Supporting information for

Fragmentation of β-Hydroxy Hydroperoxides

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General methods. Proton magnetic resonance (^{1}H NMR) spectra and carbon magnetic resonance (^{13}C NMR) spectra were recorded on a Varian Inova AS400 spectrometer operating 400 MHz. Proton chemical shifts are reported in parts per million (ppm) on δ scale relative to $CDCl_3$ (δ 7.24), CD_3OD (δ 3.30) or D_2O (δ 4.80). ^{1}H NMR spectral data are tabulated in terms of multiplicity of proton absorption (s, singlet; d, doublet; t, triplet; m, multiplet; br, broad), coupling constants (Hz), number of protons. All high resolution mass spectra were recorded on a Kratos AEI MS25 RFA high resolution mass spectrometer at 20 eV.

All solvents were distilled under a nitrogen atmosphere prior to use, and all materials were obtained from Aldrich unless specified. Chromatography was performed with ACS grade solvents. R_f values are quoted for plates of thickness 0.25 mm. The plates were visualized with iodine or phosphomolybdic acid reagent. Flash column chromatography was performed on 230-400 mesh silica gel supplied by E. Merck.

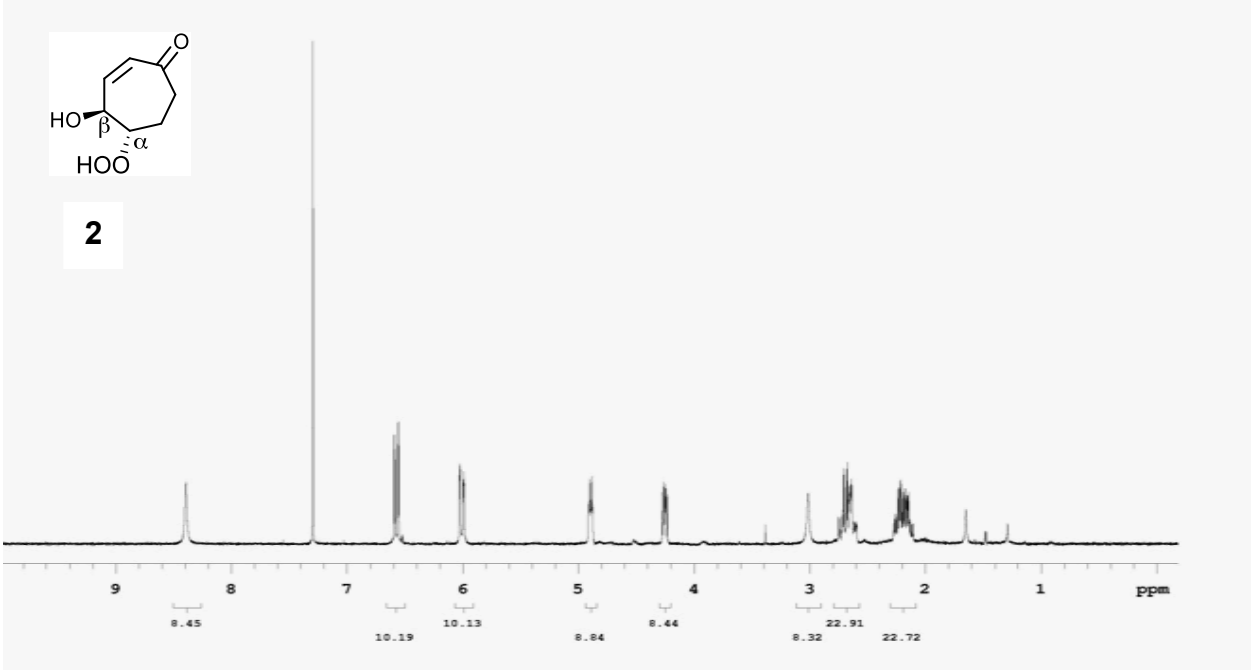

Fig S1 The 400 MHz ^{1}H NMR ($CDCl_3$) spectrum of 5-hydroperoxy-4-hydroxy-cyclohept-2-enone (**2**).

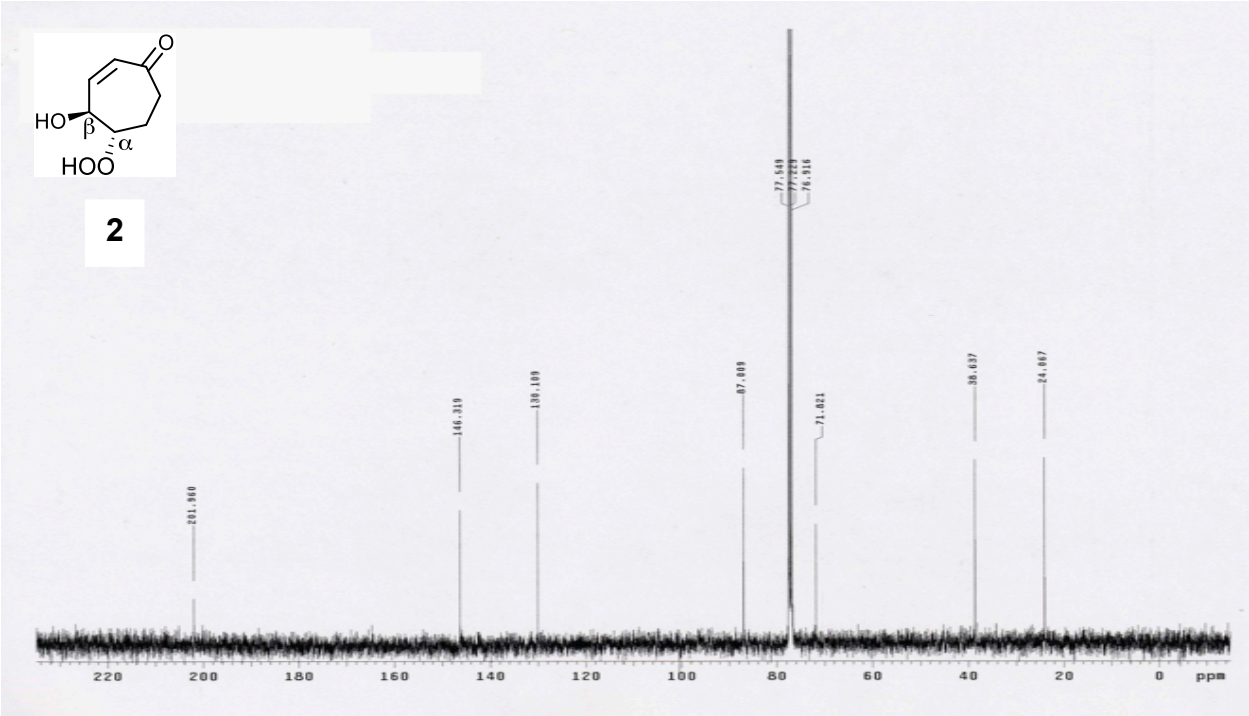

Fig S2 The 100 MHz ^{13}C NMR ($CDCl_3$) spectrum of 5-hydroperoxy-4-hydroxy-cyclohept-2-enone (**2**).

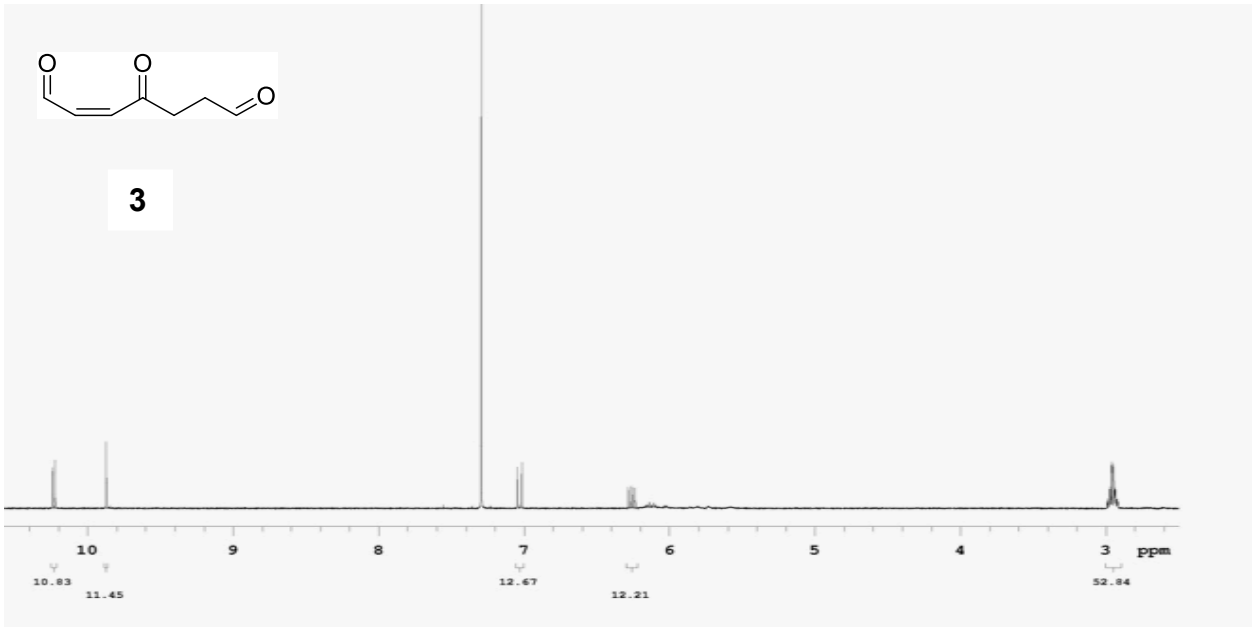

Fig S3 The 400 MHz ^{1}H NMR ($CDCl_3$) spectrum of 4-oxo-hept-2-enedial (**3**).

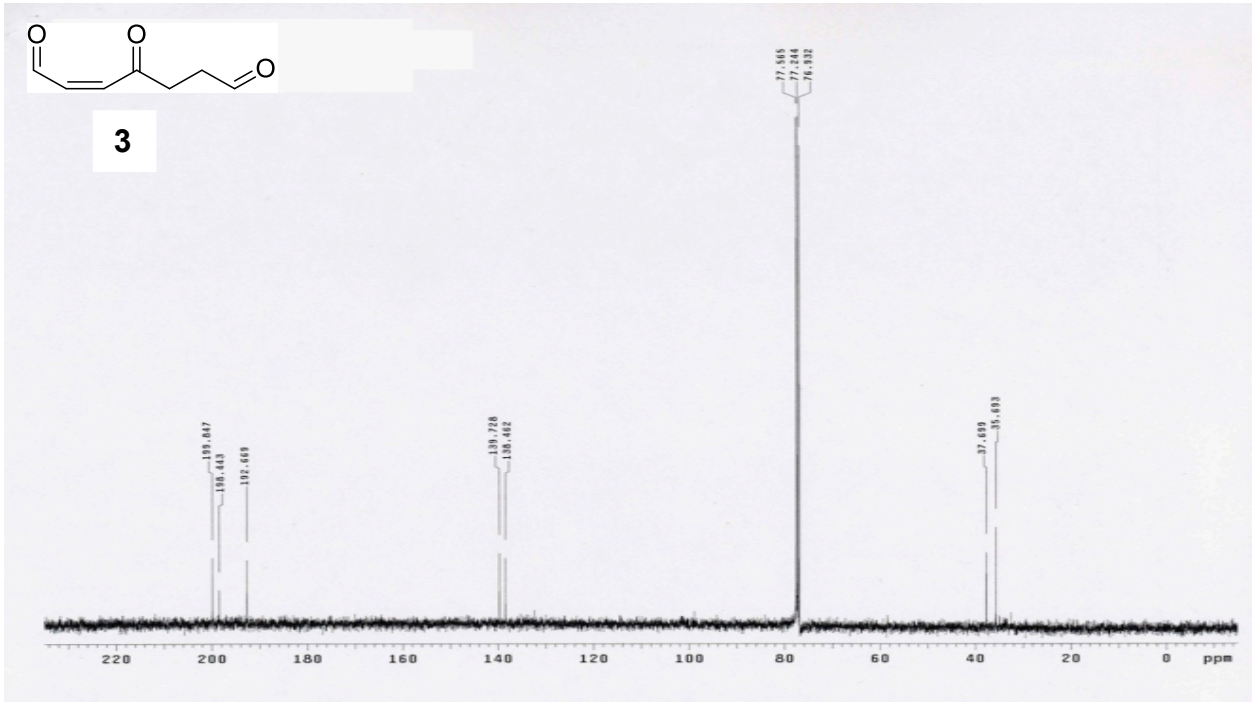

Fig S4 The 100 MHz ^{13}C NMR ($CDCl_3$) spectrum of 4-oxo-hept-2-enedial (**3**).

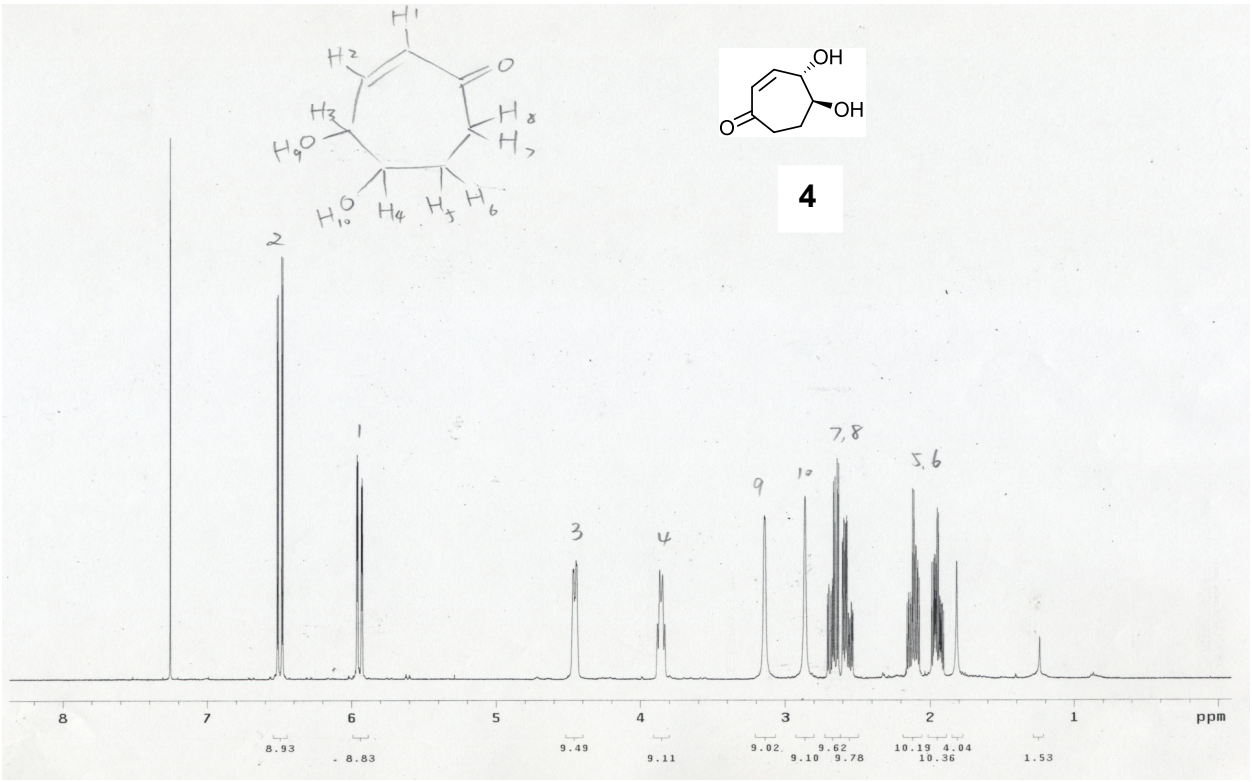

Fig S5 The 400 MHz ^{1}H NMR ($CDCl_3$) spectrum of 4,5-dihydroxy-cyclohept-2-enone (**4**).

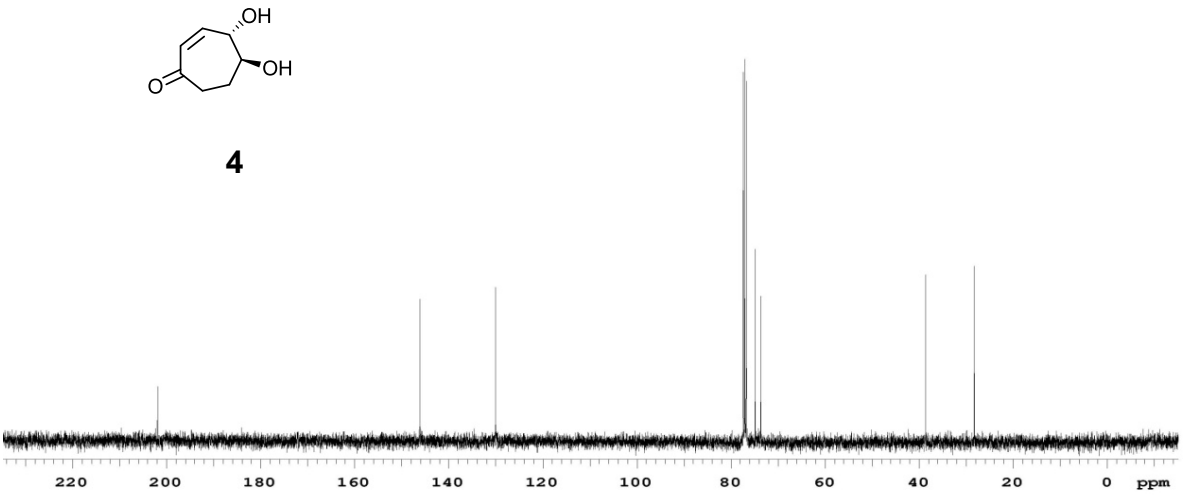

Fig S6 The 100 MHz ^{13}C NMR ($CDCl_3$) spectrum of 4,5-dihydroxy-cyclohept-2-enone (**4**).

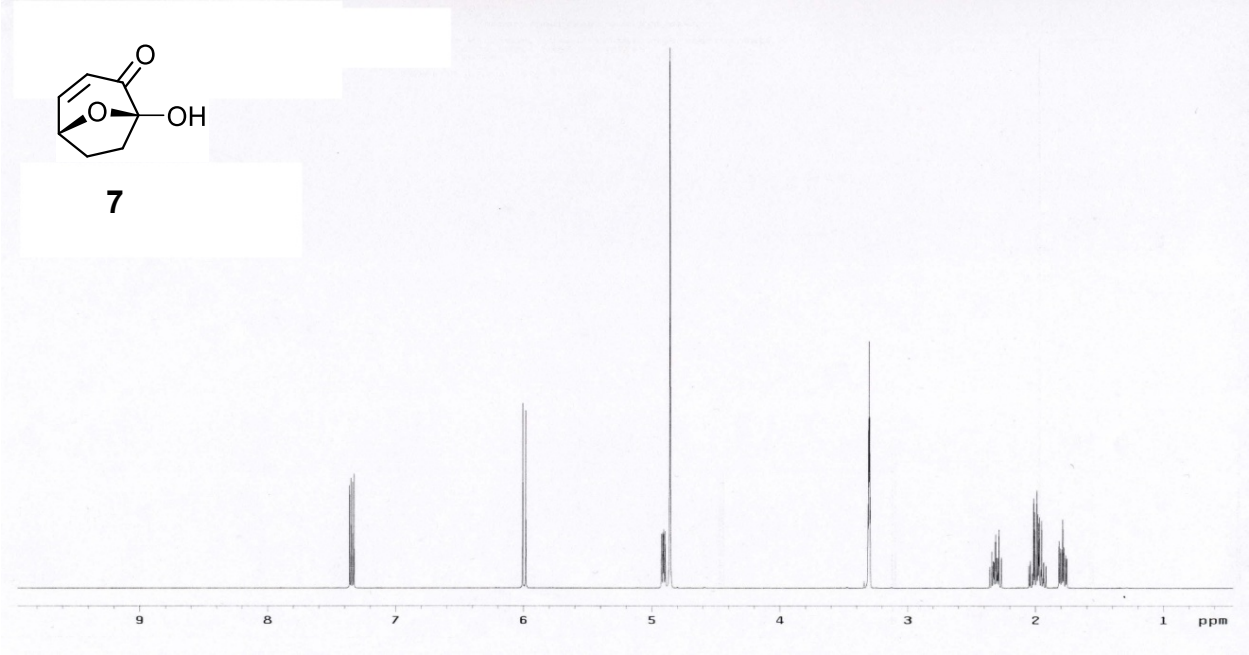

Fig S7 The 400 MHz ^{1}H NMR (CD_3OD) spectrum of 1-hydroxy-8-oxa-bicyclo[3.2.1]oct-3-en-2-one (**7**).

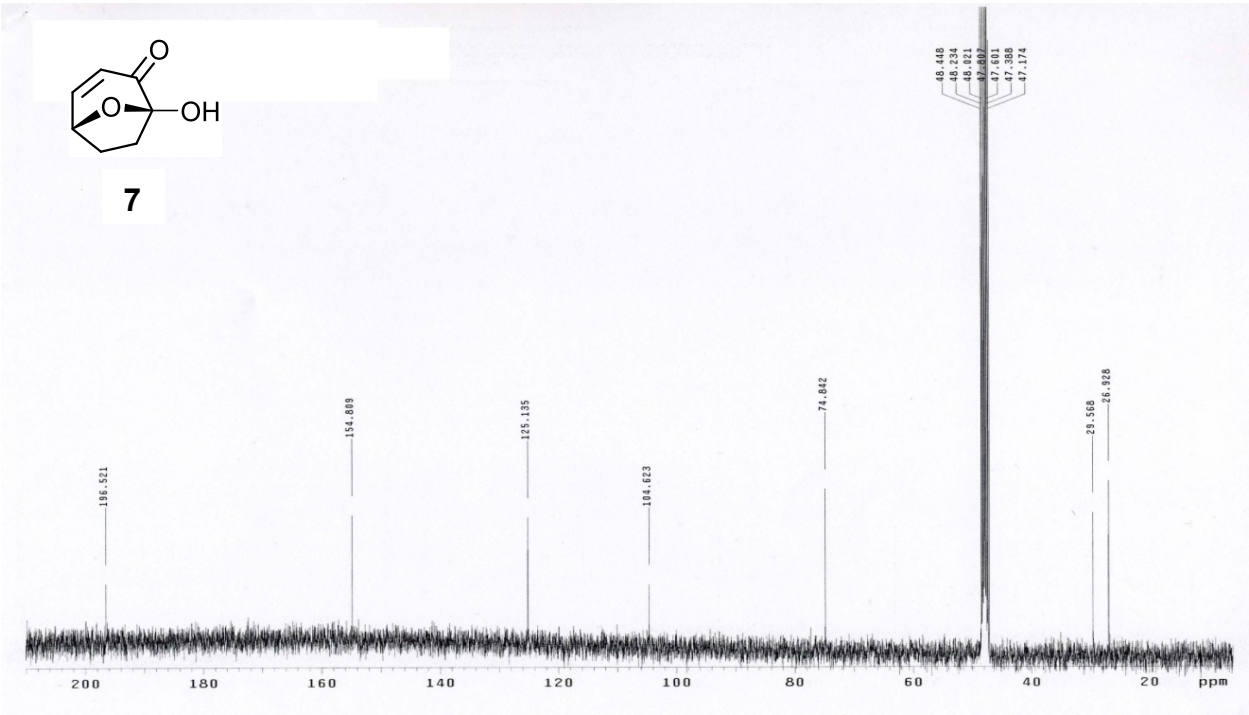

Fig S8 The 100 MHz ^{13}C NMR (CD_3OD) spectrum of 1-hydroxy-8-oxa-bicyclo[3.2.1]oct-3-en-2-one (**7**).

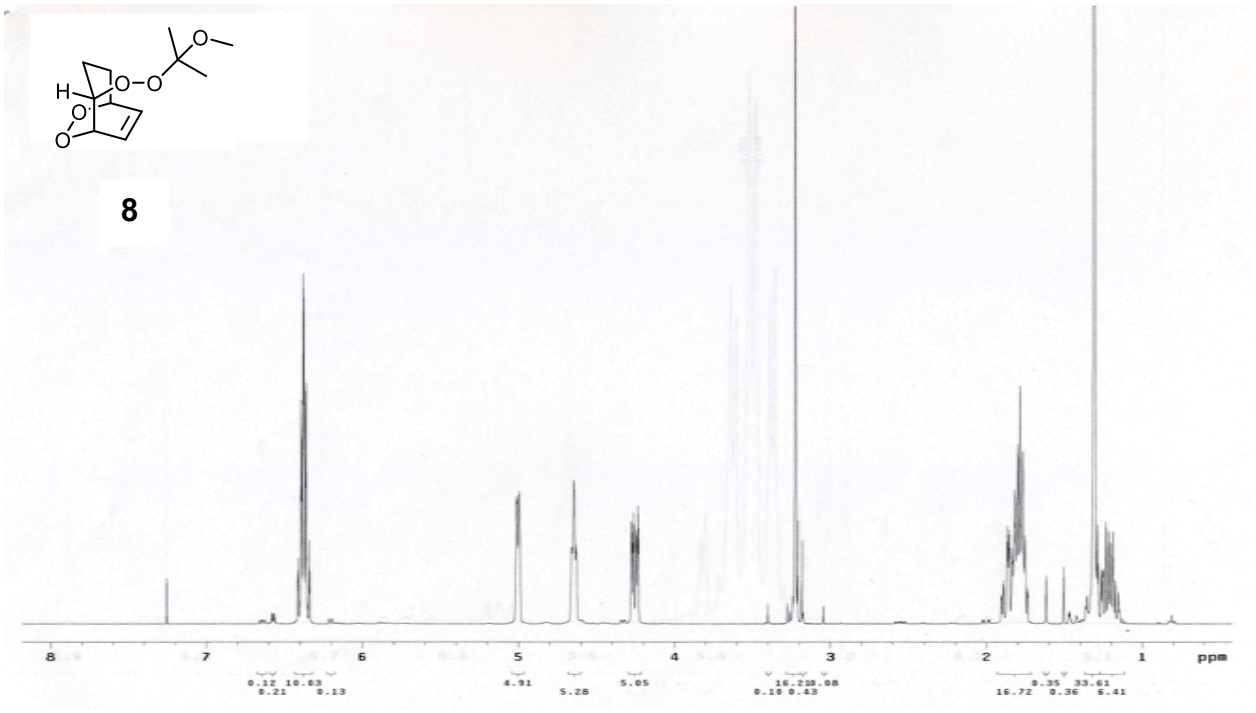

Fig S9 The 400 MHz ^{1}H NMR ($CDCl_3$) spectrum of 2-(1-methoxy-1-methyl-ethylperoxy)-6,7-dioxa-bicyclo[3.2.2]non-8-ene (**8**).

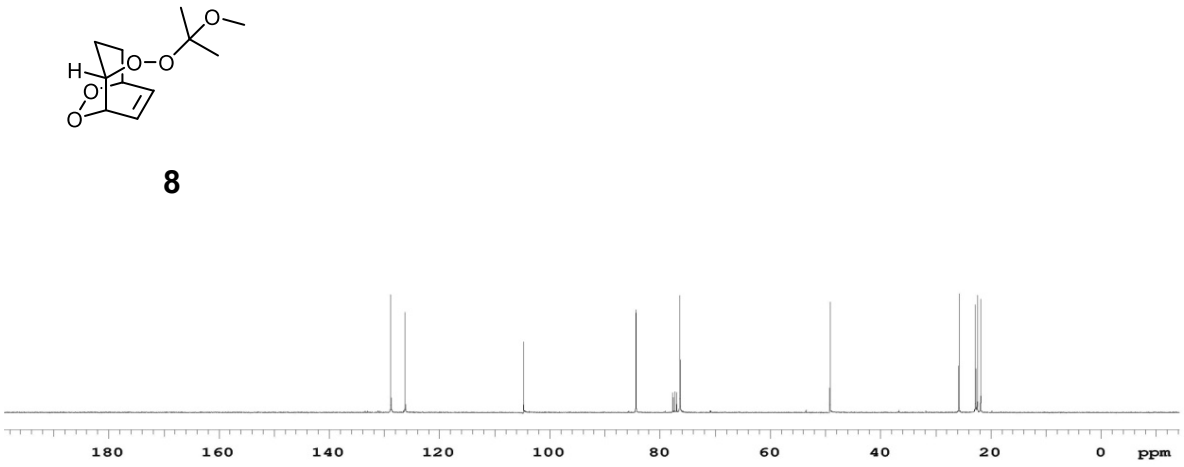

Fig S10 The 100 MHz ^{13}C NMR ($CDCl_3$) spectrum of 2-(1-methoxy-1-methyl-ethylperoxy)-6,7-dioxa-bicyclo[3.2.2]non-8-ene (**8**).

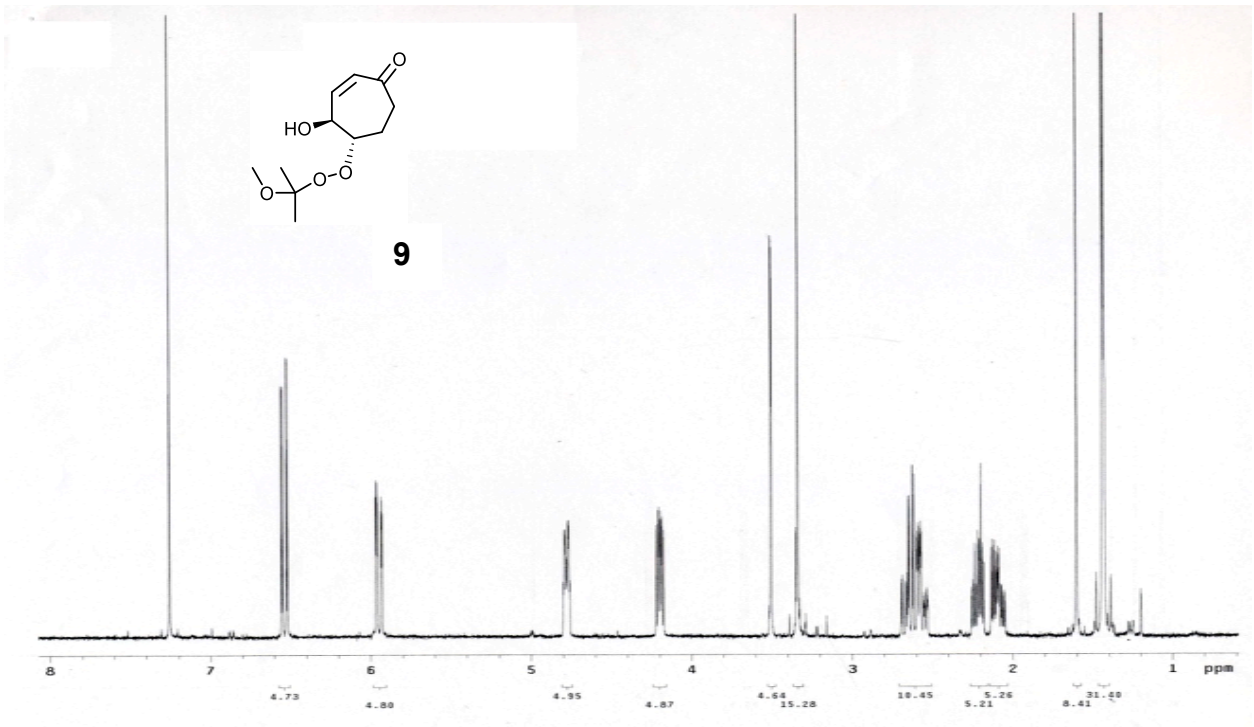

Fig S11 The 400 MHz ^{1}H NMR ($CDCl_3$) spectrum of 4-hydroxy-5-(1-methoxy-1-methyl-ethylperoxy)-cyclohept-2-enone (**9**).

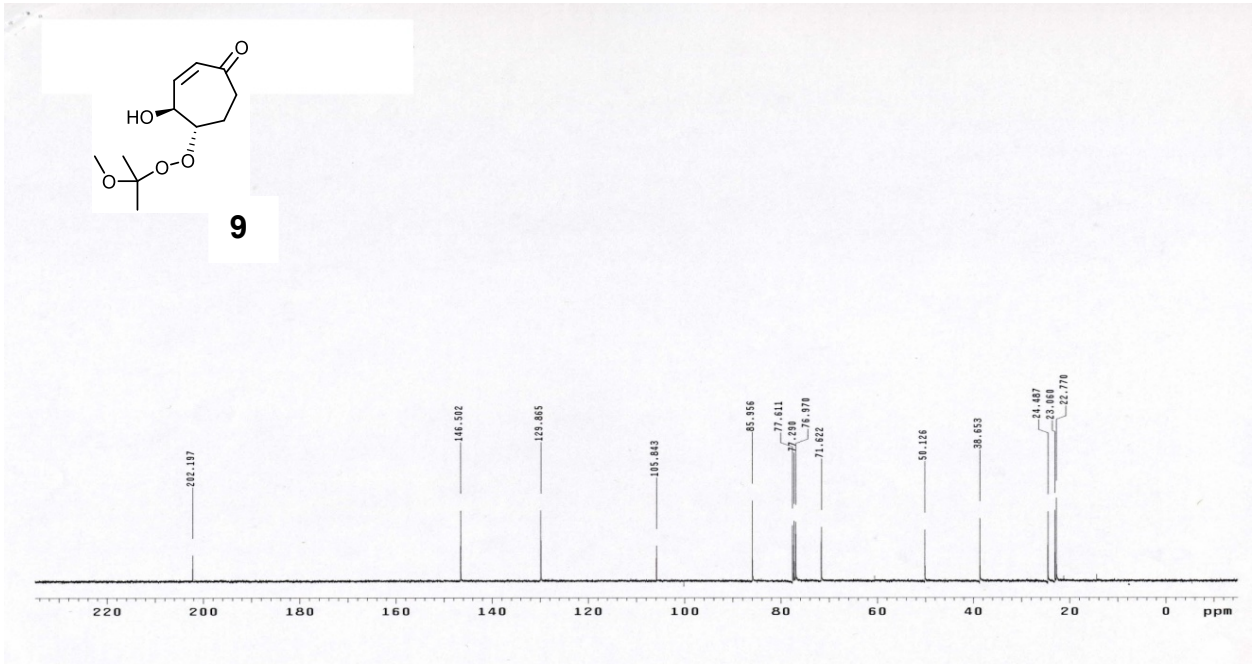

Fig S12 The 100 MHz ^{13}C NMR ($CDCl_3$) spectrum of 4-hydroxy-5-(1-methoxy-1-methyl-ethylperoxy)-cyclohept-2-enone (**9**).

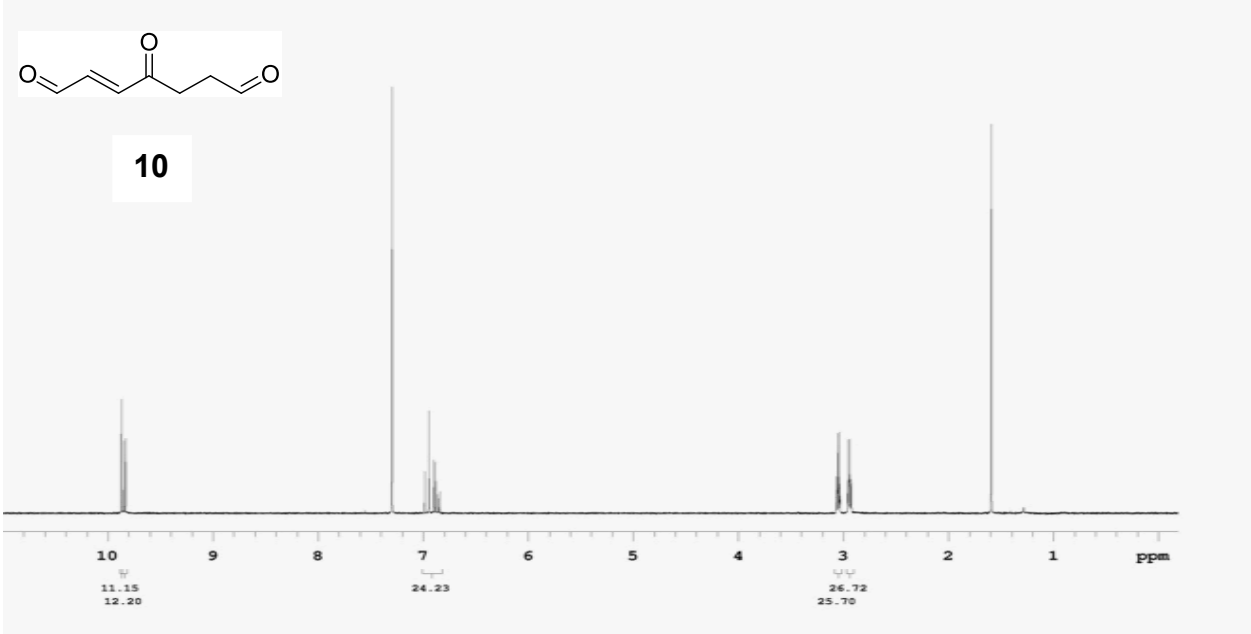

Fig S13 The 400 MHz ^{1}H NMR ($CDCl_3$) spectrum of 4-oxo-hept-2-enedial (**10**).

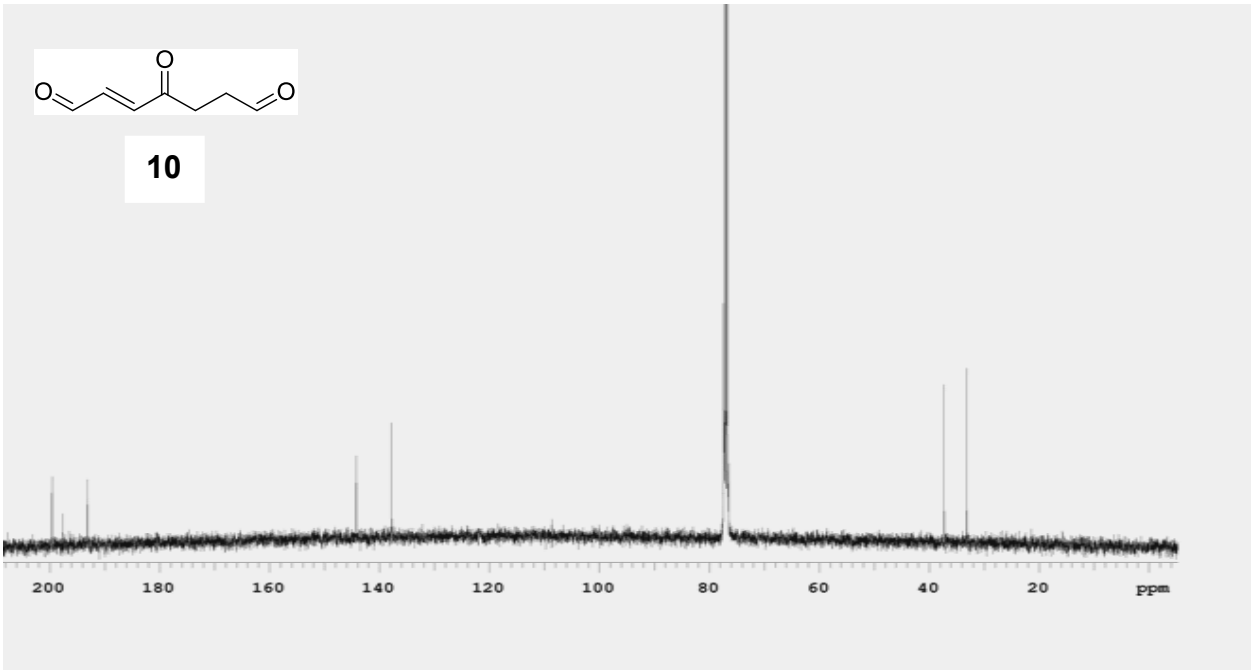

Fig S14 The 100 MHz ^{13}C NMR ($CDCl_3$) spectrum of 4-oxo-hept-2-enedial (**10**).

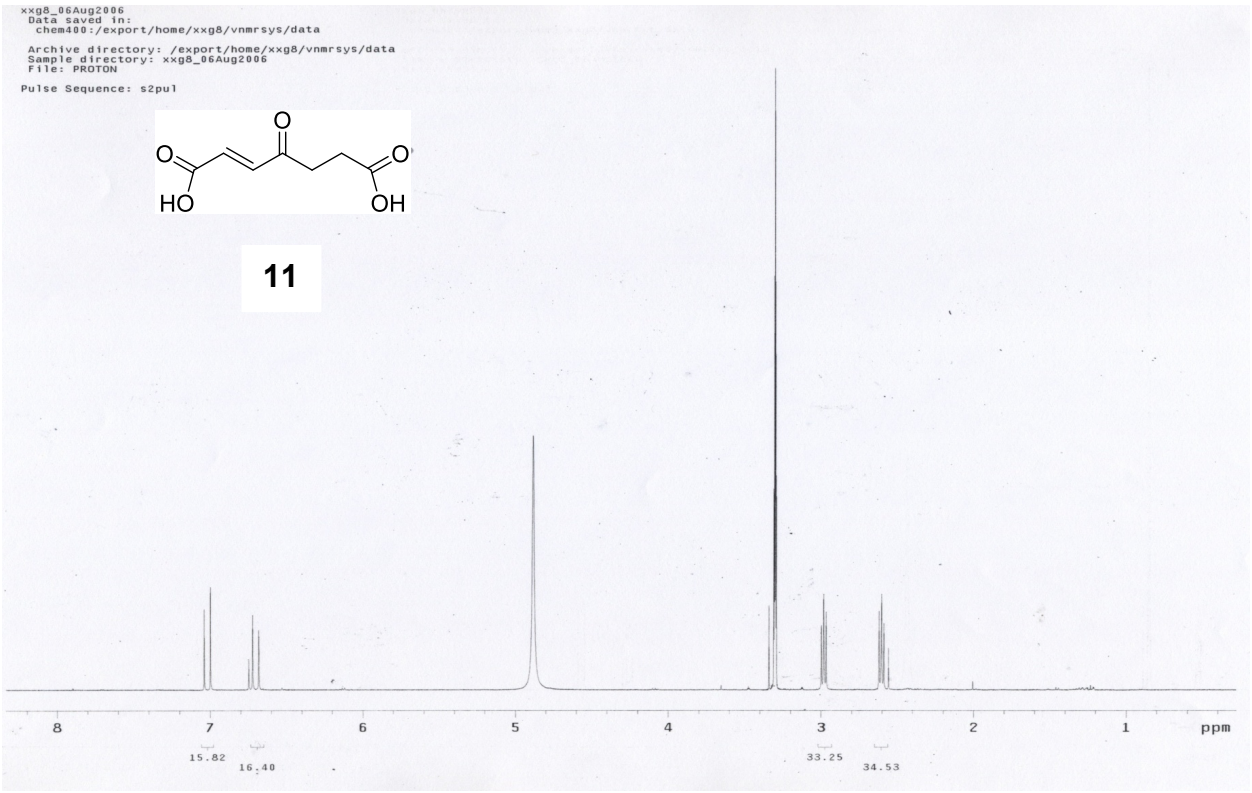

Fig S15 The 400 MHz ^{1}H NMR (CD_3OD) spectrum of 4-oxo-hept-2-enedioic acid (**11**).

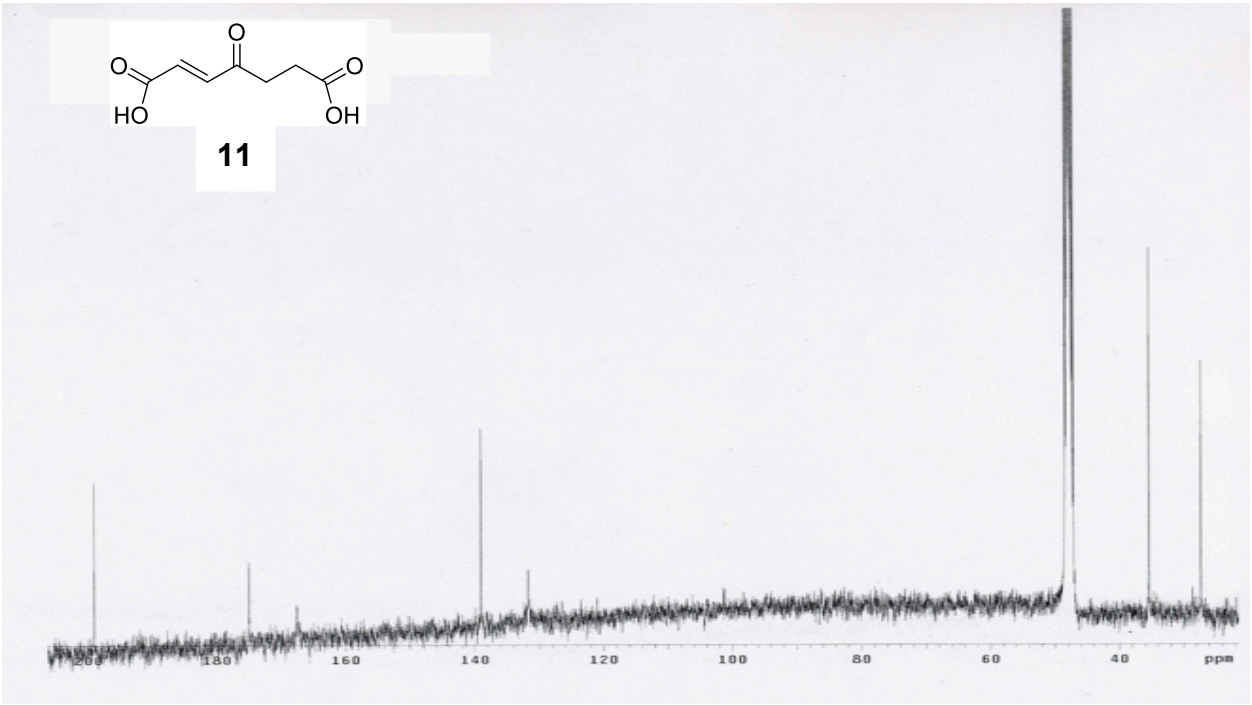

Fig S16 The 100 MHz ^{13}C NMR (CD_3OD) spectrum of 4-oxo-hept-2-enedioic acid (**11**).

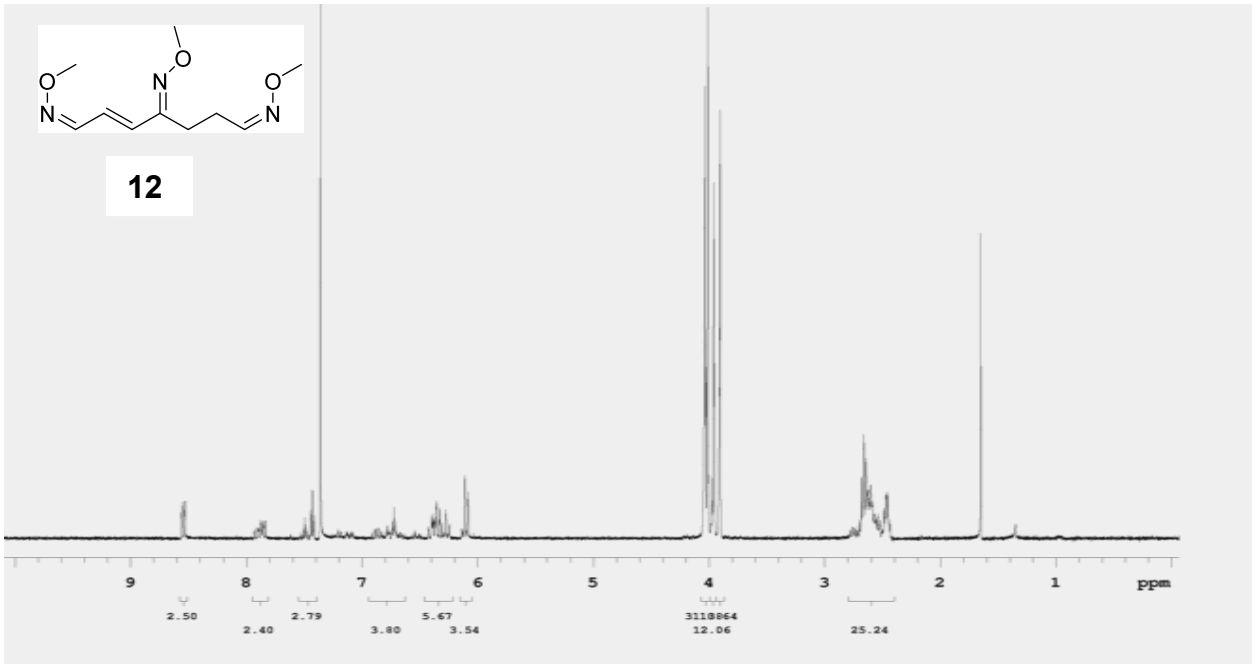

Fig S17 The 400 MHz ^{1}H NMR ($CDCl_3$) spectrum of 4-methoxyimino-hept-2-enedial bis-(O-methyl-oxime) (**12**).

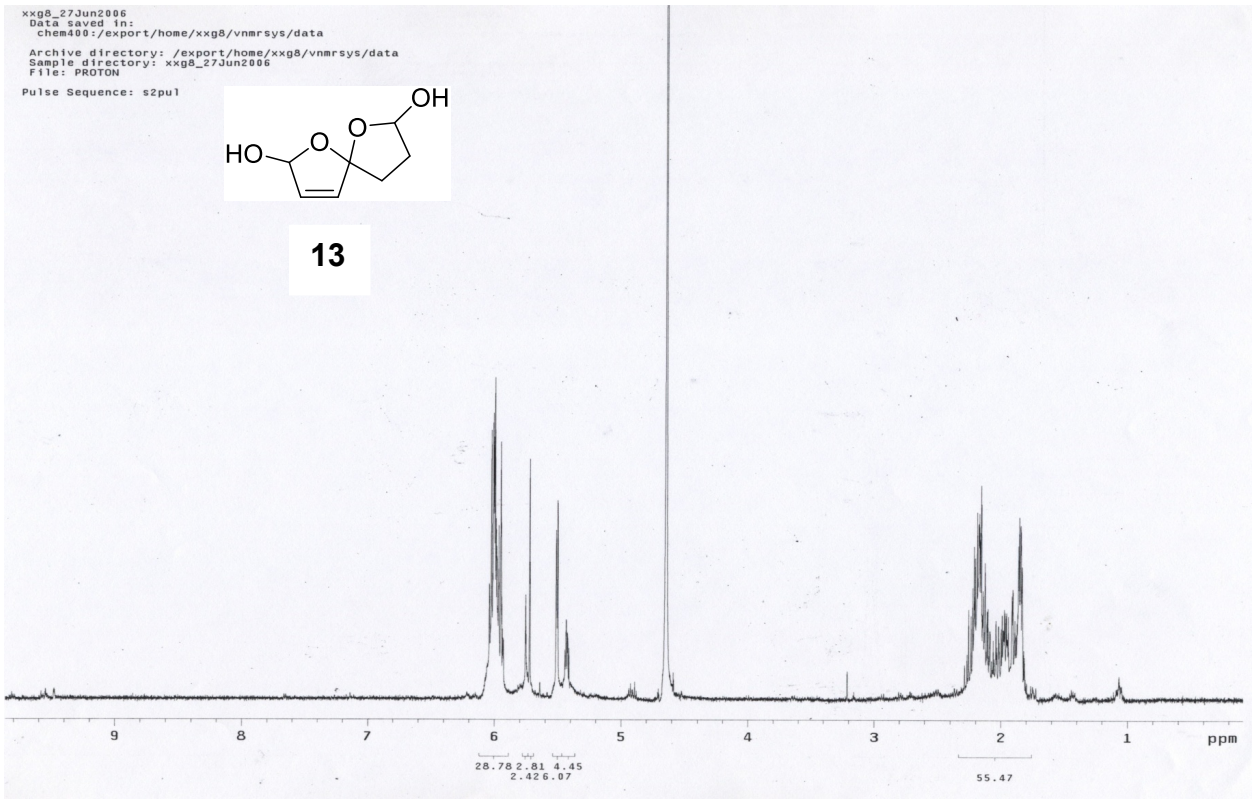

Fig S18 The 400 MHz ^{1}H NMR (D_2O) spectrum of aldehyde hydrate (**13**).