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Supplemental Information

for

Base-Promoted Synthesis of Tetrasubstituted Alkenylboronates from Propargyl Amines and B₂pin₂ via Dual 1,4-Metallate Shift and B-N Elimination

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1. General Information

All reagents and solvents were purchased from Adamas Reagent, Energy Chemical Company, Bide Pharmatech Ltd., and Tansoole, and were used without further purification. Unless otherwise stated, all reactions were accomplished in Schlenk tubes under N₂ atmosphere. The reactions were monitored by thin layer chromatography (TLC) or gas chromatography-mass spectrometry (GC-MS). Flash column chromatography was performed over silica gel (200–300 mesh). ¹H NMR spectra were recorded on a Bruker Avance III 500 MHz (or 400 MHz) NMR spectrometer, and the chemical shifts (in ppm) were referred to $CDCl_3$ ($\delta = 7.26$ ppm) as an internal standard. ¹³C NMR spectra were obtained by using the same NMR spectrometer and were calibrated with CDCl₃ (δ = 77.0 ppm). ¹¹B NMR spectra were acquired with accessories on the same NMR spectrometer using CDCl₃. ¹⁹F NMR spectra were acquired with accessories on the same NMR spectrometer using CDCl₃, too. The following abbreviations were used to illuminate the diversities: δ = chemical shifts, J = coupling constant, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS; (ESI)) were acquired with quadrupole and time-of-flight (TOF) mass spectrometers. All reagents and solvents were obtained from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC). The products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

2. General procedure for starting materials

2.1 General Synthetic Procedure for 1a-1ae^[1]

$$R = \sqrt{NH_2} + = \sqrt{NH_2} = \frac{Pd(PPh_3)_2Cl_2 (2 \text{ mol}\%), Cul (4 \text{ mol}\%)}{THF/NEt_3 = 4:1, rt., overnight} R = R = \frac{NH_2}{U}$$

To a solution of THF (8 mL)/Et₃N (2 mL) was added CuI (38.1 mg, 0.2 mmol, 4 mol%), Pd(PPh₃)₂Cl₂ (70.2 mg, 0.1 mmol, 2 mol%), and an aryl iodide (5.5 mmol, 1.1 equiv) under nitrogen. Then, a propargyl amine (5.0 mmol, 1.0 equiv) was added and the mixture was stirred overnight at room temperature. Upon the reaction was completed, a saturated NH₄Cl aqueoussolution was added and the mixture was extracted with Et₂O three times. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA/Et₃N=2:1:1%) to obtain the corresponding propargyl amine.

2.2 General Synthetic Procedure for 1af-1ag^[7-8]



2-Methyl-2-propane-sulfinamide (841 mg, 6.94 mmol, 1.00 equiv) and titanium (IV) ethoxide (3.14 mL, 13.9 mmol, 2.00 equiv) were added sequentially to a solution of corresponding ketone **S1** (10 mmol, 1 equiv) in tetrahydrofuran (17.0 mL) at 22 °C. The mixture was stirred at 80 °C for 12 h. Upon the reaction was completed, a saturated NH₄Cl aqueoussolution was added and the mixture was extracted with EA three times. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to give the crude product **S2**, which was used in the subsequent reaction without further purification.

To a solution of the phenylacetylene (4.4 mmol, 1.1 equiv) in THF (6 mL) undernitrogen gas was added n-butyllithium (2.75 mL, 4.4 mmol, 1.1 equiv, 1.60 M solution in hexane) dropwise at -78 °C. After 30 minutes' stirring, the reaction temperature was raised to 0 °C, and the solution was stirred for an hour. To the reaction mixture was added the corresponding imine (4.0 mmol, 1.1 equiv) in THF dropwise. After stirring for an hour, the reaction temperature was raised to room temperature and stirred overnight. Saturated NaHCO₃ aqueous solution was added to the reaction mixture upon completion, then extracted with EA three times. The combined organic layer was washed with brine, and then dried over anhydrous Na₂SO₄. After concentration under reduced pressure, the residue was purified by silicagel column chromatography (Hexane / EtOAc = 4 / 1). The corresponding sulfinamide with alkyne S3 was obtained in 60% - 70% yield.



To a solution of the sulfinamide with alkyne S3 (3.0 mmol, 1.0 equiv) in methanol (5 mL) was added 4.0 M HCl dioxane solution (2.25 mL, 9.0 mmol, 3.0 equiv) and stirred at room temperature overnight. Upon completion, methanol was removed under reduced pressure, and the residue was diluted with Et₂O. To the Et₂O solution was added NaOH aqueous solution (1.0 M) with stirring, and then extracted with Et₂O three times. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. After concentration under reduced pressure, the residue was purified with silicagel column chromatography (Hexane/EtOAc= 2/1). The corresponding primary propargylic amine S4 was obtained in 80% - 90% yield.

3. Condition screenings

Ph-	- $ -$	Base (0.5 equiv) MeOH (5 equiv) 100 °C, 12h, argon	Ph-Bpin
1	a 2a		3a
Entry	Base	Solvent	Yield (%)
1	K ₂ CO ₃	Toluene	15
2	K ₂ CO ₃	THF	12
3	K ₂ CO ₃	1,4-Dioxane	trace
4	K ₂ CO ₃	CH ₃ CN	15
5	K ₂ CO ₃	MeOH	60
6	КОН	MeOH	30
7	KOMe	MeOH	trace
8	Rb_2CO_3	MeOH	52
9	CsF	MeOH	40
10	Cs ₂ CO ₃	MeOH	75

4. General Process for the Synthesis of (3)

General Procedure A:



In air, B₂pin₂ (5 equiv, 1 mmol) and Cs₂CO₃ (0.5 equiv, 0.1 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Then the **1** (1 equiv, 0.2 mmol) and MeOH (0.5 mL) was added under argon atmosphere. The resulting reaction mixture was stirred vigorously at 100 °C for 12 h. Then, the reaction mixture was concentrated to dryness. The crude product was purified by silica gel chromatography to afford the products.

General Procedure B:



In air, B₂pin₂ (5 equiv, 1 mmol) and Cs₂CO₃ (0.5 equiv, 0.1 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Then the propargyl amines (1 equiv, 0.2 mmol), MeOH (5 equiv) and 2phenoxyethanol (0.5 mL)was added under argon atmosphere. The resulting reaction mixture was stirred vigorously at 100 °C for 12 h. Then, the reaction mixture was concentrated to dryness. The crude product was purified by silica gel chromatography to afford the products.

5. Mechanism studies

General Procedure C:



In air, B_2pin_2 (5 equiv, 1 mmol) and Cs_2CO_3 (0.5 equiv, 0.1 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Then the **1a** (1 equiv, 0.2 mmol) and MeOH (0.5 mL) was added under argon atmosphere. The resulting reaction mixture was stirred vigorously at 100 °C for 20 min.



General Procedure D:



In air, B₂pin₂ (5 equiv, 1 mmol) and Cs₂CO₃ (0.5 equiv, 0.1 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Then the **1** (1 equiv, 0.2 mmol) and CD₃OD (0.5 mL) was added under argon atmosphere. The resulting reaction mixture was stirred vigorously at 100 °C for 12 h. Then, the reaction mixture was concentrated to dryness. The crude product was purified by silica gel chromatography to afford the products.

General Procedure E:

	+ Bapina	Cs ₂ CO ₃ (0.5 equiv)	Bpin
	D2pin2	MeOH (0.5 mL)	Ph-
1a	2a	100 °C, 12 h, argon	2 a, 72%

In air, B₂pin₂ (5 equiv, 1 mmol), Cs₂CO₃ (0.5 equiv, 0.1 mmol) and BHT (2 equiv, 0.4 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Then the **1** (1 equiv, 0.2 mmol) and MeOH (0.5 mL) was added under argon atmosphere. The resulting reaction mixture was stirred vigorously at 100 °C for 12 h. Then, the reaction mixture was concentrated to dryness. The crude product was purified by silica gel chromatography to afford the products.

6. Scale-up Reactions and Synthetic Applications

6.1 Gram-scale reaction

General Procedure F:



In air, B_2pin_2 (5 equiv, 25 mmol) and Cs_2CO_3 (0.5 equiv, 2.5 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Then the **1** (1 equiv, 5 mmol) and MeOH (12.5 mL) was added under argon atmosphere. The resulting reaction mixture was stirred vigorously at 100 °C for 12 h. Then, the reaction mixture was concentrated to dryness. The crude product was purified by silica gel chromatography to afford the products.

6.2 Synthetic Applications

General Procedure G^[2]:



To a 25 mL Schlenk tube, was added **2a** (1 equiv, 0.2 mmol) followed by 0.3 mmol of sodium perborate monohydrate (1.5 equiv) under air. Then THF (0.8 mL) and H₂O (0.8 mL) was added in ice-bath, with that the NaOH (aq.) was added by drop wise. The reaction mixture was stirred at 0- rt until full conversion by TLC. Then, the reaction mixture was extracted with EA/H₂O. Subsequently, the organic layers were dried with Na₂SO₄, and concentrated to dryness. The crude product was purified by silica gel chromatography (silica gel, PE: EA =100:1, v/v) to afford the product with the yield of 80%.

General Procedure H^[3]:



A solution of thiophene (1 mmol, 5.0 equiv) in THF (2.0 mL) was cooled to -78 °C and treated with "BuLi (1.6 M in hexanes, 1.2 mmol, 6.0 equiv). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to -78 °C and a solution of substrate **2a** (0.2 mmol, 1.0 equiv) in THF (1 mL) was added. The mixture was stirred at -78 °C for 1 h, and then a solution of NBS (1 mmol, 5.0 equiv) in THF (2.0 mL) was added. After 10 h at room temperature, sat. Na₂S₂O₃ (aq.) (4 mL) was added. The reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over Na2SO4 and concentrated in vacuo. The crude product was purified by silica gel chromatography (silica gel, PE: EA =50:1, v/v) to afford the product with the yield of 60%.

General Procedure I^[3]:



A solution of furan (0.5 mmol, 2.5 equiv) in THF (2.0 mL) was cooled to -78 °C and treated with "BuLi (1.6 M in hexanes, 0.6 mmol, 3 equiv). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to -78 °C and a solution of **2a** (0.2 mmol, 1.0 equiv) in THF (1 mL) was added. The mixture was stirred at -78 °C for 1 h, and then a solution of NBS (0.5 mmol, 2.5 equiv) in THF (2.0 mL) was added. After 10 h at room temperature, sat. Na₂S₂O₃ (aq.) (4 mL) was added. The reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by silica gel chromatography (silica gel, PE: EA =50:1, v/v) to afford the product with the yield of 57%.

General Procedure J^[4]:



In air, $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 5.0 mol%), NaOtBu (28.8 mg, 0.3 mmol, 3.0 equiv), Ruphos (4.7 mg, 0.01 mmol, 10.0 mol%) and substrate **2a** (0.1 mmol, 1.0 equiv) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Then PhCH3 (1.0 mL), PhBr (15.7 mg, 0.1 mmol, 1.0 equiv) and H₂O (0.1 mL) was added under argon atmosphere. The mixture was stirred at 80 °C for 24 hours. Then, the mixture was cooled to room temperature and diluted with DCM (20 mL). The organic layer was separated and the aqueous phase was extracted with DCM (20 mL x 2). The combined organic layer was washed with H₂O (30 mL) and brine (30 mL). The crude product was purified by silica gel chromatography (silica gel, PE: EA =50:1, v/v) to afford the product with the yield of 89%.

General Procedure K^[5]:



To a 25 mL Schlenk tube containing a magnetic stirbar, **2a** (0.20 mmol, 1.0 equiv) and chloroiodomethane (0.6 mmol, 3.0 equiv) and THF (2.0 mL) were added under argon atmosphere. The reaction mixture was cooled to -78 °C and a solution of "BuLi (0.6 mmol, 1.6 M in hexane, 3.0 equiv) was slowly added at -78 °C. After stirring for 1 h, the reaction mixture was warmed to room temperature and additionally stirred for 24 h. The reaction was quenched with a saturated aqueous NH₄Cl solution and extracted with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (silica gel, PE: EA =100:1, v/v) to afford the product with the yield of

80%.

General Procedure L^[6]:



Under argon atmosphere, a solution of 2a (0.2 mmol, 1.0 equiv) in THF (1 mL) was added NaOH (0.3 mL, 3 M in water) via a syringe. The resulting solution was stirred at ambient temperature for 10 min, followed by adding I₂ (2.0 mL, 0.2 M in THF) dropwise. The reaction mixture was then stirred at ambient temperature for around 2 h. After completion, the reaction was quenched with aqueous sodium thiosulfate and extracted with EtOAc (10 mL x 3). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (silica gel, PE: EA =100:1, v/v) to afford the product with the yield of 35%.

Unsuccessful substrate:



7. Crystal Data

Crystal data of 3a

Method for single crystals cultivation: a pure solid sample (10-20 mg) was dissolved in ethyl acetate (2 mL) in a vial at room temperature, and petroleum ether/hexane (2-3 mL) was added into the above solution slowly while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at room temperature to allow the slow evaporation of the solvents until a single crystal was obtained.

The data were collected on a Agilent Gemini E diffractometer (Mo, 50kV 40mA) instrument using Mo-Karadiation ($\lambda = 0.71073$ Å) at 296 K and reducted by CrysAlisPro (Rigaku). The crystal structures were solved and refined using the SHELXTL software package. Refinements were performed with SHELXL-2013 using fullmatrix least-squares calculations on F2, with anisotropic displacement parameters for all the nonhydrogen atoms. The crystallographic data have already been deposited at the Cambridge Crystallographic Data Centre.

Crystallographic data for compound **3a** (CCDC-2162448) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk). Thermal ellipsoids are drawn at 50% probability level.



Bond precision:	C-C = 0.0061 A	Wavelength=0.71073	
Cell:	a=11.7662(16)	b=12.493(2)	c=14.140(2)
	alpha=90	beta=95.415(15)	gamma=90
Temperature:	298 K		
	Calculated	Reported	
Volume	2069.2(5)	2069.3(5)	
Space group	P 21/n	P 1 21/n 1	1
Hall group	-P 2yn	-P 2yn	
Moiety formula	C23 H29 B O2	C23 H29 B	02
Sum formula	C23 H29 B O2	C23 H29 B	02
Mr	348.27	348.27	
Dx,g cm-3	1.118	1.118	
Z	4	4	
Mu (mm-1)	0.068	0.068	
F000	752.0	752.0	
F000'	752.30		
h,k,lmax	16,17,19	16,16,19	
Nref	5781	4864	
Tmin,Tmax	0.984,0.988	0.593,1.00	00
Tmin'	0.983		
Correction metho	od= # Reported T L	imits: Tmin=0.593 Tm	ax=1.000
AbsCorr = MULTI-	-SCAN		
Data completenes	ss= 0.841	Theta(max) = 29.524	l
B(reflections) =	0.0919(2225)		wR2(reflections)
	0.0010(2220)		0.3361(4864)
S = 1.020	Npar=	241	

=

8. Characterization Data

2-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow solid (52.2 mg, 75%). m.p. 65-67 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 3.56 (s, 2H), 2.04 (s, 3H), 1.84 (s, 3H), 1.16 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 148.1, 141.6, 141.4, 138.3, 129.1, 128.7, 127.0, 126.8, 126.8, 82.9, 36.4, 24.8, 24.7, 21.5. ¹¹B NMR (160 MHz, CDCl₃) δ 31.40. HRMS (ESI, m/z) calcd for C₂₃H₃₀BO₂ [M+H] ⁺: 349.2333; found: 349.2336.

4,4,5,5-tetramethyl-2-(3-methyl-1-(p-tolyl)but-2-en-2-yl)-1,3,2-dioxaborolane (3b)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (41.2 mg, 72%).¹**H NMR** (500 MHz, CDCl₃) δ 7.09 (d, J = 7.8 Hz, 2H), 7.04 (d, J = 7.8 Hz, 2H), 3.49 (s, 2H), 2.30 (s, 3H), 2.03 (s, 3H), 1.80 (s, 3H), 1.17 (s, 12H).¹³**C NMR** (126 MHz, CDCl₃) δ 147.8, 139.2, 134.6, 128.7, 128.5, 82.8, 36.2, 24.7, 21.4, 21.0.¹¹**B NMR** (160 MHz, CDCl₃) δ 31.12. **HRMS** (ESI, m/z) calcd for C₁₈H₂₈BO₂ [M+H] +: 287.2177; found: 349.2336.

2-(1-(4-ethylphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (43.2 mg, 72%). ¹H NMR (500 MHz, CDCl₃) δ 7.11 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 3.49 (s, 2H), 2.60 (q, J = 7.6 Hz, 2H), 2.02 (s, 3H), 1.81 (s, 3H), 1.20 (t, J = 7.6 Hz, 3H), 1.16 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 147.5, 141.2, 139.5, 128.6, 127.5, 82.8, 36.3, 28.5, 24.8, 24.7, 21.3, 15.8. ¹¹B NMR (160 MHz, CDCl₃) δ 30.99. **HRMS** (ESI, m/z) calcd for C₁₉H₃₀BO₂ [M+H] ⁺: 301.2333; found: 301.2325.



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (52.5 mg, 80%). ¹**H NMR** (500 MHz, CDCl₃) δ 7.27 – 7.24 (m, 2H), 7.15 – 7.12 (m, 2H), 3.49 (s, 2H), 2.02 (s, 3H), 1.82 (s, 3H), 1.30 (s, 9H), 1.15 (s, 12H). ¹³**C NMR** (126 MHz, CDCl₃) δ 148.0, 147.1, 139.3, 128.4, 124.9, 82.8, 36.3, 34.3, 31.5, 24.8, 24.7, 21.3. ¹¹**B NMR** (160 MHz, CDCl₃) δ 31.05. **HRMS** (ESI, m/z) calcd for C₂₁H₃₃BNaO₂ [M+Na] ⁺: 351.2466; found: 351.2458.

2-(1-(4-butylphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (47.6 mg, 68%). ¹H NMR (500 MHz, CDCl₃) δ 7.10 (d, J = 8.1 Hz, 2H), 7.04 (d, J = 8.1 Hz, 2H), 3.49 (s, 2H), 2.57 – 2.54 (m, 2H), 2.02 (s, 3H), 1.81 (s, 3H), 1.61 – 1.53 (m, 3H), 1.36 – 1.31 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 147.3, 139.7, 139.4, 128.5, 128.1, 82.8, 36.4, 35.2, 33.8, 24.8, 24.7, 22.3, 21.3, 14.0. ¹¹B NMR (160 MHz, CDCl₃) δ 30.78. HRMS (ESI, m/z) calcd for C₂₁H₃₃BNaO₂ [M+Na] +: 351.2466; found: 351.2464.

2-(1-(4-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (45.2 mg, 78%). ¹H NMR (500 MHz, CDCl₃) δ 7.15 – 7.11 (m, 2H), 6.93 – 6.88 (m, 2H), 3.47 (s, 2H), 2.02 (s, 3H), 1.80 (s, 3H), 1.15 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 161.1 (d, J = 242.3 Hz), 148.1, 138.0 (d, J = 3.1 Hz), 129.9 (d, J = 7.7 Hz), 114.6 (d, J = 21.0 Hz), 82.9, 35.9, 24.7, 24.7, 21.3. ¹⁹F NMR (471 MHz, CDCl₃) δ -118.68. ¹¹B NMR (160 MHz, CDCl₃) δ 30.91. HRMS (ESI, m/z) calcd for C₁₇H₂₅BFO₂ [M+H] ⁺: 291.1926; found: 291.1921.

2-(1-(4-chlorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (33.6 mg, 55%).¹**H** NMR (500 MHz, CDCl₃) δ 7.21 – 7.16 (m, 2H), 7.13 – 7.08 (m, 2H), 3.47 (s, 2H), 2.03 (s, 3H), 1.79 (s, 3H), 1.16 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 148.8, 140.9, 131.0, 123.0, 128.0, 82.9, 36.1, 24.7, 21.4. ¹¹**B** NMR (160 MHz, CDCl₃) δ 30.79. **HRMS** (ESI, m/z) calcd for C₁₇H₂₅BClNaO₂ [M+Na] +: 329.1450; found: 329.1443.

4,4,5,5-tetramethyl-2-(3-methyl-1-phenylbut-2-en-2-yl)-1,3,2-dioxaborolane (3h)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (41.9 mg, 77%).¹H NMR (500 MHz, CDCl₃) δ 7.25 – 7.18 (m, 4H), 7.15 – 7.10 (m, 1H), 3.53 (s, 2H), 2.04 (s, 3H), 1.82 (s, 3H), 1.16 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 147.9, 142.4, 128.7, 128.0, 125.3, 82.9, 36.8, 24.7, 24.7, 21.4. ¹¹B NMR (160 MHz, CDCl₃) δ 31.01. HRMS (ESI, m/z) calcd for C₁₇H₂₆BO₂ [M+H] ⁺: 273.2020; found: 273.2025.

4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)aniline (3i)



The reaction was performed following the **Condition B**. The residue was purified by flash column chromatograph (PE: EA=30:1) to give the product as a yellow oil liquid (37.3 mg, 65%).¹**H NMR** (500 MHz, CDCl₃) δ 7.02 – 6.97 (m, 2H), 6.62 – 6.58 (m, 2H), 3.64 – 3.24 (m, 4H), 2.02 (s, 3H), 1.81 (s, 3H), 1.18 (s, 12H). ¹³**C NMR** (126 MHz, CDCl₃) δ 147.0, 143.8, 132.5, 129.4, 115.1, 82.8, 35.8, 24.8, 24.7, 21.2. ¹¹**B NMR** (160 MHz, CDCl₃) δ 31.12. **HRMS** (ESI, m/z) calcd for C₁₇H₂₇BNO₂ [M+H] ⁺: 288.2129; found: 288.2122.

4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)phenol (3j)



The reaction was performed following the **Condition B**. The residue was purified by flash column chromatograph (PE: EA=30:1) to give the product as a yellow solid (34.6 mg, 60%). m.p. 104-106 °C.¹H **NMR** (500 MHz, CDCl₃) δ 7.03 (d, J = 8.4 Hz, 2H), 6.68 (d, J = 8.5 Hz, 2H), 4.88 (s, 1H), 3.43 (s, 2H), 2.00 (s, 3H), 1.79 (s, 3H), 1.15 (s, 12H). ¹³C **NMR** (126 MHz, CDCl₃) δ 153.4, 147.3, 134.4, 129.7, 114.9, 82.9, 35.8, 24.8, 24.7, 21.2. ¹¹B **NMR** (160 MHz, CDCl₃) δ 30.86. **HRMS** (ESI, m/z) calcd for C₁₇H₂₆BO₃ [M+H] ⁺: 289.1970; found: 289.1969.

4,4,5,5-tetramethyl-2-(3-methyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-2-en-2-yl)-1,3,2-dioxaborolane (3k)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow solid (57.4 mg, 72%). m.p. 104-106 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.69 – 7.65 (m, 2H), 7.21 – 7.18 (m, 2H), 3.53 (s, 2H), 2.02 (s, 3H), 1.78 (s, 3H), 1.33 (d, *J* = 2.7 Hz, 12H), 1.16 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 148.9, 146.0, 134.6, 128.0, 83.5, 82.9, 36.9, 24.9, 24.7, 24.7, 21.5. ¹¹B NMR (160 MHz, CDCl₃) δ 31.53. HRMS (ESI, m/z) calcd for C₂₃H₃₆B2NaO₄ [M+Na] ⁺: 421.2692; found: 421.2686.

4,4,5,5-tetramethyl-2-(3-methyl-1-(4-(trifluoromethyl)phenyl)but-2-en-2-yl)-1,3,2-dioxaborolane (3l)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (35.4mg, 52%). ¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, J = 8.0 Hz, 2H), 7.32 – 7.27 (m, 2H), 3.56 (s, 2H), 2.04 (s, 3H), 1.80 (s, 3H), 1.15 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 149.6, 146.7, 128.8, 127.7 (q, J = 32.0 Hz), 124.9 (q, J = 3.7 Hz), 124.5 (d, J = 271.7 Hz), 83.0, 36.6, 24.8, 24.7, 21.6. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.19. ¹¹B NMR (160 MHz, CDCl₃) δ 30.88. HRMS (ESI, m/z) calcd for C₁₈H₂₅BF₃O₃ [M+H] ⁺: 341.1894; found: 341.1904.

4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)phenyl methylbenzenesulfonate (3m)

4-



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow solid (50.4 mg, 57%). m.p. 68-70 °C. ¹H **NMR** (500 MHz, CDCl₃) δ 7.72 – 7.64 (m, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.09 – 7.04 (m, 2H), 6.84 – 6.78 (m, 2H), 3.44 (s, 2H), 2.43 (s, 3H), 2.00 (s, 3H), 1.76 (s, 3H), 1.11 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 148.62, 147.47, 145.09, 141.49, 132.64, 129.67, 129.65, 128.53, 121.77, 82.91, 36.14, 24.70, 24.67, 21.70, 21.38. ¹¹B NMR (160 MHz, CDCl₃) δ 31.06. HRMS (ESI, m/z) calcd for C₂₄H₃₂BO₅S [M+H] ⁺: 443.2058; found: 443.2053.

1-(4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)phenyl)ethan-1-one (3n)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow solid (13.8 mg, 22%). m.p. 65-67 °C. ¹H **NMR** (500 MHz, CDCl₃) δ 7.85 – 7.82 (m, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 3.56 (s, 2H), 2.56 (s, 3H), 2.04 (s, 3H), 1.79 (s, 3H), 1.15 (s, 12H). ¹³C **NMR** (126 MHz, CDCl₃) δ 198.0, 149.6, 148.6, 134.7, 128.7, 128.3, 83.0, 36.8, 26.5, 24.7, 24.7, 21.6. ¹¹B **NMR** (160 MHz, CDCl₃) δ 30.96. **HRMS** (ESI, m/z) calcd for C₁₉H₂₈BO₃ [M+H] ⁺: 315.2126; found: 315.2133.

4,4,5,5-tetramethyl-2-(3-methyl-1-(4-(trifluoromethoxy)phenyl)but-2-en-2-yl)-1,3,2-dioxaborolane (30)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=50:1) to give the product as a yellow oil liquid (30.6 mg, 43%).¹**H NMR** (500 MHz, CDCl₃) δ 7.21 – 7.16 (m, 2H), 7.09 – 7.04 (m, 2H), 3.50 (s, 2H), 2.03 (s, 3H), 1.80 (s, 3H), 1.14 (s, 12H).¹³**C NMR** (126 MHz, CDCl₃) δ 148.5, 147.1, 141.3, 129.9, 120.6, 120.6 (q, *J* = 257.0 Hz), 83.0, 36.1, 24.7, 24.6, 21.4.¹⁹**F NMR** (471 MHz, CDCl₃) δ -58.00.¹¹B NMR (160 MHz, CDCl₃) δ 30.88. **HRMS** (ESI, m/z) calcd for C₁₈H₂₅BF₃O₃ [M+H] ⁺: 357.1843; found: 357.1845.

$2-(1-(4-methoxyphenyl)-3-methylbut-2-en-2-yl)-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolane \ (3p)$



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=30:1) to give the product as a yellow oil liquid (45.9 mg, 76%). ¹**H NMR** (500

MHz, CDCl₃) δ 7.12 – 7.08 (m, 2H), 6.79 – 6.76 (m, 2H), 3.77 (s, 3H), 3.45 (s, 2H), 2.01 (s, 3H), 1.80 (s, 3H), 1.15 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 157.5, 147.4, 134.5, 129.5, 113.5, 82.8, 55.3, 35.8, 24.7, 24.7, 21.3. ¹¹B NMR (160 MHz, CDCl₃) δ 31.41. HRMS (ESI, m/z) calcd for C₁₈H₂₈BO₃ [M+H] ⁺: 303.2126; found: 303.2131.

N,N-dimethyl-4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)aniline (3q)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=30:1) to give the product as a yellow oil liquid (41.0mg, 65%).¹**H NMR** (500 MHz, CDCl₃) δ 7.09 – 7.04 (m, 2H), 6.69 – 6.65 (m, 2H), 3.42 (s, 2H), 2.88 (s, 6H), 2.01 – 1.98 (m, 3H), 1.80 (s, 3H), 1.16 (s, 12H).¹³**C NMR** (126 MHz, CDCl₃) δ 148.9, 147.0, 130.9, 129.2, 113.2, 82.8, 41.2, 35.7, 24.8, 21.3.¹¹**B NMR** (160 MHz, CDCl₃) δ 31.37. **HRMS** (ESI, m/z) calcd for C₁₉H₃₁BNO₂ [M+H] +: 316.2442; found: 316.2440.

2-(1-(3-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (27.8 mg, 48%). ¹**H** NMR (500 MHz, CDCl₃) δ 7.17 (td, *J* = 7.9, 6.1 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.90 (dt, *J* = 10.2, 2.1 Hz, 1H), 6.81 (td, *J* = 8.5, 2.7 Hz, 1H), 3.50 (s, 2H), 2.03 (s, 3H), 1.80 (s, 3H), 1.17 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 162.9 (d, *J* = 244.4 Hz), 149.1, 145.2 (d, *J* = 7.6 Hz), 129.3 (d, *J* = 7.6 Hz), 124.2 (d, *J* = 2.5 Hz), 115.4 (d, *J* = 21.4 Hz), 112.1 (d, *J* = 21.4 Hz), 82.9, 36.5, 36.5, 24.69, 24.68, 21.5. ¹⁹F NMR (471 MHz, CDCl₃) δ -114.51. ¹¹B NMR (160 MHz, CDCl₃) δ 30.93. **HRMS** (ESI, m/z) calcd for C₁₇H₂₄BFNaO₂ [M+Na] ⁺: 313.1746; found: 313.1748.

$2-(1-(3-bromophenyl)-3-methylbut-2-en-2-yl)-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolane\ (3s)$



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (49.0 mg, 70%).¹**H NMR** (500 MHz, CDCl₃) δ 7.36 (d, *J* = 1.9 Hz, 1H), 7.25 (dt, *J* = 6.9, 1.9 Hz, 1H), 7.12 – 7.06 (m, 2H), 3.48 (s, 2H), 2.03 (s, 3H), 1.80 (s, 3H), 1.17 (s, 12H).¹³**C NMR** (126 MHz, CDCl₃) δ 149.1, 145.0, 131.8, 129.6,

128.4, 127.3, 122.2, 83.0, 36.5, 24.7, 21.5. ¹¹**B** NMR (160 MHz, CDCl₃) δ 30.84. **HRMS** (ESI, m/z) calcd for C₁₇H₂₄BBrNaO₂ [M+Na] ⁺: 373.0945; found: 373.0946.

2-(1-(3-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=30:1) to give the product as a yellow oil liquid (50.2 mg, 83%).¹**H NMR** (500 MHz, CDCl₃) δ 7.14 (t, *J* = 7.8 Hz, 1H), 6.81 – 6.76 (m, 2H), 6.68 (dd, *J* = 8.0, 2.7 Hz, 1H), 3.78 (s, 3H), 3.50 (s, 2H), 2.03 (s, 3H), 1.81 (s, 3H), 1.17 (s, 12H). ¹³**C NMR** (126 MHz, CDCl₃) δ 159.5, 148.4, 144.1, 128.9, 121.2, 114.3, 110.8, 82.9, 55.1, 36.8, 24.7, 21.5. ¹¹**B NMR** (160 MHz, CDCl₃) δ 31.08. **HRMS** (ESI, m/z) calcd for C₁₈H₂₈BO₃ [M+H] +: 303.2126; found: 303.2124.

3-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)benzonitrile (3u)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=50:1) to give the product as a yellow oil liquid (32.7 mg, 55%). ¹H NMR (500 MHz, CDCl₃) δ 7.48 (d, J = 1.7 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.31 (t, J = 7.7 Hz, 1H), 3.52 (s, 2H), 2.05 (s, 3H), 1.80 (s, 3H), 1.15 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 150.3, 144.0, 133.29, 132.25, 129.2, 128.7, 119.3, 111.9, 83.0, 36.3, 24.7, 24.7, 21.7. ¹¹B NMR (160 MHz, CDCl₃) δ 30.91. HRMS (ESI, m/z) calcd for C₁₈H₂₅BNO₂ [M+H] ⁺: 298.1973; found: 298.1980.

2-(1-(2-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3v)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (34.2 mg, 59%). ¹**H NMR** (500 MHz, CDCl₃) δ 7.16 (td, J = 7.6, 1.8 Hz, 1H), 7.10 (tdd, J = 7.4, 5.2, 1.8 Hz, 1H), 7.00 (td, J = 7.5, 1.3 Hz, 1H), 6.96 (ddd, J = 9.5, 8.1, 1.3 Hz, 1H), 3.52 (s, 2H), 2.03 (s, 3H), 1.77 (s, 3H), 1.17 (s, 12H). ¹³**C NMR** (126 MHz, CDCl₃) δ 161.1 (d, J = 244.7 Hz), 149.1, 130.4 (d, J = 4.9 Hz), 129.0 (d, J = 15.7 Hz), 126.9 (d, J = 8.1 Hz), 123.6 (d, J = 3.5 Hz), 114.8 (d, J = 22.3 Hz), 82.9, 29.3 (d, J = 3.0 Hz), 24.72, 24.70, 21.3. ¹⁹**F NMR** (471 MHz, CDCl₃) δ -117.23. ¹¹**B NMR** (160 MHz, CDCl₃) δ 30.93. **HRMS** (ESI, m/z) calcd for C₁₇H₂₄BFNaO₂ [M+Na] ⁺: 313.1746; found: 313.1746.

 $2-(1-(2-methoxyphenyl)-3-methylbut-2-en-2-yl)-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolane\ (3w)$



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=30:1) to give the product as a yellow solid (48.3 mg, 87%). m.p. 48-50 °C. ¹H **NMR** (500 MHz, CDCl₃) δ 7.15 – 7.09 (m, 2H), 6.87 – 6.79 (m, 2H), 3.83 (s, 3H), 3.49 (s, 2H), 2.04 (s, 3H), 1.75 (s, 3H), 1.17 (s, 12H). ¹³C **NMR** (126 MHz, CDCl₃) δ 157.5, 148.1, 130.5, 129.2, 126.4, 120.2, 109.9, 82.8, 55.3, 30.3, 24.8, 24.7, 21.2. ¹¹B **NMR** (160 MHz, CDCl₃) δ 31.09. **HRMS** (ESI, m/z) calcd for C₁₈H₂₅BNO₂ [M+H] ⁺: 303.2126; found: 303.2130.

2-(1-(2-chlorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3x)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow solid (27.6 mg, 45%). m.p. 75-77 °C. ¹H **NMR** (500 MHz, CDCl₃) δ 7.32 – 7.29 (m, 1H), 7.16 – 7.11 (m, 2H), 7.08 (ddd, *J* = 7.5, 6.5, 2.7 Hz, 1H), 3.59 (s, 2H), 2.06 (s, 3H), 1.72 (s, 3H), 1.15 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 149.6, 139.6, 134.3, 129.7, 129.0, 126.7, 126.4, 82.9, 34.0 24.72, 24.66, 21.4. ¹¹B NMR (160 MHz, CDCl₃) δ 30.98. **HRMS** (ESI, m/z) calcd for C₁₇H₂₅BClO₂ [M+H] +: 307.1631; found: 307.1632.

methyl 2-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)benzoate (3y)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (13.2 mg, 20%).¹**H NMR** (500 MHz, CDCl₃) δ 7.78 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 3.89 (d, *J* = 0.9 Hz, 3H), 3.86 (s, 2H), 2.06 – 2.03 (m, 3H), 1.73 (s, 3H), 1.09 (d, *J* = 0.9 Hz, 12H). ¹³**C NMR** (126 MHz, CDCl₃) δ 168.7, 148.6, 143.6, 131.5, 130.4, 130.0, 129.6, 125.2, 82.8, 51.8, 34.3, 24.7, 24.6, 21.3. ¹¹**B NMR** (160 MHz, CDCl₃) δ 30.99. **HRMS** (ESI, m/z) calcd for C₁₉H₂₈BO₄ [M+H] ⁺: 331.2075; found: 331.2078.

2 - (1 - (3, 4 - dichlorophenyl) - 3 - methylbut - 2 - en - 2 - yl) - 4, 4, 5, 5 - tetramethyl - 1, 3, 2 - dioxaborolane (3z) - (3z)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow solid (36.7 mg, 54%). m.p. 70-72 °C. ¹H **NMR** (500 MHz, CDCl₃) δ 7.30 – 7.26 (m, 2H), 7.01 (ddd, J = 8.1, 2.0, 0.9 Hz, 1H), 3.45 (s, 2H), 2.03 (s, 3H), 1.79 (s, 3H), 1.18 (d, J = 1.1 Hz, 12H). ¹³C **NMR** (126 MHz, CDCl₃) δ 149.9, 142.9, 131.8, 130.6, 129.8, 129.1, 128.1, 83.0, 35.9, 24.74, 24.69, 21.6. ¹¹B **NMR** (160 MHz, CDCl₃) δ 30.84. **HRMS** (ESI, m/z) calcd for C₁₇H₂₄BCl₂O₂ [M+H] ⁺: 341.1241; found: 341.1244.

2-(1-(5-chloro-2-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3aa)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (52.4 mg, 78%). ¹**H NMR** (500 MHz, CDCl₃) δ 7.10 – 7.04 (m, 2H), 6.70 (d, *J* = 8.5 Hz, 1H), 3.79 (s, 3H), 3.43 (s, 2H), 2.04 (s, 3H), 1.74 (s, 3H), 1.18 (s, 12H). ¹³**C NMR** (126 MHz, CDCl₃) δ 156.1, 149.2, 132.6, 129.3, 125.9, 125.1, 111.0, 82.9, 55.6, 30.4, 24.8, 24.8, 21.4. ¹¹**B NMR** (160 MHz, CDCl₃) δ 30.79. **HRMS** (ESI, m/z) calcd for C₁₈H₂₇BClO₃ [M+H] ⁺: 337.1736; found: 337.1731.

4,4,5,5-tetramethyl-2-(3-methyl-1-(thiophen-2-yl)but-2-en-2-yl)-1,3,2-dioxaborolane (3ab)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (23.2 mg, 65%). ¹H NMR (500 MHz, CDCl₃) δ 7.05 (dd, J = 5.1, 1.3 Hz, 1H), 6.87 (dd, J = 5.1, 3.4 Hz, 1H), 6.76 (dd, J = 3.1, 1.4 Hz, 1H), 3.67 (s, 2H), 2.03 (s, 3H), 1.83 (s, 3H), 1.21 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 149.6, 145.9, 126.4, 123.9, 122.7, 83.0, 31.1, 24.8, 24.6, 21.4. ¹¹B NMR (160 MHz, CDCl₃) δ 30.84. HRMS (ESI, m/z) calcd for C₁₅H₂₄BO₂S [M+H] ⁺: 279.1585; found: 279.1582.

4,4,5,5-tetramethyl-2-(3-methyl-1-(naphthalen-1-yl)but-2-en-2-yl)-1,3,2-dioxaborolane (3ac)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow solid (37.4 mg, 58%). m.p. 80-82 °C. ¹**H NMR** (500 MHz, CDCl₃) δ 8.15 (d, J = 8.4 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.53 (ddt, J = 8.3, 6.9, 1.2 Hz, 1H), 7.48 (ddt, J = 7.9, 6.8, 1.1 Hz, 1H), 7.38 (t, J = 7.7 Hz, 1H), 7.29 (dt, J = 7.0, 1.1 Hz, 1H), 3.98 (s, 2H), 2.13 (s, 3H), 1.79 (s, 3H), 1.08 (d, J = 1.0 Hz, 12H). ¹³**C NMR** (126 MHz, CDCl₃) δ 148.4, 137.7, 133.7, 132.5, 128.5, 126.1, 125.6, 125.5, 125.2, 125.1, 124.0, 82.9, 33.4, 24.8, 24.6, 21.3. ¹¹**B NMR** (160 MHz, CDCl₃) δ 31.29. **HRMS** (ESI, m/z) calcd for C₂₁H₂₈BO₂ [M+H] +: 323.2177; found: 323.2173.

2-(1-(9H-fluoren-2-yl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ad)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow solid (51.2 mg, 71%). m.p. 98-100 °C. ¹H **NMR** (500 MHz, CDCl₃) δ 7.76 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.53 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.37 (ddd, *J* = 15.0, 7.8, 1.3 Hz, 2H), 7.30 – 7.22 (m, 2H), 3.86 (s, 2H), 3.63 (s, 2H), 2.08 (s, 3H), 1.88 (s, 3H), 1.16 (s, 12H). ¹³C **NMR** (126 MHz, CDCl₃) δ 147., 143.3, 142.0, 141.3, 139.1, 127.4, 126.6, 126.1, 125.3, 125.0, 119.6, 119.4, 82.9, 37.0, 36.9, 24.9, 24.8, 21.4. ¹¹B **NMR** (160 MHz, CDCl₃) δ 31.30. **HRMS** (ESI, m/z) calcd for C₂₄H₃₀BO₂ [M+H] ⁺: 361.2333; found: 361.2329.

2-(1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ae)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (41.6 mg, 63%). ¹H NMR (500 MHz, CDCl₃) δ 6.73 – 6.69 (m, 2H), 6.66 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.22 – 4.19 (m, 4H), 3.40 (s, 2H), 2.00 (s, 3H), 1.79 (s, 3H), 1.18 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 148.0, 143.1, 141.3, 135.8,

121.6, 117.3, 116.6, 82.8, 64.4, 64.4, 35.9, 24.8, 24.7, 21.4. ¹¹**B** NMR (160 MHz, CDCl₃) δ 31.06. **HRMS** (ESI, m/z) calcd for C₁₉H₂₈BO₄ [M+H] +: 331.2075; found: 331.2079.

2-(3-ethyl-1-phenylpent-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3af)



The reaction was performed following the **Condition A.** The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (31.2 mg, 52%). ¹H NMR (500 MHz, CDCl3) δ 7.26 – 7.17 (m, 4H), 7.15 – 7.10 (m, 1H), 3.52 (s, 2H), 2.37 (q, J = 7.5 Hz, 2H), 2.19 (q, J = 7.6 Hz, 2H), 1.10 (s, 12H), 1.05 (t, J = 7.5 Hz, 3H), 0.99 (t, J = 7.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl3) δ 158.3, 142.4, 128.7, 128.0, 125.3, 82.7, 36.2, 28.5, 24.6, 14.8, 13.2. ¹¹B NMR (160 MHz, CDCl3) δ 31.12. HRMS (ESI, m/z) calcd for C₁₉H₃₀BO₂ [M+H] +: 301.2333; found: 301.2328.

2-(1-cyclohexylidene-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ag)



The reaction was performed following the **Condition A**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (37.5 mg, 60%).¹**H** NMR (500 MHz, CDCl3) δ 7.25 – 7.17 (m, 4H), 7.14 – 7.09 (m, 1H), 3.54 (s, 2H), 2.50 (t, J = 5.7 Hz, 2H), 2.30 (dd, J = 7.0, 5.0 Hz, 2H), 1.64 – 1.52 (m, 6H), 1.14 (s, 12H). ¹³**C** NMR (126 MHz, CDCl3) δ 155.1, 142.6, 128.7, 128.0, 125.3, 82.8, 35.8, 35.3, 31.3, 29.0, 28.2, 27.0, 24.7. ¹¹**B** NMR (160 MHz, CDCl3) δ 31.32. **HRMS** (ESI, m/z) calcd for C₂₀H₃₀BO₂ [M+H] +: 313.2333; found: 313.2335.

2-(3,4-dimethyl-1-phenylpent-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ah)



The reaction was performed following the **Condition B**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (37.5 mg, 68%).¹H NMR (500 MHz, CDCl3) δ 7.25 – 7.16 (m, 6H), 7.15 – 7.07 (m, 1H), 3.56 (s, 1H), 3.50 (s, 2H), 3.18 (m, J = 6.9 Hz, 1H), 3.05 (m, J = 6.8 Hz, 0.5H), 1.89 (s, 2H), 1.66 (s, 3H), 1.12 (s, 6H), 1.12 (s, 12H), 1.02 (d, J = 6.8 Hz, 6H), 0.96 (d, J = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl3) δ 155.7, 142.2, 128.7, 128.7, 128.0, 125.3, 125.3, 82.9, 82.8, 36.5, 35.6, 34.8, 30.3, 24.7, 24.6, 21.4, 20.5, 16.3, 12.7. ¹¹B NMR (160 MHz, CDCl3) δ 31.21. HRMS (ESI, m/z) calcd for C₁₉H₃₀BO₂ [M+H] +: 301.2333; found: 301.2335.

4,4,5,5-tetramethyl-2-(1-phenylpent-2-en-2-yl)-1,3,2-dioxaborolane (3ai)



The reaction was performed following the **Condition B**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (34.8 mg, 64%). ¹**H NMR** (500 MHz, CDCl₃) δ 7.34 (dd, *J* = 6.9, 3.2 Hz, 1.5H), 7.22 (dq, *J* = 8.6, 6.9, 5.8 Hz, 7H), 7.16 – 7.11 (m, 1.6H), 6.42 (t, *J* = 7.0 Hz, 0.7H), 6.05 (t, *J* = 7.5 Hz, 1H), 3.51 (s, 1.4H), 3.43 (s, 2H), 2.35 (q, *J* = 7.7 Hz, 2H), 2.23 (q, *J* = 7.4 Hz, 1.4H), 1.20 (s, 8H), 1.16 (s, 12H), 1.00 (dt, *J* = 10.7, 7.6 Hz, 5H). ¹³**C NMR** (126 MHz, CDCl₃) δ 148.7, 148.5, 141.9, 134.0, 129.0, 128.6, 128.04, 128.00, 125.5, 125.3, 83.2, 82.9, 42.8, 34.2, 24.80, 24.78, 24.7, 24.6, 22.9, 22.2, 14.6, 13.5. ¹¹**B NMR** (160 MHz, CDCl₃) δ 30.77. **HRMS** (ESI, m/z) calcd for C17H30BO2 [M+H] +: 273.2020; found: 273.2026.

2-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-2-en-2-yl-1,1-d2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a-d)



The reaction was performed following the **Condition D**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow solid (52.5 mg, 75%). m.p. 55-57 °C.¹H **NMR** (500 MHz, CDCl₃) δ 7.61 – 7.57 (m, 2H), 7.51 – 7.48 (m, 2H), 7.43 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.31 – 7.27 (m, 2H), 2.07 (s, 3H), 1.86 (s, 3H), 1.19 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 148.2, 141.6, 141.4, 138.3, 129.1, 128.7, 127.0, 126.9, 126.8, 82.9, 24.79, 24.75, 21.5. ¹¹B NMR (160 MHz, CDCl₃) δ 31.88. HRMS (ESI, m/z) calcd for C₂₃H₂₈D₂BO₂ [M+H] ⁺: 351.2459; found: 351.2461.

1-([1,1'-biphenyl]-4-yl)-3-methylbutan-2-one (4)



The reaction was performed following the **Condition G**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow solid (38.1 mg, 80%). m.p. 55-57 °C.¹H **NMR** (500 MHz, CDCl₃) δ 7.65 – 7.55 (m, 4H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 3.81 (s, 2H), 2.78 (p, *J* = 6.9 Hz, 1H), 1.16 (s, 3H), 1.15 (s, 3H). ¹³C **NMR** (126 MHz, CDCl₃) δ 211.9, 140.8, 139.8, 133.5, 129.9, 128.8, 127.4, 127.3, 127.1, 47.3, 40.3, 18.4. **HRMS** (ESI, m/z) calcd for C₁₇H₁₉O [M+H] +: 239.1430; found: 239.1431.

2-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-2-en-2-yl)thiophene (5)



The reaction was performed following the **Condition H**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (36.5 mg, 60%). ¹**H** NMR (500 MHz, CDCl₃) δ 7.62 – 7.58 (m, 2H), 7.53 – 7.49 (m, 2H), 7.46 – 7.41 (m, 2H), 7.36 – 7.32 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.94 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.75 (dd, *J* = 3.5, 1.2 Hz, 1H), 3.84 (s, 2H), 1.99 (s, 3H), 1.92 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 145.3, 141.1, 139.2, 138.8, 133.6, 128.8, 128.7, 127.0, 126.4, 126.3, 126.0, 123.8, 40.8, 22.9, 21.6. HRMS (ESI, m/z) calcd for C₂₁H₂₁S [M+H] ⁺: 305.1358; found: 305.1357.

2-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-2-en-2-yl)furan (6)



The reaction was performed following the **Condition I**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (32.8 mg, 57%). ¹**H NMR** (500 MHz, CDCl₃) δ 7.61 – 7.58 (m, 2H), 7.53 – 7.50 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 1.8 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.39 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.20 (d, *J* = 3.3 Hz, 1H), 3.89 (s, 2H), 2.08 (s, 3H), 1.97 (s, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 155.2, 141.2, 140.4, 139.8, 138.7, 133.3, 128.7, 128.5, 127.04, 127.00, 126.97, 123.3, 110.6, 108.4, 36.6, 23.0, 22.1. **HRMS** (ESI, m/z) calcd for C₂₁H₂₁O [M+H] ⁺: 289.1587; found: 289.1591.

4-(3-methyl-2-phenylbut-2-en-1-yl)-1,1'-biphenyl (7)



The reaction was performed following the **Condition J**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil solid (53.1 mg, 89%). m.p. 47-49 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.64 – 7.61 (m, 2H), 7.54 – 7.50 (m, 2H), 7.49 – 7.44 (m, 2H), 7.39 – 7.34 (m, 1H), 7.32 – 7.28 (m, 2H), 7.25 – 7.20 (m, 3H), 7.14 – 7.10 (m, 2H), 3.85 (s, 2H), 2.02 (s, 3H), 1.74 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 143.9, 141.2, 139.6, 138.6, 133.5, 129.8, 129.1, 129.0, 128.8, 127.9, 127.02, 126.96, 126.0, 40.2, 22.4, 21.0. HRMS (ESI, m/z) calcd for C₂₃H₂₃ [M+H] +: 299.1794; found: 299.1789.

2-(2-([1,1'-biphenyl]-4-ylmethyl)-3-methylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8)



The reaction was performed following the **Condition K**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow oil liquid (58.0 mg, 80%).¹**H** NMR (500 MHz, CDCl₃) δ 7.60 – 7.57 (m, 2H), 7.51 – 7.48 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 3.49 (s, 2H), 2.14 (t, *J* = 8.4 Hz, 2H), 1.80 (s, 3H), 1.77 (s, 3H), 1.24 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 141.3, 140.4, 138.5, 132.6, 128.9, 128.7, 127.0, 126.9, 126.9, 126.0, 83.0, 36.6, 24.9, 21.0, 20.4. ¹¹B NMR (160 MHz, CDCl₃) δ 34.01. **HRMS** (ESI, m/z) calcd for C₂₄H₃₂BO₂ [M+H] ⁺: 363.2490; found: 363.2482.

4-(2-iodo-3-methylbut-2-en-1-yl)-1,1'-biphenyl (9)



The reaction was performed following the **Condition L**. The residue was purified by flash column chromatograph (PE: EA=100:1) to give the product as a yellow solid (24.4 mg, 35%). m.p.76-78 °C. ¹H **NMR** (500 MHz, CDCl₃) δ 7.62 – 7.58 (m, 2H), 7.57 – 7.52 (m, 2H), 7.43 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.03 (s, 2H), 2.05 (s, 3H), 2.00 (s, 3H). ¹³C **NMR** (126 MHz, CDCl₃) δ 141.0, 139.5, 138.1, 137.9, 128.8, 128.7, 127.2, 127.1, 127.0, 99.2, 47.0, 31.7, 19.8. **HRMS** (ESI, m/z) calcd for C₁₇H₁₈I [M+H] ⁺: 349.0448; found: 349.0456.

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10. NMR Spectroscopic Data

 1 H spectra (CDCl₃) of 2-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**)



 ^{13}C spectra (CDCl₃) of 2-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

 ^{11}B spectra (CDCl₃) of 2-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**)



¹H spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(p-tolyl)but-2-en-2-yl)-1,3,2-dioxaborolane **(3b)**



¹³C spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(p-tolyl)but-2-en-2-yl)-1,3,2-dioxaborolane **(3b)**



¹¹B spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(p-tolyl)but-2-en-2-yl)-1,3,2-dioxaborolane **(3b)**



33



¹H spectra (CDCl₃) of 2-(1-(4-ethylphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-

 $^{13}\mathrm{C}$ spectra (CDCl₃) of 2-(1-(4-ethylphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**)



 $^{11}\mathrm{B}$ spectra (CDCl₃) of 2-(1-(4-ethylphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**)



 $^1\mathrm{H}\ \text{spectra}\ (\mathrm{CDCl}_3)\ \text{of}\ 2-(1-(4-(\mathrm{tert}-\mathrm{butyl})\mathrm{phenyl})-3-\mathrm{methylbut}-2-\mathrm{en}-2-\mathrm{yl})-4,4,5,5-\mathrm{tetramethyl}-1,3,2-\mathrm{dioxaborolane}\ \textbf{(3d)}$



 $^{13}\mathrm{C}$ spectra (CDCl₃) of 2-(1-(4-(tert-butyl)phenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**)



 $^{11}\mathrm{B}$ spectra (CDCl₃) of 2-(1-(4-(tert-butyl)phenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**)




 13 C spectra (CDCl₃) of 2-(1-(4-butylphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-



¹H spectra (CDCl₃) of 2-(1-(4-butylphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**)

 ^{11}B spectra (CDCl₃) of 2-(1-(4-butylphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**)



 $^1\mathrm{H}$ spectra (CDCl₃) of 2-(1-(4-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)



 $^{13}\mathrm{C}$ spectra (CDCl₃) of 2-(1-(4-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)



 $^{19}\mathrm{F}$ spectra (CDCl₃) of 2-(1-(4-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)



0 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)

 $^{11}\mathrm{B}$ spectra (CDCl₃) of 2-(1-(4-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)



 1 H spectra (CDCl₃) of 2-(1-(4-chlorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**)



 $^{13}\mathrm{C}$ spectra (CDCl₃) of 2-(1-(4-chlorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**)



 $^{11}\mathrm{B}$ spectra (CDCl₃) of 2-(1-(4-chlorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**)



¹H spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-phenylbut-2-en-2-yl)-1,3,2-dioxaborolane (**3h**)



¹³C spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-phenylbut-2-en-2-yl)-1,3,2-dioxaborolane (**3h**)



¹¹B spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-phenylbut-2-en-2-yl)-1,3,2-dioxaborolane **(3h)**



 $^1\mathrm{H}$ spectra (CDCl_3) of 4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)aniline (**3i**)



¹³C spectra (CDCl₃) of 4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)aniline (**3i**)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

¹¹B spectra (CDCl₃) of 4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)aniline (**3i**)



 $^1\mathrm{H}$ spectra (CDCl_3) of 4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)phenol (3j)



¹³C spectra (CDCl₃) of 4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)phenol (**3j**)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

¹¹B spectra (CDCl₃) of 4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1yl)phenol **(3j)**



 $\label{eq:linear} ^{1}H \ spectra \ (CDCl_{3}) \ of \ 4,4,5,5-tetramethyl-2-(3-methyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) but-2-en-2-yl)-1,3,2-dioxaborolane \ (\mathbf{3k})$

688 667 19 19 19 19 19 10 10 10 10 10 10 10 10 10 10 10 10 10	23	02 333 333 16
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¹³C spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-2-en-2-yl)-1,3,2-dioxaborolane **(3k)**



¹¹B spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-2-en-2-yl)-1,3,2-dioxaborolane **(3k)**







¹³C spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(4-(trifluoromethyl)phenyl)but-2-en-2-yl)-1,3,2-dioxaborolane (3l)



 19 F spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(4-(trifluoromethyl)phenyl)but-2-en-2-yl)-1,3,2-dioxaborolane (31)



 ^{11}B spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(4-(trifluoromethyl)phenyl)but-2-en-2-yl)-1,3,2-dioxaborolane (**3**)



¹H spectra (CDCl₃) of 4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)phenyl 4-methylbenzenesulfonate **(3m)**



¹³C spectra (CDCl₃) of 4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)phenyl 4-methylbenzenesulfonate (**3m**)



 $^{11}\mathrm{B}$ spectra (CDCl₃) of 4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)phenyl 4-methylbenzenesulfonate (**3m**)



 1 H spectra (CDCl₃) of 1-(4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)phenyl)ethan-1-one (**3n**)



¹³C spectra (CDCl₃) of 1-(4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1yl)phenyl)ethan-1-one (3n)



¹¹B spectra (CDCl₃) of 1-(4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1yl)phenyl)ethan-1-one (3n)





¹³C spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(4-(trifluoromethoxy)phenyl)but-2-en-2-yl)-1,3,2-dioxaborolane (**30**)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

¹⁹F spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(4-(trifluoromethoxy)phenyl)but-2-en-2-yl)-1,3,2-dioxaborolane **(30)**



¹¹B spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(4-(trifluoromethoxy)phenyl)but-2-en-2-yl)-1,3,2-dioxaborolane **(30)**



¹H spectra (CDCl₃) of 2-(1-(4-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3p**)



 $^{13}\mathrm{C}$ spectra (CDCl₃) of 2-(1-(4-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3p**)



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¹¹B spectra (CDCl₃) of 2-(1-(4-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3p**)



 1 H spectra (CDCl₃) of N,N-dimethyl-4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)aniline (**3q**)



¹³C spectra (CDCl₃) of N,N-dimethyl-4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)aniline (**3q**)



¹¹B spectra (CDCl₃) of N,N-dimethyl-4-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)aniline (**3q**)



 1 H spectra (CDCl₃) of 2-(1-(3-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3r**)



 $^{13}\mathrm{C}$ spectra (CDCl₃) of 2-(1-(3-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3r**)



 $^{19}\mathrm{F}$ spectra (CDCl₃) of 2-(1-(3-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3r**)



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)

 $^{11}\mathrm{B}$ spectra (CDCl₃) of 2-(1-(3-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3r**)



 $^1\mathrm{H}$ spectra (CDCl_3) of 2-(1-(3-bromophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s)



 ^{13}C spectra (CDCl₃) of 2-(1-(3-bromophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3s**)



 ^{11}B spectra (CDCl₃) of 2-(1-(3-bromophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3s**)



 1 H spectra (CDCl₃) of 2-(1-(3-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3t**)



 13 C spectra (CDCl₃) of 2-(1-(3-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3t**)



 $^{11}\text{B} \quad \text{spectra} \quad (\text{CDCl}_3) \quad \text{of} \quad 2-(1-(3-\text{methoxyphenyl})-3-\text{methylbut}-2-\text{en}-2-\text{yl})-4,4,5,5-\text{tetramethyl}-1,3,2-\text{dioxaborolane} \quad (\mathbf{3t})$





 $^{13}\mathrm{C}$ spectra (CDCl₃) of 3-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)benzonitrile (**3u**)



¹H spectra (CDCl₃) of 3-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1vl)benzonitrile (**3u**)

 ^{11}B spectra (CDCl₃) of 3-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)benzonitrile (**3u**)



 $^1\mathrm{H}$ spectra (CDCl_3) of 2-(1-(2-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3v**)



 ^{13}C spectra (CDCl₃) of 2-(1-(2-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3v**)



 $^{19} F\ 2\ (1\ (2\ fluorophenyl)\ -3\ methylbut\ -2\ en\ -2\ yl)\ -4, 4, 5, 5\ -tetramethyl\ -1, 3, 2\ -dioxaborolane\ (\mathbf{3v})$



0 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)

 ^{11}B spectra (CDCl₃) of 2-(1-(2-fluorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3v**)



 $^1\mathrm{H}$ spectra (CDCl_3) of 2-(1-(2-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3w**)



 ^{13}C spectra (CDCl₃) of 2-(1-(2-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3w**)



 ^{11}B spectra (CDCl₃) of 2-(1-(2-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3w**)



 1 H spectra (CDCl₃) of 2-(1-(2-chlorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3x**)



 ^{13}C spectra (CDCl₃) of 2-(1-(2-chlorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3x**)



 ^{11}B spectra (CDCl₃) of 2-(1-(2-chlorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3x**)



¹H spectra (CDCl₃) of methyl 2-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)benzoate (**3y**)



¹³C spectra (CDCl₃) of methyl 2-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)benzoate (**3y**)



¹¹B spectra (CDCl₃) of methyl 2-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)benzoate (**3y**)



¹H spectra (CDCl₃) of 2-(1-(3,4-dichlorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (3z)



¹³C spectra (CDCl₃) of 2-(1-(3,4-dichlorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (3z)



 ^{11}B spectra (CDCl₃) of 2-(1-(3,4-dichlorophenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3z**)



¹H spectra (CDCl₃) of 2-(1-(5-chloro-2-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3aa**)


¹³C spectra (CDCl₃) of 2-(1-(5-chloro-2-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3aa**)



¹¹B spectra (CDCl₃) of 2-(1-(5-chloro-2-methoxyphenyl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3aa**)



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¹H spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(thiophen-2-yl)but-2-en-2-yl)-1,3,2-dioxaborolane (**3ab**)



¹³C spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(thiophen-2-yl)but-2-en-2-yl)-1,3,2-dioxaborolane (**3ab**)



¹¹B spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(thiophen-2-yl)but-2-en-2-yl)-1,3,2-dioxaborolane (**3ab**)



 $^1\mathrm{H}$ spectra (CDCl_3) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(naphthalen-1-yl)but-2-en-2-yl)-1,3,2-dioxaborolane (**3ac**)



¹³C spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(naphthalen-1-yl)but-2-en-2-yl)-1,3,2-dioxaborolane (**3ac**)



¹¹B spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(3-methyl-1-(naphthalen-1-yl)but-2-en-2-yl)-1,3,2-dioxaborolane (**3ac**)







¹³C spectra (CDCl₃) of 2-(1-(9H-fluoren-2-yl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3ad**)



¹¹B spectra (CDCl₃) of 2-(1-(9H-fluoren-2-yl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3ad**)



 $\label{eq:linear} ^1H \ spectra \ (CDCl_3) \ of \ 2-(1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane \ \textbf{(3ae)}$



¹³C spectra (CDCl₃) of 2-(1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3ae**)



¹¹B spectra (CDCl₃) of 2-(1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3-methylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3ae**)



0 -10 f1 (ppm) 40 30 20 10 -20 -30 -40 -50 -70 90 80 70 60 50 -60 -80 -90



¹³C spectra (CDCl₃) of 2-(3-ethyl-1-phenylpent-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3af)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

¹¹B spectra (CDCl₃) of 2-(3-ethyl-1-phenylpent-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3af)



¹H spectra (CDCl₃) of 2-(1-cyclohexylidene-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3ag)**



¹³C spectra (CDCl₃) of 2-(1-cyclohexylidene-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ag)



210 200 190 180 170 160 150 140 130 120 110 100 90 f1 (ppm) 80 70 60 50 40 30 20 10 0 -10

 $^{11}B\ spectra\ (CDCl_3)\ of\ 2-(1-cyclohexylidene-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane$ (3ag)

-31.32







¹H spectra (CDCl₃) of 2-(3,4-dimethyl-1-phenylpent-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3ah)**



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

 $\label{eq:spectra} {}^{11}\text{B} \quad \text{spectra} \quad (\text{CDCl}_3) \quad \text{of} \quad 2\mbox{-}(3,4\mbox{-dimethyl-1-phenylpent-2-en-2-yl})\mbox{-}4,4,5,5\mbox{-tetramethyl-1,3,2-dioxaborolane} \eqno(3ah)$



¹H spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(1-phenylpent-2-en-2-yl)-1,3,2-dioxaborolane **(3ai)**







¹³C spectra (CDCl₃) of 4,4,5,5-tetramethyl-2-(1-phenylpent-2-en-2-yl)-1,3,2-dioxaborolane (3ai)

0 f1 (ppm) 90 80 70 60 50 40 30 20 10 -10 -20 -30 -40 -50 -60 -70 -80 -90 1 H spectra (CDCl₃) of 2-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-2-en-2-yl-1,1-d2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a-d**)



 ^{13}C spectra (CDCl₃) of 2-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-2-en-2-yl-1,1-d2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a-d**)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

 ^{11}B spectra (CDCl₃) of 2-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-2-en-2-yl-1,1-d2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a-d**)





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

¹H spectra (CDCl₃) of 2-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-2-en-2-yl)thiophene (5)





¹³C spectra (CDCl₃) of 2-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-2-en-2-yl)thiophene (5)

66

3.5

3.0

2.5

4.0 f1 (ppm)

2.03 2.09 0.90 2.12

7.5

7.0

3.0

-76.0

6.0

5.5

5.0

4.5

6.5

2.97

2.0

1.5

1.0

0.0

0.5



¹H spectra (CDCl₃) of 4-(3-methyl-2-phenylbut-2-en-1-yl)-1,1'-biphenyl (7)







¹H spectra (CDCl₃) of 2-(2-([1,1'-biphenyl]-4-ylmethyl)-3-methylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(8)**



¹³C spectra (CDCl₃) of 4-(3-methyl-2-phenylbut-2-en-1-yl)-1,1'-biphenyl (7)

¹³C spectra (CDCl₃) of 2-(2-([1,1'-biphenyl]-4-ylmethyl)-3-methylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(8)**



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

¹¹B spectra (CDCl₃) of 2-(2-([1,1'-biphenyl]-4-ylmethyl)-3-methylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(8)**



in (ppi



¹³C spectra (CDCl₃) of 4-(2-iodo-3-methylbut-2-en-1-yl)-1,1'-biphenyl (9)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)