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Supporting Information

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A Catalytic Aldol Reaction and Condensation via *In Situ* Boron "Ate"-Complex Enolate Generation in Water.

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General experimental details

All starting materials were obtained commercially from Aldrich, Lancaster or Fluka and were used as received or prepared by known methods, unless otherwise stated. Solvents were also used as received or dried by known methods, unless otherwise stated. In the case of DCM and toluene this involved refluxing over $CaCO_3$ under argon and in the case of ether and THF involved refluxing over sodium and benzophenone under argon, or using a commercial drying system. Purification by column chromatography was performed using Lancaster silica gel with pore size 60 Å, 40 Å or Florasil®. TLC was carried out using Merck aluminium-backed or plastic-backed pre-coated plates. TLC plates were analysed by UV at 254 and 365 nm, and visualisation was performed using standard solutions of 4-anisaldehyde, vanillin or PMA. NMR spectra were recorded at 200, 300 or 400 MHz using a Varian Mercury 200 MHz spectrometer, Varian Unity 300 MHz spectrometer or a Brucker 400 MHz spectrometer, respectively, unless otherwise stated. Chemical shifts are expressed as parts per million (ppm) downfield from the internal standard TMS for ^1H and ^{13}C, to external $BF_3.Et_2O$ for ^{11}B. Electrospray (ES) mass spectra were recorded using a Micromass LCT spectrometer. Infra red spectra were obtained using FT1600 series spectrometer. Ultra-violet spectra were measured using a Unicam UV-Vis UV2 spectrometer. Melting points were measured with an Electrothermal apparatus and were uncorrected. Evaporations were carried out at 20 mmHg using a Büchi rotary evaporator and water bath, followed by evaporation to dryness under vacuum (<2 mmHg).

***N*-Butyl-2-(2-boronophenyl)benzimidazole sodium hydroxide complex** 2

To a stirred solution of phenylbenzimidazoleboroxine[1] (209 mg, 0.252 mmol) in DCM (4 ml) was added 3 aqueous NaOH (45.35 μL of a 40% solution, 0.756 mmol). After 17 h stirring at RT, the resulting white precipitate was collected by filtration (filter: 0.1 μm) and dried under high vacuum to provide the "ate"-complex **2** (125.3 mg, 50%): δ_H [400 MHz, $CD_3CN:D_2O$ (1:1)] 1.36 (3H, t, *J* 7.2), 1.80 (2H, hextet, *J* 7.2), 2.28 (2H, quintet, *J* 7.2), 4.56 (2H, m), 7.81-7.89 (4H, m), 7.94-7.98 (1H, m), 8.09-8.11 (1H, m), 8.24 (1H, d, *J* 7.2) and 8.30 (1H, d, *J* 7.2) ppm. δ_c [100 MHz, $CD_3CN:D_2O$ (1:1)] 13.5, 20.2, 31.8, 44.9, 111.4 (2C), 118.7, 123.1 (2C), 125.6, 129.4, 132.2, 133.1 (2C), 135.4 and 161.3 ppm. δ_B (128 MHz, $CD_3CN:D_2O$ (1:1)) 0.3 ppm. IR (neat) ν_{max}/cm^{-1} 3049, 2874,1455, 1393, 1277 and 745. *m/z* EI (+) 667.1

(100%), 345.3 (91%). Found: C, 60.71; H, 5.94; N, 8.05. $C_{17}H_{20}O_3BN_2Na$ requires C, 61.10; H, 6.03; N, 8.38%.

General procedure with "ate" complex 2 **formed *in situ.***

A stirred solution of phenylbenzimidazoleboroxine[1] (110.4 mg, 0.13 mmol) in water (2 mL) was treated with aqueous NaOH (24 µL of a 40% NaOH solution, 0.39 mmol). This catalyst solution was added to a prepared mixture of aldehyde **3** (2 mmol) and acetone or hydroxyacetone (20 mmol). After stirring RT for time in Table 1, the solvent was evaporated and the resulting mixture was diluted with aqueous HCl (5%, 3mL). The product was extracted with DCM (3 x 10 mL) and ethyl acetate (3 x 10 mL), and the combined organic extracts dried ($MgSO_4$) and evaporated to give the crude oil. Further purification was carried out by silica gel chromatography (hexane: ethyl acetate, gradient elution) to provide the corresponding products below:

3,4-Dihydroxy-4-phenylbutan-2-one[2] ***5a***

δ_H (400 MHz, $CDCl_3$) 1.75 (3H, s), 2.02 (3H, s), 3.56 (1H, OH, br,), 3.82 (1H, OH, br), 4.14 (1H, d, *J* 2.5), 4.26 (1H, d, *J* 4.5), 4.79 (1H, d, *J* 4.5), 4.81 (1H, d, *J* 2.5) and 7.17-7.24 (5H, m) (addition of D_2O caused the signals at δ 3.56 and 3.82 to disappear). δ_C (100 MHz, $CDCl_3$) 26.6, 27.8, 74.0, 74.9, 80.8, 81.1, 126.3 (2C), 128.0, 129.0 (2C), 139.3, 140.1 and 208.7.

3,4-Dihydroxy-4-(4-nitrophenyl)butan-2-one[3] ***5b***

δ_H (400 MHz, $CDCl_3$) 1.96 (3H, s), 2.29 (3H, s), 2.70 (1H, OH, d, *J* 6.4), 2.87 (1H, OH, br), 3.61 (1H, OH, d, *J* 4.5), 3.67 (1H, OH, d, *J* 4.5), 4.35 (1H, t, *J* 2.8), 4.41 (1H, t, *J* 4.4), 5.01-5.04 (1H, m), 5.11-5.18 (1H, m), 7.54 (2H, d, *J* 8.6) and 8.18 (2H, d, *J* 8.6) [addition of D_2O caused the signals at δ 2.70, 2.87, 3.61 and 3.67 to disappear, that at δ 4.35 to change to (1H, d, *J* 2.4), that at δ 4.41 to change to (1H, d, *J* 4.4) and that at δ 5.01-5.04 to change to (1H, d, *J* 4.8)]. δ_C (100 MHz, $CDCl_3$) 25.9, 27.7, 72.9, 74.4, 80.0, 80.6, 123.7 (2C), 127.1 (2C), 147.3, 147.7 and 206.6. The *syn*-stereochemistry of the major diastereoisomer was confirmed by single crystal X-ray analysis (see below).

3,4-Dihydroxy-4-(4-methoxy)butan-2-one ***5c***

δ_H (400 MHz, $CDCl_3$) 1.92 (3H, s), 2.09 (3H, s), 2.93 (1H, OH, br), 3.05 (1H, OH, br), 3.59 (1H, OH, br), 3.66 (1H, OH, br), 3.73 (3H, s), 3.82 (3H, s), 4.25 (1H, br), 4.34 (1H, d, *J* 3.2), 4.83 (1H, br), 6.78-6.84 (2H, m) and 7.2-7.27 (2H, m) [addition of D_2O caused the signals at δ 2.93, 3.05, 3.59 and 3.66 to disappear, that at δ 4.25 to change to (1H, d, *J* 3.2) and that at δ 4.83 to change to (1H, d, *J* 2.4)]. δ_C (100 MHz, $CDCl_3$) 25.5, 26.6, 54.3, 54.6, 72.9, 73.6, 79.8, 80.0, 113.0 (2C), 113.3 (2C), 126.7 (2C), 127.0 (2C), 130.3, 131.1, 158.5, 207.1 and 207.5. IR (neat) ν_{max}/cm^{-1} 3437, 2938,1714, 1603, 1514, 1251 and 835. HRMS (ES+) $C_{11}H_{18}O_4N$ *m/z* calcd 228.1230 ($M+NH_4^+$), found 228.1230.

Syn-*3,4-dihydroxy-6-phenylhex-5-en-2-one*[4] ***5d***

δ_H (400 MHz, $CDCl_3$) 2.25 (3H, s), 2.46 (1H, OH, br), 3.73 (1H, OH, br), 4.17 (1H, br), 4.60 (1H, br), 6.27 (1H, dd, *J* 16 and 6.5), 6.63 (1H, d, *J* 16), 7.19 (1H, d, *J* 6.5), 7.24 (2H, t, *J* 7.5) and 7.32 (2H, d, *J* 7.5) [addition of D_2O caused the signals at δ_H 2.46 and 3.73 to disappear, that at δ_H 4.17 to change to (1H, d, *J* 2.8) and that at 4.60 to change to (1H, dt, *J* 5.2 and 1.2)]. δ_C (100 MHz, $CDCl_3$) 26.0, 73.0, 79.9, 127.0 (2C), 127.6, 128.1, 128.5 (2C), 132.5, 136.1, and 207.6. IR (neat) ν_{max}/cm^{-1} 3418, 3062, 3032, 2927, 2539, 1717, 1459, 1451, 1113 and 699. MS (MALDI) $C_{12}H_{14}O_3$ *m/z* calcd. 206.24, found 245 ($M+K^+$, 100%) and 229 ($M+Na^+$, 48%).

3,4-Dihydroxyhexan-2-one ***5e***

δ_H (400 MHz, $CDCl_3$) 0.94 (3H, t, *J* 7.5), 1.59 (2H, q, *J* 7.5), 2.20 (3H, s), 2.69 (1H, OH, br), 3.82 (1H, t, *J* 6.4), 3.86 (1H, OH, br), 4.04 (1H, s) and 4.18 (1H, s) (addition of D_2O caused the signal at δ 2.69 and 3.86 to disappear). δ_C (100 MHz, $CDCl_3$) 10.1, 10.2, 24.8, 25.2, 25.4, 27.1, 73.3, 74.2, 79.0, 80.4, 207.5 and 208.9. IR (neat) ν_{max}/cm^{-1} 3418, 2969, 2938, 2880, 1715, 1462, 1359, 1132, 1076 and 976. HRMS (ES+) $C_6H_{16}O_3N$ *m/z* calcd. 150.1125 ($M+NH_4^+$), found 150.1125.

3,4-Dihydroxy-5,5-dimethylhexan-2-one ***5f***

δ_H (400 MHz, $CDCl_3$) 0.97 (9H, s), 2.21 (3H, s), 3.51 (1H, br), 3.72 (1H, d, *J* 4.0), and 4.24 (1H, d, J 2.8) [addition of D_2O caused the signal at δ 3.72 to disappear and that at δ 4.24 to change to (1H, s)]; δ_C (100 MHz, $CDCl_3$) 23.9, 25.3 (3C), 34.7, 76.6, 77.5 and 207.8 ppm. IR (neat) ν_{max}/cm^{-1} 3307, 2959, 2871, 1711, 1413, 1361, 1107 and 1057. Anal. Calcd for $C_8H_{16}O_3$ C, 59.97; H, 10.07, found C,59.92; H, 10.12. The *syn*-stereochemistry of the single diastereoisomer was confirmed by single crystal X-ray analysis (see below).

4-Phenylbut-3-en-2-one[5] ***6g***

δ_H (400 MHz, $CDCl_3$) 2.22 (3H, s), 6.57 (1H, d, *J* 16), 7.24-7.27 (3H, m) and 7.35-7.40 (3H, m). δ_C (100 MHz, $CDCl_3$) 27.7, 126.8, 127.4 (2C), 127.9 (2C), 134.3, 139.0, 143.5 and 197.3.

4-Hydroxy-4-phenylbutan-2-one[3] ***5g***

δ_H (400 MHz, $CDCl_3$) 2.10 (3H, s), 2.69-2.84 (2H, m), 3.36 (1H, OH, br), 5.06 (1H, dd, *J* 9 and 3.2) and 7.17-7.27 (5H, m) (addition of D_2O caused the signal at δ 3.36 to disappear). δ_C (100 MHz, $CDCl_3$) 29.8, 51.0, 68.9, 124.7 (2C), 126.8, 127.5 (2C), 141.8 and 208.

4-(4-Nitrophenyl)but-3-en-2-one[6] ***6b***

δ_H (400 MHz, $CDCl_3$) 2.34 (3H, s), 6.75 (1H, d, J 16.4), 7.47 (1H, d, J 16.4), 7.63 (1H, d, J 8.8) and 8.16 (H, d, J 8.8). δ_C (100 MHz, $CDCl_3$) 28.0, 124.4 (2C), 129.0 (2C), 130.4, 140.4, 140.7, 148.6 and 197.5.

4-(4-Methoxyphenyl)but-3-en-2-one[7] ***6h***

δ_H (400 MHz, $CDCl_3$) 2.24 (3H, s), 3.72 (3H, s), 6.49 (1H, dd, J 16.2 and 1.6), 6.81 (2H, dd, J 8.4 and 1.6) and 7.34-7.39 (3H, m). δ_C (100 MHz, $CDCl_3$) 27.3, 55.3, 114.4 (2C), 125.0, 127.6, 129.9 (2C), 143.2, 161.6 and 206.7.

4-Hydroxy-4-(4-methoxyphenyl)butan-2-one[3] ***5h***

δ_H (400 MHz, $CDCl_3$) 2.11 (3H, s), 2.68-2.85 (2H, m), 3.17 (1H, OH, br), 3.72 (3H, s), 5.03 (1H, dd, J 9.2 and 3.2), 6.81 (2H, d, J 8.2) and 7.20 (2H, d, J 8.2) (addition of D_2O caused the signal at δ 3.17 to disappear). δ_C (100 MHz, $CDCl_3$) 30.8, 52.0, 55.3, 70.0, 113.9 (2C), 126.9 (2C), 135.0, 159.2 and 209.0 ppm.

6-Phenylhexa-3,5-dien-2-one[8] ***6i***

δ_H (400 MHz, $CDCl_3$) 2.22 (3H, s), 6.57 (1H, d, J 15.6), 6.74-6.89 (2H, m), 7.16-7.30 (4H, m) and 7.36-7.39 (2H, m). δ_C (100 MHz, $CDCl_3$) 27.4, 126.7, 127.3 (2C), 129.1 (2C), 129.1, 130.5, 135.0, 141.3, 143.0 and 197.3.

4-Hydroxy-6-phenyl-hex-5-en-2-one[9] ***5i***

δ_H (400 MHz, $CDCl_3$) 2.14 (3H, s), 2.69 (2H, d, J 6.4), 3.03 (1H, OH, br), 4.69 (1H, d, J 6.4), 6.13 (1H, dd, J_1 16.2 J_2 6.4), 6.57 (1H, d, J 15.8) and 7.16-7.31 (5H, m) (addition of D_2O caused the signal at δ 3.03 to disappear). δ_C (100 MHz, $CDCl_3$) 29.8, 50.0, 67.5, 125.5 (2C), 126.8, 127.6 (2C), 129.1, 129.5, 135.5 and 207.9.

General procedure for the kinetic studies of the aldol reaction with acetone and hydroxyacetone

Benzaldehyde (40 µl, 0.394 mmol), hydroxyacetone (271 µL, 3.93 mmol) and a water solution of catalyst (400 µL, 0.2 M cat. in water) were mixed and stirred vigorouly for the appropriate time. The reaction was quenched at a specific time with 5 % aqueous HCl (80 µL), extracted with EtOAc (3 x 4 mL), the organic solvent evaporated and to the crude product re-dissolved in DCM (4 mL) containing 1,4-dimethoxyphenyl as internal standard (6.76 mM) and analyzed by HPLC: (Chiracel OJ, Hexane:EtOH:MeOH = 90:6.6:3.3, flow rate 1.0 mL/min, λ = 210 nm) t_R = 19.89 (*anti*), 22.42 (*anti*), 24.85 (*syn*) and 29.40 (*syn*) min. t_R Internal standard = 8.78 min.

Hydroxyacetone + benzaldehyde reaction

Figure 1. Conversion *versus* time plot for the complex **2** catalysed reaction of benzaldehyde with hydroxyacetone, product formation (benzaldehyde consumption could not be followed accurately due to overlapping HPLC peaks).

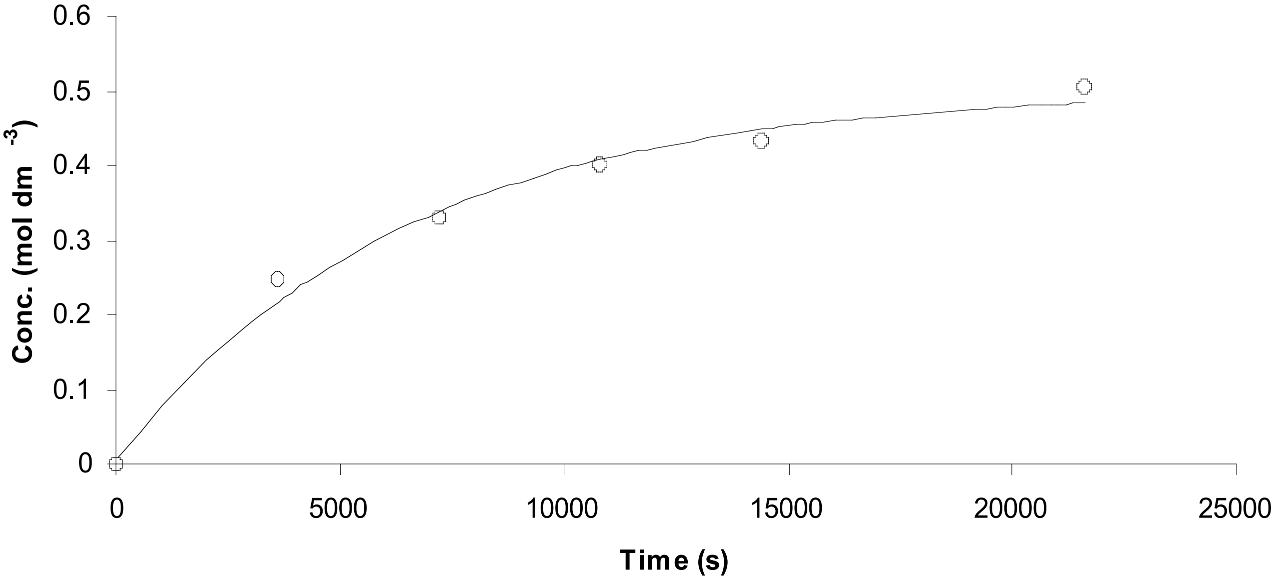


Figure 1 note: the data was fitted to first order kinetics and the observed rate constant for formation of the aldol adduct k_{obs} was found to be $k_{obs} = 1.54 \pm 0.27\times10^{-4}$ s^{-1}.

Figure 2. Conversion *versus* time plot for the NaOH catalysed reaction of benzaldehyde with hydroxyacetone, product formation (benzaldehyde consumption could not be followed accurately due to overlapping HPLC peaks).

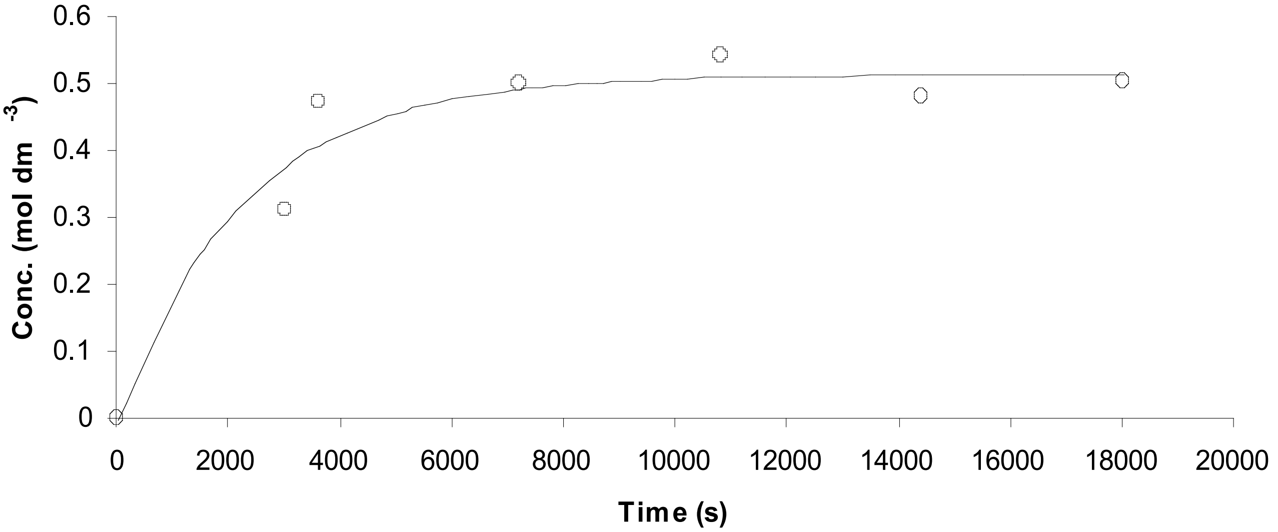


Figure 2 note: the data was fitted to first order kinetics and the observed rate constant for formation of the aldol adduct k_{obs} was found to be $k_{obs} = 4.41 \pm 1.18\times10^{-4}$ s^{-1}.

Acetone + benzaldehyde reaction

Figure 3. Phenylboronate benzimidazole **2** catalysed aldol reaction benzaldehyde with acetone, product formation and benzaldehyde consumption.

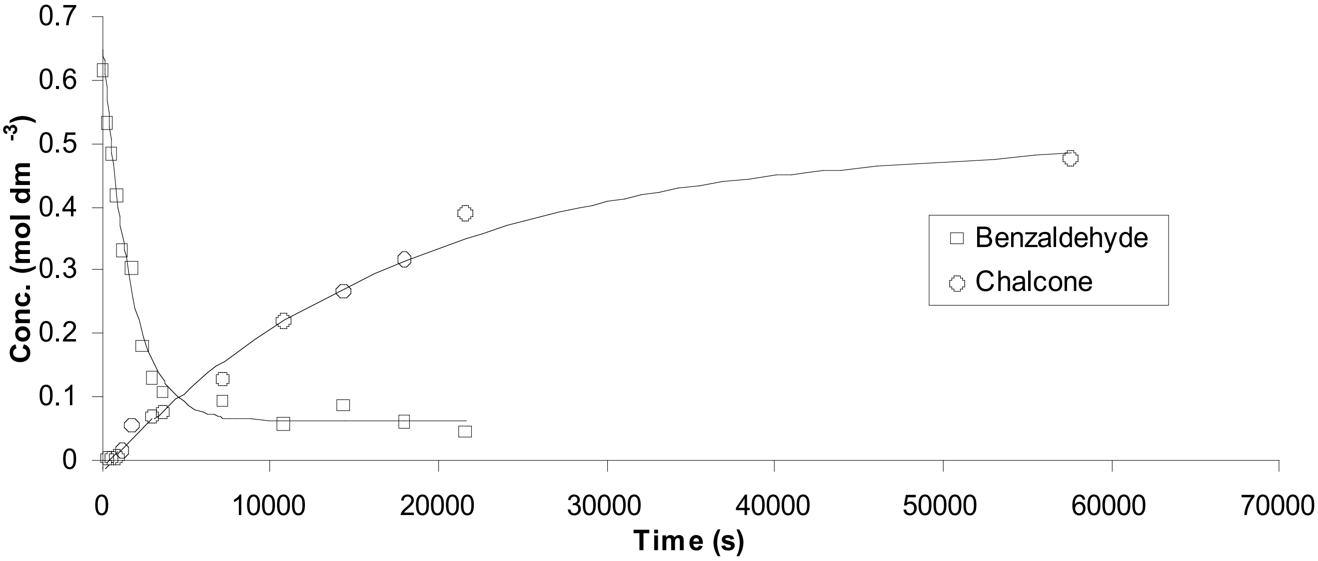


Figure 2 note: the rate of consumption of benzaldehyde is higher than that of formation of the chalcone ($k_{benzaldehyde} = 6.10 \pm 0.42 \times 10^{-4}\ s^{-1}$ and $k_{chalcone} = 5.54 \pm 0.53 \times 10^{-5}\ s^{-1}$).

Figure 4. Sodium hydroxide catalysed aldol reaction of benzaldehyde with acetone, chalcone formation and benzaldehyde consumption.

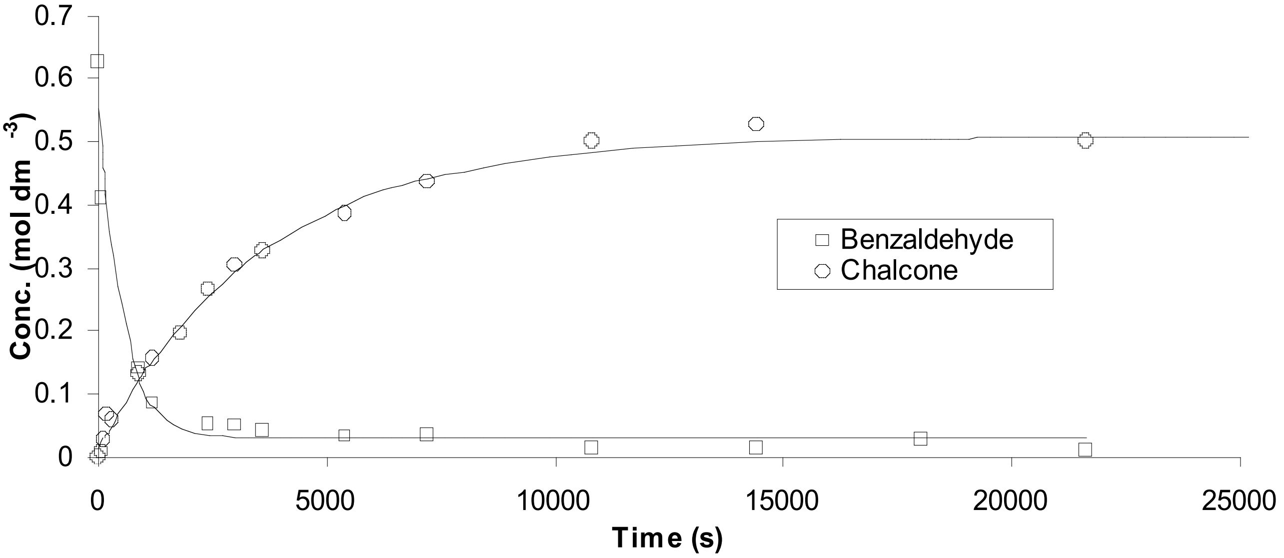
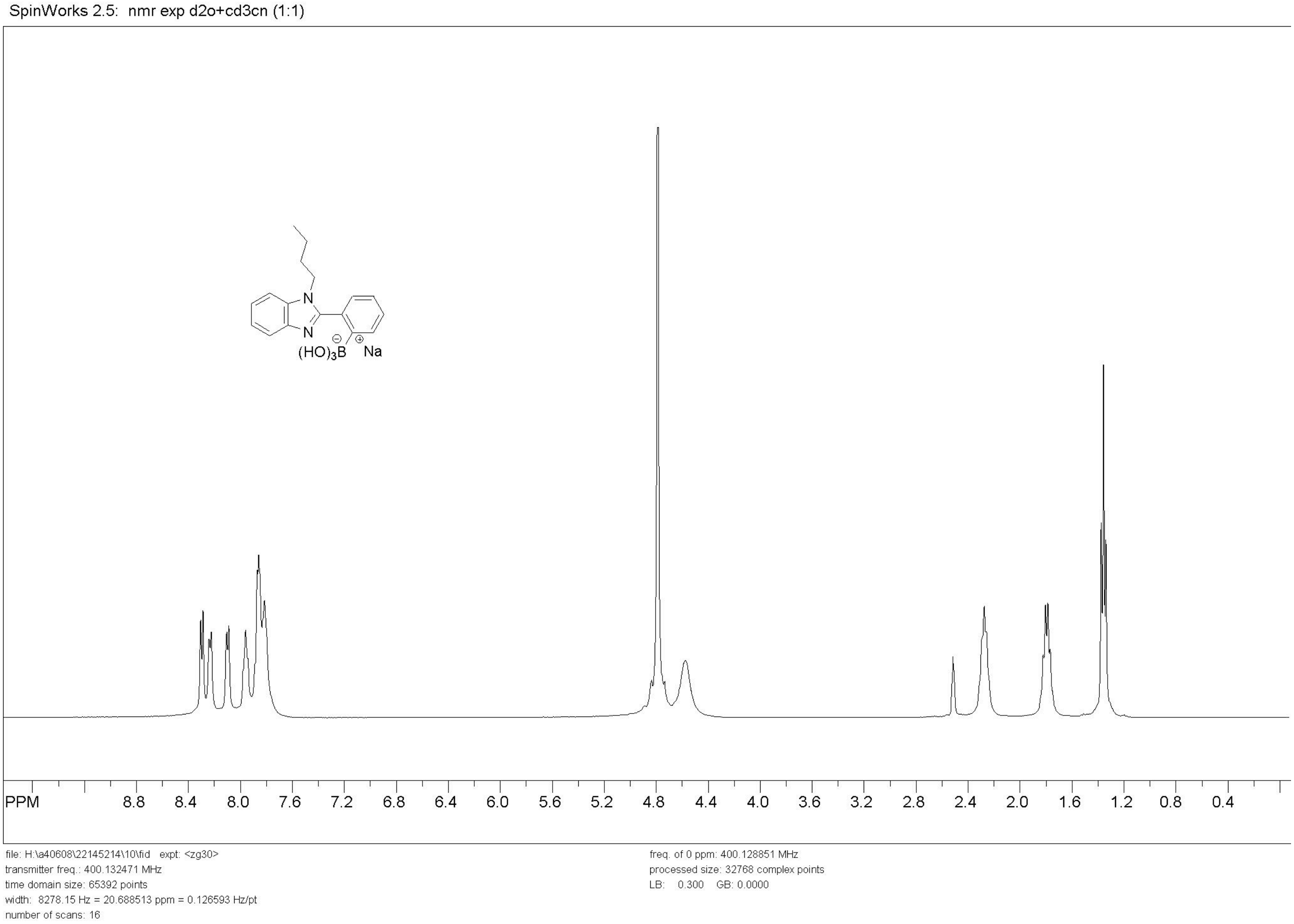


Figure 3 note: the rate of consumption of the aldehyde is significantly faster than that of formation of the chalcone, and the data can be fitted to first order kinetics although the error recorded on fitting is probably indicative of more complex kinetics ($k_{benzaldehyde} = 1.99 \pm 0.44 \times 10^{-3}\ s^{-1}$ and $k_{chalcone} = 2.81 \pm 0.16 \times 10^{-4}\ s^{-1}$). Further experiments are required to calculate the individual rate constants.

Spectrum 1. ^{1}H-NMR of **2**



Spectrum 2. ^{11}B-NMR of **2**

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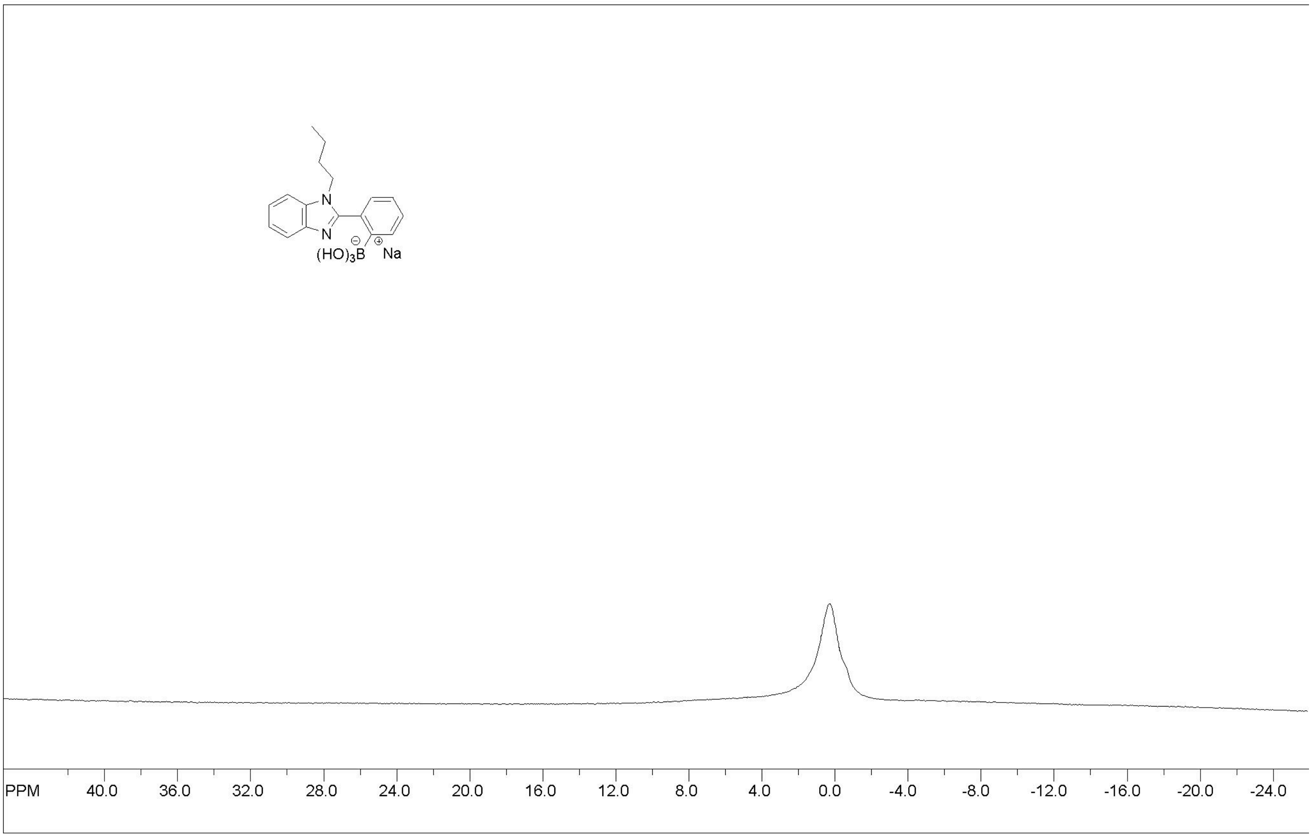

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number of scans: 128
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Spectrum 3. ^{1}H-NMR of **5a**

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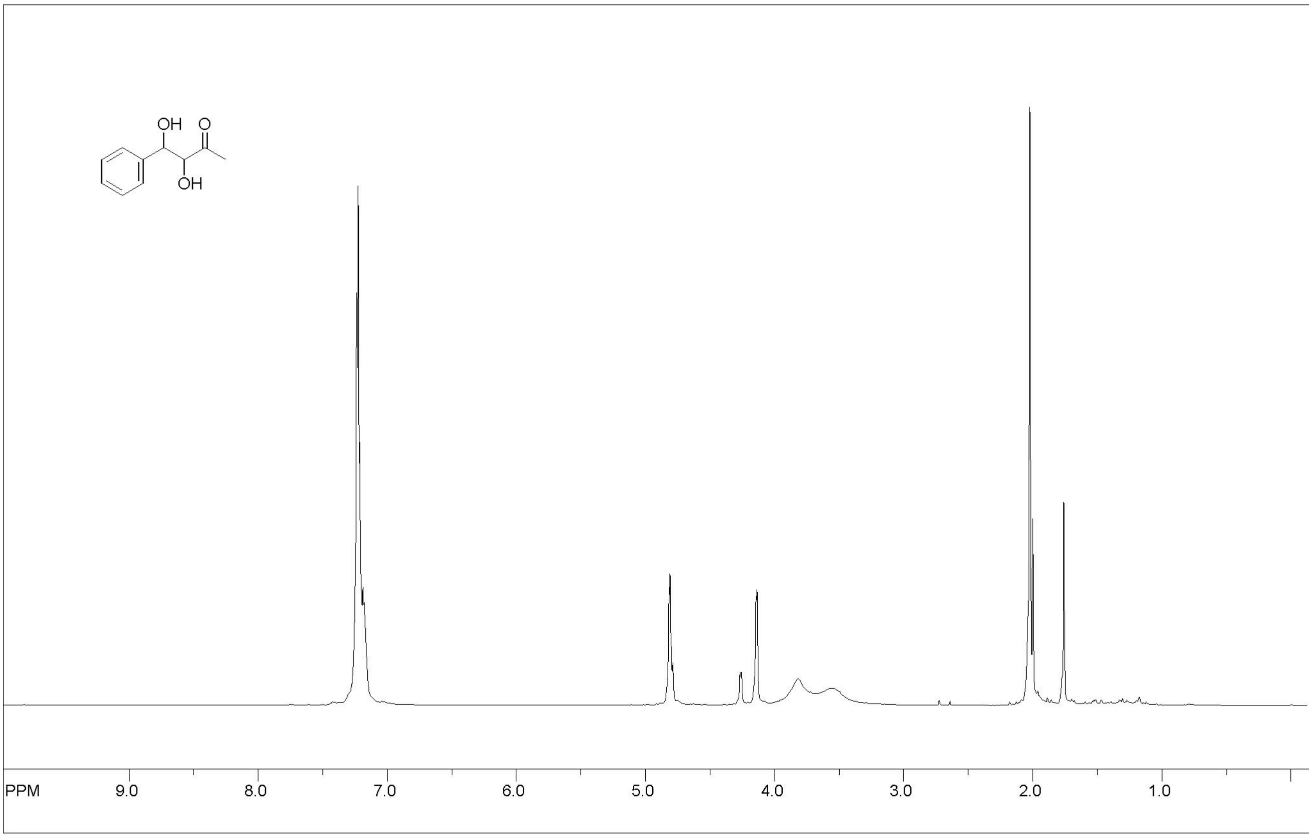

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number of scans: 16
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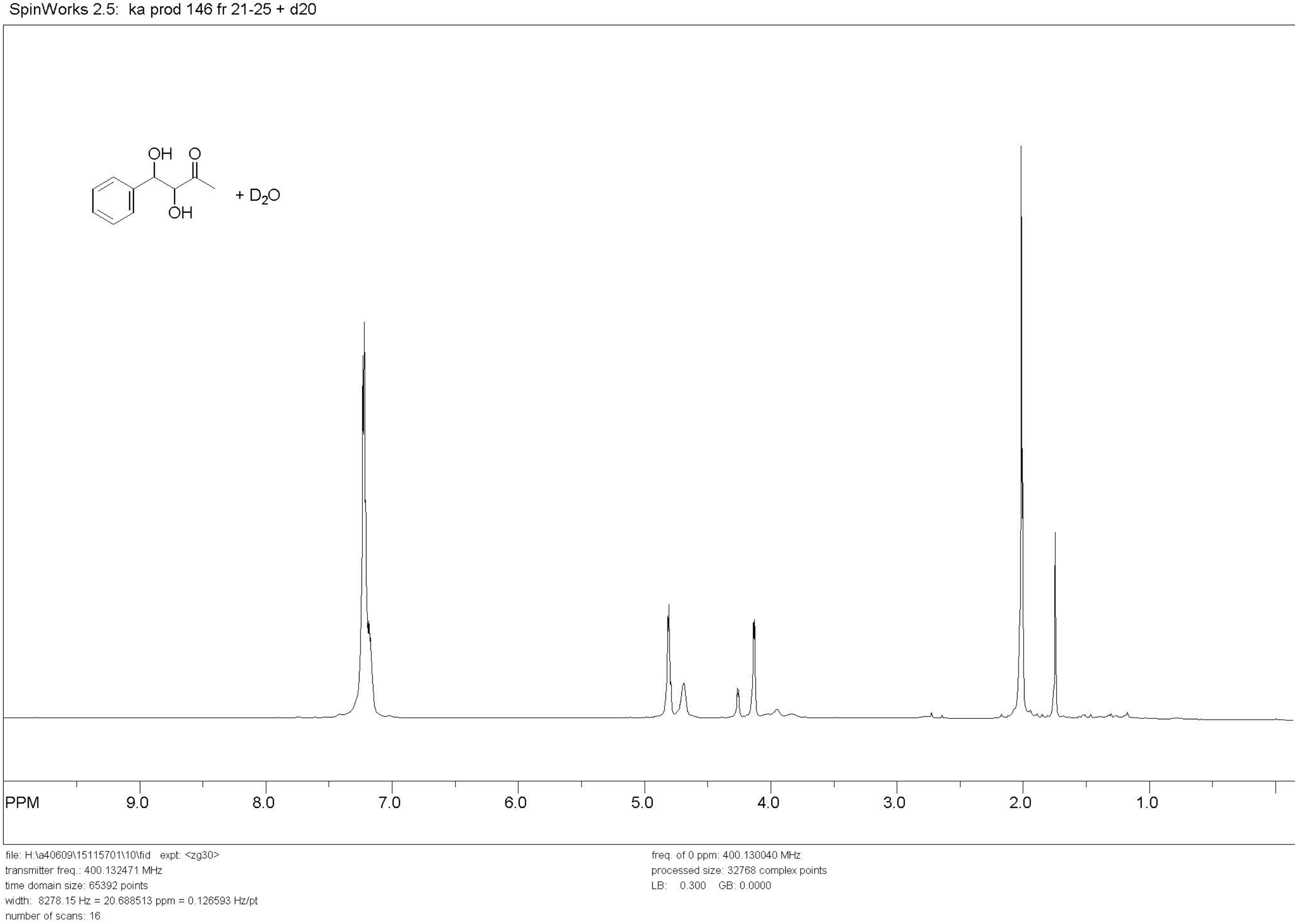
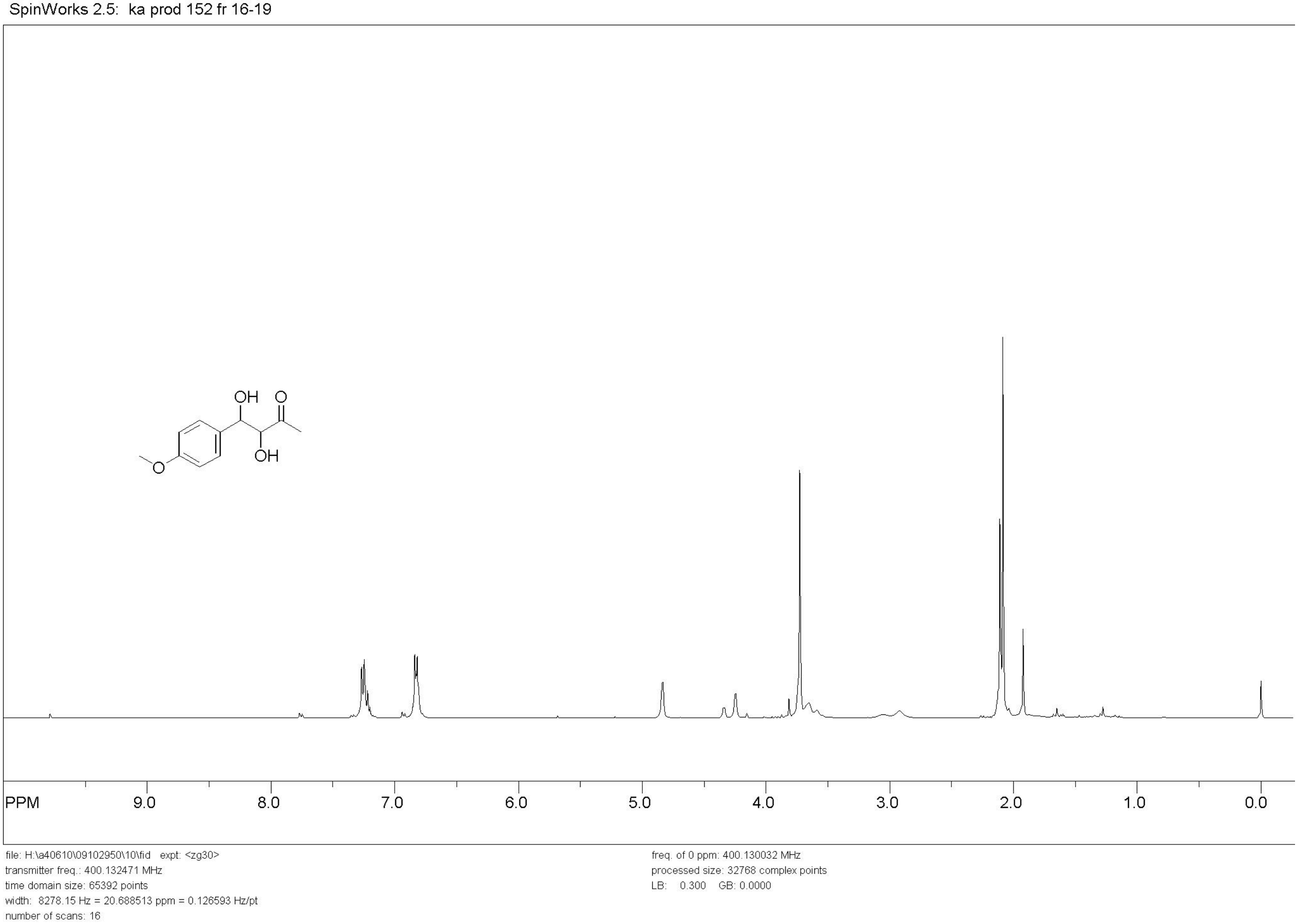
Spectrum 4. ^{1}H-NMR of **5a** with D_2O

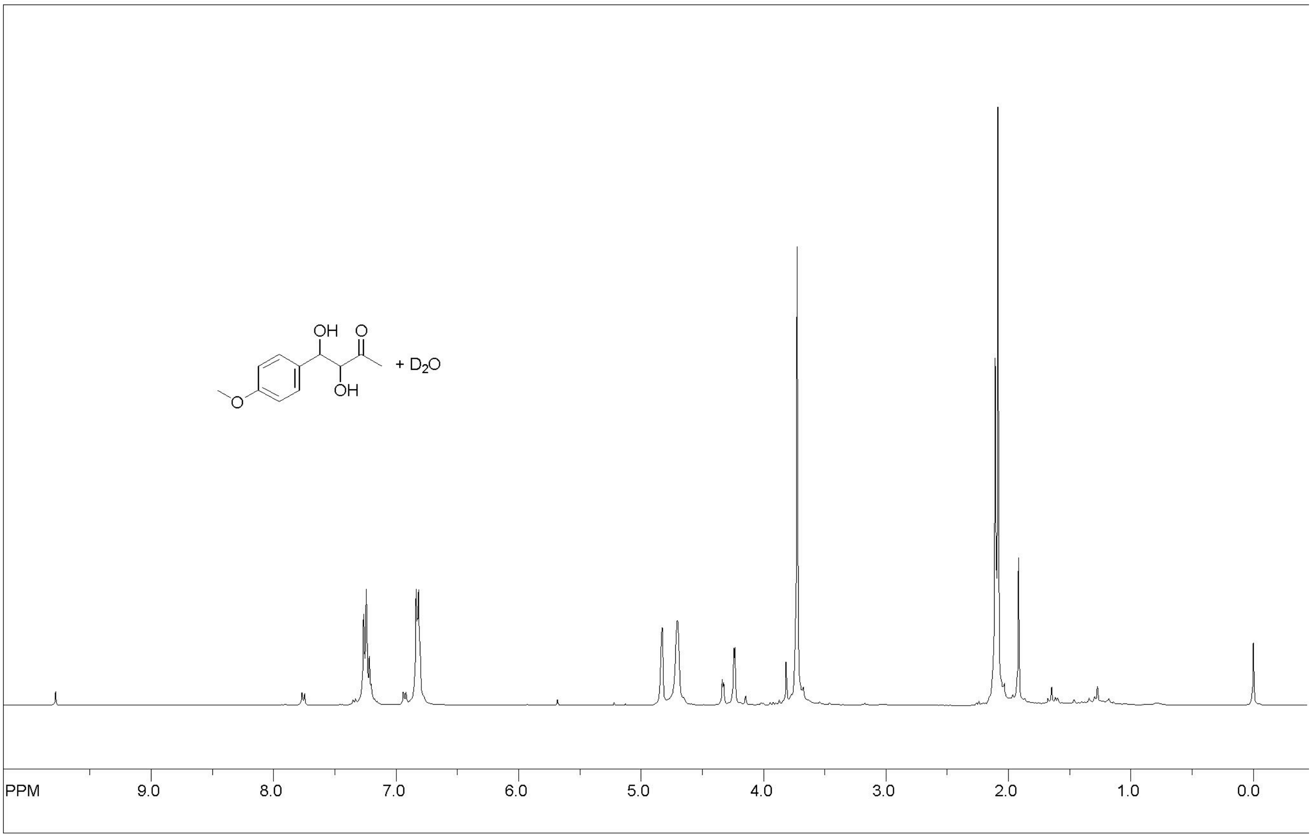


Spectrum 5. ^{1}H-NMR of **5c**



Spectrum 6. ^{1}H-NMR of **5c** in D_2O

SpinWorks 2.5: ka prod 152 fr 16-19



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number of scans: 16

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LB: 0.300 GB: 0.0000

Spectrum 7. ^{13}C-NMR of **5c**

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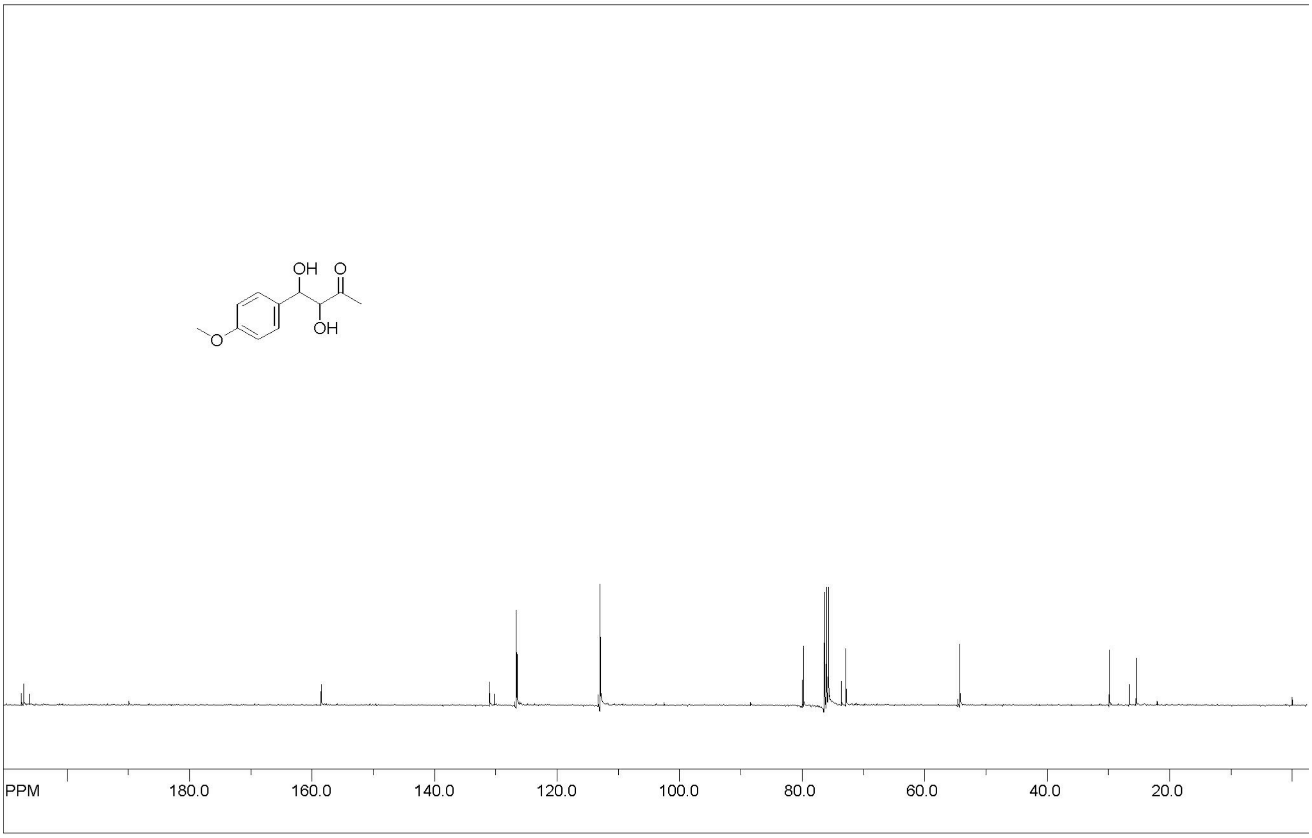

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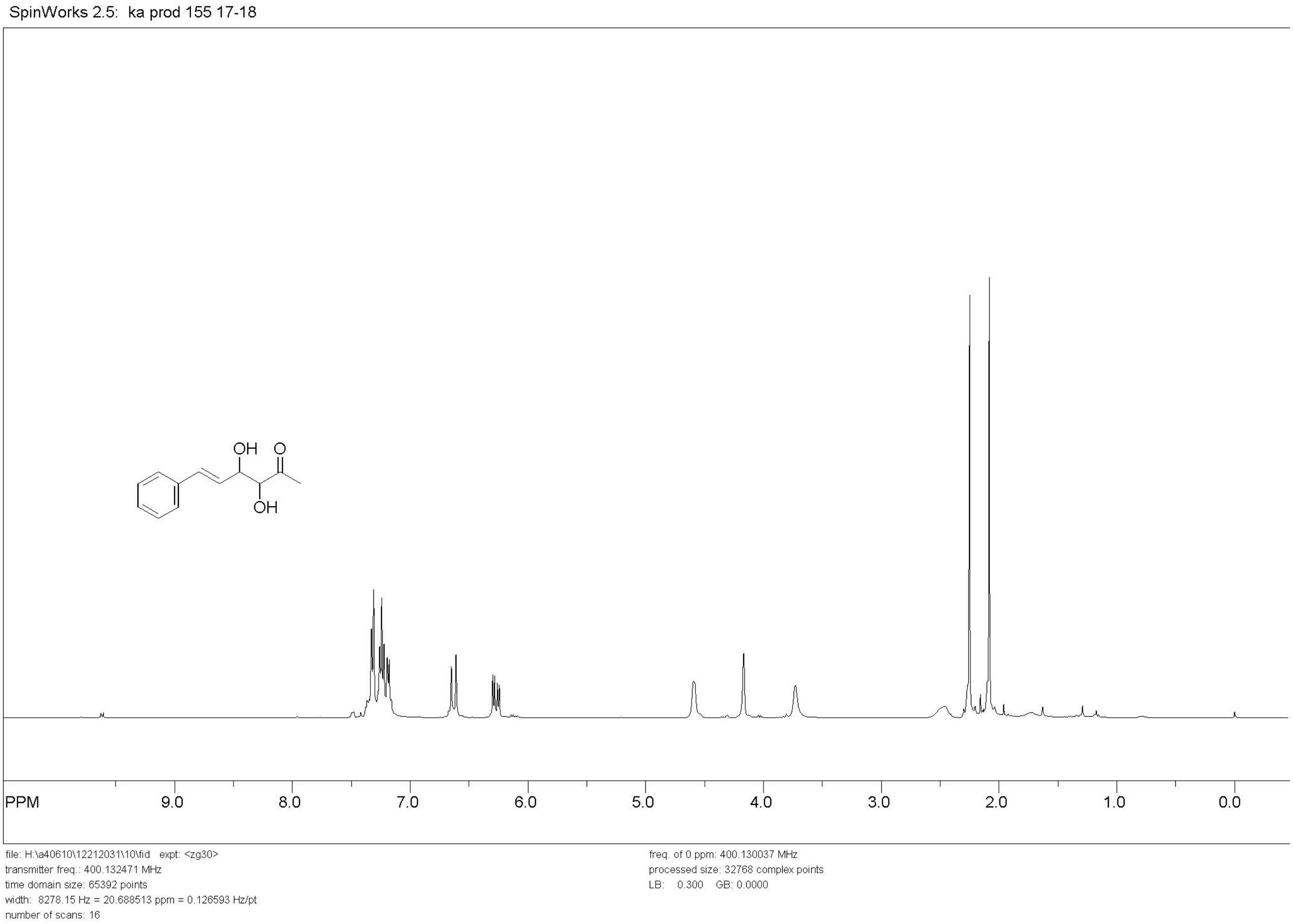
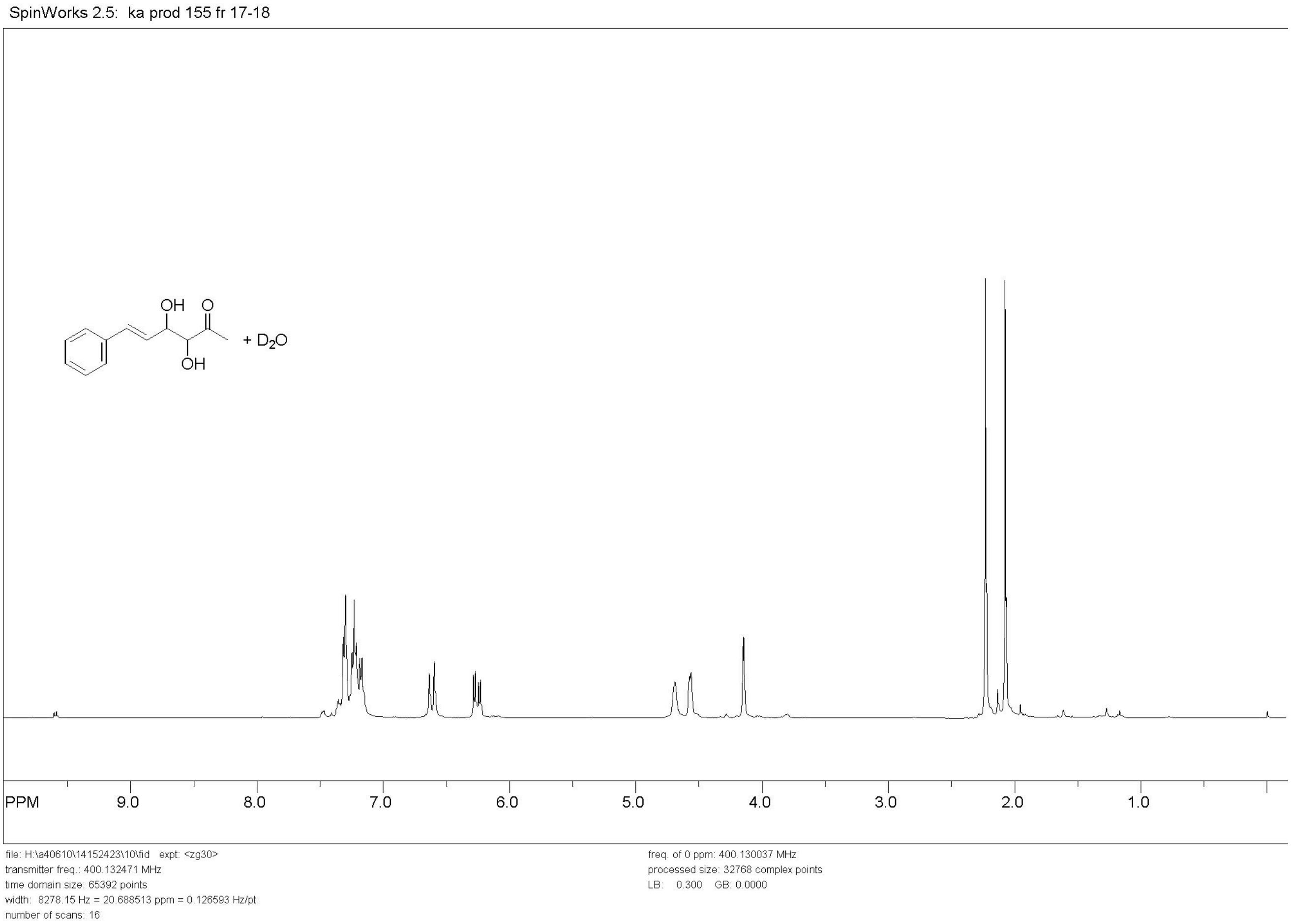
LB: 1.000 GB: 0.0000

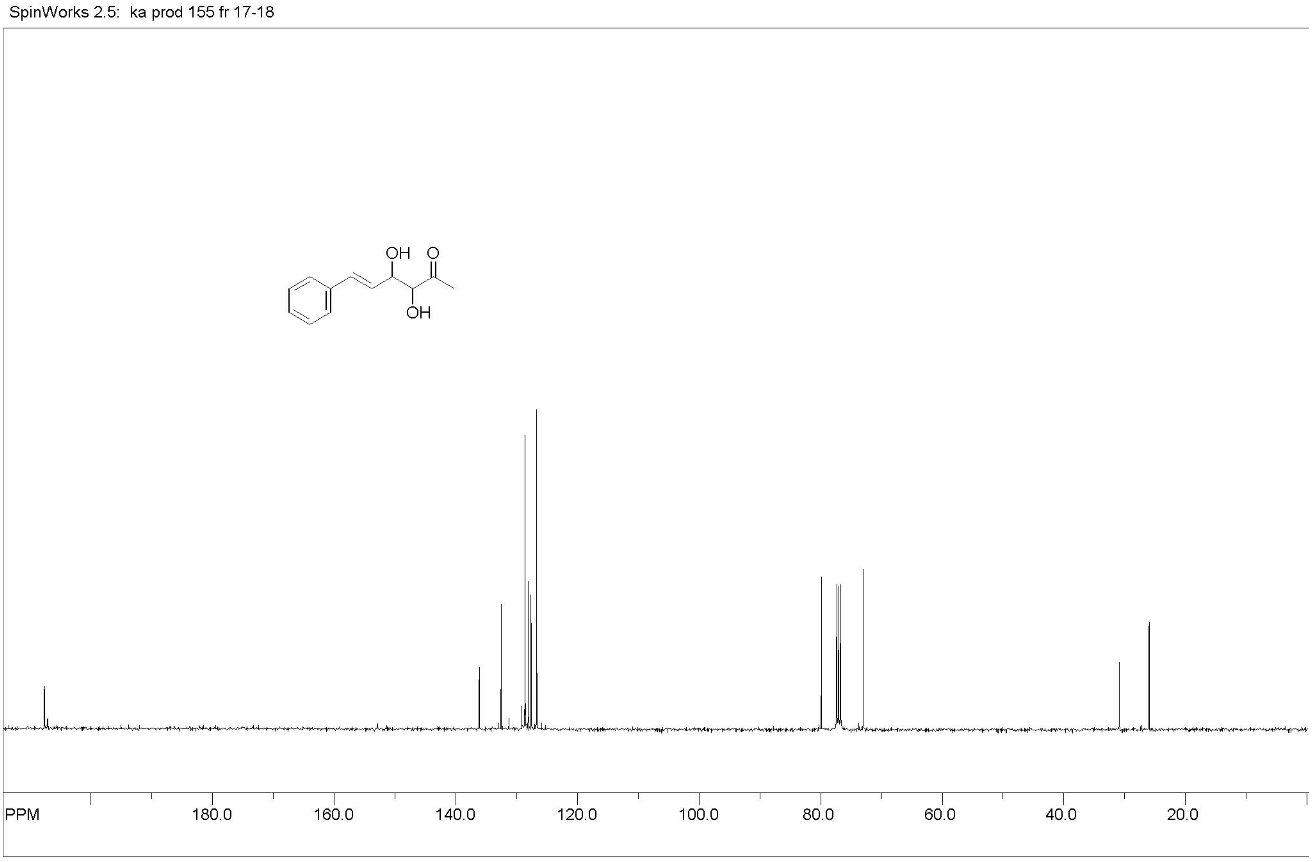
Spectrum 8. ^{1}H-NMR of **5d**



Spectrum 9. ^{1}H-NMR of **5d** in D_2O



Spectrum 10. ^{13}C-NMR of **5d**



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number of scans: 1024

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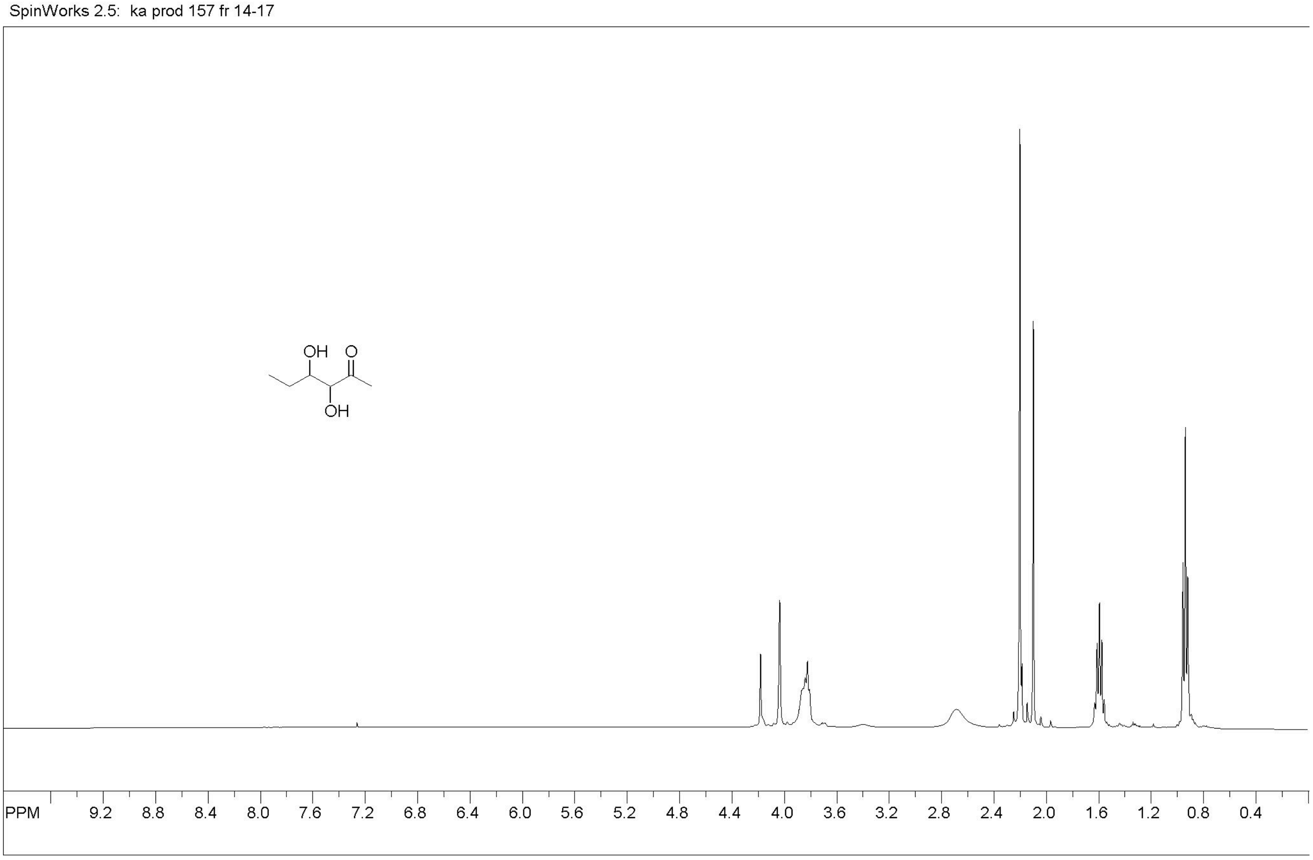
Spectrum 11. ^{1}H-NMR of **5e**



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Spectrum 12. ^{1}H-NMR of **5e** in D_2O

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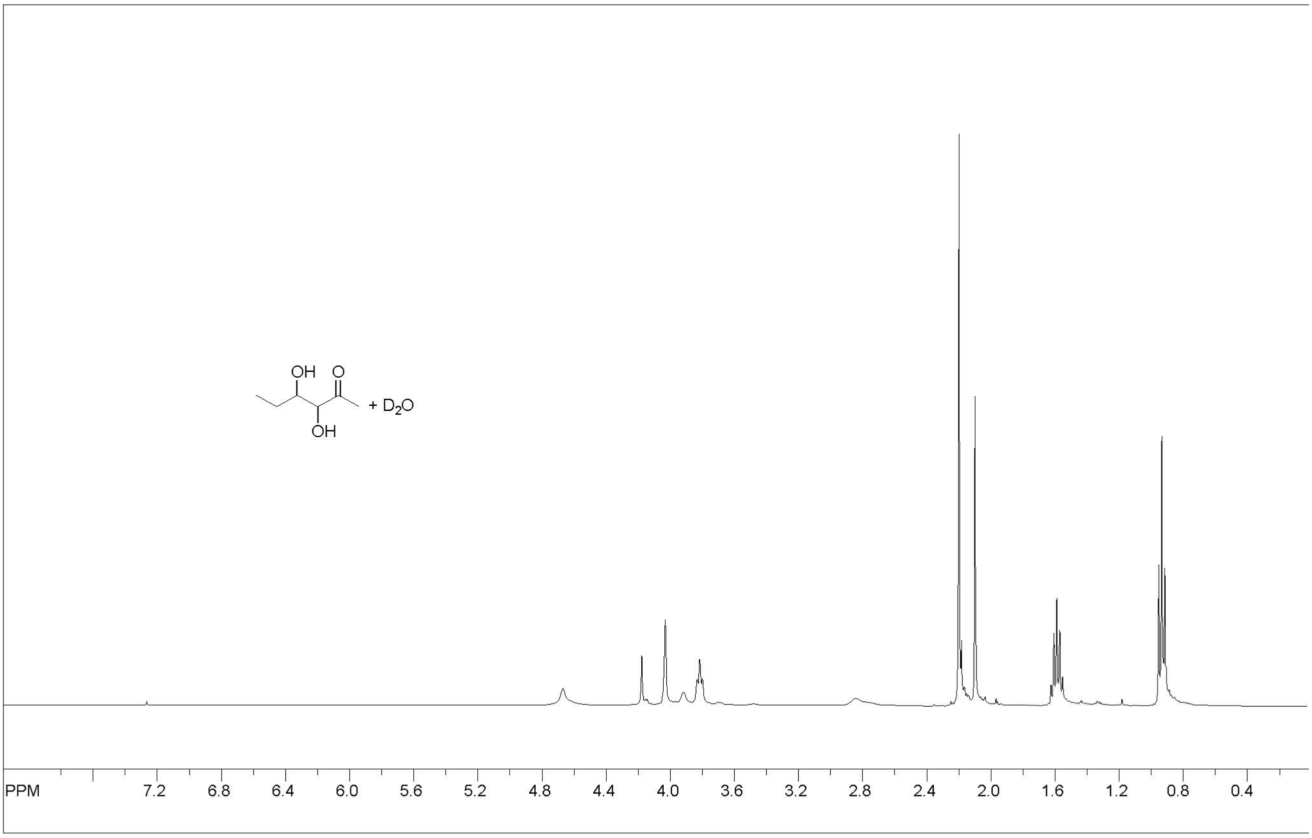

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number of scans: 16

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LB: 0.300 GB: 0.0000

Spectrum 13. ^{13}C-NMR of **5e**

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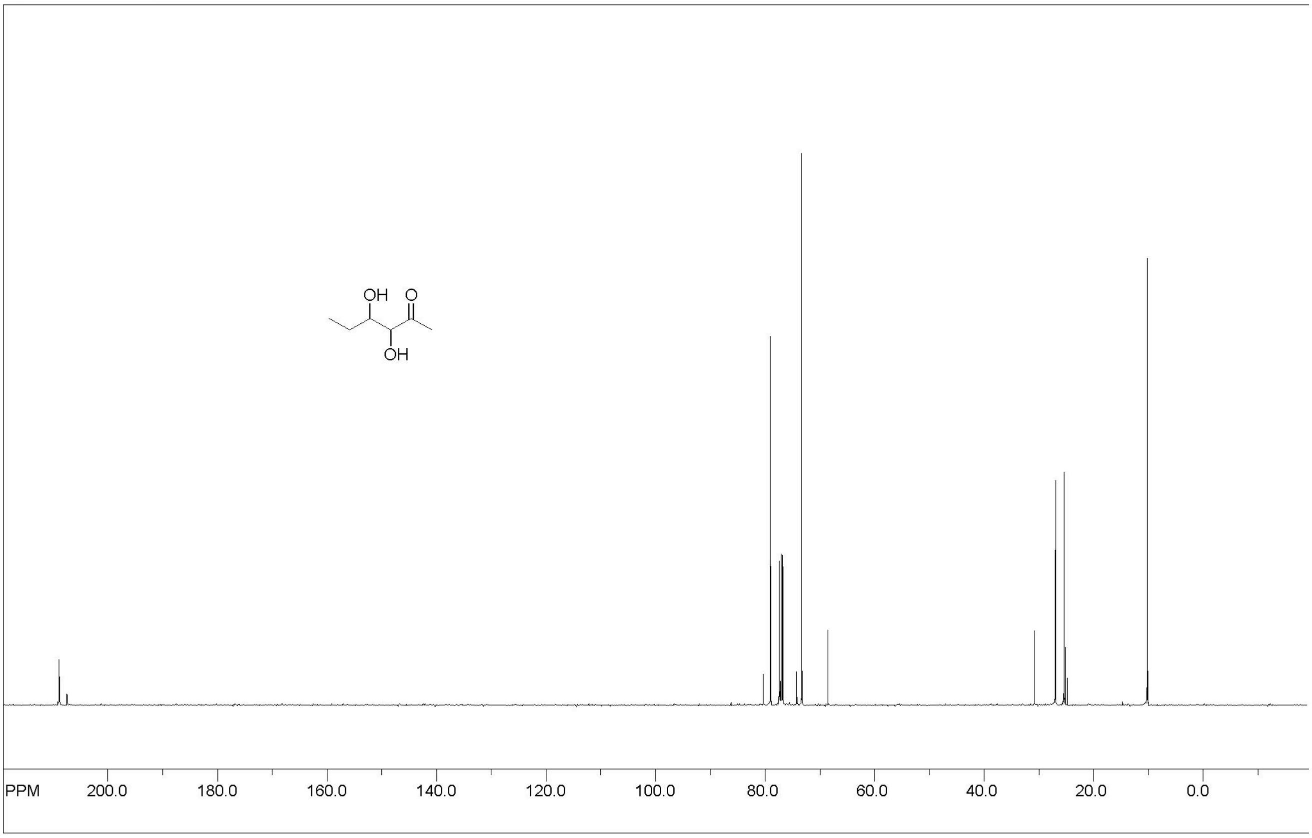

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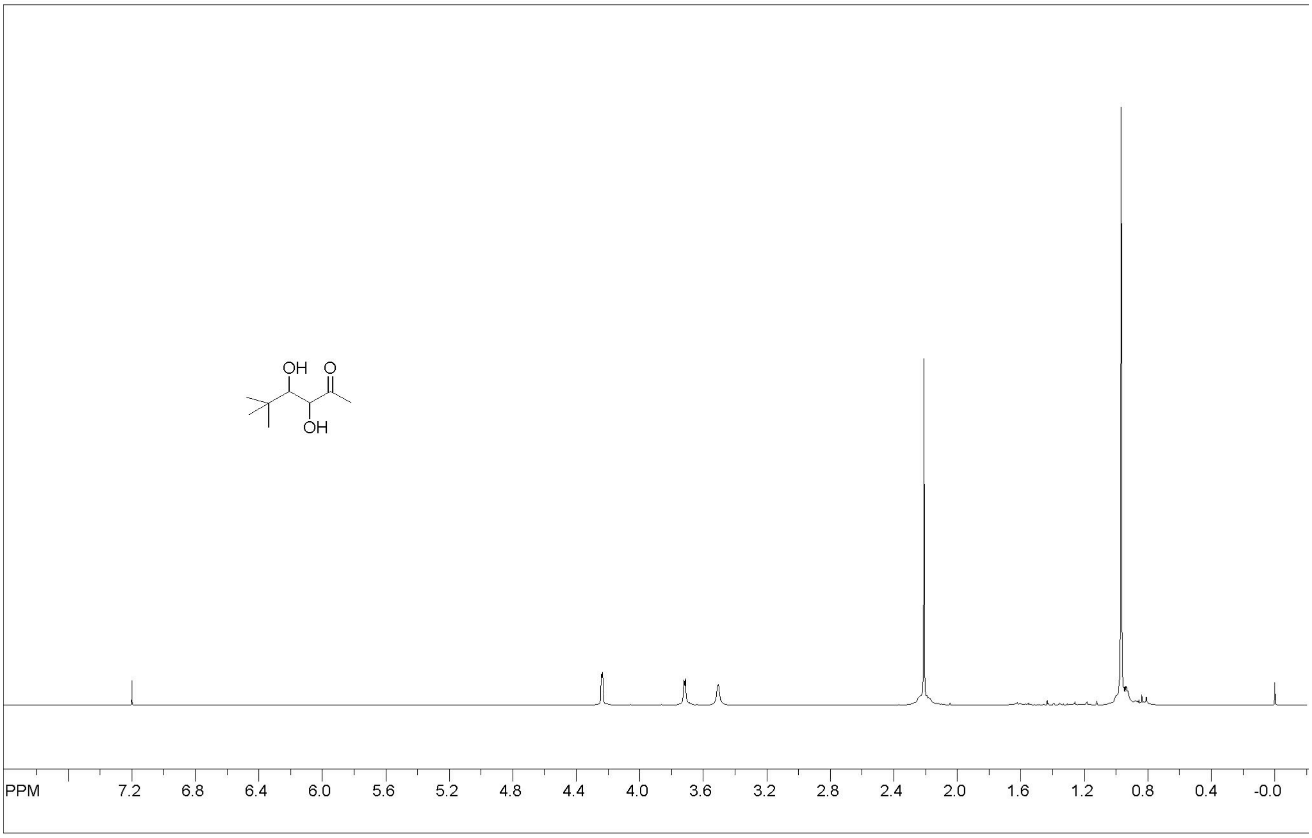
time domain size: 65418 points
width: 23980.82 Hz = 238.323802 ppm = 0.366578 Hz/pt
number of scans: 1024

freq. of 0 ppm: 100.612769 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000

Spectrum 14. ^{1}H-NMR of **5f**

SpinWorks 2.5: ka prod 158 fr 4-7



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time domain size: 65392 points
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number of scans: 16

freq. of 0 ppm: 400.130033 MHz
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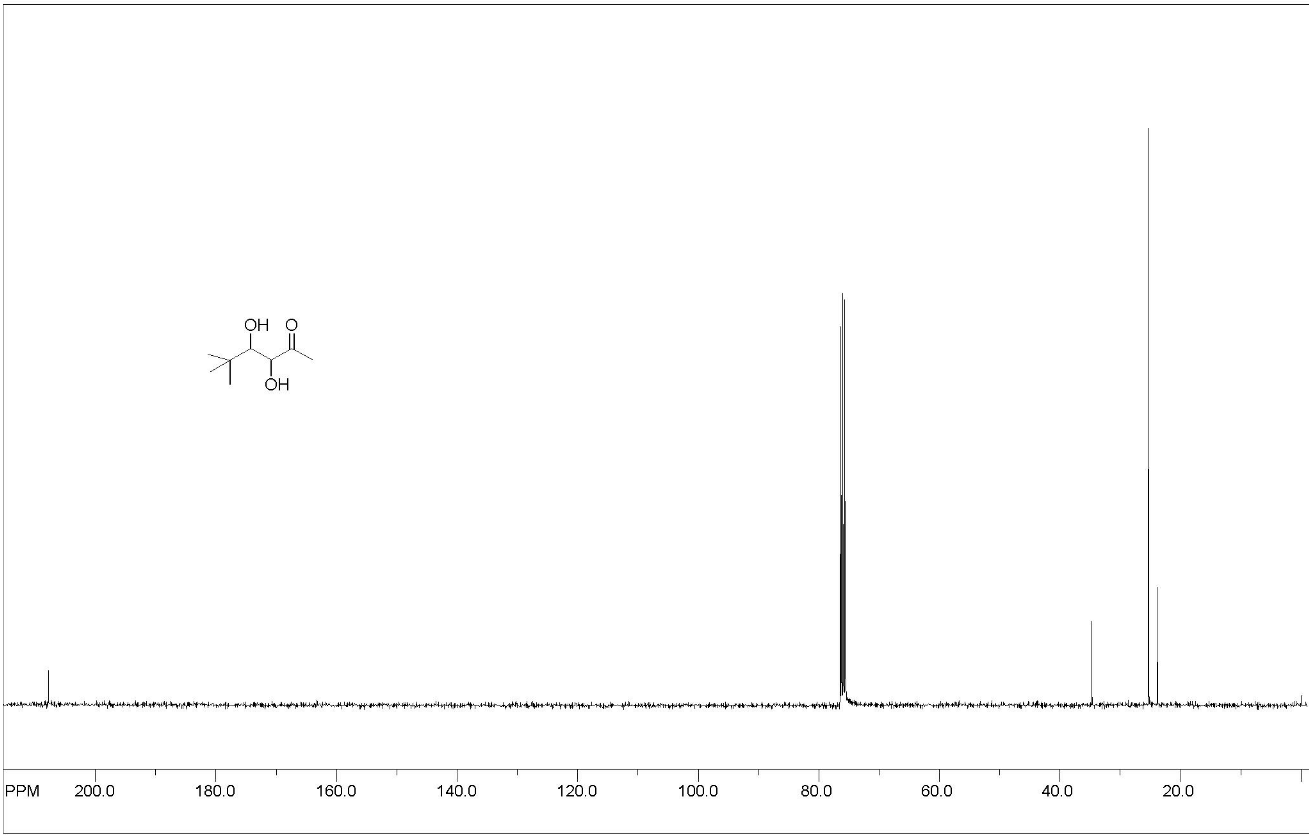
Spectrum 15. ^{13}C-NMR of **5f**

SpinWorks 2.5: ka prod 158 fr 4-7



file: H:\a40610\29170207\11\fid   expt: <zgpg30>
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number of scans: 1024

freq. of 0 ppm: 100.612869 MHz
processed size: 32768 complex points
LB: 1.000   GB: 0.0000

X-ray crystallography

Compound **5f.** The X-ray diffraction data were collected on a SMART 3-circle diffractometer with a 6K CCD area detector, using graphite-monochromated Cu-K_α radiation ($\bar{\lambda}$=1.54178 Å) and a Cryostream (Oxford Cryosystems) open-flow N_2 cryostat. The structure was solved by direct methods and refined by full-matrix least squares against F^2 of all reflections, using SHELXTL software (version 6.14, Bruker AXS, Madison WI, USA, 2003). *Crystal data*: **5f**, $C_8H_{16}O_3$, M=160.21, T=120 K, triclinic, space group $P\bar{1}$ (No. 2), a=9.4668(5), b=9.9480(5), c=10.0866(5) Å, α=78.898(9), β=83.568(9), γ=87.511(9)°, U=926.04(8) Å^3, Z=4, D_c=1.149 g cm^{-3}, μ=0.71 mm^{-1}, 4067 reflections with 2θ≤121° (2374 unique), R_{int}=0.084, final $R(F)$=0.067 [1648 data with $I\geq2\sigma(I)$], w$R(F^2)$=0.190 (all data). The asymmetric unit comprises two molecules, one of which is disordered (in fact, the site is shared in a 9:1 ratio between opposite enantiomers). Structural data in the CIF format has been deposited with the Cambridge Structural Data Centre, deposition number CCDC-657958.

Figure 9. Independent molecules *A* (top) and *B* in the crystal of **5f**. Thermal ellipsoids are drawn at the 30% probability level. Disorder is not shown.

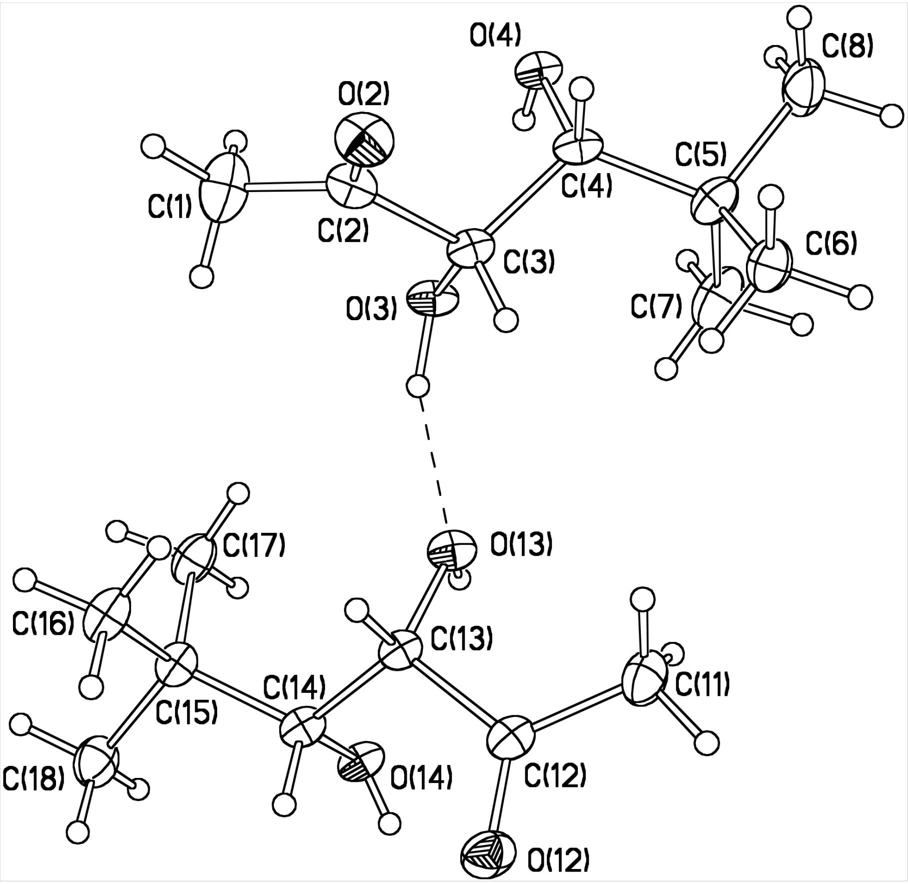
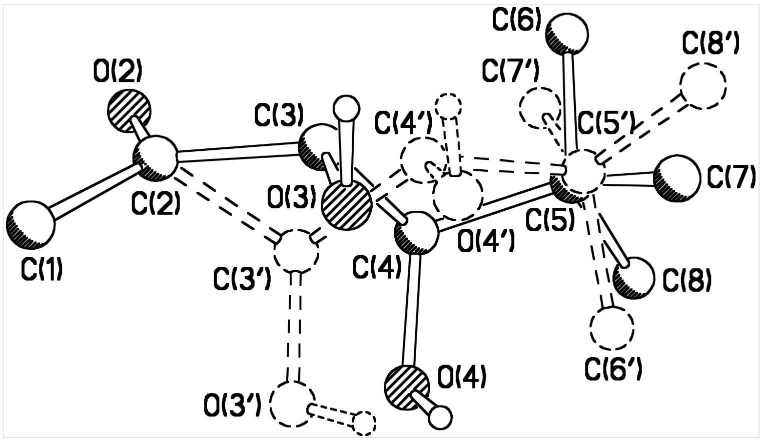
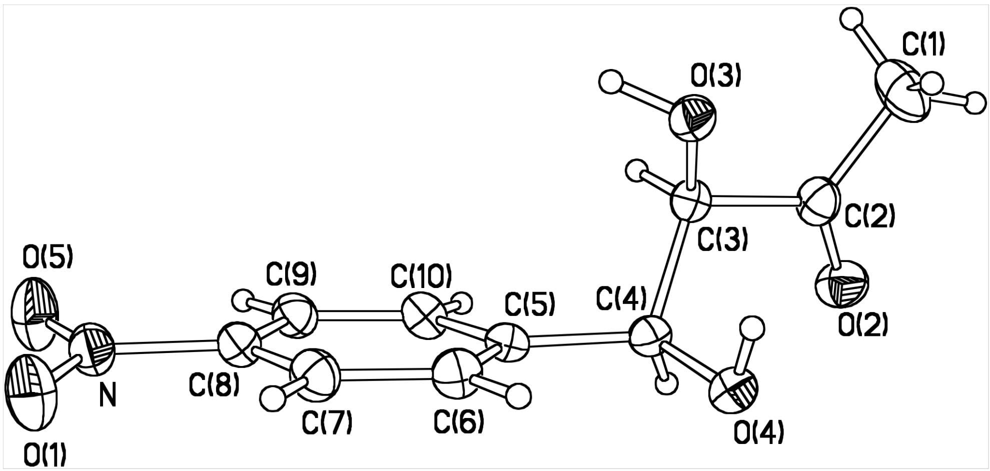


Figure 10. Disorder in molecule **5f**. The components of opposite configuration have occupancies 0.9 (solid) and 0.1 (dashed).



Compound **5b.** As above, using a SMART 3-circle diffractometer with a 1K CCD area detector and graphite-monochromated Mo-K_α radiation ($\bar{\lambda}$=0.71073 Å). *Crystal data*: **5b**, $C_{10}H_{11}NO_5$, M=225.20, T=120 K, orthorhombic, space group $P2_12_12_1$ (No. 19), a=4.6812(6), b=9.2627(11), c=23.407(3) Å, V= 1014.9(2) Å^3, Z=4, D_c=1.474 g cm^{-3}, μ=0.12 mm^{-1}, 10539 reflections with $2\theta \leq 58°$ (1601 unique and 1091 Friedel equivalents), R_{int}=0.028, final $R(F)$=0.039 [1470 unique data with $I \geq 2\sigma(I)$], w$R(F^2)$=0.107 (all data), CCDC-659031. The absolute configuration was assigned arbitrarily (the product being racemic). The structure is essentially identical with that recently determined at room temperature.[10]

Figure 11. Molecular structure of **5b** (50% thermal ellispoids).



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