Supporting Information for:

Diastereoselective β-Hydroxy Vinylsulfone Isomerizations

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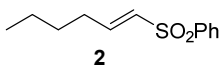
Contents:

WEC-WA-007F13.1.fid

^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



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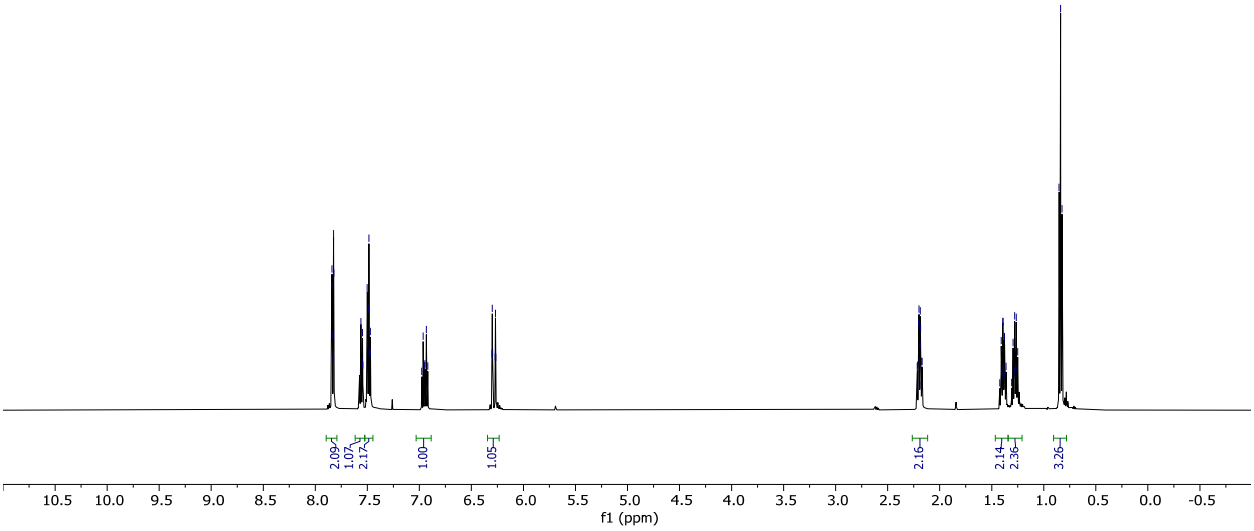
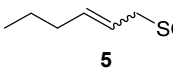


CND-C4-079.1.fid
vinylsulfone,DBU, MeCN, rt onight

^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



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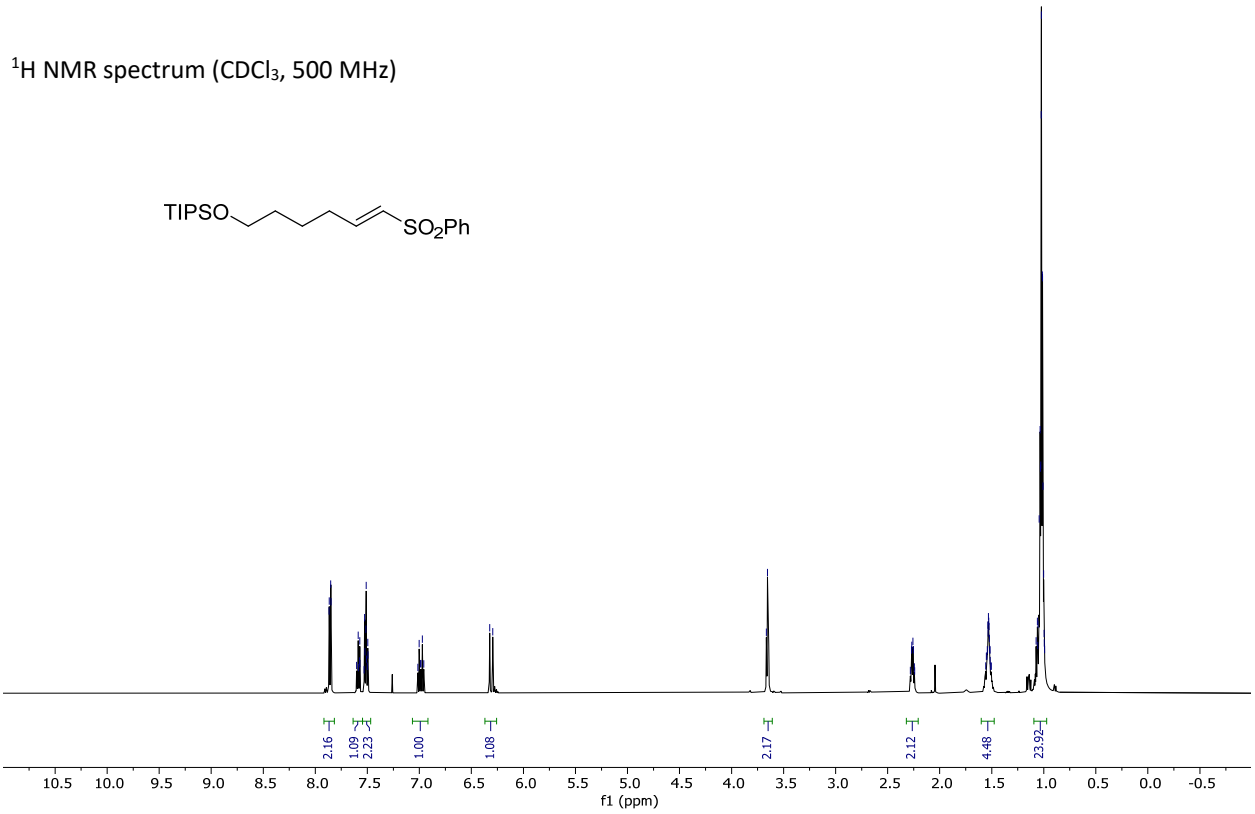
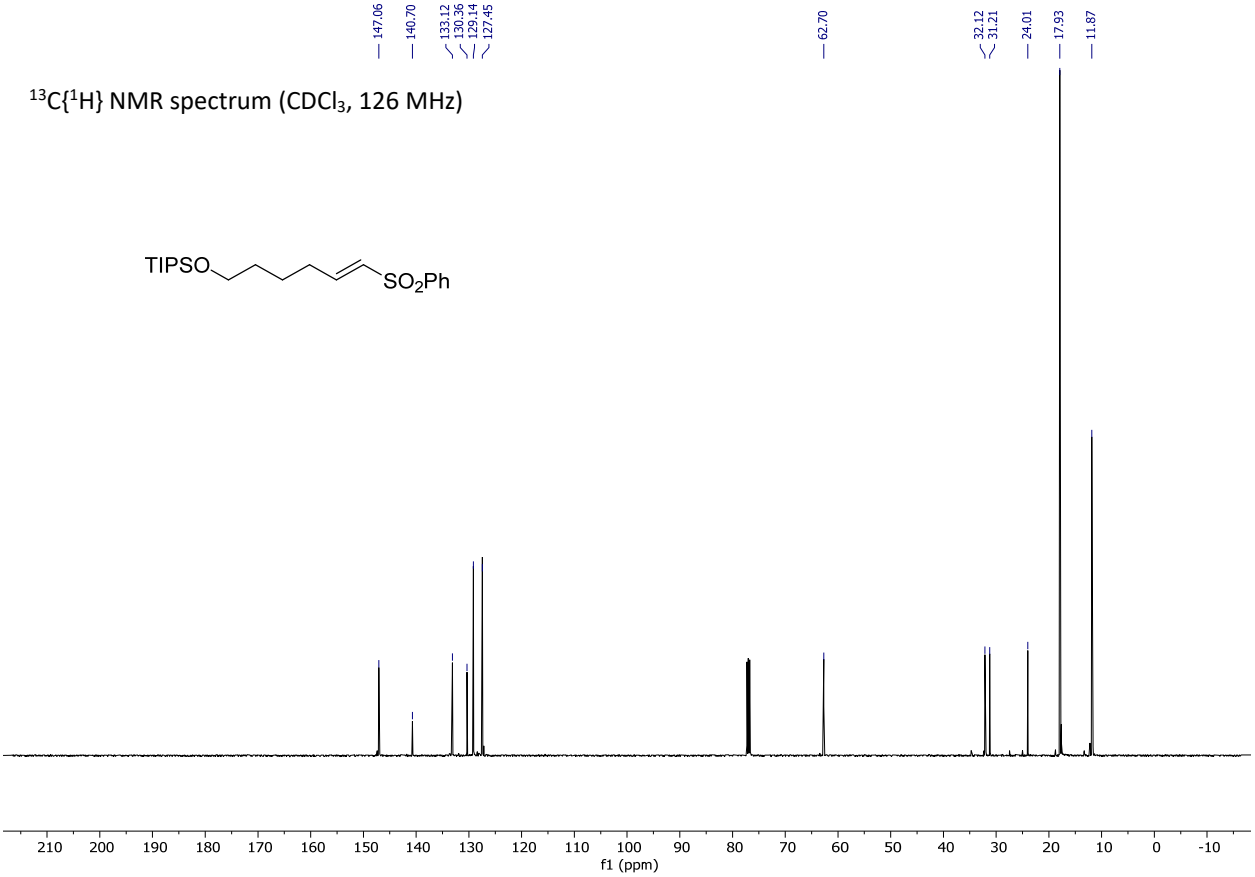
^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



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



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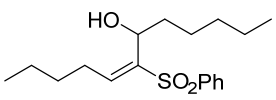
vinyl sulfone hexanal addition

^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



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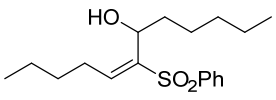
^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 126 MHz)



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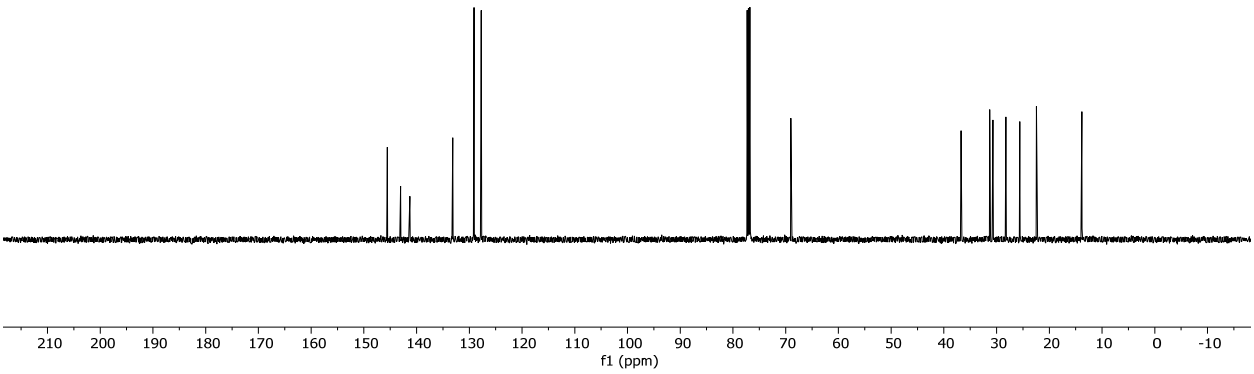

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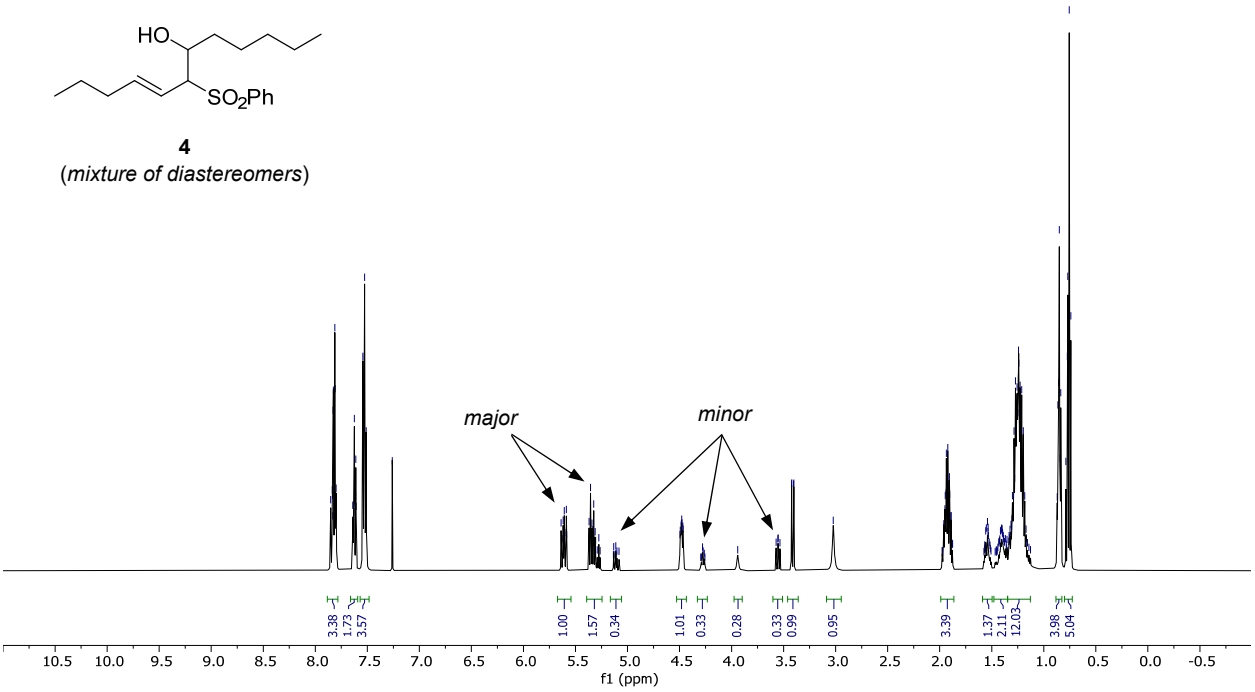
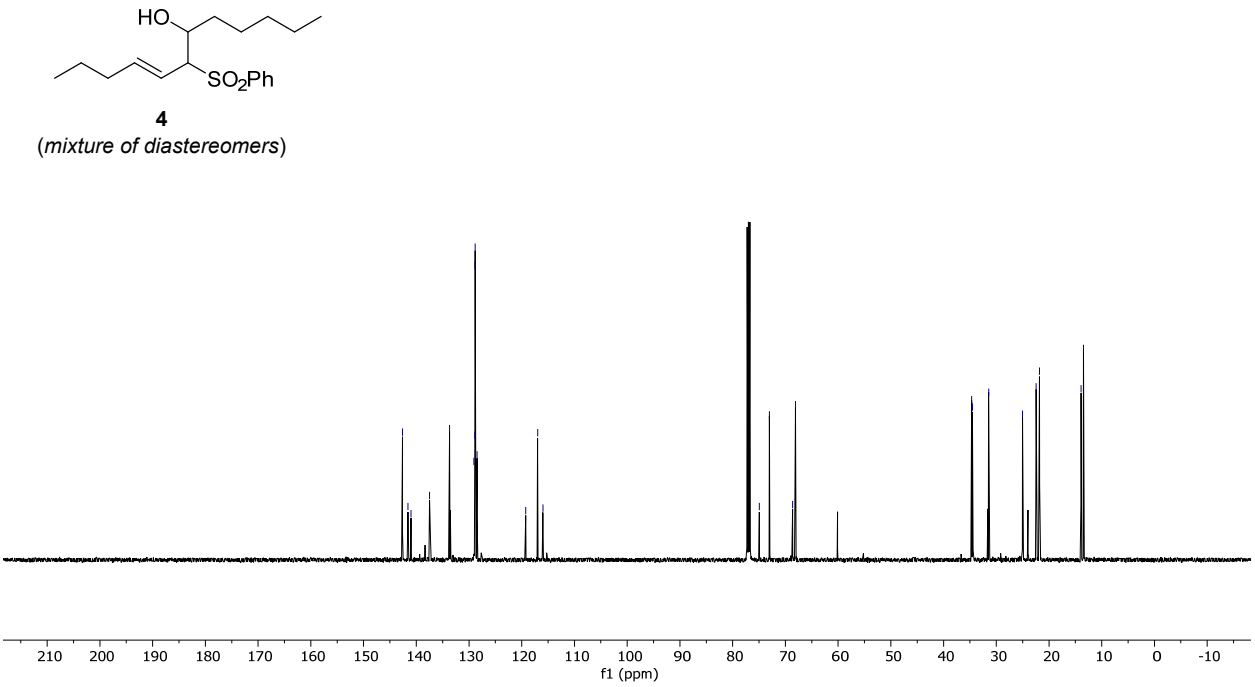


^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 126 MHz)



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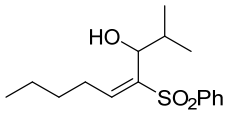

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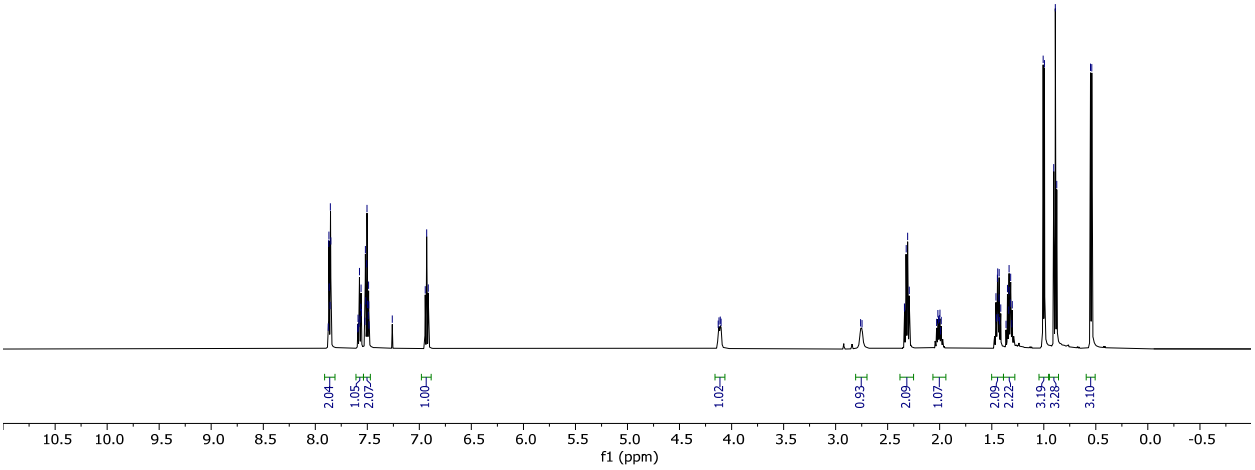
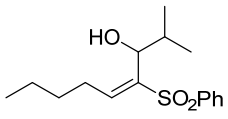


^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 126 MHz)



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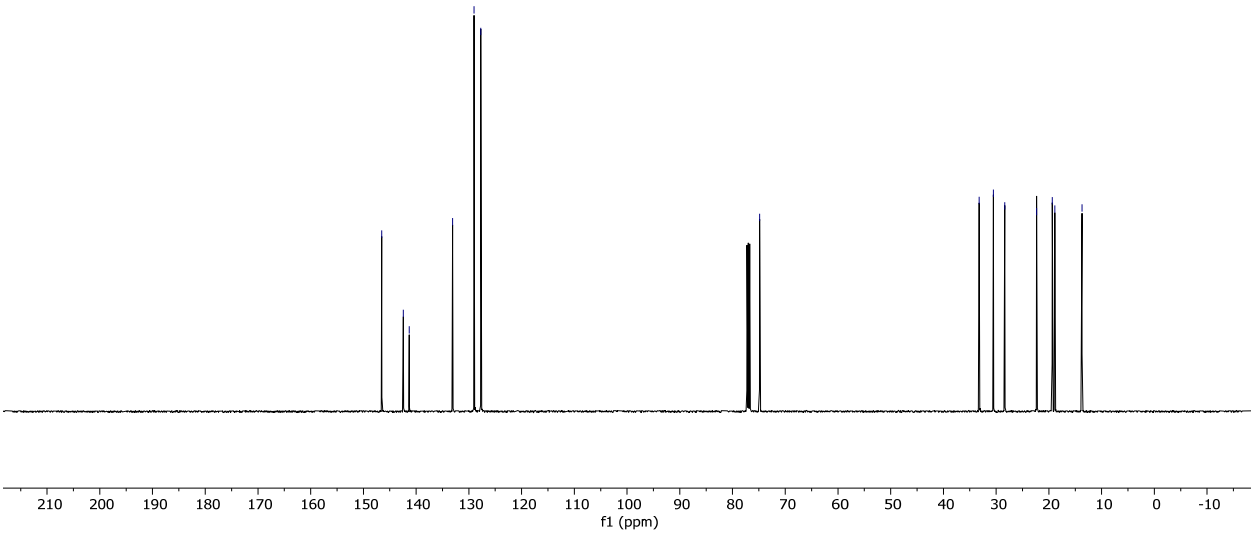
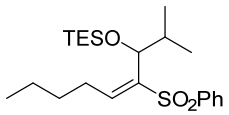
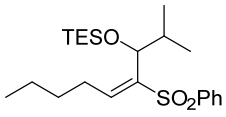


^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



6-Si

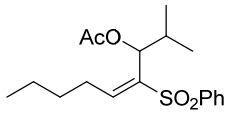
^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 126 MHz)



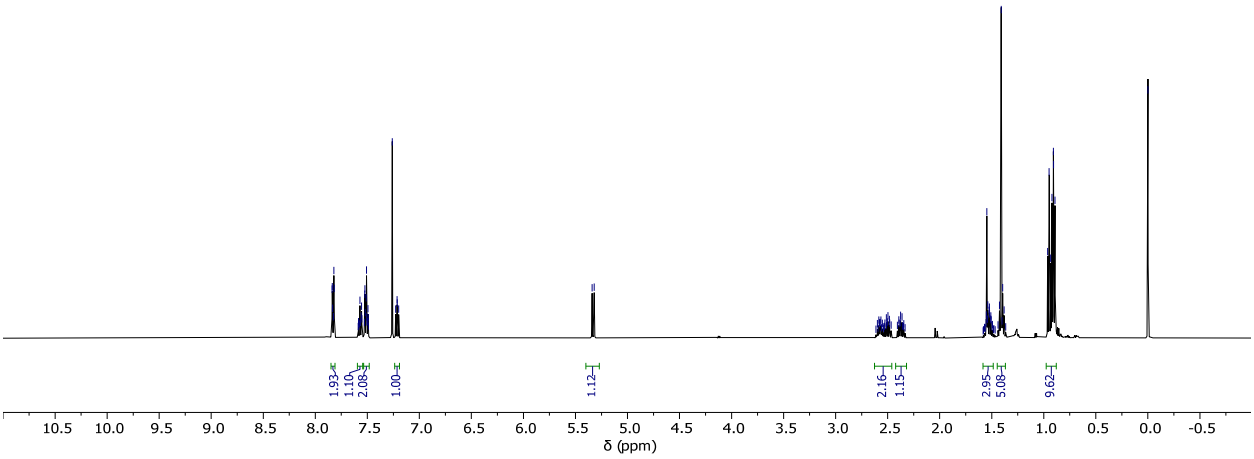
6-Si

WEC-WA-57-F8+9-2.fid

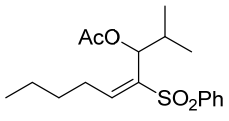
^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



6-Ac

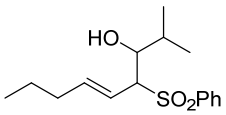


^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 126 MHz)



6-Ac

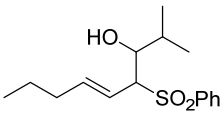
^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



7

(*major diastereomer*)

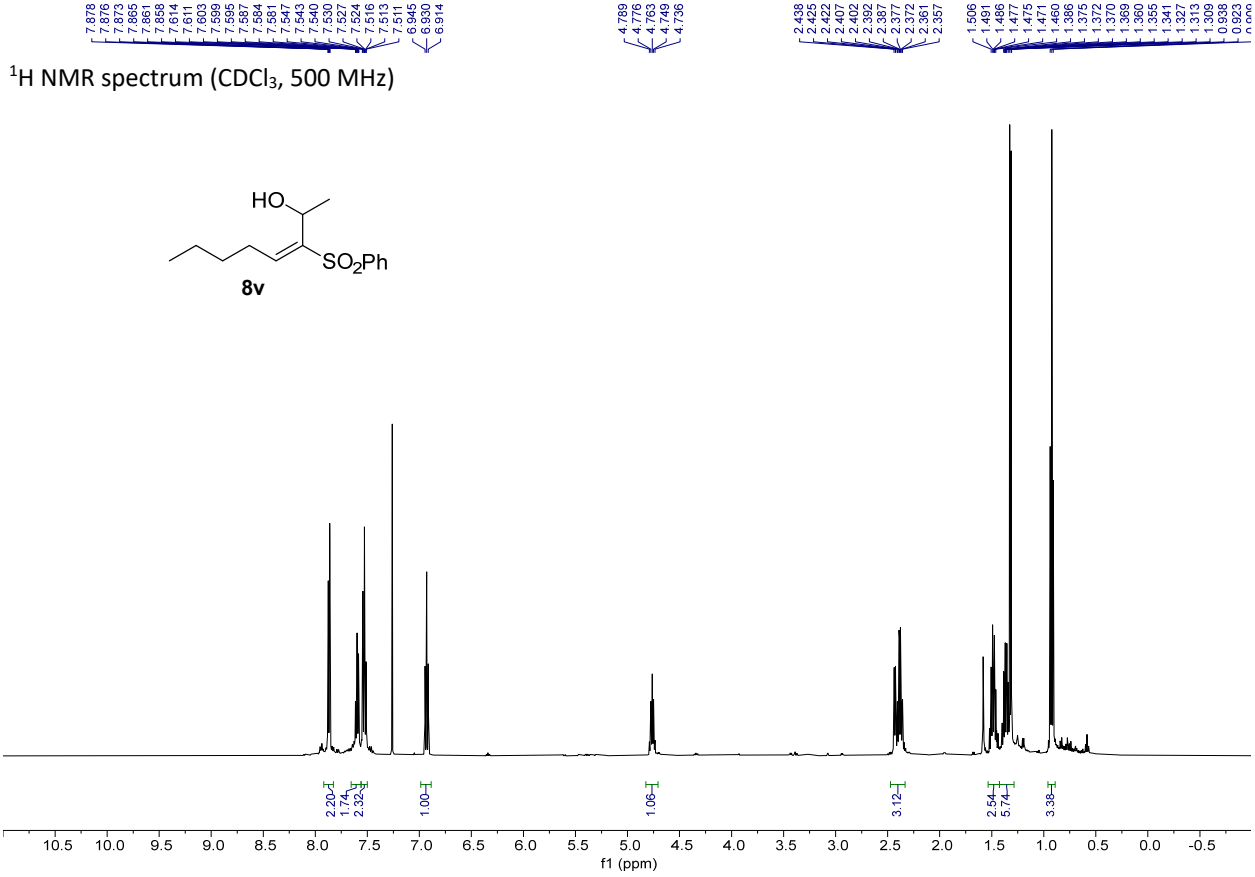
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 126 MHz)



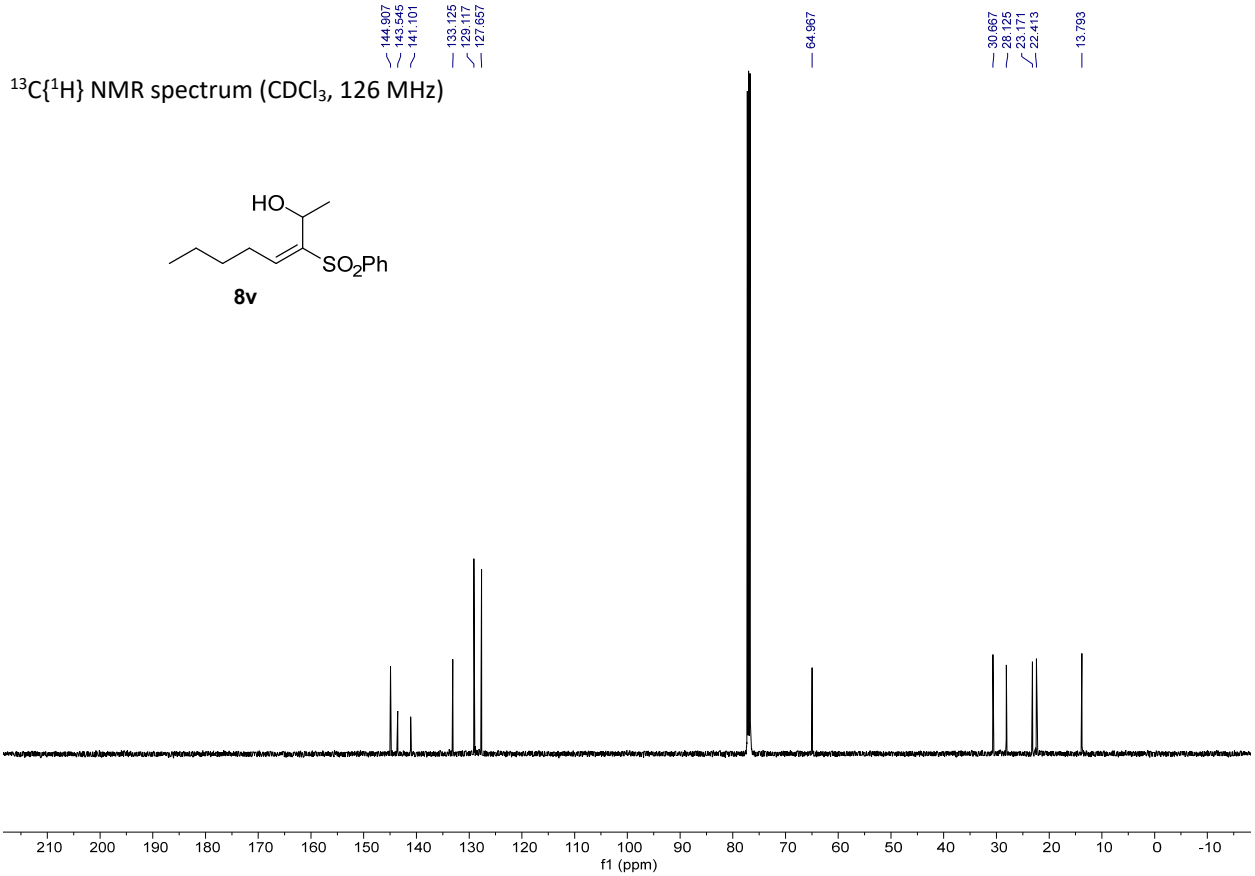
7

(*major diastereomer*)

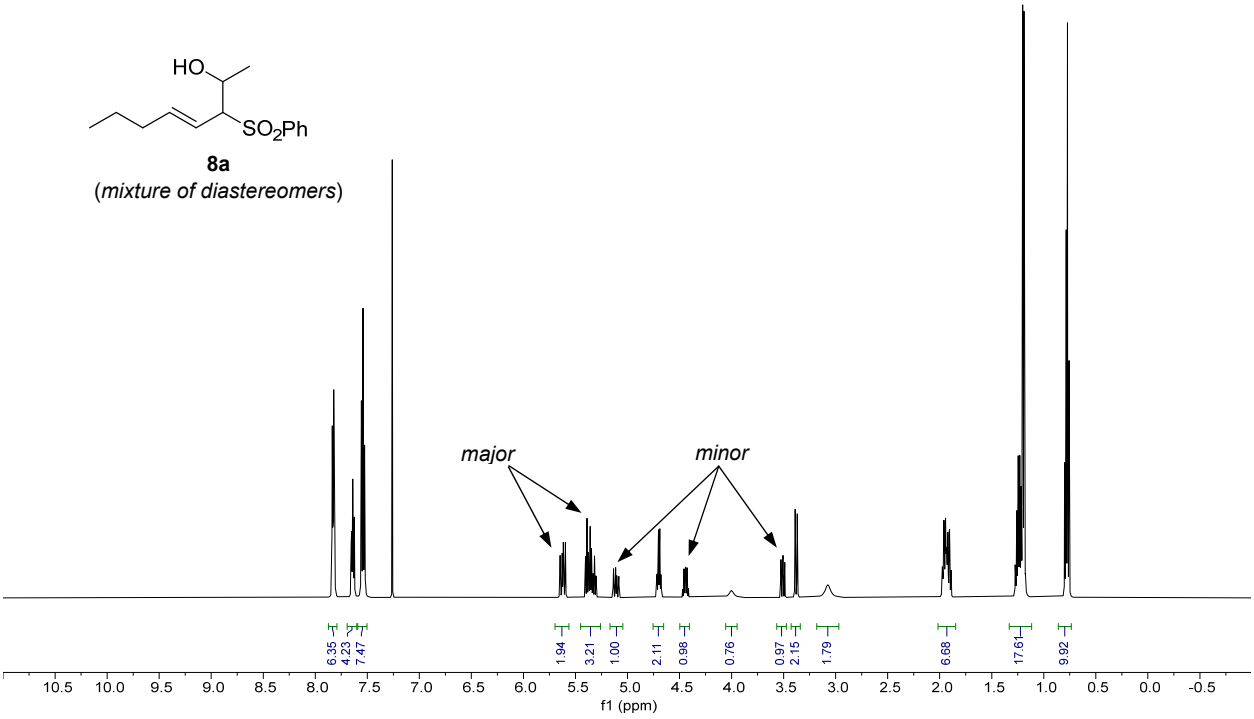
^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



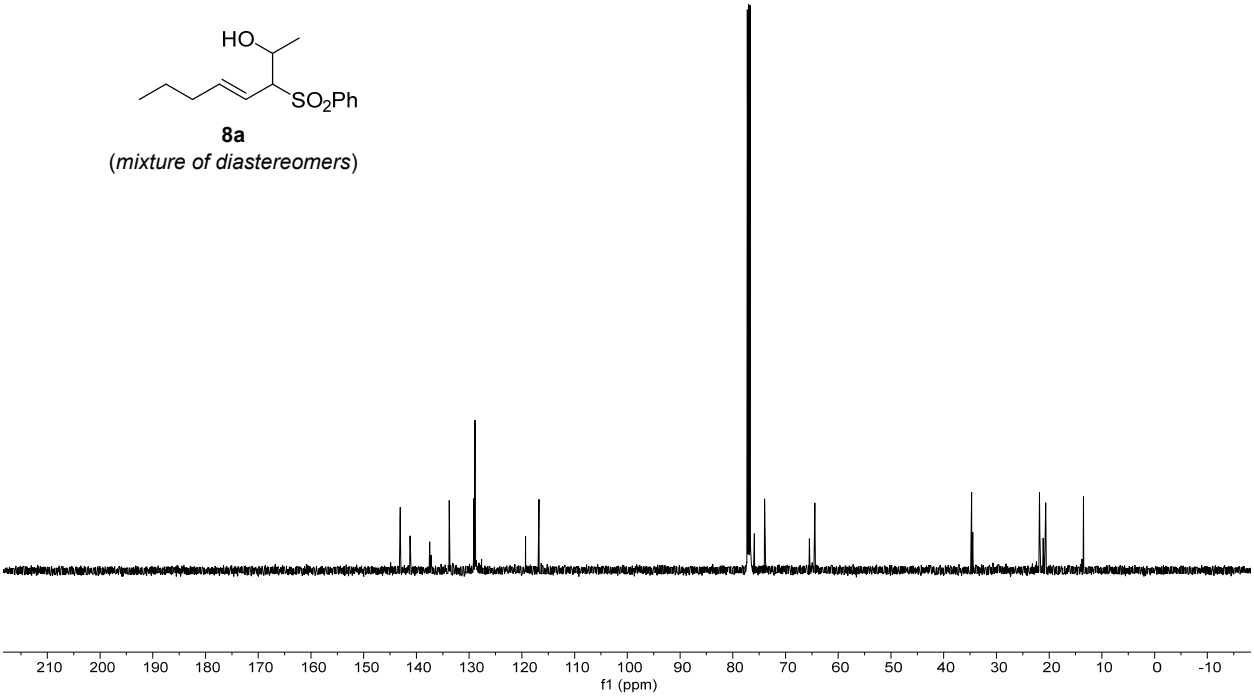
^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 126 MHz)



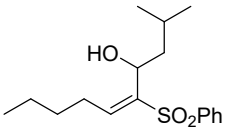
^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



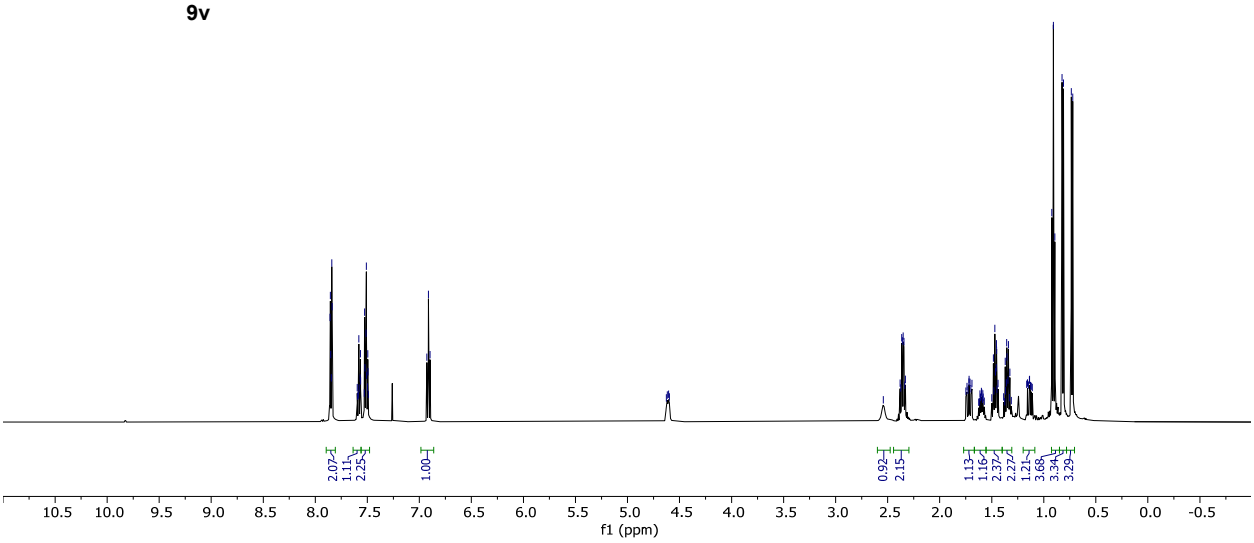
^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 126 MHz)



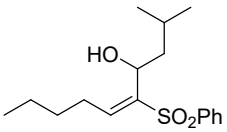
^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



9v



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



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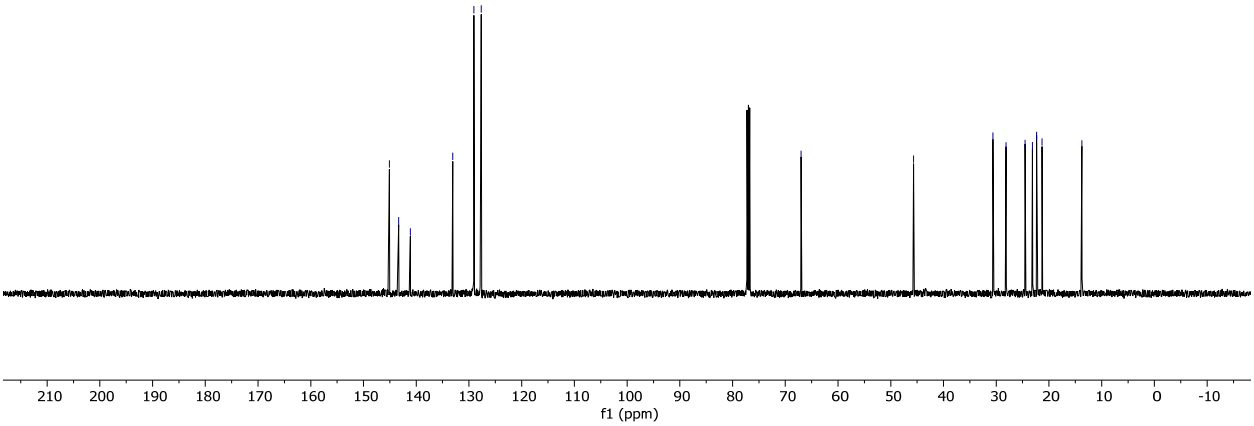
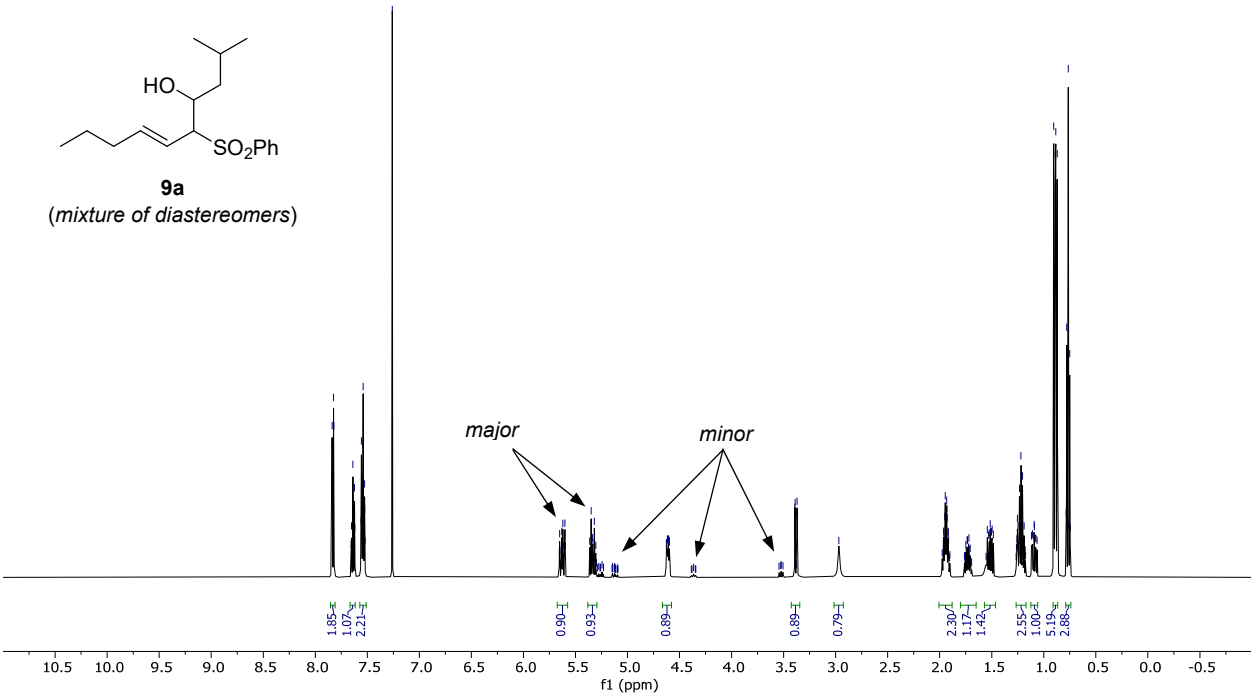
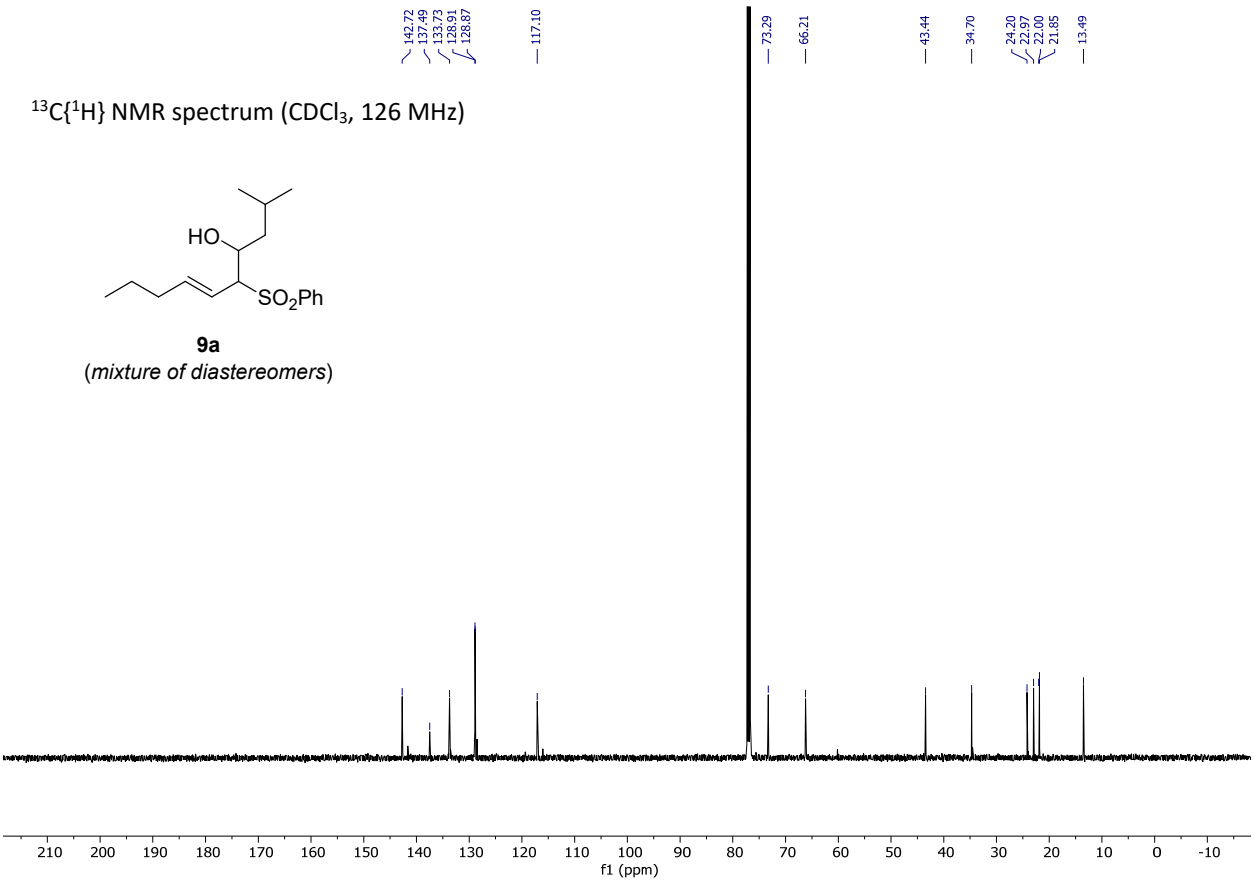


^{1}H NMR spectrum ($CDCl_3$, 500 MHz)

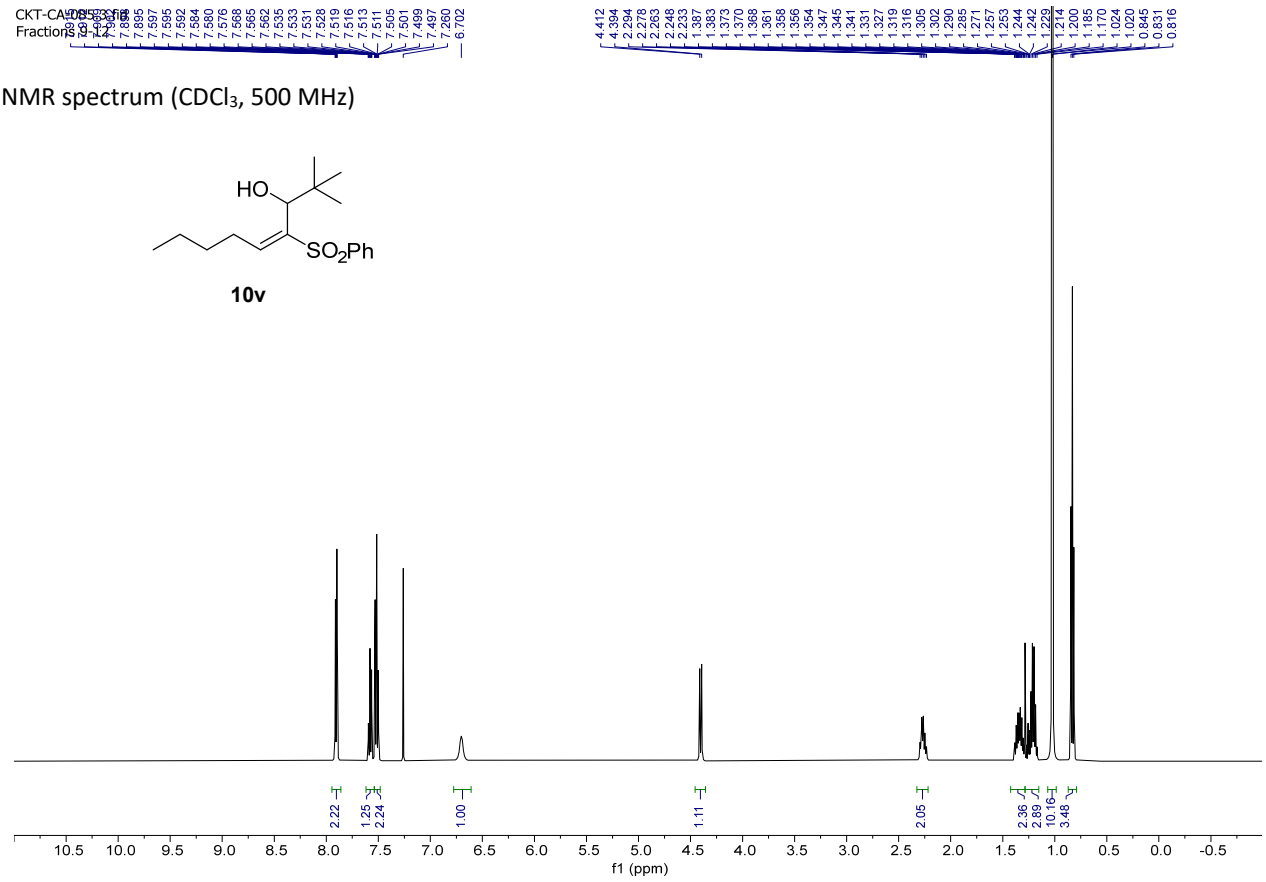


9a
(*mixture of diastereomers*)

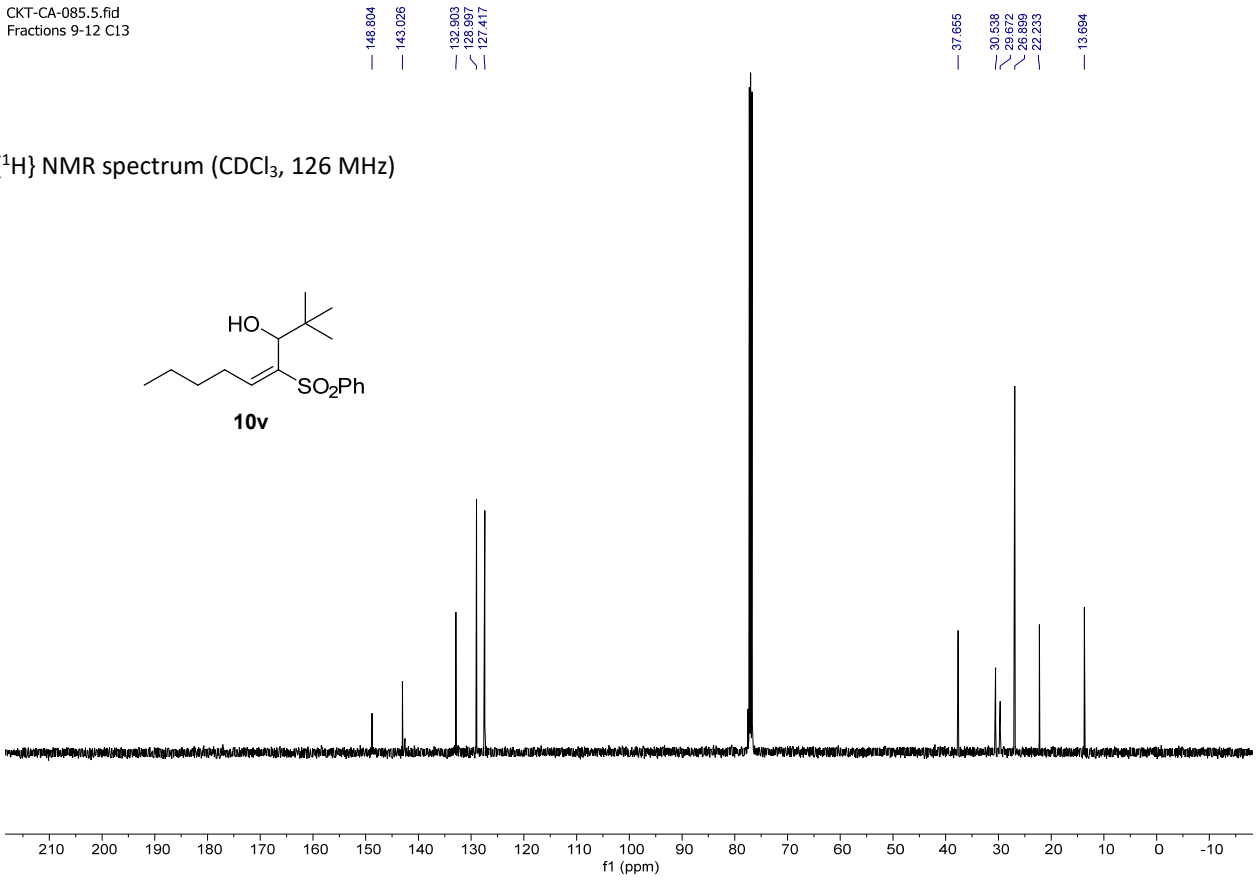
^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 126 MHz)



9a
(*mixture of diastereomers*)



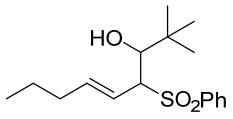
^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



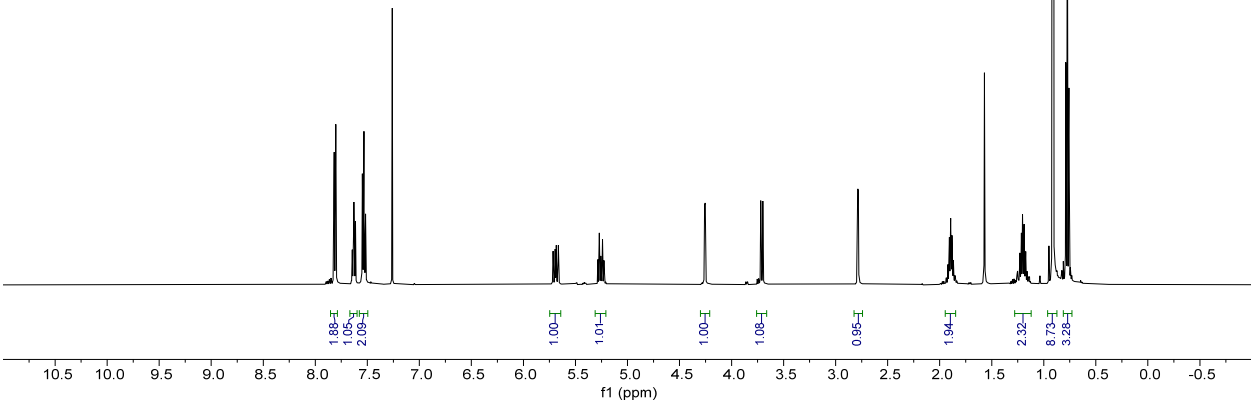
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 126 MHz)

CKT-CA-086.2.fid
Fraction 9

^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



10a



CKT-CA-086.5.fid
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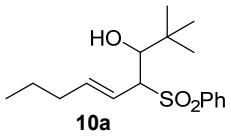
^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 126 MHz)



10a

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Fraction 13 again

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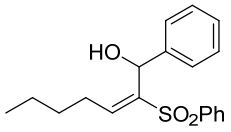

11v

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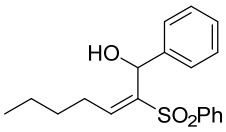
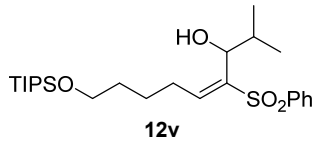


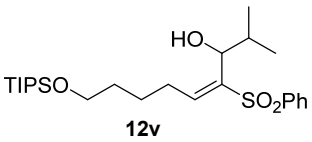
11v

^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



12v

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



12v

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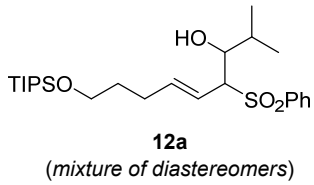
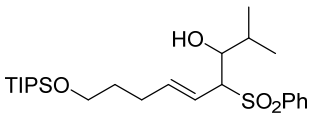
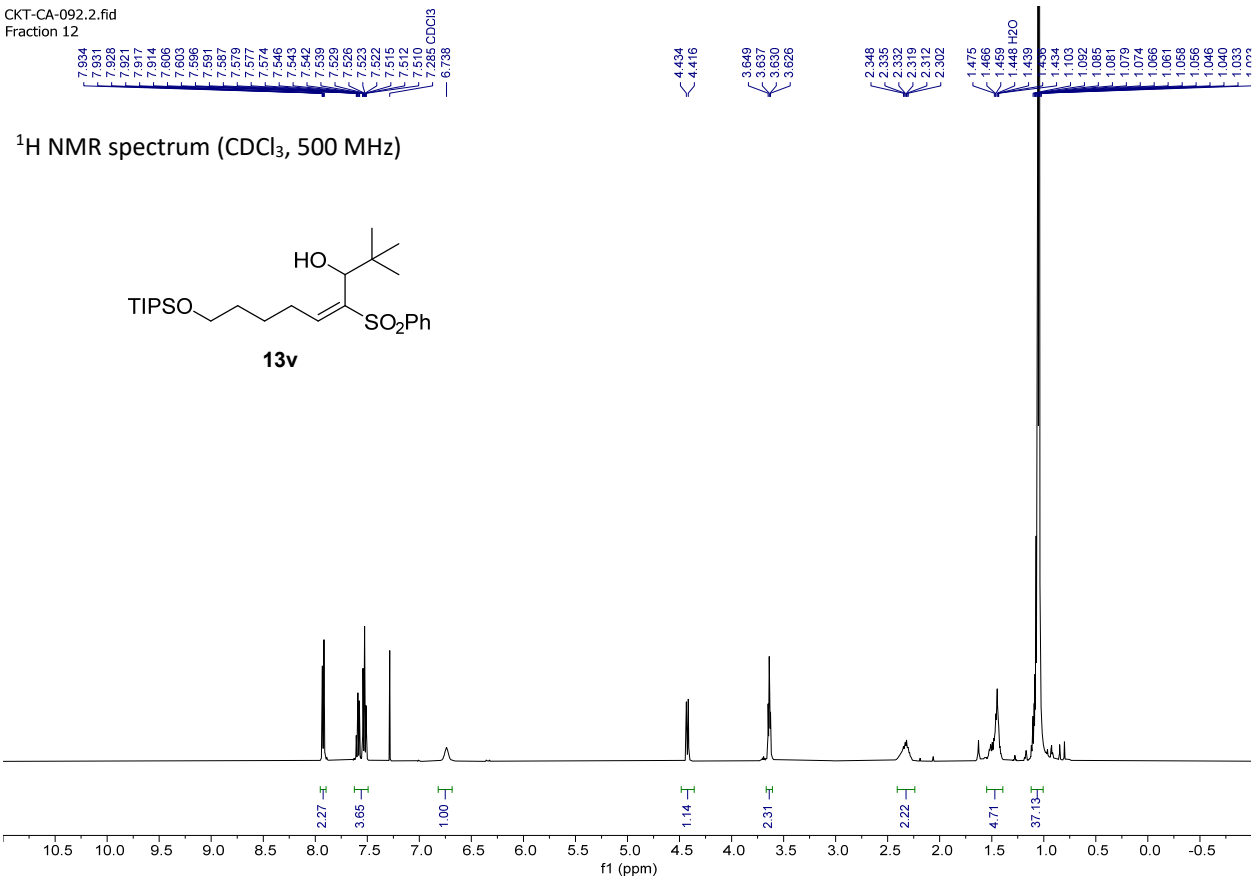


12a
(*mixture of diastereomers*)

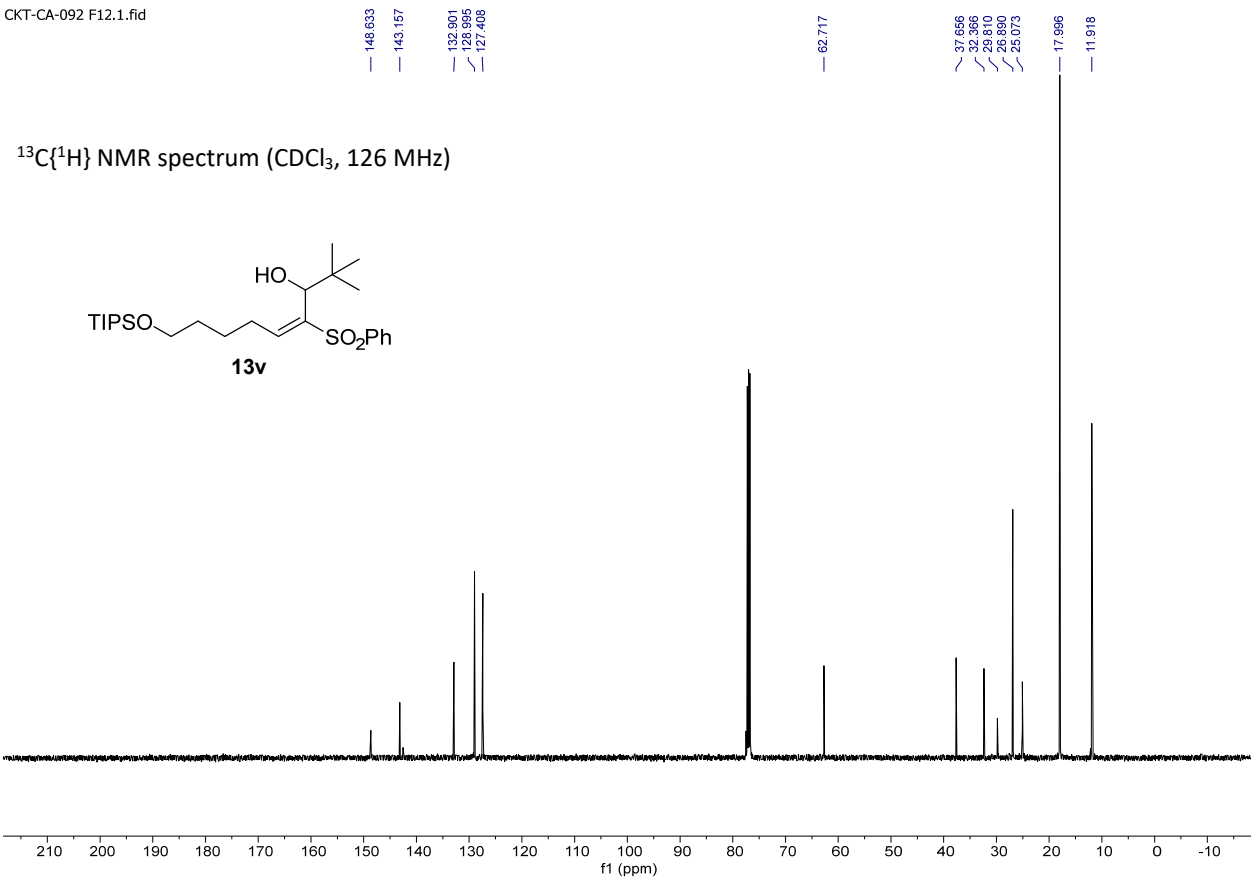
^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 126 MHz)



12a
(*mixture of diastereomers*)

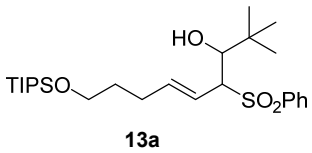


^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



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

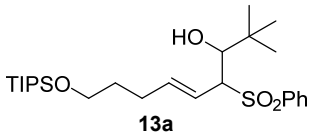
^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



13a

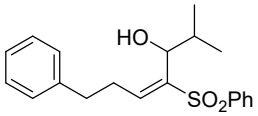
CKT-CA-093 F7-9 13C.10.fid

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

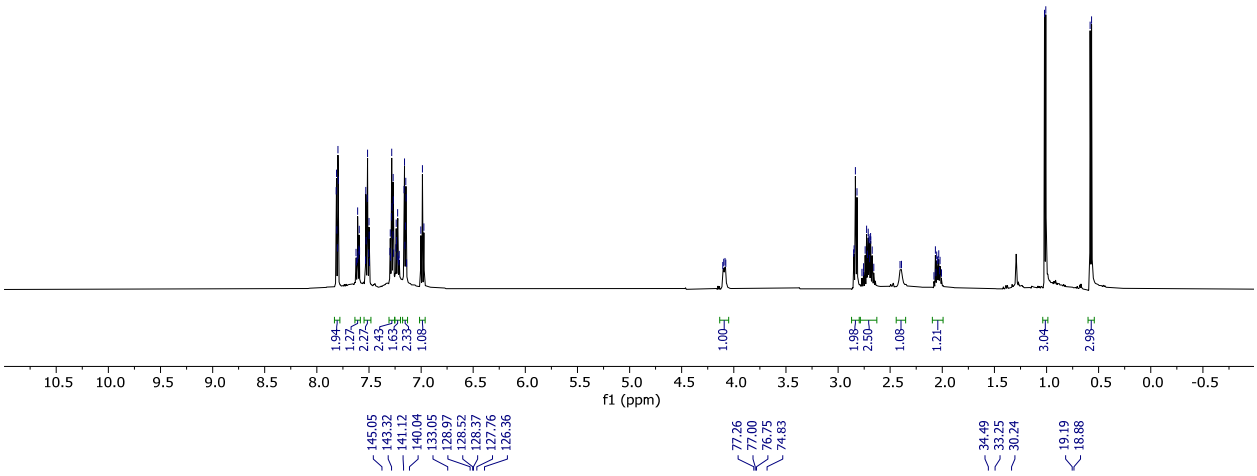


13a

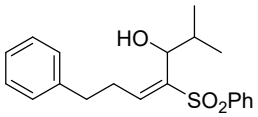
^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



14v



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



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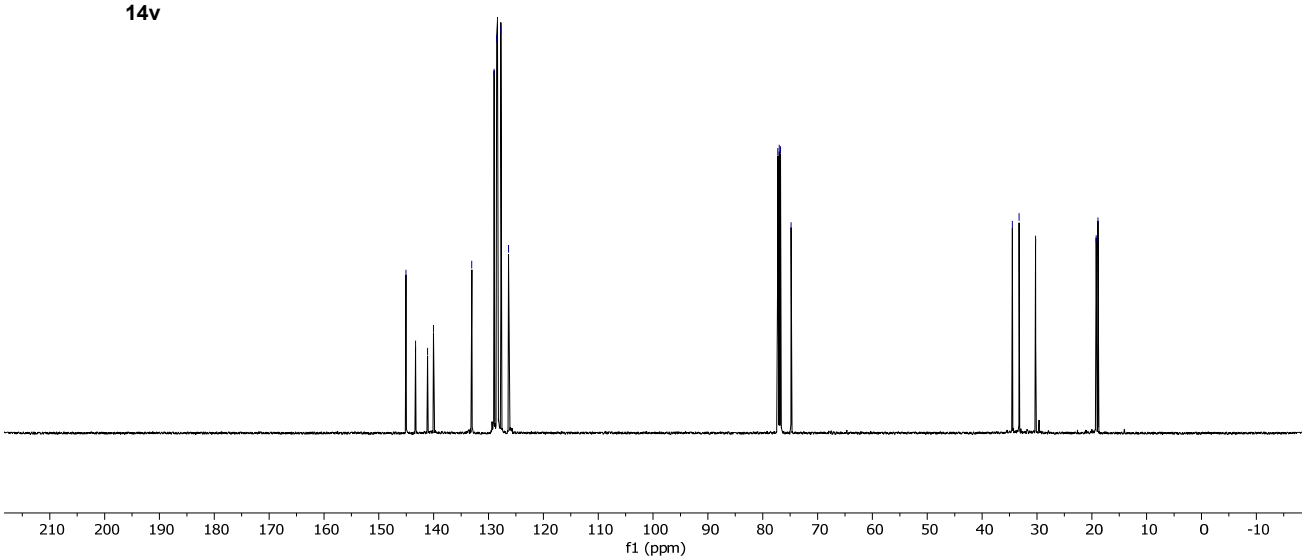
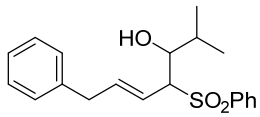
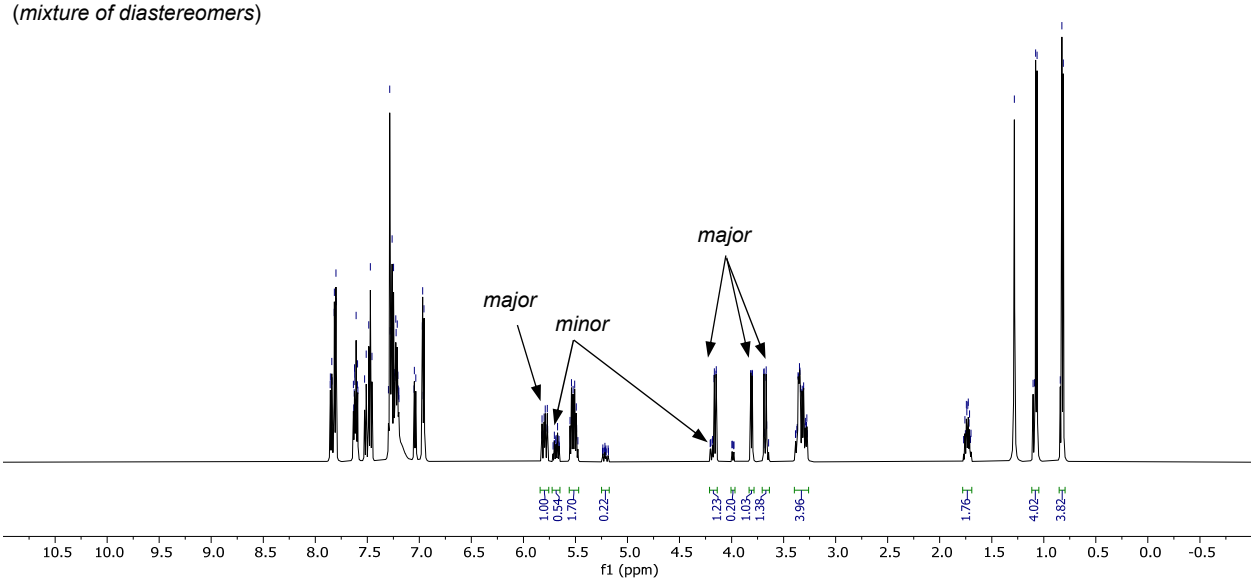


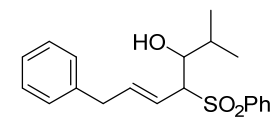
^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



14a
(*mixture of diastereomers*)

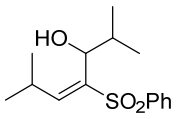


^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 126 MHz)

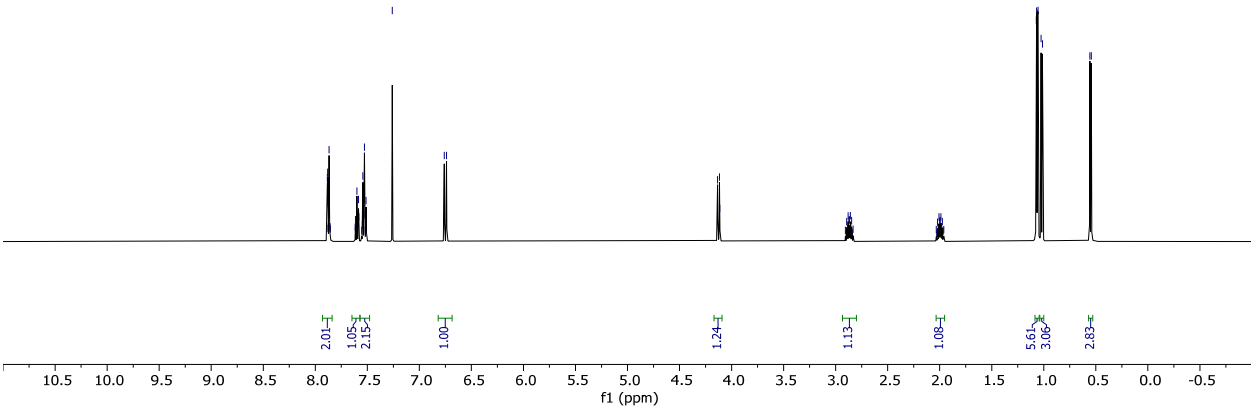


14a
(*mixture of diastereomers*)

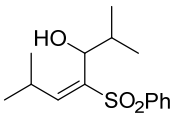
^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



15



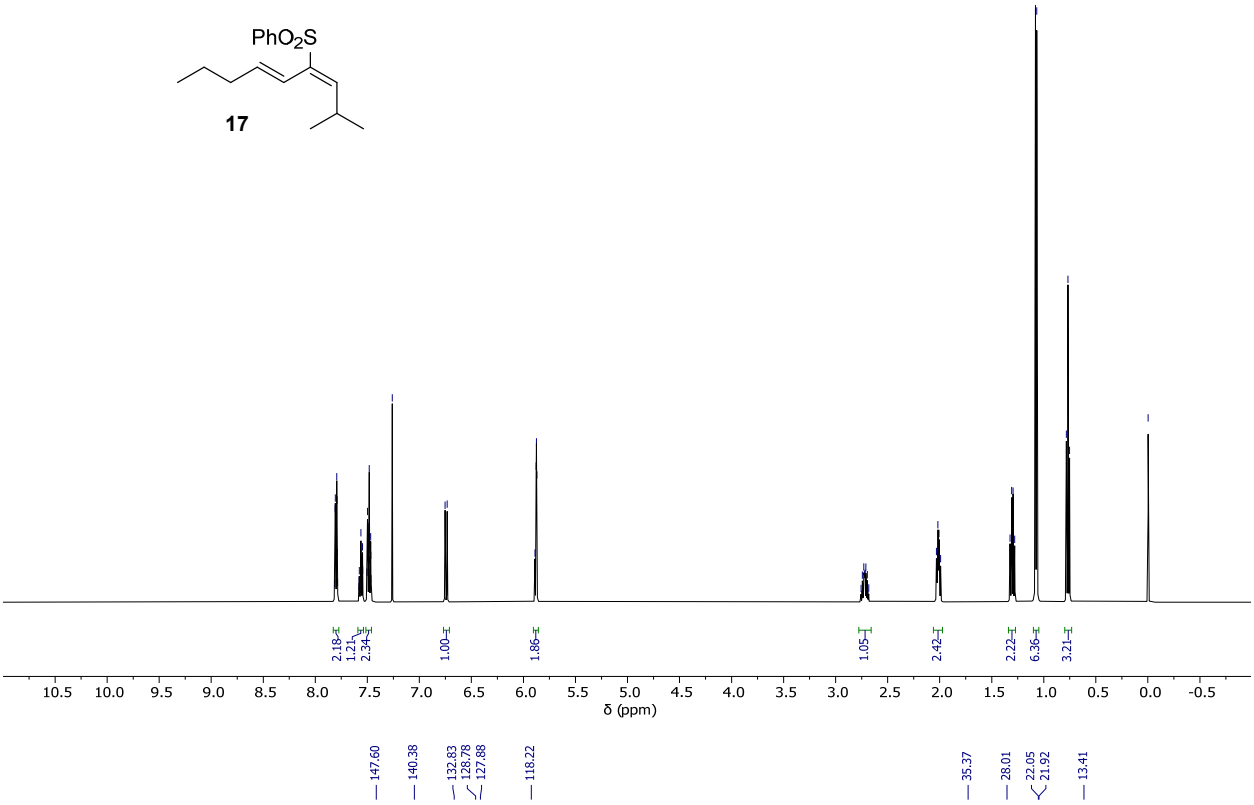
^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 126 MHz)



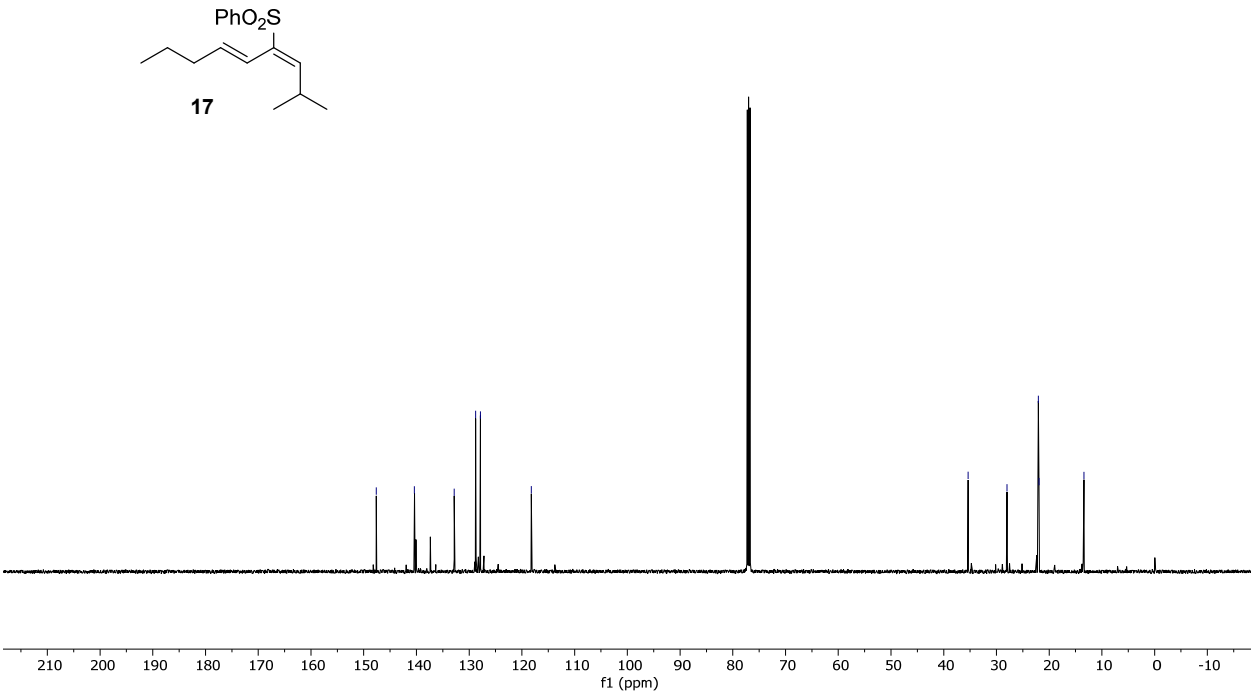
15

WEC-WA-58+59-F15_1.fid

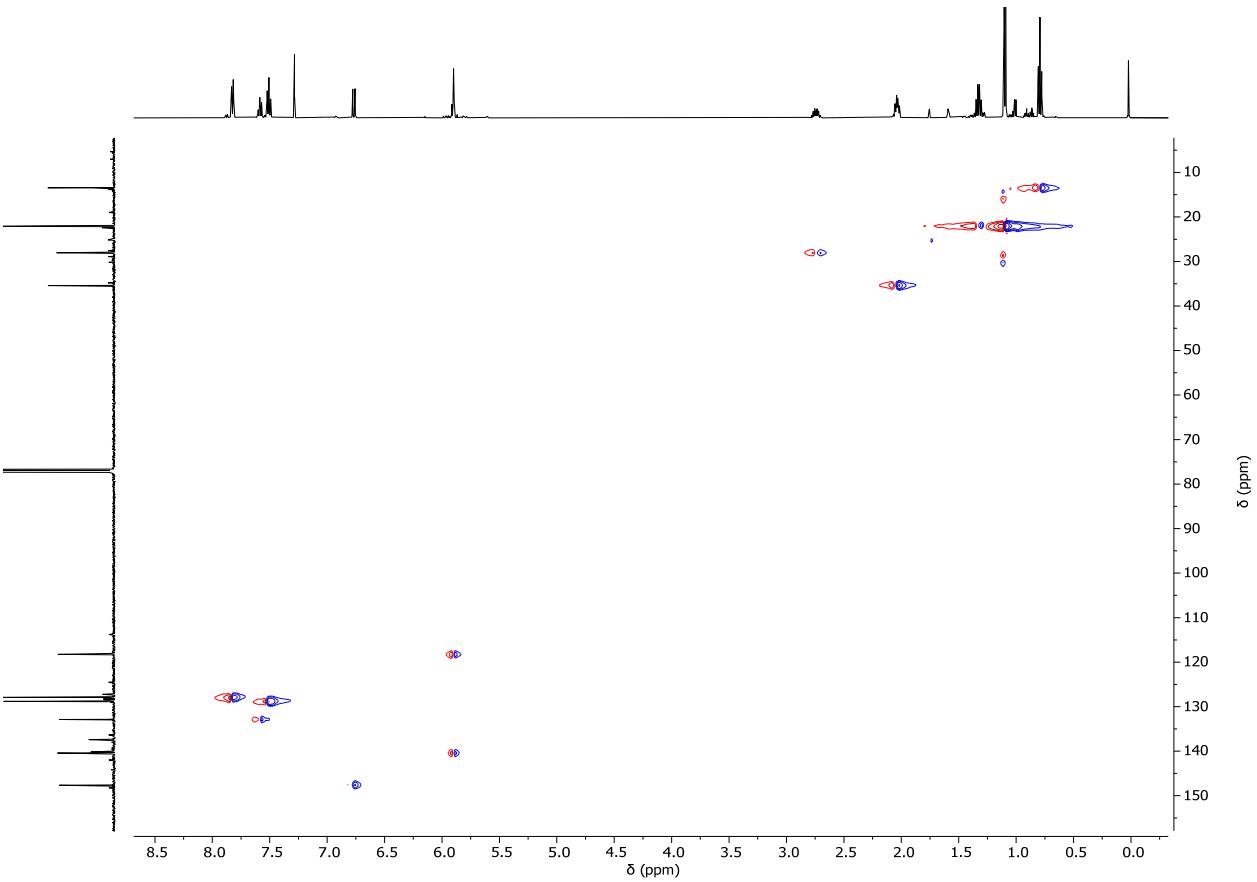
^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



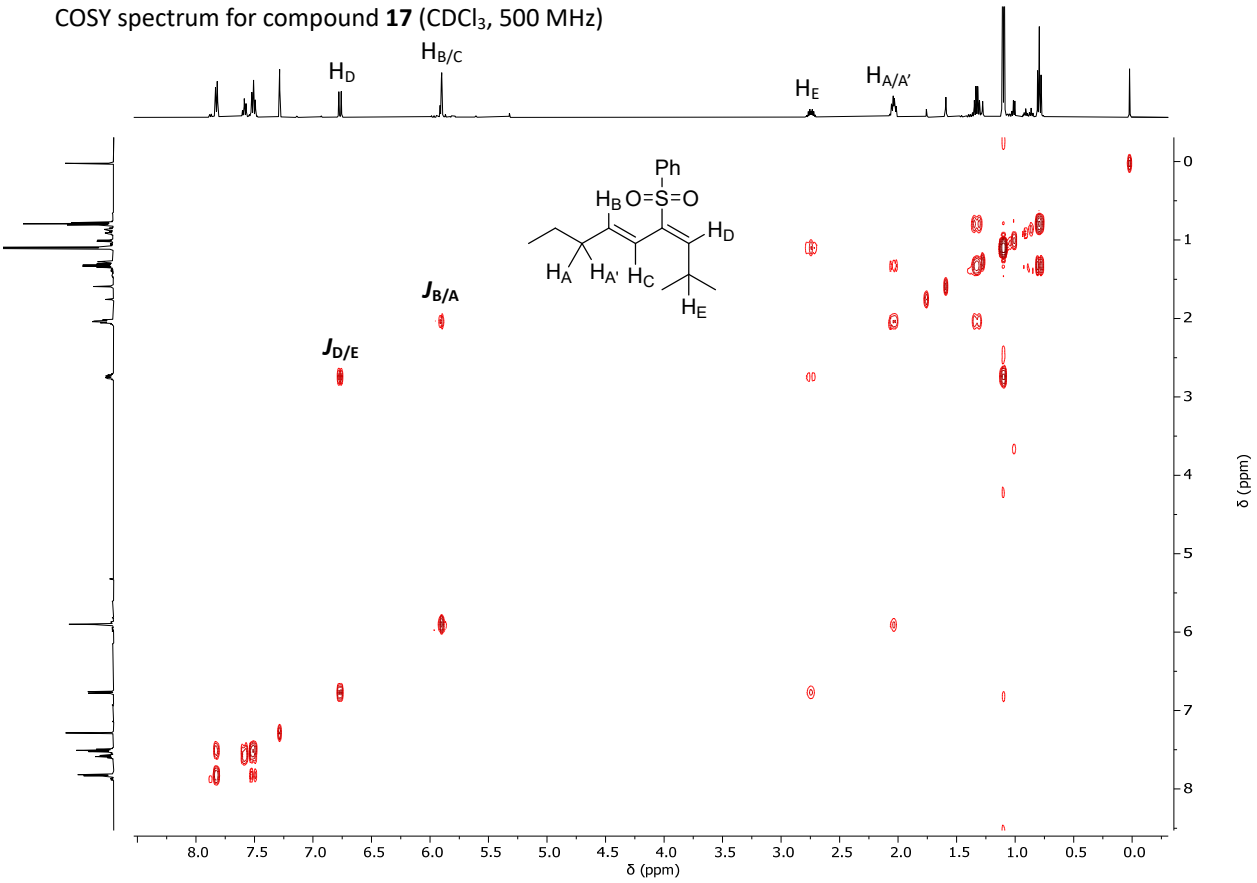
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 126 MHz)



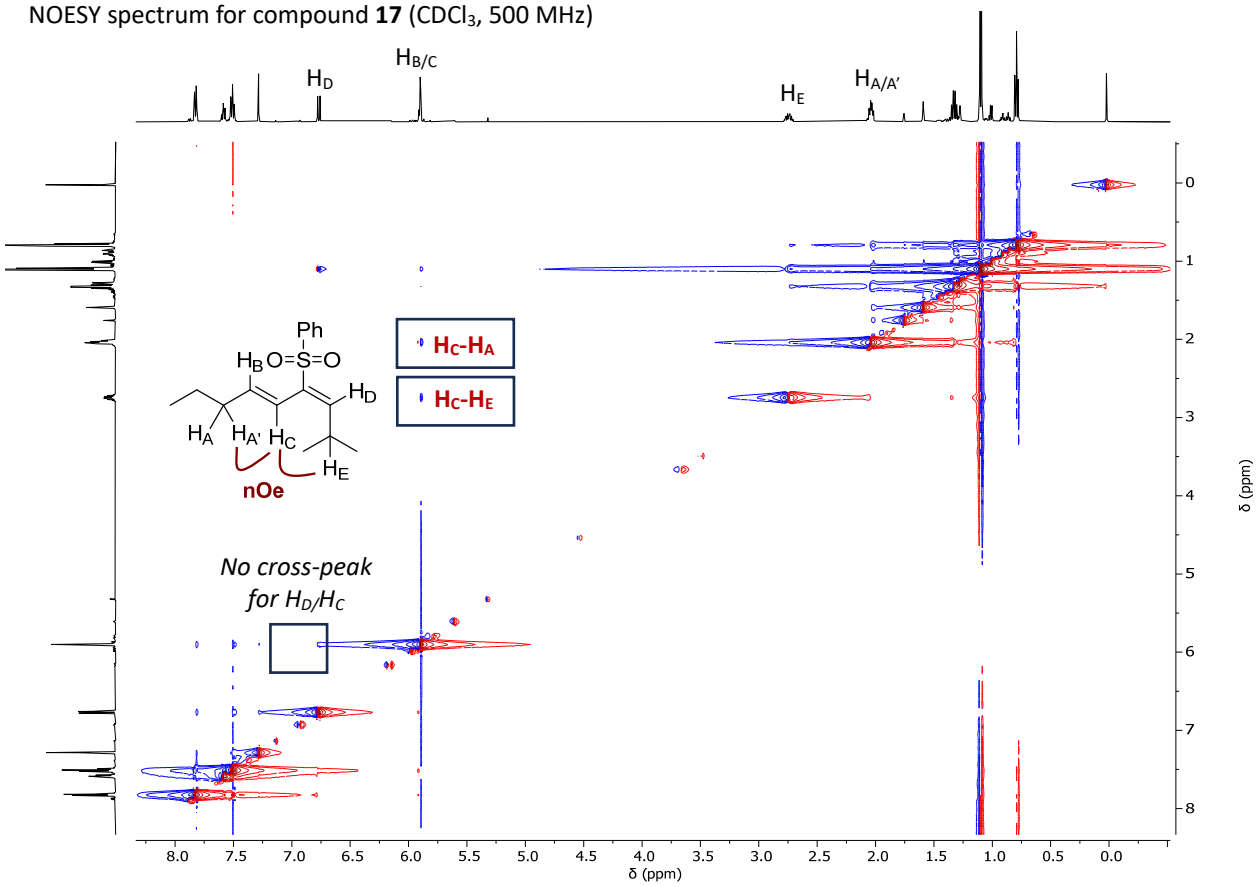
HSQC spectrum for compound **17** ($CDCl_3$, 500 MHz)



COSY spectrum for compound **17** ($CDCl_3$, 500 MHz)



NOESY spectrum for compound **17** ($CDCl_3$, 500 MHz)



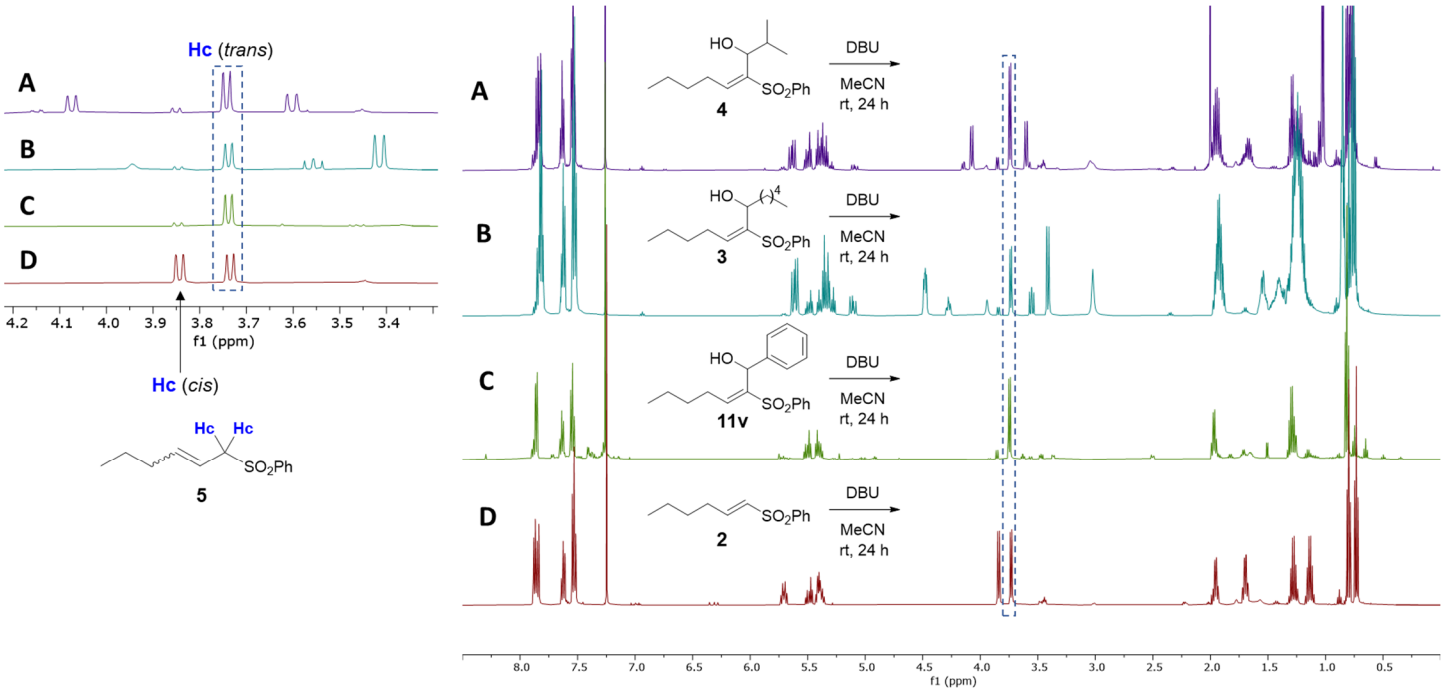
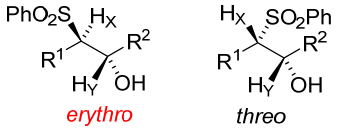


Figure S1. Comparison of crude product mixtures by ^{1}H NMR obtained from the DBU isomerization of different vinylsulfone starting materials. β-hydroxysulfones **4** (top, spectrum A) and **3** (spectrum B) gave primarily the isomerized allylic sulfone product, whereas **11v** produced almost exclusively 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 ~1:1 *cis*:*trans* mixture (spectrum D).

Table S1. Tables of ^{1}H NMR coupling constants for various beta-hydroxysulfones stereoisomers previously reported by Mase and coworkers[1] (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.



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

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

Notes for Table: ^{1}H NMR spectra were acquired in $CDCl_3$ as solvent. [a]Not 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.