Supporting information

Cobalt catalyzed hydroboration of alkenes, aldehydes, and ketones

Sem Raj Tamang, Deepika Bedi, Sara Shafiei-Haghighi, Cecilia R. Smith,
Christian Crawford, and Michael Findlater*

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX-79409

Contents

1. General Information:..... 3
2. Hydroboration of alkenes..... 4
2.1. Table S1: Optimization for hydroboration of alkenes..... 4
2.2 General procedure for hydroboration of alkenes..... 7
2.3 Spectral data for branched and linear boronate esters..... 7
3 Hydroboration of Aldehydes and Ketones..... 14
3.1. Table S3: Optimization for hydroboration of aldehydes and ketones..... 14
3.2 General procedure for hydroboration of aldehydes..... 15
3.3 General procedure for hydroboration of ketones..... 15
3.4 General procedure for chemoselective catalytic hydroboration..... 15
3.5 General procedure for competitive chemoselective hydroboration of aldehydes..... 15
3.6 General procedure for competitive chemoselective hydroboration of ketones..... 16
3.7 General procedure for catalytic intramolecular hydroboration..... 16
3.8 Spectral data for 1° alcohols inferred from reaction mixture..... 17
3.9 Spectral data for 2° alcohols inferred from reaction mixture..... 19
4. ^{1}H, ^{13}C and GC-MS of alkene hydroboration product..... 22
5. ^{11}B, ^{1}H and ^{13}C NMR of 1º alcohol..... 64
6. ^{11}B, ^{1}H and ^{13}C NMR of 2º alcohols..... 92
7. ^{1}H NMR for Chemoselective experiments..... 112
8. Deuterium labelling experiments..... 116
8.1. ^{11}B and ^{1}H NMR of synthesized DBpin..... 116

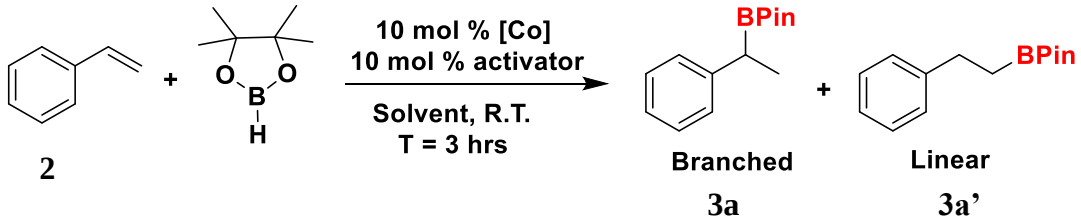
8.2 General procedure for deuterium labelling experiment 118
8.2.1 Hydroboration with THF-d_8 118
8.2.2 Hydroboration with styrene-d_8 122
8.2.3 Hydroboration with DBpin 126
9. GC-MS spectra of reaction mixtures containing 1º and 2º alcohol 130
10 References 147

1. General Information:

All reactions were performed in oven dried apparatus under the atmosphere of Argon. All reagents were purchased from commercial vendors and were used as received without any purification or drying. THF was distilled using sodium and benzophenone and stored over activated molecular sieves (4 Å) prior to usage. DBPin was synthesized according to the reported procedure.[1] ^{1}H, $^{13}C\{^{1}H\}$ and ^{11}B NMR spectra were recorded on a Jeol 400 MHz spectrometer at 300K unless otherwise noted. ^{1}H NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 7.26 ppm) and ^{13}C NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 77.16 ppm). Coupling constants *J* are reported in Hz. NMR multiplicities are as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br,s = broad singlet. MS data were acquired using Thermo Scientific™ ISQ™ Single Quadrupole system.

2. Hydroboration of alkenes

2.1. Table S1: Optimization for hydroboration of alkenes

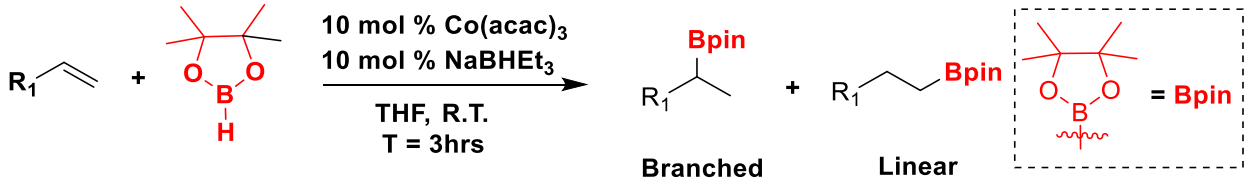


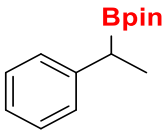
2 **3a** **3a'**

Entry	[Co]	Activator	Solvent	Yield (%)	3a:3a'
1	$Co(acac)_3$	$NaHBEt_3$	THF	66	75:25
2	$Co(acac)_3$	$NaHBEt_3$	Cyclohexane	16	65:35
3	$Co(acac)_3$	$NaBHEt_3$	neat	58	58:42
4	$Co(acac)_3$	-	THF	0	0
5	-	$NaBHEt_3$	THF	6	72: 28
6	$CoCl_2$	$NaBHEt_3$	THF	0	0
7	$Co(acac)_2$	$NaBHEt_3$	THF	56	81:19
8	$Co(PhCOOH)_2$	$NaBHEt_3$	THF	36	56:44
10	-	-	THF	0	0

* Yields and ratio of the regioisomers determined by GC-MS.

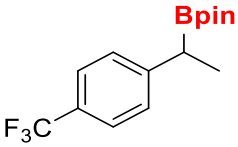
2.2 Scheme S1. Initial substrate screening with $Co(acac)_3$ (**1**)/ $NaHBEt_3$ combination





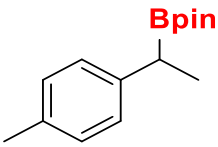
52 %

Ratio 73: 24



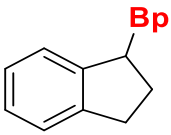
72 %

85: 15

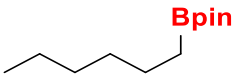


60 %

82: 18



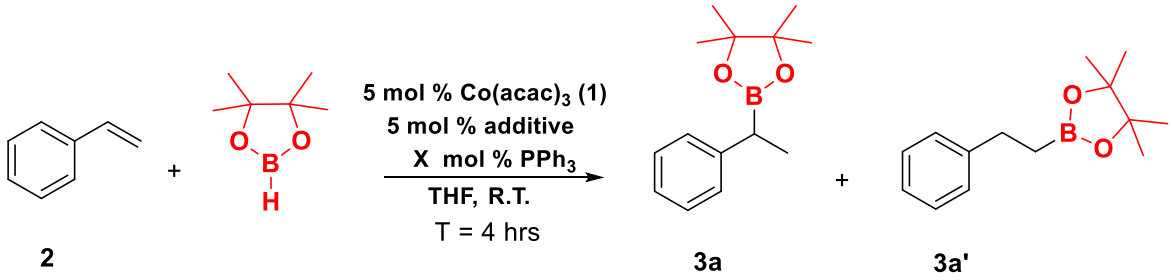
< 5 %



> 95 % selectivity

* Ratio of regioisomers determined by ^1H NMR.

2.3 Table S2: Optimization of PPh_3 with different additives



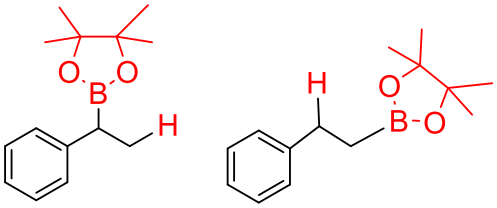
Entry	Additive	PPh_3 (mol %)	Yield (%)	Ratio (B:L)[a]
1	$NaHBEt_3$	5	55	87 : 13
2	$NaHBEt_3$	10	79	94 : 6
3	$NaHBEt_3$	15	88	93 : 7
4	NaO^tBu	5	76	94 : 6
5	NaO^tBu	10	90	94 : 6
6	NaO^tBu	15	84	94: 6

[a] Ratio of regioisomers determined by ^1H NMR.

2.2 General procedure for hydroboration of alkenes

An oven dried scintillation vial was charged with Co(acac)3 (17.8 mg, 0.05 mmol), NaO^{t}Bu (4.8 mg, 0.05 mmol), THF (1 mL) and magnetic stir bar. The reaction mixture was allowed to stir for ~ 1-2 minutes, and a change of color from dark green to purple was observed. PPh_3 (26 mg, 0.10 mmol), HBpin (153.6 mg, 174 µL, 1.2 mmol), styrene (104 mg, 114.8 µL, 1.0 mmol) was then added and the reaction mixture was then stirred inside the glove box for 4 hrs at room temperature. The reaction was quenched by opening the vial to air and adding DI H_2O (5 mL) and diethyl ether (10 mL). The organic phase was extracted, concentrated under vacuo and passed through a short pad of silica using hexanes and ethyl acetate as the eluent (95: 5). In all cases, ^{1}H NMR and GC-MS were used to determine the ratio of the regioisomers.

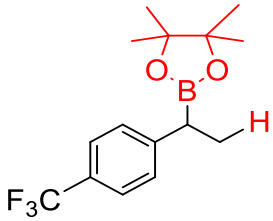
2.3 Spectral data for branched and linear boronate esters



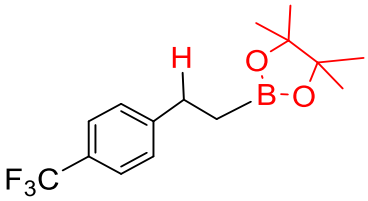
3a **3a'**

4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (3a)[2]: The two regioisomers were isolated as colorless oil (207 mg, 90%). δ_H (400 MHz; $CDCl_3$): 7.18-7.11 (4H, m), 7.05-7.01 (1H, m), 2.33 (1H, q, *J* = 7.6 Hz), 1.23 (3H, d, *J* = 7.6 Hz), 1.20 (12H, d, *J* = 5.2 Hz). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 145.0, 128.4, 127.9, 125.2, 83.4, 24.7, 24.7, 17.2. GC-MS (m/z): 232.14.

4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (3a')[3]: The presence of this material was identified by a proton resonance at 2.65 (2H, t, *J* = 8.4 Hz). The remaining proton resonances were not assigned since they are obscured by those of the major regioisomer. The amount of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane formed was too low for detection in the ^{13}C NMR spectrum recorded.



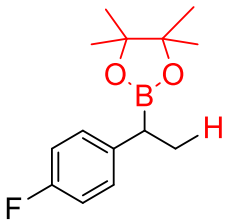
3b



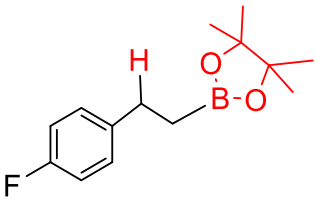
3b'

4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)ethyl)-1,3,2-dioxaborolane (3b)[4]: The two regioisomers were isolated as a white solid (287 mg, 95%). δ_H (400 MHz; $CDCl_3$): 7.52 (2H, d, *J* = 7.7 Hz), 7.32 (2H, d, *J* = 8.0 Hz), 2.51 (1H, q, *J* = 7.3 Hz), 1.35 (3H, d, *J* = 7.4 Hz). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 149.3, 128.1, 125.3 (q, *J* = 3.0 Hz), 83.7 Hz, 24.8, 24.7, 16.9. GC-MS (m/z): 300.19.

4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenethyl)-1,3,2-dioxaborolane (3b')[3]: The presence of this material was identified by a proton resonance at 2.81 (2H, t, *J* = 8.6 Hz). The remaining proton resonances were not assigned since they are obscured by those of the major regioisomer. The amount of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane formed was too low for detection in the ^{13}C NMR spectrum recorded.



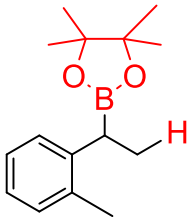
3c



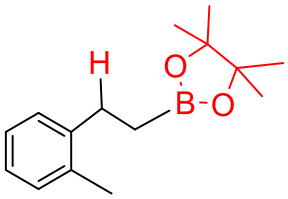
3c'

2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)[2]: The two regioisomers were isolated as colorless oil (245 mg, 98%). δ_H (400 MHz; $CDCl_3$): 7.18-7.14 (2H, m), 6.96-6.92 (2H, m), 2.41 (1H, q, *J* = 7.6 Hz), 1.31 (3H, d, *J* = 7.6 Hz), 1.21 (12H, d, *J* = 4.8 Hz). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 161.0 (d, $J_{C\text{-}F}$ = 243 Hz), 140.6 (d, $J_{C\text{-}F}$ = 2.7 Hz), 129.1 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21 Hz), 83.5, 24.8, 24.7, 17.4. GC-MS (m/z): 250.19.

2-(4-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c')[3]: The presence of this material was identified by a proton resonance at 2.72 (2H, t, *J* = 8.0 Hz). The remaining proton resonances were not assigned since they are obscured by those of the major regioisomer. The amount of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane formed was too low for detection in the ^{13}C NMR spectrum recorded. GC-MS (m/z): 250.18.



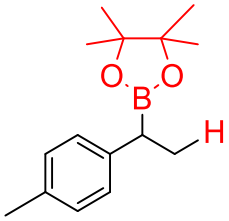
3d



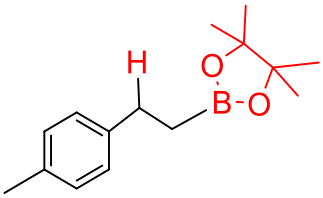
3d'

4,4,5,5-tetramethyl-2-(1-(o-tolyl)ethyl)-1,3,2-dioxaborolane (3d)[2]: The two regioisomers were isolated as colorless oil (220 mg, 90%). δ_H (400 MHz; $CDCl_3$): 7.26-7.04 (4H, m), 2.59 (1H, q, *J* = 7.0 Hz), 2.32 (3H, s), 1.32 (3H, d, *J* = 6.6 Hz), 1.22 (12 H, dd, *J* = 2.3, 7.7 Hz). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 143.5, 135.7, 130.1, 127.2, 126.2, 125.1, 83.4, 24.8, 24.7, 20.0, 16.5. GC-MS(m/z): 246.22.

4,4,5,5-tetramethyl-2-(2-methylphenethyl)-1,3,2-dioxaborolane (3d')[4]: δ_H (400 MHz; $CDCl_3$): 7.26-7.04 (3H, m), 2.72 (2H, t, *J* = 7.2 Hz), 2.32 (3H, s), 1.24 (12H, d, *J* = 2.4), 1.11 (2H, t, *J* = 7.6 Hz). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 142.6, 135.9, 130.1, 128.2, 126.0,125.7, 83.2, 27.3, 25.0, 19.4. GC-MS (m/z): 246.20.



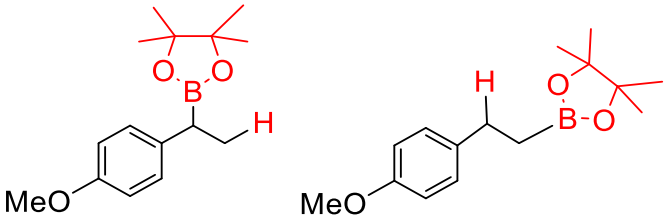
3e



3e'

4,4,5,5-tetramethyl-2-(1-(p-tolyl)ethyl)-1,3,2-dioxaborolane (3e)[5] : The two regioisomers were isolated as colorless oil (221 mg, 90%). δ_H (400 MHz; $CDCl_3$): 7.13-7.05 (4H, m), 2.39 (1H, q, *J* = 7.5 Hz), 2.30 (3H, s), 1.31 (3H, d, *J* = 7.5 Hz), 1.21 (12H, d, *J* = 5.2 Hz). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 142.0, 134.5, 129.2, 127.8, 83.4, 24.8, 24.7, 21.1, 17.4. GC-MS (m/z): 246.19

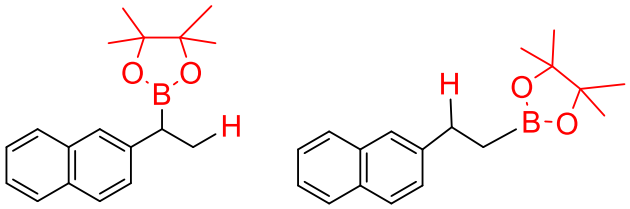
4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (3e')[6]: The presence of this material was identified by a single proton resonance at 2.71 (2H, t, *J* = 8.2 Hz). The remaining proton resonances were not assigned since they are obscured by those of the major regioisomer. The amount of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane formed was too low for detection in the ^{13}C NMR spectrum recorded. GC-MS (m/z): 246.17



3f **3f'**

2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)[2]: The two regioisomers were isolated as a pale yellow oil (250 mg, 95%). δ_H (400 MHz; $CDCl_3$): 7.14 (2H, d, *J* = 8.8 Hz), 6.81 (2H, d, *J* = 8.4 Hz), 3.77 (3H, s), 2.37 (1H, q, *J* = 7.5 Hz), 1.29 (3H, d, *J* = 7.5 Hz), 1.20 (12H, d, *J* = 5.2 Hz). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 157.3, 137.1, 128.7, 113.9, 83.3, 55.3, 24.7, 24.7, 17.5. GC-MS (m/z): 262.21.

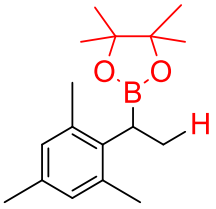
2-(4-methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f')[3]: The presence of this material was identified by a single proton resonance at 2.69 (2H, t, *J* = 8.1 Hz). The remaining proton resonances were not assigned since they are obscured by those of the major regioisomer. The amount of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane formed was too low for detection in the ^{13}C NMR spectrum recorded. GC-MS (m/z): 262.20.



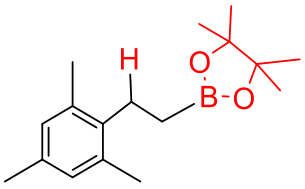
3g **3g'**

4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane(3g)[2]: The two regioisomers were isolated as a white solid (221mg, 90%). δ_H (400 MHz; $CDCl_3$): 7.79-7.74 (3H, m), 7.64 (1H, s), 7.45-7.36 (3H, m), 2.61 (1H, q, *J* = 7.4 Hz), 1.43 (3H, d, *J* = 8.0 Hz), 1.21 (12H, d, *J* = 4 Hz). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 142.7, 134.0, 131.8, 127.8, 127.6, 127.6, 127.4, 125.8, 125.4, 125.0, 83.5, 24.8, 24.7, 17.0. GC-MS (m/z): 282.25.

4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (3g')[4]: The presence of this material was identified by a single proton resonance at 2.92 (2H, t, *J* = 8.1 Hz). The remaining proton resonances were not assigned since they are obscured by those of the major regioisomer. The amount of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane formed was too low for detection in the ^{13}C NMR spectrum recorded. GC-MS (m/z): 282.23.



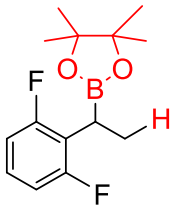
3h



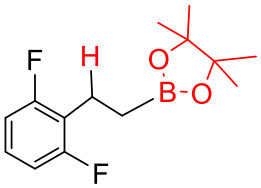
3h'

2-(1-mesitylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)[2]: The two regioisomers were isolated as colorless oil (244 mg, 89%). δ_H (400 MHz; $CDCl_3$): 6.8 (2H, s), 2.62-2.59 (1H, q), 2.28 (6H, s), 2.22 (3H, s), 1.27 (12 H, s), 1.11-1.07 (2H, m). GC-MS (m/z): 274.24

4,4,5,5-tetramethyl-2-(2,4,6-trimethylphenethyl)-1,3,2-dioxaborolane (3h')[3]: δ_H (400 MHz; $CDCl_3$): 6.8 (2H, s), 2.69-2.64 (t, 2H, *J* = 8.8 Hz), 2.29 (6H, s), 2.24 (3H, s), 1.27 (12H, s), 0.97-0.93 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): 138.6, 135.7, 134.8, 128.9, 83.2, 25.0, 23.4, 20.9, 19.8. GC-MS (m/z): 274.24.



3i

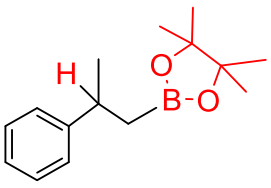


3i'

2-(1-(2,6-difluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i): The two regioisomers were isolated as pale yellow oil (137 mg, 51%). δ_H (400 MHz; $CDCl_3$): 7.12-7.04 (1H, m), 6.84-6.77 (2H, m), 2.67 (1H, q, *J* = 7.6 Hz), 1.27 (3H, d, *J* = 7.6 Hz), 1.23 (12H, s). GC-MS (m/z): 268.20

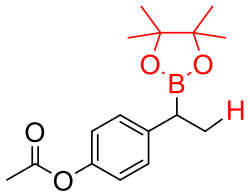
2-(2,6-difluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i'): δ_H (400 MHz; $CDCl_3$): 7.12-7.04 (1H, m), 6.84-6.77 (2H, m), 2.76 (2H, t, *J* = 8.3 Hz), 1.25 (12H, d, *J* = 6.8 Hz), 1.10 (2H, t, *J* = 8.4 Hz). GC-MS (m/z): 268.23

^{13}C NMR (101 MHz, $CDCl_3$, ppm): The assignment of peaks was difficult but two distinct peaks were observed at 162.5 and 160.1 which confirmed the formation of both the isomers **3i** and **3i'**

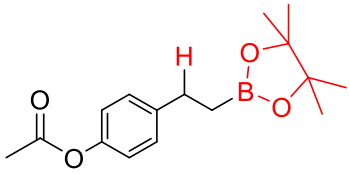


3j'

4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (3j')[3]: The product was isolated as a colorless oil (100mg, 40%). δ_H (400 MHz, $CDCl_3$): 7.27-7.22 (4H, m), 7.15-7.12 (1H, m), 3.05-2.99 (1H, m), 1.26 (3H, d, J = 6.8 Hz), 1.16-1.13 (14H, m). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): 149.3, 128.3, 126.8, 125.8, 83.1, 36.0, 25.0, 24.9, 24.8. GC-MS (m/z): 246.20.



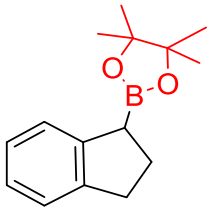
3k



3k'

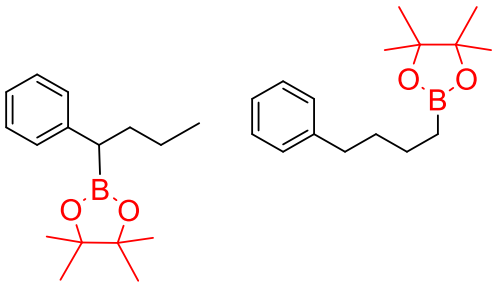
4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate(3k): The two regioisomers were isolated as pale yellow oil (111 mg, 38%).[2] δ_H (400 MHz; $CDCl_3$): 7.22-7.20 (2H, m), 6.98-6.96 (2H, m), 2.43 (1H, q, *J* = 7.4 Hz), 2.28 (3H, s), 1.31 (3H, d, *J* = 7.5 Hz), 1.20 (12H, d, *J* = 4.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): 169.8, 148.3, 142.6, 128.7, 121.2, 83.5, 24.7, 24.7, 21.3, 17.2. GC-MS (m/z): 290.22.

4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate(3k')[4]: The presence of this material was identified by a proton resonance at 2.73 (2H, t, *J* = 8.1 Hz). The remaining proton resonances were not assigned since they are obscured by those of the major regioisomer. ^{13}C NMR (101 MHz, $CDCl_3$, ppm): 148.6, 142.1, 129.0, 121.2, 83.3, 29.4, 24.9. (The remaining peaks were not observed). GC-MS (m/z): 290.19.



3l

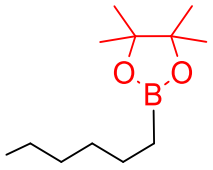
2-(2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)[7]: The compound was isolated as a pale-yellow oil (127 mg, 52%). δ_H (400 MHz; $CDCl_3$):7.32-7.26 (1H, m), 7.22-7.20 (1H, m), 7.13-7.07 (2H, m), 2.98-2.88 (2H, m), 2.73 (1H, t, *J* = 8.6 Hz), 2.27-2.18 (1H, m), 2.14-2.07 (1H, m), 1.25 (12H, d, *J* = 4.36). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): 145.2, 144.4, 126.1, 125.6, 124.5, 124.4, 83.4, 33.4, 28.0, 25.0, 24.8. GC-MS (m/z): 244.19



3m **3m'**

4,4,5,5-tetramethyl-2-(1-phenylbutyl)-1,3,2-dioxaborolane (3m)[7]: The two regioisomers were isolated as colorless oil (117 mg, 45%). δ_H (400 MHz; $CDCl_3$): 2.30 (1H, t, *J* = 8.0 Hz), 1.81-1.76 (1H, m), 1.66-1.58 (1H, m), 1.50-1.42 (2H, m), 1.18 (12 H, d, *J* = 7.2 Hz), 0.88 (3H, t, *J* = 7.6 Hz). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): 143.6, 128.5, 128.3, 125.2, 83.2, 34.9, 24.7, 24.7, 22.5, 14.3. GC-MS (m/z):260.23.

4,4,5,5-tetramethyl-2-(4-phenylbutyl)-1,3,2-dioxaborolane (3m')[7]: The presence of this material was identified by proton resonances at 2.59 (2H, t, *J* = 7.6 Hz) and 0.80 (3H, t, *J* = 7.6 Hz). The remaining proton resonances overlapped with those of the major regioisomer. ^{13}C NMR (101 MHz, $CDCl_3$, ppm): 143.0, 128.5, 128.3, 125.6, 83.0, 35.9, 34.3, 25.0, 24.0, 22.5, 14.3. GC-MS (m/z): 260.22.

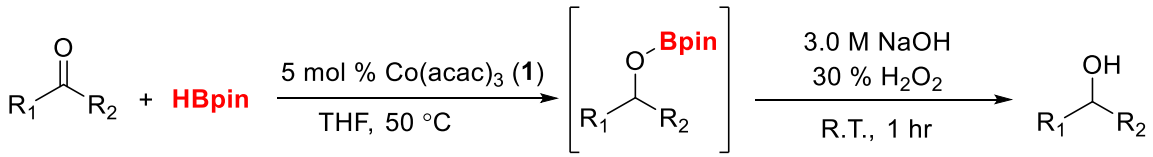


3n

2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n')[4]: The compound was isolated as a colorless oil (157 mg, 74%). The regiosisomer was identified using a proton resonance at 0.76 (2H, t, *J* = 7.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): 83.0, 32.2, 31.8, 25.0, 24.1, 22.7, 14.2. GC-MS (m/z): 212.20

3 Hydroboration of Aldehydes and Ketones

3.1. Table S3: Optimization for hydroboration of aldehydes and ketones



Entry	Substrate (1.0 mmol)	Catalyst	HBpin	Temp (°C)	Time (hrs)	Yield (%)[a]
1	4-methoxybenzaldehyde	5 mol %	1.2	R.T.	24	95
2	4-methoxybenzaldehyde	5 mol %	1.2	50	4	95
3	4-methoxybenzaldehyde	-	1.2	50	24	66
4	4-methylacetophenone	5 mol %	1.2	R.T.	24	60
5	4-methylacetophenone	5 mol %	1.2	50	4	95
6	4-methylacetophenone	-	1.2	50	24	16

[a] Yield based on ^{1}H NMR with mesitylene as internal standard

3.2 General procedure for hydroboration of aldehydes

An oven dried *J-Young* tube was charged with $Co(acac)_3$ (17.8 mg, 0.05 mmol), THF (0.7 mL), HBpin (153.6 mg, 1.2mmol, 174µL) and 4-methoxybenzaldehyde (136 mg, 1 mmol, 121.7 µL). The *J-Young* tube was then immersed into a preheated oil bath at 50 ºC. The progress of the reaction was monitored using ^{11}B NMR. After the complete consumption of HBpin, the reaction mixture was transferred to a scintillation vial and quenched by addition of diethyl ether (10 mL). Subsequently, 3 M NaOH (1 mL) and 30% H_2O_2 (1 mL) were added and allowed to stir for 1 h at room temperature. The organic layer was then extracted with diethyl ether (30 mL) and concentrated under reduced pressure. The yield of the product was calculated using mesitylene as the internal standard.

3.3 General procedure for hydroboration of ketones

An oven dried *J-Young* tube was charged with $Co(acac)_3$ (17.8 mg, 0.05 mmol), THF (0.7 mL), HBpin (153.6 mg, 1.2mmol, 174µL) and 4-methylacetophenone (134.2mg, 1 mmol, 133.6 µL). The *J-Young* tube was then immersed into a preheated oil bath at 50 ºC. The progress of the reaction was monitored using ^{11}B NMR. After the complete consumption of HBpin, the reaction mixture was transferred to a scintillation vial and quenched by addition of diethyl ether (10 mL). Subsequently, 3 M NaOH (1 mL) and 30% H_2O_2 (1 mL) were added and allowed to stir for 1 h at room temperature. The organic layer was then extracted with diethyl ether (30 mL) and concentrated under reduced pressure. The yield of the product was calculated using mesitylene as the internal standard.

3.4 General procedure for chemoselective catalytic hydroboration

An oven dried *J-Young* tube was charged with $Co(acac)_3$ (17.8 mg, 0.05 mmol), THF (0.5 mL), HBpin (128 mg, 1mmol, 145.1µL). A separate vial was then charged with benzaldehyde (106mg, 1 mmol, 101.5 µL), acetophenone (120 mg, 1 mmol, 116.5 µL), and THF (0.2 mL). The reaction mixture containing the substrates was then transferred to the J-Young tube, and it was placed on a preheated oil bath at 50 ºC. The progress of the reaction was monitored using ^{11}B NMR. After the complete consumption of HBpin, the reaction mixture was transferred to a scintillation vial and quenched by addition of diethyl ether (10 mL). Subsequently, 3 M NaOH (1 mL) and 30% H_2O_2 (1 mL) were added and allowed to stir for 1 h at room temperature. The organic layer was then extracted with diethyl ether (30 mL) and concentrated under reduced pressure. The yield of the product was calculated using mesitylene as the internal standard.

3.5 General procedure for competitive chemoselective hydroboration of aldehydes

An oven dried *J-Young* tube was charged with $Co(acac)_3$ (17.8 mg, 0.05 mmol), THF (0.5 mL), HBpin (128 mg, 1mmol, 145.1 µL). A separate vial was then charged with benzaldehyde (106 mg, 1 mmol, 101.5 µL), 4-methoxybenzaldehyde (136.mg, 1 mmol, 121.4 µL), and 4-fluorobenzaldehyde (124mg, 1 mmol, 107 µL), and THF (0.2 mL). The reaction mixture in the vial containing the substrates was then transferred to the *J-Young* tube, and placed on a preheated oil bath at 50 ºC. The progress of the reaction was monitored using ^{11}B NMR. After the complete consumption of 1 equivalent of HBpin after 1hr, an additional 1 equivalent of HBpin (128 mg, 1 mmol, 145.1 µL) was added and the reaction was heated for another 1hr. The reaction mixture was then then transferred to a 20 mL scintillation vial and quenched by addition of diethyl ether (10 mL) after 11B NMR showed the complete consumption of the 2^{nd} equivalence of HBpin.

Subsequently, 3 M NaOH (1 mL) and 30% H_2O_2 (1 mL) were added and allowed to stir for 1 h at room temperature. The organic layer was then extracted with diethyl ether (30 mL) and concentrated under reduced pressure. The yield of the product was calculated using mesitylene as the internal standard.

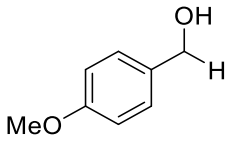
3.6 **General procedure for competitive chemoselective hydroboration of ketones**

An oven dried *J-Young* tube was charged with $Co(acac)_3$ (17.8 mg, 0.05 mmol), THF (0.5 mL), HBpin (128 mg, 1.0mmol, 145.1 µL). A separate vial was then charged with acetophenone (120.2 mg, 1 mmol, 116.7 µL), 4-methyl acetophenone (134.2.mg, 1 mmol, 133.7 µL), and 4-fluoroaceetophenone (138.1mg, 1 mmol, 121.4 µL), and THF (0.2 mL). The reaction mixture in the vial containing the substrates was then transferred to the *J-Young* tube, and placed on a preheated oil bath at 50 ºC. The progress of the reaction was monitored using ^{11}B NMR. After the complete consumption of 1 equivalent of HBpin after 1hr, an additional 1 equivalent of HBpin (128 mg, 1 mmol, 145.1 µL) was added and the reaction was heated for another 1hr. The reaction mixture was then transferred to a 20 mL scintillation vial and quenched by addition of diethyl ether (10 mL) after ^{11}B NMR showed the complete consumption of the 2nd equivalence of HBpin. Subsequently, 3 M NaOH (1 mL) and 30% H_2O_2 (1 mL) were added and allowed to stir for 1 h at room temperature. The organic layer was then extracted with diethyl ether (30 mL) and concentrated under reduced pressure. The yield of the product was calculated using mesitylene as the internal standard.

3.7 General procedure for catalytic intramolecular hydroboration

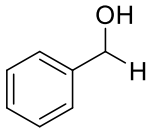
An oven dried *J-Young* tube was charged with $Co(acac)_3$ (17.8 mg, 0.05 mmol), THF (0.7 mL), HBpin (128 mg, 1.2mmol, 145.1µL) and 3-acetylbenzaldehyde(148.2mg, 1 mmol). The *J-Young* tube was then immersed into a preheated oil bath at 50 ºC. The progress of the reaction was monitored using ^{11}B NMR. After the complete consumption of HBpin, the reaction mixture was transferred to a scintillation vial and quenched by addition of diethyl ether (10 mL). Subsequently, 3 M NaOH (1 mL) and 30% H_2O_2 (1 mL) were added and allowed to stir for 1 h at room temperature. The organic layer was then extracted with diethyl ether (30 mL) and concentrated under reduced pressure. The yield of the product was calculated using mesitylene as the internal standard.

3.8 Spectral data for 1° alcohols inferred from reaction mixture



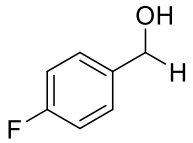
5a

4-methoxybenzyl Alcohol (5a)[8]: Yield: 95%. δ_H (400 MHz; $CDCl_3$): 3.66 (1H, br S), 3.73 (3H, S), 4.52 (2H, br S), 6.85 (2H, d, *J* = 8Hz), 7.24 (2H, d, *J* = 8 Hz). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 158.7, 133.0, 128.3, 113.5, 64.1, 54.8. GC-MS (m/z): 138.



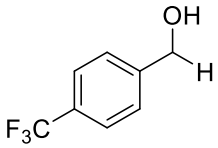
5b

Benzyl Alcohol (5b)[8]: Yield: 93%. δ_H (400 MHz; $CDCl_3$): 3.87 (1H, br S), 4.58 (2H, d, *J* = 4.0Hz), 7.22 – 7.28 (1H, m), 7.32 (4H, d, *J* = 4Hz). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 140.8, 128.2, 127.2, 126.8, 64.5. GC-MS (m/z): 108.10.



5c

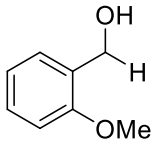
4-fluorobenzyl Alcohol (5c)[8]: Yield: 100%. δ_H (400 MHz; $CDCl_3$): 3.49 (1H, br S), 4.54 (2H, br S), 6.99 (2H, t, *J* = 8Hz), 7.26 (2H, t, *J* = 6 Hz). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 162 (d, $J_{C\text{-}F}$ = 246.4 Hz), 136.7, 128.5 (d, $J_{C\text{-}F}$ = 8.1 Hz), 114.9 (d, $J_{C\text{-}F}$ = 21 Hz), 63.8. GC-MS (m/z): 126.09.



5d

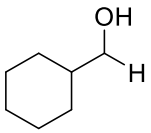
4-tri(fluoromethyl)benzyl Alcohol (5d)[9]: Yield: 99%. δ_H (400 MHz; $CDCl_3$): 4.00 (1H, br S), 4.65 (2H, d, *J* = 4 Hz), 7.40 (2H, d, *J* = 8 Hz), 7.56 (2H, d, *J* = 8 Hz). $^{13}C\{^1H\}$ NMR (101 MHz;

$CDCl_3$). 145.4, 129.6 (q, $J_{C\text{-}F}$ = 32.4 Hz), 126.9, 125.3 (q, $J_{C\text{-}F}$ = 3.0 Hz), 123.0, 63.8. GC-MS (m/z): 176.05.



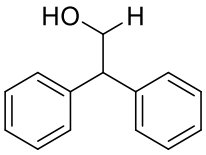
5e

2-methoxybenzyl Alcohol (5e)[8]: Yield: 99%. δ_H (400 MHz; $CDCl_3$): 3.03 (1H, br S), 3.80 (3H, S), 4.67 (2H, d, *J* = 4 Hz), 6.84 (1H, d, *J* = 8 Hz), 6.93 (1H, d, *J* = 8 Hz), 7.23-7.30 (2H, m). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 156.9, 128.9, 128.4, 128.2, 120.3, 109.8, 60.8, 54.8. GC-MS (m/z): 138.10.



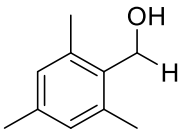
5f

Cyclohexylmethanol (5f)[8]: Yield: 96%. δ_H (400 MHz; $CDCl_3$): 0.83-0.93 (2H, m), 1.10-1.30 (4H, m), 1.31-1.51 (1H, m), 1.60-1.83 (5H, m), 3.32-3.45 (2H, m). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 68.6, 40.4, 29.5, 26.5, 25.8. GC-MS (m/z): 128.10.



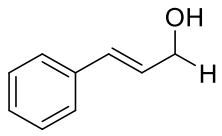
5g

2,2-diphenylethanol (5g)[8]: Yield: 97%. δ_H (400 MHz; $CDCl_3$): 1.73 (1H, br S), 4.12-4.20 (3H, m), 7.19-7.32 (10H, m). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$):141.4, 128.6, 128.2, 126.8, 66.0, 53.5. GC-MS (m/z): 198.13



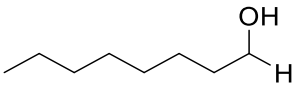
5h

Mesitylmethanol (5h)[8]: Yield:78%. δ_H (400 MHz; $CDCl_3$): 2.19 (1H, br S), 2.25 (3H, S), 2.35 (6H, S), 4.61 (2H, S), 6.83 (2H, S). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$):137.5, 137.1, 133.6, 128.9, 58.7, 20.8, 19.1. GC-MS (m/z): 150.13.



5i

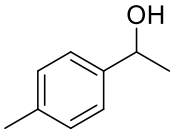
3-phenyl-2-propene-1-ol (5i)[8]: Yield: 98%. δ_H (400 MHz; $CDCl_3$): 3.10 (1H, br S), 4.26 (2H, d, *J* = 4 Hz), 6.28-6.34 (1H, m), 6.56 (1H, d, *J* = 12 Hz), 7.20-7.23 (1H, m), 7.28 (2H, t, *J* = 8 Hz), 7.34 (2H, d, *J* = 8 Hz). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$):136.6, 130.8, 128.5, 127.5, 126.3, 63.3. GC-MS (m/z): 134.10.



5j

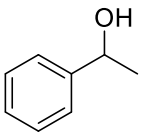
***n*-octanol (5j): Yield:** 62%. Characterized by GC-MS (See **Figure S107**)

3.9 Spectral data for 2° alcohols inferred from reaction mixture



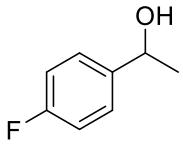
5k

1-(4-Methylphenyl)ethanol (5k)[8]: Yield: 95%. δ_H (400 MHz; $CDCl_3$): 7.22 (d, *J* = 8.0 Hz, 2H) 7.12 (d, *J* = 8.0 Hz, 2H), 4.77 (q, *J* = 4.0 Hz, 1H), 2.80 (br.s, 1H), 2.33(s, 3H), 1.43(d. *J* = 8.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 143.04, 136.68, 128.96, 125.39, 69.81, 25.09, 21.01. ^{11}B NMR (128 MHz, $CDCl_3$): 24.23. GC-MS (m/z): 136.06.



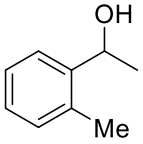
5l

1-Phenylethanol (5l)[8]: Yield: 88%. δ_H (400 MHz; $CDCl_3$): 7.32-7.23 (m, 5H), 4.80 (q, *J* = 4.0 Hz, 1H), 3.125 (d, *J* = 2.88 Hz, 1H), 1.44(d, *J* = 8.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 146.09, 128.51, 128.96, 127.42, 125.57, 70.24, 25.28. ^{11}B NMR (128 MHz, $CDCl_3$): 23.07. GC-MS (m/z): 122.11



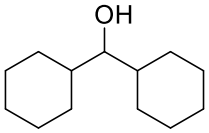
5m

1-(4-Fluorophenyl)ethanol (5m)[8]: Yield: 94%. δ_H (400 MHz; $CDCl_3$): 7.28 (t, *J* = 8.0 Hz, 2H) 6.99 (t, *J* = 8.0 Hz, 2H), 4.79 (q, *J* = 8.0 Hz, 1H), 3.31 (br, s, 1H), 1.41(d. *J* = 4.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 162.09 (d, J_{C-F} = 245.43 Hz), 141.88, 127.18 (d, J_{C-F} = 8.08 Hz), 115.16 (d, J_{C-F} = 22.22 Hz), 69.50, 25.34. ^{11}B NMR (128 MHz, $CDCl_3$): 24.49. GC-MS (m/z): 140.10



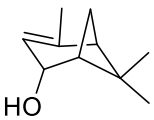
5n

1-(*O*-tolyl)ethanol (5n)[8]: Yield: 78%. δ_H (400 MHz; $CDCl_3$): 7.48 (d, *J* = 8.0 Hz, 1H) 7.22-7.08 (m, 3H), 5.03 (q, *J* = 4.0 Hz, 1H), 2.81 (br.s, 1H), 2.30(s, 3H), 1.41(m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 144.18, 134.19, 130.36, 127.10, 126.41, 124.79, 66.59, 24.07, 19.0. ^{11}B NMR (128 MHz, $CDCl_3$): 23.16. GC-MS (m/z): 136.05



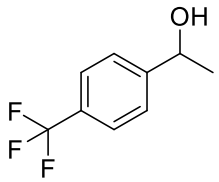
5o

Dicyclohexylmethanol (5o)[8]: Yield: 66%. δ_H (400 MHz; $CDCl_3$): 3.03 (br, s, 1H), 1.91-0.94 (m, 22H). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 80.09, 39.79, 29.91, 27.30, 26.49, 26.43, 26.12. ^{11}B NMR (128 MHz, $CDCl_3$): 22.12. GC-MS (m/z): [M-C_6H_{11}] = 113.15



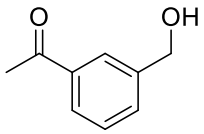
5p

Verbenol (5p)[10]: Yield: 24%. δ_H (400 MHz; $CDCl_3$): 5.34 (s, 1H), 4.44 (s, 1H), 1.98 (s, 1H), 1.71 (s, 3H), 1.47 (s, 1H), 1.35(d, *J* = 8.0 Hz, 3H), 1.31(m, 1H), 1.09 (s, 3H)
26.12. ^{11}B NMR (128 MHz, $CDCl_3$): 23.81. GC-MS (m/z): 152.19



5q

1-(4-Trifluoromethyl)phenyl)ethanol (5q)[8]: Yield: 98%. δ_H (400 MHz; $CDCl_3$): 7.56(d, *J* = 8.0 Hz, 2H) 7.44 (d, *J* = 8.0 Hz, 2H), 4.89 (q, *J* = 4.0 Hz, 1H), 2.68 (d, *J* = 4.0 Hz 1H), 1.45(d. *J* = 8.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 149.88, 129.60 (d, J_{C-F} = 33.3 Hz), 125.74, 125.61, 125.47 (d, J_{C-F} = 4.0 Hz), 69.76, 24.82. ^{11}B NMR (128 MHz, $CDCl_3$): 23.86. GC-MS (m/z): 190.11



3-Acetylbenzyl alcohol[11] (7): Yield: 90%. δ_H (400 MHz; $CDCl_3$): 7.90 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 4.68 (br, s, 1H), 3.84 (br,s, 1H), 2.55(s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 198.90, 141.90, 137.77, 131.76, 128.79, 127.47, 127.01, 64.34, 26.73. ^{11}B NMR (128 MHz, $CDCl_3$): 21.75. GC-MS (m/z): 150.10

4. ^{1}H, ^{13}C and GC-MS of alkene hydroboration product

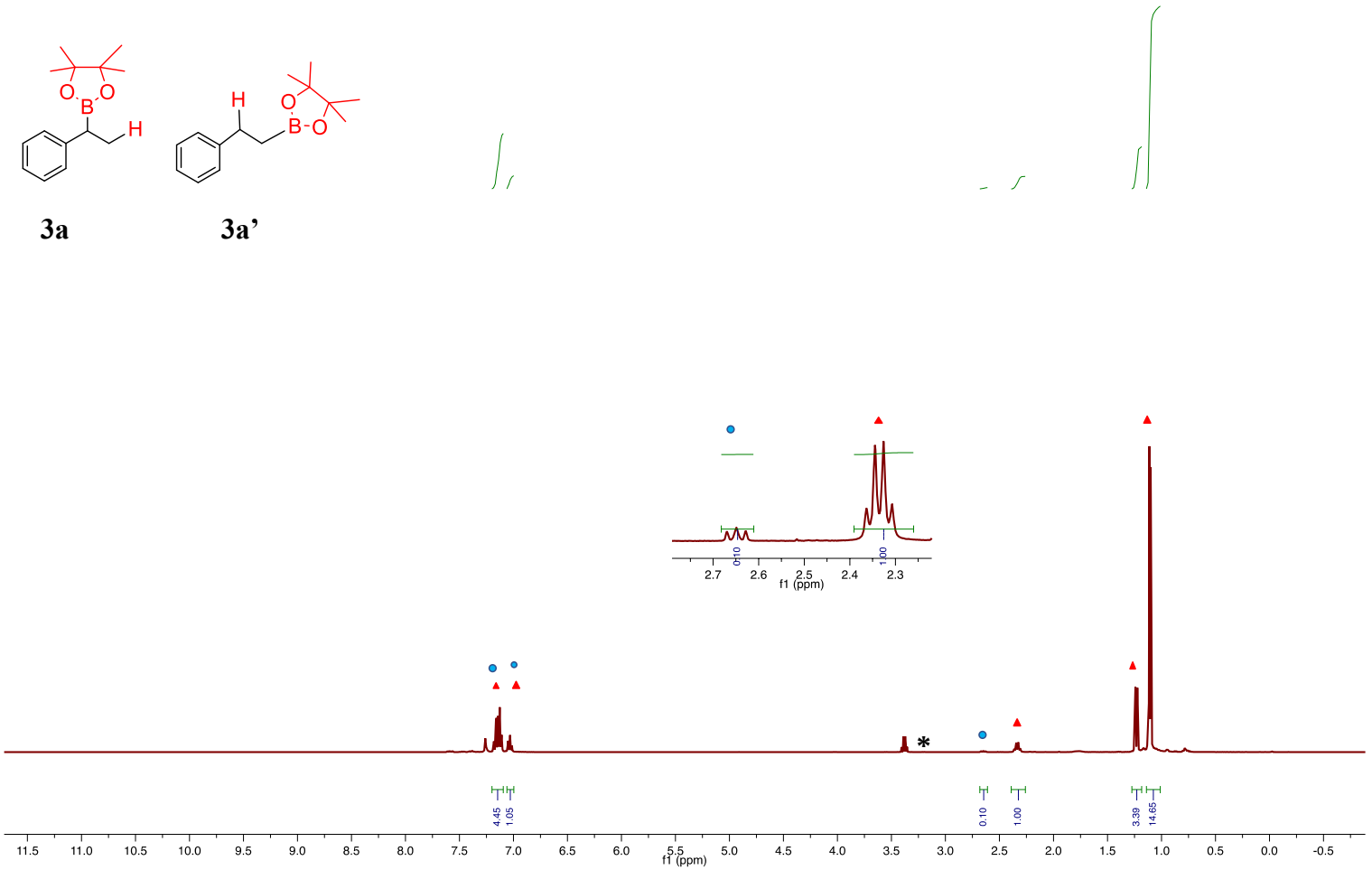


Figure S1. ^{1}H NMR of 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (**3a**) (▲) and 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (**3a'**) (●). (*) represents solvent peak.

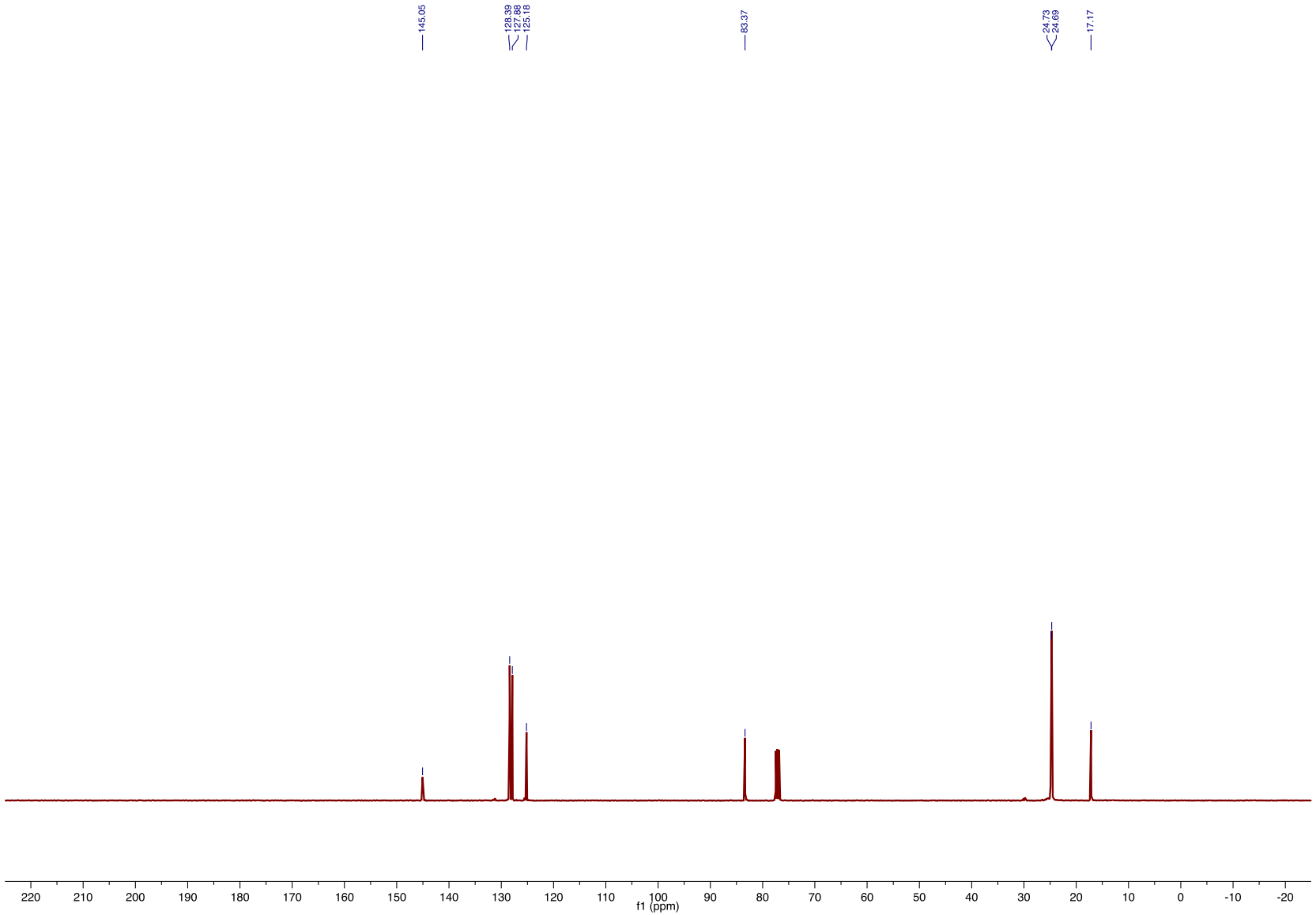


Figure S2. ^{13}C NMR of 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (**3a**)

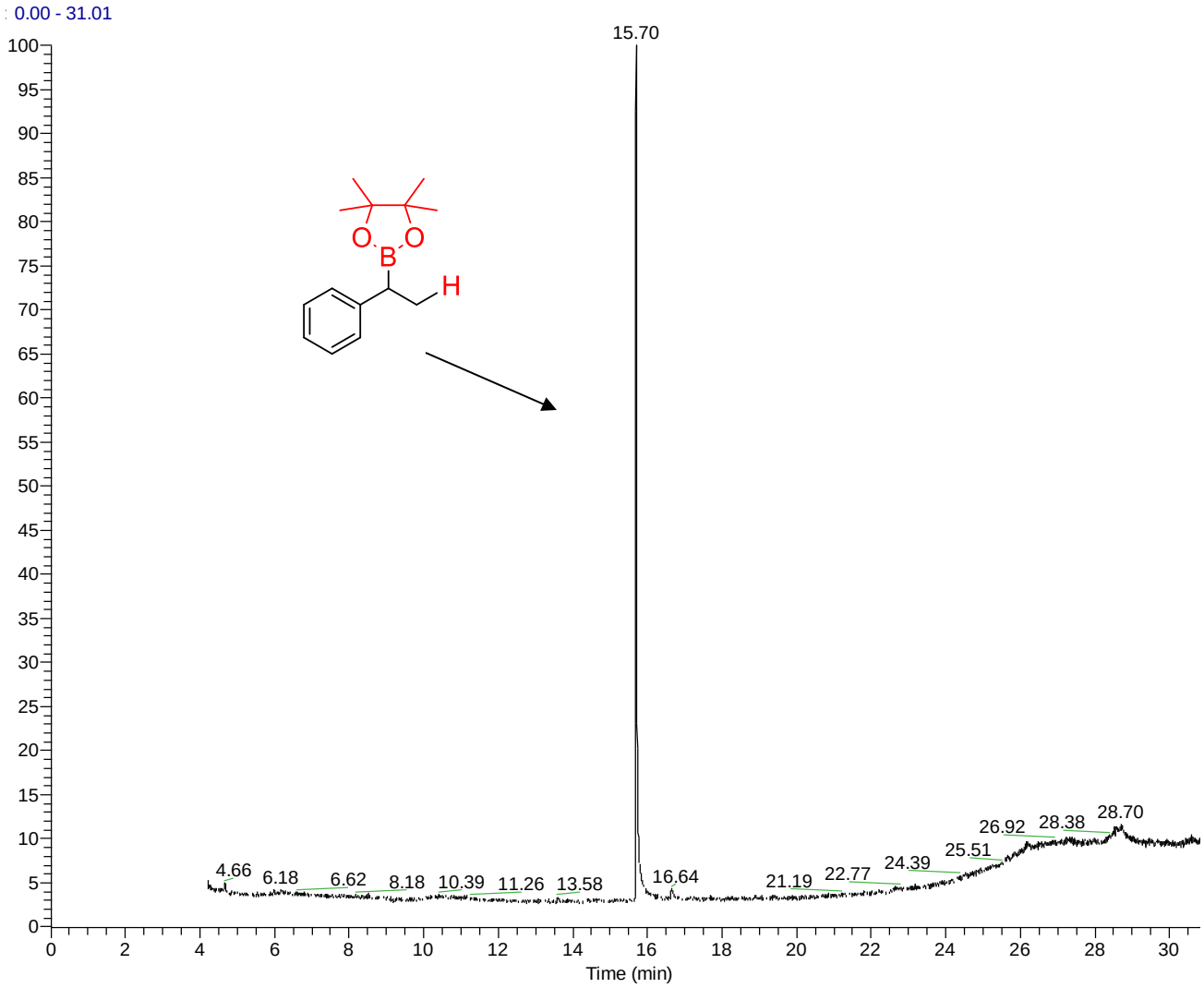


Figure S3. GC-MS of 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (**3a**).

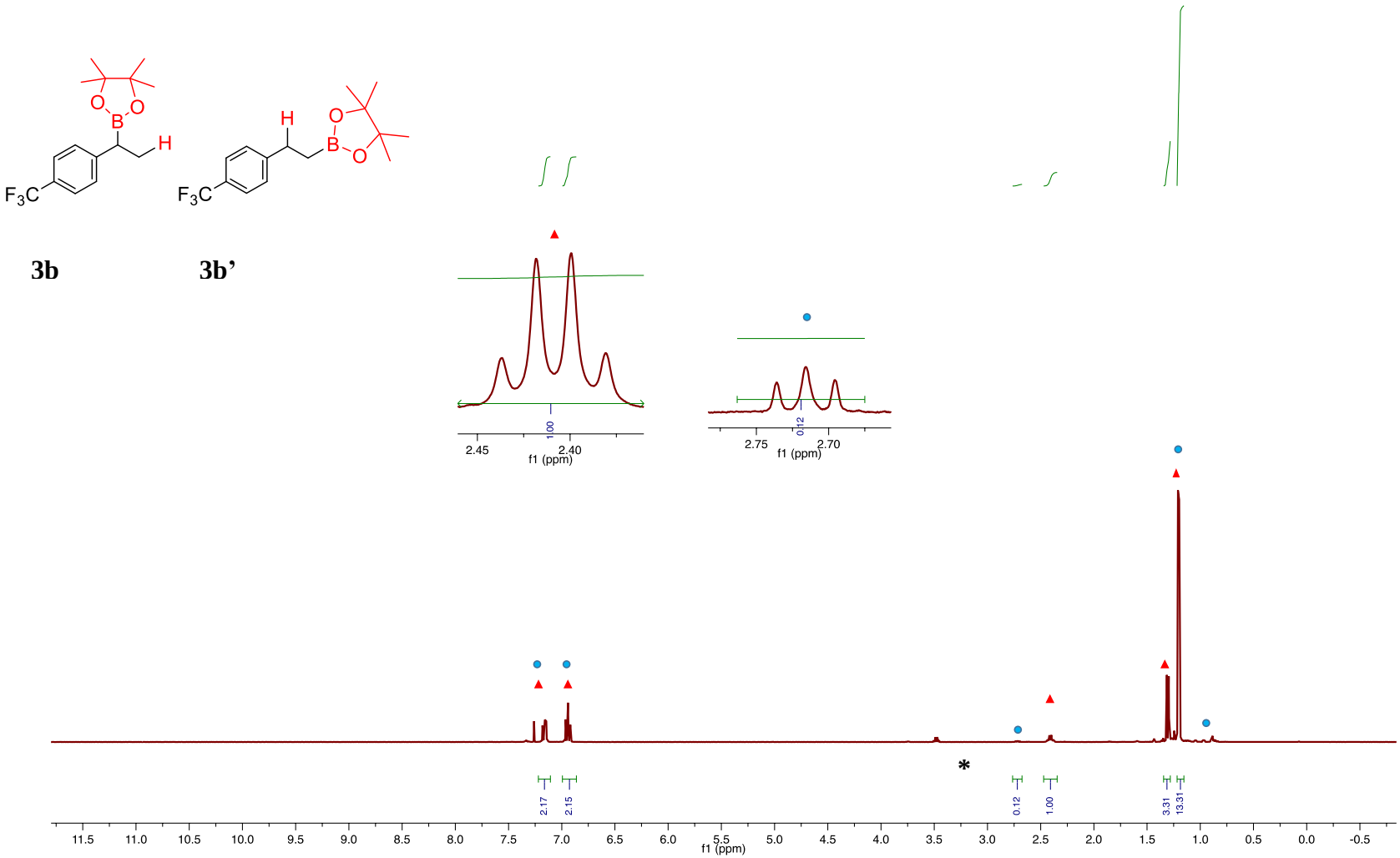


Figure S4. ^{1}H NMR of 4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)ethyl)-1,3,2-dioxaborolane (**3b**) (▲)and 4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenylethyl)-1,3,2-dioxaborolane (**3b'**) (●). (*) represents solvent peak.

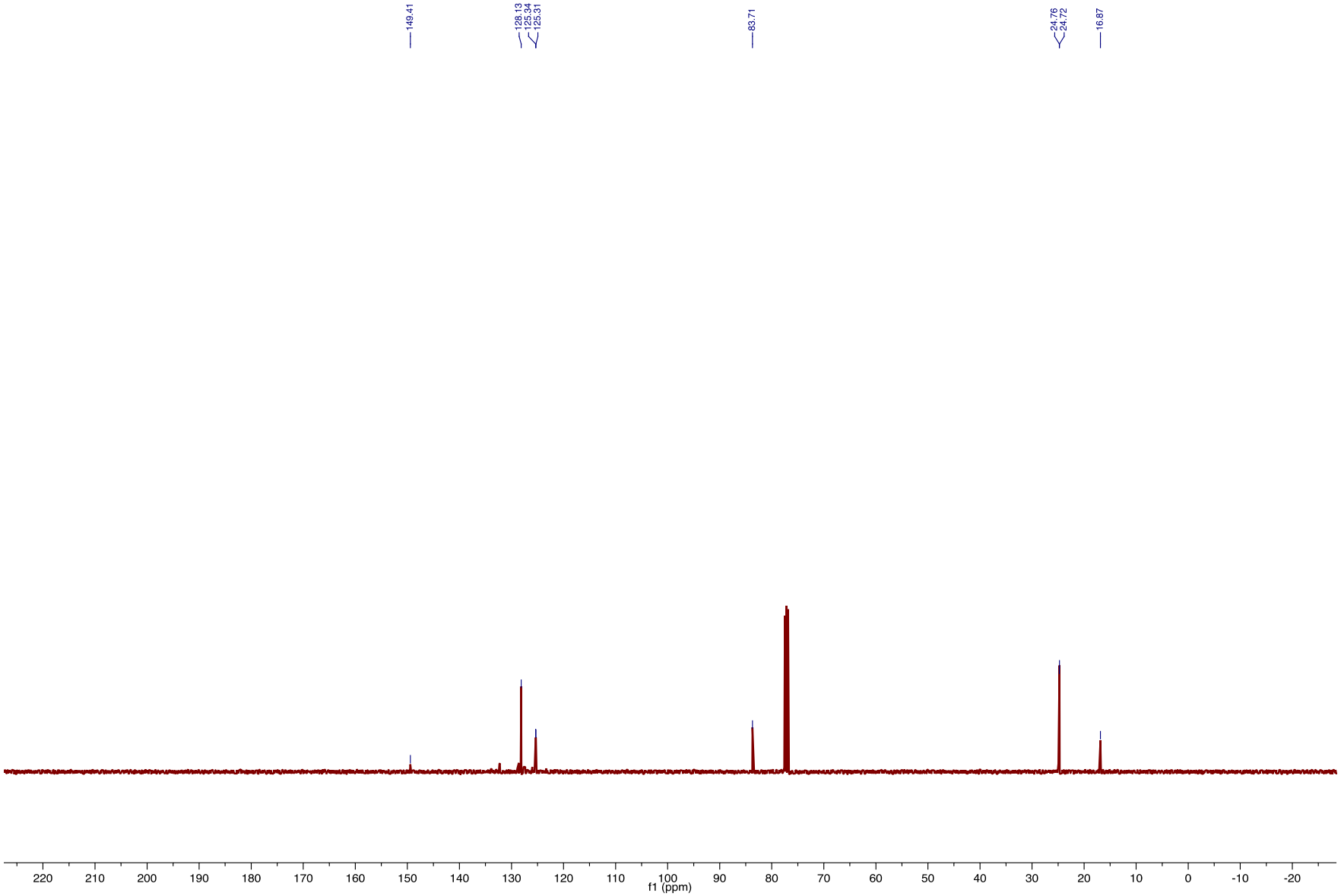


Figure S5. ^{13}C NMR of 4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)ethyl)-1,3,2-dioxaborolane (**3b)**

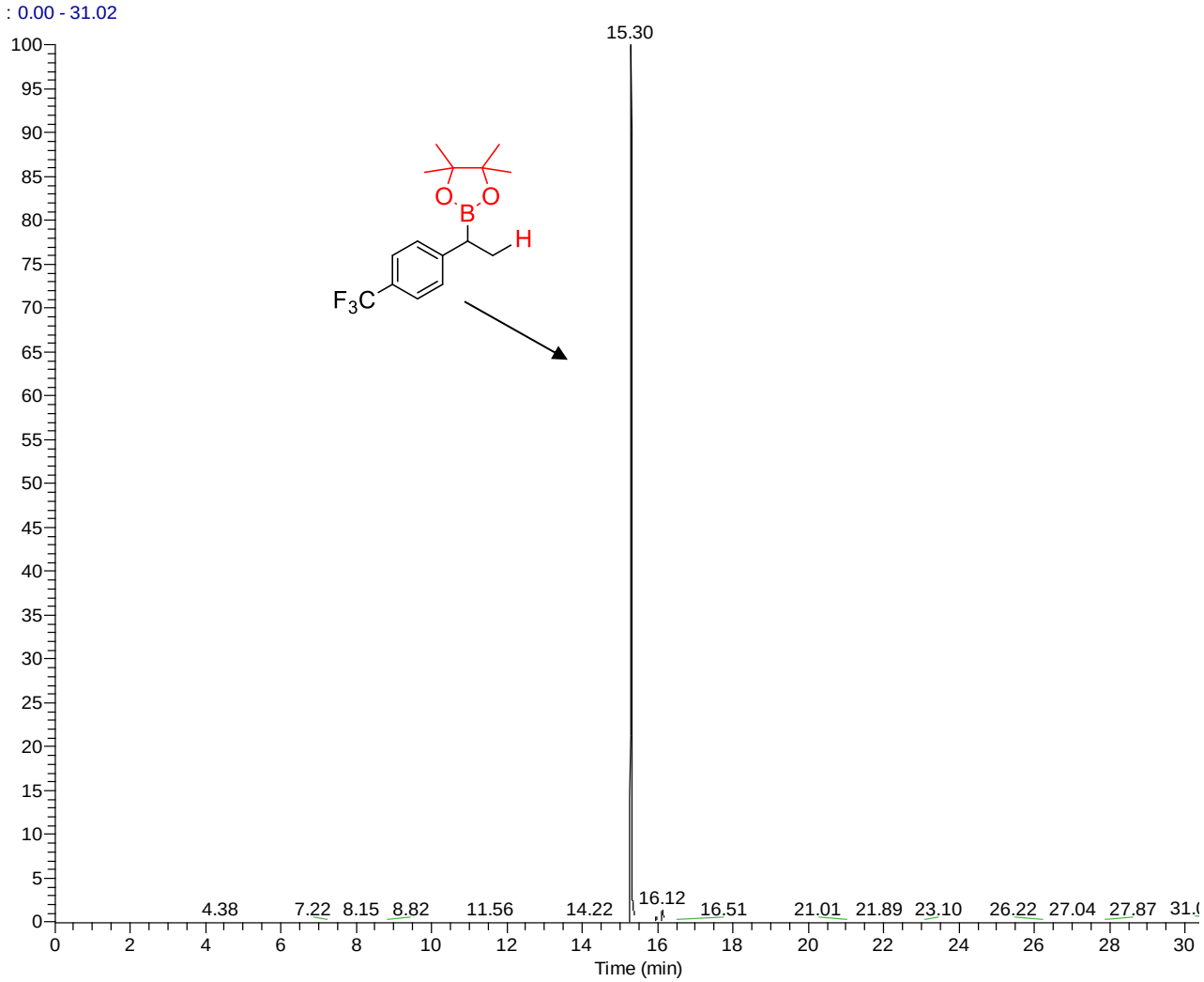


Figure S6. GC-MS of 4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)ethyl)-1,3,2-dioxaborolane (**3b**)

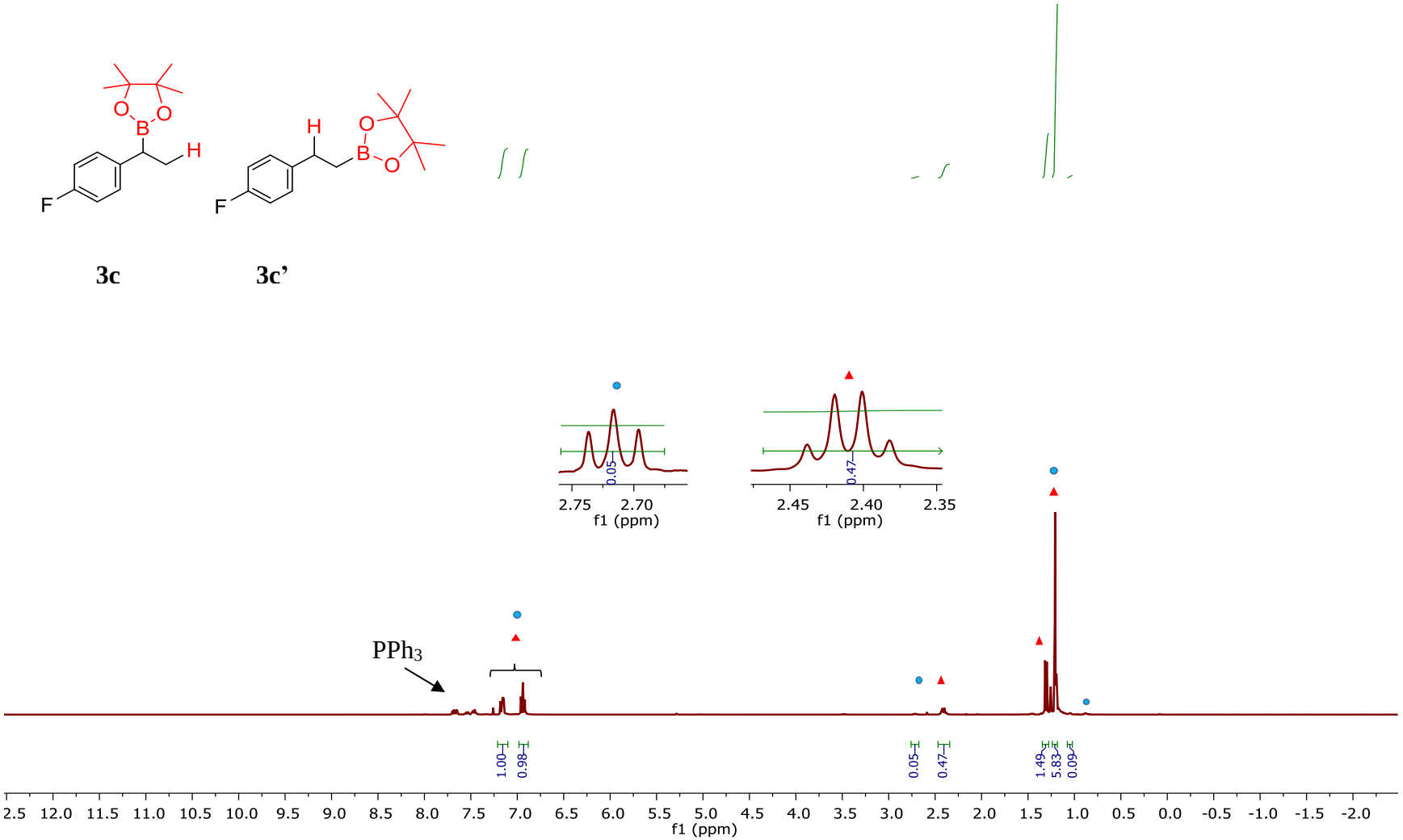


Figure S7. ^{1}H NMR of 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**) (▲) and 2-(4-fluorophenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3c')** (●)

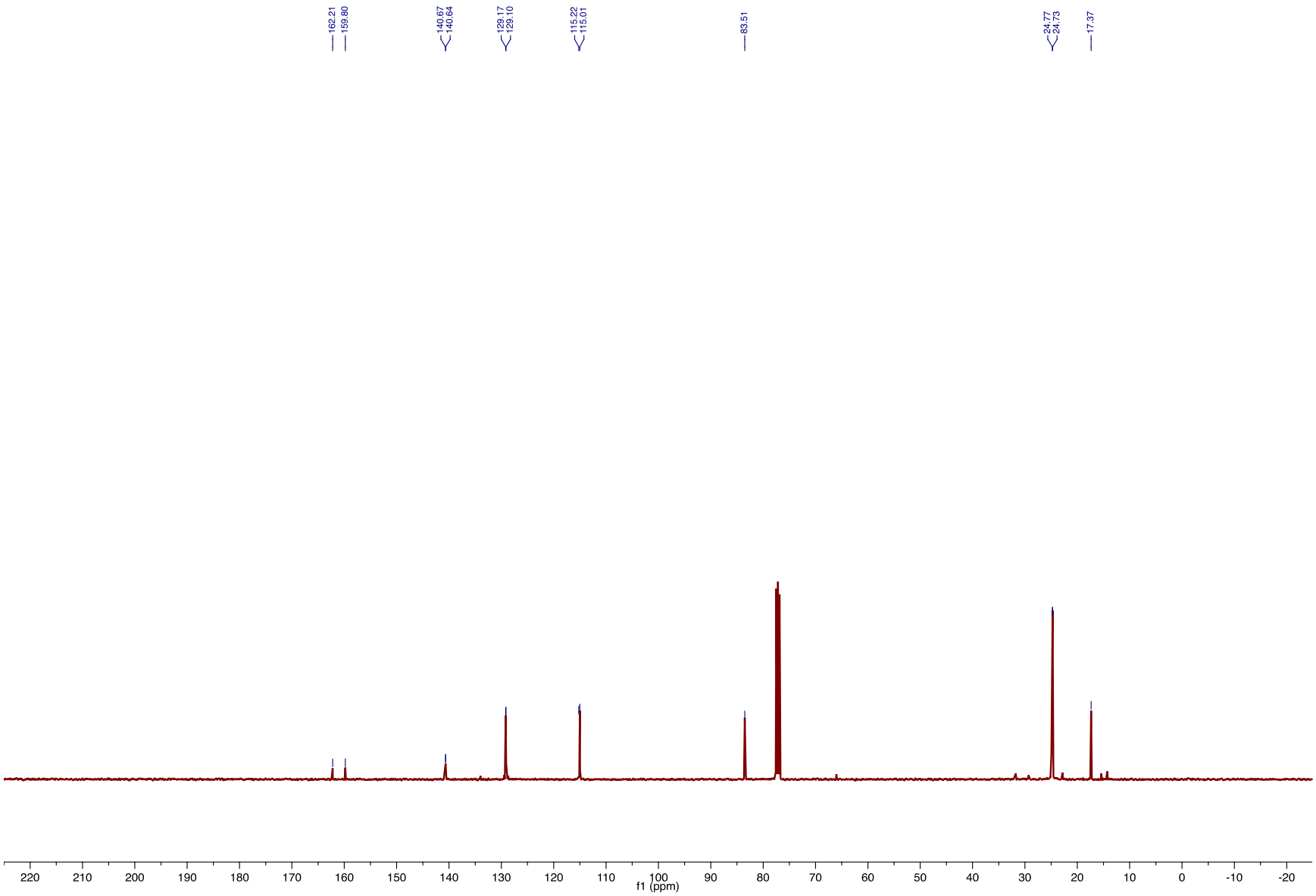


Figure S8. ^{13}C NMR of 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c)**

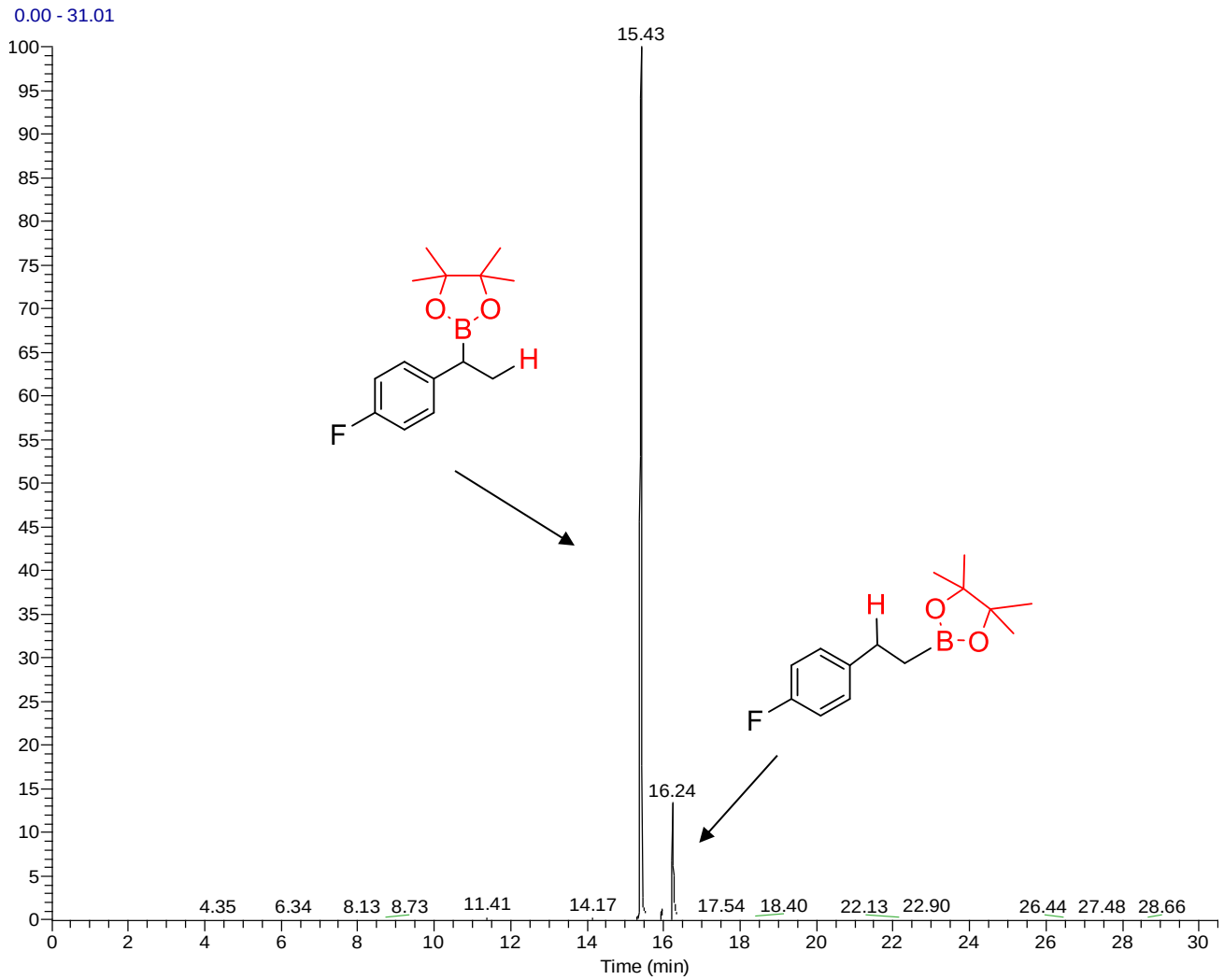


Figure S9. GC-MS of 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**) and 2-(4-fluorophenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3c')**

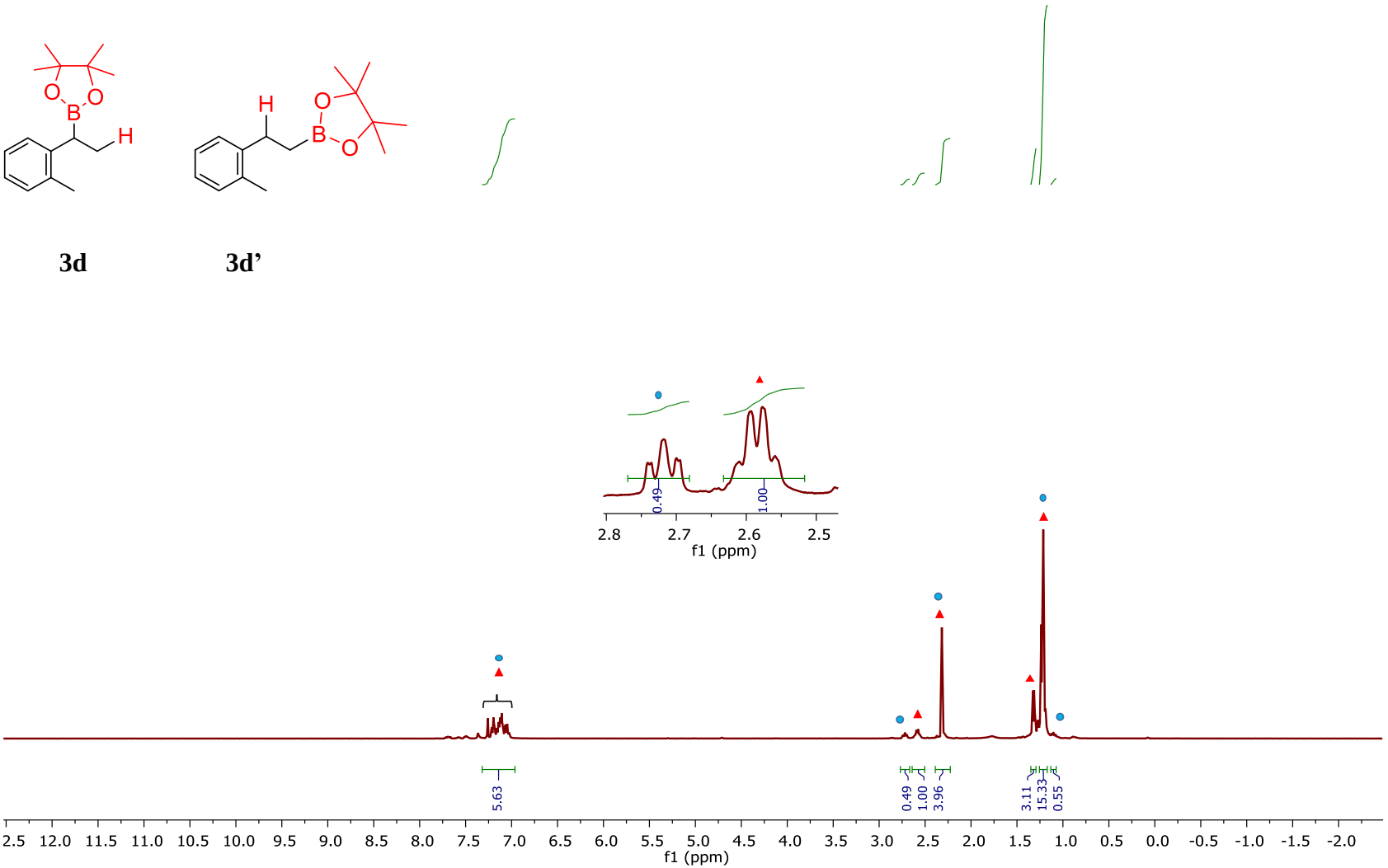


Figure S10. ^{1}H NMR of 4,4,5,5-tetramethyl-2-(1-(o-tolyl)ethyl)-1,3,2-dioxaborolane (**3d**) (▲) and 4,4,5,5-tetramethyl-2-(2-methylphenethyl)-1,3,2-dioxaborolane (**3d’**) (●)

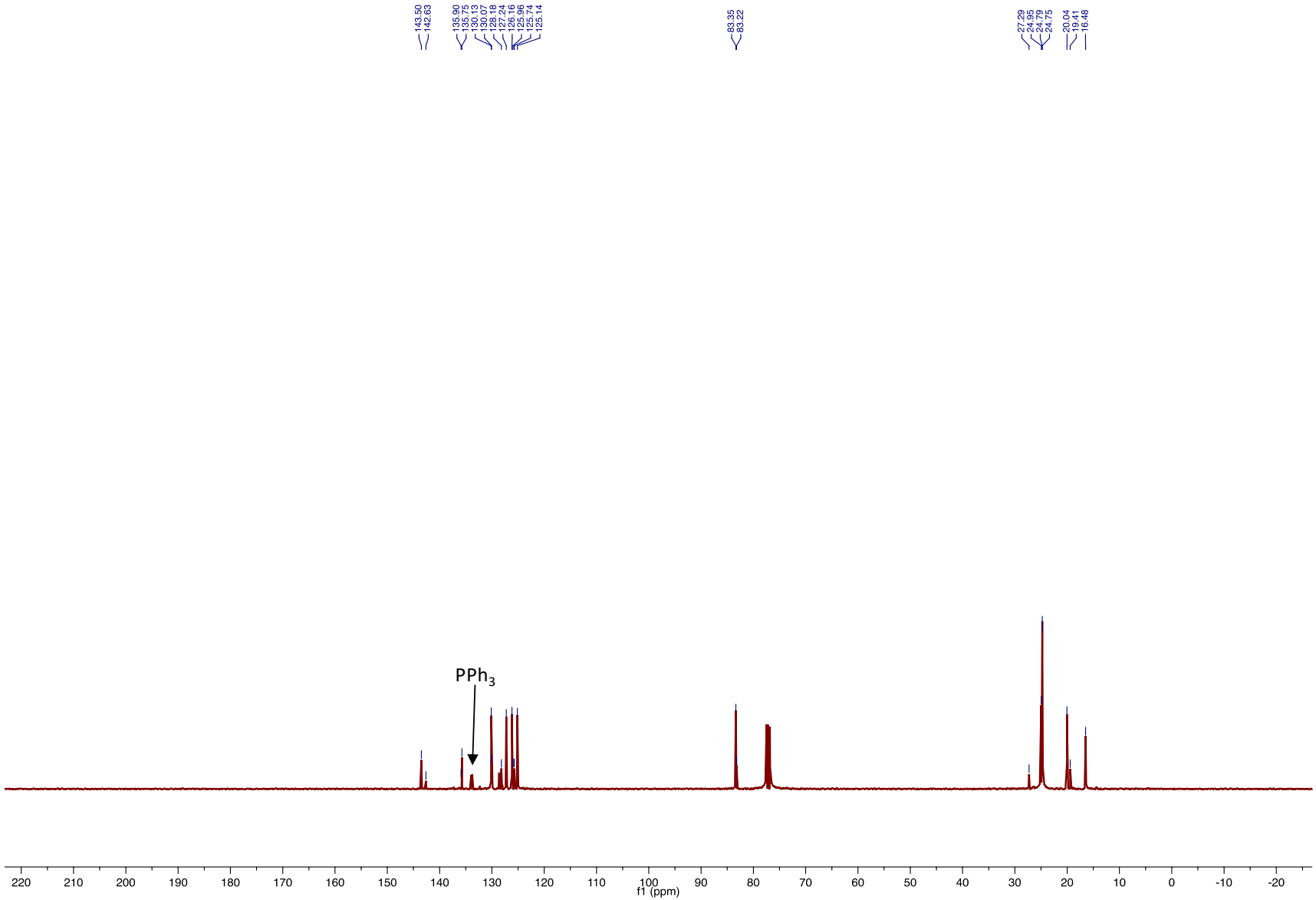


Figure S11. ^{13}C NMR of 4,4,5,5-tetramethyl-2-(1-(o-tolyl)ethyl)-1,3,2-dioxaborolane (**3d**) and 4,4,5,5-tetramethyl-2-(2-methylphenethyl)-1,3,2-dioxaborolane (**3d'**)

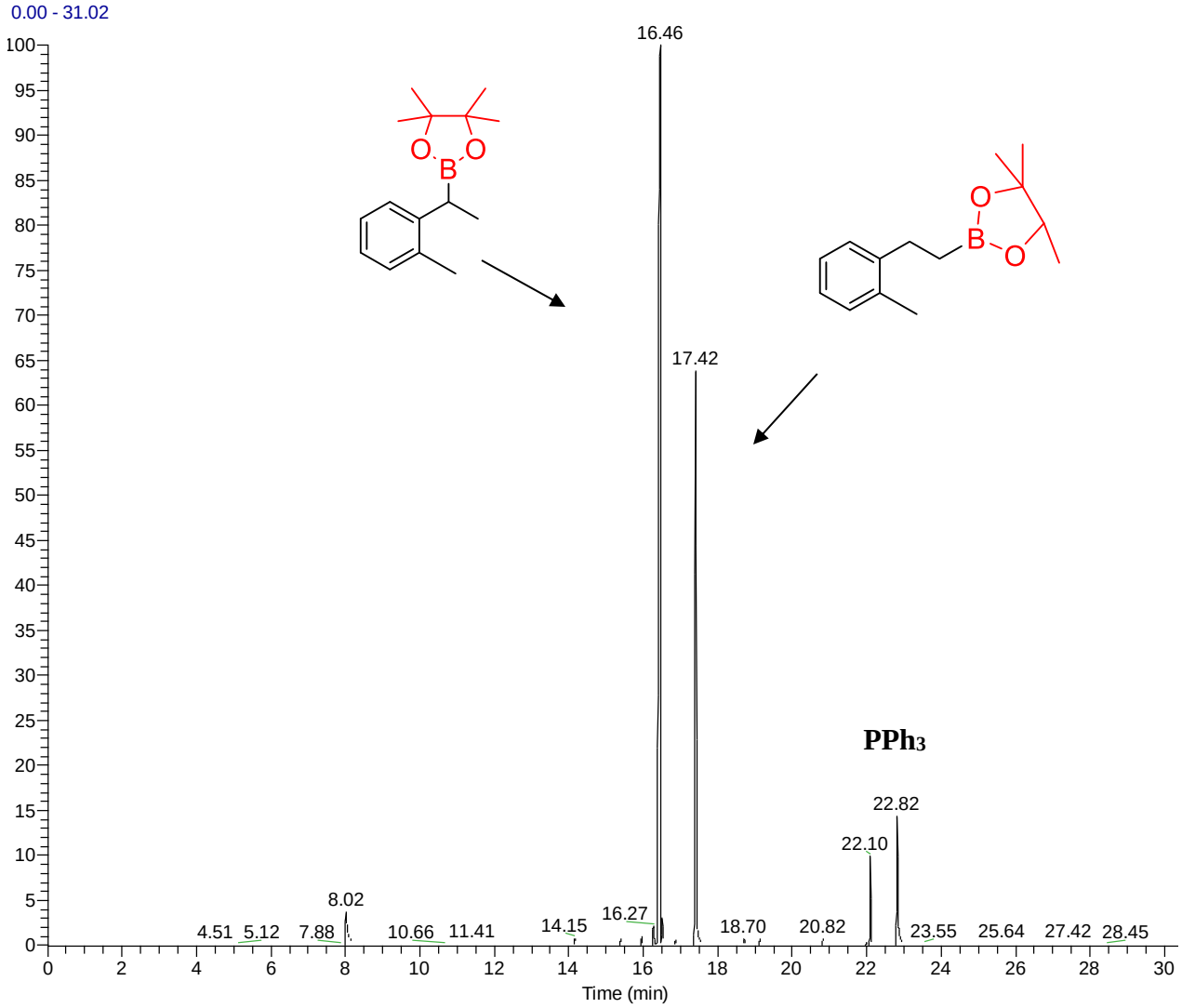


Figure S12. GC-MS of 4,4,5,5-tetramethyl-2-(1-(o-tolyl)ethyl)-1,3,2-dioxaborolane (**3d**) and 4,4,5,5-tetramethyl-2-(2-methylphenethyl)-1,3,2-dioxaborolane (**3d'**)

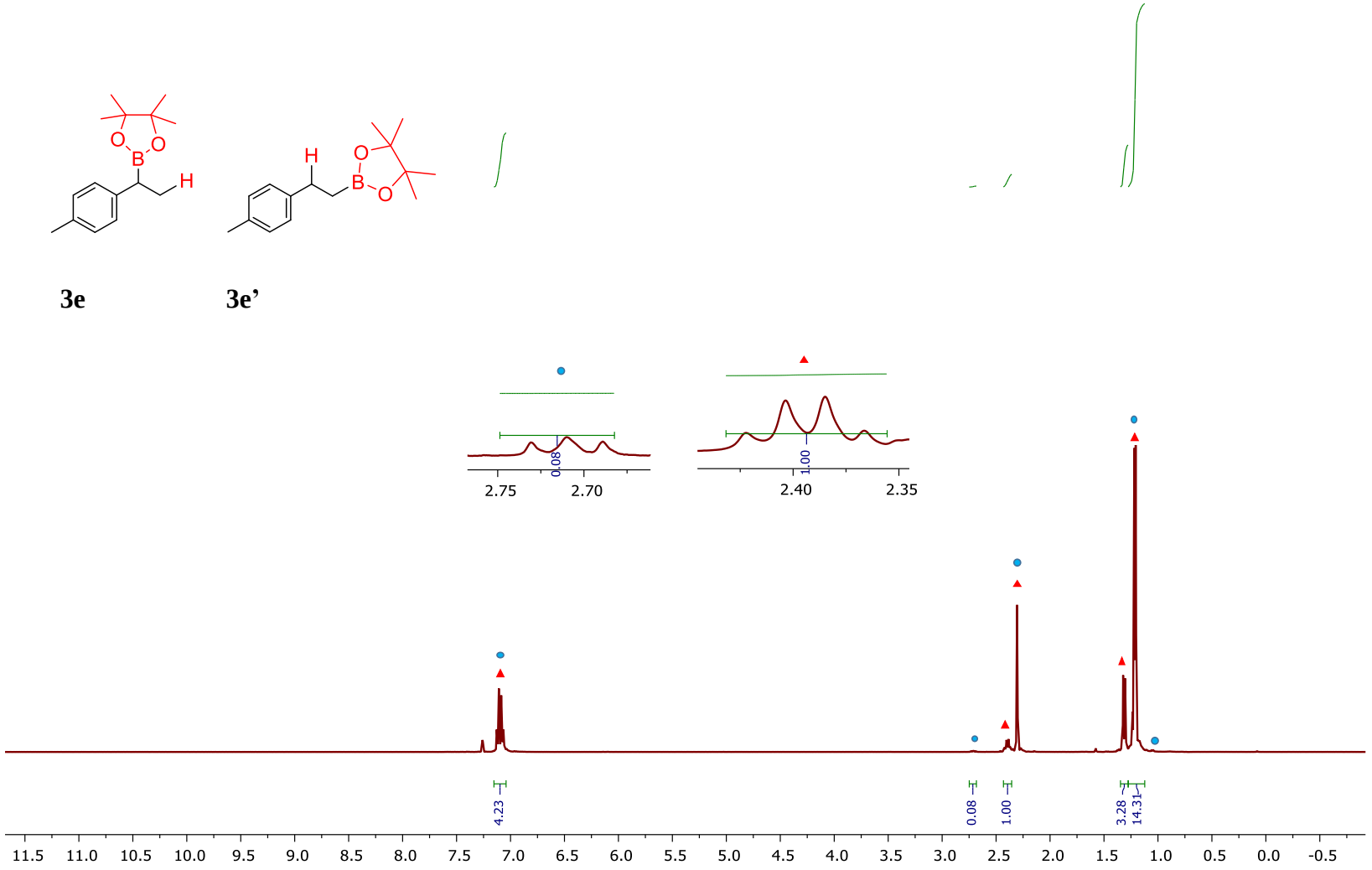


Figure S13. ^{1}H NMR of 4,4,5,5-tetramethyl-2-(1-(p-tolyl)ethyl)-1,3,2-dioxaborolane **(3e)** (▲) and 4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane **(3e')** (●)

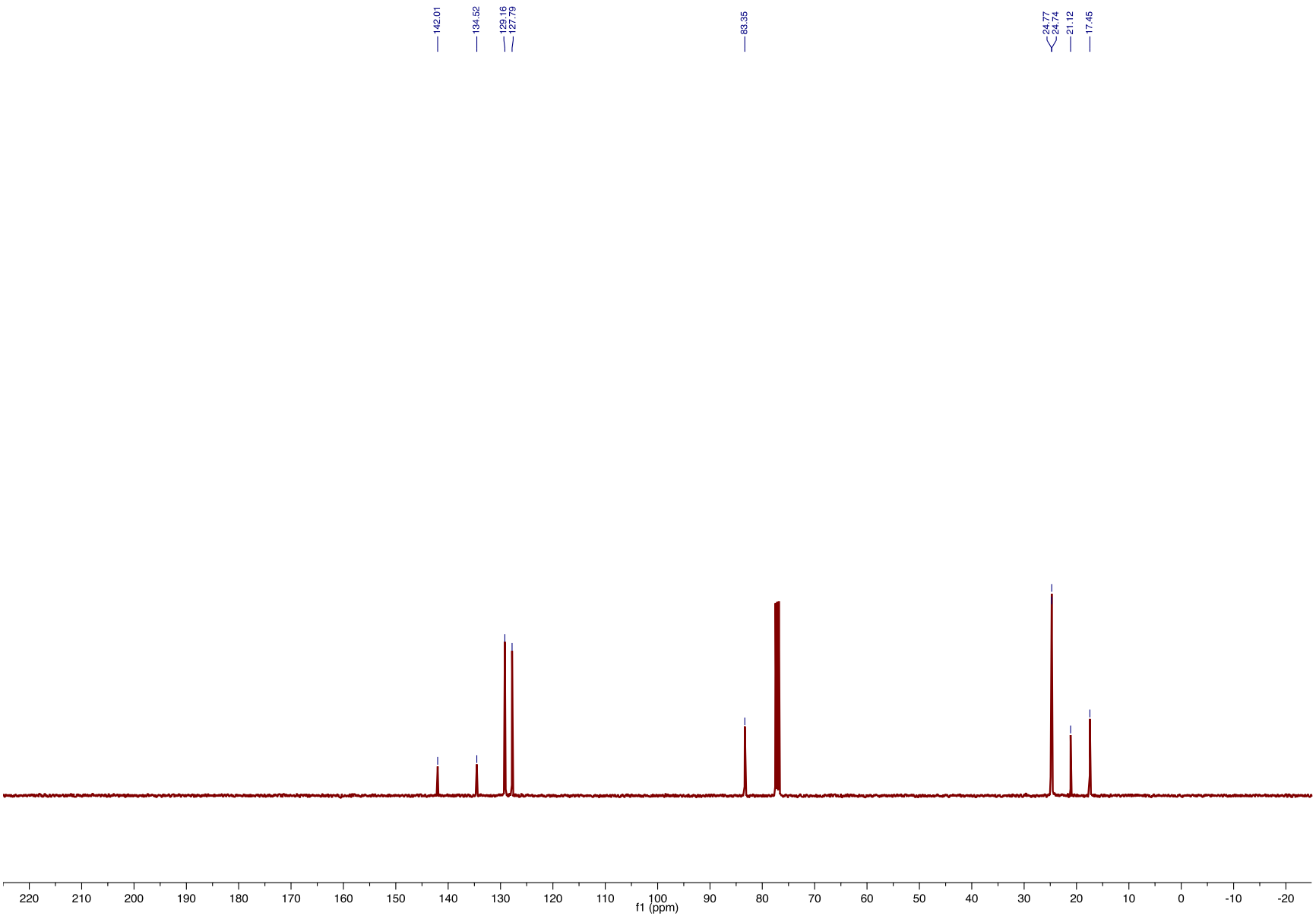


Figure S14. ^{13}C NMR of 4,4,5,5-tetramethyl-2-(1-(p-tolyl)ethyl)-1,3,2-dioxaborolane **(3e)**

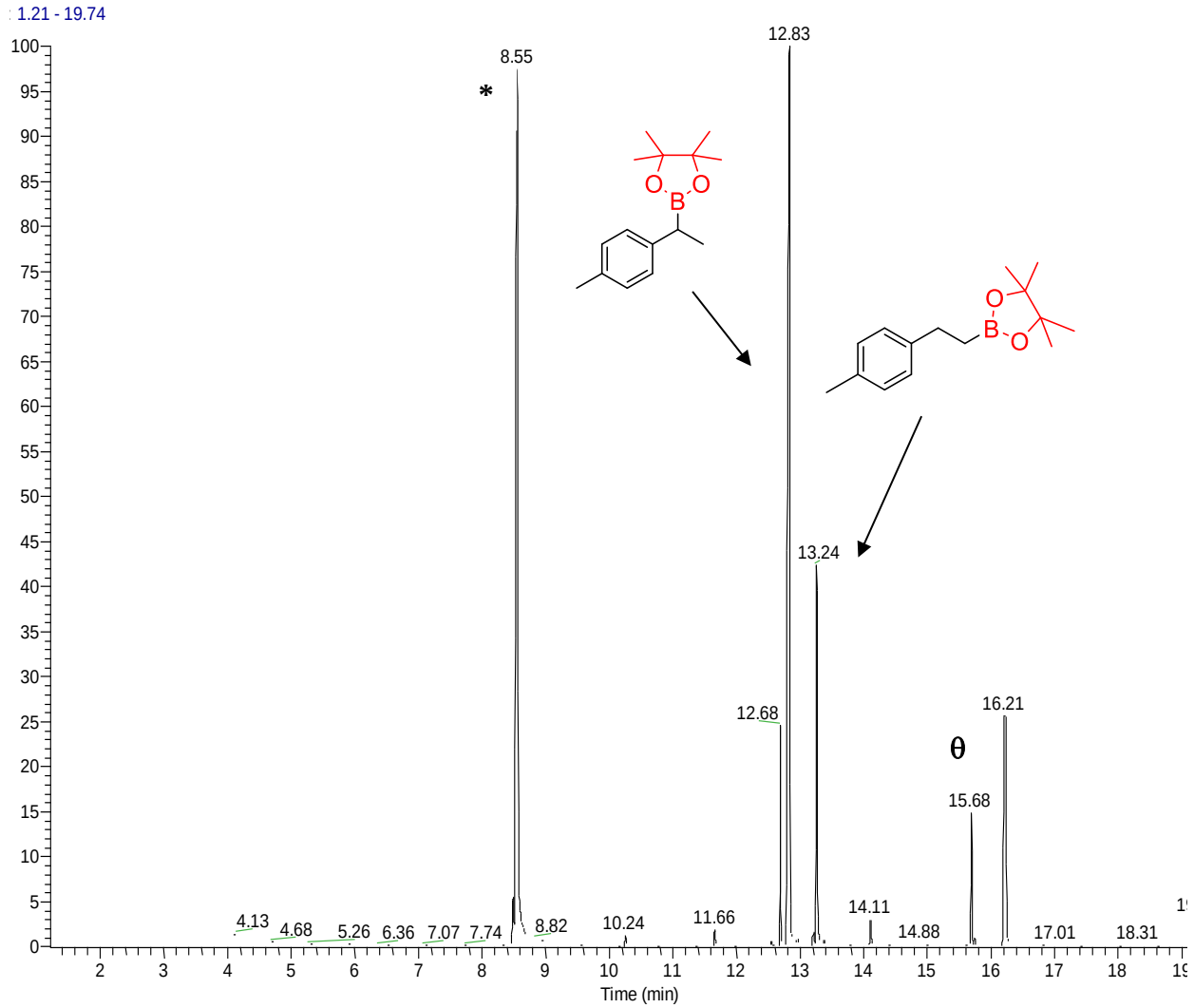


Figure S15. GC-MS of 4,4,5,5-tetramethyl-2-(1-(p-tolyl)ethyl)-1,3,2-dioxaborolane **(3e)** and 4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane **(3e')** .(*) represents internal standard and (**θ**) represents dehydrogenative borylation product.

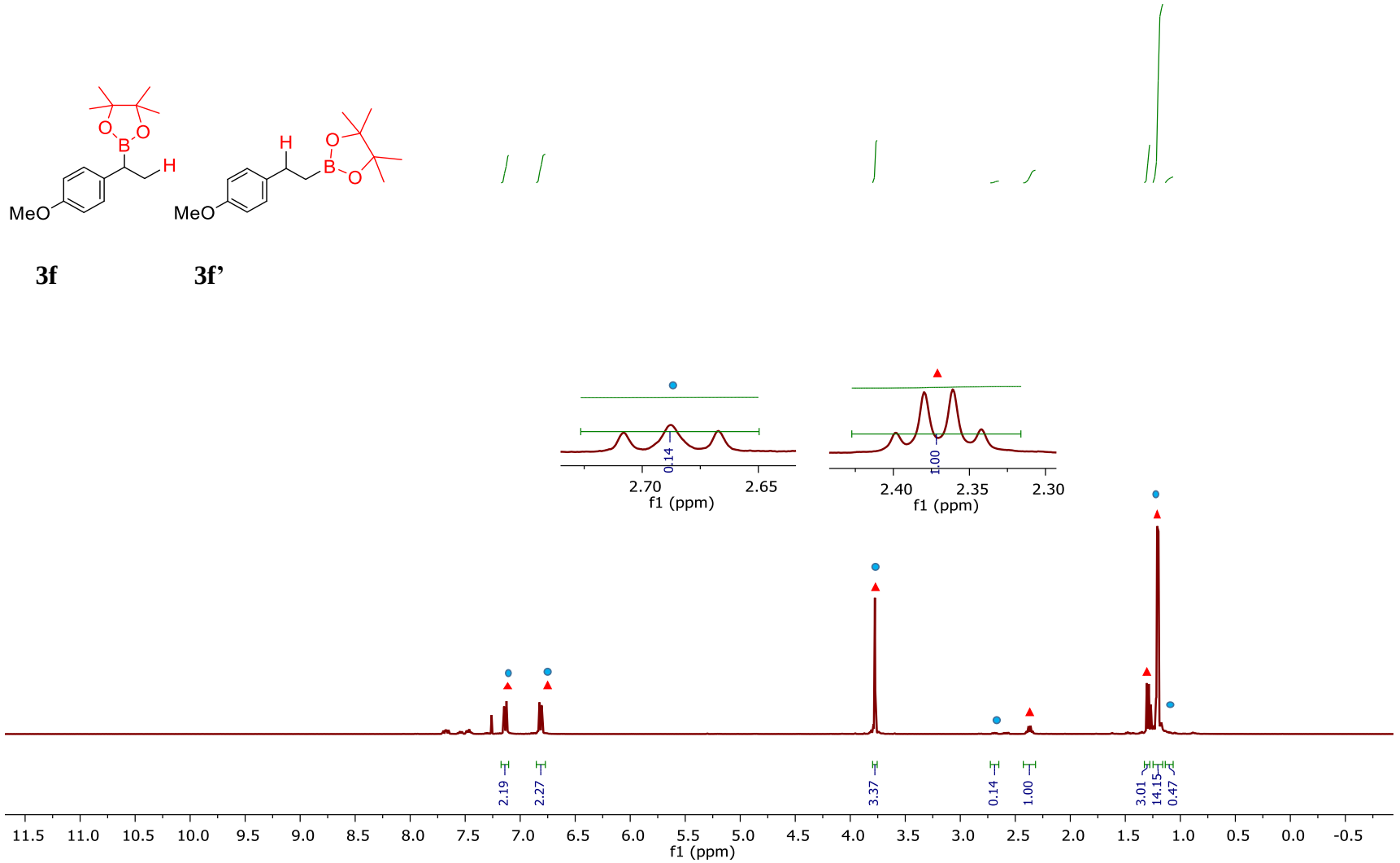


Figure S16. ^{1}H NMR of 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3f)** (▲) and 2-(4-methoxyphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f'**) (●)

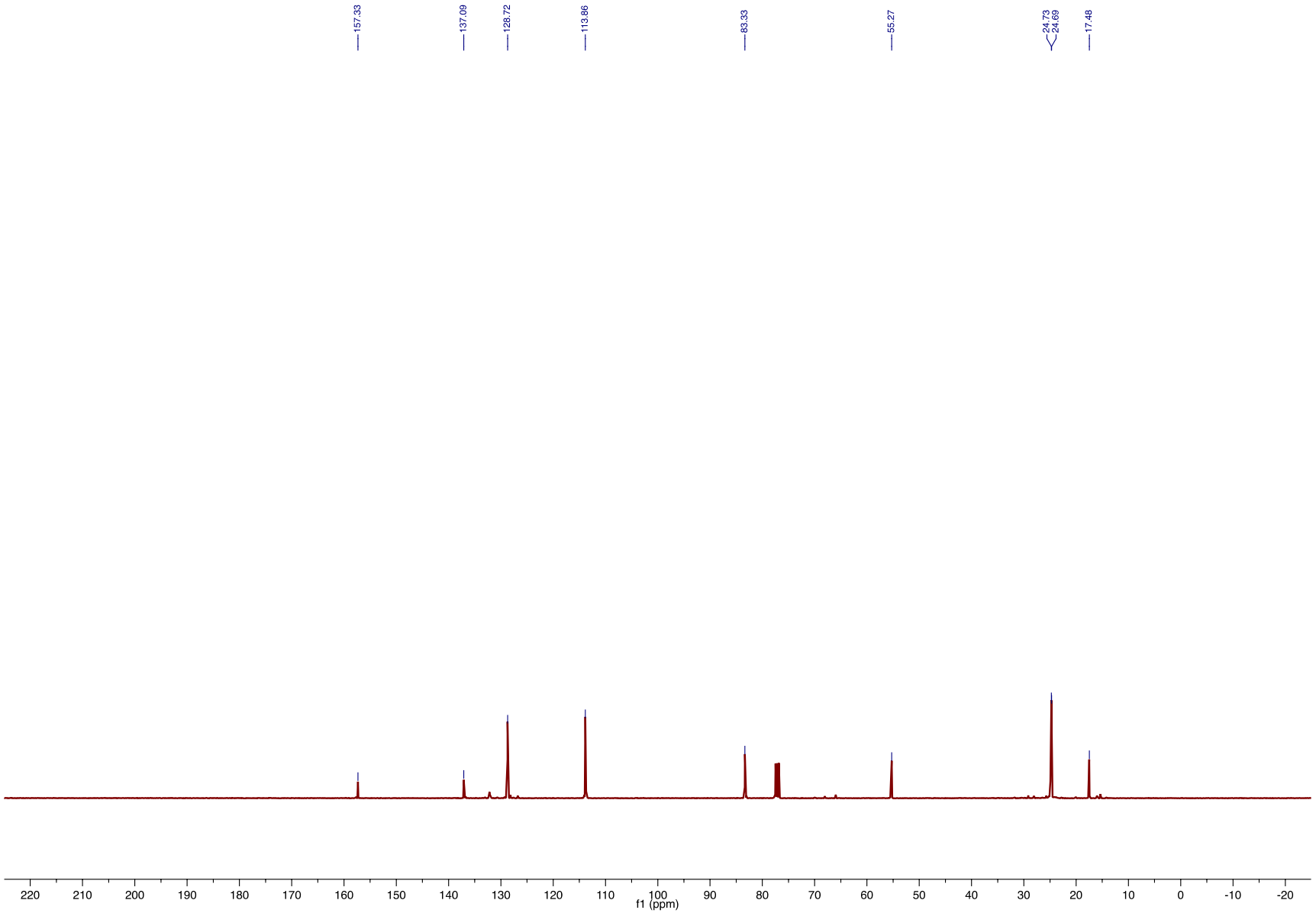


Figure S17. ^{13}C NMR of 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3f)**

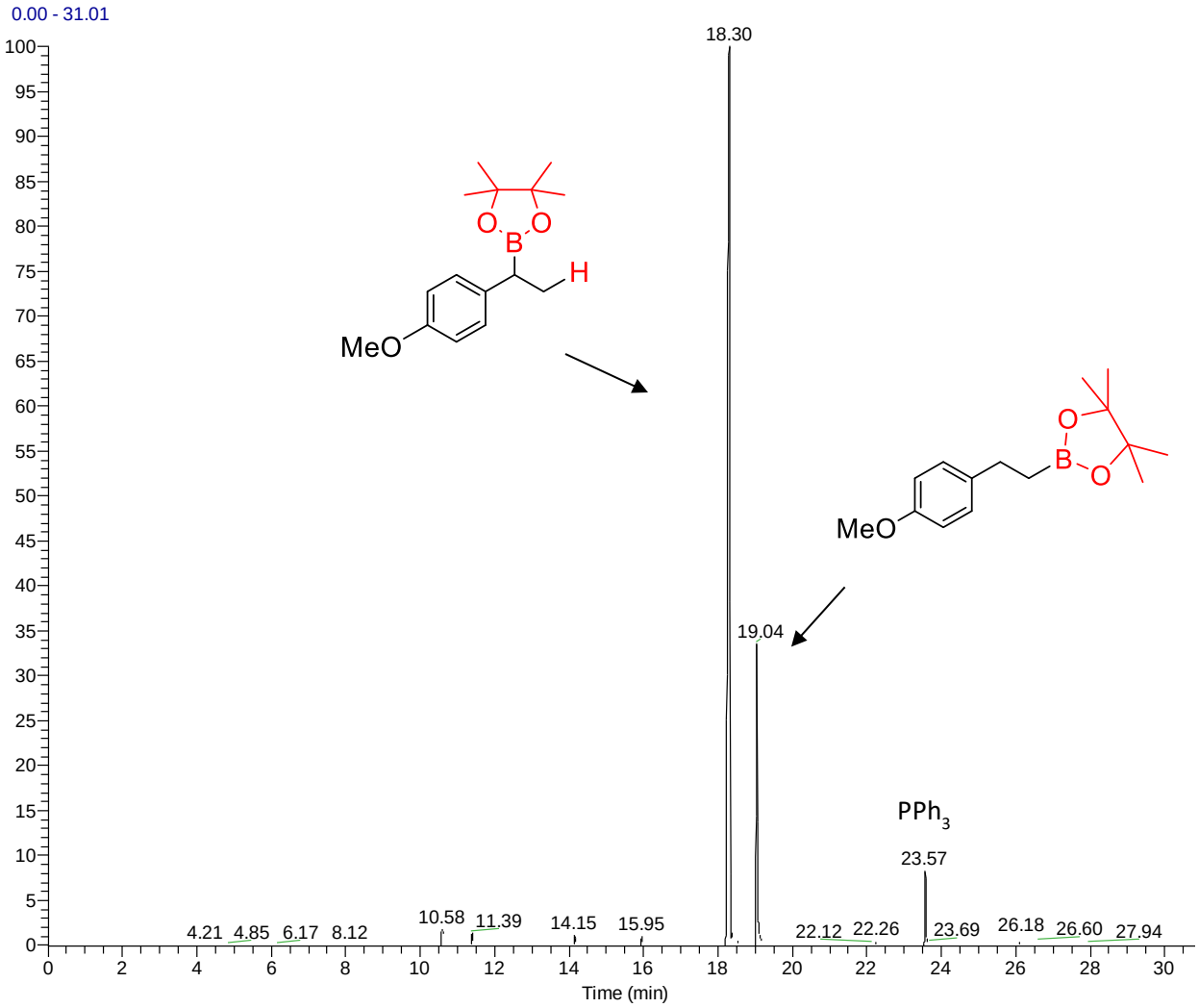


Figure S18. GC-MS of 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3f)** (▲) and 2-(4-methoxyphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f'**) (●)

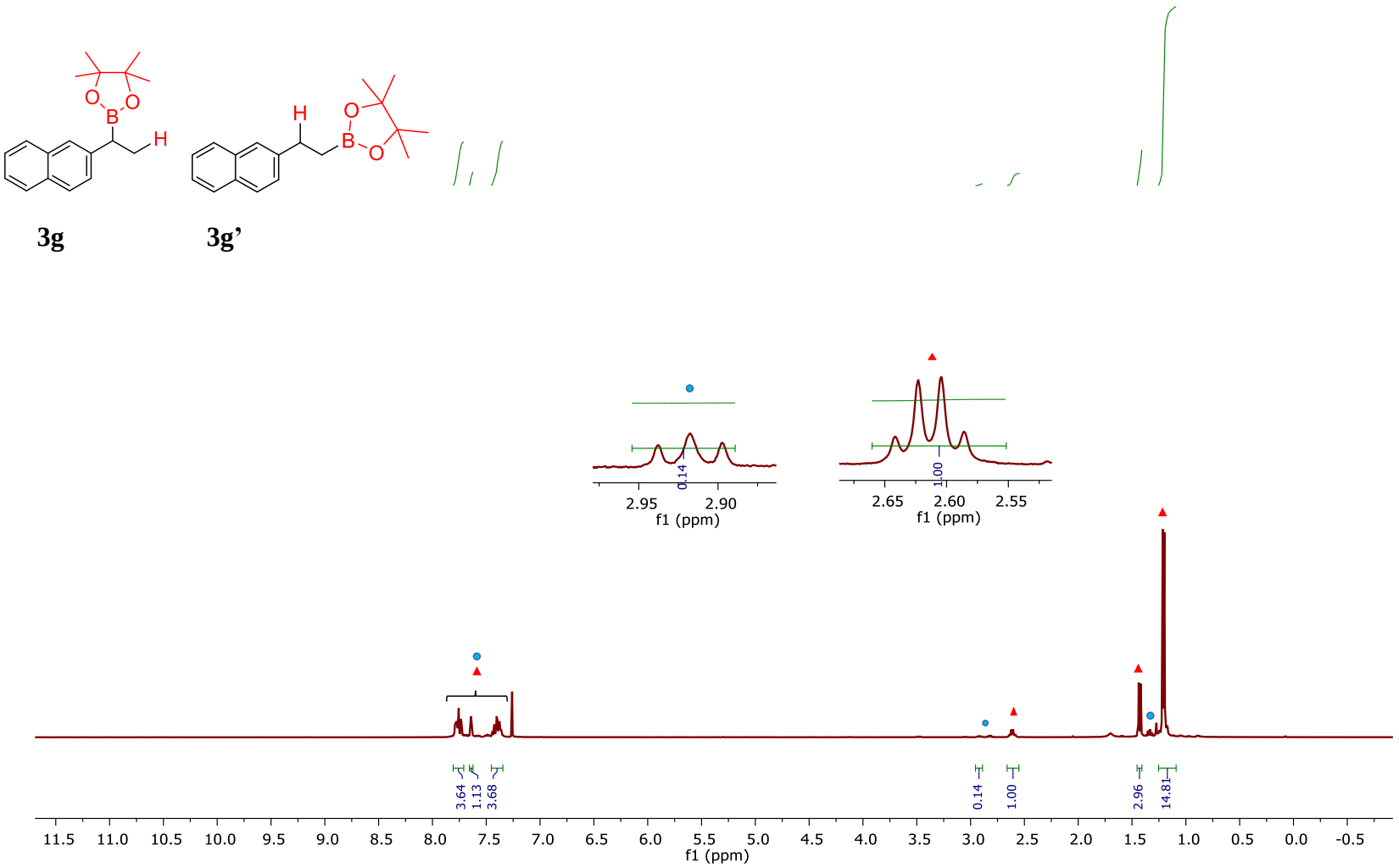


Figure S19. ^{1}H NMR of 4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane **(3g)** (▲) and 4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (**3g'**) (●)

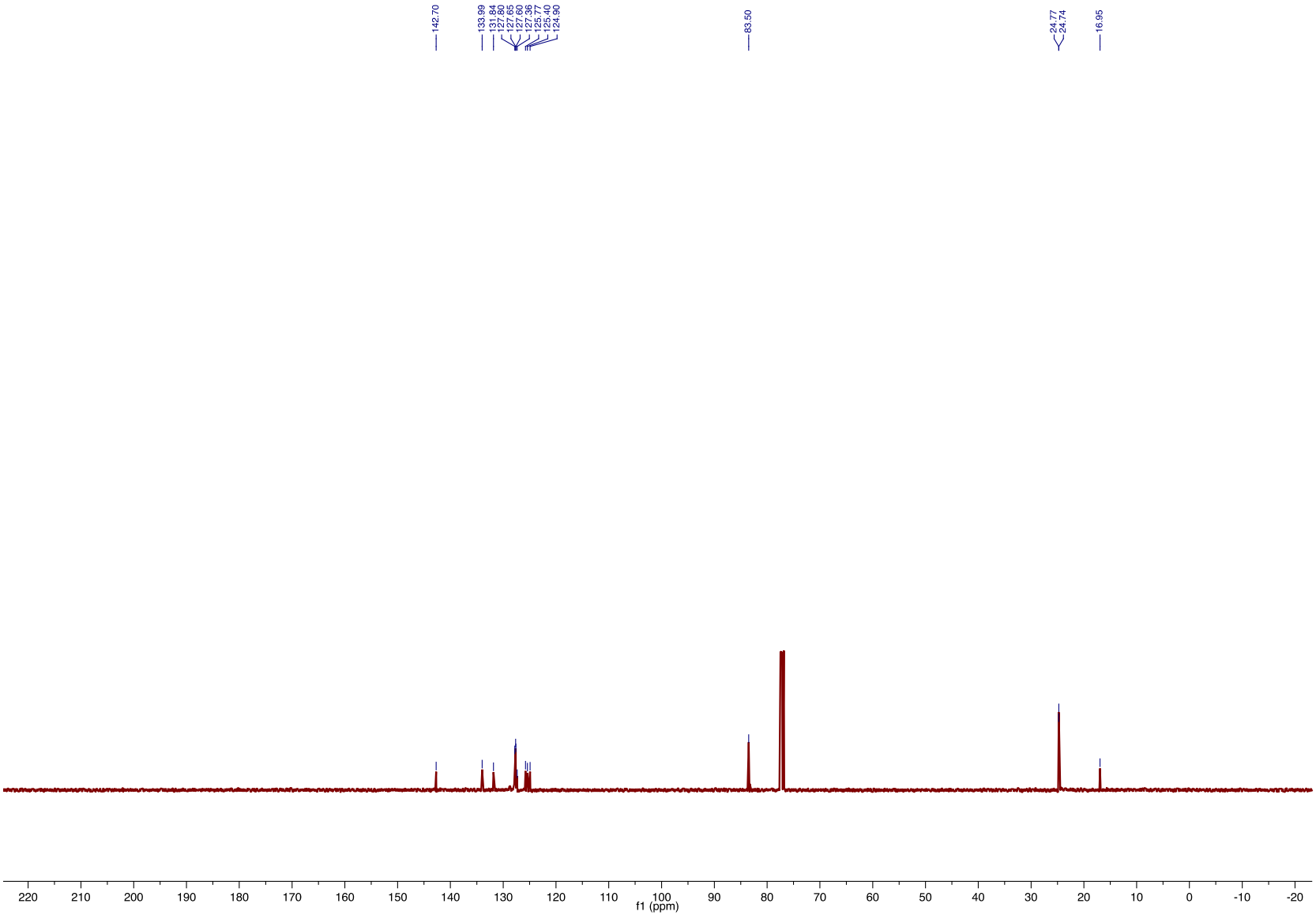


Figure S20. ^{13}C NMR of 4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane **(3g)**

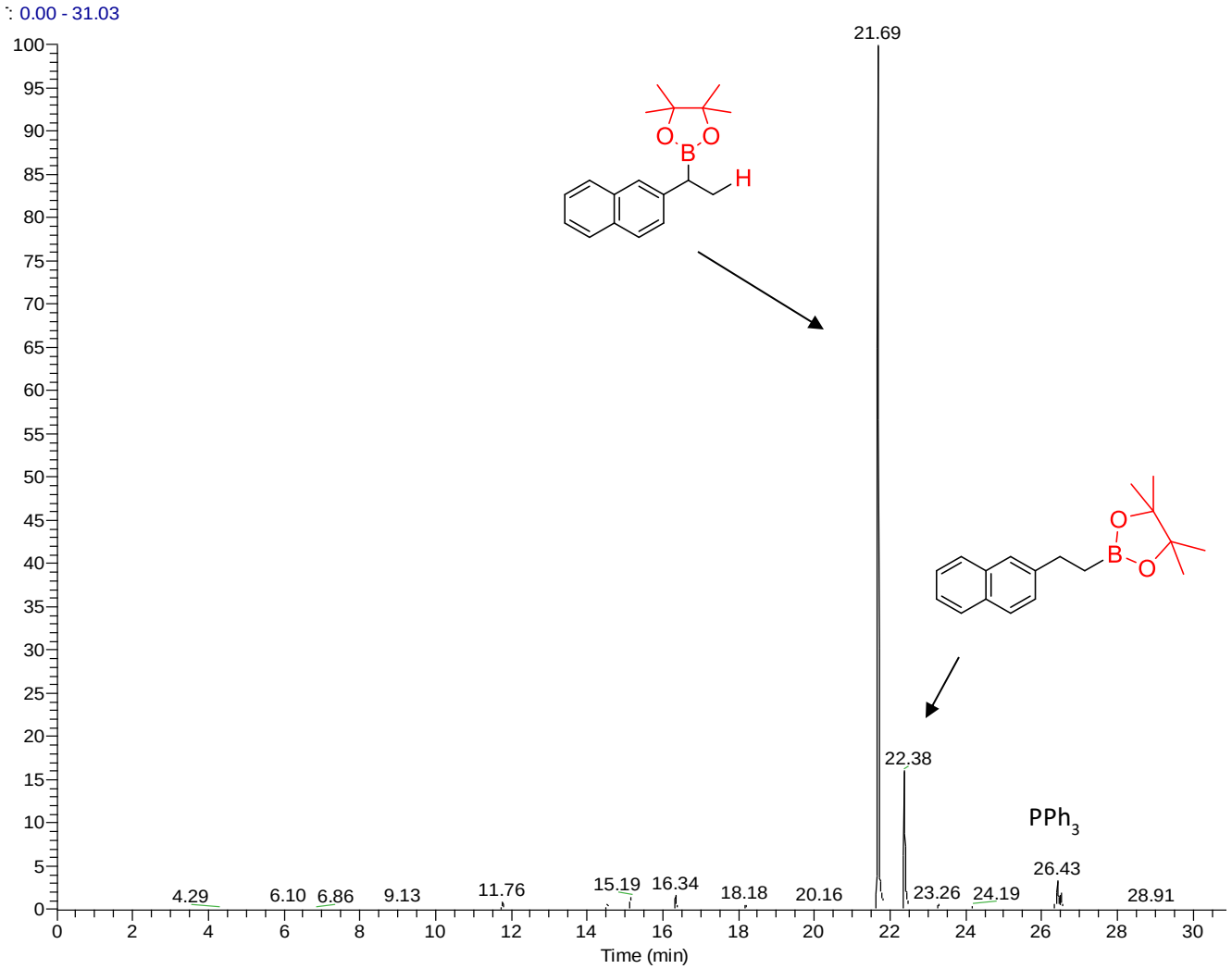


Figure S21. GC-MS of 4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane **(3g)** and 4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (**3g'**)

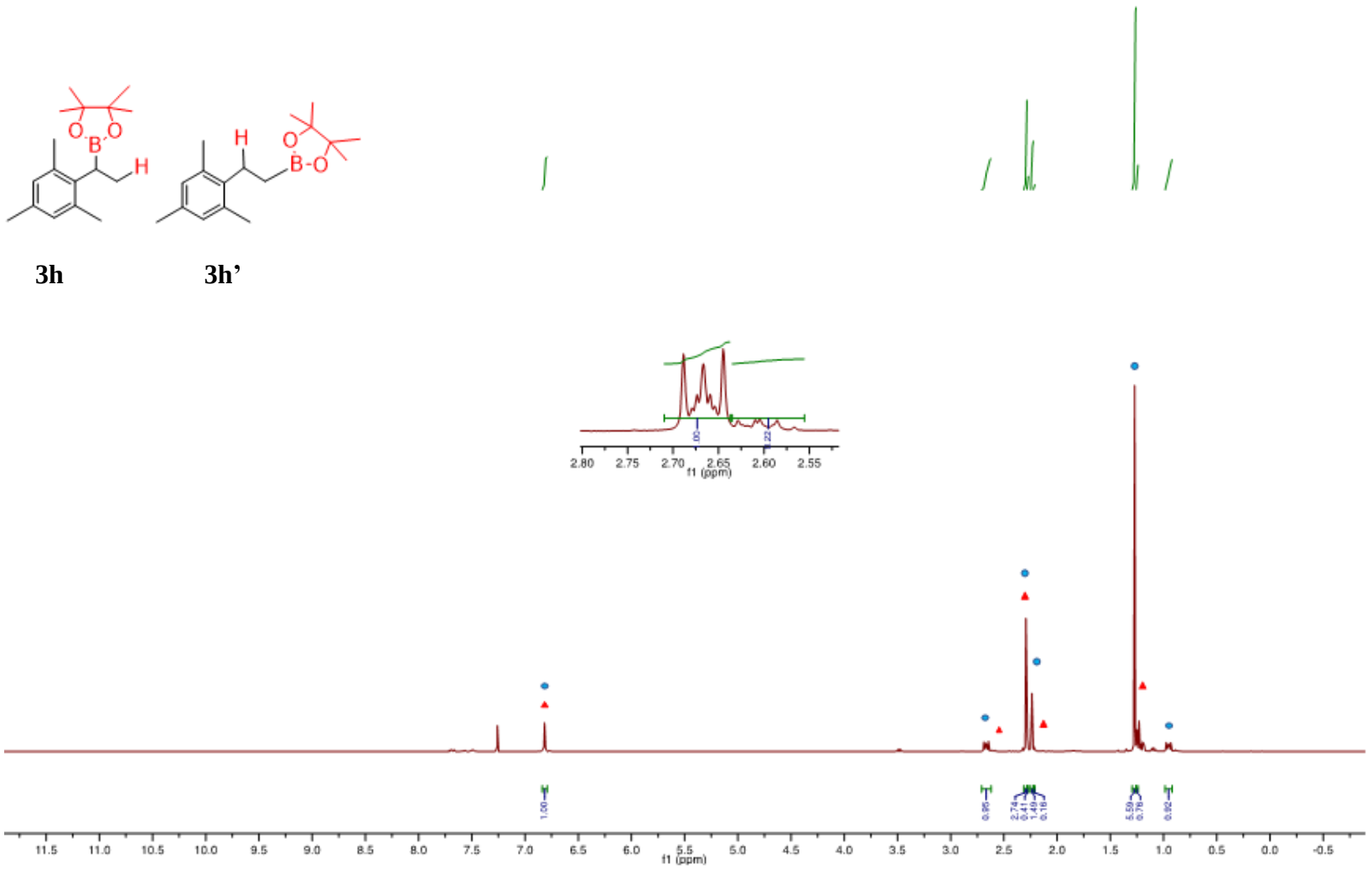


Figure S22. ^{1}H NMR of 2-(1-mesitylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3h)** (▲) and 4,4,5,5-tetramethyl-2-(2,4,6-trimethylphenethyl)-1,3,2-dioxaborolane (**3h'**) (●)

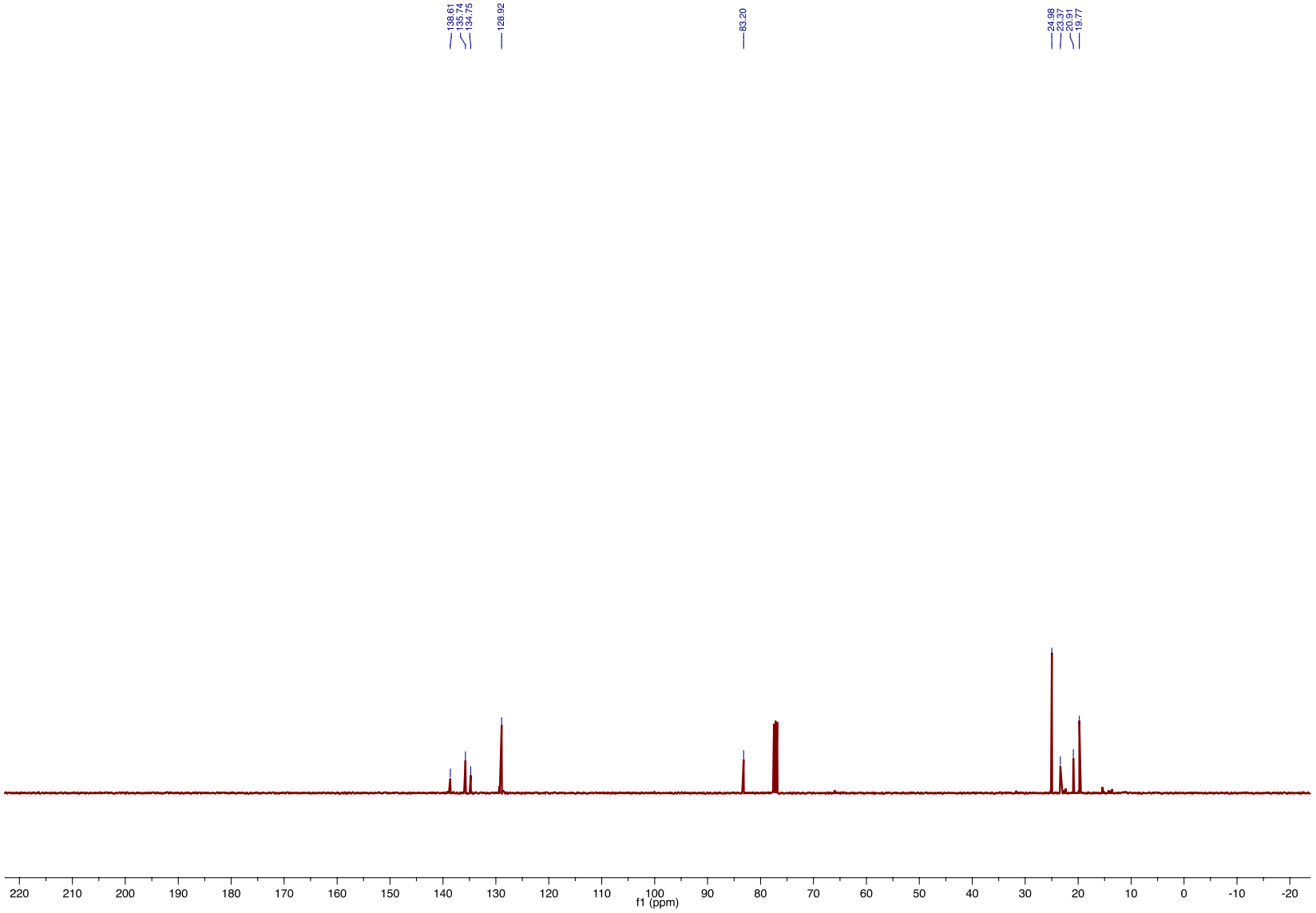


Figure S23. ^{13}C NMR of 2-(1-mesitylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3h)** and 4,4,5,5-tetramethyl-2-(2,4,6-trimethylphenethyl)-1,3,2-dioxaborolane (**3h'**)

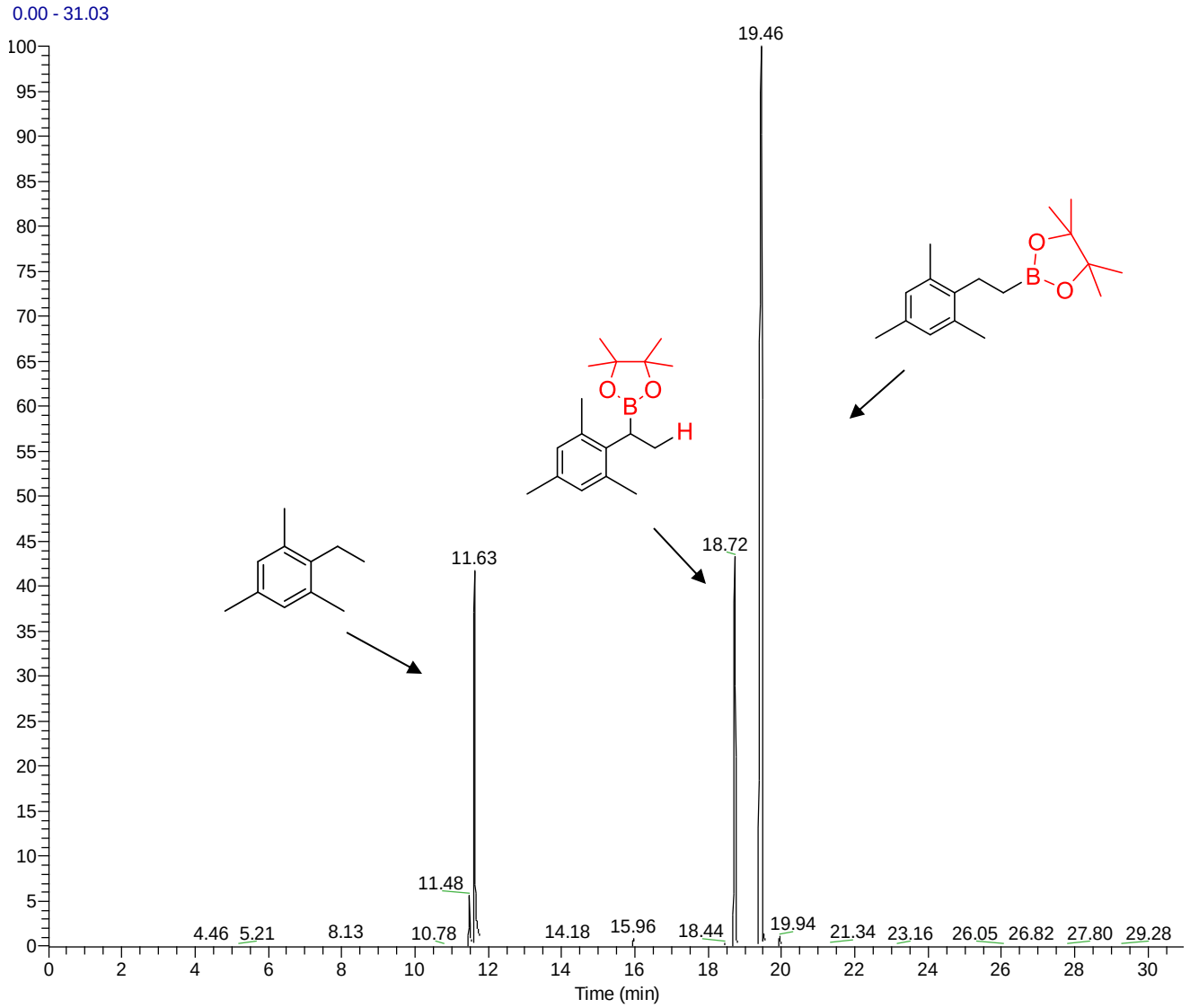


Figure S24. GC-MS of 2-(1-mesitylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3h)** and 4,4,5,5-tetramethyl-2-(2,4,6-trimethylphenethyl)-1,3,2-dioxaborolane (**3h'**)

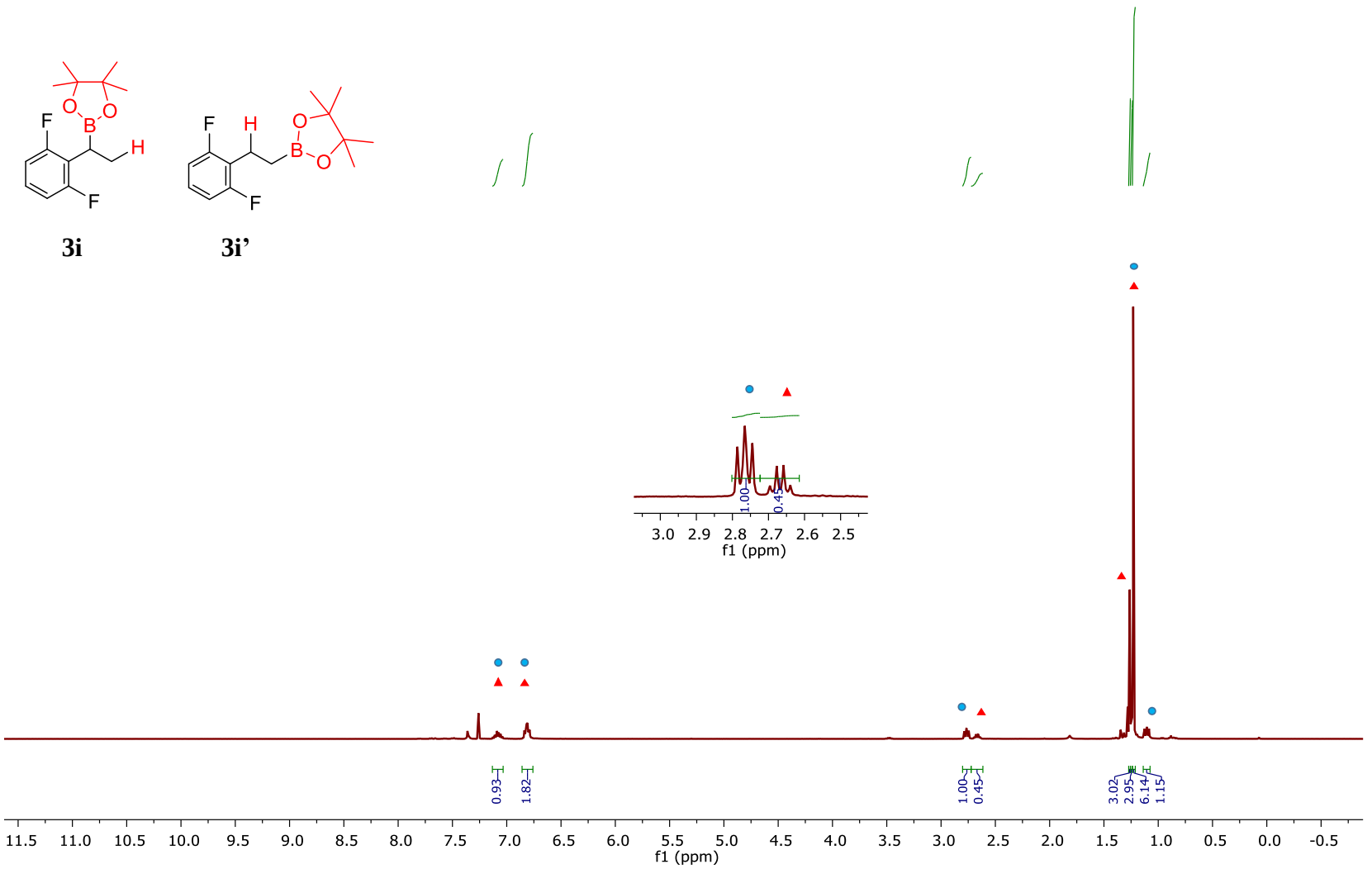


Figure S25. ^{1}H NMR of 2-(1-(2,6-difluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3i)** (▲) and 2-(2,6-difluorophenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3i')** (●)

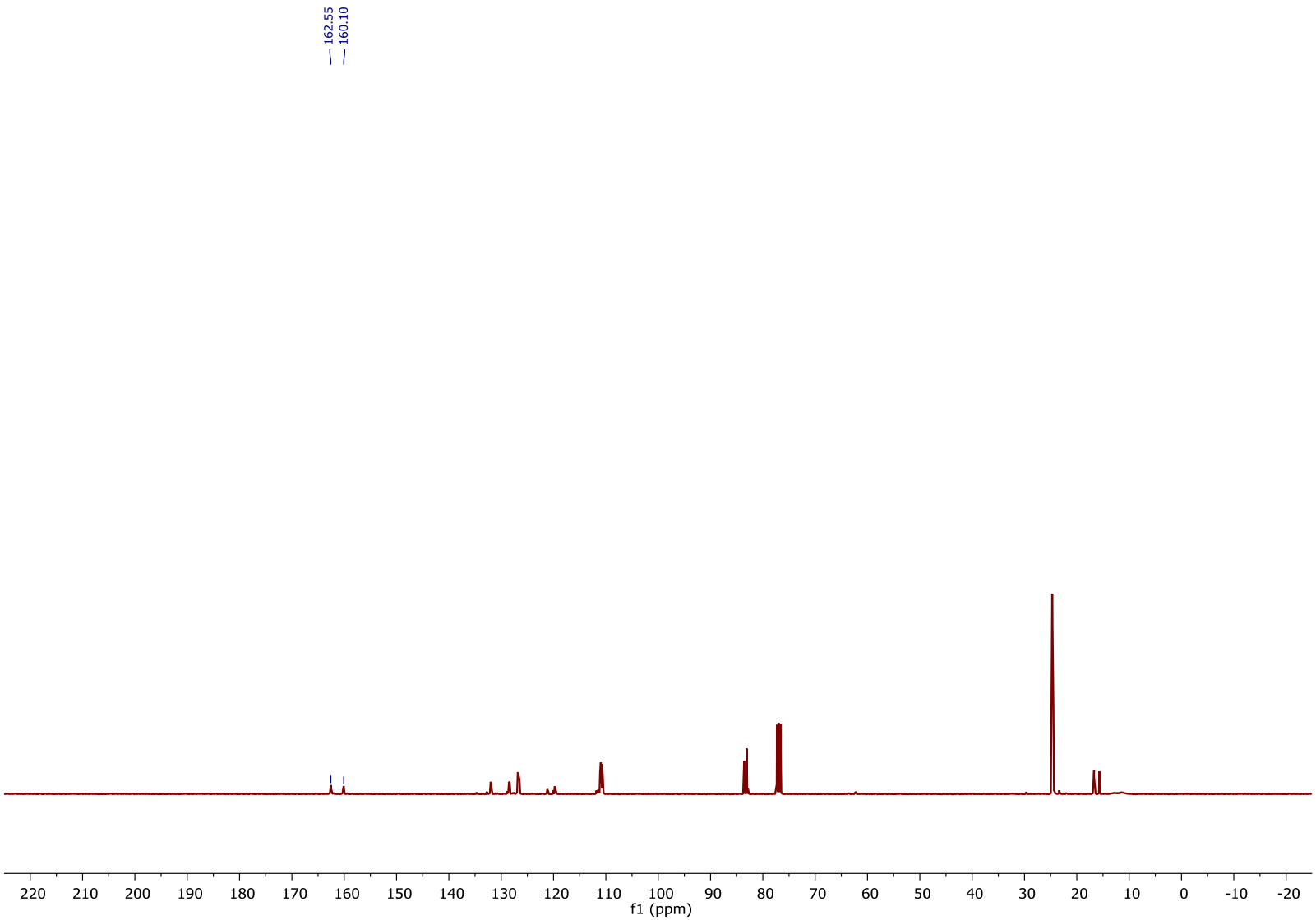


Figure S26. ^{13}C NMR of 2-(1-(2,6-difluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3i)** (▲) and 2-(2,6-difluorophenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i')** (●)

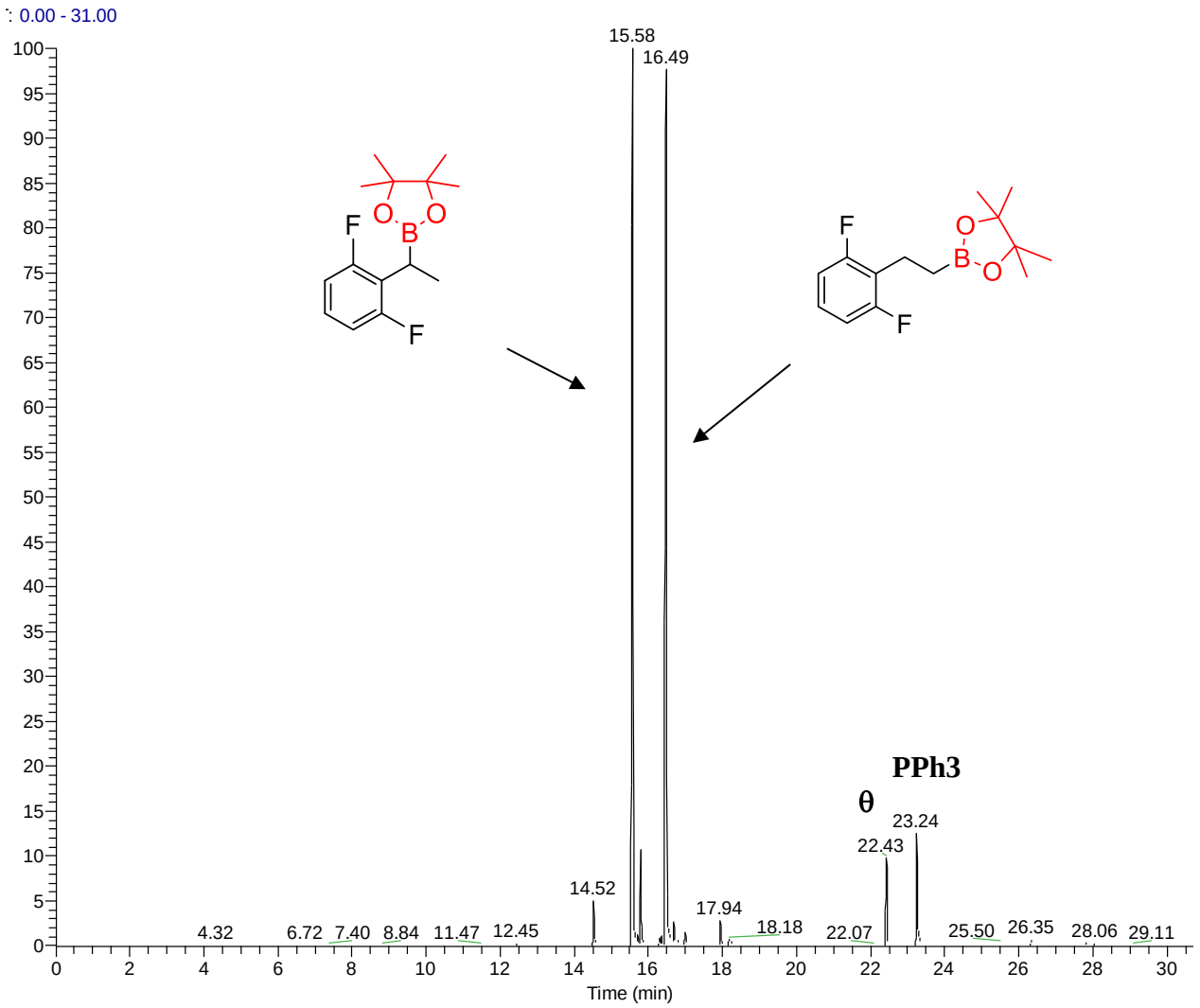


Figure S27. GC-MS of 2-(1-(2,6-difluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3i)** and 2-(2,6-difluorophenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i'). (θ)** represents the dehydrogenative borylation product.

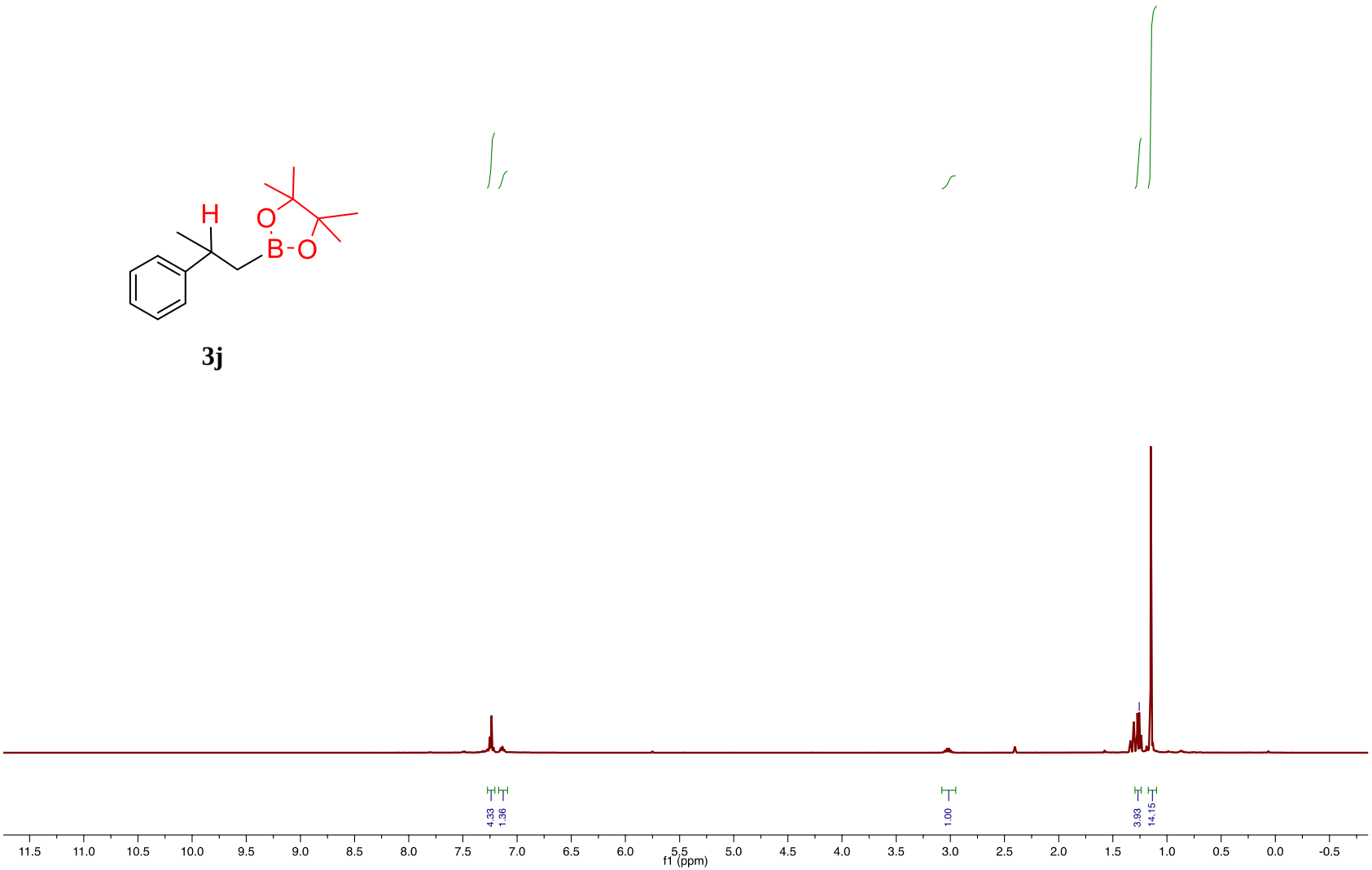


Figure S28. ^{1}H NMR of 4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (**3j**)

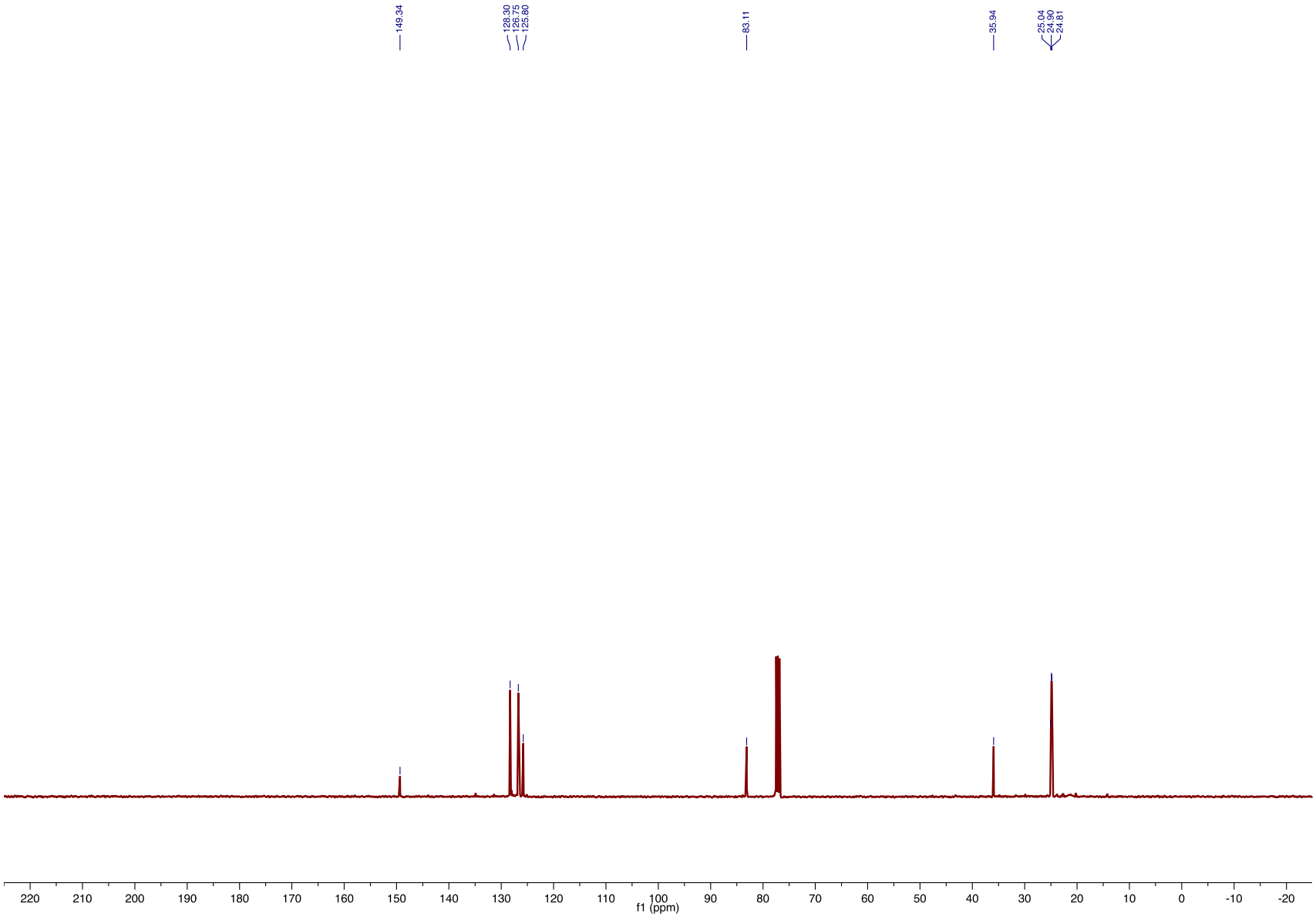


Figure S29. ^{13}C NMR of 4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (**3j**)

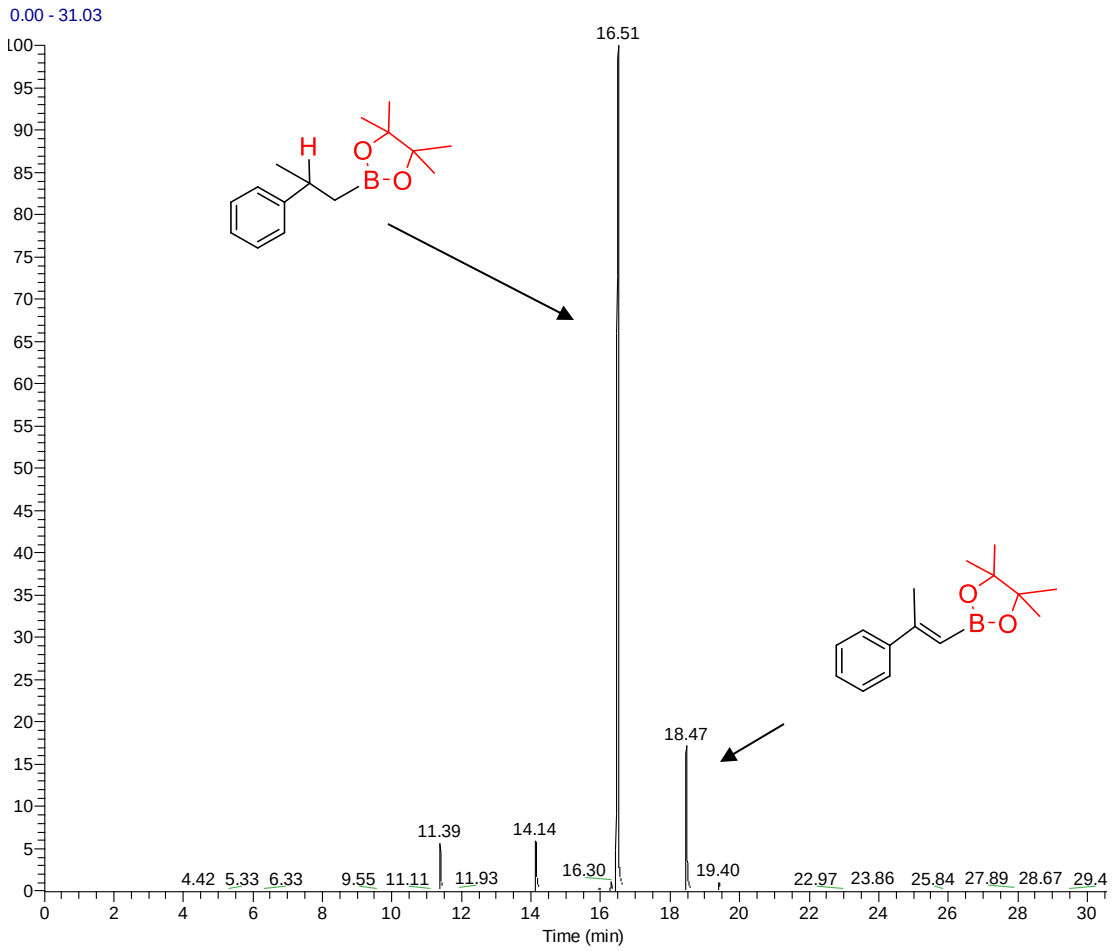


Figure S30. GC-MS of 4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (**3j**)

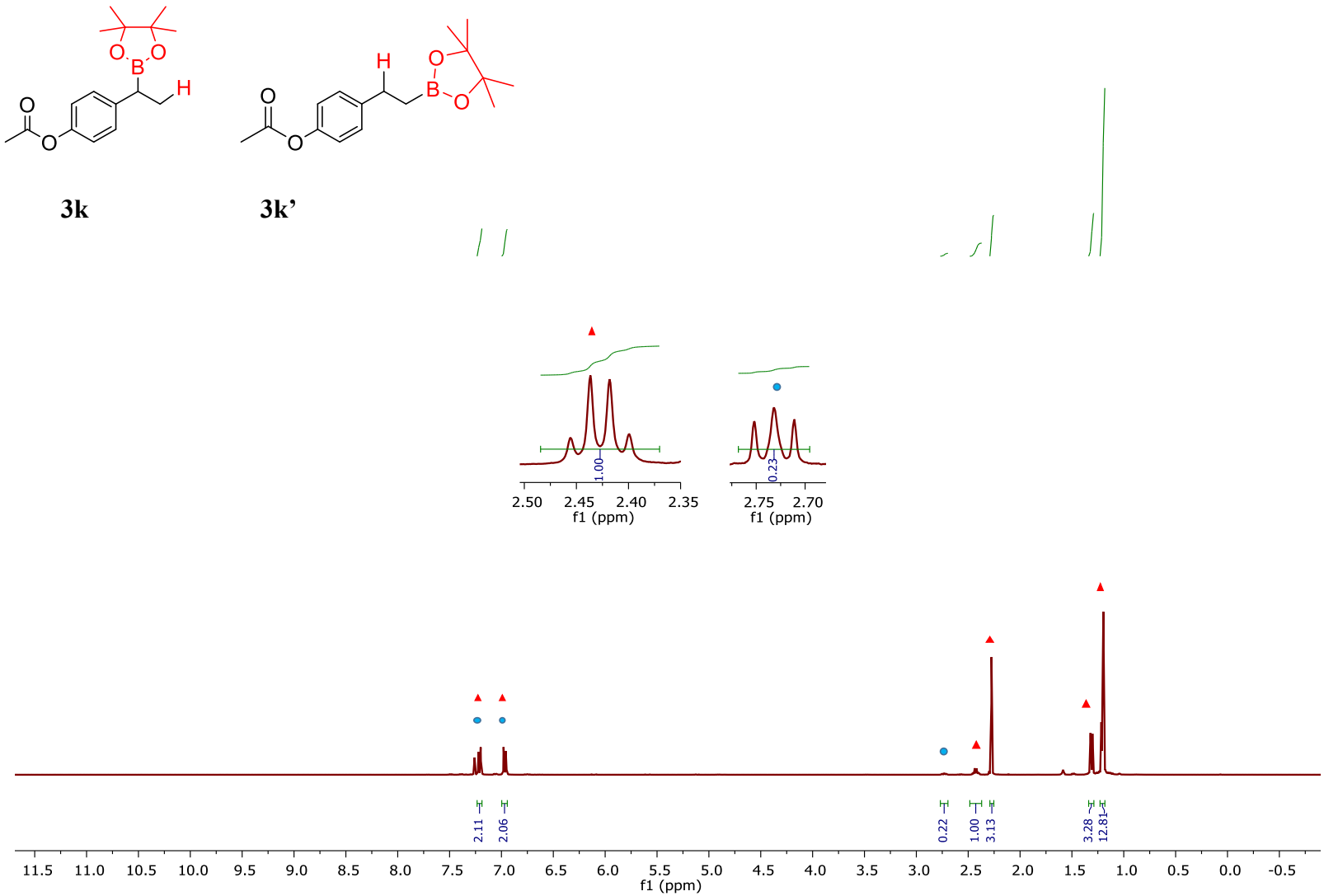


Figure S31. ^{1}H NMR of 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate **(3k)** (▲) and 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate (**3k'**) (●)

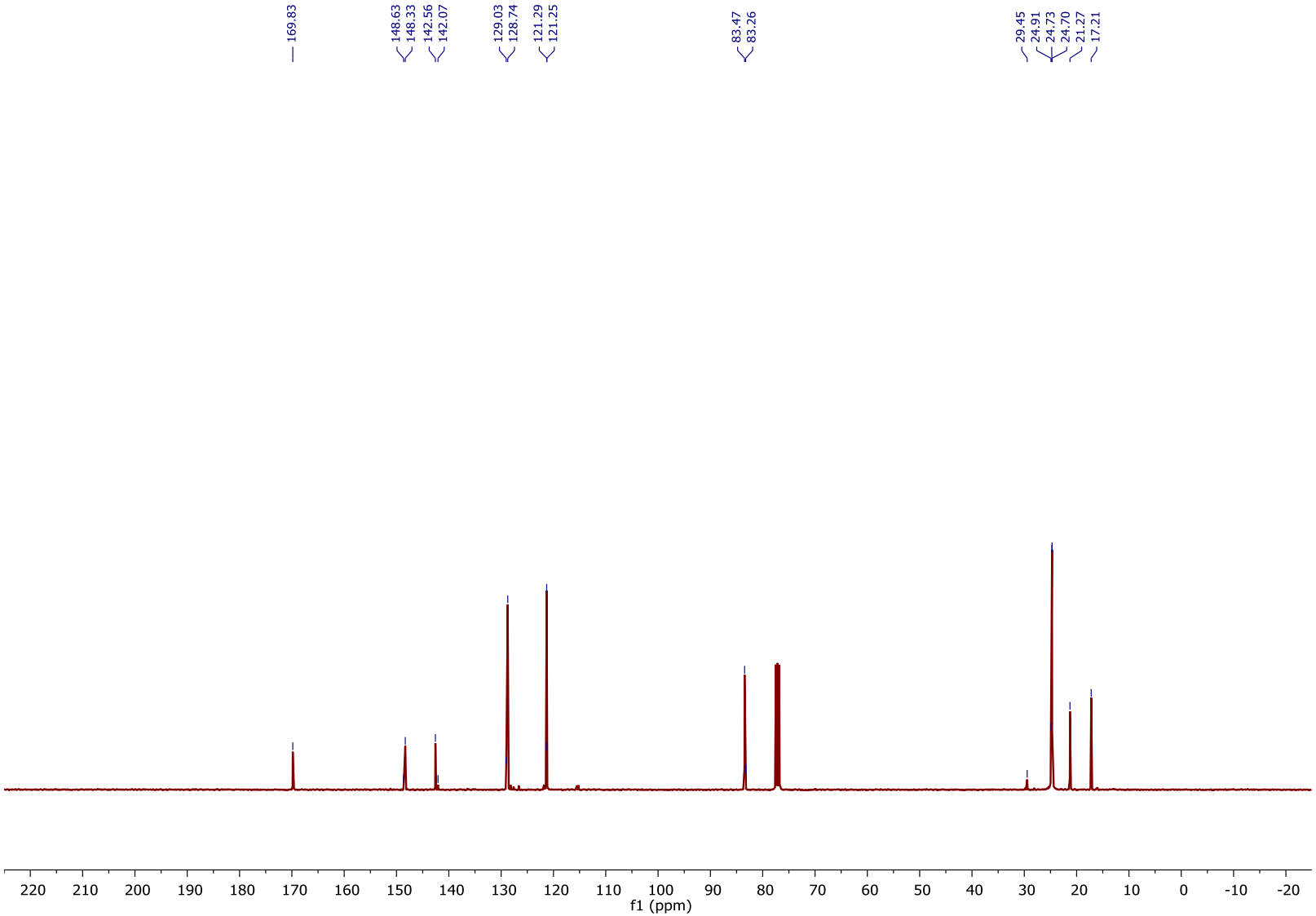


Figure S32. ^{13}C NMR of 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate **(3k)** and 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate (**3k')**

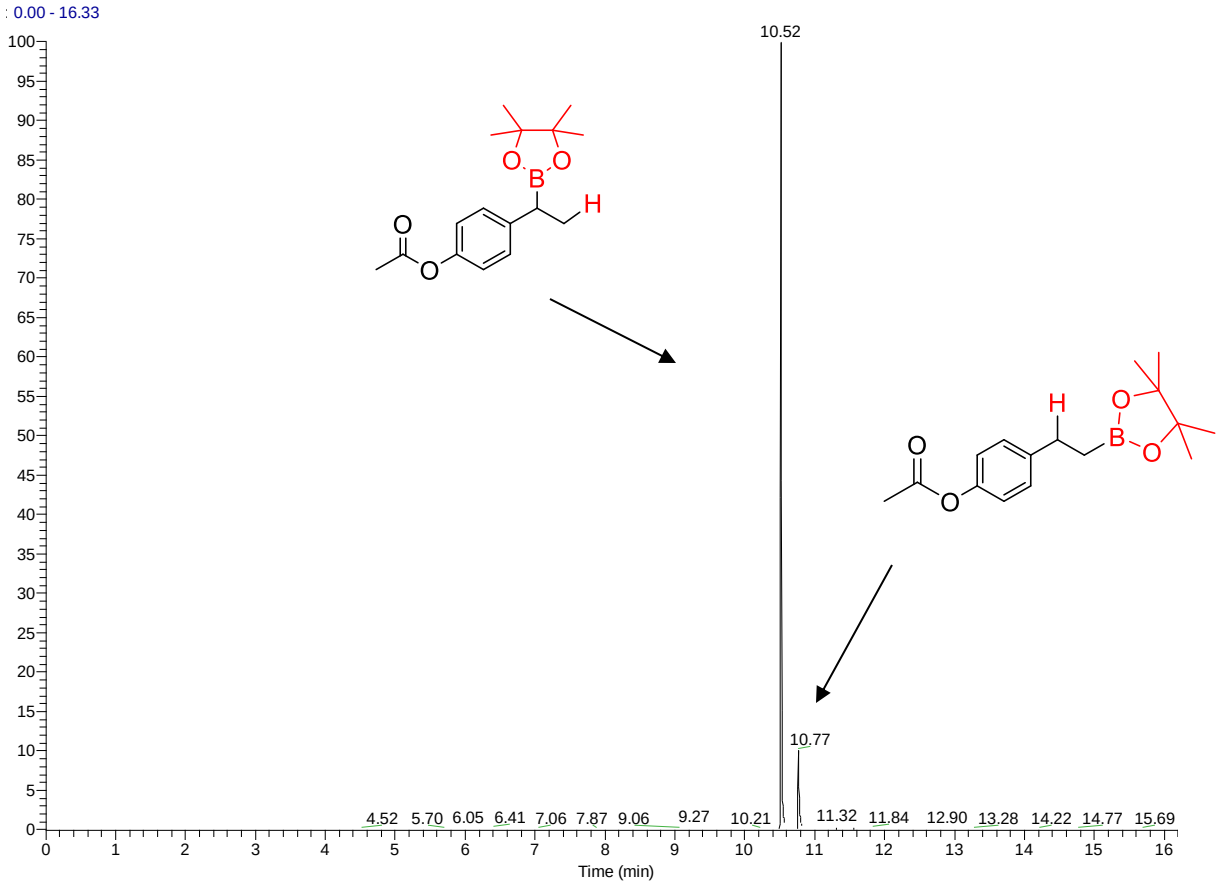


Figure S33. GC-MS of 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate **(3k)** and 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate (**3k'**)

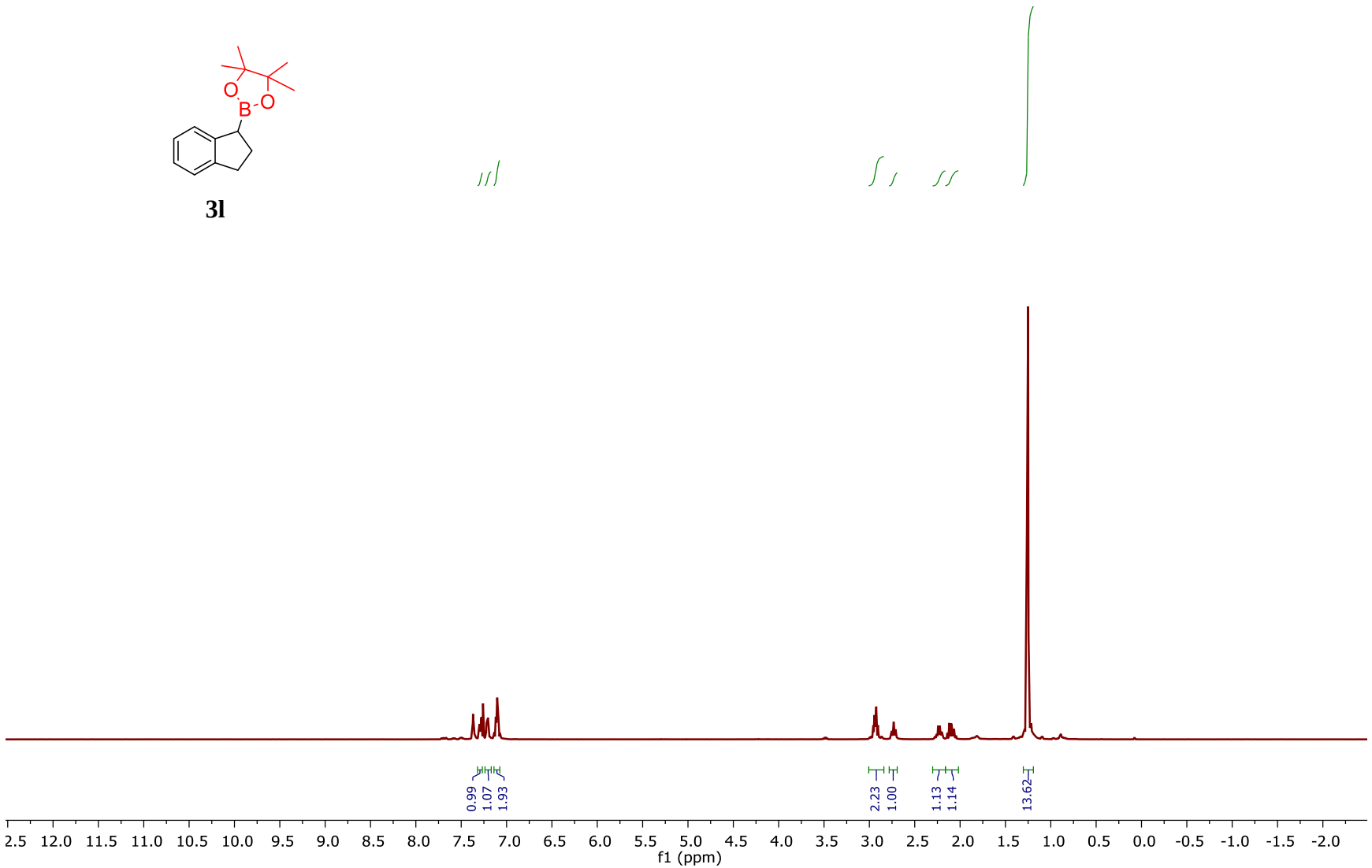


Figure S34. ^{1}H NMR of 2-(2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3l)**

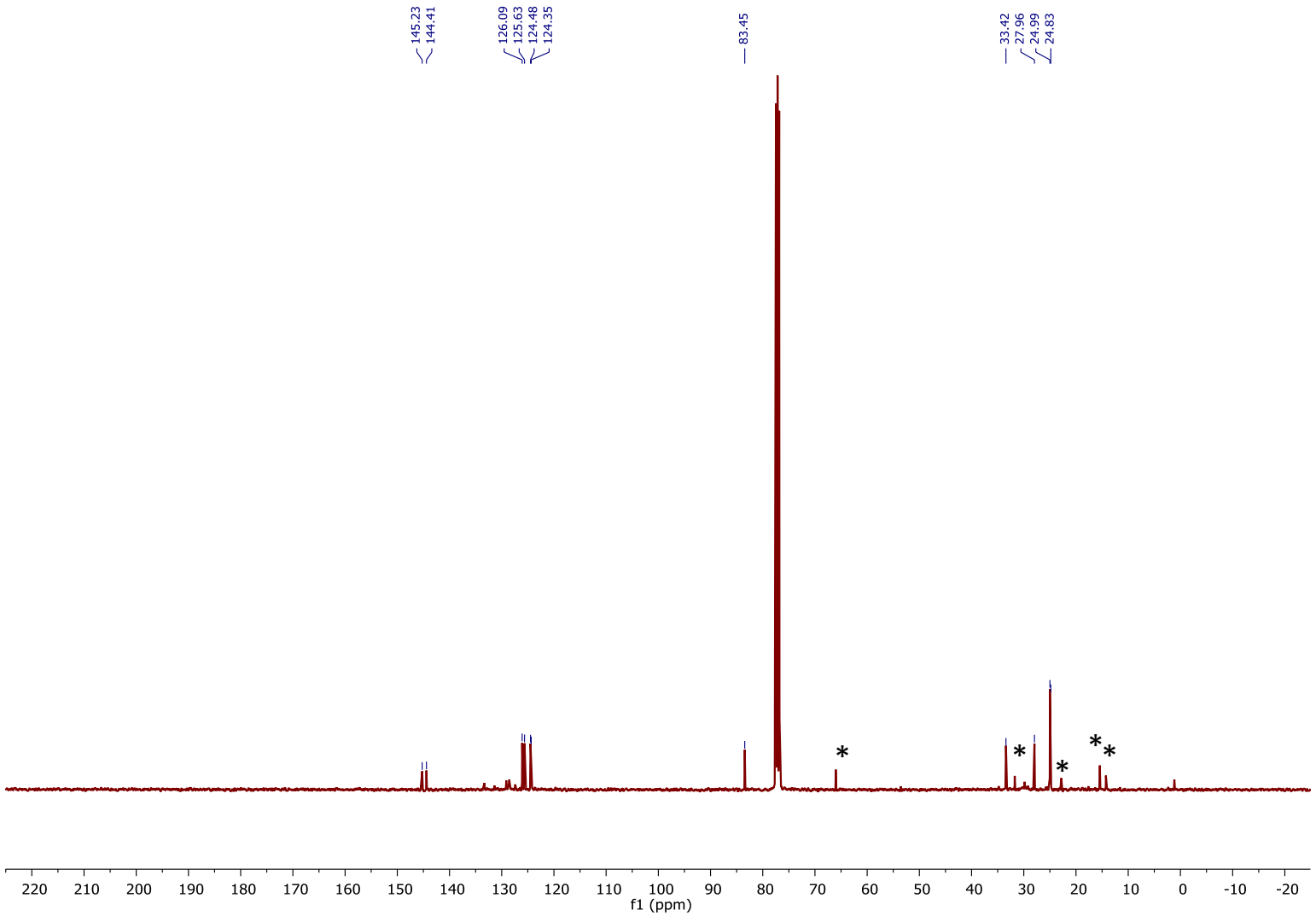


Figure S35. ^{13}C NMR of 2-(2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3l). (*)** represent solvent peaks.

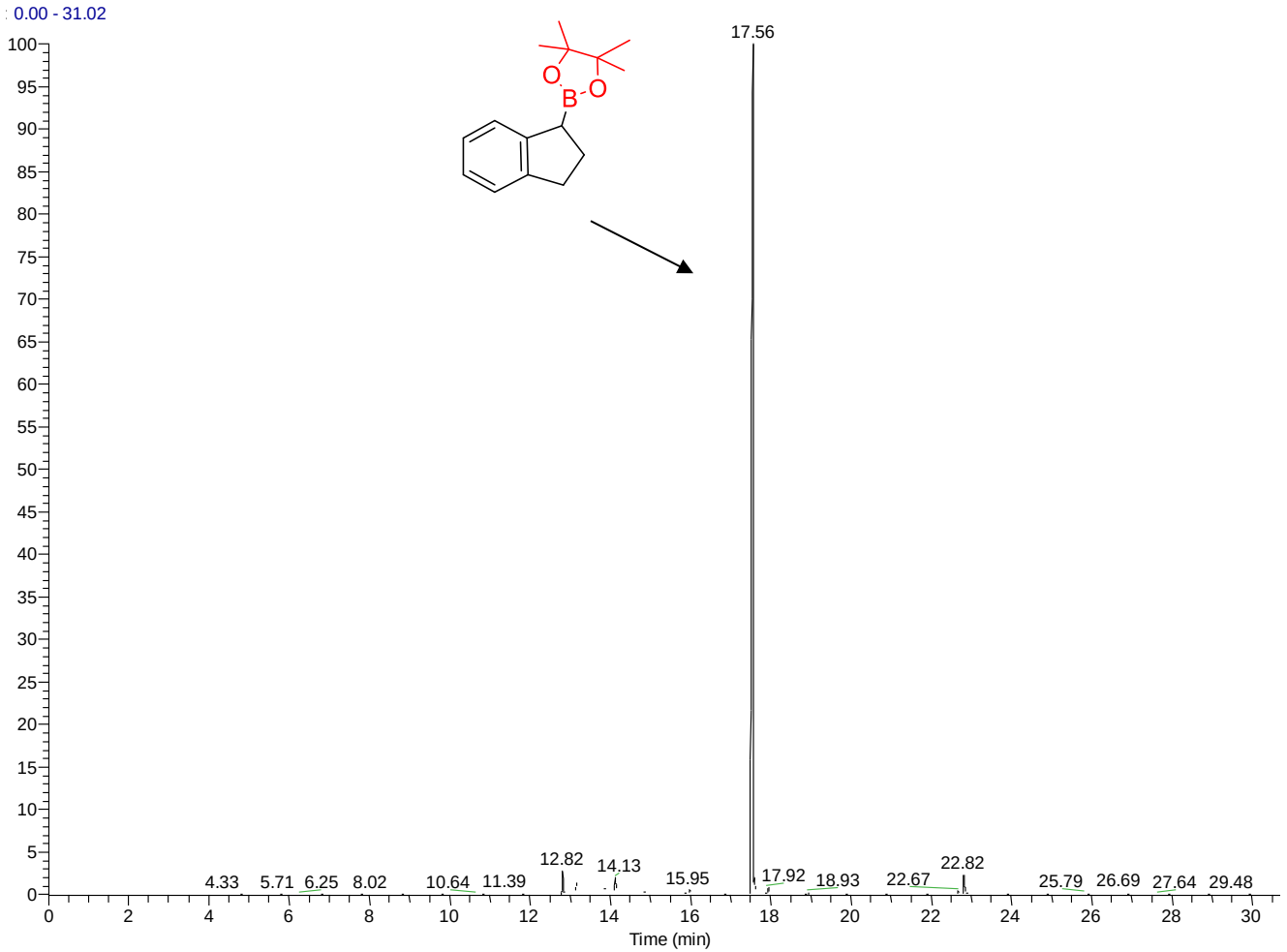


Figure S36. GC-MS of 2-(2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3l)**

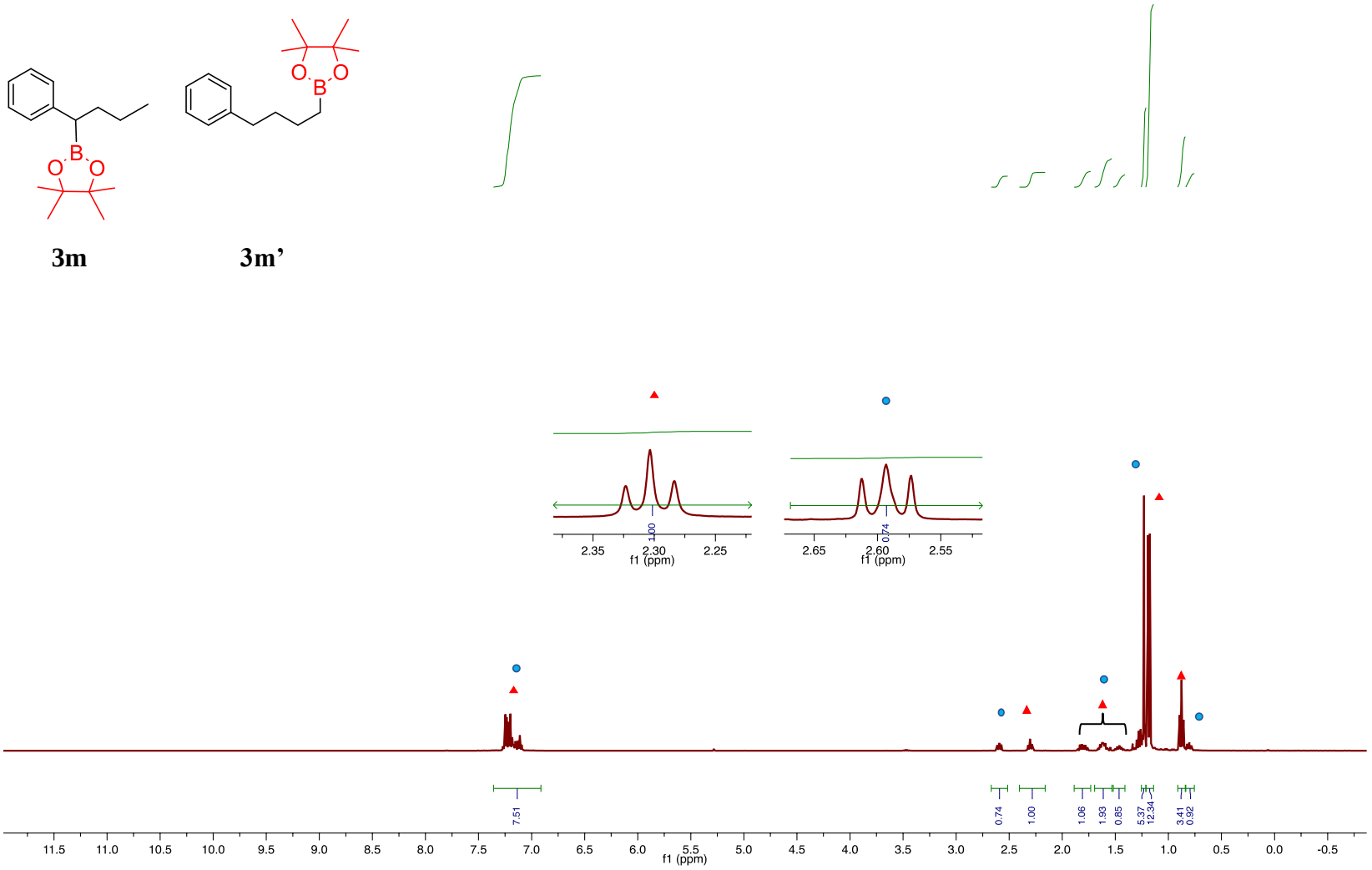


Figure S37. ^{1}H NMR of 4,4,5,5-tetramethyl-2-(1-phenylbutyl)-1,3,2-dioxaborolane **(3m)** (▲) and 4,4,5,5-tetramethyl-2-(4-phenylbutyl)-1,3,2-dioxaborolane (**3m’**) (●)

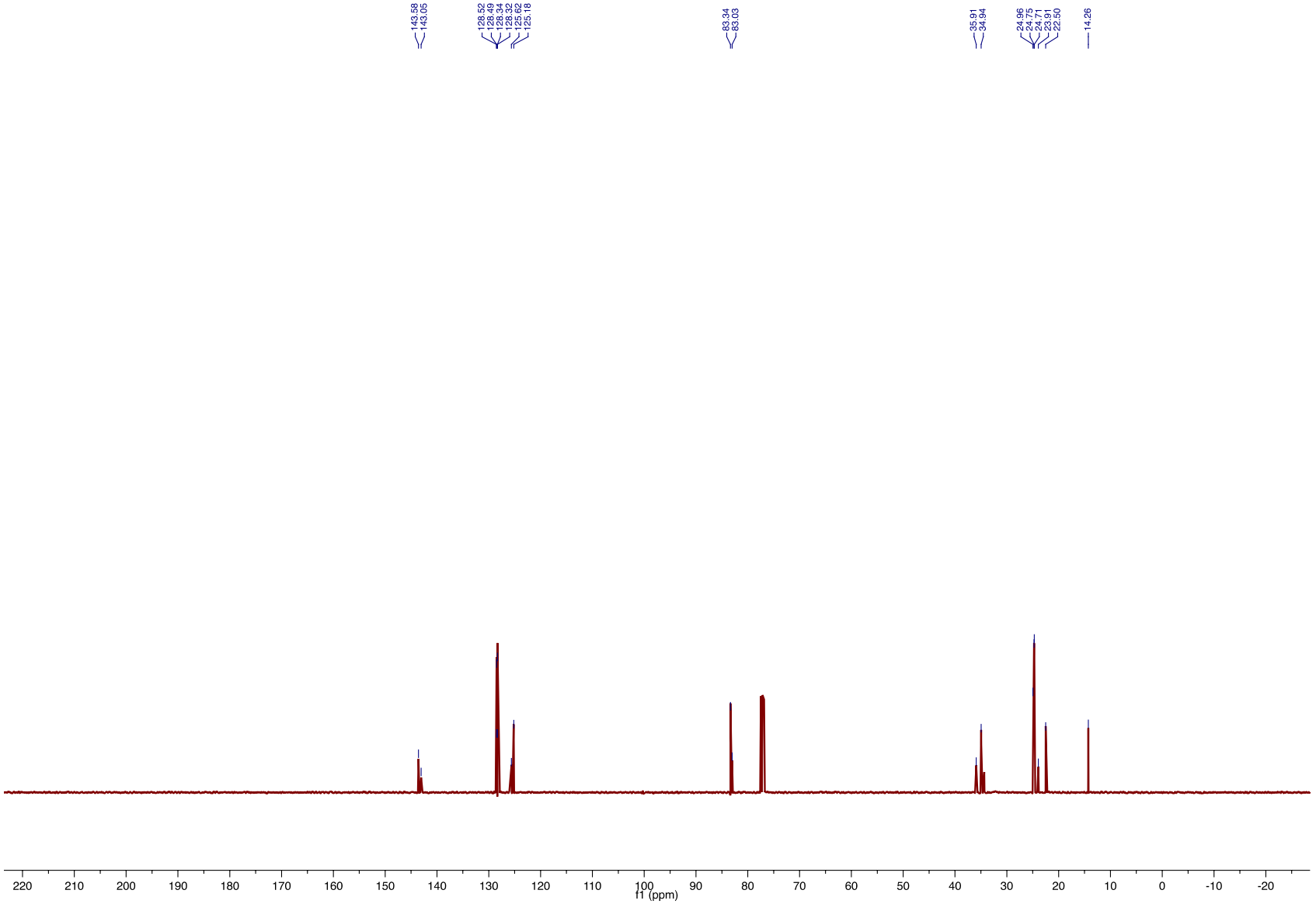


Figure S38. ^{13}C NMR of 4,4,5,5-tetramethyl-2-(1-phenylbutyl)-1,3,2-dioxaborolane **(3m)** and 4,4,5,5-tetramethyl-2-(4-phenylbutyl)-1,3,2-dioxaborolane (**3m'**)

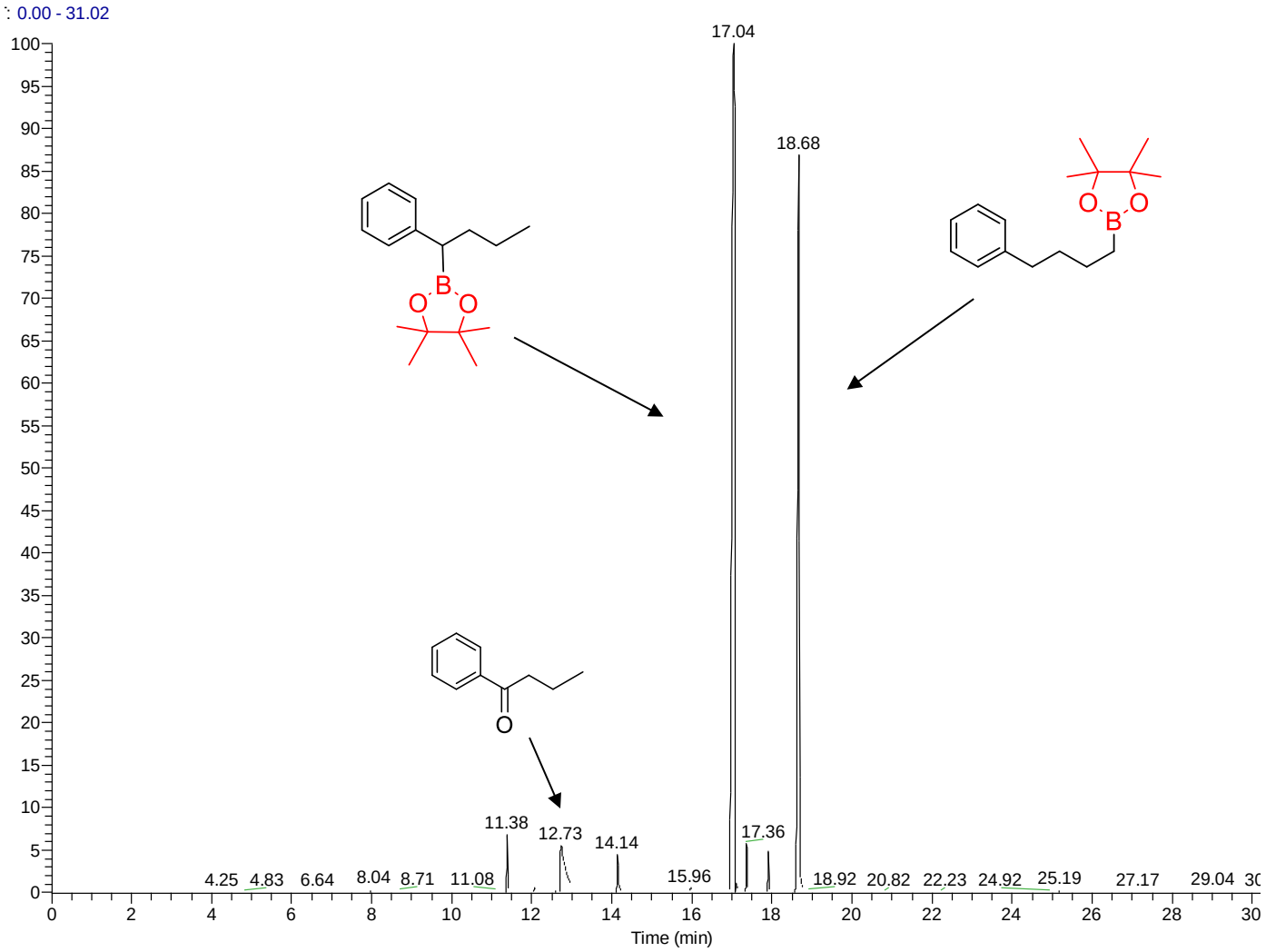


Figure S39. GC-MS of 4,4,5,5-tetramethyl-2-(1-phenylbutyl)-1,3,2-dioxaborolane **(3m)** and 4,4,5,5-tetramethyl-2-(4-phenylbutyl)-1,3,2-dioxaborolane (**3m'**)

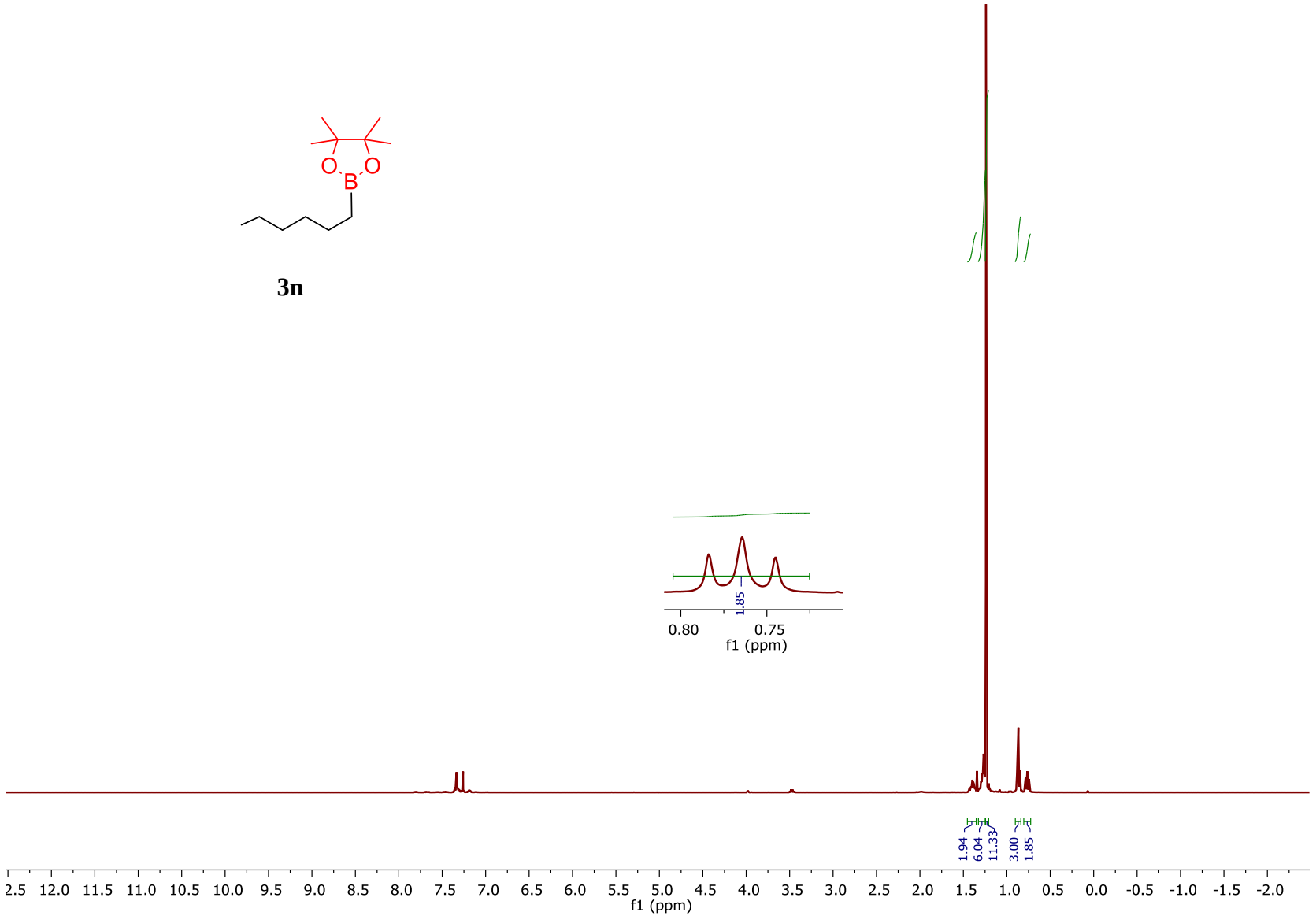


Figure S40. ^{1}H NMR of 2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3n)**

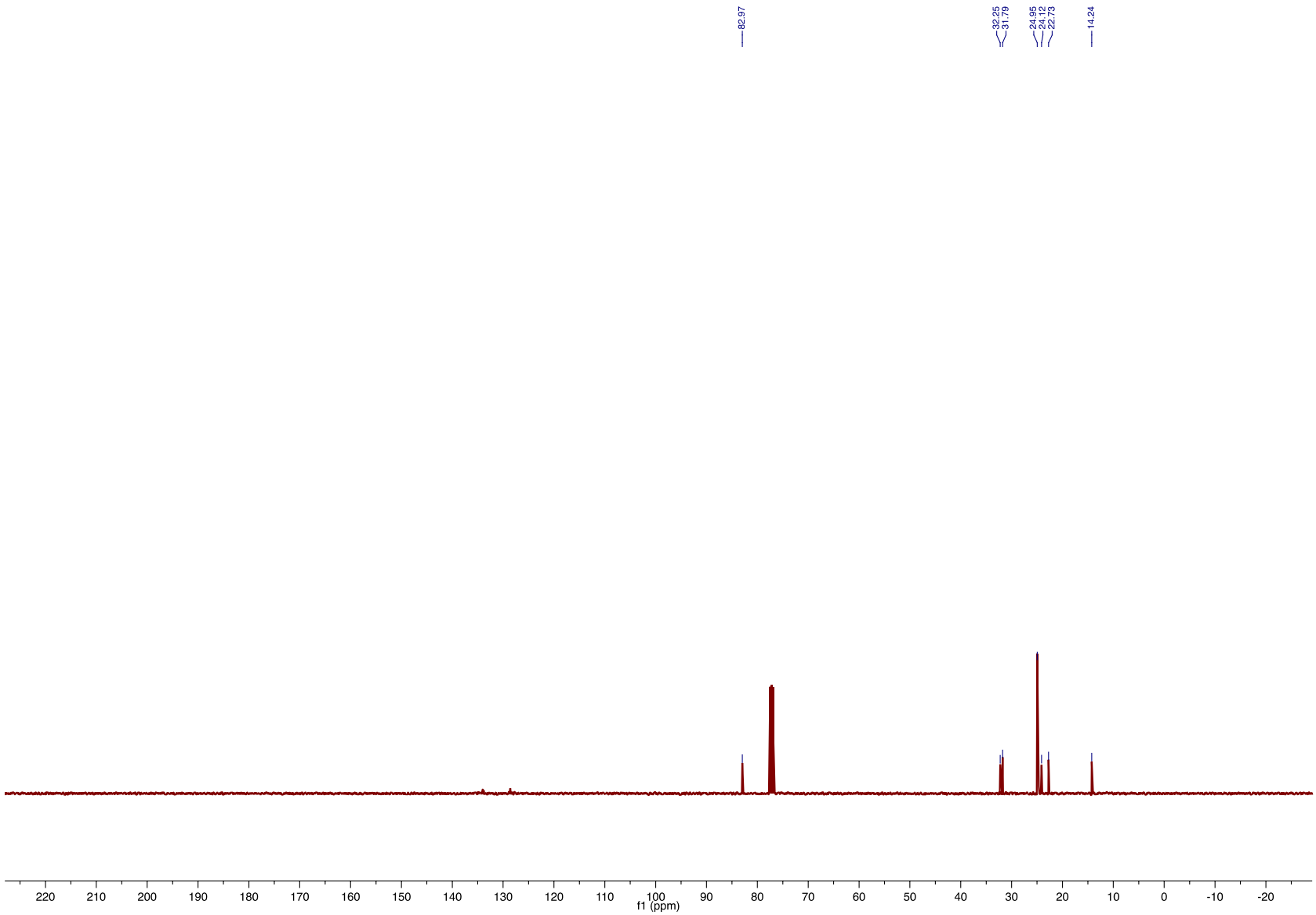


Figure S41. ^{13}C NMR of 2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3n)**

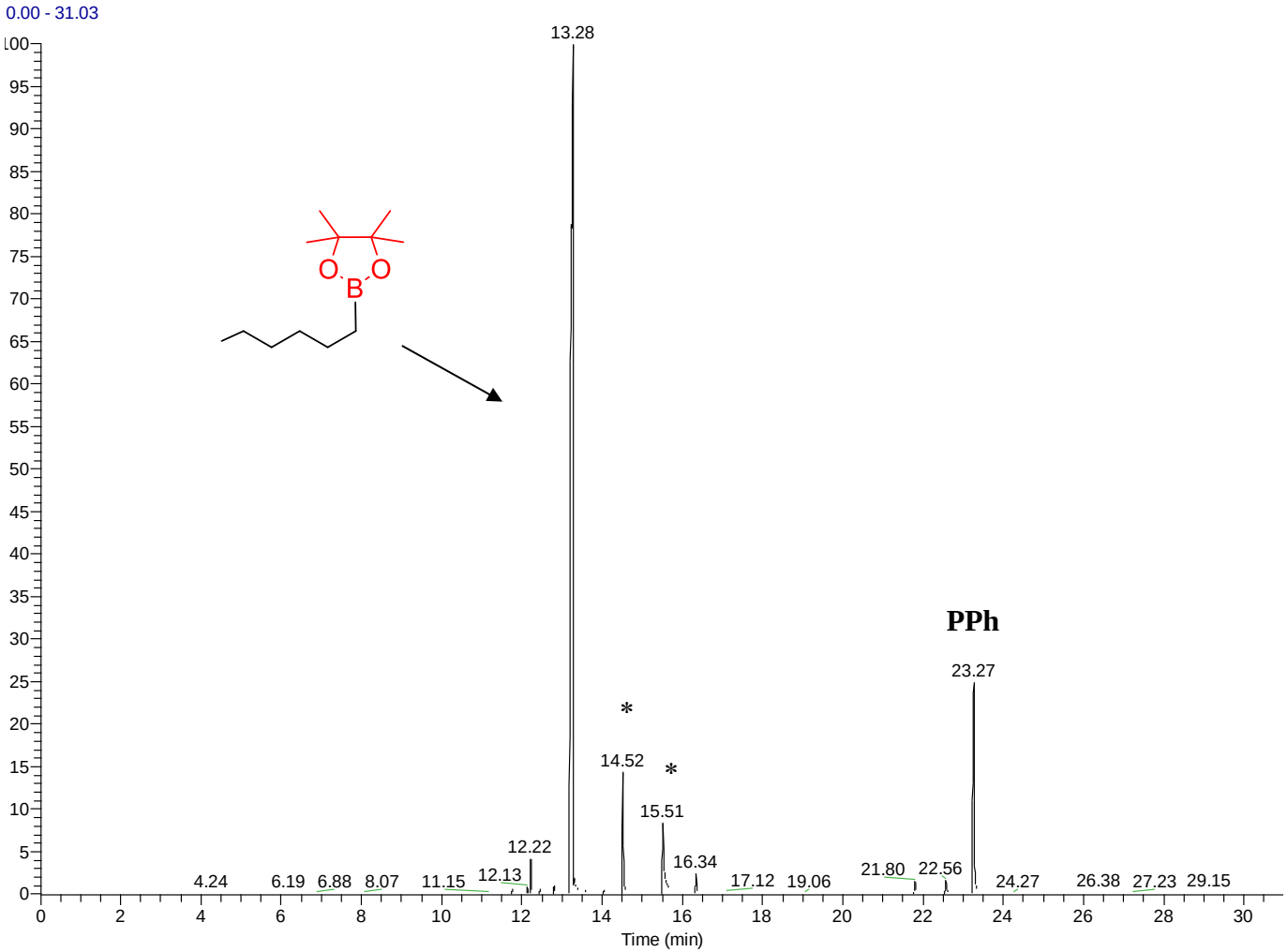


Figure S42. ^{13}C NMR of 2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3n). (∗)** represents unknown impurities

5. ^{11}B, ^{1}H and ^{13}C NMR of 1º alcohol

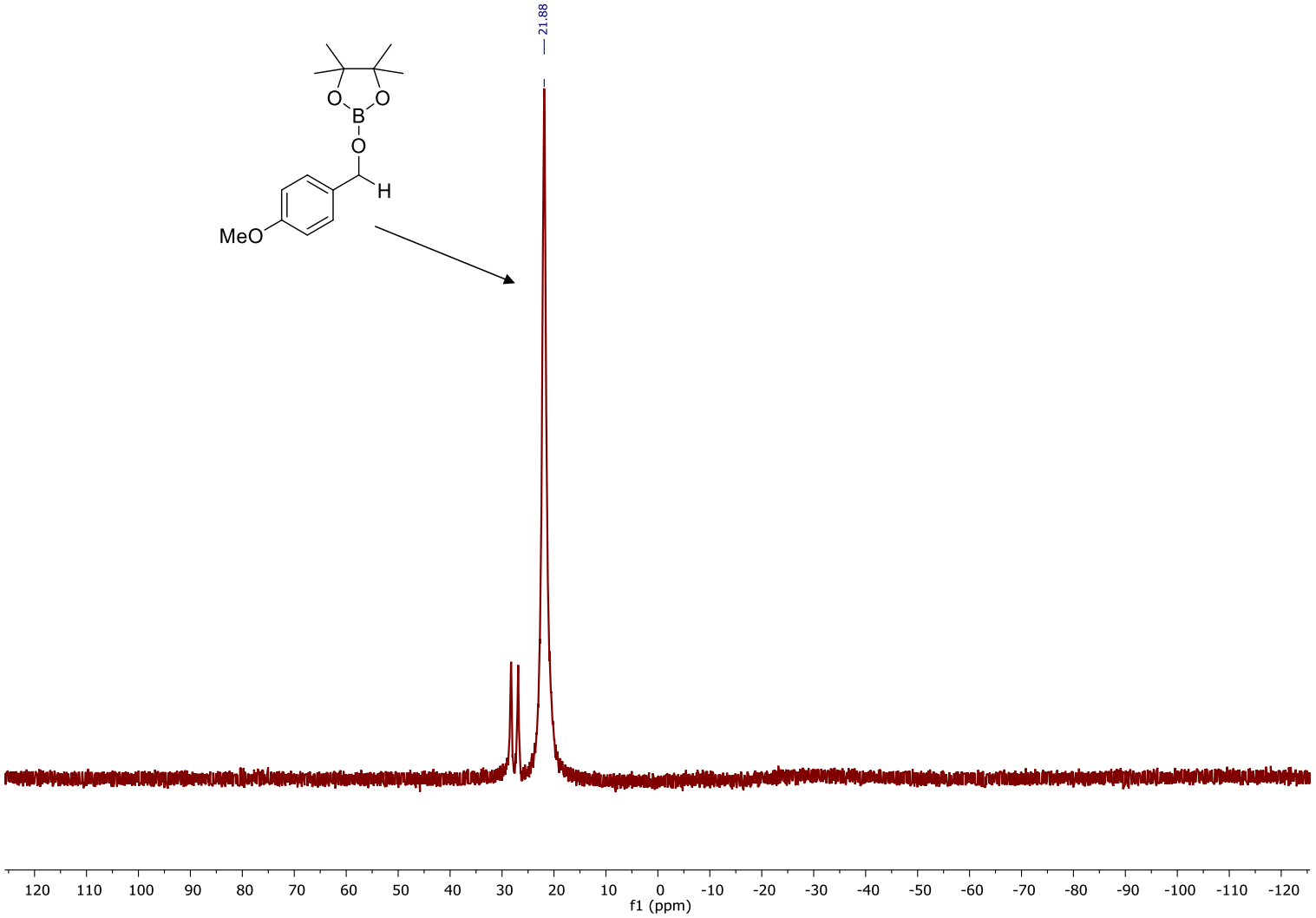


Figure S43. ^{11}B NMR resulting from catalytic hydroboration of **5a**

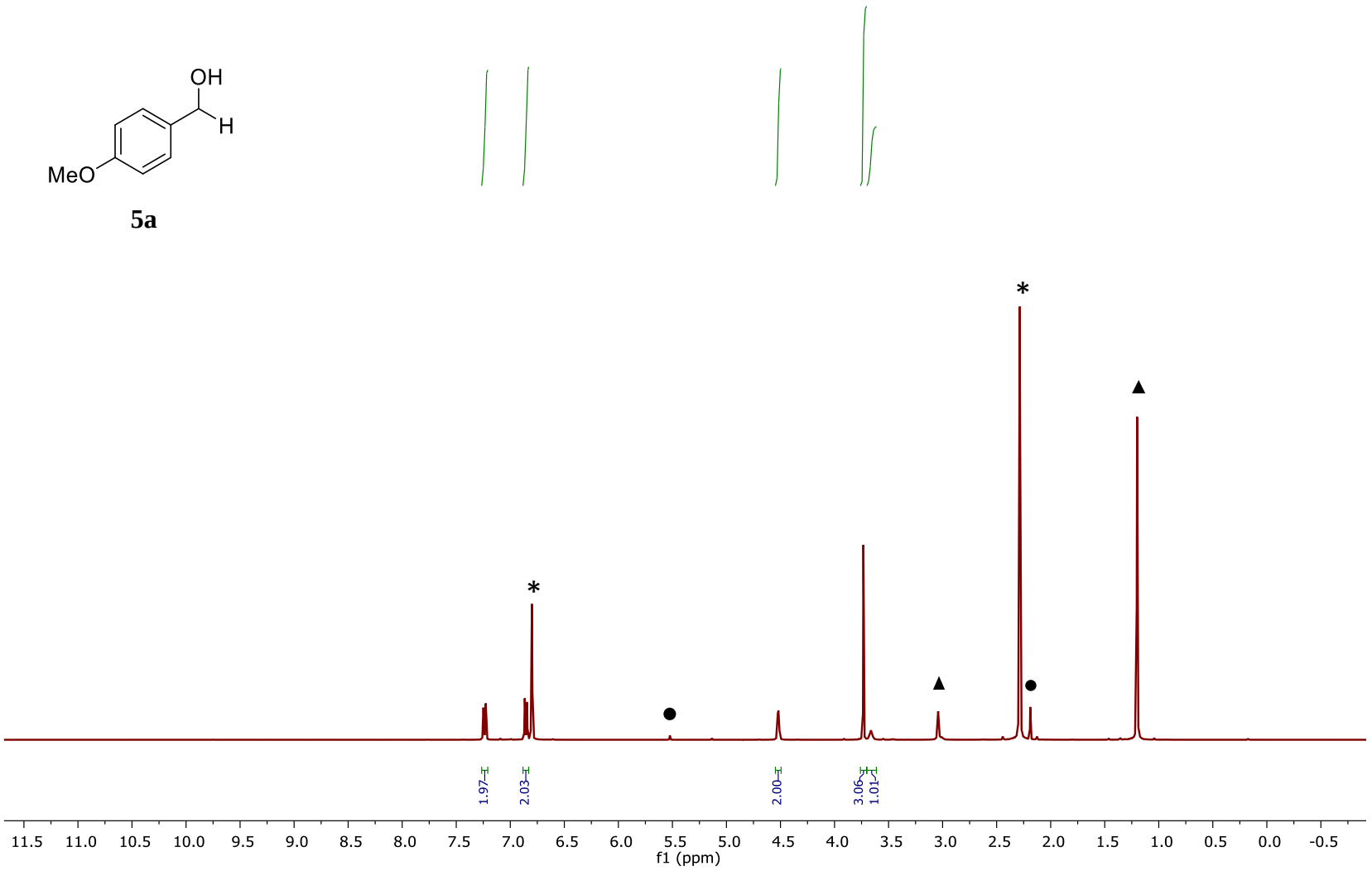


Figure S44. ^{1}H NMR of 4-methoxybenzyl alcohol (**5a**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinacol

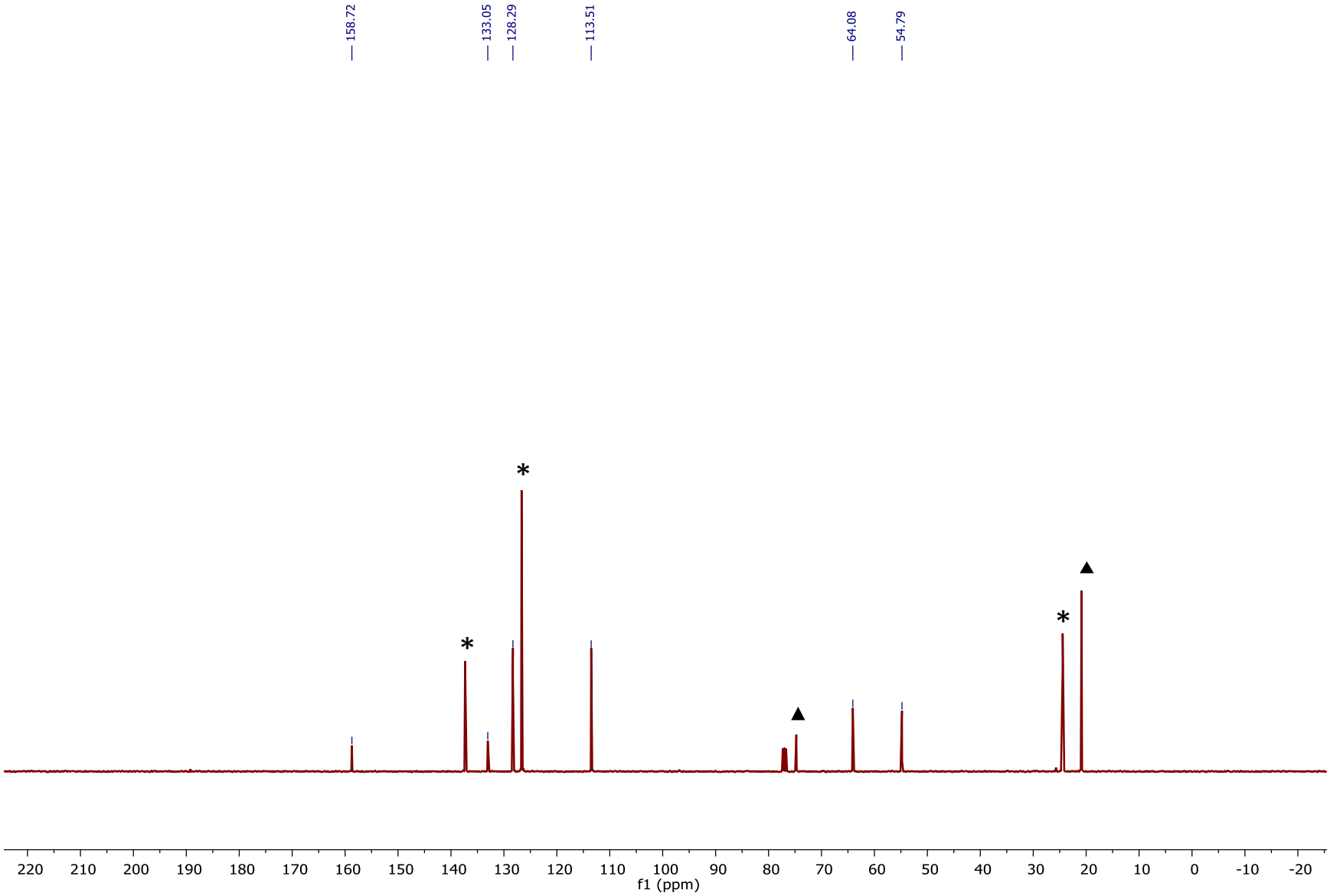


Figure S45. ^{13}C NMR of 4-methoxybenzyl alcohol (**5a**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

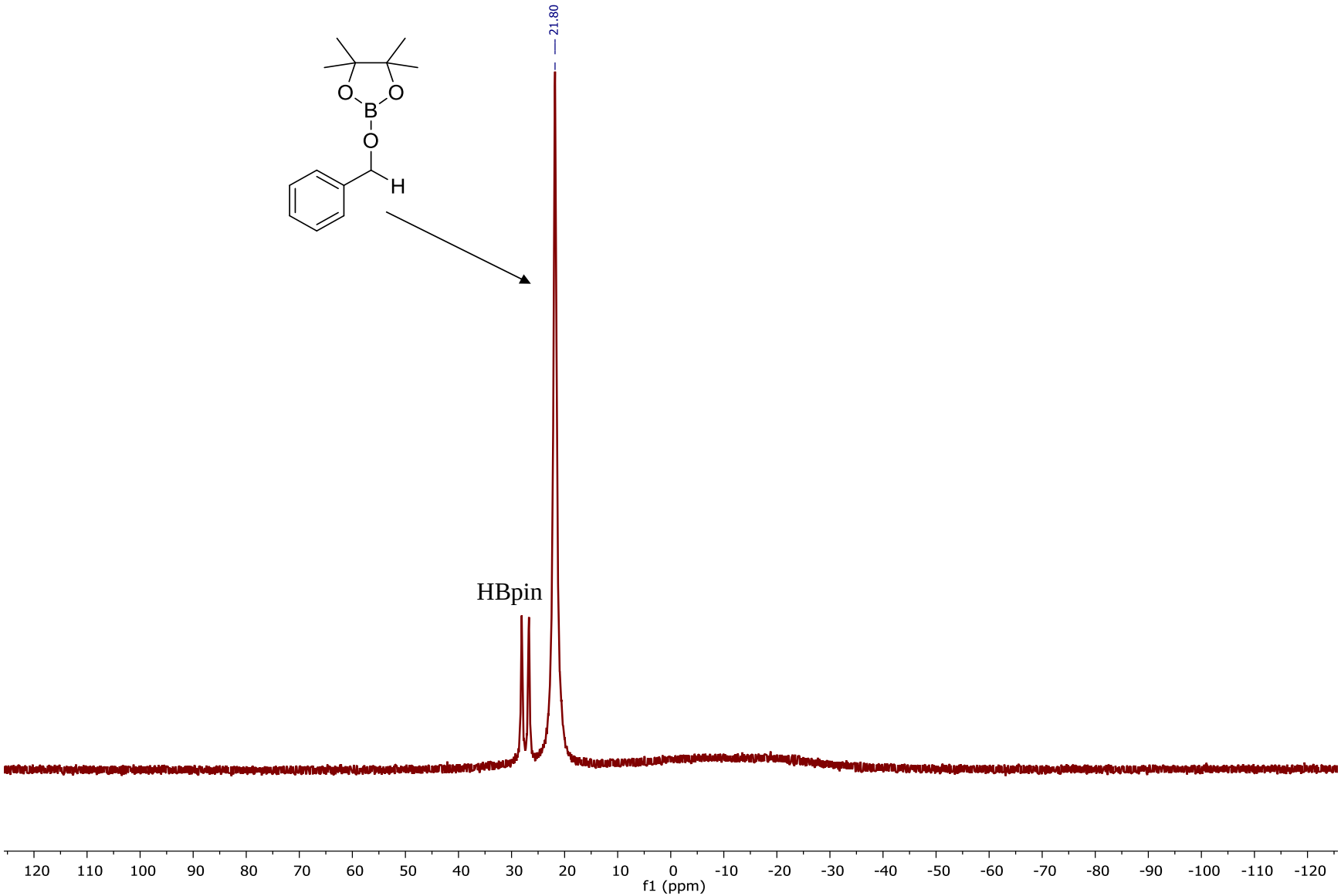


Figure S46. ^{11}B NMR resulting from catalytic hydroboration of **5b**

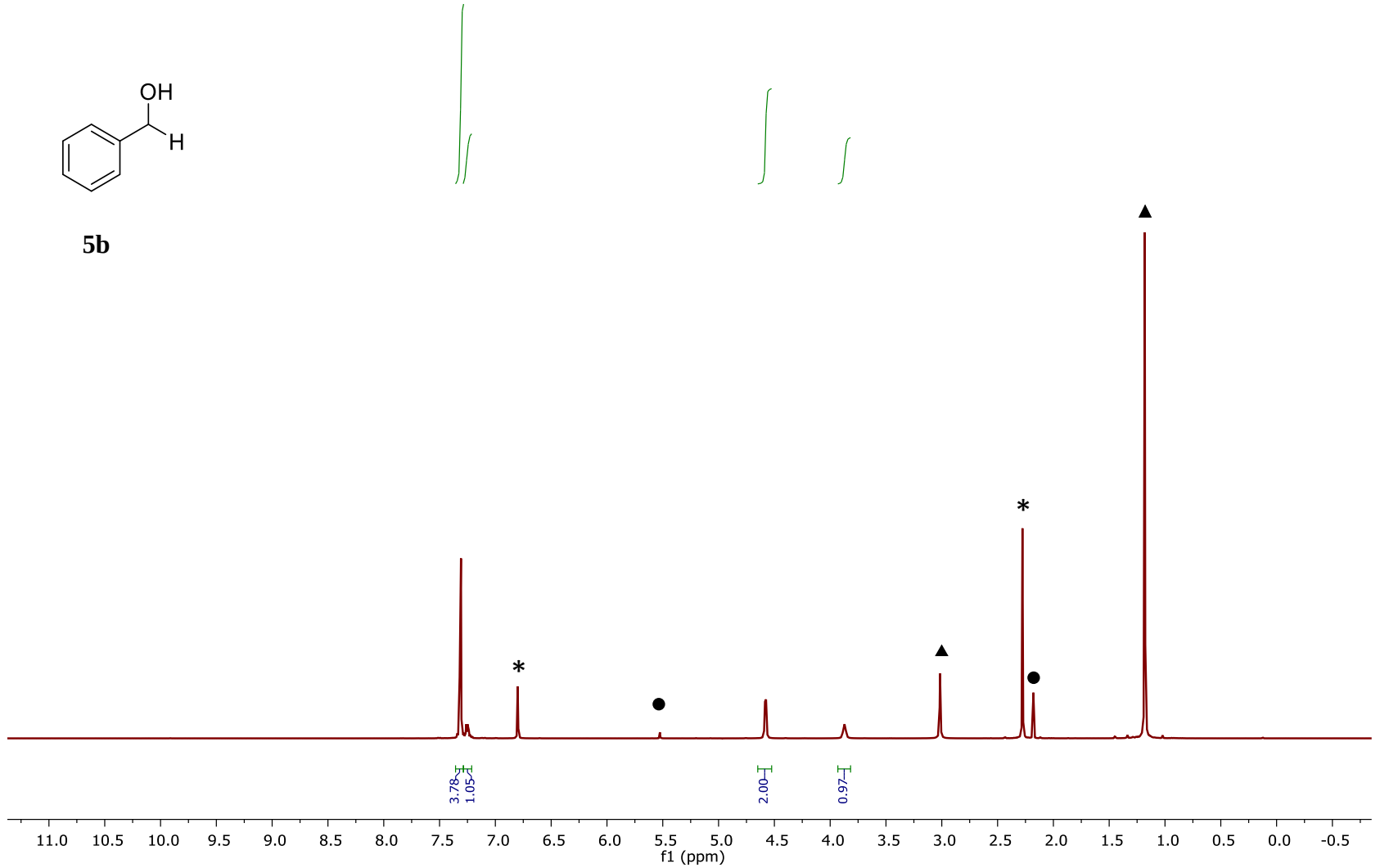


Figure S47. ^{1}H NMR of Benzyl alcohol (**5b**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

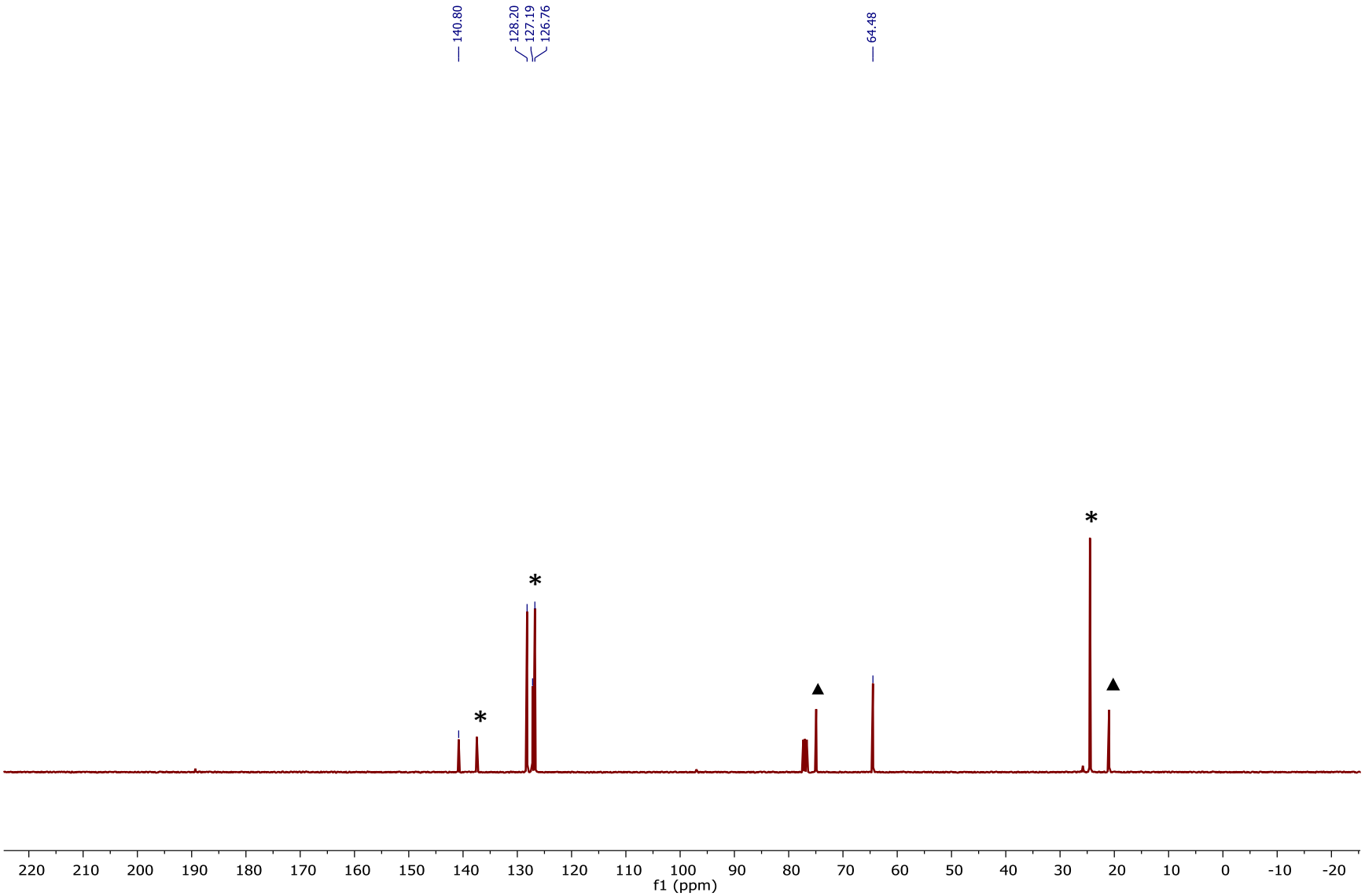


Figure S48. ^{13}C NMR of Benzyl alcohol (**5b**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

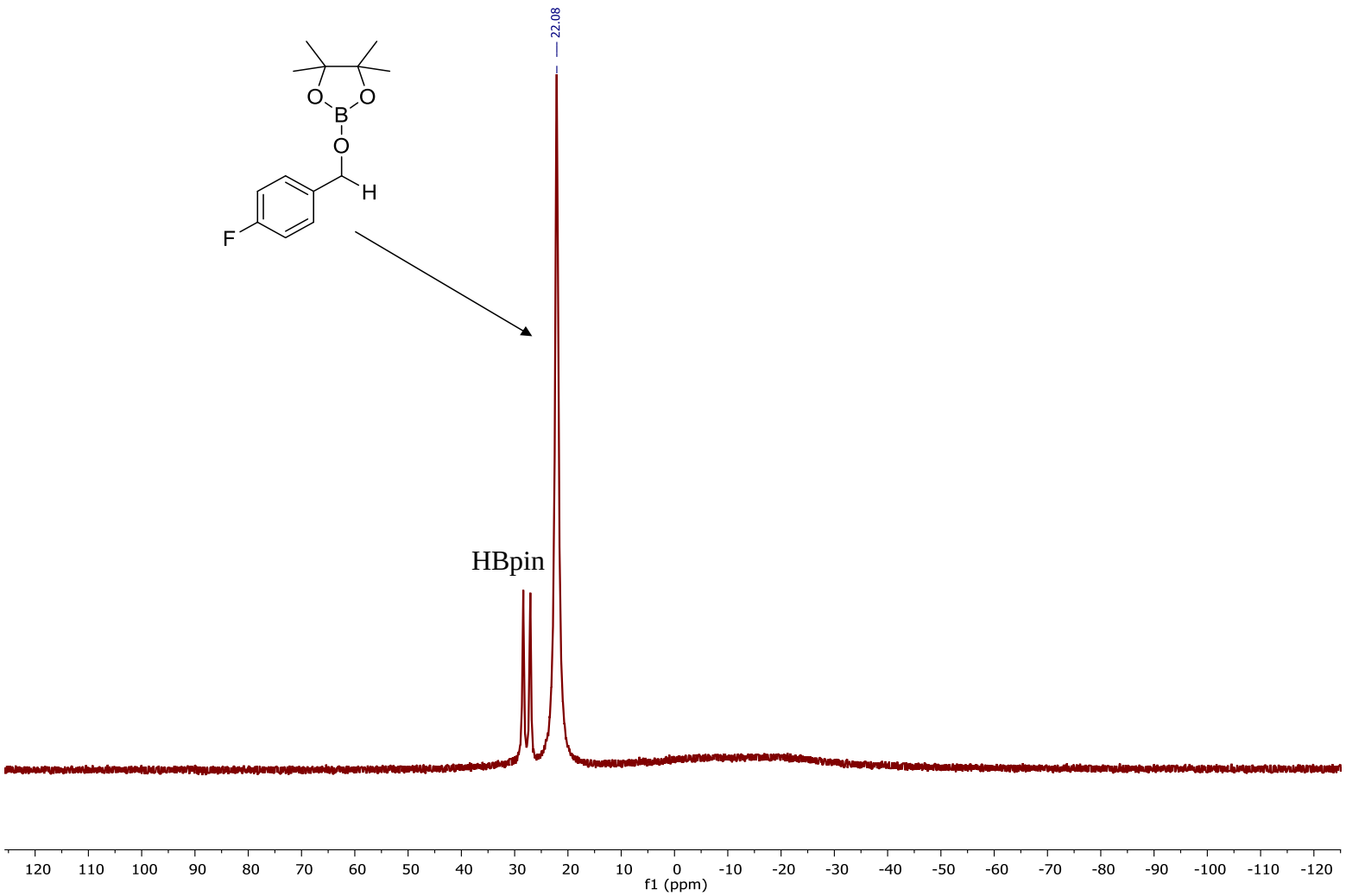
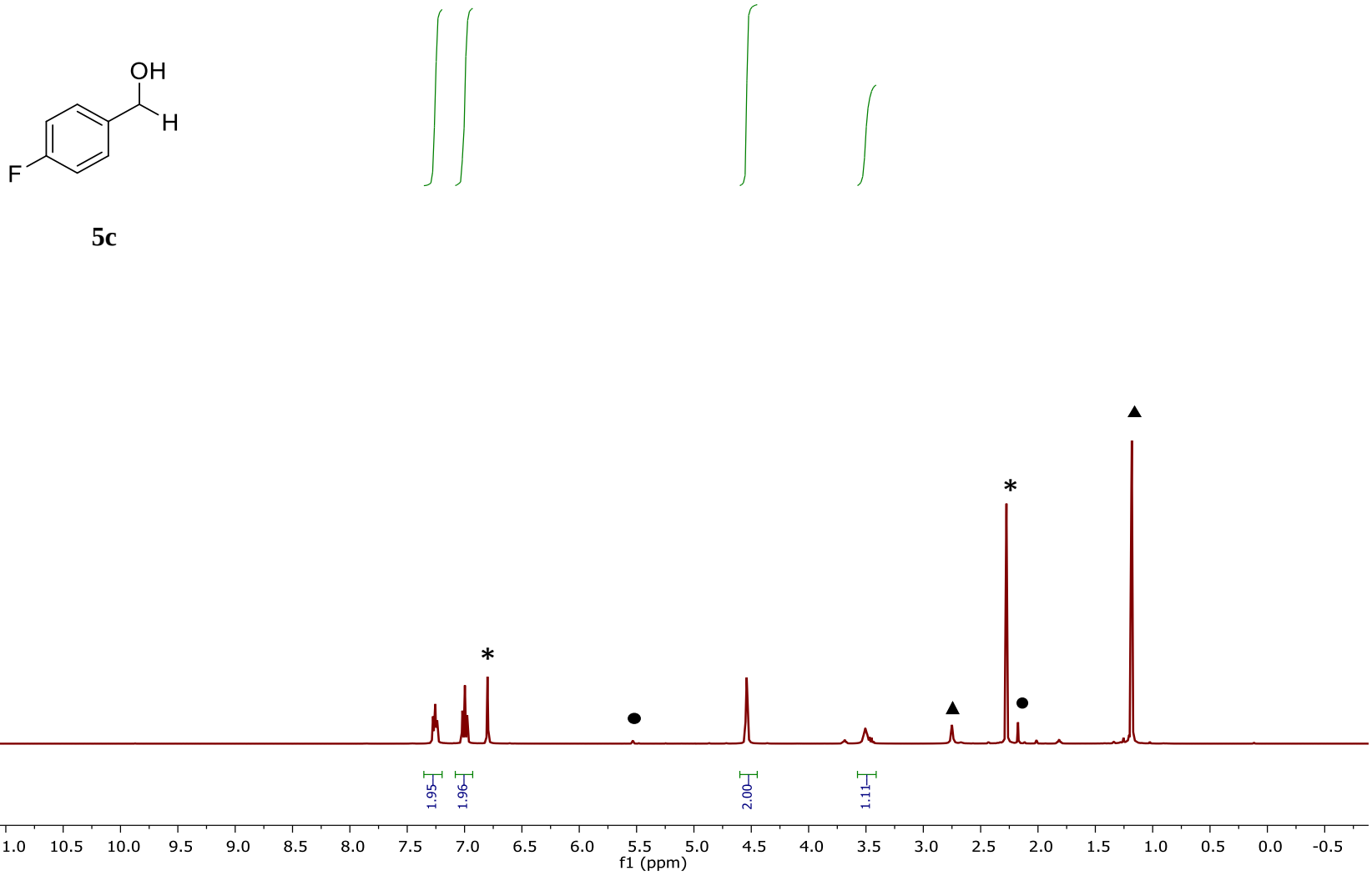


Figure S49. ^{11}B NMR resulting from catalytic hydroboration of **5c**



5c

Figure S50. ^{1}H NMR of 4-fluorobenzyl alcohol (**5c**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

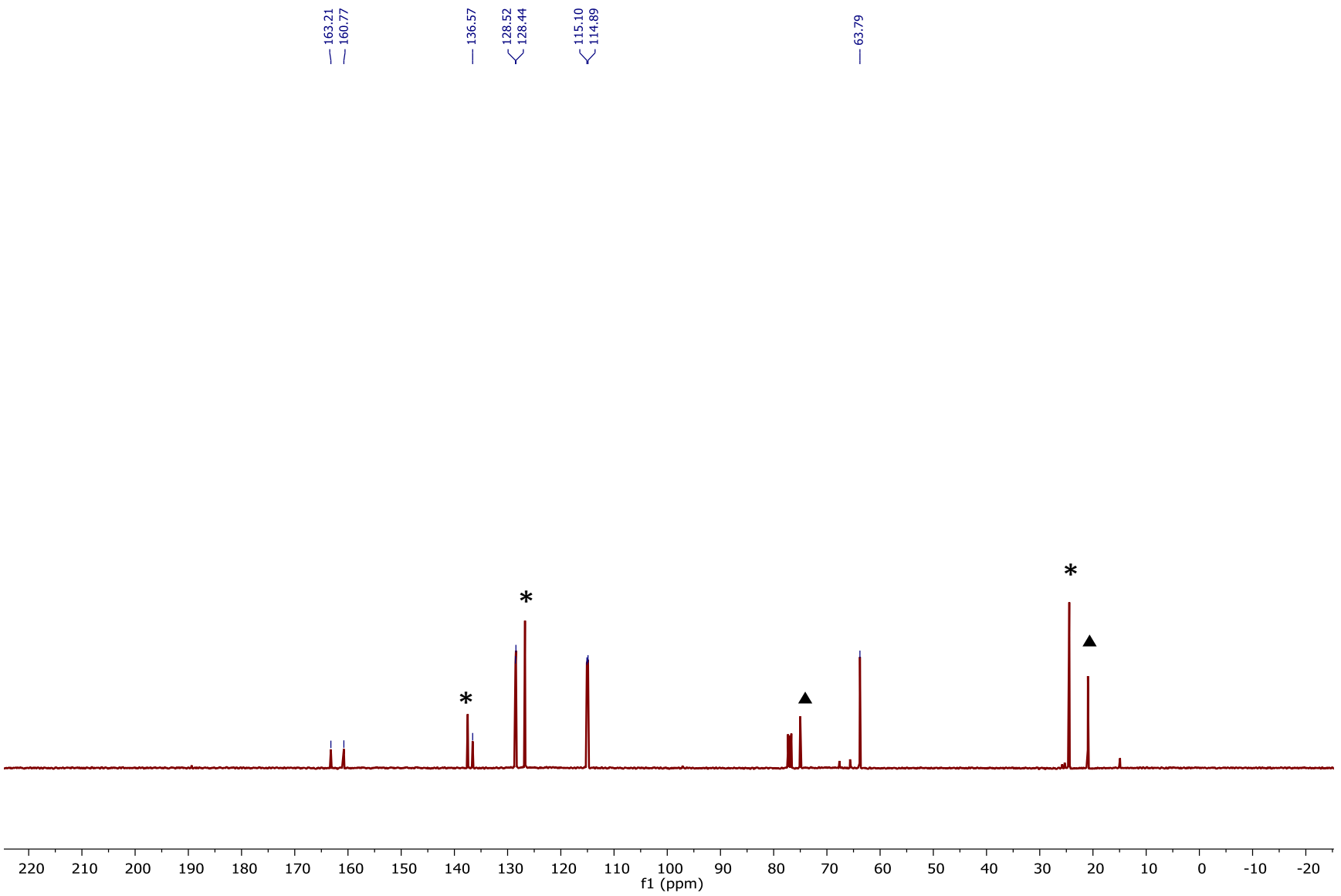


Figure S51. ^{13}C NMR of 4-fluorobenzyl alcohol (**5c**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

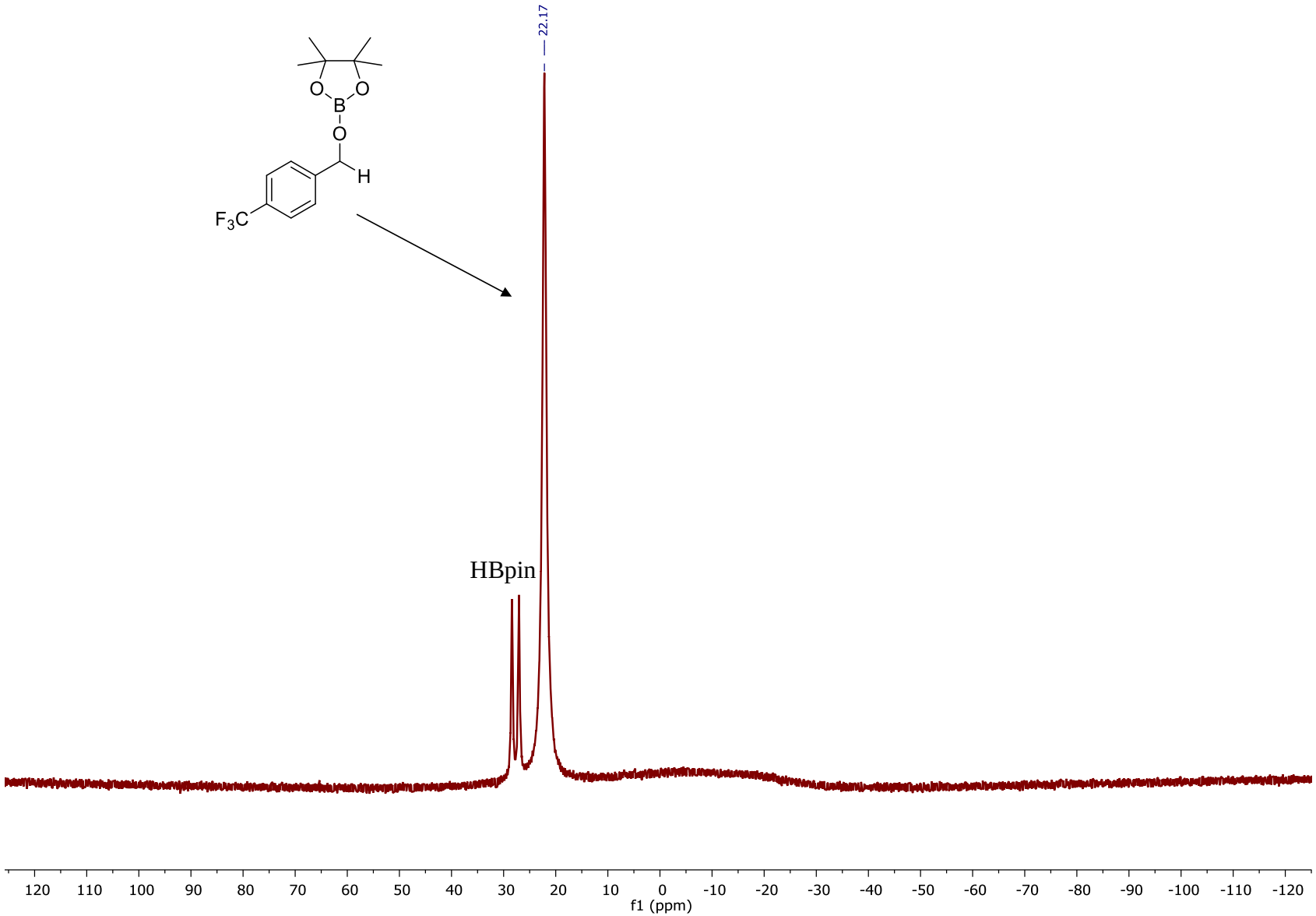


Figure S52. ^{11}B NMR resulting from catalytic hydroboration of **5d**

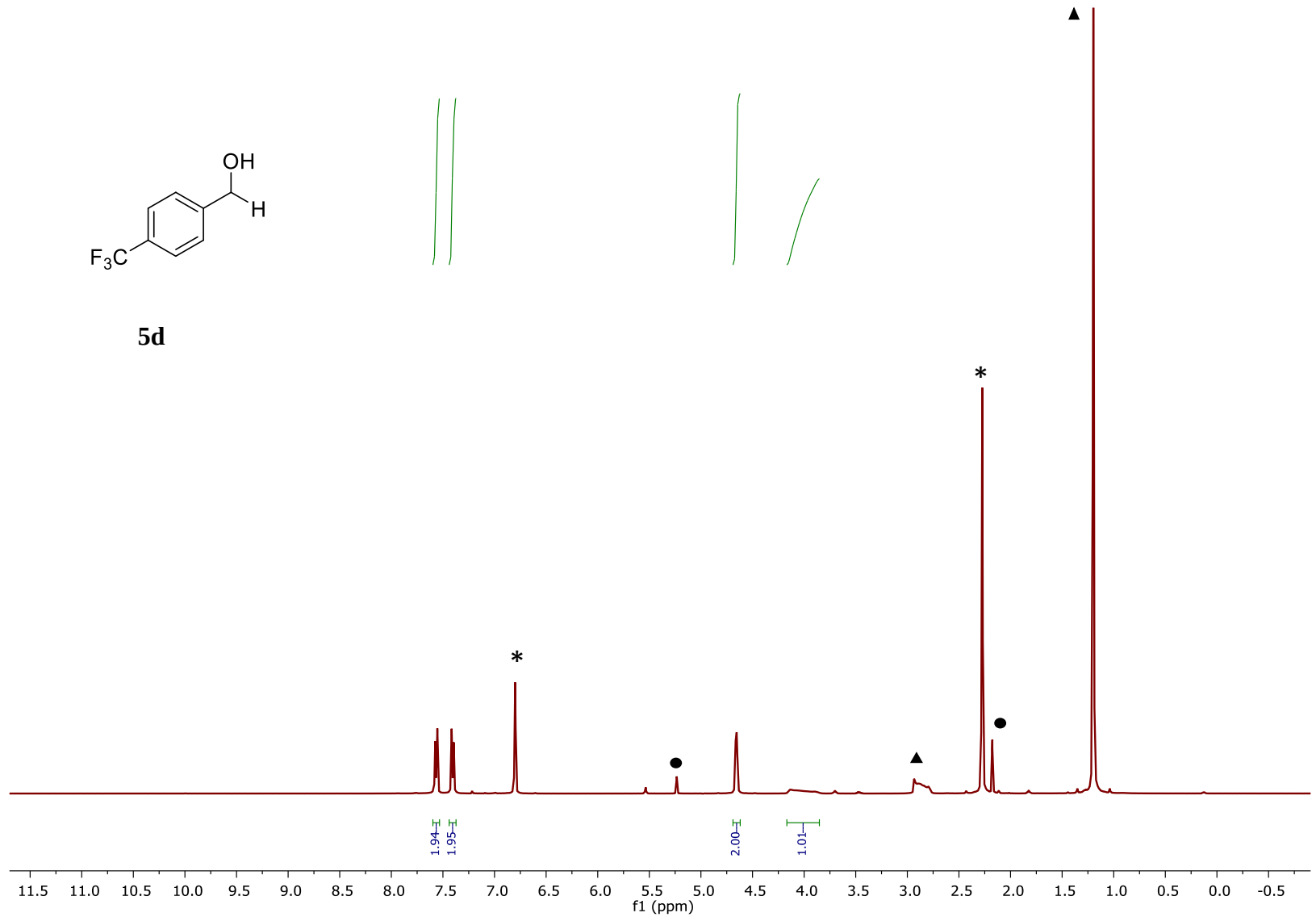


Figure S53. ^{1}H NMR of 4-trifluorobenzyl alcohol (**5d**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

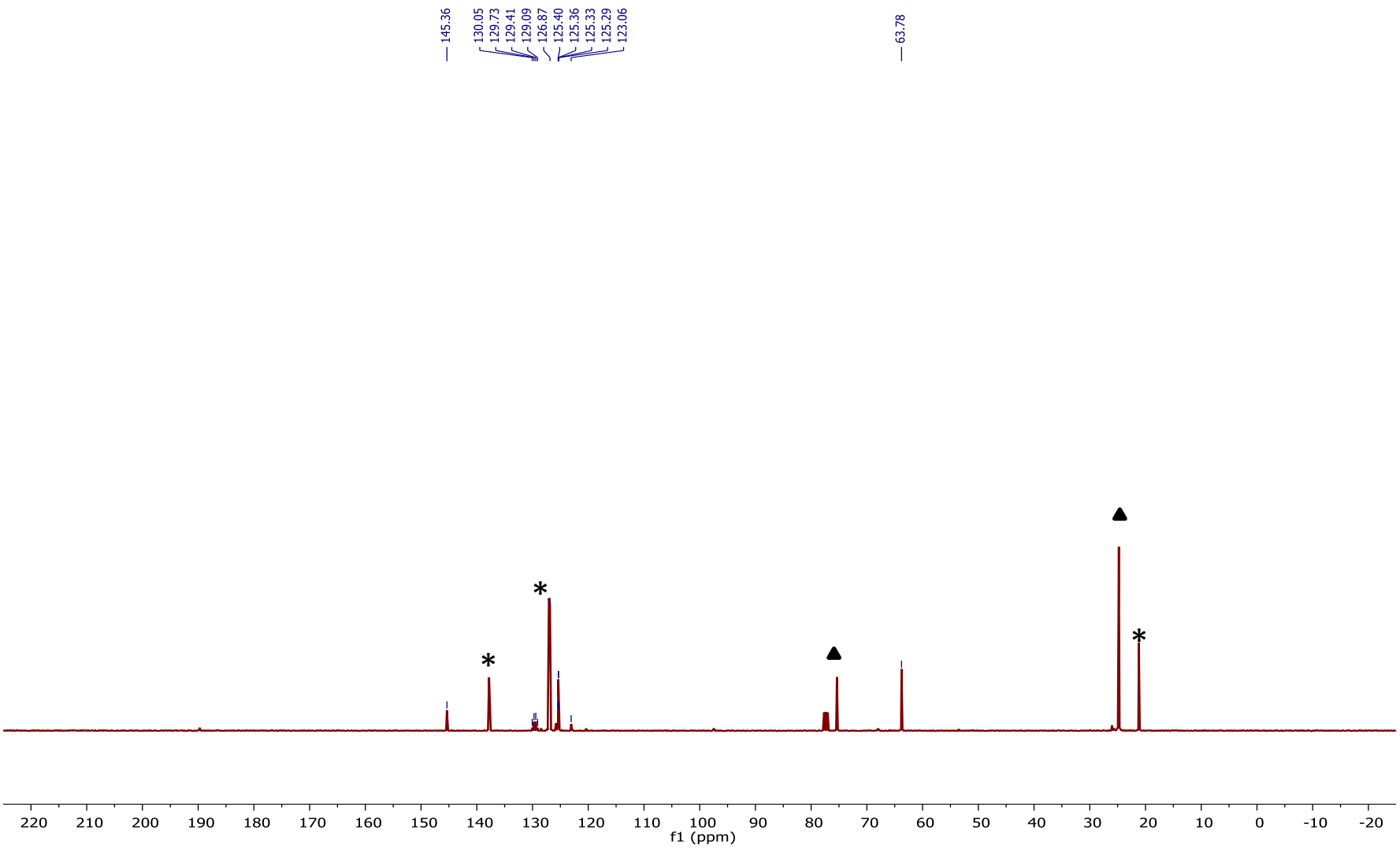


Figure S54. ^{13}C NMR of 4-trifluorobenzyl alcohol (**5d**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

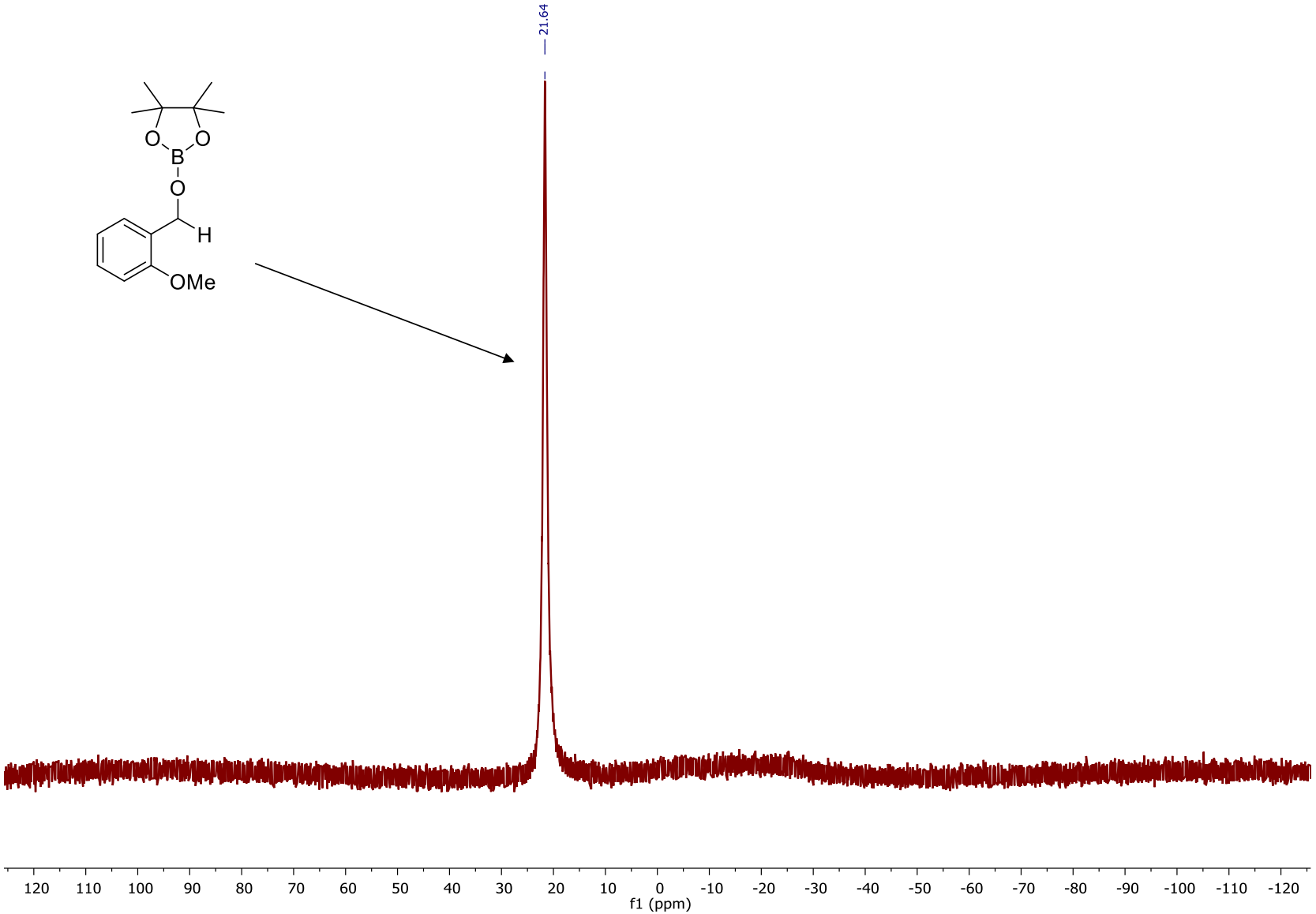


Figure S55. ^{11}B NMR resulting from catalytic hydroboration of **5e**

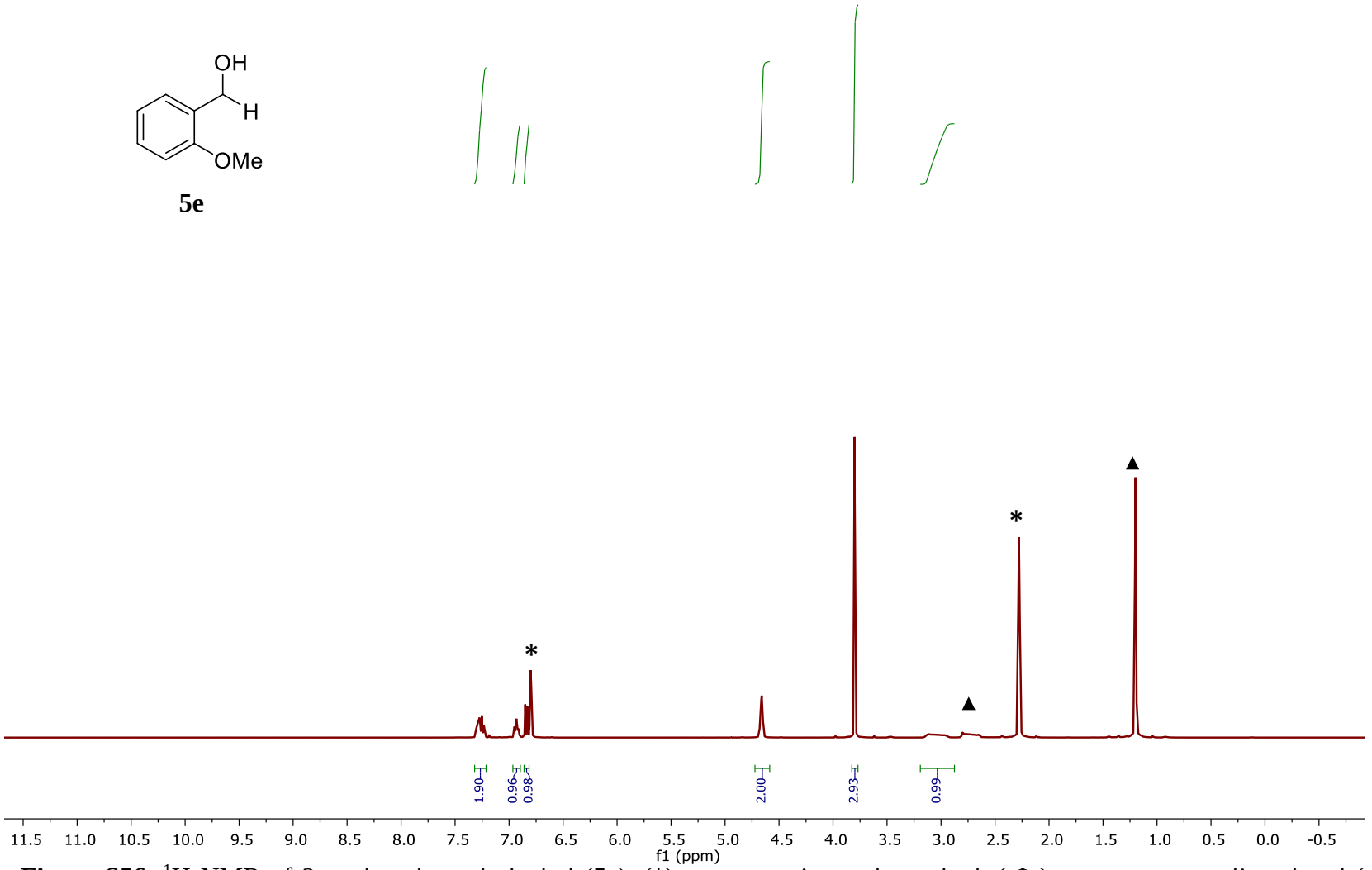


Figure S56. ^{1}H NMR of 2-methoxybenzyl alcohol (**5e**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

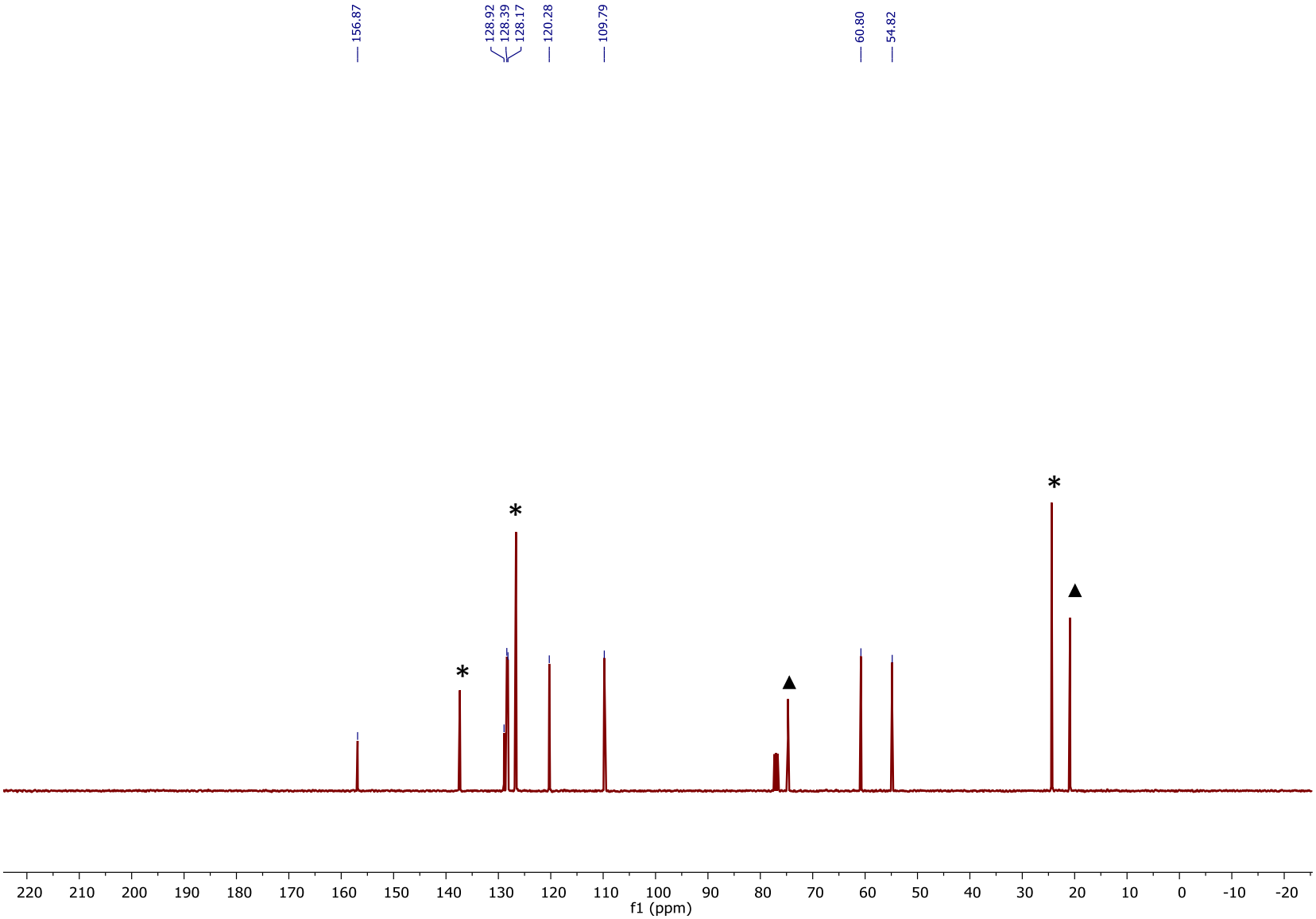


Figure S57. ^{13}C NMR of 2-methoxybenzyl alcohol (**5e**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

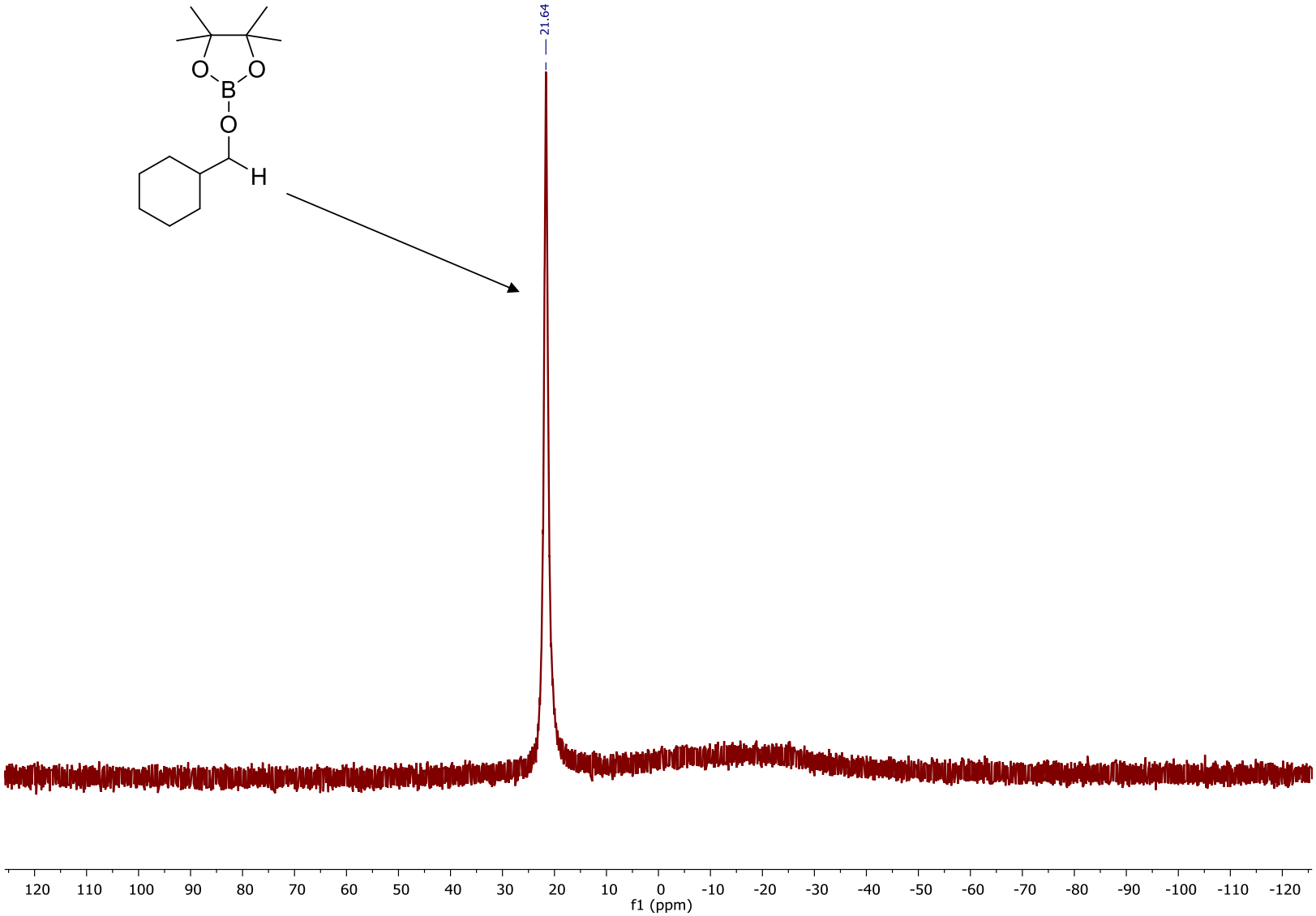


Figure S58. ^{11}B NMR resulting from catalytic hydroboration of **5f**

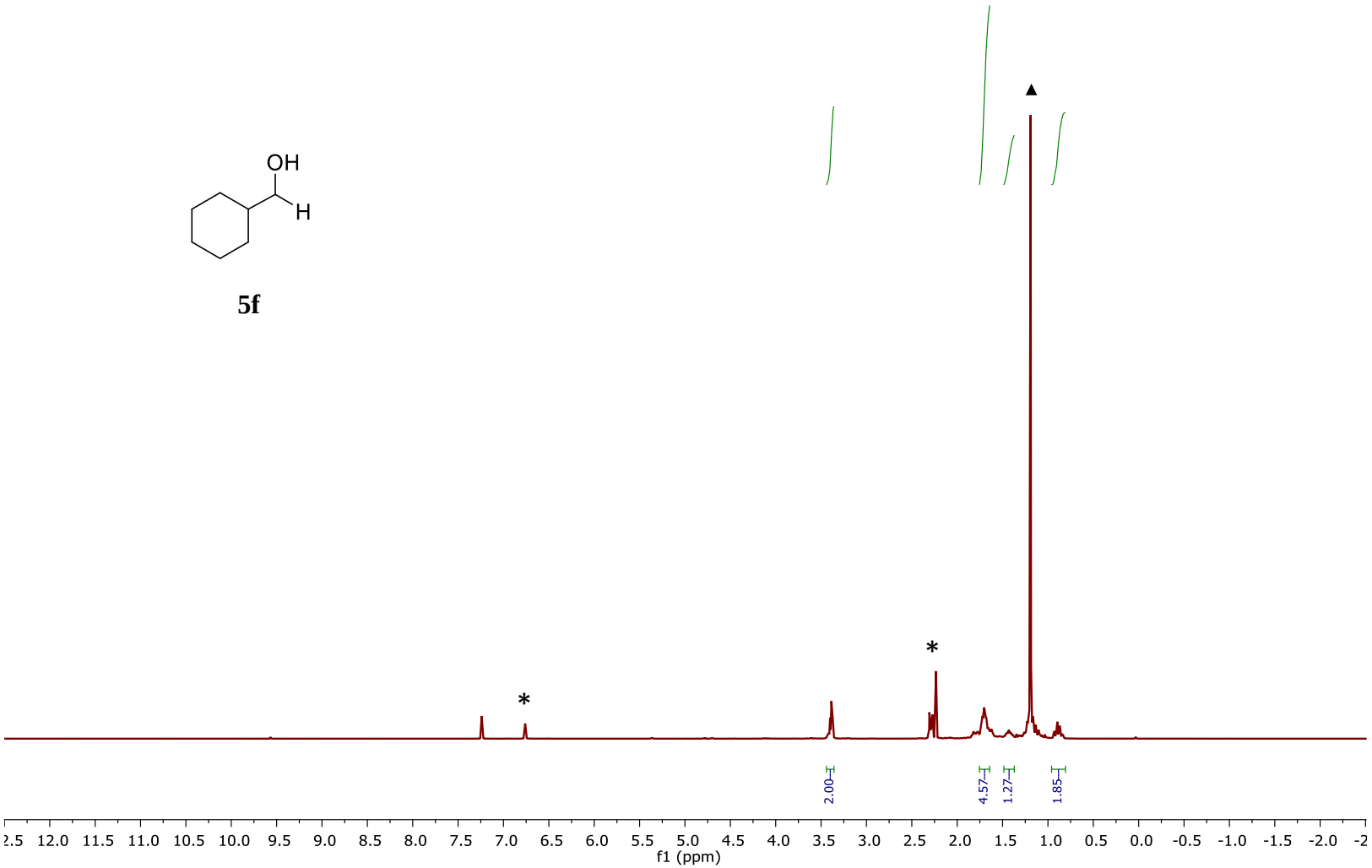


Figure S59. ^{1}H NMR of cyclohexyl methanol (**5f**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

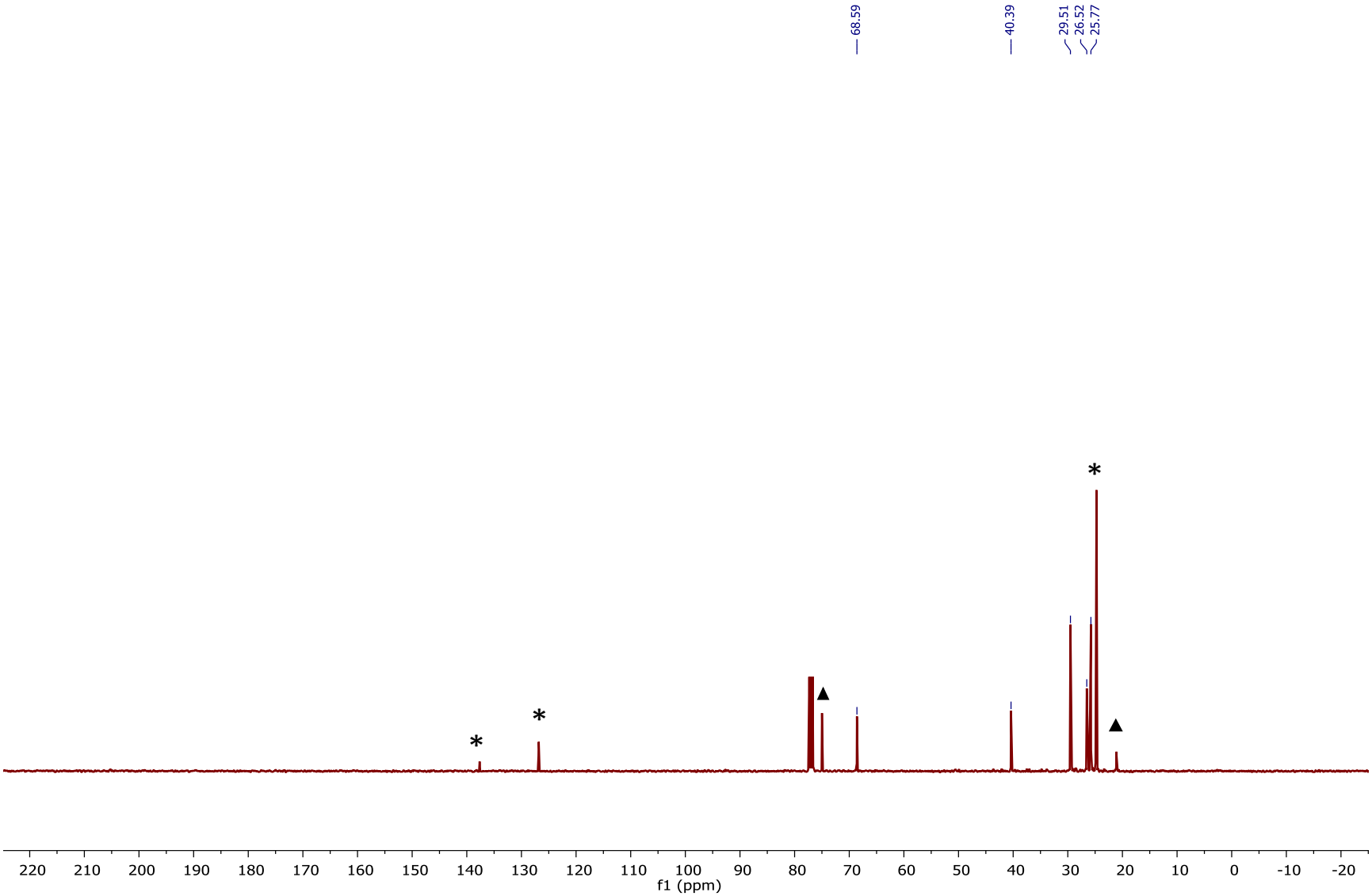


Figure S60. ^{13}C NMR of cyclohexyl methanol (**5f**). (*) represents internal standard, and (▲) represents pinnacol

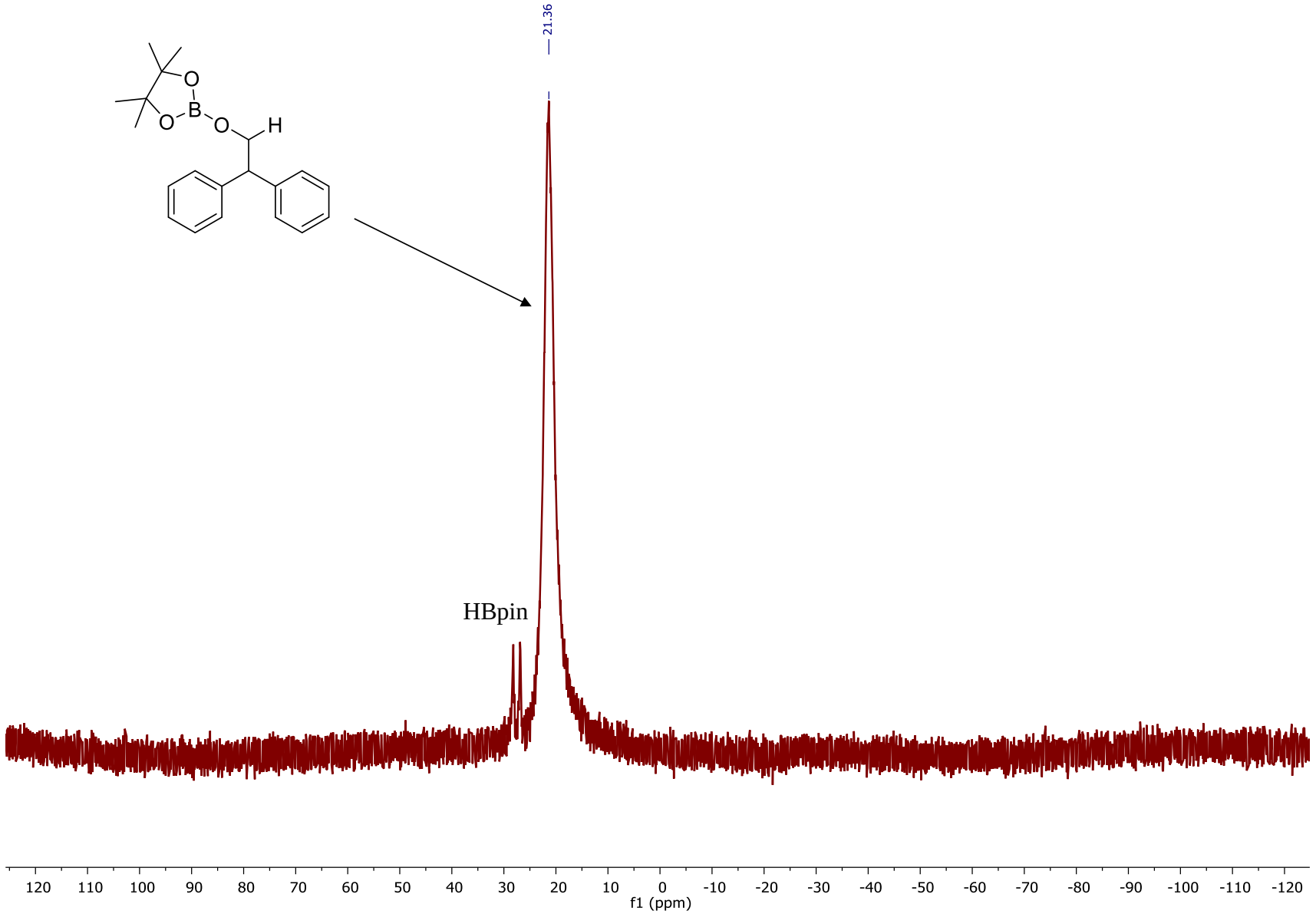


Figure S61. ^{11}B NMR resulting from catalytic hydroboration of **5g**

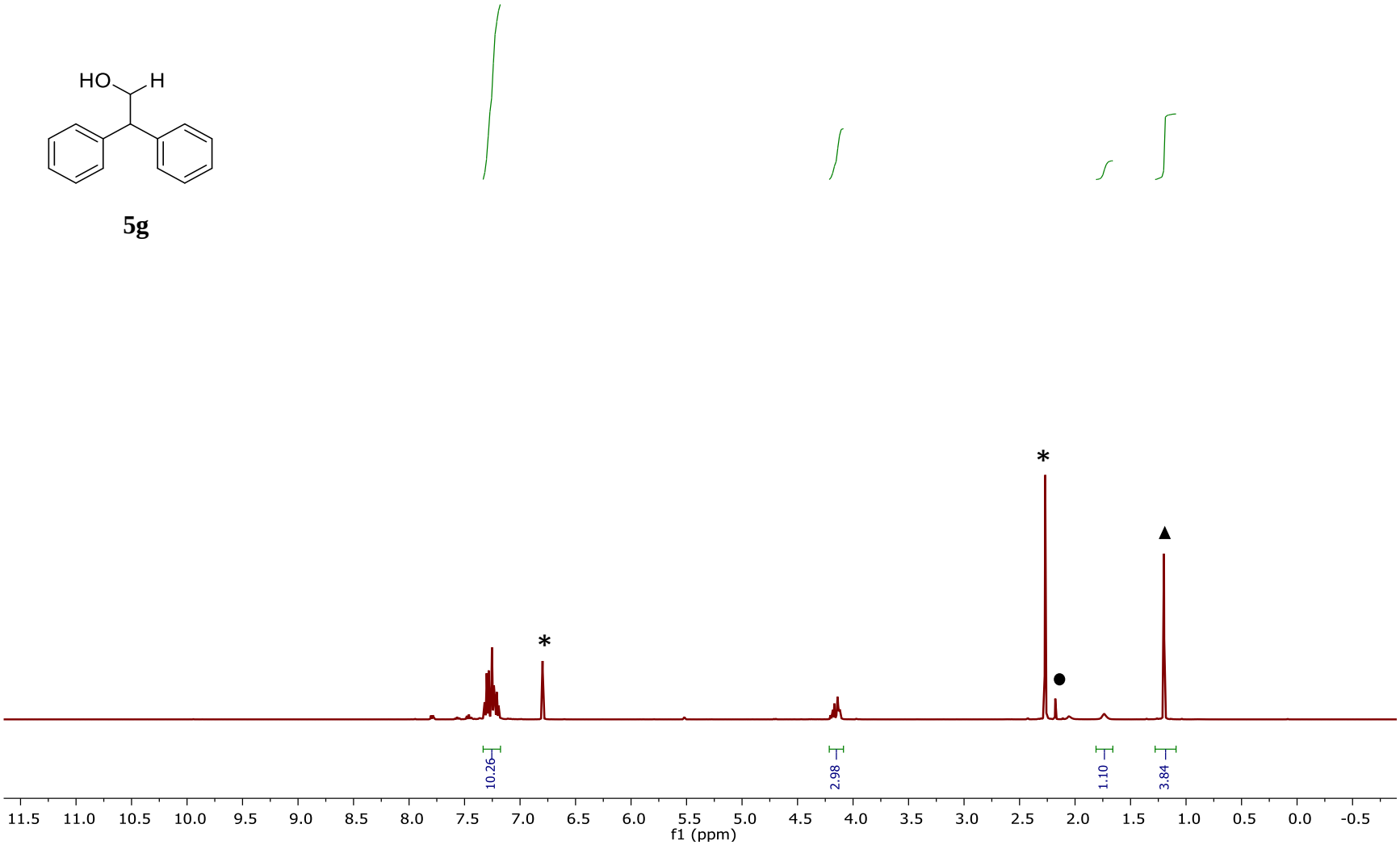


Figure S62. ^{1}H NMR of 2,2-diphenylethanol (**5g**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

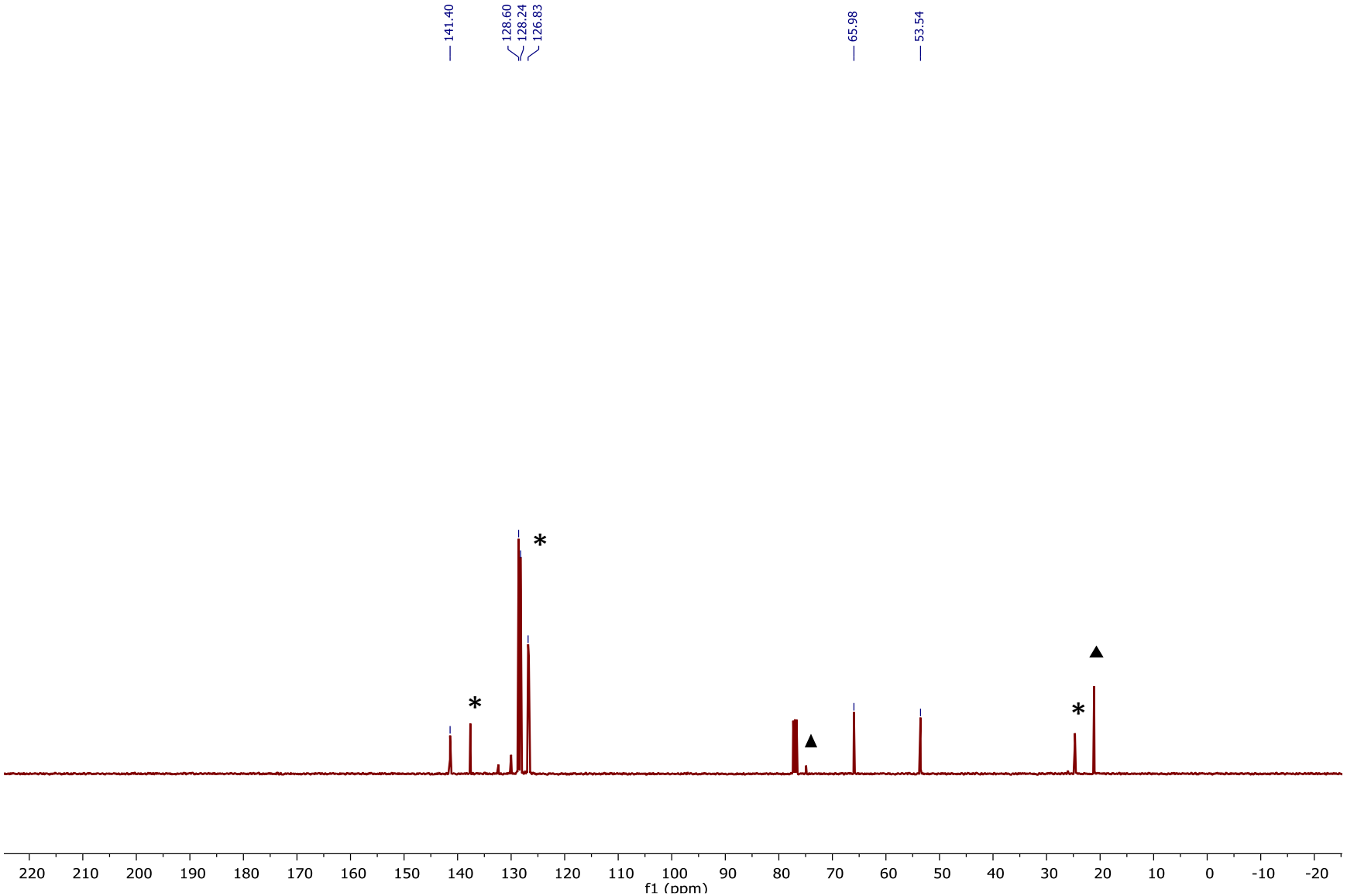


Figure S63. ^{13}C NMR of 2,2-diphenylethanol (**5g**). (*) represents internal standard and (▲) represents pinnacol

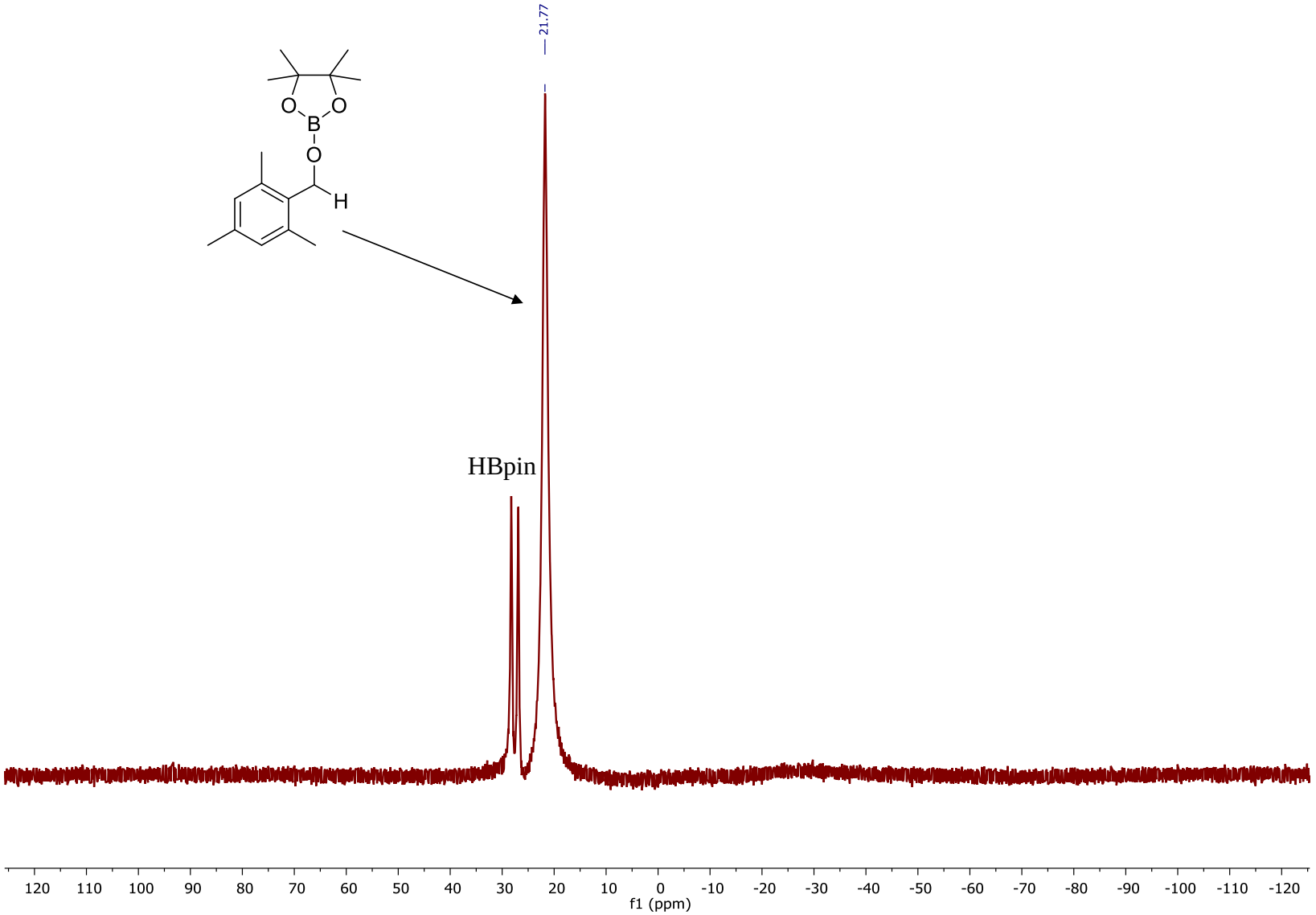


Figure S64. ^{11}B NMR resulting from catalytic hydroboration of **5h**

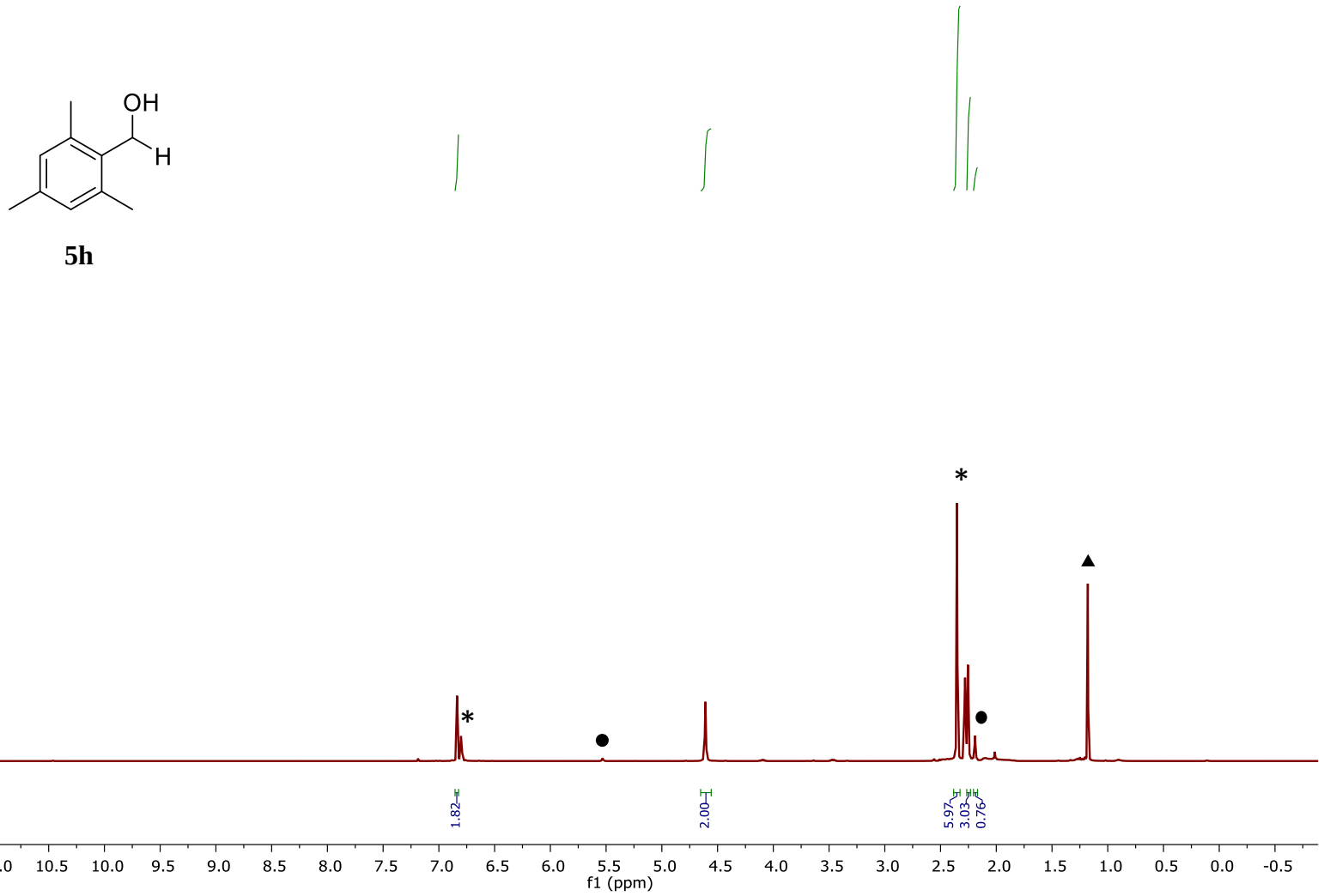


Figure S65. ^{1}H NMR of mesitylmethanol (**5h**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

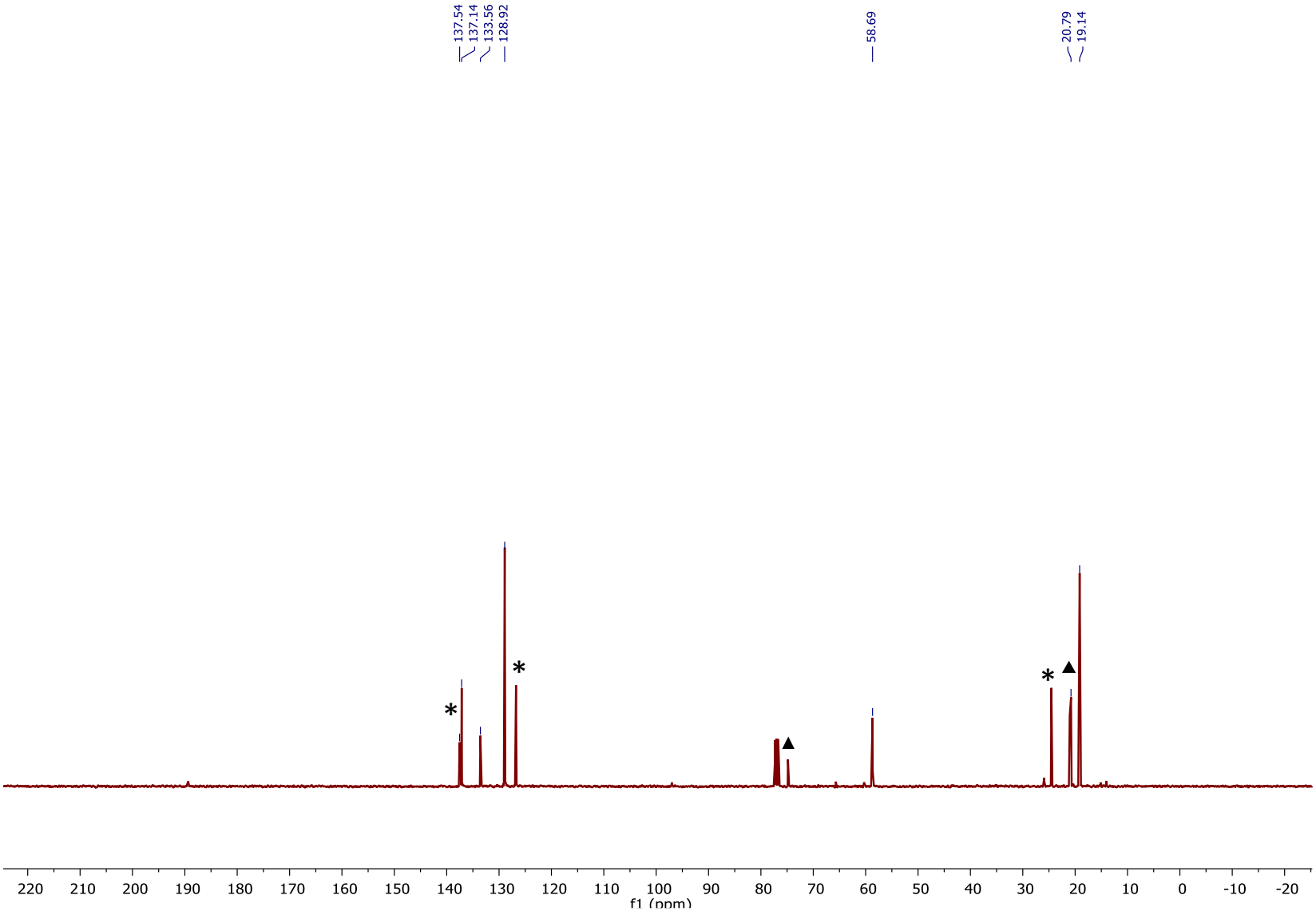


Figure S66. ^{13}C NMR of mesitylmethanol (**5h**). (*) represents internal standard and (▲) represents pinnacol

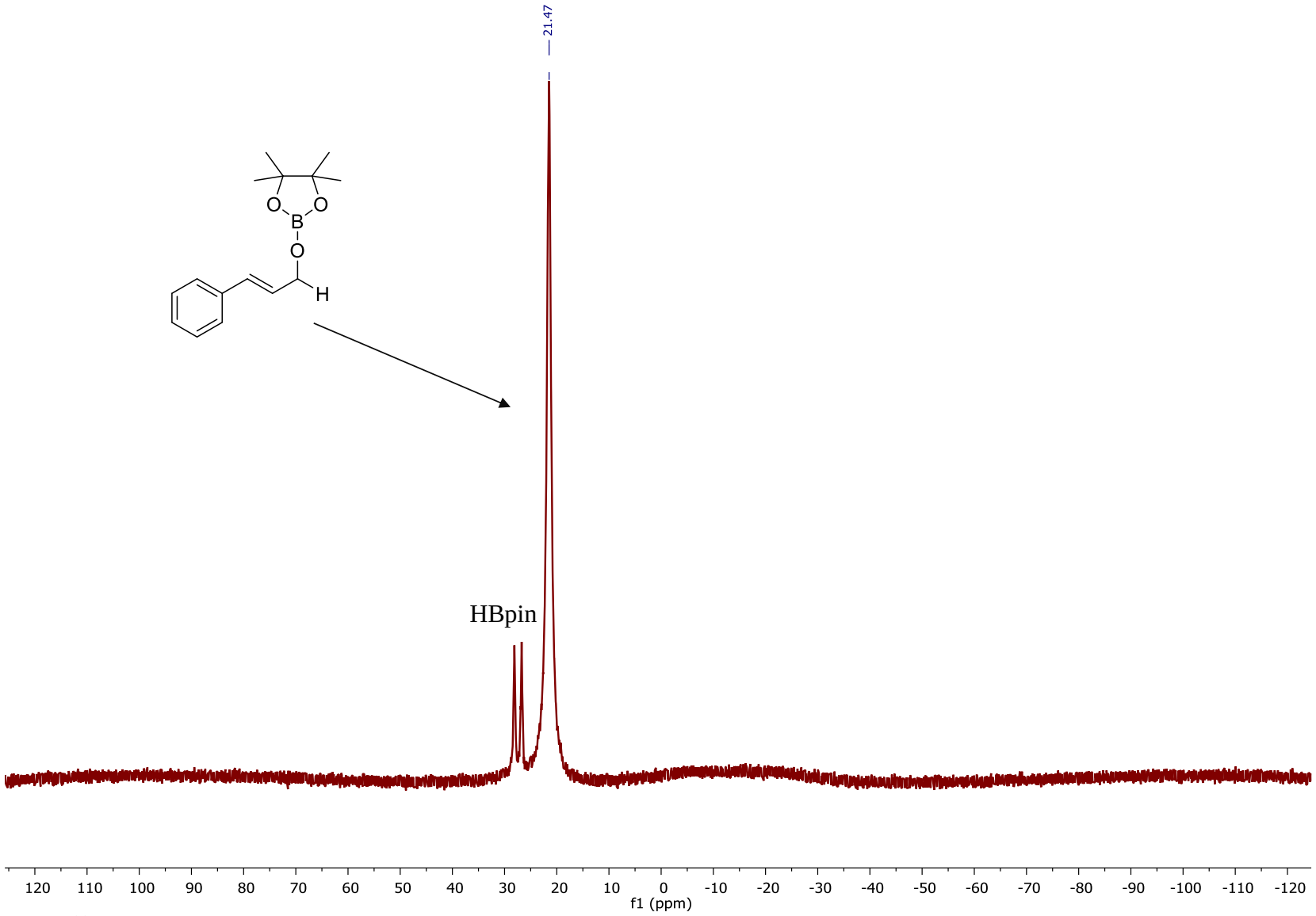


Figure S67. ^{11}B NMR resulting from catalytic hydroboration of **5i**

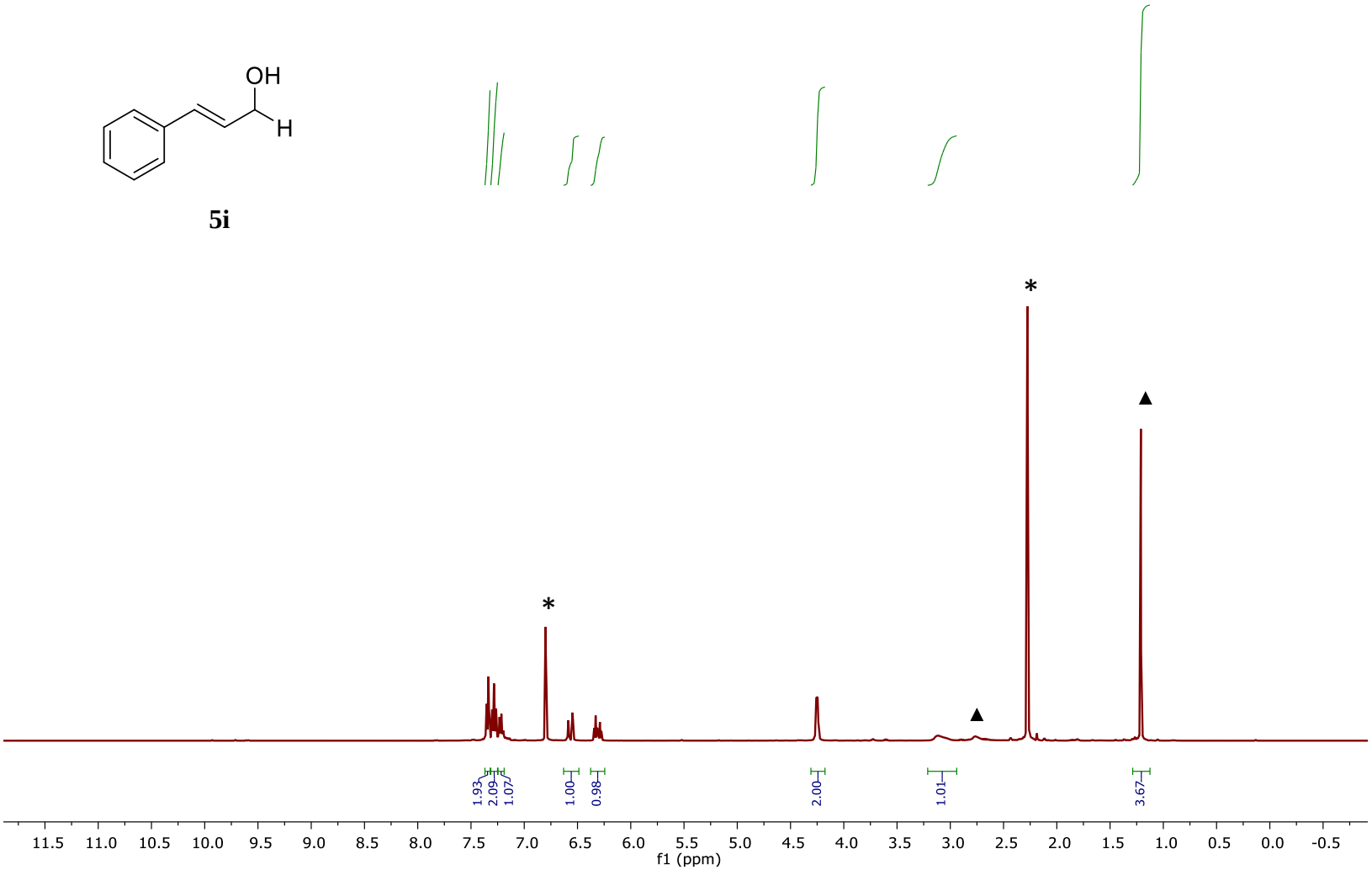


Figure S68. ^{1}H NMR of 3-phenyl-2-propene-1-ol (**5i**). (*) represents internal standard and (▲) represents pinnacol

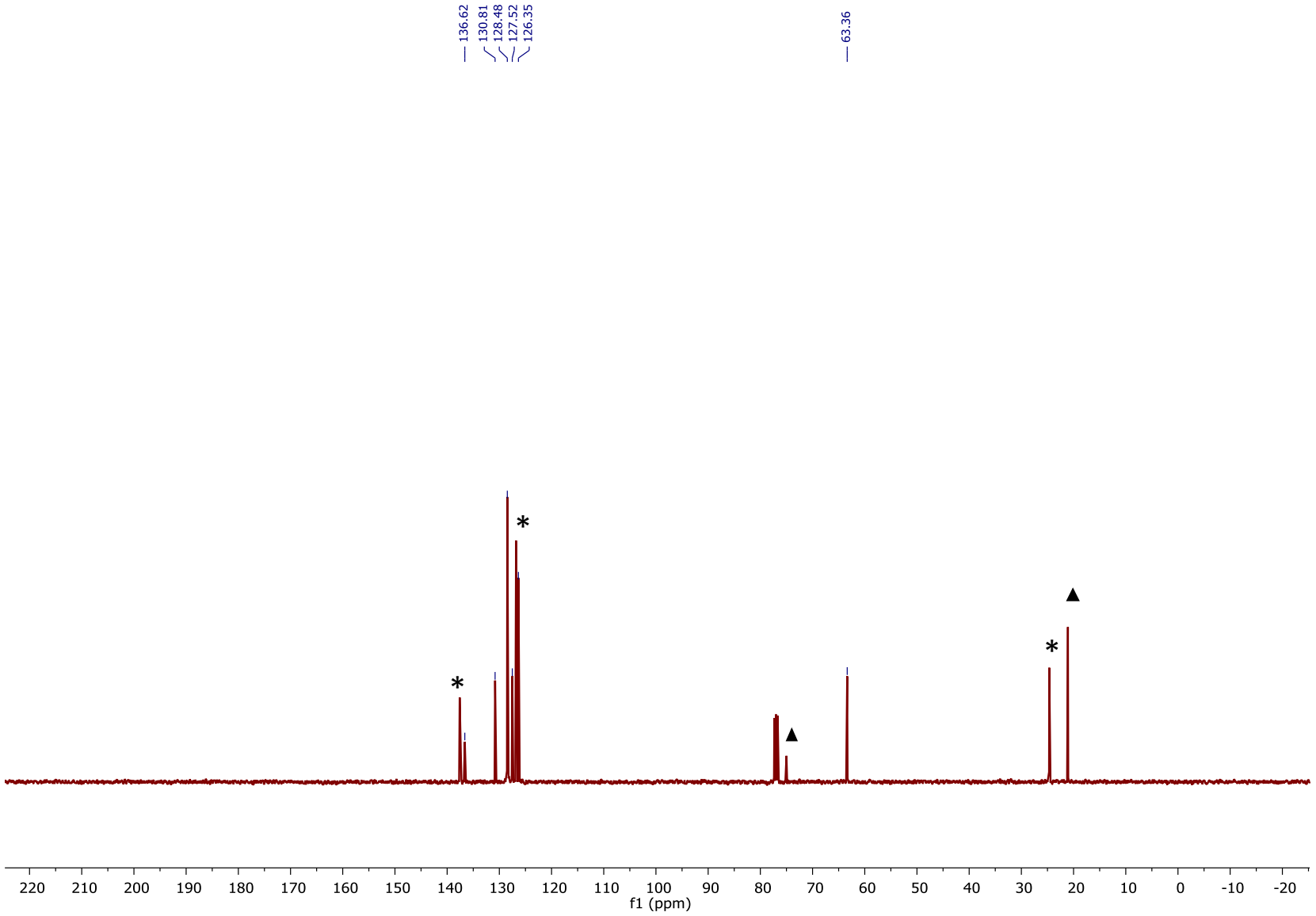


Figure S69. ^{13}C NMR of 3-phenyl-2-propene-1-ol (**5i**). (*) represents internal standard and (▲) represents pinnacol

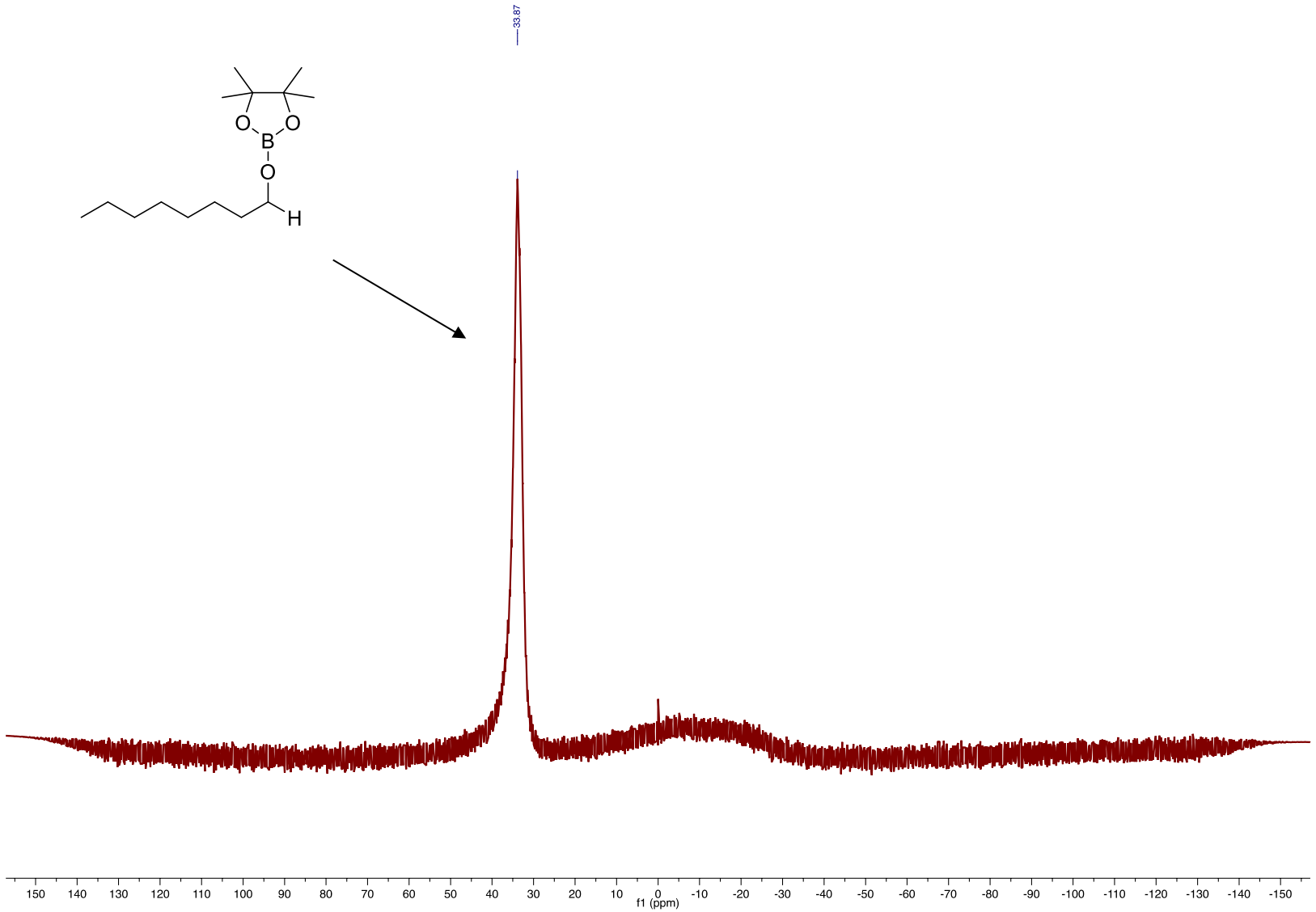


Figure S70. ^{11}B NMR resulting from catalytic hydroboration of **5j**

6. ^{11}B, ^{1}H and ^{13}C NMR of 2º alcohols

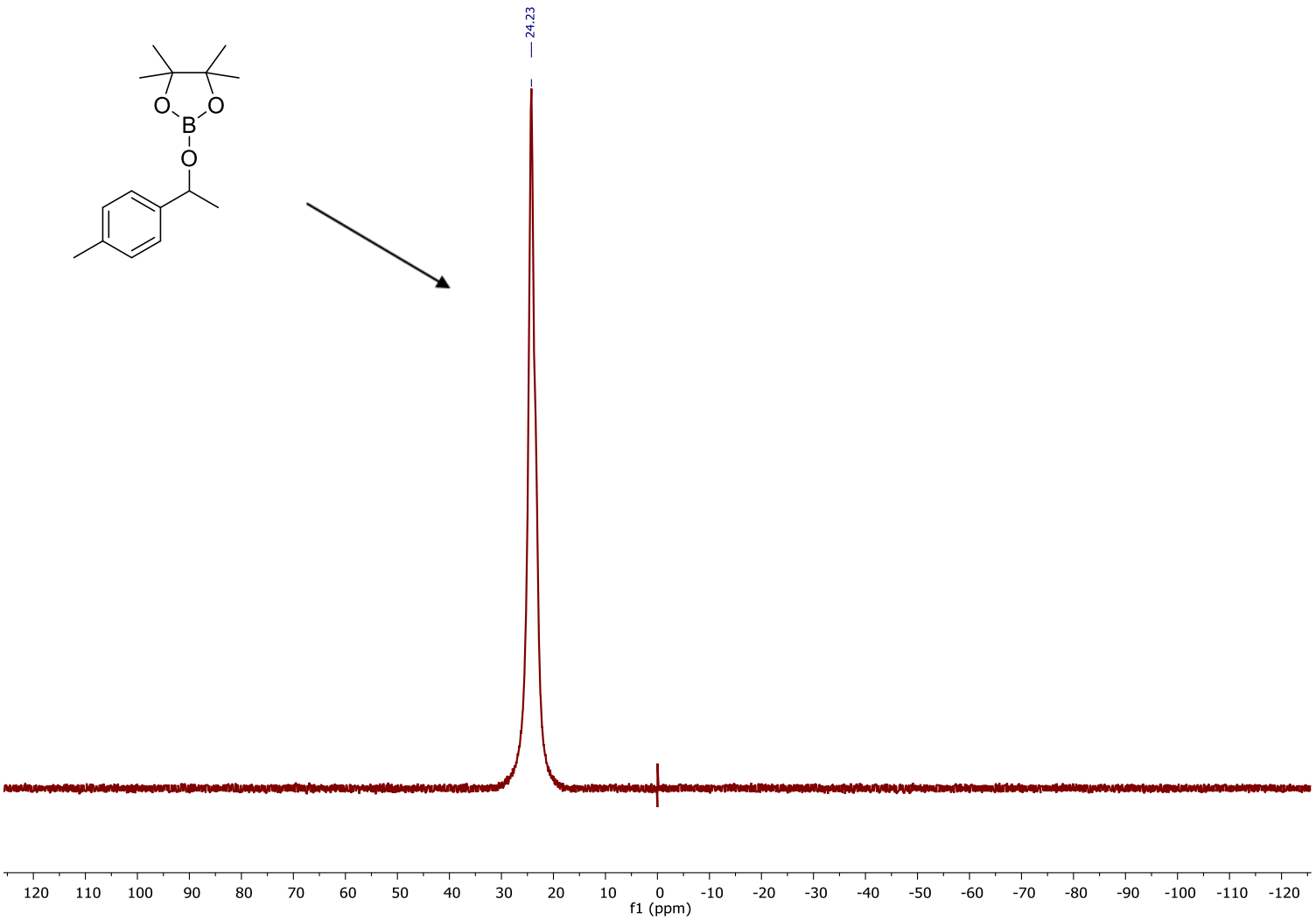


Figure S71. ^{11}B NMR resulting from catalytic hydroboration of **5k**

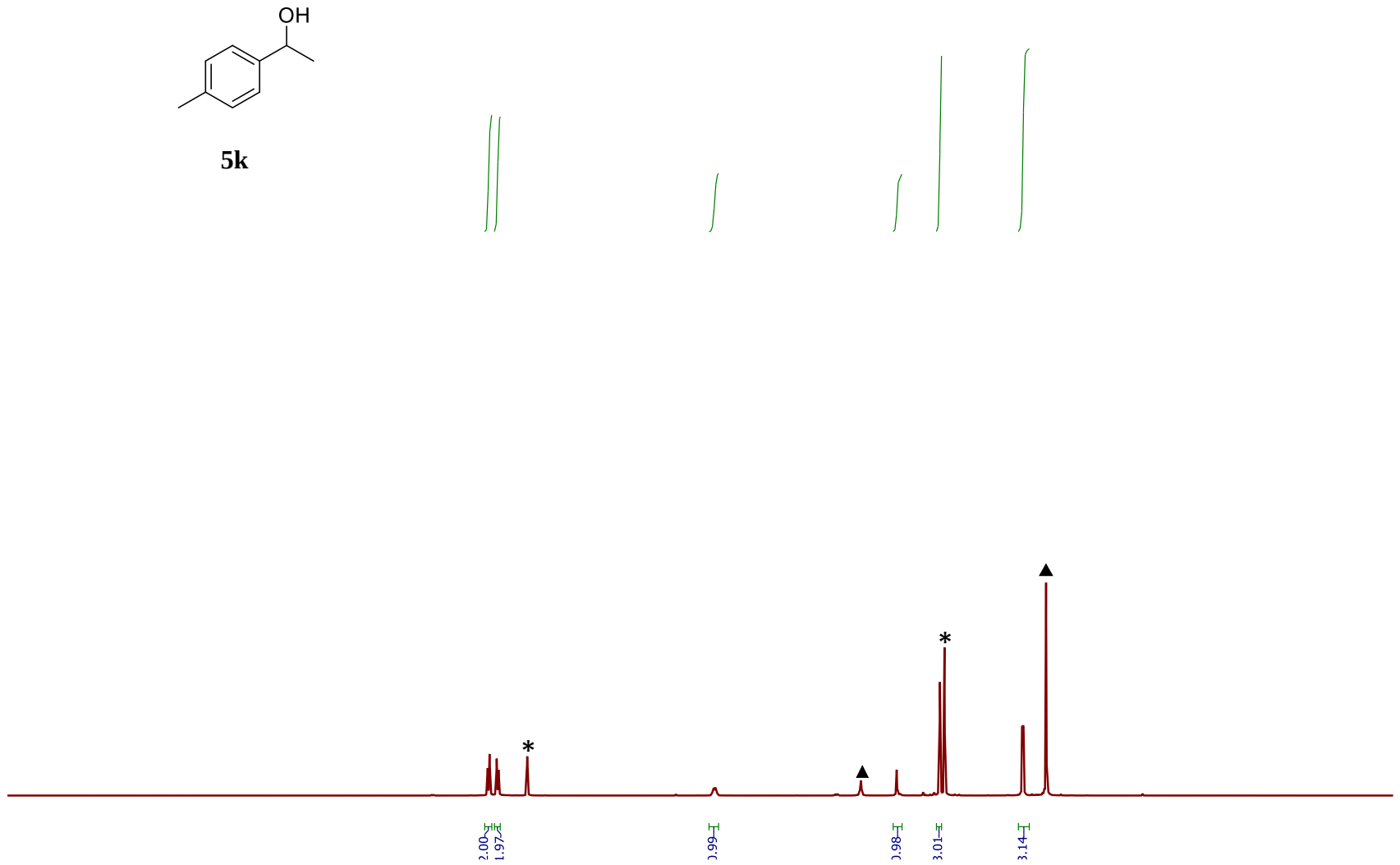


Figure S72. ^{1}H NMR of 1-(4-Methylphenyl)ethanol(**5k**). (*) represents internal standard and (▲) represents pinnacol

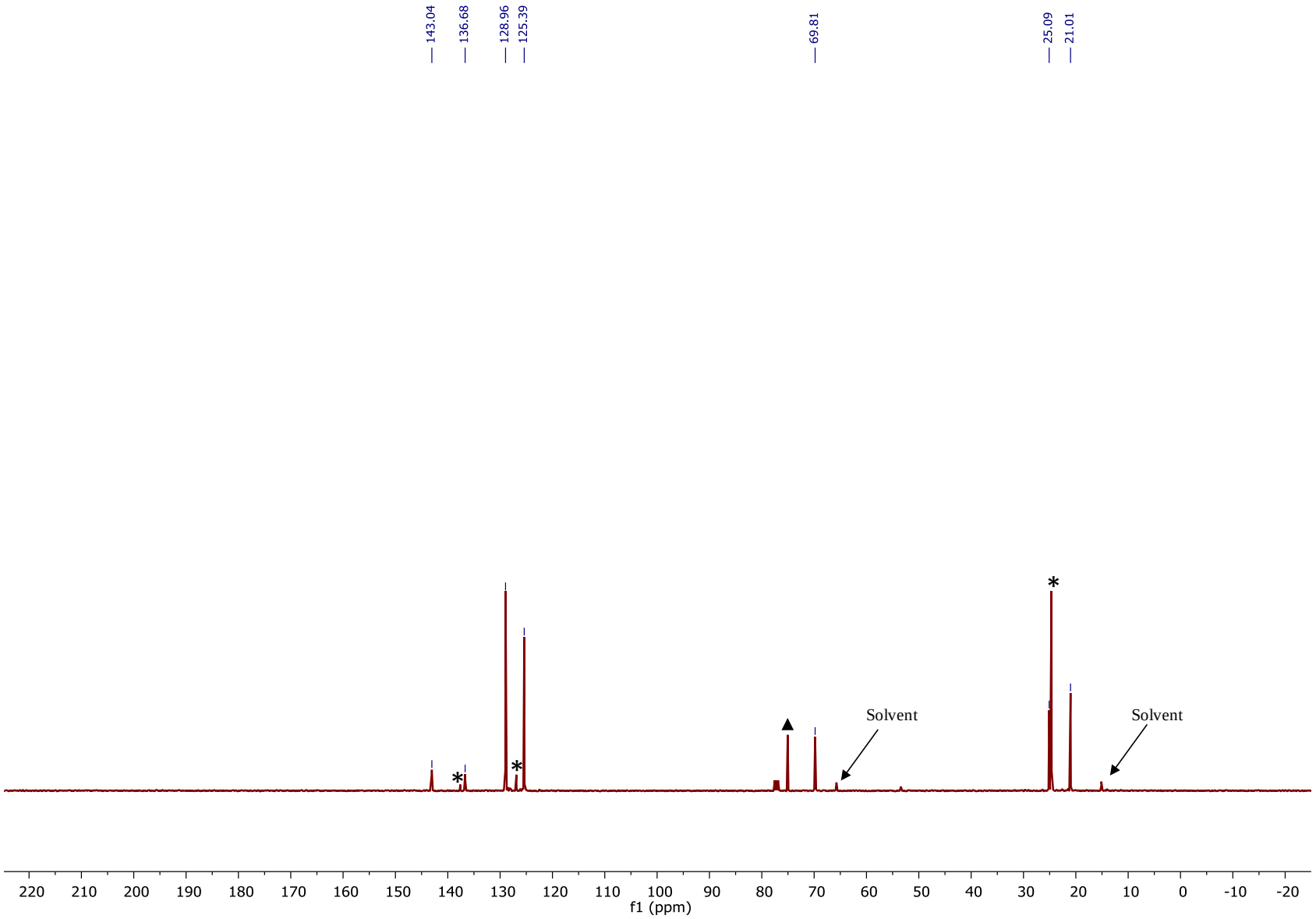


Figure S73. ^{13}C NMR of 1-(4-Methylphenyl)ethanol(**5k**). (*) represents internal standard and (▲) represents pinnacol

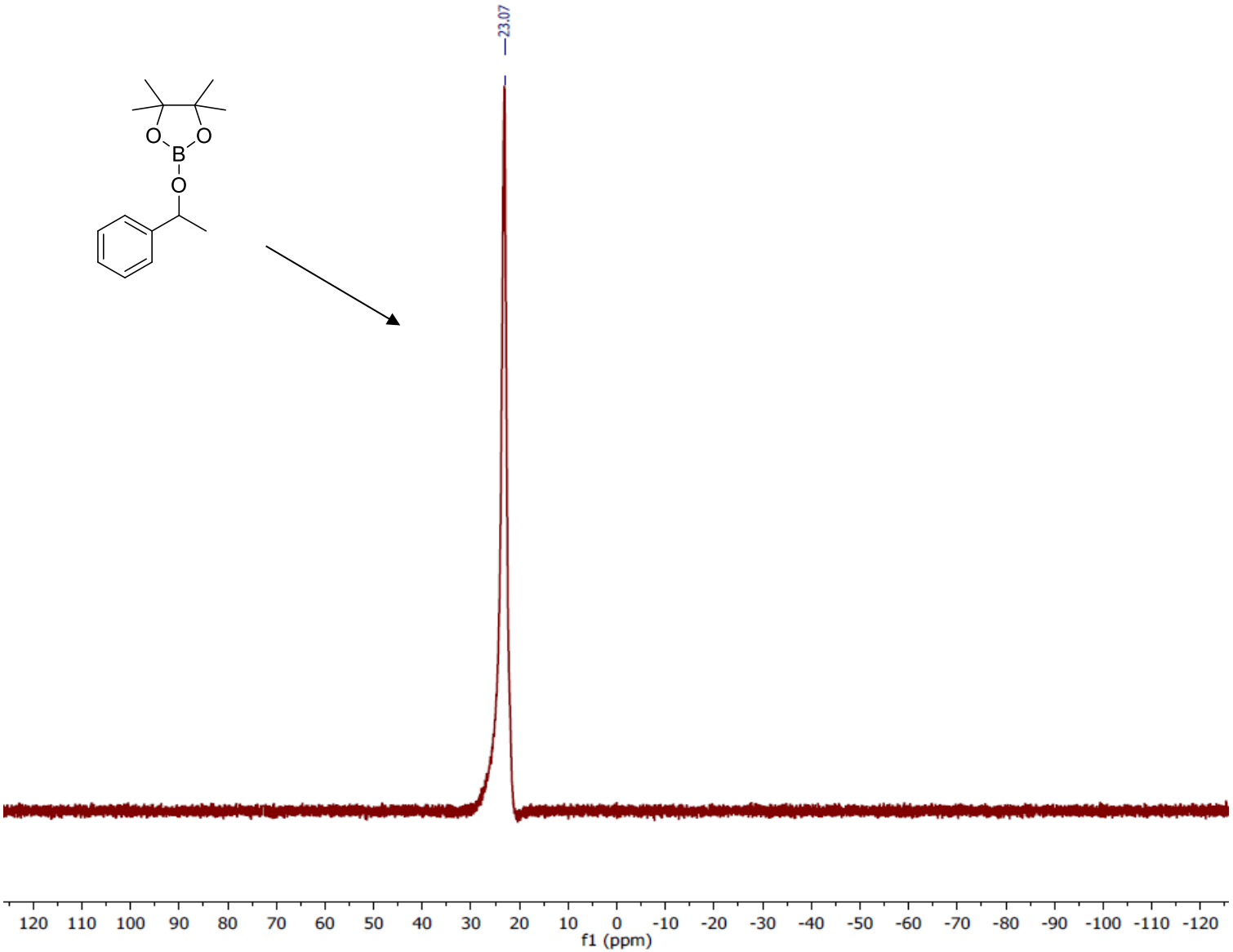


Figure S74. ^{11}B NMR resulting from catalytic hydroboration of **5l**

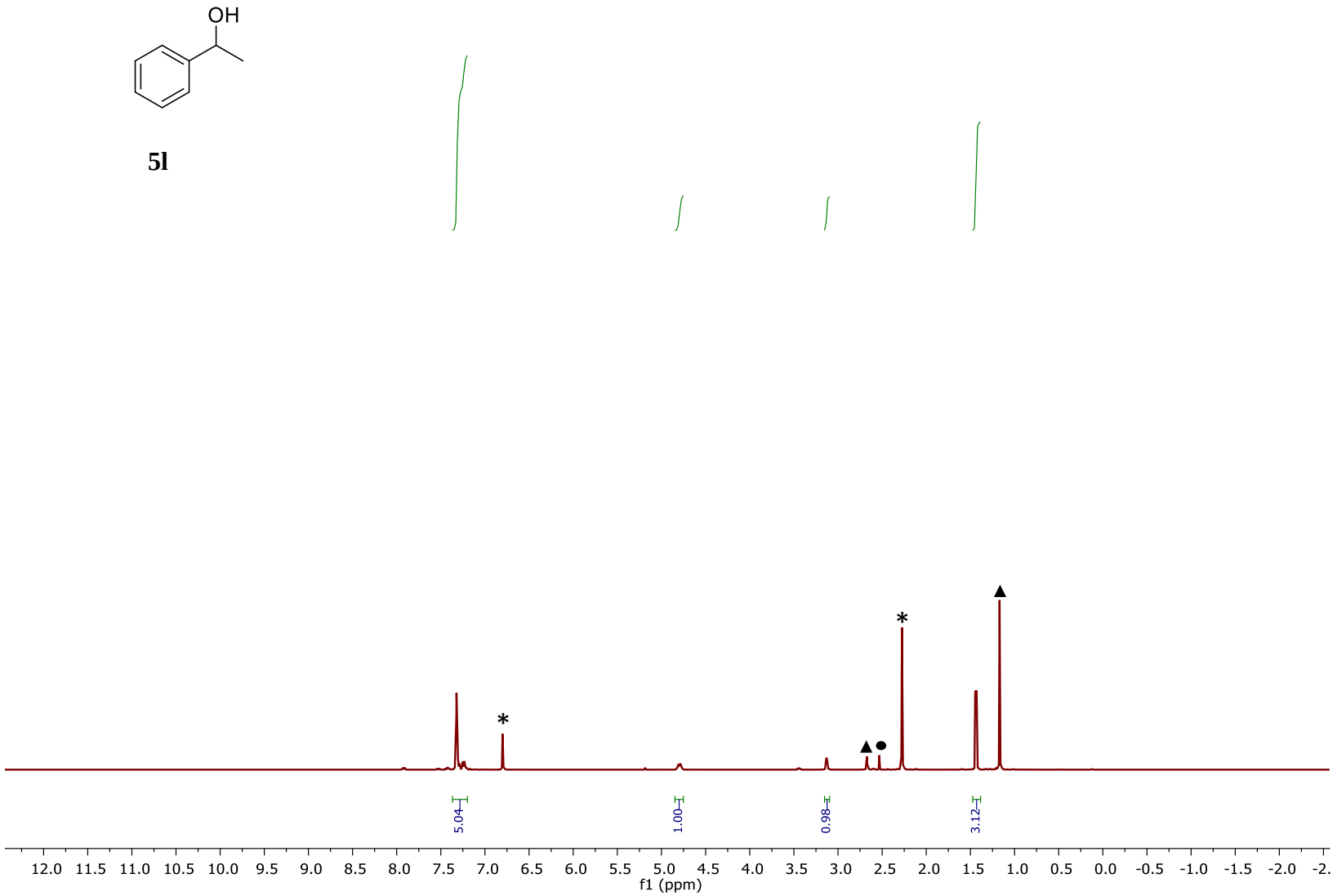


Figure S75. ^{1}H NMR of 1-Phenylethanol (**5l**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

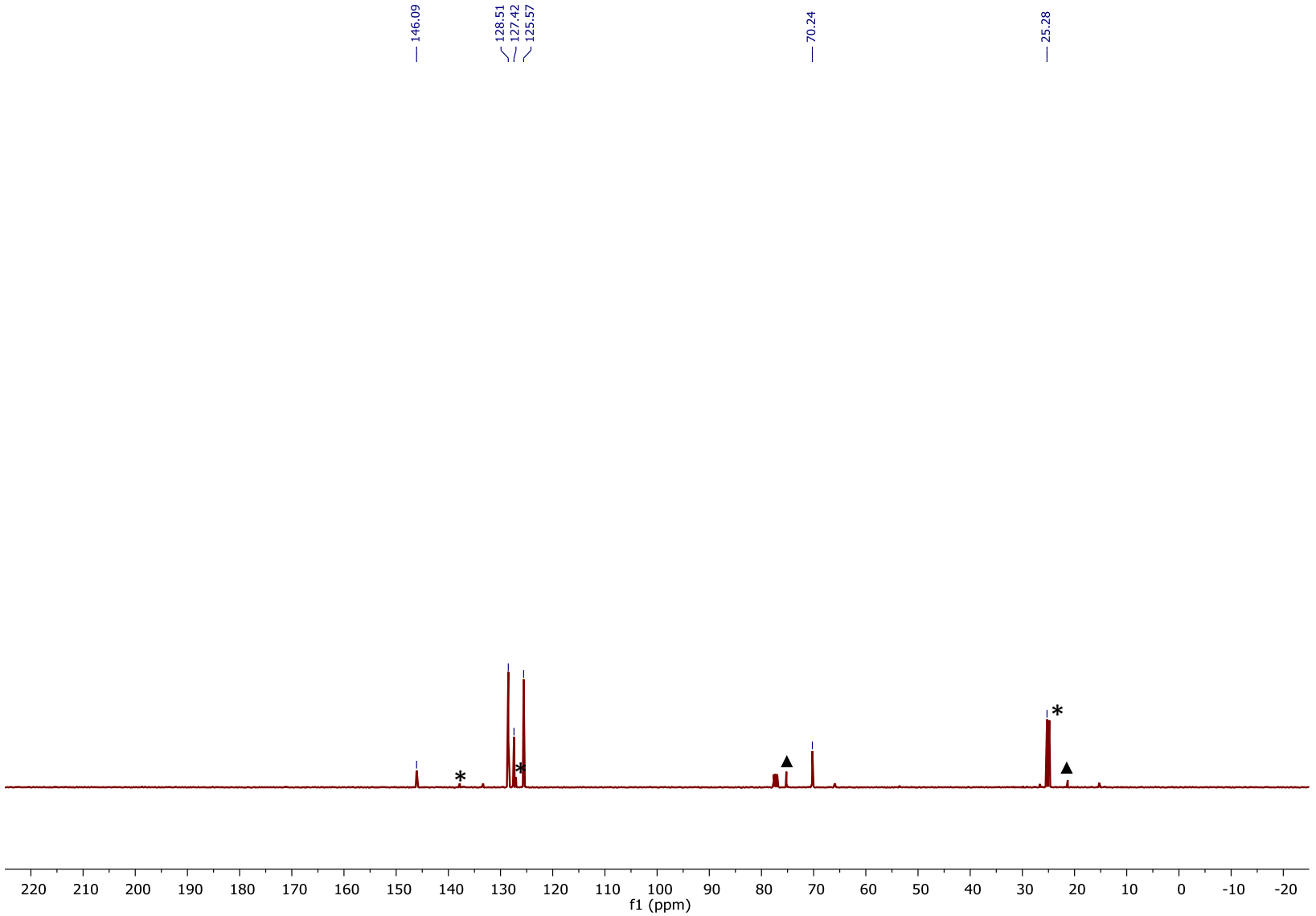


Figure S76. ^{13}C NMR of 1-Phenylethanol (**5l**). (*) represents internal standard and (▲) represents pinnacol

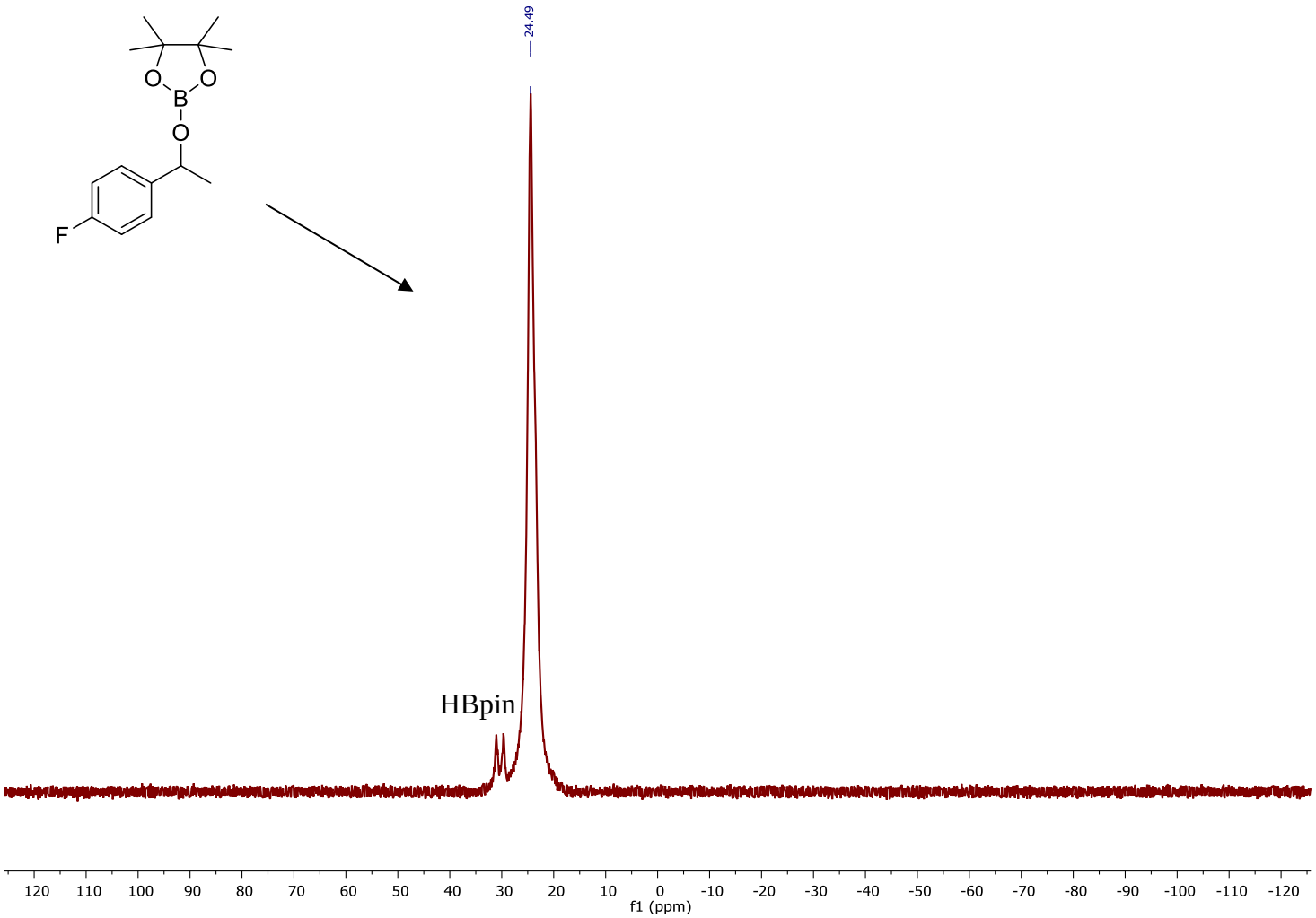


Figure S77. ^{11}B NMR resulting from catalytic hydroboration of **5m**

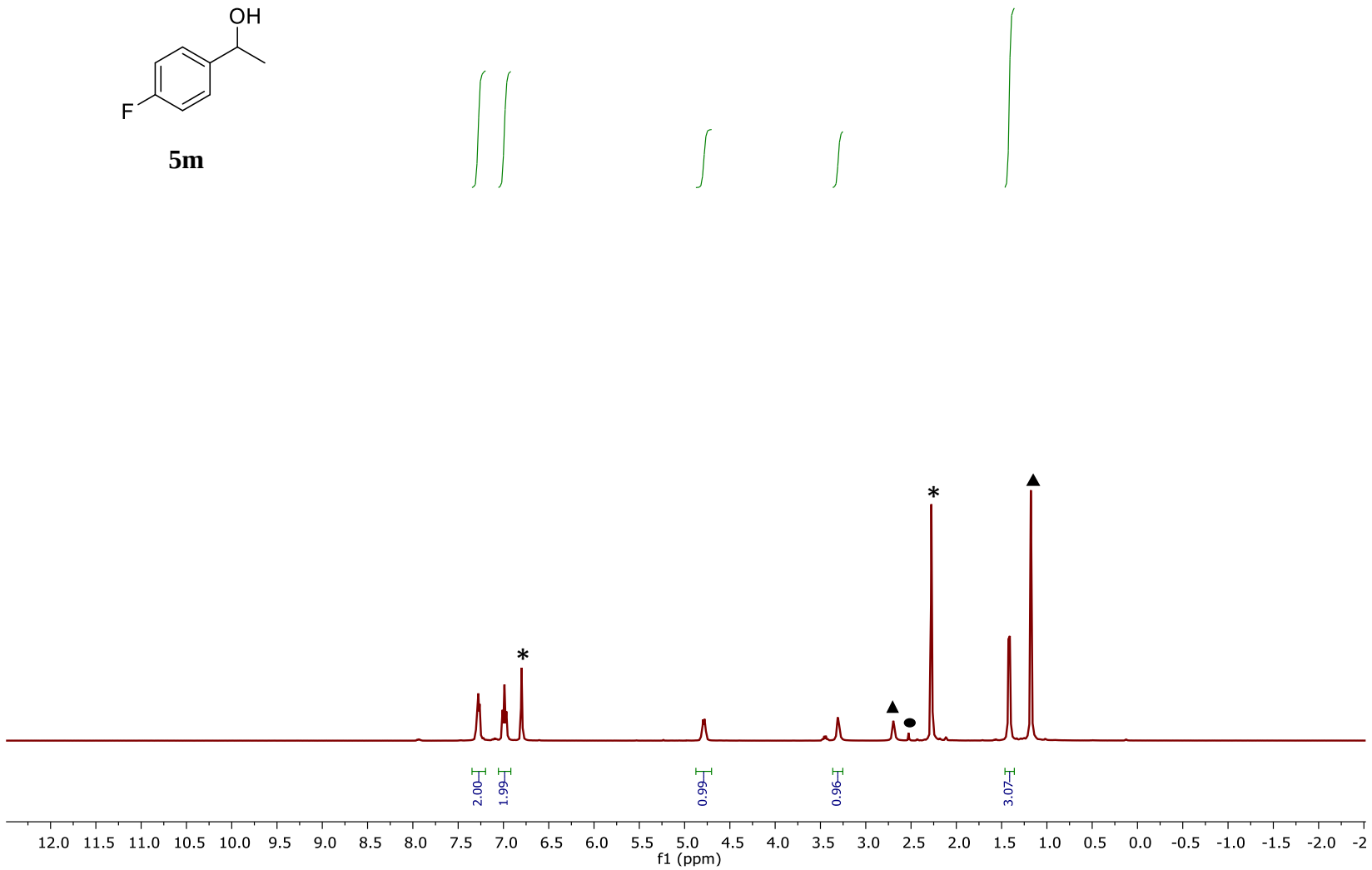


Figure S78. ^{1}H NMR of 1-(4-Fluorophenyl)ethanol (**5m**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

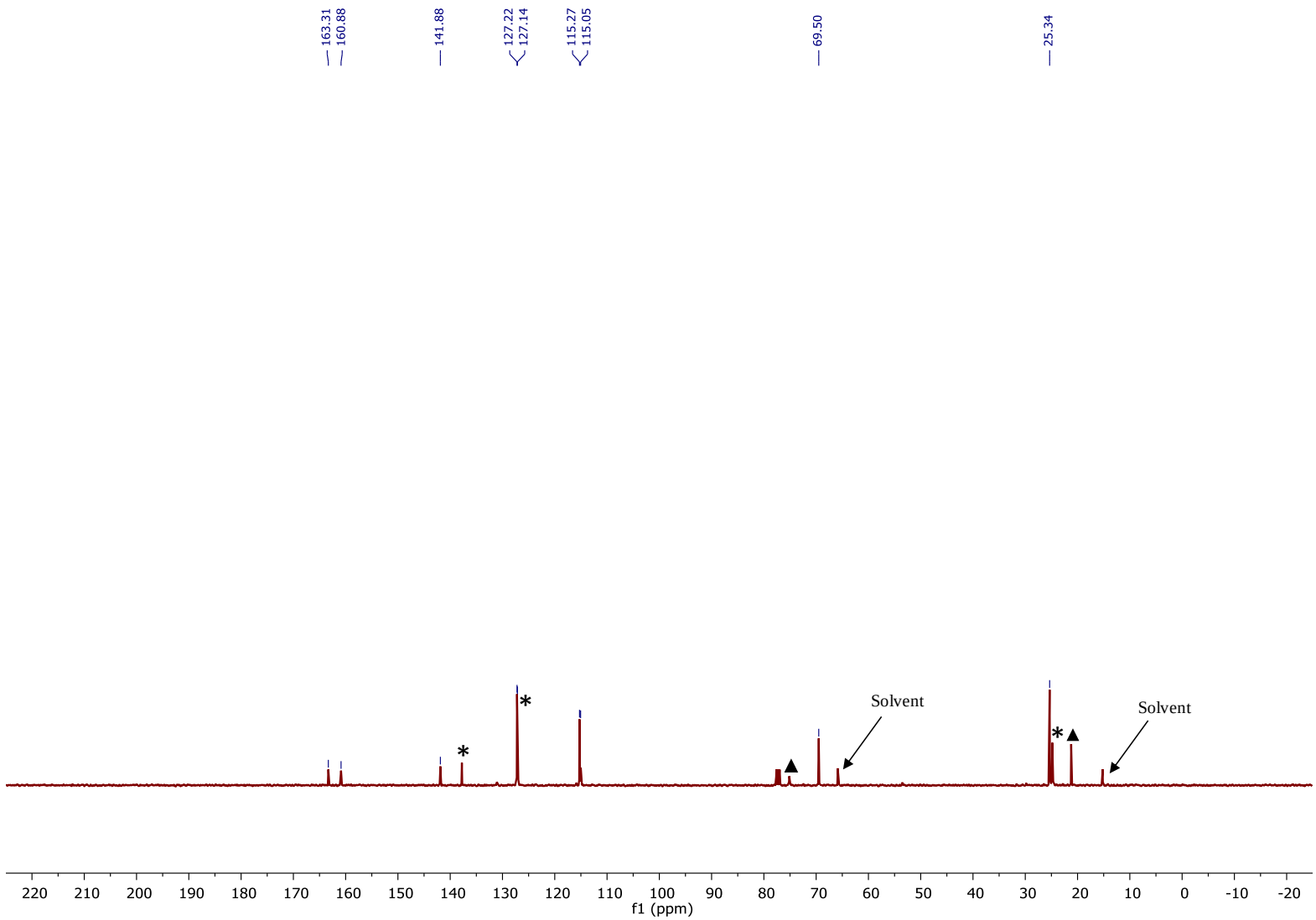


Figure S79. ^{13}C NMR of 1-(4-Fluorophenyl)ethanol (**5m**). (*) represents internal standard and (▲) represents pinnacol

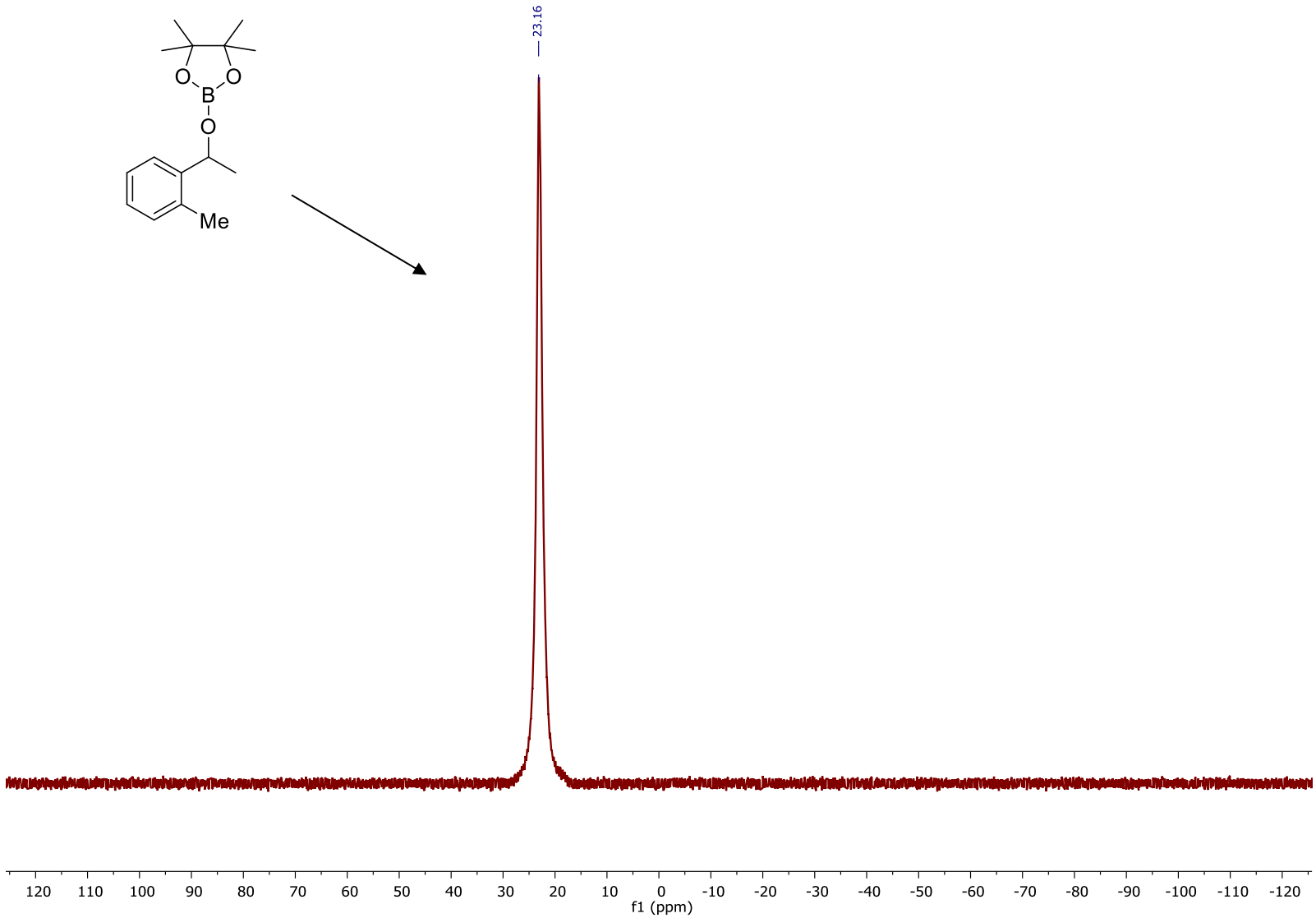


Figure S80. ^{11}B NMR resulting from catalytic hydroboration of **5n**

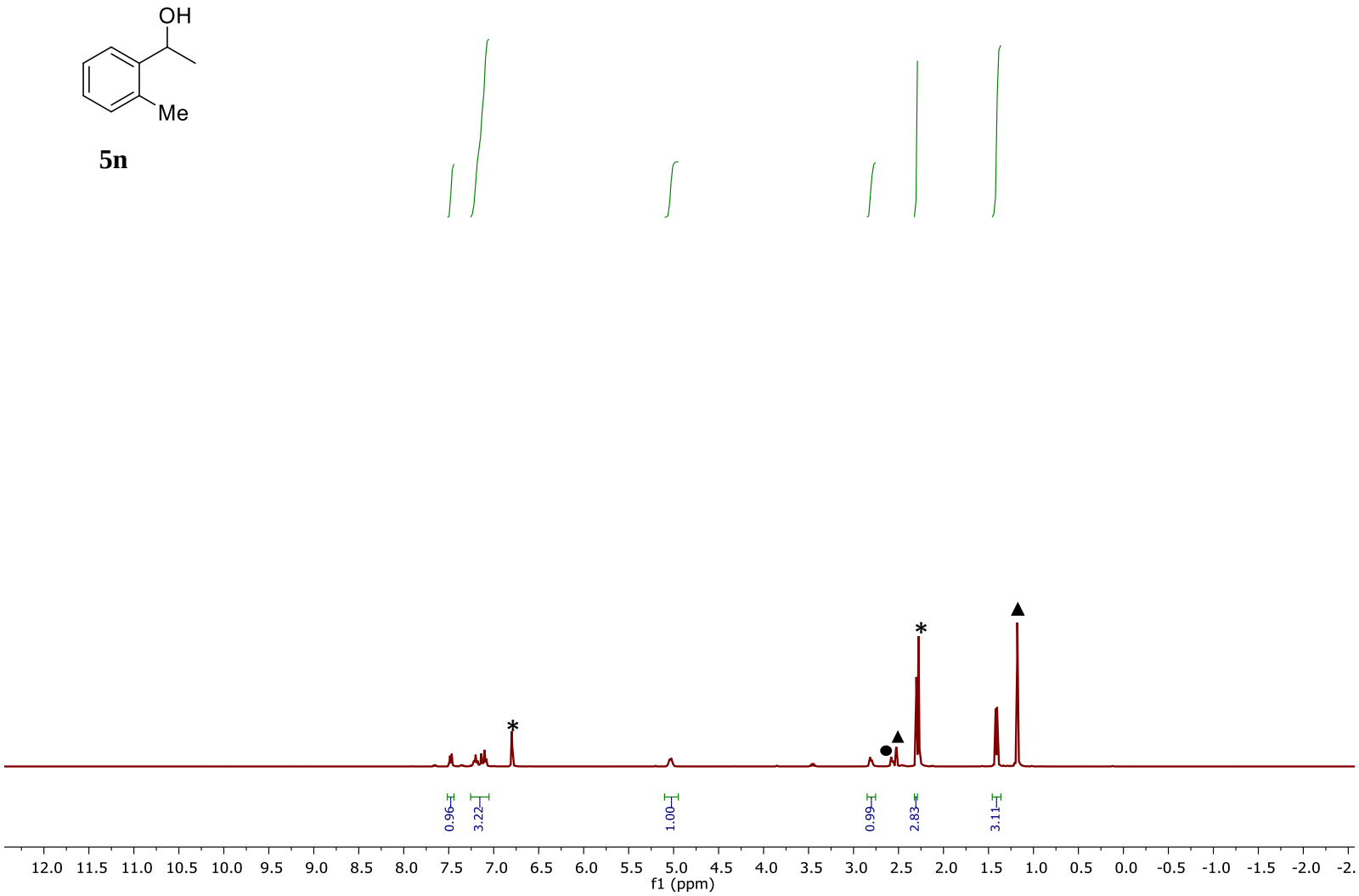


Figure S81. ^{1}H NMR of 1-(*O*-tolyl)ethanol (**5n**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

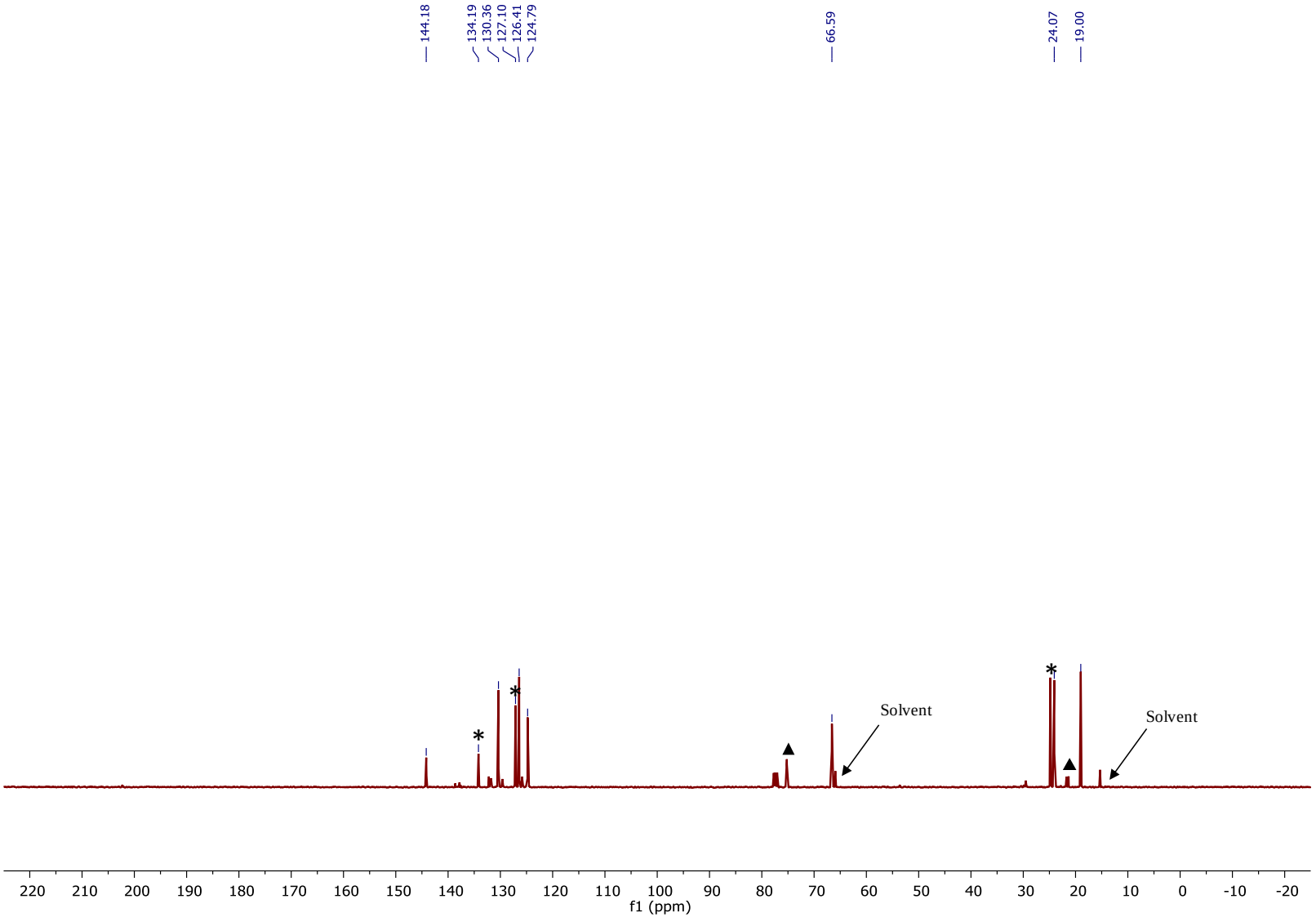


Figure S82. ^{13}C NMR of 1-(*O*-tolyl)ethanol (**5n**). (*) represents internal standard and (▲) represents pinnacol

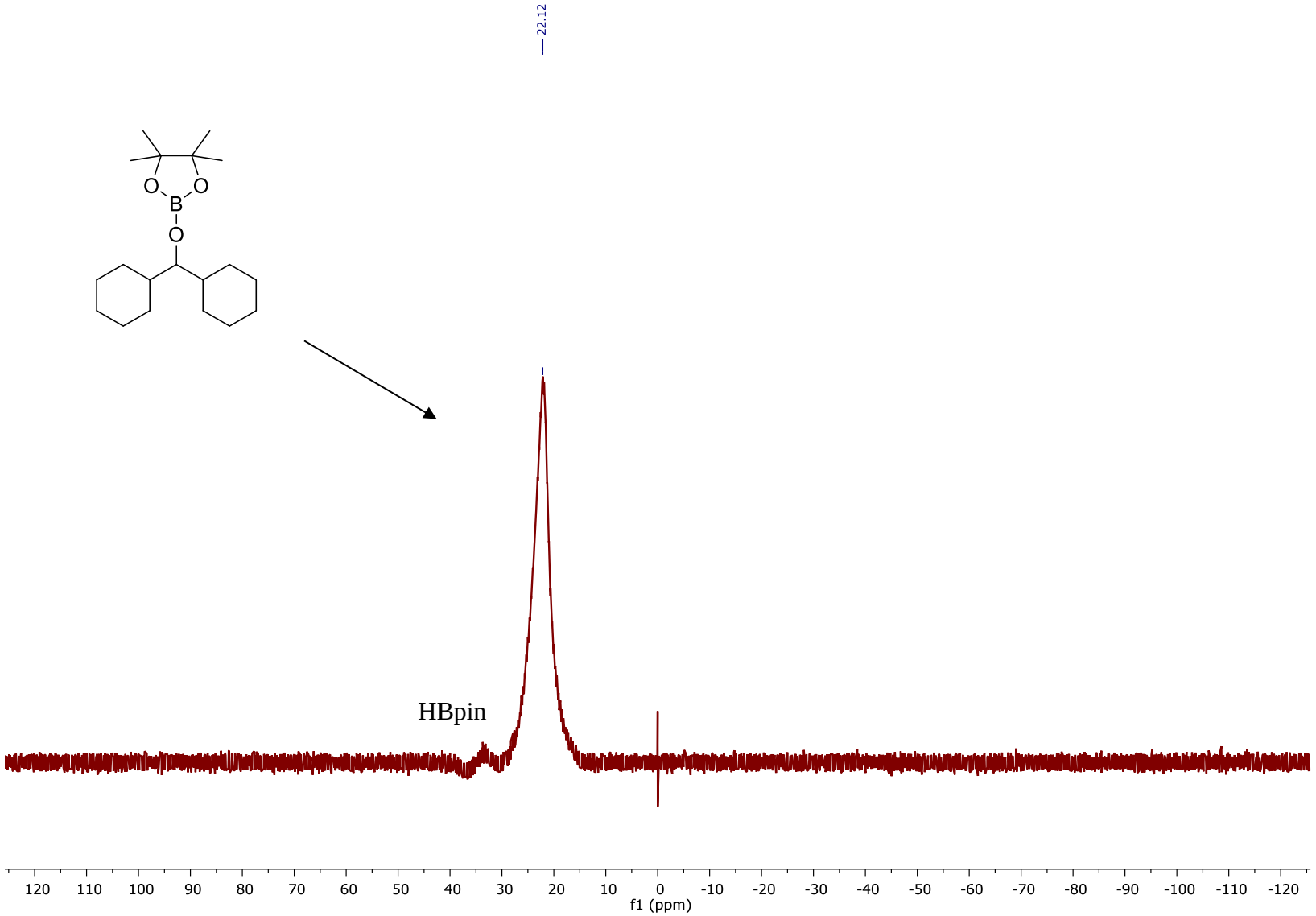


Figure S83. ^{11}B NMR resulting from catalytic hydroboration of **5o**

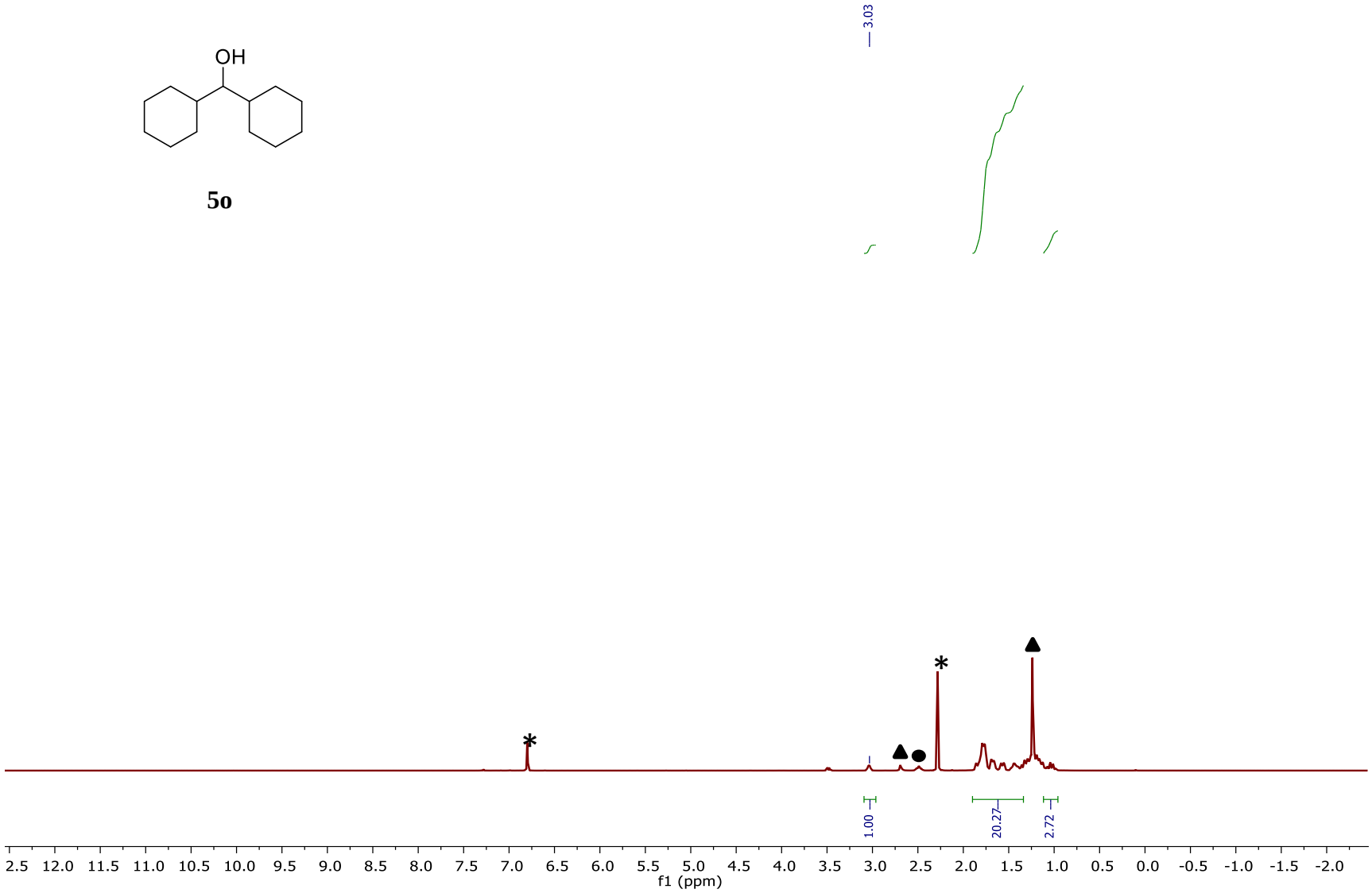


Figure S84. ^{1}H NMR of Dicyclohexylmethanol (**5o**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

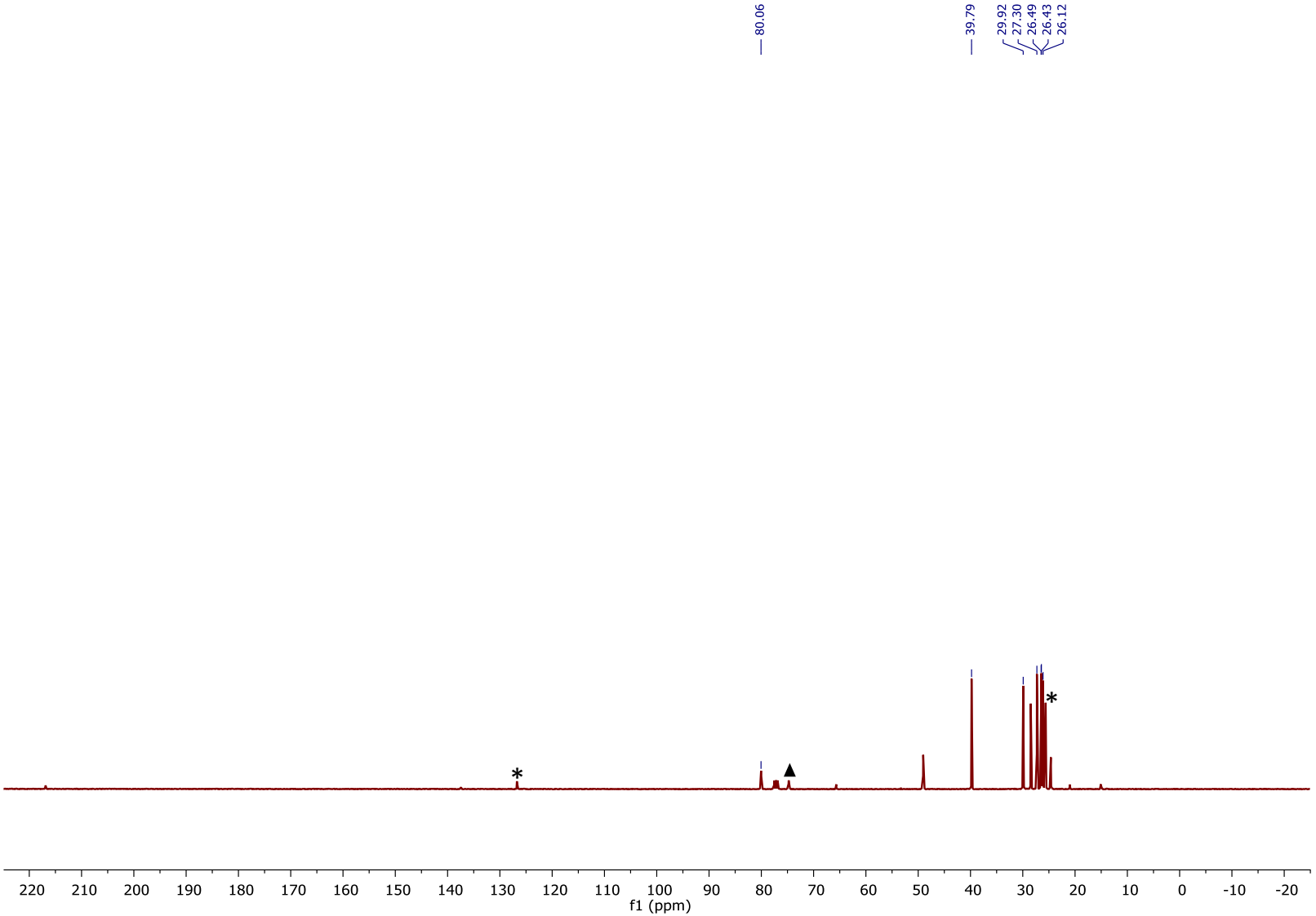


Figure S85. ^{13}C NMR of Dicyclohexylmethanol (**5o**). (*) represents internal standard and (▲) represents pinnacol

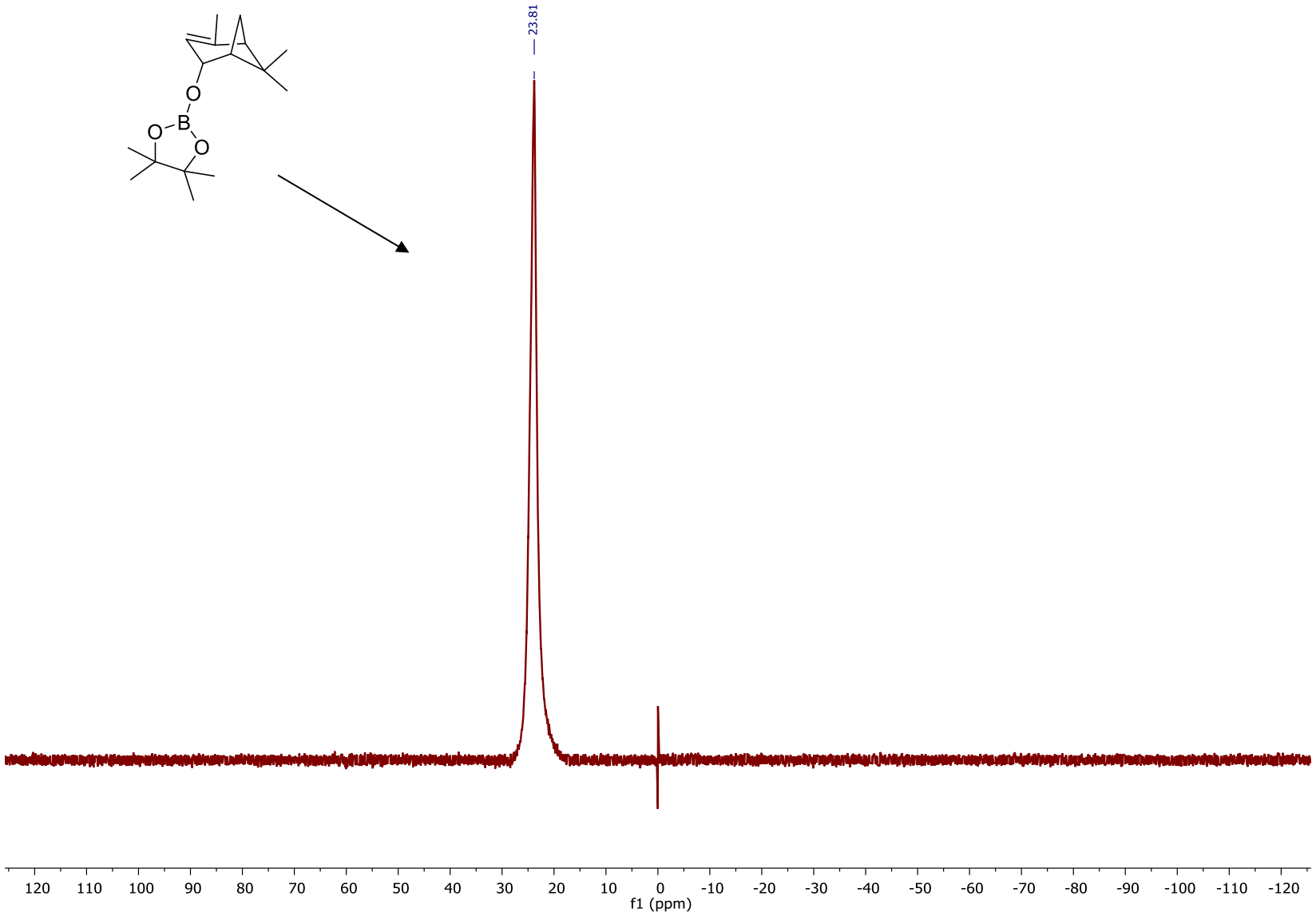


Figure S86. ^{11}B NMR resulting from catalytic hydroboration of **5p**

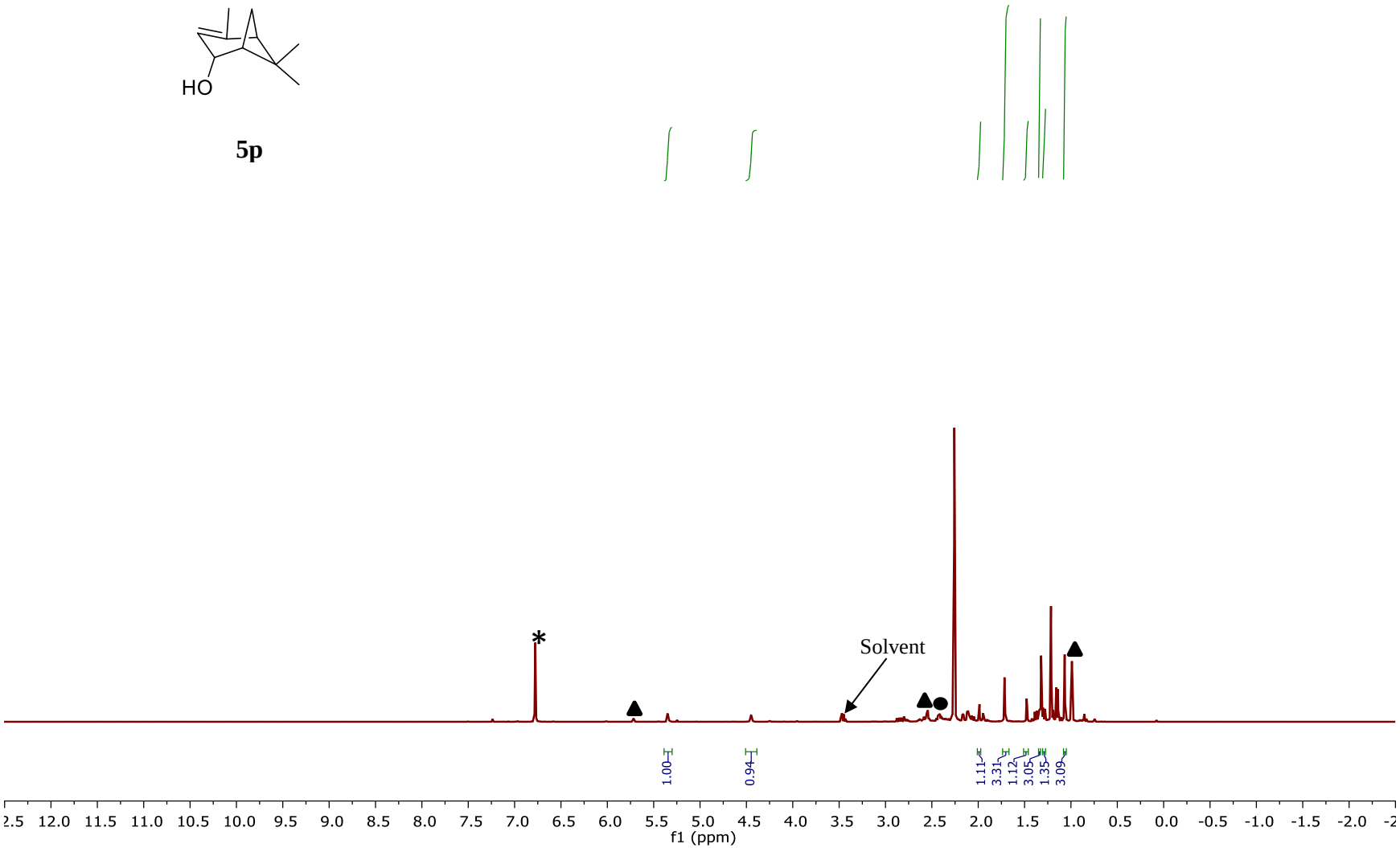


Figure S87. ^{1}H NMR of Verbenol (**5p**). (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

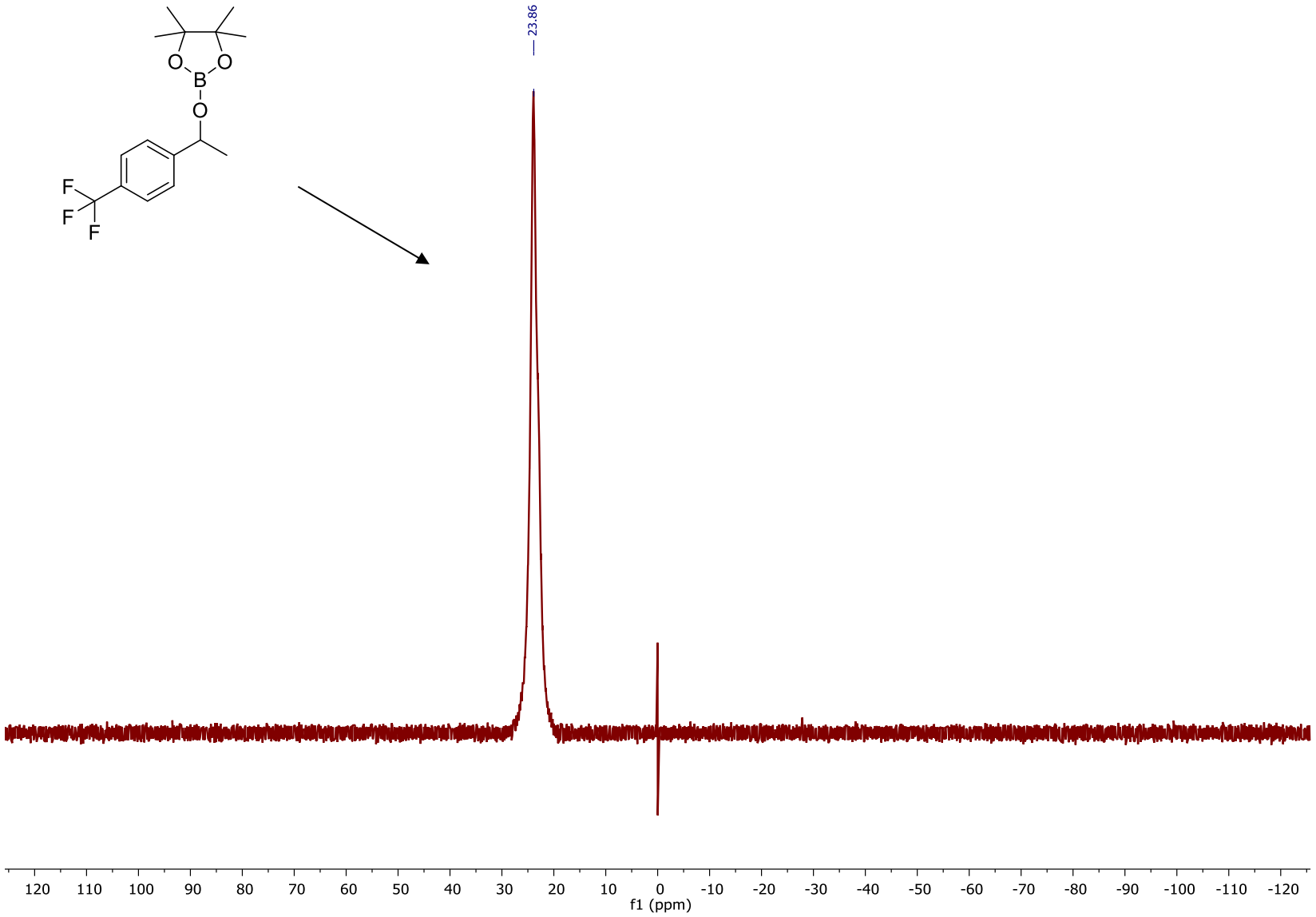


Figure S88. ^{11}B NMR resulting from catalytic hydroboration of **5q**

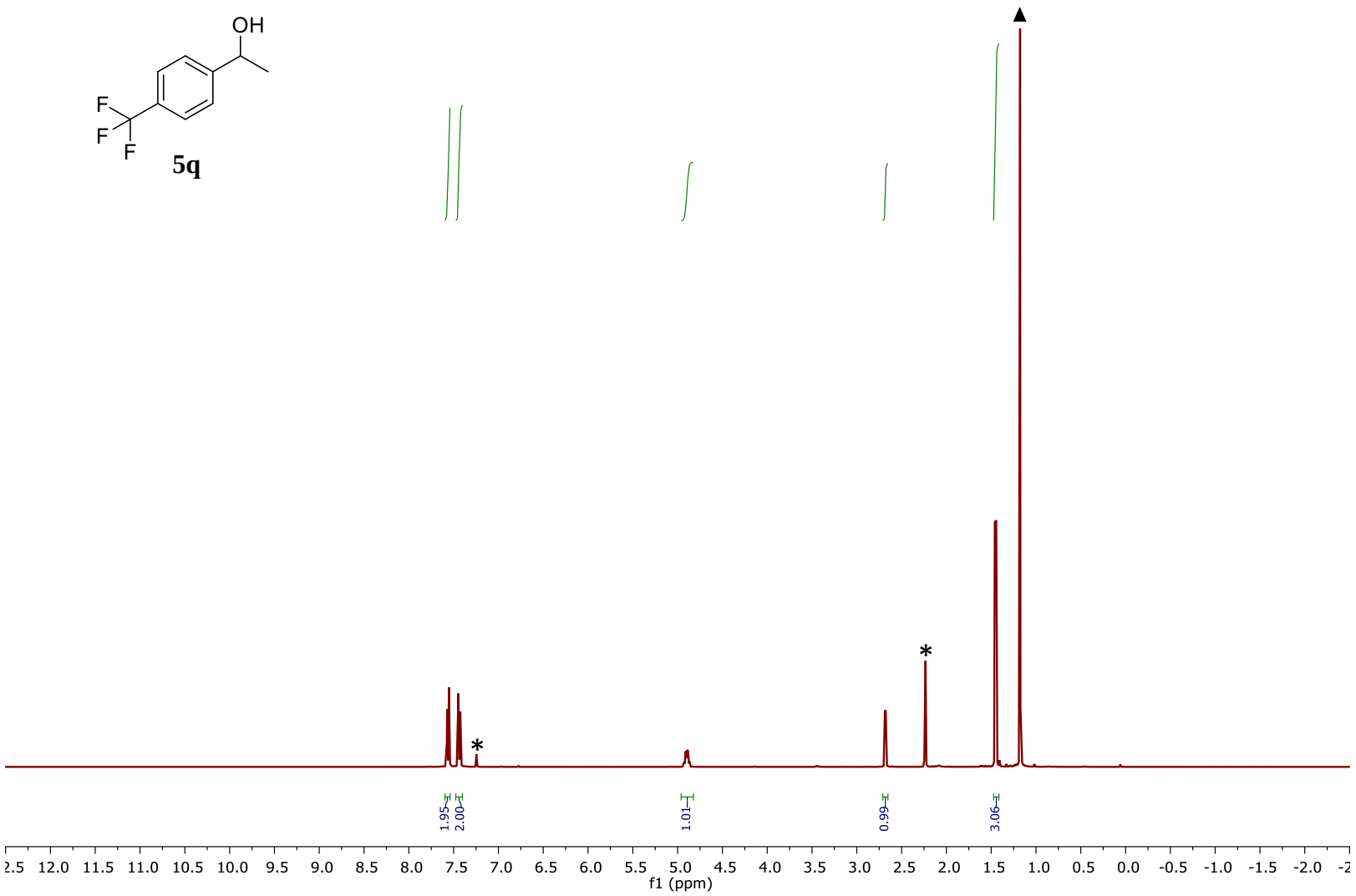


Figure S89. ^{1}H NMR of 1-(4-Trifluoromethyl)phenyl)ethanol (**5q**). (*) represents internal standard and (▲) represents pinnacol

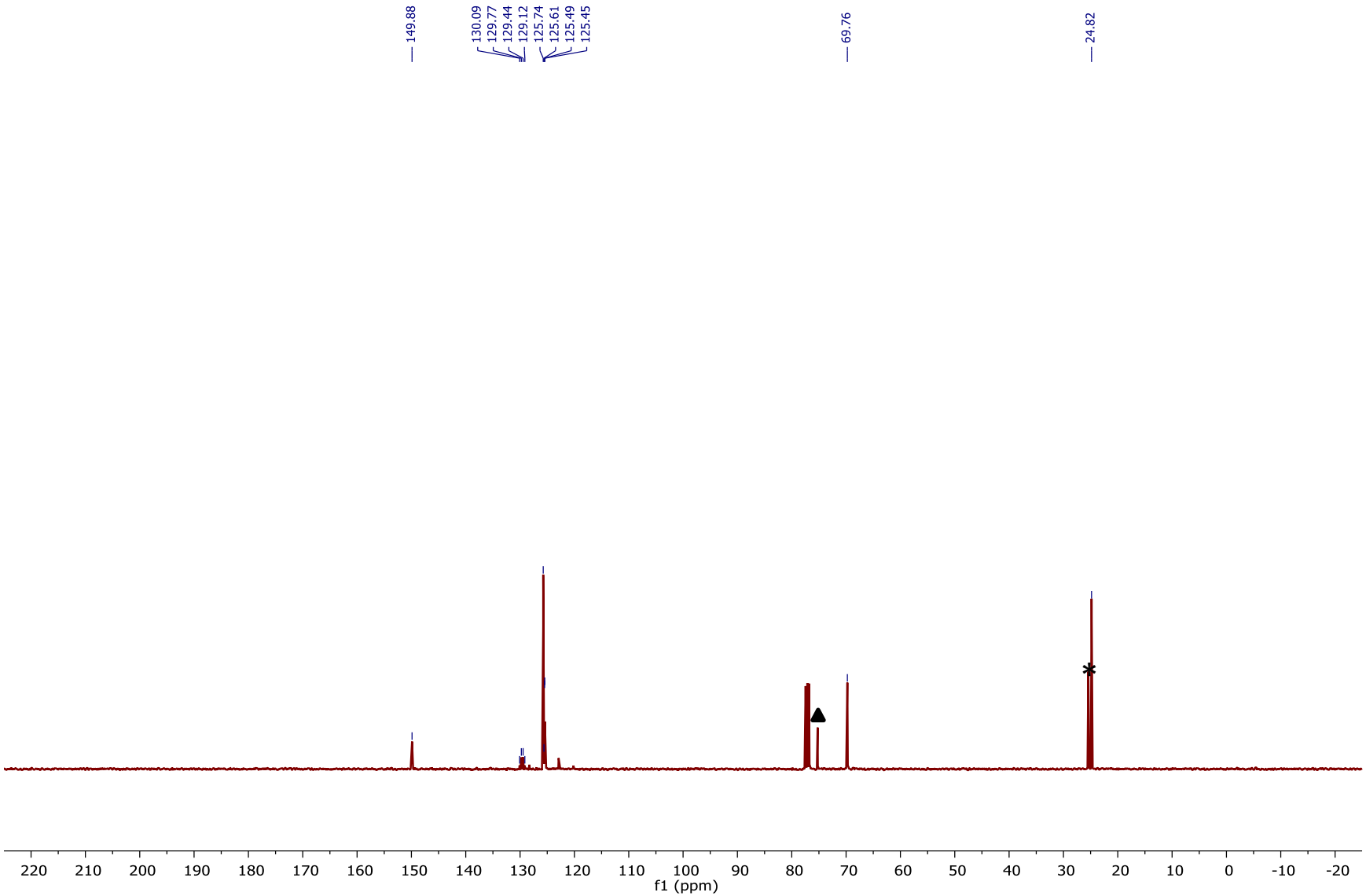


Figure S90. ^{13}C NMR of 1-(4-Trifluoromethyl)phenyl)ethanol (**5q**). (*) represents internal standard and (▲) represents pinnacol

7. ^{1}H NMR for Chemoselective experiments

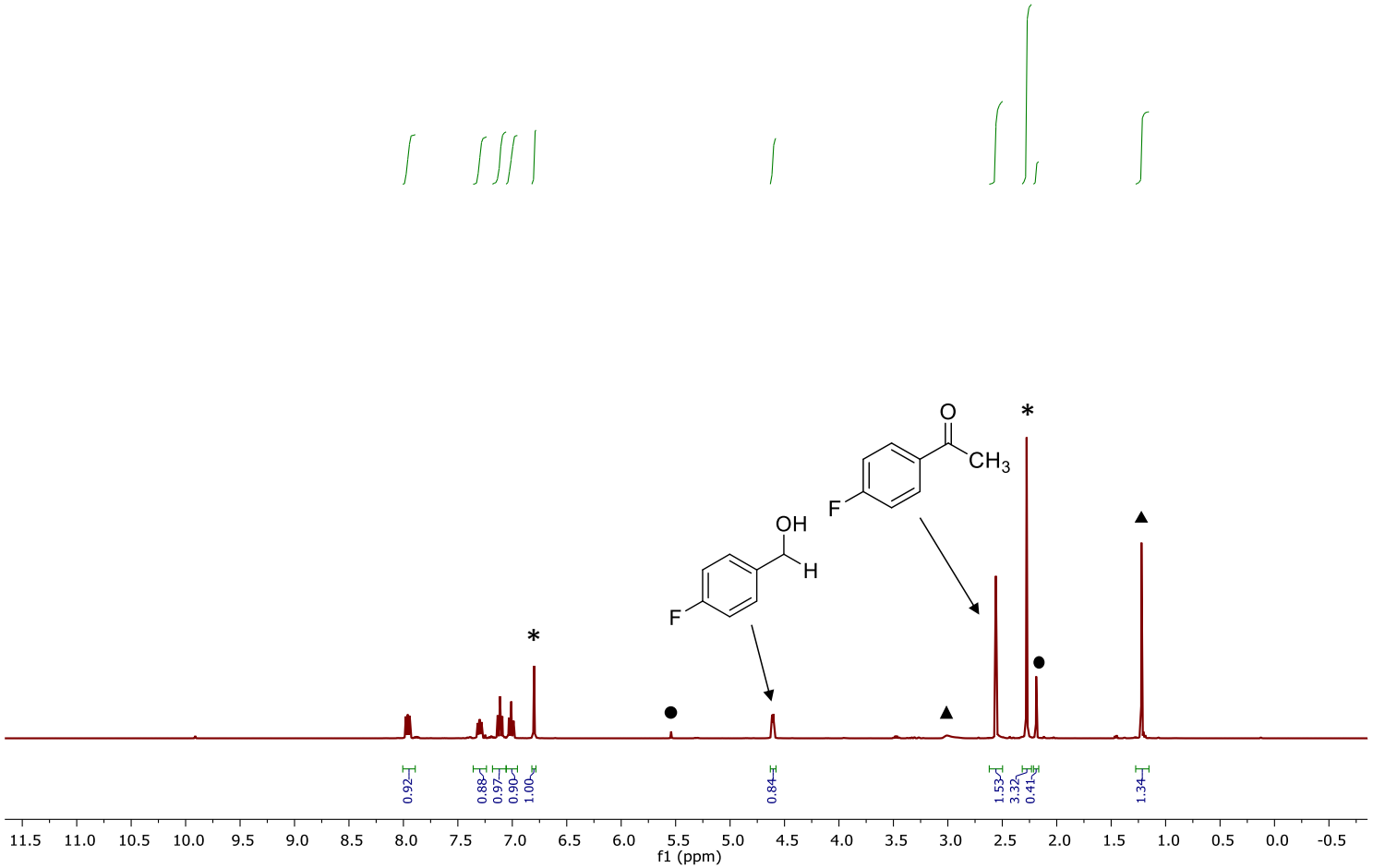


Figure S91. ^{1}H NMR of chemoselective hydroboration between 4-fluorobenzaldehyde and 4-fluoroacetophenone at T=30 minutes. (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

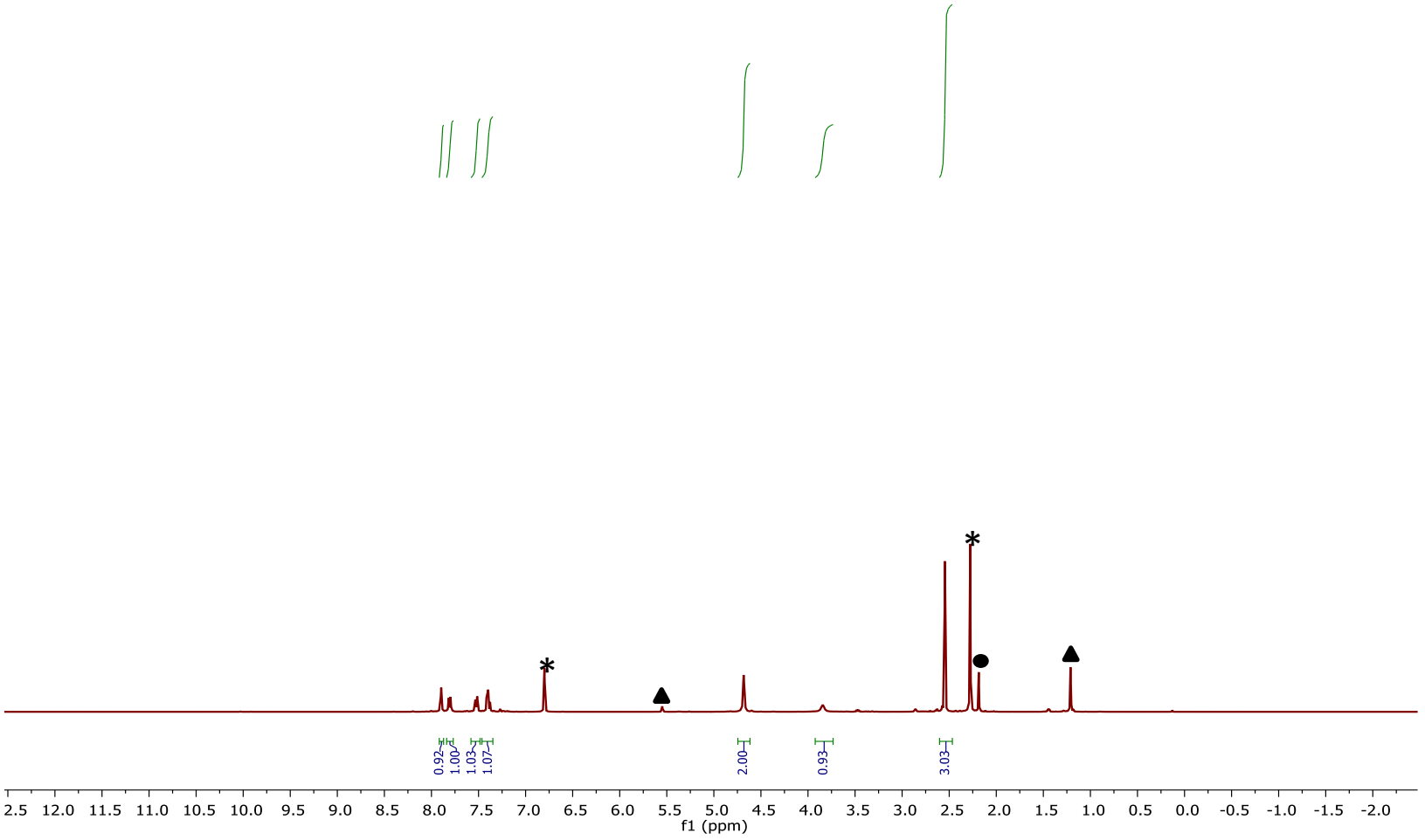


Figure S92. [1]H NMR of chemoselective hydroboration of 3-acetylbenzyl alcohol. (*) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

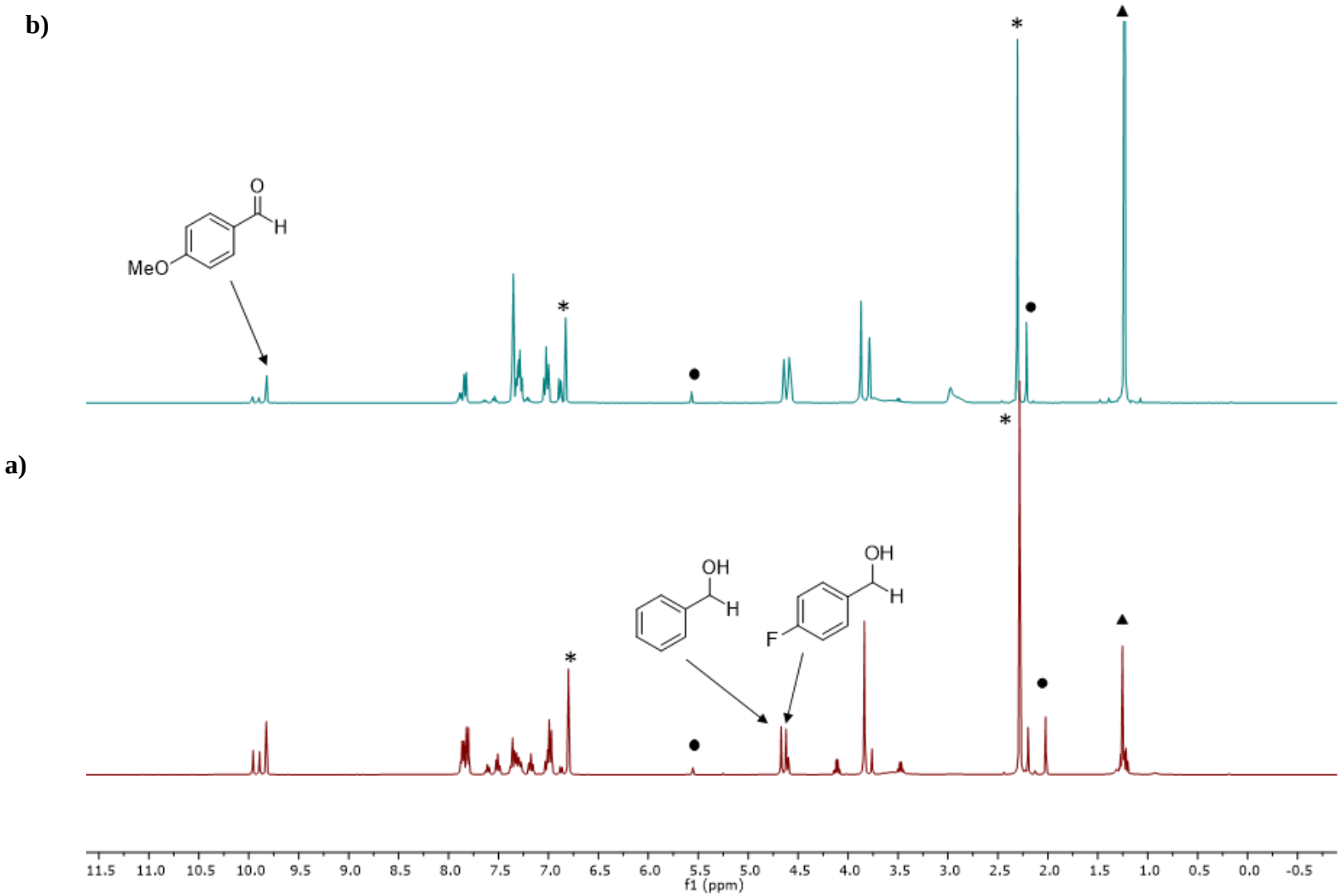


Figure S93. ^{1}H NMR of competitive chemoselective hydroboration of benzaldehyde, 4-methoxybenzaldehyde, and 4-fluorobenzaldehyde. (a) ^{1}H NMR at T= 30 minutes; (b) ^{1}H NMR at T= 1 hr after additional 1 equiv. HBpin was added. (*****) represents internal standard, (●) represents acac ligand and (▲) represents pinnacol

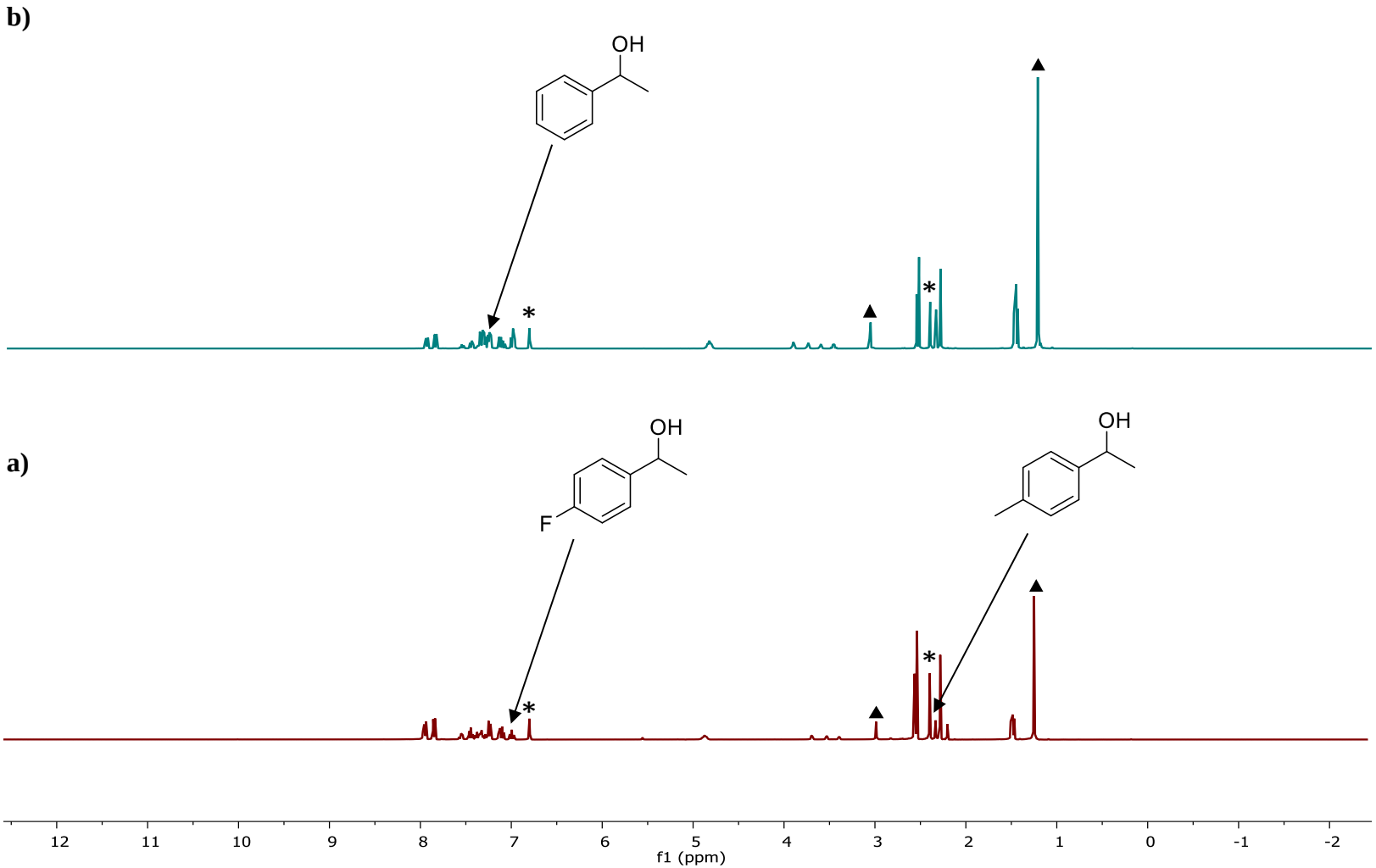


Figure S94. ^{1}H NMR of competitive chemoselective hydroboration of acetophenone, 4-methylacetophenone, and 4-fluoroacetophenone. (a) ^{1}H NMR at T= 2 hours; (b) ^{1}H NMR at T= 4 hours after additional 1 equiv. HBpin was added. (*****) represents internal standard and (▲) represents pinnacol

8. Deuterium labelling experiments

8.1. ^{11}B and ^{1}H NMR of synthesized DBpin

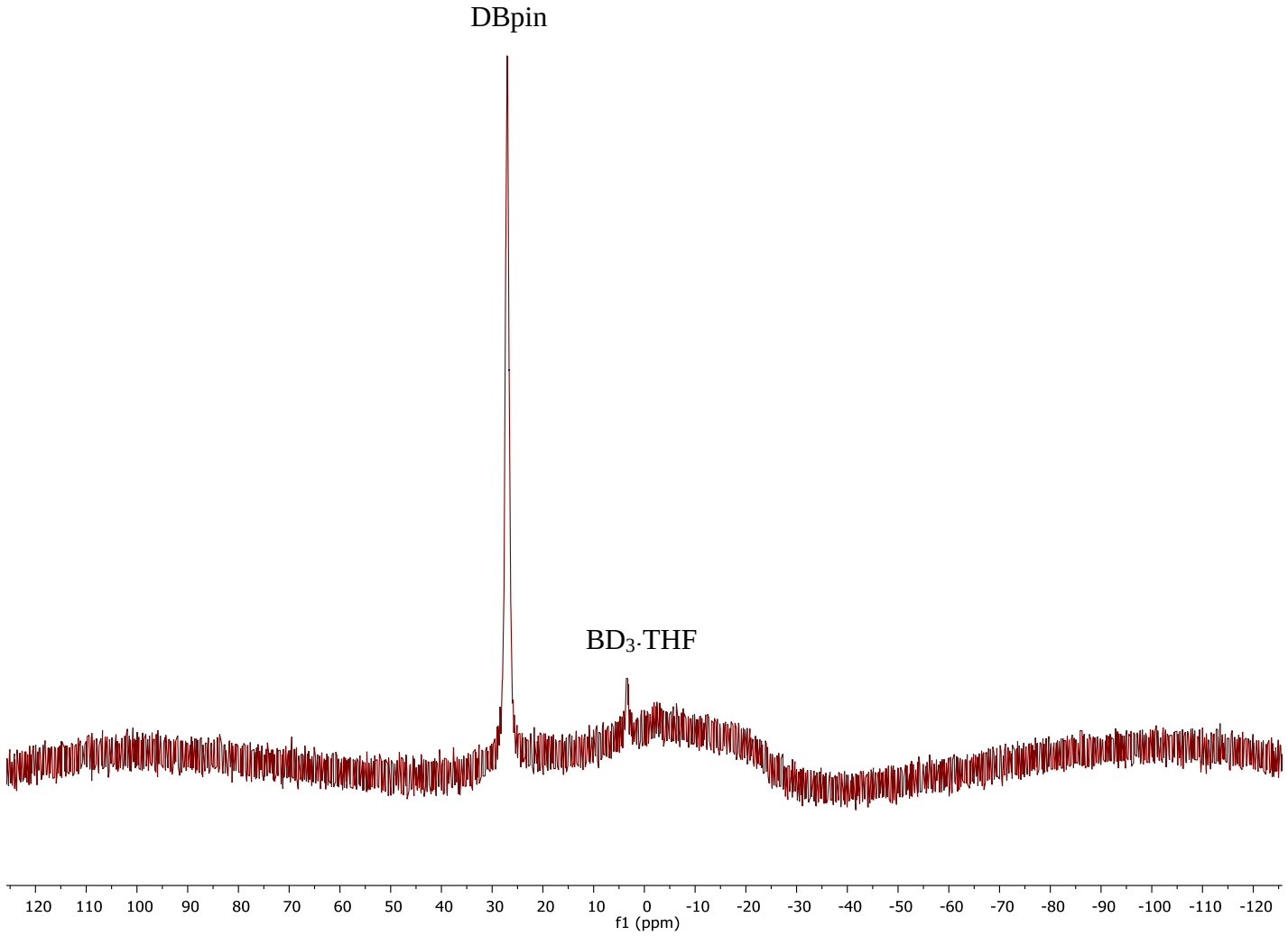


Figure S95. ^{11}B NMR of DBpin

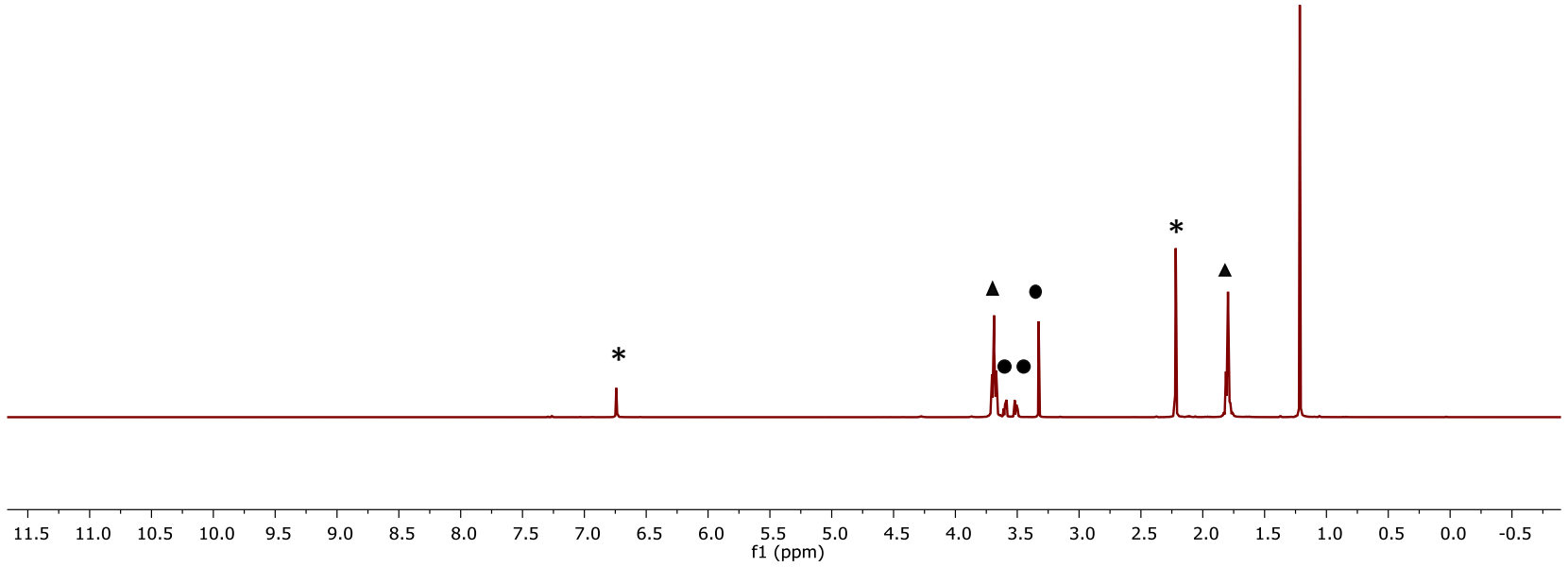
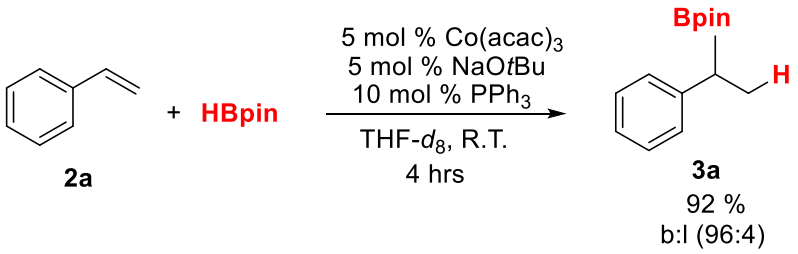


Figure S96. ^{1}H NMR of DBpin. (*) represents internal standard, (●) represents diglyme (diethylene glycol dimethyl ether) and (▲) represents THF peaks.

8.2 General procedure for deuterium labelling experiment

8.2.1 Hydroboration with THF-d_8



An oven dried scintillation vial was charged with $Co(acac)_3$ (17.8 mg, 0.05 mmol), NaO^tBu (4.8 mg, 0.05 mmol), THF-d_8 (1 mL) and magnetic stir bar. The reaction mixture was allowed to stir for ~ 1-2 minutes, and a change of color from dark green to purple was observed. PPh_3 (26 mg, 0.10 mmol), HBpin (154 mg, 174 µL, 1.2 mmol), styrene (104 mg, 115 µL, 1.0 mmol) was then added and the reaction mixture was then stirred inside the glove box for 4 hrs at room temperature. The reaction was quenched by opening the vial to air and adding DI H_2O (5 mL) and diethyl ether (10 mL). The organic phase was extracted, concentrated under vacou and passed through a short pad of silica using hexanes and ethyl acetate as the eluent (95: 5). Yield: 214 mg (92 %). ^{1}H NMR was used to determine the ratio of the regioisomers.

^{1}H NMR (400 MHz, $CDCl_3$): 7.29-7.22 (4H, m), 7.16-7.12 (1H, m), 2.45 (1H, quart, J = 7.52 Hz), 1.34 (3H, d, 7.52 Hz), 1.22 (6H, s), 1.21 (6H, s).

^{13}C NMR (101 MHz, $CDCl_3$): 145.09, 128.42, 127.91, 125.20, 83.41, 24.74, 24.71, 17.18

11B NMR (126 MHz, $CDCl_3$): 32.71 ppm

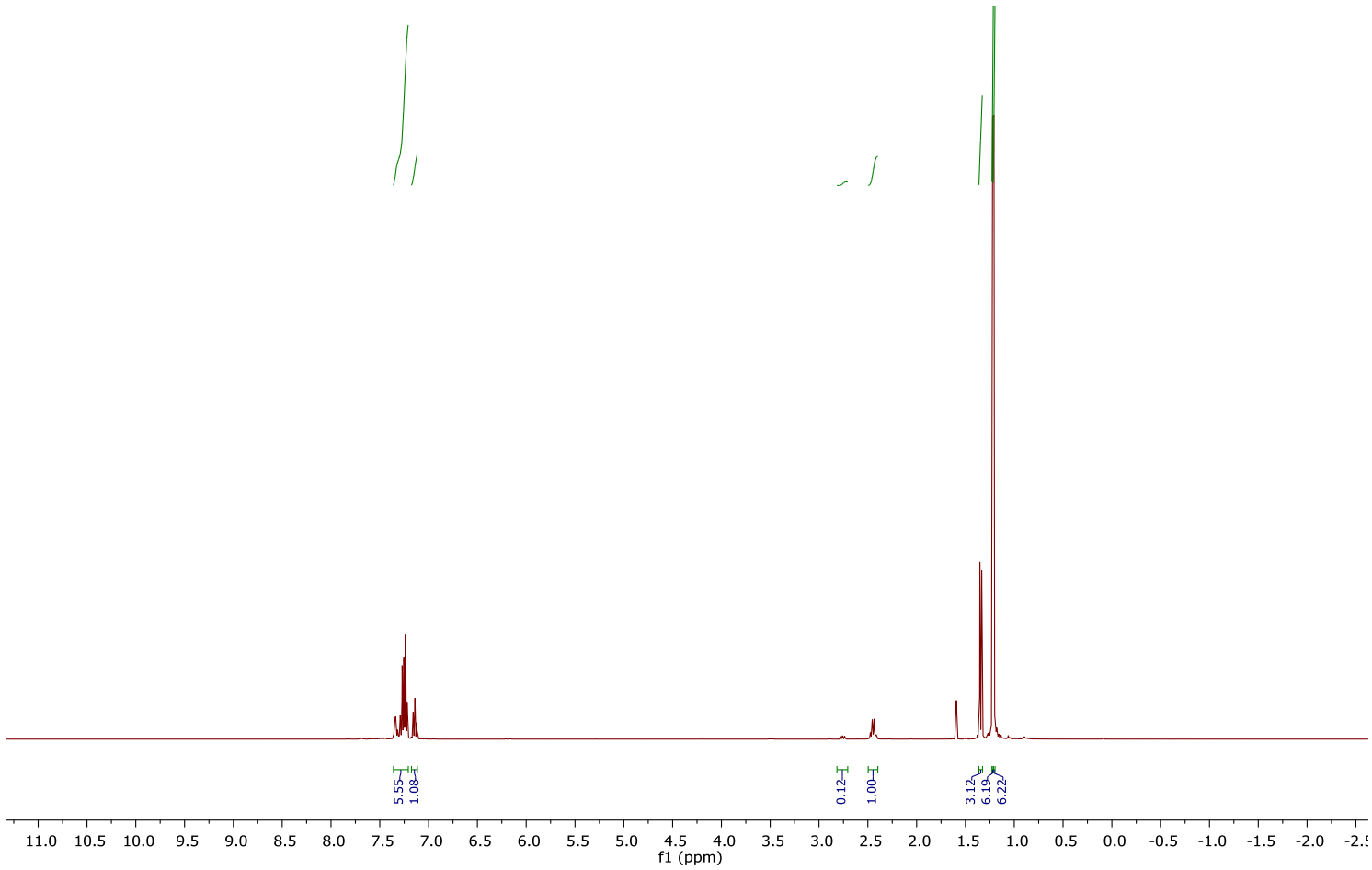


Figure S97. ^{1}H NMR of 3a

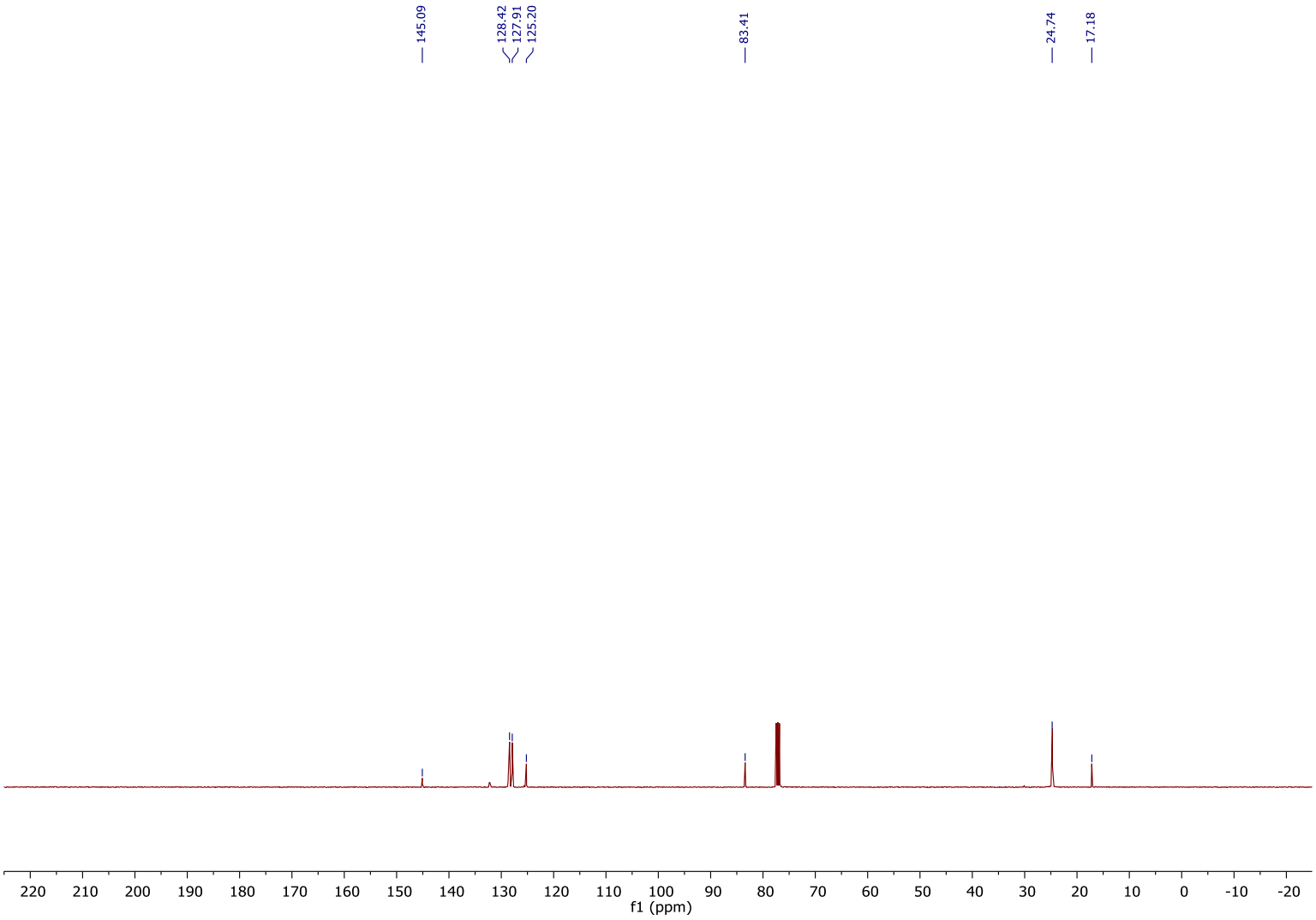


Figure S98. ^{13}C NMR of 3a.

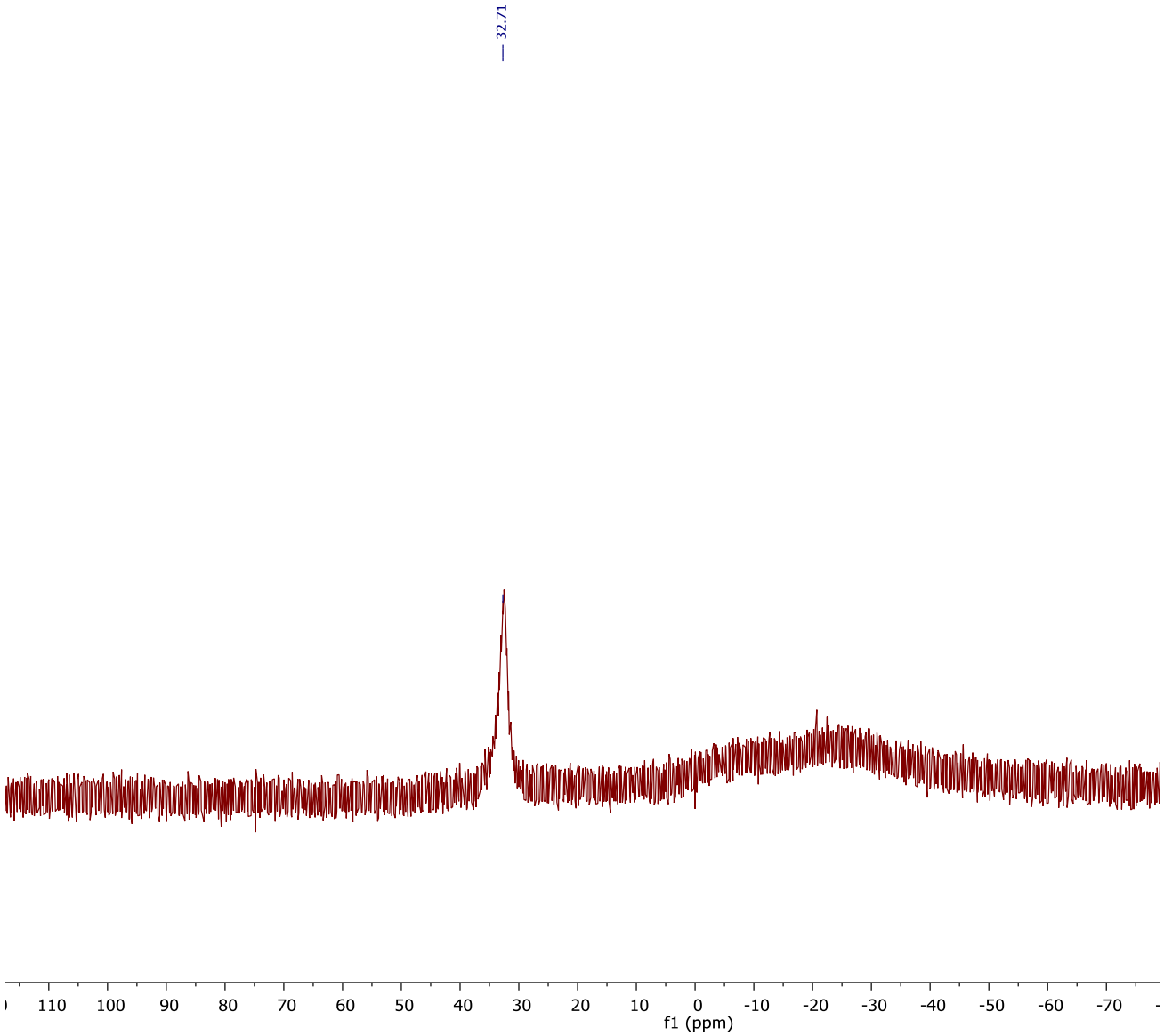
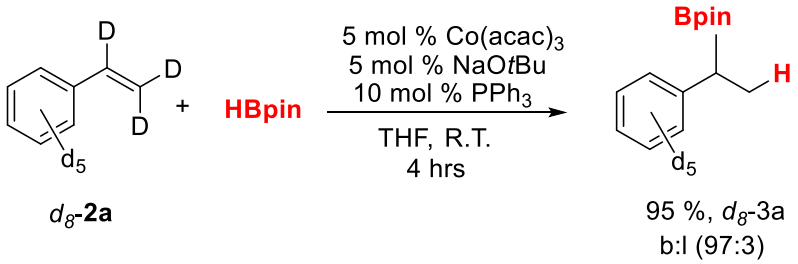


Figure S99. ^{11}B NMR of 3a.

8.2.2 Hydroboration with styrene-d_8



d_8-**2a**

95 %, d_8-3a
b:l (97:3)

An oven dried scintillation vial was charged with $Co(acac)_3$ (17.8 mg, 0.05 mmol), NaO^tBu (4.8 mg, 0.05 mmol), THF (1 mL) and magnetic stir bar. The reaction mixture was allowed to stir for ~ 1-2 minutes, and a change of color from dark green to purple was observed. PPh_3 (26 mg, 0.10 mmol), HBpin (154 mg, 174 µL, 1.2 mmol), styrene-d_8 (112.2 mg, 114.6 µL, 1.0 mmol) was then added and the reaction mixture was then stirred inside the glove box for 4 hrs at room temperature. The reaction was quenched by opening the vial to air and adding DI H_2O (5 mL) and diethyl ether (10 mL). The organic phase was extracted, concentrated under vacou and passed through a short pad of silica using hexanes and ethyl acetate as the eluent (95: 5). Yield: 221 mg (95 %). ^{1}H NMR was used to determine the ratio of the regioisomers.

^{1}H NMR (400 MHz, $CDCl_3$): 1.28 (1H, br s), 1.21 (6H, s), 1.20 (6H, s)

^{13}C NMR (101 MHz, $CDCl_3$):144.86, 127.90 (t, J = 24 Hz), 127.50 (t, J = 22.7), 124.67 (t, J = 24.2 Hz), 83.39, 24.74, 24.71, 16.5 (quint, J=19.4 Hz).

11B NMR (126 MHz, $CDCl_3$): 32.64 ppm

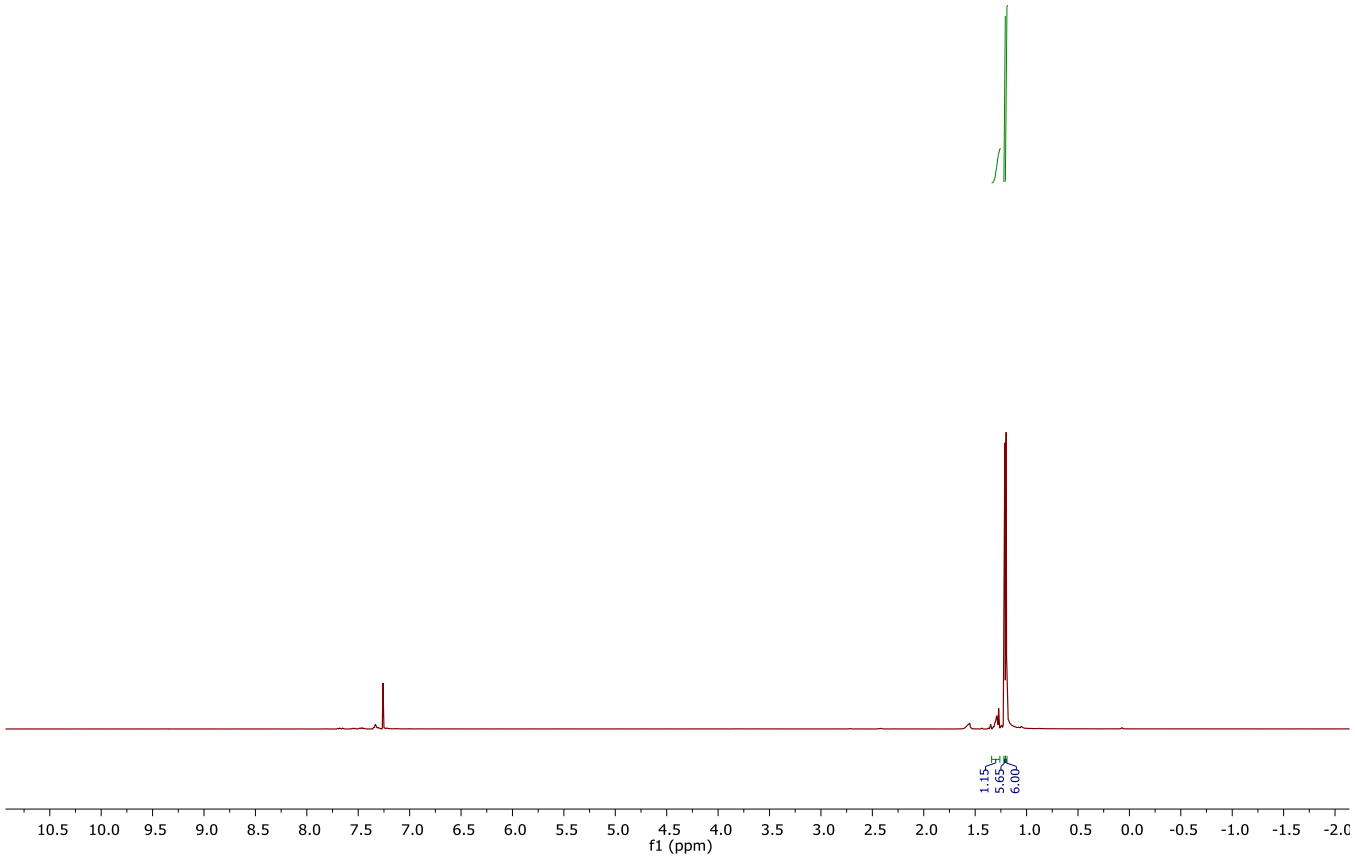


Figure S100. ^{1}H NMR of d_8-3a

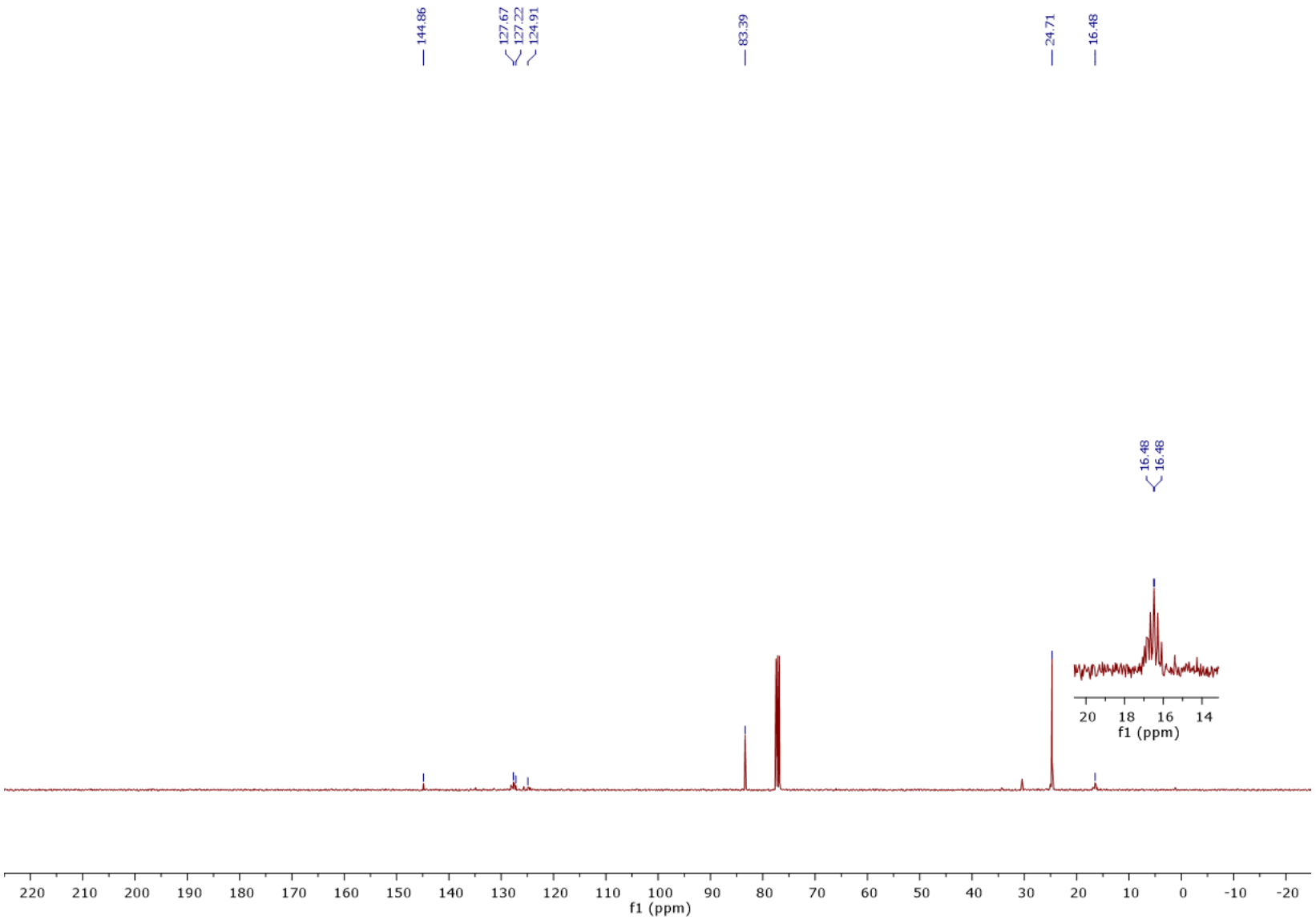


Figure S101. ^{13}C NMR of d_8-3a

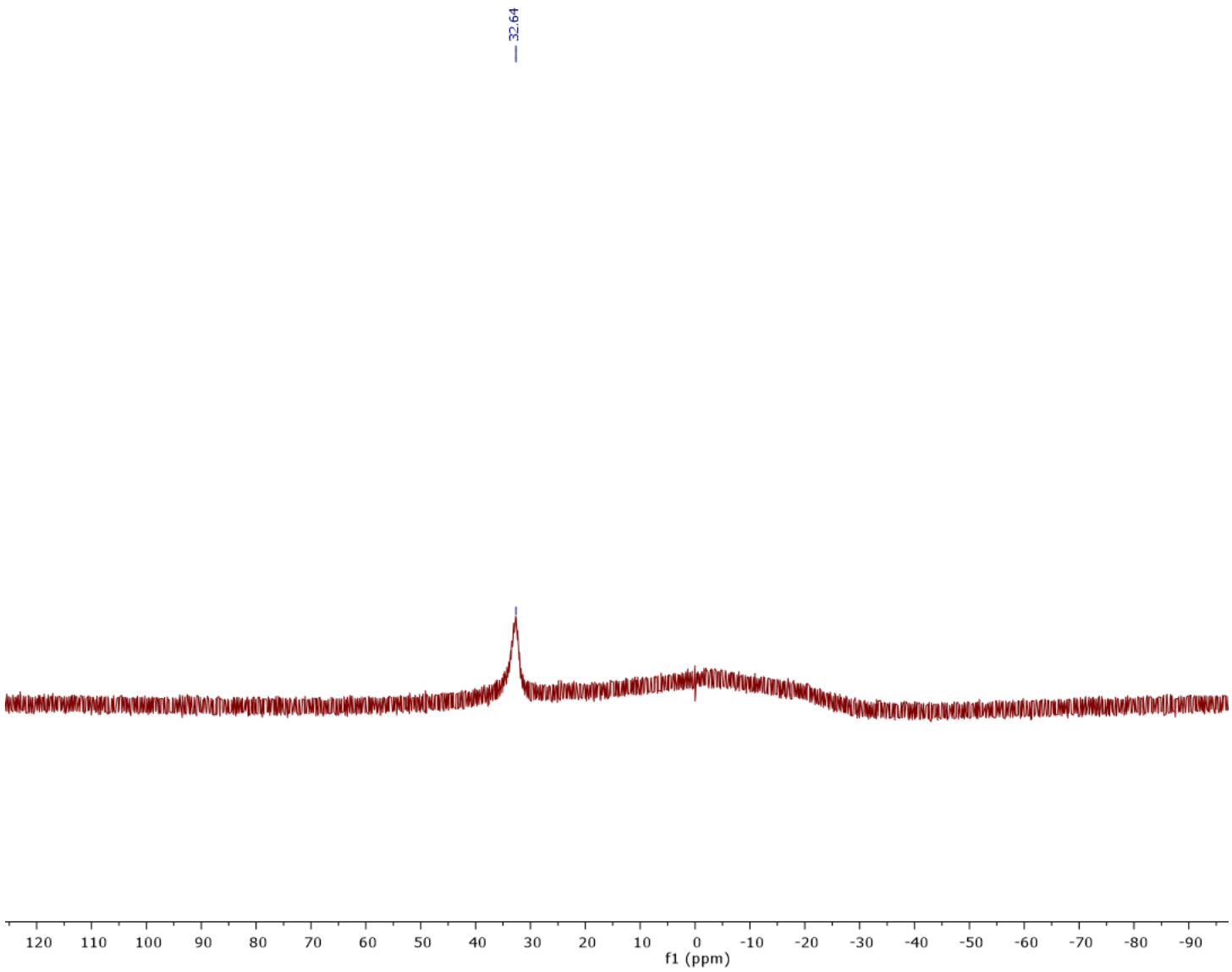
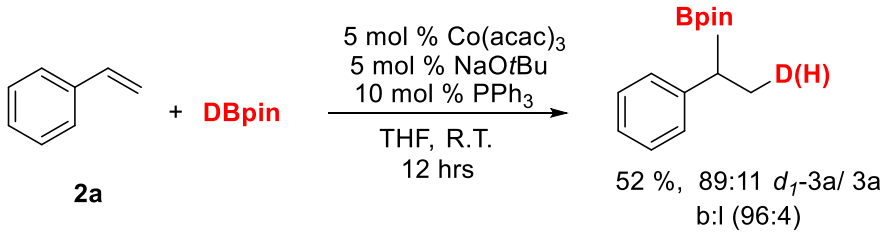


Figure S102. ^{11}B NMR of d_8-3a

8.2.3 Hydroboration with DBpin



An oven dried scintillation vial was charged with $Co(acac)_3$ (8.9 mg, 0.025 mmol), NaO^tBu (2.41 mg, 0.025 mmol), THF (1 mL) and magnetic stir bar. The reaction mixture was allowed to stir for ~ 1-2 minutes, and a change of color from dark green to purple was observed. PPh_3 (13.1 mg, 0.05 mmol), DBpin (240 µL, 0.6 mmol), styrene (52 mg, 57.5 µL, 0.5 mmol) was then added and the reaction mixture was then stirred inside the glove box for 4 hrs at room temperature. The reaction was quenched by opening the vial to air and adding DI H_2O (5 mL) and diethyl ether (10 mL). The organic phase was extracted, concentrated under vacou and passed through a short pad of silica using hexanes and ethyl acetate as the eluent (95: 5). Yield: 60 mg (52 %). 1H NMR was used to determine the ratio of the regioisomers.

^{1}H NMR (400 MHz, $CDCl_3$): 7.27- 7.22 (4H, m), 7.17-7.13 (1H, t, J = 8Hz), 2.44 (1H, quart, J =7.12 Hz), 1.35 (2.11 H, d, J = 7.68 Hz), 1.23 (6H, s), 1.22 (s, 6H)

13C NMR (101 MHz, $CDCl_3$) = 145.09, 128.43, 127.91, 125.21, 83.41, 24.75, 17.19 (s, CH_3 from protonated product, 16.88 (t, J = 19.59 Hz, H_2D from monodeuterated product)

11B NMR (126 MHz, $CDCl_3$): 32.88 ppm

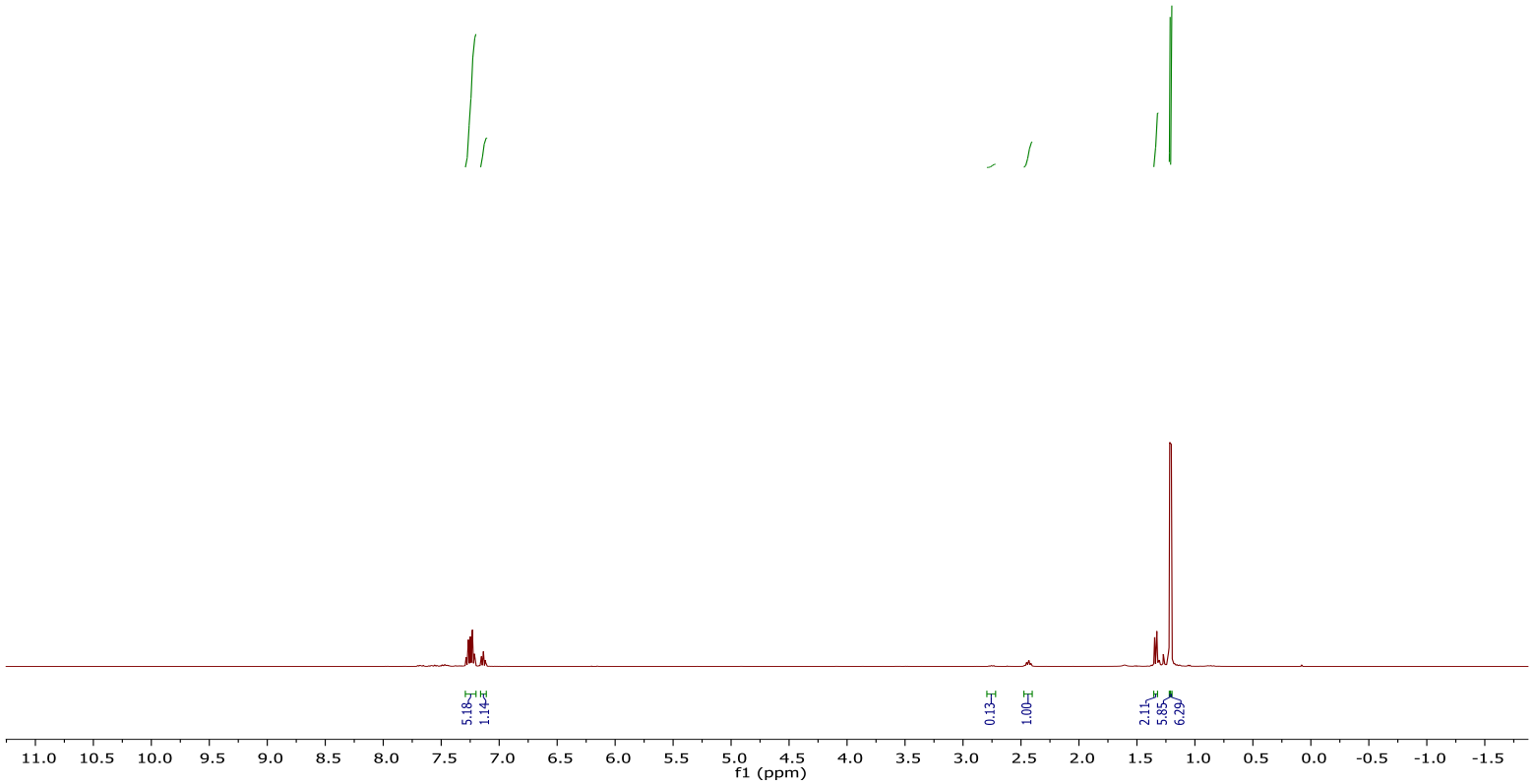


Figure S103. ^{1}H NMR of d_1- 3a/ 3a.

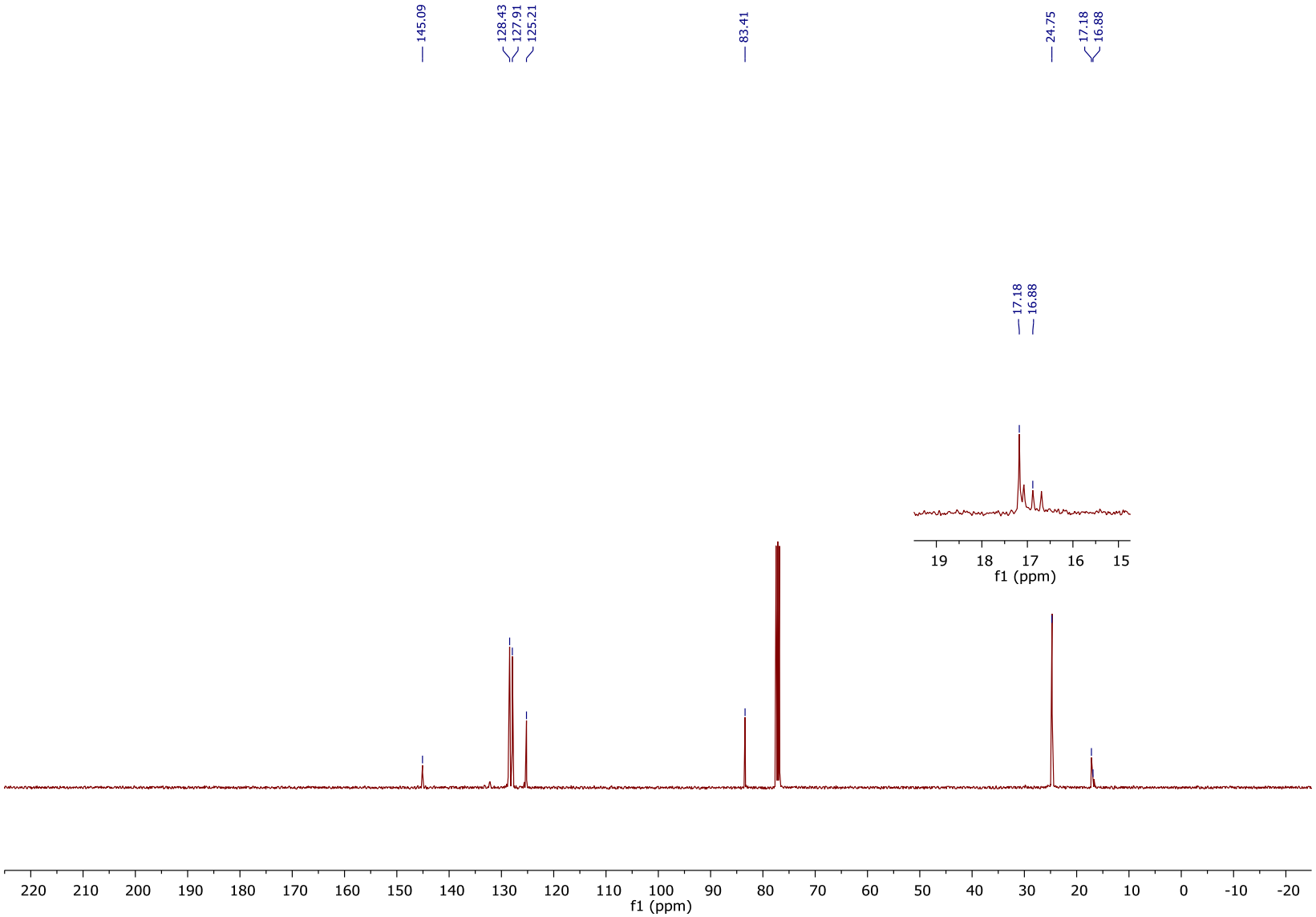


Figure S104. ^{13}C NMR of d_1- 3a/ 3a.

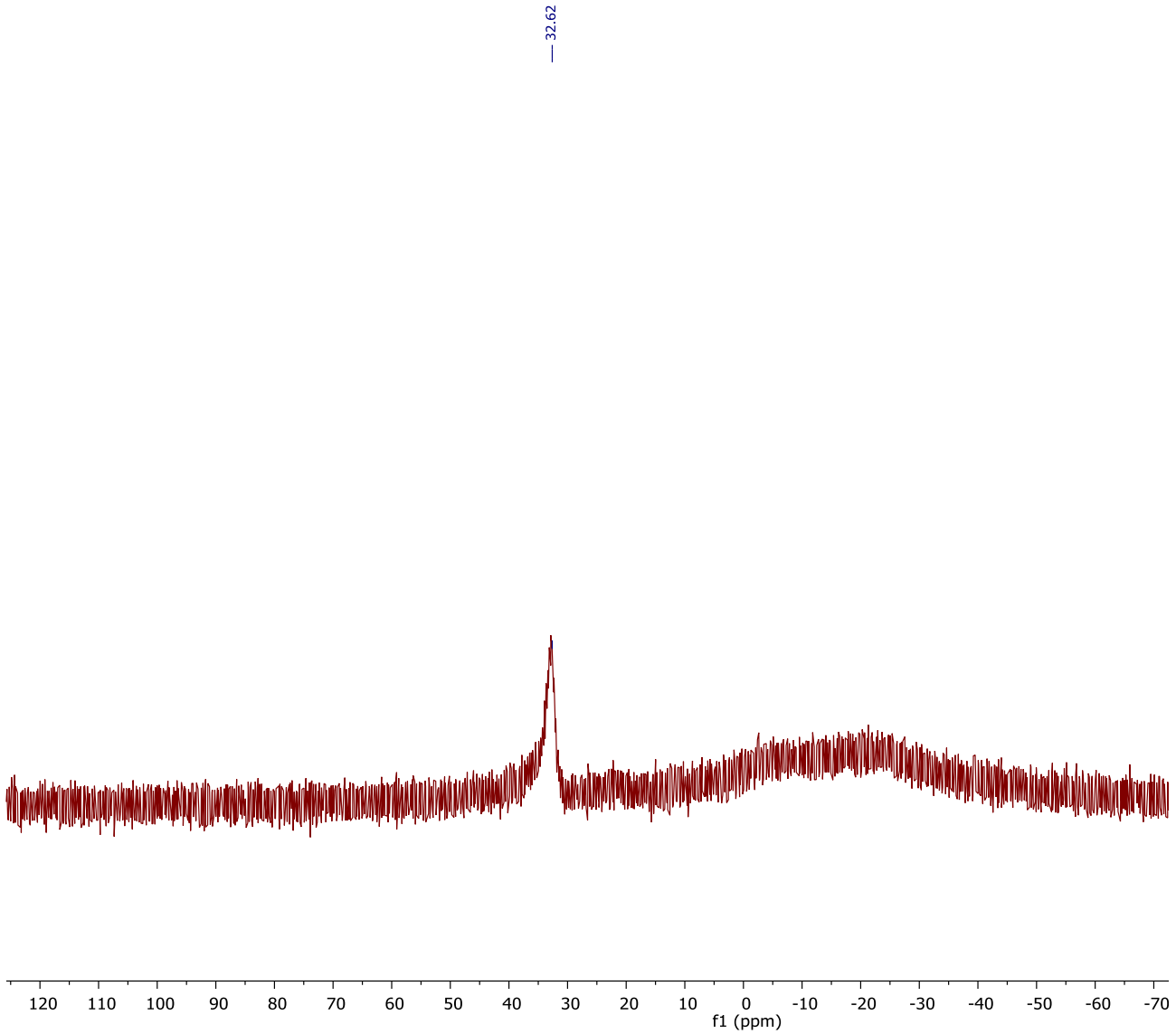


Figure S105. ^{11}B NMR of d_1- 3a/ 3a.

9. GC-MS spectra of reaction mixtures containing 1º and 2º alcohol

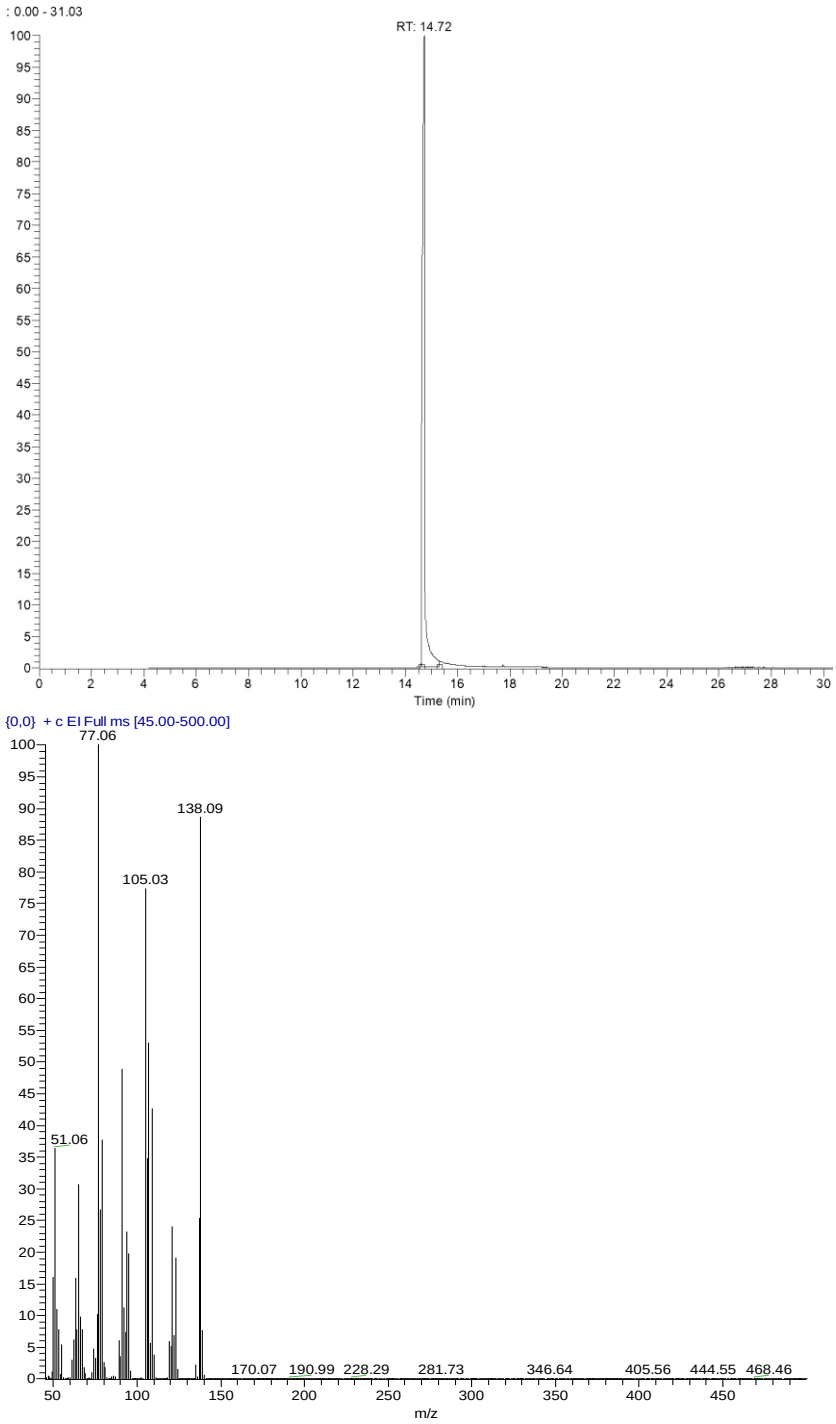


Figure S106. GC-MS data of 4-methoxybenzyl Alcohol (**5a**). GC-MS (m/z) = 138.09.

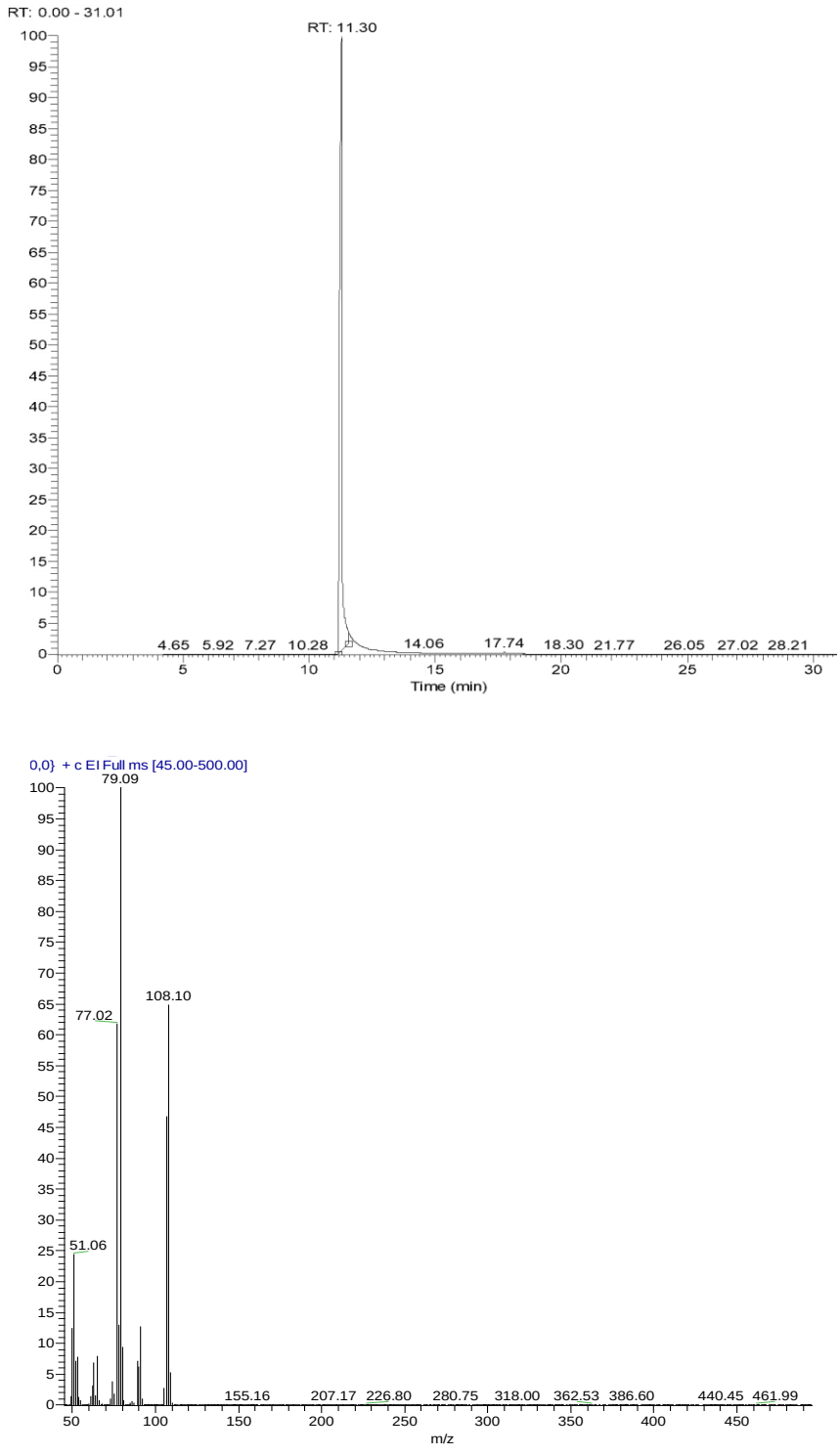


Figure S107. GC-MS data of Benzyl Alcohol (**5b**). GC-MS (m/z) = 108.10.

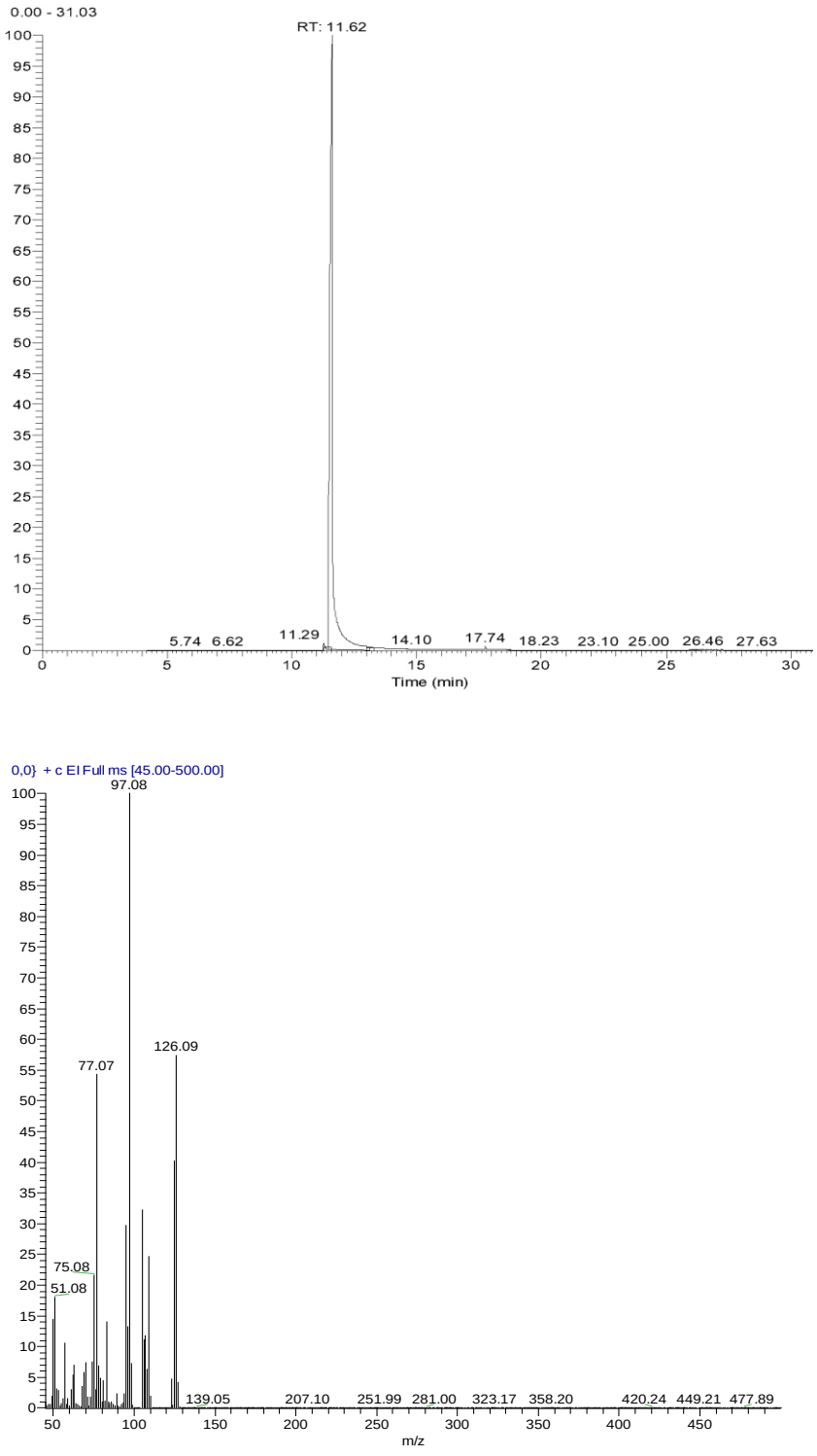


Figure S108. GC-MS data of 4-fluorobenzyl Alcohol (**5c**). GC-MS (m/z) = 126.09

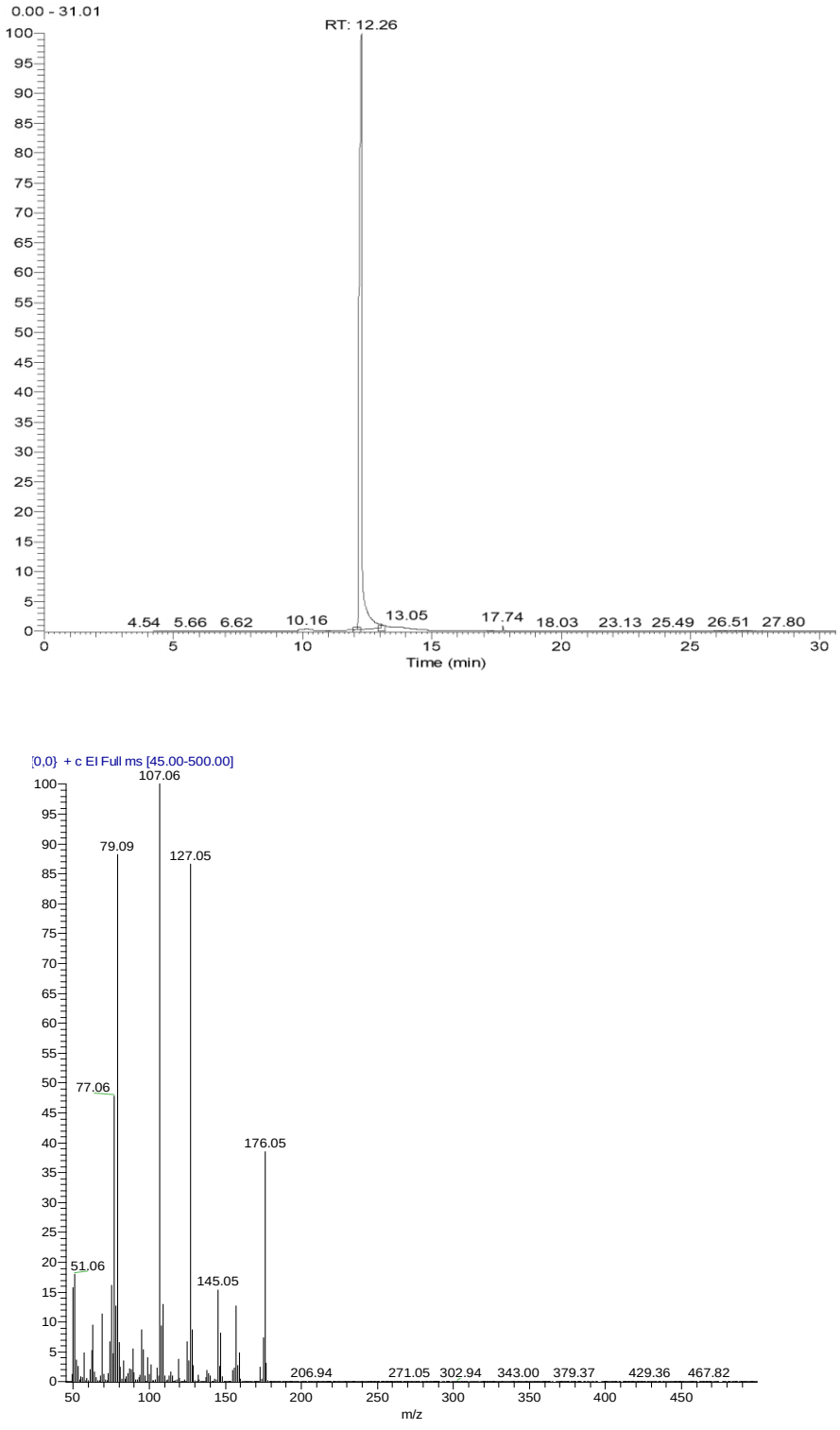


Figure S109. GC-MS data of 4-trifluorobenzyl Alcohol (**5d**). GC-MS (m/z) = 176.05.

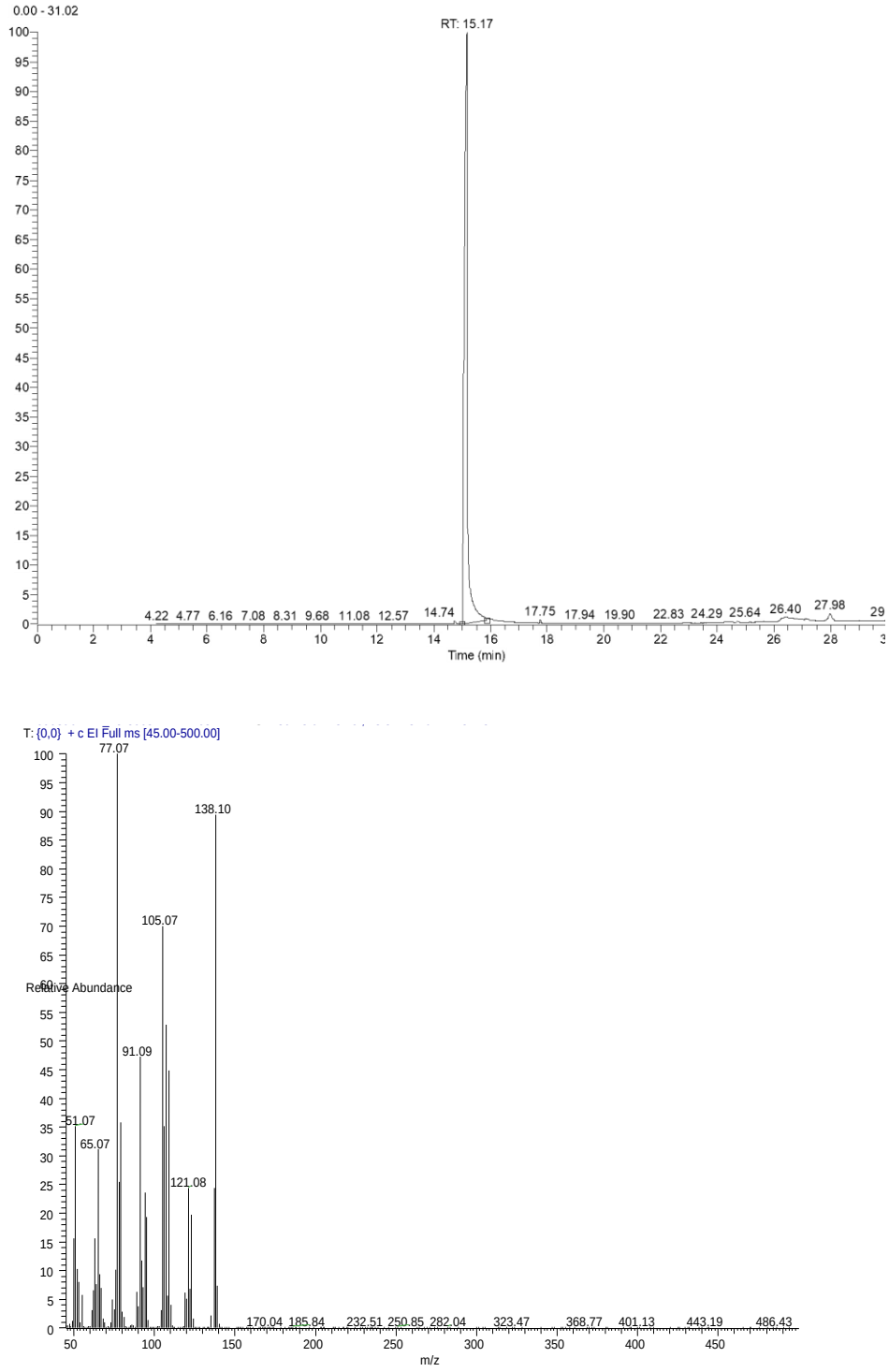


Figure S110. GC-MS data of 2-methoxybenzyl Alcohol (**5e**). GC-MS (m/z) = 138.09

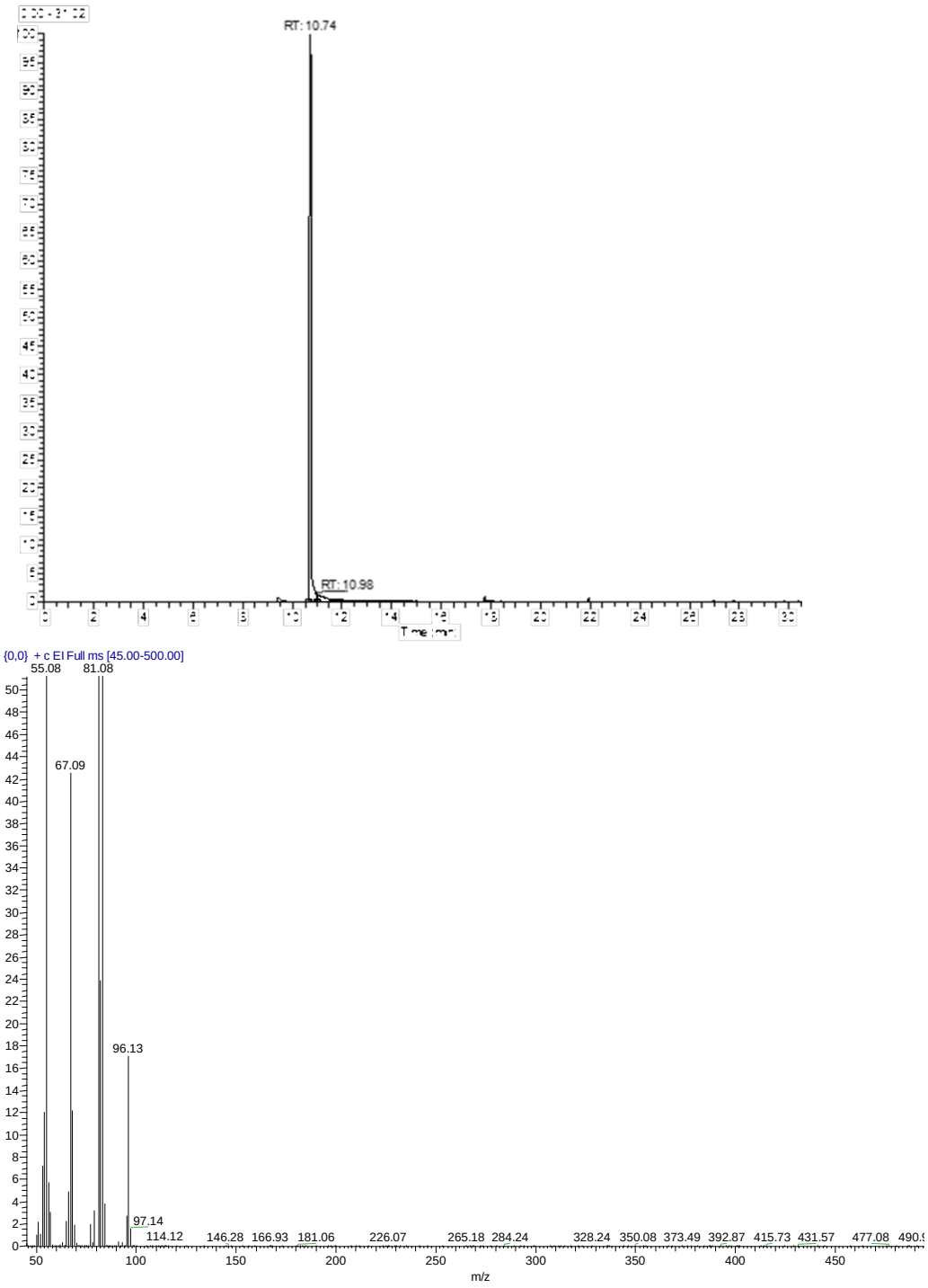


Figure S111. GC-MS data of Cyclohexyl methanol (**5f**). GC-MS (m/z) = 114.12.

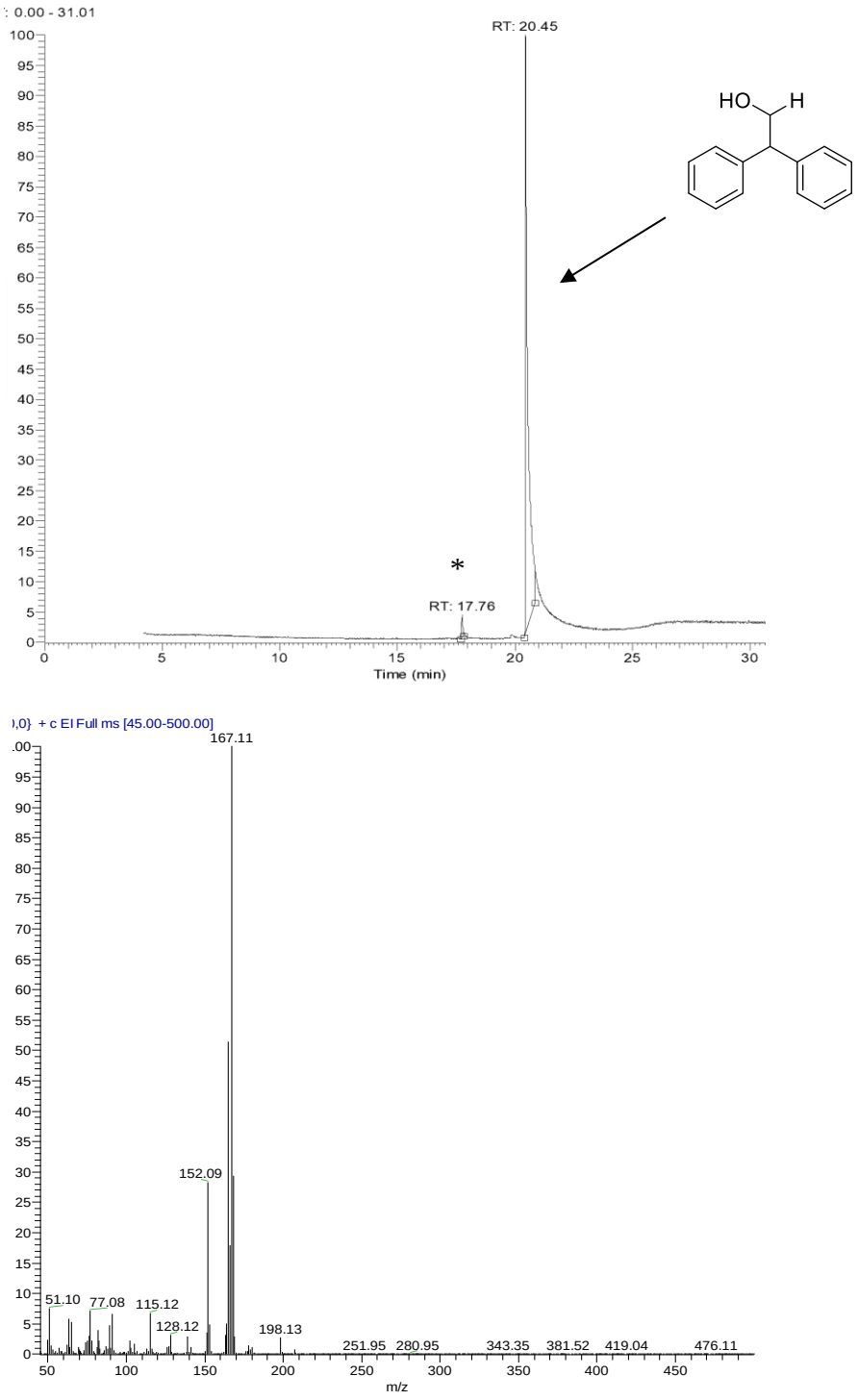


Figure S112. GC-MS for 2,2-diphenylethanol **(5g).** GC-MS (m/z): 198.13. (*) represents an unknown impurity.

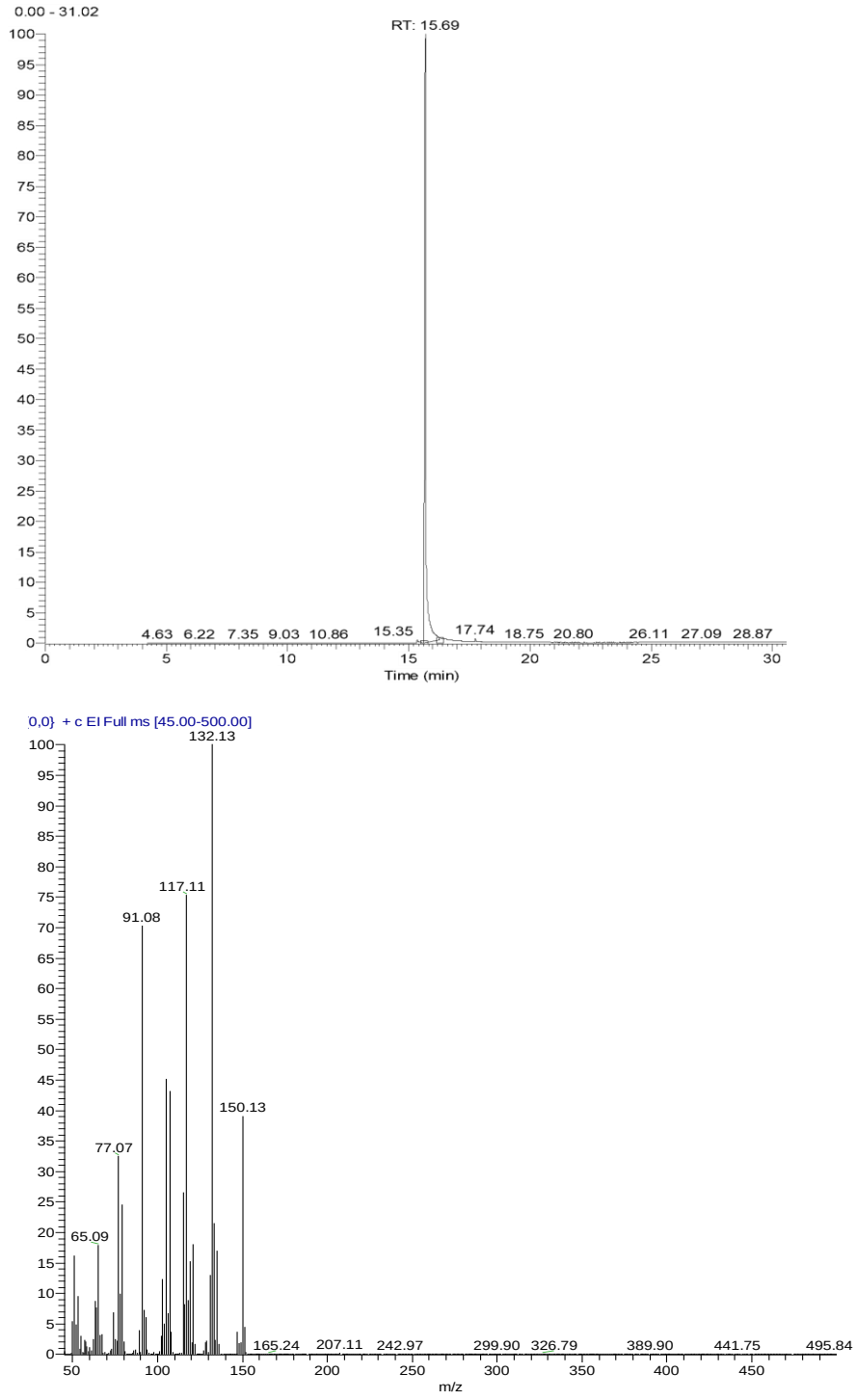


Figure S113. GC-MS for mesitylmethanol (**5h**). GC-MS (m/z) =150.13

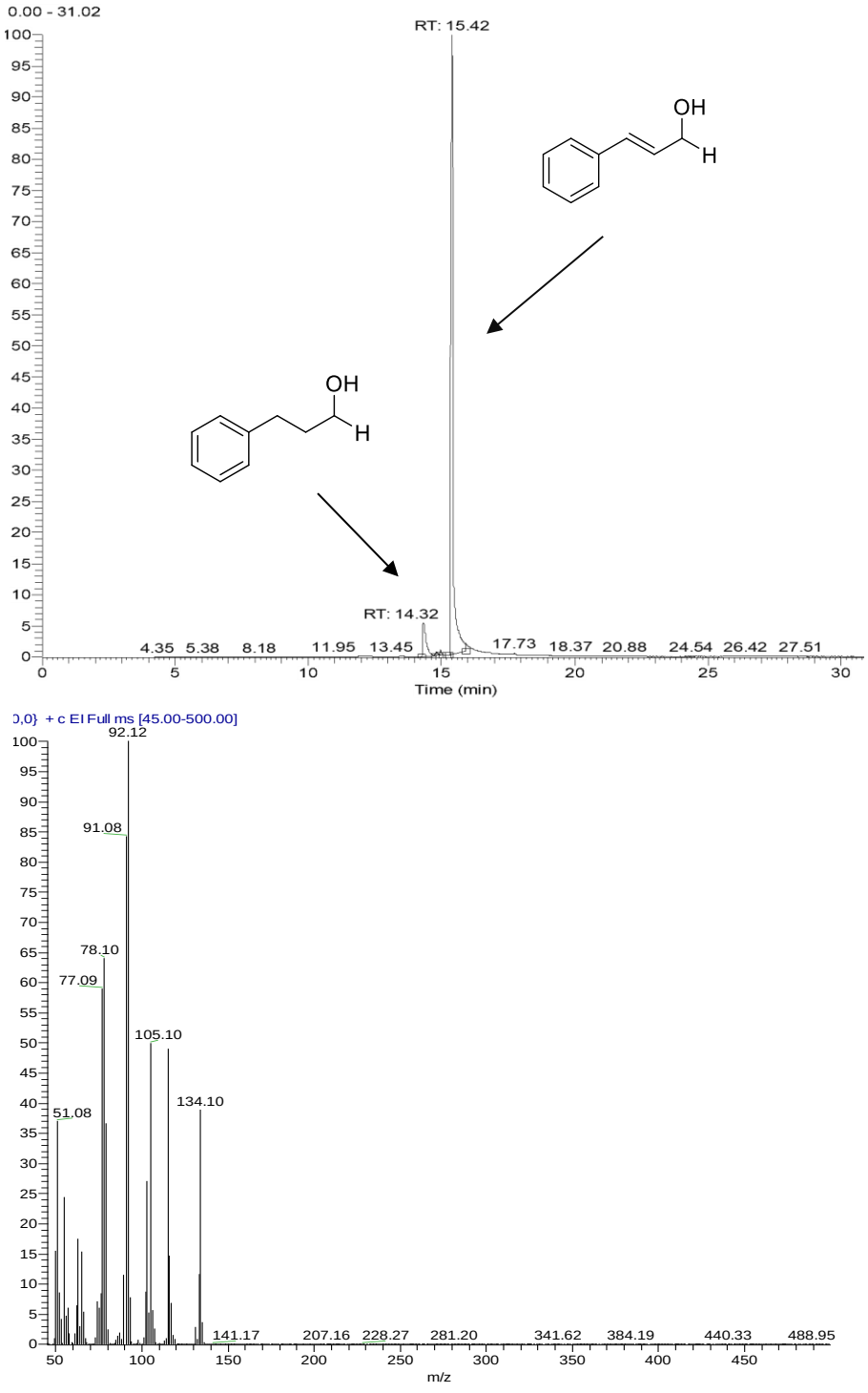


Figure S114. GC-MS data of 3-Phenyl-2-propene-1-ol (**5i)**. GC-MS (m/z): 134.14.

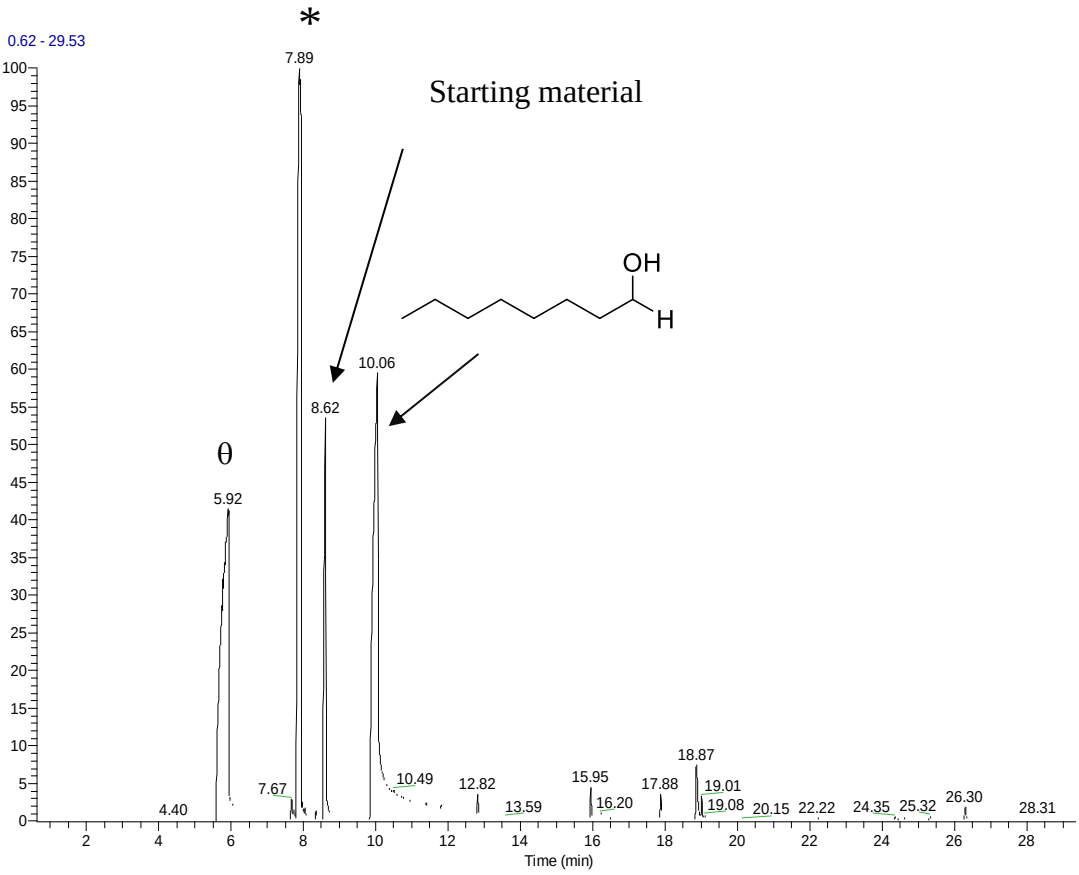


Figure S115. GC-MS data of n-octanol (**5j**). GC-MS (m/z): 130.2. (*) represents internal standard (mesitylene) and (θ) represents pinacol

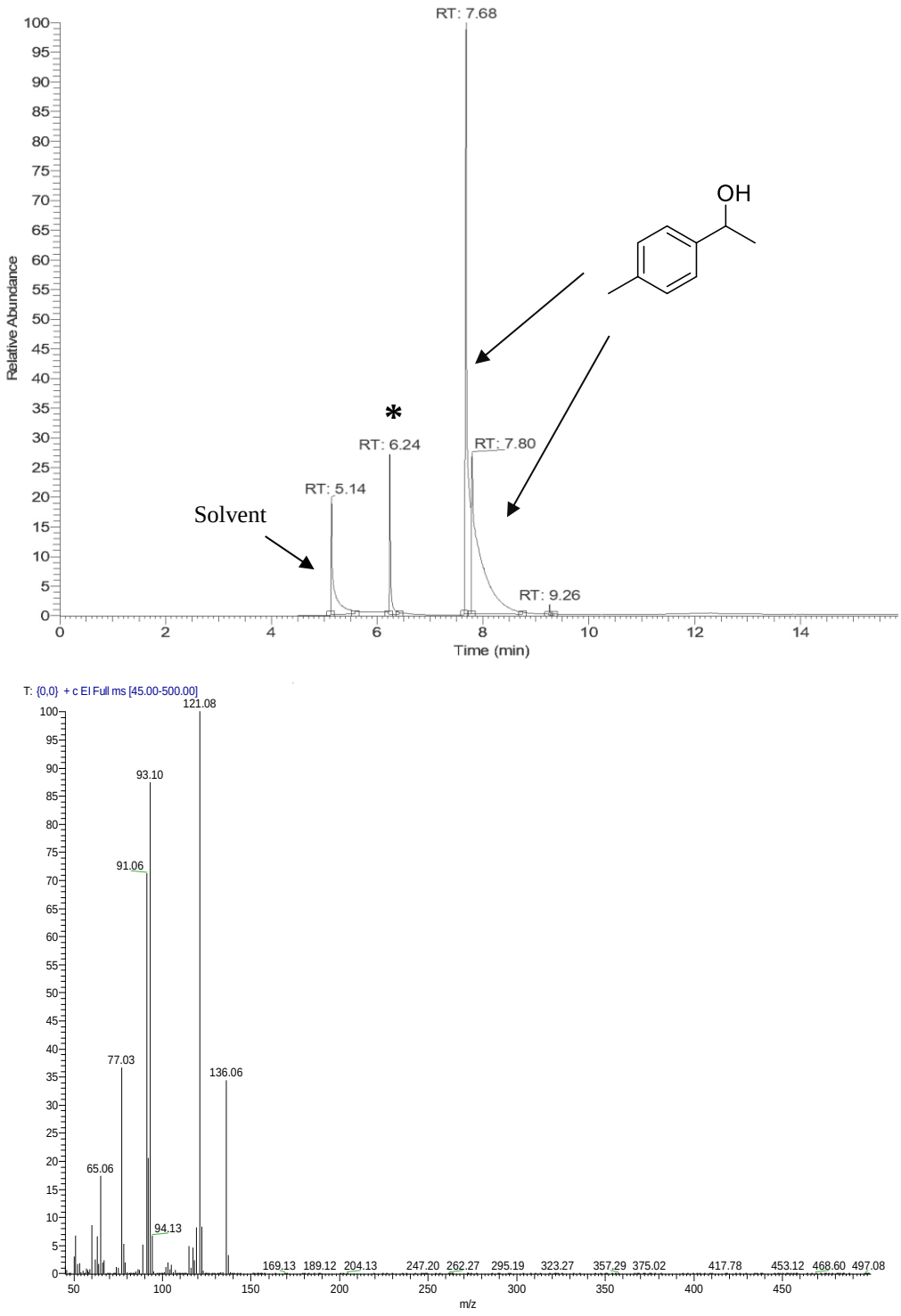


Figure S116. GC-MS data of 1-(4-Methylphenyl)ethanol (**5k**). GC-MS (m/z):136.06. (*) represents internal standard.

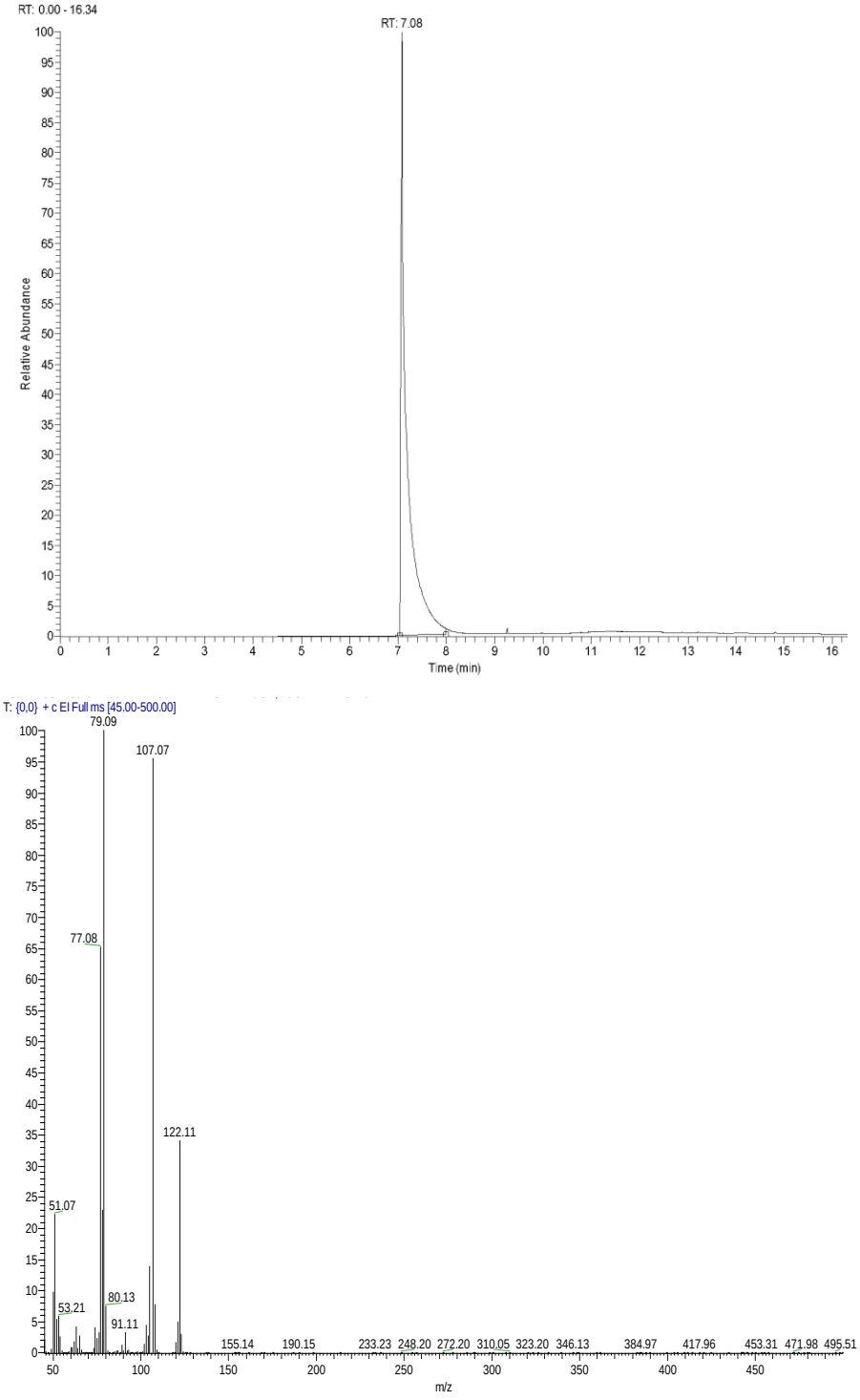


Figure S117. GC-MS data of 1-Phenylethanol (**5l**)**.** GC-MS (m/z):122.11.

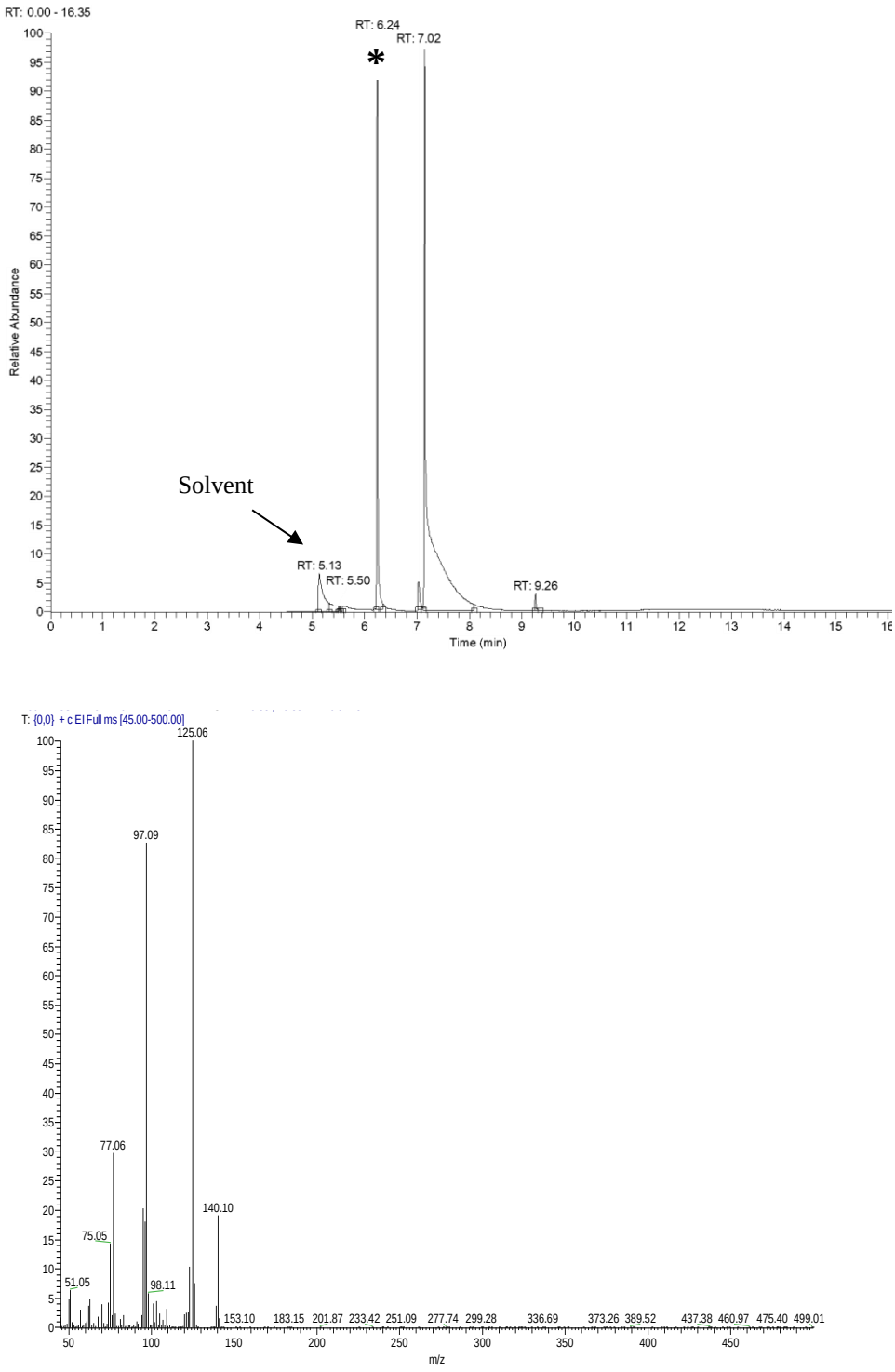


Figure S118. GC-MS data of 1-(4-Fluorophenyl)ethanol (**5m**). GC-MS (m/z):140.10. **(*)** represents internal standard.

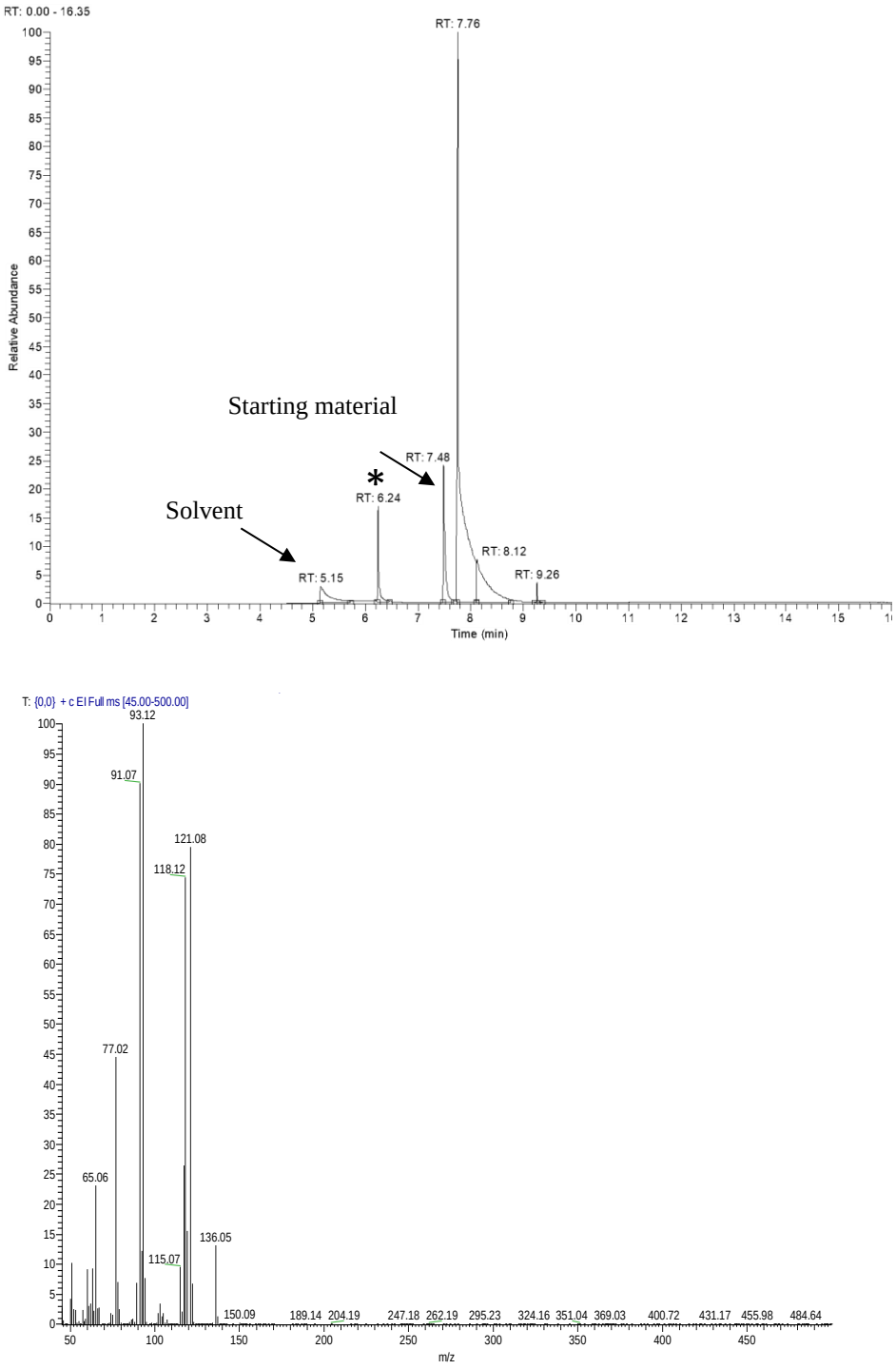


Figure S119. GC-MS data of 1-(*O*-tolyl)ethanol (**5n**). GC-MS (m/z):136.05. **(*)** represents internal standard.

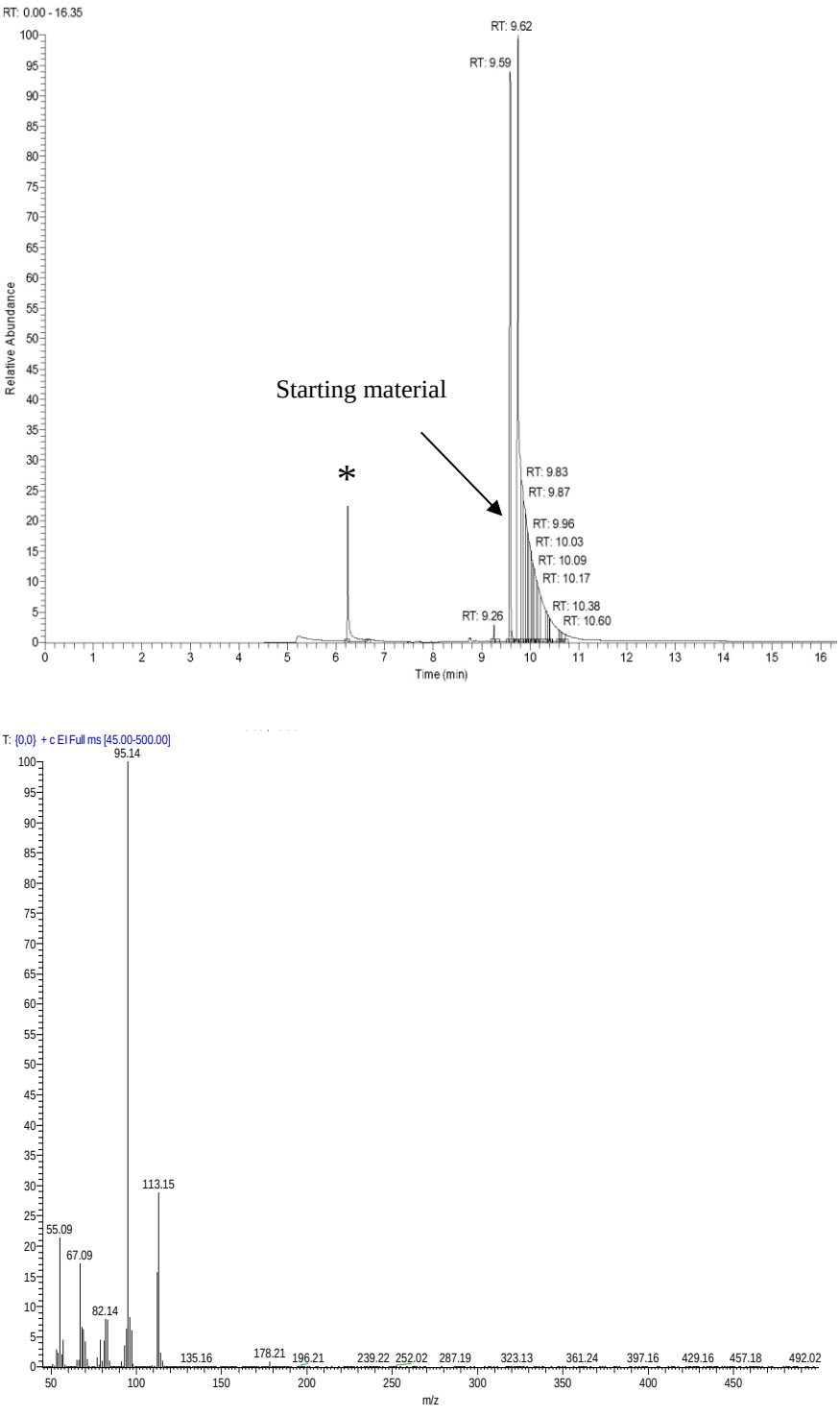


Figure S120. GC-MS data of Dicyclohexylmethanol (**5o**). GC-MS (m/z):136.05. **(*)** represents internal standard.

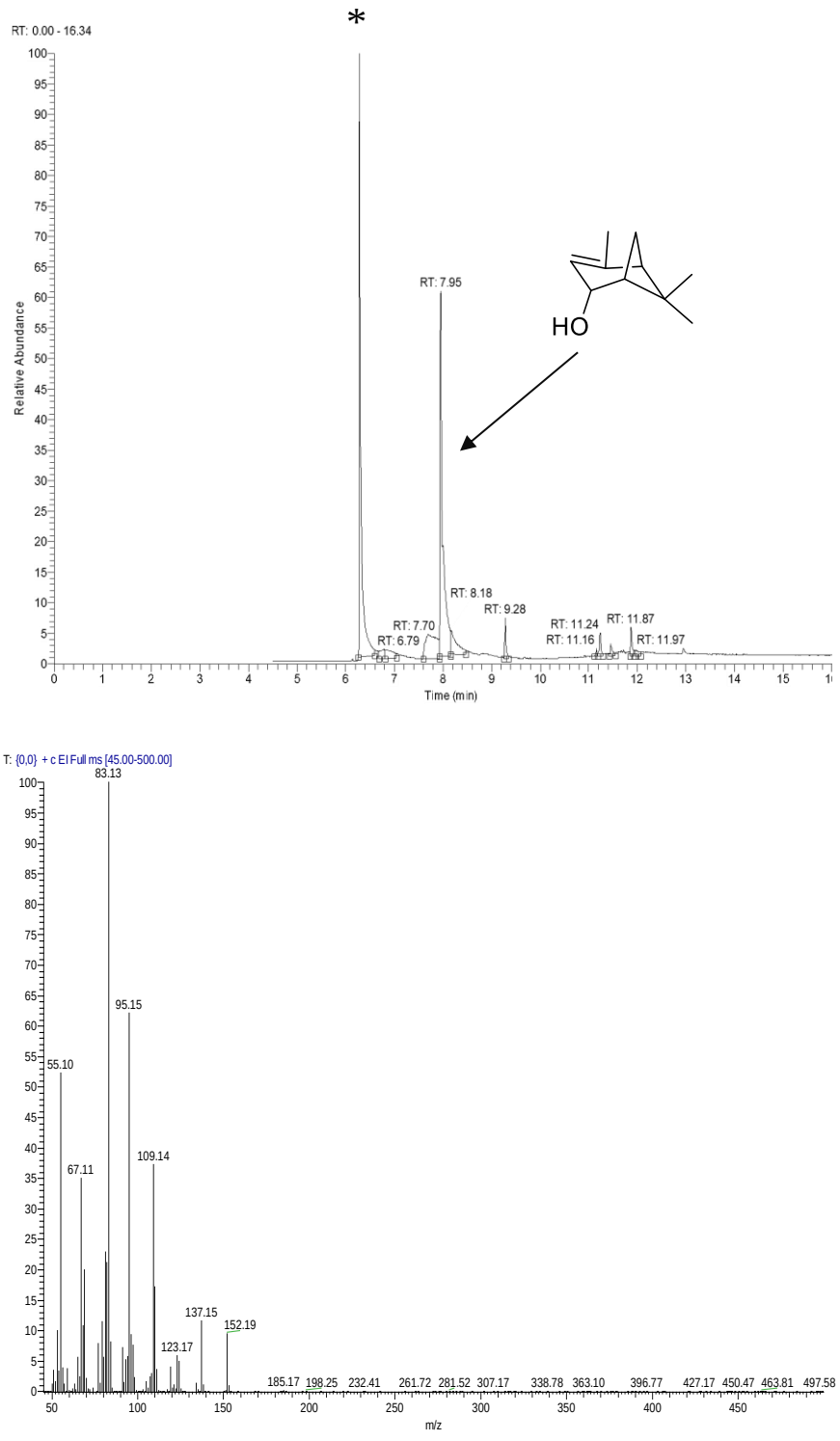
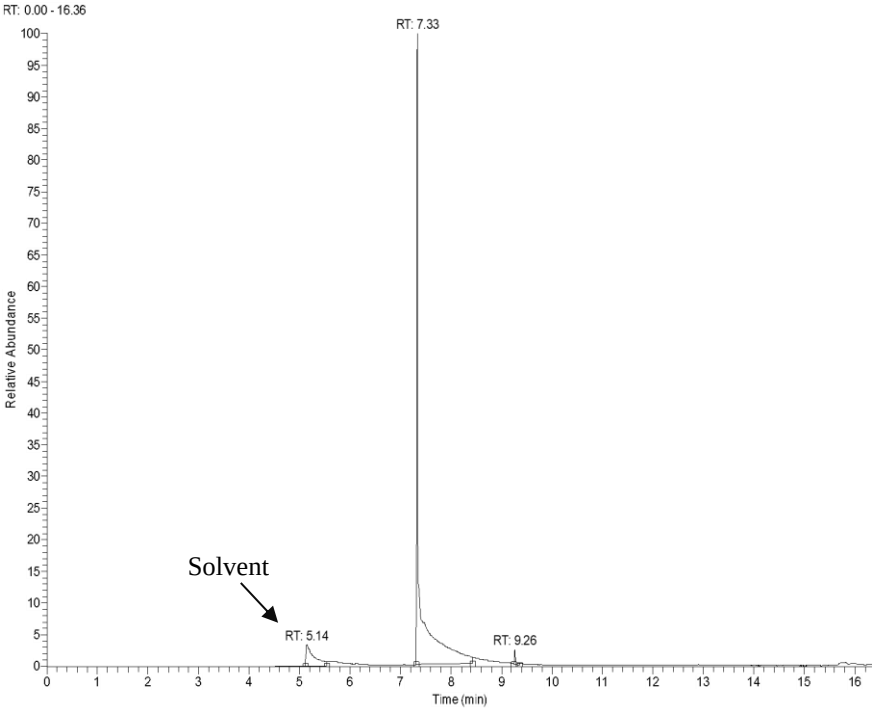


Figure S121. GC-MS data of Verbenol (**5p**). GC-MS (m/z):152.19. **(*)** represents internal standard.



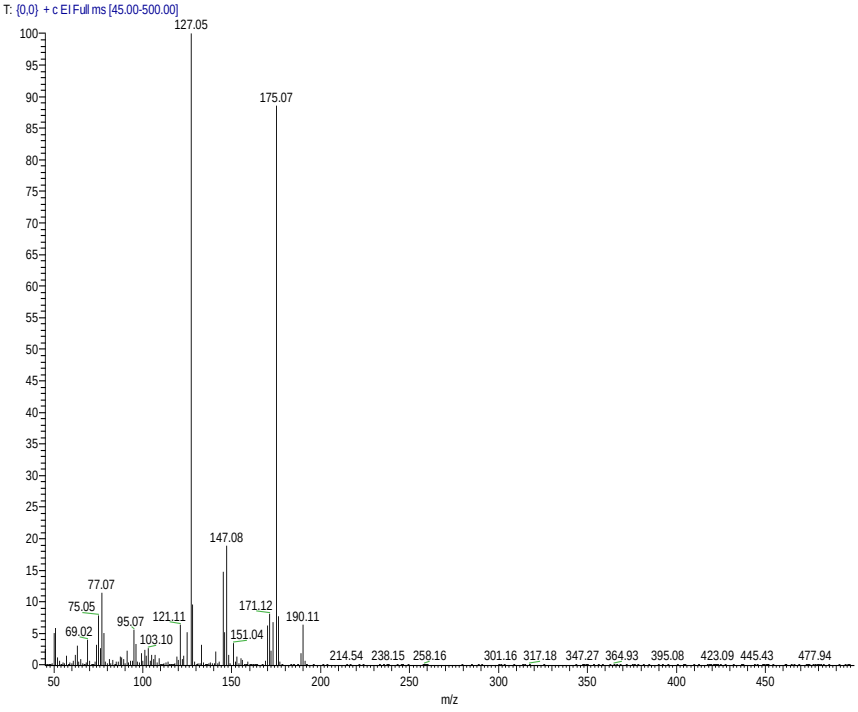


Figure S122. GC-MS data of 1-(4-Trifluoromethyl)phenyl)ethanol (**5q**). GC-MS (m/z):190.11.

10 References

1. Labre, F.; Gimbert, Y.; Bannwarth, P.; Olivero, S.; Duñach, E.; Chavant, P. Y., Application of Cooperative Iron/Copper Catalysis to a Palladium-Free Borylation of Aryl Bromides with Pinacolborane. *Org. Lett.* **2014,** *16* (9), 2366-2369.
2. Huang, J.; Yan, W.; Tan, C.; Wu, W.; Jiang, H., Palladium-catalyzed regioselective hydroboration of aryl alkenes with B2pin2. *Chem. Commun.* **2018,** *54* (14), 1770-1773.
3. Bismuto, A.; Cowley, M. J.; Thomas, S. P., Aluminum-Catalyzed Hydroboration of Alkenes. *ACS Catal.* **2018,** *8* (3), 2001-2005.
4. Zhang, G.; Wu, J.; Wang, M.; Zeng, H.; Cheng, J.; Neary, M. C.; Zheng, S., Cobalt-Catalyzed Regioselective Hydroboration of Terminal Alkenes. *Eur. J. Org. Chem.* **2017,** *2017* (38), 5814-5818.
5. Chen, X.; Cheng, Z.; Lu, Z., Iron-Catalyzed, Markovnikov-Selective Hydroboration of Styrenes. *Org. Lett.* **2017,** *19* (5), 969-971.
6. Kisan, S.; Krishnakumar, V.; Gunanathan, C., Ruthenium-Catalyzed Anti-Markovnikov Selective Hydroboration of Olefins. *ACS Catal.* **2017,** *7* (9), 5950-5954.
7. Scheuermann, M. L.; Johnson, E. J.; Chirik, P. J., Alkene Isomerization–Hydroboration Promoted by Phosphine-Ligated Cobalt Catalysts. *Org. Lett.* **2015,** *17* (11), 2716-2719.
8. Tamang, S. R.; Findlater, M., Iron Catalyzed Hydroboration of Aldehydes and Ketones. *J. Org. Chem.* **2017,** *82* (23), 12857-12862.
9. Dieskau, A. P.; Begouin, J.-M.; Plietker, B., Bu4N[Fe(CO)3(NO)]-Catalyzed Hydrosilylation of Aldehydes and Ketones. *Eur. J. Org. Chem.* **2011,** *2011* (27), 5291-5296.
10. L. L. Frolova, I. V. D., M. V. Panteleeva, E. U. Ipatova, I. N. Alekseev, and A. V. Kutchin, Favorable effect of Ce^{III} on the stereoselectivity of reduction of verbenone to *cis*-verbenol. *Russ. Chem. Bull., Int. Ed. 52* (2), 498-501.
11. Osako, T.; Torii, K.; Hirata, S.; Uozumi, Y., Chemoselective Continuous-Flow Hydrogenation of Aldehydes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Resin. *ACS Catal.* **2017,** *7* (10), 7371-7377.