Supporting Information

For

Copper-catalyzed regioselective formation of tri- and tetra-substituted vinylboronates in air

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Contents

1. Synthesis of starting materials.

1.1. Generalities

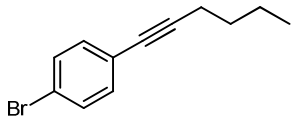
Reactions were performed in air (unless otherwise stated) and solvents were dispensed from a solvent purification system. Bis-(pinacolato)diboron was used as received. Pinacolborane was used as received and stored at -20ºC under argon. NHC-Cu complexes[1] and $[PdCl_2(PPh_3)_2]$ [2] were synthesized according to published procedures. Internal alkynes were used as received or prepared according to literature procedures.[3] ^1H and ^{13}C-$\{^1H\}$ Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE 400 Ultrashield spectrometer or on a Bruker AVANCE 300 spectrometer using the residual solvent peak as reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm) at 298K. Gas chromatography (GC) analyses were performed on an Agilent 7890A apparatus equipped with a flame ionization detector and a (5%-Phenyl)-methylpolysiloxane column (30 m, 320 μm, film: 0.25 μm). Flash chromatography was performed on silica gel 60 Å pore diameter and 40-63 μm particle size. Elemental analyses were performed at London Metropolitan University Service 166-220 Holloway Road, London, N7 8DB. Mass spectroscopy was performed by the EPSRC National Mass Spectrometry Service Centre at Swansea University, Grove Building, Singleton Park, Swansea, SA2 8PP, Wales, UK.

1.2. Synthesis of internal alkynes 5-9

$[Pd(Cl)_2(PPh_3)_2]$ was synthesized according to a published procedure.[2] Alkynes **5**, **7**, **8**, **9** were synthesised according to a general procedure shown below. **6** was synthesised according to a similar method of the literature.[3]

A Schlenk flask was charged with THF (20 mL), triethylamine (10 mL), aryl iodide, alkyne, $[PdCl_2(PPh_3)_2]$ and CuI. The reaction mixture was stirred overnight at the indicated temperature, allowed to cool to rt and quenched with MeOH (10 mL). The solution was concentrated *in vacuo* and Et_2O (100 mL) was added. After filtration, the filtrate was washed with 1N $HCl_{(aq.)}$ and H_2O. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (SiO_2).

1.2.1 Preparation of **5**



5

$[PdCl_2(PPh_3)_2]$ (50.0 mg, 0.070 mmol), CuI (13.5 mg, 0.070 mmol), 1-bromo-4-iodobenzene (4.0 g, 14.0 mmol), 1-hexyne (1.8 mL, 15.4 mmol, 1.1 equiv.) were charged in a Schlenk flask and stirred at RT for 48 h.

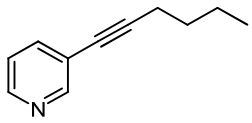
Flash chromatography (SiO_2, pentane/ethyl acetate 10:1) afforded 1.6 g of the title compound **5** (48 %) as a yellowish oil.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.35 (d, ^3J(H,H) = 8.5 Hz, 2H, C*H* phenyl), 7.20 (d, ^3J(H,H) = 8.5 Hz, 2H, C*H* phenyl), 2.35 (t, ^3J(H,H) = 6.9 Hz, 2H, CH_2), 1.59 -1.49 (m, 2H, CH_2) , 1.48-1.37 (m, 2H, CH_2), 0.91 (t, ^3J(H,H) = 7.2 Hz, 3H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 133.0 (s, *C*H phenyl), 131.4 (s, *C*H phenyl), 123.2 (s, C^{IV} phenyl), 121.6 (s, C^{IV} phenyl), 91.7 (s, C^{IV}), 79.7 (s, C^{IV}), 30.8 (s, *C*H_2), 22.1 (s, *C*H_2), 19.2 (s, *C*H_2), 13.7 (s, *C*H_3).

These data were compared and found similar to literature values.[3]

1.2.2 Preparation of **7**



7

$[PdCl_2(PPh_3)_2]$ (50.0 mg, 0.070 mmol), CuI (13.5 mg, 0.070 mmol), 3-iodopyridine (3.0 g, 14.6 mmol), 1-hexyne (2.0 mL, 17.4 mmol, 1.2 equiv.) were charged in a Schlenk flask and stirred at 50°C for 24 h.

Flash chromatography (SiO_2, pentane) afforded 2.1 g of the title compound **7** (90 %) as a dark orange oil.

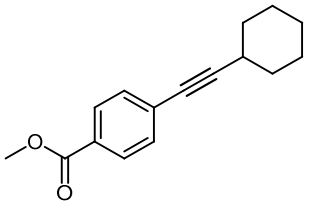
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.56 (br. s, 1H, *CH* Ar), 8.42 - 8.39 (m, 1H, C*H* Ar), 7.60 - 7.58 (dt, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.9 Hz, 1H, C*H* Ar), 7.14 - 7.10 (dd,

^{3}J(H,H) = 8.1 Hz, ^{4}J(H,H) = 5.0 Hz, 1H, C*H* Ar), 2.35 (t, ^{3}J(H,H) = 7.1 Hz, 2H, CH_2), 1.56-1.36 (m, 4H, CH_2), 0.88 (t, ^{3}J(H,H) = 7.3 Hz, 3H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 152.3 (s, *C*H Ar), 147.9 (s, *C*H Ar), 138.3 (s, *C*H Ar), 122.9 (s, *C*H Ar), 121.2 (s, C^{IV} Ar), 94.1 (s, C^{IV}), 77.3 (s, C^{IV}), 30.6 (s, *C*H_2), 22.0 (s, *C*H_2), 19.1 (s, *C*H_2), 13.6 (s, *C*H_3).

These data were compared and found similar to literature values.[3]

1.2.3. Preparation of **8**



8

[$PdCl_2(PPh_3)_2$] (50.0 mg, 0.070 mmol), CuI (13.5 mg, 0.070 mmol), 4-iodo-methylbenzoate (4.0 g, 15.3 mmol), cyclohexylacetylene (2.4 mL, 18.3 mmol, 1.2 equiv.) were charged in a Schlenk flask and stirred at 50°C for 24 h.

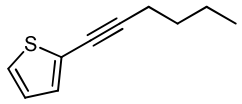
Flash chromatography (SiO_2, pentane/ethyl acetate 10:1) afforded 3.5 g of the title compound **8** (94 %) as an orange solid.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.98 - 7.92 (d, ^{3}J(H,H) = 8.1 Hz, 2H, C*H* phenyl), 7.48 - 7.42 (d, ^{3}J(H,H) = 8.1 Hz, 2H, C*H* phenyl), 3.90 (s, 3H, OCH_3), 2.66 - 2.55 (m, 1H, C*H*), 1.93 - 1.84 (m, 2H, CH_2), 1.81 - 1.69 (m, 2H, CH_2), 1.63 - 1.48 (m, 3H, CH_2), 1.43 - 1.30 (m, 3H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 166.8 (s, C^{IV} carbonyl), 131.6 (s, *C*H phenyl), 129.5 (s, *C*H phenyl), 129.1 (s, C^{IV} phenyl), 128.8 (s, C^{IV} phenyl), 98.0 (s, C^{IV}), 80.2 (s, C^{IV}), 52.2 (s, *C*H_3), 32.6 (s, *C*H), 29.9 (s, *C*H_2), 26.0 (s, *C*H_2), 25.0 (s, *C*H_2).

These data were compared and found similar to literature values.[3]

1.2.4. Preparation of **9**



9

$[PdCl_2(PPh_3)_2]$ (75.0 mg, 0.105 mmol), CuI (13.5 mg, 0.070 mmol), 2-iodo-thiophene (1.55 mL, 14.0 mmol), 1-hexyne (1.8 mL, 15.4 mmol, 1.1 equiv.) were charged in a Schlenk flask and stirred at 50°C for 24 h.

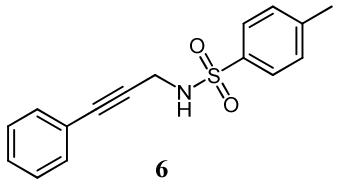
Flash chromatography (SiO_2, pentane) afforded 2.1 g of the title compound **9** (90 %) as a brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.17 - 7.16 (dd, ^3J(H,H) = 5.3 Hz, ^4J(H,H) = 1.2 Hz, 1H, C*H* Ar), 7.12 - 7.11 (m, 1H, C*H* Ar), 6.95 - 6.92 (dd, ^3J(H-H) = 5.3 Hz, ^3J(H,H) = 3.7 Hz, 1H, C*H* Ar), 2.43 (t, ^3J(H,H) = 7.0 Hz, 2H, CH_2), 1.63 - 1.56 (m, 2H, CH_2), 1.52 - 1.43 (m, 2H, CH_2), 0.95 (t, ^3J(H,H) = 7.3 Hz, 3H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 131.0 (s, *C*H Ar), 126.9 (s, *C*H Ar), 125.9 (s, *C*H Ar), 124.4 (s, C^{IV}Ar), 94.6 (s, C^{IV}), 73.8 (s, C^{IV}), 30.8 (s, *C*H_2), 22.2 (s, *C*H_2), 19.5 (s, *C*H_2), 13.7 (s, *C*H_3).

These data were compared and found similar to literature values.[3]

1.2.5. Preparation of **6**



6

A Schlenk flask was charged with 3-phenyl-2-propyn-1-amine hydrochloride (2.0 g, 11.9 mmol), tosylchloride (2.5 g, 13.1 mmol, 1.1 equiv.), DMAP (40.0 mg, 0.33 mmol) and dichloromethane (20 mL). Triethylamine was added dropwise (5.0 mL, 35.7 mmol, 3.0 equiv.). The reaction mixture was stirred at room temperature for 14 hours. The organic layer was washed with saturated $NH_4Cl_{(aq)}$ (1 x 20 mL) and H_2O (1 x 20 mL), dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. Flash chromatography (SiO_2, pentane/ethyl acetate 8:2) afforded 2.0 g of the title compound **6** (59 %) as a colorless solid.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.81 (d, ^3J(H,H) = 8.4 Hz, 2H, C*H* phenyl), 7.30 -7.22 (m, 5H, C*H* phenyl), 7.15 - 7.11 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.3 Hz, 2H, C*H* phenyl), 4.63 (br. s, 1H, N*H*), 4.08 (d, ^3J(H,H) = 5.6 Hz, 2H, CH_2), 2.36 (s, 3H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 143.9 (s, C^{IV} phenyl), 137.0 (s, C^{IV} phenyl), 131.7 (s, *C*H phenyl), 129.8 (s, *C*H phenyl), 128.6 (s, *C*H phenyl), 128.3 (s, *C*H phenyl), 127.6 (s, *C*H phenyl), 122.2 (s, C^{IV} phenyl), 84.8 (s, C^{IV}), 83.3 (s, C^{IV}) , 33.9 (s, *C*H_2), 21.6 (s, *C*H_3).

These data were compared and found similar to literature values.[4]

2. General procedure for the β-hydroboration of internal alkynes.

2.1. Procedure for Table 1.

In a glovebox, a vial was charged with the Cu catalyst, the base (0.2 mmol), bis-(pinacolato)diboron (2.2 mmol, 0.558 g, 1.1 equiv.), 1-phenyl-1-butyne **1** (2.0 mmol, 0.284 mL), the solvent (2.4 mL) and MeOH (0.180 mL, 2 equiv.). At low catalyst loading, a stock solution of Cu was prepared (0.005 mmol in CH_2Cl_2 (3.3 mL)). CH_2Cl_2 was removed *in vacuo* before addition of the other reagents. The reaction mixture was stirred at 25ºC for 16 h under inert atmosphere. The conversion was determined by GC. The volatiles were removed *in vacuo* and the products were obtained after purification by column chromatography (SiO_2). The regioselectivity of the reaction was determined by ^{1}H NMR.

Optimization of reaction conditions

Catalyst	Loading (ppm)	Base	Loading (mol%)	Solvent	Conversion (%)
[Cu(Cl)(IPr)]	50000	NaO^{t}Bu	5	THF	99
[Cu(Cl)(IPr)]	20000	NaO^{t}Bu	2	THF	99
[Cu(Cl)(IPr)]	10000	NaO^{t}Bu	1	THF	99
[Cu(Cl)(IPr)]	5000	NaO^{t}Bu	1	THF	99
[Cu(Cl)(IPr)]	1000	NaO^{t}Bu	1	THF	99
[Cu(Cl)(IPr)]	250	NaO^{t}Bu	1	THF	26
[Cu(Cl)(IPr)]	250	NaO^{t}Bu	1	Methyl THF	30
[Cu(Cl)(IPr)]	250	NaO^{t}Bu	1	toluene	13

[Cu(Cl)(IPr)]	250	NaO^{t}Bu	1	DME	20
[Cu(Cl)(IPr)]	250	NaO^{t}Bu	1	MTBE	24
[Cu(Cl)(IPr)]	250	NaO^{t}Bu	1	DCM	22
[Cu(Cl)(IPr)]	250	NaO^{t}Bu	1	Dioxane	29
[Cu(Cl)(IPr)]	250	NaO^{t}Bu	1	DMSO	31
[Cu(Cl)(IPr)]	250	NaO^{t}Bu	1	*i*PrOH	34
[CuIPr)(I^{t}Bu)(BF$_4$)]	250	/	/	Methyl THF	11
[CuIPr)(I^{t}Bu)(BF$_4$)]	250	/	/	Toluene	9
[CuIPr)(I^{t}Bu)(BF$_4$)]	250	/	/	THF	9
[CuIPr)(I^{t}Bu)(BF$_4$)]	250	/	/	DME	7
[CuIPr)(I^{t}Bu)(BF$_4$)]	250	/	/	H_2O	3
[CuIPr)(I^{t}Bu)(BF$_4$)]	250	/	/	MTBE	18
[CuIPr)(I^{t}Bu)(BF$_4$)]	250	/	/	DCM	0
[CuIPr)(I^{t}Bu)(BF$_4$)]	250	/	/	Dioxane	11
[CuIPr)(I^{t}Bu)(BF$_4$)]	250	/	/	DMSO	2
[CuIPr)(I^{t}Bu)(BF$_4$)]	250	/	/	*i*PrOH	2
[CuIPr)(I^{t}Bu)(BF$_4$)]	250	/	/	ethanol	2
[CuIPr)(P^{t}Bu$_3$)(BF$_4$)]	250	/	/	Methyl-THF	5
[CuIPr)(P^{t}Bu$_3$)(BF$_4$)]	250	/	/	Toluene	6
[CuIPr)(P^{t}Bu$_3$)(BF$_4$)]	250	/	/	THF	4
[CuIPr)(P^{t}Bu$_3$)(BF$_4$)]	250	/	/	DME	4
[CuIPr)(P^{t}Bu$_3$)(BF$_4$)]	250	/	/	MTBE	15
[CuIPr)(P^{t}Bu$_3$)(BF$_4$)]	250	/	/	DCM	0
[CuIPr)(P^{t}Bu$_3$)(BF$_4$)]	250	/	/	Dioxane	6
[CuIPr)(P^{t}Bu$_3$)(BF$_4$)]	250	/	/	DMSO	0
[CuIPr)(P^{t}Bu$_3$)(BF$_4$)]	250	/	/	*i*PrOH	3
[Cu(Cl)(I^{t}Bu)]	250	NaO^{t}Bu	1	Methyl THF	62
[Cu(Cl)(I^{t}Bu)]	250	NaO^{t}Bu	1	Toluene	43
[Cu(Cl)(I^{t}Bu)]	250	NaO^{t}Bu	1	THF	55
[Cu(Cl)(I^{t}Bu)]	250	NaO^{t}Bu	1	DME	50
[Cu(Cl)(I^{t}Bu)]	250	NaO^{t}Bu	1	MTBE	42
[Cu(Cl)(I^{t}Bu)]	250	NaO^{t}Bu	1	DCM	48

[Cu(Cl)(I^{t}Bu)]	250	NaO^{t}Bu	1	Dioxane	67
[Cu(Cl)(I^{t}Bu)]	250	NaO^{t}Bu	1	DMSO	12
[Cu(Cl)(I^{t}Bu)]	250	NaO^{t}Bu	1	*i*PrOH	46
[Cu(Cl)(ICy)]	250	NaO^{t}Bu	1	Methyl THF	63
[Cu(Cl)(ICy)]	250	NaO^{t}Bu	1	Toluene	57
[Cu(Cl)(ICy)]	250	NaO^{t}Bu	1	THF	69
[Cu(Cl)(ICy)]	250	NaO^{t}Bu	1	DME	69
[Cu(Cl)(ICy)]	250	NaO^{t}Bu	1	MTBE	65
[Cu(Cl)(ICy)]	250	NaO^{t}Bu	1	DCM	76
[Cu(Cl)(ICy)]	250	NaO^{t}Bu	1	Dioxane	74
[Cu(Cl)(ICy)]	250	NaO^{t}Bu	1	DMSO	23
[Cu(Cl)(ICy)]	250	NaO^{t}Bu	1	*i*PrOH	70
[Cu(Cl)(SIMes)]	250	NaO^{t}Bu	1	Methyl THF	95
[Cu(Cl)(SIMes)]	250	NaO^{t}Bu	1	Toluene	95
[Cu(Cl)(SIMes)]	250	NaO^{t}Bu	1	THF	98
[Cu(Cl)(SIMes)]	250	NaO^{t}Bu	1	DME	97
[Cu(Cl)(SIMes)]	250	NaO^{t}Bu	1	MTBE	97
[Cu(Cl)(SIMes)]	250	NaO^{t}Bu	1	DCM	90
[Cu(Cl)(SIMes)]	250	NaO^{t}Bu	1	Dioxane	96
[Cu(Cl)(SIMes)]	250	NaO^{t}Bu	1	DMSO	81
[Cu(Cl)(SIMes)]	250	NaO^{t}Bu	1	*i*PrOH	96
[Cu(Cl)(IMes)]	250	NaO^{t}Bu	1	Methyl THF	99
[Cu(Cl)(IMes)]	250	NaO^{t}Bu	1	Toluene	92
[Cu(Cl)(IMes)]	250	NaO^{t}Bu	1	THF	99
[Cu(Cl)(IMes)]	250	NaO^{t}Bu	1	DME	93
[Cu(Cl)(IMes)]	250	NaO^{t}Bu	1	MTBE	96
[Cu(Cl)(IMes)]	250	NaO^{t}Bu	1	DCM	92
[Cu(Cl)(IMes)]	250	NaO^{t}Bu	1	Dioxane	94
[Cu(Cl)(IMes)]	250	NaO^{t}Bu	1	DMSO	80
[Cu(Cl)(IMes)]	250	NaO^{t}Bu	1	*i*PrOH	95
[Cu(Cl)(SIMes)]	125	NaO^{t}Bu	1	Methyl THF	99
[Cu(Cl)(SIMes)]	125	NaO^{t}Bu	1	Toluene	96

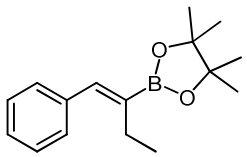
[Cu(Cl)(SIMes)]	125	NaO^{t}Bu	1	THF	95
[Cu(Cl)(SIMes)]	125	NaO^{t}Bu	1	DME	89
[Cu(Cl)(SIMes)]	125	NaO^{t}Bu	1	MTBE	97
[Cu(Cl)(SIMes)]	125	NaO^{t}Bu	1	Dioxane	97
[Cu(Cl)(SIMes)]	125	NaO^{t}Bu	1	*i*PrOH	87
[Cu(Cl)(SIMes)]	50	NaO^{t}Bu	1	Methyl THF	69
[Cu(Cl)(SIMes)]	50	NaO^{t}Bu	1	Toluene	89
[Cu(Cl)(SIMes)]	50	NaO^{t}Bu	1	THF	76
[Cu(Cl)(SIMes)]	50	NaO^{t}Bu	1	MTBE	93
[Cu(Cl)(SIMes)]	50	NaO^{t}Bu	1	dioxane	81
[Cu(Cl)(SIMes)]	50	KO^{t}Bu	1	MTBE	87
[Cu(Cl)(SIMes)]	50	CsOH	1	MTBE	89
[Cu(Cl)(SIMes)]	50	KOH	1	MTBE	93
[Cu(Cl)(SIMes)]	50	NaOH	1	MTBE	95
[Cu(Cl)(SIMes)]	50	NaOMe	1	MTBE	74
[Cu(Cl)(SIMes)]	50	K^{t}Am	1	MTBE	91
[Cu(Cl)(IMes)]	125	NaO^{t}Bu	1	Methyl THF	98
[Cu(Cl)(IMes)]	125	NaO^{t}Bu	1	THF	97
[Cu(Cl)(IMes)]	125	NaO^{t}Bu	1	MTBE	96
[Cu(Cl)(IMes)]	125	NaO^{t}Bu	1	Dioxane	96
[Cu(Cl)(IMes)]	125	NaO^{t}Bu	1	*i*PrOH	91
[Cu(Cl)(IMes)]	50	NaO^{t}Bu	1	Methyl THF	87
[Cu(Cl)(IMes)]	50	NaO^{t}Bu	1	THF	87
[Cu(Cl)(IMes)]	50	NaO^{t}Bu	1	MTBE	92
[Cu(Cl)(IMes)]	50	NaO^{t}Bu	1	dioxane	80
[Cu(Cl)(IMes)]	50	KO^{t}Bu	1	MTBE	92
[Cu(Cl)(IMes)]	50	CsOH	1	MTBE	91
[Cu(Cl)(IMes)]	50	KOH	1	MTBE	92
[Cu(Cl)(IMes)]	50	NaOH	1	MTBE	96
[Cu(Cl)(IMes)]	50	NaOMe	1	MTBE	93
[Cu(Cl)(IMes)]	50	K^{t}Am	1	MTBE	92
[Cu(Cl)(IMes)]	25	NaOH	1	MTBE	36

[Cu(Cl)(IMes)]	25	NaOH	2	MTBE	34
[Cu(Cl)(IMes)]	25	NaOH	5	MTBE	50
[Cu(Cl)(IMes)]	25	NaOH	10	MTBE	31
[Cu(Cl)(SIMes)]	25	NaOH	5	MTBE	43

2.2. General procedure for Table 2.

Catalysts and reagents were stored in air. A vial was charged in air with the Cu catalyst (stock solution 0.005 mmol in 3.3 mL of CH_2Cl_2. The latter was evaporated *in vacuo* before addition of the other reagents), the base (0.2 mmol), bis-(pinacolato)diboron (2.2 mmol, 0.558 g, 1.1 equiv.), 1-phenyl-1-butyne **1** (2.0 mmol, 0.284 mL), the solvent (2.4 mL) and MeOH (0.180 mL, 2 equiv.). The vial was closed with a screw-cap, and the reaction mixture was stirred at 25ºC for 16 h. The conversion was determined by GC analysis. The volatiles were removed *in vacuo* and the products were purified by column chromatography (SiO_2). The regioselectivity of the reactions were determined by ^{1}H NMR.

***(Z)-4,4,5,5-tetramethyl-2-(1-phenylbut-1-en-2-yl)-1,3,2-dioxaborolane* 1a**.[5]



1a

After purification (SiO_2, hexane/ethyl acetate 9:1) **1a** was isolated as a colorless oil in 98 % yield (0.263 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 7.34 - 7.22 (m, 5H, C*H* phenyl), 7.20 (br. s, 1H, C*H*), 2.39 (d, ^3J(H,H) = 7.6 Hz, 2H, CH_2), 1.31 (s, 12H), 1.10 (t, ^3J(H,H) = 7.6 Hz, 3H, CH_3).

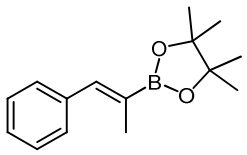
2.3. General procedure for Scheme 2.

Catalysts and reagents were stored in air. A vial was charged with [Cu(Cl)(IMes)] (stock solution 0.005 mmol in 3.3 mL of CH_2Cl_2. The latter was removed *in vacuo* before addition of other reagents), NaOH (0.025 mmol, 1 mg), bis-(pinacolato)diboron (0.55 mmol, 140 mg, 1.1 equiv.), the alkyne (0.5 mmol), CPME (0.6 mL) and MeOH (1.0 mmol, 0.05 mL). The vial was closed with a screw-cap, and the reaction mixture was stirred at 25ºC for 16 h.

Conversion was determined by GC analysis. The volatiles were removed *in vacuo* and the products were purified by column chromatography (SiO_2). The regioselectivity of the reaction was determined by ^1H NMR.

^1H and ^{13}C-{^1H} NMR data were found similar to literature values for **2a**,[3] **3a**,[6] **4a**,[7] **5a**,[3] **7a**,[3] **8a**,[3] and **9a**.[3]

(Z)-4-(4,4,5,5-Tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane, 2a [3]

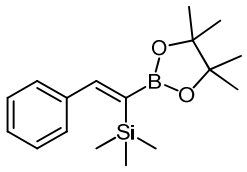


2a

After purification (SiO_2, hexane/ethyl acetate 15:1) **2a** was isolated as a colorless oil in 98% yield (0.119 g).

^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.40 - 7.32 (m, 4H, C*H* phenyl), 7.25 - 7.23 (m, 2H, C*H* phenyl and C*H*), 1.99 (d, *J*(H,H) = 1.8 Hz, 3H, CH_3), 1.32 (s, 12H).

(Z)-trimethyl-(2-phenyl-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane, 3a [6]

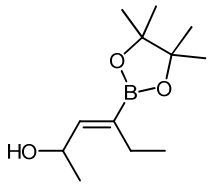


3a

After purification (SiO_2, pentane) **3a** was isolated as a colorless solid in 70 % yield (0.105 g).

^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.39 (br s, 1H, C*H*=C-Si), 7.32 - 7.31 (m, 4H, C*H* phenyl), 7.23 - 7.18 (m, 1H, C*H* phenyl), 1.26 (s, 12H), -0.12 (s, 9H, CH_3-Si).

(Z)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hex-3-en-2-ol, 4a [7]

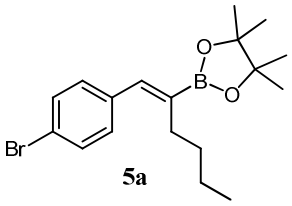


4a

After purification (SiO_2, hexane/ethyl acetate 7:3) **4a** was isolated as a colorless oil in 90 % yield (0.102 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 6.20 (d, ^3J(H,H) = 8.8 Hz, 1H, C*H*), 4.76 - 4.64 (m, 1H, C*H*-OH), 2.18 (q, ^3J(H,H) = 7.2 Hz, 2H, CH_2), 1.28 - 1.26 (m, 15H), 0.98 (t, ^3J(H,H) = 7.2 Hz, CH_3-CH_2).

(Z)-2-(1-(4-bromophenyl)hex-1-en-2-yl)-4,4,5,5-Tetramethyl-1,3,2-dioxaborolane, 5a [3]

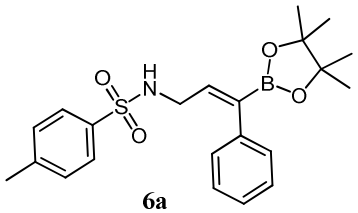


5a

After purification (SiO_2, hexane/ethyl acetate 20:1) **5a** was isolated as yellowish oil in 93 % yield (0.170 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 7.45 (d, ^3J(H,H) = 8.5 Hz, 2H, C*H* phenyl), 7.18 (d, ^3J(H,H) = 8.5 Hz, 2H, C*H* phenyl), 7.11 (br. s, 1H, C*H*), 2.33 (t, ^3J(H,H) = 7.0 Hz, 2H, C-CH_2-CH_2), 1.51 - 1.26 (m, 16H), 0.88 (t, ^3J(H,H) = 7.0 Hz, 3H, CH_3).

(Z)-4-methyl-N-(3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ally)benzene sulfonamide, 6a



6a

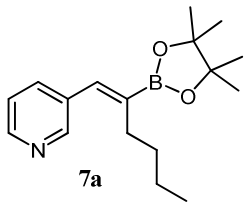
After purification (SiO_2, hexane/ethyl acetate 8:2) **6a** was isolated as a colorless solid in 90 % yield (0.186 g, mixture of *α*- and *β*-products).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ = 7.63 (d, ^{3}J(H,H) = 8.4 Hz, 2H, C*H* phenyl), 7.36-7.28 (m, 4H, C*H* phenyl), 7.24-7.18 (m, 5H, C*H* phenyl), 5.33 (t, ^{3}J(H,H) = 6.0 Hz, 1H, C*H*-CH_2), 3.96 (dd, ^{3}J(H,H) = 6.0 Hz, ^{3}J(H,H) = 1.2 Hz, 2H, CH_2-NH), 2.42 (s, 3H, CH_3), 1.26 (s, 12H).

^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K, TMS): δ = 145.8 (s, *C*H phenyl), 143.2 (s, C^{IV} phenyl), 137.2 (s, C^{IV} phenyl), 136.2 (s, C^{IV} phenyl), 129.6 (s, *C*H phenyl), 129.2 (s, *C*H phenyl), 128.5 (s, *C*H phenyl), 128.3 (s, *C*H-CH_2), 127.5 (s, *C*H phenyl), 84.2 (s, C^{IV}-O), 42.9 (s, *C*H_2-NH), 24.9 (s, *C*H_3-C-O), 21.7 (s, *C*H_3, tosyl).

HRMS calcd. for $C_{22}H_{28}BNO_4S$ $(M+H)^+$ 413.1942 found 413.1941.

(Z)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-2-yl)pyridine, 7a [3]

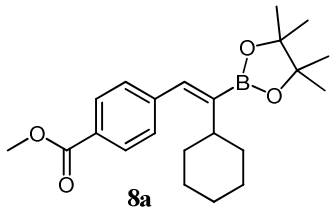


7a

After purification (SiO_2, hexane/ethyl acetate 6:4) **7a** was isolated as a dark orange oil in 95 % yield (0.151 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 8.55 (br. s, 2H, C*H* Ar), 7.62 (d, ^{3}J(H,H) = 7.9 Hz, 1H, C*H* Ar), 7.30 (br. s, 1H, C*H* Ar), 7.14 (br. s, 1H, C*H*=C), 2.37-2.30 (m, 2H, CH_2-C=C), 1.52-1.34 (m, 4H, CH_2), 1.31 (s, 12H), 1.29-1.25 (m, 2H, CH_2), 0.88 (t, ^{3}J(H,H) = 7.2 Hz, 3H, CH_3-CH_2).

(Z)-methyl-4-(2-cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate, 8a [3]

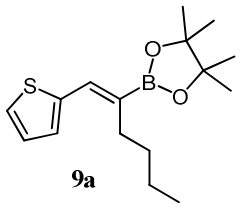


8a

After purification (SiO_2, hexane/ethyl acetate 8:2) **8a** was isolated as a colorless solid in 92 % yield (0.144 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 8.00 (d, ^3J(H,H) = 8.2 Hz, 2H, C*H* phenyl), 7.31 (d, ^3J(H,H) = 8.2 Hz, 2H, C*H* phenyl), 7.13 (s, 1H, C*H*-C phenyl), 3.91 (s, 3H, CH_3), 2.63-2.54 (m, 1H, CH_2-C*H*-CH_2), 1.72-1.62 (m, 5H CH_2 cyclohexyl), 1.56-1.49 (m, 2H, CH_2 cyclohexyl), 1.31 (s, 12H), 1.27-1.09 (m, 3H, CH_2 cyclohexyl).

(Z)- 4,4,5,5-tetramethyl-2-(1-(thiophen-2-yl)hex-1-en-2-yl)-1,3,2-dioxaborolane, 9a [3]



9a

After purification (SiO_2, hexane/ethyl acetate 15:1) **9a** was isolated as a dark orange oil in 93 % yield (0.136 g).

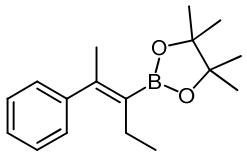
^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 7.32-7.31 (m, 2H, C*H* Ar and C*H*=C), 7.12 (d, ^3J(H,H) = 3.7 Hz, 1H, C*H* Ar), 7.01 (dd, ^3J(H,H) = 3.7 Hz, ^3J(H,H) = 3.5 Hz, 1H, C*H* Ar), 2.52 (t, ^3J(H,H) = 7.7 Hz, 2H, CH_2-C=C), 1.50-1.38 (m, 4H, CH_2), 1.29 (s, 12H), 0.94 (t, ^3J(H,H) = 7.7 Hz, 3H, CH_3).

3. General procedure for the carboboration of internal alkynes

3.1. General procedure for Table 3.

Catalysts and reagents were stored in air. A vial was charged in air with [Cu(Cl)(IMes)], NaO*t*Bu, bis-(pinacolato)diboron, 1-phenyl-1-butyne **1** (0.5 mmol, 0.071 mL), CPME (1.4 mL) and MeI. The vial was closed with a screw-cap, and the reaction mixture was stirred at 60°C for 24 h. The conversion was determined by GC analysis using an aliquot of the crude mixture. The volatiles were then removed *in vacuo* and the products were purified by column chromatography (SiO_2). The regioselectivity of the product was determined by ^{1}H NMR.

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



1b

After purification (SiO_2, hexane/ethyl acetate 8:2) **1b** was isolated as a colorless solid in 90 % yield (0.122 g).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ = 7. 30 (m, 2H, C*H* phenyl), 7.24-7.19 (m, 1H, C*H* phenyl), 7.11 (d, ^3J(H,H) = 7.3 Hz, 2H, C*H* phenyl), 2.20 (s, 3H, CH_3-C=C), 1.98 (q, ^3J(H.H) = 7.5 Hz, 2H, CH_2-CH_3), 1.33 (s, 12H), 0.89 (t, ^3J(H.H) = 7.5 Hz, 3H, CH_3-CH_2).

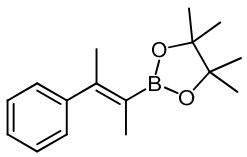
^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K, TMS): δ = 149.0 (C^{IV} phenyl), 144.9 (C^{IV}, C=C), 128.1 (*C*H phenyl), 127.3 (*C*H phenyl), 126.3 (*C*H phenyl), 83.2 (C^{IV}, *C*-O-B), 25.7 (CH_2-CH_3), 24.9 (CH_3-C-O), 24.6 (CH_3-C=C), 15.2 (CH_3-CH_2).

HRMS calcd. for $C_{17}H_{25}BO_2$ $(M-2H+H)^+$ 270.1904 found 270.1900

3.2. General procedure for Scheme 4.

Catalysts and reagents were stored in air. A vial was charged in air with [Cu(Cl)(IMes)] (4.1 mg, 2 mol%), NaO^{t}Bu (0.55 mmol, 53 mg, 1.1 equiv.), bis-(pinacolato)diboron (0.65 mmol, 165 mg, 1.3 equiv.), alkyne (0.5 mmol), CPME (1.4 mL) and the electrophile (3-4 equiv.). The vial was closed with a screw-cap, and the reaction mixture was stirred at 60°C for 24 h. The conversion was determined by GC analysis using an aliquot of the crude mixture. The volatiles were then removed *in vacuo* and the products were purified by column chromatography (SiO_2). The regioselectivity of the product was determined by ^{1}H NMR.

(Z)- 4,4,5,5-tetramethyl-2-(3-phenylbut-2-en-3-yl)-1,3,2-dioxaborolane, 2b[8]

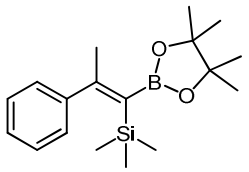


2b

After purification (SiO_2, hexane/ethyl acetate 15:1) **2b** was isolated as a colorless oil in 91 % yield (0.117 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 7.35-7.30 (m, 2H, C*H* phenyl), 7.24-7.19 (m, 1H, C*H* phenyl), 7.13-7.11 (2H, C*H* phenyl), 2.23 (q, ^5J(H,H) = 1.6 Hz, 3H, CH_3), 1.59 (q, ^5J(H,H) = 1.6 Hz, CH_3), 1.33 (s, 12H, CH_3CO).

(Z)-trimethyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl) silane, 3b



3b

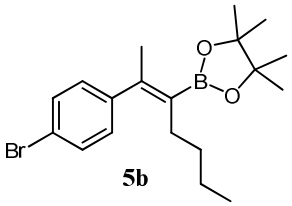
After purification (SiO_2, gradient pentane/diethyl ether 100:0 to 8:2) **3b** was isolated as a colorless solid in 32 % yield (0.051 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.31-7.22 (m, 3H, C*H* phenyl), 7.17-7.13 (m, 2H, C*H* phenyl), 2.10 (s, 3H, CH_3-C=C), 1.30 (s, 12H), -0.16 (s, 9H, CH_3-Si).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 151.8 (s, C^{IV} phenyl), 144.1 (s, *C*=C-Si), 128.5 (s, *C*H phenyl), 127.8 (s, *C*H phenyl), 126.1 (s, *C*H phenyl), 83.6 (s, C^{IV}-O), 60.5 (s, C^{IV}-Si), 24.8 (s, *C*H_3-C-O), 23.2 (s, *C*H_3-C=C), -0.13 (s, *C*H_3-Si).

HRMS calcd. for $C_{18}H_{33}BNO_2Si$ $(M+NH_4)^+$ 333.2409 found 333.2404.

(Z)-2-(2-(4-bromophenyl)hept-2-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 5b



5b

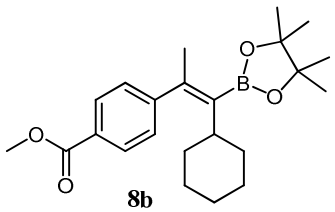
After purification (SiO_2, pentane/dichloromethane 7:3) **5b** was isolated as a colorless solid in 85 % yield (0.161 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 7.43 (d, ^3J(H,H) = 8.5 Hz, 2H, C*H* phenyl), 6.98 (d, ^3J(H,H) = 8.5 Hz, 2H, C*H* phenyl), 2.15 (s, 3H, CH_3-C=C), 1.94 (t, ^3J(H,H) = 7.0 Hz, 2H, C=C-CH_2), 1.33 (s, 12H, CH_3CO), 1.30-1.12 (m, 4H, CH_2), 0.77 (t, ^3J(H,H) = 7.0 Hz, 3H, CH_3-CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 147.2 (s, C^{IV} phenyl), 143.8 (s, C^{IV} phenyl), 131.3 (s, C*H* phenyl), 129.4 (s, C*H* phenyl), 120.2 (s, C^{IV} C=C), 83.4 (s, C^{IV}-O), 32.8 (s, CH_2), 32.2 (s, CH_2), 25.1 (s, CH_3-C=C), 25.0 (s, CH_3-C-O), 22.7 (s, CH_2), 14.1 (s, CH_3).

HRMS calcd. for $C_{19}H_{28}BBrO_2$ $(M+H)^+$ 378.1466 found 378.1475.

(Z)-methyl-4-(1-cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl) benzoate, 8b



8b

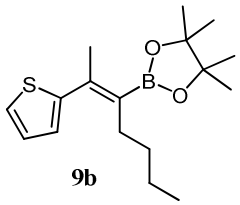
After purification (SiO_2, hexane/ethyl acetate 15:1) **8b** was isolated as a colorless solid in 93 % yield (0.152 g).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ = 7.99 (d, ^{3}J(H,H) = 8.4 Hz, 2H, C*H* phenyl), 7.17 (d, ^{3}J(H,H) = 8.4 Hz, 2H, C*H* phenyl), 3.91 (s, 3H, CH_3-O=CO), 2.07 (s, 3H, CH_3-C=C), 1.96-1.90 (m, 1H, C*H*), 1.72-1.51 (m, 6H, CH_2), 1.37 (s, 12H), 1.28-1.19 (m, 2H, CH_2), 1.06-0.92 (m, 2H, CH_2).

^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): δ = 167.3 (s, C^{IV} carbonyl), 149.9 (s, C^{IV} phenyl), 142.8 (s, C^{IV} phenyl), 129.6 (s, *C*H phenyl), 129.5 (s, *C*H phenyl), 128.9 (s, *C*H phenyl), 128.2 (s, C^{IV} C=C), 127.7 (s, *C*H phenyl), 83.6 (s, C^{IV}-O), 52.2 (s, CH_3-C=O), 42.2 (s, *C*H-C=C), 32.8 (s, CH_2), 26.4 (s, CH_2), 26.2 (s, CH_2), 25.3 (s, CH^3-C-O), 25.2 (S, CH_3-C-O), 24.9 (s, CH_3-C=C).

HRMS calcd. for $C_{23}H_{33}BO_4$ $(M+H)^+$ 384.2582 found 384.2581.

(Z)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)hex-2-en-3-yl)-1,3,2-dioxaborolane, 9b



9b

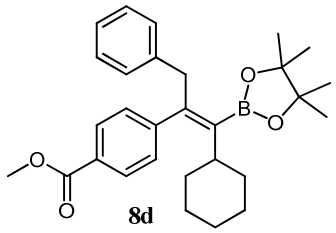
After purification (SiO_2, hexane/ethyl acetate 40:1) **9b** was isolated as a dark orange oil in 97 % yield (0.148 g).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ = 7.22 (dd, ^3J(H,H) = 5.1 Hz, ^4J(H,H) = 1.1 Hz, 1H, C*H* Ar), 6.97 (dd, ^3J(H,H) = 3.5 Hz, ^3J(H,H) = 5.1 Hz, 1H, C*H*-CH-S), 6.87 (dd, ^3J(H,H) = 3.5 Hz, ^4J(H,H) = 1.1 Hz, 1H, CH Ar), 2.27-2.23 (m, 5H, CH_3-C=C and CH_2-C=C), 1.32 (s, 12H), 1.29-1.24 (m, 4H, CH_2), 0.85 (t, ^3J(H,H) = 7.0 Hz, 3H, CH_3-CH_2).

^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): δ = 145.5 (s, CH-C^{IV}-S), 139.6 (C^{IV}-C-S), 126.5 (s, *C*H=CH-S), 125.1 (s, *C*H Ar), 124.2 (s, *C*H Ar), 83.4 (C^{IV}-O), 32.8 (s, *C*H_2-CH_2), 32.6 (s, *C*H_2), 24.9 (s, *C*H_3-C-O), 24.6 (s, *C*H_3-C=C), 22.8 (s, *C*H_2-CH_3), 14.1 (s, *C*H_3-CH_2).

HRMS calcd. for $C_{17}H_{27}BO_2S$ $(M+H)^+$ 306.1938 found 306.1934.

(Z)-methyl-4-(1-cyclohexyl-3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)benzoate, 8b



8d

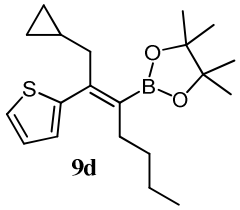
After purification (SiO_2, hexane/ethyl acetate 15:1) **8b** was isolated as a colorless solid in 93% yield (0.152 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 7.84 (d, ^3J(H,H) = 8.3 Hz, 2H, C*H* phenyl), 7.17-7.04 (m, 5H, C*H* phenyl), 6.86 (d, ^3J(H,H) = 8.3 Hz, 2H, C*H* phenyl), 3.86 (s, 3H, CH_3-OOC), 3.71 (s, 2H, CH_2-C=C), 1.92-1.82 (m, 1H, C*H*-C=C), 1.63-1.53 (m, 4H, CH_2), 1.37 9s, 12H), 1.09-0.87 (m, 4H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 167.3 (s, C^{IV} carbonyl), 147.7 (s, C^{IV} phenyl), 146.0 (s, C^{IV} phenyl), 139.2 (s, C^{IV} phenyl), 129.2 (s, *C*H phenyl), 129.1 (s, *C*H phenyl), 128.4 (s, *C*H phenyl), 128.1 (s, *C*H phenyl), 126.0 (s, *C*H phenyl), 83.8 (s, C^{IV}-O), 52.0 (s, CH_3-C=O), 45.2 (s, CH_2-C=C), 42.3 (s, *C*H-C=C), 32.8 (s, CH_2), 26.3 (s, CH_2), 26.1 (s, CH_2), 25.1 (s, CH^3-C-O).

HRMS calcd. for $C_{29}H_{37}BO_4$ $(M+NH_4)^+$ 477.3155 found 477.3159.

(Z)-2-(1-cyclopropyl-2-(thiophen-2-yl)hept-2-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 9d



9d

After purification (SiO_2, pentane/dichloromethane 6:4) **9d** was isolated as an orange oil in 60 % yield (0.104 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 7.23 (dd, ^{3}J(H,H) = 5.1 Hz, ^{4}J(H,H) = 1.1 Hz, 1H, C*H* Ar), 6.98 (dd, ^{3}J(H,H) = 3.5 Hz, ^{3}J(H,H) = 5.1 Hz, 1H, C*H*-CH-S), 6.83 (dd, ^{3}J(H,H) = 3.5 Hz, J(H,H) = 1.1 Hz, 1H, C*H* Ar), 2.48 (d, ^{3}J(H,H) = 7.0 Hz, 2H, CH-CH_2-C=C), 2.17 (t, ^{3}J(H,H) = 6.9 Hz, 2H, CH_2-CH_2-C=C), 1.35-1.21 (m, 4H, CH_2), 1.30 (s, 12H), 0.82 (t, ^{3}J(H,H) = 7.4 Hz, 3H, CH_3), 0.76-0.71 (m, 1H, C*H*-CH_2-CH_2), 0.35-0.30 (m, 2H, CH_2-CH_2-CH), 0.10-0.06 (m, 2H, CH_2-CH_2-CH).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 144.2 (s, CH-C^{IV}-S), 126.5 (s, *C*H=CH-S), 125.6 (s, *C*H Ar), 124.2 (s, *C*H Ar), 83.4 (C^{IV}-O), 43.6 (s, CH_2-CH-CH_2), 32.9 (s, CH_2-CH_2), 32.5 (s, CH_2), 24.9 (s, CH_3-C-O), 22.8 (s, CH_2-CH_3), 14.1 (s, CH_3-CH_2), 10.9 (s, *C*H-CH_2-CH_2), 4.4 (s, CH_2, cyclopropane).

HRMS calcd. for $C_{20}H_{31}BO_2S$ $(M+H)^+$ 346.2253 found 346.2247.

4. General procedure for α-hydroboration of internal alkynes

4.1.General procedure for Table 4.

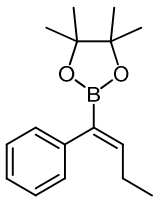
In a glovebox, a vial was charged with the Cu catalyst, the base, 1-phenyl-1-butyne **1** (0.50 mmol, 0.071 mL) and the solvent (0.6 mL). The reaction mixture was stirred for 5 minutes at RT, cooled down to -30°C and then pinacolborane HB(pin) was added slowly (0.75 mmol, 0.11 mL, 1.5 equiv.). The reaction mixture was allowed to warm up to RT for 20 h under inert atmosphere. The conversion was determined by GC analysis using an aliquot of the crude mixture. The volatiles were then removed *in vacuo* and the products were purified by column chromatography (SiO_2). The regioselectivity and the (*α:β*) ratio of the products were determined by ^{1}H NMR.

4.2. General procedure for Table 5.

Catalysts and reagents were stored in air, with the exception of HB(pin) which was kept under argon to avoid decomposition. A vial was charged in air with [Cu(Cl)(IMes)], NaOH (2.5 mg, 12 mol%), 1-phenyl-1-butyne **1** (0.50 mmol, 0.071 mL) and CPME (0.6 mL). The mixture was stirred for 5 minutes and cooled down to -30°C and then pinacolborane HB(pin) was added slowly (0.75 mmol, 0.11 mL, 1.5 equiv.). The vial was closed with a screw-cap, and the reaction mixture was stirred at the required temperature for 20 h. The conversion was determined by GC analysis using an aliquot of the crude mixture. The volatiles were then removed *in vacuo* and the products were purified by column chromatography (SiO_2). The regioselectivity and the (*α:β*) ratio of the products were determined by ^{1}H NMR.

^{1}H and ^{13}C-{^{1}H} NMR data were found similar to literature values for **1c**.[5]

(Z)- 4,4,5,5-tetramethyl-2-(1-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane, 1c[5]



1c

After purification (SiO_2, hexane/ethyl acetate 20:1) **1c** was isolated as a yellowish oil in 94 % yield (0.121 g).

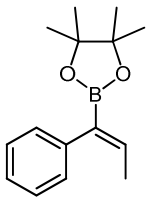
^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 7.33-7.28 (m, 2H, C*H* phenyl), 7.22-7.12 (m, 3H, C*H* phenyl), 6.57 (t, ^3J(H,H) = 7.3 Hz, 1H, C*H*-CH_2), 2.17 (q, ^3J(H,H) = 7.3 Hz, 2H, CH-CH_2-CH_3), 1.27 (s, 12H), 1.00 (t, ^3J(H,H) = 7.3 Hz, 3H, CH_3-CH_2).

4.3. General procedure for Scheme 6.

Catalysts and reagents were stored in air, with the exception of HB(pin) which was kept under argon to avoid decomposition. A vial was charged in air with [Cu(Cl)(IMes)], NaOH (2.5 mg, 12 mol%), alkyne (0.50 mmol) and CPME (0.6 mL). The mixture was stirred for 5 minutes, cooled down to -30°C and then pinacolborane HB(pin) was added slowly (0.75 mmol, 0.11 mL, 1.5 equiv.). The vial was closed with a screw-cap and the reaction mixture was stirred at 80°C for 20 h. The conversion was determined by GC analysis using an aliquot of the crude mixture. The volatiles were then removed *in vacuo* and the products were purified by column chromatography (SiO_2). The regioselectivity and the (*α:β*) ratio of the products were determined by ^{1}H NMR.

^{1}H and ^{13}C-{^{1}H} NMR data were found similar to literature values for **2c**,[3] **3c**,[3] **5c**,[3] **7c**,[3] **8c**,[3] and **9c**.[3]

(Z)- 4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane, 2c[3]

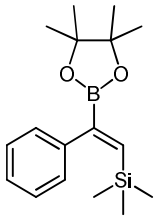


2c

After purification (SiO_2, hexane/ethyl acetate 30:1) **2c** was isolated as a yellowish oil in 70 % yield (0.085 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 7.34-7.29 (m, 2H, C*H* phenyl), 7.22-7.14 (m, 3H, C*H* phenyl), 6.72 (q, ^3J(H,H) = 6.9 Hz, 1H, C*H*-CH_3), 1.77 (d, ^3J(H,H) = 6.9 Hz, 3H, CH_3-CH), 1.27 (s, 12H).

(Z)-trimethyl(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane, 3c[3]

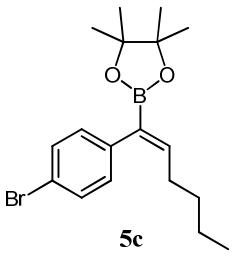


3c

After purification (SiO_2, hexane/ethyl acetate 40:1) **3c** was isolated as a colorless solid in 87% yield (0.132 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 8.01 (s, 1H, C*H*-Si), 7.29-7.27 (m, 3H, C*H* phenyl), 7.26-7.23 (m, 2H, C*H* phenyl), 1.30 (s, 12H), 0.00 (s, (9H, Si-CH_3).

(Z)- 4,4,5,5-tetramethyl-2-(1-phenylhex-1-en-1-yl)-1,3,2-dioxaborolane, 5c[3]

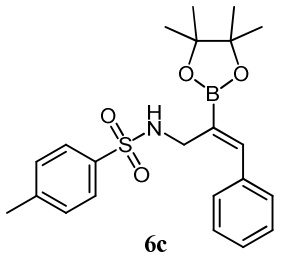


5c

After purification (SiO_2, hexane/ethyl acetate 30:1) **5c** was isolated as a yellowish oil in 91% yield (0.166 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 7.42 (d, ^3J(H,H) = 8.6 Hz, 2H, C*H* phenyl), 7.00 (d, ^3J(H,H)= 8.6 Hz, 2H, C*H* phenyl), 6.59 (t, ^3J(H,H) = 7.5 Hz, 1H, C*H*-CH_2), 2.17-2.05 (m, 2H, CH_2), 1.40-1.19 (m, 4H, CH_2), 1.26 (s, 12H), 0.83 (t, ^3J(H,H) = 7.1 Hz, 3H, CH_3-CH_2).

(Z)-4-methyl-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)allyl) benzenesulfonamide, 6c



6c

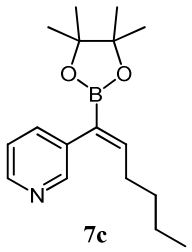
Following the procedure described in 4.2, compounds **6c** and **6a** were obtained as a mixture 75:25 as a yellowish solid after purification (SiO_2, dichloromethane/diethylether 20:1) in 65 % yield (0.134 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS) of **6a**: δ = 7.63 (d, ^3J(H,H) = 8.4 Hz, 2H, C*H* phenyl), 7.36-7.28 (m, 4H, C*H* phenyl), 7.24-7.18 (m, 5H, C*H* phenyl), 5.33 (t, ^3J(H,H) = 6.0 Hz, 1H, C*H*-CH_2), 3.96 (dd, ^3J(H,H) = 6.0 Hz, ^3J(H,H) = 1.2 Hz, 2H, CH_2-NH), 2.42 (s, 3H, CH_3), 1.26 (s, 12H).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS) of **6c**: δ = 7.81 (d, ^3J(H,H) = 8.6 Hz, 2H, C*H* phenyl), 7.72 (d, ^3J(H,H) = 8.6 Hz, 2H, C*H* phenyl), 7.68-7.66 (m, 1H, C*H* phenyl), 7.09 (d, ^3J(H,H) = 7.5 Hz, 2H, C*H* phenyl), 7.00 (d, ^3J(H,H) = 7.5 Hz, 2H, C*H* phenyl), 5.60-5.52 (m, 1H, C*H*=C-B), 4.78 (broad m, 1H, N*H*), 3.88-3.83 (m, 2H, CH_2-NH), 2.43 (s, 3H, CH_3 tosyl), 1.24 (s, 12H).

HRMS calcd. for $C_{22}H_{28}BNO_4S$ $(M+H)^+$ 413.1936 found 413.1941.

(Z)-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)pyridine, 7c[3]

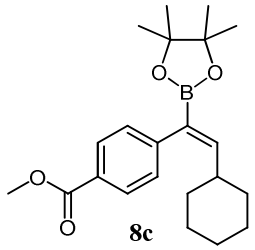


7c

After purification (SiO_2, hexane/ethyl acetate 7:3) **7c** was isolated as a dark brown oil in 99 % yield (0.142 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 8.43 (br. s, 2H, C*H* Ar), 7.48 (d, ^3J(H,H) = 7.5 Hz, 1H, C*H* Ar), 7.26 (br. s, 1H, C*H* Ar), 6.69 (t, ^3J(H,H) = 7.5 Hz, 1H, C*H*-CH_2), 2.14 (q, ^3J(H,H) = 7.4 Hz, 2H, CH_2-CH_3), 1.46-1.32 (m, 4H, CH_2), 1.24 (s, 12H), 0.83 (t, ^3J(H,H) = 7.4 Hz, 3H, CH_3-CH_2).

(Z)-methyl-4-(2-cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate, 8c[3]

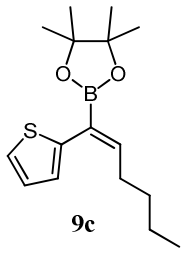


8c

After purification (SiO_2, hexane/ethyl acetate 15:1) **8c** was isolated as a colorless solid in 99 % yield (0.184 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 7.98 (d, ^3J(H,H) = 8.2 Hz, 2H, C*H* phenyl), 7.18 (d, ^3J(H,H) = 8.2 Hz, 2H, C*H* phenyl), 6.40 (d, ^3J(H,H) = 10.4 Hz, 1H, C*H*=C-B), 3.91 (s, 3H, CH_3-O-CO), 2.29 - 2.16 (m, 1H, C*H*-CH=C), 1.67 - 1.57 (m, 4H, CH_2), 1.26 (s, 12H), 1.18 - 1.10 (m, 6H, CH_2).

(Z)- 4,4,5,5-tetramethyl-2-(1-thiophen-2-yl)-hex-1-en-1-yl)-1,3,2-dioxaborolane, 9c[3]



9c

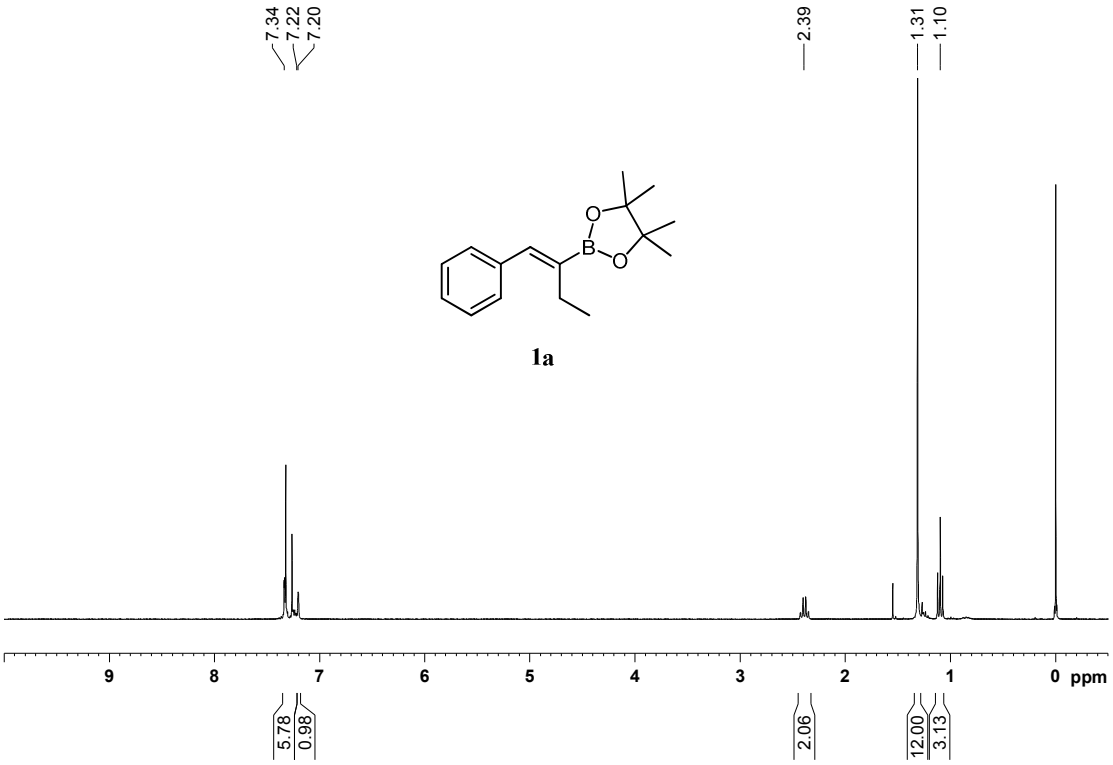
After purification (SiO_2, hexane/ethyl acetate 20:1) **9c** was isolated as a dark orange oil in 78% yield (0.114 g).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 7.24 (dd, ^3J(H,H) = 5.1 Hz, ^4J(H,H) = 1.1 Hz, 1H, C*H*-S), 7.13 (dd, ^3J(H,H) = 3.5Hz, ^4J(H,H) = 1.1 Hz, 1H, C*H*-C-S), 7.01 (dd, ^3J(H,H) = 5.1 Hz, ^3J(H,H) = 3.5 Hz, 1H, C*H*-CH-S), 6.55 (t, ^3J(H,H) = 7.1 Hz, 1H, C*H*=C-

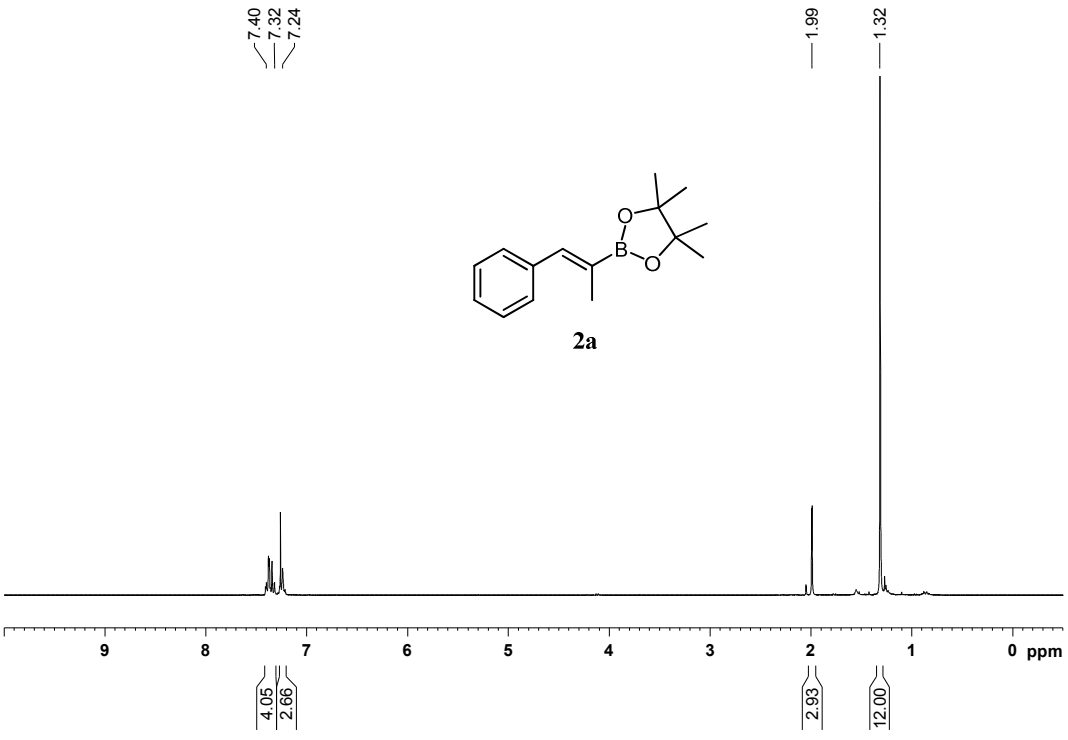
B), 2.46-2.39 (m, 2H, CH_2-CH=C), 1.54-1.32 (m, 4H, CH_2), 1.30 (s, 12H), 0.90 (t, ^3J(H,H) = 7.2 Hz, 3H, CH_3).

5. ^{1}H and ^{13}C-{^{1}H} NMR spectra

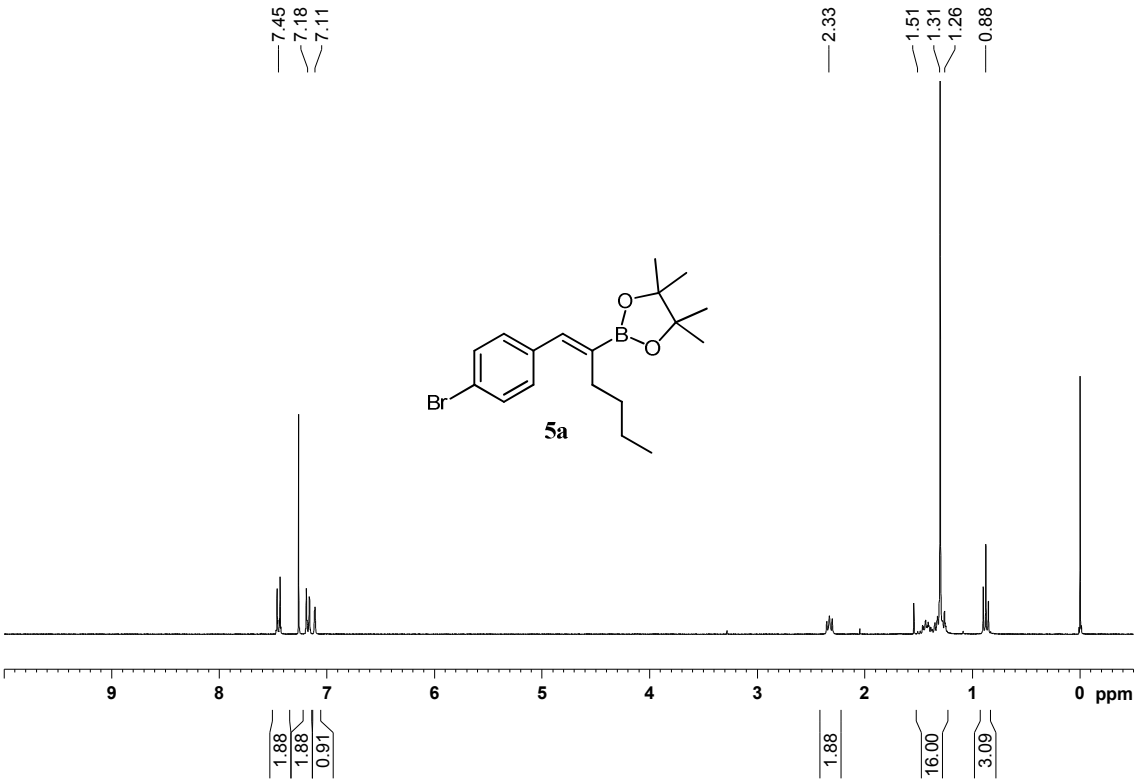
^{1}H and ^{13}C-{^{1}H} NMR spectra of products 1a-9a

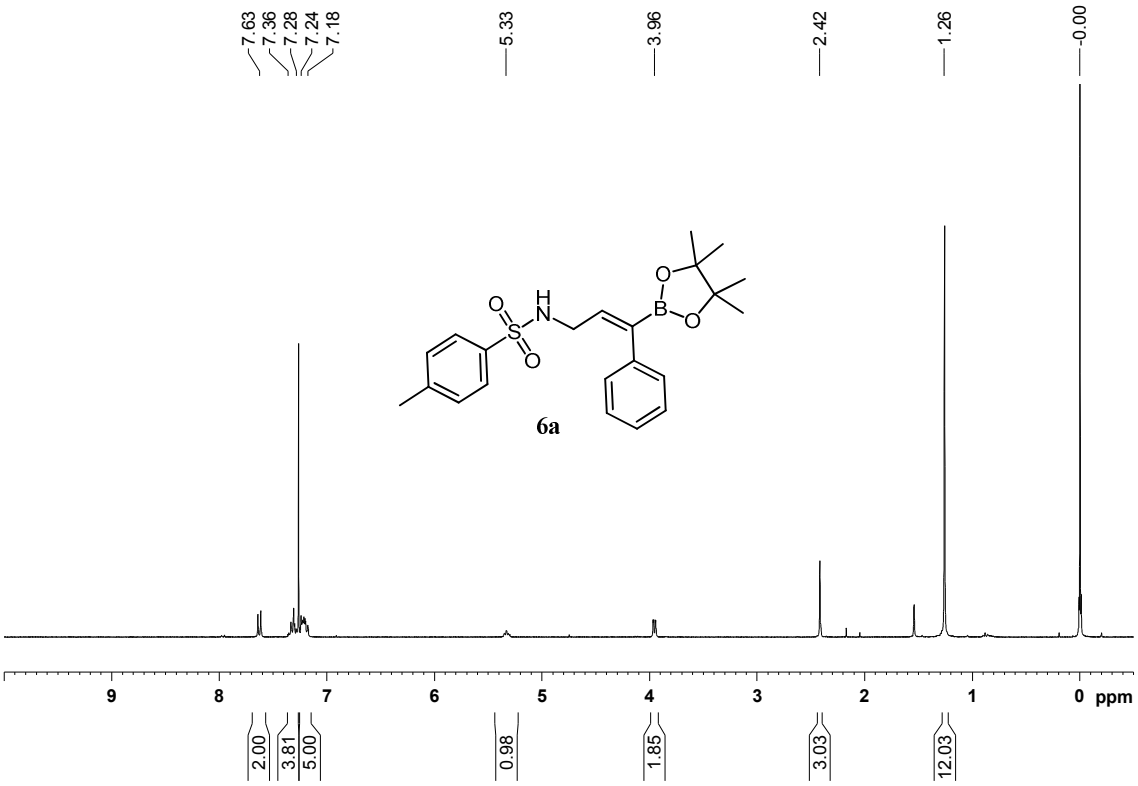


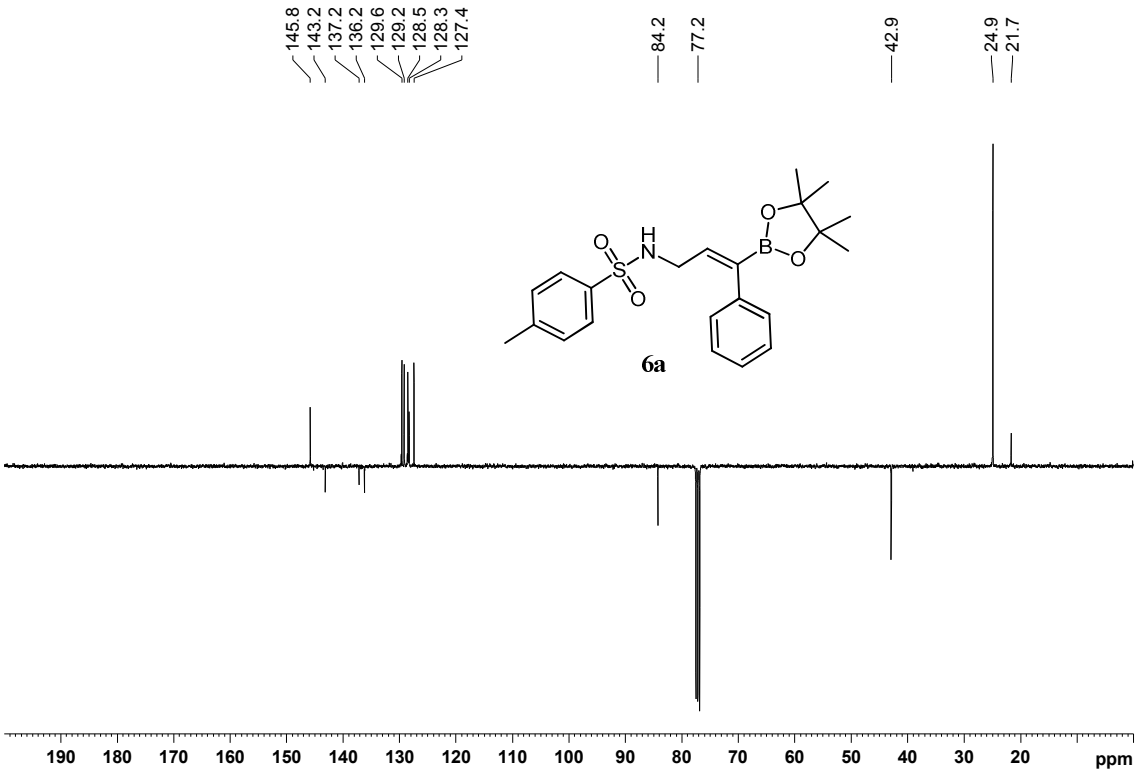
1a



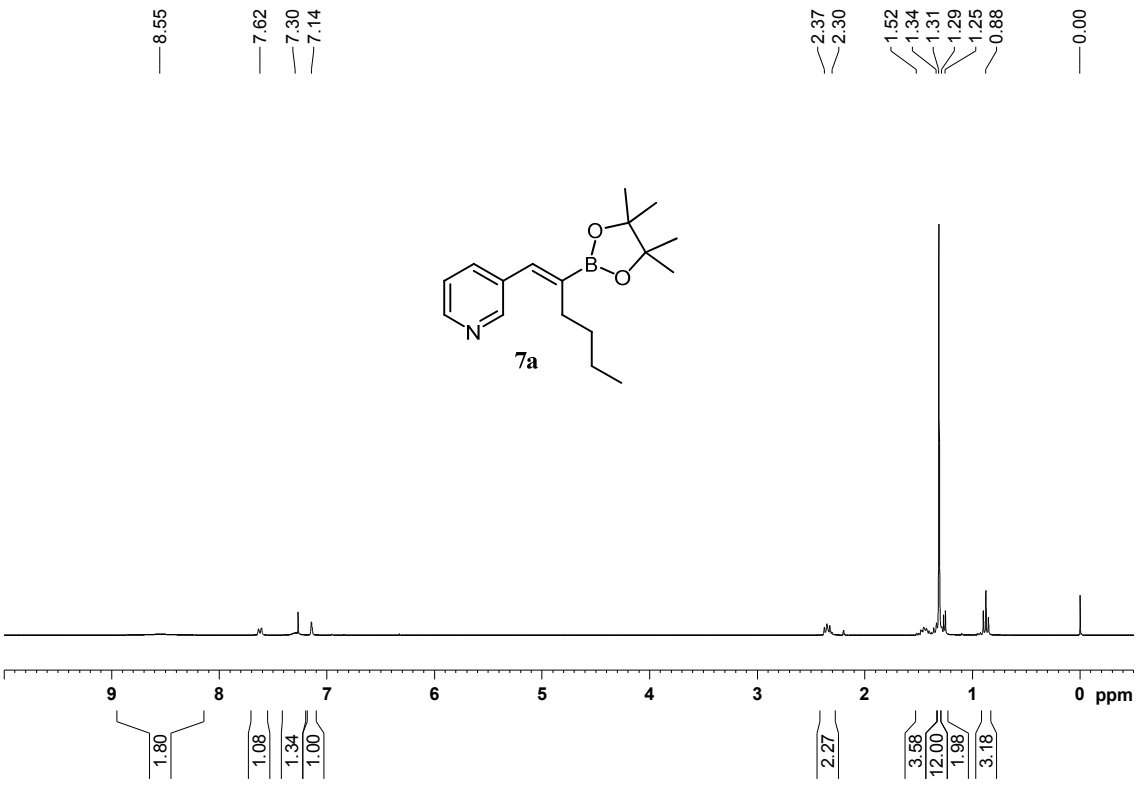
2a


7.45
7.18
7.11
2.33
1.51
1.31
1.26
0.88
Br
O
B
O
5a
9
8
7
6
5
4
3
2
1
0 ppm
1.88
1.88
0.91
1.88
16.00
3.09

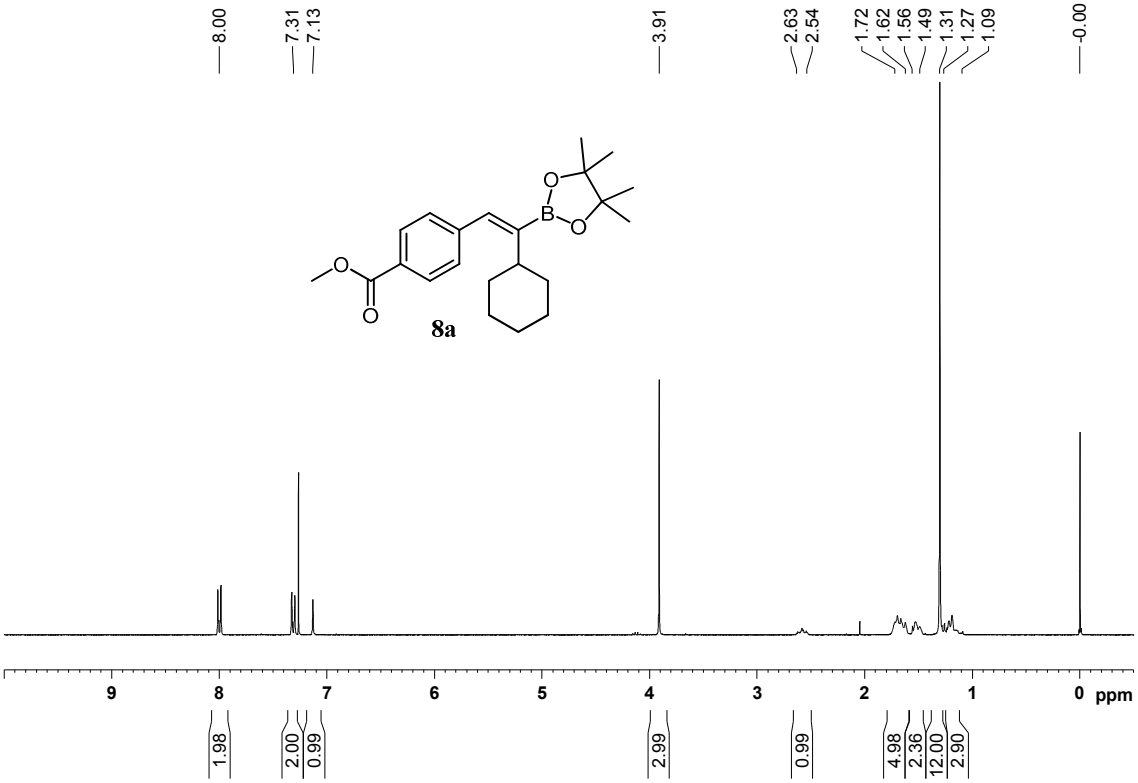

7.63
7.36
7.28
7.24
7.18
5.33
3.96
2.42
1.26
-0.00
O
S
O
H
N
O
B
O
6a
9
8
7
6
5
4
3
2
1
0 ppm
2.00
3.81
5.00
0.98
1.85
3.03
12.03

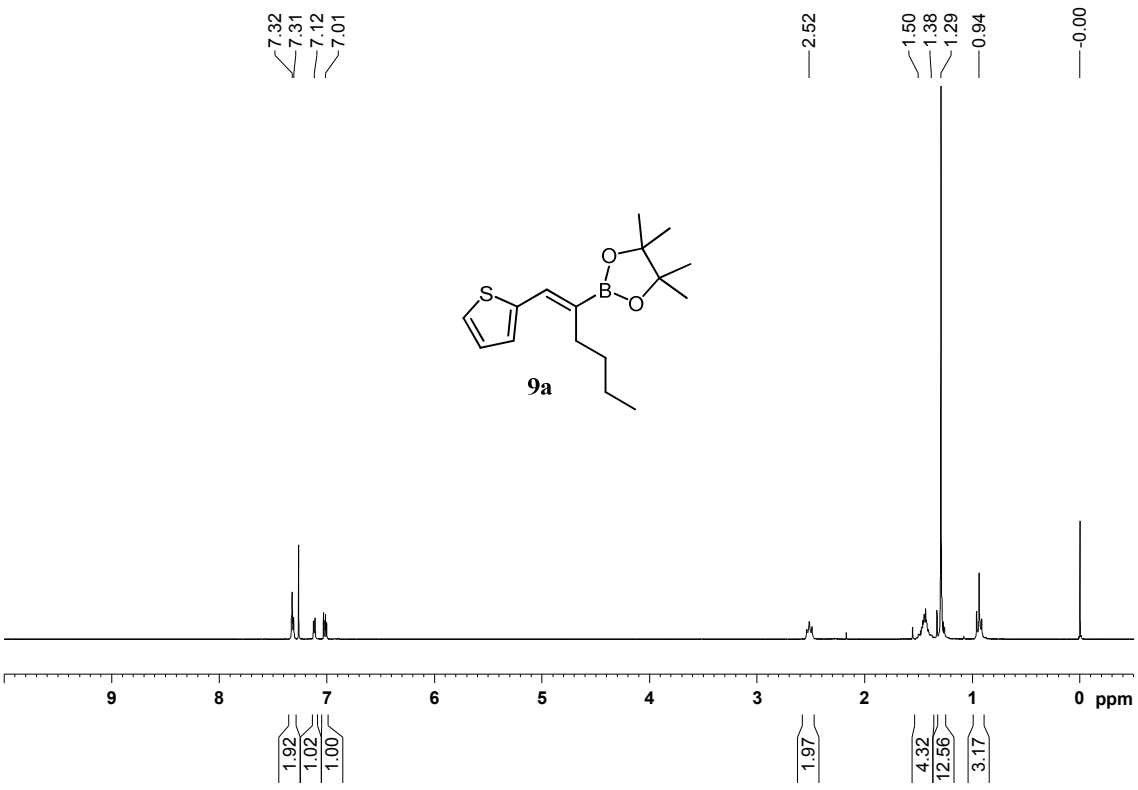

145.8
143.2
137.2
136.2
129.6
129.2
128.5
128.3
127.4
84.2
77.2
42.9
24.9
21.7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

6a

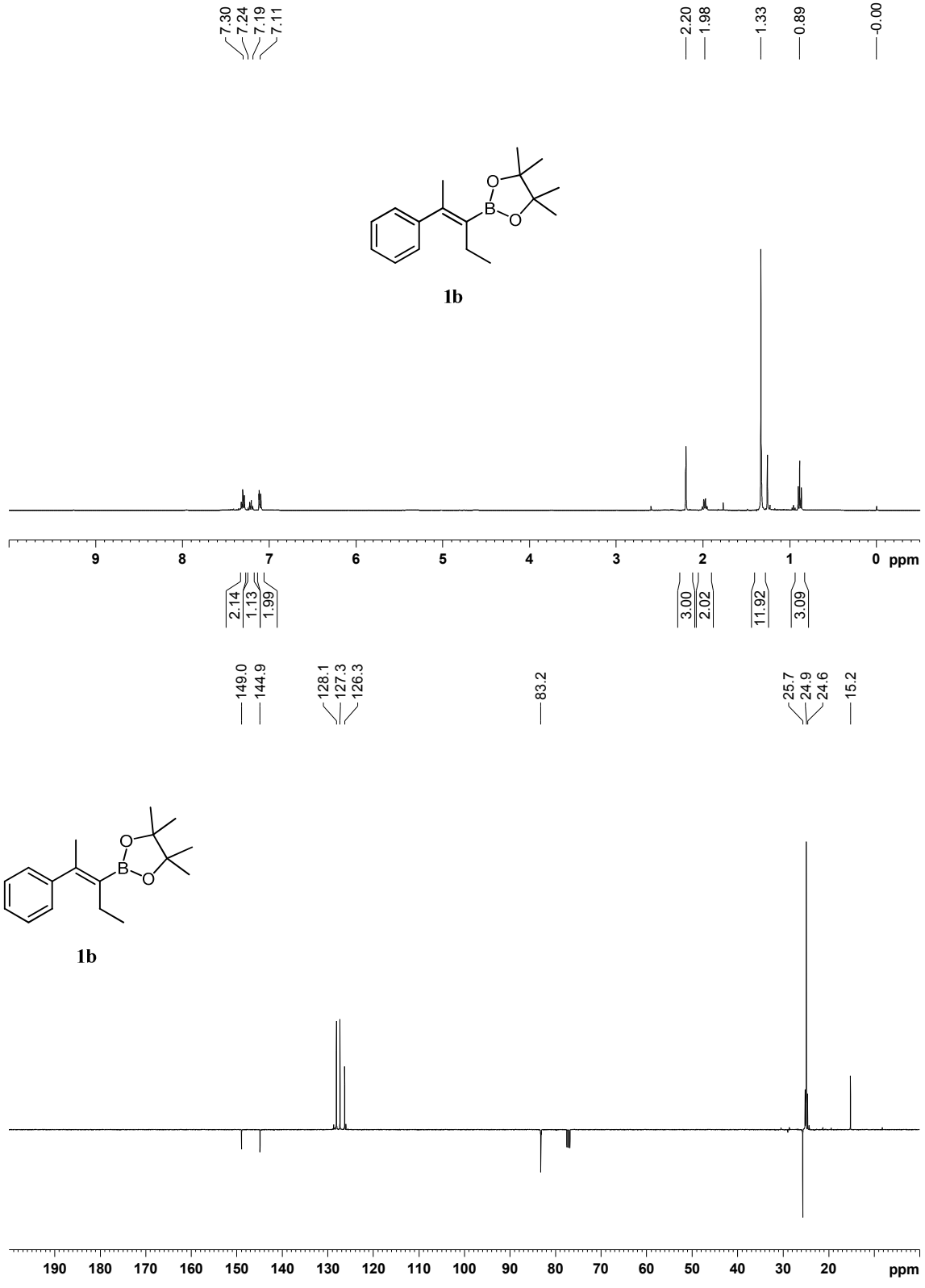

8.55
7.62
7.30
7.14
2.37
2.30
1.52
1.34
1.31
1.29
1.25
0.88
0.00
9 8 7 6 5 4 3 2 1 0 ppm
1.80
1.08
1.34
1.00
2.27
3.58
12.00
1.98
3.18

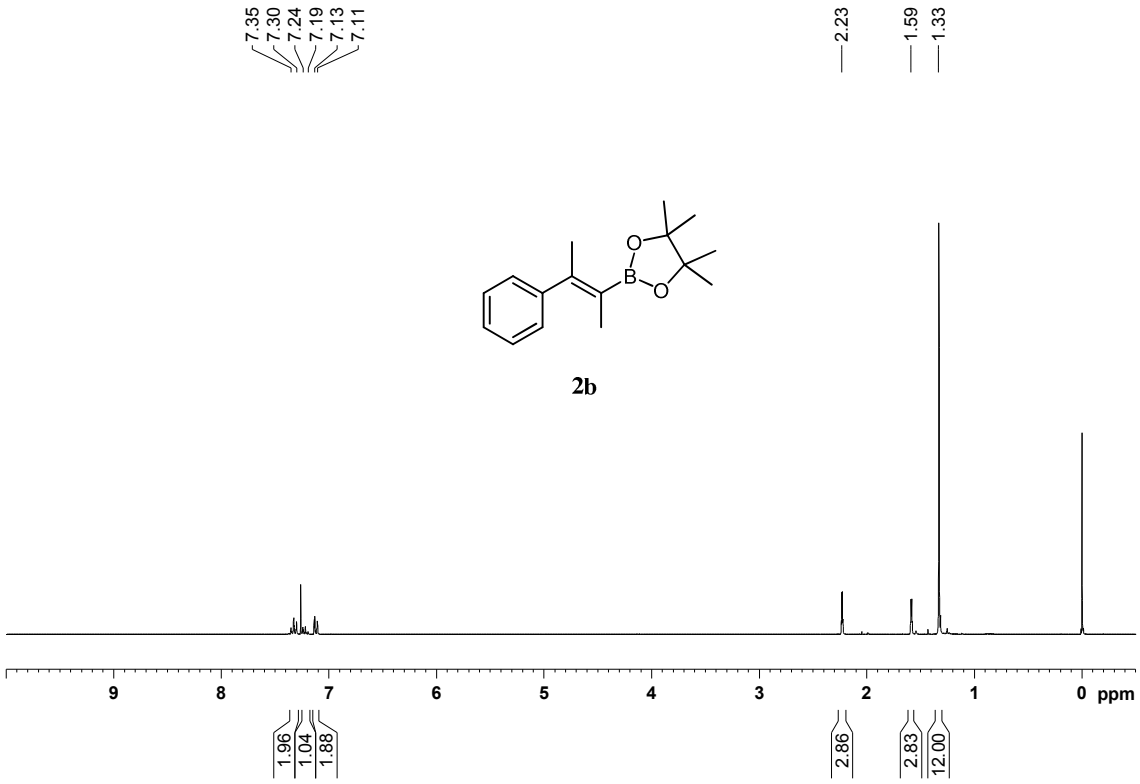
7a


8.00
7.31
7.13
3.91
2.63
2.54
1.72
1.62
1.56
1.49
1.31
1.27
1.09
-0.00
O
B
O
O
O
8a
9
8
7
6
5
4
3
2
1
0 ppm
1.98
2.00
0.99
2.99
0.99
4.98
2.36
12.00
2.90

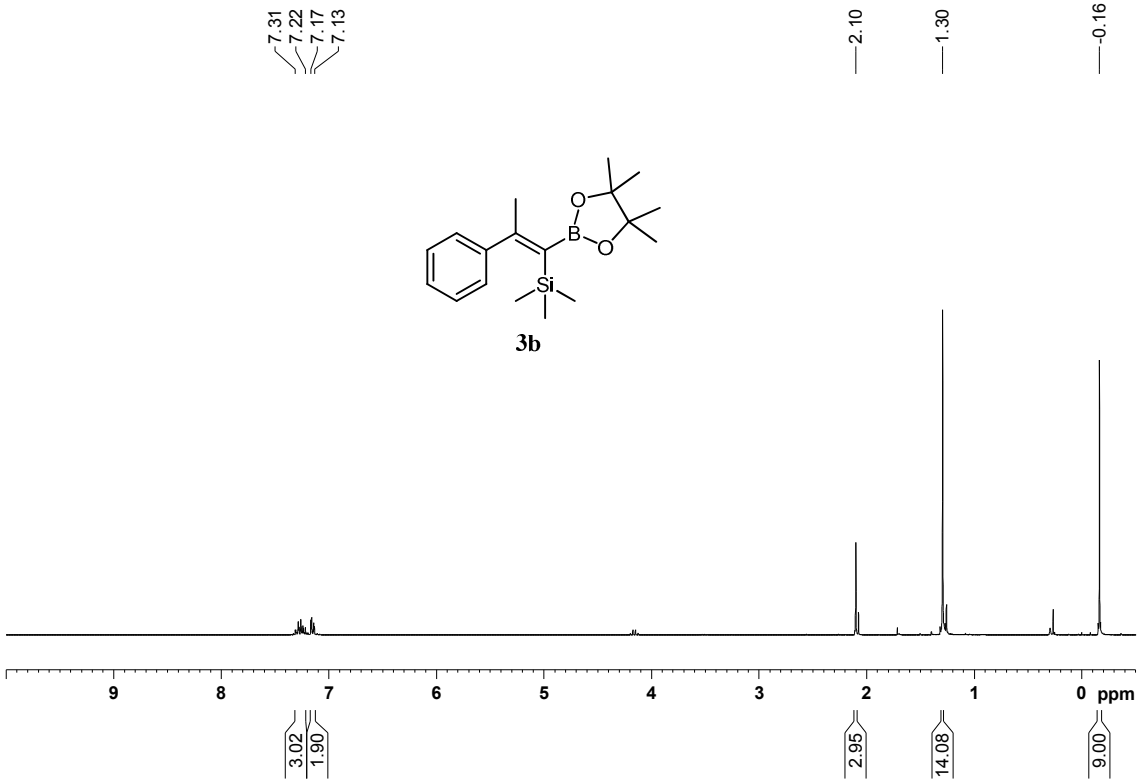

7.32
7.31
7.12
7.01
2.52
1.50
1.38
1.29
0.94
-0.00
S
O
B
O
9a
9
8
7
6
5
4
3
2
1
0 ppm
1.92
1.02
1.00
1.97
4.32
12.56
3.17

^{1}H and ^{13}C-{^{1}H} NMR spectra of products 1b-9b, 8d and 8f.

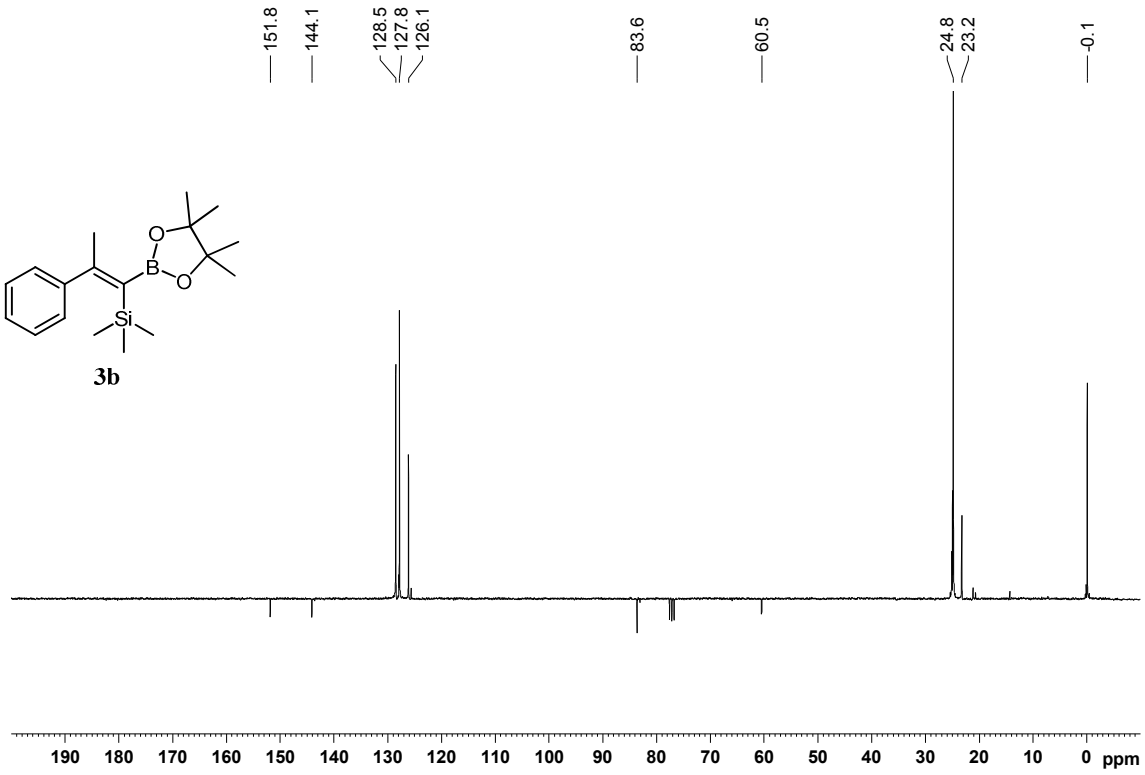



7.35
7.30
7.24
7.19
7.13
7.11
2.23
1.59
1.33
O
B
O
O
9
8
7
6
5
4
3
2
1
0 ppm
1.96
1.04
1.88
2.86
2.83
12.00

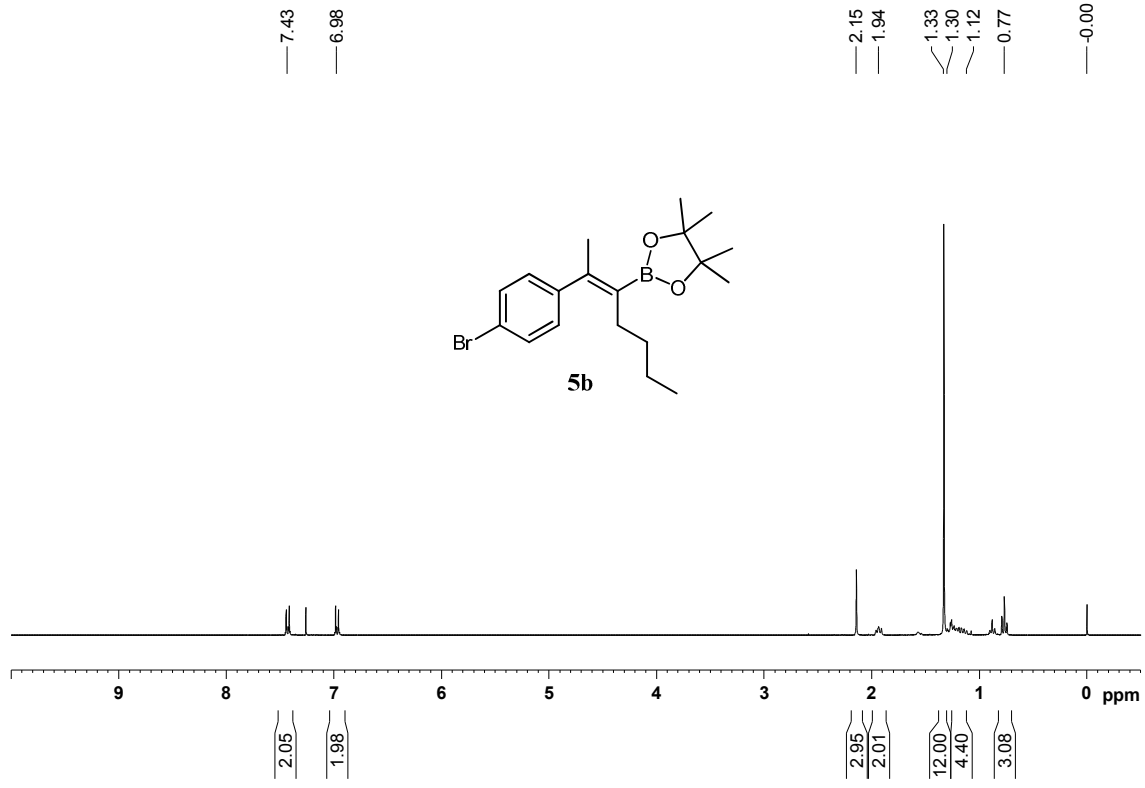
2b


7.31
7.22
7.17
7.13
2.10
1.30
-0.16
O
B
O
Si
9
8
7
6
5
4
3
2
1
0 ppm
3.02
1.90
2.95
14.08
9.00

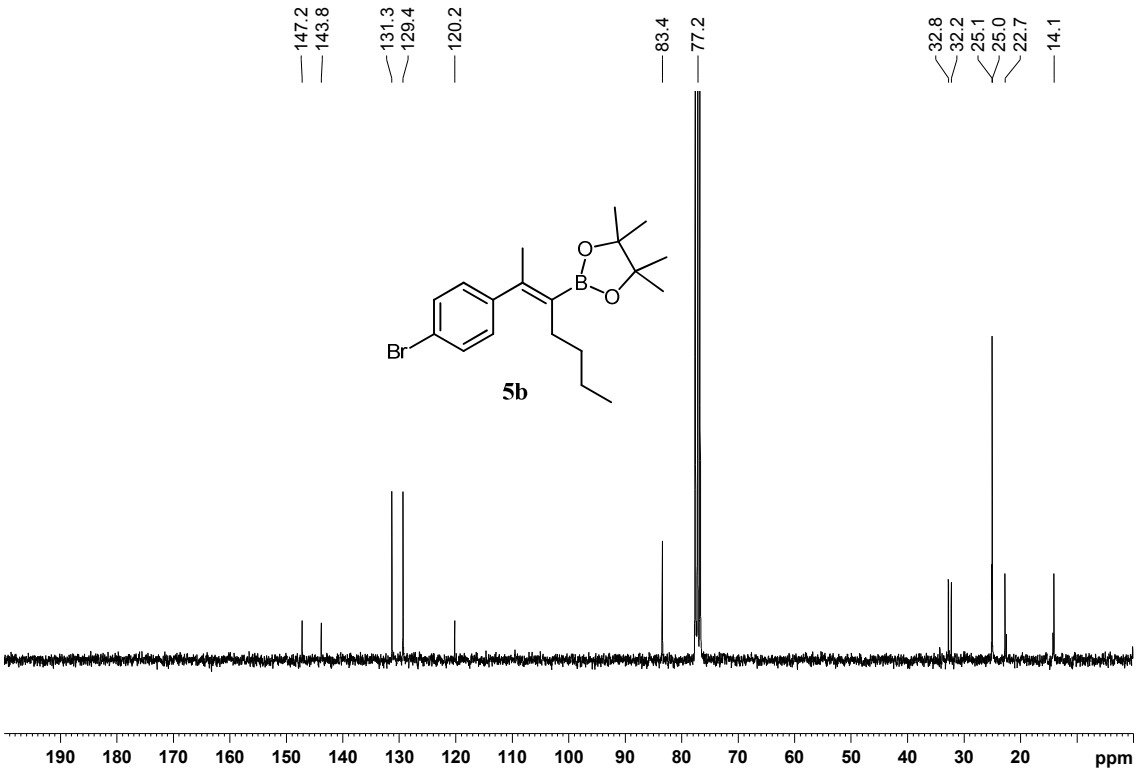
3b

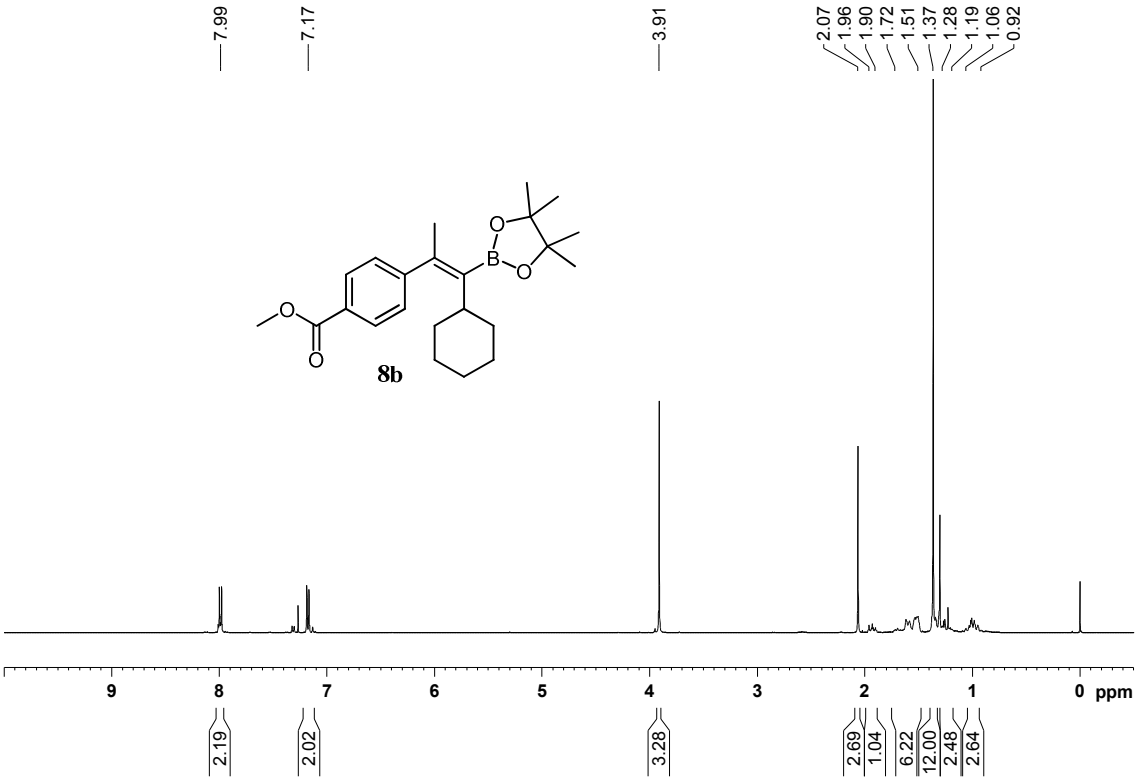

151.8
144.1
128.5
127.8
126.1
83.6
60.5
24.8
23.2
-0.1
O
B
O
Si
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

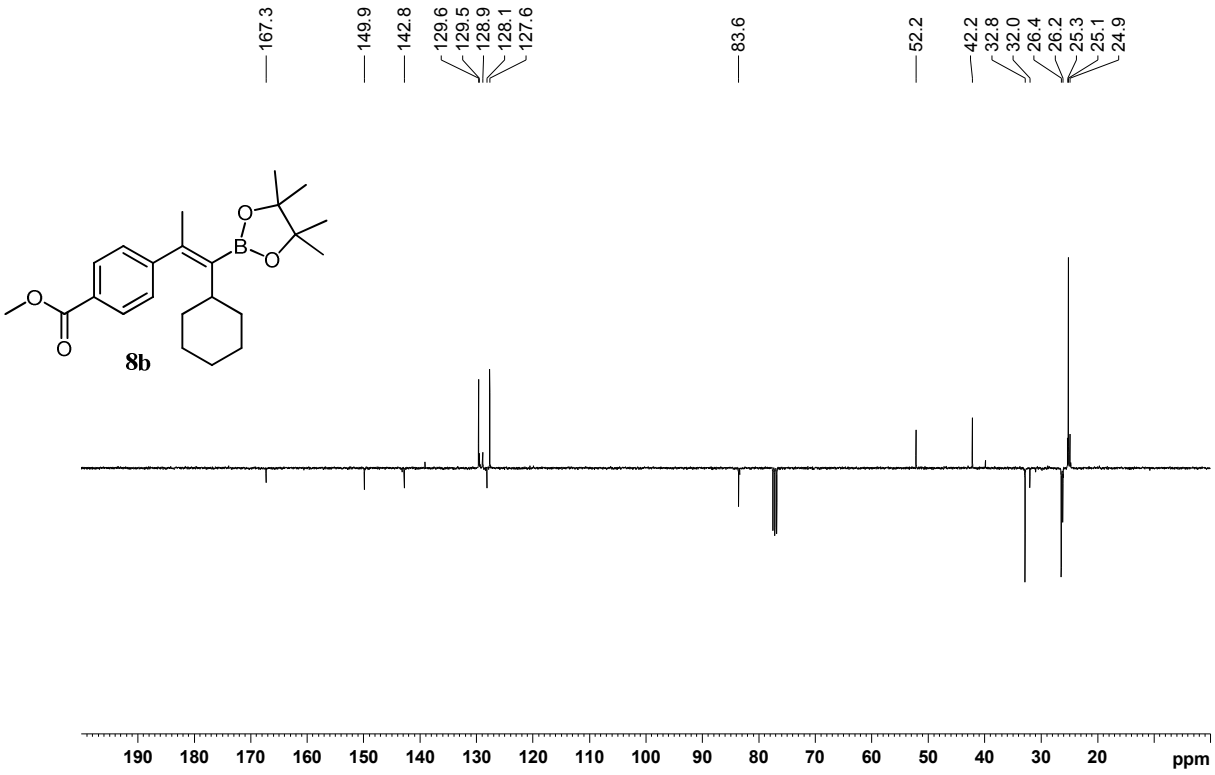
3b

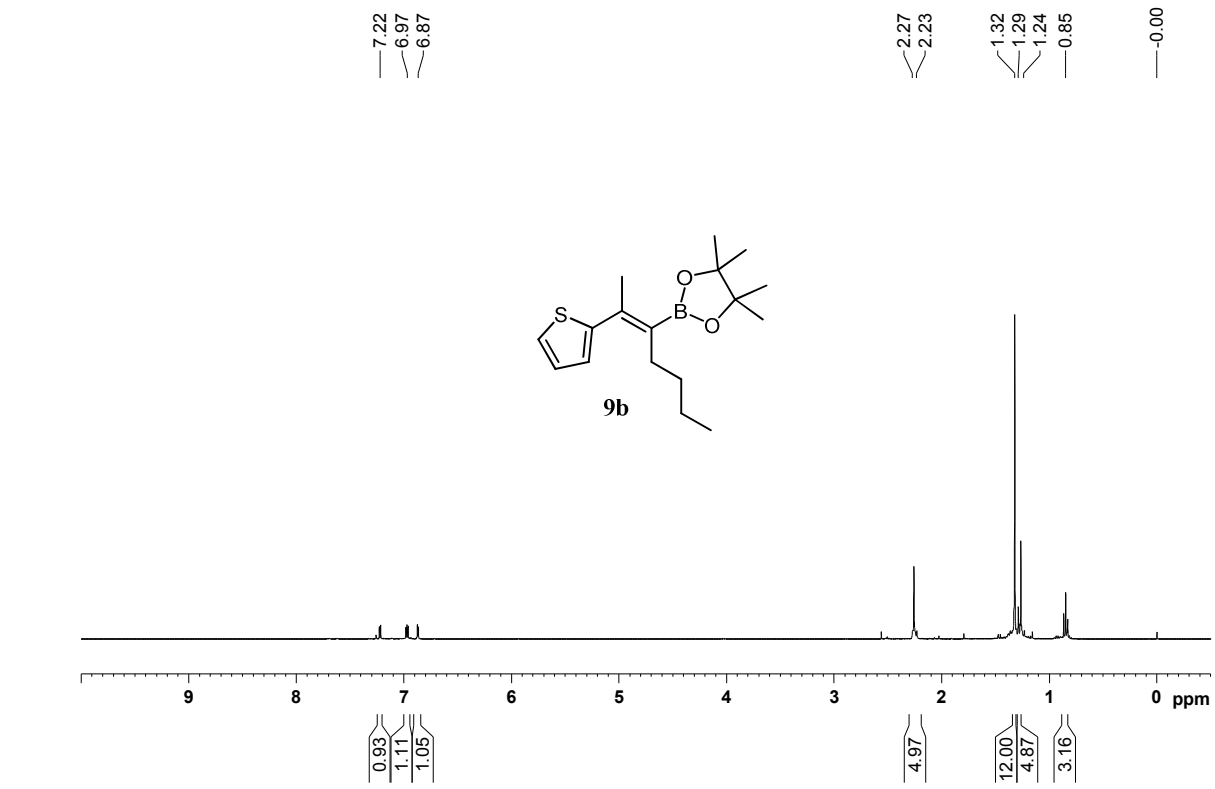

7.43
6.98
2.15
1.94
1.33
1.30
1.12
0.77
-0.00
O
B
O
Br
9 8 7 6 5 4 3 2 1 0 ppm
2.05
1.98
2.95
2.01
12.00
4.40
3.08

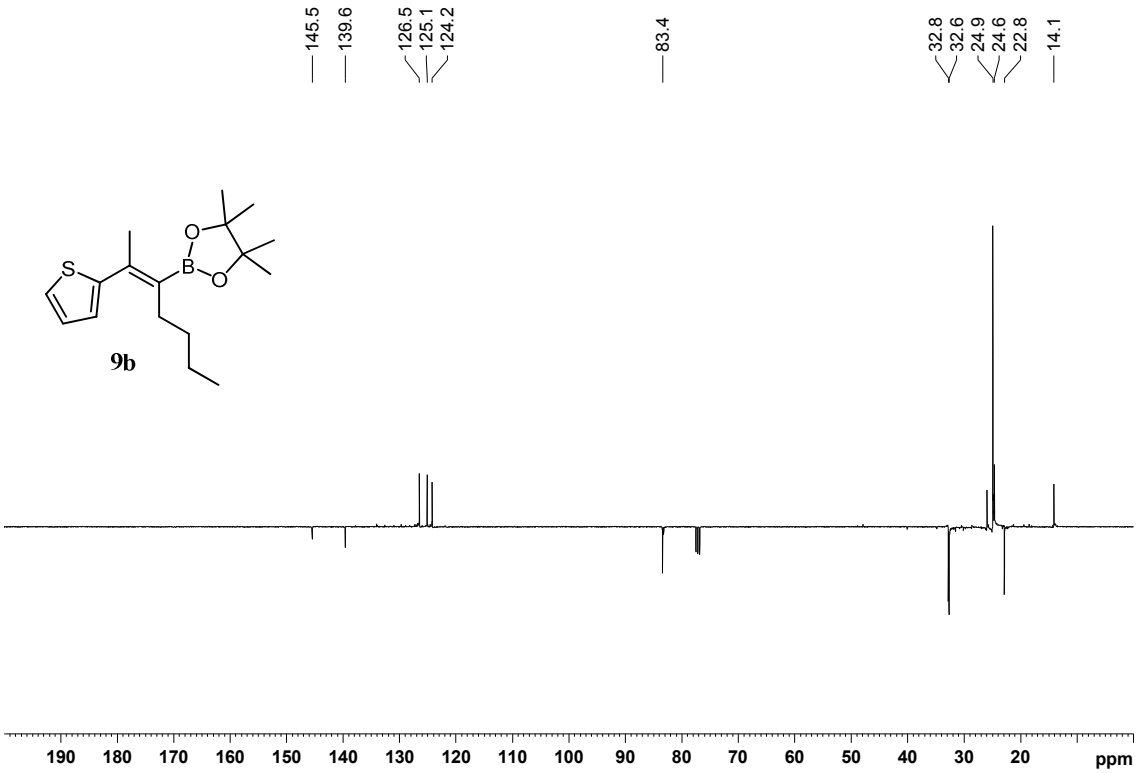
5b

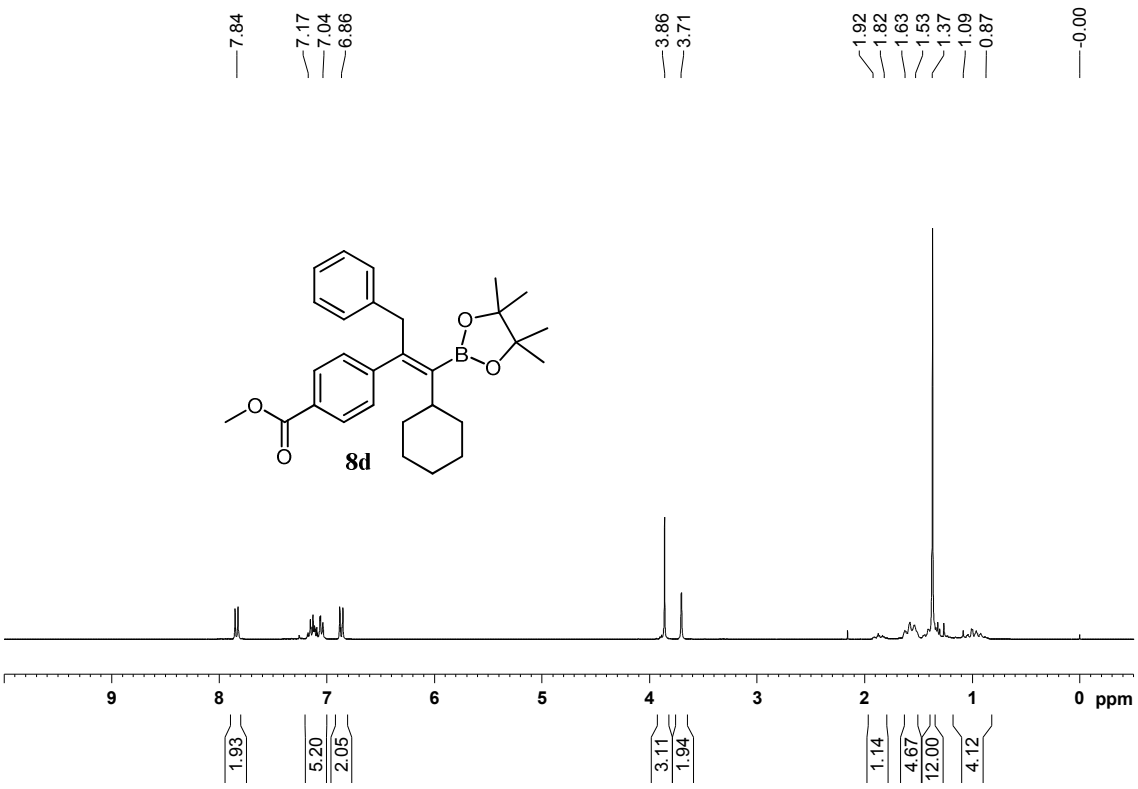

147.2
143.8
131.3
129.4
120.2
83.4
77.2
32.8
32.2
25.1
25.0
22.7
14.1
Br
5b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

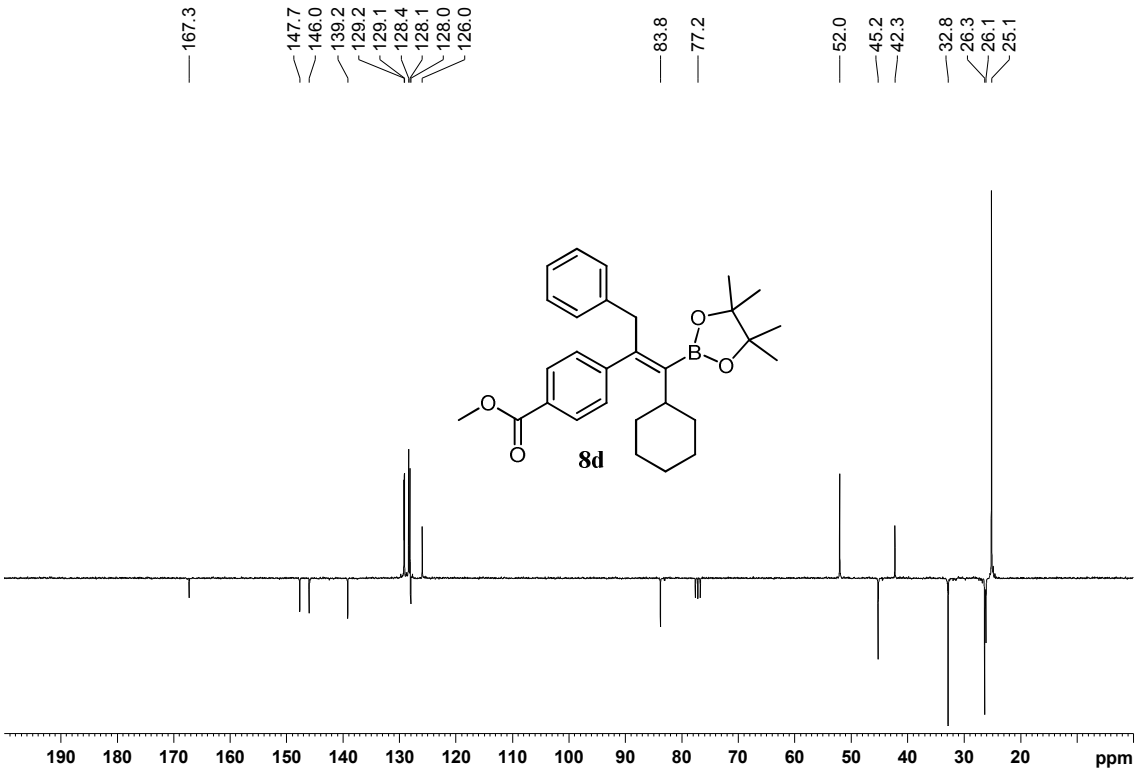

7.99
7.17
3.91
2.07
1.96
1.90
1.72
1.51
1.37
1.28
1.19
1.06
0.92
8b
9 8 7 6 5 4 3 2 1 0 ppm
2.19
2.02
3.28
2.69
1.04
6.22
12.00
2.48
2.64

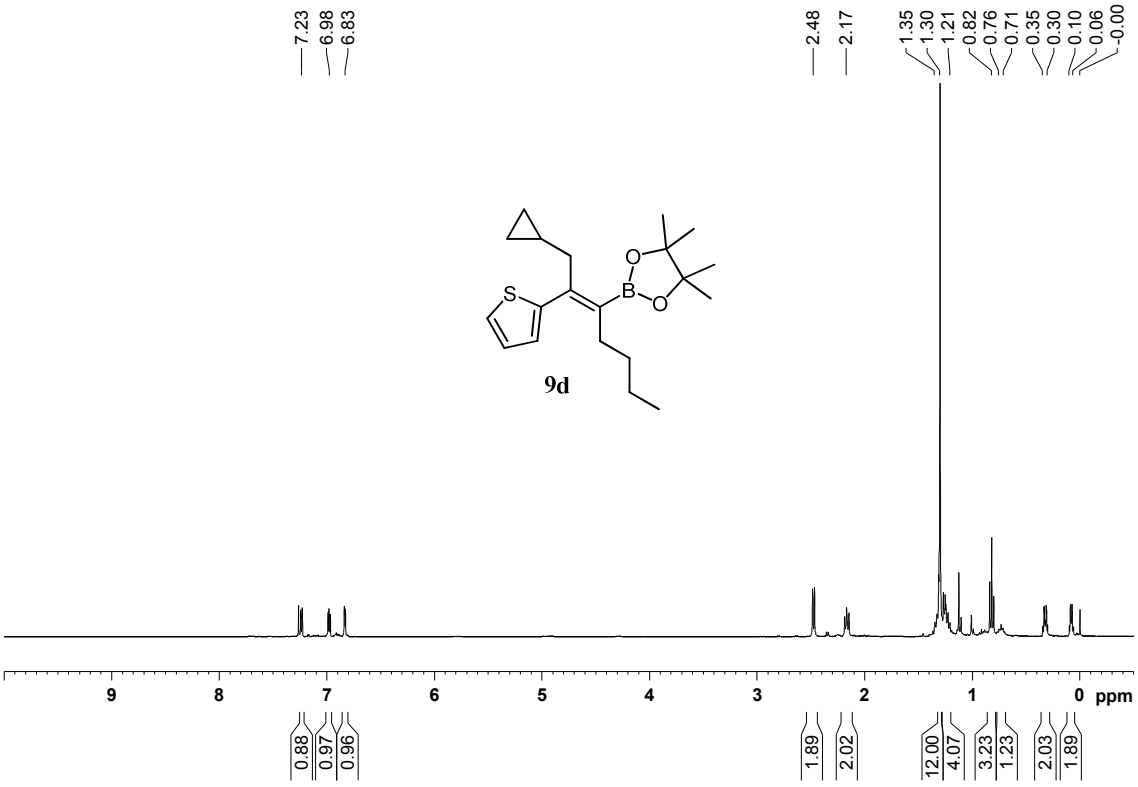

167.3
149.9
142.8
129.6
129.5
128.9
128.1
127.6
83.6
52.2
42.2
32.8
32.0
26.4
26.2
25.3
25.1
24.9
O
B
O
O
O
8b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

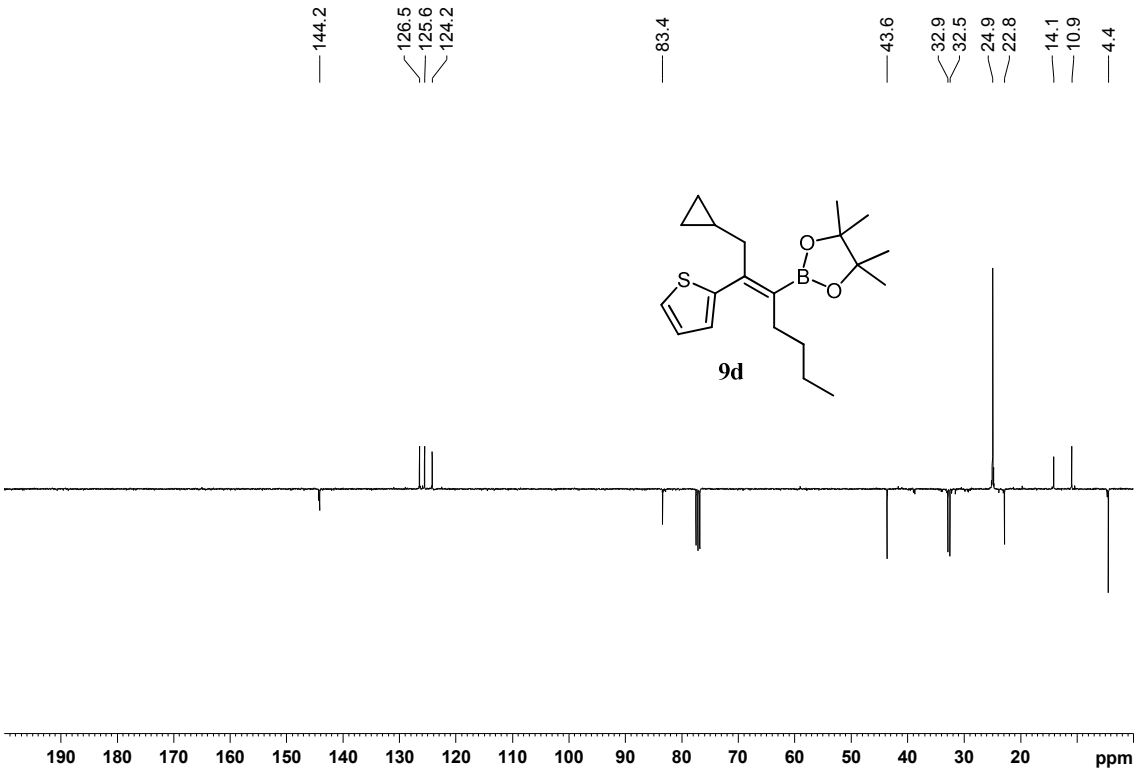

7.22
6.97
6.87
2.27
2.23
1.32
1.29
1.24
0.85
-0.00
S
O
B
O
9b
9
8
7
6
5
4
3
2
1
0
ppm
0.93
1.11
1.05
4.97
12.00
4.87
3.16


145.5
139.6
126.5
125.1
124.2
83.4
32.8
32.6
24.9
24.6
22.8
14.1
9b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

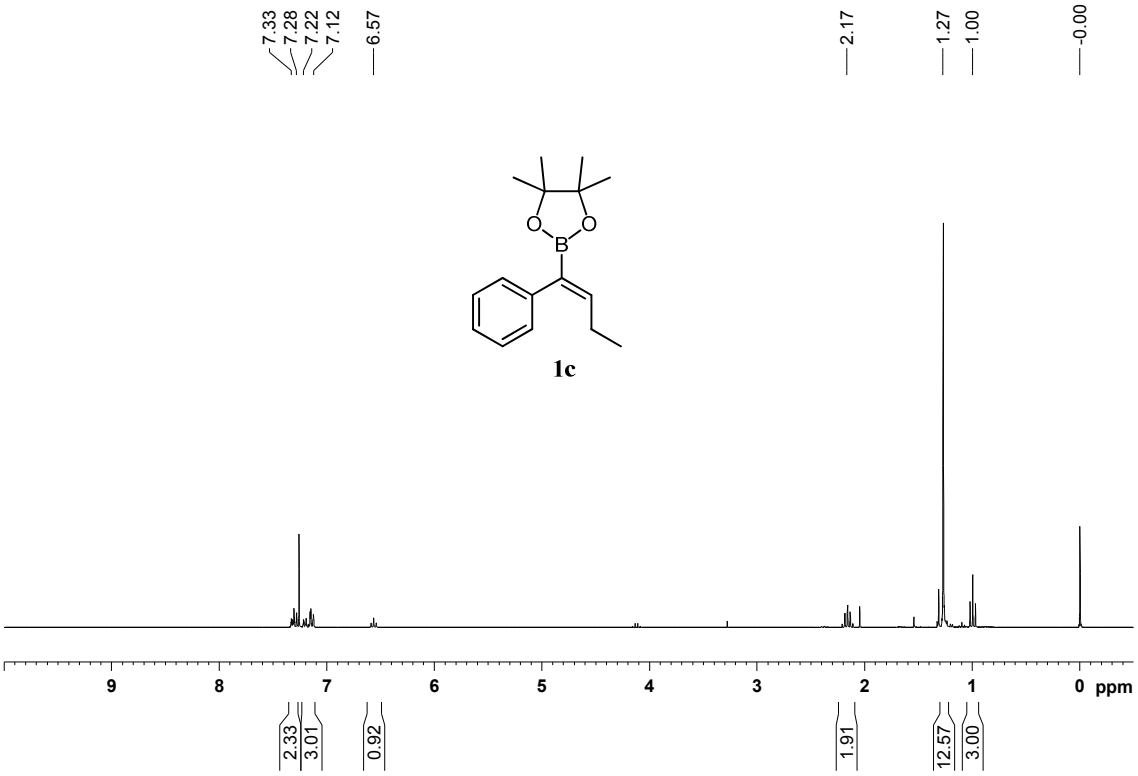

7.84
7.17
7.04
6.86
3.86
3.71
1.92
1.82
1.63
1.53
1.37
1.09
0.87
-0.00
8d
9 8 7 6 5 4 3 2 1 0 ppm
1.93
5.20
2.05
3.11
1.94
1.14
4.67
12.00
4.12

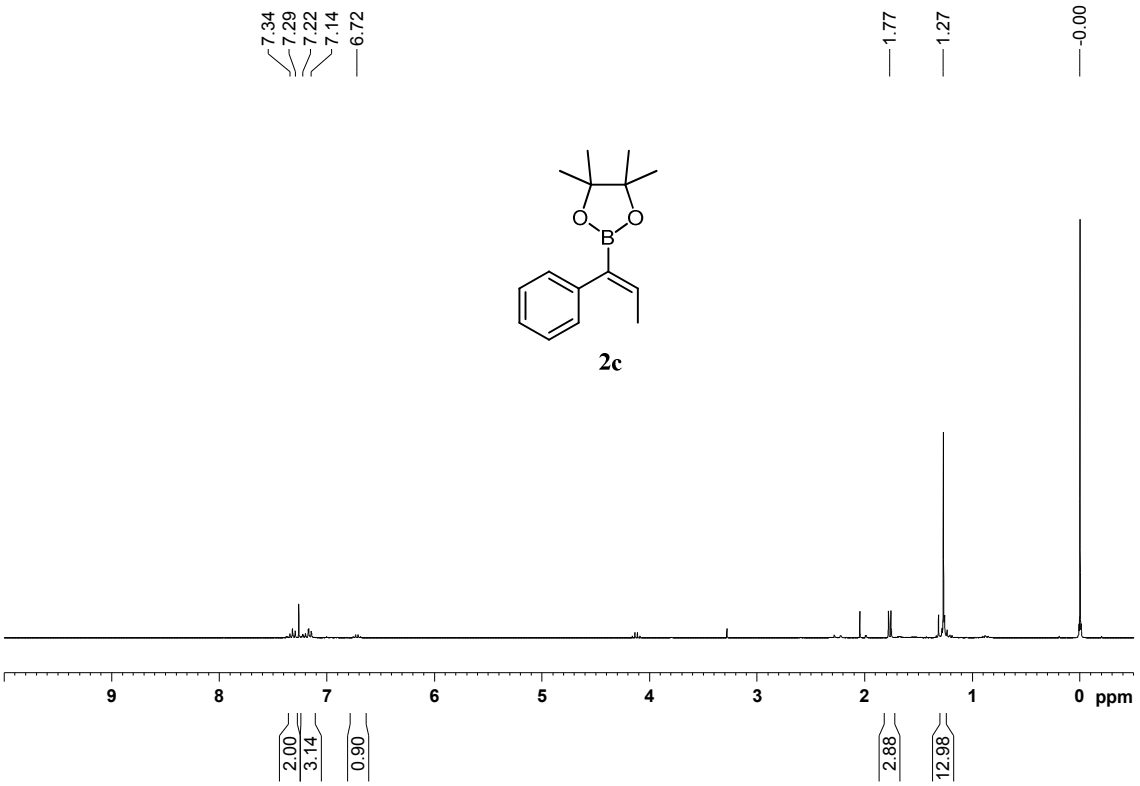

167.3
147.7
146.0
139.2
129.2
129.1
128.4
128.1
128.0
126.0
83.8
77.2
52.0
45.2
42.3
32.8
26.3
26.1
25.1
8d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.23
6.98
6.83
2.48
2.17
1.35
1.30
1.21
0.82
0.76
0.71
0.35
0.30
0.10
0.06
-0.00
9d
9 8 7 6 5 4 3 2 1 0 ppm
0.88
0.97
0.96
1.89
2.02
12.00
4.07
3.23
1.23
2.03
1.89

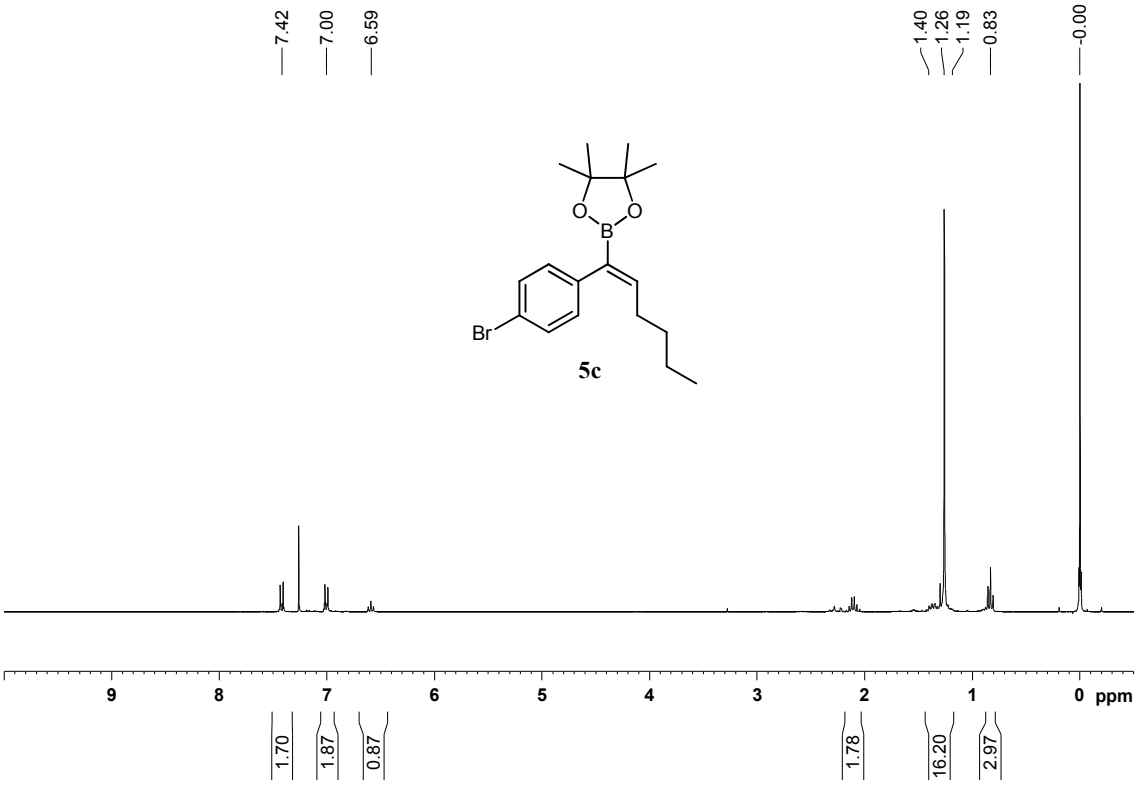


^{1}H and ^{13}C-{^{1}H} NMR spectra of products 1c-9c

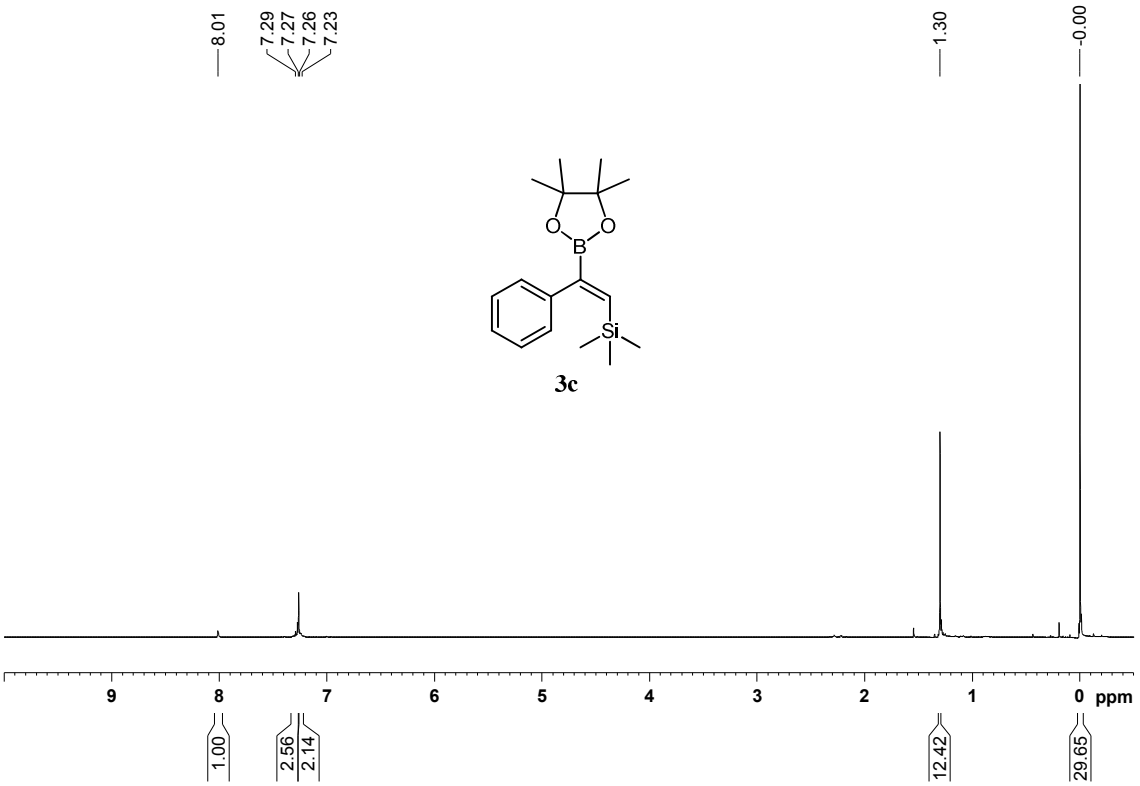



7.34
7.29
7.22
7.14
6.72
1.77
1.27
-0.00
9
8
7
6
5
4
3
2
1
0 ppm
2.00
3.14
0.90
2.88
12.98

2c


7.42
7.00
6.59
1.40
1.26
1.19
0.83
-0.00
9
8
7
6
5
4
3
2
1
0 ppm
1.70
1.87
0.87
1.78
16.20
2.97

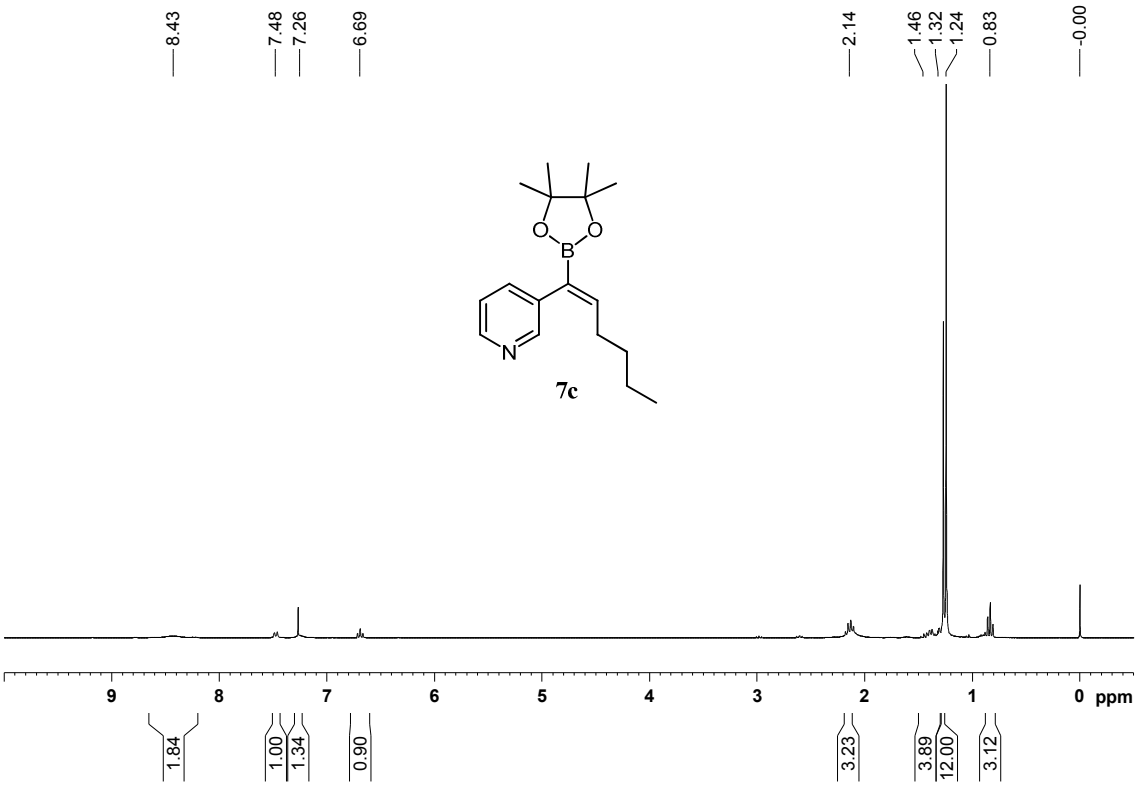
5c

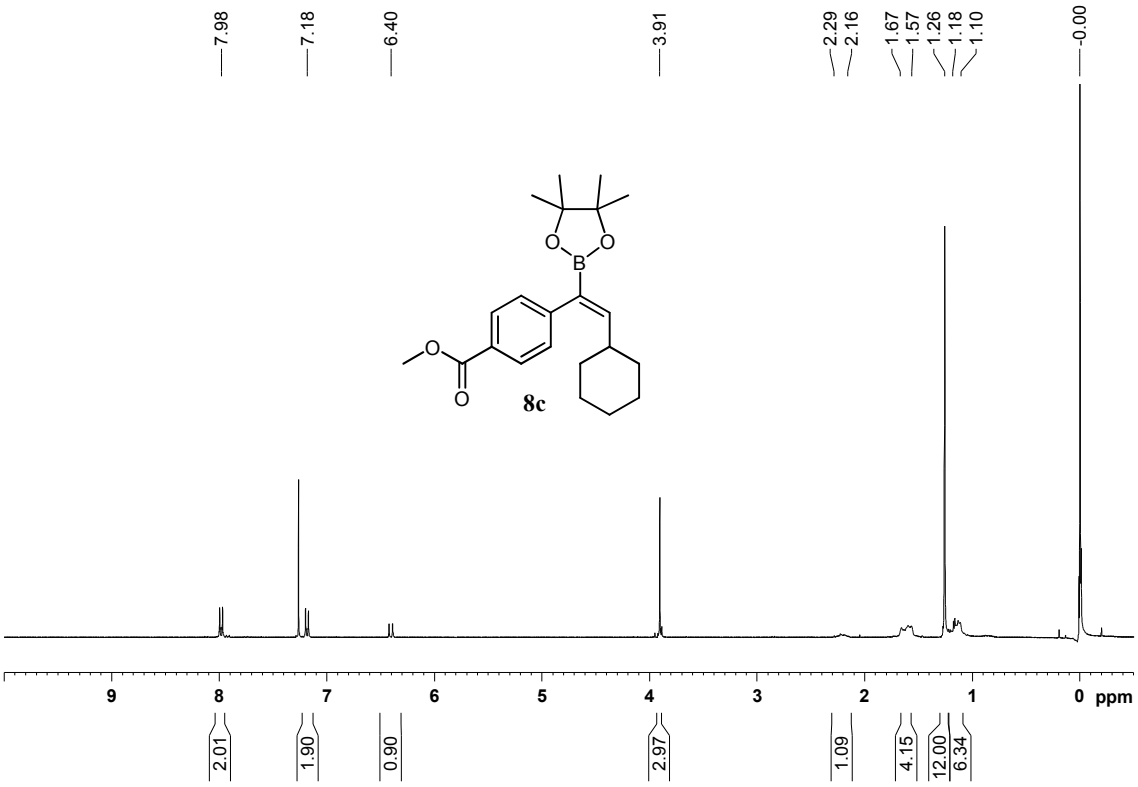

8.01
7.29
7.27
7.26
7.23
1.30
-0.00
O
B
O
Si
9
8
7
6
5
4
3
2
1
0 ppm
1.00
2.56
2.14
12.42
29.65

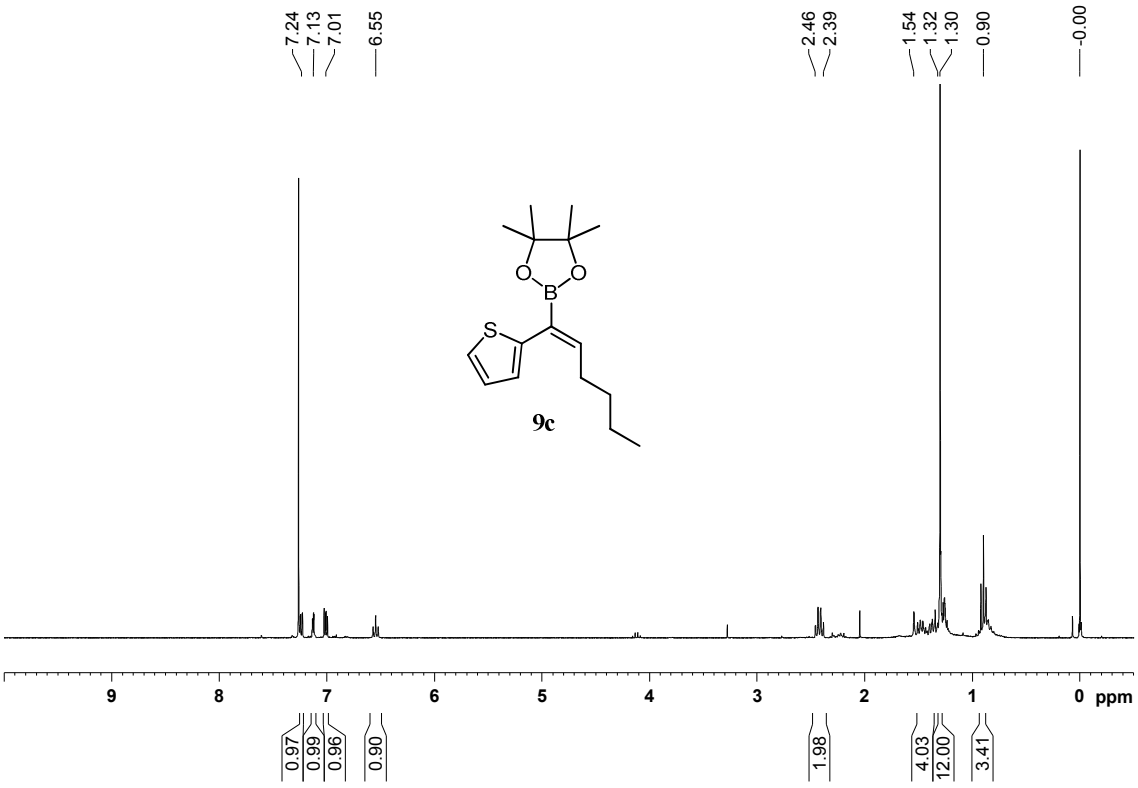
3c


7.81
7.72
7.68
7.66
7.09
7.00
5.60
5.52
4.78
3.88
3.83
2.43
1.24
-0.00
O
B
O
H
N
O
S
O
9
8
7
6
5
4
3
2
1
0 ppm
2.00
2.32
1.52
2.16
1.88
0.70
1.26
2.21
3.82
15.13

6c


8.43
7.48
7.26
6.69
2.14
1.46
1.32
1.24
0.83
-0.00
7c
9
8
7
6
5
4
3
2
1
0 ppm
1.84
1.00
1.34
0.90
3.23
3.89
12.00
3.12


7.98
7.18
6.40
3.91
2.29
2.16
1.67
1.57
1.26
1.18
1.10
-0.00
8c
9
8
7
6
5
4
3
2
1
0 ppm
2.01
1.90
0.90
2.97
1.09
4.15
12.00
6.34


7.24
7.13
7.01
6.55
2.46
2.39
1.54
1.32
1.30
0.90
-0.00
O
B
O
S
9c
9
8
7
6
5
4
3
2
1
0 ppm
0.97
0.99
0.96
0.90
1.98
4.03
12.00
3.41

6. References

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