Electronic Supporting Information of the Manuscript:

Highly Diastereoselective Oxidation of β-Thioglycosides: The *exo*-anomeric effect Paves the Way

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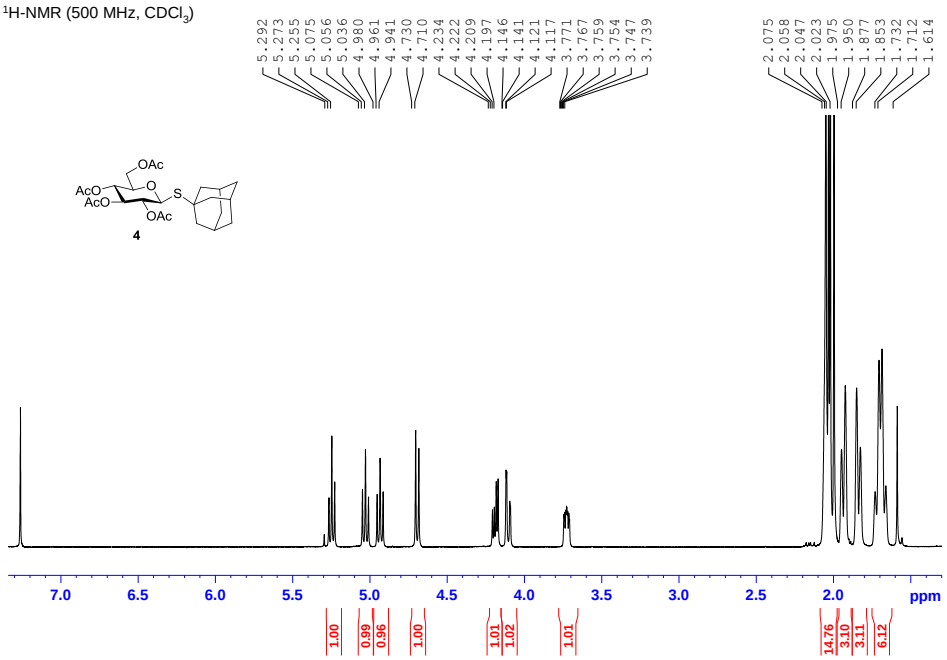
^{1}H-NMR (500 MHz, $CDCl_3$)



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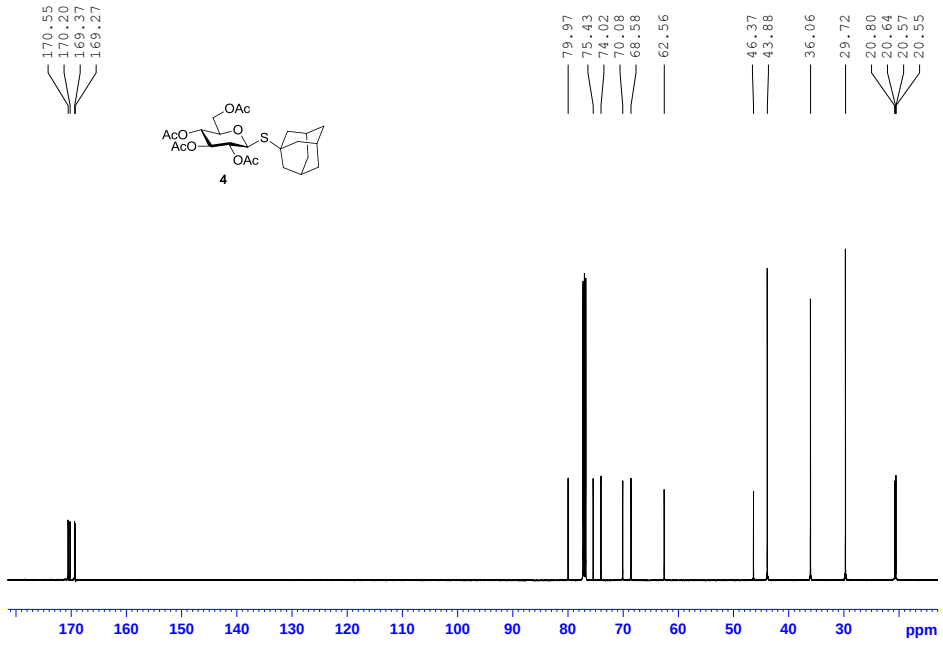

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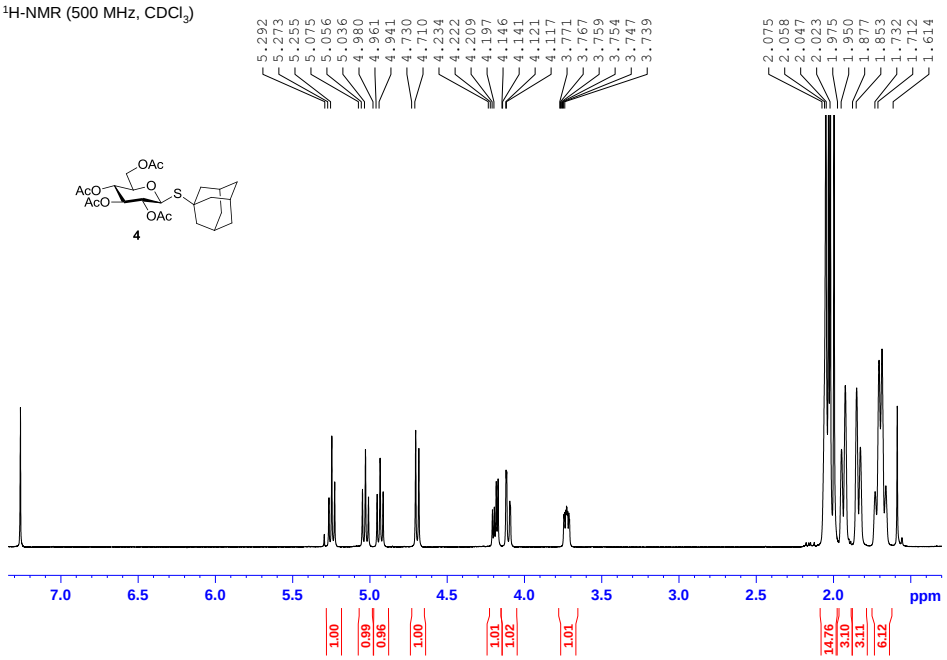

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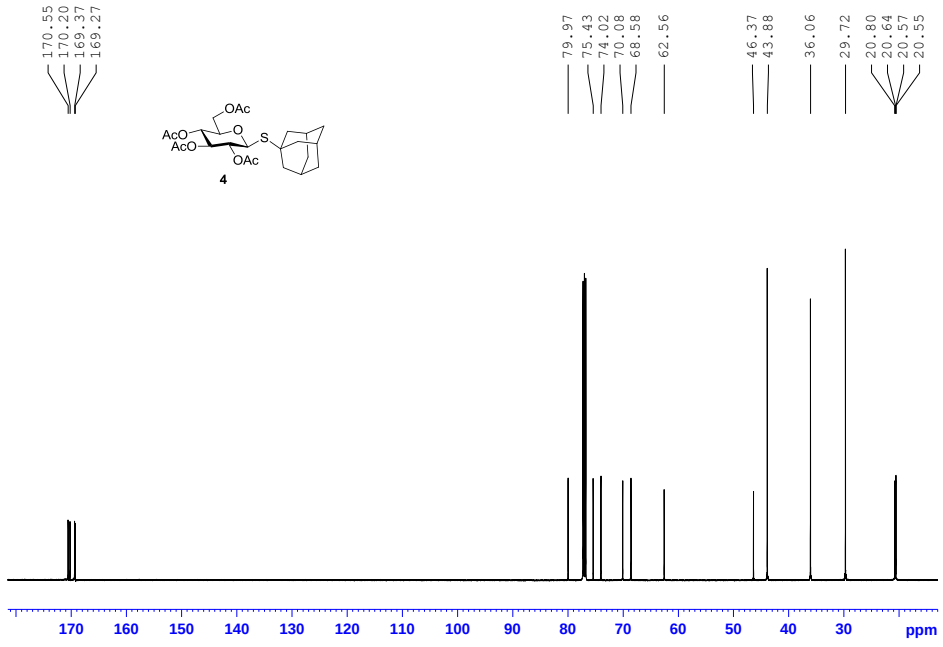

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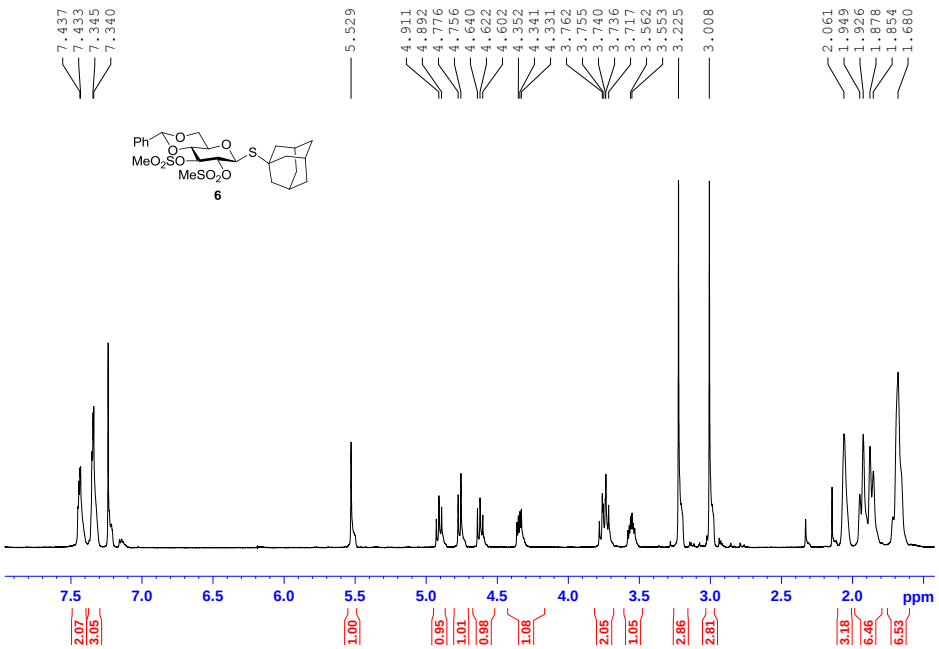

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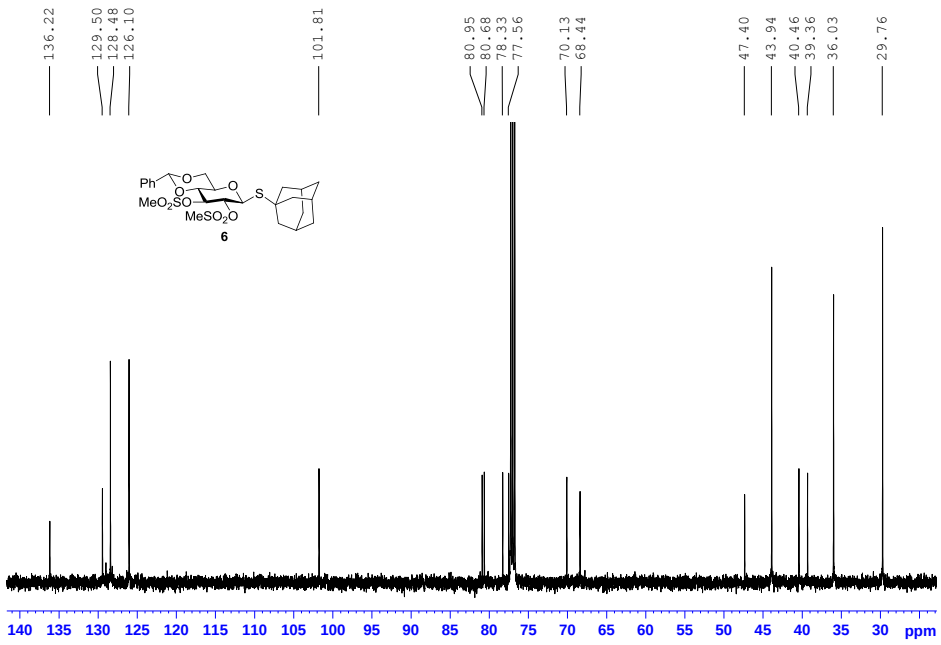

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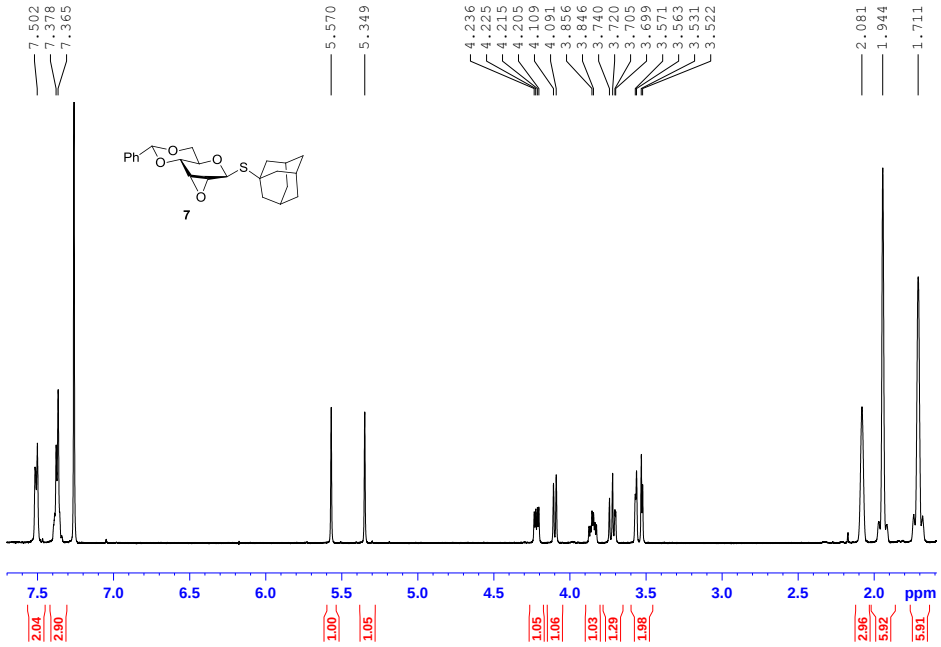

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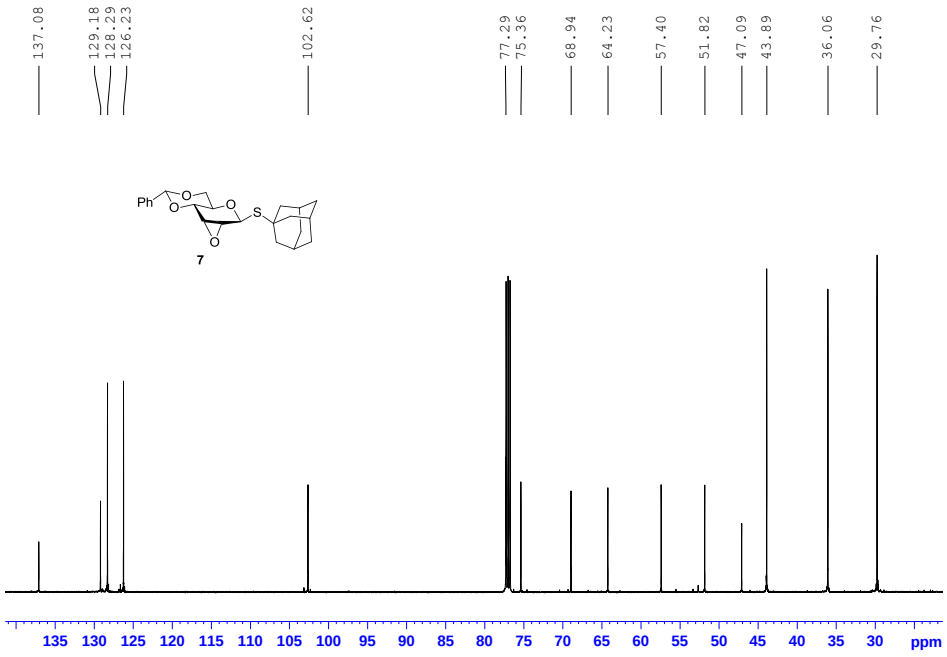

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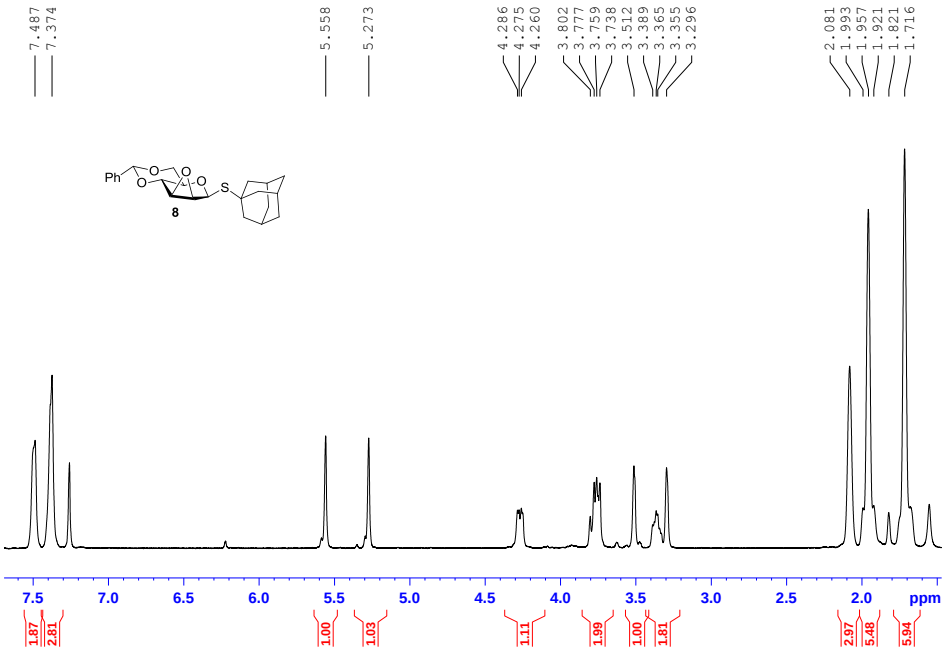

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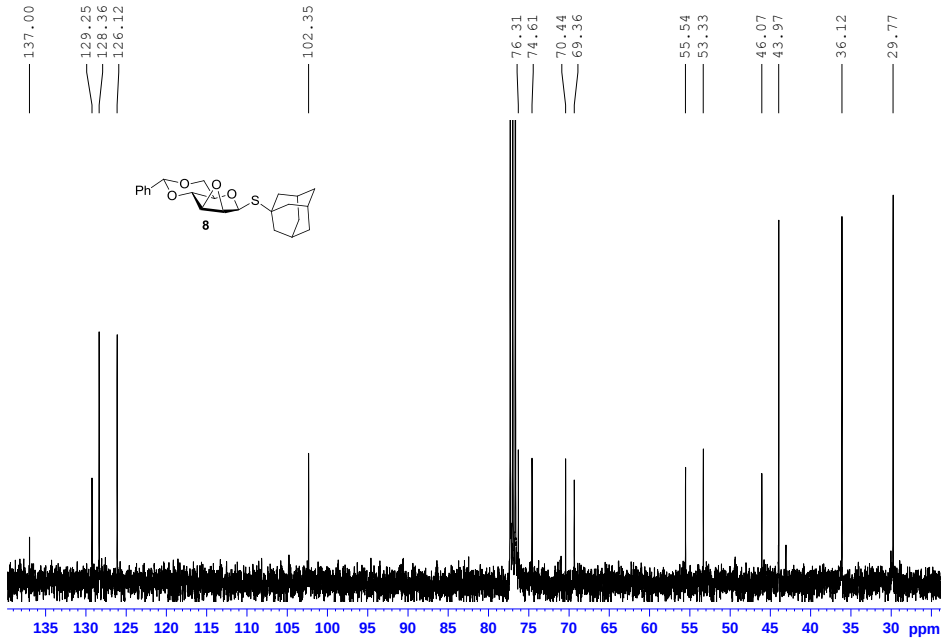

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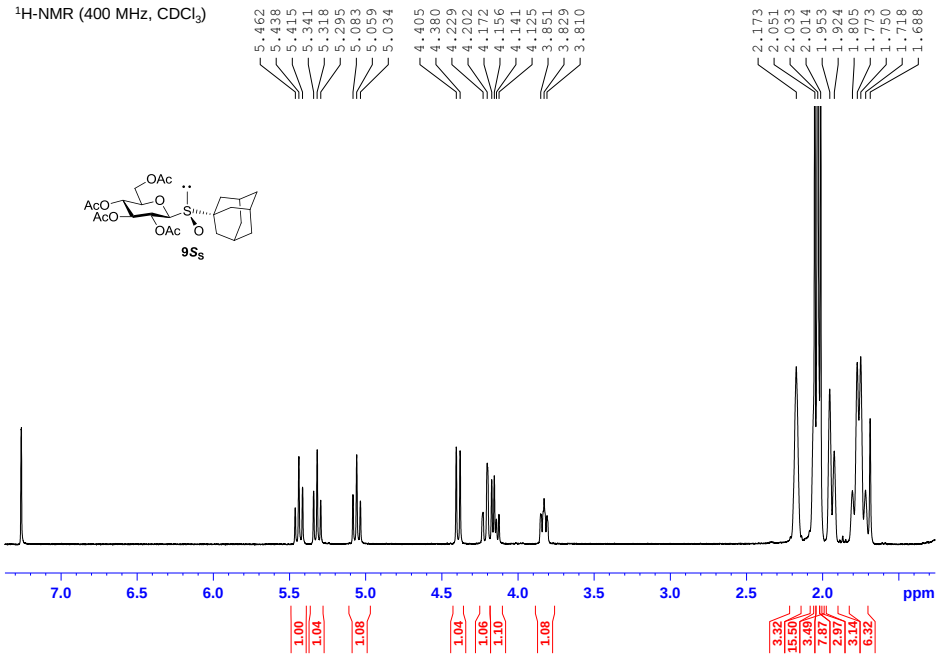

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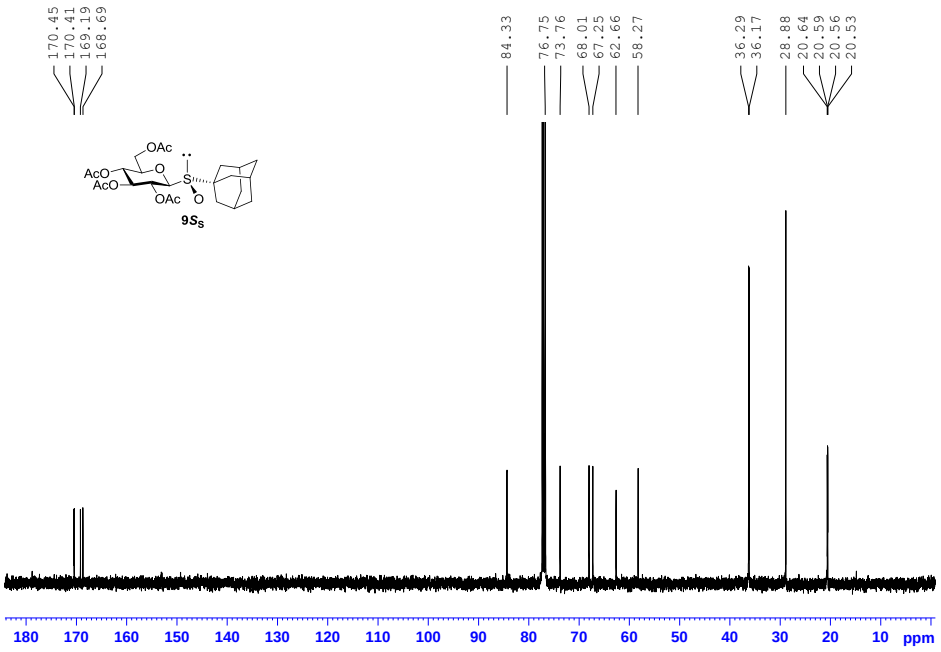

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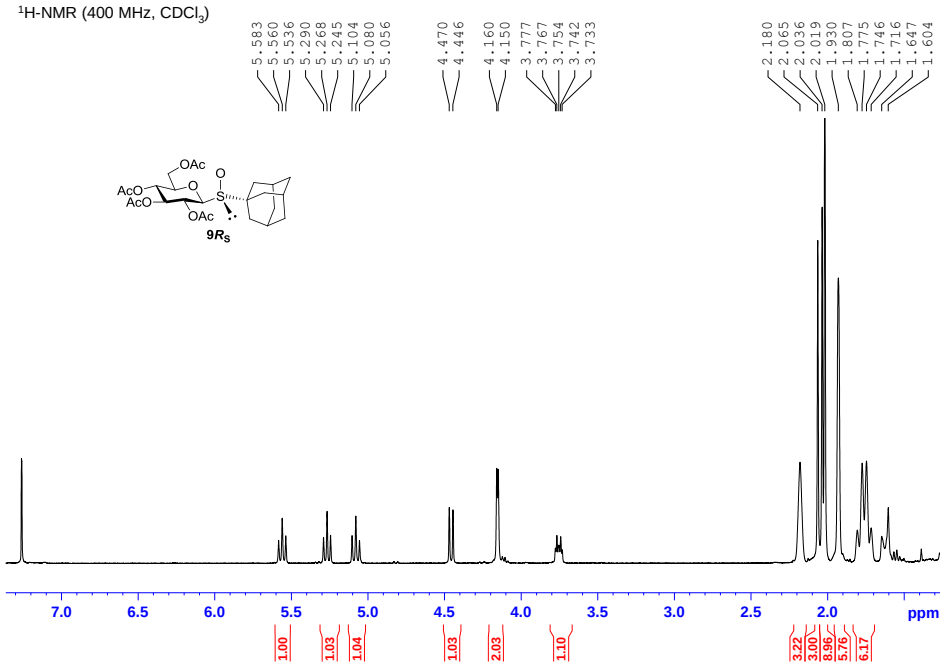

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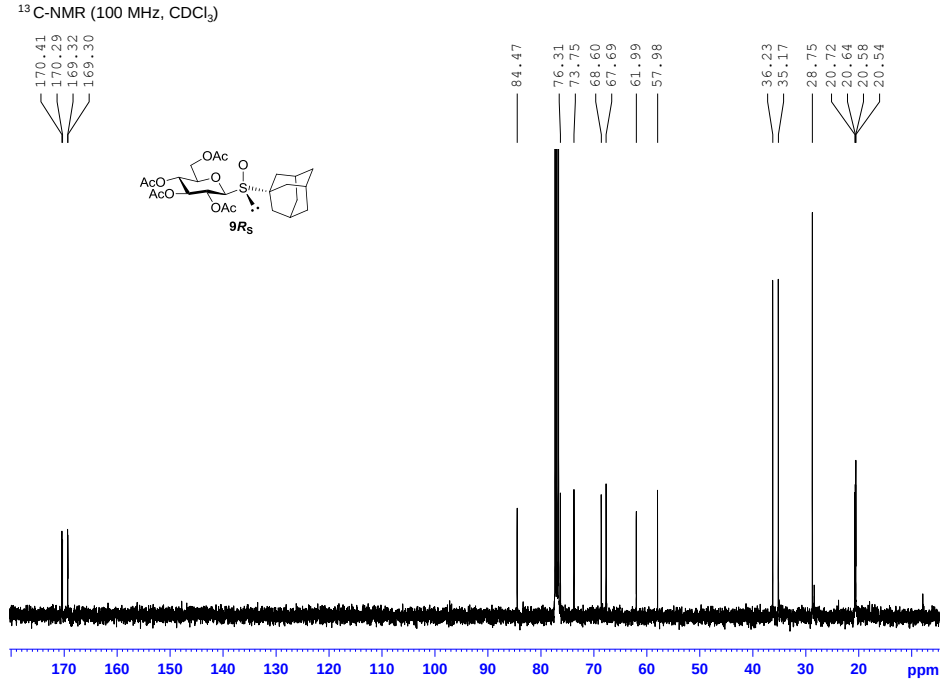

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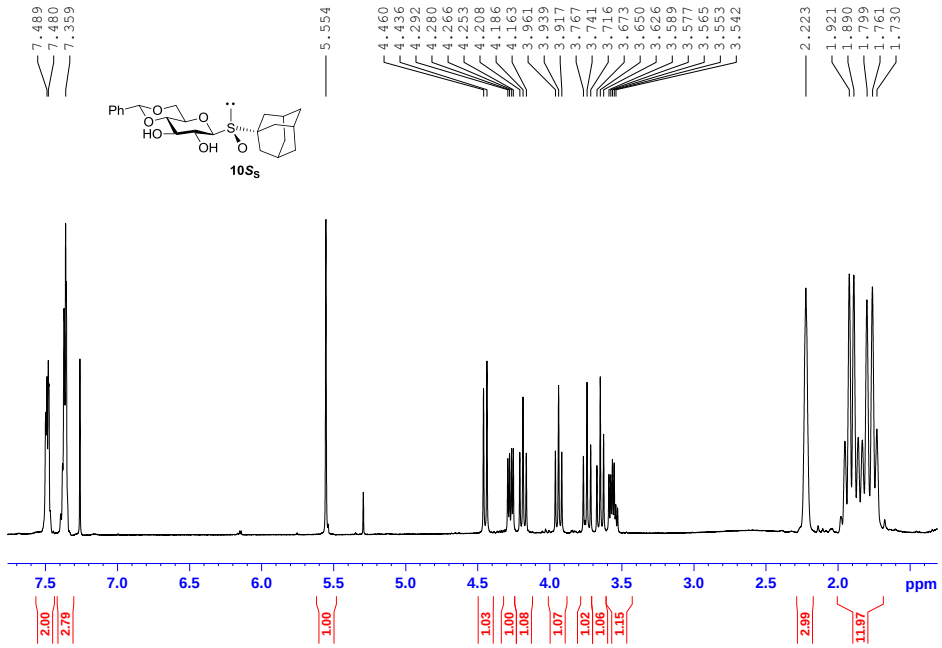

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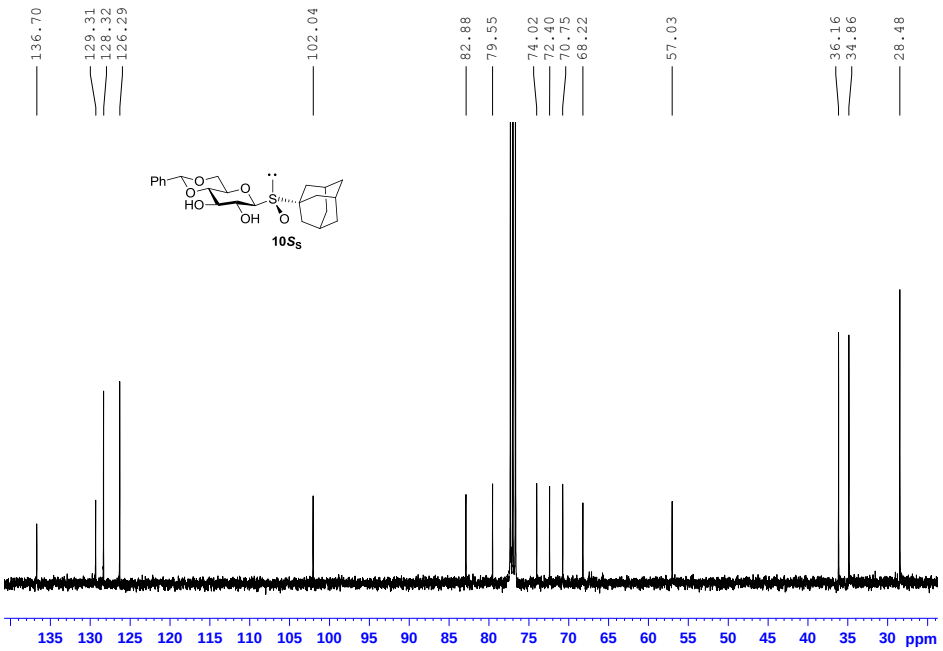

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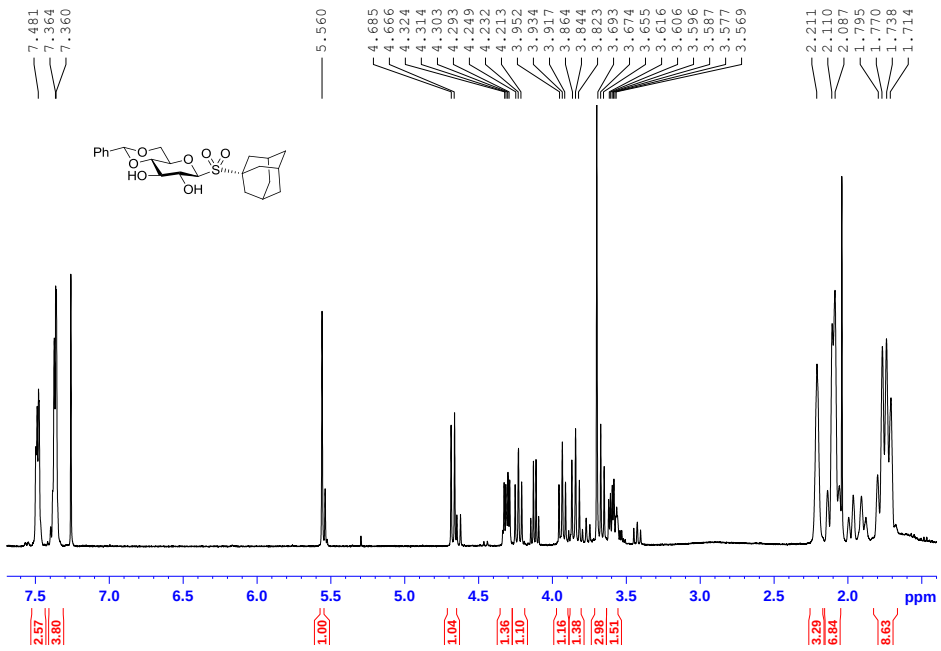

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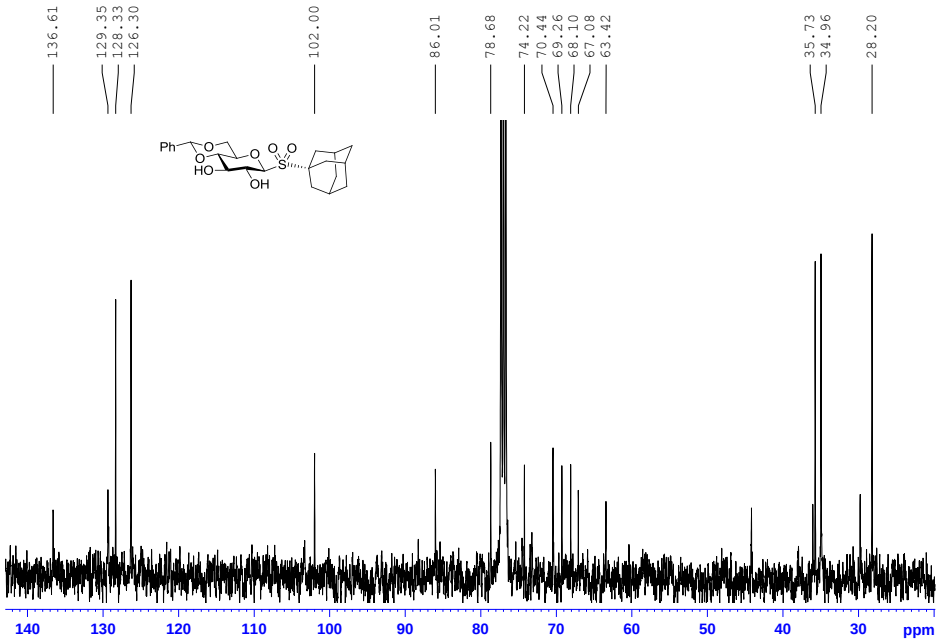

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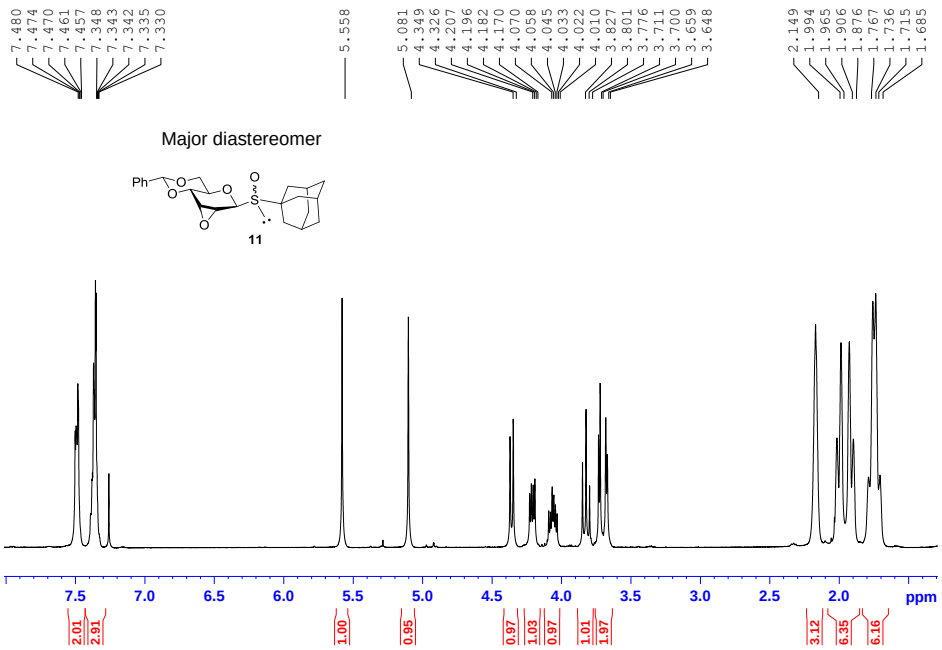

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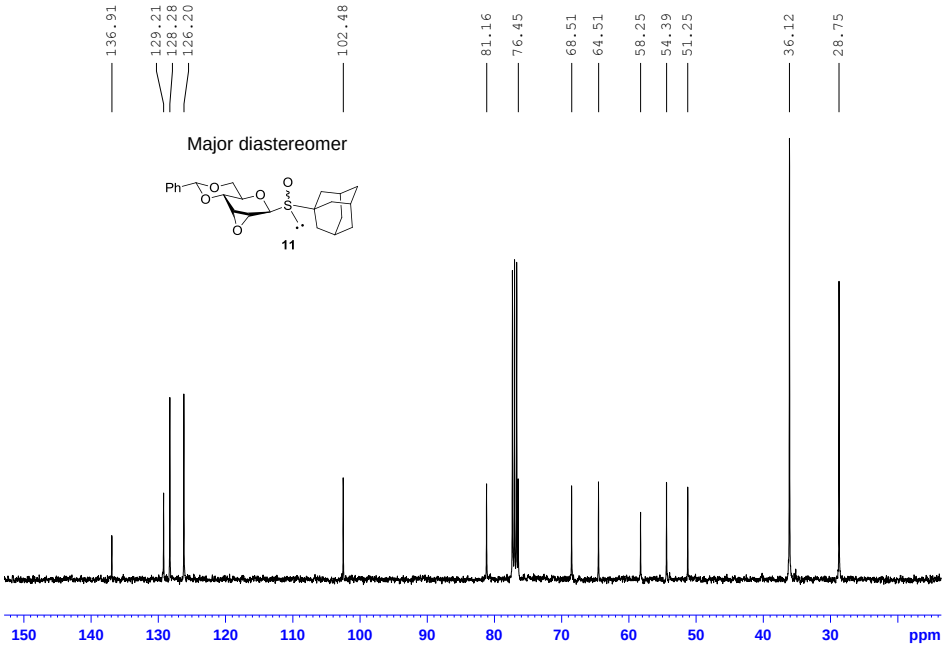

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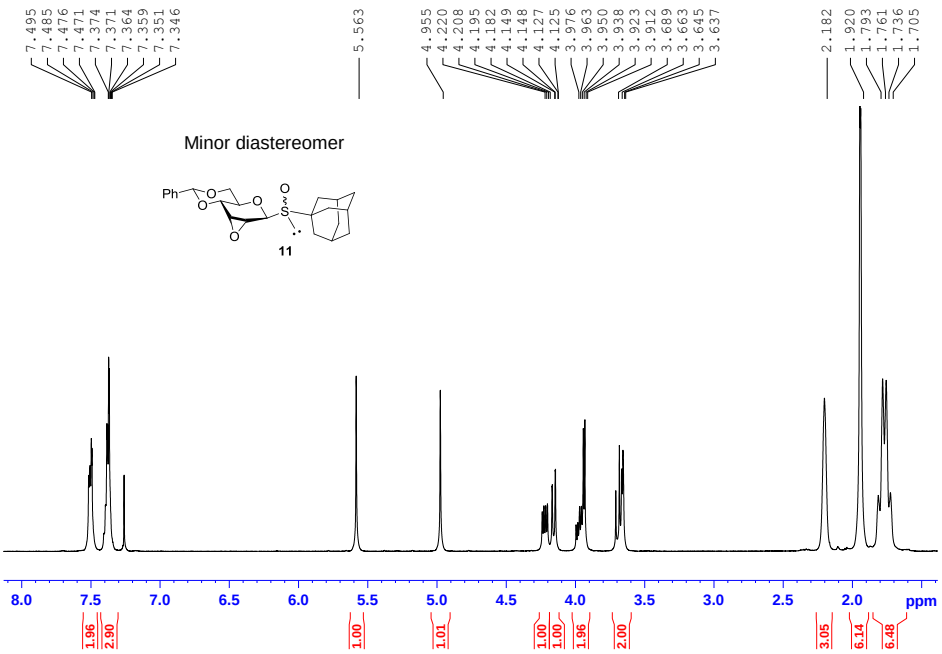

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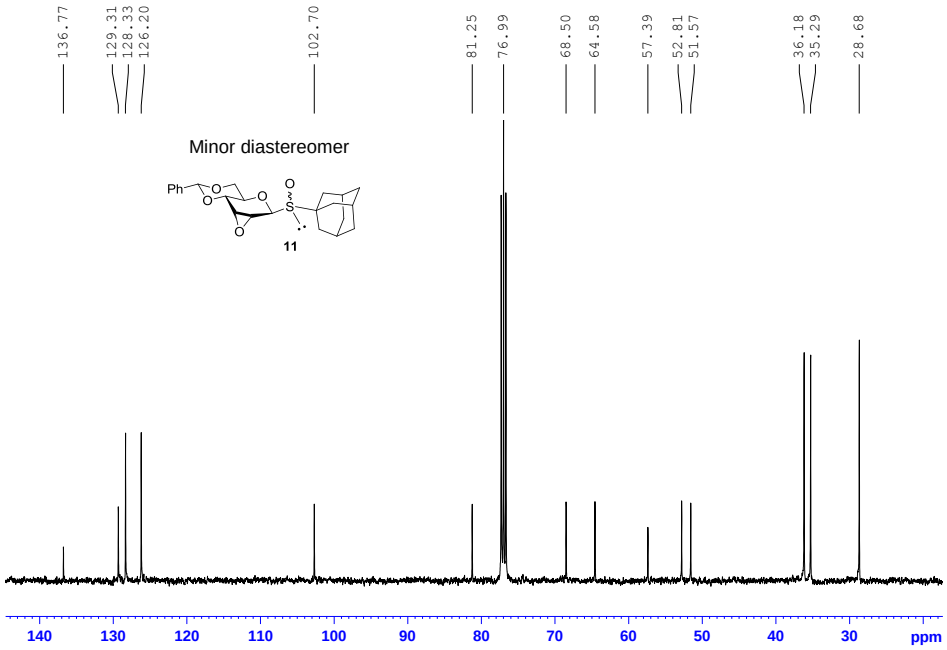

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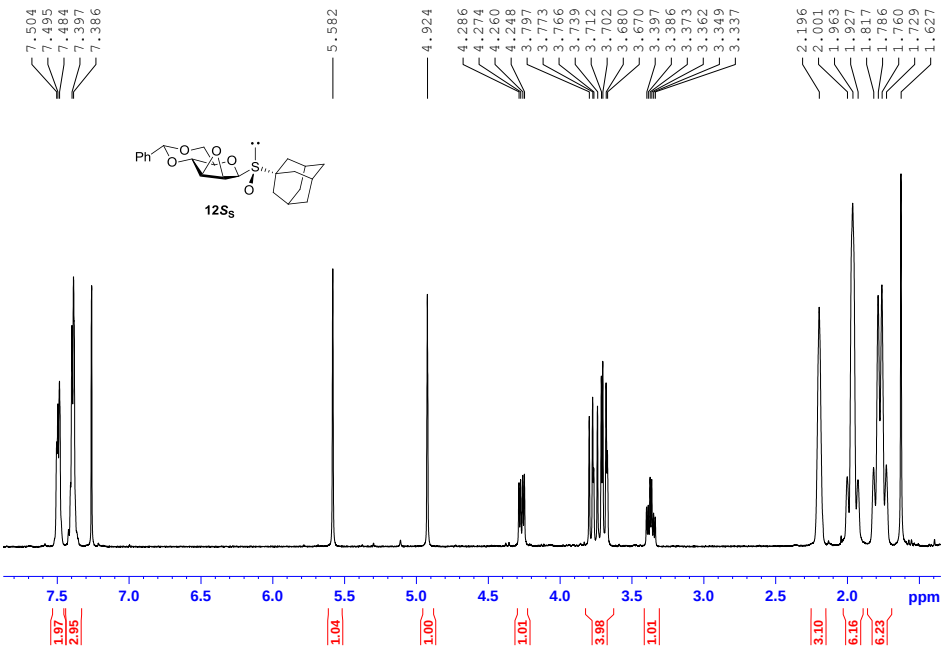

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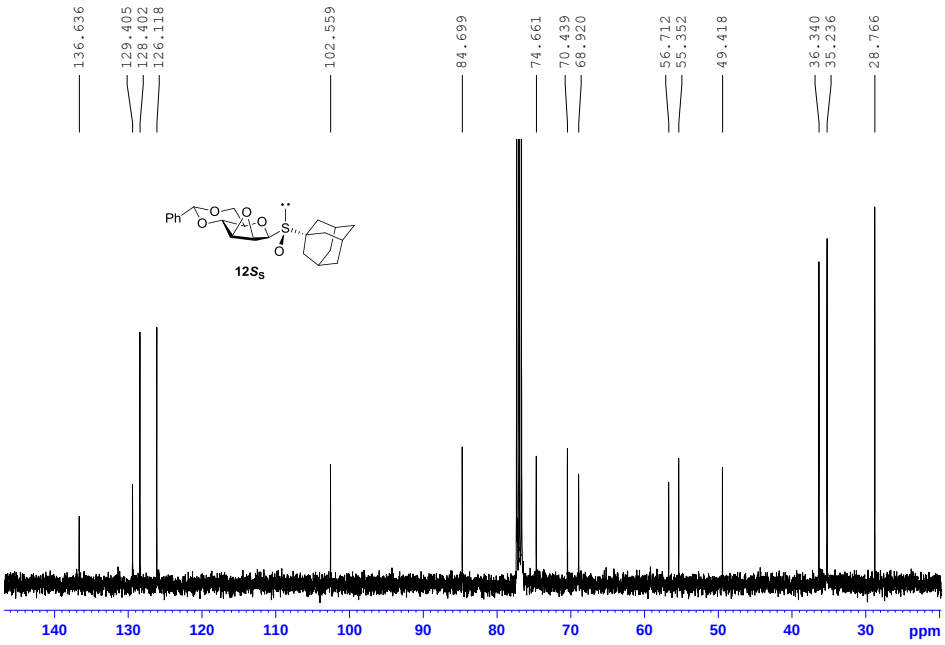

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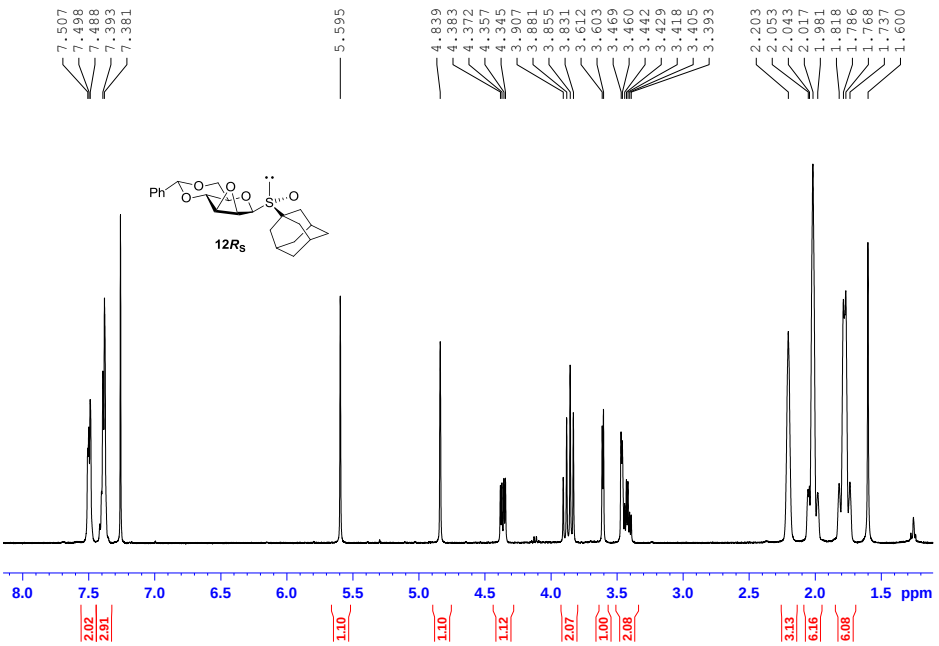

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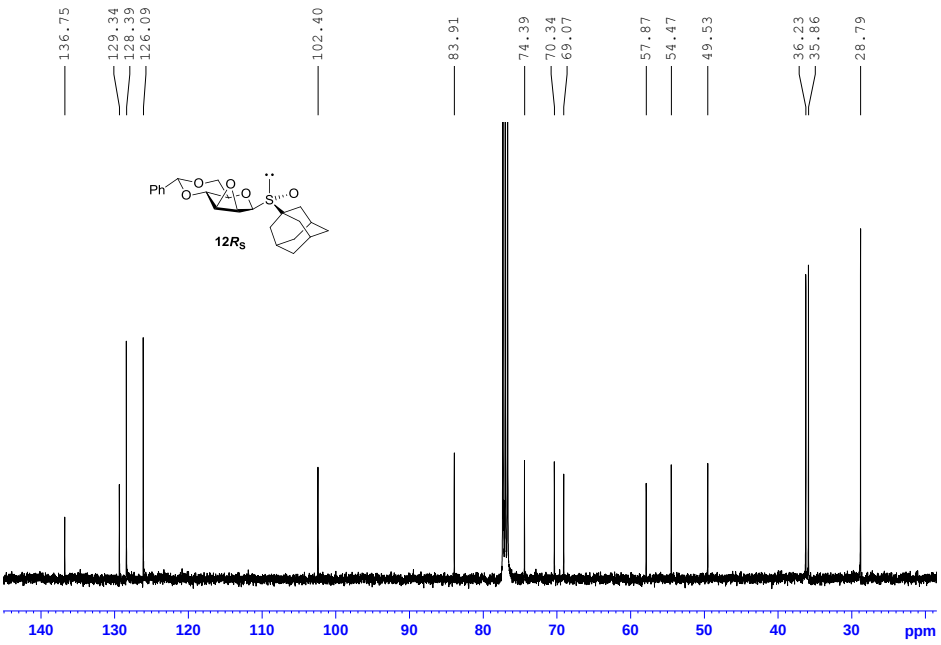

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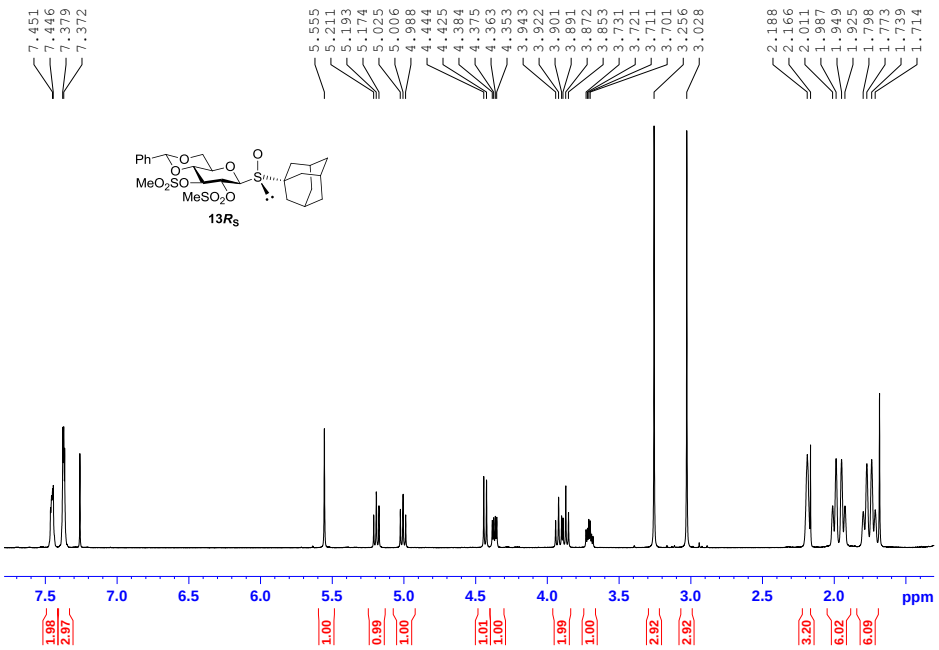

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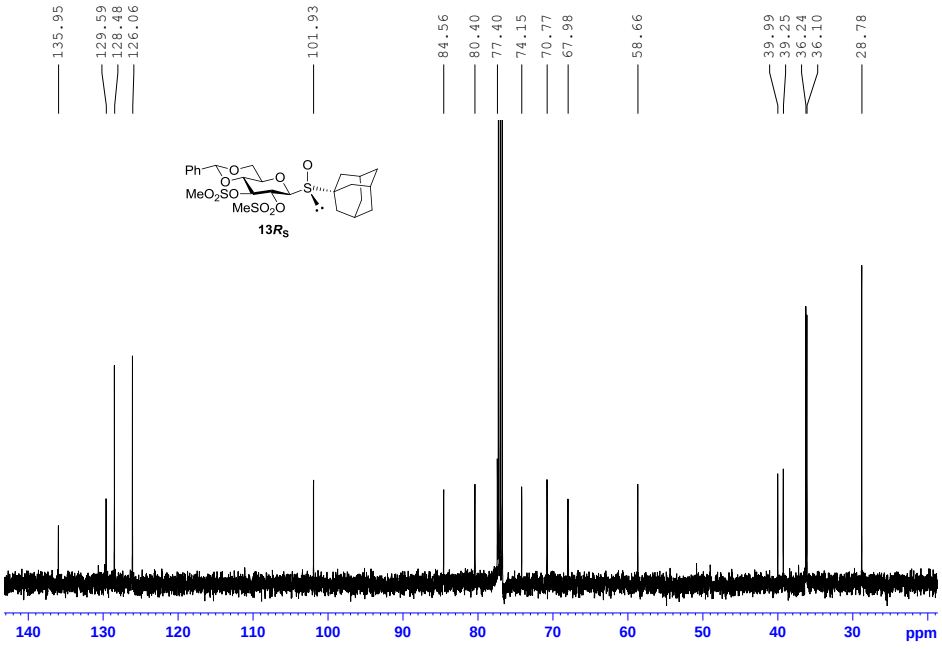

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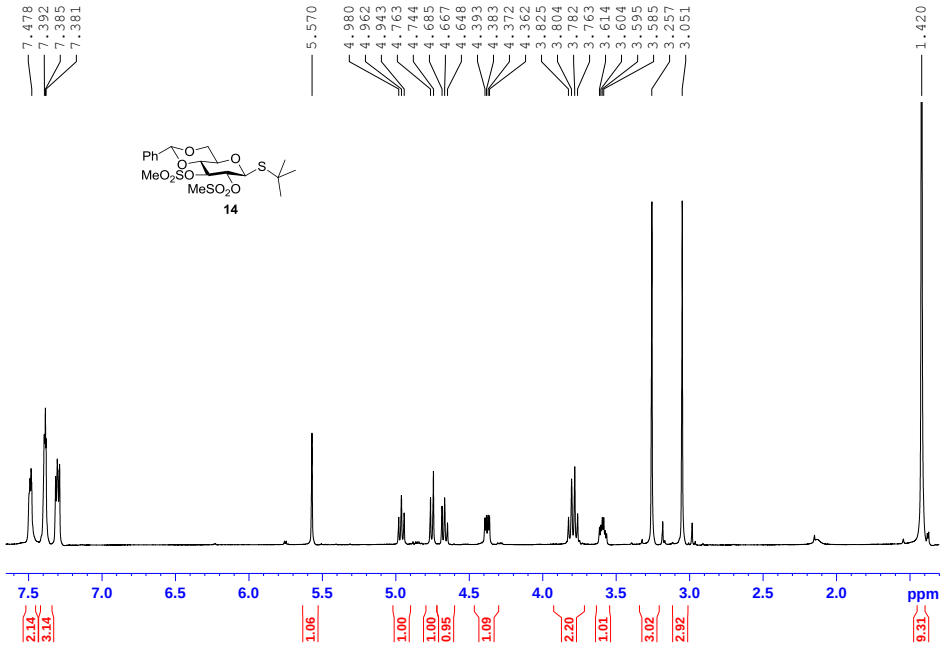

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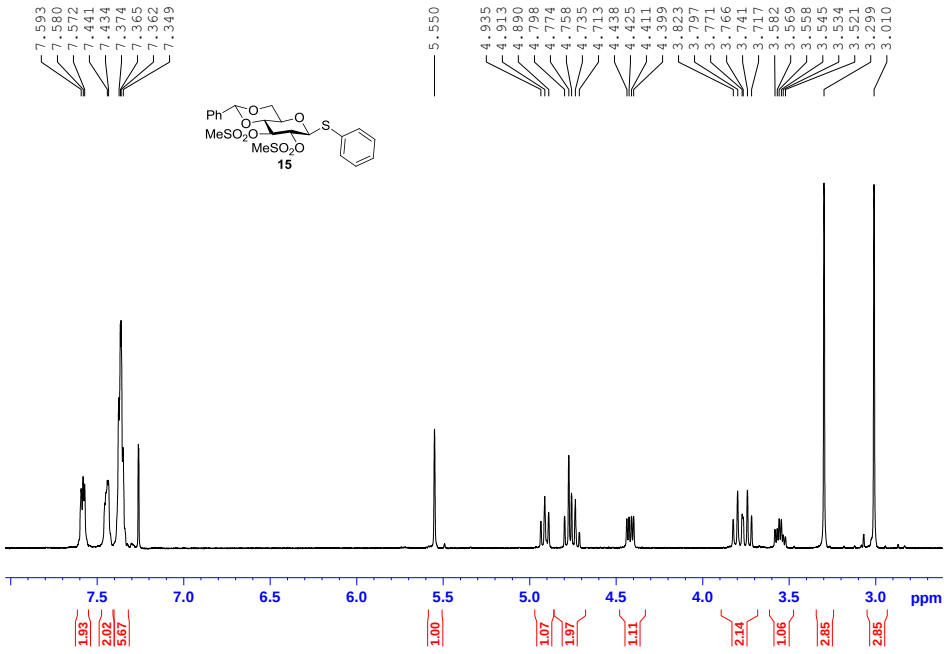

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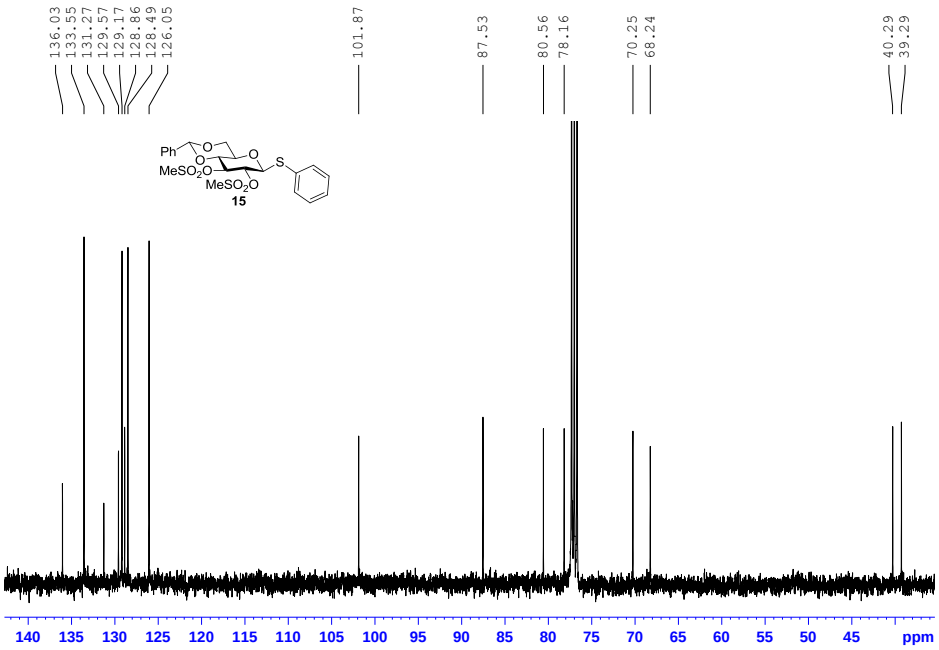

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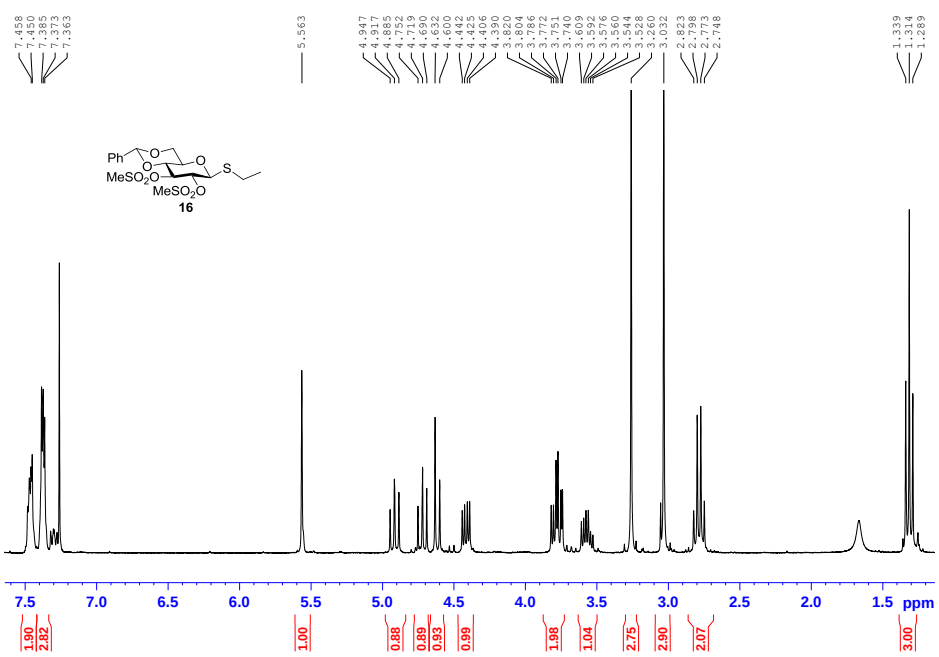

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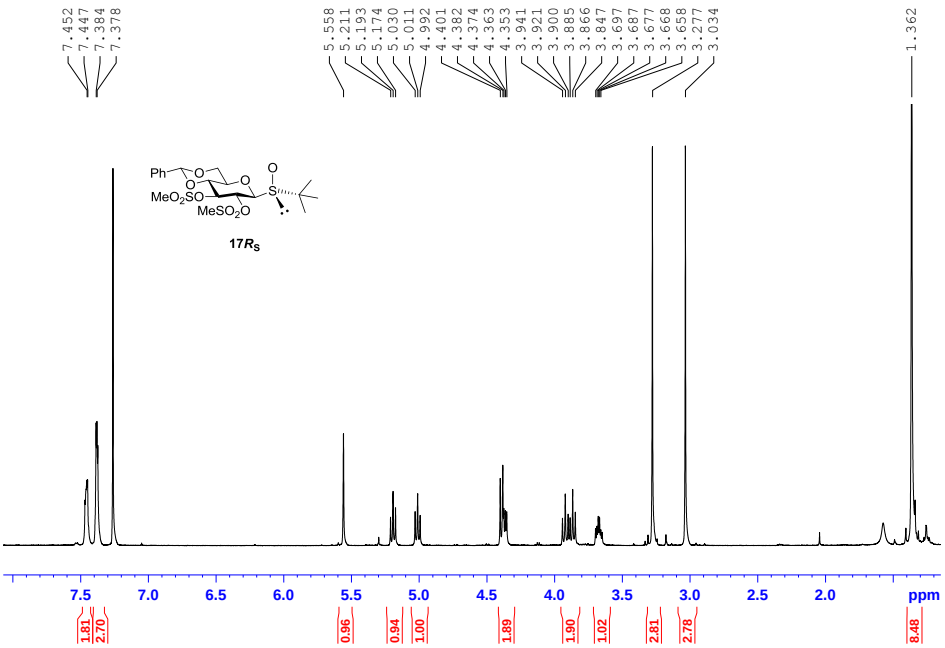

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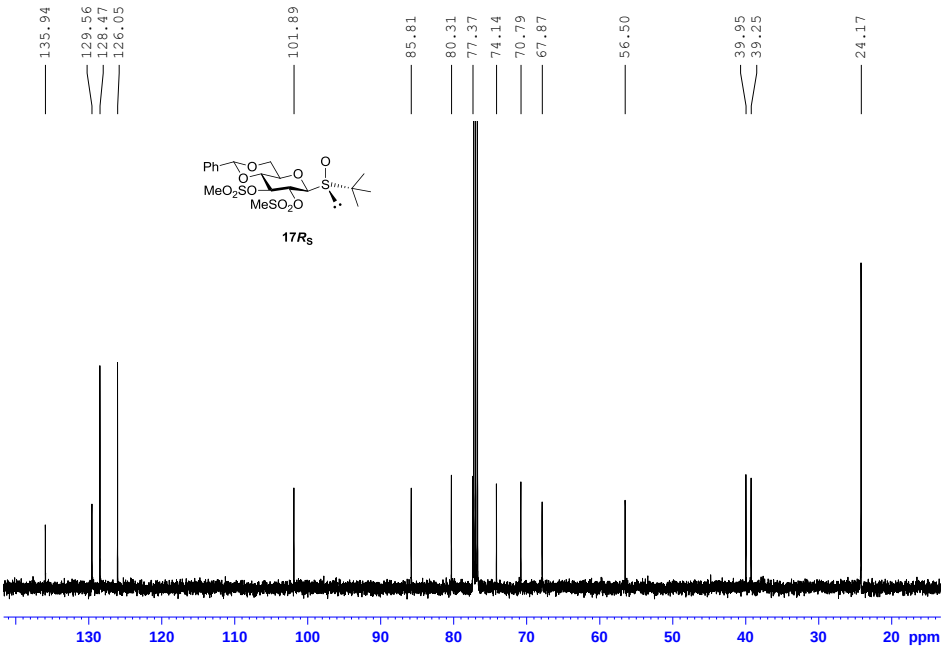

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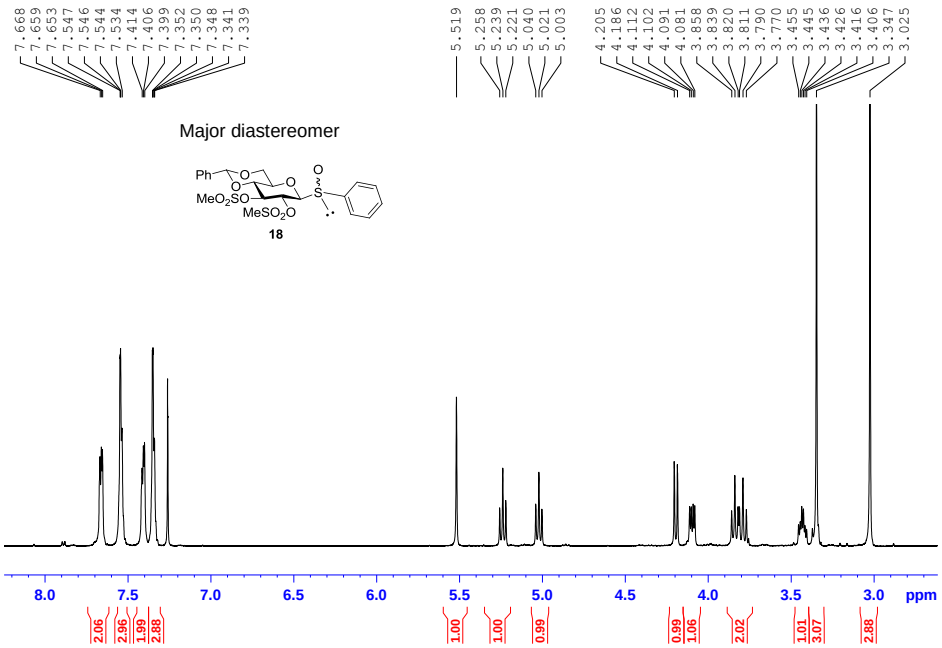

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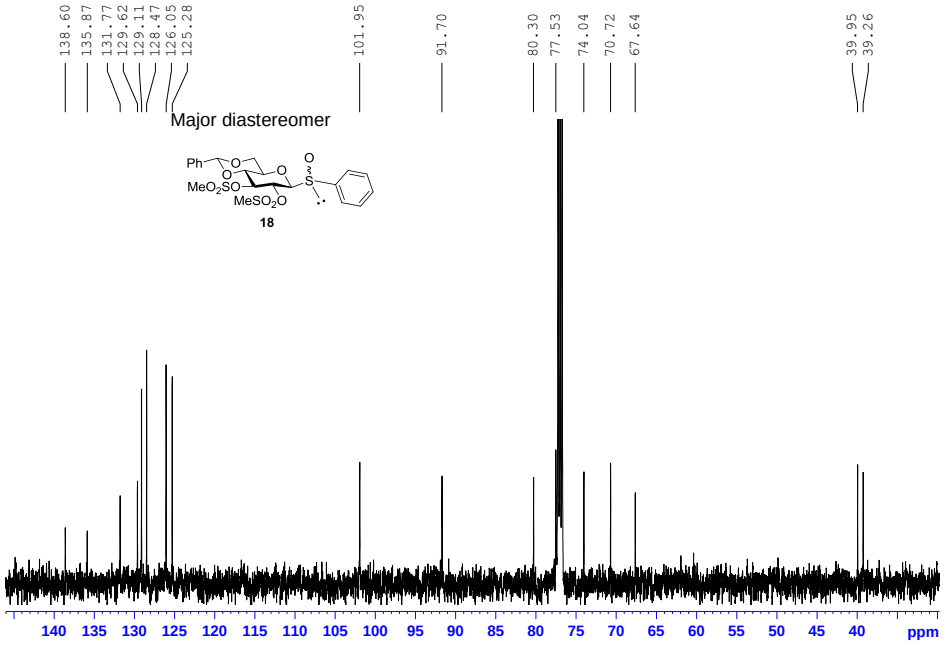

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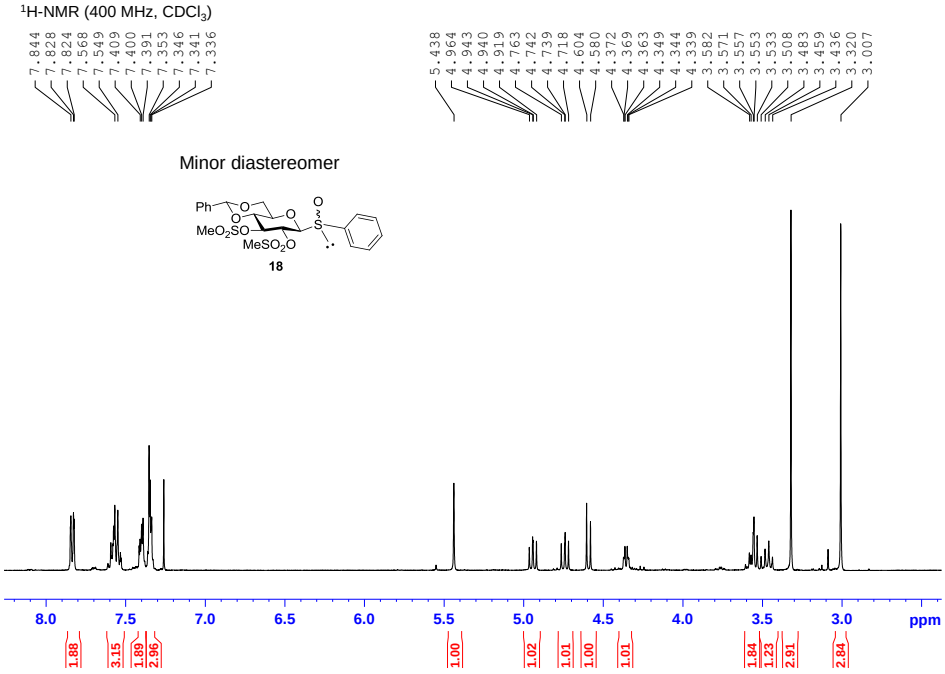

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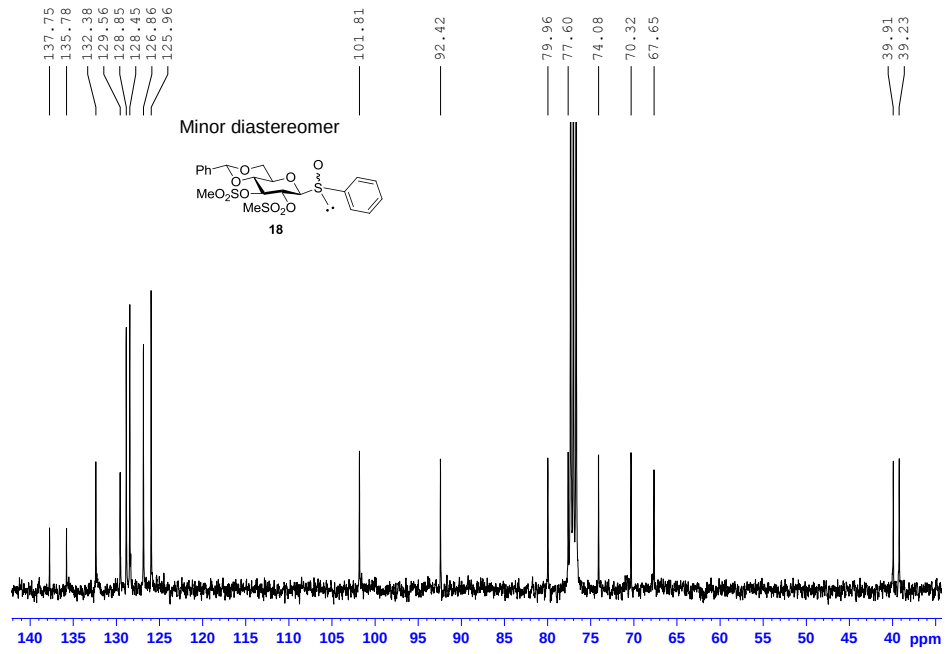

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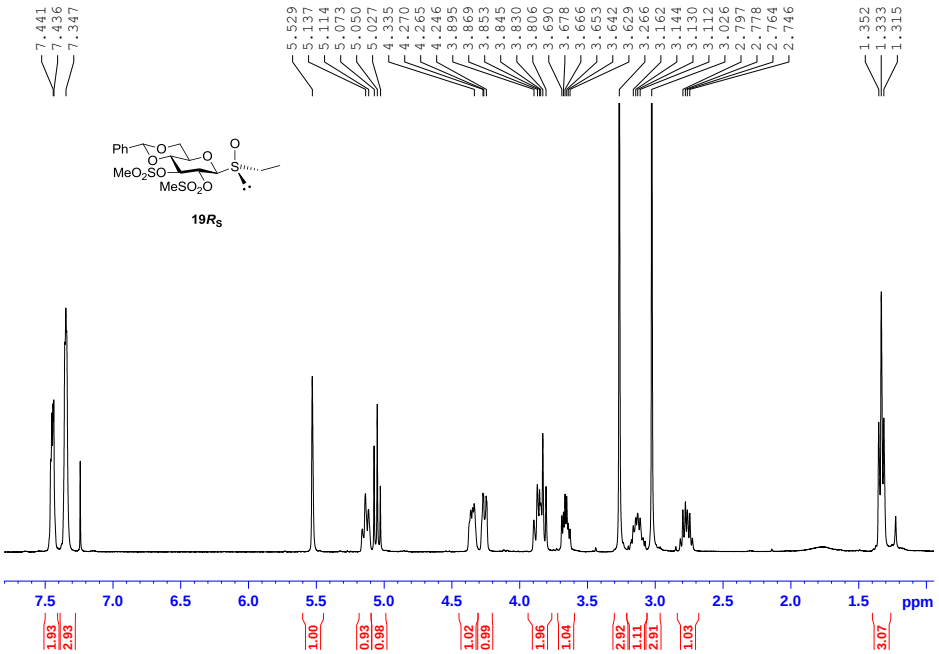

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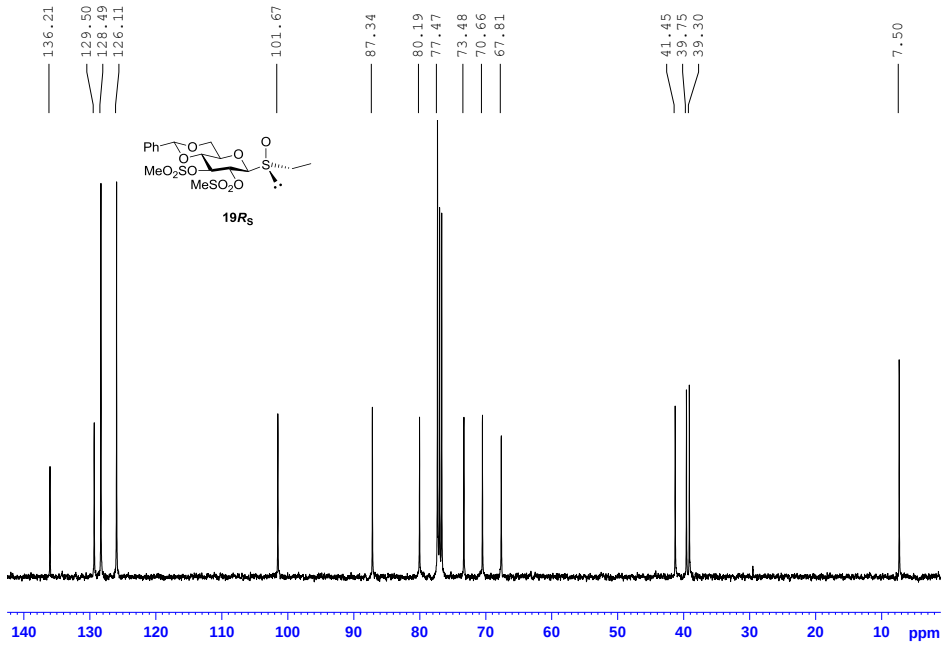

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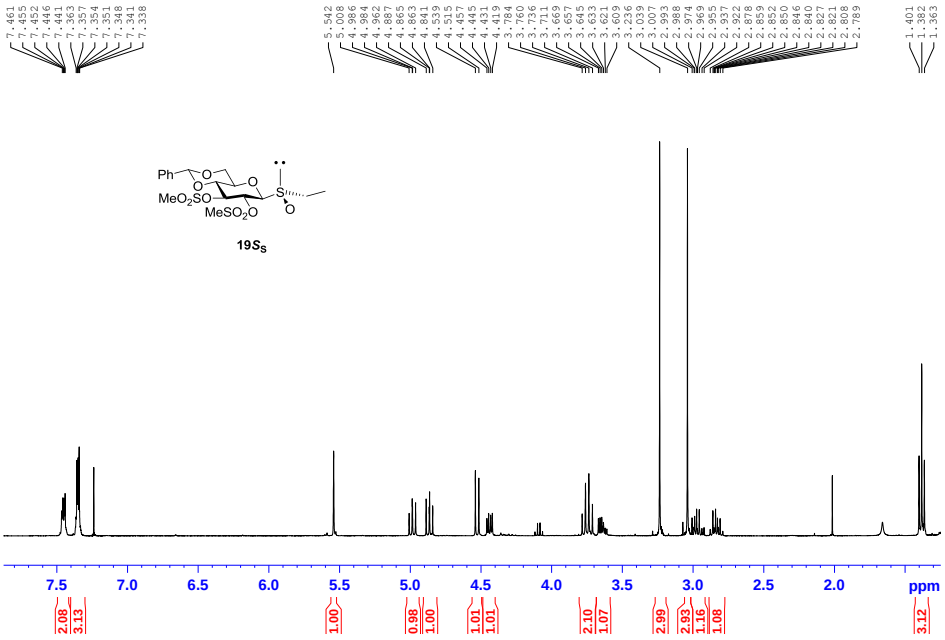

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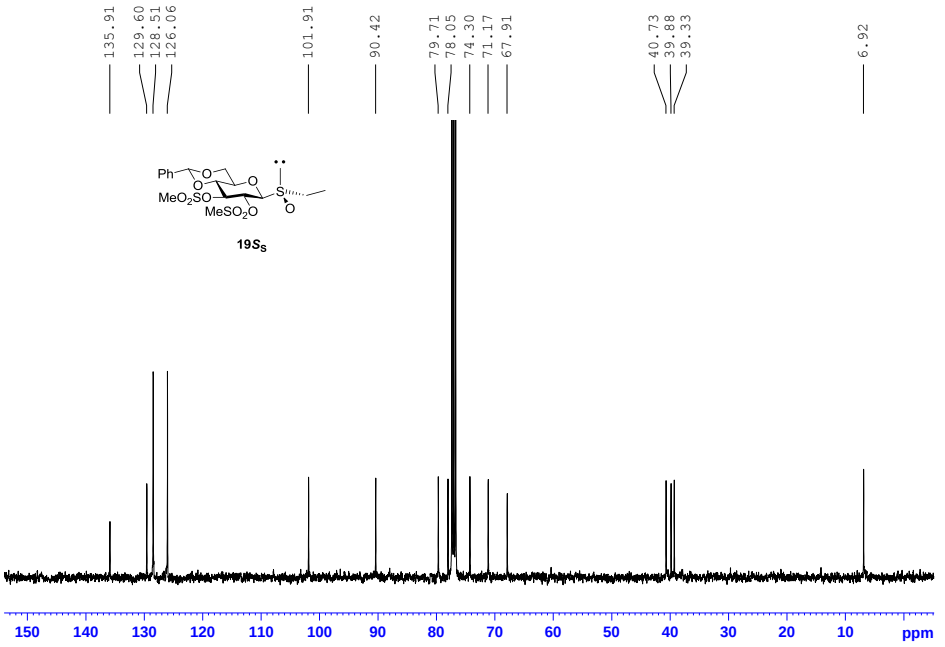

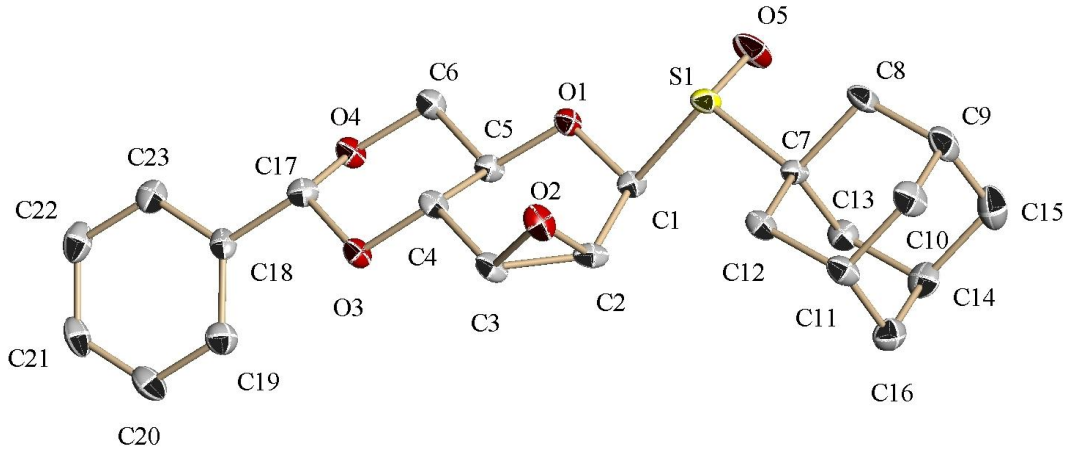

Table S1. Crystal data and structure refinement for compound **12*R*$_S$**.

Empirical formula	$C_{23}H_{28}O_5S$	
Formula weight	416.51	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 20.294(3) Å	α= 90°.
	b = 6.4701(8) Å	β= 96.306(4)°.
	c = 15.4757(17) Å	γ = 90°.
Volume	2019.7(4) Å^3	
Z	4	
Density (calculated)	1.370 Mg/m^3	
Absorption coefficient	0.193 mm^{-1}	
F(000)	888	
Crystal size	0.45 x 0.15 x 0.15 mm^3	
Theta range for data collection	3.15 to 25.22°.	
Index ranges	-17<=h<=24, -7<=k<=7, -13<=l<=18	
Reflections collected	10600	
Independent reflections	3042 [R(int) = 0.0391]	

Completeness to theta = 25.22°	95.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9714 and 0.9660
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3042 / 1 / 262
Goodness-of-fit on F^2	1.170
Final R indices [I>2sigma(I)]	R1 = 0.0598, wR2 = 0.1608
R indices (all data)	R1 = 0.0768, wR2 = 0.1720
Absolute structure parameter	-0.05(15)
Largest diff. peak and hole	0.506 and -0.479 e.$Å^{-3}$

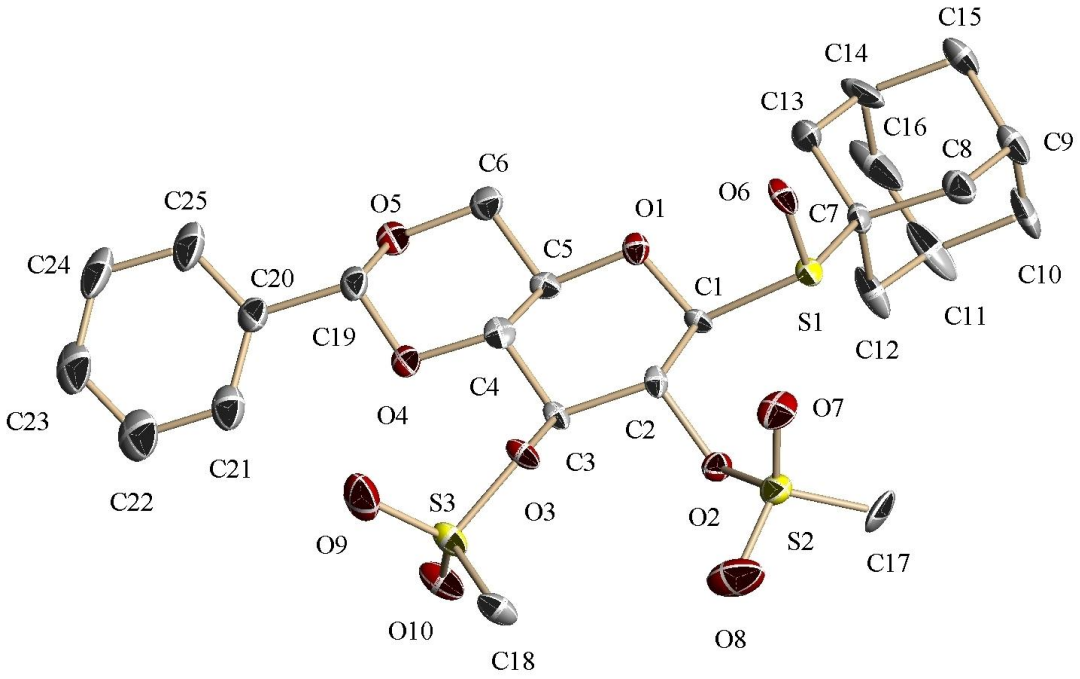

Table S2. Crystal data and structure refinement for compound **13*R*S**.

Empirical formula	$C_{29}H_{42}O_{12}S_3$	
Formula weight	678.81	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1	
Unit cell dimensions	a = 10.4931(8) Å	α= 90°.
	b = 11.5171(10) Å	β= 91.379(4)°.
	c = 28.284(2) Å	γ = 90°.
Volume	3417.1(5) $Å^3$	
Z	4	
Density (calculated)	1.319 Mg/m^3	
Absorption coefficient	0.275 mm^{-1}	
F(000)	1440	
Crystal size	0.50 x 0.30 x 0.20 mm^3	
Theta range for data collection	1.44 to 25.25°.	

Index ranges	-12<=h<=11, -13<=k<=10, -33<=l<=33
Reflections collected	39325
Independent reflections	9661 [R(int) = 0.0800]
Completeness to theta = 25.25°	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9471 and 0.9049
Refinement method	Full-matrix-block least-squares on F^2
Data / restraints / parameters	9661 / 0 / 801
Goodness-of-fit on F^2	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0605, wR2 = 0.1574
R indices (all data)	R1 = 0.0843, wR2 = 0.1826
Absolute structure parameter	0.06(3)
Largest diff. peak and hole	1.136 and -1.068 e.$Å^{-3}$

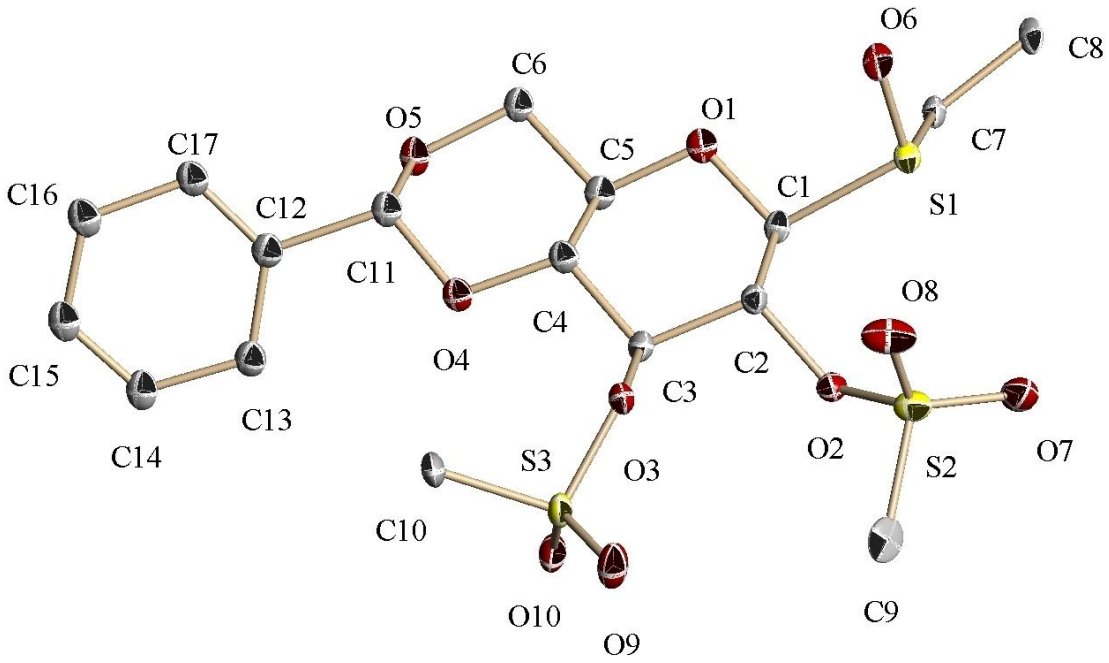

Table S3. Crystal data and structure refinement for compound **19*R*S**.

Empirical formula	$C_{17}H_{24}O_{10}S_3$	
Formula weight	484.54	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1	
Unit cell dimensions	a = 5.2270(6) Å	α= 90°.
	b = 25.122(3) Å	β= 99.08°.
	c = 16.5667(18) Å	γ = 90°.
Volume	2148.2(4) $Å^3$	
Z	4	
Density (calculated)	1.498 Mg/m^3	
Absorption coefficient	0.397 mm^{-1}	
F(000)	1016	
Crystal size	0.50 x 0.40 x 0.10 mm^3	
Theta range for data collection	1.62 to 25.25°.	
Index ranges	-6<=h<=6, -30<=k<=29, -19<=l<=18	
Reflections collected	17443	

Independent reflections	5111 [R(int) = 0.0427]
Completeness to theta = 25.25°	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9614 and 0.8262
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5111 / 0 / 547
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0674, wR2 = 0.1116
R indices (all data)	R1 = 0.0896, wR2 = 0.1632
Absolute structure parameter	-0.01(3)
Largest diff. peak and hole	0.856 and -1.198 e.$Å^{-3}$