Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

A Ruthenium-catalysed Domino Hydroformylation-Hydrogenation-Esterification of Olefins

Ricarda Dühren,[a] Peter Kucmierczyk,[b,c] Carolin Schneider,[a] Ralf Jackstell,[a]* Robert Franke[b,c] and Matthias Beller[a]*

[a] *Leibniz-Institut für Katalyse e.V., Albert-Einstein-Straße 29a, 18059 Rostock, Germany. E-Mail:* matthias.beller@catalysis.de

[b] **Evonik Performance Materials GmbH, Paul-Baumann-Straße 1, 45772 Marl, Germany*

[c] **Lehrstuhl für Theoretische Chemie Ruhr-Universität Bochum, 44780 Bochum, Germany. E-Mail: robert.franke@evonik.com*

*Corresponding author Email: matthias.beller@catalysis.de, ralf.jackstell@catalysis.de.

Content

General considerations

All air- and moisture sensitive syntheses were performed under an argon atmosphere in heating gun dried glassware using Schlenk techniques. Chemicals were purchased from commercial sources and used as received unless the purity was less than 98%. All olefins were stored under argon. 1-octene, di-iso-butene and 3,3-dimethyl-1-butene were distilled under argon before use. Oxygen-free and dry solvents were prepared by distillation. Di-iso-butene was obtained from Evonik Performance Materials GmbH and. CO and synthesis gas are purchased from Linde (CO=4.7; H_2=5.0; N_2=5.0; H_2/CO 1:1+/-1%).

The products were characterised by ^{1}H NMR and ^{13}C NMR spectroscopy. NMR spectra were recorded on either a Bruker AV 400 (400 MHz), AV 300 (MHz) or Fourier 300 (MHz) spectrometer. Chemical shifts δ (ppm) are reported relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H-NMR) and 77.16 ppm (^{13}C-NMR). ^{13}C NMR spectra were acquired on a broad band decouple method. Signals were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublets) and m (multiplet).

GC analysis was performed on a 7890A GC-System with a 30 m HP-5 column from Agilent Technologies. Argon was used as carrier gas. The products were measured by MS an GC analysis or isolated from the reaction mixture by solvent evaporation and further purified by column chromatography on silica gel. Isolated yields refer to the yield of inseparable mixture and n- and iso- acetate esters. GC yields were calculated using hexadecane as the internal standard.

General procedure for the catalytic conversion of alkenes

In general, the catalytic experiments were performed in 4 mL screw cap vials, closed with a polytetrafluoroethylene (PTFE)/white rubber septum (Wheaton 13 mm Septa) and phenolic cap. The connection with the atmosphere was achieved by a needle. The reaction scale for those reactions was 2 mL. The vials were placed inside a 300 mL Parr autoclave and stirred with a magnetic stirring bar.

In a typical catalytic experiment, the reaction vial was charged with $Ru_3(CO)_{12}$ (5 mol%), **L6** (5.5 mol%), PTSA·H_2O (20.6 mol%) and an oven-dried stirring bar. The vial was closed by (PTFE)/white rubber septum (Wheaton 13 mm Septa) and phenolic cap, fixed in an alloy plate and connected to atmosphere with a needle. The vial was then evacuated and recharged with argon for three times. Acetic acid (1.17 mL), H_2O (0.35 mL) and 1-Octene (3 mmol) were injected by Hamilton syringe. Under argon atmosphere the vial was transferred into Parr4560 series 300 mL autoclave. After the autoclave was flushed three times with 10 bar CO at room temperature, it was charged with 40 bar CO, placed in an aluminium block on a heating plate with magnetic stirring and heated to 140 °C for 20 hours. Afterwards, the autoclave is cooled to room temperature and pressure was released carefully. Hexadecane (100 µL) was added to the reaction solution as internal standard. The yield was determined by GC analysis.

Data for the Optimization of Reaction Conditions

Table S1: Acid Screening.

Entry	Acid	Yield [%]	n/iso [%]
1	PTSA	53	29/71
2	H_2SO_4	11	48/52
3	H_3PO_4	7	33/67
4	$Al(OTf)_3$	14	43/57

Conditions: 1-octene (3 mmol), $[Ru_3(CO)_{12}]$ (5 mol% Ru), PCy_3:Ru (1.1:1, 5.5 mol%), acid:PCy_3 (3.75:1, 20.6 mol%), H_2O:1-octene (6.5:1), HOAc:1-octene (6.75:1), CO (40 bar), V_R= 2 mL.

Table S2: Screening gas mixture, pressure and temperature.

Entry	T [°C]	$p(CO/H_2)$ [bar]	Yield [%]	n/iso [%]
1	120	60 bar CO	9	45/55
2	140	15 bar CO	11	45/55
3		20 bar CO	19	45/55
4		30 bar CO	24	45/55
5		40 bar CO	25	45/55
6		60 bar CO	29	48/52
7		80 bar CO	31	35/65
8	160	40 bar CO	26	47/53
9		60 bar CO	27	47/53
10	100	40 bar H_2/CO	21	55/45
11	120	40 bar H_2/CO	56	48/52
12	140	60 bar H_2/CO	52	49/51
13		40 bar H_2/CO + 20 bar N_2	55	48/52
14		40 bar H_2/CO	61	48/52
15		30 bar H_2/CO + 10 bar H_2 (= 15 CO + 25 H2)	50	47/53
16		10 bar CO + 30 bar H_2/CO (= 25 CO + 15 H_2)	50	46/54

17		30 bar CO + 10 bar H_2	39	45/55
18		10 bar CO + 30 bar H_2	35	48/52
19		20 bar CO + 30 bar H_2	57	47/53
20		20 bar CO + 40 bar H_2	62	52/48
21		20 bar CO + 60 bar H_2	61	49/51
22		20 bar H_2 + 40 bar CO	38	38/62
23		20 bar H_2 + 60 bar CO	42	41/59
24	160	40 bar H_2/CO	44	50/50

Conditions: 1-octene (3 mmol), $[Ru_3(CO)_{12}]$ (5 mol% Ru), PCy_3:Ru (1.1:1, 5.5 mol%), acid:PCy_3 (3.75:1, 20.6 mol%), H_2O:1-octene (6.5:1), HOAc:1-octene (6.75:1), mixtures of CO/N_2 or CO/H2 (V_G=40-80 bar), V_R= 2 mL.

Table S3: Screening of Acid:Ligand.

Entry	Acid:L [mmol:mmol]	Yield [%]	n/iso [%]
1	1	61	51/49
2	2	59	49/51
3	3,75	61	48/52
4	6	48	49/51
5	8	40	50/50

Conditions: 1-octene (3 mmol), $[Ru_3(CO)_{12}]$ (5 mol% Ru), PCy_3:Ru (1.1:1, 5.5 mol%), PTSA·H_2O:PCy_3 (1:1-8:1), H_2O:1-octene (6.5:1), HOAc:1-octene (6.75:1), H_2/CO (1:1, 40 bar), V_R=2 mL.

Table S4: Screening of H2O:Substrate.

Entry	H_2O:Sub [mmol:mmol]	Yield [%]	n/iso [%]
1	0	0	-
2	1	65	48/52
3	2	70	49/51
4	4	64	49/51
5	6.5	61	51/49
6	8	59	54/46
7	10	58	55/45

Conditions: 1-octene, $[Ru_3(CO)_{12}]$ (5 mol% Ru), PCy_3:Ru (1.1:1, 5.5 mol%), PTSA·H_2O:PCy_3 (1:1, 5,5 mol%), H_2O:1-octene (1:1-10:1), HOAc:1-octene (6.75:1), H_2/CO (1:1, 40 bar), V_R=2 mL.

Table S5: Screening of HOAc:Substrate.

Entry	HOAc:Sub [mmol:mmol]	Yield [%]	n/iso [%]
1	2	49	51/49
2	4	62	59/51
3	6.75	70	49/51
4	8	66	48/52
5	10	70	49/51

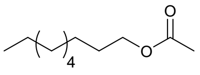
Conditions: 1-octene, [$Ru_3(CO)_{12}$] (5 mol% Ru), PCy_3:Ru (1.1:1, 5.5 mol%), PTSA·H_2O:PCy_3 (1:1, 5.5 mol%), H_2O:1-octene (2:1), HOAc:1-octene (2:1-10:1), H_2/CO (1:1, 40 bar), V_R=2 mL.

Table S6: Influence of halide additives.

Entry	Additive	Mol% (Additive)	Yield [%]	n/iso [%]
1	none	-	70	49/51
2	LiCl	2	57	48/52
3	CsF	2	69	49/51
4	LiBr	2	60	47/53

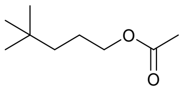
Conditions: 1-octene (3 mmol), [$Ru_3(CO)_{12}$] (5 mol% Ru), PCy_3:Ru (1.1:1, 5.5 mol%), PTSA·H_2O:PCy_3 (1:1, 5.5 mol%), H_2O:1-octene (6.5:1), HOAc:1-octene (6.75:1), additive (2 mol%), H_2/CO (1:1, 40 bar), V_R=2 mL.

Characterization of the Acetate Esters



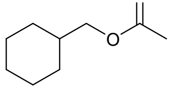
Nonyl acetate (70% yield)

^{1}H NMR (300 MHz, $CDCl_3$) and **^{13}C NMR** (300 MHz, $CDCl_3$) show a 49:51 mixture of n- and iso-nonyl acetate.



4,4-Dimethylpentyl acetate (75% yield)

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.89-3.84 (m, 2H), 1.87 (s, 3H), 1.49-1.38 (m, 2H), 1.12-1.03 (m, 2H), 0.74 (s, 9H) ppm. **^{13}C NMR** (300 MHz, $CDCl_3$) δ 170.58, 65.01, 39.84, 29.07, 23.86, 20.63 ppm.



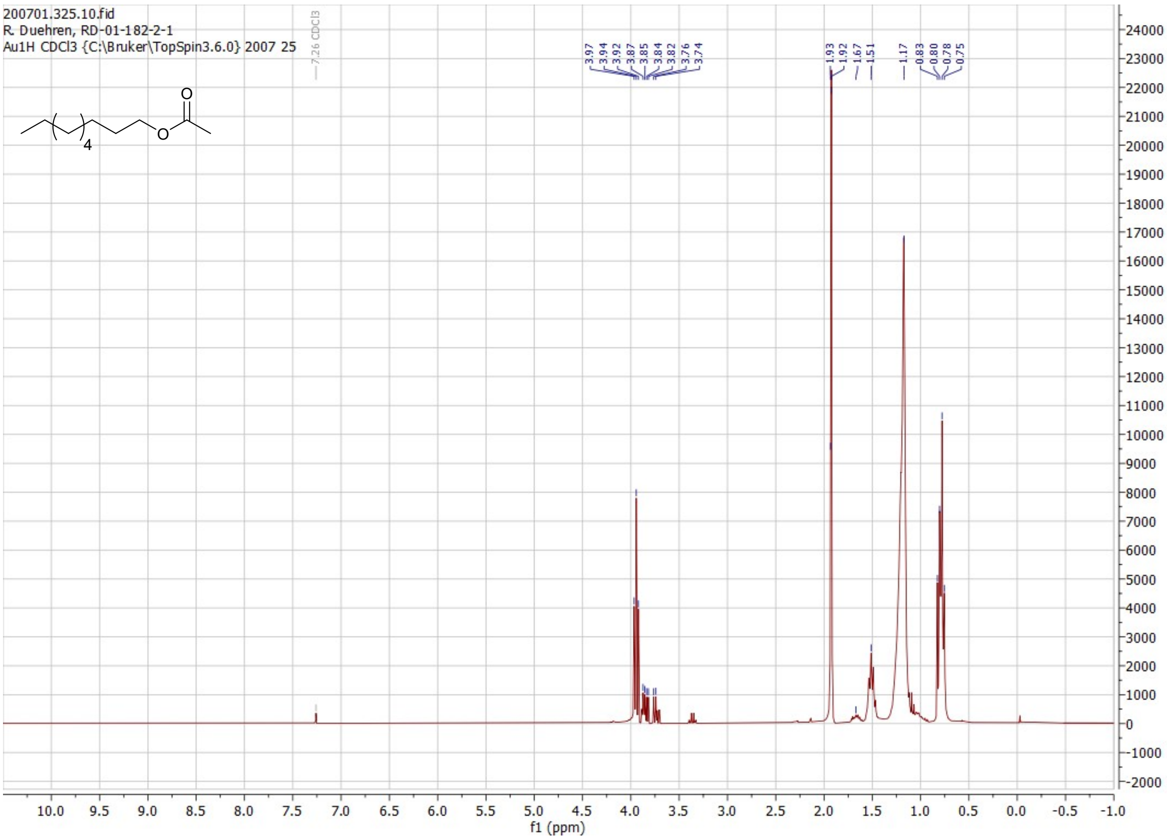
Cyclohexylmethyl acetate (55% yield)

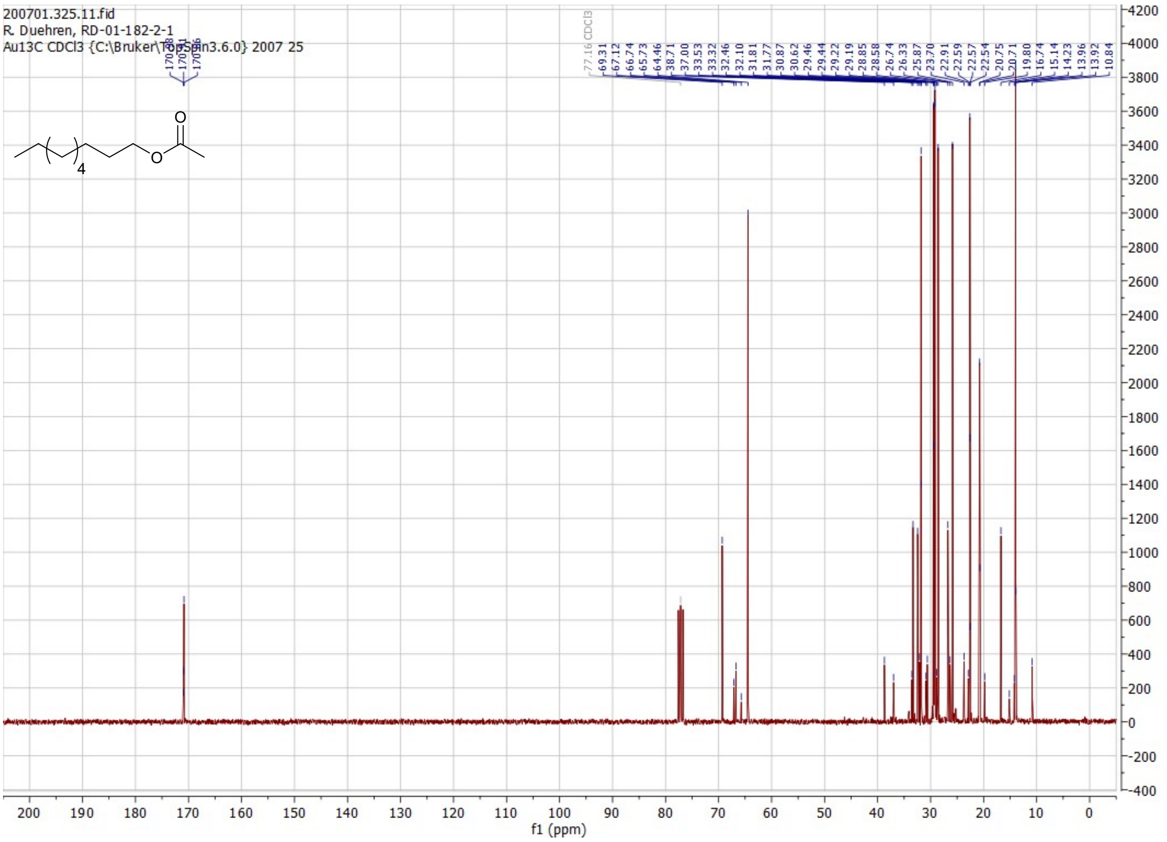
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.77-3.75 (m, 2H), 1.92 (s, 3H), 1.64-0.83 (m, 11H) ppm. **^{13}C NMR** (300 MHz, $CDCl_3$) δ 170.87, 69.45, 36.99, 29.57, 26.27, 25.57, 20.67 ppm.

Spectroscopic Data

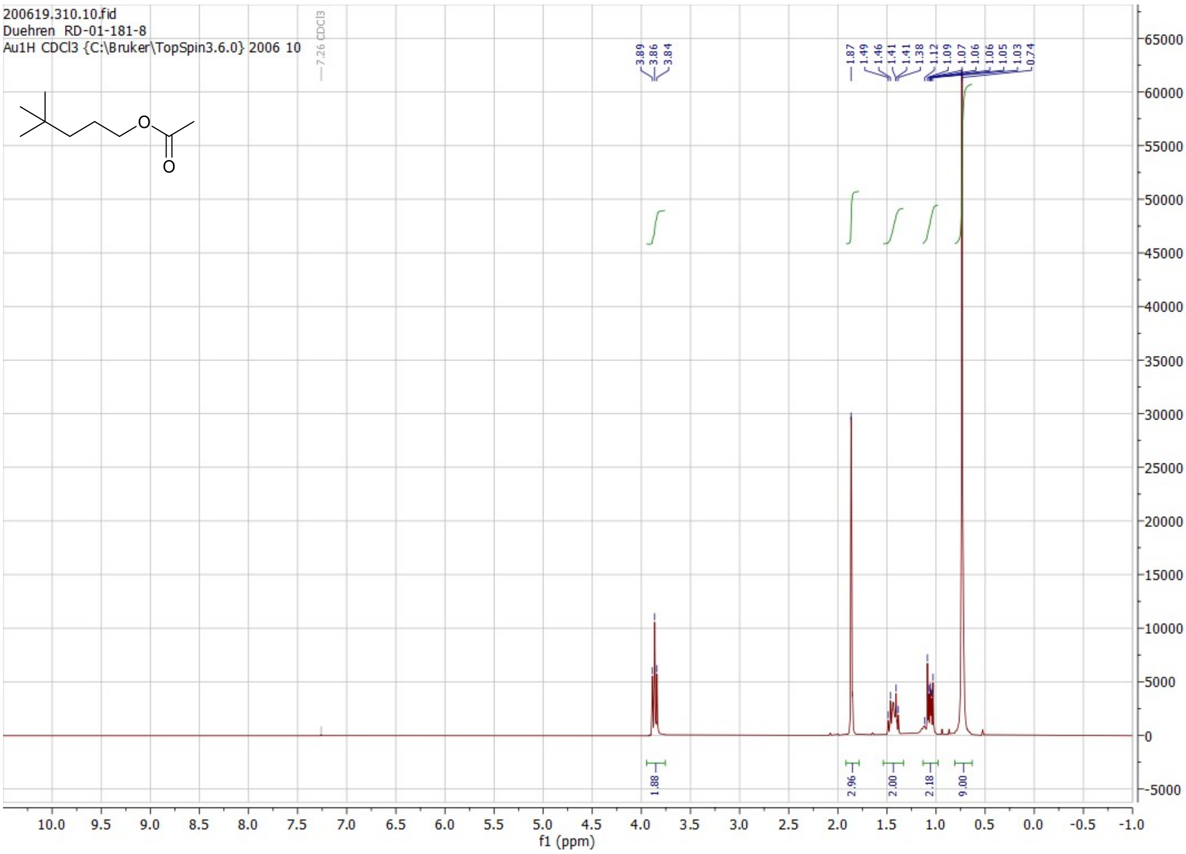
NMR Spectra

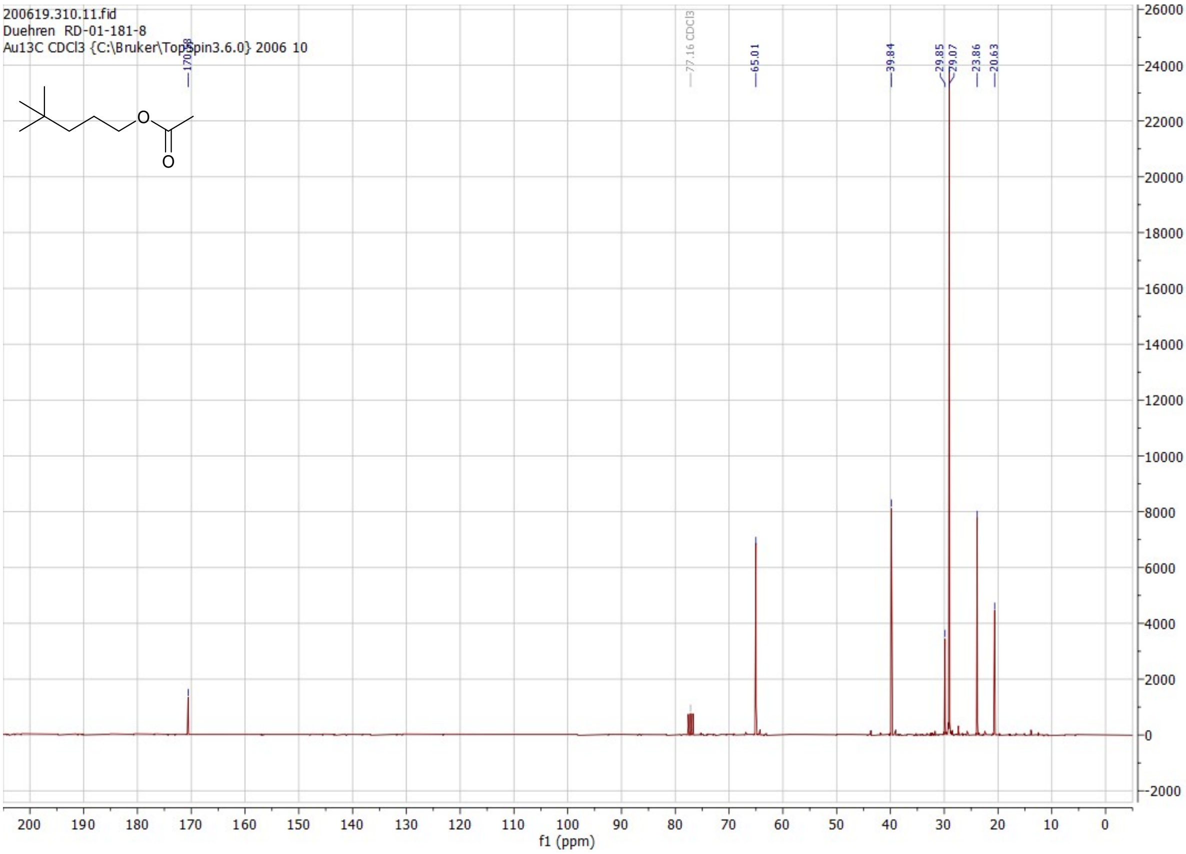
Nonyl acetate (+isomers)

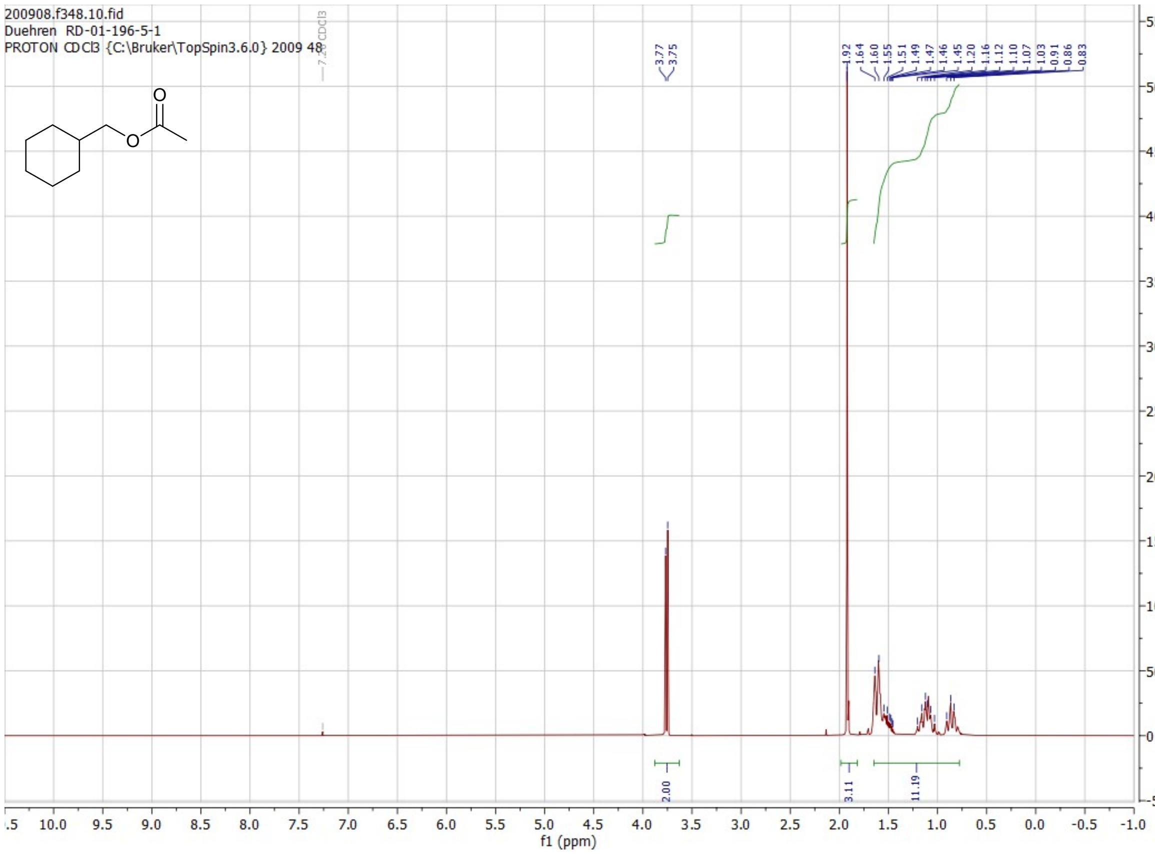




4,4-Dimethylpentyl acetate

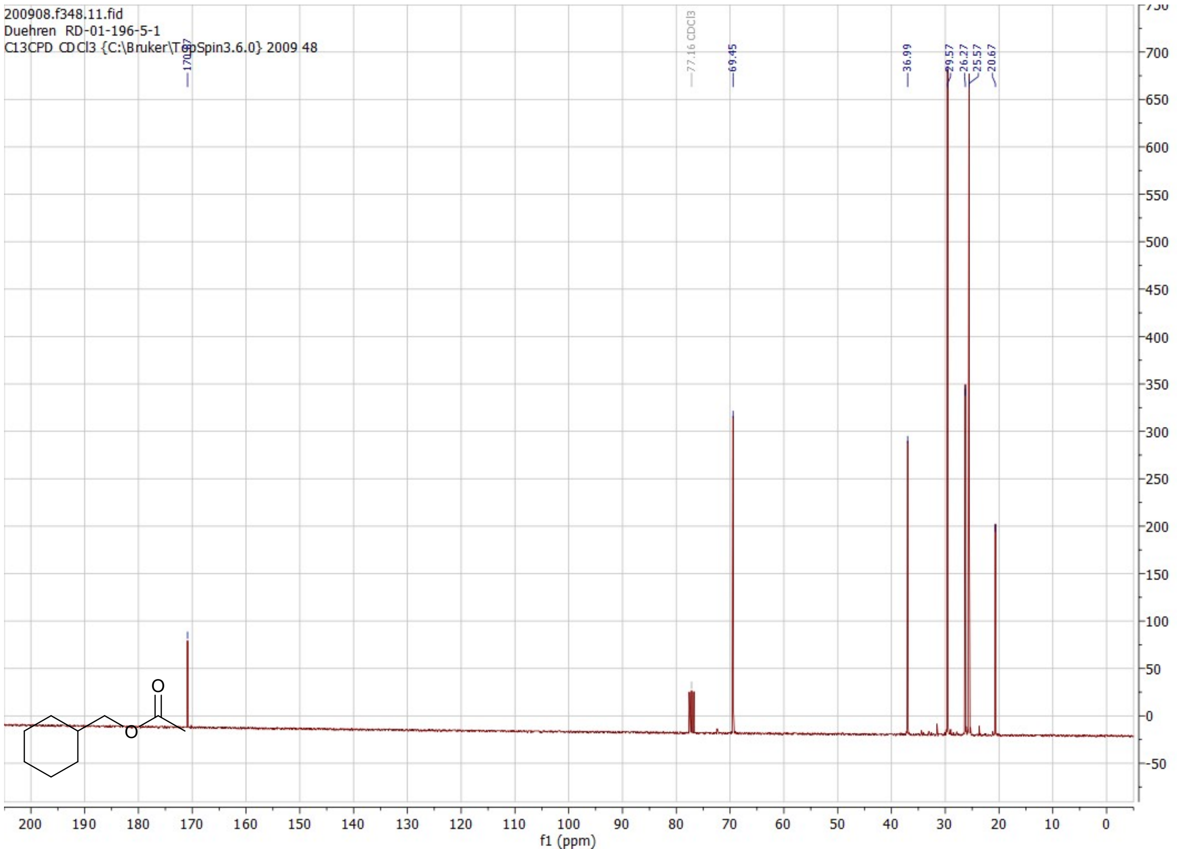




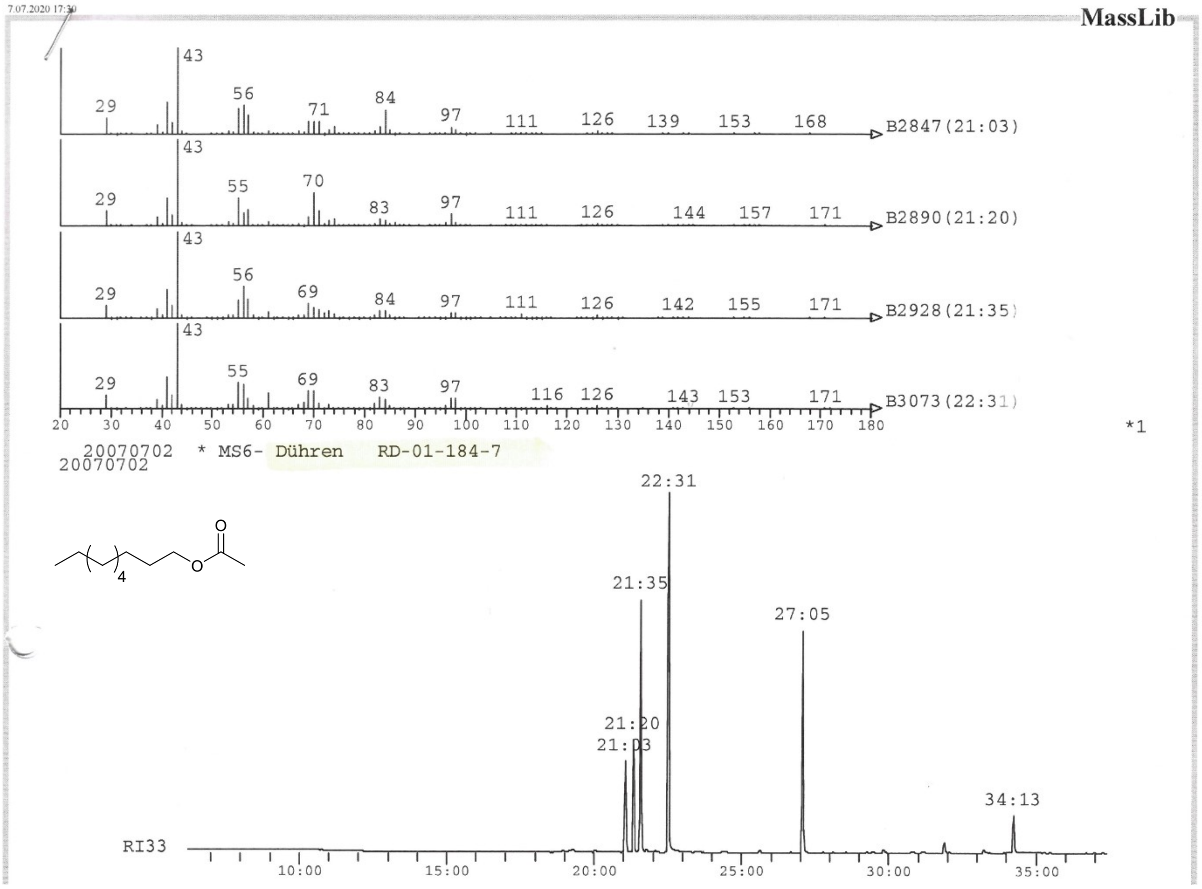


Cyclohexylmethyl acetate

GC/MS



Nonyl acetate



Signal identification:

21:03 – 22:31	isomerised acetate
27:05	internal standard hexadecane
34:13	ligand PCy_3