

Supporting Information

Ruthenium-catalysed Hydroxycarbonylation of Olefins

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Content

General considerations	S2	
General procedure for hydroxycarbonylation of olefins	S2	
Data for the Optimization of Reaction Conditions		S3
Spectroscopic Data		S5
NMR of catalytic experiments	S5	
GC-MS of catalytic experiments	S6	

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%. 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:99,997%; H₂/CO 1:1+/-1%).

The products were characterised by ¹H NMR and ¹³C 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 CDCl₃ were 7.26 ppm (¹H-NMR) and 77.16 ppm (¹³C-NMR). ¹³C NMR spectra were acquired on a broad band decouple method. Signals were assigned as s (singlet), d (doublet), t (triplet), dd (double of doublet) 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 iso- and n- carboxylic acids. GC yields were calculated using hexadecane as the internal standard.

General procedure for hydroxycarbonylation 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 Ru₃(CO)₁₂ (5 mol%), **L6** (5.5 mol%), PTSA·H₂O (20.79 m%) 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. Solvent HFIP (1.44 mL), H₂O (0.24 mL) and 1-Octene (2 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 120 °C for 3.5 hours. Afterwards, the autoclave is cooled to room temperature and pressure was released carefully. Hexadecane (100 μ L) 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: Solvent Screening.

Entry	Solvent	Additive	Yield [%]	n/iso [%]
1	HOAc	-	0	
2	HFIP	-	70	19/81
3	TFA	-	38	25/75
4	Trifluoroethanol	-	0	-
5	Dioxane	-	0	-
6	Dioxane	5 mol% CsF	0	-
7	Anisole	-	0	-
8	Anisole	5 mol% CsF	0	-
9	THF	-	0	-
10	THF	5 mol% CsF	0	-
11	Sulfolane	-	0	-
12	Sulfolane	5 mol% CsF	0	-
13	NMP	-	0	-
14	NMP	5 mol% CsF	0	-
15	2-MTHF	-	0	-
16	2-MTHF	5 mol% CsF	0	-
17	DMF	-	0	-
18	DMF	5 mol% CsF	0	-
19	DMSO	-	0	-
20	DMSO	5 mol% CsF	0	-

Conditions: 1-octene (2 mmol), [Ru₃(CO)₁₂] (5 mol% Ru), PCy₃:Ru (1.1:1, 5.5 mol%), PTSA·H₂O:PCy₃ (3.75:1, 20.79 mol%), H₂O:1-octene (6.5:1), Solvent:1-octene (6.75:1), CO (40 bar), V_R=2 mL.

Table S2: Precursor Screening.

Entry	Acid	Yield [%]	n/iso [%]
1	Ru ₃ (CO) ₁₂	70	19/81
2	RuCl ₃ ·H ₂ O	0	-
3	(Ru(p-Cymene)Cl ₂) ₂	0	-
4	RuCl ₂ (DMSO) ₄	0	-
5	Ru(acac) ₃	63	15/85
6	Benzene-ru-(II)chloride dimer	0	-
7	Ru(II)chlorid-1,5-cyclooctadien	0	-
8	Ru-carbonylhydrido-tris-pph ₃	0	-

Conditions: 1-octene (2 mmol), Ru-precursor (5 mol% Ru), PCy₃:Ru (1.1:1, 5.5 mol%), PTSA·H₂O:PCy₃ (3.75:1, 20.79 mol%), H₂O:1-octene (6.5:1), HFIP:1-octene (6.75:1), CO (40 bar), V_R= 2 mL.

Table S3: Screening of c(Ru), L:M and amount of water.

Entry	c(Ru) mol%	L:M mmol:mmol	H ₂ O:substrate mmol:mmol	Yield [%]	n/iso [%]
1	5	2.2	6.5	69	23/77
2	5	1.1	6.5	70	19/81
3	5	1.1	2	75	22/78
4	5	0.55	6.5	62	13/87
5	5	no L	6.5	65	16/84
6	5	no L	2	60	13/87
7	3	2.2	6.5	39	13/87
8	3	1.1	6.5	67	19/81
9	3	1.1	2	65	15/85
10	3	0,55	6.5	67	16/84
11	3	no L	6.5	66	12/88
12	3	no L	2	54	14/86
13	1	2.2	6.5	32	6/94
14	1	1.1	6.5	40	6/94
15	1	0.55	6.5	26	>1/99
16	1	no L	6.5	39	21/79

Conditions: 1-octene (2 mmol), [Ru₃(CO)₁₂] (5 mol% Ru), PCy₃:Ru (1.1:1, 5.5 mol%), PTSA·H₂O:PCy₃ (3.75:1, 20.79 mol%), H₂O:1-octene (6.5:1), HFIP:1-octene (6.75:1), CO (40 bar), V_R= 2 mL.

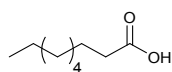
Table S4: Screening gas mixture, pressure and temperature.

Entry	T [°C]	p(CO/H ₂) [bar]	Yield [%]	n/iso [%]
1	100	40 bar CO	59	13/87

2		15 bar CO + 25 bar N ₂	55	16/84
3		40 bar CO	75	22/78
4	120	60 bar CO	63	16/84
5		40 bar CO + 5 bar H ₂	64	20/80
6		35 bar CO + 5 bar H ₂	57	18/82

7	140	40 bar CO	57	22/78

Conditions: 1-octene (2 mmol), [Ru₃(CO)₁₂] (5 mol% Ru), PCy₃:Ru (1.1:1, 5.5 mol%), PTSA·H₂O:PCy₃ (3.75:1, 20.79 mol%), H₂O:1-octene (2:1), HFIP:1-octene (6.75:1), mixtures of CO/N₂ or CO/H₂ (V_G=40-60 bar), V_R= 2 mL.

Characerization of the Acids

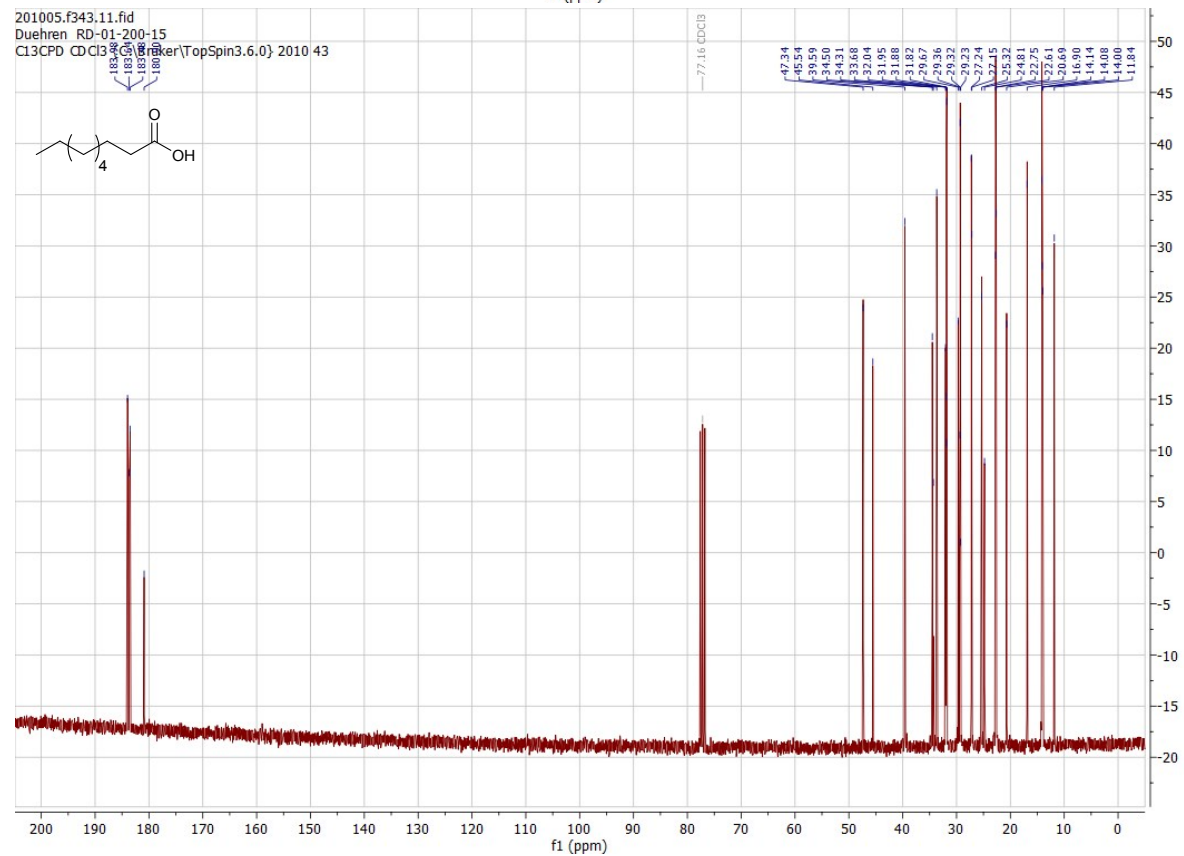
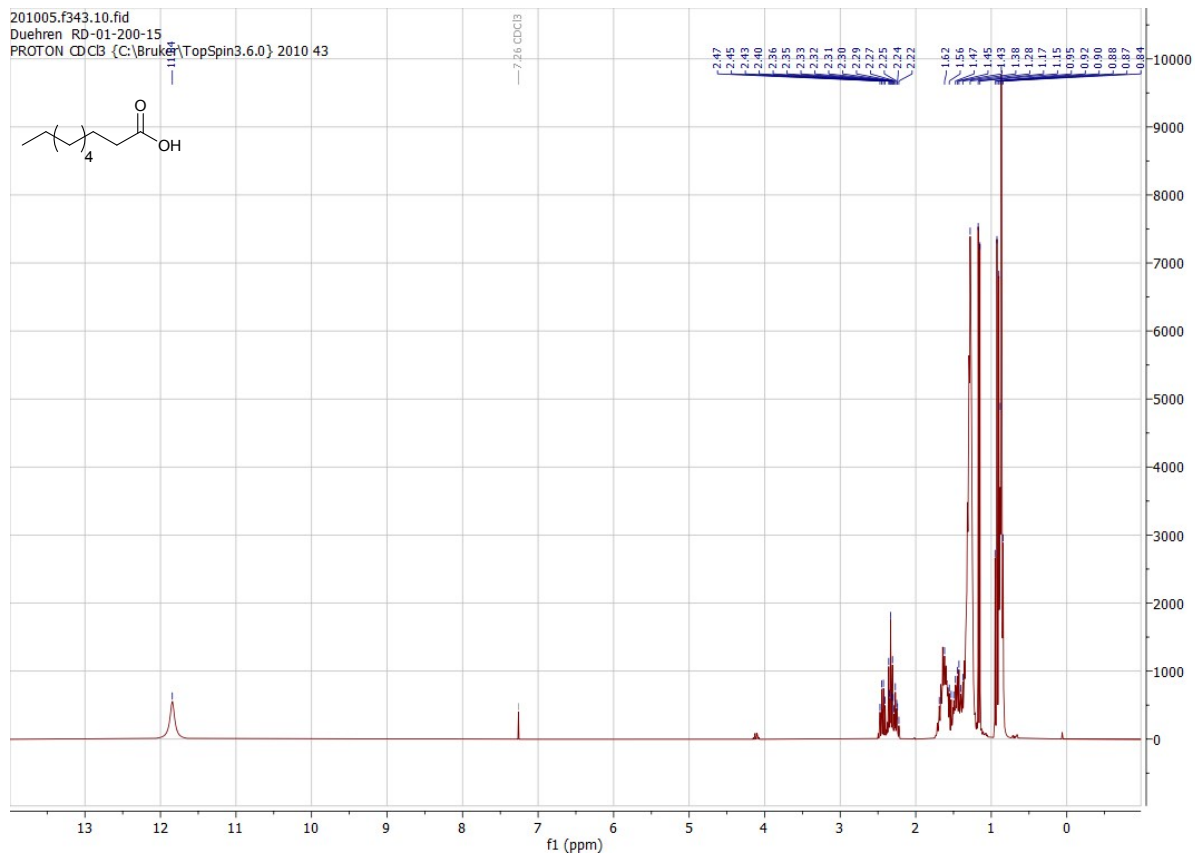
Nonanoic acid (75% GC-yield, 68 % isolated yield)

¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (300 MHz, CDCl₃) show a 22:78 mixture of n/iso nonanoic acid.

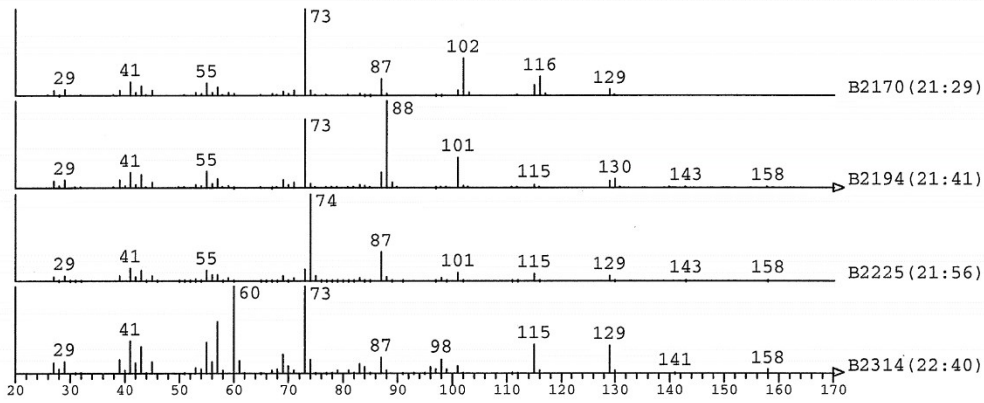
Spectroscopic Data

NMR Spectra

Nonanoic acid (+isomers)

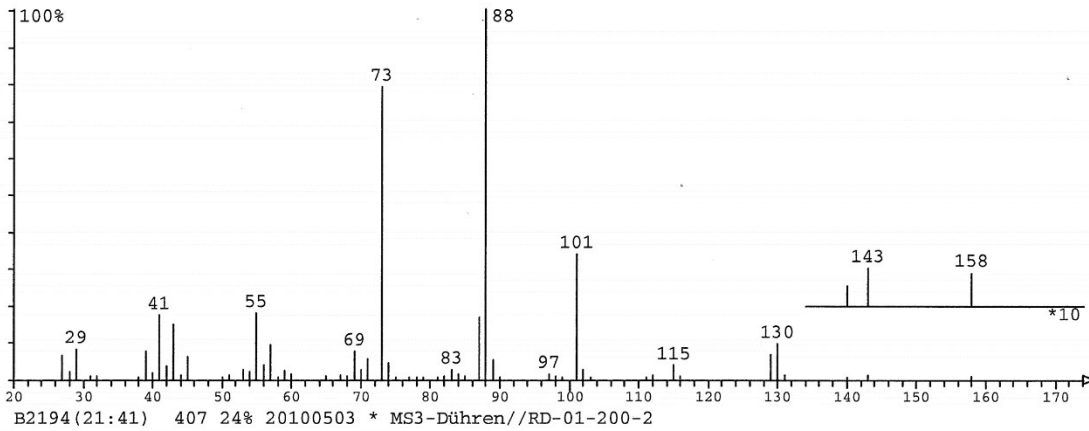
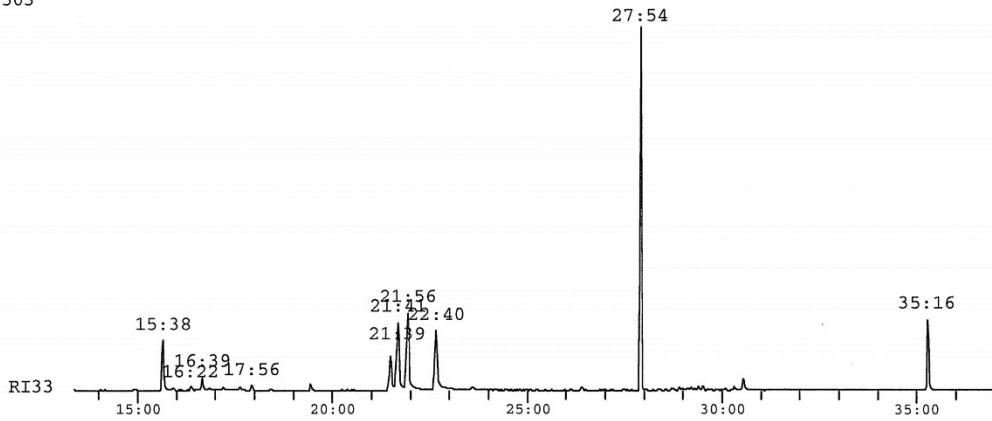


GC/MS



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27	6.37	59	2.16	89	5.30
28	1.84	60	1.39	90	0.63
29	7.99	65	0.71	97	1.37
31	0.75	67	1.20	98	0.80
32	0.67	68	0.91	99	0.63
38	0.47	69	7.48	101	34.00
39	7.46	70	2.66	102	2.45
40	1.62	71	5.55	103	0.40
41	17.28	73	79.24	111	0.64
42	3.44	74	4.19	112	1.00
43	14.63	75	0.63	115	3.58
44	0.99	77	0.51	116	0.67
45	5.88	78	0.39	129	6.62
50	0.37	79	0.66	130	9.55
51	1.07	81	0.56	131	1.13
53	2.54	82	0.68	140	0.53
54	1.87	83	2.61	143	1.00
55	17.85	84	1.45	158	0.88
56	3.77	85	0.85		
57	9.28	87	16.88		
58	0.56	88	100.00		

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