

Markovnikov Selective Hydroboration of Olefins Catalyzed by a Copper N-Heterocyclic Carbene Complex

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Supporting Information

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1. General information

1.1 Reagents

Metal Complexes

Unless otherwise noted, all organometallic compounds were prepared and handled under a nitrogen atmosphere using standard Schlenk and glovebox techniques.

Ligands

(*1E, 2E*)-*N*¹, *N*²-bis(2,6-diisopropylphenyl)ethane-1,2-diimine **A** was synthesized according to the literature procedure.¹ 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene **B** was synthesized according to the literature procedure.²

Solvents

Anhydrous tetrahydrofuran (THF) was obtained from an Innovative Technology PS-MD-6 solvent purification system and this was degassed by three freeze-pump-thaw cycles and stored in a nitrogen glovebox. THF-*d*₈ and chloroform-*d* (CDCl₃) were purchased from Cambridge Isotopes. CDCl₃ was used without further purification. THF-*d*₈ was degassed by three freeze-pump-thaw cycles and stored over activated 3 Å molecular sieves inside a nitrogen glovebox. Solvents for the preparation of the *N*-heterocyclic carbene salt and the copper precursor were obtained from Fisher Scientific and used without further purification.

Other reagents

Reagents were used as received from the following sources: 2,4,6-trimethylbenzaldehyde (Combi Blocks), α,α,α-trifluorotoluene (Sigma Aldrich), 4-fluorobenzoic acid (Sigma Aldrich), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Sigma Aldrich), bis(pinacolato)diboron (Combi Blocks), styrene (Sigma Aldrich), 4-cyanostyrene (Alfa Aesar), 4-methylstyrene (Sigma Aldrich), 4-trifluoromethylstyrene (Combi Blocks), 4-ethoxystyrene (Combi Blocks), 4-methoxystyrene (Sigma Aldrich), 4-aminostyrene (Combi Blocks), 4-fluorostyrene (Combi Blocks), 2-(4-ethenylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Combi Blocks), 3-methylstyrene (Sigma Aldrich), 3-chlorostyrene (Combi Blocks), 2-methylstyrene (Fluka), 2-chlorostyrene (Combi Blocks), α-methylstyrene (Sigma Aldrich), ethynylbenzene (Sigma Aldrich), 1-ethynyl-2-methylbenzene (Combi Blocks), 3-ethynylpyridine (Combi Blocks), 1-ethynyl-4-methoxybenzene (Sigma Aldrich), methyl 4-ethynylbenzoate (Combi Blocks), 1,2-dihydronaphthalene (Sigma Aldrich), ethyl acrylate (Sigma Aldrich), 4-vinylpyridine (Sigma Aldrich), triisopropyl(prop-1-yn-1-yl)silane (Sigma Aldrich), 1-ethynylcyclohex-1-ene (Sigma Aldrich), 4-bromostyrene (Combi Blocks), 1-ethynyl-4-(trifluoromethyl)benzene (Sigma Aldrich), 1-ethynyl-4-methylbenzene (Sigma Aldrich), 1-chloro-3-ethynylbenzene (Sigma Aldrich), 2,6-diisopropylaniline (TCI), glyoxal (Alfa Aesar), formic acid (Fisher Scientific), paraformaldehyde (Sigma Aldrich), hydrogen chloride 4M in dioxane (Oakwood), copper(I) oxide (Fisher Scientific), cesium hydroxide monohydrate (Sigma Aldrich)

1.2 Methods

NMR spectroscopy

¹H NMR spectra were recorded on 400 and 500 MHz Bruker Avance NMR instruments. NMR chemical shifts are reported in ppm and are referenced to the residual solvent peak CDCl₃ (δ = 7.26) and THF-*d*₈ (δ = 3.58). Coupling constants (*J*) are reported in Hertz.

GC-MS analysis

GC-MS spectra were recorded on a Shimadzu QP2010 instrument equipped with a SH-Rxi-5ms column (15 M \times 0.25 mm ID \times 0.25 μ film). Column flow = 0.7 mL/min, temperature program: 3 min at 50 °C, then increase at 20 °C/min to 235 °C and hold for 3.5 min.

Chromatography

Chromatography was performed on silica gel (EMD, silica gel 60, particle size 0.040-0.063 mm) using standard flash techniques. Products were visualized by UV.

Elemental analysis

Elemental analyses were obtained from the CENTC Elemental Analysis Facility at the University of Rochester using a Perkin Elmer PerkinElmer 2400 Series II Analyzer.

2. Optimization of hydroboration reaction workup

The general procedure was followed for the setup of the following optimization reactions.

Work-up 1: After 24 h, the reaction was filtered through a celite plug and CDCl₃ (0.6 mL) was used to wash the reaction vial. The washings were filtered through the plug and the crude was analyzed by ¹H NMR spectroscopy utilizing 2,4,6-trimethylbenzaldehyde as the internal standard.

Work-up 2: After 24 h, the reaction was filtered through a silica plug and CDCl₃ (0.6 mL) was used to wash the reaction vial. The washings were filtered through the plug and the crude was analyzed by ¹H NMR spectroscopy utilizing 2,4,6-trimethylbenzaldehyde as the internal standard.

Work-up 3: After 24 h, the reaction was filtered through a celite plug and the reaction vial was washed with DCM (5x 0.5 mL) and the washings were filtered through the plug. The crude reaction was concentrated *in vacuo* and analyzed by ¹H NMR spectroscopy utilizing 2,4,6-trimethylbenzaldehyde as the internal standard.

Work-up 4: After 24 h, the reaction was filtered through a silica plug and the reaction vial was washed with DCM (5x 0.5 mL) and the washings were filtered through the plug. The crude reaction was concentrated *in vacuo* and analyzed by ¹H NMR spectroscopy utilizing 2,4,6-trimethylbenzaldehyde as the internal standard.

Table S1. Yields for various workup procedures

entry ^a	catalyst loading	Work-up #	wash solvent	3a (%) ^b
1	0.50 mol %	1	CDCl ₃	68
2	0.50 mol %	2	CDCl ₃	62
3	0.50 mol %	3	DCM	>99
4	0.50 mol %	4	DCM	86

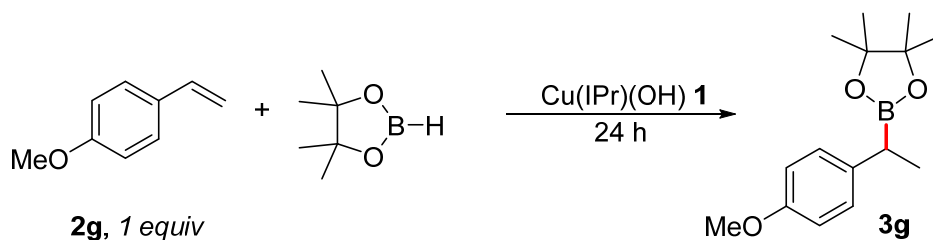
^aReaction conditions: alkene (0.5 mmol), HBpin (0.5 mmol), catalyst **1**, rt, 24 h. ^bYield determined via ¹H NMR vs 2,4,6-trimethylbenzaldehyde as an internal standard.

Work-up 3 (entry 3) proved to be optimal for analyzing catalytic reactions.

3. Optimization of electron rich substrates

The general reaction setup was followed for the optimization of electron rich substrates. Under mild atom economical (equimolar) conditions, the reaction between *para*-methoxystyrene and HBpin does not afford a high yield. The use of excess HBpin or B₂Pin₂ (entries 3-4) does result in an increase in yield. From our observations, the yield of the borylated product is likely dependent upon how much excess boron is available. When there is no excess boron available (1:1 ratio of alkene to boron), the ¹H NMR spectrum and GC-MS chromatogram shows full consumption of the boron species and remaining starting alkene and product.

Table S2. Optimization of conditions



Entry ^a	Catalyst Loading	THF (mL)	Boron Reagent	Boron mmol	Temperature	Yield ^b
1	1 mol %	0.5	HBpin	0.5 mmol	RT	43%
2	1 mol %	0.5	B ₂ Pin ₂	0.5 mmol	RT	56%
3	1 mol %	0.5	HBpin	1 mmol	RT	49%
4	1 mol %	0.5	B ₂ Pin ₂	0.6 mmol	RT	69%
5	1 mol %	--	HBpin	0.5 mmol	RT	34%
6	1.5 mol %	--	HBpin	0.5 mmol	RT	33%
7	1 mol %	0.25	HBpin	0.5 mmol	RT	30%
8	1.5 mol %	0.25	HBpin	0.5 mmol	RT	23%

^aReaction conditions: alkene (0.5 mmol), HBpin (0.5 mmol), catalyst **1**, THF (mL), rt, 24 h. ^bYield determined via ¹H NMR spectroscopy vs 2,4,6-trimethylbenzaldehyde as an internal standard.

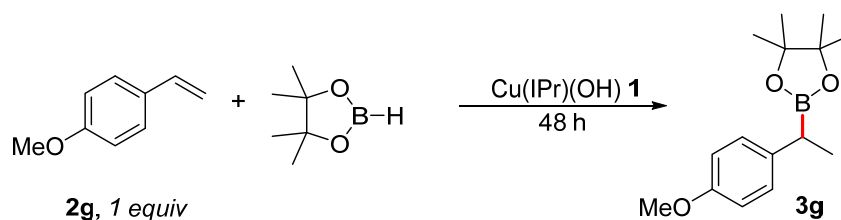
3.1 Time release optimization of electron rich substrates

The general reaction setup was followed for the time release studies. Reactions were run for 48 h.

Entry 1: HBpin (0.5 mmol, 1.0 equiv, 72.6 μ L) was added over 3 portions (24.2 μ L per portion). The first portion was added at the beginning of the reaction ($t = 0$ min), the next portion was added at 2 h and the last was added at 24 h. The reaction was then allowed to stir another 24 h before workup.

Entry 2: HBpin (0.5 mmol, 1.0 equiv, 72.6 μ L) was added at the beginning of the reaction. After 24 h HBpin (0.5 mmol, 1.0 equiv, 72.6 μ L) was added again for a total of 2 equiv. The reaction was then allowed to stir another 24 h before workup.

Table S3. Effect of Boron loading on products

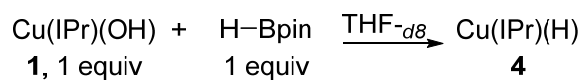


Entry ^a	Catalyst Loading	Boron mmol	Temperature	(2g : 3g) ^b
1	1 mol %	0.5 mmol	RT	(1.29:1)
2	1 mol %	1 mmol	RT	(1:1.38)

^aReaction conditions: alkene (0.5 mmol), HBpin (0.5 mmol), catalyst **1**, rt, 48 h. ^bRatio of (**2**:**3**) determined via ¹H NMR spectroscopy vs 2,4,6-trimethylbenzaldehyde as an internal standard.

4. General procedure for stoichiometric studies

Stoichiometric reaction of **1** with HBpin in THF-*d*₈



In a nitrogen-filled glovebox: an oven-dried J-Young NMR test tube was charged with Cu(IPr)(OH) (0.05 mmol, 1.0 equiv, 23.5 mg) and THF-*d*₈ (0.6 mL) resulting in a colorless solution. Next, HBpin (0.05 mmol, 1.0 equiv, 6.5 mg, 7.3 μ L) was added and upon mixing the solution immediately became bright yellow in color. The tube was capped and brought out of the glovebox and the ¹H NMR spectrum was recorded as soon as possible (*ca.* 5 min) thereafter.

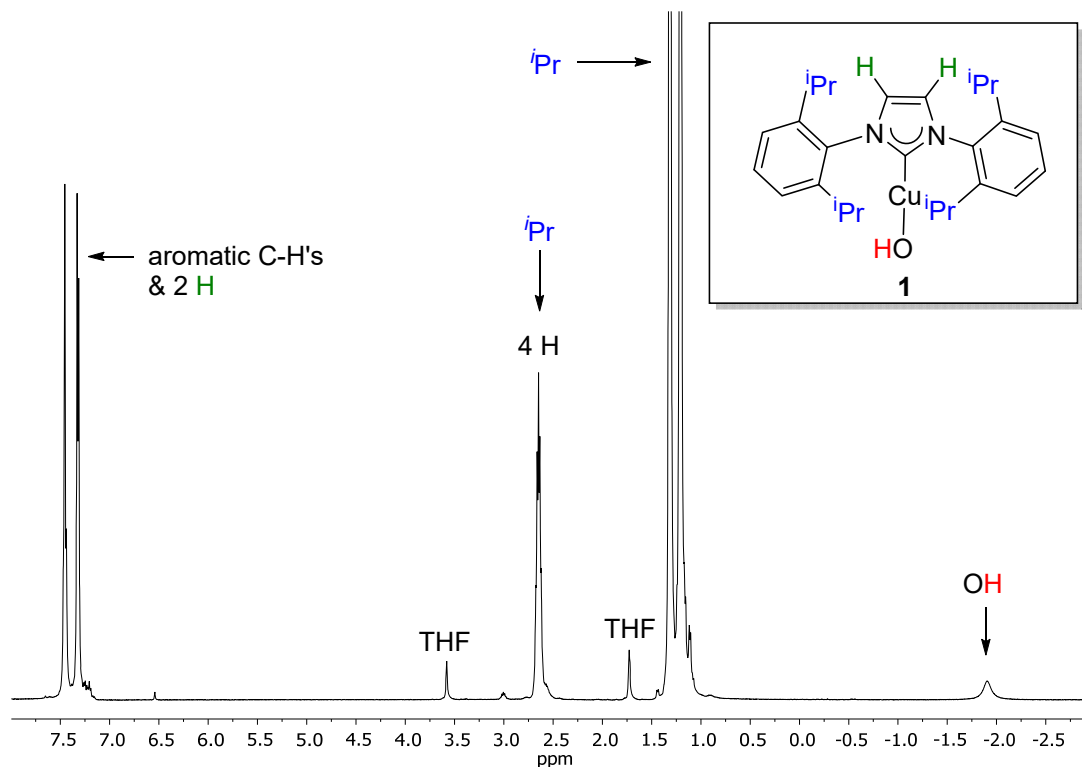


Figure S1. ¹H NMR spectra of **1** in THF-*d*₈.

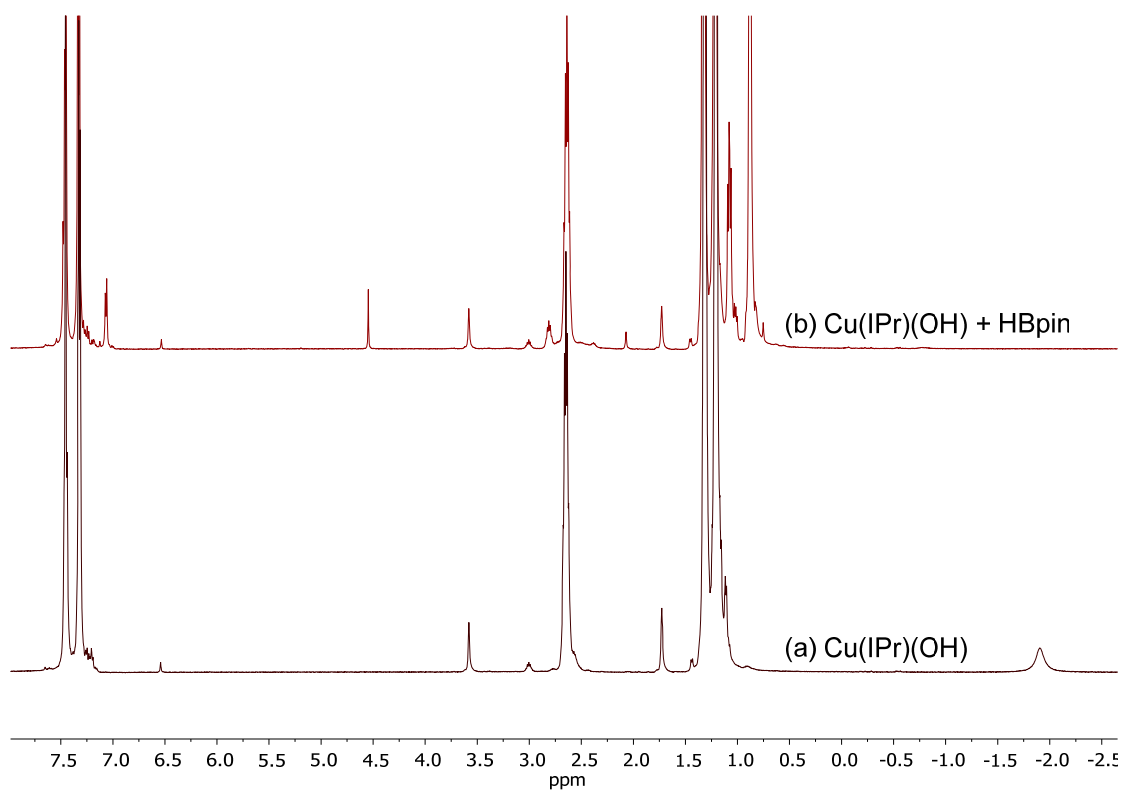
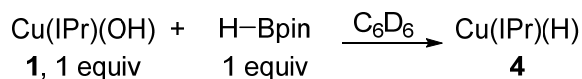


Figure S2. ^1H NMR spectra in THF- d_8 of the stoichiometric reaction of **1** with HBpin. (a) before the addition of HBpin. (b) after the addition of HBpin (*ca.* 5 min).

Stoichiometric reaction of **1** with HBpin in C₆D₆



In a nitrogen-filled glovebox: an oven-dried J-Young NMR test tube was charged with Cu(IPr)(OH) (0.05 mmol, 1.0 equiv, 23.5 mg) and C₆D₆ (0.6 mL) resulting in a colorless solution. Next, HBpin (0.05 mmol, 1.0 equiv, 6.5 mg, 7.3 μ L) was added and upon mixing the solution immediately became bright yellow in color. The tube was capped and brought out of the glovebox and the ¹H NMR spectrum was recorded as soon as possible (*ca.* 5 min) thereafter.

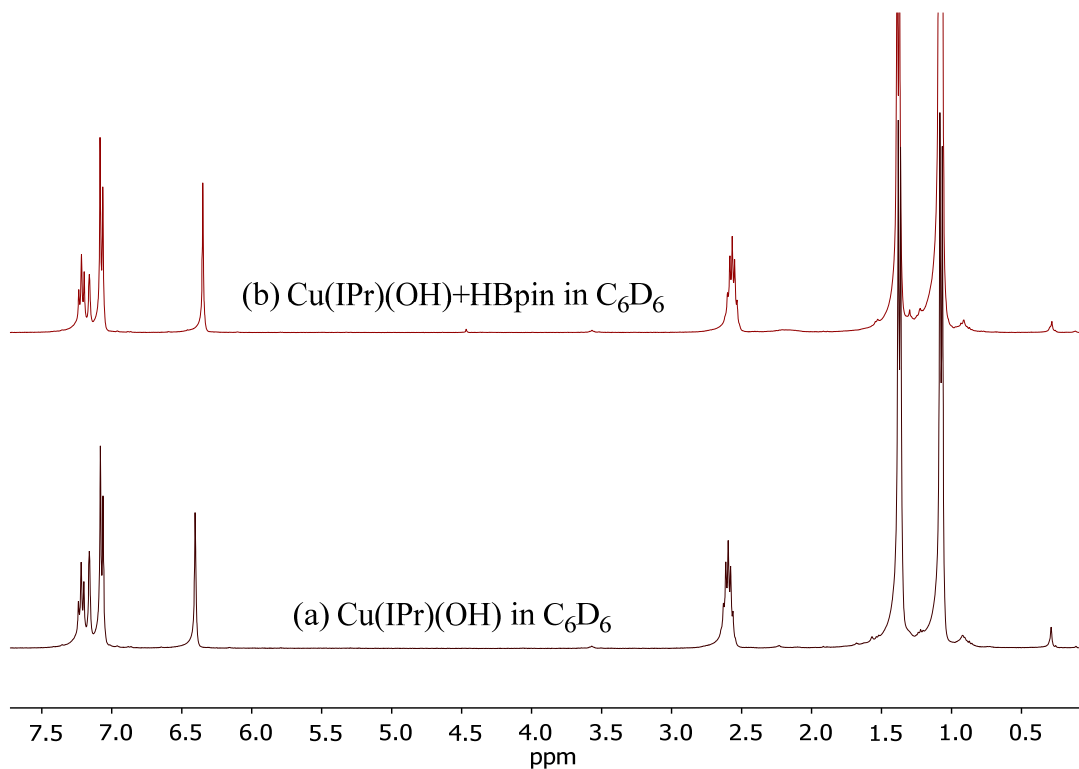
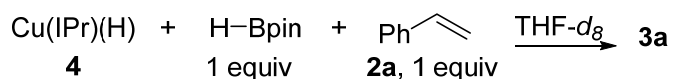


Figure S3. ¹H NMR spectra in C₆D₆ of the stoichiometric reaction of **1** with HBpin. (a) before the addition of HBpin. (b) after the addition of HBpin (*ca.* 5 min).

Stoichiometric reaction of **4** with HBpin and alkene **2a**



In a nitrogen-filled glovebox: an oven-dried J-Young NMR test tube was charged with Cu(IPr)(OH) (0.05 mmol, 1 equiv, 23.5 mg) and THF-*d*₈ (0.6 mL) resulting in a colorless solution. Next, HBpin (0.05 mmol, 1 equiv, 6.5 mg, 7.3 μ L) was added and upon mixing the solution immediately became bright yellow in color. The bright yellow solution indicates the formation of **4**. Next, **2a** (0.05 mmol, 1 equiv, 5.2 mg, 5.7 μ L) and HBpin (0.05 mmol, 1 equiv, 6.5 mg, 7.3 μ L) were quickly added and the tube was capped and brought out of the glovebox and reaction progress was monitored by ¹H NMR spectroscopy.

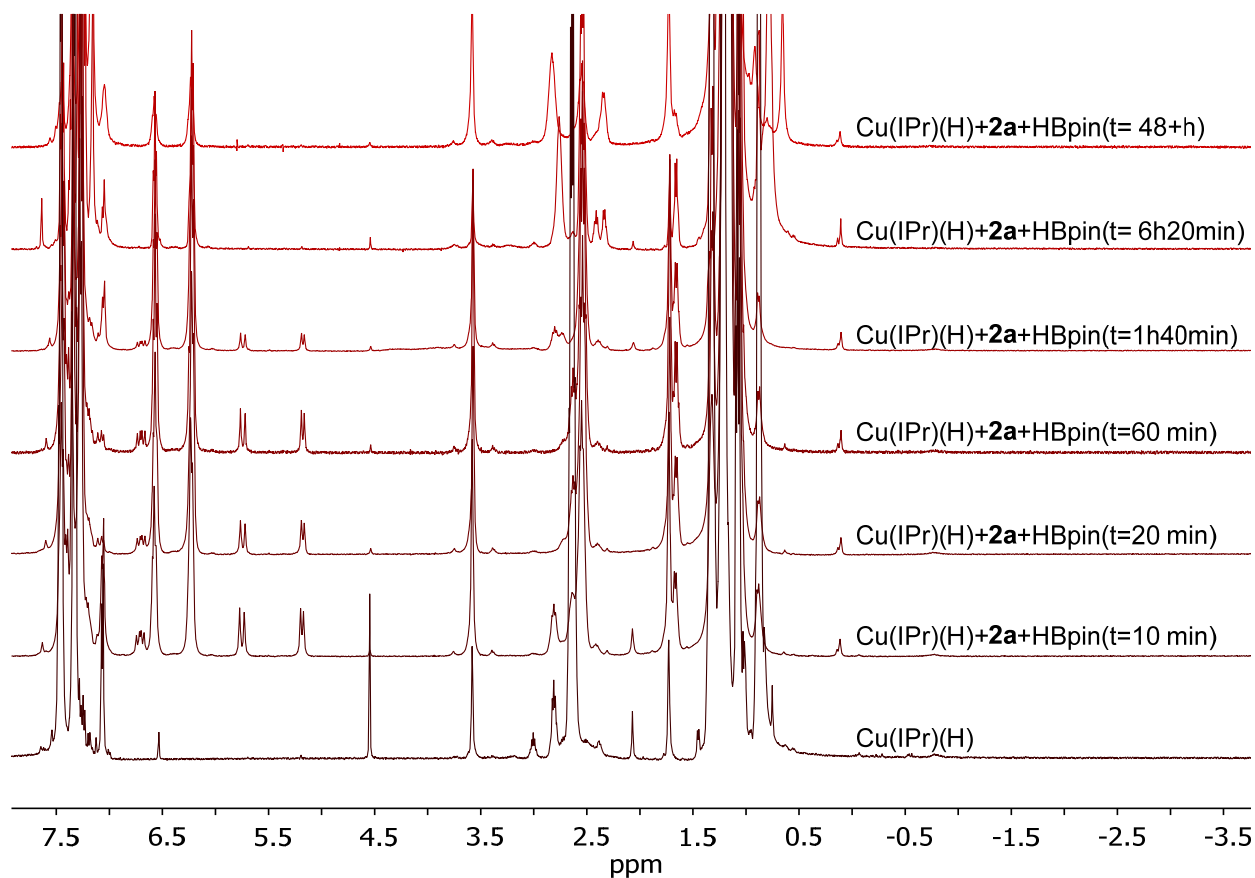
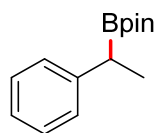


Figure S4. ¹H NMR spectra in THF-*d*₈ of the stoichiometric reaction of **4** with HBpin and **2a**.

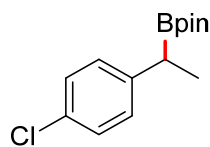
5. Product characterization



3a

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

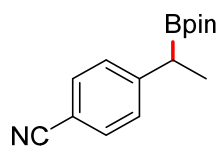
The general procedure for hydroboration was followed with styrene (0.5 mmol, 1.0 equiv, 57.5 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.³



3b

2-(1-(4-chlorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

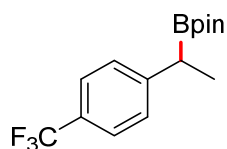
The general procedure for hydroboration was followed with 4-chlorostyrene (0.5 mmol, 1.0 equiv, 60.0 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.⁴



3c

4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile

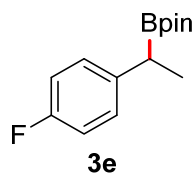
The general procedure for hydroboration was followed with 4-cyanostyrene (0.5 mmol, 1.0 equiv, 60.0 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.⁵



3d

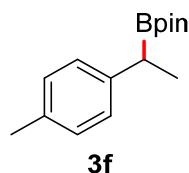
4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)ethyl)-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 4-trifluoromethylstyrene (0.5 mmol, 1.0 equiv, 73.9 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.⁴



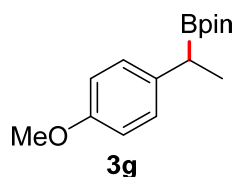
2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 4-fluorostyrene (0.5 mmol, 1.0 equiv, 59.6 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.^{5,6}



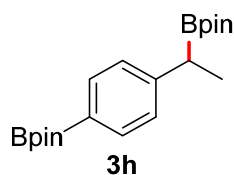
4,4,5,5-tetramethyl-2-(1-(p-tolyl)ethyl)-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 4-methylstyrene (0.5 mmol, 1.0 equiv, 65.9 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.⁷



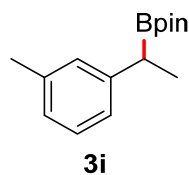
2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 4-methoxystyrene (0.5 mmol, 1.0 equiv, 66.5 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.⁴



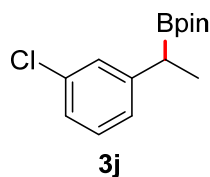
4,4,5,5-tetramethyl-2-(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 2-(4-ethenylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 0.115g) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.⁸



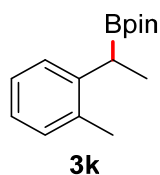
4,4,5,5-tetramethyl-2-(1-(m-tolyl)ethyl)-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 3-methylstyrene (0.5 mmol, 1.0 equiv, 66.4 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.⁵



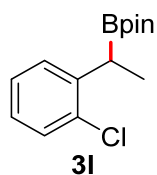
2-(1-(3-chlorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 3-chlorostyrene (0.5 mmol, 1.0 equiv, 63.6 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.⁹



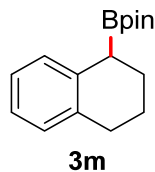
4,4,5,5-tetramethyl-2-(1-(o-tolyl)ethyl)-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 2-methylstyrene (0.5 mmol, 1.0 equiv, 64.6 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.⁴



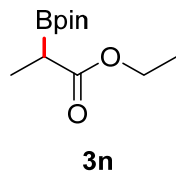
2-(1-(2-chlorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 2-chlorostyrene (0.5 mmol, 1.0 equiv, 64.2 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.⁴



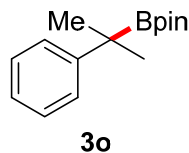
4,4,5,5-tetramethyl-2-(1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 1,2-dihydronaphthalene (0.5 mmol, 1.0 equiv, 65.3 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.¹⁰



ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate

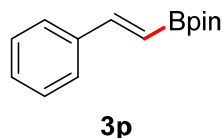
The general procedure for hydroboration was followed with ethyl acrylate (0.5 mmol, 1.0 equiv, 54.5 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.¹¹



4,4,5,5-tetramethyl-2-(2-phenylpropan-2-yl)-1,3,2-dioxaborolane

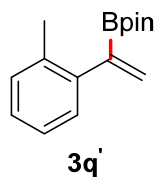
The general procedure for hydroboration was followed with α -methylstyrene (0.5 mmol, 1.0 equiv, 65.0 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L).

NOTE: no borylation (branched or linear) of the alkene was observed by NMR spectroscopy, but some (<5%) branched isomer was seen by GCMS.



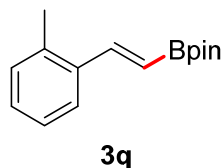
(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with ethynylbenzene (0.5 mmol, 1.0 equiv, 54.9 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.¹²



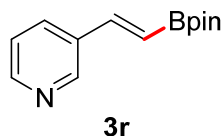
4,4,5,5-tetramethyl-2-(1-(o-tolyl)vinyl)-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 1-ethynyl-2-methylbenzene (0.5 mmol, 1.0 equiv, 63.0 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.¹²



(E)-4,4,5,5-tetramethyl-2-(2-methylstyryl)-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 1-ethynyl-2-methylbenzene (0.5 mmol, 1.0 equiv, 63.0 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.¹²



(E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine

The general procedure for hydroboration was followed with 3-ethynylpyridine (0.5 mmol, 1.0 equiv, 0.052 g) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.¹³

¹H NMR (400 MHz, CDCl₃) δ 8.57 (s, 1H), 8.39 (d, J = 4.4 Hz, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.26 (d, J = 18.4 Hz, 1H), 7.14 (dd, J = 7.6, 4.9 Hz, 1H), 6.14 (d, J = 18.5 Hz, 1H), 1.20 (s, 12H).

GC-MS: 231 (M⁺)

Line#:1 R.Time:10.358(Scan#:1243)
MassPeaks:424
RawMode:Single 10.358(1243) BasePeak:132.10(9820971)
BG Mode:None

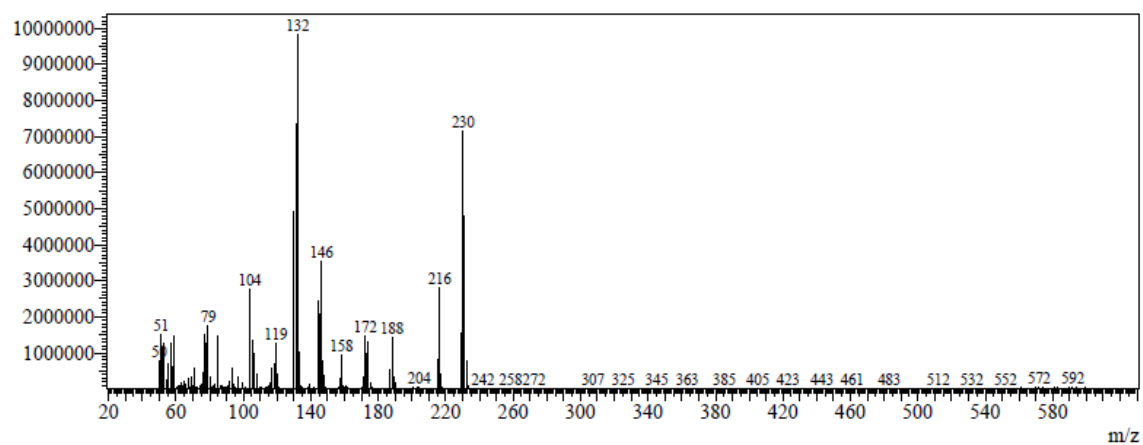
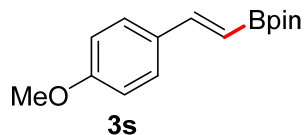
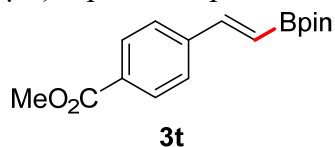


Figure S5. GC-MS chromatogram of borylated product **3r**.



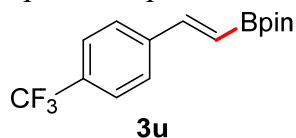
(E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 1-ethynyl-4-methoxybenzene (0.5 mmol, 1.0 equiv, 64.8 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.¹²



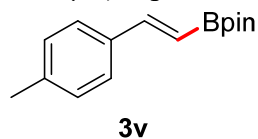
methyl (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate

The general procedure for hydroboration was followed with methyl 4-ethynylbenzoate (0.5 mmol, 1.0 equiv, 0.080 g) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.¹⁴



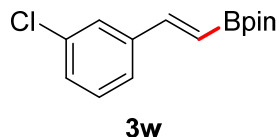
(E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 1-ethynyl-4-(trifluoromethyl)benzene (0.5 mmol, 1.0 equiv, 81.6 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.¹²



(E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane

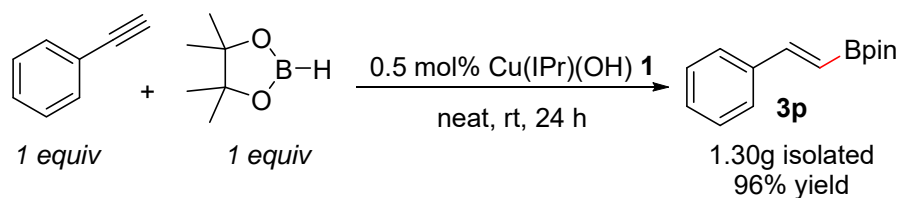
The general procedure for hydroboration was followed with 1-ethynyl-4-methylbenzene (0.5 mmol, 1.0 equiv, 63.4 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.¹²



(E)-2-(3-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure for hydroboration was followed with 1-chloro-3-ethynylbenzene (0.5 mmol, 1.0 equiv, 61.6 μ L) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 1.0 equiv, 72.6 μ L). Spectroscopic data matches the reported literature.¹²

6. Large scale reaction



General procedure for hydroboration was followed for the large scale reaction, with slight modifications (vial size, workup). In a glovebox, an oven-dried 2-dram vial containing a stir bar was charged with Cu(IPr)(OH) (0.50 mol %, 0.05 equiv), phenylacetylene (5.9 mmol, 1.0 equiv, 0.648mL), and HBpin (5.9 mmol, 1.0 equiv, 0.856mL). Note the reaction was highly exothermic and was allowed to cool enough to touch the vial before the reaction was capped and removed from the glovebox and stirred at room temperature for 24h. The reaction was then filtered through a celite (5mL)/silica (5mL) plug. The vial was washed with an eluent of 8:2 hexanes/ethyl acetate and added to the plug. The plug was then washed with 350mL of the 8:2 hexanes/ethyl acetate eluent. The combined washings were concentrated *in vacuo* and dried on a vacuum line to afford **3p** (1.30g, 96% yield). Spectroscopic data matches the reported data.¹²

¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 7.0 Hz, 2H), 7.38 (d, *J* = 18.5 Hz, 1H), 7.34 – 7.20 (m, 3H), 6.15 (d, *J* = 18.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 149.65, 137.59, 129.03, 128.70, 127.19, 83.49, 24.94.

¹³C NMR DEPT-135 (101 MHz, CDCl₃) δ 149.50, 128.89, 128.56, 127.05, 24.81.

Substrate 3p
 Avance 400
 Proton NMR
 CDCl₃

¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 7.0 Hz, 2H), 7.38 (d, *J* = 18.5 Hz, 1H),
 7.34 – 7.20 (m, 3H), 6.15 (d, *J* = 18.4 Hz, 1H).

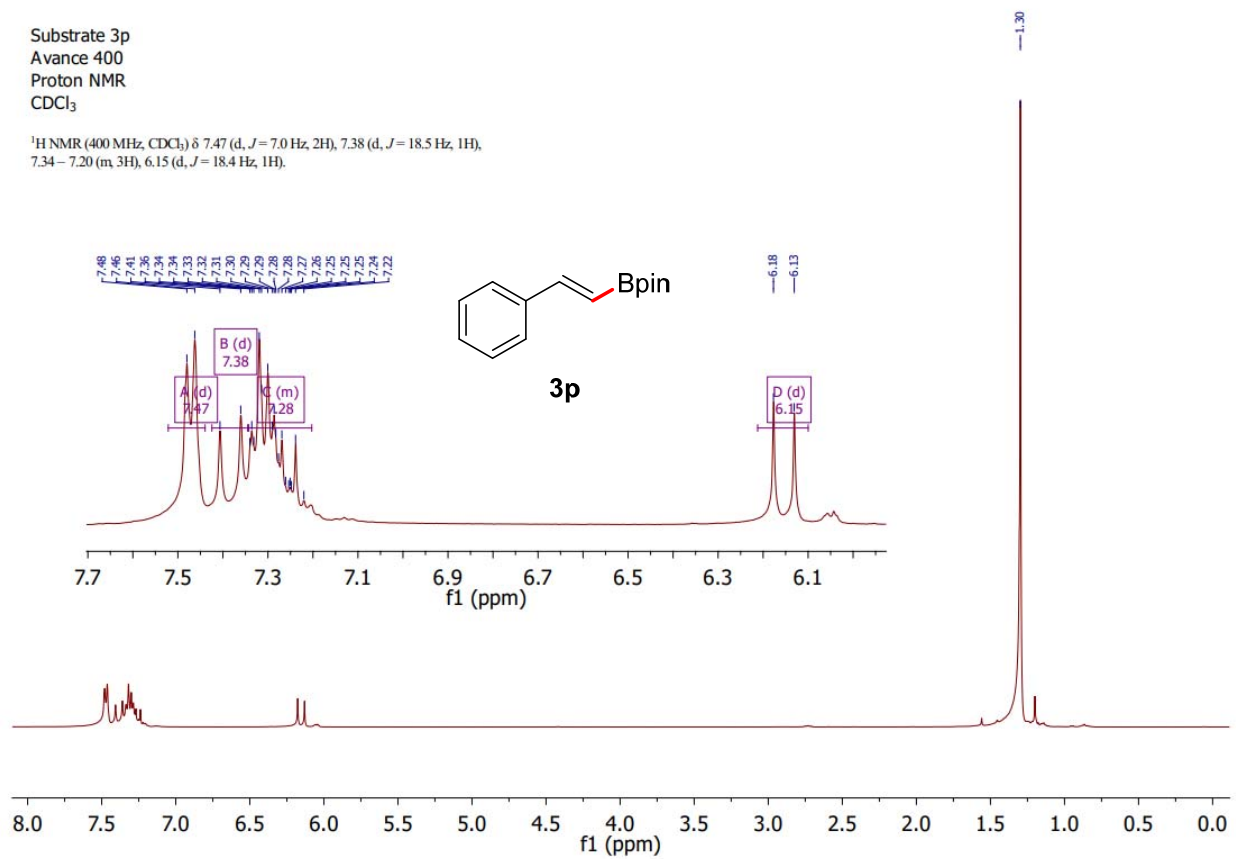
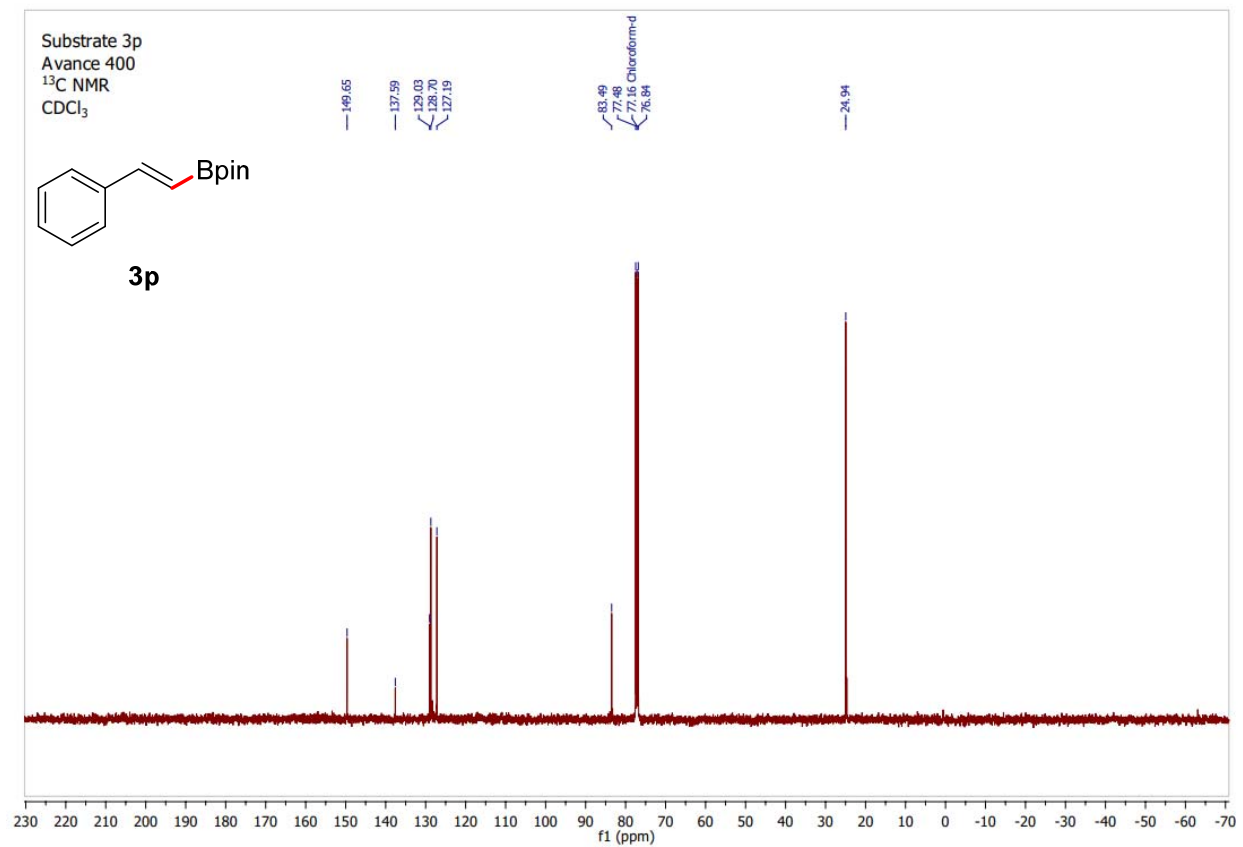


Figure S6. ¹H NMR spectrum of borylated product **3p**.



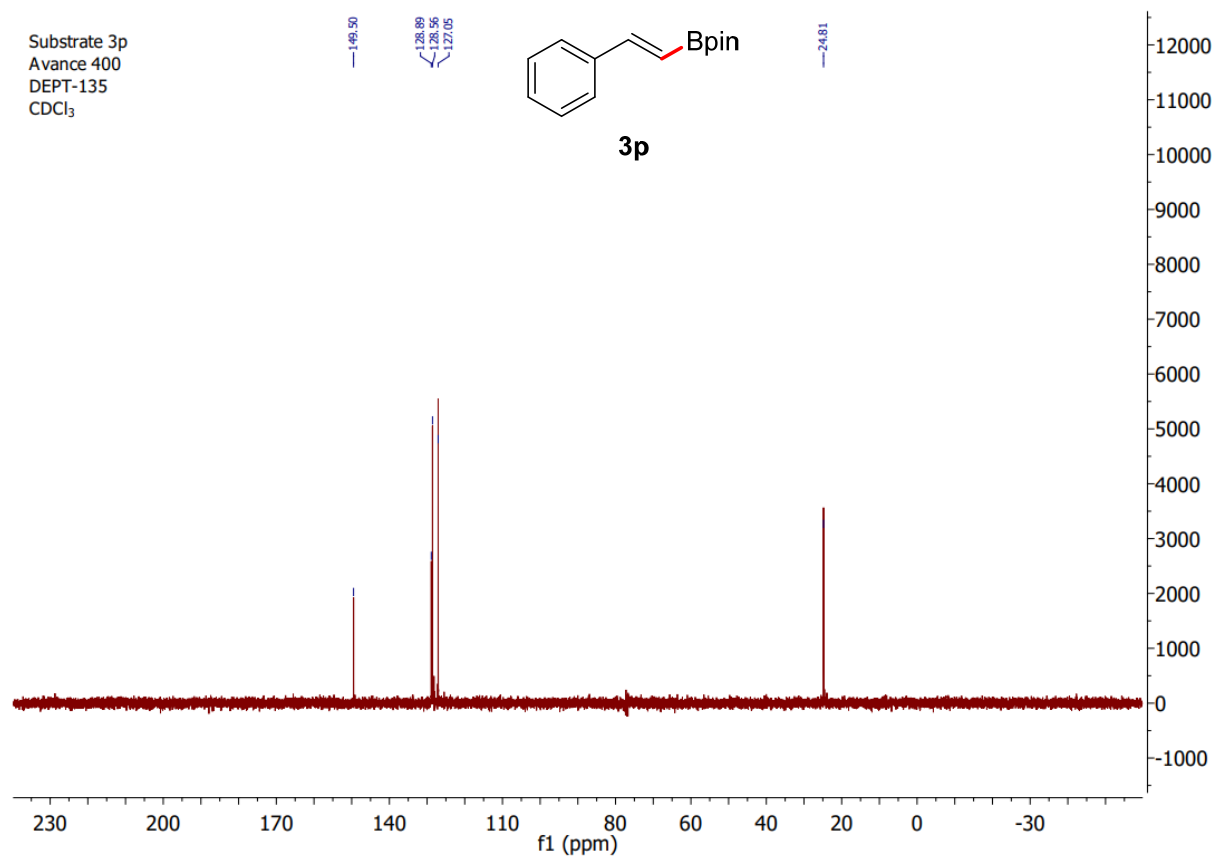
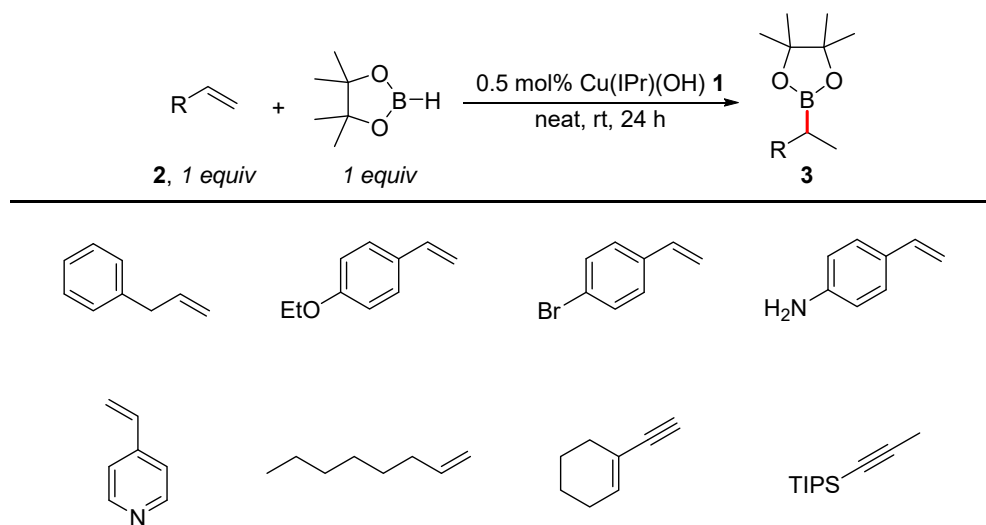


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum and $^{13}\text{C}\{^1\text{H}\}$ NMR DEPT-135 spectrum of borylated product **3p**.

7. Unsuccessful substrates

The substrates shown below were run following the general procedure for hydroboration. Note that the substrates that ended up in this table showed less than a 25% yield by ^1H NMR spectroscopy using 2,4,6-trimethylbenzaldehyde as the internal standard. For 4-bromostyrene and 1-ethynylcyclohex-1-ene, two hydroboration products were observed. In the case of 4-bromostyrene we saw competition for borylation at both the alkene and the bromide, and for 1-ethynylcyclohex-1-ene we saw competition for borylation at both the alkene and alkyne. The unselective borylation made the determination of yields by ^1H NMR spectroscopy unreliable; the GCMS chromatograms showed many products.

Table S4. Unsuccessful substrates



8. GCMS Data

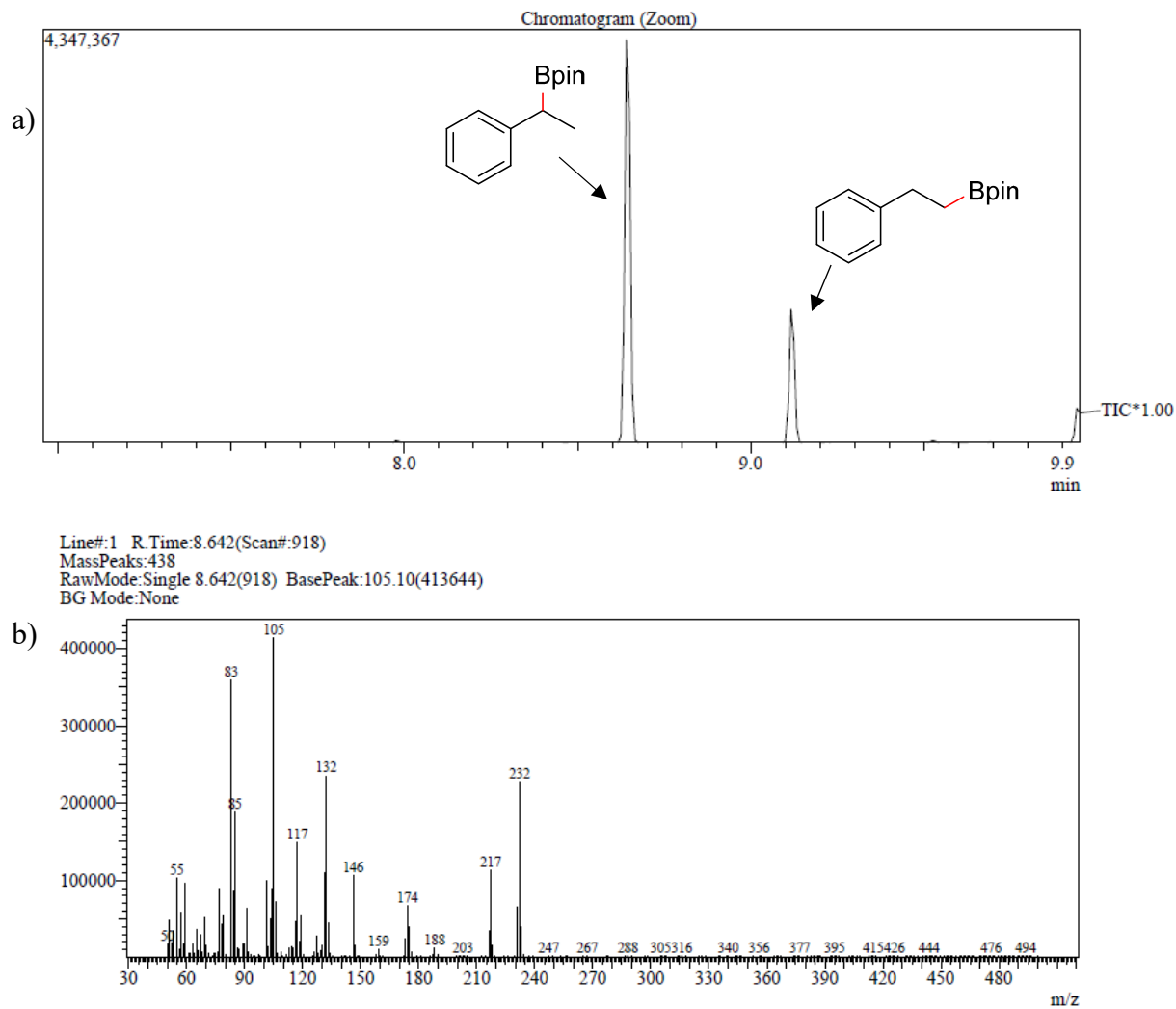


Figure S8. GC-MS chromatograms of authentic samples of the branched and linear borylated products.

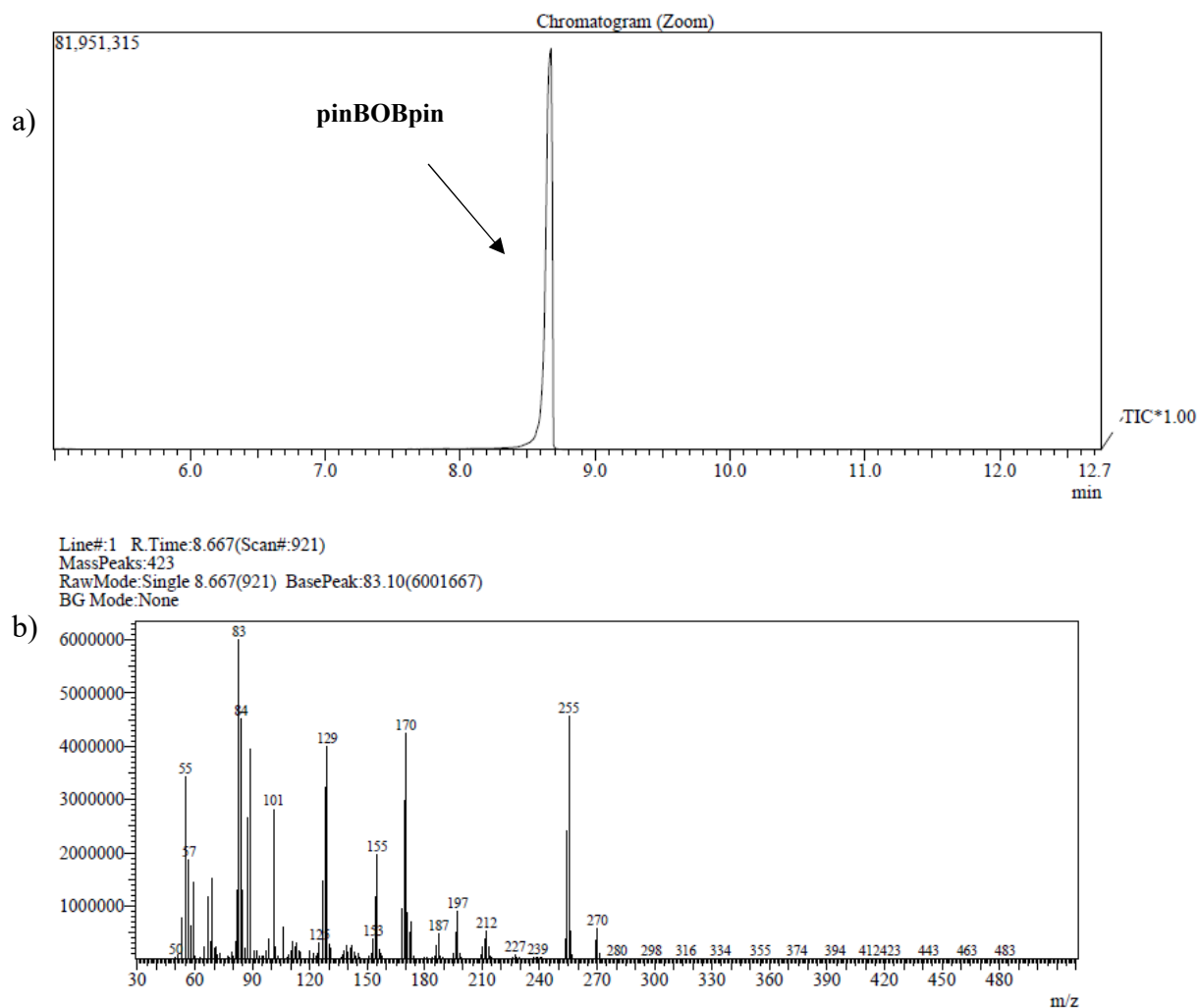


Figure S9. GC-MS chromatograms of authentic sample of 2,2'-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). The compound was independently synthesized according to Stephan's procedure see ref. 16.¹⁵

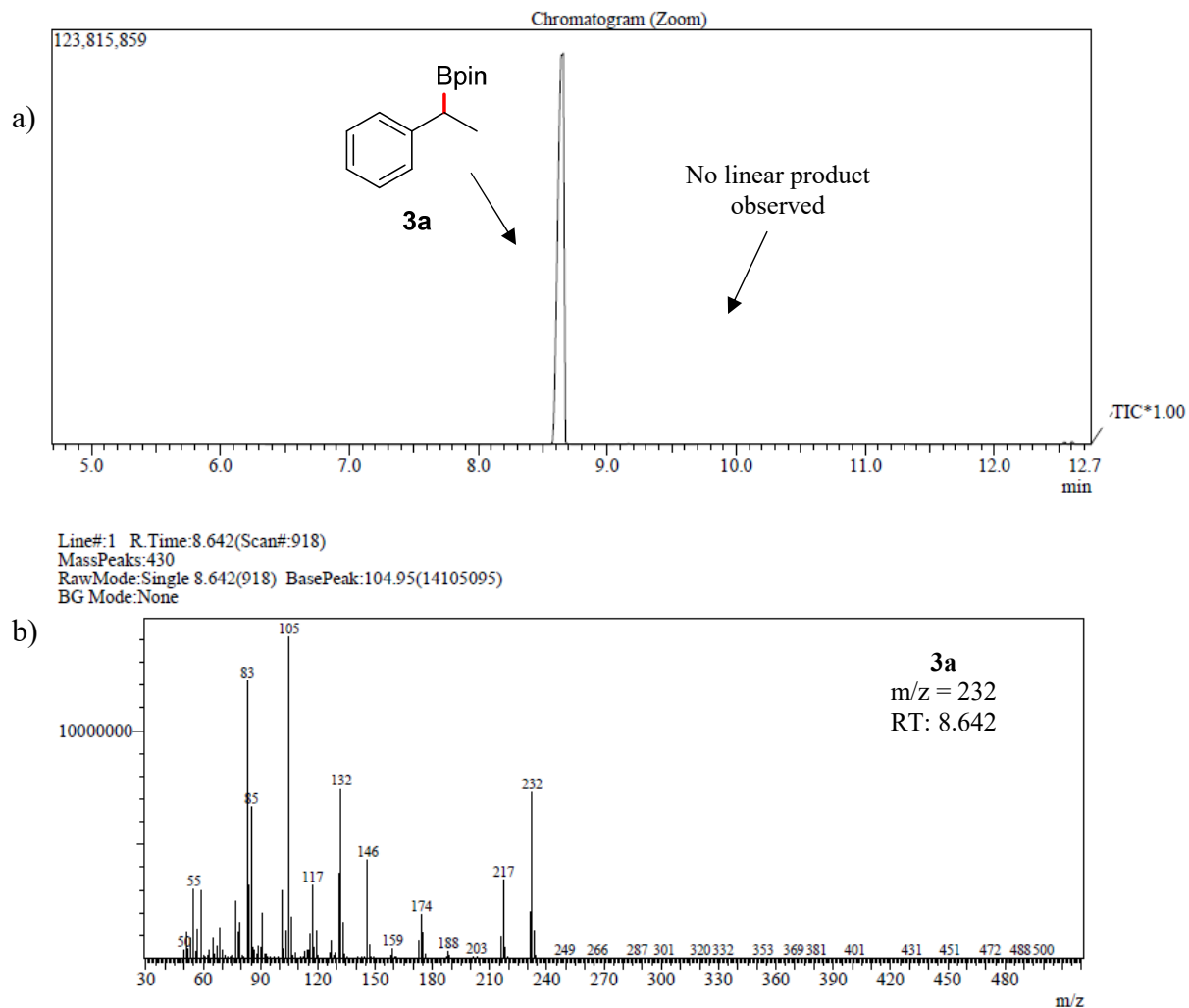
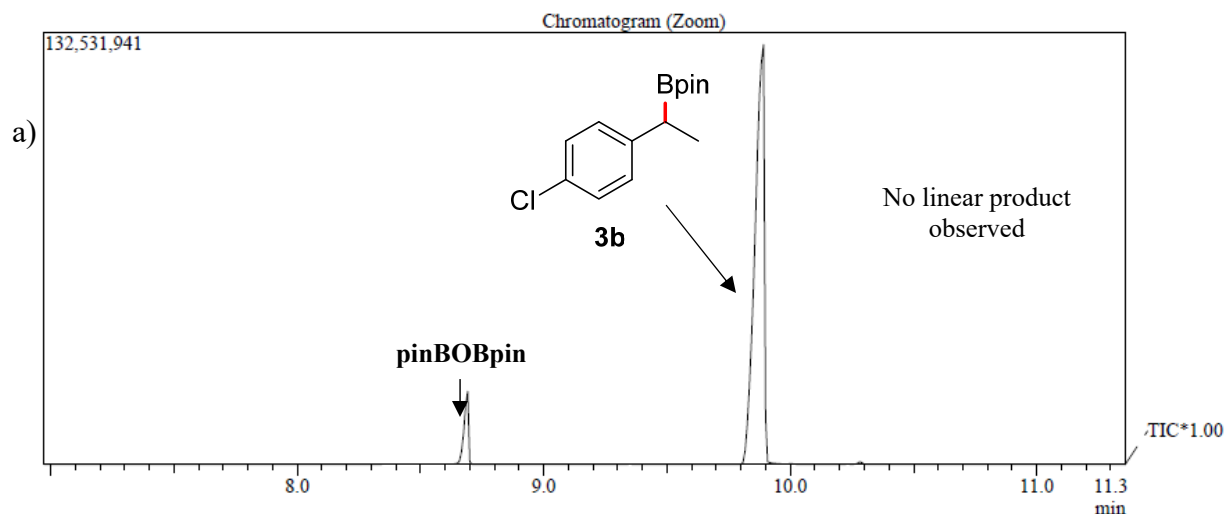
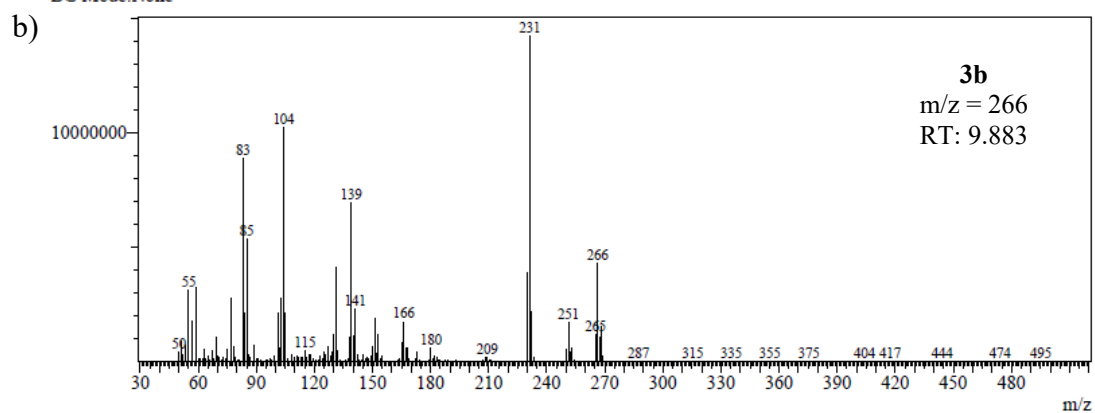


Figure S10. GC-MS chromatograms of product **3a**.



Line#:1 R.Time:9.883(Scan#:1067)
 MassPeaks:434
 RawMode:Single 9.883(1067) BasePeak:231.15(14238739)
 BG Mode:None



Line#:1 R.Time:8.683(Scan#:923)
 MassPeaks:437
 RawMode:Single 8.683(923) BasePeak:255.20(1446225)
 BG Mode:None

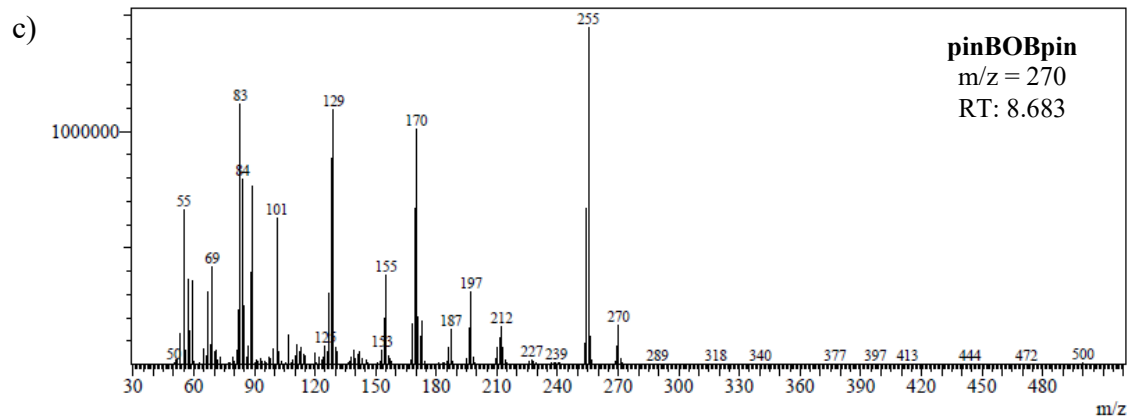
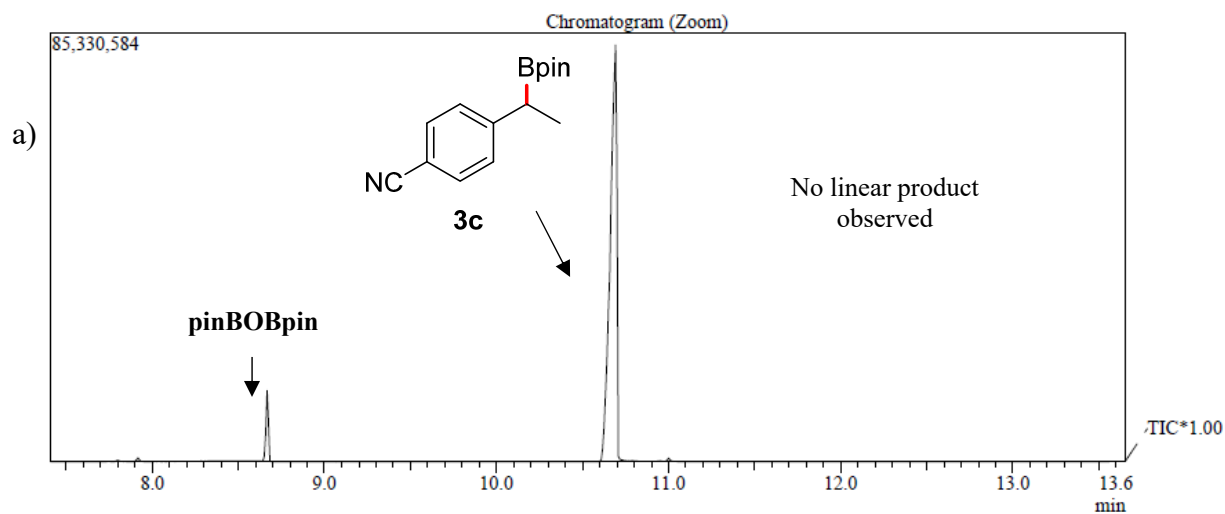
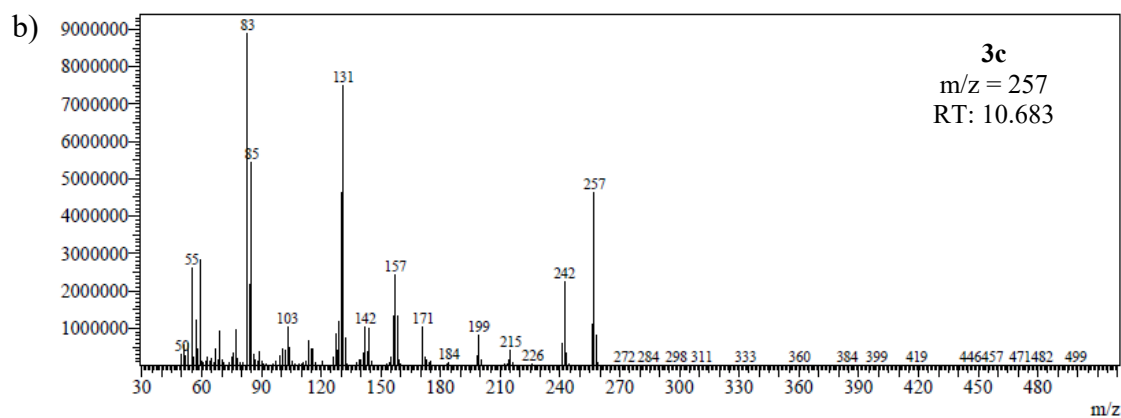


Figure S11. GC-MS chromatograms of product **3b** and pinBOBpin.



Line#:1 R.Time:10.683(Scan#:1163)
 MassPeaks:436
 RawMode:Single 10.683(1163) BasePeak:83.10(8881072)
 BG Mode:None



Line#:1 R.Time:8.667(Scan#:921)
 MassPeaks:438
 RawMode:Single 8.667(921) BasePeak:255.25(1074646)
 BG Mode:None

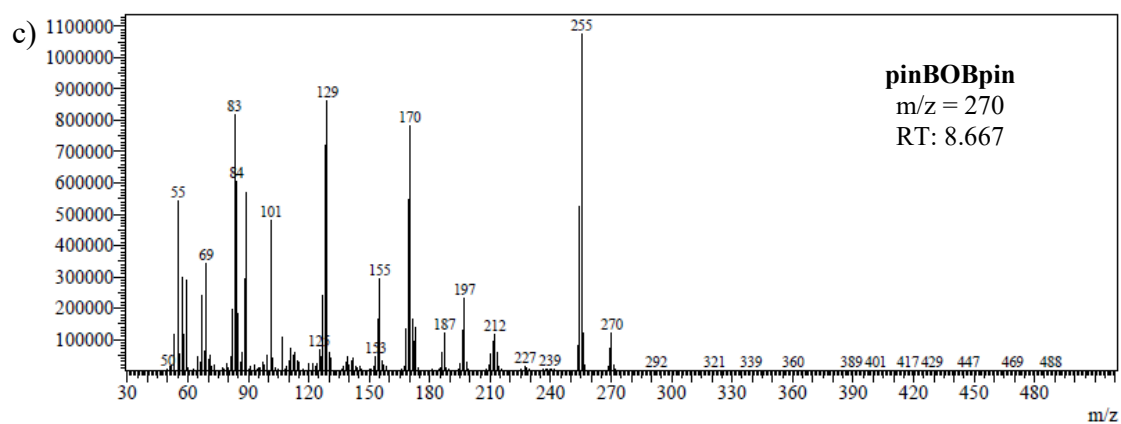
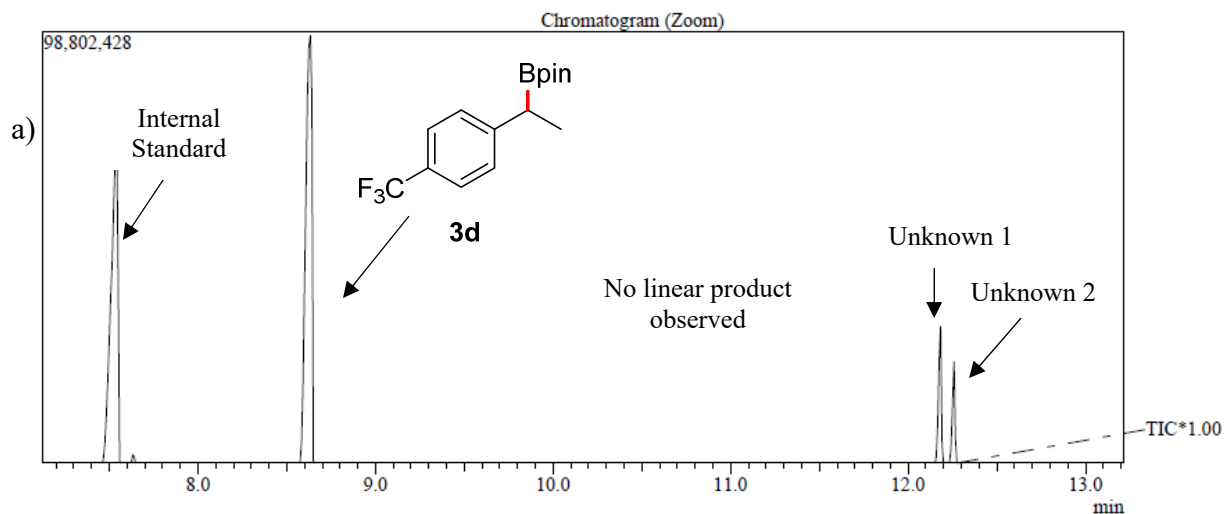
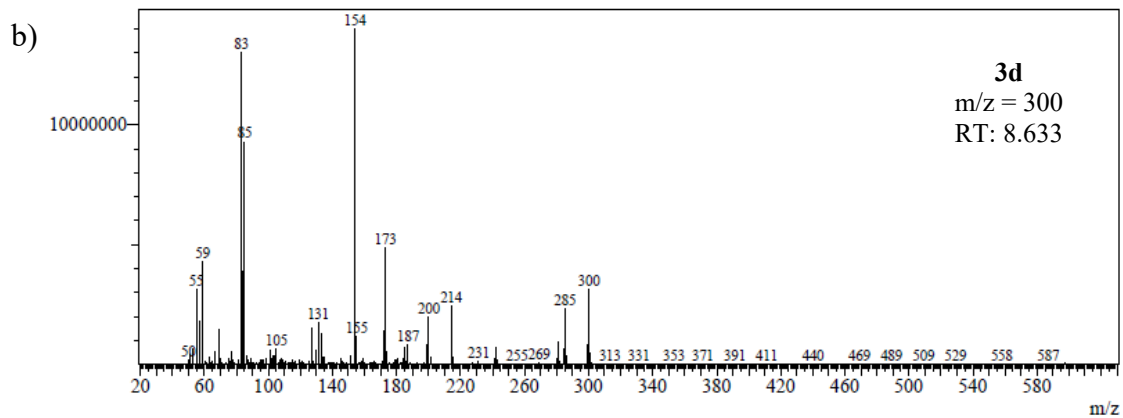


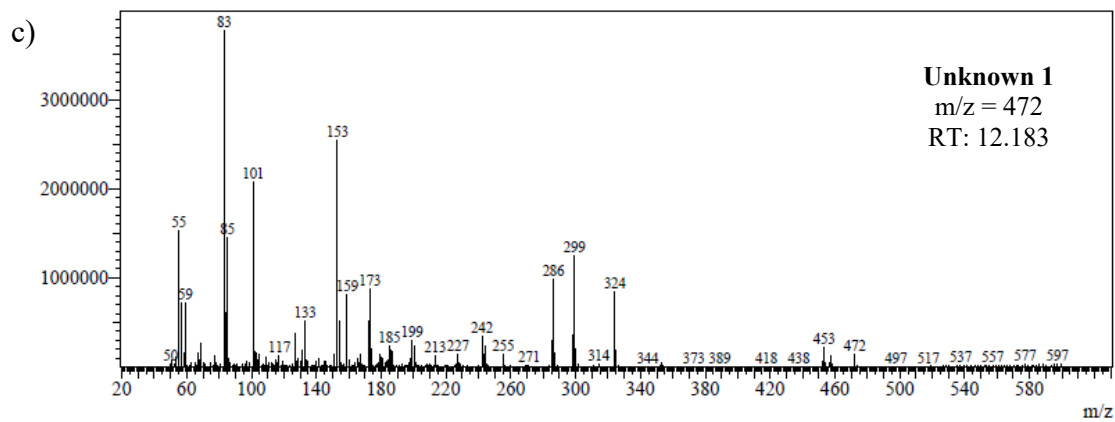
Figure S12. GC-MS chromatograms of product **3c** and pinBOBpin.



Line#1 R.Time:8.633(Scan#:1036)
 MassPeaks:413
 RawMode:Single 8.633(1036) BasePeak:153.95(13998804)
 BG Mode:None



Line#1 R.Time:12.183(Scan#:1462)
 MassPeaks:448
 RawMode:Single 12.183(1462) BasePeak:83.05(3770516)
 BG Mode:None



Line#:1 R.Time:12.258(Scan#:1471)
MassPeaks:446
RawMode:Single 12.258(1471) BasePeak:83.05(2612904)
BG Mode:None

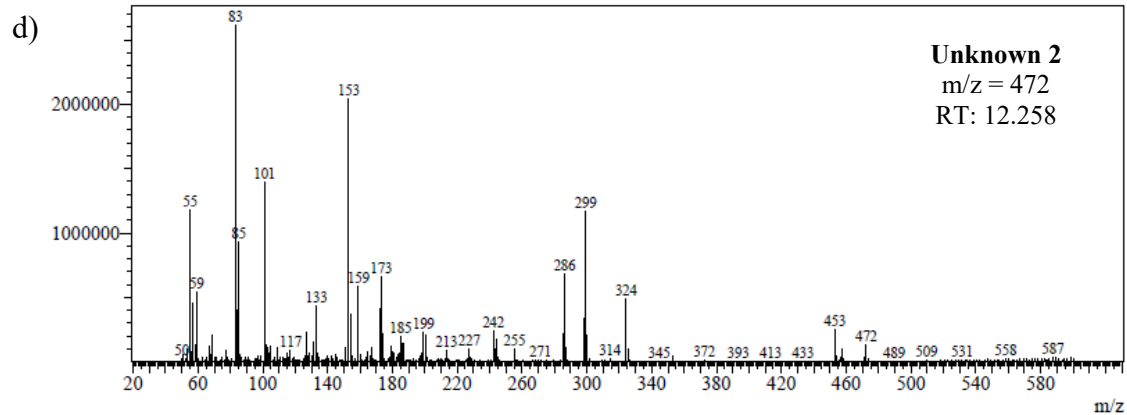
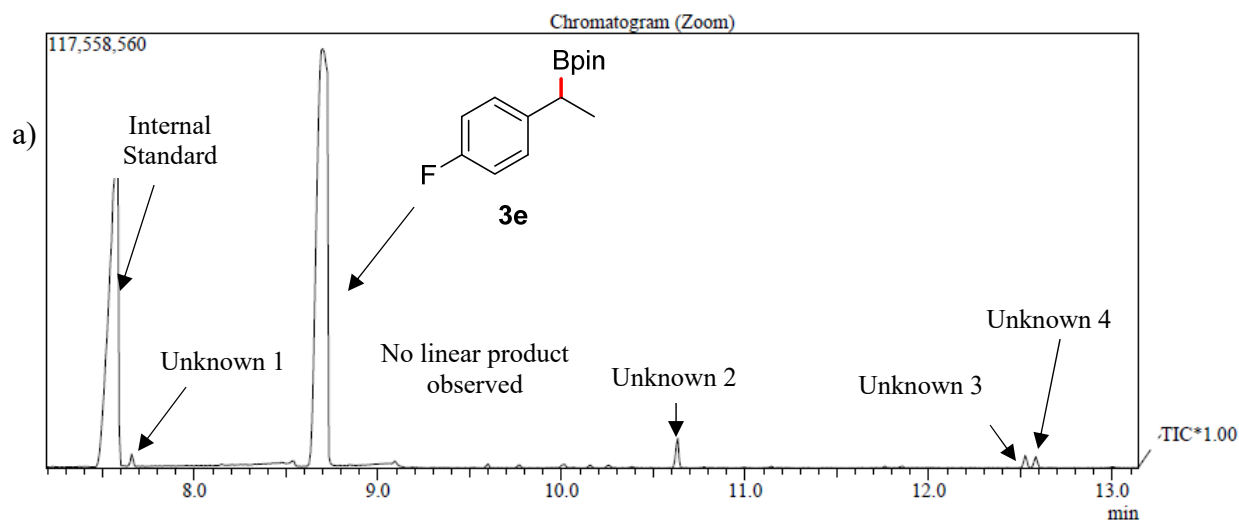
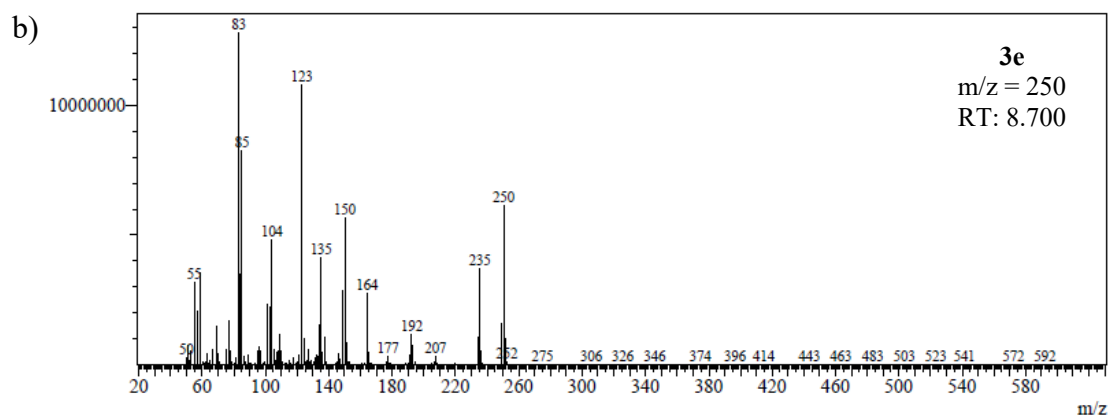


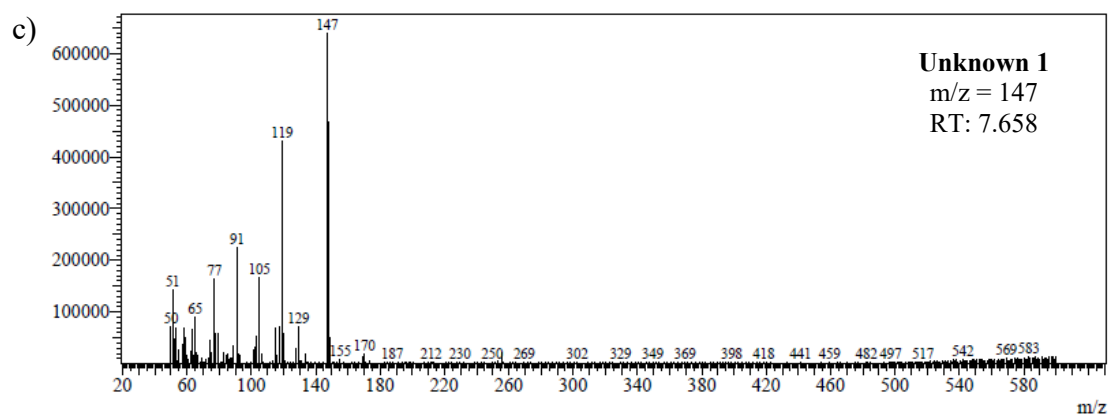
Figure S13. GC-MS chromatograms of product **3d** and 2 unknowns.



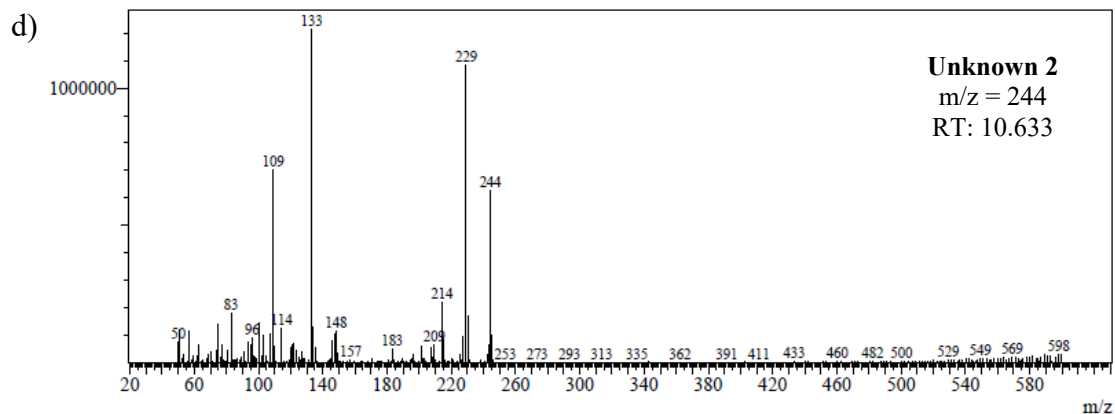
Line#1 R.Time:8.700(Scan#:1044)
 MassPeaks:411
 RawMode:Single 8.700(1044) BasePeak:83.05(12792463)
 BG Mode:None



Line#1 R.Time:7.658(Scan#:919)
 MassPeaks:453
 RawMode:Single 7.658(919) BasePeak:147.15(638476)
 BG Mode:None



Line#1 R.Time:10.633(Scan#:1276)
MassPeaks:410
RawMode:Single 10.633(1276) BasePeak:133.10(1212694)
BG Mode:None



Line#1 R.Time:12.525(Scan#:1503)
MassPeaks:408
RawMode:Single 12.525(1503) BasePeak:83.10(288981)
BG Mode:None

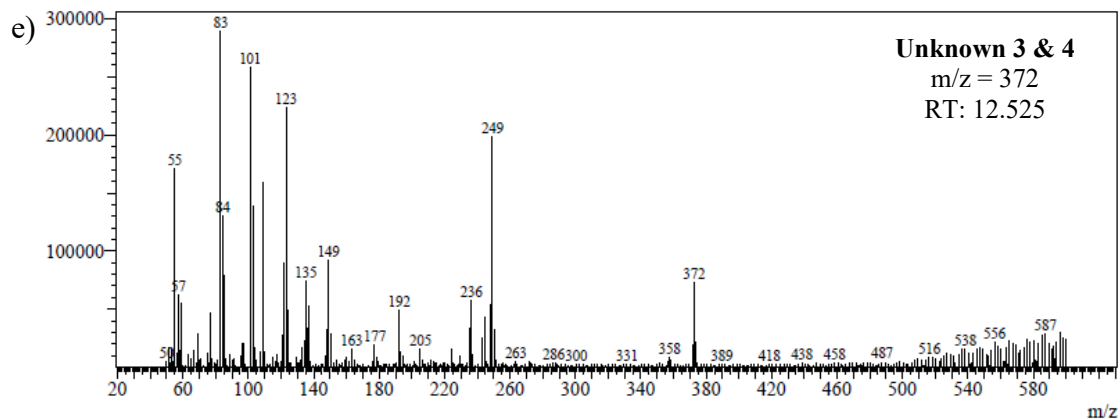
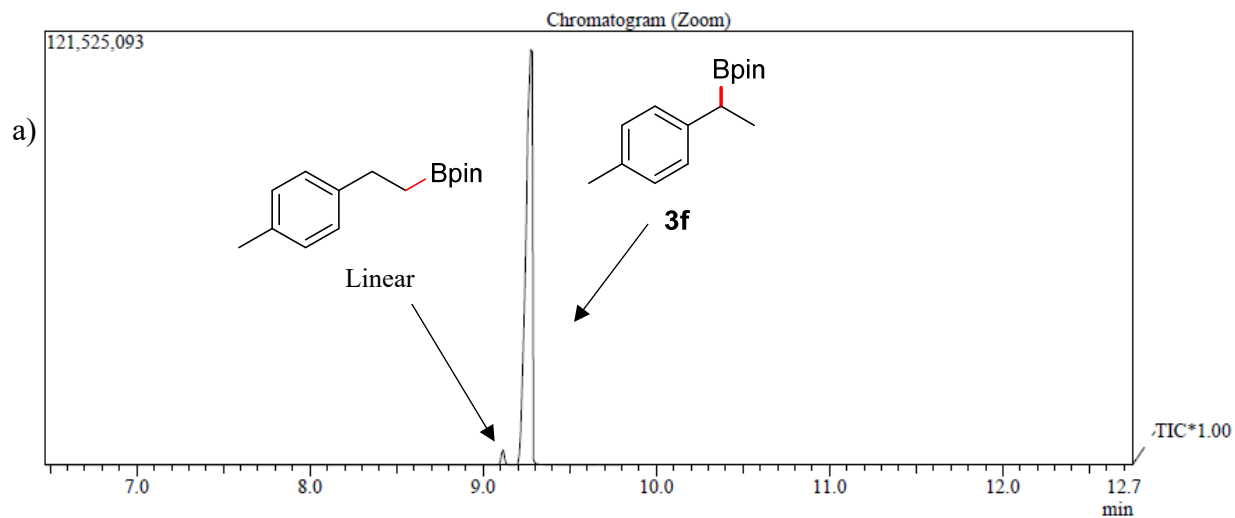
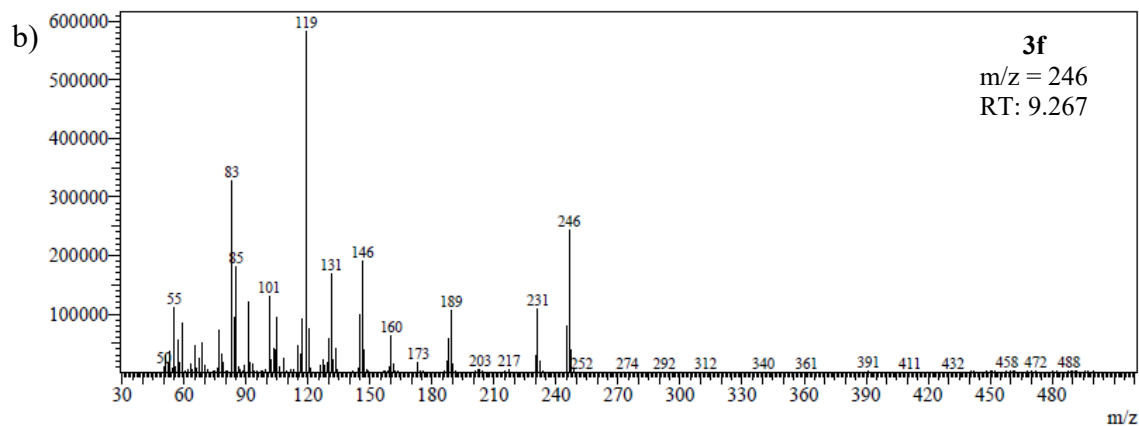


Figure S14. GC-MS chromatograms of product **3e** and several unknowns.



Line#1 R.Time:9.117(Scan#:975)
 MassPeaks:435
 RawMode:Single 9.117(975) BasePeak:119.00(582652)
 BG Mode:None



Line#1 R.Time:9.267(Scan#:993)
 MassPeaks:426
 RawMode:Single 9.267(993) BasePeak:119.15(11447471)
 BG Mode:None

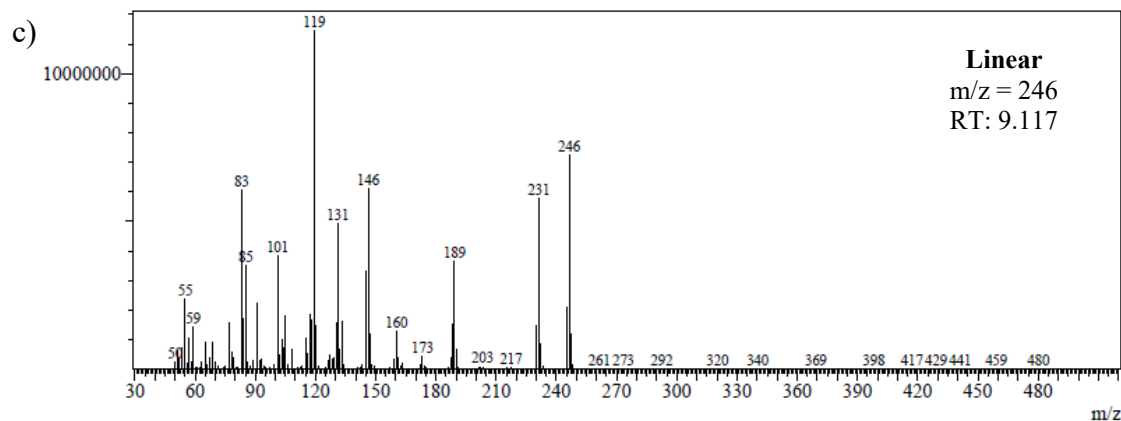
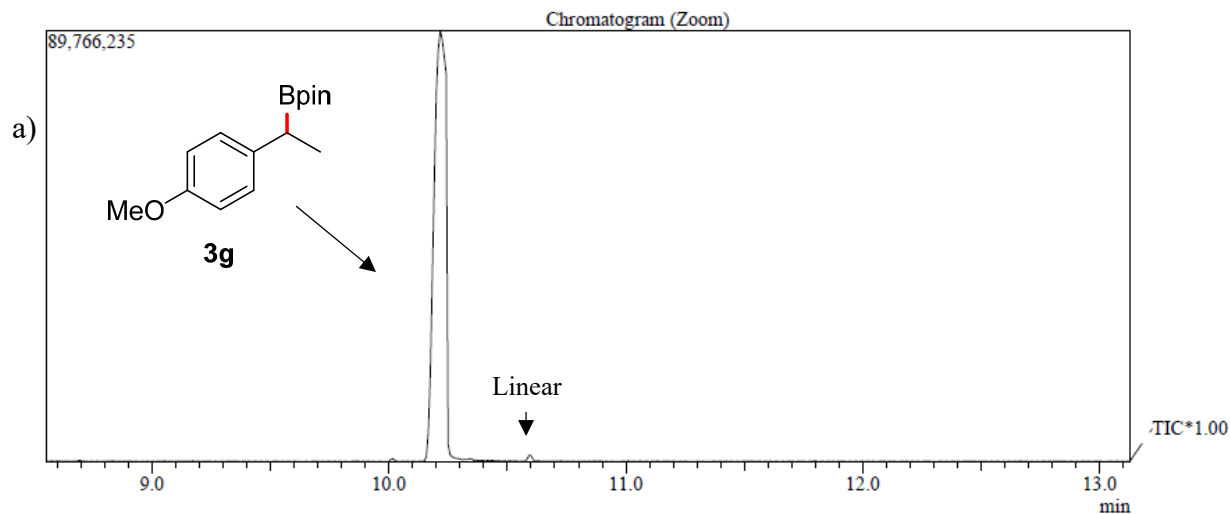
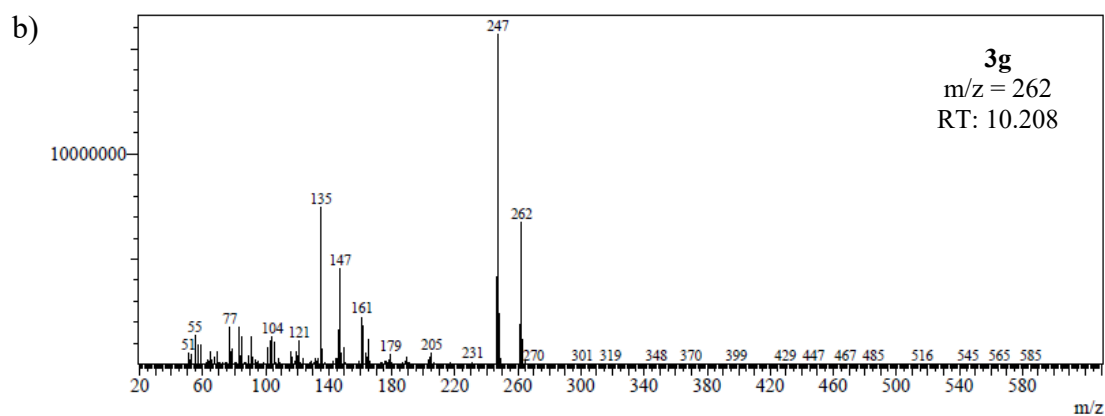


Figure S15. GC-MS chromatograms of product **3f** and linear isomer.



Line#:1 R.Time:10.208(Scan#:1225)
 MassPeaks:441
 RawMode:Single 10.208(1225) BasePeak:247.25(15673430)
 BG Mode:None



Line#:1 R.Time:10.600(Scan#:1272)
 MassPeaks:418
 RawMode:Single 10.600(1272) BasePeak:121.10(269142)
 BG Mode:None

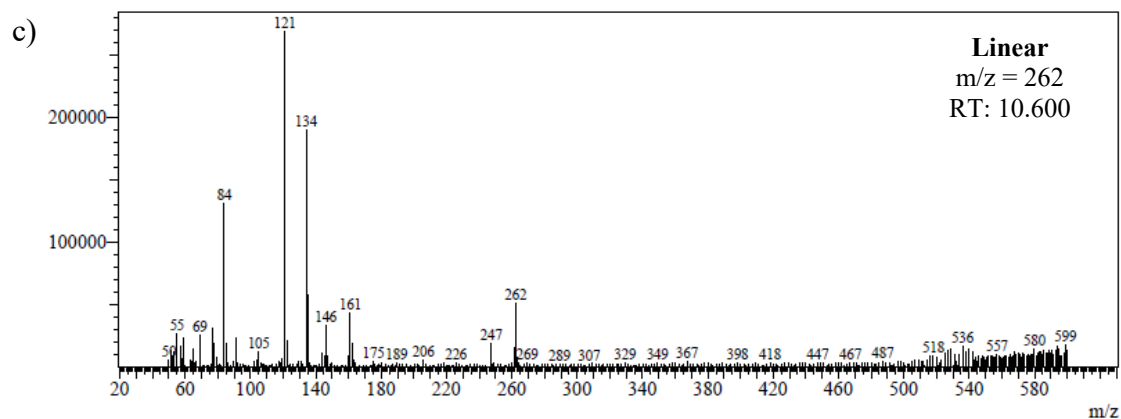
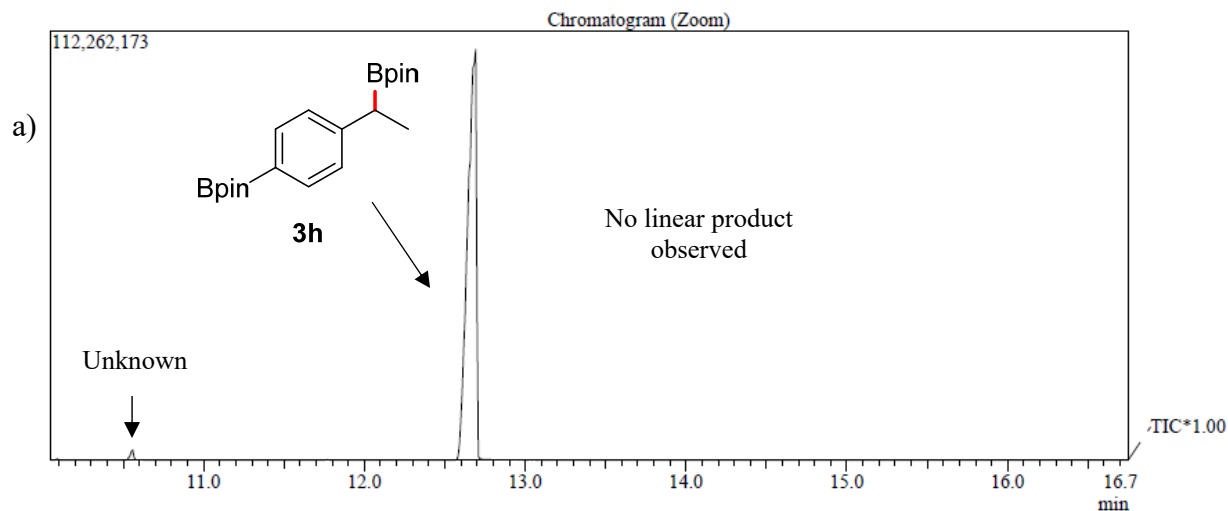
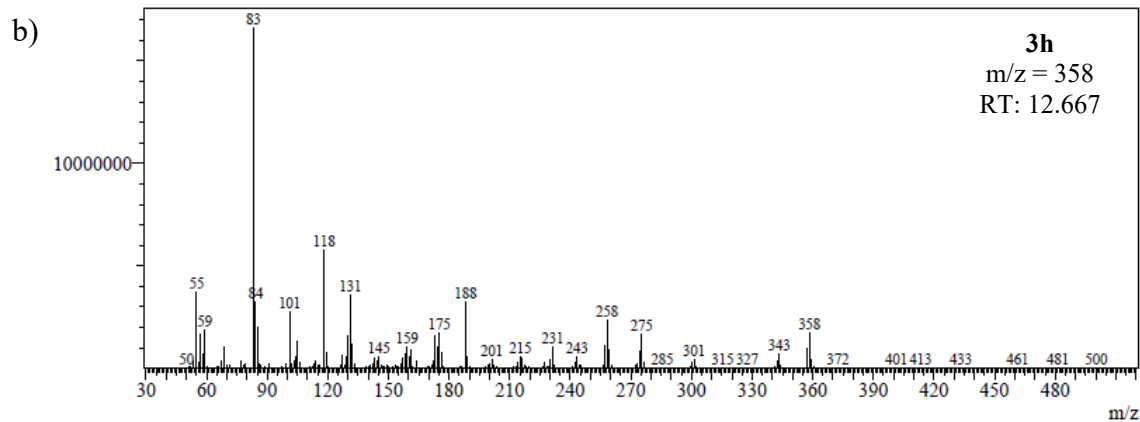


Figure S16. GC-MS chromatograms of product **3g** and linear isomer.



Line#:1 R.Time:12.667(Scan#:1401)
 MassPeaks:420
 RawMode:Single 12.667(1401) BasePeak:83.05(16606880)
 BG Mode:None



Line#:1 R.Time:10.550(Scan#:1147)
 MassPeaks:431
 RawMode:Single 10.550(1147) BasePeak:231.15(380656)
 BG Mode:None

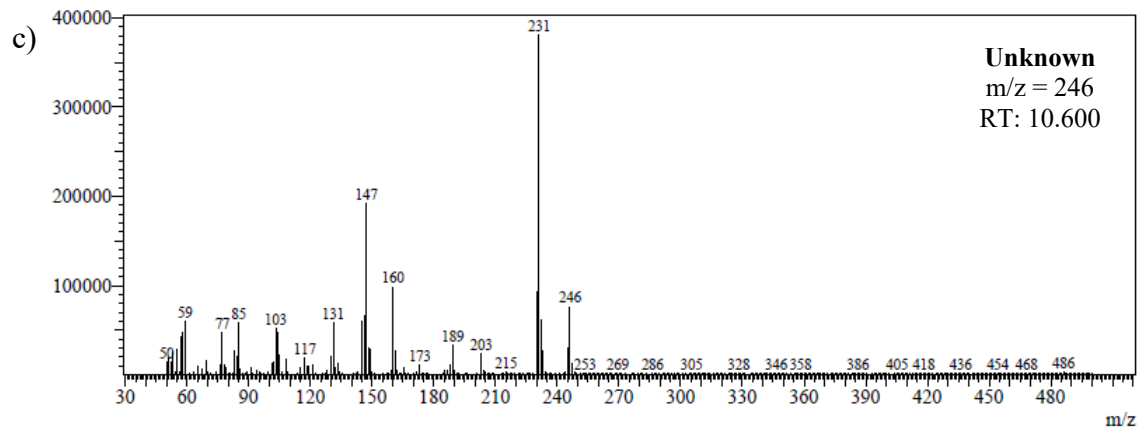
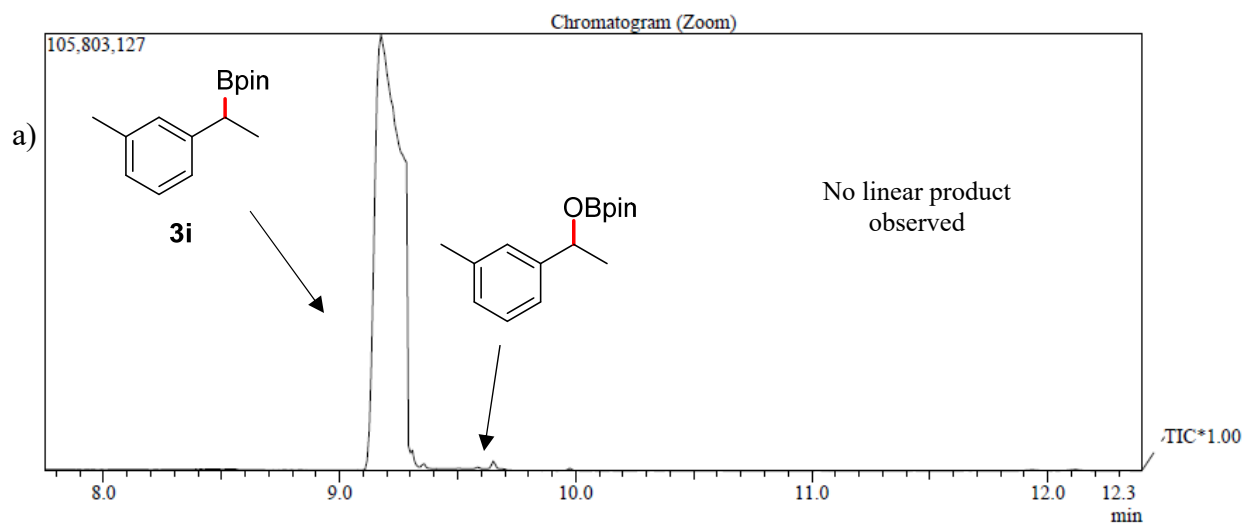
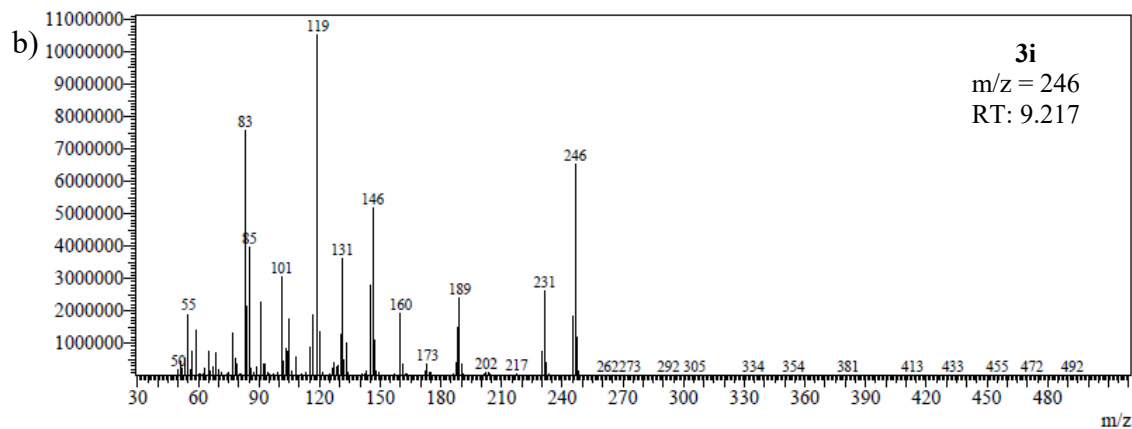


Figure S17. GC-MS chromatograms of product **3h** and an unknown.



Line#:1 R.Time:9.217(Scan#:1106)
 MassPeaks:423
 RawMode:Single 9.217(1106) BasePeak:118.95(10515452)
 BG Mode:None



Line#:1 R.Time:9.658(Scan#:1159)
 MassPeaks:430
 RawMode:Single 9.658(1159) BasePeak:84.00(316170)
 BG Mode:None

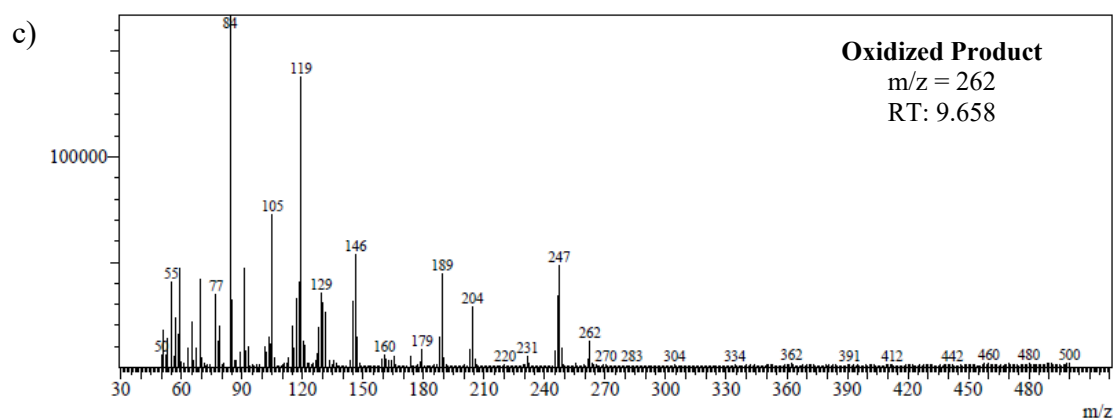
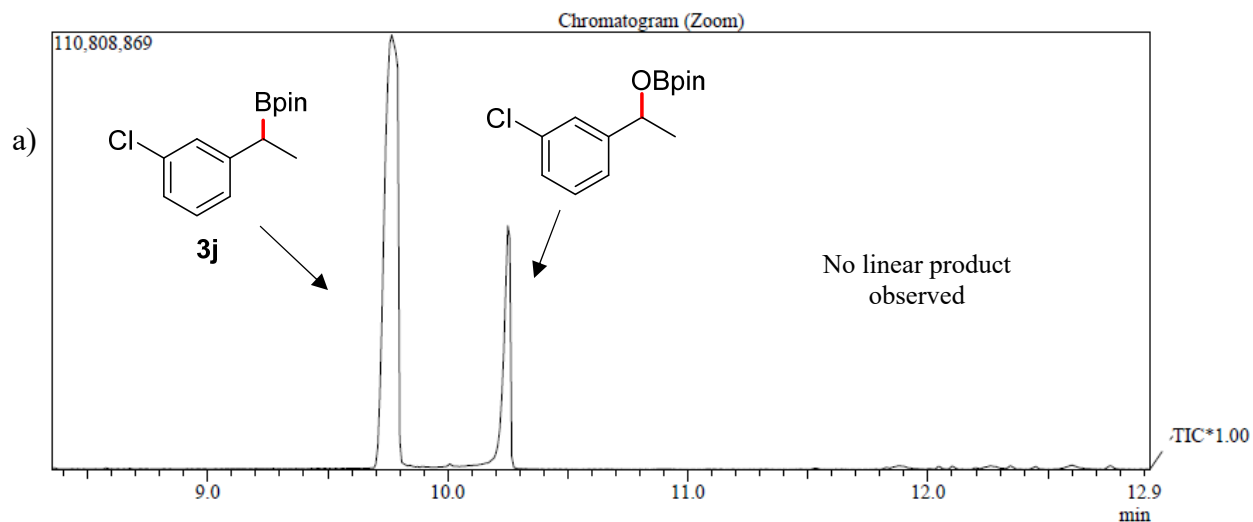
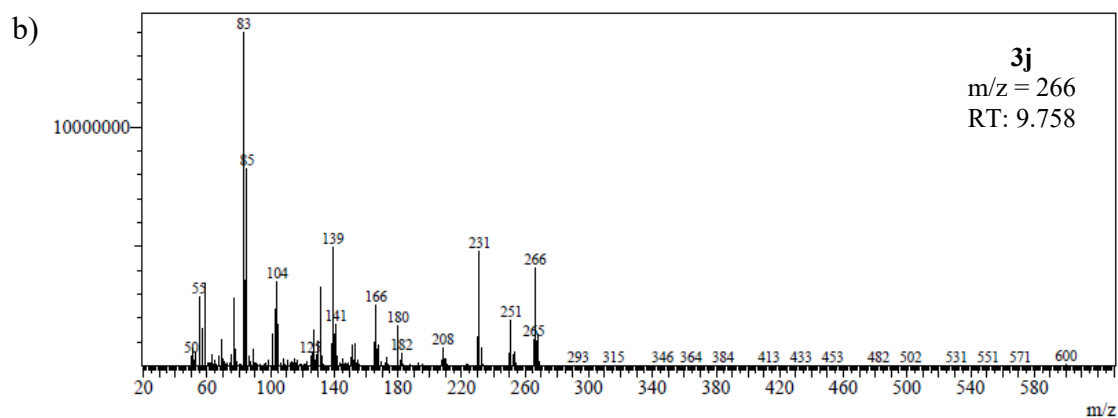


Figure S18. GC-MS chromatograms of product **3i** and oxidized product. Assignment of oxidized product is tentative.



Line#1 R.Time:9.758(Scan#:1171)
 MassPeaks:417
 RawMode:Single 9.758(1171) BasePeak:83.05(13964098)
 BG Mode:None



Line#1 R.Time:10.250(Scan#:1230)
 MassPeaks:421
 RawMode:Single 10.250(1230) BasePeak:138.95(6382807)
 BG Mode:None

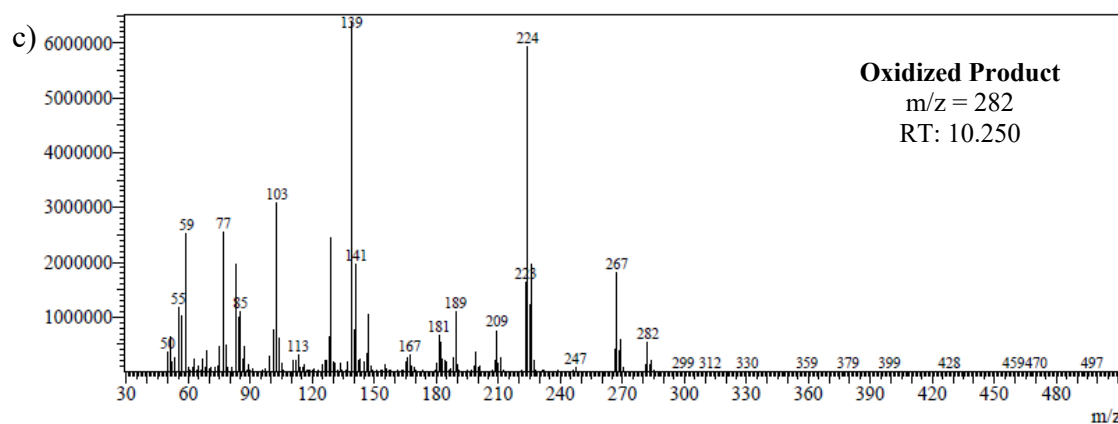
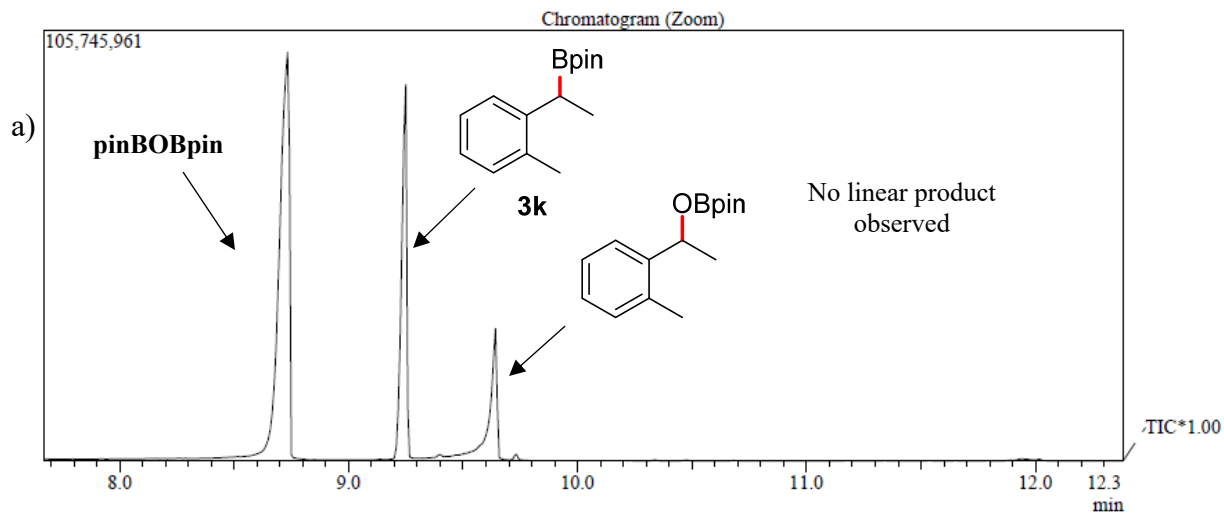
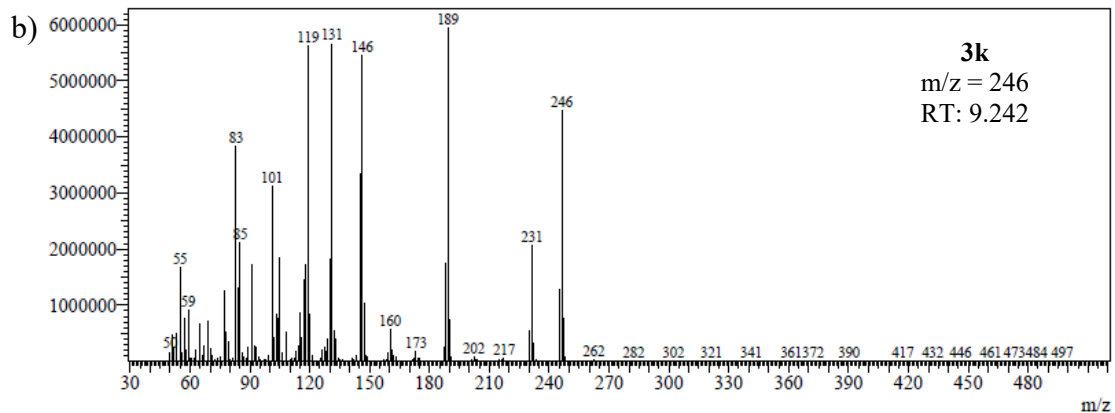


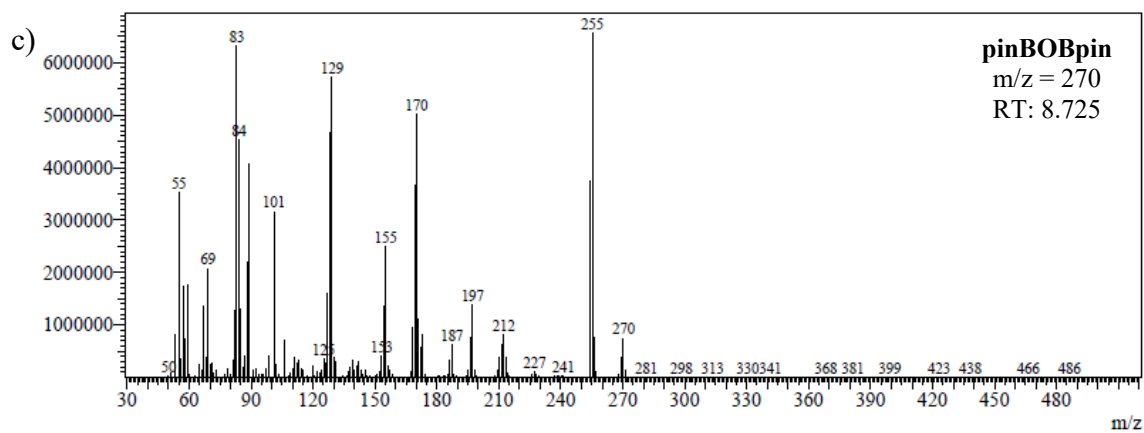
Figure S19. GC-MS chromatogram of product **3j** and oxidized product. Assignment of oxidized product is tentative.



Line#:1 R.Time:9.242(Scan#:1109)
 MassPeaks:434
 RawMode:Single 9.242(1109) BasePeak:189.20(5942153)
 BG Mode:None



Line#:1 R.Time:8.725(Scan#:1047)
 MassPeaks:427
 RawMode:Single 8.725(1047) BasePeak:255.20(6560777)
 BG Mode:None



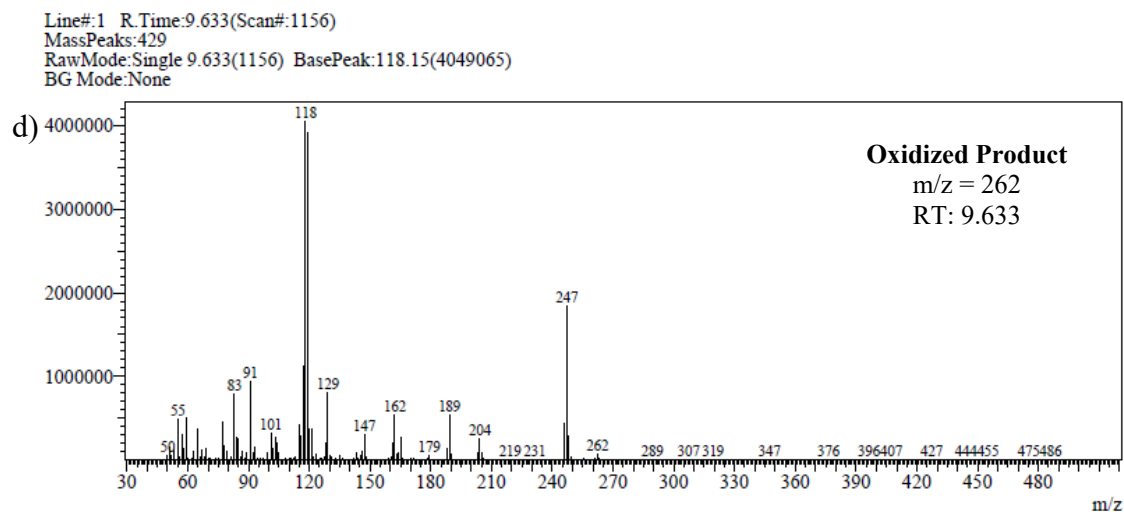
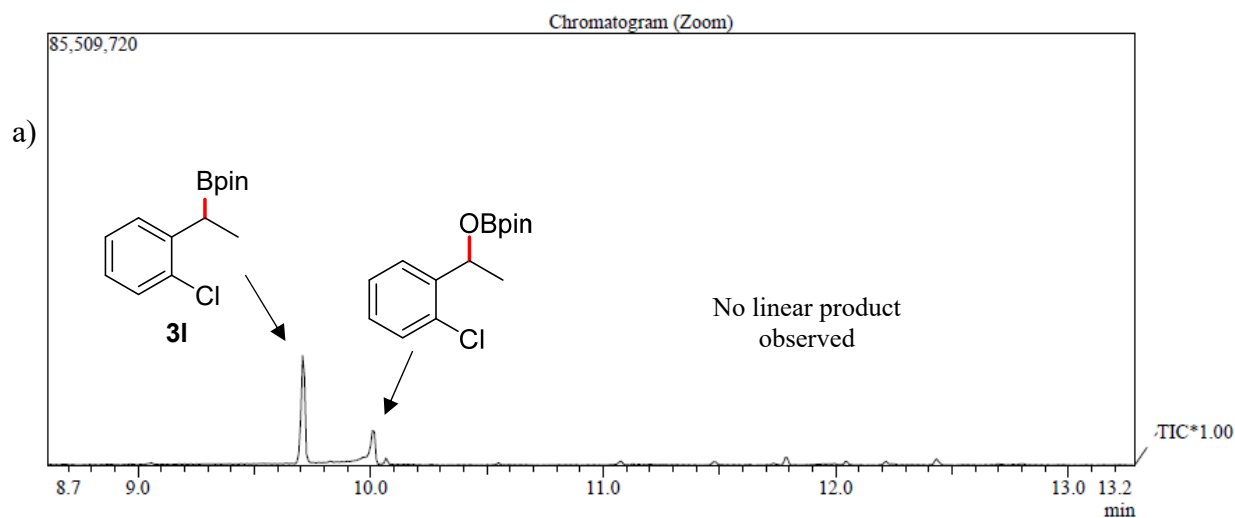
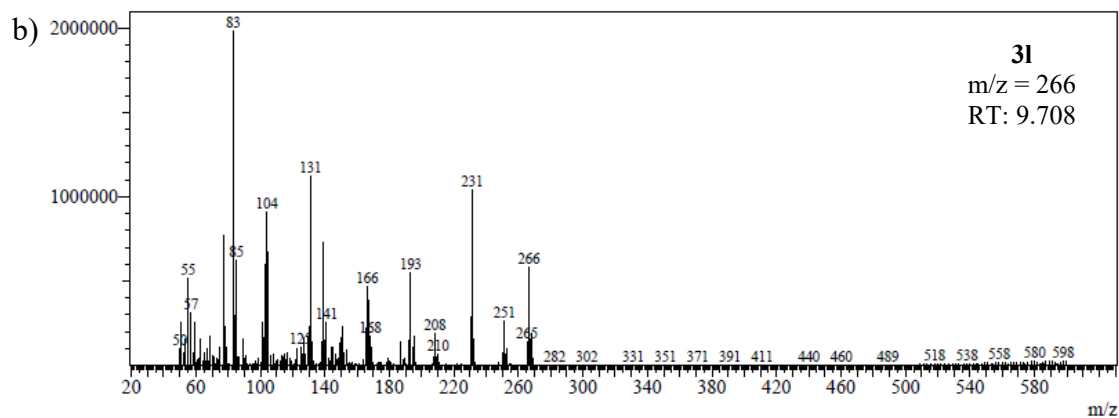


Figure S20. GC-MS chromatogram of product **3k**, pinBOBpin, and oxidized product. Assignment of oxidized product is tentative.



Line#1 R.Time:9.708(Scan#:1165)
 MassPeaks:431
 RawMode:Single 9.708(1165) BasePeak:83.05(1979955)
 BG Mode:None



Line#1 R.Time:10.008(Scan#:1201)
 MassPeaks:476
 RawMode:Single 10.008(1201) BasePeak:139.00(607436)
 BG Mode:None

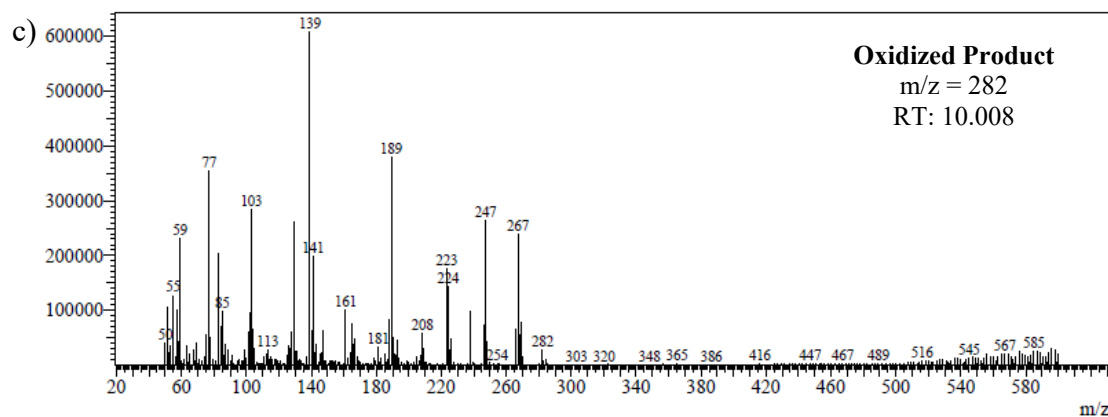


Figure S21. GC-MS chromatograms of product **3I** and oxidized product. Assignment of oxidized product is tentative.

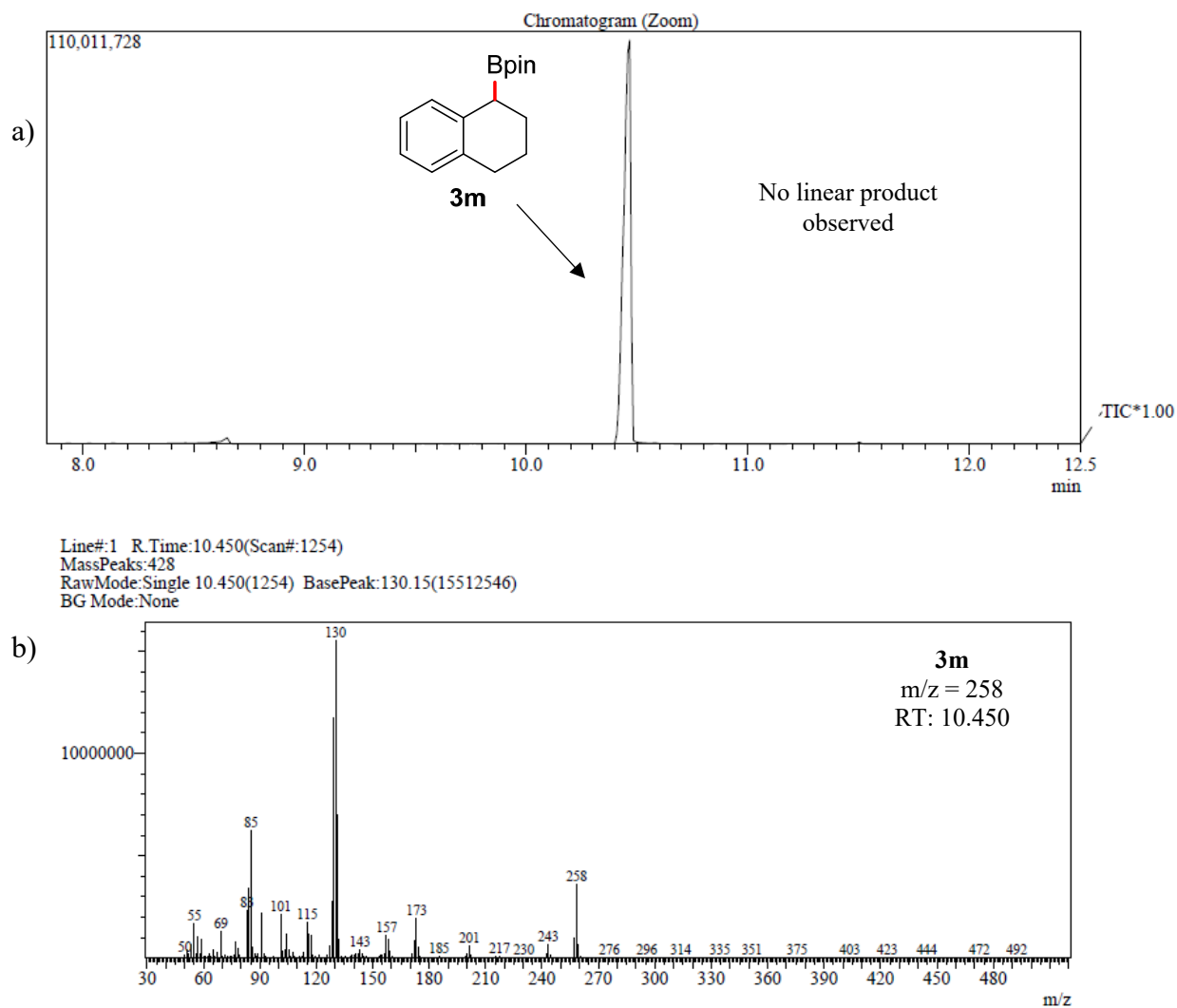
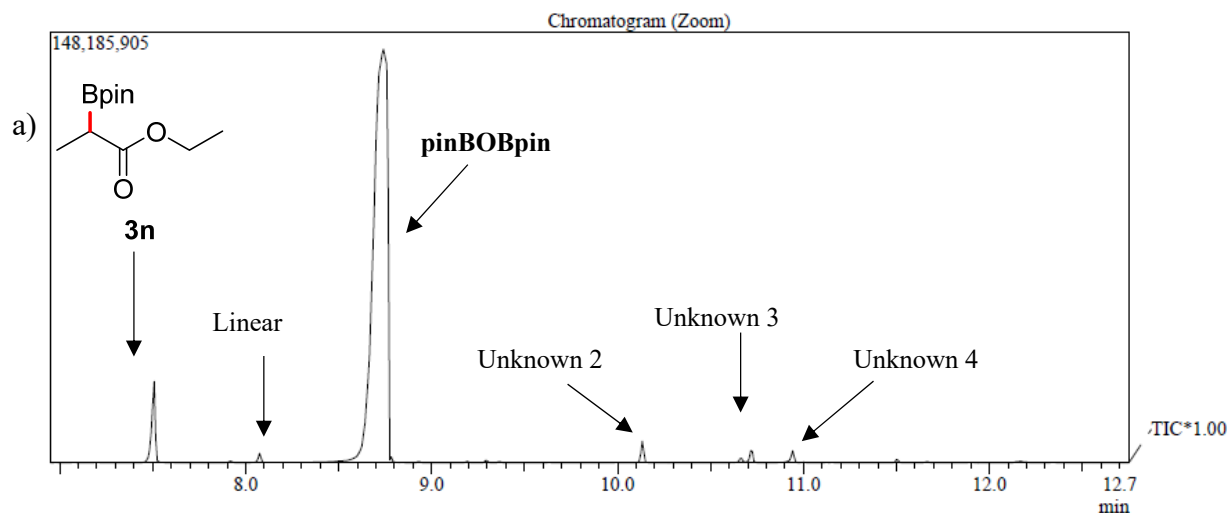
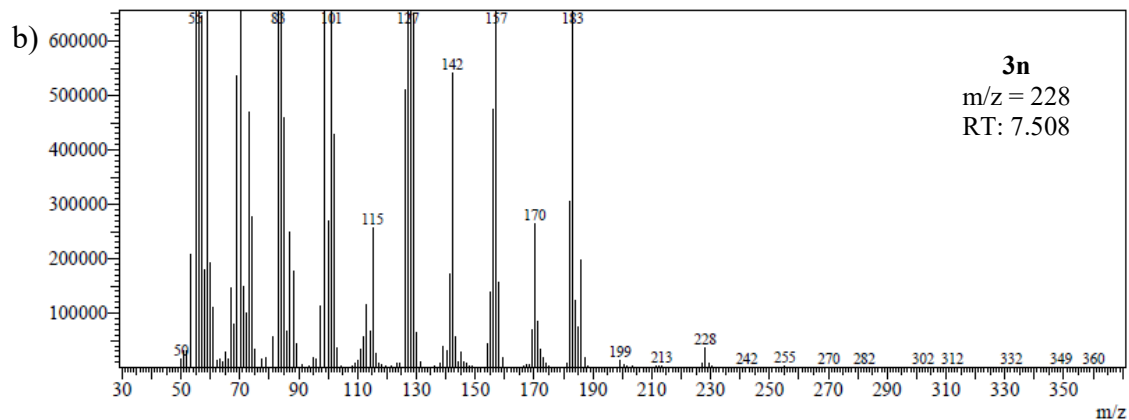


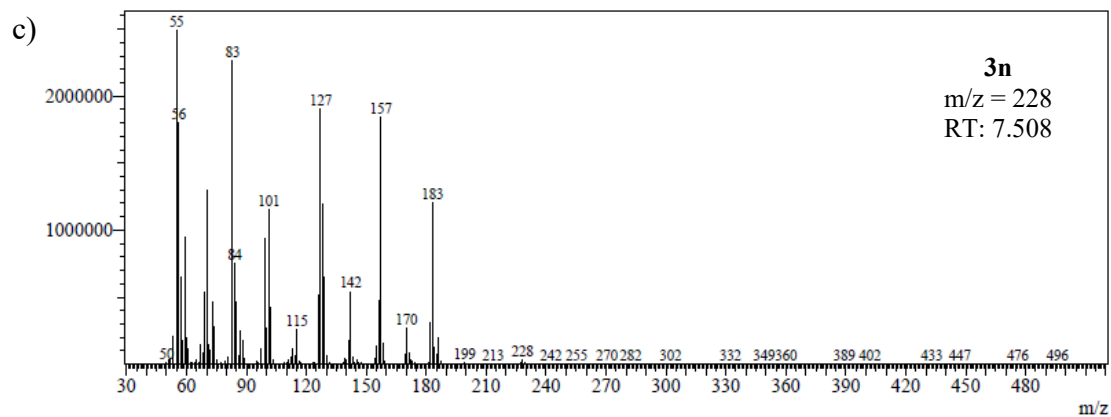
Figure S22. GC-MS chromatograms of product **3m**.



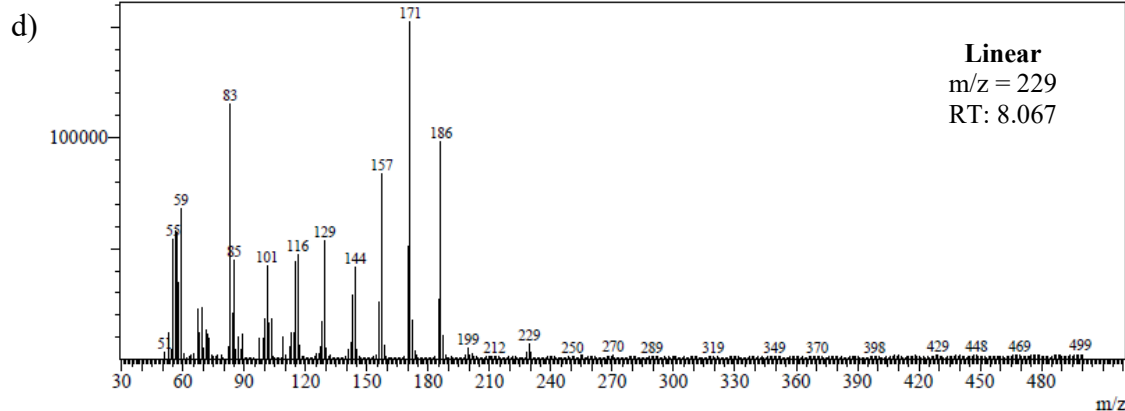
Line#:1 R.Time:7.508(Scan#:782)
 MassPeaks:437
 RawMode:Single 7.508(782) BasePeak:55.00(2489137)
 BG Mode:None



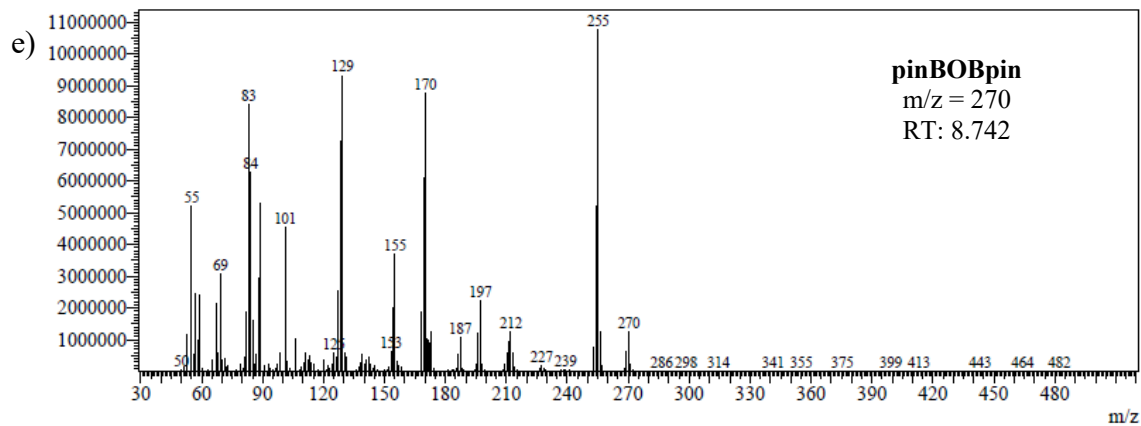
Line#:1 R.Time:7.508(Scan#:782)
 MassPeaks:437
 RawMode:Single 7.508(782) BasePeak:55.00(2489137)
 BG Mode:None



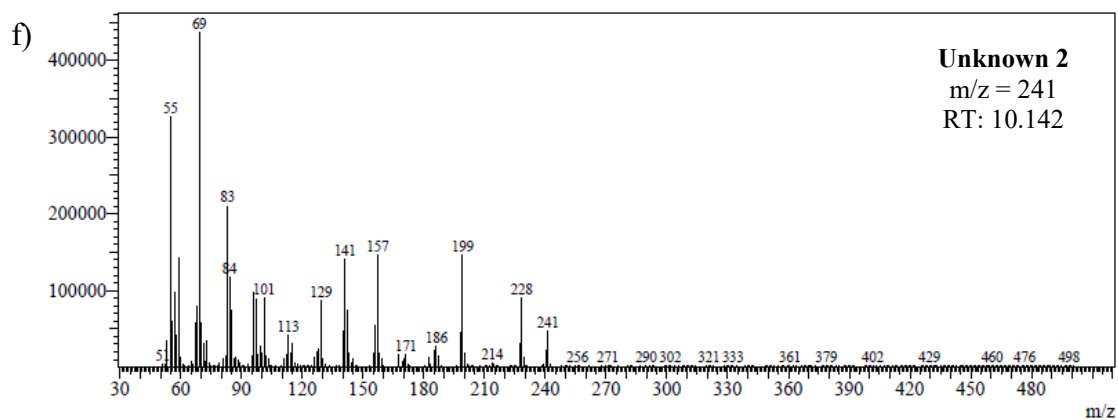
Line#1 R.Time:8.067(Scan#:849)
MassPeaks:438
RawMode:Single 8.067(849) BasePeak:171.20(152277)
BG Mode:None



Line#1 R.Time:8.742(Scan#:930)
MassPeaks:425
RawMode:Single 8.742(930) BasePeak:255.20(10760149)
BG Mode:None



Line#1 R.Time:10.142(Scan#:1098)
MassPeaks:435
RawMode:Single 10.142(1098) BasePeak:69.10(436505)
BG Mode:None



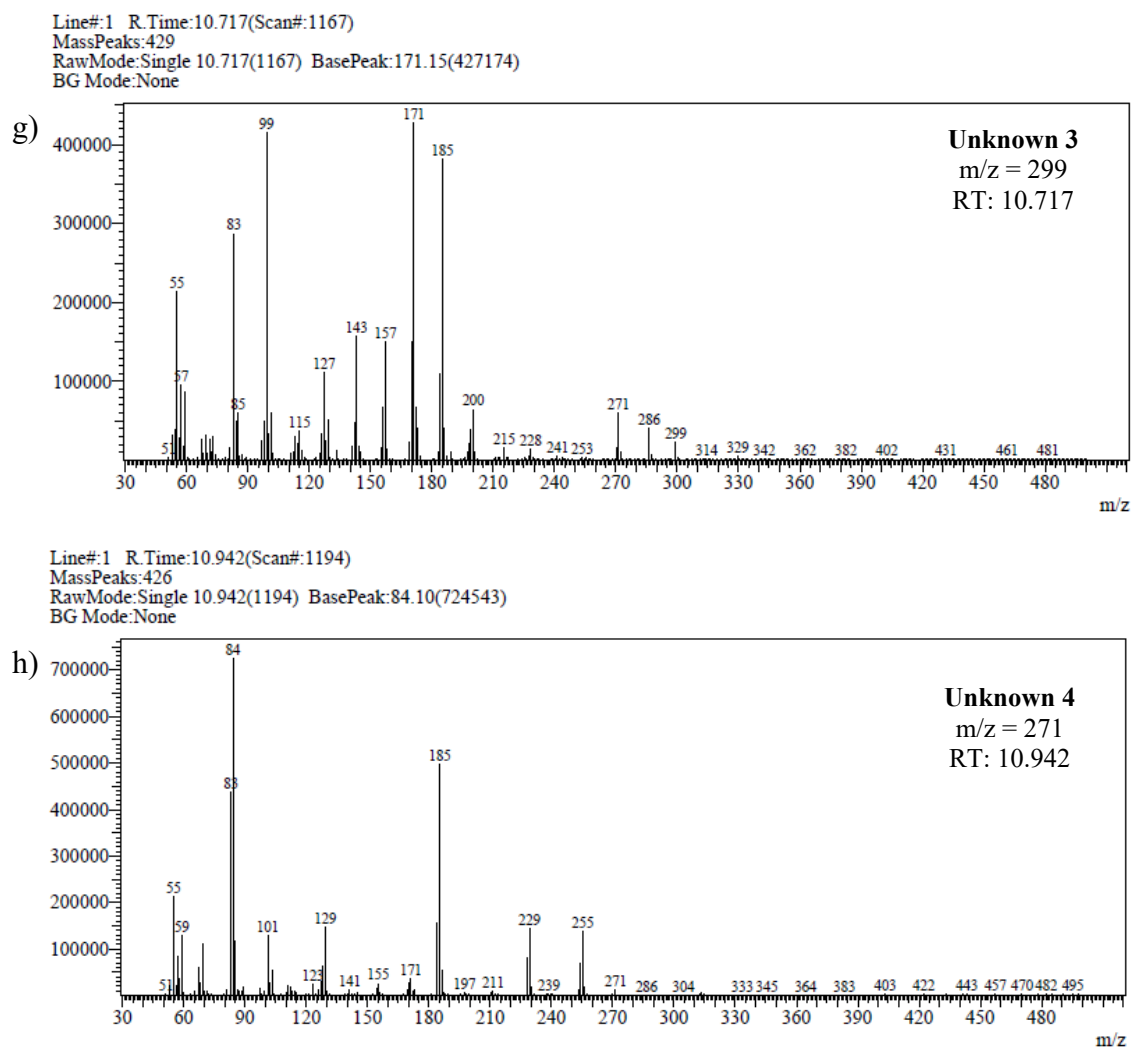
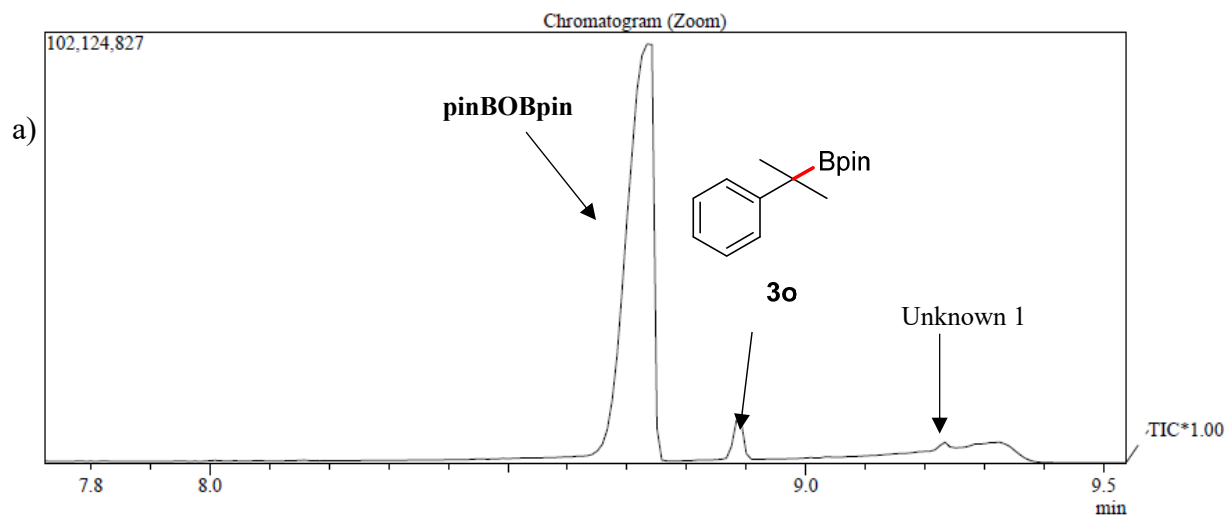
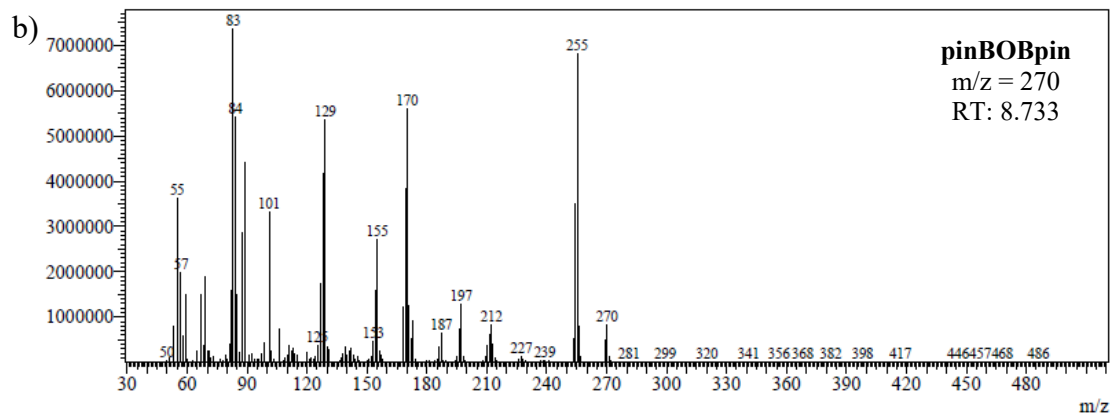


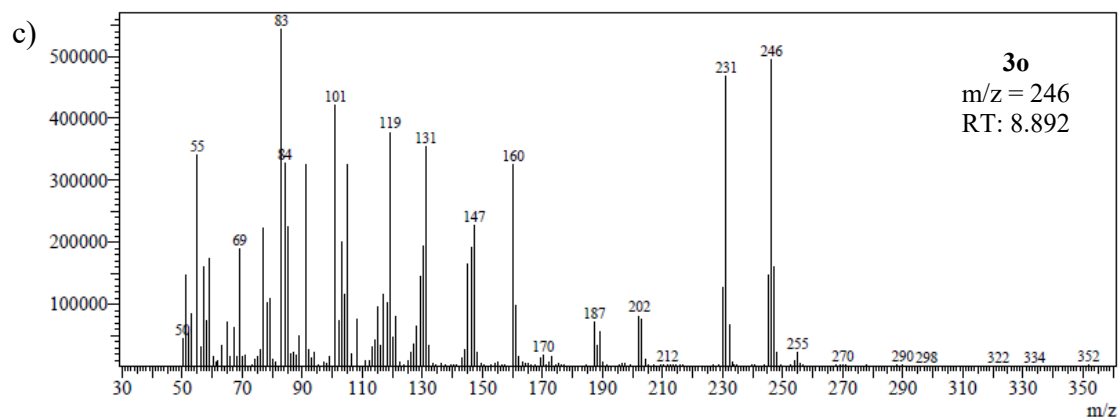
Figure S23. GC-MS chromatograms of product **3n**, linear isomer, pinBOBpin, and unknowns.



Line#:1 R.Time:8.733(Scan#:1048)
 MassPeaks:326
 RawMode:Single 8.733(1048) BasePeak:83.10(7360378)
 BG Mode:Averaged 8.150-8.650(978-1038)



Line#:1 R.Time:8.892(Scan#:1067)
 MassPeaks:429
 RawMode:Single 8.892(1067) BasePeak:83.05(543948)
 BG Mode:None



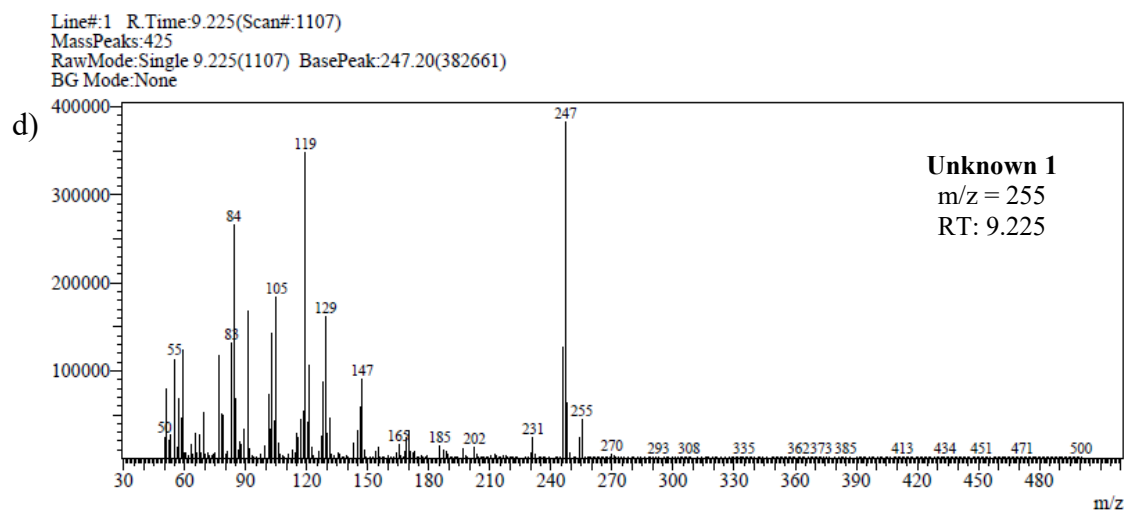
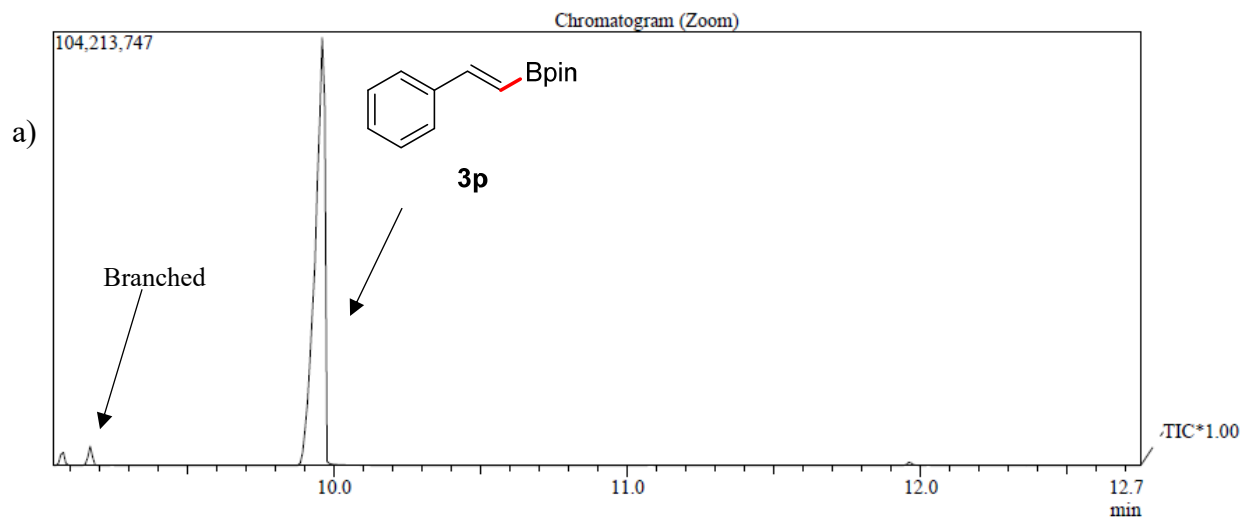
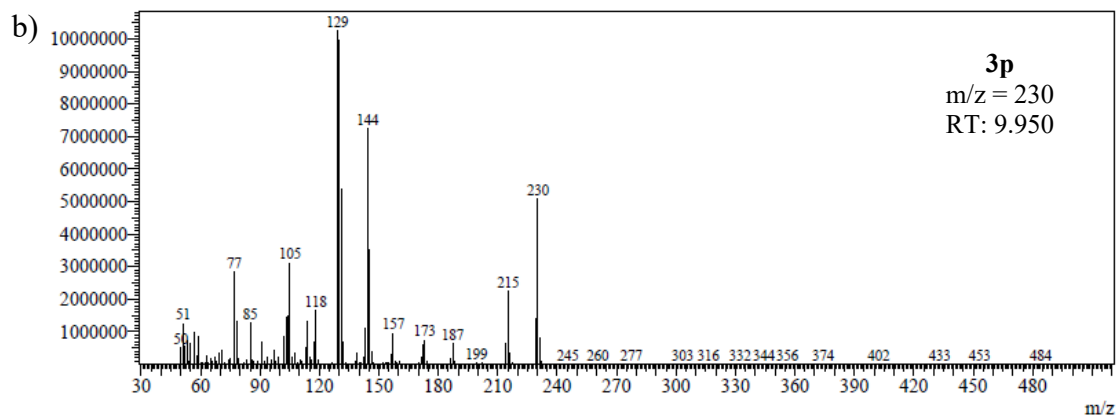


Figure S24. GC-MS chromatograms of product **3o**, pinBOBpin, and an unknown.



Line#:1 R.Time:9.950(Scan#:1075)
 MassPeaks:429
 RawMode:Single 9.950(1075) BasePeak:129.05(10247794)
 BG Mode:None



Line#:1 R.Time:9.167(Scan#:981)
 MassPeaks:435
 RawMode:Single 9.167(981) BasePeak:129.15(450981)
 BG Mode:None

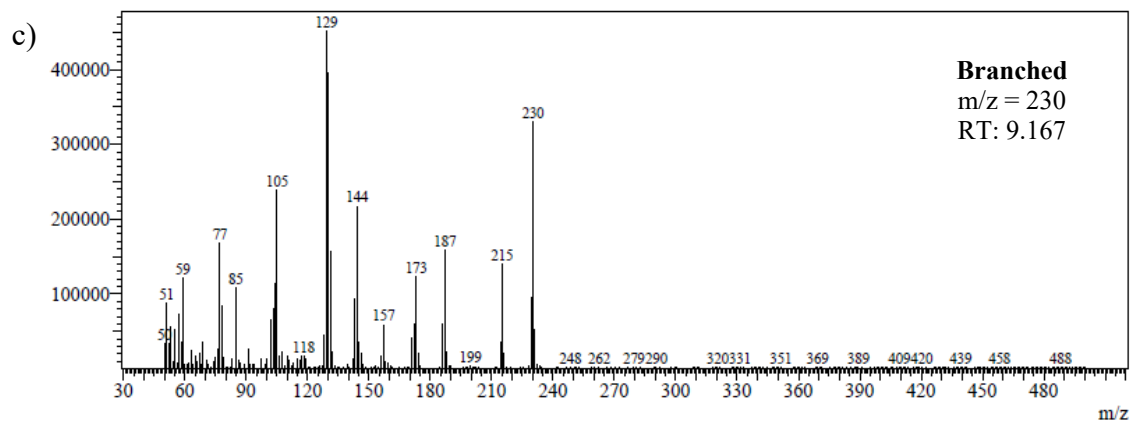
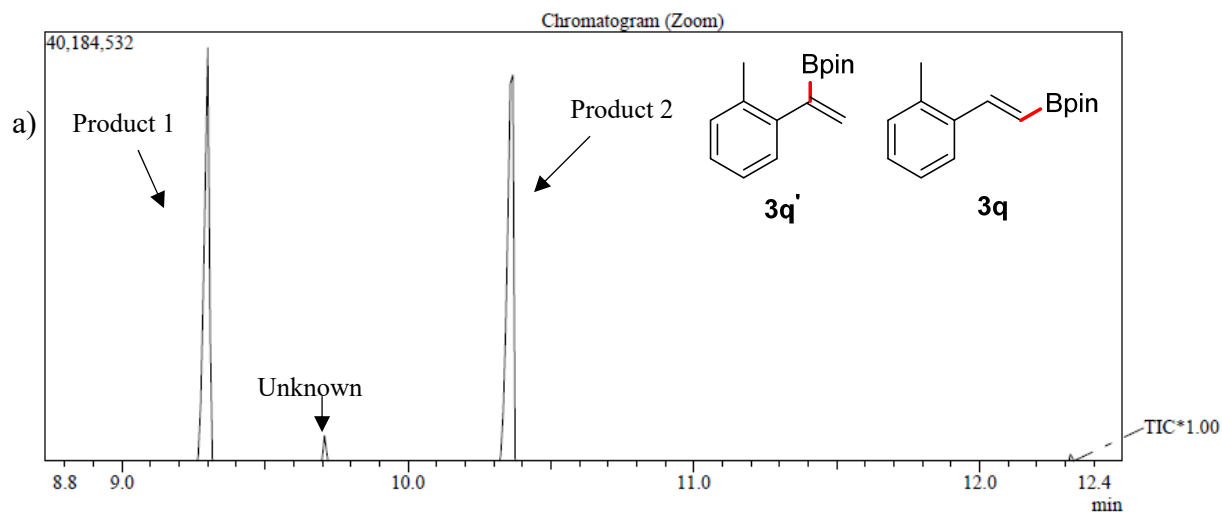
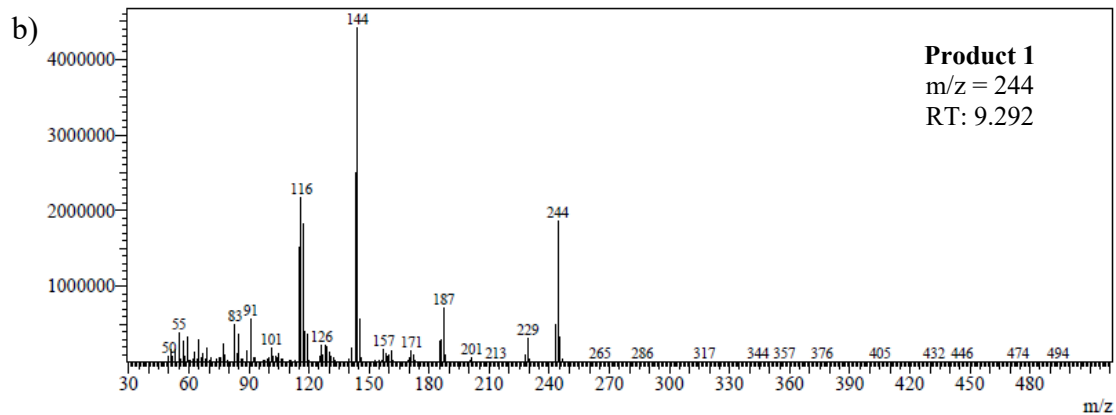


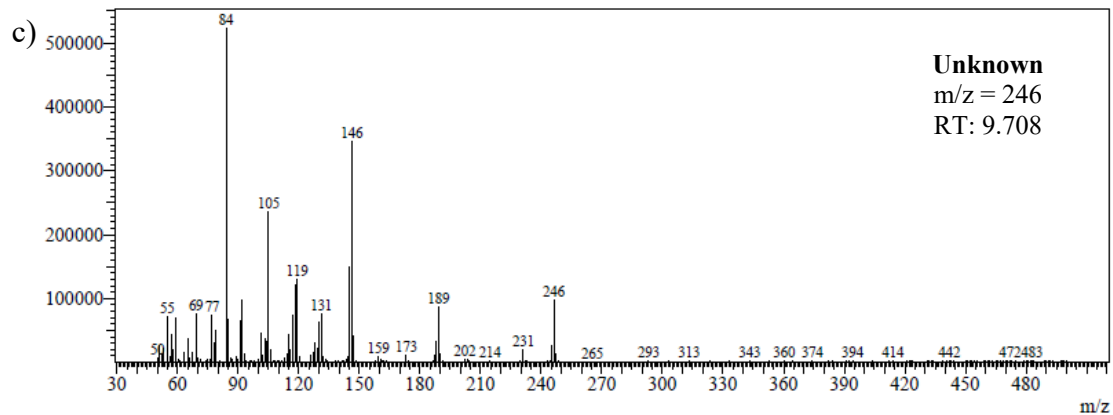
Figure S25. GC-MS chromatograms of product **3p** and branched isomer.



Line#1 R.Time:9.292(Scan#:996)
 MassPeaks:433
 RawMode:Single 9.292(996) BasePeak:144.15(4411612)
 BG Mode:None



Line#1 R.Time:9.708(Scan#:1046)
 MassPeaks:437
 RawMode:Single 9.708(1046) BasePeak:84.00(522551)
 BG Mode:None



Line#:1 R.Time:10.358(Scan#:1124)
MassPeaks:435
RawMode:Single 10.358(1124) BasePeak:144.15(5498231)
BG Mode:None

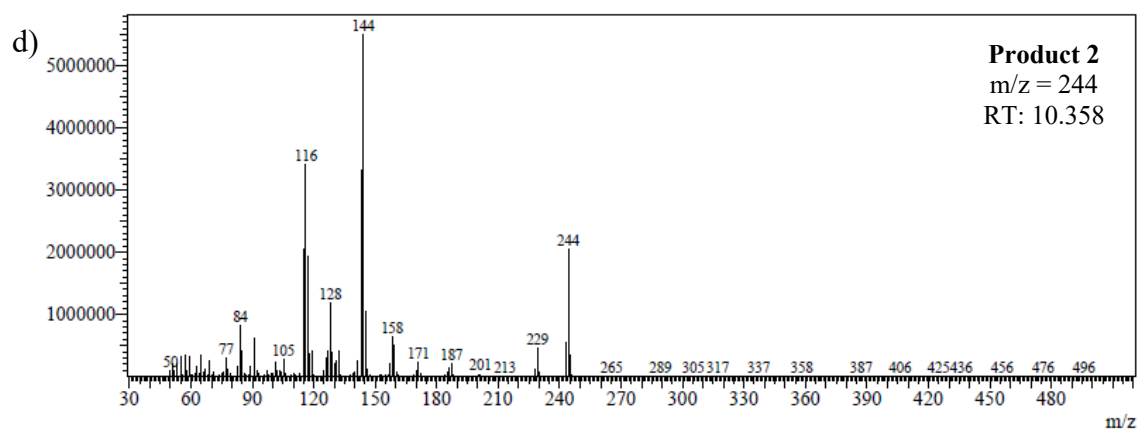
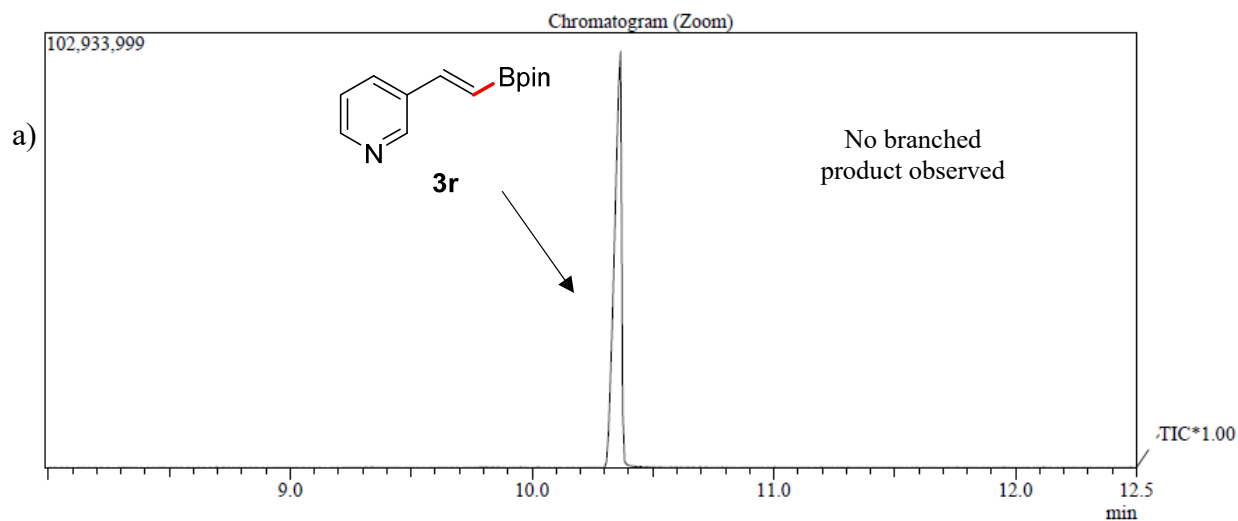


Figure S26. GC-MS chromatograms of product **3q**, **3q'**, an isomer, and an unknown.



Line#:1 R.Time:10.358(Scan#:1243)
 MassPeaks:424
 RawMode:Single 10.358(1243) BasePeak:132.10(9820971)
 BG Mode:None

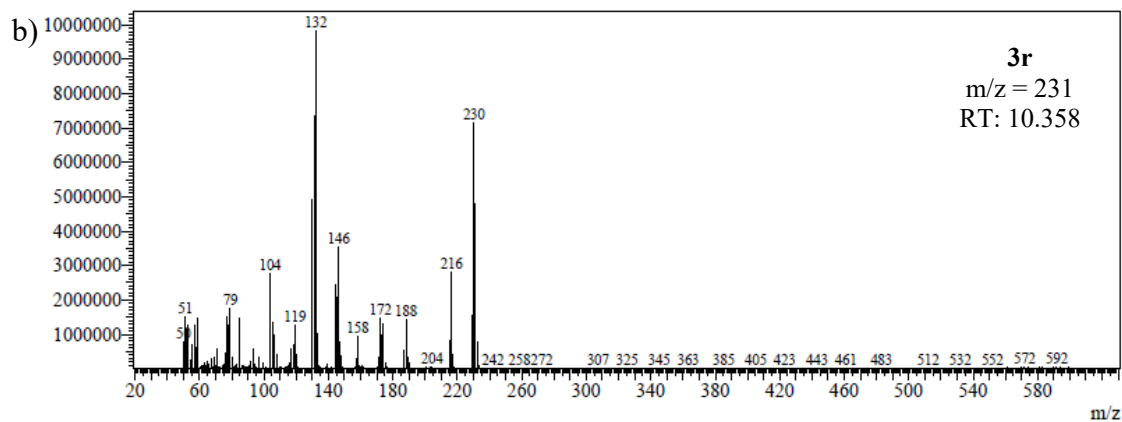
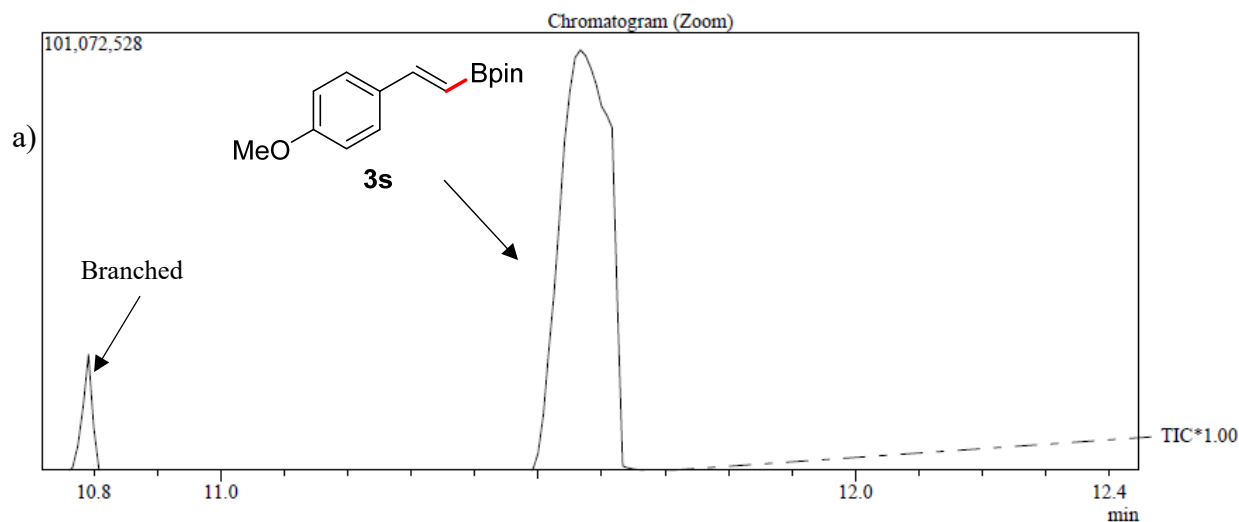
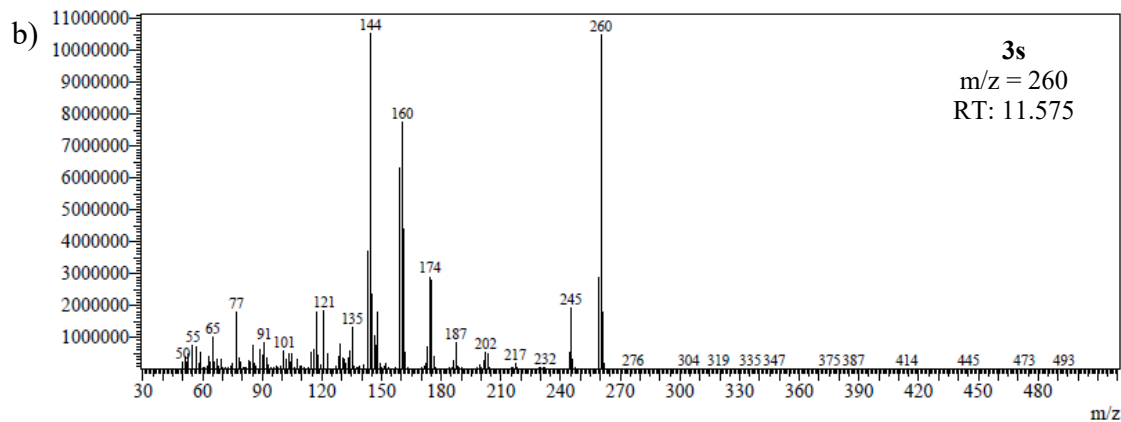


Figure S27. GC-MS chromatograms of product **3r**.



Line#1 R.Time:11.575(Scan#:1389)
 MassPeaks:430
 RawMode:Single 11.575(1389) BasePeak:144.15(10527417)
 BG Mode:None



Line#1 R.Time:10.792(Scan#:1295)
 MassPeaks:433
 RawMode:Single 10.792(1295) BasePeak:260.20(4005936)
 BG Mode:None

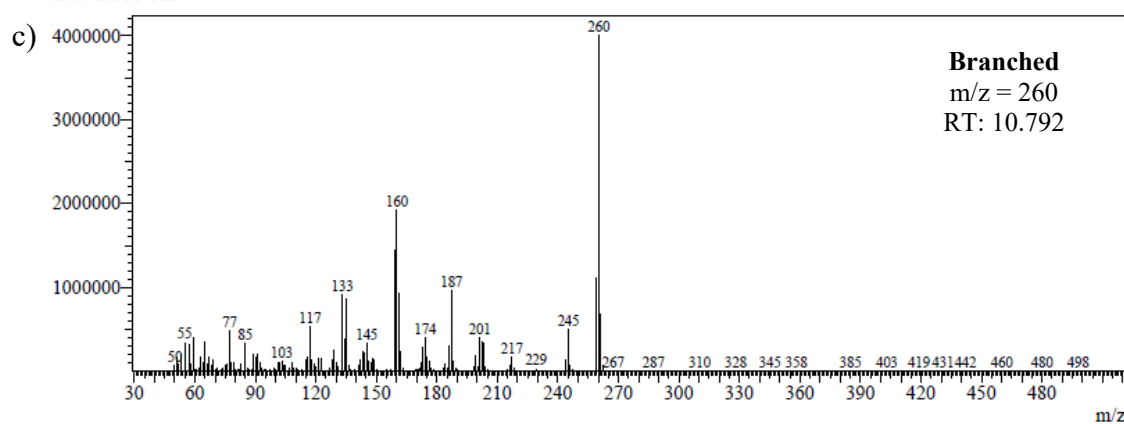
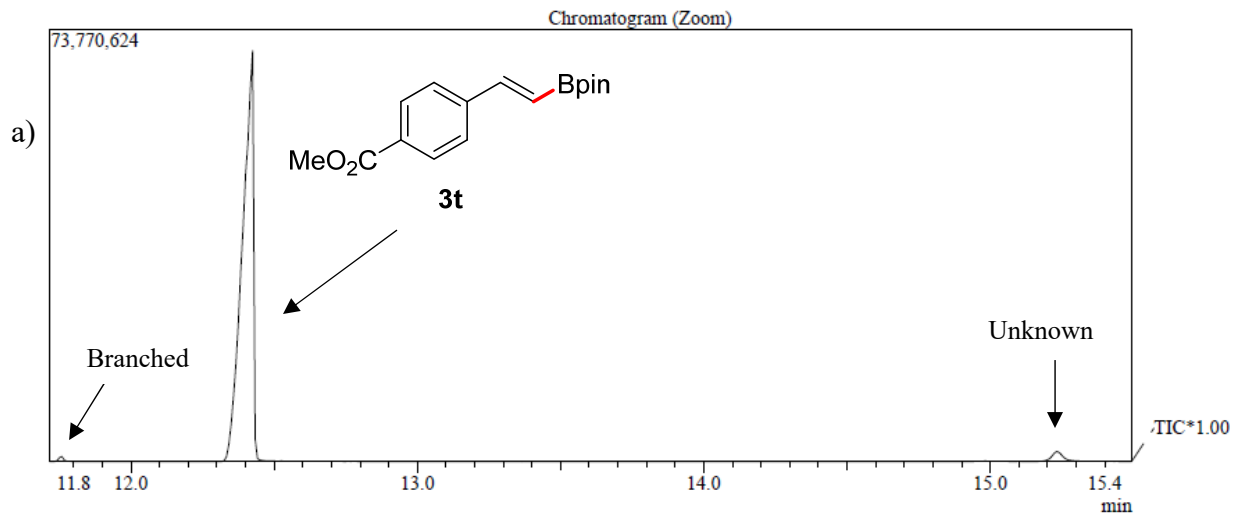
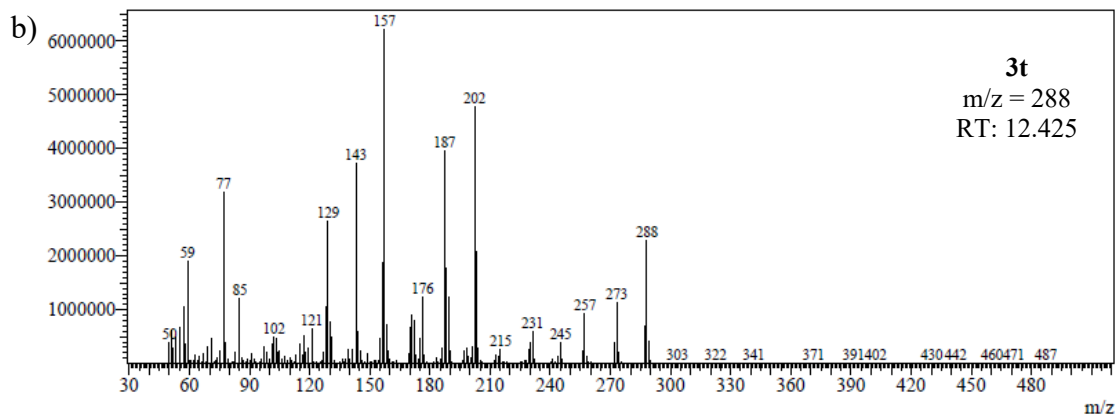


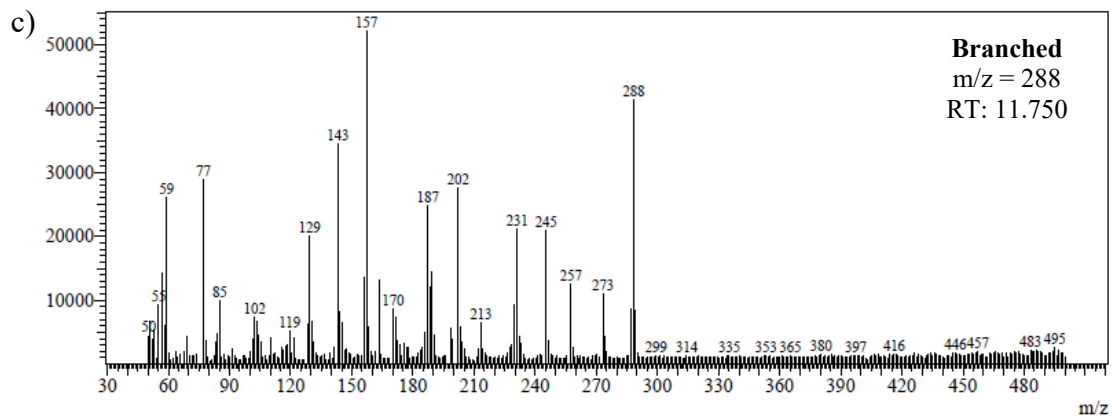
Figure S28. GC-MS chromatograms of product **3s** and an isomer.



Line#1 R.Time:12.425(Scan#:1372)
 MassPeaks:429
 RawMode:Single 12.425(1372) BasePeak:157.10(6212676)
 BG Mode:None



Line#1 R.Time:11.750(Scan#:1291)
 MassPeaks:432
 RawMode:Single 11.750(1291) BasePeak:157.15(52128)
 BG Mode:None



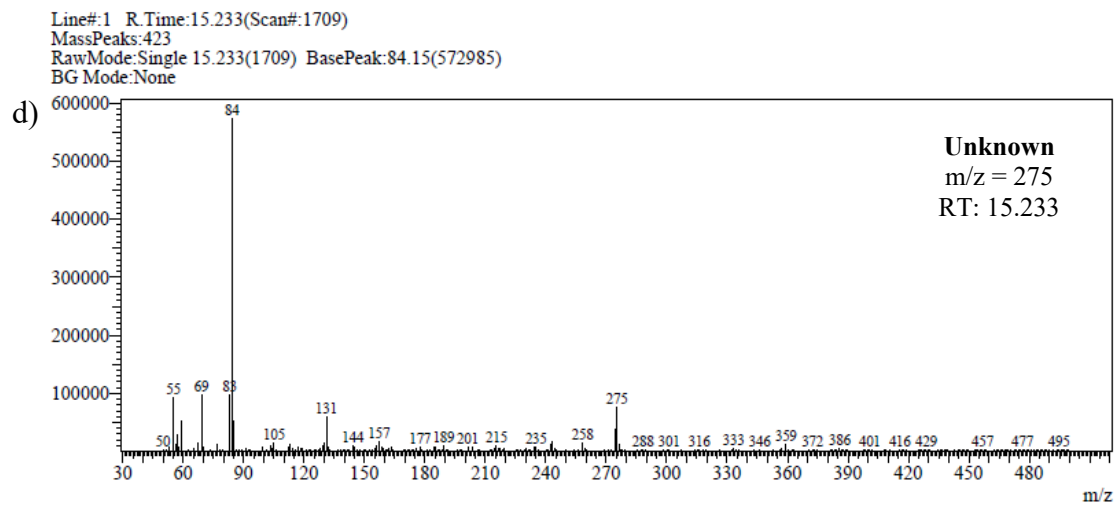
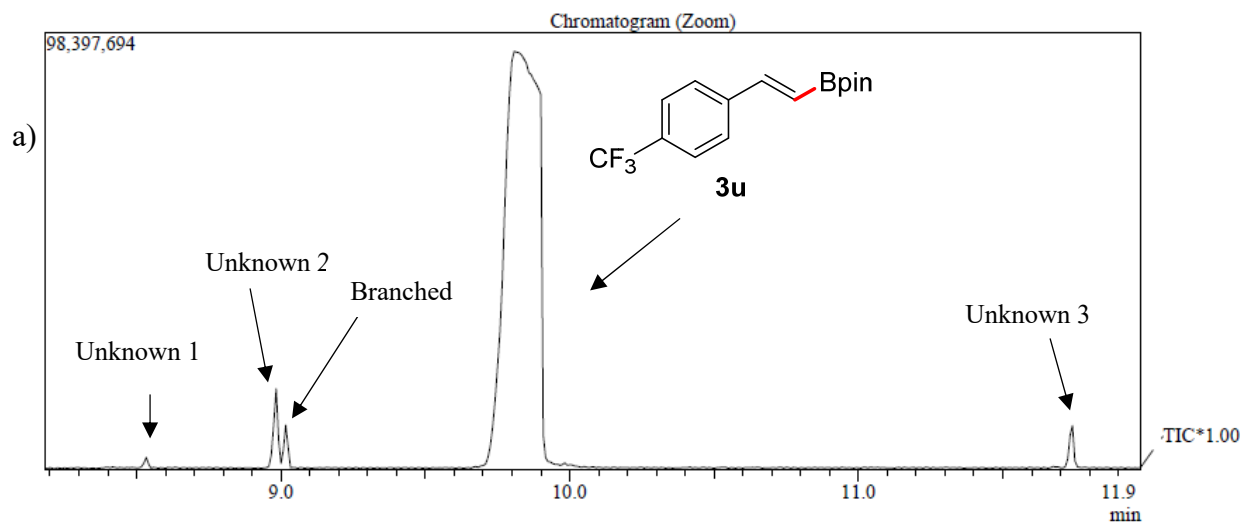
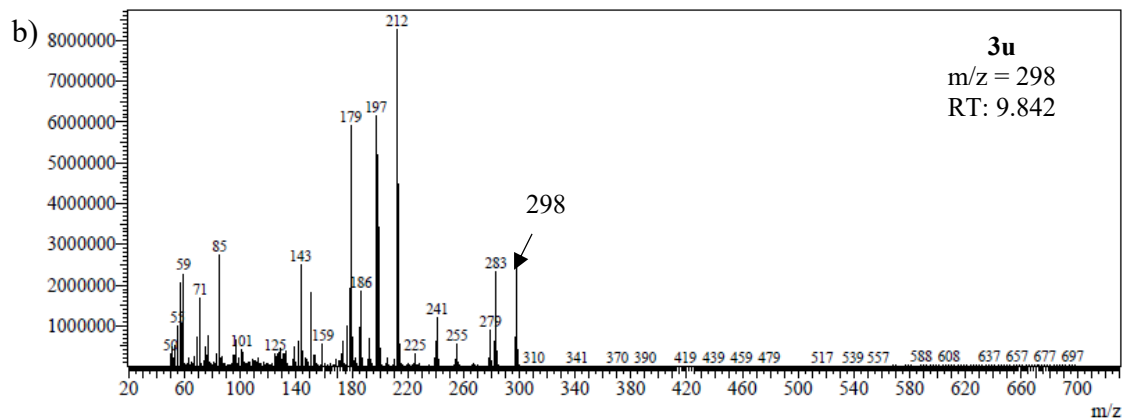


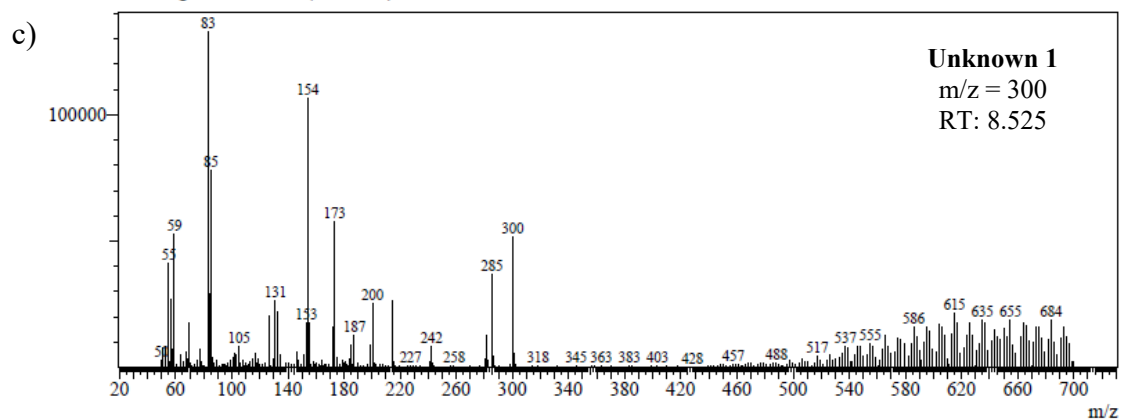
Figure S29. GC-MS chromatogram of product **3t**, isomer, and unknown



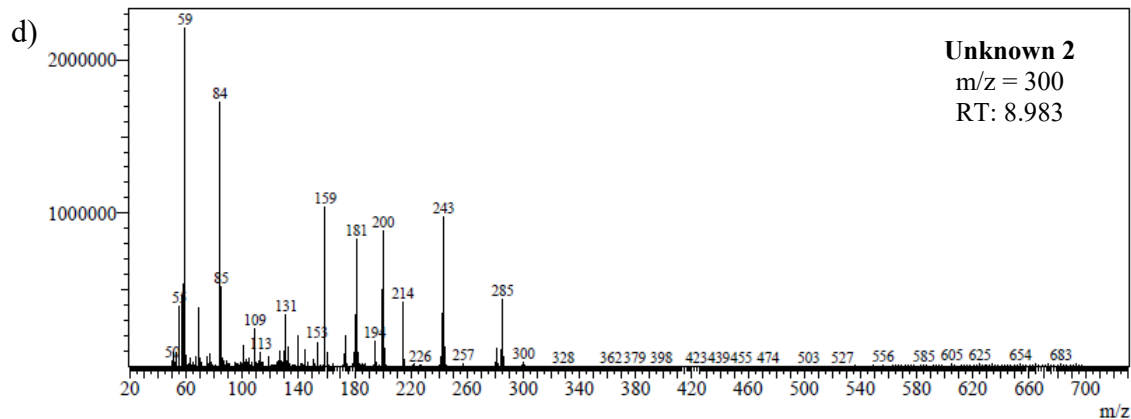
Line#:1 R.Time:9.842(Scan#:1181)
 MassPeaks:503
 RawMode:Single 9.842(1181) BasePeak:212.05(8265192)
 BG Mode:None



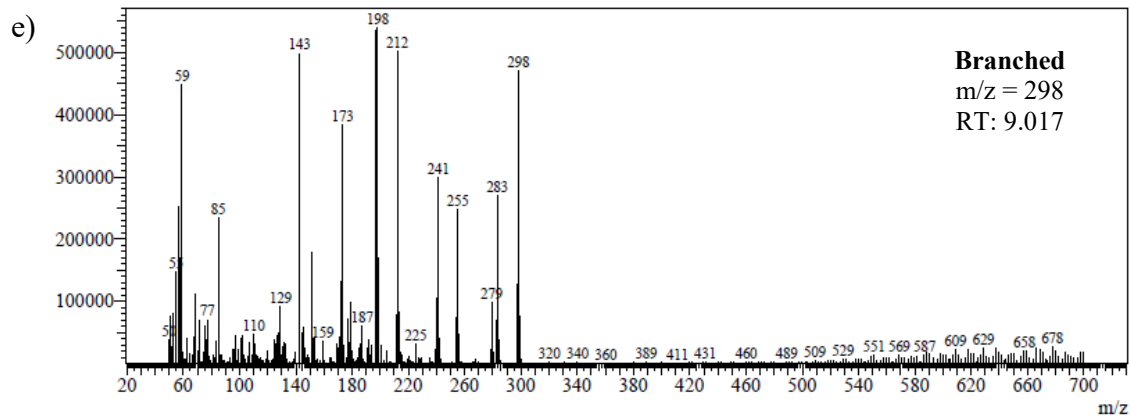
Line#:1 R.Time:8.525(Scan#:1023)
 MassPeaks:356
 RawMode:Single 8.525(1023) BasePeak:83.05(132738)
 BG Mode:Averaged 8.092-8.475(971-1017)



Line#:1 R.Time:8.983(Scan#:1078)
 MassPeaks:364
 RawMode:Single 8.983(1078) BasePeak:59.05(2205776)
 BG Mode:Averaged 8.408-8.950(1009-1074)



Line#:1 R.Time:9.017(Scan#:1082)
 MassPeaks:399
 RawMode:Single 9.017(1082) BasePeak:198.10(539154)
 BG Mode:Averaged 8.200-8.950(984-1074)



Line#:1 R.Time:11.742(Scan#:1409)
 MassPeaks:404
 RawMode:Single 11.742(1409) BasePeak:84.10(2707619)
 BG Mode:Averaged 9.975-11.692(1197-1403)

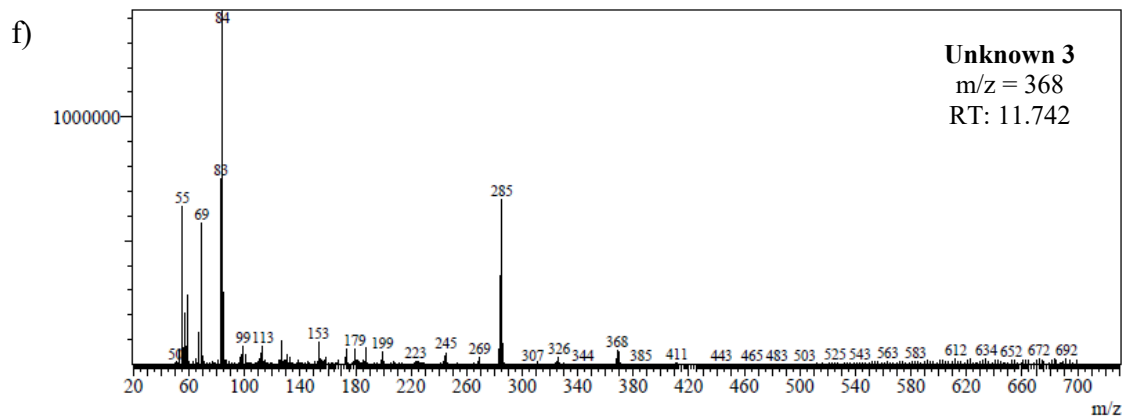
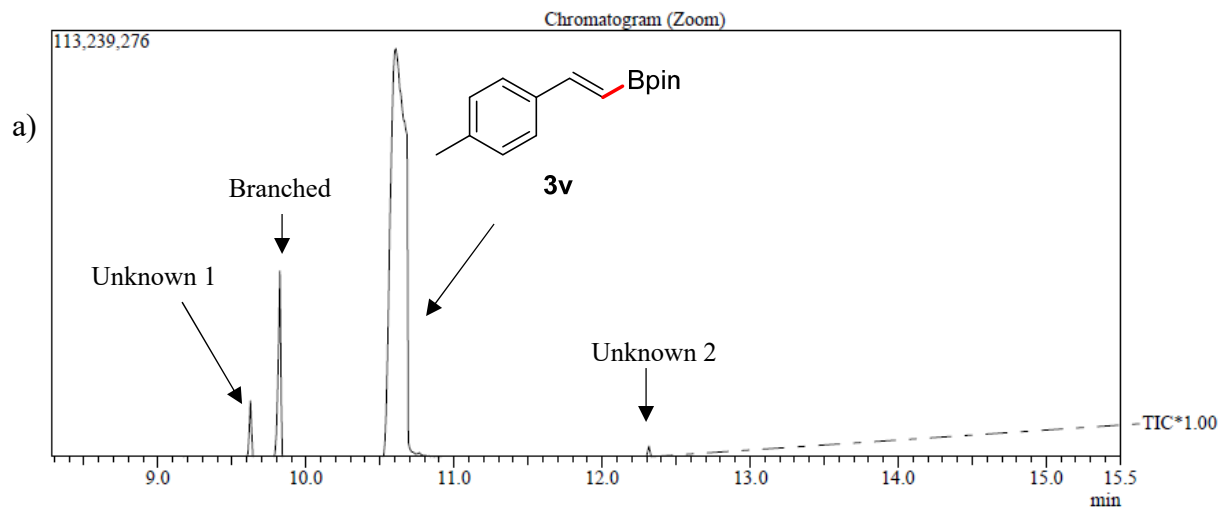
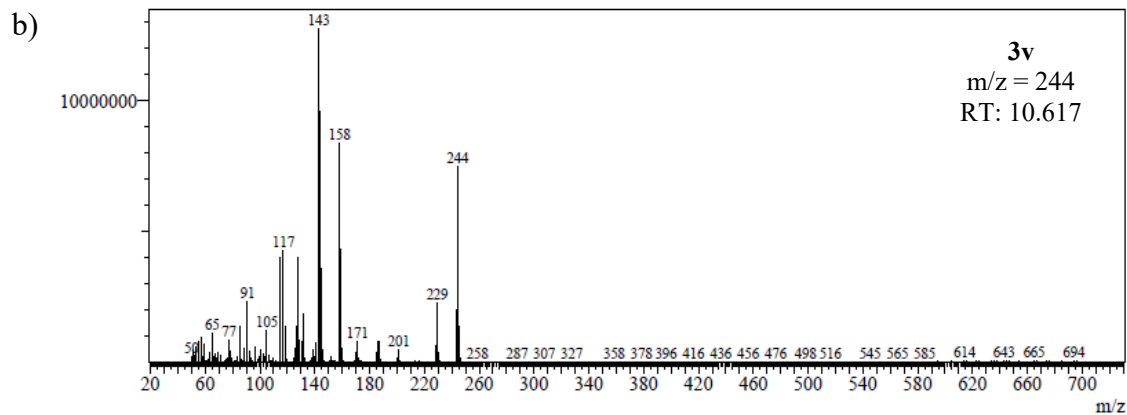


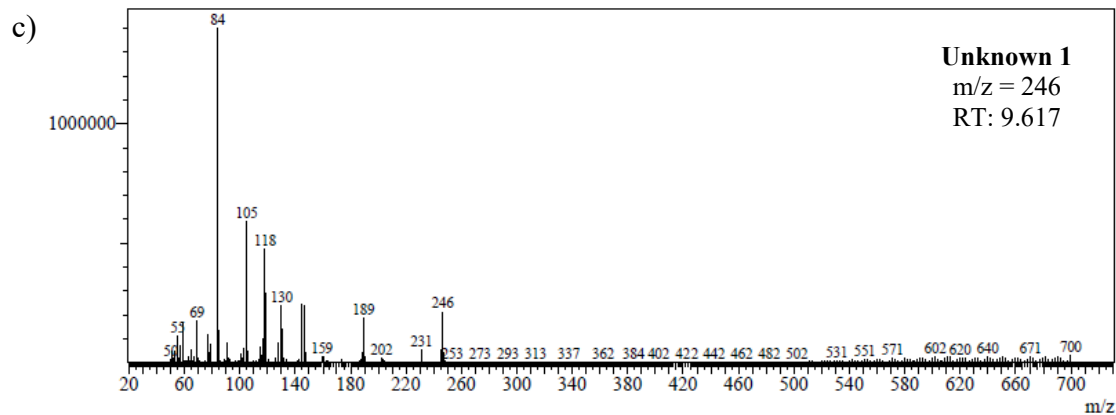
Figure S30. GC-MS chromatogram of product **3u**, branched isomer and 3 unknowns.



Line#1 R.Time:10.617(Scan#:1274)
 MassPeaks:533
 RawMode:Single 10.617(1274) BasePeak:143.05(12758577)
 BG Mode:None



Line#1 R.Time:9.617(Scan#:1154)
 MassPeaks:366
 RawMode:Single 9.617(1154) BasePeak:84.05(1399237)
 BG Mode:Averaged 8.450-9.575(1014-1149)



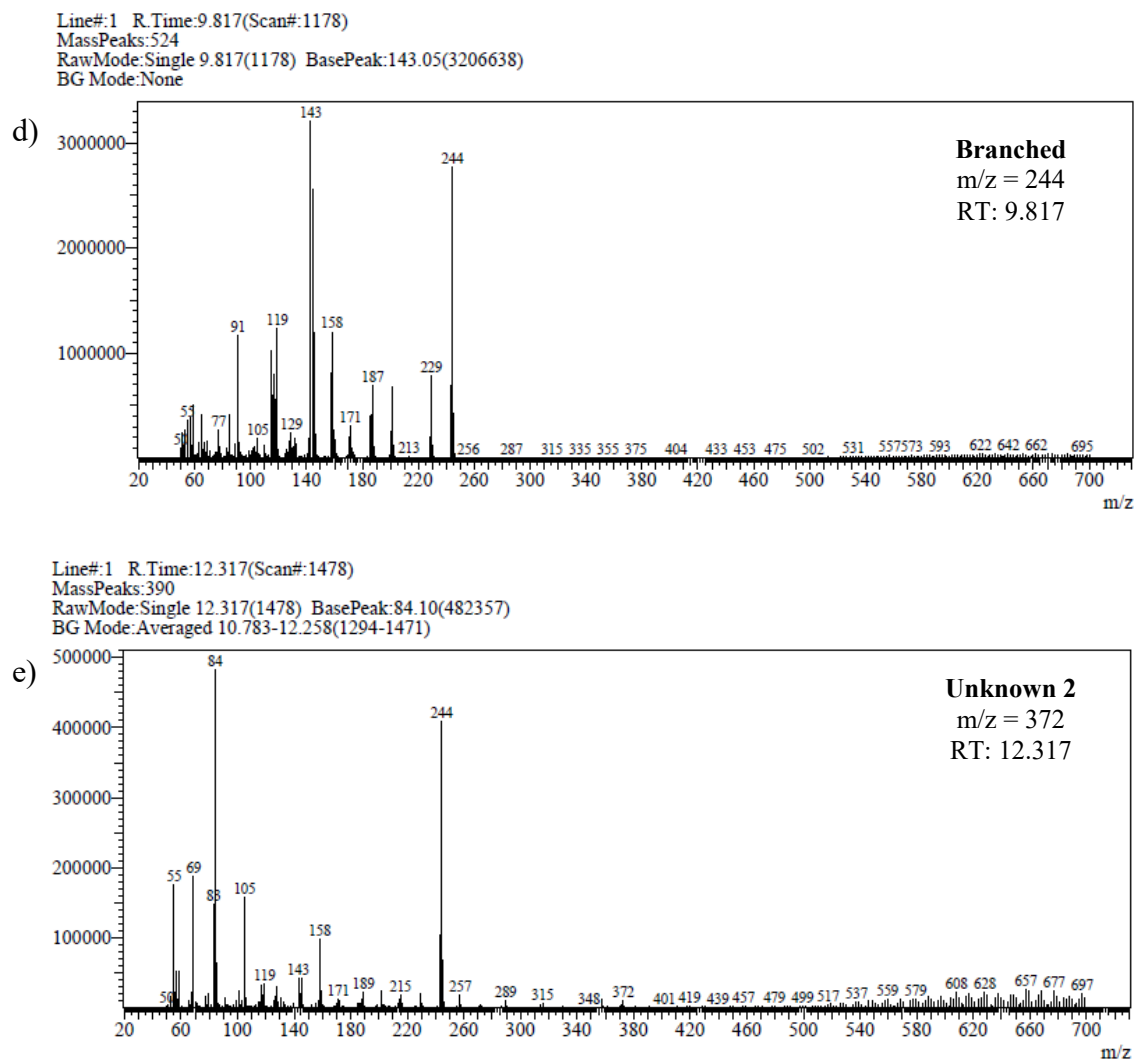
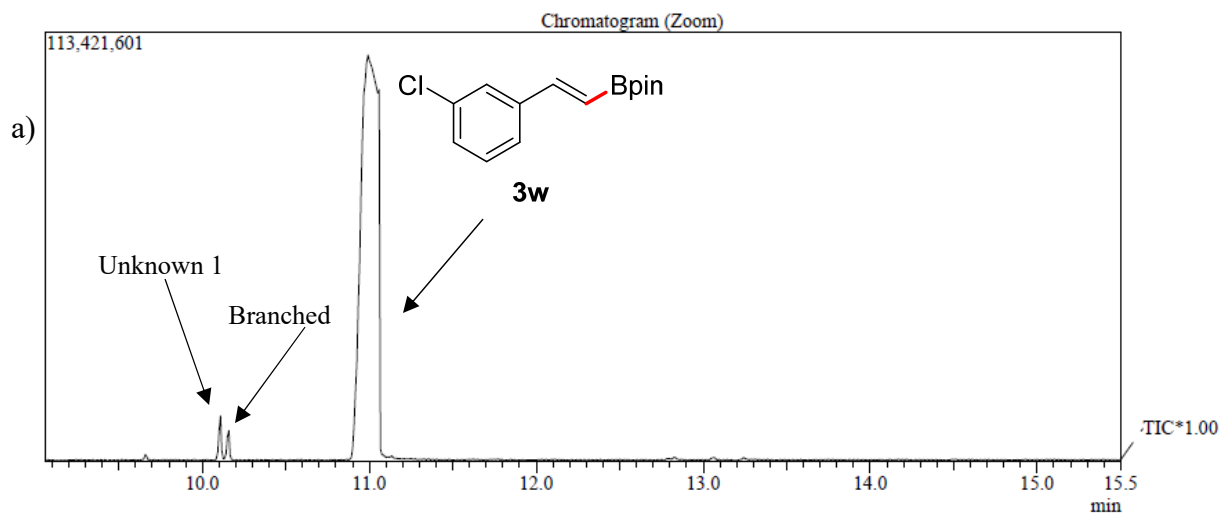
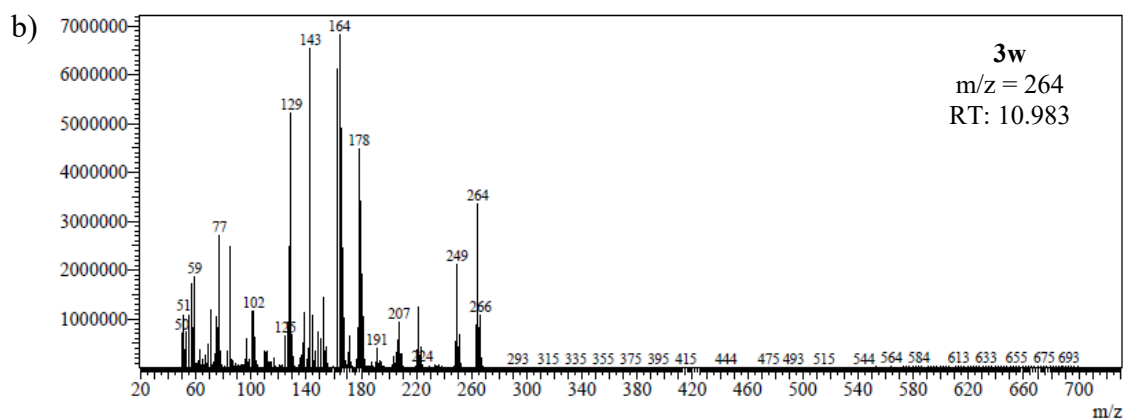


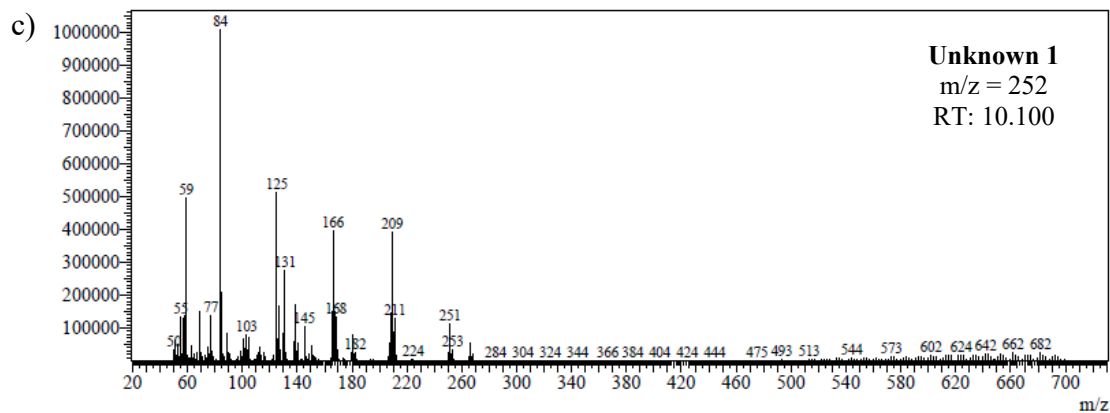
Figure S31. GC-MS chromatograms of product **3v**, branched isomer, and 2 unknowns.



Line#1 R.Time:10.983(Scan#:1318)
 MassPeaks:485
 RawMode:Single 10.983(1318) BasePeak:164.10(6819146)
 BG Mode:None



Line#1 R.Time:10.100(Scan#:1212)
 MassPeaks:378
 RawMode:Single 10.100(1212) BasePeak:84.05(1006613)
 BG Mode:Averaged 9.208-10.058(1105-1207)



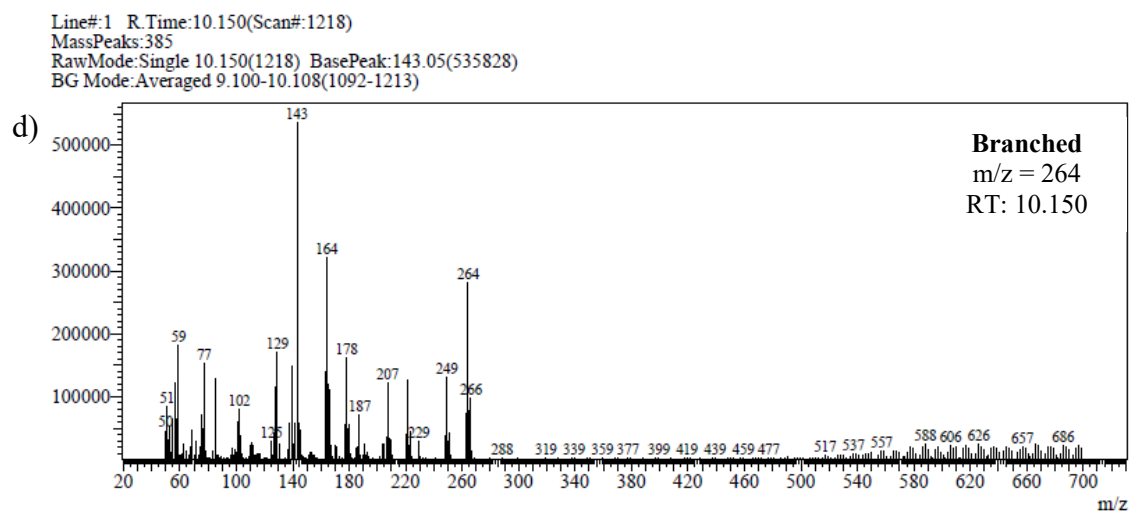


Figure S32. GC-MS chromatogram of product **3w**, branched isomer, and an unknown.

9. NMR data

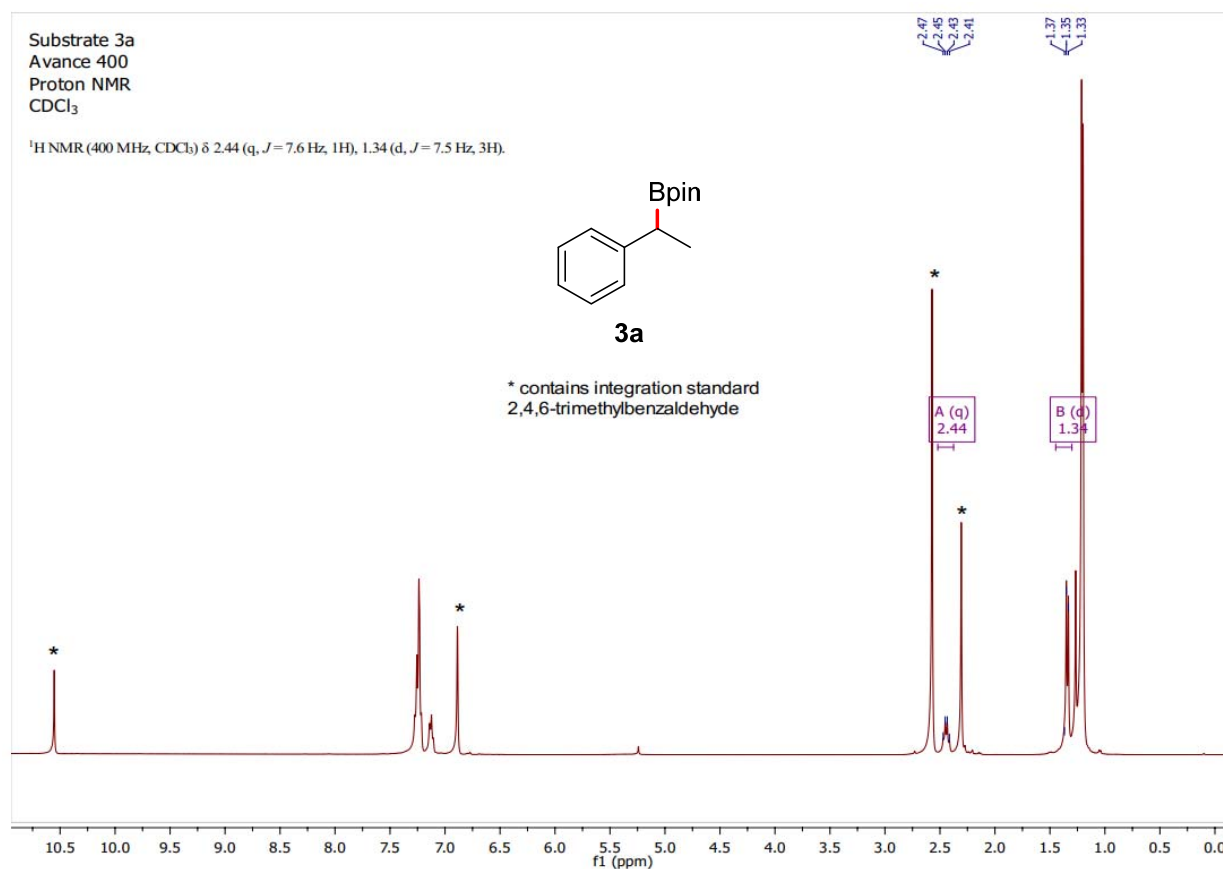


Figure S33. NMR spectra of product **3a**.

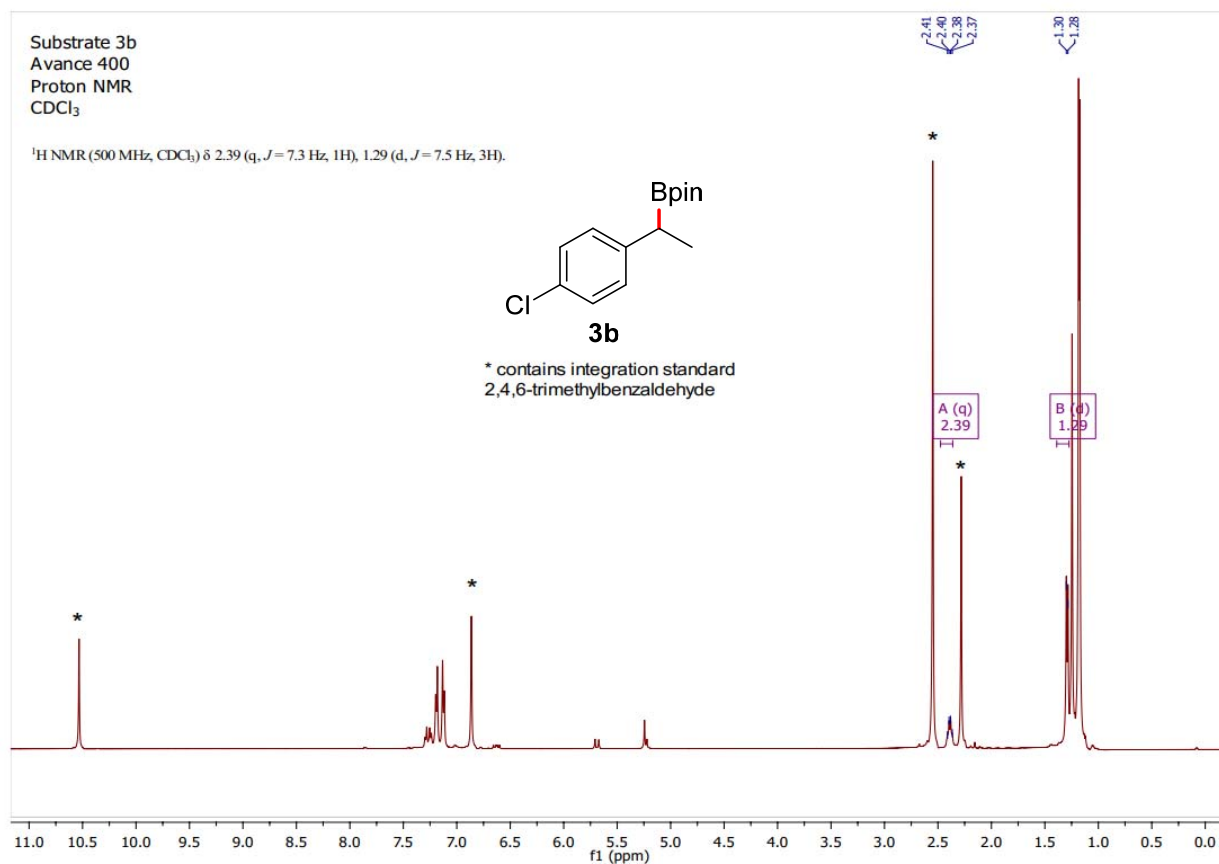


Figure S34. NMR spectra of product **3b**.

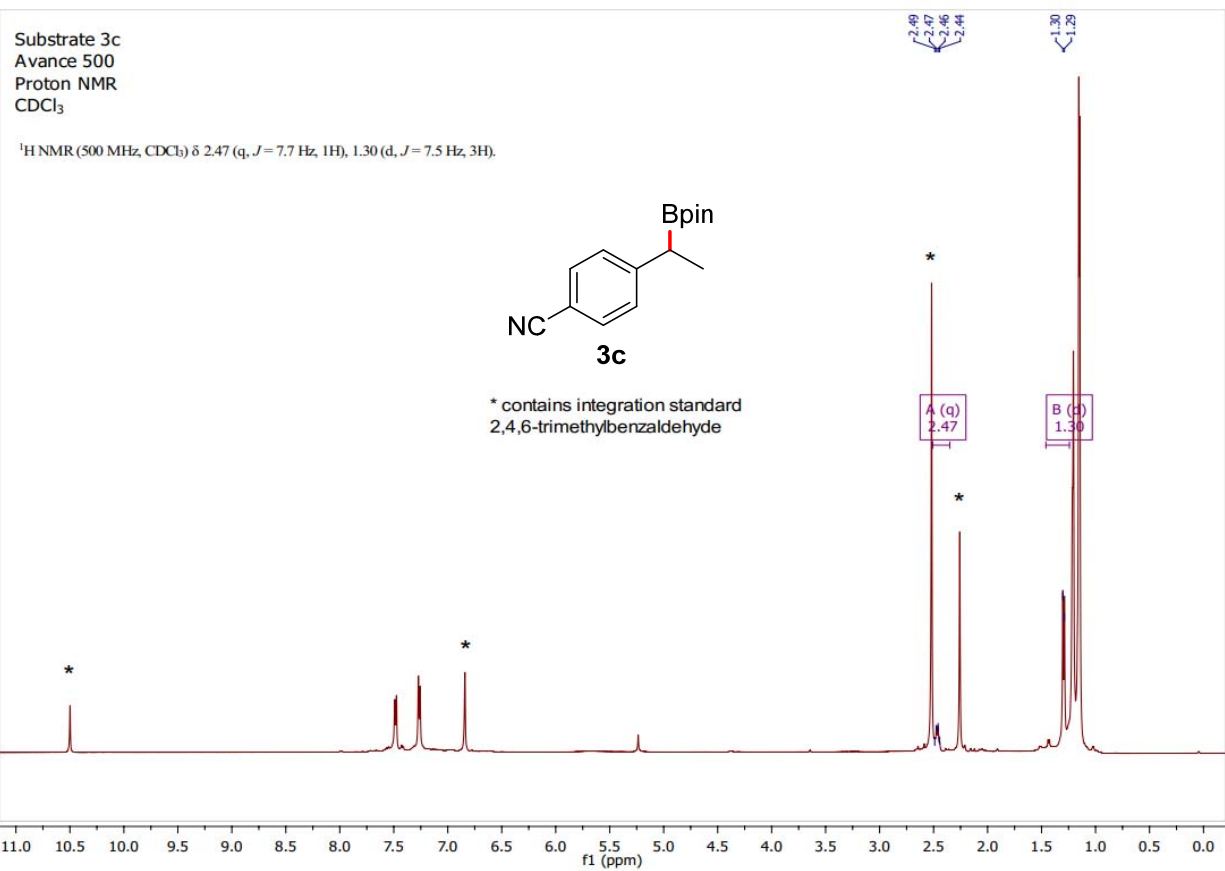


Figure S35. NMR spectra of product **3c**.

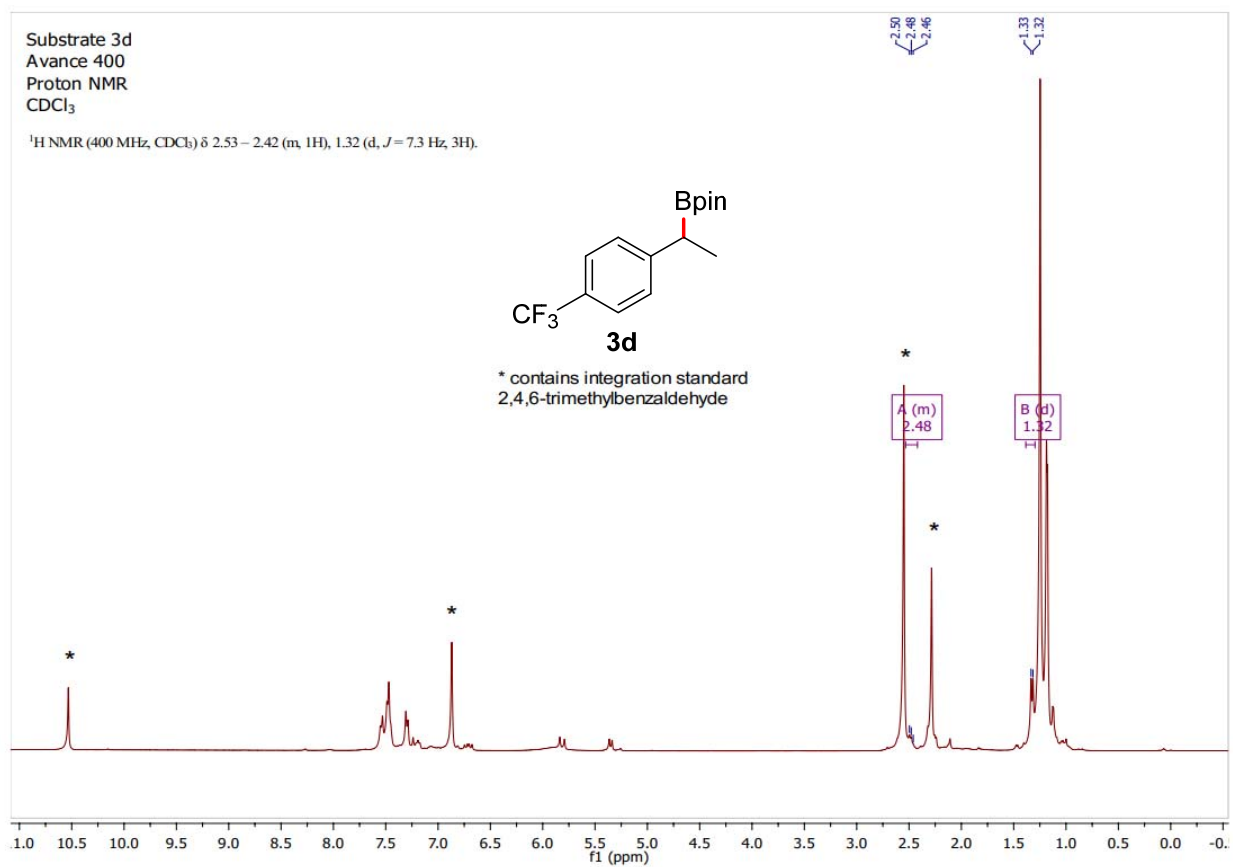


Figure S36. NMR spectra of product **3d**.

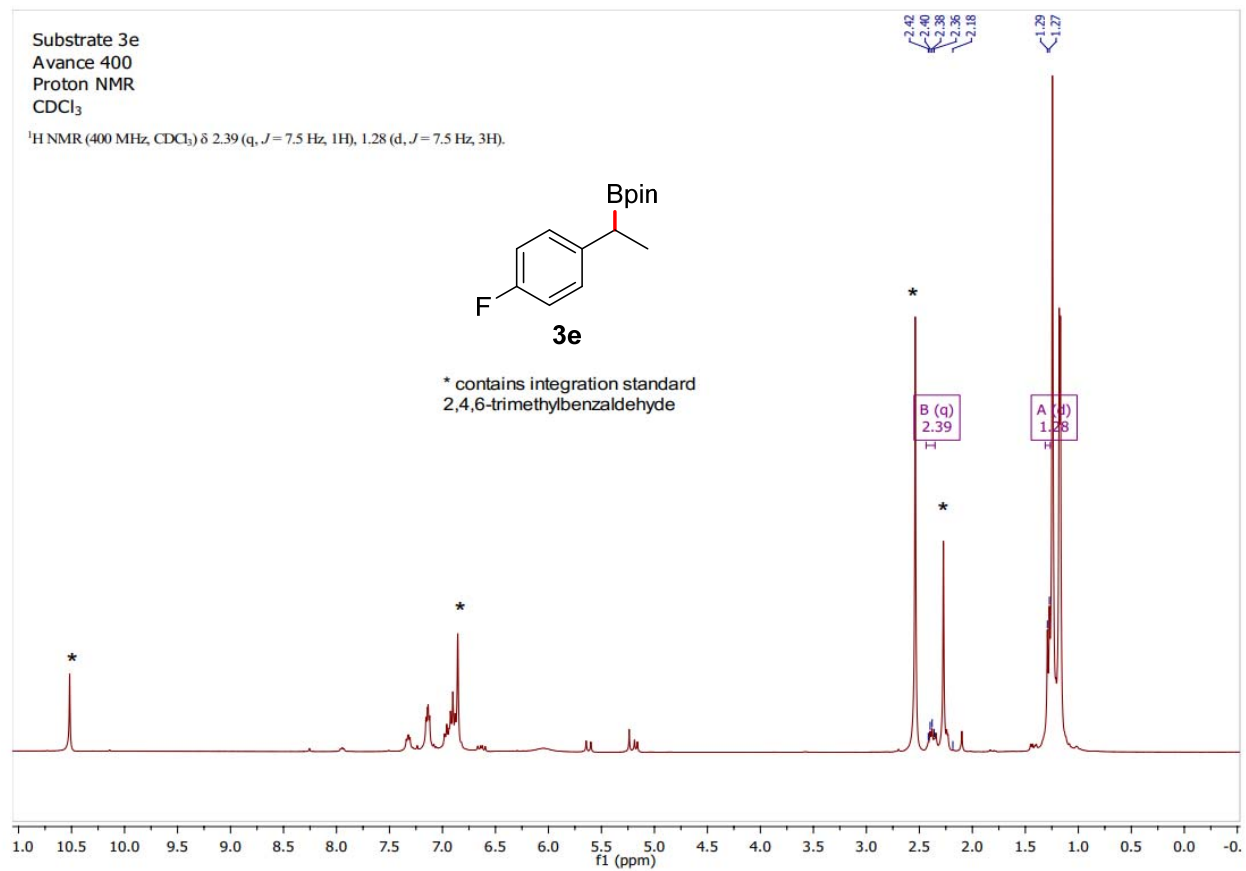


Figure S37. NMR spectra of product **3e**.

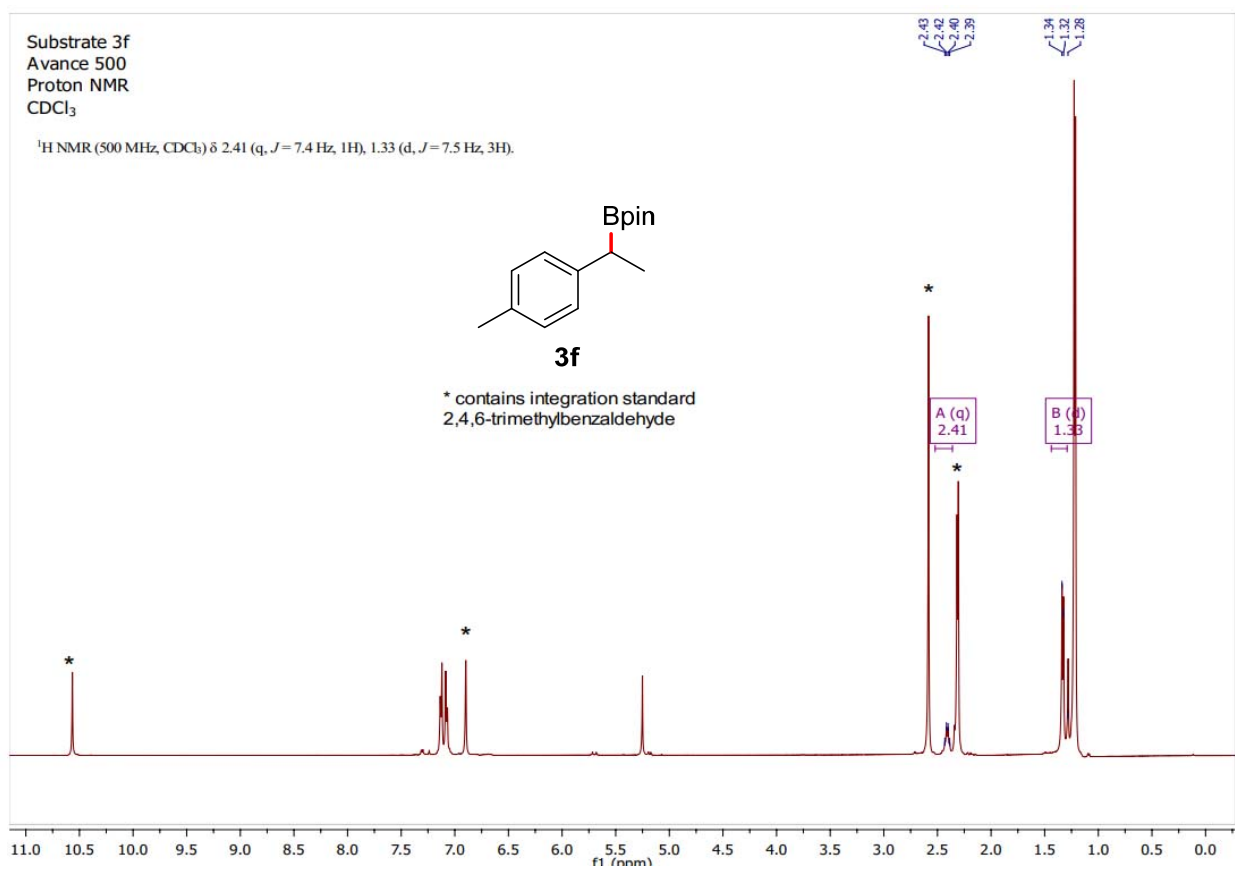


Figure S38. NMR spectra of product **3f**.

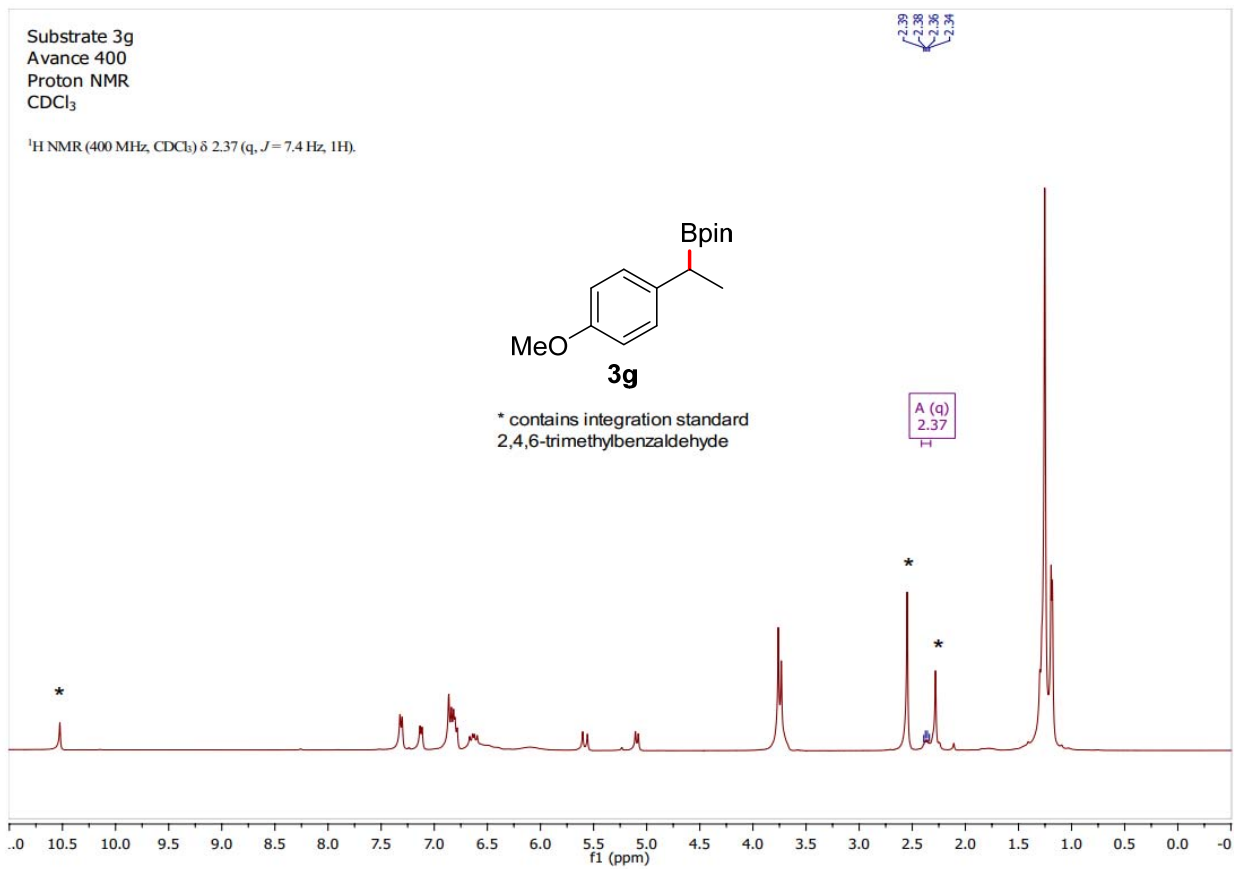


Figure S39. NMR spectra of product **3g**.

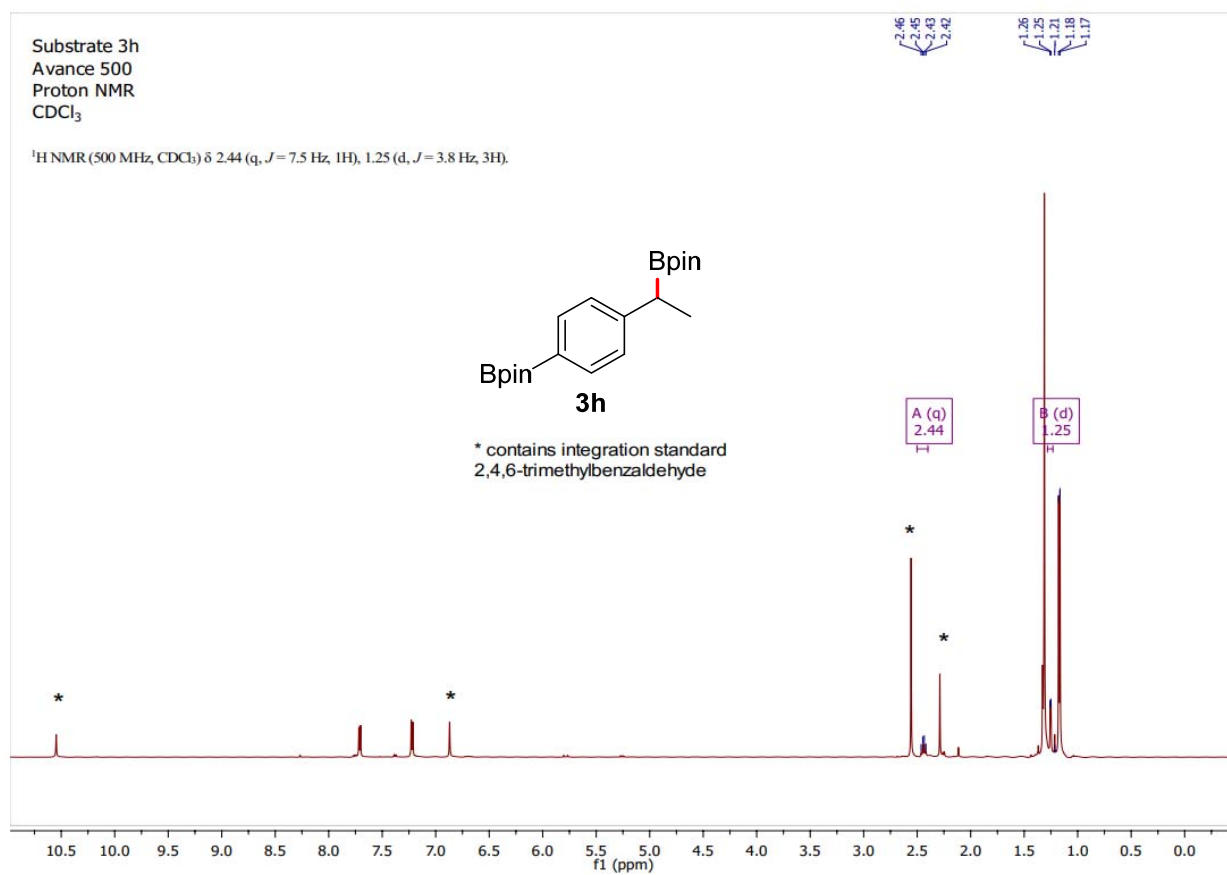


Figure S40. NMR spectra of product **3h**.

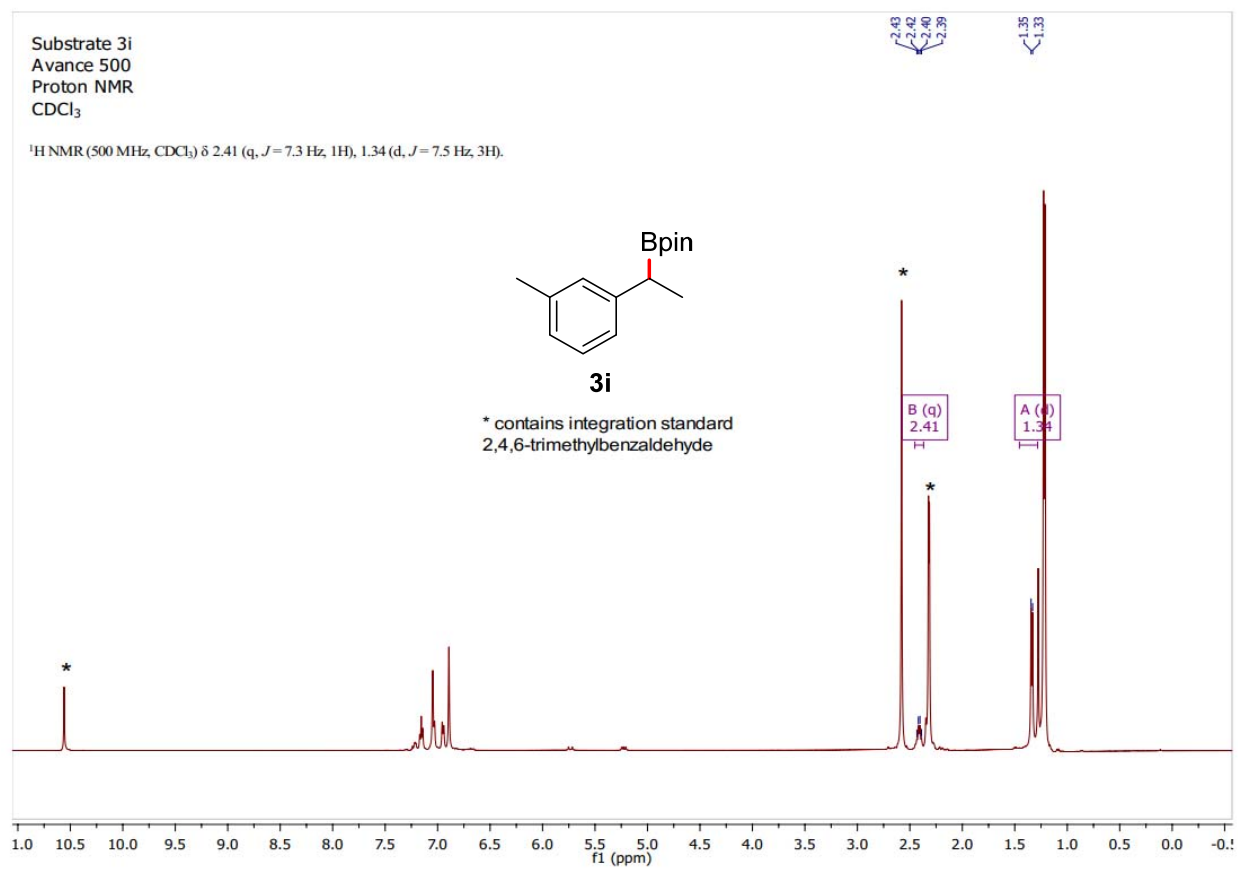


Figure S41. NMR spectra of product **3i**.

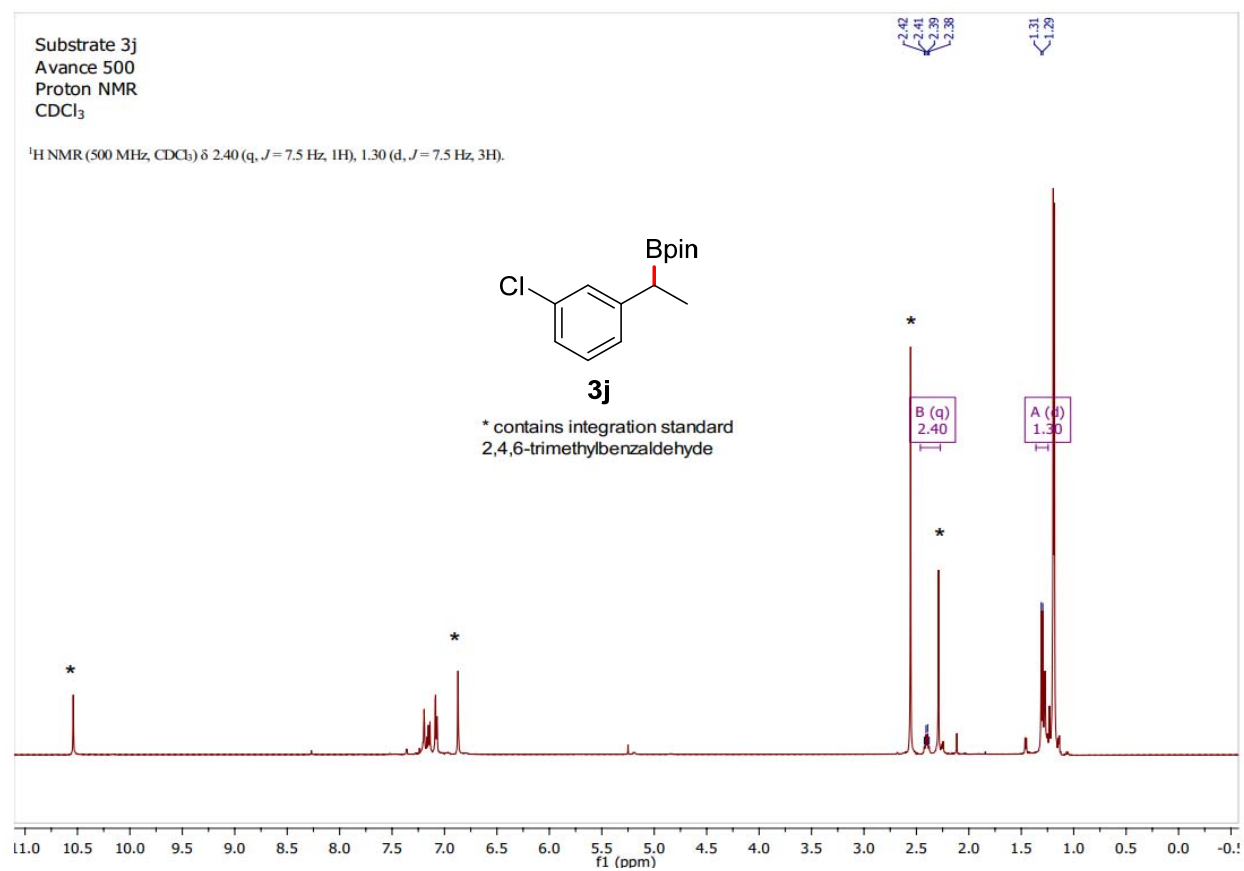


Figure S42. NMR spectra of product **3j**.

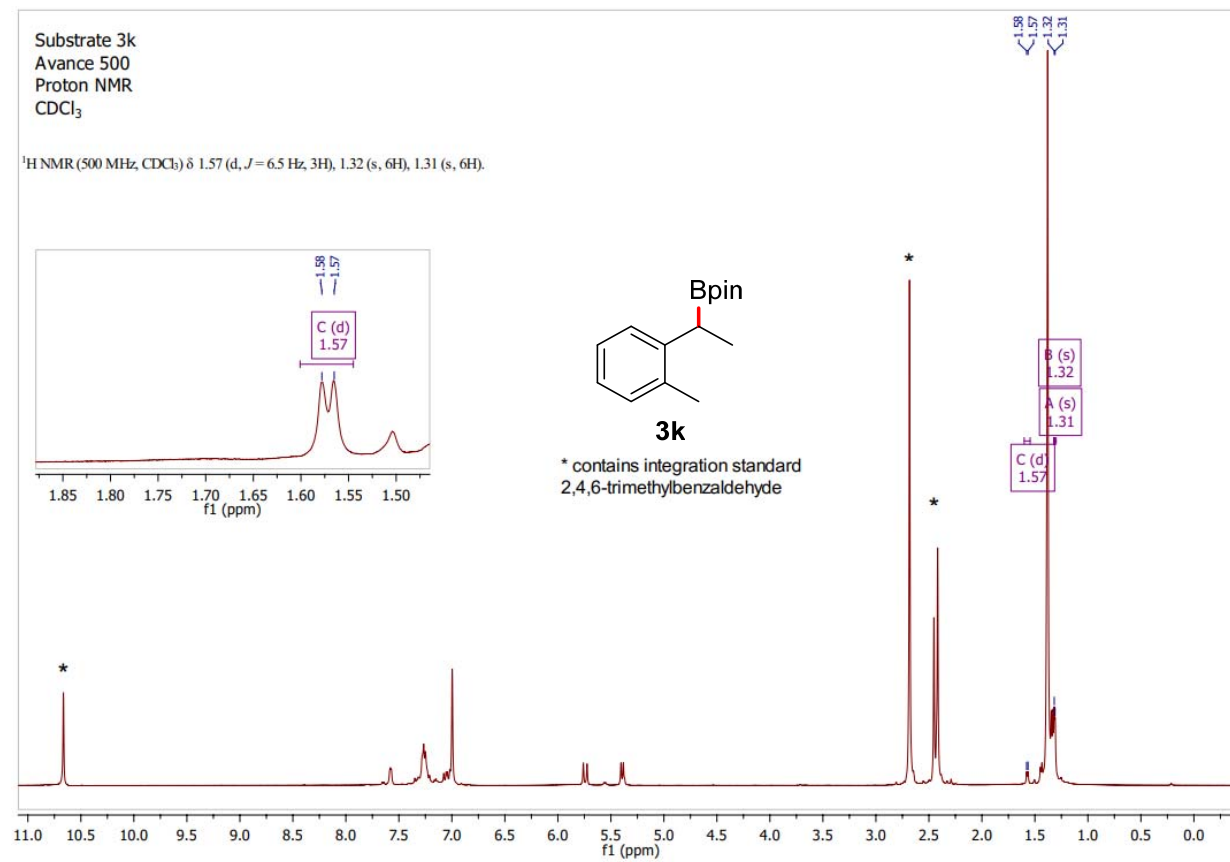


Figure S43. NMR spectra of product **3k**.

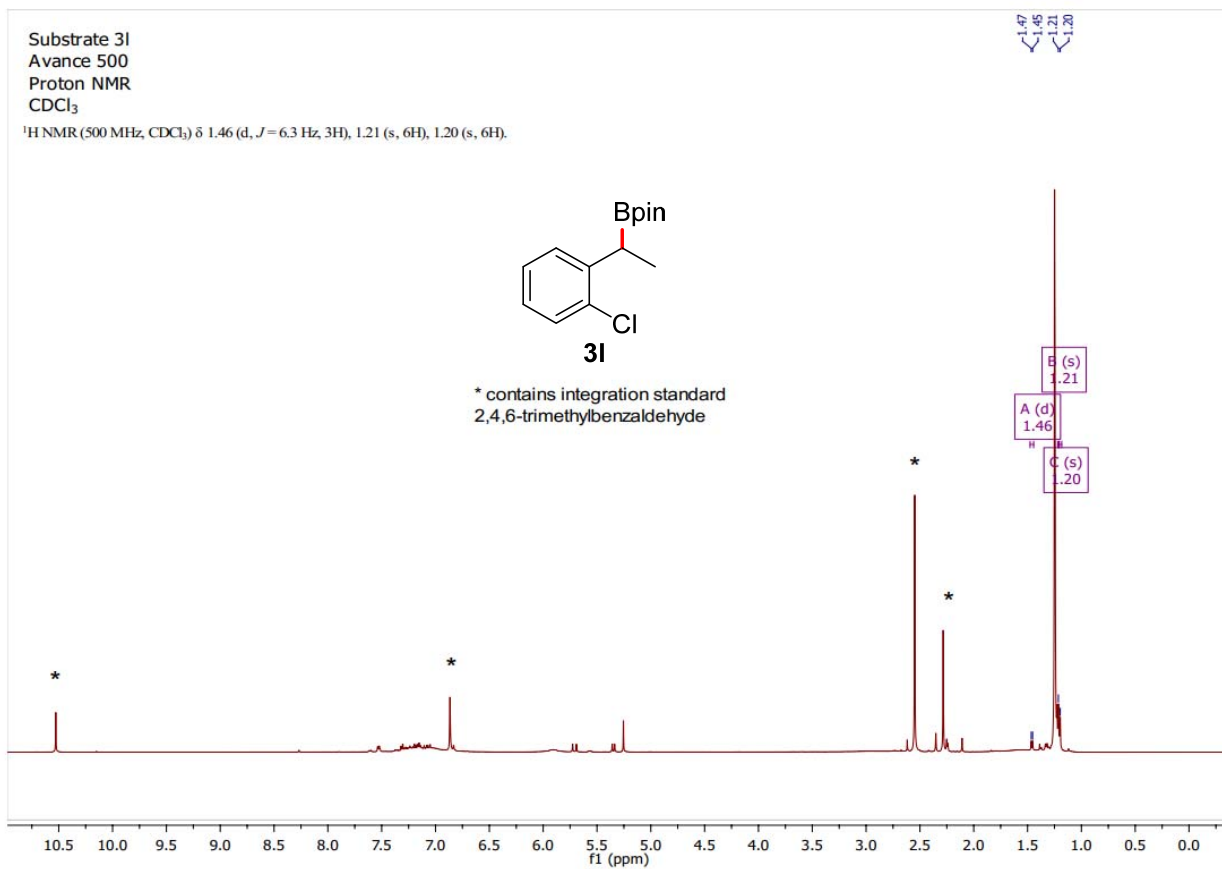


Figure S44. NMR spectra of product **3l**.

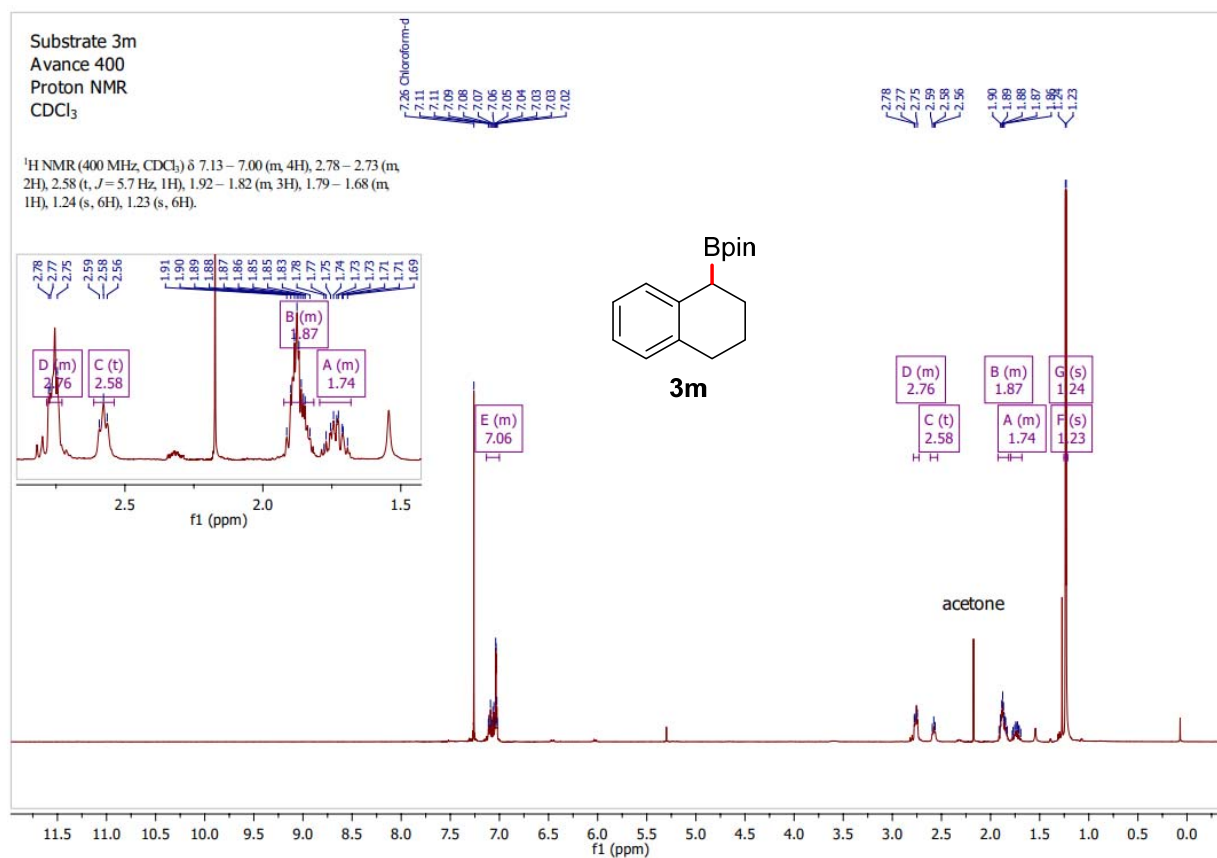


Figure S45. NMR spectra of product **3m**.

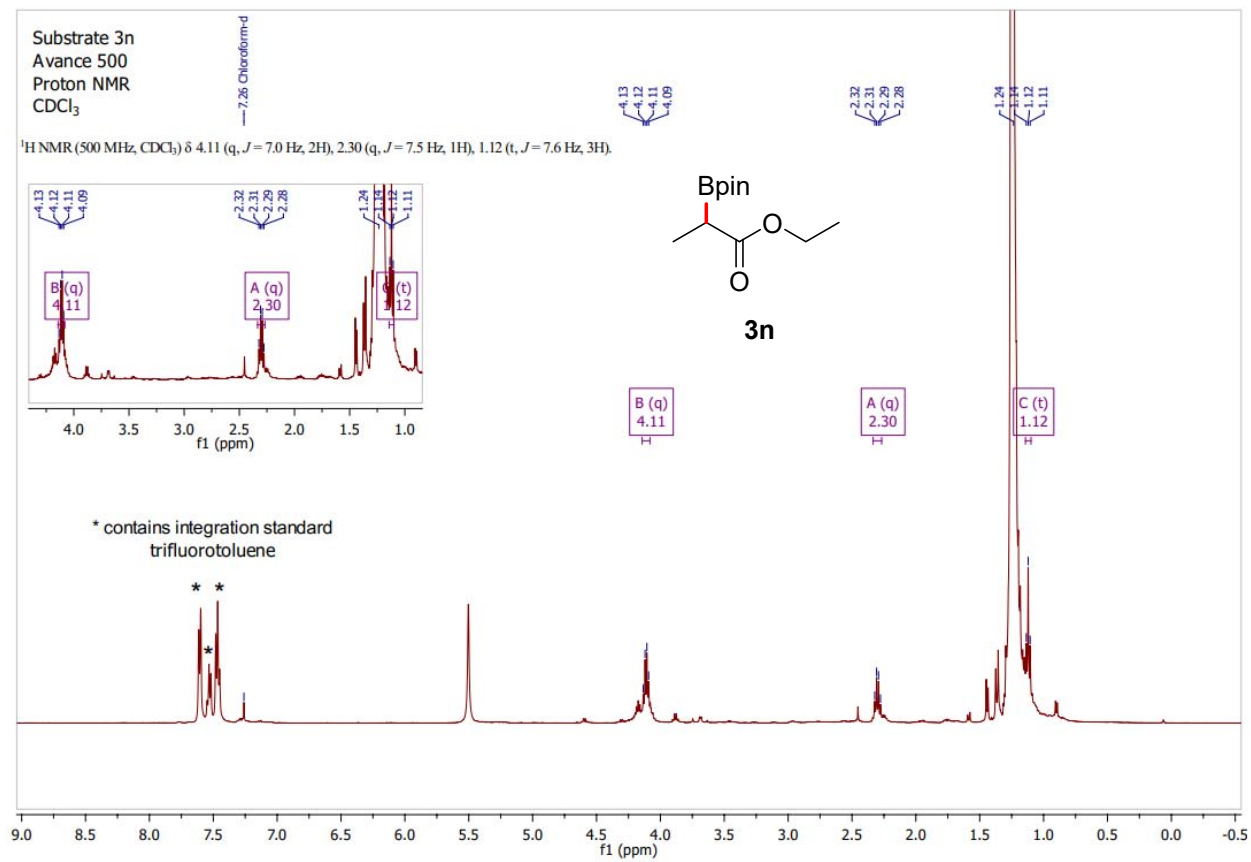


Figure S46. NMR spectra of product **3n**.

Substrate 3p
 Avance 400
 Proton NMR
 CDCl₃

¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 7.0 Hz, 2H), 7.38 (d, *J* = 18.5 Hz, 1H), 7.34 – 7.20 (m, 3H), 6.15 (d, *J* = 18.4 Hz, 1H).

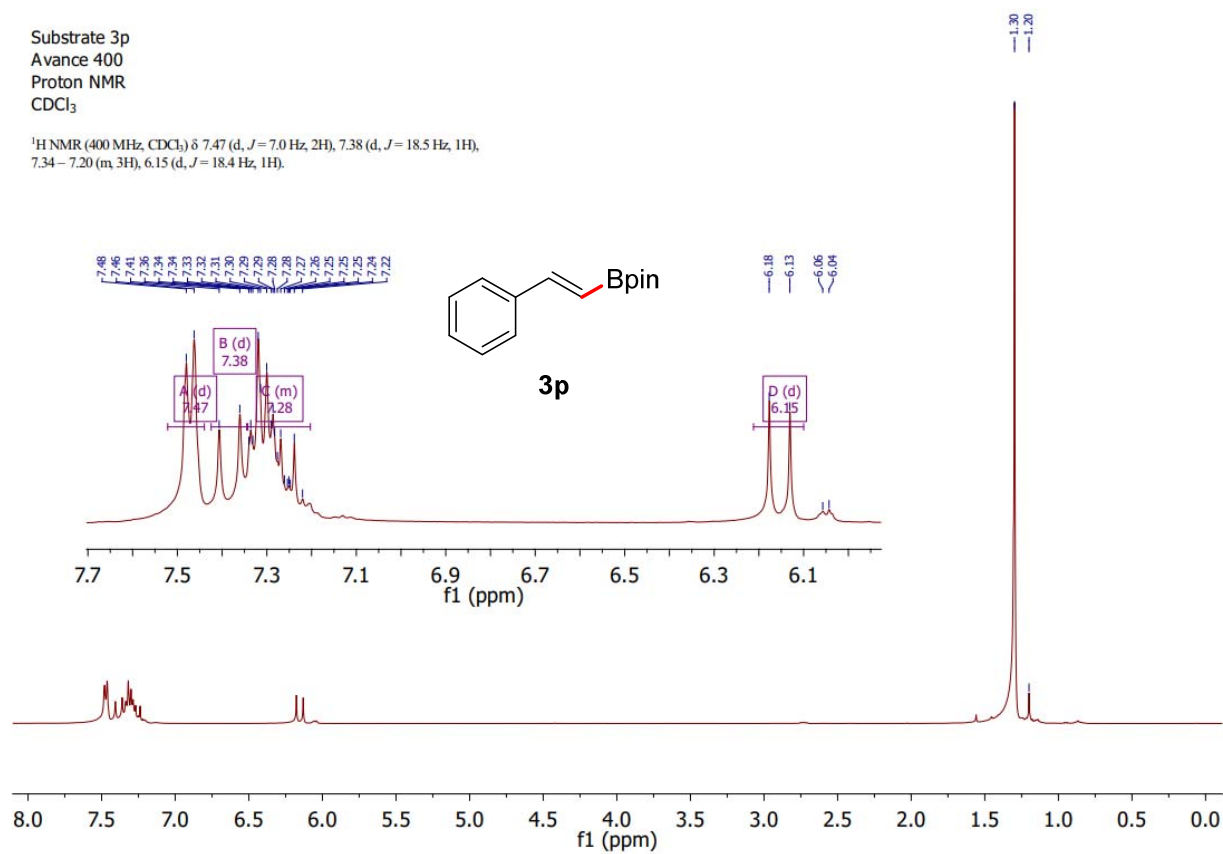


Figure S47. NMR spectra of product 3p.

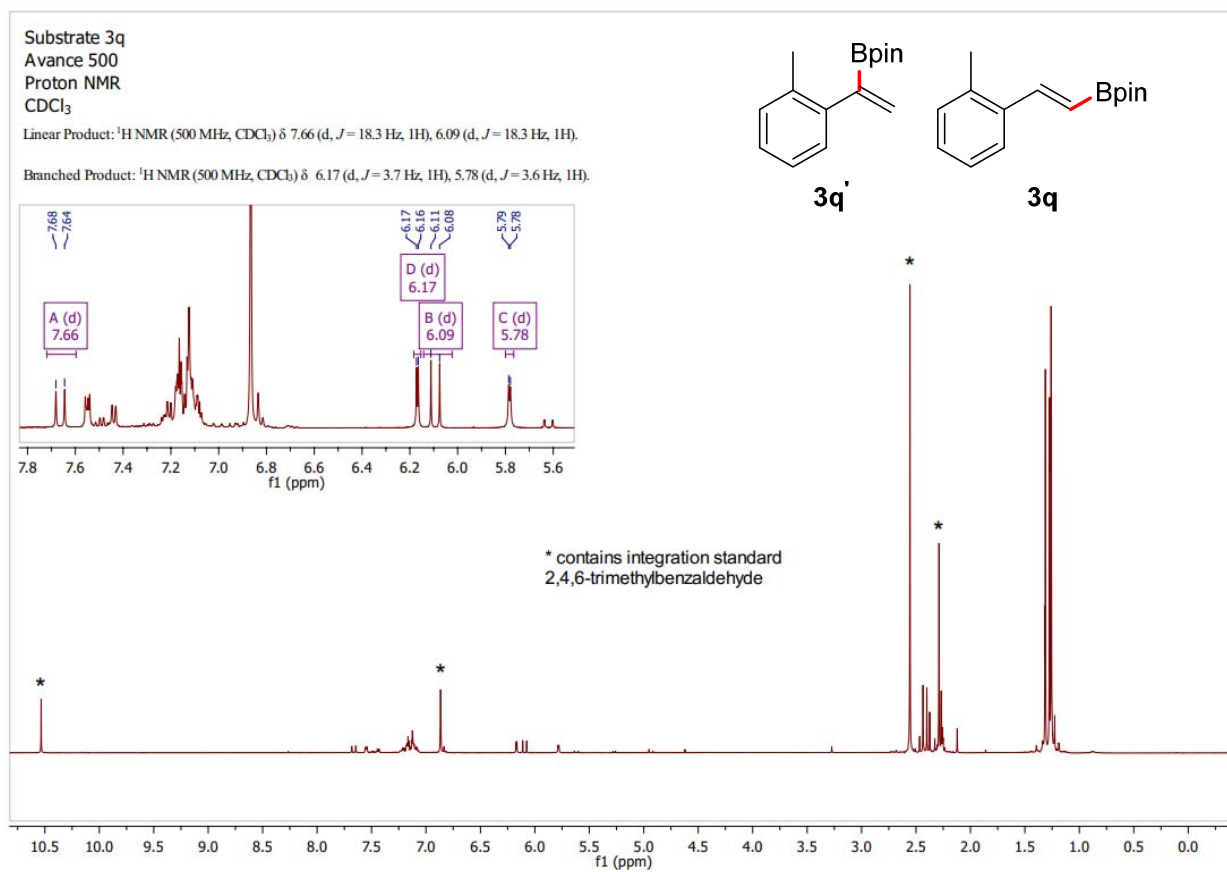


Figure S48. NMR spectra of product **3q**.

Substrate 3r
 Avance 400
 Proton NMR
 CDCl₃

¹H NMR (400 MHz, CDCl₃) δ 8.57 (s, 1H), 8.39 (d, *J* = 4.4 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 18.4 Hz, 1H), 7.14 (dd, *J* = 7.6, 4.9 Hz, 1H), 6.14 (d, *J* = 18.5 Hz, 1H), 1.20 (s, 12H).

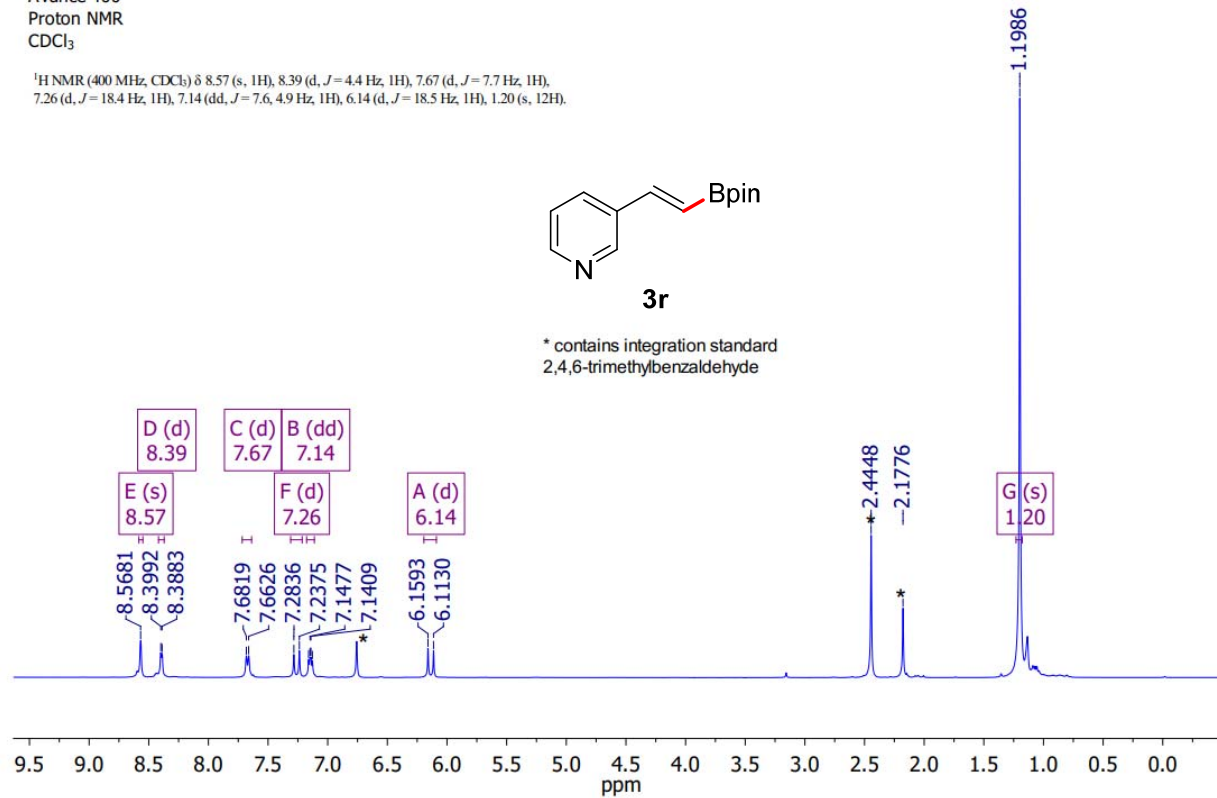


Figure S49. NMR spectra of product 3r.

Substrate 3t
Avance 400
Proton NMR
CDCl₃

¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 18.4 Hz, 1H), 6.24 (d, *J* = 18.4 Hz, 1H).

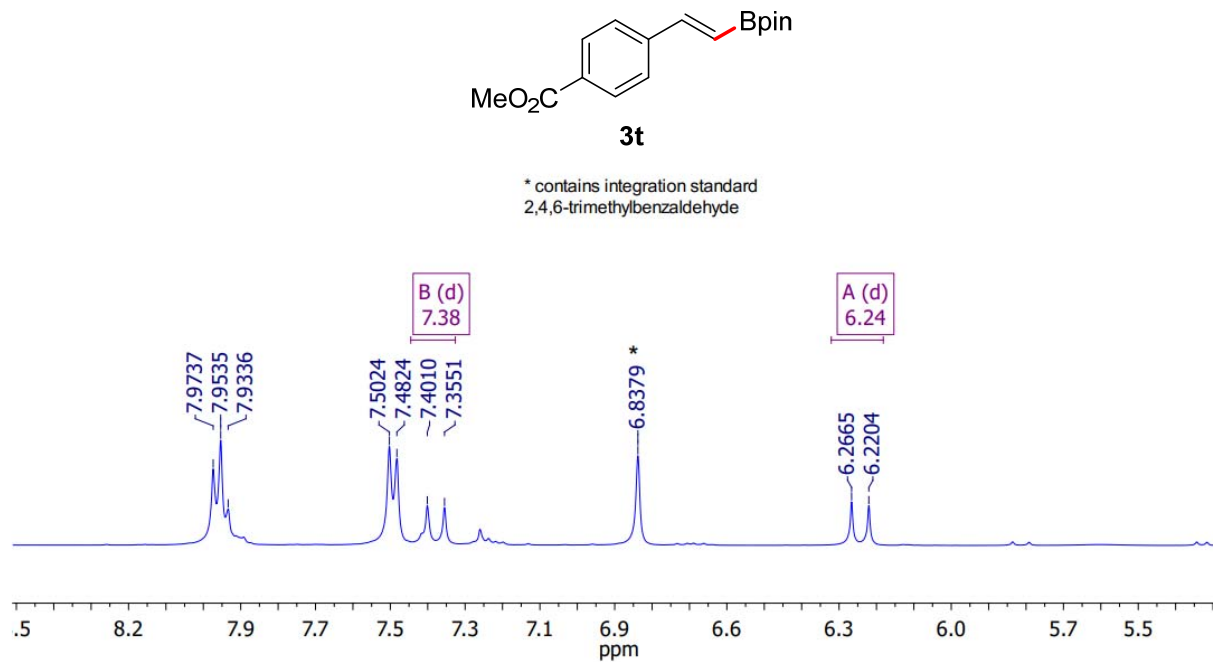


Figure S51. NMR spectra of product **3t**.

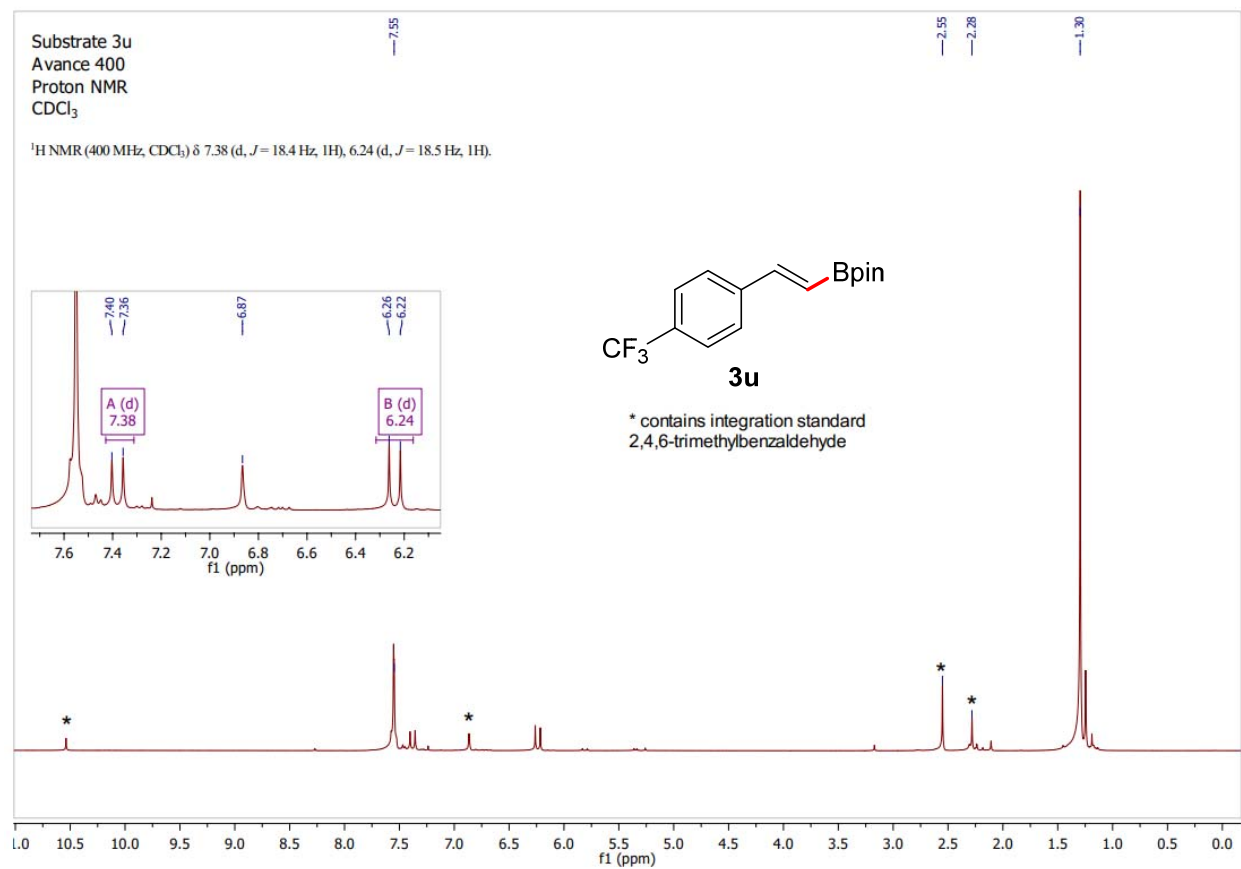


Figure S52. NMR spectra of product **3u**.

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