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## Supporting Information

for

### **The hydrolysis of geminal ethers: a kinetic appraisal of orthoesters and ketals**

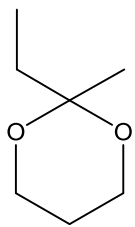
Sonia L. Repetto<sup>1</sup>, James F. Costello\*<sup>1</sup>, Craig P. Butts<sup>2</sup>, Joseph K. W. Lam<sup>3</sup> and Norman M. Ratcliffe<sup>1</sup>

Address: <sup>1</sup>Faculty of Applied Sciences, University of the West of England, Bristol, BS16 1QY, UK, <sup>2</sup>School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK and <sup>3</sup>Airbus Operations Ltd., Filton, Bristol, BS34 7PA, UK

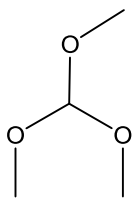
Email: James F. Costello - James.Costello@uwe.ac.uk

\*Corresponding author

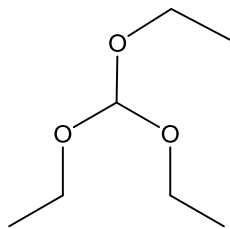
### **Analytical data**



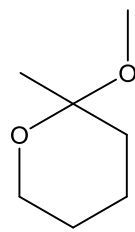
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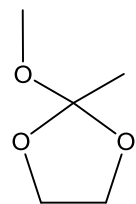
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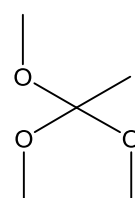
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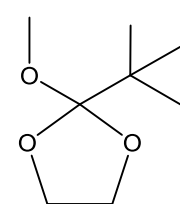
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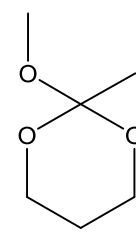
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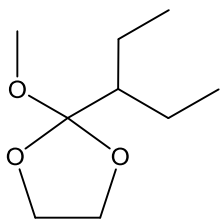
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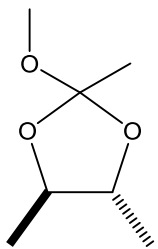
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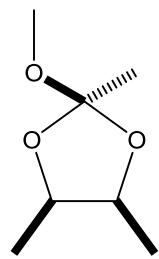
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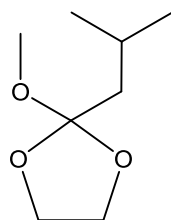
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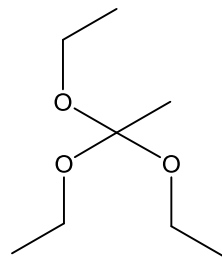
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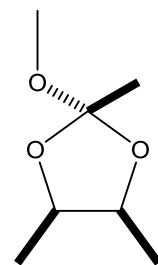
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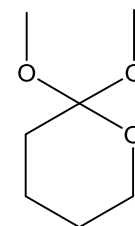
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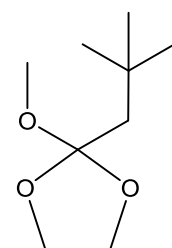
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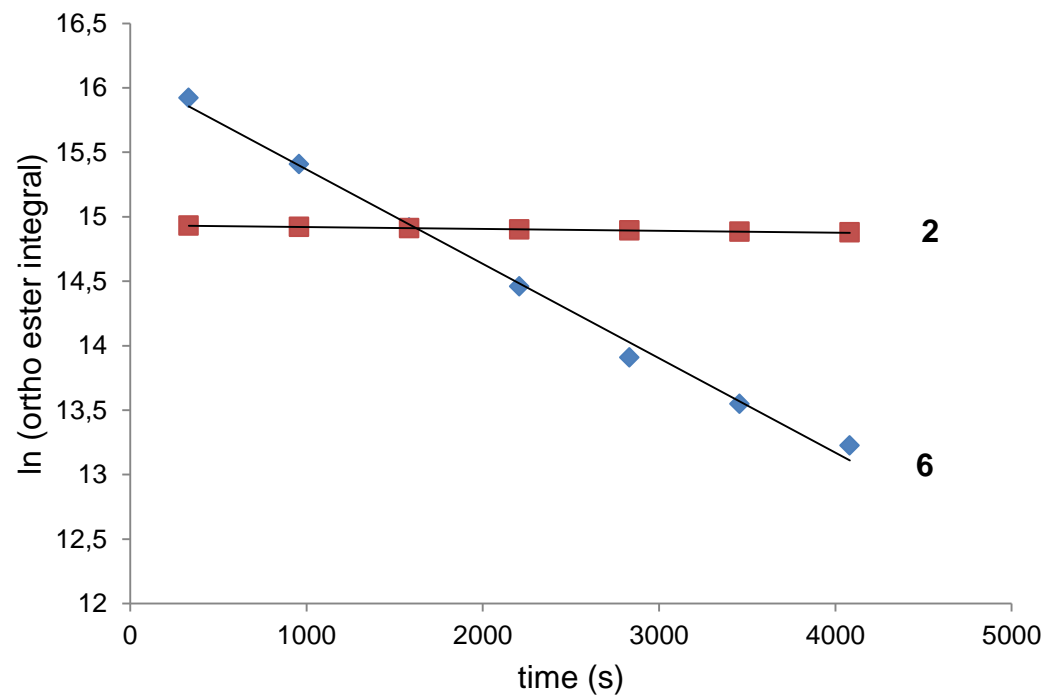
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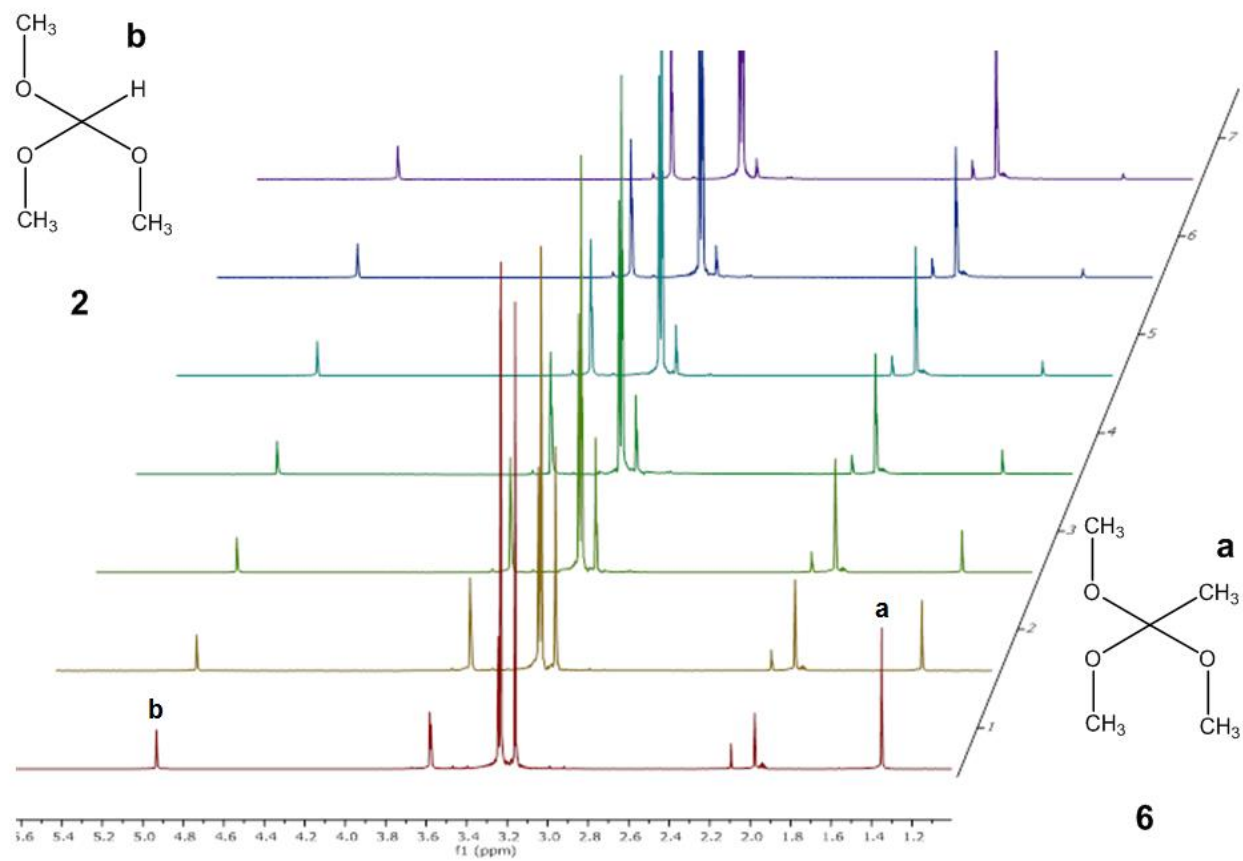
15



16



Indicative plot of  $\ln(\text{integral})$  for **6** ( $k_{\text{obs}} = 7 \times 10^{-4}$ ;  $R^2 = 0.9944$ ), and **2** ( $k_{\text{obs}} = 1.46 \times 10^{-5}$ ;  $R^2 = 0.9932$ ), versus time (s).



Indicative stacked plot of **6** and **2** versus time (300 MHz  $^1\text{H}$  NMR in  $\text{D}_2\text{O}/\text{CD}_3\text{CN}$  (1:4), 625 s intervals,  $T= 25^\circ\text{C}$ ,  $[\text{HCl}] = 9.56 \times 10^{-5}$  M).

**Table S1:** The concentration of acid catalyst used to determine values of  $k_{H^+}$  for the following mixtures of reacting ortho esters.

Reacting substrates	$[H^+] \times 10^{-4} \text{ M}$
<b>6:2</b>	4.78
<b>3:2</b>	4.78
<b>6:13</b>	1.98
<b>6:5</b>	1.98
<b>6:8</b>	1.98
<b>6:10:11:14</b>	1.98
<b>6:16</b>	0.125

**Table S2:** Experimentally determined values of  $k_{H^+}$  for the reacting mixtures of geminal ethers: [6 + 2], [3 + 2], [6 + 13], [6 + 5], [6 + 8], [6 + 10 + 11 + 14], [6 + 16].

The corresponding values of  $k_{H^+}$  (including standard deviations) in Figure 1 (main article) were calculated from an average of these experiments. Thus,  $k_{H^+}$  for **5** calculated using entries (x–xii). Also,  $k_{H^+}$  for **6** calculated from entries (i–iii), (vii–ix), and (x–xxi) respectively, along with data from Table 1 of main article.

	<b>6</b>	<b>2</b>
(i)	7.32	0.153
(ii)	6.74	0.145
(iii)	7.20	0.151

	<b>3</b>	<b>2</b>
(iv)	1.650	0.147
(v)	1.675	0.155
(vi)	1.730	0.143

	<b>6</b>	<b>13</b>
(vii)	6.91	19.44
(viii)	7.20	19.74
(ix)	6.89	21.18

	<b>6</b>	<b>5</b>
(x)	7.50	6.70
(xi)	6.70	6.30
(xii)	7.20	6.60

	<b>6</b>	<b>8</b>
(xiii)	6.84	9.77
(xiv)	6.99	10.00
(xv)	6.52	9.57



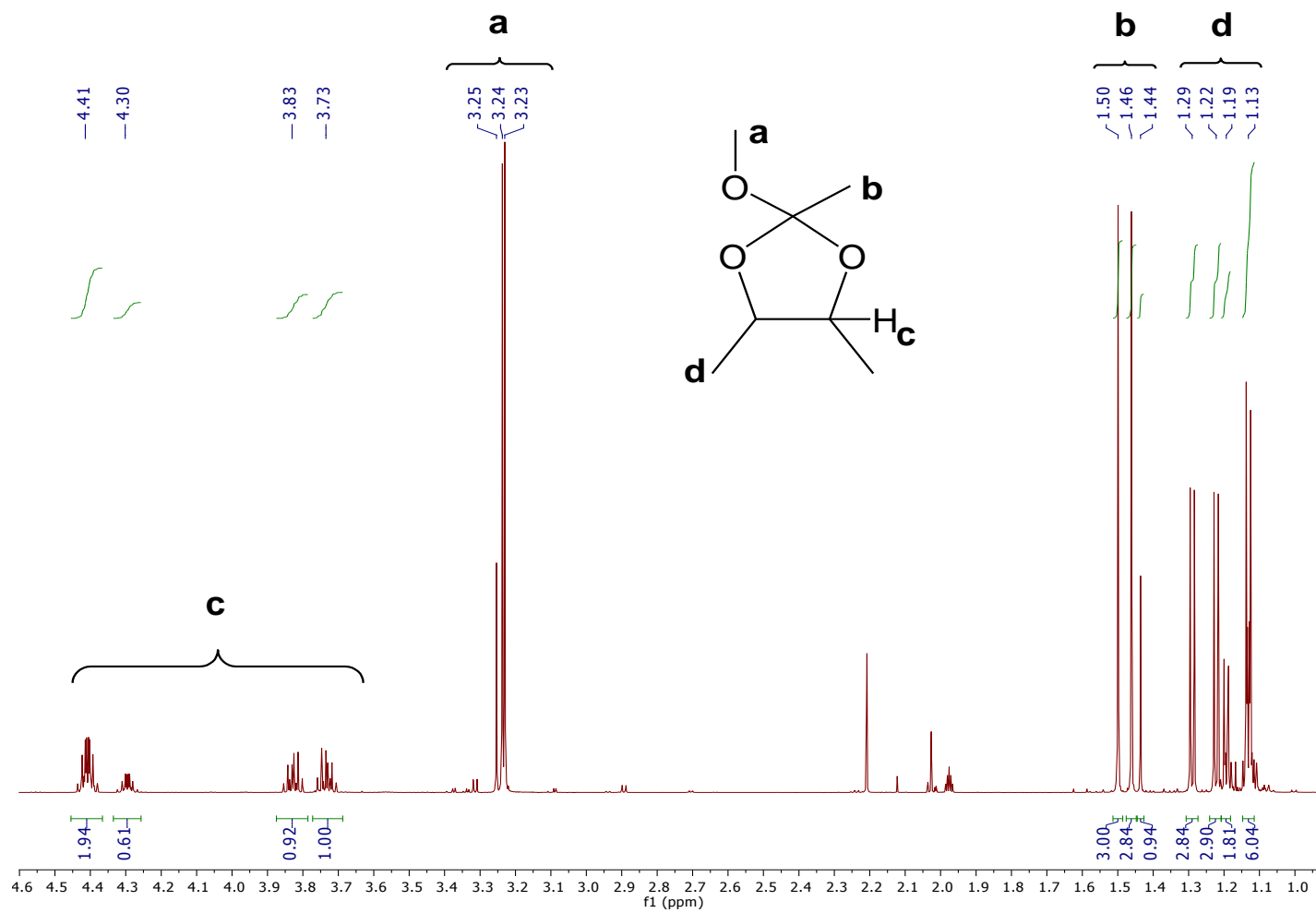
	<b>6</b>	<b>10</b>	<b>11</b>	<b>14</b>
(xvi)	7.07	13.10	13.99	29.80
(xvii)	7.01	11.76	12.78	27.38
(xviii)	6.90	11.38	12.07	26.62

	<b>6</b>	<b>16</b>
(xix)	7.00	70.63
(xx)	7.20	73.10
(xxi)	6.74	84.00

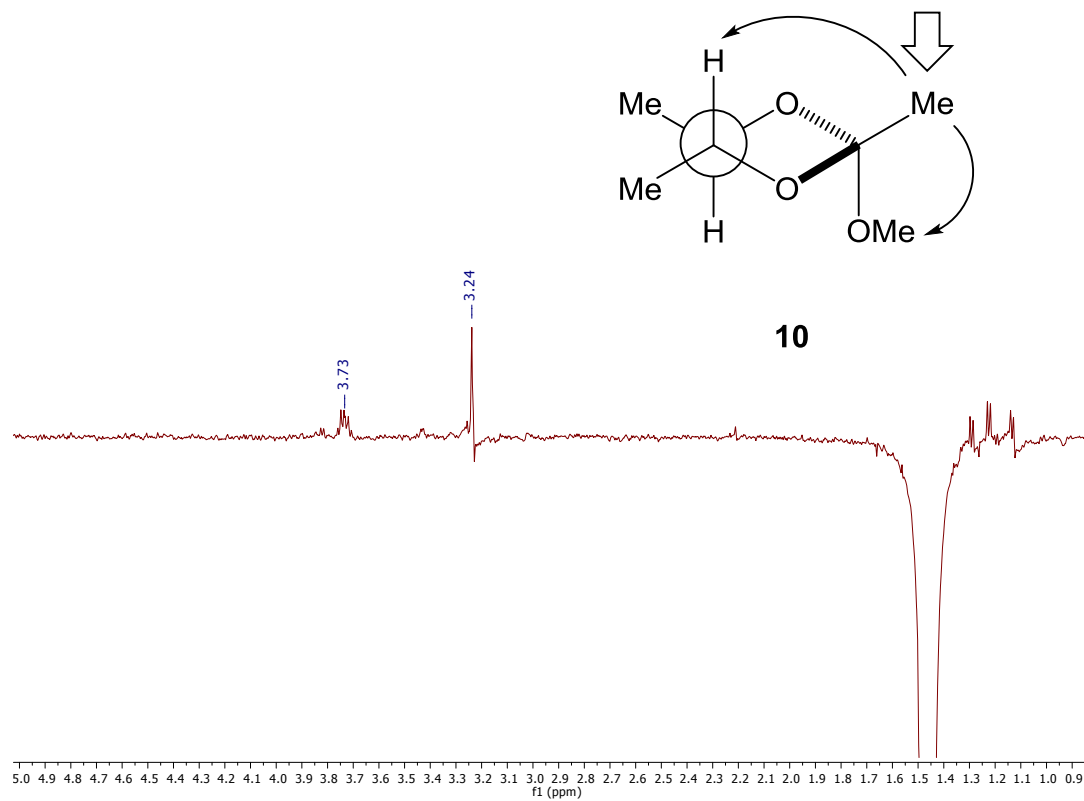
**Table S3:** Corresponding values of  $k_{H^+}$  ( $M^{-1}s^{-1}$ ) obtained from calibration of data obtained from different workers.

Ortho ester	Relative rate <sup>a</sup>	$k_{H^+}$ ( $M^{-1}s^{-1}$ )
<b>1</b>	1	$4 \times 10^{-3b}$
<b>4</b>	649	$2.79^b$
<b>8</b>	2270	$9.78^c$
<b>15</b>	11351	$48.90^b$

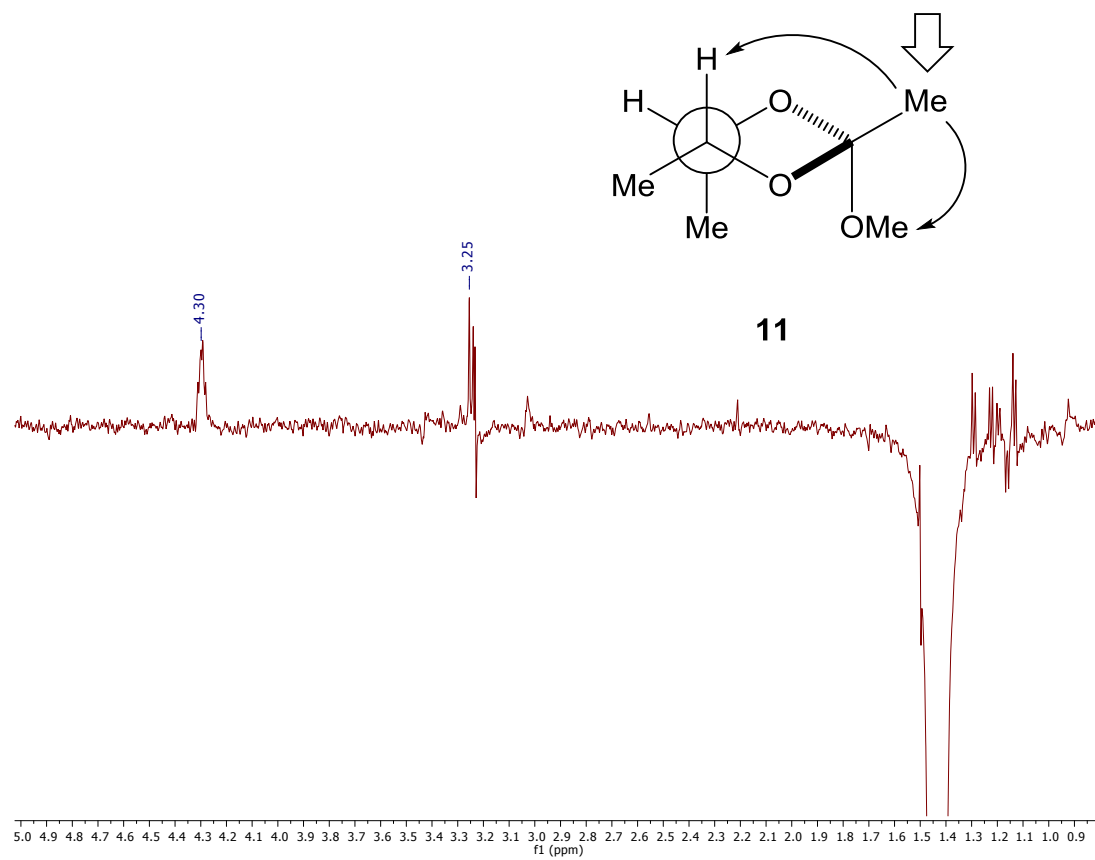
Ortho ester	$k_{1H^+}$ ratios <sup>a</sup>	$k_{H^+}$ ( $M^{-1}s^{-1}$ ) <sup>b</sup>	$k_{H^+}$ ( $M^{-1}s^{-1}$ ) <sup>c</sup>	$k_{H^+}$ ( $M^{-1}s^{-1}$ ) <sup>d</sup>
<b>5</b>	1	6.53	–	$6.5 \pm 0.2$
<b>6</b>	–	–	–	$7.0 \pm 0.2$
<b>7</b>	2.0	$\approx 13$	$\approx 8$	–
<b>9</b>	2.6	$\approx 17$	$\approx 11$	–
<b>12</b>	3.4	$\approx 22$	$\approx 14$	–
<b>16</b>	18.8	$\approx 123$	$\approx 76$	$75.9 \pm 7.1$



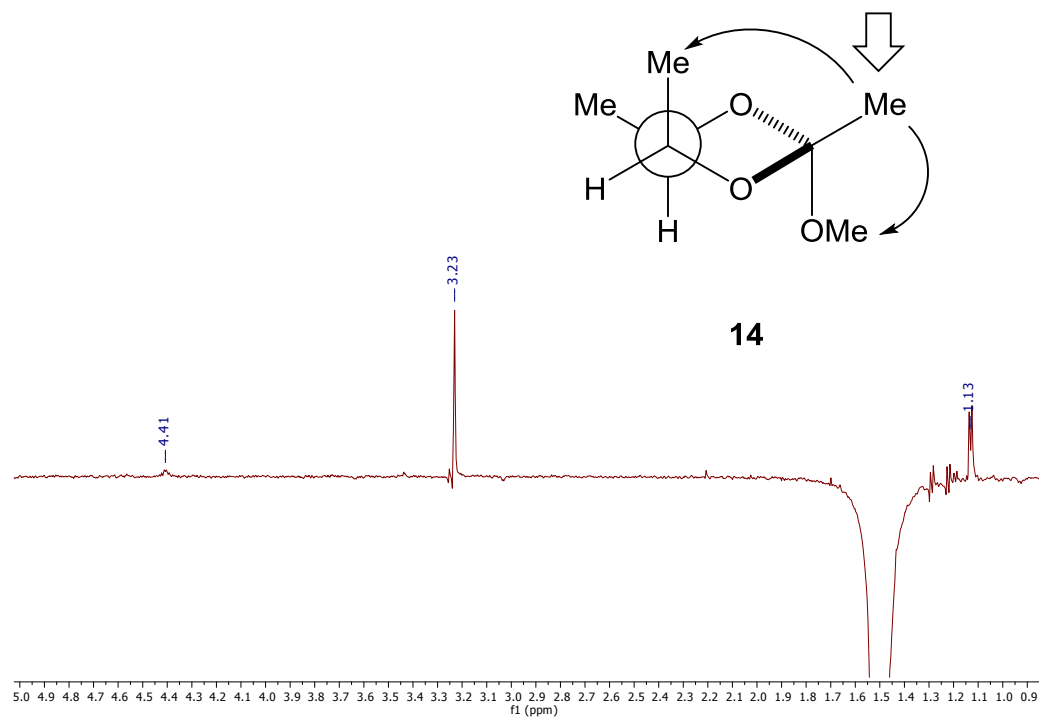
500 MHz <sup>1</sup>H NMR spectrum of a mixture of **10**, **11** and **14** in CD<sub>3</sub>CN.



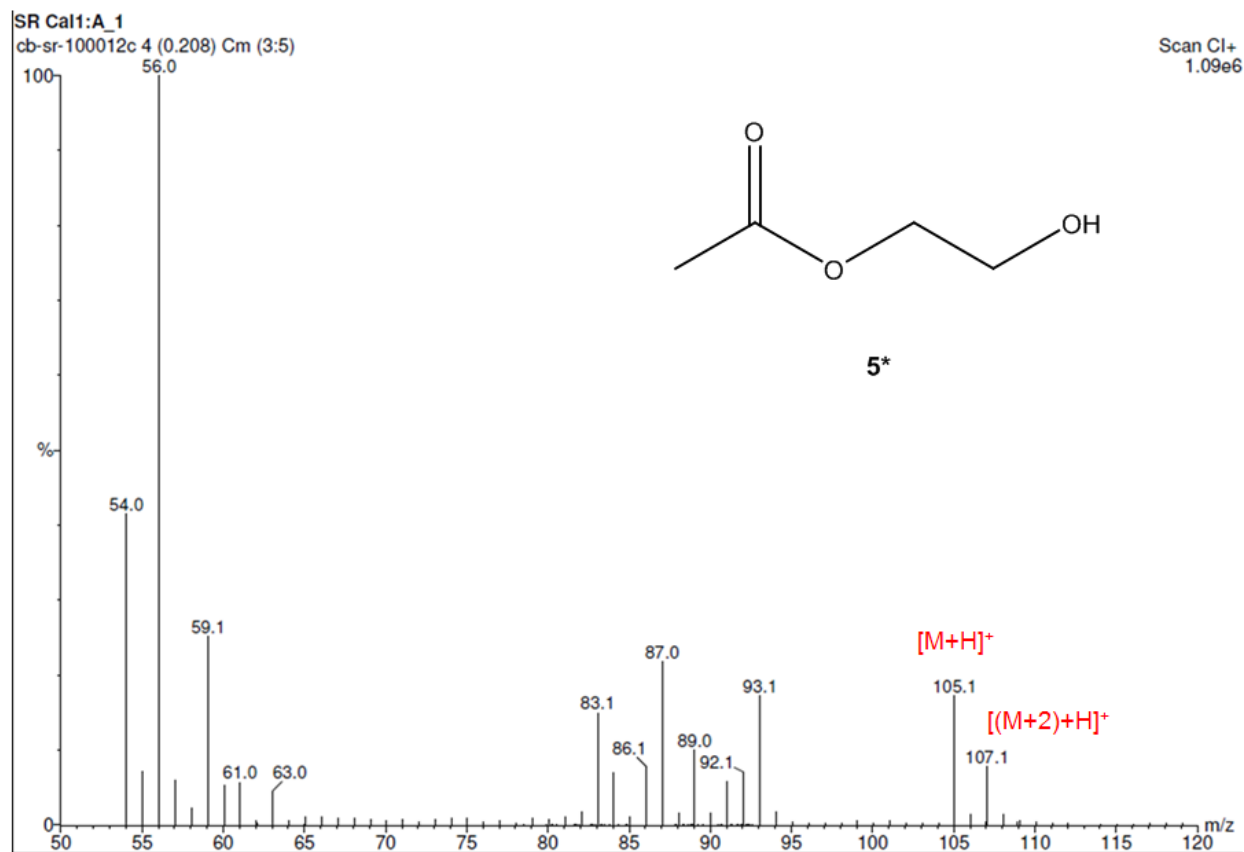
1D-NOESY <sup>1</sup>H NMR spectrum of a mixture of **10**, **11** and **14** (3:1:3.2, respectively) irradiated at 1.46 ppm.



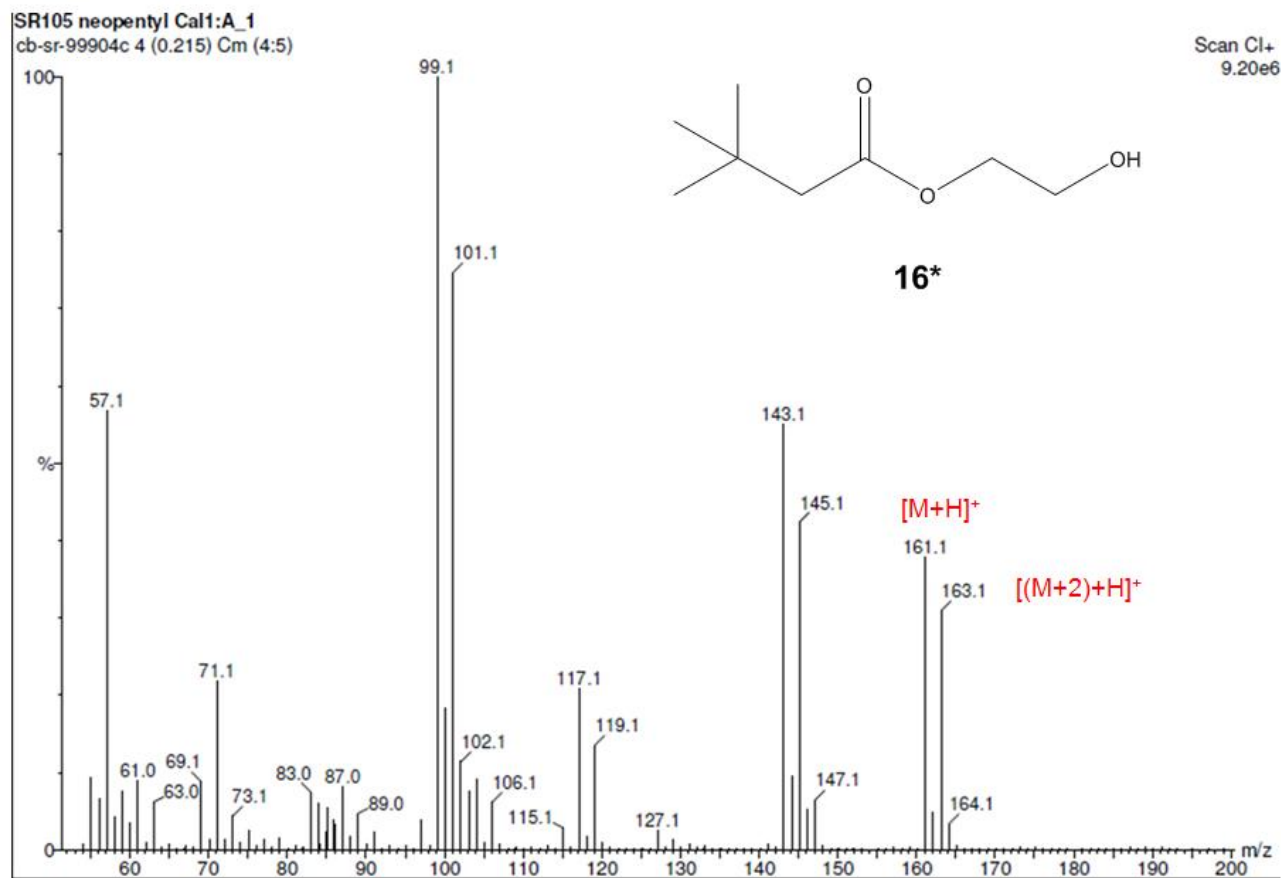
1D-NOESY  $^1\text{H}$  NMR spectrum of a mixture of **10**, **11** and **14** (3:1:3.2, respectively) irradiated at 1.44 ppm.



1D-NOESY <sup>1</sup>H NMR spectrum of a mixture of **10**, **11** and **14** (3:1:3.2, respectively) irradiated at 1.50 ppm.

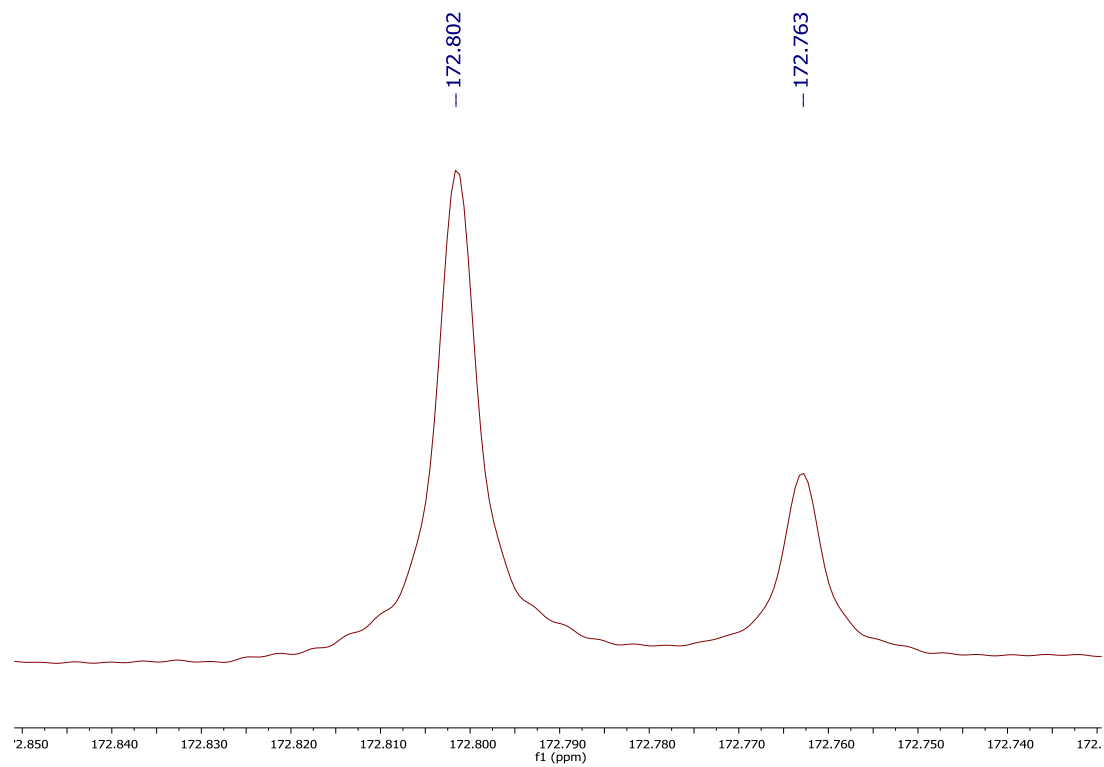


MS(Cl) spectrum of hydroxy ester the derived from 1,3-dioxolan-2-ylum cation **5\*** and H<sub>2</sub><sup>16/18</sup>O.



MS(Cl) spectrum of the hydroxy ester derived from 1,3-dioxolan-2-ylum cation **16\*** and H<sub>2</sub><sup>16/18</sup>O.





Partial <sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>) of hydroxy ester derived from **16** illustrating resonances associated with <sup>13</sup>C=<sup>18</sup>O ( $\delta_C = 172.76\text{ppm}$ ) and <sup>13</sup>C=<sup>16</sup>O ( $\delta_C = 172.80\text{ ppm}$  *i.e.*,  $\Delta\delta_C = 0.04\text{ ppm}$ ) nuclei.

## Full literature reference for Gaussian 09

**Gaussian 09**, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

### Cartesian coordinates of conformer 16a

C	-2.03182000	-1.48965000	0.70785400
C	-0.65026000	0.10995800	-0.22370600
C	-2.71696200	-0.93745800	-0.54025600
H	-1.53976800	-2.45194700	0.50530200
H	-2.69624900	-1.60348600	1.56830100
H	-3.55058500	-0.27027400	-0.28049700
H	-3.08107900	-1.71225000	-1.22112000
O	-1.07539300	-0.48067000	1.00366400
O	-1.66994800	-0.21260100	-1.18009900
C	2.01132200	-0.13827700	-0.02606300
C	-1.70594500	2.18082800	0.31258800
C	0.67229700	-0.46586200	-0.74446500
H	0.74833500	-0.16286400	-1.79470500
H	0.52920700	-1.55318900	-0.74953900
C	3.06375700	-1.11795600	-0.58936700
H	2.80847500	-2.15785700	-0.35469200
H	3.14739800	-1.03077900	-1.67892100
H	4.05146400	-0.91215200	-0.16254300
C	1.91375000	-0.33679700	1.49828200
H	2.89471900	-0.17794900	1.96086300
H	1.20598200	0.36262600	1.94880800
H	1.58261300	-1.34987200	1.74977800
C	2.47793900	1.29981200	-0.33099000
H	2.57498300	1.46087300	-1.41114800
H	1.77454100	2.03795400	0.05597000
H	3.45981200	1.48242600	0.12108900
O	-0.52029200	1.47759800	-0.05540900
H	-2.10822200	1.81140500	1.26113000
H	-2.46727000	2.09899700	-0.47042200
H	-1.41375100	3.22613200	0.42382600

### Cartesian coordinates of conformer 16b

C	2.38968800	-1.37618000	-0.58742300
C	0.65369300	0.12175600	-0.27113300
C	2.27342700	-1.08285900	0.90637300
H	1.91707900	-2.33428600	-0.84817000
H	3.41693000	-1.37254000	-0.96145000
H	3.08183200	-0.42462900	1.25333400
H	2.25165200	-1.97980500	1.53181300
O	1.68860200	-0.28655300	-1.17061100
O	1.01185700	-0.42378900	1.00060800
C	-2.01088200	-0.13476500	0.00804900
C	1.76908600	2.17713900	0.20309800
C	-0.69264300	-0.42218600	-0.76409500
H	-0.56063700	-1.50891700	-0.83061300
H	-0.80009600	-0.05595300	-1.79119400
C	-1.93898400	-0.60490100	1.47351100
H	-1.67068700	-1.66512400	1.53981700
H	-1.19613600	-0.04224300	2.04237900
H	-2.91421100	-0.47521200	1.95722100
C	-3.11714400	-0.93625700	-0.71278700
H	-4.08823900	-0.77068900	-0.23356100
H	-3.20829200	-0.63589500	-1.76296700
H	-2.91244300	-2.01286900	-0.68825700
C	-2.38886300	1.35911000	-0.03438000
H	-1.66131100	1.97239700	0.49890100
H	-2.43886200	1.72540400	-1.06596300
H	-3.37390600	1.51031000	0.42230100
O	0.59430000	1.50544700	-0.24707400
H	2.63111000	1.93027200	-0.42475100
H	1.98820100	1.92961300	1.24752000
H	1.55567700	3.24418000	0.12297800

### Cartesian coordinates of conformer 16c

C	1.89106600	-1.62860600	-0.60508300
C	0.70638100	0.24111600	-0.17460500
C	2.00325600	-1.31263500	0.90460600
H	1.68891600	-2.68057200	-0.81852900
H	2.78172900	-1.30766800	-1.15468900
H	3.02099100	-1.02455900	1.18911700
H	1.67908700	-2.14381600	1.53859600
O	0.75043600	-0.87067000	-1.01760200
O	1.09432100	-0.22422200	1.10544500
C	-1.95450000	0.02730500	0.03190700
C	2.00317400	2.26227600	0.12712600
C	-0.67408400	0.89747500	-0.11627700
H	-0.76624600	1.50331000	-1.02443600
H	-0.63111200	1.59724500	0.72578800
C	-3.10852700	0.99775800	0.36487900
H	-2.94503100	1.49856400	1.32609400
H	-3.21411600	1.77242400	-0.40361600
H	-4.06057800	0.45932900	0.42632800
C	-1.83563600	-1.00419600	1.16910700
H	-2.79635200	-1.51176700	1.31362500
H	-1.08407200	-1.76409400	0.94337400
H	-1.55599000	-0.52978700	2.11497200
C	-2.29071700	-0.69270300	-1.28985000
H	-2.42633500	0.02729200	-2.10541700
H	-1.49754600	-1.38314400	-1.58032100
H	-3.22472600	-1.25723200	-1.18760200
O	1.69011400	1.13564200	-0.68186000
H	2.18922200	1.97067500	1.16665100
H	1.20940700	3.02082400	0.10491700
H	2.91130600	2.70023100	-0.29357500