Supporting Information

Direct Synthesis of Alkenylboronates from Alkenes and Pinacol Diboron via Copper Catalysis

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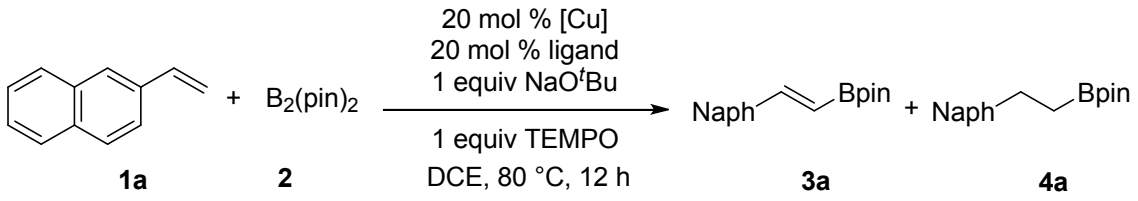
Experimental Procedures

I. General procedure

Commercial reagents were purchased from Aldrich or Energy unless otherwise addressed, and all solvents were dried and distilled before use according to the standard methods. Analytical thin layer chromatography (TLC) was performed on percolated silica gel 60 F254 plates. Visualization on TLC was achieved with UV light (254 nm) and potassium permanganate as visualization methods. ^{1}H NMR spectra were recorded on Mercury Plus-400 (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ shift), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublet, ddd = double of dd, dt = double of triplet, td = triple of doublet), integration, coupling constant (Hz), and assignment. ^{13}C NMR spectra were also recorded on Mercury Plus-400 (100 MHz). Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d* or a heptet at 39.5 ppm of dimethyl sulfoxide-*d*6. High resolution mass spectra were obtained with ACQUITY^{TM} UPLC & Q-TOF MS Premier Spectrometer. Gas chromatograph-mass spectra analysis was performed on LECO Pegasus 4D GC×GC-TOFMS. Gas chromatograph analysis was carried on Shimadzu GC-2014 machine.

II. Optimization of reaction conditions

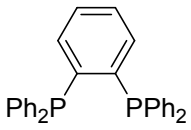
Table *S1.* Optimization of reaction for the dehydrogenative borylation[a]



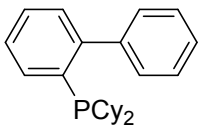
1a **2** **3a** **4a**

entry	[Cu]	Ligand	solvent	Yield of (**3a**+**4a**) (%)[b]	**3a**/**4a**[c]
1	$Cu(CH_3CN)_4PF_6$	dppbz	DMF	24	61:39
2	$Cu(CH_3CN)_4PF_6$	dppbz	DMA	26	70:30
3	$Cu(CH_3CN)_4PF_6$	dppbz	DMSO	19	72:28
4	$Cu(CH_3CN)_4PF_6$	dppbz	NMP	24	68:32
5	$Cu(CH_3CN)_4PF_6$	dppbz	CH_3CN	19	75:25
6	$Cu(CH_3CN)_4PF_6$	dppbz	THF	12	52:48
7	$Cu(CH_3CN)_4PF_6$	dppbz	toluene	14	66:34
8	$Cu(CH_3CN)_4PF_6$	dppbz	$CHCl_3$	38	81:19
9	$Cu(CH_3CN)_4PF_6$	dppbz	DCM	24	88:12
10	$Cu(CH_3CN)_4PF_6$	dppbz	DCE	38	92:8
11	CuSCN	dppbz	DCE	36	100:0
12[d]	CuSCN	dppbz	DCE	52	100:0
13[e]	CuSCN	dppbz	DCE	60	100:0
14[d,f]	**CuSCN**	**CyJohnPhos**	**DCE**	**85**	**100:0**

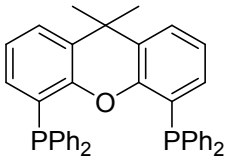
[a] Conditions: **1a** (0.15 mmol), $B_2(pin)_2$ (1 equiv), NaO^{t}Bu (1 equiv), TEMPO (1 equiv), catalyst (20 mol %),80 °C, DCE (1 mL). [b] Total yield of **3a** and **4a** after chromatographic purification. [c] The ratio of **3a/4a** determined by ^{1}H NMR analysis. [d] Using $B_2(pin)_2$ (2 equiv), TEMPO (2 equiv), and LiO^{t}Bu (1 equiv)instead of NaO^{t}Bu. [e] Using LiO^{t}Bu (2 equiv). [f] Using CuSCN (10 mol %), CyJohnPhos (22 mol %), 18 h.



dppbz

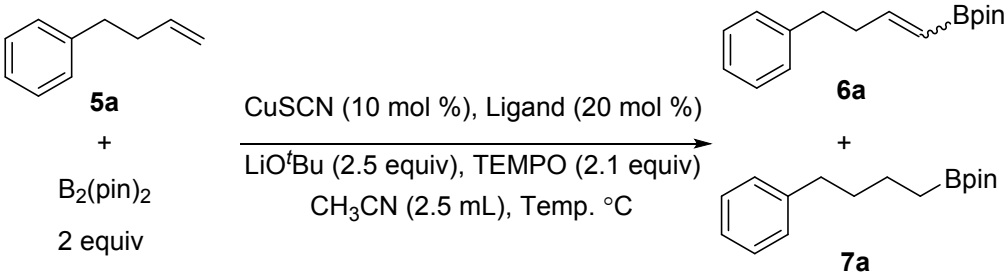


CyJohnPhos



XantPhos

Table *S2*. Optimization of for the synthesis of aliphatic alkenylboronates[a]

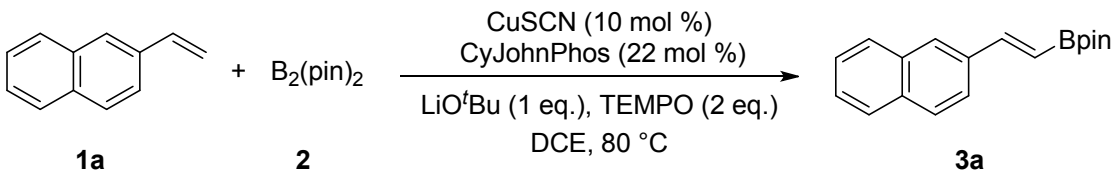


entry	ligand	T °C	yield of **6a** (%)[b]	**6a** (*E*/*Z*) / **7a**[b]
1	10 mol % XantPhos	80	48	(78:22):0
2	20 mol % XantPhos	80	57	(77:23):0
3	20 mol % XantPhos	90	75	(83:17):0
4	20 mol % XantPhos	100	93	(87:13):0
5	20 mol % XantPhos	110	67	(78:22):0

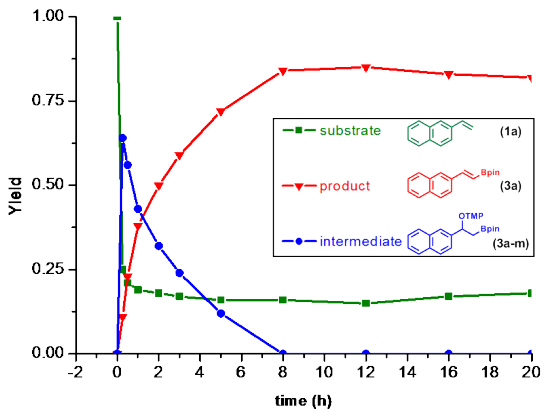
[a] Conditions: **5a** (0.15 mmol, 1 equiv), $B_2(pin)_2$ (2 equiv), LiO^{t}Bu (2.5 equiv), TEMPO (2.1 equiv), catalyst (10 mol %), CH_3CN (2.5 mL). [b] Isolated yield and the ratio determined by ^{1}H NMR analysis.

III. Mechanistic studies

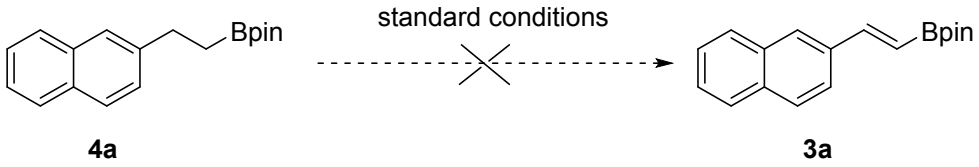
1. Figure *S1*. Reaction profile using 1a as a model substrate



1a **2** **3a**



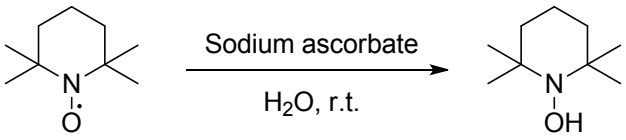
2. Hydroborylation product **4a** was subjected to standard conditions, and no desired product was obtained. This result excludes the possibility of alkenyl boronic esters coming from hydroborylation product **4a**.



4a **3a**

3. Detection of TEMPOH

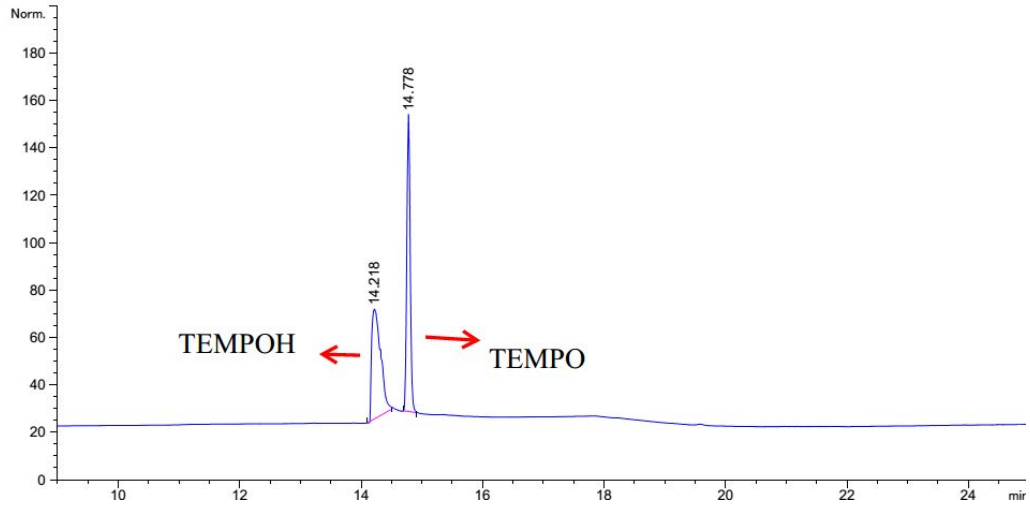
(1) Synthesis and Characterization of TEMPOH



TEMPOH

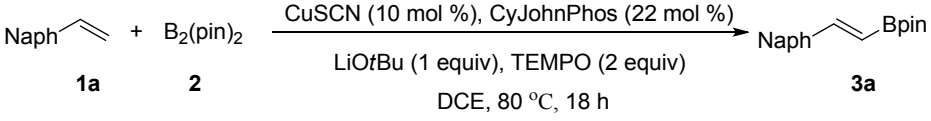
Based on the procedure reported by Tidwell,[17] TEMPO (1 g, 6.4 mmol) was added into a round flask charged with sodium ascorbate (2.1 g, 10.6 mmol) and H_2O (18 mL). Then, the suspension was stirred vigorously at room temperature until completely decolorized with the appearance of a white precipitate. The resulting suspension was extracted with diethyl ether. Afterward, the ether extracts were washed with water and brine, dried over anhydrous sodium sulfate and evaporated under reduced pressure to provide white solid TEMPOH (0.96 g, 96% yield). As shown in Figure S1, the retention time of TEMPOH **at GC** was obtained. Notably, part of TEMPOH was oxidized to TEMPO at GC.

Figure S2. **GC spectrum of TEMPOH**

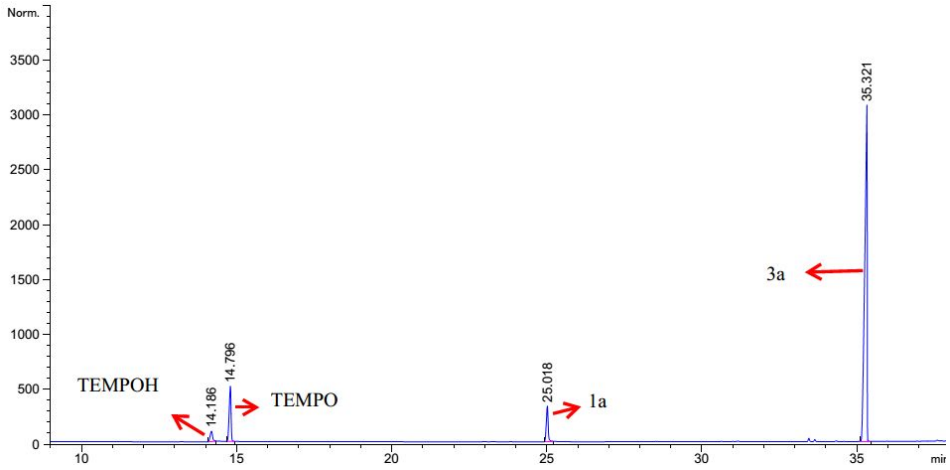


(2) Detection of TEMPOH

Figure S3. **GC spectrum of dehydrogenative borylation reaction after 18 h**



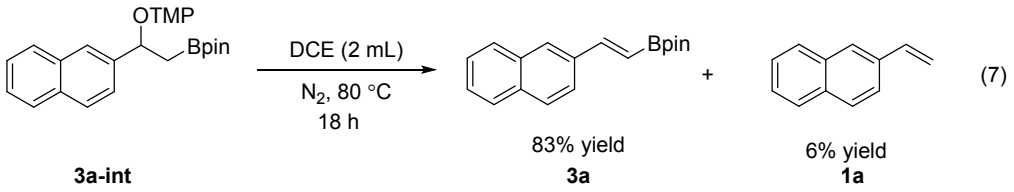
1a **2** **3a**



1a: 2-Vinylnaphthalene
3a: (*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalene-2-yl)vinyl)-1,3,2-dioxaborolane

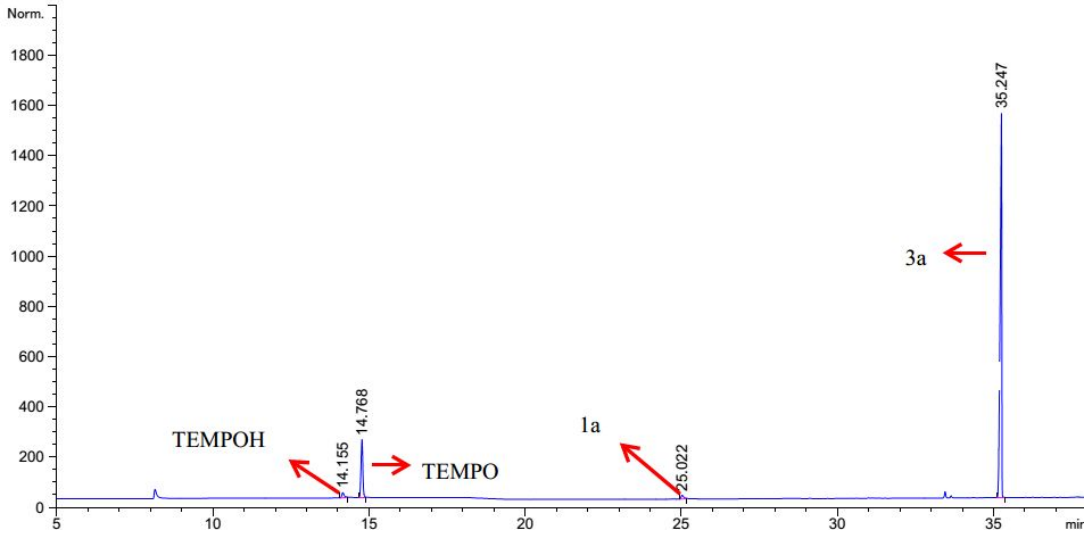
TEMPOH was formed during the course of dehydrogenative borylation reaction under the stardard conditions (determined by GC) by the comparison of TEMPOH retention time at GC.

(3) Detection of TEMPOH when heating the intermediate 3a-int.



In a nitrogen-filled glove-box, **3a-int** (87.4 mg, 0.2 mmol) and DCE (2 mL) were added to an oven-dried 25 mL Schlenk tube containing a stirring bar. The Schlenk tube was sealed with a Teflon-lined screw cap. Heating up to 80 °C for 18 h, the resulting red brown mixture was allowed to cool to room temperature, diluted with CH_2Cl_2, and washed with H_2O. The aqueous layer was extracted with CH_2Cl_2 (15 mL× 3). The combined organic layers were dried over $MgSO_4$, and the filtrate was concentrated. The crude was purified by column chromatography to afford product **3a** (47 mg, 85% yield) and **1a** (2 mg, 6%).

Figure S4. GC spectrum of intermediate 3a-int after heating for 18 hours

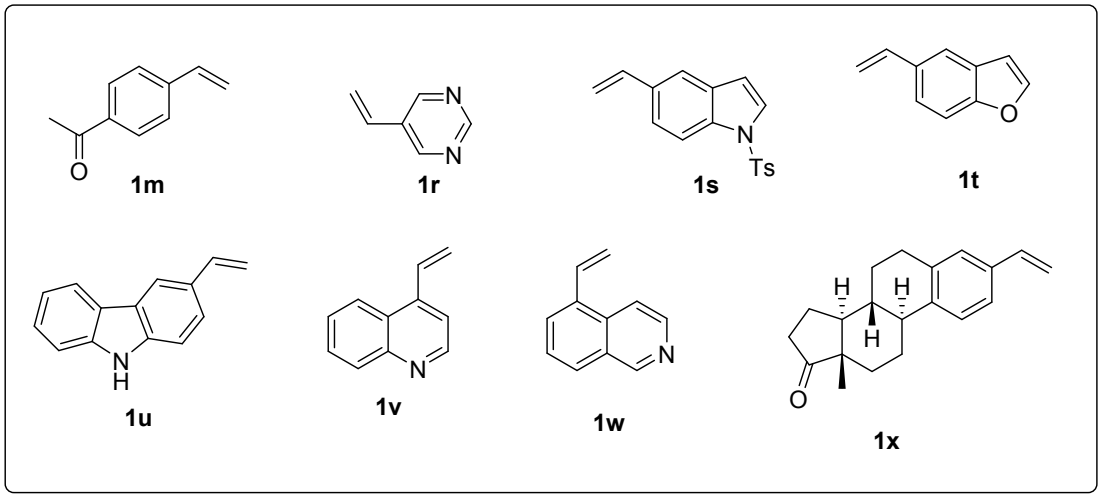


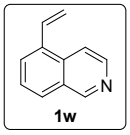
1a: 2-Vinylnaphthalene
3a: (*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalene-2-yl)vinyl)-1,3,2-dioxaborolane

During the course of above reaction, TEMPOH and TEMPO were determined by GC by the comparison of TEMPOH and TEMPO retention time at GC. We considered that TEMPO was formed from TEMPOH by oxidation.

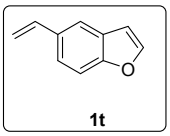
IV. Preparation of Substrates

Substrates **1m**[1], **1r**[1], **1s**[1], **1t**[2], **1u**[2], **1v**[2], **1w**[2] and **1x**[3] were prepared based on reported literatures. Other substrates without mention below are commercially available.

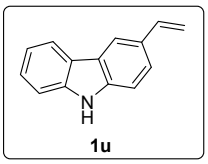




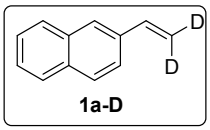
5-Vinylisoquinoline (**1w**). Based on the reported procedure,[2] potassium vinyltrifluoroborate (134 mg, 1.0 mmol) was reacted with 5-bromoisoquinoline (208 mg, 1.0 mmol) to yield 5-vinyl-isoquinoline as a colorless liquid (120 mg, 0.774 mmol, 77%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94-8.92 (m, 1H), 8.47-8.45 (m, 1H), 8.08-8.04 (m, 1H), 7.72-7.68 (m, 2H), 7.45-7.36 (m, 2H), 5.83 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.34 (dd, *J* = 10.8, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.6, 142.9, 133.9, 133.1, 132.1, 128.3, 127.1, 126.9, 126.6, 117.7, 116.2; HRMS (ESI): m/z calcd for $C_{11}H_{10}N^+$ [M+H$^+$]: 156.0808, Found: 156.0804.



5-Vinylbenzofuran (**1t**). Based on the reported procedure, [2] potassium vinyltrifluoroborate (134 mg, 1.0 mmol) was reacted with 5-bromo-1-benzofuran (197 mg, 1.0 mmol) to yield 5-vinyl-isoquinoline as a colorless liquid (100 mg, 0.694 mmol, 69%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 1.2 Hz, 1H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.34-7.31 (m, 1H), 6.76 (dd, *J* = 17.6, 11.2 Hz, 1H), 6.63-6.62 (m, 1H), 5.68 (d, *J* = 17.6 Hz, 1H), 5.17 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.7, 145.3, 136.9, 132.6, 127.6, 122.5, 119.0, 112.5, 111.2, 106.6; HRMS (ESI): m/z calcd for $C_{10}H_9O^+$ [M+H$^+$]: 145.0648, Found: 145.0651.

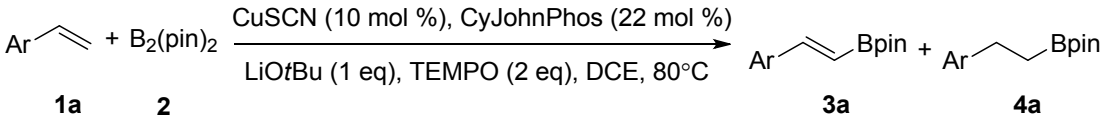


3-Vinyl-9H-carbazole (**1u**). Based on the reported procedure, [2] potassium vinyltrifluoroborate (134 mg, 1.0 mmol) was reacted with 3-bromo-9*H*-carbazole (246 mg, 1.0 mmol) to yield 3-vinyl-9*H*-carbazole as a colorless solid (100 mg, 0.518 mmol, 52%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.06 (m, 2H), 7.99 (br, 1H,), 7.54-7.51 (m, 1H), 7.43-7.36 (m, 2H), 7.33(d, *J* = 8.8 Hz, 1H), 7.25-7.21 (m, 1H), 6.90 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.77 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.20 (dd, *J* = 10.8, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.1, 139.5, 137.7, 129.7, 126.2, 124.4, 123.8, 123.6, 120.6, 119.8, 118.6, 111.5, 111.0, 110.8; HRMS (ESI): m/z calcd for $C_{14}H_{12}N^+$ [M+H$^+$]: 194.0964, Found: 194.0965.



2-(Vinyl-2,2-d2)naphthalene (**1a-D**). An over-dried re-sealable tube with a magnetic stirrer was charged with PPh_3 (2 mmol, 526 mg). The tube fitted with a rubber spetum was evacuated and backfilled with nitrogen three times. Anhydrous THF (4 mL) was added to the tube. Then, CD_3I (2 mmol, 290 mg) was added dropwise to the solution at room tempeture overnight. The mixture was filtered and concentrated in vacuo. Freshly distilled 1-naphthaldehydein (2 mmol, 312 mg) in dry THF (8 mL) and KO*t*Bu (2 mmol, 224 mg) were added to a suspension of methyl-d_3-triphenylphosphonium iodide (2 mmol, 816 mg) at 0°C. The reaction was stirred at rt overnight. The mixture was diluted with CH_2Cl_2 (15 mL), washed with brine (3×15 mL), dried with Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by column chromatography to afford deuterium-labeled 1-vinylnaphthalene (**1a-D**) [4] (200 mg, 60%) as white solid (D/H=9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.79 (m, 3H,), 7.75 (br, 1H), 7.65-7.63 (m, 1H), 7.48-7.43 (m, 2H), 6.87 (br, 1H).

V. Typical procedure for direct synthesis of alkenylboronates from aromatic alkenes and diboron via copper catalysis

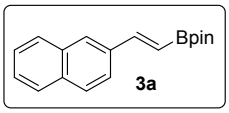


1a **2** **3a** **4a**

In a nitrogen-filled glove-box, CuSCN (3.7 mg, 10 mol %), CyJohnPhos (23.1 mg, 22 mol %), and DCE (1 mL) were added to an oven-dried 25 mL Schlenk tube containing a stirring bar. The solution was stirred at room temperature until a colorless solution is formed. Then, Li*O*^{t}Bu (24 mg, 0.3 mmol), 2-vinylnaphthalene (46.3 mg, 0.3 mmol), TEMPO (93.6 mg, 0.6 mmol), pinacolborane (152.3 mg, 0.6 mmol) and DCE (1 mL) were added to the above mixture. The Schlenk tube was sealed with a Teflon-lined screw cap and taken out of the glove-box. Heating up to 80 °C for 18 h, the resulting red brown mixture was allowed to cool to room temperature, diluted with CH_2Cl_2, and washed with H_2O. The aqueous layer was extracted with CH_2Cl_2 (15 mL× 3). The combined organic layers were dried over $MgSO_4$, and the filtrate was concentrated. The crude was purified by column chromatography with eluent (petroleum ether/ethyl acetate = 100/1) to afford the product **3a.**

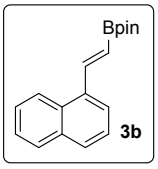
VI. Characterization data

(*E*)-4,4,5,5-Tetramethyl-2-(2-(naphthalene-2-yl)vinyl)-1,3,2-dioxaborolane (3a)[5]



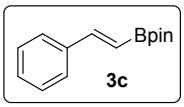
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 100/1) to afford the product **3a** (71 mg, 85% yield) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.79 (m, 4H), 7.71-7.69 (m, 1H), 7.57 (d, *J* = 18.4 Hz, 1H), 7.48-7.43 (m, 2H), 6.29 (d, *J* = 18.4 Hz, 1H), 1.33 (s, 12H); MS (ESI+) m/z: 281.2 $(M+H)^+$.

(*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalene-1-yl)vinyl)-1,3,2-dioxaborolane (3b)



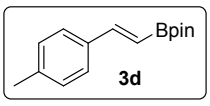
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 100/1) to afford the product **3b** (67 mg, 80% yield) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (m, 2H), 7.83-7.72 (m, 3H), 7.52-7.43 (m, 3H), 6.27 (d, *J* = 18.4 Hz, 1H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.3, 135.2, 133.4, 130.9, 128.9, 128.3, 126.0, 125.7, 125.4, 123.9, 123.6, 83.3, 24.7; HRMS (ESI): m/z calcd for $[M+H^+]$: 281.1707, Found: 281.1698.

(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (3c)[5]



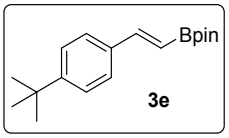
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 100/1) to afford product **3c** (48 mg, 70% yield) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H), 7.40 (d, *J* = 18.4 Hz, 1H), 7.36-7.28 (m, 3H), 6.17 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H); MS (ESI+) m/z: 231.2 $(M+H)^+$.

(*E*)-4,4,5,5-tetramethyl-2-(4-methylstyry)-1,3,2-dioxaborolane (3d).[8]



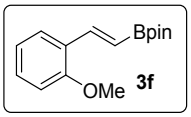
The reaction was conducted with general procedure **1d** in 0.3 mmol scale. Heating up to 80 °C for 24 h, The residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 50/1) to afford product **3d** (63 mg, 86% yield) as light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.35 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.11 (d, *J* = 18.4 Hz, 1H), 2.33 (s, 3H), 1.31 (s, 12H); MS (ESI+) m/z: 245.3 $(M+H)^+$.

(*E*)-2-(4-(*tert*-butyl)styry)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e).[12]



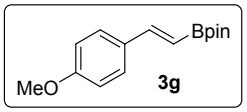
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 30/1) to afford product **3e** (76 mg, 89% yield) as colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.41 (m, 3H), 7.37-7.35 (m, 2H), 6.12 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 21H); HRMS (ESI): m/z calcd for $C_{18}H_{28}BO_3^+$ $[M+H^+]$: 287.2177, Found: 287.2176.

(*E*)-2-(2-methoxystyry)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f).[9]



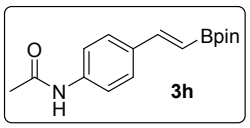
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 100/1) to afford product **3f** (68 mg, 87% yield) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 18.8 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.28-7.24 (m, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.11 (d, *J* = 18.8 Hz, 1H), 3.84 (s, 3H), 1.31 (s, 12H); MS (ESI+) m/z: 261.3 $(M+H)^+$.

(*E*)-2-(4-methoxystyry)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g).[11]



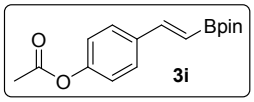
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 100/1) to afford product **3g** (33 mg, 42% yield) as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.43 (m, 2H), 7.36 (d, *J* = 18.4 Hz, 1H), 6.88-6.85 (m, 2H), 6.02 (d, *J* = 18.4 Hz, 1H), 3.81 (s, 3H), 1.31 (s, 12H); MS (ESI+) m/z: 261.3 $(M+H)^+$.

***(E)*-*N*-(4-(2(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetamide (3h).**



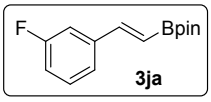
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 24 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 2/1) to afford product **3h** (69 mg, 80% yield) as colorless solid; m.p. 145-147 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 4H), 7.35 (d, *J* = 18.4 Hz, 1H), 7.21 (s, 1H), 6.09 (d, *J* = 18.4 Hz, 1H), 2.19 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.2, 148.7, 138.4, 133.5, 127.8, 119.6, 83.3, 24.8, 24.7; HRMS (ESI): m/z calcd for $C_{16}H_{23}BNO_3^+$ $[M+H^+]$: 288.1766, Found: 288.1761.

(*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl acetate (3i).



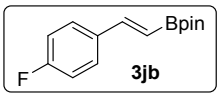
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, The residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 10/1) to afford product **3i** (73 mg, 84% yield) as colorless solid; m.p. 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.48 (m, 2H), 7.37 (d, *J* = 18.8 Hz, 1H), 7.08-7.05 (m, 2H), 6.11 (d, *J* = 18.4 Hz, 1H), 2.30 (s, 3H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.3, 151.0, 148.3, 135.2, 128.0, 121.6, 83.3, 24.7, 21.1; HRMS (ESI): m/z calcd for $C_{16}H_{22}BO_4^+$ $[M+H^+]$: 289.1606, Found: 289.1603.

(*E*)-2-(3-fluorostyry)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ja).[6]



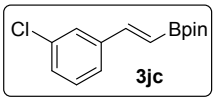
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, The residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 50/1) to afford product **3ja** (50 mg, 67% yield) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 18.4 Hz, 1H), 7.31-7.29 (m, 1H), 7.23 (s, 1H), 7.19-7.16 (m, 1H), 7.01-6.96 (m, 1H), 6.16 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -232.0; MS (ESI+) m/z: 249.2 $(M+H)^+$.

(*E*)-2-(4-fluorostyry)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3jb).[7]



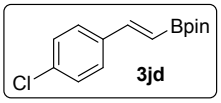
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, The residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 50/1) to afford product **3jb** (56 mg, 75% yield) as colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.43 (m, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 7.05-6.99 (m, 2H), 6.07 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -230.8; MS (ESI+) m/z: 249.2 $(M+H)^+$.

(*E*)-2-(3-chlorostyry)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3jc).[8]



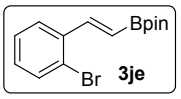
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 24 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 50/1) to afford product **3jc** (63 mg, 79% yield) as pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.36-7.34 (m, 2H), 7.27-7.26 (m, 2H), 6.17 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); MS (ESI+) m/z: 265.1 $(M+H)^+$.

(*E*)-2-(4-chlorostyry)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3jd). [7]



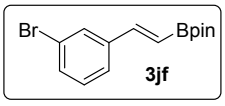
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 24 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 50/1) to afford product **3jd** (60 mg, 76% yield) as yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.39 (m, 2H), 7.36-7.29 (m, 3H), 6.13 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); MS (ESI+) m/z: 265.1 $(M+H)^+$.

(*E*)-2-(2-bromostyry)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3je).[9]



The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 24 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 50/1) to afford product **3je** (75 mg, 81% yield) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 18.4 Hz, 1H), 7.62-7.60 (m, 1H), 7.57-7.54 (m, 1H), 7.31-7.29 (m, 1H,), 7.16-7.12 (m, 1H,), 6.13 (d, *J* = 18.4 Hz, 1H,), 1.32 (s, 12H,); MS (ESI+) m/z: 309.1 $(M+H)^+$.

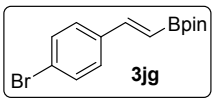
(*E*)-2-(3-bromostyry)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3jf).[10]



The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 24 h, The residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 50/1) to afford product **3jf** (74 mg, 80% yield) as pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 18.4 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.16 (d, *J* = 18.4 Hz, 1H), 1.31 (s,

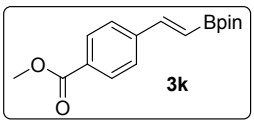
12H); MS (ESI+) m/z: 309.1 $(M+H)^+$.

(*E*)-2-(4-bromostyry)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3jg).[9]



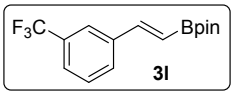
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 24 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 50/1) to afford product **3jg** (78 mg, 84% yield) as yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.45 (m, 2H), 7.36-7.30 (m, 3H), 6.15 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); MS (ESI+) m/z: 309.1 $(M+H)^+$.

(*E*)-methyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (3k).[13]



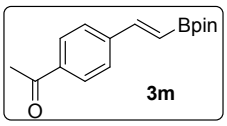
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 12 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 10/1) to afford product **3k** (65 mg, 75% yield) as colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.99 (m, 2H), 7.55-7.52 (m, 2H), 7.41 (d, *J* = 18.4 Hz, 1H), 6.28 (d, *J* = 18.4 Hz, 1H), 3.91 (s, 3H), 1.32 (s, 12H); MS (ESI+) m/z: 289.2 $(M+H)^+$.

(*E*)-4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)styryl)-1,3,2-dioxaborolane(3l).[9]



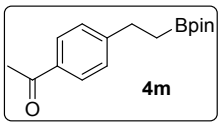
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 12 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 50/1) to afford product **3l** (64 mg, 72% yield) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.47-7.38 (m, 1H), 7.32 (d, *J* = 18.4 Hz, 1H), 6.24 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -181.4; MS (ESI+) m/z: 299.2 $(M+H)^+$.

(*E*)-1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)ethanone (3m).



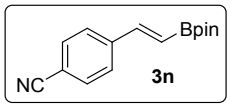
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 5/1) to afford product **3m** and **4m** (65 mg, 80% yield) as light yellow solid (**3m/4m**=57:43); m.p. 73-75 °C; **3m**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 18.8 Hz, 1H), 6.29 (d, *J* = 18.4 Hz, 1H), 2.60 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.6, 148.0, 128.8, 128.5, 128.2, 127.1, 83.6, 26.7, 24.8; HRMS (ESI): m/z calcd for $C_{16}H_{22}BO_3^+$ $[M+H^+]$: 273.1657, Found: 273.1663.

1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethanone (4m).



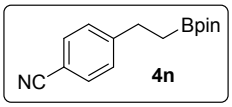
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.58 (s, 3H), 1.22 (s, 12H), 1.16 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.0, 150.3, 141.8, 137.0, 134.8, 83.3, 30.0, 26.7, 26.6, 24.8; HRMS (ESI): m/z calcd for $C_{16}H_{24}BO_3^+$ $[M+H^+]$: 275.1813, Found: 275.1809.

(*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (3n).[11]



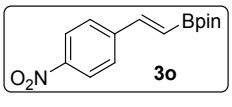
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 4 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 10/1) to afford product **3n** and **4n** (46 mg, 60% yield) as brown solid (**3n/4n** = 53:47); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 18.8 Hz, 1H), 6.29 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H); MS (ESI+) m/z: 256.3 $(M+H)^+$.

4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (4n).[14]



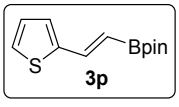
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 1.21 (s, 12H), 1.14 (t, *J* = 8.0 Hz, 2H); MS (ESI+) m/z: 258.3 $(M+H)^+$.

(*E*)-4,4,5,5-tetramethyl-2-(4-nitrostyryl)-1,3,2-dioxaborolane (**3o).**[11]



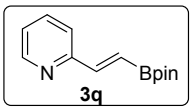
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 1 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 10/1) to afford product **3o** and **4o** (22 mg, 27% yield) as light yellow solid (**3o/4o**=95:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22-8.19 (m, 2H), 7.63-7.59 (m, 2H), 7.42 (d, *J* = 18.4 Hz, 1H), 6.34 (d, *J* = 18.4 Hz, 1H), 1.33 (s, 12H); MS (ESI+) m/z: 276.2 $(M+H)^+$.

(*E*)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (3p).[15]



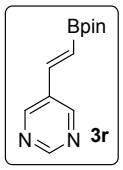
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 30/1) to afford product **3p** (52 mg, 73% yield) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 18.0 Hz, 1H), 7.24 (d, *J* = 4.8 Hz, 1H), 7.08 (d, *J* = 3.6 Hz, 1H), 6.99-6.97 (m, 1H), 5.91 (d, *J* = 18.0 Hz, 1H), 1.30 (s, 12H); MS (ESI+) m/z: 237.1 $(M+H)^+$.

(*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (3q).[6]



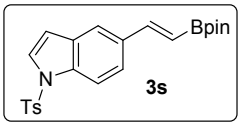
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 5/1) to afford product **3q** (45 mg, 65% yield) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 4.4 Hz, 1H), 7.66 (td, *J* = 7.6, 2.0 Hz, 1H), 7.46 (d, *J* = 18.0 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.20-7.17 (m, 1H), 6.63 (d, *J* = 18.0 Hz, 1H), 1.31 (s, 12H); MS (ESI+) m/z: 232.2 $(M+H)^+$.

(*E*)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyrimidine (3r).



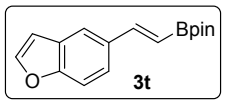
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 12 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 2/1) to afford product **3r** (45 mg, 65% yield) as yellow solid; m.p. 97-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (s, 1H), 8.83 (s, 2H), 7.31 (d, *J* = 18.4 Hz, 1H), 6.36 (d, *J* = 18.4 Hz, 1H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 154.9, 141.9, 130.7, 83.8, 24.8; HRMS (ESI): m/z calcd for $C_{12}H_{18}BN_2O_2^+$ $[M+H^+]$: 233.1456, Found: 233.1456.

(*E*)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1-tosyl-1*H*-indole (3s).



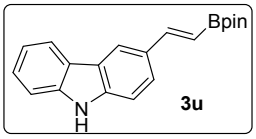
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 12 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 5/1) to afford product **3s** (96 mg, 76% yield) as colorless solid; m.p. 69-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.78-7.74 (m, 2H), 7.60 (d, *J* = 1.2 Hz, 1H), 7.55 (d, *J* = 4.0 Hz, 1H), 7.49 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.44 (d, *J* = 18.4 Hz, 1H), 7.23-7.21 (m, 2H), 6.64 (d, *J* = 4.0 Hz, 1H), 6.13 (d, *J* = 18.4 Hz, 1H), 2.34 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 144.9, 135.01, 134.97, 132.9, 130.9, 130.0, 129.8, 126.7, 123.4, 120.3, 113.5, 109.2, 83.2, 24.7, 21.4; HRMS (ESI): m/z calcd for $C_{23}H_{27}BNO_4S^+$ $[M+H^+]$: 424.1748, Found: 424.1749.

(*E*)-2-(2-(benzofuran-5-yl)vinyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t).



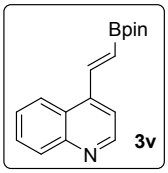
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 24 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 50/1) to afford product **3t** (40 mg, 49% yield) as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.52-7.44 (m, 3H), 6.77-6.76 (m, 1H), 6.15 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.4, 149.8, 145.5, 132.7, 127.7, 123.4, 120.2, 111.4, 106.8, 83.3, 24.8; HRMS (ESI): m/z calcd for $C_{16}H_{20}BO_3^+$ $[M+H^+]$: 271.1500, Found: 271.1494.

(*E*)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-9*H*-carbazole (3u).



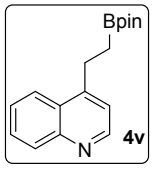
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 24 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 10/1) to afford product **3u** (50 mg, 52% yield) as brown solid; m.p. 135-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 8.13 (br, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.63-7.58 (m, 2H), 7.43-7.37 (m, 3H), 7.25-7.23 (m, 1H), 6.19 (d, *J* = 18.4 Hz, 1H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.8, 140.0, 139.8, 129.4, 126.1, 125.0, 123.5, 123.3, 120.3, 119.7, 119.6, 110.7, 110.6, 83.2, 24.8; HRMS (ESI): m/z calcd for $C_{20}H_{23}BNO_2^+$ $[M+H^+]$: 320.1816, Found: 320.1819.

(*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)quinoline (3v).



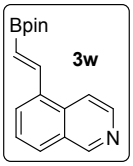
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 12 h, The residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 5/1) to afford product **3v** and **4v** (82 mg, 97% yield) as brown solid (**3v**/**4v**=78:22); **3v**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.91 (br, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.15-8.10 (m, 2H), 7.74-7.67 (m, 1H), 7.59-7.53 (m, 2H), 6.44 (d, *J* = 18.0 Hz, 1H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 148.6, 143.6, 143.2, 129.9, 129.3, 126.6, 126.1, 123.6, 117.5, 83.8, 24.8; HRMS (ESI): m/z calcd for $C_{17}H_{21}BNO_2^+$ $[M+H^+]$: 282.1660. Found: 282.1668.

4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)quinoline (4v).



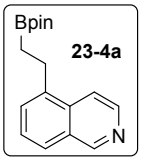
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (br, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.14-8.10 (m, 1H), 7.74-7.67 (m, 1H), 7.59-7.53 (m, 2H), 3.21 (t, *J* = 8.0 Hz, 1H), 1.29 (t, *J* = 8.0 Hz, 2H), 1.23 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 148.6, 143.2, 130.0, 129.9, 128.9, 126.0, 123.6, 83.3, 26.0, 24.8, 24.7; HRMS (ESI): m/z calcd for $C_{17}H_{23}BNO_2^+$ $[M+H^+]$: 284.1816, Found: 284.1819.

(*E*)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)isoquinoline (3w).



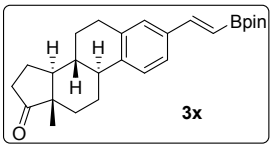
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 12 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 5/1) to afford product **3w** and **4w** (85 mg, 100% yield) as yellow oil (**3w**/**4w**=80:20); **3w**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (d, *J* = 4.0 Hz, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 8.13-8.07 (m, 2H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.44-7.41 (m, 1H), 6.30 (d, *J* = 18.0 Hz, 1H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 150.2, 148.2, 144.6, 135.5, 132.3, 130.1, 129.0, 125.4, 124.2, 120.9, 83.5, 24.8; HRMS (ESI): m/z calcd for $C_{17}H_{21}BNO_2^+$ $[M+H^+]$: 282.1660, Found: 282.1653.

5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)isoquinoline (23-4a).



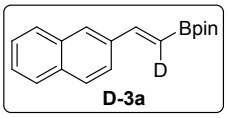
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (d, *J* = 4.0 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.64-7.60 (m, 1H), 7.42-7.38 (m, 2H), 3.19 (t, *J* = 8.0 Hz, 2H), 1.28 (t, *J* = 8.0 Hz, 2H), 1.22 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 148.2, 132.3, 127.5, 126.1, 120.4, 83.1, 26.1, 24.8; HRMS (ESI): m/z calcd for $C_{17}H_{23}BNO_2^+$ [M+H$^+$]: 284.1816, Found: 284.1819.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (3x).



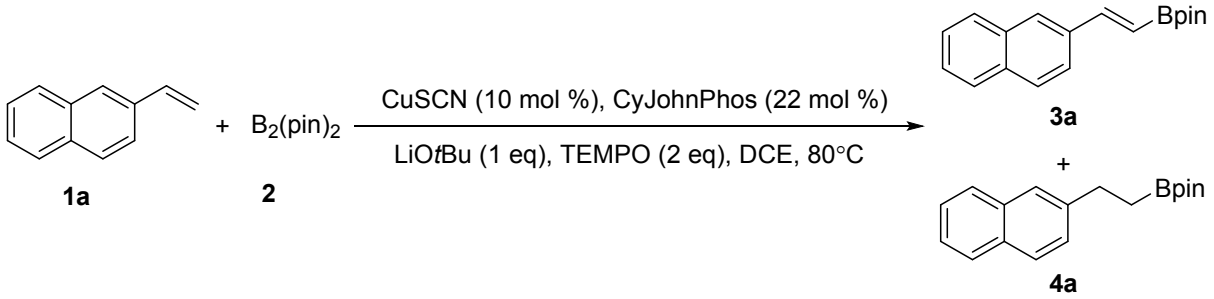
The reaction was conducted with general procedure in 0.15 mmol scale. Heating up to 80 °C for 12 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 5/1) to afford product **3x** (46 mg, 76% yield) as light yellow solid; m.p. 228-231 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 18.4 Hz, 1H), 7.29-7.27 (m, 2H), 7.22 (s, 1H), 6.11 (d, *J* = 18.4 Hz, 1H), 2.93-2.90 (m, 2H), 2.51 (dd, *J* = 19.2, 8.0 Hz, 1H), 2.45-2.40 (m, 1H), 2.34-2.28 (m, 1H), 2.20-2.13 (m, 1H) , 2.11-2.00 (m, 2H), 1.98-1.95 (m, 1H), 1.68-1.40 (m, 6H), 1.31 (s, 12H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 220.8, 149.3, 140.7, 136.5, 135.0, 127.7, 125.5, 124.4, 83.2, 50.4, 47.9, 44.4, 38.0, 35.8, 31.5, 29.3, 26.4, 25.6, 24.8, 21.5, 13.8; HRMS (ESI): m/z calcd for $C_{26}H_{36}BO_3^+$ [M+H$^+$]: 407.2752, Found: 407.2758.

(*Z*)-2-(1-*D*-2(naphthalene-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*D*-1a).



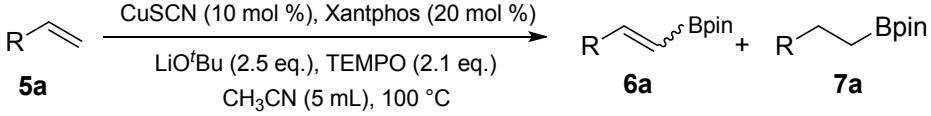
The reaction was conducted with general procedure in 0.3 mmol scale. Heating up to 80 °C for 18 h, the residue was purified by column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 100/1) to afford product **D-3a** (68 mg, 80% yield) as colorless solid (D/H=13:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.79 (m, 4H), 7.71-7.69 (m, 1H), 7.56 (s, 1H), 7.48-7.44 (m, 2H), 1.33 (s, 12H); MS (ESI+) m/z: 282.2 (M+H)$^+$.

One example of the detailed procedure for 1 mmol scale:



In a nitrogen-filled glove-box, CuSCN (12.2 mg, 10 mol %), CyJohnPhos (77 mg, 22 mol %), and DCE (4 mL) were added to an oven-dried 25 mL Schlenk tube containing a stirring bar. The solution was stirred at room temperature until a colorless solution is formed. Then, LiO^{t}Bu (80 mg, 1 mmol), 2-vinylnaphthalene (154 mg, 1 mmol), TEMPO (312 mg, 2 mmol), pinacolborane (508 mg, 2 mmol) and DCE (4 mL) were added to the above mixture. The Schlenk tube was sealed with a Teflon-lined screw cap and taken out of the glove-box. Heating up to 80 °C for 18 h, the resulting red brown mixture was allowed to cool to room temperature, diluted with CH_2Cl_2, and washed with H_2O. The aqueous layer was extracted with CH_2Cl_2 (20 mL× 3). The combined organic layers were dried over $MgSO_4$, and the filtrate was concentrated. The crude was purified by column chromatography first with eluent petroleum ether (150 mL), then with the eluent 600 mL (petroleum ether/ethyl acetate = 100/1) to afford the product **3a** as colorless oil (202 mg, 72%), and the recovery of the substrate **1a** as colorless solid was 27 mg (18%).

VII. Typical procedure for direct synthesis of alkenylboronates from terminal aliphatic alkenes and diboron via copper catalysis

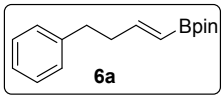


5a **6a** **7a**

In a nitrogen-filled glove-box, CuSCN (3.7 mg, 10 mol%), XantPhos (34.8 mg, 20 mol%), and CH_3CN (2.5 mL) were added to an oven-dried 25 mL Schlenk tube containing a stirring bar. The solution was stirred at room temperature for 30 minutes. Then, LiO^{t}Bu (60 mg, 0.75 mmol), 4-Phenyl-1-butene (39.6 mg, 0.3 mmol), TEMPO (98.3 mg, 0.63 mmol), pinacolborane (152.3 mg, 0.6 mmol) and CH_3CN (2.5 mL) were added to the above mixture. The Schlenk tube was sealed with a Teflon-lined screw cap and taken out of the glove-box. Heating up to 100 °C for 24 h, the resulting red brown mixture was allowed to cool to room temperature, diluted with CH_2Cl_2, and washed with H_2O. The aqueous layer was extracted with CH_2Cl_2 (15 mL× 3). The combined organic layers were dried over $MgSO_4$, and the filtrate was concentrated. The crude reaction mixture was analyzed by ^{1}H NMR to determine the *E/Z* ratio. The crude material was purified by column chromatography on boric acid (0.5 %) impregnated silica gel (as prepared above) in the indicated solvent combination.

VIII. Characterization data

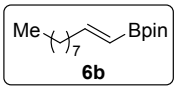
(*E*)-4,4,5,5-tetramethyl-2-(4-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane (6a).[16]



6a

The reaction was conducted in 0.3 mmol scale. ^{1}H NMR analysis of the crude reaction mixture determined a ratio of *E/Z* = 87:13. The residue was purified by column chromatography on boric acid impregnated silica gel with eluent (petroleum ether/ diethyl ether = 100/1) to afford the product **6a** (72 mg, 93% yield) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.20-7.16 (m, 3H), 6.70 (dt, *J* = 18.0, 6.0 Hz, 1H), 5.50 (dt, *J* = 18.0, 1.6 Hz, 1H), 2.76-2.72 (m, 2H), 2.51-2.45 (m, 2H), 1.27 (s, 12H); MS (ESI+) m/z: 259.3 $(M+H)^+$.

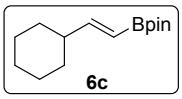
(*E*)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6b**).[12]



6b

The reaction was conducted in 0.3 mmol scale. ^{1}H NMR analysis of the crude reaction mixture determined a ratio of *E/Z* = 91:9. The residue was purified by silica column chromatography on boric acid impregnated silica gel with eluent (petroleum ether/ diethyl ether = 200/1) to afford product **6b** (76 mg, 95% yield) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.42 (dt, *J* = 17.6, 1.6 Hz, 1H), 2.17-2.11 (m, 2H), 1.43-1.37 (m, 2H), 1.29-1.23 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H); MS (ESI+) m/z: 284.4 $(M+NH_4)^+$.

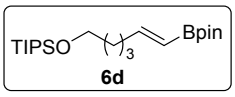
(*E*)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6c**).[16]



6c

The reaction was conducted in 0.3 mmol scale. ^{1}H NMR analysis of the crude reaction mixture determined a ratio of *E/Z*= 93:7. The residue was purified by silica column chromatography on boric acid impregnated silica gel with eluent (petroleum ether/ diethyl ether = 150/1) to afford product **6c** (65 mg, 85% yield) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.58 (dd, *J* = 18.0, 6.0 Hz, 1H), 5.38 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.05-2.01 (m, 1H), 1.75-1.71 (m, 4H), 1.67-1.63 (m, 2H), 1.27 (s, 12H), 1.17-1.08 (m, 4H); MS (ESI+) m/z: 254.3 $(M+NH_4)^+$.

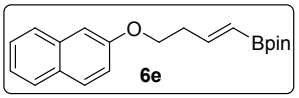
(*E*)-triisopropyl((6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)hex-5-en-1-yl)oxy)silane (**6d**).[12]



6d

The reaction was conducted in 0.3 mmol scale. ^{1}H NMR analysis of the crude reaction mixture determined a ratio of *E/Z* = 96:4. The residue was purified by silica column chromatography on boric acid impregnated silica gel with eluent (petroleum ether/ diethyl ether = 100/1) to afford product **6d** (86 mg, 75% yield) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.43 (dt, *J* = 18.0, 1.6 Hz, 1H), 3.67 (t, *J* = 6.4 Hz, 2H), 2.21-2.15 (m, 2H), 1.57-1.47 (m, 4H), 1.27 (s, 12H), 1.11-1.02 (m, 21H); MS (ESI+) m/z: 383.4 $(M+H)^+$.

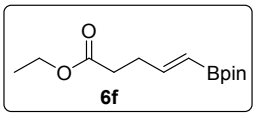
(*E*)-4,4,5,5-tetramethyl-2-(4-(naphthalen-2-yloxy)but-1-en-1-yl)-1,3,2-dioxaborolane (6e).



6e

The reaction was conducted in 0.3 mmol scale. ^{1}H NMR analysis of the crude reaction mixture determined a ratio of *E/Z* = 82:18. The residue was purified by silica column chromatography on boric acid impregnated silica gel with eluent (petroleum ether/ diethyl ether = 80/1) to afford product **6e** (63 mg, 65% yield) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.70 (m, 3H), 7.45-7.40 (m, 1H), 7.34-7.30 (m, 1H), 7.16-7.11 (m, 2H), 6.74 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.63 (dt, *J* = 18.4, 1.2 Hz, 1H), 4.16 (t, *J* = 6.4 Hz, 2H), 2.74-2.69 (m, 2H), 1.28 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 149.5, 134.5, 129.3, 128.9, 127.6, 126.7, 126.3, 123.5, 119.0, 104.5, 83.2, 66.4, 35.4, 24.8; HRMS (ESI): m/z calcd for $C_{20}H_{26}BO_3^+$ $[M+H^+]$: 325.1970, Found: 325.1973.

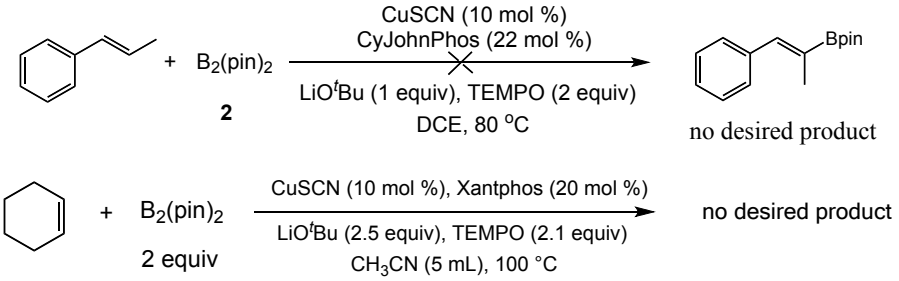
(*E*)-ethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (6f).



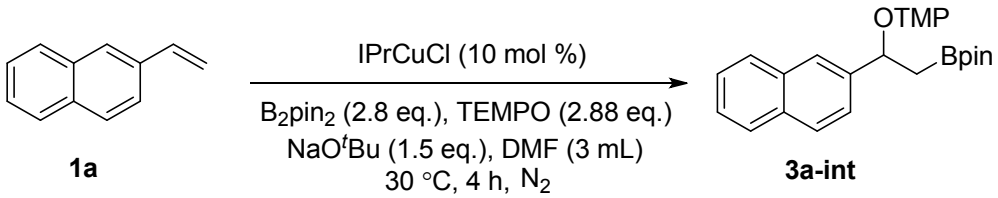
6f

The reaction was conducted in 0.3 mmol scale. ^{1}H NMR analysis of the crude reaction mixture determined a ratio of *E/Z* = 99:1. The residue was purified by silica column chromatography on boric acid impregnated silica gel with eluent (petroleum ether/ diethyl ether = 80/1) to afford product **6f** (52 mg, 68% yield) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.62 (dt, *J* = 18.0, 5.6 Hz, 1H), 5.47 (dt, *J* = 18.0, 1.2 Hz, 1H), 4.13 (q, *J* = 14.4, 7.2 Hz, 2H), 2.51-2.40 (m, 4H), 1.27-1.24 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 151.7, 83.1, 60.4, 32.7, 30.6, 24.7, 14.2; HRMS (ESI): m/z calcd for $C_{13}H_{24}BO_4^+$ $[M+H^+]$: 255.1762, Found: 255.1767.

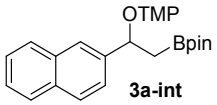
We subjected the following internal alkenes as substrates to the standard conditions. However, no corresponding desired products were observed.



The synthesis of compound 3a-int



2,2,6,6-tetramethyl-1-(1-(naphthalene-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethoxy)piperidine[18]



In glovebox, IPrCuCl (14.6 mg, 10 mol %), TEMPO (134.8 mg, 0.86 mmol), NaO^{t}Bu (43.2 mg, 0.45 mmol), **1a** (46.2 mg, 0.3 mmol), and DMF (3 mL) were added to a dried tube. The resulting mixture was stirred at ambient temperature with B_2pin_2 (213.4 mg, 0.84 mmol) added dropwise for 20 min. The resulting mixture was stirred at ambient temperature for 4 h. The tube was taken out of glovebox. The reaction was quenched with water, and then extracted three times with ether. The combined organic layers were washed with aqueous sodium hydroxide and water, and dried over Na_2SO_4. The desired product **3a-int** was obtained by recrystallization (100 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.77 (m, 3H), 7.73-7.69 (m, 1H), 7.58-7.56 (m, 1H), 7.48-7.39 (m, 2H), 5.06 (dd, *J* = 11.2, 4.0 Hz, 1H), 1.89 (dd, *J* = 14.4, 4.0 Hz, 1H), 1.51-1.45 (m, 4H), 1.36-1.34 (m, 6H), 1.18 (s, 3H), 0.99-0.96 (m, 15H), 0.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 132.9, 132.7, 127.9, 127.5, 127.4, 126.0, 125.8, 125.5, 125.2, 84.4, 82.8, 59.7, 59.4, 40.3, 34.8, 34.4, 24.8, 24.4, 20.3, 17.2; HRMS (ESI): m/z calcd for $C_{27}H_{41}BNO_3^+$ [M+H$^+$]: 438.3174, Found: 438.3192.

IX. References

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14. Endo, K.; Ohkubo, T.; Ishioka, T.; Shibata, T. *J. Org. Chem*. **2012**, *77*, 4826-4831.
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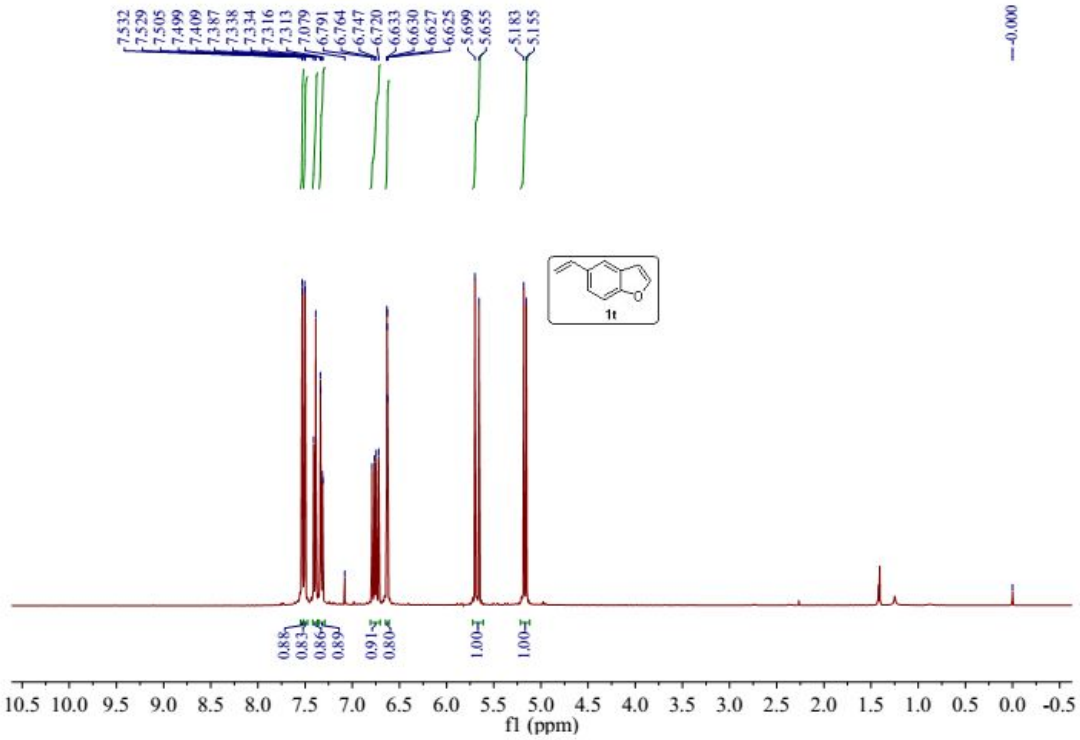
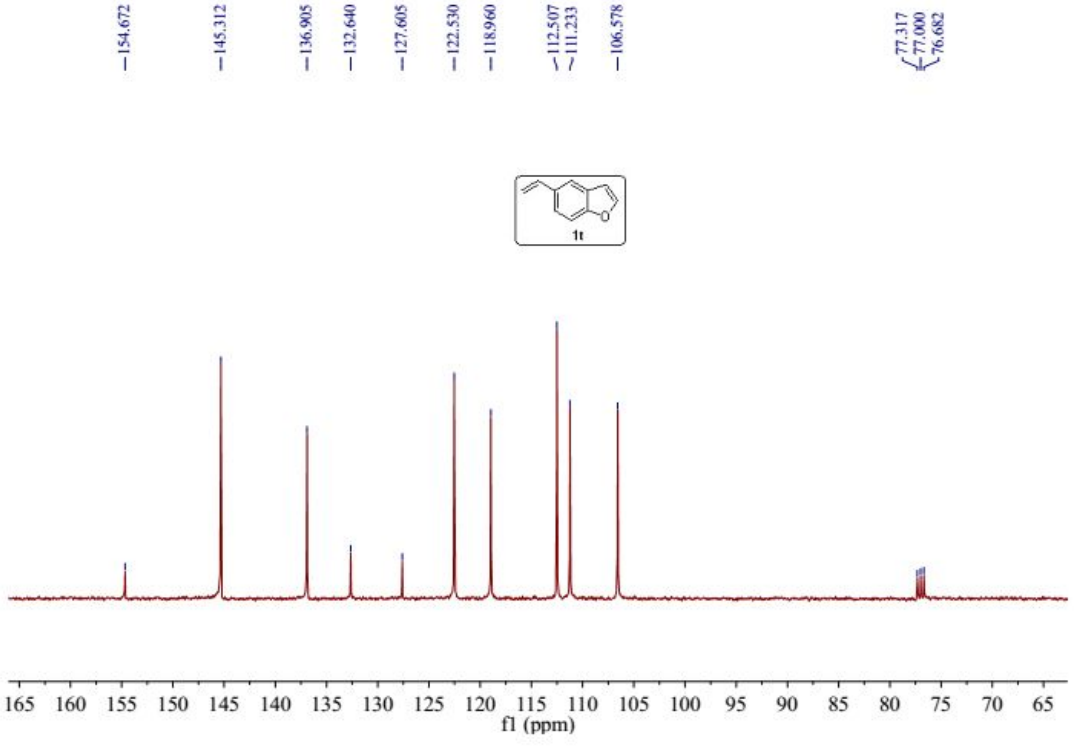
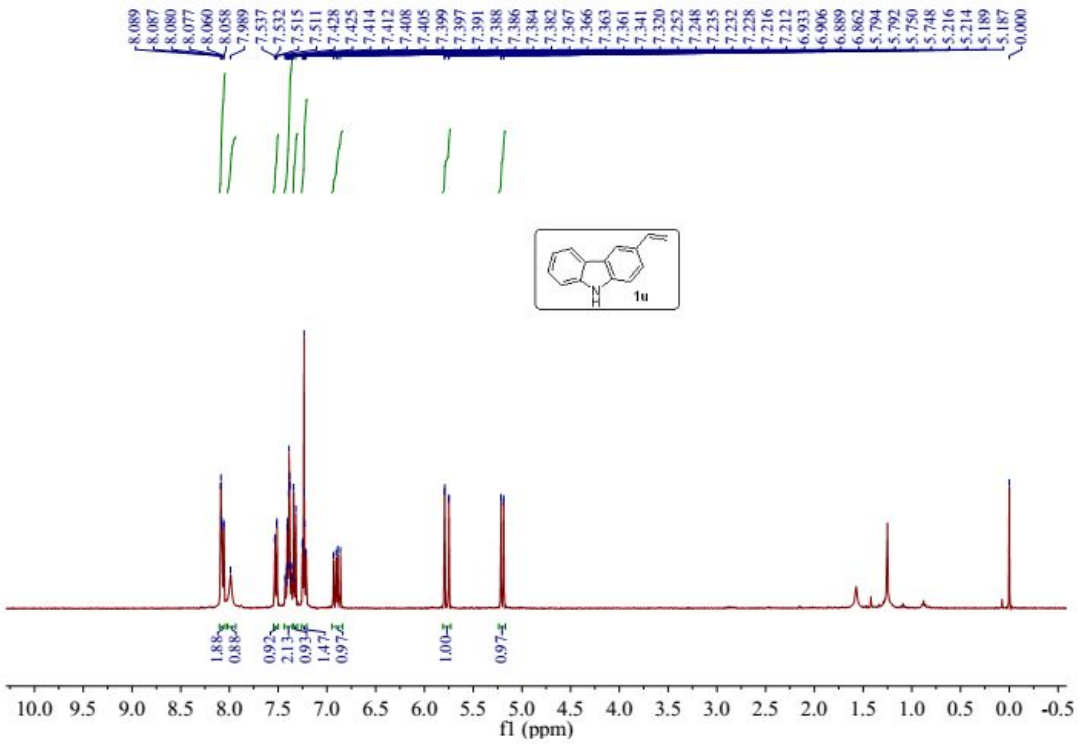
18. Itoh, T.; Matsueda, T.; Shimizu, Y.; Kanai, M. *Chem. - Eur. J.* **2015**, *21*, 15955-15959.

X. Copies of NMR spectra of products



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7.399
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7.382
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6.862
5.794
5.792
5.750
5.748
5.216
5.214
5.189
5.187
0.000
1u
1.88
0.88
0.92
2.13
0.93
1.47
0.97
1.00
0.97
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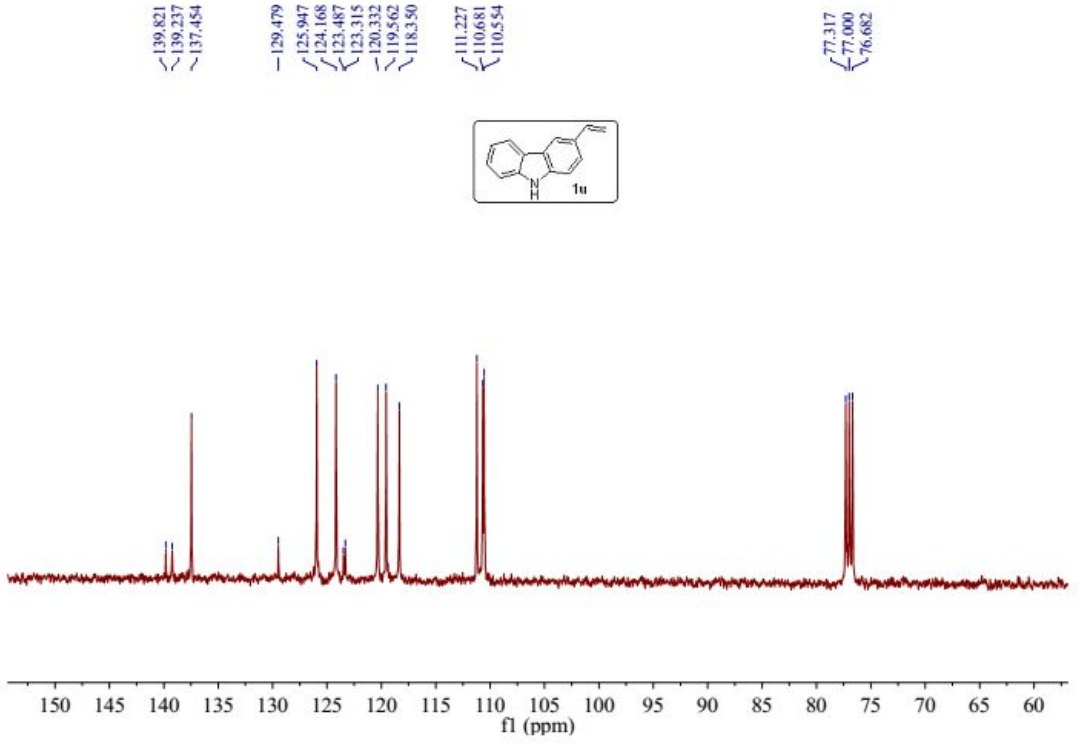
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76.682
1u
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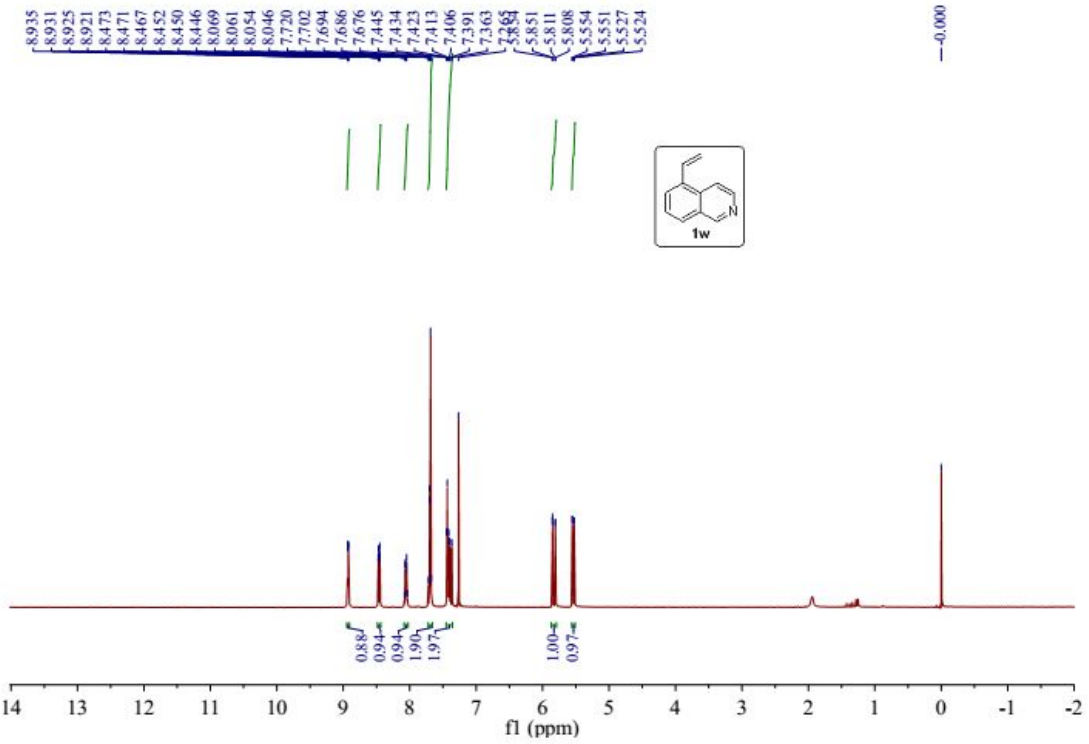
f1 (ppm)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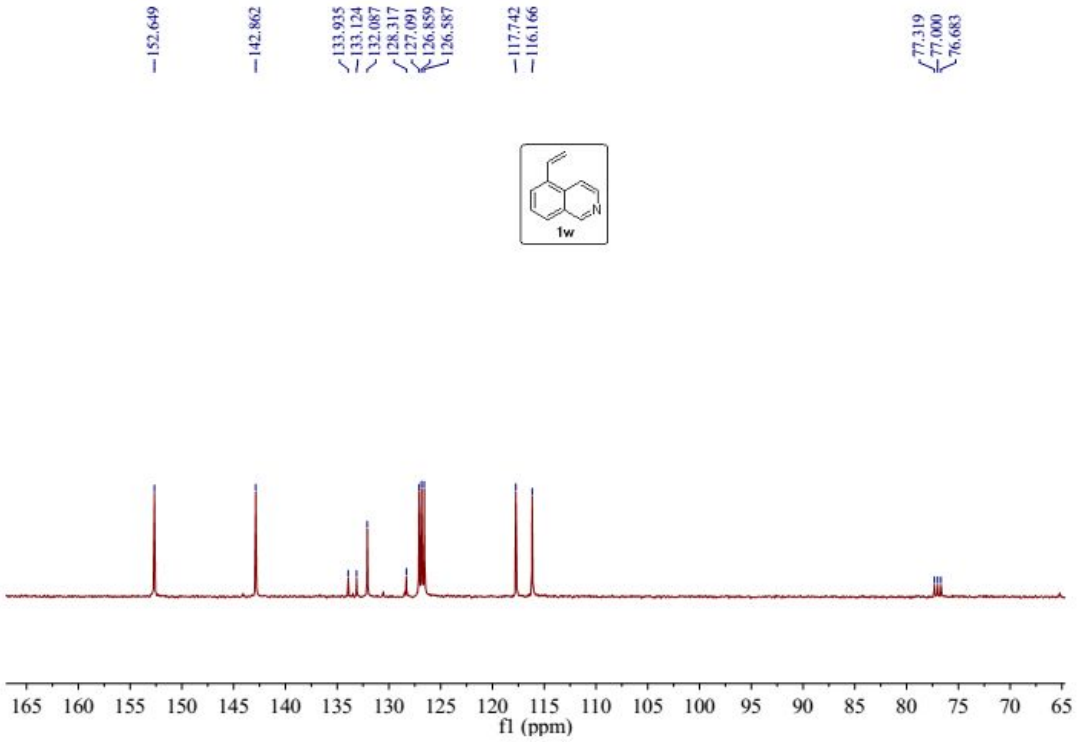
fl (ppm)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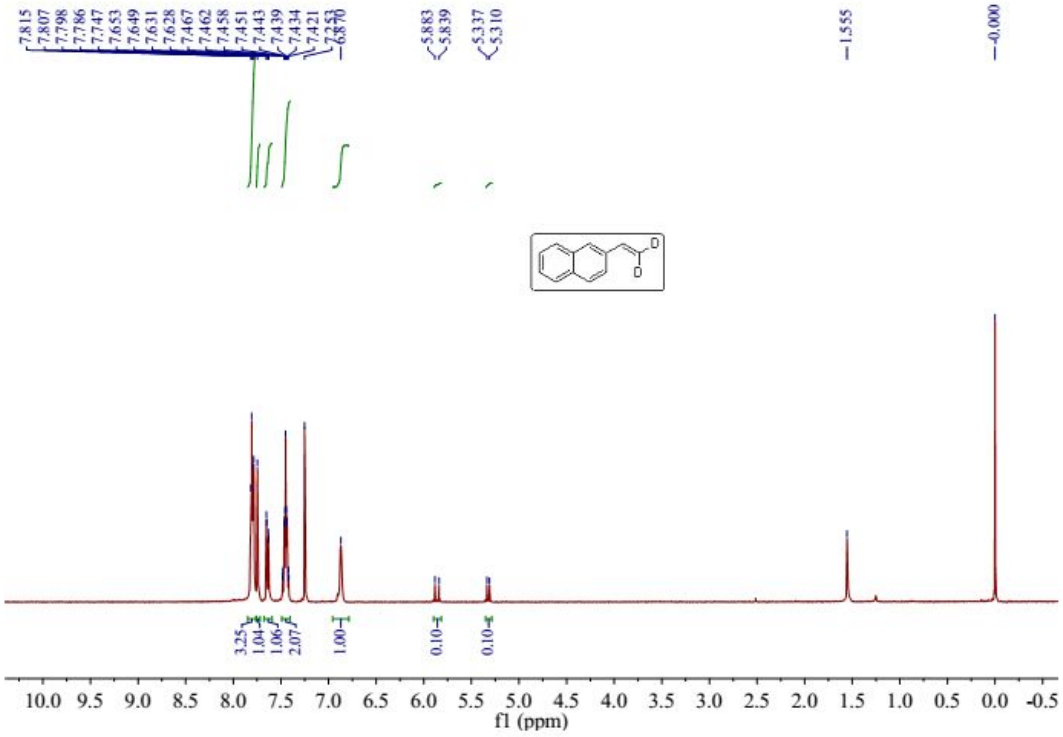
1w
fl (ppm)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1.06
2.07
1.00
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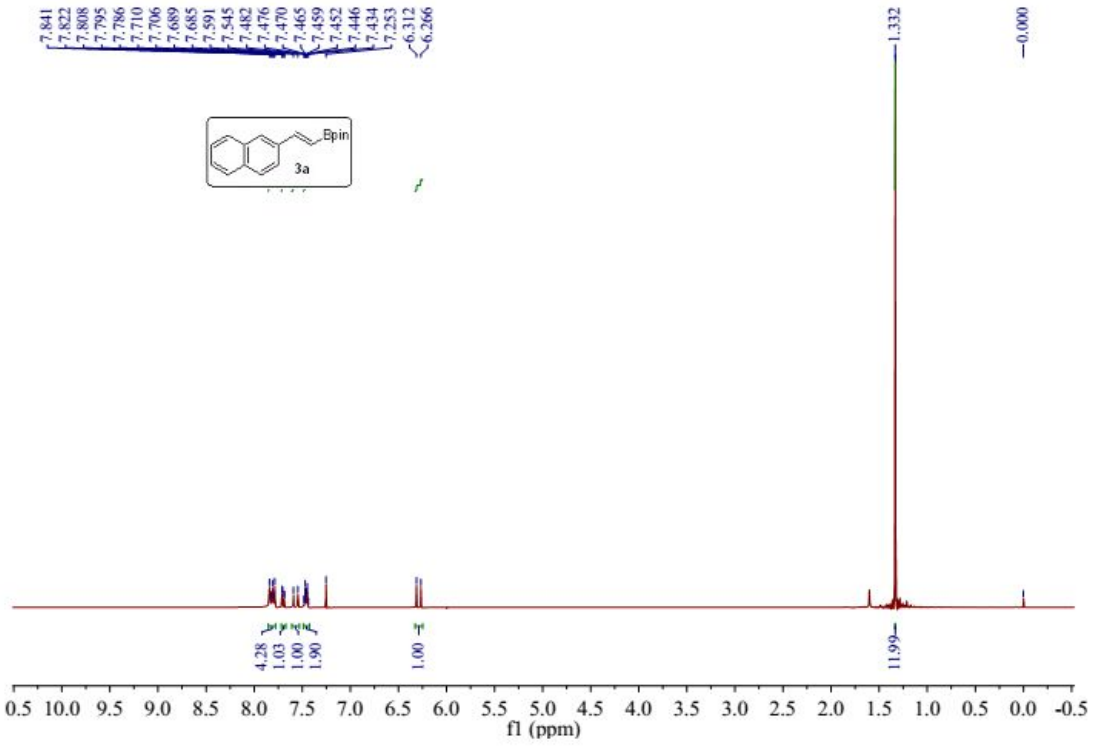
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1.00
11.99
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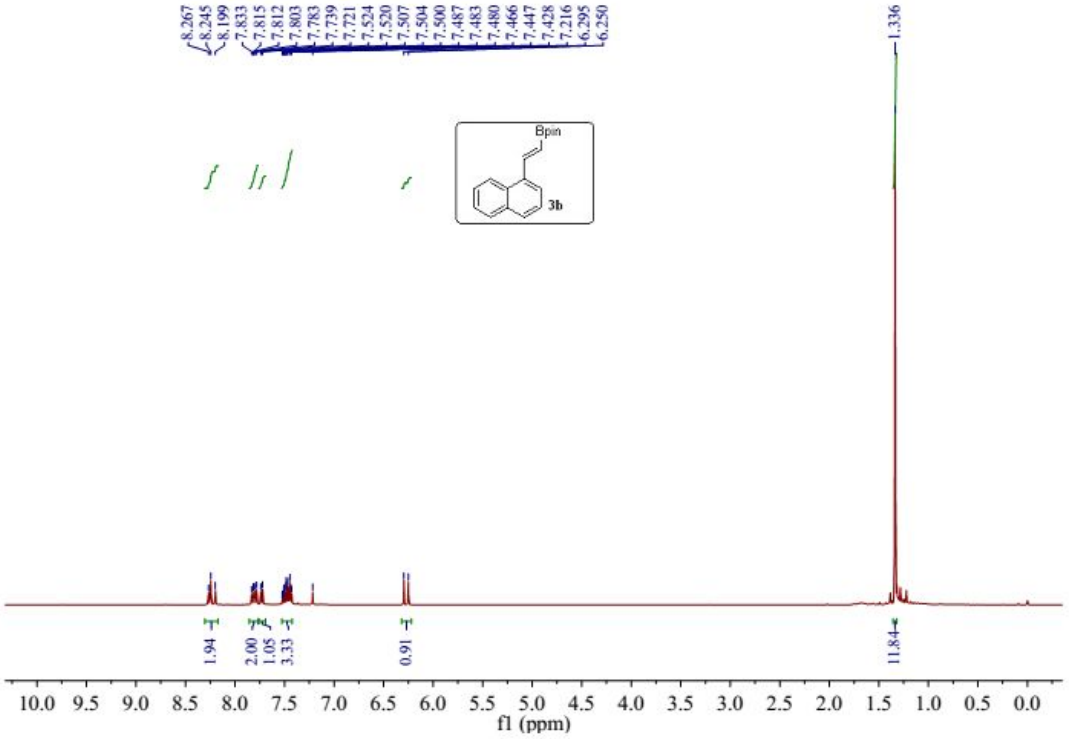
f1 (ppm)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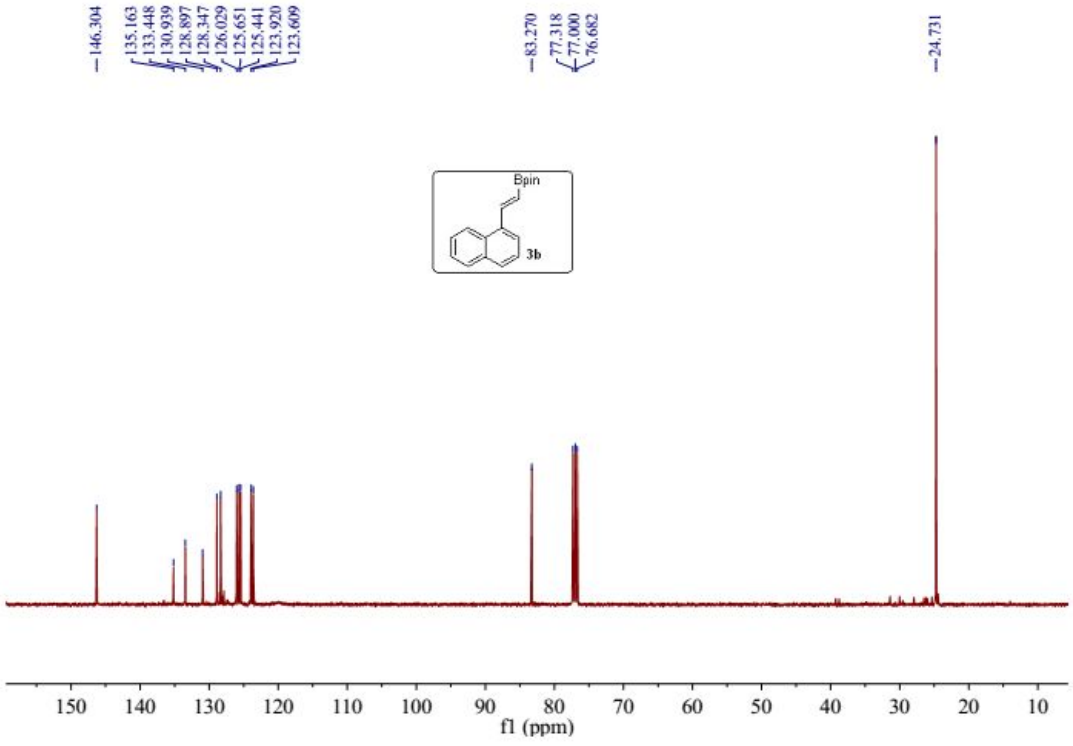
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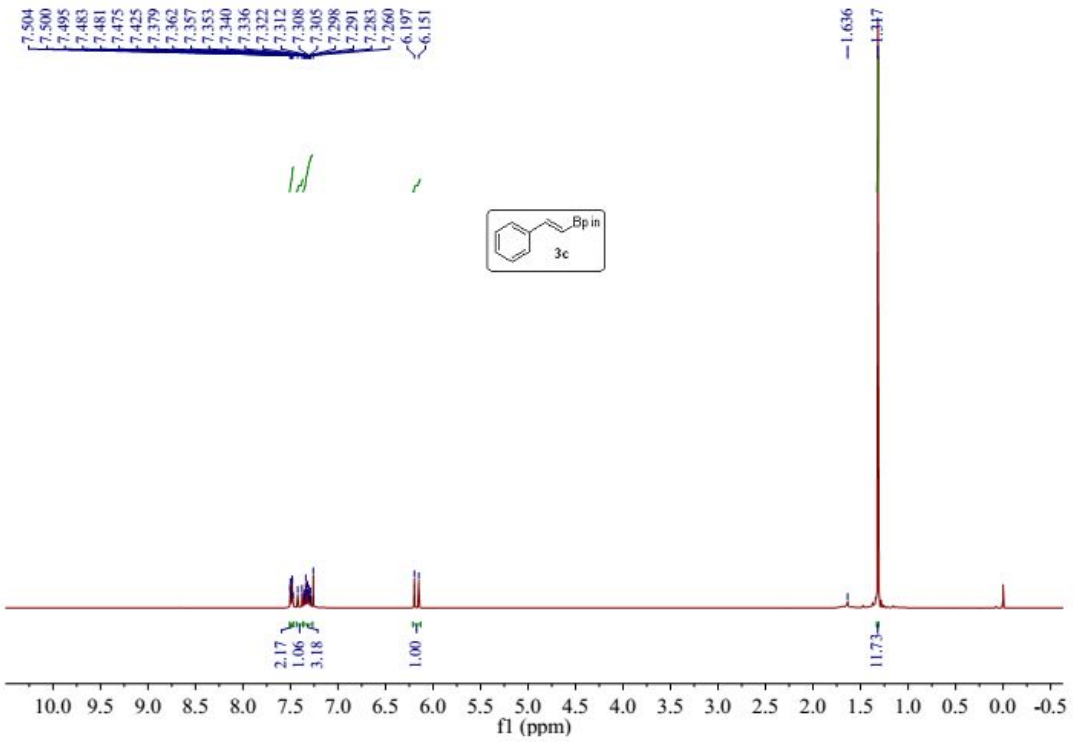
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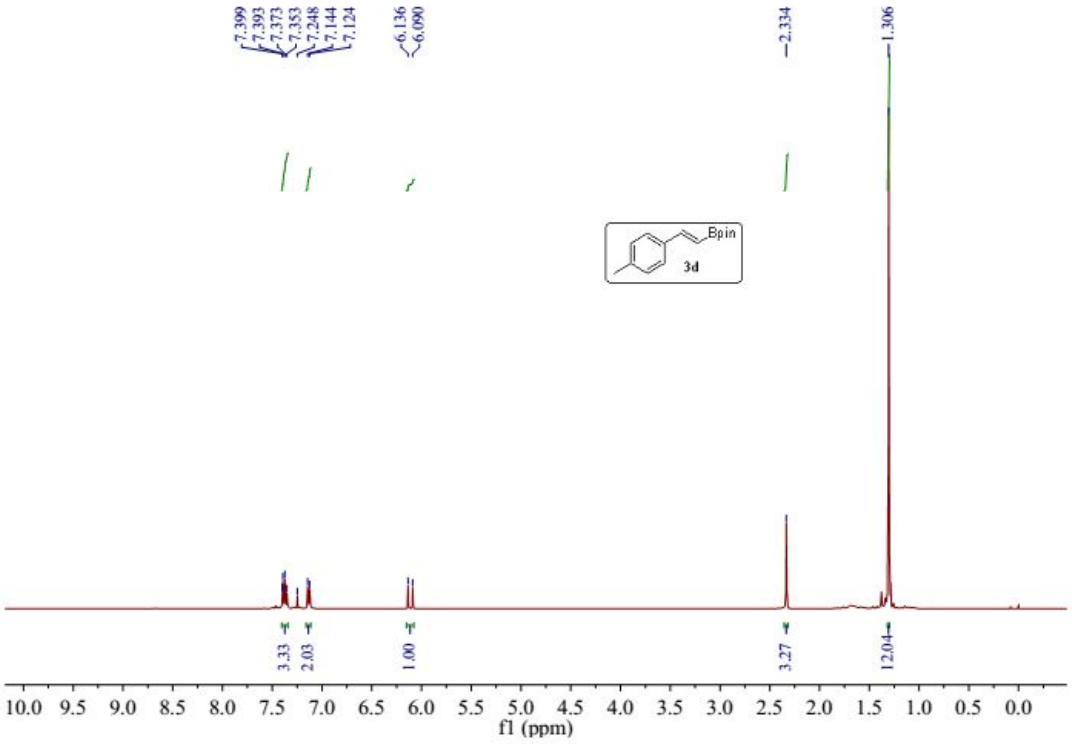
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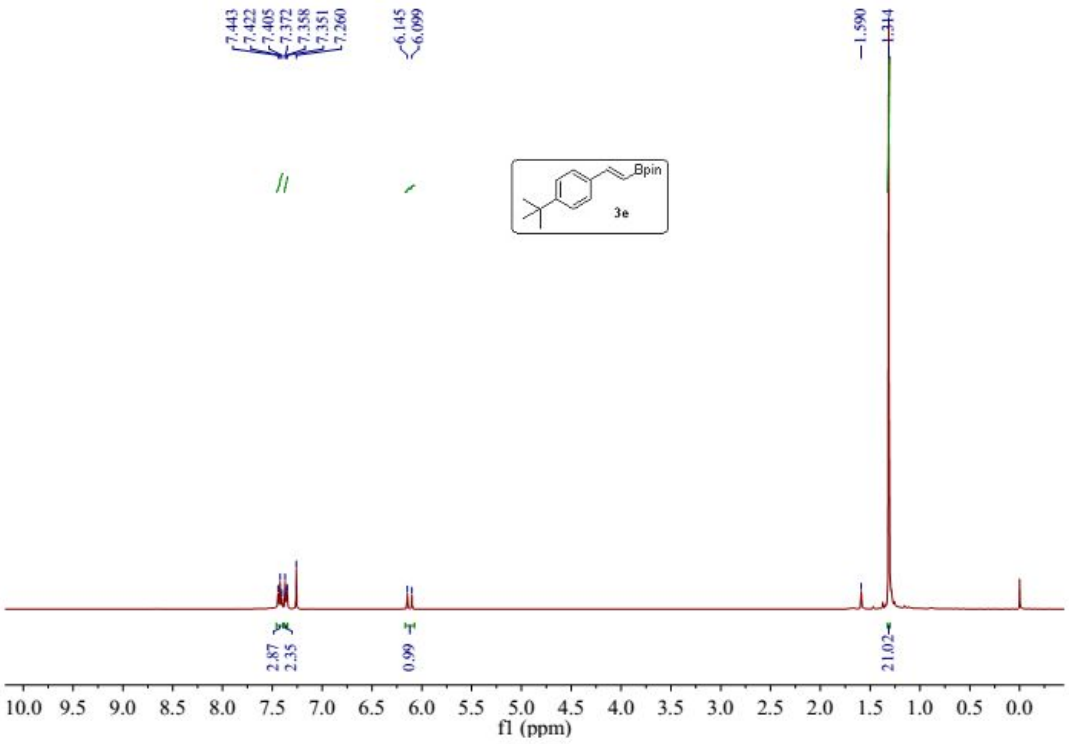
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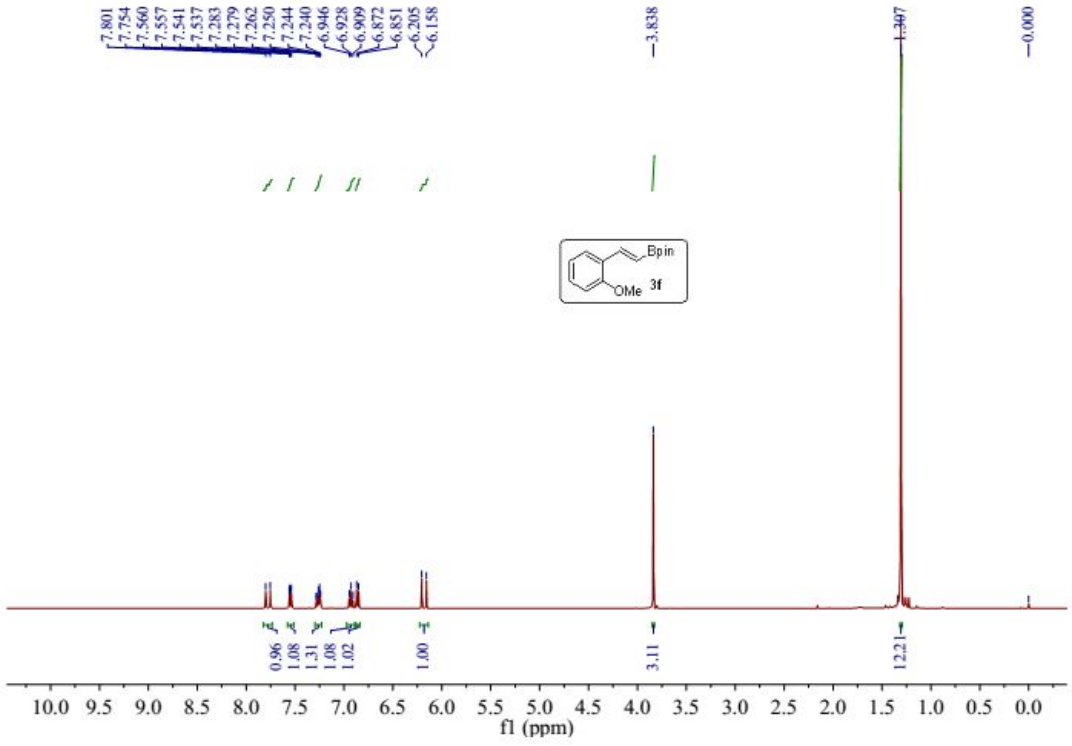
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OMe
3f
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1.31
1.08
1.02
1.00
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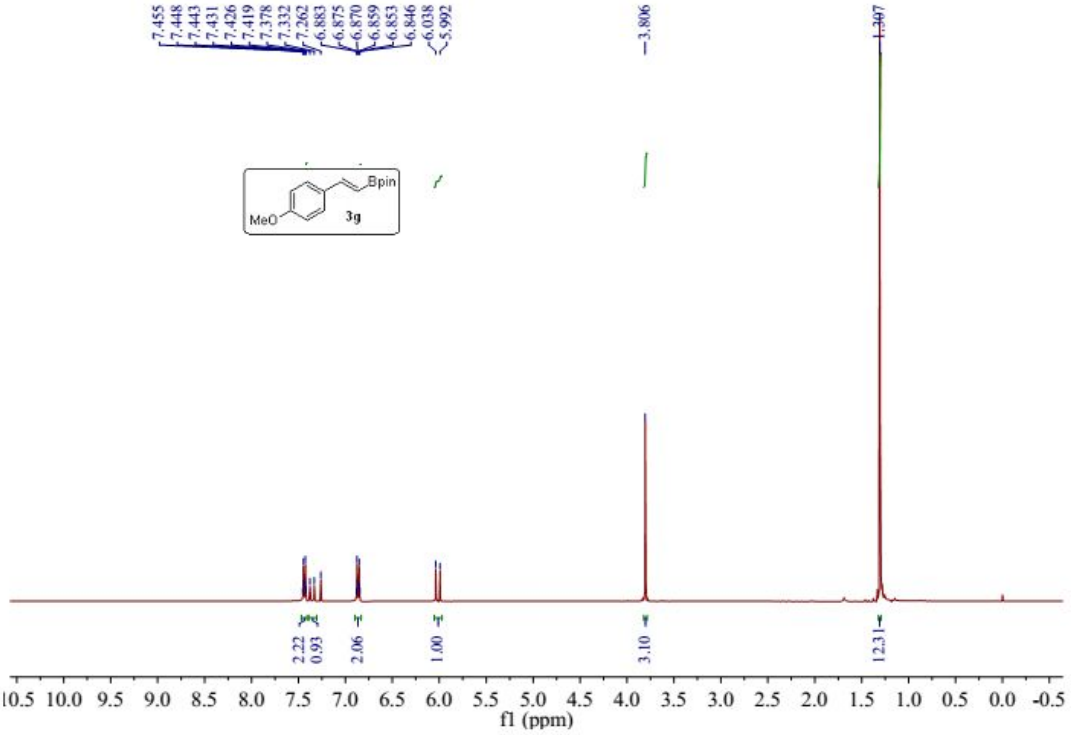
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3.806
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2.06
1.00
3.10
12.31
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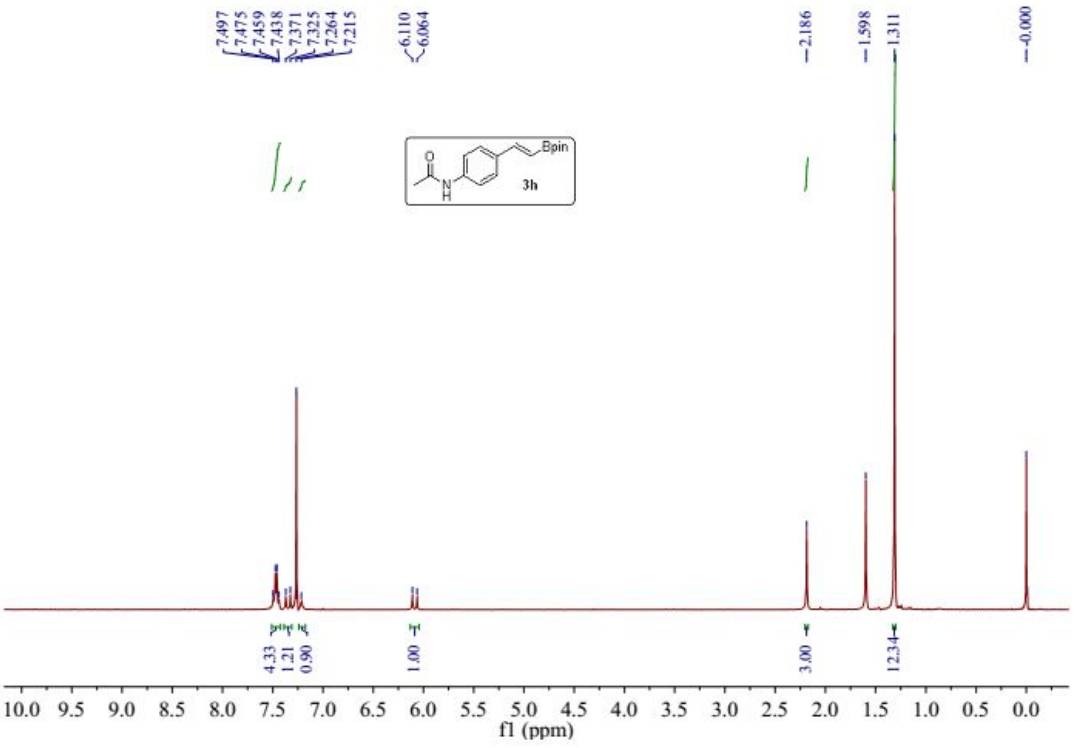
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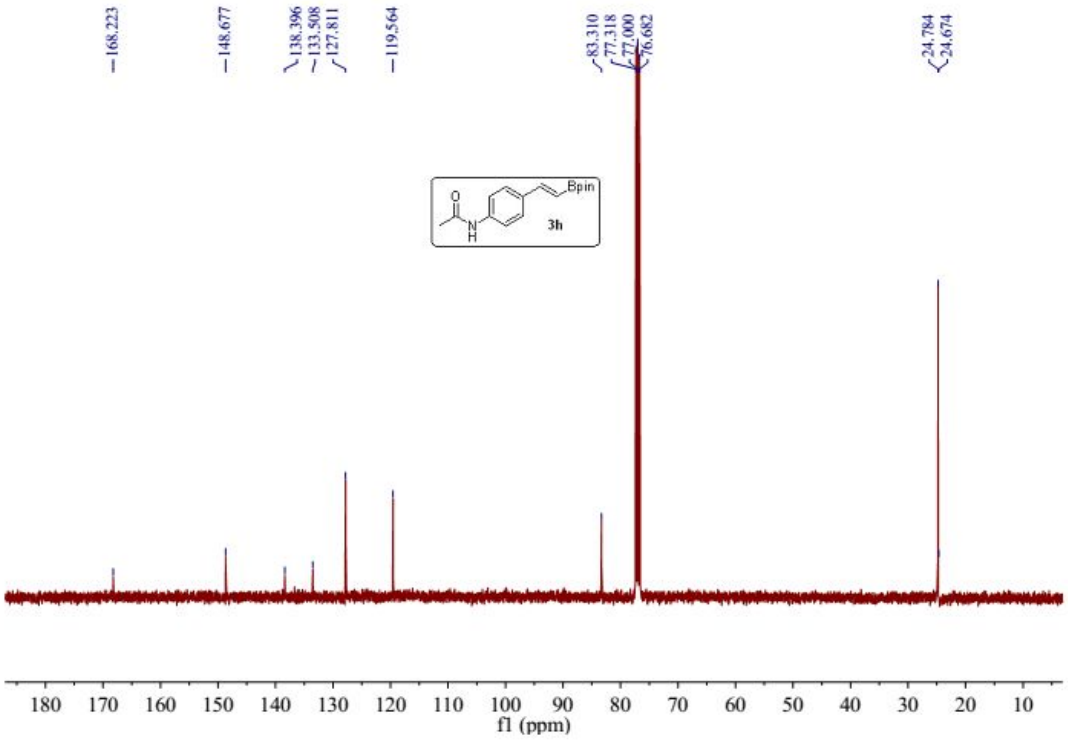
3.00
12.34
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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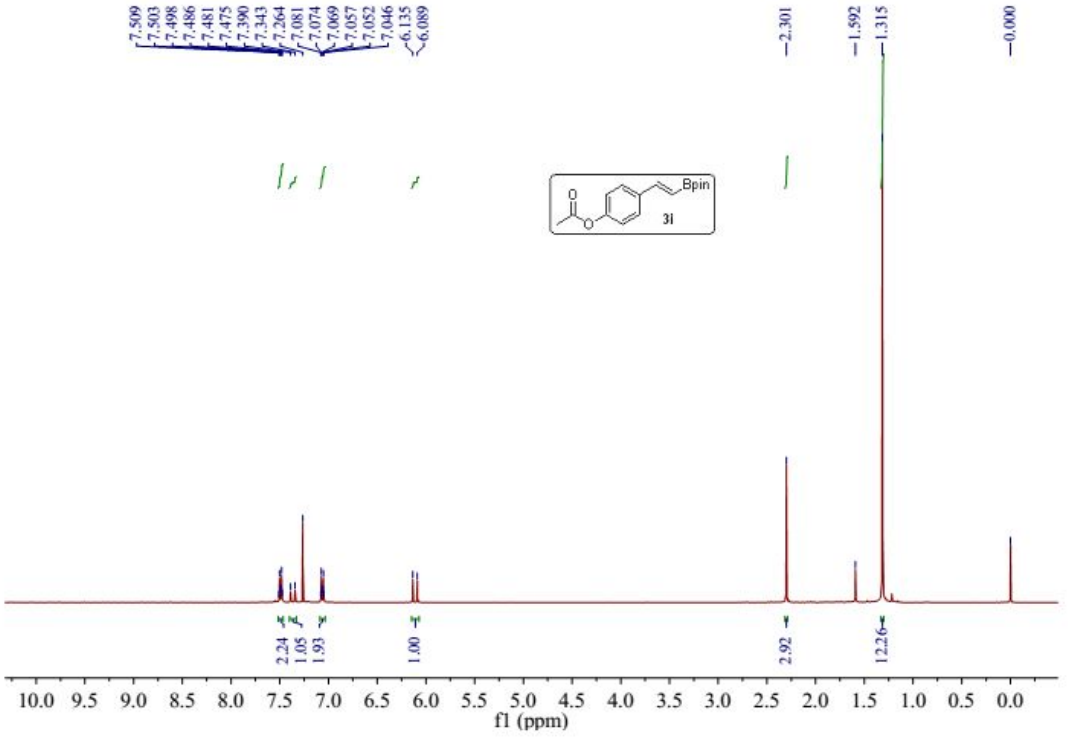
148.677
138.396
133.508
127.811
119.564
83.310
77.318
77.000
76.682
24.784
24.674
Bpin
3h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.498
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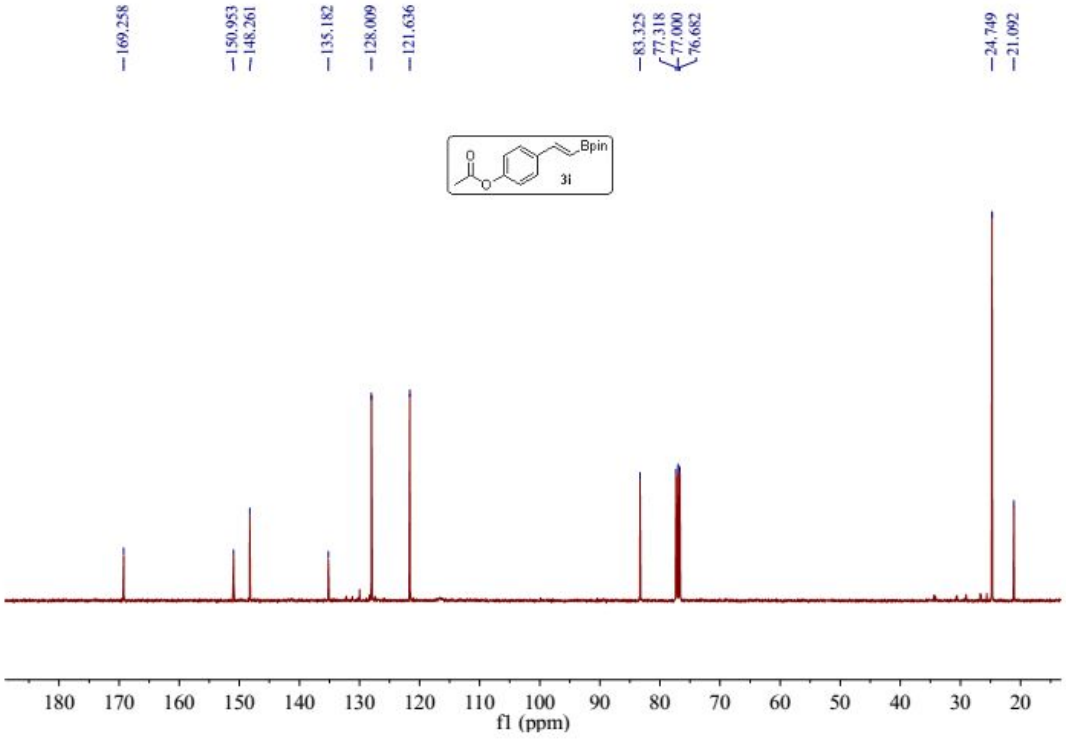
7.390
7.343
7.264
7.081
7.074
7.069
7.057
7.052
7.046
6.135
6.089
2.301
1.592
1.315
0.000
Bpin
3l
2.24
1.05
1.93
1.00
2.92
12.26
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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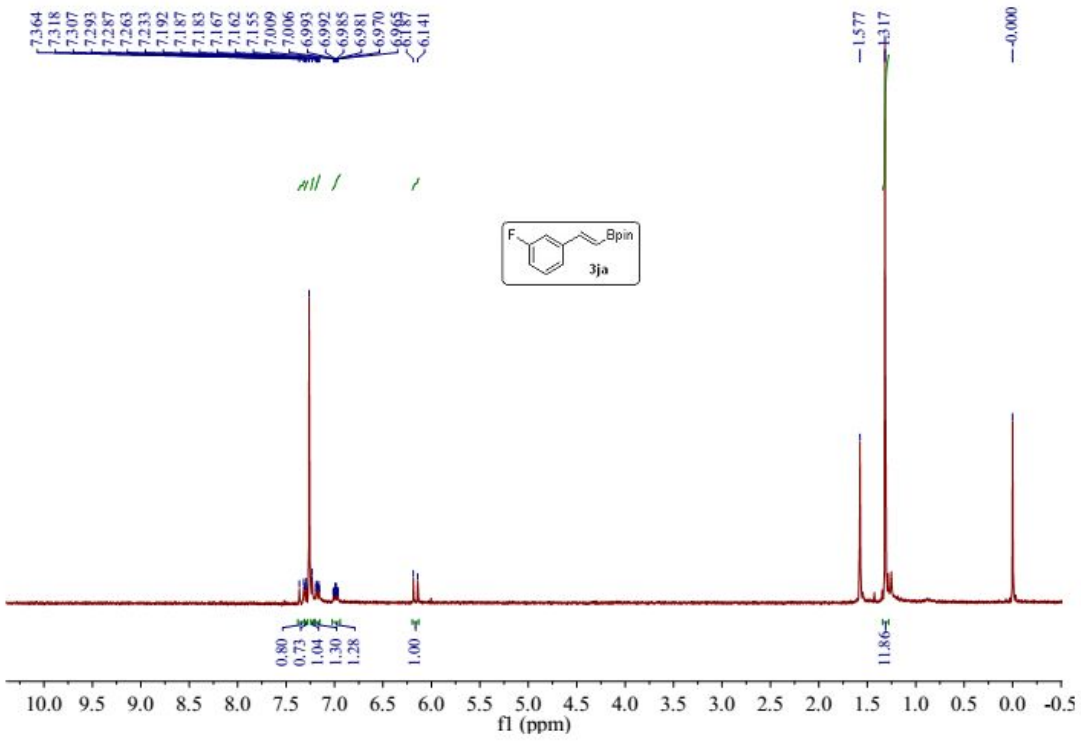
150.953
148.261
135.182
128.009
121.636
83.325
77.318
77.000
76.682
24.749
21.092
Bpin
3i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)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7.318
7.307
7.293
7.287
7.263
7.233
7.192
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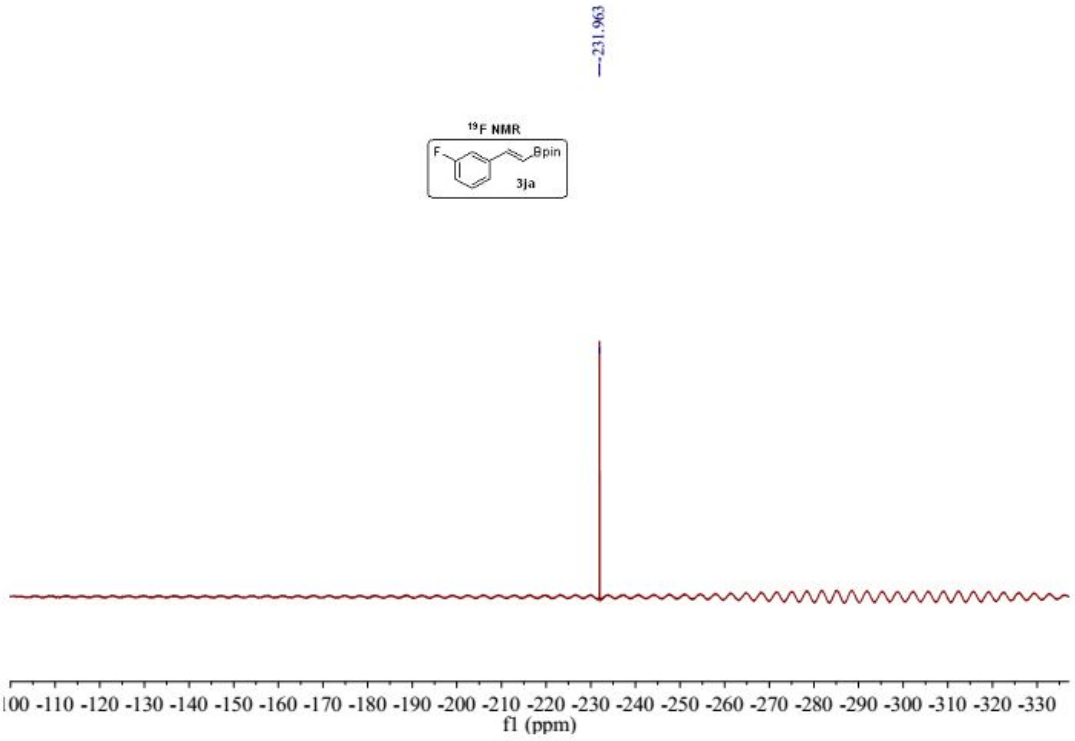
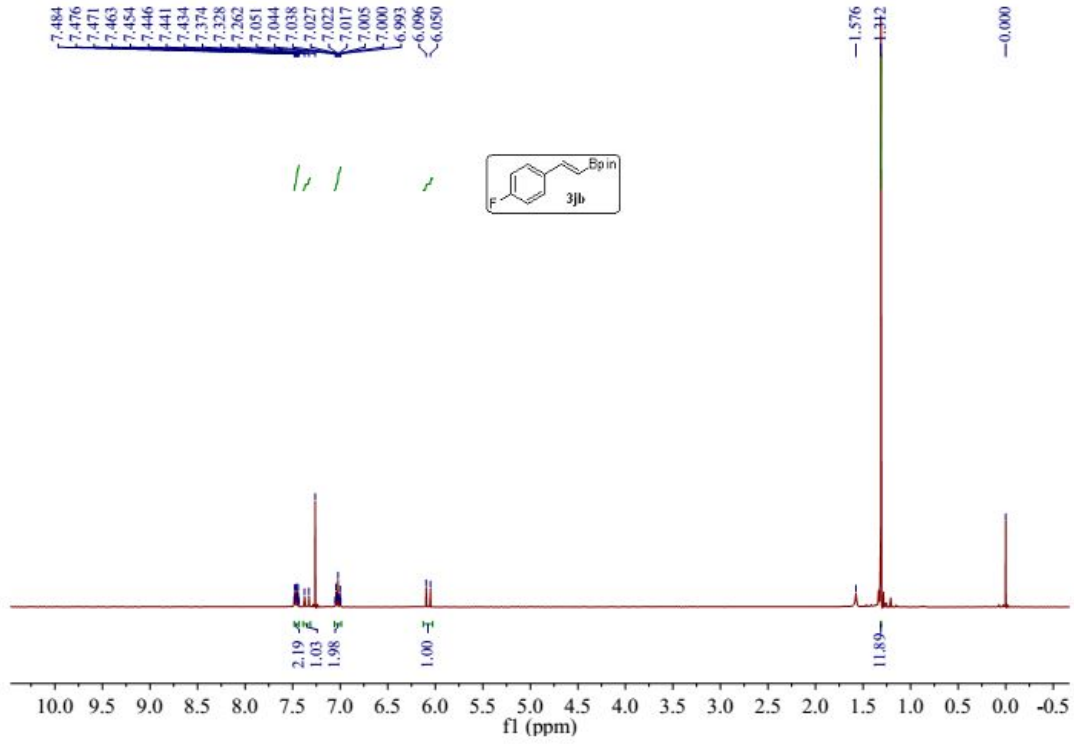
7.183
7.167
7.162
7.155
7.009
7.006
6.993
6.992
6.985
6.981
6.970
6.965
6.187
6.141
1.577
1.317
-0.000
F
Bpin
3ja
0.80
0.73
1.04
1.30
1.28
1.00
11.86
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


-231.963
19F NMR
F
Bpin
3ja
100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310 -320 -330
f1 (ppm)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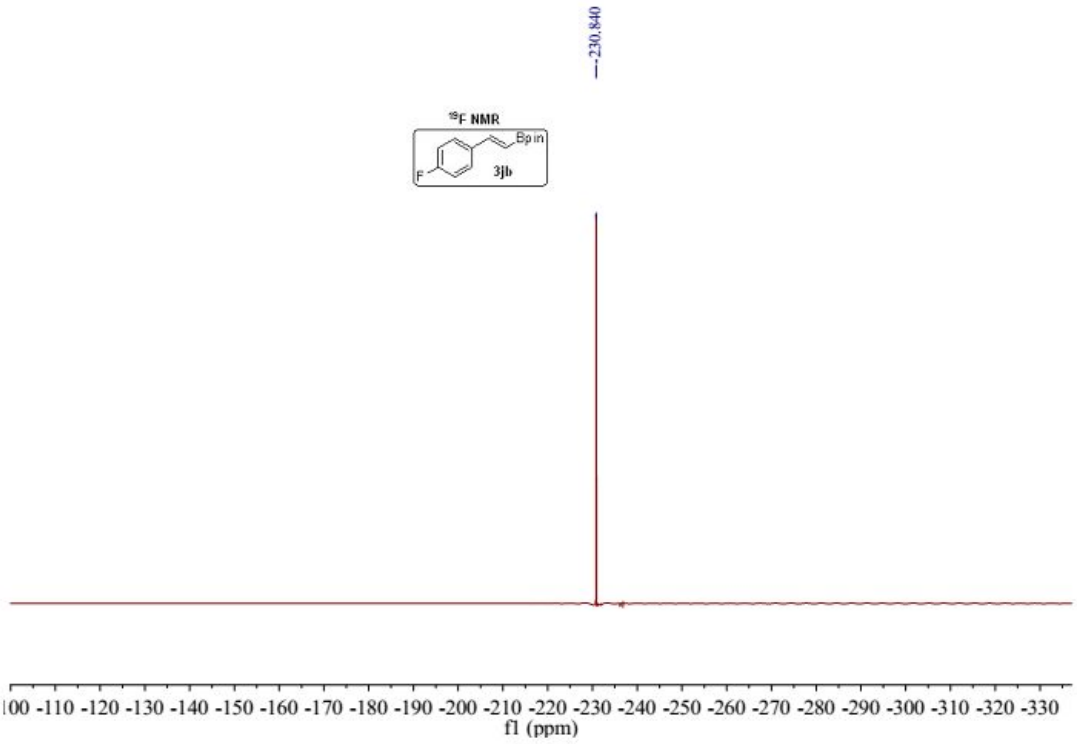
7.471
7.463
7.454
7.446
7.441
7.434
7.374
7.328
7.262
7.051
7.044
7.038
7.027
7.022
7.017
7.005
7.000
6.993
6.096
6.050
1.576
1.342
0.000
Bpin
F
3jb
2.19
1.03
1.98
1.00
11.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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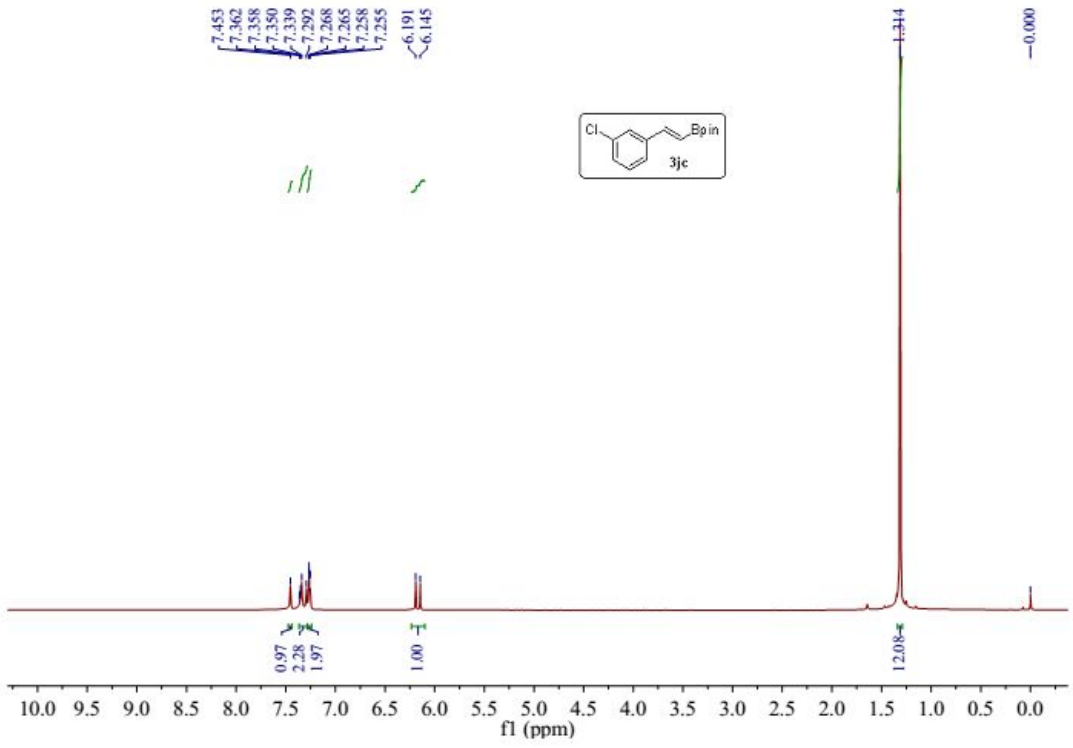
^{19}F NMR
Bpin
F
3jb
100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310 -320 -330
f1 (ppm)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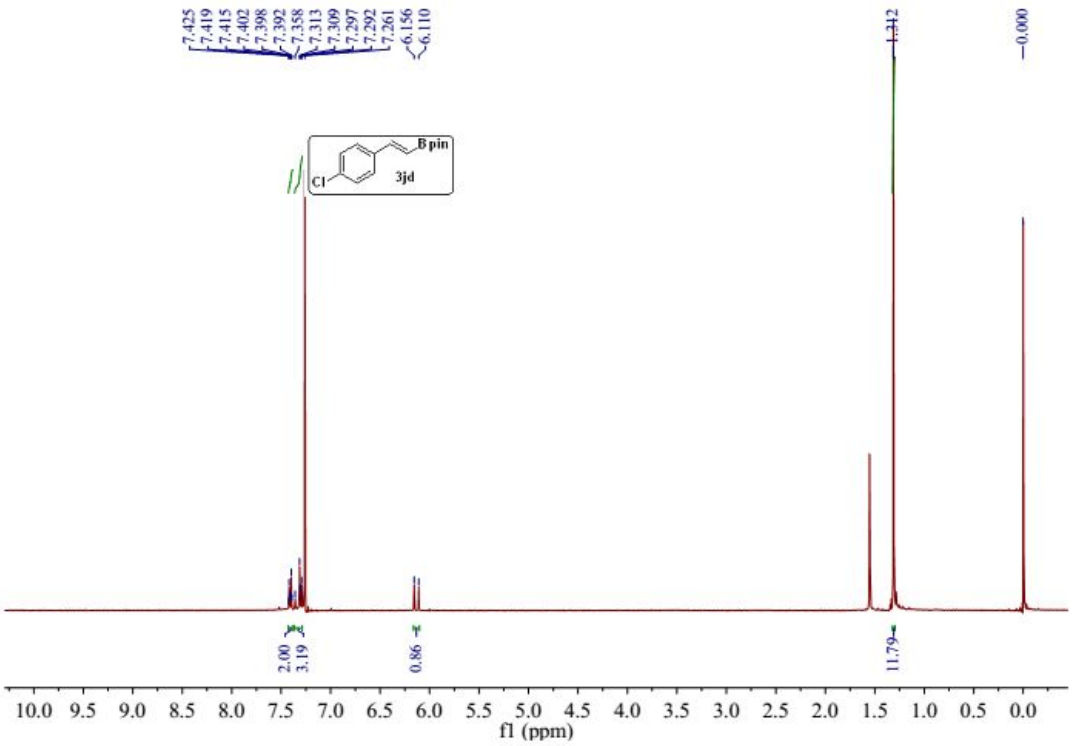
7.362
7.358
7.350
7.339
7.292
7.268
7.265
7.258
7.255
6.191
6.145
1.314
0.000
Cl
Bpin
3jc
0.97
2.28
1.97
1.00
12.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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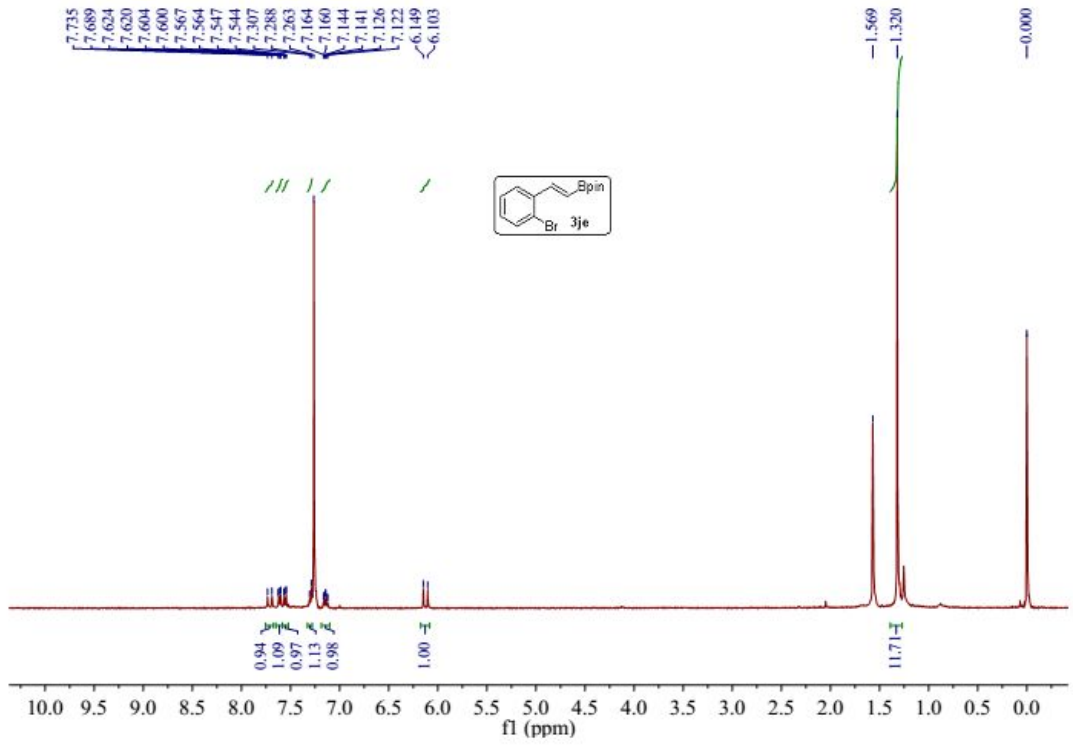
7.419
7.415
7.402
7.398
7.392
7.358
7.313
7.309
7.297
7.292
7.261
6.156
6.110
1.312
0.000
B pin
Cl
3jd
2.00
3.19
0.86
11.79
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.689
7.624
7.620
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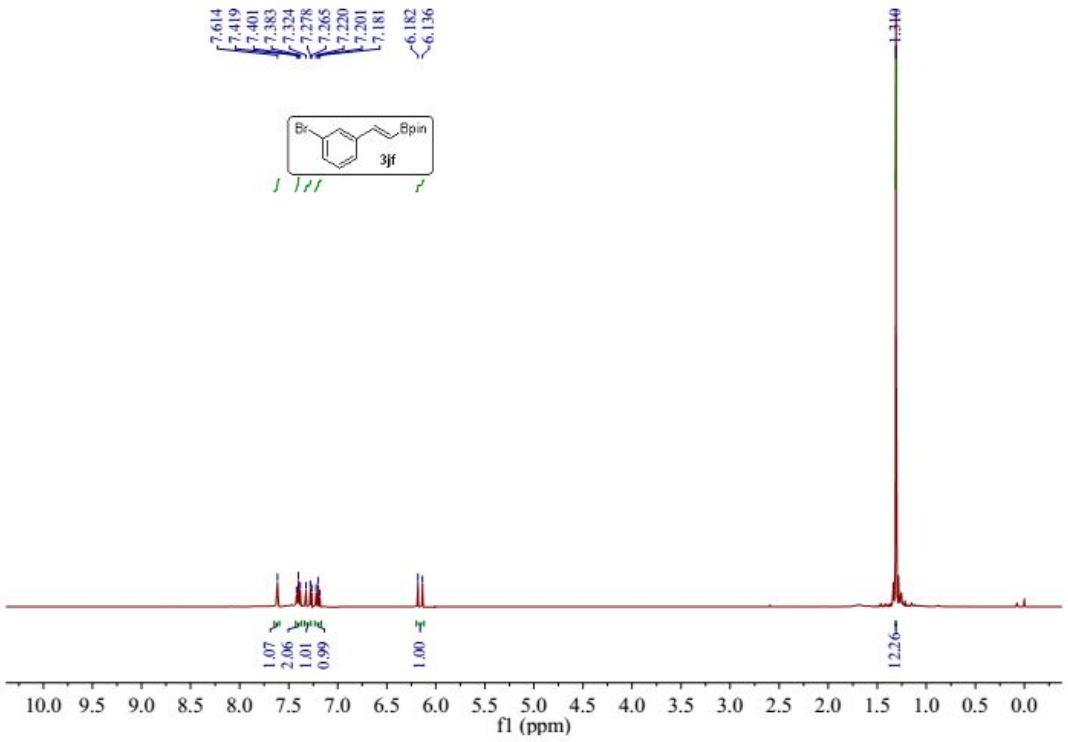
7.600
7.567
7.564
7.547
7.544
7.307
7.288
7.263
7.164
7.160
7.144
7.141
7.126
7.122
6.149
6.103
1.569
1.320
0.000
Bpin
Br
3je
0.94
1.09
0.97
1.13
0.98
1.00
11.71
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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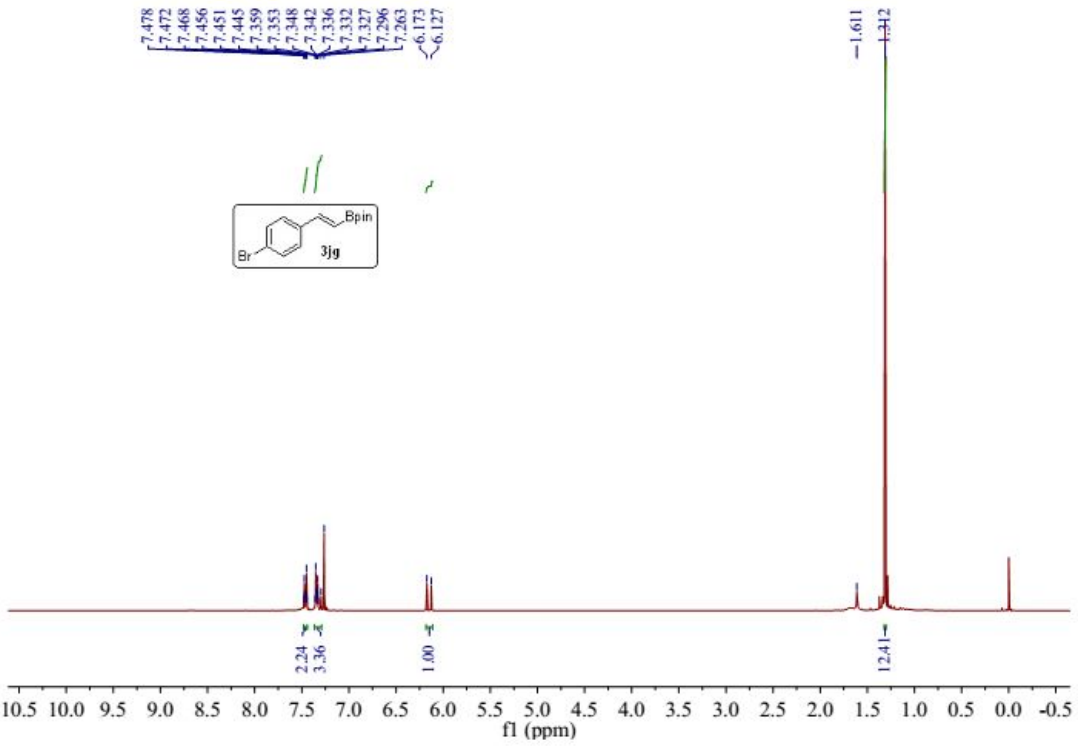
7.419
7.401
7.383
7.324
7.278
7.265
7.220
7.201
7.181
6.182
6.136
1.340
Br
Bpin
3jf
1.07
2.06
1.01
0.99
1.00
12.26
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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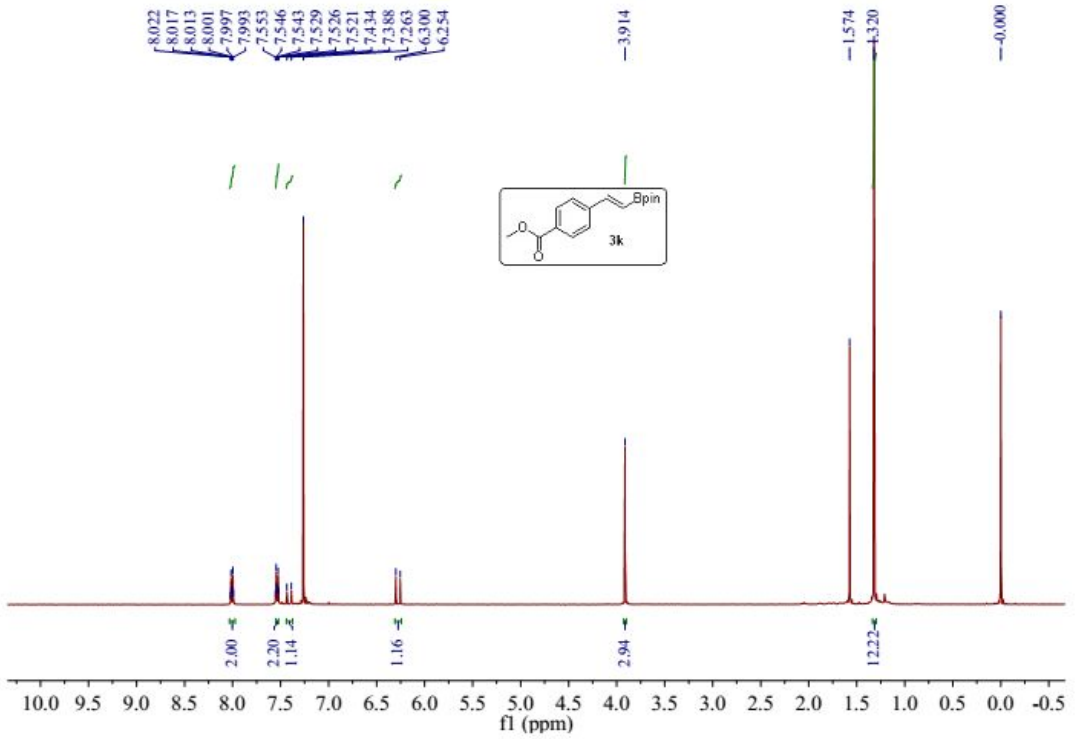
7.451
7.445
7.359
7.353
7.348
7.342
7.336
7.332
7.327
7.296
7.263
6.173
6.127
1.611
1.342
Bpin
Br
3jg
2.24
3.36
1.00
12.41
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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7.993
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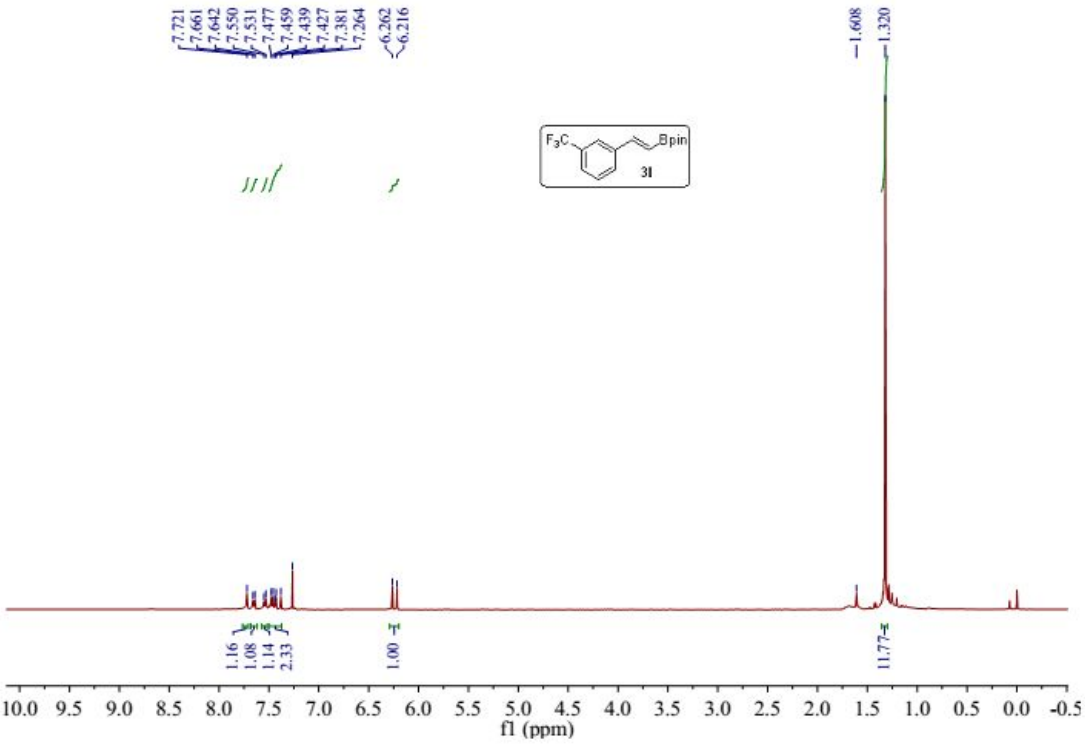
7.546
7.543
7.529
7.526
7.521
7.434
7.388
7.263
6.300
6.254
3.914
1.574
1.320
0.000
Bpin
3k
2.00
2.20
1.14
1.16
2.94
12.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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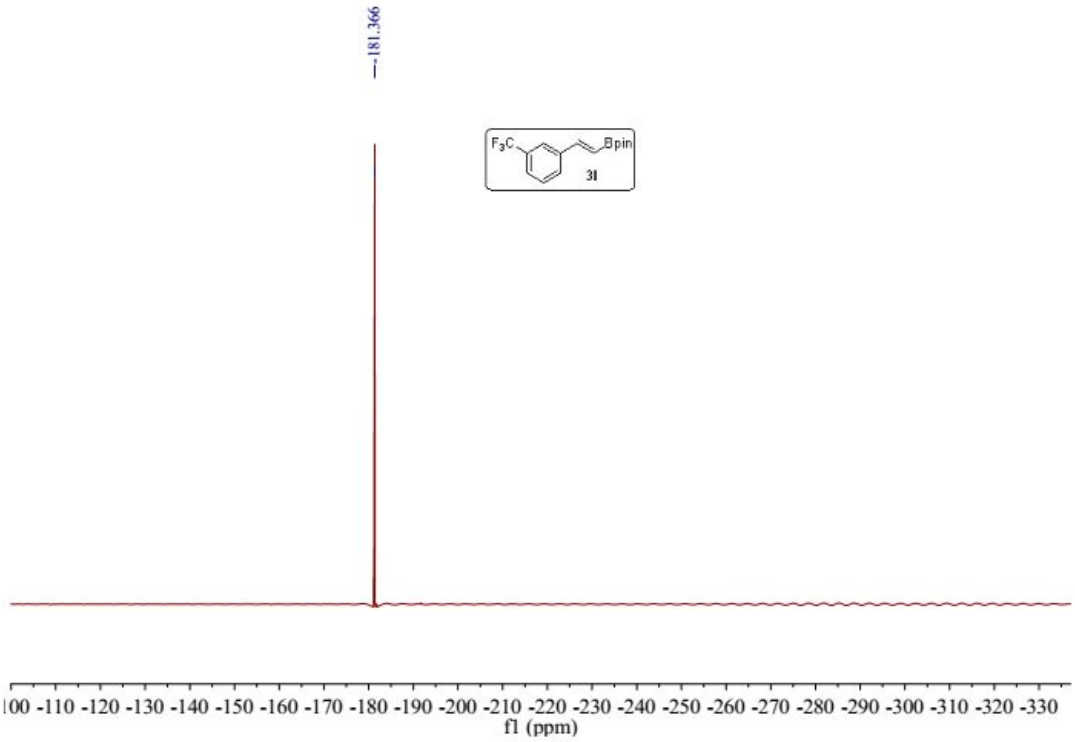
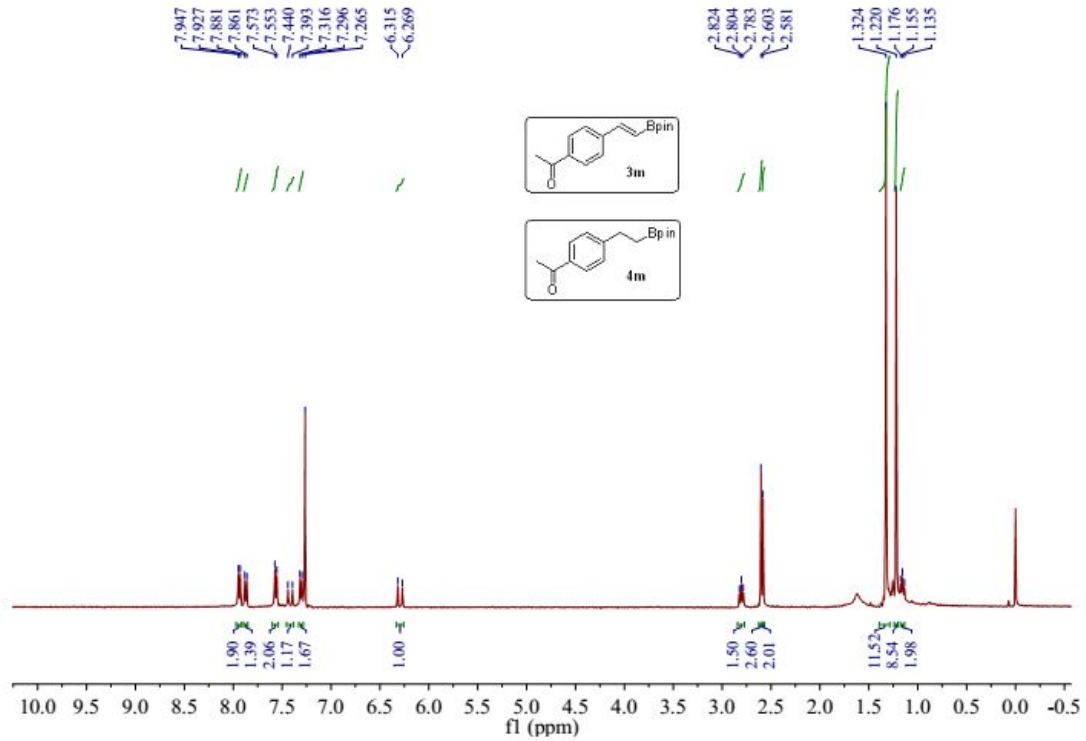
7.531
7.477
7.459
7.439
7.427
7.381
7.264
6.262
6.216
1.608
1.320
F3C
Bpin
3l
1.16
1.08
1.14
2.33
1.00
11.77
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


-181.366
F3C
Bpin
3l
100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310 -320 -330
f1 (ppm)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7.296
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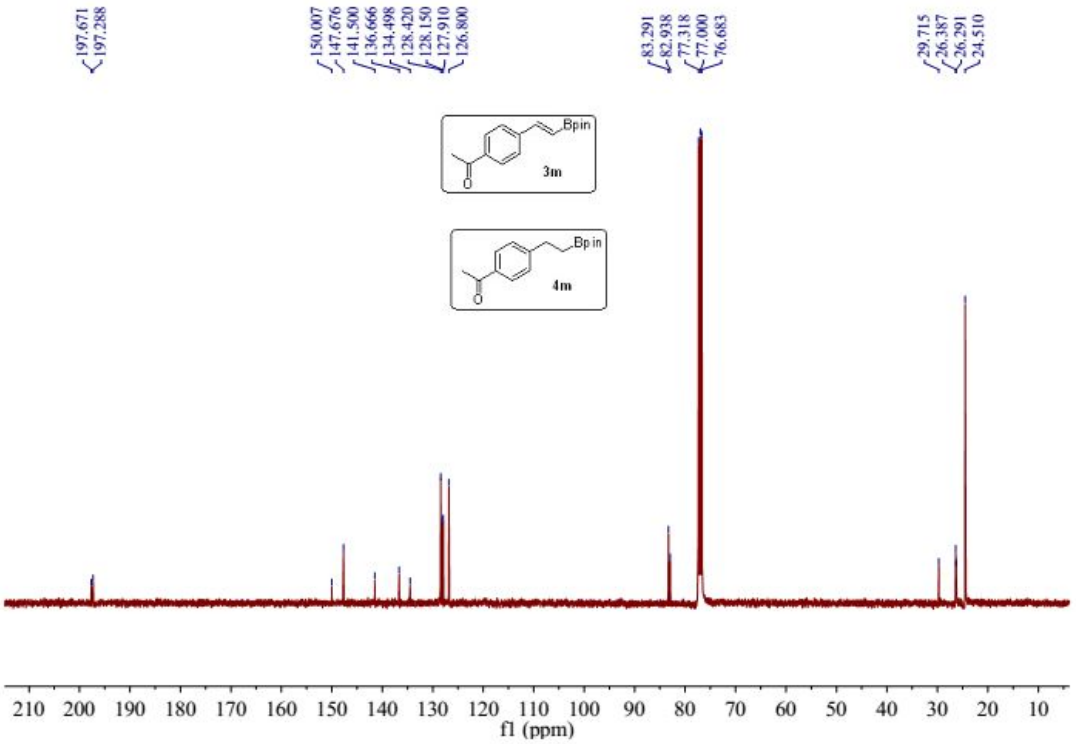
6.315
6.269
2.824
2.804
2.783
2.603
2.581
1.324
1.220
1.176
1.155
1.135
Bpin
3m
Bpin
4m
1.90
1.39
2.06
1.17
1.67
1.00
1.50
2.60
2.01
11.52
8.54
1.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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197.288
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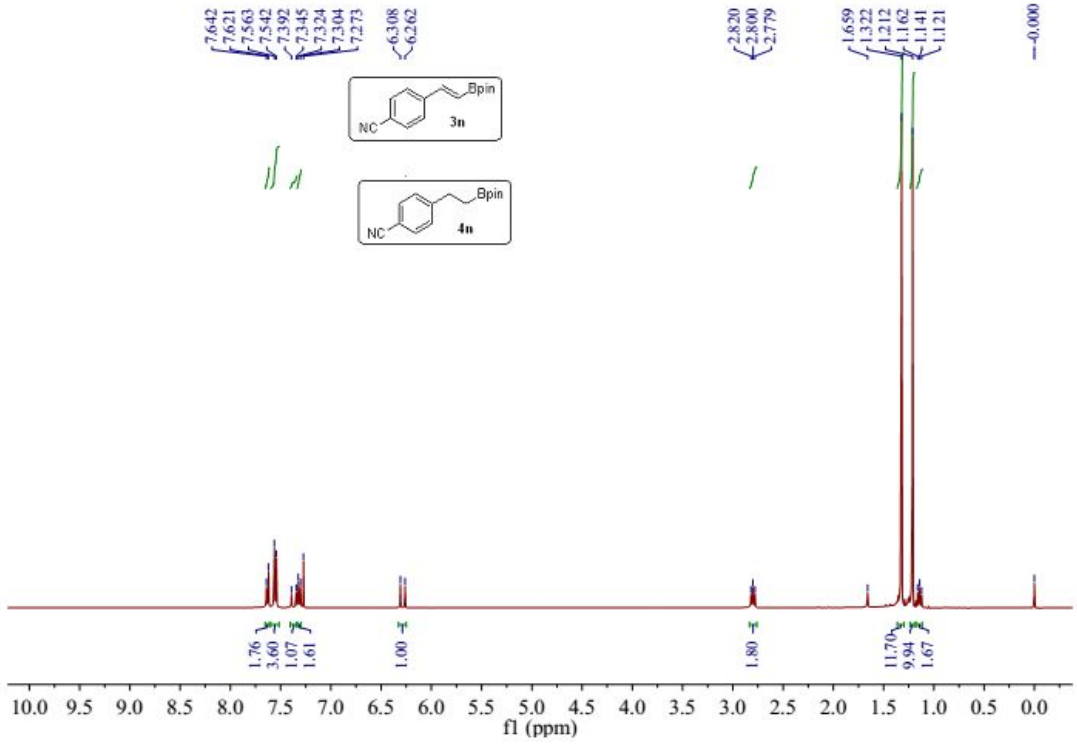
147.676
141.500
136.666
134.498
128.420
128.150
127.910
126.800
83.291
82.938
77.318
77.000
76.683
29.715
26.387
26.291
24.510
Bpin
3m
Bpin
4m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.304
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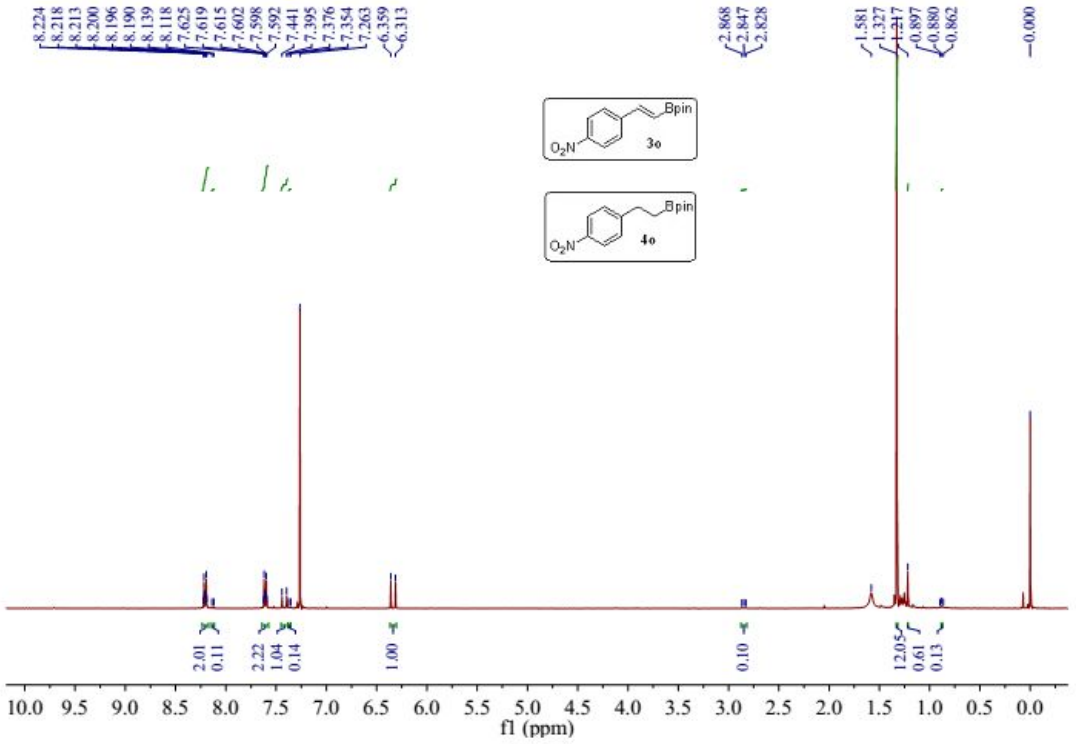
6.308
6.262
2.820
2.800
2.779
1.659
1.322
1.212
1.162
1.141
1.121
-0.000
Bpin
NC
3n
Bpin
NC
4n
1.76
3.60
1.07
1.61
1.00
1.80
11.70
9.94
1.67
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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8.218
8.213
8.200
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8.190
8.139
8.118
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7.619
7.615
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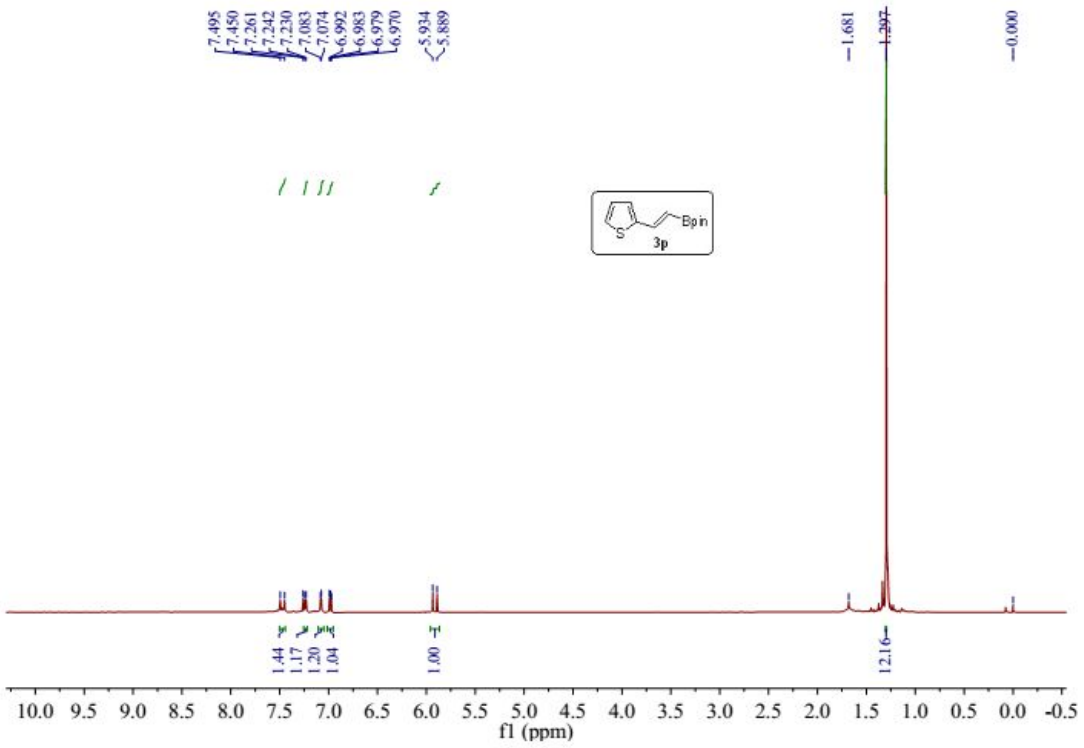
7.598
7.592
7.441
7.395
7.376
7.354
7.263
6.359
6.313
2.868
2.847
2.828
1.581
1.327
1.317
0.897
0.880
0.862
0.000
Bpin
O2N
3o
Bpin
O2N
4o
2.01
0.11
2.22
1.04
0.14
1.00
0.10
12.05
0.61
0.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.230
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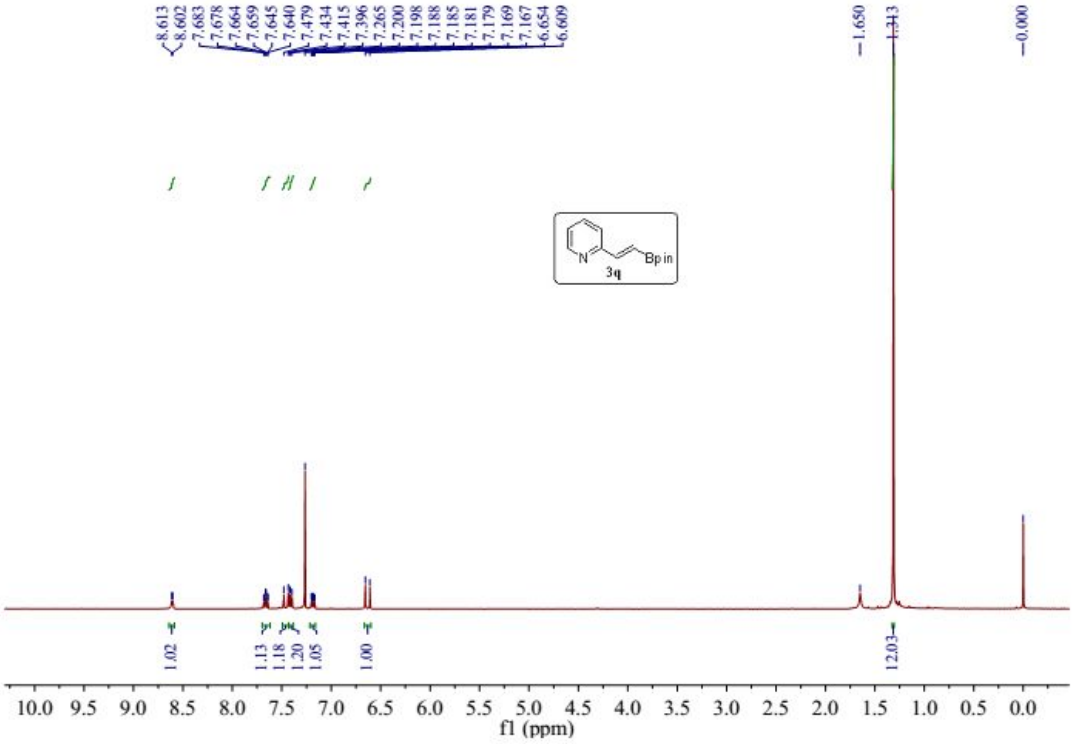
7.074
6.992
6.983
6.979
6.970
5.934
5.889
1.681
1.297
0.000
S
Bpin
3p
1.44
1.17
1.20
1.04
1.00
12.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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7.640
7.479
7.434
7.415
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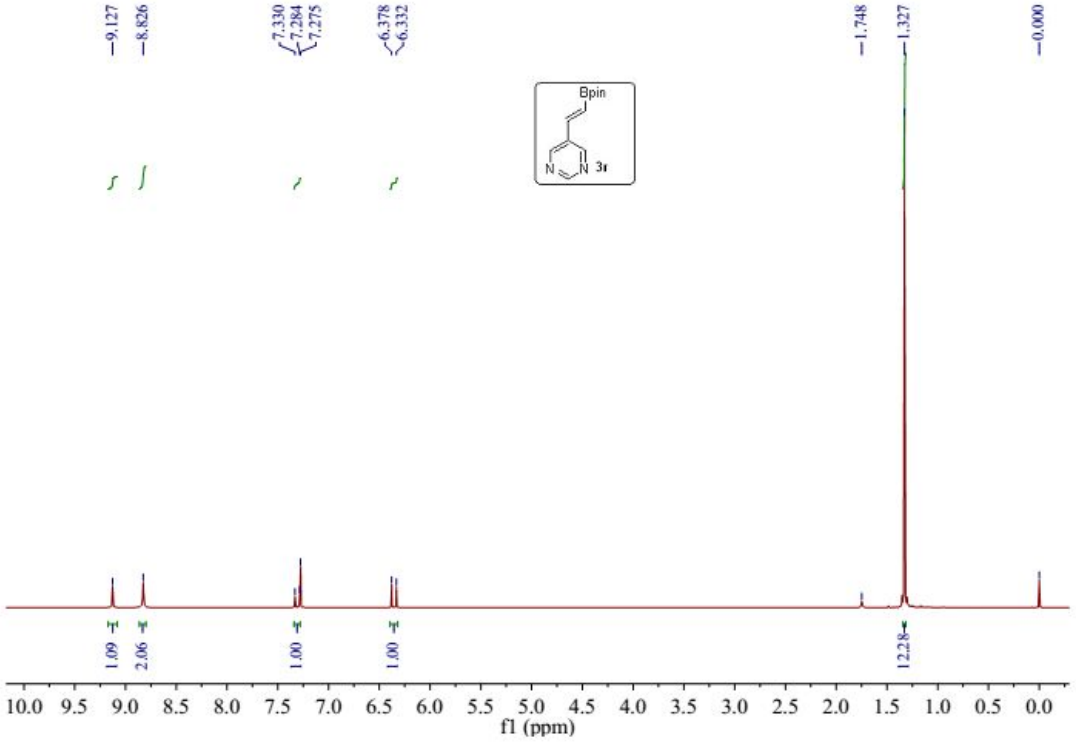
7.265
7.200
7.198
7.188
7.185
7.181
7.179
7.169
7.167
6.654
6.609
1.650
1.343
0.000
Bpin
3q
1.02
1.13
1.18
1.20
1.05
1.00
12.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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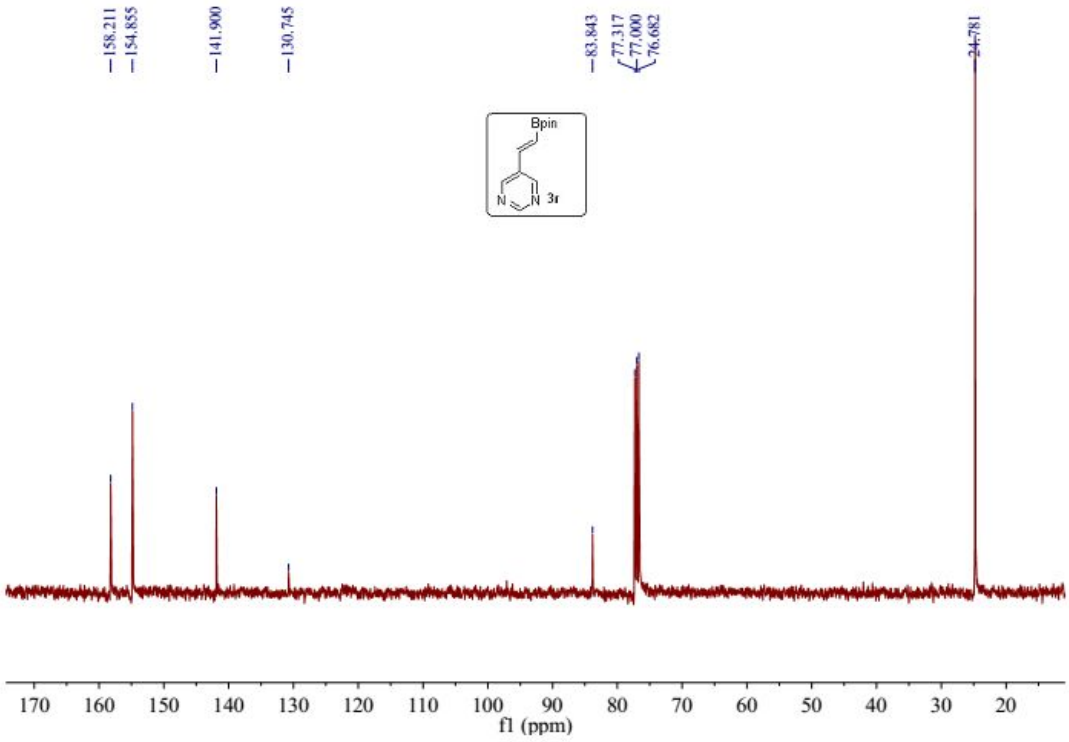
6.378
6.332
1.748
1.327
0.000
Bpin
3r
1.09
2.06
1.00
1.00
12.28
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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141.900
130.745
83.843
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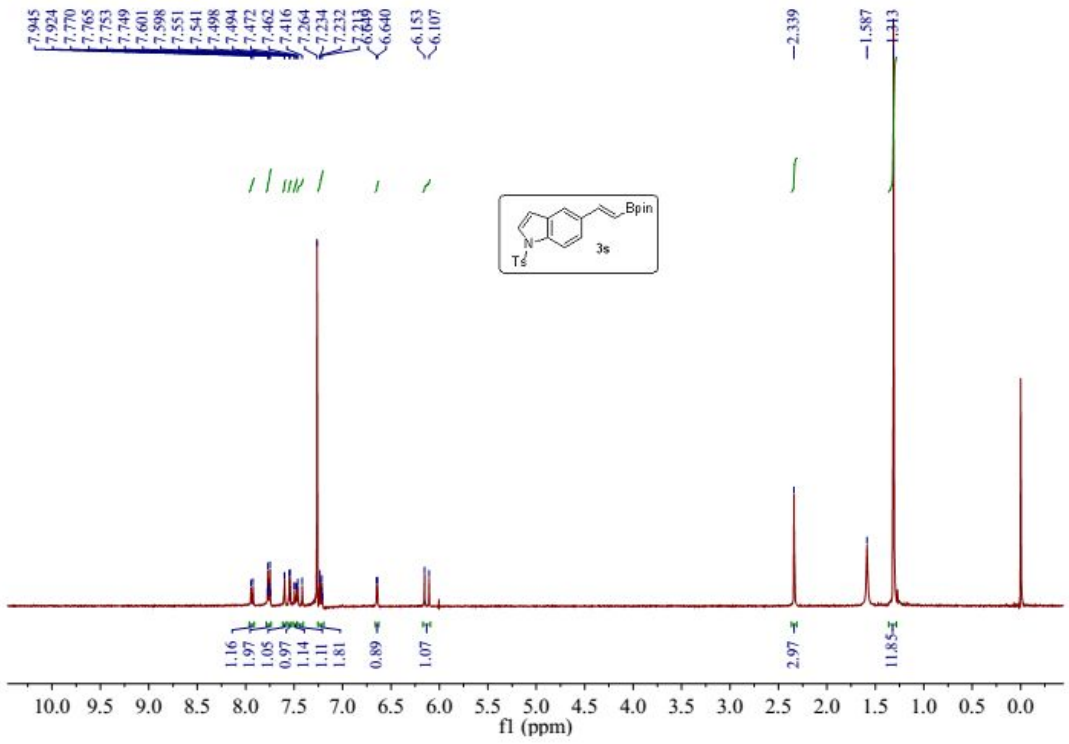
77.000
76.682
24.781
Bpin
3r
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)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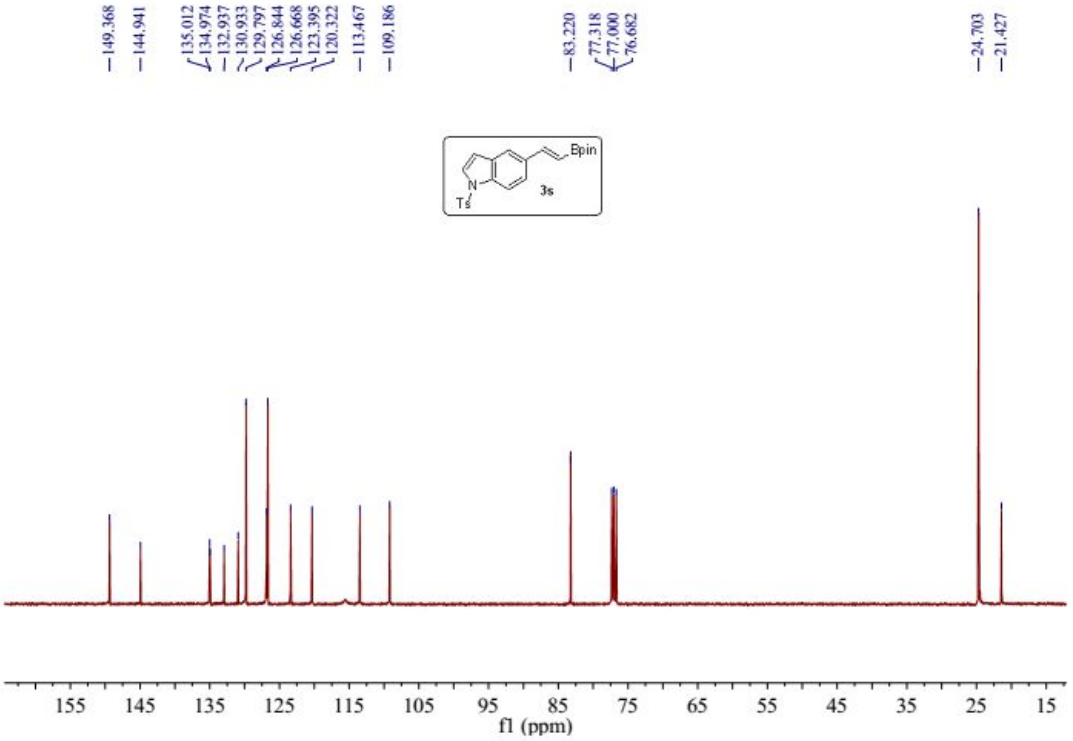
7.472
7.462
7.416
7.264
7.234
7.232
7.213
6.649
6.640
6.153
6.107
2.339
1.587
1.343
Bpin
Ts
3s
1.16
1.97
1.05
0.97
1.14
1.11
1.81
0.89
1.07
2.97
11.85
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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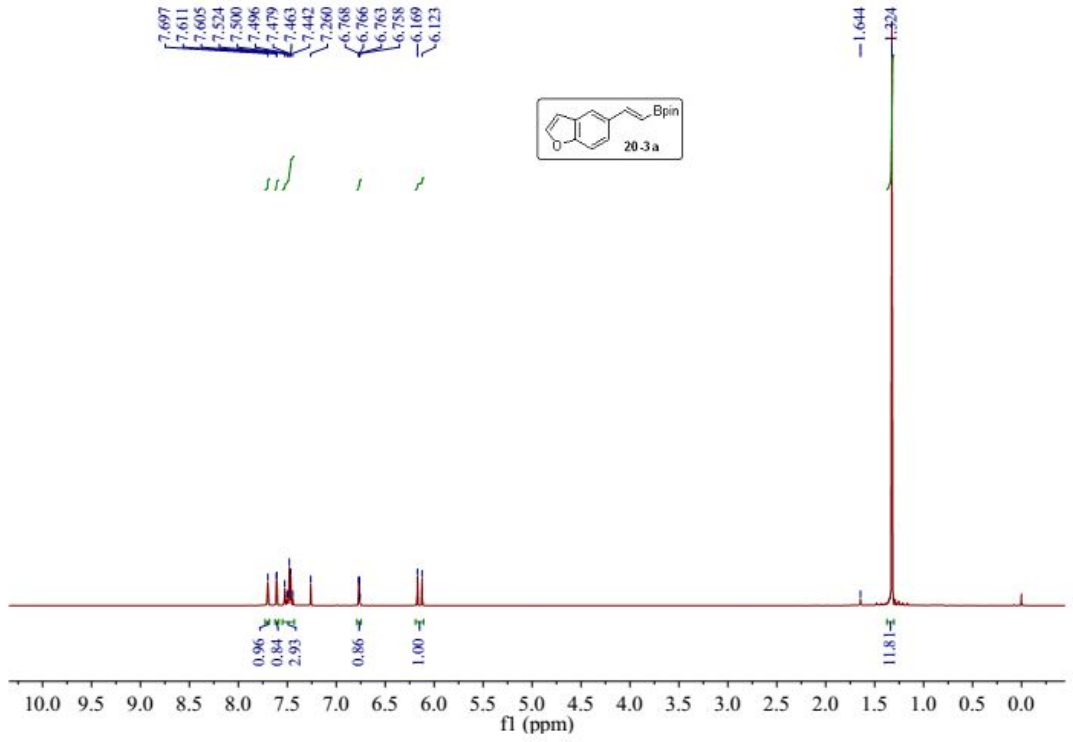
135.012
134.974
132.937
130.933
129.797
126.844
126.668
123.395
120.322
113.467
109.186
83.220
77.318
77.000
76.682
24.703
21.427
Bpin
N
Ts
3s
155 145 135 125 115 105 95 85 75 65 55 45 35 25 15
f1 (ppm)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7.611
7.605
7.524
7.500
7.496
7.479
7.463
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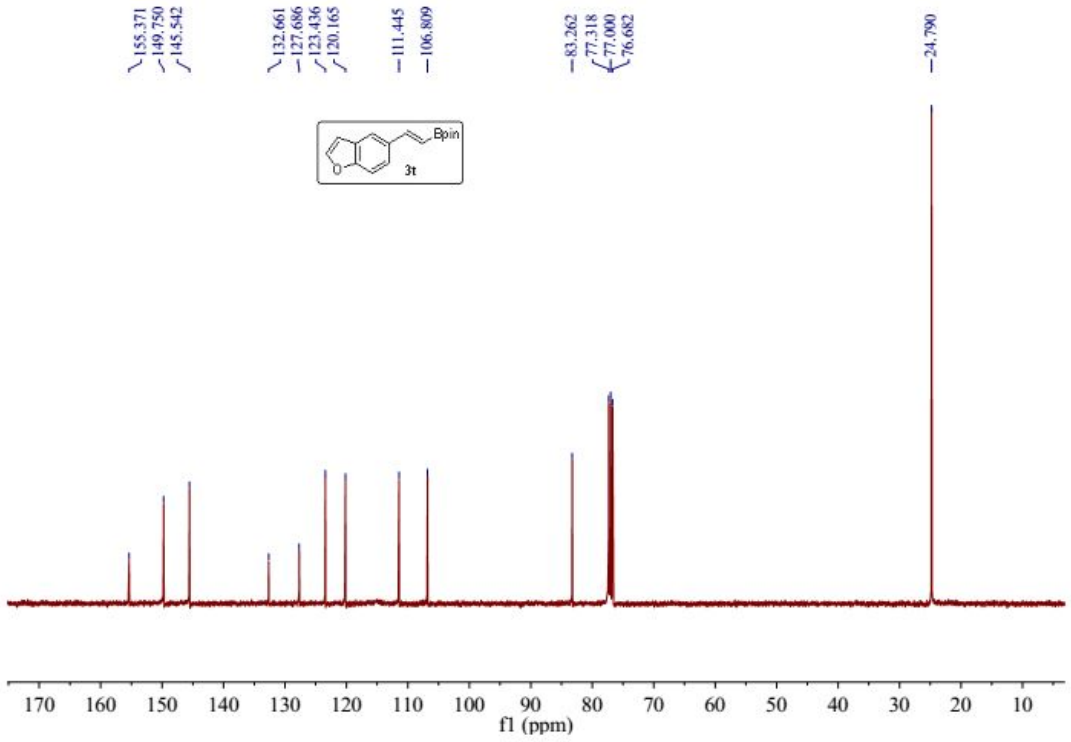
7.260
6.768
6.766
6.763
6.758
6.169
6.123
1.644
1.324
Bpin
O
20-3a
0.96
0.84
2.93
0.86
1.00
11.81
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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149.750
145.542
132.661
127.686
123.436
120.165
111.445
106.809
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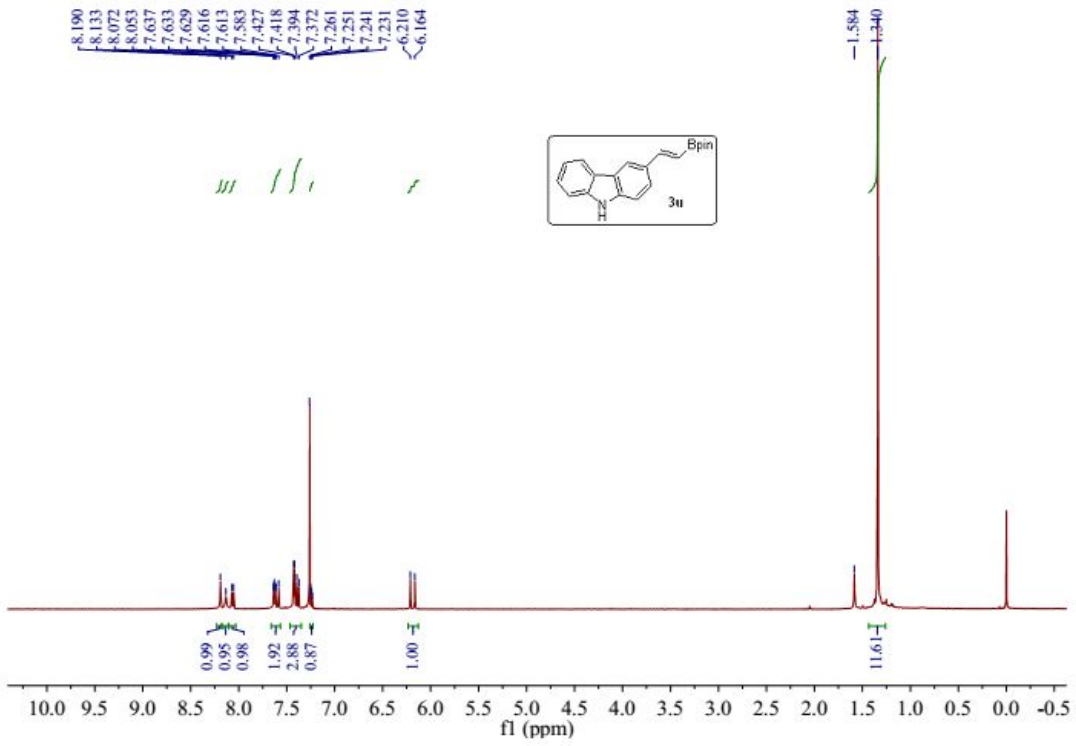
77.318
77.000
76.682
24.790
Bpin
3t
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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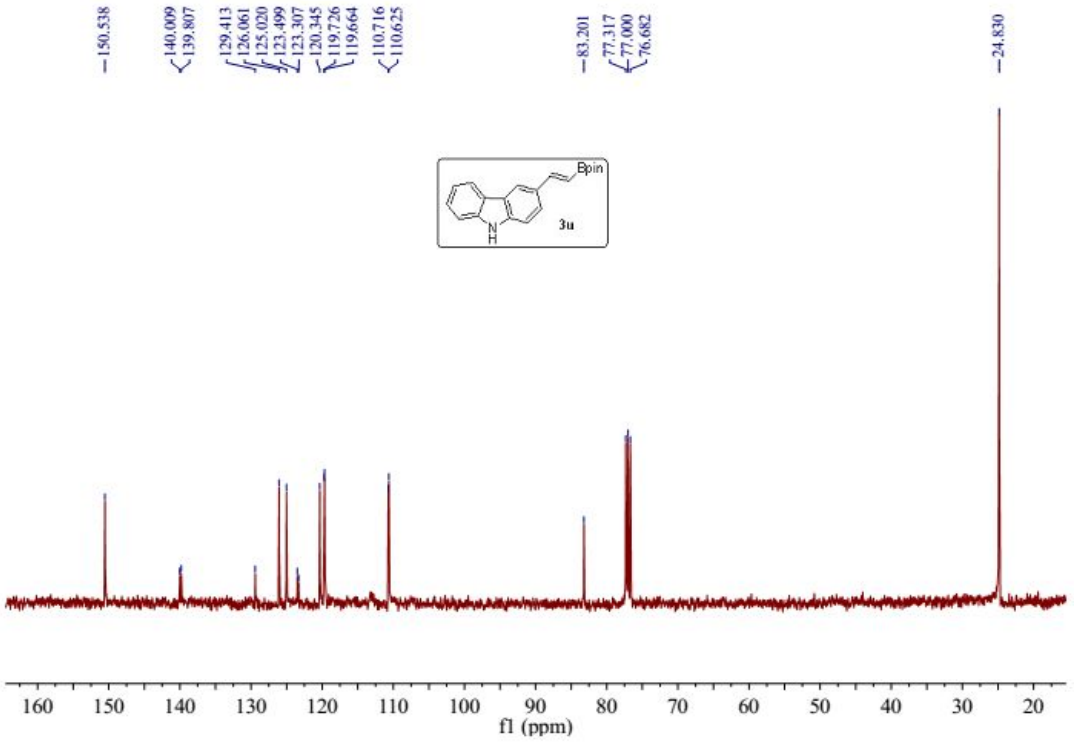
8.072
8.053
7.637
7.633
7.629
7.616
7.613
7.583
7.427
7.418
7.394
7.372
7.261
7.251
7.241
7.231
6.210
6.164
1.584
1.340
Bpin
3u
0.99
0.95
0.98
1.92
2.88
0.87
1.00
11.61
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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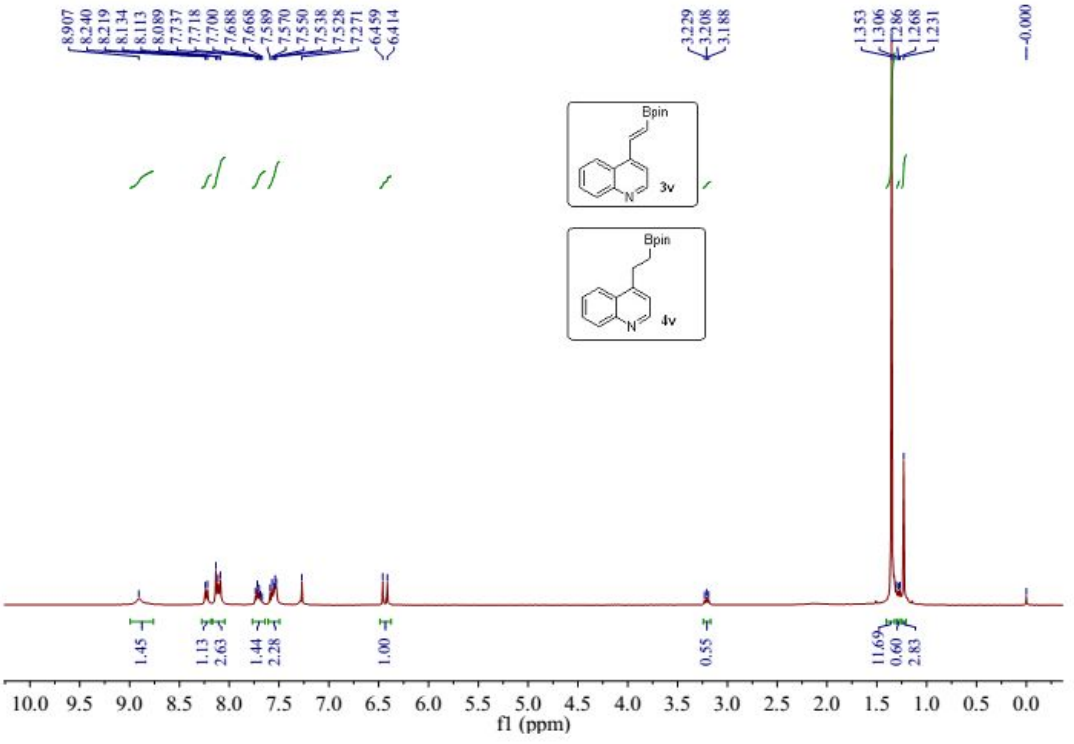
140.009
139.807
129.413
126.061
125.020
123.499
123.307
120.345
119.726
119.664
110.716
110.625
83.201
77.317
77.000
76.682
24.830
Bpin
3u
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)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8.219
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8.113
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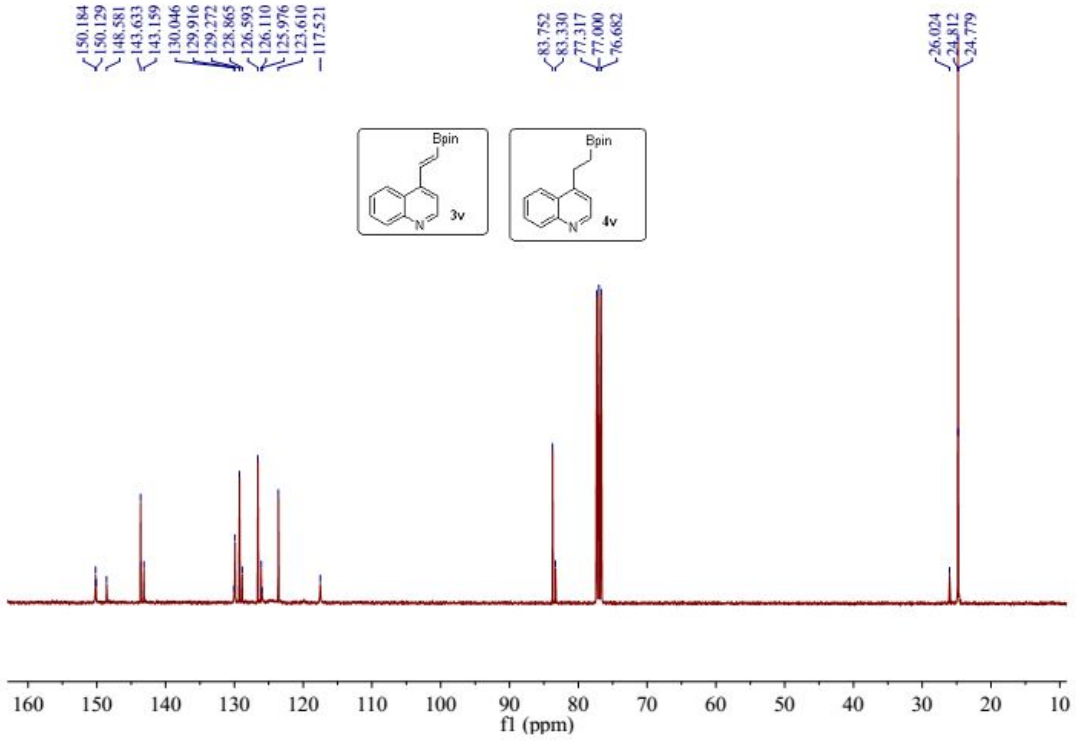
7.737
7.718
7.700
7.688
7.668
7.589
7.570
7.550
7.538
7.528
7.271
6.459
6.414
3.229
3.208
3.188
1.353
1.306
1.286
1.268
1.231
-0.000
Bpin
3v
Bpin
4v
1.45
1.13
2.63
1.44
2.28
1.00
0.55
11.69
0.60
2.83
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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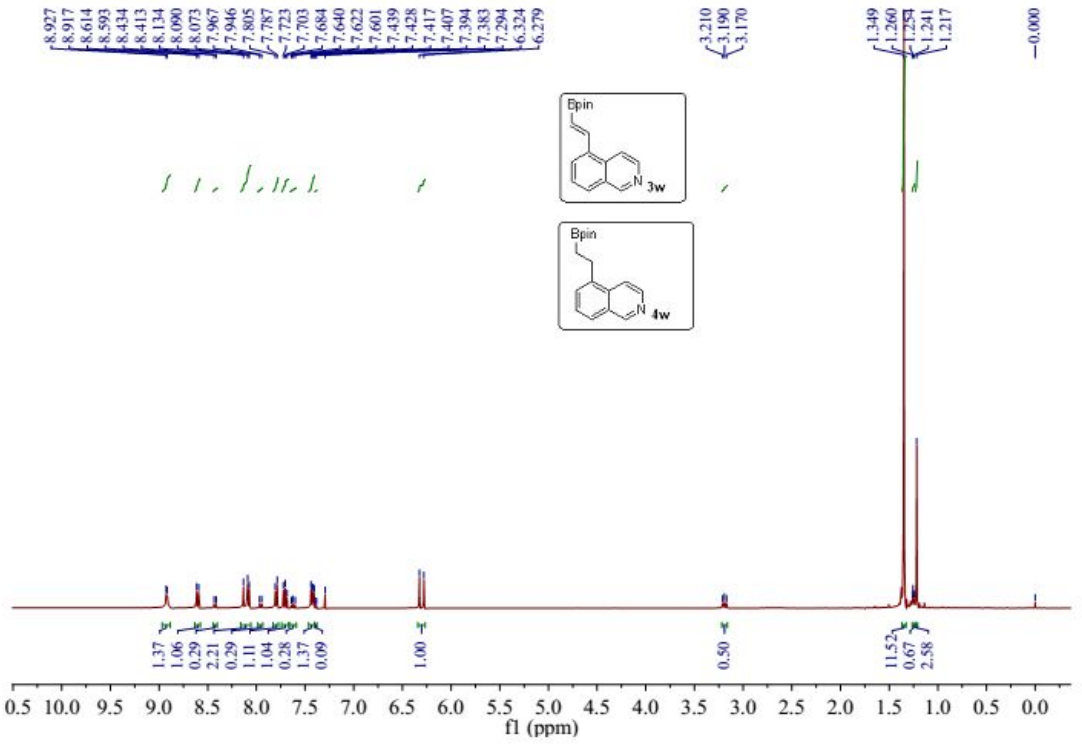
150.129
148.581
143.633
143.159
130.046
129.916
129.272
128.865
126.593
126.110
125.976
123.610
117.521
83.752
83.330
77.317
77.000
76.682
26.024
24.812
24.779
Bpin
3v
Bpin
4v
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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8.614
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8.434
8.413
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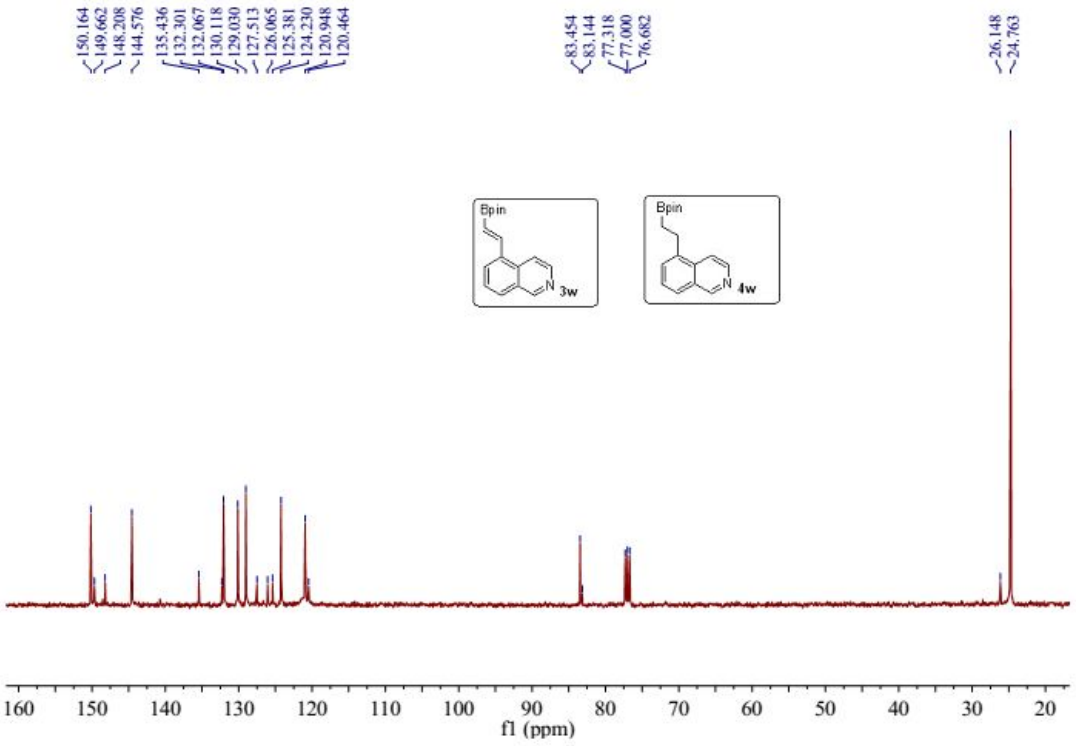
8.090
8.073
7.967
7.946
7.805
7.787
7.723
7.703
7.684
7.640
7.622
7.601
7.439
7.428
7.417
7.407
7.394
7.383
7.294
6.324
6.279
3.210
3.190
3.170
1.349
1.260
1.253
1.241
1.217
0.000
Bpin
3w
Bpin
4w
1.37
1.06
0.29
2.21
0.29
1.11
1.04
0.28
1.37
0.09
1.00
0.50
11.52
0.67
2.58
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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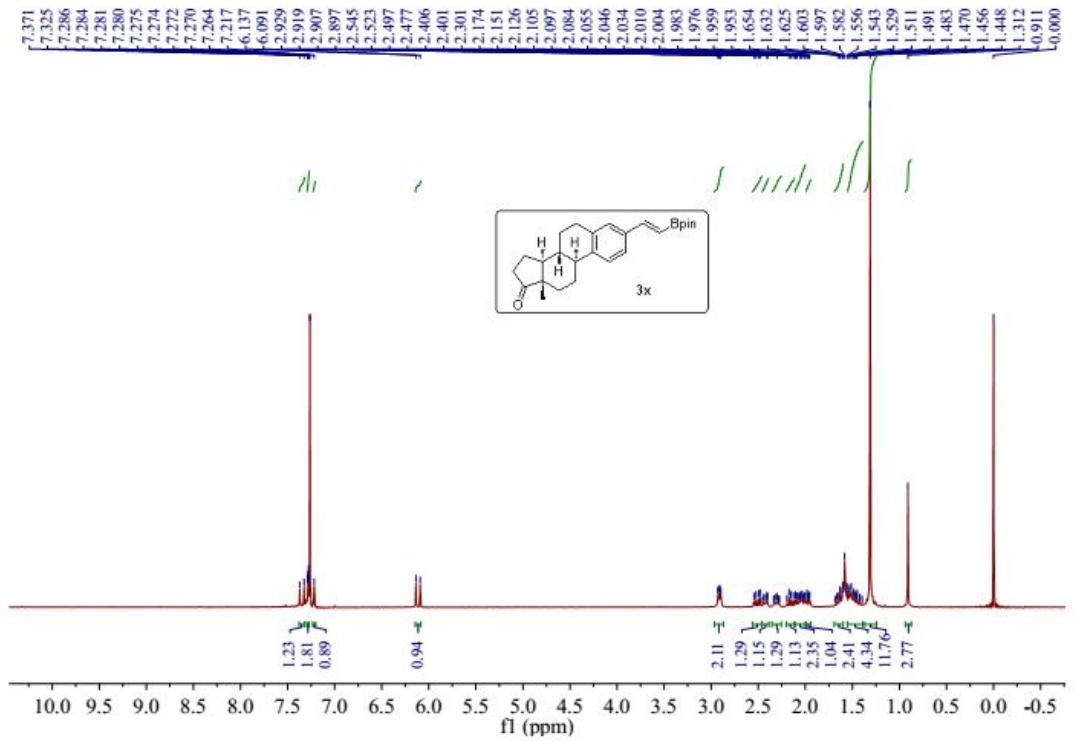
132.301
132.067
130.118
129.030
127.513
126.065
125.381
124.230
120.948
120.464
83.454
83.144
77.318
77.000
76.682
26.148
24.763
Bpin
3w
Bpin
4w
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)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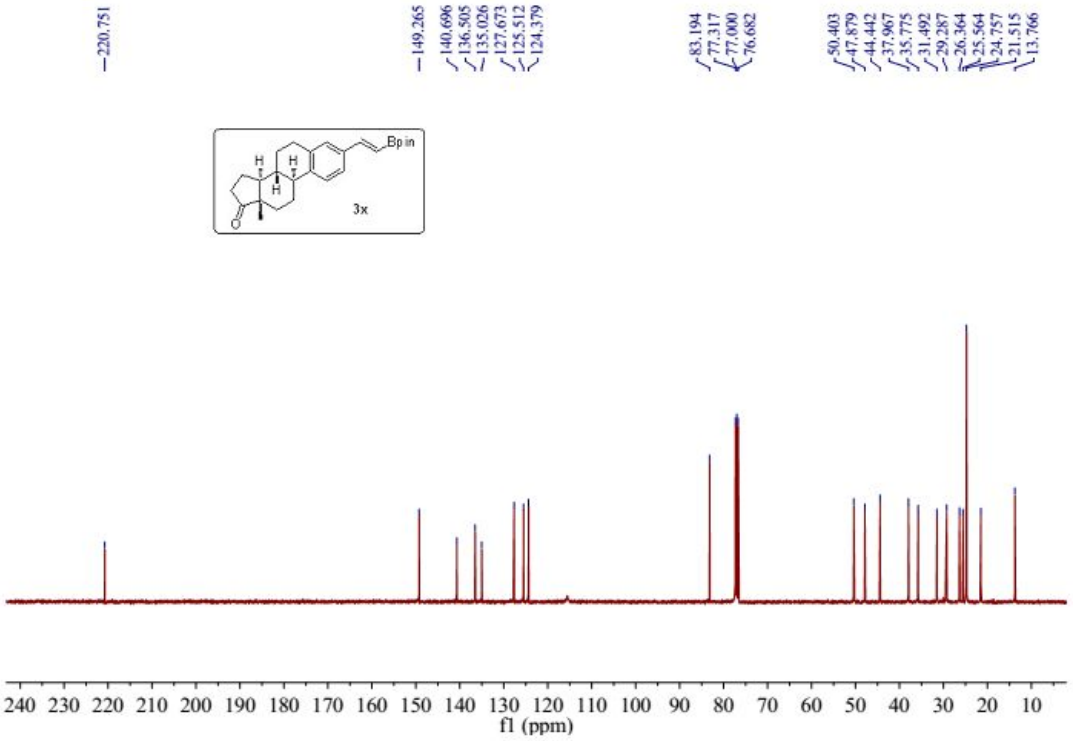
7.286
7.284
7.281
7.280
7.275
7.274
7.272
7.270
7.264
7.217
6.137
6.091
2.929
2.919
2.907
2.897
2.545
2.523
2.497
2.477
2.406
2.401
2.301
2.174
2.151
2.126
2.105
2.097
2.084
2.055
2.046
2.034
2.010
2.004
1.983
1.976
1.959
1.953
1.654
1.632
1.625
1.603
1.597
1.582
1.556
1.543
1.529
1.511
1.491
1.483
1.470
1.456
1.448
1.312
0.911
0.000
Bpin
3x
1.23
1.81
0.89
0.94
2.11
1.29
1.15
1.29
1.13
2.35
1.04
2.41
4.34
11.76
2.77
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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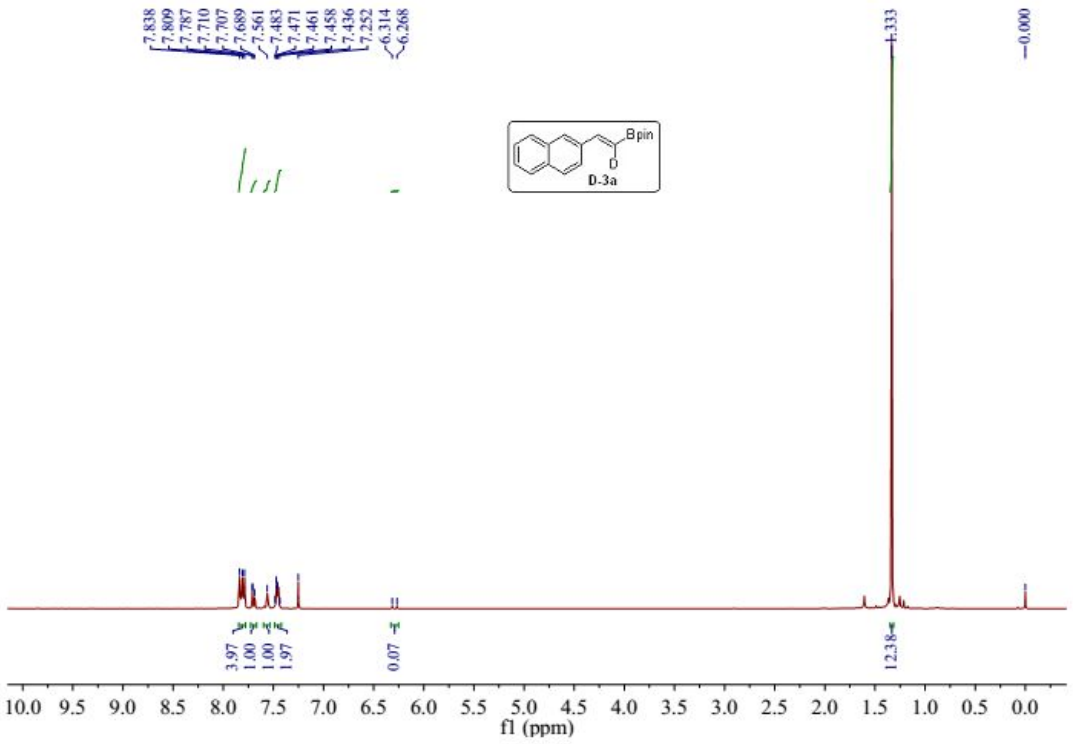
127.673
125.512
124.379
83.194
77.317
77.000
76.682
50.403
47.879
44.442
37.967
35.775
31.492
29.287
26.364
25.564
24.757
21.515
13.766
Bpin
3x
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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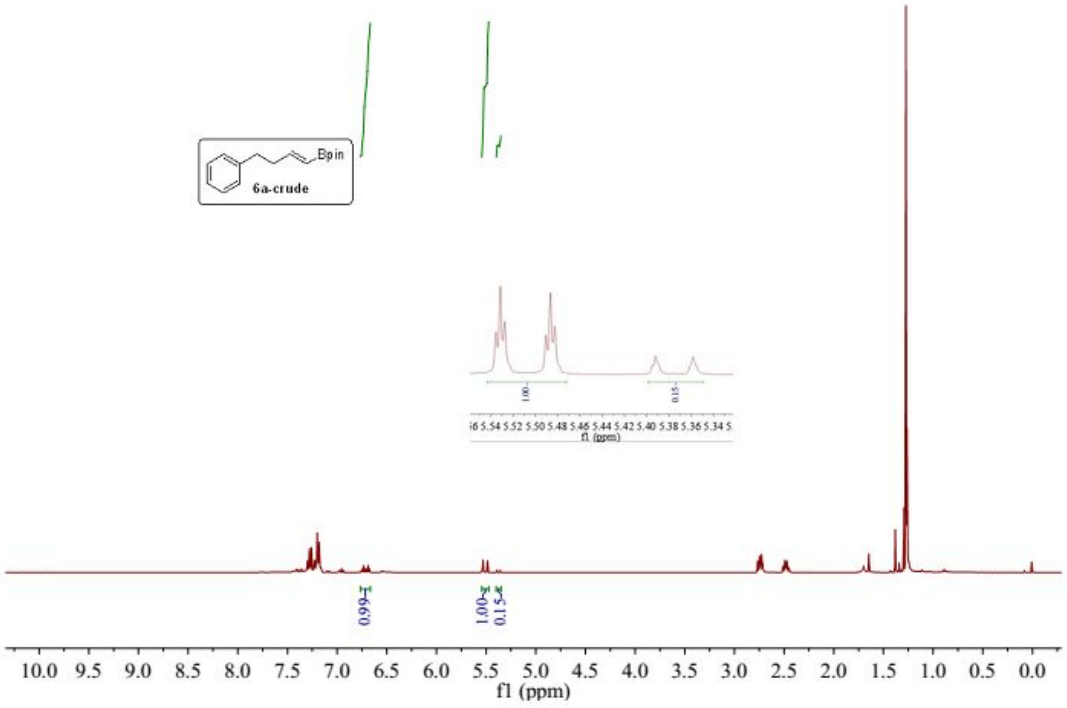
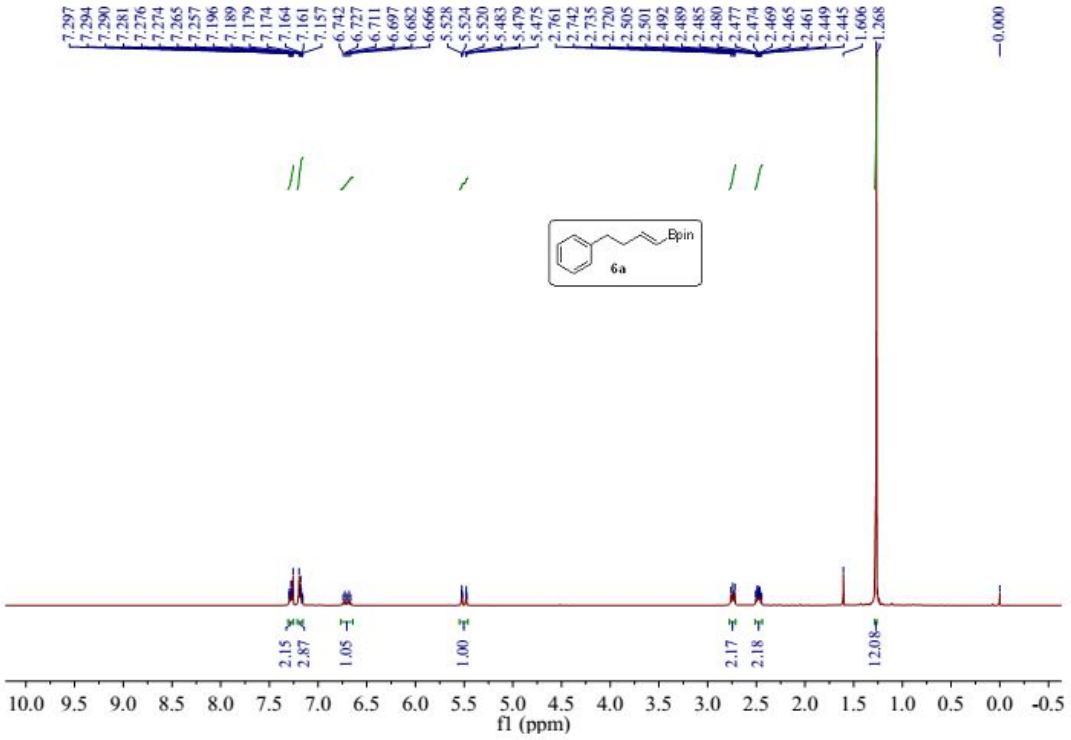
7.707
7.689
7.561
7.483
7.471
7.461
7.458
7.436
7.252
6.314
6.268
1.333
0.000
Bpin
D-3a
3.97
1.00
1.00
1.97
0.07
12.38
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Bpin
6a-crude
0.99
1.00
0.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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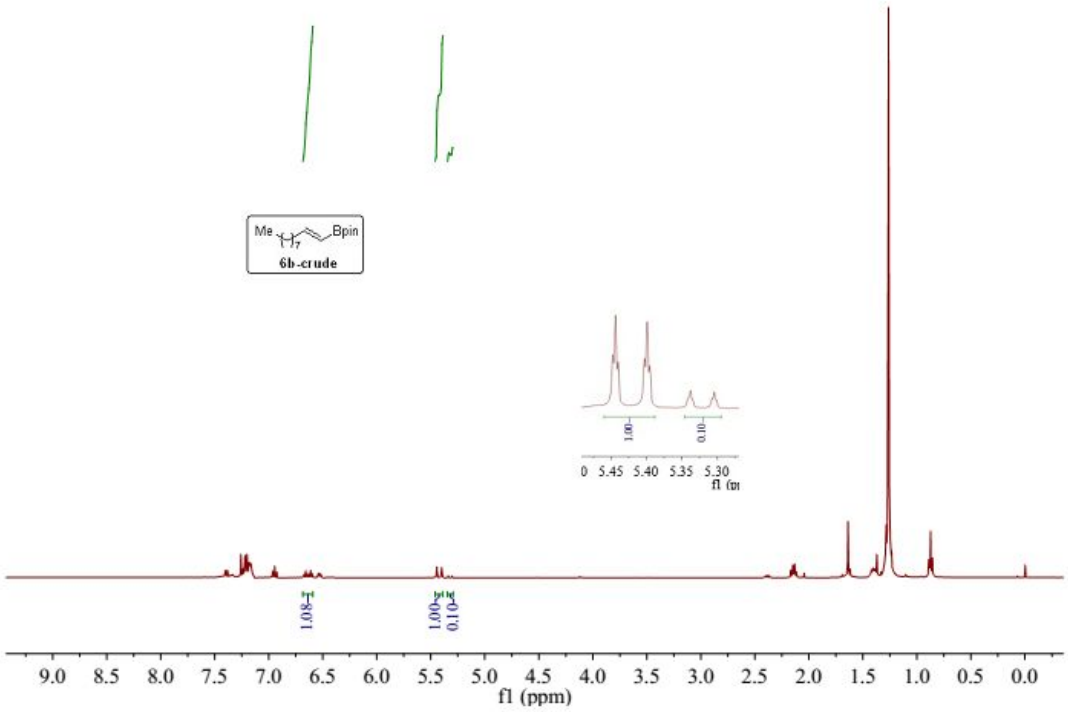
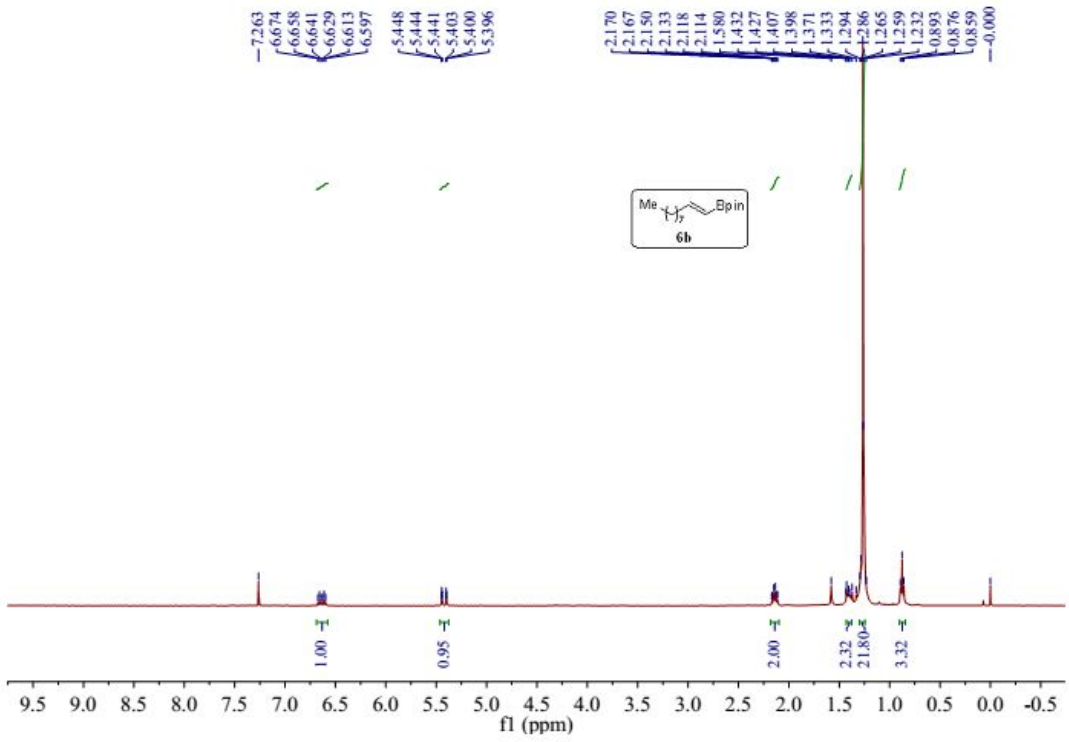
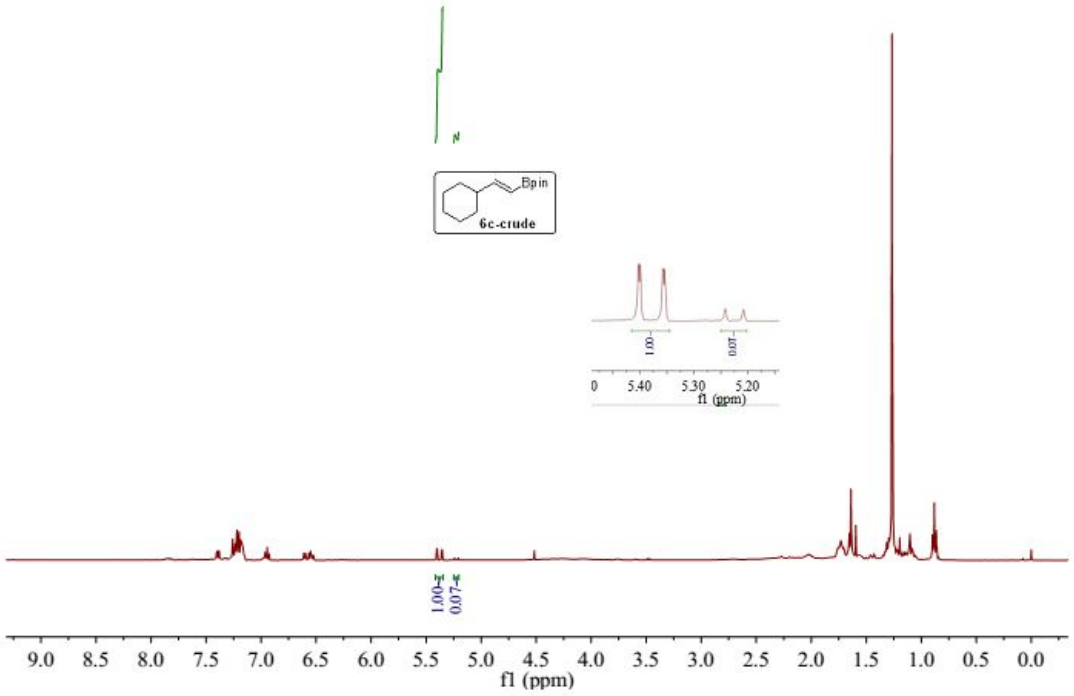
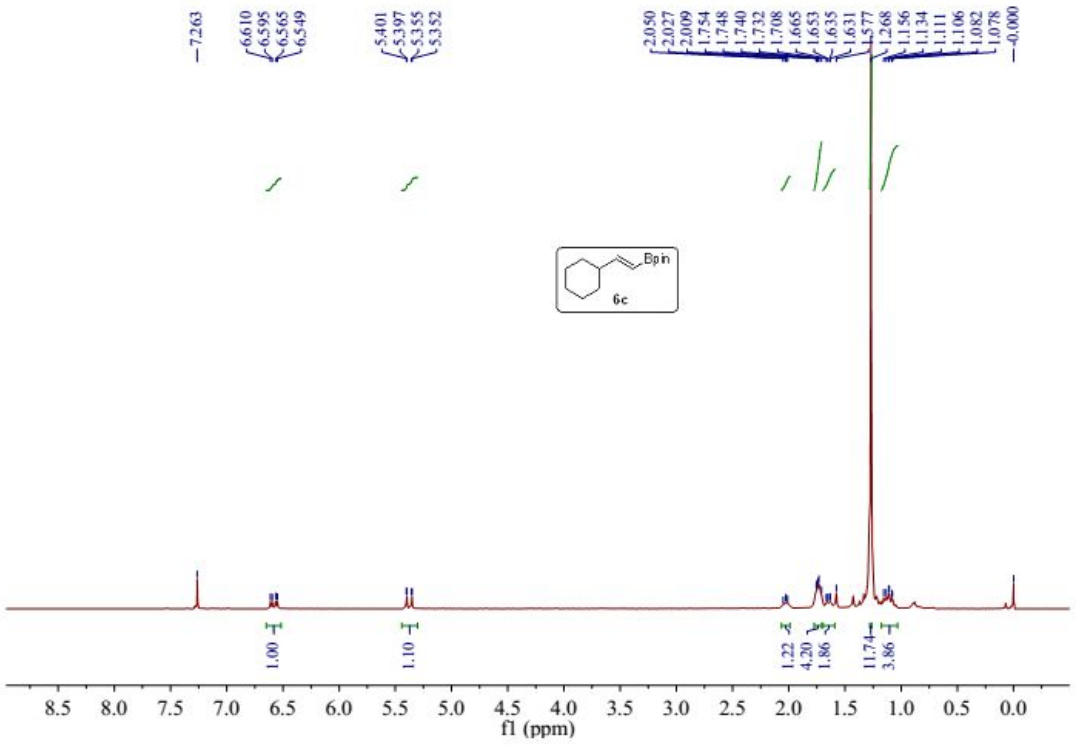
7.274
7.265
7.257
7.196
7.189
7.179
7.174
7.164
7.161
7.157
6.742
6.727
6.711
6.697
6.682
6.666
5.528
5.524
5.520
5.483
5.479
5.475
2.761
2.742
2.735
2.720
2.505
2.501
2.492
2.489
2.485
2.480
2.477
2.474
2.469
2.465
2.461
2.449
2.445
1.606
1.268
-0.000
Bpin
6a
2.15
2.87
1.05
1.00
2.17
2.18
12.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Me
Bpin
6b-crude
1.08
1.00
0.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.263
6.674
6.658
6.641
6.629
6.613
6.597
5.448
5.444
5.441
5.403
5.400
5.396
2.170
2.167
2.150
2.133
2.118
2.114
1.580
1.432
1.427
1.407
1.398
1.371
1.333
1.294
1.286
1.265
1.259
1.232
0.893
0.876
0.859
-0.000
Me
Bpin
6b
1.00
0.95
2.00
2.32
21.80
3.32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Bpin
6c-crude
1.00
0.07
0
5.40
5.30
5.20
f1 (ppm)
1.00
0.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


7.263
6.610
6.595
6.565
6.549
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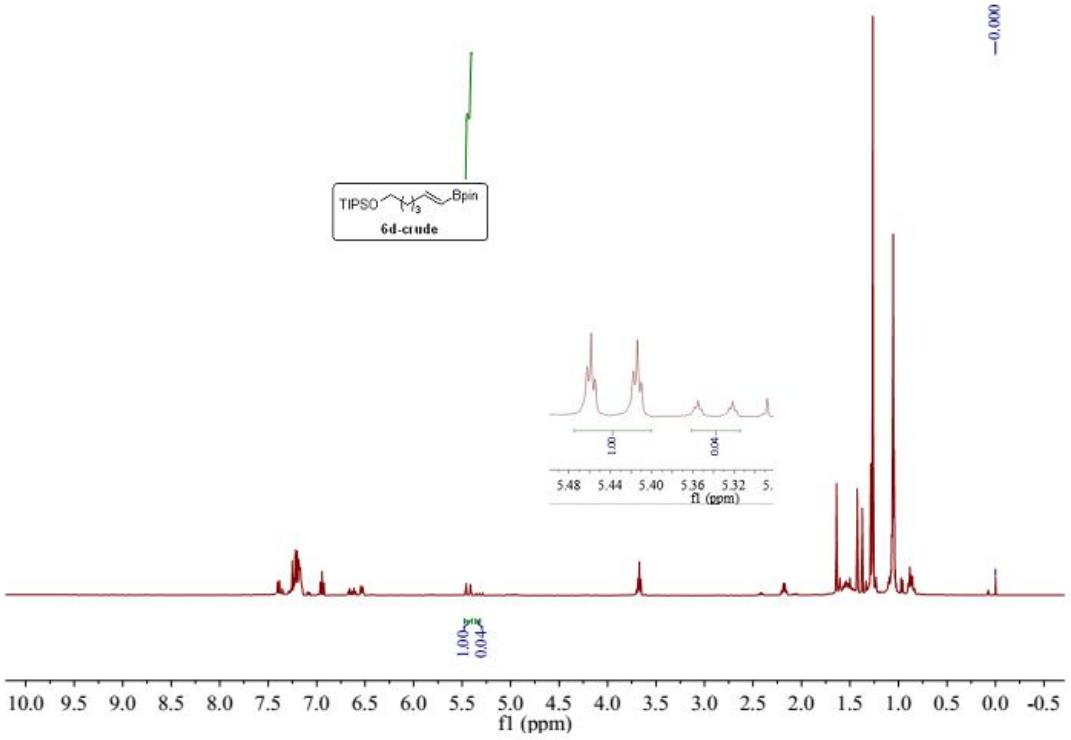
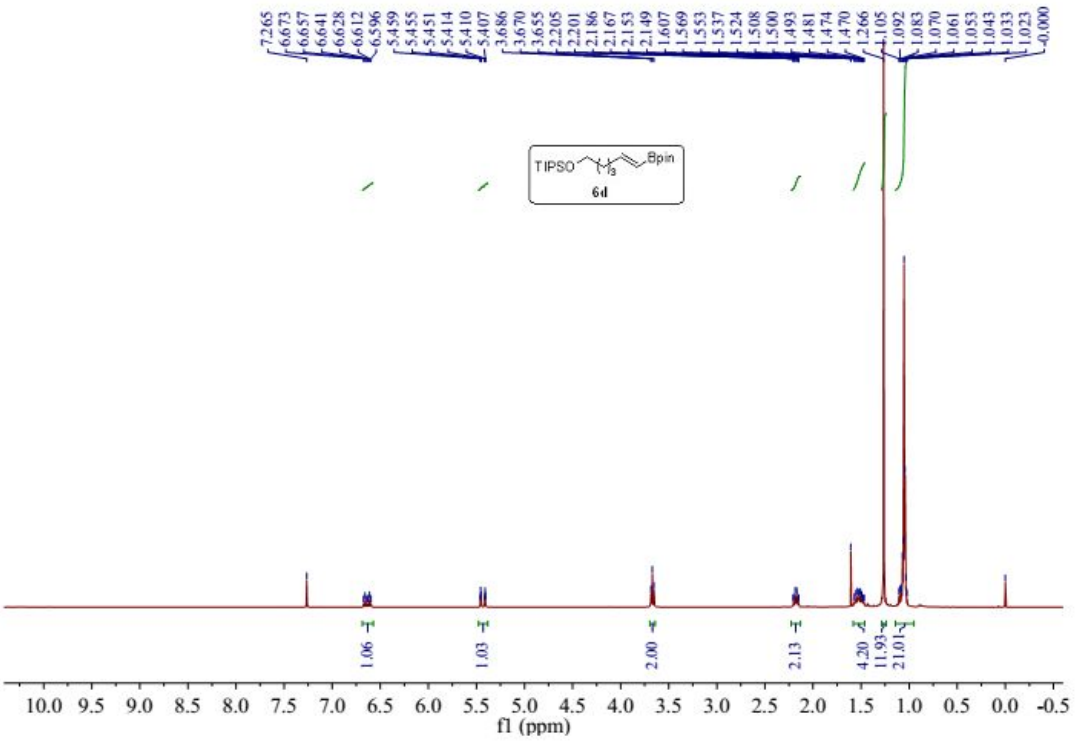
5.355
5.352
2.050
2.027
2.009
1.754
1.748
1.740
1.732
1.708
1.665
1.653
1.635
1.631
1.577
1.268
1.156
1.134
1.111
1.106
1.082
1.078
-0.000
Bpin
6c
1.00
1.10
1.22
4.20
1.86
11.74
3.86
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


TIPSO
Bpin
6d-crude
1.00
0.04
5.48 5.44 5.40 5.36 5.32 5.
f1 (ppm)
-0.000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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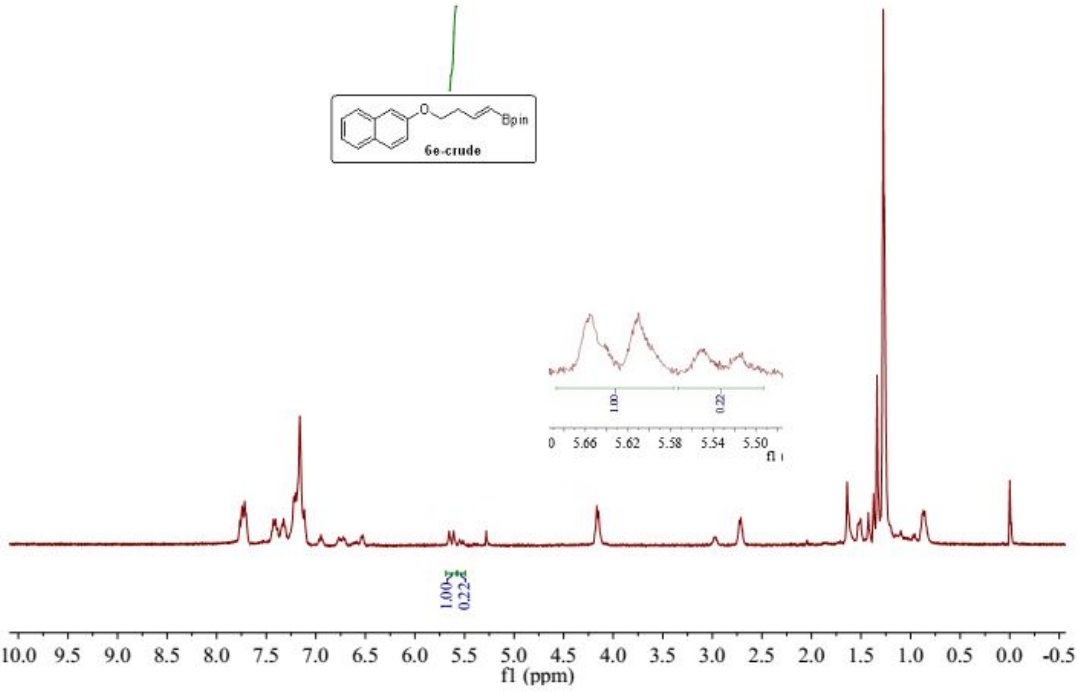
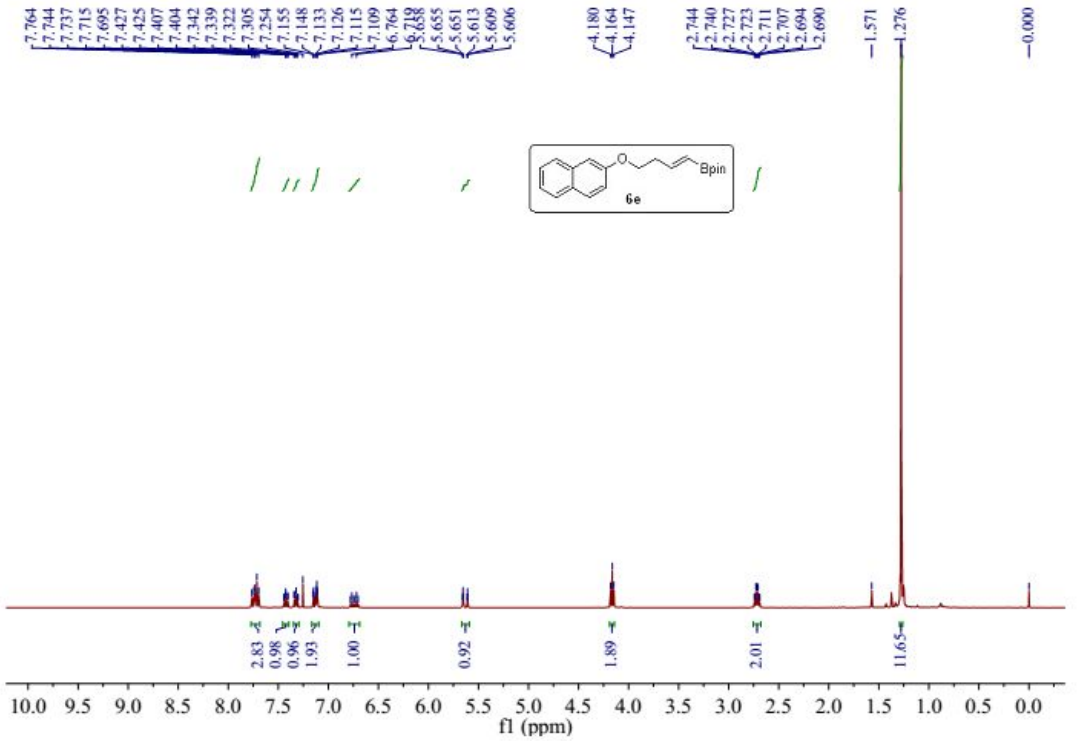
6.657
6.641
6.628
6.612
6.596
5.459
5.455
5.451
5.414
5.410
5.407
3.686
3.670
3.655
2.205
2.201
2.186
2.167
2.153
2.149
1.607
1.569
1.553
1.537
1.524
1.508
1.500
1.493
1.481
1.474
1.470
1.266
1.105
1.092
1.083
1.070
1.061
1.053
1.043
1.033
1.023
-0.000
TIPSO
Bpin
6d
1.06
1.03
2.00
2.13
4.20
11.93
21.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


6e-crude
Bpin
1.00
0.22
0 5.66 5.62 5.58 5.54 5.50
f1
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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7.427
7.425
7.407
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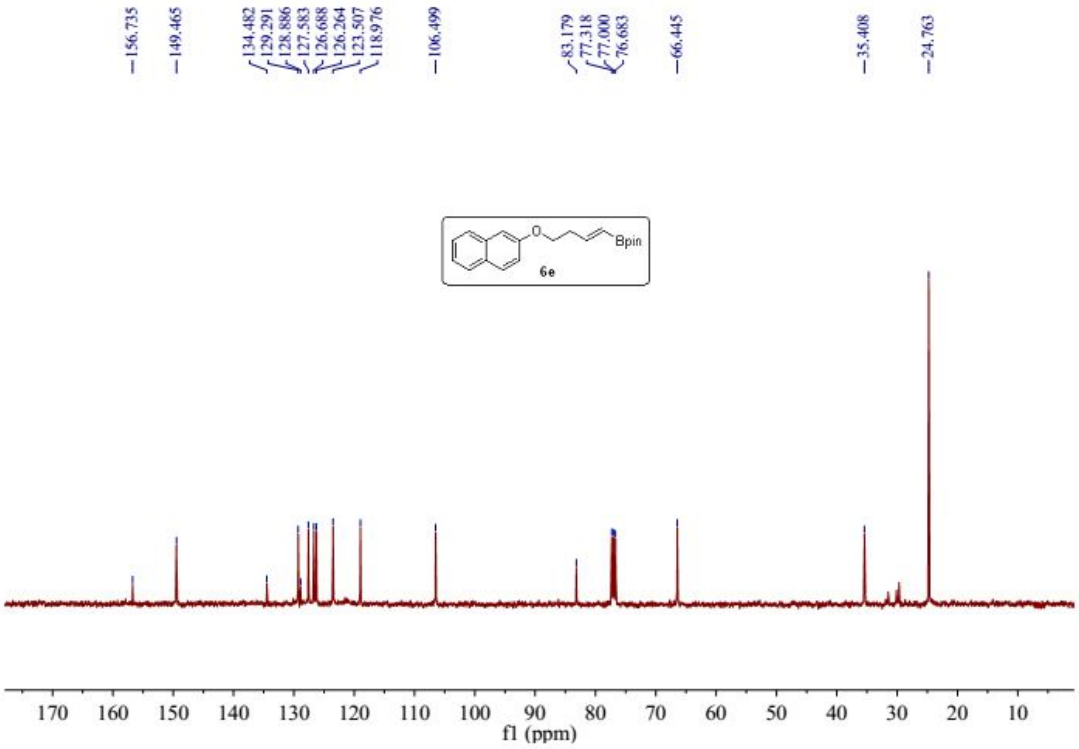
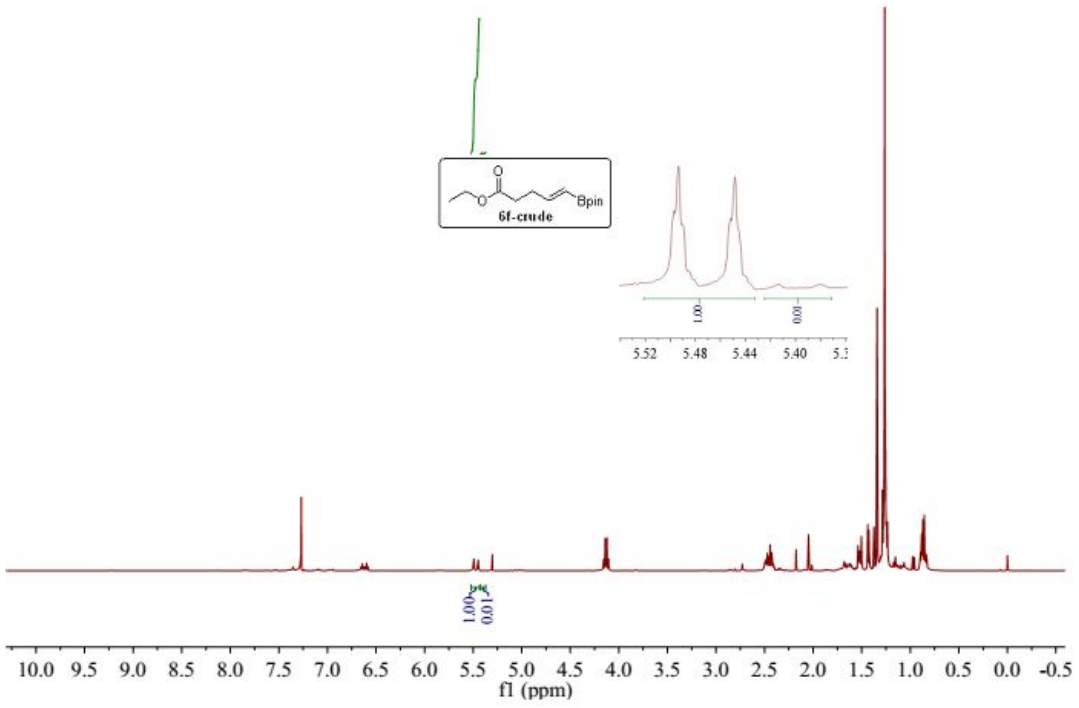
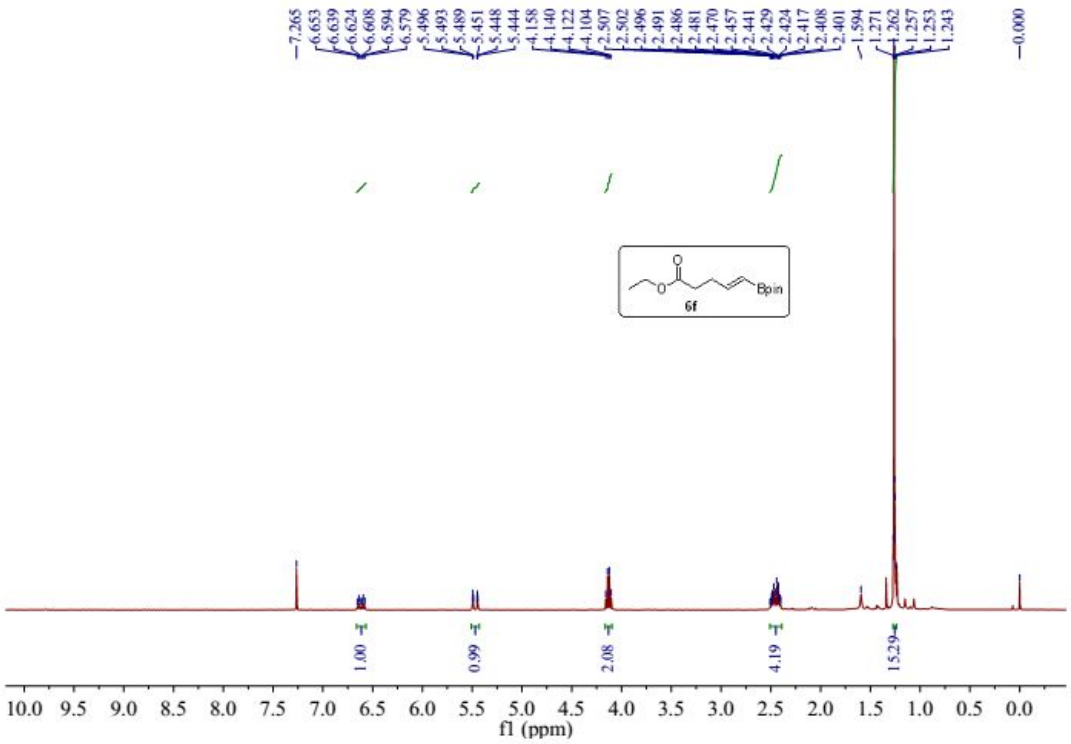
7.342
7.339
7.322
7.305
7.254
7.155
7.148
7.133
7.126
7.115
7.109
6.764
6.719
6.658
5.655
5.651
5.613
5.609
5.606
4.180
4.164
4.147
2.744
2.740
2.727
2.723
2.711
2.707
2.694
2.690
1.571
1.276
0.000
6e
Bpin
2.83
0.98
0.96
1.93
1.00
0.92
1.89
2.01
11.65
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


156.735
149.465
134.482
129.291
128.886
127.583
126.688
126.264
123.507
118.976
106.499
83.179
77.318
77.000
76.683
66.445
35.408
24.763
Bpin
6e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Bpin
6f-crude
1.00
0.01
5.52 5.48 5.44 5.40
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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6.653
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6.624
6.608
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6.579
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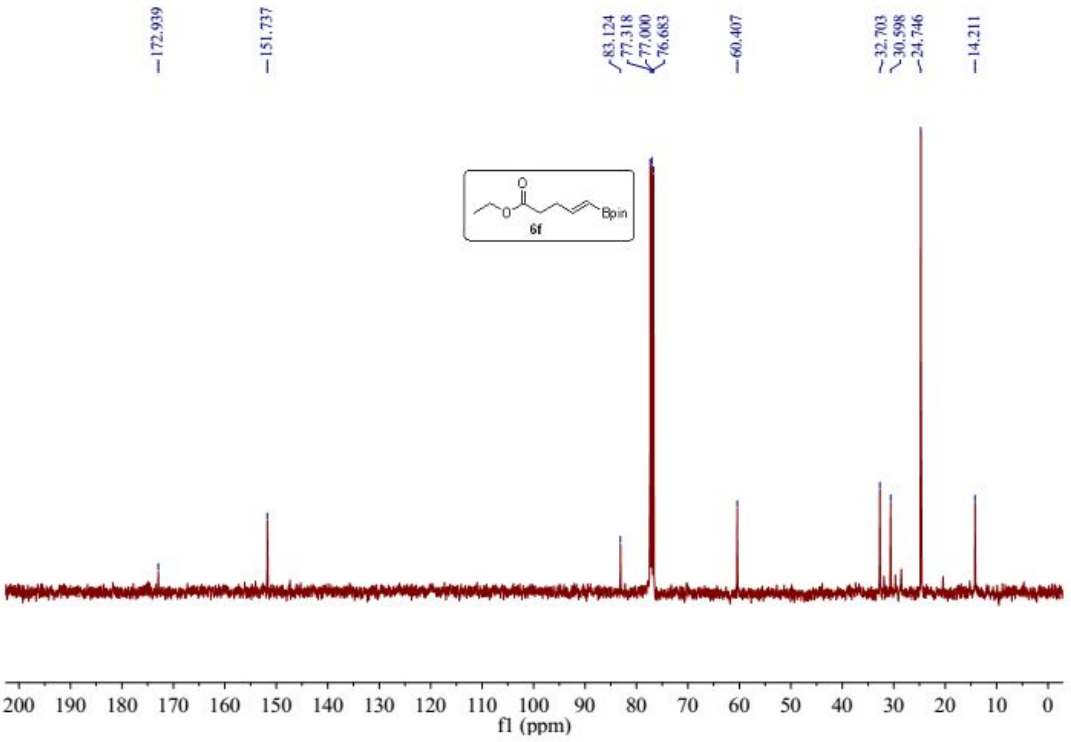
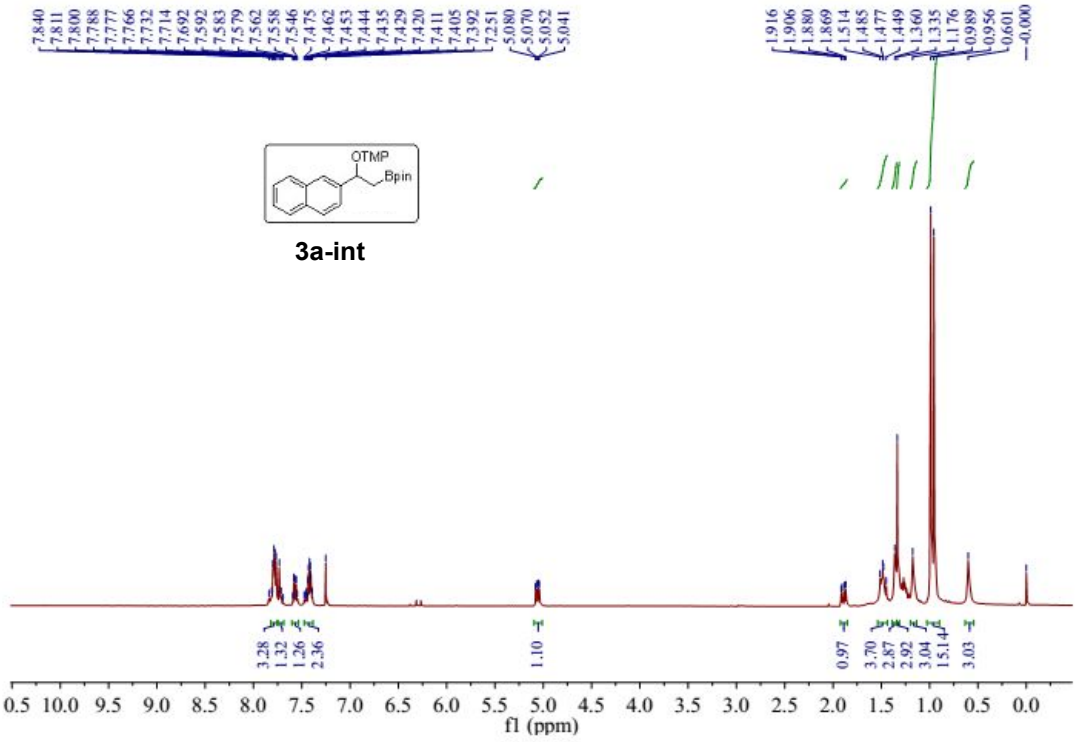
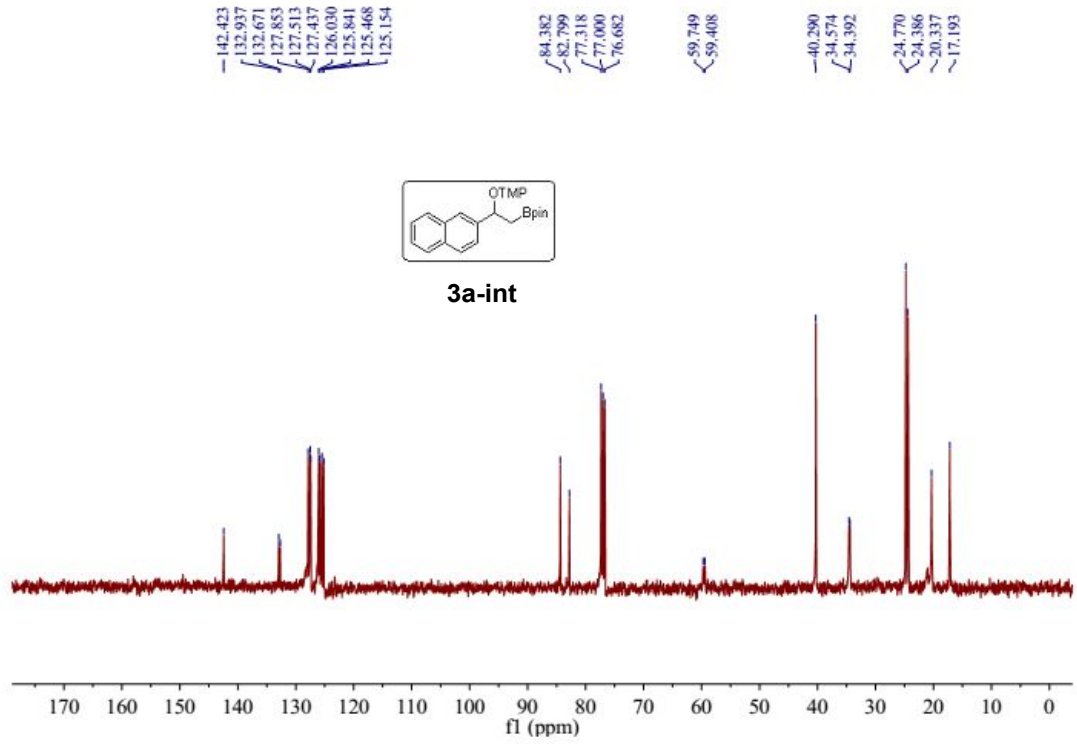
5.493
5.489
5.451
5.448
5.444
4.158
4.140
4.122
4.104
2.507
2.502
2.496
2.491
2.486
2.481
2.470
2.457
2.441
2.429
2.424
2.417
2.408
2.401
1.594
1.271
1.262
1.257
1.253
1.243
0.000
Bpin
6f
1.00
0.99
2.08
4.19
15.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.939
151.737
83.124
77.318
77.000
76.683
60.407
32.703
30.598
24.746
14.211
Bpin
6f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OTMP
Bpin
3a-int
fl (ppm)


OTMP
Bpin
3a-int
fl (ppm)