Supporting information.

Kinetic and structural studies on ‘tethered’ Ru(II) arene ketone reduction catalysts

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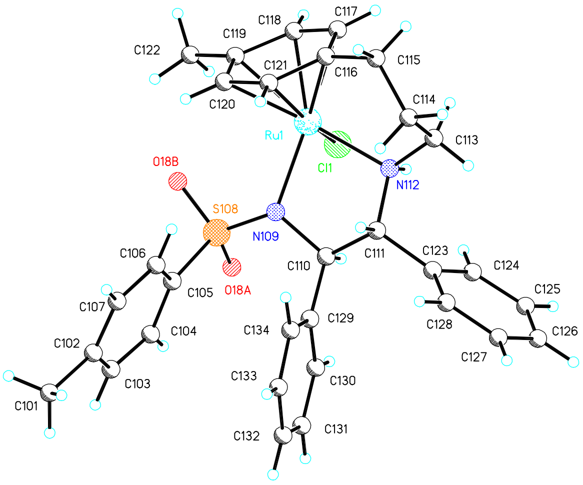
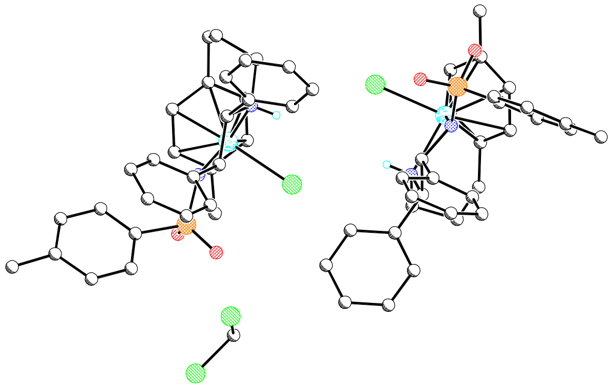
Contents:

1. X-ray structural data.

X-ray crystallography of 4-methyl reverse tethered catalyst (**5**)



One of the crystallographic independent molecules in the asymmetric unit. The other one is labelled from 201. The asymmetric unit contains two complexes (which appear to be the same) and a molecule of methylene chloride.



The two complexes face each other and there are rather long contacts (over 3 Å) between the NH of one complex and the Cl of the other which is reciprocated.

The asymmetric unit contains two crystallographic independant complexes and a molecule of dichloromethane so eight complexes and four DCMs in the cell. The polar face of each complex faces towards the other with very very long interactions between the NH of one complex and the Cl of the other. The hydrogens on the amines N112 and N212 were located in a difference map and their positions allowed to refine freely but their isotropic displacement parameters were fixed at 1.5 times the equivalent isotropic displacement parameter of the parent nitrogen. The very long reciprical contacts between the NH of one complex and the Cl of the other complex are tabulated below and the internal interaction with its own chloride.

Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)	
0.844(19)	3.24(4)	3.939(4)	142(5)	N112-H112...Cl2
0.844(19)	2.58(5)	3.054(4)	117(4)	N112-H112...Cl1
0.830(19)	3.27(4)	3.932(4)	138(5)	N212-H212...Cl1
0.830(19)	2.54(5)	3.047(4)	121(5)	N212-H212...Cl2

The torsion angles between the N-H and the Ru-Cl are tabulated below
Dihedral angle TORS
14.25 (3.78) degrees H112 - N112 - Ru1 - Cl1
9.81 (4.11) degrees H212 - N212 - Ru2 - Cl2

There is a possible intramolecular pi pi interaction between the tosyl sulphonamide group and one of the phenyls of the diamine. The angle between mean planes through these rings and the closest atomic distance for each complex is shown below

C102 C103 C104 C105 C106 C107
C129 C130 C131 C132 C133 C134
angle between planes 24.87 (0.21) degrees
closest atomic distance 3.07 A (C105-C134)

C202 C203 C204 C205 C206 C207
C229 C230 C231 C232 C233 C234
angle between planes 22.63 (0.22) degrees
closest atomic distance 3.20 A (C205-C234)

Crystal Data
C31.50 H34 Cl2 N2 O2 Ru S, M = 676.64, Orthorhombic, space group P2(1)2(1)2(1)
a = 13.2206(17), b = 17.179(2), c = 25.789(3) A ,
alpha = 90 deg., beta = 90 deg., gamma = 90 deg.,
U = 5857.2(13) A^3 (by least squares refinement on 2776 reflection positions),
T =180(2)K, lambda = 0.71073 A, Z = 8,
D(cal) = 1.535 Mg/m^3, F(000) = 2776.
mu(MoK-alpha) = 0.822 mm^-1.
Crystal character:orange block.
Crystal dimensions 0.40 x 0.22 x 0.18 mm,

Data Collection and Processing.
Oxford Diffraction Gemini four-circle system with Ruby CCD area detector.
The crystal was held at 180(2) K with the Oxford Cryosystem Cryostream Cobra.
Maximum theta was 29.20 deg.
The hkl ranges were -17/ 17, -23/ 22, -34/ 34.

58808 reflections measured, 14480 unique [R(int) = 0.0570].
Absorption correction by Semi-empirical from equivalents;
minimum and maximum transmission factors: 0.7346; 0.8662.
no crystal decay

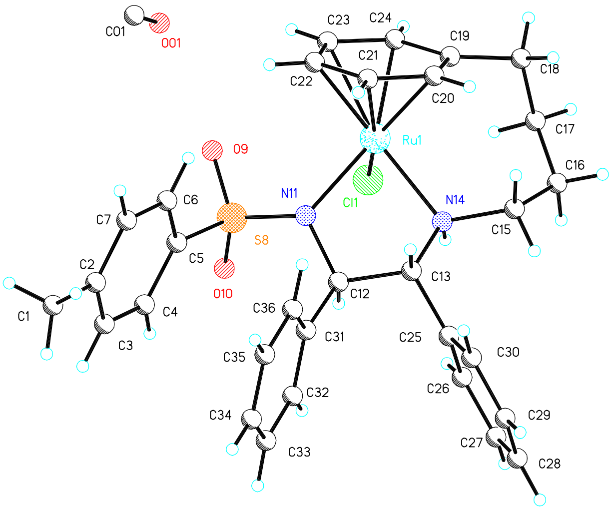
Structure Analysis and Refinement.
Systematic absences indicated space group P2(1)2(1)2(1) and shown to be correct by successful refinement.
The structure was solved by direct methods using SHELXS (Sheldrick, 1990) (TREF) with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model except the amine hydrogens which were located in a difference map. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameter equal to 1.2 (or 1.5 for methyl and NH H-atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

The absolute structure of the individual crystal chosen was checked by refinement of a delta-f" multiplier. Absolute structure parameter x = 0.02(3). The weighting scheme was calc w=1/[\s^2^(Fo^2^)+(0.0668P)^2^+2.5821P] where P=(Fo^2^+2Fc^2^)/3. Goodness-of-fit on F^2 was 1.042, R1[for 11570 reflections with I>2sigma(I)] = 0.0513, wR2 = 0.1231. Data / restraints / parameters 14480/ 3/ 722. Largest difference Fourier peak and hole 1.078 and -1.007 e.A^-3 . Refinement used SHELXL 97 (Sheldrick, 1997). Additional material available from the Cambridge

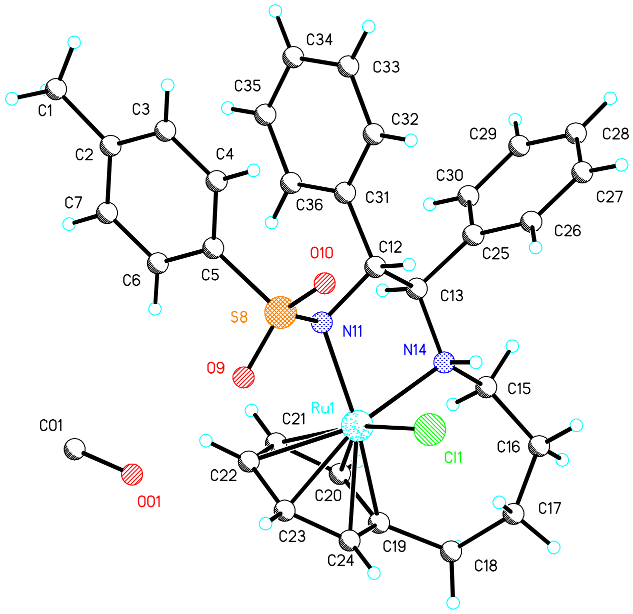
Crystallographic Data
Centre comprises H-atom coordinates, thermal parameters and the remaining bond lengths and angles. We thank EPSRC and Siemens Analytical Instruments for grants in support of the diffractometer.

References
For relevant information for the SHELXTL suite of programmes used to solve, refine and produce the files for this structure, please refer to "A Short History of Shelx, G. M. Sheldrick, Acta Cryst. 2008, 64, 112-122"
Use Mercury (Free from CCDC at www.ccdc.cam.ac.uk/products/mercury) to view

X-ray crystallography of 4-carbon reverse tethered catalyst (**3**)



solid state structure of (**3**) showing the partially occupied methanol solvent and another view below



The asymmetric unit contains the complex and a solvent methanol.

The methanol was modelled at 50% occupancy. No hydrogens were found for the methanol but were included for the unit cell instructions so as to generate the correct density.

The methanol oxygen is in close contact with O9 of the sulphonamide presumably forming a hydrogen bond (O01 - O9 distance 2.7892 (0.0067)Angstroms).

The hydrogen was located on N11 and its position was allowed to refine freely but its thermal parameters were fixed at 1.5 times the nitrogen it rides on.

It may form a 5 membered Hydrogen bond with the chlorine tabulated below

Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)	
0.88(5)	2.54(5)	2.968(4)	111(3)	N14-H14...Cl1

The torsion angle between H14-N14-Ru1-CL1 is
Dihedral angle TORS
3.04 (3.13) degrees H14 - N14 - Ru1 - Cl1

There is a possible off set pi stacking interaction between the tosyl group and one of the phenyls of the diamine. Centroid - centroid distance 3.64 A with the closest atomic contact of 3.14 A (using Mercury).

Crystal Data

C31.50 H35 Cl N2 O2.50 Ru S, M = 650.20, Orthorhombic, space group P2(1)2(1)2(1)
a = 7.0703(3), b = 11.9645(6), c = 34.9758(18) A ,
alpha = 90 deg., beta = 90 deg., gamma = 90 deg.,
U = 2958.7(2) A^3 (by least squares refinement on 25686 reflection positions),
T =120(2)K, lambda = 0.71073 A, Z = 4,
D(cal) = 1.460 Mg/m^3, F(000) = 1340.
mu(MoK-alpha) = 0.724 mm^-1.
Crystal character:orange rod.
Crystal dimensions 0.80 x 0.14 x 0.12 mm,

Data Collection and Processing.

The data was recorded by the EPSRC crysrallographic service at Southampton as detailed in the cif file.
Maximum theta was 27.48 deg.
The hkl ranges were -8/ 9, -15/ 15, -45/ 45.
21250 reflections measured, 6734 unique [R(int) = 0.0594].
No absorption correction;
Absorption correction by Semi-empirical from equivalents; minimum and maximum transmission factors: 0.5849; 0.9182.
no crystal decay

Structure Analysis and Refinement.

Systematic absences indicated space group P2(1)2(1)2(1) and shown to be correct by successful refinement.
The structure was solved by direct methods using SHELXS (Sheldrick, 1990) (TREF) with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model except the amine H which was located in a difference map. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameter equal to 1.2 (or 1.5 for methyl or NH H-atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached

The absolute structure of the individual crystal chosen was checked by refinement of a delta-f'' multiplier.
Absolute structure parameter x = 0.01(3).
The weighting scheme was calc w=1/[\s^2^(Fo^2^)+(0.0265P)^2^+3.2074P] where P=(Fo^2^+2Fc^2^)/3.
Goodness-of-fit on F^2 was 1.018,
R1[for 5765 reflections with
I>2sigma(I)] = 0.0392, wR2 = 0.0876.
Data / restraints / parameters 6734/ 13/ 366.
Largest difference Fourier peak and hole 0.599 and -0.883 e.A^-3 .

Refinement used SHELXL 97 (Sheldrick, 1997).
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and the remaining bond lengths and angles. The Oxford Diffraction Gemini XRD system was obtained through the Science City Advanced Materials project: Creating and Characterising Next Generation Advanced Materials, with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF)

References

For relevant information for the SHELXTL suite of programmes used to solve, refine and produce the files for this structure, please refer to "A Short History of Shelx, G. M. Sheldrick, Acta Cryst. 2008, 64, 112-122"
Use Mercury (Free from CCDC at www.ccdc.cam.ac.uk/products/mercury) to view the structure.

2. Kinetic data for reductions at varying concentrations of ketone.

The following tables show the measured data for two runs at each concentration.
Because the 6M and 4.5M runs did not go to completion, the data was not fitted to theoretical models and no RMS error was calculated.

For the other runs, the original data is shown, followed by the calculated vs theoretical conversions, and the square of the difference i.e.:

[D]= experimental values of product concentration, [D]*=calculated values of product concentration, d[D]^2 = square of difference between [D] and [D]*.

For the 3M-0.1M runs, the final table shows the calculated k1 and k2 values and the RMS error obtained by averaging the two runs, i.e.:

A0 = total catalyst concentration.
[A]= initial concentation of RuH.
[D] = initial concentration of product alcohol.
[C0] = initial concentration of ketone.

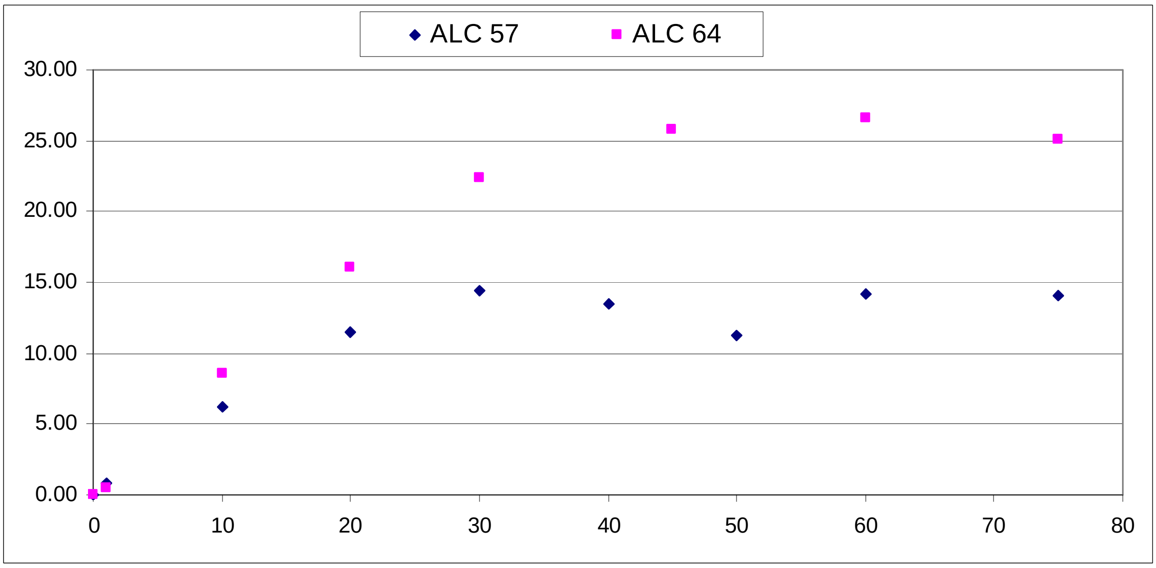
At 6M run 1 (ALC 57):

time (min)	%ketone	%alcohol	% conversion			
0	100.00	0.00	0.00	ee=	97.16312	%
1	99.20	0.80	0.80			
10	93.80	6.20	6.20			
20	88.50	11.50	11.50	ketone =	1.4	ml
30	85.60	14.40	14.40	FA/TEA =	0.6	ml
40	86.50	13.50	13.50	CAT =	14.4	mg
50	88.70	11.30	11.30			
60	85.80	14.20	14.20			
75	85.90	14.10	14.10			

At 6M run 2 (ALC 64):

time (min)	%ketone	%alcohol	% conversion			
0	100.00	0.00	0.00	ee=	96.8254	%
1	99.50	0.50	0.50			
10	91.50	8.50	8.50			
20	84.00	16.00	16.00	ketone =	1.4	ml
30	77.60	22.40	22.40	FA/TEA =	0.6	ml
45	73.80	25.80	25.80	CAT =	14.3	mg
60	73.40	26.60	26.60			
75	74.90	25.10	25.10			

Data not fitted using theoretical model hence no RMS calculation.



At 4.5M run 1 (ALC 56):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	99.00	1.00	1.00
10	81.50	18.50	18.50
20	80.20	19.80	19.80
30	69.00	31.00	31.00
40	62.20	37.80	37.80
50	61.70	38.30	38.30
60	54.30	45.70	45.70
75	54.10	45.90	45.90
90	55.30	44.70	44.70
105	53.90	46.10	46.10
120	54.80	45.20	45.20

ee= 97.34513 %

ketone = 1.05 ml

FA/TEA = 0.95 ml

CAT = 14.2 mg

At 4.5M run 2 (ALC 63):

time (min)	%ketone	%alcohol	% conversion	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00	100.00	0.00	0.00
1	99.30	0.70	0.70	99.20	0.80	0.80
10	88.70	11.30	11.30	88.50	11.50	11.50
20	81.60	18.40	18.40	78.00	22.00	22.00
30	75.20	24.80	24.80	63.00	37.00	37.00
40	73.50	26.60	26.60	57.10	42.90	42.90
50	74.20	25.80	25.80	50.90	49.10	49.10
60	74.40	25.70	25.70	48.40	51.60	51.60
75	74.60	25.40	25.40	48.30	51.70	51.70

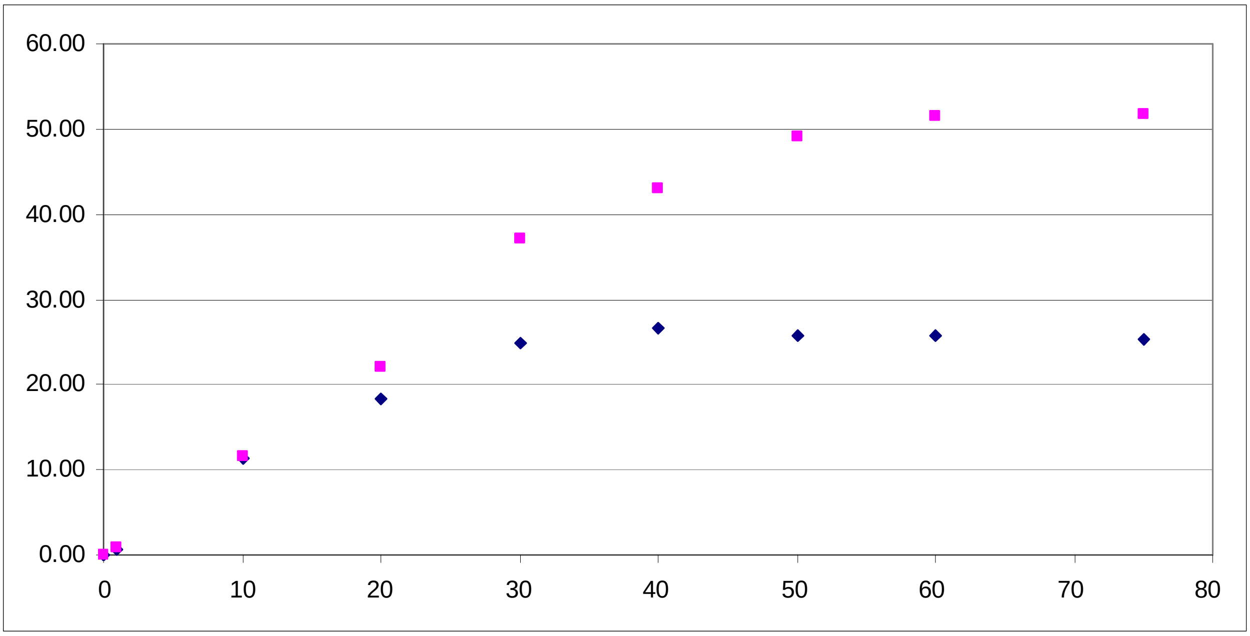
ee= 97.34513 %

ketone = 1.05 ml

FA/TEA = 0.95 ml

CAT = 14.3 mg

Data not fitted using theoretical model hence no RMS calculation.



At 3M run 1 (ALC 39):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	99.10	0.90	0.90
10	87.10	12.90	12.90
20	66.70	33.30	33.30
30	56.40	43.50	43.50
50	25.20	74.80	74.80
60	15.20	84.70	84.70
75	3.40	96.50	96.50
90	0.30	99.70	99.70
105	0.10	99.90	99.90
120	0.00	100.00	100.00

ee= 97 %

ketone = 0.7 ml
FA/TEA = 1.3 ml
CAT = 14.3 mg

Data and Error Analysis in theoretical model.

Time	[D]	[D]*	d[D]^2
0	0	0	0
1	0.027	0.055321	0.000802
10	0.387	0.491247	0.010867
20	0.999	0.952276	0.002183
30	1.305	1.382658	0.006031
50	2.244	2.11807	0.015858
60	2.541	2.403699	0.018852
75	2.895	2.709476	0.034419
90	2.991	2.877949	0.01278

At 3M run 2 (ALC 51):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	98.60	1.40	1.40
10	85.10	14.90	14.90

ee= 97.4 %

20	69.70	30.30	30.30
30	60.50	39.50	39.50
40	43.10	56.90	56.90
50	28.60	71.40	71.40
60	17.90	82.10	82.10
75	6.90	93.10	93.10
90	1.40	98.60	98.60
120	0.00	100.00	100.00

ketone = 0.7 ml
FA/TEA = 1.3 ml
CAT = 14 mg

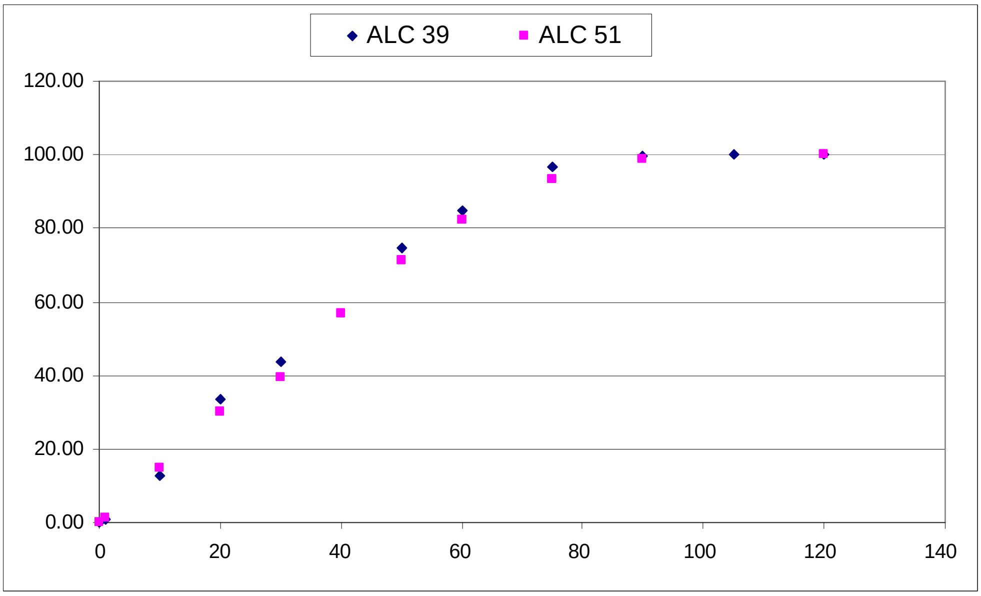
Data and Error Analysis

Time	[D]	[D]*	d[D]^2
0	0	0	0
1	0.042	0.055321	0.000177
10	0.447	0.491247	0.001958
20	0.909	0.952276	0.001873
30	1.185	1.382658	0.039069
40	1.707	1.774431	0.004547
50	2.142	2.11807	0.000573
60	2.463	2.403699	0.003517
75	2.793	2.709476	0.006976
90	2.958	2.877949	0.006408

Total calculated RMS for combined runs = 0.093721

Parameters:	k1:	7
	k2:	6.5
	A0:	0.01
Case1 ICs:	[A]:	0.01
	[D]:	0
	[C0]:	3
Case2 ICs:	[A]:	0.01
	[D]:	0
	[C0]:	3

RMS : 0.093721



At 2M run 1 (ALC 40):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	99.20	0.80	0.80
10	77.40	22.60	22.60
20	67.70	32.30	32.30
30	34.60	65.40	65.40
40	22.80	77.20	77.20
50	8.40	91.60	91.60
65	1.20	98.80	98.80
75	0.40	99.60	99.60
90	0.00	100.00	100.00

ee= 96.8 %

ketone = 0.466 ml

FA/TEA = 1.534 ml

CAT = 14.3 mg

Data and Error Analysis

Time	[D]	[D]*	d[D]^2
0	0	0	0
1	0.016	0.056565	0.001646
10	0.452	0.501549	0.002455
20	0.646	0.942874	0.088134
30	1.308	1.312358	1.9E-05
40	1.544	1.594694	0.00257
50	1.832	1.784822	0.002226
65	1.976	1.929094	0.0022
75	1.992	1.968302	0.000562
90	2	1.99091	8.26E-05

At 2M run 2(ALC 52):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	98.90	1.10	1.10
10	75.50	24.50	24.50

ee= 96.8 %

20	51.50	48.50	48.50
30	30.20	69.80	69.80
40	13.10	86.90	86.90
50	4.00	96.00	96.00
60	0.80	99.20	99.20
75	0.00	100.00	100.00

ketone = 0.466 ml
FA/TEA = 1.534 ml
CAT = 14.1 mg

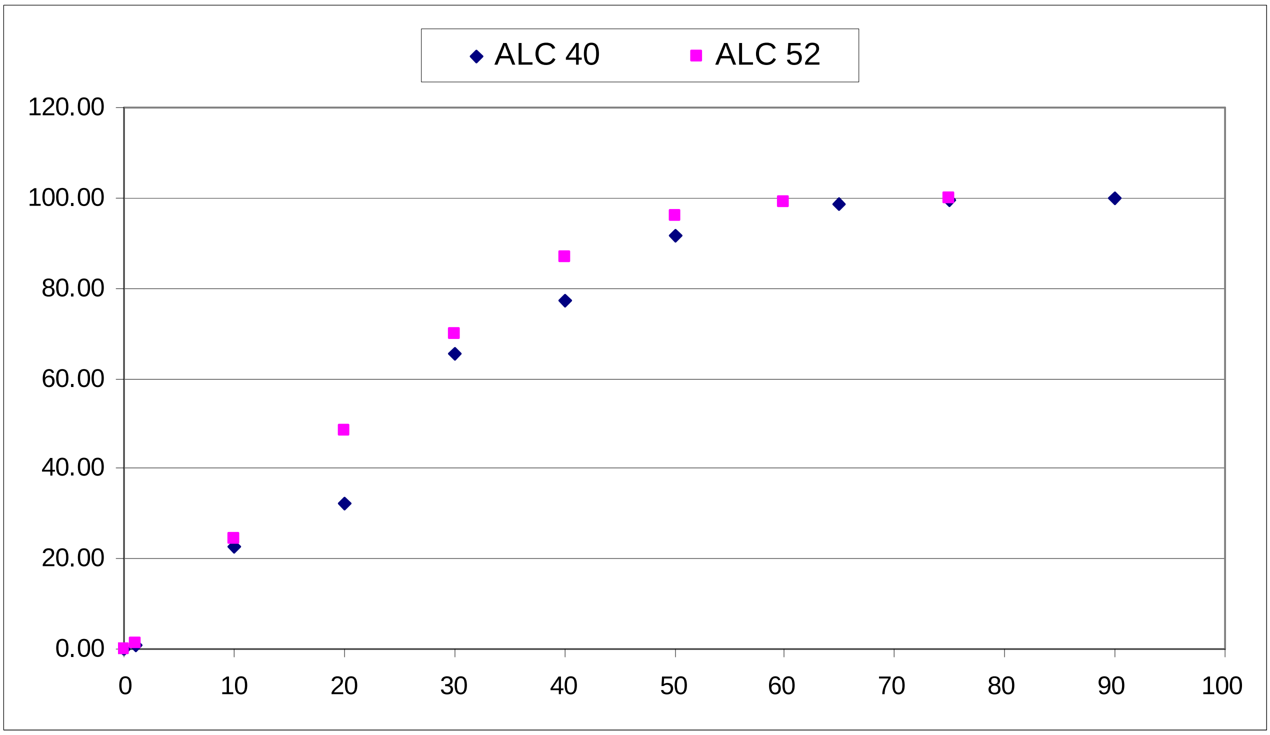
Data and Error Analysis

Time	[D]	[D]*	d[D]^2
0	0	0	0
1	0.022	0.056565	0.001195
10	0.49	0.501549	0.000133
20	0.97	0.942874	0.000736
30	1.396	1.312358	0.006996
40	1.738	1.594694	0.020537
50	1.92	1.784822	0.018273
60	1.984	1.895618	0.007811
75	2	1.968302	0.001005

Parameters:	k1:	8.5
	k2:	7.5
	A0:	0.01
Case1 ICs:	[A]:	0.01
	[D]:	0
	[C0]:	2
Case2 ICs:	[A]:	0.01
	[D]:	0
	[C0]:	2

RMS : 0.09078

Total calculated RMS for combined runs = 0.09078



At 1M run 1 (ALC 41):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	98.80	1.20	1.20
10	69.30	30.70	30.70
20	43.10	56.90	56.90
30	25.80	74.20	74.20
40	7.60	92.40	92.40
50	3.30	96.70	96.70
60	0.80	99.20	99.20
70	0.30	99.70	99.70
80	0.00	100.00	100.00

ee= 97.6 %

ketone = 0.234 ml
FA/TEA = 1.766 ml
CAT = 14.2 mg

Data and Error Analysis

Time	[D]	[D]*	d[D]^2
0	0	0	0
1	0.012	0.039642	0.000764
10	0.307	0.338563	0.000996
20	0.569	0.600943	0.00102
30	0.742	0.78319	0.001697
40	0.924	0.892899	0.000967
50	0.967	0.950596	0.000269
60	0.992	0.978101	0.000193
70	0.997	0.990485	4.24E-05
80	1	0.995904	1.68E-05

At 1M run 2 (ALC53):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	96.70	3.30	3.30
10	70.00	30.00	30.00
20	39.20	60.80	60.80
30	16.60	83.40	83.40
40	5.80	94.20	94.20
50	2.00	98.00	98.00
60	0.70	99.30	99.30
75	0.00	100.00	100.00

ee=	97.2	%
ketone =	0.234	ml
FA/TEA =	1.766	ml
CAT =	14.1	mg

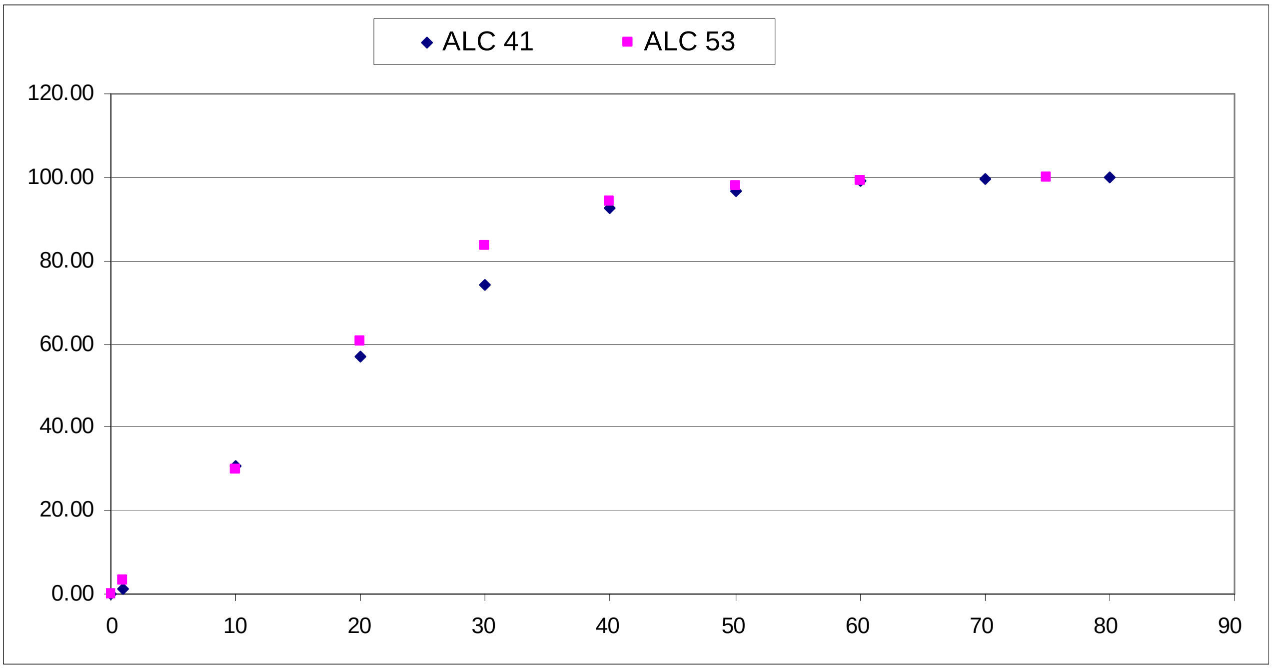
Data and Error Analysis

Time	[D]	[D]*	d[D]^2
0	0	0	0
1	0.033	0.039642	4.41E-05
10	0.3	0.338563	0.001487
20	0.608	0.600943	4.98E-05
30	0.834	0.78319	0.002582
40	0.942	0.892899	0.002411
50	0.98	0.950596	0.000865
60	0.993	0.978101	0.000222
75	1	0.993753	3.9E-05

Parameters:	k1:	8.5
	k2:	6.5
	A0:	0.01
Case1 ICs:	[A]:	0.01
	[D]:	0
	[C0]:	1
Case2 ICs:	[A]:	0.01
	[D]:	0
	[C0]:	1

RMS : 0.026818

Total calculated RMS for combined runs = 0.026818



At 0.5M run 1 (ALC 42):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	98.70	1.30	1.30
10	79.60	20.40	20.40
20	58.10	41.90	41.90
40	14.70	85.30	85.30
50	7.00	93.00	93.00
60	2.50	97.50	97.50
70	1.10	98.90	98.90
80	0.30	99.70	99.70
90	0.00	100.00	100.00

ee= 97 %

ketone = 0.116 ml
FA/TEA = 1.884 ml
CAT = 14.5 mg

Data and Error Analysis			
Time	[D]	[D]*	d[D]^2
0	0	0	0
1	0.0065	0.019871	0.000179
10	0.102	0.166186	0.00412
20	0.2095	0.287802	0.006131
40	0.4265	0.424578	3.69E-06
50	0.465	0.45695	6.48E-05
60	0.4875	0.475826	0.000136
70	0.4945	0.486559	6.31E-05
80	0.4985	0.49257	3.52E-05
90	0.5	0.495906	1.68E-05

At 0.5M run 2 (ALC 54):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	98.40	1.60	1.60

ee= 96.8 %

10	73.80	26.20	26.20
20	39.00	61.00	61.00
30	18.50	81.50	81.50
40	7.50	92.50	92.50
50	2.20	97.80	97.80
60	0.70	99.30	99.30
80	0.10	99.90	99.90
90	0.00	100.00	100.00

ketone = 0.116 ml
FA/TEA = 1.884 ml
CAT = 14.2 mg

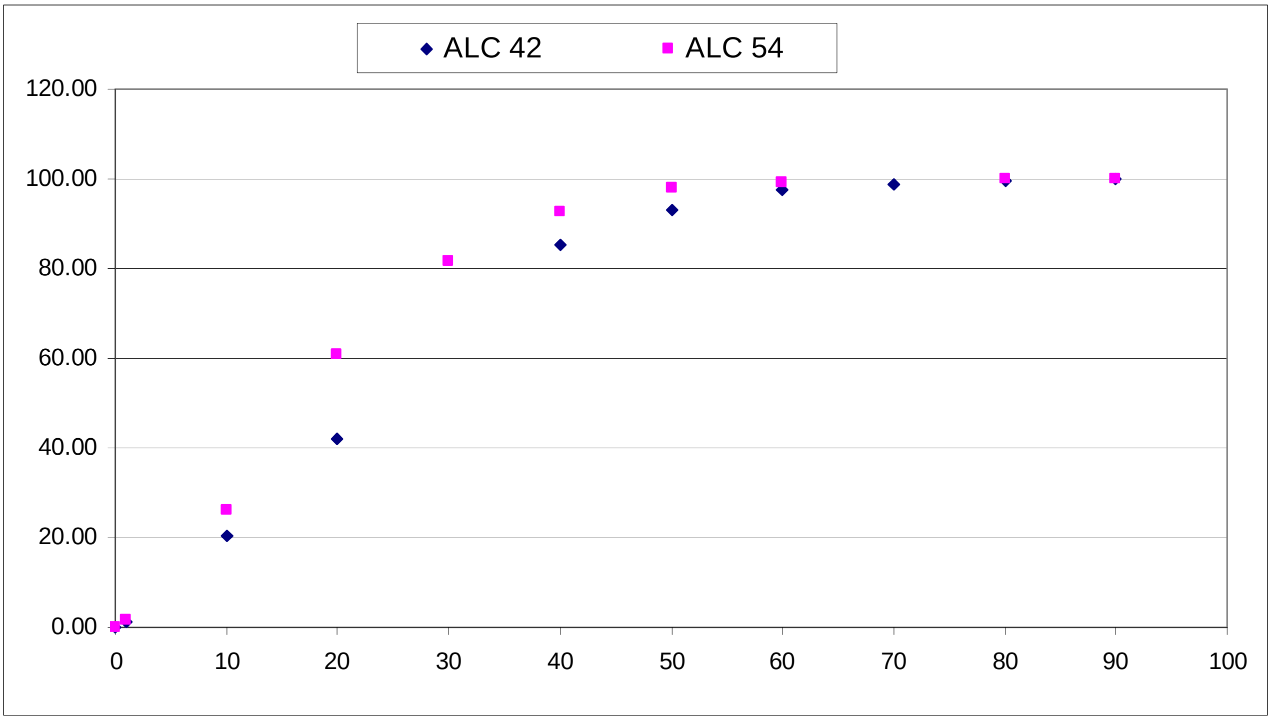
Data and Error Analysis

Time	[D]	[D]*	d[D]^2
0	0	0	0
1	0.008	0.019871	0.000141
10	0.131	0.166186	0.001238
20	0.305	0.287802	0.000296
30	0.4075	0.371181	0.001319
40	0.4625	0.424578	0.001438
50	0.489	0.45695	0.001027
60	0.4965	0.475826	0.000427
80	0.4995	0.49257	4.8E-05
90	0.5	0.495906	1.68E-05

Parameters:	k1:	6
	k2:	5
	A0:	0.01
Case1 ICs:	[A]:	0.01
	[D]:	0
	[C0]:	0.5
Case2 ICs:	[A]:	0.01
	[D]:	0
	[C0]:	0.5

RMS : 0.028897

Total calculated RMS for combined runs = 0.028897



At 0.1M run 1 (ALC 43):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	96.40	3.60	3.60
10	65.70	34.30	34.30
20	42.60	57.40	57.40
30	27.20	72.80	72.80
40	10.30	89.70	89.70
50	3.80	96.20	96.20
60	2.10	97.90	97.90
70	0.80	99.20	99.20
80	0.20	99.80	99.80
90	0.00	100.00	100.00

ee= 96.8 %

ketone = 0.024 ml
FA/TEA = 1.976 ml
CAT = 14.3 mg

Data and Error Analysis			
Time	[D]	[D]*	d[D]^2
0	0	0	0
1	0.0036	0.004282	4.66E-07
10	0.0343	0.034174	1.59E-08
20	0.0574	0.057616	4.67E-08
30	0.0728	0.073246	1.99E-07
40	0.0897	0.083348	4.03E-05
50	0.0962	0.089734	4.18E-05
60	0.0979	0.093709	1.76E-05
70	0.0992	0.096161	9.24E-06
80	0.0998	0.097662	4.57E-06
90	0.1	0.098579	2.02E-06

At 0.1M run 2 (ALC 55):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	99.10	0.90	0.90
10	85.20	14.80	14.80
20	52.90	47.10	47.10
30	16.50	83.50	83.50
40	8.20	91.80	91.80
50	2.40	97.60	97.60
60	0.80	99.20	99.20
80	0.00	100.00	100.00

ee=	96.6	%
ketone =	0.024	ml
FA/TEA =	1.976	ml
CAT =	14	mg

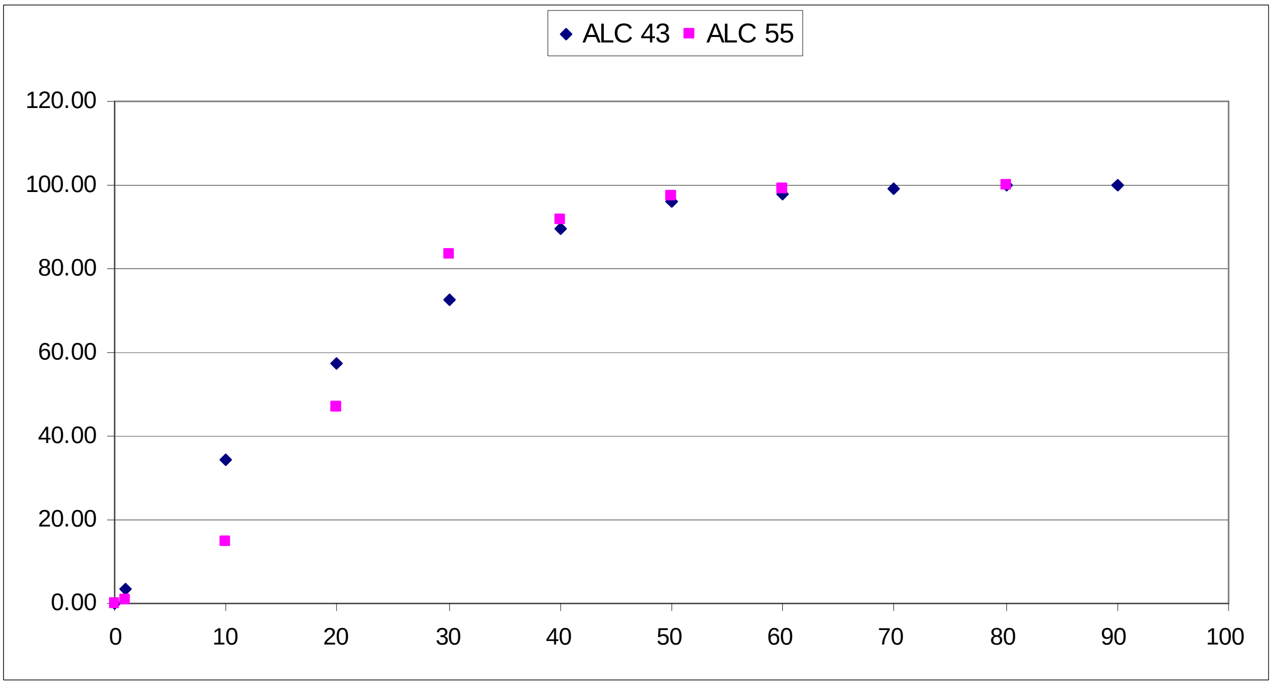
Data and Error Analysis

Time	[D]	[D]*	d[D]^2
0	0	0	0
1	0.0009	0.004282	1.14E-05
10	0.0148	0.034174	0.000375
20	0.0471	0.057616	0.000111
30	0.0835	0.073246	0.000105
40	0.0918	0.083348	7.14E-05
50	0.0976	0.089734	6.19E-05
60	0.0992	0.093709	3.01E-05
80	0.1	0.097662	5.46E-06

Parameters:	k1:	5
	k2:	2
	A0:	0.01
Case1 ICs:	[A]:	0.01
	[D]:	0
	[C0]:	0.1
Case2 ICs:	[A]:	0.01
	[D]:	0
	[C0]:	0.1

RMS : 0.006662

Total calculated RMS for combined runs = 0.006662


◆ ALC 43
■ ALC 55
120.00
100.00
80.00
60.00
40.00
20.00
0.00
0
10
20
30
40
50
60
70
80
90
100

Summary: Kinetic data used in measurements (two runs used in theoretical model):

3M

conversion	time (min)	%ketone	%alcohol	% conversion	time (min)	%ketone	%alcohol	% conversion	conc ketone
0	0	100.00	0.00	0.00	0	100.00	0.00	0.00	0
1.15	1	99.10	0.90	0.90	1	98.60	1.40	1.40	0.0345
13.9	10	87.10	12.90	12.90	10	85.10	14.90	14.90	0.417
31.8	20	66.70	33.30	33.30	20	69.70	30.30	30.30	0.954
41.5	30	56.40	43.50	43.50	30	60.50	39.50	39.50	1.245
56.90	40				40	43.10	56.90	56.90	1.707
78.05	50	25.20	74.80	74.80	50	28.60	71.40	71.40	2.3415
89.3	60	15.20	84.70	84.70	60	17.90	82.10	82.10	2.679
96.4	75	3.40	96.50	96.50	75	6.90	93.10	93.10	2.892
99.25	90	0.30	99.70	99.70	90	1.40	98.60	98.60	2.9775
99.90	105	0.10	99.90	99.90					2.997
100	120	0.00	100.00	100.00	120	0.00	100.00	100.00	3

			6M					4.5M	
time (min)	%ketone	%alcohol	% conversion		time (min)	%ketone	%alcohol	% conversion	
0	100.00	0.00	0.00	0	0	100.00	0.00	0.00	0
1	99.50	0.50	0.50	0.03	1	99.20	0.80	0.80	0.036
10	91.50	8.50	8.50	0.51	10	88.50	11.50	11.50	0.5175
20	84.00	16.00	16.00	0.96	20	78.00	22.00	22.00	0.99
30	77.60	22.40	22.40	1.344	30	63.00	37.00	37.00	1.665
45	73.80	25.80	25.80	1.548	40	57.10	42.90	42.90	1.9305
60	73.40	26.60	26.60	1.596	50	50.90	49.10	49.10	2.2095
75	74.90	25.10	25.10	1.506	60	48.40	51.60	51.60	2.322
					75	48.30	51.70	51.70	2.3265

2M

conversion	time (min)	%ketone	%alcohol	% conversion	time (min)	%ketone	%alcohol	% conversion	
0	0	100.00	0.00	0.00	0	100.00	0.00	0.00	0
0.95	1	99.20	0.80	0.80	1	98.90	1.10	1.10	0.019

23.55	10	77.40	22.60	22.60	10	75.50	24.50	24.50	0.471
40.4	20	67.70	32.30	32.30	20	51.50	48.50	48.50	0.808
67.6	30	34.60	65.40	65.40	30	30.20	69.80	69.80	1.352
82.05	40	22.80	77.20	77.20	40	13.10	86.90	86.90	1.641
93.8	50	8.40	91.60	91.60	50	4.00	96.00	96.00	1.876
99	65	1.20	98.80	98.80	60	0.80	99.20	99.20	1.98
99.8	75	0.40	99.60	99.60	75	0.00	100.00	100.00	1.996
100	90	0.00	100.00	100.00	90	0.00	100.00	100.00	2

1M

conversion	time (min)	%ketone	%alcohol	% conversion	time (min)	%ketone	%alcohol	% conversion	
0	0	100.00	0.00	0.00	0	100.00	0.00	0.00	0
2.25	1	98.80	1.20	1.20	1	96.70	3.30	3.30	0.0225
30.35	10	69.30	30.70	30.70	10	70.00	30.00	30.00	0.3035
58.85	20	43.10	56.90	56.90	20	39.20	60.80	60.80	0.5885
78.8	30	25.80	74.20	74.20	30	16.60	83.40	83.40	0.788
93.3	40	7.60	92.40	92.40	40	5.80	94.20	94.20	0.933
97.35	50	3.30	96.70	96.70	50	2.00	98.00	98.00	0.9735
99.25	60	0.80	99.20	99.20	60	0.70	99.30	99.30	0.9925
99.70	70	0.30	99.70	99.70					0.997
100	80	0.00	100.00	100.00	80	0.00	100.00	100.00	1

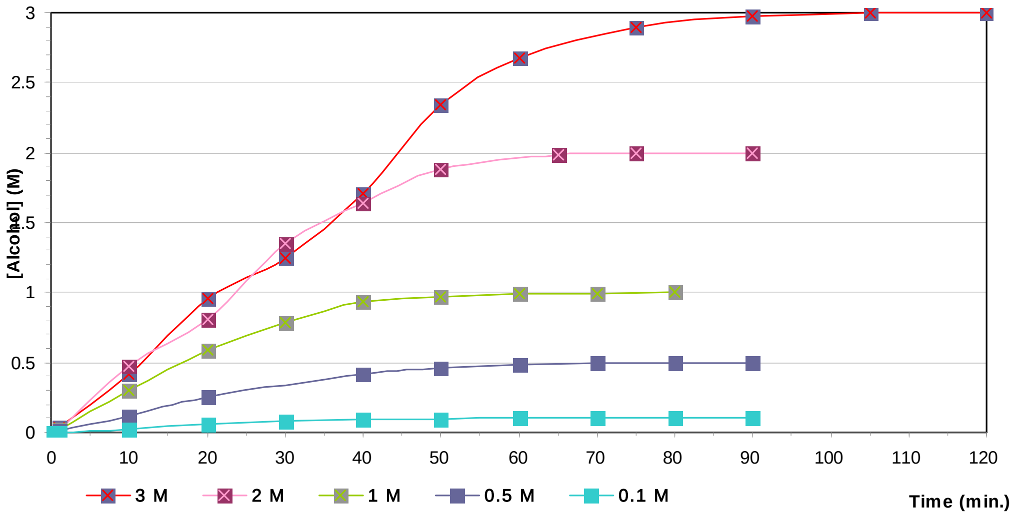
0.5M

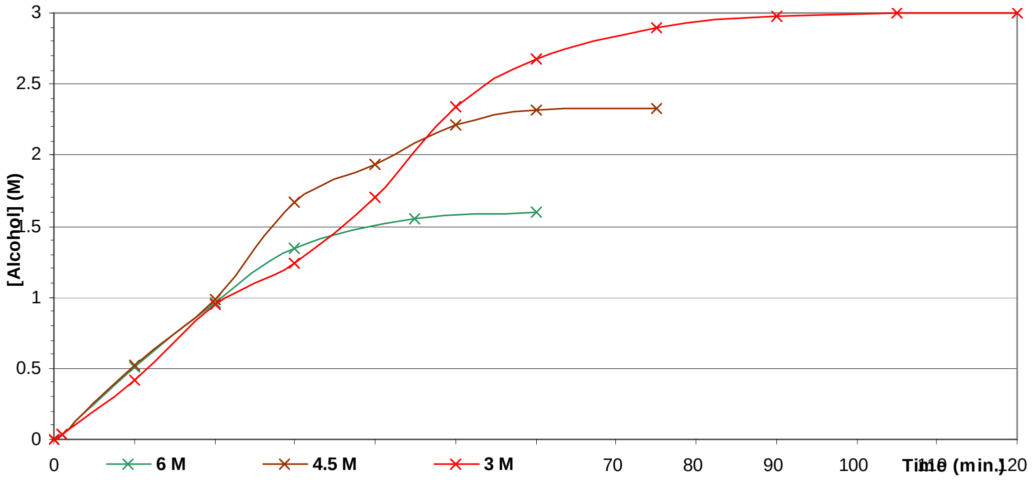
conversion	time (min)	%ketone	%alcohol	% conversion	time (min)	%ketone	%alcohol	% conversion	
0	0	100.00	0.00	0.00	0	100.00	0.00	0.00	0
1.45	1	98.70	1.30	1.30	1	98.40	1.60	1.60	0.00725
23.3	10	79.60	20.40	20.40	10	73.80	26.20	26.20	0.1165
51.45	20	58.10	41.90	41.90	20	39.00	61.00	61.00	0.25725
83.4	40	14.70	85.30	85.30	30	18.50	81.50	81.50	0.417
92.75	50	7.00	93.00	93.00	40	7.50	92.50	92.50	0.46375
97.65	60	2.50	97.50	97.50	50	2.20	97.80	97.80	0.48825
99.1	70	1.10	98.90	98.90	60	0.70	99.30	99.30	0.4955
99.8	80	0.30	99.70	99.70	80	0.10	99.90	99.90	0.499
100	90	0.00	100.00	100.00	90	0.00	100.00	100.00	0.5

0.1M

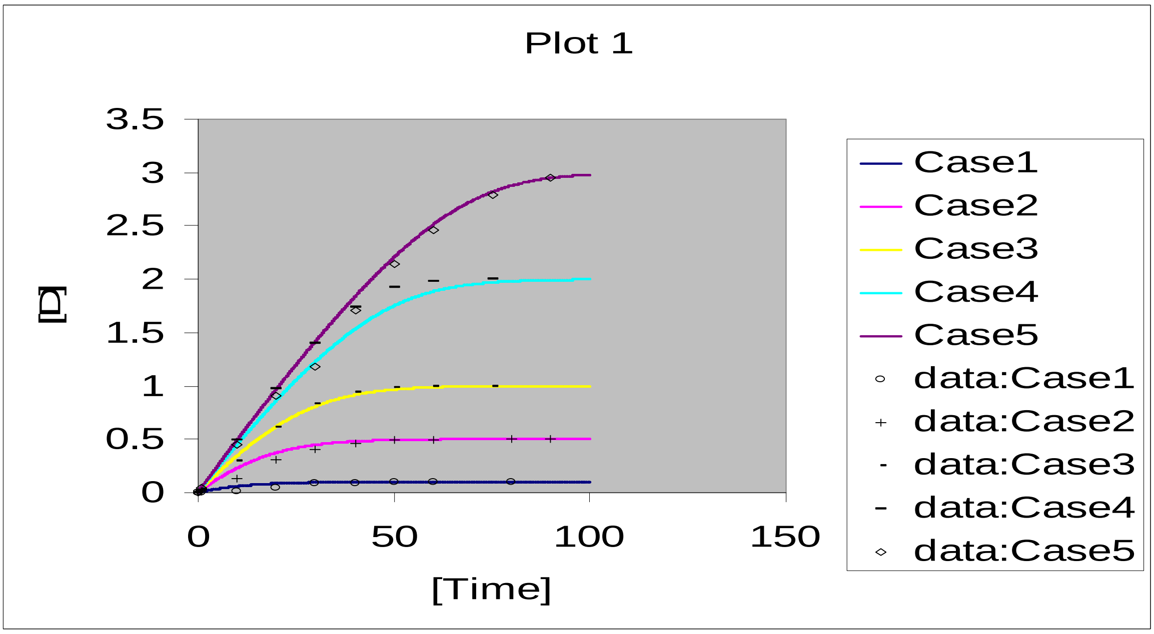
conversion	time (min)	%ketone	%alcohol	% conversion	time (min)	%ketone	%alcohol	% conversion	
0	0	100.00	0.00	0.00	0	100.00	0.00	0.00	0
2.25	1	96.40	3.60	3.60	1	99.10	0.90	0.90	0.00225
24.55	10	65.70	34.30	34.30	10	85.20	14.80	14.80	0.02455
52.25	20	42.60	57.40	57.40	20	52.90	47.10	47.10	0.05225
78.15	30	27.20	72.80	72.80	30	16.50	83.50	83.50	0.07815
90.75	40	10.30	89.70	89.70	40	8.20	91.80	91.80	0.09075
96.9	50	3.80	96.20	96.20	50	2.40	97.60	97.60	0.0969
98.55	60	2.10	97.90	97.90	60	0.80	99.20	99.20	0.09855
99.20	70	0.80	99.20	99.20					0.0992
99.9	80	0.20	99.80	99.80	80	0.00	100.00	100.00	0.0999
100.00	90	0.00	100.00	100.00					0.1

Summary graphs (unsmoothed):





Kinetic data fitting plots for 0.1-3.0M runs (using averaged data from duplicate runs in each case, see reference 5a in main paper for full details of how these are carried out):



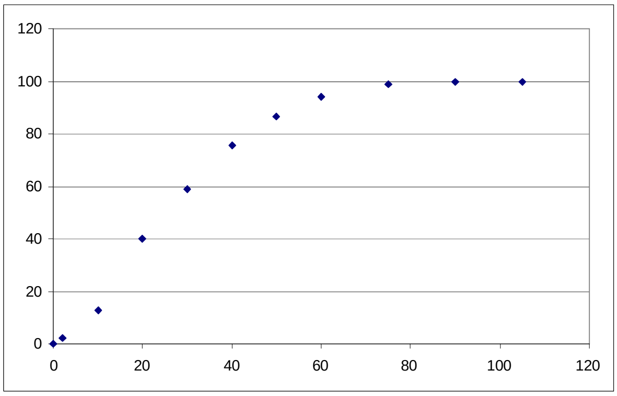
3. Kinetic data for reduction of different ketones.

p-H (acetophenone) (ALC 29):

ee (%) = 96.40

time (min)	% ketone	% alcohol	% conversion
0	100.00	0.00	0.00
1	97.80	2.20	2.20
10	87.30	12.70	12.70
20	59.10	40.20	40.20
30	41.40	58.90	58.90
40	24.60	75.40	75.40
50	13.10	86.80	86.80
60	5.80	94.20	94.20
75	0.90	99.10	99.10
90	0.30	99.70	99.70
105	0.00	100.00	100.00

ketone = 0.466 ml
FA/TEA = 2 ml
CAT = 14.1 mg

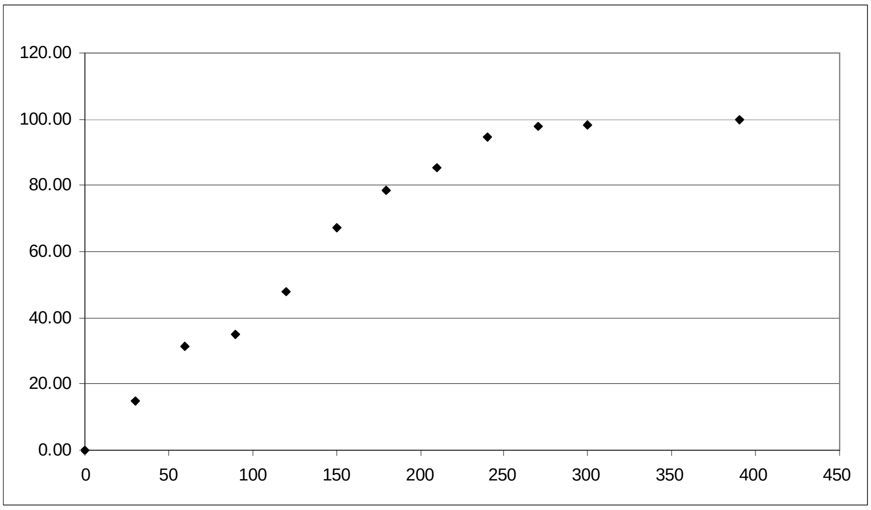


p-OMe (ALC 45):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
30	85.00	15.00	15.00
60	68.70	31.30	31.30
90	64.90	35.00	35.00
120	51.90	48.10	48.10
150	32.80	67.20	67.20
180	21.60	78.40	78.40
210	14.70	85.30	85.30
240	5.40	94.60	94.60
270	2.30	97.80	97.80
300	1.60	98.40	98.40
390	0.00	100.00	100.00

ee= 96.34146 %

ketone = 598.4 mg
FA/TEA = 2 ml
CAT = 14 mg

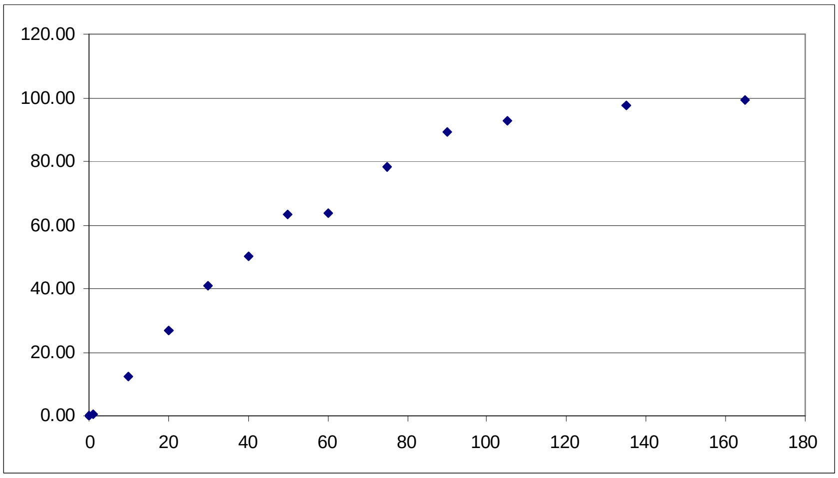


p-Me (ALC 49):

time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	99.4	0.6	0.60
10	87.70	12.30	12.30
20	74.40	26.60	26.60
30	59.10	41.00	41.00
40	50.10	49.90	49.90
50	36.60	63.40	63.40
60	36.30	63.70	63.70
75	21.90	78.10	78.10
90	10.80	89.20	89.20
105	7.10	92.90	92.90
135	2.40	97.60	97.60
165	0.50	99.50	99.50

ee= 92.0082 %

ketone = 0.534 ml
FA/TEA = 2 ml
CAT = 14.2 mg



pCl (ALC 50):

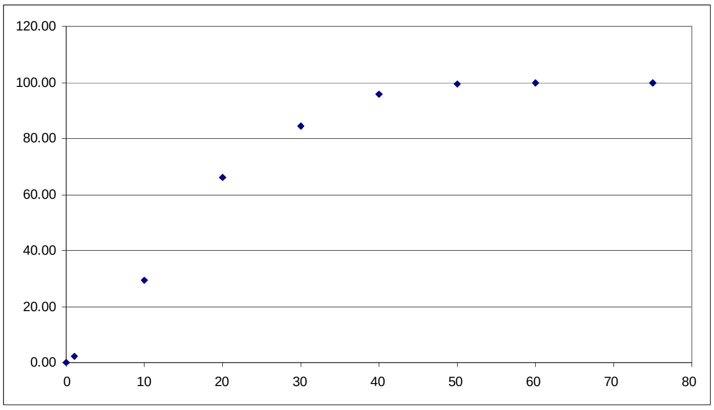
time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	97.9	2.1	2.10
10	70.60	29.40	29.40
20	34.10	65.90	65.90
30	15.70	84.30	84.30
40	4.30	95.70	95.70
50	0.70	99.30	99.30
60	0.10	99.90	99.90
75	0.00	100.00	100.00

ee= 91.99199 %

ketone = 0.518 ml

FA/TEA = 2 ml

CAT = 14.3 mg



p-CN (ALC 60).

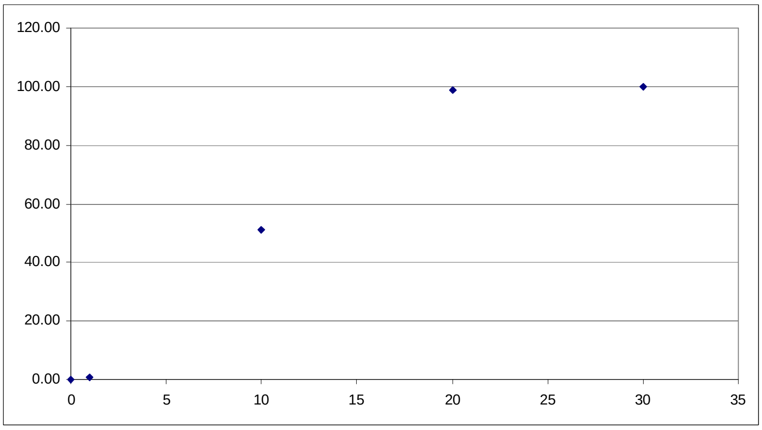
time (min)	%ketone	%alcohol	% conversion
0	100.00	0.00	0.00
1	99.2	0.7	0.70
10	48.80	51.20	51.20
20	1.10	98.90	98.90
30	0.00	100.00	100.00

ee= 83.4 %

ketone = 540 mg

FA/TEA = 2 ml

CAT = 14.2 mg



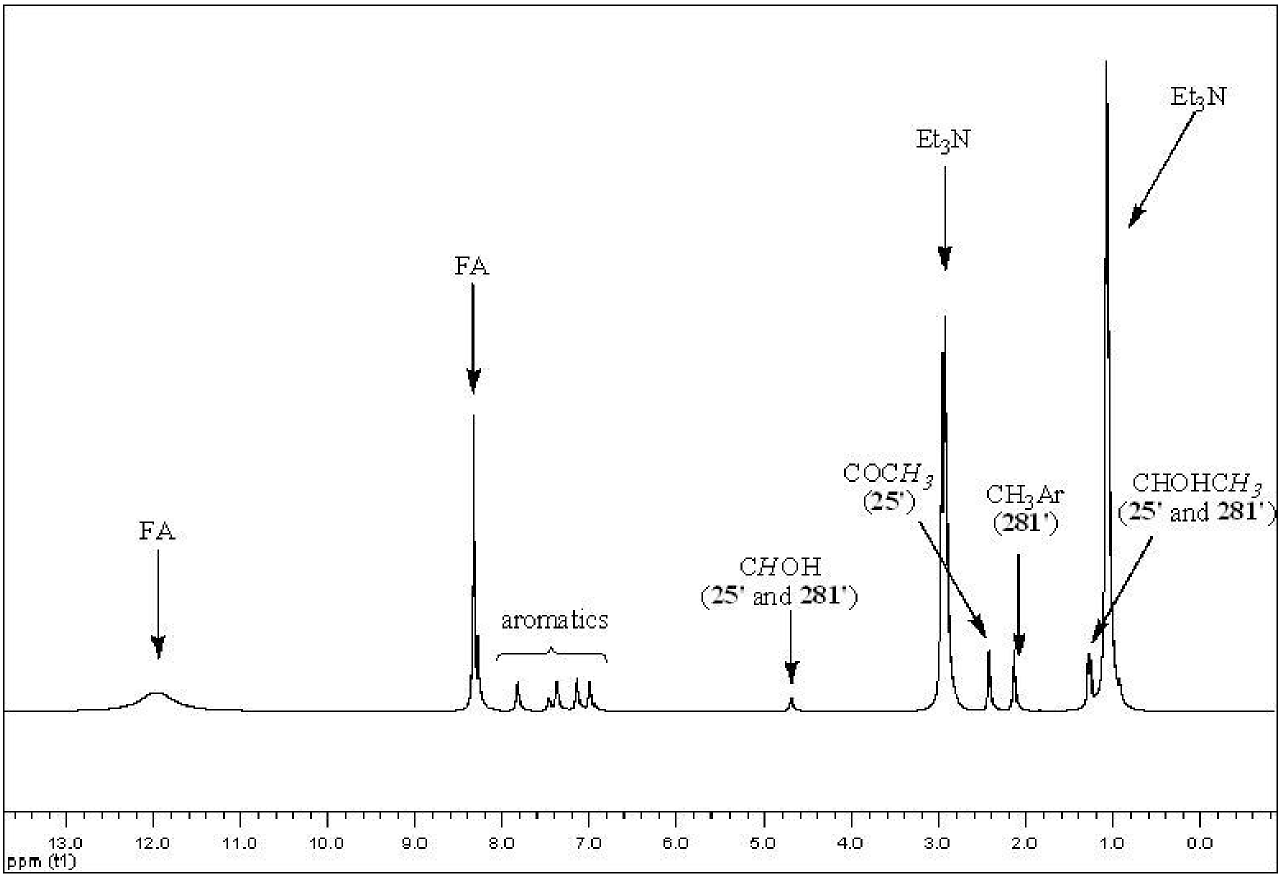
4. Crossover ketone reduction / oxidation test.

Procedure for the attempted crossover reaction (MW187):

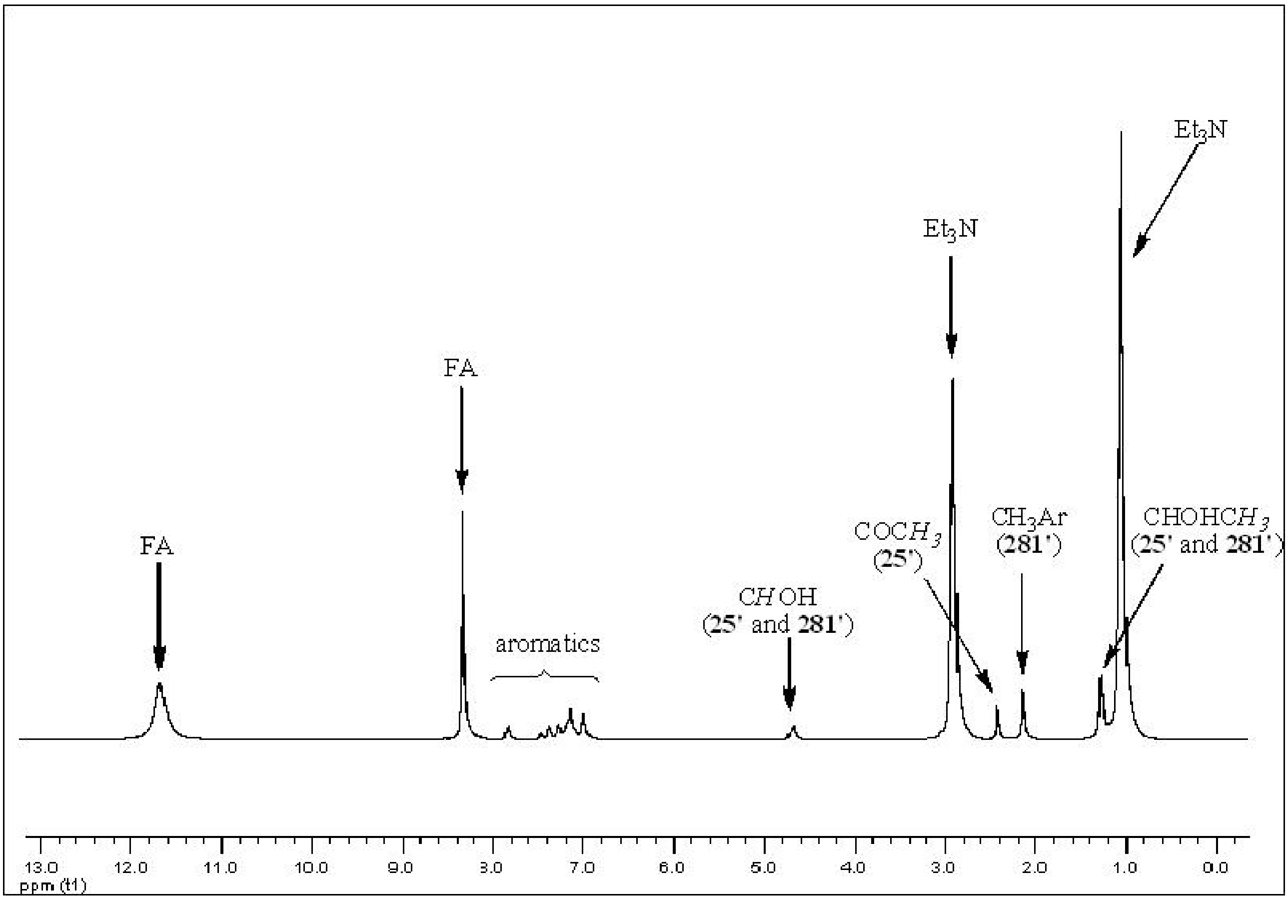
To a solution of acetophenone (120 mg, 1 mmol) and 1-(4-methylphenyl)ethanol (136 mg, 1 mmol) in formic acid:triethylamine (5:2, 1 mL) and d6-benzene (0.05 mL) in an NMR tube (with a perforated top) was added catalyst **3** (6.2 mg, 0.01 mmol). The first NMR spectrum was recorded within 15 min and subsequent NMR spectra were recorded at 20 min intervals. The reduction of acetophenone could be clearly observed, whilst there was no evidence of concommitant oxidation of the alcohol. At the end of the reaction an authentic sample of 4-methylacetophenone was added to identify the positions it occupied in the NMR spectrum..

Results and sample spectra:

The spectra below illustrate the ^{1}H NMR taken at the beginning, during, and at the end of the reduction reaction. In the spectra, 25'=acetophenone and 181'=1-(4-methylphenyl)-ethanol. No formation of 4-methylacetophenone **13** was observed at any stage. However to confirm that it was not being missed due to overlapping peaks, an authentic sample of 4-methyl acetophenone (**13**) was added at the end (Last spectrum).



^{1}H NMR spectrum at the beginning of the reaction: The methylene and methyl doublet signal at this stage are entirely due to the 4-(methylphenyl)ethanol (281'). Acetophenone = 25'.



^{1}H NMR spectrum taken during the reaction. The level of acetophenone (25') relative to the 1-(4-methylphenyl)ethanol **17** (281') has decreased (comparison of methyl singlet peaks).

Move figures 6-9 to SI and change the discussion.

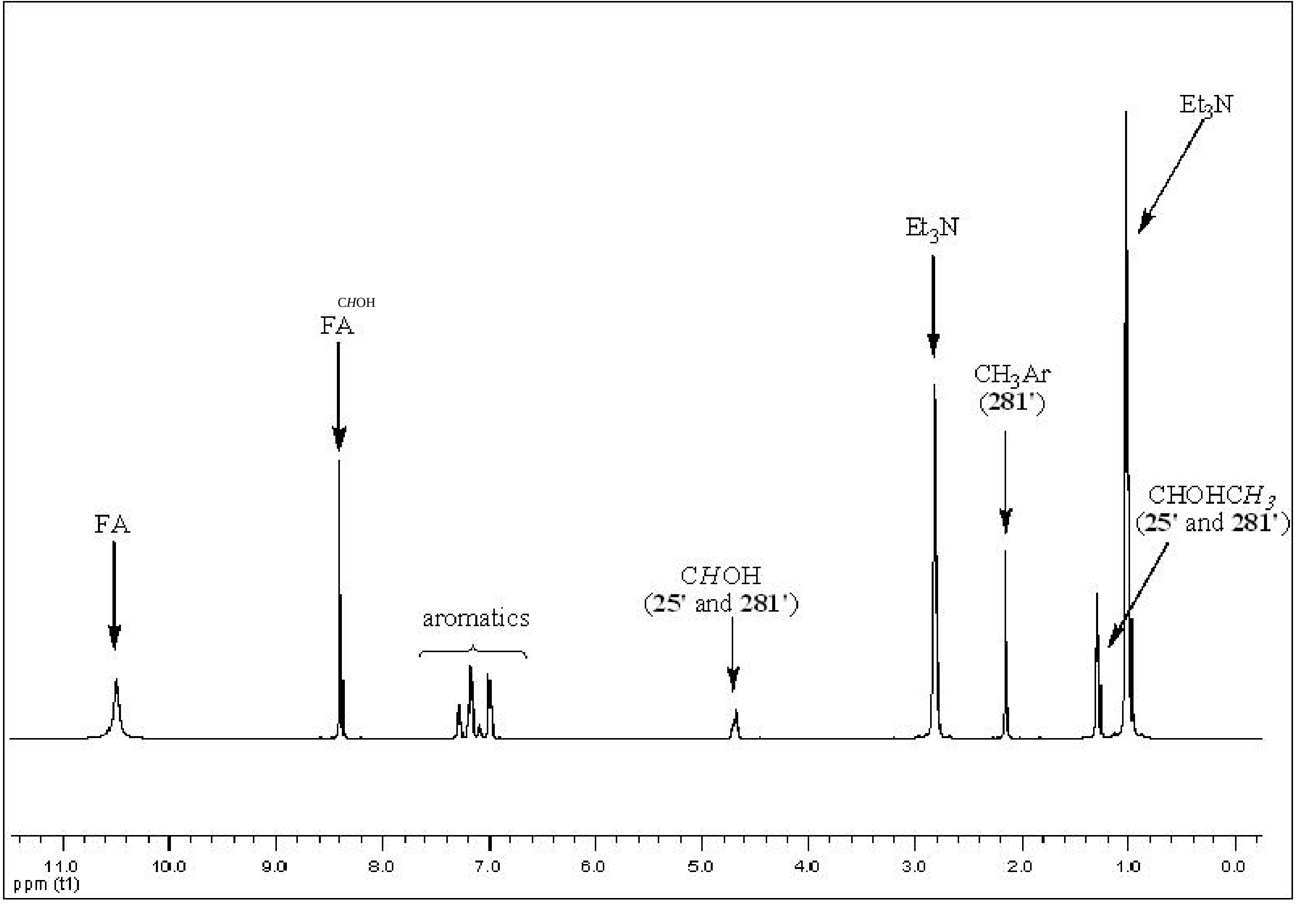


Figure 8: ^{1}H NMR spectrum at the end of the reaction. Acetophenone (25’) has been fully reduced, and the CH of the 1phenylethanol now overlaps with that of the 1-(4-methylphenyl)ethanol (281’).

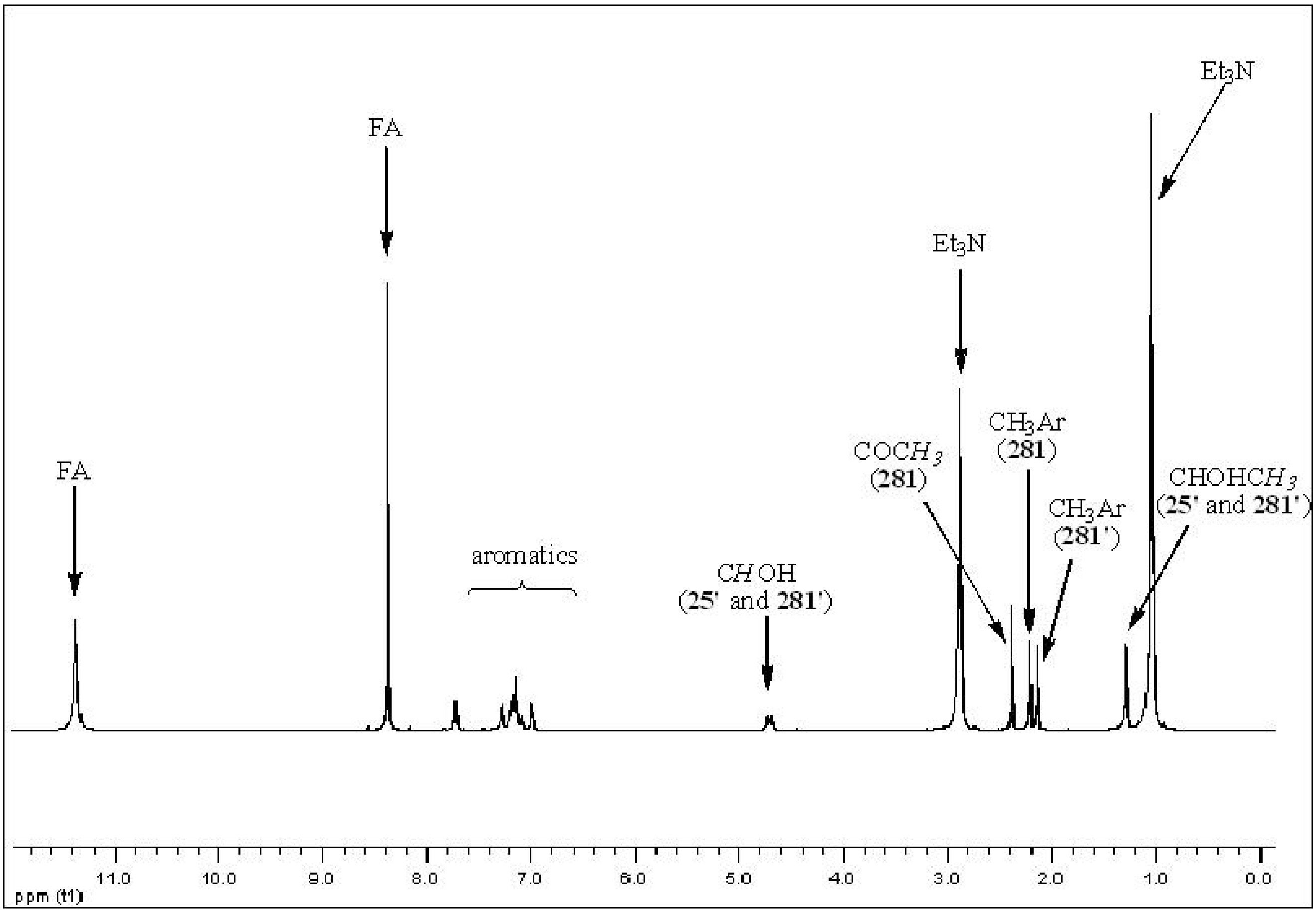


Figure 9: ^{1}H NMR spectrum at the end of the reaction with the addition of authentic 4-(methylphenyl)-acetophenone (**13**) (281) to eliminate the possibility of overlapping peaks.

The pCH_3 peak in **13** clearly appears at a different position to the same signal in **17** and would have been clearly visible if it had formed during the reduction. Hence there was no evidence for the oxidation of 1-(4-methylphenyl)ethanol (**17**) to 4-methyl acetophenone (**13**) during the course of acetophenone reduction to 1-phenylethanol.

5. Following hydride reactions by 700 MHz 1H NMR.

Monitoring of formic acid decomposition and hydride formation during reduction (MW 191): To a mixture of formic acid:triethylamine (5:2, 1 mL) and d6-benzene (0.05 mL) in an NMR tube (with a perforated cap) was added catalyst **3** (6.2 mg, 0.01 mmol). The first NMR spectrum was recorded within 10 min and subsequent 700 MHz NMR spectra were recorded at 5 min intervals. The decomposition of formic acid could be clearly observed and measured by integration of the formic acid:triethylamine ratio. After 300 minutes, acetophenone (240 mg, 2 mmol); reduction of acetophenone could be clearly observed and was followed by 1H-NMR.

SPECTRUM	TIME	REL TIME	HCO2H(1H)	Et3N(6H)	small hydride	large hydride	total cat	ketone	alcohol
11	9.34		2.42	6					
41	9.37	0	2.20654	6	0	0	0.00000		
42	9.43	5	2.1356	6	0	0.00011	0.00011		
43		10	2.0966	6	0	0.00012	0.00012		
44		15	2.04368	6	0	0.00011	0.00011		
45		20	2.00327	6	0	0.0002	0.00020		
46		25	1.97002	6	0	0.00023	0.00023		
47		30	1.92872	6	0	0.00026	0.00026		
48		35	1.93499	6	0	0.00029	0.00029		
49		40	1.90057	6	0	0.00024	0.00024		
50	10.22	45	1.87833	6	0	0.00036	0.00036		
51		50	1.87646	6	0.00003	0.00048	0.00051		
52		55	1.85507	6	0.0001	0.00045	0.00055		
53		60	1.84319	6	0.00009	0.00049	0.00058		
54		65	1.83096	6	0.00009	0.00049	0.00058		
55		70	1.82519	6	0.00009	0.0005	0.00059		
56		75	1.80471	6	0.0001	0.0005	0.00060		
57		80	1.79924	6	0.0001	0.0005	0.00060		
58		85	1.78713	6	0.00012	0.00052	0.00064		
59		90	1.77471	6	0.00011	0.00055	0.00066		
60	11.1	95	1.76583	6	0.00009	0.00054	0.00063		
61		100	1.76113	6	0.00011	0.00057	0.00068		
62		105	1.75418	6	0.00012	0.00056	0.00068		
63		110	1.74564	6	0.00015	0.00058	0.00073		
64		115	1.73941	6	0.00016	0.00054	0.00070		
65		120	1.72906	6	0.00012	0.00057	0.00069		
66		125	1.72282	6	0.0002	0.0006	0.00080		
67		130	1.71748	6	0.00013	0.0006	0.00073		
68		135	1.70781	6	0.00012	0.00053	0.00065		
69		140	1.70853	6	0.00016	0.00057	0.00073		
70	11.58	145	1.69777	6	0.00013	0.00059	0.00072		
71		150	1.68701	6	0.00012	0.00048	0.00060		
72		155	1.67957	6	0.00012	0.00048	0.00060		
73		160	1.67967	6	0.00019	0.00053	0.00072		
74		165	1.67297	6	0.00012	0.00055	0.00067		
75		170	1.67086	6	0.00012	0.00054	0.00066		
76		175	1.66491	6	0.00015	0.00055	0.00070		
77		180	1.6561	6	0.00012	0.00053	0.00065		
78		185	1.65133	6	0.00016	0.00062	0.00078		
79		190	1.64663	6	0.00012	0.00055	0.00067		
80	12.46	195	1.64475	6	0.00015	0.00055	0.00070		
81		200	1.64144	6	0.00012	0.00054	0.00066		
82		205	1.6373	6	0.00015	0.00054	0.00069		
83		210	1.63195	6	0.00015	0.00053	0.00068		

84		215	1.6251	6	0.00015	0.00055	0.00070		
85		220	1.62122	6	0.00018	0.00057	0.00075		
86		225	1.61981	6	0.00015	0.00059	0.00074		
87		230	1.61566	6	0.00021	0.00059	0.00080		
88		235	1.60926	6	0.00016	0.00058	0.00074		
89		240	1.60463	6	0.00013	0.00055	0.00068		
90	13.34	245	1.61141	6	0.00015	0.00051	0.00066		
91		250	1.60212	6	0.00013	0.00055	0.00068		
92		255	1.59826	6	0.00015	0.00057	0.00072		
93		260	1.5994	6	0.00014	0.00061	0.00075		
94		265	1.59728	6	0.00016	0.00057	0.00073		
95		270	1.59182	6	0.00018	0.00063	0.00081		
96		275	1.58616	6	0.00014	0.00054	0.00068		
97		280	1.58363	6	0.00014	0.00057	0.00071		
98		285	1.57959	6	0.00015	0.00057	0.00072		
99		290	1.57207	6	0.00013	0.00052	0.00065		
100	14.22	295	1.57623	6	0.00015	0.00054	0.00069		
KETONE IN	14.25								0
101									
102									
103	14.37		1.45709	6	0.00013	0.00019	0.00032	1.9291	0.10589
104			1.40131	6	0.00014	0.00017	0.00031	1.79004	0.15979
105			1.35392	6	0.00015	0.00018	0.00033	1.60969	0.20757
106			1.29506	6	0.00013	0.00023	0.00036	1.51336	0.26104
107			1.2411	6	0.00013	0.00021	0.00034	1.34789	0.3086
108			1.19036	6	0.0001	0.00019	0.00029	1.21014	0.35487
109			1.14184	6	0.00015	0.00021	0.00036	1.08027	0.3964
110			1.10446	6	0.00012	0.00031	0.00043	0.95762	0.43258
111			1.07078	6	0.00016	0.00027	0.00043	0.85976	0.47606
112	15.21		1.03949	6	0.00017	0.00022	0.00039	0.76442	0.51521
113			1.00615	6	0.00013	0.00022	0.00035	0.65164	0.54843
114			0.98545	6	0.00018	0.00022	0.0004	0.59898	0.60206
115			0.95511	6	0.00015	0.00025	0.0004	0.5022	0.61703
116			0.93473	6	0.0001	0.00021	0.00031	0.45321	0.64094
117			0.90794	6	0.00012	0.00022	0.00034	0.39717	0.67348
118			0.89917	6	0.00013	0.00023	0.00036	0.32516	0.68861
119			0.89473	6	0.00018	0.00024	0.00042	0.28501	0.71735
120			0.88235	6	0.00019	0.00036	0.00055	0.24407	0.7345
121			0.86468	6	0.00015	0.00034	0.00049	0.1846	0.7538
122			0.86013	6	0.00014	0.0003	0.00044	0.13829	0.76912
123			0.85702	6	0.0002	0.00036	0.00056	0.10188	0.78964
124	16.18		0.84471	6	0.00017	0.0003	0.00047	0.08926	0.78571
125			0.83492	6	0.00022	0.0004	0.00062	0.06348	0.80116
126			0.8493	6	0.00021	0.00038	0.00059	0.09042	0.80182

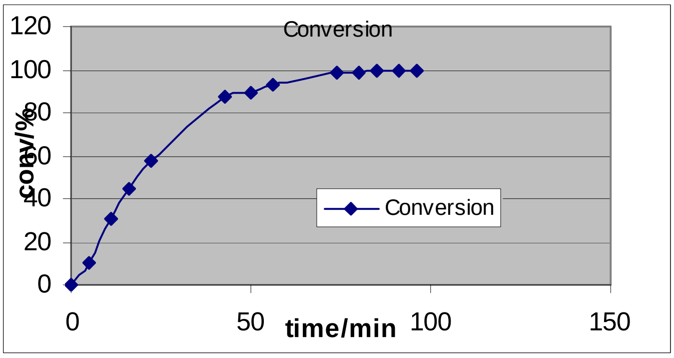
700 MHz NMR study of hydride (MW183):

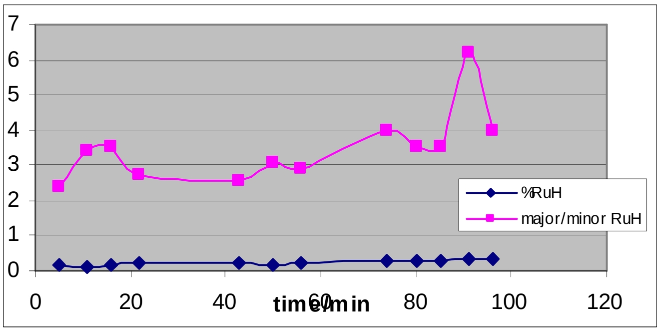
To a solution of acetophenone (240 mg, 2 mmol) in formic acid:triethylamine (5:2, 1 mL) and d6-benzene (0.05 mL) in an NMR tube (with a perforated cap) was added catalyst **3** (6.2 mg, 0.01 mmol). The first NMR spectrum was recorded after 5 minutes and subsequent spectra were recorded at 15-20 minute intervals. The ratio of the hydride peak to the starting material and product could be clearly monitored over time.

700 MHz NMR study of acetophenone reduction. (0.5 mol% cat measured)

time	elapsed	conv	mi H	Ma H	total RuH	Ma/Mi	% RuH in reaction. {(ma/Mi)/alc+acet)
10.47	0	0					
10.52	5	9.887937	0.00499	0.01195	0.01694	2.39479	0.167502
10.58	11	31.13648	0.00102	0.00348	0.0045	3.411765	0.140114
11.03	16	44.96403	0.00074	0.00261	0.00335	3.527027	0.150629
11.09	22	57.84805	0.00093	0.00254	0.00347	2.731183	0.200733
11.31	43	87.01832	0.00076	0.00195	0.00271	2.565789	0.23582
11.37	50	89.45077	0.00052	0.00161	0.00213	3.096154	0.19053
11.43	56	93.32131	0.00056	0.00161	0.00217	2.875	0.202507
12.01	74	98.22604	0.00058	0.00231	0.00289	3.982759	0.283873
12.07	80	98.88393	0.00061	0.00216	0.00277	3.540984	0.273908
12.12	85	99.30881	0.00067	0.00237	0.00304	3.537313	0.301899
12.18	91	99.11883	0.00045	0.00278	0.00323	6.177778	0.320154
12.23	96	99.99757	0.06541	0.26228	0.32769	4.009784	0.327682

Mi H = minor RuH peak, Ma H = major RuH peak.





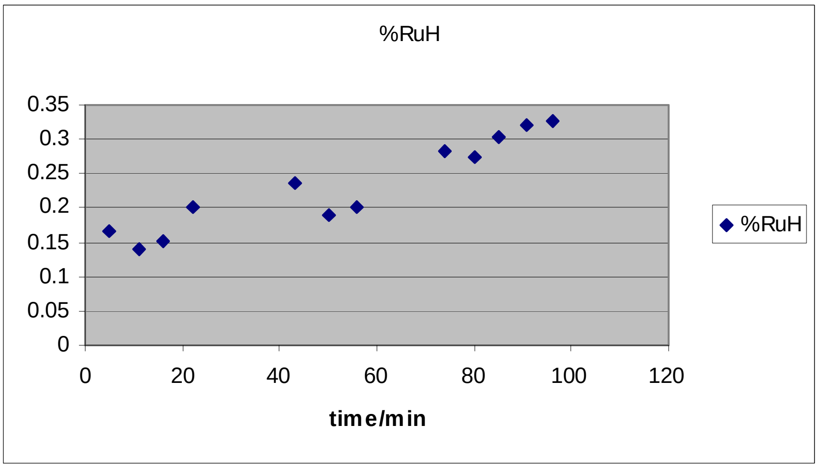
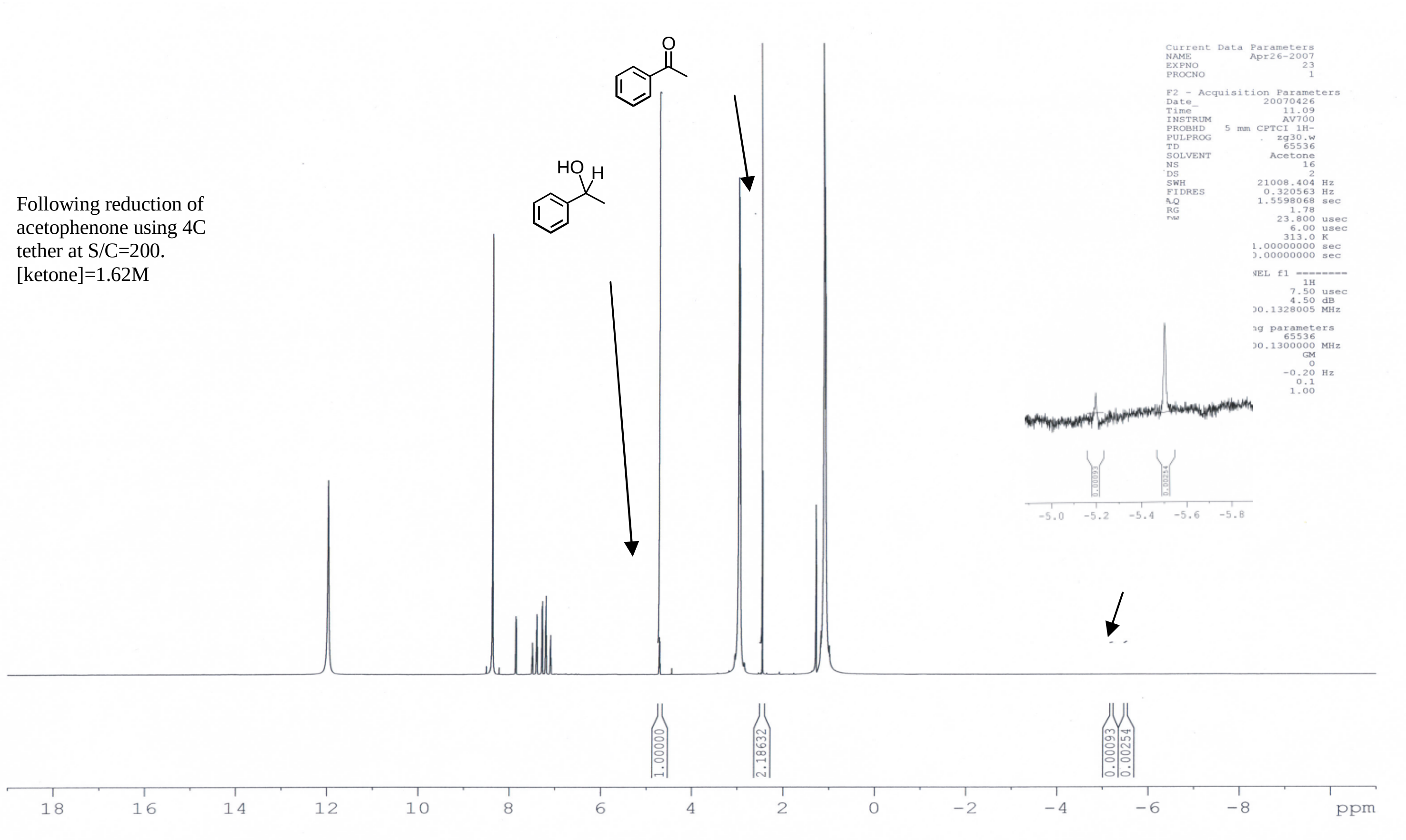


Illustration of a sample spectrum showing peaks which are integrated:



Following reduction of acetophenone using 4C tether at S/C=200. [ketone]=1.62M

```
Current Data Parameters
NAME          Apr26-2007
EXPNO                 23
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070426
Time               11.09
INSTRUM            AV700
PROBHD   5 mm CPTCI 1H-
PULPROG        .  zg30.w
TD                 65536
SOLVENT          Acetone
NS                    16
DS                     2
SWH            21008.404 Hz
FIDRES          0.320563 Hz
AQ             1.5598068 sec
RG                  1.78
                  23.800 usec
                    6.00 usec
                   313.0 K
              1.00000000 sec
              ).00000000 sec

             NEL f1 ========
                      1H
                    7.50 usec
                    4.50 dB
             )0.1328005 MHz

             ng parameters
                   65536
             )0.1300000 MHz
                      GM
                       0
                   -0.20 Hz
                     0.1
                    1.00
```