Efficient *trans*-Selectivity in the Cyclocondensation of (*S*)-2-[2-(*p*-Tolylsulfinyl)phenyl]acetaldehyde with Activated Dienes Catalyzed by $Yb(OTf)_3$.

José L. García Ruano, M. Ángeles Fernández-Ibáñez, M. Carmen Maestro.**

Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco,

28049-Madrid, SPAIN.

joseluis.garcia.ruano@uam.es; carmen.maestro@uam.es

Supporting Information

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General Experimental Methods

Unless stated otherwise, NMR spectra were recorded in $CDCl_3$ solutions at 300 and 75 MHz for ^1H and ^{13}C NMR, respectively (*J* values are given in hertz). Melting points were measured in open capillary tubes and are uncorrected. Mass spectra (MS) were determined by FAB^+ (fast atom bombardment), ES^+ (electrospray; MeOH + 0.1 formic acid) or EI^+ (electron impact; 70 eV). De´s were evaluated by integration of well-separated signals of the NMR spectra or by chiral HPLC (retention times in minutes). HDA reactions were carried out under argon atmosphere in anhydrous solvents. CH_2Cl_2 was distilled from P_2O_5. Flash-column chromatography was performed using silica gel (230-400 mesh). Dienes **5**, **8** and **11** were synthesized according literature procedures.[1]

*Mukaiyama adducts from **1** and Danishefsky's diene***:**

A 88:12 mixture of **12** and **13** was obtained from Danishefsky's diene following the general procedure at -40 ºC for 5 min, when the reaction was quenched with water. The residue was purified by flash chromatography (ethyl acetate-hexane, 3:1). Combined yield 72%. White solid. They could not be isolated and were characterized from the above mixture. ^1H-NMR: 7.82 [m, 1H (**12**) + 1H (**13**)], 7.59-7.22 [m, 8H (**12**) + 8H (**13**)], 5.57 [d, *J* 13.3 Hz, 1H (**13**)], 5.52 [d, *J* 12.9 Hz, 1H (**12**)], 4.26 [m, 1H (**12**) + 1H (**13**)], 3.70 [s, 3H (**12**) + 3H (**13**)], 3.00 [dd, *J* 14.0 and 6.5 Hz, 1H (**12**) + 1H (**13**)], 2.91 [dd, *J* 14.5 and 5.9 Hz, 1H (**12**) + 1H (**13**)], 2.60 [dd, *J* 16.7 and 3.8 Hz, 1H (**12**) + 1H (**13**)], 2.48 [dd, *J* 16.7 and 8.1 Hz, 1H (**12**) + 1H (**13**)], 2.35 [s, 3H (**12**) + 3H (**13**)]. MS

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[1] (a) Mikami, K.; Matsumoto, S.; Okubo, Y.; Fujitsuka, M.; Ito, O.; Suenobu, T.; Fukuzumi. S. *J. Am . Chem. Soc*. **2000**, *122*, 2236. (b) Danishefsky, S.; Yan, C.-F.; Singh, R. K.; Gammill, R. B.; McCurry, P. M.; Fritsch, N.; Clardy. J. *J. Am. Chem. Soc.* **1979**, *101*, 7001.

(EI$^+$) *m/z*: 357 [M-1] (0.2), 341 (1), 327 (7), 326 (6), 309 (61), 214 (90), 113 (100), 91 (50). HRMS (EI$^+$) [M-17]: calcd for $C_{20}H_{21}O_3S$: 341.1211; found: 341.1200.

*Mukaiyama adducts from **1** and diene **8**:*

A 90:10 mixture of **14** and **15** was obtained from diene **8** at -40 ºC for 3 h, following the general procedure in the presence of MS 4Å, when the reaction was quenched with water. The residue was purified by flash column chromatography (ethyl acetate-hexane, 1:1) to afford a mixture of diastereoisomers **14** and **15** as a (Combined yield: 51%). White solid. They were characterized from the corresponding mixture. ^{1}H-NMR (200 MHz): 7.76 [m, 1H (**14**) + 1H (**15**)], 7.46-7.33 [m, 4H (**14**) + 4H (**15**)], 7.27-7.21 [m, 4H (**14**) + 4H (**15**)], 3.89-3.86 [m, 1H (**14**) + 1H (**15**)], 3.87 [s, 3H (**14**)], 3.86 [s, 3H (**15**)], 3.04-2.80 [m, 3H (**14**) + 3H (**15**)], 2.35 [s, 3H (**14**) + 3H (**15**)], 1.69 [s, 3H (**14**)], 1.67 [s, 3H (**15**)], 1.22 [d, *J* 7.5 Hz, 3H (**14**)], 1.18 [d, *J* 7.0 Hz, 3H (**15**)]. MS (EI$^+$) *m/z*: 385 (0.6) [M-1], 354 (9), 337 (80), 253 (27), 241 (44), 211 (100), 141 (46), 91 (46). HRMS (EI$^+$) [M-1]: calcd for $C_{22}H_{25}O_4S$: 385.1474; found: 385.1466.

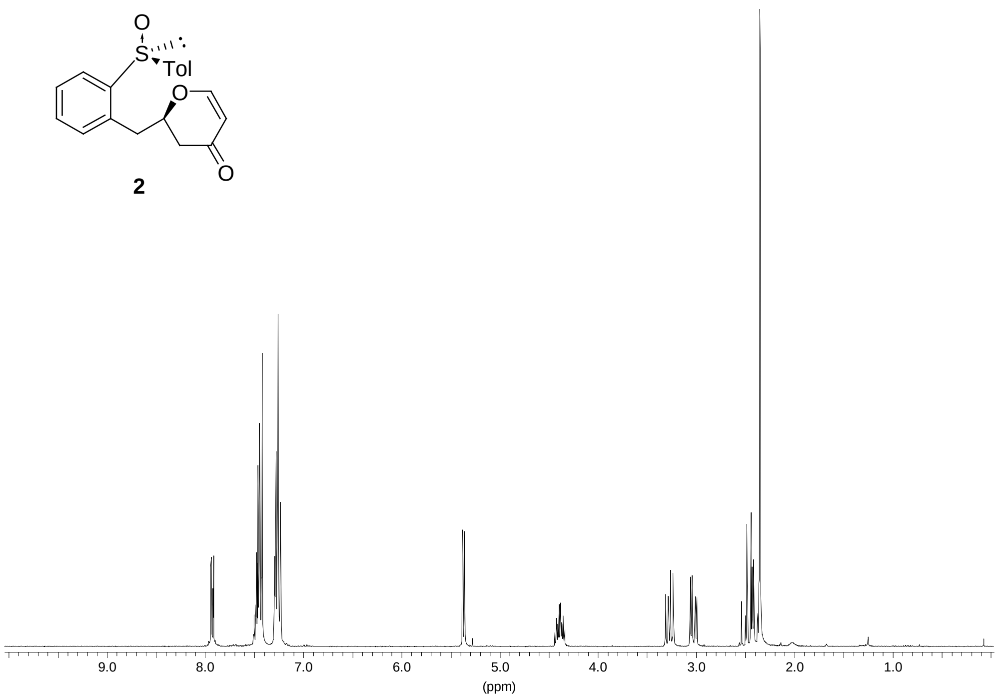
*Sulfinyl group oxidation of HDA adducts **9** and **10** :*

To a 60:40 mixture of diastereoisomers **9** and **10** (17 mg, 0.05 mmol) respectively in CH_2Cl_2 (1 mL), cooled at 0 ºC was added a solution of *m*-CPBA (17 mg 0.1 mmol) in CH_2Cl_2 (0.5 mL). The reaction mixture was stirred for 1 h, starting from 0 ºC to room temperature. Then, the mixture was treated with saturated aqueous Na_2SO_3 (2 mL). The organic layer was separated, washed with saturated aqueous $NaHCO_3$ (2 mL), dried (Na_2SO_4), and the solvent was removed under reduced pressure. The resulting 60:40 mixture of sulfones **16** and **17** was characterized without further purification. ^{1}H-NMR (200 MHz)**:** 8.18-7.11 [m, 1H (**16**) + 1H (**17**)], 7.69 and 7.29 [sistema AA´BB´, 4H (**16**) + 4H (**17**)], 7.57-7.36 [m, 3H (**16**) + 3H (**17**)], 7.06 [s, 1H (**16**)], 7.01 (s, 1H, (**16**)], 4.35-4.24 [m, 1H (**16**) + 1H (**17**)], 3.39 [dd, *J* 14.5 and 2.7 Hz, 1H, (**16**)], 3.21 [dd, *J* 14.5 and

3.2 Hz, 1H (**17**)], 3.12-2.94 [m, 1H (**16**) + 1H (**17**)], 2.46-2.34 [m, 1H (**16**) + 1H (**17**)], 2.39 [s, 3H (**16**) + 3H (**17**)], 1.62 [s, 3H (**16**)], 1.60 [s, 3H (**17**)], 1.22 [d, *J* 7.0 Hz, 3H (**16**)], 1.11 [d, *J* 7.5 Hz, 3H (**17**)]. HRMS (ES^+) [M+1]: calcd for $C_{21}H_{23}O_4S$: 371.1311; found: 371.1320.

*Hydroxy group oxidation of Mukaiyama adducts **14** and **15**:*

A mixture of PCC (11 mg, 0.05 mmol) and Celite (10 mg) was added, at room temperature, to a 90:10 mixture of **14** and **15** (10 mg, 0.03 mmol), in CH_2Cl_2 (1 mL). The mixture was stirred for 3 h at the same temperature and then filtered through Celite. The solvent was removed under vacuum. The residue was purified by flash column chromatography (ethyl acetate-hexane, 1:1) to yield a 82:18 mixture of **18** and **19** as a white solid (combined yield 31%). ^{1}H-NMR (200 MHz): 7.88-7.85 [m, 1H (**18**) + 1H (**19**)], 7.72-7.64 [m, 1H (**18**) + 1H (**19**)], 7.57-7.34 [m, 3H (**18**) + 3H (**19**)], 7.27-7.10 [m, 3H (**18**) + 3H (**19**)], 6.19 [s, 1H (**18** or **19**)], 6.16 [s, 1H (**19** or **18**)], 4.18-3.78 [m, 3H (**18**) + 3H (**19**)], 3.89 [s, 3H (**19**)], 3.86 [s, 3H (**18**)], 2.37 [s, 3H (**18**) + 3H (**19**)], 1.73 [s, 3H], 1.70 [s, 3H], 1.35 [d, *J* 7.0 Hz, 3H (**18**)], 1.34 [d, *J* 7.0 Hz, 3H].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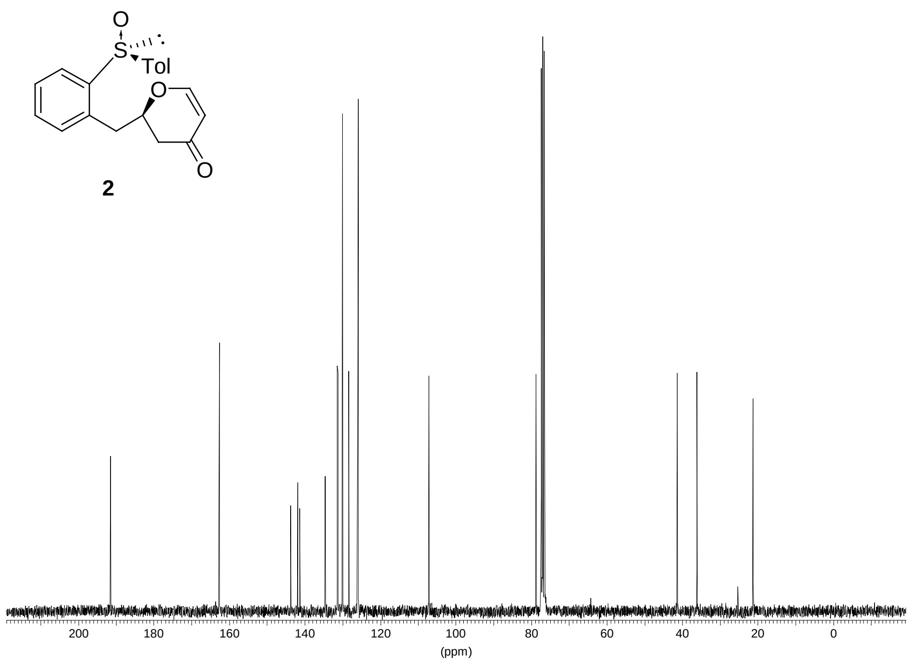
(ppm)

2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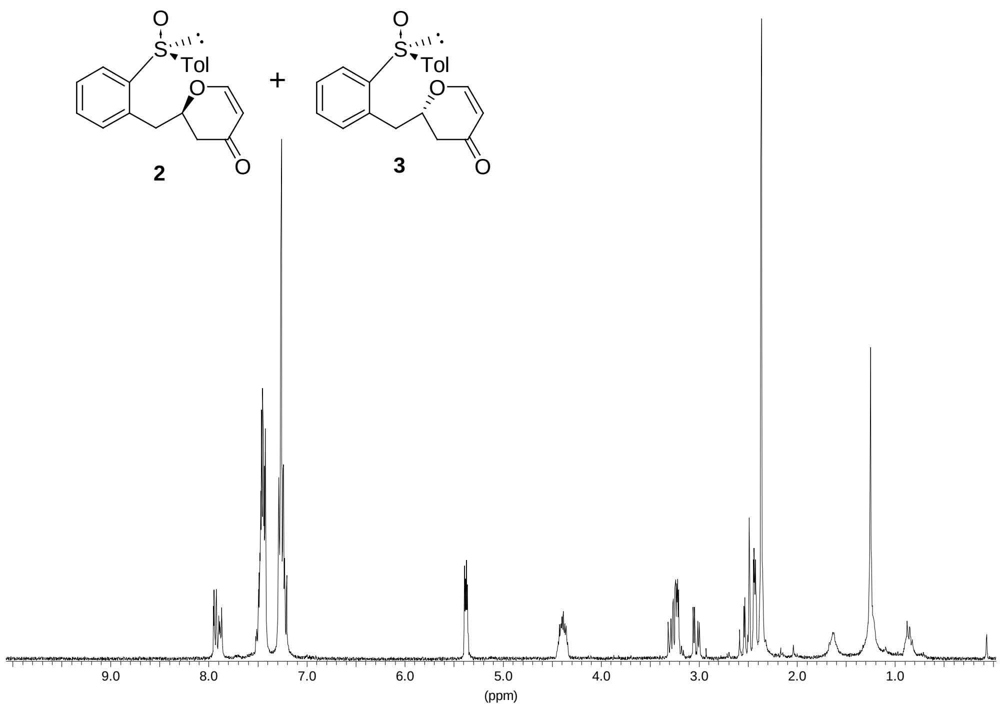
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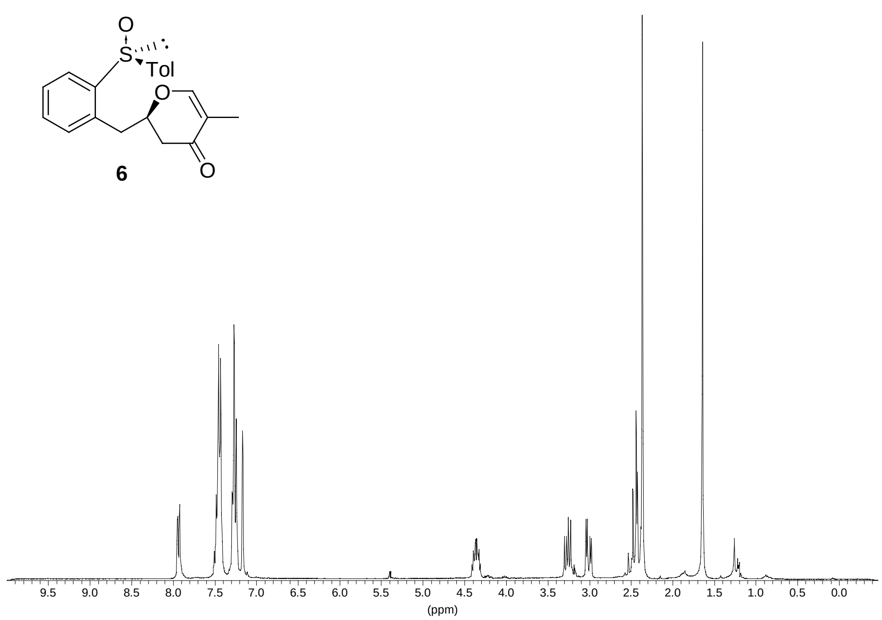
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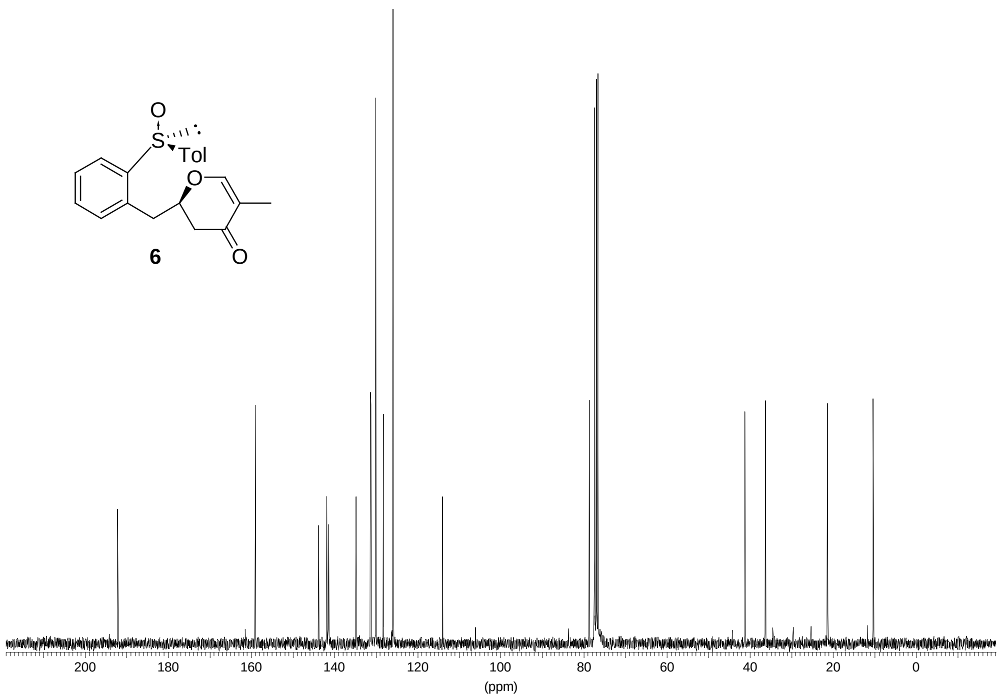
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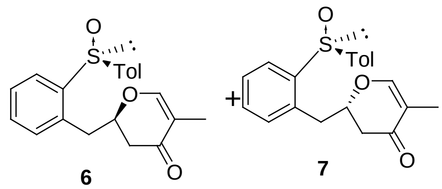
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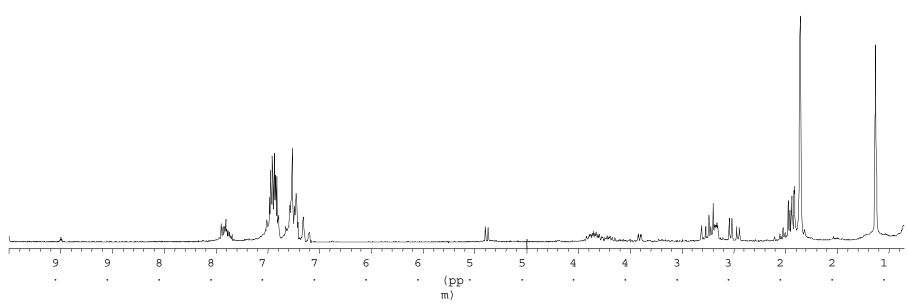

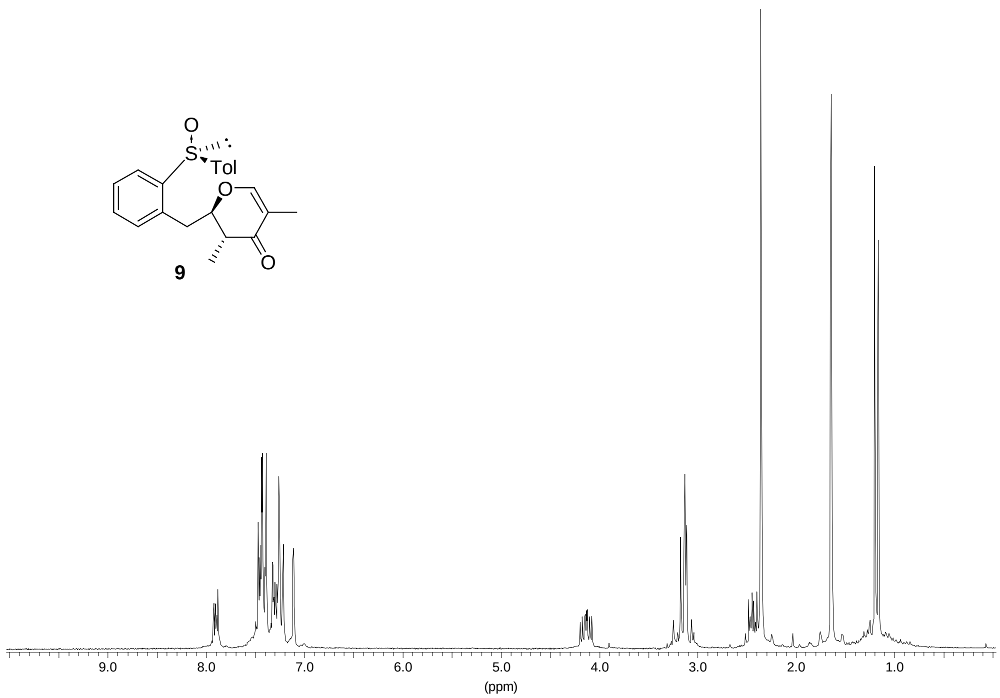
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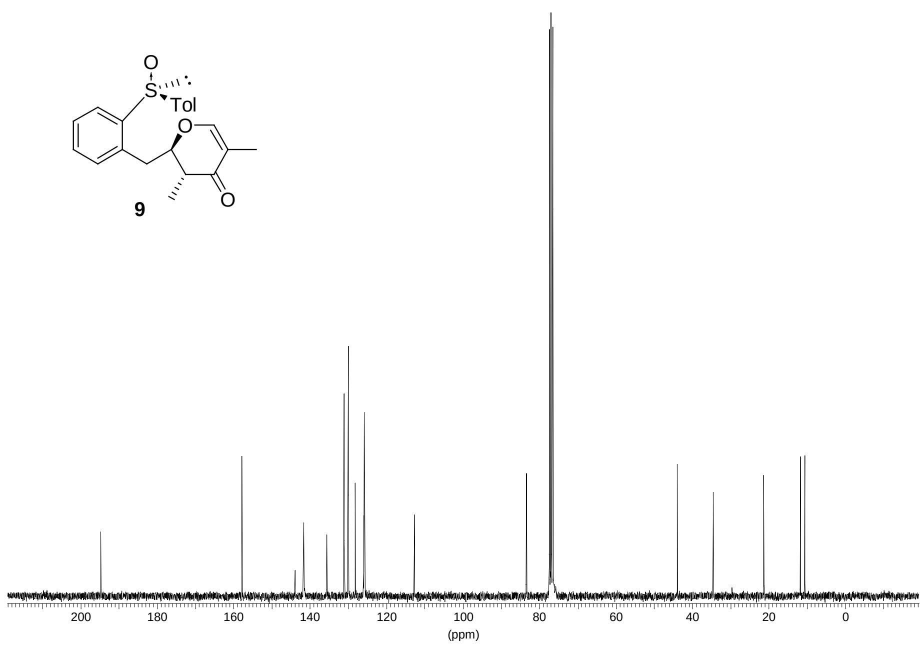
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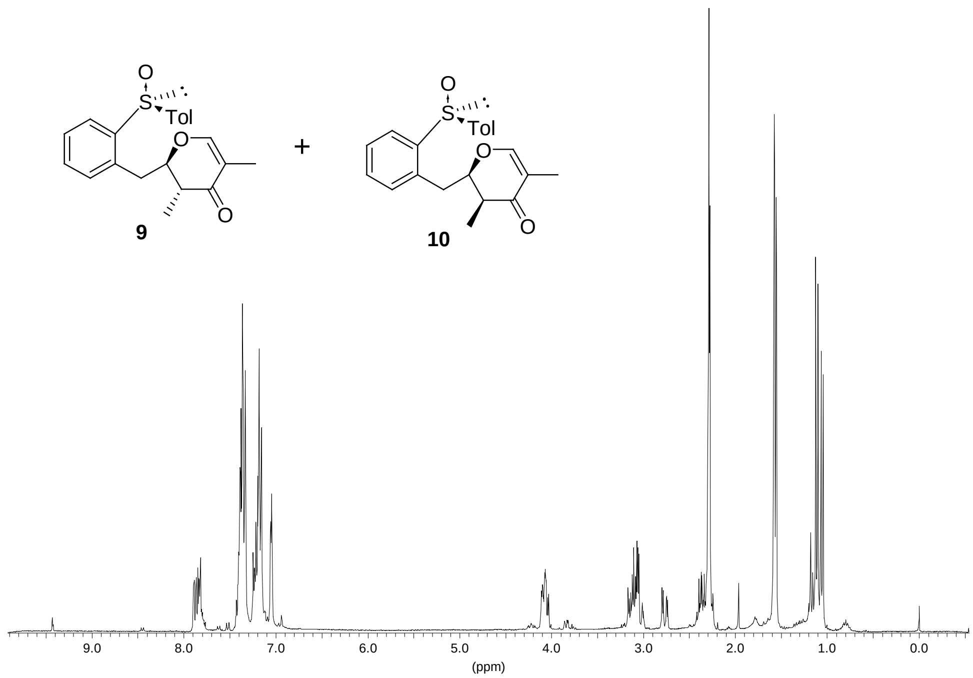
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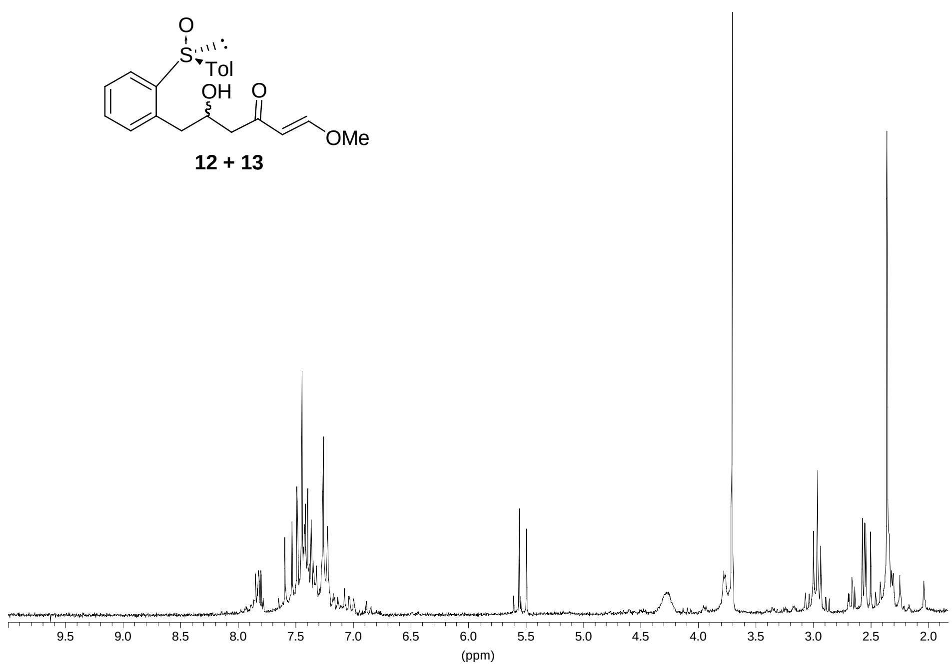
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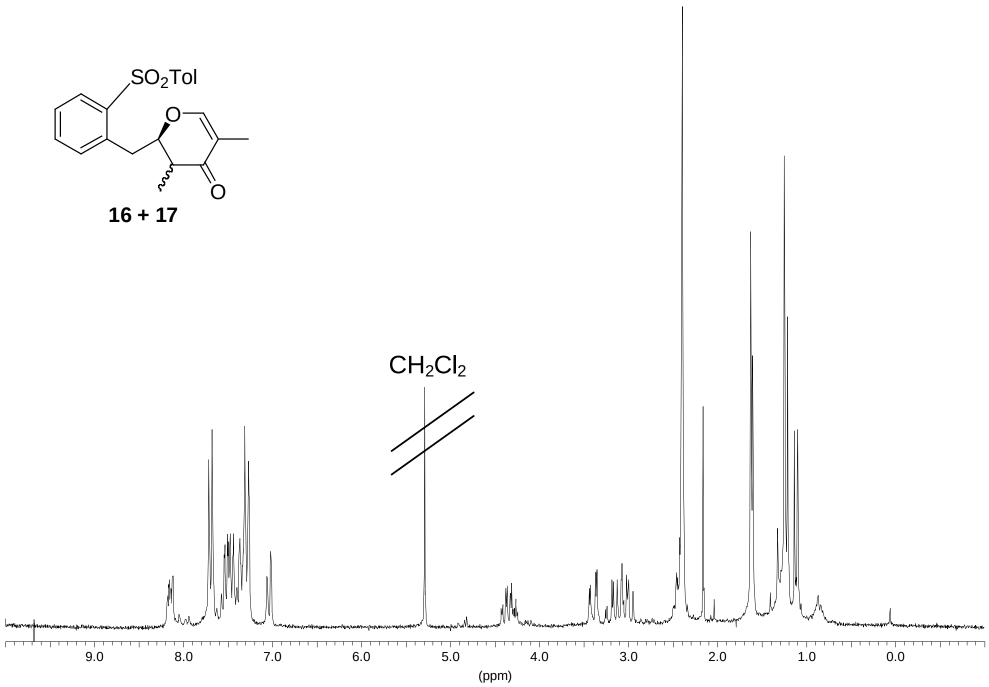
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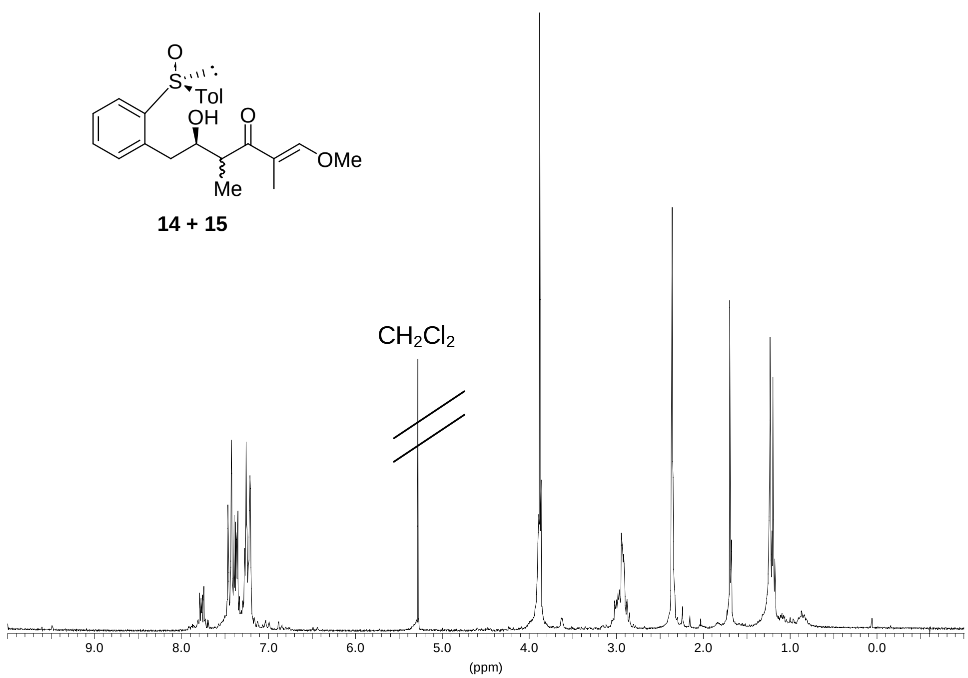
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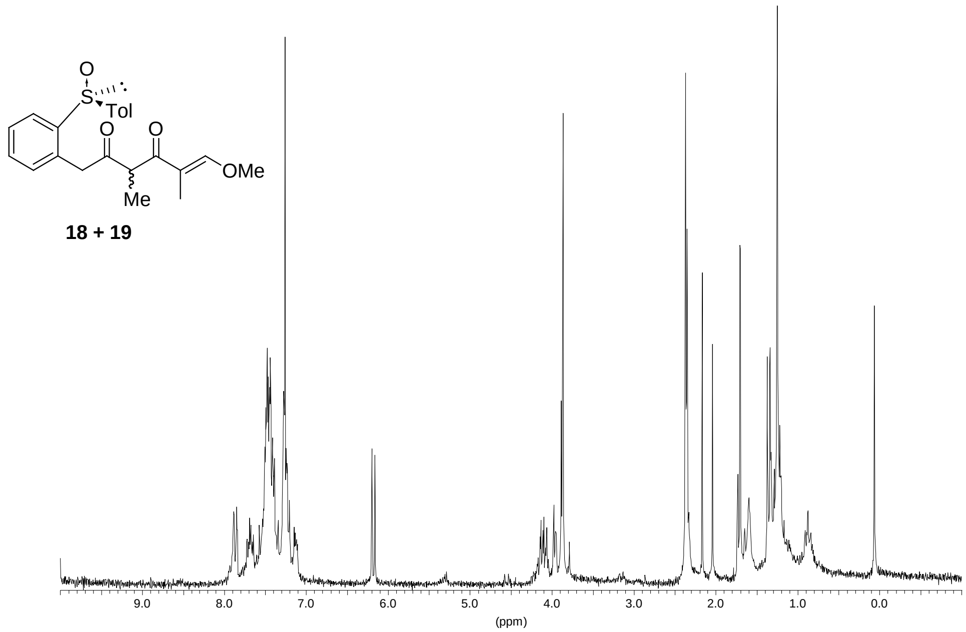
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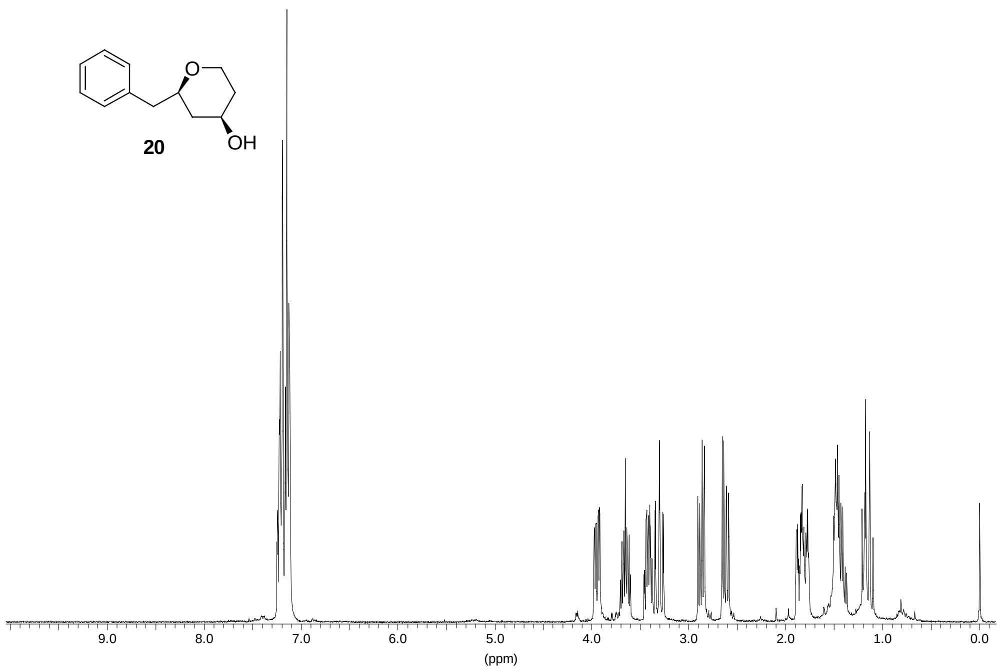
18 + 19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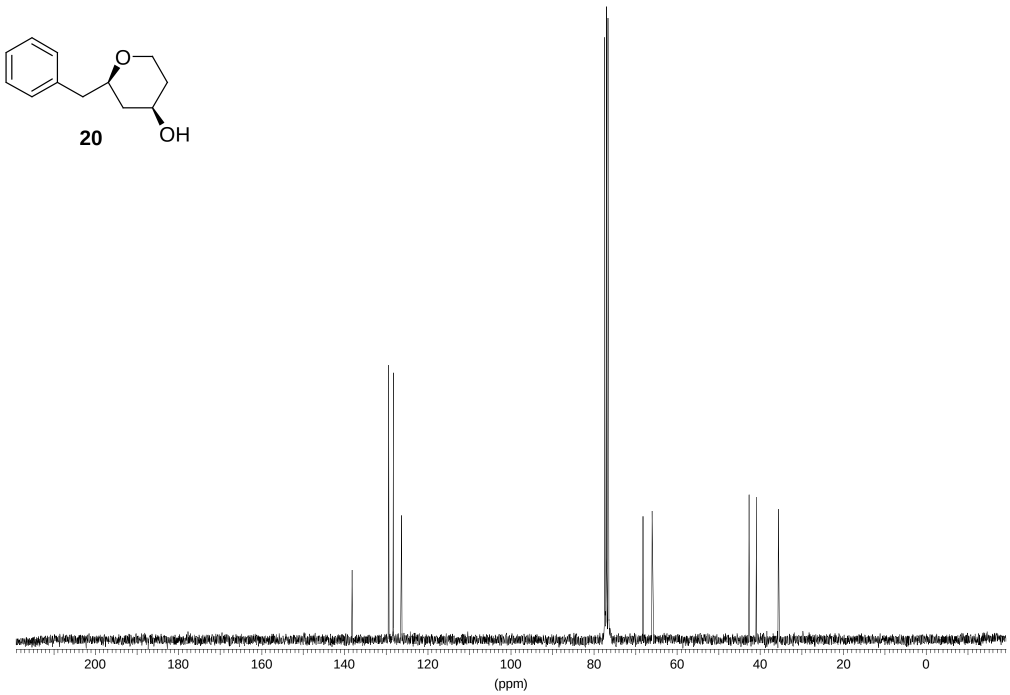
20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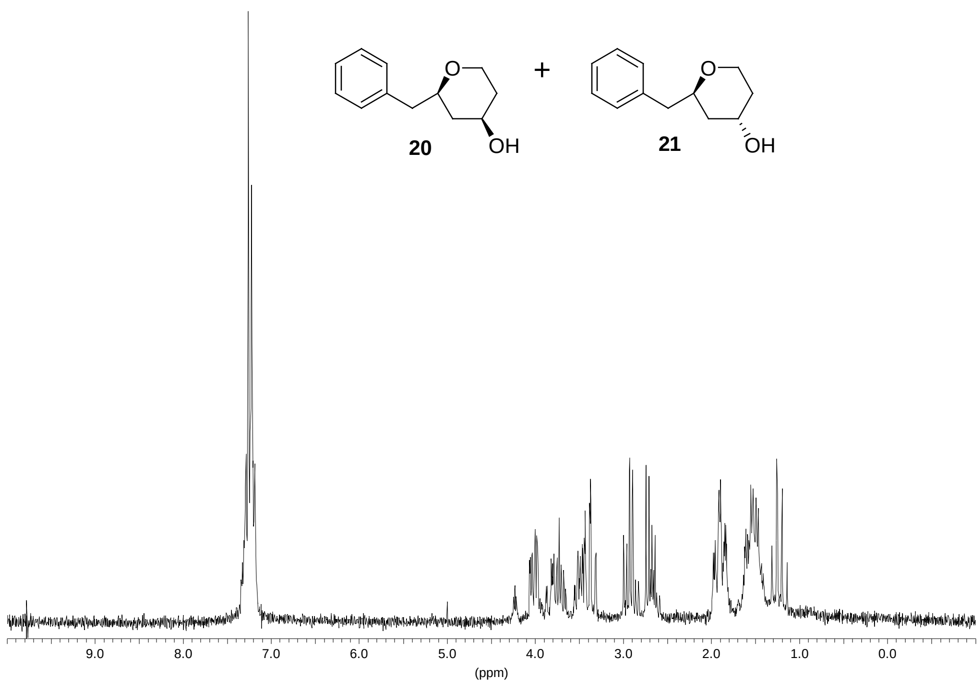
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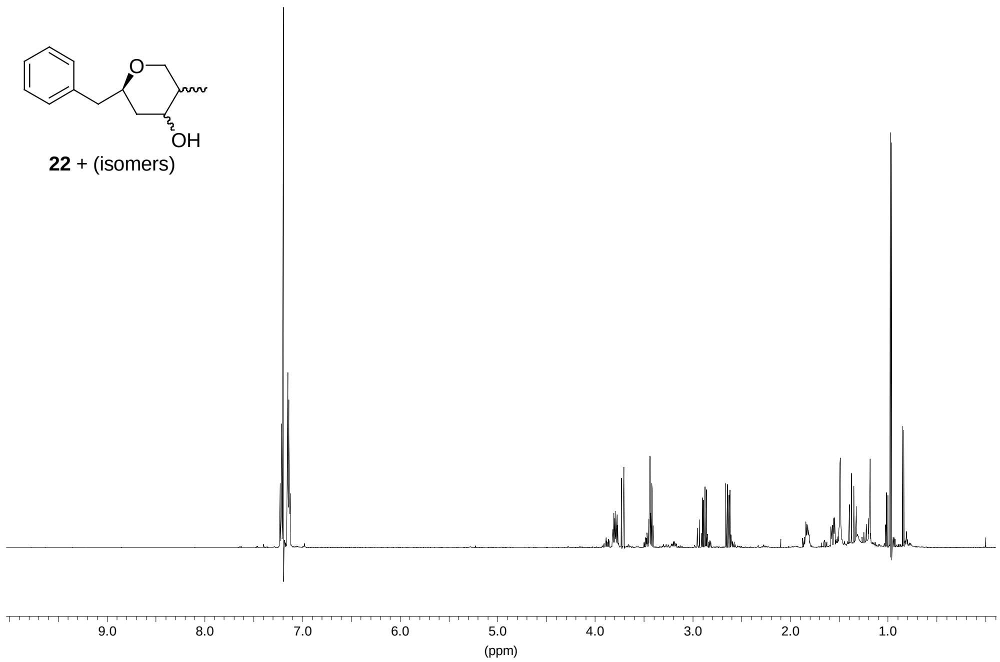
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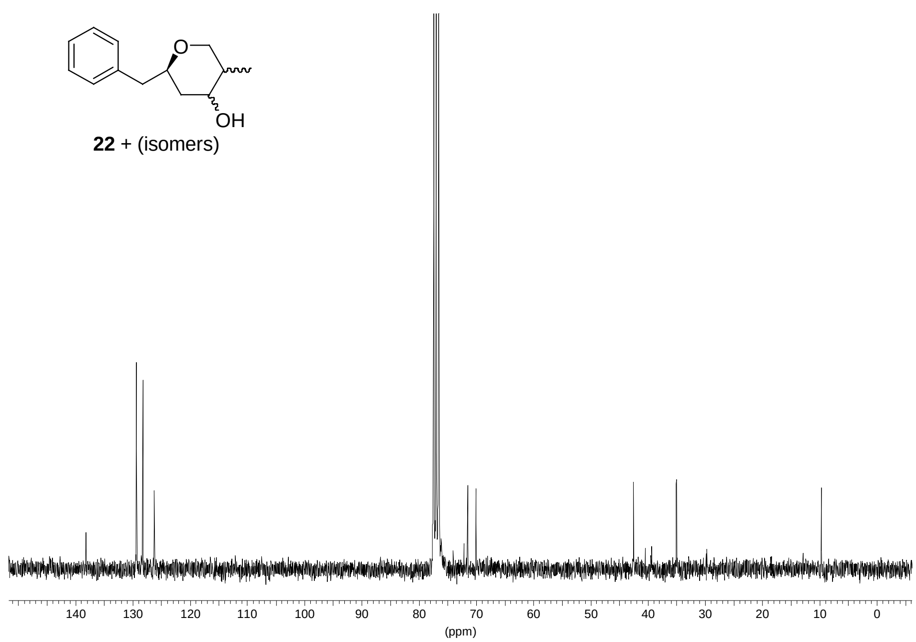
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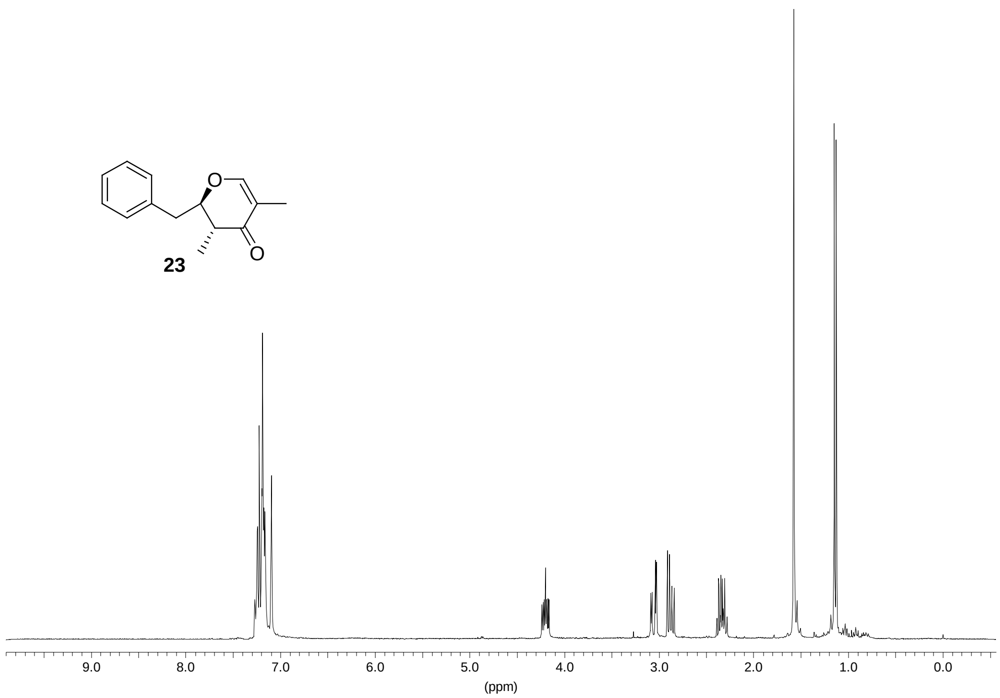
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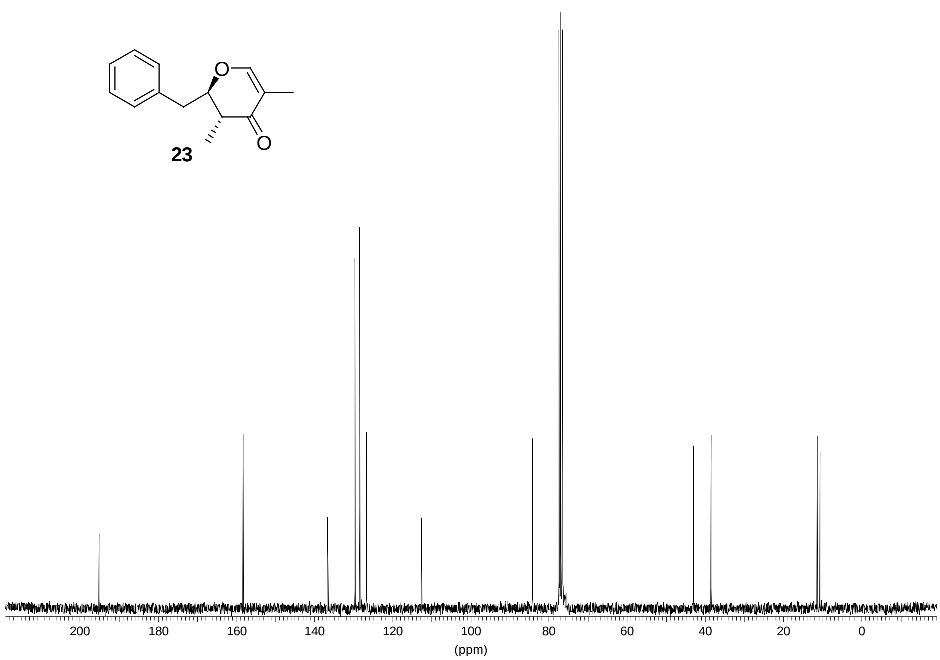
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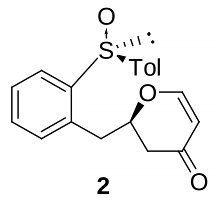

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O

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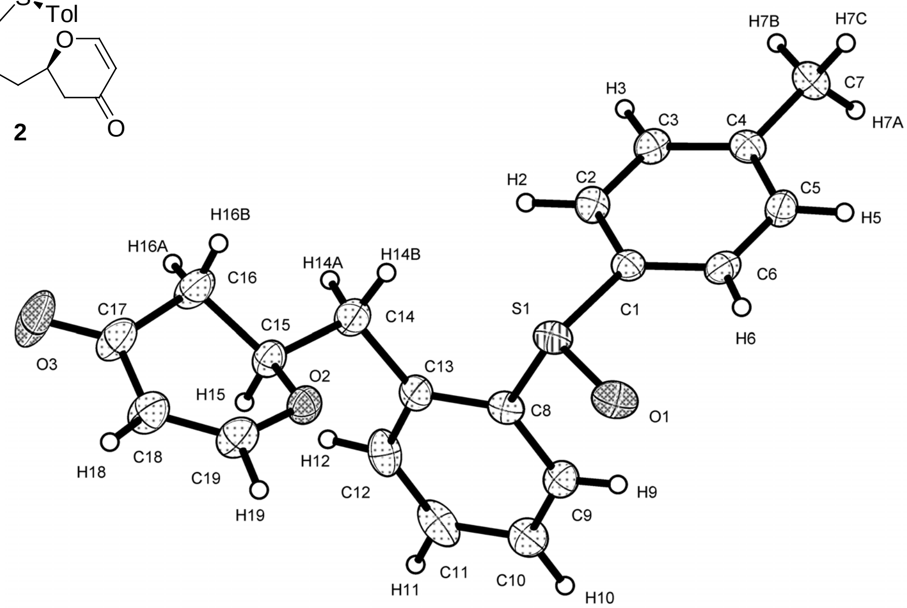

H7B
H7C
C7
H7A
H3
C3
C4
H2
C2
C5
H5
H16B
H16A
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H14B
C14
C6
C1
S1
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C17
C15
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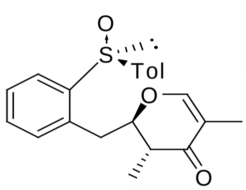
C11
C10
H10



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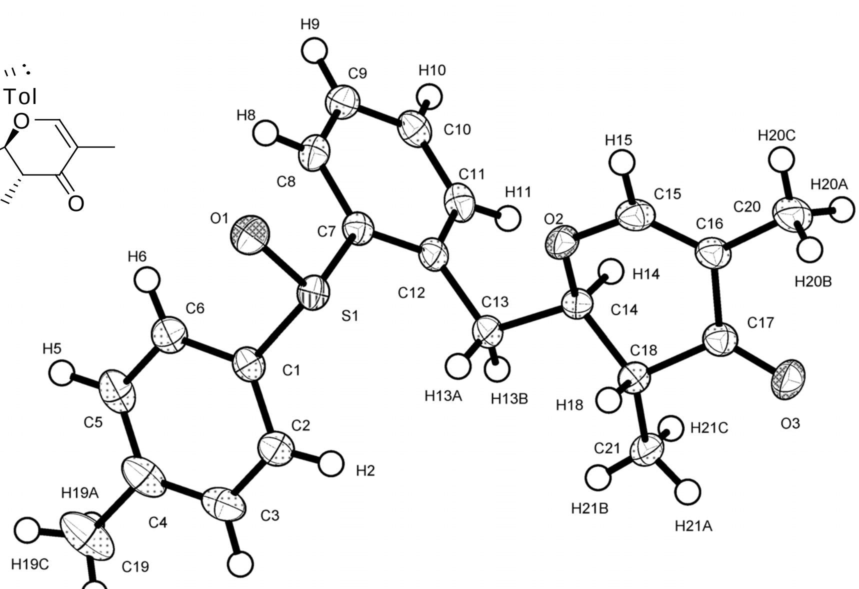

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H8
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C8
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H11
H15
C15
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H18
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C5
C2
H21C
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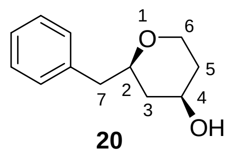
C19
H3
H19B

Configurational assignment of **20**:

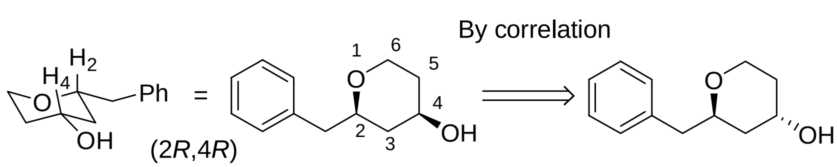


20

Representative [1]H-NMR signals from **20**:

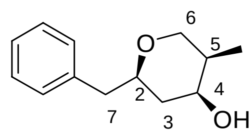
Entry	proton	δ (ppm)	Multiplicity	J (Hz)
1	H_6	3.94	ddd	11.9, 4.7, 1.7
2	H_4	3.65	tt	10.9, 4.5
3	H_2	3.41	dtd	11.1, 6.4, 1.9
4	$H_{6'}$	3.29	dt	12.4, 2.1
5	H_7	2.87	dd	13.6, 6.6
6	$H_{7'}$	2.62	dd	13.7, 7.0

Trans coupling constants were observed for H_2 (11.1 Hz) and H_4 (10.9 Hz), showing their axial arrangement in alcohol **20.** Therefore, the compound presents (2*R*,4*R*) configuration.



20 **21**

Configurational assignment of **22**:

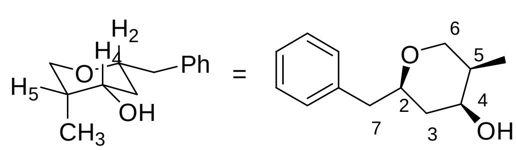


22

Representative ^{1}H-NMR signals from **22**:

Entry	proton	δ (ppm)	Multiplicity	*J* (Hz)
1	H_{4ax}	3.79	dt	11.3, 5.0
2	H_6	3.72	dd	11.5, 1.6
3	$H_{6'}$	3.42	dd	11.5, 2.2
4	H_2	3.42	dtd	13.2, 6.6, 2.2
5	H_7	2.87	dd	13.7, 6.3
6	H_7	2.64	dd	13.7, 6.6
8	H_{3ec}	1.56	dddd	12.6, 4.7, 2.2, 0.9
9	H_{3ax}	1.36	q	11.0
10	CH_3	0.97	d	6.9

H_6 and $H_{6'}$protons appear as double doublets, with a high coupling constant (11.5 Hz), related to their *geminal* relationship, and low coupling constants with H_5 (1.6, 2.2 Hz, respectively), indicating the equatorial position of this proton. Then, methyl group adopts the axial arrangement. On the other hand, both H_4 and H_2 present a high constant, indicating that both protons are in axial position. Therefore, compound **22** presents (2*R*,4*S*,5*R*) configuration.



22 (2*R*,4*S*,5*R*)