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Phosphine-free Pincer Cobalt Catalyst Precursors for Selective Hydrogenation of Olefins

Supporting Information

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1. General Information

Reagents and solvents were obtained from commercial sources and used as received unless noted otherwise. Dry solvents were obtained from a solvent purification system, or purchased water-free in a bottle with septum (isopropanol). Complexes were prepared using standard Schlenk techniques. Stock solutions for high-throughput screening were prepared and distributed using a Zinsser Lissy liquid handling robot equipped with 4 probes inside a glove box (see Figure **S1a**). High-throughput screening was carried out in a Premex 96-Multi Reactor that can accommodate 96 reactions vessels at the same temperature and hydrogen pressure (see Figure **S1b**). This reactor was developed by Premex in cooperation with DSM.[1]

Figure S1: Hardware available at InnoSyn for high throughput screening: a) Liquid handling robot (Zinsser Lissy) and b) Premex 96-Multi Reactor.[1]

GC analysis was carried out on an Agilent 7890B GC system with a HP-5 normal-phase silica column, using He as a carrier gas and dodecane as internal standard. NMR spectra were recorded on a Bruker AV400, Bruker AV300 or Bruker Fourier300 NMR spectrometer. ^{1}H and ^{13}C-NMR spectra were referenced w.r.t. the solvent signal. All chemical shifts are in ppm, coupling constants in Hz. HR-MS measurements were recorded on an Agilent 6210 Time-of-Flight LC/MS (ESI) instrument; peaks as listed correspond to the highest abundant peak and are of the expected isotope pattern.

X-ray diffraction data for **1** and **2** were collected on a Bruker Kappa APEX II Duo and a Bruker D8 VENTURE diffractometer, respectively. The structures were solved by direct methods (SHELXS-97[2] and SHELXT[3], resp.) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2014 and SHELXL-2018, resp[3]). XP (Bruker AXS) was used for molecular graphics. CCDC 1864013-1864014 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

2. Results and Discussion

2.1 High-throughput screening

An initial screening was carried out at 0.2 mmol scale, with 2 mol% catalyst and 4 mol% of additives. Complexes **1** and **2** were initially screened for activity in the hydrogenation of 1-octene, acetophenone and 1-octen-3-one in toluene and THF. Three bases (KO^tBu, NaOMe, and NaOH), and four reductants (Zn, $NaBEt_3H$, $NaBH_4$ and $AlEt_3$) were screened for activation. Additionally, two monodentate ligands (pyridine and PMe_3) were screened based on the assumption that these ligands expedite the dissociation of the dimeric complex **1**. The results of this screening are summarised in Table **S1** (1-octene and acetophenone, which were dissolved in the same stock solution) and Table **S2** (1-octen-3-ol). In several cases, the results were not interpretable due to broad or overlapping peaks in the GC trace, or other experimental artefacts (listed as 'n.a.').

Table S1. High throughput screening of **1** and **2** in the hydrogenation of 1-octene and acetophenone.

#[a]	Cat	Solvent	Additive 1	Additive 2	% octane[b]	% 1-phenylethanol
1	1	THF	KO^{t}Bu		n.a.	0%
2	1	THF	KO^{t}Bu	PMe_3	Isomerisation	0%
3	1	THF	NaOMe		n.a.	0%
4	1	THF	NaOMe	PMe_3	Isomerisation	0%
5	1	THF	NaOH		Isomerisation	0%
6	1	THF	NaOH	PMe_3	n.a.	0%
7	1	THF	KO^{t}Bu	$NaBEt_3H$	n.a.	0%
8	1	THF	KO^{t}Bu	Pyridine	n.a.	0%
9	1	THF	NaOMe	$NaBEt_3H$	n.a.	0%
10	1	THF	NaOMe	Pyridine	n.a.	0%
11	1	THF	NaOH	$NaBEt_3H$	n.a.	0%
12	1	THF	NaOH	Pyridine	n.a.	0%
13	1	toluene	KO^{t}Bu		0%	0%
14	1	toluene	KO^{t}Bu	PMe_3	0%	0%
15	1	toluene	NaOMe		0%	0%
16	1	toluene	NaOMe	PMe_3	Isomerisation	0%
17	1	toluene	NaOH		0%	0%
18	1	toluene	NaOH	PMe_3	Isomerisation	0%
19	1	toluene	KO^{t}Bu	$NaBEt_3H$	0%	0%
20	1	toluene	KO^{t}Bu	Pyridine	0%	0%
21	1	toluene	NaOMe	$NaBEt_3H$	0%	0%
22	1	toluene	NaOMe	Pyridine	0%	0%
23	1	toluene	NaOH	$NaBEt_3H$	0%	0%
24	1	toluene	NaOH	Pyridine	0%	0%
25	1	THF		$AlEt_3$	95%	0%
26	1	THF	KO^{t}Bu	$AlEt_3$	90%	0%
27	1	Toluene		$AlEt_3$	0%	0%
28	1	Toluene	KO^{t}Bu	$AlEt_3$	0%	0%
29	2	THF	KO^{t}Bu		n.a.	0%
30	2	THF	KO^{t}Bu	$NaBEt_3H$	Isomerisation	0%
31	2	toluene	KO^{t}Bu		0%	0%
32	2	toluene	KO^{t}Bu	$NaBEt_3H$	Isomerisation	0%
33	2	THF	KO^{t}Bu		n.a.	0%
34	2	THF	NaOMe	$NaBEt_3H$	Isomerisation	0%
35	2	toluene	NaOMe		n.a.	0%
36	2	toluene	NaOMe	$NaBEt_3H$	n.a.	0%
37	2	THF			n.a.	0%
38	2	THF	KO^{t}Bu		n.a.	0%
39	2	Toluene			0%	0%
40	2	Toluene	KO^{t}Bu		0%	0%
41	2	THF		$NaBEt_3H$	50% + isomerisation	0%
42	2	THF	KO^{t}Bu	$NaBEt_3H$	30% + isomerisation	0%
43	2	Toluene		$NaBEt_3H$	80% + isomerisation	0%
44	2	Toluene	KO^{t}Bu	$NaBEt_3H$	80% + isomerisation	0%
45	2	THF		$NaBH_4$	80% + isomerisation	0%
46	2	THF	KO^{t}Bu	$NaBH_4$	40% + isomerisation	0%
47	2	Toluene		$NaBH_4$	0%	0%
48	2	Toluene	KO^{t}Bu	$NaBH_4$	0%	0%
49	2	THF		Zn^0	80%	0%
50	2	THF	KO^{t}Bu	Zn^0	100%	0%
51	2	Toluene		Zn^0	0%	0%
52	2	Toluene	KO^{t}Bu	Zn^0	0%	0%

[a]Reaction conditions: 1-octene (0.2 mmol), acetophenone (0.2 mmol), solvent (2.5 mL), catalyst (1 mol% **1** or 2 mol% **2**), additives (5 mol%), 50 bar H_2, 100 °C, 16 h reaction time. [b]Area percentages; n.a. indicates the results were not interpretable.

Table S2. High throughput screening of **1** and **2** in the hydrogenation of 1-octen-3-ol.

#	Cat	Solvent	Additive 1	Additive 2	% 3-octanol[b]
1	1	THF	KO^{t}Bu		0%
2	1	THF	KO^{t}Bu	PMe_3	n.a.
3	1	THF	NaOMe		n.a.
4	1	THF	NaOMe	PMe_3	n.a.
5	1	THF	NaOH		40%
6	1	THF	NaOH	PMe_3	60%
7	1	THF	KO^{t}Bu	$NaBEt_3H$	20%
8	1	THF	KO^{t}Bu	Pyridine	0%
9	1	THF	NaOMe	$NaBEt_3H$	10%
10	1	THF	NaOMe	Pyridine	0%
11	1	THF	NaOH	$NaBEt_3H$	90%
12	1	THF	NaOH	Pyridine	5%
13	1	toluene	KO^{t}Bu		0%
14	1	toluene	KO^{t}Bu	PMe_3	40%
15	1	toluene	NaOMe		0%
16	1	toluene	NaOMe	PMe_3	n.a.
17	1	toluene	NaOH		50%
18	1	toluene	NaOH	PMe_3	full conversion
19	1	toluene	KO^{t}Bu	$NaBEt_3H$	50%
20	1	toluene	KO^{t}Bu	Pyridine	0%
21	1	toluene	NaOMe	$NaBEt_3H$	20%
22	1	toluene	NaOMe	Pyridine	0%
23	1	toluene	NaOH	$NaBEt_3H$	95%
24	1	toluene	NaOH	Pyridine	95%
25	1	THF		$AlEt_3$	full conversion
26	1	THF	KO^{t}Bu	$AlEt_3$	full conversion
27	1	Toluene		$AlEt_3$	full conversion
28	1	Toluene	KO^{t}Bu	$AlEt_3$	full conversion
29	2	THF	KO^{t}Bu		0%
30	2	THF	KO^{t}Bu	$NaBEt_3H$	60%
31	2	toluene	KO^{t}Bu		0%
32	2	toluene	KO^{t}Bu	$NaBEt_3H$	full conversion
33	2	THF	NaOMe		0%
34	2	THF	NaOMe	NaBet3H	60%
35	2	toluene	NaOMe		0%
36	2	toluene	NaOMe	NaBet3H	50%
37	2	THF			broad
38	2	THF	KOtBu		broad
39	2	Toluene			broad
40	2	Toluene	KOtBu		broad
41	2	THF		$NaBEt_3H$	60%
42	2	THF	KO^{t}Bu	$NaBEt_3H$	50%
43	2	Toluene		$NaBEt_3H$	60%
44	2	Toluene	KO^{t}Bu	$NaBEt_3H$	95%
45	2	THF		$NaBH_4$	30%
46	2	THF	KO^{t}Bu	$NaBH_4$	100%
47	2	Toluene		$NaBH_4$	n.a.
48	2	Toluene	KO^{t}Bu	$NaBH_4$	n.a.
49	2	THF		Zn^0	10%
50	2	THF	KO^{t}Bu	Zn^0	n.a.
51	2	Toluene		Zn^0	n.a.
52	2	Toluene	KO^{t}Bu	Zn^0	n.a.

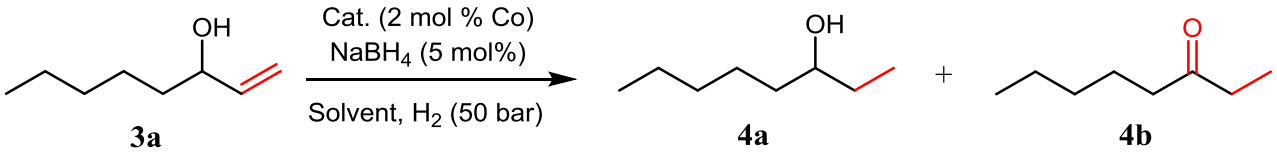
[a]Reaction conditions: 1-octen-3-ol (0.2 mmol), solvent (2.5 mL), catalyst (1 mol% **1** or 2 mol% **2**), additives (5 mol%), 50 bar H_2, 100 °C, 16 h reaction time. [b]Area percentages; 'n.a.' indicates the results were not interpretable, whereas 'full conversion' indicates no starting material was observed after the reaction, but the products could not be determined.

It was concluded from this preliminary screening that **2**, in combination with base and borohydride reducing agent was active in the hydrogenation of 1-octene as well as 1-octen-3-ol, although isomerisation was observed as side reaction. Reactions where **1** was employed as catalyst typically gave no appreciable quantities of octane, with the notable exception where Et_3Al was used as a reductant in THF. In no single case was 1-phenylethanol observed from the reduction of acetophenone.

2.2 Solvent optimisation

Several representative reaction solvents were screened for conversion and selectivity in the hydrogenation/isomerisation of 1-octen-3-ol (Table S3). The reaction in isopropanol led to full conversion with >99% selectivity towards the hydrogenated product **4a**.

Table S3. Solvent screening for the hydrogenation of 1-octen-3-ol by catalyst **2**.



#[a)]	Cat.	Solvent	Yield **4a**:**4b** (%)[b)]
1	**2**	THF	95:1
2	**2**	Toluene	1:2
3	**2**	MeOH	58:30
4	**2**	iPrOH	>99:0
5	**2**	HFIP[c)]	0:0

[a)] Reaction conditions: 0.33 mmol 1-octen-3-ol, 1.0 mL solvent, 2 mol% **2**, 5 mol% of $NaBH_4$, 50 bar H_2, 100 °C, 16 h reaction time. [b)] Determined by GC using dodecane as internal standard. [c)] HFIP = hexafluoroisopropanol.

2.3 Kinetics and Poisoning Experiments

After a typical experiment, a black residue was observed in the reaction vials (example in Figure **S2**), which prompted us to investigate the formation of nanoparticles.

Figure S2: Black residue after the reaction.

The reaction was followed by monitoring the hydrogen consumption over time, at 5 mmol scale (15 mL solvent), with 1 mol % of catalyst loading (Figure **S3**), which is often indicative of nanoparticle-catalysed reactions.

In order to assess whether the reaction was catalysed by nanoparticles, two types of poisoning experiments were performed. Firstly, the reactions were repeated in the presence of mercury on the optimisation scale (section 3.3). This led to lower conversions, but did not quench the reactivity completely (Table **S4**).

Table S4. Mercury poisoning experiments

#[a]	Cat	Hg loading (%)	Conversion (%)
1	2	10	57
2	2	30	44

[a)]Reaction conditions: 0.33 mmol 1-octen-3-ol, 1.0 mL ^{i}PrOH, 2 mol% **2**, 5 mol% of $NaBH_4$, 50 bar H_2, 100 °C, 16 h reaction time.

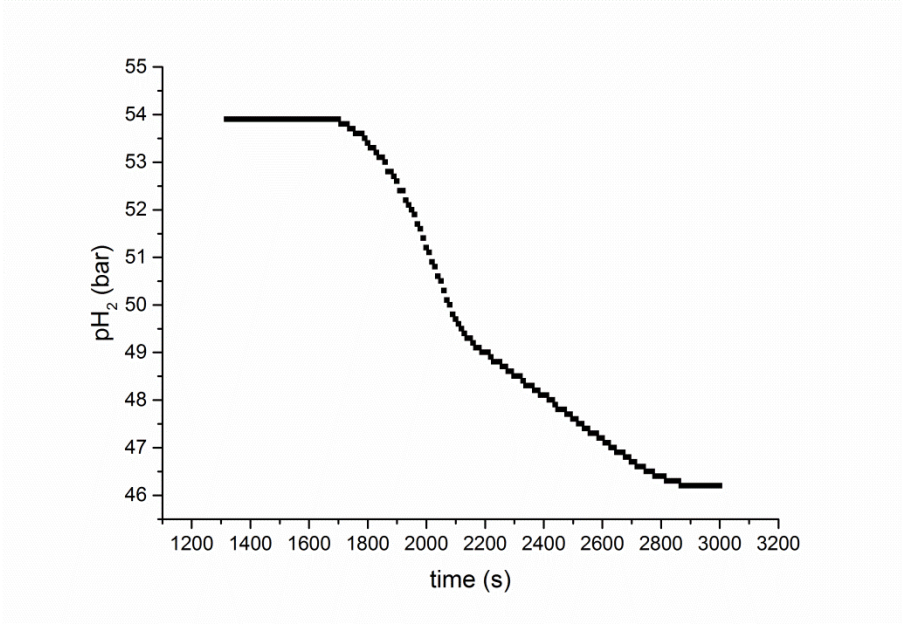


Figure S3: H_2 uptake for the reduction of 1-octen-3-ol with 1 mol % of **2**.

Based on the reportedly low solubility of cobalt in mercury, it was decided that another poisoning experiment using trimethylphosphine was in order.[4] The reaction was repeated on a 10 mmol scale (30 mL of iPrOH, 1 mol% **2**, 5 mol% $NaBH_4$), and after the induction period was over and the reaction had started, trimethylphosphine (300 µL,0.05 M in toluene, 15% w.r.t. cobalt) was injected under pressure. The hydrogen uptake curves are depicted in Figure **S6** and clearly show after injection of trimethylphosphine, the reaction stopped at 65% conversion (determined by GC with dodecane as internal standard).

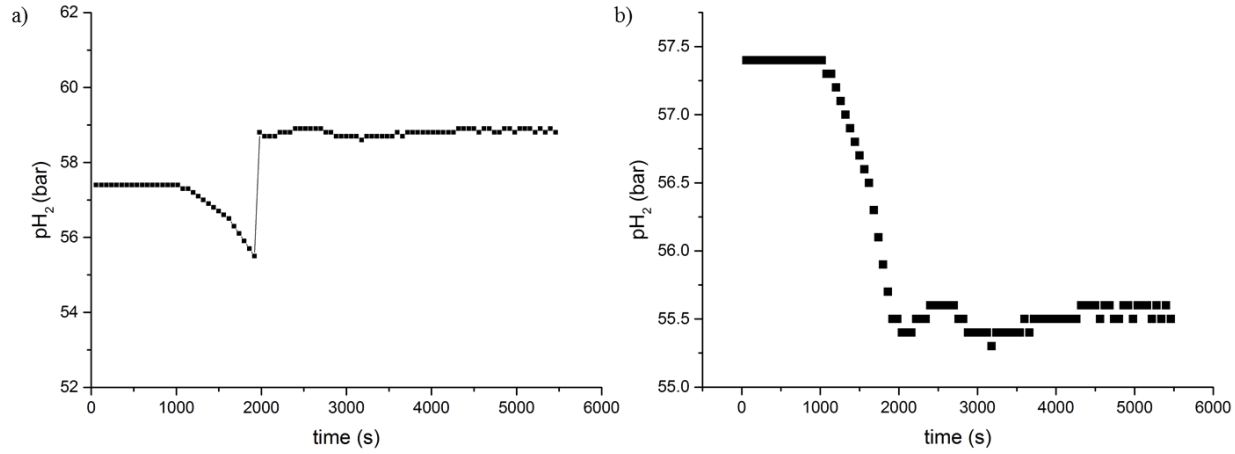


Figure S6: H_2 uptake curve with injection of trimethylphosphine solution after an induction period. Graph a) shows the pressure values as measured; b) is corrected for the pressure spike that resulted from the addition of the solution under additional pressure.

3. Experimental procedures

3.1 Complex synthesis

L1 (NN^HS) and **L2 ($NN^{Me}S$)** were synthesised according to previously reported procedures.[5]

$Co_2Cl_4(NN^HS)_2$ (1): In a schlenk flask, $CoCl_2$ (300 mg, 2.3 mmol) was dissolved in ethanol (40 mL). Upon addition of **L1** (420 µL, 450 mg, 1 eq.) the colour of the reaction mixture changed from blue to indigo, and the mixture was stirred overnight. The solvent was removed *in vacuo*, after which the resulting dark blue oil was redissolved in dichloromethane (1.0 mL). Et_2O (10 mL) was added, crashing out the majority of the material as a dark blue powder. While cooling on a dry ice/isopropanol bath, the Et_2O/DCM mixture was filtered off. The product was washed with Et_2O (2 x 10 mL) and dried *in vacuo*, yielding **1** (645 mg, 95%)

as a dark blue crystalline material. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of heptane into a solution of **1** in dichloromethane.

HRMS (ESI+): m/z calcd. for $C_{10}H_{16}ClCoN_2S$: 290.0049 $[M\text{-}Cl]^+$; found: 290.0046. *N.b.* $[M]^+$ or $[M\text{-}Cl]^+$ for the dimeric complex were not observed. The complex supposedly dissociated on ionisation.

Elemental analysis calcd. (%) for $C_{20}H_{32}Cl_4Co_2N_4S_2$: C 36.83, H 4.95, N 8.59; found: C 36.96, H 4.89 N 8.43.

ATR-IR (cm^{-1}): ν(NH) 3203, ν(CH) 2967, ν(CH) 2925, ν(CH) 2867, 1604 (m), 1442 (m), 1051 (m), 1017 (m), 940 (m), 764 (s), 418 (m)

Crystal data for complex **1**: $C_{20}H_{32}Cl_4Co_2N_4S_2$, M = 652.27, triclinic, space group $P\bar{1}$, a = 7.6862(3), b = 11.1085(4), c = 17.7851(6) Å, α = 72.8236(10), β = 88.0499(11), γ = 70.2746(10)°, V = 1362.03(9) $Å^3$, T = 150(2) K, Z = 2, 54839 reflections measured, 6586 independent reflections (R_{int} = 0.0219), final R values ($I > 2\sigma(I)$): R_1 = 0.0214, wR_2 = 0.0537, final R values (all data): R_1 = 0.0236, wR_2 = 0.0554, 299 parameters. The asymmetric unit contains two molecules; in the main text, only one is depicted.

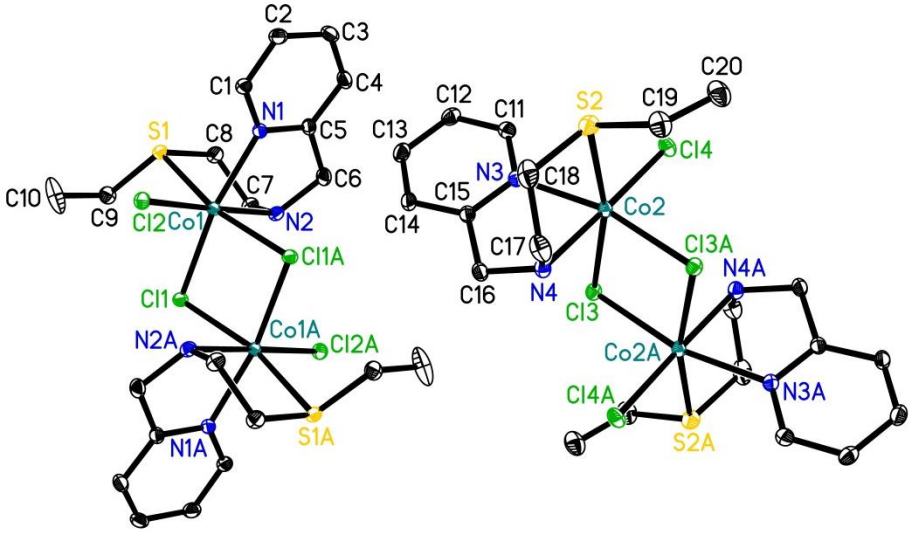


Figure S2: Molecular structure of **1** in the crystal. Displacement ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity. Operators for generating equivalent atoms are -x, -y+1, -z+1 and -x+1, -y+1, -z+2, respectively.

$CoCl_2$(NN^{Me}S) (2): 2 (400 mg, 94%) was obtained as an ultramarine powder from $CoCl_2$ (160 mg, 1.25 mmol) and **L2** (240 µL, 260 mg, 1 eq.), analogously to the synthesis of **1**. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of heptane into a solution of **2** in dichloroethane.

HRMS (ESI+): m/z calcd. for $C_{11}H_{18}Cl_2CoN_2S$: 304.0206 $[M\text{-}Cl]^+$; found: 304.0204.

Elemental analysis calcd. (%) for $C_{11}H_{18}Cl_2CoN_2S$: C 38.84, H 5.33, N 8.24; found: C 37.95 H 4.90 N 7.19. *N.b.* These values are outside of the commonly accepted margin of 0.4%. A contamination of $CoCl_2$ is likely present in the obtained powder - when excess of ligand was used to prevent this, it was observed that two equivalents of ligand may coordinate to cobalt.

ATR-IR (cm^{-1}): ν(CH) 2972, ν(CH) 2928, ν(CH) 2853, 1603(m), 1447(m), 1436(m), 1298(m), 1000 (m), 980 (m), 762 (s), 732(m), 473(m), 420(m)

Crystal data for complex **2**: $C_{11}H_{18}Cl_2CoN_2S$, M = 340.16, triclinic, space group $P\bar{1}$, a = 7.0681(9), b = 9.0140(12), c = 12.2372(15) Å, α = 108.210(4), β = 98.899(4), γ = 99.291(5)°, V = 713.18(16) $Å^3$, T = 150(2) K, Z = 2, 14675 reflections measured, 3215 independent reflections (R_{int} = 0.029), final R values ($I > 2\sigma(I)$): R_1 = 0.0336, wR_2 = 0.0838, final R values (all data): R_1 = 0.0364, wR_2 = 0.0852, 156 parameters.

3.2 Hydrogenation reactions (high-throughput screening, 0.2 mmol scale)

In oven-dried 5 mL headspace vials with crimp neck, **1** or **2** (1.3 mg, 2 mol% Co w.r.t. substrate) was weighed off in the glovebox, and the vials were capped. Stock solutions of the substrates (0.1 M) and additives (0.08 M) were prepared, and injected to the

reaction vials by robot. These were then transferred to a parallel reactor, pressurised with H_2 (50 bar) and heated to 100 °C overnight. The results were analysed by GC based on area percentages and used as a starting point for identifying the desired reaction conditions.

3.3 Hydrogenation reactions (optimisation, 0.33 mmol scale)

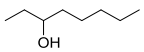
In a typical reaction, 4 mL glass vials were dried in the oven and closed with PTFE septa and screw caps. In the glovebox, catalyst, base, and additive were weighed off. Solvent (1.0 mL), dodecane (150 µL) and 1-octen-3-ol (50 µL, 0.33 mmol) were added, and the septum pierced with a needle. The vial was transferred to an autoclave, which was flushed with inert gas and then pressurised with H_2 (50 bar), and stirred at 100 °C overnight. Yields were determined by GC using dodecane as an internal standard.

3.4 Hydrogenation reactions (substrate scope, 5 mmol scale)

Small-scale reactions were performed in vials as described under **2.2**. Reactions performed at a 5 mmol scale were carried out in a 100 mL hastelloy autoclave vessel, to which **2** (31 mg, 2 mol%) and $NaBH_4$ (9.5 mg, 5 mol%) were added. Under a flow of argon, isopropanol (15 mL) and substrate (5 mmol) were added, the vessel was closed, purged with N_2 and pressurised with H_2 (50 bar). After cooling down, the autoclave was depressurised, and the reaction mixture filtered over a short column of silica. The solvent was evaporated, yielding the product directly unless stated otherwise. Yields refer to isolated yields, the products were analysed by ^{1}H- and ^{13}C-NMR spectroscopy, as well as GC-MS. Analytical data correspond to those reported in literature, where reported. (See section 4 for analytical data, yields and spectra.)

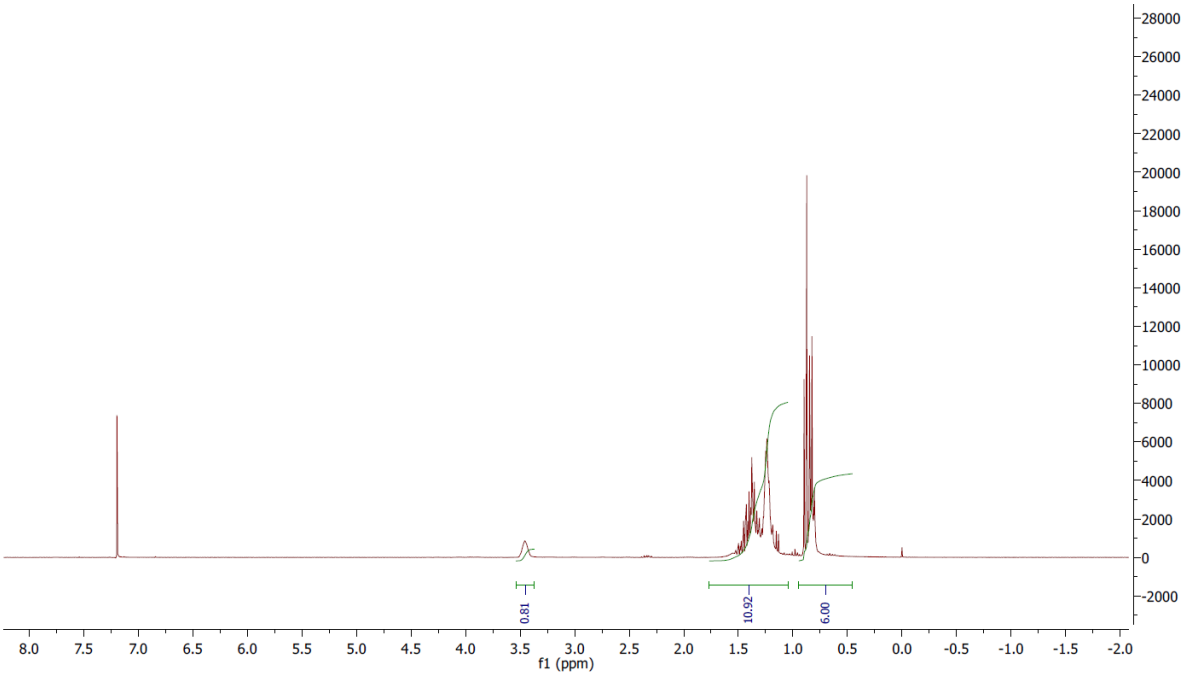
4 Characterisation of isolated products

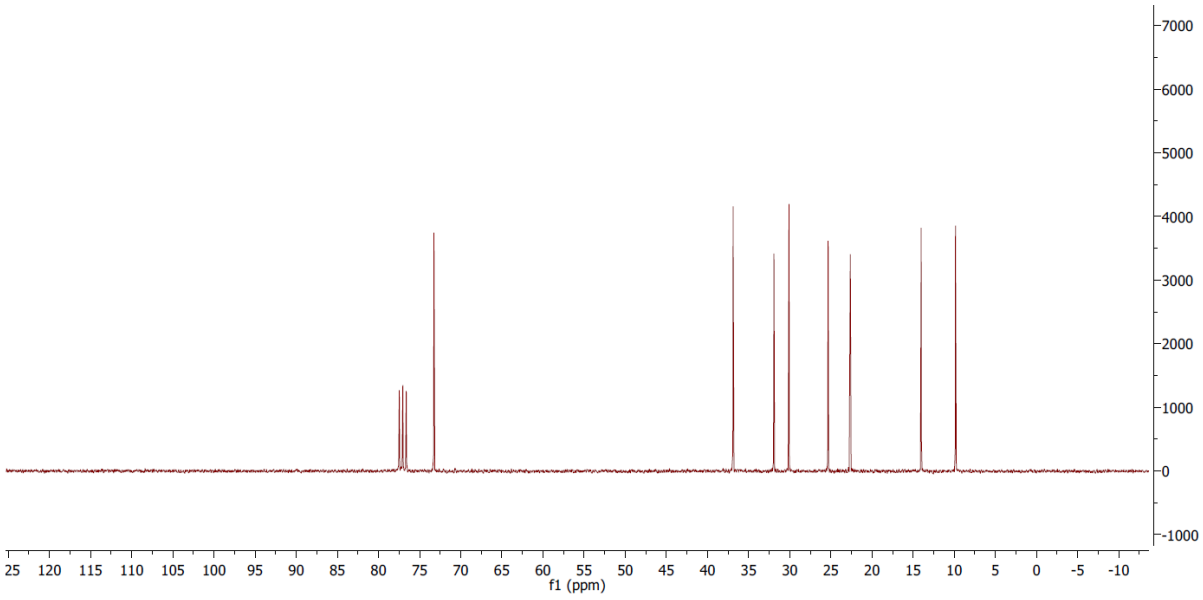
3-Octanol (4a)



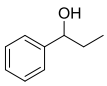
1-Octen-3-ol (**3a**, 0.76 mL, 5.00 mmol) was converted to 635 mg (4.88 mmol, 98 %) of 3-octanol (**4a**).[6]

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.45 (broad, 1H), 1.62 – 1.10 (m, 11H, CH_2, CH, OH), 0.87 (t, *J* = 7.4 Hz, 3H, CH_3), 0.83 (t, *J* = 7.3 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 73.3, 36.9, 31.9, 31.9, 30.1, 25.3, 22.6, 14.0, 9.9. GC-MS: m/z calcd. for $C_8H_{18}O$: 130 $[M]^+$; found: 130.



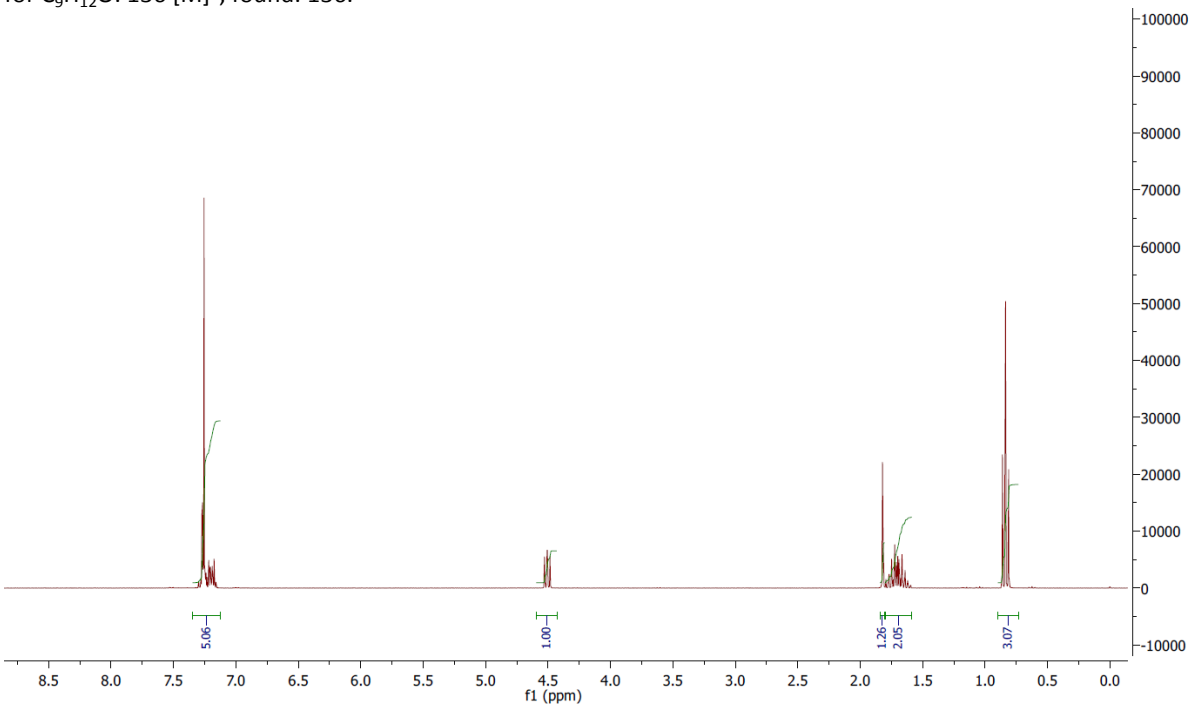


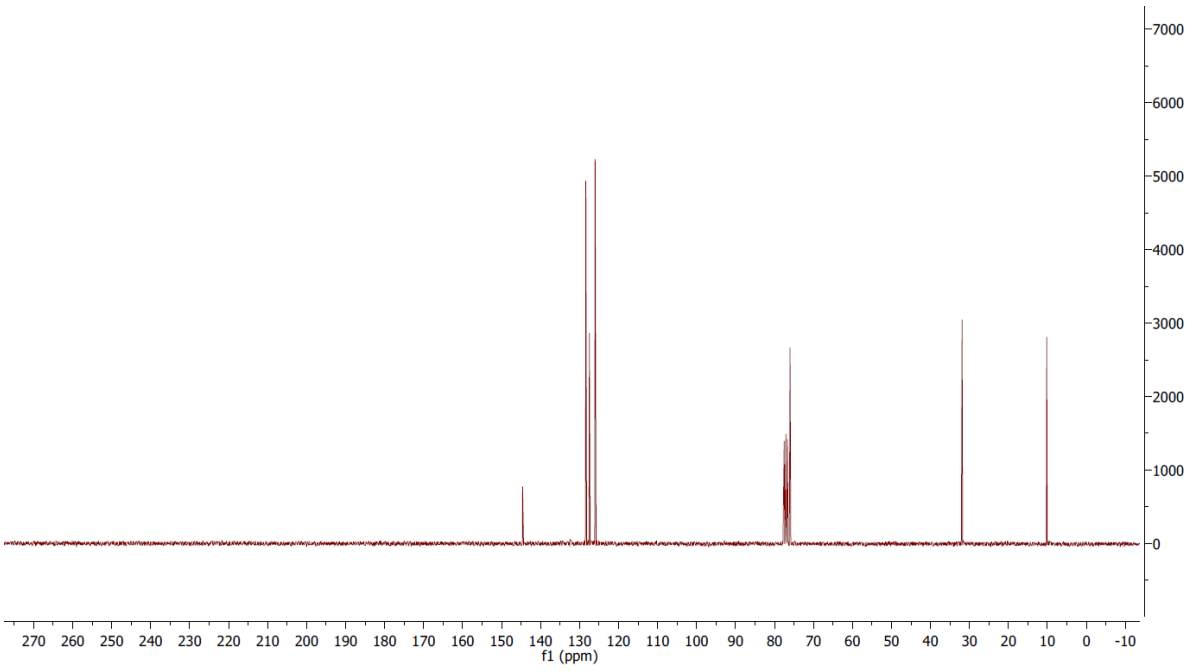
1-phenyl-1-propanol (4b)



α-Vinylbenzyl alcohol (**3b**, 0.66 mL, 5.00 mmol) was converted to 641 mg (4.85 mmol, 97 %) of 1-phenyl-1-propanol (**4b**).[6]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 – 7.13 (m, 5H, CH_{arom}), 4.51 (t, *J* = 6.6 Hz, 1H, CH), 1.82 (d, *J* = 0.8 Hz, 1H, OH), 1.80 – 1.59 (m, 2H, CH_2), 0.84 (t, *J* = 7.4 Hz, 3H, CH_3).^{13}C NMR (75 MHz, $CDCl_3$): δ 144.6, 128.4, 127.5, 126.0, 76.0, 31.9, 10.2. GC-MS: m/z calcd. for $C_9H_{12}O$: 136 $[M]^+$; found: 136.

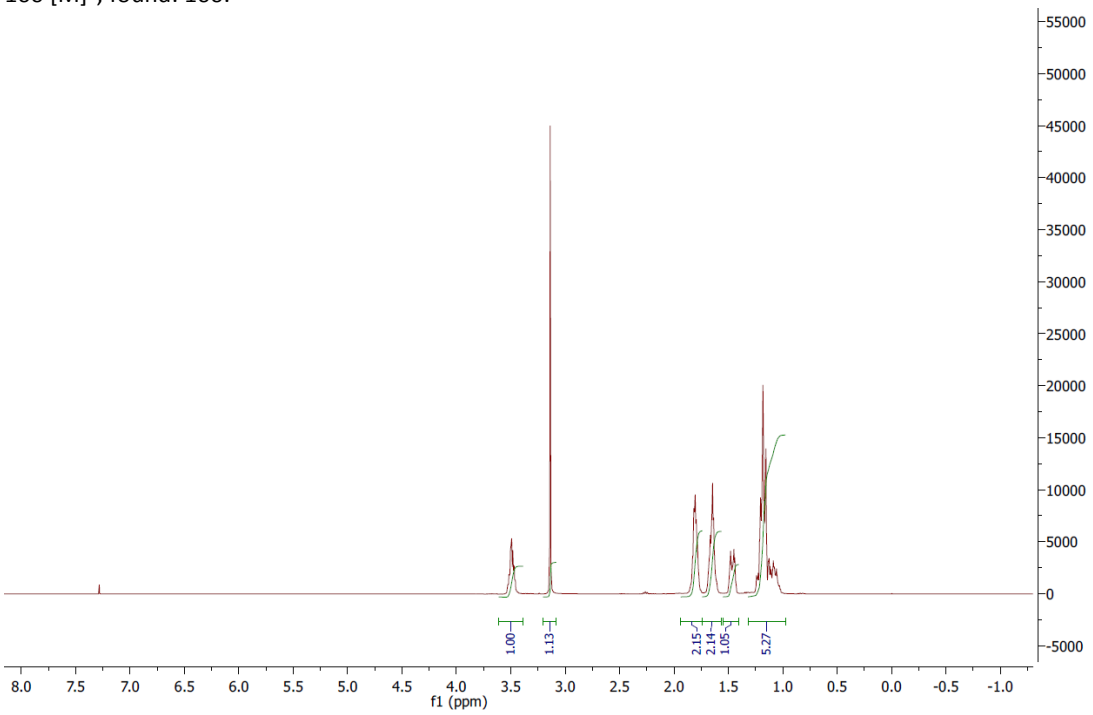


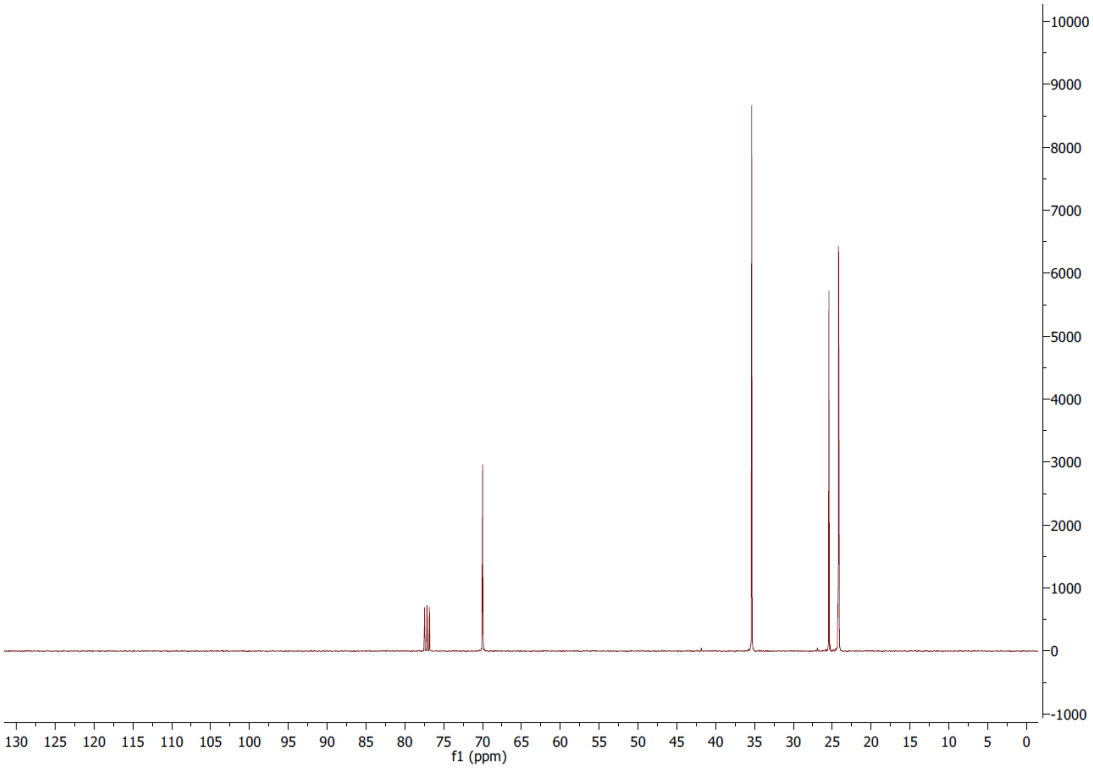


Cyclohexanol (4c)

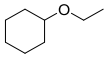
2-Cyclohexen-1-ol (**3c**, 0.49 mL, 5.00 mmol) was converted to 236 mg (2.35 mmol, 47 %) of cyclohexanol (**4c**).[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.49 (tt, *J* = 9.2, 4.1 Hz, 1H, CH), 3.14 (s, 1H, OH), 1.88 – 1.75 (m, 2H, CH_2), 1.65 (m, 2H, CH_2), 1.46 (m, 1H, CH_2), 1.32 – 0.98 (m, 5H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 70.0, 35.4 (2C), 25.4, 24.2 (2C). GC-MS: m/z calcd. for $C_6H_{12}O$: 100 $[M]^+$; found: 100.



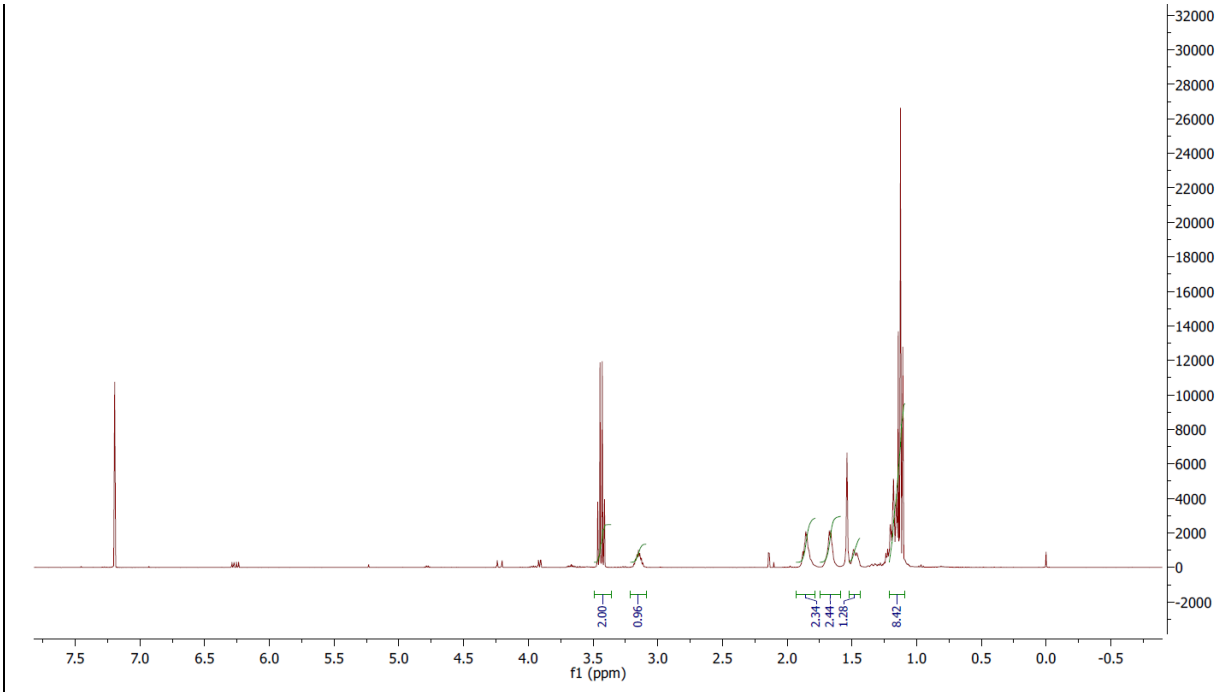


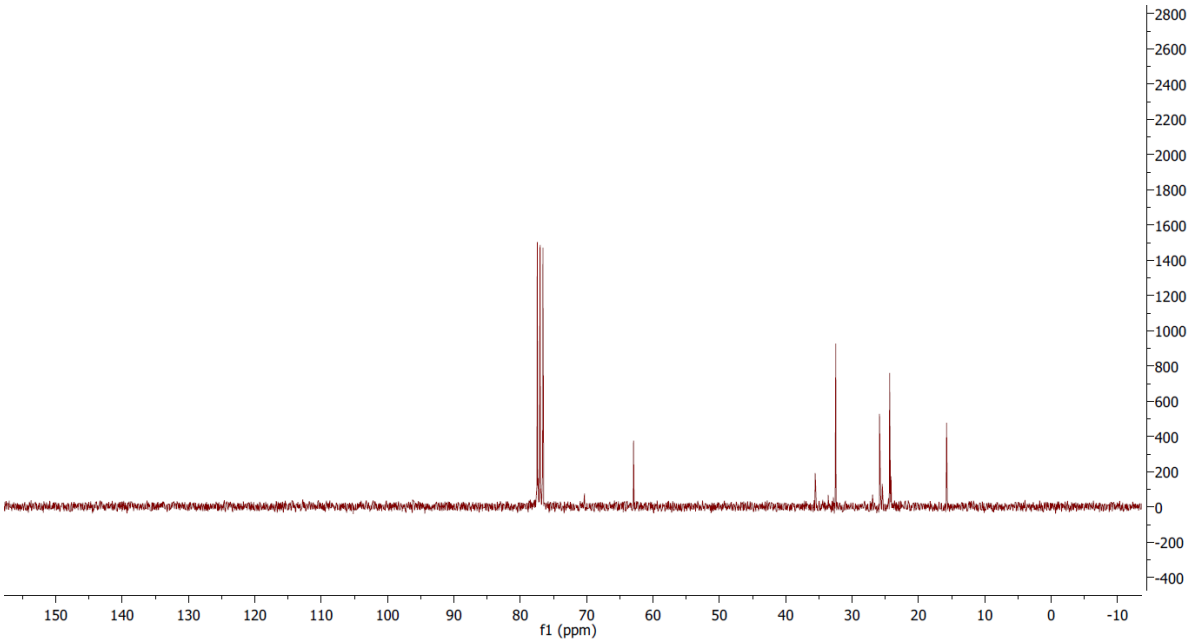
Cyclohexylethylether (4d)



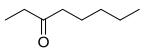
Cyclohexylvinylether (**3d**, 0.71 mL, 5.00 mmol) was converted to 542 mg (4.30 mmol, 86 %) of cyclohexylethylether (**4d**).[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 (q, *J* = 7.0 Hz, 2H, O-CH_2), 3.15 (m, 1H, CH), 1.85 (m, 2H), 1.67 (m, 2H), 1.52 – 1.43 (m, 1H), 1.21 – 1.10 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 77.3, 62.9, 32.4 (2C), 25.7, 24.3 (2C), 15.7. GC-MS: m/z calcd. for $C_6H_{12}O$: 128 $[M]^+$; found: 128.



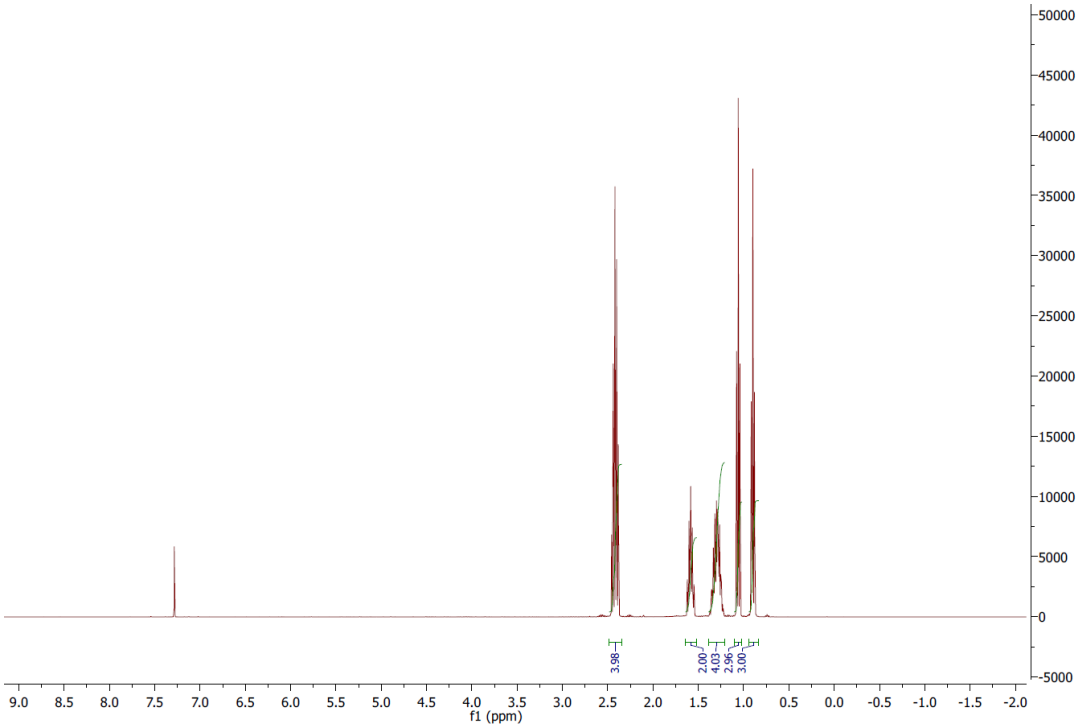


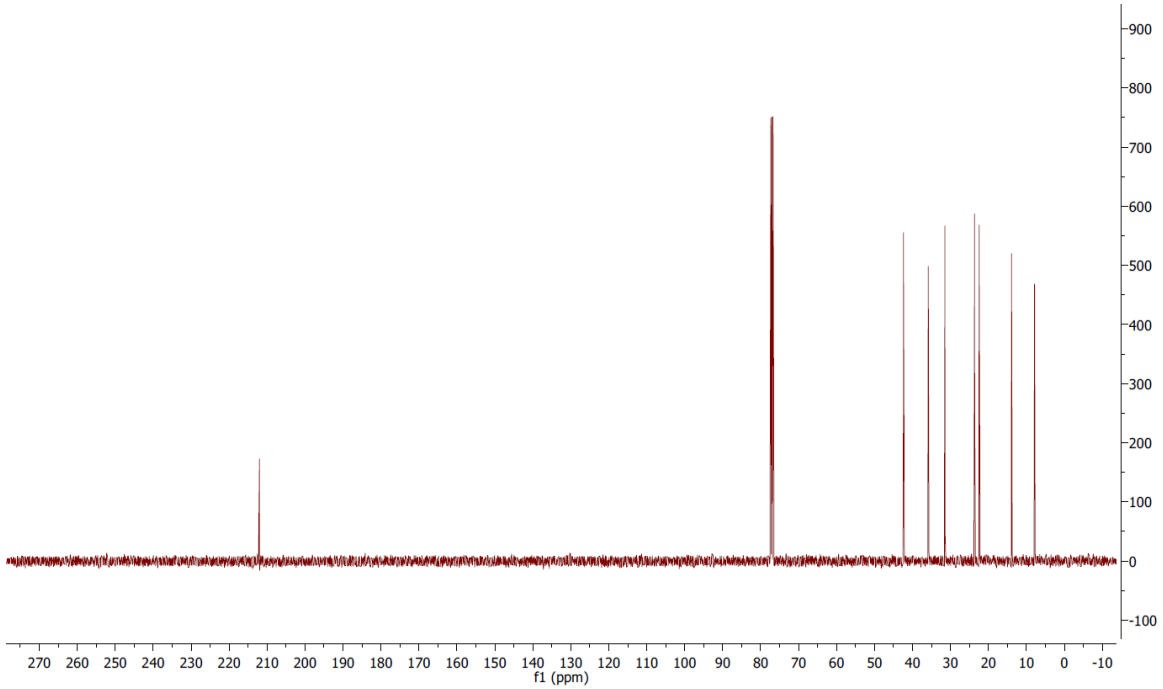
3-Octanone (4e)



1-Octen-3-one (**3e**, 0.76 mL, 5.00 mmol) was converted to 606 mg (4.80 mmol, 96 %) of 3-octanone (**4e**).[8]

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.45 (bs, 1H, OH), 1.62 – 1.10 (m, 11H, CH_2 and CH), 0.87 (t, *J* = 7.4 Hz, 3H, CH_3), 0.83 (t, *J* = 7.3 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 73.3, 36.9, 31.9, 31.9, 30.1, 25.3, 22.6, 14.0, 9.9. GC-MS: m/z calcd. for $C_8H_{16}O$: 128 $[M]^+$; found: 128.

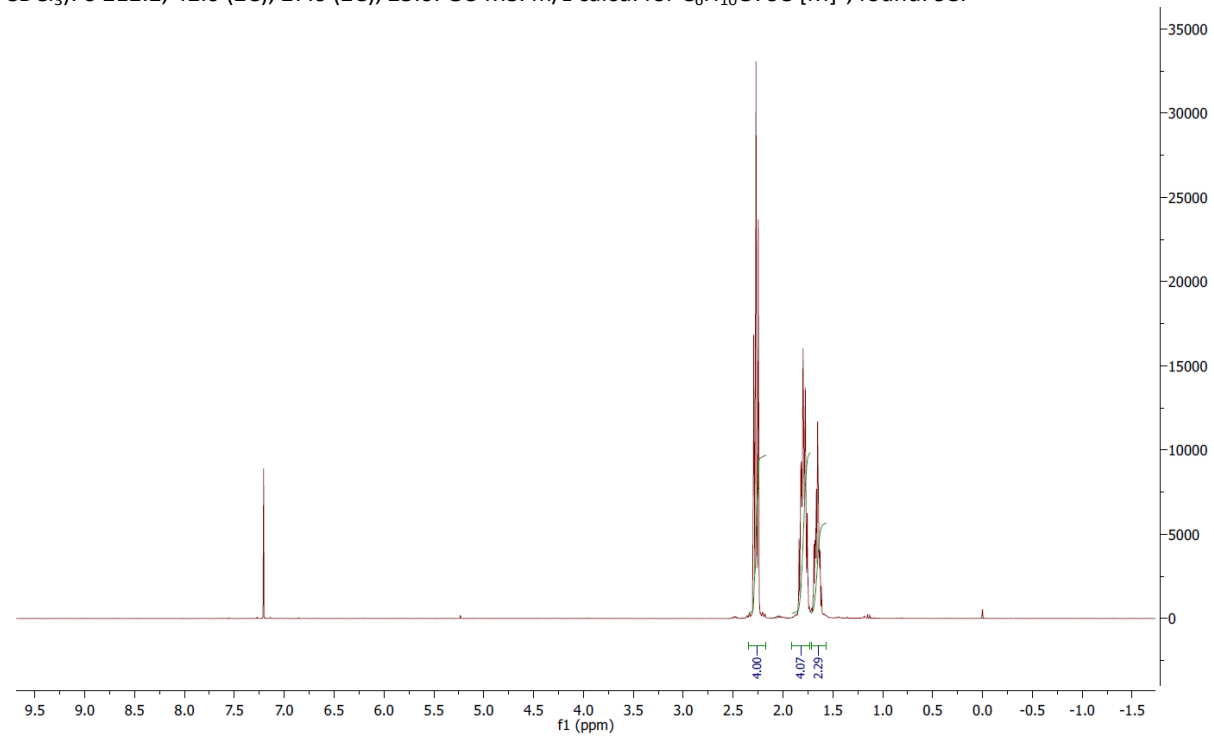


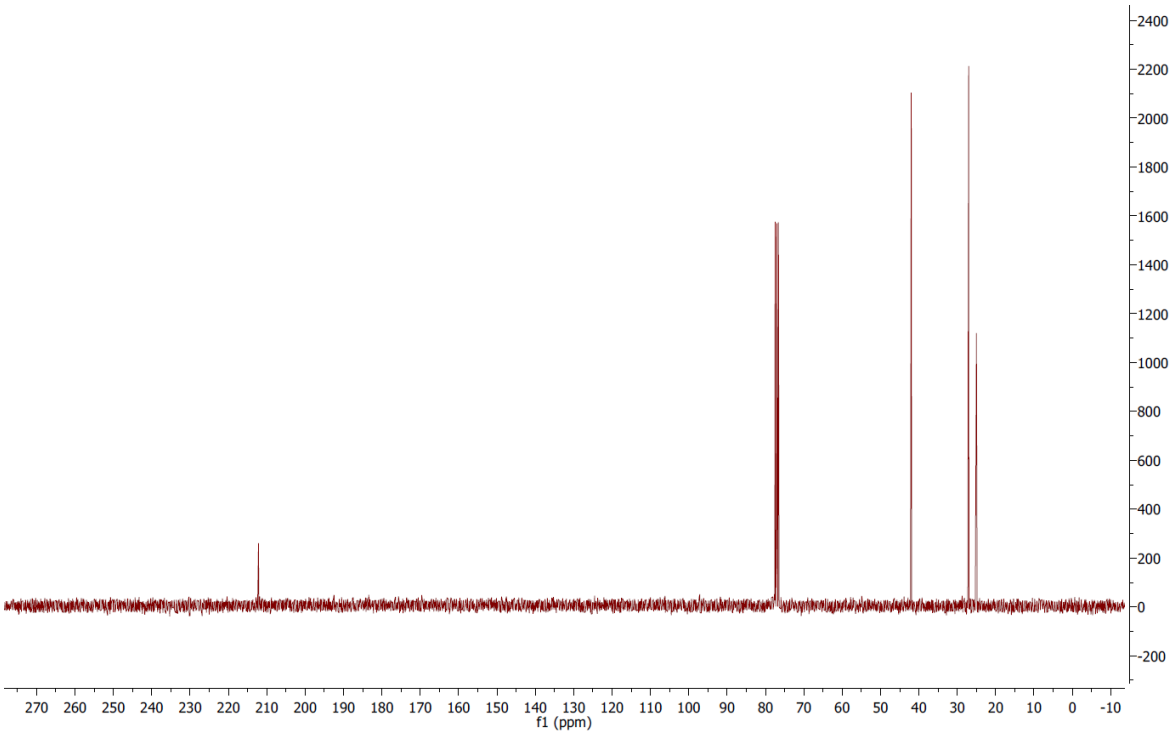


Cyclohexanone (4f)

2-Cyclohexen-1-one (**3f**, 0.48 mL, 5.00 mmol) was converted to 275 mg (2.80 mmol, 56 %) of cyclohexanone (**4f**).[7]

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (t, J = 6.7, 6.1 Hz, 4H, CH_2), 1.90 – 1.73 (m, 4H, CH_2), 1.72 – 1.56 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 212.2, 42.0 (2C), 27.0 (2C), 25.0. GC-MS: m/z calcd. for $C_6H_{10}O$: 98 $[M]^+$; found: 98.

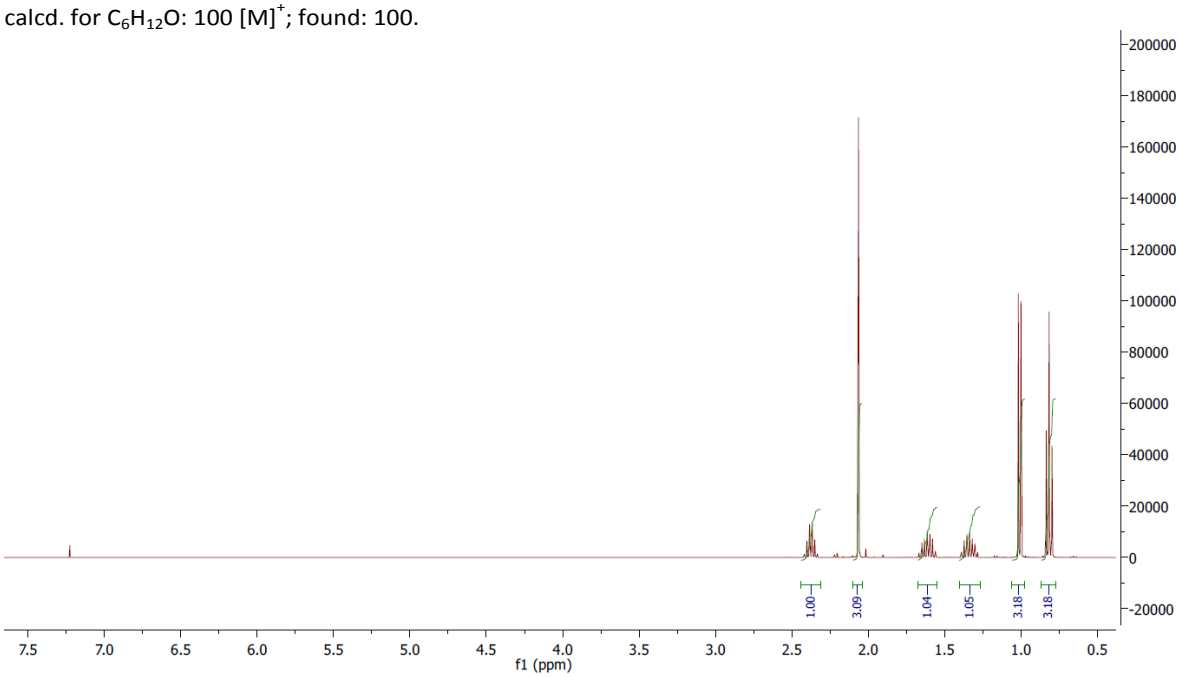


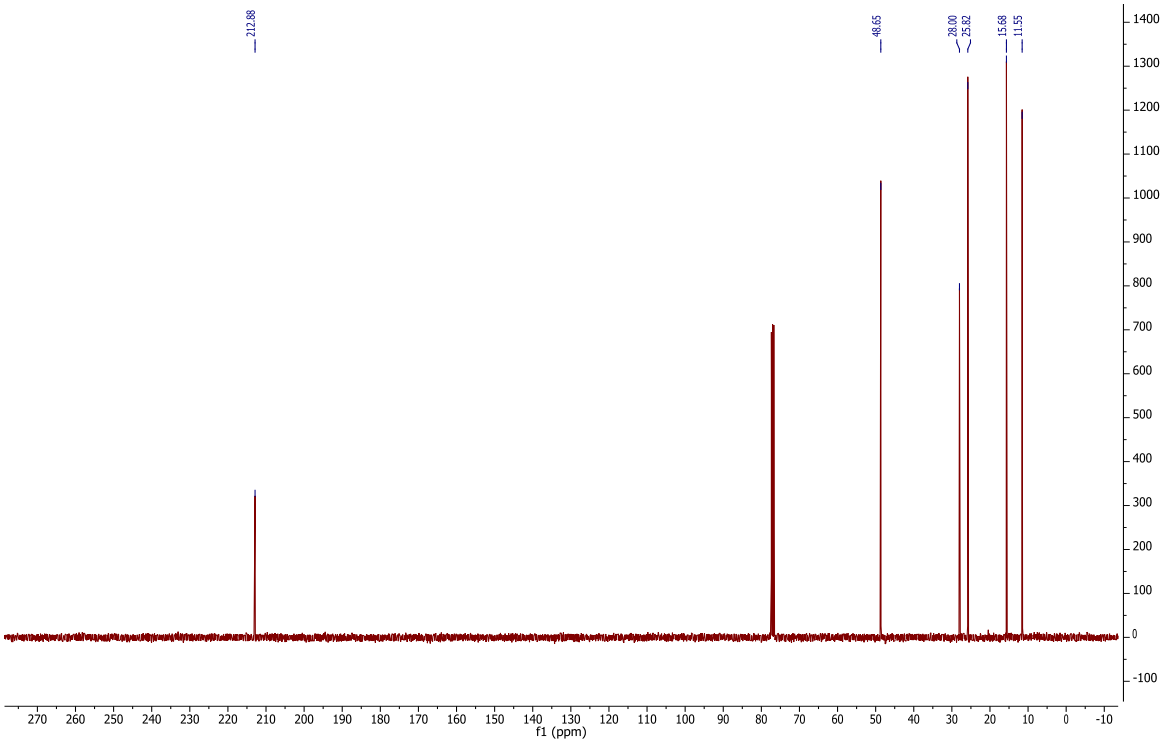


3-Methyl-2-pentanone (4g)

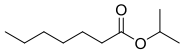
3-Methyl-2-penten-2-one (**3g**, 0.56 mL, 5.00 mmol) was converted to 391 mg (3,90 mmol, 78 %) of 1-phenyl-1-propanol (**4g**).[9]

^{1}H NMR (400 MHz, $CDCl_3$): 2.38 (h, *J* = 6.9 Hz, 1H, CH), 2.06 (s, 3H, CH_3), 1.68 – 1.55 (m, 1H, CH_2), 1.40 – 1.28 (m, 1H, CH_2), 1.01 (d, *J* = 7.0 Hz, 3H, CH_3), 0.82 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 212.9, 48.7, 28.0, 25.8, 15.7, 11.6. GC-MS: m/z calcd. for $C_6H_{12}O$: 100 $[M]^+$; found: 100.



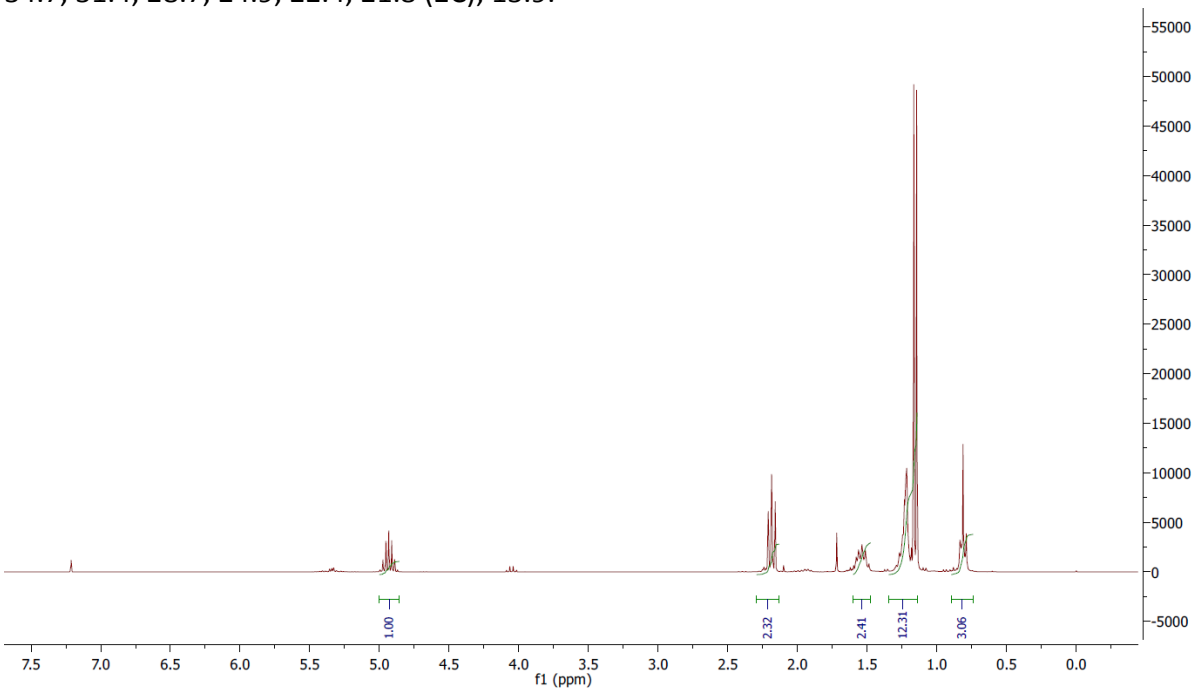


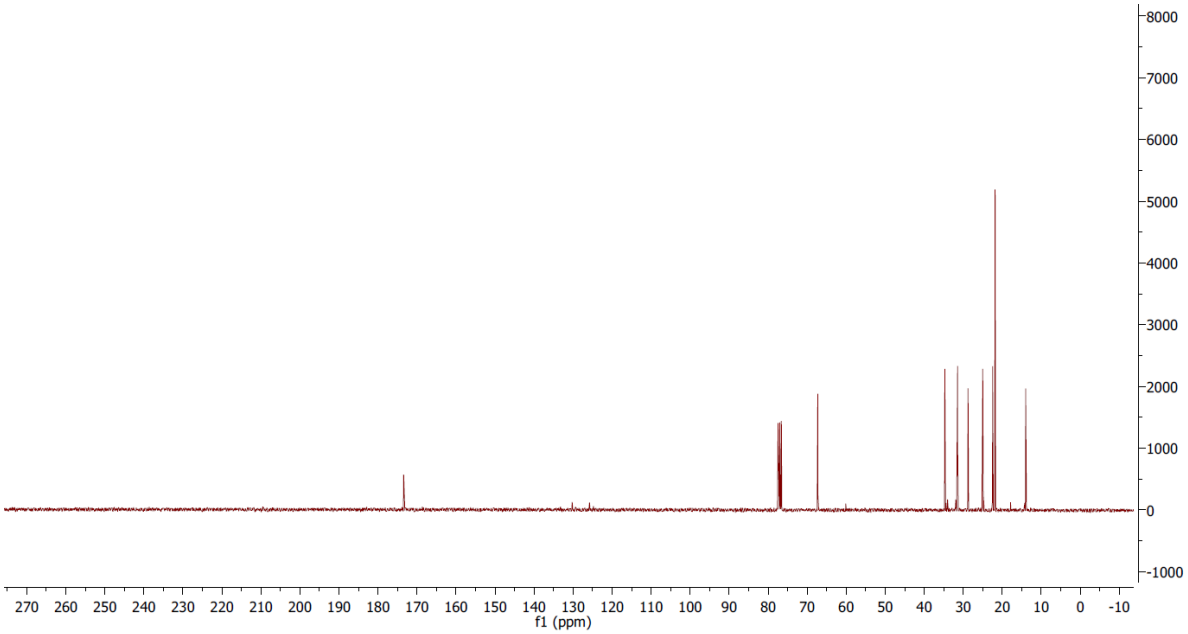
Isopropyl heptanoate (4h)



Methyl 6-heptenoate (**3h**, 0.78 mL, 5.00 mmol) was converted to 740 mg (4.30 mmol, 86 %) of isopropyl heptanoate (**4h**).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.93 (hept, *J* = 6.3 Hz, 1H, CH), 2.29 – 2.13 (m, 2H, CH_2), 1.60 – 1.47 (m, 2H, CH_2), 1.35 – 1.14 (m, 12H, CH_2, CH_3), 0.90 – 0.74 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 67.2, 34.7, 31.4, 28.7, 24.9, 22.4, 21.8 (2C), 13.9.

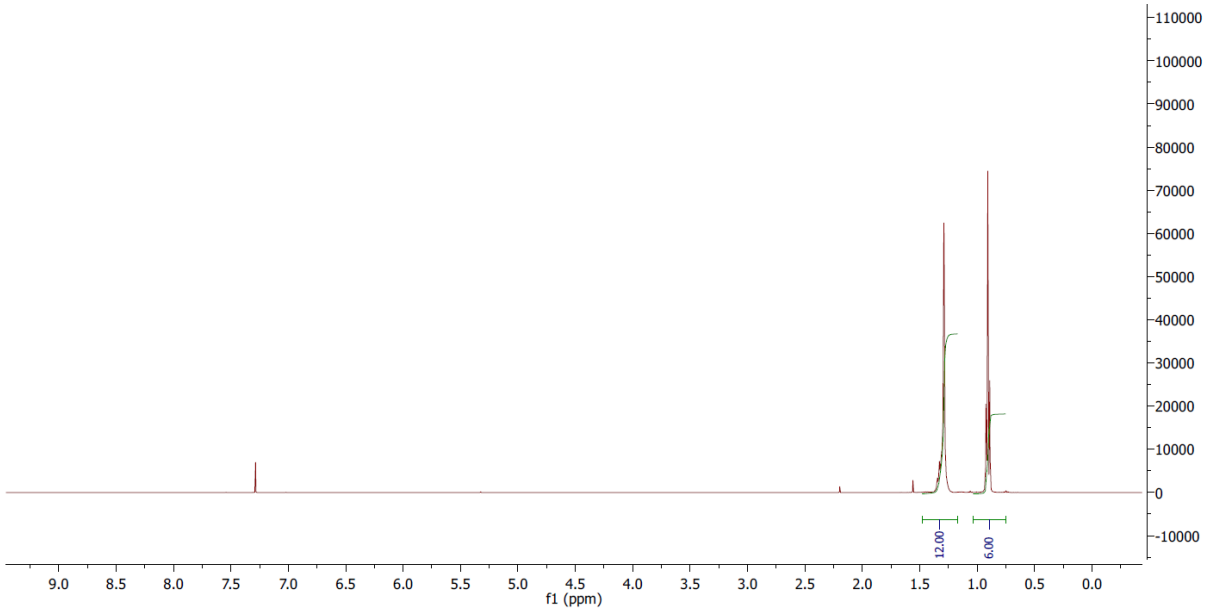


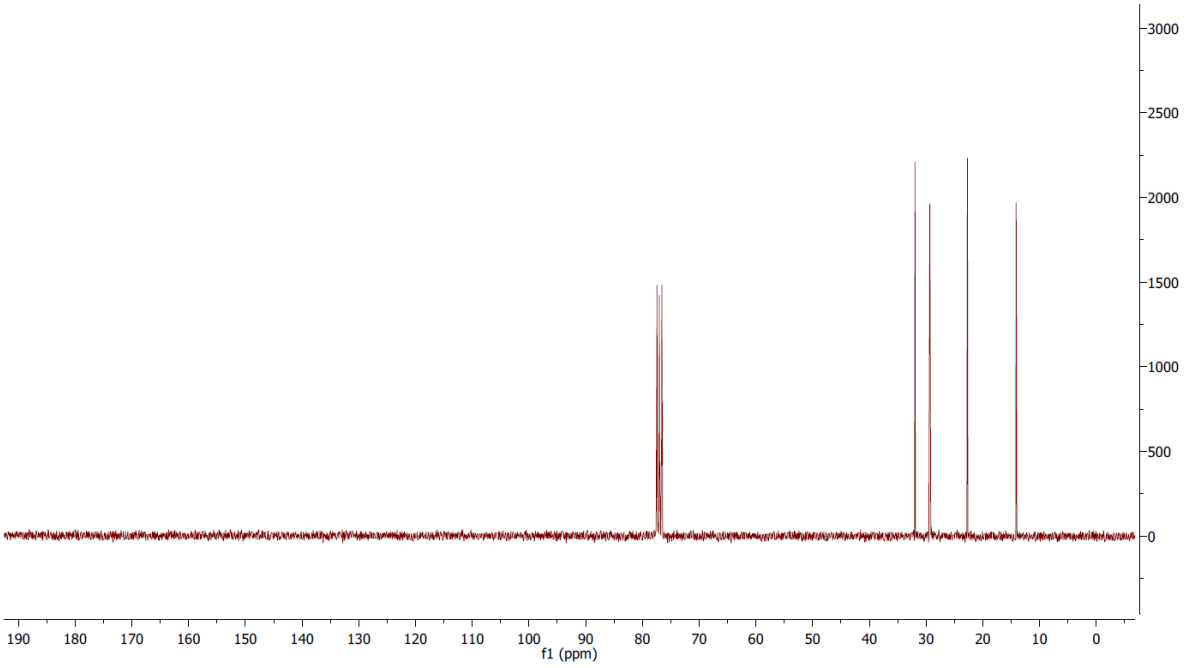


***n*-Octane (4i)**

1-Octene (**3i**, 0.67 mL, 5.00 mmol) was converted to 531 mg (4.65 mmol, 93 %) of *n*-octane (**4i**).[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 – 1.22 (m, 12H, CH_2), 0.91 (t, *J* = 6.8 Hz, 6H, CH_3). ^{13}C NMR (75 MHz, CDCl3): δ 31.9 (2C), 29.3 (2C), 22.7 (2C), 14.1 (2C). GC-MS: m/z calcd. for C_8H_{18}: 114 $[M]^+$; found: 114.





4. References

1 See: http://www.premex-reactorag.ch/index.php?page=464
2 Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.
3 Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3-8.
4 a) C. Guminki, *J. Phase Equil.* **1993**, *14*, 643-644; b) J.A. Widegren, R.G. Finke, *J. Mol. Catal. A: Chemical* **2003**, *198*, 317-341; c) R. Crabtree, *Chem. Rev.* **2012**, *112*, 1536-1554.
5 P. Puylaert, R. van Heck, Y. Fan, A. Spannenberg, W. Bauman, M. Beller, J. Medlock, W. Bonrath, L. Lefort, S. Hinze, J.G. de Vries, *Chem.- Eur. J.* **2017**, 23, 8473-8481.
6 J. W. Kim, T. Koike, M. Kotani, K. Yamaguchi, N. Mizuno, *Chem. Eur. J.* **2008**, *14*, 4104-4109.
7 Mannepalli L. Kantam, R. Kishore, J. Yadav, M. Sudhakar, A. Venugopala, *Adv. Synth. Catal.* **2012**, *354*, 663-669.
8 N. Rios-Lombardía, C. Vidal, M. Cocina, F. Morís, J. García-Álvarez, J. González-Sabín, *Chem. Commun.* **2015**, *51*, 10937-10940.
9 P. N. Liu, K. D. Ju, C. Po Lau, *Adv. Synth. Catal.* **2011**, *353*, 275-280.
10 E. Kleinpeter, J. Thielemann, *Tetrahedron* **2007**, *63*, 9071-9081.

