# Supporting information

# Synthetic efforts toward the spiroketal core of spirangien A

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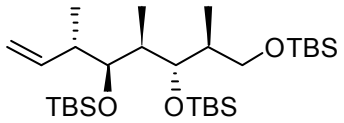
General

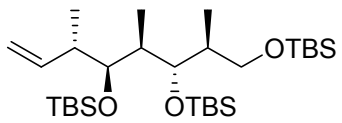
Wave-numbers are indicated in $cm^{-1}$. $^{1}H$ NMR spectra were recorded at 400 MHz or at 600 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane as an internal standard with the residual solvent peak as an internal indicator ($CDCl_3$ δ: 7.26), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non-equivalent resonances), integration. $^{13}C$ NMR spectra were recorded at 100 MHz or at 150 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator ($CDCl_3$ δ = 77.1 ppm), multiplicity with respect to proton (deduced from DEPT experiments, s = quaternary C, d = CH, t = $CH_2$, q = $CH_3$). $CH_2Cl_2$ was distilled from $CaH_2$. THF and $Et_2O$ were dried over sodium/benzophenone prior to distillation. TLC were performed on silica gel plates visualized either with a UV lamp (254 nm), or using solutions of *p*-anisaldehyde/sulfuric acid/acetic acid in EtOH followed by heating. Mass spectra with electronic impact (MS-EI) were recorded on a GC/MS (70 eV).

$CDCl_3$, 400 MHz




**3**

$CDCl_3$, 100 MHz




**3**

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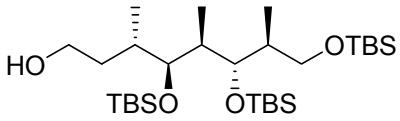


**4**

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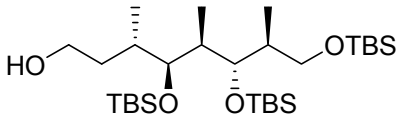


**4**

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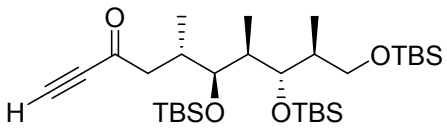


**5**

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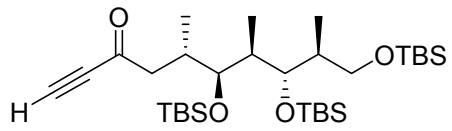


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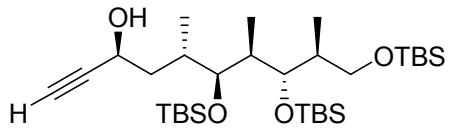


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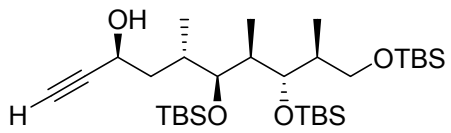


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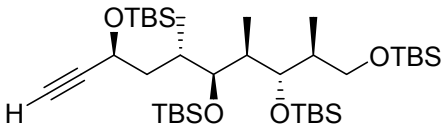
$CDCl_3$, 400 MHz

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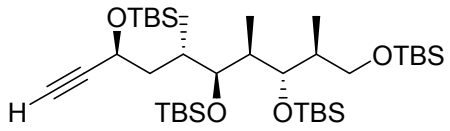


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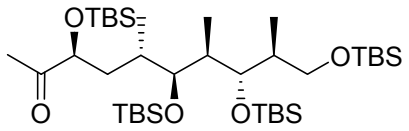


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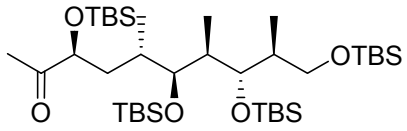
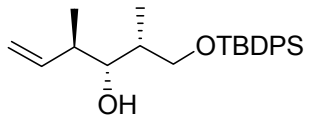


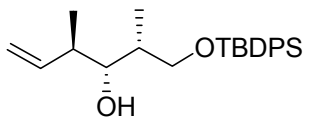

**8**

$CDCl_3$, 400 MHz



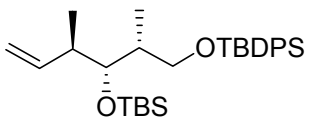

**10**

$CDCl_3$, 100 MHz



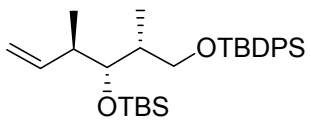

**10**

$CDCl_3$, 400 MHz



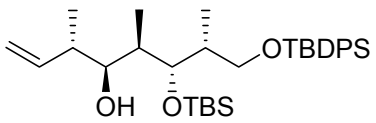

**11**

$CDCl_3$, 100 MHz



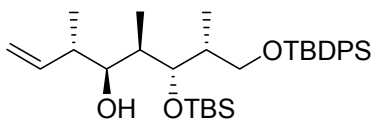

**11**

$CDCl_3$, 400 MHz



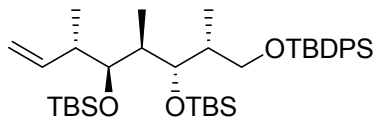

**12**

$CDCl_3$, 100 MHz



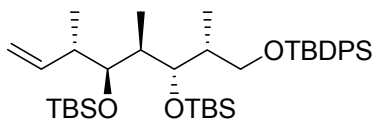

**12**

$CDCl_3$, 400 MHz



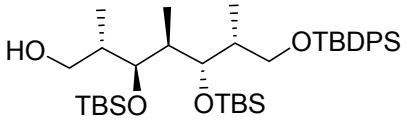

**13**

$CDCl_3$, 100 MHz



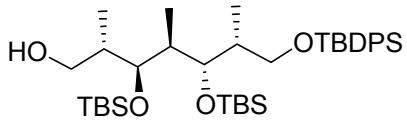

**13**

$CDCl_3$, 400 MHz



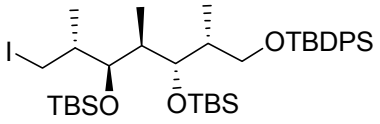

**14**

$CDCl_3$, 100 MHz



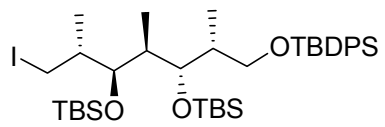

**14**

$CDCl_3$, 400 MHz



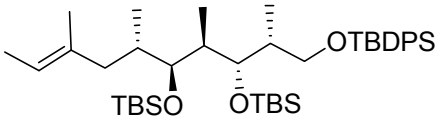

**15**

$CDCl_3$, 100 MHz



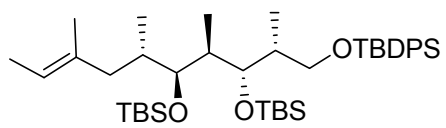

**15**

$CDCl_3$, 400 MHz



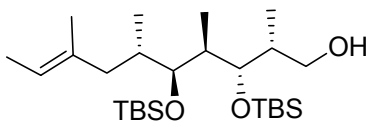

**16**

$CDCl_3$, 100 MHz



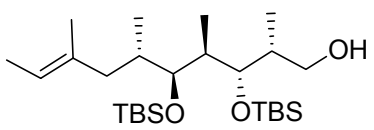

**16**

$CDCl_3$, 400 MHz



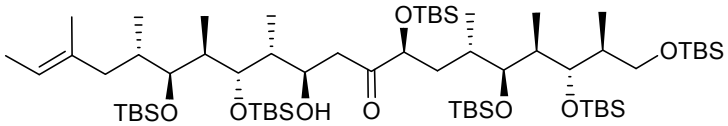

**17**

$CDCl_3$, 100 MHz



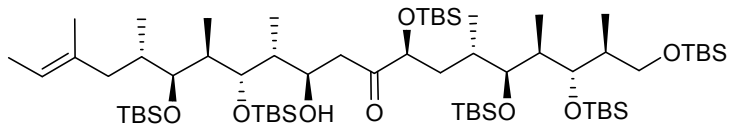

**17**

$CDCl_3$, 400 MHz



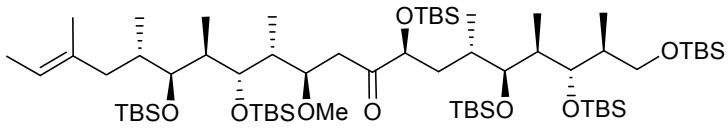

**19**

$CDCl_3$, 100 MHz



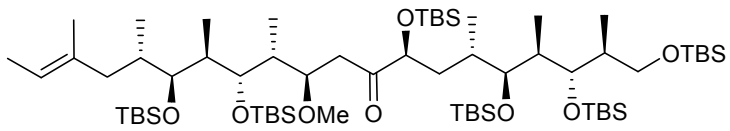

**19**

$CDCl_3$, 400 MHz



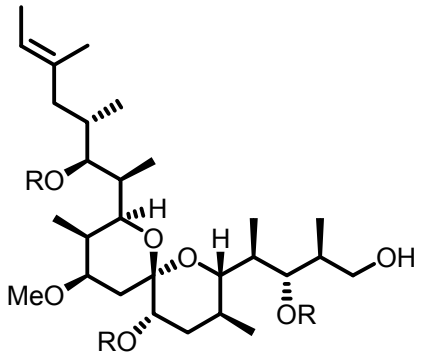

**20**

$CDCl_3$, 100 MHz




**20**

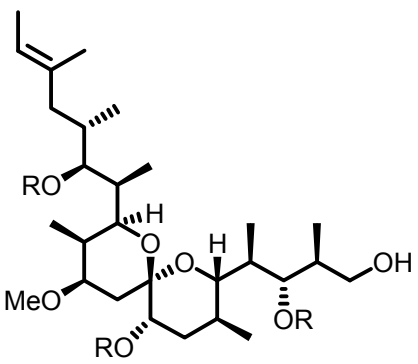
$C_6D_6$, 600 MHz




R : H or TBS
2 remaining TBS

**22** + unknowm impurity

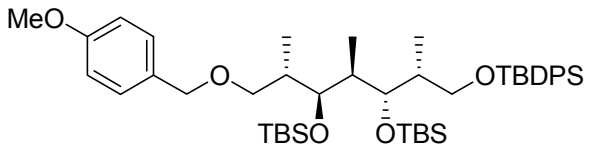
$C_6D_6$, 100 MHz




R : H or TBS
2 remaining TBS

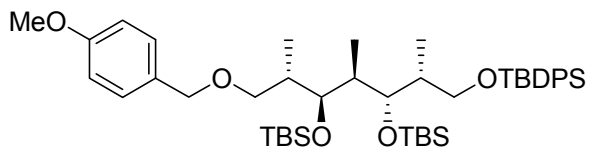
**22** + unknowm impurity

$CDCl_3$, 400 MHz



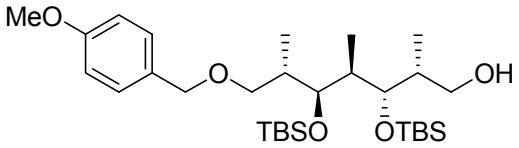

**23**

$CDCl_3$, 100 MHz



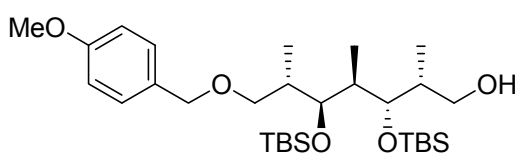

**23**

$CDCl_3$, 400 MHz



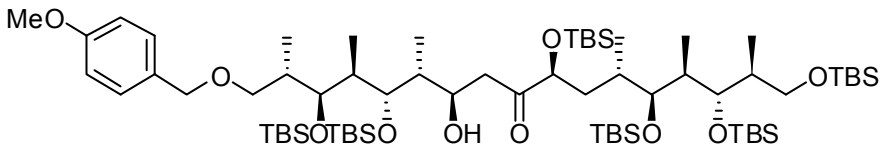

**24**

$CDCl_3$, 100 MHz



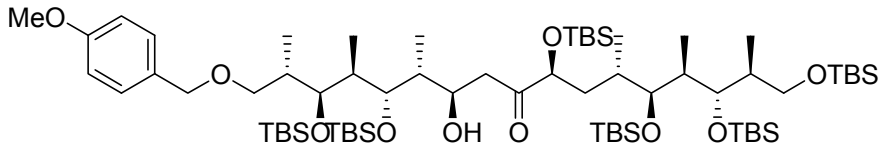

**24**

$CDCl_3$, 400 MHz



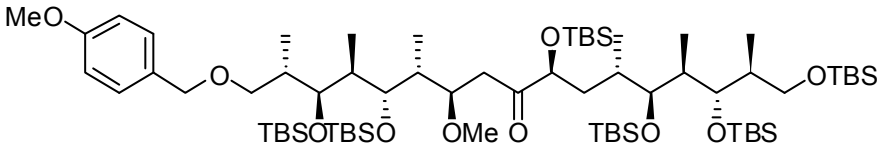

**26**

$CDCl_3$, 100 MHz



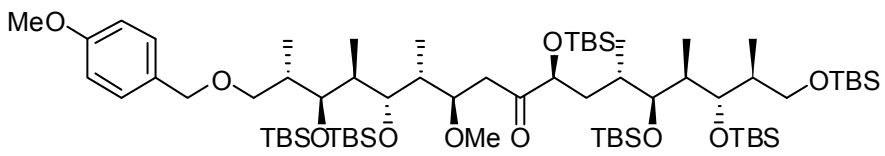

**26**

$CDCl_3$, 400 MHz




**27**

$CDCl_3$, 100 MHz




**27**

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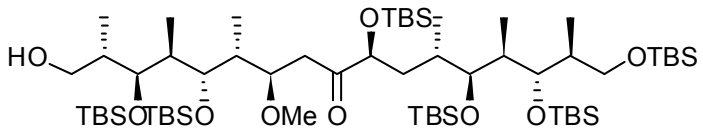
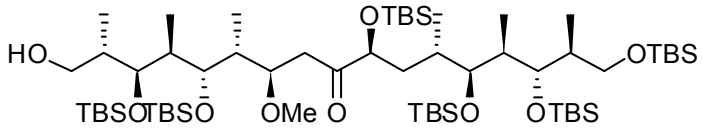


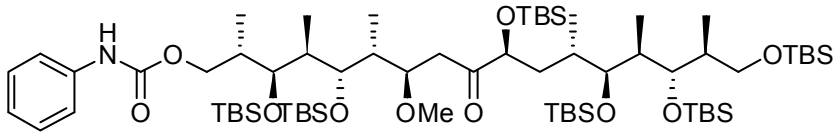

**29**

$CDCl_3$, 100 MHz



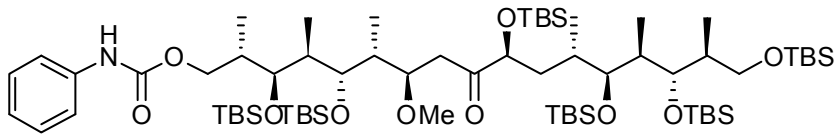

**29**

$CDCl_3$, 400 MHz



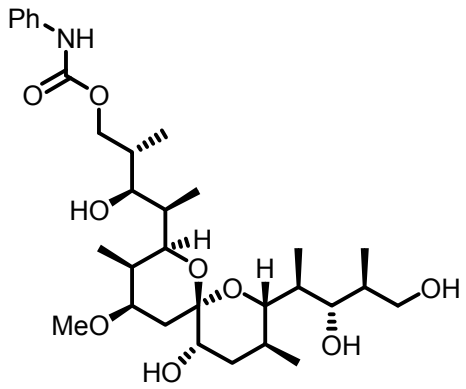

**30**

$CDCl_3$, 100 MHz



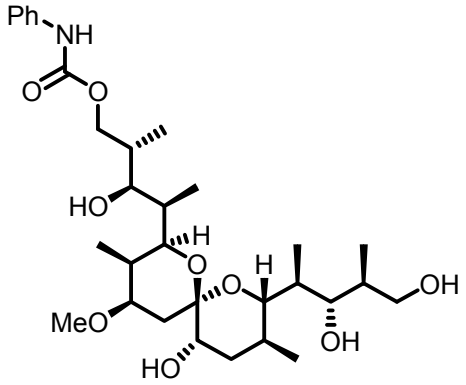

**30**

$CDCl_3$, 600 MHz



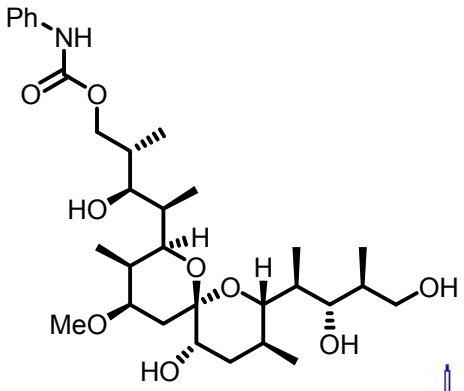

**31**

$CDCl_3$, 600 MHz



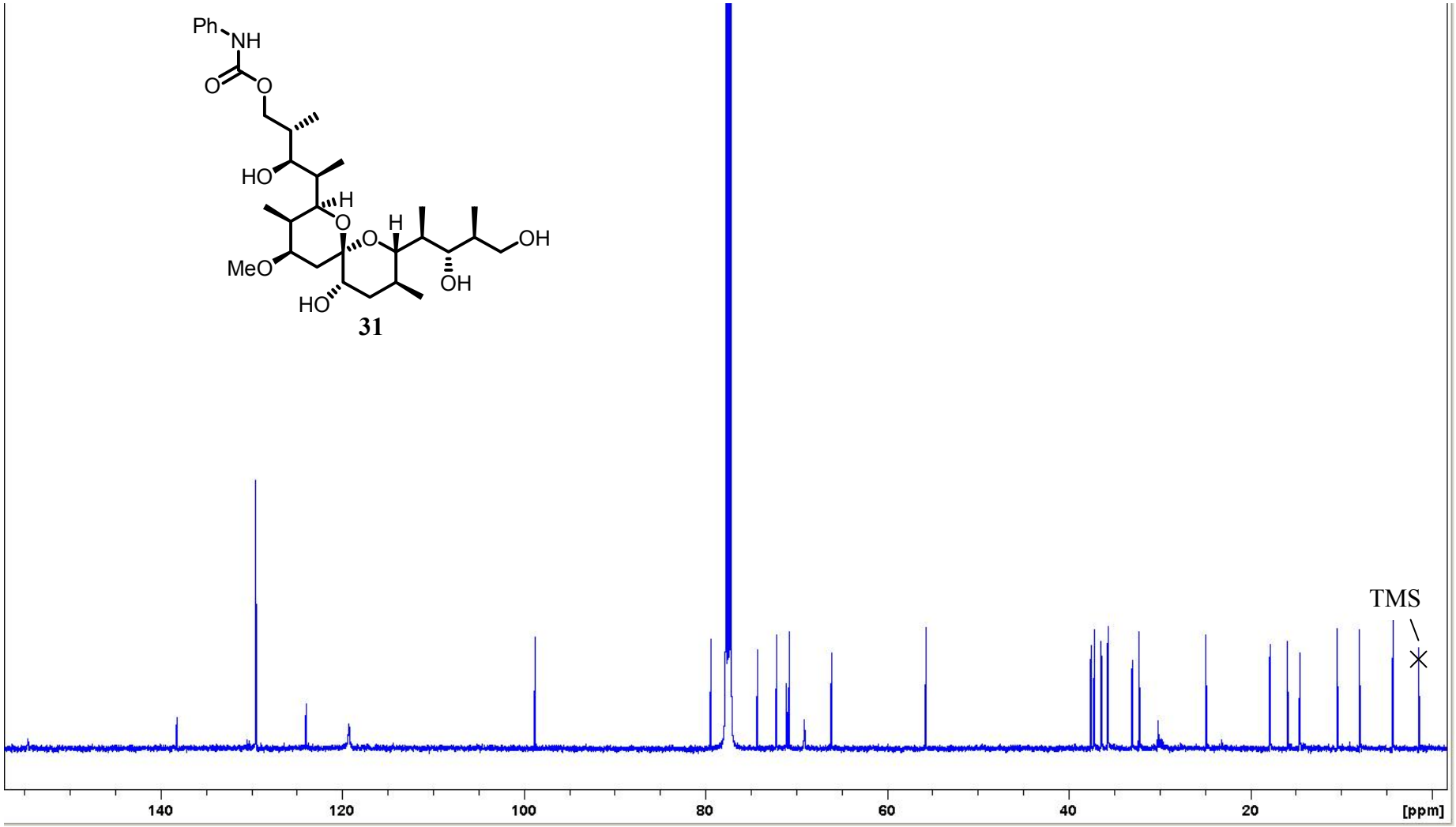

**31**

$CDCl_3$, 600 MHz



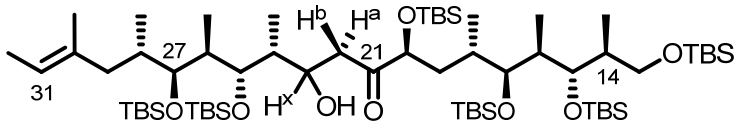

**31**

$CDCl_3$, 150 MHz



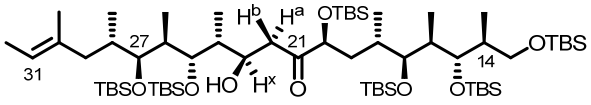

**31**

**NMR assignment of the diastereomers obtained during the aldolisation reactions**[1]

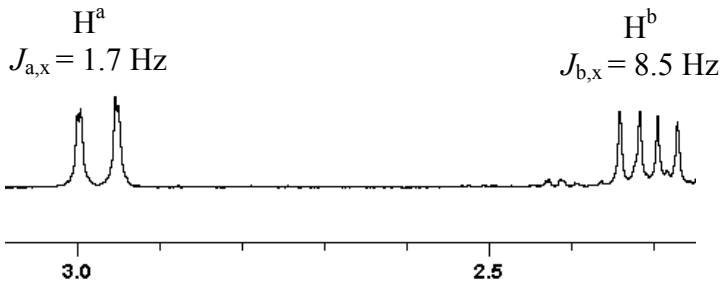



**19** and **19'**

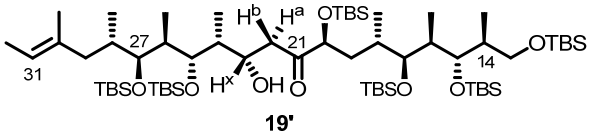
Major product : anti Felkin aldol adduct



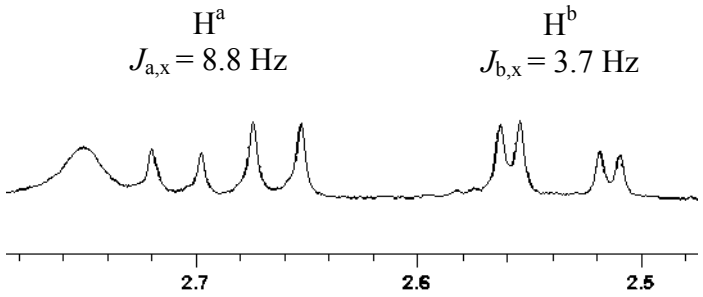

**19**



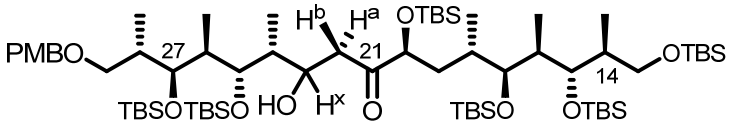

Minor product : Felkin aldol adduct




**19'**

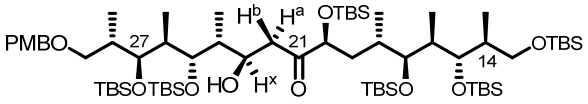



[1] Roush, W. R.; Bannister, T. D.; Wendt, M. D.; VanNieuwenhze, M. S.; Gustin, D. J.; Dilley, G. J.; Lane, G. C.; Scheidt, K. A.; Smith, W. J. *J. Org. Chem.* **2002**, *67*, 4284.




**25** and **25'**

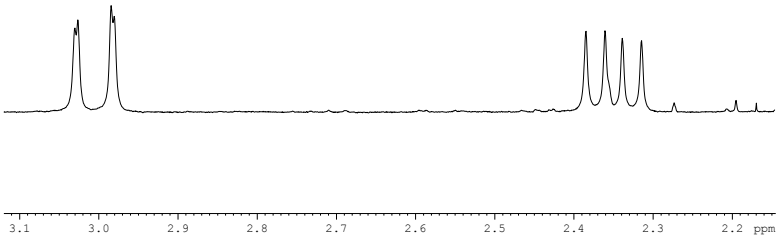
Major product : anti Felkin aldol adduct



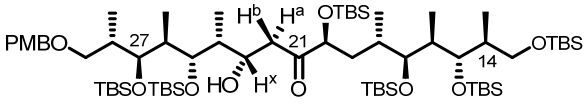

**25**

$H^a$
$J_{a,x}$ = 1.9 Hz

$H^b$
$J_{b,x}$ = 9.4 Hz



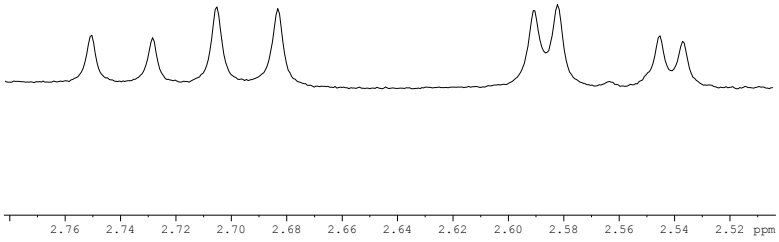

Minor product : Felkin aldol adduct



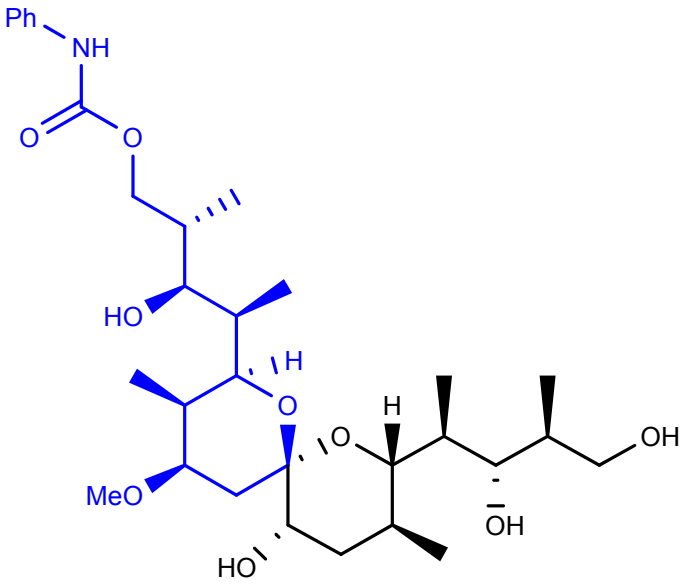

**25'**

$H^a$
$J_{a,x}$ = 8.8 Hz

$H^b$
$J_{b,x}$ = 2.6 Hz



**Mesurable coupling constants in $^{1}$H NMR and nOe diagnostics for the spiroketal core of 31**




**31**