Supporting Information

Palladium-Catalyzed Oxidative Allylation of Bis[(pinacolato)boryl]methane: Synthesis of Homoallylicboronic Esters

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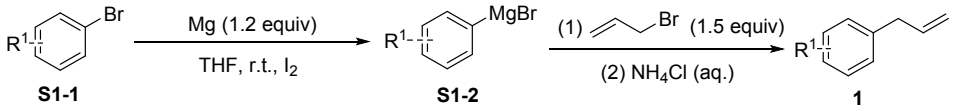
A. General Information

^1H and ^{13}C NMR spectra were recorded using a 400 MHz NMR spectrometer. Chemical shifts were reported in ppm from the solvent resonance as the internal reference ($CDCl_3$ δ_H = 7.26 ppm, downfield from TMS, δ_C = 77.16 ppm. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). IR spectra were obtained as potassium bromide pellets between two potassium bromide pellets with a spectrometer. GC-MS was obtained using electron ionization. HRMS was obtained with a LCMS-IT-TOF mass spectrometer or recorded on an EI-ion trap High Resolution mass spectrometer. TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. X-ray structural analyses were conducted on an x-ray analysis instrument.

Materials. Toluene and tetrahydrofuran were distilled from sodium/benzophenone. Acetonitrile was distilled from phosphorus pentoxide. Other commercially available reagents were purchased and used without further purification. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF_{254}) using UV light as a visualizing agent. Flash column chromatography was conducted using silica gel (200–300 mesh) with the indicated solvent system. All the reaction temperatures reported are oil bath temperatures. Bis[(pinacolato)boryl]methane were commercially available.

B. Typical Procedures for the Synthesis of Substrates

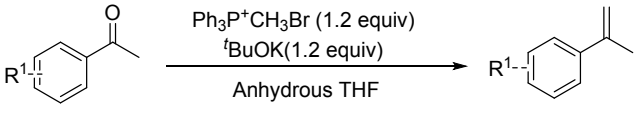
(a). General Procedure for the Synthesis of Allylbenzenes[1]



S1-1 **S1-2** **1**

Aryl bromide (5 mmol) was reacted with magnesium (1.2 equiv) in 10 mL anhydrous THF using I_2 as initiator at room temperature. After the reaction was finished, the combined organics was added to the anhydrous THF solution of allyl bromide. After stirring for 1 h, NH_4Cl (aq.) was added to the reaction mixture, washing with water and then concentrated for further purification. Purification by column chromatography over silica gel (230-400 mesh) using petroleum ether as eluent afforded **1c**, **1d**, **1g**, **1j**, **1m**, **1n**, **1o**, **1q**, **1t** as a colorless oil.

(b). General Procedure for Synthesis of *α*-Methyl Styrenes [2]



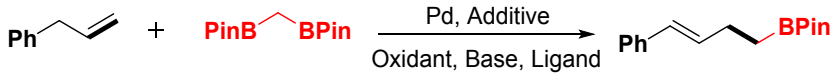
S4-1 **4**

In an oven dried flask, methyl triphenylphosphonium bromide (1.2 equiv) in THF (1.6 mL/mmol) was added. The suspension was cooled to 0 °C, KO^{t}Bu (1.2 equiv) was added and the resulting yellow suspension was stirred at 0 °C for 45 min. To this suspension, a solution of acetophenone (1.0 equiv) in THF (0.7 mL/mmol) was added dropwise and the resulting mixture was warmed

gradually to r.t. and stirred at r.t. for 16 h. Reaction mixture was concentrated under reduced pressure and filtered. The filtrate was concentrated under reduced pressure to yield a yellow oil. Purification by column chromatography over silica gel (230-400 mesh) using petroleum ether as eluent afforded **4b**, **4c**, **4d**, **4e**, **4f**, **4g**, **4h** as a colorless oil.

C. Optimization of Reaction Conditions [a]

In a 25 mL sealed test tube, a mixture of allylbenzene **1a** (0.25 mmol), bis[(pinacolato)boryl]methane **2a** (0.1 mmol), catalyst (10 mol %), ligand (15 mol %), base (2 equiv), additive (20 mol %), oxidant (2 equiv) in 2 mL solvent was vigorously stirred together for 24 h. After completion of the reaction and quenched by saturated brines, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate layer was then dried over anhydrous sodium sulfate and concentrated in vacuum. Further purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded the pure product **3a,** and calculated the isolated yield.



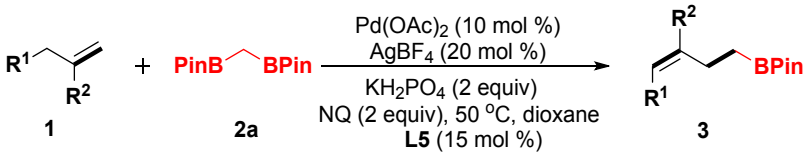
1a **2a** **3a**

entry	catalyst	additive	base	ligand	oxidant	solvent	yield[b] (%)
1	$Pd(OAc)_2$	AgOTf	^tBuOK	-	O_2	1,4-dioxane	N.D.
2	$Pd(OAc)_2$	AgTFA	^tBuOK	-	O_2	1,4-dioxane	N.D.
3	$Pd(OAc)_2$	AgOAc	^tBuOK	-	O_2	1,4-dioxane	N.D.
4	$Pd(OAc)_2$	$AgBF_4$	^tBuOK	-	O_2	1,4-dioxane	Trace
5	$Pd(OAc)_2$	$AgBF_4$	Cs_2CO_3	-	O_2	1,4-dioxane	Trace
6	$Pd(OAc)_2$	$AgBF_4$	CF_3COONa	-	O_2	1,4-dioxane	12
7	$Pd(OAc)_2$	$AgBF_4$	KPF_6	-	O_2	1,4-dioxane	23
8	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	O_2	1,4-dioxane	30
9	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	$PhI(OAc)_2$	1,4-dioxane	N.D.
10	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	BQ	1,4-dioxane	Trace
11	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	DDQ	1,4-dioxane	Trace
12	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	DMBQ	1,4-dioxane	Trace
13[c]	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	BQ/DDQ	1,4-dioxane	35
14[d]	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	BQ/DDQ	1,4-dioxane	55
15	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	NQ	1,4-dioxane	60
16	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	NQ	DMSO	N.D.
17	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	NQ	DMF	N.D.
18	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	NQ	Toluene	32
19	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	NQ	MeCN	N.D.
20	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	NQ	DMA	N.D.
21	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	-	NQ	THF	32
22	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	L1	NQ	1,4-dioxane	N.D.
23	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	L2	NQ	1,4-dioxane	N.D.

24	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	L3	NQ	1,4-dioxane	N.D.
25	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	L4	NQ	1,4-dioxane	43
26	**$Pd(OAc)_2$**	**$AgBF_4$**	**KH_2PO_4**	**L5**	**NQ**	**1,4-dioxane**	**83**
27[e]	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	L5	NQ	1,4-dioxane	53
28[f]	$Pd(OAc)_2$	$AgBF_4$	KH_2PO_4	L5	NQ	1,4-dioxane	12

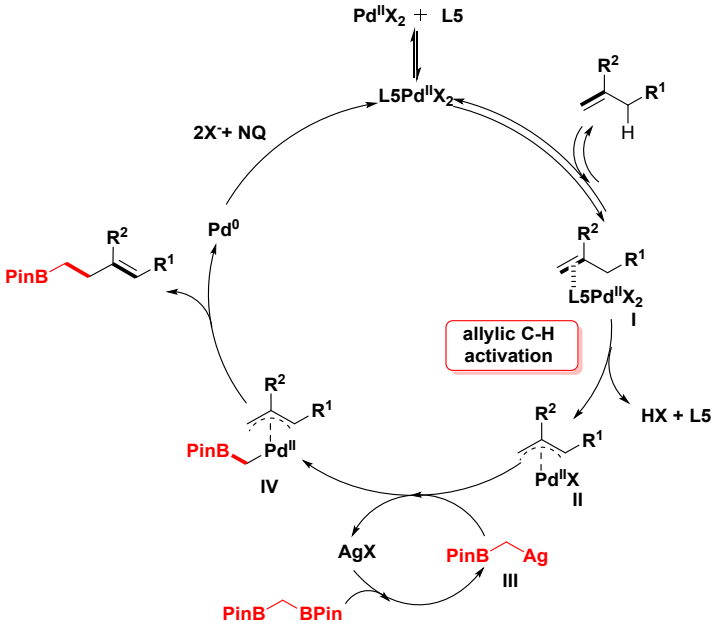
[a] A mixture of **1a** (0.25 mmol, 2.5 equiv), **2a** (0.1 mmol, 1 equiv), base (0.2 mmol, 2 equiv), catalyst (10 mol %), additive (20 mol %), ligand (15 mol %), oxidant (2 equiv)and solvent (2 mL) was sealed in a 25 mL Schlenk tube at 50 °C for 24 h. N.D. = not detected. **L1**: PPh_3. **L2**: dppf. **L3**: 4,4'-bipyridine. **L4:** 1,2-bis(phenylsulphonyl)ethane. **L5**: 1,2-bis(phenylsulfinyl)ethane. [b] Isloated yields based on **2a**. [c] BQ:DDQ=2:1; [d] BQ:DDQ=4:1. [e] The reaction was at room temperature. [f] The temperature was 100 °C.

D. General Procedure for the Synthesis of Homoallylic Organoboronic Esters



In a 25 mL sealed test tube, a mixture of olefins **1** (0.25 mmol), bis[(pinacolato)boryl]methane **2a** (0.1 mmol), $Pd(OAc)_2$ (10 mol %), $AgBF_4$ (20 mol %), KH_2PO_4 (2 equiv), NQ (2 equiv), 1,2-bis(phenylsulfinyl)ethane (10 mol %) and 2 mL of anhydrous 1,4-dioxane was vigorously stirred together at 50 °C for 24 h. After completion of the reaction and quenched by saturated brine, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate layer was then dried over anhydrous sodium sulfate and concentrated in vacuum. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) afforded the pure product **3**.

E. Possible Reaction Mechanism

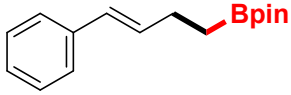


In light of the previous literature, a plausible mechanism is outlined in the manuscript. In this

catalytic cycle, KH_2PO_4 represents an important additive in this oxidative allylic alkylation reaction. When screening for the optimal reaction conditions, various bases were surveyed and KH_2PO_4 was found to be the most effective base for this reaction. Based on these results and the literatures (*Angew. Chem. Int. Ed.* **2011**, *50*, 12236, *Chem. Eur. J.* **2011**, *17*, 14371, *Chem. Commun.* **2017**, *53*, 8316), we supposed that KH_2PO_4 behaved as an important additive in the step of allylic C-H activation. Furthermore, 1,1-bis[(pinacolato)boryl]methane underwent a deborylative transmetallation process to form an alkyl silver species **III**. In this process, 'PinB-X' should be appended as a releasing byproduct in the smaller catalytic cycle. Unfortunately, we are not able to detect or isolate this byproduct in our reaction.

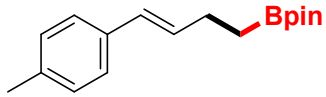
F. Analysis Data for the Products

(*E*)-4,4,5,5-Tetramethyl-2-(4-phenylbut-3-en-1-yl)-1,3,2-dioxaborolane (3a)



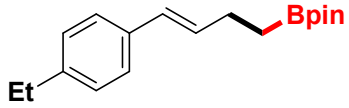
21.4 mg, 83% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.28 (m, 3H), 7.25 (s, 1H), 7.19 - 7.14 (m, 1H), 6.38 (d, J = 16.0 Hz, 1H), 6.27 (dt, J = 16.0, 6.0 Hz, 1H), 2.33 (dd, J = 15.2, 7.6 Hz, 2H), 1.24 (s, 12H), 0.98 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 132.8, 128.8, 128.4, 126.6, 125.9, 83.1, 27.3, 24.8; IR (KBr): 3883, 3606, 3296, 2924, 1736, 1456, 1145, 801, 694 cm^{-1}; HRMS (EI, m/z): $[M]^+$ Calcd. for $C_{16}H_{23}BNaO_2$, 281.1683, found, 281.1684.

(*E*)-4,4,5,5-Tetramethyl-2-(4-(*p*-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3b)



23.9 mg, 88% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.35 (d, J = 16.0 Hz, 1H), 6.22 (dt, J = 16.0, 6.0 Hz, 1H), 2.38 - 2.27 (m, 5H), 1.24 (s, 12H), 0.98 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 135.2, 131.7, 129.1, 128.6, 125.8, 83.0, 27.3, 24.8, 21.1; IR (KBr): 3883, 3593, 3297, 2920, 1736, 1371, 1144, 797, 712 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{17}H_{25}BNaO_2$, 295.1840, found, 295.1847.

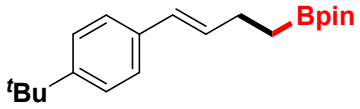
(*E*)-2-(4-(4-Ethylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)



24.3 mg, 85% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.18; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.35 (d, J = 16.0 Hz, 1H), 6.22 (dt, J = 16.0, 6.0 Hz, 1H), 2.61 (q, J = 8.0 Hz, 2H), 2.32 (q, J = 8.0 Hz, 2H), 1.24 (s, 12H), 1.20 (d, J = 8.0 Hz, 3H), 0.97 (t, J = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 135.5, 131.8, 128.7, 127.9, 125.9, 83.0, 28.5, 27.3, 24.8, 15.6; IR (KBr): 3881, 3729, 3610, 2928, 1745, 1370, 1143, 803, 707 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{18}H_{27}BNaO_2$, 309.1996,

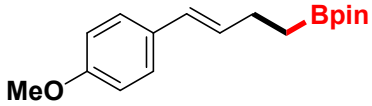
found, 309.1996.

(*E*)-2-(4-(4-(*tert*-Butyl)phenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)



19.2 mg, 79% yield; yellow oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.23 (m, 4H), 6.35 (d, J = 16.0 Hz, 1H), 6.23 (dt, J = 16.0, 6.4 Hz, 1H), 2.32 (q, J = 8.0 Hz, 2H), 1.30 (s, 9H), 1.24 (s, 12H), 0.97 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 135.2, 132.0, 128.5, 125.6, 125.3, 83.0, 34.4, 31.3, 27.3, 24.8; IR (KBr): 3893, 3611, 3296, 2949, 1744, 1462, 1141, 803, 707 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{20}H_{31}BNaO_2$, 337.2313, found, 337.2310.

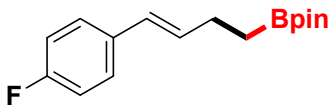
(*E*)-2-(4-(4-Methoxyphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)



In a 25 mL sealed test tube, a mixture of olefins **1a** (0.25 mmol), bis[(pinacolato)boryl]methane **2a** (0.1 mmol), $Pd(OAc)_2$ (10 mol %), $AgBF_4$ (20 mol %), KH_2PO_4 (2 equiv), BQ (4 equiv), DDQ (1 equiv), 1,2-bis(phenylsulfinyl)ethane (10 mol %) and 2 mL of anhydrous dioxane was vigorously stirred together at 50 °C for 24 h. After completion of the reaction and quenched by saturated brines, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate layer was then dried over anhydrous sodium sulfate and concentrated in vacuum. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) afforded the pure product **3e**.

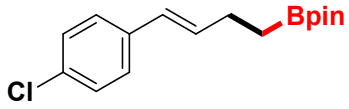
22.2 mg, 88% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.31; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 4.0 Hz, 2H), 6.83 - 6.78 (m, 2H), 6.32 (d, J = 16.0 Hz, 1H), 6.13 (dt, J = 16.0, 6.4 Hz, 1H), 3.79 (s, 3H), 2.31 (dd, J = 14.0, 6.4 Hz, 2H), 1.24 (s, 12H), 0.97 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 130.9, 130.7, 128.2, 127.0, 113.9, 83.1, 55.3, 27.3, 24.9; IR (KBr): 3885, 3607, 3295, 2924, 1520, 1370, 1238, 803, 705 cm^{-1}; HRMS (ESI, m/z): $[M+ Na]^+$ Calcd. for $C_{17}H_{25}BNaO_3$, 311.1789, found, 311.1794.

(*E*)-2-(4-(4-Fluorophenyl)but-3-en-1y-l)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)



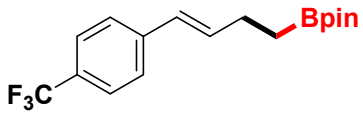
19.6 mg, 71% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.17; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.23 (m, 2H), 6.99 - 6.93 (m, 2H), 6.33 (d, J = 16.0 Hz, 1H), 6.18 (dt, J = 16.0, 6.4 Hz, 1H), 2.32 (q, J = 8.0 Hz, 2H), 1.24 (s, 12H), 0.97 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, J = 245.2 Hz), 134.1 (d, J = 3.0 Hz), 132.5 (d, J = 3.0 Hz), 127.7, 127.3 (d, J = 8.0 Hz), 115.2 (d, J = 21.5 Hz), 83.1, 27.2, 24.8; IR (KBr): 3882, 3614, 3205, 2924, 1756, 1372, 1144, 799, 703 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{16}H_{22}BFNaO_2$, 299.1589, found, 299.1587.

(*E*)-2-(4-(4-Chlorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)



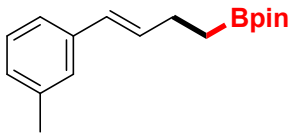
22.2 mg, 76% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.38; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 4H), 6.32 (d, J = 16.0 Hz, 1H), 6.25 (dt, J = 16.0, 6.4 Hz, 1H), 2.33 (q, J = 8.0 Hz, 2H), 1.24 (s, 12H), 0.97 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 133.5, 132.2, 128.5, 127.7, 127.1, 83.1, 27.3, 24.8; IR (KBr): 3886, 3618, 2924, 1742, 1372, 1322, 1145, 839, 681 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{16}H_{22}BClNaO_2$, 315.1294, found, 315.1294.

(*E*)-4,4,5,5-Tetramethyl-2-(4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3h)



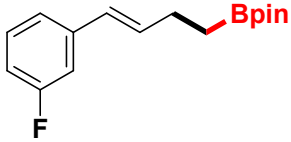
22.8 mg, 70% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.31; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 6.40 - 6.38 (m, 2H), 2.39 - 2.34 (m, 2H), 1.24 (s, 12H), 0.99 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 135.6, 128.5 (q, J = 32.0 Hz), 127.7, 126.0, 125.4 (q, J = 3.8 Hz), 123.0, 83.1, 27.3, 24.8; IR (KBr): 3884, 3296, 2980, 1616, 1323, 1133, 843, 803, 711 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{17}H_{22}BF_3NaO_2$, 349.1555, found, 349.1560.

(*E*)-4,4,5,5-Tetramethyl-2-(4-(m-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3i)



22.6 mg, 83% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.19; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 - 7.11 (m, 3H), 7.00 (d, J = 8.0 Hz, 1H), 6.36 (d, J = 16.0 Hz, 1H), 6.27 (dt, J = 16.0, 6.0 Hz, 1H), 2.38 - 2.27 (m, 5H), 1.26 (s, 12H), 0.99 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 137.9, 132.6, 128.9, 128.3, 127.4, 126.7, 123.1, 83.0, 27.3, 24.8, 21.4; IR (KBr): 3916, 3621, 3298, 2922, 1748, 1371, 1143, 796, 705 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{17}H_{25}BNaO_2$, 295.1840, found, 294.1842.

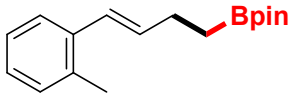
(*E*)-2-(4-(3-Fluorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)



17.4 mg, 63% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.21; ^{1}H NMR (400 MHz, CDCl3) δ 7.25 - 7.19 (m, 1H), 7.10 - 6.97 (m, 2H), 6.89 - 6.82 (m, 1H), 6.38 - 6.24 (m, 2H), 2.33 (td, J = 8.0, 5.6 Hz, 2H), 1.24 (s, 12H), 0.98 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, J = 243.0 Hz), 140.4 (d, J = 8.0 Hz), 134.2, 129.8 (d, J = 8.0 Hz), 127.9

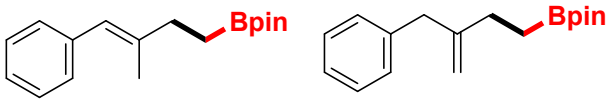
(d, J = 3.0 Hz), 121.8 (d, J = 3.0 Hz), 113.4 (d, J = 21.0 Hz), 112.32 (d, J = 22.0 Hz), 83.1, 27.3, 24.8; IR (KBr): 3882, 3620, 3296, 2922, 1754, 1372, 1143, 798, 679 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{22}BFNaO_2$, 299.1589, found, 299.1589.

(*E*)-4,4,5,5-Tetramethyl-2-(4-(o-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3k)



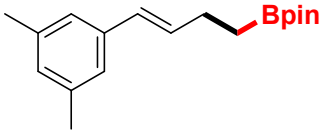
21.2 mg, 78% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.23; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.2 Hz, 1H), 7.18 - 7.08 (m, 3H), 6.59 (d, J = 16.0 Hz, 1H), 6.16 (dt, J = 16.0, 6.0 Hz, 1H), 2.41 - 2.35 (m, 2H), 2.33 (s, 3H), 1.26 (s, 12H), 1.01 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 134.9, 134.1, 130.1, 126.6, 126.6, 125.9, 125.4, 83.0, 27.6, 24.8, 19.8; IR (KBr): 3886, 3601, 3294, 2922, 1641, 1371, 1145, 795, 709 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{17}H_{25}BNaO_2$, 295.1840, found, 295.1841.

(*E*)-4,4,5,5-tetramethyl-2-(3-methyl-4-phenylbut-3-en-1-yl)-1,3,2-dioxaborolane (3l)



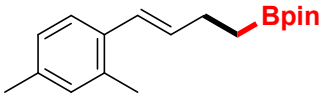
19.6 mg, 72% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.30; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 6.0 Hz, 3H), 7.24 (d, J = 12.0 Hz, 3H), 7.21 - 7.13 (m, 5H), 6.28 (s, 1.2H), 4.85 (s, 1H), 4.68 (s, 1H), 3.35 (s, 2H), 2.29 (t, J = 8.0 Hz, 2.4H), 2.18 - 2.05 (m, 2H), 1.85 (s, 3H), 1.24 (s, 14.4H), 1.22 (s, 12H), 1.06 - 1.00 (m, 2.4H), 0.97 - 0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 140.9, 140.0, 138.8, 129.0, 128.8, 128.2, 127.9, 125.9, 125.6, 123.6, 110.0, 83.0, 82.9, 43.0, 34.6, 29.6, 24.8, 24.8, 17.7; IR (KBr): 3885, 3614, 3296, 2921, 1646, 1370, 1144, 797, 704 cm^{-1};HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{17}H_{25}BNaO_2$, 295.1840; found, 295.1847.

(*E*)-2-(4-(3,5-Dimethylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)



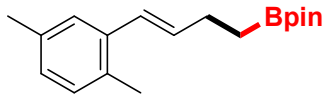
23.5 mg, 82% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.28; ^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.83 (s, 1H), 6.33 (d, J = 16.0 Hz, 1H), 6.25 (dt, J = 16.0, 6.4 Hz, 1H), 2.40 - 2.21 (m, 8H), 1.26 (s, 12H), 0.98 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 137.8, 132.4, 128.9, 128.4, 123.9, 83.1, 27.4, 24.9, 21.3; IR (KBr): 3889, 3618, 3425, 2922, 1736, 1371, 1141, 801, 704 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{18}H_{27}BNaO_2$, 309.1996, found, 309.2004.

(*E*)-2-(4-(2,4-Dimethylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n)



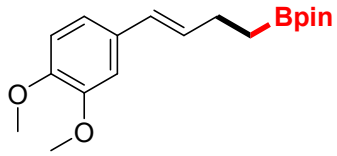
23.5 mg, 81% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.44; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 2H), 6.53 (d, J = 16.0 Hz, 1H), 6.10 (dt, J = 16.0, 6.4 Hz, 1H), 2.35 - 2.31 (m, 2H), 2.28 (s, 6H), 1.24 (s, 12H), 0.98 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 134.7, 134.2, 133.2, 130.8, 126.7, 126.4, 125.4, 83.0, 27.6, 24.8, 21.0, 19.7; IR (KBr): 3887, 3620, 2921, 1748, 1545, 1370, 1141, 801, 709 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{18}H_{27}BNaO_2$, 309.1996, found, 309.2002.

(*E*)-2-(4-(2,5-Dimethylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)



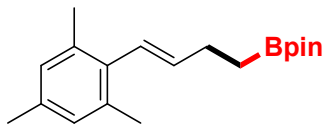
24.3 mg, 85% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.54 (d, J = 16.0 Hz, 1H), 6.13 (dt, J = 16.0, 6.4 Hz, 1H), 2.35 (q, J = 8.0 Hz, 2H), 2.29 (s, 3H), 2.27 (s, 3H), 1.25 (s, 12H), 0.99 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 135.2, 133.8, 131.8, 130.0, 127.4, 126.7, 126.1, 83.0, 27.6, 24.8, 21.0, 19.3; IR (KBr): 3914, 3727, 3065, 2927, 1617, 1371, 1321, 1144, 825 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{18}H_{27}BNaO_2$, 309.1996, found, 309.2002.

(*E*)-2-(4-(3,4-Dimethoxyphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p)



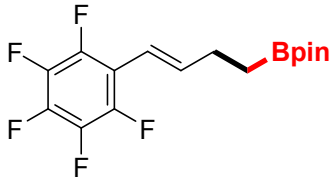
15.3 mg, 48% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.21; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, J = 4.0 Hz, 1H), 6.85 (dd, J = 8.0, 2.0 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.31 (d, J = 16.0 Hz, 1H), 6.14 (dt, J = 16.0, 6.4 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 2.37 - 2.26 (m, 2H), 1.24 (s, 12H), 0.98 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.2, 131.2, 130.9, 128.5, 118.8, 111.2, 108.6, 83.1, 55.9, 55.8, 27.2, 24.8; IR (KBr): 3986, 3623, 3418, 2923, 1731, 1373, 1141, 797, 708 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{18}H_{27}BNaO_4$, 341.1895, found, 341.1895.

(*E*)-2-(4-Mesitylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3q)



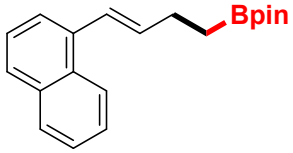
23.7 mg, 79% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.38; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 2H), 6.29 (d, J = 16.0 Hz, 1H), 5.73 (dt, J = 16.0, 6.4 Hz, 1H), 2.37 (q, J = 8.0 Hz, 2H), 2.27 (s, 9H), 1.27 (s, 12H), 1.01 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 135.8, 135.4, 134.7, 128.3, 126.0, 83.0, 27.7, 24.8, 20.8; IR (KBr): 3886, 3608, 3295, 2923, 1732, 1372, 1144, 797, 703 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{29}BNaO_2$, 323.2153, found, 323.2158.

(*E*)-4,4,5,5-Tetramethyl-2-(4-(perfluorophenyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3r)



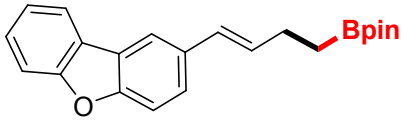
32.4 mg, 93% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (dt, J = 16.0, 6.4 Hz, 1H), 6.27 (d, J = 16.0 Hz, 1H), 2.39 (q, J = 8.0 Hz, 2H), 1.25 (s, 12H), 0.99 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5 (dm, J = 249.1 Hz), 142.7 (td, J = 7.4, 2.0 Hz), 139.2 (dm, J = 252.7 Hz), 137.6 (dm, J =251.3 Hz), 113.18 (t, J =1.0 Hz), 112.62 (td, J = 14.3, 4.0 Hz), 83.2, 28.6, 24.7; IR (KBr): 3850, 3620, 2982, 2925, 1647, 1376, 1144, 842, 669 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{18}BF_5NaO_2$, 371.1212, found, 371.1210.

(*E*)-4,4,5,5-Tetramethyl-2-(4-(naphthalen-1-yl)but-3-en-1-yl)-1,3,2-dioxaborolane (3s)



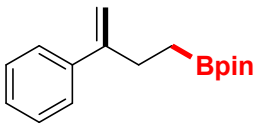
21.3 mg, 78% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.14; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 - 8.10 (m, 1H), 7.82 (dd, J = 6.4, 2.8 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.49 - 7.36 (m, 3H), 7.12 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 16.0, 6.4 Hz, 1H), 2.49 - 2.42 (m, 2H), 1.25 (s, 12H), 1.07 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 135.8, 133.6, 131.2, 128.4, 127.1, 125.9, 125.6, 125.6, 125.5, 124.0, 123.4, 83.1, 27.7, 24.9; IR (KBr): 3876, 3607, 3296, 2925, 1471, 1372, 1144, 828, 680 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{25}BNaO_2$, 331.1840, found, 331.1846.

(*E*)-2-(4-(Dibenzo[b,d]furan-2-yl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)



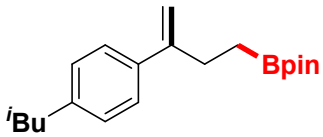
24.4 mg, 70% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 - 7.87 (m, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.43 (ddd, J = 8.0, 4.4, 2.0 Hz, 3H), 7.32 (td, J = 8.0, 0.8 Hz, 1H), 6.52 (d, J = 16.0 Hz, 1H), 6.32 (dt, J = 16.0, 6.4 Hz, 1H), 2.38 (td, J = 8.0, 1.2 Hz, 2H), 1.25 (s, 12H), 1.03 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 155.4, 133.1, 132.0, 128.7, 127.0, 125.4, 124.4, 124.3, 122.6, 120.6, 117.7, 111.6, 111.4, 83.1, 27.4, 24.8; IR (KBr): 3066, 2973, 1672, 1590, 1463, 1369, 1189, 964, 747, 664 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{22}H_{25}BNaO_3$, 371.1789, found, 371.1790.

4,4,5,5-Tetramethyl-2-(3-phenylbut-3-en-1-yl)-1,3,2-dioxaborolane (5a)



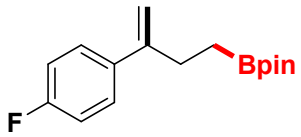
23.2 mg, 90% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.38 (m, 2H), 7.32 - 7.28 (m, 2H), 7.26 - 7.21 (m, 1H), 5.23 (s, 1H), 5.07 (d, J = 1.2 Hz, 1H), 2.63 - 2.58 (m, 2H), 1.23 (s, 12H), 1.02 - 0.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 141.7, 128.1, 127.1, 126.2, 111.0, 83.0, 29.3, 24.8; IR (KBr): 3835, 3742, 3620, 2923, 1691, 1533, 1142, 793, 707 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{16}H_{23}BNaO_2$, 281.1683, found, 281.1682.

2-(3-(4-*iso*Butylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b)



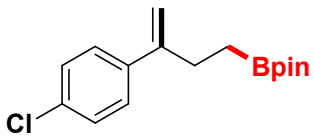
25.5 mg, 81% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.47; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 5.22 (s, 1H), 5.03 (d, J = 1.2 Hz, 1H), 2.62 - 2.56 (m, 2H), 2.45 (d, J = 8.0 Hz, 2H), 1.85 (dt, J = 13.2, 6.8 Hz, 1H), 1.23 (s, 12H), 1.02 - 0.96 (m, 2H), 0.90 (d, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 140.7, 138.9, 128.9, 125.8, 110.2, 83.0, 45.1, 30.2, 29.3, 24.8, 22.4; IR (KBr): 3894, 3457, 3293, 2924, 1743, 1371, 1142, 800, 712 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{20}H_{31}BNaO_2$, 337.2309, found, 337.2317.

2-(3-(4-Fluorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c)



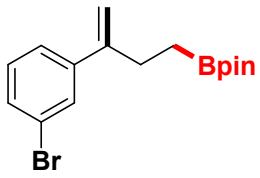
19.6 mg, 71% yield; light yellow oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.33 (m, 2H), 6.98 (t, J = 8.0 Hz, 2H), 5.18 (s, 1H), 5.05 (d, J = 1.2 Hz, 1H), 2.60 - 2.53 (m, 2H), 1.23 (s, 12H), 1.01 - 0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, J = 245.0 Hz), 149.3, 137.7 (d, J = 3.0 Hz), 127.7 (d, J = 8.0 Hz), 114.9 (d, J = 21.0 Hz), 111.0, 83.1, 29.5, 24.8; IR (KBr): 3887, 3800, 3627, 2929, 1508, 1372, 1146, 836, 719 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{16}H_{22}BFNaO_2$, 299.1589, found, 299.1590.

2-(3-(4-Chlorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d)



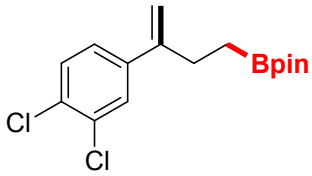
24.2 mg, 83% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50:1, v/v): R_f = 0.38; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.31 (m, 2H), 7.29 - 7.27 (m, 2H), 5.22 (s, 1H), 5.08 (d, J = 1.2 Hz, 1H), 2.61 - 2.51 (m, 2H), 1.23 (s, 12H), 1.01 - 0.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 140.1, 132.9, 128.3, 127.5, 111.6, 83.1, 29.3, 24.8; IR (KBr): 3883, 3802, 3459, 2924, 1737, 1370, 1135, 805, 707 cm^{-1}; HRMS (ESI, m/z): $[M+ Na]^+$ Calcd. for $C_{16}H_{22}BClNaO_2$, 315.1294, found, 315.1293.

2-(3-(3-Bromophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e)



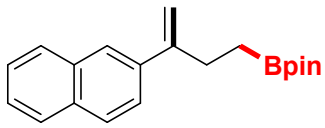
20.8 mg, 62% yield; light yellow oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (t, J = 1.6 Hz, 1H), 7.39 - 7.36 (m, 1H), 7.33 - 7.30 (m, 1H), 7.17 (t, J = 8.0 Hz, 1H), 5.23 (s, 1H), 5.10 (d, J = 1.2 Hz, 1H), 2.56 (t, J = 8.0 Hz, 2H), 1.23 (s, 12H), 1.03 - 0.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 144.0, 130.1, 129.7, 129.3, 124.8, 122.4, 112.2, 83.1, 29.2, 24.8; IR (KBr): 3889, 3612, 3298, 2924, 1641, 1552, 1143, 796, 708 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{16}H_{22}BBrNaO_2$, 359.0788, found, 359.0786.

2-(3-(3,4-dichlorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5f)



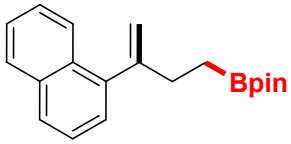
25.8 mg, 79% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.36; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 2.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.23 (dd, J = 8.4, 2.0 Hz, 1H), 5.24 (s, 1H), 5.12 (s, 1H), 2.54 (t, J = 8.0 Hz, 2H), 1.23 (s, 12H), 1.01 - 0.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 141.8, 132.2, 130.9, 130.0, 128.1, 125.6, 112.6, 83.1, 29.1, 24.8; IR (KBr): 3883, 3612, 3296, 2925, 1471, 1372, 1144, 797, 703 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{16}H_{21}BCl_2NaO_2$, 349.0904, found, 349.0903.

4,4,5,5-Tetramethyl-2-(3-(naphthalen-2-yl)but-3-en-1-yl)-1,3,2-dioxaborolane (5g)



25.3 mg, 82% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 - 7.76 (m, 4H), 7.60 (dd, J = 8.4, 1.6 Hz, 1H), 7.48 - 7.41 (m, 2H), 5.40 (s, 1H), 5.20 (d, J = 1.2 Hz, 1H), 2.77 - 2.70 (m, 2H), 1.25 (s, 12H), 1.11 - 1.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 138.9, 133.4, 132.7, 128.1, 127.6, 127.5, 125.9, 125.6, 124.9, 124.7, 111.6, 83.0, 29.3, 24.8; IR (KBr): 3884, 3296, 3060, 2927, 1735, 1371, 1237, 1146, 965 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{20}H_{25}BNaO_2$, 331.1840, found, 331.1849.

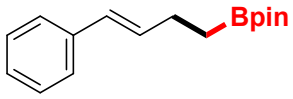
4,4,5,5-Tetramethyl-2-(3-(naphthalen-1-yl)but-3-en-1-yl)-1,3,2-dioxaborolane (5h)



24.0 mg, 78% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.28; ^{1}H

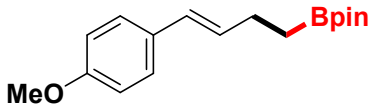
NMR (400 MHz, $CDCl_3$) δ 8.07 - 8.03 (m, 1H), 7.84 - 7.80 (m, 1H), 7.73 (d, J = 8.0 Hz, 3H), 7.48 - 7.38 (m, 1H), 7.29 - 7.22 (m, 1H), 5.38 (s, 1H), 5.02 (d, J = 1.2 Hz, 1H), 2.60 (t, J = 8.0 Hz, 2H), 1.22 (s, 12H), 1.03 - 0.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 141.8, 133.7, 131.5, 128.1, 127.0, 126.1, 125.6, 125.5, 125.2, 125.1, 113.7, 83.1, 32.7, 24.9; IR (KBr): 3919, 3617, 3454, 2920, 1642, 1368, 1138, 794, 707 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{20}H_{25}BNaO_2$, 331.1840, found, 331.1849.

(*E*)-4,4,5,5-Tetramethyl-2-(4-phenylbut-3-en-1-yl)-1,3,2-dioxaborolane (3a)



20.4 mg, 79% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.28 (m, 3H), 7.25 (s, 1H), 7.19 - 7.14 (m, 1H), 6.38 (d, J = 16.0 Hz, 1H), 6.27 (dt, J = 16.0, 6.0 Hz, 1H), 2.33 (dd, J = 15.2, 7.6 Hz, 2H), 1.24 (s, 12H), 0.98 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 132.8, 128.8, 128.4, 126.6, 125.9, 83.1, 27.3, 24.8; IR (KBr): 3883, 3606, 3296, 2924, 1736, 1456, 1145, 801, 694 cm^{-1}; HRMS (EI, m/z): $[M]^+$ Calcd. for $C_{16}H_{23}BNaO_2$, 281.1683, found, 281.1684.

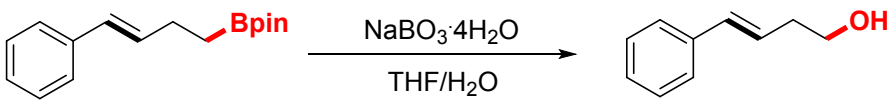
(*E*)-2-(4-(4-Methoxyphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)



In a 25 mL sealed test tube, a mixture of olefins **4j** (0.25 mmol), bis[(pinacolato)boryl]methane **2a** (0.1 mmol), $Pd(OAc)_2$ (10 mol %), $AgBF_4$ (20 mol %), KH_2PO_4 (2 equiv), BQ (4 equiv), DDQ (1 equiv), 1,2-bis(phenylsulfinyl)ethane (10 mol %) and 2 mL of anhydrous dioxane was vigorously stirred together at 50 °C for 24 h. After completion of the reaction and quenched by saturated brines, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate layer was then dried over anhydrous sodium sulfate and concentrated in vacuum. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) afforded the pure product **7b**.

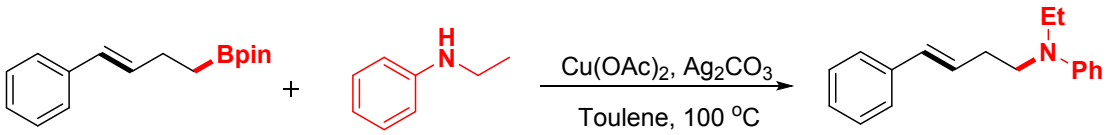
19.7 mg, 78% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.31; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 4.0 Hz, 2H), 6.83 - 6.78 (m, 2H), 6.32 (d, J = 16.0 Hz, 1H), 6.13 (dt, J = 16.0, 6.4 Hz, 1H), 3.79 (s, 3H), 2.31 (dd, J = 14.0, 6.4 Hz, 2H), 1.24 (s, 12H), 0.97 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 130.9, 130.7, 128.2, 127.0, 113.9, 83.1, 55.3, 27.3, 24.9; IR (KBr): 3885, 3607, 3295, 2924, 1520, 1370, 1238, 803, 705 cm^{-1}; HRMS (ESI, m/z): $[M+ Na]^+$ Calcd. for $C_{17}H_{25}BNaO_3$, 311.1789; found, 311.1794.

G. Elaboration of Homoallyl Boronates



3a **8**, 86%

A solution of **3a** (52 mg, 0.20 mmol) in THF (2.0 mL) and H_2O (2.0 mL) was added $NaBO_3 \cdot 4H_2O$ (0.18 g, 1.2 mmol, 6.0 equiv) at room temperature. The reaction mixture was stirred for 12 h and quenched by addition of saturated aq. $Na_2S_2O_3$ (5.0 mL). The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4) and concentrated in vacuo to give a crude product. Purification by flash column chromatography (silica gel, eluting with petroleum ether/ethyl acetate) afforded the (*E*)-4-phenylbut-3-en-1-ol (**8**) as yellow oil (25.5 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 6.20 (dt, J = 16.0, 6.0 Hz, 1H), 3.75 (t, J = 8.0 Hz, 2H), 2.48 (q, J = 8.0 Hz, 2H), 1.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 132.8, 128.5, 127.2, 126.3, 126.0, 62.0, 36.4; IR (KBr): 3779, 3267, 2829, 2400, 1807, 1397, 1188, 913, 555 cm^{-1}; HRMS (EI, m/z): [M]+ Calcd. for $C_{10}H_{12}NaO$, 171.0780, found, 171.0778.



3a **9**, 78%

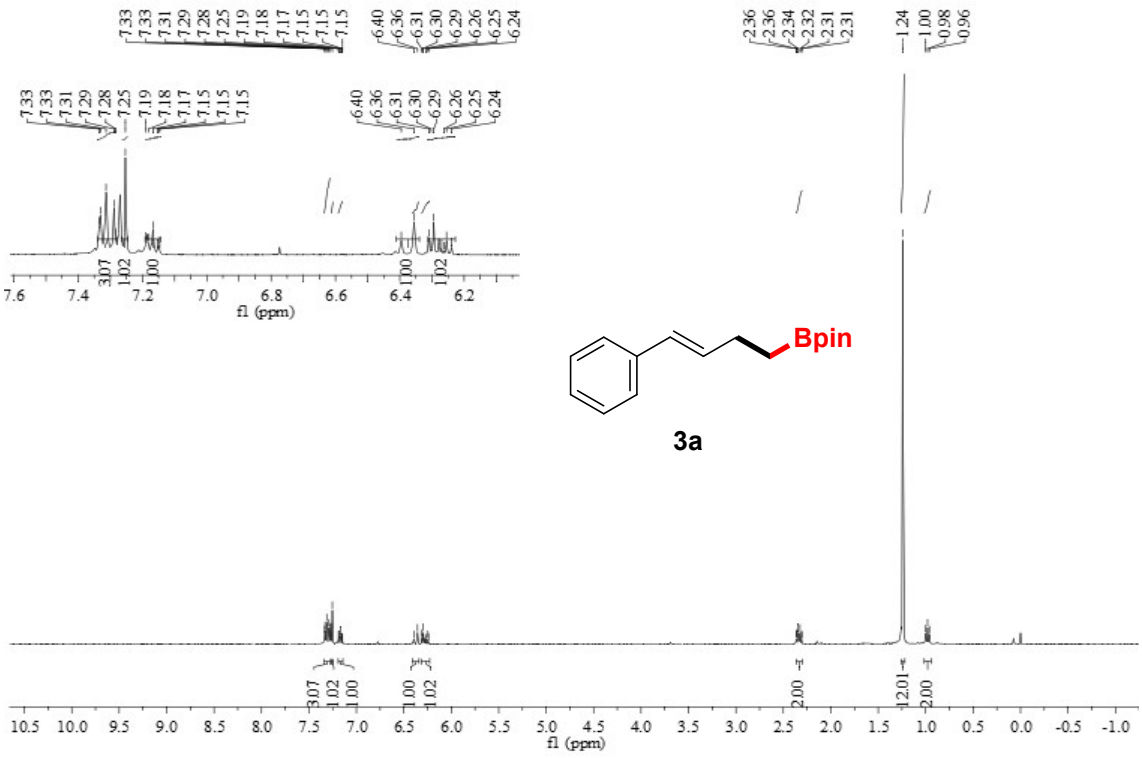
A solution of **3a** (52 mg, 0.20 mmol) in toluene (1.0 mL) and $Cu(OAc)_2$ (10 mol %), Ag_2CO_3 (2.0 equiv) was added. The reaction mixture was stirred for 20 h at 100 °C. After the completion of the reaction, the mixture was extracted with ethyl acetate (3 × 10 mL mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4) and concentrated in vacuo to give a crude product. Purification by flash column chromatography (silica gel, eluting with petroleum ether/ethyl acetate) afforded the (*E*)-*N*-ethyl-*N*-(4-phenylbut-3-en-1-yl)aniline (**9**) as yellow oil (39.2 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.27 (m, 4H), 7.22 (dd, J = 16.0, 7.2 Hz, 3H), 6.75 - 6.63 (m, 3H), 6.46 (d, J = 16.0 Hz, 1H), 6.23 (dt, J = 16.0, 6.0 Hz, 1H), 3.47 - 3.34 (m, 4H), 2.50 (dd, J = 14.4, 7.2 Hz, 2H), 1.17 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 137.5, 131.6, 129.3, 128.5, 127.7, 127.1, 126.0, 115.6, 111.9, 50.3, 45.0, 31.3, 12.4; IR (KBr): 3666, 3359, 2866, 1806, 1382, 1184, 949, 529 cm^{-1}; HRMS (EI, m/z): [M]+ Calcd. for $C_{18}H_{22}N$, 252.1747, found, 252.1748.

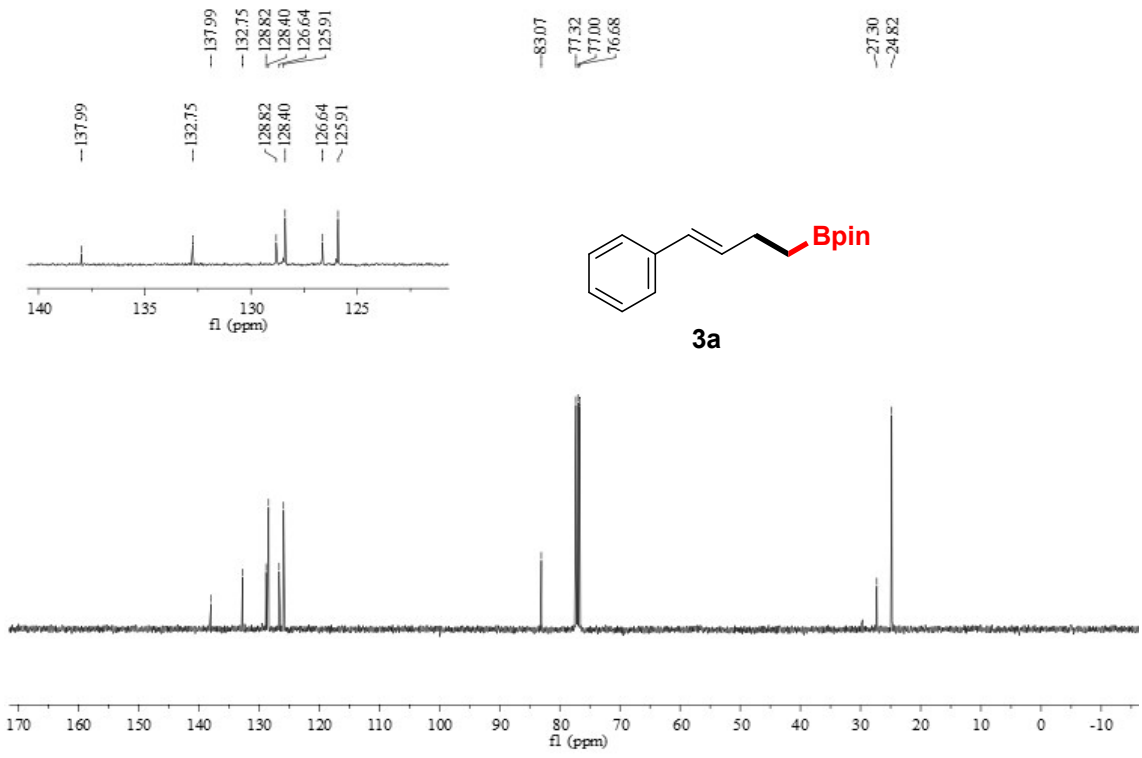
H. References

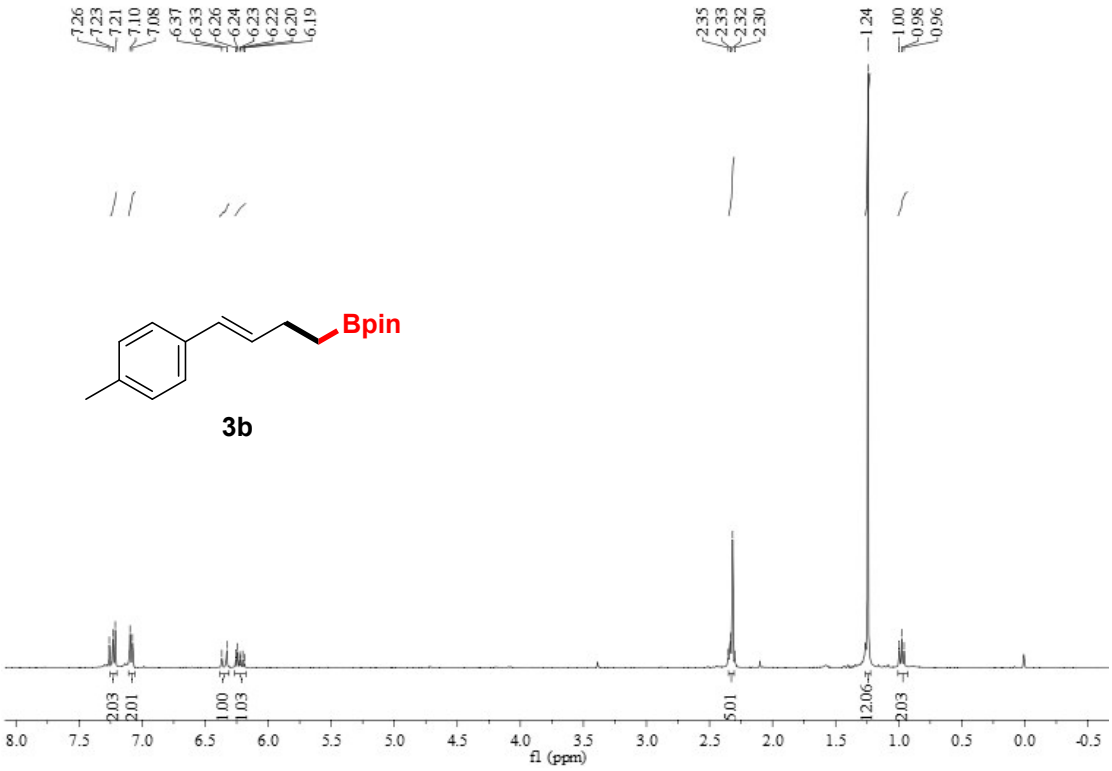
(1) Yang, W.; Chen, H.; Li, J.; Li, C.; Wu, W.; Jiang, H. *Chem. Commun.* **2015**, *51*, 9575.

(2) Tripathi, C.; Mukherjee, S. *Angew. Chem. Int. Ed.* **2013**, *52,* 8450.

I. NMR Spectra for New Compounds



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7.10
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6.26
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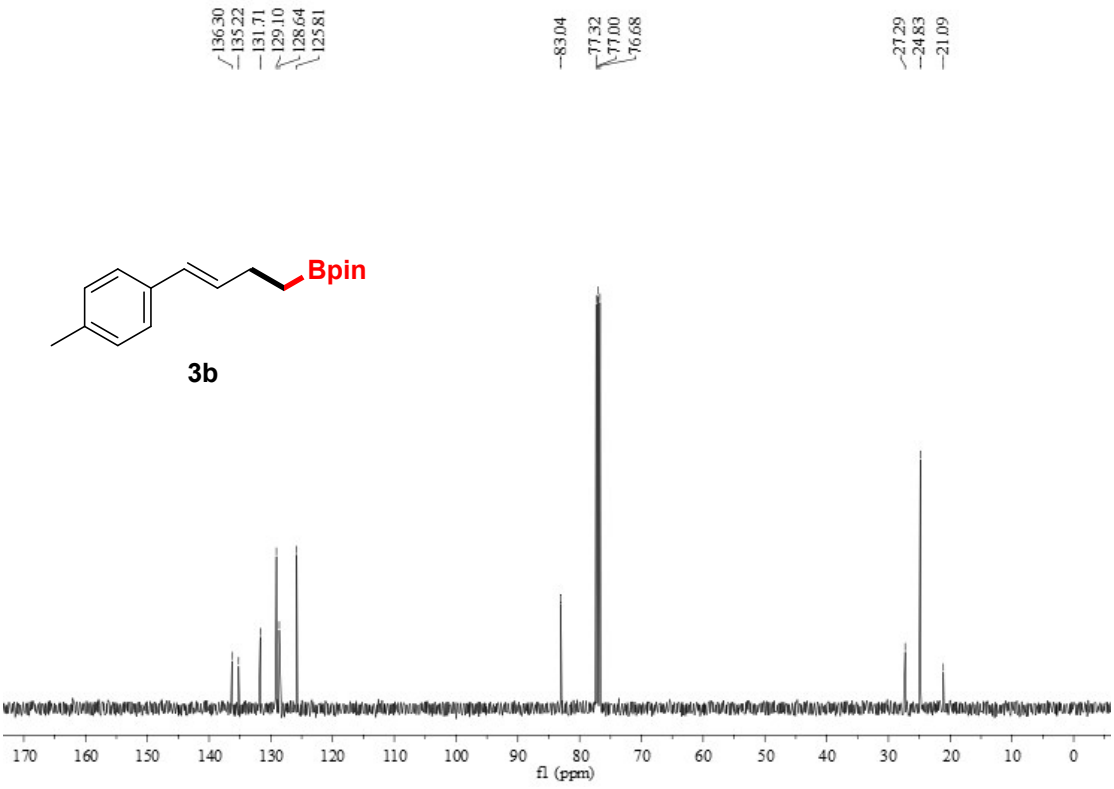
6.23
6.22
6.20
6.19
2.35
2.33
2.32
2.30
1.24
1.00
0.98
0.96
Bpin
3b
2.03
2.01
1.00
1.03
5.01
12.06
2.03
f1 (ppm)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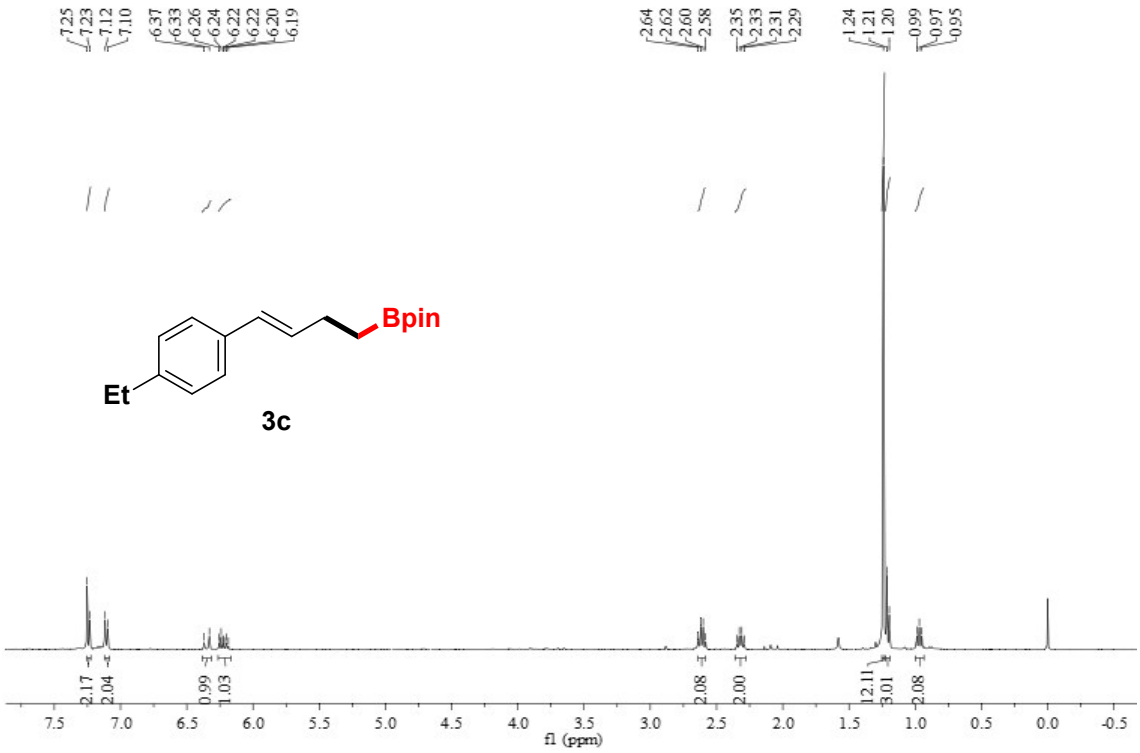
24.83
21.09
Bpin
3b
f1 (ppm)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2.62
2.60
2.58
2.35
2.33
2.31
2.29
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1.20
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0.97
0.95
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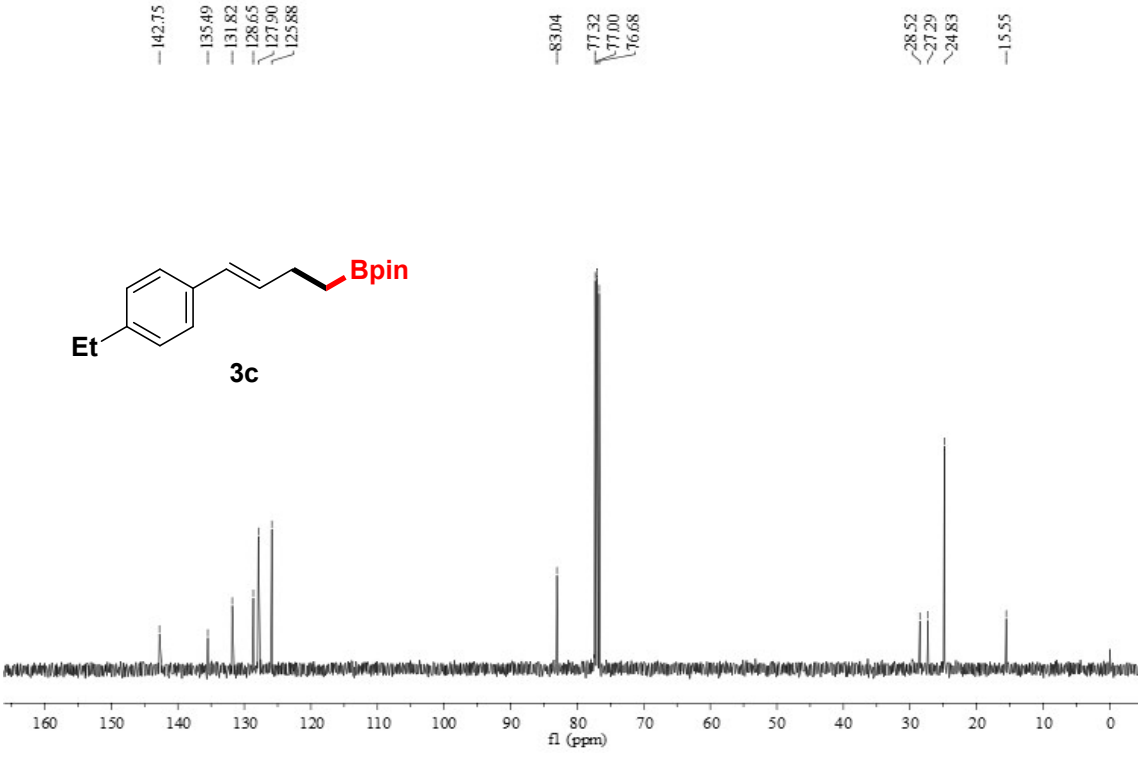
fl (ppm)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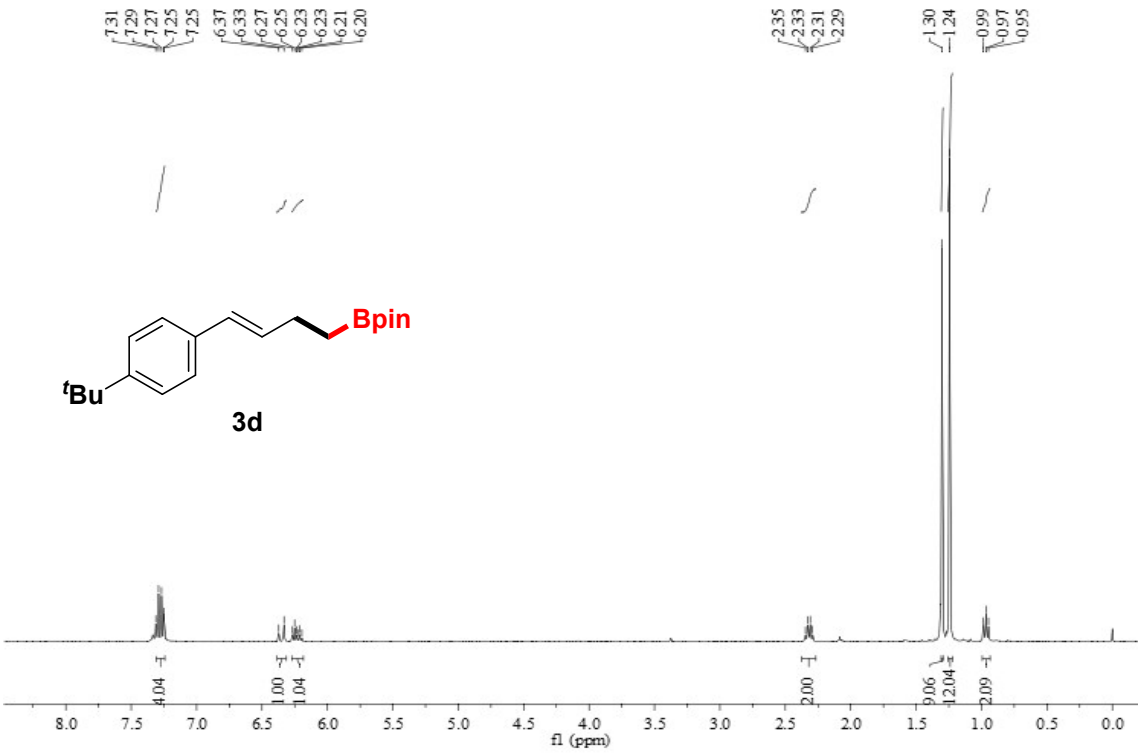
Et
3c
fl (ppm)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2.33
2.31
2.29
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0.95
Bpin
tBu
3d
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1.00
1.04
2.00
9.06
12.04
2.09
8.0
7.5
7.0
6.5
6.0
5.5
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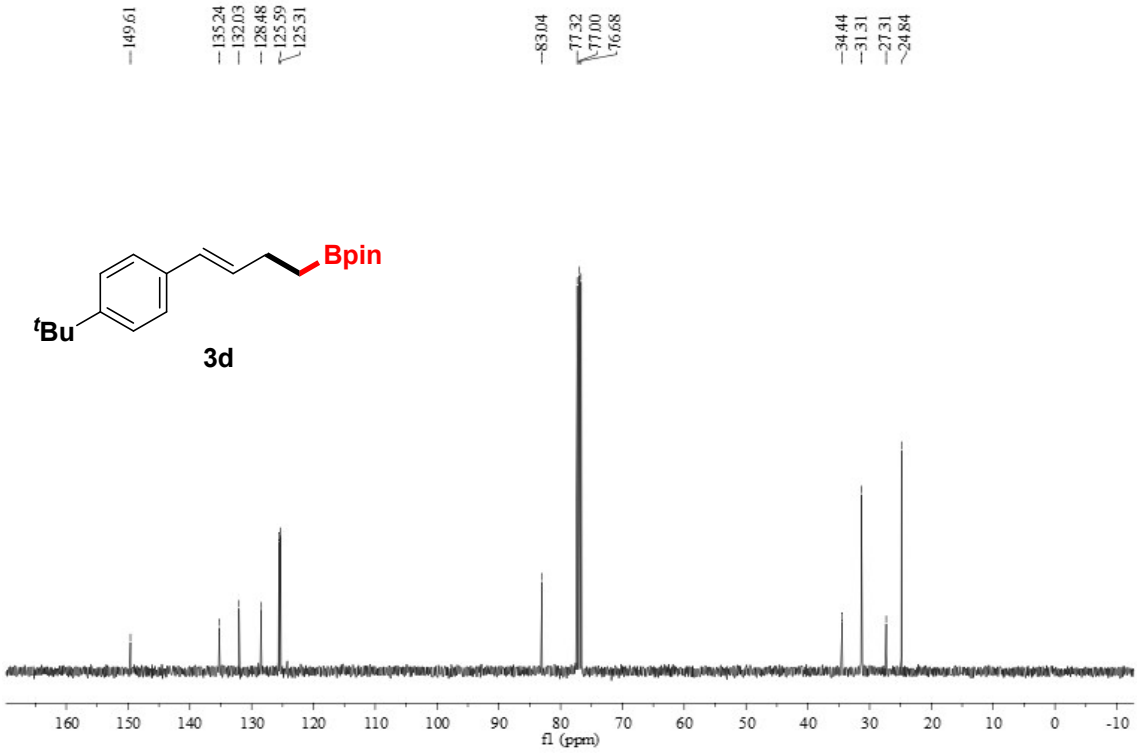
0.0
f1 (ppm)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24.84
Bpin
tBu
3d
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140
130
120
110
100
90
80
70
60
50
40
30
20
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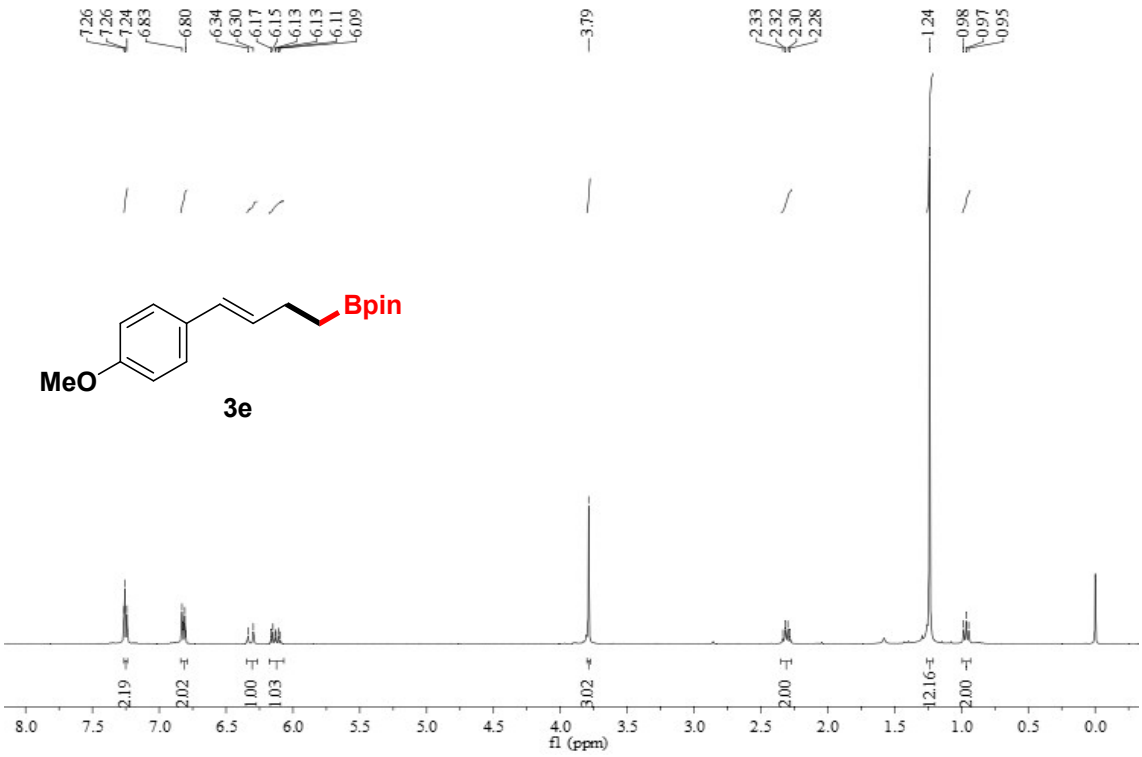
0
-10
f1 (ppm)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2.30
2.28
1.24
0.98
0.97
0.95
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MeO
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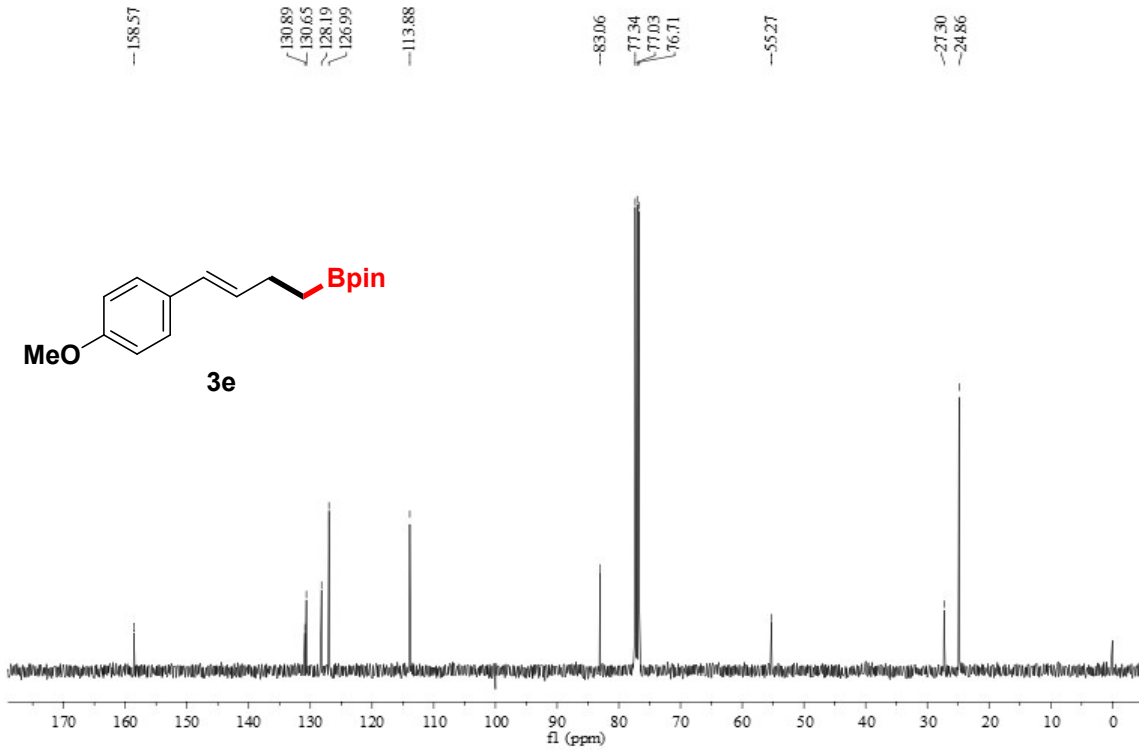
f1 (ppm)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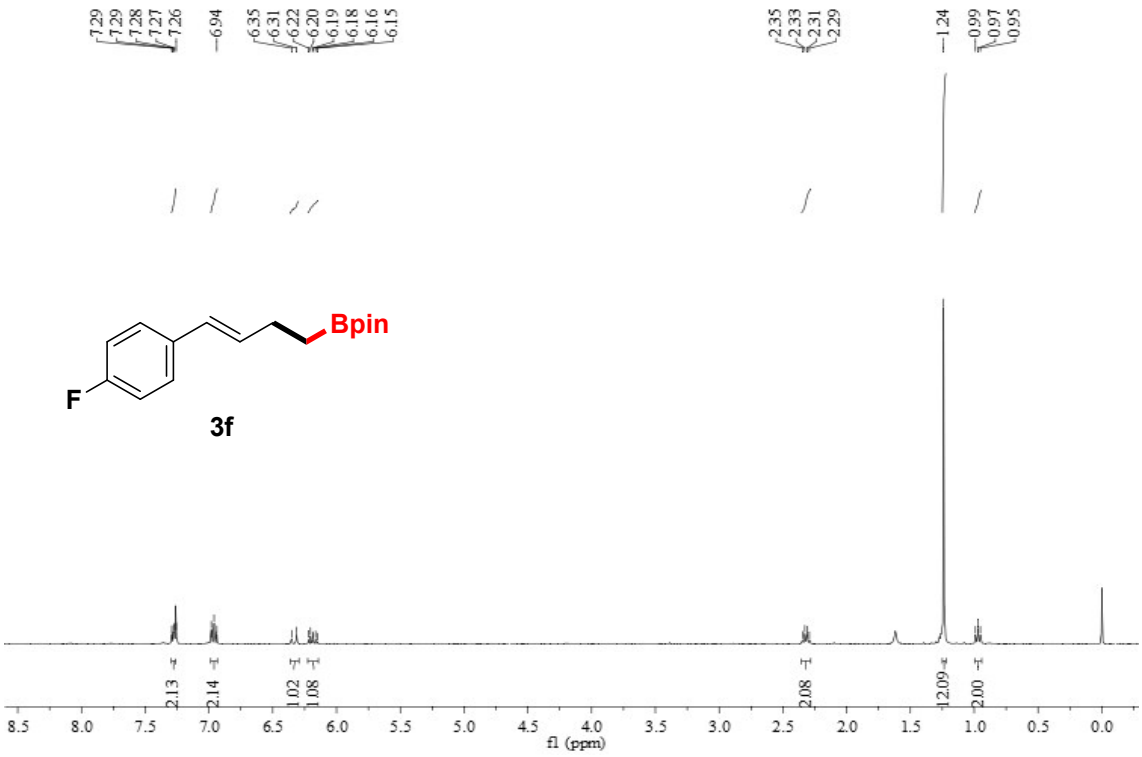
MeO
3e
f1 (ppm)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2.29
1.24
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1.08
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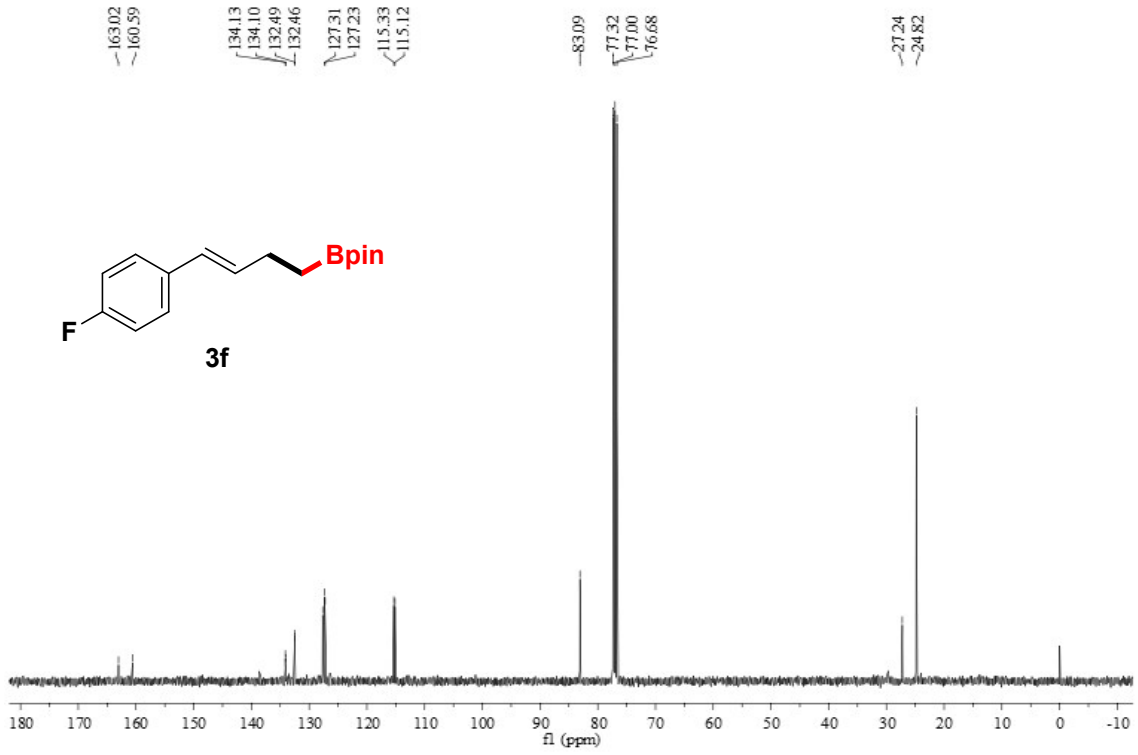
fl (ppm)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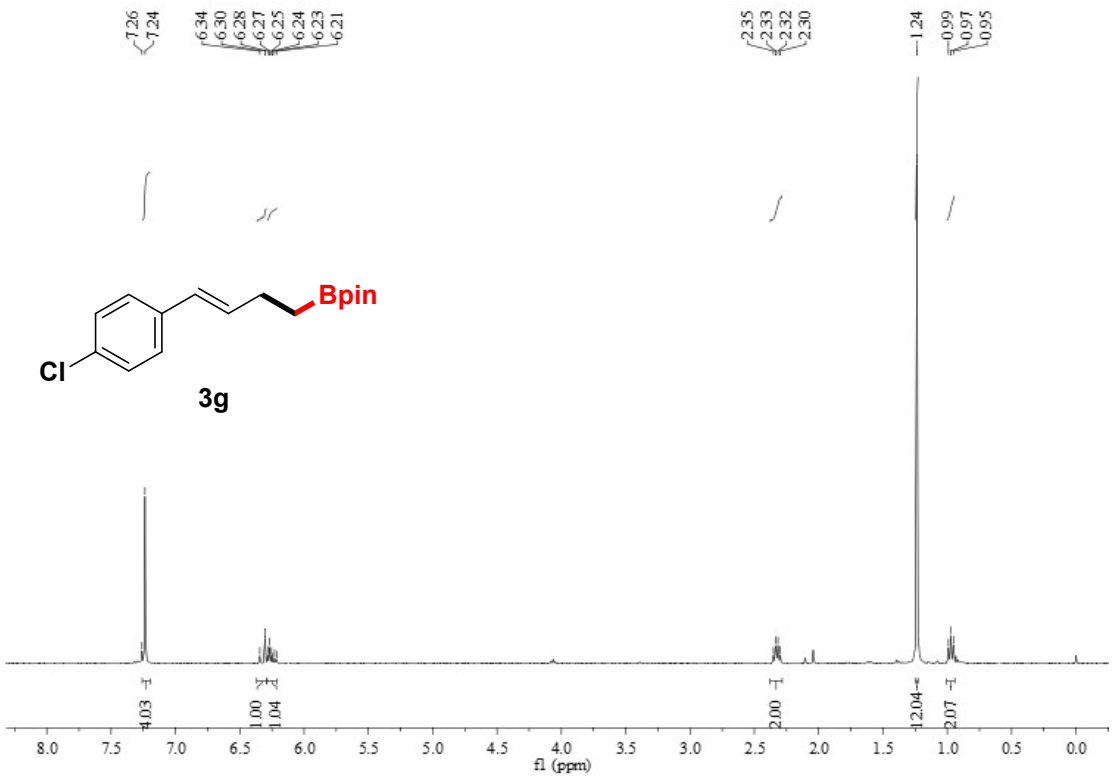
Bpin
F
3f
fl (ppm)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7.24
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6.27
6.25
6.24
6.23
6.21
2.35
2.33
2.32
2.30
1.24
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Cl
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1.04
2.00
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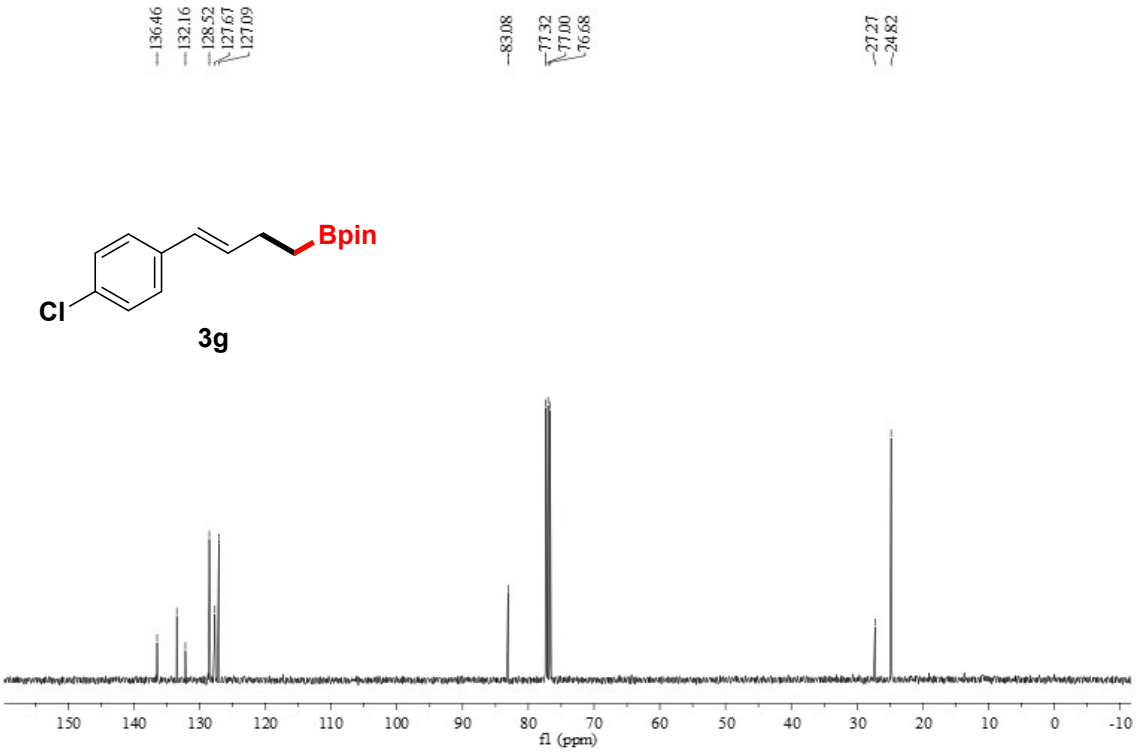
2.07
fl (ppm)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27.27
24.82
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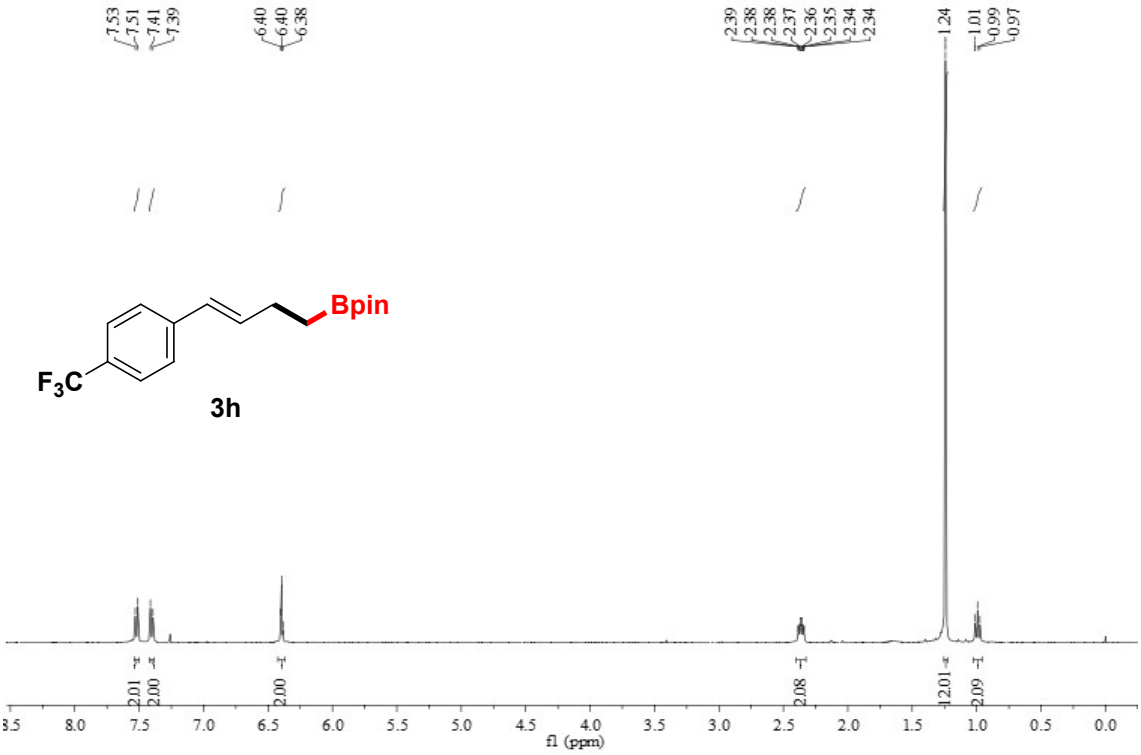
Cl
3g
fl (ppm)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2.35
2.34
2.34
1.24
1.01
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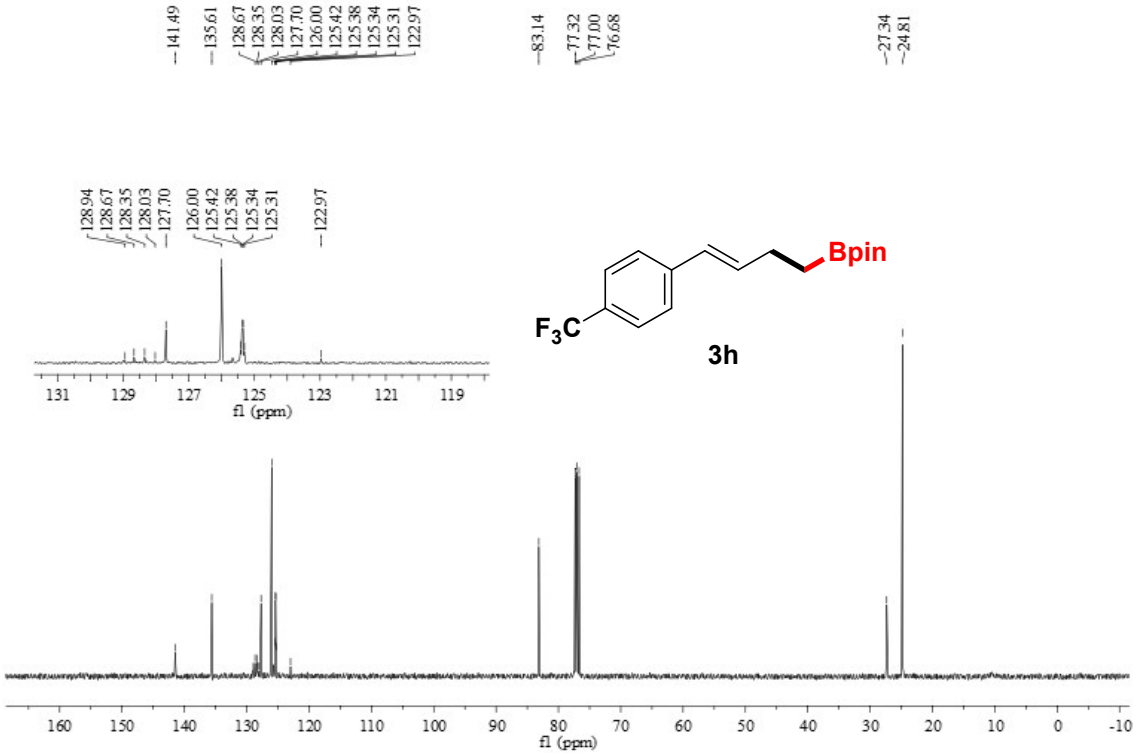
F3C
3h
2.01
2.00
2.00
2.08
12.01
2.09
fl (ppm)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77.32
77.00
76.68
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24.81
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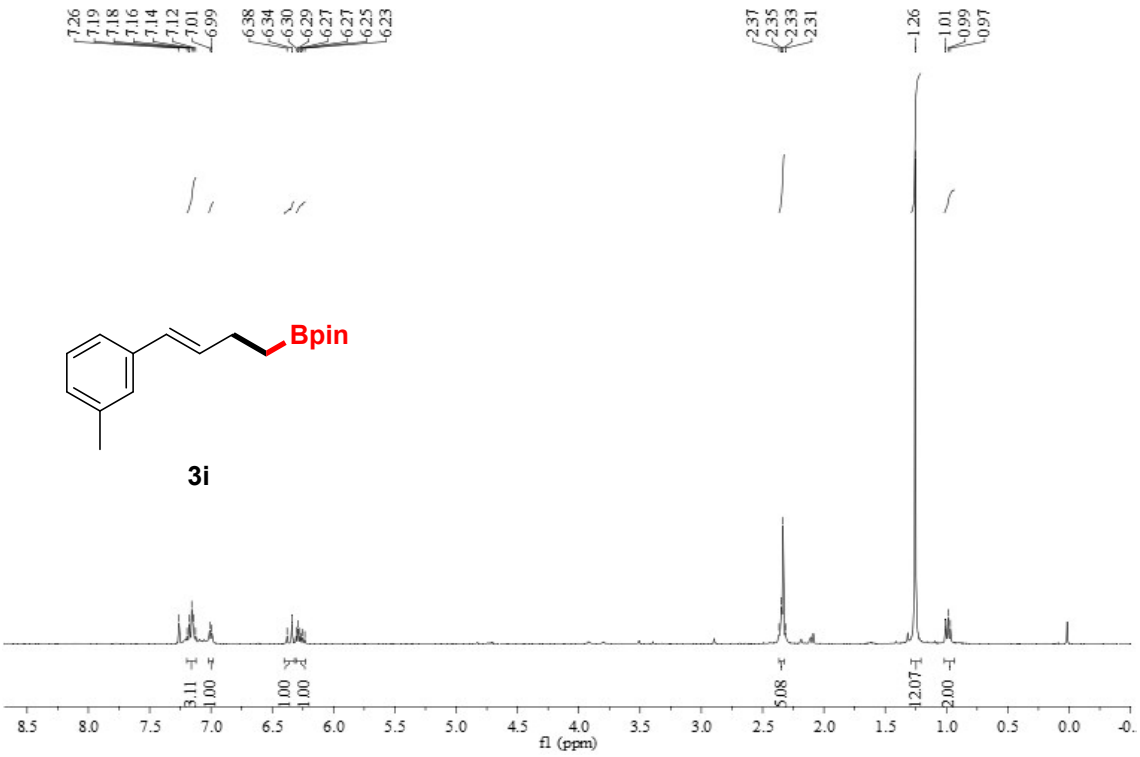
F3C
3h
fl (ppm)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6.29
6.27
6.27
6.25
6.23
2.37
2.35
2.33
2.31
1.26
1.01
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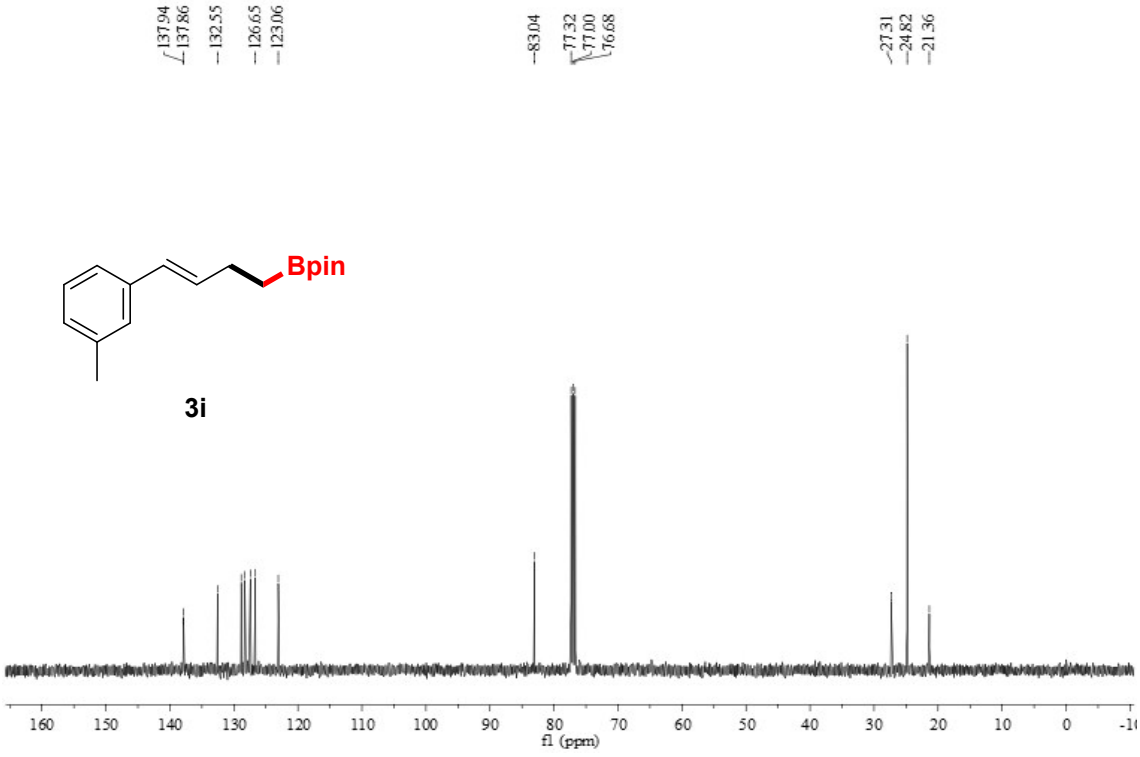
3i
3.11
1.00
1.00
1.00
5.08
12.07
2.00
fl (ppm)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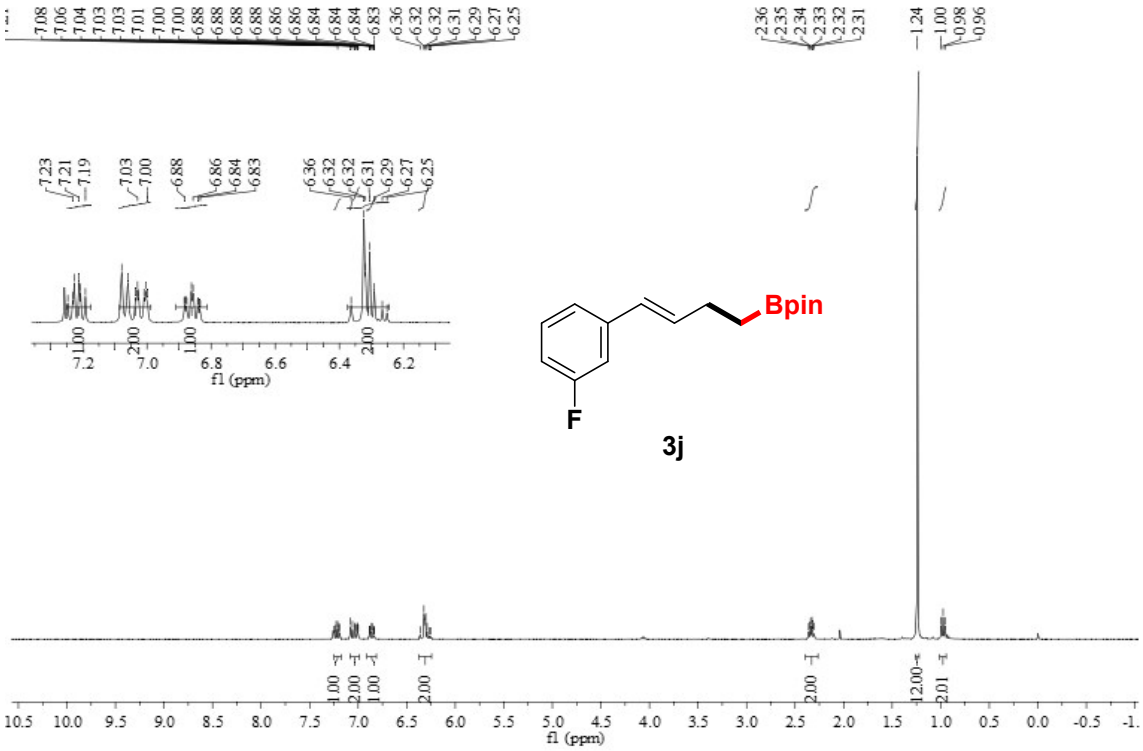
Bpin
3i
fl (ppm)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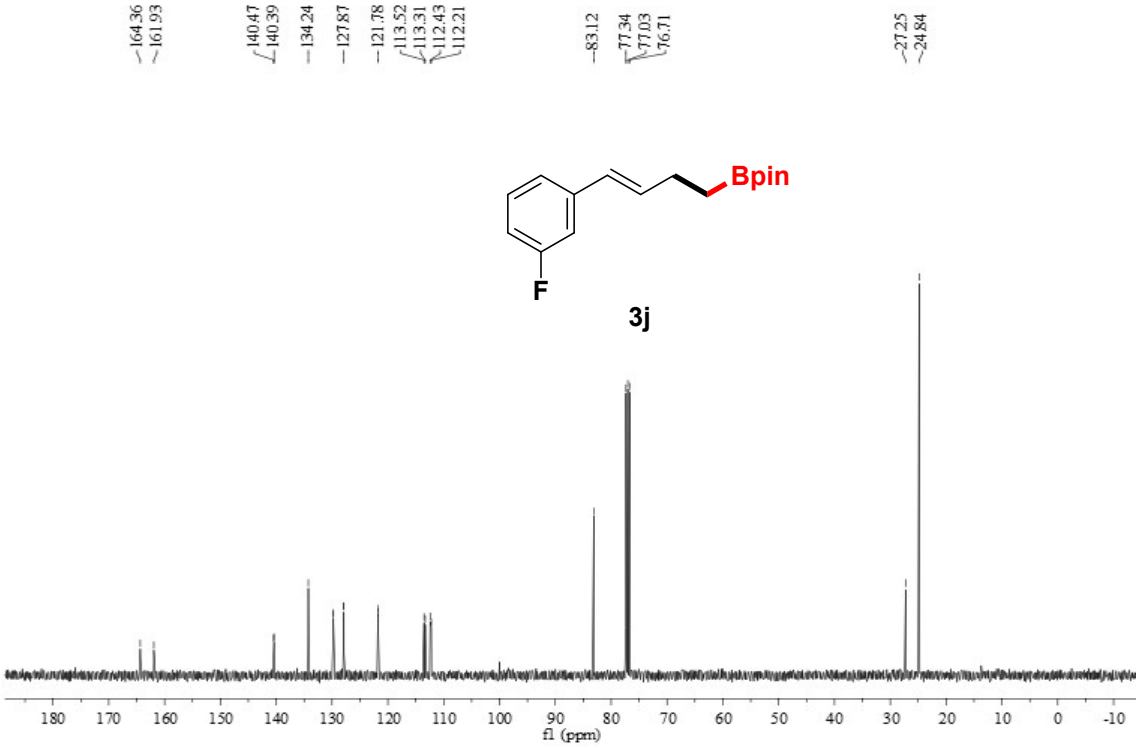
F
3j
fl (ppm)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F
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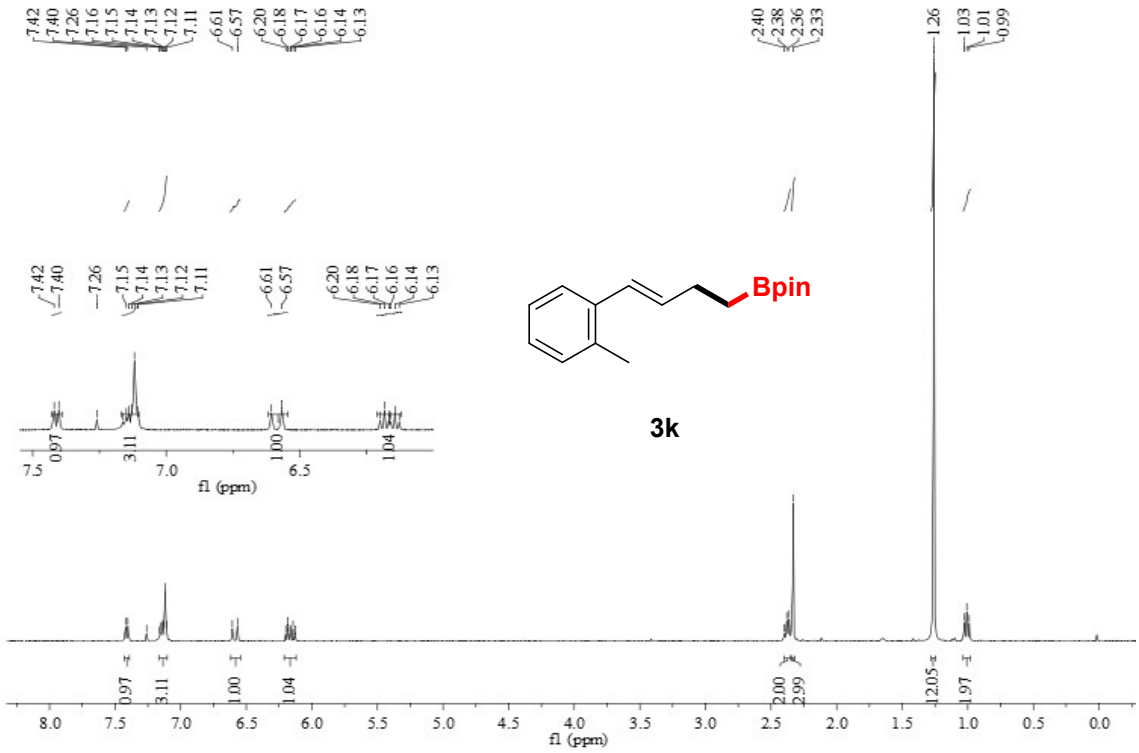
fl (ppm)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6.17
6.16
6.14
6.13
2.40
2.38
2.36
2.33
1.26
1.03
1.01
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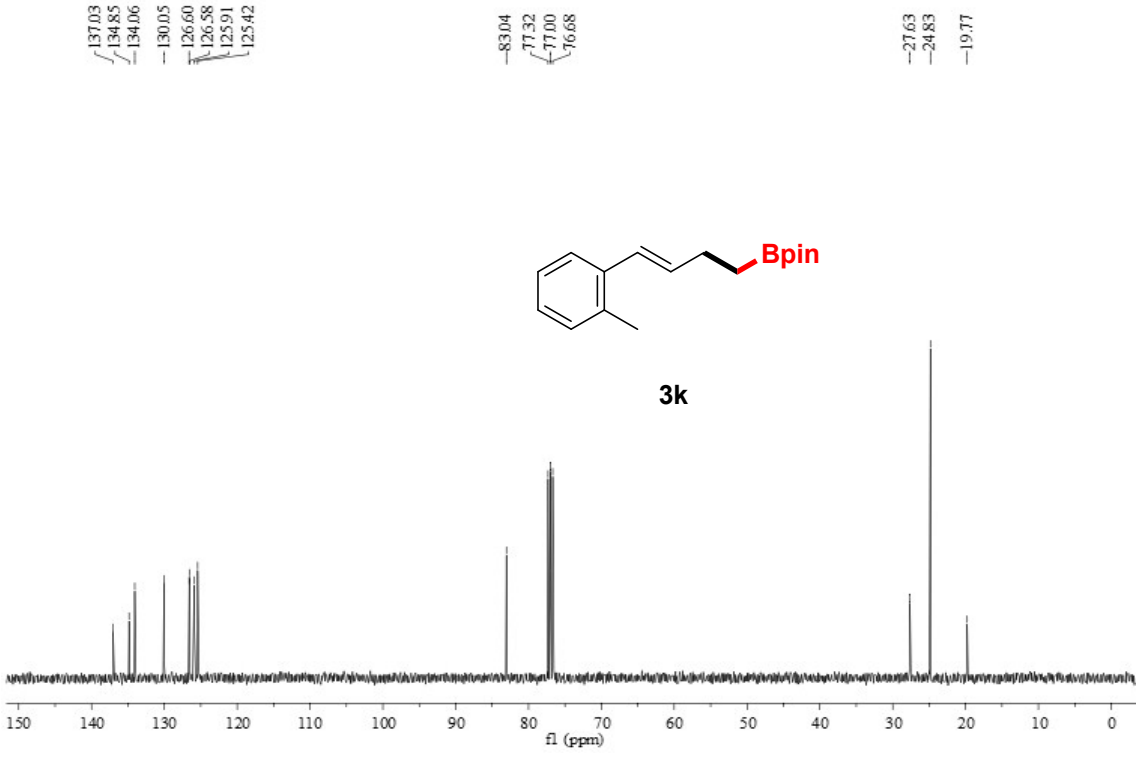
1.00
1.04
2.00
2.99
12.05
1.97
f1 (ppm)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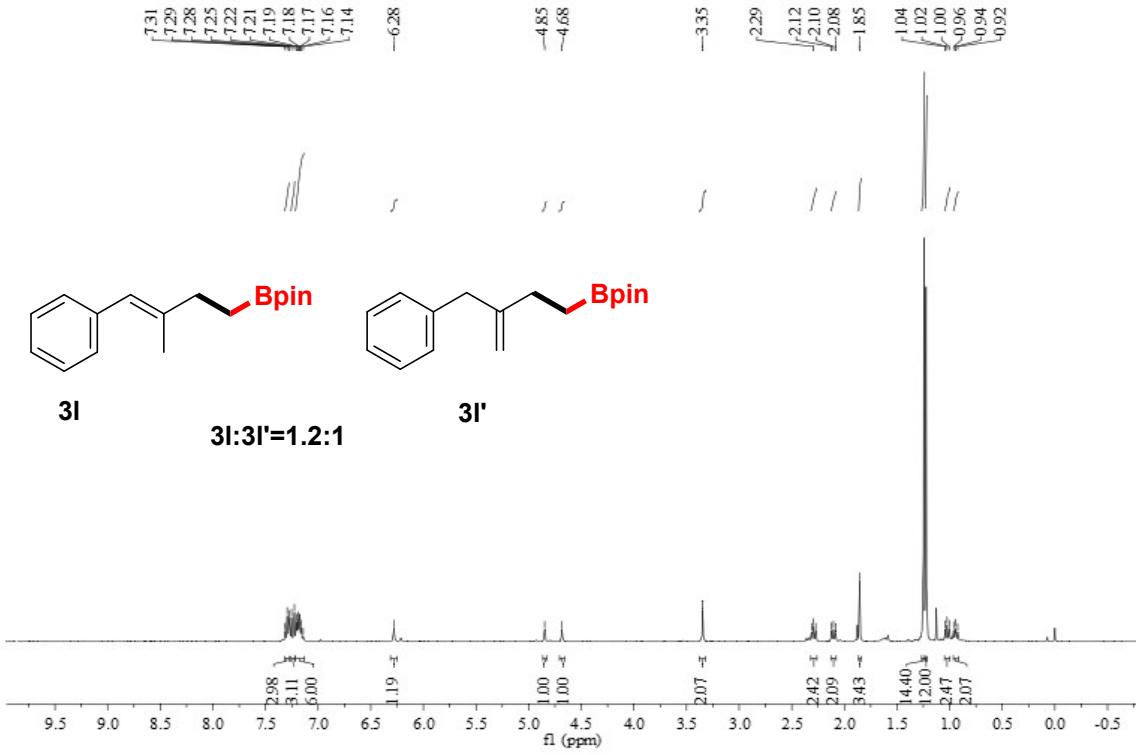
24.83
19.77
Bpin
3k
f1 (ppm)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7.16
7.14
6.28
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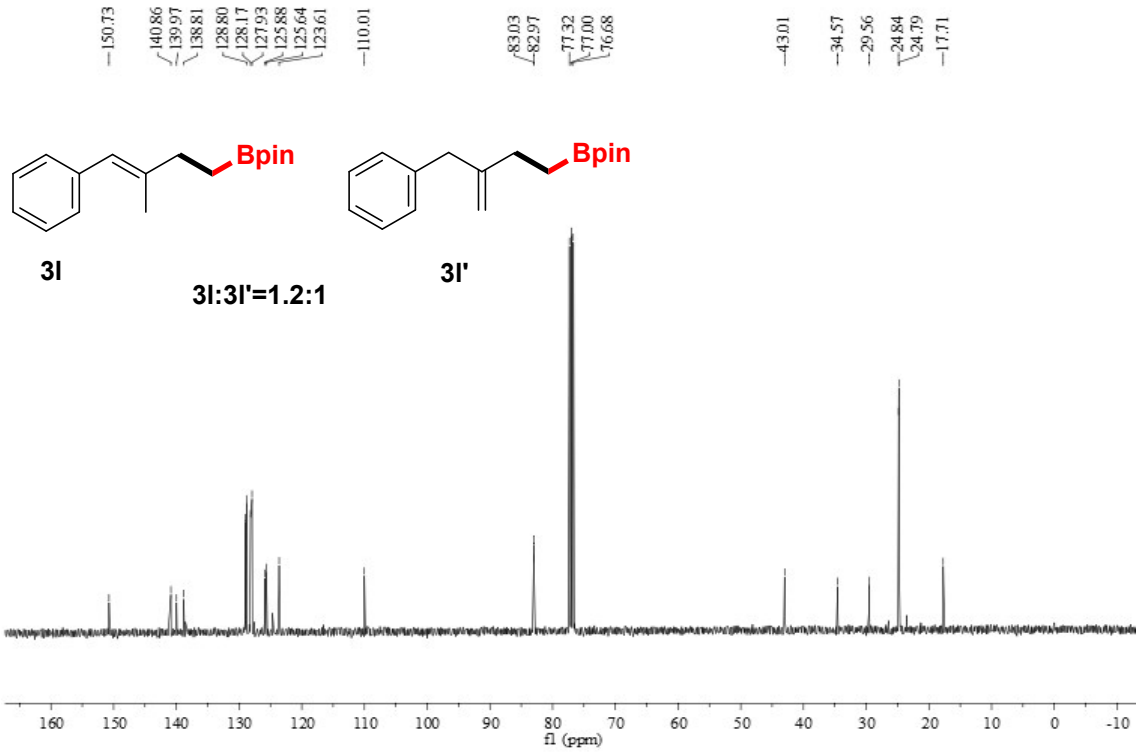
4.68
3.35
2.29
2.12
2.10
2.08
1.85
1.04
1.02
1.00
0.96
0.94
0.92
Bpin
Bpin
3l
3l:3l'=1.2:1
3l'
2.98
3.11
6.00
1.19
1.00
1.00
2.07
2.42
2.09
3.43
14.40
12.00
2.47
2.07
f1 (ppm)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127.93
125.88
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123.61
110.01
83.03
82.97
77.32
77.00
76.68
43.01
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29.56
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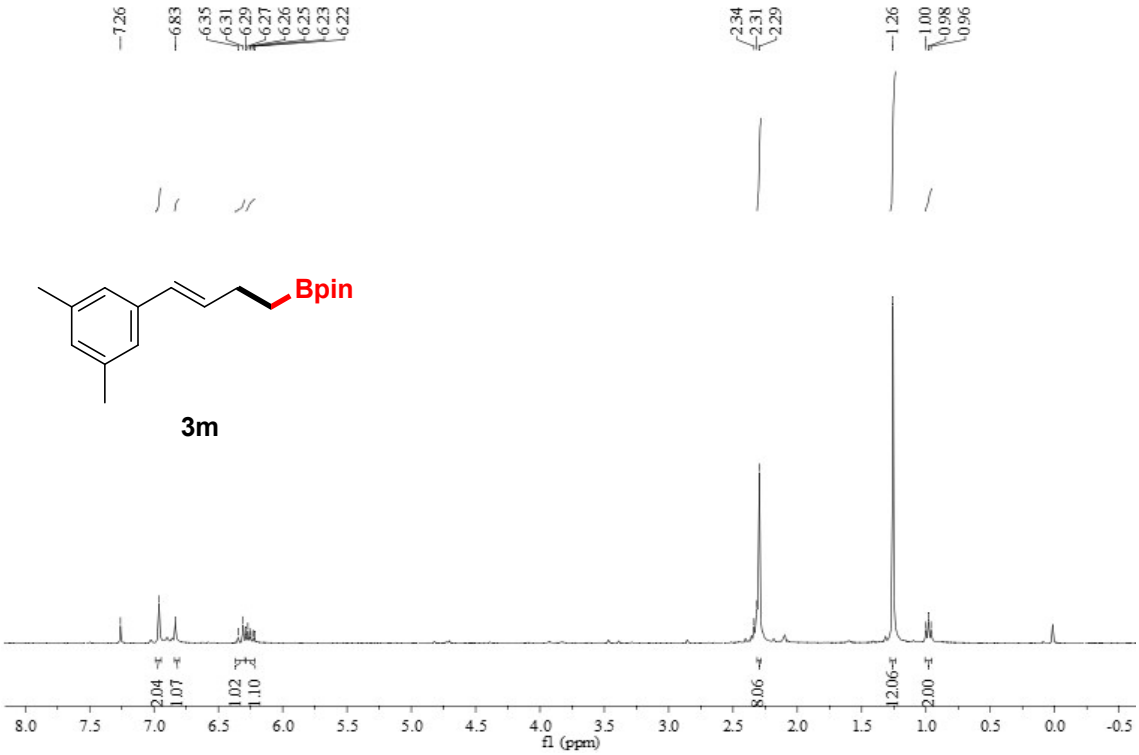
24.79
17.71
Bpin
Bpin
3l
3l:3l'=1.2:1
3l'
f1 (ppm)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6.29
6.27
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6.25
6.23
6.22
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2.31
2.29
1.26
1.00
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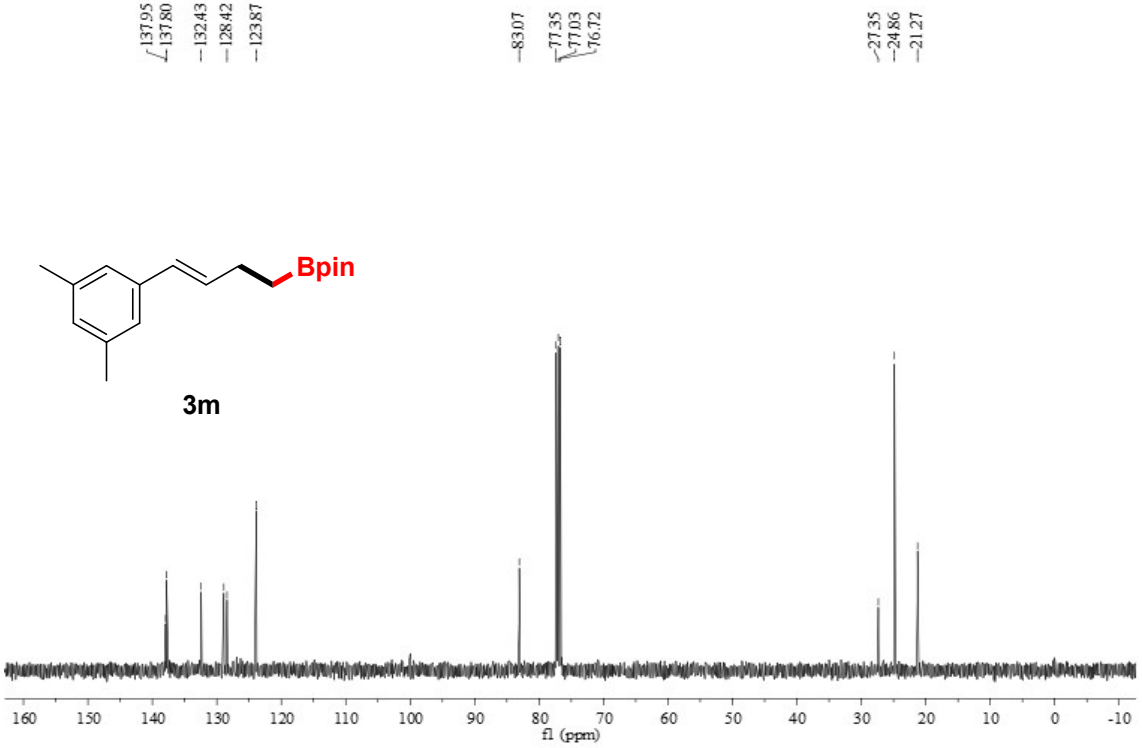
Bpin
3m
2.04
1.07
1.02
1.10
8.06
12.06
2.00
f1 (ppm)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24.86
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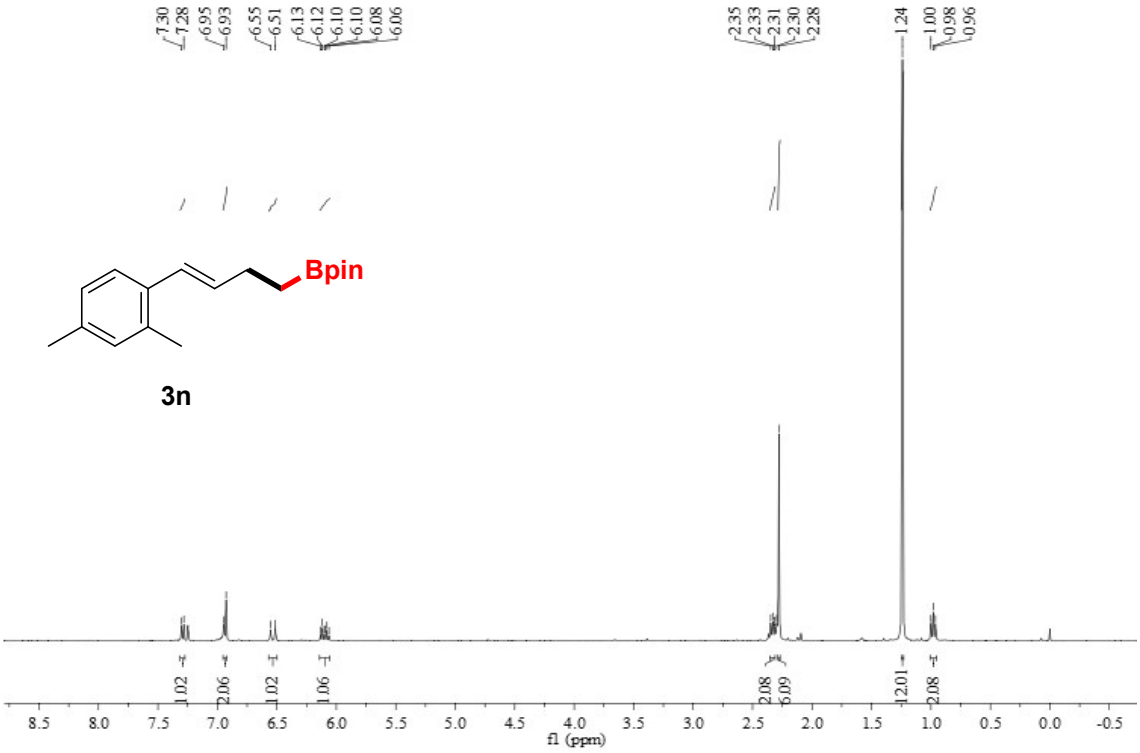
Bpin
3m
f1 (ppm)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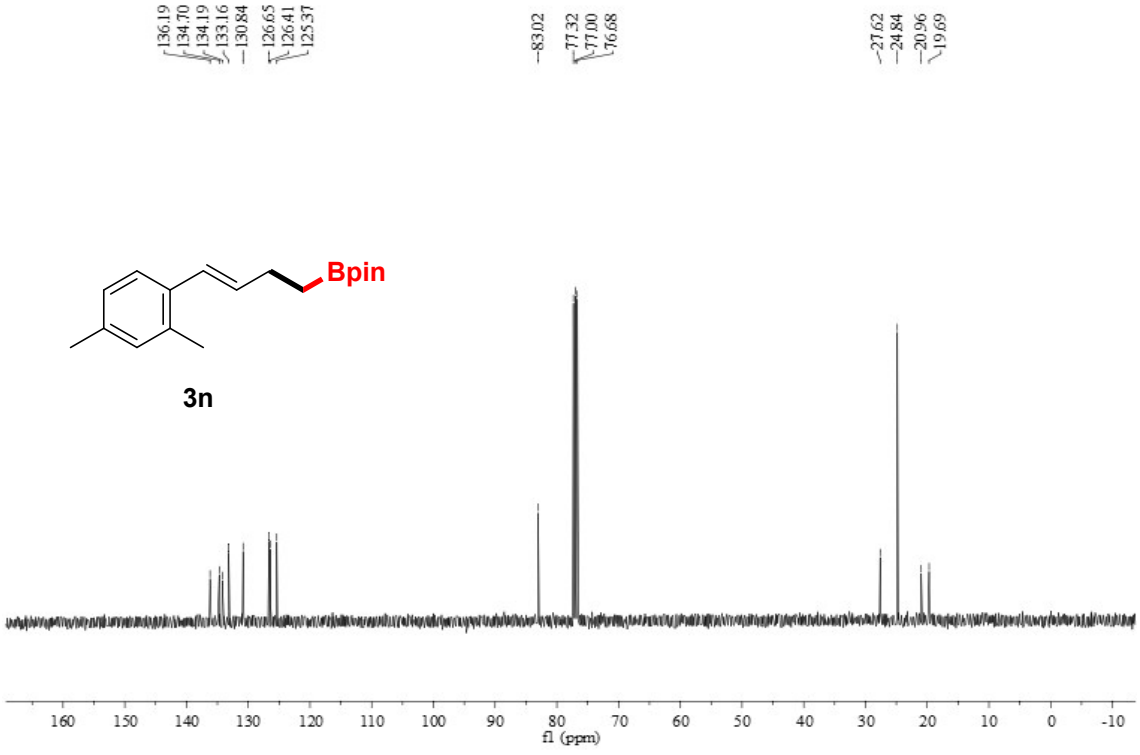
6.12
6.10
6.08
6.06
2.35
2.33
2.31
2.30
2.28
1.24
1.00
0.98
0.96
Bpin
3n
1.02
2.06
1.02
1.06
2.08
6.09
12.01
2.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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125.37
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77.32
77.00
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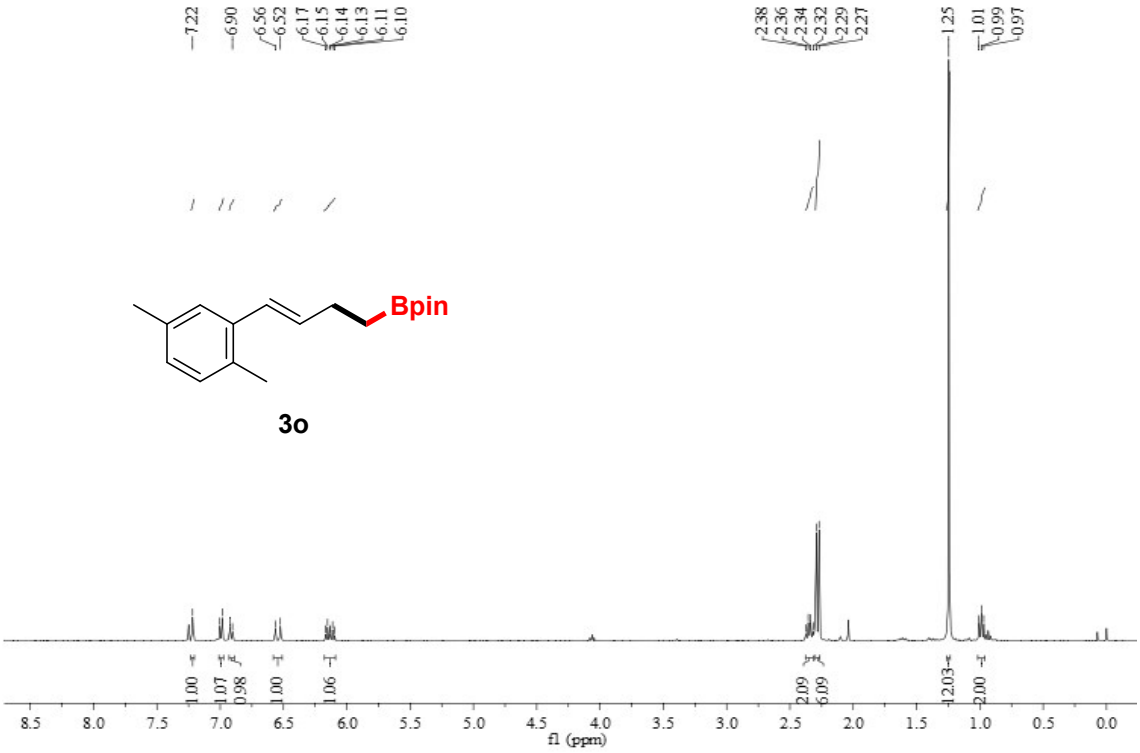
20.96
19.69
Bpin
3n
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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2.34
2.32
2.29
2.27
1.25
1.01
0.99
0.97
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1.07
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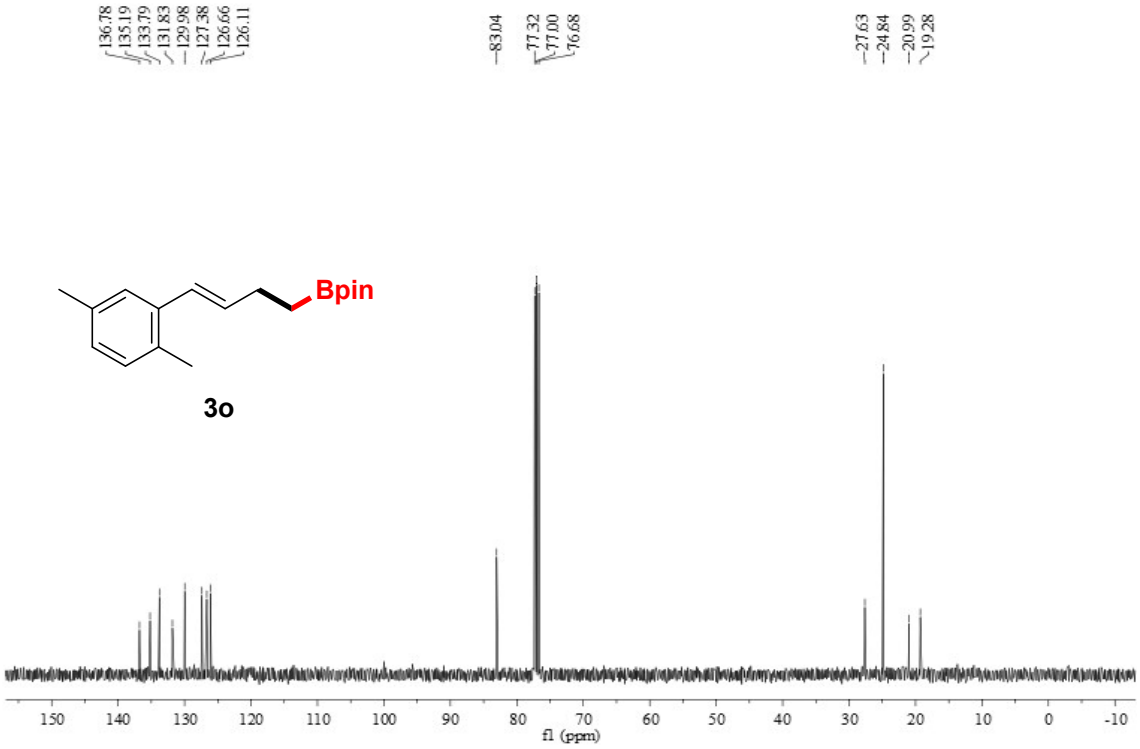
1.00
1.06
2.09
6.09
12.03
2.00
f1 (ppm)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20.99
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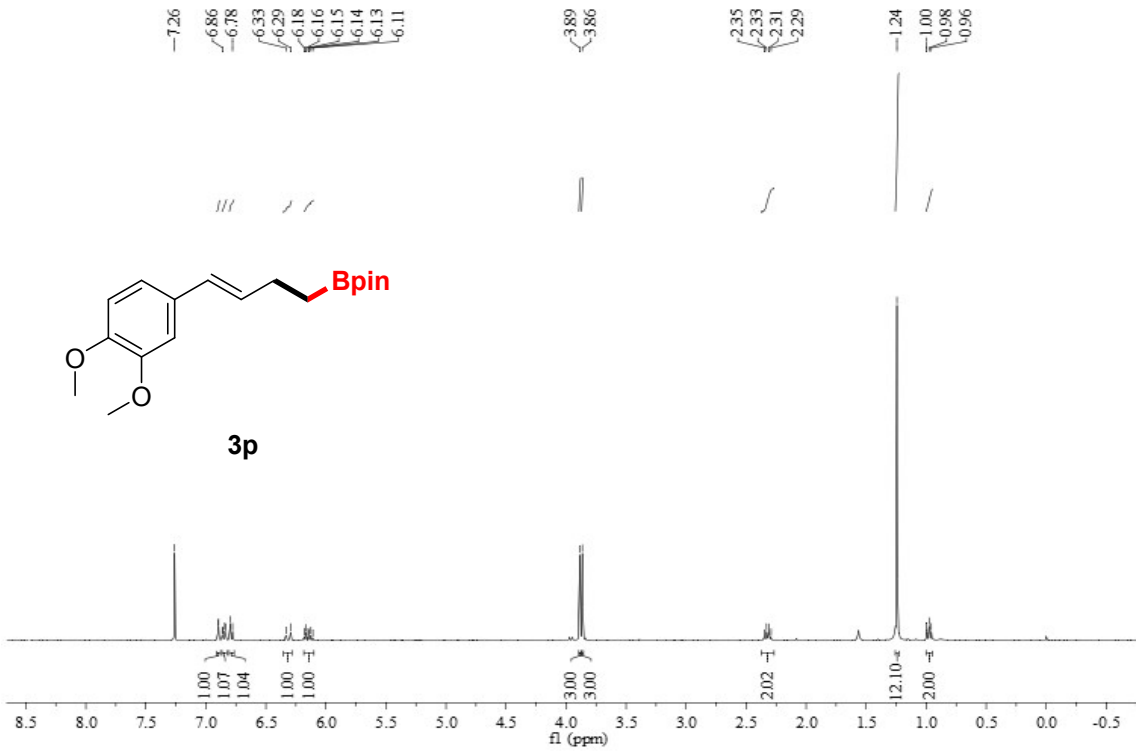
Bpin
3o
f1 (ppm)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6.13
6.11
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3.86
2.35
2.33
2.31
2.29
1.24
1.00
0.98
0.96
Bpin
O
O
3p
1.00
1.07
1.04
1.00
1.00
3.00
3.00
2.02
12.10
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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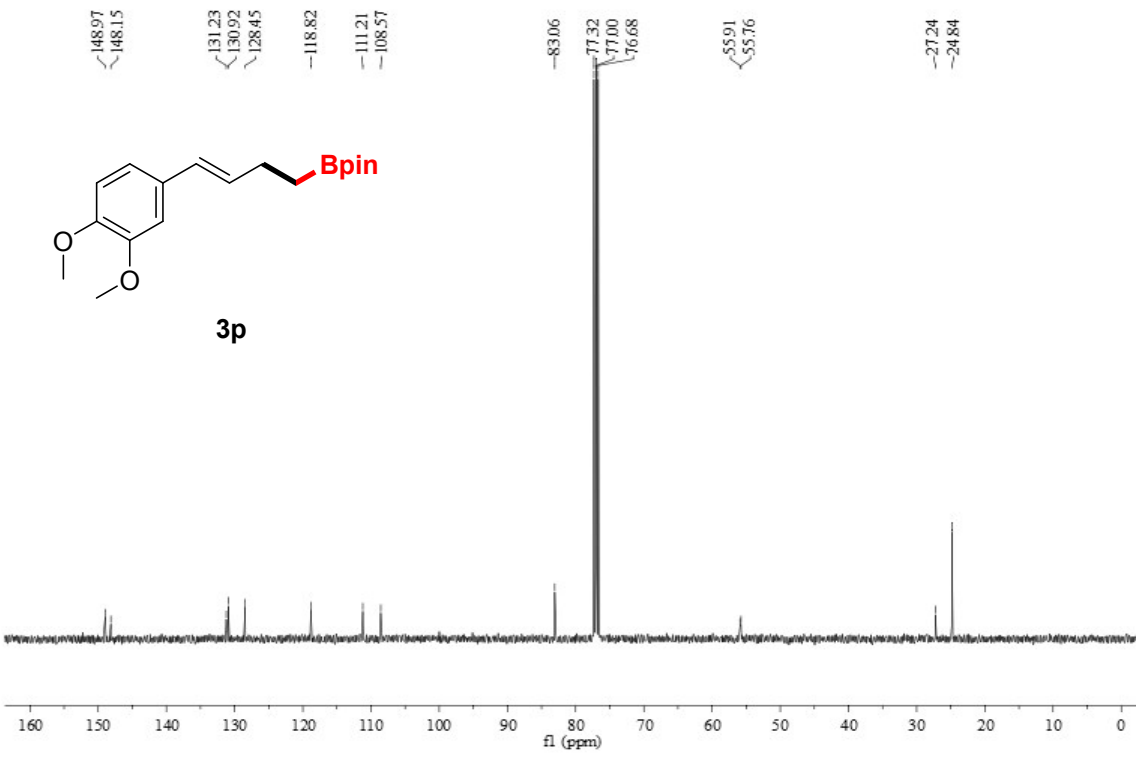
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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77.32
77.00
76.68
55.91
55.76
27.24
24.84
Bpin
O
O
3p
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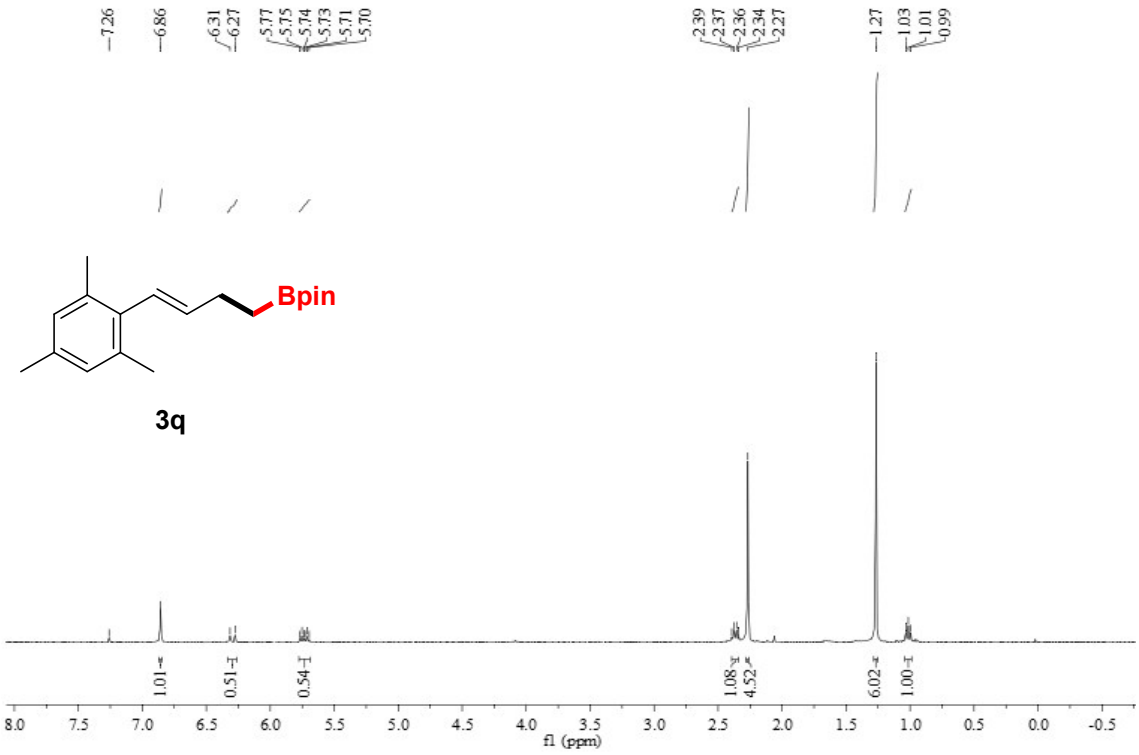
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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2.34
2.27
1.27
1.03
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4.52
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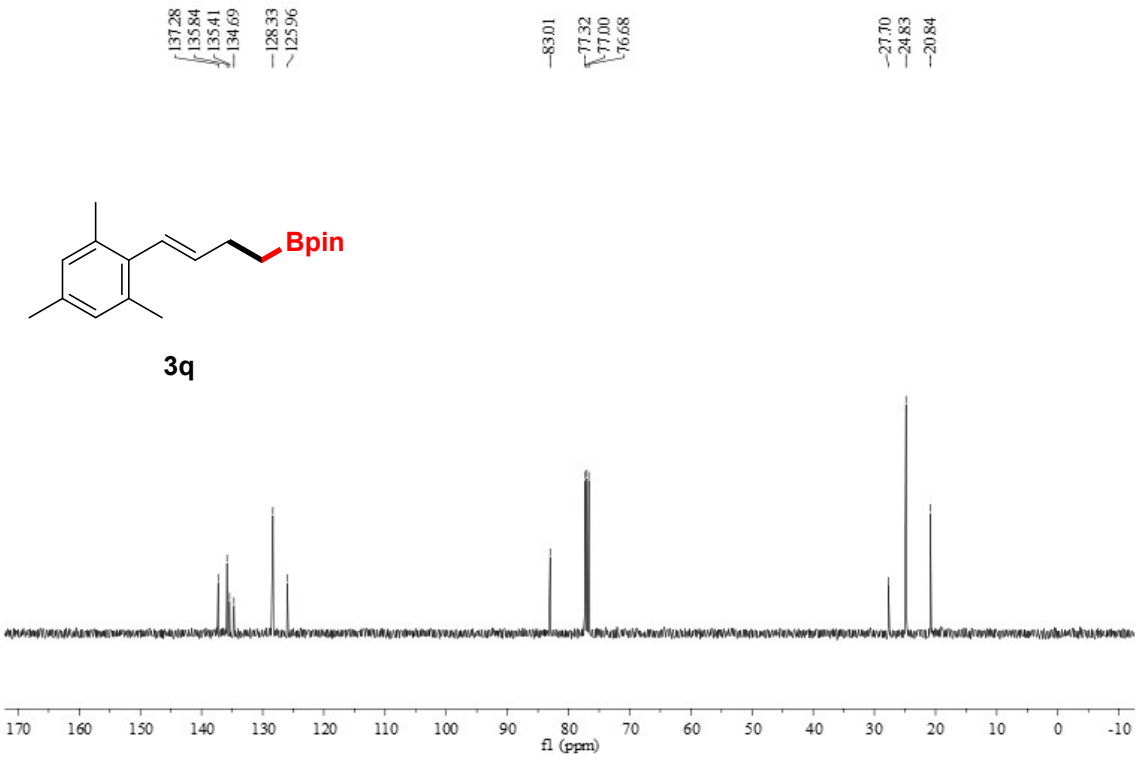
1.00
f1 (ppm)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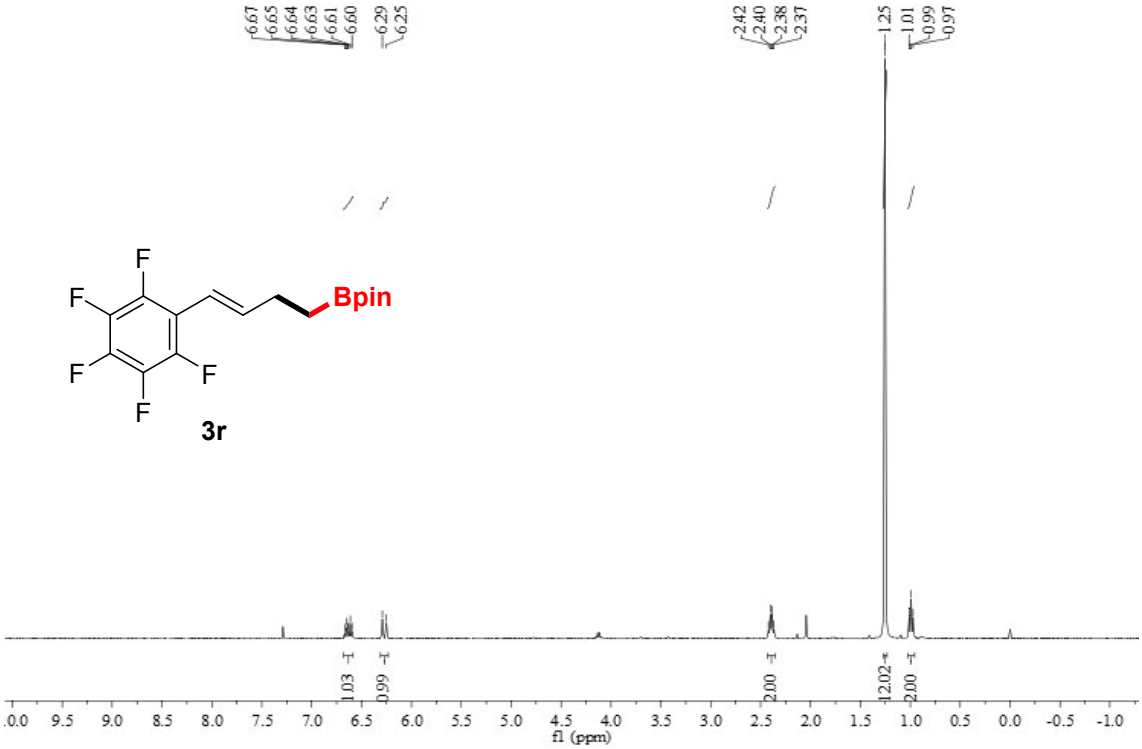
24.83
20.84
Bpin
3q
f1 (ppm)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2.38
2.37
1.25
1.01
0.99
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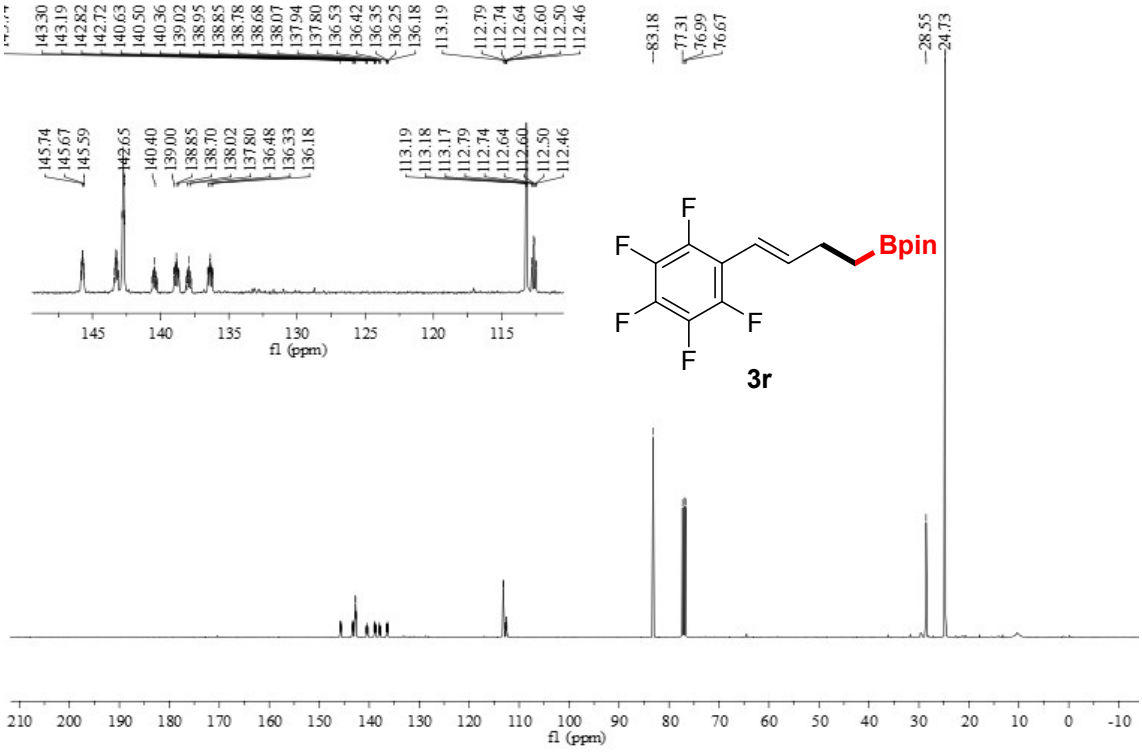
F
F
F
F
F
Bpin
3r
1.03
0.99
2.00
12.02
2.00
fl (ppm)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136.35
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112.60
112.50
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76.99
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138.02
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113.19
113.18
113.17
112.79
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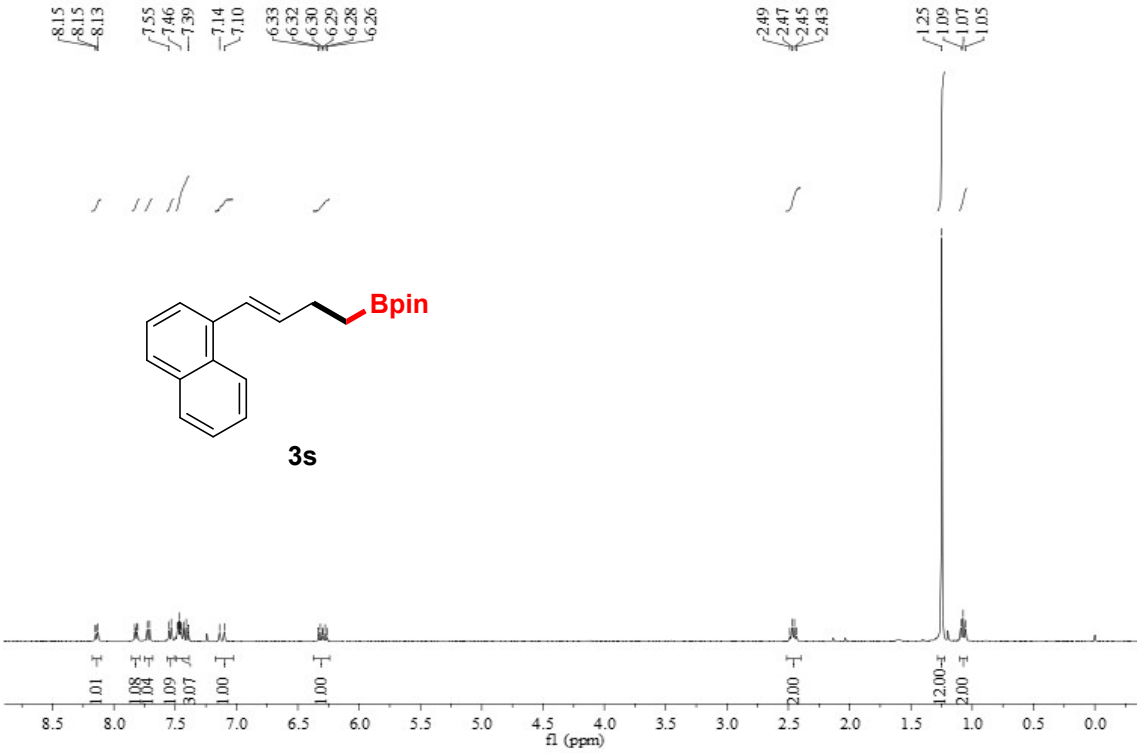
112.50
112.46
fl (ppm)
F
F
F
F
F
Bpin
3r
fl (ppm)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6.26
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2.47
2.45
2.43
1.25
1.09
1.07
1.05
Bpin
3s
1.01
1.08
1.04
1.09
3.07
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1.00
2.00
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8.0
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6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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1.0
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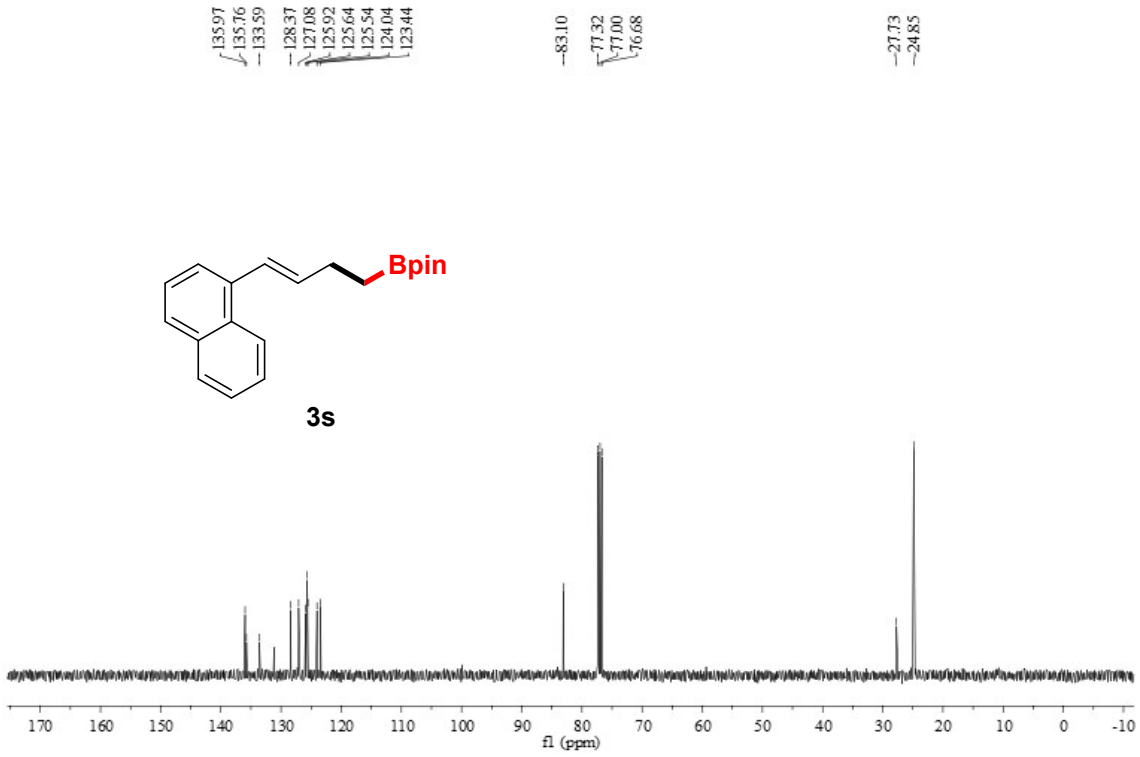
0.0
f1 (ppm)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76.68
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24.85
Bpin
3s
170
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120
110
100
90
80
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60
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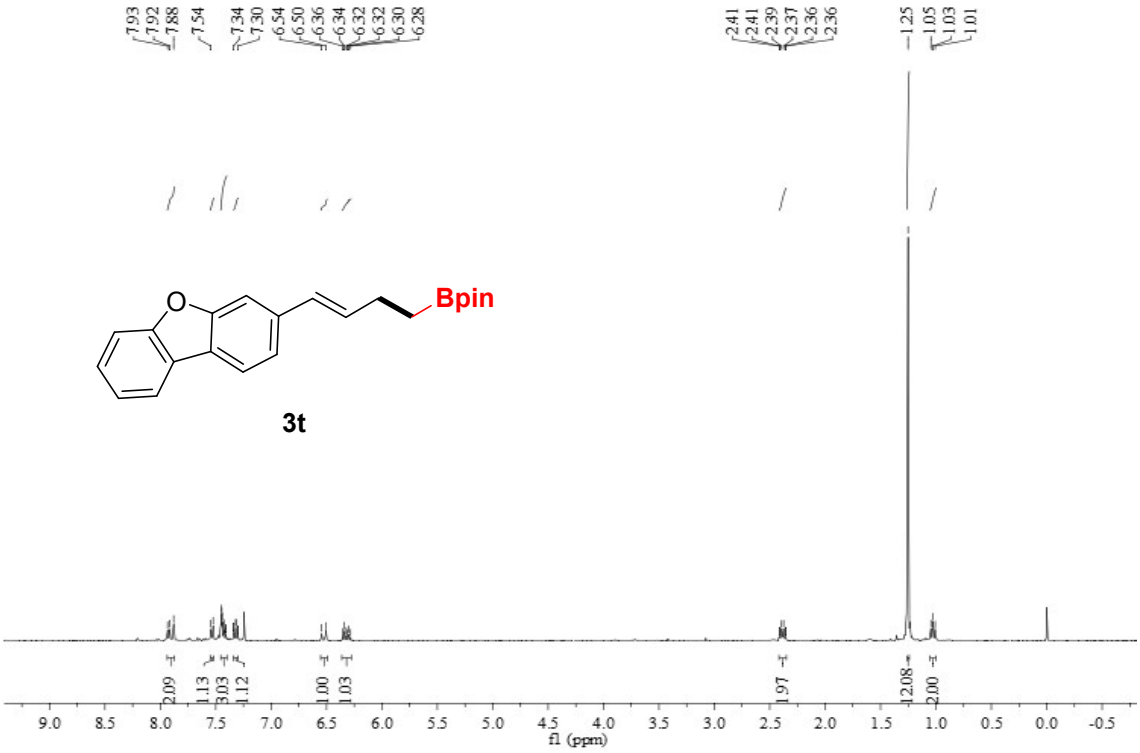
40
30
20
10
0
-10
f1 (ppm)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2.41
2.39
2.37
2.36
2.36
1.25
1.05
1.03
1.01
Bpin
O
2.09
1.13
3.03
1.12
1.00
1.03
1.97
12.08
2.00
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
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1.5
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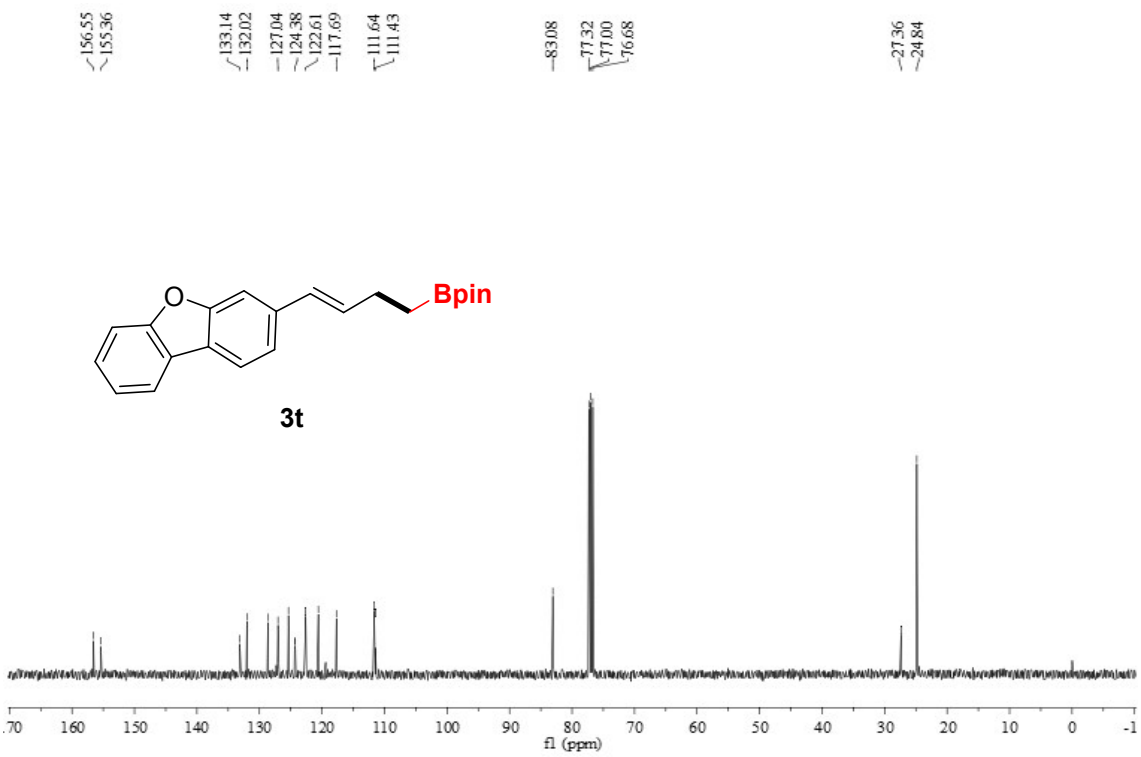
-0.5
f1 (ppm)

3t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111.43
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77.32
77.00
76.68
27.36
24.84
Bpin
O
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100
90
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60
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40
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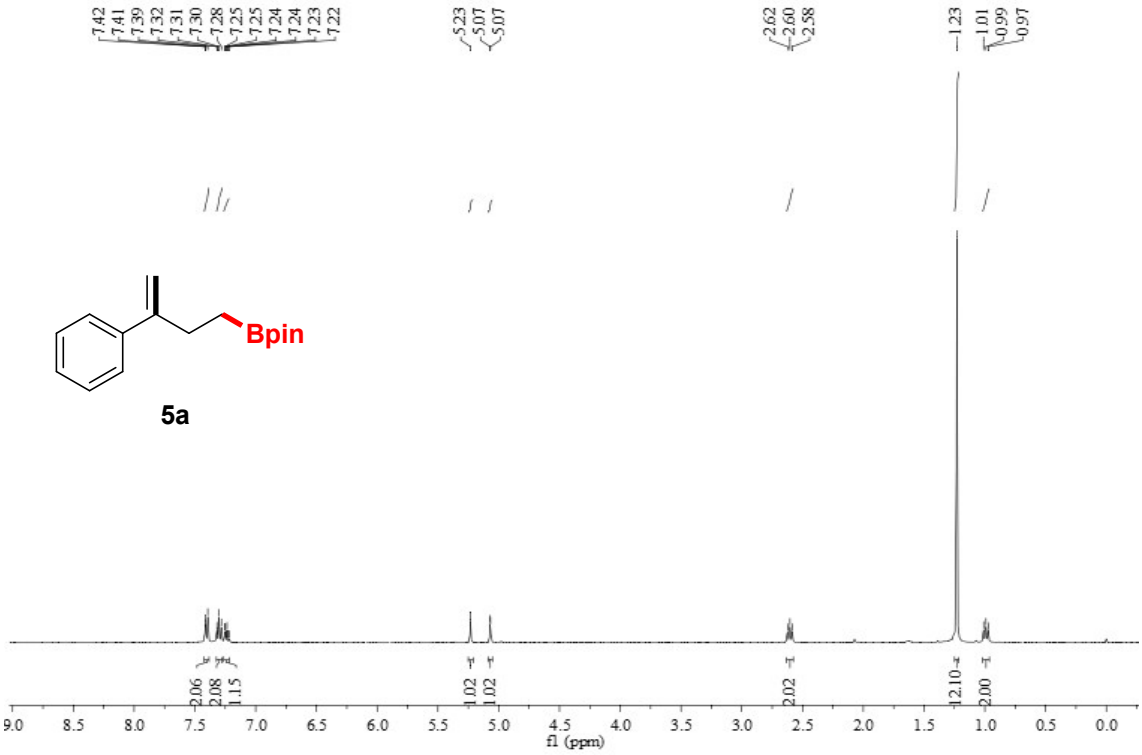
20
10
0
-1
f1 (ppm)

3t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7.22
5.23
5.07
5.07
2.62
2.60
2.58
1.23
1.01
0.99
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2.08
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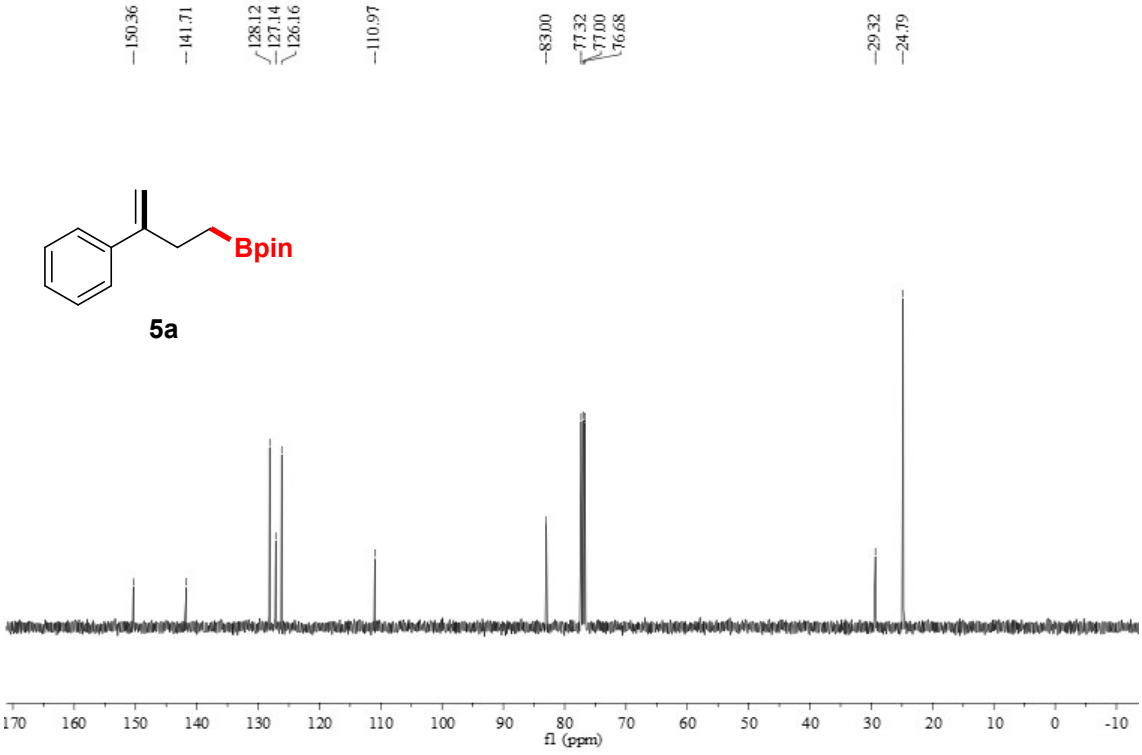
1.02
1.02
2.02
12.10
2.00
f1 (ppm)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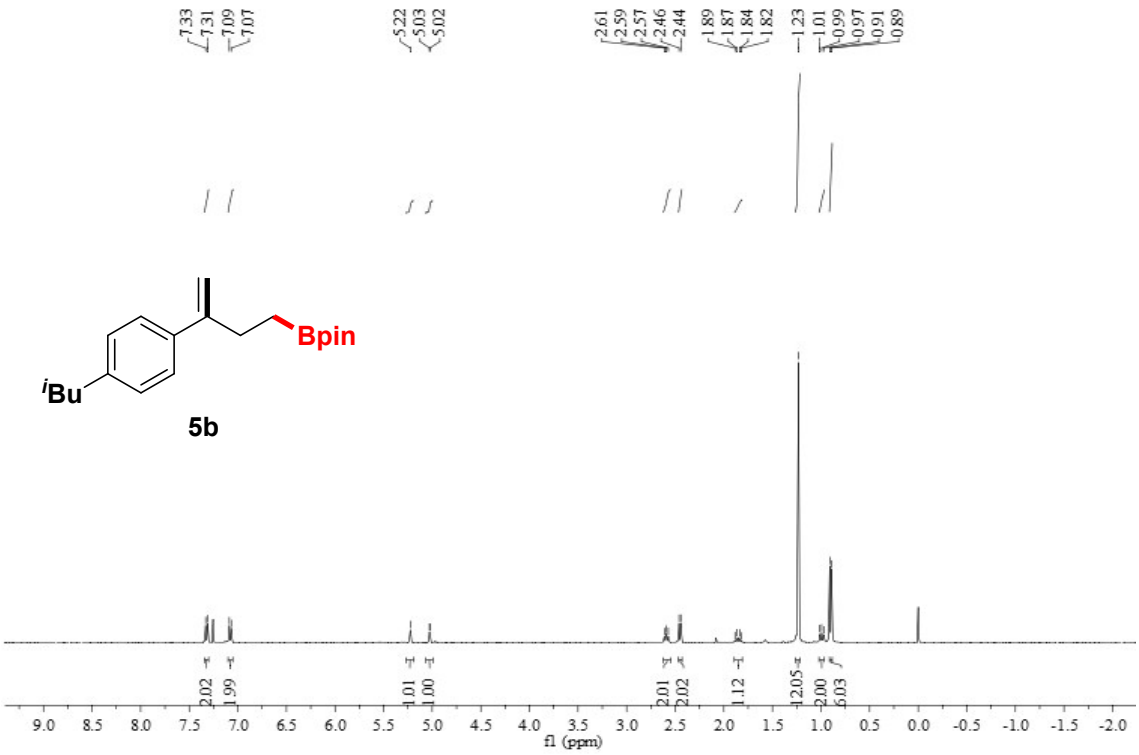
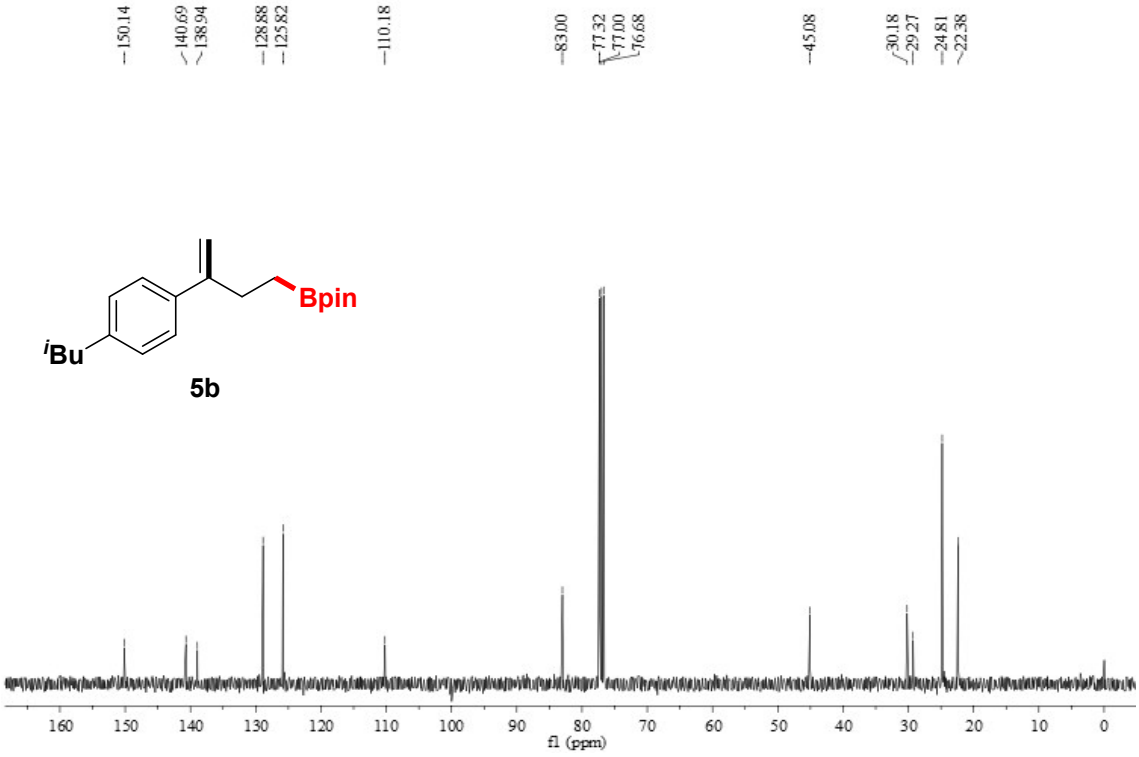
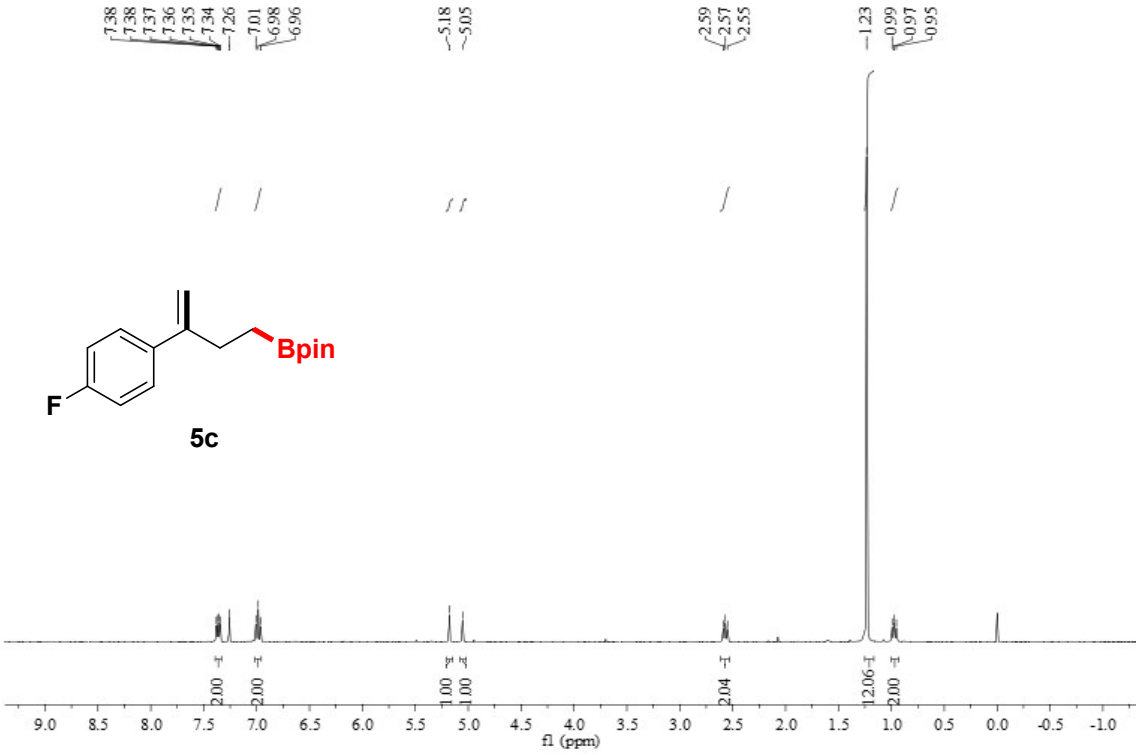
77.00
76.68
29.32
24.79
Bpin
5a
f1 (ppm)


7.33
7.31
7.09
7.07
5.22
5.03
5.02
2.61
2.59
2.57
2.46
2.44
1.89
1.87
1.84
1.82
1.23
1.01
0.99
0.97
0.91
0.89
Bpin
iBu
5b
2.02
1.99
1.01
1.00
2.01
2.02
1.12
12.05
2.00
6.03
fl (ppm)


150.14
140.69
138.94
128.88
125.82
110.18
83.00
77.32
77.00
76.68
45.08
30.18
29.27
24.81
22.38
Bpin
iBu
5b
fl (ppm)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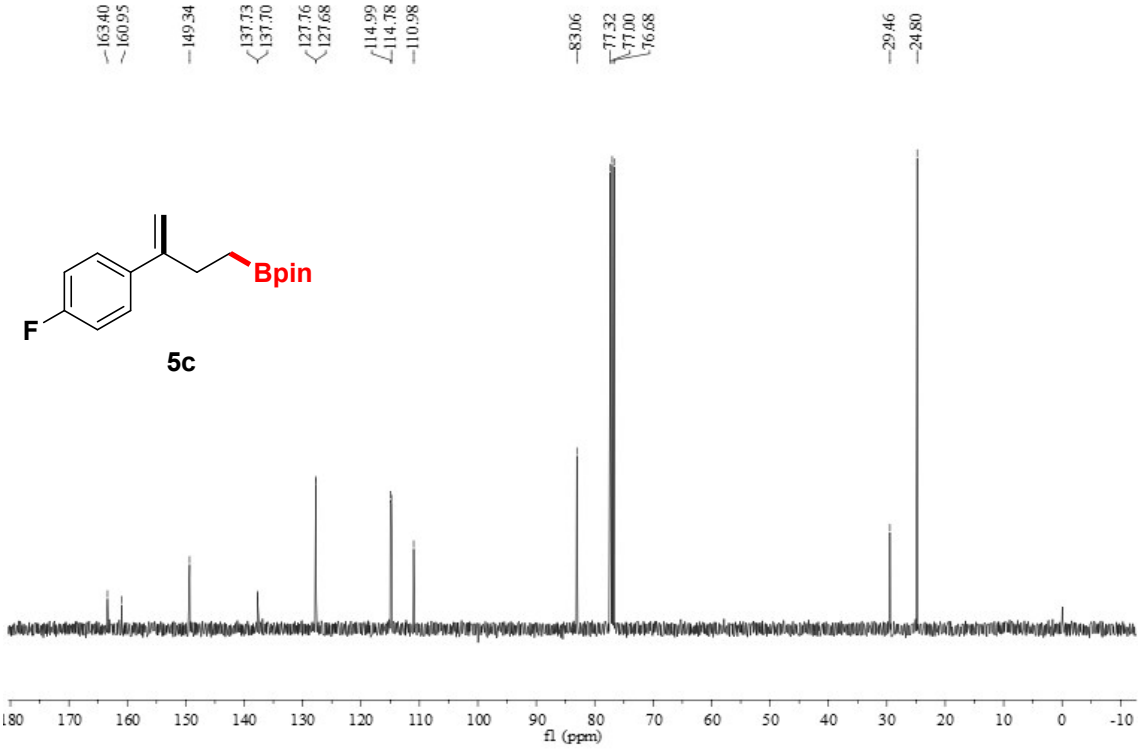
7.38
7.37
7.36
7.35
7.34
7.26
7.01
6.98
6.96
5.18
5.05
2.59
2.57
2.55
1.23
0.99
0.97
0.95
Bpin
F
5c
2.00
2.00
1.00
1.00
2.04
12.06
2.00
fl (ppm)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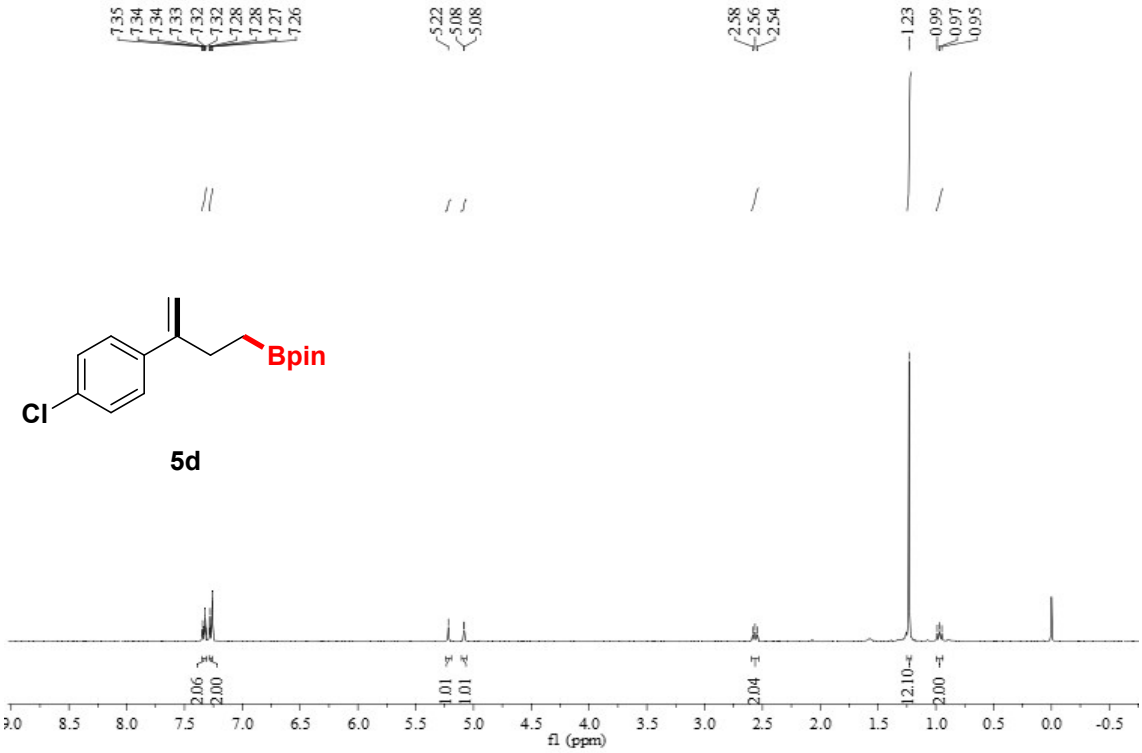
160.95
149.34
137.73
137.70
127.76
127.68
114.99
114.78
110.98
83.06
77.32
77.00
76.68
29.46
24.80
Bpin
F
5c
fl (ppm)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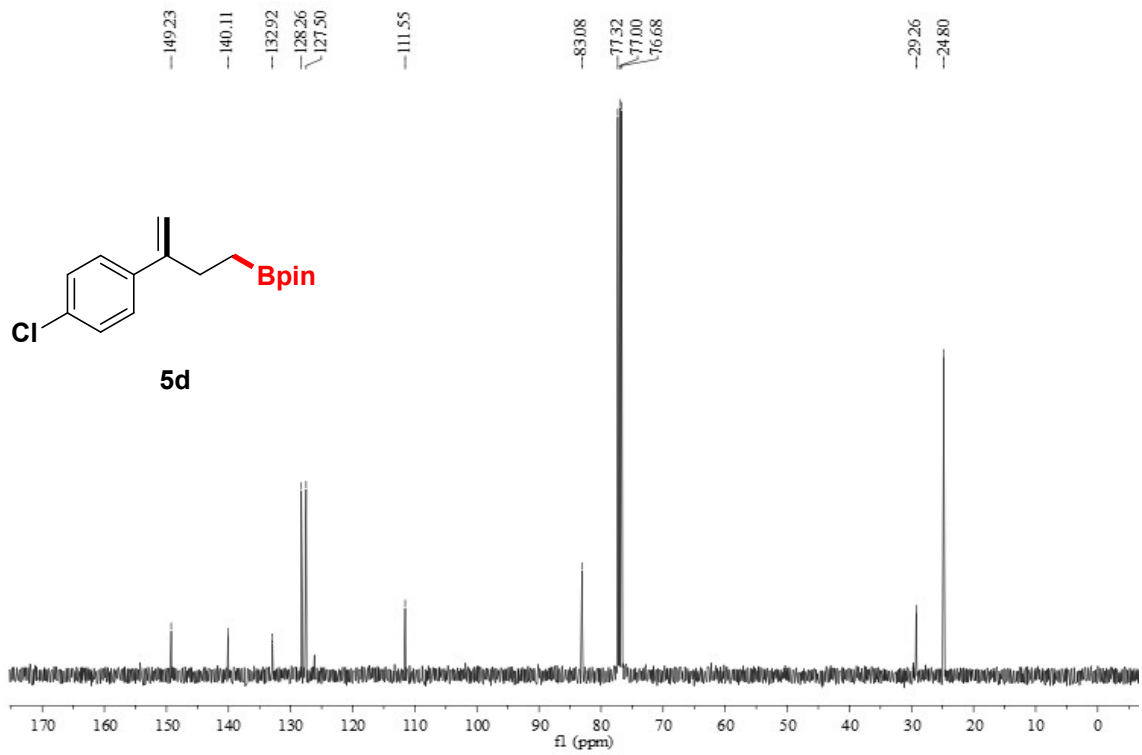
7.34
7.34
7.33
7.32
7.32
7.28
7.28
7.27
7.26
5.22
5.08
5.08
2.58
2.56
2.54
1.23
0.99
0.97
0.95
Bpin
Cl
5d
2.06
2.00
1.01
1.01
2.04
12.10
2.00
fl (ppm)


149.23
140.11
132.92
128.26
127.50
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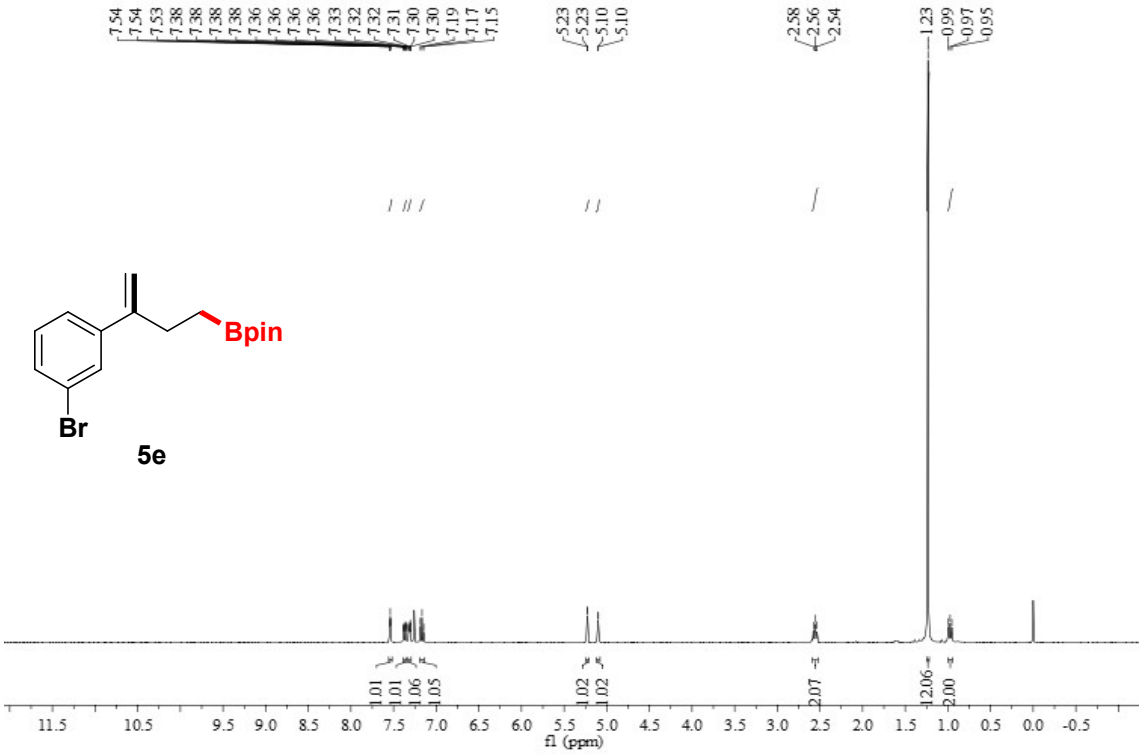
83.08
77.32
77.00
76.68
29.26
24.80
Bpin
Cl
5d
fl (ppm)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7.36
7.33
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7.32
7.31
7.30
7.30
7.19
7.17
7.15
5.23
5.23
5.10
5.10
2.58
2.56
2.54
1.23
0.99
0.97
0.95
Bpin
Br
5e
1.01
1.01
1.06
1.05
1.02
1.02
2.07
12.06
2.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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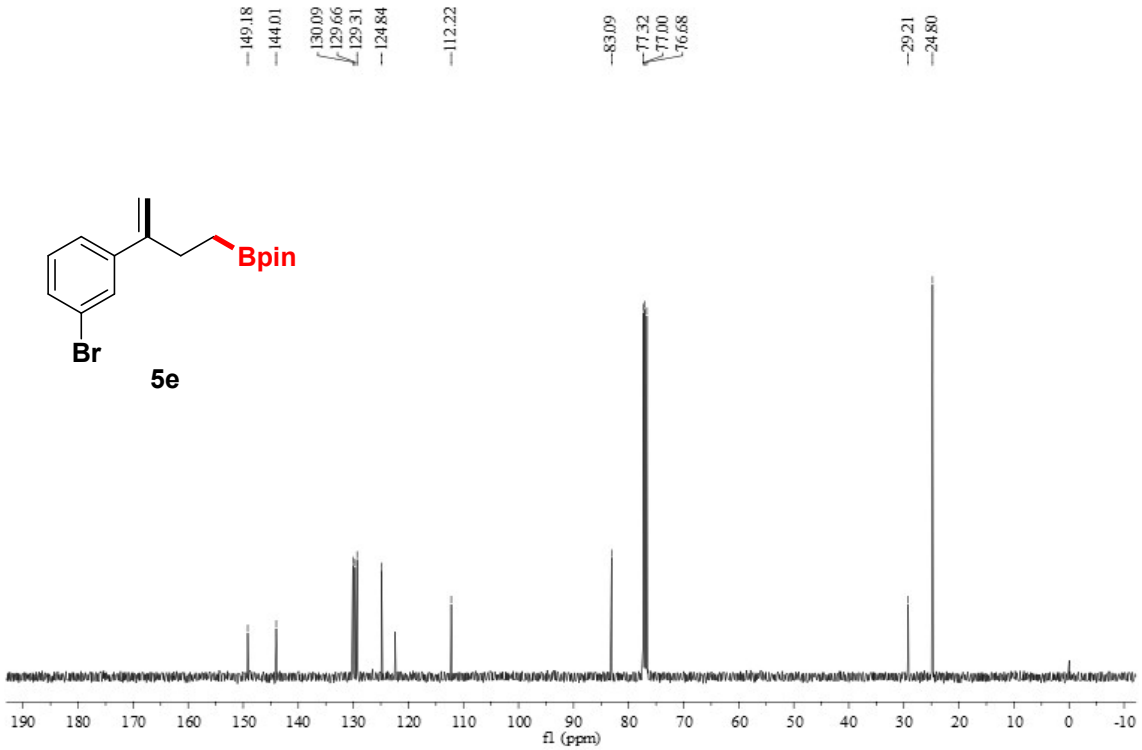
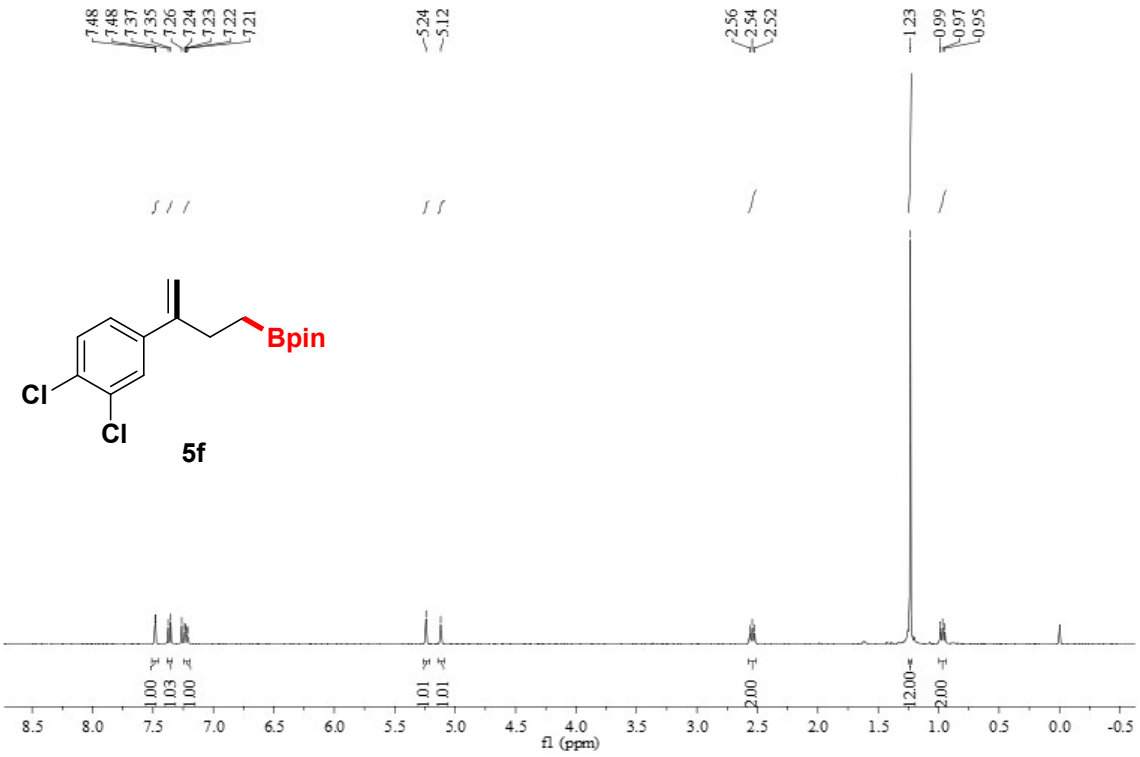
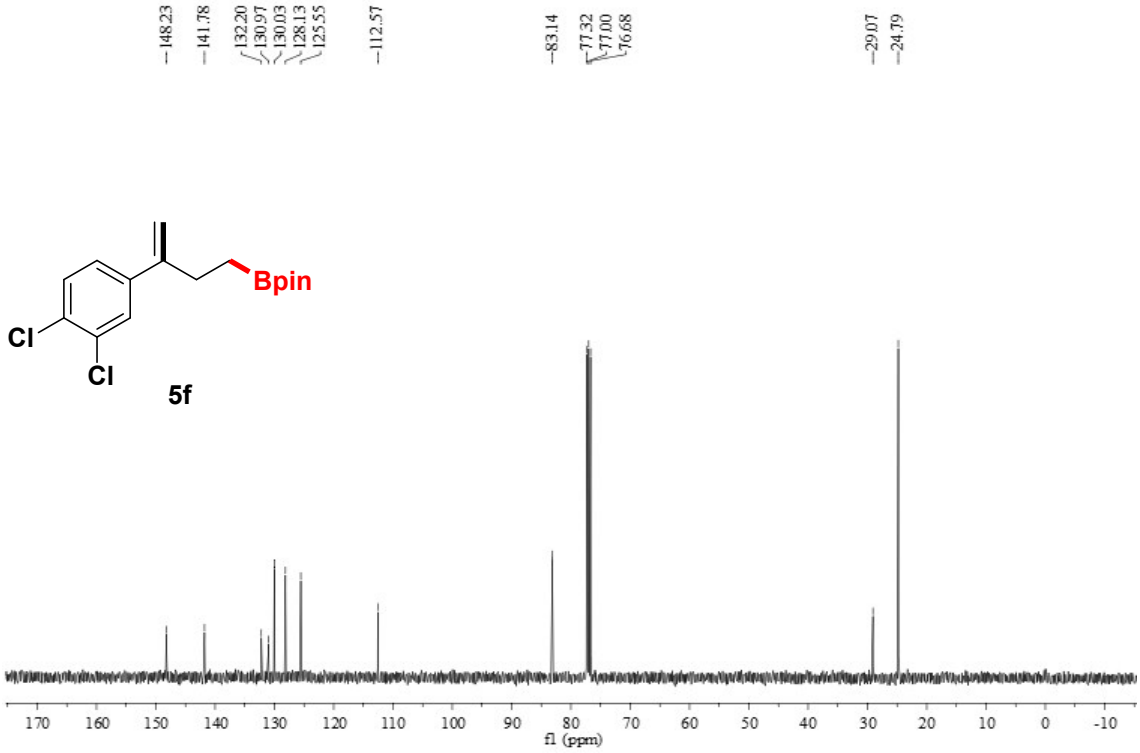
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


149.18
144.01
130.09
129.66
129.31
124.84
112.22
83.09
77.32
77.00
76.68
29.21
24.80
Bpin
Br
5e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.48
7.48
7.37
7.35
7.26
7.24
7.23
7.22
7.21
5.24
5.12
2.56
2.54
2.52
1.23
0.99
0.97
0.95
Bpin
Cl
Cl
5f
1.00
1.03
1.00
1.01
1.01
2.00
12.00
2.00
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)


148.23
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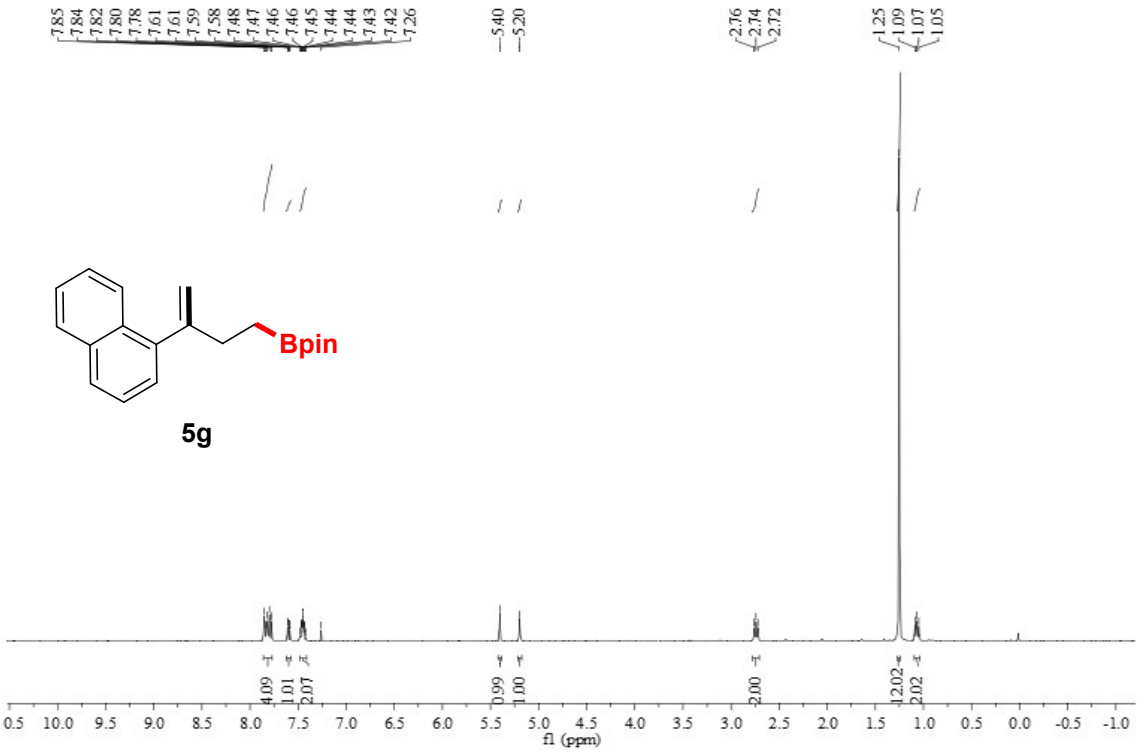
132.20
130.97
130.03
128.13
125.55
112.57
83.14
77.32
77.00
76.68
29.07
24.79
Bpin
Cl
Cl
5f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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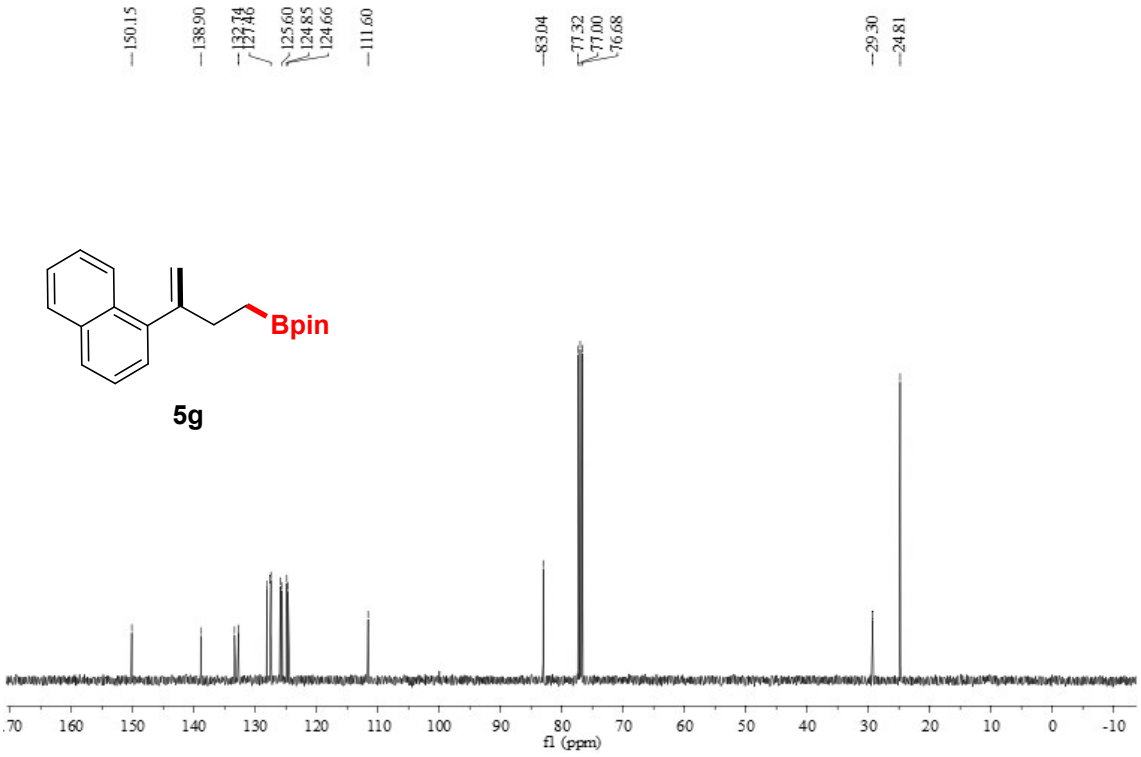
7.84
7.82
7.80
7.78
7.61
7.61
7.59
7.58
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.26
5.40
5.20
2.76
2.74
2.72
1.25
1.09
1.07
1.05
Bpin
4.09
1.01
2.07
0.99
1.00
2.00
12.02
2.02
f1 (ppm)

5g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138.90
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125.60
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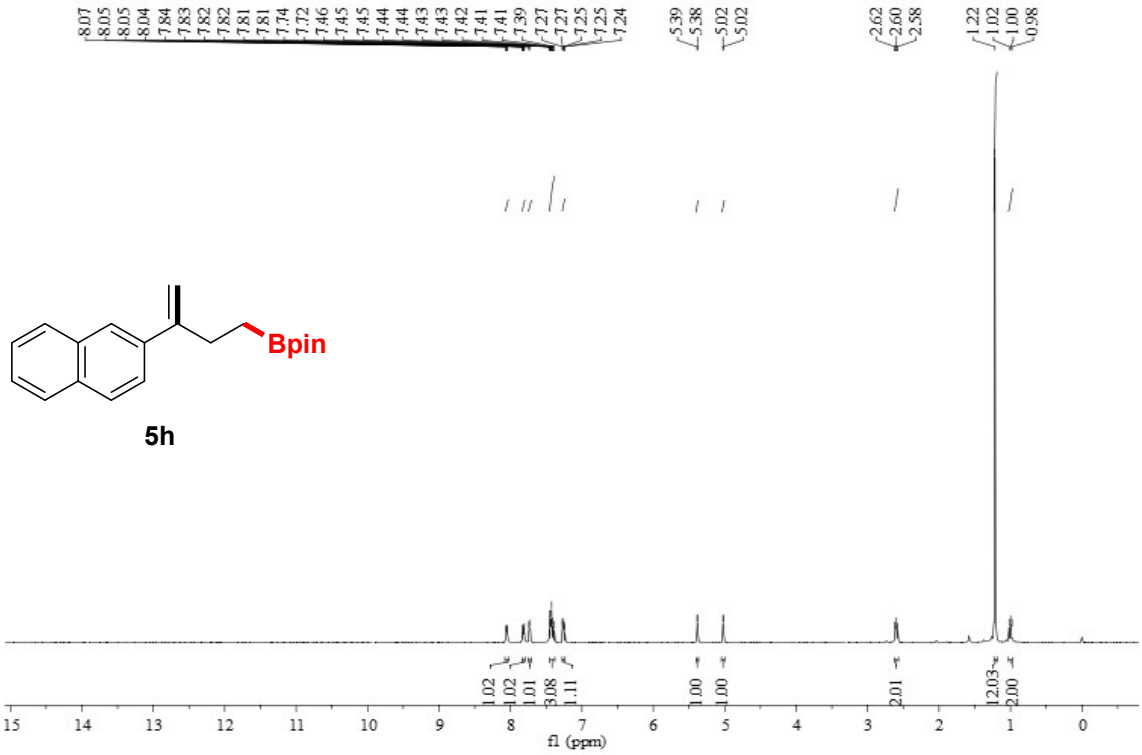
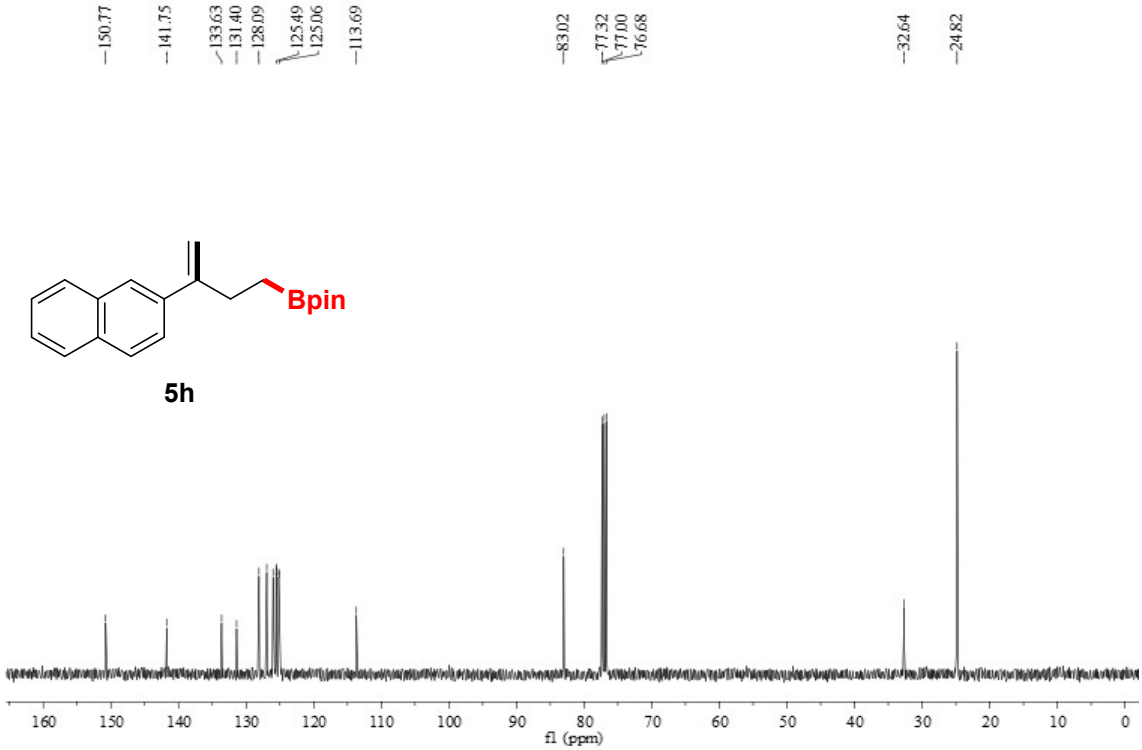
124.66
111.60
83.04
77.32
77.00
76.68
29.30
24.81
Bpin
f1 (ppm)

5g


8.07
8.05
8.05
8.04
7.84
7.83
7.82
7.82
7.81
7.81
7.74
7.72
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.41
7.39
7.27
7.27
7.25
7.25
7.24
5.39
5.38
5.02
5.02
2.62
2.60
2.58
1.22
1.02
1.00
0.98
Bpin
5h
1.02
1.02
1.01
3.08
1.11
1.00
1.00
2.01
12.03
2.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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128.09
125.49
125.06
113.69
83.02
77.32
77.00
76.68
32.64
24.82
Bpin
5h
160
150
140
130
120
110
100
90
80
70
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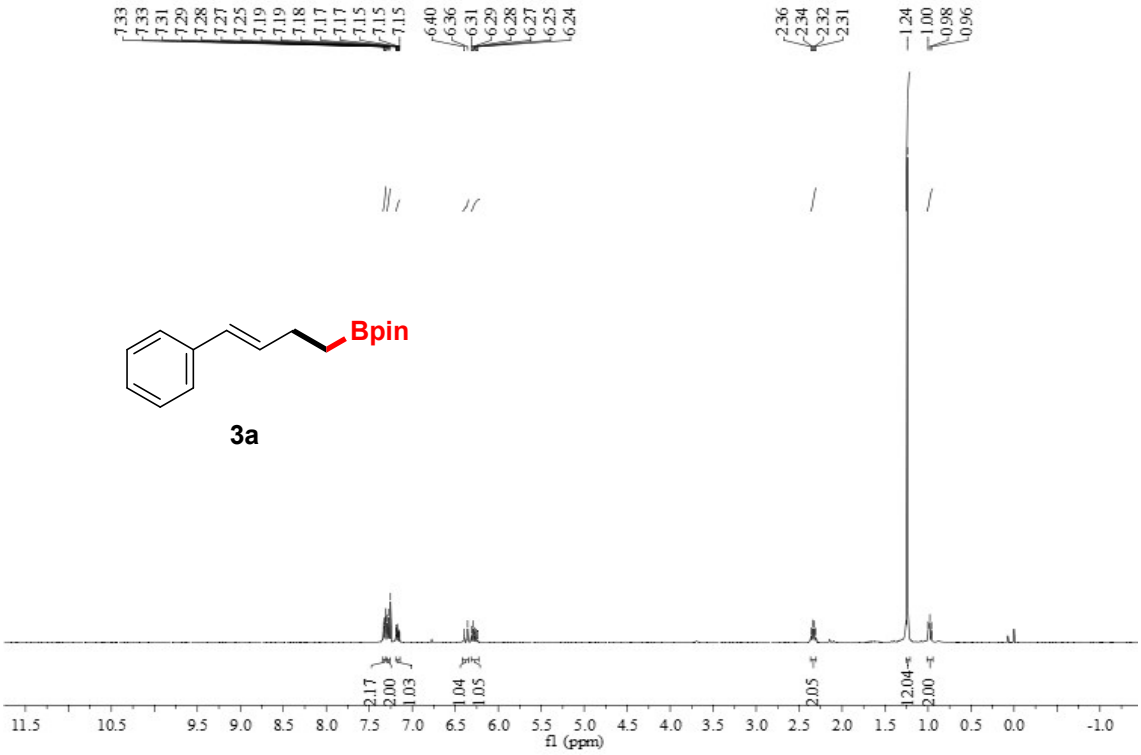
50
40
30
20
10
0
f1 (ppm)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7.33
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7.19
7.19
7.18
7.17
7.17
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7.15
7.15
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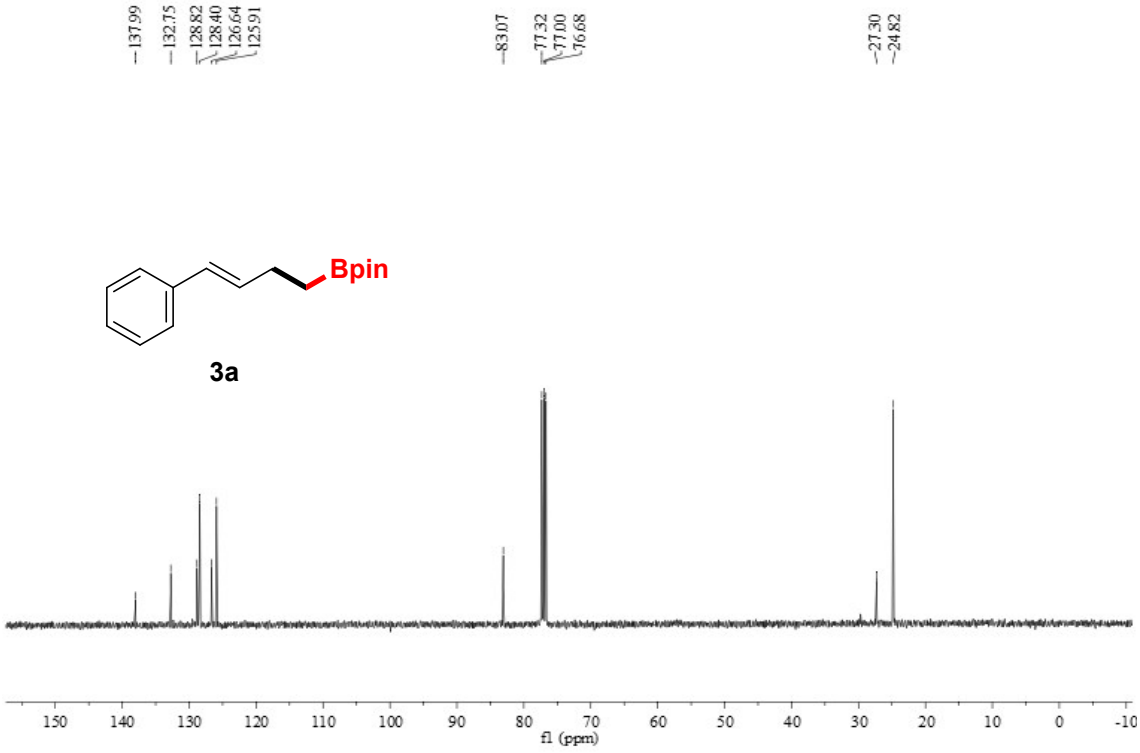
6.36
6.31
6.29
6.28
6.27
6.25
6.24
2.36
2.34
2.32
2.31
1.24
1.00
0.98
0.96
Bpin
3a
2.17
2.00
1.03
1.04
1.05
2.05
12.04
2.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)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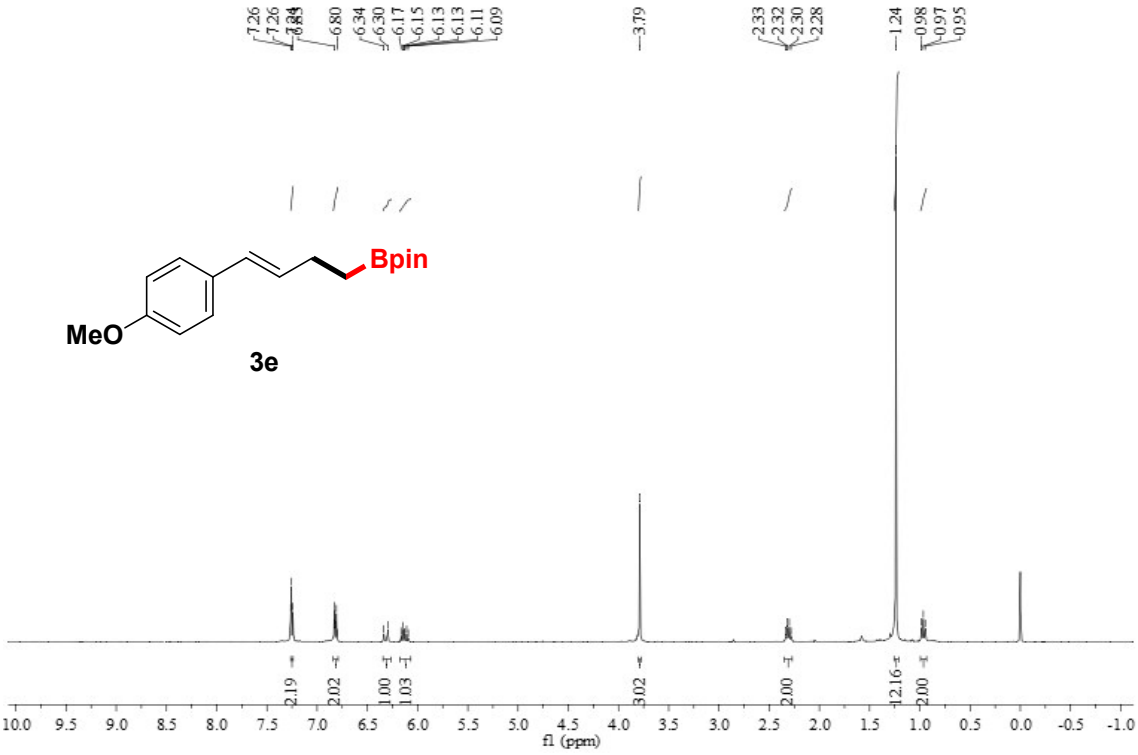
132.75
128.82
128.40
126.64
125.91
83.07
77.32
77.00
76.68
27.30
24.82
Bpin
3a
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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6.80
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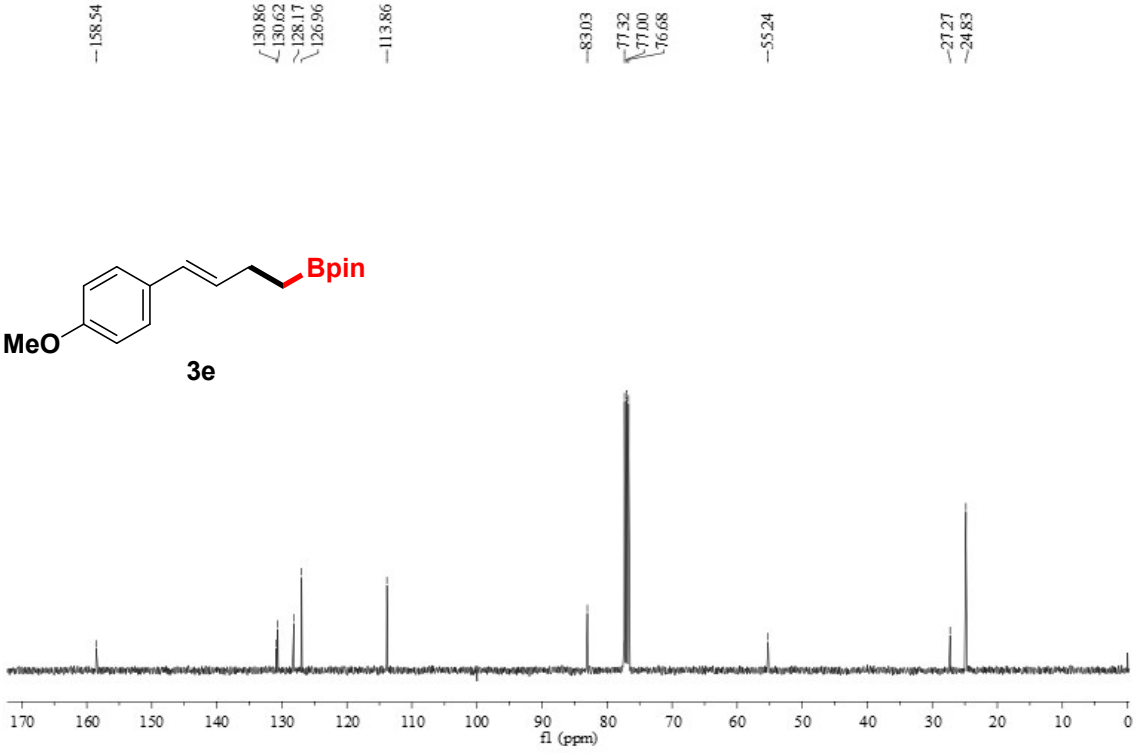
6.30
6.17
6.15
6.13
6.11
6.09
3.79
2.33
2.32
2.30
2.28
1.24
0.98
0.97
0.95
Bpin
MeO
3e
2.19
2.02
1.00
1.03
3.02
2.00
12.16
2.00
f1 (ppm)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128.17
126.96
113.86
83.03
77.32
77.00
76.68
55.24
27.27
24.83
Bpin
MeO
3e
f1 (ppm)