Supporting Information

Palladium-Catalyzed Oxidative Borylation of Allylic C-H Bonds in Alkenes

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Contents

I. General Information

All reagents were purchased from Alfa-Aesar, Aldrich, ABCR or VWR, and were checked for purity by GC-MS and/or ^{1}H NMR spectroscopy and used as received. B_2pin_2 was kindly provided by AllylChem Co. Ltd. (Dalian, China). HPLC grade solvents were argon saturated, dried using an Innovative Technology Inc. Pure-Solv Solvent Purification System, and further deoxygenated using the freeze-pump-thaw method. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, and dried over 4Å molecular sieves, deoxygenated using the freeze-pump-thaw method and vacuum transferred into a sealed vessel.

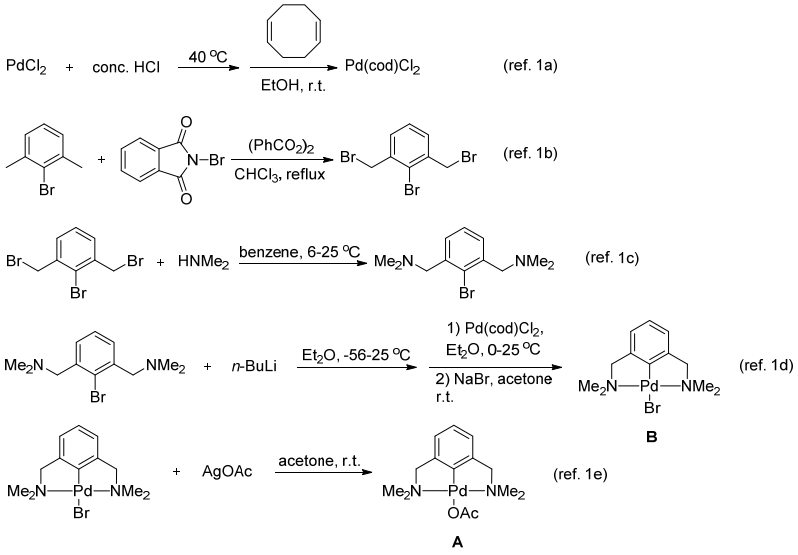
Automated flash chromatography was performed using a Biotage® Isolera Four system, on silica gel (Biotage SNAP cartridge KP-Sil 10 g and KP-Sil 25 g). Commercially available, precoated TLC plates (Polygram® Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 30 °C.

GC-MS analyses were performed using an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 10 m, Ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C (20 °C min^{-1}); carrier gas: He (1.2 mL min^{-1})) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. HRMS analyses were performed using a Thermo Fischer Scientific Exactive Plus Orbitrap MS system (ASAP, ESI or HESI probe). Elemental analyses were performed on a Leco CHNS-932 Elemental Analyzer in our Institute.

All NMR spectra were recorded at ambient temperature using Bruker Avance III HD 300 NMR (^{1}H, 300 MHz; ^{13}C{^{1}H}, 75 MHz; ^{11}B, 96 MHz), or Bruker Avance 400 NMR (^{1}H, 400 MHz; ^{13}C{^{1}H}, 100 MHz; ^{11}B, 128 MHz), or Bruker Avance 500 NMR (^{1}H, 500 MHz; ^{13}C{^{1}H}, 125 MHz; ^{11}B, 160 MHz; ^{19}F, 470 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS *via* the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm). ^{11}B NMR chemical shifts are quoted relative to $BF_3{\cdot}Et_2O$ as external standard. ^{19}F NMR chemical shifts are quoted relative to $CFCl_3$ as external standard. All ^{13}C NMR spectra were broad-band ^{1}H decoupled.

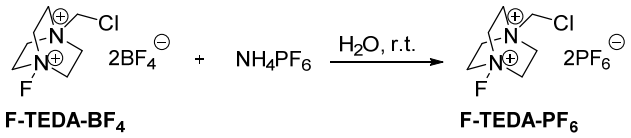
II. Preparation of Pd-pincer complexes A and B

The Pd-pincer complexes A and B were prepared via the following method. The characterization data (^{1}H, ^{13}C NMR and elemental analysis) are in accordance with those in the literature.[1]



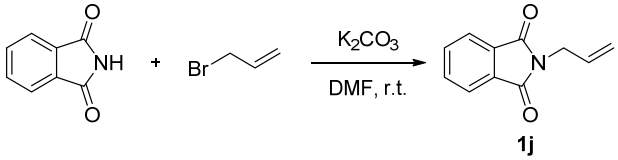
III. Preparation of F-TEDA-PF_6

F-TEDA-PF_6 was prepared via anion exchange from the commercial BF_4^- salt. The characterization data (^{1}H, ^{13}C and ^{19}F NMR) are in accordance with those in the literature.[2]



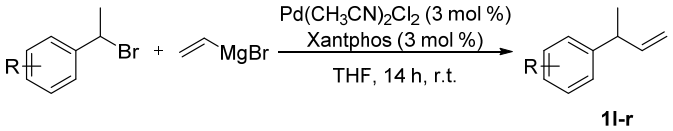
IV. Preparation of Compound 1j

Compound **1j** was prepared via the following method. The characterization data (^{1}H and ^{13}C NMR) are in accordance with those in the literature.[3]



V. Preparation of Compounds 1l-r

Compounds **1l-r** were prepared via the following method. Their characterization data (^{1}H and ^{13}C NMR) are in accordance with those in the literature.[4]

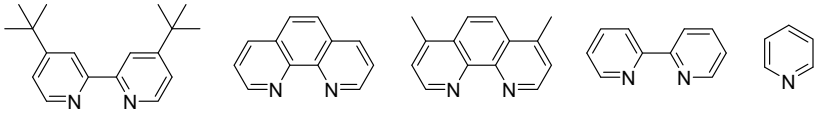


VI. Optimization of Conditions

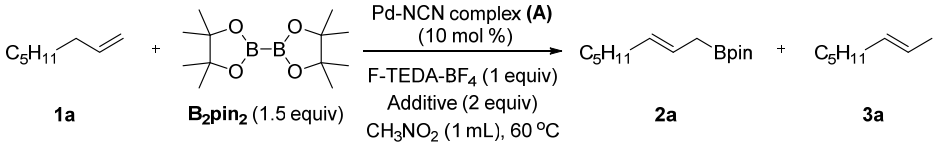
1. Catalysts and ligands[a]

Entry	Catalyst	Ligand	% 2a[b]	*E*:*Z*[c]	% 3a[d]	% Conversion
1	**A**	-	89%	50:1	-	100%
2	$Pd(OAc)_2$	-	N.D.[e]	-	21%	24%
3	$PdCl_2$	-	N.D.[e]	-	43%	48%
4	$Pd(TFA)_2$	-	N.D.[e]	-	34%	39%
5	$Pd(PPh_3)_4$	-	N.D.[e]	-	68%	73%
6	$Pd(dba)_2$	-	N.D.[e]	-	72%	79%
7	$Pd(OAc)_2$	dtbpy	N.D.[e]	-	29%	33%
8	$Pd(OAc)_2$	1,10-Phen	N.D.[e]	-	24%	29%
9	$Pd(OAc)_2$	4,4'- Me_2Phen	N.D.[e]	-	29%	33%
10	$Pd(OAc)_2$	bpy	N.D.[e]	-	24%	27%
11	$Pd(OAc)_2$	Py	N.D.[e]	-	21%	25%

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **1a** (1.0 equiv), B_2pin_2 (1.5 equiv), Catalyst (10 mol %), Ligand, K_2CO_3 (2.0 equiv), F-TEDA-BF_4 (1.0 equiv), CH_3NO_2 (1.0 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] *E*/*Z* isomer ratios were determined by ^{1}H NMR spectroscopy of the crude product. [d] Yields were determined by ^{1}H NMR analysis *vs.* an internal standard and are averages of two experiments. [e] N.D. = not detected.



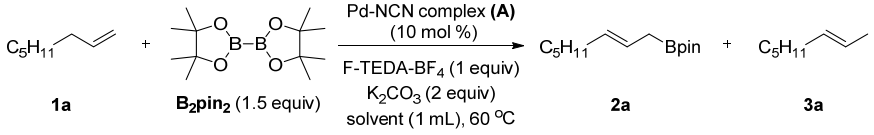
2. Additives[a]



Entry	Base	% 2a[b]	*E*:*Z*[c]	% 3a[d]	% Conversion
1	K_2CO_3	89%	50:1	-	100%
2	Li_2CO_3	61%	44:1	-	68%
3	Cs_2CO_3	74%	47:1	-	79%
4	LiF	58%	41:1	-	64%
5	NaF	52%	48:1	-	55%
6	CsF	55%	43:1	-	59%
7	$NaHCO_3$	43%	45:1	-	49%
8	$KHCO_3$	49%	50:1	-	56%
9	KO^{t}Bu	N.D.[e]	-	47%	53%

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **1a** (1.0 equiv), B_2pin_2 (1.5 equiv), Pd-NCN complex **(A)** (10 mol %), Additive (2.0 equiv), F-TEDA-BF_4 (1.0 equiv), CH_3NO_2 (1.0 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] *E*/*Z* isomer ratios were determined by ^{1}H NMR spectroscopy of the crude product. [d] Yields were determined by ^{1}H NMR analysis *vs.* an internal standard and are averages of two experiments. [e] N.D. = not detected.

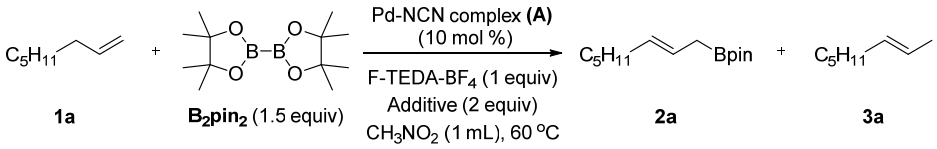
3. Solvents[a]



Entry	Solvent	% 2a[b]	*E*:*Z*[c]	% 3a[d]	% Conversion
1	CH_3NO_2	89%	50:1	-	100%
2	toluene	49%	43:1	27%	81%
3	benzene	54%	47:1	29%	85%
4	MTBE	N.D.[e]	-	34%	39%
5	CH_3CN	N.D.[e]	-	42%	48%

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **1a** (1.0 equiv), B_2pin_2 (1.5 equiv), Pd-NCN complex **(A)** (10 mol %), K_2CO_3 (2.0 equiv), F-TEDA-BF_4 (1.0 equiv), solvent (1.0 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c] *E*/*Z* isomer ratios were determined by ^{1}H NMR spectroscopy of the crude product. [d] Yields were determined by ^{1}H NMR analysis *vs.* an internal standard and are averages of two experiments. [e] N.D. = not detected.

4. Temperature[a]

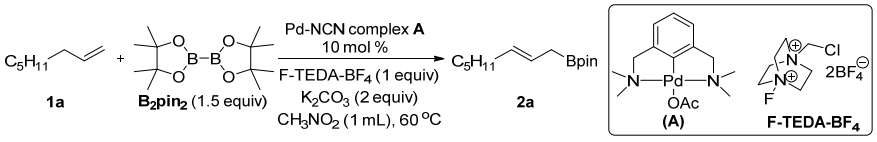


1a **B_2pin_2** (1.5 equiv) **2a** **3a**

Entry	Temperature (°C)	% 2a[b]	*E*:*Z*	% 3a[c]	% Conversion
1	80	74%	48:1	21%	100%
2	60	89%	50:1	-	100%
3	40	63%	50:1	32%	100%
4	room temperature	39%	43:1	35%	79%

[a] Standard conditions: Reactions were carried out on a 0.2 mmol scale. **1a** (1.0 equiv), B_2pin_2 (1.5 equiv), Pd-NCN complex **(A)** (10 mol %), K_2CO_3 (2.0 equiv), F-TEDA-BF_4 (1.0 equiv), CH_3NO_2 (1.0 mL). [b] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [c]Yields were determined by ^{1}H NMR analysis *vs.* an internal standard and are averages of two experiments.

VII. Allylic C-H Borylation of Alkenes

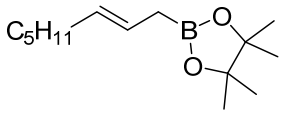


Pd-NCN complex **A** (10 mol %, 7 mg) and F-TEDA-BF_4 (1 equiv, 71 mg, 0.2 mmol) were dissolved in 0.5 mL of CH_3NO_2 in a dried vial in a glove-box under argon and the reaction was stirred for 5 min. Then, B_2pin_2 (1.5 equiv, 76 mg, 0.3 mmol), **1a** (1.0 equiv, 31 μL, 0.2 mmol), and K_2CO_3 (2.0 equiv, 55 mg, 0.4 mmol) were added in this order. Finally, another 0.5 mL of CH_3NO_2 was added to the mixture. The reaction was heated at 60 °C under argon until the starting material was completely consumed (determined by GC-MS). The crude mixture was filtered through a pad of Celite. Then, the solvent was slowly removed on a rotary evaporator (30 °C, 300 mbar). A colorless oil in 83% yield (40 mg, *E*:*Z* = 50:1) was obtained via purification with flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs.

The reaction was scaled up to 1 mmol according to the following procedure:

Pd-NCN complex **A** (10 mol %, 36 mg) and F-TEDA-BF_4 (1 equiv, 354 mg, 1 mmol) were dissolved in 2 mL of CH_3NO_2 in a dried vial in a glove-box under argon and the reaction was stirred for 5 min. Then, B_2pin_2 (1.5 equiv, 381 mg, 1.5 mmol), **1a** (1.0 equiv, 157 μL, 1 mmol), and K_2CO_3 (2.0 equiv, 276 mg, 2 mmol) were added in this order. Finally, another 3 mL of CH_3NO_2 was added to the mixture. The reaction was heated at 60 °C under argon until the starting material was completely consumed (determined by GC-MS). The crude mixture was filtered through a pad of Celite. Then, the solvent was slowly removed on a rotary evaporator (30 °C, 300 mbar). A colorless oil in 79% yield (188 mg, *E*:*Z* = 50:1) was obtained via purification with flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs.

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



2a-*major (E)-isomer*

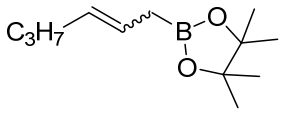
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48–5.33 (m, 2H), 1.99-1.92 (m, 2H), 1.63 (d, *J* = 6 Hz, 2H), 1.37–1.19 (m, 6H), 1.24 (s, 12H), 0.87 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 131.2, 124.8, 83.3, 32.8, 31.5, 29.5, 24.9, 22.7, 16.4 (broad, low intensity), 14.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* for $C_{14}H_{28}BO_2$ [M+H$^+$] calcd: 239.2177, found: 239.2172.

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



Following the above method, a colorless oil in 84% yield (35 mg, *E*:*Z* = 20:1) from **1b** (25 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

2b-*major (E)-isomer*

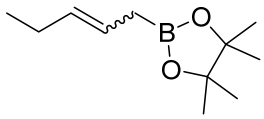
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47–5.33 (m, 2H), 1.99–1.90 (m, 2H), 1.65–1.61 (m, 2H), 1.34 (tq, J_1 = 7 Hz, J_2 = 7 Hz, 2H), 1.24 (s, 12H), 0.86 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 130.9, 125.0, 83.3, 35.0, 24.9, 22.9, 16.1 (broad, low intensity), 13.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* for $C_{12}H_{24}BO_2$ [M+H$^+$] calcd: 211.1864, found: 211.1860.

4,4,5,5-Tetramethyl-2-(pent-2-en-1-yl)-1,3,2-dioxaborolane (2c)



Following the above method, a colorless oil in 79% yield (31 mg, *E*:*Z* = 17:1) from **1c** (22 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

2c-*major (E)-isomer*

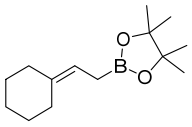
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50–5.33 (ov. m, 2H), 2.04–1.93 (m, 2H), 1.66–1.58 (ov. m, 2H), 1.24 (s, 12H), 0.94 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 132.8, 123.8, 83.3, 25.9, 24.9, 16.3 (broad, low intensity), 14.2.

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* for $C_{11}H_{22}BO_2$ [M+H$^+$] calcd: 197.1707, found: 197.1704.

2-(2-Cyclohexylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)



Following the above method, a colorless oil in 86% yield (41 mg) from **1d** (31 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

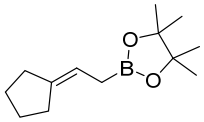
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (tquint, J_1 = 8 Hz, J_2 = 1 Hz, 1H), 2.12–2.04 (m, 4H), 1.60 (d, *J* = 8 Hz, 2H), 1.54–1.45 (m, 6H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 139.9, 115.1, 83.2, 37.2, 28.8, 28.7, 27.8, 27.1, 24.9, 11.2 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* for $C_{14}H_{26}BO_2$ [M+H$^+$] calcd: 237.2020, found: 237.2018.

2-(2-Cyclopentylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)



Following the above method, a colorless oil in 78% yield (35 mg) from **1e** (28 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

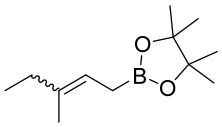
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.33 (tquint., J_1 = 8 Hz, J_2 = 1 Hz, 1H), 2.25–2.12 (m, 4H), 1.71–1.53 (ov. m, 6H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.7, 114.1, 83.2, 33.7, 28.9, 26.8, 26.4, 24.9, 11.0 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* for $C_{13}H_{24}BO_2$ [M+H$^+$] calcd: 223.1864, found: 223.1861.

4,4,5,5-Tetramethyl-2-(3-methylpent-2-en-1-yl)-1,3,2-dioxaborolane (2f)



Following the above method, a colorless oil in 83% yield (35 mg, *E*:*Z* = 2:1) from **1f** (25 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

2f-a mixture of isomers

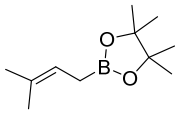
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26–5.16 (m, 1H), 2.04–1.95 (m, 2H), 1.68–1.66 and 1.62–1.56 (m, 5H), 1.23 (s, 12H), 0.99–0.92 (m, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.24, 137.21, 118.1, 117.2, 83.20, 83.17, 32.6, 24.89, 24.88, 23.0, 15.9, 13.1, 12.6, 11.9 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* for $C_{12}H_{24}BO_2$ [M+H$^+$] calcd: 211.1864, found: 211.1860.

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



Following the above method, a colorless oil in 68% yield (27 mg) from **1g** (22 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

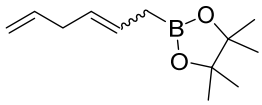
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.22 (tqq, J_1 = 8 Hz, J_2 = 2 Hz, J_3 = 1 Hz, 1H), 1.69–1.68 (m, 3H), 1.62–1.57 (m, 5H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 131.7, 118.7, 83.2, 25.9, 24.9, 17.8, 12.0 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.2.

HRMS (ASAP): *m/z* for $C_{11}H_{22}BO_2$ [M+H$^+$] calcd: 197.1707, found: 197.1703.

2-(Hexa-2,5-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)



Following the above method, a colorless oil in 72% yield (30 mg, *E*:*Z* = 11:1) from **1h** (24 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

2h-*major (E)-isomer*

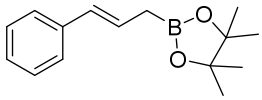
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88–5.75 (m, 1H), 5.54–5.35 (m, 2H), 5.04–4.98 (m, 1H), 4.97–4.91 (m, 1H), 2.78–2.70 (m, 2H), 1.66 (d, *J* = 7 Hz, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 137.8, 128.3, 126.4, 114.7, 83.3, 37.0, 27.7 (broad, low intensity), 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* for $C_{12}H_{22}BO_2$ [M+H$^+$] calcd: 209.1707, found: 209.1700.

(*E*)-2-Cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i)



Following the above method, a colorless oil in 69% yield (34 mg) from **1i** (27 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:Et_2O = 97:3), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

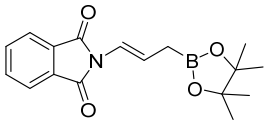
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.31 (m, 2H), 7.30–7.23 (m, 2H), 7.19–7.13 (m, 1H), 6.41–6.24 (m, 2H), 1.87 (d, *J* = 7 Hz, 2H), 1.26 (s, 12H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.3, 130.4, 128.5, 126.6, 126.4, 126.0, 83.5, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* for $C_{15}H_{22}BO_2$ [M+H$^+$] calcd: 245.1707, found: 245.1702.

(*E*)-2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)isoindoline-1,3-dione (2j)



Following the above method, a colorless oil in 69% yield (43 mg) from **1j** (37 mg, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

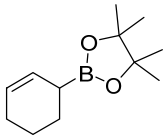
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86–7.81 (m, 2H), 7.73–7.68 (m, 2H), 6.67–6.57 (m, 2H), 1.81 (d, *J* = 6 Hz, 2H), 1.26 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 166.8, 134.3, 131.9, 123.5, 119.0, 117.9, 83.7, 24.9, 14.4 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.9.

HRMS (ASAP): *m/z* for $C_{17}H_{20}BNO_4$ [M+H$^+$] calcd: 313.1485, found: 313.1481.

2-(Cyclohex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



Following the above method, a colorless oil in 71% yield (30 mg) from **1k** (20 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

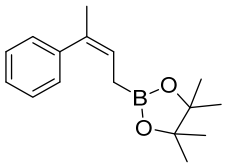
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75–5.64 (m, 2H), 2.02–1.95 (m, 2H), 1.83–1.72 (m, 2H), 1.70–1.56 (m, 3H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 127.7, 126.2, 83.3, 25.1, 24.9, 24.8, 24.3, 22.7, 21.4 (broad, low intensity).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.5.

HRMS (ASAP): *m/z* for $C_{12}H_{22}BO_2$ [M+H$^+$] calcd: 209.1707, found: 209.1701.

(*Z*)-4,4,5,5-Tetramethyl-2-(3-phenylbut-2-en-1-yl)-1,3,2-dioxaborolane (2l)



Following the above method, a colorless oil in 71% yield (36.7 mg) from **1l** (26.4 mg, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

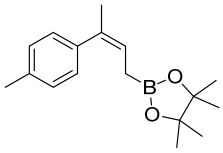
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2H), 7.23–7.18 (m, 3H), 5.60 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.03 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.62 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.23 (s, 12H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 142.2, 136.1, 128.3, 128.2, 126.4, 122.0, 83.3, 25.7, 24.9, 13.6 (broad, low intensity).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.0.

HRMS (ASAP): *m/z* for $C_{16}H_{24}BO_2$ [M+H$^+$] calcd: 259.1864, found: 259.1861.

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



Following the above method, a colorless oil in 74% yield (40.3 mg) from **1m** (29.2 mg, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 °C.

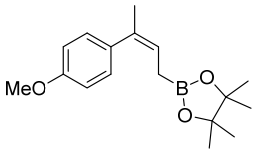
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17–7.07 (m, 4H), 5.58 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.34 (s, 3H), 2.03 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.64 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.2, 135.9 (2C), 128.8, 128.2, 121.7, 83.3, 25.7, 24.9, 21.3, 13.8 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* for $C_{17}H_{26}BO_2$ [M+H$^+$] calcd: 273.2020, found: 273.2016.

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



Following the above method, a colorless oil in 79% yield (45.5 mg) from **1n** (32.4 mg, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

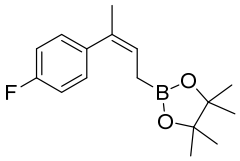
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20–7.13 (m, 2H), 6.90–6.83 (m, 2H), 5.56 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 3.80 (s, 3H), 2.02 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.65 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 158.1, 135.4, 134.5, 129.3, 121.5, 113.5, 83.2, 55.3, 25.7, 24.9, 13.7 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.2.

HRMS (ASAP): *m/z* for $C_{17}H_{26}BO_3$ [M+H$^+$] calcd: 289.1970, found: 289.1965.

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



Following the above method, a colorless oil in 70% yield (38.7 mg) from **1o** (30.0 mg, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.13 (m, 2H), 7.04–6.95 (m, 2H), 5.59 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.01 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.60 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.23 (s, 12H).

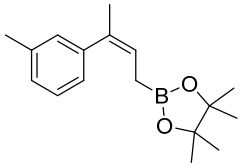
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 161.6 (d, $J_{C\text{-}F}$ = 244 Hz), 138.1 (d, $J_{C\text{-}F}$ = 3 Hz), 135.1, 129.8 (d, $J_{C\text{-}F}$ = 8 Hz), 122.4, 114.9 (d, $J_{C\text{-}F}$ = 21 Hz), 83.3, 25.7, 24.9, 13.6 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ -116.7 (tt, J_1 = 6 Hz, J_2 = 9 Hz, 1F).

HRMS (ASAP): *m/z* for $C_{16}H_{23}BFO_2$ [M+H$^+$] calcd: 277.1770, found: 277.1764.

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



Following the above method, a colorless oil in 73% yield (39.7 mg) from **1p** (29.2 mg, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.17 (m, 1H), 7.08–7.00 (m, 3H), 5.59 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.35 (s, 3H), 2.03 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.64 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.25 (s, 12H).

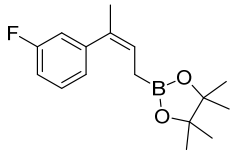
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.2, 137.5, 136.1, 129.0, 128.0, 127.2, 125.3, 121.8, 83.3,

25.7, 24.9, 21.6, 13.7 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* for $C_{17}H_{26}BO_2$ [M+H$^+$] calcd: 273.2020, found: 273.2018.

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



Following the above method, a colorless oil in 74% yield (40.9 mg) from **1q** (30.0 mg, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.22 (m, 1H), 7.02–6.85 (m, 3H), 5.61 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.01 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.62 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.24 (s, 12H).

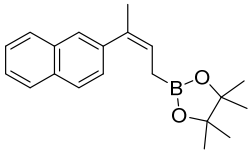
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 245 Hz), 144.6 (d, $J_{C\text{-}F}$ = 7 Hz), 134.9 (d, $J_{C\text{-}F}$ = 2 Hz), 129.6 (d, $J_{C\text{-}F}$ = 8 Hz), 123.9 (d, $J_{C\text{-}F}$ = 3 Hz), 122.9, 115.2 (d, $J_{C\text{-}F}$ = 21 Hz), 113.2 (d, $J_{C\text{-}F}$ = 21 Hz), 83.4, 25.5, 24.9, 13.8 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ -114.0 (ddd, J_1 = 1.5 Hz, J_2 = 6 Hz, J_3 = 9 Hz, 1F).

HRMS (ASAP): *m/z* for $C_{16}H_{23}BFO_2$ [M+H$^+$] calcd: 277.1770, found: 277.1766.

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



Following the above method, a colorless oil in 64% yield (39.5 mg) from **1r** (36.5 mg, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 95:5), during which some decomposition occurs. The reaction was complete within 9 h at 60 ºC.

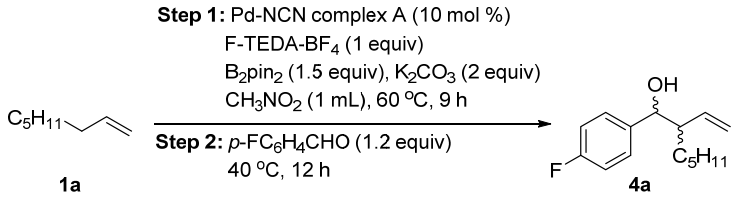
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.77 (m, 3H), 7.70 (s, 1H), 7.48–7.37 (m, 3H), 5.71 (tq, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 2.14 (dt, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 3H), 1.71 (dq, J_1 = 8 Hz, J_2 = 1.5 Hz, 2H), 1.25 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.7, 136.0, 133.5, 132.3, 127.9, 127.7, 127.6, 126.9, 126.8, 125.9, 125.5, 122.6, 83.3, 25.7, 24.9, 14.0 (broad, low intensity).

^{11}B NMR (96 MHz, $CDCl_3$) δ 33.1.

HRMS (ASAP): *m/z* for $C_{20}H_{26}BO_2$ [M+H$^+$] calcd: 309.2020, found: 309.2016.

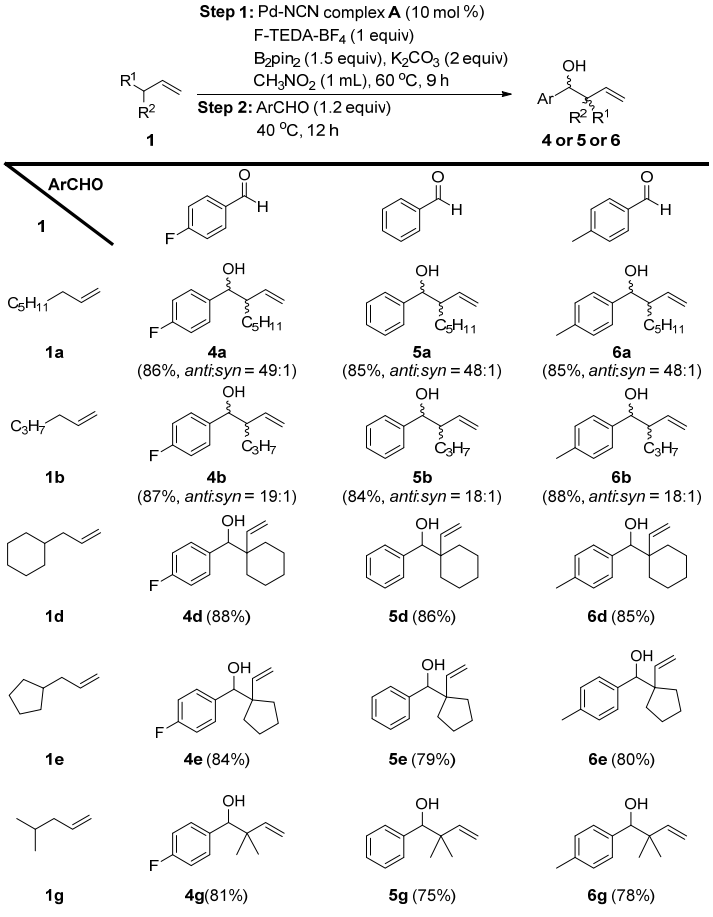
VIII. Application in One-pot Carbonyl Allylation Reactions



Step 1: Pd-NCN complex **A** (10 mol %, 7 mg) and F-TEDA-BF_4 (1 equiv, 71 mg, 0.2 mmol) were dissolved in 0.5 mL of CH_3NO_2 in a dried vial in a glove-box under argon and the reaction was stirred for 5 min. Then, B_2pin_2 (1.5 equiv, 76 mg, 0.3 mmol), **1a** (1.0 equiv, 31 μL, 0.2 mmol), and K_2CO_3 (2.0 equiv, 55 mg, 0.4 mmol) were added in this order. Finally, another 0.5 mL of CH_3NO_2 was added to the mixture. The reaction was heated at 60 °C under argon until the starting material was completely consumed (determined by GC-MS).

Step 2: 4-Fluorobenzaldehyde (1.2 equiv, 26 μL, 0.24 mmol) was added to the reaction mixture after it cooled to room temperature, and the reaction was heated at 40 °C for 12 h. The crude mixture was filtered through a pad of Celite. Then, the solvent was removed on a rotary evaporator. A colorless oil in 86% yield (41 mg, *anti*:*syn* = 49:1) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

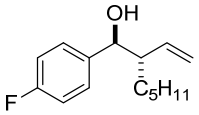
Scheme S1. Application in One-pot Carbonyl Allylation Reactions[a,b,c]



[a] Step **1**: **1** (0.2 mmol, 1 equiv), Pd-NCN complex **A** (10 mol %), F-TEDA-BF_4 (0.2 mmol, 1 equiv), K_2CO_3 (0.4 mmol, 2 equiv), B_2pin_2 (0.3 mmol, 1.5 equiv), CH_3NO_2 (1 mL), 60 °C. Step **2**: ArCHO (0.24 mmol, 1.2 equiv), 40 °C. [b] Isolated yield. [c] The *anti*/*syn* ratios were determined by ^{1}H NMR spectroscopy of the crude product.

The allylic C-H borylation of **1a**, accomplished under the standard conditions, followed by addition of 1.2 equiv of an aldehyde, such as 4-fluorobenzaldehyde, benzaldehyde, and *p*-tolualdehyde, gave homoallyl alcohols **4a**, **5a** and **6a** in overall yields of 86%, 85% and 85%, respectively. When we employed **1b** as the substrate, the one-pot, two-step carbonyl allylation reactions also proceeded with high efficiency, affording **4b**, **5b** and **6b** in overall yields of 87%, 84% and 88%, respectively. When acyclic alkyl groups were replaced with cyclohexyl (**1d**) or cyclopentyl (**1e**) groups, the allylation reactions proceeded smoothly giving the desired homoallyl alcohols (**4-6)d** and (**4-6)e** in high overall yields. With disubstituted alkene **1g** as starting material, products **4g, 5g** and **6g** were obtained in overall yields of 75%-81%.

1-(4-Fluorophenyl)-2-vinylheptan-1-ol (4a)



4a-major-anti-isomer

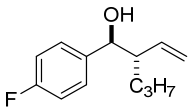
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 7.05–6.99 (m, 2H), 5.63 (ddd, J_1 = 9 Hz, J_2 = 10 Hz, J_3 = 17 Hz, 1H), 5.25 (dd, J_1 = 2 Hz, J_2 = 10 Hz, 1H), 5.17 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 17 Hz, 1H), 4.35 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 2.33–2.30 (m, 1H), 2.26–2.19 (m, 1H), 1.37–1.04 (ov. m, 8H, slightly overlapped with the *syn* isomer), 0.83 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 245 Hz), 139.3, 138.4 (d, $J_{C\text{-}F}$ = 3 Hz), 128.6 (d, $J_{C\text{-}F}$ = 8 Hz), 119.0, 115.1 (d, $J_{C\text{-}F}$ = 21 Hz), 76.1, 53.1, 31.8, 30.4, 26.9, 22.6, 14.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ -115.1 (tt, J_1 = 5 Hz, J_2 = 8 Hz, 1F).

HRMS (ASAP): *m/z* for $C_{15}H_{22}FO$ [M+H$^+$] calcd: 237.1649, found: 237.1646.

1-(4-Fluorophenyl)-2-vinylpentan-1-ol (4b)



Following the above method, a colorless oil in 87% yield (39 mg, *anti*:*syn* = 19:1) from **1b** (25 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

4b-major-anti-isomer

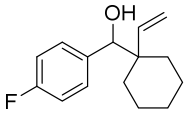
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 7.05–7.00 (m, 2H), 5.63 (ddd, J_1 = 9 Hz, J_2 = 10 Hz, J_3 = 17 Hz, 1H), 5.25 (dd, J_1 = 2 Hz, J_2 = 10 Hz, 1H), 5.17 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 17 Hz, 1H), 4.36 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 2.32–2.28 (m, 1H), 2.28–2.21 (m, 1H), 1.41–1.06 (ov. m, 4H, slightly overlapped with the *syn* isomer), 0.79 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 245 Hz), 139.3, 138.4 (d, $J_{C\text{-}F}$ = 3 Hz), 128.6 (d, $J_{C\text{-}F}$ = 8 Hz), 119.1, 115.1 (d, $J_{C\text{-}F}$ = 21 Hz), 76.1, 52.8 (d, J = 1 Hz), 32.6, 20.4, 14.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ -115.1 (tt, J_1 = 5 Hz, J_2 = 8 Hz, 1F).

HRMS (ASAP): *m/z* for $C_{13}H_{18}FO$ [M+H$^+$] calcd: 209.1336, found: 209.1333.

(4-Fluorophenyl)(1-vinylcyclohexyl)methanol (4d)



Following the above method, a colorless oil in 88% yield (41 mg) from **1d** (31 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

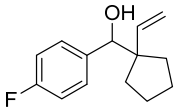
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24–7.18 (m, 2H), 7.01–6.95 (m, 2H), 5.53 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.41 (dd, J_1 = 2 Hz, J_2 = 11 Hz, 1H), 5.10 (dd, J_1 = 2 Hz, J_2 = 18 Hz, 1H), 4.33 (d, J = 5 Hz, 1H), 2.13 (d, J = 5 Hz, 1H), 1.93–1.83 (m, 1H), 1.61-1.27 (m, 8 H), 1.16–1.05 (m, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 247 Hz), 141.8, 136.5 (d, $J_{C\text{-}F}$ = 3 Hz), 129.6 (d, $J_{C\text{-}F}$ = 8 Hz), 117.9, 114.3 (d, $J_{C\text{-}F}$ = 21 Hz), 80.5, 45.8 (d, J = 1 Hz), 33.0, 31.2, 26.5, 22.2, 22.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ -115.5 (tt, J_1 = 5 Hz, J_2 = 8 Hz, 1F).

HRMS (ASAP): *m/z* for $C_{15}H_{20}FO$ [M+H$^+$] calcd: 235.1493, found: 235.1490.

(4-Fluorophenyl)(1-vinylcyclopentyl)methanol (4e)



Following the above method, a colorless oil in 84% yield (37 mg) from **1e** (28 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

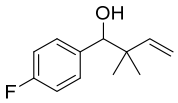
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27–7.22 (m, 2H), 7.01–6.94 (m, 2H), 5.74 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.18 (dd, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.02 (dd, J_1 = 1 Hz, J_2 = 18 Hz, 1H), 4.51 (d, J = 4 Hz, 1H), 2.17–2.12 (m, 1H), 1.84–1.76 (m, 1H), 1.71–1.49 (m, 6H), 1.43–1.35 (m, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.2 (d, $J_{C\text{-}F}$ = 246 Hz), 141.5, 137.8 (d, $J_{C\text{-}F}$ = 3 Hz), 129.1 (d, $J_{C\text{-}F}$ = 8 Hz), 115.3, 114.5 (d, $J_{C\text{-}F}$ = 21 Hz), 79.8, 55.3 (d, J = 1 Hz), 34.3, 33.2, 23.50, 23.48.

^{19}F NMR (470 MHz, $CDCl_3$) δ -115.5 (tt, J_1 = 5 Hz, J_2 = 8 Hz, 1F).

HRMS (ASAP): *m/z* for $C_{14}H_{18}FO$ [M+H$^+$] calcd: 221.1336, found: 221.1331.

1-(4-Fluorophenyl)-2,2-dimethylbut-3-en-1-ol (4g)



Following the above method, a colorless oil in 81% yield (31 mg) from **1g** (31 μL, 0.2 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

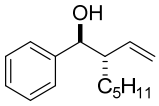
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.23 (m, 2H), 7.03–6.96 (m, 2H), 5.89 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.15 (dd, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.07 (dd, J_1 = 1 Hz, J_2 = 18 Hz, 1H), 4.41 (d, J = 3 Hz, 1H), 2.07–2.02 (m, 1H), 0.99 (s, 3H), 0.94 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 245 Hz), 145.0, 136.5 (d, $J_{C\text{-}F}$ = 3 Hz), 129.4 (d, $J_{C\text{-}F}$ = 8 Hz), 114.5 (d, $J_{C\text{-}F}$ = 21 Hz), 114.3, 80.1, 42.4 (d, J = 1 Hz), 24.6, 21.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ -115.4 (tt, J_1 = 5 Hz, J_2 = 8 Hz, 1F).

HRMS (ASAP): *m/z* for $C_{12}H_{16}FO$ [M+H$^+$] calcd: 195.1180, found: 195.1177.

1-Phenyl-2-vinylheptan-1-ol (5a)



Following the above method, a colorless oil in 85% yield (37 mg, *anti*:*syn* = 48:1) from **1a** (31 μL, 0.2 mmol) and benzaldehyde (1.2 equiv, 24 μL, 0.24 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7). The characterization data (^{1}H and ^{13}C NMR) are in accordance with those in the literature.[5]

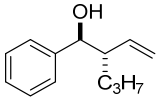
5a-major-anti-isomer

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.25 (m, 5H, slightly overlapped with *syn* isomer), 5.67 (ddd, J_1 = 9 Hz, J_2 = 10 Hz, J_3 = 17 Hz, 1H), 5.25 (dd, J_1 = 2 Hz, J_2 = 10 Hz, 1H), 5.18 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 17 Hz, 1H), 4.39 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 2.37–2.20 (ov. m, 2H), 1.38–1.05 (m, 8H, slightly overlapped with *syn* isomer), 0.85 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.7, 139.5, 128.3, 127.6, 127.0, 118.7, 76.8, 52.8, 31.8, 30.5, 26.9, 22.6, 14.1.

HRMS (ASAP): *m/z* for $C_{15}H_{23}O$ [M+H$^+$] calcd: 219.1743, found: 219.1740.

1-Phenyl-2-vinylpentan-1-ol (5b)



Following the above method, a colorless oil in 84% yield (32 mg, *anti*:*syn* = 18:1) from **1b** (25 μL, 0.2 mmol) and benzaldehyde (1.2 equiv, 24 μL, 0.24 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

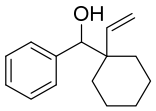
5b-major-anti-isomer

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.25 (m, 5H, slightly overlapped with *syn* isomer), 5.69 (ddd, J_1 = 9 Hz, J_2 = 10 Hz, J_3 = 17 Hz, 1H), 5.28 (dd, J_1 = 2 Hz, J_2 = 10 Hz, 1H), 5.20 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 17 Hz, 1H), 4.41 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 2.50–2.31 (m, 1H), 2.30 (d, J = 2 Hz, 1H), 1.63–1.08 (m, 4H, slightly overlapped with *syn* isomer), 0.83 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.7, 139.5, 128.3, 127.7, 127.1, 118.7, 76.8, 52.6, 32.7, 20.4, 14.0.

HRMS (ASAP): *m/z* for $C_{13}H_{19}O$ [M+H$^+$] calcd: 191.1430, found: 191.1427.

Phenyl(1-vinylcyclohexyl)methanol (5d)



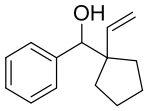
Following the above method, a colorless oil in 86% yield (37 mg) from **1d** (31 μL, 0.2 mmol) and benzaldehyde (1.2 equiv, 24 μL, 0.24 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7). The characterization data (^{1}H and ^{13}C NMR) are in accordance with those in the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.22 (m, 5H), 5.56 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.41 (dd, J_1 = 2 Hz, J_2 = 11 Hz, 1H), 5.11 (dd, J_1 = 2 Hz, J_2 = 18 Hz, 1H), 4.35 (d, J = 5 Hz, 1H), 2.12 (d, J = 5 Hz, 1H), 1.96–1.86 (m, 1H), 1.58–1.27 (m, 9H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 142.0, 140.9, 128.2, 127.5, 127.4, 117.7, 81.2, 45.9, 33.0, 31.5, 26.5, 22.24, 22.15.

HRMS (ASAP): *m/z* for $C_{15}H_{21}O$ [M+H$^+$] calcd: 217.1587, found: 217.1583.

Phenyl(1-vinylcyclopentyl)methanol (5e)



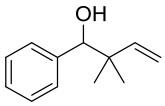
Following the above method, a colorless oil in 79% yield (32 mg) from **1e** (28 μL, 0.2 mmol) and benzaldehyde (1.2 equiv, 24 μL, 0.24 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

^1H NMR (300 MHz, $CDCl_3$) δ 7.35–7.22 (m, 5H), 5.78 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.19 (dd, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.05 (dd, J_1 = 1 Hz, J_2 = 18 Hz, 1H), 4.54 (d, J = 4 Hz, 1H), 2.09 (d, J = 4 Hz, 1H), 1.67–1.87 (m, 2H), 1.51–1.65 (m, 5H), 1.90–1.36 (m, 8H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 142.1, 141.8, 127.7, 127.6, 127.5, 115.1, 80.4, 55.4, 34.3, 33.3, 23.53, 23.51.

HRMS (ASAP): *m/z* for $C_{14}H_{19}O$ [M+H$^+$] calcd: 203.1430, found: 203.1427.

2,2-Dimethyl-1-phenylbut-3-en-1-ol (5g)



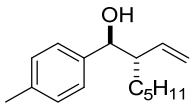
Following the above method, a colorless oil in 75% yield (26 mg) from **1g** (31 μL, 0.2 mmol) and benzaldehyde (1.2 equiv, 24 μL, 0.24 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

^1H NMR (300 MHz, $CDCl_3$) δ 7.36–7.23 (m, 5H), 5.92 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.15 (dd, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.08 (dd, J_1 = 1 Hz, J_2 = 18 Hz, 1H), 4.43 (d, J = 3 Hz, 1H), 2.03 (br. d, J = 3 Hz, 1H), 1.02 (s, 3H), 0.97 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 145.2, 140.9, 127.9, 127.63, 127.55, 114.0, 80.8, 42.4, 24.6, 21.2.

HRMS (ASAP): *m/z* for $C_{12}H_{17}O$ [M+H$^+$] calcd: 177.1274, found: 177.1271.

1-(*p*-Tolyl)-2-vinylheptan-1-ol (6a)



Following the above method, a colorless oil in 85% yield (39 mg, *anti*:*syn* = 48:1) from **1a** (31 μL, 0.2 mmol) and *p*-tolualdehyde (1.2 equiv, 28 μL, 0.24 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

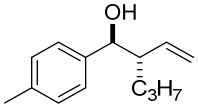
^1H NMR (300 MHz, $CDCl_3$) δ 7.25–7.20 (m, 2H), 7.19–7.13 (m, 2H), 5.67 (ddd, J_1 = 9 Hz, J_2 = 10 Hz, J_3 = 17 Hz, 1H), 5.26 (dd, J_1 = 2 Hz, J_2 = 10 Hz, 1H), 5.18 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 17 Hz, 1H), 4.36 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 2.37 (s, 3H), 2.34–2.23 (ov. m, 2H), 1.39–1.05 (m, 8H, slightly overlapped with the *syn* isomer), 0.85 (t, J = 7 Hz, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 139.7, 137.2, 129.0, 126.9, 118.5, 76.6, 52.7, 31.8, 30.5, 26.9,

22.6, 21.2, 14.1.

HRMS (ASAP): *m/z* for $C_{16}H_{25}O$ [M+H$^+$] calcd: 233.1900, found: 233.1897.

1-(*p*-Tolyl)-2-vinylpentan-1-ol (6b)



Following the above method, a colorless oil in 88% yield (36 mg, *anti*:*syn* = 18:1) from **1b** (25 μL, 0.2 mmol) and *p*-tolualdehyde (1.2 equiv, 28 μL, 0.24 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

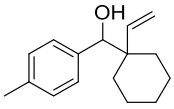
6b-major-anti-isomer

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.20 (m, 2H), 7.17–7.13 (m, 2H), 5.67 (ddd, J_1 = 9 Hz, J_2 = 10 Hz, J_3 = 17 Hz, 1H), 5.25 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 10 Hz, 1H), 5.19 (ddd, J_1 = 1 Hz, J_2 = 2 Hz, J_3 = 17 Hz, 1H), 4.35 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 2.36 (s, 3H), 2.35-2.25 (m, 1H), 2.22 (dd, J_1 = 1 Hz, J_2 = 2 Hz, 1H), 1.44–1.10 (m, 4H, slightly overlapped with *syn* isomer), 0.81 (t, J = 7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.7 (2C), 137.3, 129.0, 127.0, 118.6, 76.6, 52.6, 32.7, 21.2, 20.4, 14.0.

HRMS (ASAP): *m/z* for $C_{14}H_{21}O$ [M+H$^+$] calcd: 205.1587, found: 205.1583.

***p*-Tolyl(1-vinylcyclohexyl)methanol (6d)**



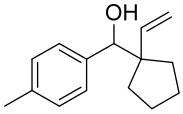
Following the above method, a colorless oil in 81% yield (37 mg) from **1d** (31 μL, 0.2 mmol) and *p*-tolualdehyde (1.2 equiv, 28 μL, 0.24 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17–7.07 (m, 4H), 5.56 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.39 (dd, J_1 = 2 Hz, J_2 = 11 Hz, 1H), 5.11 (dd, J_1 = 2 Hz, J_2 = 18 Hz, 1H), 4.31 (d, J = 5 Hz, 1H), 2.34 (s, 3H), 2.08 (d, J = 5 Hz, 1H), 1.95–1.84 (m, 1H), 1.62–1.25 (m, 9H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.1, 138.0, 137.0, 128.2, 128.0, 117.5, 81.0, 45.9, 33.0, 31.5, 26.5, 22.24, 22.15, 21.2.

HRMS (ASAP): *m/z* for $C_{16}H_{23}O$ [M+H$^+$] calcd: 231.1743, found: 231.1740.

***p*-Tolyl(1-vinylcyclopentyl)methanol (6e)**



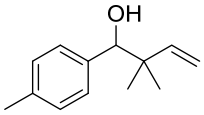
Following the above method, a colorless oil in 80% yield (35 mg) from **1e** (28 μL, 0.2 mmol) and *p*-tolualdehyde (1.2 equiv, 28 μL, 0.24 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.15 (m, 2H), 7.15–7.08 (m, 2H), 5.79 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.18 (dd, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.04 (dd, J_1 = 1 Hz, J_2 = 18 Hz, 1H), 4.51 (d, J = 4 Hz, 1H), 2.35 (s, 3H), 2.08 (d, J = 4 Hz, 1H), 1.87–1.37 (m, 8H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 142.0, 139.1, 137.0, 128.4, 127.5, 114.9, 80.3, 55.3, 34.3, 33.3, 23.5 (2C), 21.2.

HRMS (ASAP): *m/z* for $C_{15}H_{21}O$ [M+H$^+$] calcd: 217.1587, found: 217.1583.

2,2-Dimethyl-1-(p-tolyl)but-3-en-1-ol (6g)



Following the above method, a colorless oil in 78% yield (30 mg) from **1g** (31 μL, 0.2 mmol) and *p*-tolualdehyde (1.2 equiv, 28 μL, 0.24 mmol) was obtained via purification with flash chromatography on silica gel (pentane:EtOAc = 93:7).

^1H NMR (300 MHz, $CDCl_3$) δ 7.21−7.16 (m, 2H), 7.15−7.09 (m, 2H), 5.92 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 5.13 (dd, J_1= 1 Hz, J_2 = 11 Hz, 1H), 5.07 (dd, J_1 = 1 Hz, J_2 = 18 Hz, 1H), 4.41 (d, J = 3 Hz, 1H), 2.34 (s, 3H), 1.94 (d, J = 3 Hz, 1H), 1.01 (s, 3H), 0.96 (s, 3H).

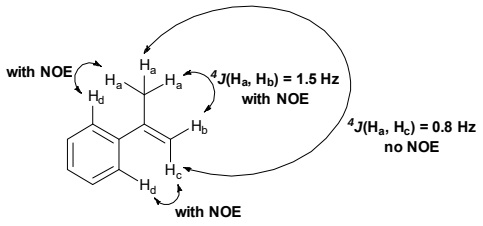
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 145.4, 138.0, 137.2, 128.4, 127.8, 113.9, 80.7, 42.4, 24.7, 21.3, 21.2.

HRMS (ASAP): *m/z* for $C_{13}H_{19}O$ [M+H$^+$] calcd: 191.1430, found: 191.1426.

IX. NOE Studies

1. Assignment of the Geometry of the C=C Bond in Compound 2l

To assign the geometry of the C=C bond in compound **2l**, we used α-methyl styrene as a model compound to investigate the relationship between ^4J coupling constants and the geometry of the C=C bond, as well as the NOE study (*vide infra*). In α-methyl styrene, $^4J(H_a, H_b)$ = 1.5 Hz, and $^4J(H_a, H_c)$ = 0.8 Hz. The $^4J(H_a, H_b)$ coupling constant is identical to the $^4J(H_e, H_f)$ coupling constant in compound **2l**. A $^1H,^1H$ NOESY study of α-methyl styrene also suggests that there is NOE between H_a and H_b, H_a and H_d, as well as H_c and H_d.

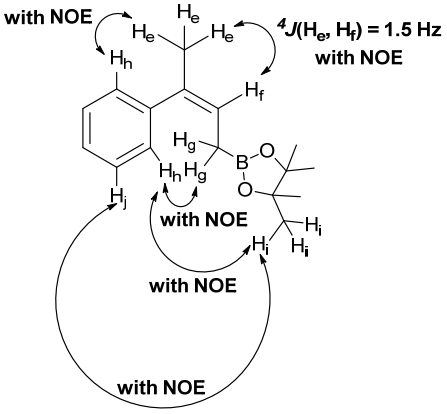


NOE-enhancements in [%]

irrad.	H_a	H_b	H_c	H_d
H_a		0.7	0	1.7
H_b	1.5		-3.7	-0.3
H_c	0	-2.5		2.8
H_d	H_d is not irradiated.			

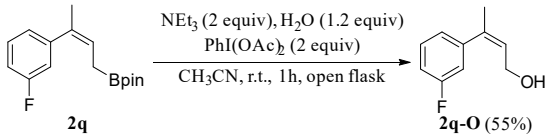
Due to fact that the NOE is strongly correlated with dipolar relaxation phenomena of two nuclei and the protons of the CH_3 group relax mainly by spin rotation, the NOE's in this compound are small. The relaxation process involved is thus not only dipolar, but due to the rotation of methyl group, the residual NOE of the three protons is also averaged. This leads to a small NOE between H_a and H_b which is of the same order of magnitude as that between H_a and H_c.

A $^1H,^1H$ NOESY study has also been carried out on compound **2l**. There is also NOE between H_e and H_f, H_e and H_h, H_h and H_i, as well as H_i and H_j. The NOE between H_g and H_h, H_h and H_i as well as H_i and H_j in combination with $^4J(H_e, H_f)$ = 1.5 Hz suggests that the C=C bond has the *Z* configuration. Additionally, the ^1H and ^{13}C NMR data of compound **2l** are identical to those in a literature report.[6a]



2. Assignment of the Geometry of the C=C Bond in Compound 2q

According to a literature procedure,[6b] **2q** was oxidized to provide the corresponding allylic alcohol **2q-O** in a 55% yield (46 mg). The NMR data are in agreement with the known compound (*Z*)-3-(3-fluorophenyl)but-2-en-1-ol.[6c]



2q **2q-O** (55%)

Characterization data of **2q-O** are listed below:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.25 (m, 1H), 6.98-6.92 (m, 2H), 6.90-6.86 (m, 1H), 5.70 (tq, J_1 = 7 Hz, J_2 = 1.5 Hz, 1H), 4.04 (dq, J_1 = 7 Hz, J_2 = 1 Hz, 2H), 3.07 (br.s, 1H), 2.05 (dt, J_1 = 1 Hz, J_2 = 0.5 Hz, 3H).

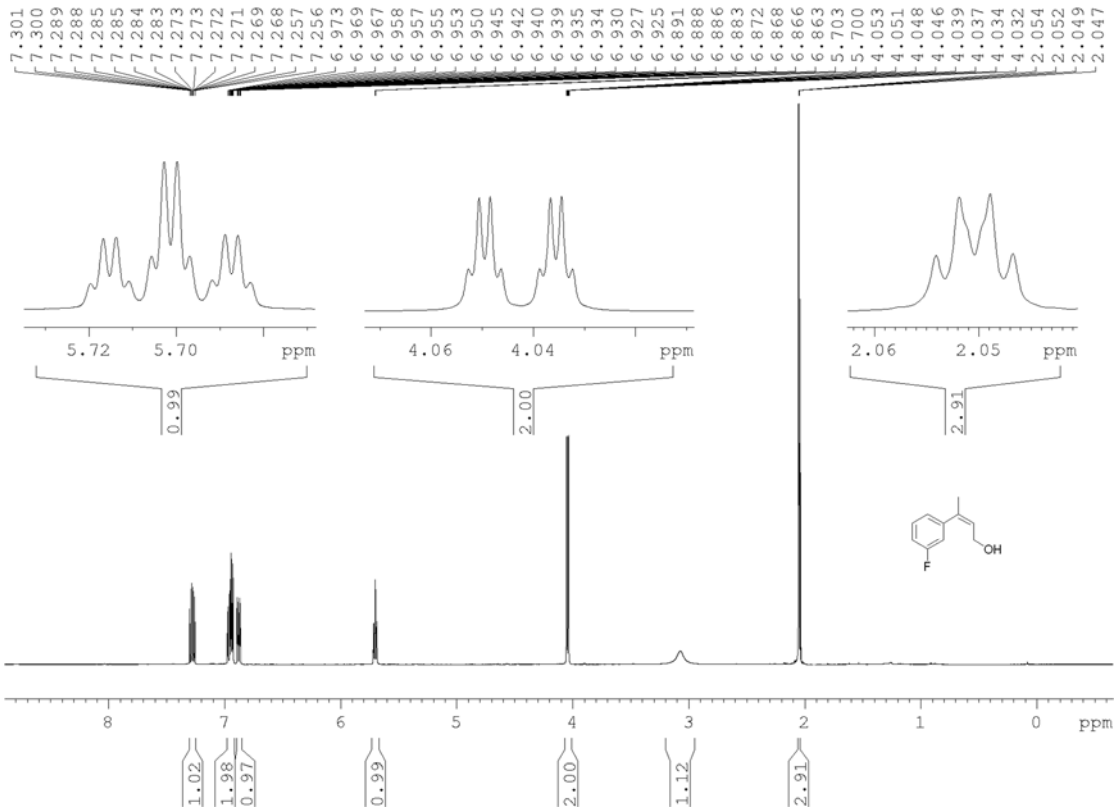
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 246 Hz), 143.1 (d, $J_{C\text{-}F}$ = 8 Hz), 138.8, 129.7 (d, $J_{C\text{-}F}$ = 8 Hz), 126.9, 123.6 (d, $J_{C\text{-}F}$ = 3 Hz), 114.8 (d, $J_{C\text{-}F}$ = 21 Hz), 114.1 (d, $J_{C\text{-}F}$ = 21 Hz), 60.0, 25.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ -113.3 (ddd, J_1 = 1.5 Hz, J_2 = 6 Hz, J_3 = 9 Hz, 1F).

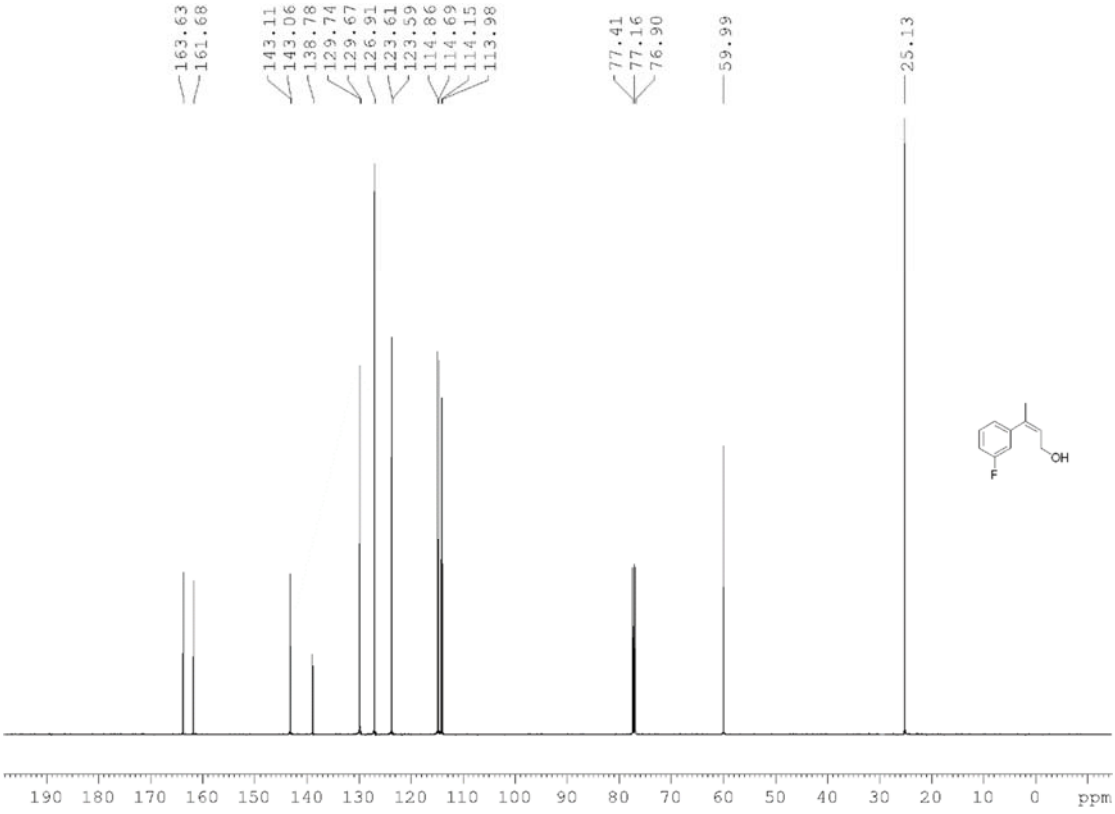
HRMS (ASAP) *m/z* for $C_{10}H_{12}FO$ [$M+H^+$] calcd: 167.0867, found: 167.0864.

Spectra of 2q-O

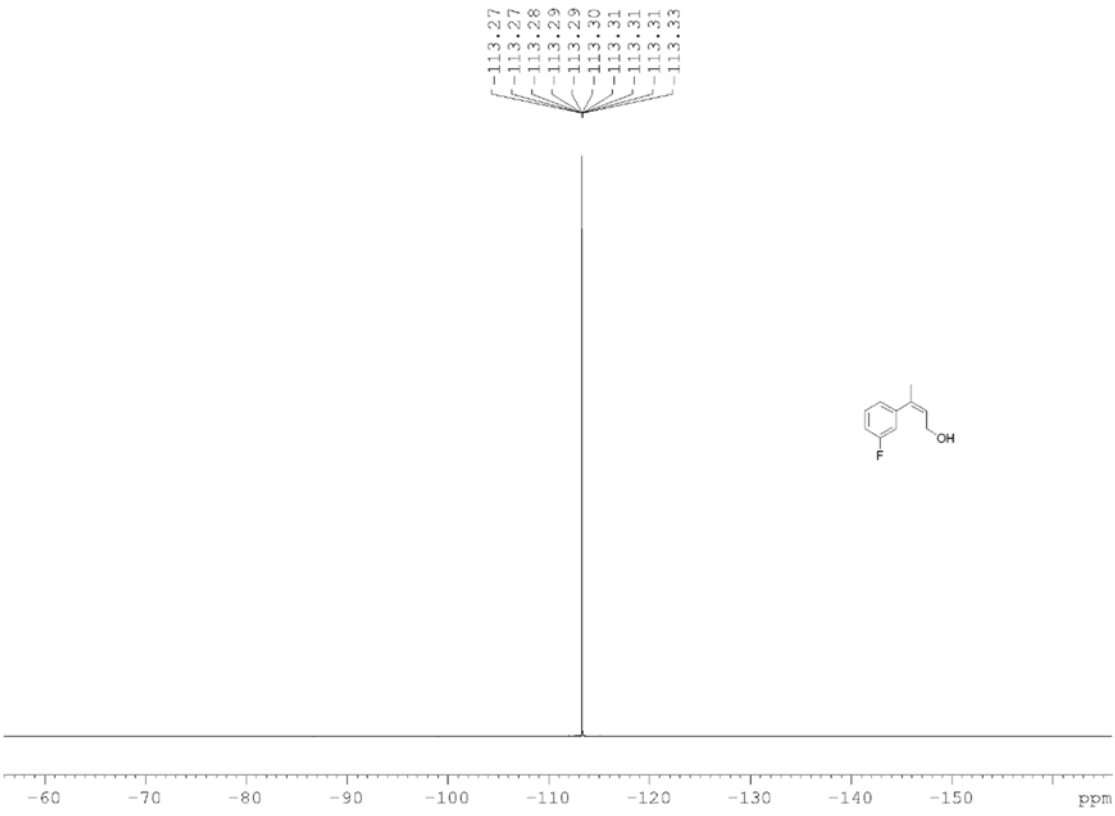
^{1}H NMR (500 MHz, $CDCl_3$)



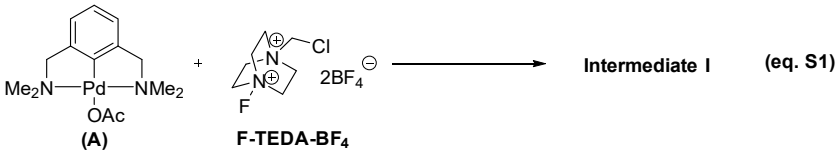
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$)

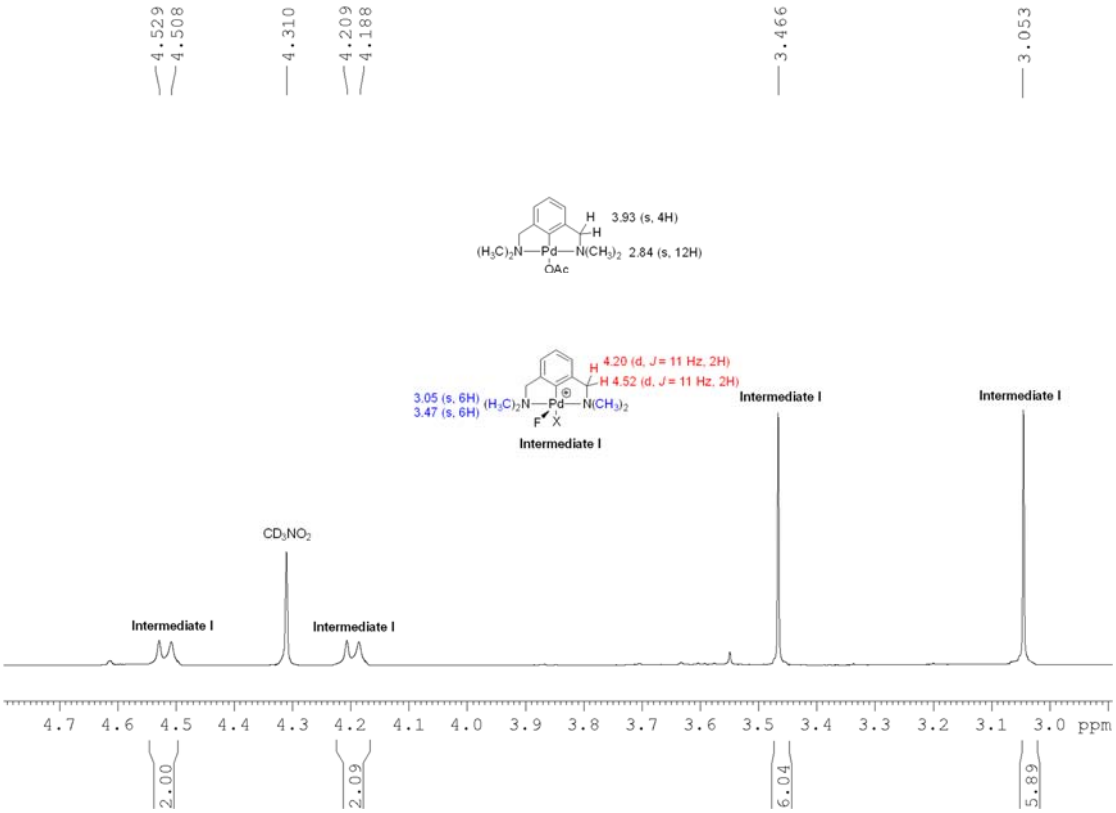


X. Mechanistic Study

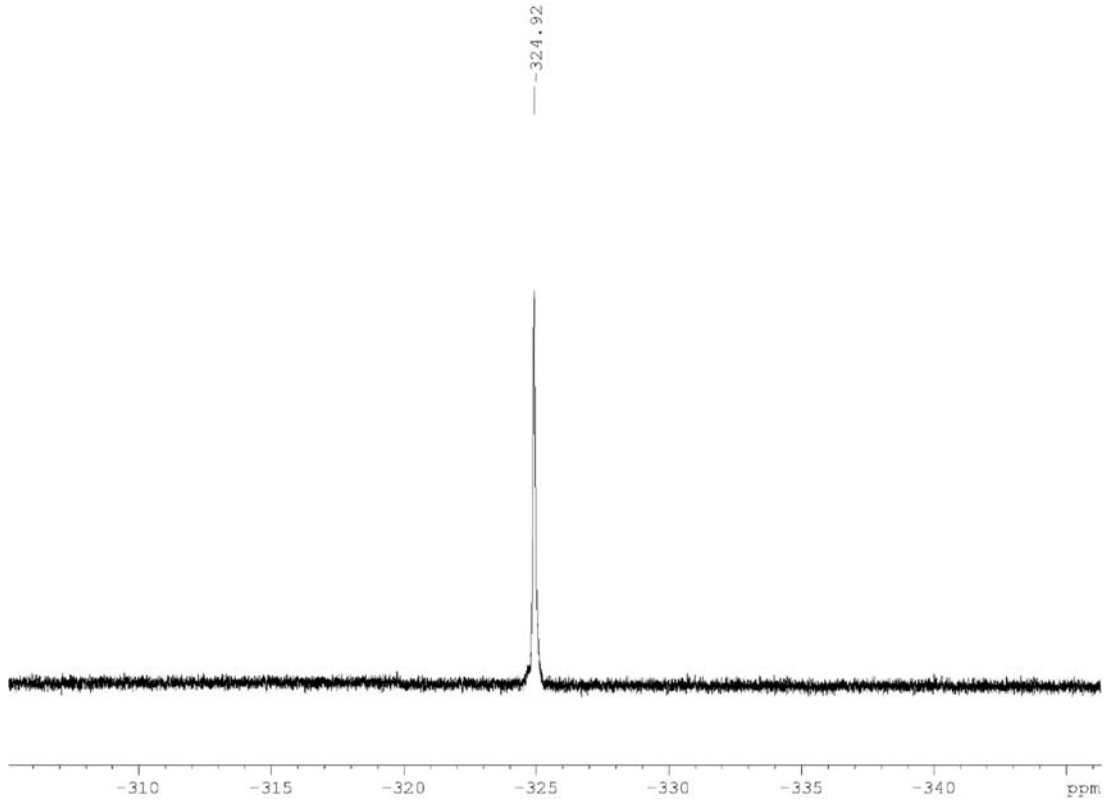


Palladium complex **A** (38 mg, 0.1 mmol, 1 equiv) was dissolved in CD_3NO_2 (0.5 mL), and F-TEDA-BF_4 (53 mg, 0.15 mmol, 1.5 equiv) was added. The sample was vigorously stirred for 5 min. to give a homogeneous solution. *In situ* ^1H and ^{19}F NMR were recorded at room temperature. Spectroscopic data for the relevant benzyl and methyl protons of proposed intermediate **I**: ^1H NMR (500 MHz, CD_3NO_2): δ 4.52 (d, J = 11 Hz, 2H, Ar-CH_2), 4.20 (d, J = 11 Hz, 2H, Ar-CH_2), 3.47 (s, 6H, NCH_3), 3.05 (s, 6H, NCH_3). The inequivalence of the benzylic protons and also the NMe_2 groups indicates that the Pd no longer has a square planar geometry and is likely square pyramidal with a vacant coordination site or octahedral with the two axial ligands being different. A single peak at -324.9 ppm was found by an *in situ* ^{19}F NMR study of the reaction mixture of **A** and F-TEDA-BF_4 in CD_3NO_2 at room temperature. These results suggest that a Pd(IV) intermediate was generated *in situ* from the reaction of palladium pincer-complex **A** with F-TEDA-BF_4.[7]

^1H NMR (500 MHz, CD_3NO_2)



^{19}F NMR (470 MHz, CD_3NO_2)



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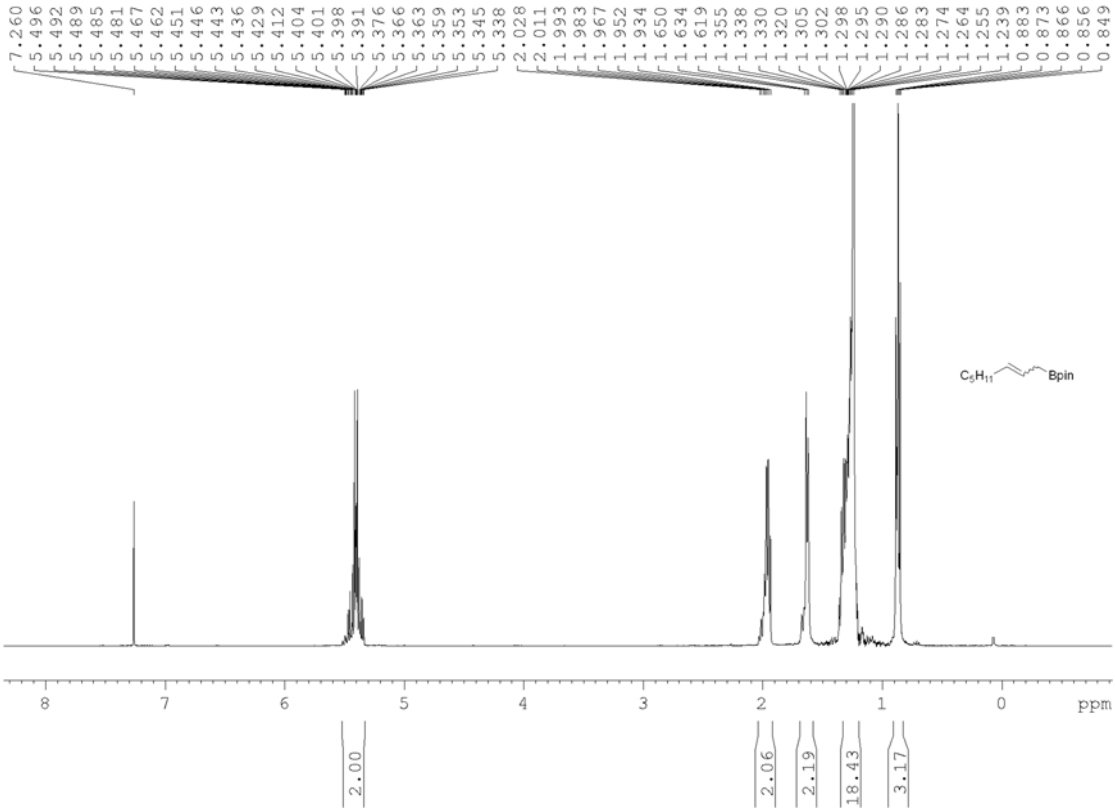
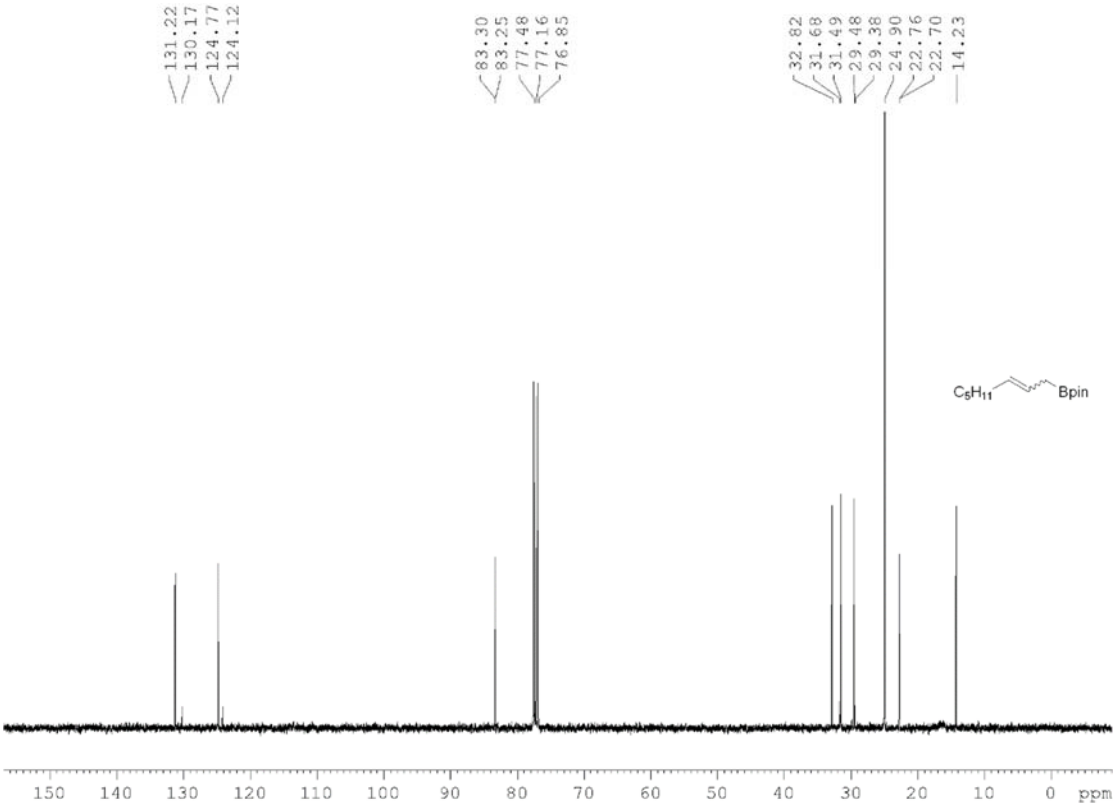
XI. ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR Spectra

Compound 2a

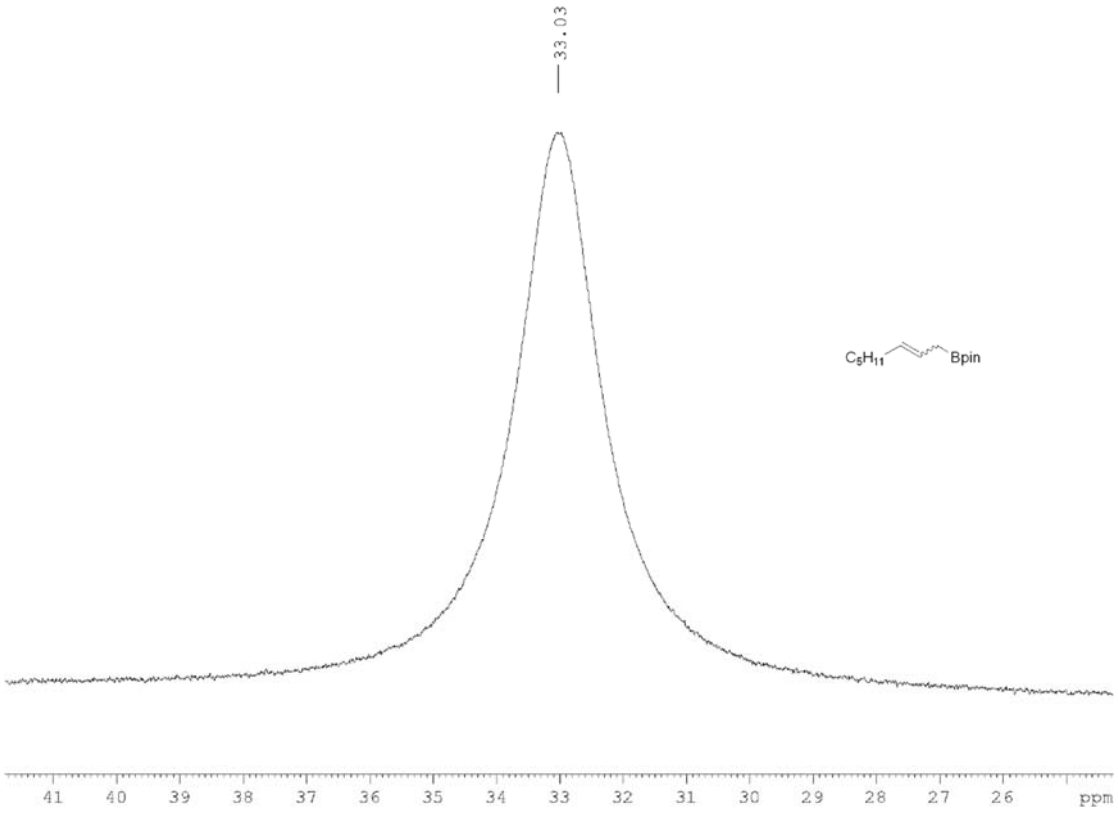
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

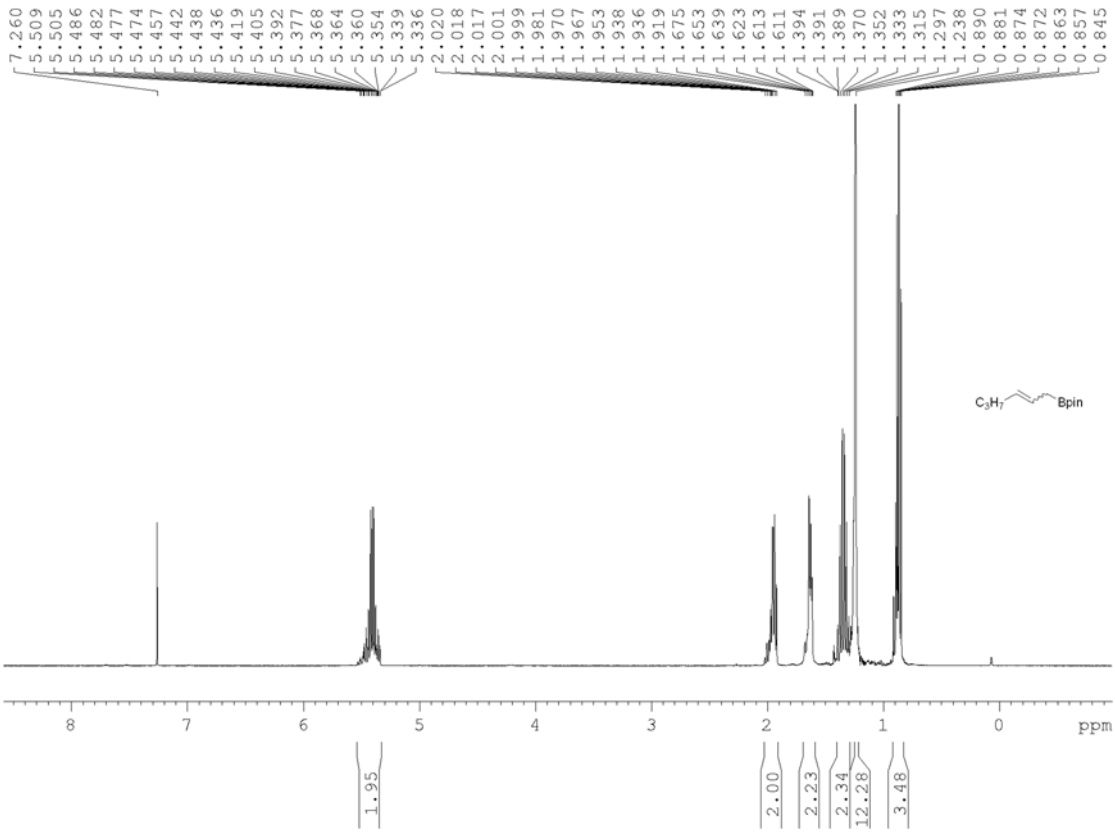


^{11}B NMR (128 MHz, $CDCl_3$)

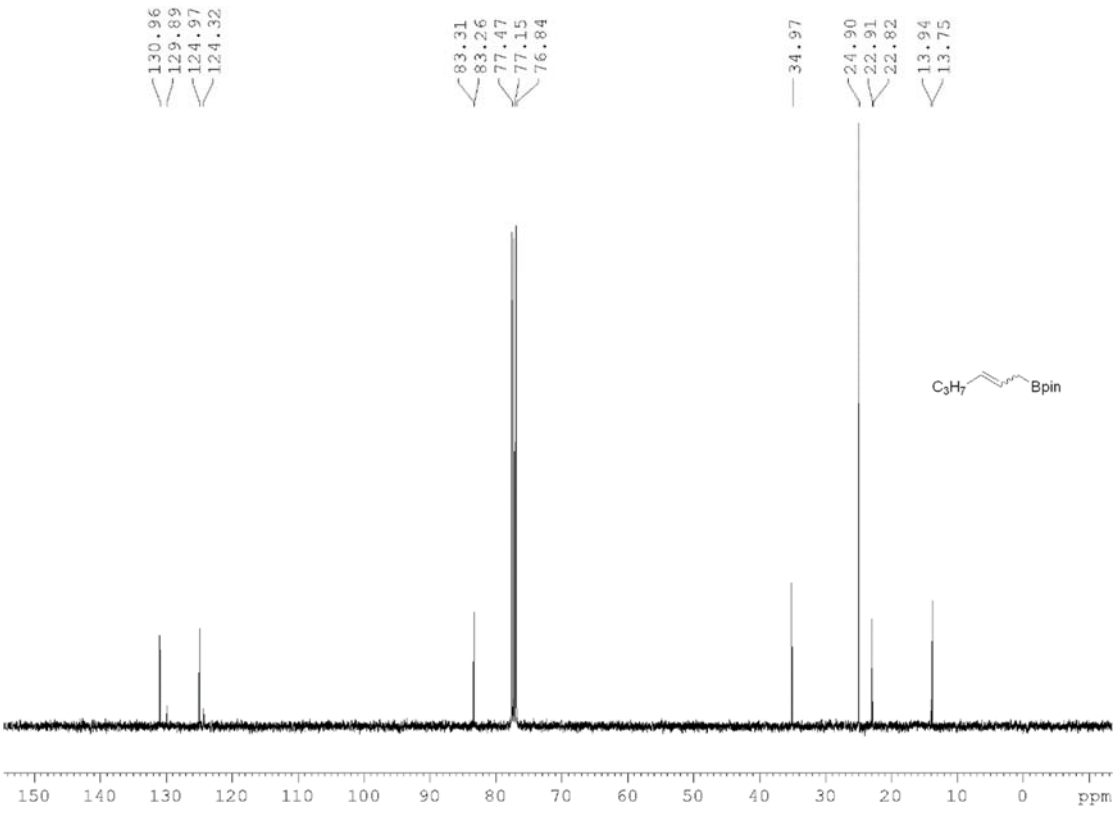


Compound 2b

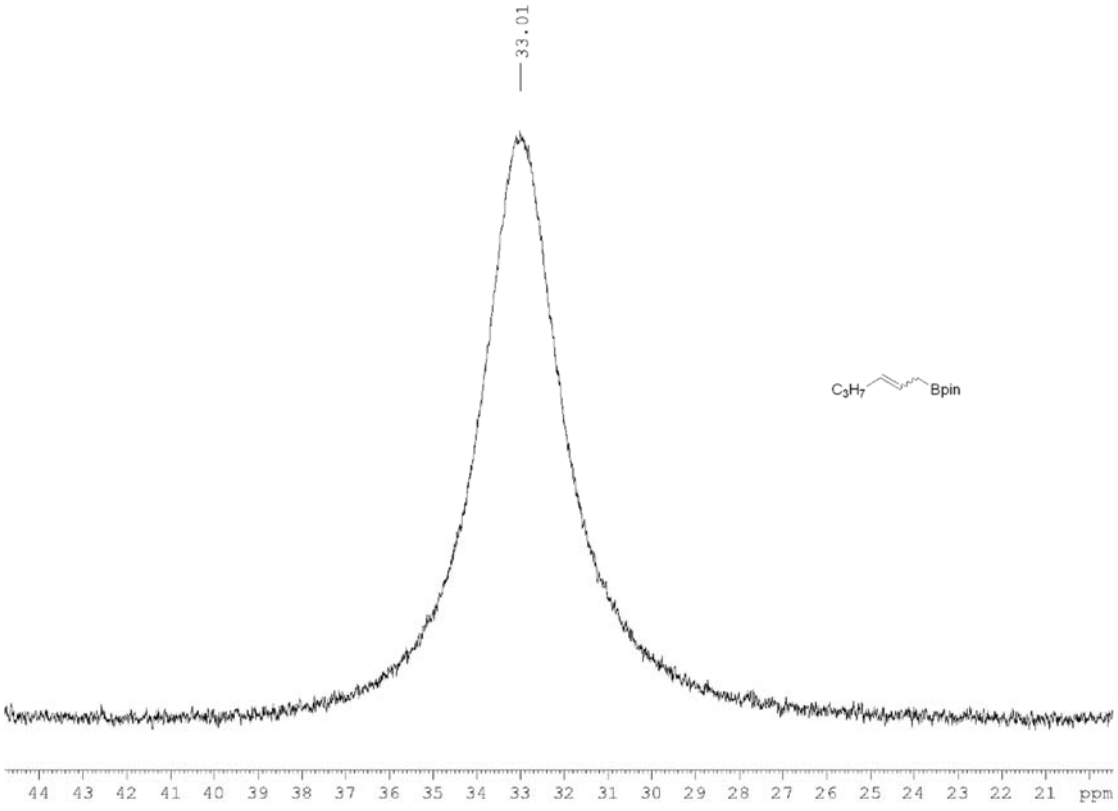
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

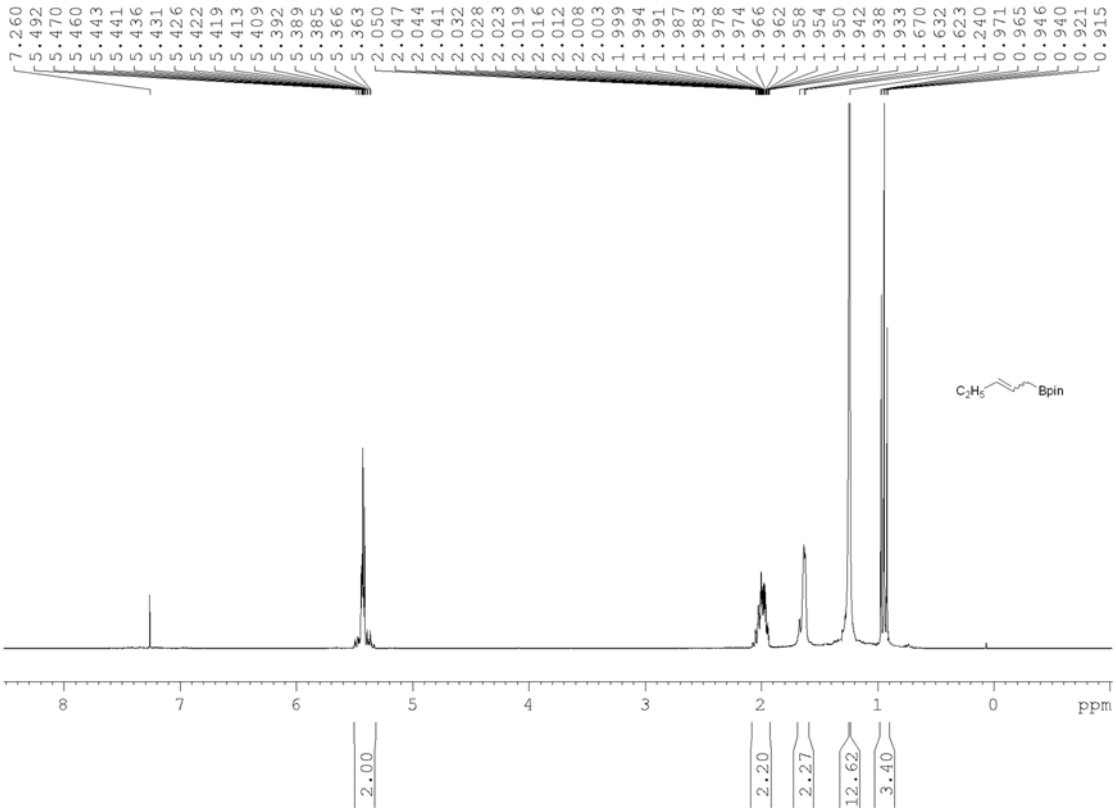


^{11}B NMR (128 MHz, $CDCl_3$)

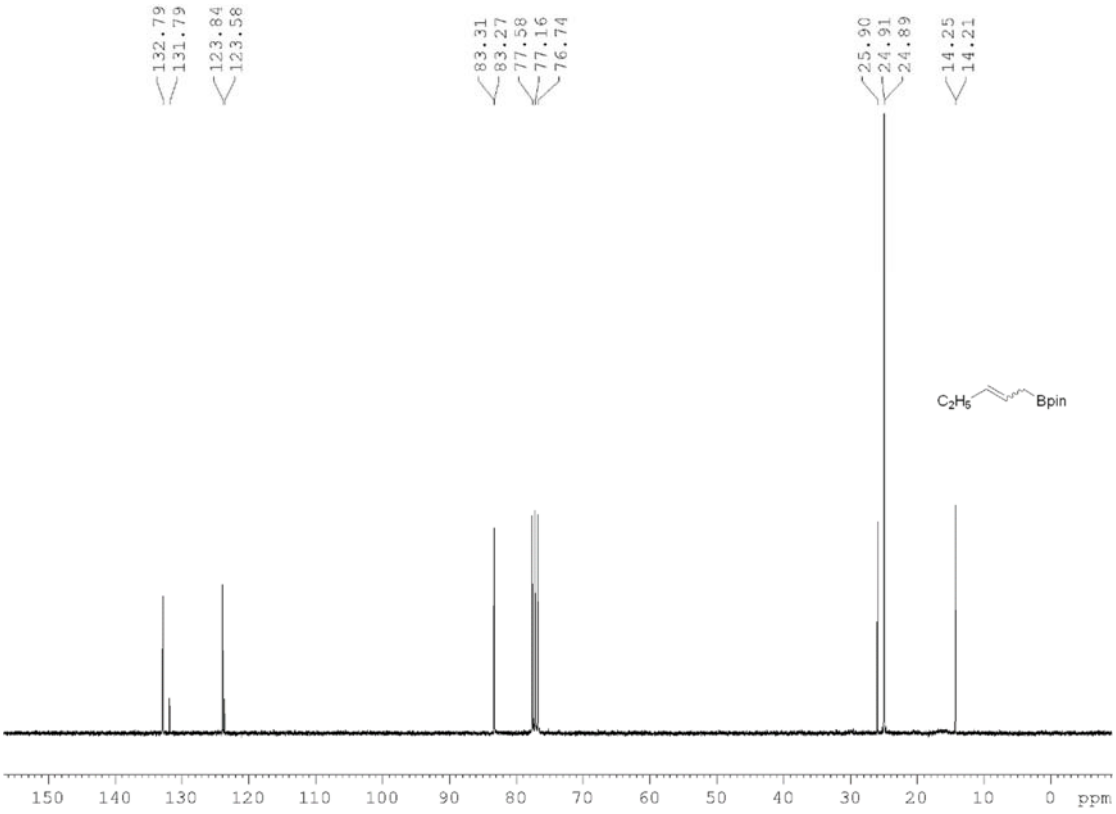


Compound 2c

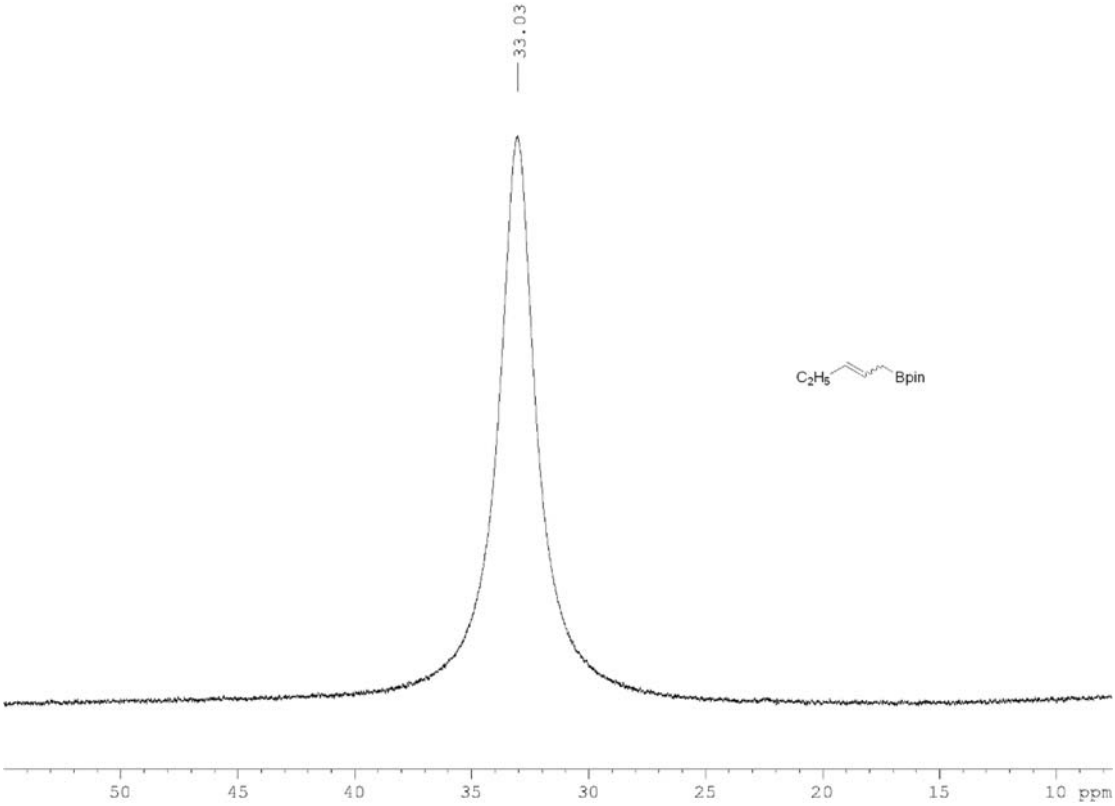
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

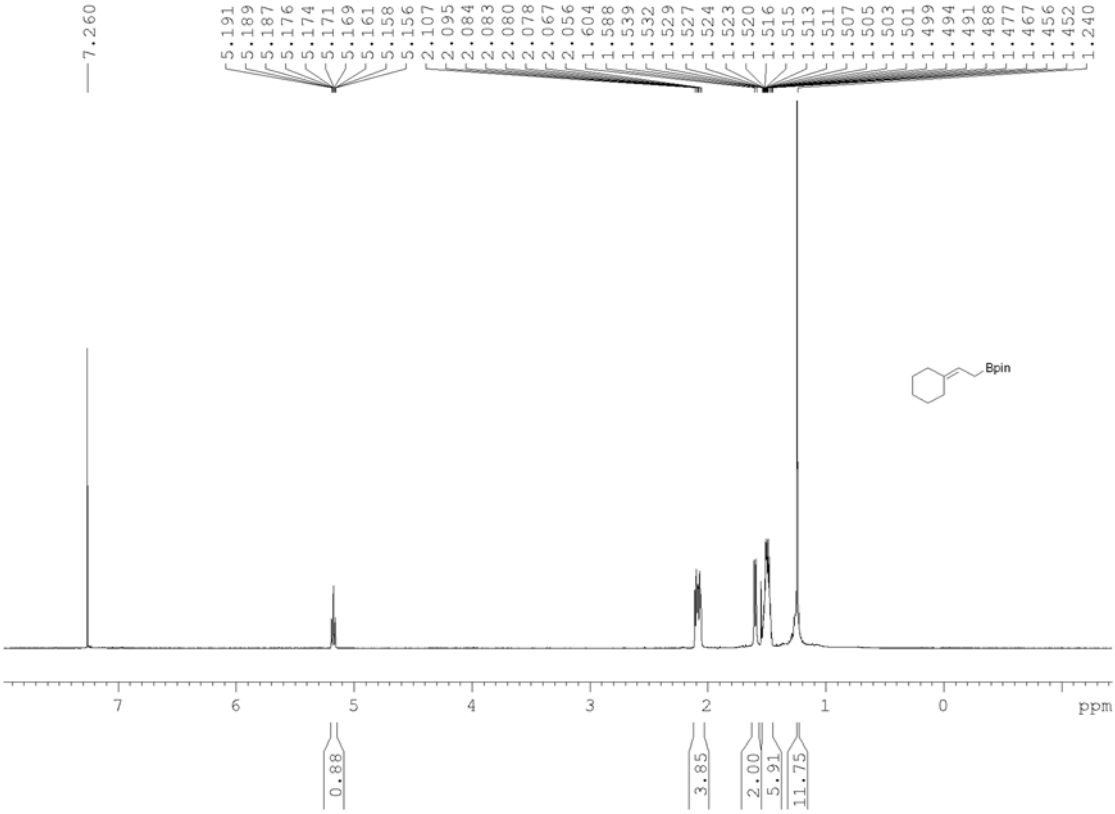


^{11}B NMR (96 MHz, $CDCl_3$)

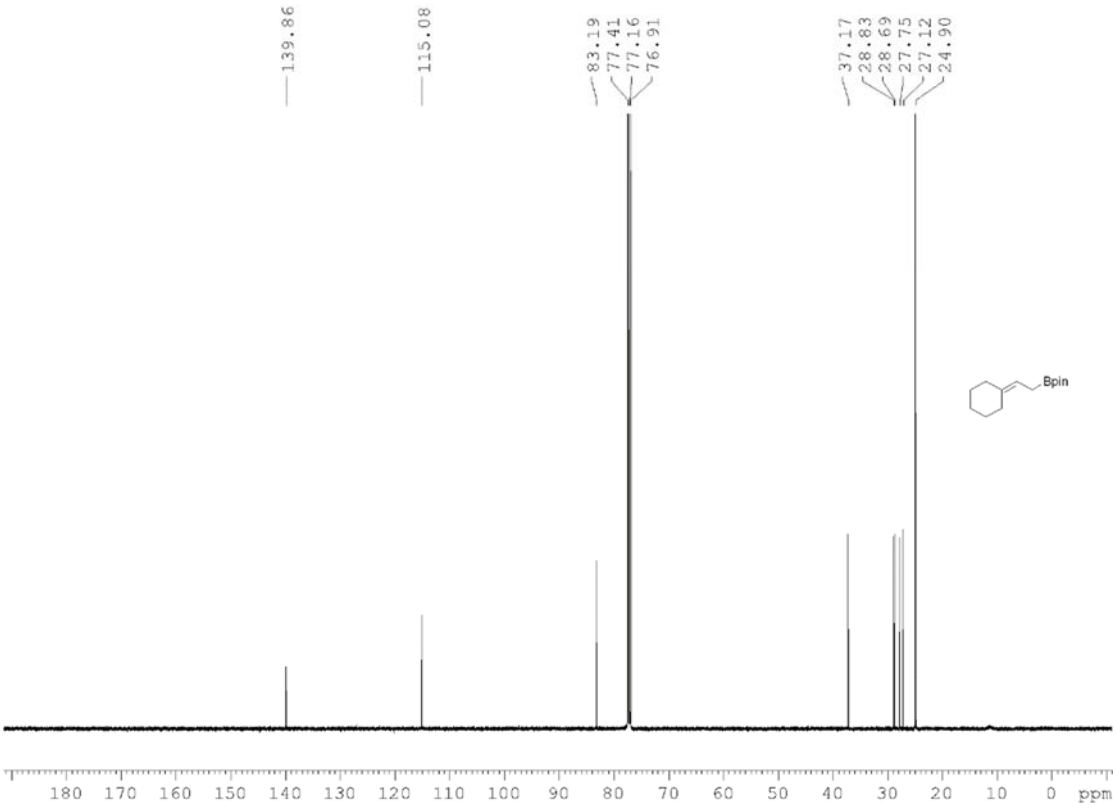


Compound 2d

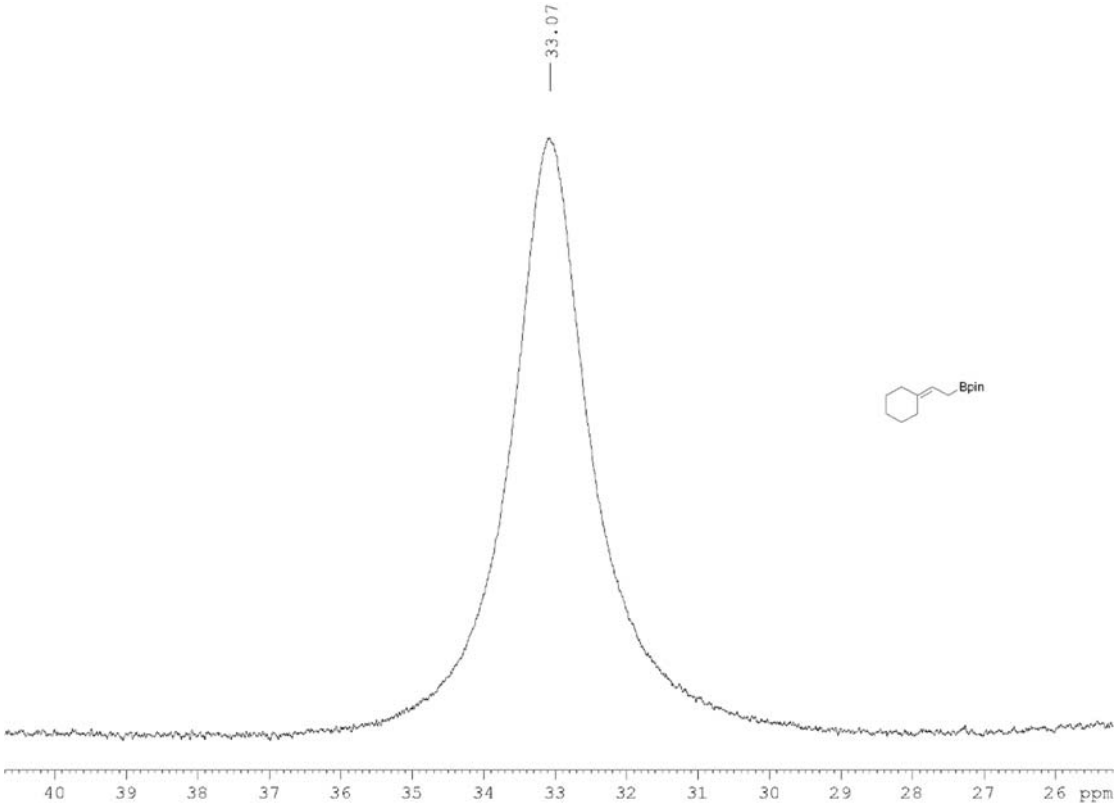
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

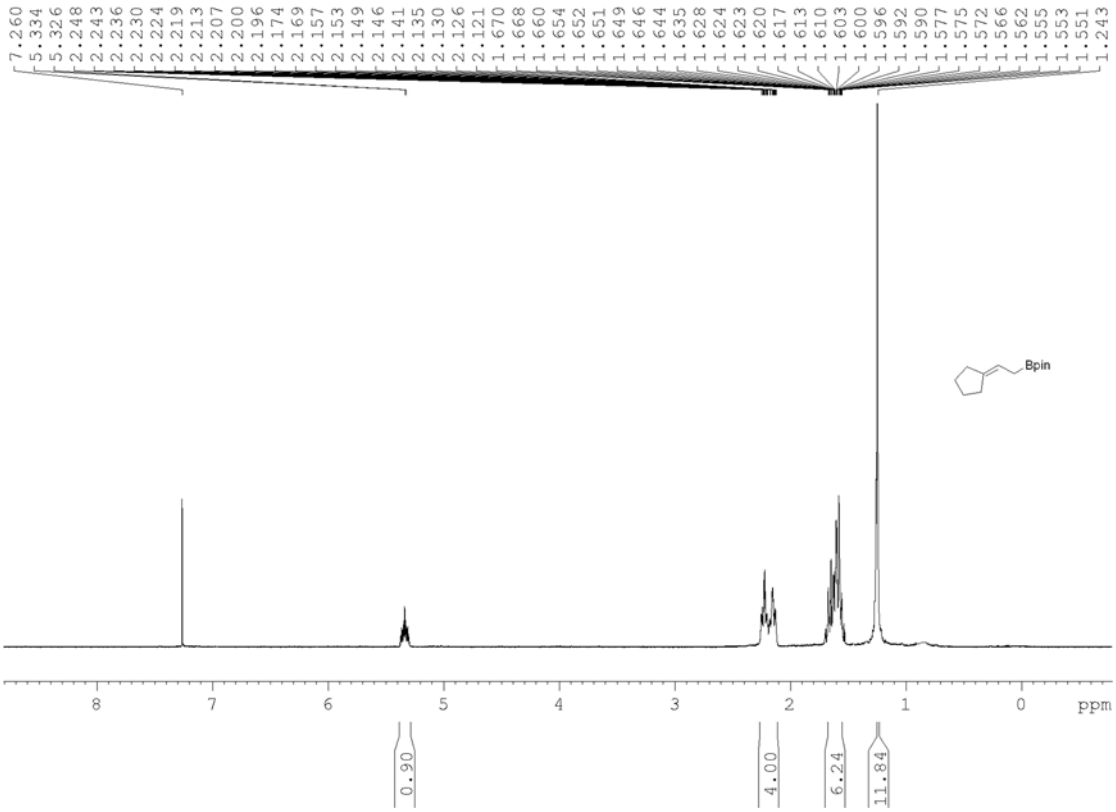


^{11}B NMR (160 MHz, $CDCl_3$)

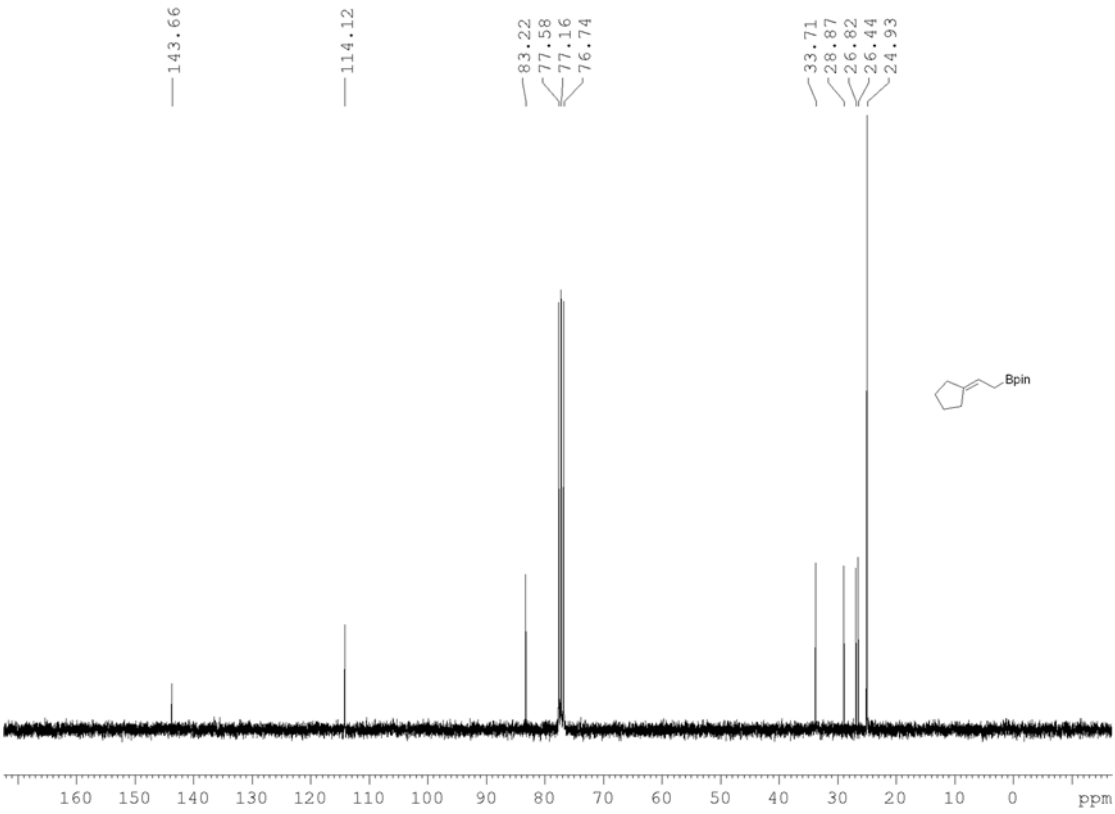


Compound 2e

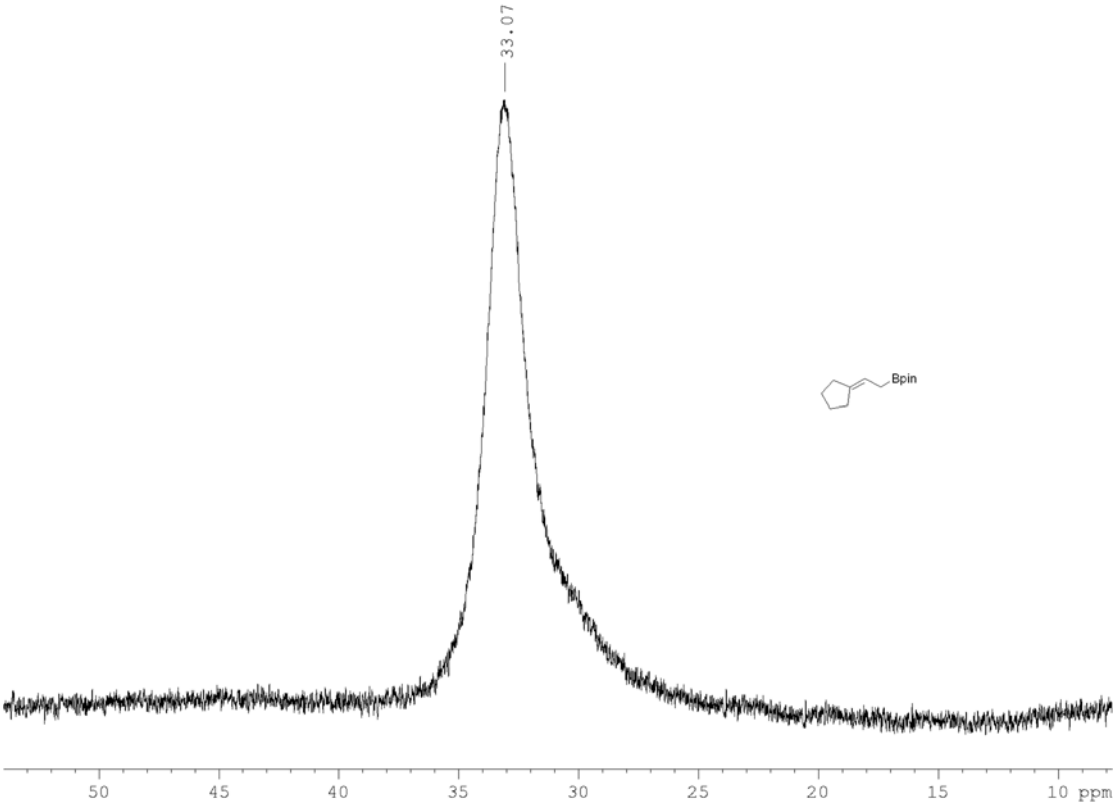
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

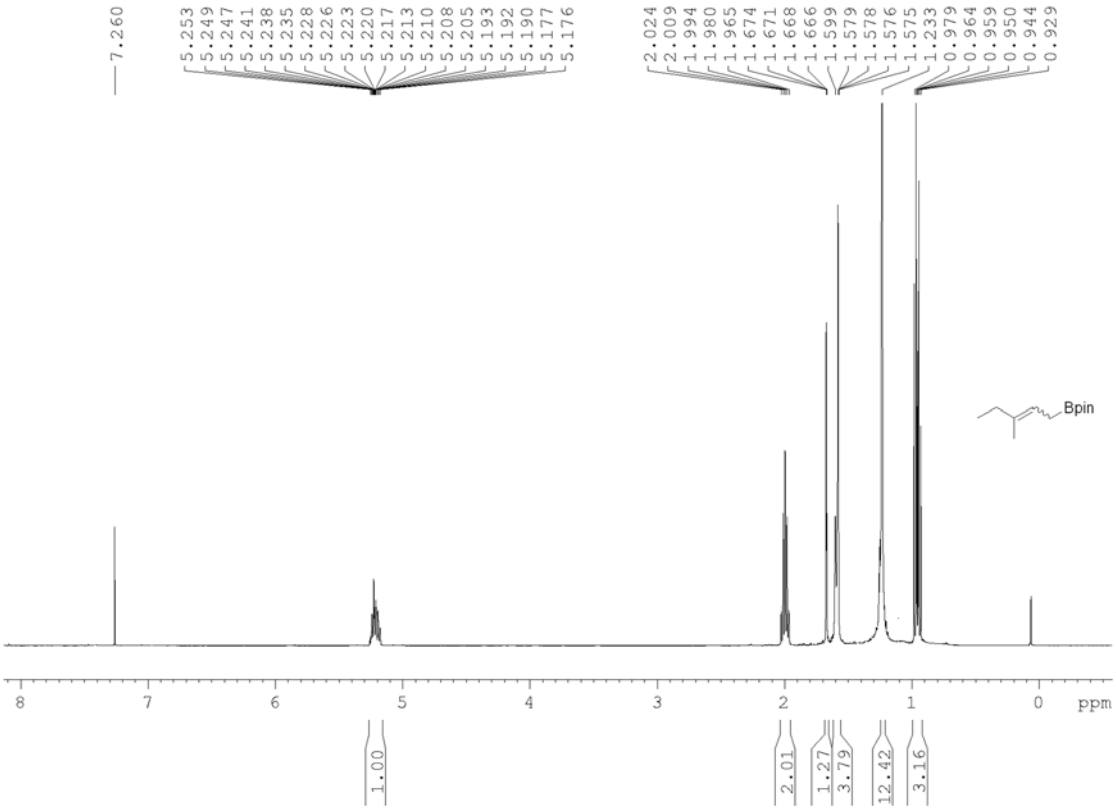


^{11}B NMR (96 MHz, $CDCl_3$)

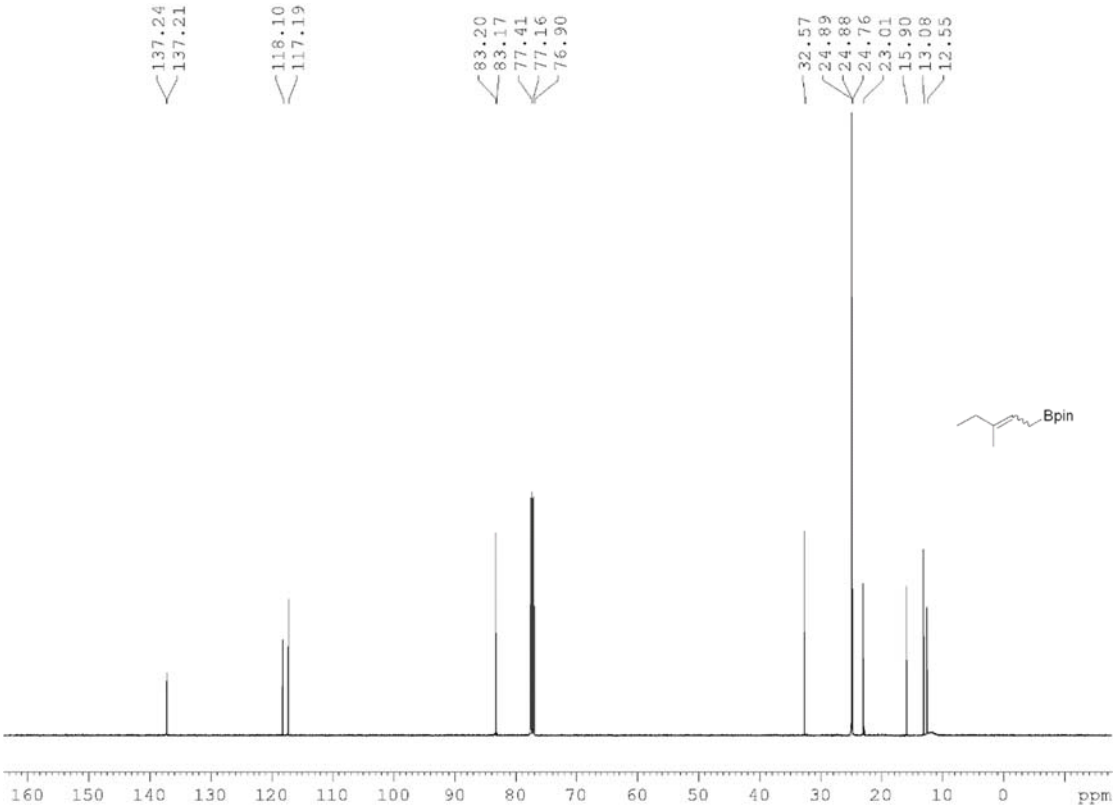


Compound 2f

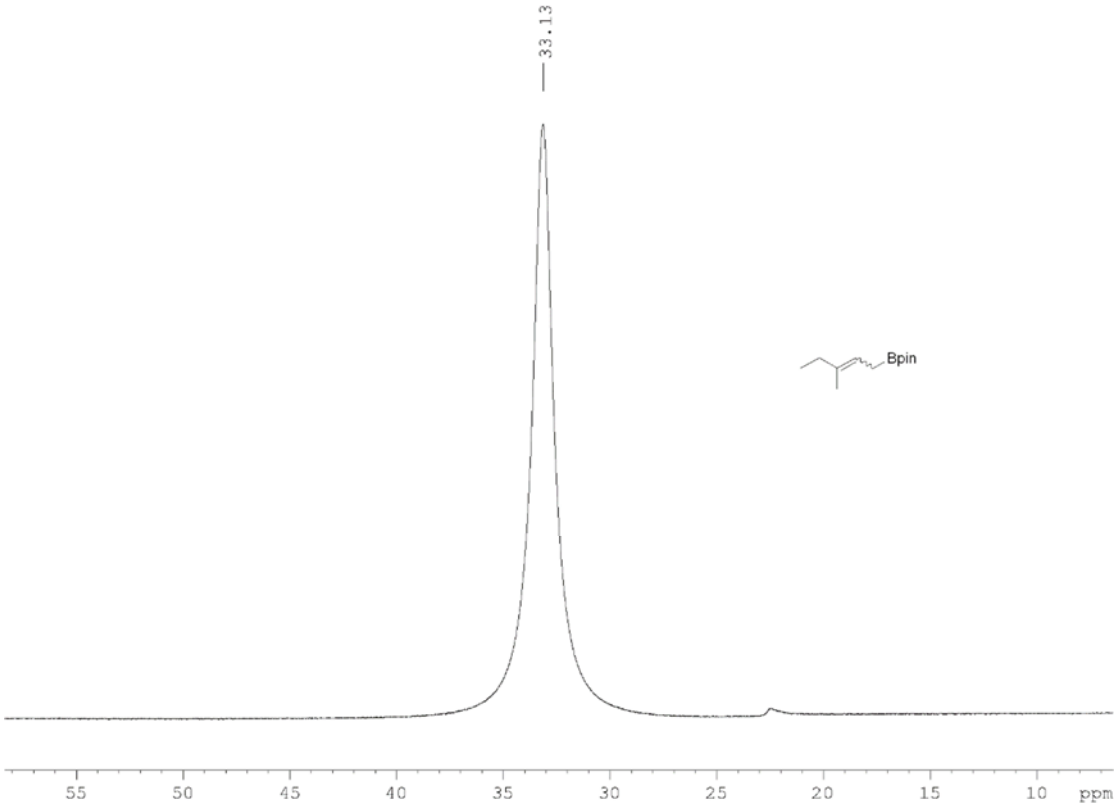
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

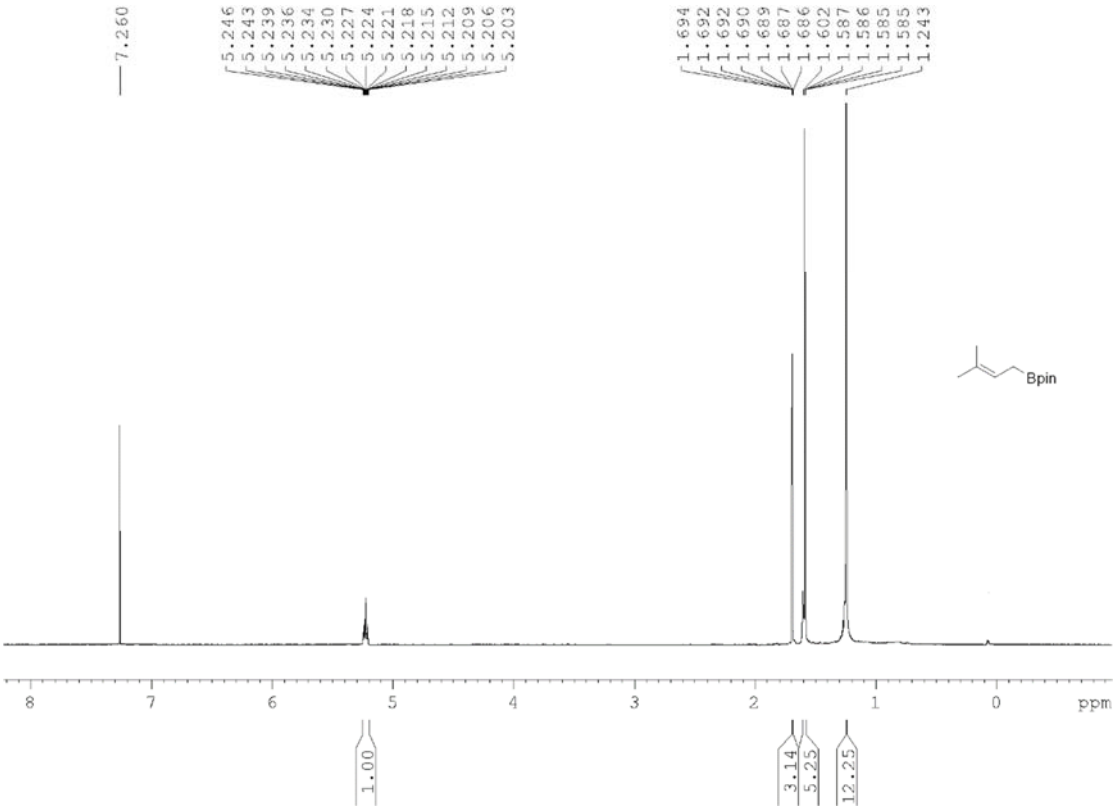


^{11}B NMR (160 MHz, $CDCl_3$)

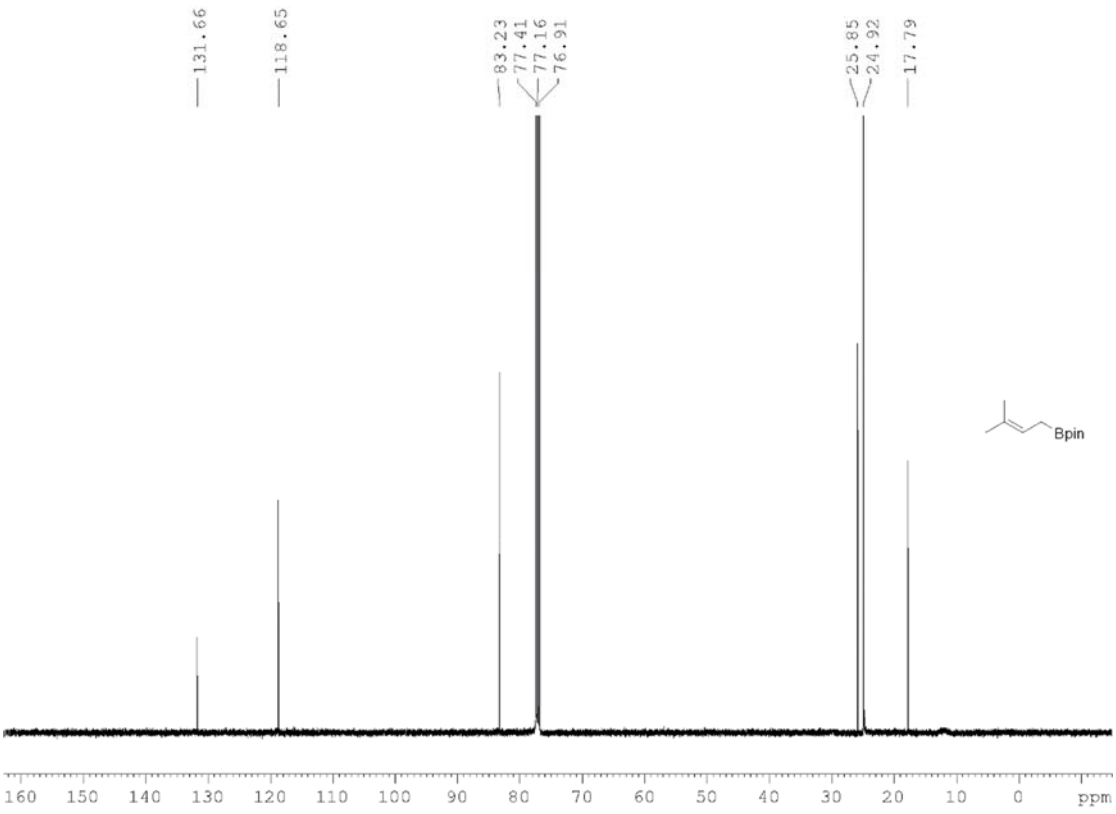


Compound 2g

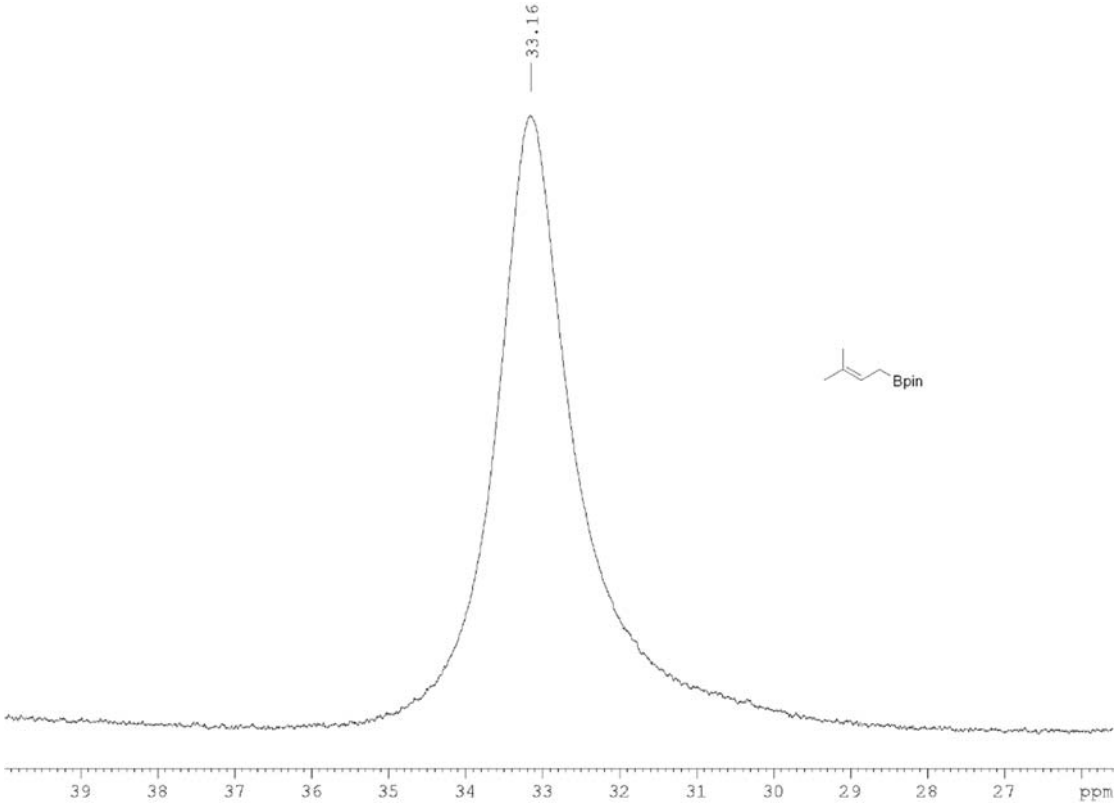
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

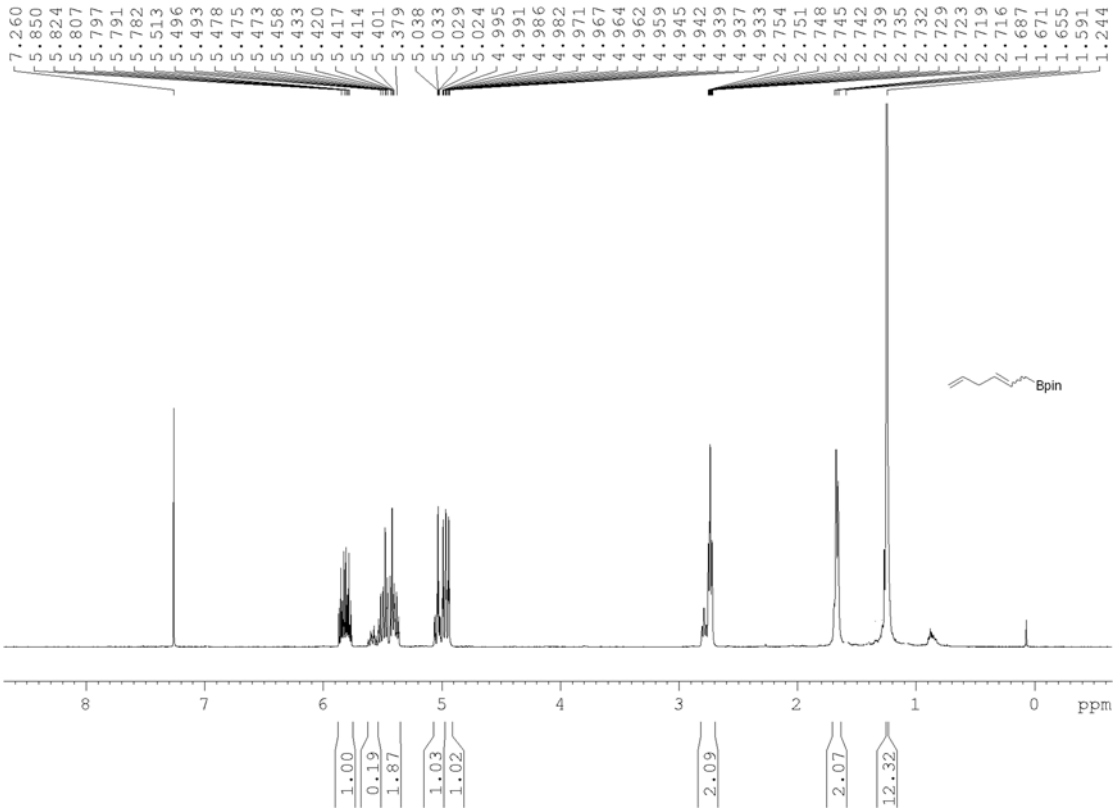


^{11}B NMR (160 MHz, $CDCl_3$)

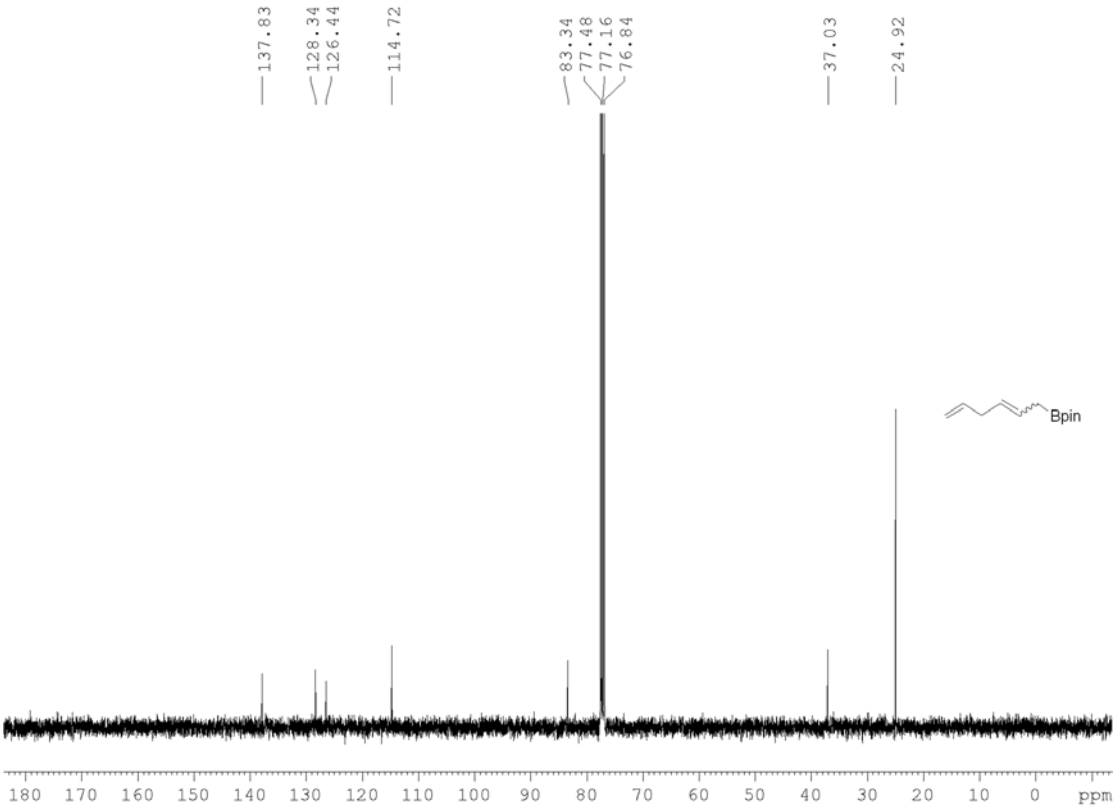


Compound 2h

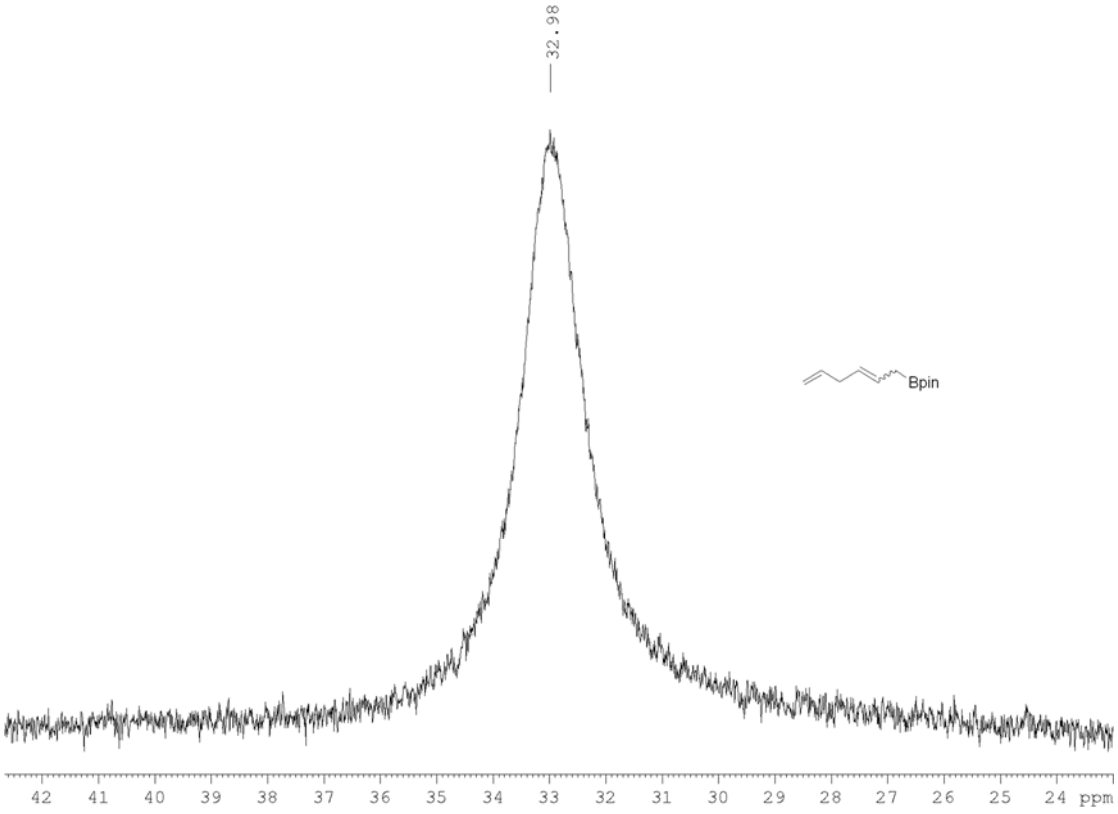
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

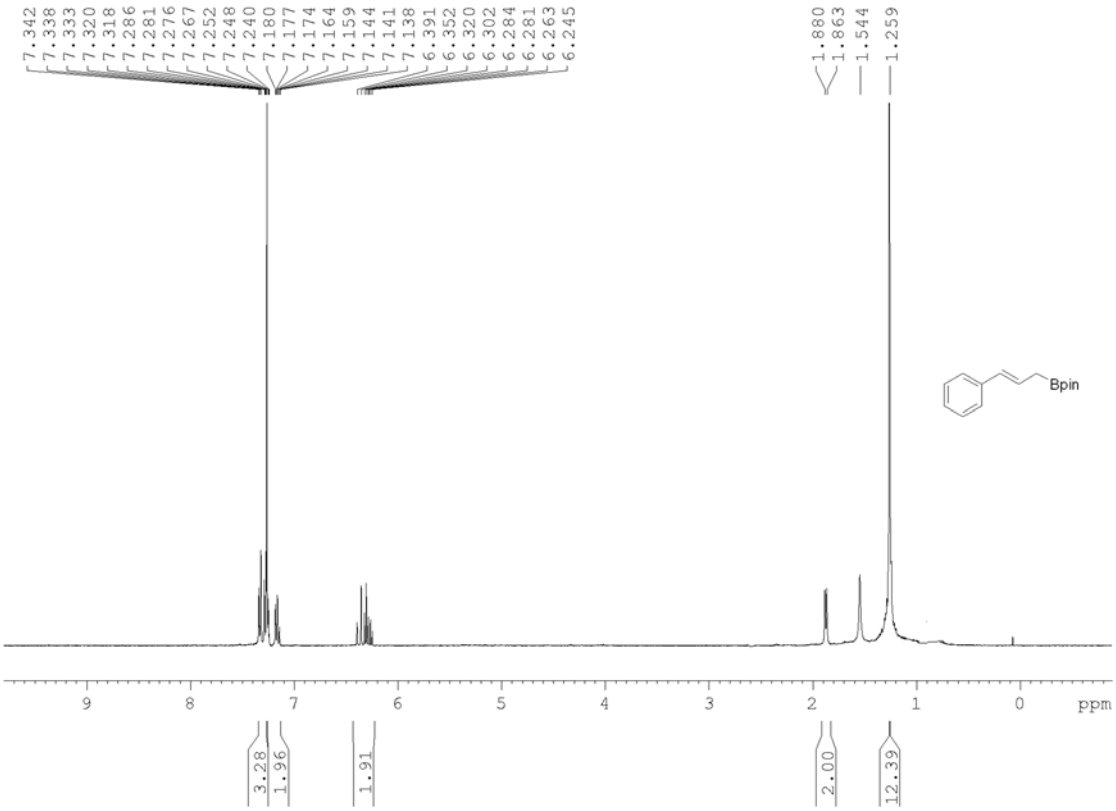


^{11}B NMR (128 MHz, $CDCl_3$)

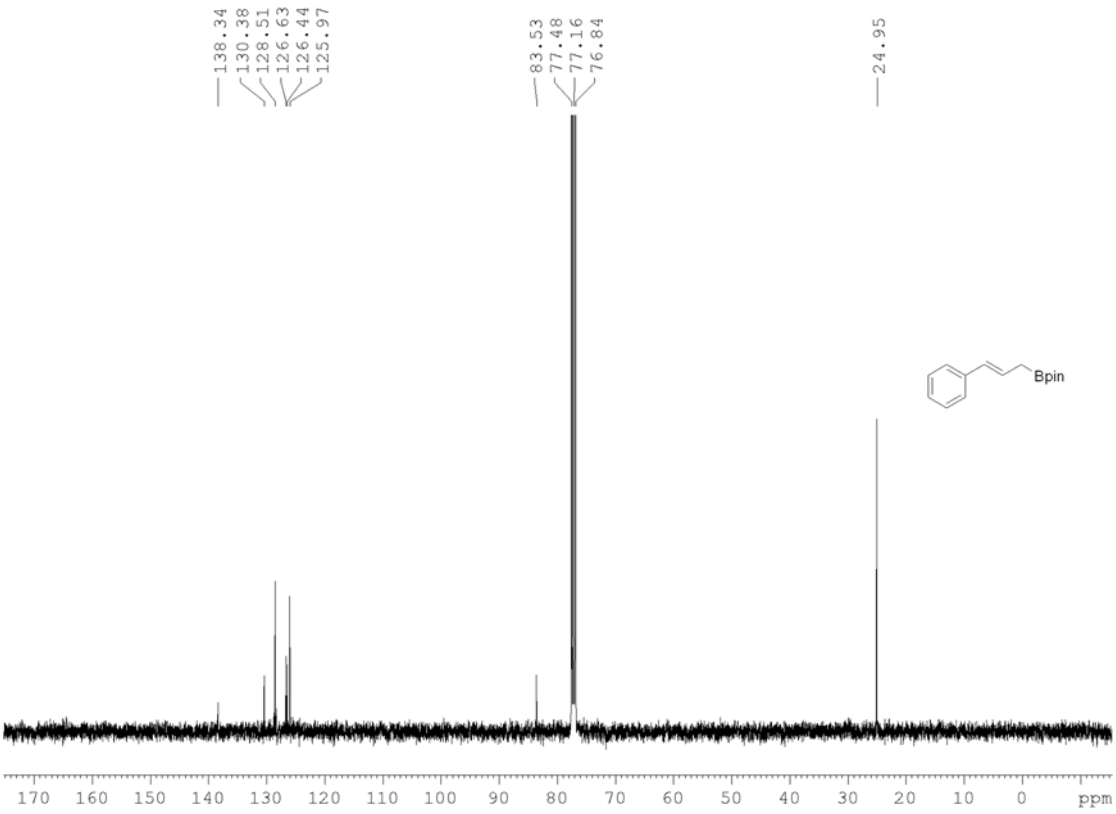


Compound 2i

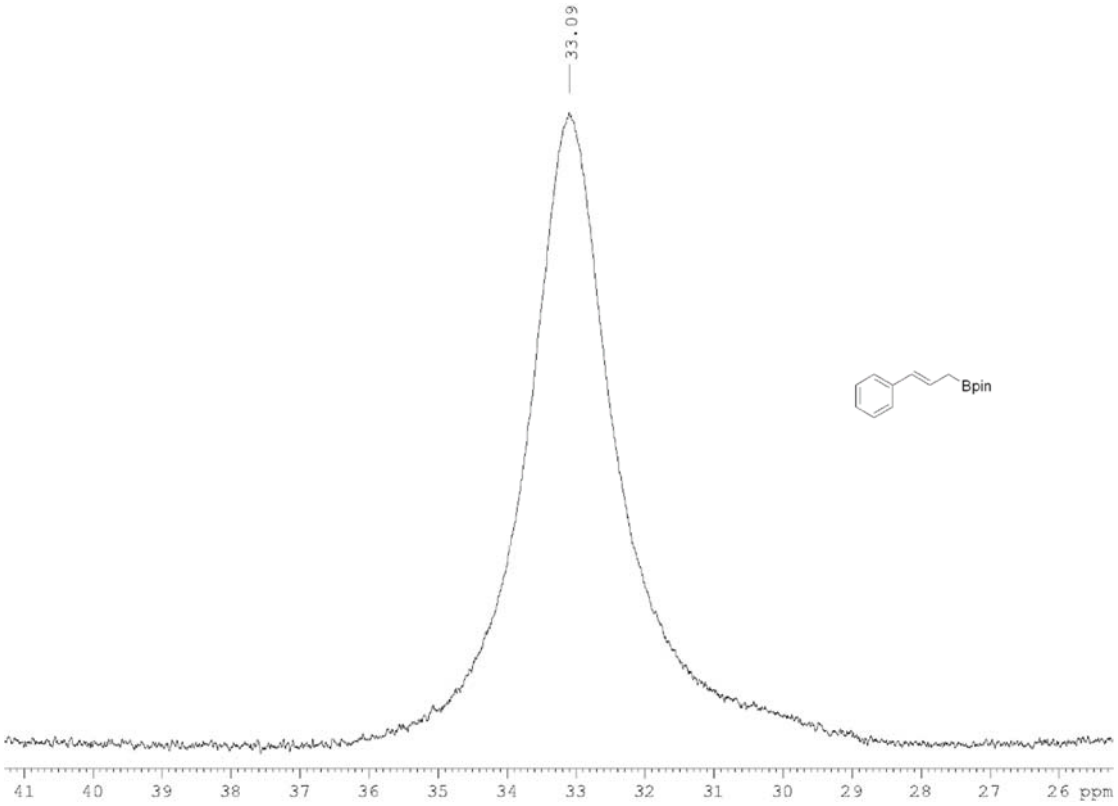
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

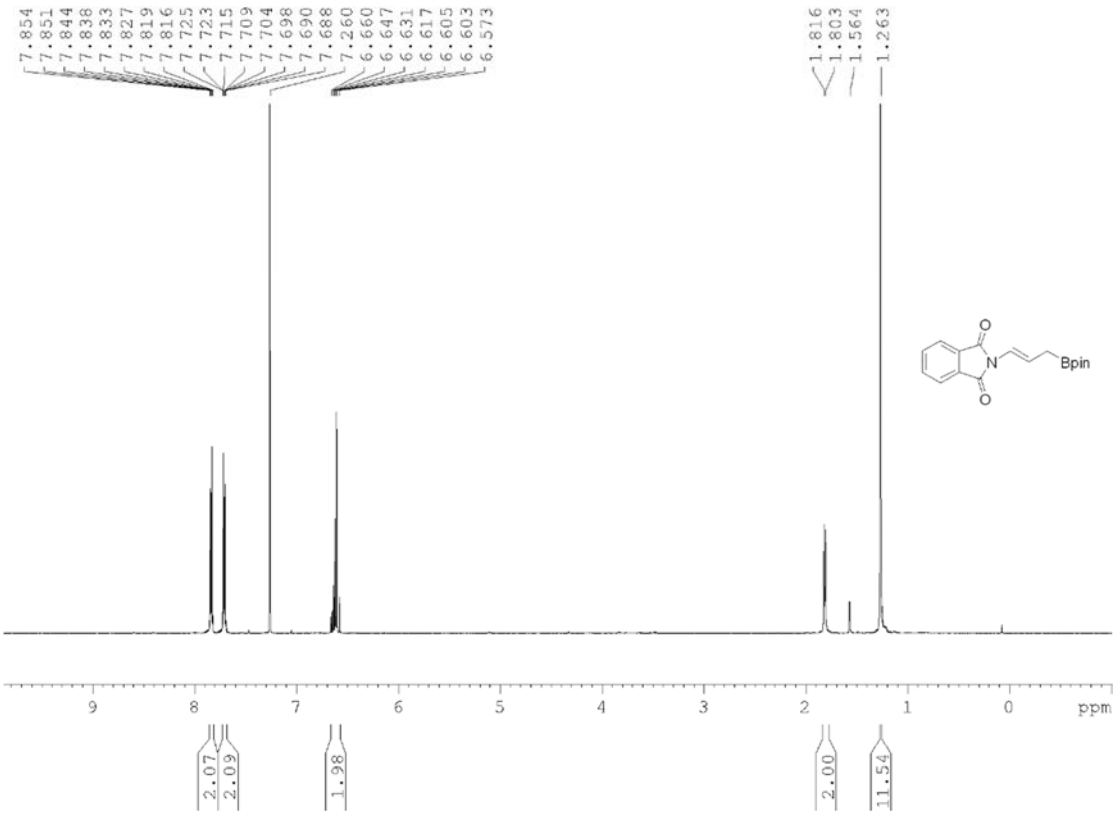


^{11}B NMR (128 MHz, $CDCl_3$)

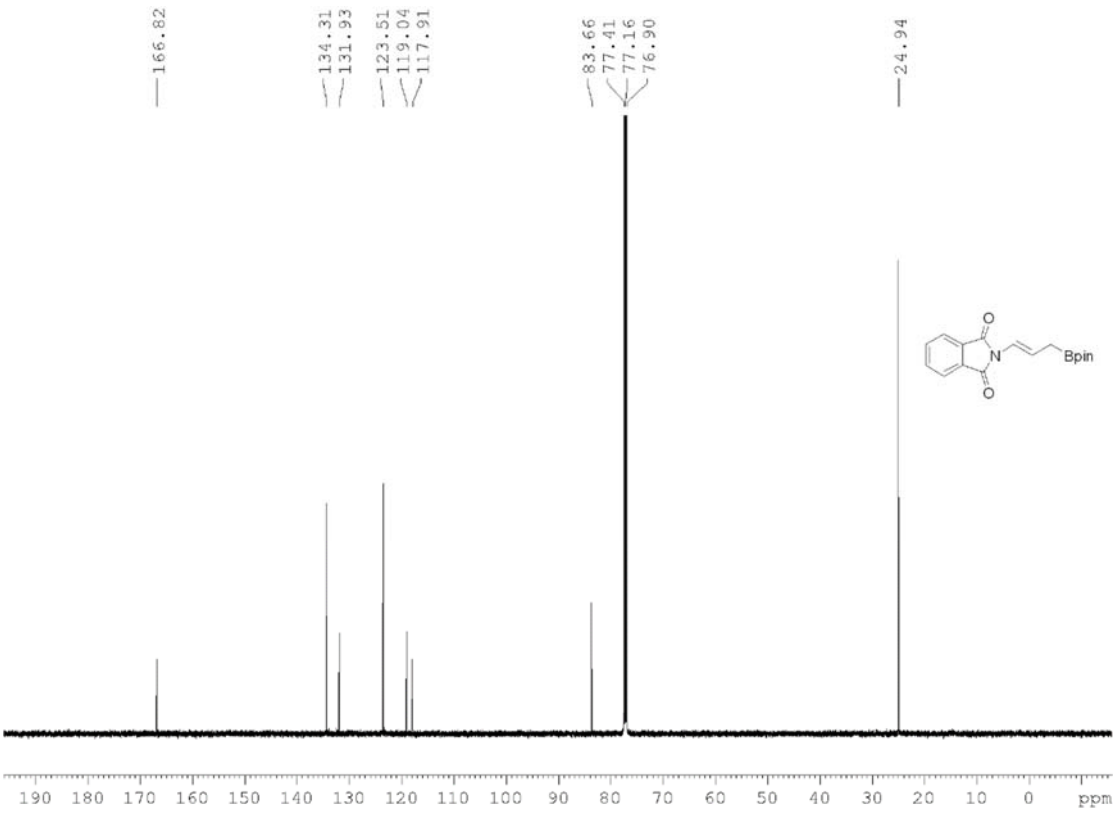


Compound 2j

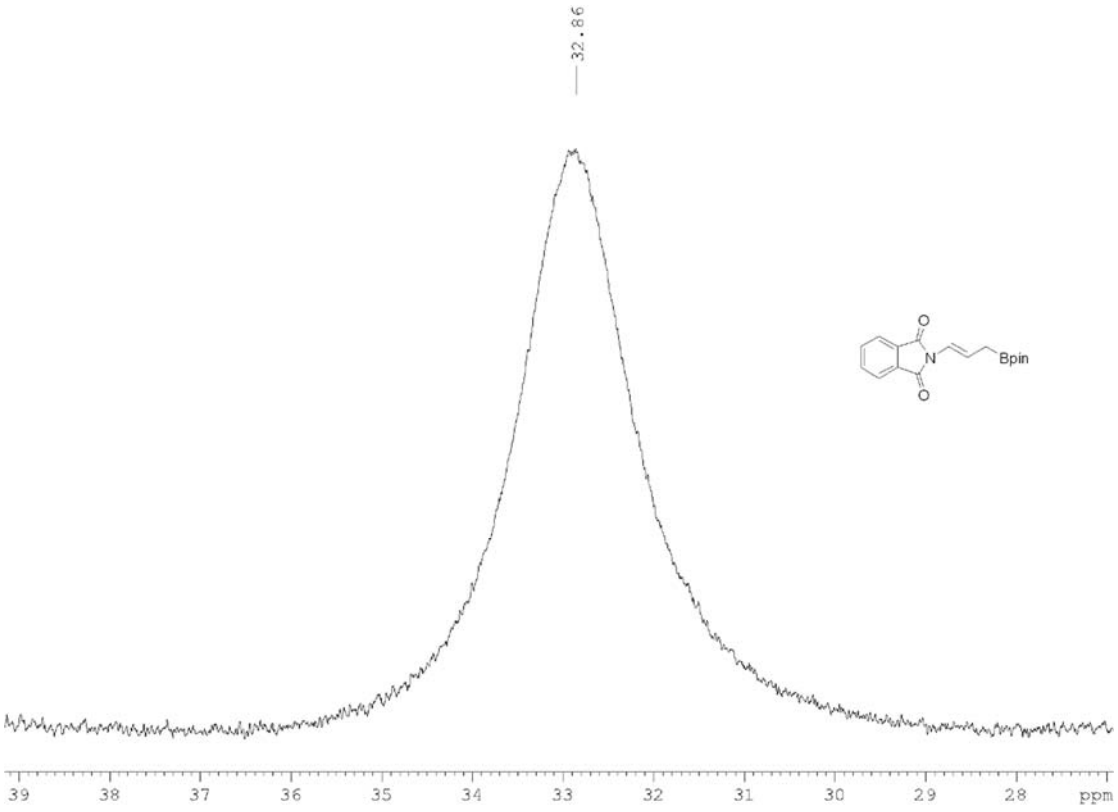
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

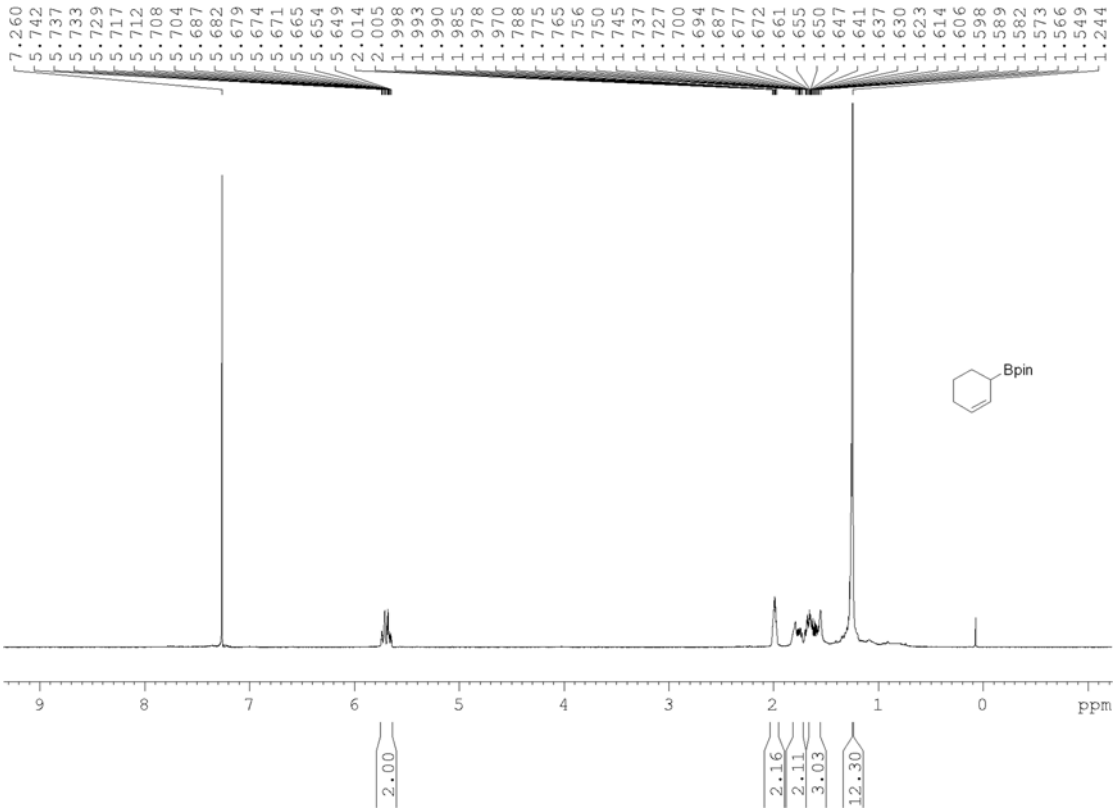


^{11}B NMR (160 MHz, $CDCl_3$)

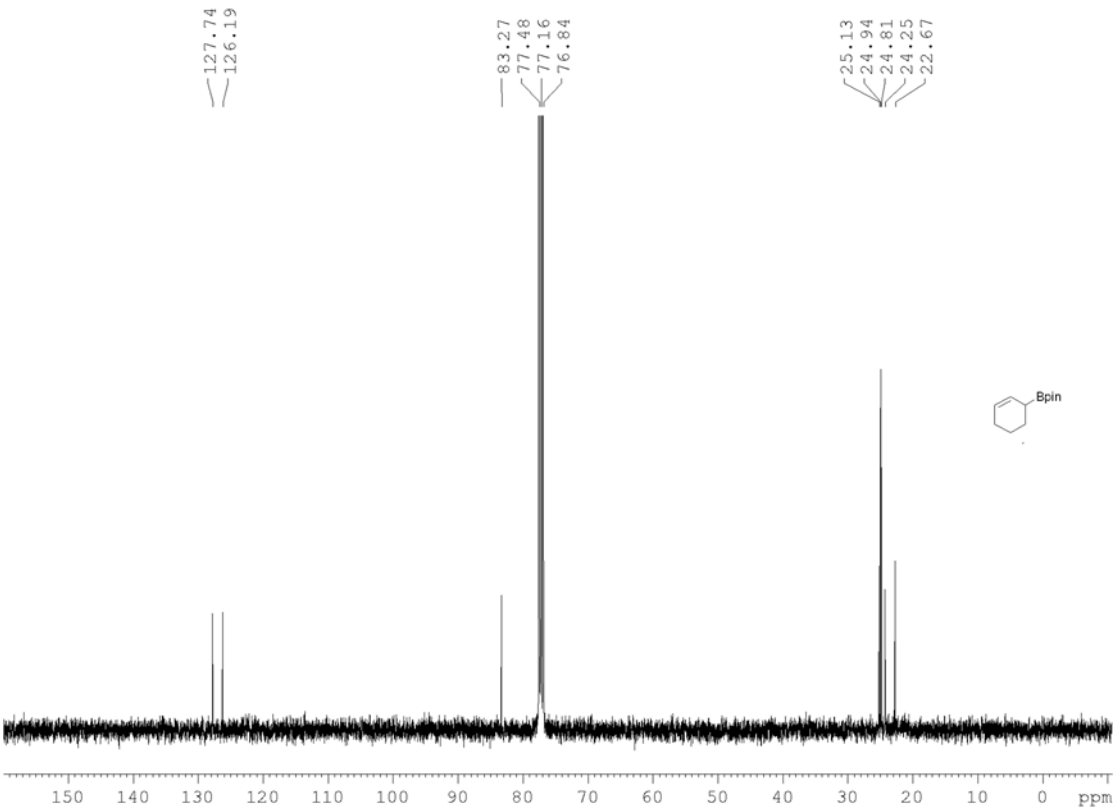


Compound 2k

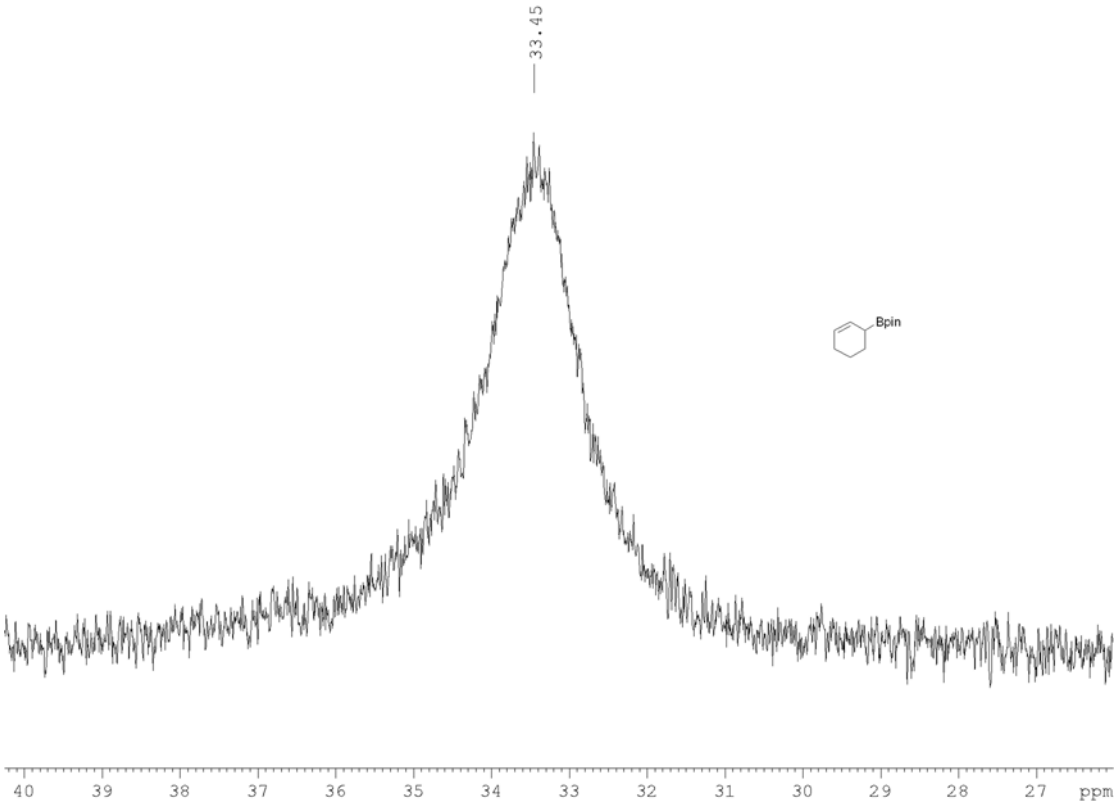
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

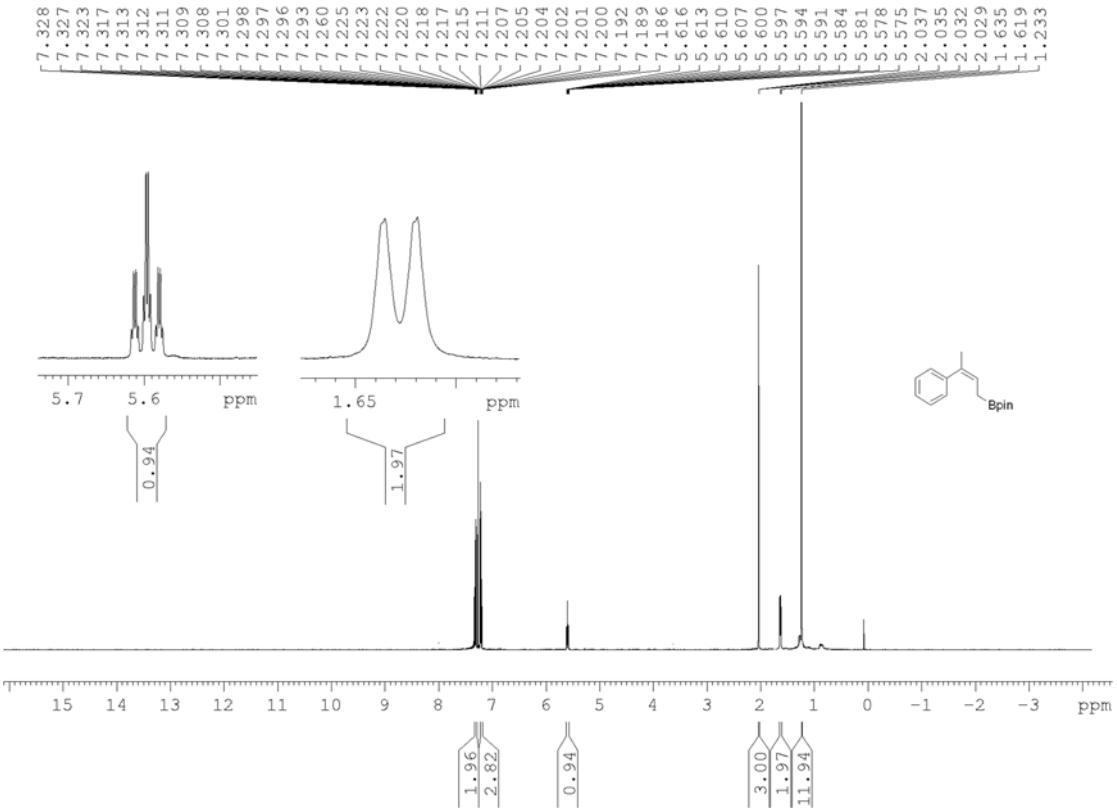


^{11}B NMR (128 MHz, $CDCl_3$)

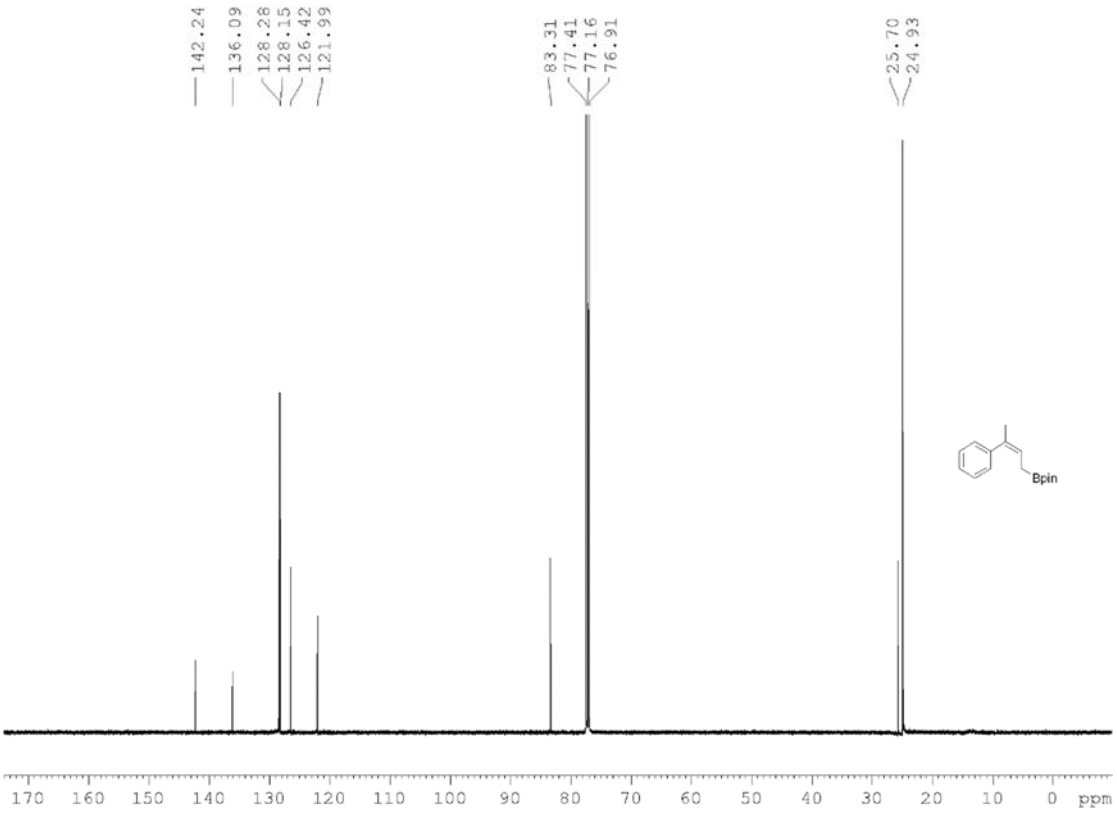


Compound 2l

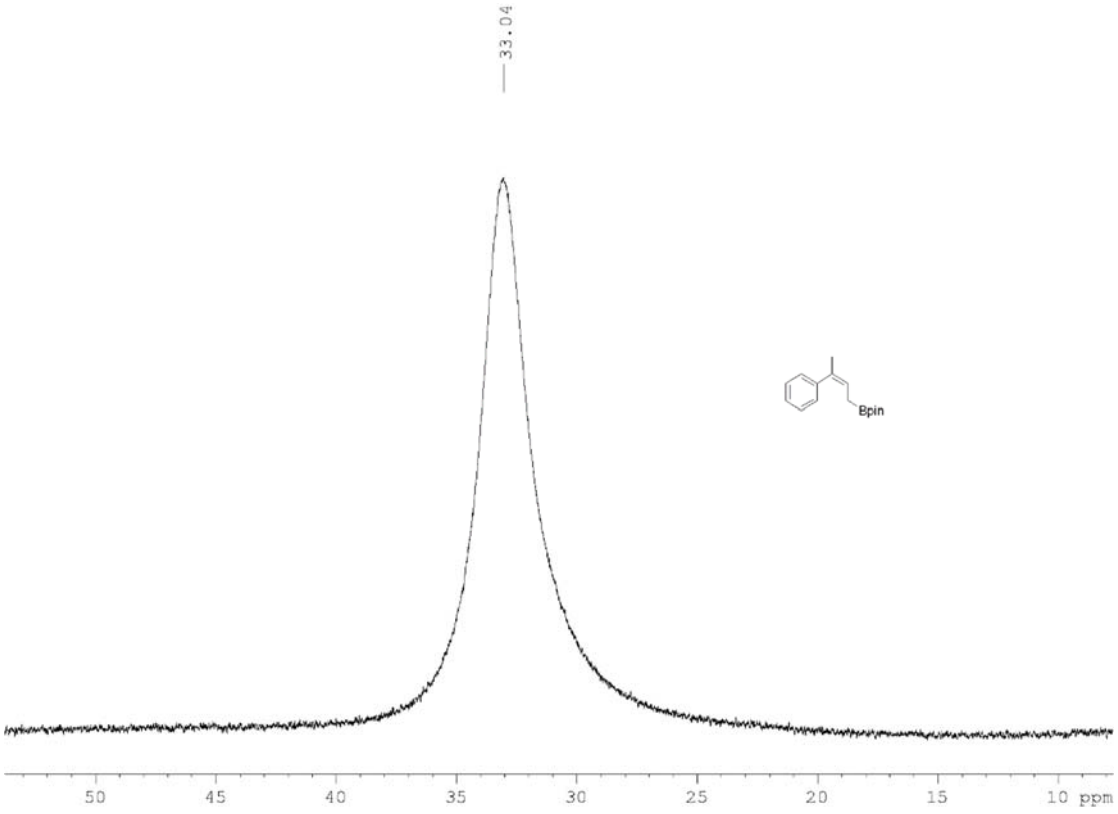
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

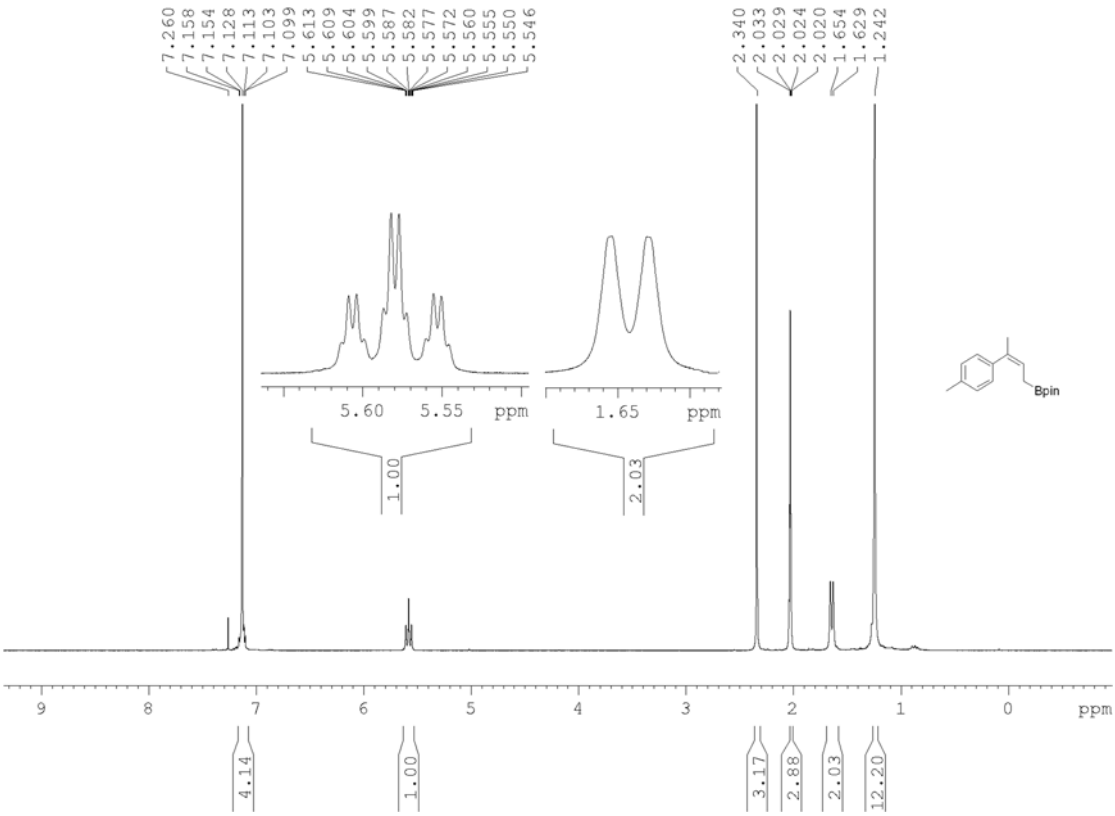


^{11}B NMR (160 MHz, $CDCl_3$)

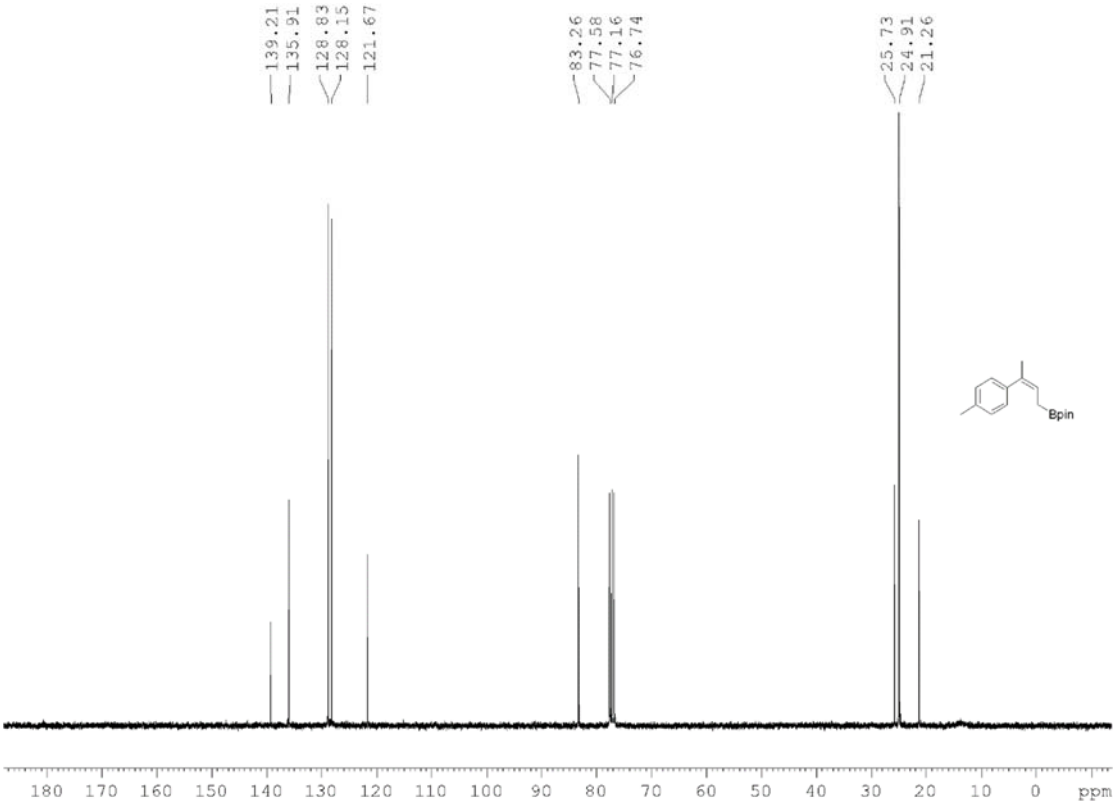


Compound 2m

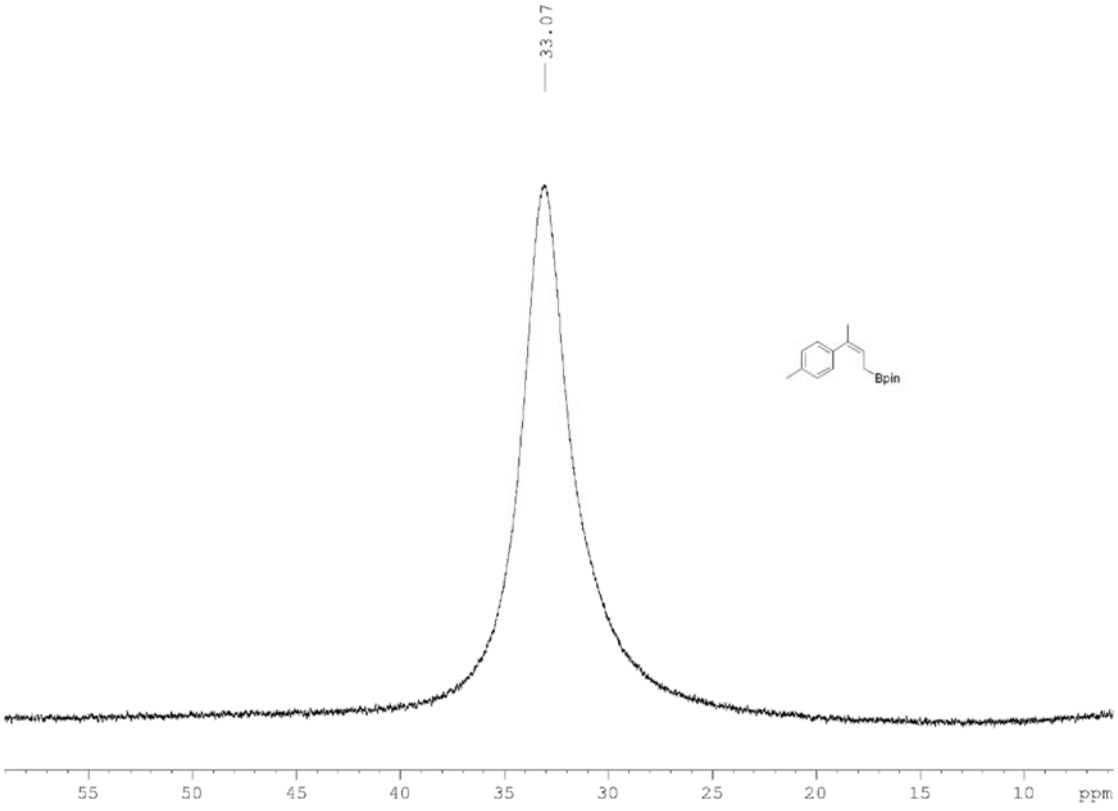
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

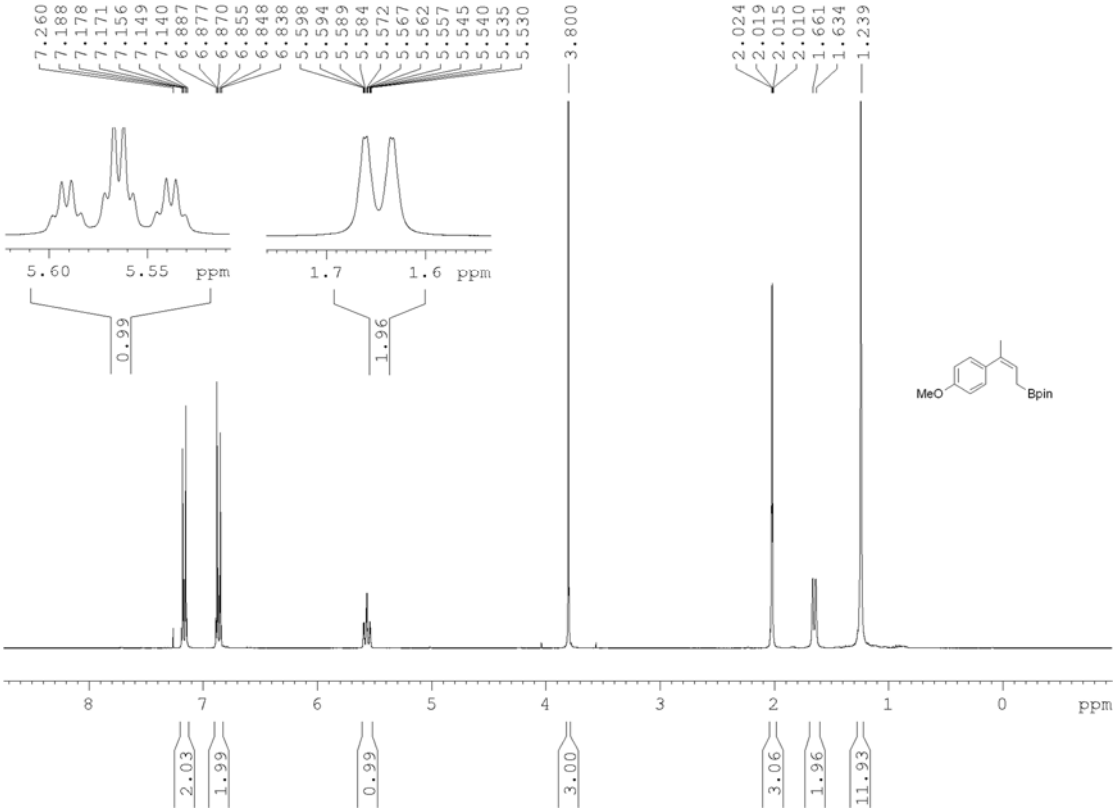


^{11}B NMR (96 MHz, $CDCl_3$)

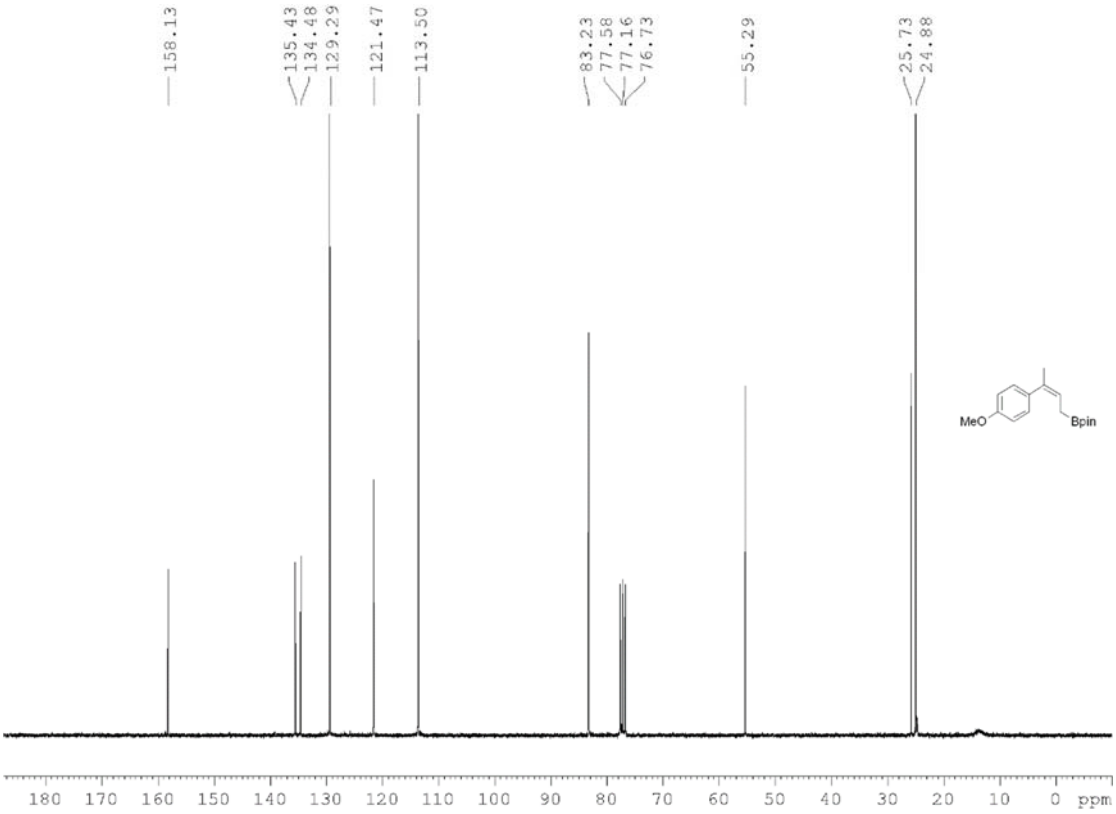


Compound 2n

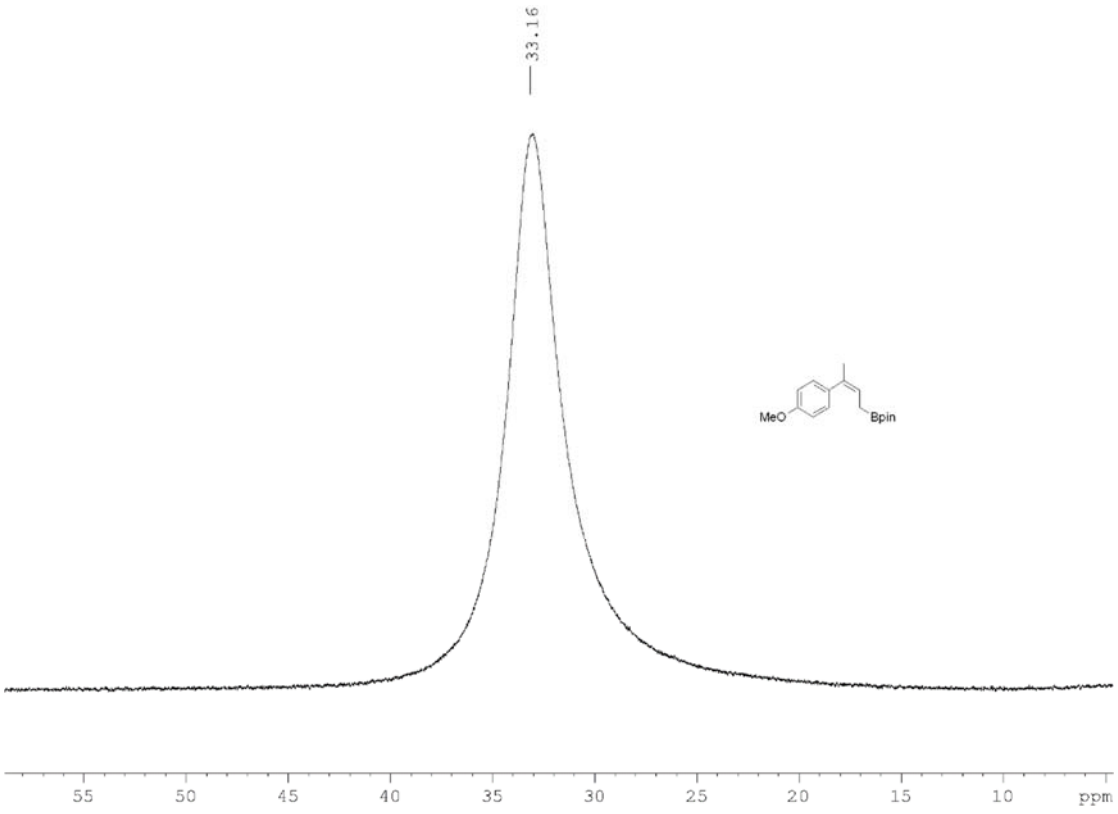
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

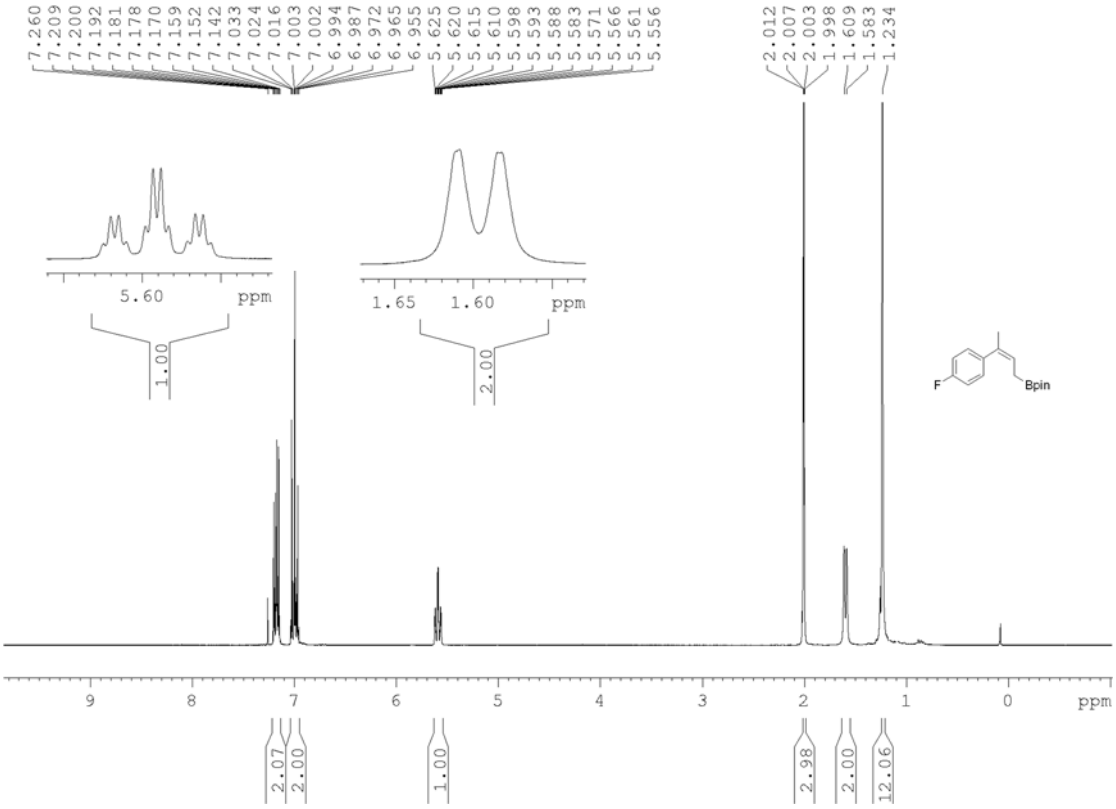


^{11}B NMR (96 MHz, $CDCl_3$)

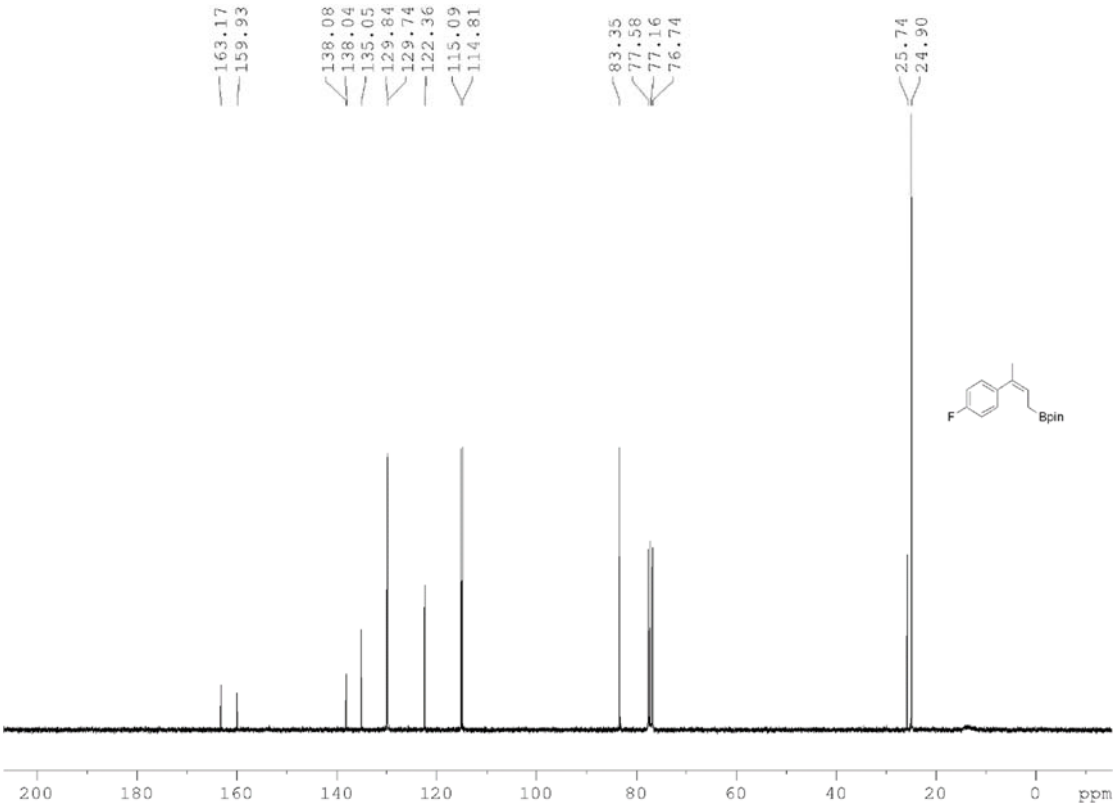


Compound 2o

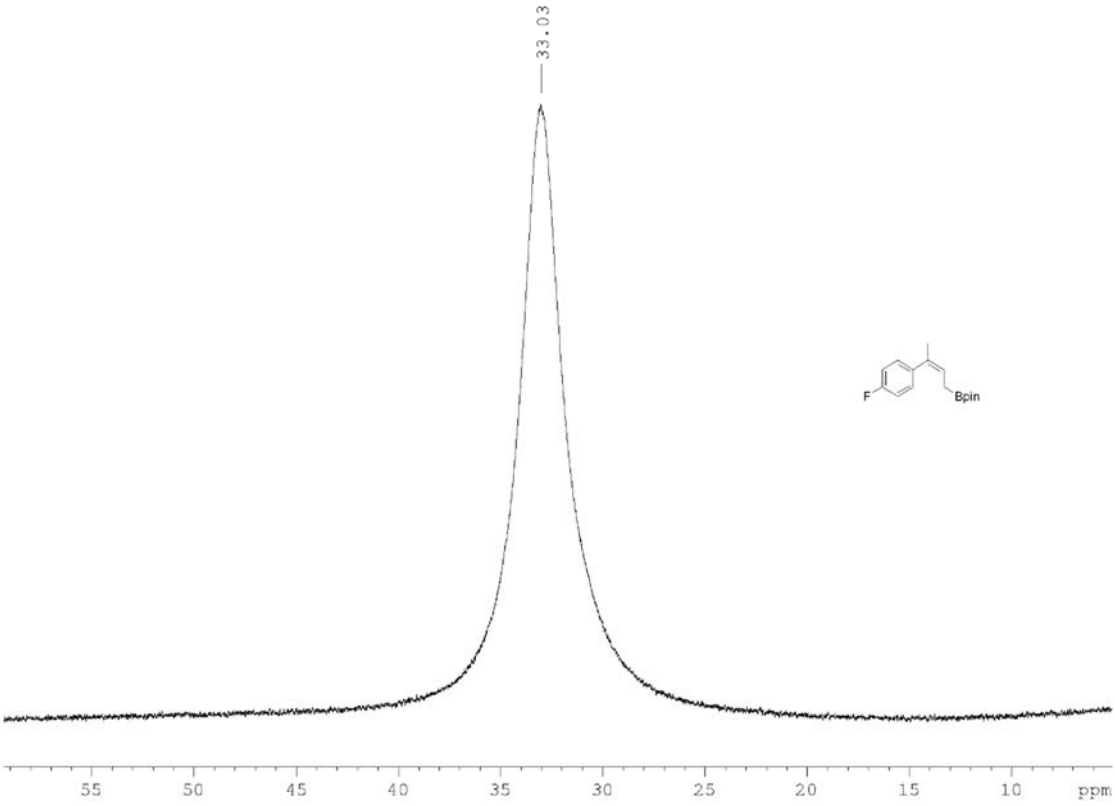
^{1}H NMR (300 MHz, $CDCl_3$)



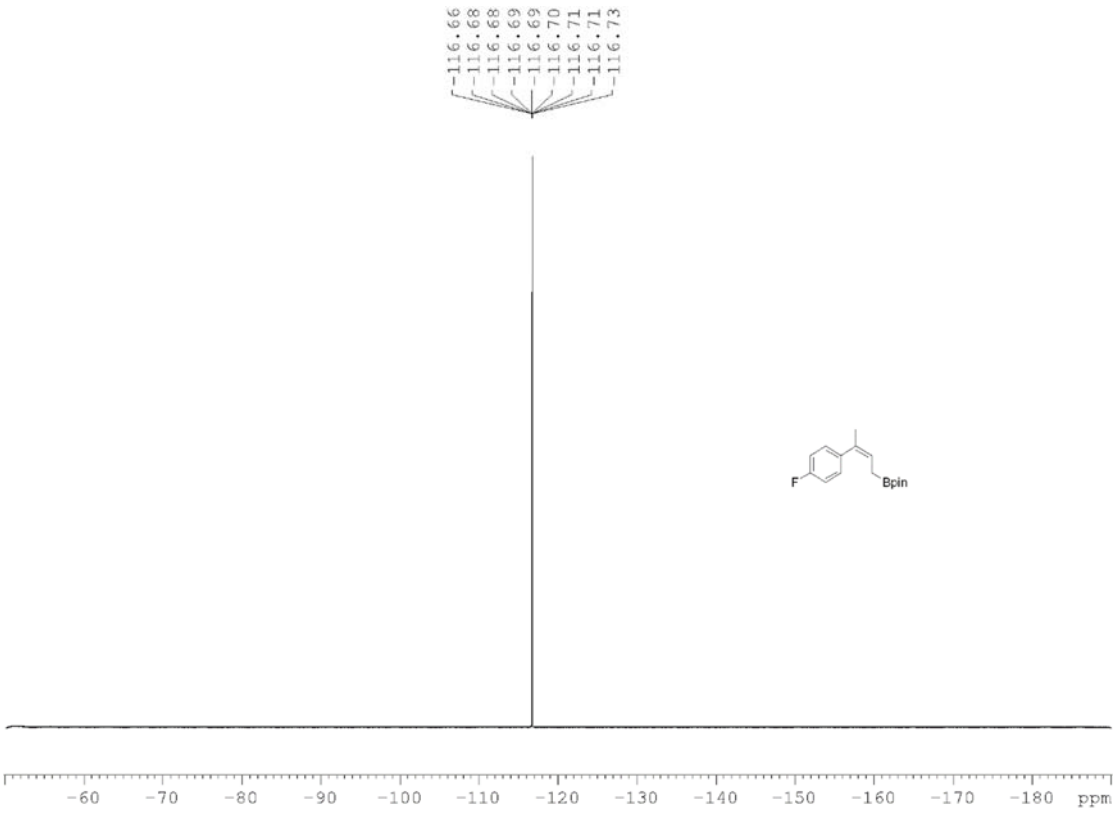
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



^{11}B NMR (96 MHz, $CDCl_3$)

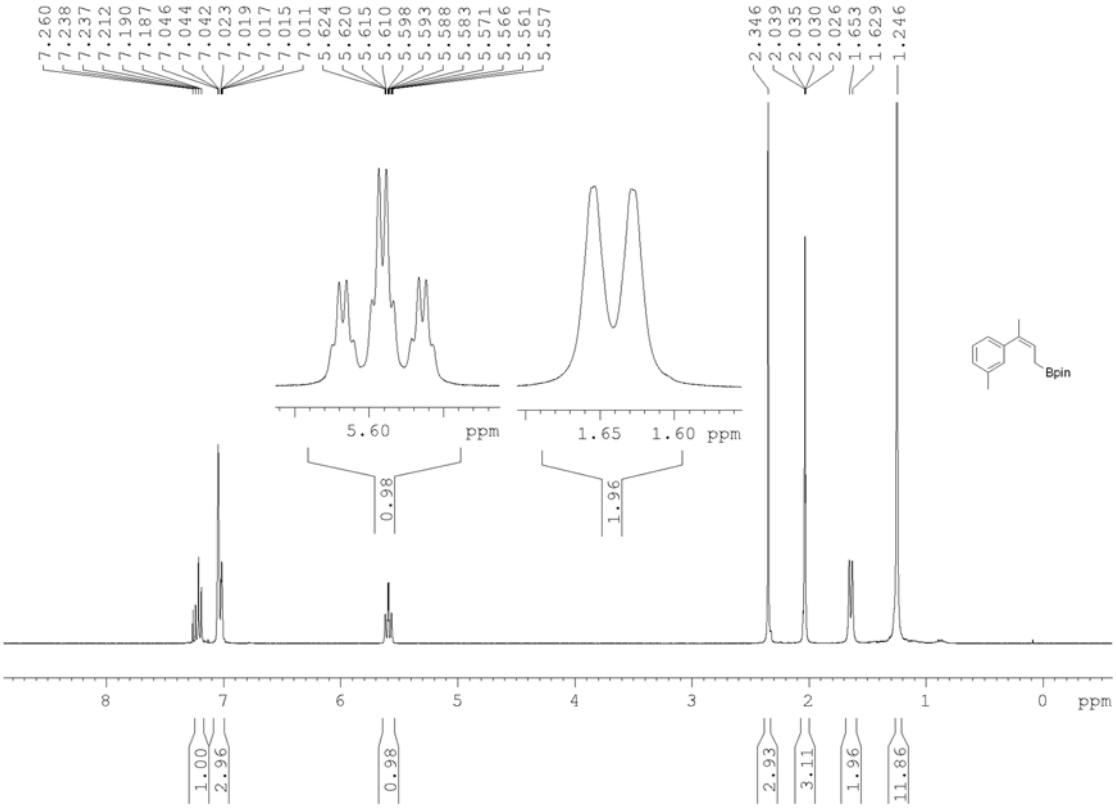


^{19}F NMR (470 MHz, $CDCl_3$)

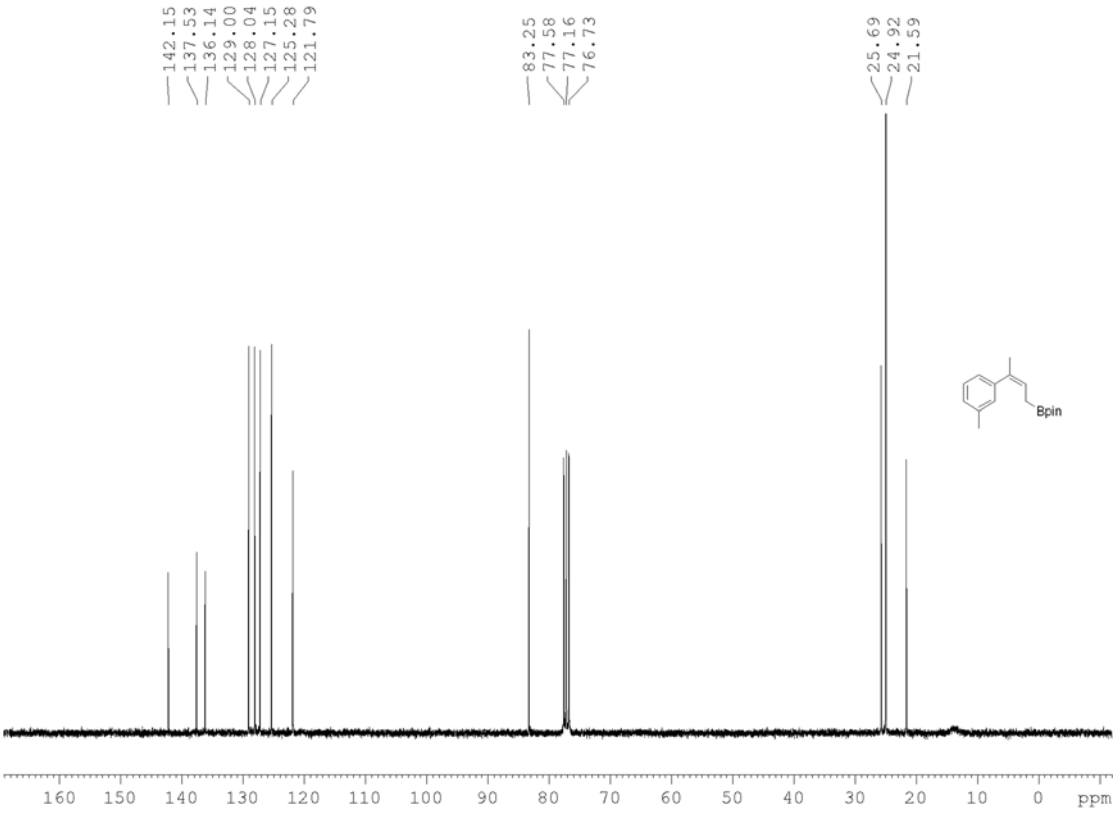


Compound 2p

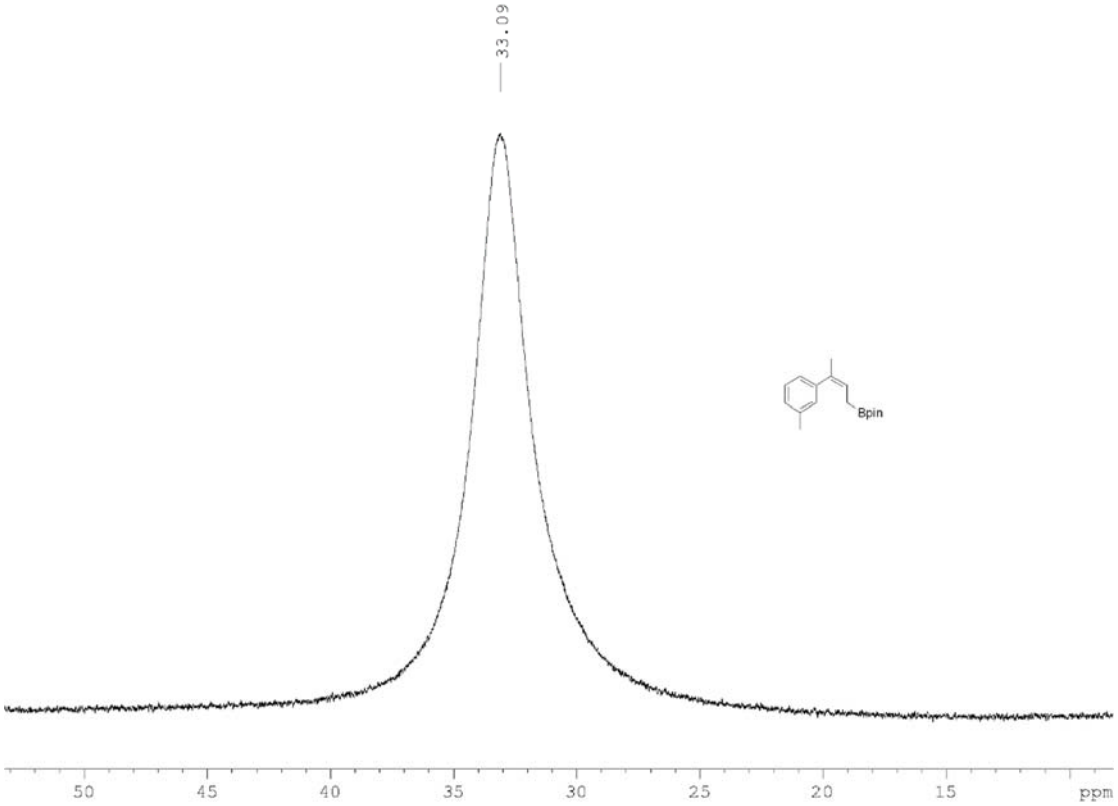
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

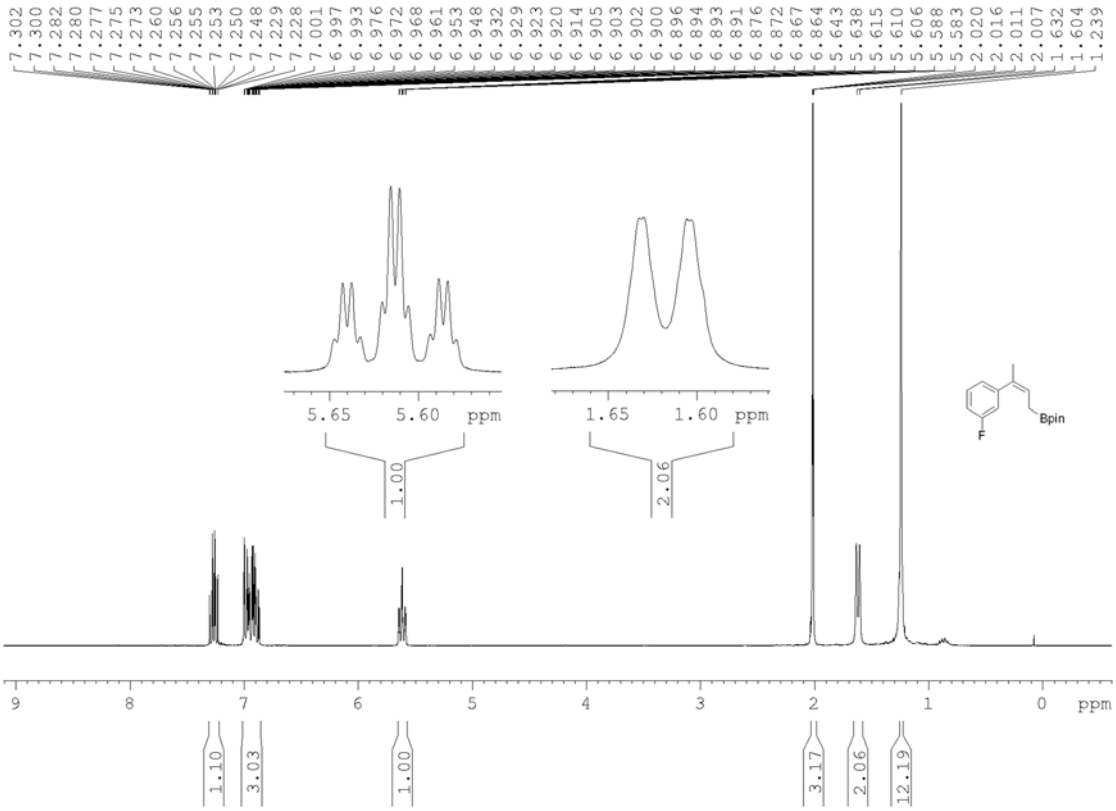


^{11}B NMR (96 MHz, $CDCl_3$)

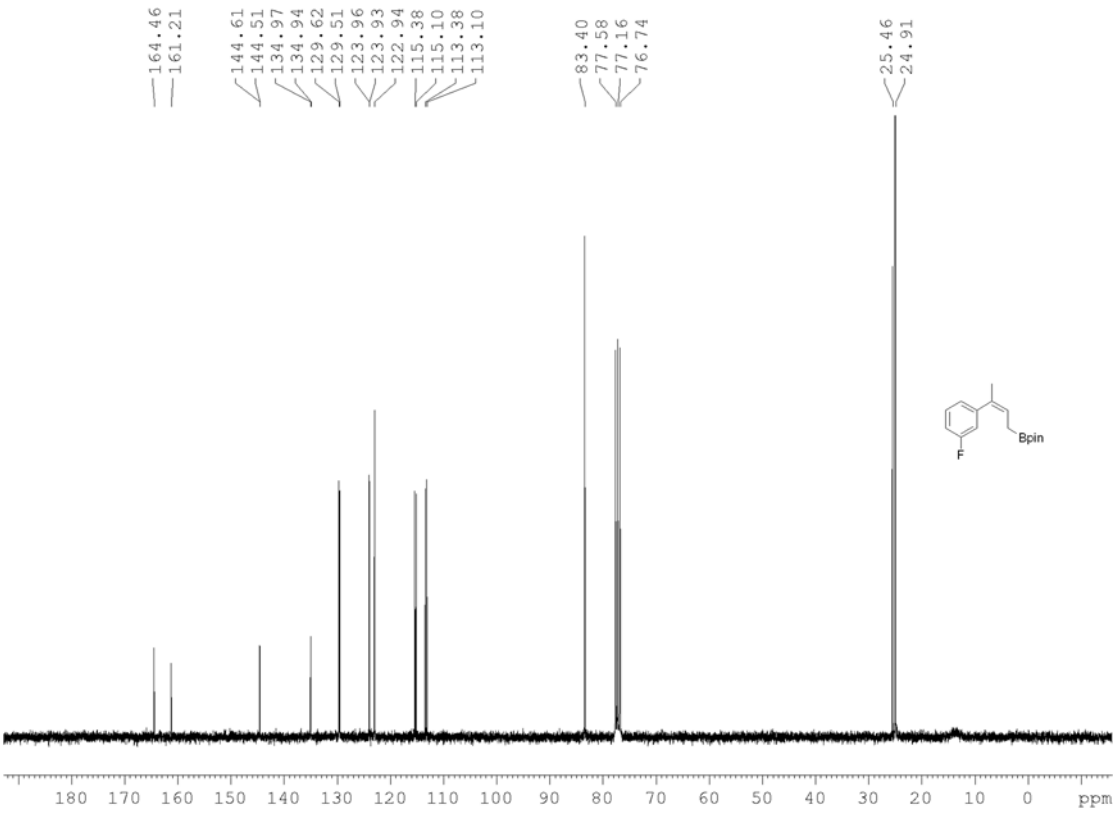


Compound 2q

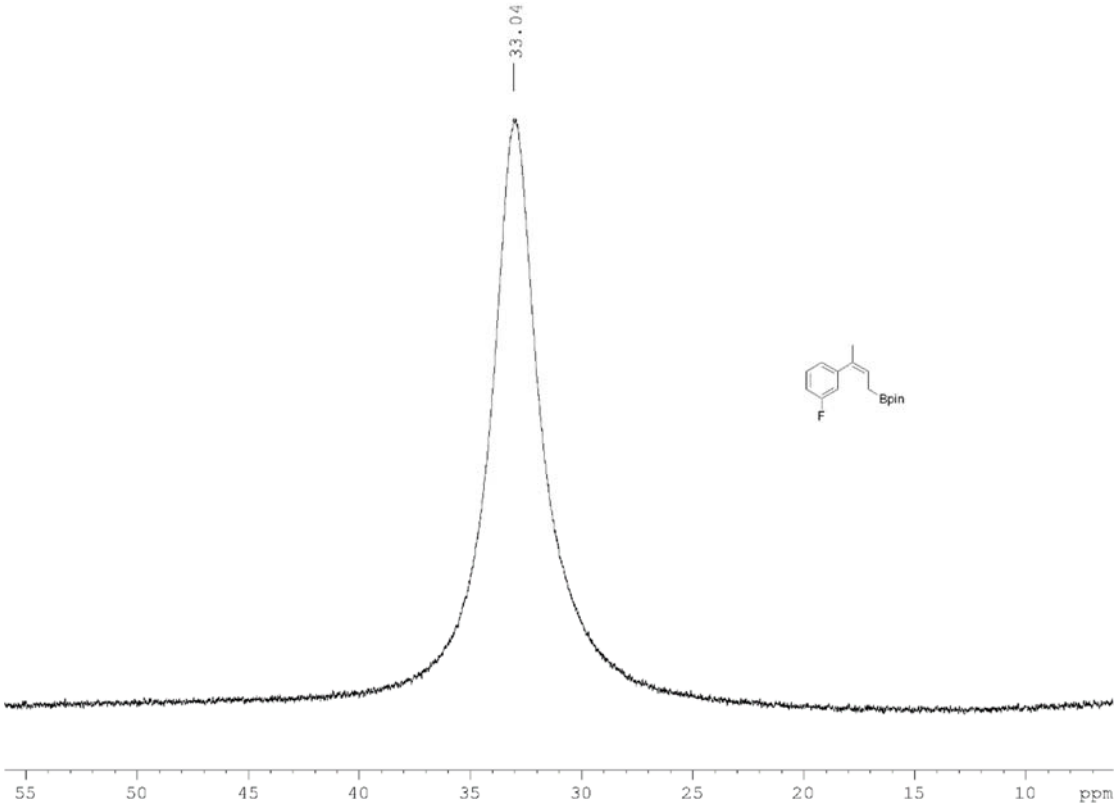
^{1}H NMR (300 MHz, $CDCl_3$)



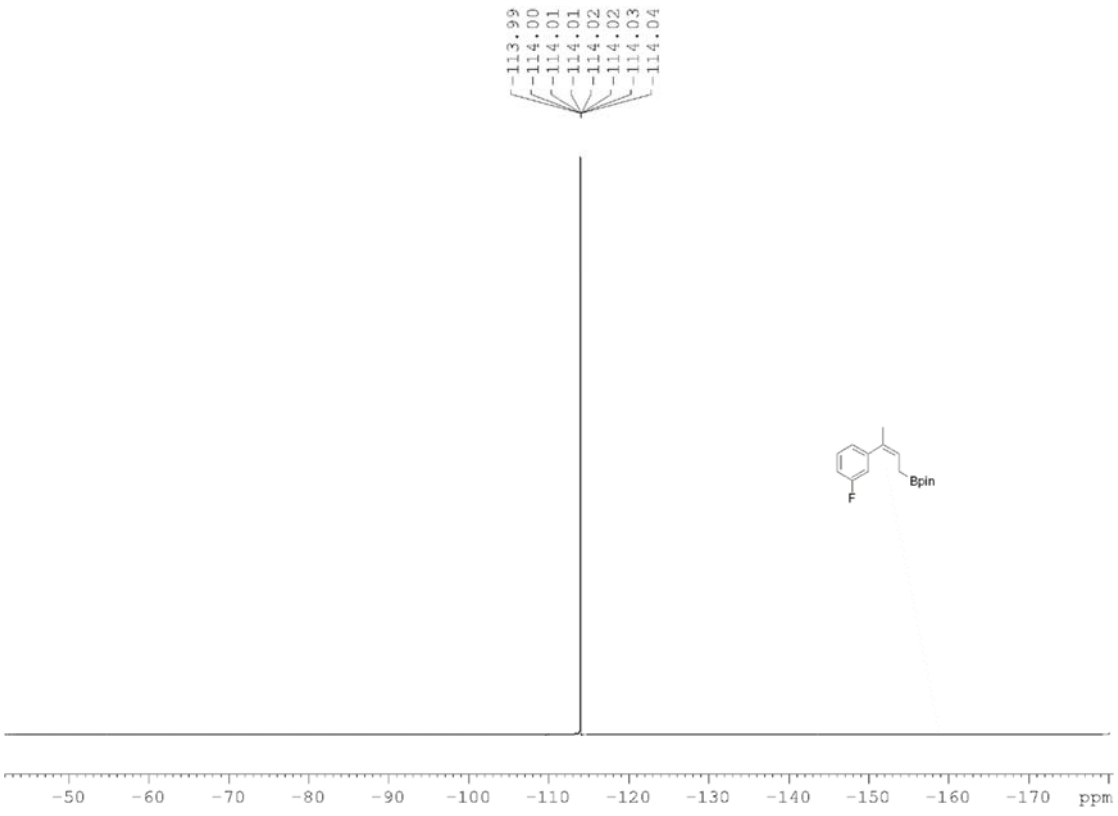
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



^{11}B NMR (96 MHz, $CDCl_3$)

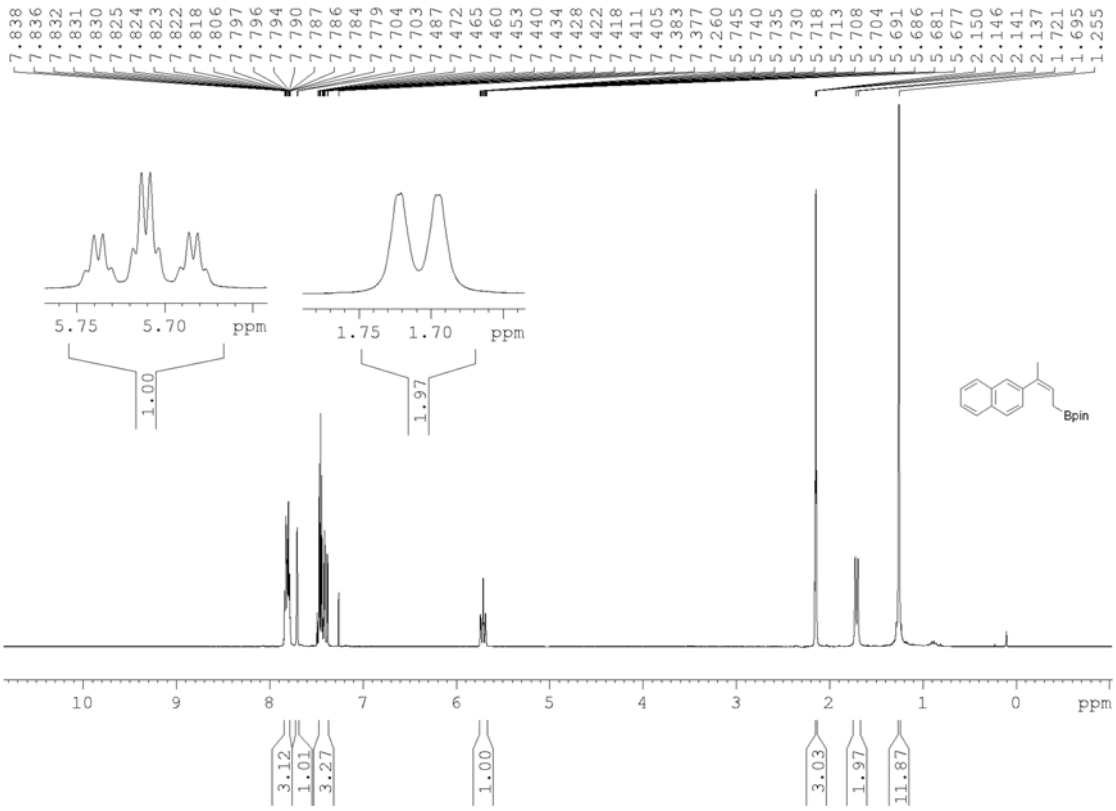


^{19}F NMR (470 MHz, $CDCl_3$)

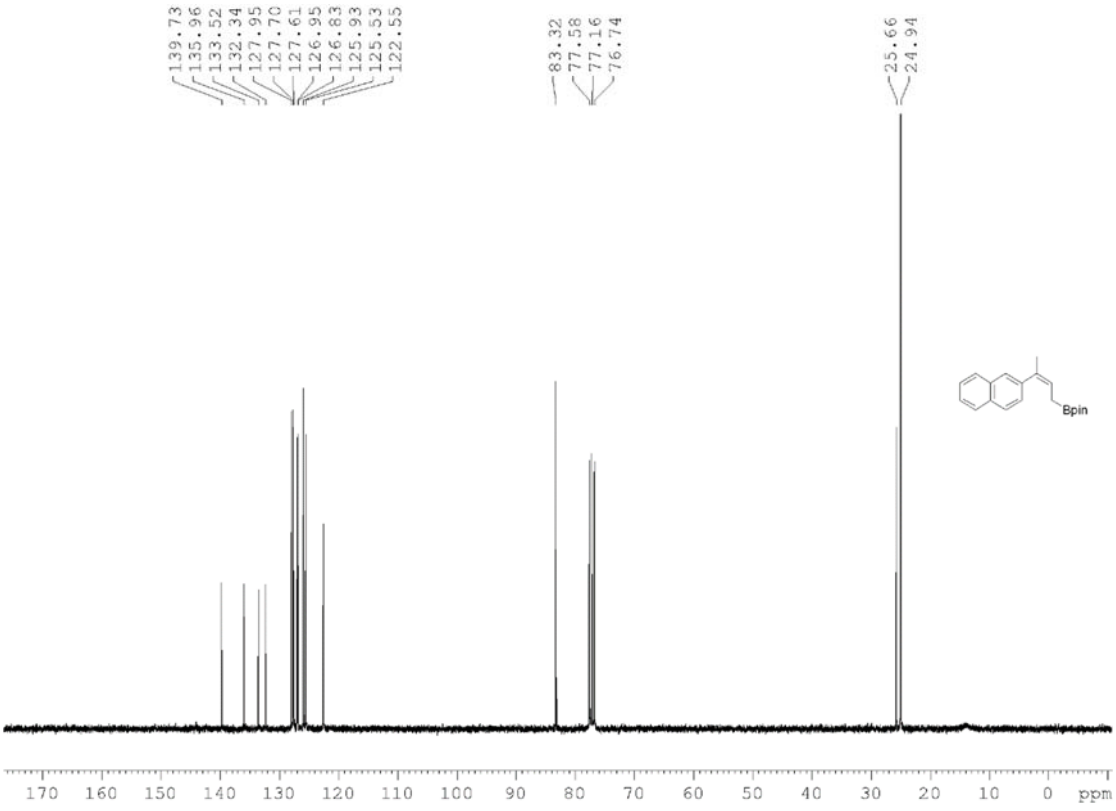


Compound 2r

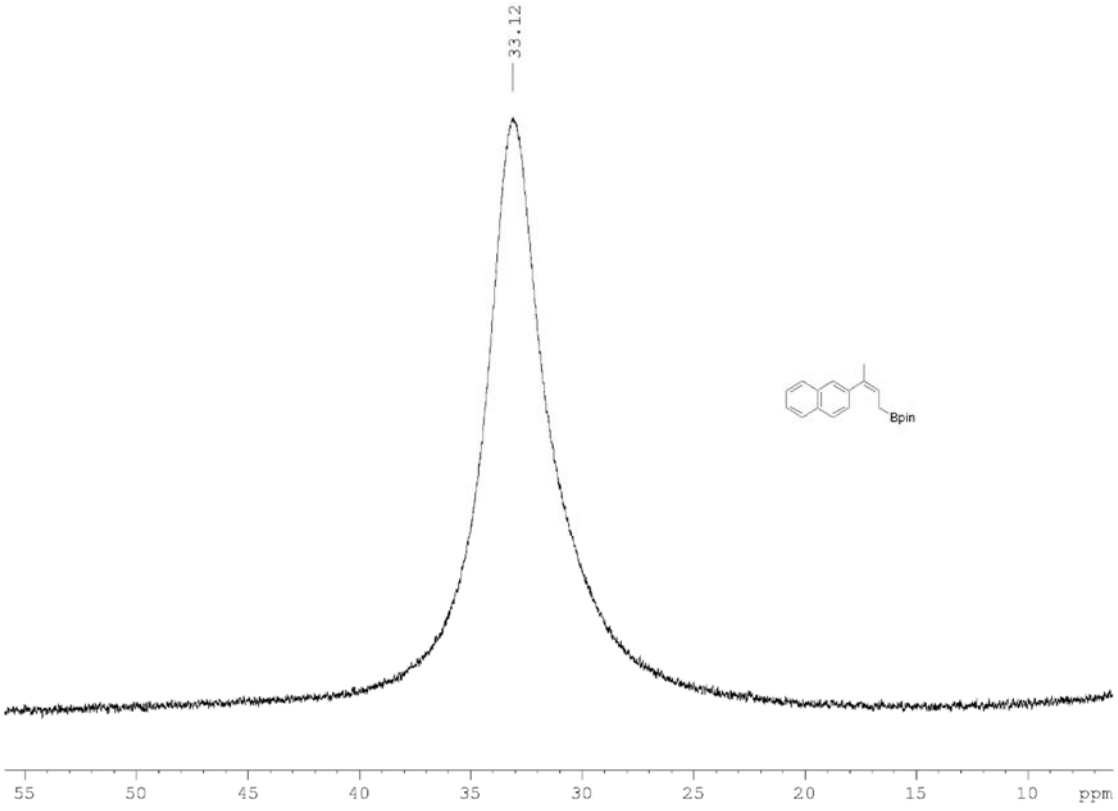
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

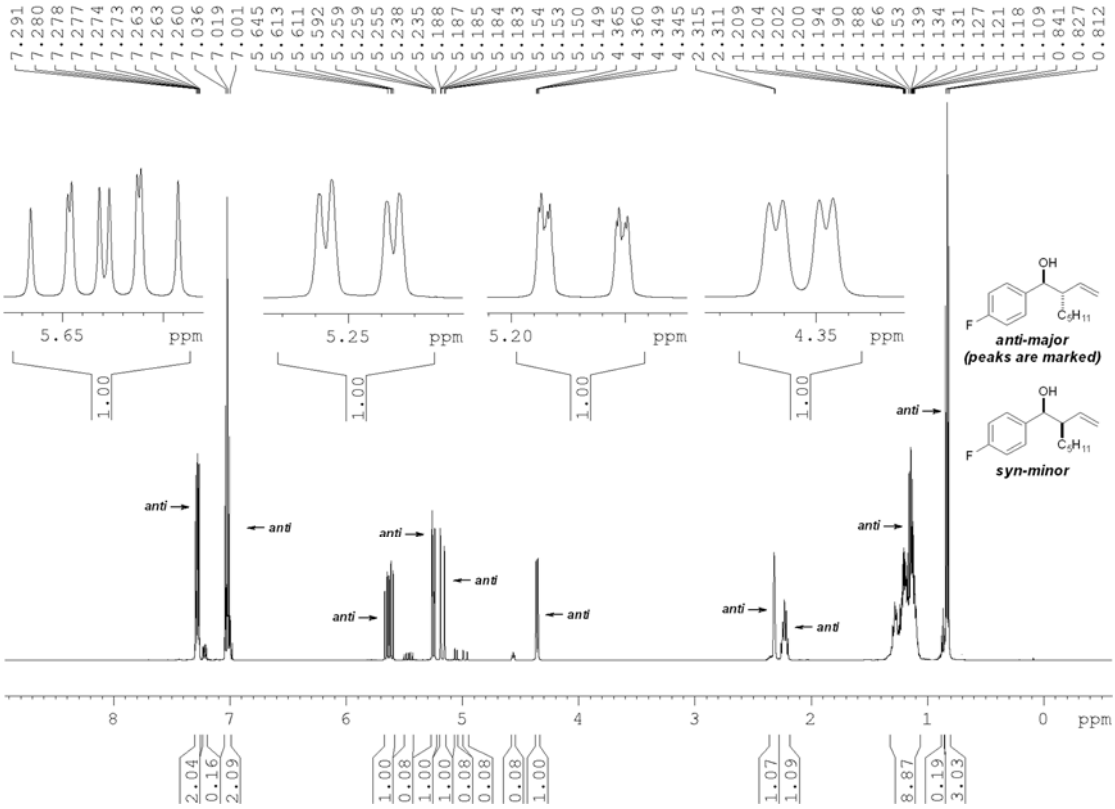


^{11}B NMR (96 MHz, $CDCl_3$)

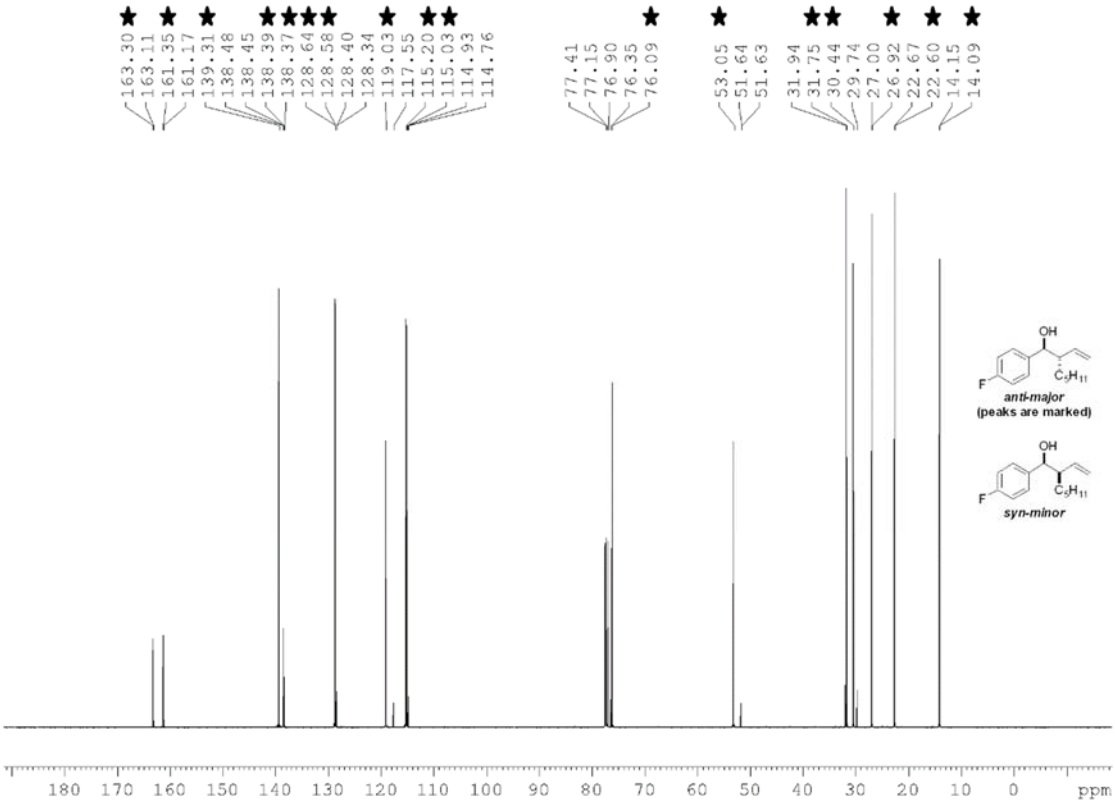


Compound 4a

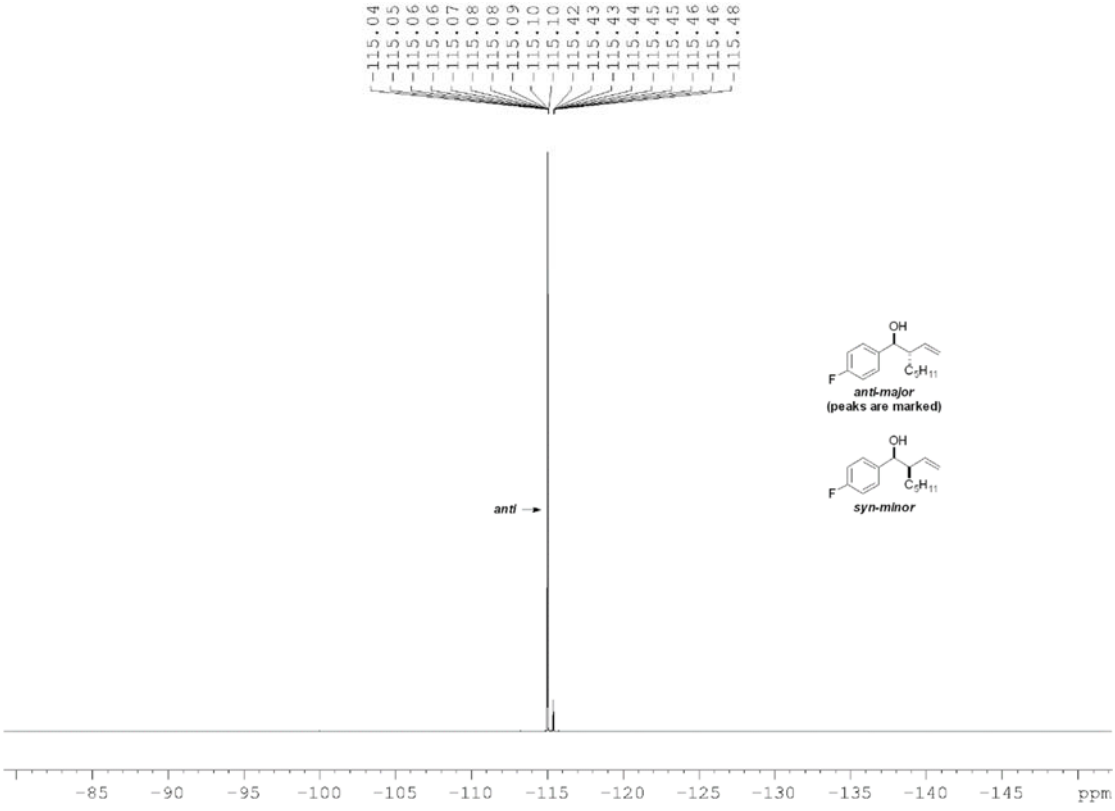
^{1}H NMR (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

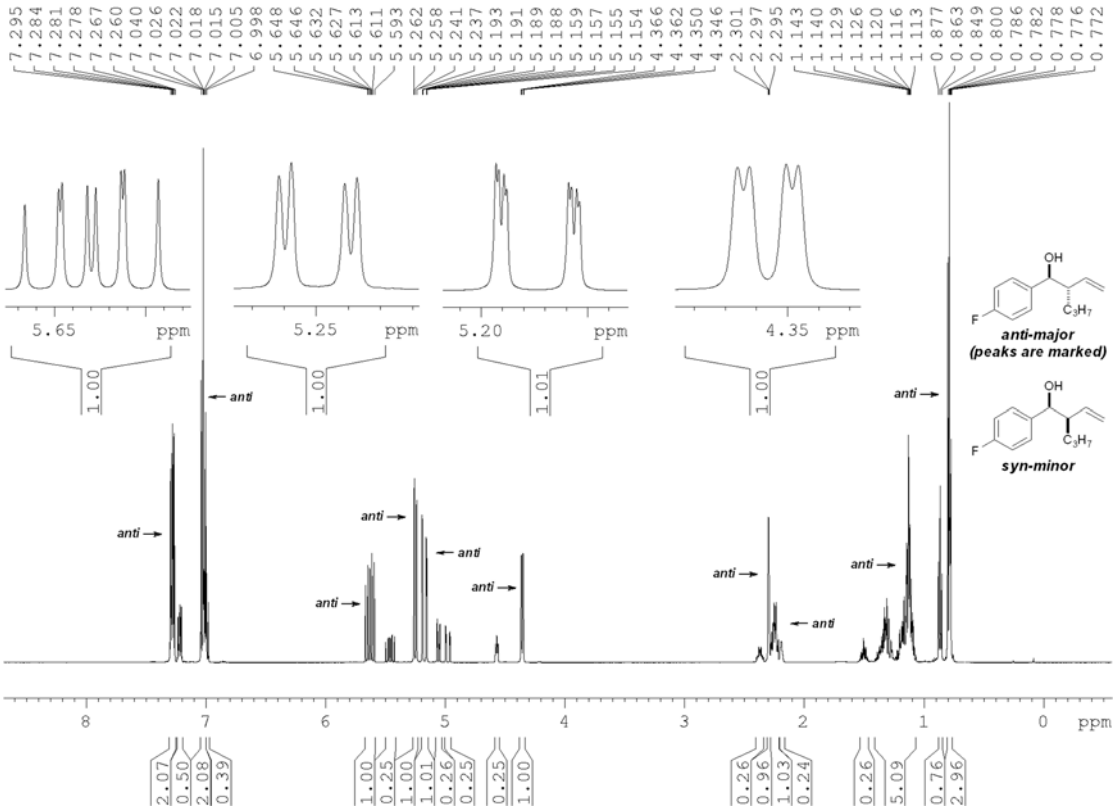


^{19}F NMR (470 MHz, $CDCl_3$)

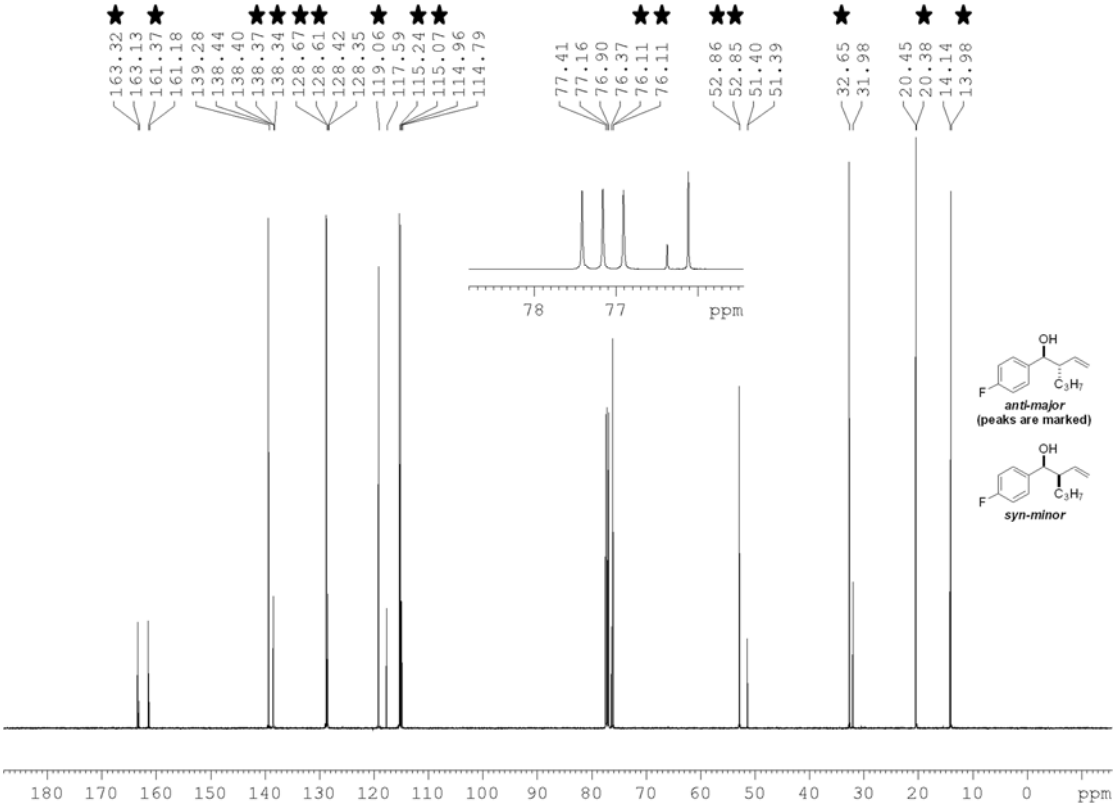


Compound 4b

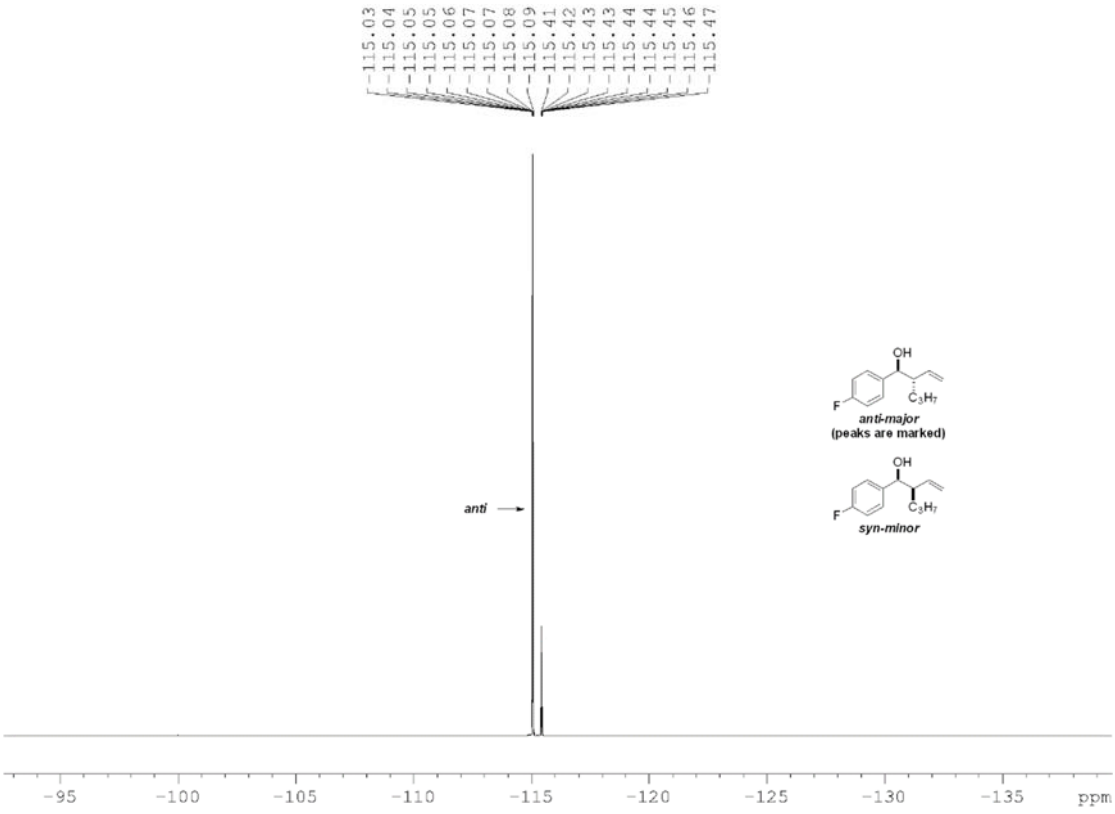
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

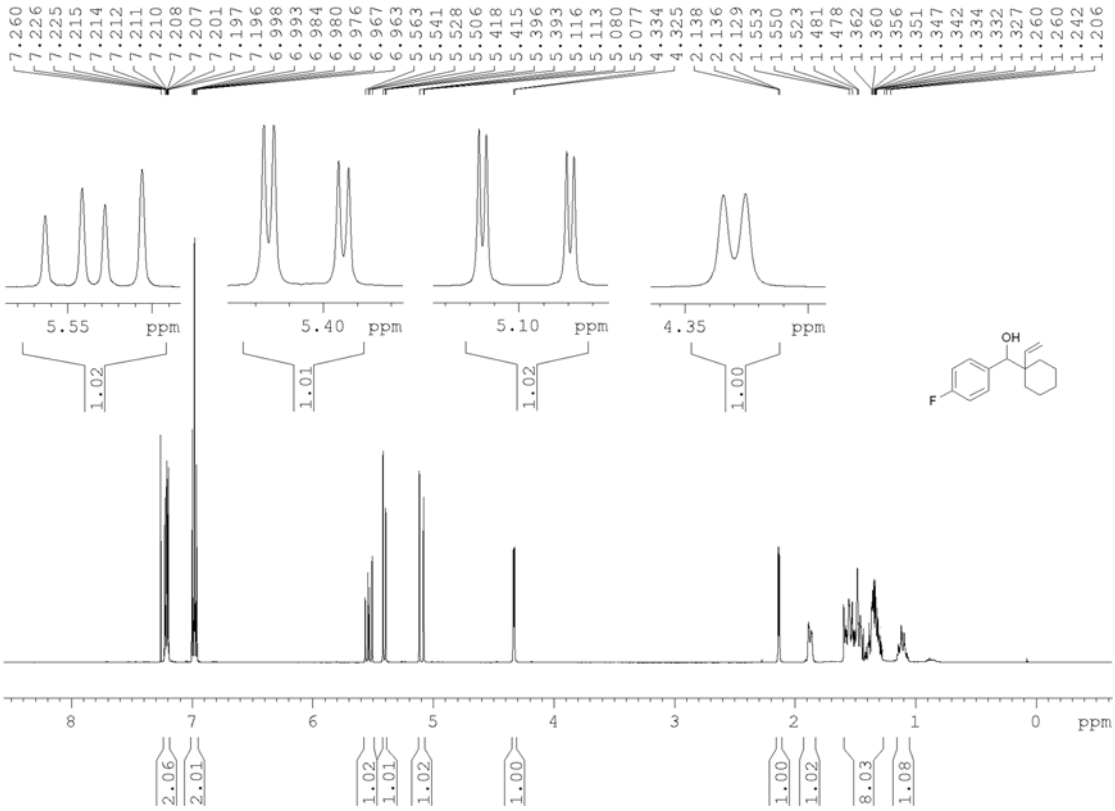


^{19}F NMR (470 MHz, $CDCl_3$)

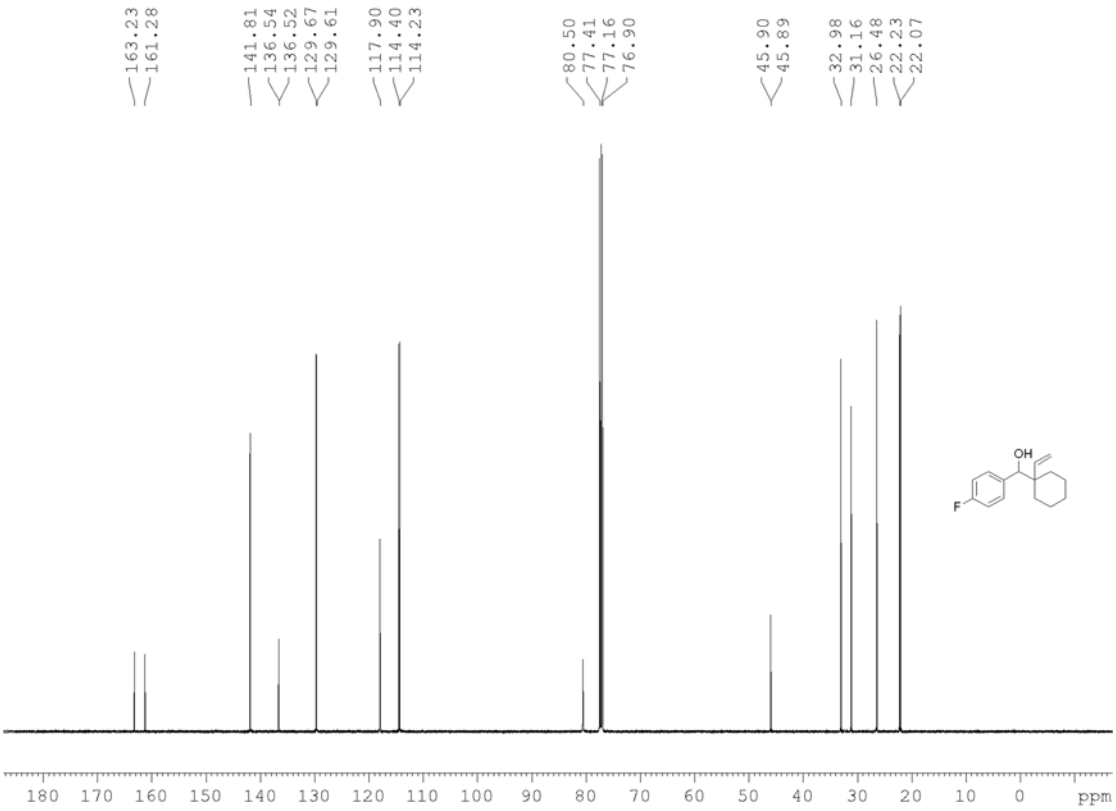


Compound 4d

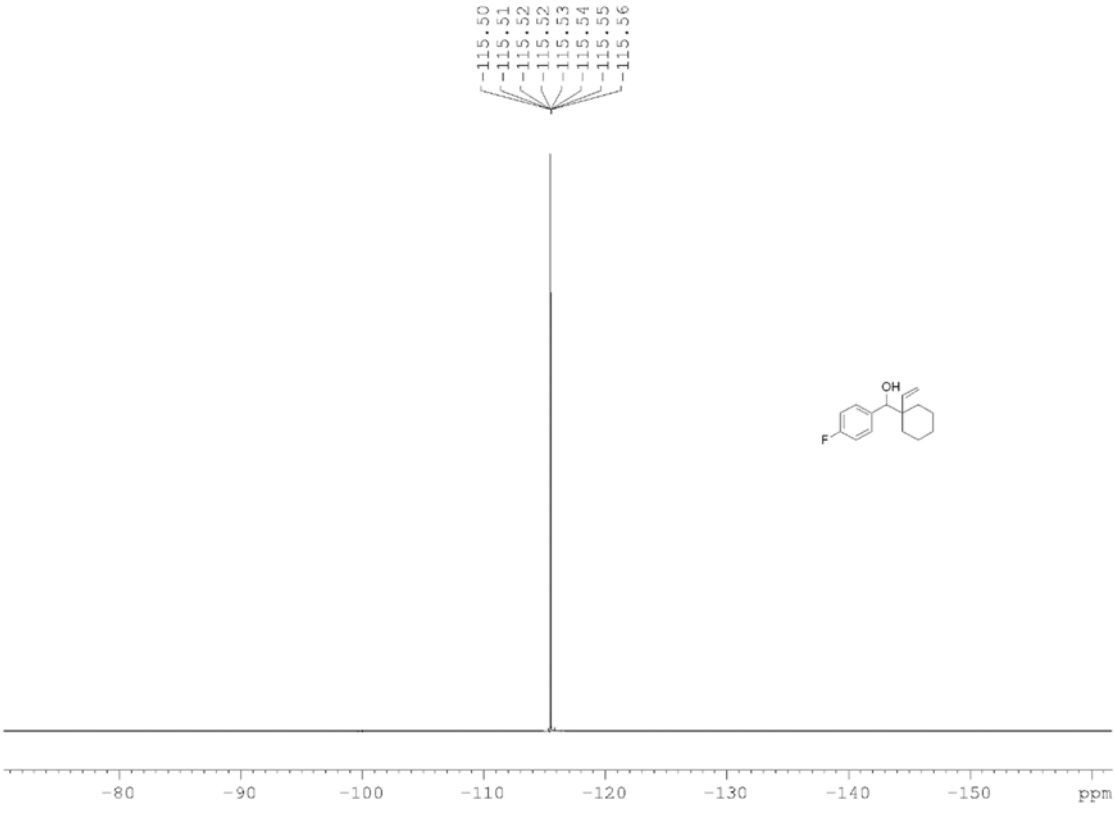
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

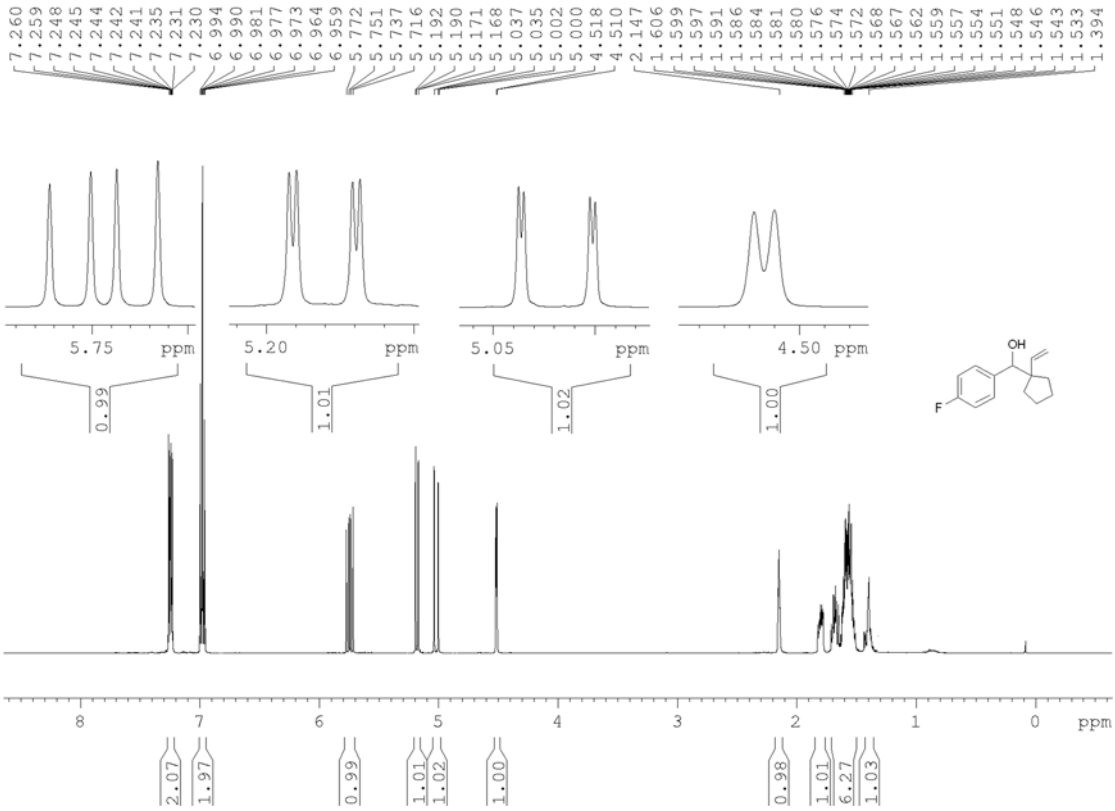


^{19}F NMR (470 MHz, $CDCl_3$)

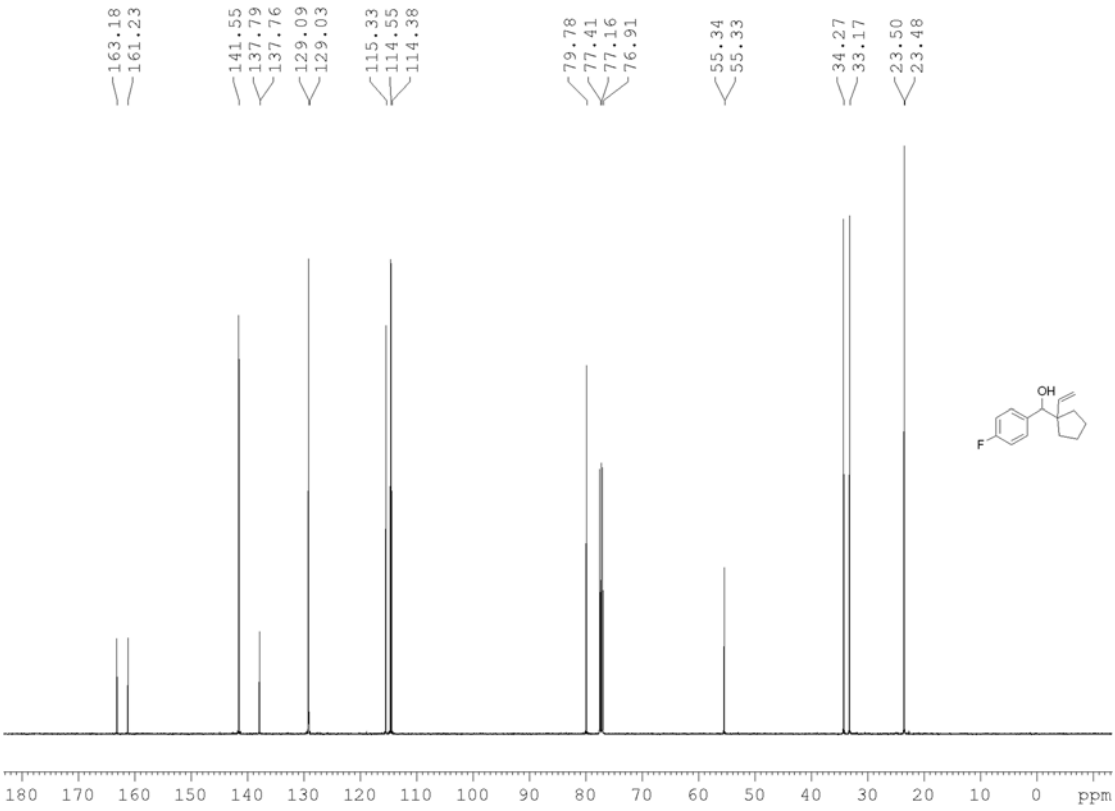


Compound 4e

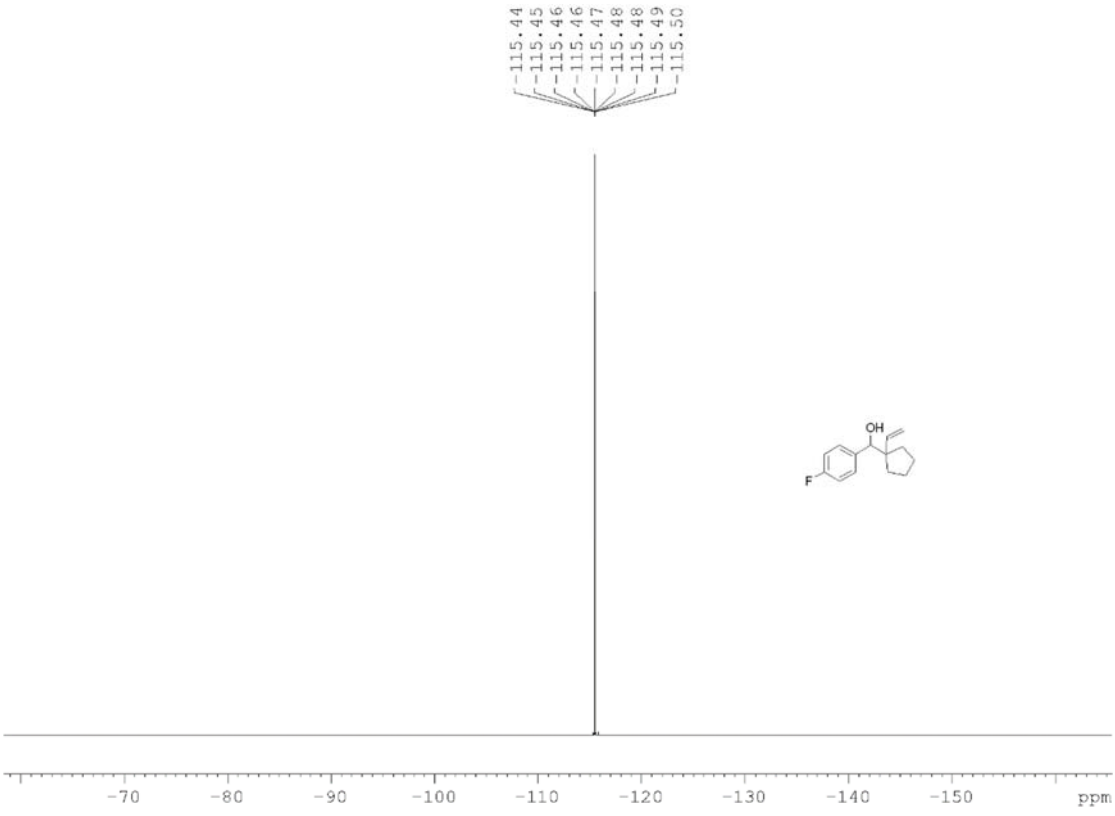
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

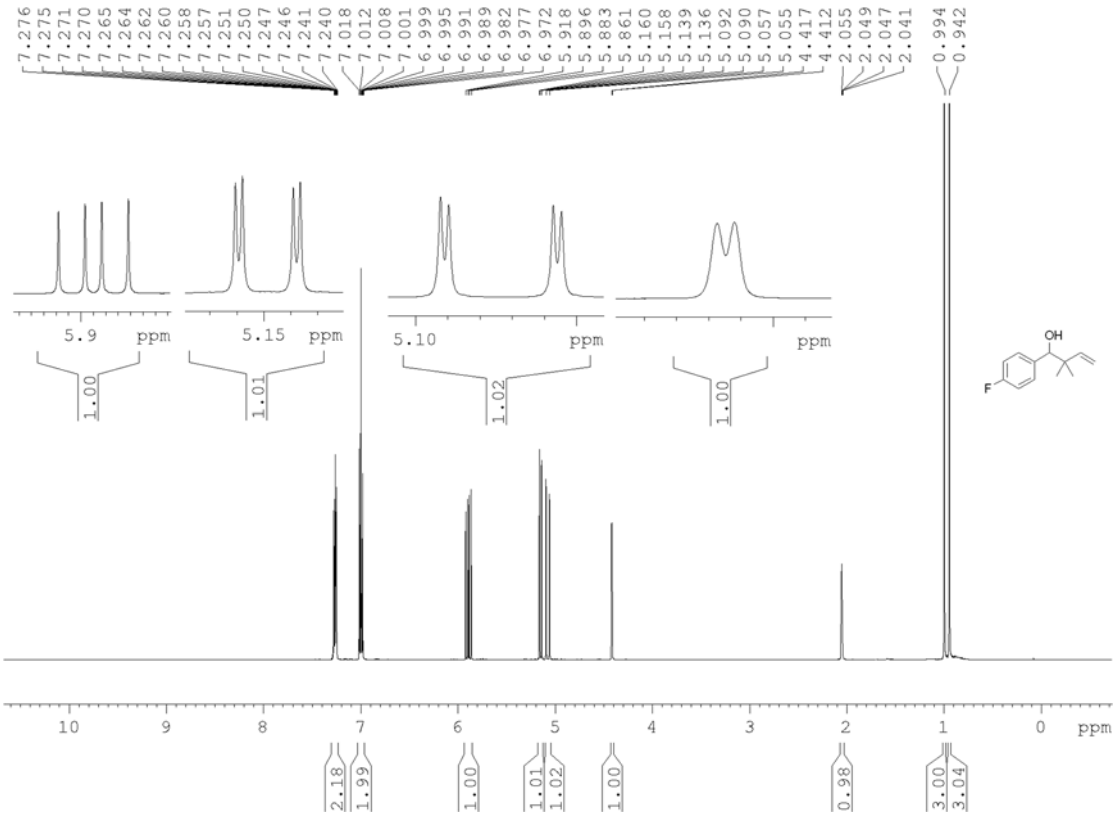


^{19}F NMR (470 MHz, $CDCl_3$)

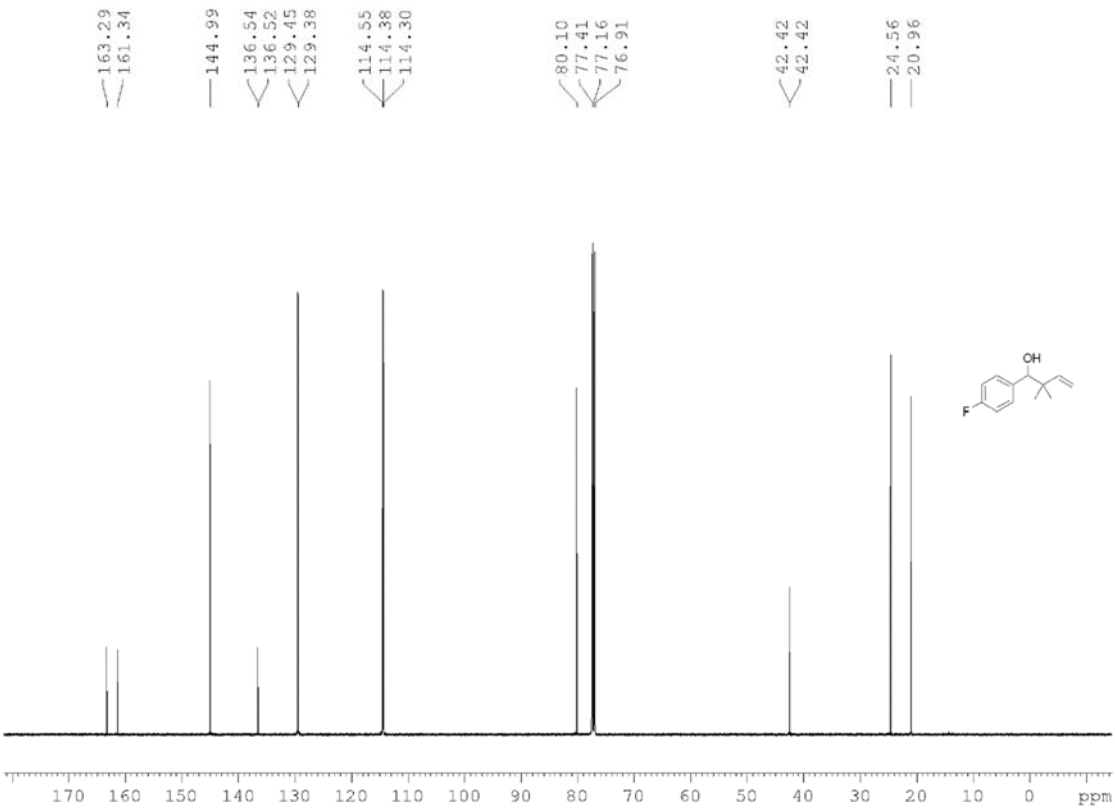


Compound 4g

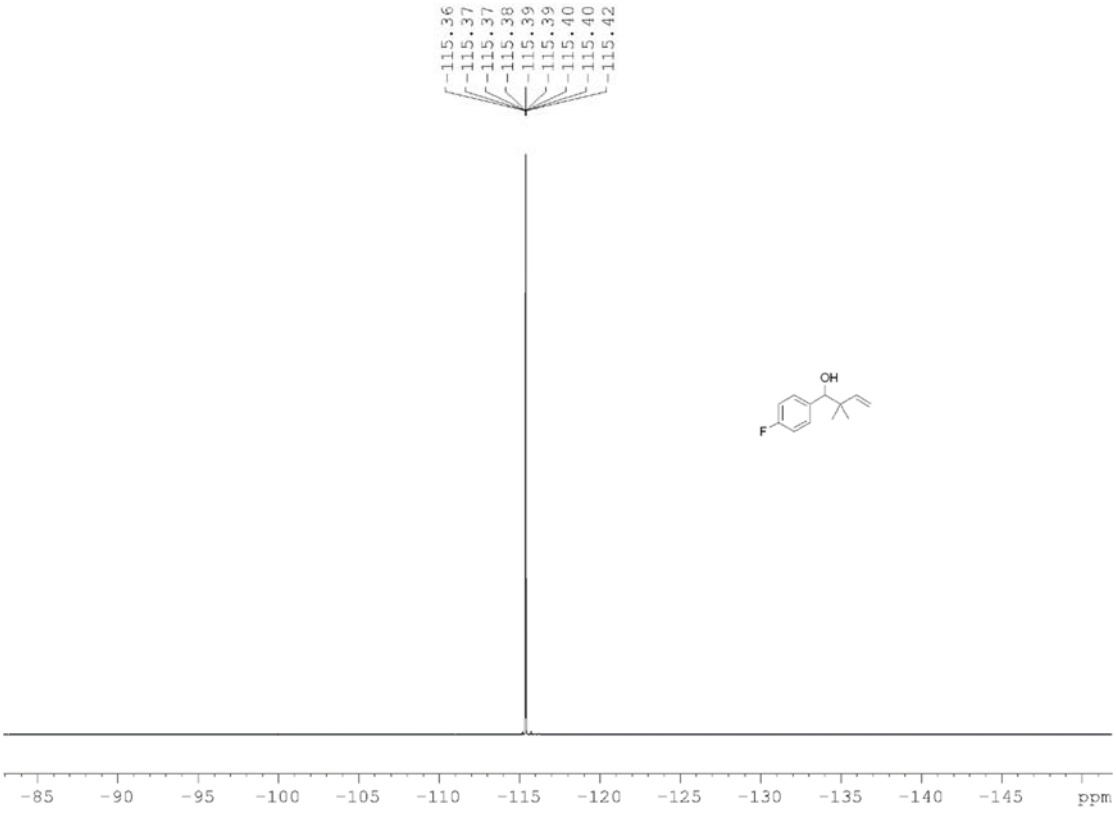
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

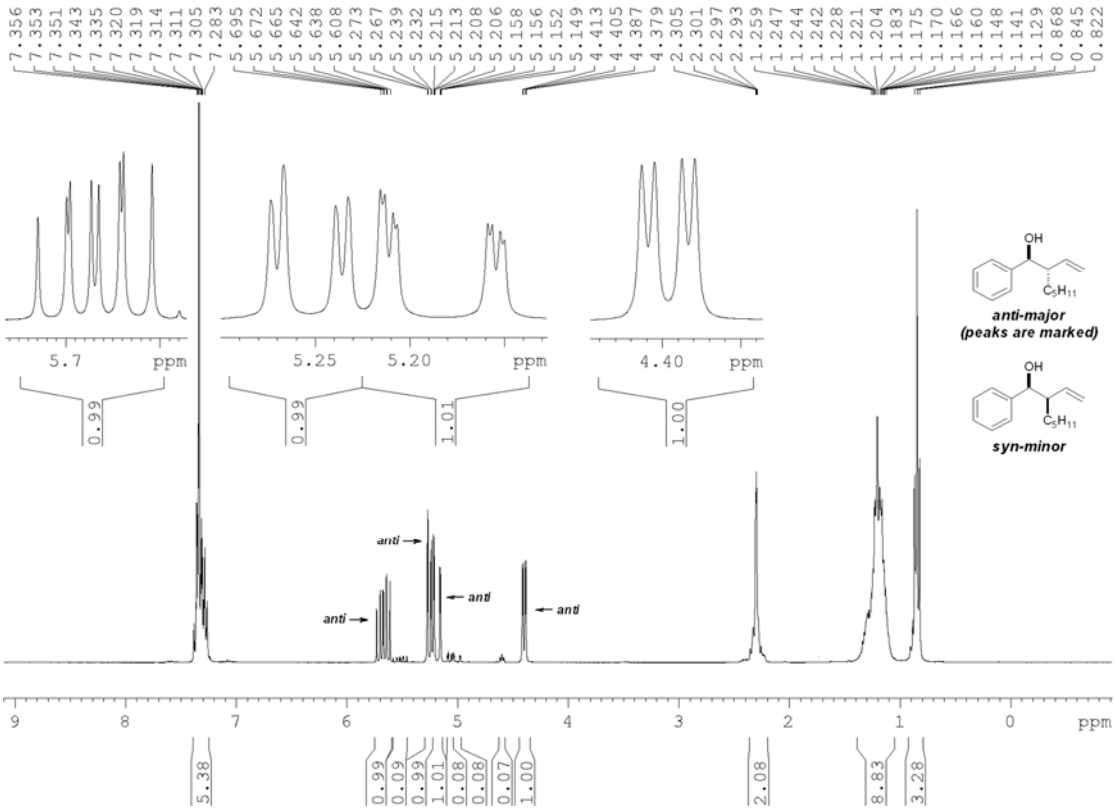


^{19}F NMR (470 MHz, $CDCl_3$)

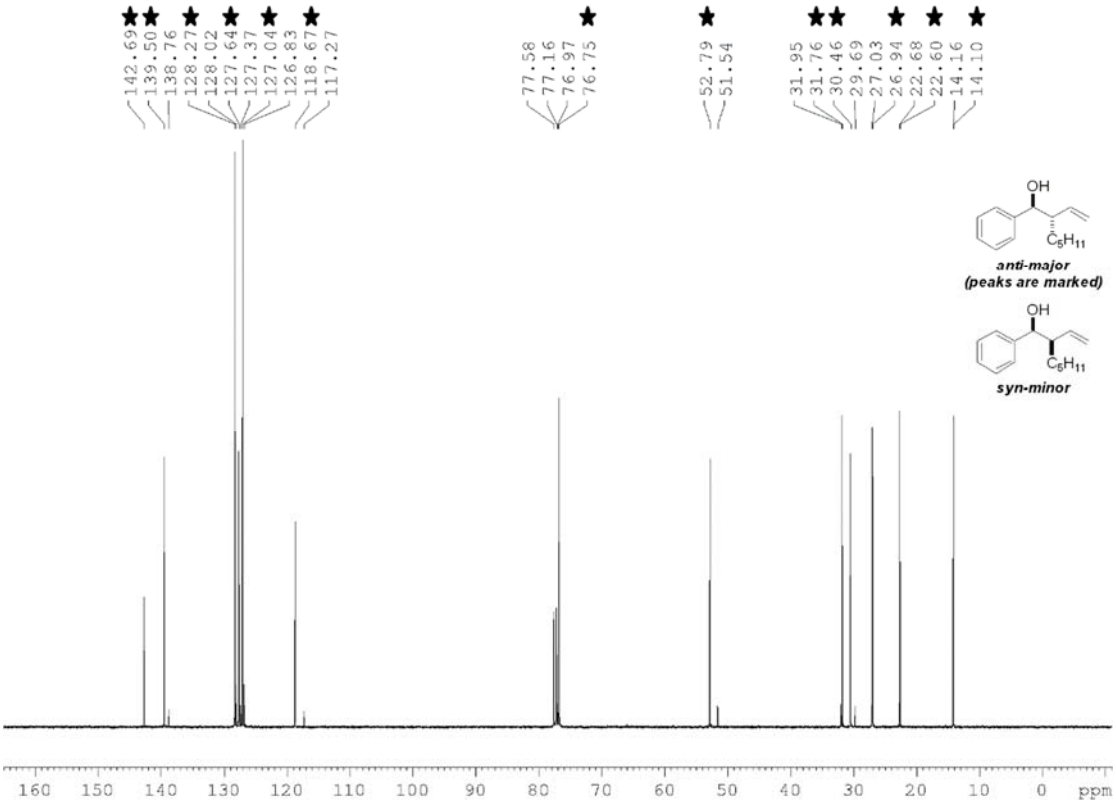


Compound 5a

^{1}H NMR (300 MHz, $CDCl_3$)

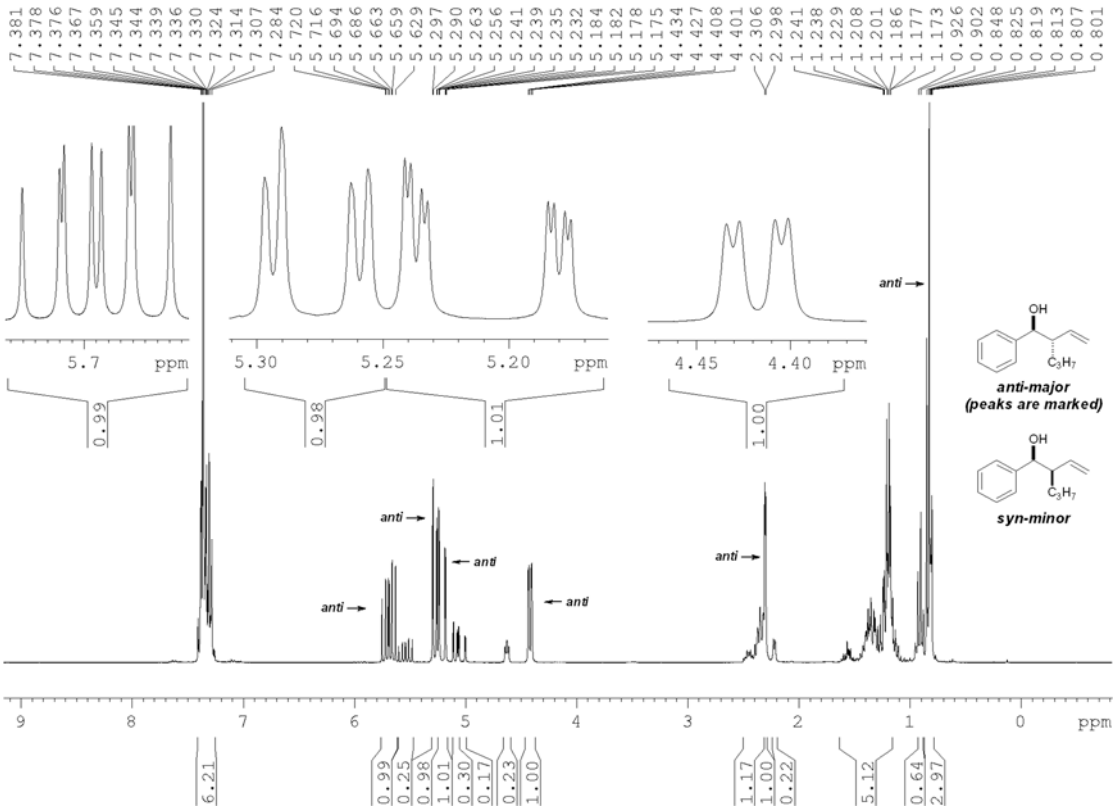


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

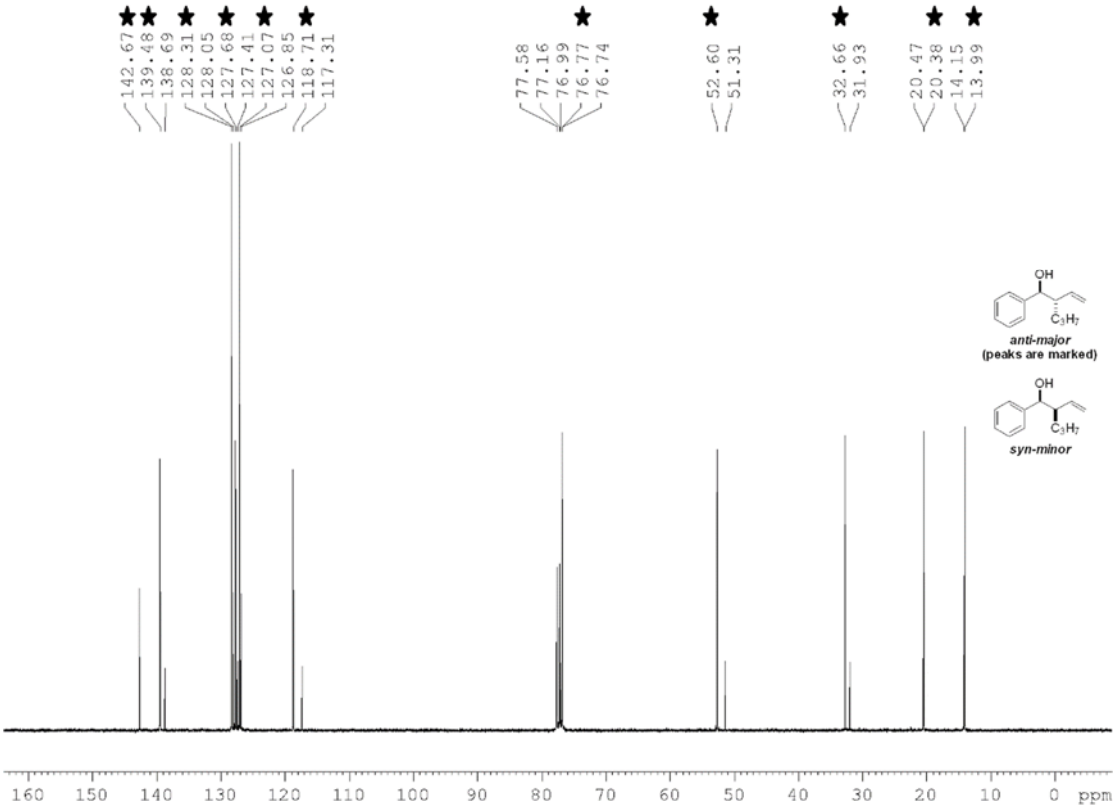


Compound 5b

^{1}H NMR (300 MHz, $CDCl_3$)

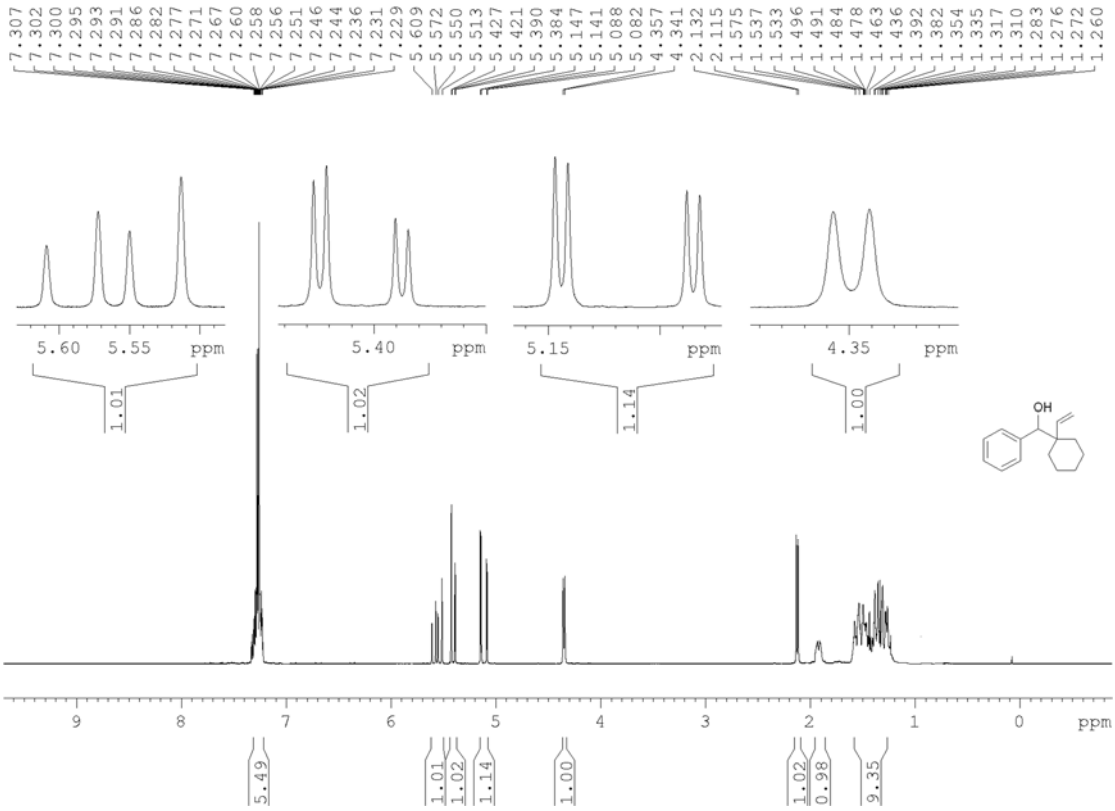


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

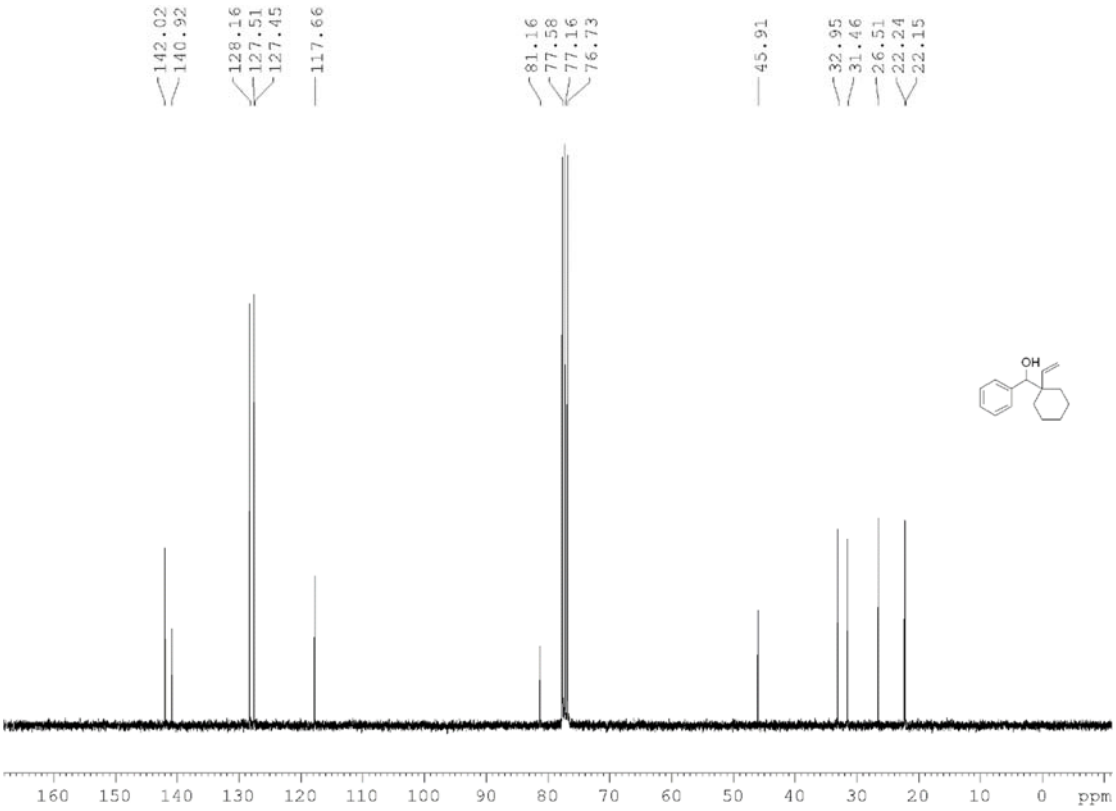


Compound 5d

^{1}H NMR (300 MHz, $CDCl_3$)

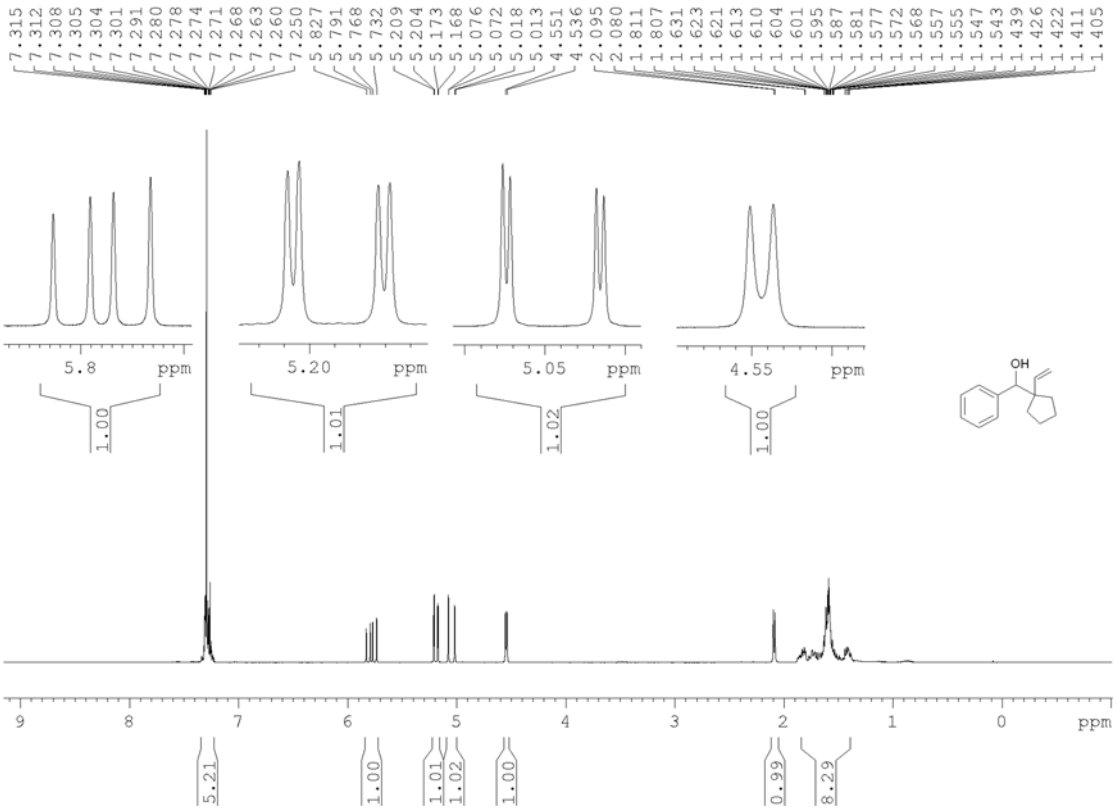


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

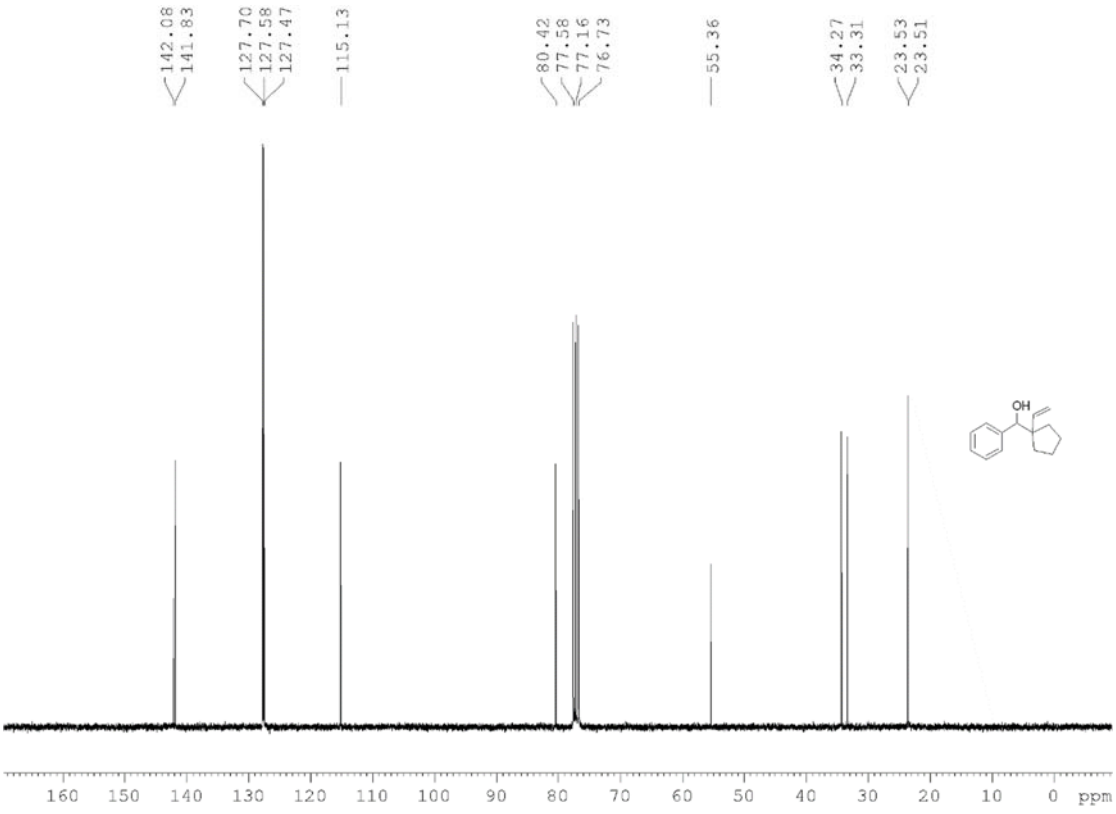


Compound 5e

^{1}H NMR (300 MHz, $CDCl_3$)

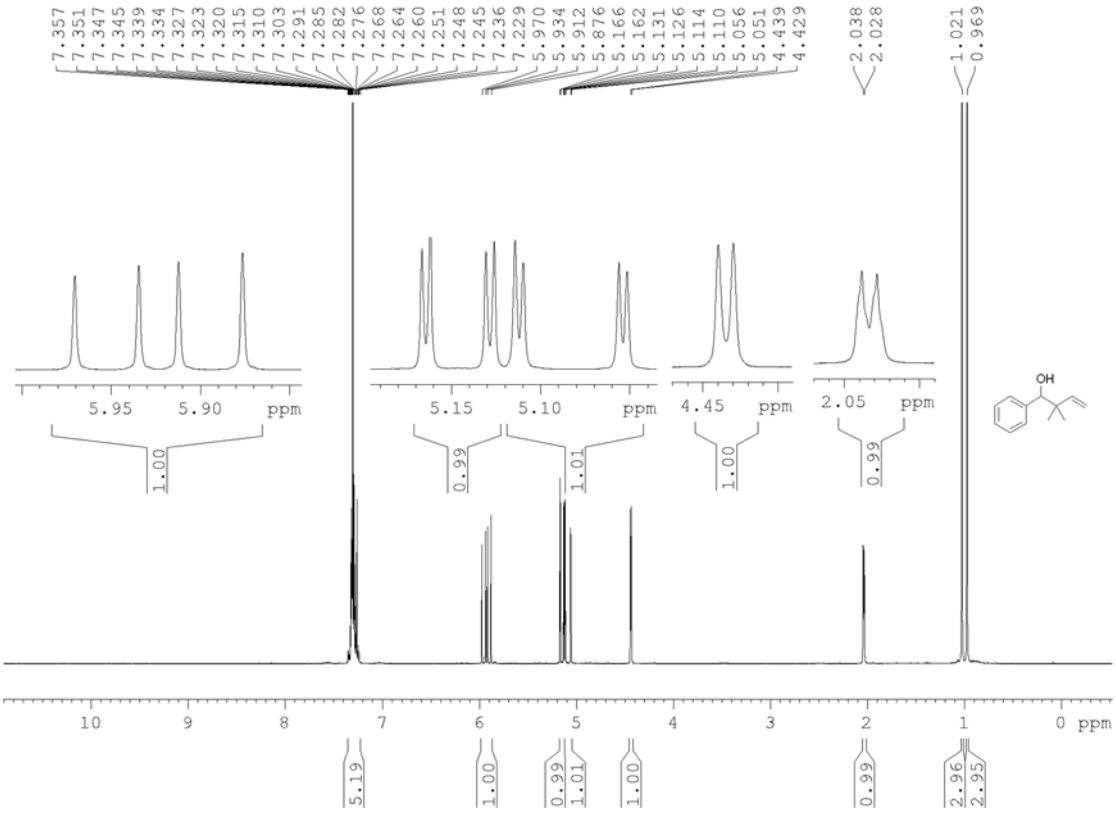


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

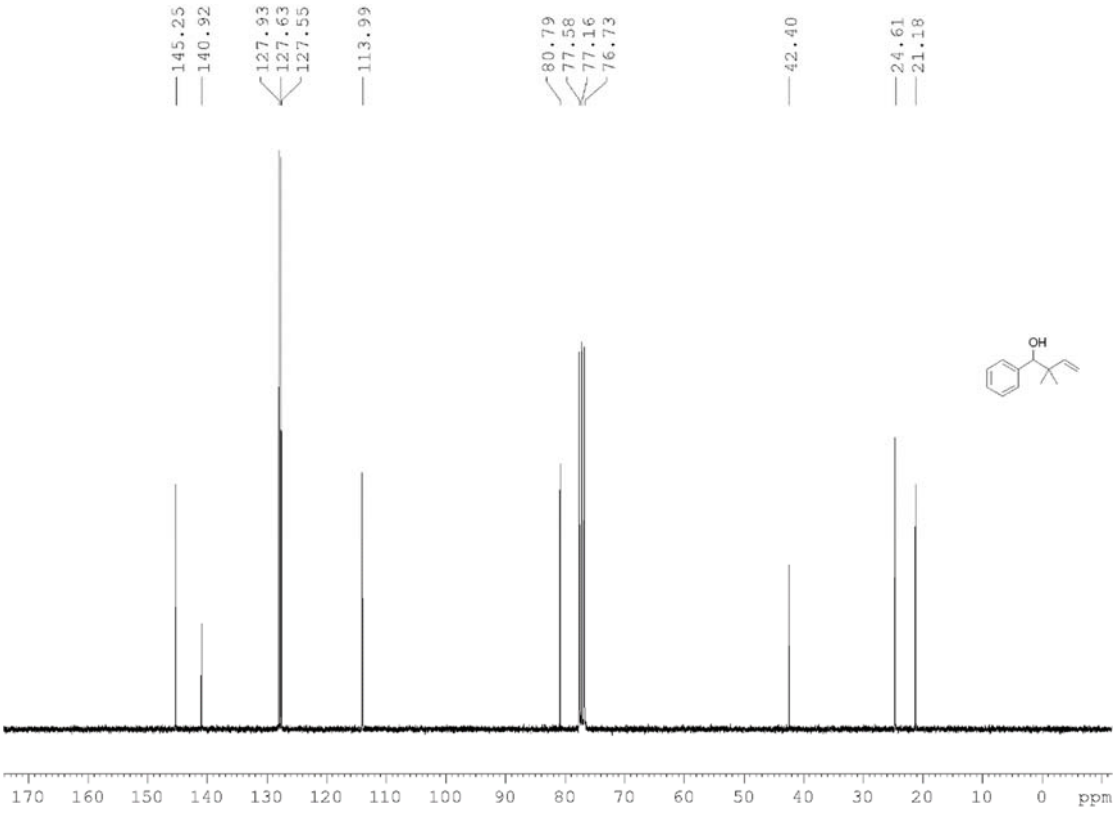


Compound 5g

^{1}H NMR (300 MHz, $CDCl_3$)

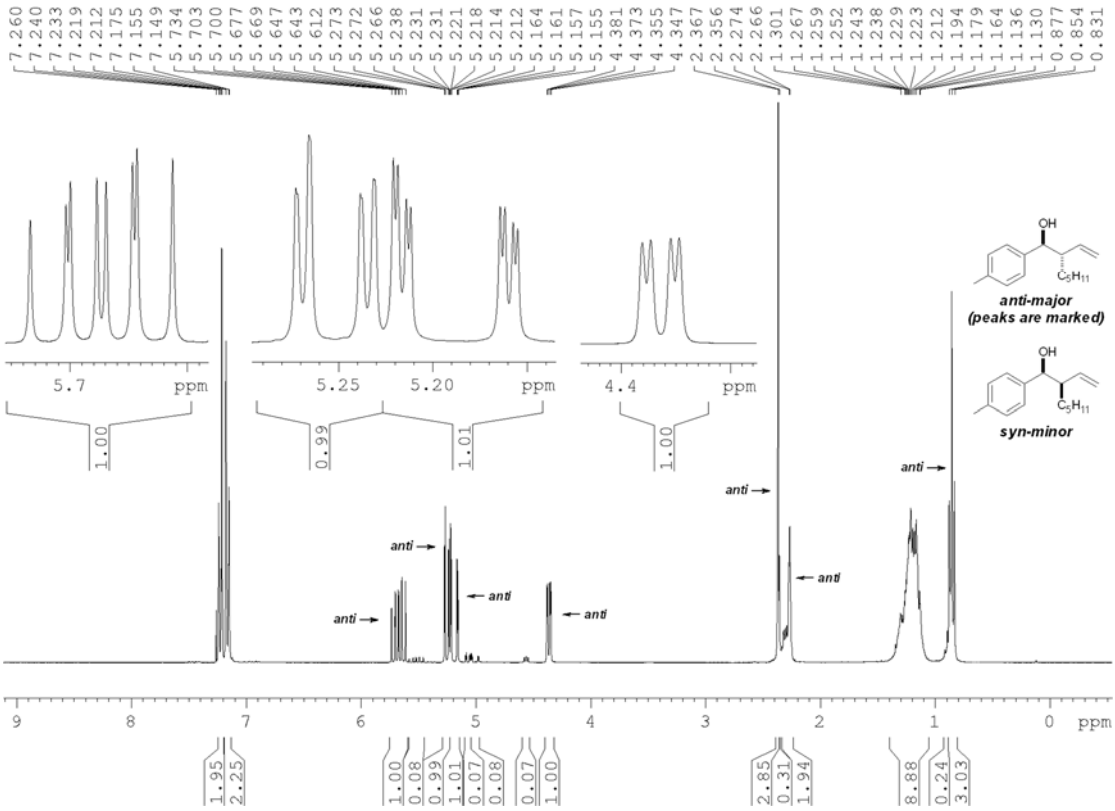


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

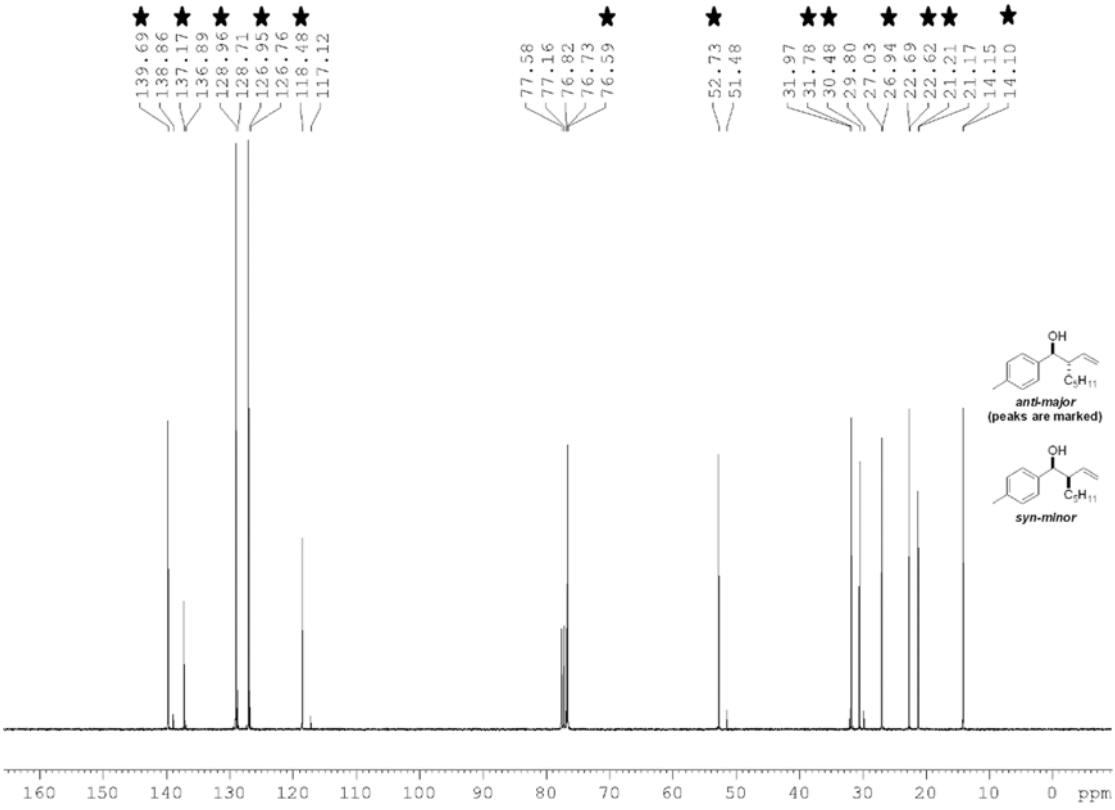


Compound 6a

^{1}H NMR (300 MHz, $CDCl_3$)

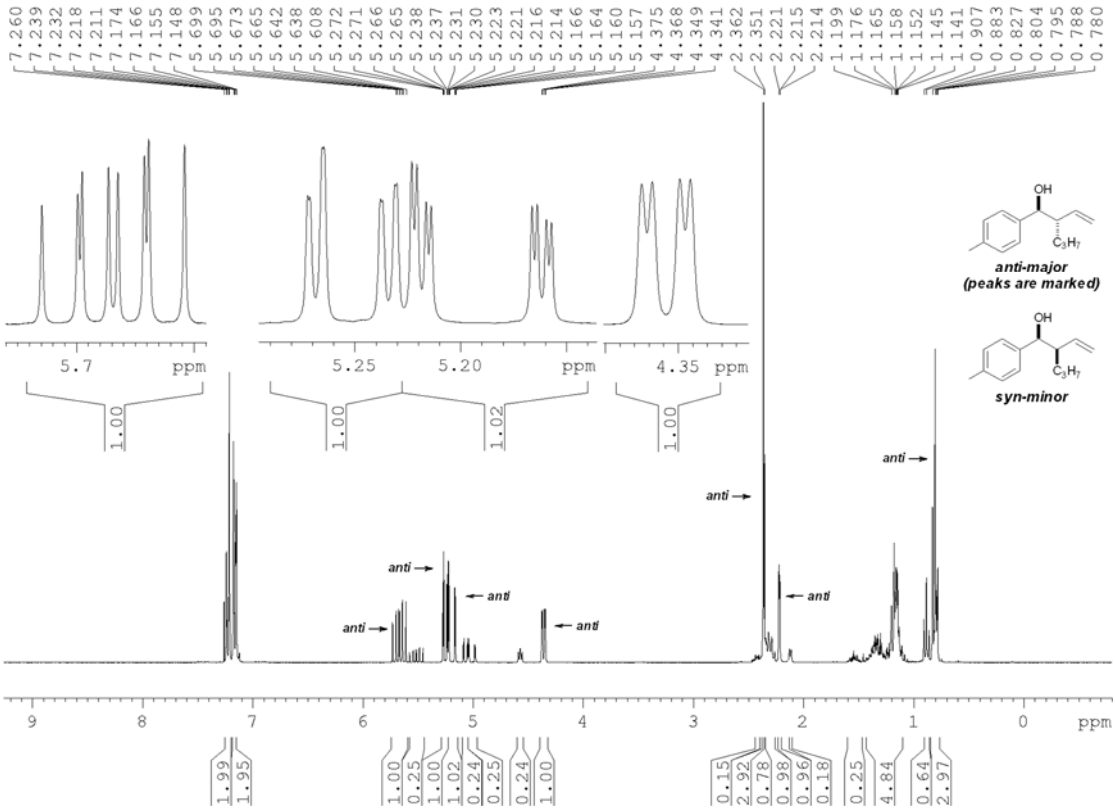


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

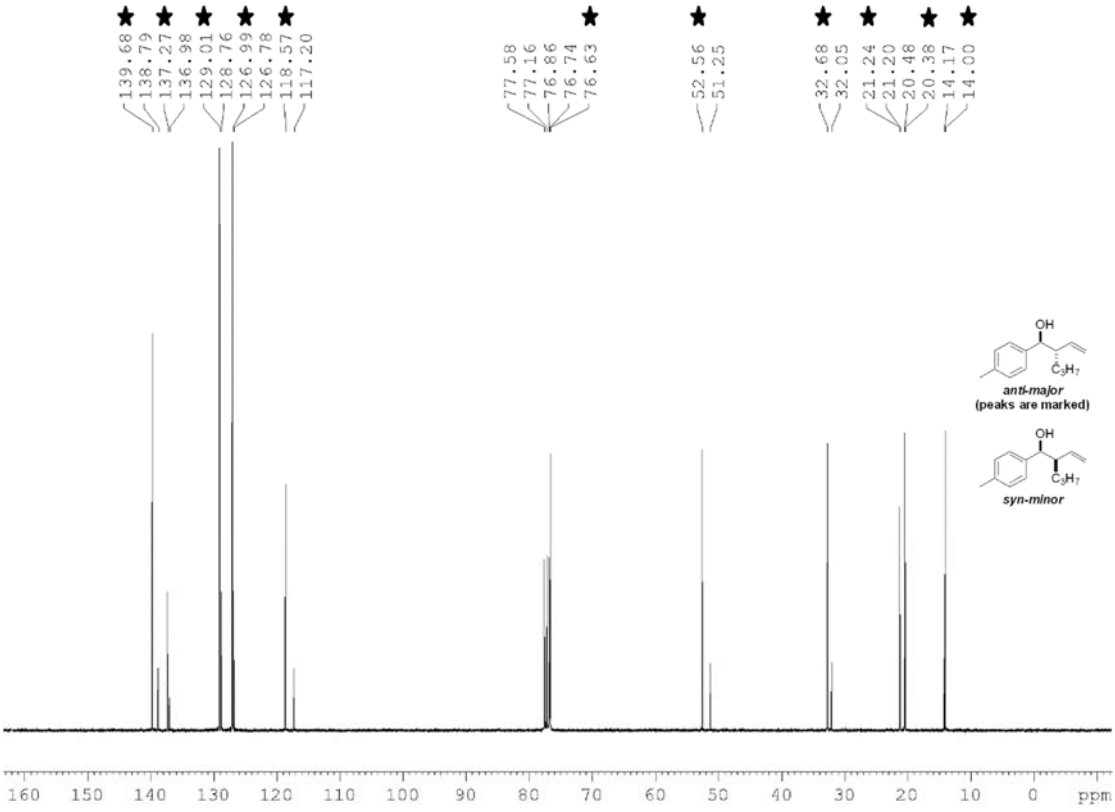


Compound 6b

^{1}H NMR (300 MHz, $CDCl_3$)

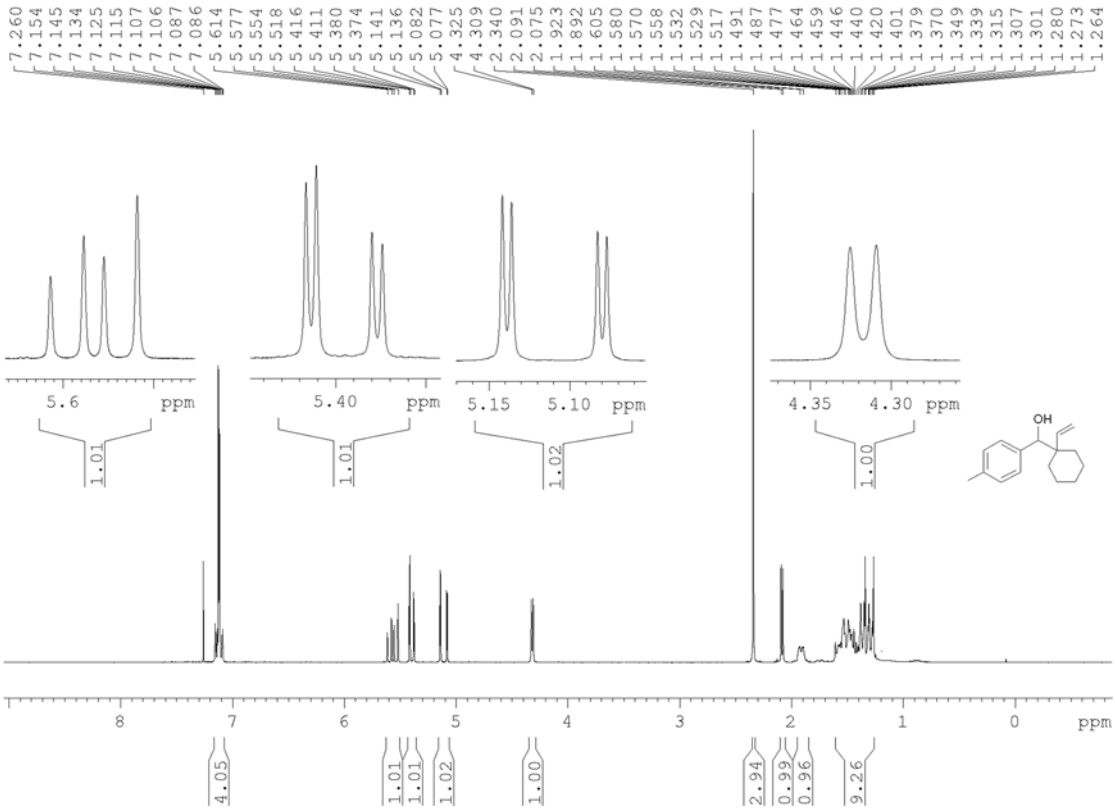


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

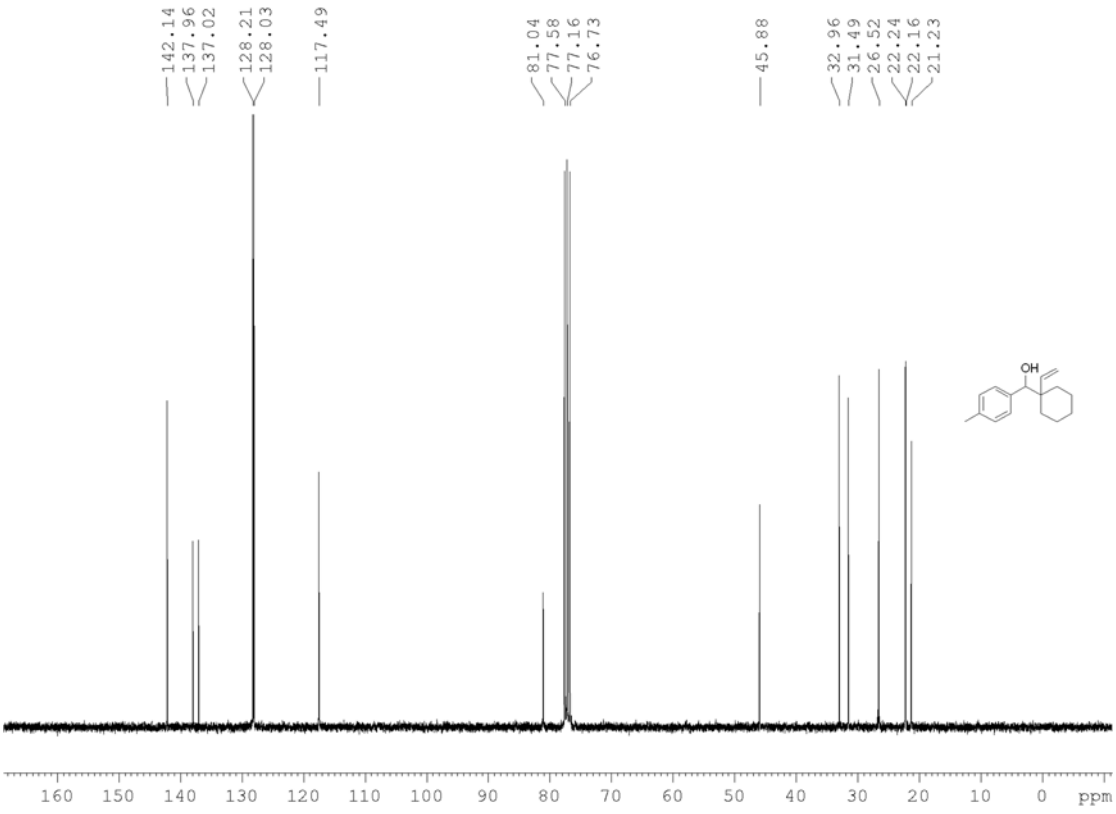


Compound 6d

^{1}H NMR (300 MHz, $CDCl_3$)

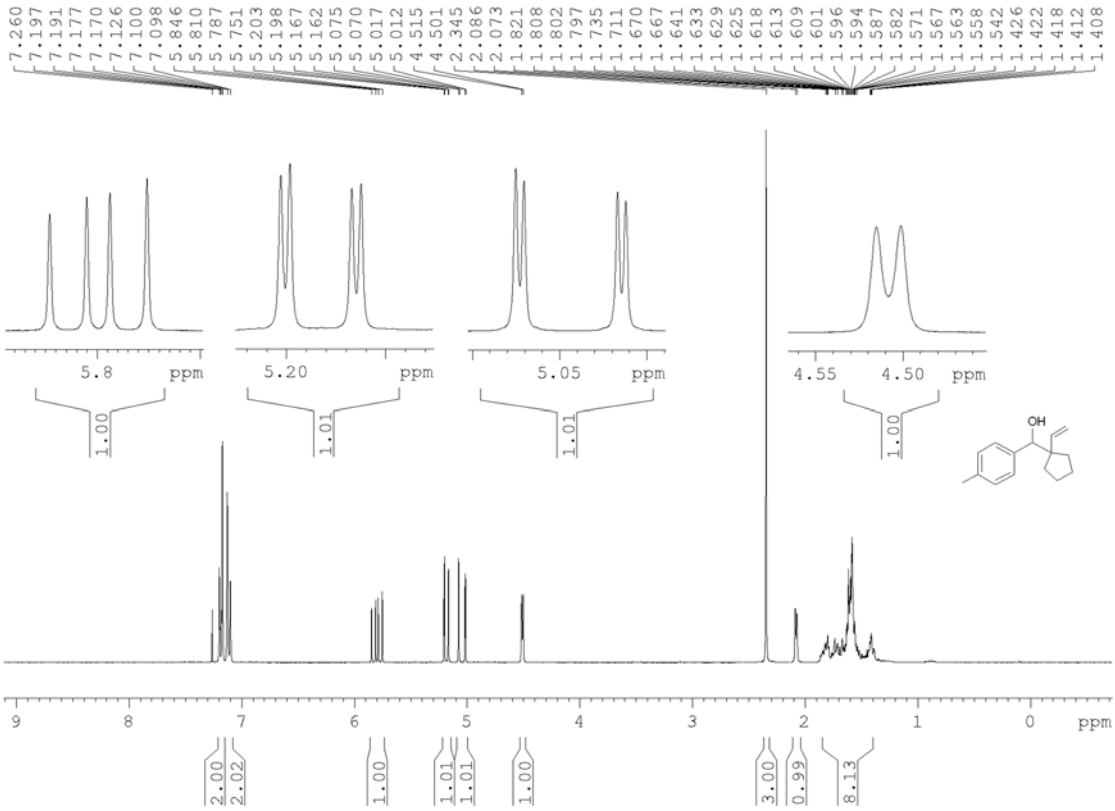


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

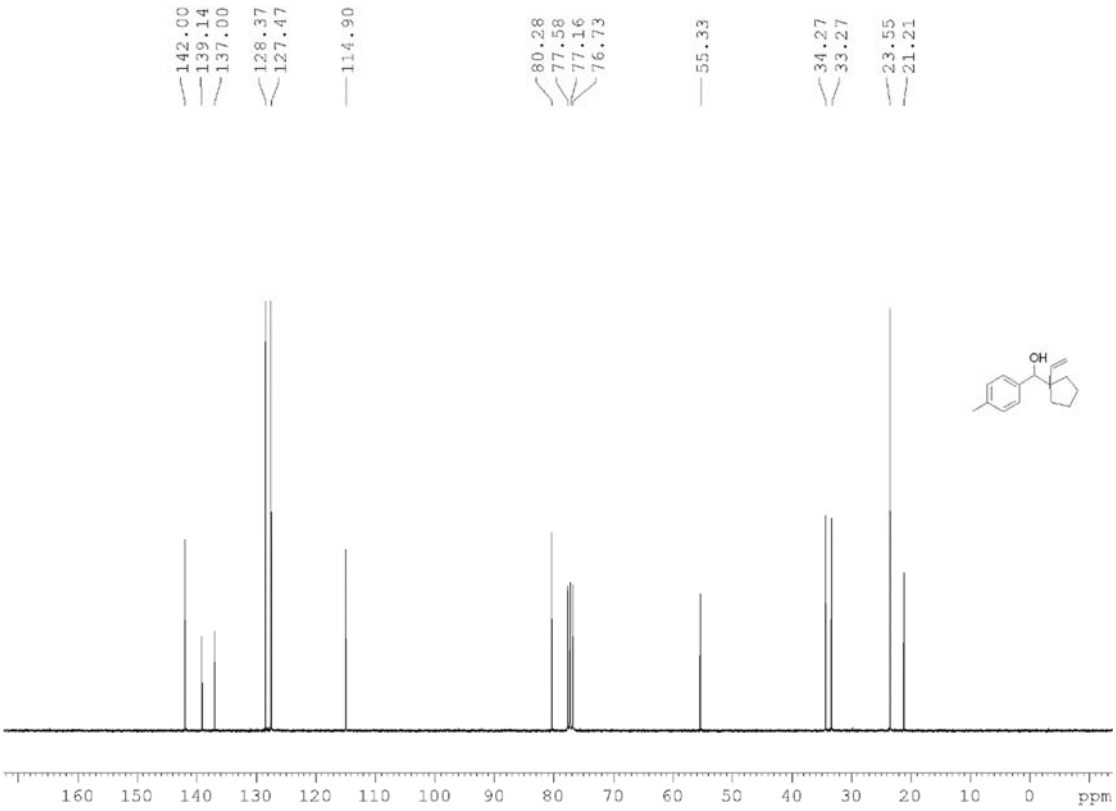


Compound 6e

^{1}H NMR (300 MHz, $CDCl_3$)

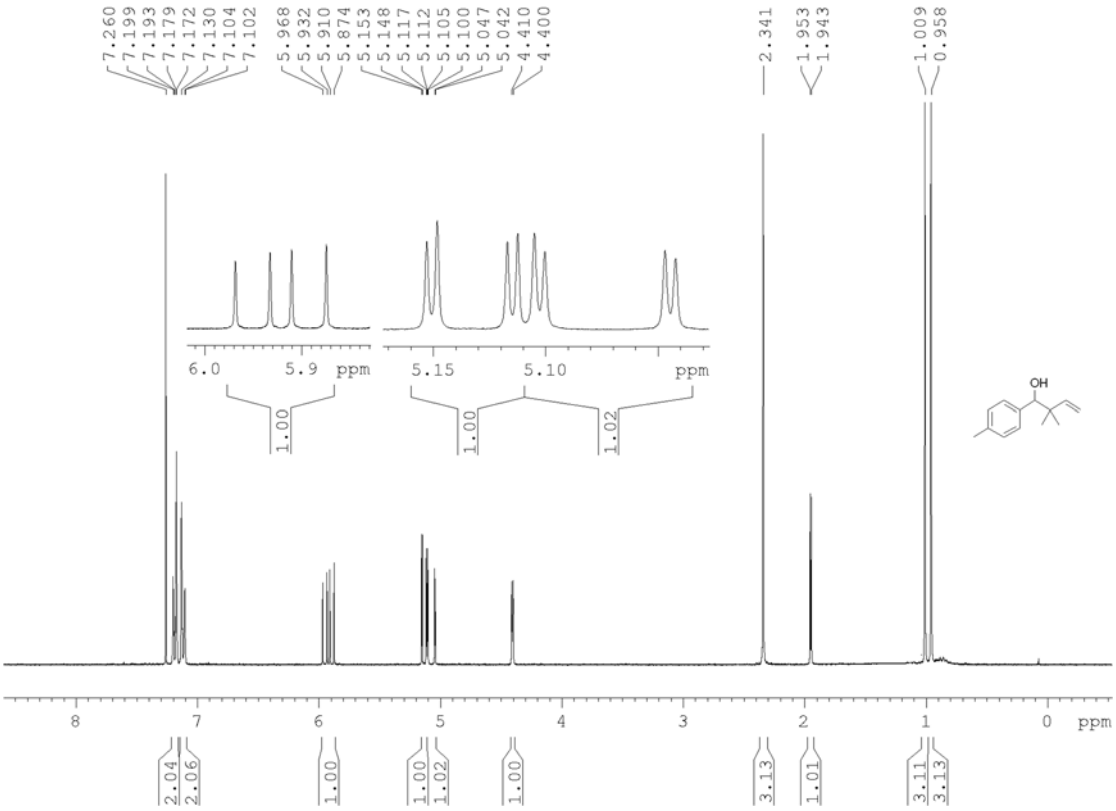


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



Compound 6g

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)