Supporting information

Pd-Catalysed Cross-Coupling of Allenylic Carbonates with *gem*-Diborylalkanes: Efficient Synthesis of Isoprenylboronates

Xin-Ru Ma, Qian-Cheng Zhang, Hua-Xing Hu, Ma-Hong Yu, Qin Zhong* and Jian Zhao*

Department of Chemical Engineering, School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China.

Email: zq304@njust.edu.cn; jzhao@njust.edu.cn

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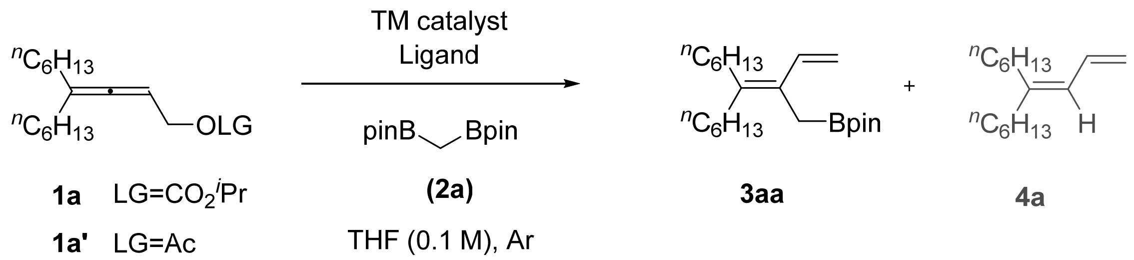
General Information. ^1H NMR and ^{13}C NMR spectra were recorded on BRUKER AVANCE III (500 MHz) spectrometers. ^1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d =doublet, t = triplet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on BRUKER AVANCE III (126 MHz) spectrometers with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77.0 ppm. High resolution mass spectra (HRMS) were obtained on a BRUKER autoflex maX MALDI-TOF(TOF) instrument. Column chromatography and filtration via silica plug were carried out employing silica gel (Qingdao Haiyang Chem, neutral, 300-400 Mesh). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

Materials. Unless otherwise noted, commercially available chemicals were used as received. The structures of all products were determined by ^1H, ^{13}C NMR, and HRMS.

Experimental Procedures and Spectral Data

1. Table S1. Detailed optimization of reaction conditions[a]



Entry	TM catalyst (2.5 mol%)	Ligand (10 mol%)	Conversion of **1a** /%[b]	Yield of **3aa** /%[b]	Yield of **4a** /%[b]
1	Pd(PPh$_3$)$_4$[c]	-	100	74	25
2	Pd$_2$dba$_3$	PPh$_3$	48	39	3
3	Pd$_2$dba$_3$	P(C$_6$H$_4$-*p*-OMe)$_3$	91	44	9
4	Pd$_2$dba$_3$	TFP	100	54	12
5	Pd$_2$dba$_3$	PCy$_3$	47	33	1
6	Pd$_2$dba$_3$	P(Cy)Ph$_2$	100	81 (80)[d]	4
7	Pd$_2$dba$_3$	xantphos	24	trace	13
8	Pd$_2$dba$_3$	dppe	41	trace	19
9	Pd$_2$dba$_3$	binap	16	trace	9
10	Pd$_2$dba$_3$	dppbz	0	0	0
11	Pd$_2$dba$_3$	P(OEt)$_3$	88	20	7
12	Pd$_2$dba$_3$	Dibenzyl *N,N*-diisopropylphosphoramidite	73	6	3
13[e]	Pd$_2$dba$_3$	P(Cy)Ph$_2$	56	40	0
14[f]	Pd$_2$dba$_3$	P(Cy)Ph$_2$	74	62	1
15[g]	Pd$_2$dba$_3$	P(Cy)Ph$_2$	15	0	0
16	NiI$_2$[c]	P(Cy)Ph$_2$	<5	0	0
17	ICyCuCl[c]	-	16	0	0
18	CuI[c]	P(Cy)Ph$_2$	0	0	0
19	Pd$_2$dba$_3$	-	5	0	0
20	-	P(Cy)Ph$_2$	0	0	0

[a] General reaction condition: a mixture of **1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 equiv), TM catalyst (2.5 mol%) and Ligand (10 mol%) in THF (0.1 M, 2 mL) was reacted at 50 °C for 24 h under Ar. [b] The conversion of **1a** and yields of **3aa**/**4a** were determined by crude ^{1}H NMR spectrum with naphthalene as an internal standard. [c] 5 mol% of TM catalyst was used. [d] The yield of isolated **3aa** is given in parentheses. [e] Reacted at 40 °C. [f] Reacted for 12 h. [g] Allenyl acetate (**1a'**) was used in the reaction. TFP = tri(2-furyl)phosphine. xantphos= 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene. dppe = 1,2-bis(diphenylphosphino)ethane. binap= 2,2'-Bis-(diphenylphosphino)-1,1'-binaphthyl. dppbz = 1,2-bis(diphenylphosphino)benzene. ICyCuCl = chloro[1,3 - bis(2,6 - diisopropylphenyl)imidazol - 2 - ylidene]copper(I).

2. General procedure for the synthesis of isoprenylboronates with unsubstituted *gem*-diborylalkanes

General method A (Synthesis of **3aa, 3ba, 3ca, 3da, 3ea, 3fa, 3ga**)

An oven-dried Schlenk flask was equipped with a Teflon coated stirrer bar and charged with Pd_2dba_3 (4.6 mg, 0.005 mmol, 2.5 mol%), $P(Cy)Ph_2$ (5.4 mg, 0.02 mmol, 10 mol%), bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane **2a** (107.2 mg, 0.40 mmol, 2 equiv.), and THF (1 mL) under Ar atmosphere. The resulted solution was stirred for 10 min, then a THF solution (1 mL) of corresponding **1** (0.2 mmol, 1 equiv.) was added to the reaction mixture via syringe. The final reaction mixture was stirred at 50 °C for 24 hours. Completion of the reaction was checked by TLC. After a complete conversion of **1**, the reaction mixture was diluted by petroleum ether (about 5 mL). The precipitate was filtered off by a short silica pad (Qingdao Haiyang Chem, neutral, 300-400 Mesh, about 2-3 cm in pipette) using EtOAc/petroleum ether (1:10 v/v) as an eluent. The solvent was removed and the residue was purified by a rapid silica gel chromatography (typically within 10 min) using a mixture of EtOAc/petroleum ether (1:500-1:50 v/v) as eluent affording pure product **3**.

Please note:

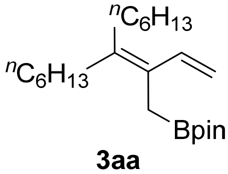
For the case of isoprenylboronates **3fa** and **3ga**, 5 mol% of Pd_2dba_3 (9.2 mg, 0.01 mmol) and 20 mol% of $P(Cy)Ph_2$ (10.7 mg, 0.04 mmol) were used. The crude reaction mixtures were directly oxidized to the corresponding alcohols (**3fa-OH** or **3ga-OH**) using the following procedure: The crude reaction mixture was dissolved in a 1:1 mixture of THF and H_2O and charged with $NaBO_3{\cdot}4H_2O$ (3 equiv.). The resulting heterogeneous mixture was allowed to stir vigorously at ambient temperature for 3 hours and then quenched by the addition of petroleum ether. The aqueous layer was extracted three times with petroleum ether and the combined organic extracts were dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification by silica gel chromatography using a mixture of EtOAc/petroleum ether (1:100-1:10 v/v) yielded the alcohol.

General method B (Synthesis of **3ha**)

An oven-dried Schlenk flask was equipped with a Teflon coated stirrer bar and charged with $Pd(PPh_3)_4$ (23.1mg, 0.02 mmol, 10 mol%), bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane **2a** (107.2 mg, 0.40 mmol, 2 equiv.), and THF (0.5 mL) under Ar atmosphere. The resulted solution was stirred for 10 min, then a THF solution (0.5 mL) of **1h** (0.2 mmol, 1 equiv.) was added to the reaction mixture via syringe. The final reaction mixture was stirred at 50 °C for 24 hours. Completion of the reaction was checked by TLC. After a complete conversion of **1h**, the reaction mixture was diluted by petroleum ether (about 5 mL). The precipitate was filtered off by a short silica pad (Qingdao Haiyang Chem, neutral, 300-400 Mesh, about 2-3 cm in pipette) using EtOAc/petroleum ether (1:10 v/v) as an eluent. The solvent was removed and the residue was purified by a rapid silica gel chromatography (typically within 10 min) using a mixture of EtOAc/petroleum ether (1:500-1:50 v/v) as eluent affording pure product **3ha**.

Analytical data:

2-(3-Hexyl-2-vinylnon-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3aa)

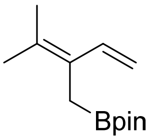


3aa

This product was prepared according to the above general method A.

Colorless oil (58.4 mg, 80%). R_f = 0.65 (EA/PE = 1:20 v/v). NMR data: ^1H NMR (500 MHz, $CDCl_3$) δ 6.82 (dd, *J* = 17.2, 10.9 Hz, 1H), 5.05 (d, *J* = 17.1 Hz, 1H), 4.93 (d, *J* = 10.9 Hz, 1H), 2.17 (t, *J* = 7.2 Hz, 2H), 2.06 (t, *J* = 7.2 Hz, 2H), 1.85 (s, 2H), 1.41–1.33 (m, 4H), 1.33–1.22 (m,12H), 1.20 (s, 12H), 0.87 (app. t, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0, 135.9, 127.7, 110.9, 82.9, 34.2, 32.3, 31.8(9), 31.8(1), 29.7, 29.5, 29.4, 28.5, 24.6, 22.6(7), 22.6(3), 14.1 (C×2); Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z $[M+H]^+$ calcd. for $[C_{23}H_{44}BO_2]^+$ 363.34289, found 363.34158.

2-(3-Methyl-2-vinylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ba)

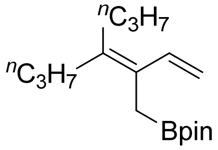


3ba

This product was prepared according to the above general method A.

Colorless oil (16.9 mg, 38%). R_f = 0.76 (EA/PE = 1:20 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (dd, *J* = 17.2, 10.9 Hz, 1H), 5.05 (d, *J* = 17.1 Hz, 1H), 4.93 (d, *J* = 10.9 Hz, 1H), 1.85 (s, 2H), 1.84 (s, 3H), 1.77 (s, 3H), 1.21 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.8, 130.4, 127.7, 110.7, 82.9, 24.6, 22.1, 20.3; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z $[M+H]^+$ calcd. for $[C_{13}H_{24}BO_2]^+$ 223.18639, found 223.18506.

2-(3-Propyl-2-vinylhex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ca)

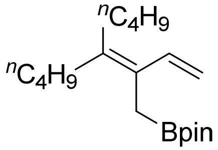


3ca

This product was prepared according to the above general method A.

Colorless oil (35.6 mg, 64%). R_f = 0.72 (EA/PE = 1:20 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (dd, *J* = 17.2, 10.9 Hz, 1H), 5.06 (d, *J* = 17.2 Hz, 1H), 4.93 (d, *J* = 10.9 Hz, 1H), 2.16 (t, *J* = 7.8 Hz, 2H), 2.06 (t, *J* = 7.8 Hz, 2H), 1.86 (s, 2H), 1.46-1.34 (m, 4H), 1.19 (s, 12H), 0.94-0.84 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.5, 135.9, 128.1, 111.0, 82.9, 36.2, 34.3, 24.6, 22.7, 21.6, 14.4, 14.1;Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{17}H_{31}BO_2Na]^+$ 301.23093, found 301.23062.

2-(3-Butyl-2-vinylhept-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3da)

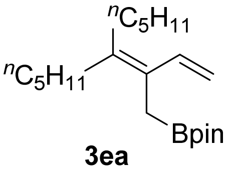


3da

This product was prepared according to the above general method A.

Colorless oil (47.8 mg, 78%). R_f = 0.70 (EA/PE = 1:20 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (dd, *J* = 17.2, 10.9 Hz, 1H), 5.06 (dd, *J* = 17.1, 0.9 Hz, 1H), 4.93 (dd, *J* = 10.9, 1.0 Hz, 1H), 2.18 (t, *J* = 7.1 Hz, 2H), 2.08 (t, *J* = 7.0 Hz, 2H), 1.85 (s, 2H), 1.40-1.26 (m, 8H), 1.20 (s, 12H), 0.90 (t, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H);^{13}C NMR (126 MHz, $CDCl_3$) δ 139.9, 135.9, 127.7, 110.9, 82.9, 33.9, 32.0, 31.8, 30.7, 24.6, 23.1, 22.8, 14.0(7), 14.0(1); Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{19}H_{35}BO_2Na]^+$ 329.26223, found 329.26205.

2-(3-Pentyl-2-vinyloct-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ea)

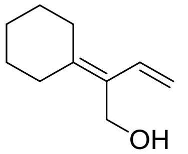


3ea

This product was prepared according to the above general method A.

Colorless oil (46.2 mg, 83%). R_f = 0.65 (EA/PE = 1:20 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (dd, *J* = 16.8, 10.9 Hz, 1H), 5.05 (d, *J* = 17.1 Hz, 1H), 4.92 (d, *J* = 10.8 Hz, 1H), 2.17 (t, *J* = 7.1 Hz, 2H), 2.06 (t, *J* = 7.3 Hz, 2H), 1.85 (s, 2H), 1.44-1.34 (m, 4H), 1.34-1.23 (m, 8H), 1.19 (s, 12H), 0.92-0.82 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0, 135.9, 127.7, 110.9, 82.9, 34.1, 32.3, 32.2, 31.9, 29.2, 28.2, 24.6, 22.6(9), 22.6(2), 14.0(8), 14.0(7);Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{21}H_{39}BO_2Na]^+$ 357.29353, found 357.29294.

2-Cyclohexylidenebut-3-en-1-ol (3fa-OH)

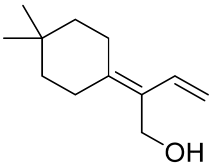


3fa-OH

This product was prepared according to the above general method A.

Colorless oil (16.1 mg, 53%). R_f = 0.25 (EA/PE = 1:10 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.35 (d, *J* = 17.4 Hz, 1H), 5.10 (d, *J* = 11.2 Hz, 1H), 4.39 (s, 2H), 2.39-2.33 (m, 4H), 1.64-1.55 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 133.2, 128.0, 112.6, 57.9, 31.5, 30.4, 28.6, 28.1, 26.7. HRMS (ESI): m/z $[M-(H_2O)+H]^+$ calcd. for $[C_{10}H_{15}]^+$ 135.11683, found 135.11659.

2-(4,4-Dimethylcyclohexylidene)but-3-en-1-ol (3ga-OH)

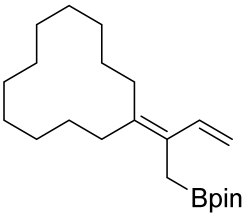


3ga-OH

This product was prepared according to the above general method A.

Colorless oil (18 mg, 50%). R_f = 0.25 (EA/PE = 1:10 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.34 (d, *J* = 17.5 Hz, 1H), 5.10 (d, *J* = 11.1 Hz, 1H), 4.38 (s, 2H), 2.41-2.32 (m, 4H), 1.60-1.54 (m, 1H), 1.43-1.34 (m, 4H), 0.96 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 133.2, 128.1, 112.6, 58.0, 40.9, 40.4, 30.3, 28.1, 27.1, 26.0. HRMS (ESI): m/z calcd. for $[C_{12}H_{20}ONa]^+$ 203.14064, found 203.14026.

2-(2-Cyclododecylidenebut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ha)



3ha

This product was prepared according to the above general method B.

Colorless oil (39.5 mg, 57%). R_f = 0.55 (EA/PE = 1:40 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (dd, *J* = 17.1, 10.9 Hz, 1H), 5.08 (dd, *J* = 17.2, 0.9 Hz, 1H), 4.94 (dd, *J* = 10.9, 0.9 Hz, 1H), 2.21 (t, *J* = 7.5 Hz, 2H), 2.12 (t, *J* = 7.6 Hz, 2H), 1.88 (s, 2H), 1.53-1.44 (m, 4H), 1.44-1.37 (m, 8H), 1.37-1.29 (m, 6H), 1.20 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.6, 136.0, 128.4, 111.2, 82.9, 29.4, 27.6, 25.9, 25.7(7), 25.7(4), 24.6, 23.8, 23.2, 22.2, 22.1, 22.0(5), 22.0(3); Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{22}H_{39}BO_2Na]^+$ 369.29353, found 369.29285.

3. General procedure for the synthesis of isoprenylboronates with substituted *gem*-diborylalkanes

General method C (Synthesis of isoprenylboronates **3ab-3ag, 3ai-3aj**)

An oven-dried Schlenk flask was equipped with a Teflon coated stirrer bar and charged with Pd_2dba_3 (9.2 mg, 0.01 mmol, 5 mol%), $P(Cy)Ph_2$ (10.7 mg, 0.04 mmol, 20 mol%), corresponding substituted *gem*-diborylalkane **2** (0.40 mmol, 2 equiv.), KOH (2 M, 0.2 mL, 2 equiv.) and THF (1 mL) under Ar atmosphere. The resulted solution was stirred for 10 min, then a THF solution (1 mL) of **1a** (64.9 mg, 0.2 mmol, 1 equiv.) was added to the reaction mixture via syringe. The final reaction mixture was stirred at room temperature for 24 hours. Completion of the reaction was checked by TLC and/or crude ^{1}H NMR spectrum. After a complete conversion of **1a**, the reaction mixture was diluted by petroleum ether (about 5 mL). The precipitate was filtered off by a short silica pad (Qingdao Haiyang Chem, neutral, 300-400 Mesh, about 2-3 cm in pipette) using EtOAc/petroleum ether (1:10 v/v) as an eluent. The solvent was removed and the residue was purified by a rapid silica gel chromatography (within 10 min) using a mixture of EtOAc/petroleum ether (1:500-1:50 v/v) as eluent affording pure product **3**.

Please note:

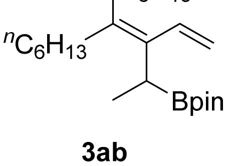
For the case of isoprenylboronates **3ac**, **3af** and **3aj**, the crude reaction mixtures were further oxidized to the corresponding alcohols using the following procedure: The crude reaction mixture was dissolved in a 1:1 mixture of THF and H_2O and charged with $NaBO_3{\cdot}4H_2O$ (3 equiv.). The resulting heterogeneous mixture was allowed to stir vigorously at ambient temperature for 3 hours and then quenched by the addition of petroleum ether. The aqueous layer was extracted three times with petroleum ether and the combined organic extracts were dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification by silica gel chromatography using a mixture of EtOAc/petroleum ether (1:100-1:10 v/v) as eluent afforded pure alcohol.

General method D (Synthesis of isoprenylboronates **3ah**)

An oven-dried Schlenk flask was equipped with a Teflon coated stirrer bar and charged with $Pd(PPh_3)_4$ (23.1mg, 0.02 mmol, 10 mol%), *gem*-Diborylalkane **2h** (0.40 mmol, 2 equiv.), KOH (2 M, 0.2 mL, 2 equiv.) and THF (0.5 mL) under Ar atmosphere. The resulted solution was stirred for 10 min, then a THF solution (0.5 mL) of **1a** (64.9 mg, 0.2 mmol, 1 equiv.) was added to the reaction mixture via syringe. The final reaction mixture was stirred at room temperature for 24 hours. Completion of the reaction was checked by TLC and/or crude ^{1}H NMR spectrum. After a complete conversion of **1a**, the reaction mixture was diluted by petroleum ether (about 5 mL). The precipitate was filtered off by a short silica pad (Qingdao Haiyang Chem, neutral, 300-400 Mesh, about 2-3 cm in pipette) using EtOAc/petroleum ether (1:10 v/v) as an eluent. The solvent was removed and the residue was purified by a rapid silica gel chromatography (within 10 min) using a mixture of EtOAc/petroleum ether (1:500-1:50 v/v) as eluent affording pure product **3ah.**

Analytical data:

2-(4-Hexyl-3-vinyldec-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ab)

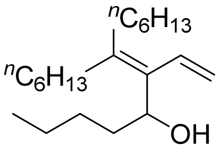


3ab

This product was prepared according to the above general method C.

Colorless oil (56.5 mg, 75%). R_f = 0.70 (EA/PE = 1:20 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.60 (dd, *J* = 17.5, 11.2 Hz, 1H), 5.04 (d, *J* = 17.5 Hz, 1H), 4.94 (d, *J* = 11.2 Hz, 1H), 2.31-2.21 (m, 2H), 2.15-2.06 (m, 1H), 2.06-1.95 (m, 2H), 1.45-1.24 (m, 16H), 1.22 (s, 6H), 1.21 (s, 6H), 1.12 (d, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 6.4 Hz, 3H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 134.9, 134.6, 111.6, 82.9, 34.1, 32.6, 31.8(6), 31.8(1), 29.8, 29.5, 29.4, 28.9, 24.7(5), 24.7(2), 22.6(7), 22.6(3), 15.6, 14.0(9), 14.0(8); Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. For $[C_{24}H_{45}BO_2Na]^+$ 399.34048, found 399.33960.

7-Hexyl-6-vinyltridec-6-en-5-ol (3ac-OH)

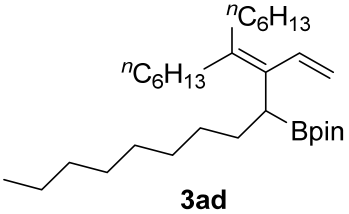


3ac-OH

This product was prepared according to the above general method C.

Colorless oil (54.2 mg, 82%). R_f = 0.25 (EA/PE = 1:10 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.36 (dd, *J* = 17.9, 11.7 Hz, 1H), 5.32 (d, *J* = 17.9 Hz, 1H), 5.19 (d, *J* = 11.7 Hz, 1H), 4.61 (t, *J* = 7.0 Hz, 1H), 2.19-2.00 (m, 4H), 1.79-1.67 (m, 1H), 1.43-1.17 (m, 21H), 0.96-0.80 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 134.1, 132.9, 116.7, 70.8, 35.6, 33.3, 32.3, 31.7(2), 31.7(1), 29.7, 29.5(5), 29.5(1), 29.0, 28.4, 22.6(9), 22.6(2), 22.6(1), 14.0 (C×3). HRMS (ESI): m/z $[M-(H_2O)+H]^+$ calcd. For $[C_{21}H_{39}]^+$ 291.30463, found 291.30411.

2-(7-Hexyl-8-vinylheptadec-7-en-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ad)

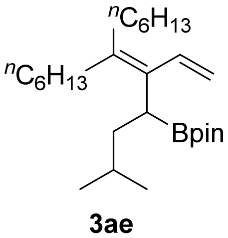


3ad

This product was prepared according to the above general method C.

Colorless oil (71.2 mg, 75%). R_f = 0.68 (EA/PE = 1:20 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.56 (dd, *J* = 17.5, 11.2 Hz, 1H), 5.07 (d, *J* = 17.5 Hz, 1H), 4.95 (d, *J* = 11.3 Hz, 1H), 2.33-2.23 (m, 1H), 2.22-2.12 (m, 2H), 2.06-1.90 (m, 2H), 1.48-1.24 (m, 22H), 1.24-1.21 (m, 8H), 1.20 (s, 6H), 1.19 (s, 6H), 0.92-0.83 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.3, 135.4, 132.9, 112.4, 82.8, 34.0, 32.8, 31.9(2), 31.9(0), 31.8, 30.0, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3(6), 29.3(4), 28.8, 24.7, 24.6, 22.7, 22.6(9), 22.6(3), 14.0 (C×3); Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. For $[C_{31}H_{59}BO_2Na]^+$ 497.45003, found 497.44955.

2-(6-Hexyl-2-methyl-5-vinyldodec-5-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ae)

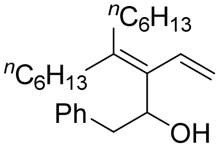


3ae

This product was prepared according to the above general method C.

Colorless oil (61.0 mg, 73%). R_f = 0.65 (EA/PE = 1:20 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.53 (dd, *J* = 17.5, 11.3 Hz, 1H), 5.09 (d, *J* = 17.6 Hz, 1H), 4.97 (d, *J* = 11.2 Hz, 1H), 2.34-2.22 (m, 2H), 2.22-2.13 (m, 1H), 2.06-1.90 (m, 2H), 1.56-1.45 (m, 3H), 1.45-1.34 (m, 4H), 1.34-1.22 (m, 12H), 1.20 (s, 6H), 1.18 (s, 6H), 0.91-0.86 (m, 6H), 0.84 (app. t, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 135.6, 133.2, 112.7, 82.7, 39.2, 33.9, 32.7, 31.8(7), 31.8(2), 29.8, 29.4(9), 29.4(5), 28.7, 27.0, 24.7, 24.6, 23.2, 22.6(9), 22.6(4), 22.6(2), 14.1(1), 14.1(0); Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. For $[C_{27}H_{51}BO_2Na]^+$ 441.38743, found 441.38654.

4-Hexyl-1-phenyl-3-vinyldec-3-en-2-ol (3af-OH)

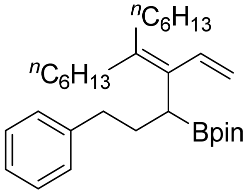


3af-OH

This product was prepared according to the above general method C.

Colorless oil (45.9 mg, 67%). R_f = 0.28 (EA/PE = 1:10 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 2H), 7.28-7.21 (m, 3H), 6.50 (dd, *J* = 17.9, 11.7 Hz, 1H), 5.53 (d, *J* = 17.9 Hz, 1H), 5.30 (d, *J* = 11.7 Hz, 1H), 4.88 (t, *J* = 7.2 Hz, 1H), 3.08 (dd, *J* = 13.4, 8.1 Hz, 1H), 2.95 (dd, *J* = 13.3, 5.9 Hz, 1H), 2.22-2.13 (m, 1H), 2.13-2.04 (m, 1H), 2.02-1.93 (m, 2H), 1.36-1.24 (m, 16H), 1.24-1.14 (m, 1H), 0.97-0.86 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 138.9, 132.8, 132.6, 129.3, 128.3, 126.2, 116.7, 72.2, 42.4, 33.4, 32.4, 31.7, 31.6, 29.7, 29.5, 29.1, 29.0, 22.6(2), 22.6(0), 14.0 (C × 3) . HRMS (ESI): m/z calcd. For $[C_{24}H_{38}Ona]^+$ 365.28149, found 365.28043.

2-(5-Hexyl-1-phenyl-4-vinylundec-4-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ag)

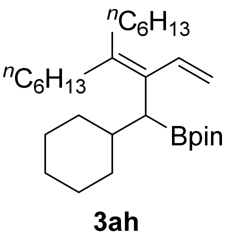


3ag

This product was prepared according to the above general method C.

Colorless oil (75.0 mg, 80%). R_f = 0.70 (EA/PE = 1:20 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2H), 7.17-7.11 (m, 3H), 6.59 (dd, *J* = 17.2, 11.4 Hz, 1H), 5.09 (d, *J* =17.6 Hz, 1H), 4.98 (d, *J* =11.3 Hz, 1H), 2.61-2.48 (m, 2H), 2.35-2.27 (m, 1H), 2.25 (t, *J* = 7.7 Hz, 1H), 2.12-1.96 (m, 3H), 1.95-1.85 (m, 1H), 1.79-1.68 (m, 1H), 1.42–1.22 (m, 16H), 1.21 (s, 12H), 0.88 (app. t, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 140.8, 135.2, 132.4, 128.5, 128.0, 125.3, 112.5, 82.9, 35.4, 34.0, 32.8, 32.1, 31.8(6), 31.8(2), 29.7, 29.6, 29.5, 28.8, 24.7(3), 24.7(0), 22.6(9), 22.6(2), 14.1(2), 14.1(0); Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z [M+H]$^+$ calcd. For $[C_{31}H_{51}BO_2]^+$ 467.40549, found 467.40430.

2-(1-Cyclohexyl-3-hexyl-2-vinylnon-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ah)



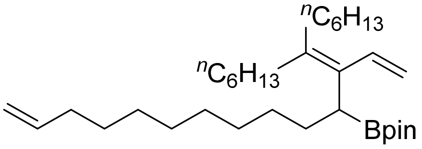
3ah

This product was prepared according to the above general method D.

Colorless oil (54.2 mg, 61%). R_f = 0.70 (EA/PE = 1:20 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.48 (dd, *J* = 17.6, 11.5 Hz, 1H), 5.19 (d, *J* = 17.6 Hz, 1H), 4.98 (d, *J* = 11.3 Hz, 1H), 2.25-2.11 (m, 2H), 2.11-1.94 (m, 3H), 1.90 (d, *J* = 12.0 Hz, 1H), 1.74-1.63 (m, 2H), 1.63-1.51 (m, 4H), 1.47-1.22 (m, 20H), 1.19 (s, 6H), 1.17

(s, 6H), 0.93-0.80 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 136.2, 131.4, 113.4, 82.6, 36.7, 34.4, 33.4, 33.0, 31.9(5), 31.9(0), 31.8, 29.7, 29.5(6), 29.5(0), 28.6, 26.8, 26.7, 26.6, 24.8, 24.4, 22.6(9), 22.6(3), 14.1(3), 14.1(0); Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. For $[C_{29}H_{53}BO_2Na]^+$ 467.40308, found 467.40268.

2-(7-Hexyl-8-vinylnonadeca-7,18-dien-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ai)

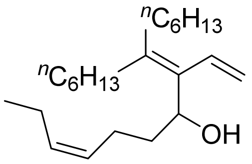


3ai

This product was prepared according to the above general method C.

Colorless oil (80.1 mg, 80%). R_f = 0.72 (EA/PE = 1:20 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.56 (dd, *J* = 17.5, 11.2 Hz, 1H), 5.85-5.75 (m, 1H), 5.07 (d, *J* = 17.5 Hz, 1H), 5.01-4.89(m, 3H), 2.33-2.23 (m, 1H), 2.23-2.11 (m, 2H), 2.06-1.99 (m, 2H), 1.99-1.90 (m, 2H), 1.73-1.61 (m, 1H), 1.50-1.40 (m, 1H), 1.40-1.21 (m, 28H), 1.20 (s, 6H), 1.19 (s, 6H), 0.91-0.84 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 139.2, 135.3, 132.8, 114.0, 112.3, 82.8, 34.1, 33.8, 32.8, 31.8(9), 31.8(4), 29.9, 29.8, 29.7, 29.6, 29.5, 29.4(9), 29.4(7), 29.3, 29.1, 28.9, 28.8, 24.7, 24.6, 22.7, 22.6, 14.1(2), 14.1(1). Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. For $[C_{33}H_{61}BO_2Na]^+$ 523.46568, found 523.46509.

(Z)-9-Hexyl-8-vinylpentadeca-3,8-dien-7-ol (3aj-OH)

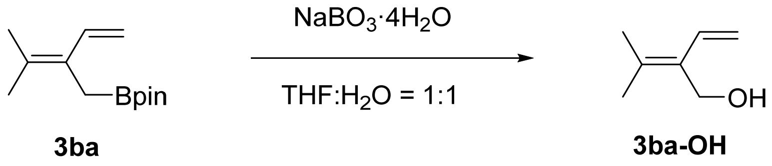


3aj-OH

This product was prepared according to the above general method C.

Colorless oil (40.1 mg, 60%). R_f = 0.25 (EA/PE = 1:10 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.37 (dd, *J* = 18.0, 11.8 Hz, 1H), 5.43-5.30 (m, 3H), 5.19 (d, *J* = 11.6 Hz, 1H), 4.63 (t, *J* = 7.7 Hz, 1H), 2.19-1.97 (m, 8H), 1.87-1.77 (m, 1H), 1.63-1.56 (m, 1H), 1.51-1.47 (m, 1H), 1.39-1.22 (m, 16H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.92-0.83 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 133.9, 132.8, 132.2, 128.5, 116.7, 70.2, 36.0, 33.3, 32.3, 31.7, 29.7, 29.5(5), 29.5(2), 29.1, 23.9, 22.6, 20.4, 14.3, 14.0 (C×2); Two carbons are missing due to overlapping signals. HRMS (ESI): m/z calcd. for $[C_{23}H_{42}ONa]^+$ 357.31279, found 357.31146.

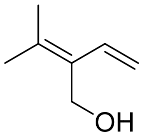
4. Synthesis of reported compound 3ba-OH



Compound **3ba-OH** was obtained by oxidation of isoprenylboronate **3ba**. Isoprenylboronate **3ba** (44.4 mg, 0.2 mmol) dissolved in a 1:1 mixture of THF (1 mL) and H_2O (1 mL) and charged with $NaBO_3{\cdot}4H_2O$ (92.3 mg, 3 equiv.). The resulting heterogeneous mixture was allowed to stir vigorously at ambient temperature for 3 hours and then quenched by the addition of petroleum ether. The aqueous layer was extracted three times with petroleum ether and the combined organic extracts were dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification by silica gel chromatography (EA/PE = 1:100-1:10 v/v) yielded the alcohol **3ba-OH** (20.2 mg, 90%). The products **3ba-OH** were confirmed by ^{1}H comparing with the reported literature[1].

Analytical data:

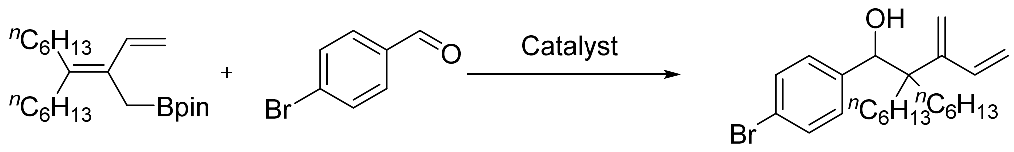
3-Methyl-2-vinylbut-2-en-1-ol (3ba-OH)



3ba-OH

Colorless oil. R_f = 0.30 (EA/PE = 1:10 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.71 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.31 (d, *J* = 17.5 Hz, 1H), 5.08 (d, *J* = 11.1 Hz, 1H), 4.38 (s, 2H), 1.90 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 133.6, 130.9, 112.0, 58.4, 21.3, 20.4. HRMS (ESI): m/z $[M-(H_2O)+H]^+$ calcd. for $[C_7H_{11}]^+$ 95.08553, found 95.08569.

5. Table S2. Detailed optimization for isoprenylboration with *p*-bromobenzaldehyde[a]



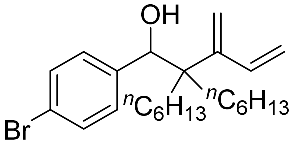
3aa **5**

Entry	Catalyst	Solvent	Temperature	Time	Conversion of **3aa** /%[b]	Yield of **5** /%[b]
1	-	toluene	rt	48h	70	50
2	$BF_3\cdot Et_2O$ (100 mol%)	DCM	-78 °C to rt	12h	100	0
3	Sc(OTf)$_3$ (20 mol%)	toluene	-78 °C to rt	18h	100	36
4	(NaphthO)$_2$P(O)OH (20 mol%)	toluene	-78 °C to rt	18h	75	64
5	C_6F_5COOH (20 mol%)	toluene	0 °C to rt	20h	100	74 (67)[c]

[a] General reaction condition: a mixture of **3aa** (0.2 mmol), *p*-bromobenzaldehyde (0.3 mmol, 1.5 equiv.) and catalyst in solvent (0.1 M, 2 mL) was reacted under Ar. [b] The conversions of **3aa** and yield of **5** were determined by crude ^{1}H NMR spectrum with naphthalene as an internal standard. [c] The yield of isolated **5** is given in parentheses. DCM = dichloromethane.

Procedure and Analytical data:

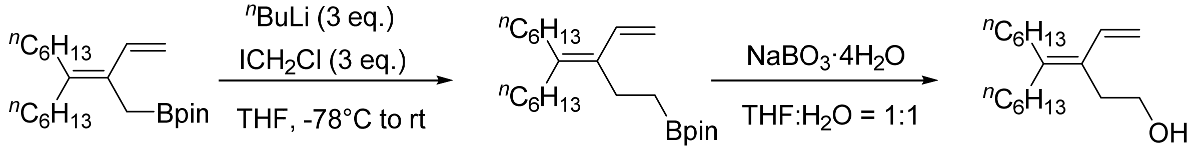
1-(4-Bromophenyl)-2-(buta-1,3-dien-2-yl)-2-hexyloctan-1-ol (5)



5

An oven-dried Schlenk flask was equipped with a Teflon coated stirrer bar and charged with pentafluorobenzoic acid (8.4 mg, 0.04 mmol, 0.2 equiv.), *p*-bromobenzaldehyde (55.5 mg, 0.30 mmol, 1.5 equiv.) and toluene (1 mL) under Ar atmosphere. The resulted solution was stirred for 10 min at 0 °C, then a toluene solution (1 mL) of **3aa** (72.4 mg, 0.2 mmol, 1 equiv.) was added to the reaction mixture via syringe. The final reaction mixture was stirred at room temperature for 20 hours. Completion of the reaction was checked by TLC and/or crude ^{1}H NMR spectrum. After a complete conversion of **3aa**, the reaction mixture was quenched with sat. NaHCO$_3$ (aq.) and extracted with EtOAc. The organic phase was dried over MgSO$_4$, filtered and evaporated under reduced pressure. Purification by silica gel chromatography (EA/PE = 1:100-1:10 v/v) yielded the compound **5** as a colorless oil (37.6 mg, 67%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.32 (dd, *J* = 16.9, 10.6 Hz, 1H), 5.40 (s, 1H), 5.38 (dd, *J* = 17.1, 1.8 Hz, 1H), 4.99 (dd, *J* = 10.6, 1.6 Hz, 1H), 4.69 (s, 1H), 4.61 (s, 1H), 2.05 (s, 1H), 1.62-1.52 (m, 2H), 1.32-1.19 (m, 18H), 0.91-0.85 (m, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 150.2, 140.3, 138.5, 130.4, 129.4, 121.1, 115.1, 114.3, 78.0, 49.3, 32.6, 31.8(3), 31.8(0), 31.7, 30.1, 29.6, 23.8, 23.7, 22.6(8), 22.6(4), 14.0 (C×2). HRMS (ESI): m/z calcd. for [C$_{24}$H$_{37}$BrONa]$^+$ 443.19200, found 443.19037.

6. Procedure for homologation



3aa **6**

To an oven-dried Schlenk flask was equipped with a Teflon coated stirrer bar, isoprenylboronate **3aa** (72.4 mg, 0.20 mmol, 1 equiv.), chloroiodomethane (106 mg, 0.60 mmol, 3 equiv.) and THF (2 mL) were added under Ar atmosphere. The reaction mixture was cooled to -78 °C and a solution of *n*-BuLi (0.37 mL, 0.60 mmol, 1.6 M in hexane) was slowly added at the same temperature. After stirring for 10 min, the reaction mixture was warmed to room temperature and additionally stirred for 12 hours. The reaction mixture was quenched with saturated aqueous NH_4Cl solution (10 mL) and extracted with CH_2Cl_2 (10 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Then, the crude reaction mixture was dissolved in a 1:1 mixture of THF (1 mL) and H_2O (1 mL) and charged with $NaBO_3·4H_2O$ (92.3 mg, 3 equiv.). The resulting heterogeneous mixture was allowed to stir vigorously at ambient temperature for 3 hours and then quenched by the addition of petroleum ether. The aqueous layer was extracted three times with petroleum ether and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude reaction mixture was purified by silica gel chromatography (EA/PE = 1:50-1:10 v/v) to give the alcohol **6** as a colorless oil (26.2 mg, 50 %).

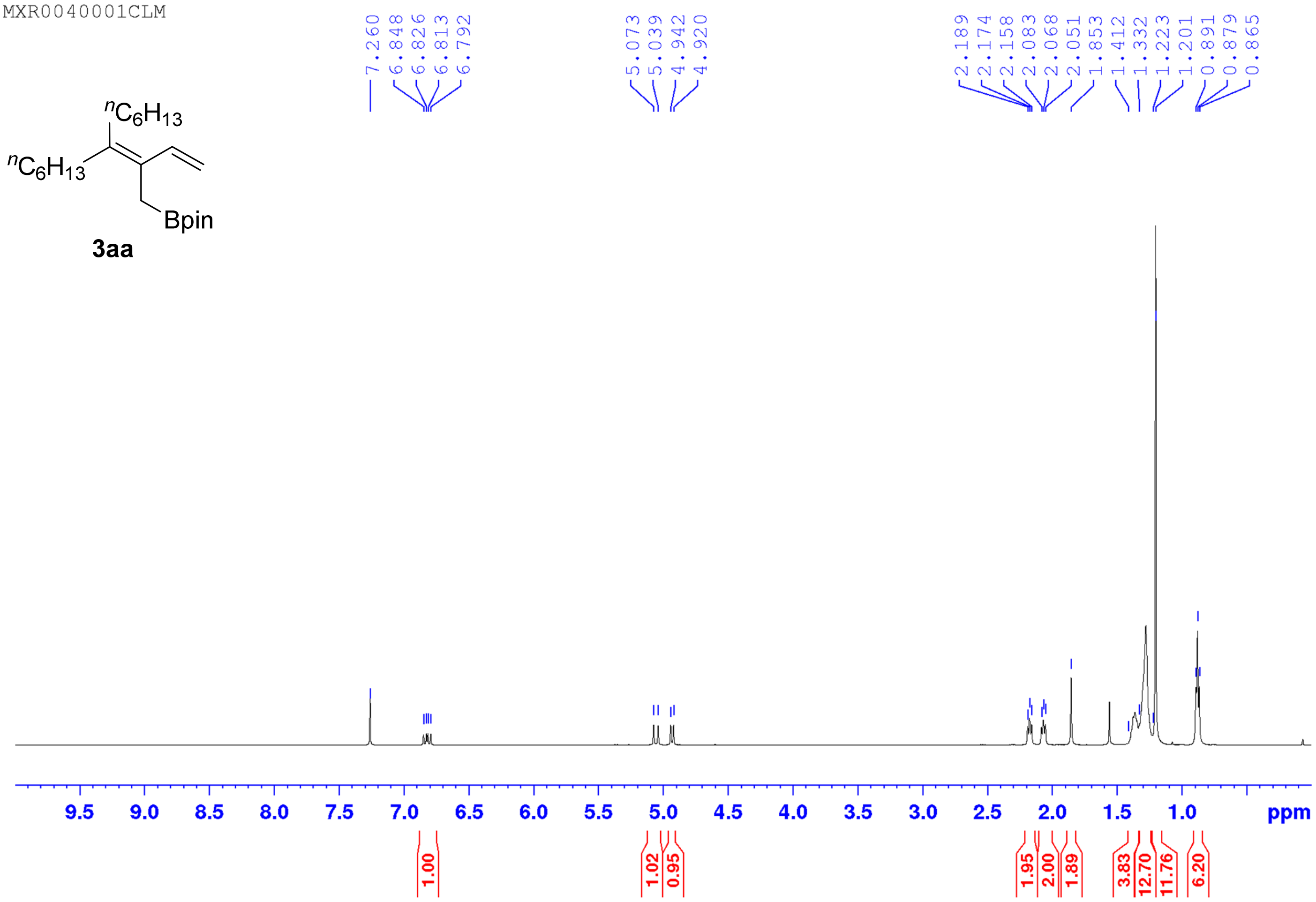
Analytical data:

4-hexyl-3-vinyldec-3-en-1-ol (6): R_f = 0.25 (EA/PE = 1:10 v/v) ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (dd, *J* = 17.4, 11.1 Hz, 1H), 5.17 (d, *J* = 17.4 Hz, 1H), 4.99 (d, *J* = 11.2 Hz, 1H), 3.63 (t, *J* = 7.2 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.18-2.09 (m, 4H), 1.40-1.33 (m, 4H), 1.33-1.23 (m, 12H), 0.92-0.84 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 134.5, 126.7, 111.5, 61.9, 33.6, 32.0, 31.7(8), 31.7(0), 30.6, 29.7, 29.6(6), 29.6(0), 28.9, 22.6(3), 22.6(2), 14.0(7), 14.0(6). HRMS (ESI): m/z $[M+H]^+$ calcd. for $[C_{18}H_{35}O]^+$ 267.26824, found 267.26685.

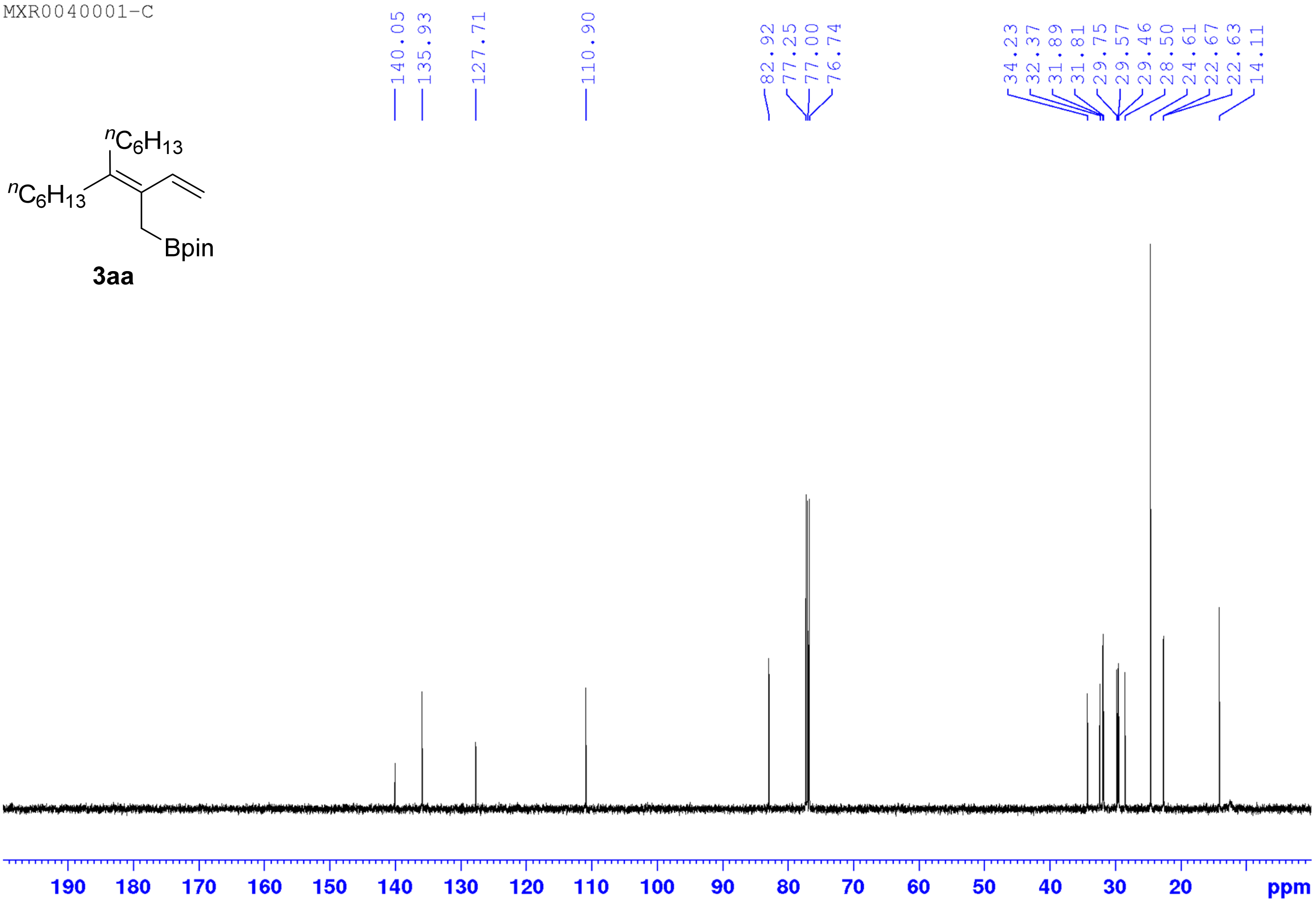
7. References:

1. G. Frater; J. Wenger. *Helv. Chim. Acta.* **1984**, *67*, 1702-1706.

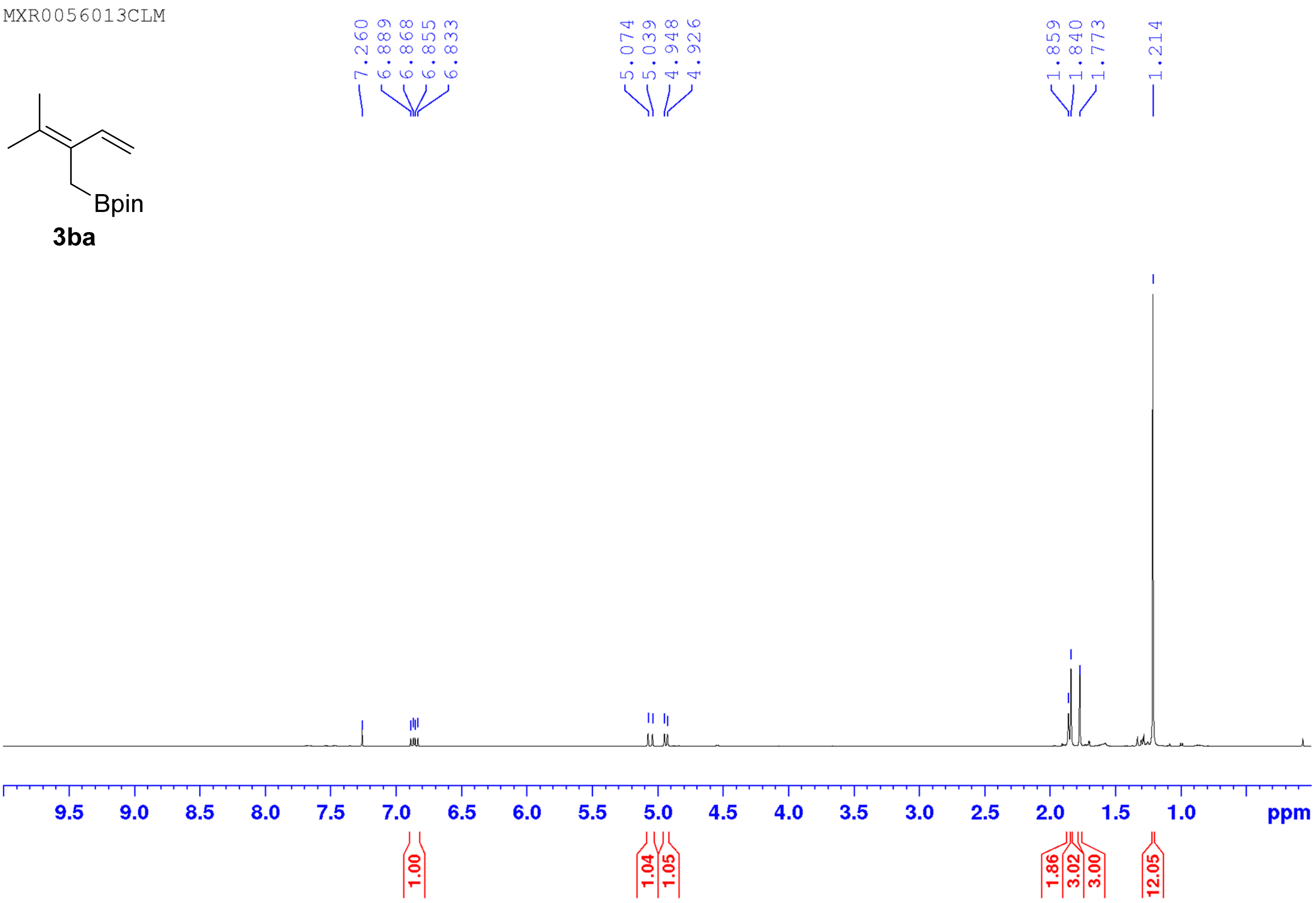
^{1}H and ^{13}C NMR Spectra of 3, 5 and 6



3aa



3aa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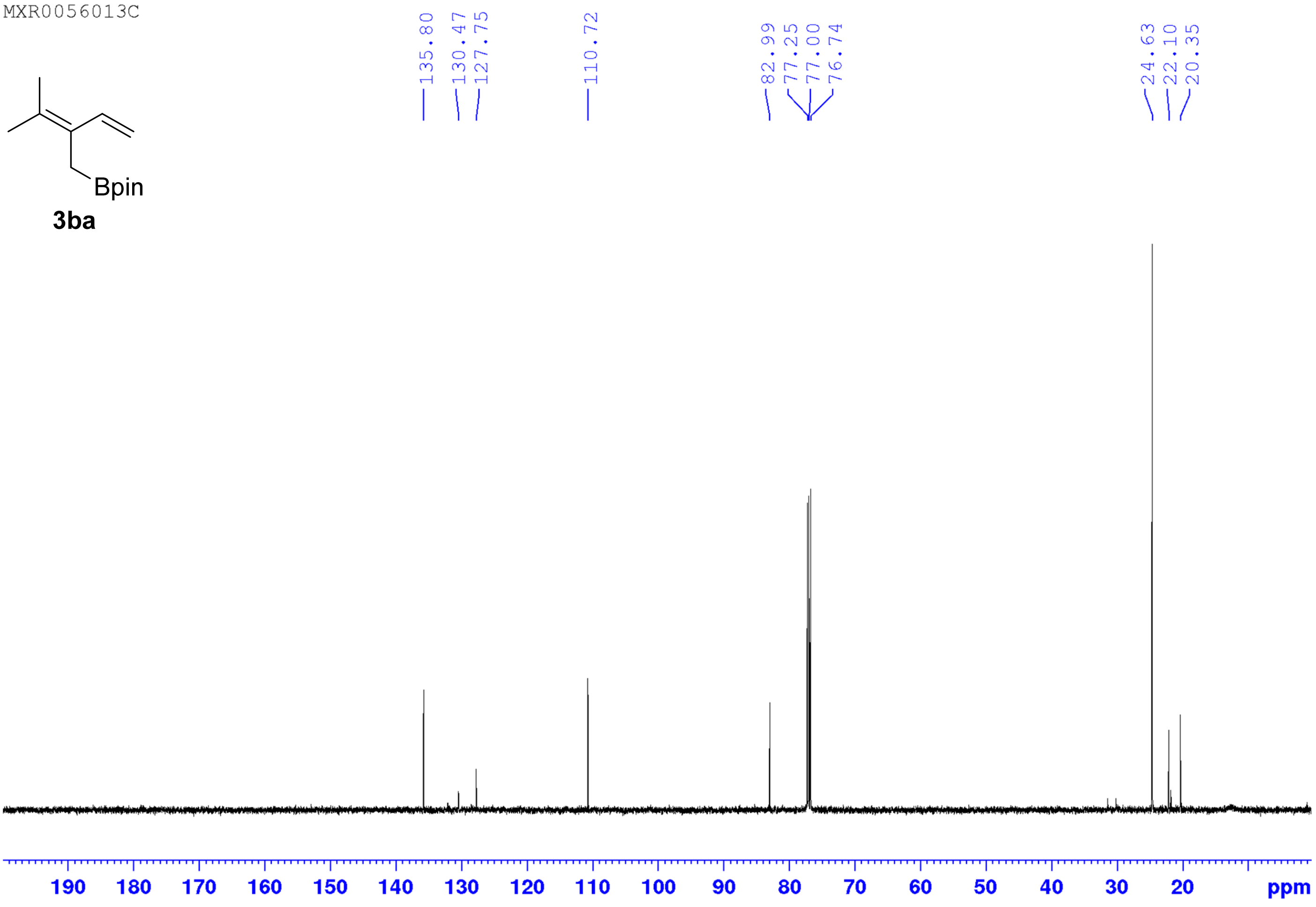
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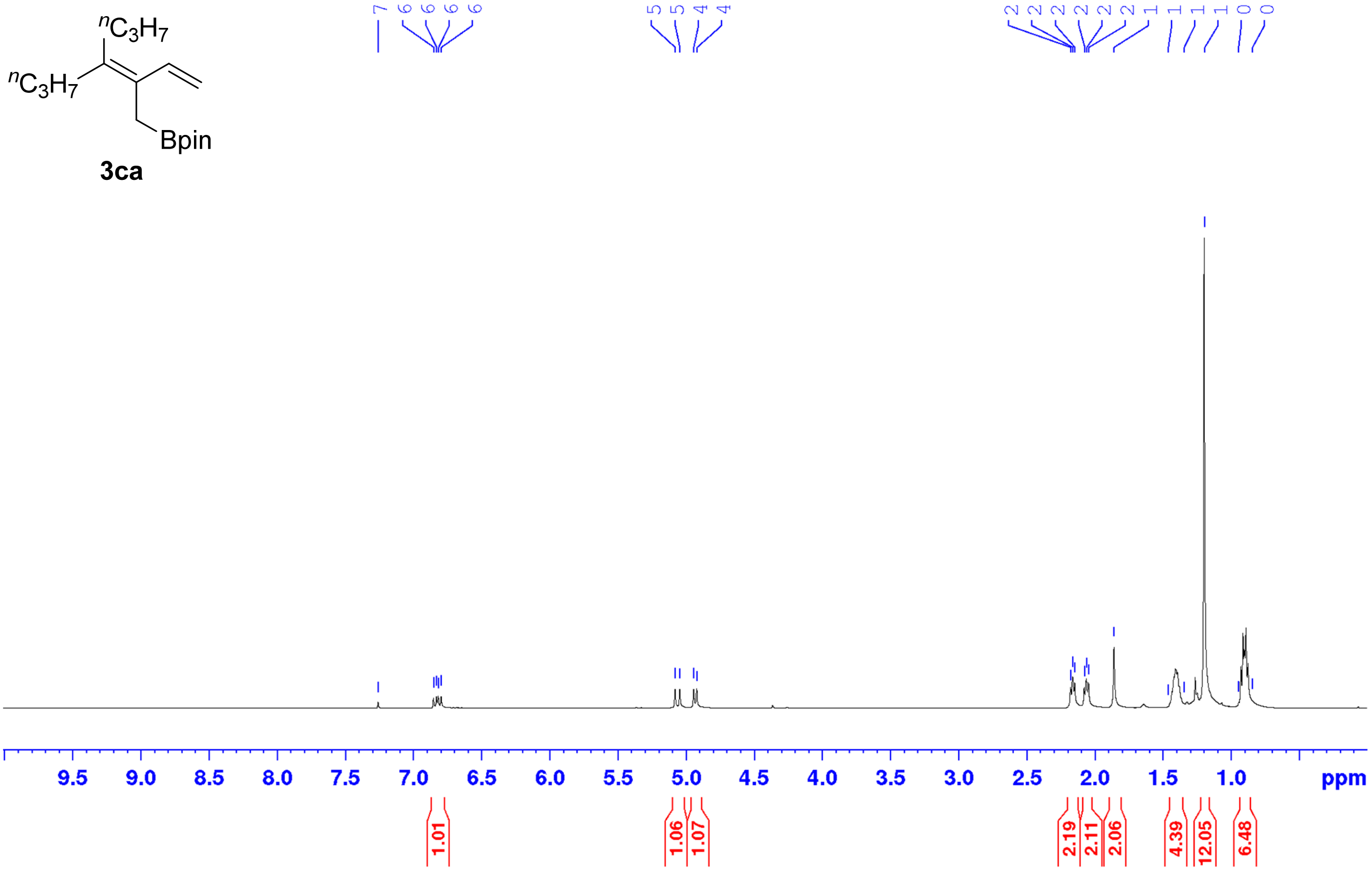
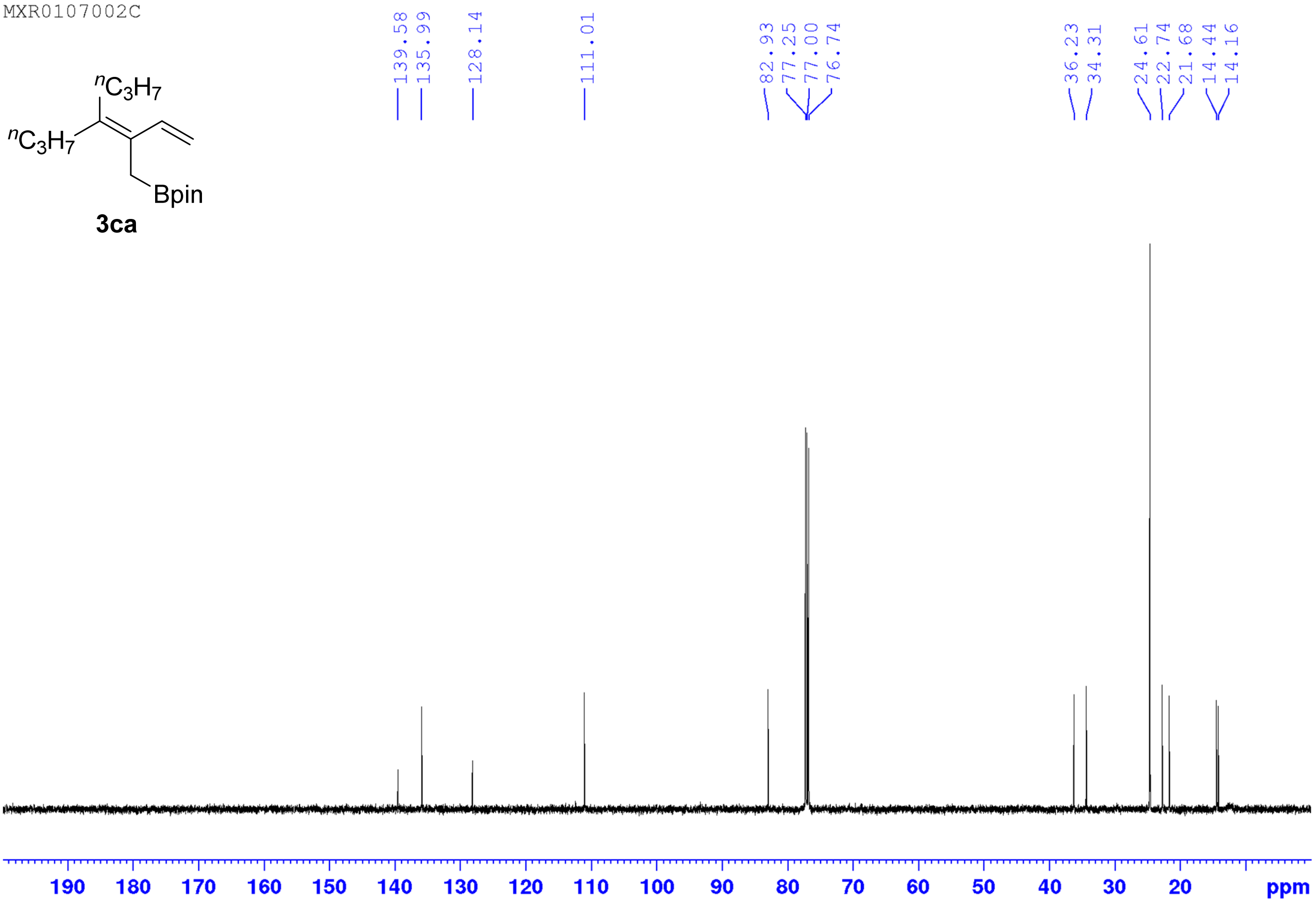


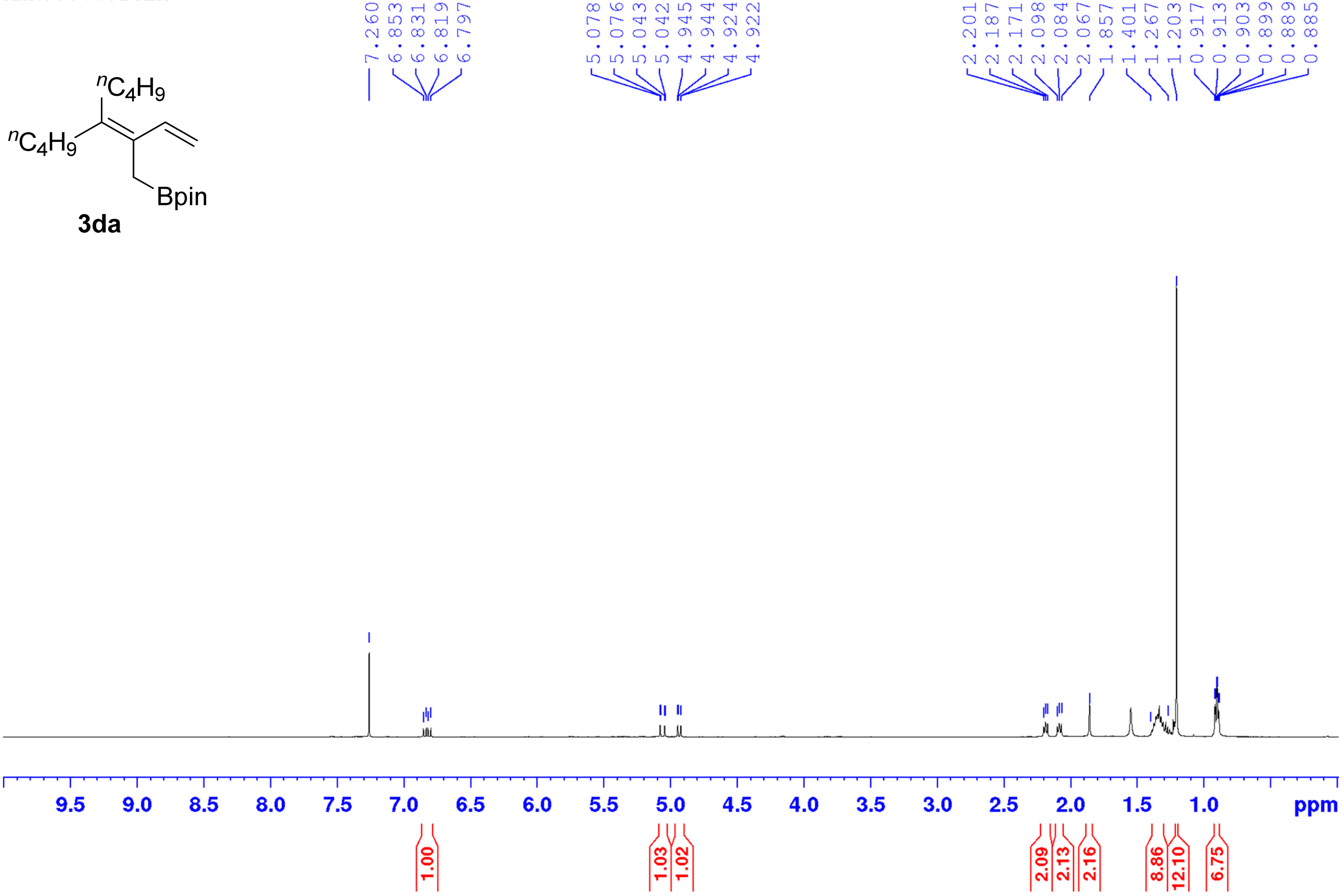
3ca

MXR0107002C

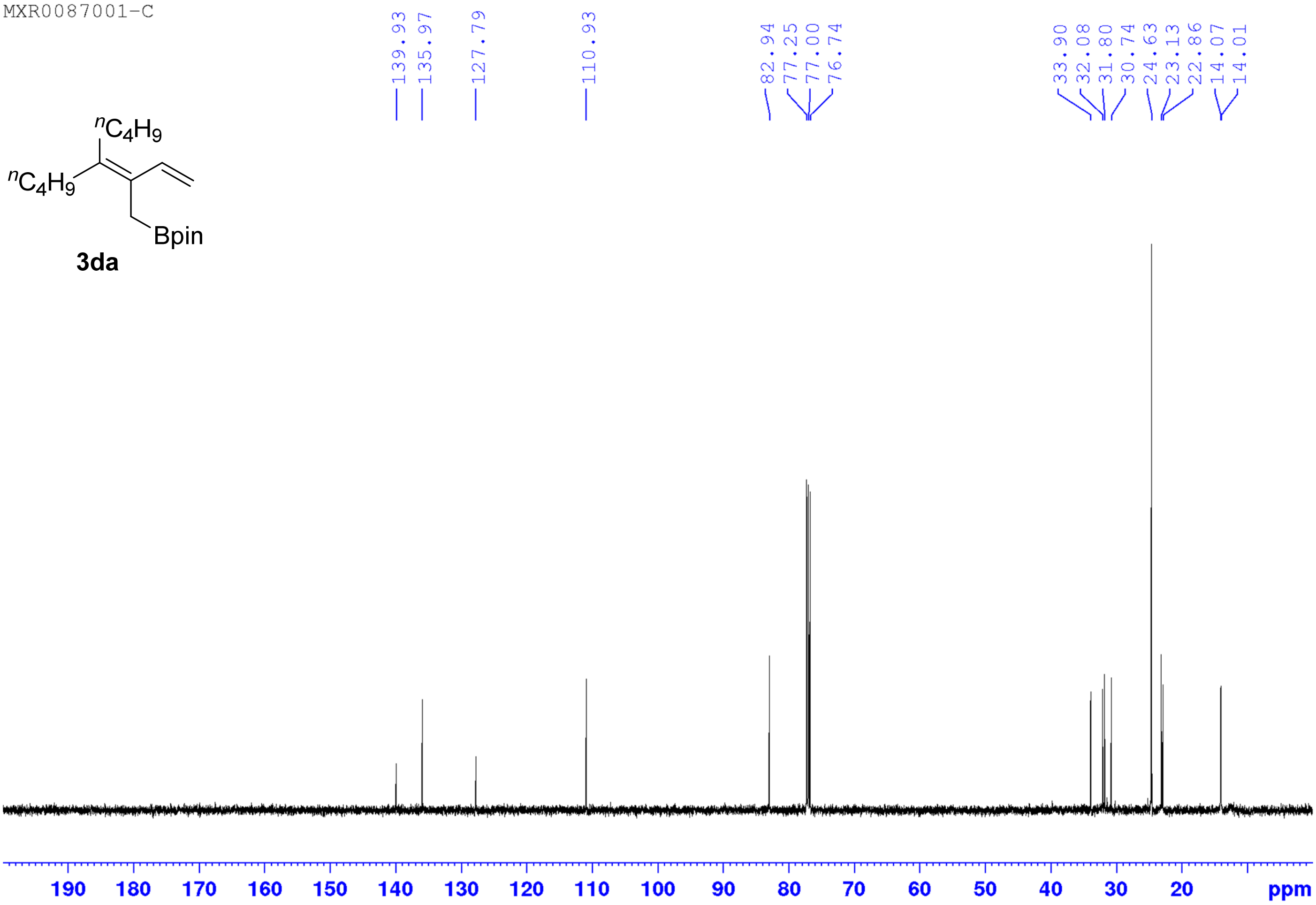


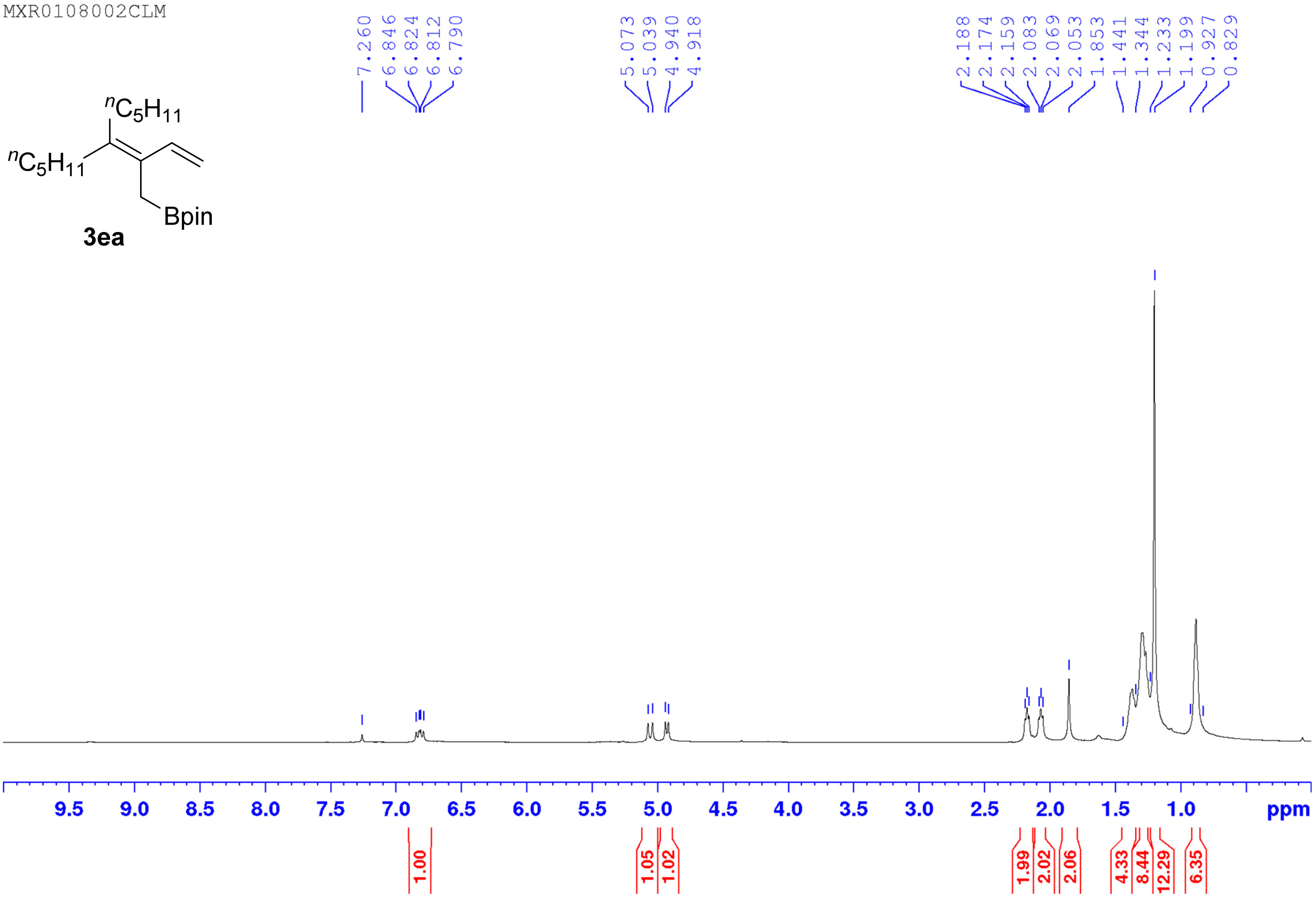
3ca

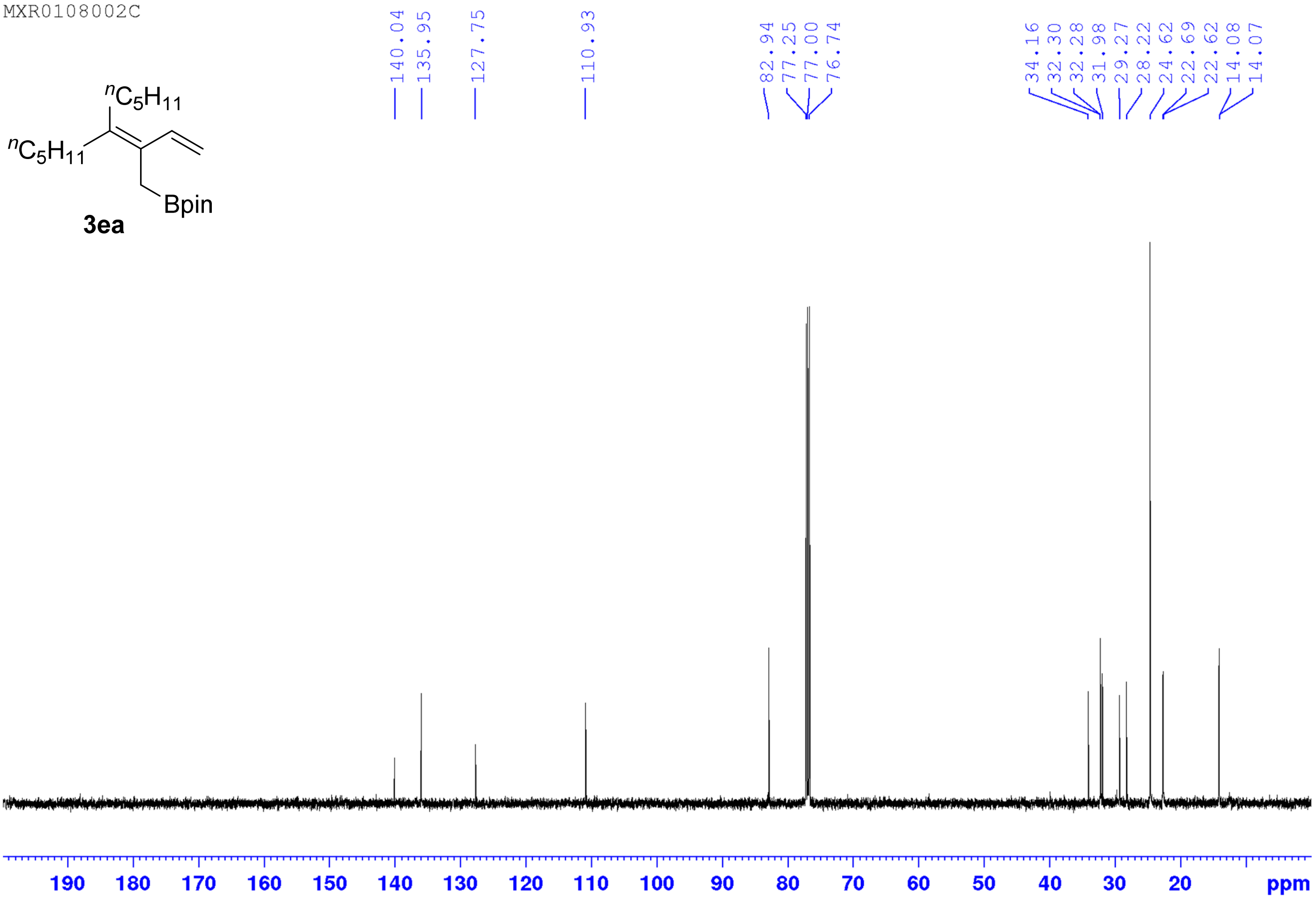
MXR0087001CLM

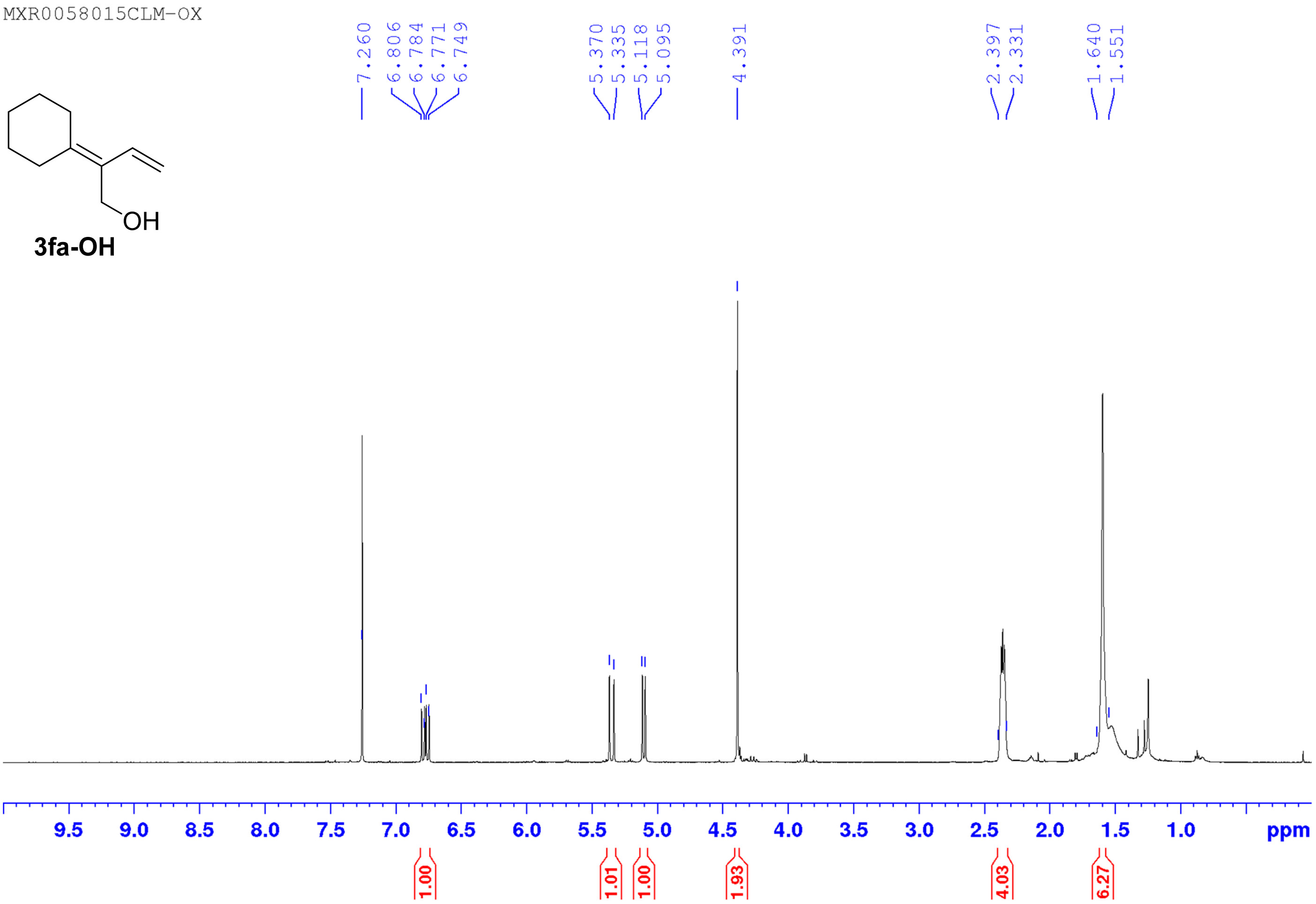


MXR0087001-C

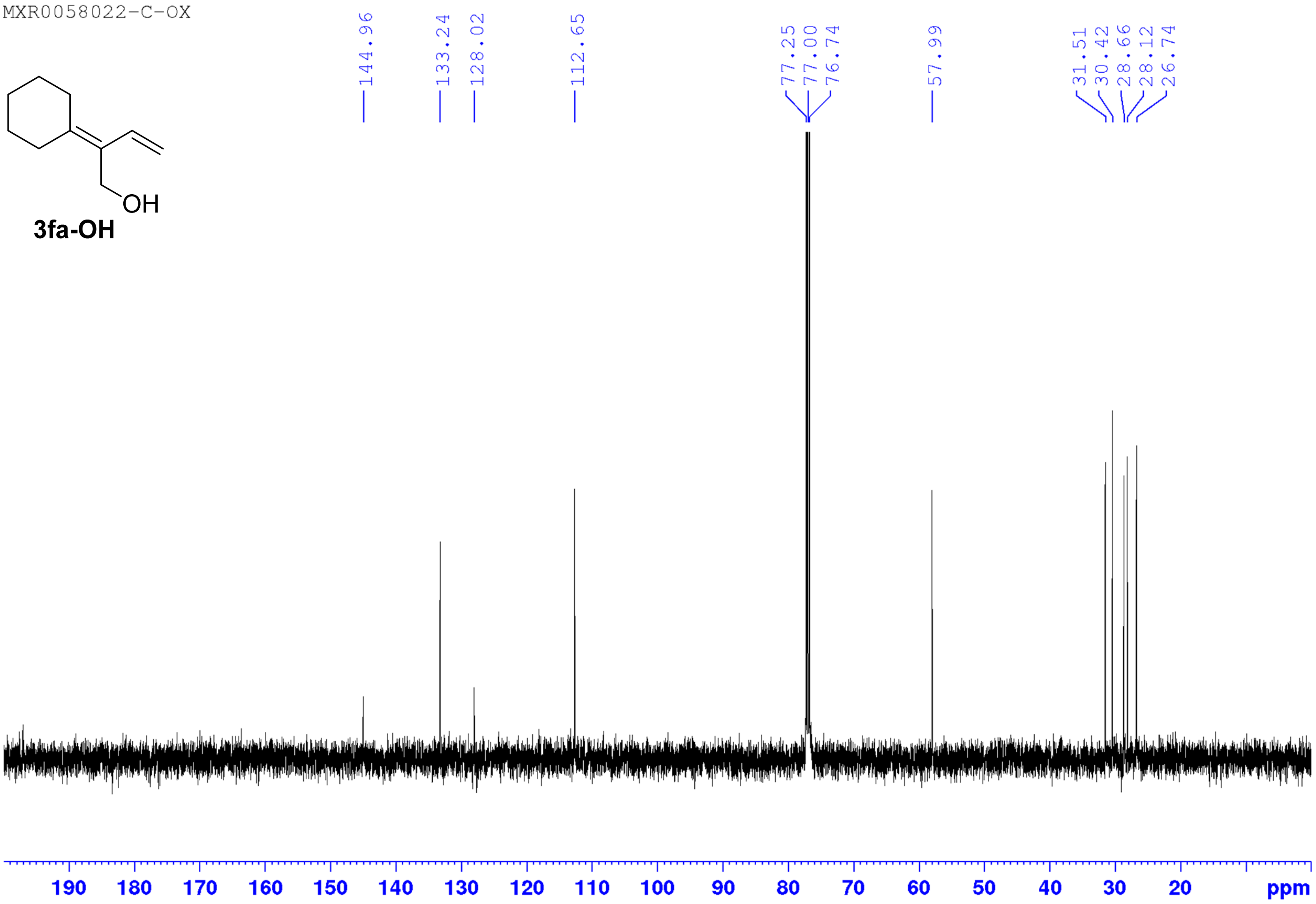



MXR0108002CLM
^{n}C5H11
^{n}C5H11
Bpin
3ea
7.260
6.846
6.824
6.812
6.790
5.073
5.039
4.940
4.918
2.188
2.174
2.159
2.083
2.069
2.053
1.853
1.441
1.344
1.233
1.199
0.927
0.829
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.05
1.02
1.99
2.02
2.06
4.33
8.44
12.29
6.35

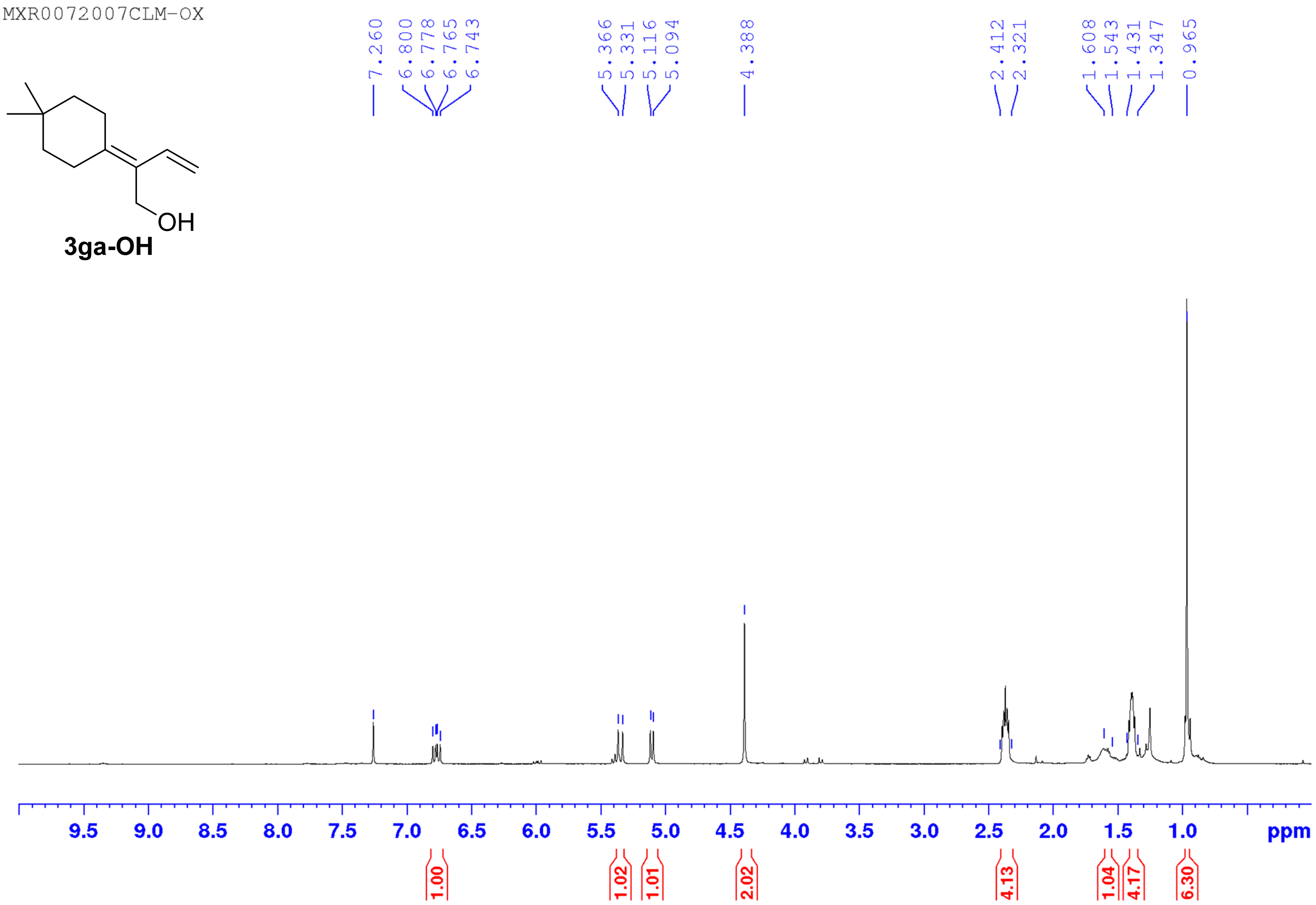

MXR0108002C
^{n}C5H11
^{n}C5H11
Bpin
3ea
140.04
135.95
127.75
110.93
82.94
77.25
77.00
76.74
34.16
32.30
32.28
31.98
29.27
28.22
24.62
22.69
22.62
14.08
14.07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

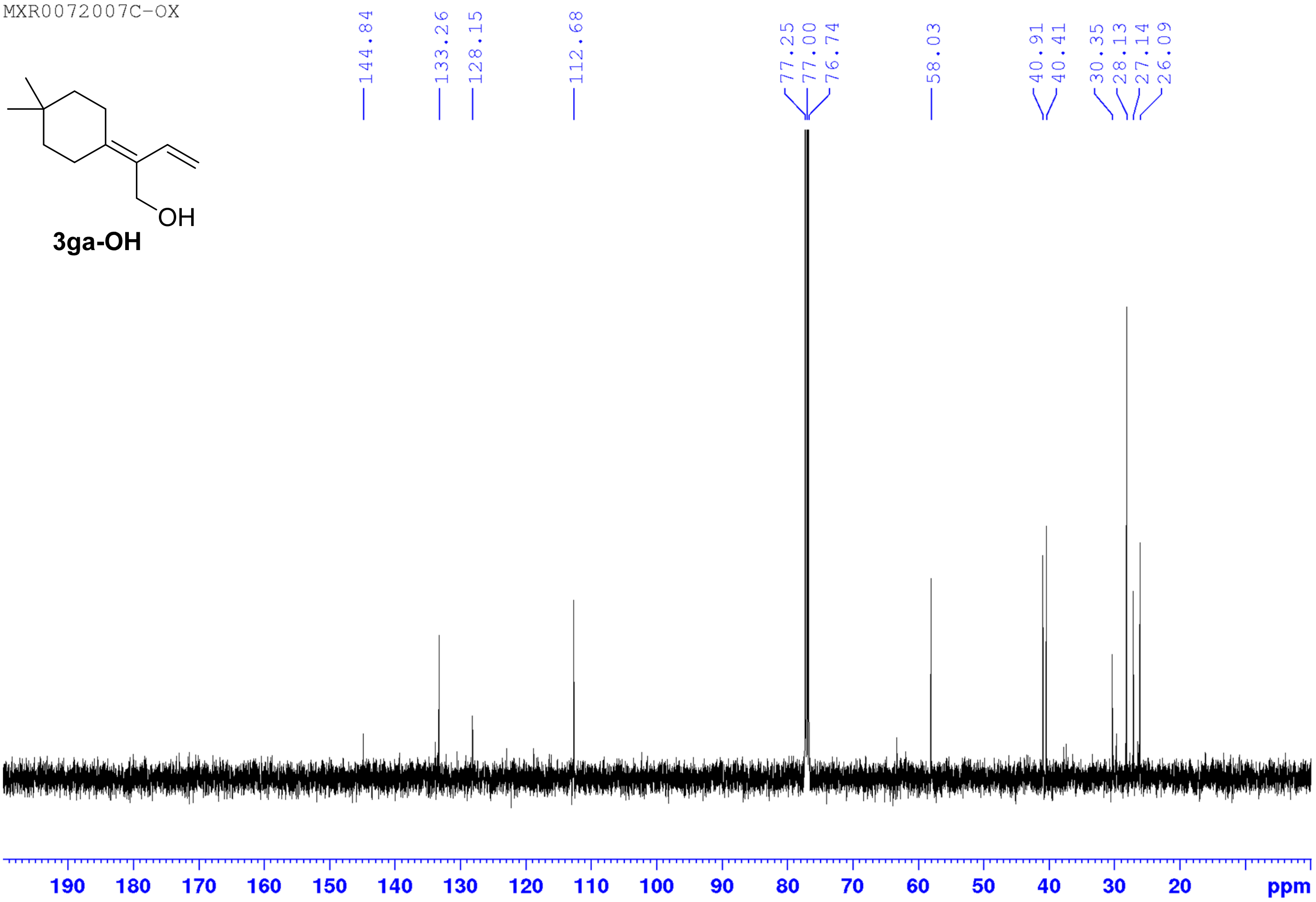

3fa-OH

MXR0058015CLM-OX
OH
7.260
6.806
6.784
6.771
6.749
5.370
5.335
5.118
5.095
4.391
2.397
2.331
1.640
1.551
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.01
1.00
1.93
4.03
6.27

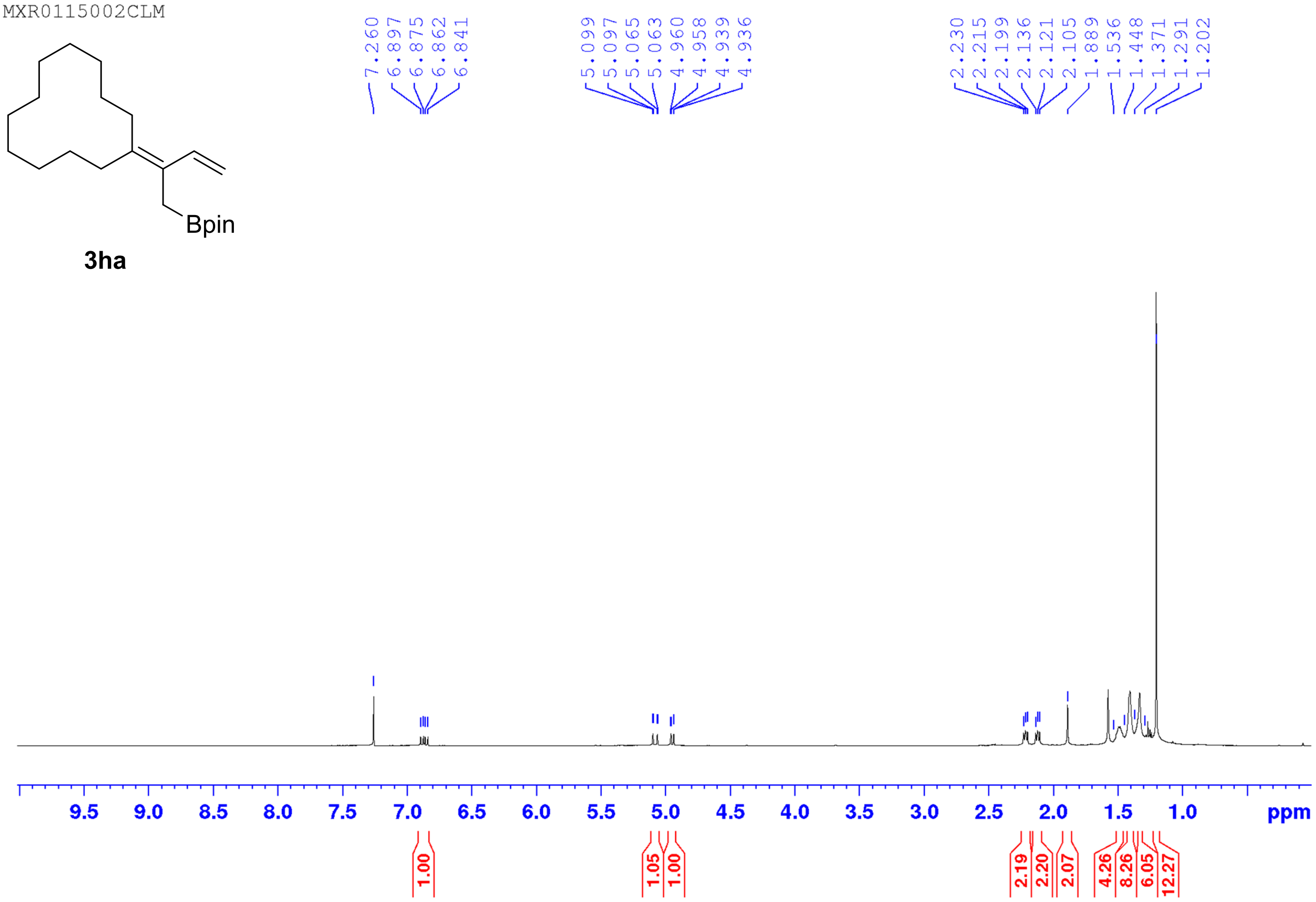

3fa-OH

MXR0058022-C-OX
OH
144.96
133.24
128.02
112.65
77.25
77.00
76.74
57.99
31.51
30.42
28.66
28.12
26.74
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


MXR0072007CLM-OX
OH
3ga-OH
7.260
6.800
6.778
6.765
6.743
5.366
5.331
5.116
5.094
4.388
2.412
2.321
1.608
1.543
1.431
1.347
0.965
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.02
1.01
2.02
4.13
1.04
4.17
6.30

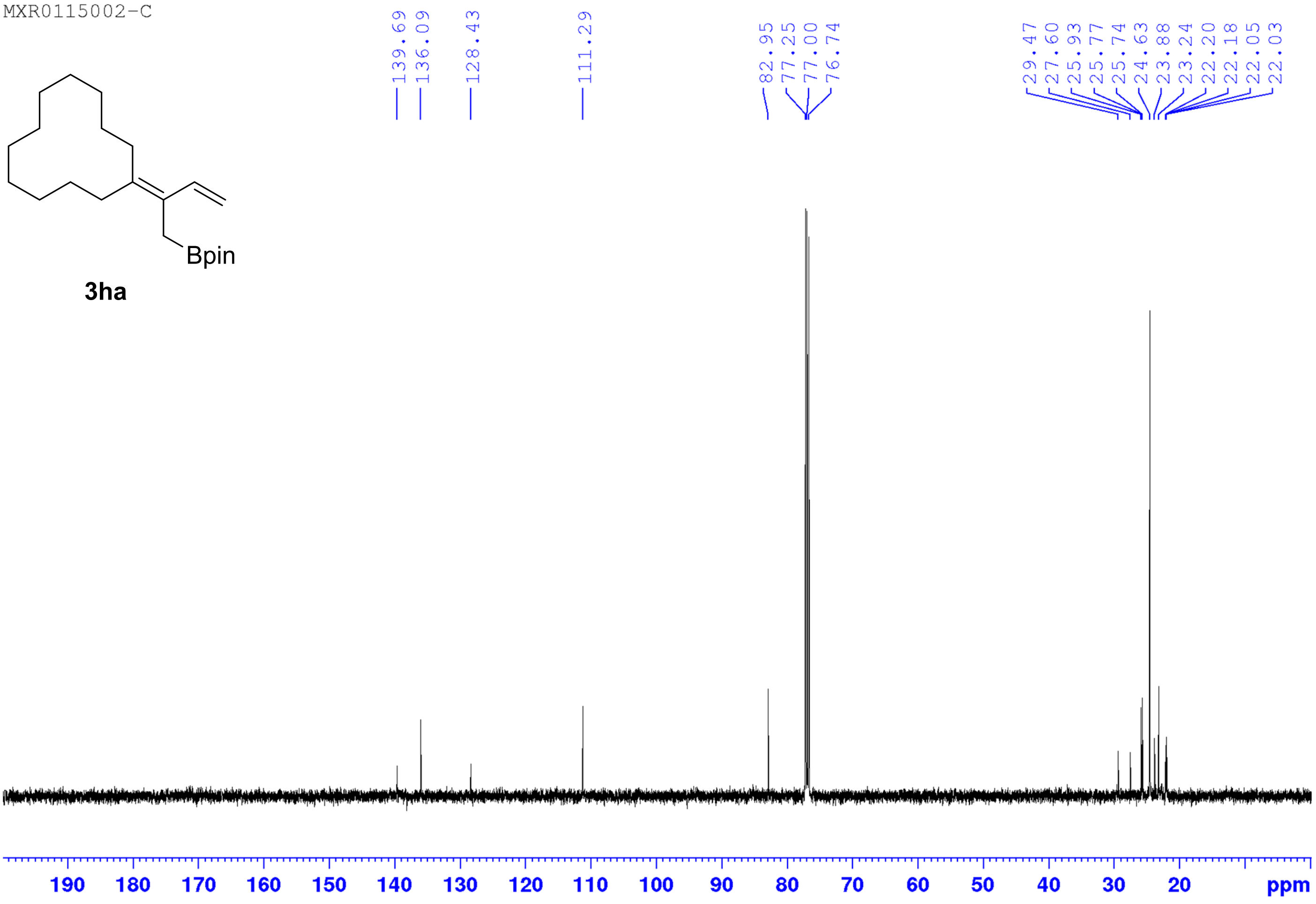

MXR0072007C-OX
OH
3ga-OH
144.84
133.26
128.15
112.68
77.25
77.00
76.74
58.03
40.91
40.41
30.35
28.13
27.14
26.09
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

MXR0115002CLM

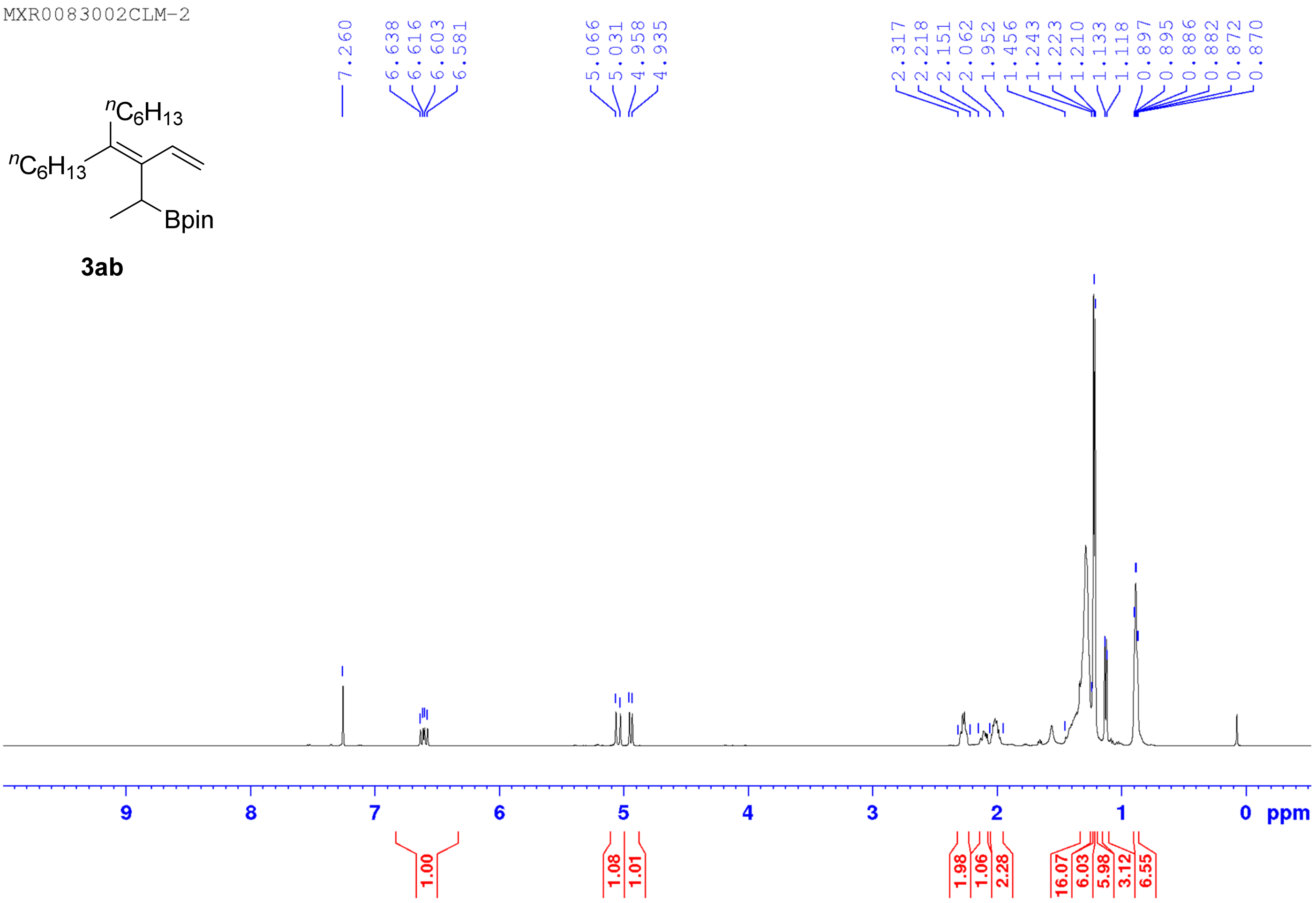


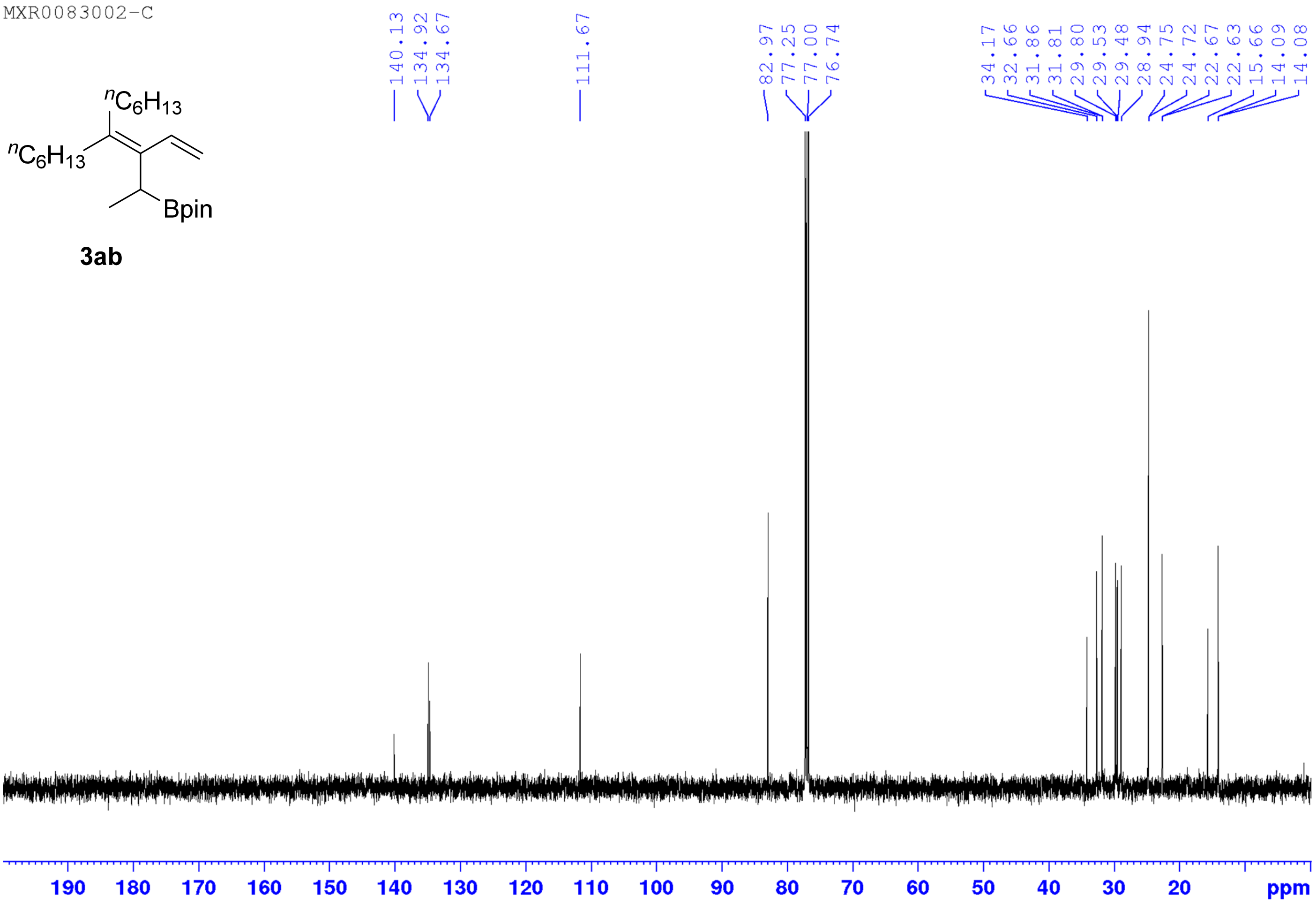
3ha

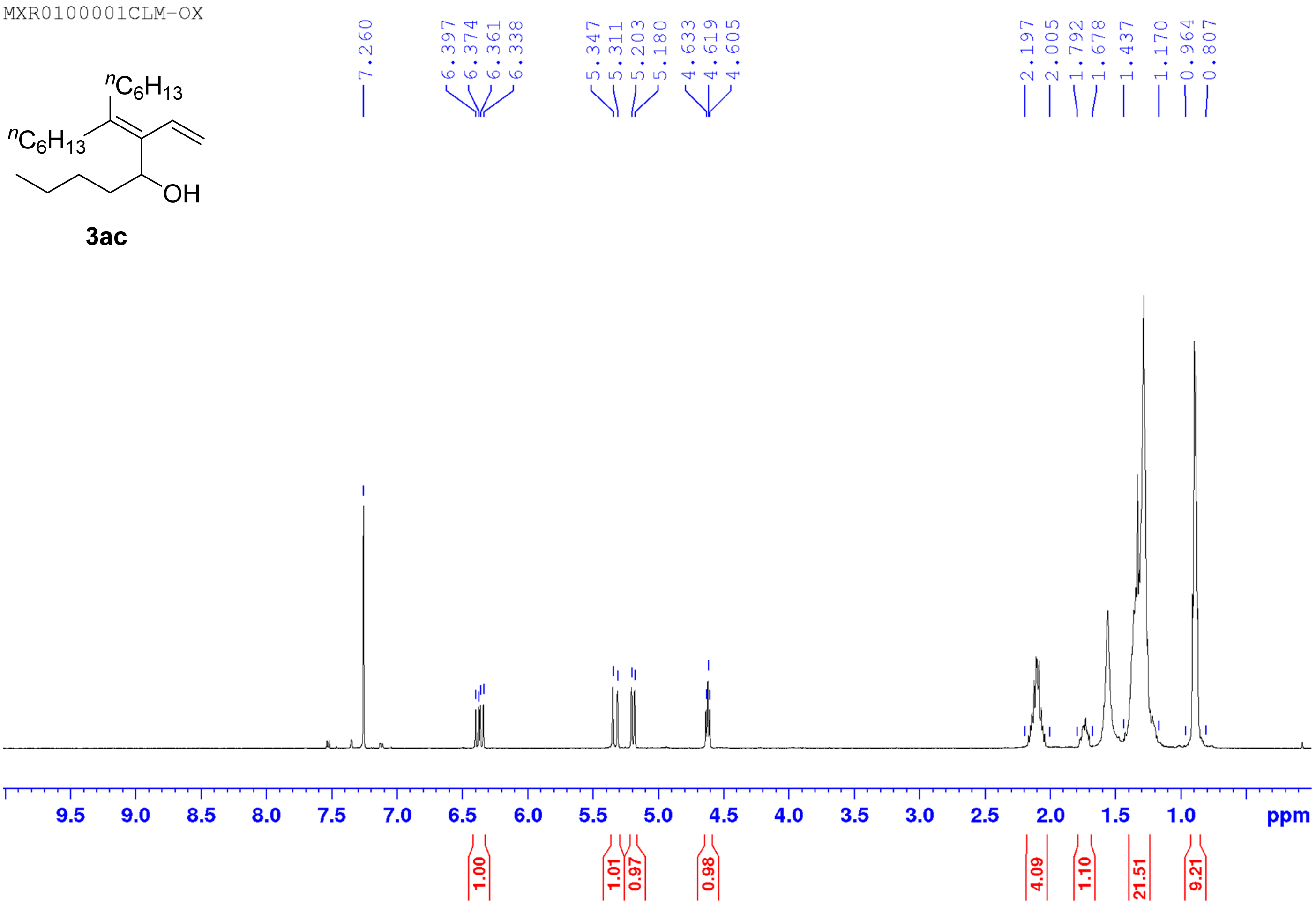
MXR0115002-C



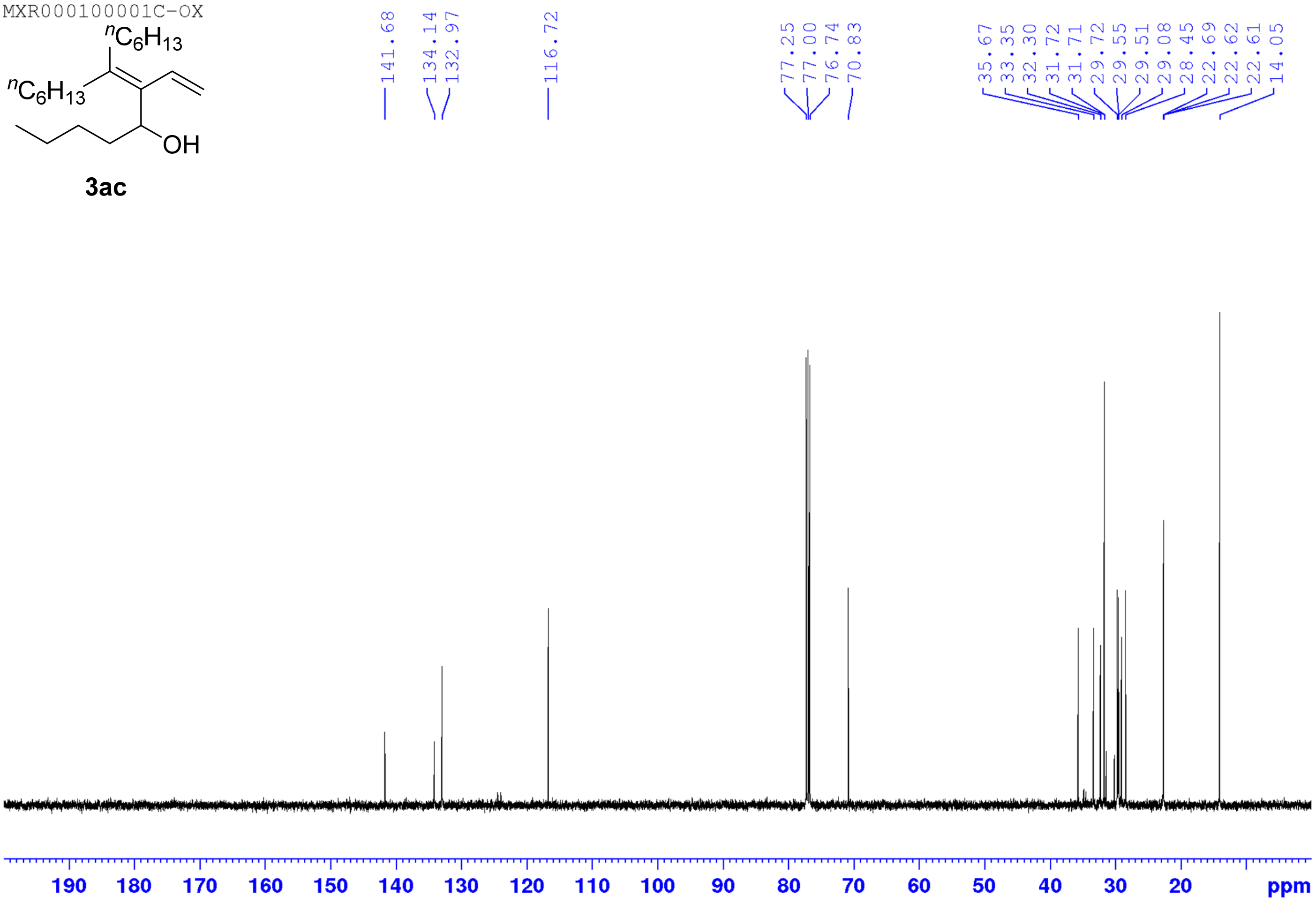
3ha


MXR0083002CLM-2
7.260
6.638
6.616
6.603
6.581
5.066
5.031
4.958
4.935
2.317
2.218
2.151
2.062
1.952
1.456
1.243
1.223
1.210
1.133
1.118
0.897
0.895
0.886
0.882
0.872
0.870
$^{n}C_6H_{13}$
$^{n}C_6H_{13}$
Bpin
3ab
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.08
1.01
1.98
1.06
2.28
16.07
6.03
5.98
3.12
6.55

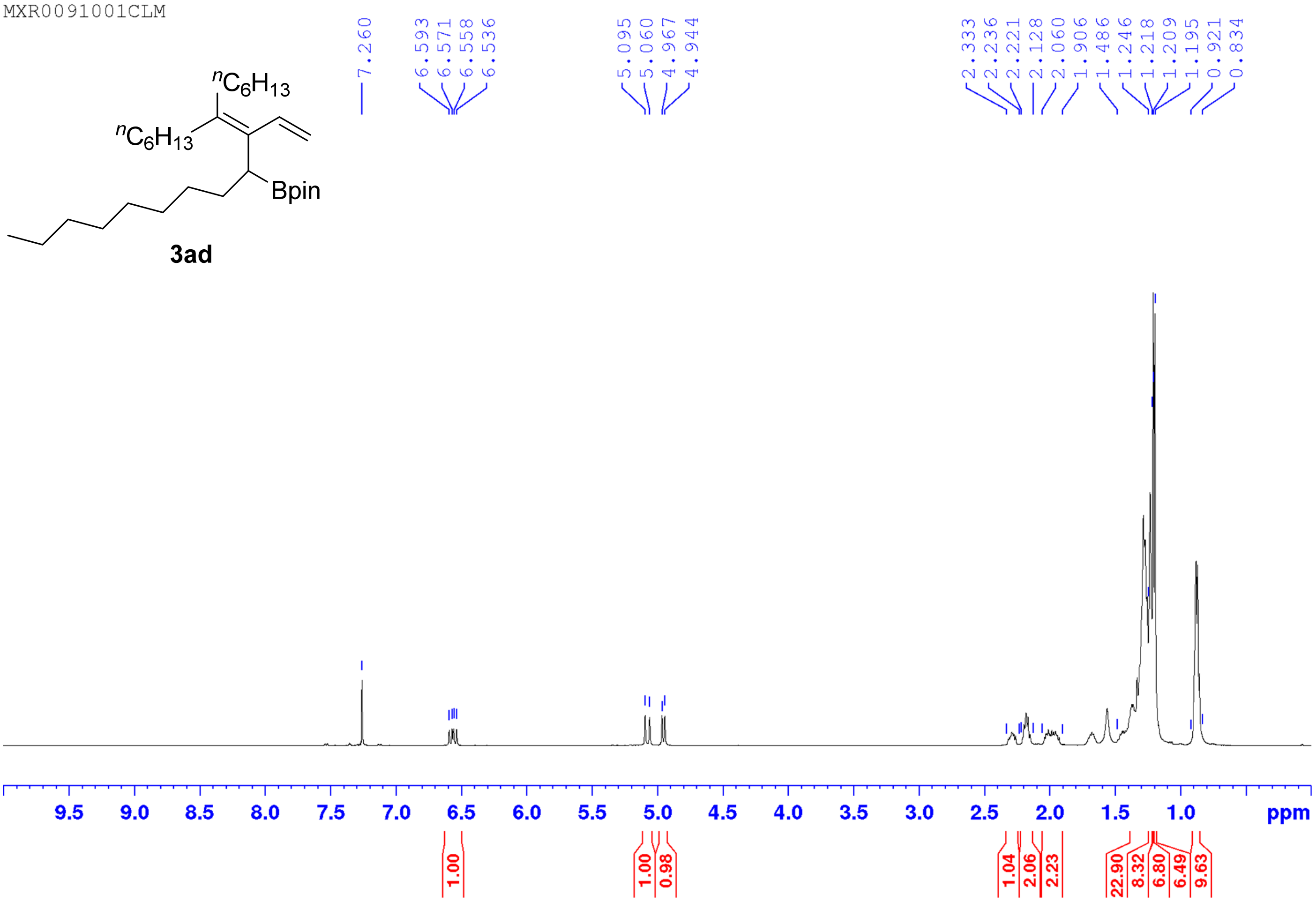

MXR0083002-C
140.13
134.92
134.67
111.67
82.97
77.25
77.00
76.74
34.17
32.66
31.86
31.81
29.80
29.53
29.48
28.94
24.75
24.72
22.67
22.63
15.66
14.09
14.08
$^{n}C_6H_{13}$
$^{n}C_6H_{13}$
Bpin
3ab
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

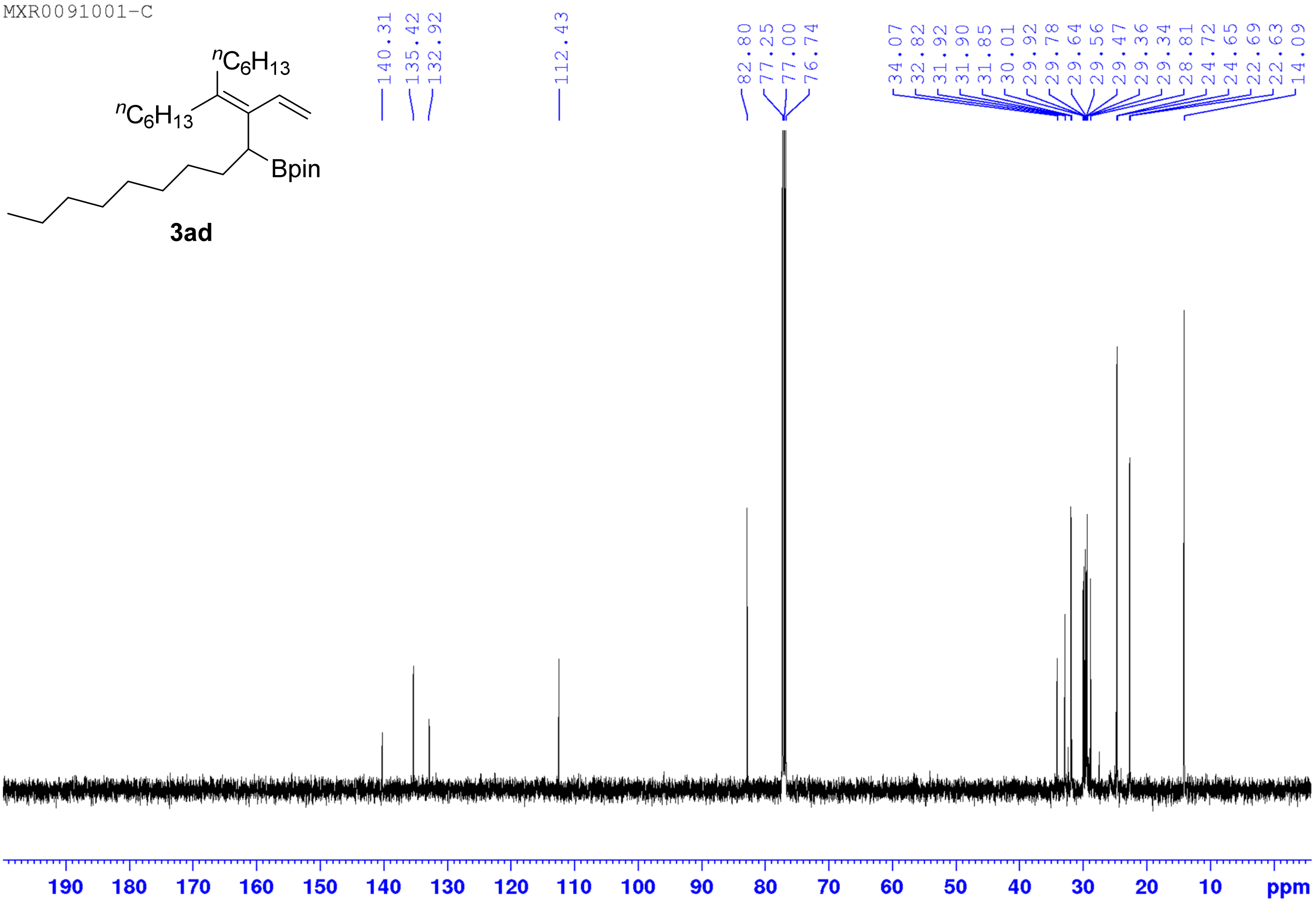

MXR0100001CLM-OX
$^{n}C_6H_{13}$
$^{n}C_6H_{13}$
OH
7.260
6.397
6.374
6.361
6.338
5.347
5.311
5.203
5.180
4.633
4.619
4.605
2.197
2.005
1.792
1.678
1.437
1.170
0.964
0.807
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.01
0.97
0.98
4.09
1.10
21.51
9.21

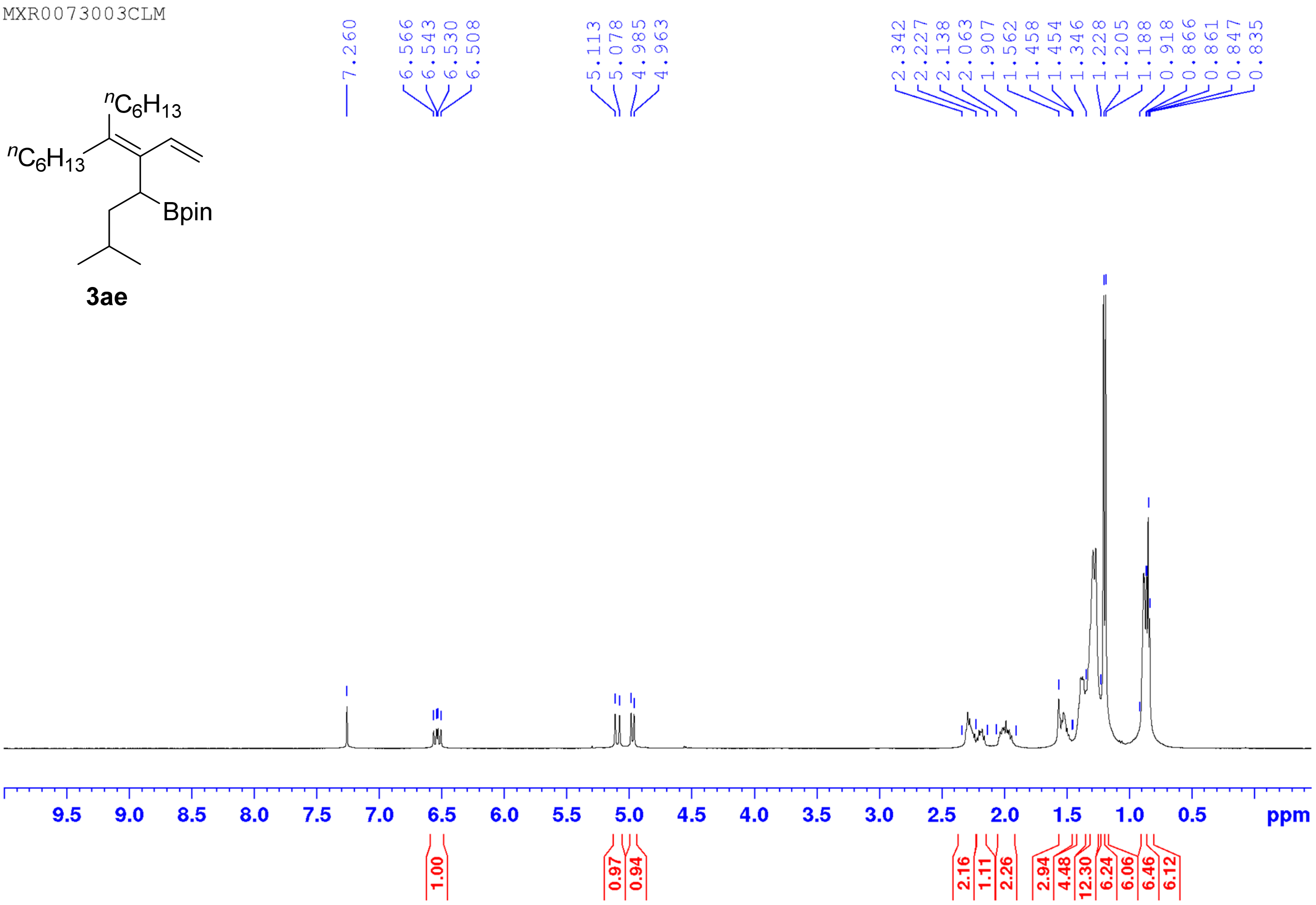
3ac

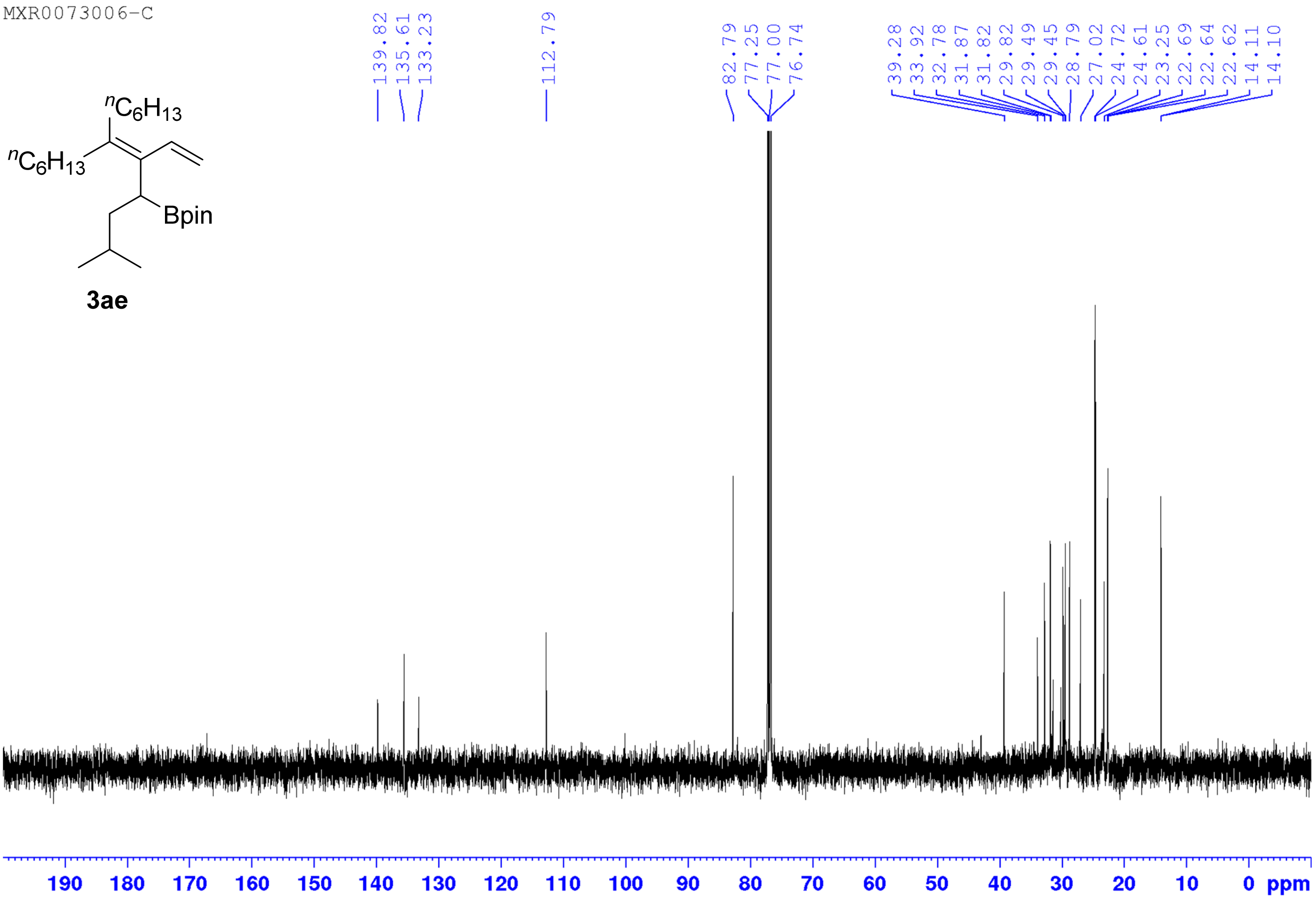

MXR000100001C-OX
$^{n}C_6H_{13}$
$^{n}C_6H_{13}$
OH
141.68
134.14
132.97
116.72
77.25
77.00
76.74
70.83
35.67
33.35
32.30
31.72
31.71
29.72
29.55
29.51
29.08
28.45
22.69
22.62
22.61
14.05
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

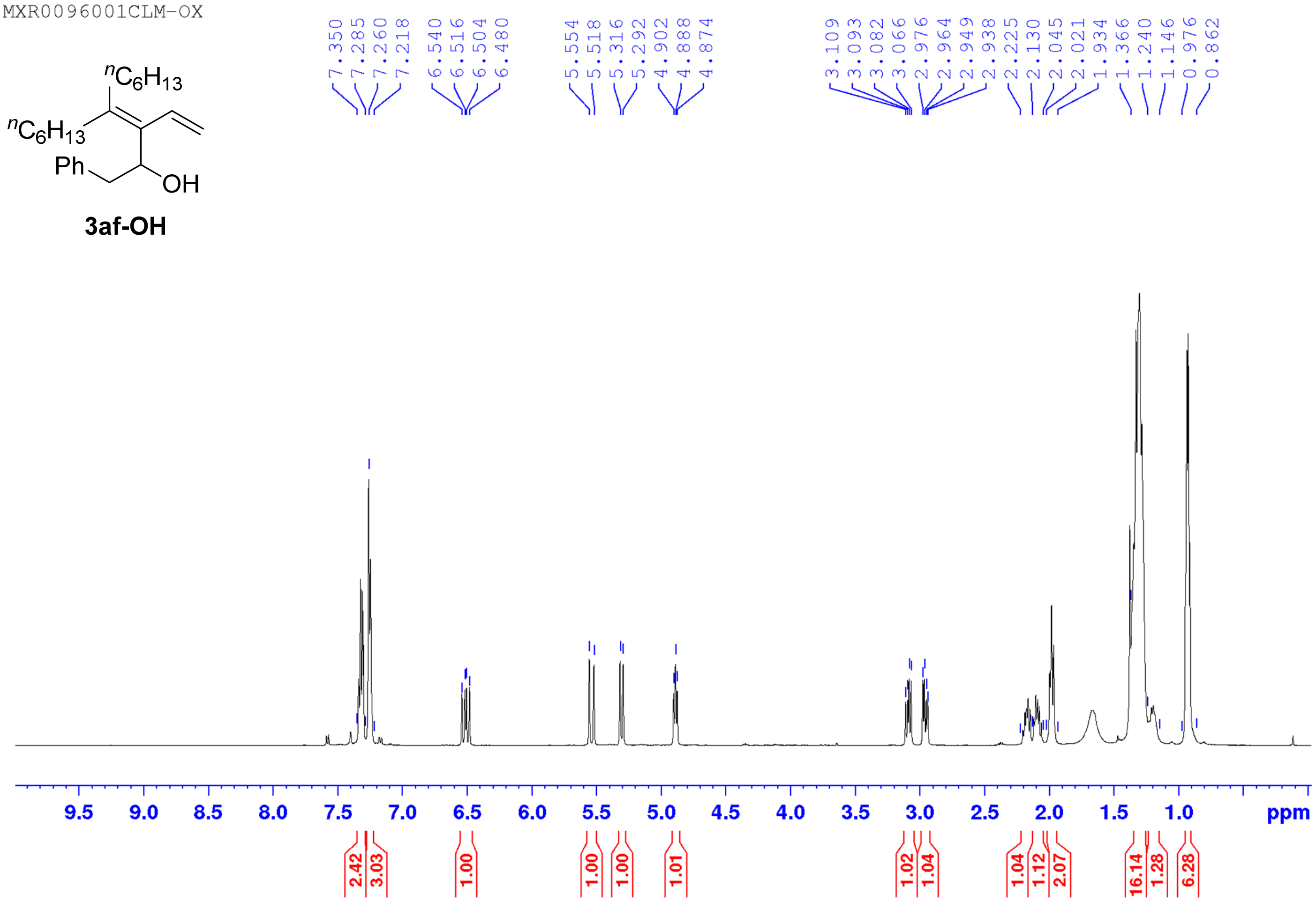
3ac

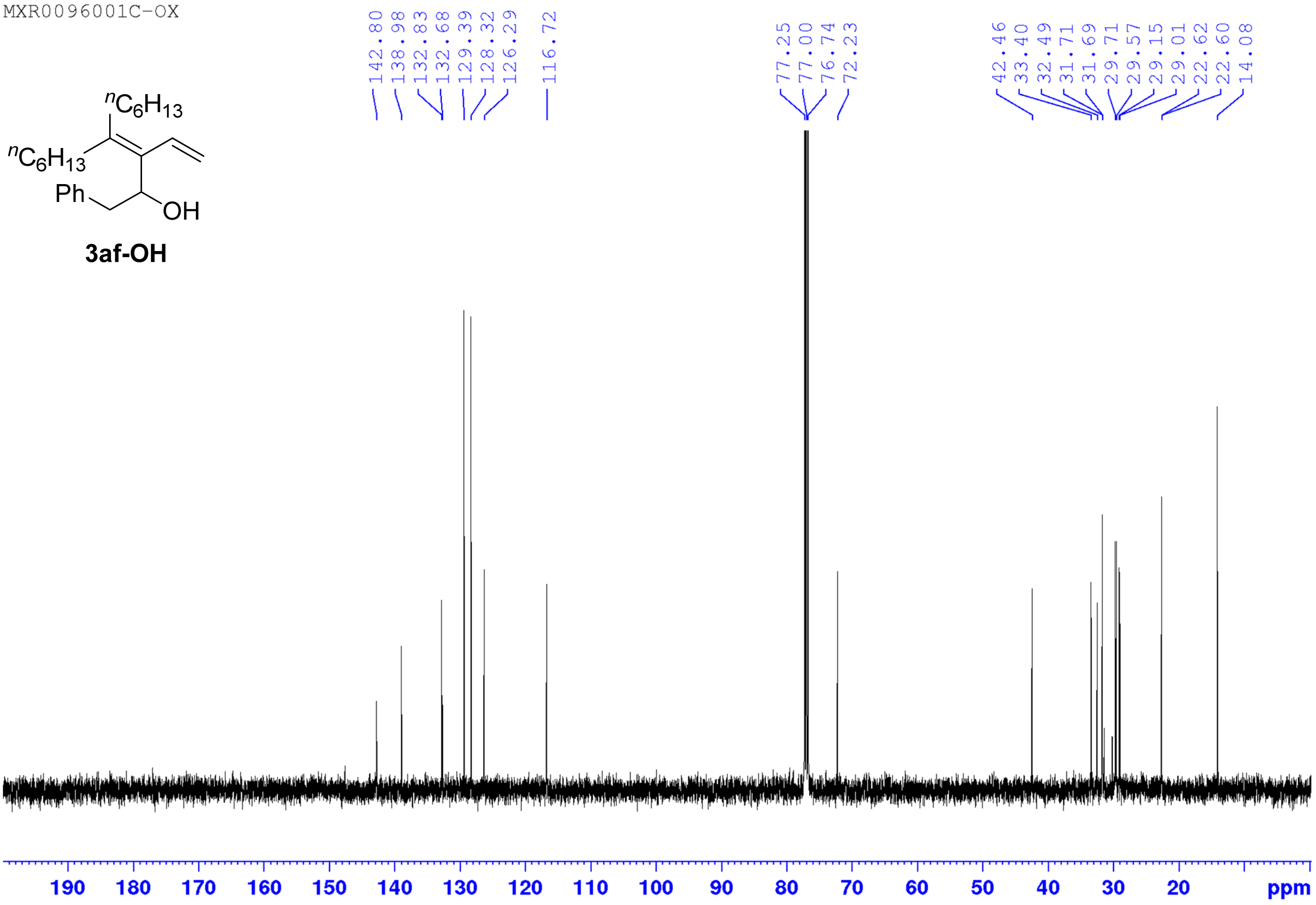

MXR0091001CLM
^{n}C$_6$H$_{13}$
^{n}C$_6$H$_{13}$
Bpin
3ad
7.260
6.593
6.571
6.558
6.536
5.095
5.060
4.967
4.944
2.333
2.236
2.221
2.128
2.060
1.906
1.486
1.246
1.218
1.209
1.195
0.921
0.834
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
0.98
1.04
2.06
2.23
22.90
8.32
6.80
6.49
9.63

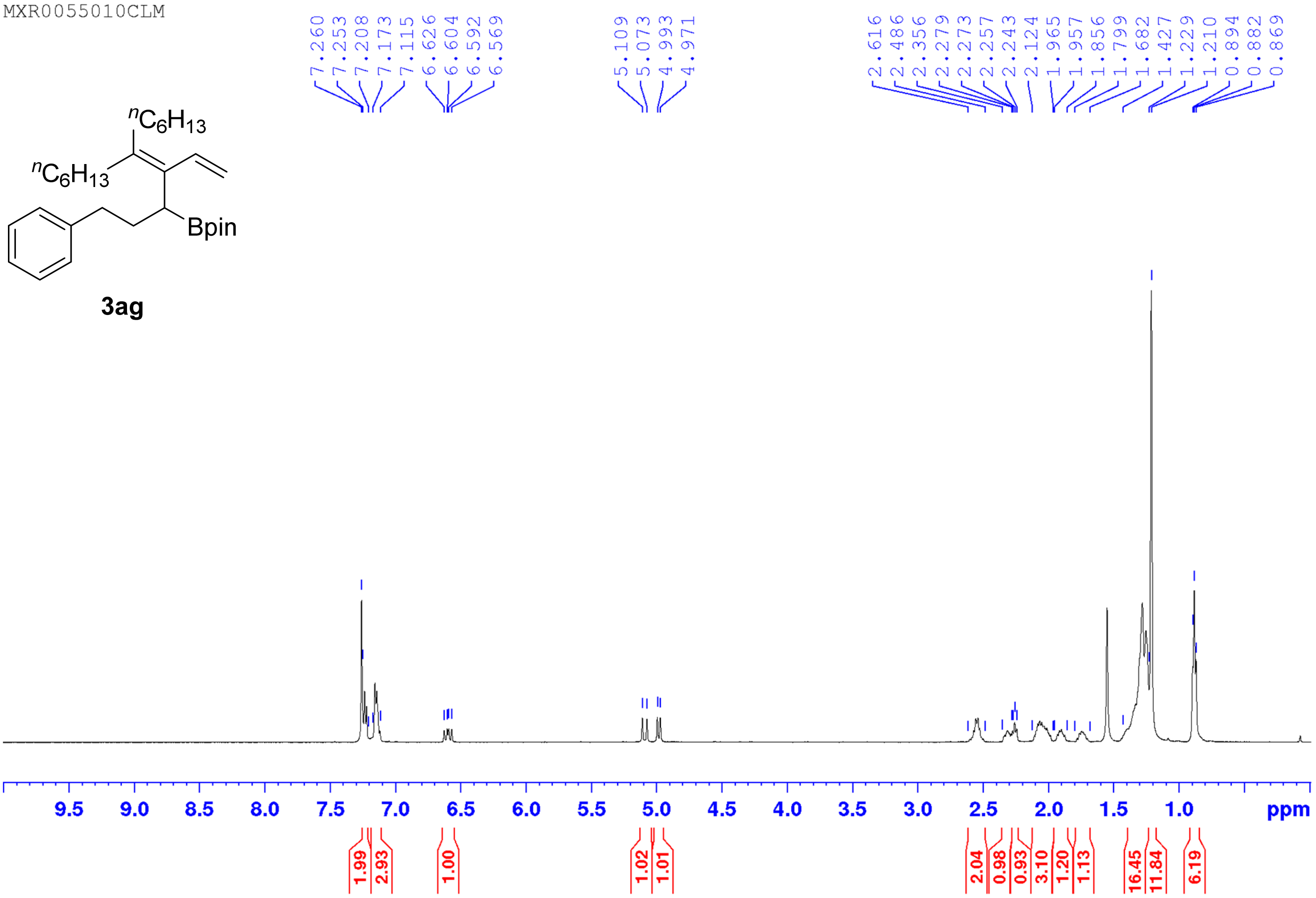

MXR0091001-C
^{n}C$_6$H$_{13}$
^{n}C$_6$H$_{13}$
Bpin
3ad
140.31
135.42
132.92
112.43
82.80
77.25
77.00
76.74
34.07
32.82
31.92
31.90
31.85
30.01
29.92
29.78
29.64
29.56
29.47
29.36
29.34
28.81
24.72
24.65
22.69
22.63
14.09
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


MXR0073003CLM
7.260
6.566
6.543
6.530
6.508
5.113
5.078
4.985
4.963
2.342
2.227
2.138
2.063
1.907
1.562
1.458
1.454
1.346
1.228
1.205
1.188
0.918
0.866
0.861
0.847
0.835
$^nC_6H_{13}$
$^nC_6H_{13}$
Bpin
3ae
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.97
0.94
2.16
1.11
2.26
2.94
4.48
12.30
6.24
6.06
6.46
6.12

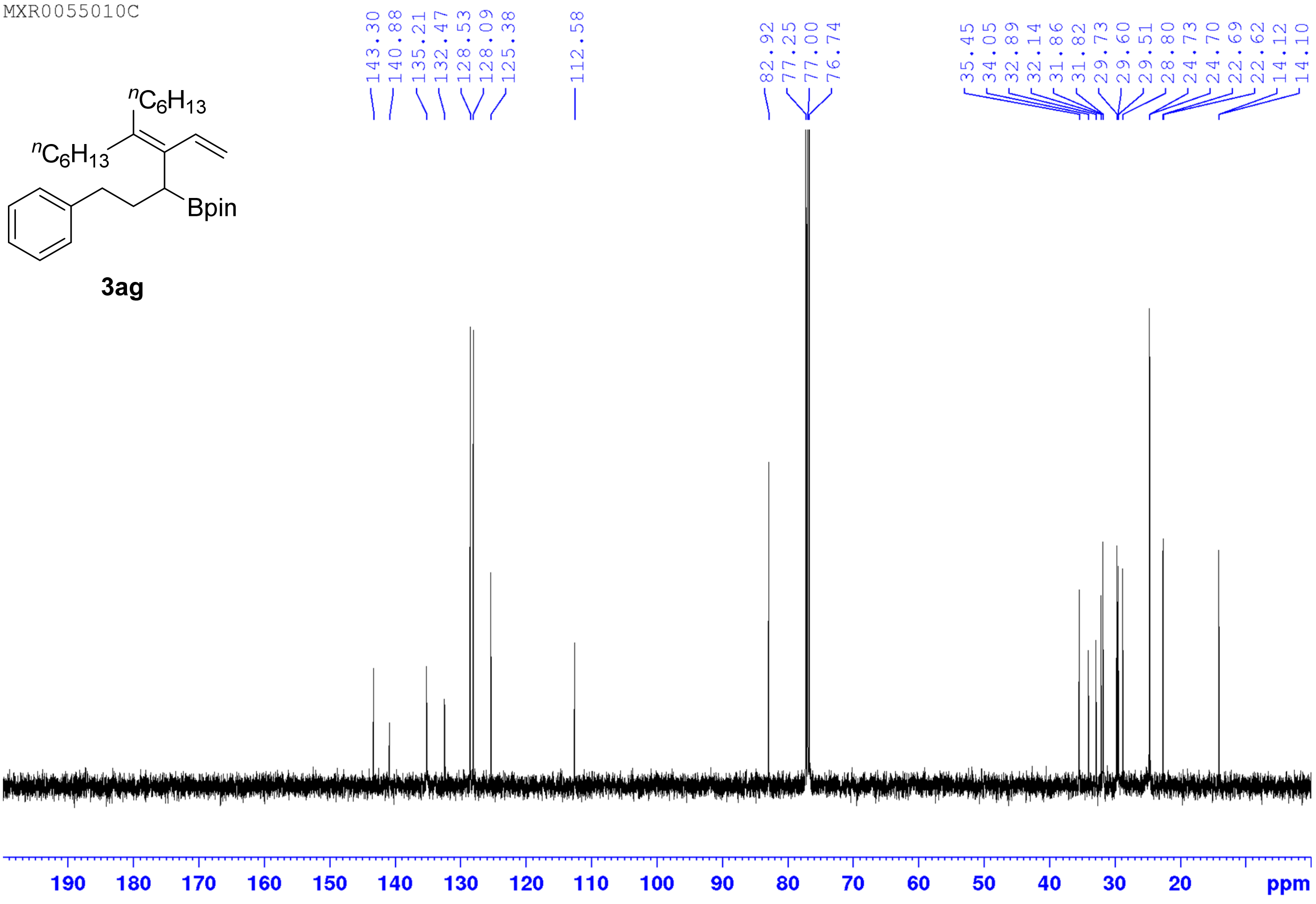

MXR0073006-C
139.82
135.61
133.23
112.79
82.79
77.25
77.00
76.74
39.28
33.92
32.78
31.87
31.82
29.82
29.49
29.45
28.79
27.02
24.72
24.61
23.25
22.69
22.64
22.62
14.11
14.10
$^nC_6H_{13}$
$^nC_6H_{13}$
Bpin
3ae
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


MXR0096001CLM-OX
$^nC_6H_{13}$
$^nC_6H_{13}$
Ph
OH
3af-OH
7.350
7.285
7.260
7.218
6.540
6.516
6.504
6.480
5.554
5.518
5.316
5.292
4.902
4.888
4.874
3.109
3.093
3.082
3.066
2.976
2.964
2.949
2.938
2.225
2.130
2.045
2.021
1.934
1.366
1.240
1.146
0.976
0.862
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.42
3.03
1.00
1.00
1.00
1.01
1.02
1.04
1.04
1.12
2.07
16.14
1.28
6.28

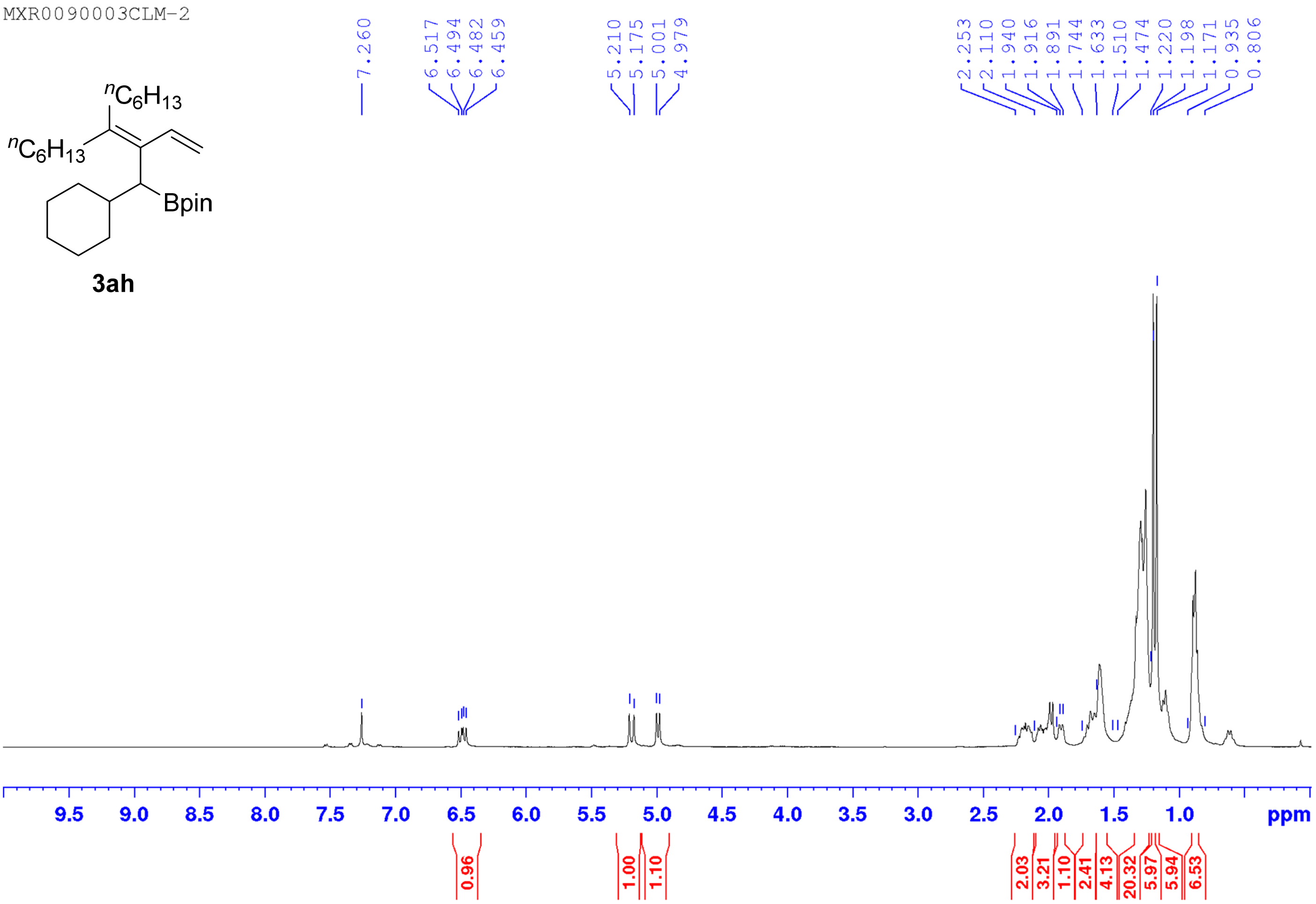

MXR0096001C-OX
$^nC_6H_{13}$
$^nC_6H_{13}$
Ph
OH
3af-OH
142.80
138.98
132.83
132.68
129.39
128.32
126.29
116.72
77.25
77.00
76.74
72.23
42.46
33.40
32.49
31.71
31.69
29.71
29.57
29.15
29.01
22.62
22.60
14.08
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

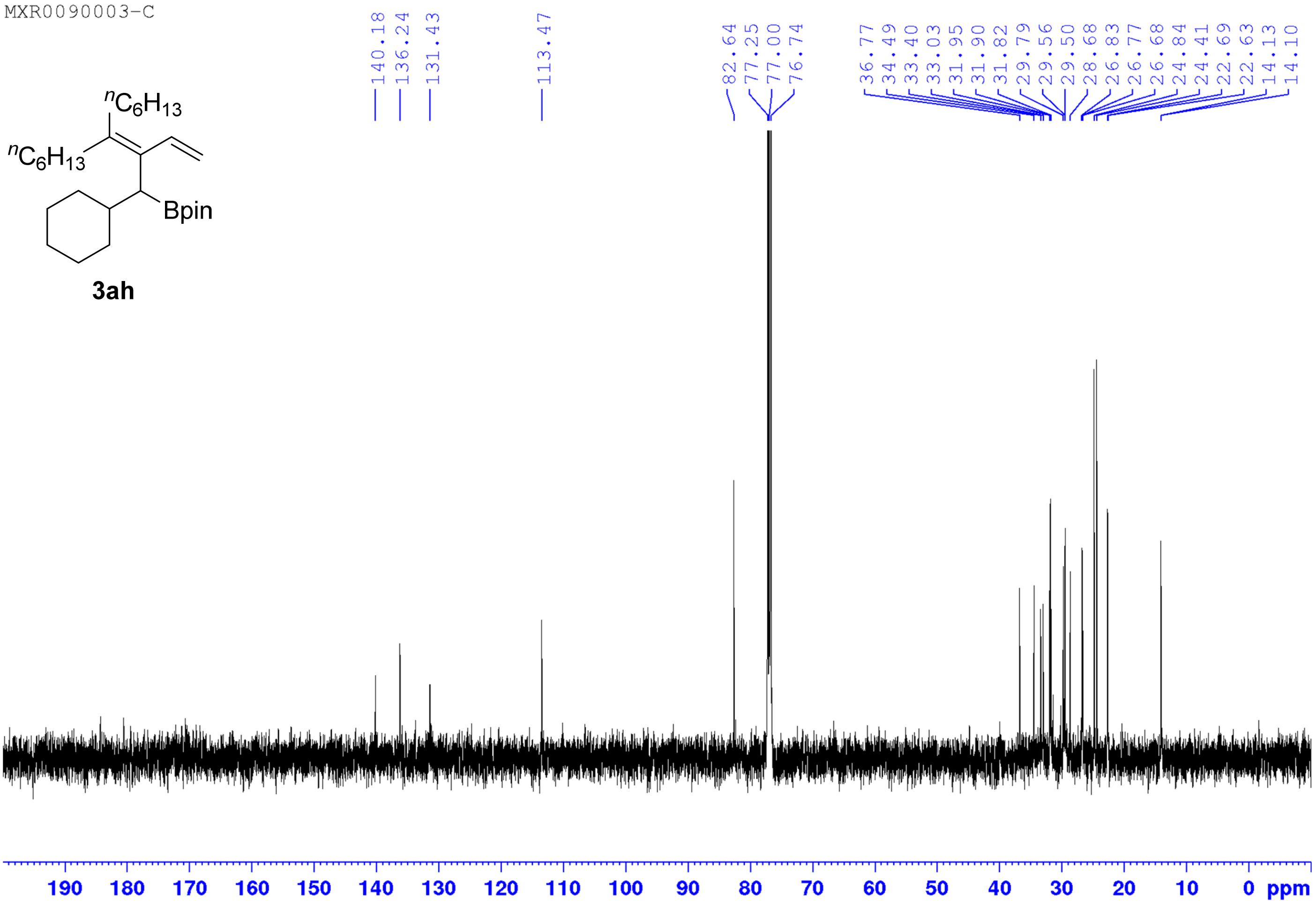

MXR0055010CLM
7.260
7.253
7.208
7.173
7.115
6.626
6.604
6.592
6.569
5.109
5.073
4.993
4.971
2.616
2.486
2.356
2.279
2.273
2.257
2.243
2.124
1.965
1.957
1.856
1.799
1.682
1.427
1.229
1.210
0.894
0.882
0.869
^{n}C$_6$H$_{13}$
^{n}C$_6$H$_{13}$
Bpin
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.99
2.93
1.00
1.02
1.01
2.04
0.98
0.93
3.10
1.20
1.13
16.45
11.84
6.19

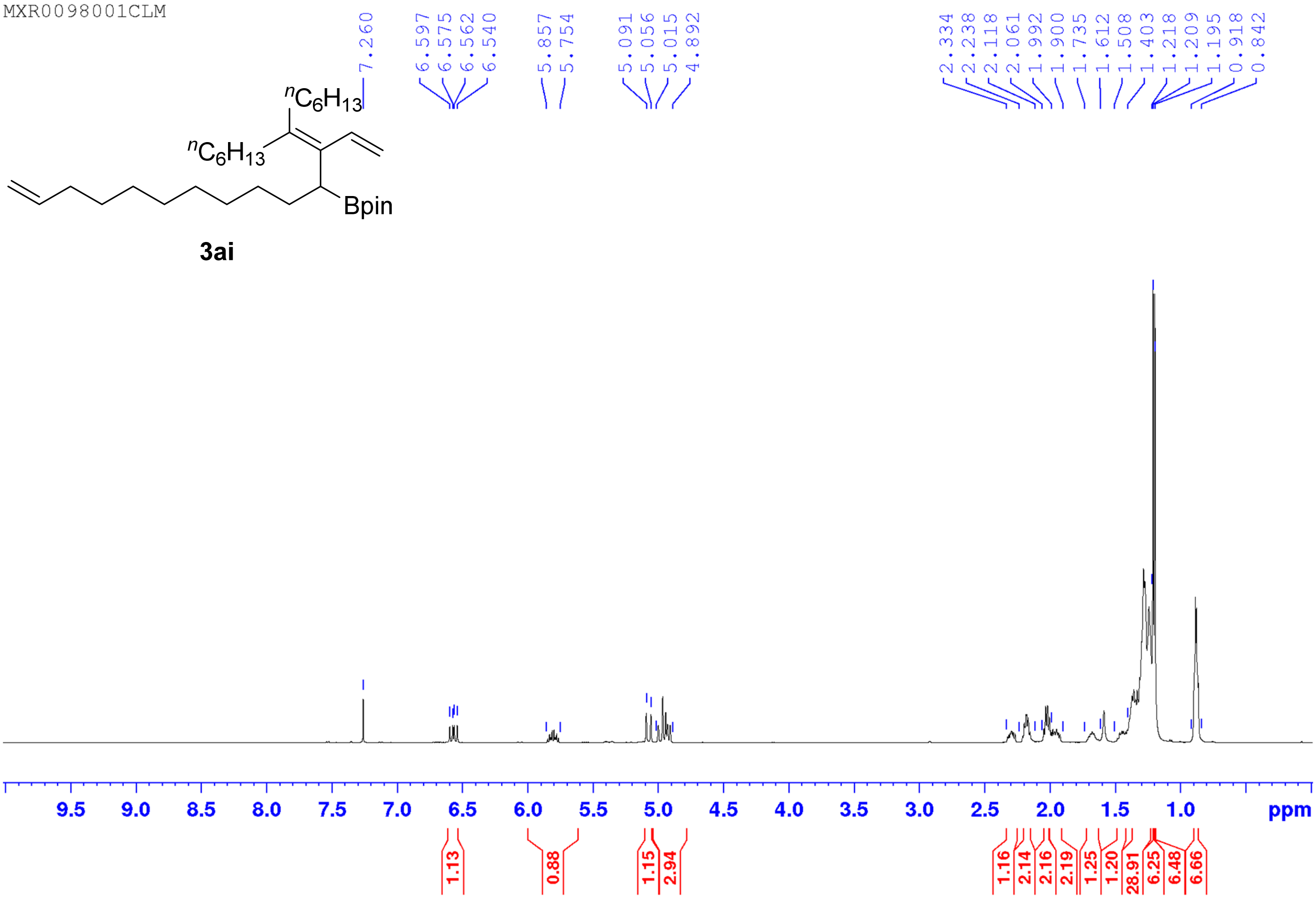
3ag

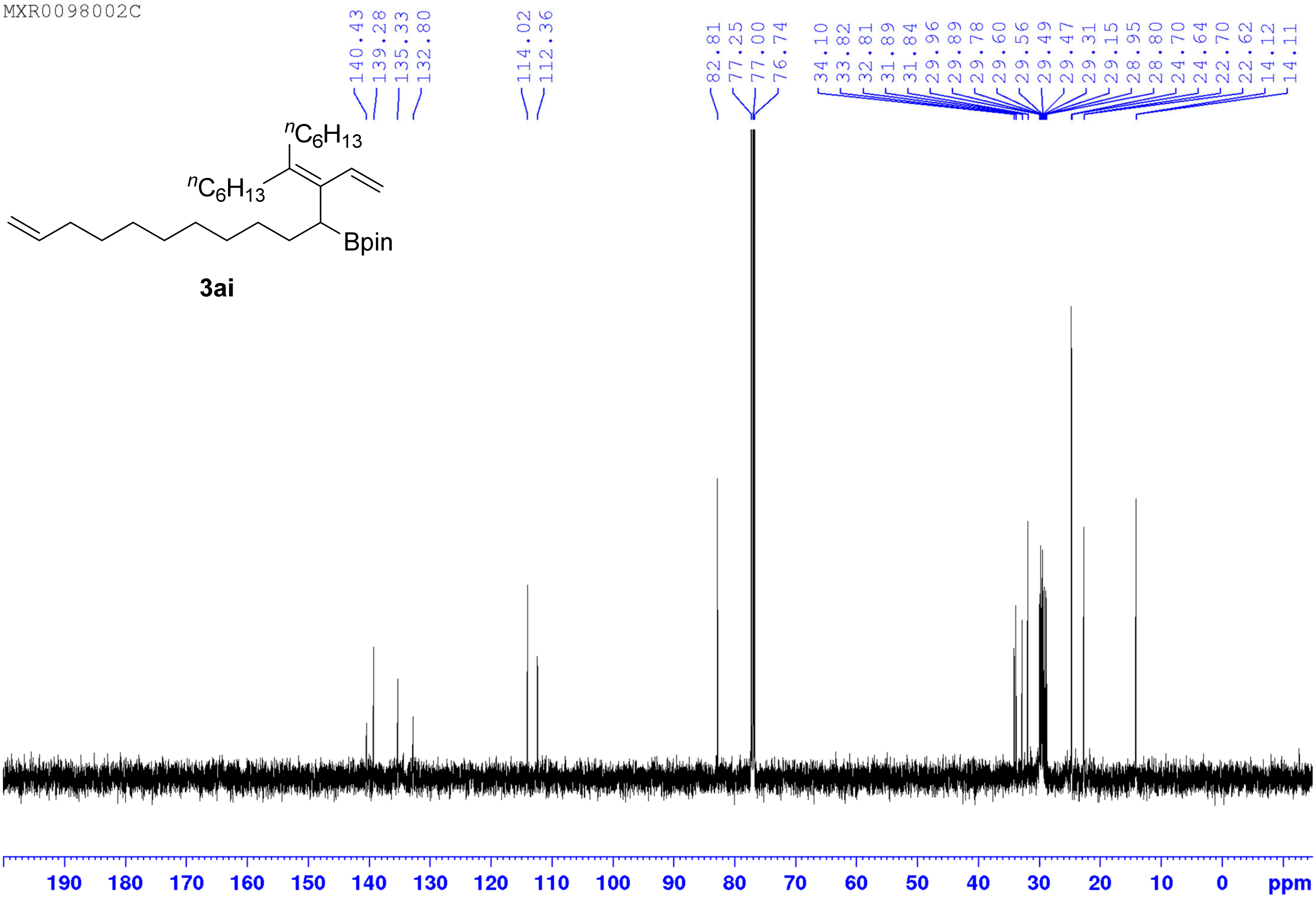

MXR0055010C
143.30
140.88
135.21
132.47
128.53
128.09
125.38
112.58
82.92
77.25
77.00
76.74
35.45
34.05
32.89
32.14
31.86
31.82
29.73
29.60
29.51
28.80
24.73
24.70
22.69
22.62
14.12
14.10
^{n}C$_6$H$_{13}$
^{n}C$_6$H$_{13}$
Bpin
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

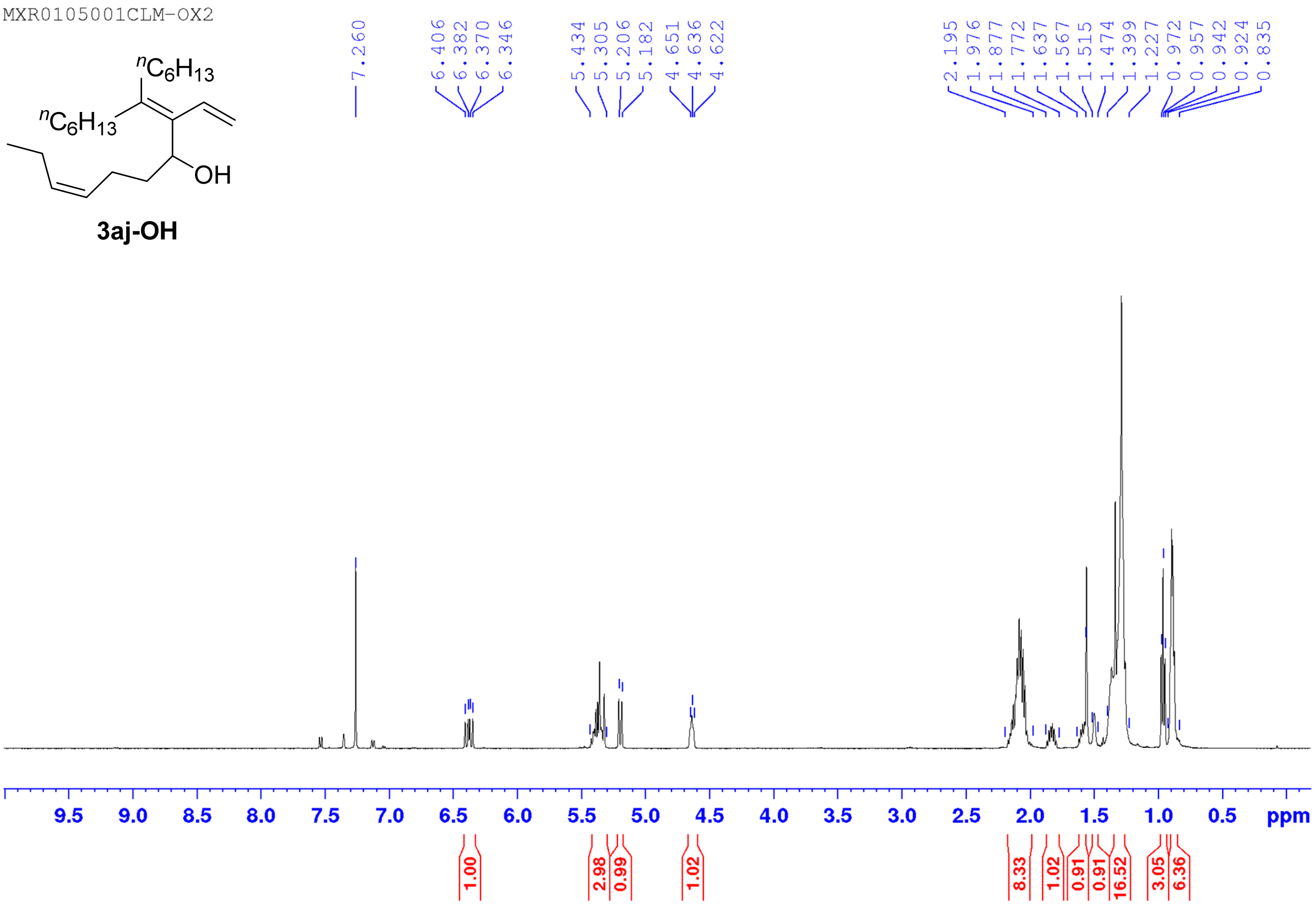
3ag

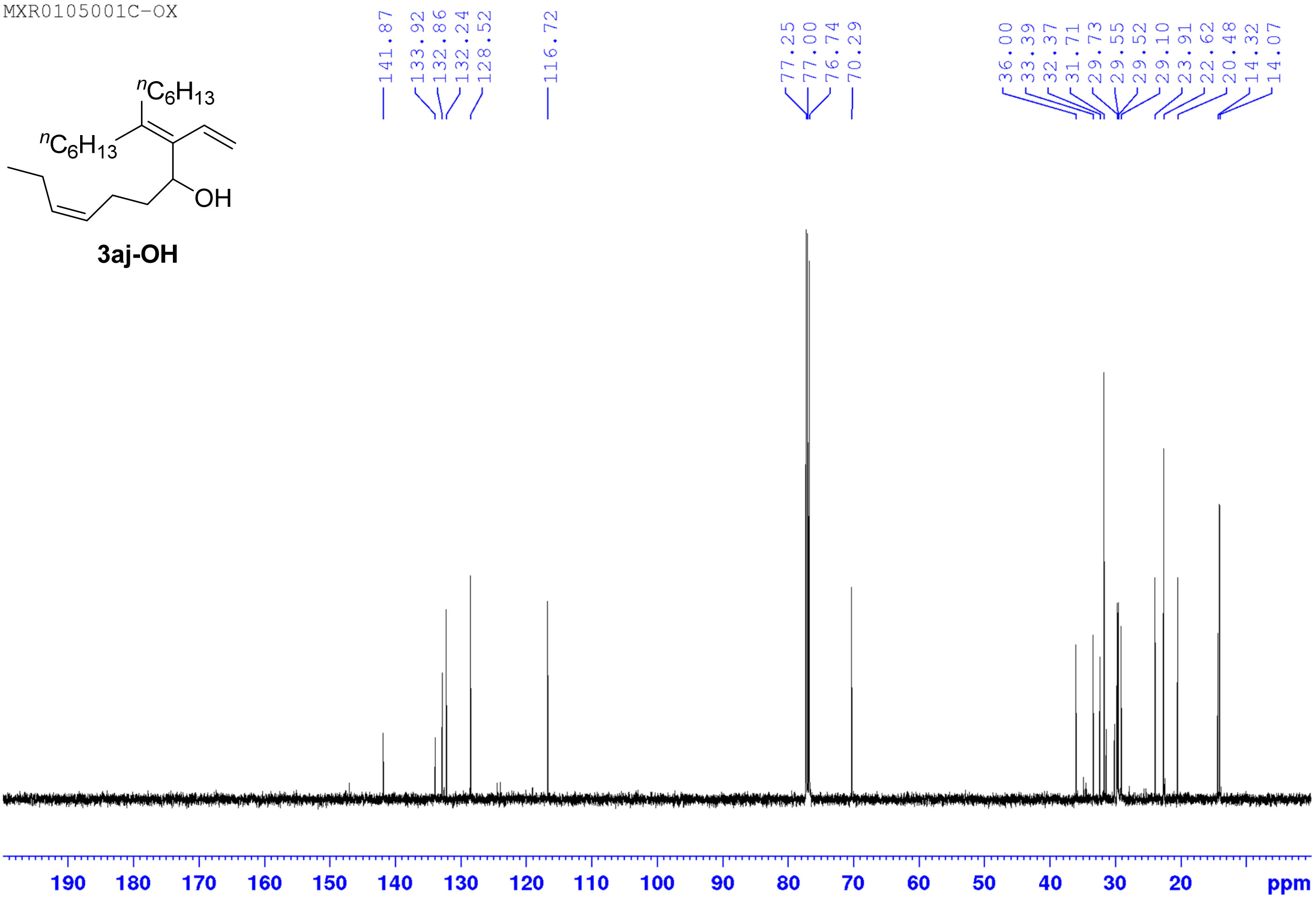

MXR0090003CLM-2
^{n}C$_6$H$_{13}$
^{n}C$_6$H$_{13}$
Bpin
3ah
7.260
6.517
6.494
6.482
6.459
5.210
5.175
5.001
4.979
2.253
2.110
1.940
1.916
1.891
1.744
1.633
1.510
1.474
1.220
1.198
1.171
0.935
0.806
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.96
1.00
1.10
2.03
3.21
1.10
2.41
4.13
20.32
5.97
5.94
6.53

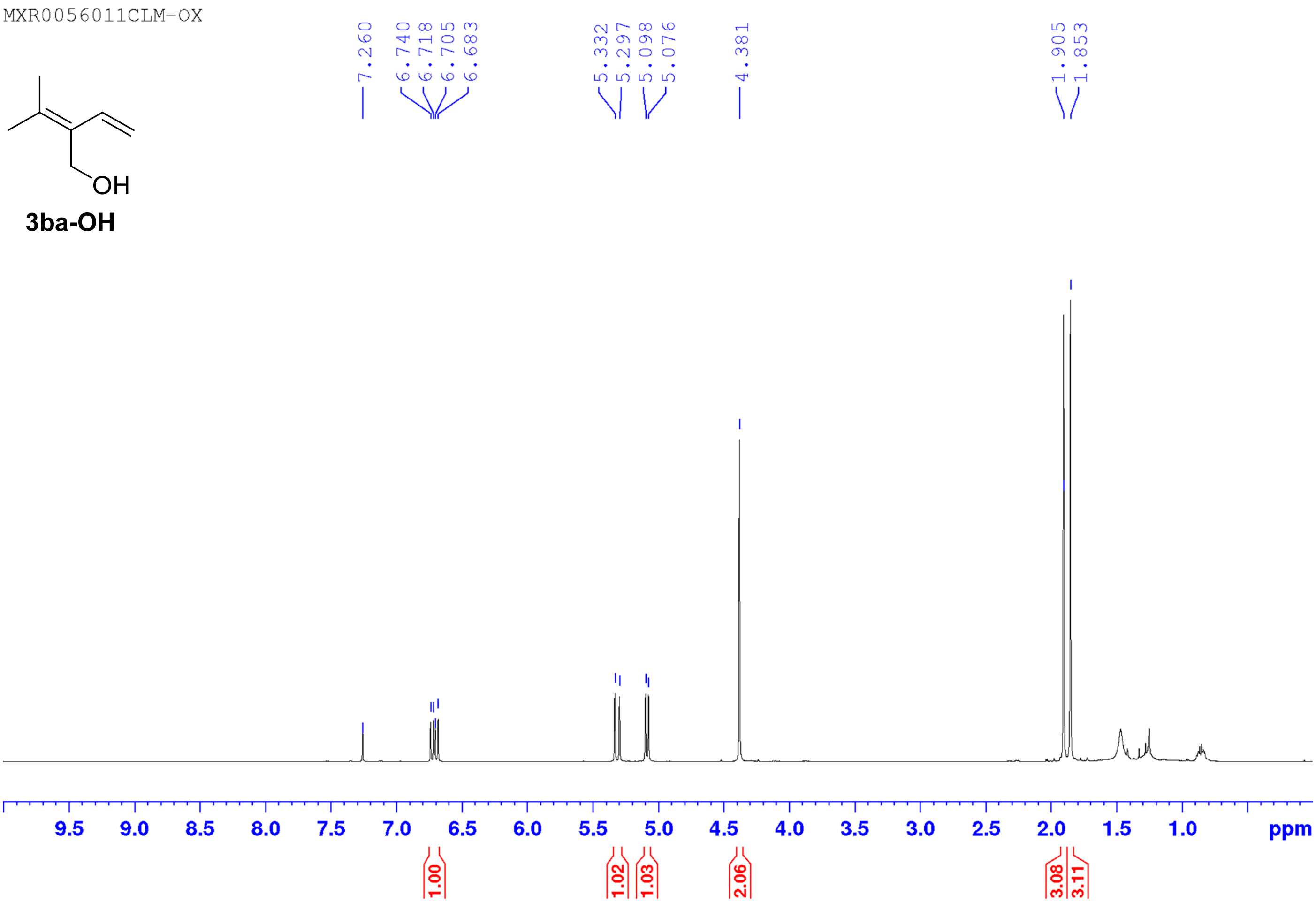

MXR0090003-C
^{n}C$_6$H$_{13}$
^{n}C$_6$H$_{13}$
Bpin
3ah
140.18
136.24
131.43
113.47
82.64
77.25
77.00
76.74
36.77
34.49
33.40
33.03
31.95
31.90
31.82
29.79
29.56
29.50
28.68
26.83
26.77
26.68
24.84
24.41
22.69
22.63
14.13
14.10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

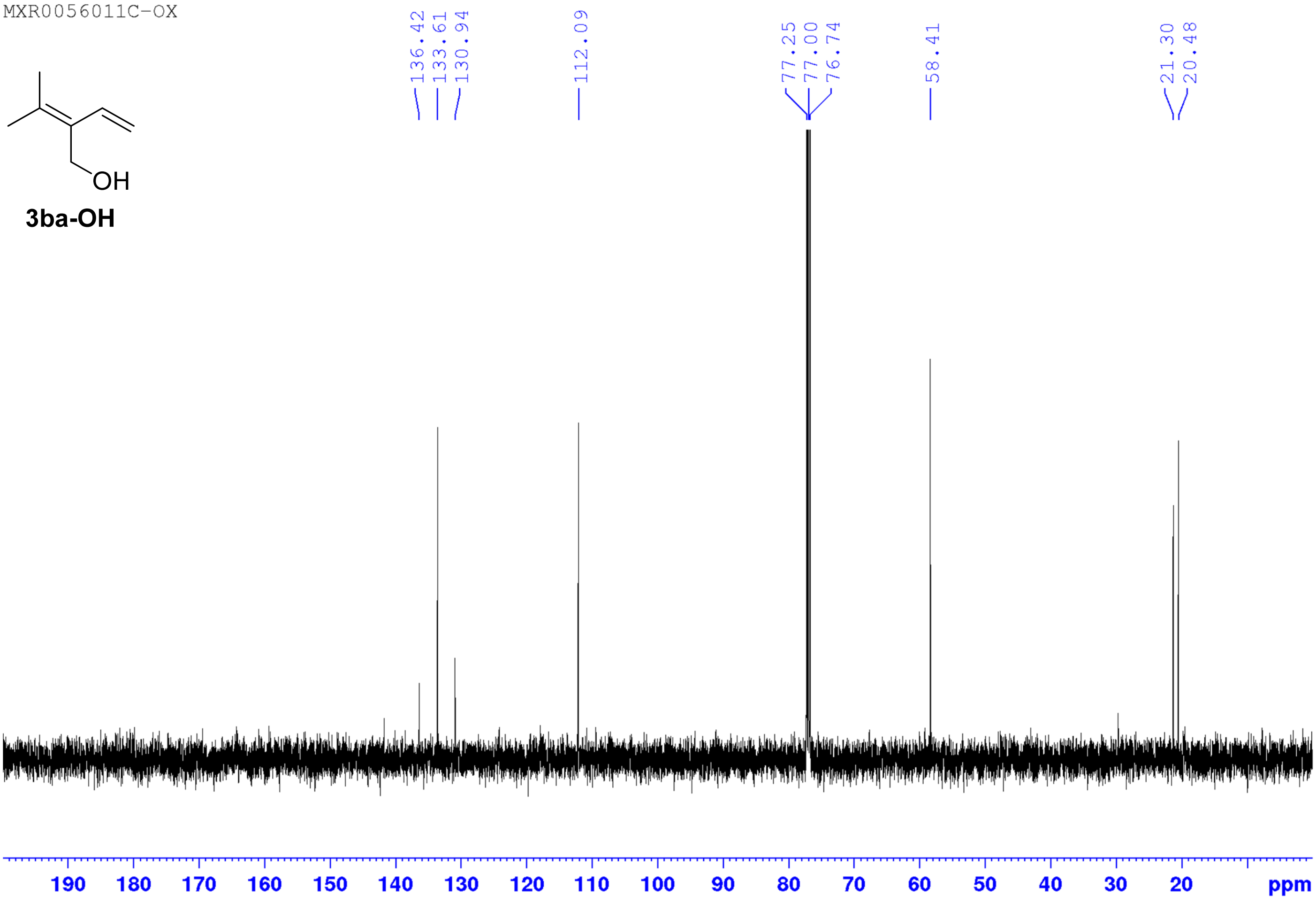

MXR0098001CLM
7.260
6.597
6.575
6.562
6.540
5.857
5.754
5.091
5.056
5.015
4.892
2.334
2.238
2.118
2.061
1.992
1.900
1.735
1.612
1.508
1.403
1.218
1.209
1.195
0.918
0.842
$^{n}C_6H_{13}$
$^{n}C_6H_{13}$
Bpin
3ai
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.13
0.88
1.15
2.94
1.16
2.14
2.16
2.19
1.25
1.20
28.91
6.25
6.48
6.66

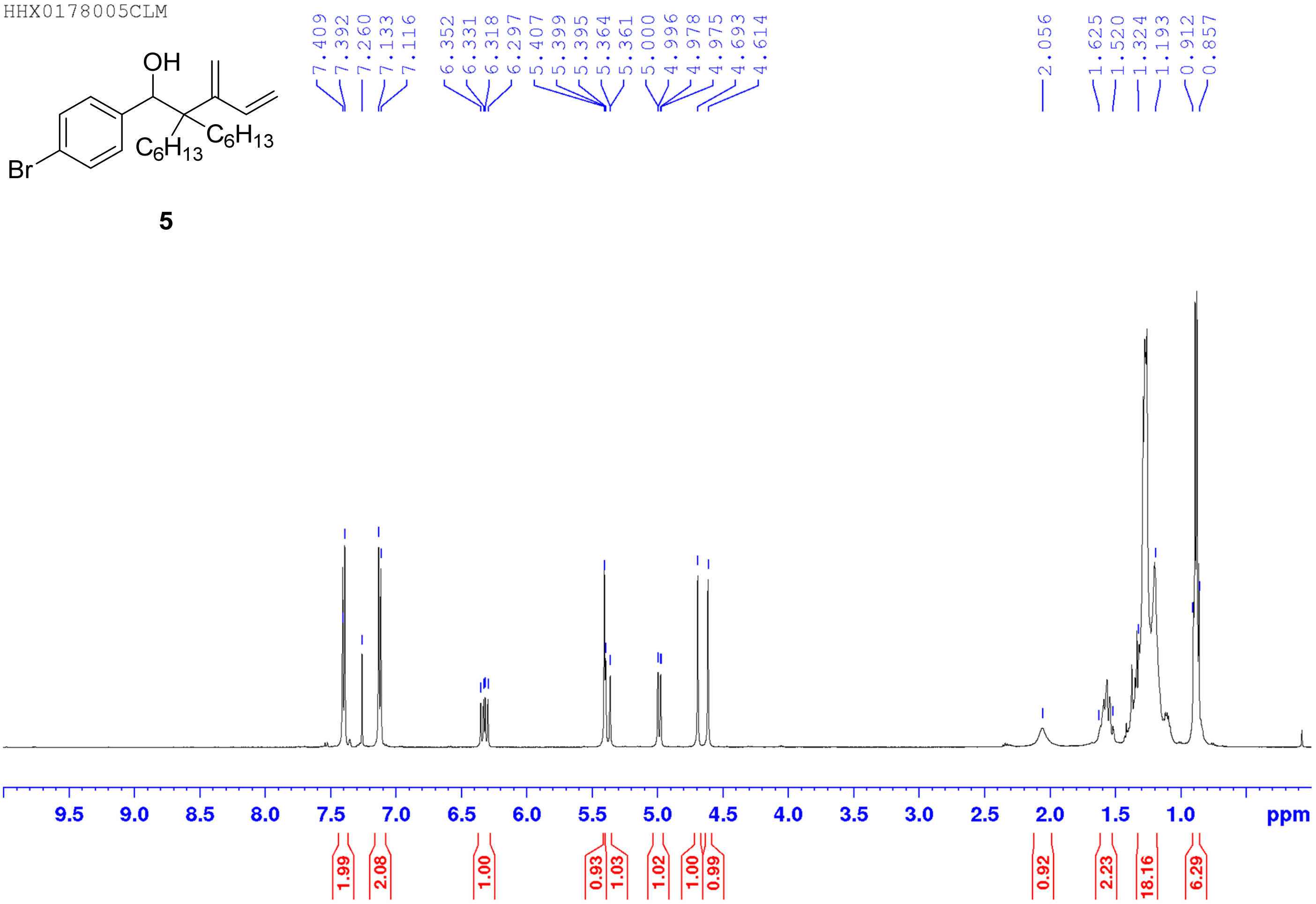

MXR0098002C
140.43
139.28
135.33
132.80
114.02
112.36
82.81
77.25
77.00
76.74
34.10
33.82
32.81
31.89
31.84
29.96
29.89
29.78
29.60
29.56
29.49
29.47
29.31
29.15
28.95
28.80
24.70
24.64
22.70
22.62
14.12
14.11
$^{n}C_6H_{13}$
$^{n}C_6H_{13}$
Bpin
3ai
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

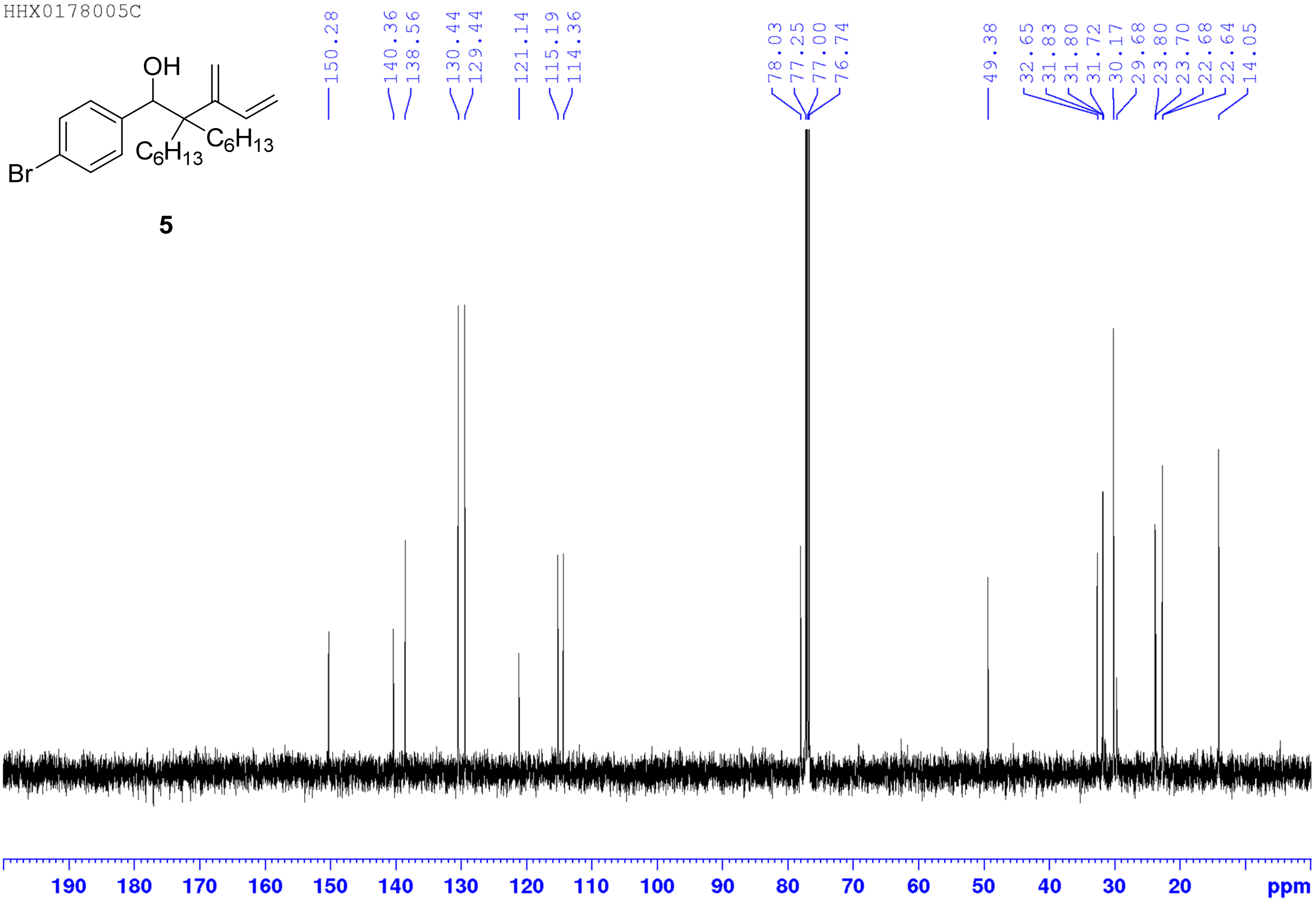

MXR0105001CLM-OX2
$^{n}C_6H_{13}$
$^{n}C_6H_{13}$
OH
3aj-OH
7.260
6.406
6.382
6.370
6.346
5.434
5.305
5.206
5.182
4.651
4.636
4.622
2.195
1.976
1.877
1.772
1.637
1.567
1.515
1.474
1.399
1.227
0.972
0.957
0.942
0.924
0.835
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.98
0.99
1.02
8.33
1.02
0.91
0.91
16.52
3.05
6.36

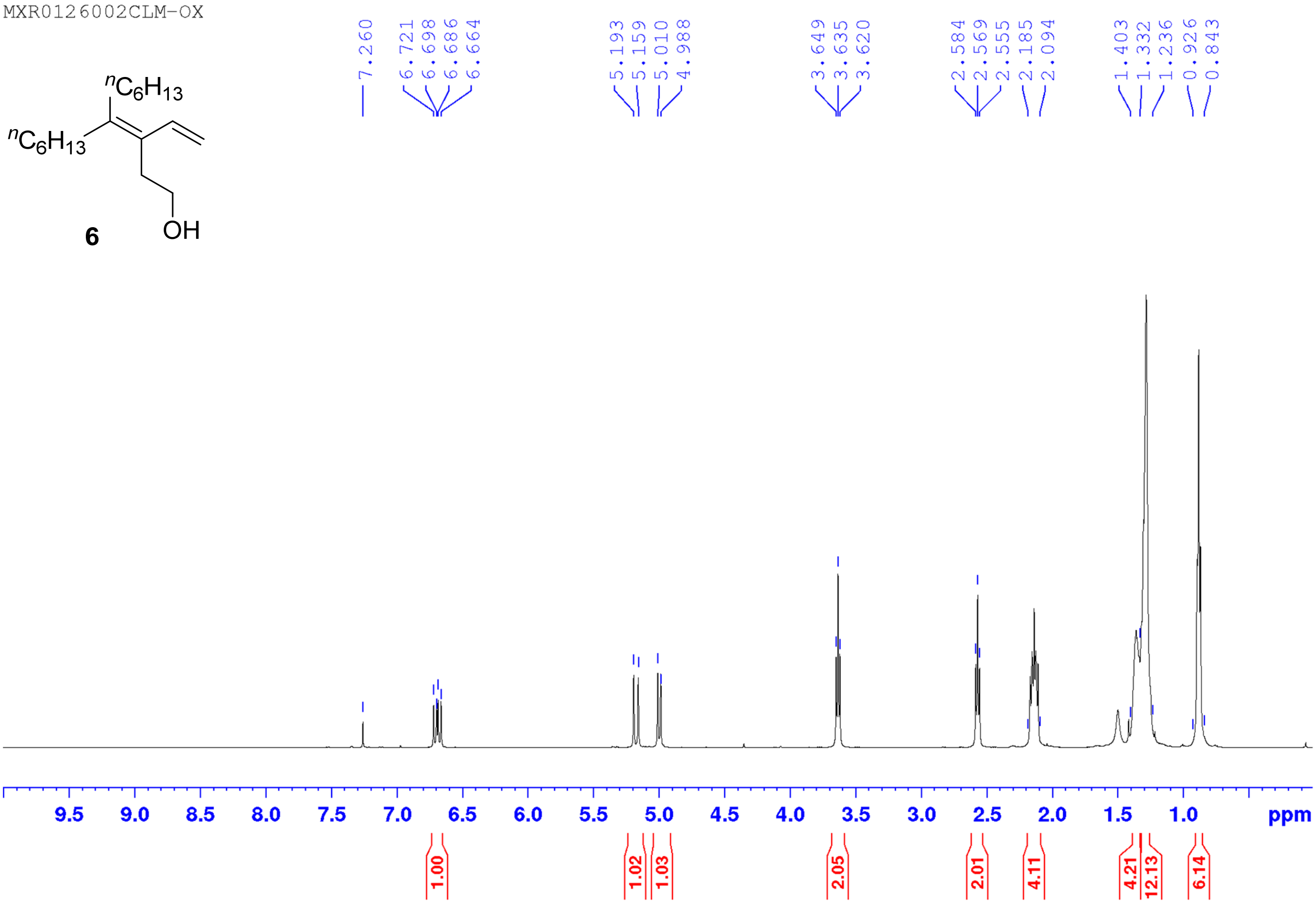

MXR0105001C-OX
$^{n}C_6H_{13}$
$^{n}C_6H_{13}$
OH
3aj-OH
141.87
133.92
132.86
132.24
128.52
116.72
77.25
77.00
76.74
70.29
36.00
33.39
32.37
31.71
29.73
29.55
29.52
29.10
23.91
22.62
20.48
14.32
14.07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

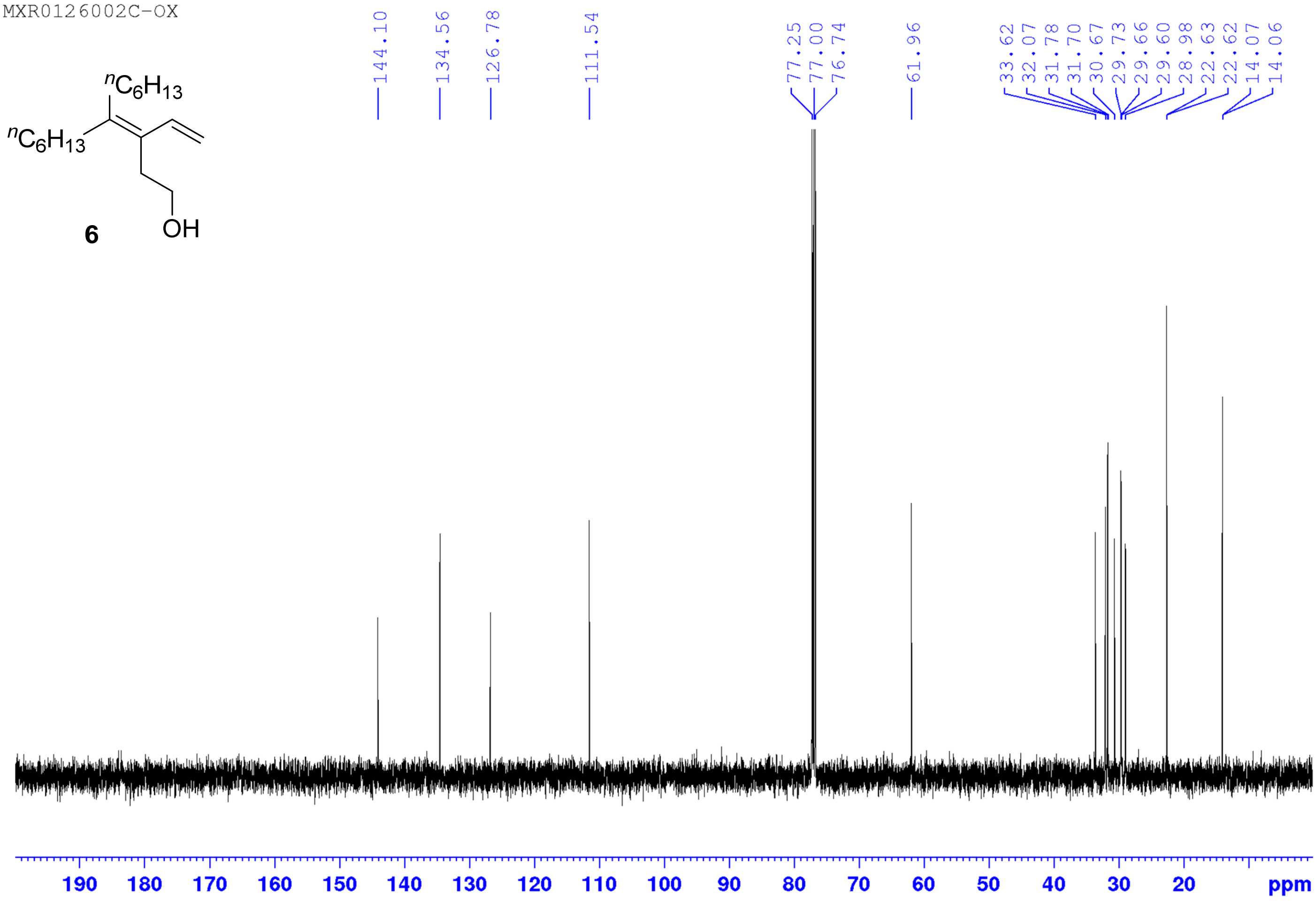

MXR0056011CLM-OX
OH
3ba-OH
7.260
6.740
6.718
6.705
6.683
5.332
5.297
5.098
5.076
4.381
1.905
1.853
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.02
1.03
2.06
3.08
3.11


MXR0056011C-OX
OH
3ba-OH
136.42
133.61
130.94
112.09
77.25
77.00
76.74
58.41
21.30
20.48
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


HHX0178005CLM
OH
Br
C6H13
C6H13
5
7.409
7.392
7.260
7.133
7.116
6.352
6.331
6.318
6.297
5.407
5.399
5.395
5.364
5.361
5.000
4.996
4.978
4.975
4.693
4.614
2.056
1.625
1.520
1.324
1.193
0.912
0.857
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.99
2.08
1.00
0.93
1.03
1.02
1.00
0.99
0.92
2.23
18.16
6.29


HHX0178005C
OH
Br
C6H13
C6H13
5
150.28
140.36
138.56
130.44
129.44
121.14
115.19
114.36
78.03
77.25
77.00
76.74
49.38
32.65
31.83
31.80
31.72
30.17
29.68
23.80
23.70
22.68
22.64
14.05
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


MXR0126002CLM-OX
$^{n}C_6H_{13}$
$^{n}C_6H_{13}$
OH
6
7.260
6.721
6.698
6.686
6.664
5.193
5.159
5.010
4.988
3.649
3.635
3.620
2.584
2.569
2.555
2.185
2.094
1.403
1.332
1.236
0.926
0.843
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.02
1.03
2.05
2.01
4.11
4.21
12.13
6.14


MXR0126002C-OX
$^{n}C_6H_{13}$
$^{n}C_6H_{13}$
OH
6
144.10
134.56
126.78
111.54
77.25
77.00
76.74
61.96
33.62
32.07
31.78
31.70
30.67
29.73
29.66
29.60
28.98
22.63
22.62
14.07
14.06
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm