

3-Chloro-1-lithiopropene - a Functional Organolithium Reagent - and its Reactions with Alkylboronates to Give 3-Alkylprop-1-en-3-ols

Keith Smith,^{*} Mark C. Elliott,^{*} and D. Heulyn Jones

School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK
AUTHOR EMAIL ADDRESS: smithk13@cardiff.ac.uk; elliottmc@cardiff.ac.uk

Supporting Information

Copies of ¹ H, ¹³ C and ¹¹ B NMR Spectra	3
Comment regarding ¹¹ B NMR spectra of new compounds	3
2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3, R = cyclohexyl)	3
2-Isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3, R = isopropyl)	5
2-Butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3, R = <i>n</i> -butyl)	7
2-(2,3-Dimethylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3, R = <i>thexyl</i>)	9
(<i>E</i>)-1-Bromo-3-chloroprop-1-ene (5)	11
2- <i>tert</i> -Butyl-1,3,2-dioxaborolane (6)	12
2- <i>tert</i> -Butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7, R = <i>t</i> -Bu)	13
2-(2,3-Dimethylbutan-2-yl)-1,3,2-dioxaborolane (11)	16
2-(2,3-Dimethylbutan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (12)	18
(<i>E</i>)-2-(1,1-Dicyclohexyl-3-phenylallyl)-5,5-dimethyl-1,3,2-dioxaborinane (13, R ^C = cyclohexyl, R ^D = PhCH=CH)	20
2-Butyl-5,5-dimethyl-1,3,2-dioxaborinane (13, R ^C = H, R ^D = <i>n</i> -propyl)	22
2-(3-Ethylpentan-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane (13, R ^C = R ^D = ethyl)	24
5,5-Dimethyl-2-(9-octylheptadecan-9-yl)-1,3,2-dioxaborinane (13, R ^C = R ^D = <i>n</i> -octyl)	26
2-(Tricyclopentylmethyl)-1,3,2-dioxaborolane (13, R ^C = R ^D = cyclopentyl)	28
1-(4-Methoxyphenyl)but-3-en-2-ol (9, R = 4-methoxybenzyl)	30

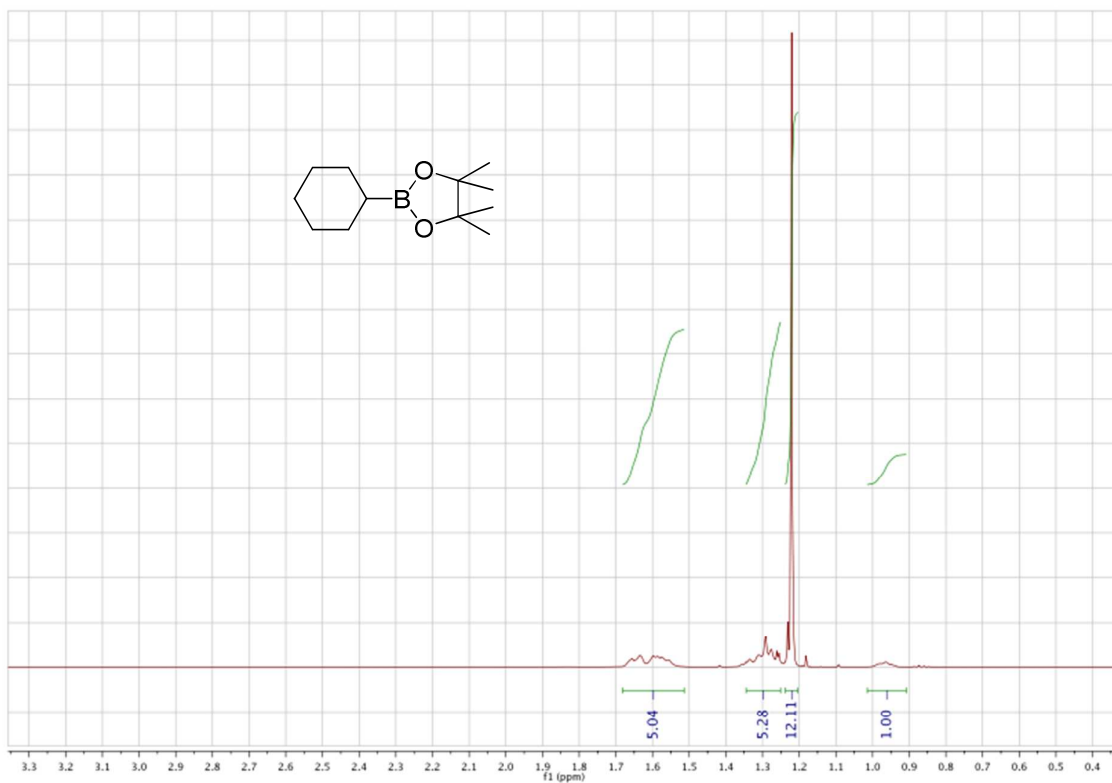
1-Phenylbut-3-en-2-ol (9, R = benzyl)	31
1-Cyclohexylprop-2-en-1-ol (9, R = cyclohexyl)	32
4-Methylpent-1-en-3-ol (9, R = isopropyl)	33
Hept-1-en-3-ol (9, R = <i>n</i>-butyl)	34
4,4-Dimethylpent-1-en-3-ol (8, R = <i>t</i>-Bu)	35
4,4,5-Trimethylhex-1-en-3-ol (9, R = hexyl)	36
4,4-Diethylhex-1-en-3-ol (14, R^C = R^D = ethyl)	37
Product mixture from reaction of 5,5-dimethyl-2-(9-octylheptadecan-9-yl)-1,3,2-dioxaborinane (13, R^C = R^D = <i>n</i>-octyl) with 1-lithio-3-chloropropene to give a mixture of 4,4-dioctyldodec-1-en-3-ol (14, R^C = R^D = <i>n</i>-octyl) and 9-octylheptadecan-9-ol	38
(<i>E</i>)-1,1-Dicyclohexyl-3-phenylprop-2-en-1-ol	39
Tricyclopentylmethanol	40
<i>tert</i>-Butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (15)	41
<i>tert</i>-Butyl 5-hydroxyhept-6-enoate (17)	43
6-Vinyltetrahydro-2H-pyran-2-one (18)	44

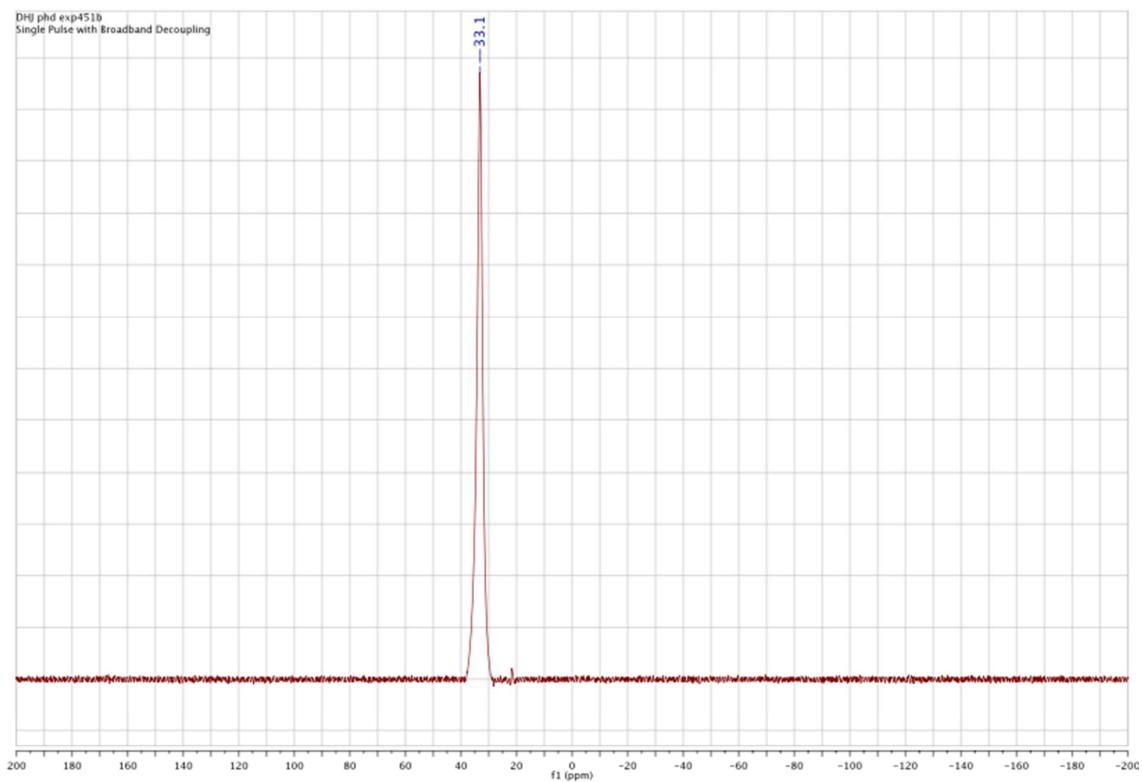
Copies of ^1H , ^{13}C and ^{11}B NMR Spectra

Comment regarding ^{11}B NMR spectra of new compounds

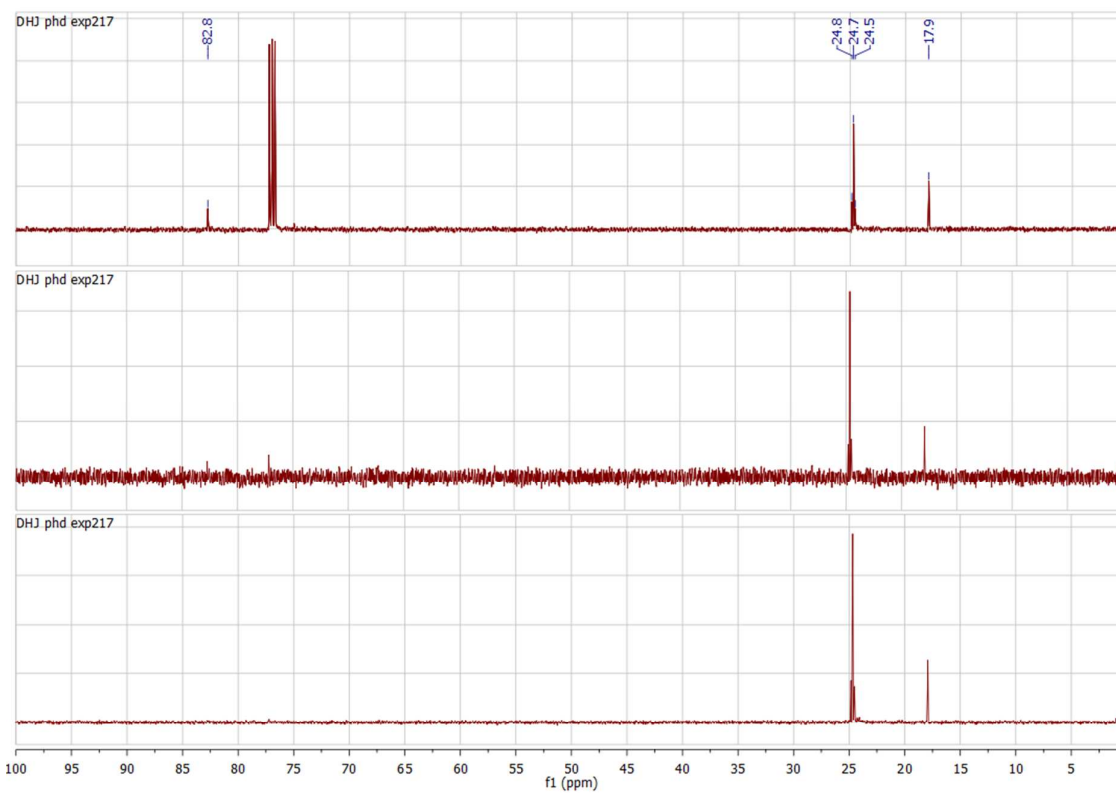
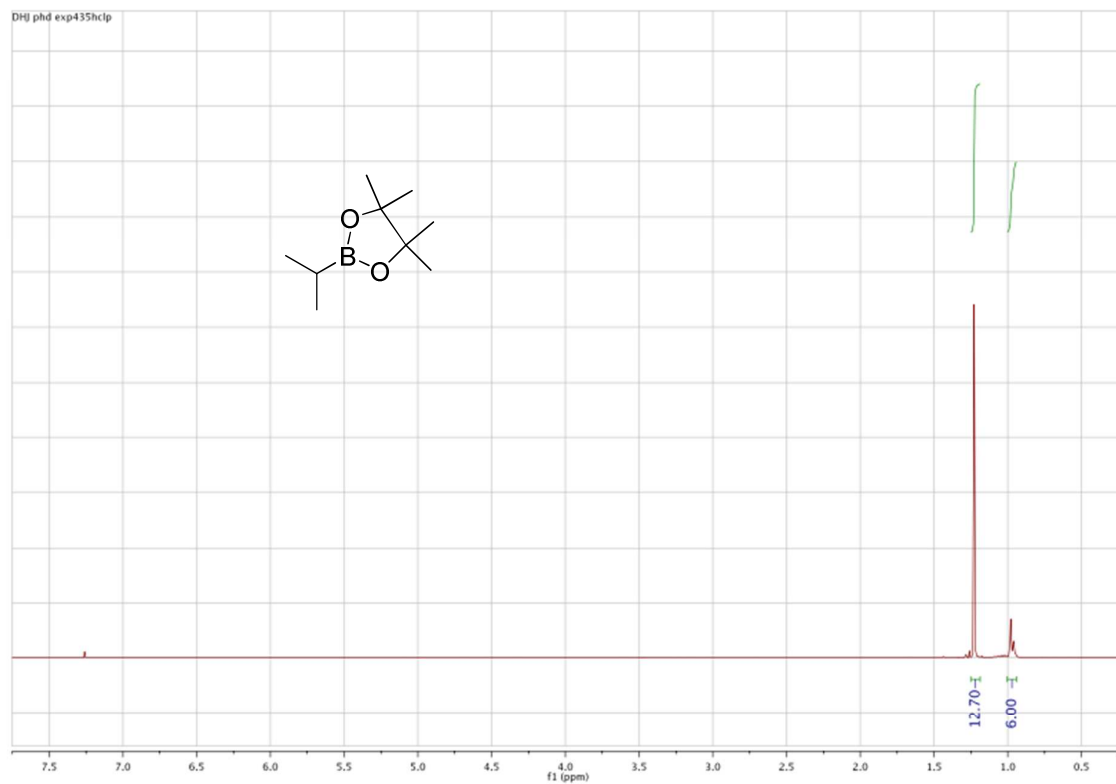
Because of the system for measuring NMR spectra, samples were initially submitted for ^1H and ^{13}C spectra and subsequently submitted for ^{11}B spectra. Sometimes there was a significant time delay before the boron spectrum was run and this resulted in an additional peak in the spectrum due to oxidized product.

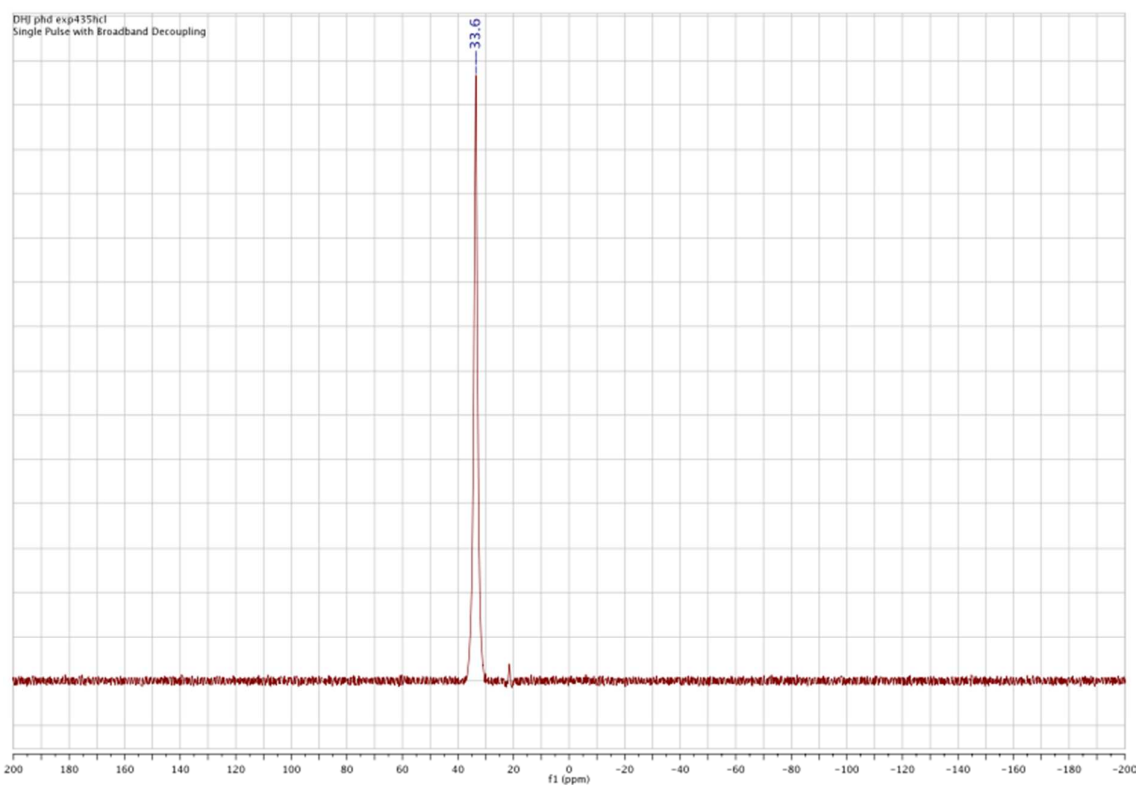
2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3, R = cyclohexyl)



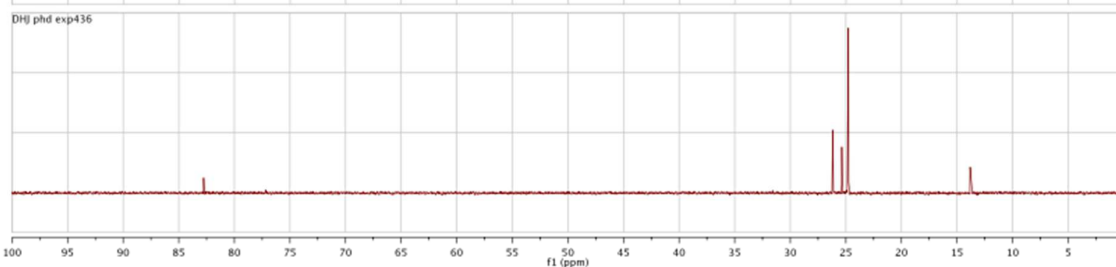
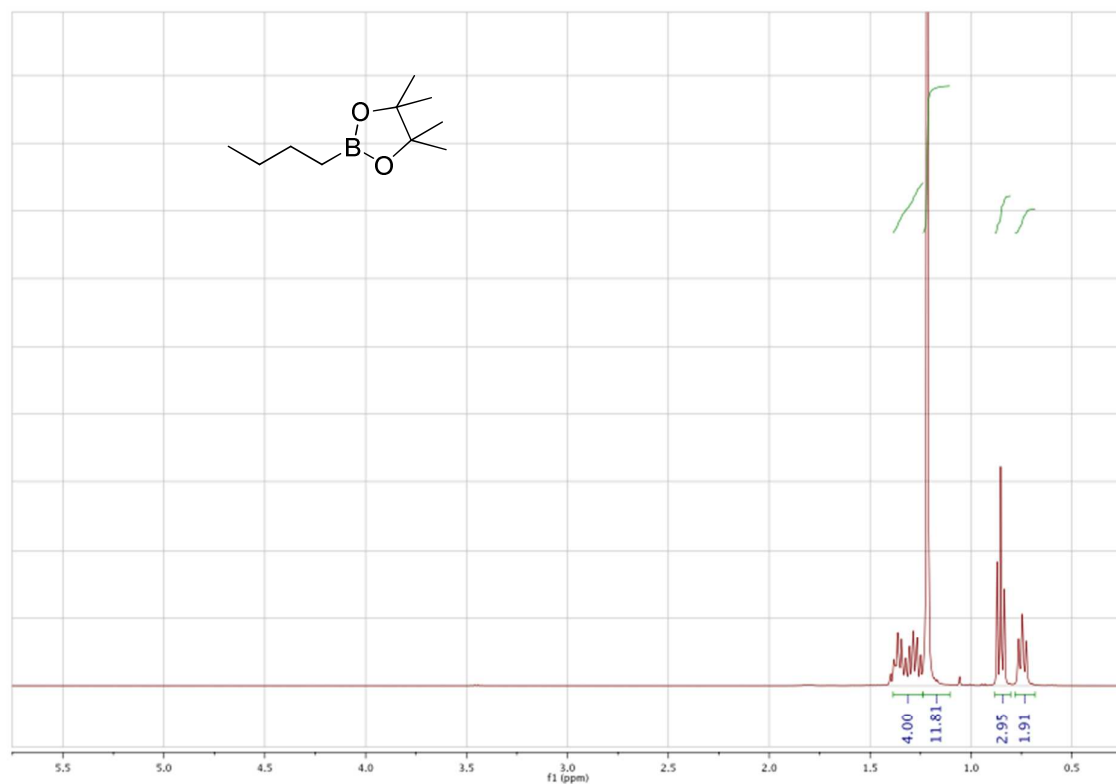


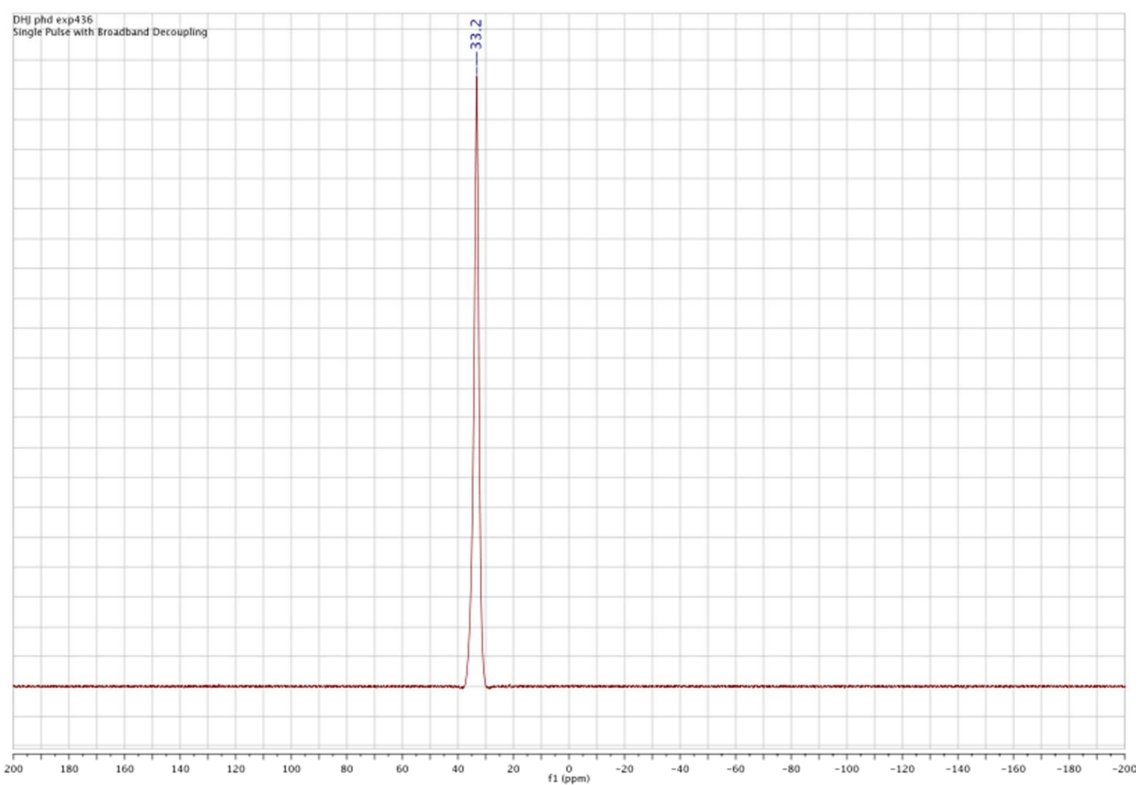
2-Isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3, R = isopropyl)



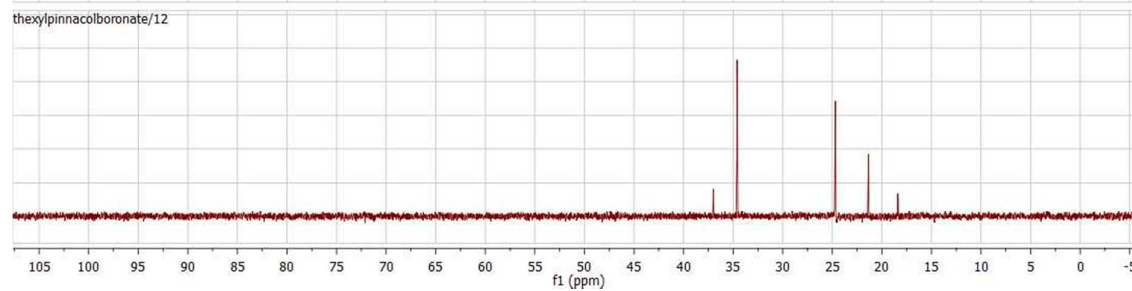
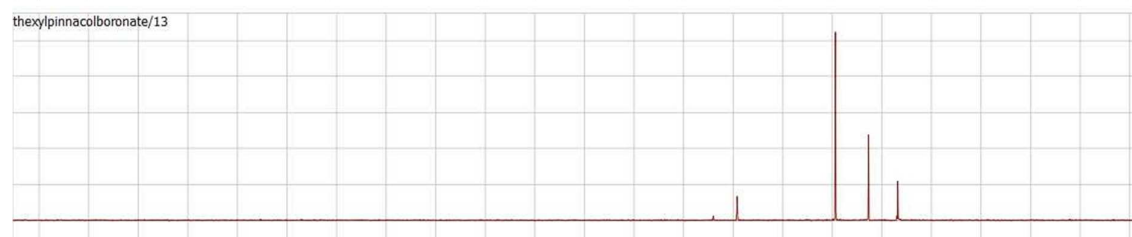
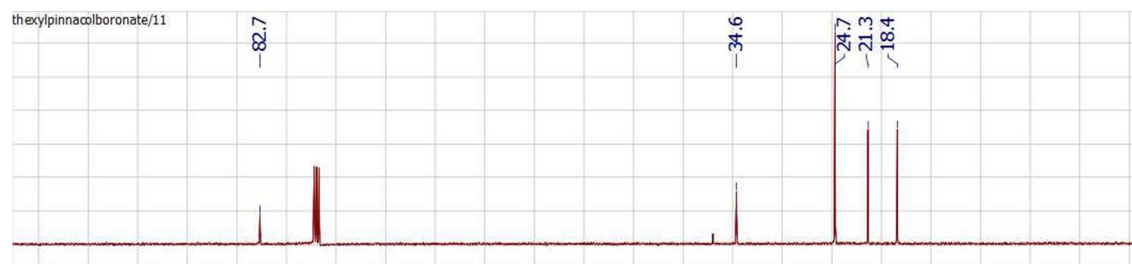
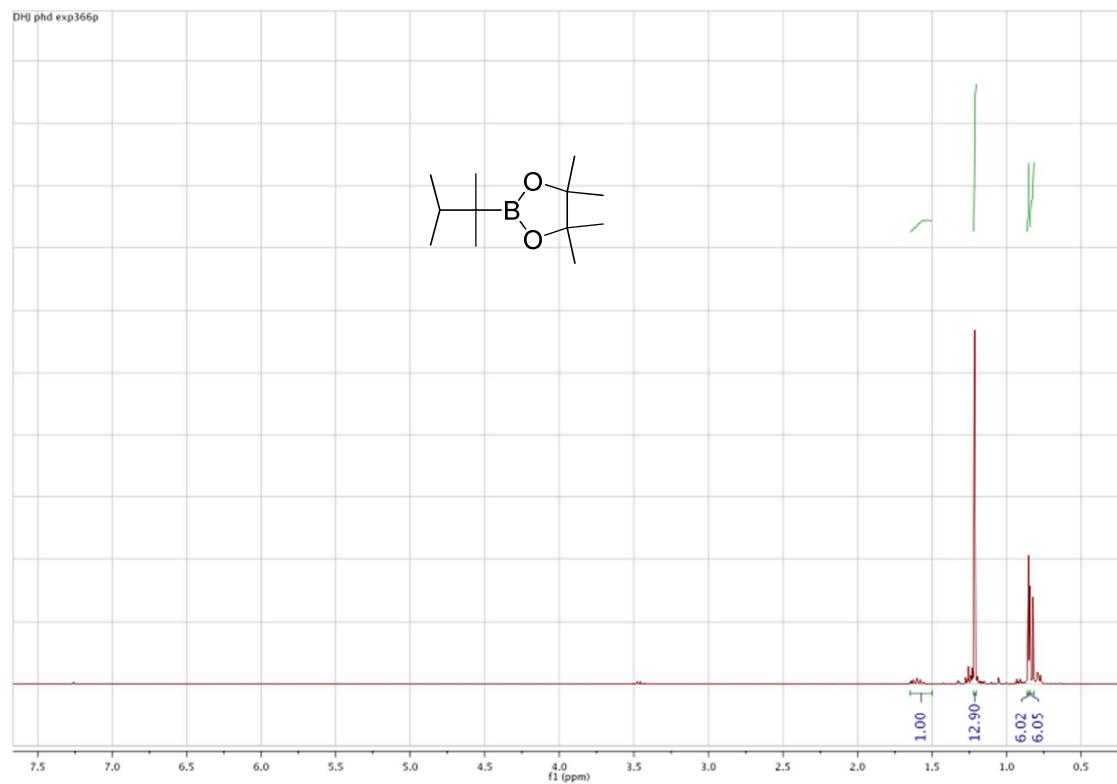


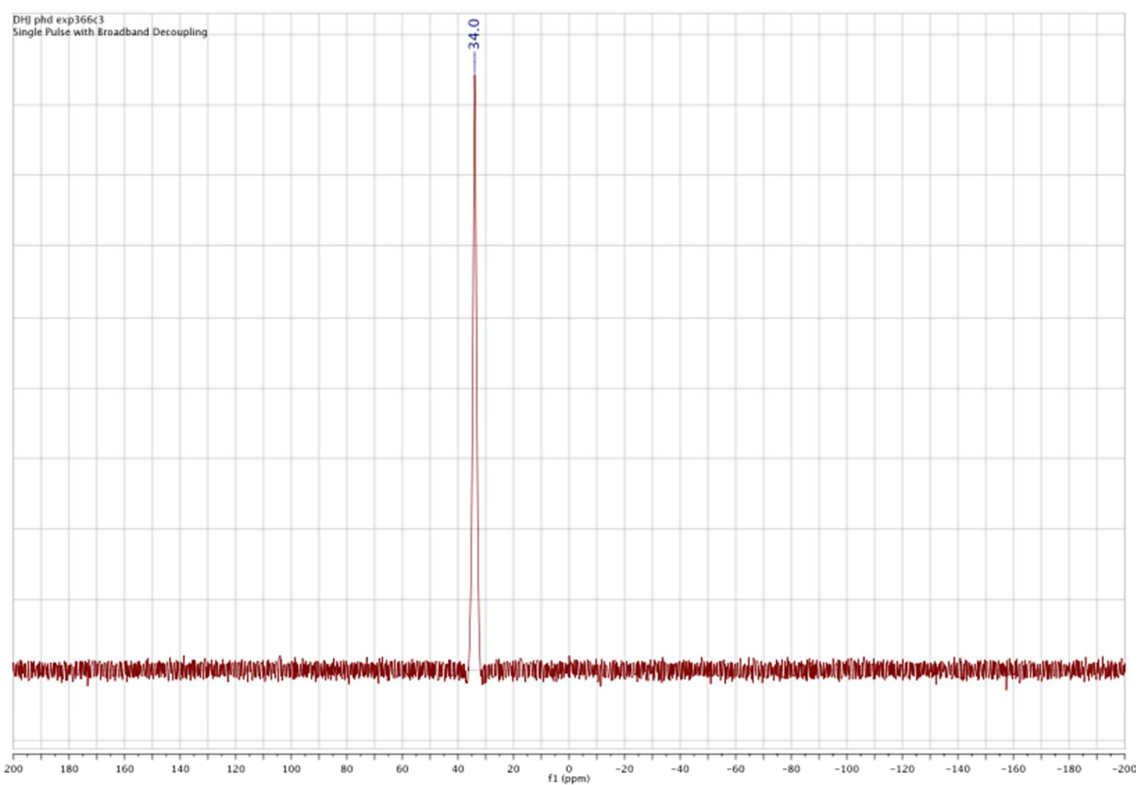
2-Butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3, R = *n*-butyl)



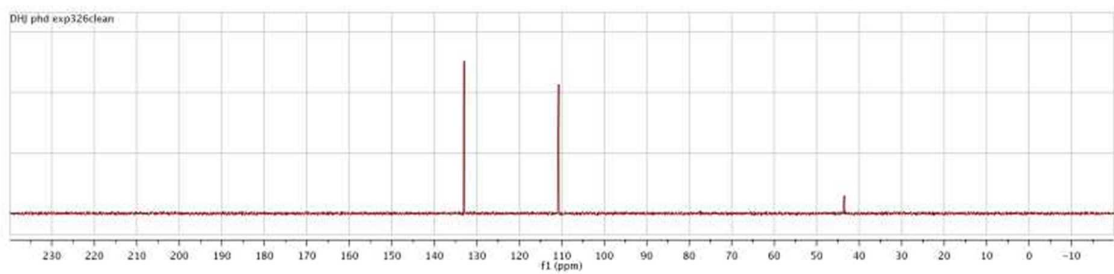
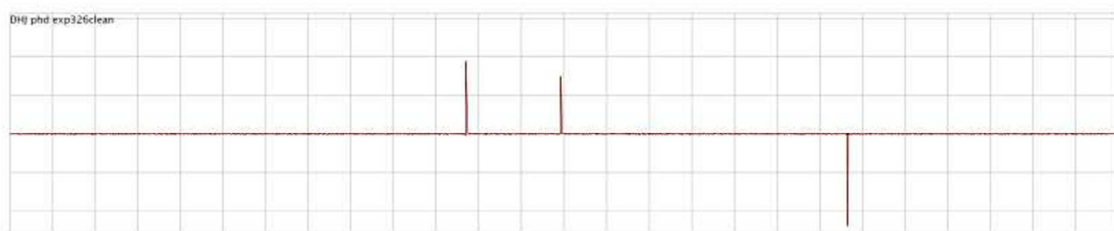
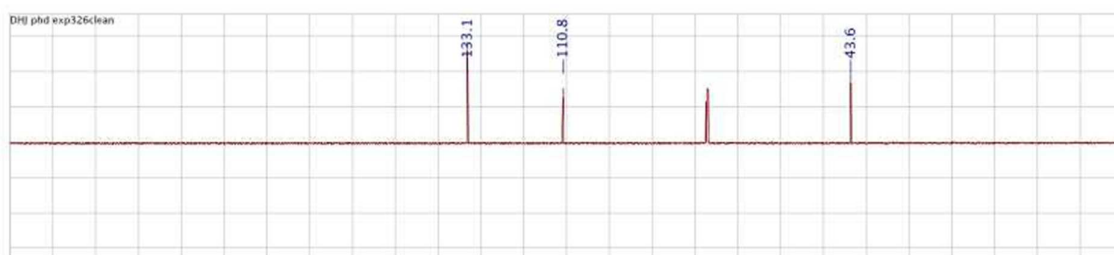
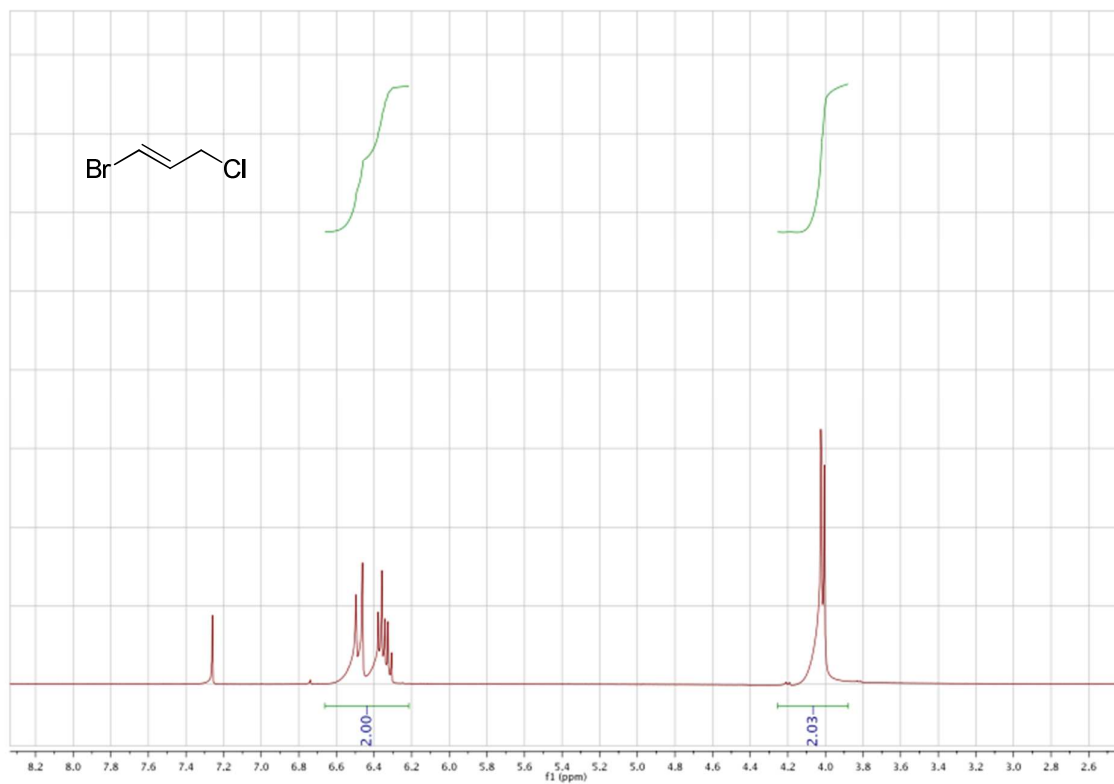


2-(2,3-Dimethylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3, R = hexyl)

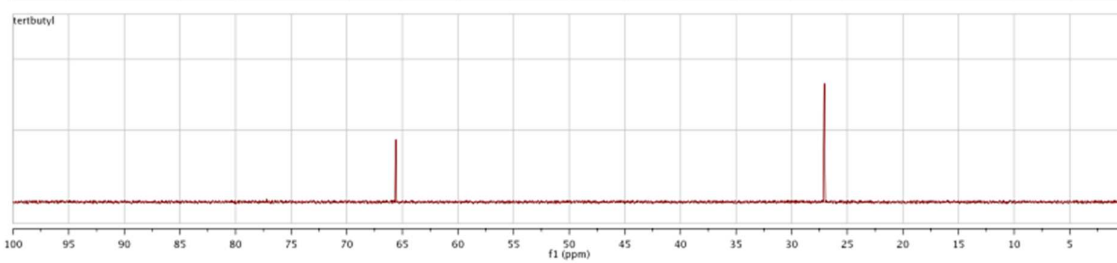
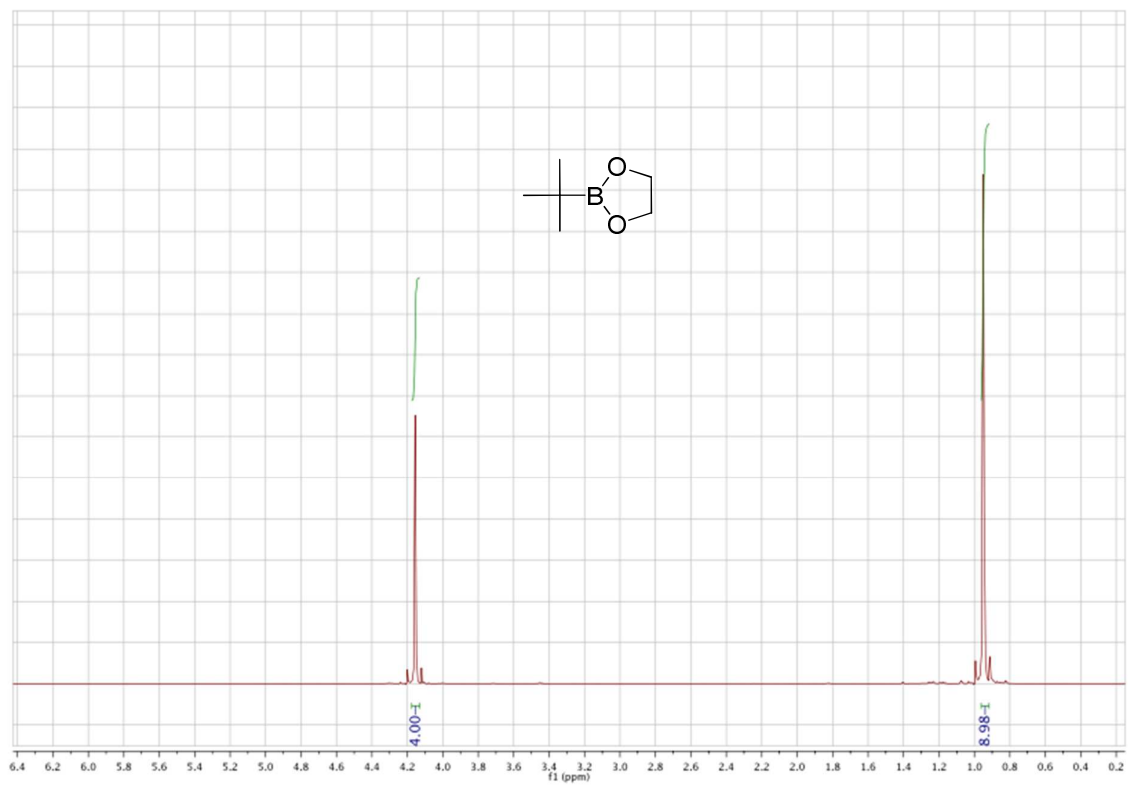


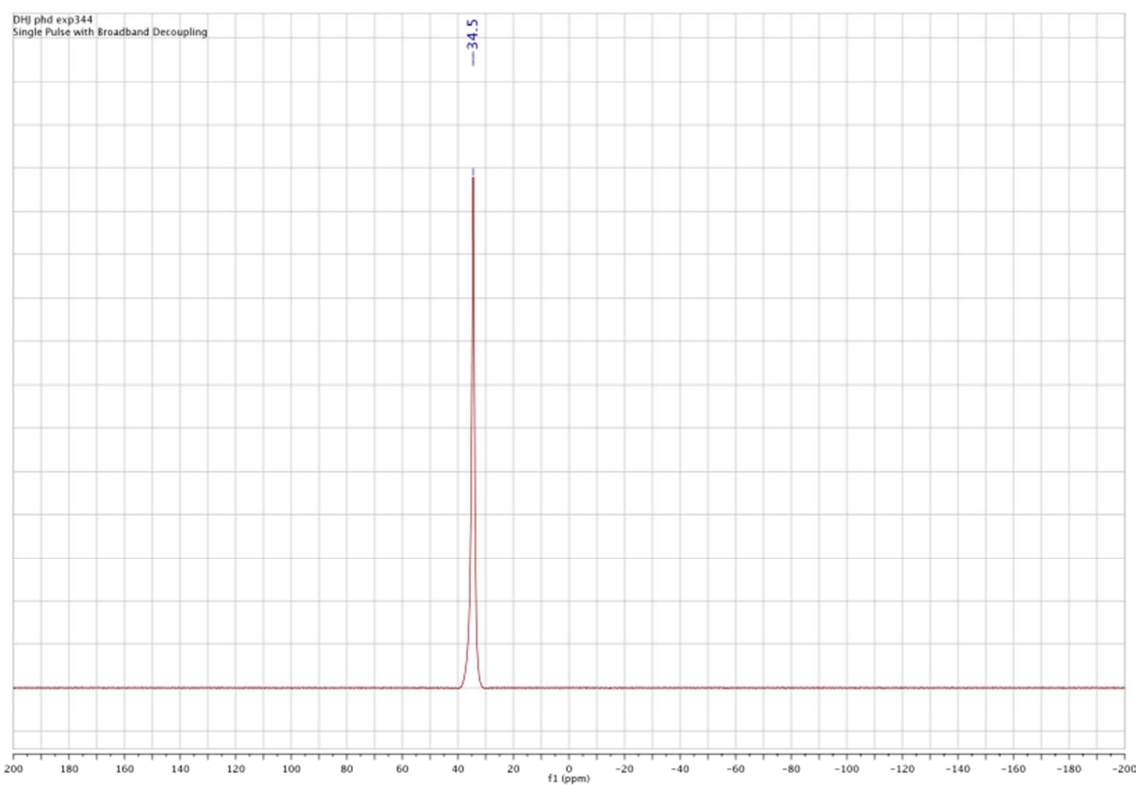


(E)-1-Bromo-3-chloroprop-1-ene (5)

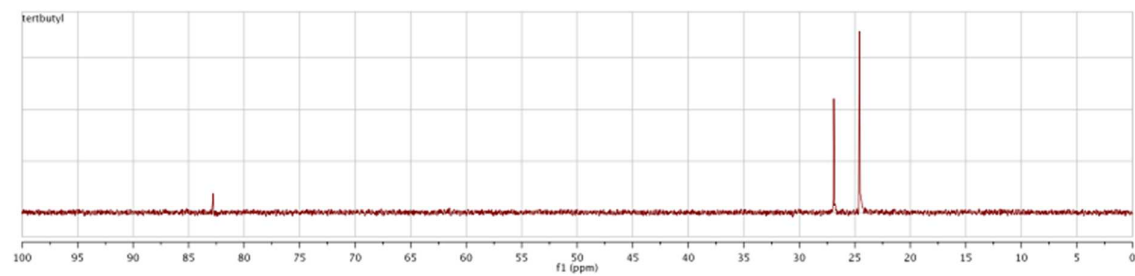
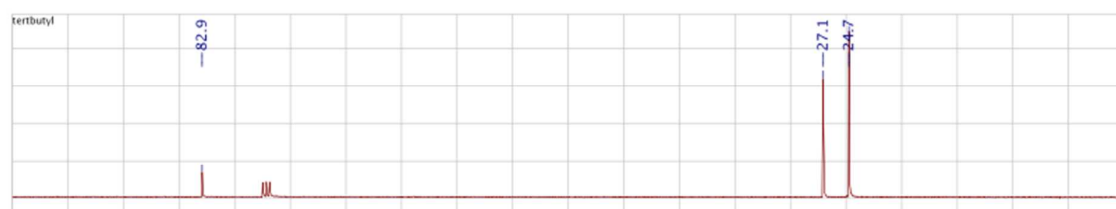
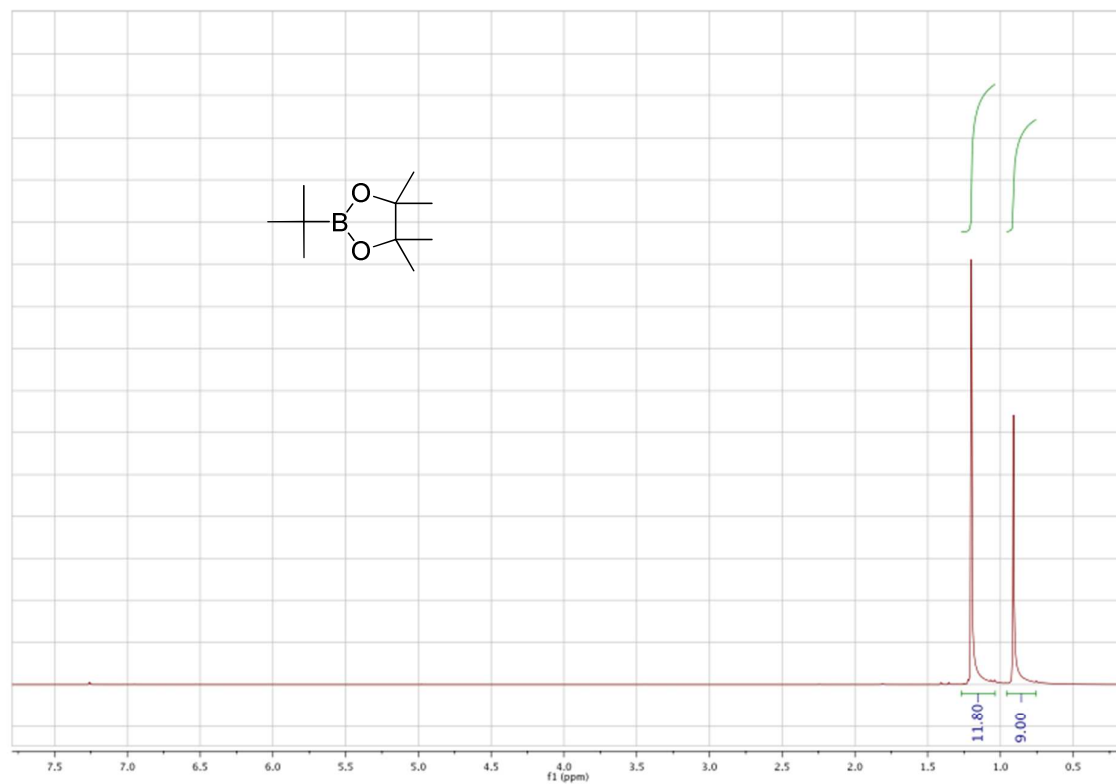


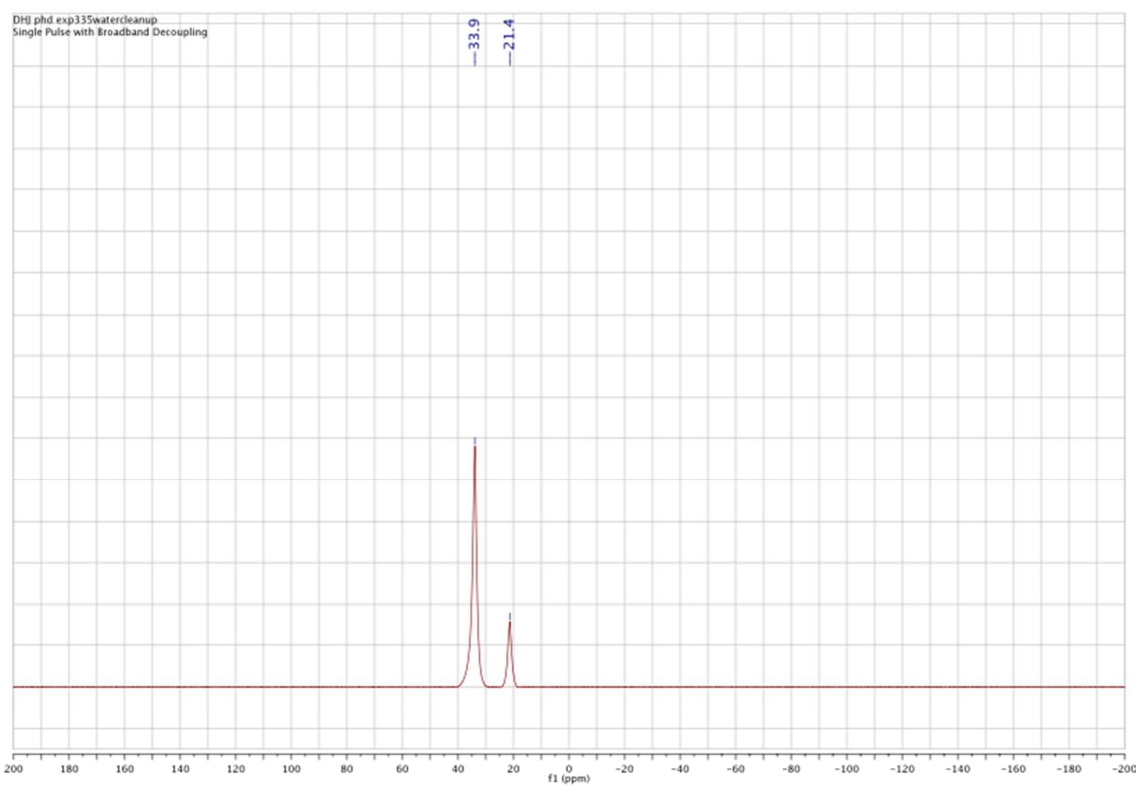
2-*tert*-Butyl-1,3,2-dioxaborolane (6)



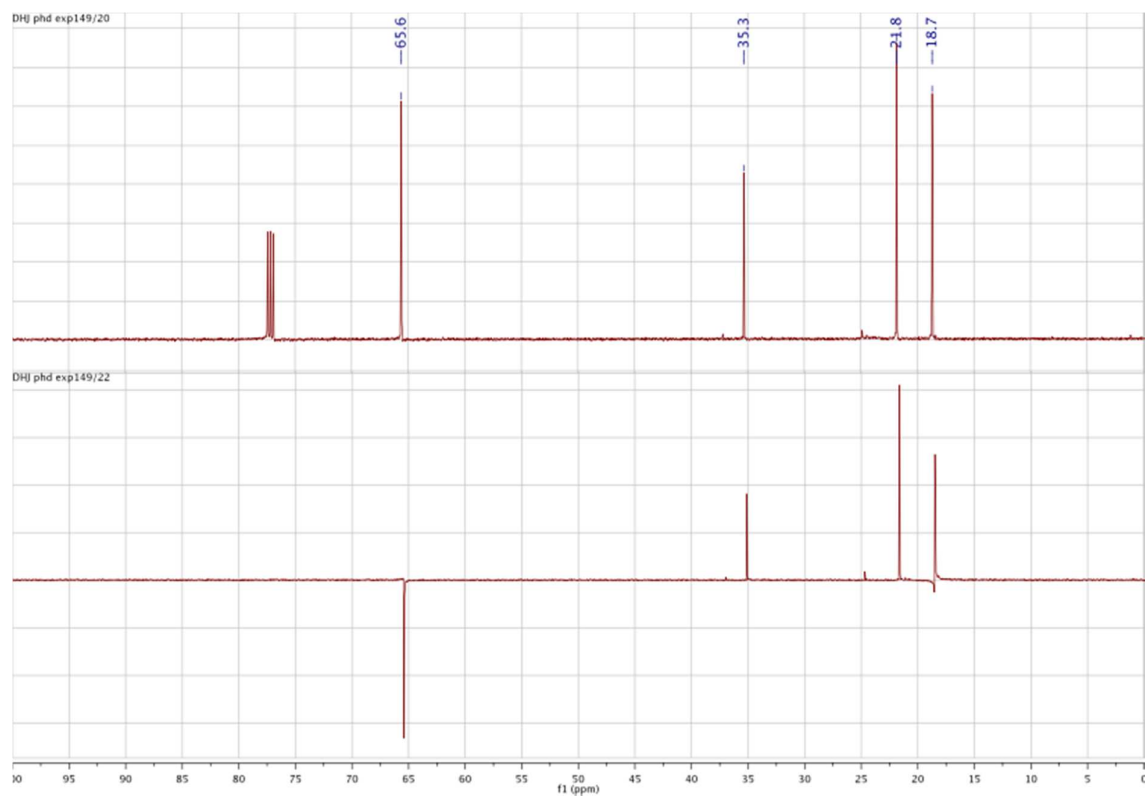
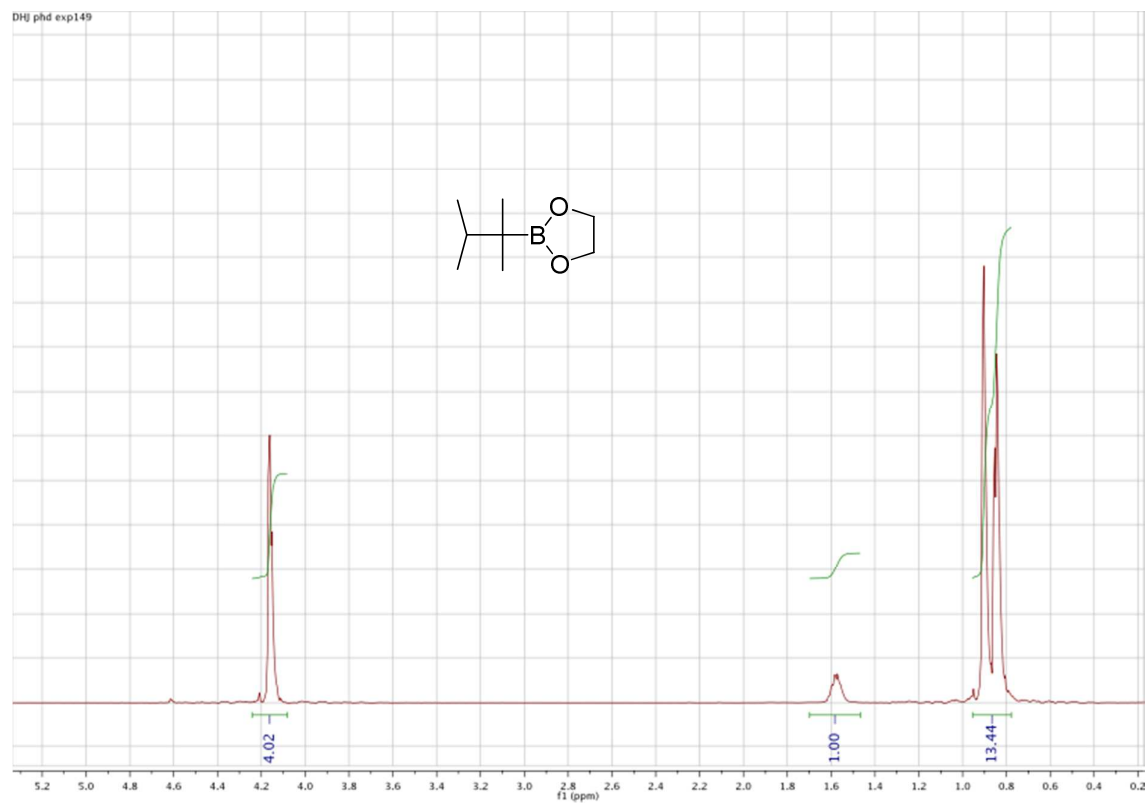


2-*tert*-Butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7, R = *t*-Bu)

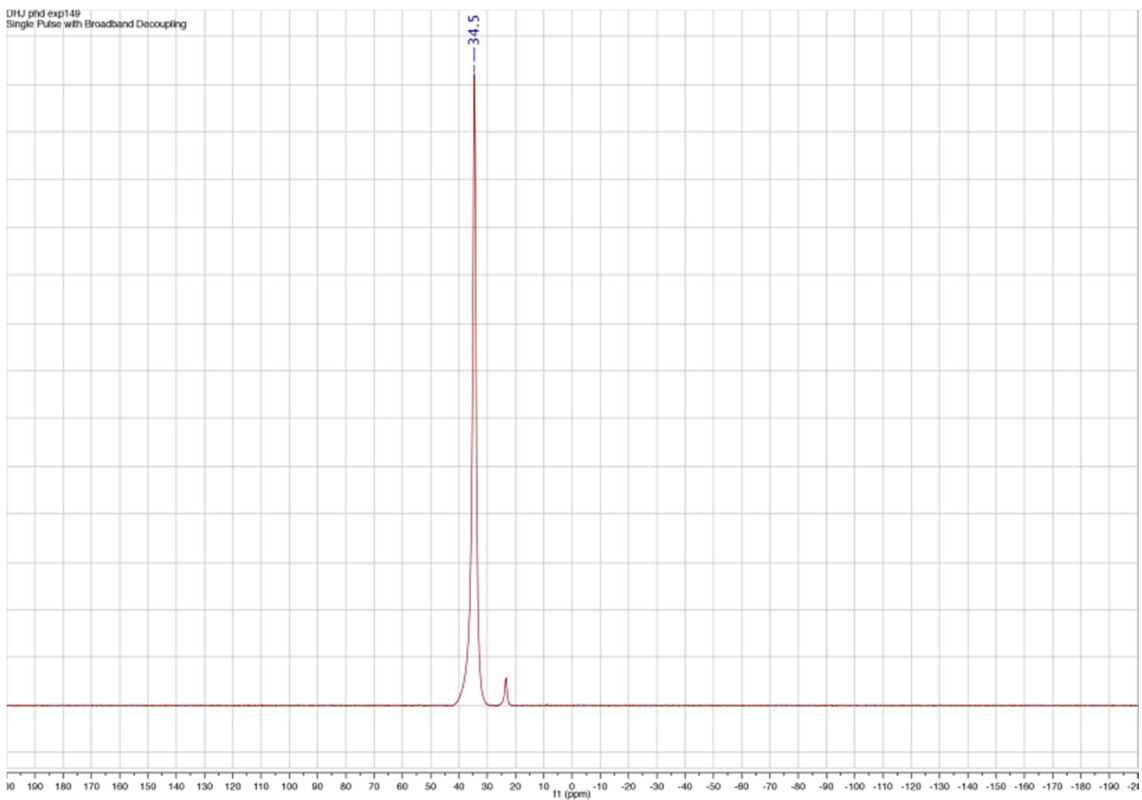




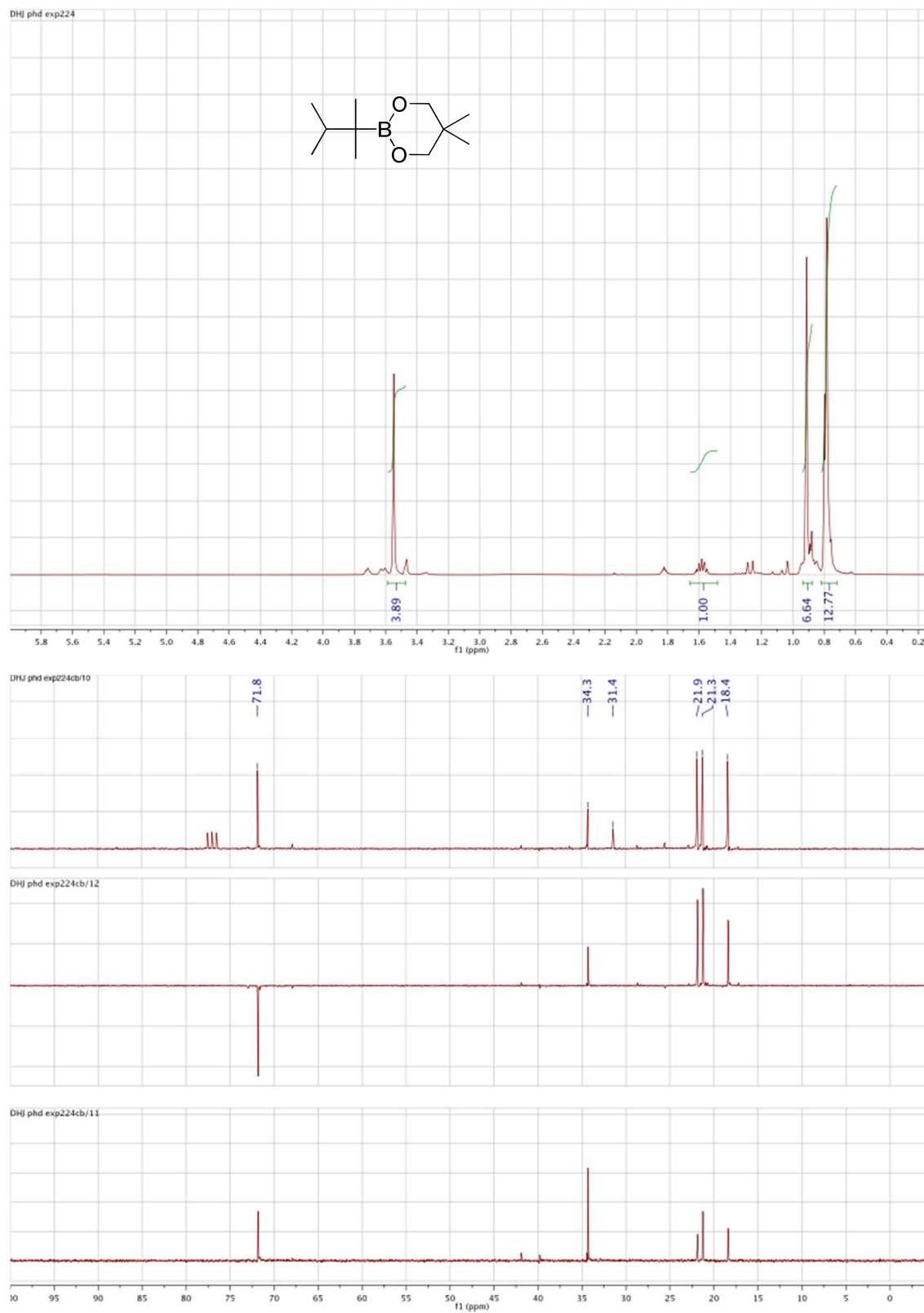
2-(2,3-Dimethylbutan-2-yl)-1,3,2-dioxaborolane (11)

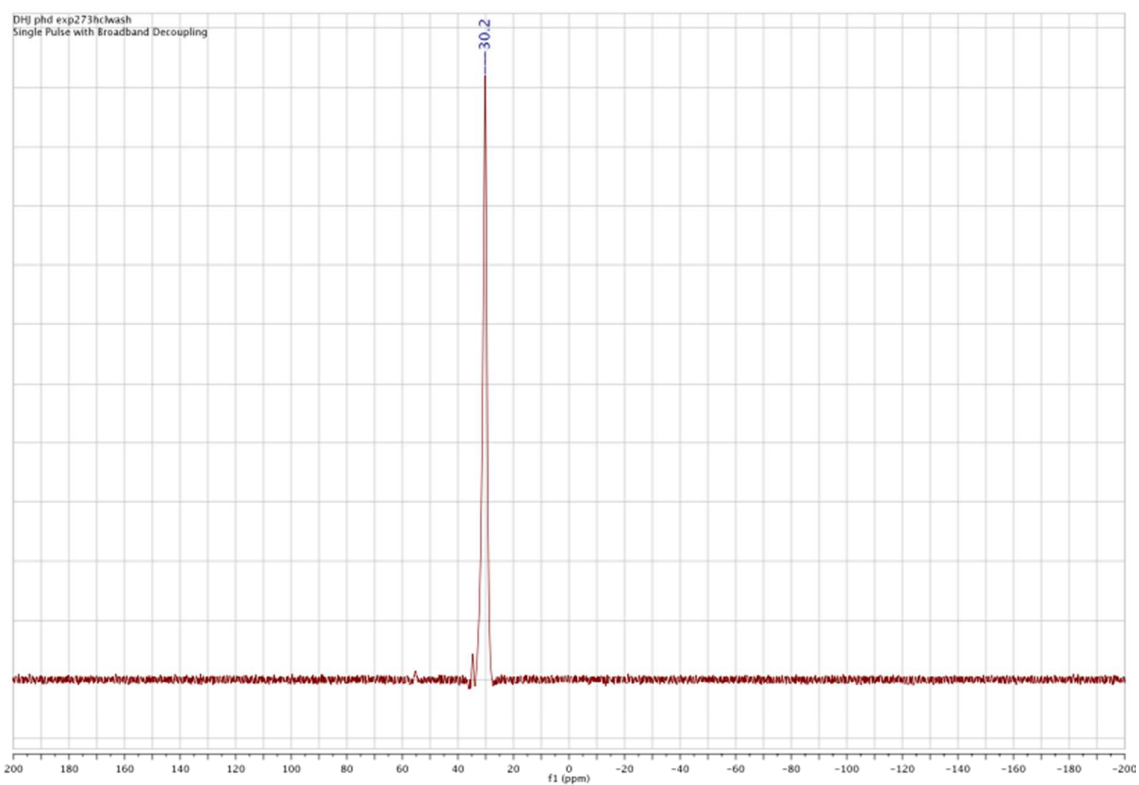


DMU ghd exp148
Single Pulse with Broadband Decoupling

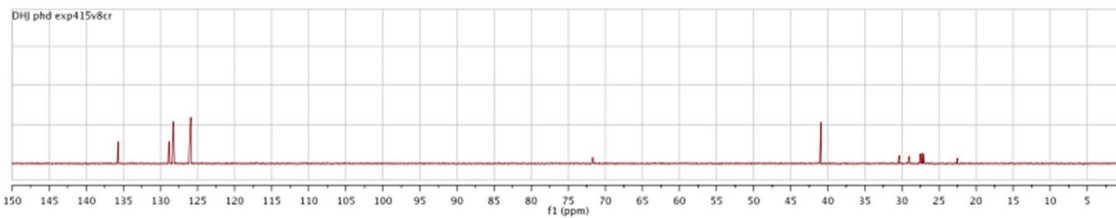
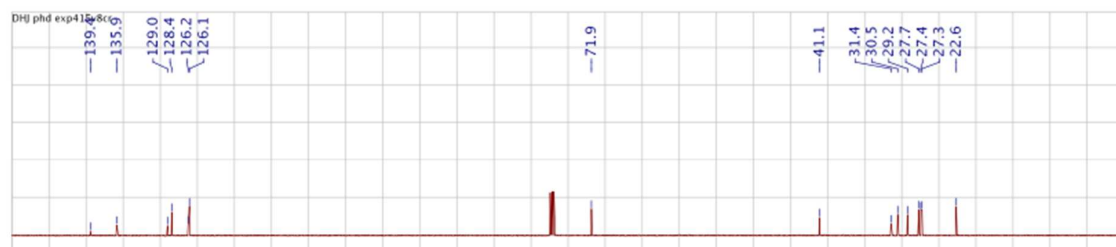
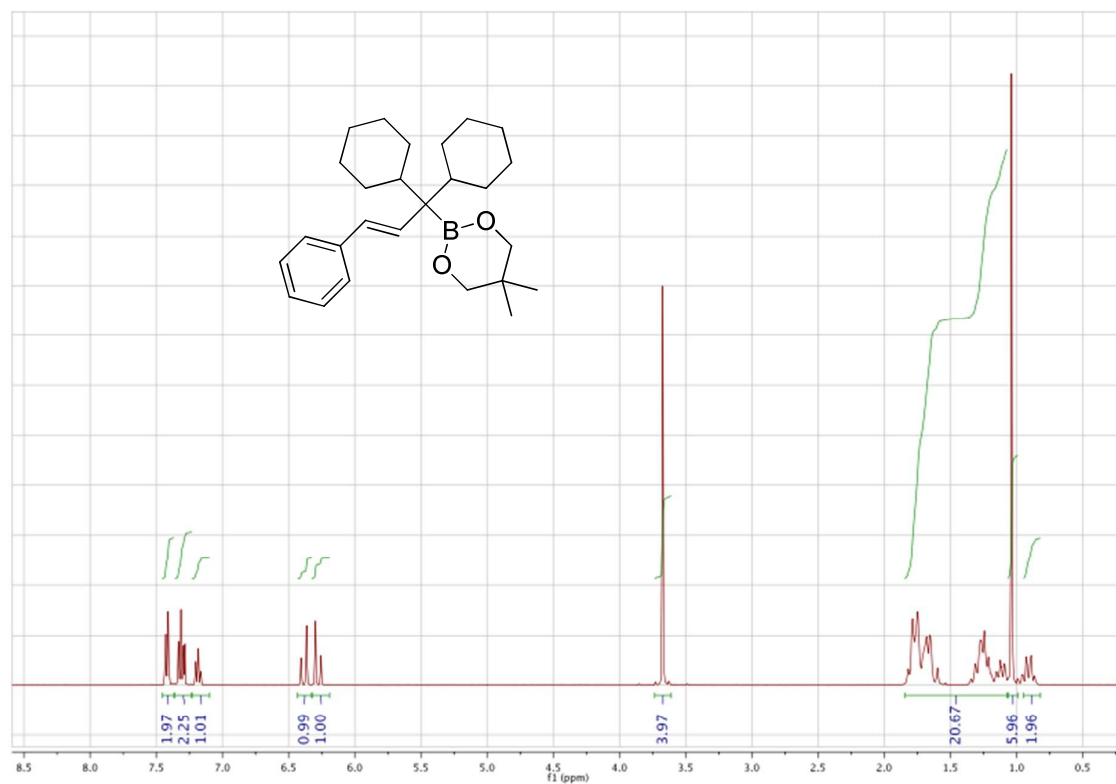


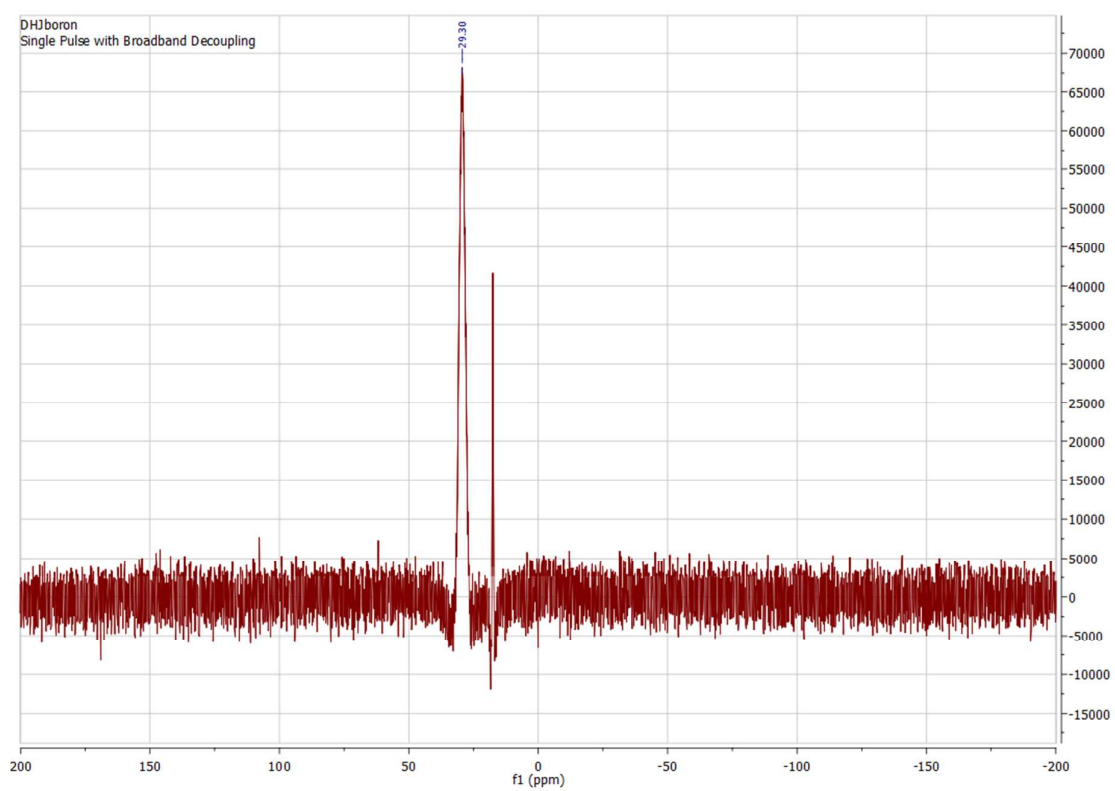
2-(2,3-Dimethylbutan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (12)



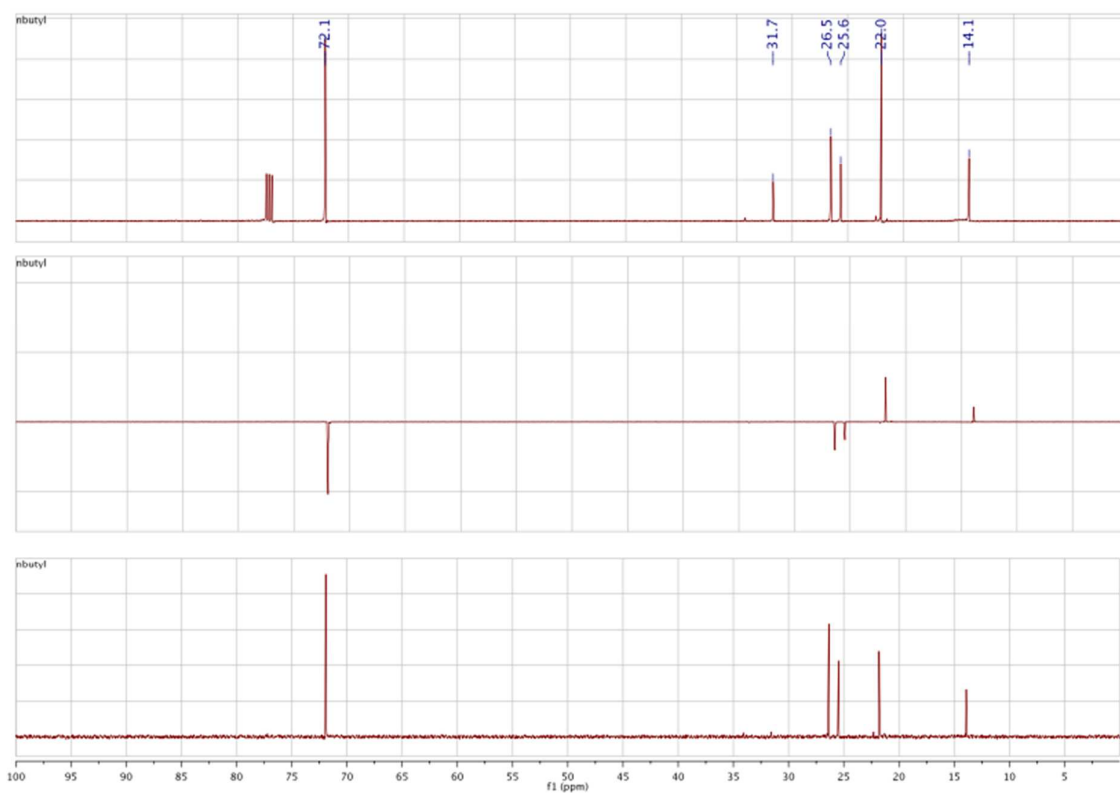
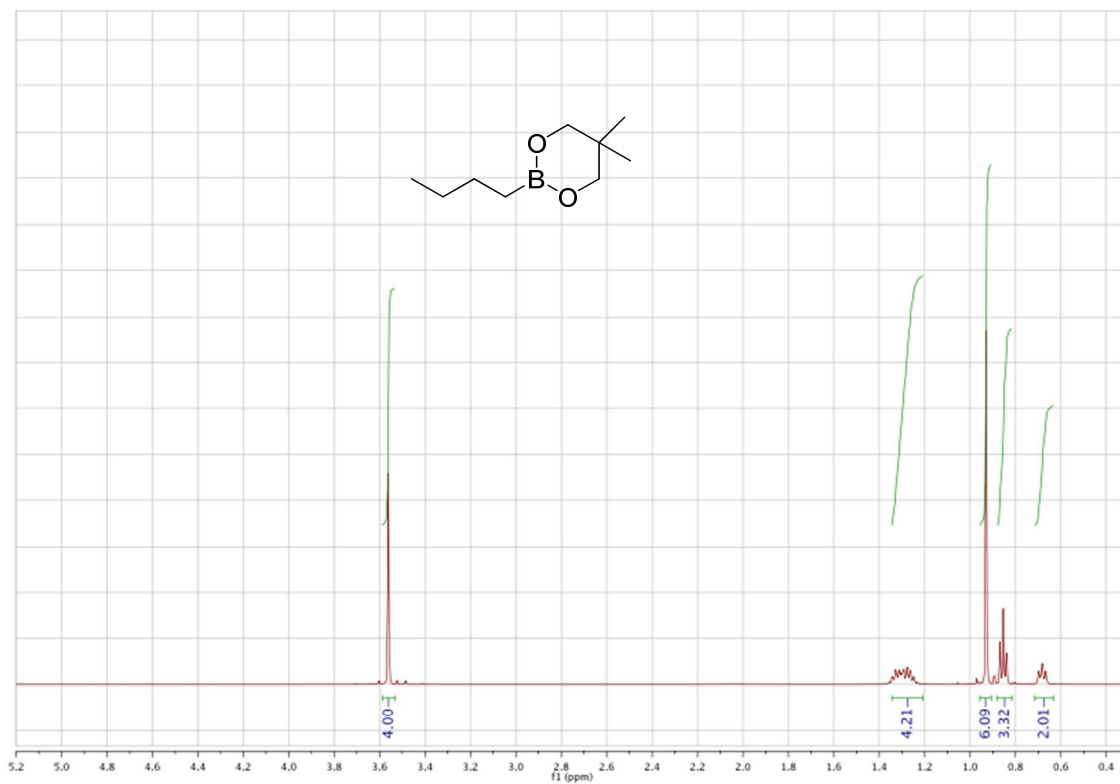


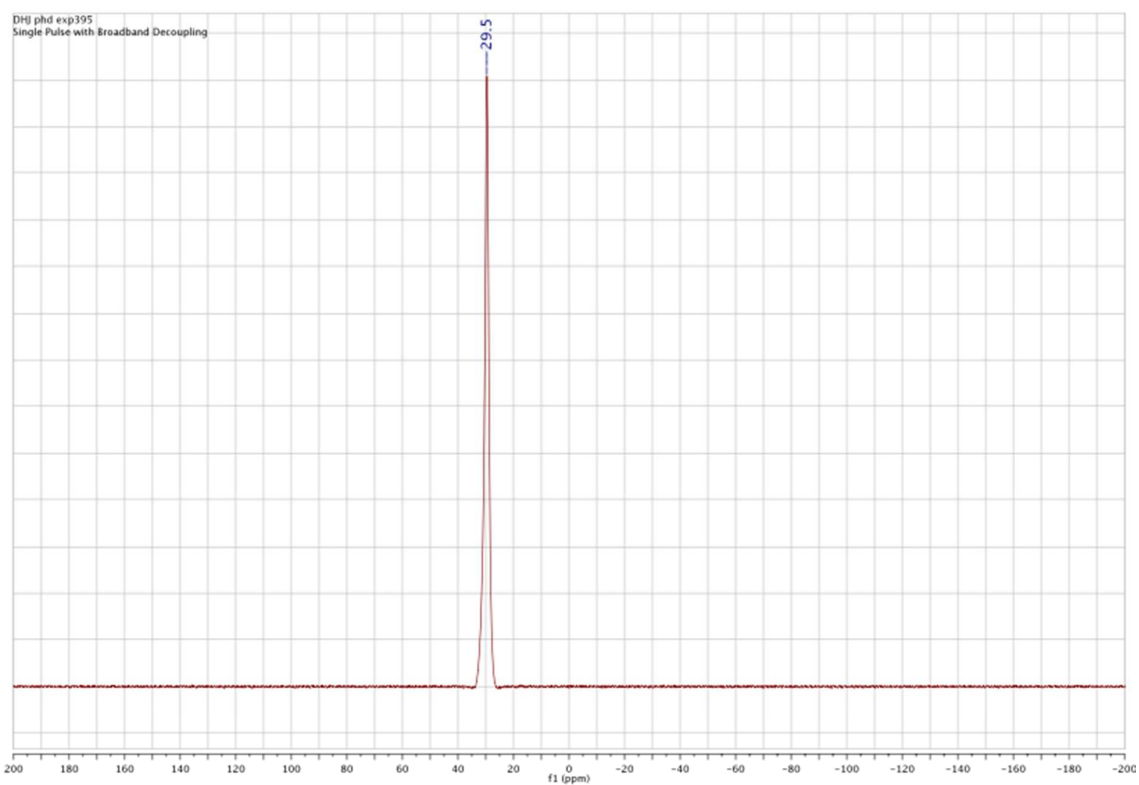
(*E*)-2-(1,1-Dicyclohexyl-3-phenylallyl)-5,5-dimethyl-1,3,2-dioxaborinane (13, R^C = cyclohexyl, R^D = PhCH=CH)



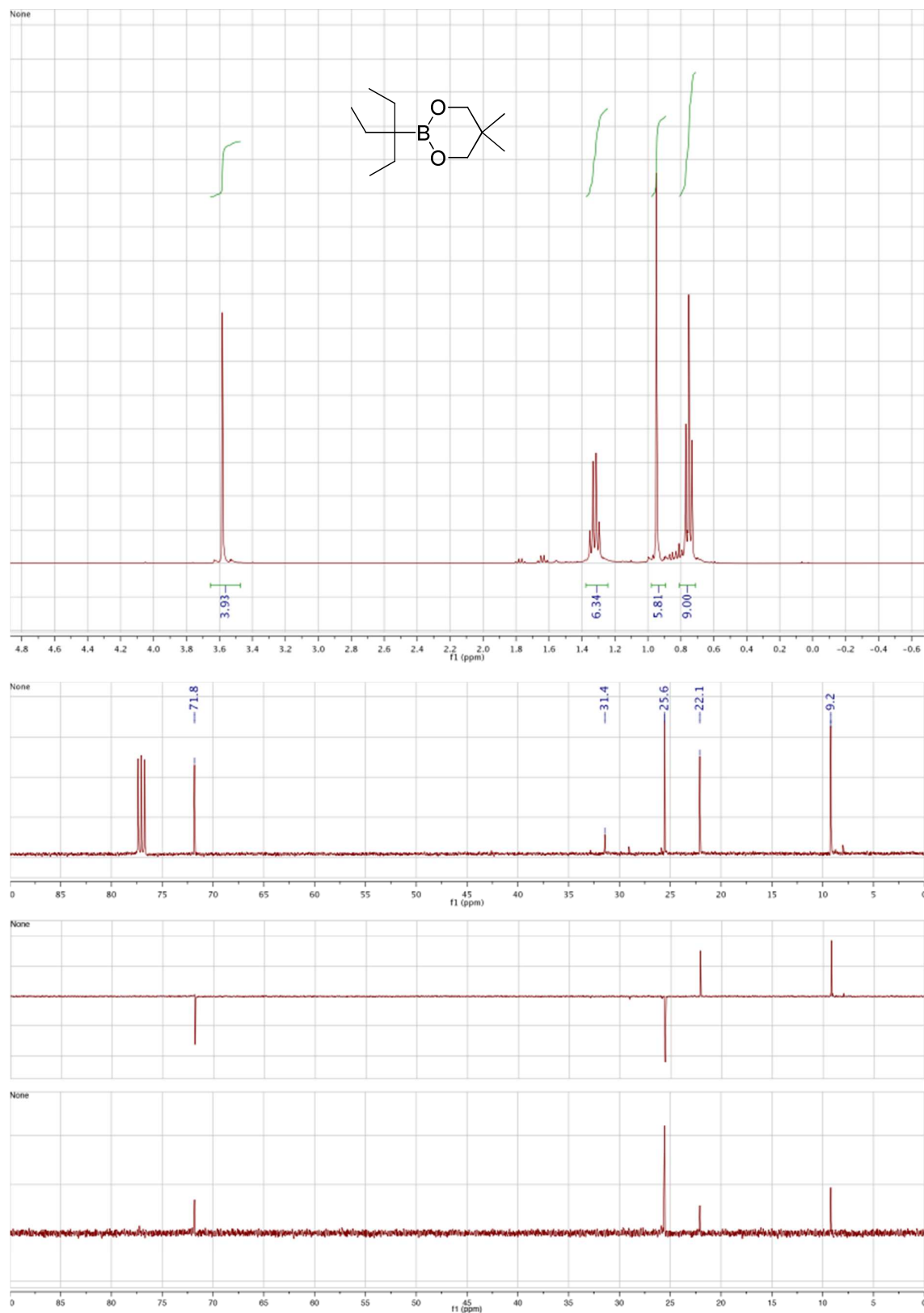


2-Butyl-5,5-dimethyl-1,3,2-dioxaborinane (13, $R^C = H$, $R^D = n$ -propyl)

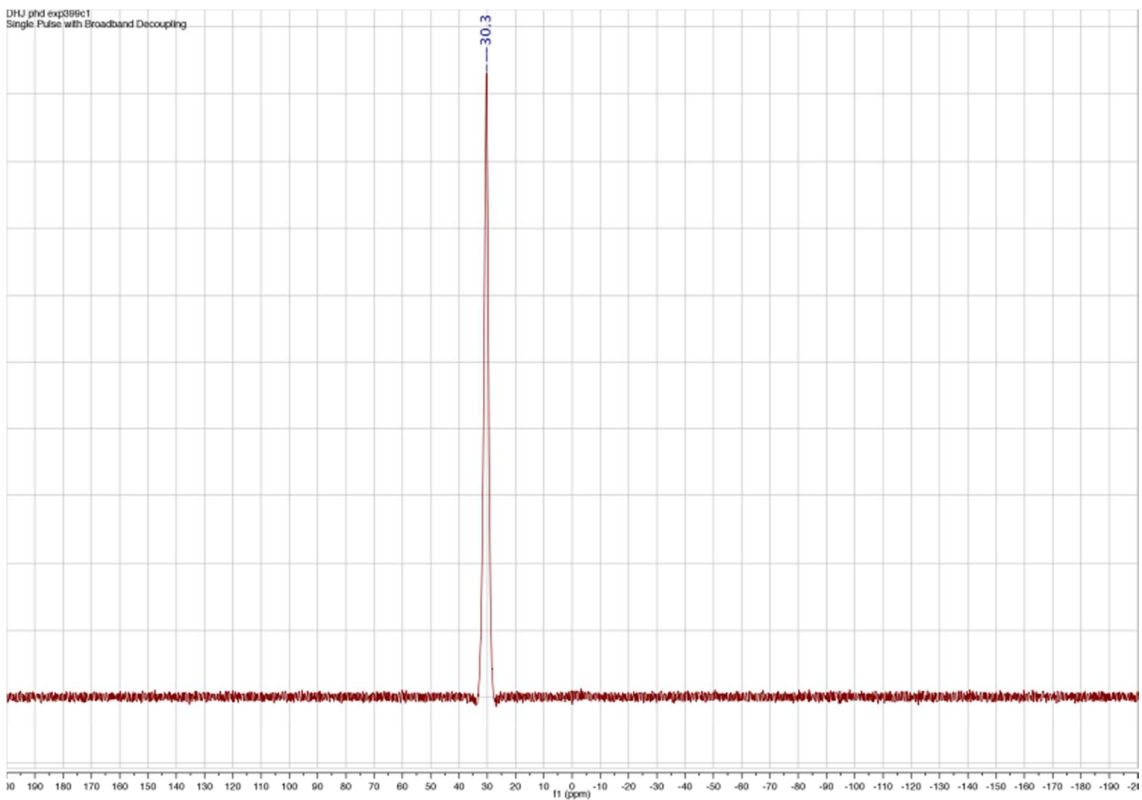




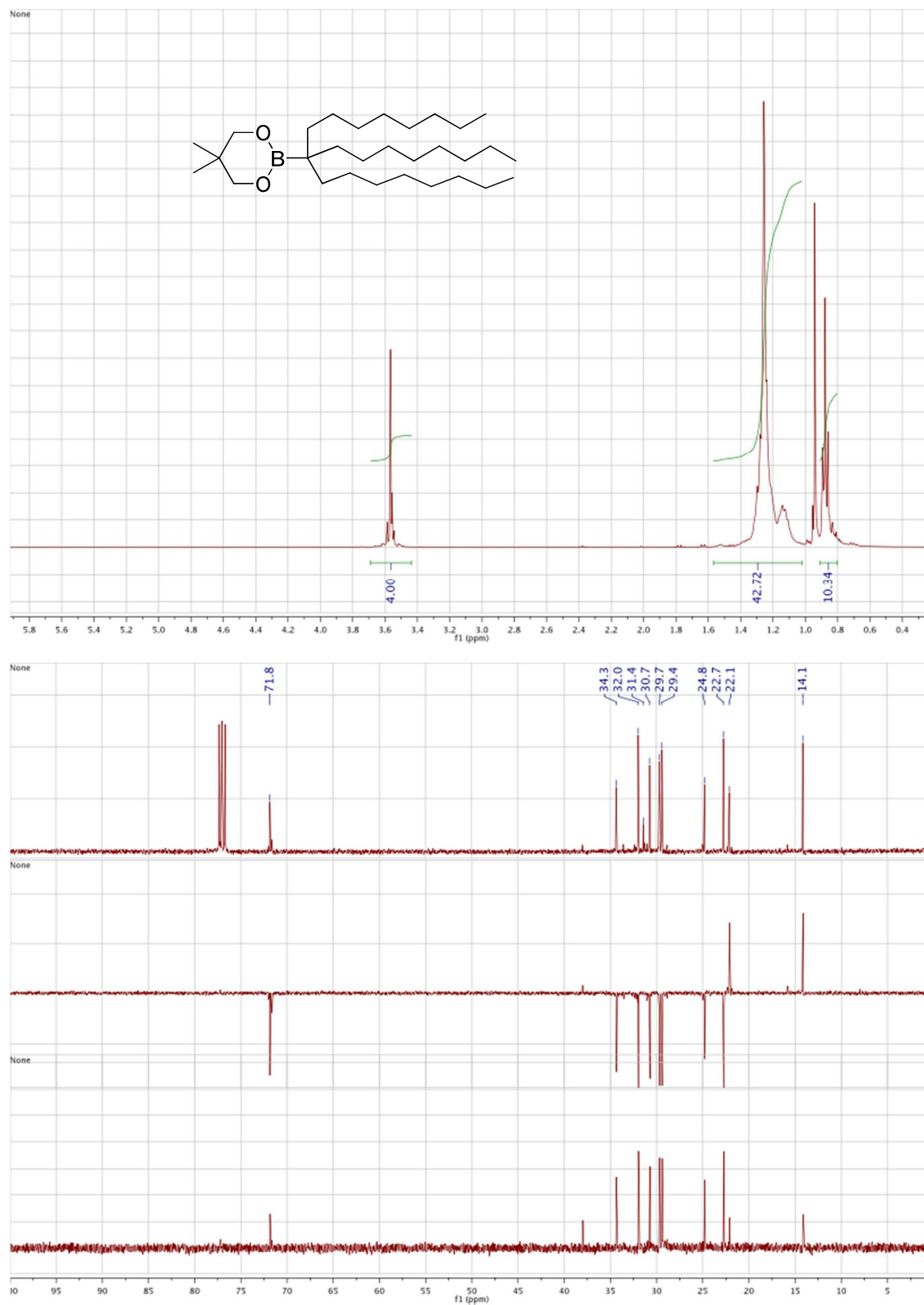
2-(3-Ethylpentan-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane (13, $R^C = R^D = \text{ethyl}$)

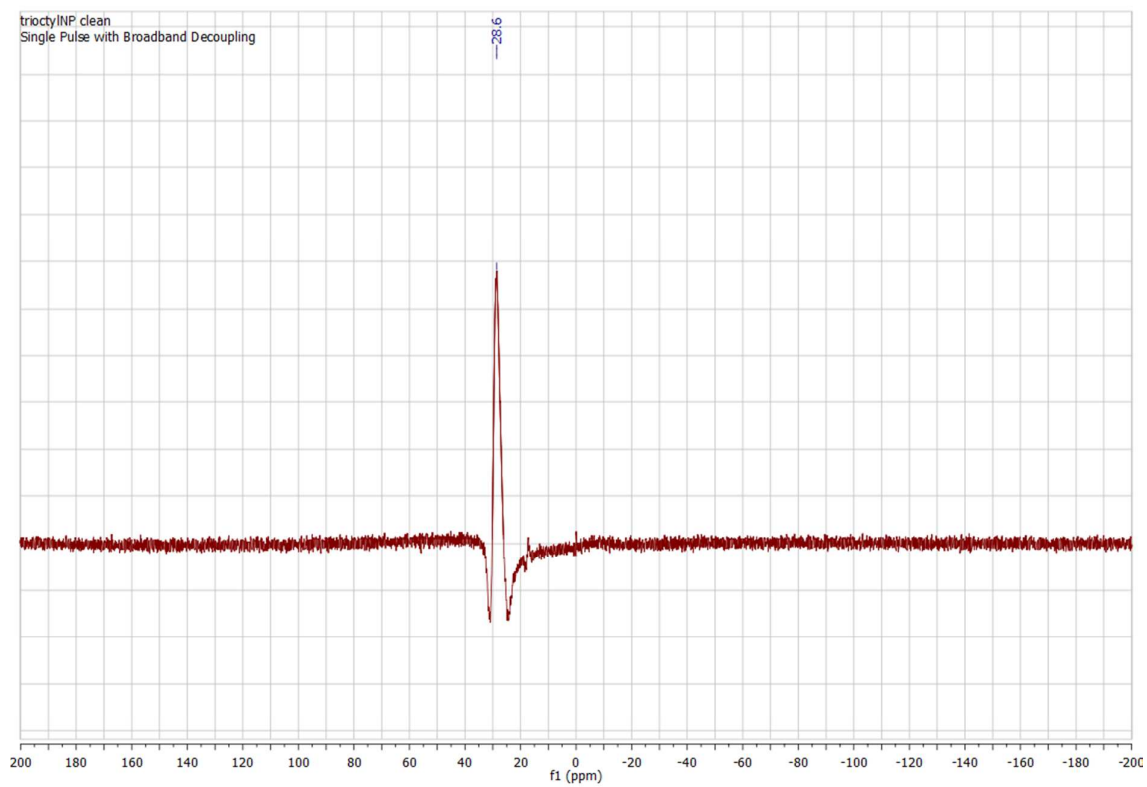


DNJ ghd eng359c1
Single Pulse with Broadband Decoupling

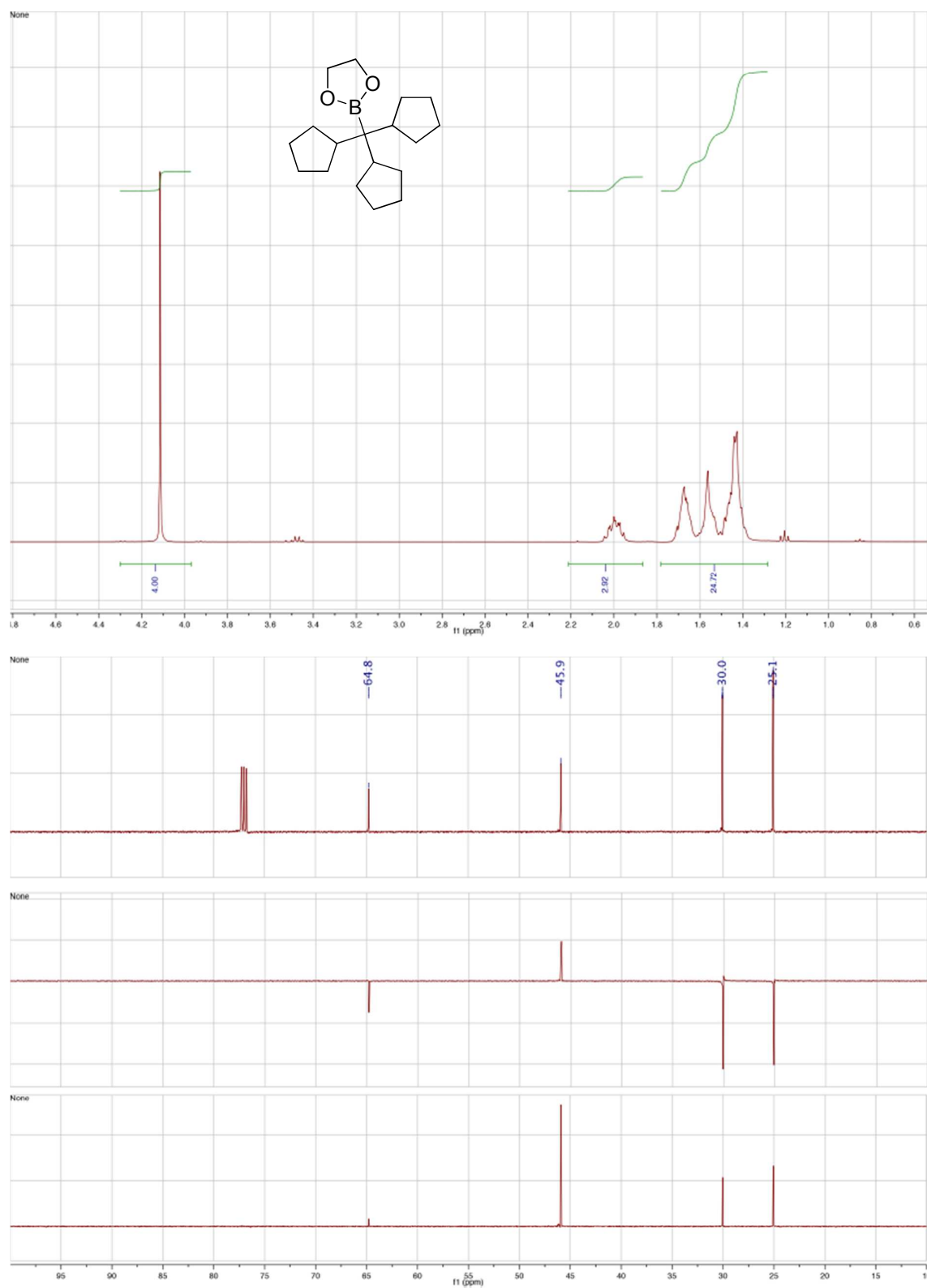


5,5-Dimethyl-2-(9-octylheptadecan-9-yl)-1,3,2-dioxaborinane (13, $R^C = R^D = n\text{-octyl}$)

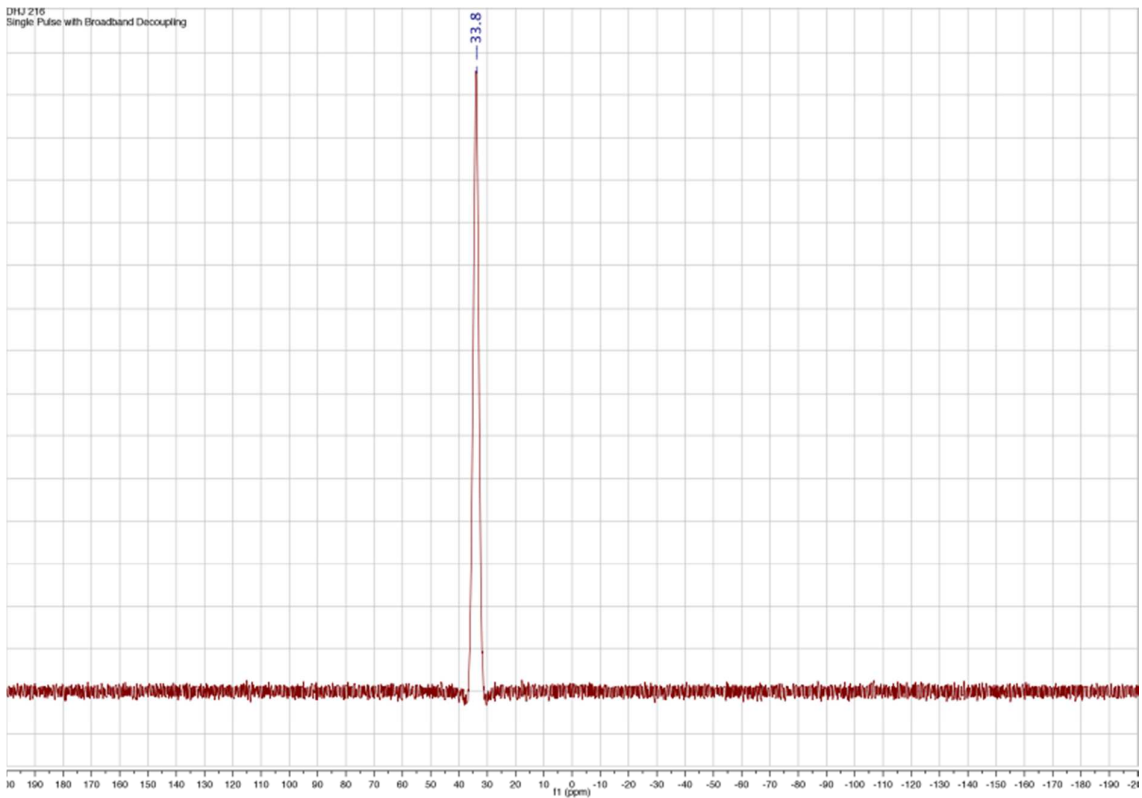




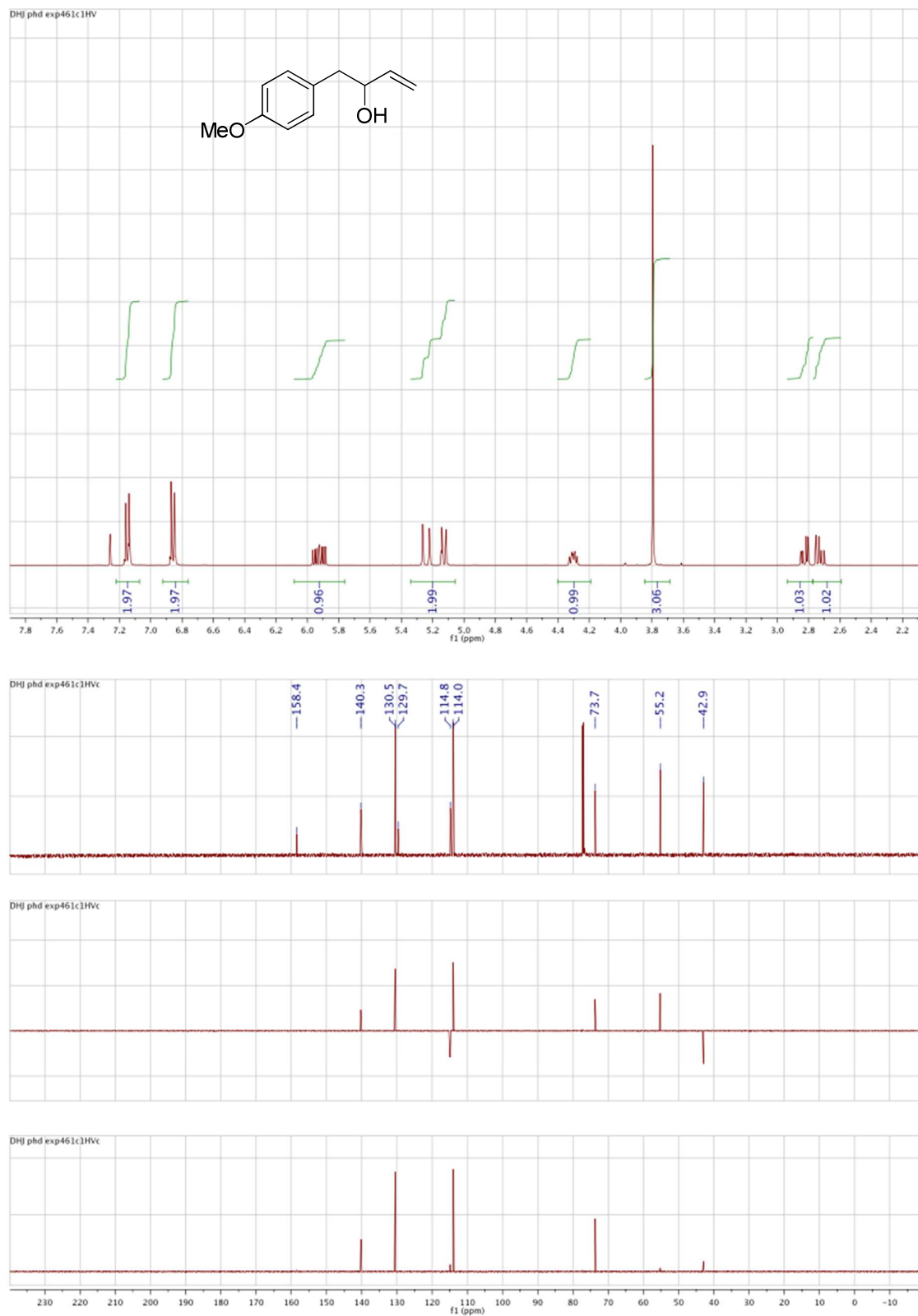
2-(Tricyclopentylmethyl)-1,3,2-dioxaborolane



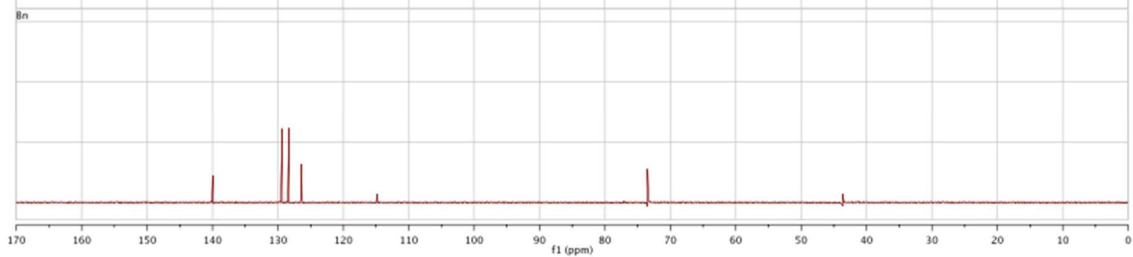
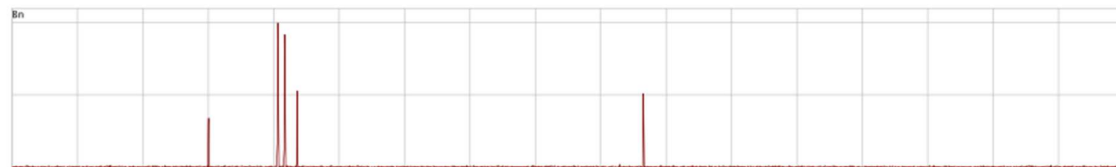
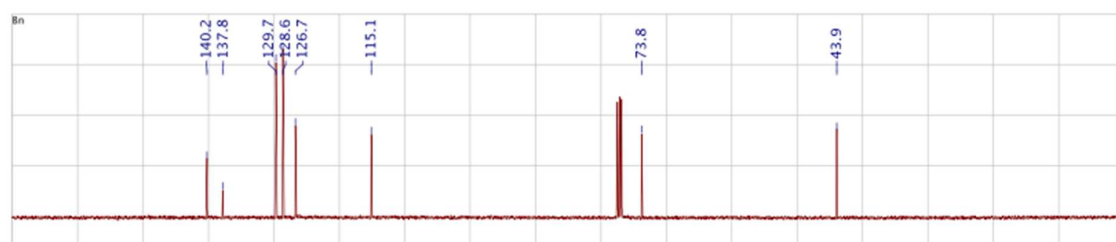
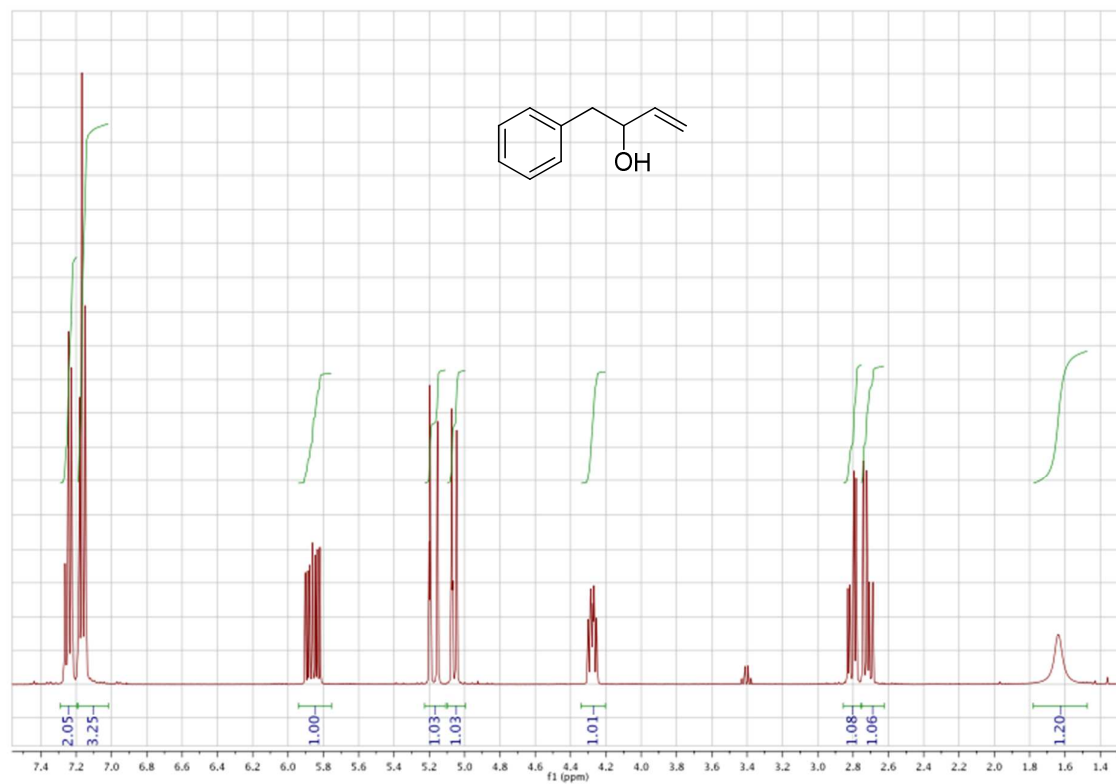
DMJ 215
Single Pulse with Broadband Decoupling



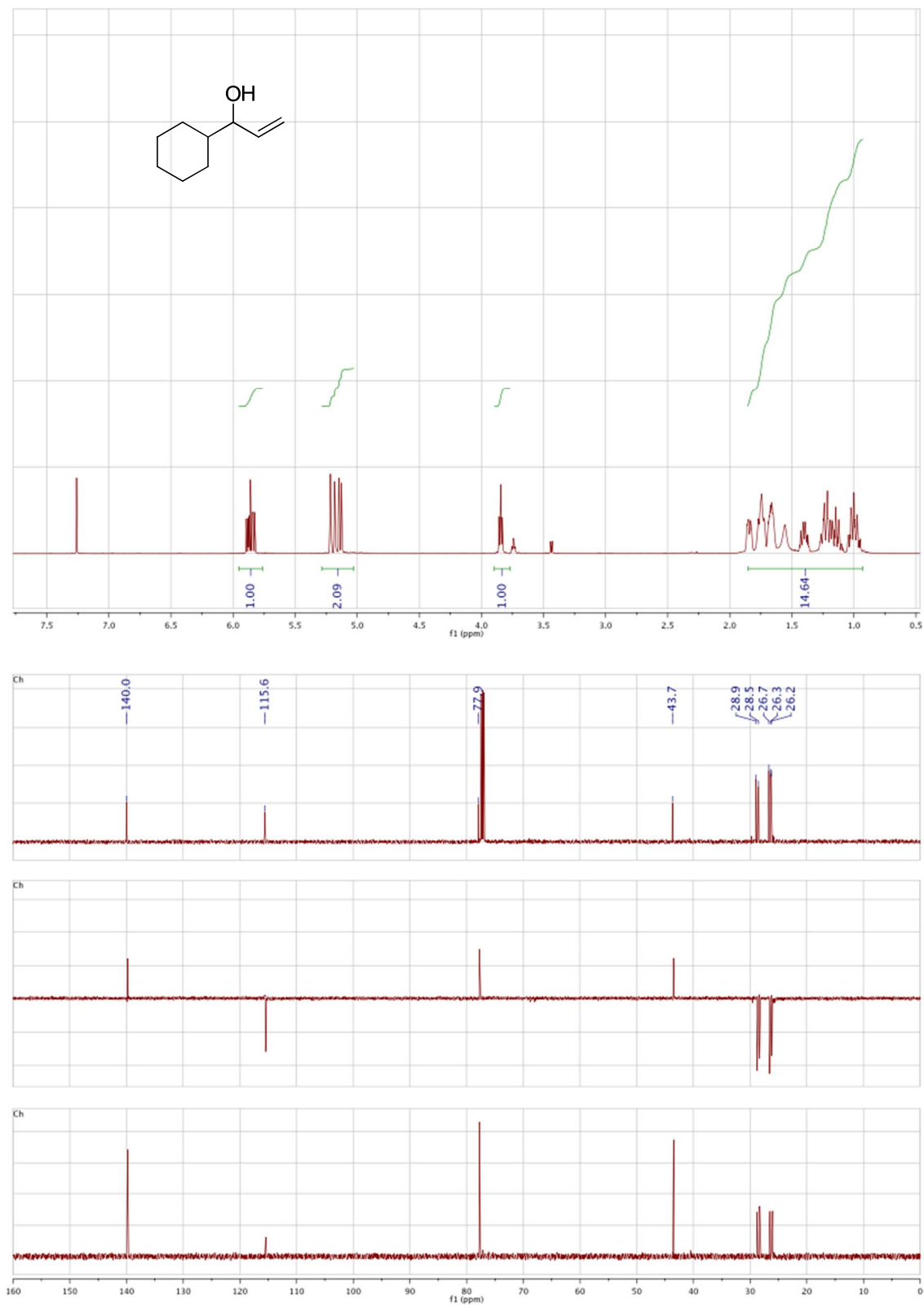
1-(4-Methoxyphenyl)but-3-en-2-ol (9, R = 4-methoxybenzyl)



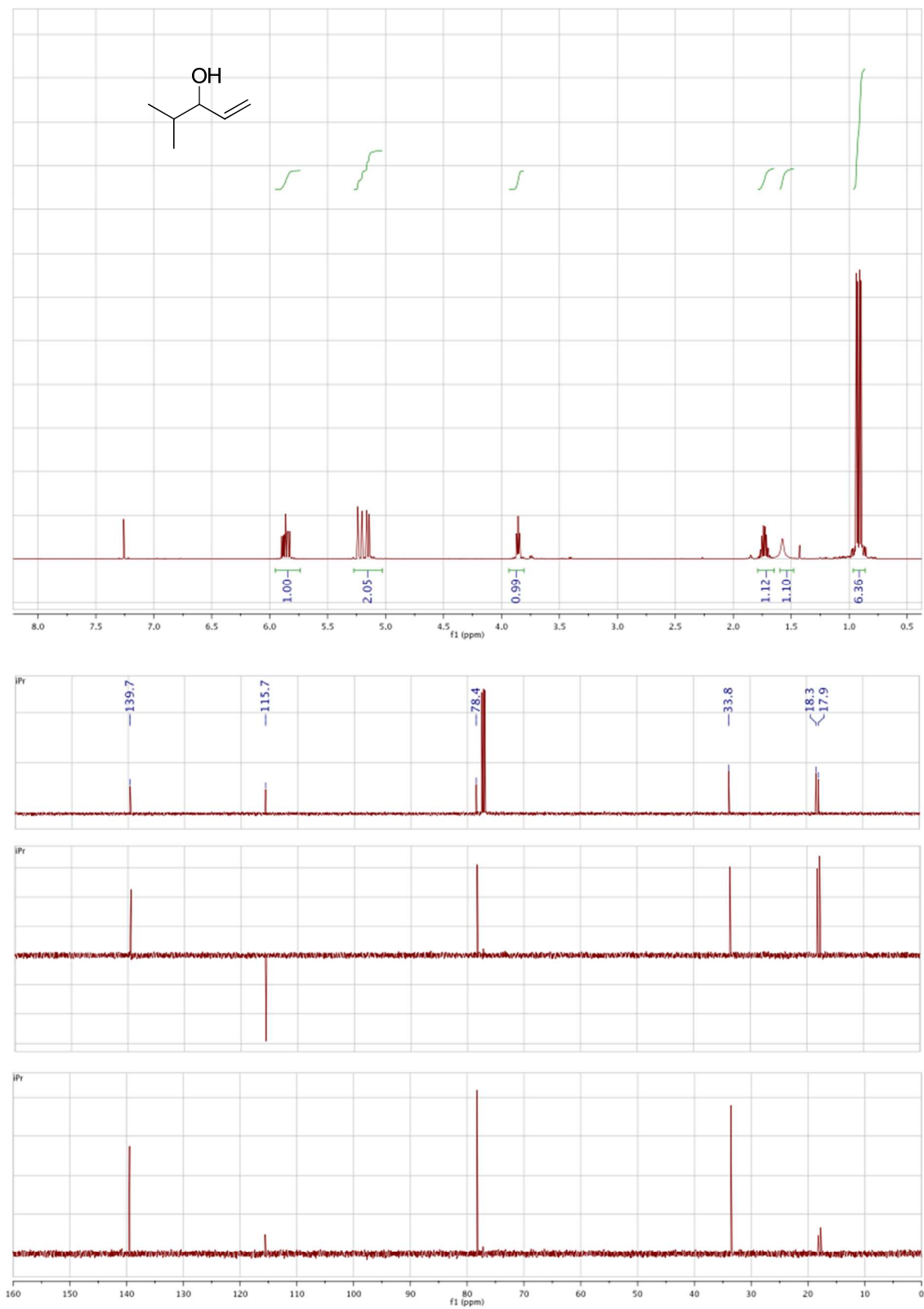
1-Phenylbut-3-en-2-ol (9, R = benzyl)



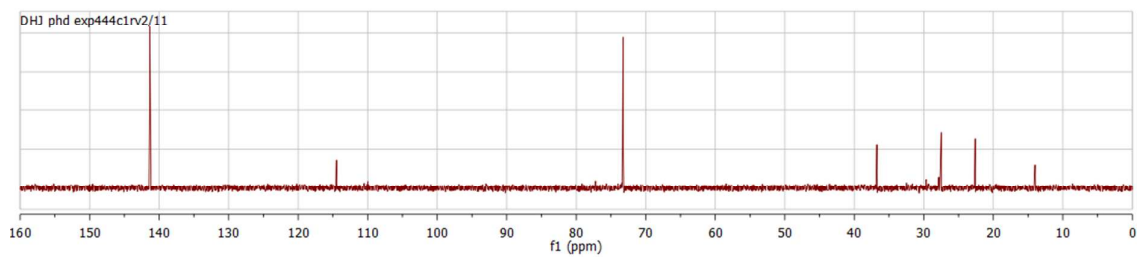
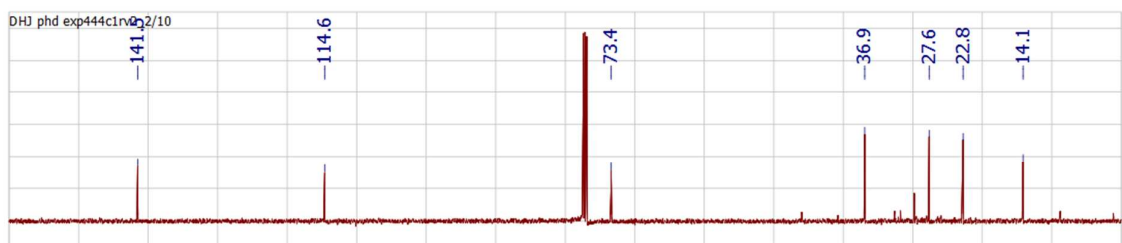
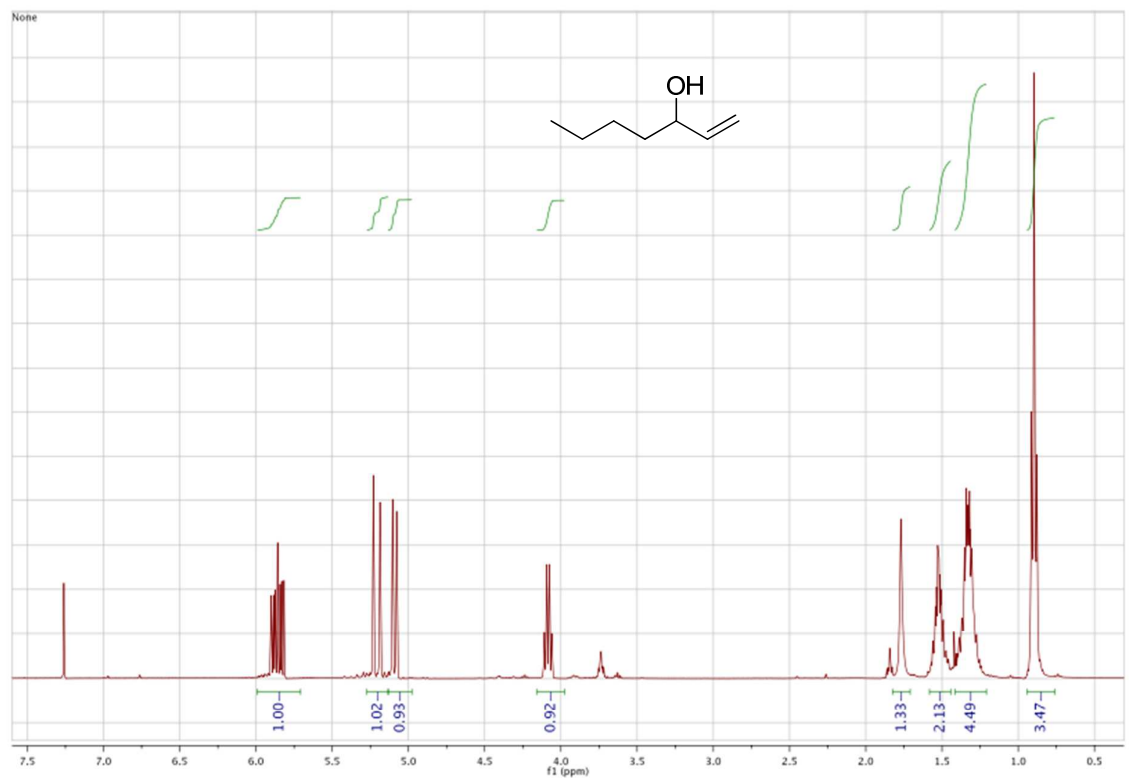
1-Cyclohexylprop-2-en-1-ol (9, R = cyclohexyl)



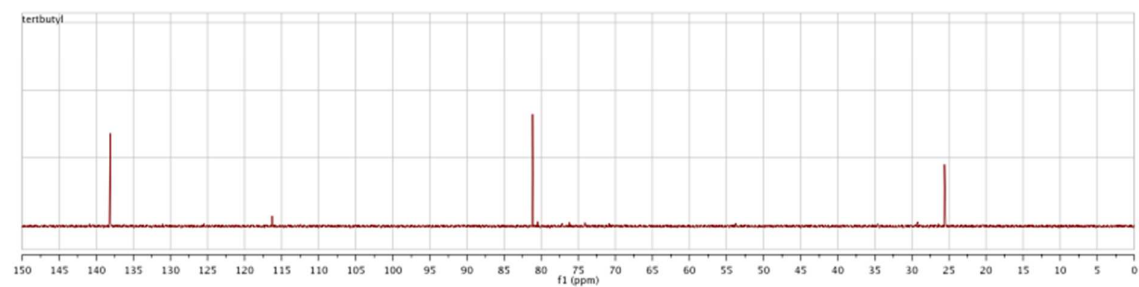
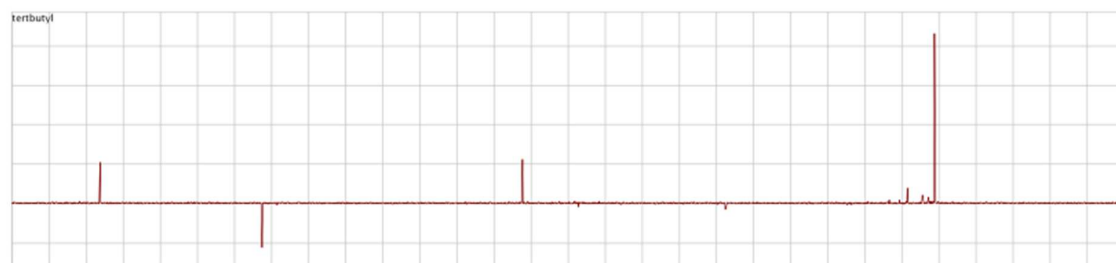
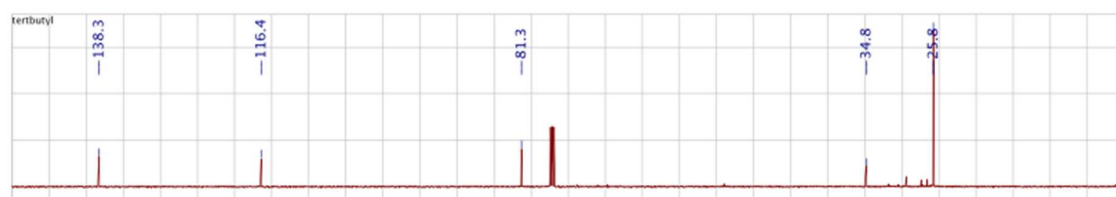
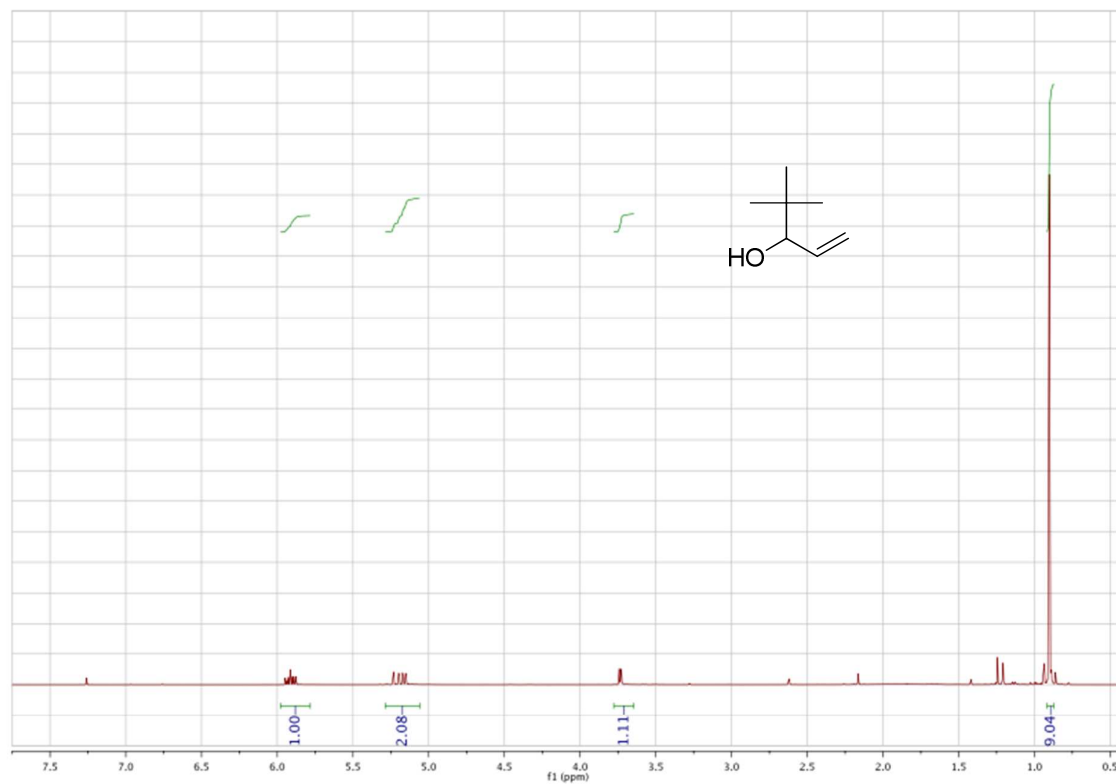
4-Methylpent-1-en-3-ol (9, R = isopropyl)



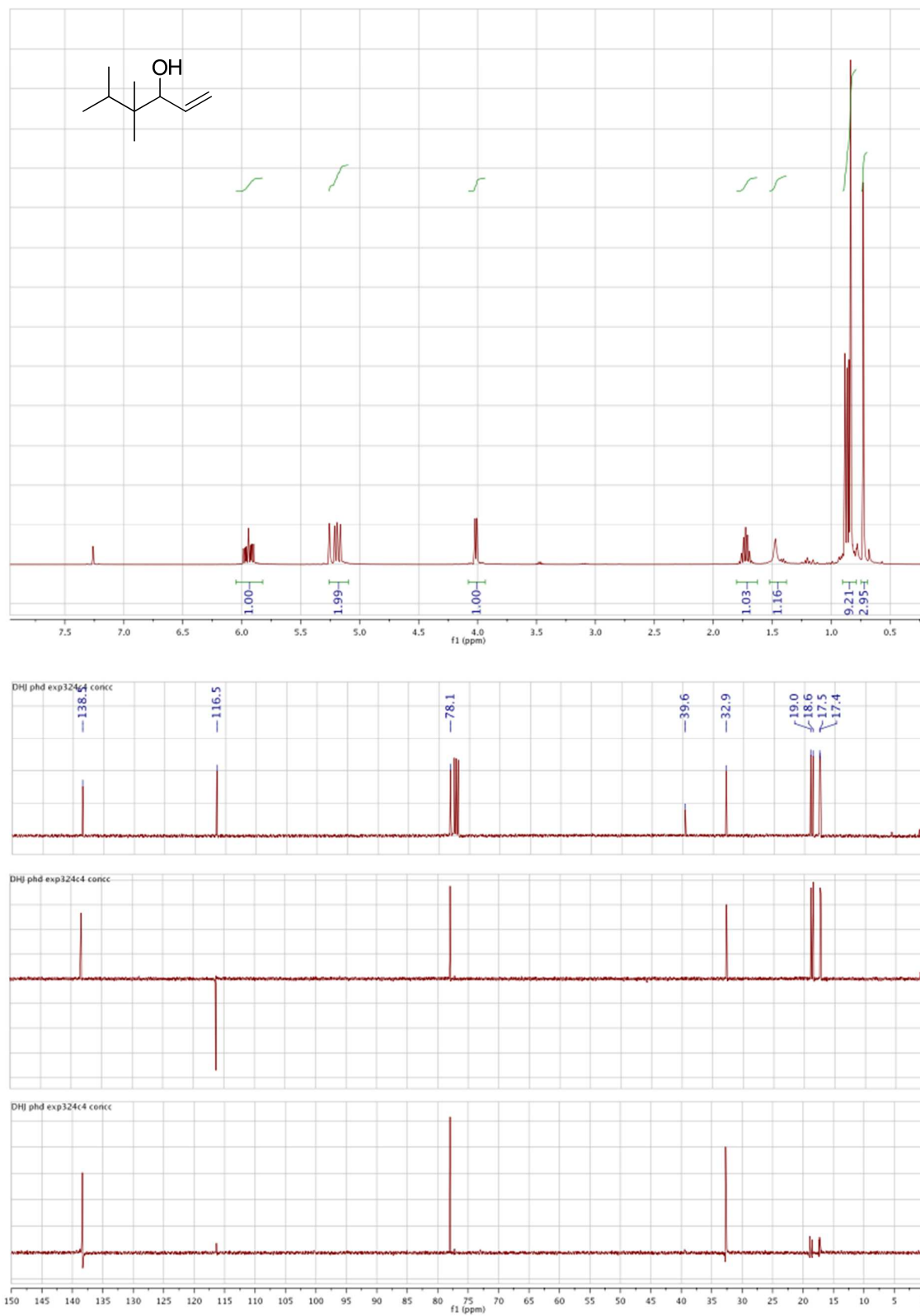
Hept-1-en-3-ol (9, R = *n*-butyl)



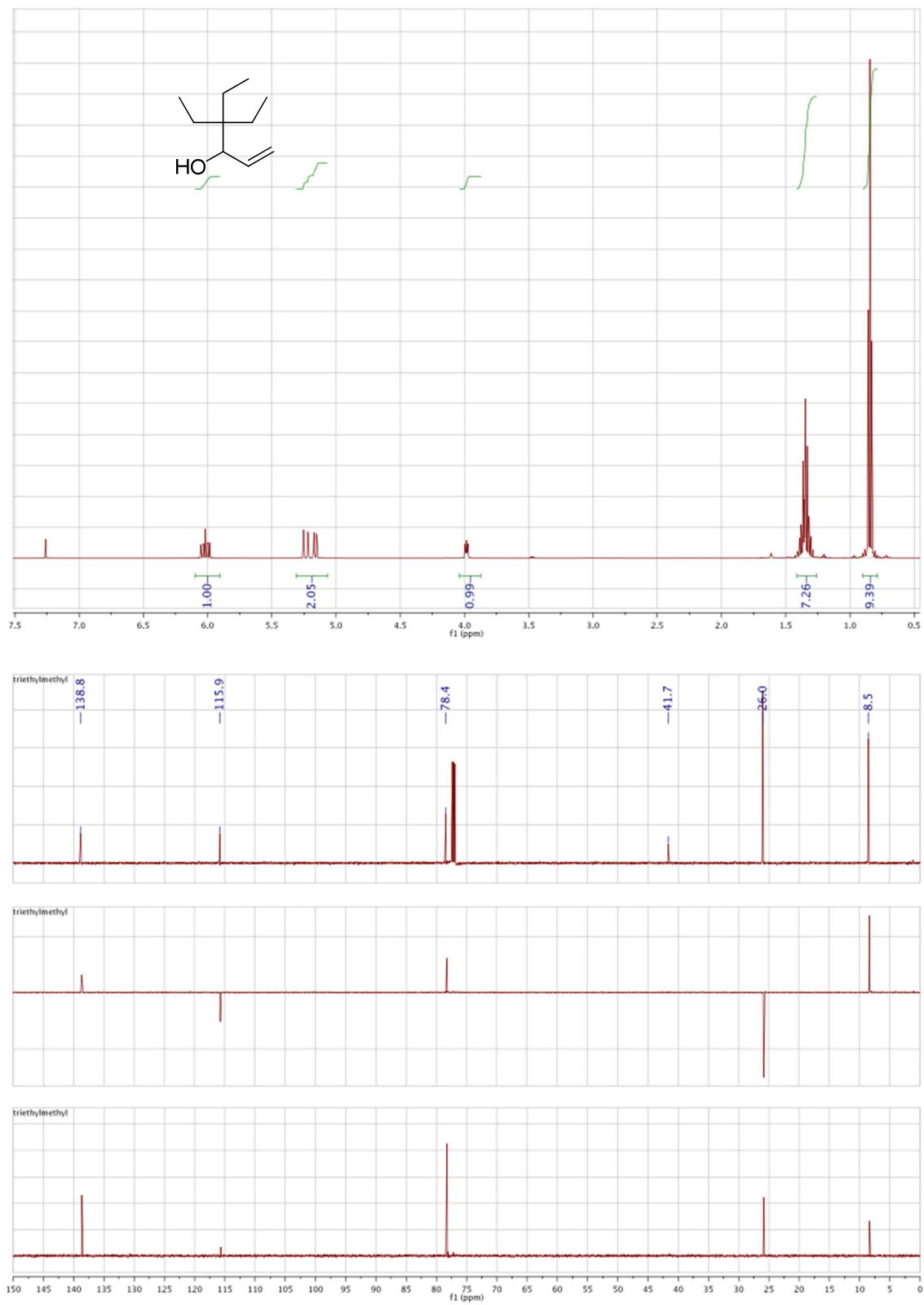
4,4-Dimethylpent-1-en-3-ol (8, R = *t*-Bu)



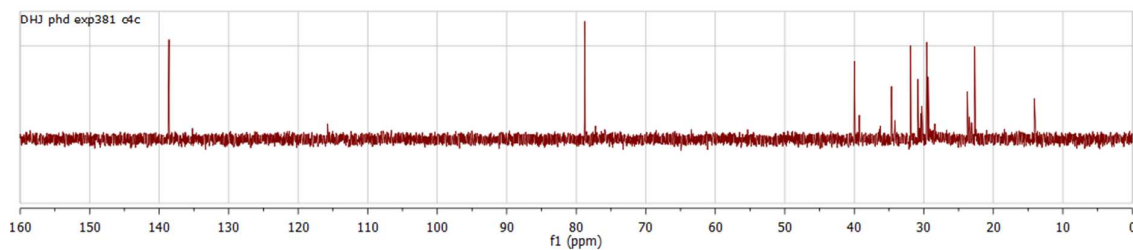
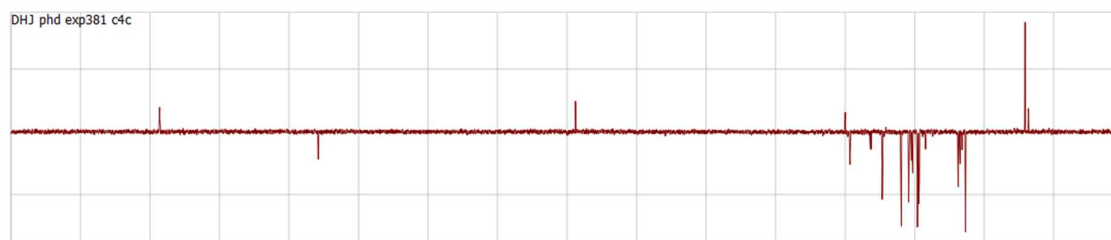
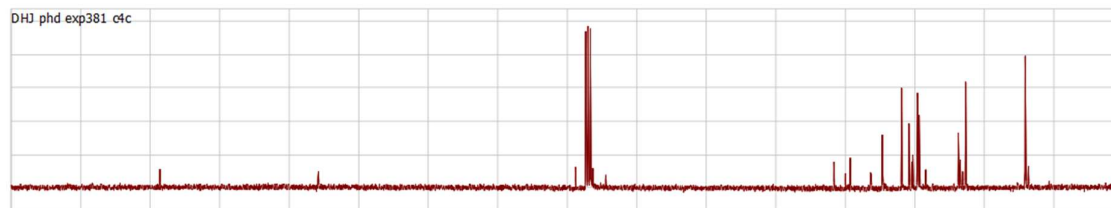
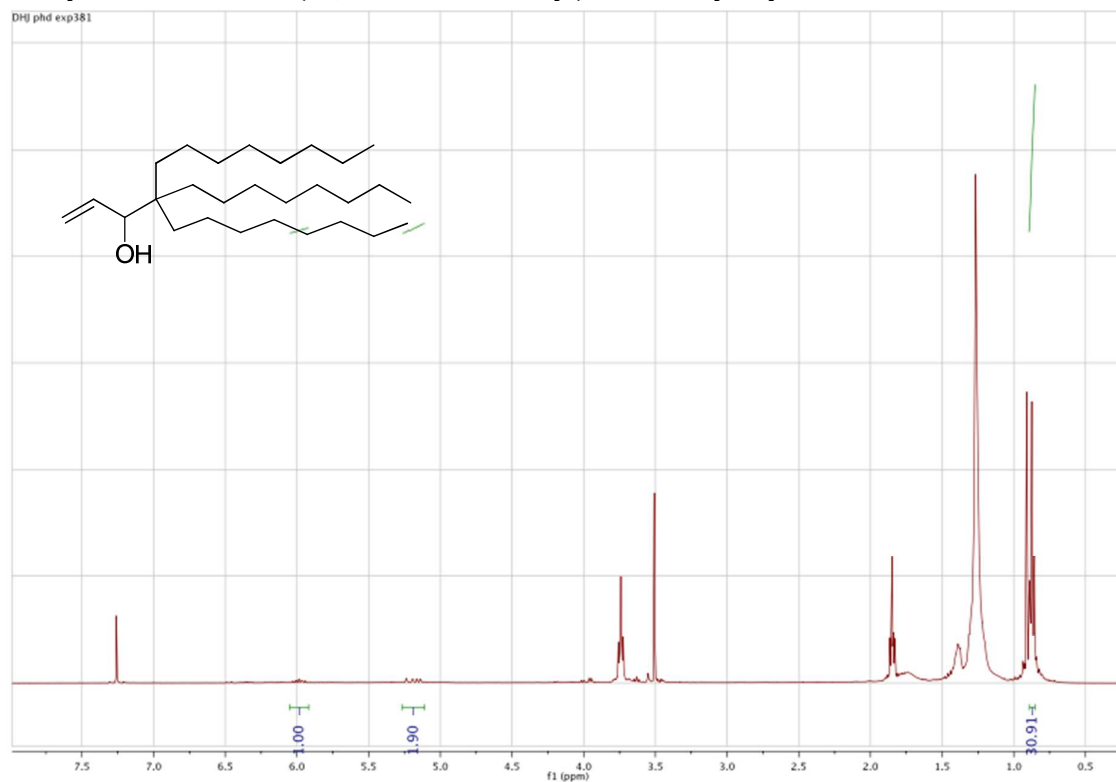
4,4,5-Trimethylhex-1-en-3-ol (9, R = hexyl)



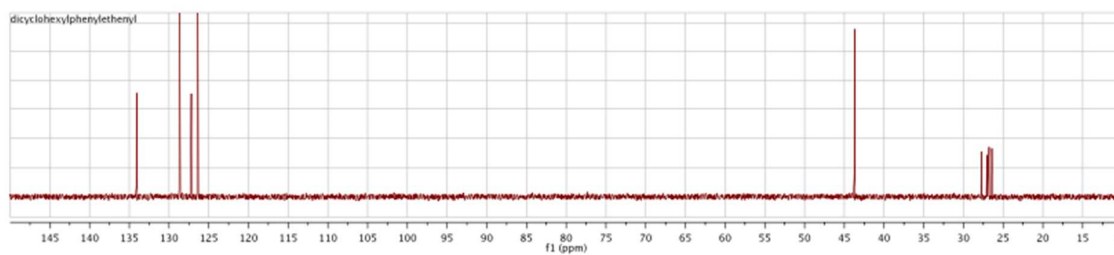
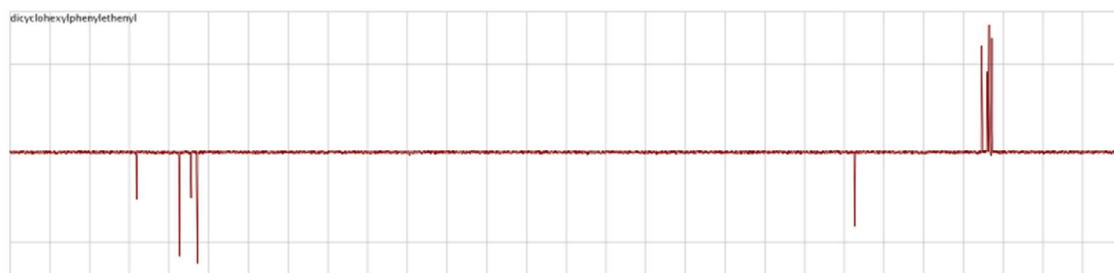
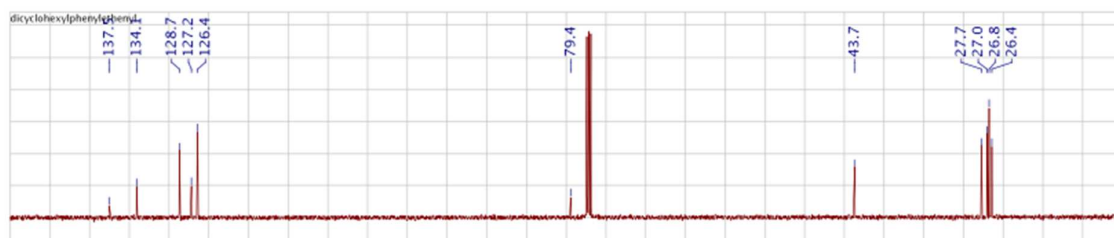
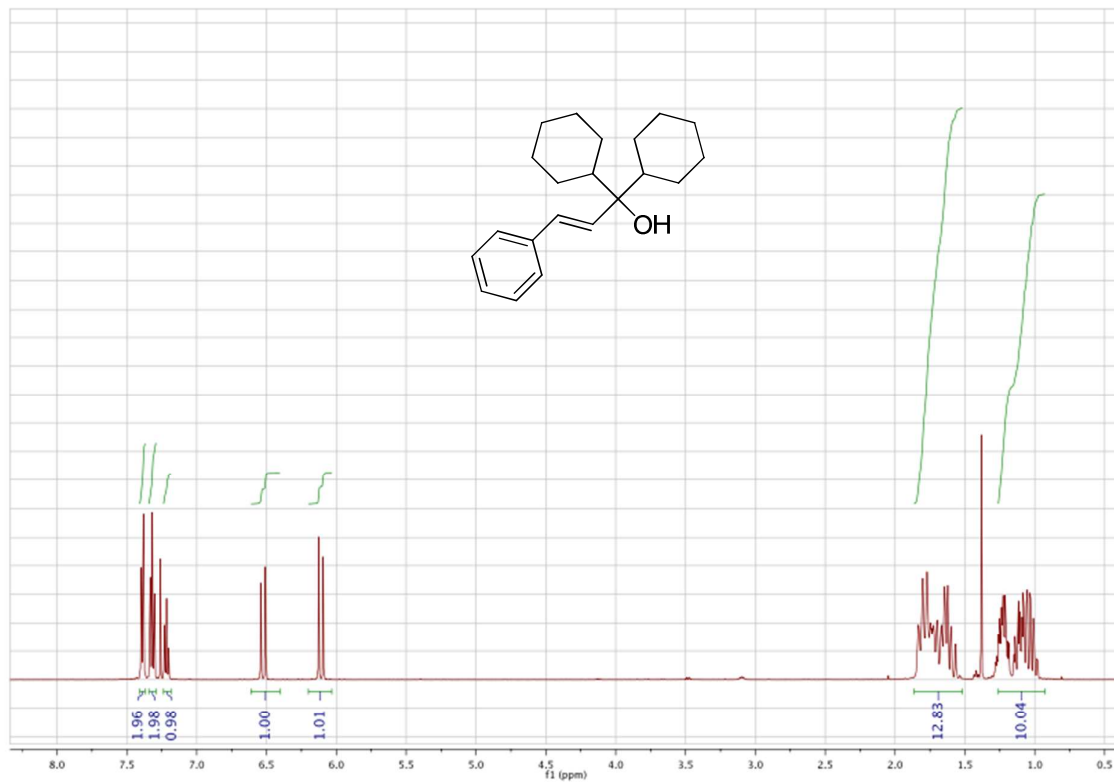
4,4-Diethylhex-1-en-3-ol (14, $R^C = R^D = \text{ethyl}$)



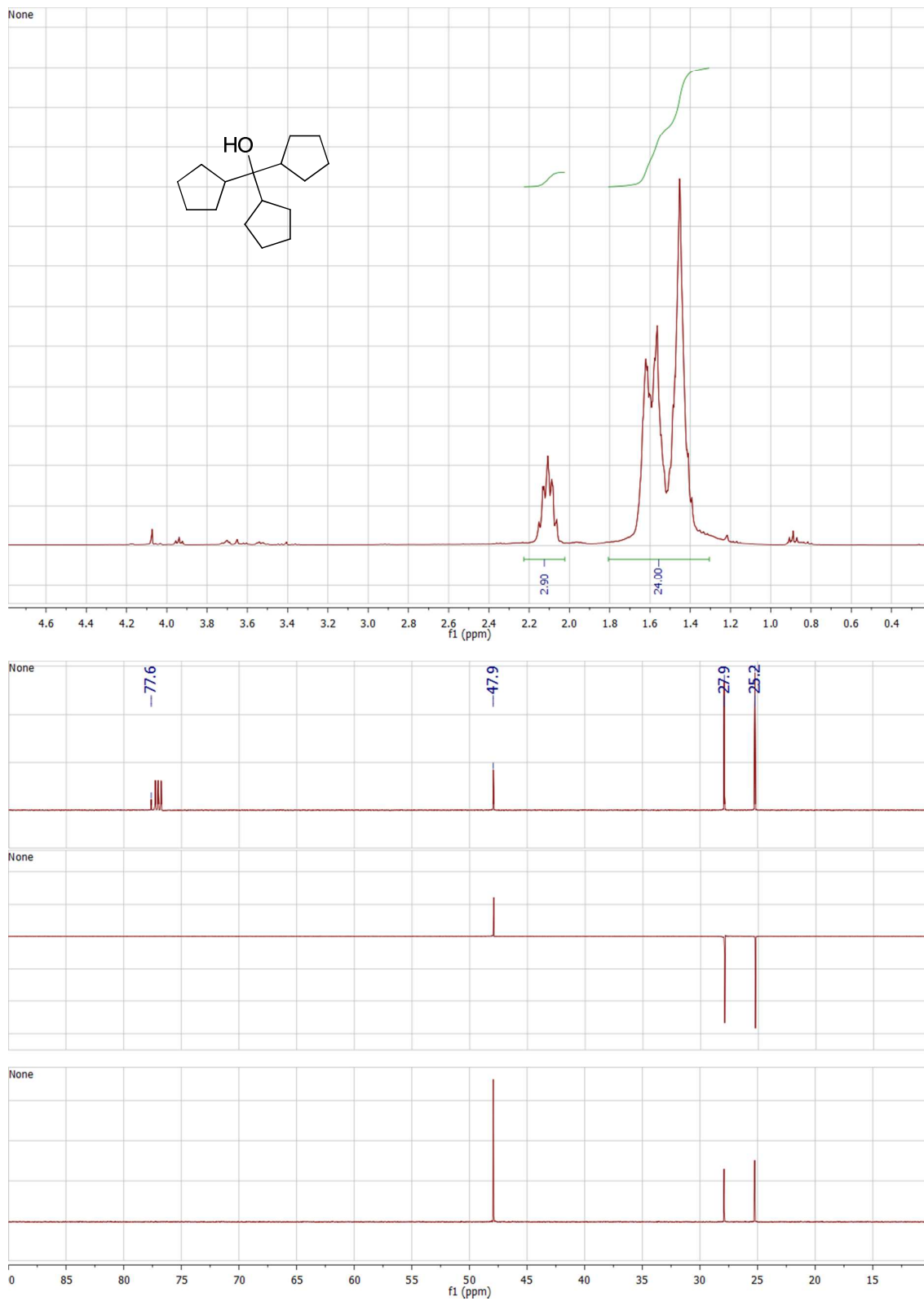
Product mixture from reaction of 5,5-dimethyl-2-(9-octylheptadecan-9-yl)-1,3,2-dioxaborinane (13, $R^C = R^D = n\text{-octyl}$) with 1-lithio-3-chloropropene to give a mixture of 4,4-dioctyldodec-1-en-3-ol (14, $R^C = R^D = n\text{-octyl}$) and 9-octylheptadecan-9-ol



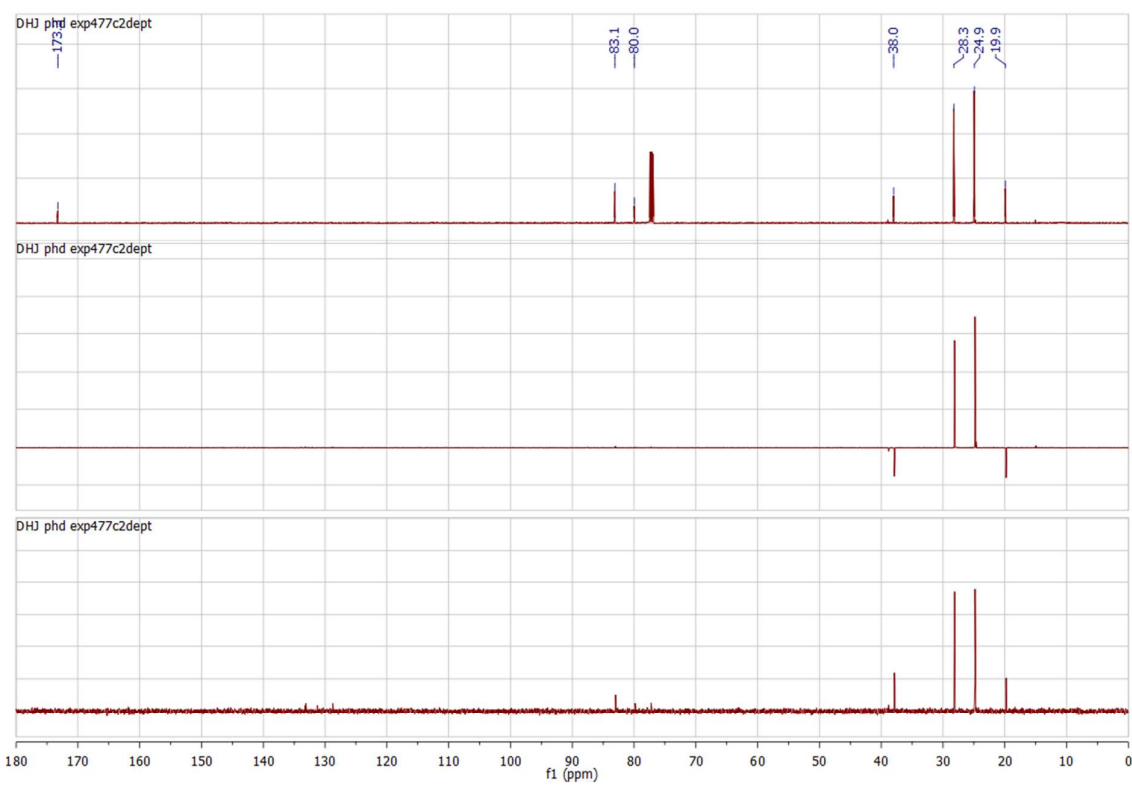
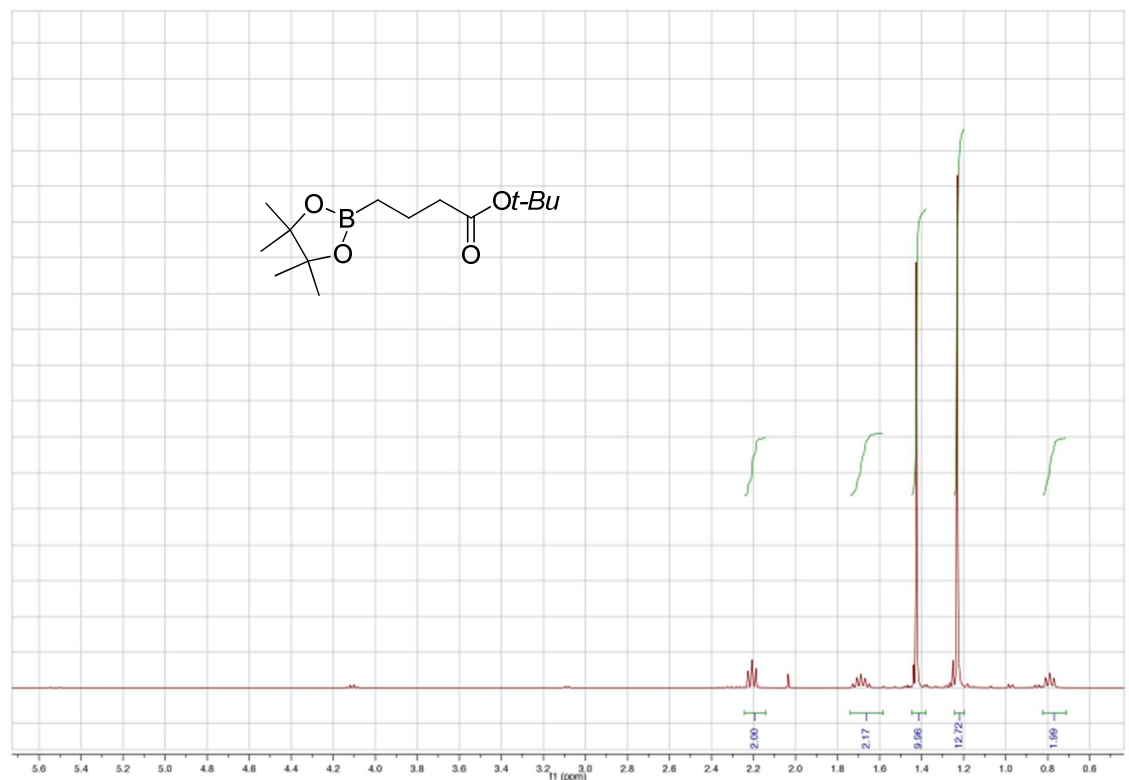
(E)-1,1-Dicyclohexyl-3-phenylprop-2-en-1-ol

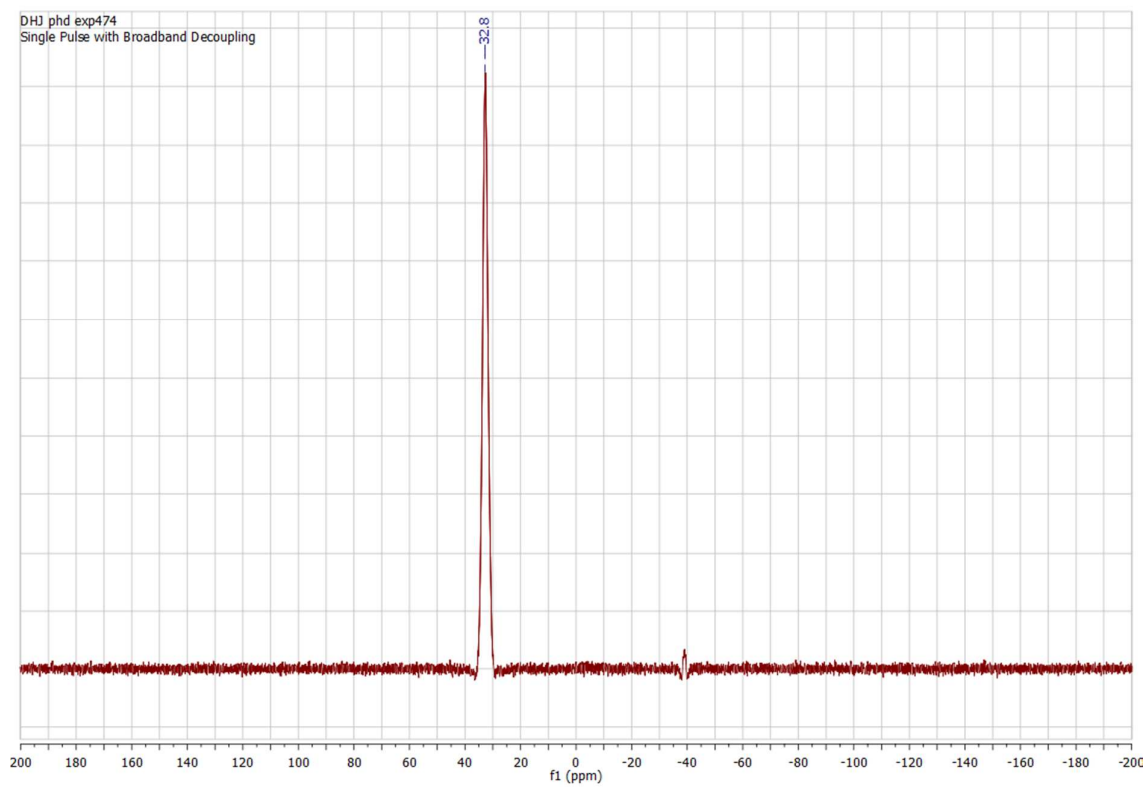


Tricyclopentylmethanol

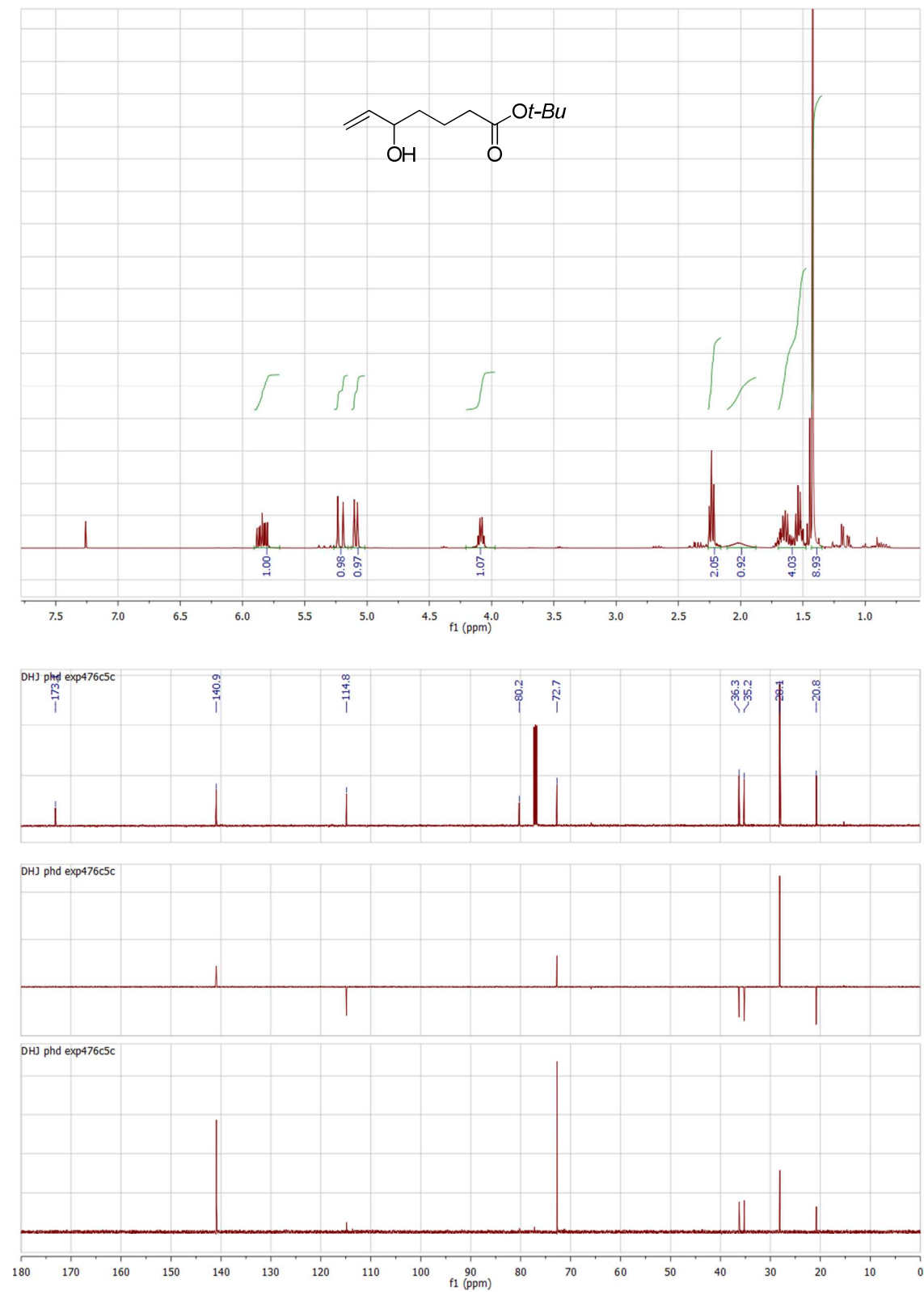


***tert*-Butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (15)**





***tert*-Butyl 5-hydroxyhept-6-enoate (17)**



6-Vinyltetrahydro-2H-pyran-2-one (18)

