

Supporting Information for:

Diastereoselective β -Hydroxy Vinylsulfone Isomerizations

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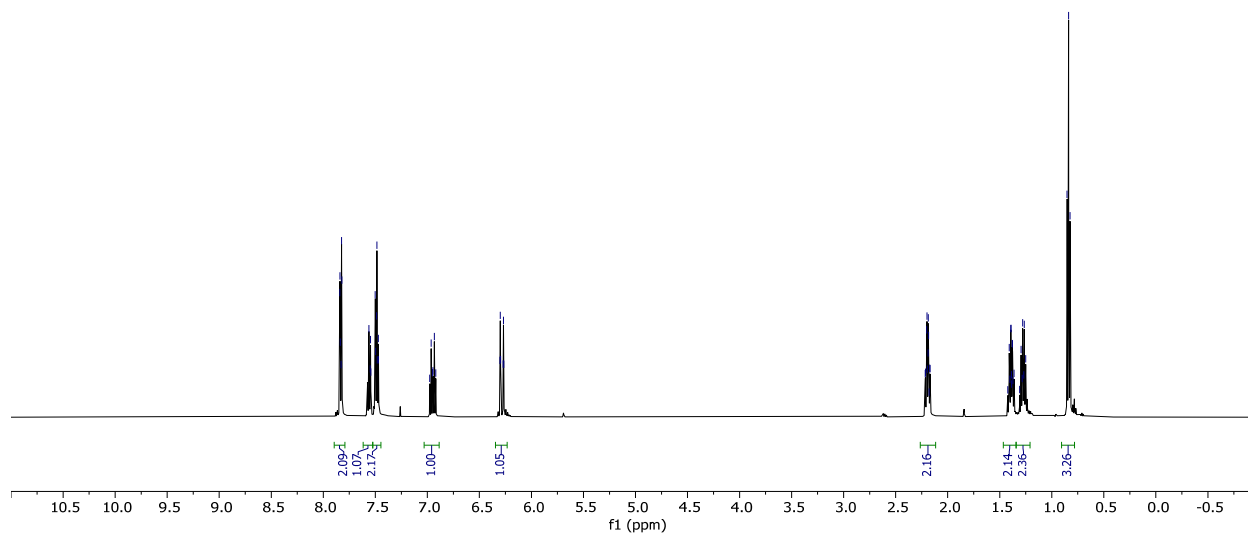
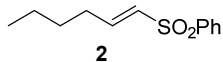
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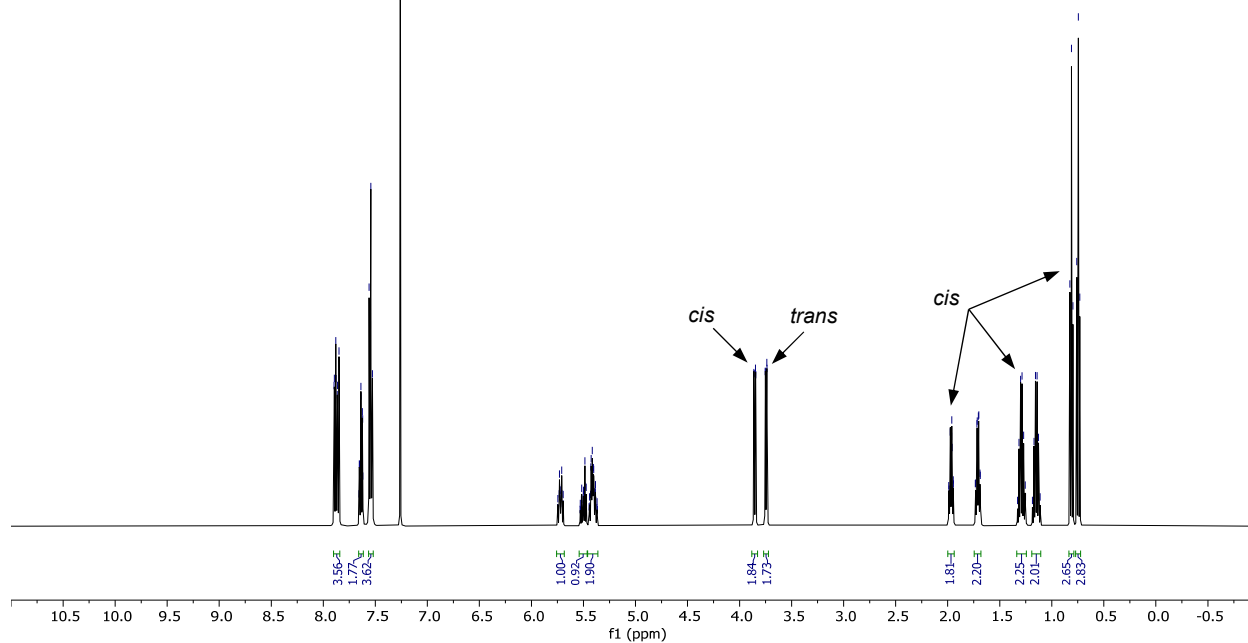
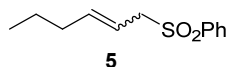
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1.39
1.39
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1.38
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1.26
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0.82

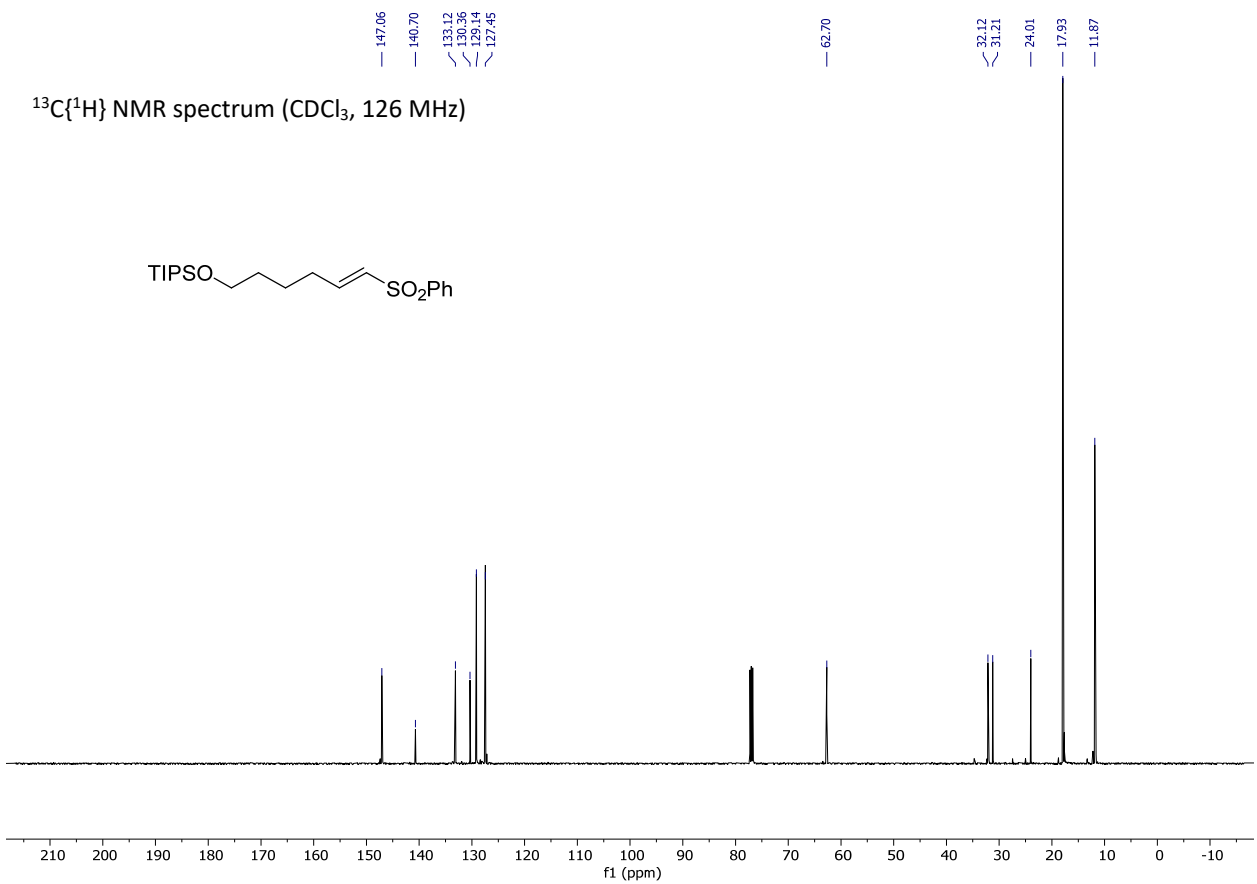
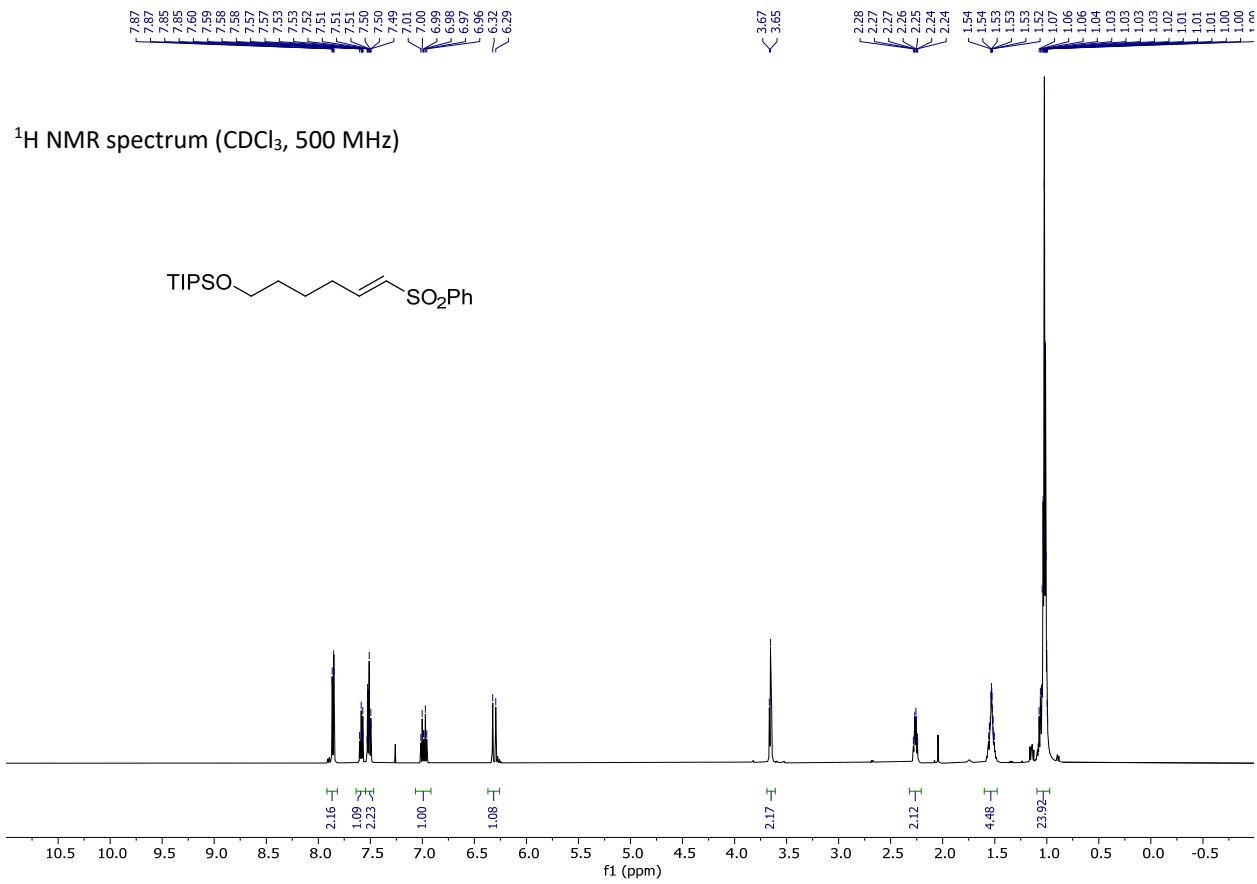
¹H NMR spectrum (CDCl₃, 500 MHz)



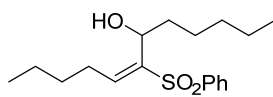
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5.42
5.41
5.41
5.41
5.40
5.40
5.38
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3.75
3.74
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1.69
1.30
1.29
1.27
1.26
1.26
1.17
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1.13
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0.76
0.75

¹H NMR spectrum (CDCl₃, 500 MHz)

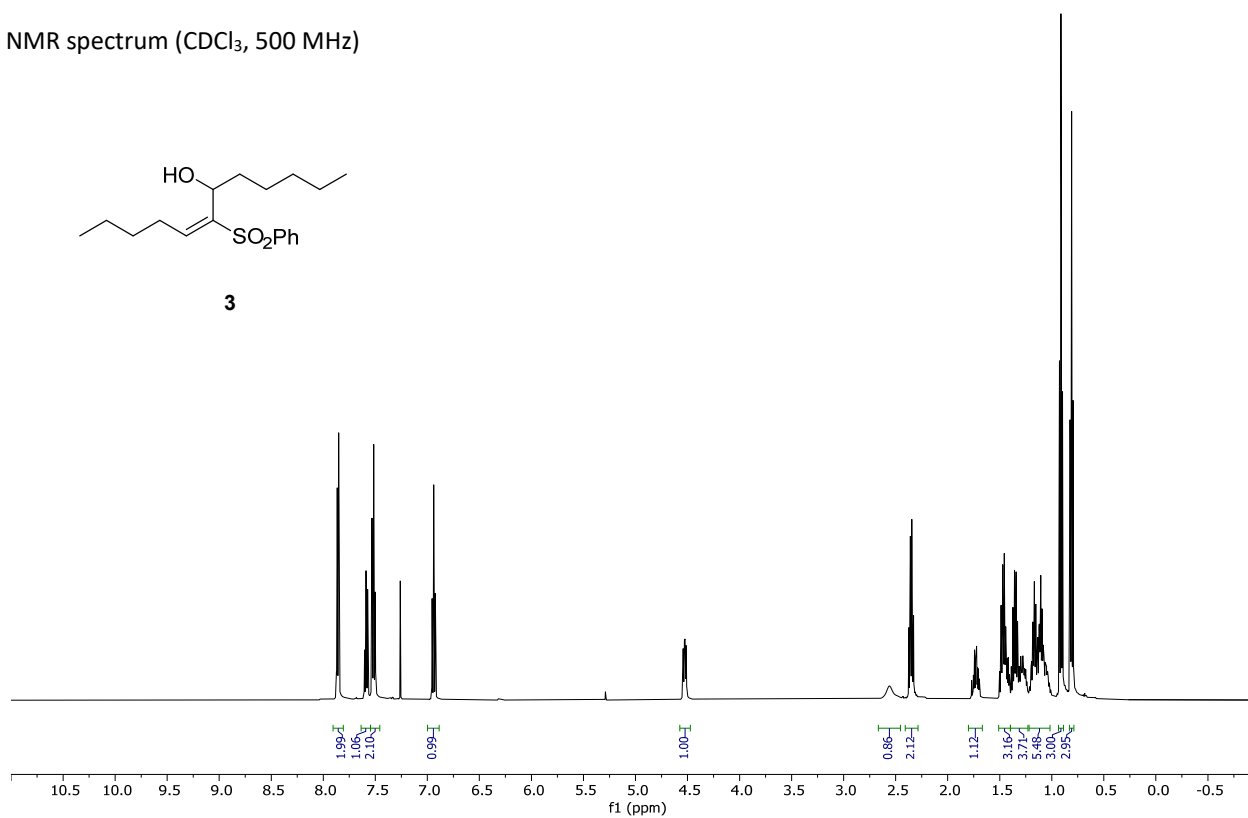




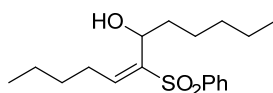
^1H NMR spectrum (CDCl_3 , 500 MHz)



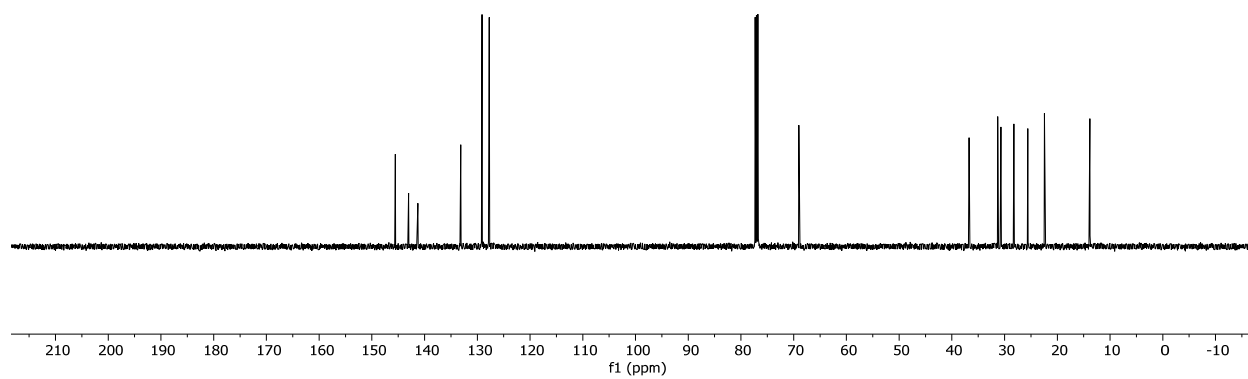
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$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 126 MHz)



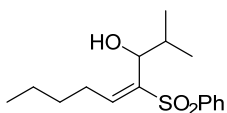
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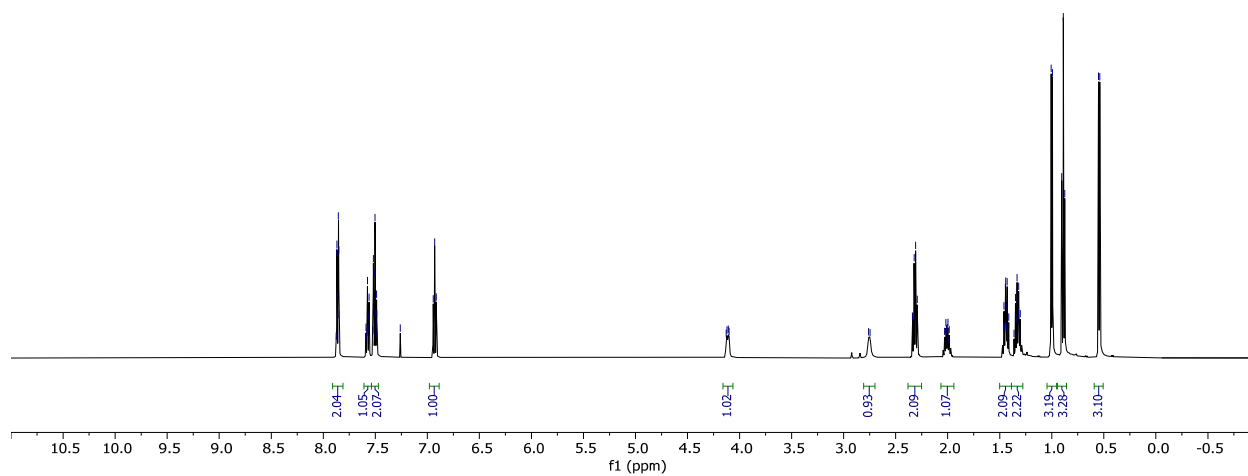
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2.29
2.03
2.02
2.01
2.00
1.99
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1.46
1.45
1.44
1.43
1.41
1.35
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1.01
0.99
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0.85
0.84

¹H NMR spectrum (CDCl₃, 500 MHz)



6

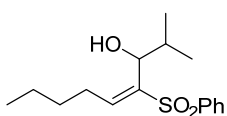


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127.74

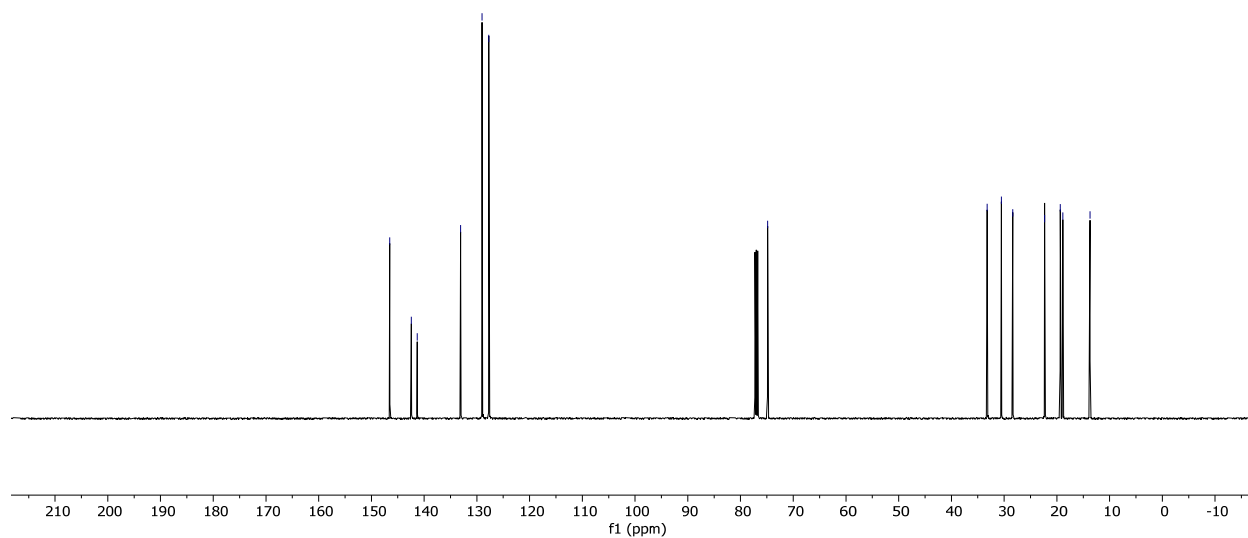
74.87

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¹³C{¹H} NMR spectrum (CDCl₃, 126 MHz)

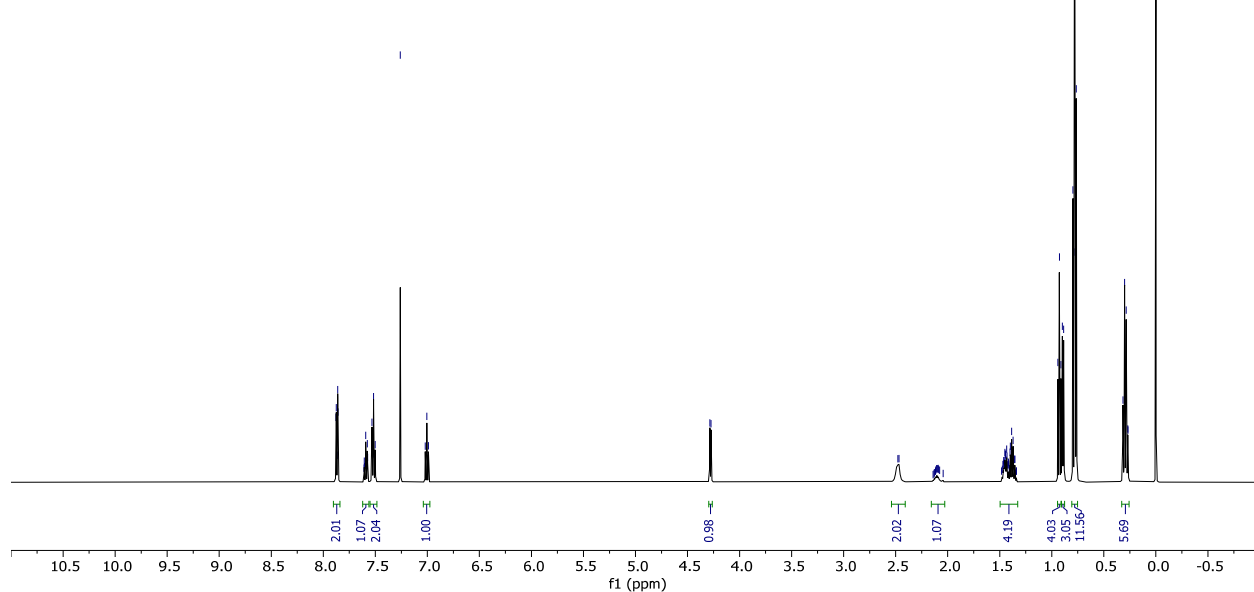
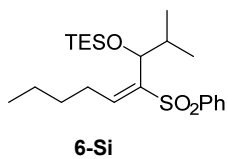


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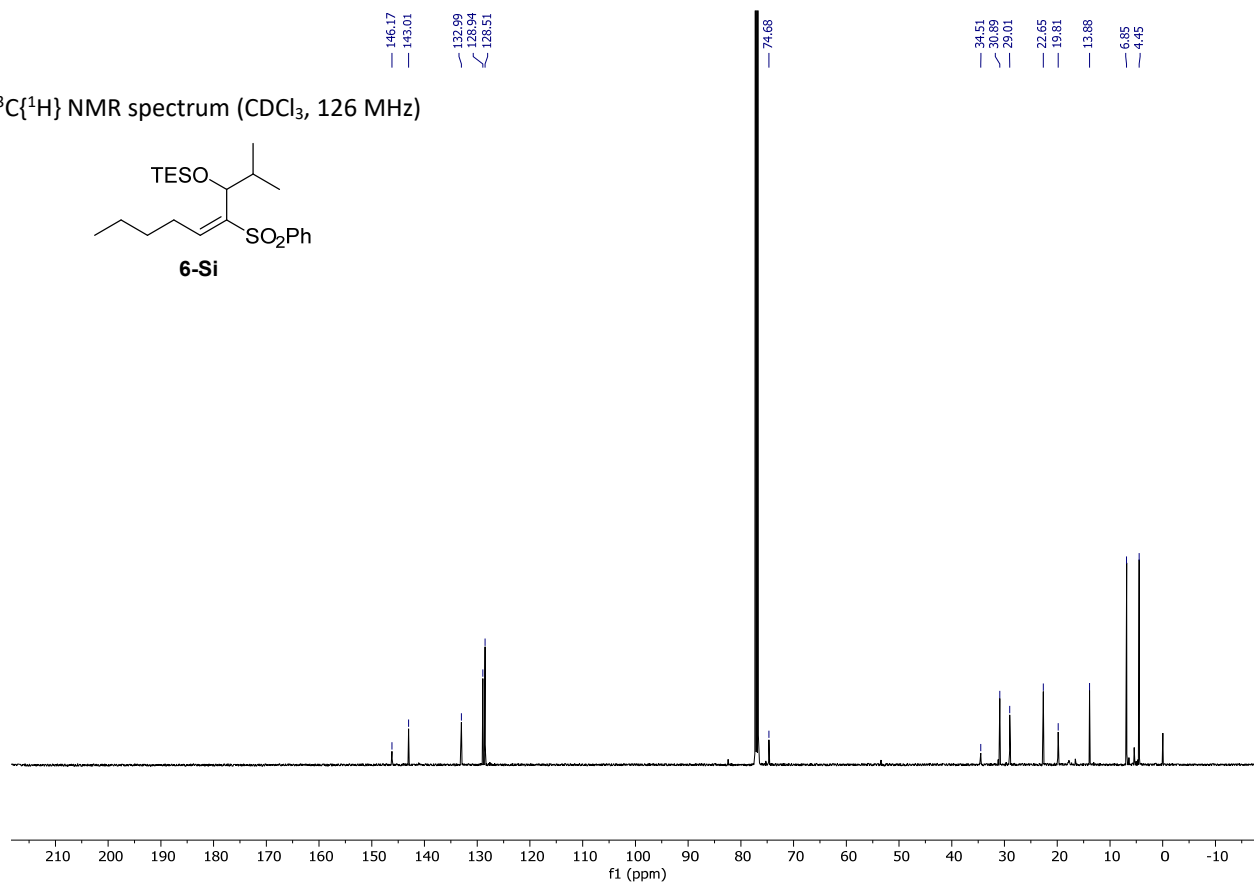
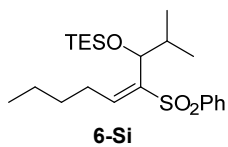


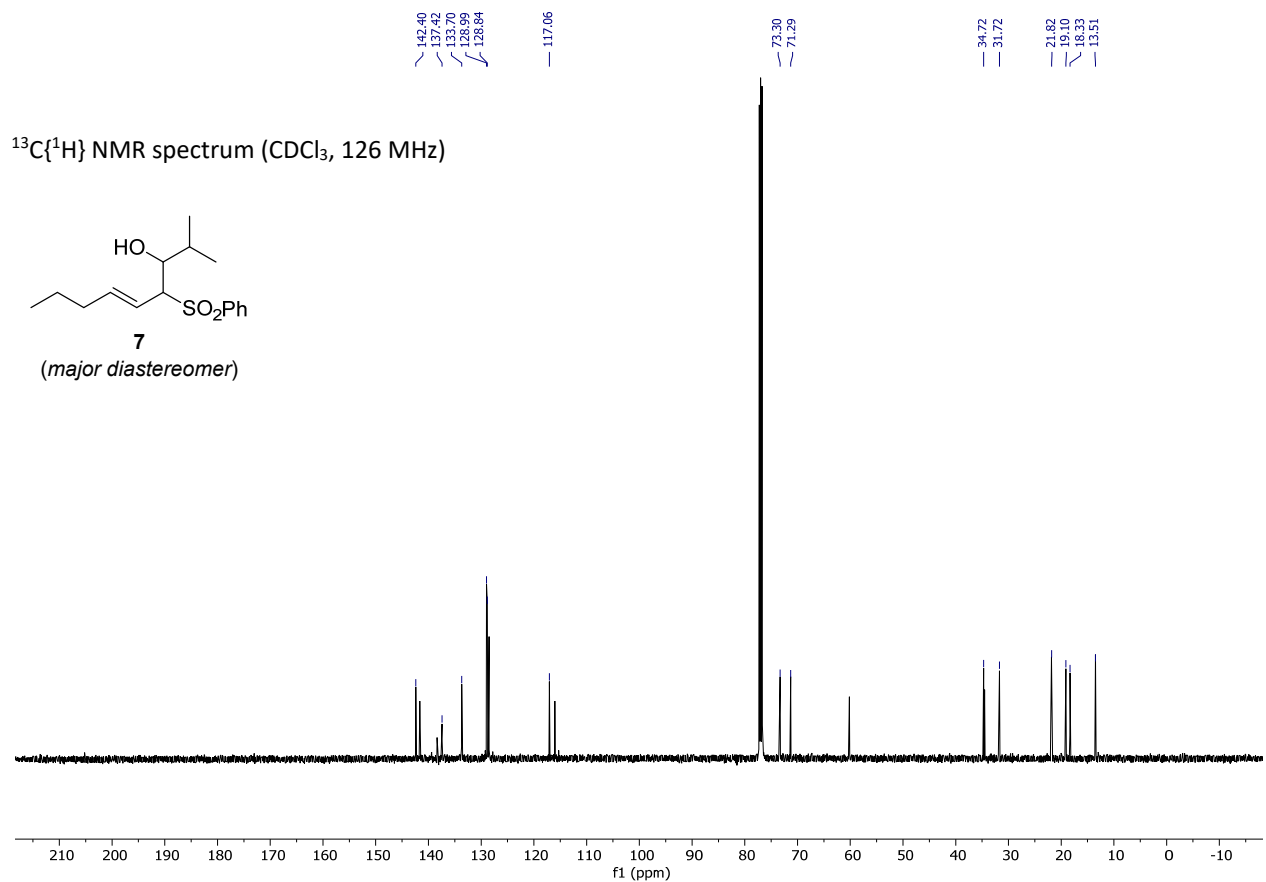
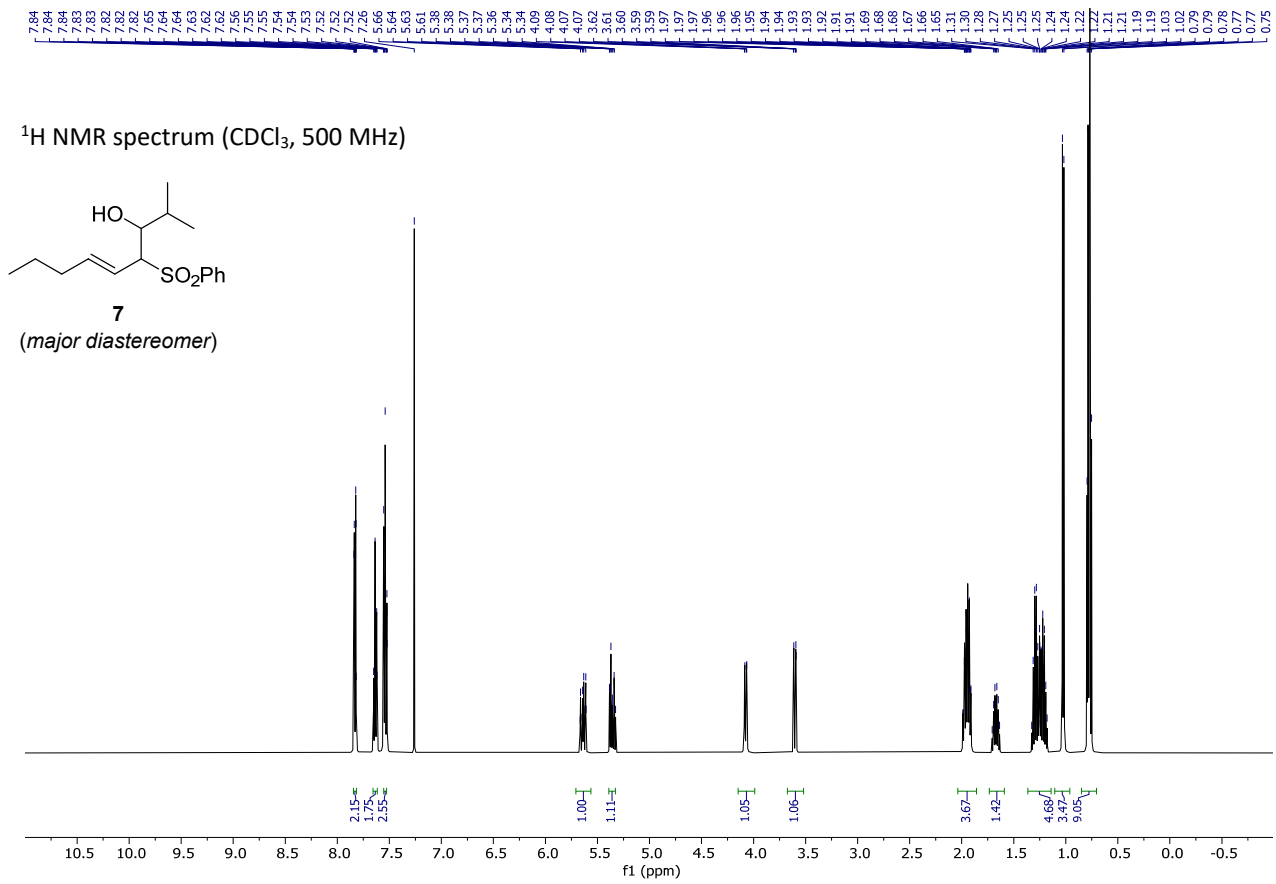
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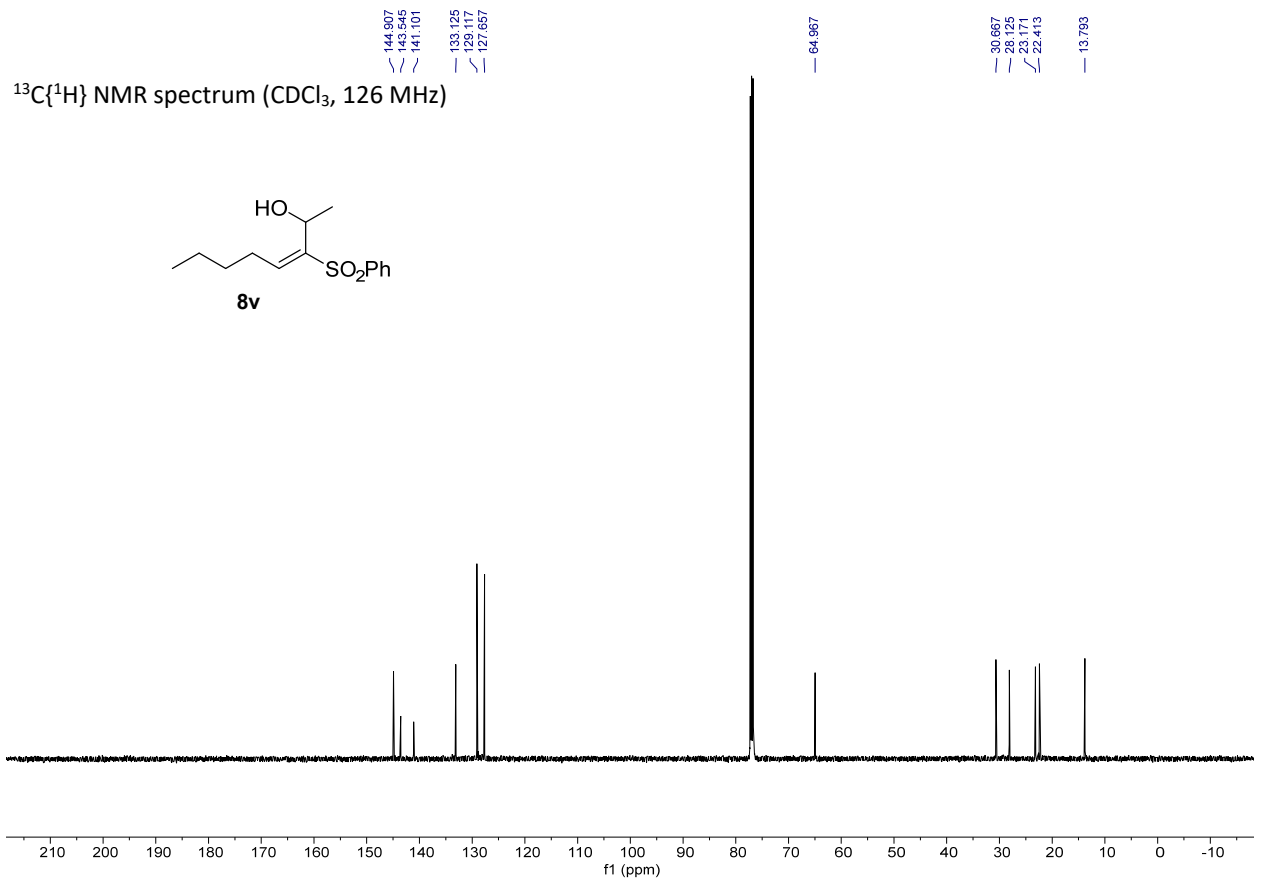
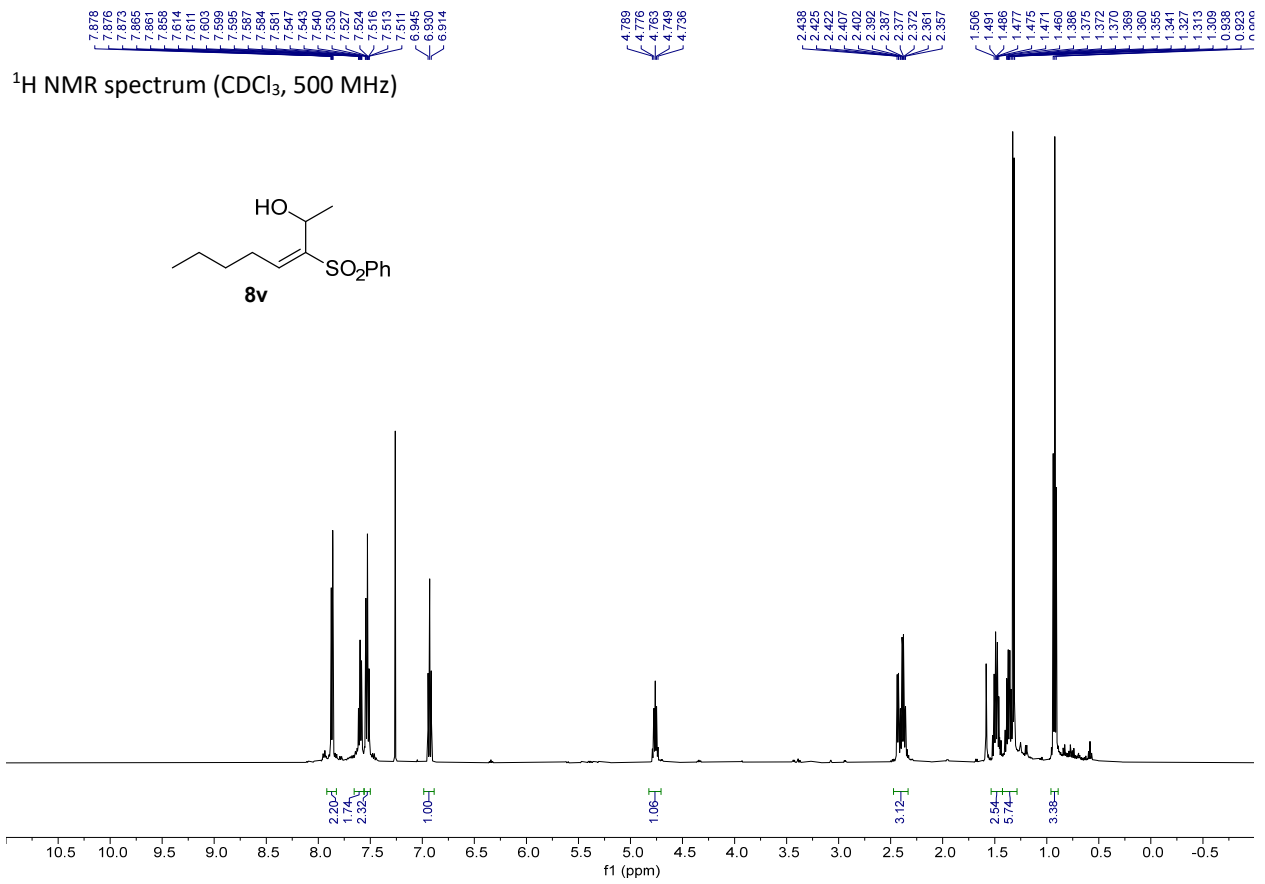
¹H NMR spectrum (CDCl₃, 500 MHz)

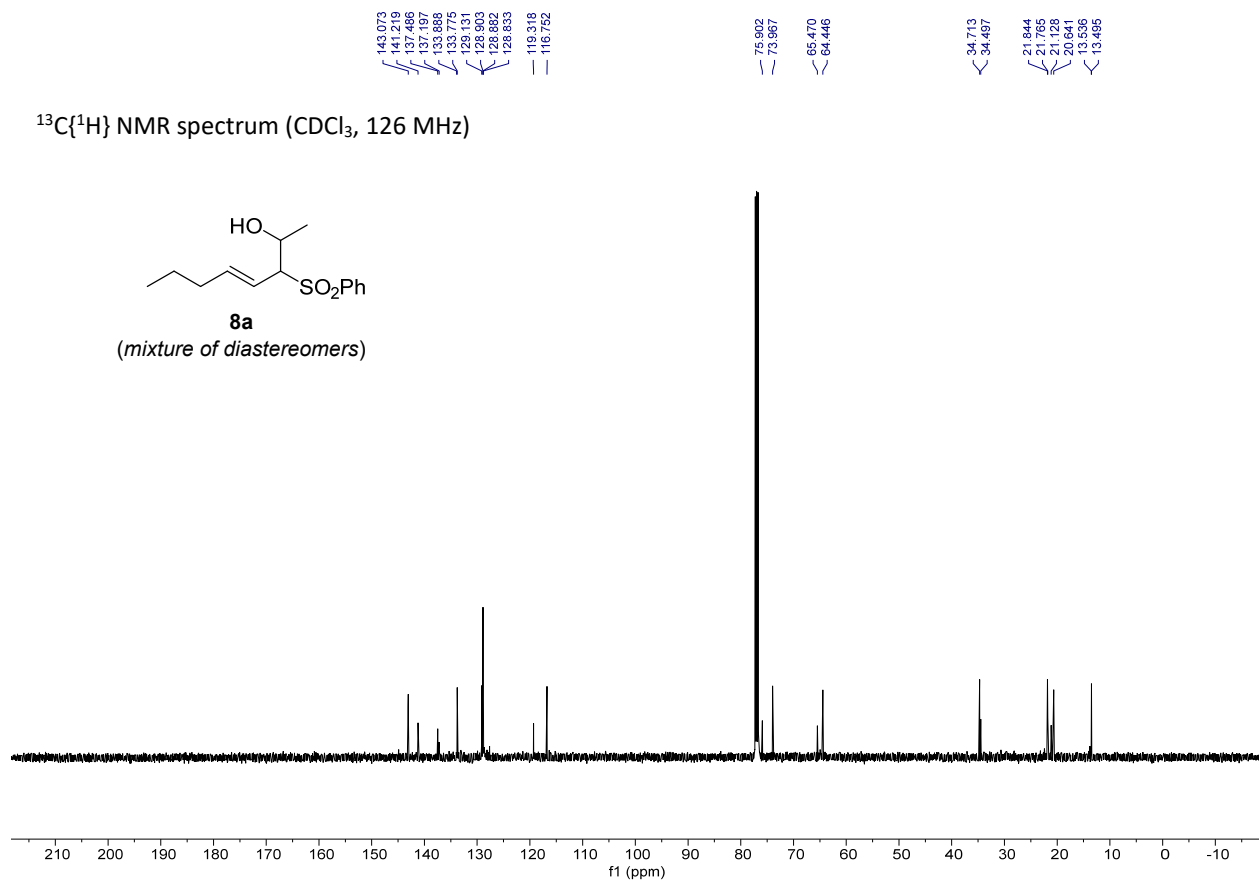
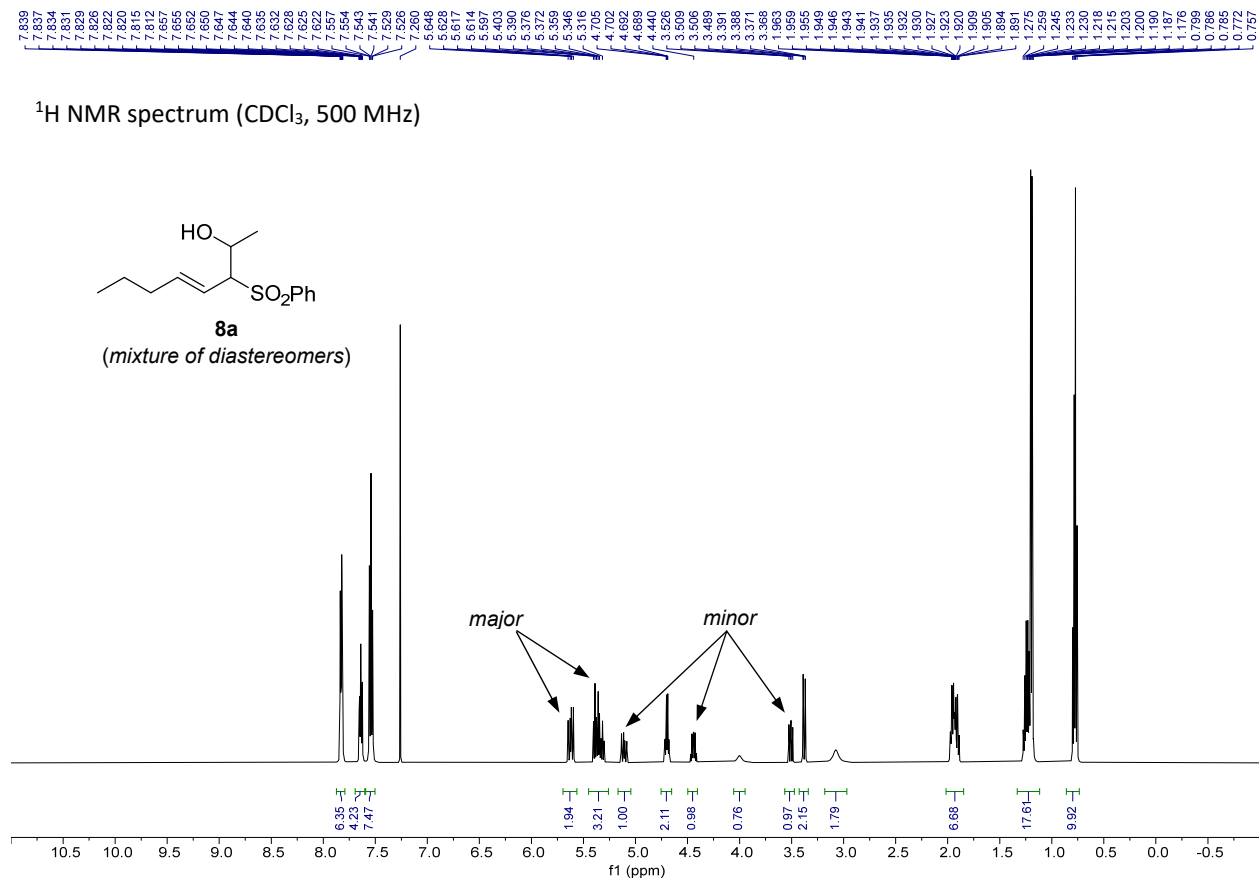


¹³C{¹H} NMR spectrum (CDCl₃, 126 MHz)



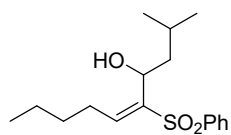




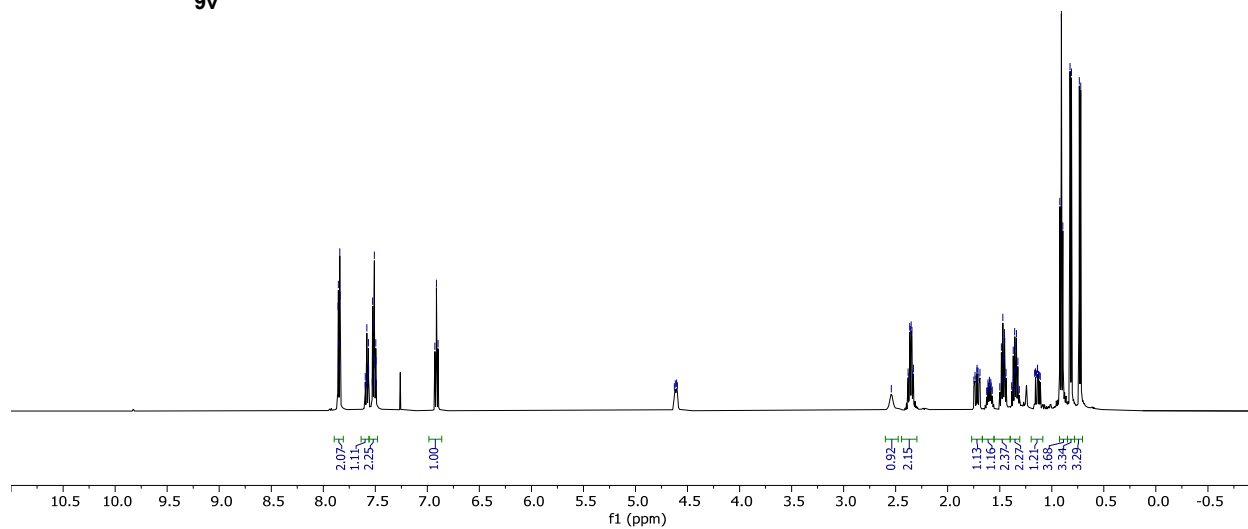


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1.12
1.12
1.11
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0.74
0.74

^1H NMR spectrum (CDCl_3 , 500 MHz)

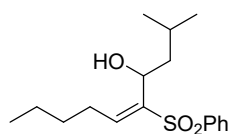


9v

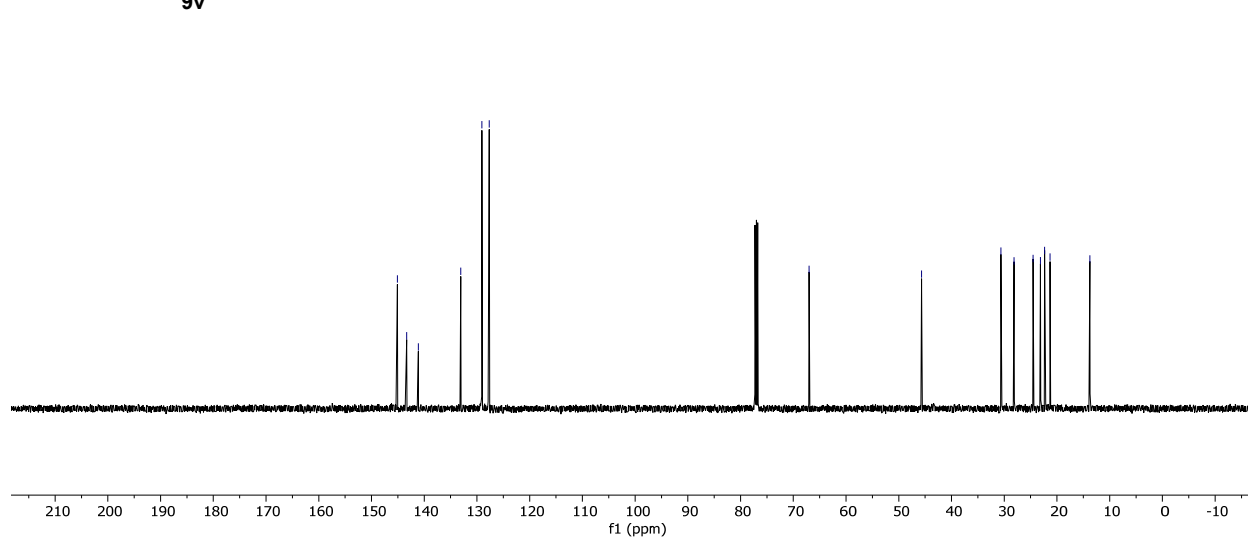


145.08
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132.07
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127.67
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45.68
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$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 126 MHz)

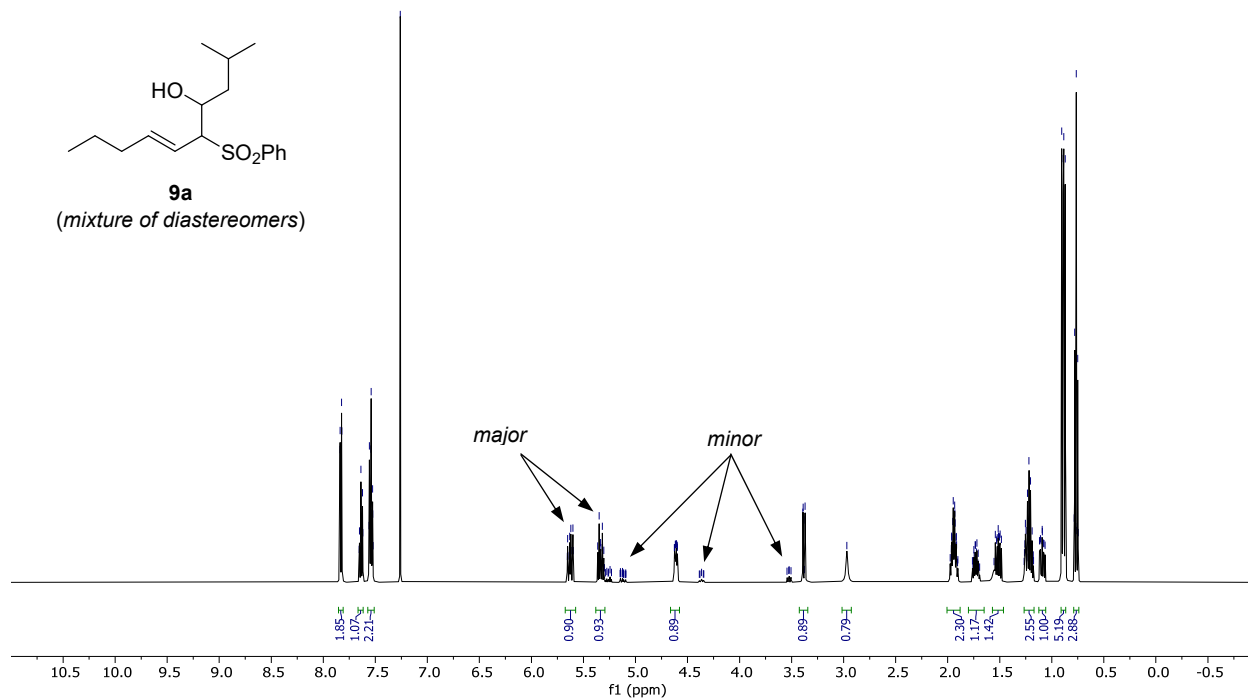


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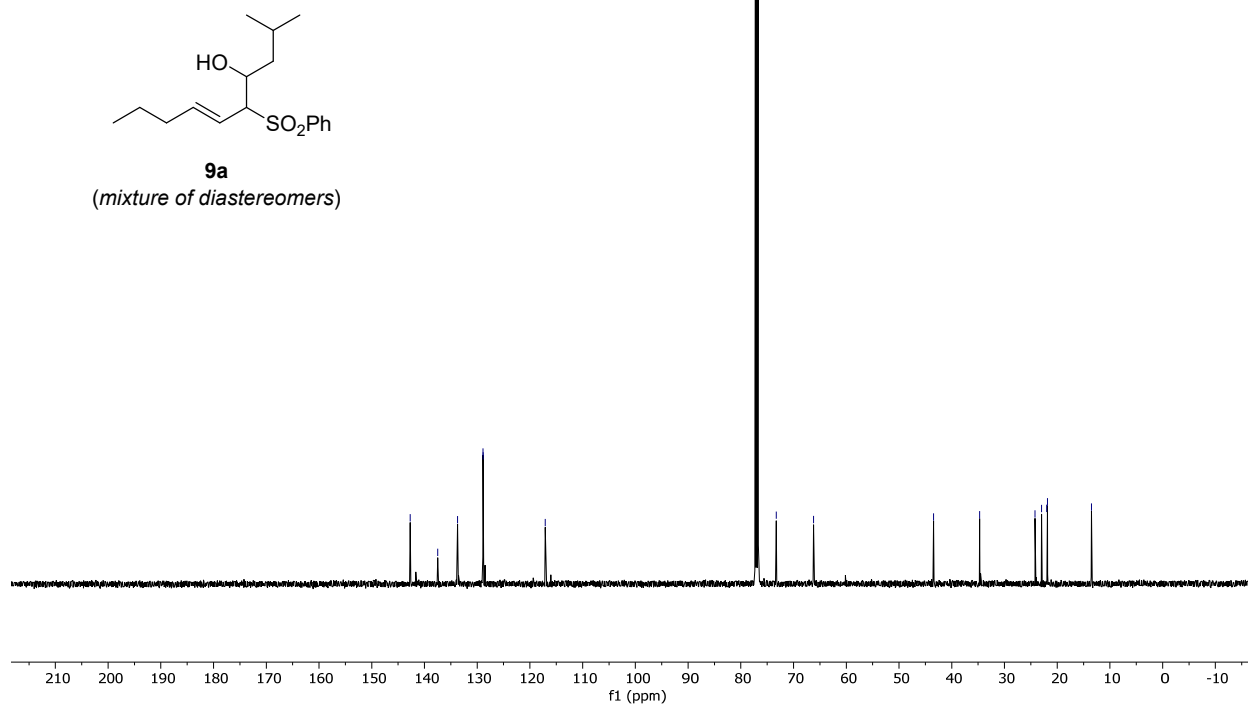


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0.75

^1H NMR spectrum (CDCl_3 , 500 MHz)



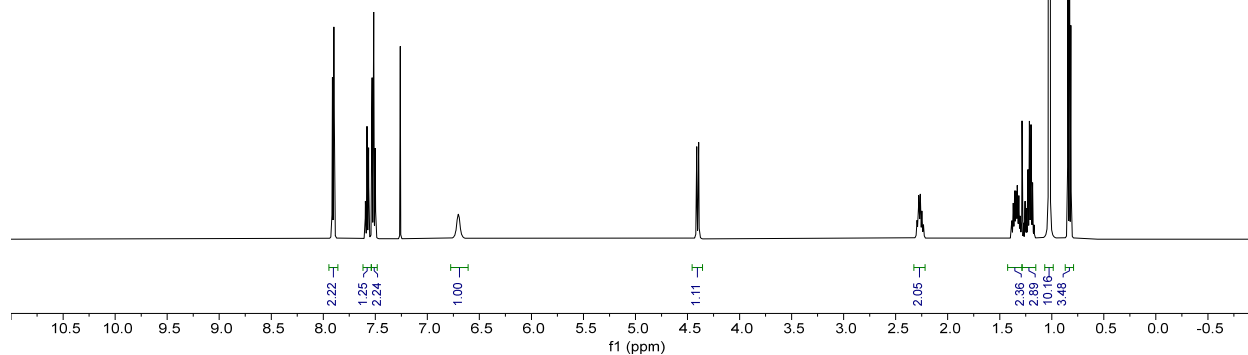
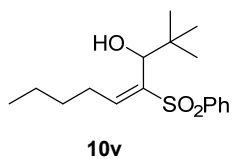
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 126 MHz)



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Fractions 9-12 C13

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2.262
2.233
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1.354
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1.345
1.341
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1.327
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1.229
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^1H NMR spectrum (CDCl_3 , 500 MHz)

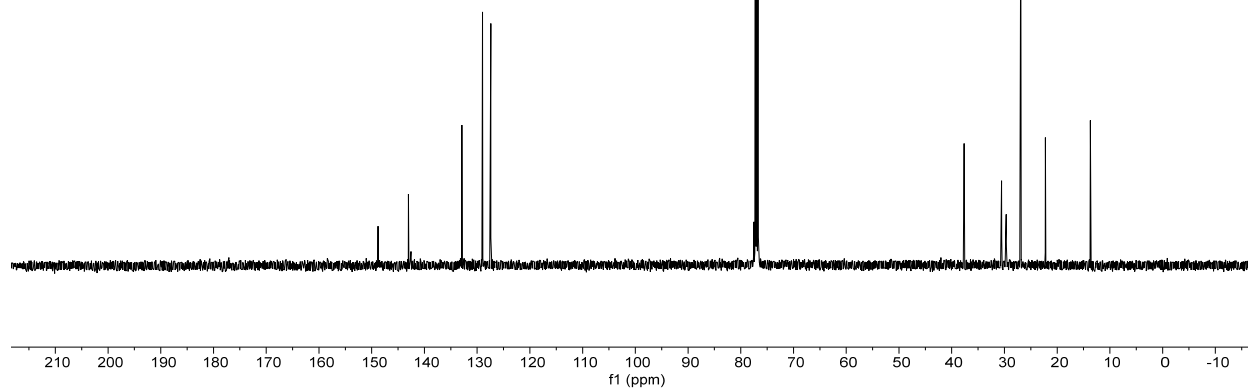
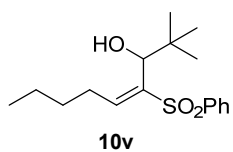


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Fractions 9-12 C13

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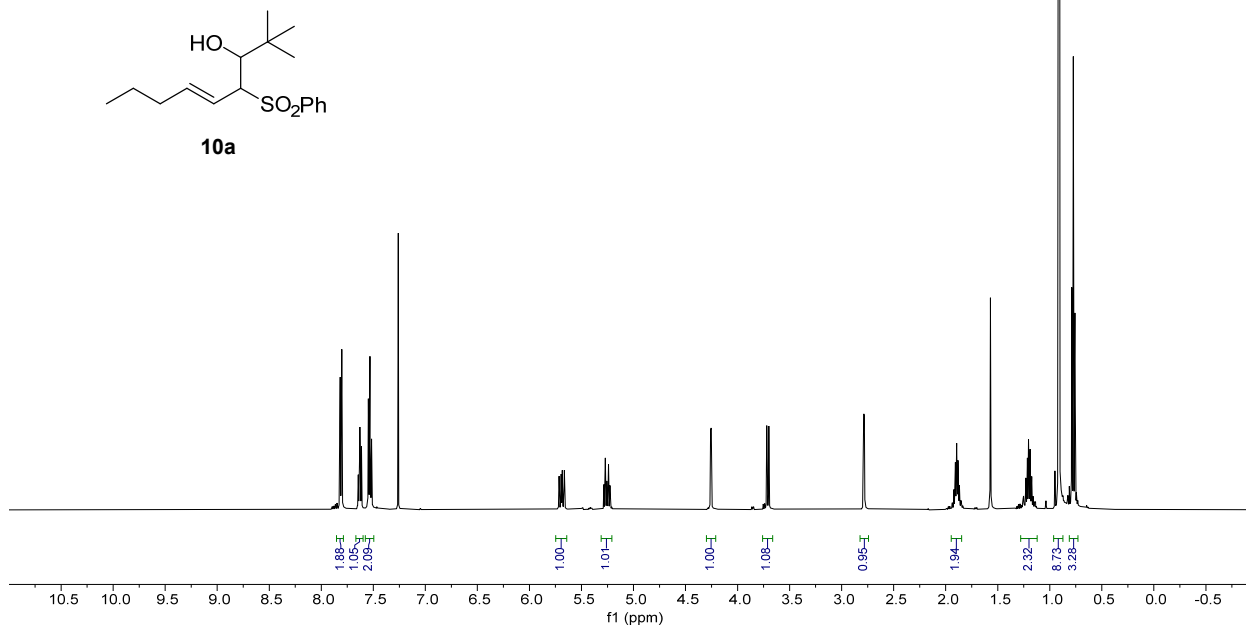
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$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 126 MHz)



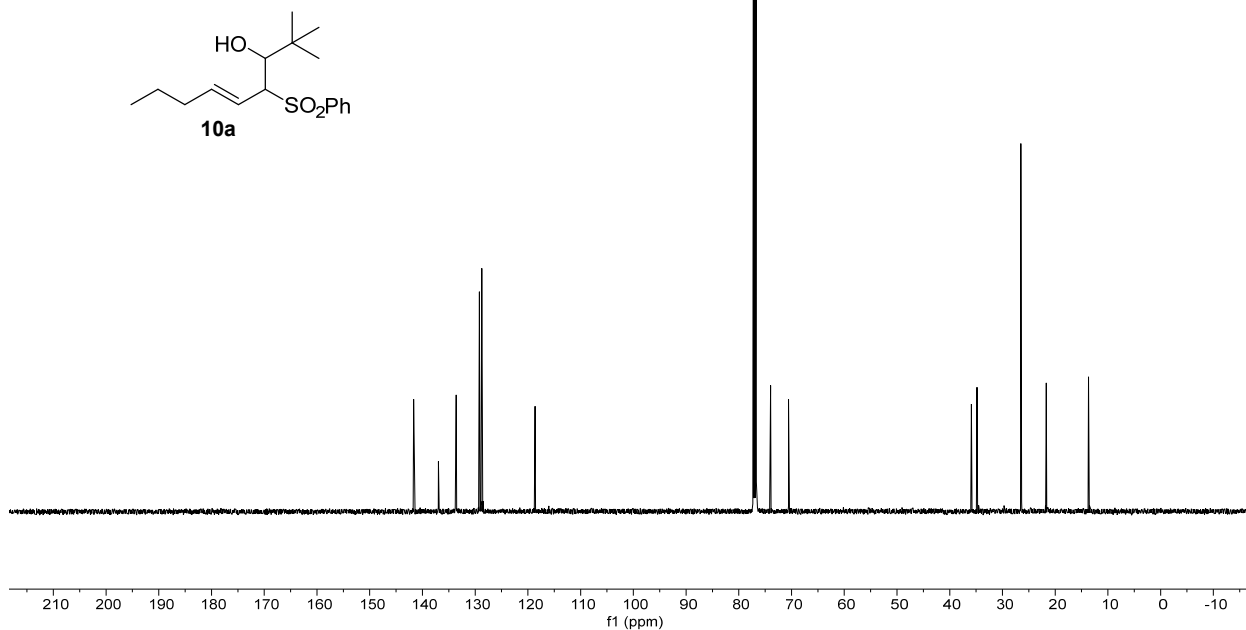
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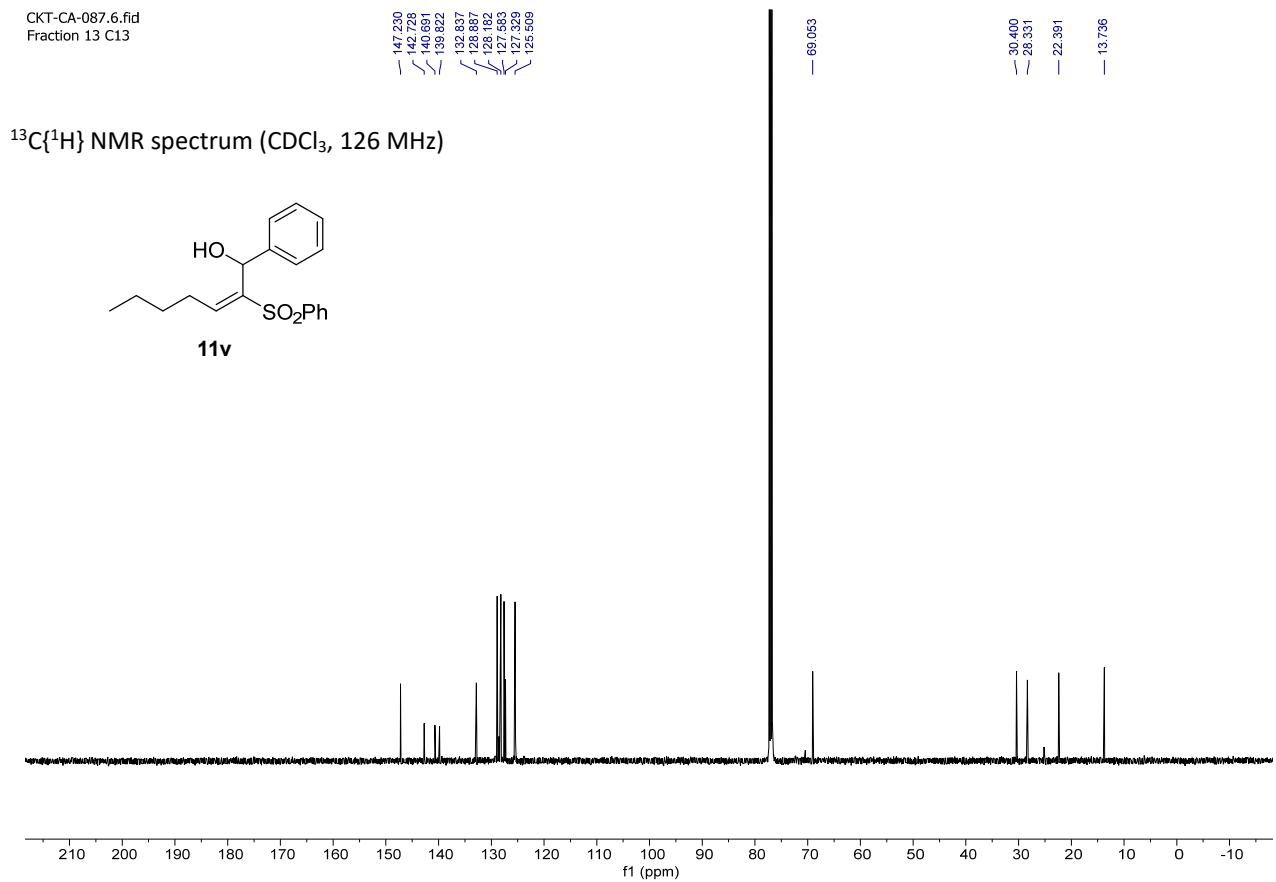
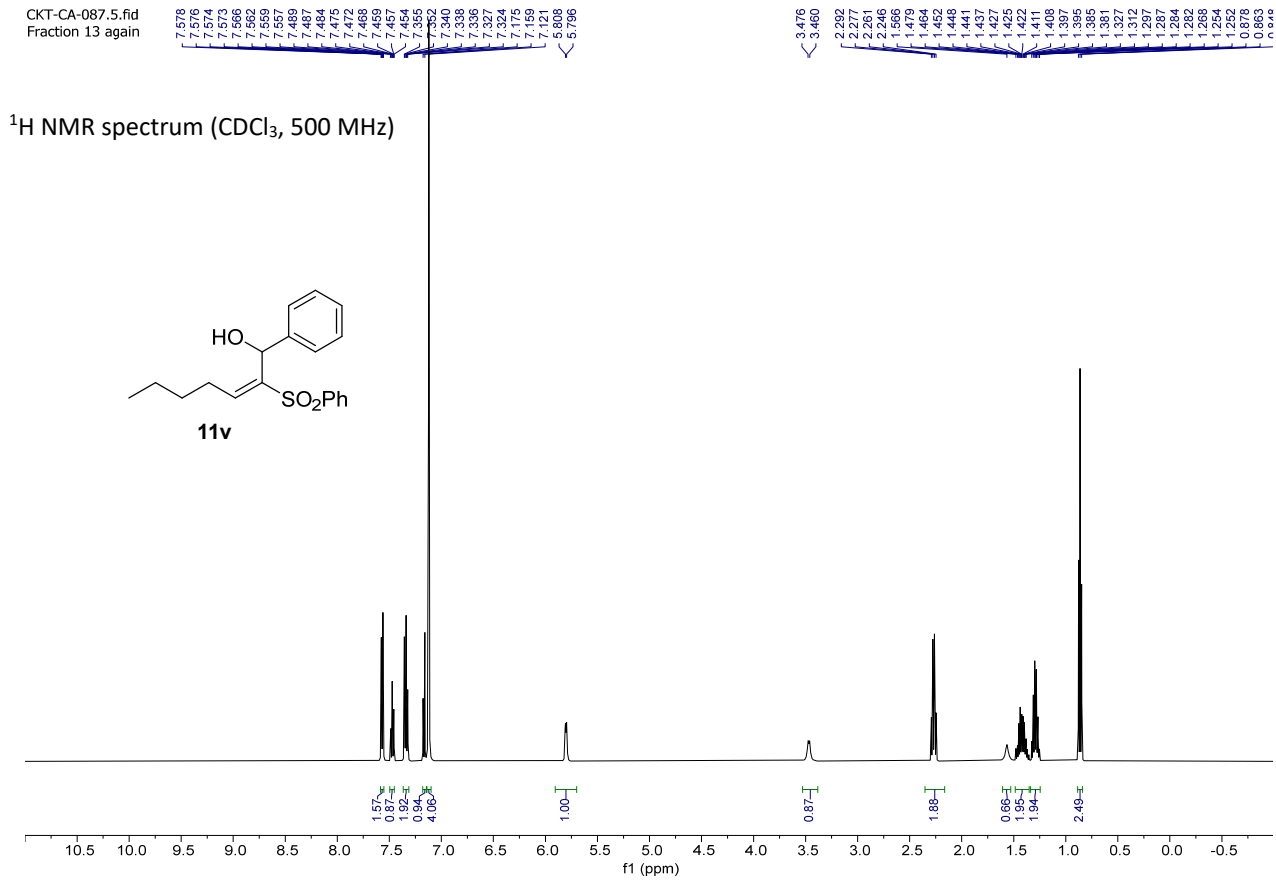
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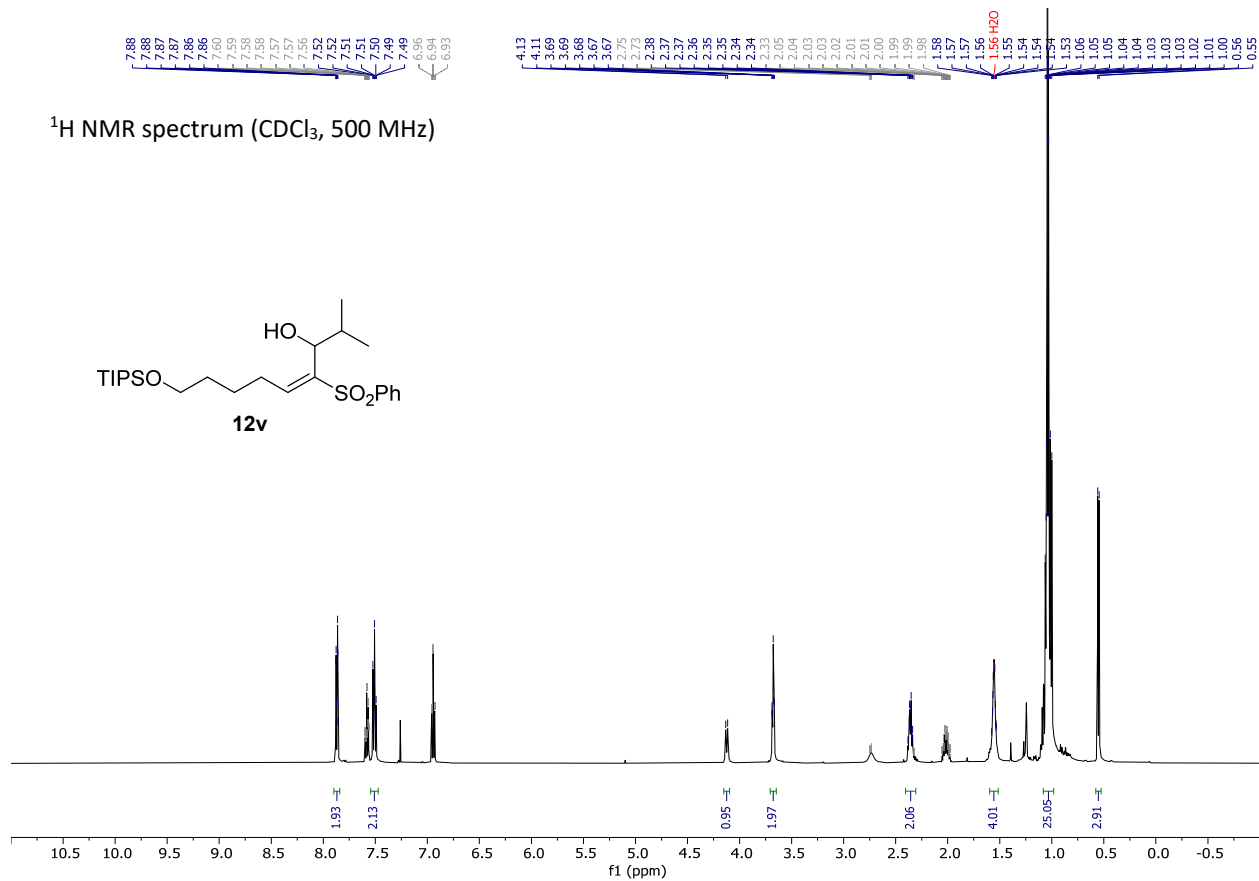
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$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 126 MHz)

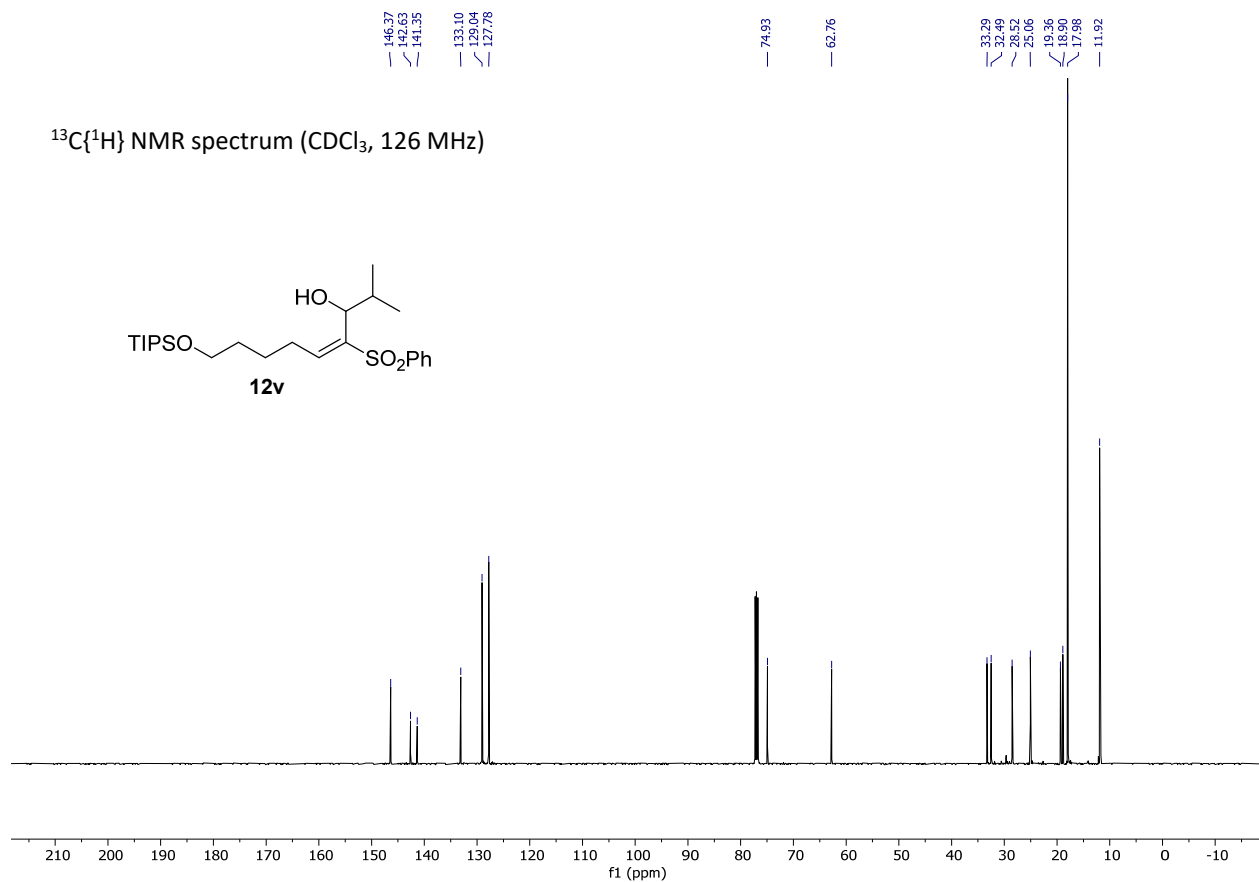




¹H NMR spectrum (CDCl₃, 500 MHz)

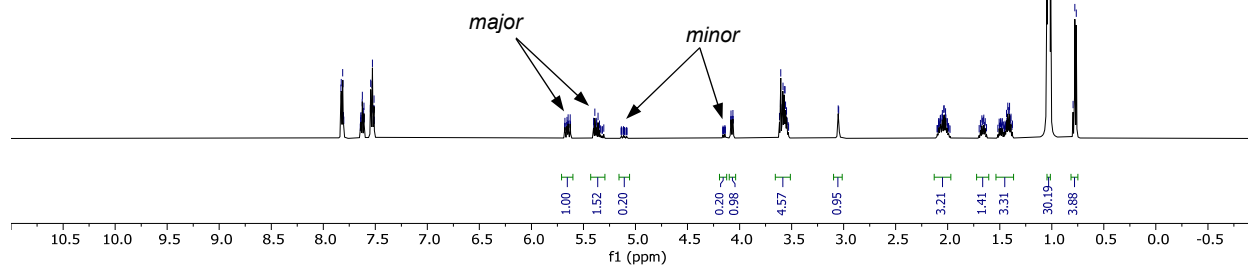
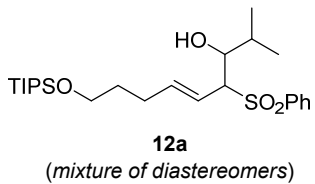


¹³C{¹H} NMR spectrum (CDCl₃, 126 MHz)

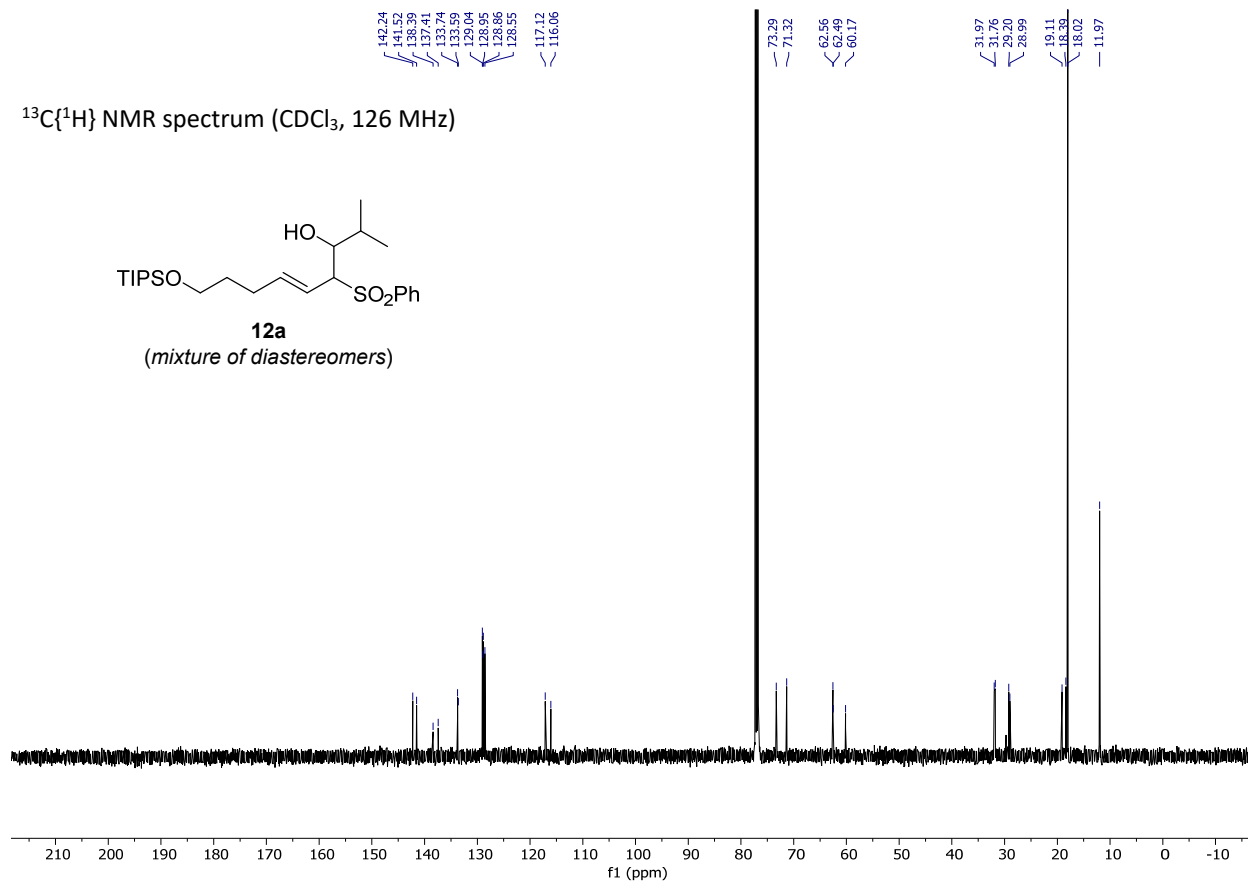
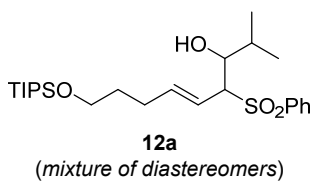


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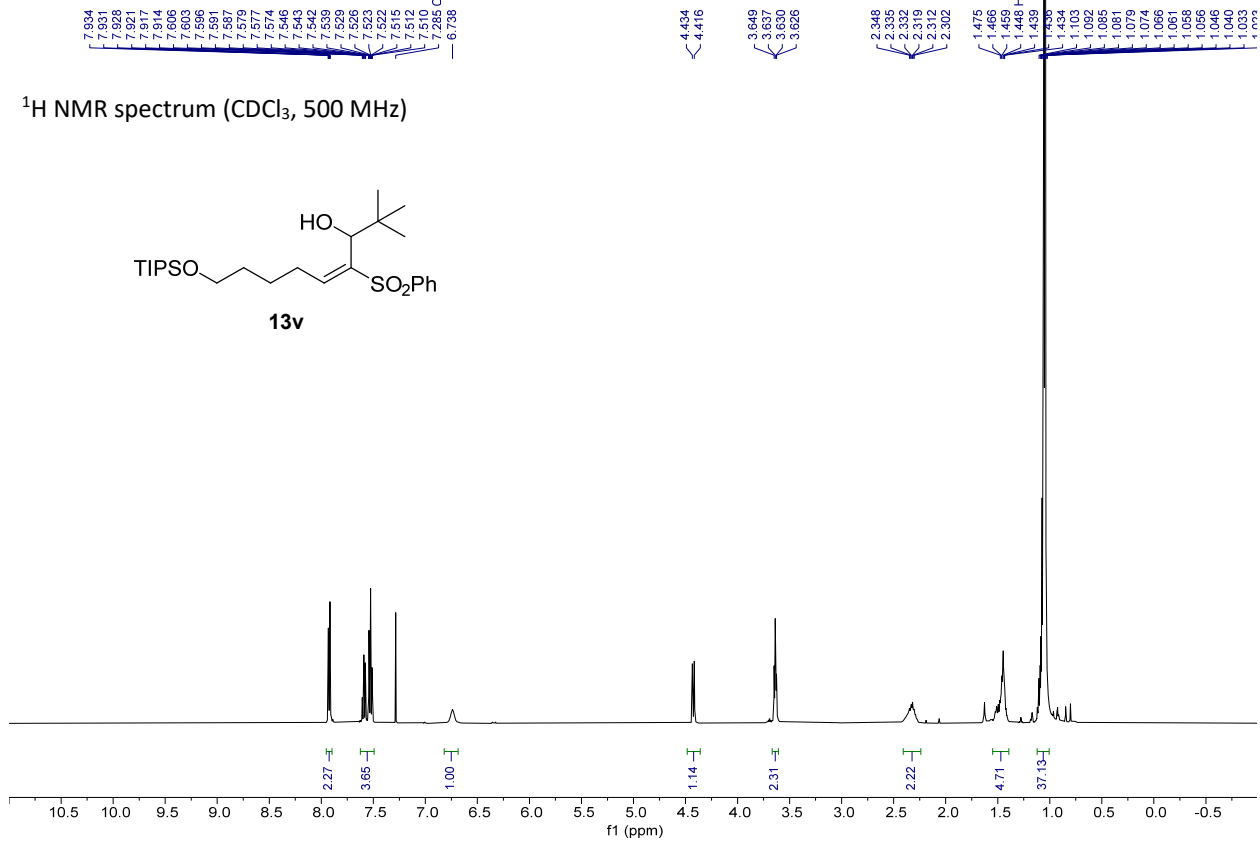
¹H NMR spectrum (CDCl₃, 500 MHz)



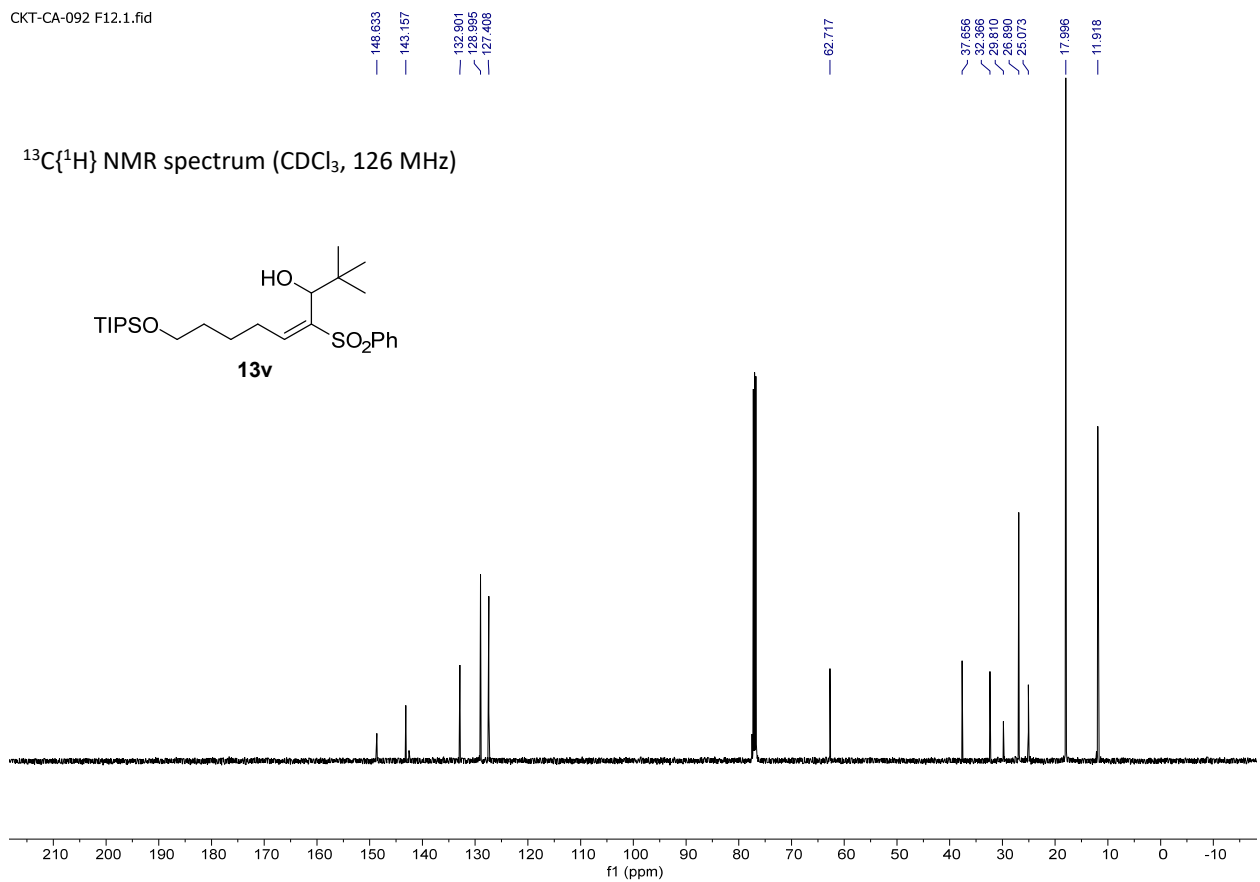
¹³C{¹H} NMR spectrum (CDCl₃, 126 MHz)



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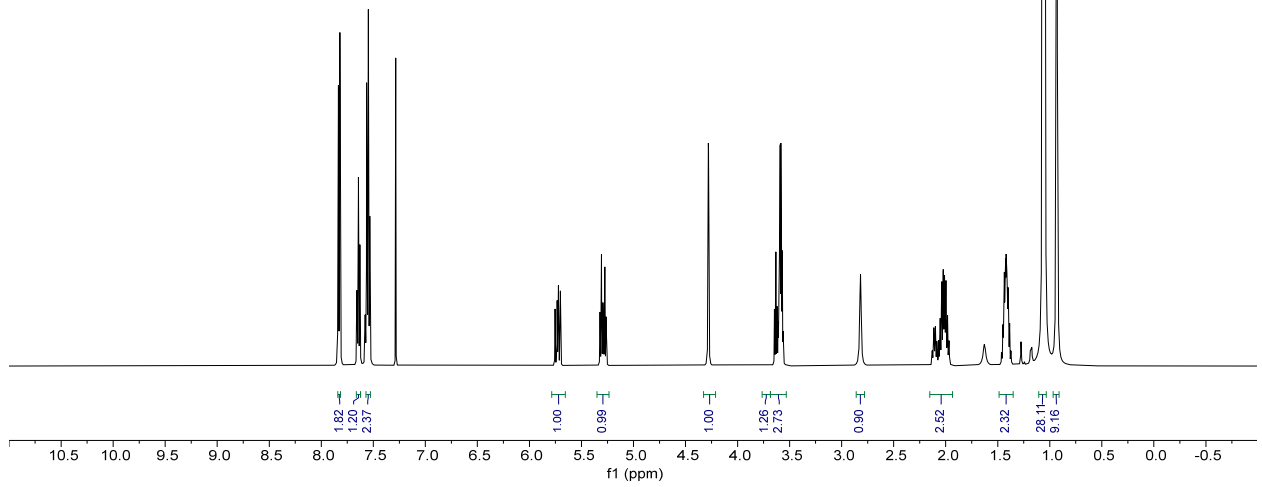
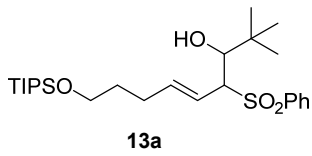


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CKT-CA-093 F7-9 13C.10.fid
 141.402 136.919 133.620 129.202 128.729 118.706 73.947 70.564 62.639 38.976 31.728 28.520 17.987 11.930

¹H NMR spectrum (CDCl₃, 500 MHz)



CKT-CA-093 F7-9 13C.10.fid

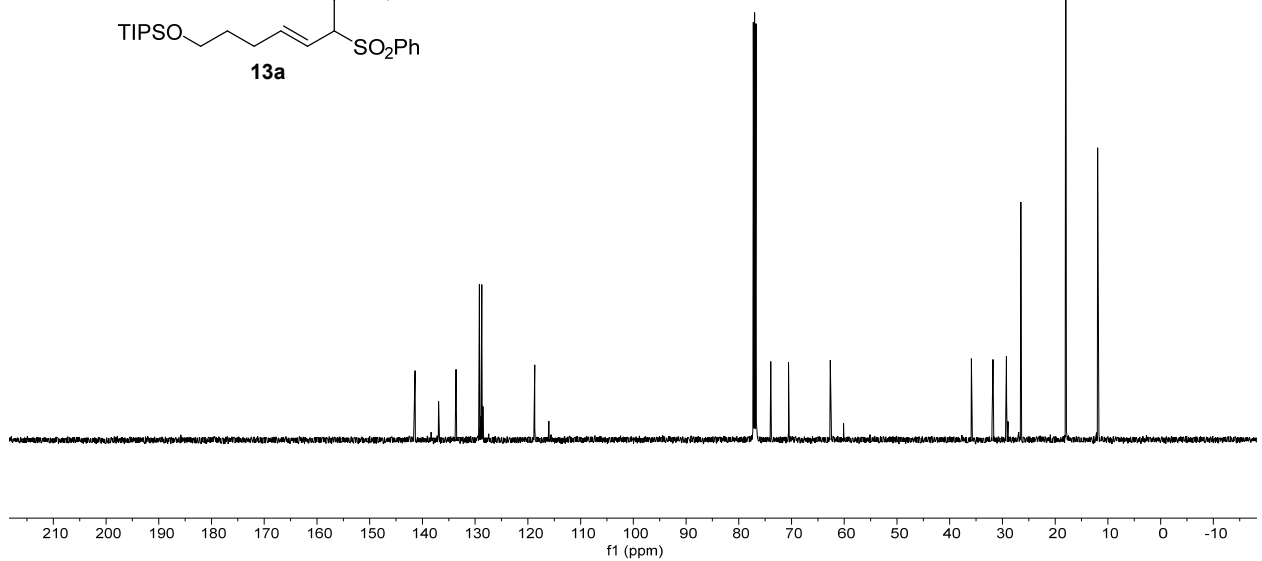
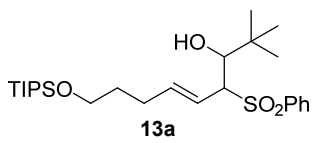
141.402
 136.919
 133.620
 129.202
 128.729
 118.706

73.947
 70.564
 62.639

38.976
 31.728
 28.520

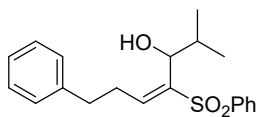
17.987
 11.930

¹³C{¹H} NMR spectrum (CDCl₃, 126 MHz)

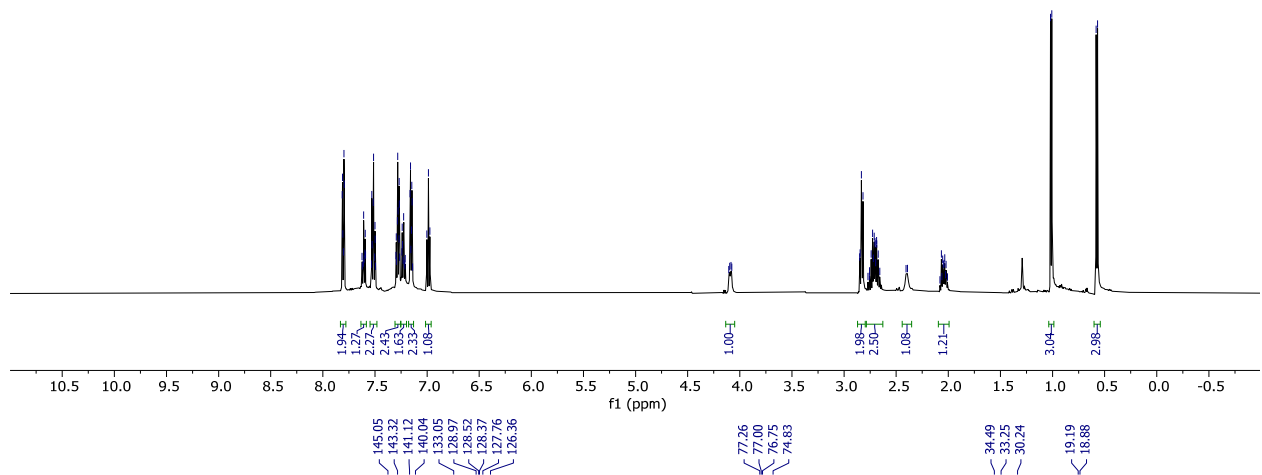


7.81 7.81 7.80 7.79 7.62 7.62 7.61 7.60 7.59 7.59 7.53 7.53 7.52 7.51 7.50 7.50 7.50 7.50 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.24 7.24 7.24 7.23 7.22 7.22 7.21 7.21 7.16 7.16 7.15 7.15 7.14 7.14 7.00 7.00 6.99 6.97 4.11 4.10 4.09 4.08 2.85 2.85 2.83 2.82 2.77 2.76 2.76 2.74 2.74 2.72 2.71 2.70 2.70 2.70 2.69 2.69 2.67 2.66 2.66 2.07 2.07 2.06 2.06 2.05 2.05 2.04 2.04 2.03 2.03 1.01 1.01 0.57 0.57

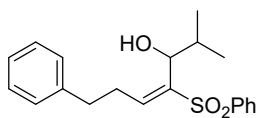
^1H NMR spectrum (CDCl_3 , 500 MHz)



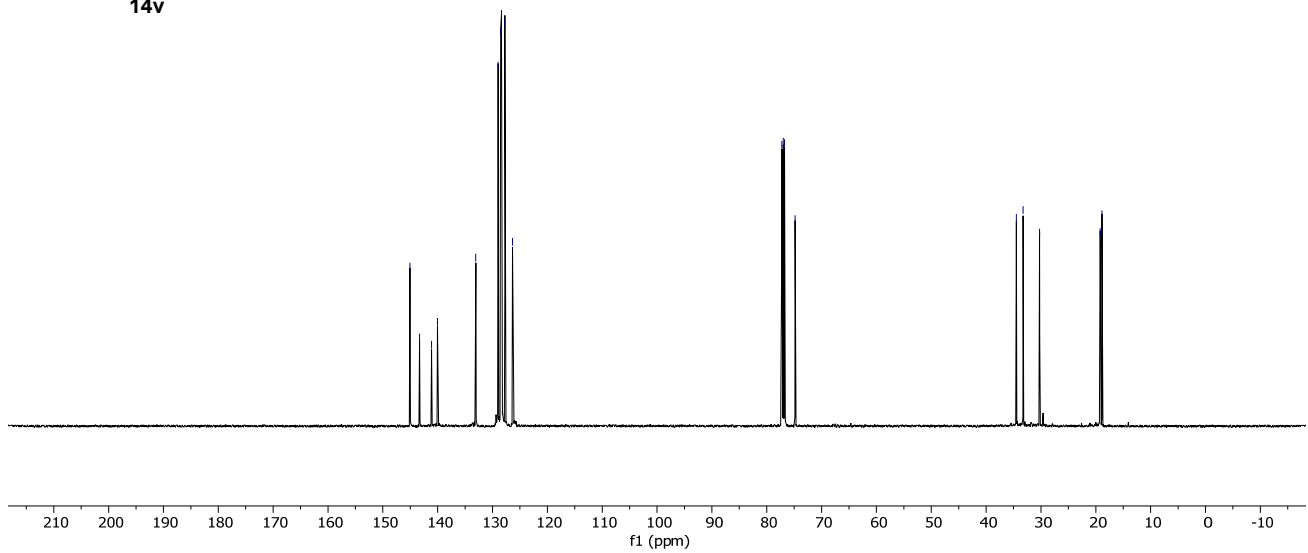
14v



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 126 MHz)

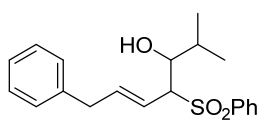


14v

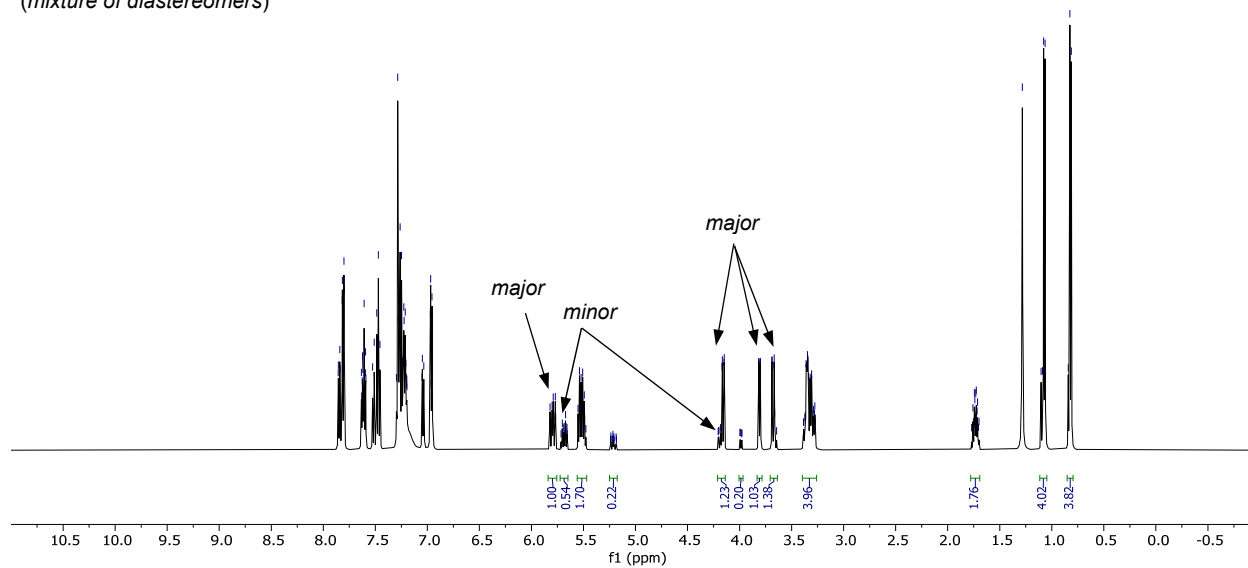


7.86 7.84 7.82 7.81 7.80 7.63 7.62 7.61 7.60 7.59 7.58 7.57 7.56 7.55 7.54 7.53 7.51 7.49 7.48 7.47 7.46 7.45 7.44 7.43 7.42 7.41 7.40 7.39 7.38 7.28 7.27 7.27 7.27 7.26 7.26 7.25 7.24 7.24 7.24 7.23 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.05 7.05 7.03 7.03 6.97 6.97 6.96 6.95 5.54 5.52 5.51 5.51 4.17 4.17 4.15 4.15 3.82 3.82 3.80 3.80 3.69 3.69 3.67 3.67 3.36 3.36 3.35 3.35 3.34 3.34 3.32 3.32 3.31 3.31 3.28 3.28 1.10 1.10 1.08 1.08 0.84 0.84 0.83 0.81

^1H NMR spectrum (CDCl_3 , 500 MHz)



14a
(mixture of diastereomers)



140.48 139.91 138.85 138.82 138.17 137.24 133.65 133.55 133.55 128.87 128.90 128.46 128.44 128.35 126.31 118.57 117.48

73.28 71.02

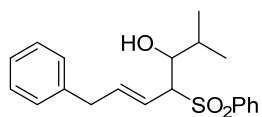
59.93

39.14 38.82

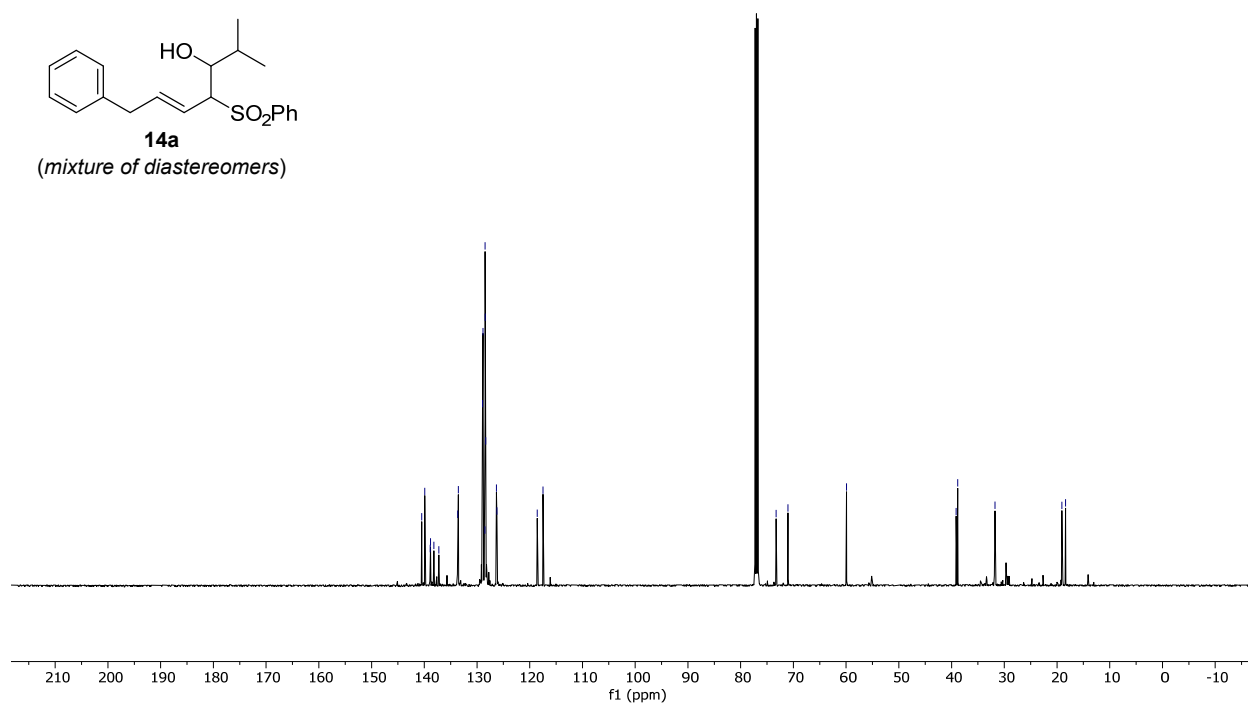
31.77

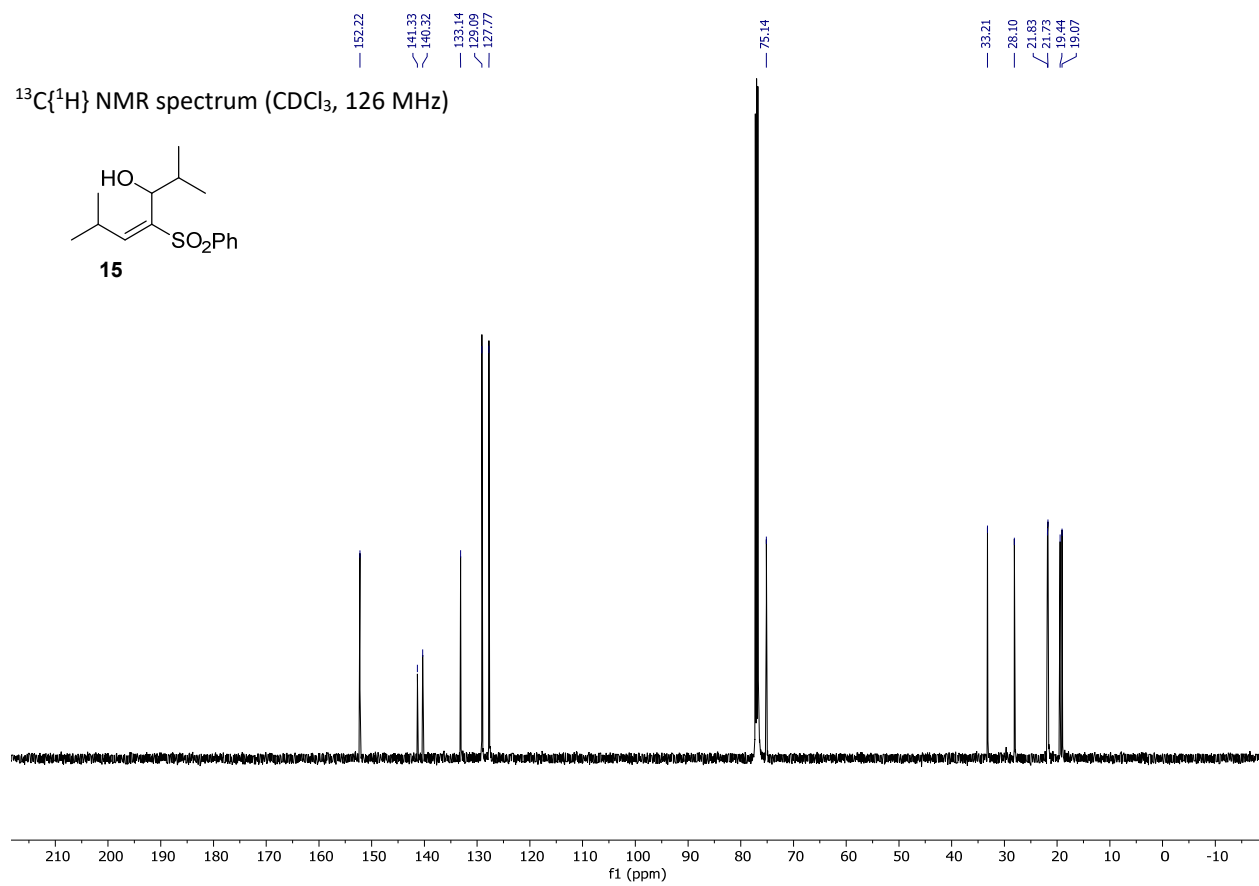
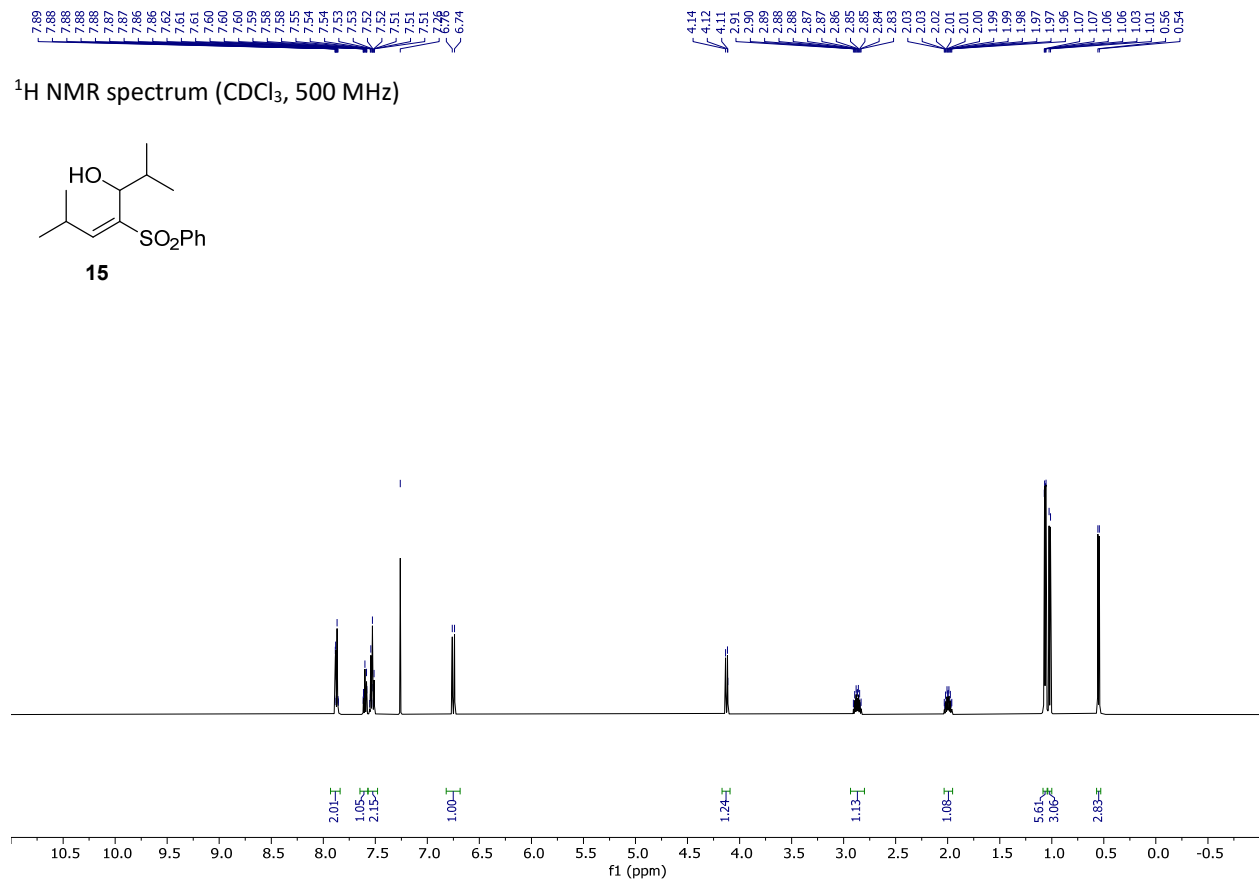
19.09 18.38

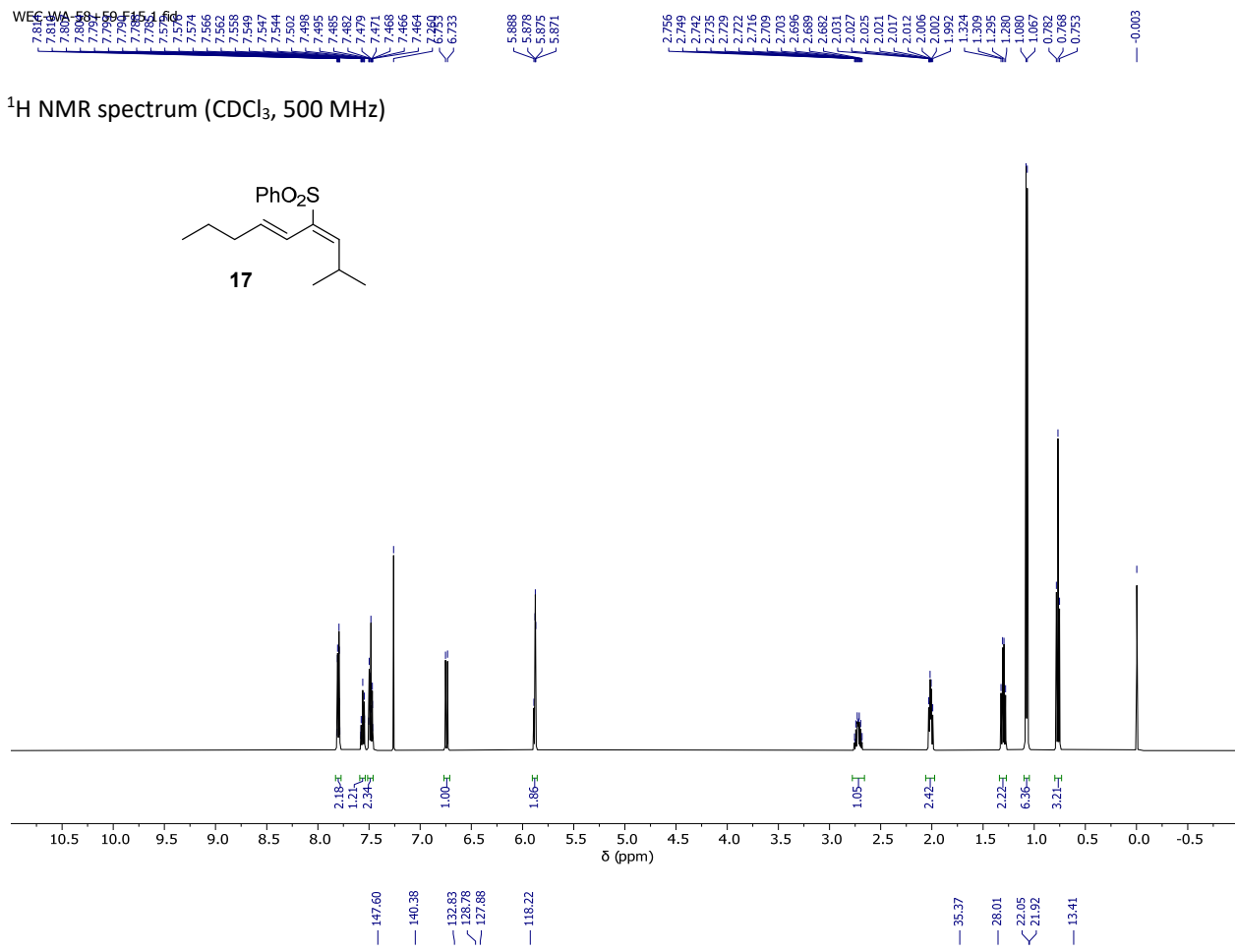
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 126 MHz)



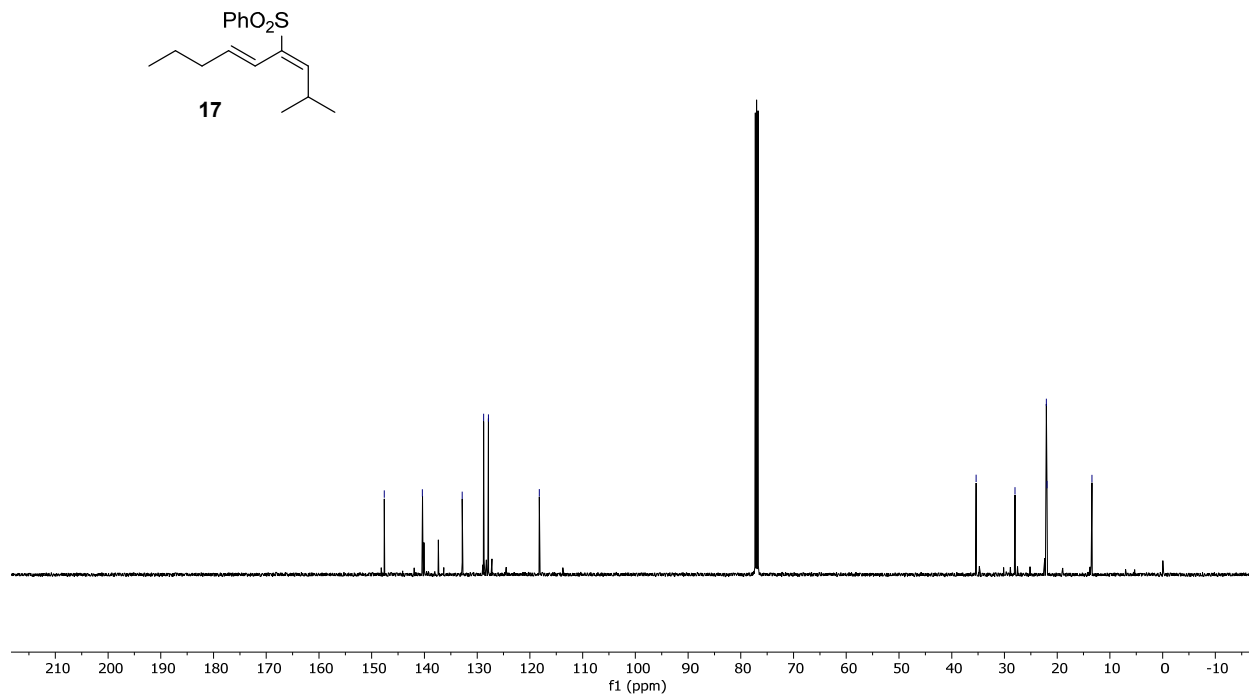
14a
(mixture of diastereomers)



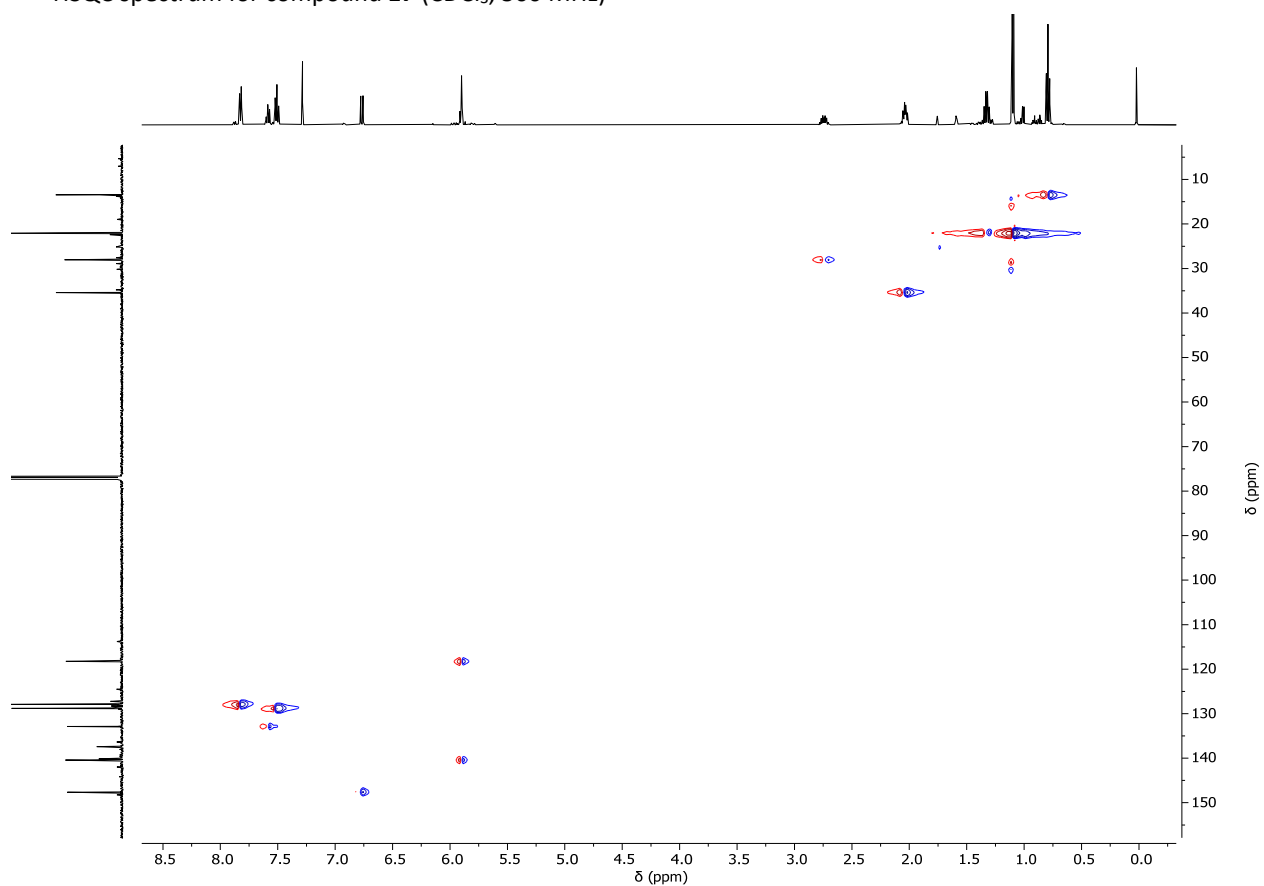




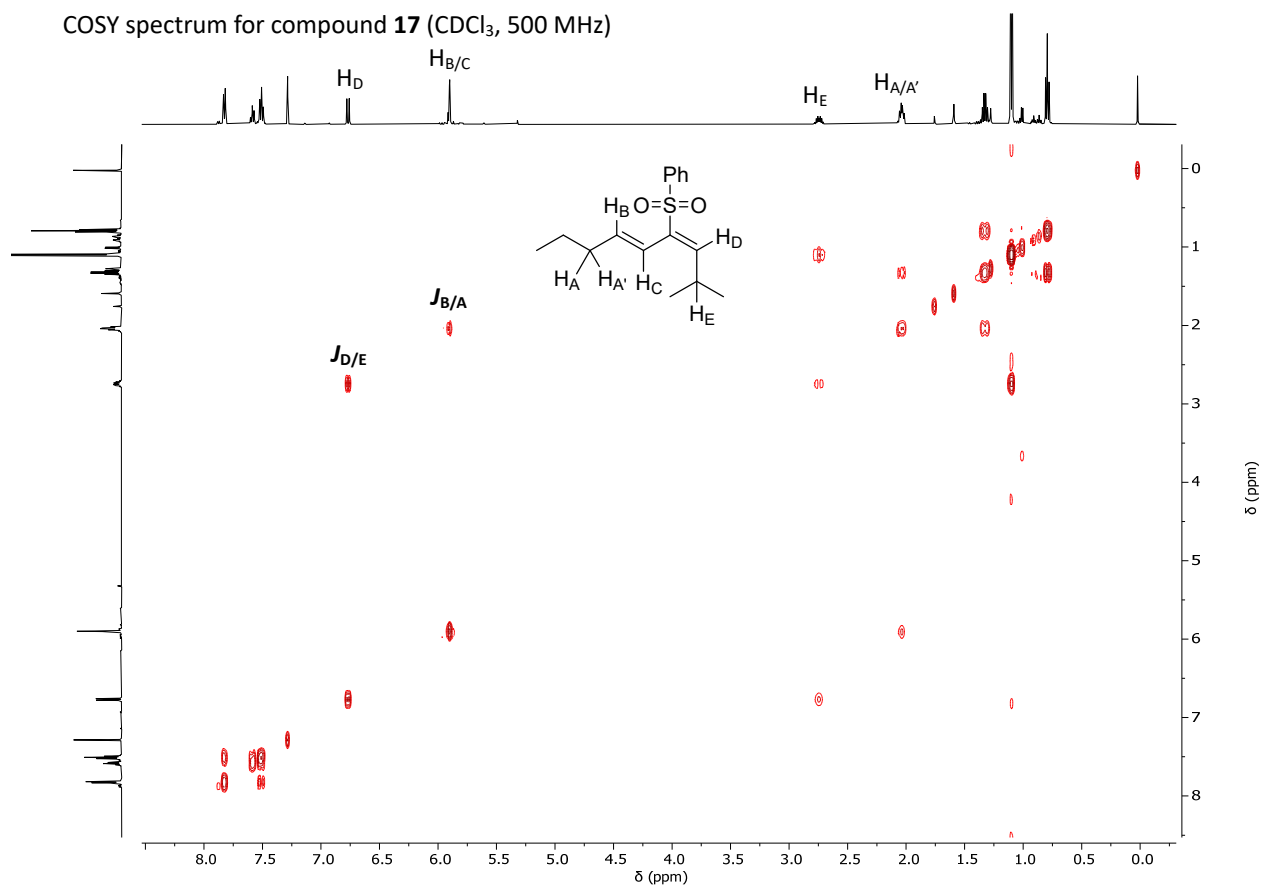
¹³C{¹H} NMR spectrum (CDCl₃, 126 MHz)



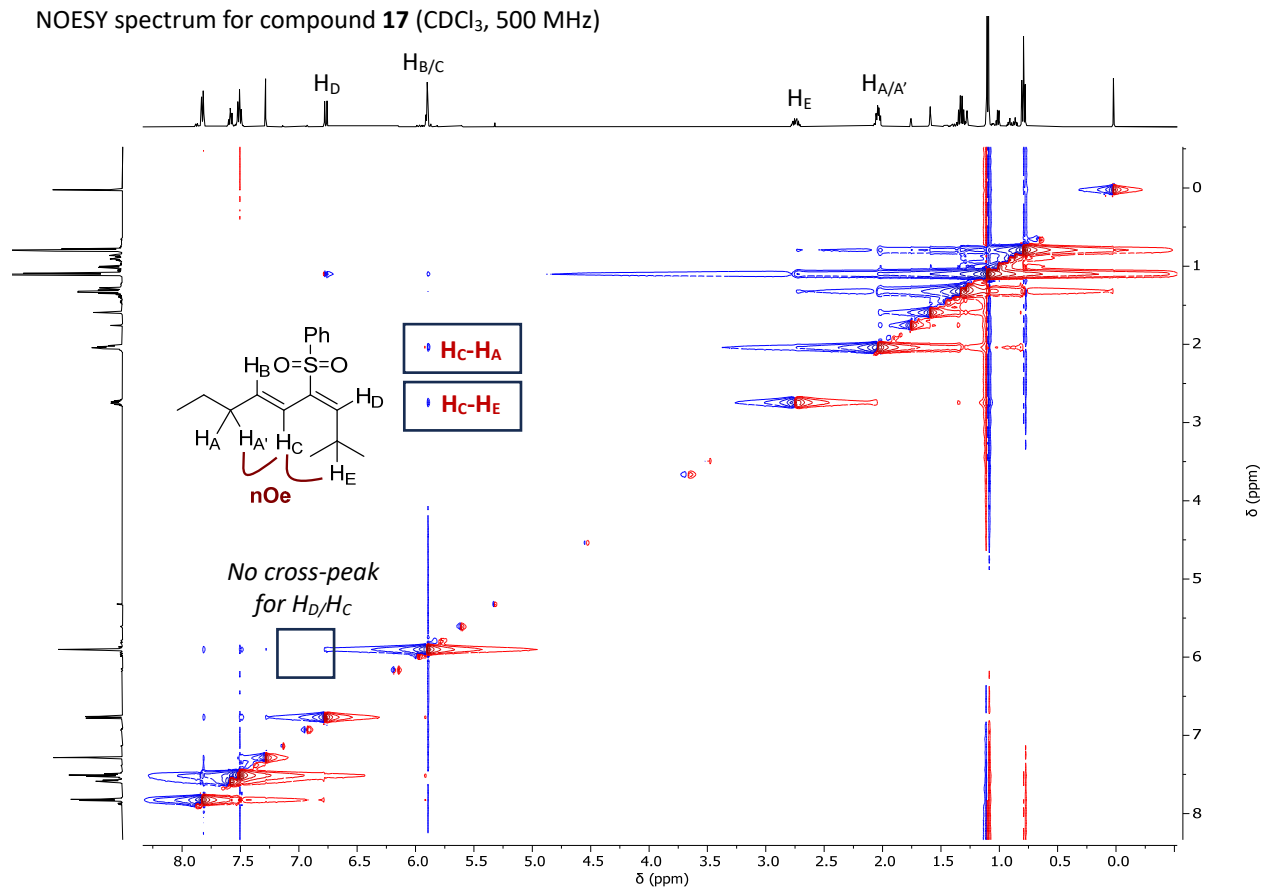
HSQC spectrum for compound **17** (CDCl₃, 500 MHz)



COSY spectrum for compound **17** (CDCl₃, 500 MHz)



NOESY spectrum for compound **17** (CDCl₃, 500 MHz)



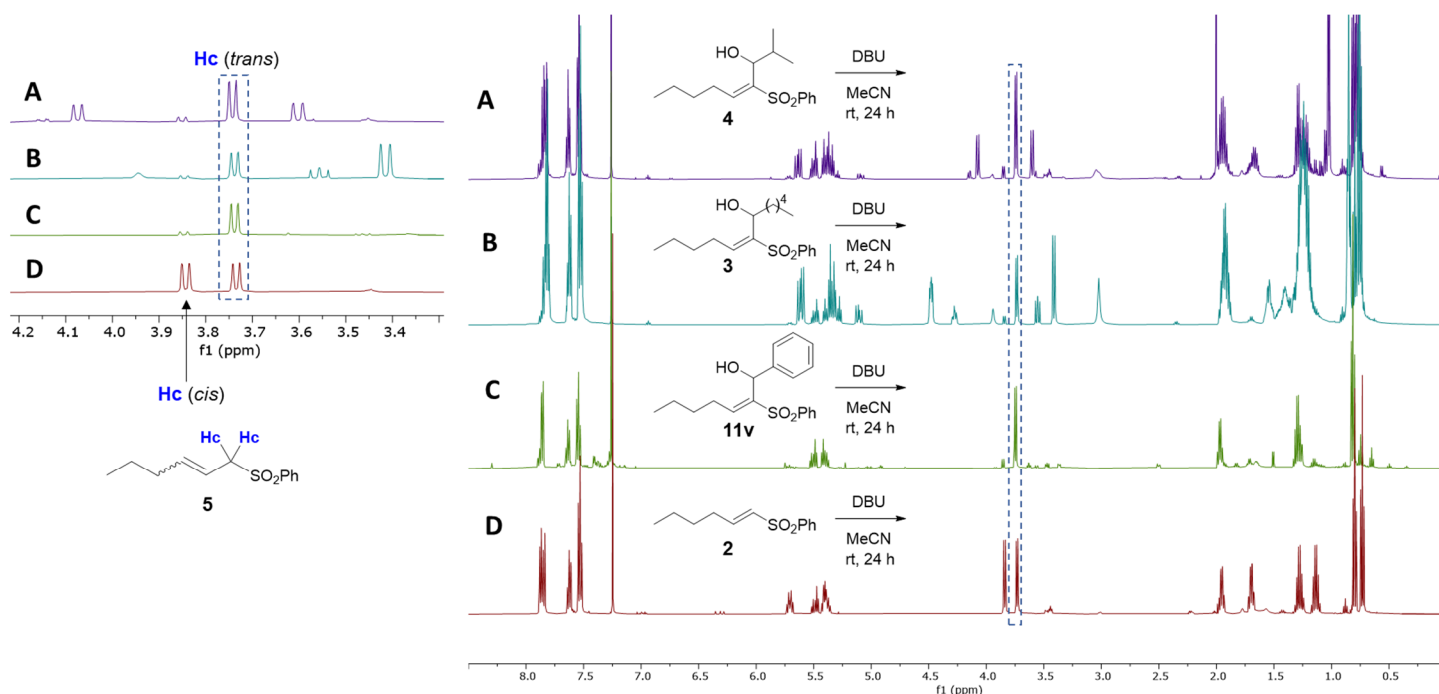


Figure S1. Comparison of crude product mixtures by ^1H NMR obtained from the DBU isomerization of different vinylsulfone starting materials. β -hydroxysulfones **4** (top, spectrum A) and **3** (spectrum B) gave primarily the isomerized allylic sulfone product, whereas **11v** produced almost exclusively the C-C bond cleavage product **5** (spectrum C). All β -hydroxysulfones gave **5** with high *trans*-selectivity, whereas vinylsulfone **2** produced **5** as a \sim 1:1 *cis:trans* mixture (spectrum D).

Table S1. Tables of ^1H NMR coupling constants for various beta-hydroxysulfones stereoisomers previously reported by Mase and coworkers¹ (left) and from our work (right). Across both data sets, a clear trend can be observed where the *major/erythro*-isomer displayed smaller coupling constants (0.9-1.5 Hz) than the *minor/threo*-isomer.

erythro

threo

R^1	R^2		J_{XY} (Hz)
Ph	<i>i</i> -Pr	<i>erythro</i>	1.2
		<i>threo</i>	8.6
Ph	Et	<i>erythro</i>	1.2
		<i>threo</i>	8.8
Me	<i>i</i> -Pr	<i>erythro</i>	1.4
		<i>threo</i>	6.7
Me	Bu	<i>erythro</i>	1.4
		<i>threo</i>	6.7
Me	Et	<i>erythro</i>	1.4
		<i>threo</i>	6.7

R^1	R^2		J_{XY} (Hz)
Pr	Me	<i>major</i>	1.5
		<i>minor</i>	8.6
Pr	<i>n</i> -pent	<i>major</i>	1.4
		<i>minor</i>	8.3
Pr	<i>i</i> -Bu	<i>major</i>	1.3
		<i>minor</i>	8.4
Pr	<i>i</i> -Pr	<i>major</i>	1.4
		<i>minor</i>	9.5
Pr	<i>t</i> -Bu	<i>major</i>	0.9
		<i>minor</i>	NA ^a

Notes for Table: ^1H NMR spectra were acquired in CDCl_3 as solvent. ^aNot available since only a single diastereomer was obtained as detected by NMR.

¹ Mase, N.; Watanabe, Y.; Toru, T.; Kakumoto, T.; Hagiwara, T. Diastereoselective Radical Hydrogenation of α -(1-Hydroxyalkyl)vinyl Sulfoxides and Sulfones Controlled by Intramolecular Hydrogen Bonding. *J. Org. Chem.* **2000**, *65*, 7083-7090.