SUPLEMENTARY MATERIAL

for

"On-Water" Rhodium-Catalysed Hydroformylation for the Production of Linear Alcohols.

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Experimental details

General:
Gas chromatography (GC) analyses were performed on a Shimadzu GC-17A gas chromatograph equipped with a flame ionization detector (FID) on an Ultra-2 column (HP?) (25 m, 200 μm, film thickness: 0.33 μm).

Method:
80ºC to 280ºC with a slope of 10ºC min^{-1}, then holding the temperature at 280ºC for 2 min.

1-octene (Aldrich) was distilled before use. Ethanol and isopropanol were dried on molecular sieves and degassed before use. Rhodium sources were purchased from commercial sources, stored under argon and used as received.

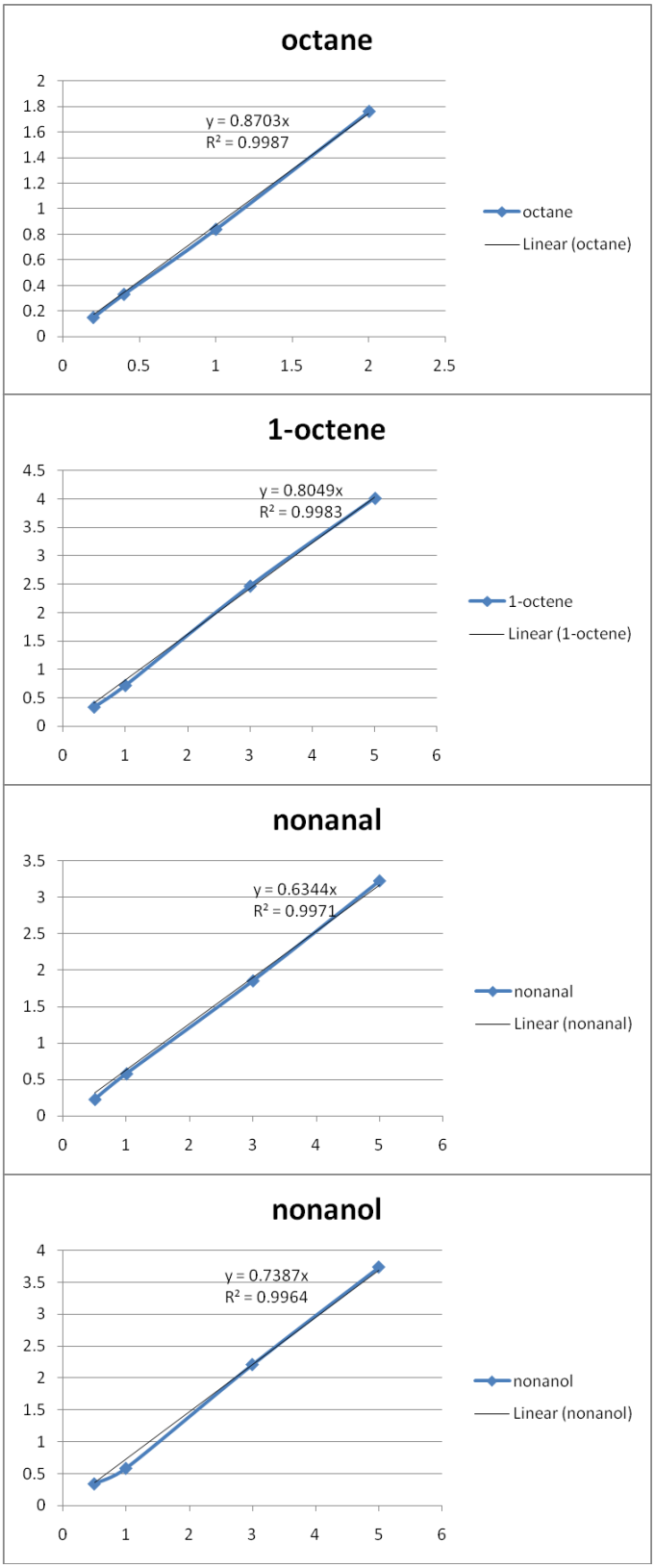
General procedure for nonanal hydrogenation:
Reactions were performed in home-made 10 mL autoclaves equipped with a magnetic stirrer bar. The autoclave was charged with $[Rh(CO)_2(acac)]$ (10 μmol; cod = 1,5-cyclooctadiene), alkene (2 mmol, S/Rh=200) and ligand (30 μmol, L/Rh= 3 for Xantphos; 40 μmol, L/Rh = 4 for PBu_3) and the desired solvent under argon atmosphere. The autoclave was purged three times with H_2 (P=10 bar) to remove the remaining argon from the autoclave. Subsequently, the autoclave was pressurised with CO and H_2 to the desired pressure and heated to reaction temperature using an oil bath. After a certain reaction time, the autoclave was cooled to room temperature. One drop of the reaction mixture was extracted with ether, the organic phase poured into a GC vial, diluted with dichloromethane and analysed by GC.

General procedure for 1-octene hydroformylation-hydrogenation:

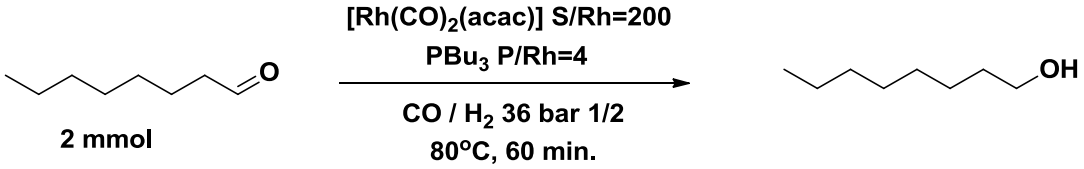
The reaction profiles were obtained using a home-made magnetically stirred 75 mL autoclave equipped with a high pressure sampling system. The solids were introduced first into the autoclave, previously purged with argon, after which the liquids were added (solvent, 1-octene, P^nBu_3). The autoclave was then purged three times with H_2 (P=10 bar) to remove the remaining argon. Subsequently, the autoclave was pressurised with CO and H_2 to the desired pressure and heated to reaction temperature. Samples were taken out regularly and analysed by GC.

When using Xantphos as ligand, the solvent (water-isopropanol mixtures) did not need to be degassed, the reaction giving similar results with non-degassed solvents.

Calibration curves. Internal standard is n-dodecane



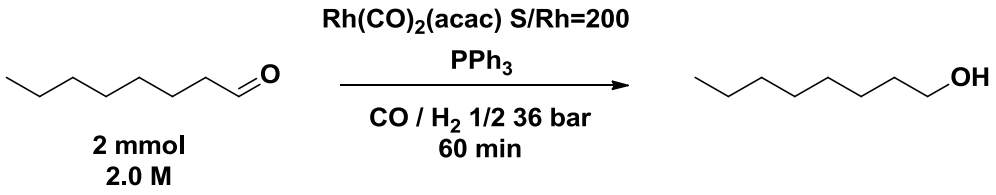
Nonanal reduction using PBu_3 as ligand



entry	solvent	conversion	alcohol selectivity (%)
1	MeOH	**61.7**	**5.7**[a]
2	H_2O/MeOH **1/1**	**7.3**	**>98**
3	H_2O/MeOH **3/1**	**62.2**	**>98**
4	H_2O/MeOH **9/1**	**42.0**	**>98**

[a] 36.1% of 1,1'-dimethoxynonane was formed.

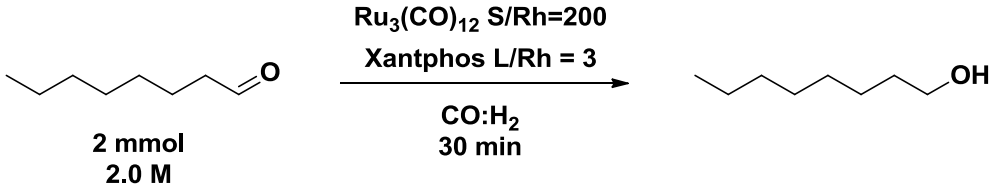
Nonanal reduction using PPh_3 as ligand



entry	solvent	P/Rh ratio	T	conversion	alcohol selectivity (%)[b]	catalyst decomposition[a]
1	H_2O/MeOH 3/1	5	**110**	**13.2**	**68.1**	No
2	H_2O/MeOH 3/1	5	**130**	**13.8**	**61.7**	Yes
3	H_2O/MeOH 3/1	5	**150**	**75.0**	**7.5**	Yes
4	**MeOH**	5	110	**11.0**	**46.2**	No
5	**H_2O/MeOH 1/1**	5	110	**14.3**	**44.7**	No
6	**H_2O/MeOH 9/1**	5	110	**27.4**	**18.0**	No
7	H_2O/**EtOH** 3/1	5	110	**6.6**	**61.7**	Yes
8	H_2O/**iPrOH** 3/1	5	110	**6.1**	**48.1**	Yes
9	H_2O/**toluene** 3/1	5	110	**7.2**	**31.4**	Yes
10	H_2O/MeOH 3/1	5	**90**	**13.6**	**57.3**	No
11	H_2O/MeOH 3/1	**10**	90	**8.2**	**35.7**	No
12	H_2O/MeOH 3/1	**10**	110	**20.0**	**54.9**	Yes
13	H_2O/MeOH 3/1	**20**	110	**15.4**	**55.4**	Yes
14	H_2O/MeOH 3/1	**30**	110	**13.5**	**71.8**	No
15	H_2O/MeOH 3/1	**50**	110	**11.6**	**64.9**	No

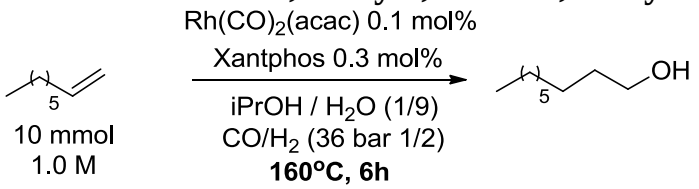
[a] acetals are present as traces and mainly aldol condensation products are formed. [b] black colloidal solution obtained at the end of the reaction.

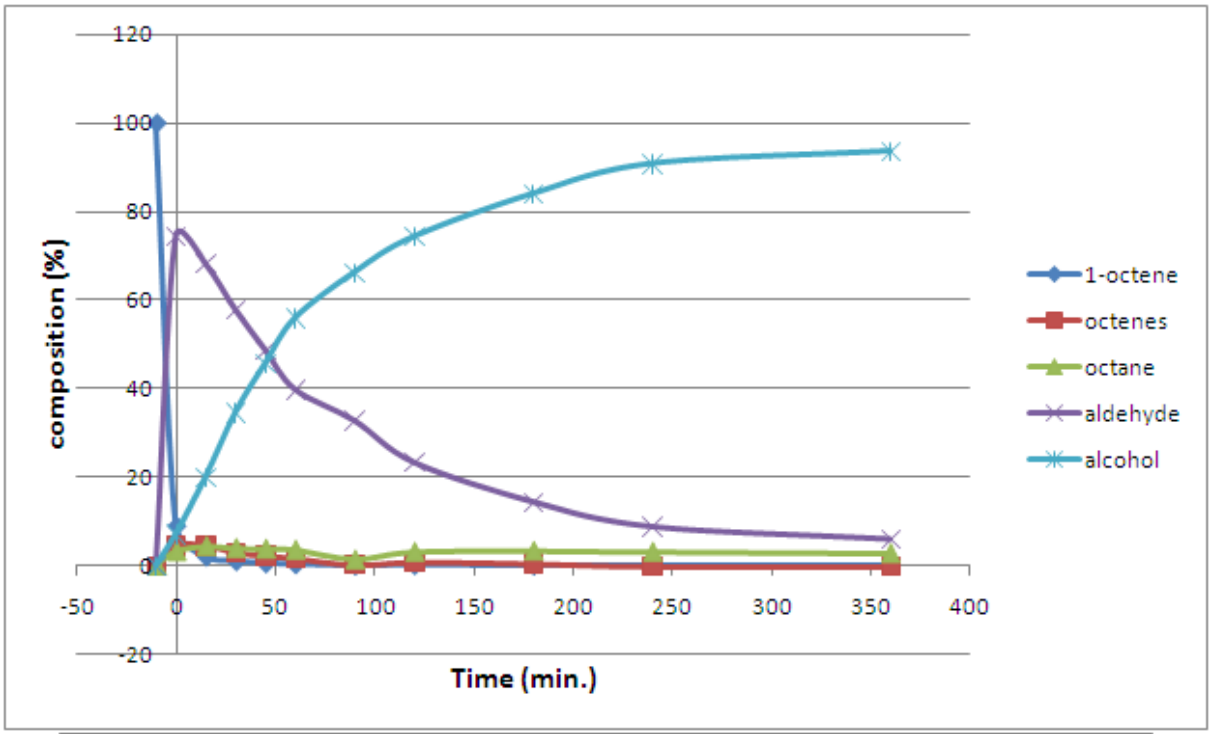
Nonanal reduction using $Ru_3(CO)_{12}$ / Xantphos

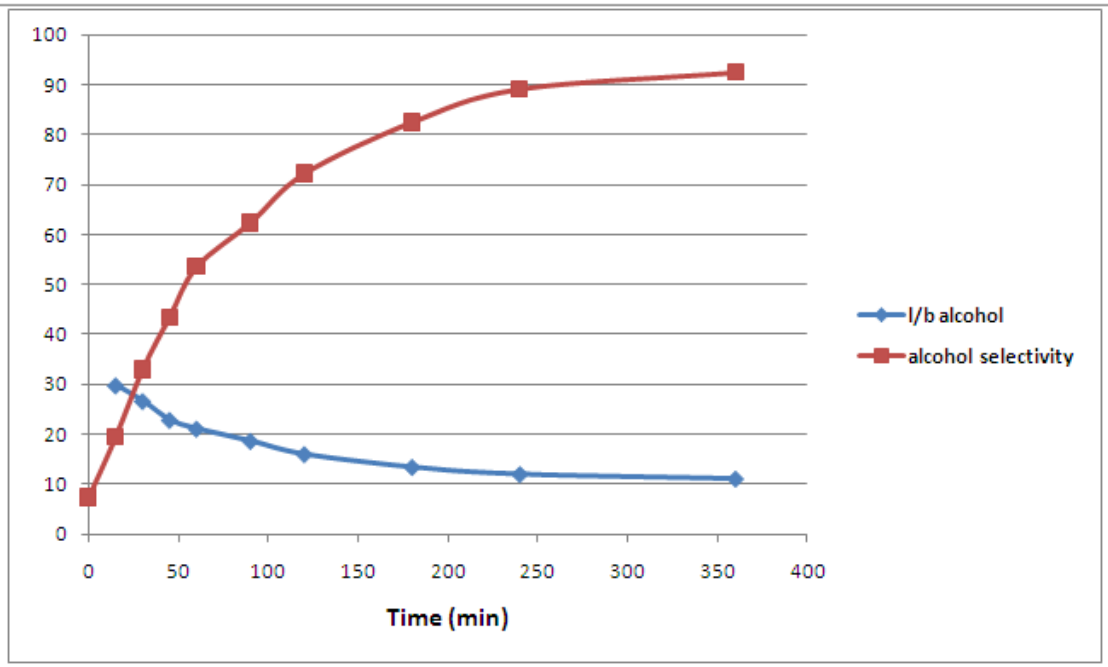


entry	T (^oC)	P (CO/H_2)	solvent	**Alcohol yield**	**Acetal yield**
1	110	**20 (0/20)**	iPrOH	**78**	**<0.2**
2	110	**36 (12/24)**	iPrOH	**0.4**	**<0.2**
3	**140**	36 (12/24)	iPrOH	**0.5**	**0.3**
4	**160**	36 (12/24)	**iPrOH**	**1.8**	**3.5**
5	160	36 (12/24)	**iPrOH/H_2O (9/1)**	**5.4**	**2**
6	160	36 (12/24)	**iPrOH/H_2O (1/1)**	**6.9**	**0.9**
7	160	36 (12/24)	**iPrOH/H_2O (1/9)**	**17.4**	**0.4**
8	160	36 (12/24)	**MeOH/H_2O (1/9)**	**21.8**	**0**
9	160	36 (12/24)	**toluene/H_2O (1/9)**	**23**	/
10	160	36 (12/24)	**EtOH/H_2O (1/9)**	**46.4**	**0**
11	160	36 (12/24)	**tAmOH/H_2O (1/9)**	**29.2**	**0**
12	160	36 (12/24)	**THF/H_2O (1/9)**	**28.4**	/
13	160	36 (12/24)	**H_2O**	**29.8**	/

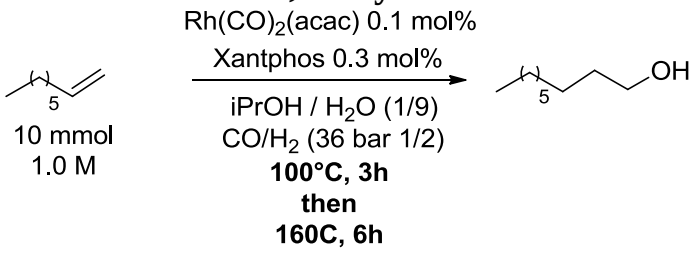
Reaction profile of reaction Table 2, entry 1, Table 3, entry 1.

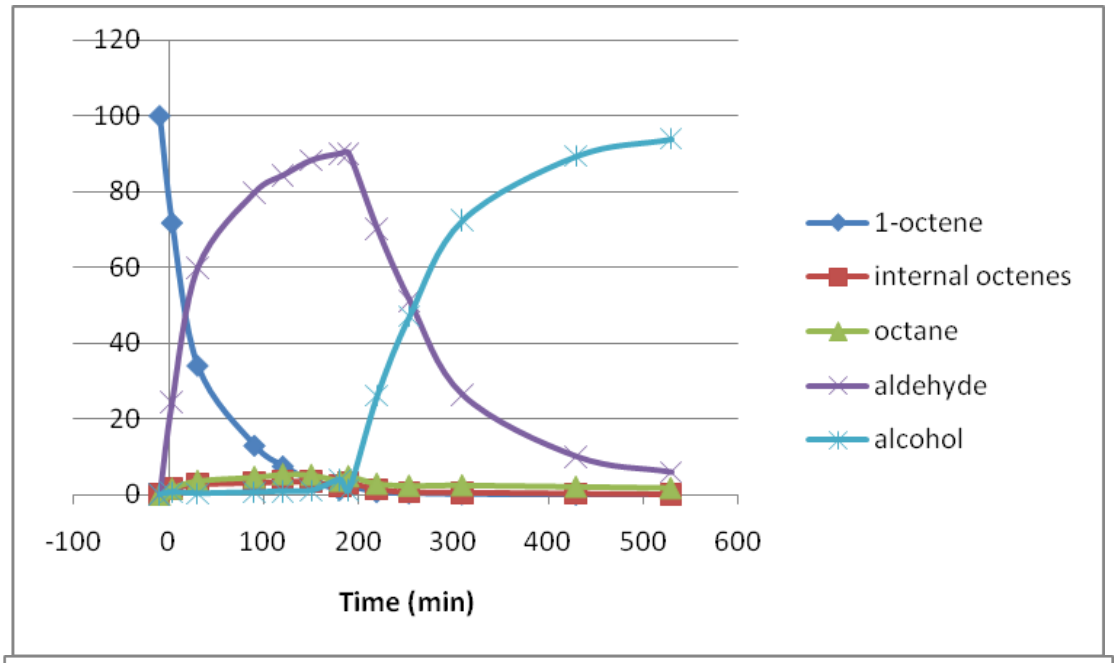


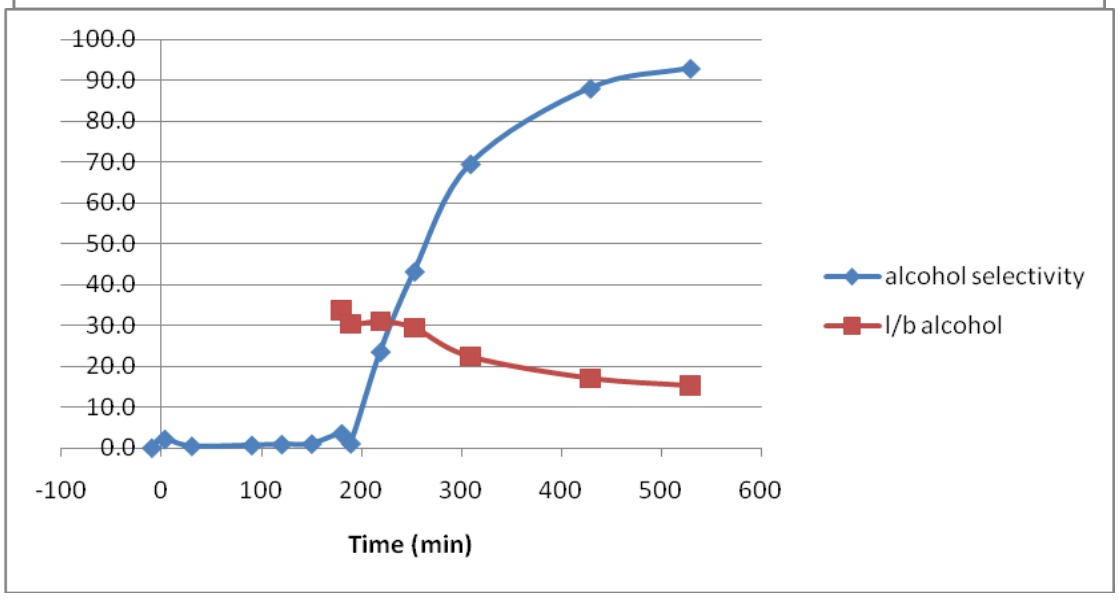




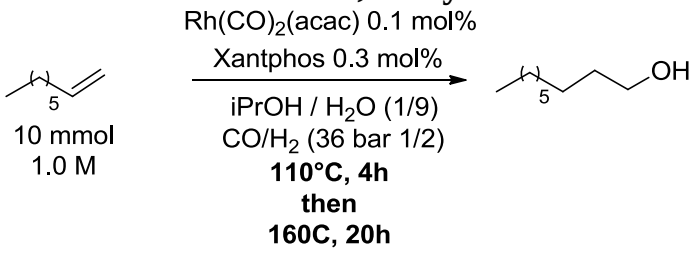
Reaction profile of reaction Table 2, entry 2.

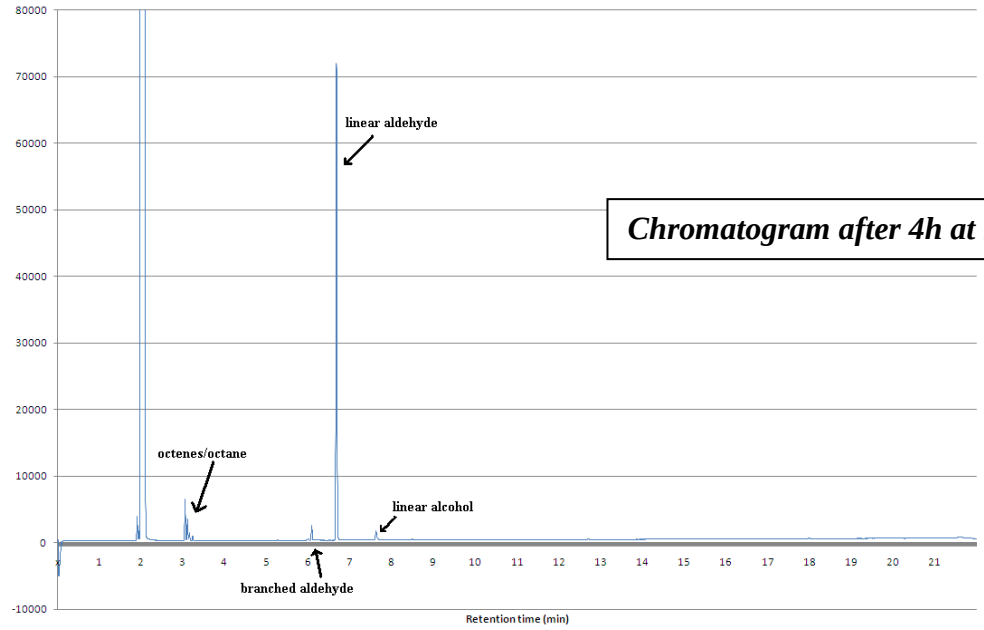




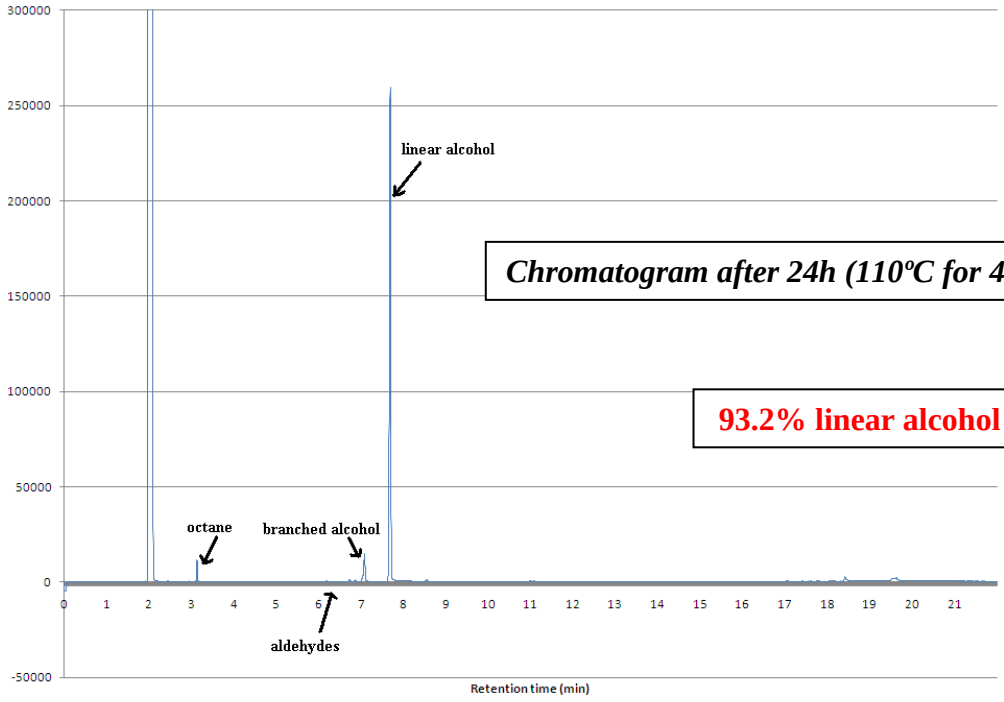


Gas chromatograms of reaction Table 2, entry 3.





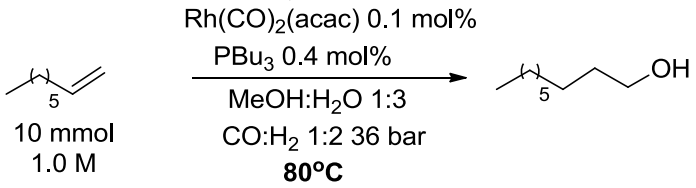
Chromatogram after 4h at 110ºC

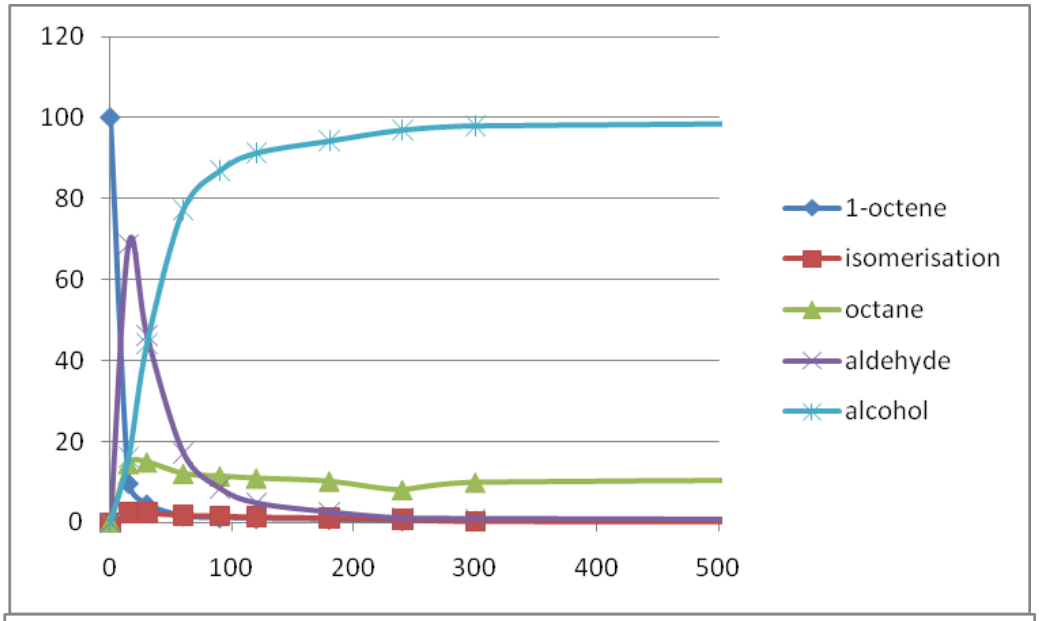


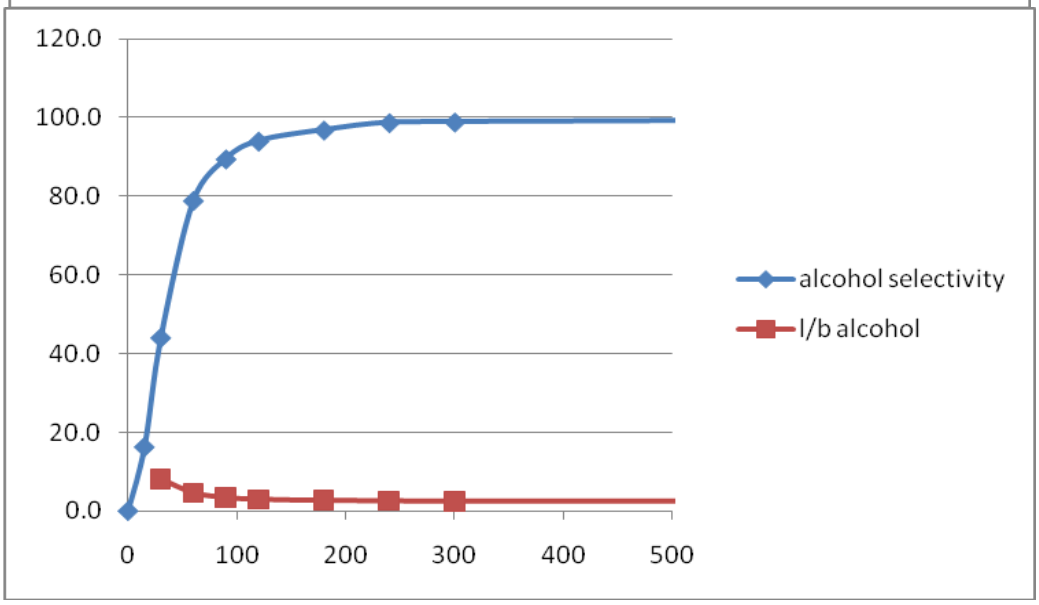
Chromatogram after 24h (110ºC for 4h, then 20h at 160ºC)

93.2% linear alcohol

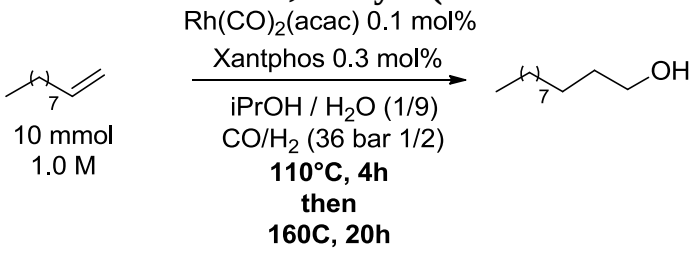
Reaction profile of reaction Table 3, entries 3 and 4.

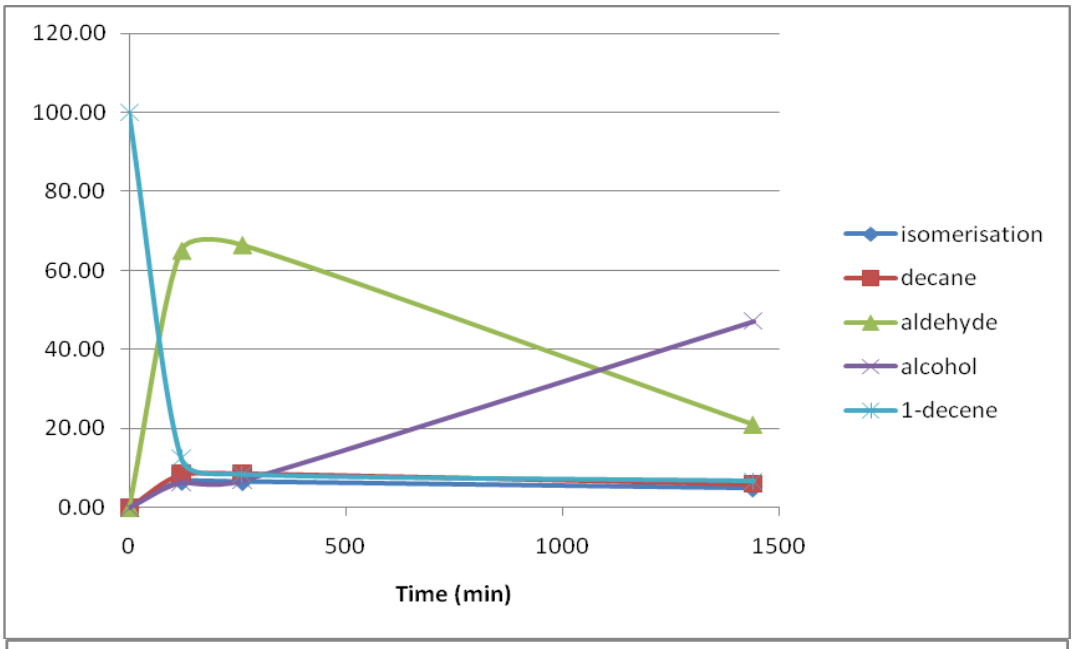


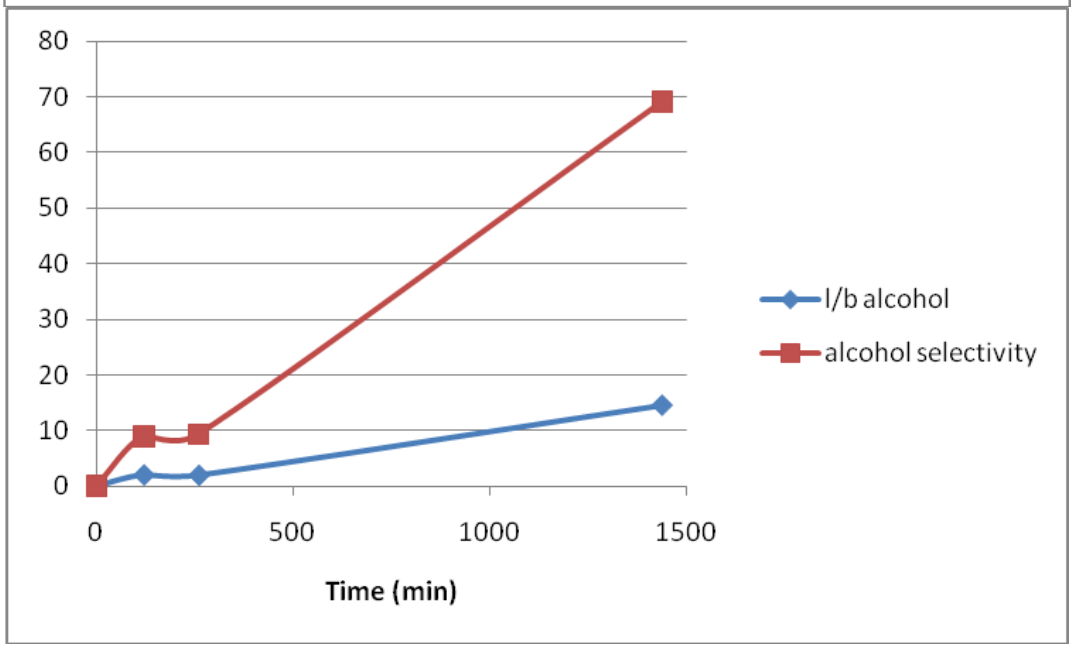




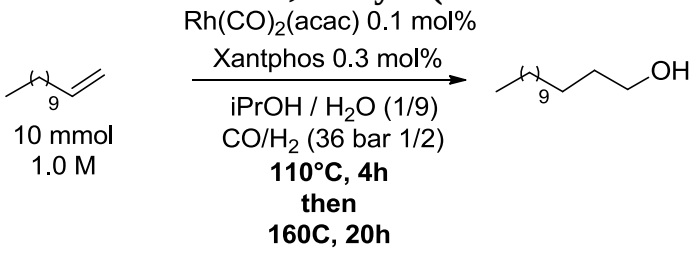
Reaction profile of reaction Table 3, entry 5 (1-decene used as substrate).

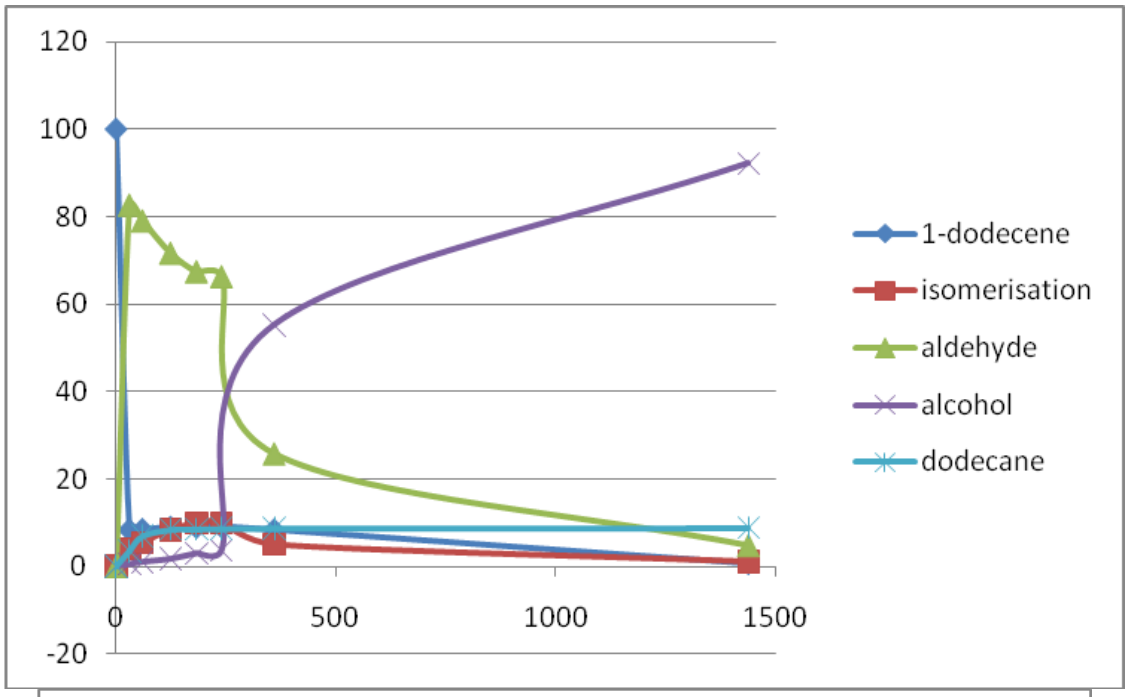


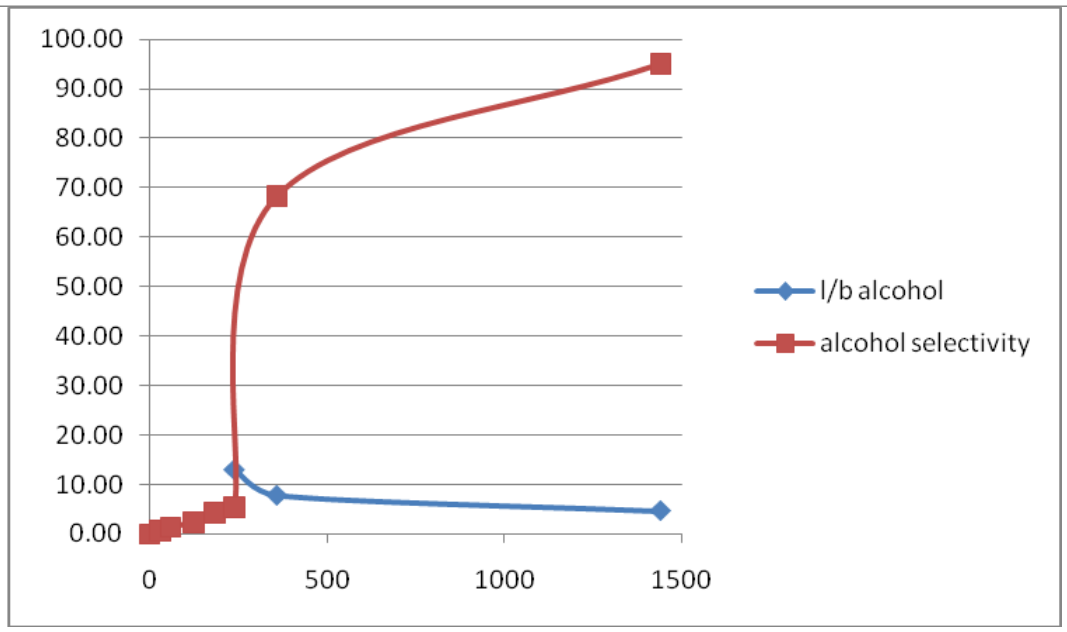




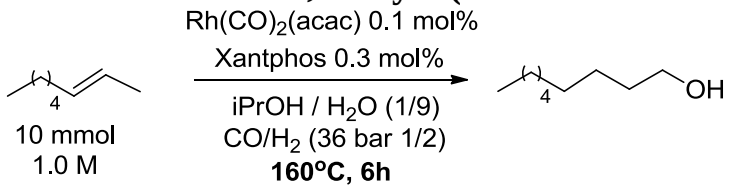
Reaction profile of reaction Table 3, entry 6 (1-dodecene used as substrate).

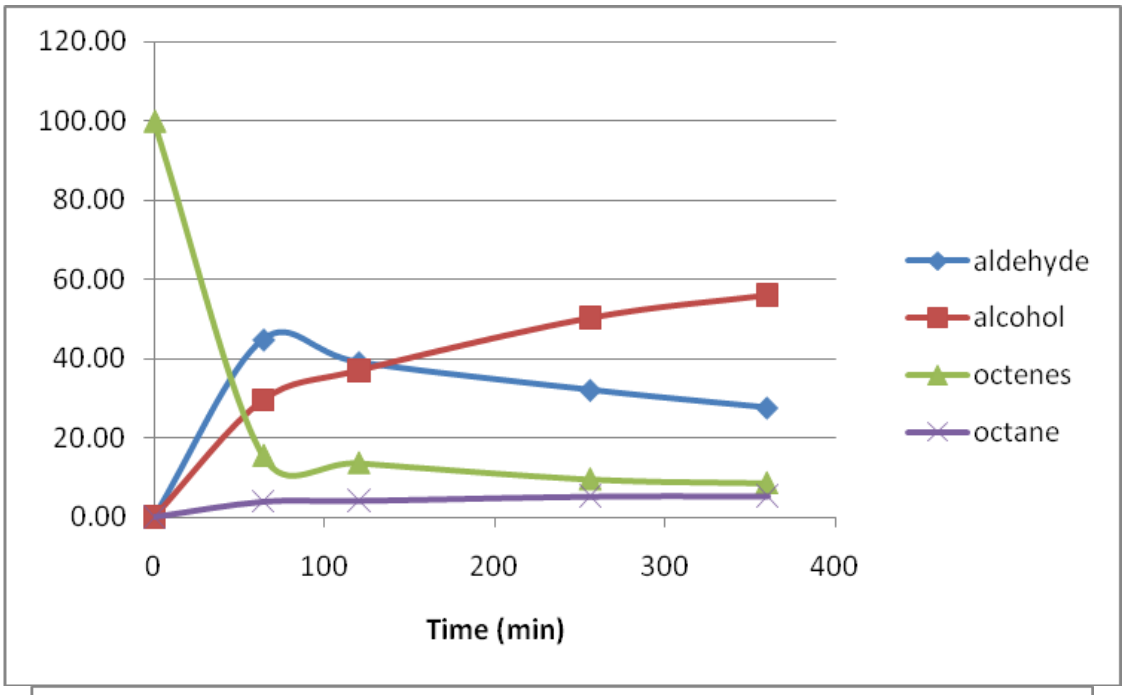


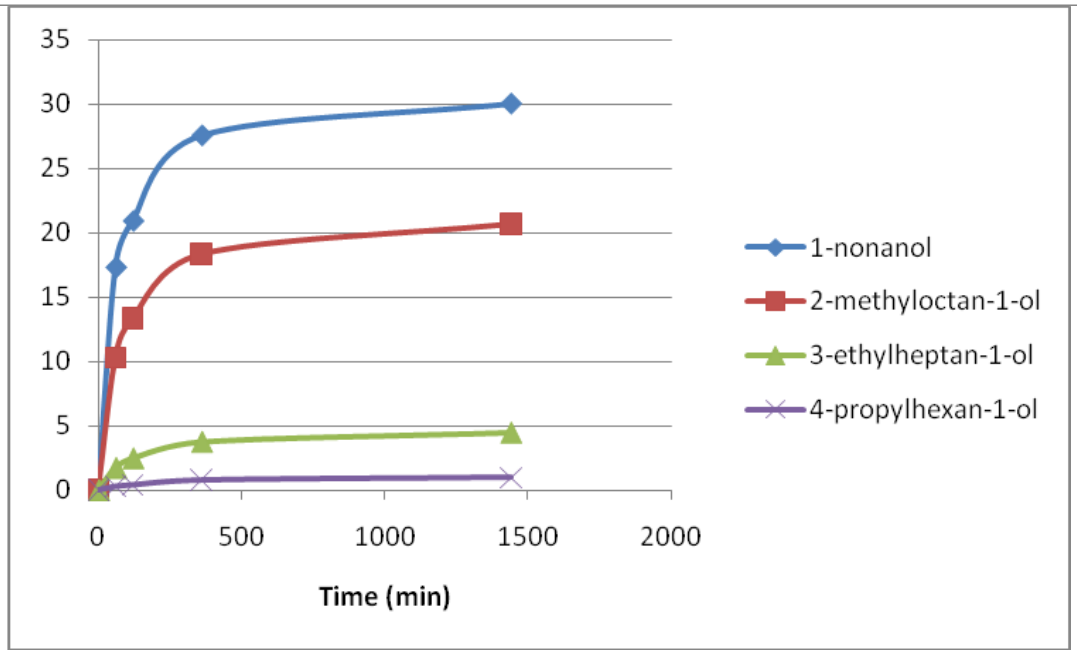




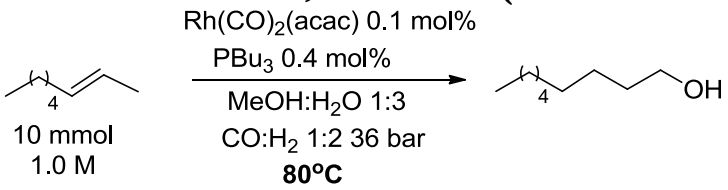
Reaction profile of reaction Table 3, entry 7 (2-octene used as substrate).

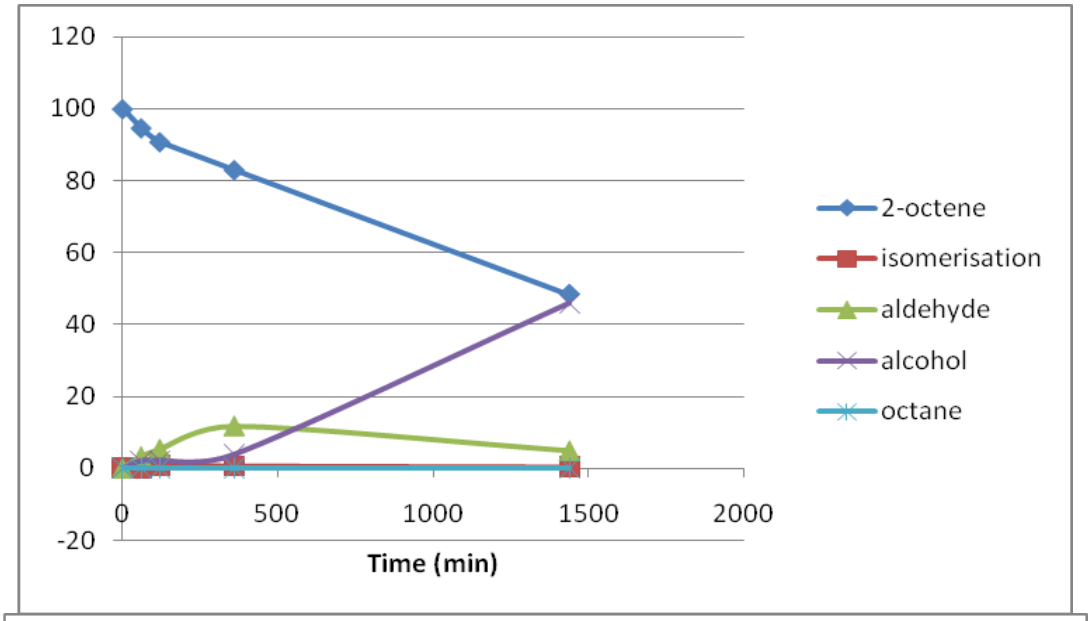


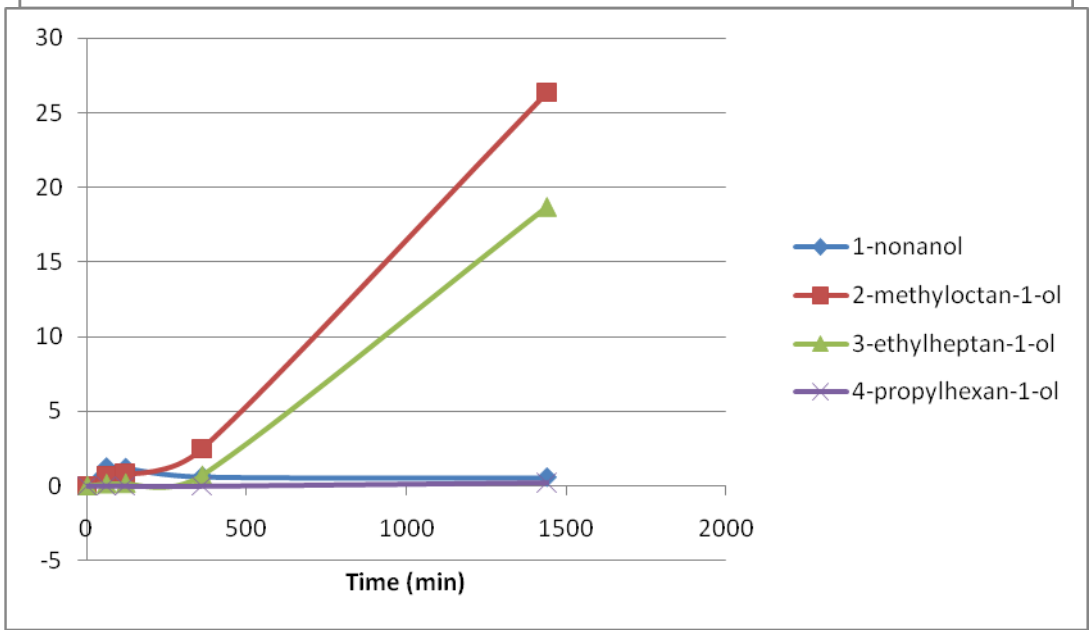




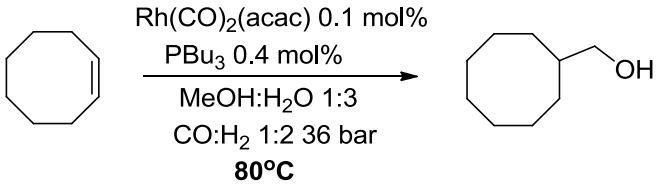
Reaction profile of reaction Table 3, entries 8-9 (2-octene used as substrate).

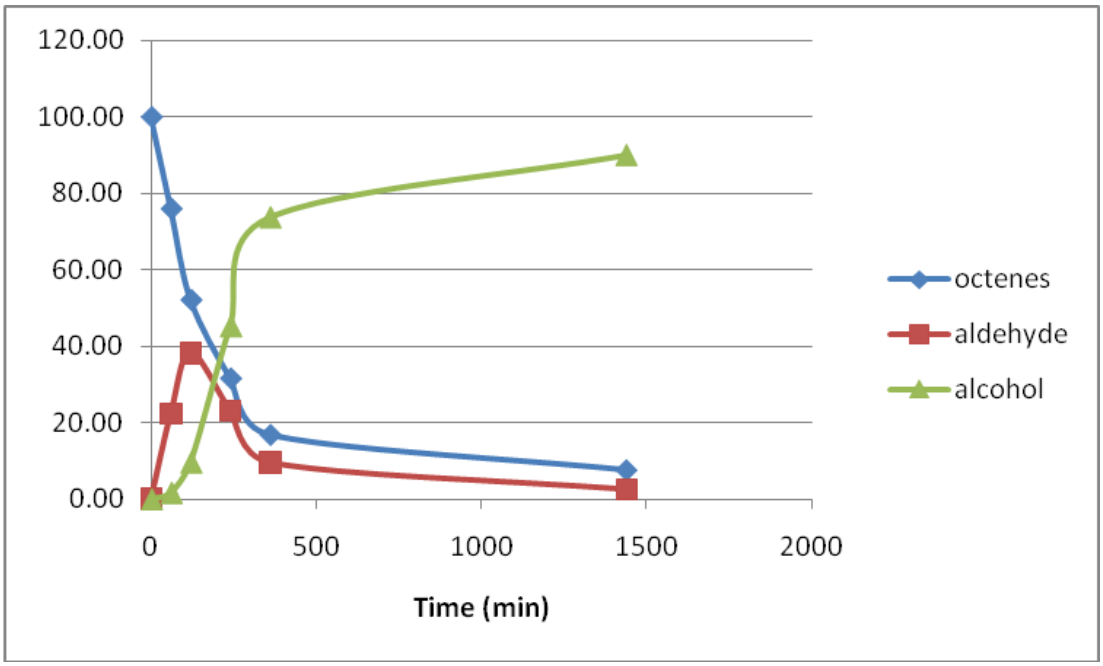






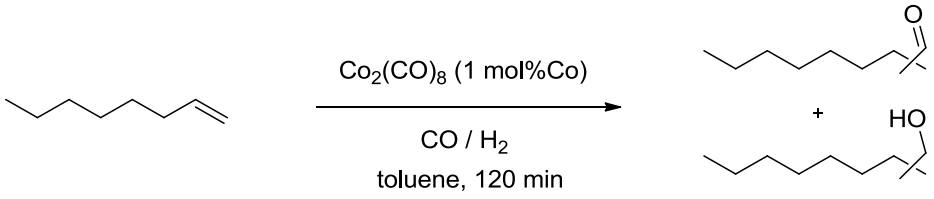
Reaction profile of reaction Table 3, entries 10-11 (*cis*-cyclooctene used as substrate).





Parameter screening for cobalt-catalyzed hydroformylation of 1-octene

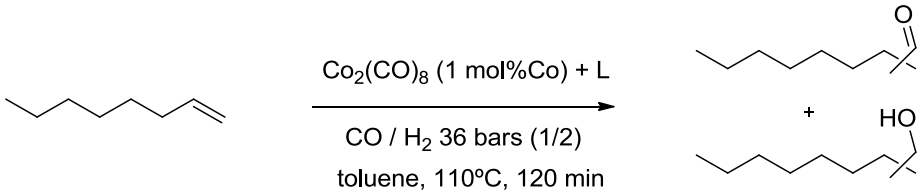
Table S7. Pressure and temperature optimization using $Co_2(CO)_8$ as catalyst.



entry	T°C	P(H_2) (bar)	P(CO) (bar)	Conv.	octane	aldehyde/ alcohol	l/b ratio*
1	170	50	25	100	2.9	0.9	1.0
2	170	24	12	100	6.8	0.1	1.0
3	150	24	12	100	6.3	3.0	1.0
4	130	24	12	93.8	9.9	18.6	1.4
5	110	24	12	89.5	9.5	65.7	1.8
6	110	18	18	87.4	13.4	>100	1.7

* ratio linear branched for combined aldehydes and alcohols products

Table S8. Various ligands at 110°C.



entry	L (L/Co ratio)	Conv.	octane	aldehyde/ alcohol	l/b ratio*
1	None	89.5	9.5	65.7	1.8
2	2,6-Ph_2-pyridine (4)	91.1	8.7	>100	2.0
3	P^nBu_3 (1)	0	0	n.d.	n.d.
4	IPr (1)	0	0	n.d.	n.d.
5	NBD (10)	91.9	9.5	82.3	1.8
6	PBr_3 (1)	4.0	0	>100	n.d.

* ratio linear branched for combined aldehydes and alcohols products

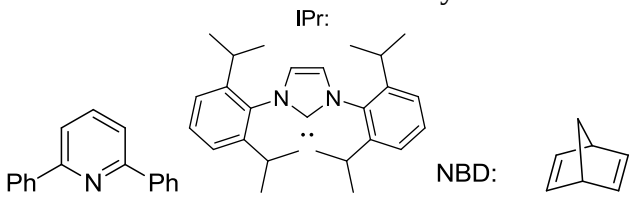
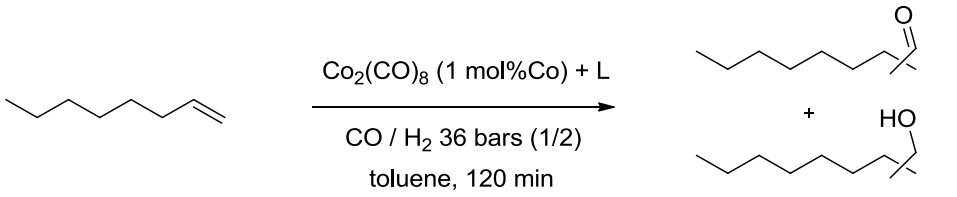


Table S9. Various ligands at 110ºC and 150ºC.



Entry	TºC	L (L/Co ratio)	conv.	octane	aldehyde/ alcohol	l/b ratio*
1	110	none	89.5	9.5	65.7	1.8
2	110	P^nBu_3 (1)	0	0	n.d.	n.d.
3	150	none	100	6.3	3.0	1.0
4	150	P^nBu_3 (2)	37	14	7.7	7.5
5	150	PPh_3 (2)	58.8	22	12.3	2.2
6	150	P(N-pyrrolyl)$_3$ (2)	16.1	4.5	>100	1.2
7	150	PPh_2(2-OMe-C_6H_4) (2)	75.5	19.8	12.9	1.7
8	150	P(O-2,4-^{t}Bu$_2$-C_6H_3)$_3$ (2)	99.3	7.7	6.0	1.4
9	150	PCy_3 (2)	42.5	20.4	6.8	5.9

* ratio linear branched for combined aldehydes and alcohols products