Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Homoallenylboration of Carbonyl Compounds Using Inert 2-Pinacolateboryl 1,3-Butadienes via in-situ Generated Borinic-TFA Mixed Anhydrides: Efficient Synthesis of Homoallenyl Alcohols

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Electronic Supplementary Information

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1 General Information.

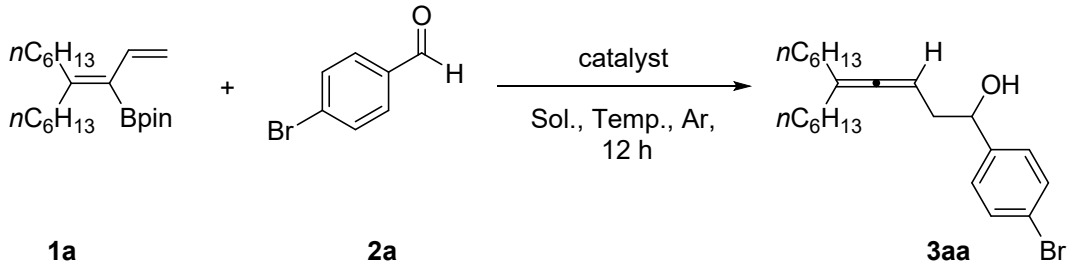
^{1}H NMR and ^{13}C NMR spectra were recorded on BRUKER AVANCE III (500 MHz) or JEOL JNM-ECZ400S/L1 (400 MHz) spectrometers. ^{11}B NMR spectra were recorded on JEOL JNM-ECZ400S/L1 (400 MHz) spectrometers. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ (internal standard: 7.26 ppm, ^{1}H; 77.0 ppm, ^{13}C), THF-d_8 (internal standard: 3.58, 1.72 ppm,^{1}H; 67.4, 25.3 ppm, ^{13}C), and DMSO-d_6 (internal standard: 2.49 ppm, ^{1}H; 39.5 ppm,^{13}C). High-resolution mass spectra (HRMS) were obtained on a Thermo Scientific Q Exactive Combined Quadrupole Orbitrap Mass Spectrometer and Waters Xevo G2QTOF Mass Spectrometer. 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).

2 Materials

Unless otherwise noted, commercially available chemicals were used as received. 2-pinacolateboyl 1,3-butadienes **1** were prepared according to reported procedures by Tsuji[1] and us[2]. The product **3be** was unambiguously confirmed by ^{1}H- and ^{13}C NMR comparing with the reported literature.[3] The structures of new products were determined by ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and high-resolution mass.

3 Experimental Procedures and Spectral Data

3.1 Initial attempts of homoallenylboration of 4-bromobenzaldehyde 2a with 2-pinacolateboyl 1,3-butadiene 1a.



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

Table S1. Initial optimization of homoallenylboration.[a]

Entry	Catalyst (20 mol%)	Temp.	Sol.	Recovery of **1a** /%[b]	Yield of **3aa** /%[b]
1	-[c]	r.t.	Toluene	100	0
2	-[c]	80 °C	Toluene	96	0
3	C_6F_5COOH	80 °C	Toluene	93	0
4	$(PhO)_2P(O)OH$	80 °C	Toluene	95	0
5[d]	$Sc(OTf)_3$	r.t.	Toluene	0	0
6[d]	$AlCl_3$	r.t.	Toluene	0	0
7[d]	$BF_3{\cdot}OEt_2$	-78 °C to r.t.	DCM	0	0

[a] Unless otherwise stated: **1a** (0.1 mmol) in solvent (1 mL), catalyst (20 mol%) and **2a** (0.15 mmol) were added into the mixture, the resulting solution performed at rt. or 80 °C for 12 hours. [b] Determined by ^1H NMR yield using Naphthene as inert standard. [c] without catalyst. [d] **1a** was completely decomposed in the reaction.

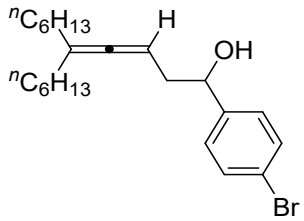
3.2 Representative Procedure for the synthesis of homoallenyl alcohols: Homoallenylboration of aldehydes 2 with 2-pinacolboryl 1,3-butadienes 1.

Step 1: To a stirred solution of 2-pinacolboryl 1,3-butadiene **1a** (104 mg, 0.30 mmol, 1.0 equiv.) in THF (1.5 mL) under Ar at –78 °C was added *n*BuLi (0.24 mL, 1.6 M, 0.375 mmol, 1.25 equiv.) dropwise. The solution was then stirred for 20 min at –78 °C, at which point TFAA (84μL, 0.60 mmol, 2.0 equiv.) was added dropwise. The reaction mixture was stirred at −78 °C for 45 min. Then, a solution of aldehyde **2a** (83 mg, 0.45 mmol) In THF (1.5 ml) was added at −78°C dropwise. The final reaction mixture was stirred at −78 °C for 30 min, then allowed to warm slowly to RT for 14 hours. After completion of reaction, the reaction was quenched with sat. $NaHCO_3$ (aq.) and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuo and used for deprotection of partially formed **3aa-TFA** directly.

Step 2: The crude residue was dissolved in MeOH (5 mL), $NaHCO_3$ (126 mg, 1.5 mmol, 5.0 equiv.) was added into the solution in one-pot. The mixture was stirred at r.t. for 12 hours. After completion of deprotection reaction, the reaction was quenched with sat. NaCl (aq.) and extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was purified by flash chromatography using EtOAc/PE (1:200-1:20) as eluent to afford pure **3aa**.

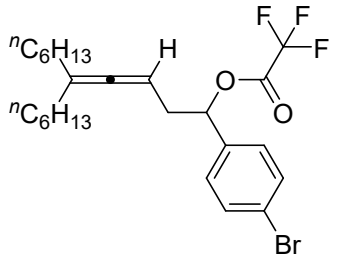
Analytical Data:

1-(4-Bromophenyl)-5-hexylundeca-3,4-dien-1-ol (3aa)



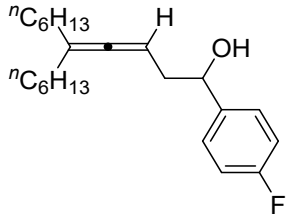
Colorless oil (110 mg, 90%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.46 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 5.34 (d, *J* = 3.8 Hz, 1H), 5.01-4.92 (m, 1H), 4.55 (dd, *J* =10.4, 5.5, Hz, 1H), 2.36-2.28 (m, 1H), 2.27-2.19 (m, 1H), 1.78-1.65 (m, 4H), 1.26-1.12 (m, 16H), 0.83 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.3, 144.6, 130.6, 128.3, 119.6, 102.8, 87.4, 71.8, 39.5, 31.8(4), 31.8(1), 31.1, 28.3(7), 28.3(5), 26.9, 26.8, 22.1, 13.9; HRMS (APCI): m/z [M-(H_2O)+H]$^+$ calcd. for [$C_{23}H_{34}Br$]$^+$ 389.18384, found 389.17432.

1-(4-Bromophenyl)-5-hexylundeca-3,4-dien-1-yl 2,2,2-trifluoroacetate (3aa-TFA)



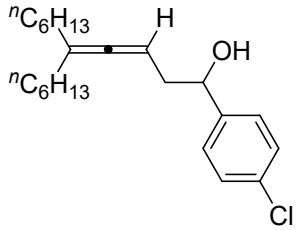
Colorless oil. NMR data:^{1}H NMR (500 MHz, THF-d_8) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.95 (t, *J* = 6.7 Hz, 1H), 5.07-4.90 (m, 1H), 2.77-2.67 (m, 1H), 2.67-2.58 (m, 1H), 1.91-1.78 (m, 4H), 1.37-1.20 (m, 16H), 0.89 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (126 MHz, THF-d_8) δ 203.5, 157.0 (q, *J* = 41.8 Hz), 138.1, 132.6, 129.7, 123.5, 115.7 (q, *J* = 286.4 Hz), 106.2, 86.5, 80.5, 36.6, 33.3, 33.2, 32.7, 30.0(4), 30.0(2), 28.5(1), 28.5(0), 23.6, 14.4; HRMS (ESI): m/z [M-OTFA]$^+$ calcd. for $[C_{23}H_{34}Br]^+$ 389.18384, found 389.18225.

1-(4-Fluorophenyl)-5-hexylundeca-3,4-dien-1-ol (3ab)



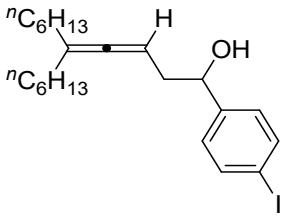
Colorless oil (67 mg, 64%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.30 (dd, *J* = 7.9, 7.9 Hz, 2H), 7.08 (dd, *J* = 8.8, 8.8 Hz, 2H), 5.27 (d, *J* = 4.1 Hz, 1H), 5.01-4.92 (m, 1H), 4.56 (dd, *J* = 10.4, 5.7 Hz, 1H), 2.37-2.28 (m, 1H), 2.27-2.19 (m, 1H), 1.78-1.65 (m, 4H), 1.26-1.13 (m, 16H), 0.83 (t, *J* = 6.5 Hz, 6H);^{13}C NMR (126 MHz, DMSO-d_6) δ 201.3, 161.1 (d, *J* = 242.1 Hz), 141.3 (d, *J* = 2.8 Hz), 127.9 (d, *J* = 8.2 Hz), 114.3 (d, *J* = 20.9 Hz), 102.7, 87.6, 71.9, 39.7, 31.8(5), 31.8(1), 31.1, 28.3(4), 28.3(2), 26.8, 22.1(1), 22.1(0), 13.8; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for $[C_{23}H_{34}F]^+$ 329.26391,found 329.26346.

1-(4-Chlorophenyl)-5-hexylundeca-3,4-dien-1-ol (3ac)



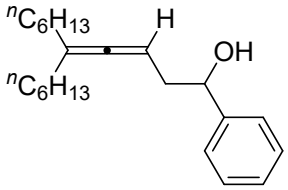
Colorless oil (81mg, 75%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.32 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 5.33 (d, *J* = 3.9 Hz, 1H), 5.01-4.92 (m, 1H), 4.57 (dd, *J* = 10.6, 5.7 Hz, 1H), 2.37-2.28 (m, 1H), 2.28-2.20 (m, 1H), 1.81-1.64 (m, 4H), 1.27-1.14 (m, 16H), 0.83 (t, *J* = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.3, 144.1, 131.1, 127.9, 127.7, 102.8, 87.4, 71.8, 39.7, 31.8, 31.7, 31.1, 28.3(3), 28.3(1), 26.8(9), 26.8(7), 22.1, 13.9; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for $[C_{23}H_{34}Cl]^+$ 345.23436, found 345.23373.

5-Hexyl-1-(4-iodophenyl)undeca-3,4-dien-1-ol (3ad)



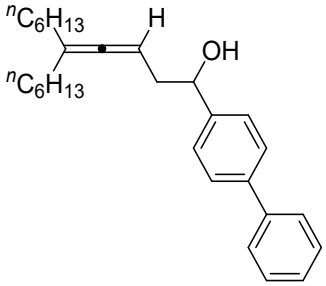
Colorless oil (82 mg, 60%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 5.31 (d, *J* = 3.7 Hz, 1H), 5.01-4.92 (m, 1H), 4.53 (dd, *J* = 10.4, 5.9 Hz, 1H), 2.36-2.28 (m, 1H), 2.27-2.19 (m, 1H), 1.78-1.65 (m, 4H), 1.26-1.12 (m, 16H), 0.84 (t, *J* = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.3, 145.0, 136.4, 128.5, 102.8, 92.3, 87.4, 71.9, 39.7, 31.8, 31.7, 31.1, 28.3, 26.9, 26.8, 22.1, 13.9; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for [$C_{23}H_{34}I$]$^+$ 437.16997, found 437.16852.

5-Hexyl-1-phenylundeca-3,4-dien-1-ol (3ae)



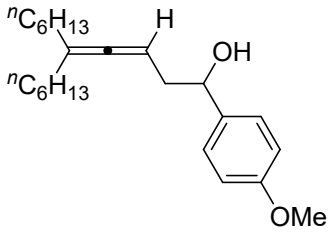
Colorless oil (63 mg, 64%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.27 (d, *J* = 4.2 Hz, 4H), 7.22-7.17 (m, 1H), 5.23 (d, *J* = 4.0 Hz, 1H), 5.01-4.92 (m, 1H), 4.54 (dd, *J* = 10.6, 6.1 Hz, 1H), 2.35-2.29 (m, 1H), 2.26-2.20 (m, 1H),1.80-1.70 (m, 4H), 1.27-1.15 (m, 16H), 0.84 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.3, 145.3, 127.7, 126.6, 126.0, 102.7, 87.9, 72.7, 39.8, 31.8(6), 31.8(3), 31.1, 28.3, 26.9, 22.1, 13.9; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for [$C_{23}H_{35}$]$^+$ 311.27333, found 311.27161.

1-([1,1'-Biphenyl]-4-yl)-5-hexylundeca-3,4-dien-1-ol (3af)



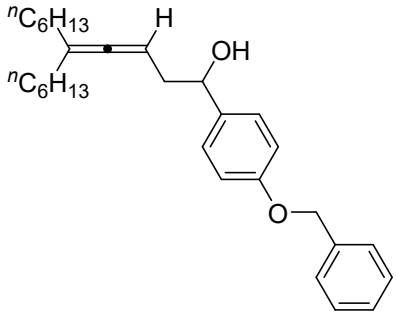
White solid (92 mg, 76%), mp 50.6-50.9 °C; NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 5.27 (d, *J* = 4.0 Hz, 1H), 5.04-4.97 (m, 1H), 4.60 (dd, *J* = 10.3, 5.8 Hz, 1H), 2.41-2.34 (m, 1H), 2.33-2.25 (m, 1H), 1.78-1.69 (m, 4H), 1.22-1.10 (m, 16H), 0.78 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.3, 144.5, 140.1, 138.5, 128.8, 127.1, 126.7, 126.4, 126.0, 102.8, 87.8, 72.4, 39.7, 31.8(9), 31.8(6), 31.1(7), 31.1(6), 28.4, 26.9, 22.1, 13.8; HRMS (ESI): m/z calcd. for [$C_{29}H_{40}ONa$]$^+$ 427.29714, found 427.29572.

5-Hexyl-1-(4-methoxyphenyl)undeca-3,4-dien-1-ol (3ag)



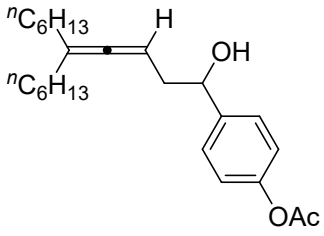
Colorless oil (63 mg, 59%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.18 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.2 Hz, 2H), 5.10 (d, *J* = 4.0 Hz, 1H), 4.98-4.91 (m, 1H), 4.48 (dd, *J* = 10.5, 6.0 Hz, 1H), 3.70 (s, 3H), 2.34-2.27 (m, 1H), 2.23-2.16 (m, 1H), 1.79-1.71 (m, 4H), 1.25-1.16 (m, 16H), 0.83 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.2, 158.0, 137.3, 127.1, 113.1, 102.7, 88.0, 72.3, 54.8, 39.7, 31.8(6), 31.8(4), 31.1(4), 31.1(1), 28.3, 26.9, 22.1, 13.9; HRMS (ESI): m/z calcd. for $[C_{24}H_{38}O_2Na]^+$ 381.27640, found 381.27509.

1-(4-(Benzyloxy)phenyl)-5-hexylundeca-3,4-dien-1-ol (3ah)



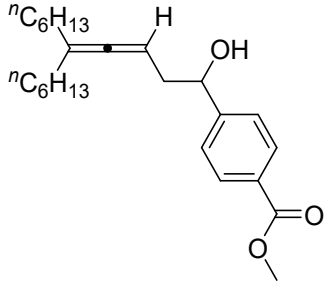
Colorless oil (87 mg, 67%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 5.10 (d, *J* = 4.0 Hz, 1H), 5.05 (s, 2H), 4.99-4.91 (m, 1H), 4.48 (dd, *J* = 10.5, 6.0 Hz, 1H), 2.35-2.27 (m, 1H), 2.25-2.17 (m, 1H), 1.79-1.71 (m, 4H), 1.25-1.16 (m, 16H), 0.82 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.2, 157.2, 137.6, 137.2, 128.3, 127.7, 127.4, 127.2, 114.0, 102.7, 88.0, 72.3, 69.0, 39.7, 31.8(8), 31.8(4), 31.1(7), 31.1(5), 28.3, 26.9, 22.1, 13.9; HRMS (APCI): m/z $[M-(H_2O)+H]^+$ Calcd. for $[C_{30}H_{41}O]^+$ 417.31519; found 417.30786.

4-(5-hexyl-1-hydroxyundeca-3,4-dien-1-yl)phenyl acetate (3ai)



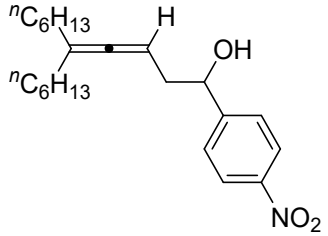
Colorless oil (65mg, 56%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 5.28 (d, *J* = 4.0 Hz, 1H), 5.02-4.92 (m, 1H), 4.55 (dd, *J* = 10.5, 5.9 Hz, 1H), 2.36-2.28 (m, 1H), 2.27-2.19 (m, 1H), 2.23 (s, 3H), 1.82-1.70 (m, 4H), 1.26-1.16 (m, 16H), 0.83 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.3, 169.1, 149.2, 127.0, 121.0, 102.8, 87.8, 72.1, 39.7, 31.8(5), 31.8(2), 31.1, 28.3, 26.9, 22.1, 20.8, 13.9; HRMS (ESI): m/z calcd. for $[C_{25}H_{38}O_3Na]^+$ 409.27132, found 409.26969.

Methyl 4-(5-hexyl-1-hydroxyundeca-3,4-dien-1-yl)benzoate (3aj)



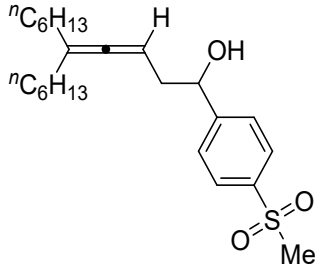
Colorless oil (87 mg, 75%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.89 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 5.43 (d, *J* = 3.7 Hz, 1H), 5.03-4.95 (m, 1H), 4.66 (dd, *J* = 10.3, 5.9 Hz, 1H), 3.81 (s, 3H), 2.39-2.33 (m, 1H), 2.25-2.32 (m, 1H), 1.72-1.64 (m, 4H), 1.25-1.09 (m, 16H), 0.82 (t, *J* = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.3, 166.1, 150.8, 128.7, 128.0, 126.4, 102.9, 87.3, 72.1, 51.8, 39.7, 31.8(9), 31.8(5), 31.1, 28.4, 26.9, 26.8, 22.1, 13.8; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for [$C_{25}H_{37}O_2$]$^+$ 369.27881, found 369.27780.

5-Hexyl-1-(4-nitrophenyl)undeca-3,4-dien-1-ol (3ak)



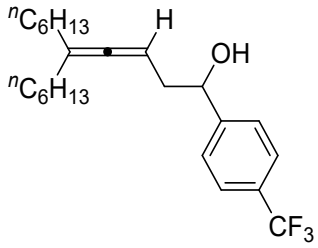
Yellow oil (72 mg, 64%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 5.60 (d, *J* = 4.0 Hz, 1H), 5.05-4.96 (m, 1H), 4.76 (dd, *J* = 10.5, 5.7 Hz, 1H), 2.41-2.28 (m, 2H), 1.71-1.63 (m, 4H), 1.22-1.05 (m, 16H), 0.82 (t, *J* = 7.0 Hz, 3H), 0.81 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.4, 153.2, 146.2, 127.3, 122.9, 103.0, 86.9, 71.5, 39.7, 31.8(3), 31.8(0), 31.1, 28.3, 26.9, 26.8, 22.1, 13.8; HRMS (ESI): m/z calcd. for [$C_{23}H_{35}NO_3Na$]$^+$ 396.25092, found 396.25012.

5-Hexyl-1-(4-(methylsulfonyl)phenyl)undeca-3,4-dien-1-ol (3al)



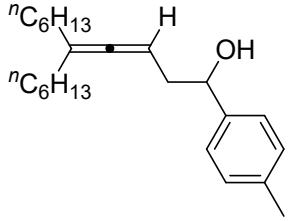
Colorless oil (61 mg, 50%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 5.50 (d, *J* = 4.1 Hz, 1H), 5.04-4.95 (m, 1H), 4.68 (dd, *J* = 10.5, 5.8 Hz, 1H), 3.15 (s, 3H), 2.39-2.25 (m, 2H), 1.79-1.69 (m, 4H), 1.26-1.14 (m, 16H), 0.83 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.4, 151.2, 139.1, 126.9, 126.6, 102.9, 87.3, 71.9, 43.6, 39.7, 31.7, 31.1, 28.2, 26.8, 22.1, 13.9; HRMS (ESI): m/z calcd. for [$C_{24}H_{38}O_3SNa$]$^+$ 429.24339, found 429.24268.

5-Hexyl-1-(4-(trifluoromethyl)phenyl)undeca-3,4-dien-1-ol (3am)



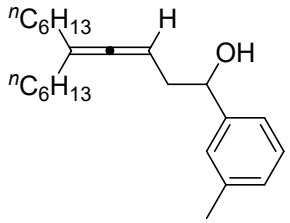
Brown oil (73 mg, 61%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 5.48 (d, *J* = 3.9 Hz, 1H), 5.03-4.95 (m, 1H), 4.68 (dd, *J* = 10.6, 6.0 Hz, 1H), 2.40-2.33 (m, 1H), 2.32-2.25 (m, 1H), 1.73-1.64 (m, 4H), 1.24-1.10 (m, 16H), 0.82 (t, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.4, 149.9, 127.3 (q, *J* = 32.2 Hz), 126.8, 124.6 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 272.1 Hz), 102.8, 87.2, 71.8, 39.7, 31.7(7), 31.7(3), 31.0, 28.2, 26.8(7), 26.8(4), 22.1, 13.8; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for [$C_{24}H_{34}F_3$]$^+$ 379.26071, found 379.25940.

5-Hexyl-1-(p-tolyl)undeca-3,4-dien-1-ol (3an)



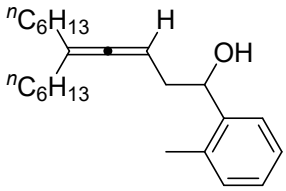
Colorless oil (75mg, 73%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.15 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 5.15 (d, *J* = 4.0 Hz, 1H), 5.00-4.90 (m, 1H), 4.49 (dd, *J* = 10.4, 5.8 Hz, 1H), 2.34-2.27 (m, 1H), 2.25 (s, 3H), 2.25-2.17 (m, 1H), 1.79-1.70 (m, 4H), 1.25-1.15 (m, 16H), 0.83 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.2, 142.3, 135.5, 128.3, 126.0, 102.7, 87.9, 72.5, 39.7, 31.8(4), 31.8(1), 31.1, 28.3, 26.8, 22.1(3), 22.1(1), 20.6, 13.9; HRMS (ESI): m/z calcd. for [$C_{24}H_{38}ONa$]$^+$ 365.28149, found 365.28067.

5-Hexyl-1-(*m*-tolyl)undeca-3,4-dien-1-ol (3ao)



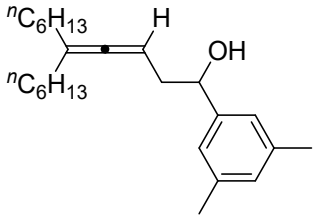
Colorless oil (67 mg, 65%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.15 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.08 (s, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 5.17 (d, *J* = 4.0 Hz, 1H), 5.00-4.94 (m, 1H), 4.49 (dd, *J* = 10.3, 5.7 Hz, 1H), 2.35-2.28 (m, 1H), 2.26 (s, 3H), 2.25-2.18 (m, 1H), 1.80-1.68 (m, 4H), 1.26-1.15 (m, 16H), 0.83 (t, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.2, 145.2, 136.6, 127.6, 127.2, 126.7, 123.1, 102.7, 87.9, 72.7, 39.7, 31.8(6), 31.8(3), 31.1, 28.3, 26.9, 22.1(5), 22.1(3), 21.0, 13.9; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for [$C_{24}H_{37}$]$^+$ 325.28898, found 325.28827.

5-Hexyl-1-(*o*-tolyl)undeca-3,4-dien-1-ol (3ap)



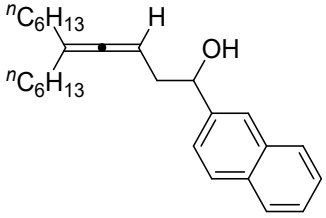
Colorless oil (64 mg, 62%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.38 (d, *J* = 7.5 Hz, 1H), 7.18-7.11 (m, 1H), 7.11-7.04 (m, 2H), 5.10 (d, *J* = 3.9 Hz, 1H), 5.07-5.01 (m, 1H), 4.77 (dd, *J* = 10.8, 6.1 Hz, 1H), 2.28-2.20 (m, 5H), 1.81-1.72 (m, 4H), 1.28-1.16 (m, 16H), 0.83 (t, *J* = 6.5 Hz, 3H), 0.82 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.1, 143.4, 133.7, 129.6, 126.2, 125.6, 125.5, 102.8, 88.2, 69.0, 38.7, 31.8, 31.1(7), 31.1(3), 28.3(6), 28.3(0), 26.9(9), 26.9(1), 22.0, 18.6, 13.8; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for $[C_{24}H_{37}]^+$ 325.28898, found 325.28806.

1-(3,5-Dimethylphenyl)-5-hexylundeca-3,4-dien-1-ol (3aq)



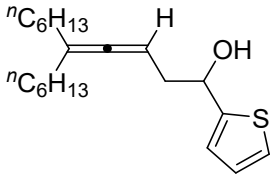
Colorless oil (99 mg, 93%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 6.86 (s, 2H), 6.81 (s, 1H), 5.11 (d, *J* = 3.9 Hz, 1H), 5.00-4.93 (m, 1H), 4.45 (dd, *J* = 10.4, 5.9 Hz, 1H), 2.32-2.25 (m, 1H), 2.22 (s, 6H), 2.22-2.16 (m, 1H), 1.80-1.71 (m, 4H), 1.26-1.15 (m, 16H), 0.83 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.2, 145.2, 136.4, 127.9, 123.8, 102.6, 88.0, 72.8, 39.7, 31.8(7), 31.8(3), 31.1(7), 31.1(6), 28.3, 26.8, 22.1(4), 22.1(2), 20.9, 13.8; HRMS (APCI): m/z [M-(H_2O)+H]$^+$ calcd. for $[C_{25}H_{39}]^+$ 339.30463, found 339.29694.

5-Hexyl-1-(naphthalen-2-yl)undeca-3,4-dien-1-ol (3ar)



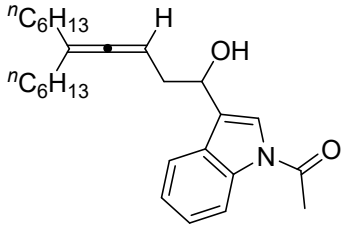
Colorless oil (45 mg, 40%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.88-7.80 (m, 3H), 7.76 (s, 1H), 7.50-7.40 (m, 3H), 5.38 (d, *J* = 3.4 Hz, 1H), 5.07-4.98 (m, 1H), 4.73 (dd, *J* = 10.4, 6.6 Hz, 1H), 2.46-2.33 (m, 2H), 1.71-1.61 (m, 4H), 1.20-1.00 (m, 16H), 0.80 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.3, 142.7, 132.7, 132.3, 127.6, 127.4, 127.3, 125.8, 125.3, 124.7, 124.5, 102.8, 87.7, 72.7, 39.7, 31.8, 31.7, 31.0(6), 31.0(4), 28.2, 26.8(7), 26.8(6), 22.1(2), 22.1(1), 13.9; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for $[C_{27}H_{37}]^+$ 361.28898, found 361.28711.

5-Hexyl-1-(thiophen-2-yl)undeca-3,4-dien-1-ol (3as)



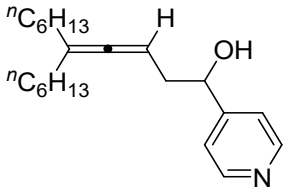
Colorless oil (42 mg, 42%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.35 (d, *J* = 4.8 Hz 1H), 6.95-6.87 (m, 2H), 5.61 (d, *J* = 4.5 Hz, 1H), 5.05-4.98 (m, 1H), 4.77 (dd, *J* = 11.1, 6.1 Hz, 1H), 2.42-2.34 (m, 1H), 2.33-2.25 (m, 1H), 1.84-1.76 (m, 4H), 1.28-1.17 (m, 16H), 0.83 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.3, 149.7, 126.2, 123.9, 123.0, 103.0, 87.7, 68.7, 39.7, 31.8(5), 31.8(2), 31.1, 28.3(3), 28.3(2), 26.9, 22.1, 13.9; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for [$C_{21}H_{33}S$]$^+$ 317.22975, found 317.22925.

1-(3-(5-Hexyl-1-hydroxyundeca-3,4-dien-1-yl)-1H-indol-1-yl)ethan-1-one (3at)



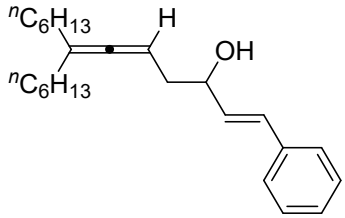
Colorless oil (65mg, 53%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.70-7.59 (m, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 5.31 (d, *J* = 4.4 Hz, 1H), 5.16-5.04 (m, 1H), 4.84 (dd, *J* = 11.3, 6.2 Hz, 1H), 2.60 (s, 3H), 2.56-2.42 (m, 2H), 1.72-1.63 (m, 4H), 1.21-1.09 (m, 16H), 0.81 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.1, 169.0, 135.5, 128.9, 125.4, 124.4, 123.1, 122.8, 119.9, 115.9, 102.9, 88.0, 66.3, 37.8, 31.8, 31.0, 28.3, 26.8(7), 26.8(4), 23.7, 22.0, 13.8; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for [$C_{27}H_{38}NO$]$^+$ 392.29479, found 392.29315.

5-Hexyl-1-(pyridin-4-yl)undeca-3,4-dien-1-ol (3au)



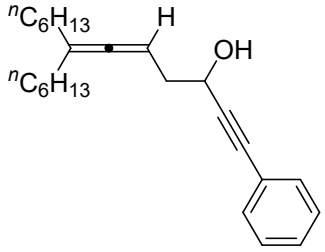
Colorless oil (48 mg, 49%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 8.46 (s, 2H), 7.28 (d, *J* = 4.8 Hz, 2H), 5.48 (d, *J* = 4.3 Hz, 1H), 5.04-4.95 (m, 1H), 4.59 (dd, *J* = 10.5, 5.6 Hz, 1H), 2.35-2.24 (m, 2H), 1.78-1.67 (m, 4H), 1.25-1.14 (m, 16H), 0.83 (t, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.4, 153.7, 149.1, 121.3, 102.9, 87.1, 71.2, 39.1, 31.7, 31.0(9), 31.0(7), 28.2, 26.8(6), 26.8(2), 22.1, 13.9; HRMS (APCI): m/z [M+H]$^+$ calcd. for [$C_{22}H_{36}NO$]$^+$, 330.27914, found 330.27231.

7-Hexyl-1-phenyltrideca-1,5,6-trien-3-ol 3(av)



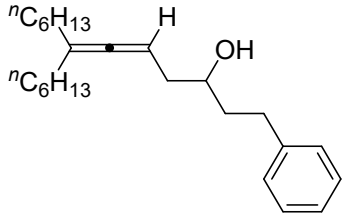
Colorless oil (66 mg, 62%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.26 (dd, *J* = 15.9, 5.9 Hz, 1H), 5.12-5.04 (m, 1H), 4.98 (d, *J* = 4.3 Hz, 1H), 4.19-4.12 (m, 1H), 2.25-2.16 (m, 1H), 2.16-2.07 (m, 1H), 1.89-1.78 (m, 4H), 1.35-1.27 (m, 4H), 1.25-1.15 (m, 12H), 0.81 (t, *J* = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.2, 136.8, 133.4, 128.4(7), 128.4(6), 127.1, 126.0, 102.9, 87.8, 71.0, 38.0, 31.9(7), 31.9(4), 31.1(3), 31.1(0), 28.3, 27.0, 22.1, 13.8; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for [$C_{25}H_{37}$]$^+$ 337.28898, found 337.28821.

7-Hexyl-1-phenyltrideca-5,6-dien-1-yn-3-ol (3aw)



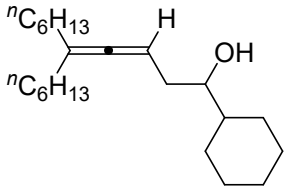
Colorless oil (76mg, 72%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.50-7.20 (m, 5H), 5.56 (s, 1H), 5.21-5.05 (m, 1H), 4.44 (t, *J* = 6.6 Hz, 1H), 2.40-2.20 (m, 2H), 1.94-1.78 (m, 4H), 1.40-1.29 (m, 4H), 1.24-1.12 (m, 12H), 0.80 (t, *J* = 6.3 Hz, 3H), 0.79 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.4, 131.1, 128.5, 128.2, 122.5, 103.4, 92.0, 87.1, 83.2, 61.2, 38.3, 31.9(5), 31.9(0), 31.1(1), 31.1(0), 28.3(7), 28.3(5), 27.0, 22.1(1), 22.1(0), 13.8; HRMS (ESI): m/z calcd. for [$C_{25}H_{36}ONa$]$^+$ 375.26584, found 375.26474.

7-Hexyl-1-phenyltrideca-5,6-dien-3-ol (3ax)



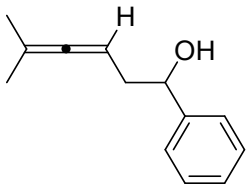
Colorless oil (96 mg, 90%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.23 (t, *J* = 7.4 Hz, 2H), 7.20-7.08 (m, 3H), 5.11-5.03 (m, 1H), 4.58 (d, *J* = 5.0 Hz, 1H), 3.50-3.43 (m, 1H), 2.75-2.65 (m, 1H), 2.57-2.52 (m, 1H), 2.11-2.05 (m, 1H), 2.04-1.97 (m, 1H), 1.89-1.79 (m, 4H), 1.76-1.69 (m, 1H), 1.60-1.51 (m, 1H), 1.34-1.15 (m, 16H), 0.82 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.1, 142.3, 128.0, 125.4, 102.6, 88.2, 69.3, 38.0, 37.8, 32.0, 31.9, 31.4, 31.1(6), 31.1(5), 28.3, 27.0, 22.1, 13.8; HRMS (ESI): m/z calcd. for [$C_{25}H_{40}ONa$]$^+$ 379.29714, found 379.29529.

1-Cyclohexyl-5-hexylundeca-3,4-dien-1-ol (3ay)



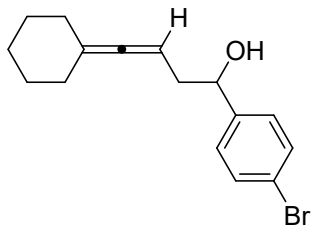
Colorless oil (67 mg, 67%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 5.14-5.02 (m, 1H), 4.33 (d, *J* = 5.1 Hz, 1H), 3.25-3.18 (m, 1H), 2.08-1.96 (m, 2H), 1.91-1.80 (m, 4H), 1.75-1.64 (m, 3H), 1.58 (d, *J* = 10.4 Hz, 1H), 1.51 (d, *J* = 11.6 Hz, 1H), 1.36-1.21 (m, 16H), 1.16-0.99 (m, 5H), 0.97-0.91 (m, 1H), 0.83 (t, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 200.9, 102.4, 88.4, 74.0, 41.8, 34.7, 32.0, 31.9, 31.2(1), 31.2(0), 29.1, 28.3(8), 28.3(4), 27.0, 26.9, 26.2, 26.0, 25.8, 22.1, 13.8; HRMS (ESI): m/z [M+H]$^{+}$ calcd. for [$C_{23}H_{43}O$]$^{+}$ 335.33084, found 335.32932.

5-Methyl-1-phenylhexa-3,4-dien-1-ol (3be)



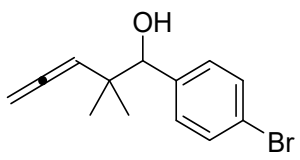
Colorless oil (45 mg, 80%). NMR data:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.31 (m, 4H), 7.30-7.24 (m, 1H), 5.00-4.92 (m, 1H), 4.74 (dd, *J* = 6.4, 6.4 Hz, 1H), 2.49-2.35 (m, 2H), 2.19 (br s, 1H), 1.65 (d, *J* = 2.0 Hz, 3H), 1.63 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.2, 143.7, 128.2, 127.3, 125.9, 95.5, 84.6, 73.5, 39.2, 20.6, 20.4; HRMS (ESI): m/z calcd. for [$C_{13}H_{16}ONa$]$^{+}$ 211.10934, found 211.10927.

1-(4-Bromophenyl)-4-cyclohexylidenebut-3-en-1-ol (3ca)



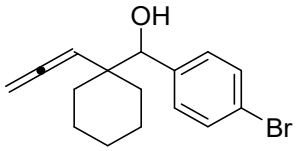
Colorless oil (73 mg, 79%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* =8.0 Hz, 2H), 5.43 (d, *J* = 4.1 Hz, 1H), 4.89-4.80 (m, 1H), 4.55 (dd, *J* = 10.5, 5.5 Hz, 1H), 2.33-2.25 (m, 1H), 2.25-2.17 (m, 1H), 1.89-1.78 (m, 4H), 1.47-1.35 (m, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 199.3, 144.6, 130.5, 128.4, 119.5, 100.9, 84.7, 71.8, 39.7, 30.8, 26.8(9), 26.8(7), 25.5; HRMS (ESI): m/z [(M-(H_2O)+H]$^{+}$ calcd. for [$C_{16}H_{18}Br$]$^{+}$ 289.05864, found 289.05780.

1-(4-Bromophenyl)-2,2-dimethylpenta-3,4-dien-1-ol (3da)



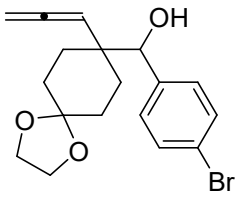
Colorless oil (49 mg, 61%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.46 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* =8.1 Hz, 2H), 5.43 (d, *J* = 4.0 Hz, 1H), 5.25 (t, *J* = 6.6 Hz, 1H), 4.65 (d, *J* = 6.6 Hz, 2H), 4.29 (d, *J* = 3.8 Hz, 1H), 0.93 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 206.5, 142.2, 129.9, 129.8, 119.7, 97.3, 78.7, 76.4, 39.7, 24.4, 24.0; HRMS (ESI): m/z [(M-(H_2O)+H]$^+$ calcd. for [$C_{13}H_{14}Br$]$^+$ 249.02734, found 249.02701.

(4-Bromophenyl)(1-(propa-1,2-dien-1-yl)cyclohexyl)methanol (3ea)



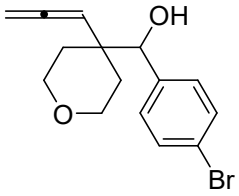
Colorless oil (57 mg, 62%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* =8.0 Hz, 2H), 5.34 (d, *J* = 3.9 Hz, 1H), 4.86 (t, *J* = 6.5 Hz, 1H), 4.60 (dd, *J* = 10.1, 6.8 Hz, 1H), 4.53 (dd, *J* = 10.1, 6.7 Hz, 1H), 4.26 (d, *J* = 3.6 Hz, 1H), 1.63 (d, *J* = 11.3 Hz, 1H), 1.55-1.44 (m, 2H), 1.45-1.27 (m, 5H), 1.17-1.05 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 208.3, 141.8, 130.1, 129.6, 119.6, 93.7, 79.5, 75.7, 43.0, 32.2, 31.8, 25.7, 21.9, 21.6; HRMS (ESI): m/z [(M-(H_2O)+H]$^+$ calcd. for [$C_{16}H_{18}Br$]$^+$ 289.05864, found 289.05817.

(4-Bromophenyl)(8-(propa-1,2-dien-1-yl)-1,4-dioxaspiro[4.5]decan-8-yl)methanol (3fa)



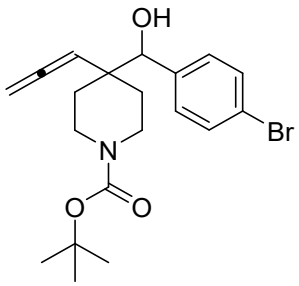
Colorless oil (77mg, 70%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.40 (d, *J* = 4.1 Hz, 1H), 4.90 (t, *J* = 6.4 Hz, 1H), 4.64 (dd, *J* = 10.3, 6.8 Hz, 1H), 4.57 (dd, *J* = 10.3, 6.8 Hz, 1H), 4.28 (d, *J* = 3.5 Hz, 1H), 3.85-3.77 (m, 4H), 1.71-1.45 (m, 7H), 1.19-1.10 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 208.1, 141.8, 130.1, 129.7, 119.8, 108.1, 92.7, 79.1, 76.0, 63.5, 63.4, 42.3, 30.8, 30.5, 29.7, 29.2; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for [$C_{18}H_{20}BrO_2$]$^+$ 347.06412, found 347.06345.

(4-Bromophenyl)(4-(propa-1,2-dien-1-yl)tetrahydro-2H-pyran-4-yl)methanol (3ga)



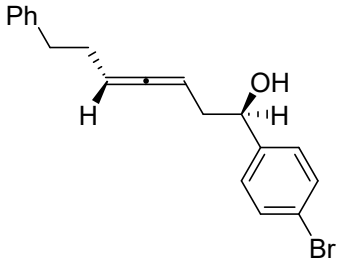
Colorless oil (71mg, 77%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.47 (d, *J* = 4.2 Hz, 1H), 4.91 (t, *J* = 6.6 Hz, 1H), 4.65 (dd, *J* = 10.3, 6.8 Hz, 1H), 4.56 (dd, *J* = 10.3, 6.8 Hz, 1H), 4.29 (d, *J* = 4.1 Hz, 1H), 3.73-3.64 (m, 1H), 3.64-3.56 (m, 1H), 3.39-3.29 (m, 2H), 1.74-1.59 (m, 2H), 1.58-1.50 (m, 1H), 1.03-0.94 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 208.6, 141.2, 130.1, 129.7, 119.8, 92.3, 79.4, 76.3, 63.6, 63.1, 40.9, 32.8, 32.0; HRMS (ESI): m/z [M-(H_2O)+H]$^+$ calcd. for [$C_{15}H_{16}BrO$]$^+$ 291.03790, found 291.03763.

Tert-butyl4-((4-bromophenyl)(hydroxy)methyl)-4-(propa-1,2-dien-1-yl)piperidine-1-carboxylate (3ha)



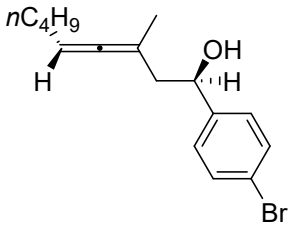
Colorless oil (64mg, 52%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.49 (d, *J* = 3.9 Hz, 1H), 4.90 (t, *J* = 6.3 Hz, 1H), 4.67 (dd, *J* = 10.4, 6.8 Hz, 1H), 4.59 (dd, *J* = 10.3, 6.7 Hz, 1H), 4.28 (d, *J* = 3.4 Hz, 1H), 3.86-3.64 (m, 2H), 2.87-2.60 (m, 2H), 1.60 (d, *J* = 11.7 Hz, 1H), 1.55-1.43 (m, 2H), 1.36 (s, 9H), 1.08 (d, *J* = 12.6 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 208.5, 153.8, 141.2, 130.1, 129.7, 119.9, 91.9, 78.9, 78.3, 76.4, 41.7, 39.7, 31.6, 28.0; HRMS (ESI): m/z [(M-BOC)+H]$^{+}$ calcd. for [$C_{15}H_{19}BrNO$]$^{+}$ 308.06445, found 308.06369.

1-(4-Bromophenyl)-7-phenylhepta-3,4-dien-1-ol (3ia)



Colorless oil (62 mg, 61%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.28-7.21 (m, 4H), 7.18-7.10 (m, 3H), 5.38 (d, *J* = 4.1 Hz, 1H), 5.09-4.98 (m, 2H), 4.51 (dd, *J* = 10.7, 6.0 Hz, 1H), 2.53-2.49 (m, 2H), 2.33-2.24 (m, 1H), 2.20-2.12 (m, 1H), 2.12-2.00 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 204.4, 144.7, 141.4, 130.7, 128.3(7), 128.3(3), 128.1, 125.7, 119.7, 89.7, 87.6, 71.7, 39.7, 34.4, 29.8; HRMS (APCI): m/z [M-(H_2O)+H]$^{+}$ calcd. For [$C_{19}H_{18}Br$]$^{+}$ 325.05864, found 325.05051.

1-(4-Bromophenyl)-3-methylnona-3,4-dien-1-ol (3ja)



Colorless oil (58 mg, 63%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.28 (d, *J* = 4.1 Hz, 1H), 4.88-4.81 (m, 1H), 4.61 (dd, *J* = 11.1, 6.4 Hz, 1H), 2.31 (dd, *J* = 13.4, 6.5 Hz, 1H), 2.16 (dd, *J* = 13.2, 7.5 Hz, 1H), 1.71-1.52 (m, 5H), 1.23-1.16 (m, 2H), 1.14-1.07 (m, 2H), 0.81 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 202.4, 145.0, 130.6, 128.3, 119.6, 95.1, 89.1, 70.5, 44.2, 30.7, 28.1, 21.5, 19.0, 13.7; HRMS (ESI): m/z [M-(H_2O)+H]$^{+}$ calcd. for [$C_{16}H_{20}Br$]$^{+}$ 291.07429, found 291.07391.

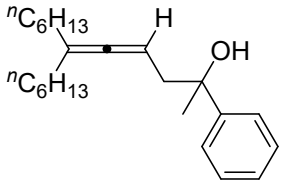
3.3 Procedure for the synthesis of homoallenyl tertiary alcohols (5aa-5ad and 5af-5ah)

Step 1: To a stirred solution of 2-pinacolboryl 1,3-butadiene **1a** (70 mg, 0.20 mmol, 1.0 equiv.) in THF (1.0 mL) under Ar at –78 °C was added *n*BuLi (0.16 mL, 1.6 M, 0.25 mmol, 1.25 equiv.) dropwise. The solution was then stirred for 20 min at –78 °C, at which point TFAA (34 µL, 0.24 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was stirred at −78 °C for 1 hour. Subsequently, the solvent was carefully removed in vacuo and the resulting residue was taken up in dry toluene (2 mL). After a sequential addition of ketone **4** (0.6 mmol, 3.0 equiv.), DIPEA (35 µL, 0.20 mmol, 1.0 equiv.) and TFAA (56 µL, 0.4 mmol, 2.0 equiv.) at 0°C dropwise, the final reaction mixture was stirred at 0°C for 30 min, then allowed to warm to RT for 14 hours. After completion of reaction, the reaction was quenched with sat. $NaHCO_3$ (aq.) and extracted with EtOAc (3x10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuo and used for deprotection of partially formed **5-TFA** directly.

Step 2: The crude residue was dissolved in MeOH (5 mL), $NaHCO_3$ (84 mg, 1.0 mmol, 5.0 equiv.) was added into the solution in one-pot. The mixture was stirred at r.t. for 12 hours. After completion of deprotection reaction, the reaction was quenched with sat. NaCl (aq.) and extracted with EtOAc (3x10 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was purified by flash chromatography using EtOAc/PE (1:200-1:50) as eluent to afford **5 (5aa,5ab and 5af)**. **5ac** and **5ad** could not be purified by flash chromatography.

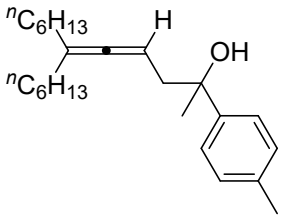
Analytical data

6-Hexyl-2-phenyldodeca-4,5-dien-2-ol (5aa)



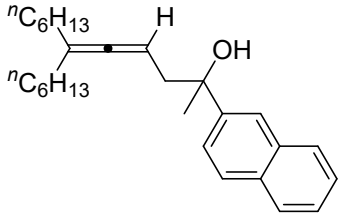
Colorless oil (34 mg, 49%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.39 (d, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 2H), 4.95 (s, 1H), 4.94-4.88 (m, 1H), 2.36-2.25 (m, 2H), 1.82-1.74 (m, 2H), 1.74-1.66 (m, 2H), 1.43 (s, 3H), 1.27-1.12 (m, 16H), 0.84 (t, *J* = 6.8 Hz, 3H), 0.83 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.6, 148.6, 127.4, 125.7, 125.0, 102.1, 87.3, 72.7, 44.8, 31.8, 31.1, 31.0, 29.1, 28.2, 26.9, 26.8, 22.0, 13.8; HRMS (ESI): m/z calcd. for $[C_{24}H_{38}ONa]^+$ 365.28149, found 365.28043.

6-Hexyl-2-(p-tolyl)dodeca-4,5-dien-2-ol (5ab)



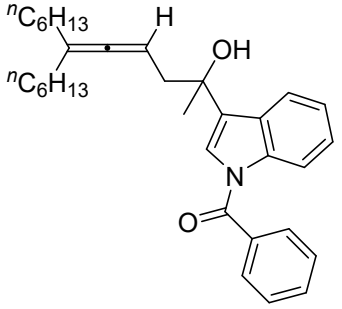
Colorless oil (38 mg, 53%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.95-4.89 (m, 1H), 4.88 (s, 1H), 2.30 (d, *J* = 7.4 Hz, 2H), 2.24 (s, 3H), 1.81-1.75 (m, 2H), 1.73-1.66 (m, 2H), 1.40 (s, 3H), 1.25-1.13 (m, 16H), 0.84 (t, *J* = 7.0 Hz, 3H), 0.83 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.6, 145.7, 134.5, 128.0, 124.9, 102.1, 87.4, 72.6, 44.9, 31.8(7), 31.8(4), 31.1, 31.0, 29.2, 28.3(3), 28.3(0), 26.9, 26.8, 22.0(9), 22.0(7), 20.5, 13.8; HRMS (ESI): m/z calcd. for $[C_{25}H_{40}ONa]^+$ 379.29714, found 379.29587.

6-Hexyl-2-(naphthalen-2-yl)dodeca-4,5-dien-2-ol (5af)



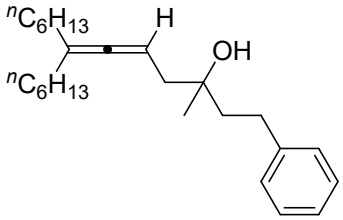
Colorless oil (49mg, 62%). NMR data:^{1}H NMR (500 MHz, DMSO-d_6) δ 7.88 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.55 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.48-7.38 (m, 2H), 5.14 (s, 1H), 5.03-4.94 (m, 1H), 2.48-2.39 (m, 2H), 1.75-1.67 (m, 2H), 1.60-1.54 (m, 2H), 1.53 (s, 3H), 1.22-1.10 (m, 10H), 1.01-0.92 (m, 6H), 0.82 (t, *J* = 7.1 Hz, 3H), 0.77 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.6, 146.1, 132.6, 131.6, 127.8, 127.1, 126.9, 125.6, 125.2, 124.3, 123.2, 102.2, 87.3, 73.0, 44.7, 31.8, 31.7, 31.1, 30.9, 29.3, 28.2(8), 28.2(4), 26.9, 26.7, 22.0, 13.9, 13.8; HRMS (ESI): m/z $[M-(H_2O)+H]^+$ calcd. for $[C_{28}H_{39}]^+$ 375.30463 found 375.30341.

(3-(6-Hexyl-2-hydroxydodeca-4,5-dien-2-yl)-1H-indol-1-yl)(phenyl)methanone (5ag)



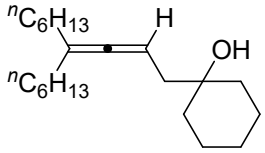
Yellow oil (35 mg, 36%). NMR data:^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.60 (dd, *J* =7.2, 7.2 Hz, 1H), 7.53 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.38 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.32 (dd, *J* =7.4, 7.4 Hz, 1H), 7.22 (s, 1H), 4.96-4.88 (m, 1H), 2.76 (dd, *J* = 13.9, 6.8 Hz, 1H), 2.54 (dd, *J* = 13.9, 8.3 Hz, 1H), 2.35 (br s, 1H), 1.90-1.77 (m, 4H), 1.66 (s, 3H), 1.30-1.20 (m, 16H), 0.89-0.83 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.2, 168.5, 137.1, 134.6, 131.8, 129.1, 128.7, 128.6, 128.4, 124.8, 123.6(9), 123.6(7), 120.8, 116.6, 104.4, 85.7, 71.9, 42.8, 32.5, 32.4, 31.6, 28.9, 28.4, 27.6, 27.5, 22.6, 14.0; HRMS (ESI): m/z calcd. for $[C_{33}H_{43}NO_2Na]^+$ 508.31860, found 508.31760.

7-Hexyl-3-methyl-1-phenyltrideca-5,6-dien-3-ol (5ah)



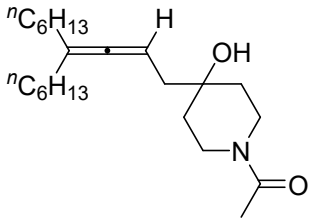
Colorless oil (42mg, 57%). NMR data:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.21 (m, 2H), 7.21-7.10 (m, 3H), 5.15-4.98 (m, 1H), 2.74-2.60 (m, 2H), 2.17 (d, *J* = 5.9 Hz, 2H), 1.97-1.84 (m, 4H), 1.83-1.72 (m, 2H), 1.58 (brs, 1H), 1.39-1.33 (m, 4H), 1.28-1.21 (m, 15H), 0.84 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.9, 142.5, 128.3, 128.2, 125.6, 104.0, 86.1, 72.3, 43.4, 42.4, 32.6, 31.7, 30.3, 29.0, 27.7, 26.5, 22.6, 14.0; HRMS (ESI): m/z $[M+H]^+$ calcd. for $[C_{26}H_{43}O]^+$, 371.3314 found 371.3314.

1-(4-Hexyldeca-2,3-dien-1-yl)cyclohexan-1-ol (5ai)



Colorless oil (34mg, 53%). NMR data:^{1}H NMR (500 MHz, $CDCl_3$) δ 5.13-5.03 (m, 1H), 2.12 (d, *J* = 7.7 Hz, 2H), 1.91 (t, *J* = 7.0 Hz, 4H), 1.66-1.59 (m, 2H), 1.57-1.52 (m, 4H), 1.51-1.44 (m, 4H), 1.44-1.34 (m, 5H), 1.33-1.26 (m, 12H), 0.88 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.8, 103.6, 85.9, 71.2, 42.6, 37.2, 32.6, 31.7, 29.0, 27.7, 25.8, 22.6, 22.2, 14.0; HRMS (ESI): m/z $[M+H]^+$ calcd. for $[C_{22}H_{41}O]^+$, 321.3157 found 321.3161.

1-(4-(4-Hexyldeca-2,3-dien-1-yl)-4-hydroxypiperidin-1-yl)ethan-1-one (5aj)



Colorless oil (51 mg, 70%). NMR data:^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09-5.01 (m, 1H), 4.45-4.15 (m, 1H), 3.75-3.51 (m, 1H), 3.45 (t, *J* = 11.6 Hz, 1H), 3.04 (t, *J* = 11.6 Hz, 1H), 2.13 (d, *J* = 7.7 Hz, 2H), 2.08 (s, 3H), 1.92 (t, *J* = 7.6 Hz, 2H), 1.91(t, *J* = 7.6 Hz, 2H), 1.84 (br s, 1H), 1.68-1.58 (m, 2H), 1.57-1.47 (m, 2H), 1.43-1.34 (m, 4H), 1.33-1.22 (m, 12H), 0.87 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.1, 168.7, 104.2, 84.8, 69.2, 43.3, 42.5, 37.6, 37.0, 36.3, 32.5, 31.6, 28.9, 27.6, 22.5, 21.3, 14.0; HRMS (ESI): m/z calcd. for $[C_{23}H_{41}NO_2Na]^+$ 386.30295, found 386.30161.

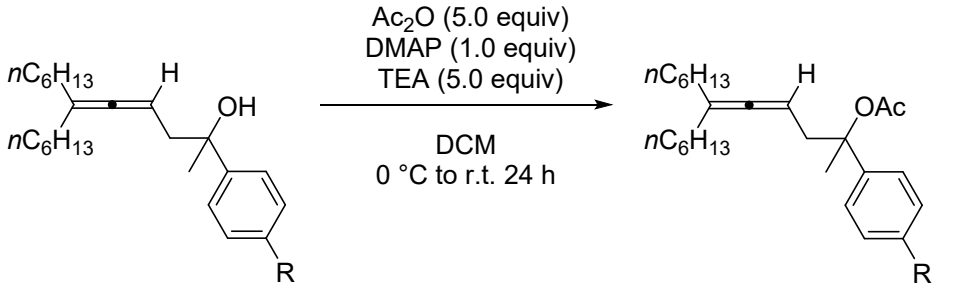
3.4 Procedure for the synthesis of homoallenyl tertiary alcohols 5ae

Step 1: To a stirred solution of 2-pinacolboryl 1,3-butadiene **1a** (70 mg, 0.20 mmol, 1.0 equiv.) in THF (1.0 mL) under Ar at –78 °C was added *n*BuLi (0.16 mL, 1.6 M, 0.25 mmol, 1.25 equiv.) dropwise. The solution was then stirred for 20 min at –78 °C, at which point TFAA (34 µL, 0.24 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was stirred at −78 °C for 1 hour. Subsequently, the solvent was carefully removed in vacuo and the resulting residue was taken up in dry Toluene (1.5 mL). After a sequential addition of ketone **4e** (119 mg 0.6 mmol 3.0 equiv.) solution in toluene (0.5 mL) and TFAA (56 µL, 0.4 mmol, 2.0 equiv.) at 0°C dropwise, the final reaction mixture was stirred at 0°C for 24 hours. After completion of reaction, the reaction was quenched with sat. $NaHCO_3$ (aq.) and extracted with EtOAc (3x10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuo and used for deprotection of partially formed **5ae-TFA** directly.

Step 2: The crude residue was dissolved in MeOH (5 mL), $NaHCO_3$ (84 mg, 1.0 mmol, 5.0 equiv.) was added into the solution in one-pot. The mixture was stirred at r.t. for 12 hours. After completion of deprotection reaction, the reaction was quenched with sat. NaCl (aq.) and extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was partly purified by flash chromatography using EtOAc/PE (1:200-1:50) as eluent to afford **5ae** accompanying ketone **4e** with an NMR yield of 52%.

3.5 Procedure for the synthesis of acetyl-protected derivatives (5ac-Ac, 5ad-Ac and 5ae-Ac)

Due to the same polarity of **5ac**-**5ae** and their corresponding ketones (**4c**-**4e**) on analytical thin-layer chromatography (TLC) in homoallenylboration reactions, the purification of **5ac**-**5ae** was not feasible by regular flash chromatography. Therefore, we decided to further transform **5ac**-**5ae** to their acetyl-protected derivatives (**5ac-Ac**, **5ad-Ac** and **5ae-Ac**) and implement their data characterization and analysis.

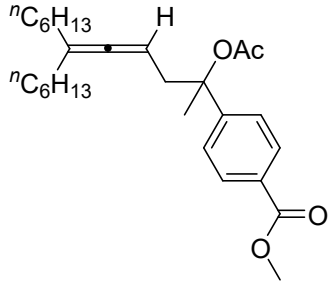


5ac-**5ae** **5ac-Ac**, **5ad-Ac** and **5ae-Ac**

The acetyl-protected homoallenyl alcohols were synthesized according to reported procedures by Wang and co-works.[4] Representative procedure: A flask was charged with **5ac** (~40 mg, 0.1 mmol, 1.0 equiv.) accompanied with *p*-chloroacetophenone **4c**, DMAP (12.2 mg, 0.1 mmol, 1.0 equiv.) and DCM (1.5 ml) then cooled to 0 °C. Subsequently, triethylamine (70 μL, 0.5 mmol, 5.0 equiv.) was added dropwise to the solution and stirred for 5 min. Then, Ac_2O (47 μL, 0.5 mmol, 5.0 equiv.) was added dropwise and the resulted solution was stirred for 24 hours at room temperature. The reaction was then quenched with saturated NH_4Cl solution and extracted with EtOAc and the organic phase was dried over anhydrous $MgSO_4$. After filtration the solvent was removed in vacuo. The crude material was purified by flash chromatography using EtOAc/PE (1:200-1:50) as eluent to afford pure **5ac**-**Ac.**

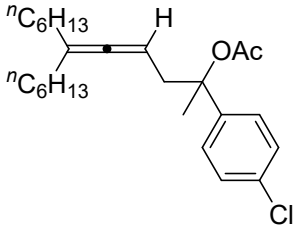
Analytical Data:

Methyl 4-(2-acetoxy-6-hexyldodeca-4,5-dien-2-yl)benzoate (5ac-Ac)



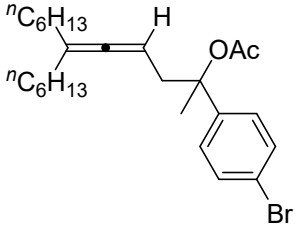
Colorless oil (33.7mg, 76%). NMR data:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 4.87-4.76 (m, 1H), 3.90 (s, 3H), 2.65 (ABqd, *J* =14.0, 7.3 Hz, 2H), 2.07 (s, 3H), 1.87 (s, 3H), 1.85-1.78 (m, 4H), 1.28-1.19 (m, 16H), 0.88 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.9, 169.4, 166.7, 149.7, 129.5, 128.7, 124.8, 104.1, 85.2, 83.1, 51.9, 43.3, 32.4(8), 32.4(5), 31.7, 29.0, 28.9, 27.5(8), 27.5(5), 24.3, 22.6, 22.0, 14.0; HRMS (ESI): m/z $[M\text{-}OAc]^+$ calcd. for $[C_{26}H_{39}O_2]^+$ 383.29446 found 383.29214.

2-(4-Chlorophenyl)-6-hexyldodeca-4,5-dien-2-yl acetate (5ad-Ac)



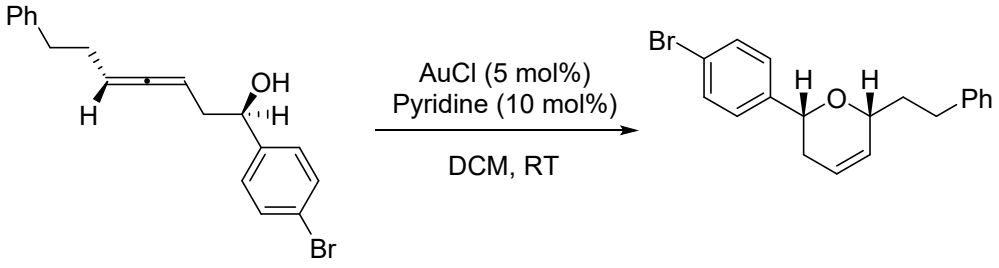
Colorless oil (24mg, 57%). NMR data:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2H), 7.28-7.25 (m, 2H), 4.87-4.80 (m, 1H), 2.65 (ABqd, *J* =13.9, 7.4 Hz, 2H), 2.07 (s, 3H), 1.86 (s, 3H),1.88-1.80 (m, 4H), 1.32-1.26 (m, 16H), 0.90 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.9, 169.5, 143.0, 132.7, 128.2, 126.3, 104.1, 85.3, 83.0, 43.4, 32.5, 32.4, 31.7, 29.0(3), 29.0(2), 27.6, 27.5, 24.3, 22.6, 22.1, 14.0; HRMS (ESI): m/z $[M\text{-}OAc]^+$ calcd. for $[C_{24}H_{36}Cl]^+$ 359.25001 found 359.24854.

2-(4-Bromophenyl)-6-hexyldodeca-4,5-dien-2-yl acetate (5ae-Ac)



Colorless oil (29mg, 62%). NMR data:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 4.88-4.76 (m, 1H), 2.62 (ABqd, *J* = 13.9, 7.7 Hz, 2H), 2.04 (s, 3H), 1.83 (s, 3H),1.84-1.79 (m, 4H), 1.36-1.18 (m, 16H), 0.88 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.9, 169.4, 143.6, 131.2, 126.6, 120.8, 104.1, 85.3, 83.0, 43.3, 32.4(9), 32.4(6), 31.7, 29.0(2), 29.0(1), 27.6, 27.5, 24.3, 22.6, 22.1, 14.0; HRMS (ESI): m/z calcd. for $[C_{26}H_{39}BrO_2Na]^+$ 485.20256, found 485.20050.

3.6 Gold-catalyzed cycloisomerization of homoallenyl alcohol 3ia to 3ia-dihydropyran

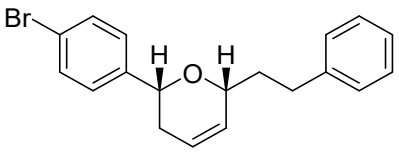


3ia **3ia**-dihydropyran
74%

3ia-dihydropyran was synthesized according to reported procedures by Krause and co-works.[5] To a solution of the homoallenyl alcohol **3ia** (34 mg, 0.1 mmol, 1.0 equiv.) in 1 mL of dry solvent under argon was added the catalyst AuCl (1.2 mg, 0.005 mmol, 5 mol%) and pyridine (1 μL, 0.01 mmol, 10 mol%). The reaction mixture was stirred at room temperature and monitored by TLC. After completion, the mixture was filtered through celite to remove trace solid, then solvent was removed in vacuo. Product **3ia-dihydropyran** was purified by flash column chromatography on silica gel with EtOAc/PE (1:100-1:50) as eluent.

Analytical data:

***cis*-2-(4-Bromophenyl)-6-phenethyl-3,6-dihydro-2H-pyran (3ia-dihydropyran)**



Colorless oil (28 mg, 74% yield). NMR data:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.32-7.26 (m, 4H), 7.25-7.16 (m, 3H), 5.95-5.87 (m, 1H), 5.73 (d, *J* = 10.5 Hz, 1H), 4.57 (t, *J* = 6.8 Hz, 1H), 4.40-4.30 (m, 1H), 2.90-2.75 (m, 2H), 2.29-2.20 (m, 2H), 1.99-1.90 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 142.0, 131.3, 130.2, 128.5, 128.2, 127.3, 125.6, 124.6, 120.9, 74.7, 74.5, 37.0, 33.1, 31.2; HRMS (ESI): m/z $[M+H]^+$ calcd. for $[C_{19}H_{20}BrO]^+$ 343.06920, found 343.06839.

3.7 Determination of the stereochemistry of 3ia-dihydropyran using a NOESY spectrum

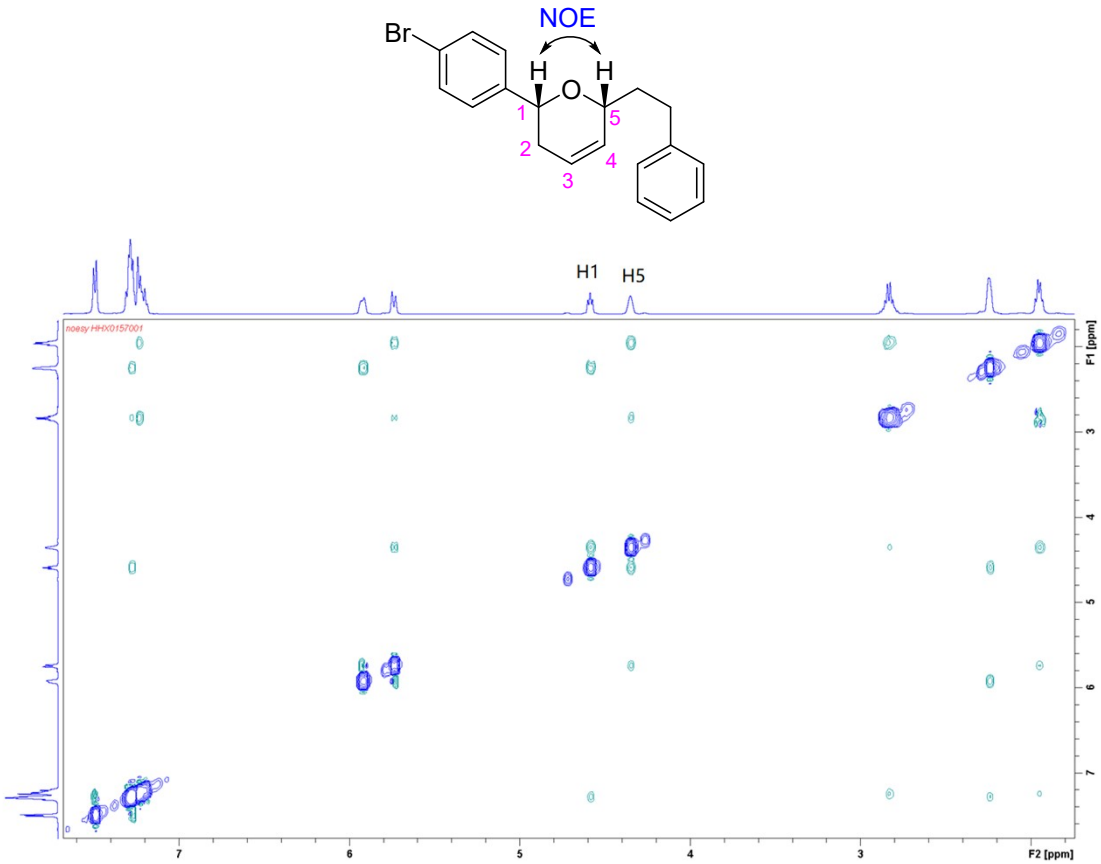
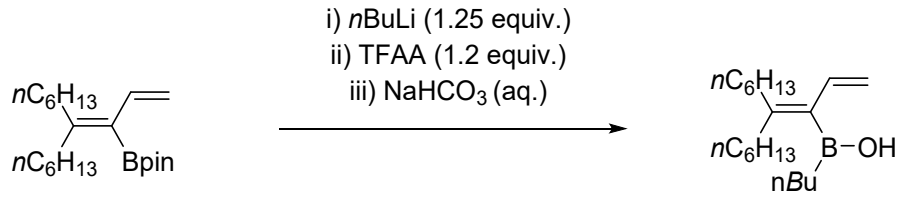


Figure S1. Observed NOESY effect between the C1 proton and C5 proton

The NOESY experiment (Figure S1) indicated a through space NOE effect between C1-H and C5-H. This indicates that C1-H and C5-H are close in space. Therefore, the relative configuration of **3ia**-dihydropyran is *cis*.

3.8 Procedure for the synthesis of 1a-BOH

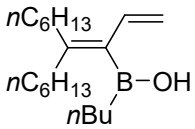


1a **1a**-BOH

To a stirred solution of 2-pinacolateboryl 1,3-butadiene **1a** (104 mg, 0.30 mmol, 1.0 equiv.) in THF (1.5 mL) under Ar at –78 °C was added *n*BuLi (0.24 mL, 1.6 M, 0.375 mmol, 1.25 equiv.) dropwise. The solution was then stirred for 20 min at –78 °C, at which point TFAA (50 µL, 0.36 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was stirred at −78 °C for 45 min and allowed to warm to 0 °C for 30 min. Then, the reaction was quenched with sat. $NaHCO_3$ (aq.) at 0 °C and extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuo. No further purification was performed since the borinic acid product **1a**-BOH decomposed during flash chromatography.

Analytical data:

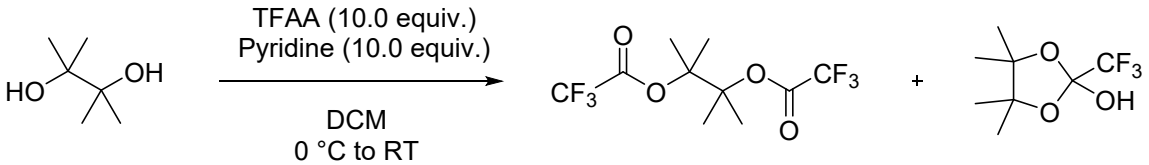
Butyl(4-hexyldeca-1,3-dien-3-yl)(hydroxy)borane (1a-BOH)



NMR data:^{1}H NMR (500 MHz, THF-d_8) δ 8.45 (s, 1H), 7.66 (dd, *J* = 17.6 Hz, 10.6 Hz, 1H), 4.87 (d, *J* = 10.7 Hz, 1H), 4.80 (d, *J* = 17.8 Hz, 1H), 2.14 (t, *J* = 7.3 Hz, 2H), 1.97 (t, *J* = 7.4 Hz, 2H), 1.42-1.28 (m, 20H), 0.92 (t, *J* = 7.7 Hz, 2H), 0.90-0.85 (m, 9H); ^{11}B NMR (128 MHz, THF-d_8) δ 52.

HRMS (ESI): m/z calcd. for $[C_{20}H_{39}BONa]^{+}$ 329.2991, found 329.2982.

3.9 Procedure for the synthesis of 2,3-dimethylbutane-2,3-diyl bis(2,2,2-trifluoroacetate) 6



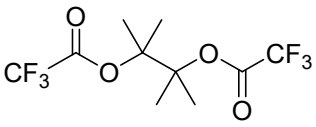
6 **S1**

The bis-TFA protected pinacol **6** accompanying with **S1**[6] were synthesized according to reported procedures by Buddrus and co-works.[7]

To a stirred solution of pinacol (236 mg, 2 mmol, 1.0 equiv.) in DCM (2 mL) under Ar at 0 °C was added pyridine (1.6 mL, 20 mmol, 10 equiv.) and trifluoroacetic anhydride (2.8 ml, 20 mmol, 10 equiv.) dropwise. Then, the reaction solution was warmed to room temperature and stirred for 24 hours. The reaction was quenched with water at 0°C and extracted with DCM (3 x 5 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. No further purification was performed since **6** decomposed during flash chromatography.

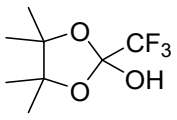
Analytical data:

2,3-dimethylbutane-2,3-diyl bis(2,2,2-trifluoroacetate) (6)



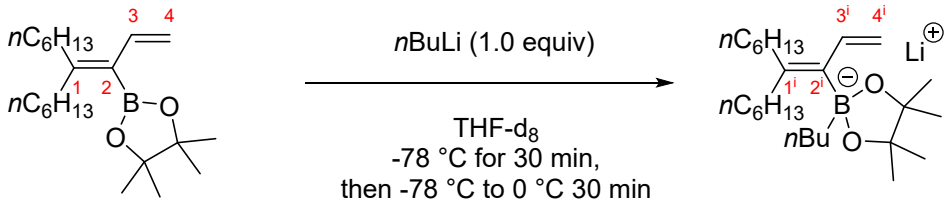
NMR data:^{1}H NMR (500 MHz, THF-d_8) δ 1.70 (s, 12H); ^{13}C NMR (126 MHz, THF-d_8) δ156.0 (q, *J* = 41.5 Hz), 115.4 (q, *J* = 286.4 Hz), 91.5, 20.1; HRMS (ESI): m/z $[M+H]^+$ calcd. for $[C_{10}H_{13}F_6O_4]^+$ 311.0718, found 311.0721.

4,4,5,5-tetramethyl-2-(trifluoromethyl)-1,3-dioxolan-2-ol (S1)



NMR data:^{1}H NMR (500 MHz, THF-d_8) δ 1.36 (s, 6H), 1.22 (s, 6H); ^{13}C NMR (126 MHz, THF-d_8) δ 121.6 (q, *J* = 287.8 Hz), 112.0 (q, *J* = 35.5 Hz), 86.2, 24.7, 24.0; HRMS (ESI): m/z calcd. for $[C_8H_{13}F_3O_3Na]^+$ 237.0714, found 237.0723.

3.10 Evidence for the formation of 1a-ate：^{1}H and ^{11}B NMR analysis of reaction



1a

^{11}B NMR : 30 ppm

1a-ate

^{11}B NMR : 7 ppm

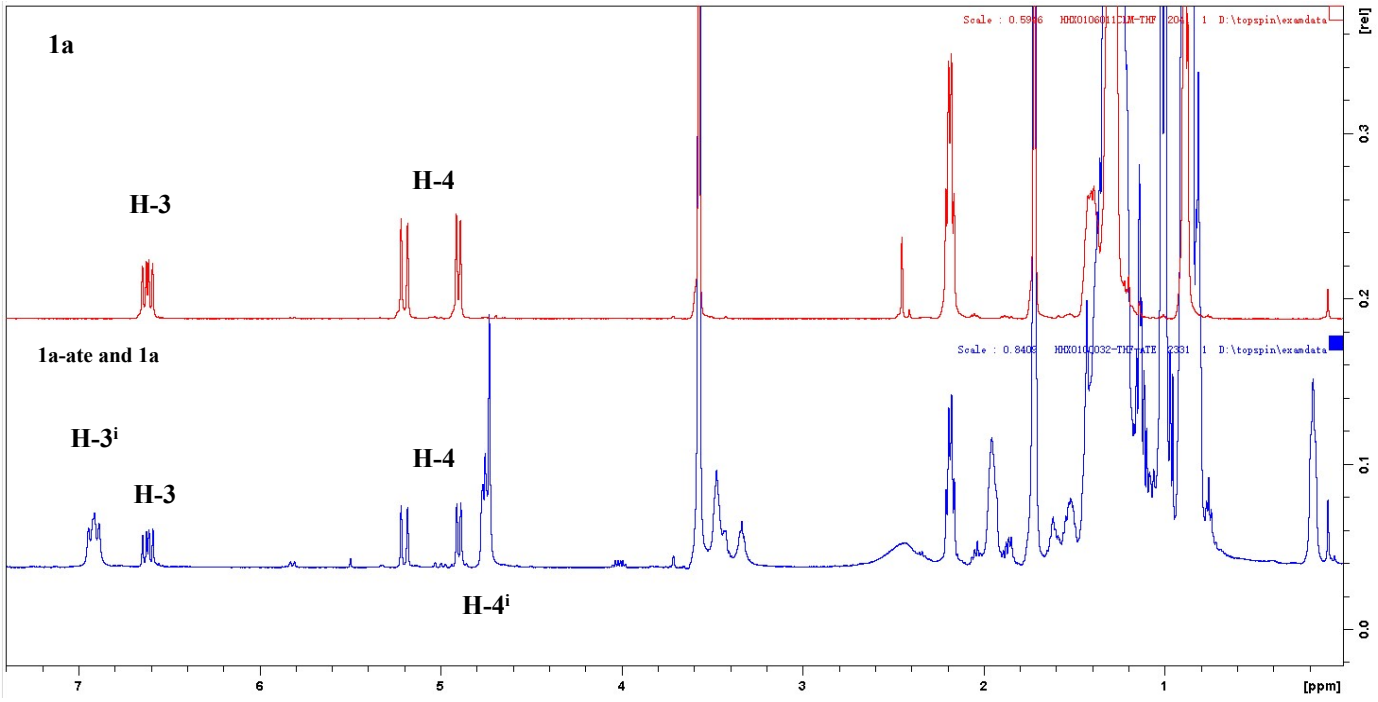


Figure S2. Changes of ^{1}H NMR after addition of *n*BuLi

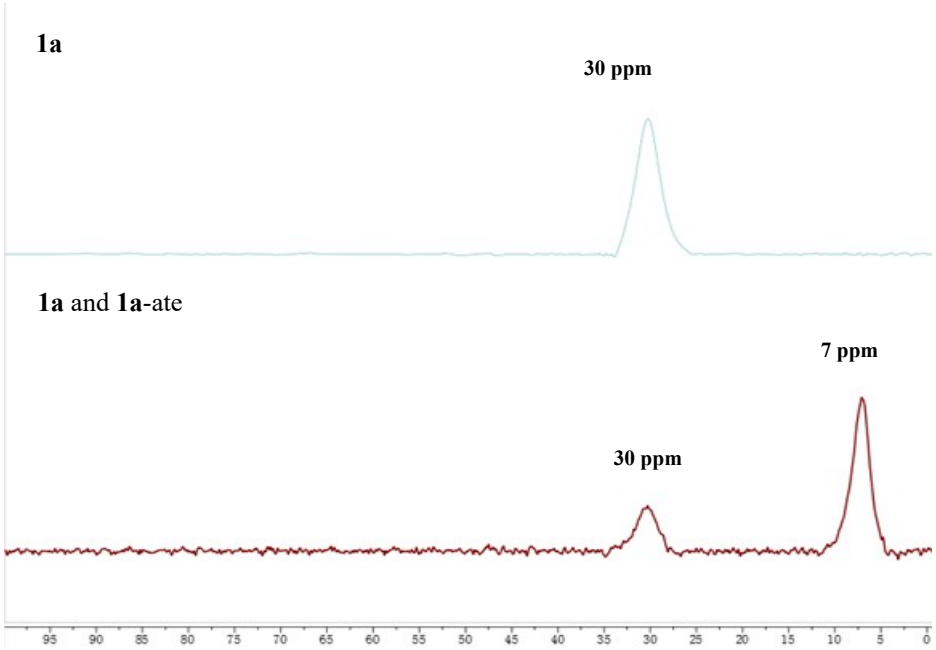
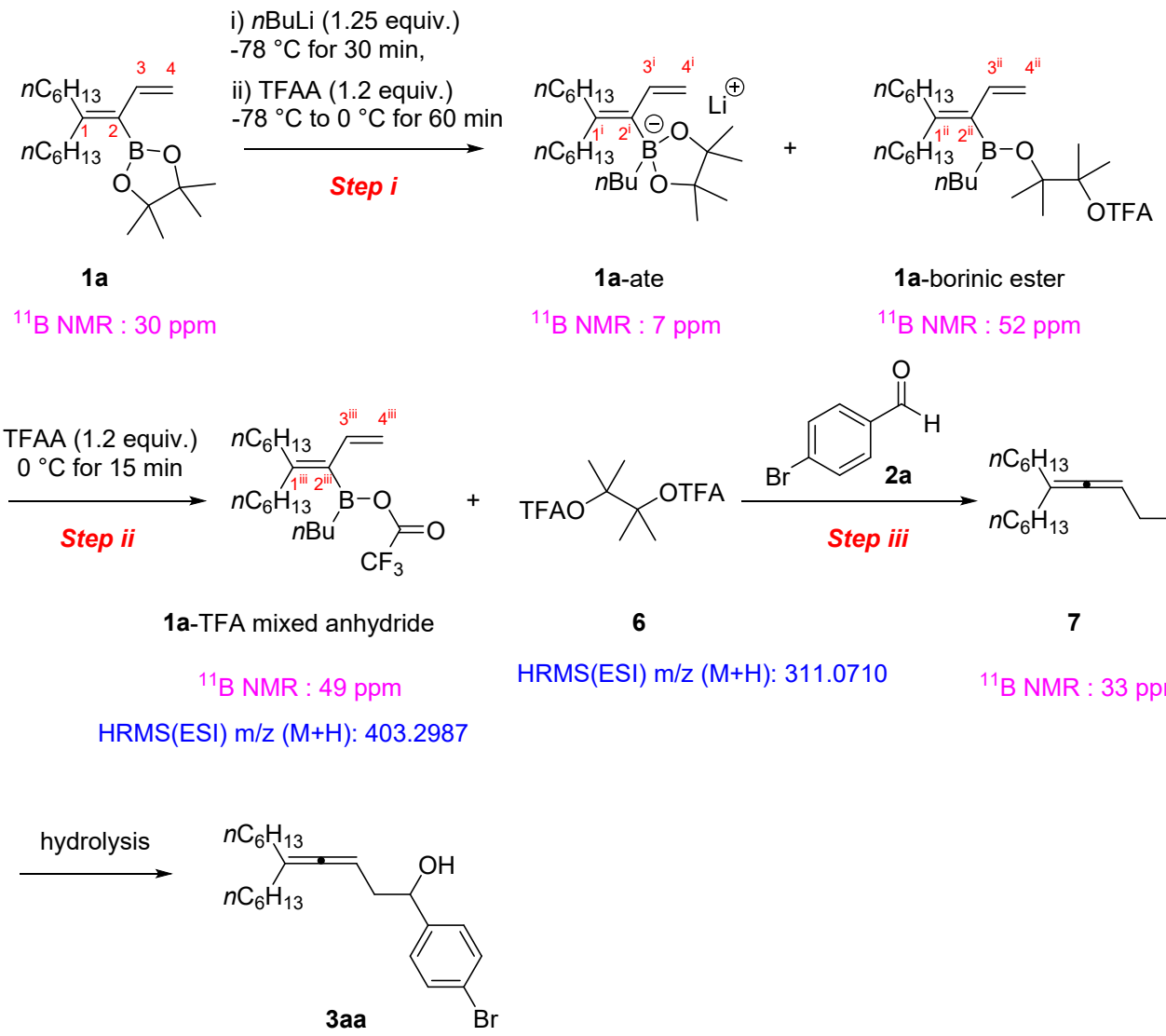


Figure S3. Changes of ^{11}B NMR after addition of *n*BuLi

3.11 Monitoring the course of the reaction by ^{1}H and ^{11}B NMR

Homoallenylboration reaction was performed in THF-d_8. The reaction mixture was transferred to the NMR tube and analysed directly.



^{11}B NMR : 30 ppm

^{11}B NMR : 7 ppm

^{11}B NMR : 52 ppm

^{11}B NMR : 49 ppm

HRMS(ESI) m/z (M+H): 403.2987

HRMS(ESI) m/z (M+H): 311.0710

^{11}B NMR : 33 ppm

Sequential addition of *n*BuLi/TFAA (1.25 and 1.20 equiv. respectively) and TFAA (1.2 equiv.) to a solution of **1a** in THF-d_8, protons' signals of C-3 and C-4 continuously changed in crude ^{1}H NMR spectra (Figure S4).

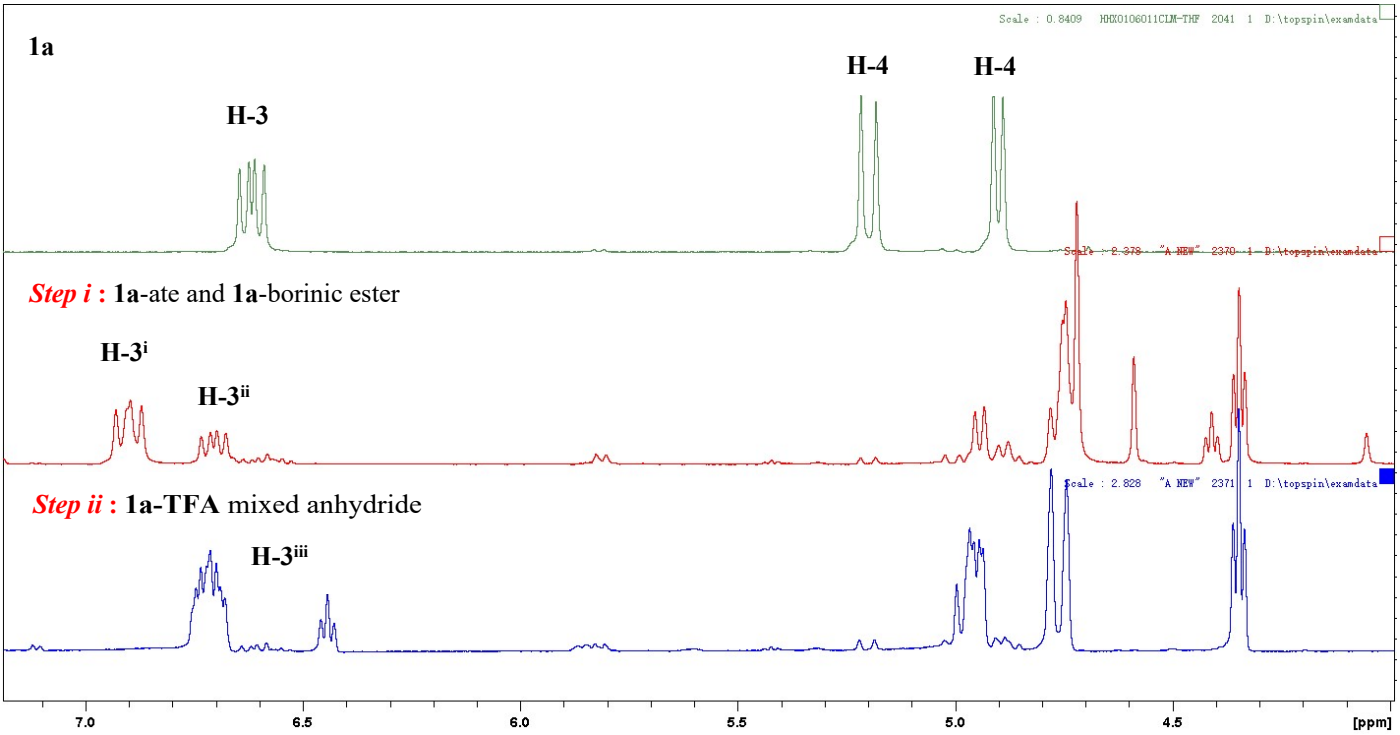


Figure S4. Changes of ^{1}H NMR after sequential addition of *n*BuLi/TFAA and following TFAA

Addition of *n*BuLi/TFAA (1.25 and 1.2 equiv. respectively) to a solution of **1a** in THF-d_8, signals at 7 ppm, 33 ppm and 52 ppm were first observed and by ^{11}B NMR analysis conducted at 0 ºC. Then, following TFAA (1.2 equiv.) was injected into the reaction mixture, signal at 7 ppm disappeared and broad signal at 52 ppm changed to 49 ppm. Besides, signal at 33 pm in ^{11}B NMR indicated the formation of *n*BuBpin in the transformation, compared with the standard sample (Figure S5).

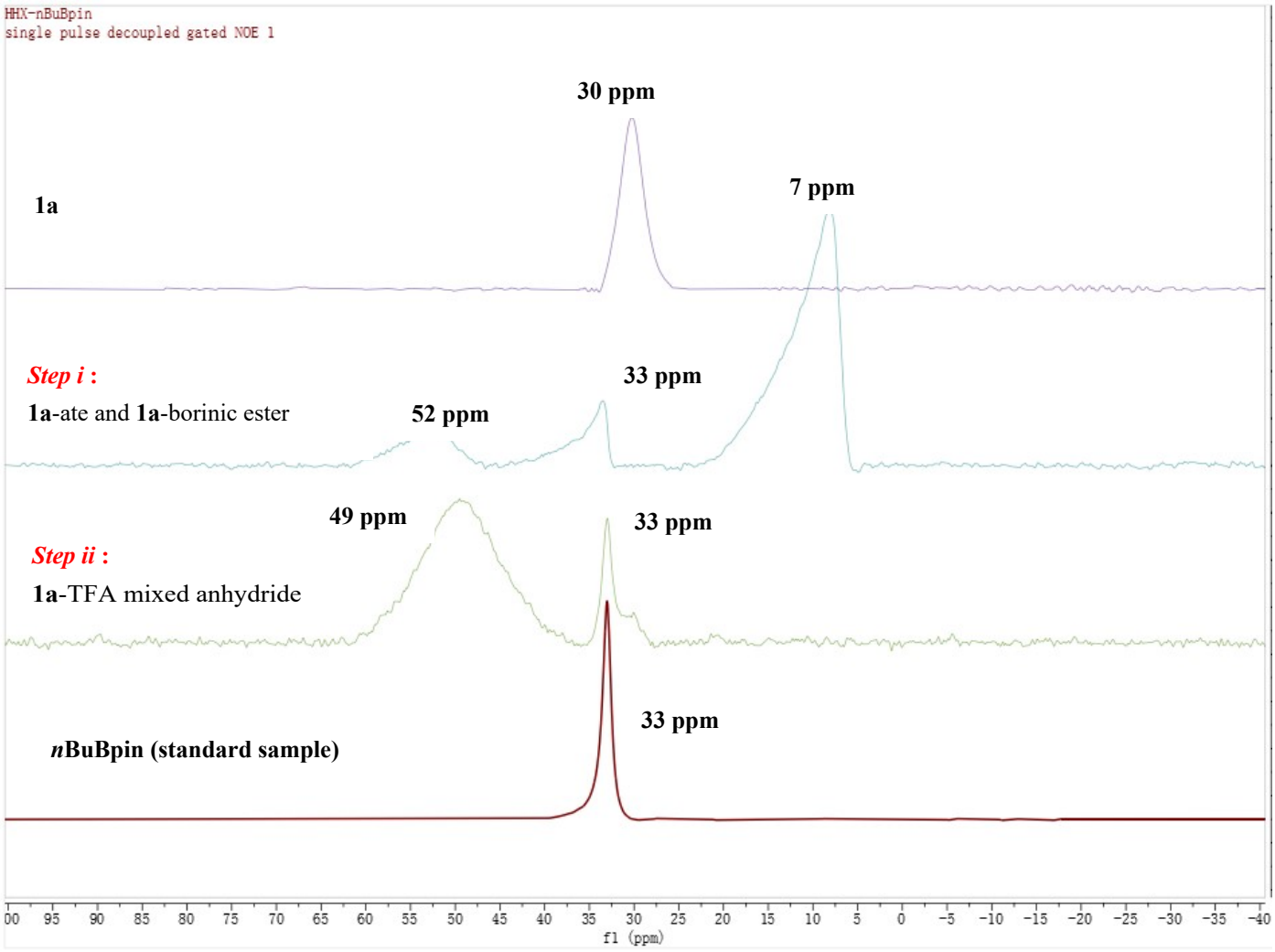


Figure S5. Changes of ^{11}B NMR after sequential addition of *n*BuLi/TFAA and additional TFAA

Following addition of *p*-bromobenzaldehyde **2a** (***Step iii***), protons' signals of C-3 and C-4 continuously declined over time in crude ^{1}H NMR spectra (Figure S6). New signals appeared and increased simultaneously in the aromatic region. Then, following addition of water, protons' signals of **3aa** appeared after hydrolysis of intermediates **7**.

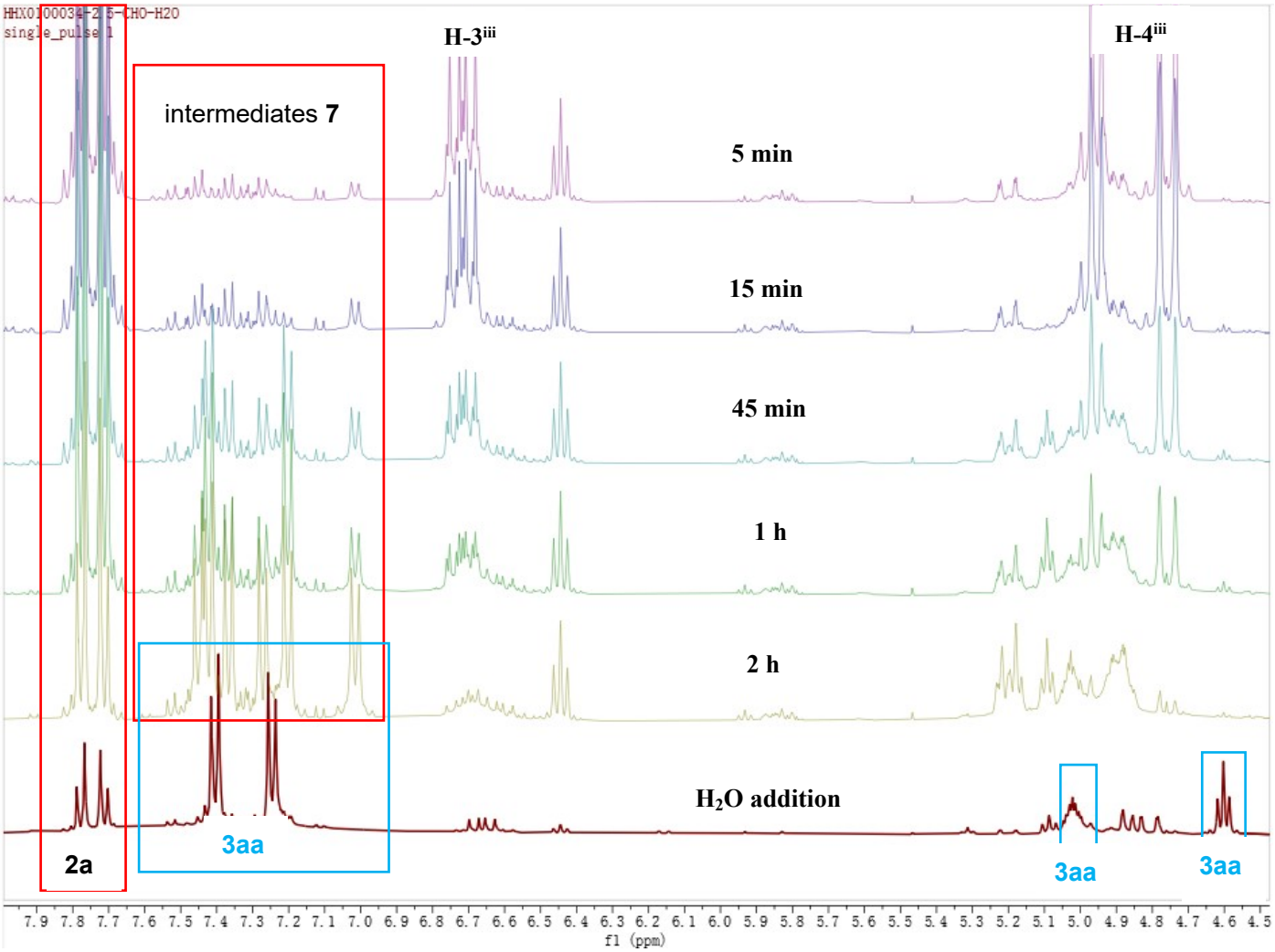


Figure S6. Changes of ^{1}H NMR after addition of *p*-bromobenzaldehyde **2a**

Following addition of *p*-bromobenzaldehyde **2a** (***Step iii***), signal of **1a**-TFA mixed anhydride continuously declined over time in ^{11}B NMR spectra (Figure S7). Simultaneously, signal at 33 ppm increased dramatically. Then, following addition of water, no significant change in ^{11}B NMR spectra was observed, indicating the formation of *n*-butylboronates.

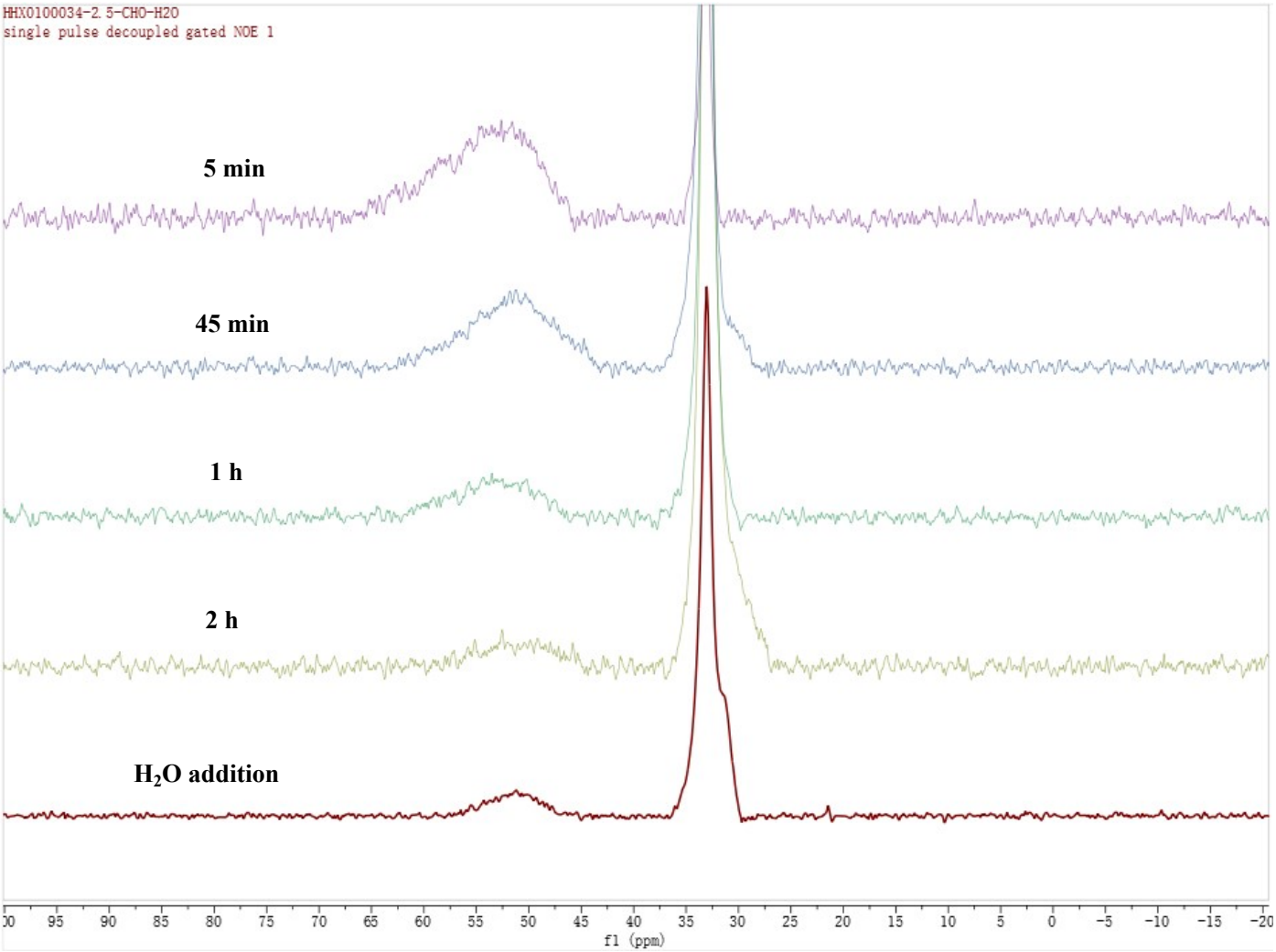
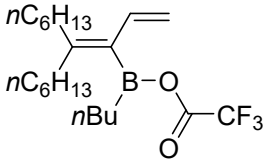


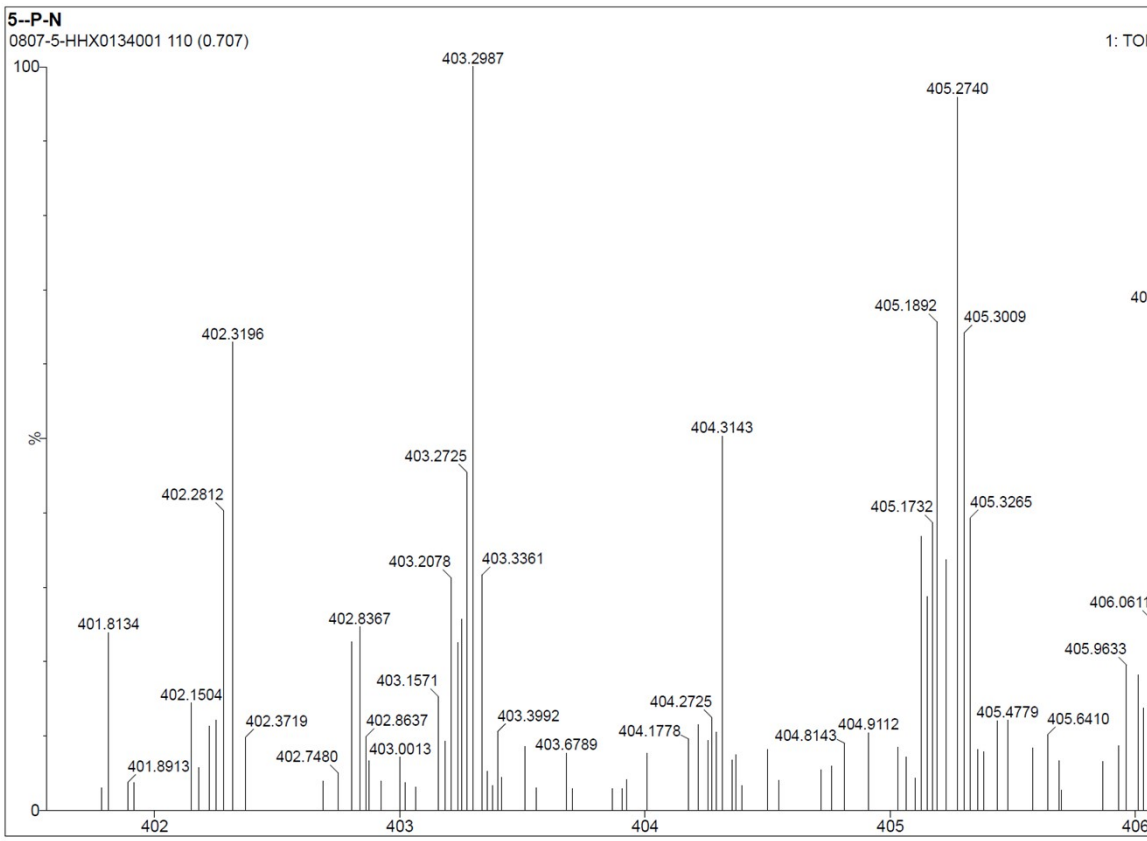
Figure S7. Changes of ^{11}B NMR after addition of *p*-bromobenzaldehyde **2a**

3.12 HRMS measurement of reaction mixture after secondary injection of additional TFAA: Evidence for the formation of 1a-TFA mixed anhydride and 6



1a-TFA mixed anhydride

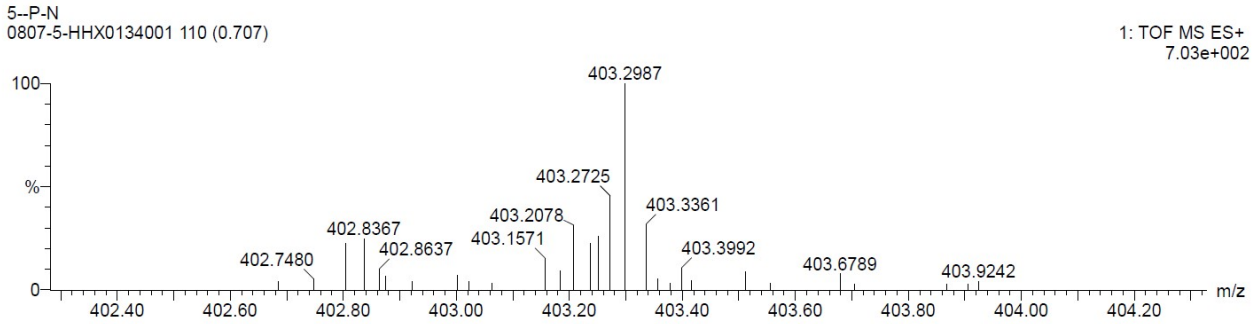
HRMS (ESI): m/z $[M+H]^+$ calcd. for $[C_{22}H_{39}BF_3O_2]^+$ 403.2995, found 403.2987.



Elemental Composition Report **Page 1**

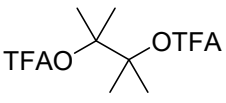
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
7788 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 22-22 H: 0-50 N: 0-11 O: 0-18 P: 0-3 F: 3-3 B: 0-20



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
403.2987	403.2995	-0.8	-2.0	2.5	106.9	n/a	n/a	C22 H39 O2 F3 B

Figure S8. HRMS spectra of **1a-TFA mixed anhydride**



6

HRMS (ESI): m/z $[M+H]^+$ calcd. for $[C_{10}H_{13}F_6O_4]^+$ 311.0718, found 311.0710

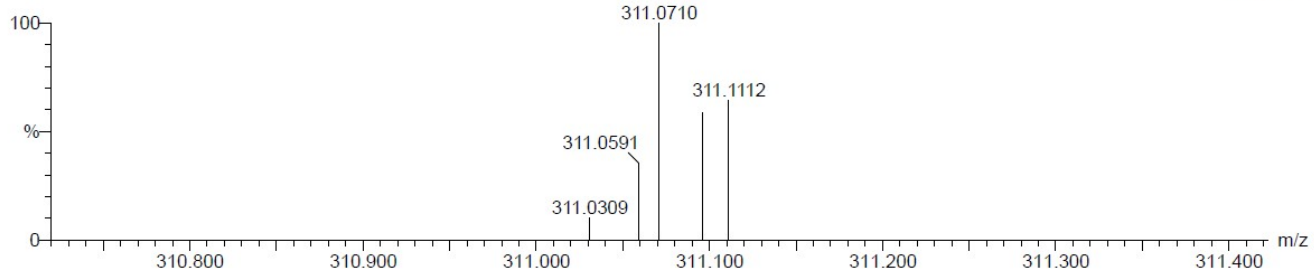
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
249 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 10-10 H: 0-50 N: 0-11 O: 0-18 F: 6-6 P: 0-3

5--P-N
0807-5-HHX0134001 42 (0.286)

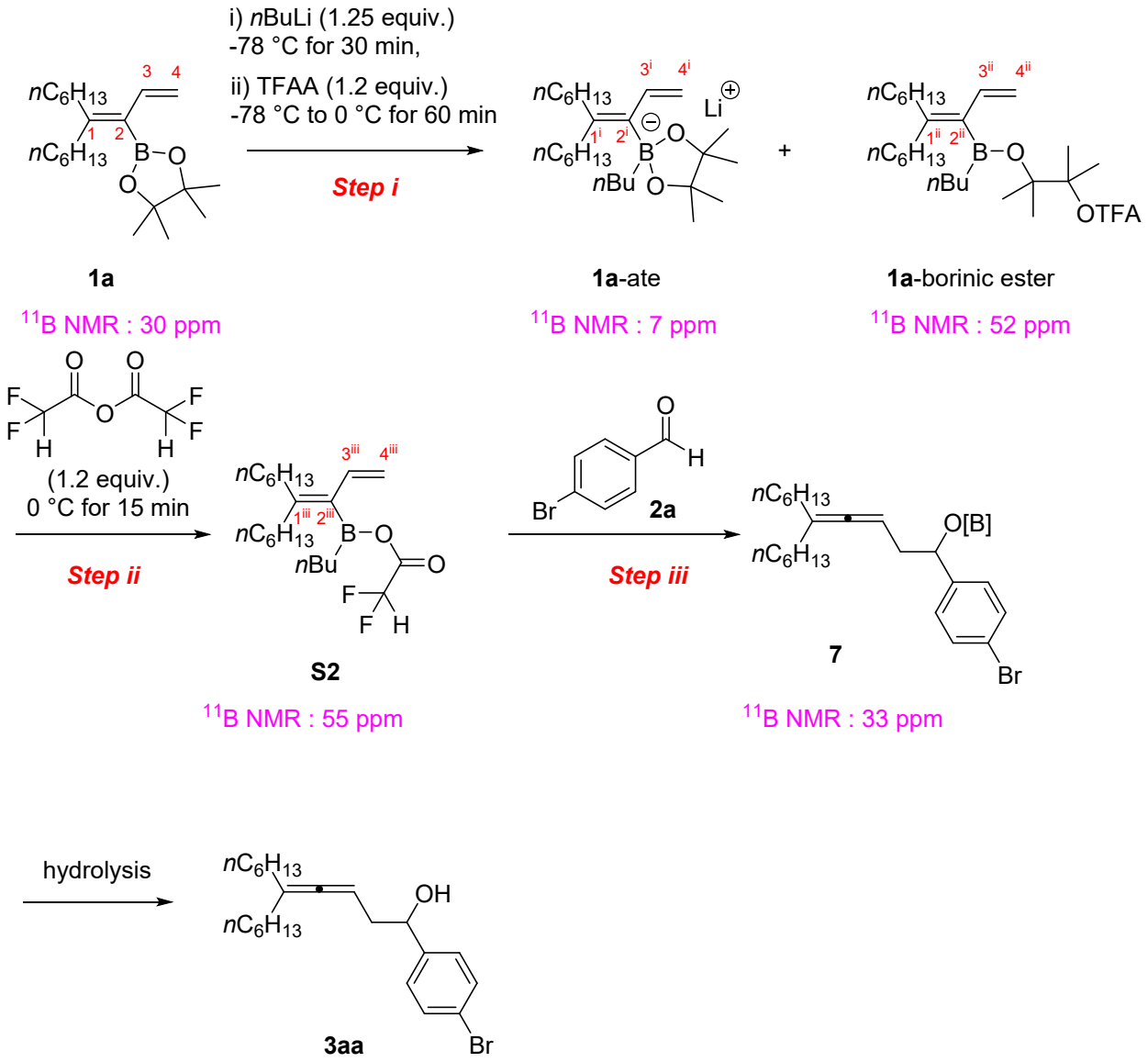
1: TOF MS ES+
2.37e+002



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
311.0710	311.0718	-0.8	-2.6	1.5	39.0	n/a	n/a	C10 H13 O4 F6

Figure S9. HRMS spectra of **6**

3.13 ^{11}B NMR analysis of reaction with $(CHF_2CO)_2O$: Evidence for reactive specie S2



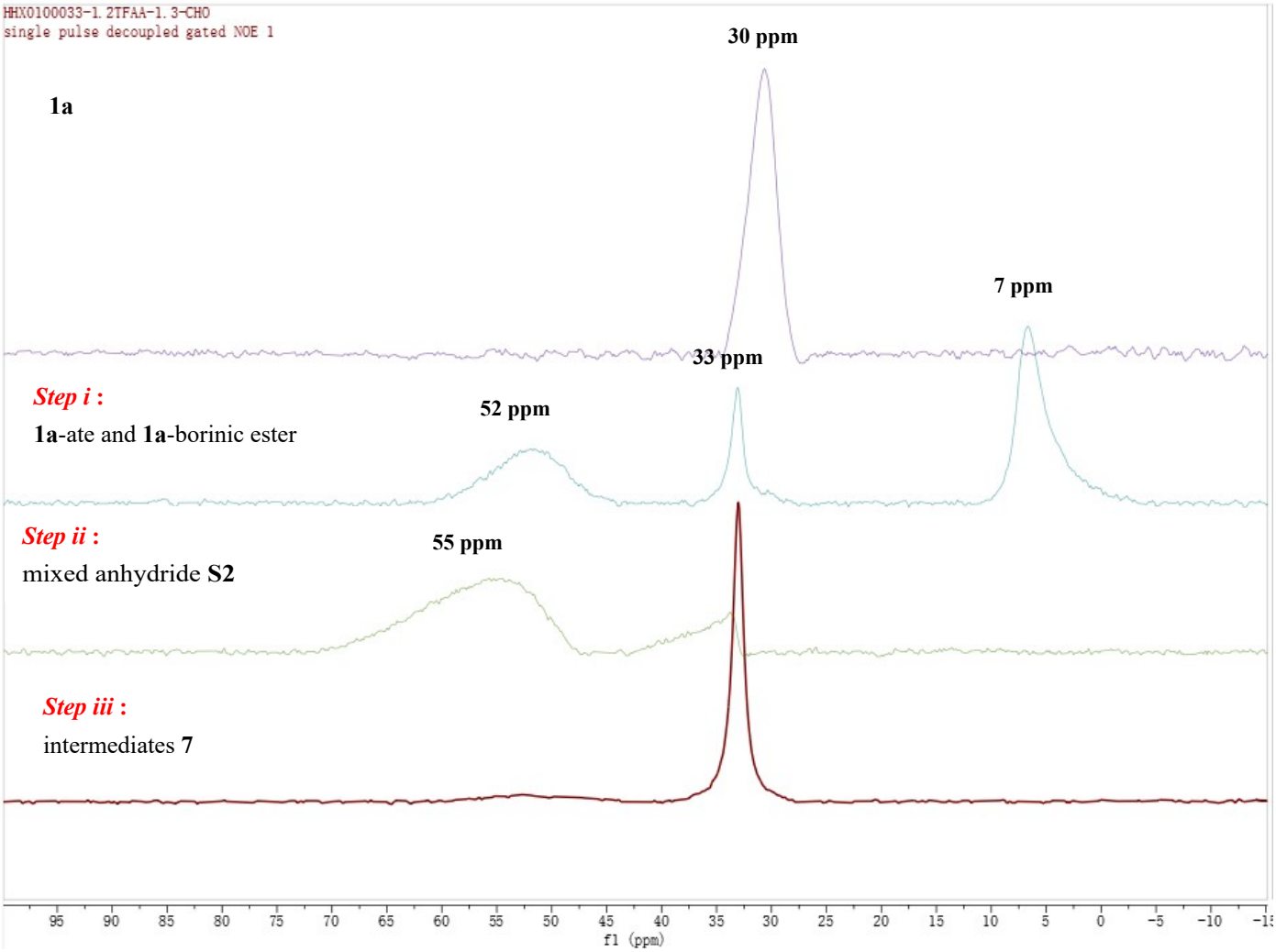
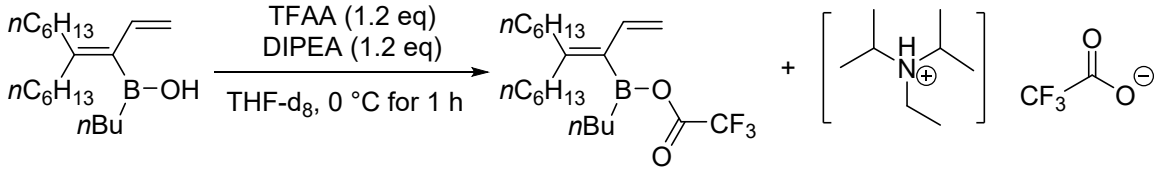


Figure S10. Changes of ^{11}B NMR in the course of the reaction using $(CHF_2CO)_2O$

3.14 ^{11}B NMR analysis of reaction for the synthesis of 1a-TFA mixed anhydride using crude 1a-BOH and TFAA

In the reaction, after sequential addition of DIPEA and TFAA to the solution of crude **1a**-BOH in THF-d_8 at 0 °C, two new species (49 ppm and 6 ppm) was apparently formed in the mixture according to the ^{11}B NMR spectrum. The signal at 49 ppm indicated the formation of **1a**-TFA. The other signal at 6 ppm was assigned as tetracoordinated boron species **S4,** which was probably produced by the further coordination of TFA anion with **1a**-TFA due to the strong Lewis acidity of **1a**-TFA.



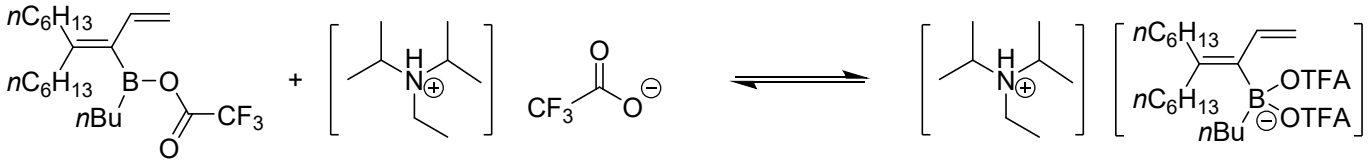
1a-BOH

^{11}B NMR : 52 ppm

1a-TFA
mixed anhydride

^{11}B NMR : 49 ppm

S3



1a-TFA
mixed anhydride

^{11}B NMR : 49 ppm

S3

S4

^{11}B NMR : 6 ppm

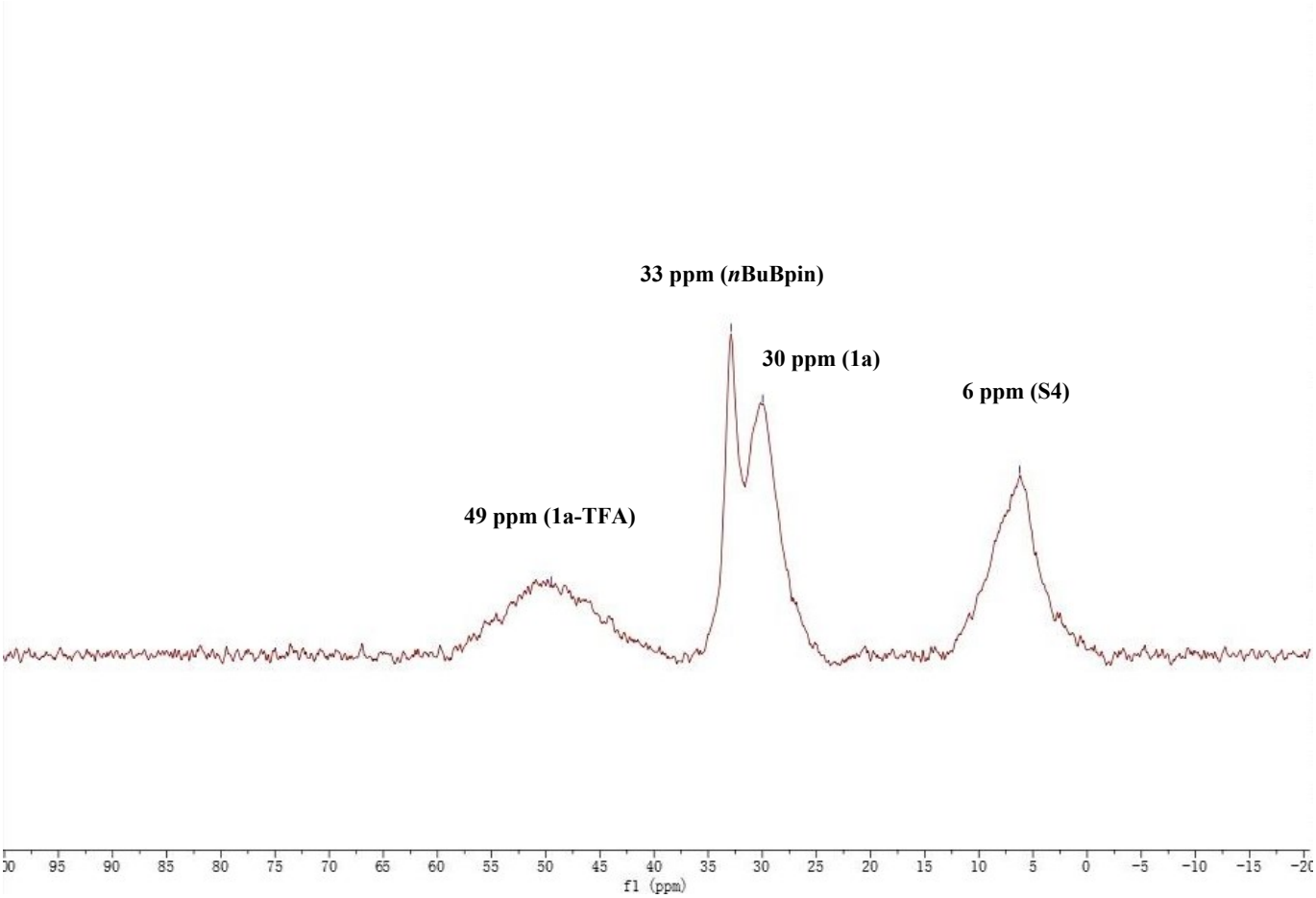


Figure S11. ^{11}B NMR of reaction mixture after addition of DIPEA and TFAA

4 References

[1] K. Semba, T. Fujihara, J. Terao, Y. Tsuji, *Angew. Chem. Int. Ed.* **2013**, *52*, 12400-12403.

[2] W.-D. Zhang, J.-Y. Zou, Q. Zhong, S.-S. Li, J. Zhao, *Chem. Commun.* **2022**, *58*, 1037-1040.

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[4] M. Shen, Y. Tu, G. Xie, Q. Niu, H. Mao, T. Xie, R. A. Flowers, X. Lv, X. Wang, *J. Org. Chem.* **2015**, *80*, 52-61.

[5] B. Gockel, N. Krause, *Org. Lett.* **2006**, *8*, 4485-4488.

[6] J. Hine, D. Ricard, R. Perz, *J. Org. Chem.* **1973**, *38*, 110-112.

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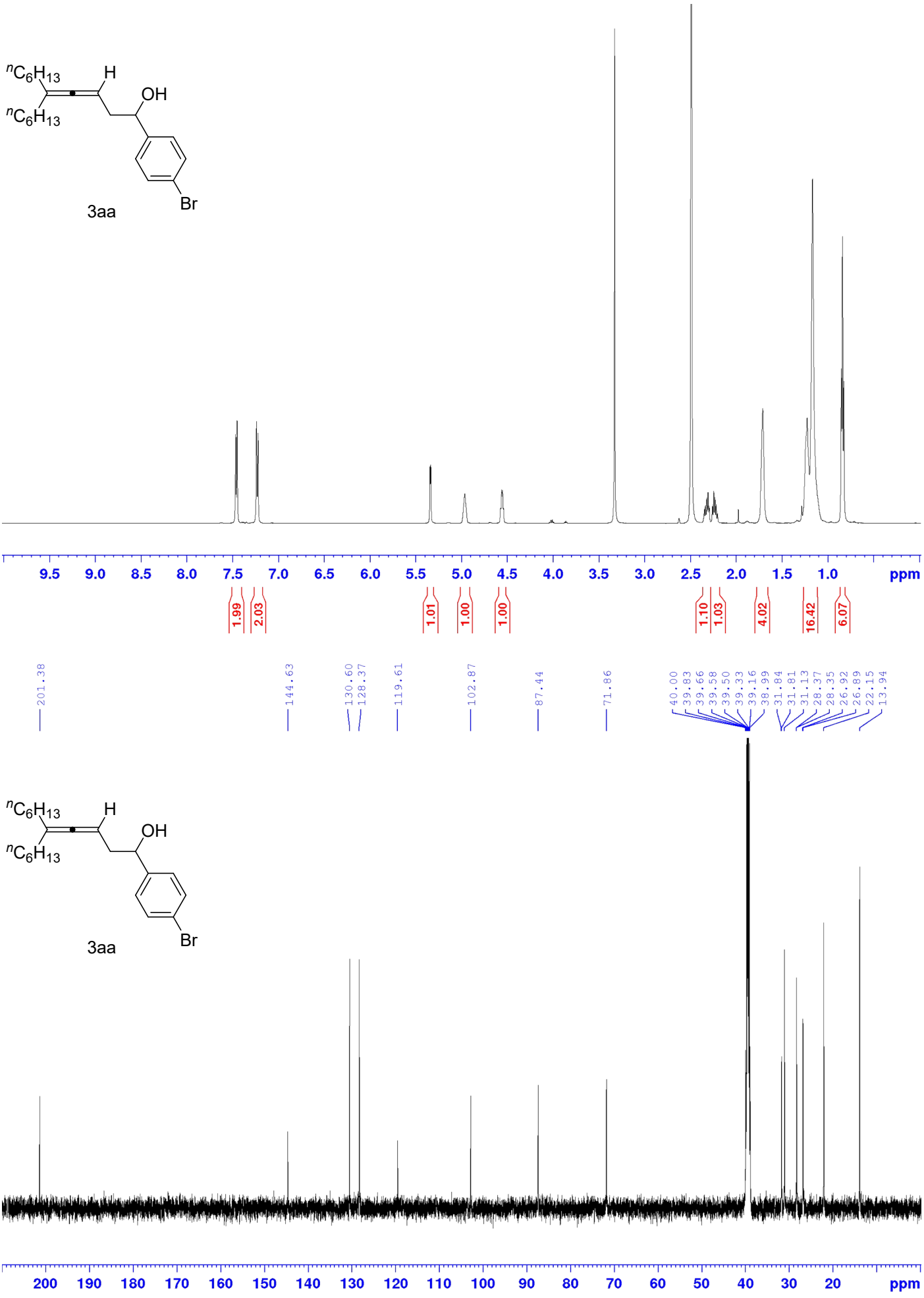
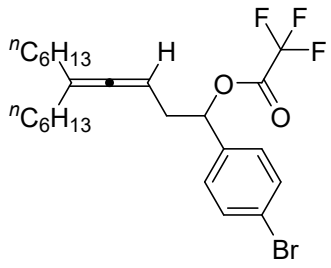
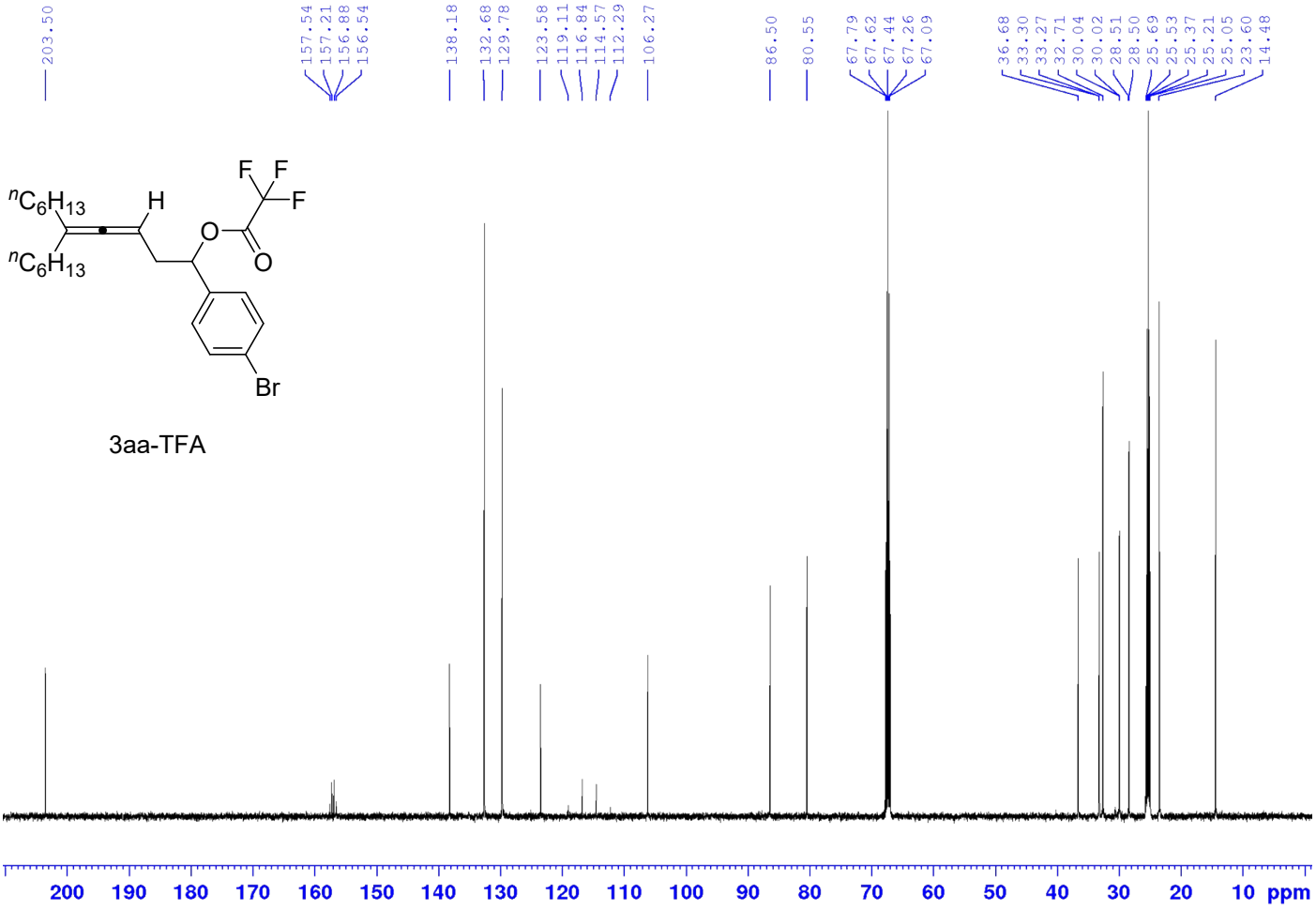
5 ^{1}H, ^{13}C and ^{11}B NMR Spectra

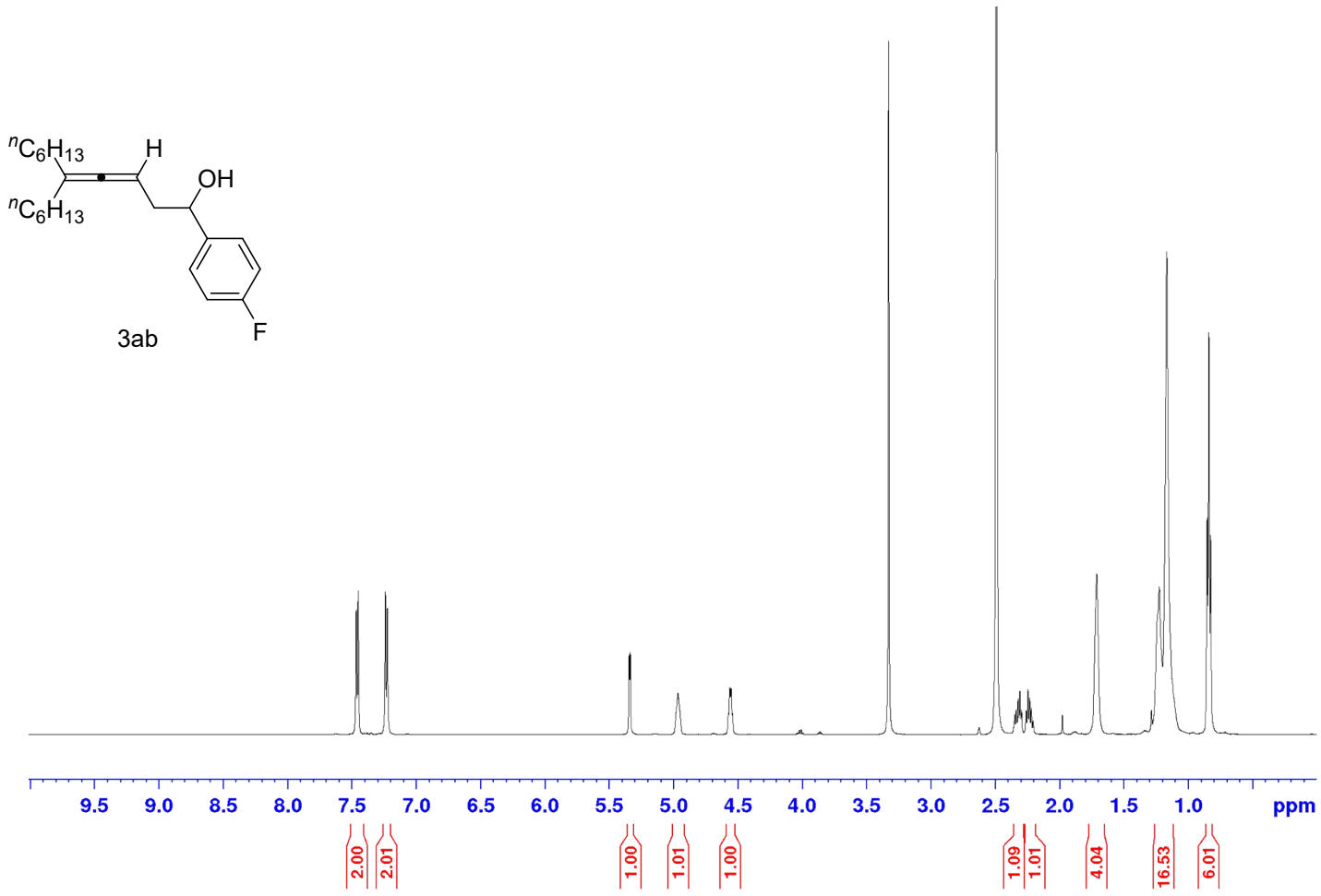


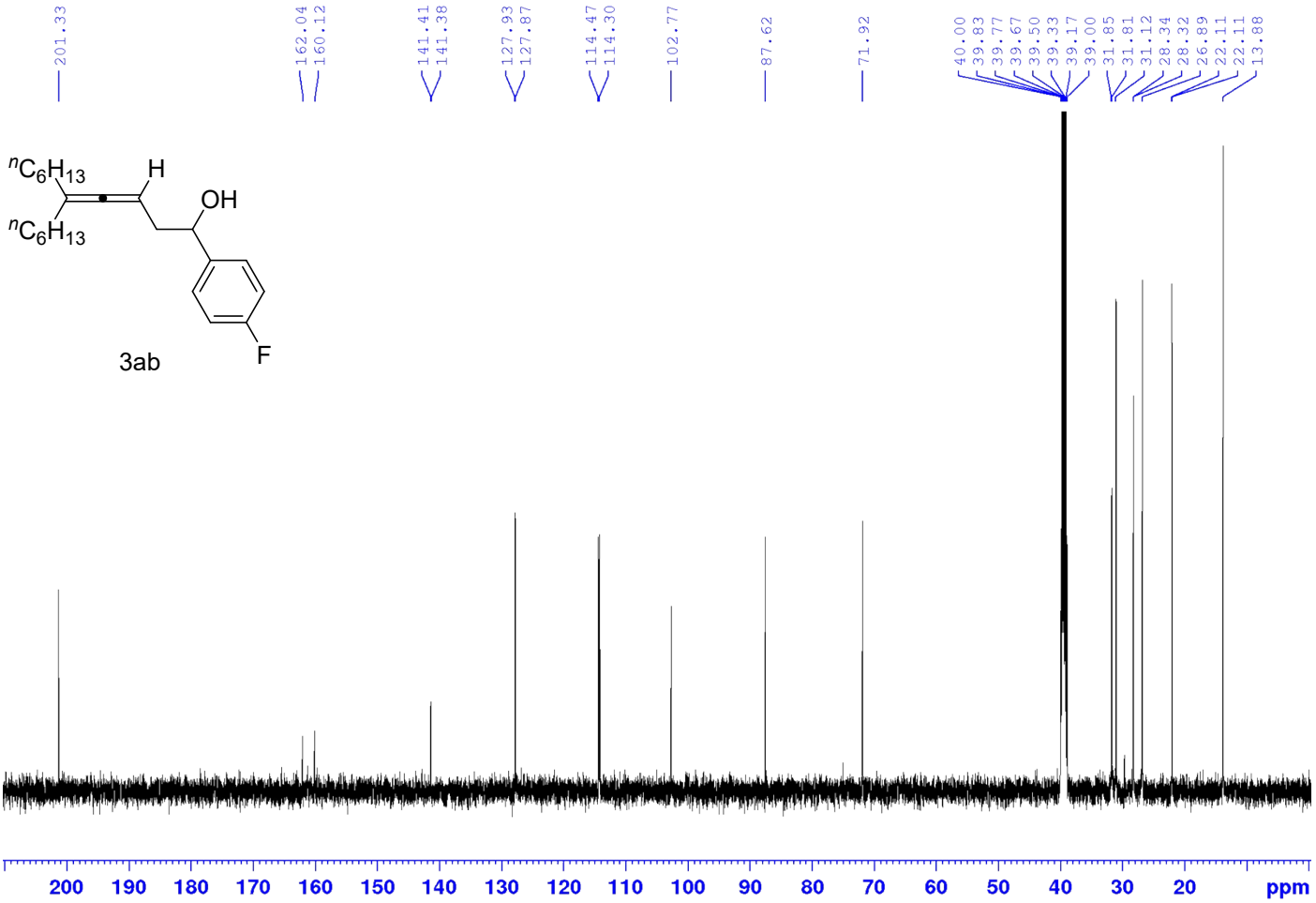


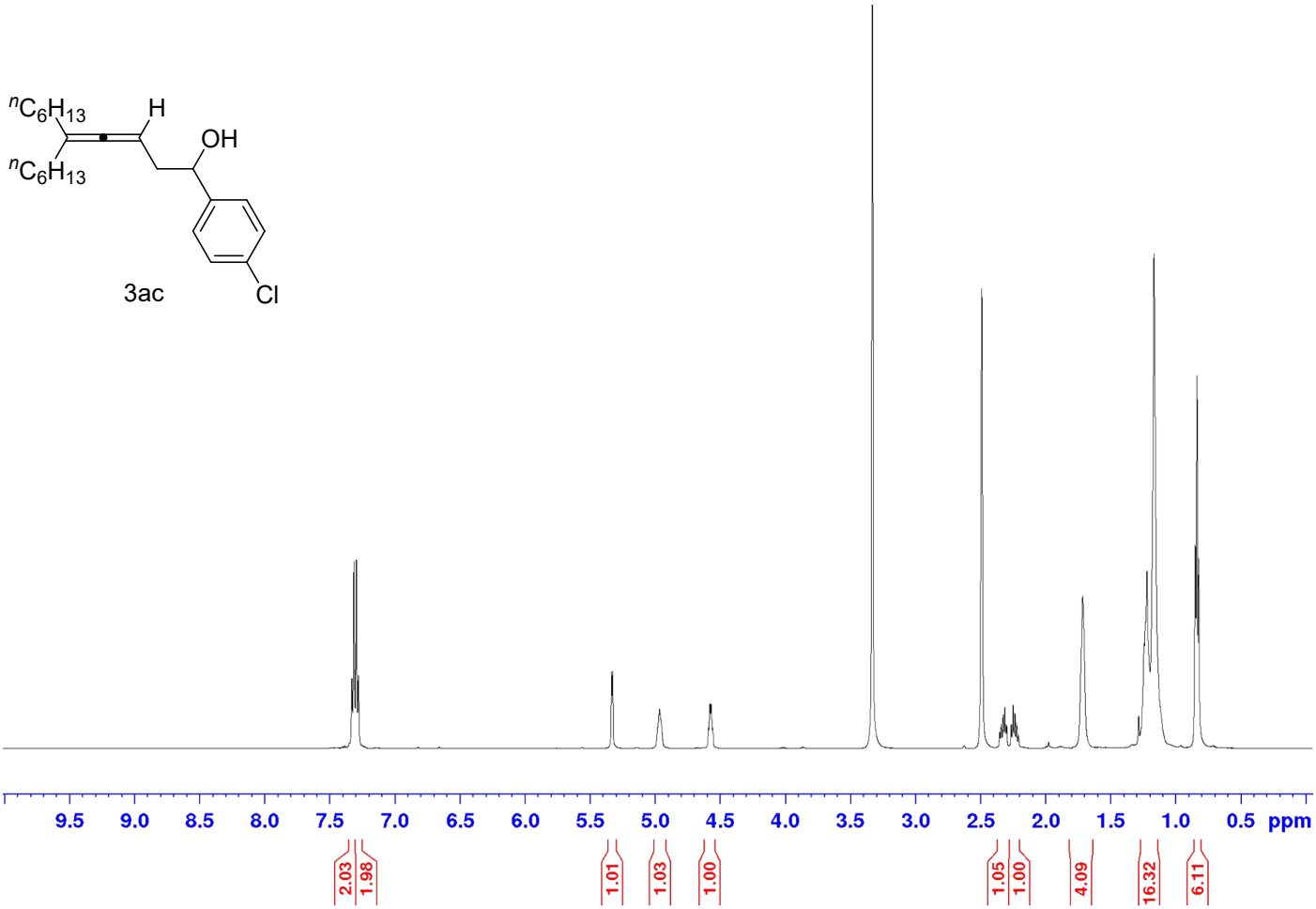
3aa-TFA

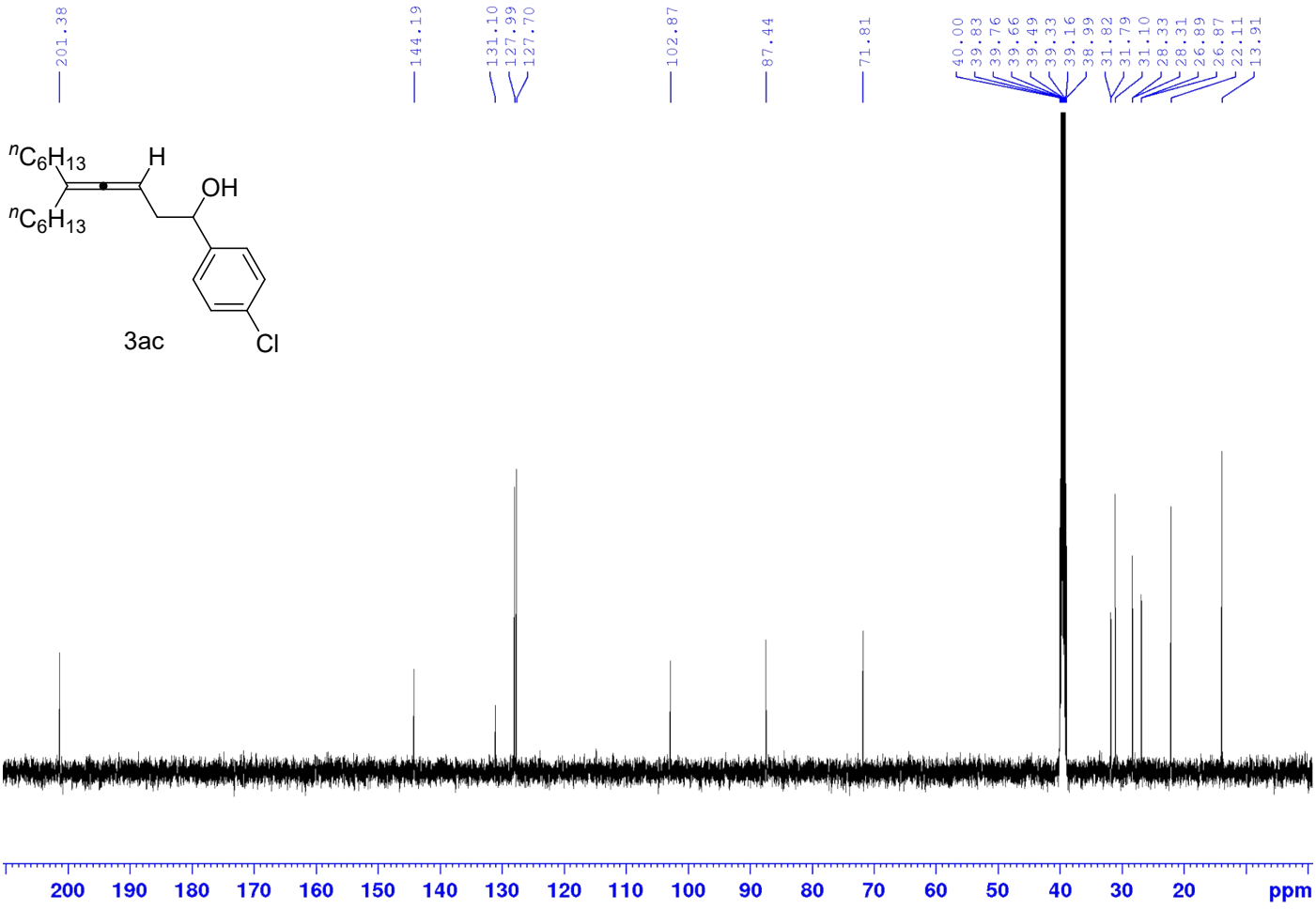


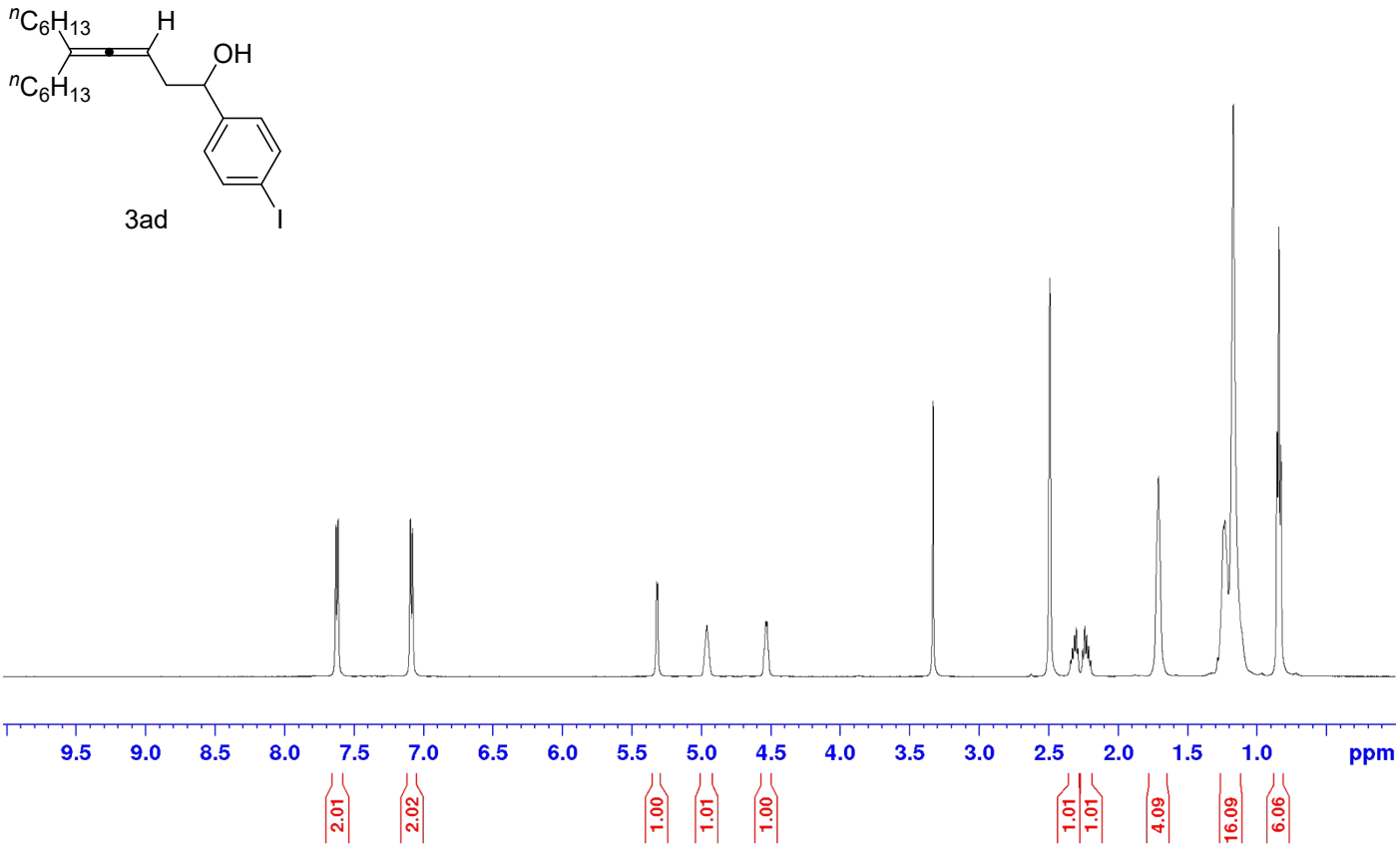
3aa-TFA

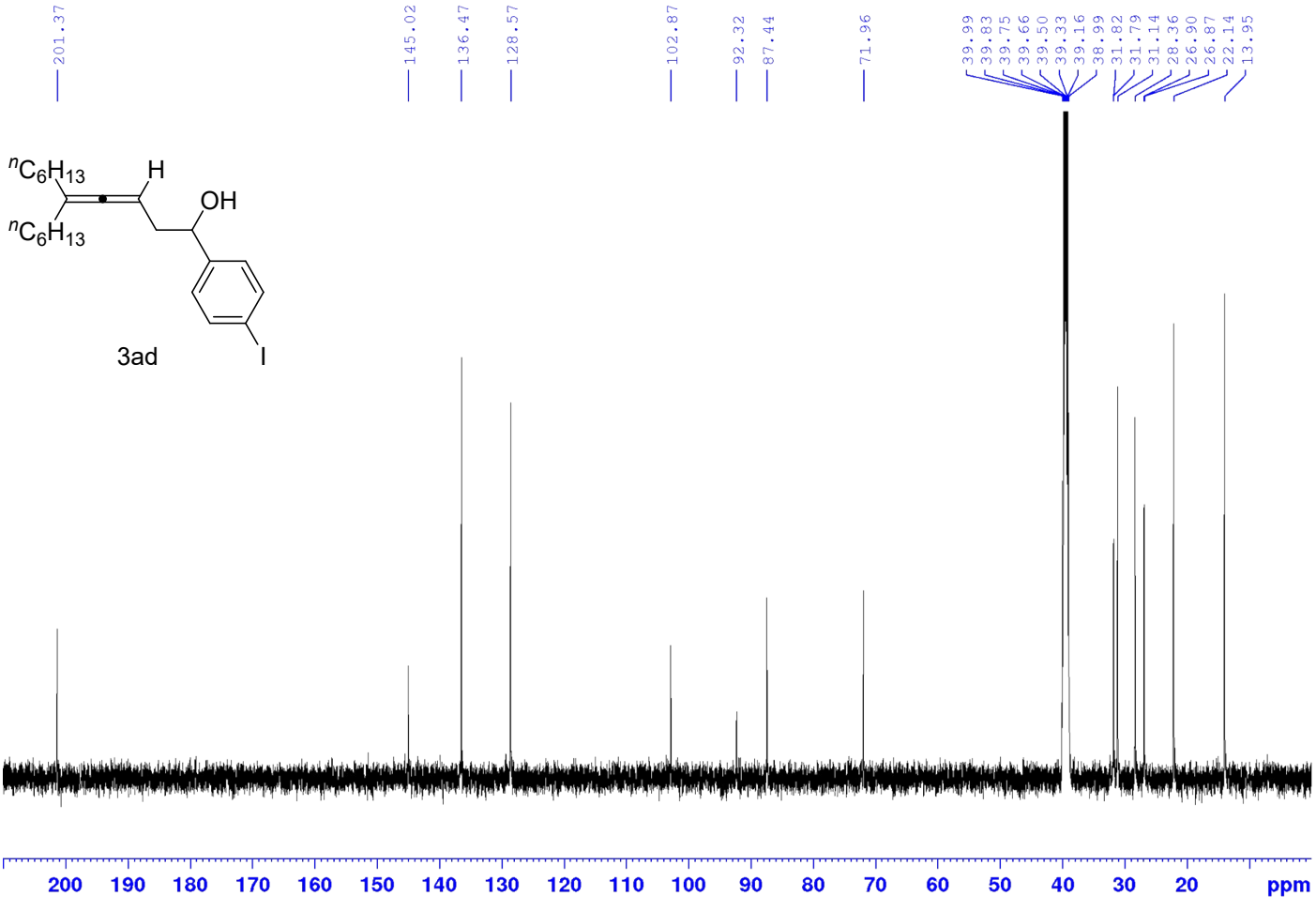

nC6H13
H
OH
nC6H13
F
3ab
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00 2.01 1.00 1.01 1.00 1.09 1.01 4.04 16.53 6.01

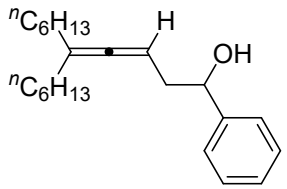

201.33
162.04
160.12
141.41
141.38
127.93
127.87
114.47
114.30
102.77
87.62
71.92
40.00
39.83
39.77
39.67
39.50
39.33
39.17
39.00
31.85
31.81
31.12
28.34
28.32
26.89
22.11
22.11
13.88
nC6H13
H
OH
nC6H13
F
3ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
3ac
Cl
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
2.03
1.98
1.01
1.03
1.00
1.05
1.00
4.09
16.32
6.11

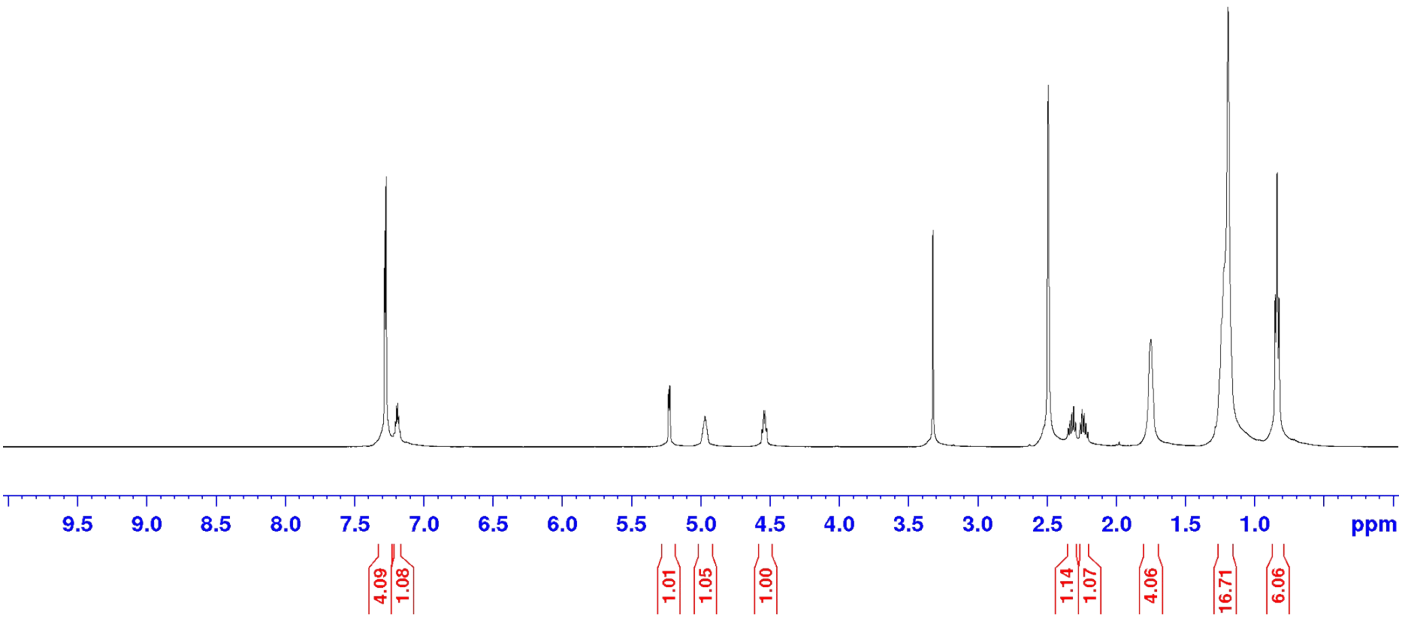

201.38
144.19
131.10
127.99
127.70
102.87
87.44
71.81
40.00
39.83
39.76
39.66
39.49
39.33
39.16
38.99
31.82
31.79
31.10
28.33
28.31
26.89
26.87
22.11
13.91
^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
3ac
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
3ad
I
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
2.01 2.02 1.00 1.01 1.00 1.01 1.01 4.09 16.09 6.06


201.37
145.02
136.47
128.57
102.87
92.32
87.44
71.96
39.99
39.83
39.75
39.66
39.50
39.33
39.16
38.99
31.82
31.79
31.14
28.36
26.90
26.87
22.14
13.95
^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
3ad
I
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$

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 ppm
4.09
1.08
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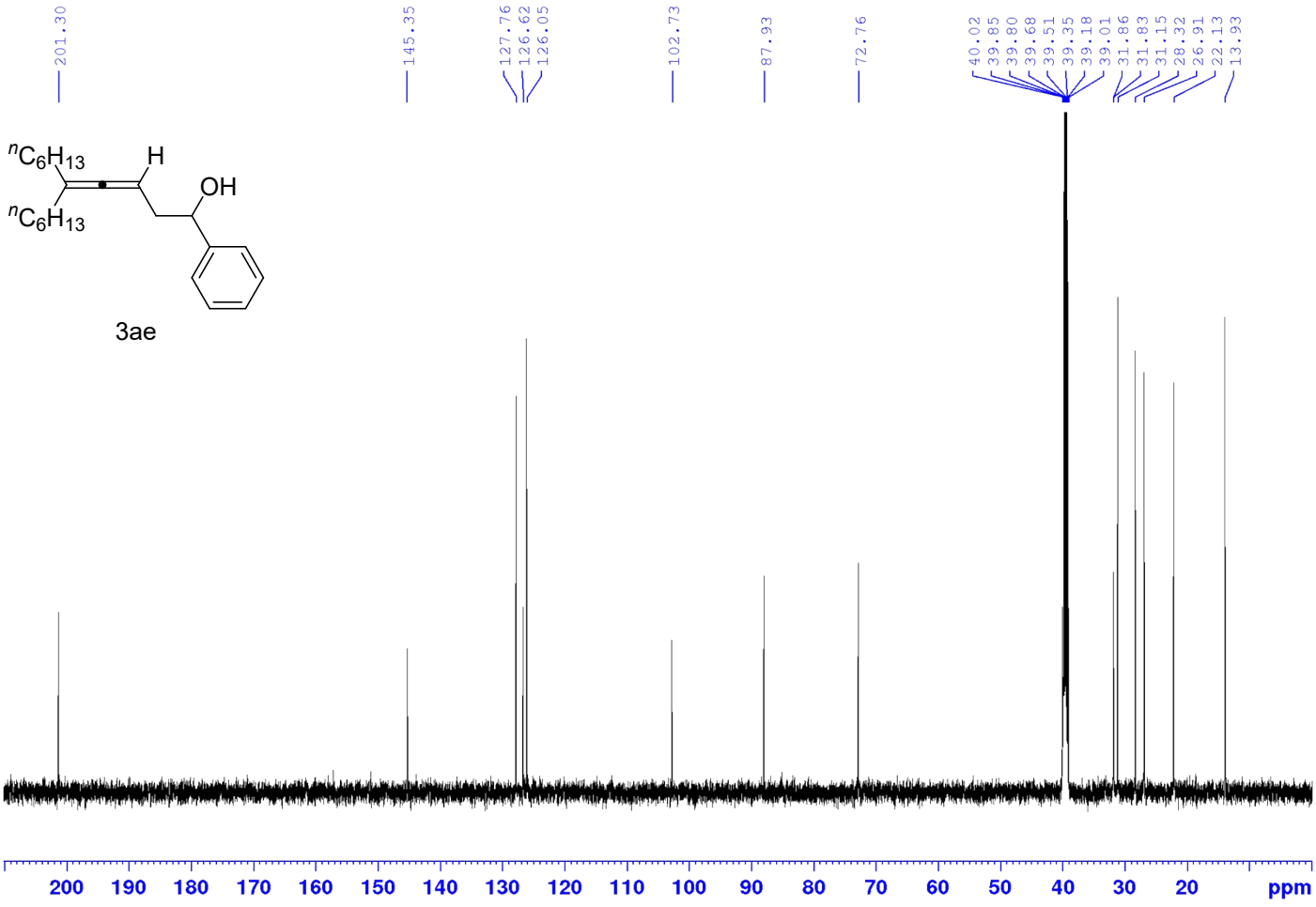
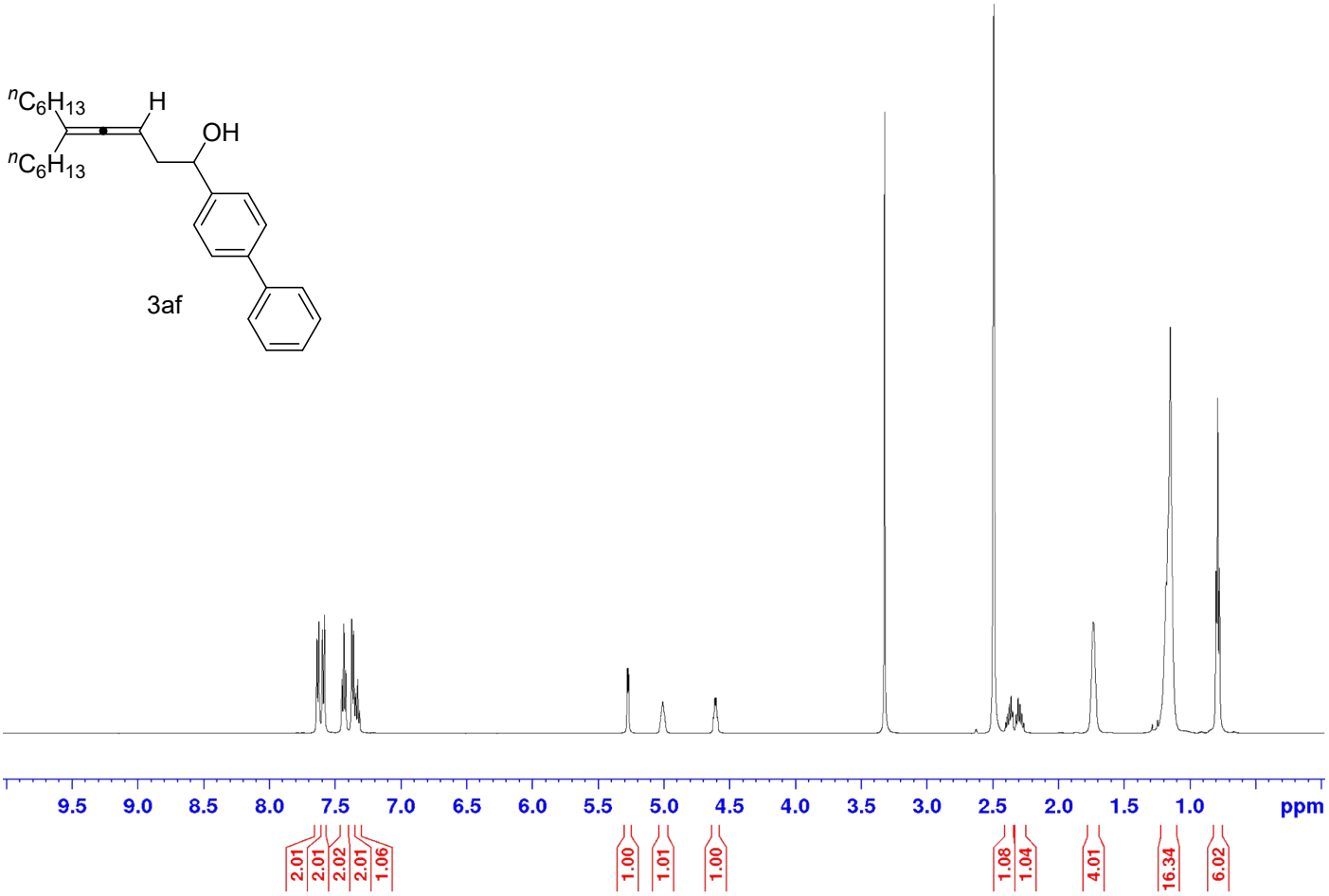
1.00
1.14
1.07
4.06
16.71
6.06


201.30
145.35
127.76
126.62
126.05
102.73
87.93
72.76
40.02
39.85
39.80
39.68
39.51
39.35
39.18
39.01
31.86
31.83
31.15
28.32
26.91
22.13
13.93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$

3ae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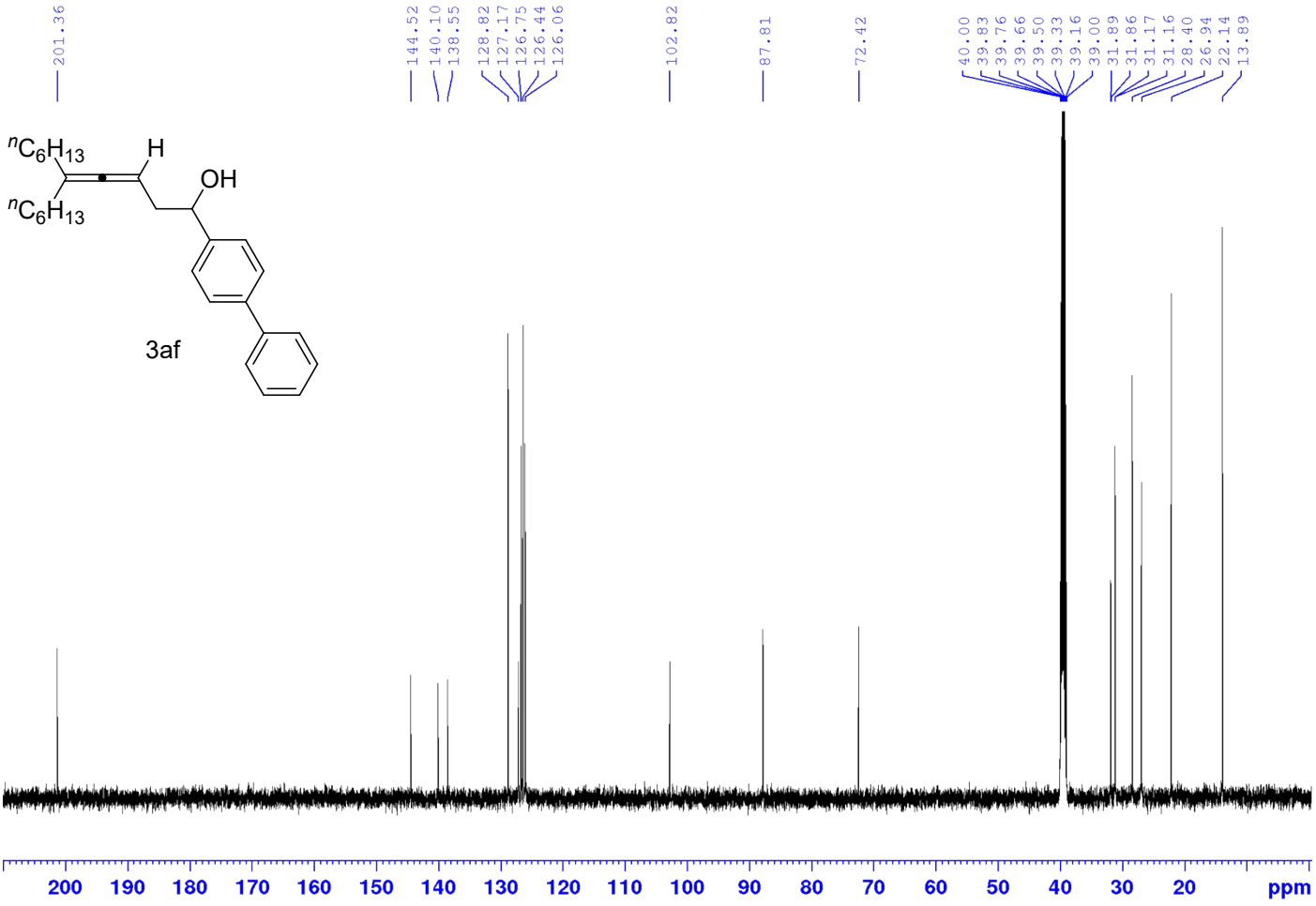
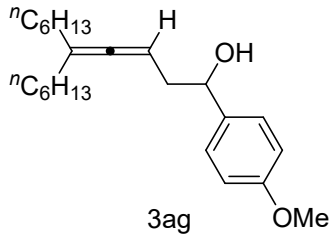
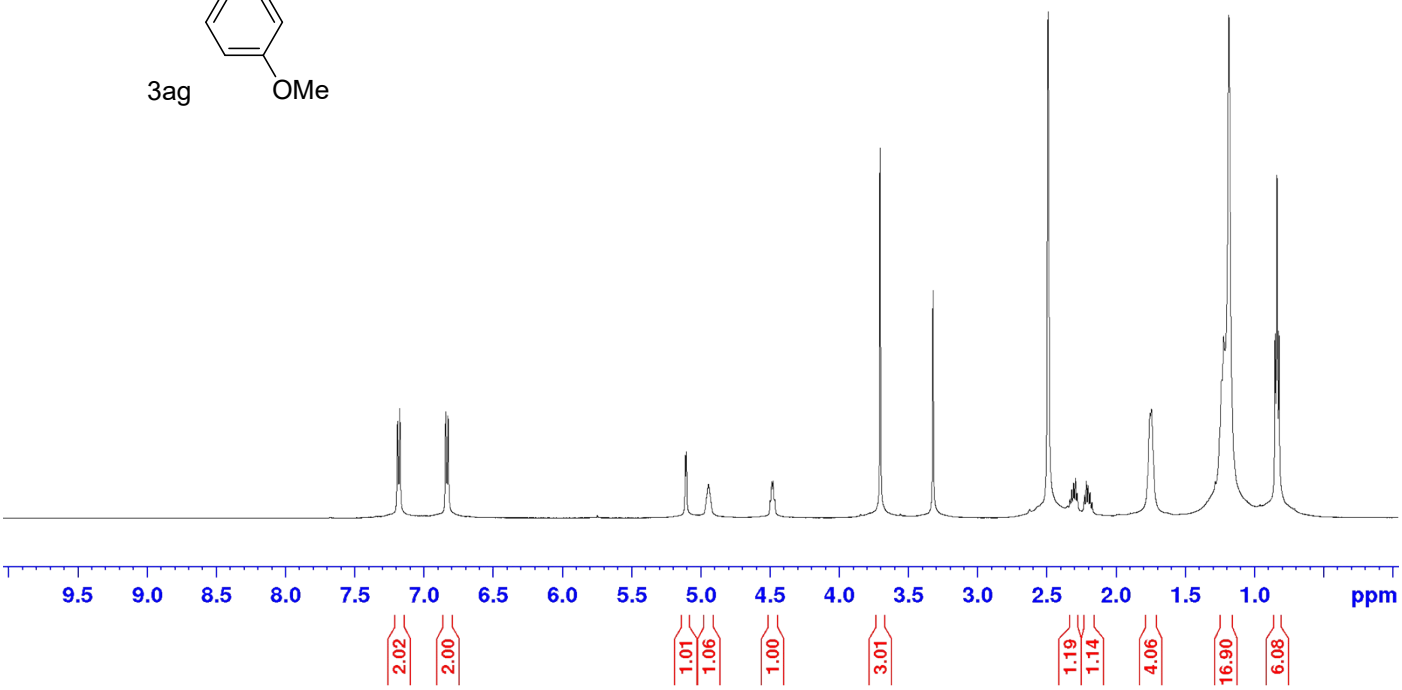
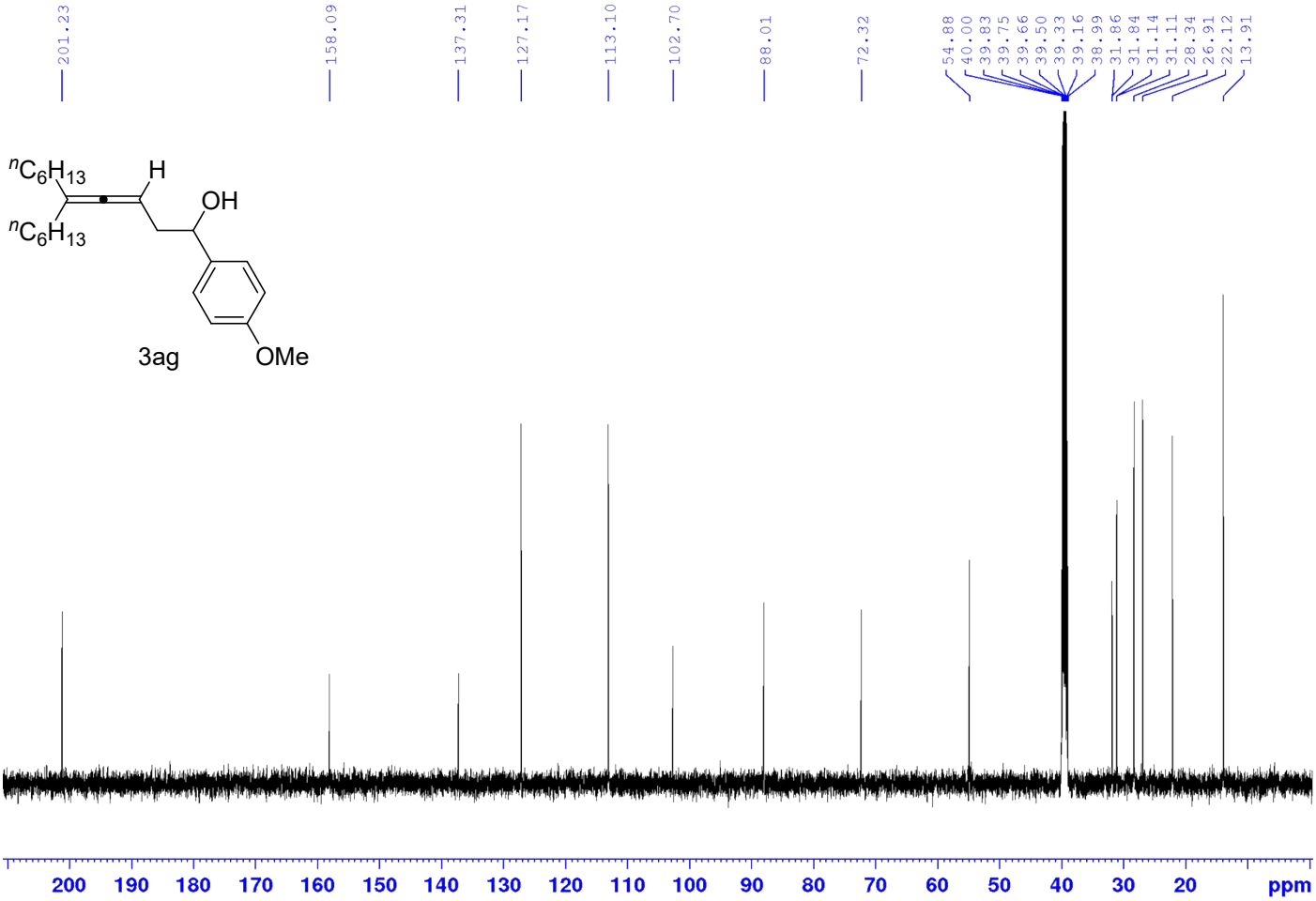
H
OH
$^{n}C_6H_{13}$
3af
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.01 2.01 2.02 2.01 1.06 1.00 1.01 1.00 1.08 1.04 4.01 16.34 6.02


201.36
144.52 140.10 138.55 128.82 127.17 126.75 126.44 126.06 102.82 87.81 72.42
40.00 39.83 39.76 39.66 39.50 39.33 39.16 39.00 31.89 31.86 31.17 31.16 28.40 26.94 22.14 13.89
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3af
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

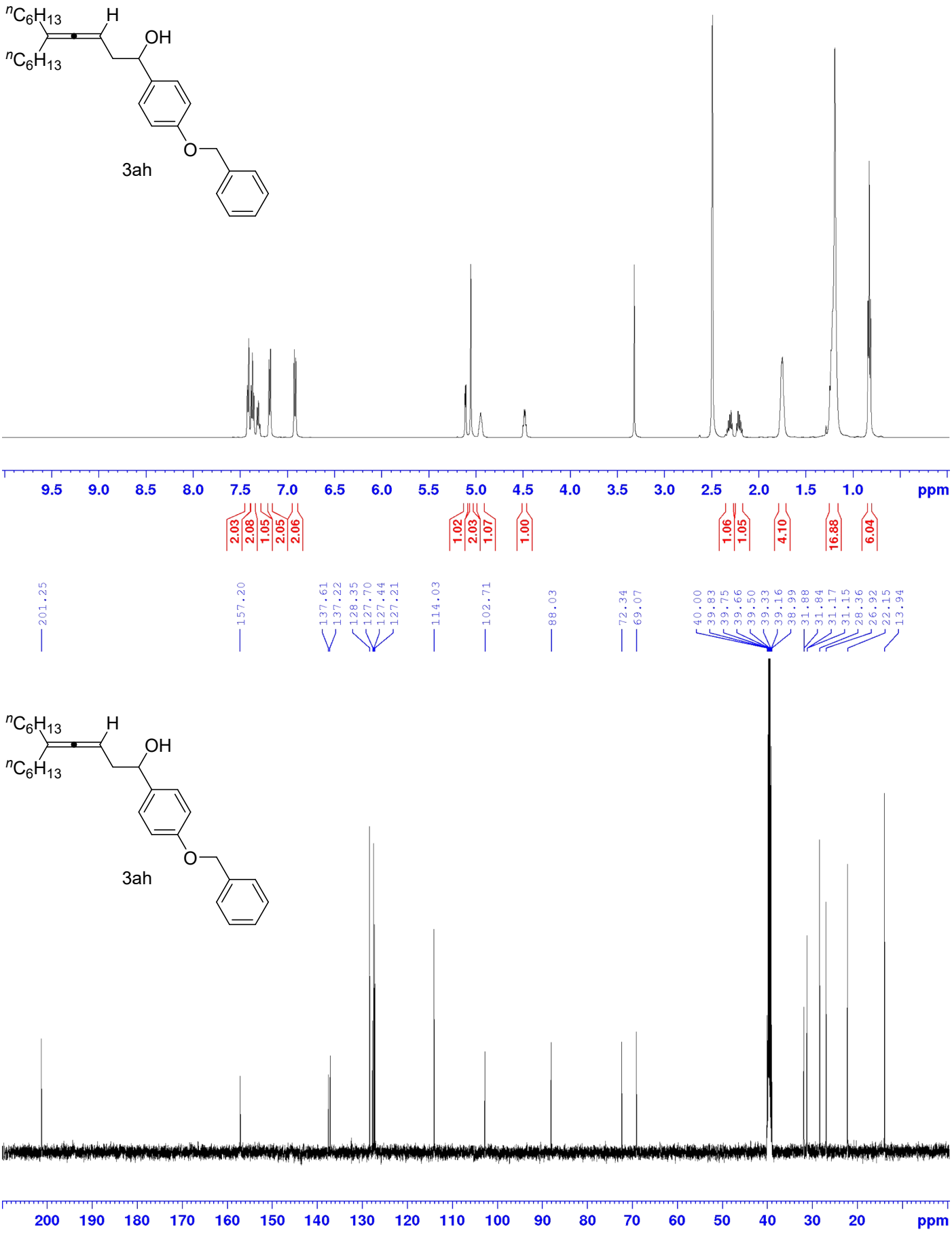


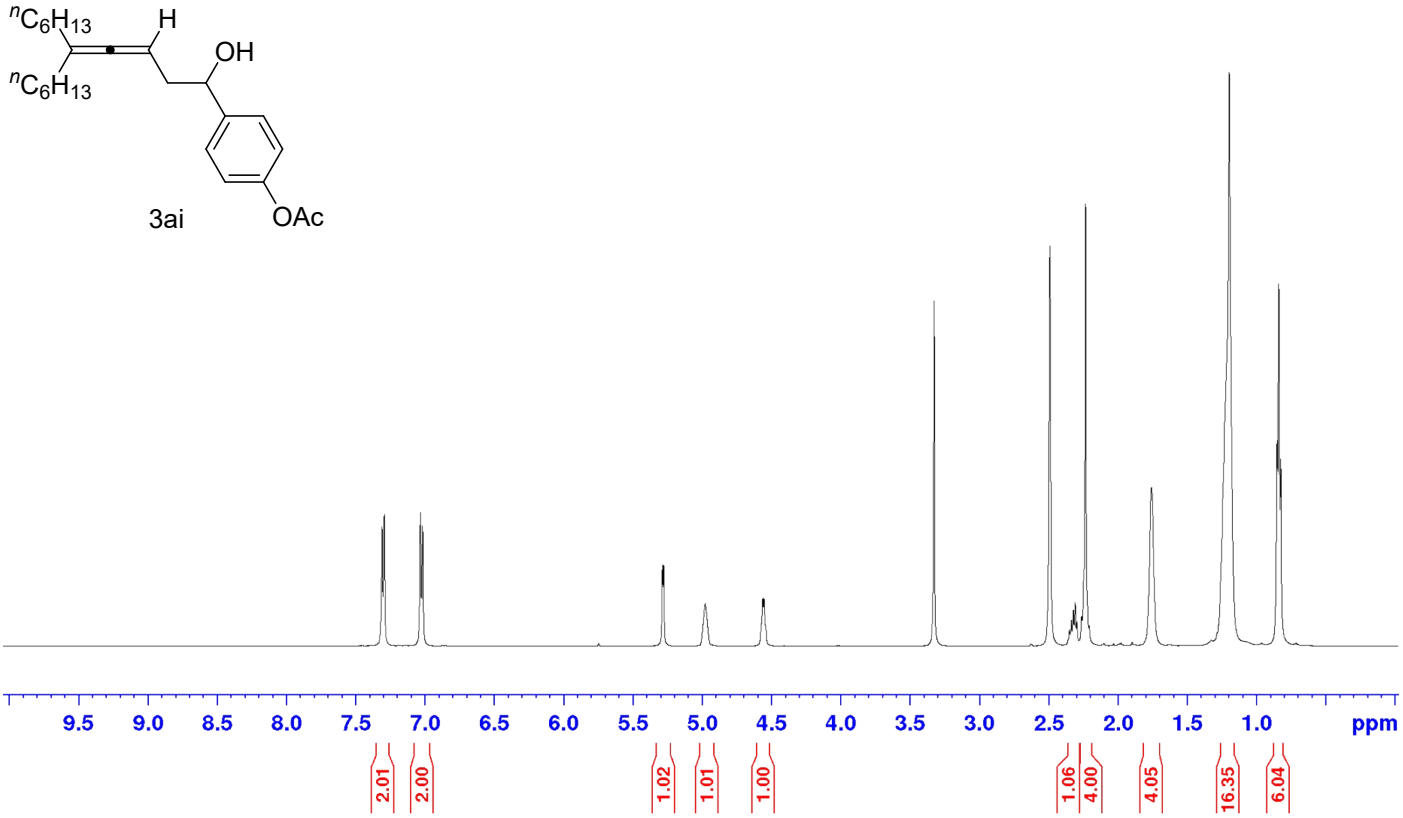
3ag

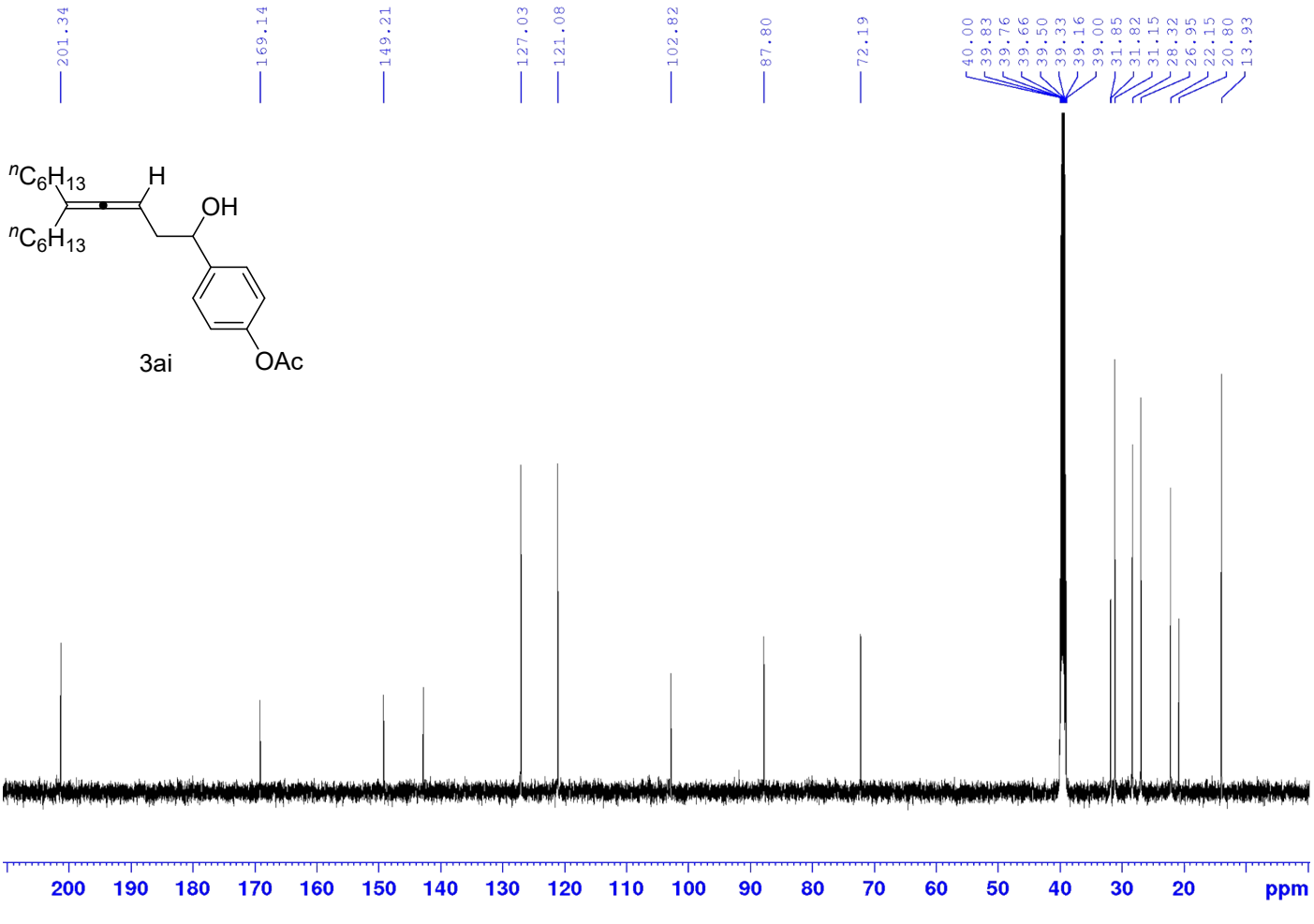


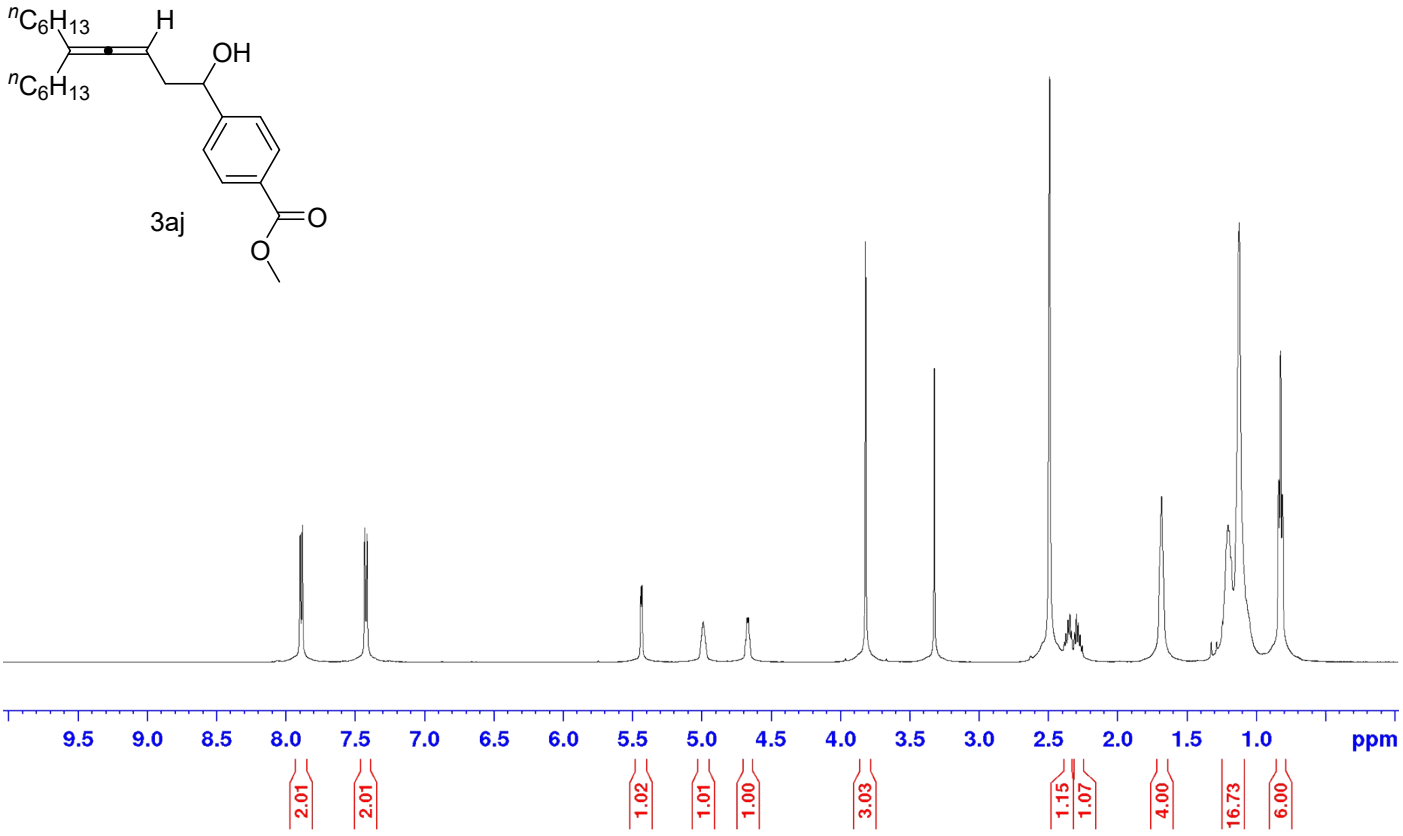


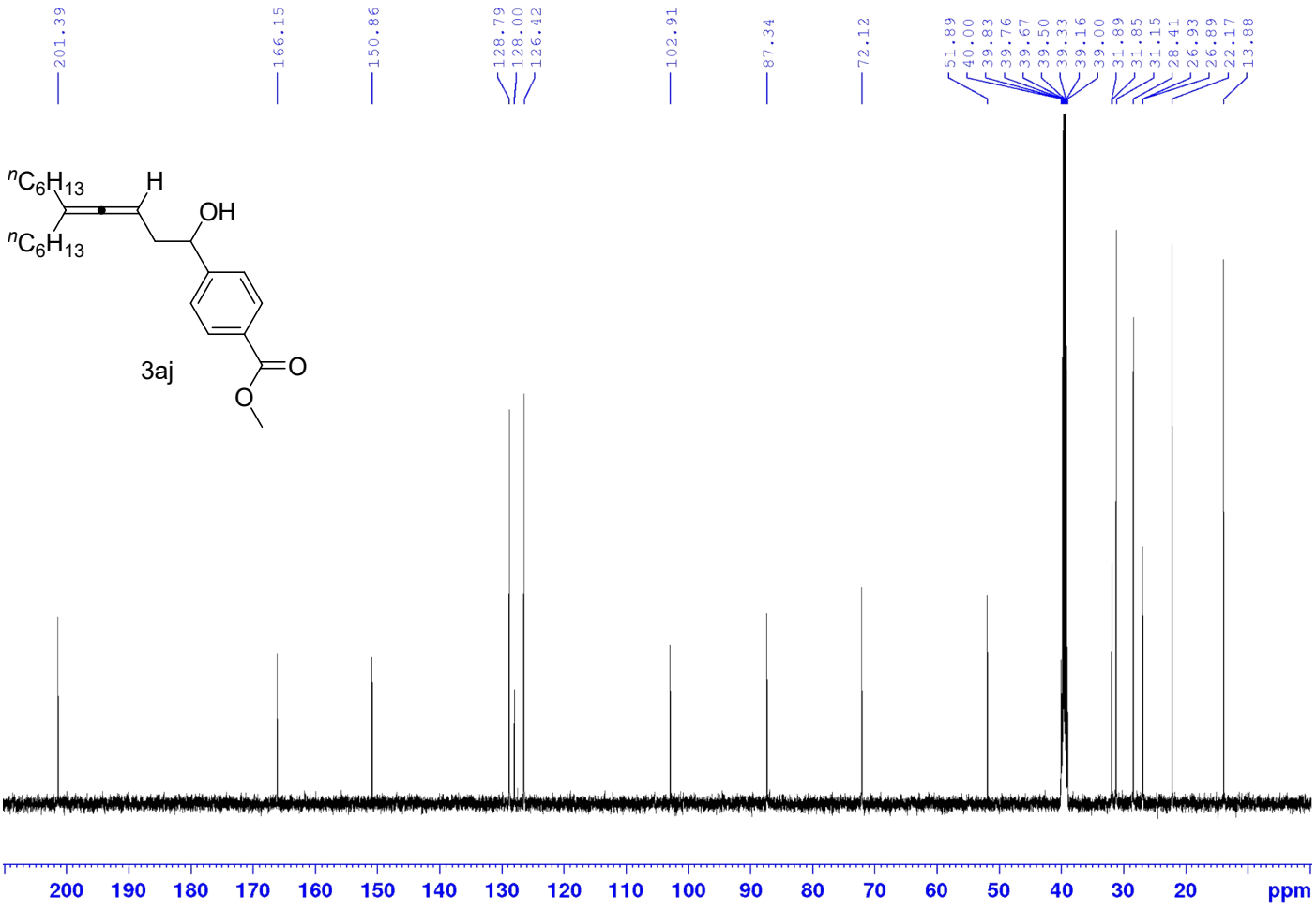
nC6H13
H
OH
nC6H13
3ag
OMe

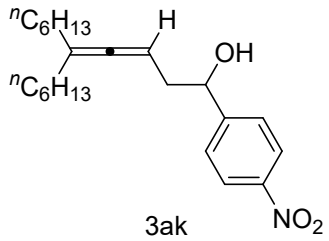

$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
O
3ah
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.03 2.08 1.05 2.05 2.06 1.02 2.03 1.07 1.00 1.06 1.05 4.10 16.88 6.04
201.25 157.20 137.61 137.22 128.35 127.70 127.44 127.21 114.03 102.71 88.03 72.34 69.07 40.00 39.83 39.75 39.66 39.50 39.33 39.16 38.99 31.88 31.84 31.17 31.15 28.36 26.92 22.15 13.94
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
O
3ah
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3ai
OAc
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
2.01 2.00 1.02 1.01 1.00 1.06 4.00 4.05 16.35 6.04


201.34 169.14 149.21 127.03 121.08 102.82 87.80 72.19
40.00 39.83 39.76 39.66 39.50 39.33 39.16 39.00 31.85 31.82 31.15 28.32 26.95 22.15 20.80 13.93
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3ai
OAc
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

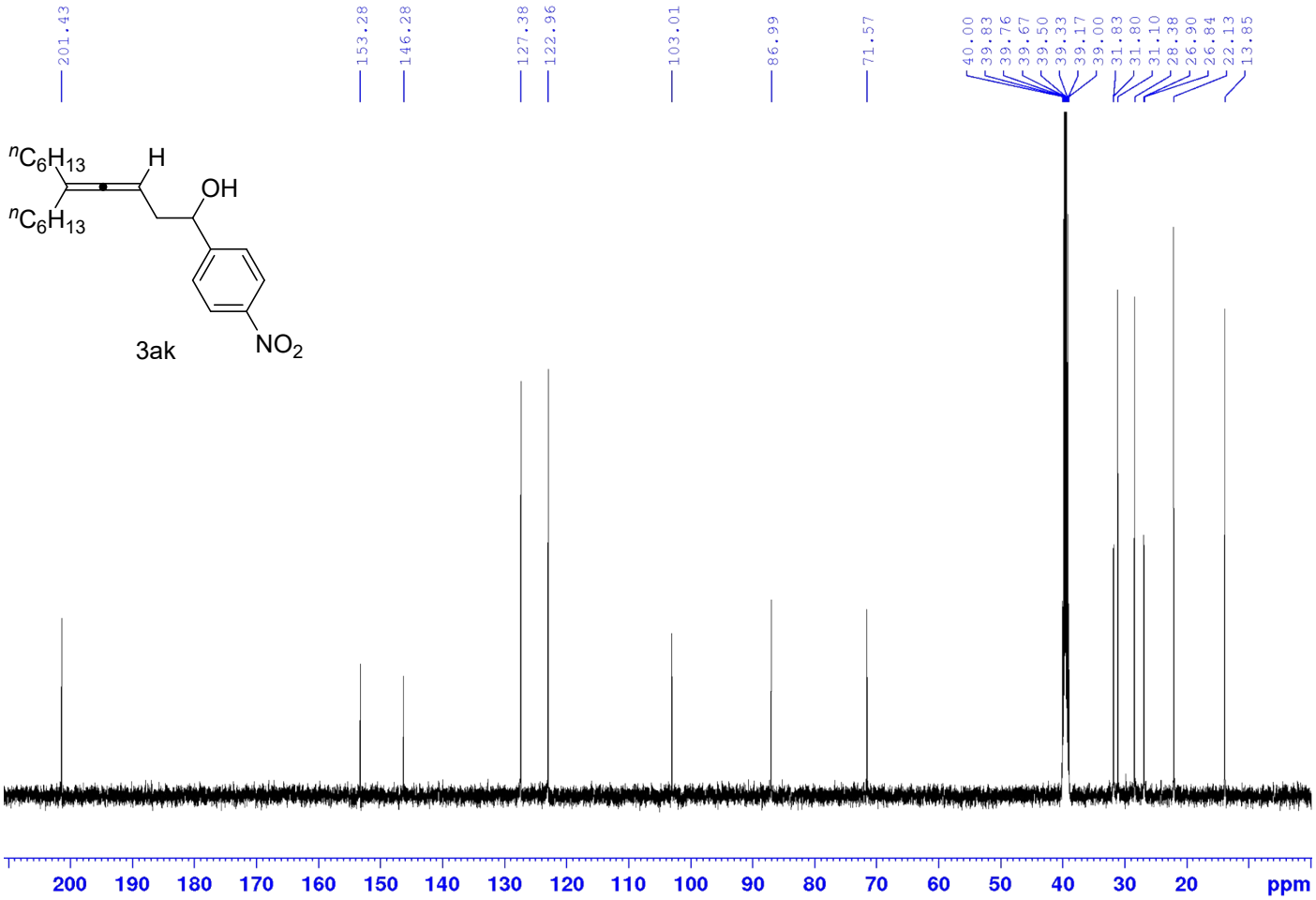

^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
3aj
O
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.01 2.01 1.02 1.01 1.00 3.03 1.15 1.07 4.00 16.73 6.00


201.39
166.15
150.86
128.79
128.00
126.42
102.91
87.34
72.12
51.89
40.00
39.83
39.76
39.67
39.50
39.33
39.16
39.00
31.89
31.85
31.15
28.41
26.93
26.89
22.17
13.88
^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
3aj
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
NO$_2$

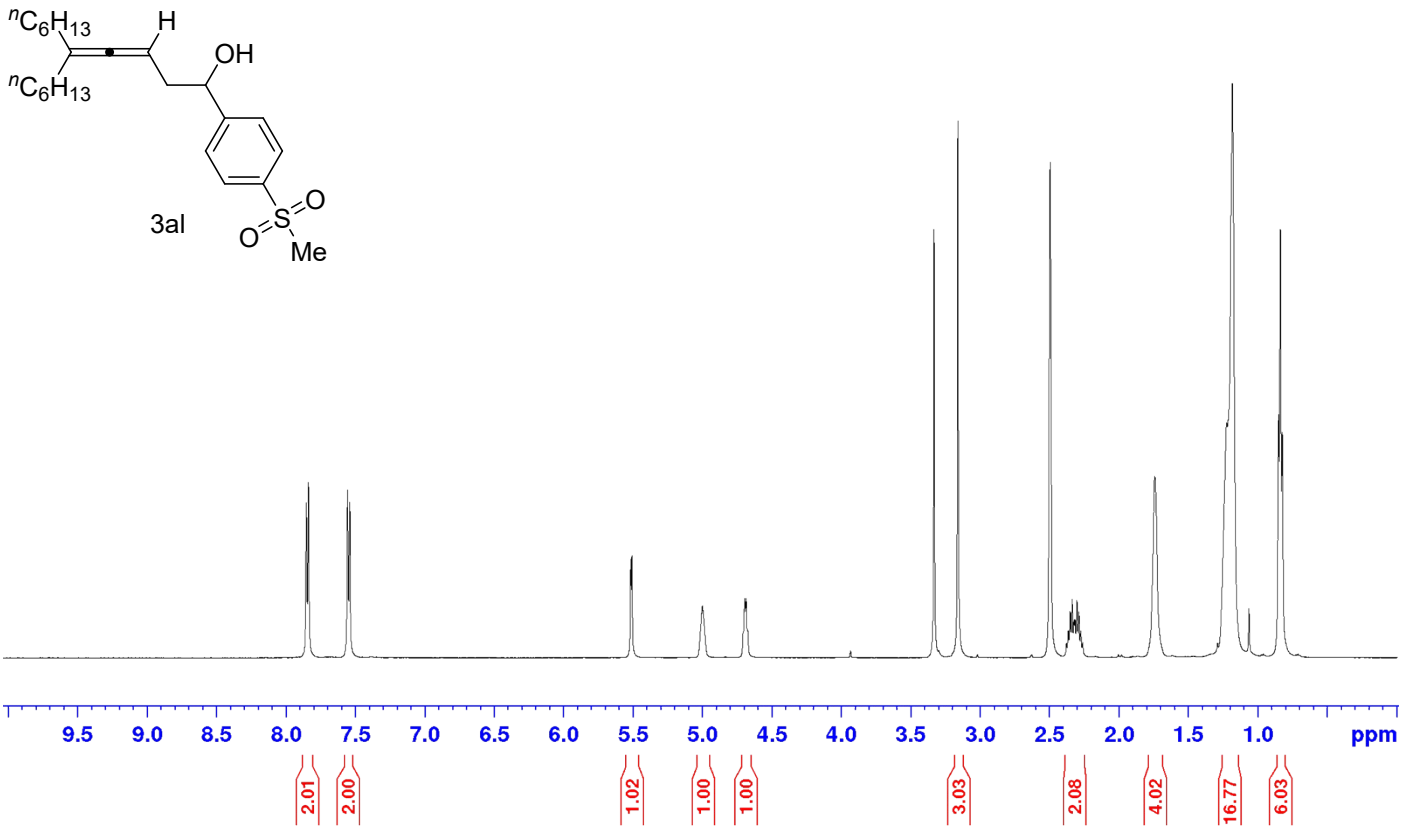
3ak

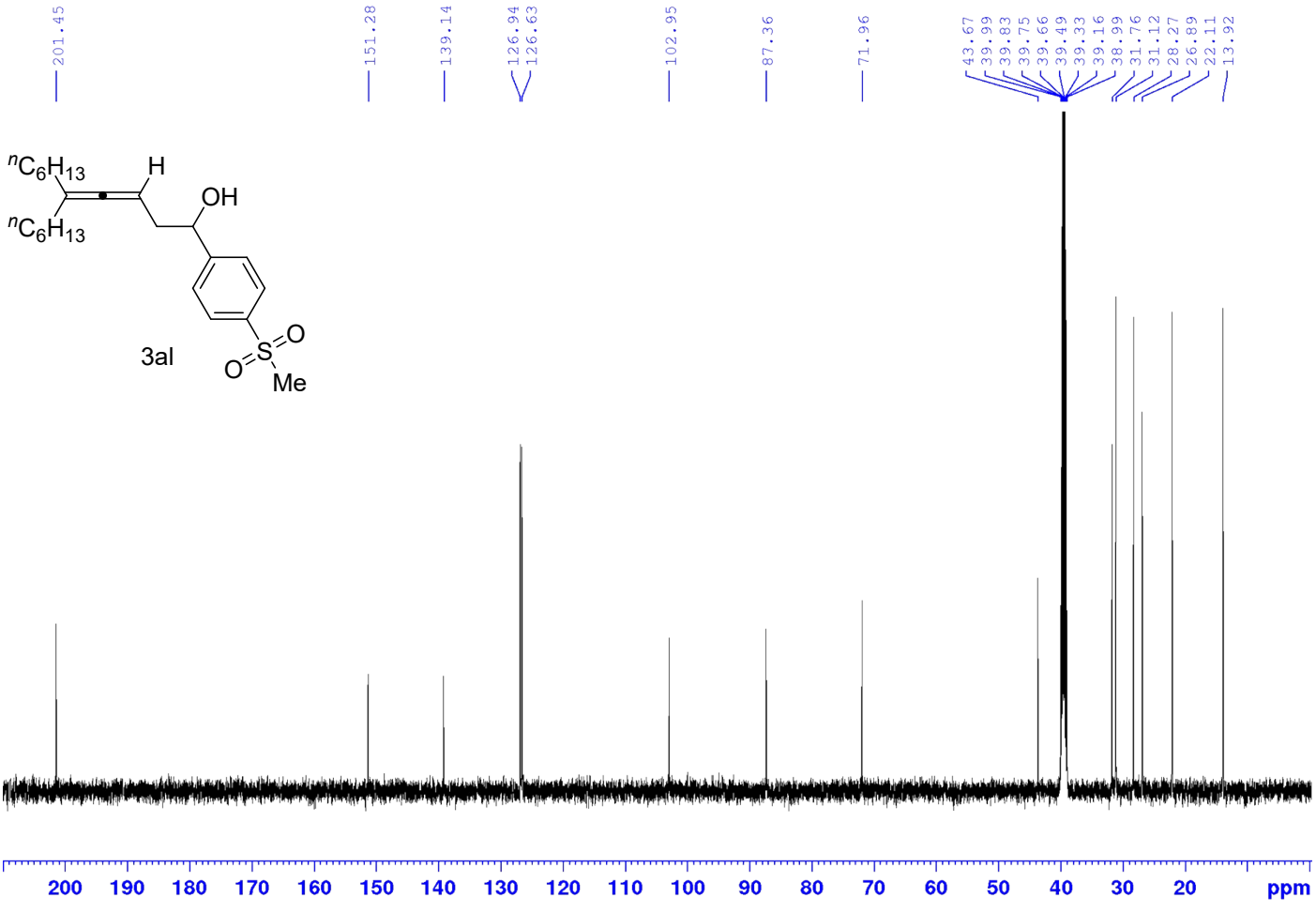
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.06
2.07
1.01
1.01
1.00
2.08
4.06
16.53
6.01

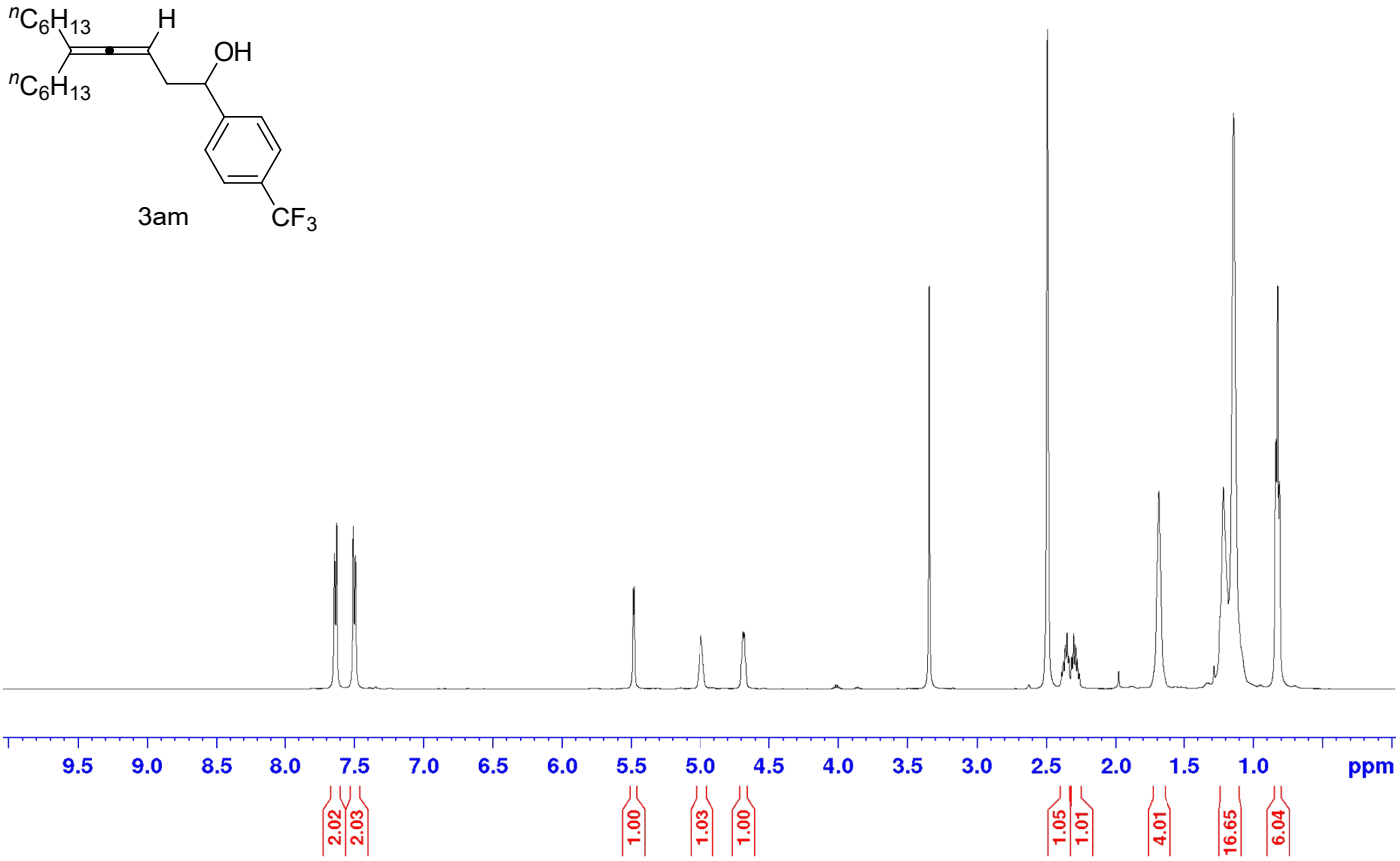

201.43
153.28
146.28
127.38
122.96
103.01
86.99
71.57
40.00
39.83
39.76
39.67
39.50
39.33
39.17
39.00
31.83
31.80
31.10
28.38
26.90
26.84
22.13
13.85
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

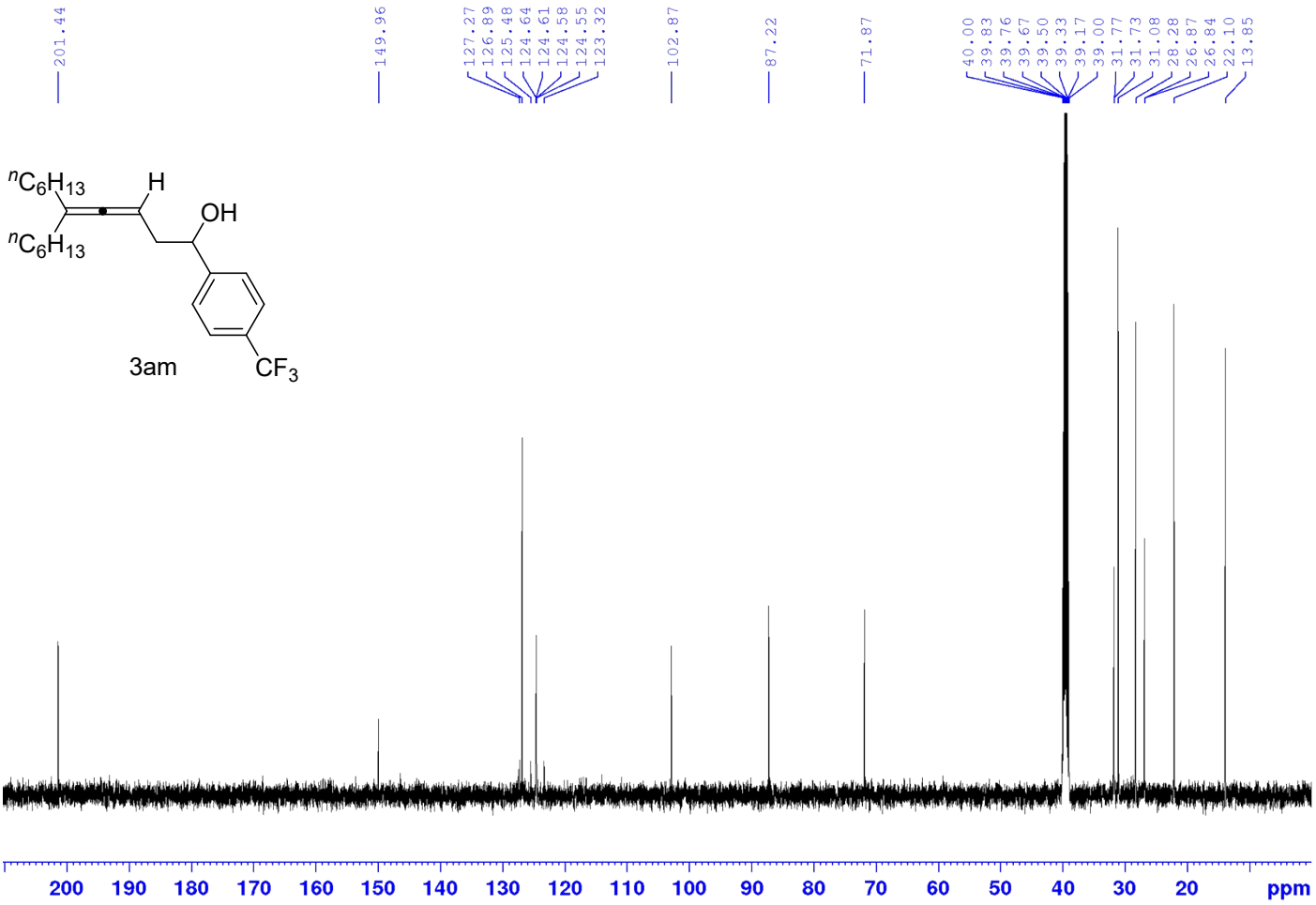
^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
NO$_2$

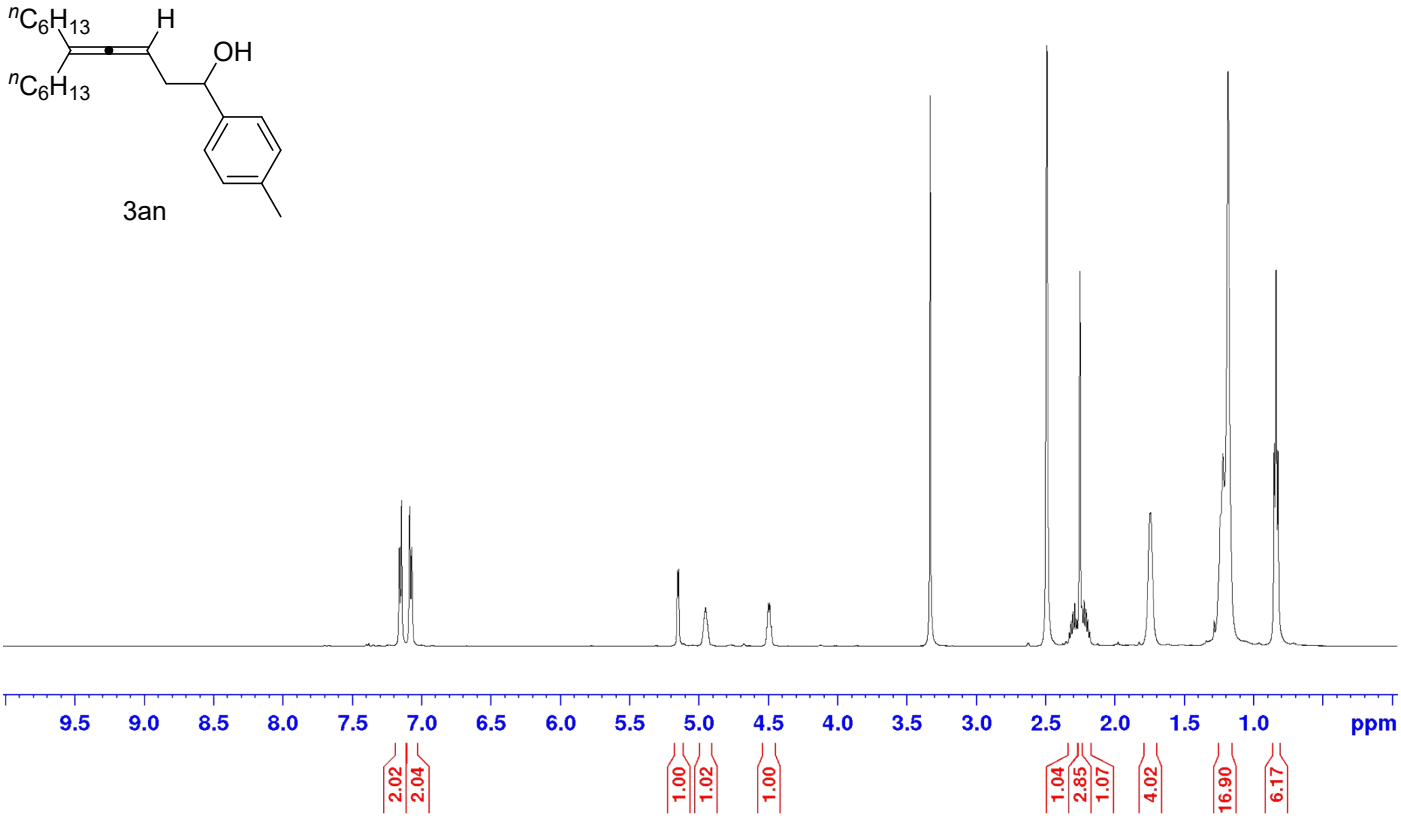
3ak

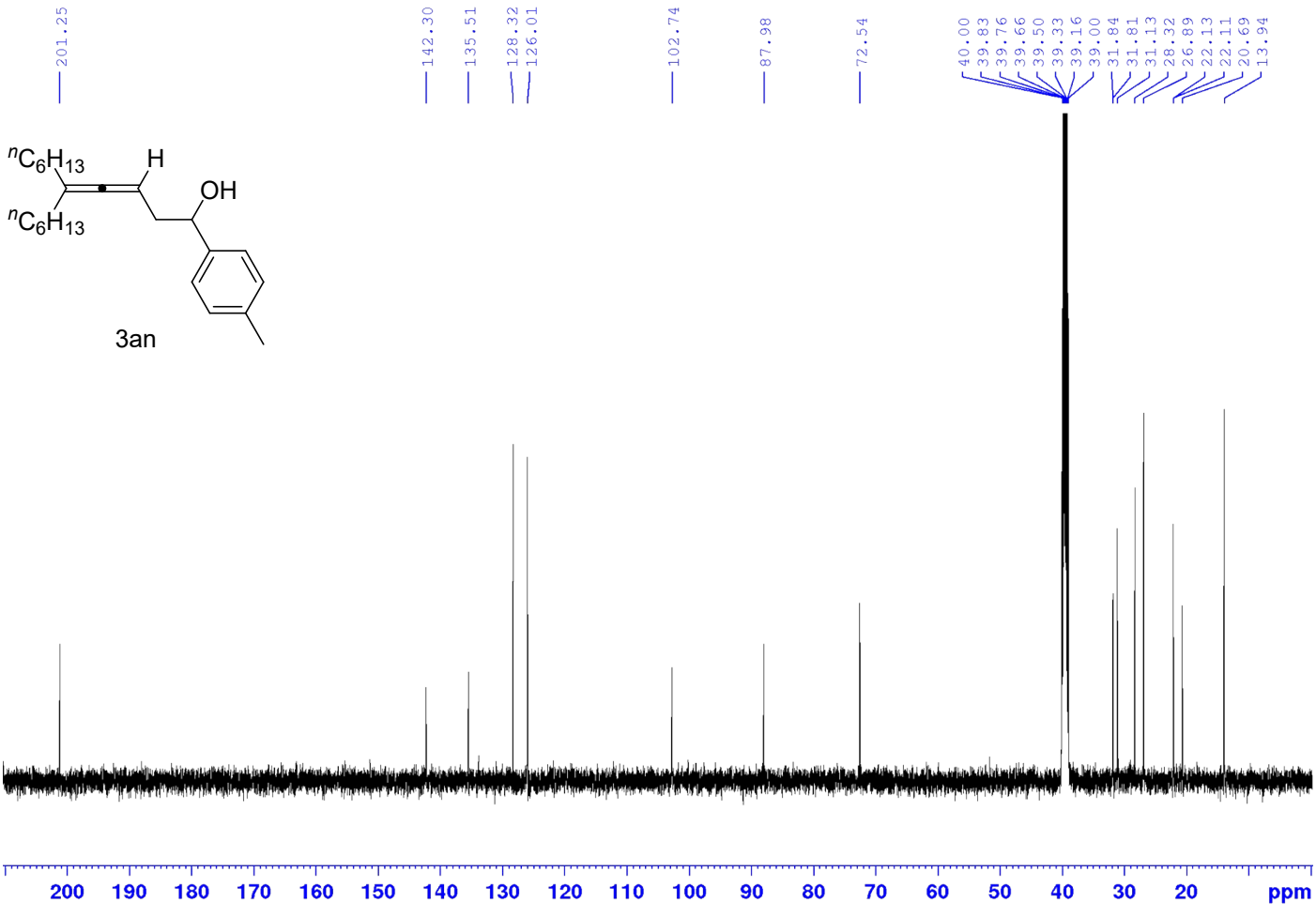

^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
3al
O
S
O
Me
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.01
2.00
1.02
1.00
1.00
3.03
2.08
4.02
16.77
6.03

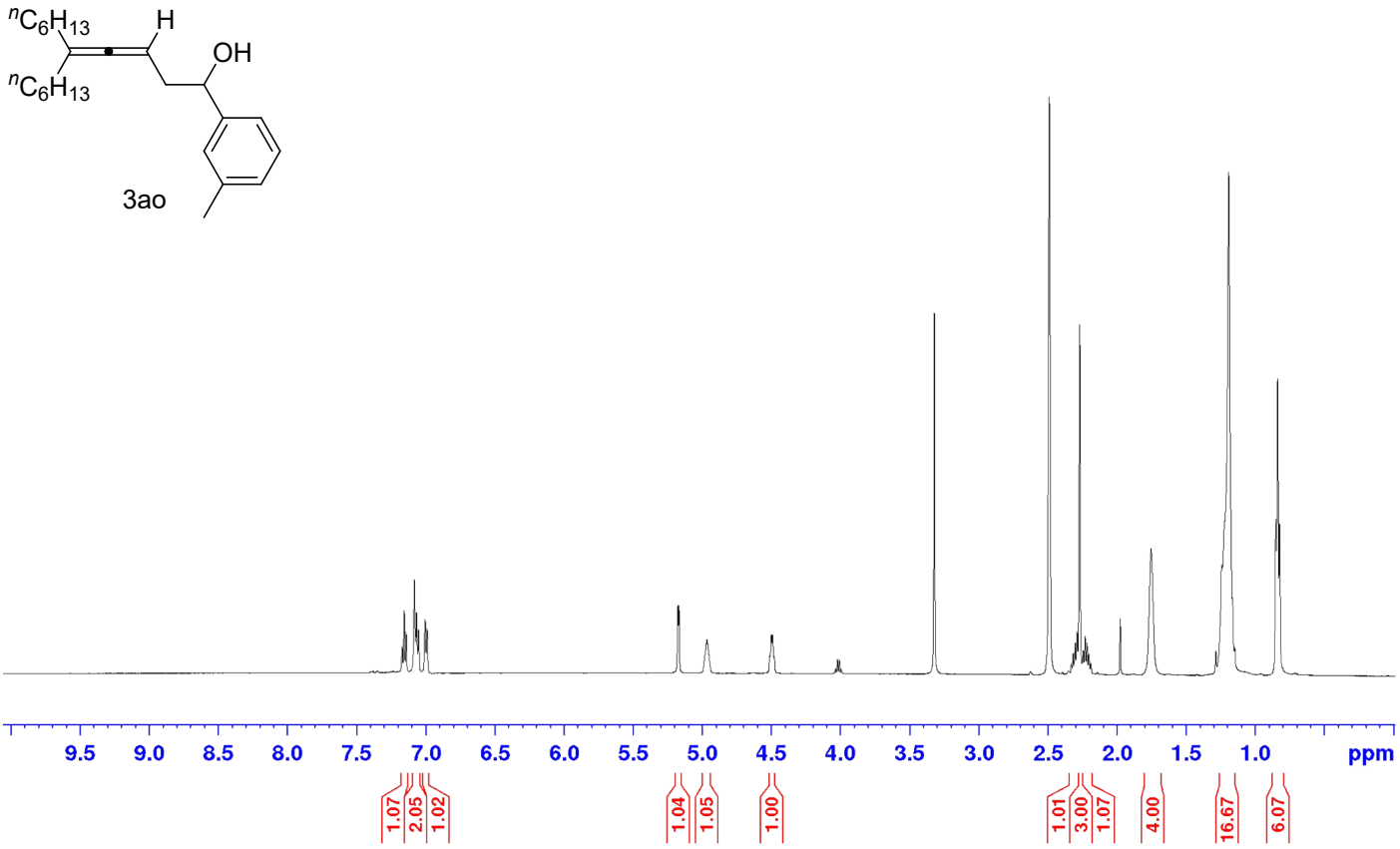

201.45
151.28
139.14
126.94
126.63
102.95
87.36
71.96
43.67
39.99
39.83
39.75
39.66
39.49
39.33
39.16
38.99
31.76
31.12
28.27
26.89
22.11
13.92
^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
3al
O
S
O
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

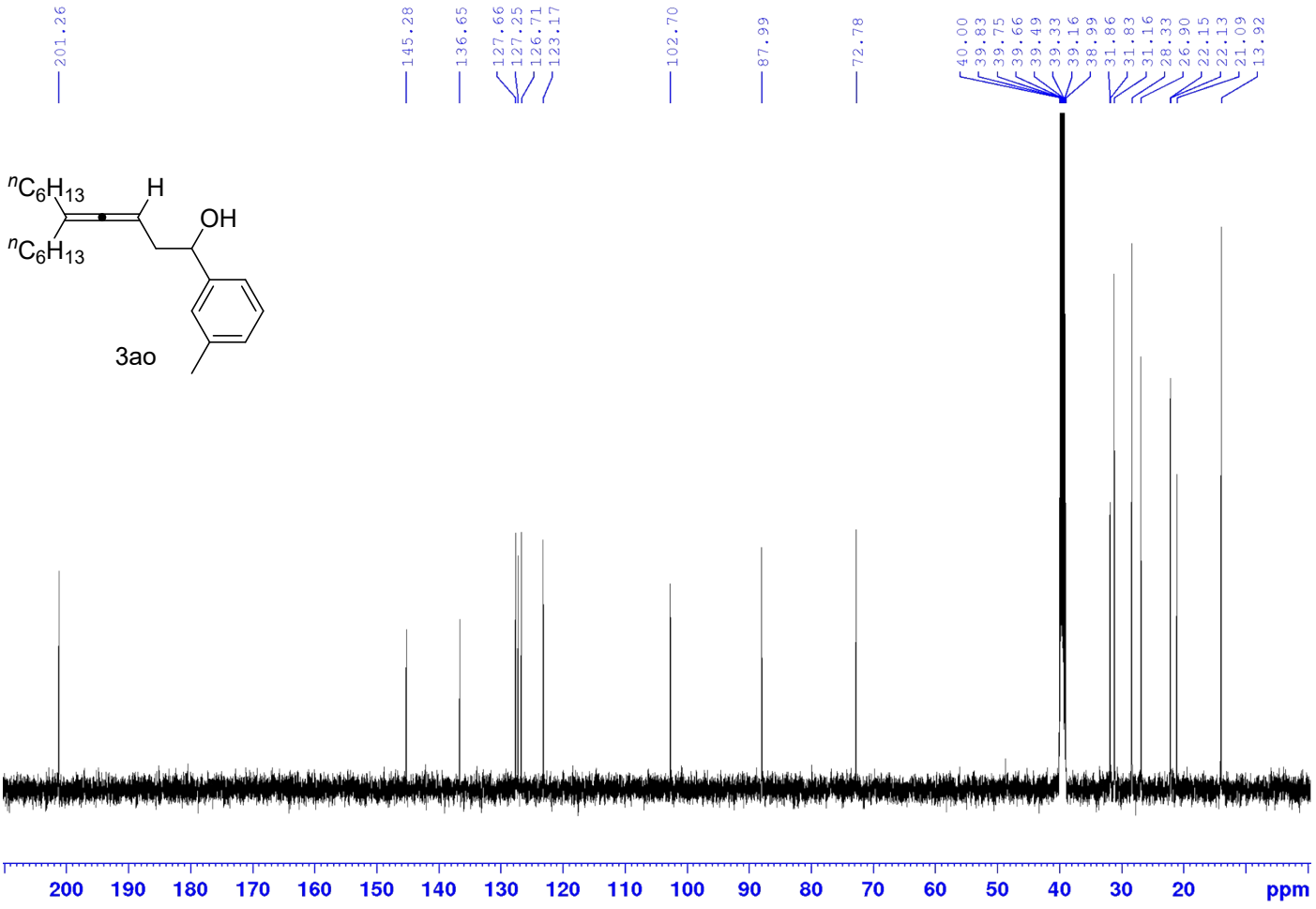

^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
3am
CF$_3$
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.02 2.03 1.00 1.03 1.00 1.05 1.01 4.01 16.65 6.04

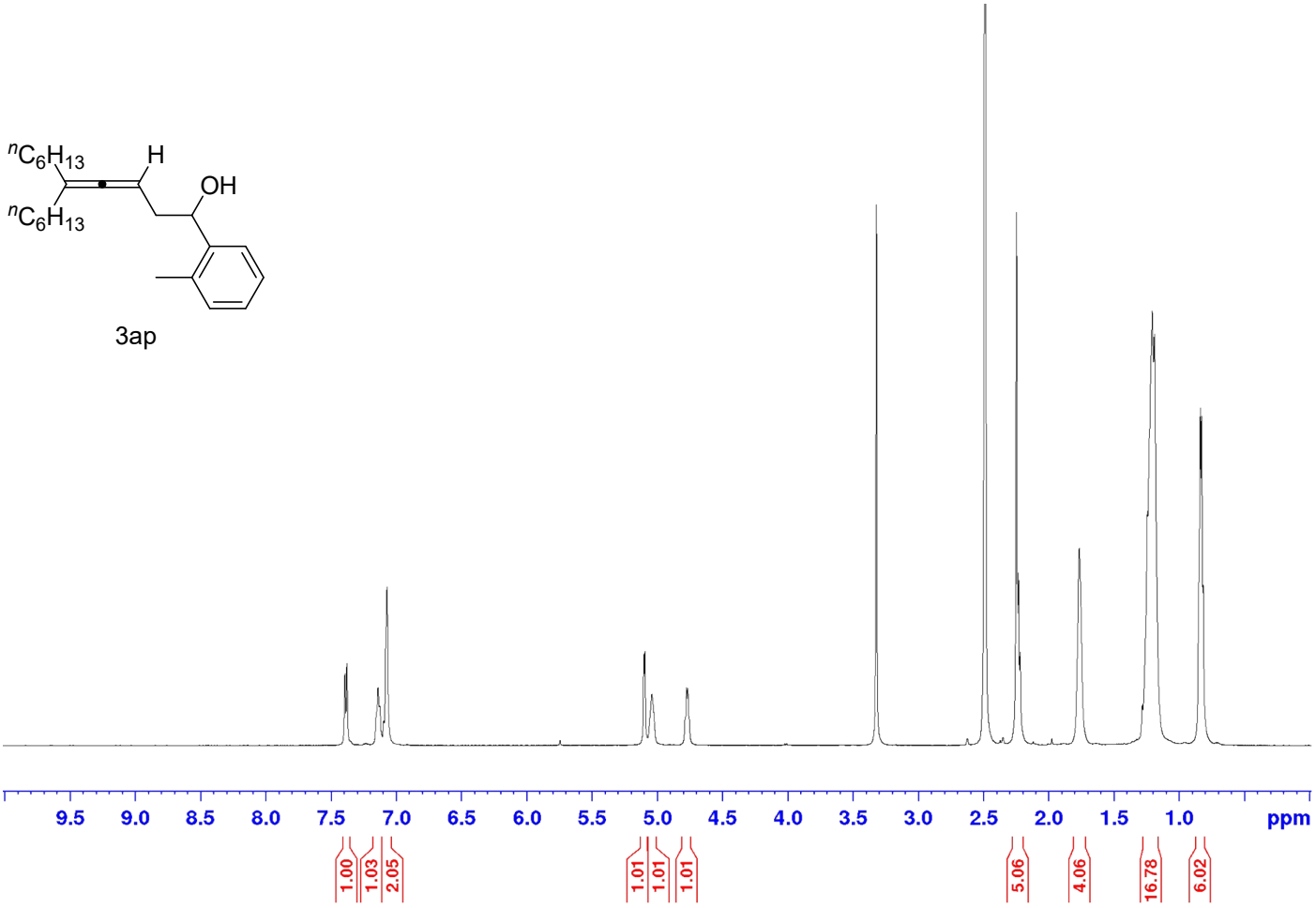

201.44
149.96
127.27
126.89
125.48
124.64
124.61
124.58
124.55
123.32
102.87
87.22
71.87
40.00
39.83
39.76
39.67
39.50
39.33
39.17
39.00
31.77
31.73
31.08
28.28
26.87
26.84
22.10
13.85
^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
3am
CF$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

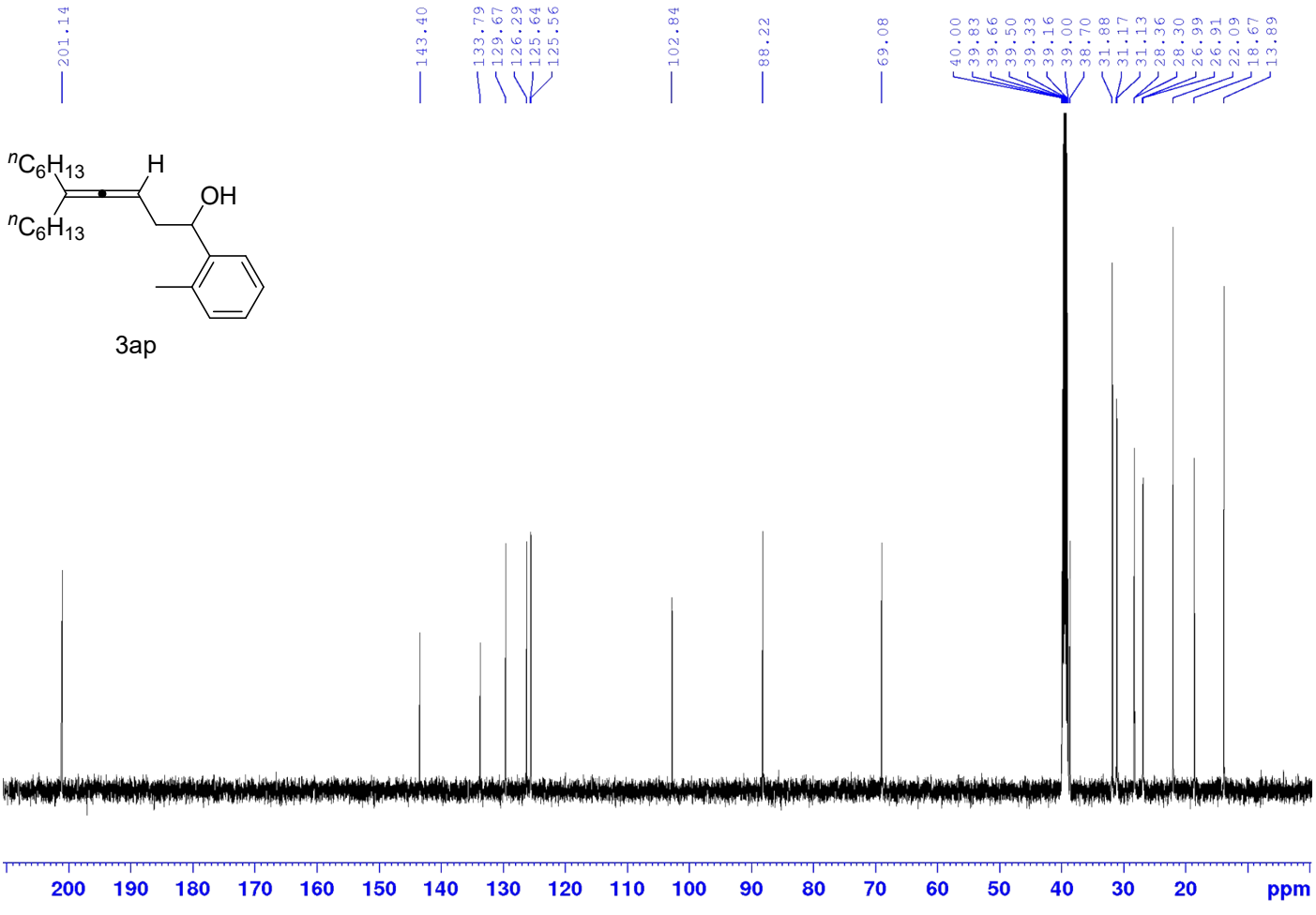

^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
3an
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.02 2.04 1.00 1.02 1.00 1.04 2.85 1.07 4.02 16.90 6.17

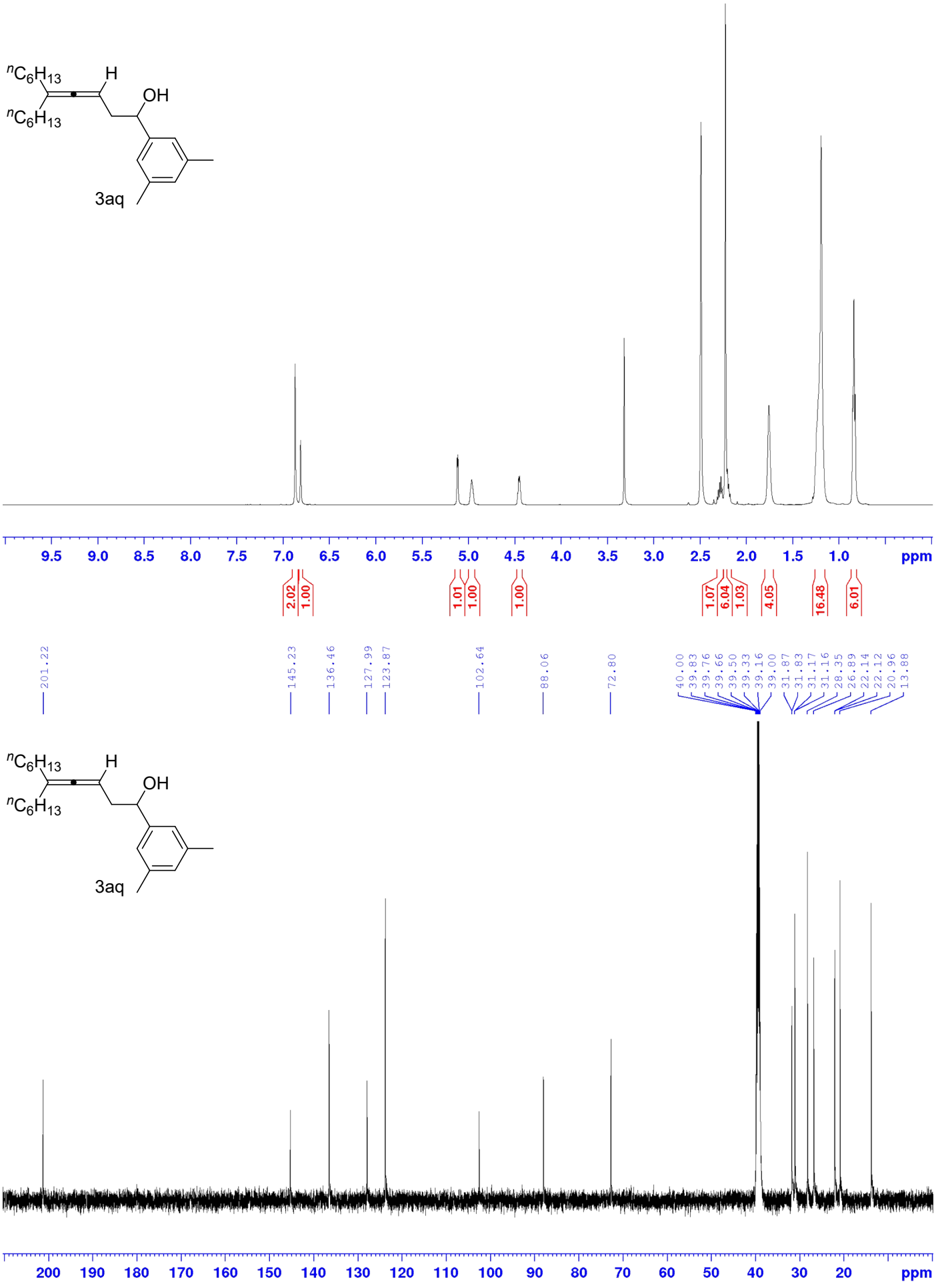

201.25
142.30
135.51
128.32
126.01
102.74
87.98
72.54
40.00
39.83
39.76
39.66
39.50
39.33
39.16
39.00
31.84
31.81
31.13
28.32
26.89
22.13
22.11
20.69
13.94
^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
3an
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

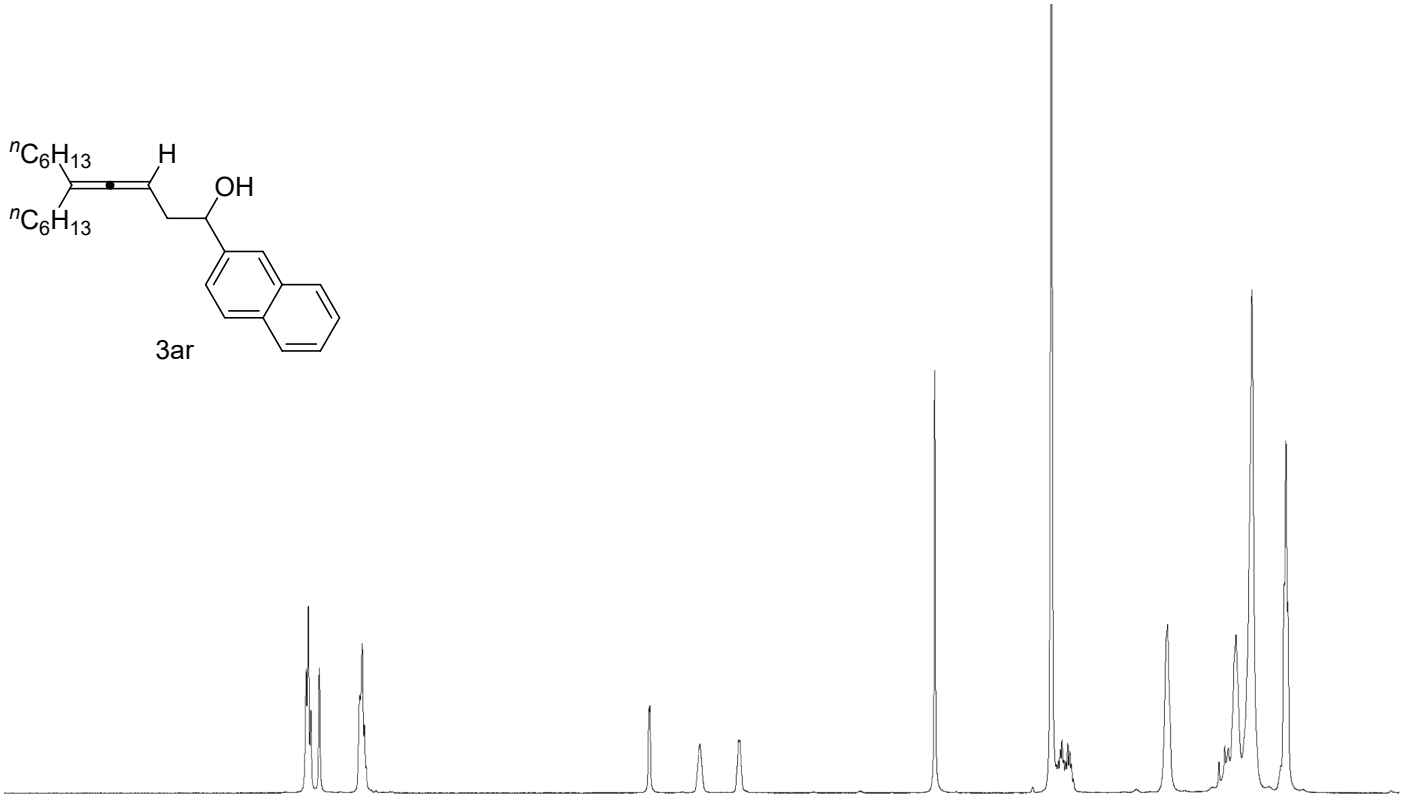

$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3ao
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.07 2.05 1.02 1.04 1.05 1.00 1.01 3.00 1.07 4.00 16.67 6.07

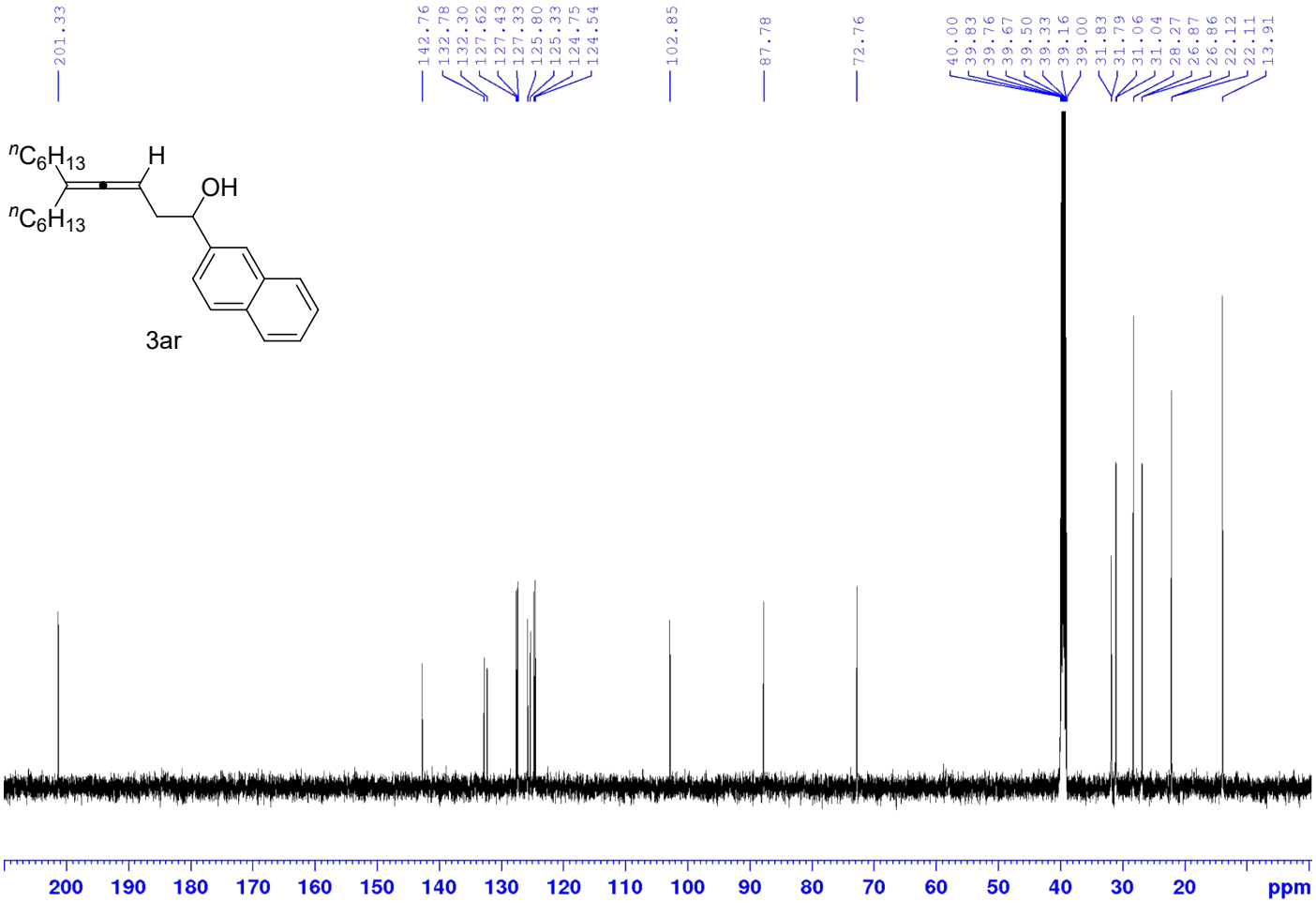

201.26
145.28
136.65
127.66
127.25
126.71
123.17
102.70
87.99
72.78
40.00
39.83
39.75
39.66
39.49
39.33
39.16
38.99
31.86
31.83
31.16
28.33
26.90
22.15
22.13
21.09
13.92
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3ao
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

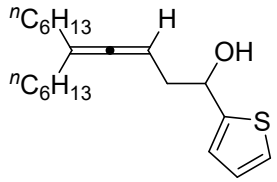

$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3ap
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00 1.03 2.05 1.01 1.01 1.01 5.06 4.06 16.78 6.02


201.14
143.40
133.79
129.67
126.29
125.64
125.56
102.84
88.22
69.08
40.00
39.83
39.66
39.50
39.33
39.16
39.00
38.70
31.88
31.17
31.13
28.36
28.30
26.99
26.91
22.09
18.67
13.89
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3ap
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3aq
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
2.02 1.00 1.01 1.00 1.00 1.07 6.04 1.03 4.05 16.48 6.01
201.22 145.23 136.46 127.99 123.87 102.64 88.06 72.80
40.00 39.83 39.76 39.66 39.50 39.33 39.16 39.00 31.87 31.83 31.17 31.16 28.35 26.89 22.14 22.12 20.96 13.88
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3aq
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

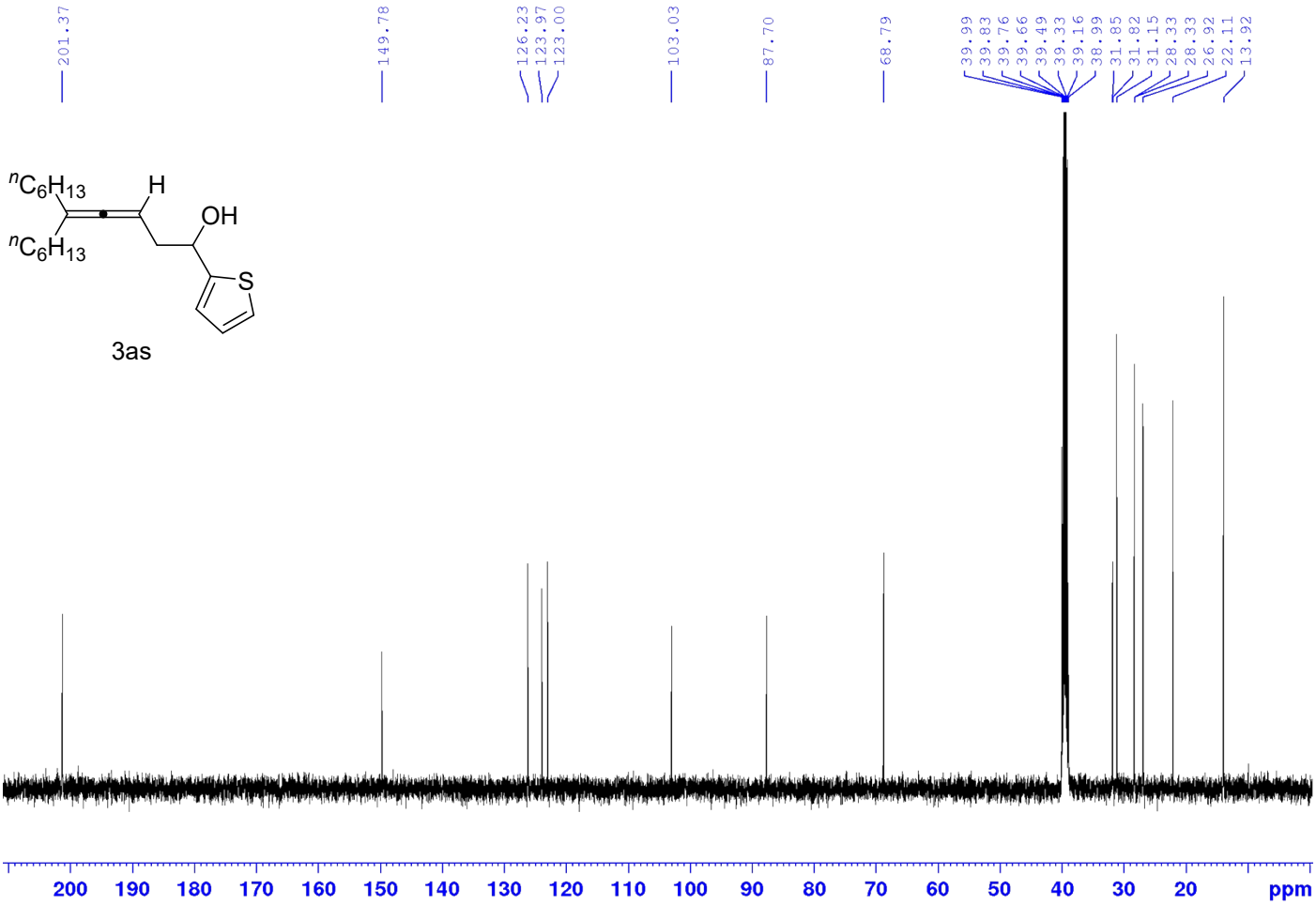

$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3ar
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.00 1.00 3.03 1.00 1.01 1.00 2.28 4.01 16.55 6.05


201.33
142.76 132.78 132.30 127.62 127.43 127.33 125.80 125.33 124.75 124.54
102.85
87.78
72.76
40.00 39.83 39.76 39.67 39.50 39.33 39.16 39.00 31.83 31.79 31.06 31.04 28.27 26.87 26.86 22.12 22.11 13.91
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3ar
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
S

3as

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
2.02
1.00
1.02
1.00
1.07
1.03
4.07
16.79
6.08


201.37
149.78
126.23
123.97
123.00
103.03
87.70
68.79
39.99
39.83
39.76
39.66
39.49
39.33
39.16
38.99
31.85
31.82
31.15
28.33
28.33
26.92
22.11
13.92
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

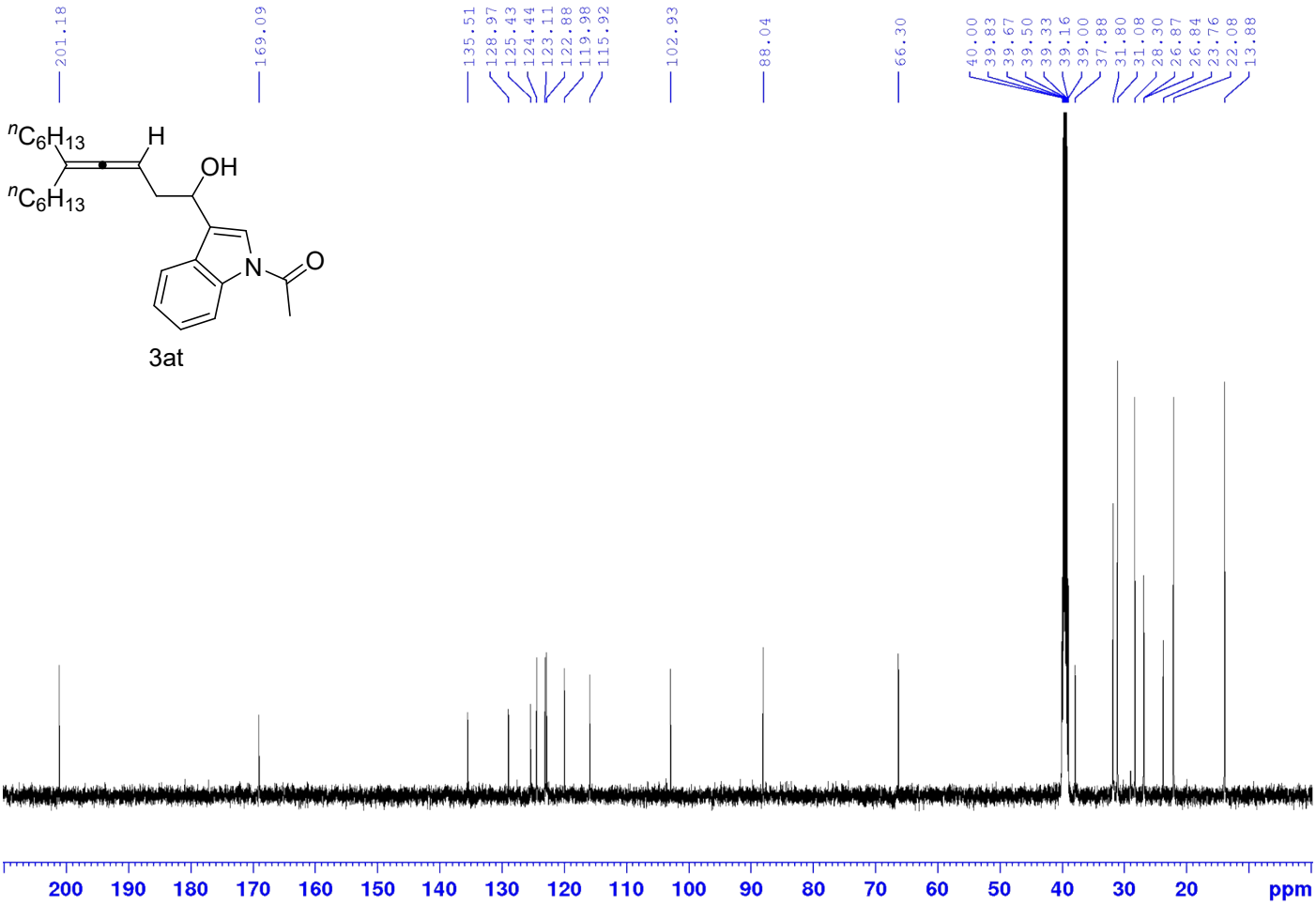
^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
S

3as


^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
N
O

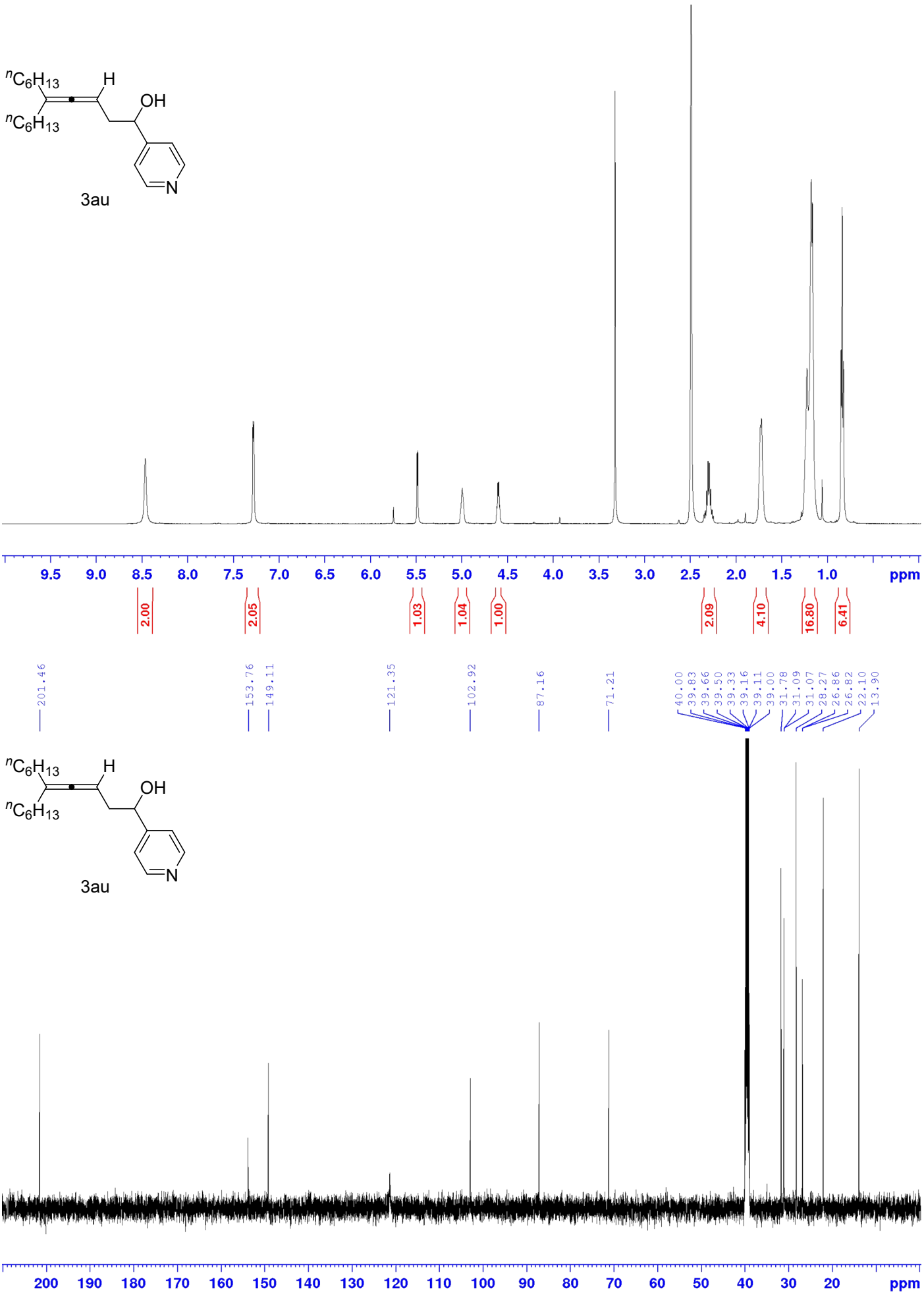
3at

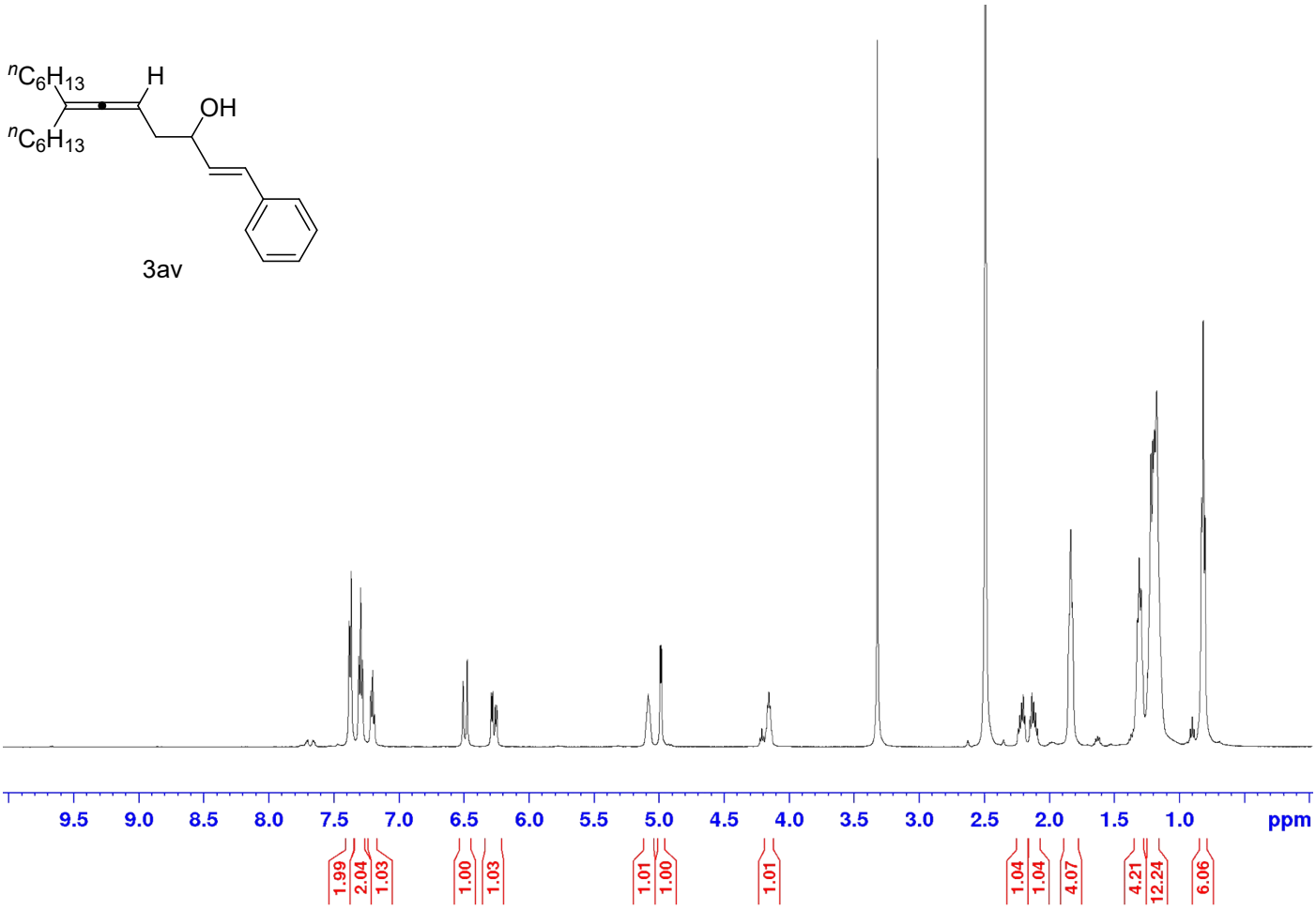
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.02
1.99
1.03
1.03
1.02
1.05
1.00
3.00
1.09
1.07
4.08
16.58
6.28

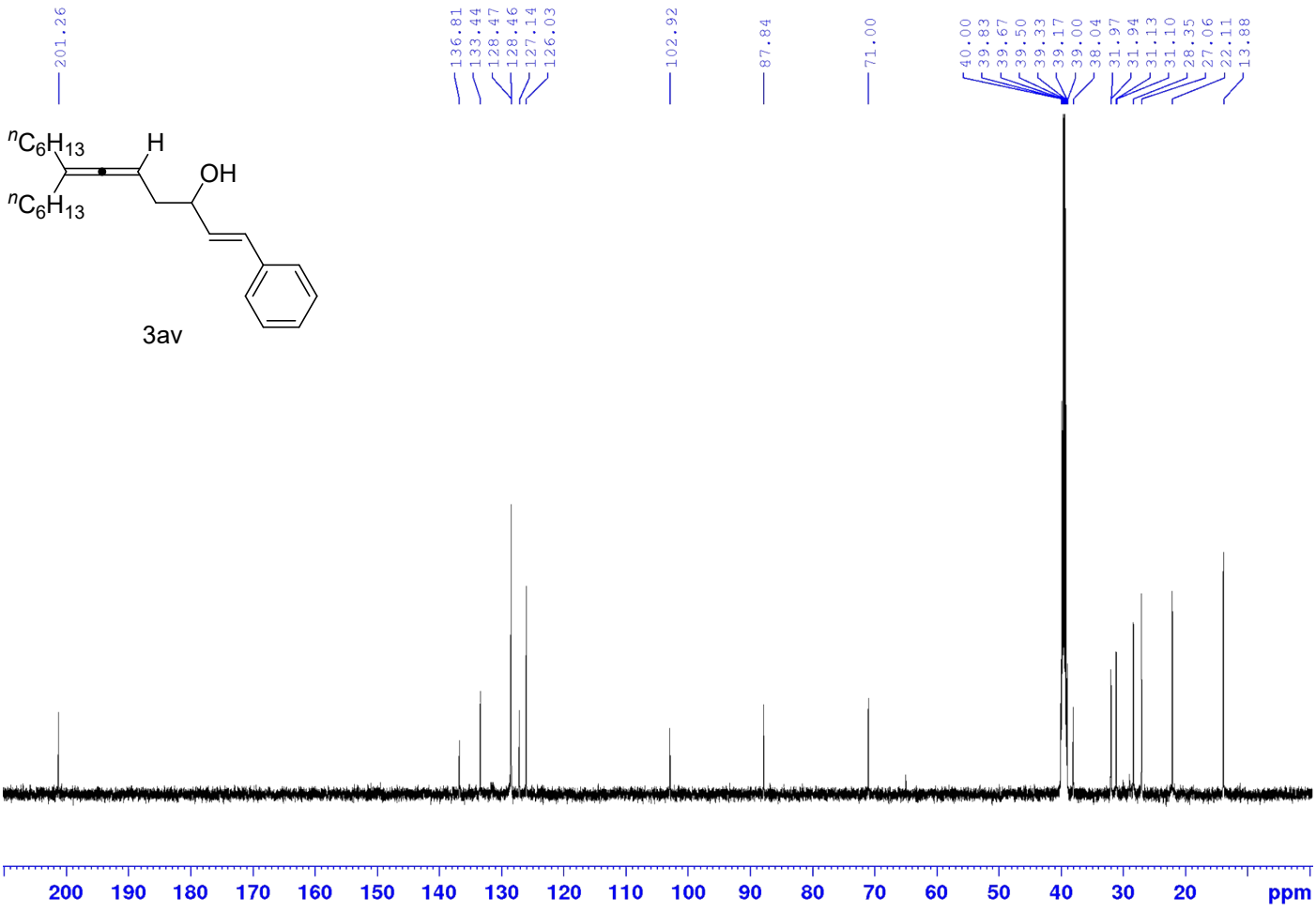

201.18
169.09
135.51
128.97
125.43
124.44
123.11
122.88
119.98
115.92
102.93
88.04
66.30
40.00
39.83
39.67
39.50
39.33
39.16
39.00
37.88
31.80
31.08
28.30
26.87
26.84
23.76
22.08
13.88
^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
N
O

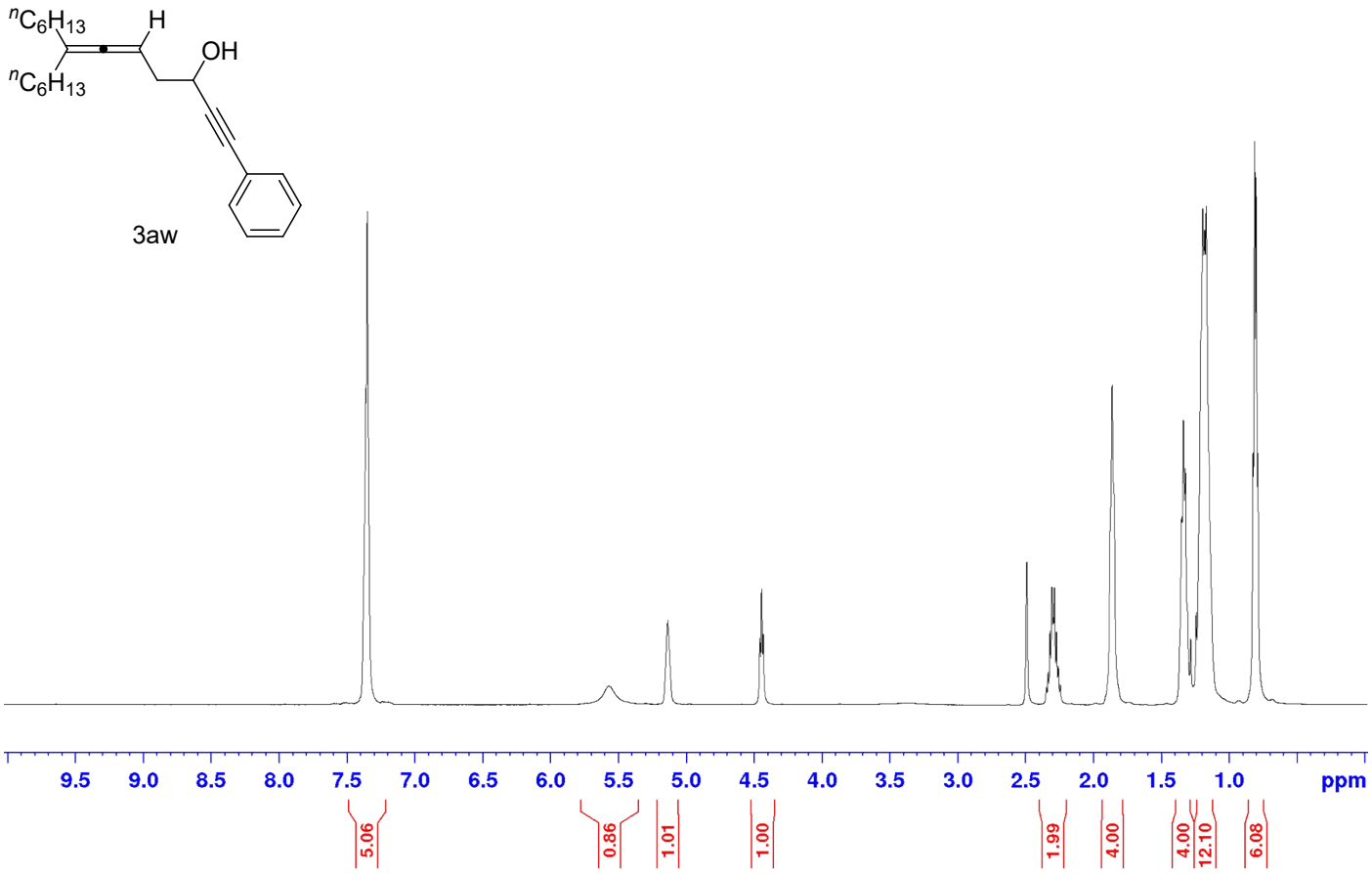
3at

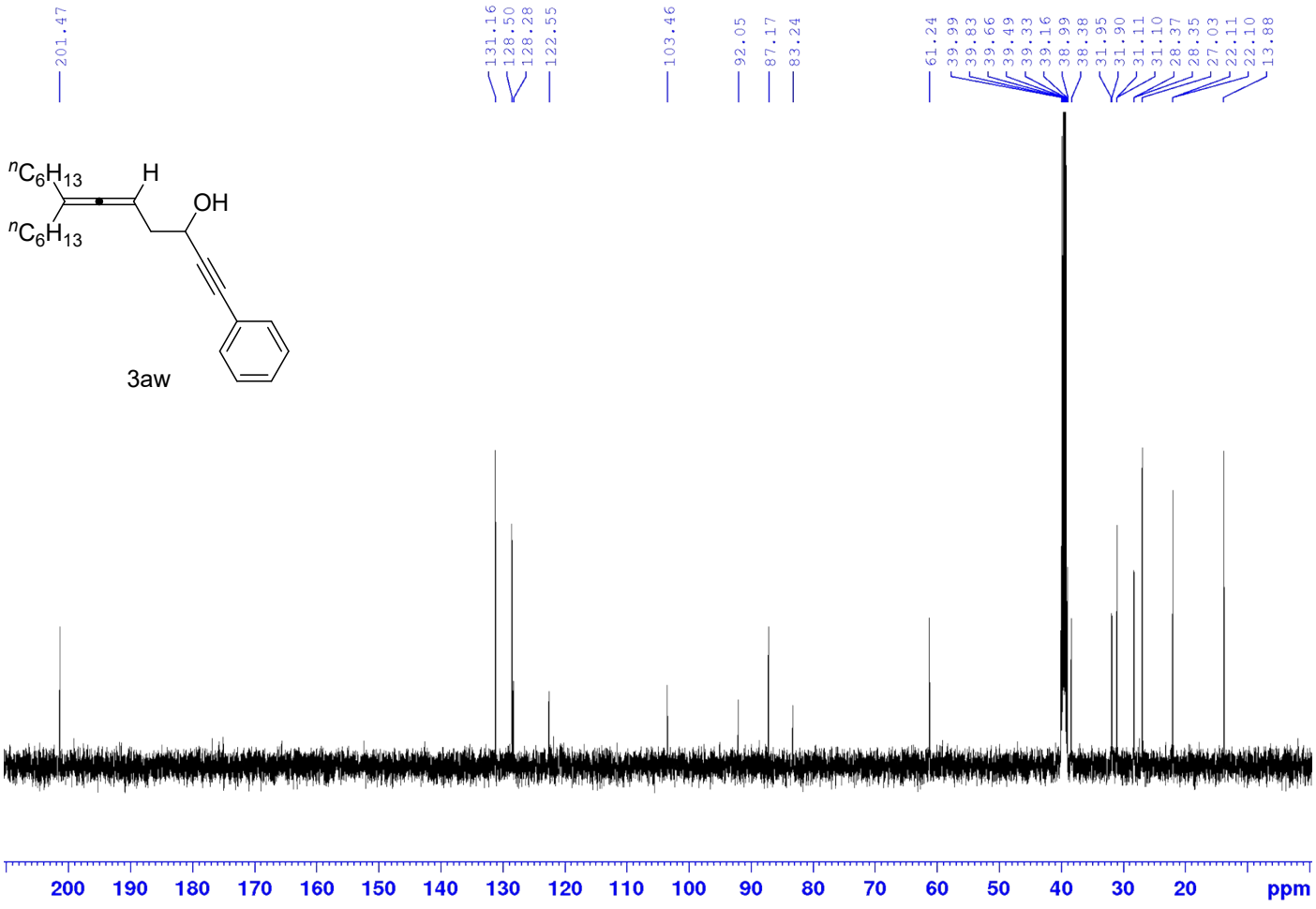
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

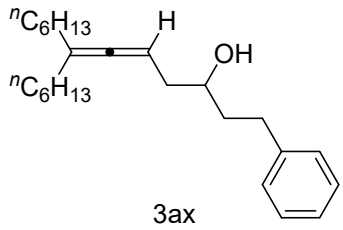

$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
N
3au
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00 2.05 1.03 1.04 1.00 2.09 4.10 16.80 6.41
201.46 153.76 149.11 121.35 102.92 87.16 71.21
40.00 39.83 39.66 39.50 39.33 39.16 39.11 39.00 31.78 31.09 31.07 28.27 26.86 26.82 22.10 13.90
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
N
3au
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3av
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 2.04 1.03 1.00 1.03 1.01 1.00 1.01 1.04 1.04 4.07 4.21 12.24 6.06


201.26
136.81 133.44 128.47 128.46 127.14 126.03
102.92
87.84
71.00
40.00 39.83 39.67 39.50 39.33 39.17 39.00 38.04
31.97 31.94 31.13 31.10 28.35 27.06 22.11 13.88
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3av
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

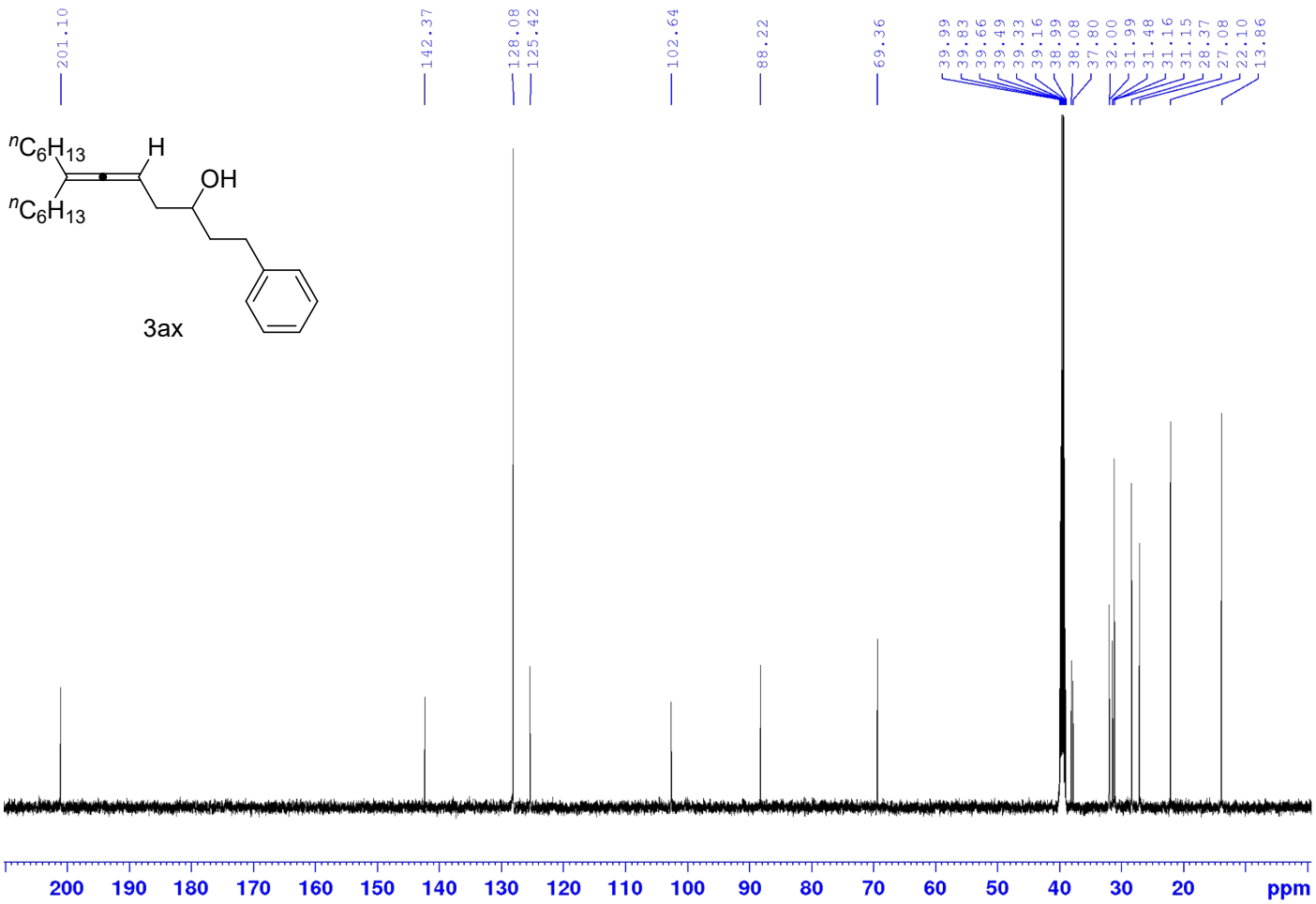

$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3aw
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
5.06
0.86
1.01
1.00
1.99
4.00
4.00
12.10
6.08


201.47
131.16
128.50
128.28
122.55
103.46
92.05
87.17
83.24
61.24
39.99
39.83
39.66
39.49
39.33
39.16
38.99
38.38
31.95
31.90
31.11
31.10
28.37
28.35
27.03
22.11
22.10
13.88
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3aw
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$

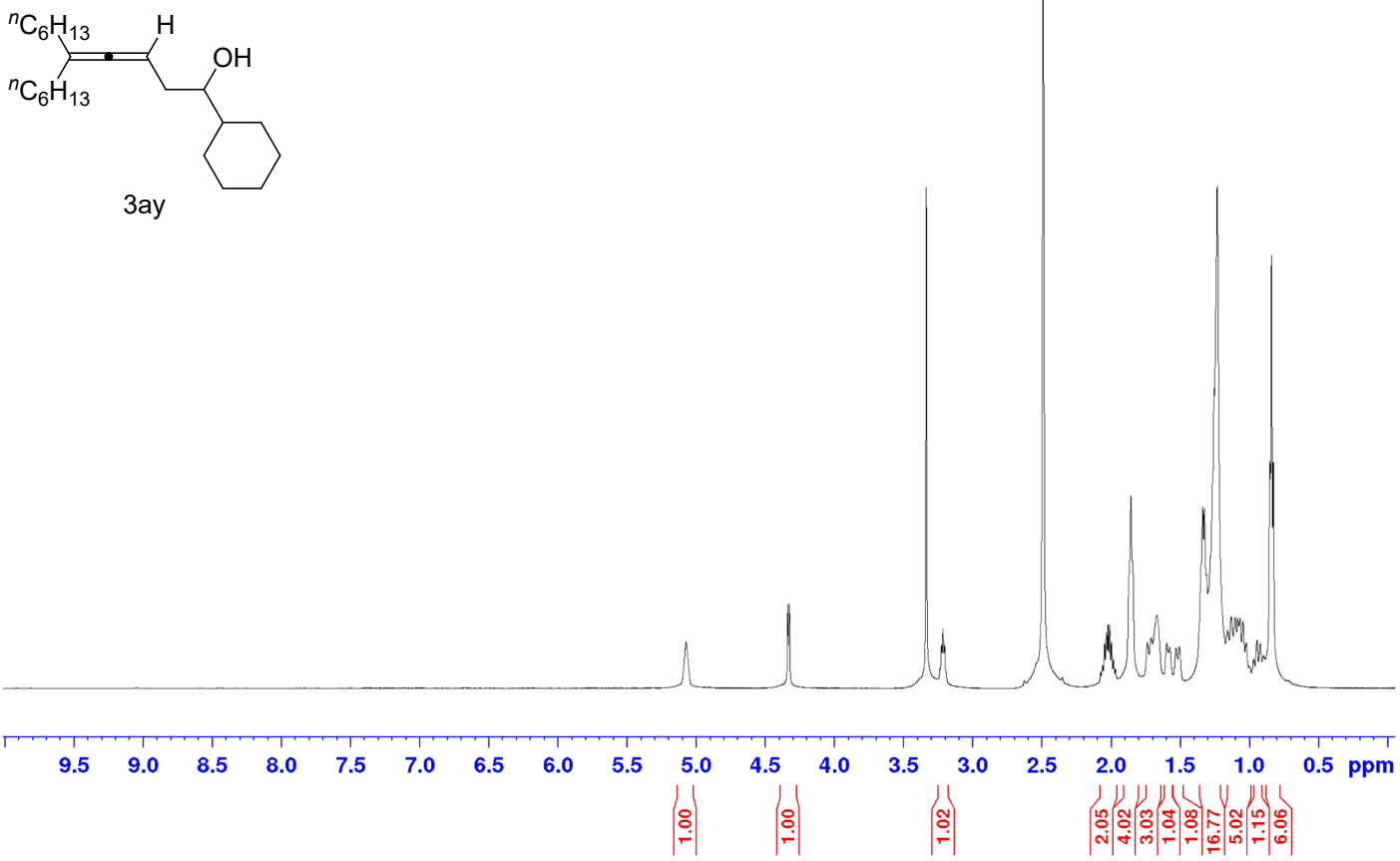
3ax

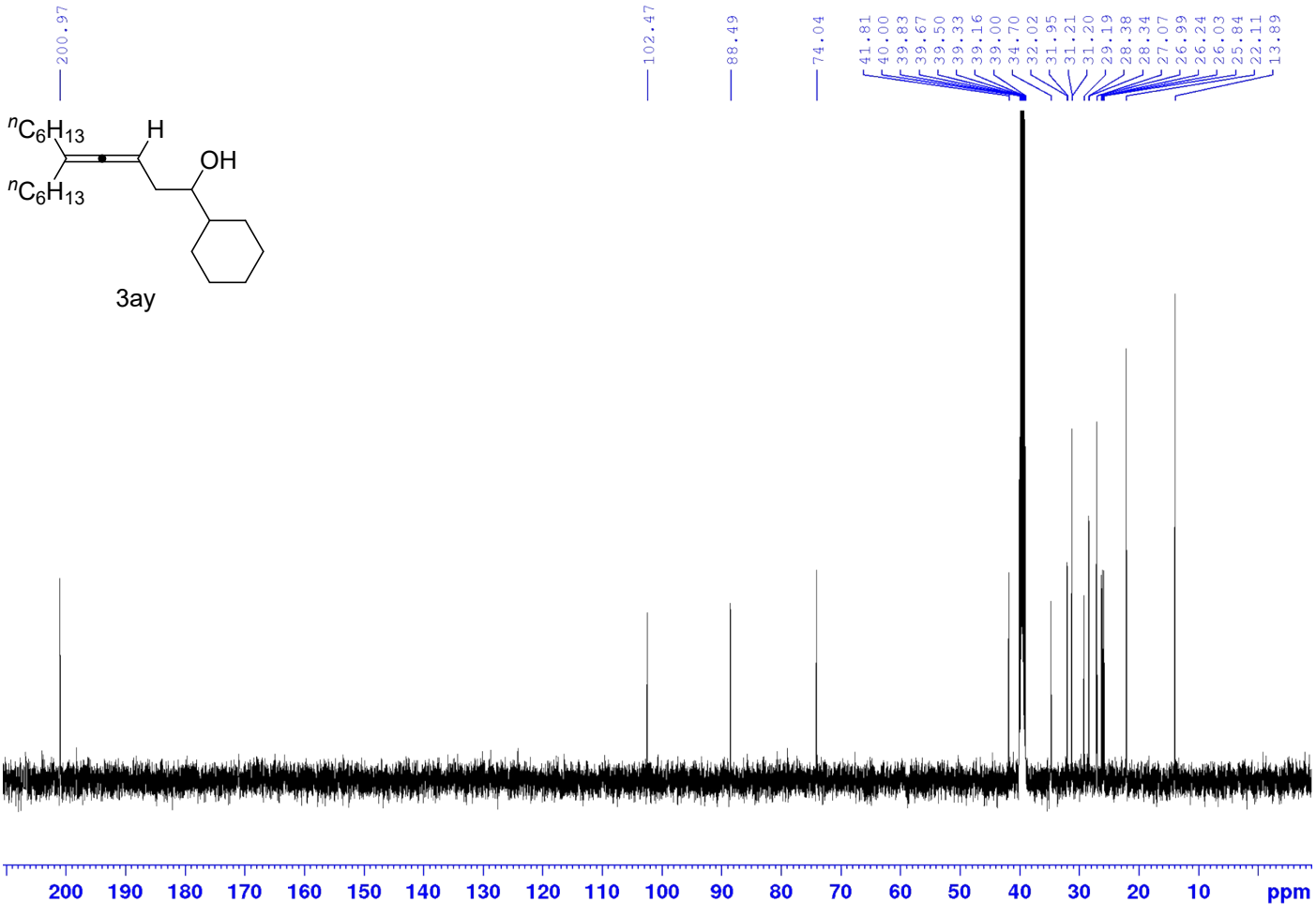
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.06 3.05 1.01 1.00 1.00 1.00 1.15 1.00 1.04 4.00 1.02 1.04 16.97 6.02

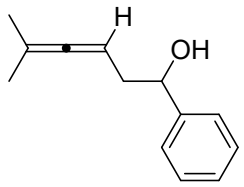

201.10
142.37
128.08
125.42
102.64
88.22
69.36
39.99
39.83
39.66
39.49
39.33
39.16
38.99
38.08
37.80
32.00
31.99
31.48
31.16
31.15
28.37
27.08
22.10
13.86
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$

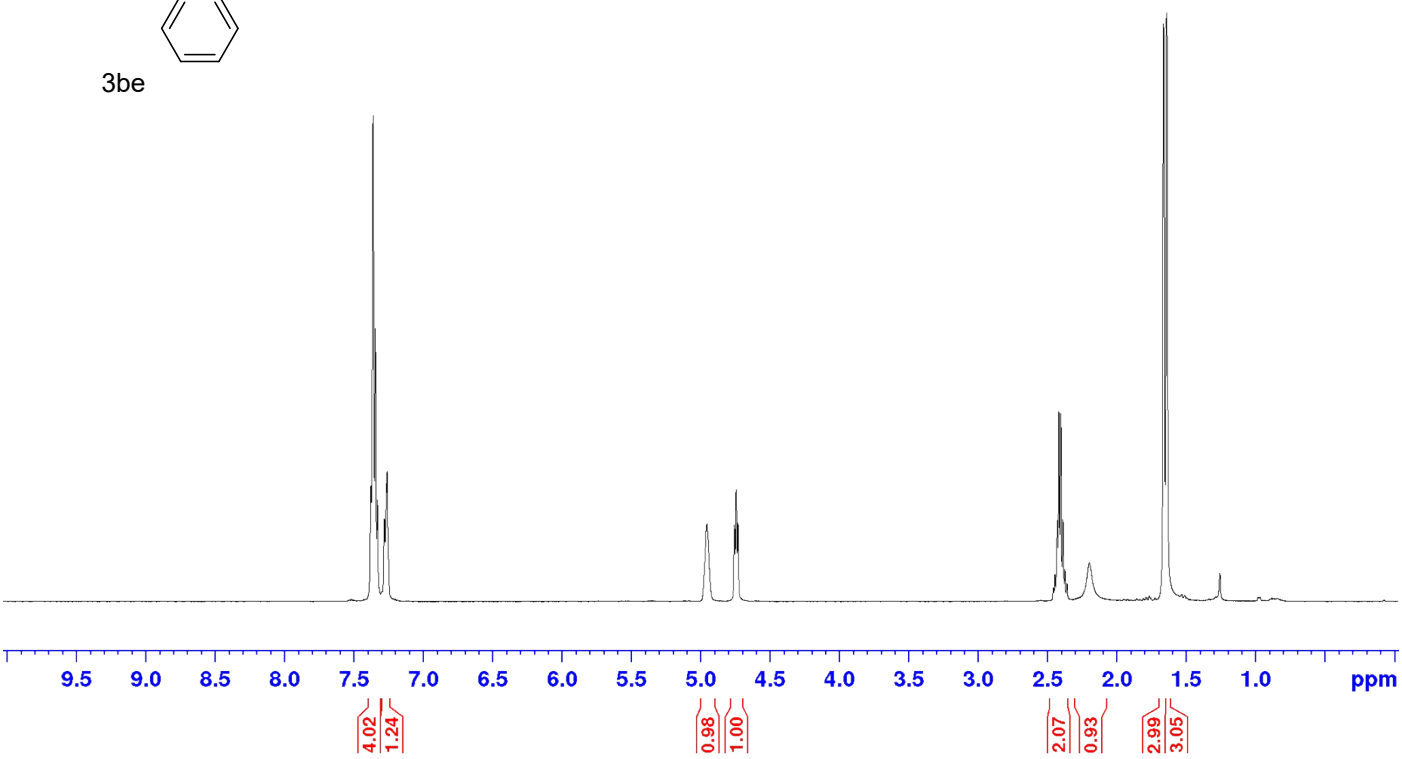
3ax


$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3ay
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 1.00 1.02 2.05 4.02 3.03 1.04 1.08 16.77 5.02 1.15 6.06

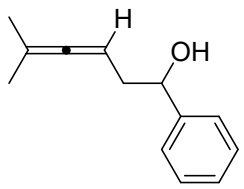

200.97
102.47
88.49
74.04
41.81
40.00
39.83
39.67
39.50
39.33
39.16
39.00
34.70
32.02
31.95
31.21
31.20
29.19
28.38
28.34
27.07
26.99
26.24
26.03
25.84
22.11
13.89
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
3ay
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


H
OH

3be

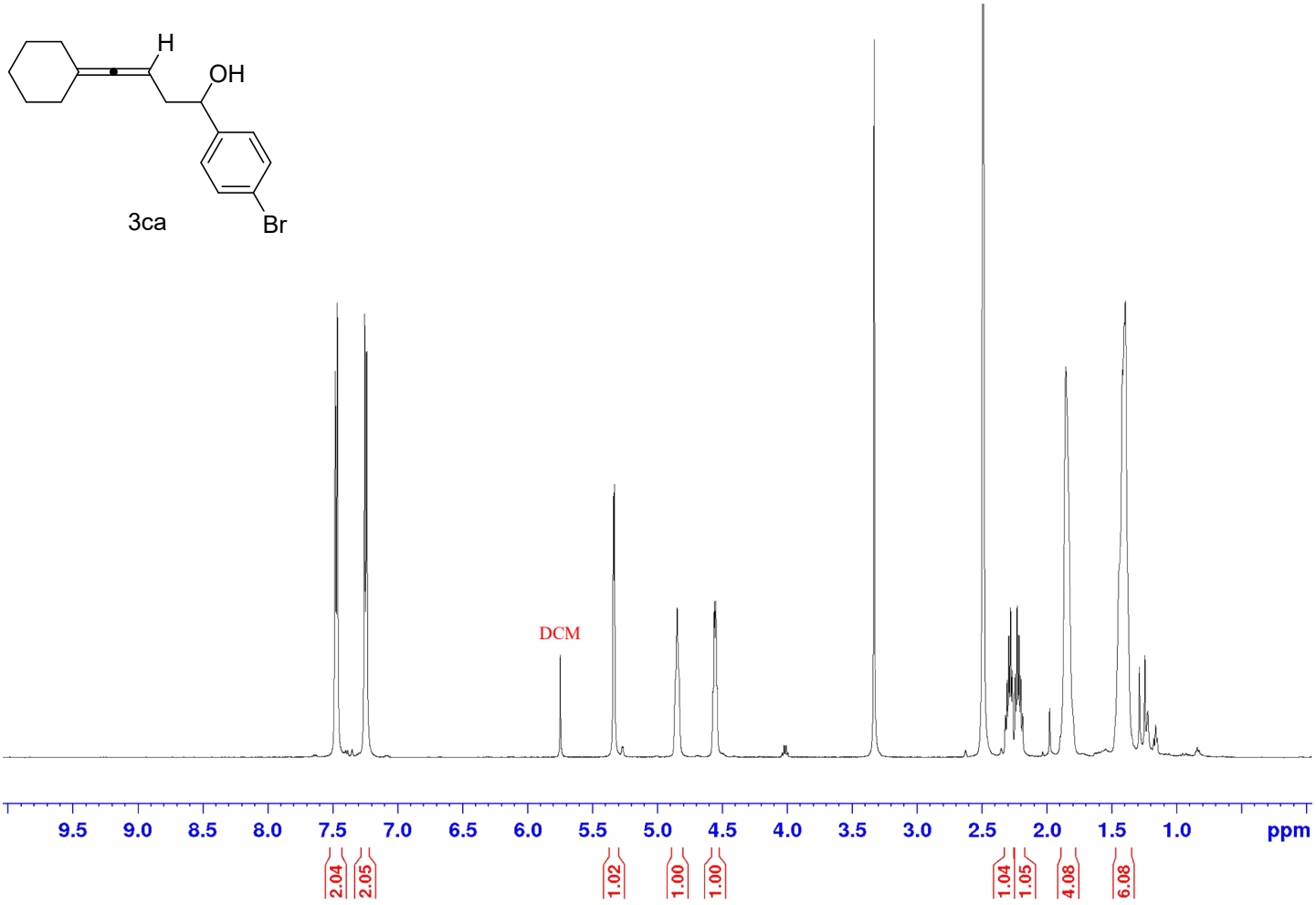

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.02
1.24
0.98
1.00
2.07
0.93
2.99
3.05

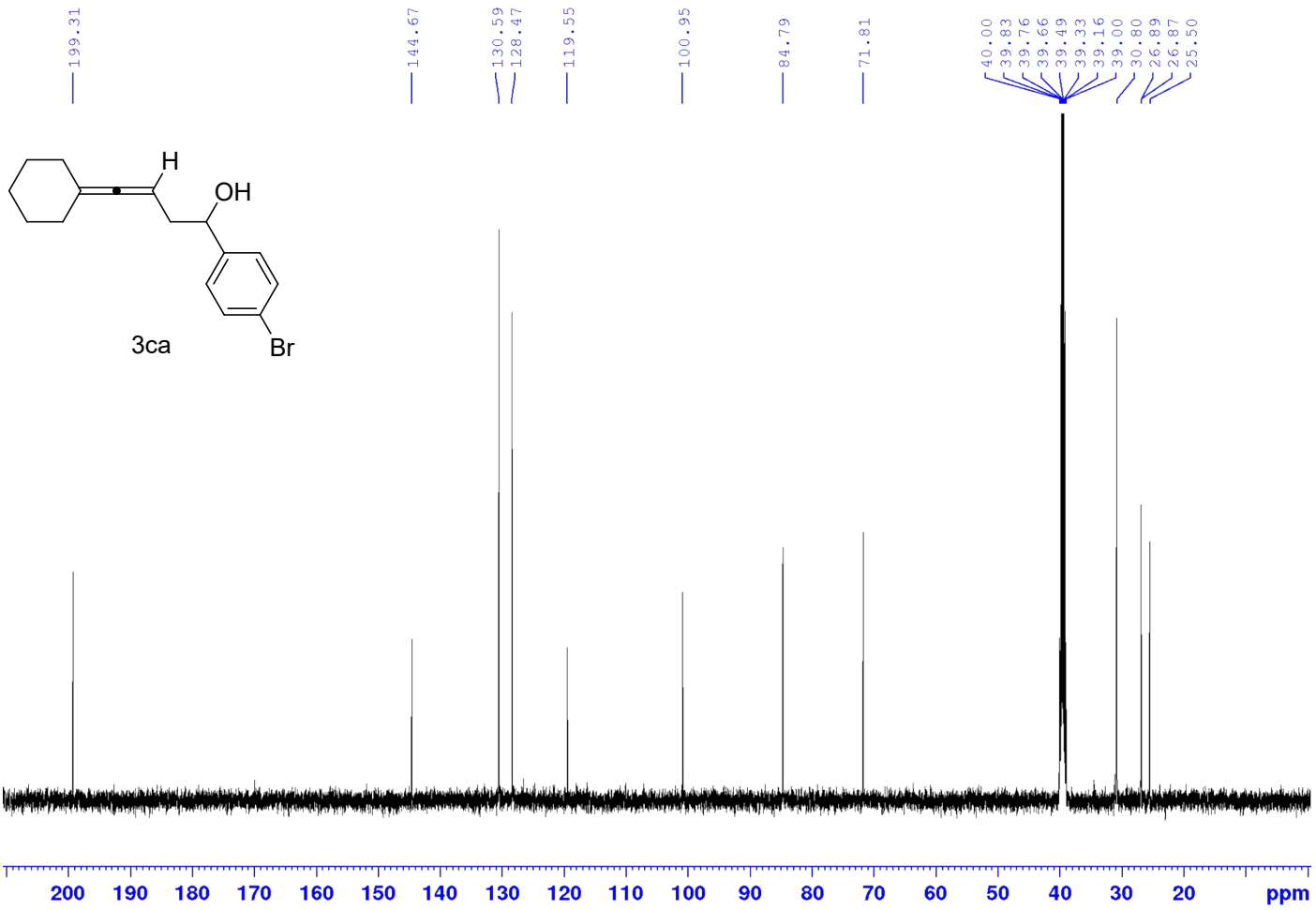

203.22
143.73
128.26
127.36
125.93
95.55
84.63
77.25
77.00
76.74
73.59
39.26
20.60
20.45

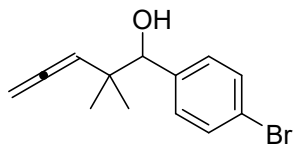

H
OH

3be

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

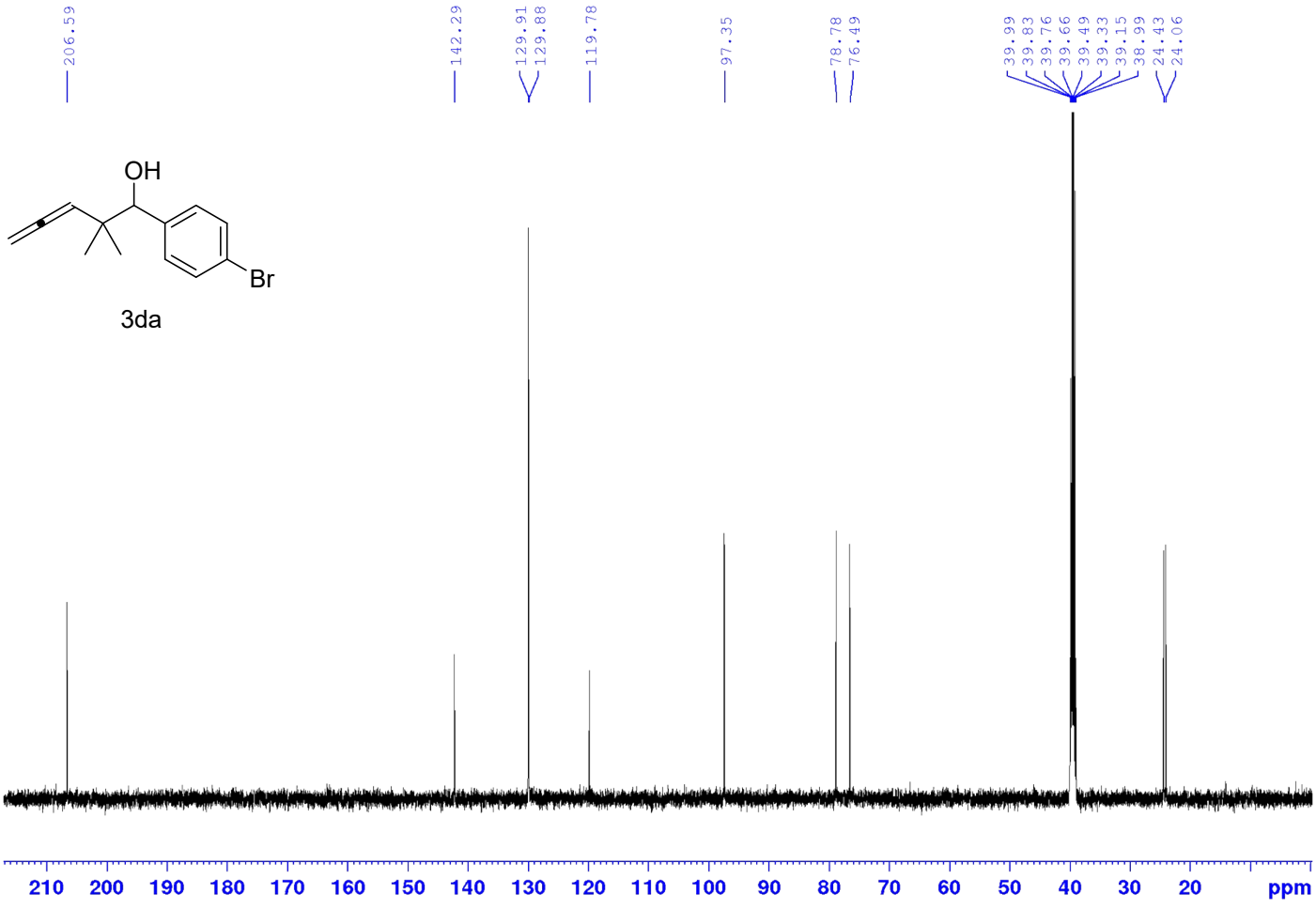

H
OH
Br
3ca
DCM
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.04
2.05
1.02
1.00
1.00
1.04
1.05
4.08
6.08


199.31
144.67
130.59
128.47
119.55
100.95
84.79
71.81
40.00
39.83
39.76
39.66
39.49
39.33
39.16
39.00
30.80
26.89
26.87
25.50
H
OH
Br
3ca
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


OH
Br

3da

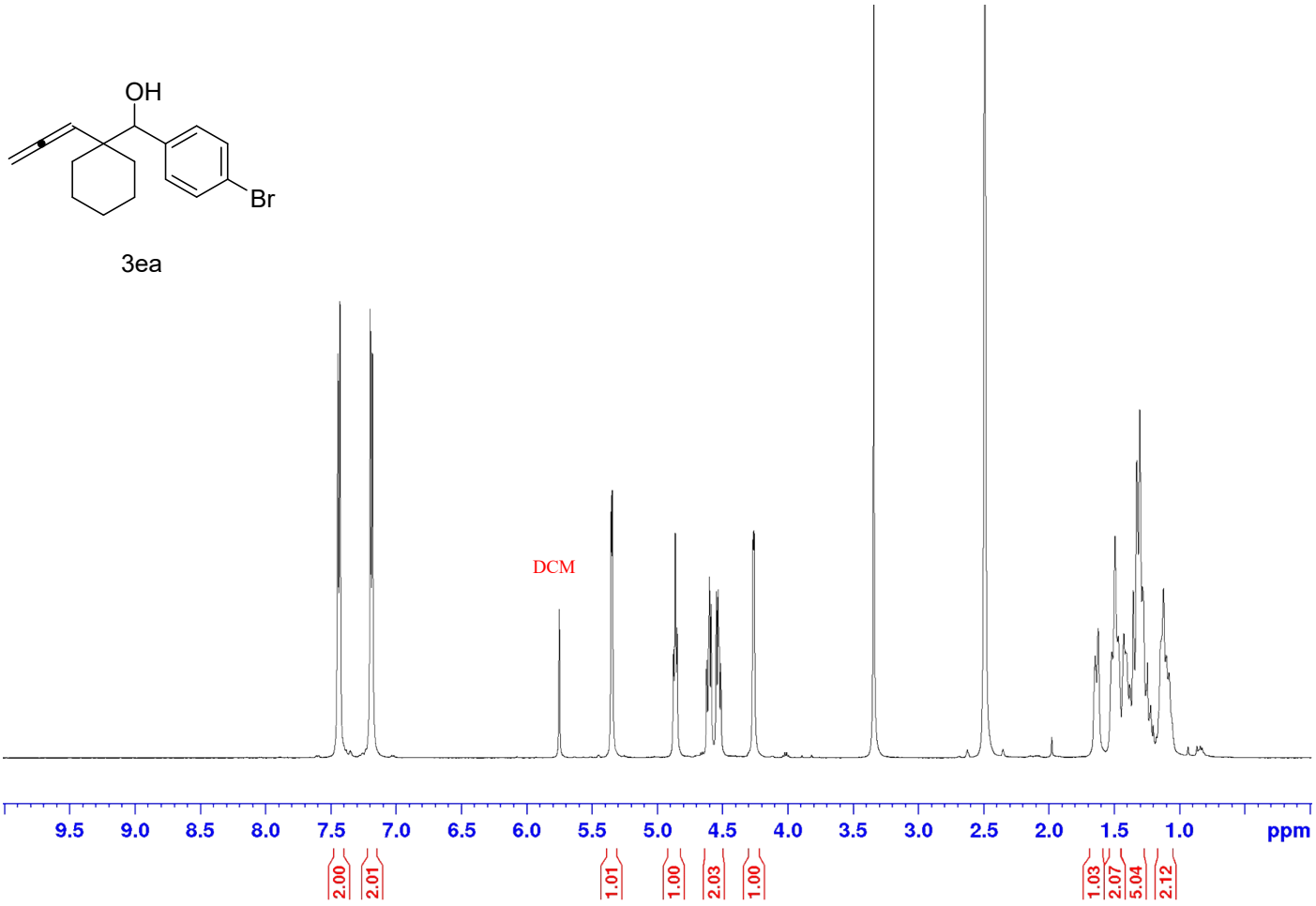
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.03
2.04
1.04
1.04
2.00
1.00
3.07
3.04

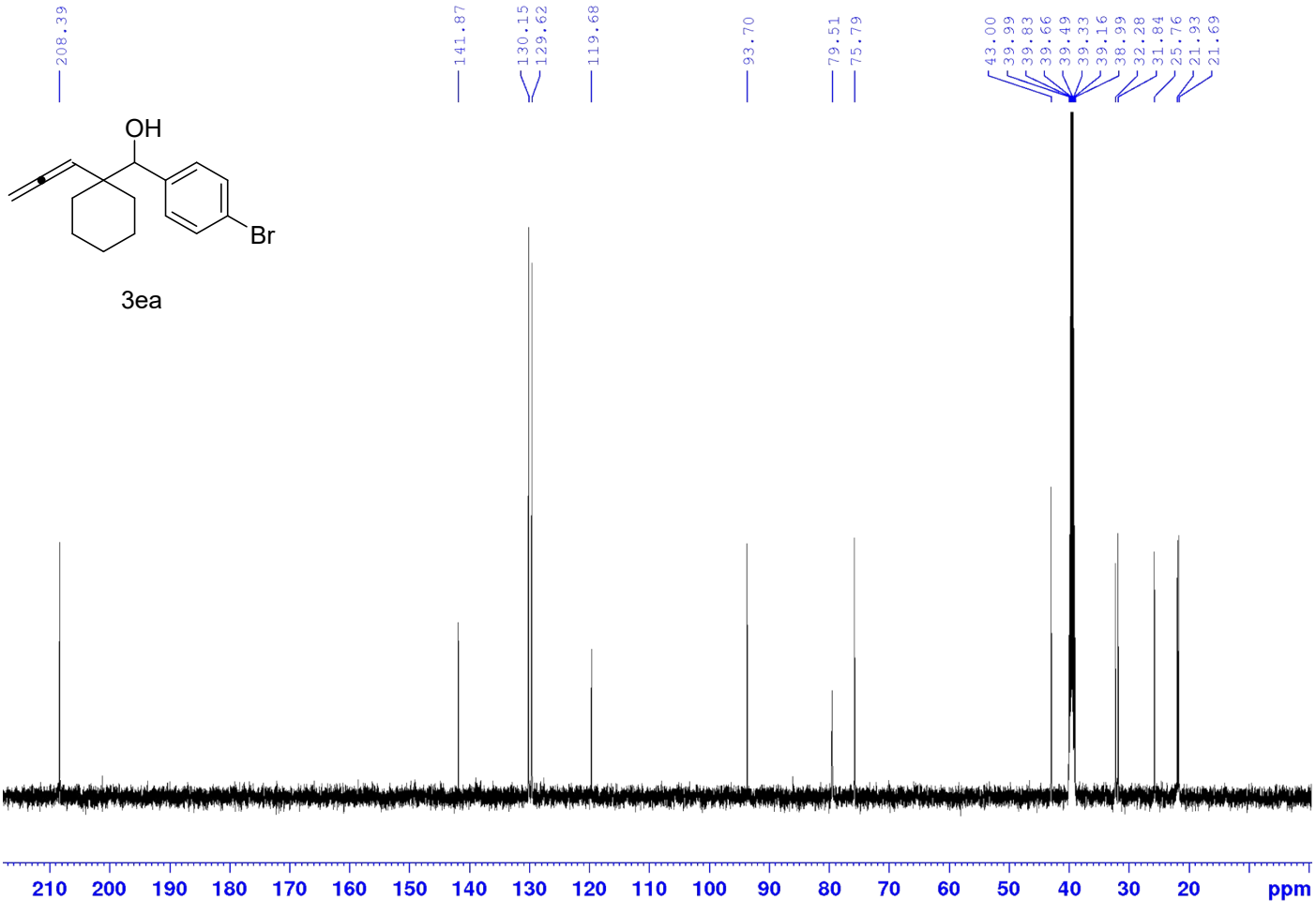

206.59
142.29
129.91
129.88
119.78
97.35
78.78
76.49
39.99
39.83
39.76
39.66
39.49
39.33
39.15
38.99
24.43
24.06

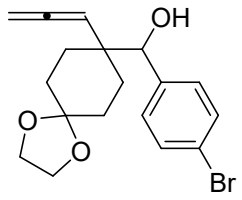
OH
Br

3da

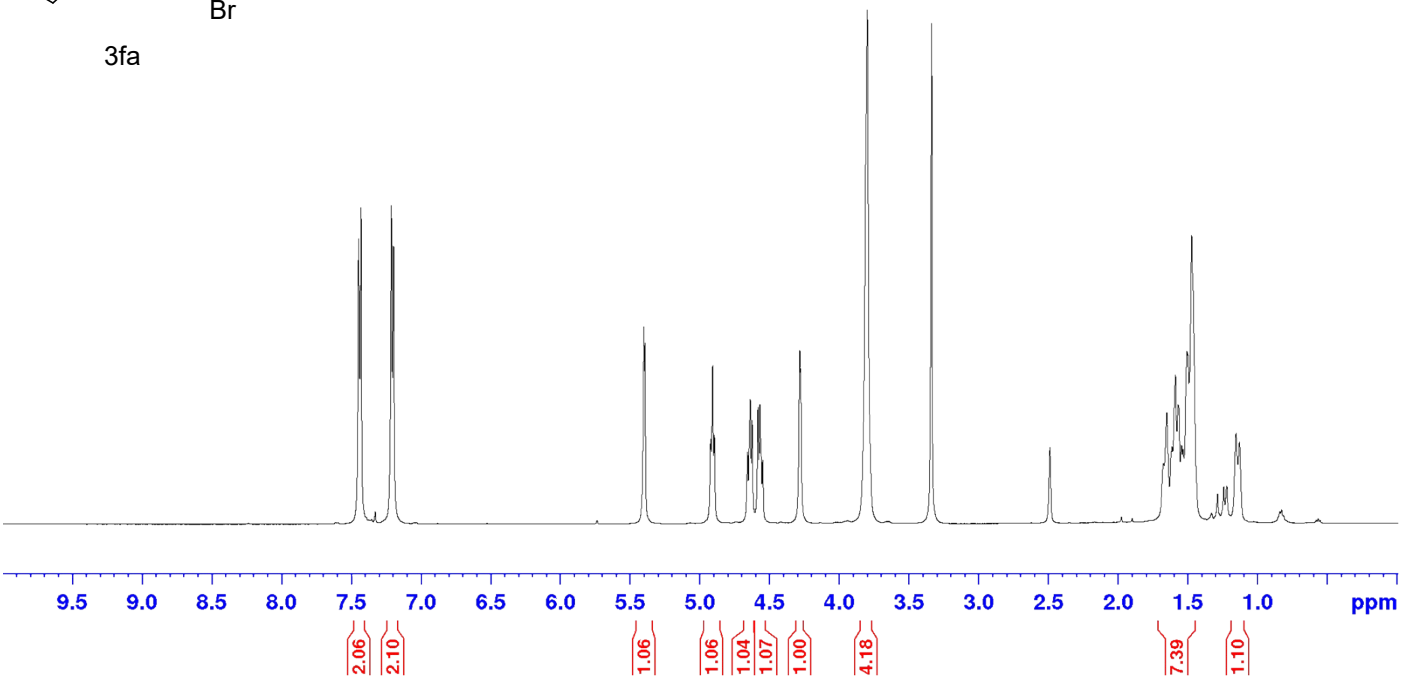
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

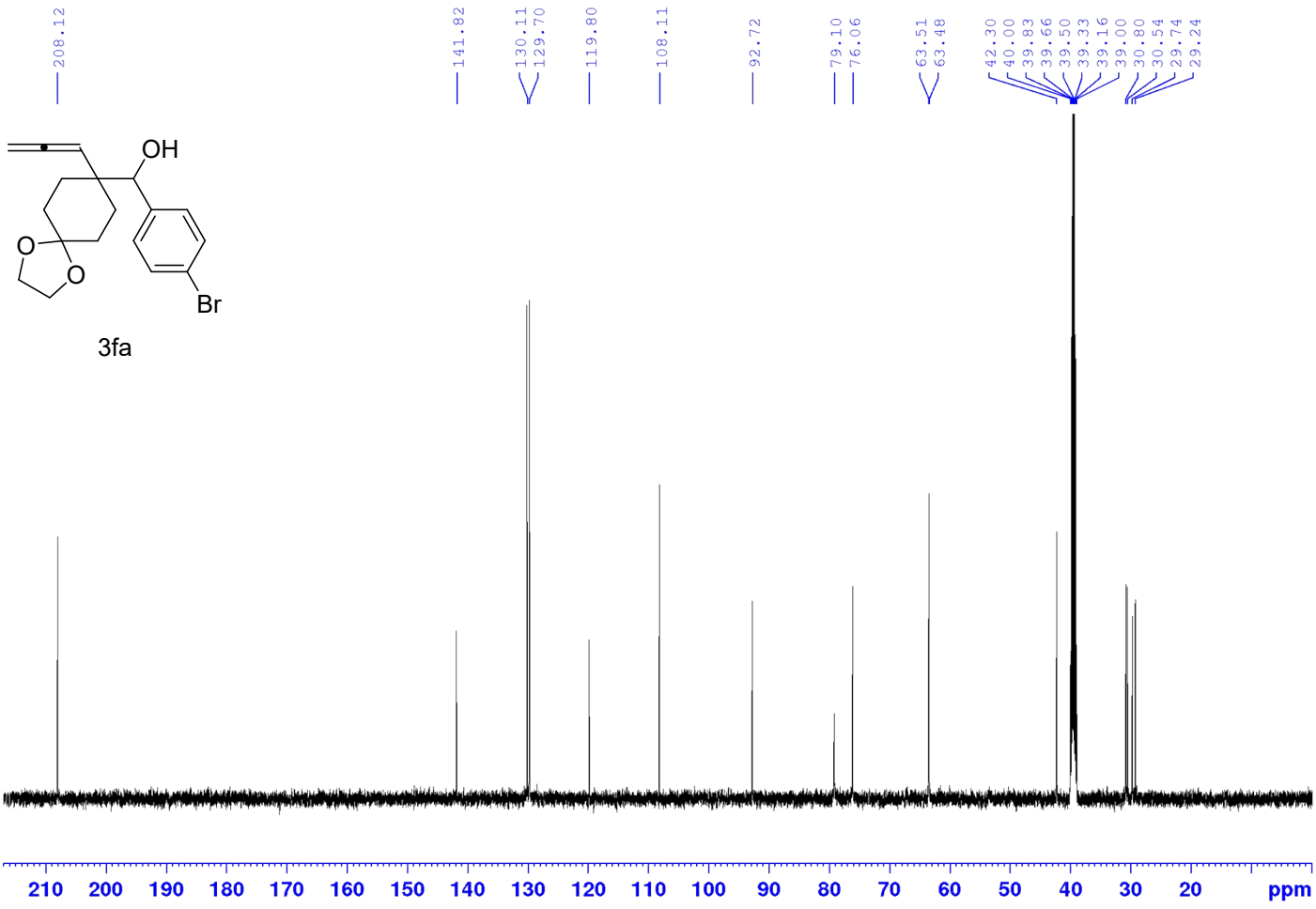

OH
Br
3ea
DCM
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00 2.01 1.01 1.00 2.03 1.00 1.03 2.07 5.04 2.12


208.39
141.87
130.15
129.62
119.68
93.70
79.51
75.79
43.00
39.99
39.83
39.66
39.49
39.33
39.16
38.99
32.28
31.84
25.76
21.93
21.69
OH
Br
3ea
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


OH
O
O
Br

3fa

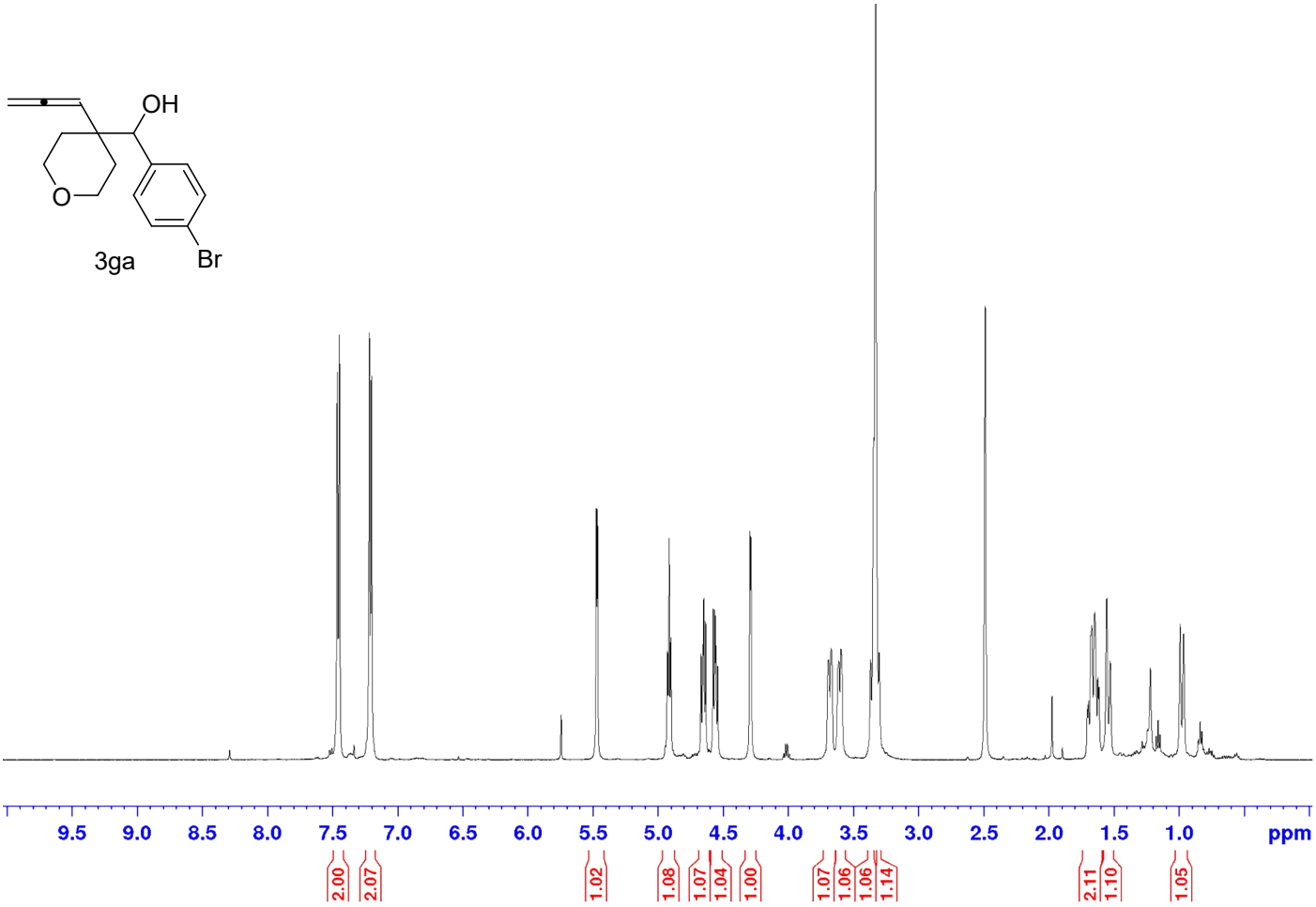

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.06
2.10
1.06
1.06
1.04
1.07
1.00
4.18
7.39
1.10

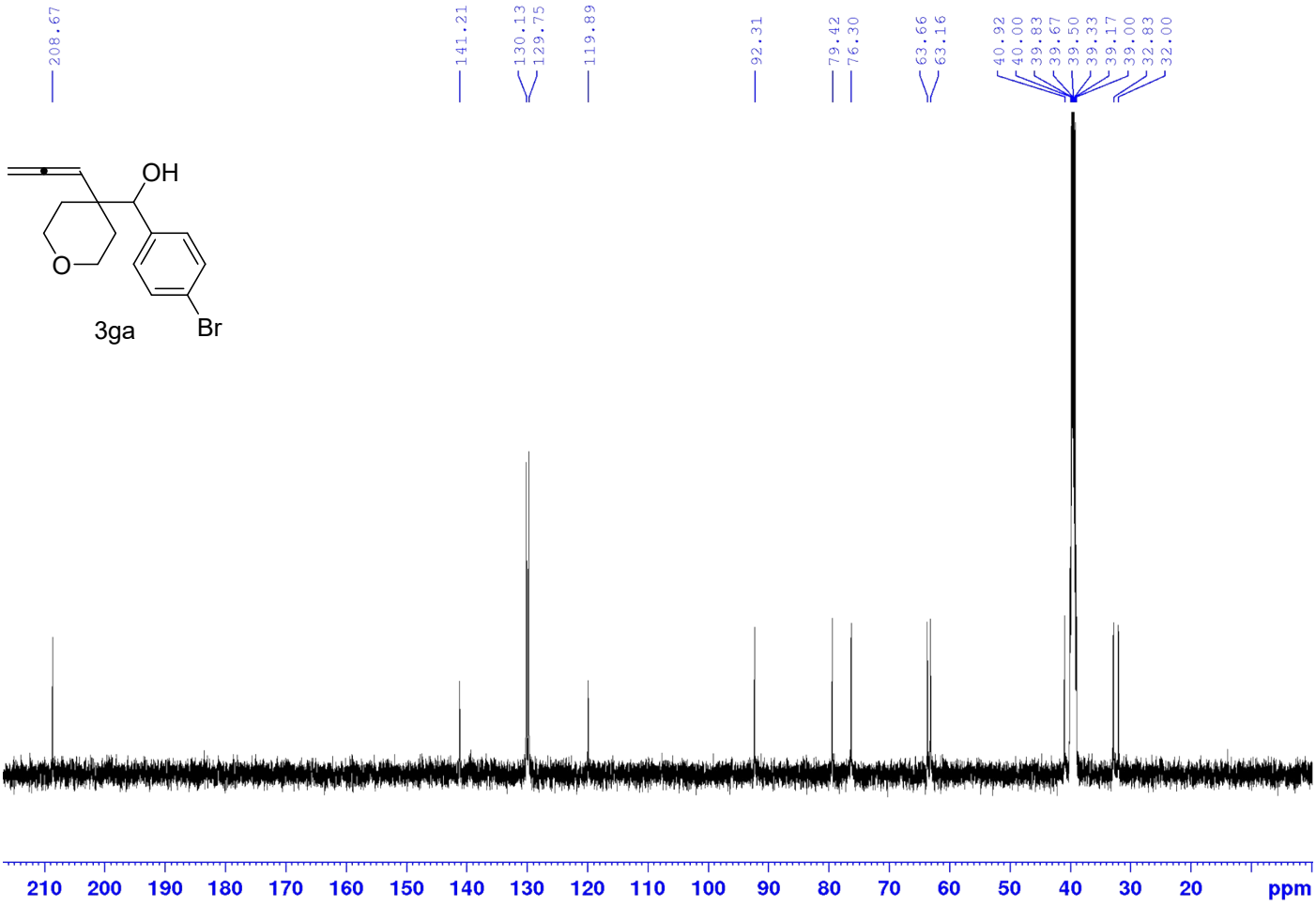

208.12
141.82
130.11
129.70
119.80
108.11
92.72
79.10
76.06
63.51
63.48
42.30
40.00
39.83
39.66
39.50
39.33
39.16
39.00
30.80
30.54
29.74
29.24

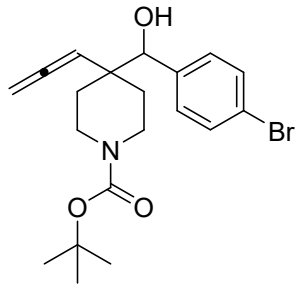
OH
O
O
Br

3fa

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

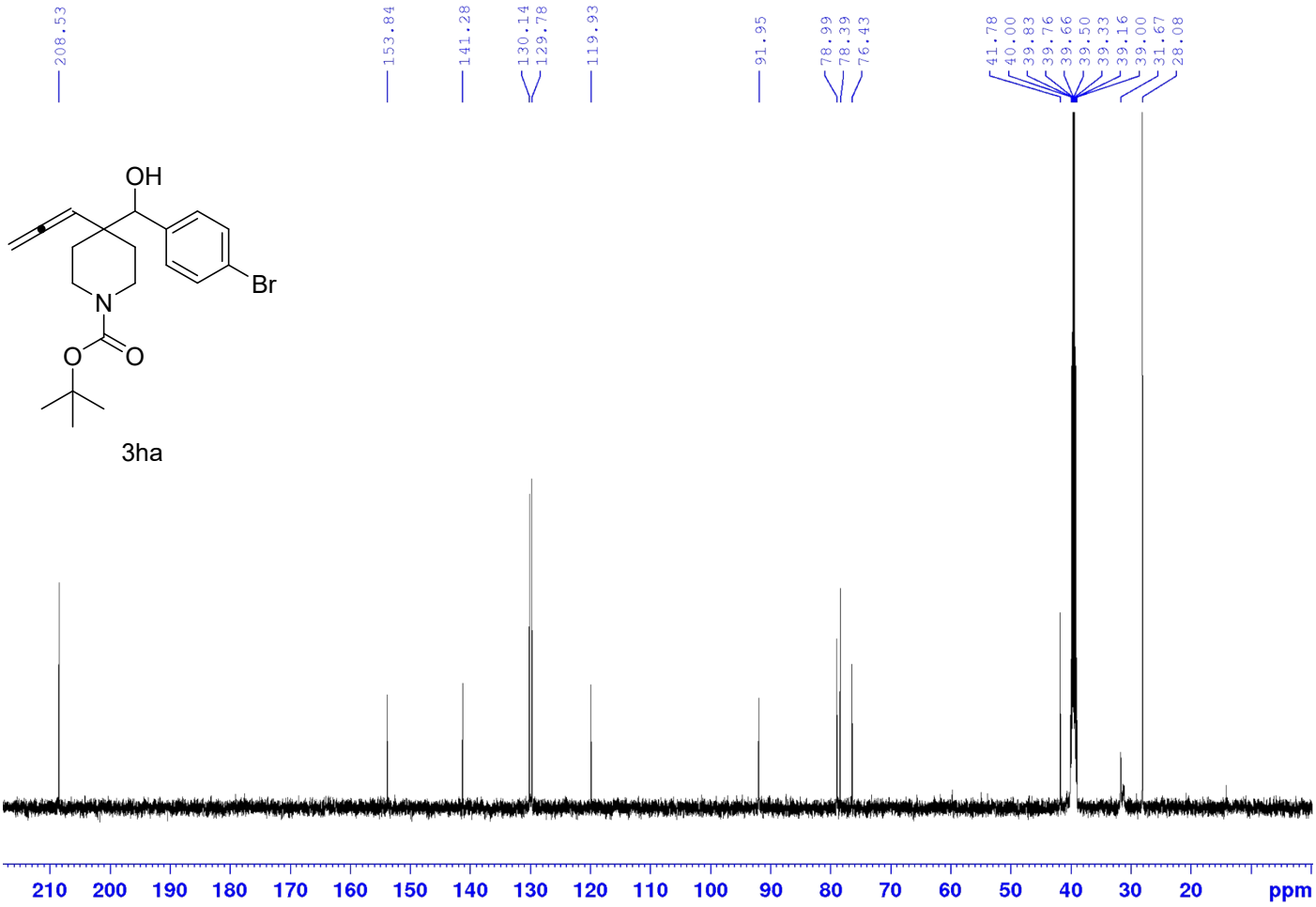

OH
O
Br
3ga
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00 2.07 1.02 1.08 1.07 1.04 1.00 1.07 1.06 1.06 1.14 2.11 1.10 1.05


208.67
141.21
130.13
129.75
119.89
92.31
79.42
76.30
63.66
63.16
40.92
40.00
39.83
39.67
39.50
39.33
39.17
39.00
32.83
32.00
OH
O
Br
3ga
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


OH
Br
N
O
O

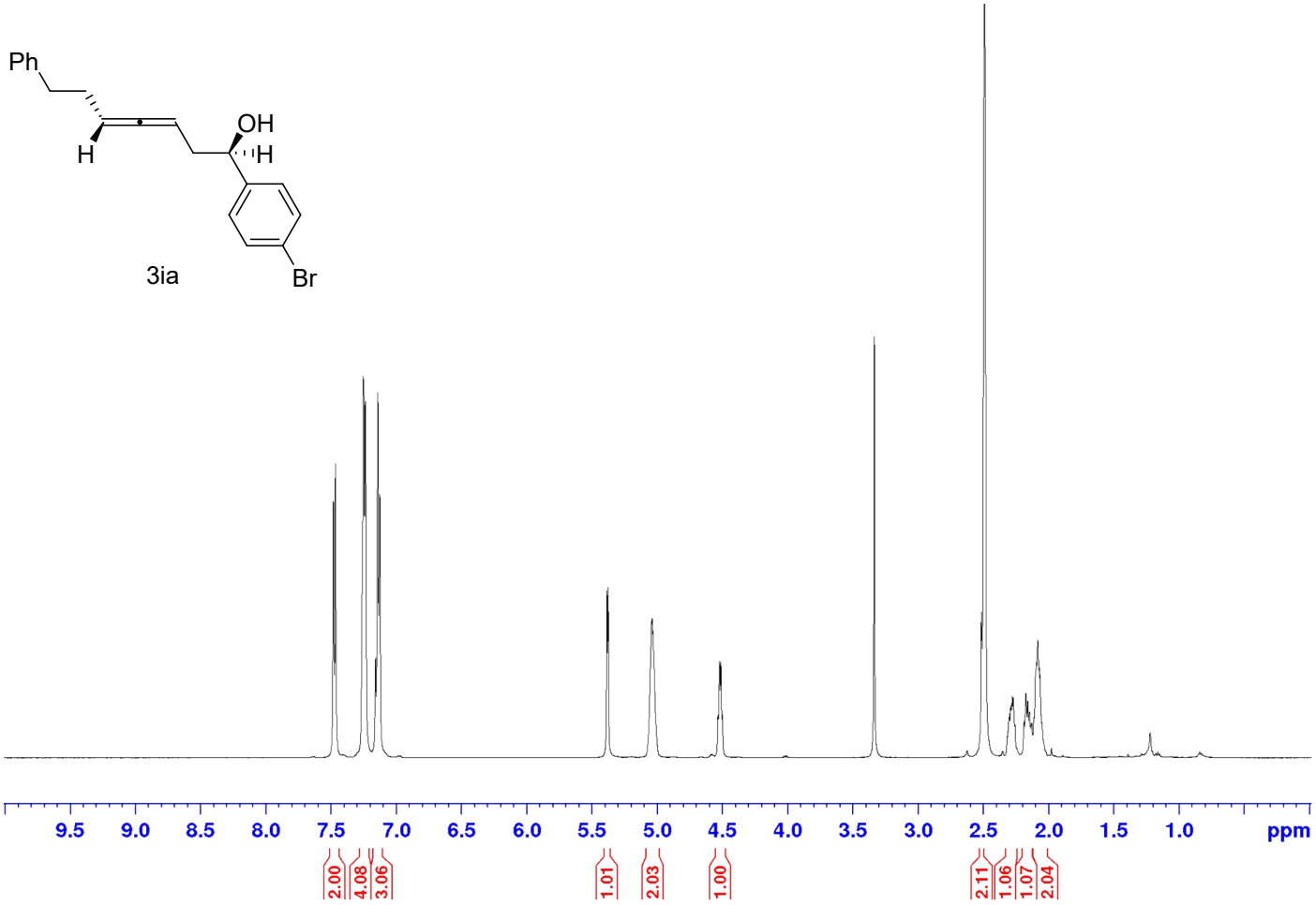
3ha

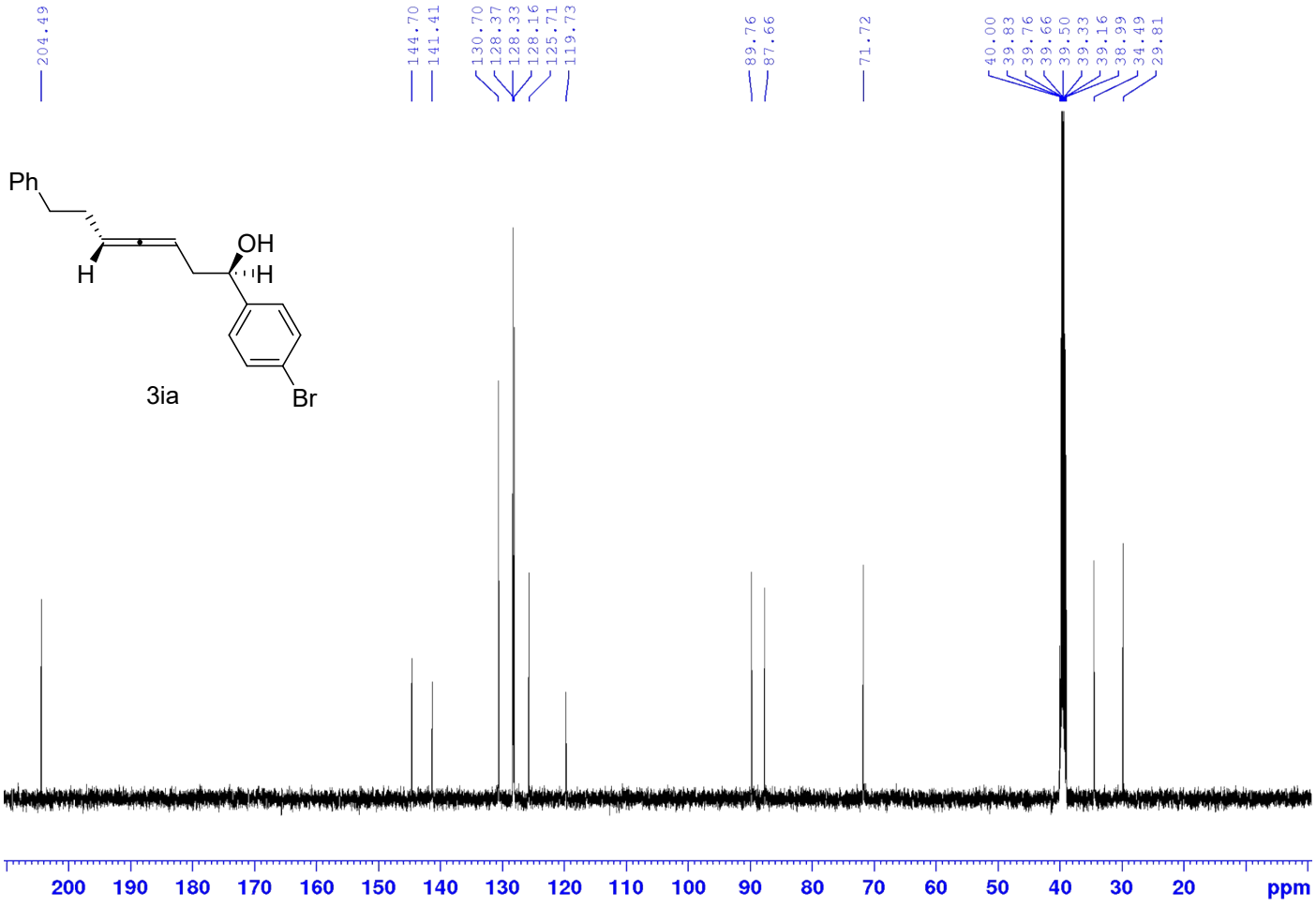
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.01 2.04 1.01 1.00 1.01 1.01 1.00 2.04 2.03 1.02 2.13 9.04 1.04

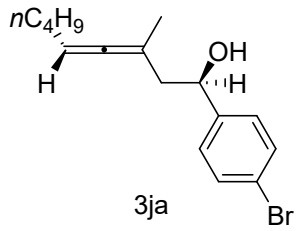

208.53
153.84
141.28
130.14
129.78
119.93
91.95
78.99
78.39
76.43
41.78
40.00
39.83
39.76
39.66
39.50
39.33
39.16
39.00
31.67
28.08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

OH
Br
N
O
O

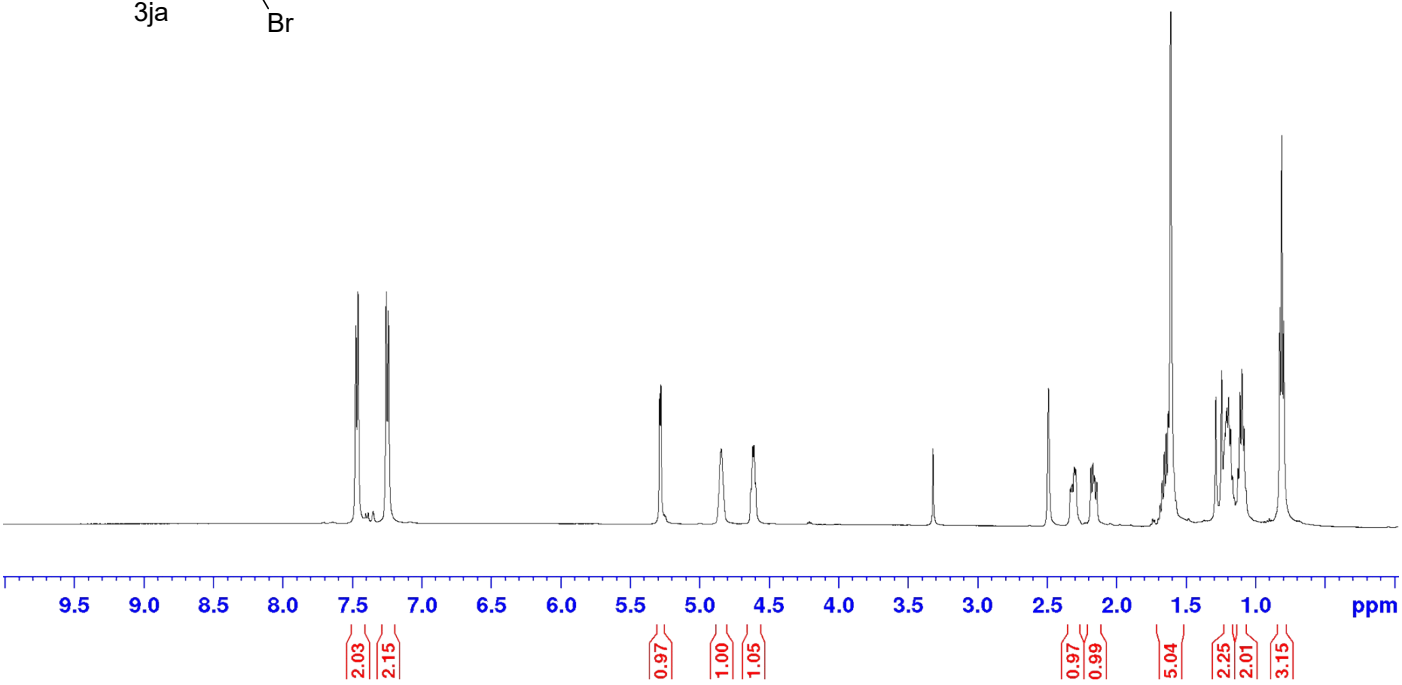
3ha

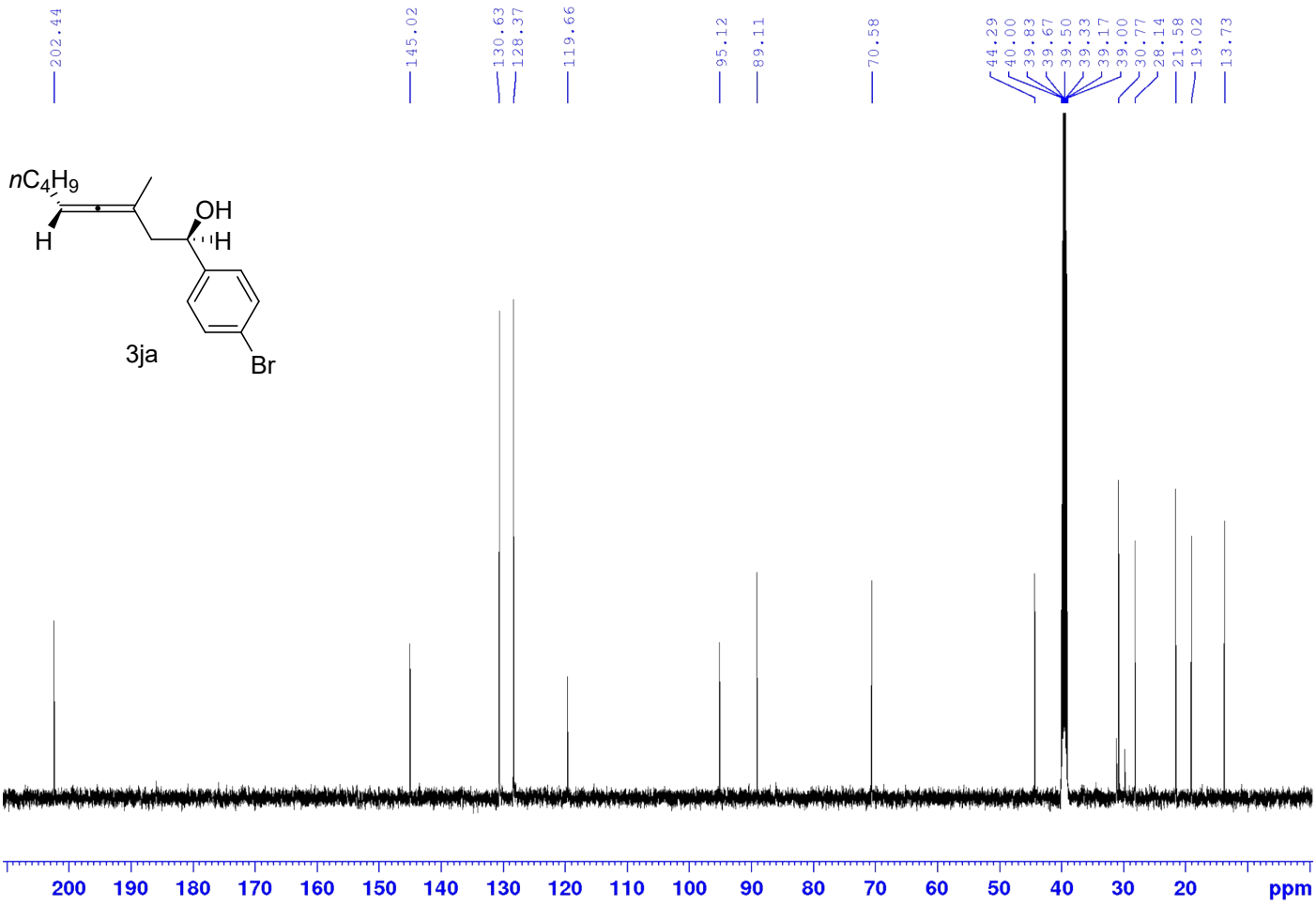

Ph
OH
H
H
Br
3ia
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00 4.08 3.06 1.01 2.03 1.00 2.11 1.06 1.07 2.04


204.49
144.70
141.41
130.70
128.37
128.33
128.16
125.71
119.73
89.76
87.66
71.72
40.00
39.83
39.76
39.66
39.50
39.33
39.16
38.99
34.49
29.81
Ph
OH
H
H
Br
3ia
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


nC4H9
OH
H
H
Br

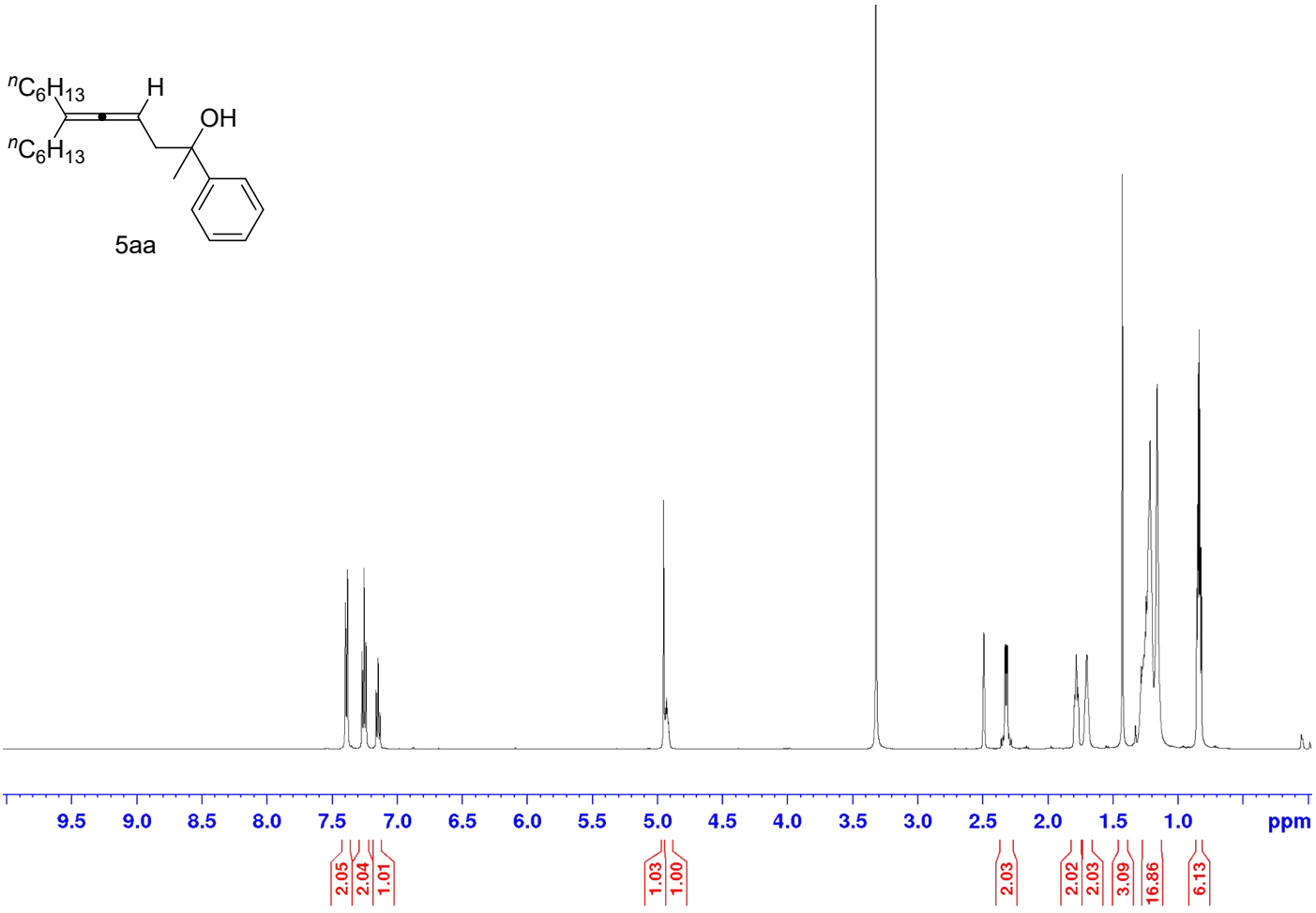
3ja

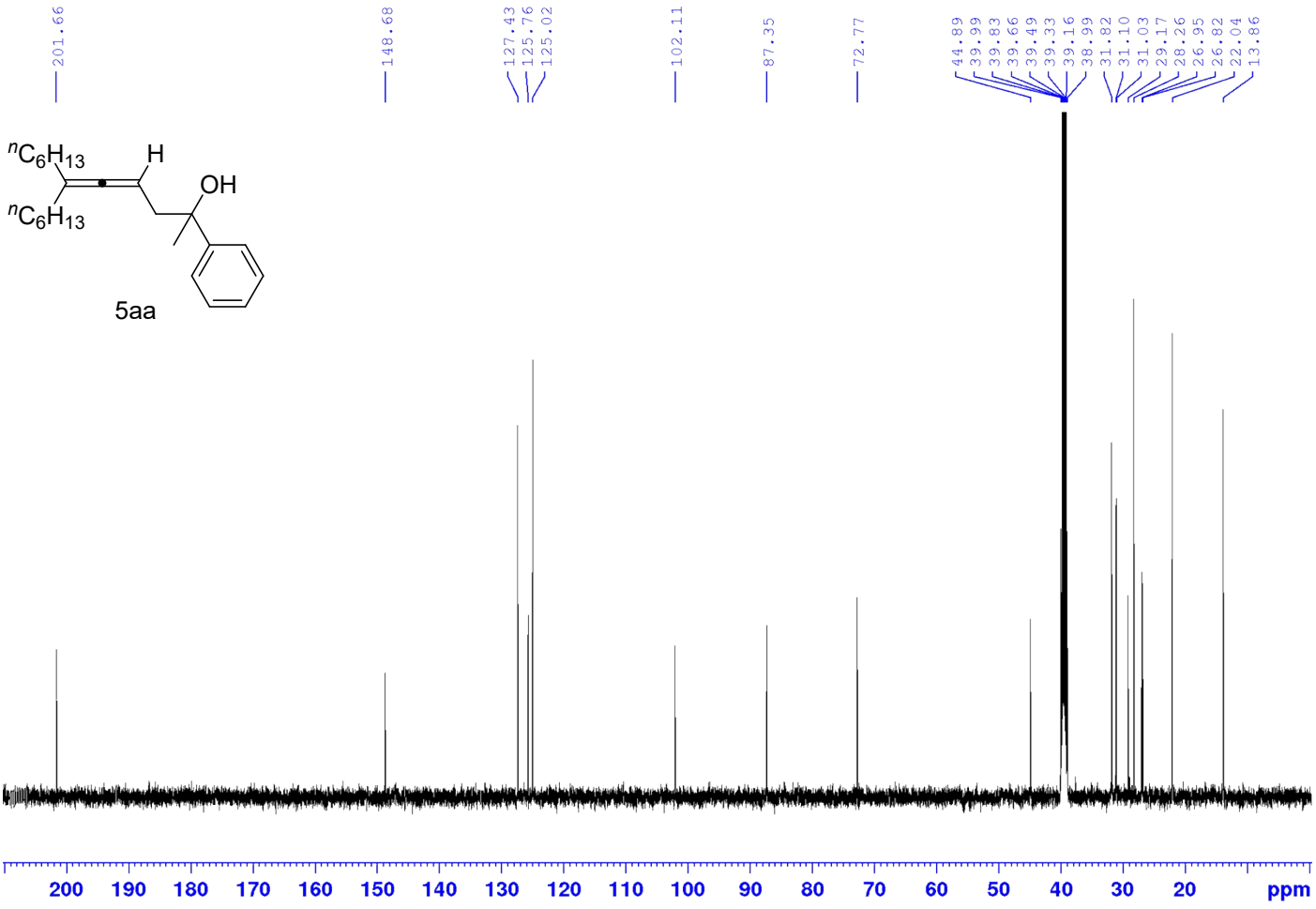

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.03
2.15
0.97
1.00
1.05
0.97
0.99
5.04
2.25
2.01
3.15

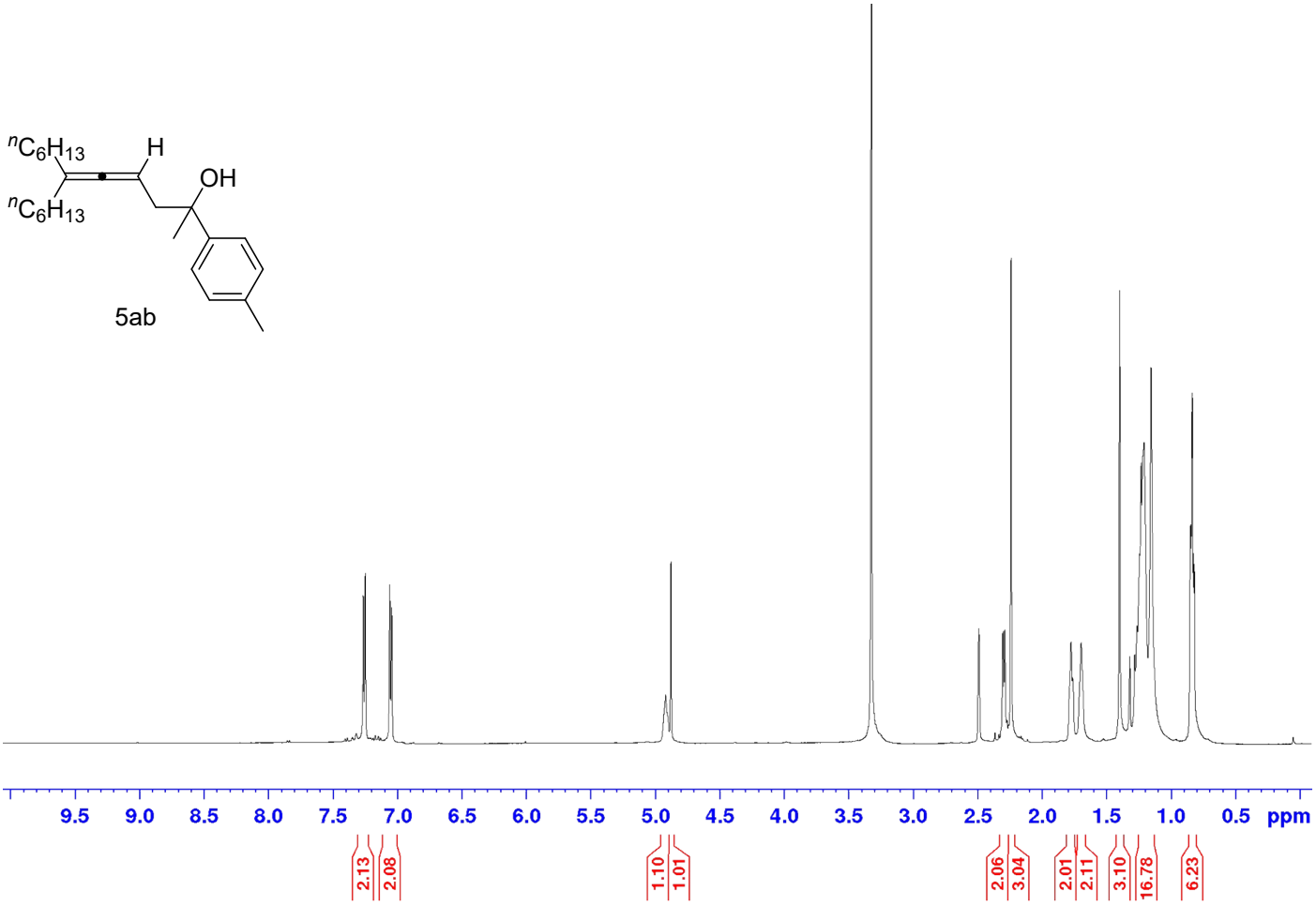

202.44
145.02
130.63
128.37
119.66
95.12
89.11
70.58
44.29
40.00
39.83
39.67
39.50
39.33
39.17
39.00
30.77
28.14
21.58
19.02
13.73
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

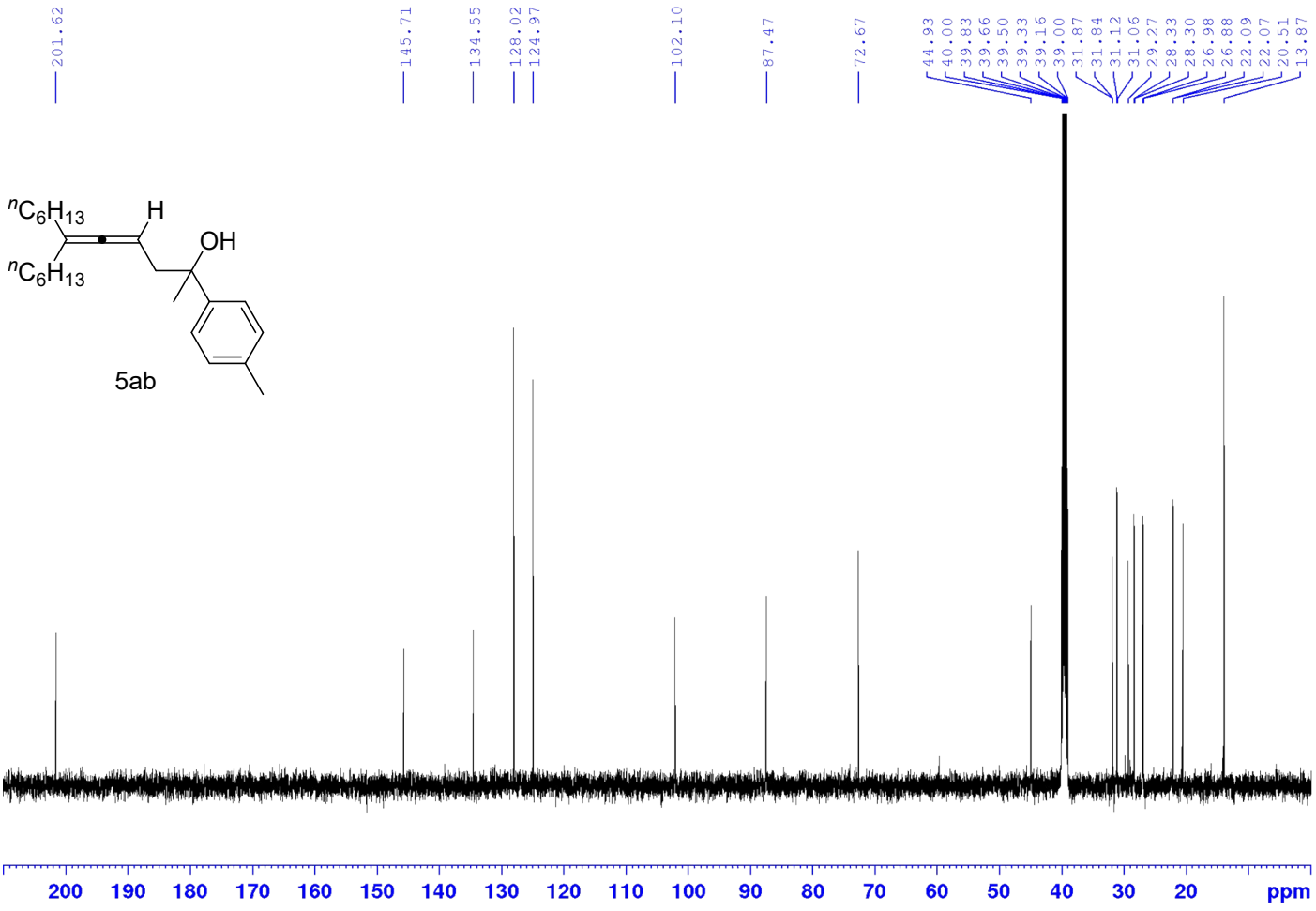
nC4H9
OH
H
H
Br

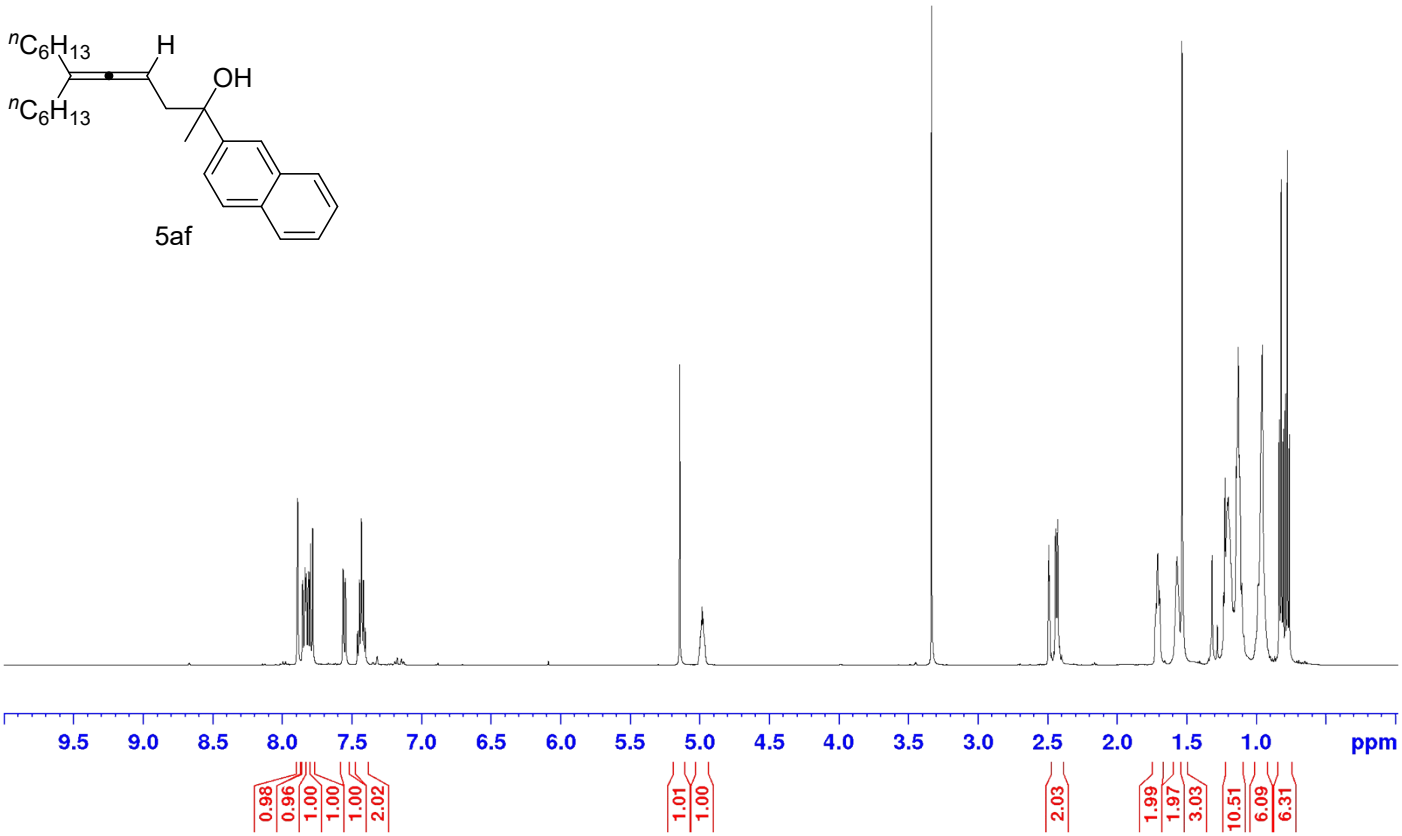
3ja

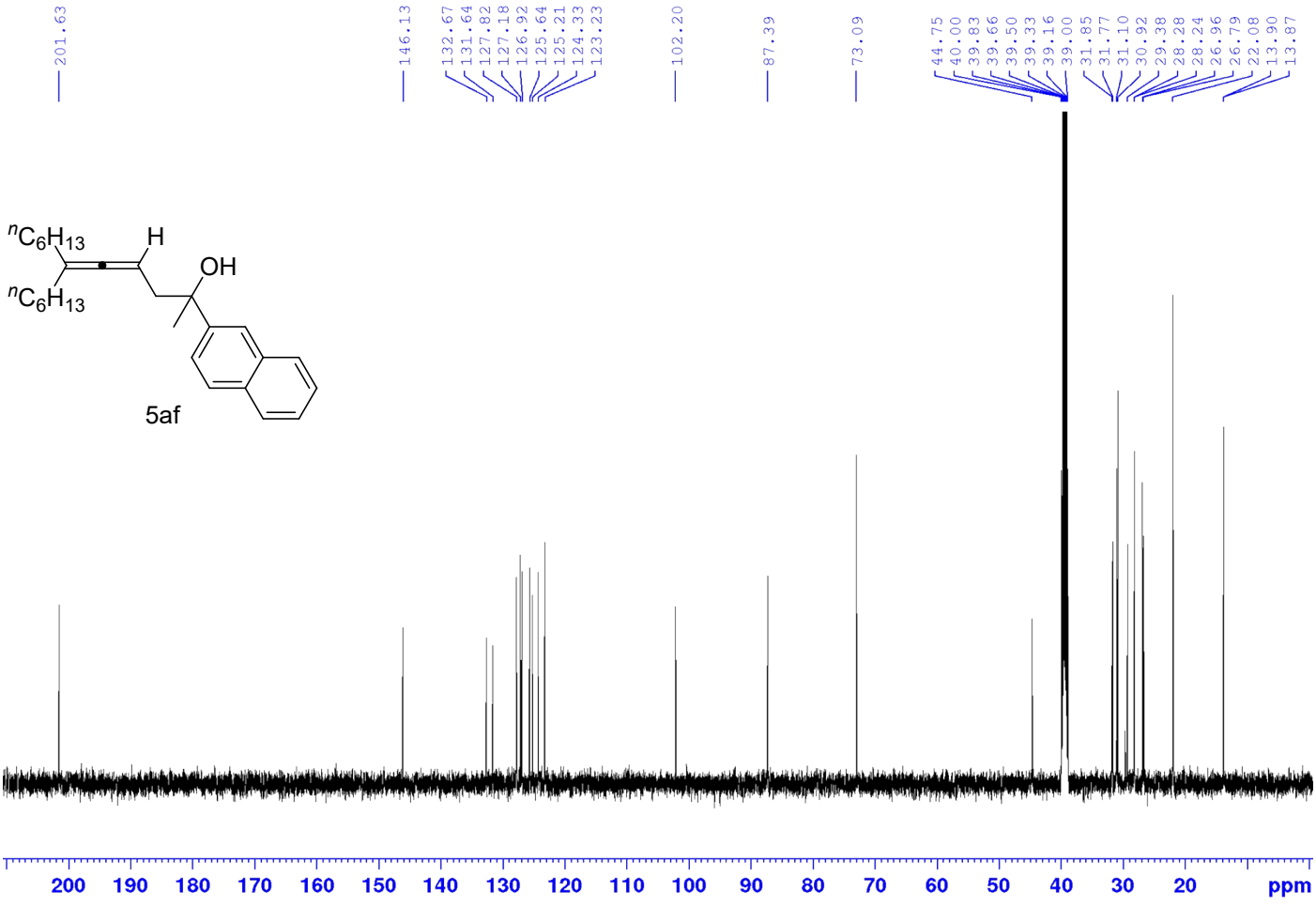

nC6H13
H
OH
nC6H13
5aa
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.05 2.04 1.01 1.03 1.00 2.03 2.02 2.03 3.09 16.86 6.13

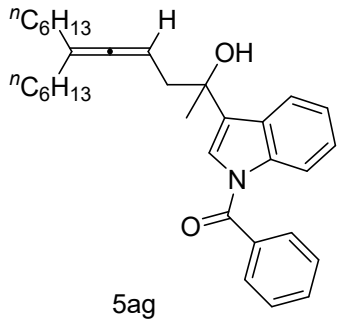

201.66
148.68
127.43
125.76
125.02
102.11
87.35
72.77
44.89
39.99
39.83
39.66
39.49
39.33
39.16
38.99
31.82
31.10
31.03
29.17
28.26
26.95
26.82
22.04
13.86
nC6H13
H
OH
nC6H13
5aa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
5ab
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
2.13
2.08
1.10
1.01
2.06
3.04
2.01
2.11
3.10
16.78
6.23

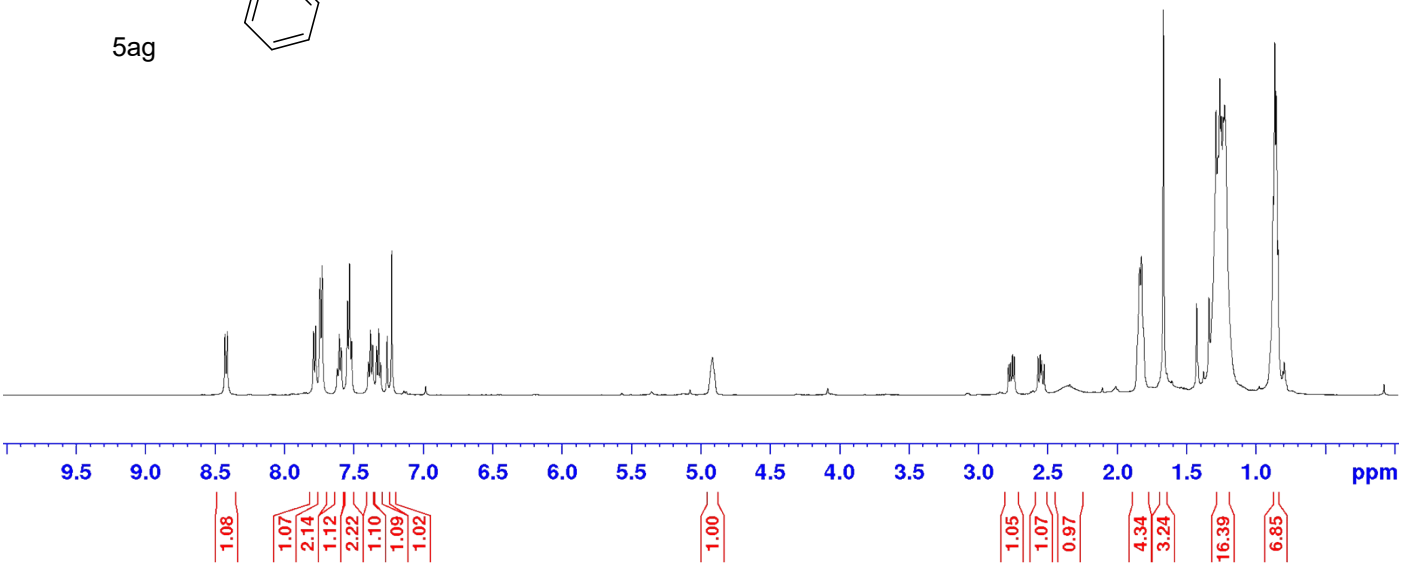

201.62
145.71
134.55
128.02
124.97
102.10
87.47
72.67
44.93
40.00
39.83
39.66
39.50
39.33
39.16
39.00
31.87
31.84
31.12
31.06
29.27
28.33
28.30
26.98
26.88
22.09
22.07
20.51
13.87
^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
5ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

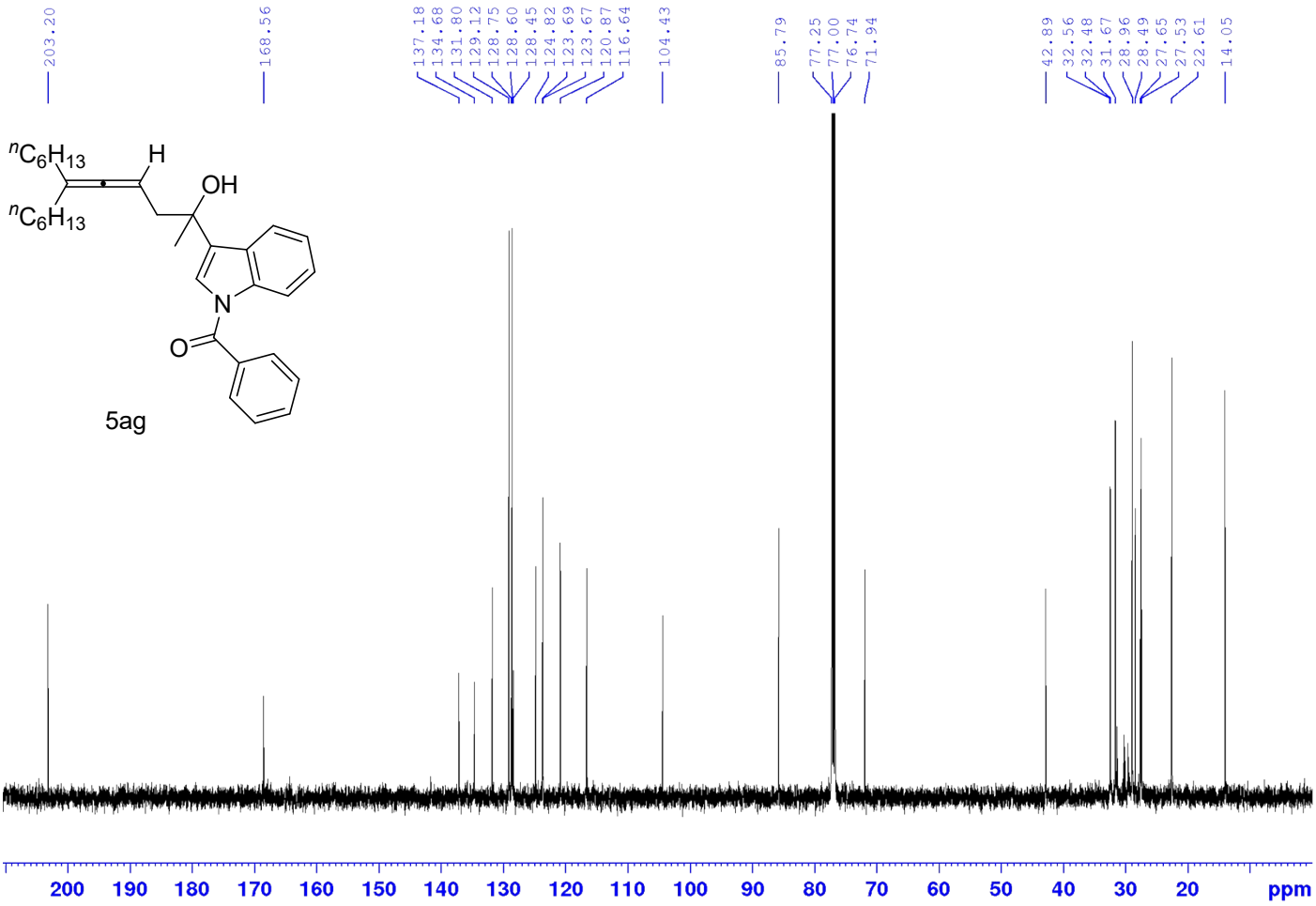

$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
5af
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.98 0.96 1.00 1.00 1.00 2.02
1.01 1.00
2.03
1.99 1.97 3.03
10.51 6.09 6.31


201.63
146.13
132.67
131.64
127.82
127.18
126.92
125.64
125.21
124.33
123.23
102.20
87.39
73.09
44.75
40.00
39.83
39.66
39.50
39.33
39.16
39.00
31.85
31.77
31.10
30.92
29.38
28.28
28.24
26.96
26.79
22.08
13.90
13.87
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
5af
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
N
O

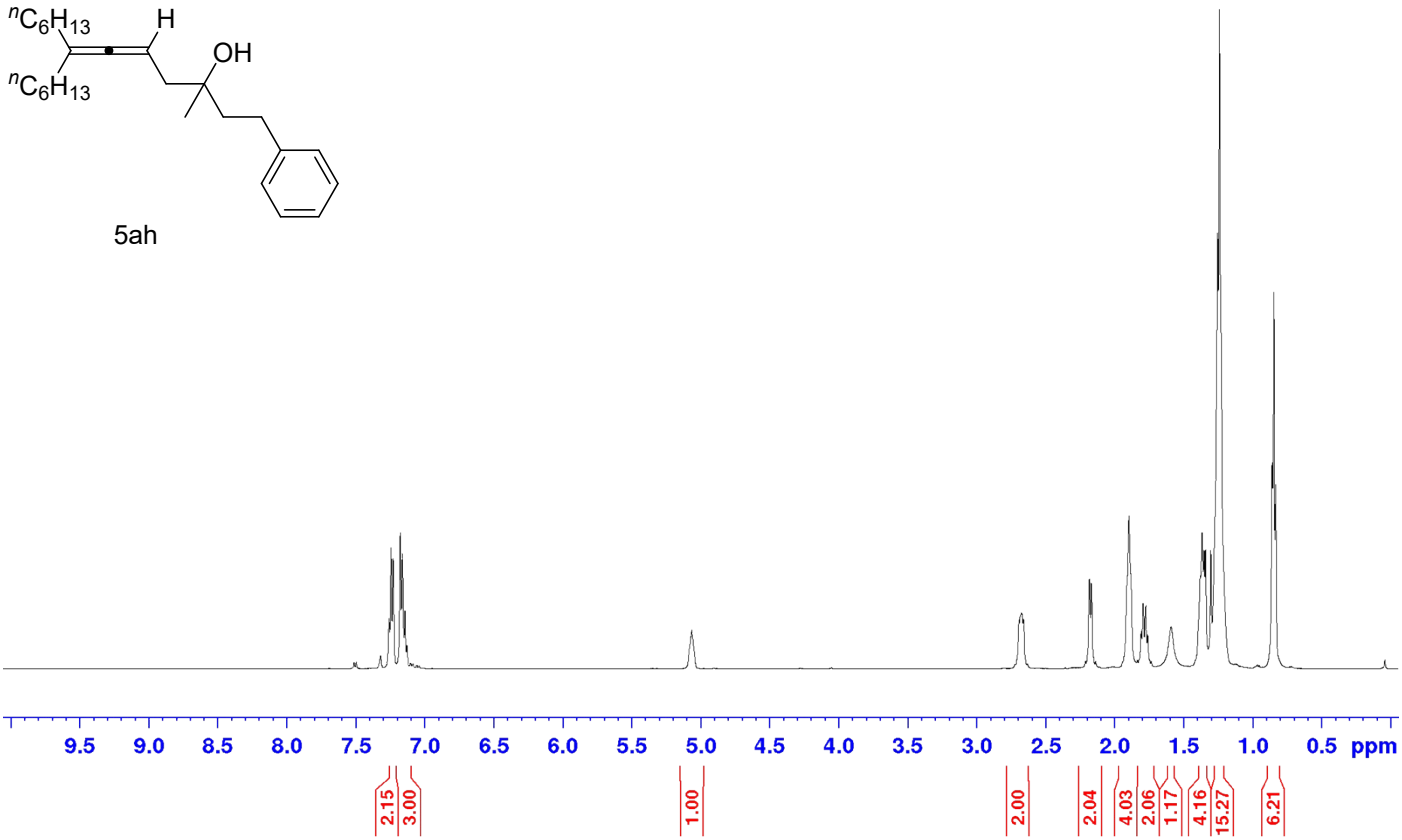
5ag

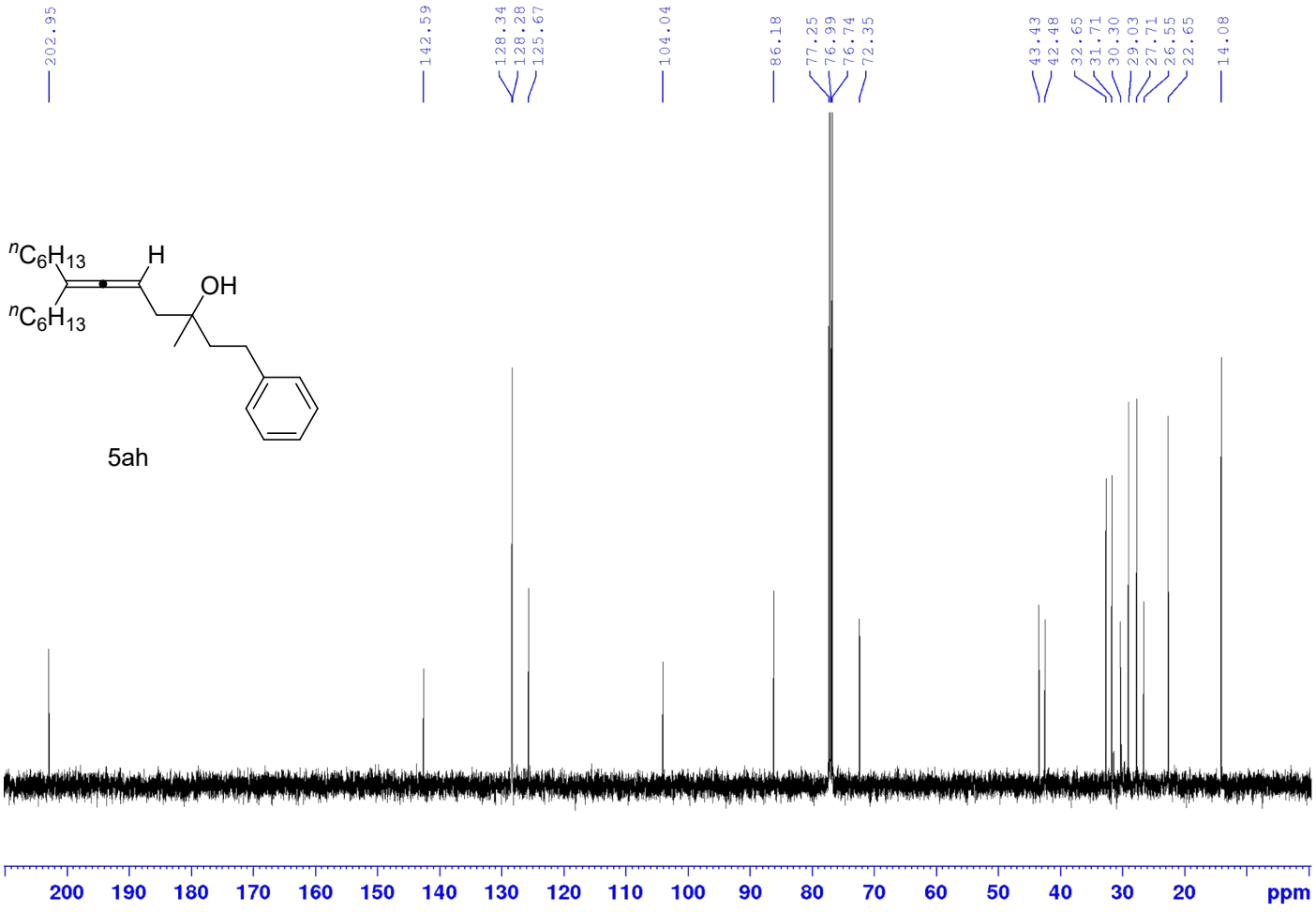

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.08
1.07
2.14
1.12
2.22
1.10
1.09
1.02
1.00
1.05
1.07
0.97
4.34
3.24
16.39
6.85

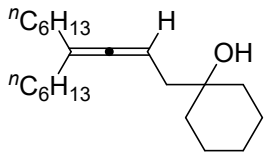

203.20
168.56
137.18
134.68
131.80
129.12
128.75
128.60
128.45
124.82
123.69
123.67
120.87
116.64
104.43
85.79
77.25
77.00
76.74
71.94
42.89
32.56
32.48
31.67
28.96
28.49
27.65
27.53
22.61
14.05
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$
N
O

5ag

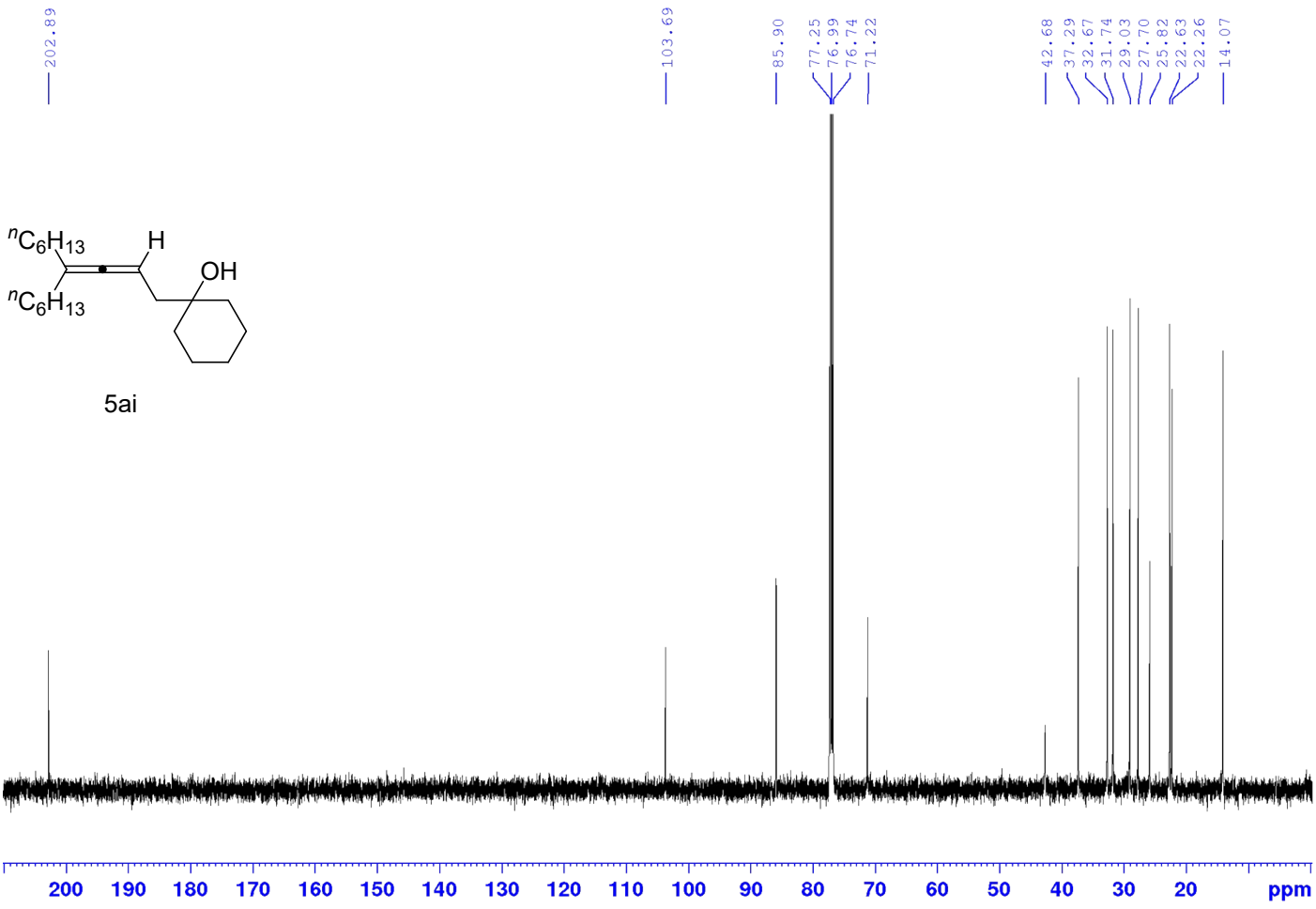

$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
5ah
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.15
3.00
1.00
2.00
2.04
4.03
2.06
1.17
4.16
15.27
6.21


202.95
142.59
128.34
128.28
125.67
104.04
86.18
77.25
76.99
76.74
72.35
43.43
42.48
32.65
31.71
30.30
29.03
27.71
26.55
22.65
14.08
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
5ah
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$

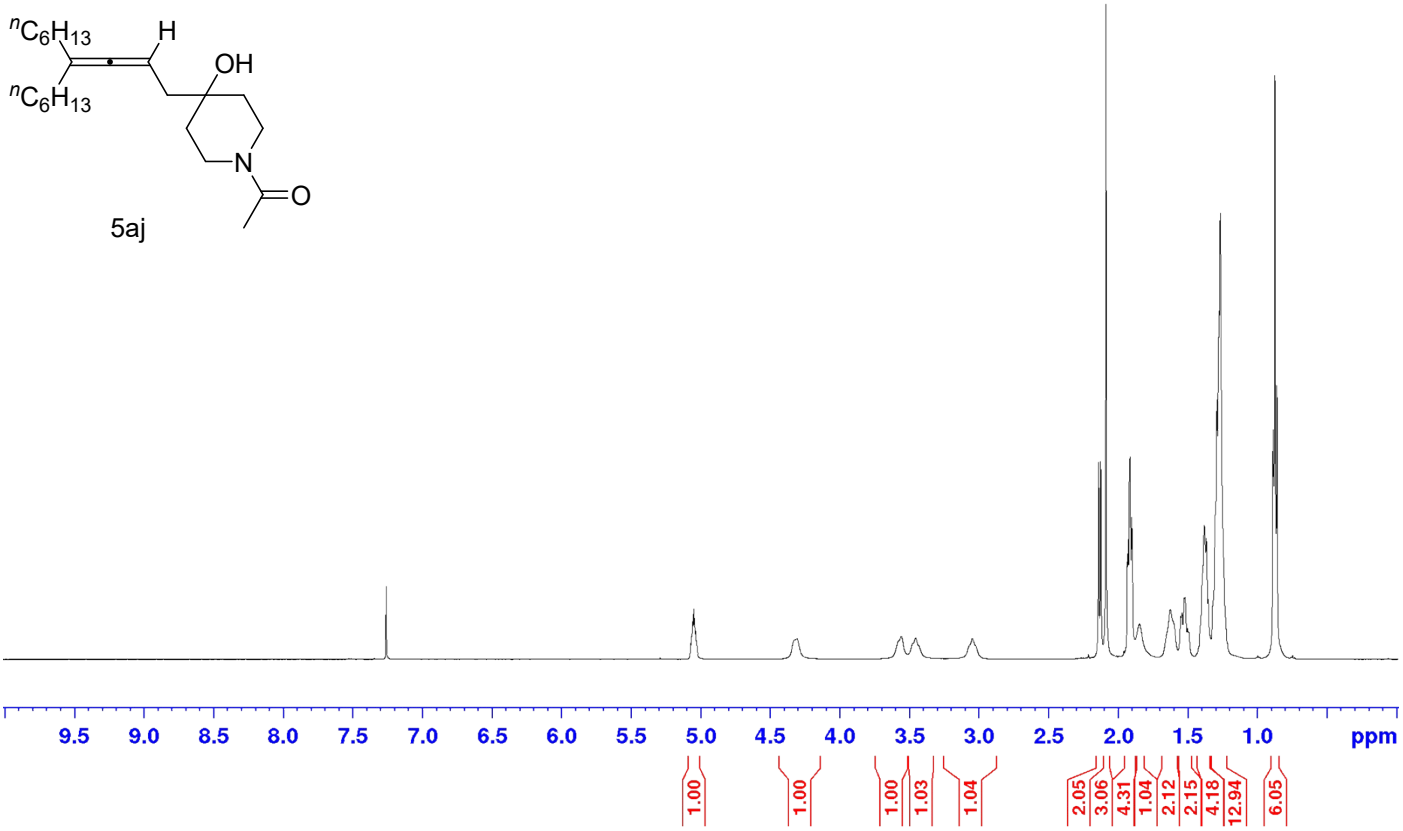
5ai

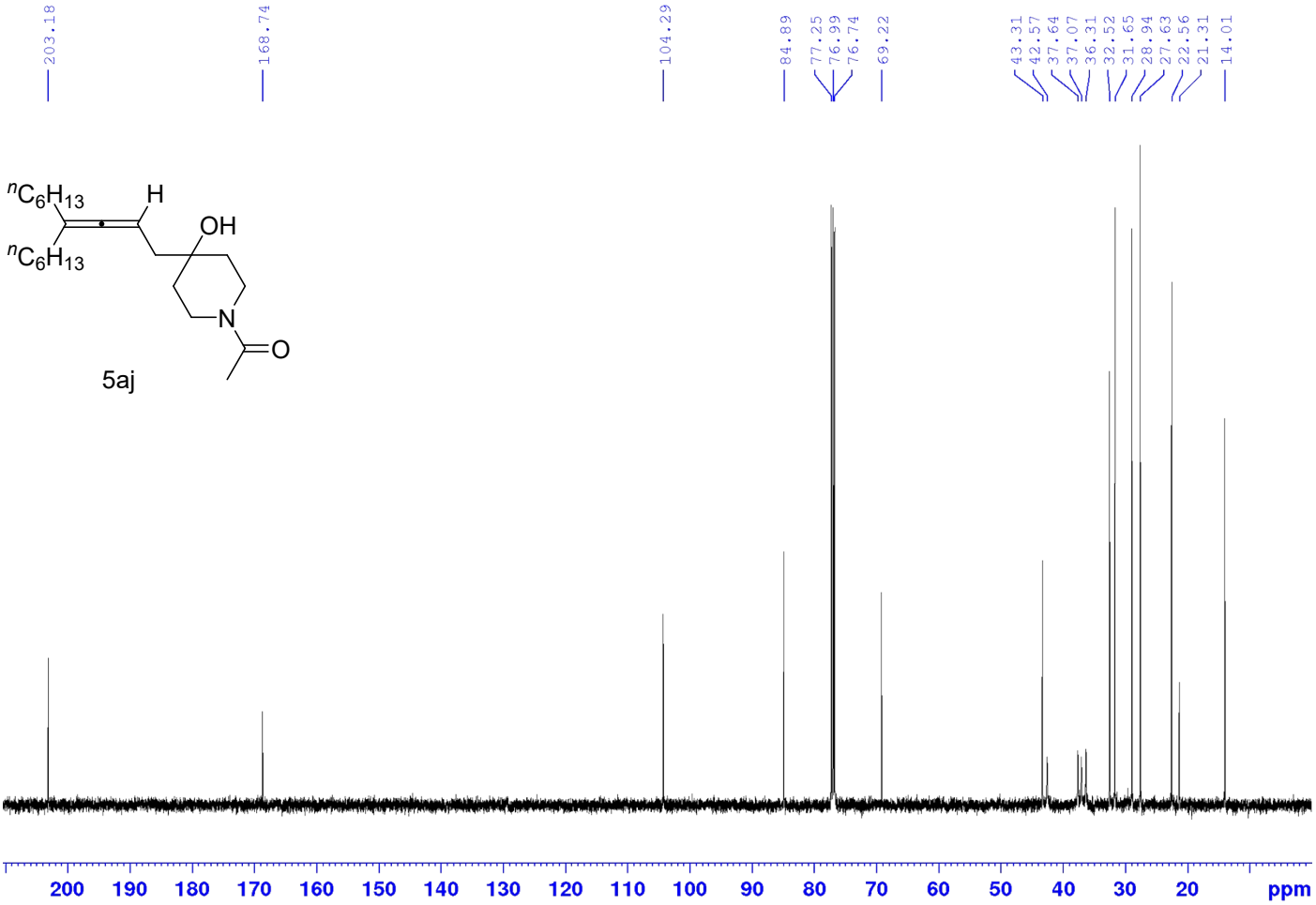
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
2.06
4.02
2.09
4.11
9.02
12.37
6.32

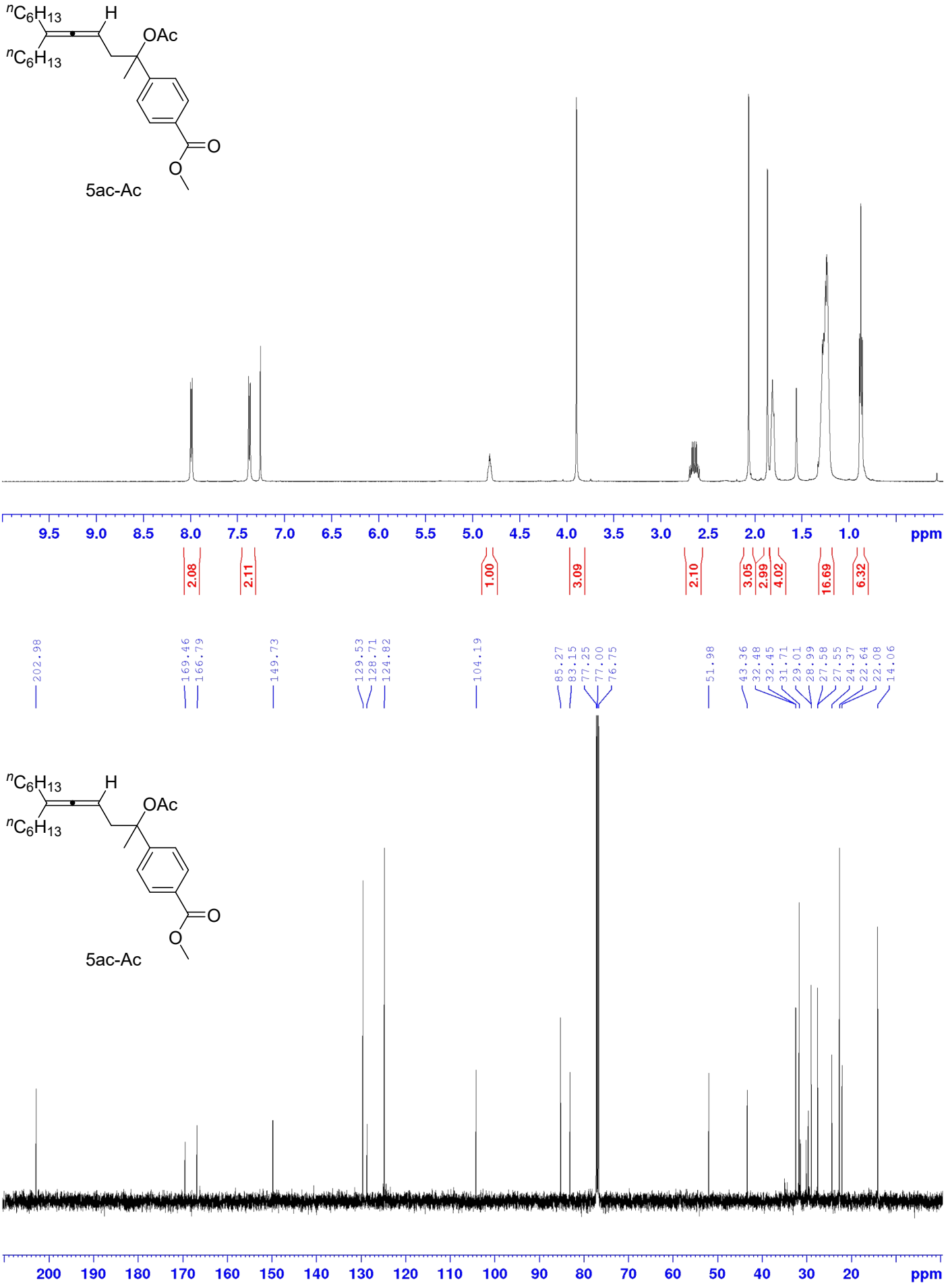

202.89
103.69
85.90
77.25
76.99
76.74
71.22
42.68
37.29
32.67
31.74
29.03
27.70
25.82
22.63
22.26
14.07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

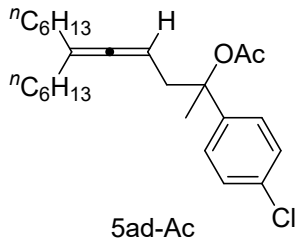
^{n}C$_6$H$_{13}$
H
OH
^{n}C$_6$H$_{13}$

5ai


$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
N
O
5aj
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 1.00 1.03 1.04 2.05 3.06 4.31 1.04 2.12 2.15 4.18 12.94 6.05

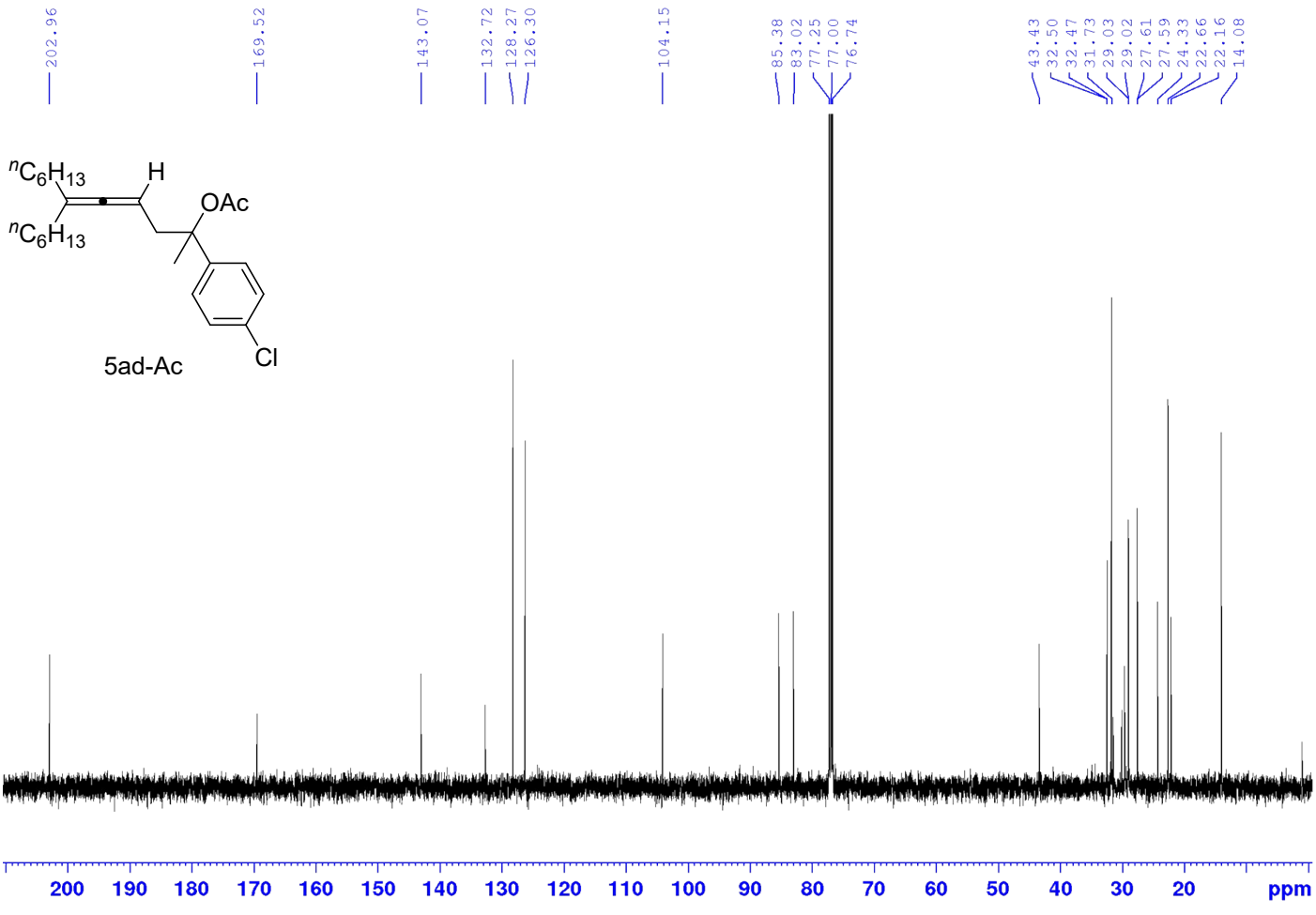

203.18
168.74
104.29
84.89
77.25
76.99
76.74
69.22
43.31
42.57
37.64
37.07
36.31
32.52
31.65
28.94
27.63
22.56
21.31
14.01
$^{n}C_6H_{13}$
H
OH
$^{n}C_6H_{13}$
N
O
5aj
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


nC6H13
H
OAc
nC6H13
O
O
5ac-Ac
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
2.08
2.11
1.00
3.09
2.10
3.05
2.99
4.02
16.69
6.32
202.98
169.46
166.79
149.73
129.53
128.71
124.82
104.19
85.27
83.15
77.25
77.00
76.75
51.98
43.36
32.48
32.45
31.71
29.01
28.99
27.58
27.55
24.37
22.64
22.08
14.06
nC6H13
H
OAc
nC6H13
O
O
5ac-Ac
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


^{n}C$_6$H$_{13}$
H
OAc
^{n}C$_6$H$_{13}$
Cl

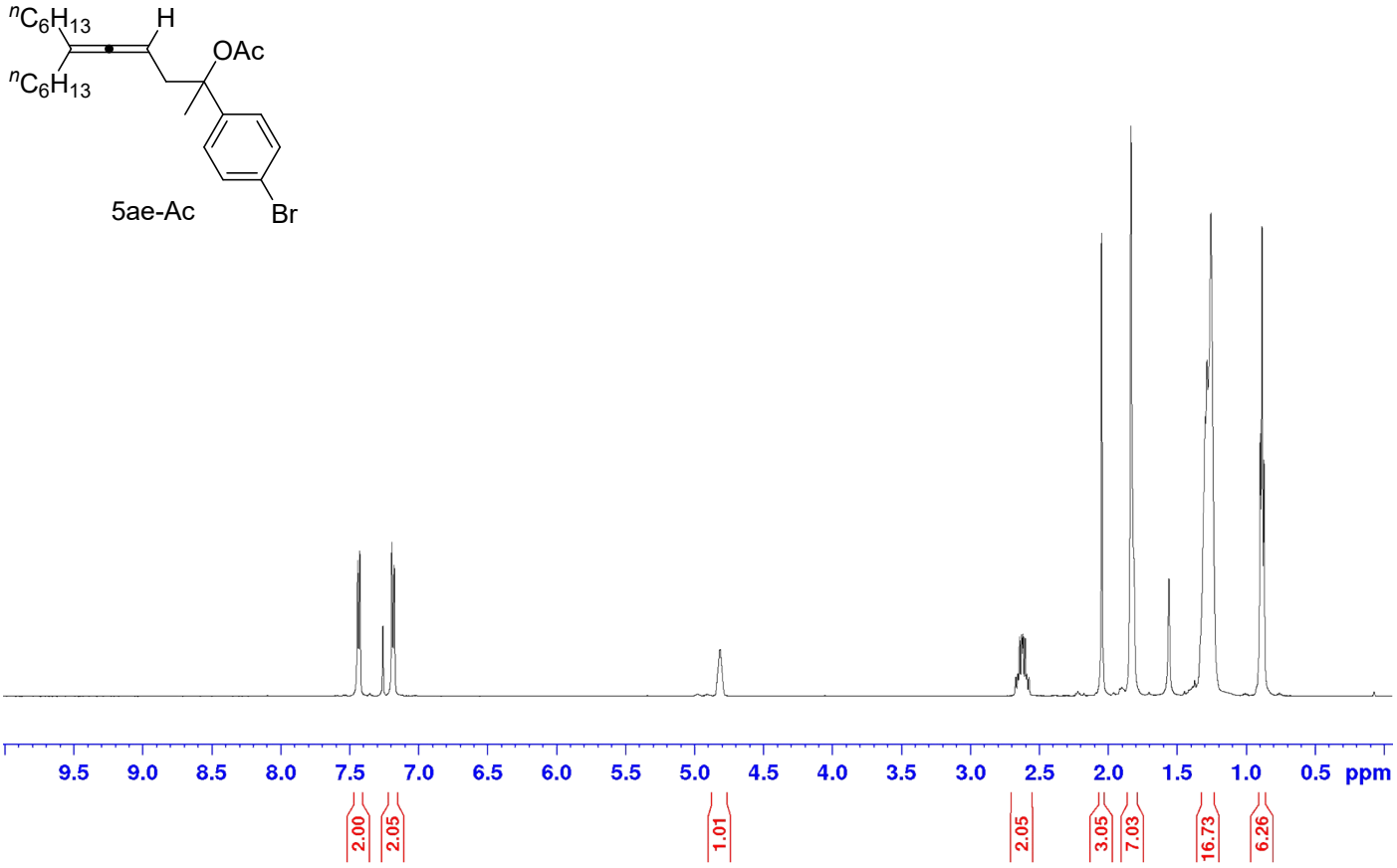
5ad-Ac

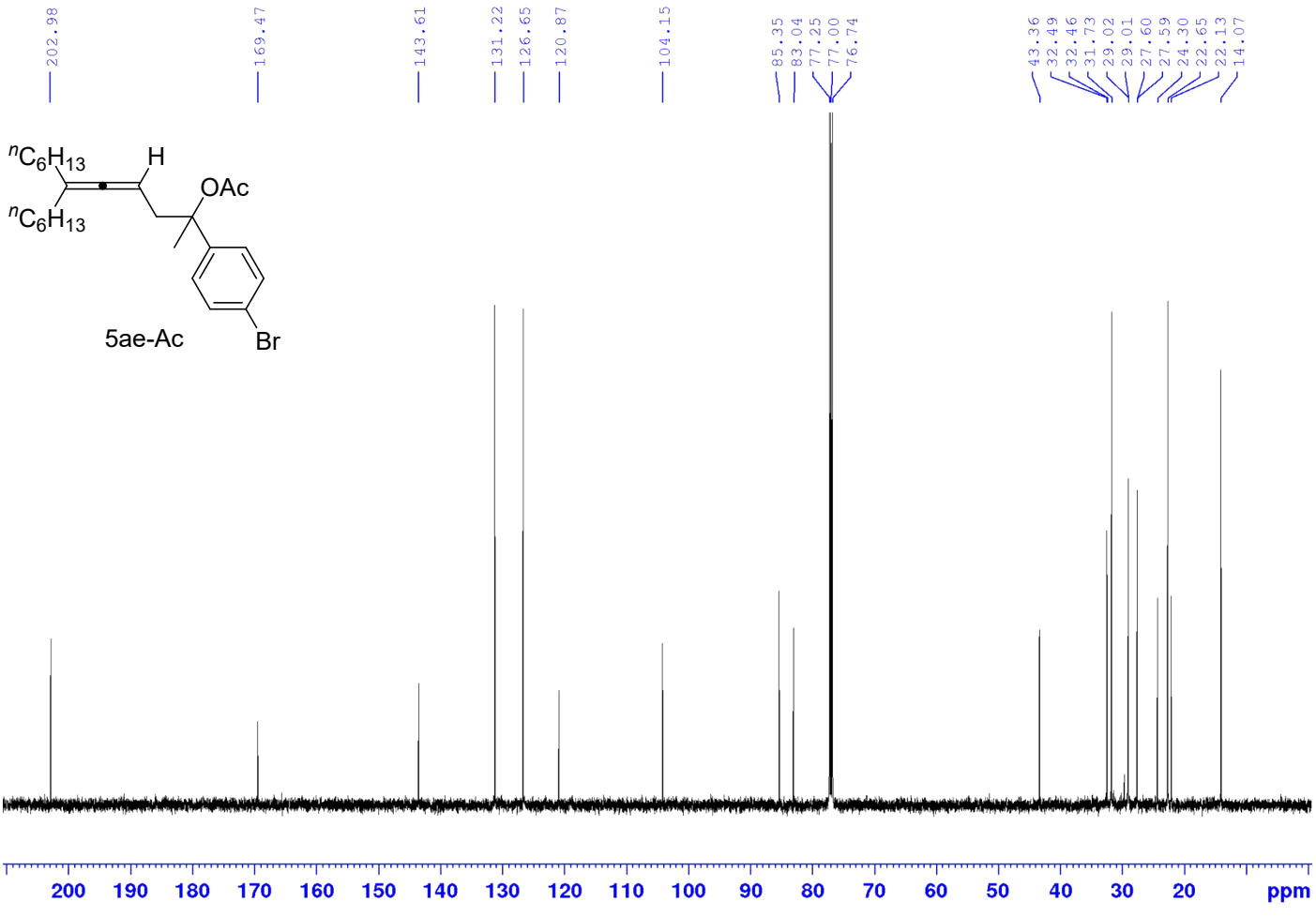
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.02
2.15
1.00
2.05
3.11
7.12
16.77
6.18

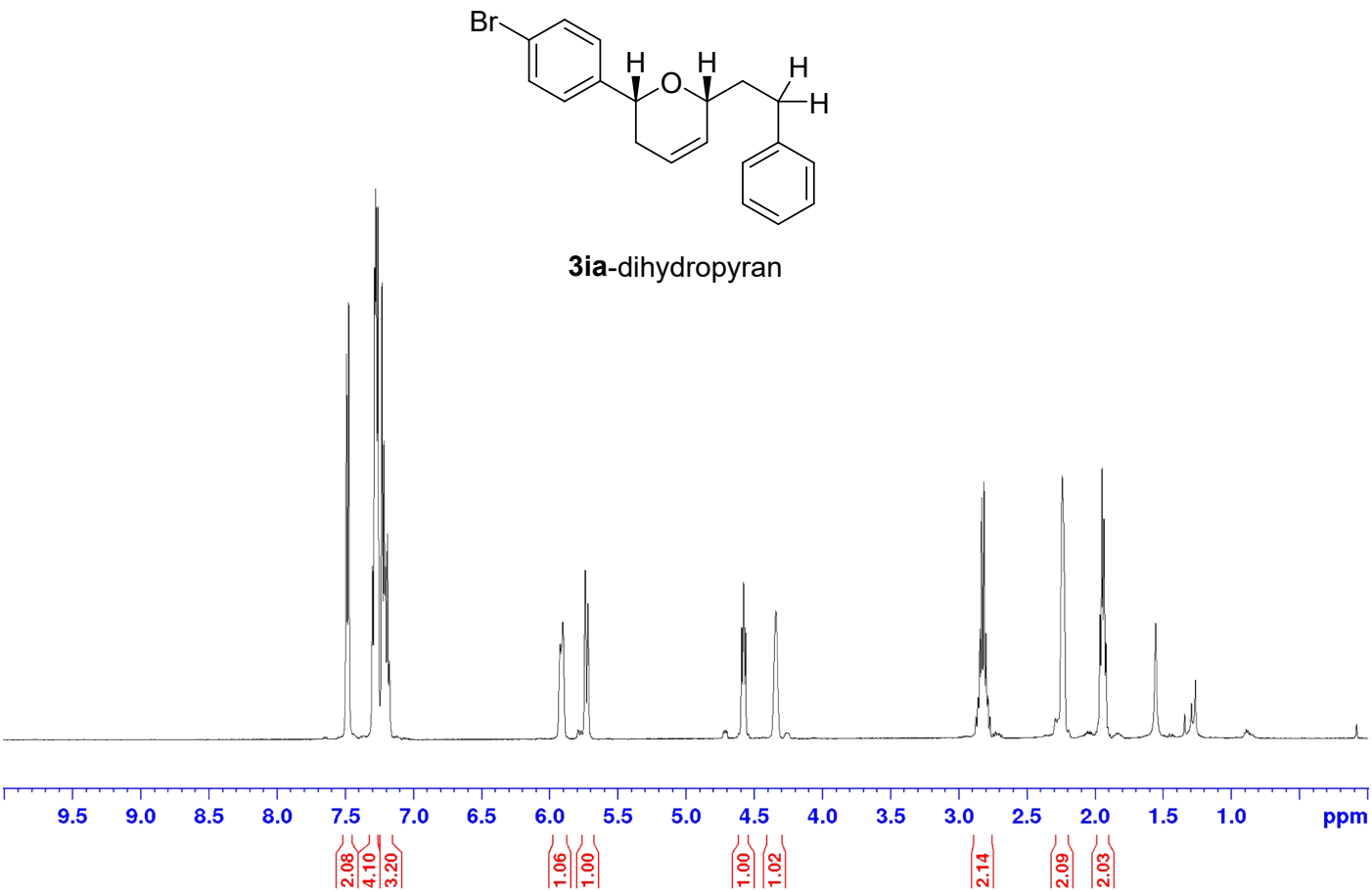

202.96
169.52
143.07
132.72
128.27
126.30
104.15
85.38
83.02
77.25
77.00
76.74
43.43
32.50
32.47
31.73
29.03
29.02
27.61
27.59
24.33
22.66
22.16
14.08
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

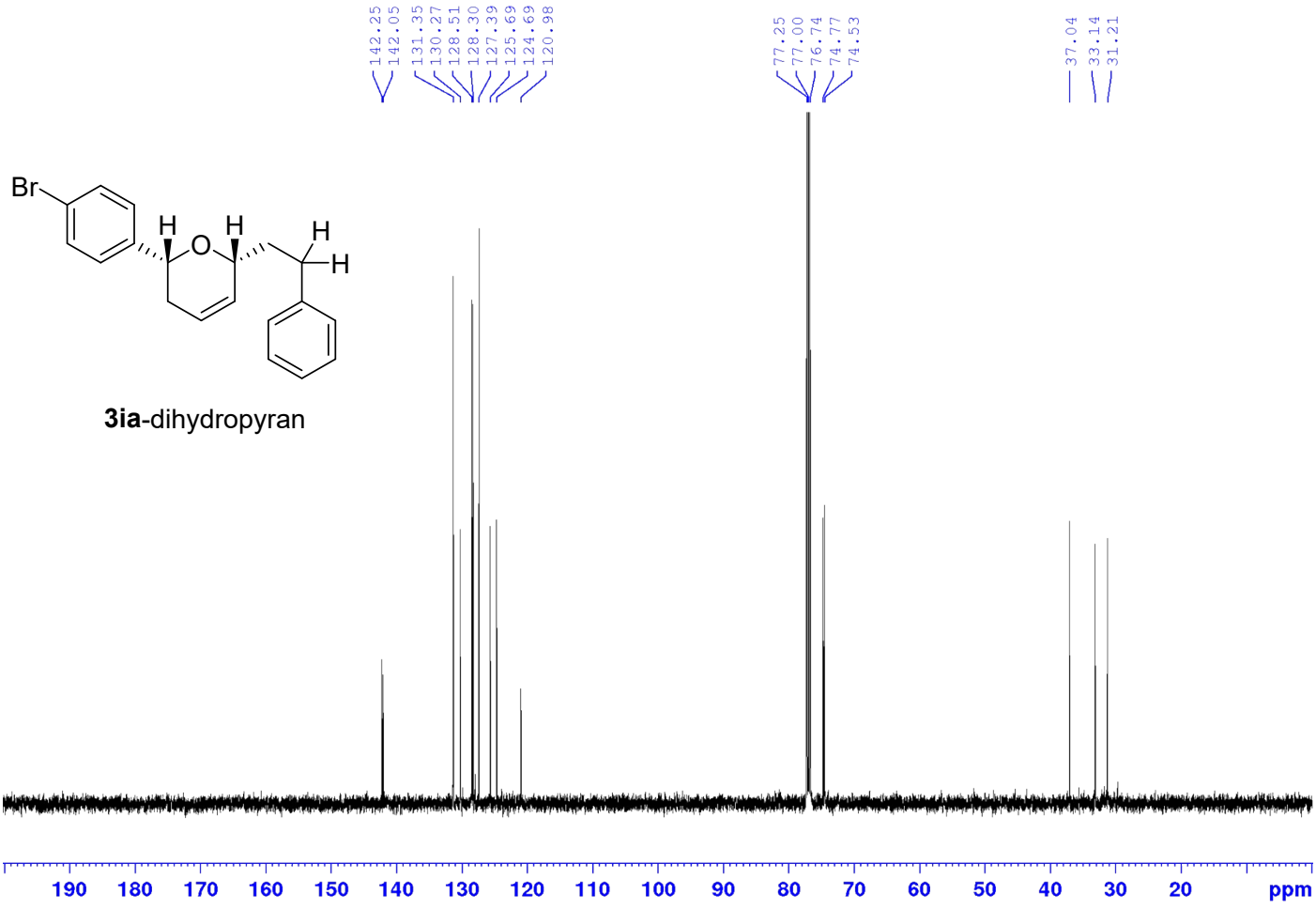
^{n}C$_6$H$_{13}$
H
OAc
^{n}C$_6$H$_{13}$
Cl

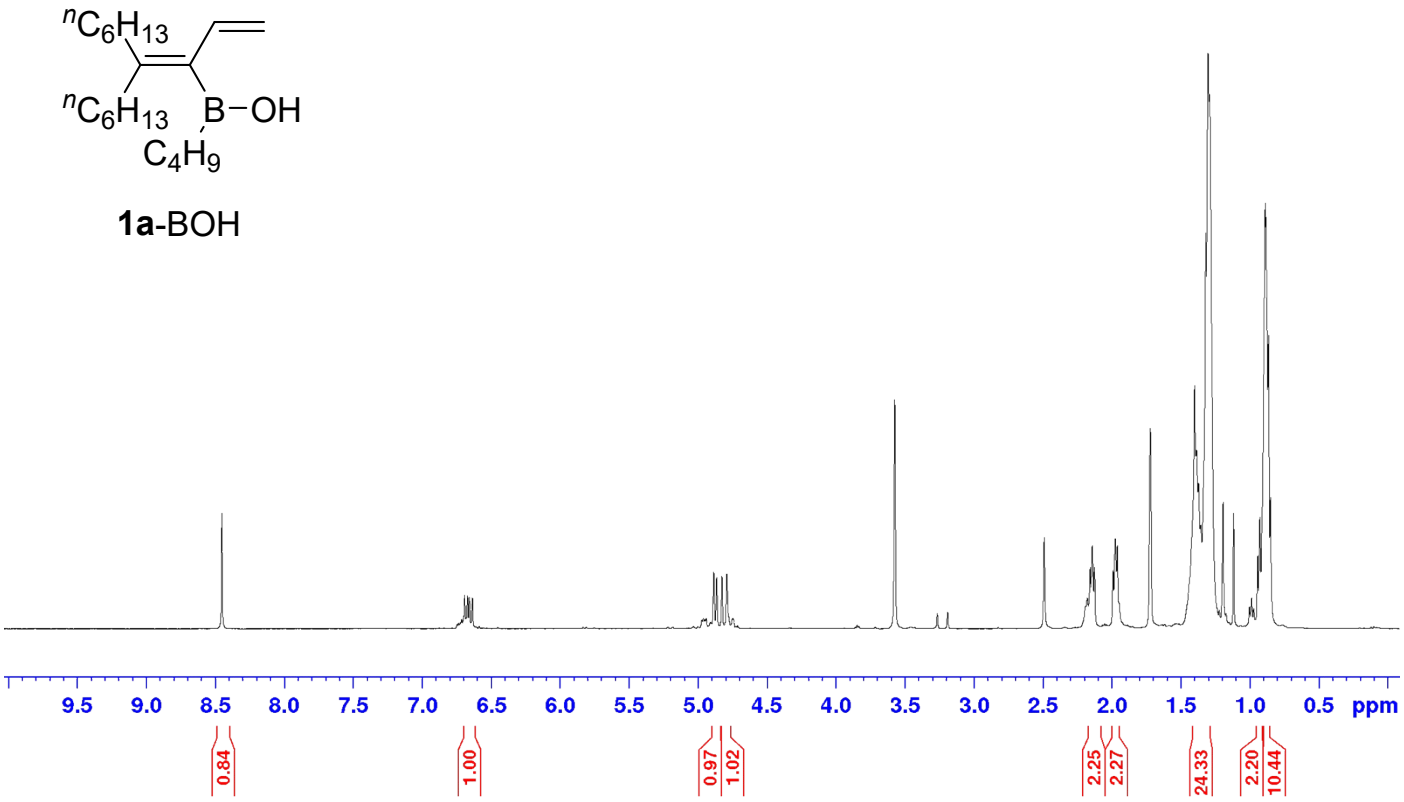
5ad-Ac

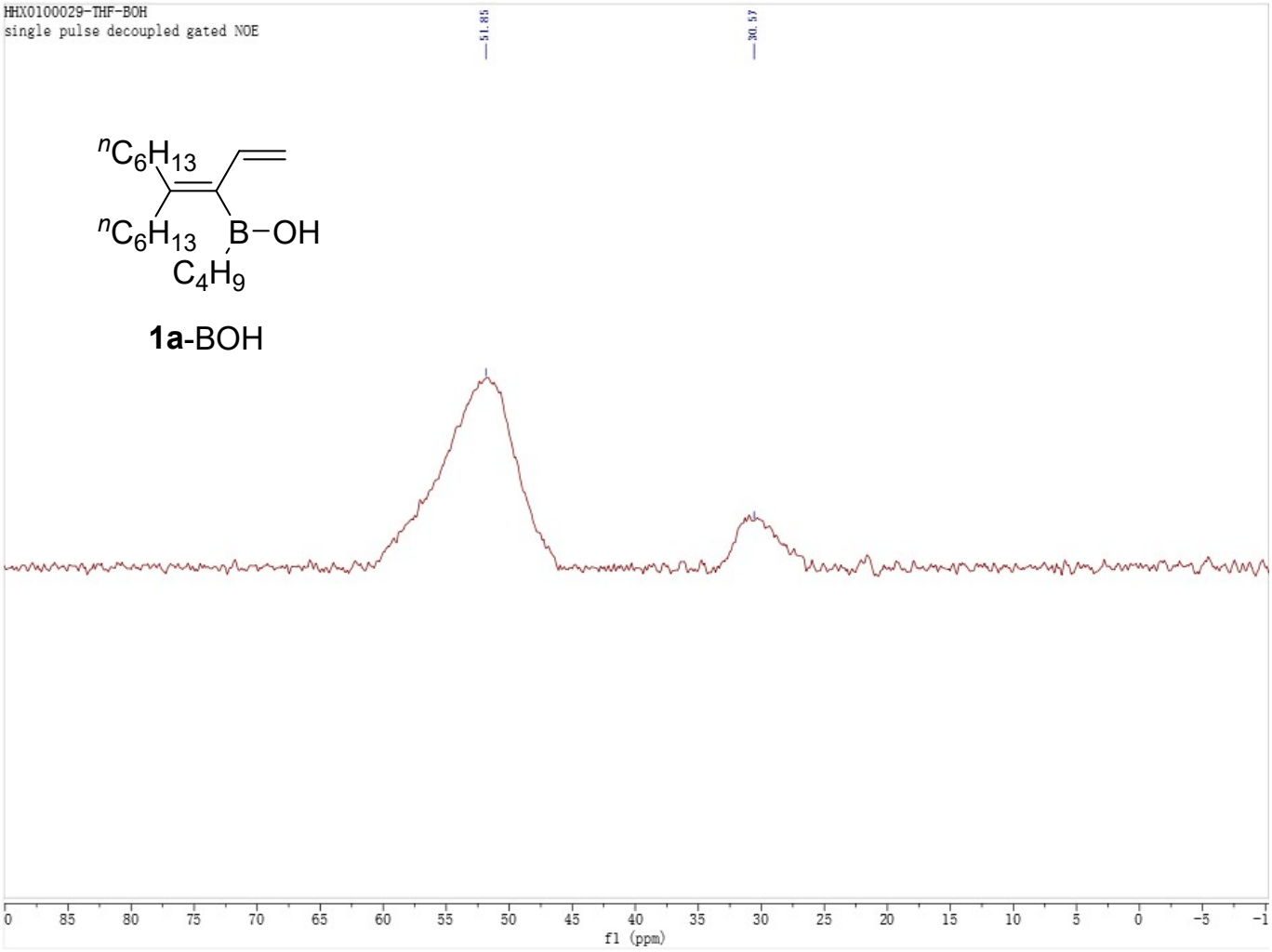

^{n}C$_6$H$_{13}$
H
OAc
^{n}C$_6$H$_{13}$
5ae-Ac
Br
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.05
1.01
2.05
3.05
7.03
16.73
6.26

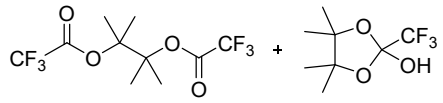

202.98
169.47
143.61
131.22
126.65
120.87
104.15
85.35
83.04
77.25
77.00
76.74
43.36
32.49
32.46
31.73
29.02
29.01
27.60
27.59
24.30
22.65
22.13
14.07
^{n}C$_6$H$_{13}$
H
OAc
^{n}C$_6$H$_{13}$
5ae-Ac
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


Br
H
O
H
H
H
3ia-dihydropyran
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
2.08
4.10
3.20
1.06
1.00
1.00
1.02
2.14
2.09
2.03


142.25
142.05
131.35
130.27
128.51
128.30
127.39
125.69
124.69
120.98
77.25
77.00
76.74
74.77
74.53
37.04
33.14
31.21
Br
H
O
H
H
H
3ia-dihydropyran
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

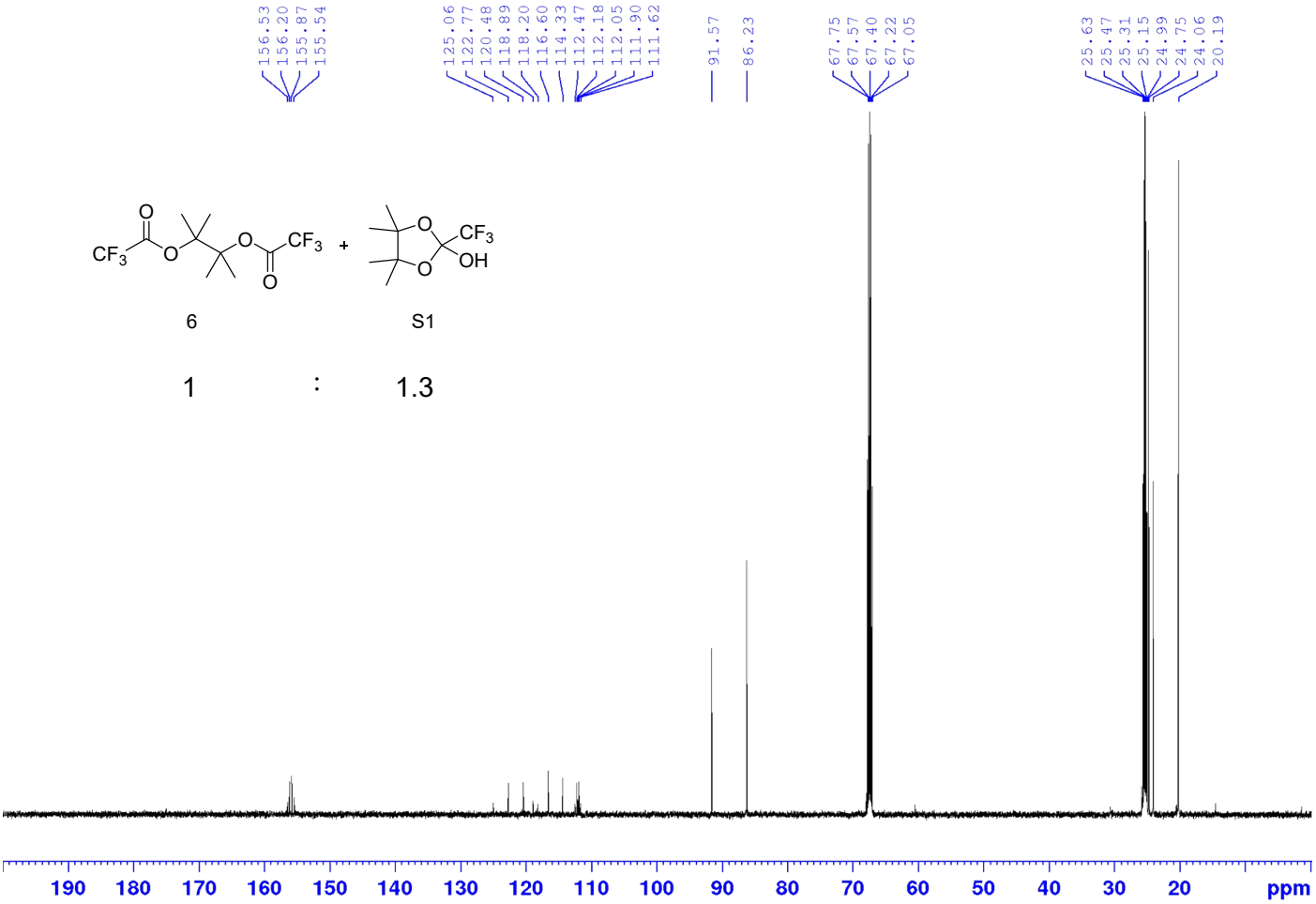

^{n}C$_6$H$_{13}$
^{n}C$_6$H$_{13}$
B−OH
C$_4$H$_9$
1a-BOH
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.84
1.00
0.97
1.02
2.25
2.27
24.33
2.20
10.44


HHX0100029-THF-BOH
single pulse decoupled gated NOE
51.85
30.57
^{n}C$_6$H$_{13}$
^{n}C$_6$H$_{13}$
B−OH
C$_4$H$_9$
1a-BOH
f1 (ppm)



6 S1

1 : 1.3



6 S1

1 : 1.3