Experimental Section

General Methods: Unless otherwise stated, all chemicals were purchased from commercial suppliers and were used without further purification. Dry dichloromethane were used. Chemical shifts were referenced to residual solvent protons. Signal multiplicity as follows: s (singlet), d (doublet), t (triplet), q (quartet), qu (quintet), m (multiplet).

1. General procedure for the synthesis of Dimethyl (2*E*)-but-2-en-1-yl(prop-2-yn-1-yl) propanedioate 4

Propargyl bromide (4.24 g, 80% solution in toluene, 28.5 mmol), 2-allylmaloninc acid dimethylester (3.47 g, 18.7 mmol) and Cs_2CO_3 (12.6 g, 38.7 mmol) were dissolved in acetone (45 mL). The reaction mixture was stirred at room temperature for 20 h. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (PE/EA = 20:1) to yield 3.98 g (17.8 mmol, 95%) of the product as colourless oil.

R_f (PE/EA = 20:1) = 0.44; ^1H NMR (250 MHz, $CDCl_3$, 25°C): δ = 5.50-5.70 (m, 1H), 5.11-5.30 (m, 1H), 3.76 (s, 6H), 2.78 (d, J = 2.6, 2H), 2.73 (d, *J* = 7.5 Hz, 2H), 2.01 (t, *J* = 2.0 Hz, 1H), 1.65 (d, *J* = 6.2 Hz, 3H).
The spectroscopic data corresponds to that reported in the literature.[1]

2. General procedure for the synthesis of 4-methyl-N-((5-methylfuran-2-yl)methyl)-N-(prop-2-yn-1-yl)benzenesulfonamide 7

To (5-methylfuran-2-yl)methanamine (2.80 g, 25.2 mmol) and triethylamine (2.5 g, 25.2 mmol) in dichloromethane (40 mL) at room temperature TsCl (4.83 g, 25.2 mmol) was added in small portions and then stirred overnight. After the slow addition of water (30 mL), separation of the organic layer, two extractions of the aqueous layer with dichloromethane (2 X 20 mL), the combined organic layers were dried over MgSO4 and then filtered. After the solvent was removed under vacuum and the residue was recrystallised from diethyl ether, 6.0 g of 4-methyl-*N*-((5-methylfuran-2-yl)methyl)benzenesulfonamide were isolated as white crystals (22.7 mmol, 90%).

The previously obtained tosylamine (4.70 g, 17.7 mmol) was dissolved in acetone (30 mL), K_2CO_3 (4.88 g, 35.4 mmol) and propargyl bromide (3.42 g, 80% solution in toluene, 21.2 mmol) were added and the mixture was stirred at room temperature for 24 h. Then the solvent was removed under vacuum, the residue was taken up in water (30 mL) and dichloromethane (20 mL) and the product was extracted with two additional portions of dichloromethane (20 mL). After removal of the solvent, the residue was recrystallised from diethyl ether to afford 5.06 g compound **7** (16.7 mmol, 94%).

R_f (PE/EA = 2:1) = 0.44; ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C): δ = 7.73 (d, J=8.4 Hz, 2H), 7.28 (d, J=8.4 Hz, 2H), 6.15 (d, J=3.1 Hz, 1 H), 5.86 (d, J=3.1 Hz, 1 H), 4.37 (s, 2H), 4.01 (d, J=2.5 Hz, 2 H), 2.42 (s, 3 H), 2.19 (s, 3 H), 2.06 (t, J=2.5 Hz, 1 H).
The spectroscopic data corresponds to that reported in the literature.[2]

3. General procedure for the synthesis of 2-(5-Hydroxypent-1-ynyl)benzyl alcohol 9

In a dry schlenk flask, 2-iodobenzyl alcohol (4.68 g, 20.0 mmol), 4-pentyn-1-ol (2.02 g, 24.0 mmol) and triethylamine (60 mL) were added. The solution was degassed *via* three freeze-pump-thaw cycles. After the addition of [$Pd(PPh_3)_4$] (0.23 g, 0.200 mmol) and CuI (76.2 mg, 0.400 mmol) the reaction mixture was stirred under nitrogen at room temperature overnight. Finally the reaction mixture was filtrated over celite and the solvent removed in *vacuo* to give the crude product as a thick oil. The crude product was purified by column chromatography (Petrolether:Ethylacetate, 1:1) to afford **9** as white crystals (3.50 g, 18.4 mmol, 92%).

R_f=0.40 (Petrolether/Ethyl acetate 2:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 7.39 (t, J = 7.0 Hz, 2H), 7.26 (m, 2H), 4.78 (s, 2H), 3.83 (t, J = 6.0 Hz, 2H), 2.59 (t, J = 6.9 Hz, 2H), 1.92 (br s, 2H), 1.88 (qu, J = 6.5 Hz, 2H).
The ^{1}H NMR corresponds to that reported in the literature. [3]

4. General Procedure for the Catalytic Activity

4.1 General Procedure for the Preparation of Substrate Stock Solution

In a 5 mL volumetric flask were added 1 mmol) of the corresponding substrate and 12.3 mg (50 µmol) of 1,3,5-tri-tert-butylbenzene as internal standard in deuterated dichloromethane. For each NMR-scale catalytic experiment, 500 µL of this stock solution were used (0.1 mmol).

4.2 General Procedure for the Preparation of Gold Catalysts Stock Solutions

Initially, 1.0 µmol of the gold catalyst were diluted in 1 mL CD_2Cl_2, producing the general stock solution 0.001 M. From the latter different dilutions were made. First, taking an aliquot of 100 µL and making a dilution in 1 mL volumetric flask to produce the 0.0001 M solution, and then, by the same manner, successive dilutions until reaching the desired concentration.

4.3 General Procedure for the Preparation of $AgSbF_6$ Stock Solutions

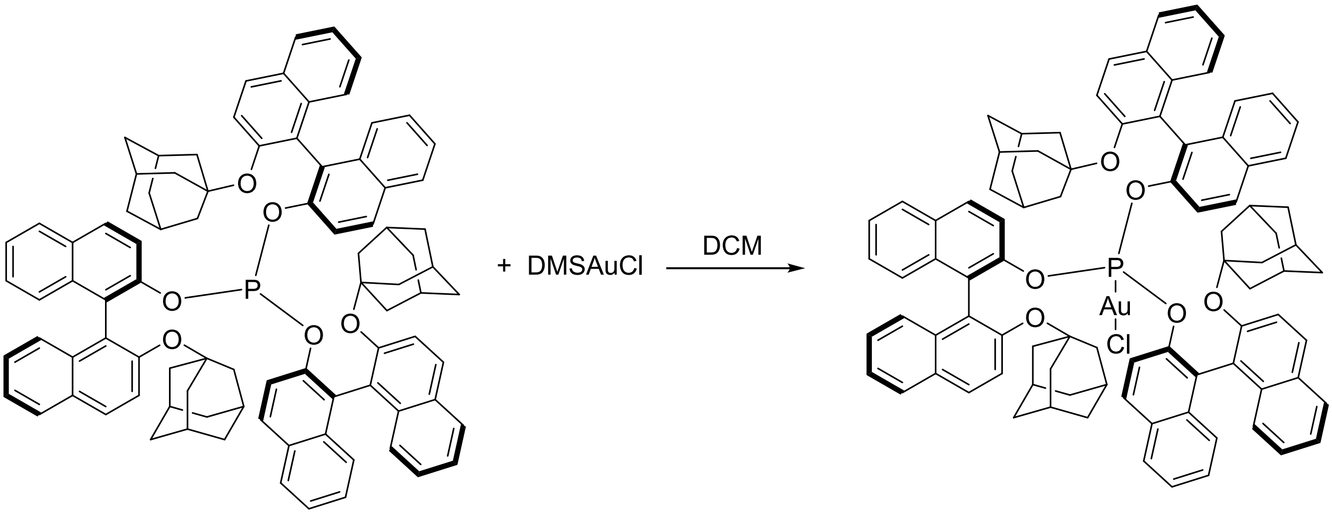
Initially, 1.717 mg (5.0 µmol) of $AgSbF_6$ were diluted in 5 mL CD_2Cl_2, producing the general stock solution 0.001 M. From the latter different dilutions were made. First, taking an aliquot of 100 µL and making a dilution in 1 mL volumetric flask to produce the 0.0001 M solution, and then, by the same manner, successive dilutions until reaching the desired concentration.

4.4 General Procedure for an NMR-Scale Catalytic Procedure.

In a typical experiment, 500 µL of the stock solution previously prepared (substrate 0.1 mmol) and 1,3,5-tri-tert-butylbenzene (1.23 mg, 5.0 µmol, 5mol%)), were added in a NMR tube. After addition of the corresponding stock solution of the catalyst and the silver salt, the reaction mixture was allowed to stir during the denounced time at the denounced temperature. Conversion of the starting material to product, as well as the yield of the reaction was determined by integration in the ^{1}HNMR spectrum of the product relative to the internal standard. Complete conversion was taken to be the time where no remaining substrate was detected.

5. Synthesis and Characterization of the Phosphite Catalysts

5.1 Catalyst 1

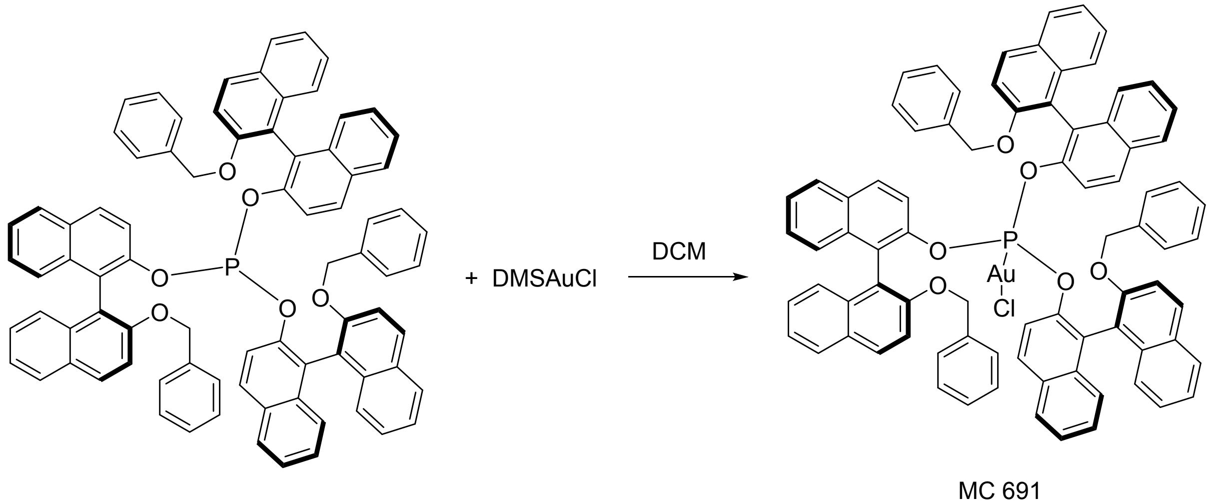


MC 695

In a flame dried Schlenk flask protected from the light, the phosphite ligand (7.00 mg, 5.43 µmol) was dissolved in dried dichloromethane (500 µL) and the DMSAuCl (1.60 mg, 5.43 µmol) was slowly added. The reaction mixture was stirred during 1 h at room temperature. After completion of the reaction, the volatiles were removed in vacuum and the crude product was purified by flash chromatography (1:1, DCM: PE). After recrystallization from pentane/DCM, the gold complex **MC 695** was obtained as colorless crystals (6.10 mg, 4.01 µmol, 74 %).

R_f (DCM/PE=1:1) = 0.28; ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.89 (dd, J = 8.4, 4.2 Hz, 6H), 7.71 (d, J = 8.3 Hz, 3H), 7.42 (d, J = 8.8 Hz, 3H), 7.39-7.30 (m, 6H), 7.23-7.12 (m, 6H), 7.02 (dd, J = 8.4, 4.4 Hz, 6H), 6.88 (d, J = 8.8 Hz, 3H), 6.19 (d, J = 8.8 Hz, 3H), 1.92 (s, 9H), 1.59 – 1.25 (m, 36H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 152.2 (3C), 145.8 (3C), 134.0 (3C), 133.6 (3C), 130.8 (3C), 130.0 (3C), 129.2 (3C), 128.8 (3C), 127.9 (3C), 127.7 (3C), 126.7 (3C), 126.5 (3C), 126.2 (3C), 125.0 (3C), 124.7 (3C), 124.2 (3C), 124.2 (3C), 124.1 (3C), 123.9 (3C), 118.70 (3C), 79.1 (3C), 43.2 (9C), 36.0 (9C), 30.9 (9C); ^{31}P NMR (162 MHz, $CDCl_3$, 25°C): δ = 107.96; IR (KBr-Pressling): 3357, 3056, 2957, 2925, 2853, 1943, 1792, |746, 1660, 1621, 1590, 1557, 1540, 1505, 1458 cm^{-1}; HRMS (ESI): $[C_{90}H_{81}AuO_6P]^+$: calcd 1485.5431, found 1485.5459.

5.2 Catalyst 2

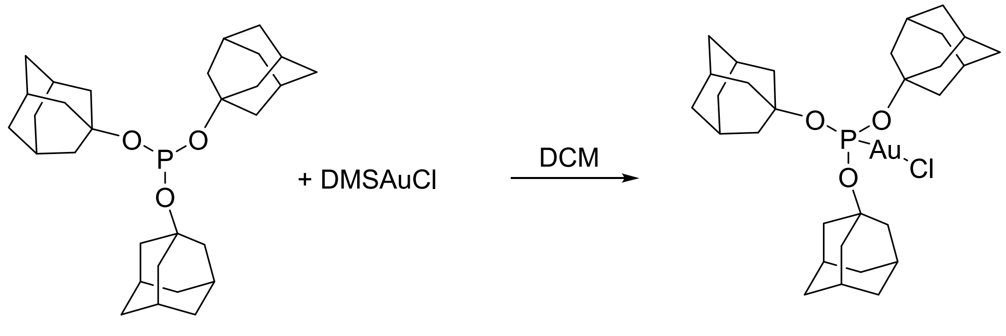


MC 691

In a flame dried Schlenk flask protected from the light, the phosphite ligand (23.15 mg, 20.0 µmol) was dissolved in dried dichloromethane (1.00 mL) and the DMSAuCl (5.90 mg, 20.0 µmol) was slowly added. The reaction mixture was stirred during 2 h at room temperature. After completion of the reaction, the volatiles were removed in vacuum and the crude product was purified by flash chromatography (1:1, DCM: PE). After recrystallization from pentane/DCM, the gold complex **MC 691** was obtained as colorless crystals (21.8 mg, 15.69 µmol, 78 %).

R_f (DCM/PE=1:1) = 0.10; ^{1}H-NMR (500 MHz, CD_2Cl_2, 25°C, TMS): δ = 7.92 (dd, J = 8.6, 3.2 Hz, 6H), 7.80 (d, J = 8.2 Hz, 3H), 7.44 (t, J = 7.5 Hz, 3H), 7.36 (t, J = 7.5 Hz, 3H), 7.27 (d, J = 9.1 Hz, 3H), 7.25 – 7.18 (m, 6H), 7.06 – 7.01 (m, 12H), 7.00 (d, J = 9.0 Hz, 3H), 6.95 (d, J = 8.5 Hz, 3H), 6.83 (dd, *J* = 7.3, 1.8 Hz, 6H), 6.00 (d, *J* = 9.0 Hz, 3H), 5.00 (d, *J* = 12.7 Hz, 3H), 4.87 (d, *J* = 12.7 Hz, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2, 25°C, TMS): δ = 154.2 (3C), 145.4 (3C), 137.1 (3C), 133.7 (3C), 133.5 (3C), 131.1 (3C), 130.3 (3C), 129.4 (3C), 129.2 (3C), 128.1 (6C), 128.0 (3C), 127.9 (3C), 127.5 (3C), 127.4 (3C), 126.8 (6C), 126.7 (3C), 126.0 (3C), 125.5 (3C), 125.1 (3C), 124.1 (3C), 119.1 (3C), 117.7 (3C), 115.2 (3C), 70.5 (3C); ^{31}P NMR (202 MHz, CD_2Cl_2, 25°C): δ = 108.48; IR (KBr-Pressling): 3433, 2928, 1623, 1507, 1455, 1273, 1208, 1187, 1147 cm^{-1}; HRMS (FAB, NBA) $[C_{81}H_{57}AuO_6PCl]^+$: calcd 1388.3247, found 1388.3280.

5.3 Catalyst 3

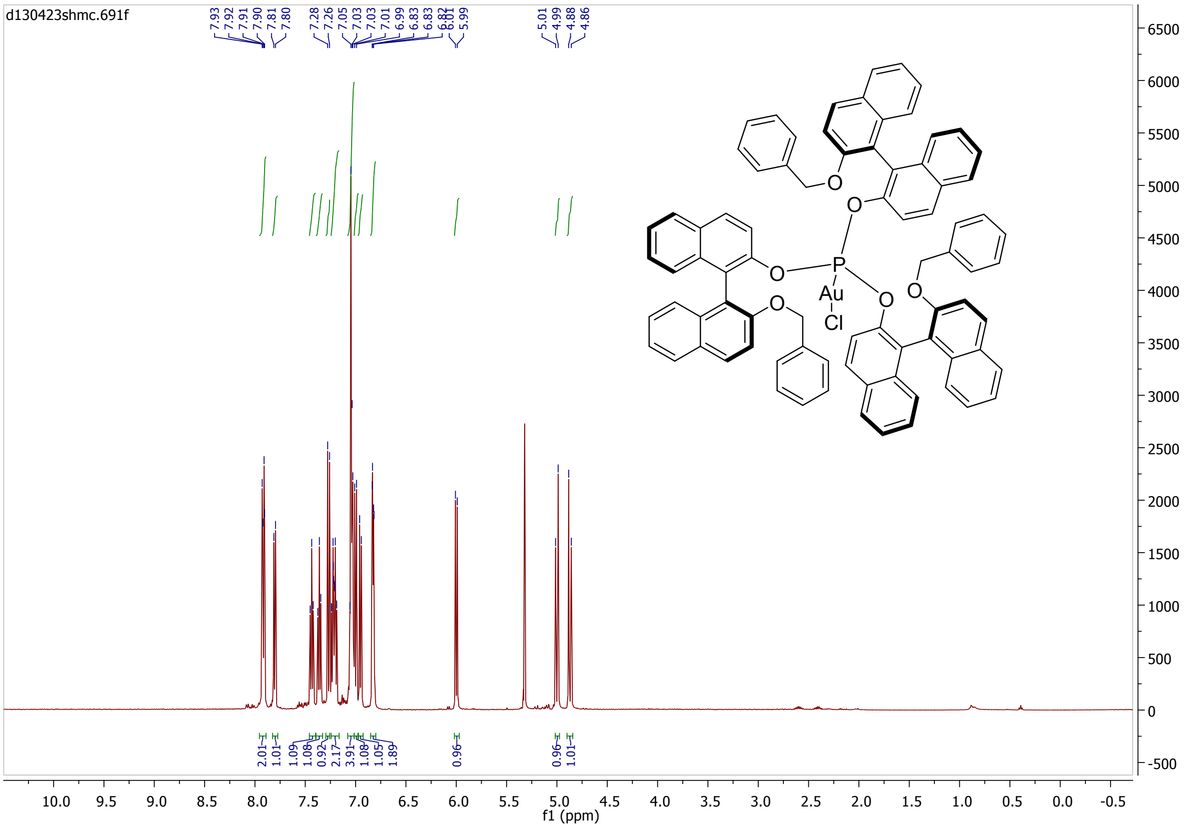


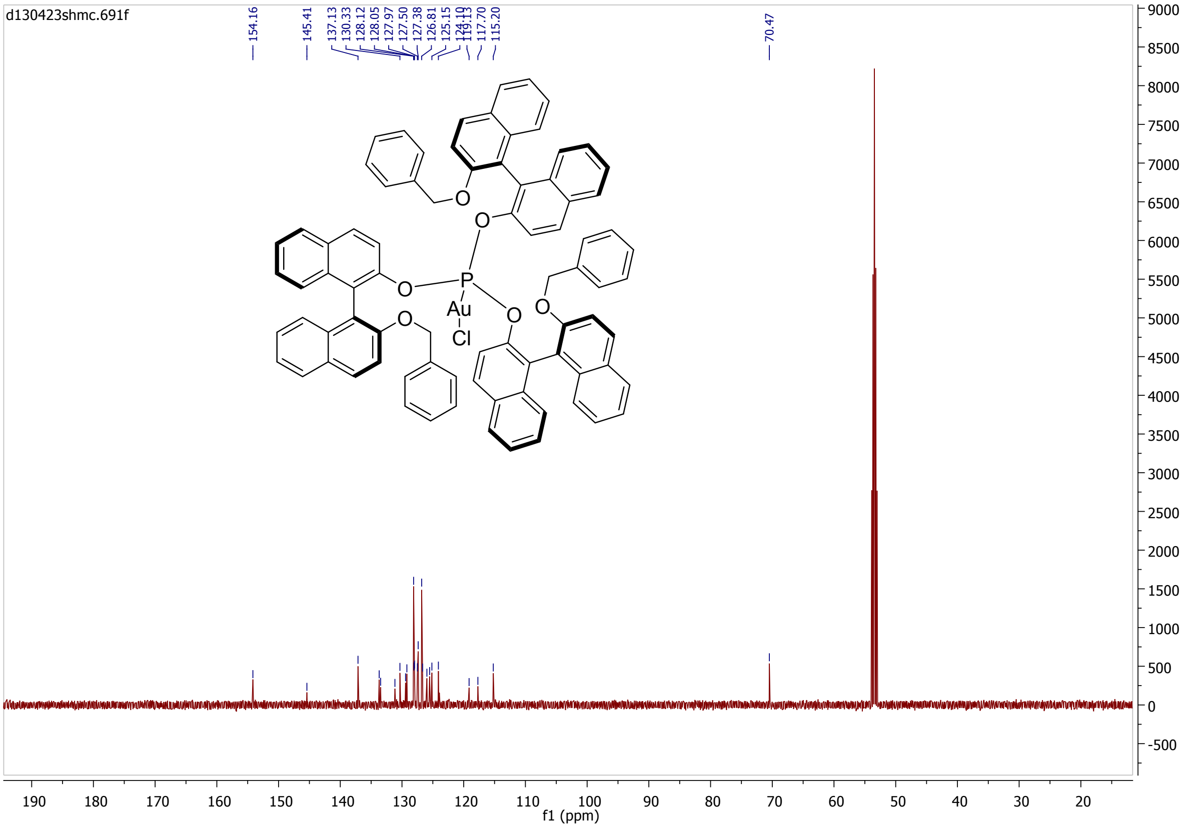
MC 680

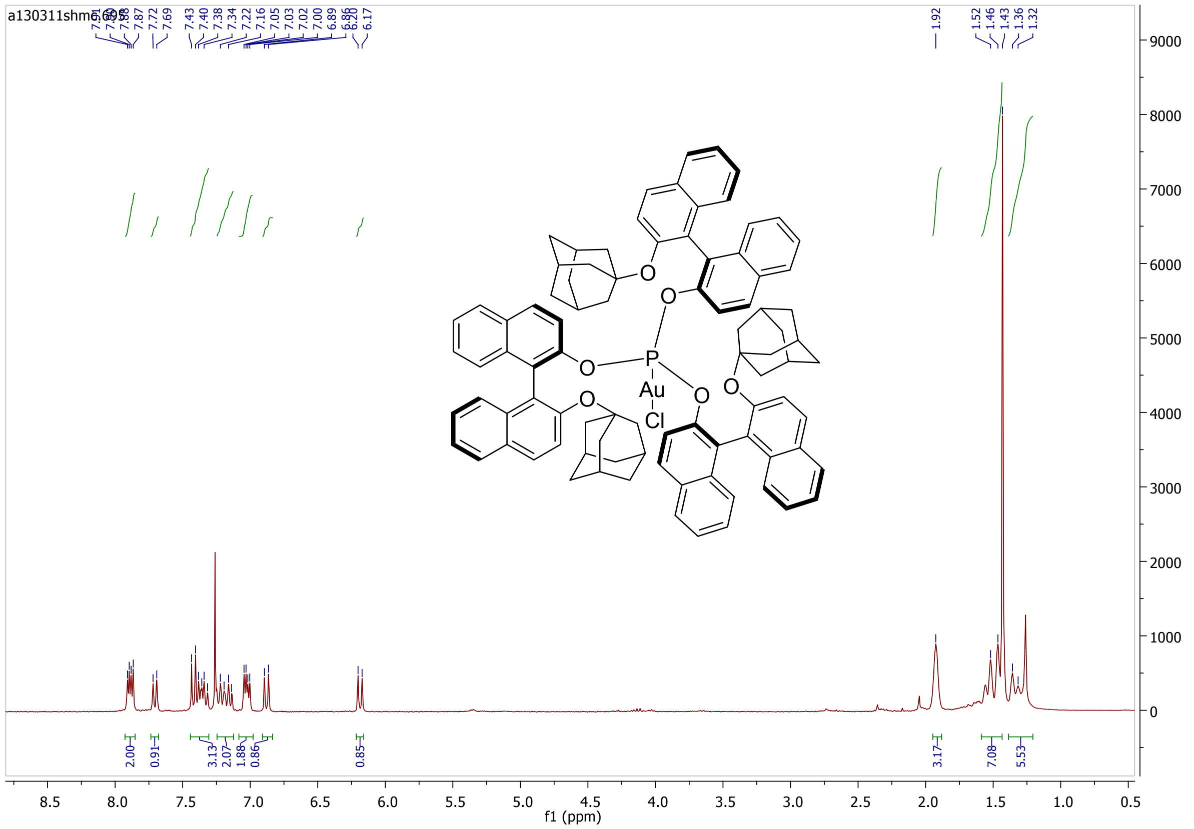
In a flame dried Schlenk flask protected from the light, the phosphite ligand (48.46 mg, 100.0 µmol) was dissolved in dried dichloromethane (5.00 mL) and the DMSAuCl (29.42 mg, 100.0 µmol) was slowly added. The reaction mixture was stirred during 1 h at room temperature. After completion of the reaction, the volatiles were removed in vacuum and the crude product was purified by flash chromatography (1:1, DCM: PE). After recrystallization from pentane/DCM, the gold complex **MC 680** was obtained as colorless crystals (54.0 mg, 75.31 µmol, 75 %).

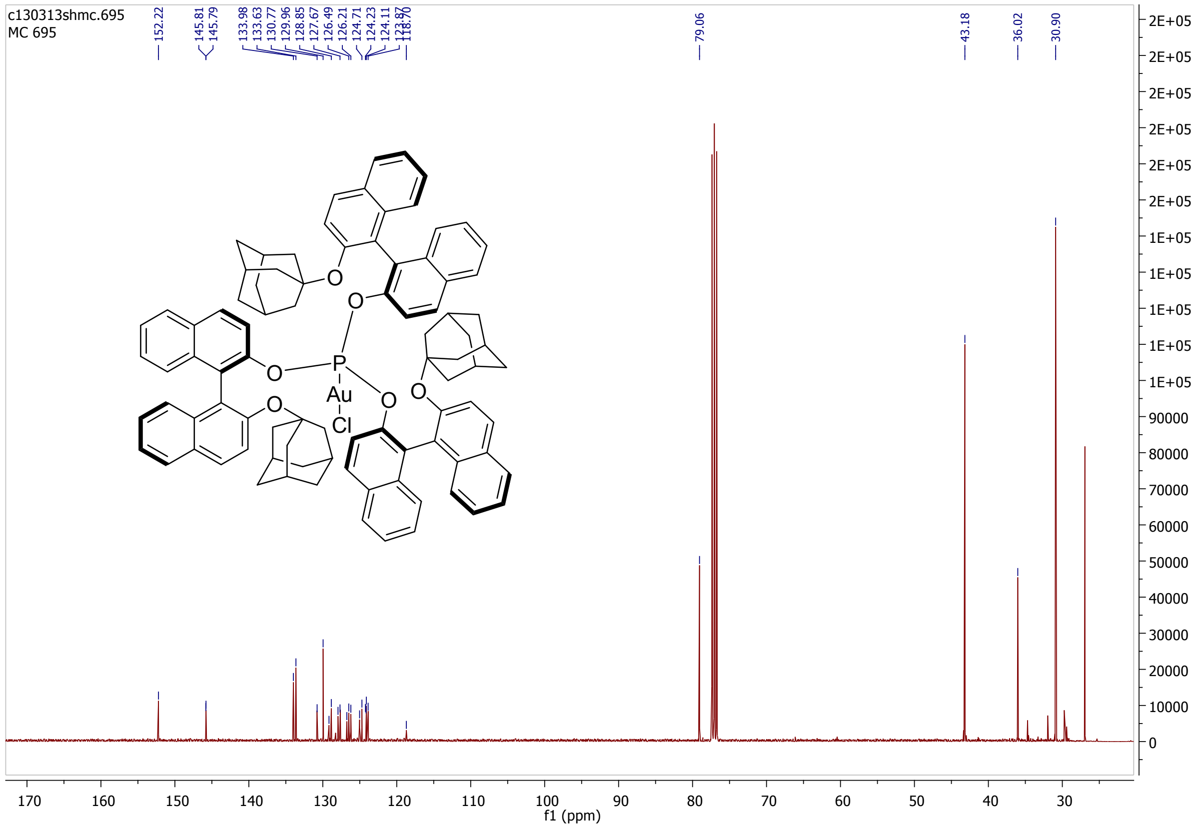
R_f (DCM/PE=1:1) = 0.20; ^{1}H-NMR (600 MHz, C_6D_6, 25°C, TMS): δ = 2.27 (s, 18H), 1.91 (s, 9H), 1.43 (d, *J* = 12.4 Hz, 9H), 1.35 (d, *J* = 12.4 Hz, 9H); ^{13}C NMR (151 MHz, C_6D_6, 25°C, TMS): δ = 83.2 (3C), 45.0 (9C), 35.55 (9C), 31.12 (9C); ^{31}P NMR (243 MHz, C_6D_6, 25°C): δ = 92.10; IR (KBr-Pressling): 3445, 2912, 2852, 1638, 1455, 1369, 1353, 1316, 1300, 1272, 1186 cm^{-1}; HRMS (FAB, NBA): $[C_{30}H_{45}AuO_3PCl]^+$: calcd 716.2461, found 716.2510.

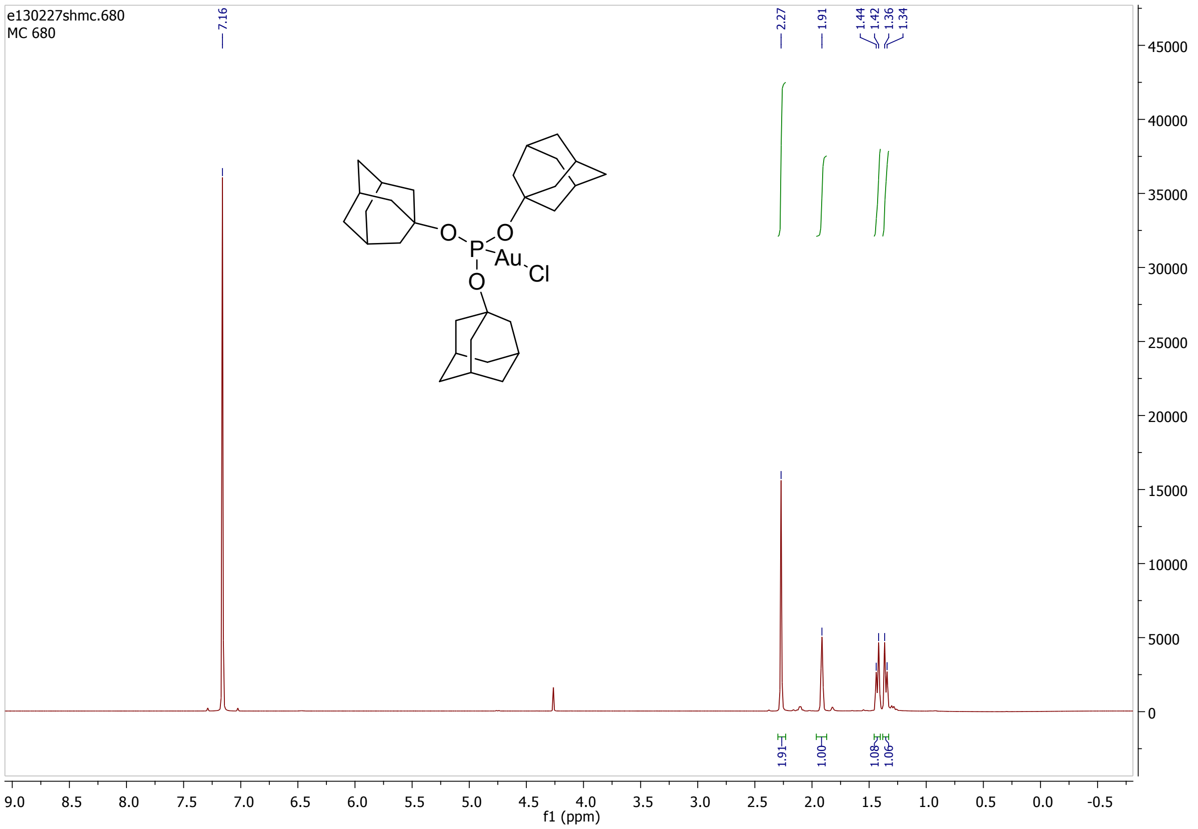
6. ^{1}H and ^{13}C NMR Spectra of Catalysts 1-3

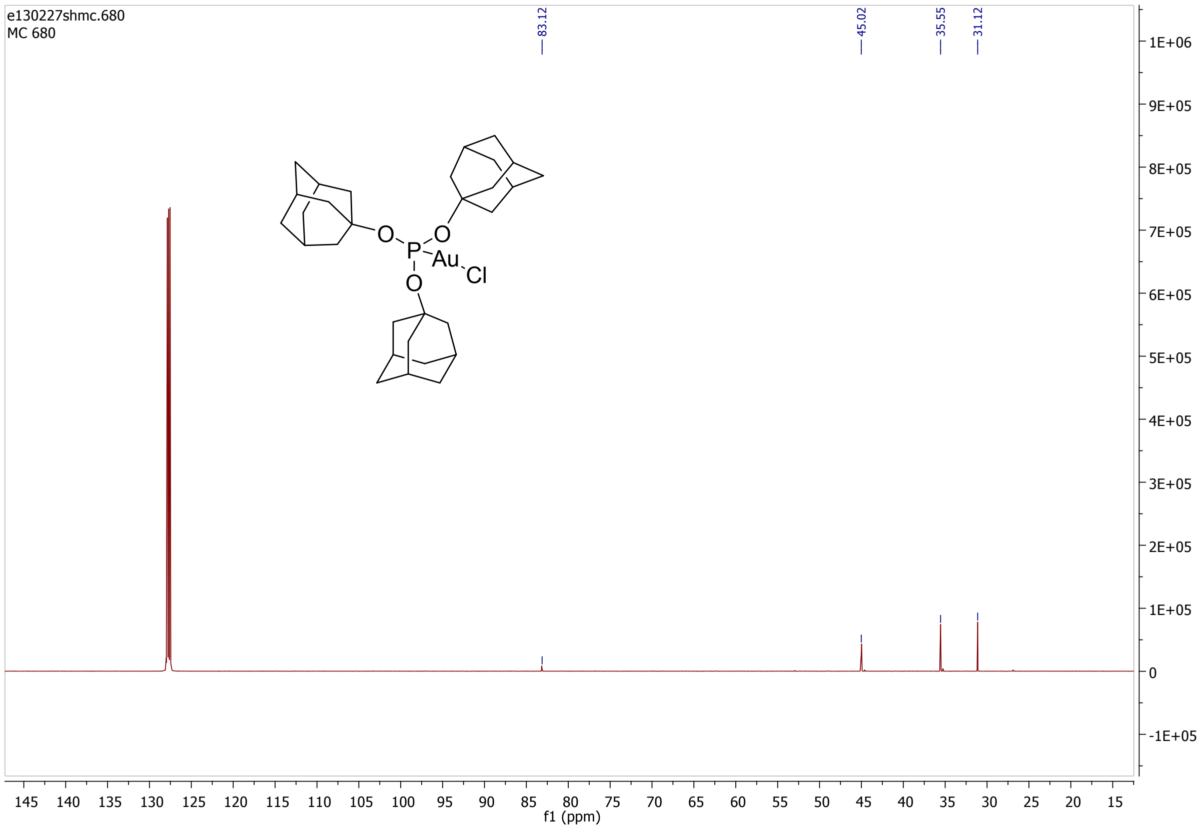





a130311shmc.695
7.91
7.90
7.88
7.87
7.72
7.69
7.43
7.40
7.38
7.34
7.22
7.16
7.05
7.03
7.02
7.00
6.89
6.86
6.20
6.17
1.92
1.52
1.46
1.43
1.36
1.32
O
P
Au
Cl
2.00
0.91
3.13
2.07
1.88
0.86
0.85
3.17
7.08
5.53
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


c130313shmc.695
MC 695
152.22
145.81
145.79
133.98
133.63
130.77
129.96
128.85
127.67
126.49
126.21
124.71
124.23
124.11
123.87
118.70
79.06
43.18
36.02
30.90
O
P
Au
Cl
2E+05
2E+05
2E+05
2E+05
2E+05
2E+05
1E+05
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

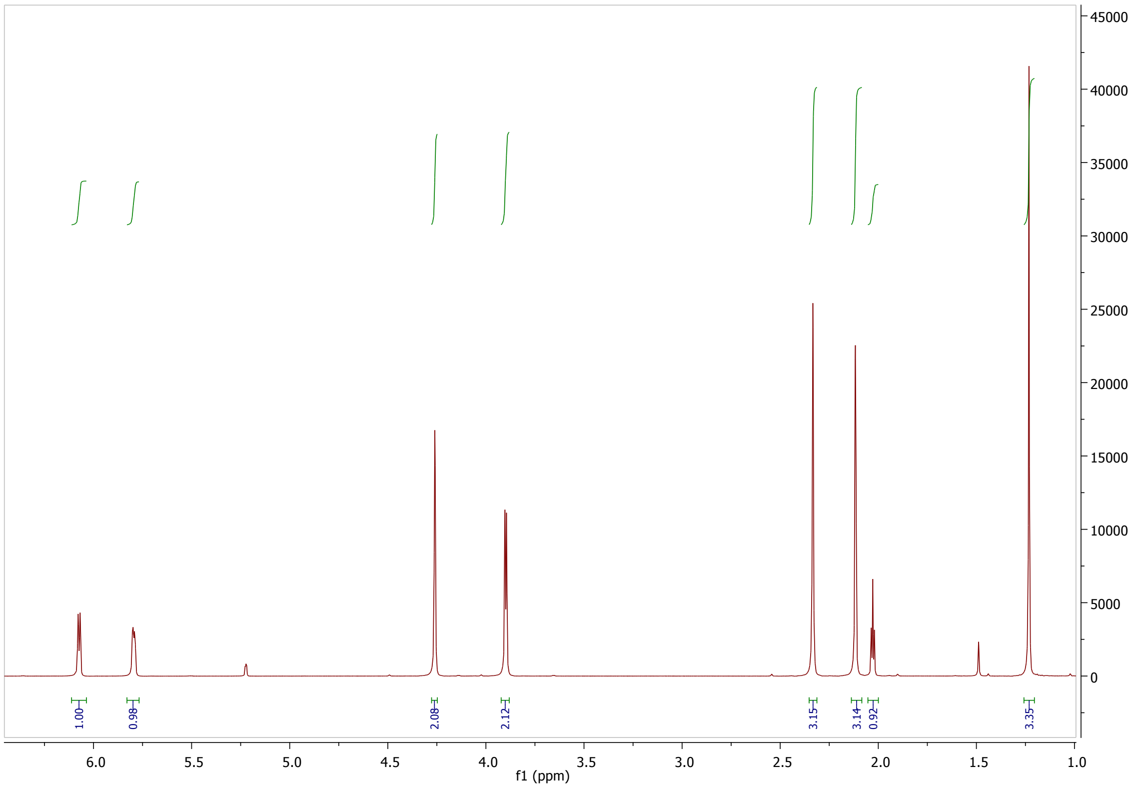

e130227shmc.680
MC 680
7.16
2.27
1.91
1.44
1.42
1.36
1.34
O
P
Au
Cl
1.91
1.00
1.08
1.06
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


e130227shmc.680
MC 680
83.12
45.02
35.55
31.12
O
P
Au
Cl
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
-1E+05
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

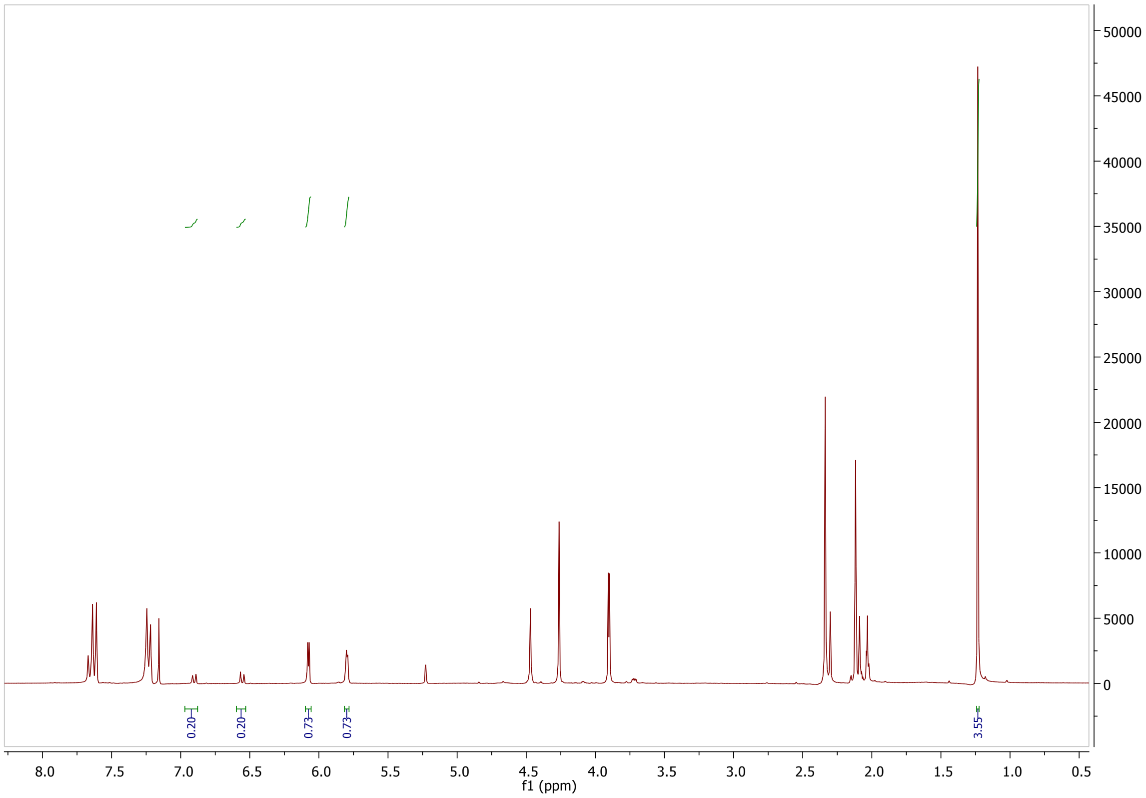
7. NMR Spectra Catalytic Conversions for Substrate 7.

7.1 Catalyst: 1. Catalyst loading: 0,001 mol%.

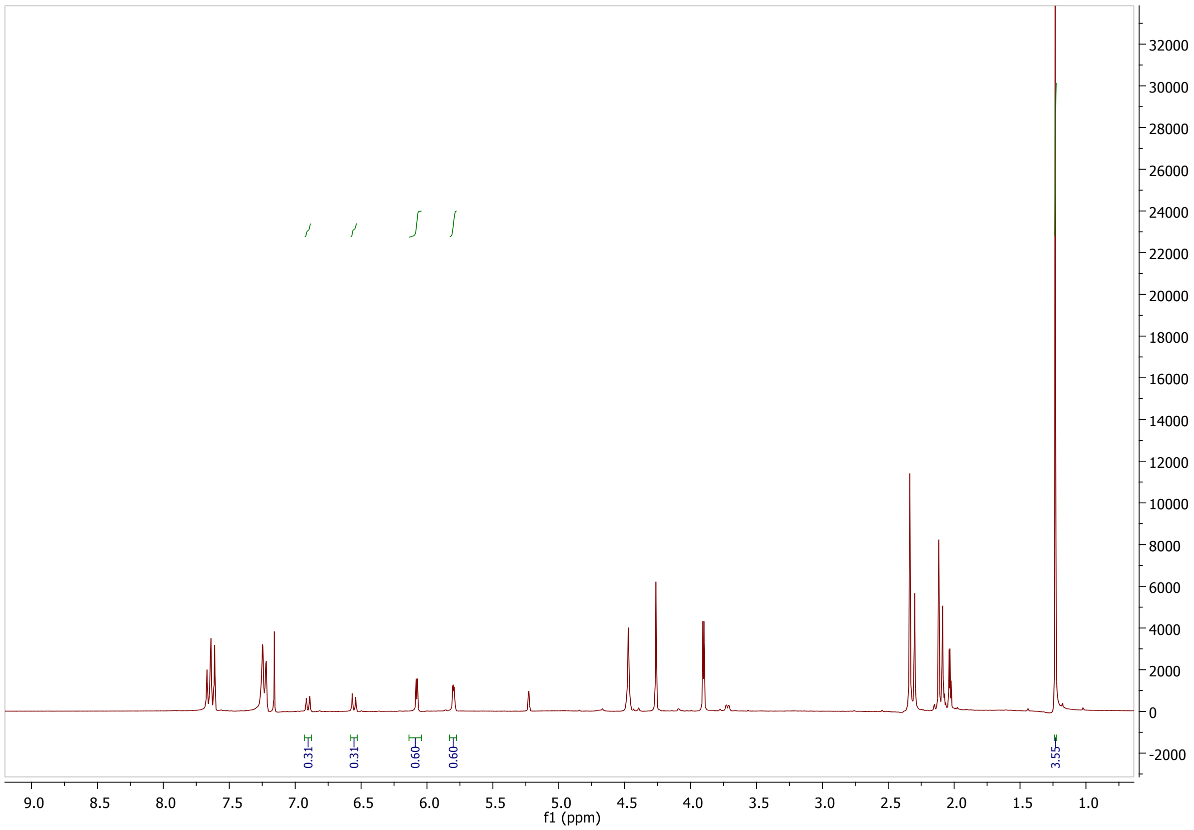
Time: 0 h, Conversion 0%



Time: 20 h, Conversion 27%, yield 20%

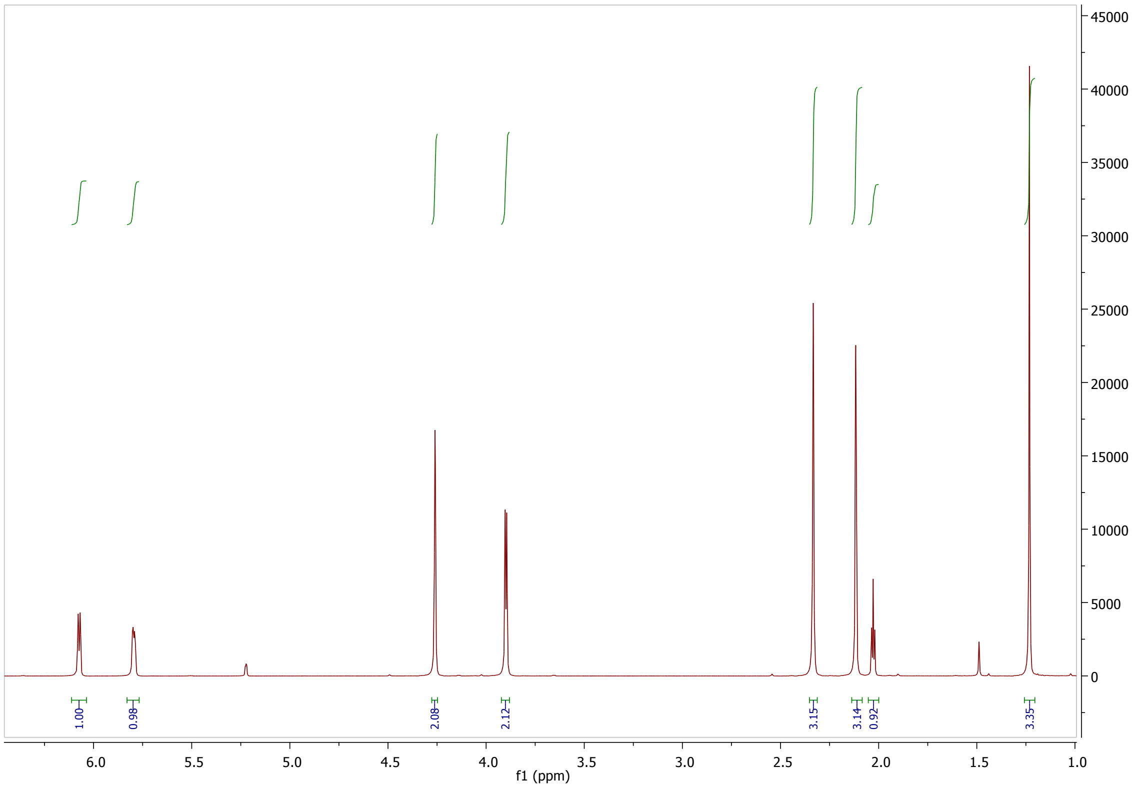


Time: 40 h, Conversion 40%, yield 31%

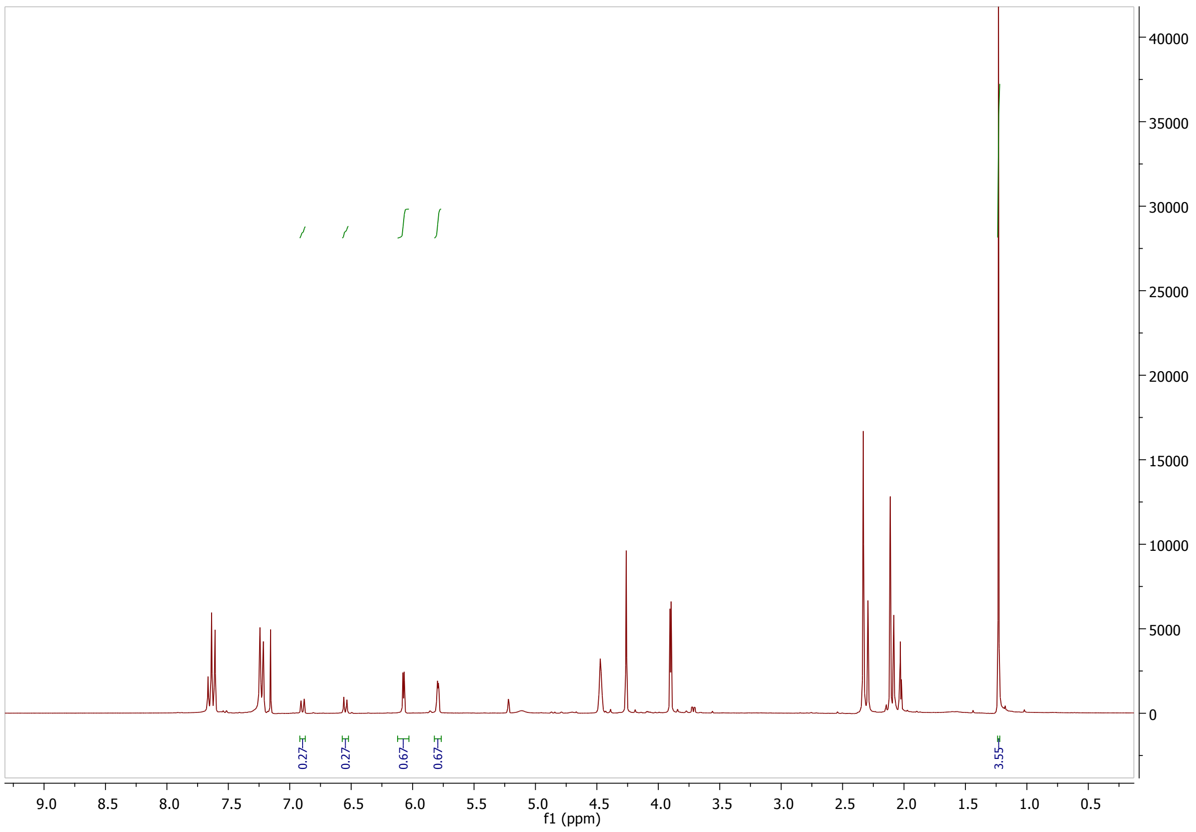


7.2 Catalyst: 2. Catalyst loading: 0,001 mol%.

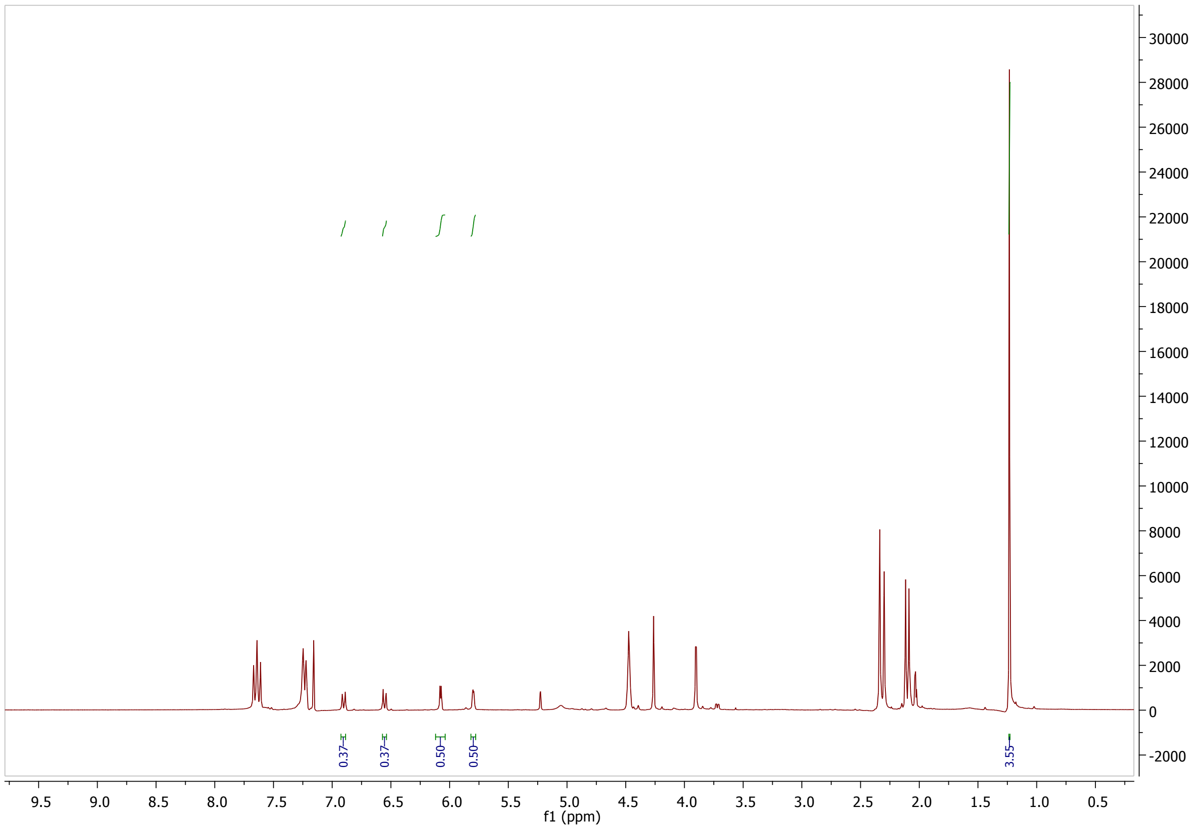
Time: 0 h, Conversion 0%



Time: 20 h, Conversion 33%, yield 27%

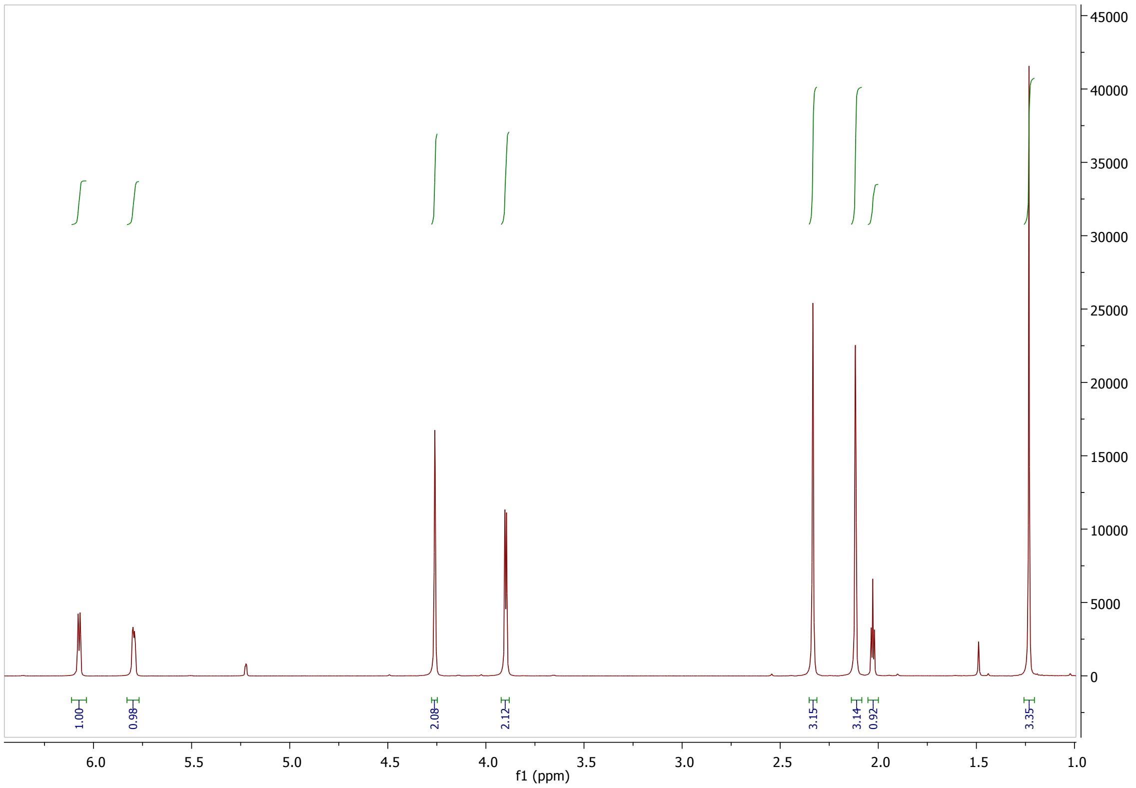


Time: 40 h, Conversion 50%, yield 37%

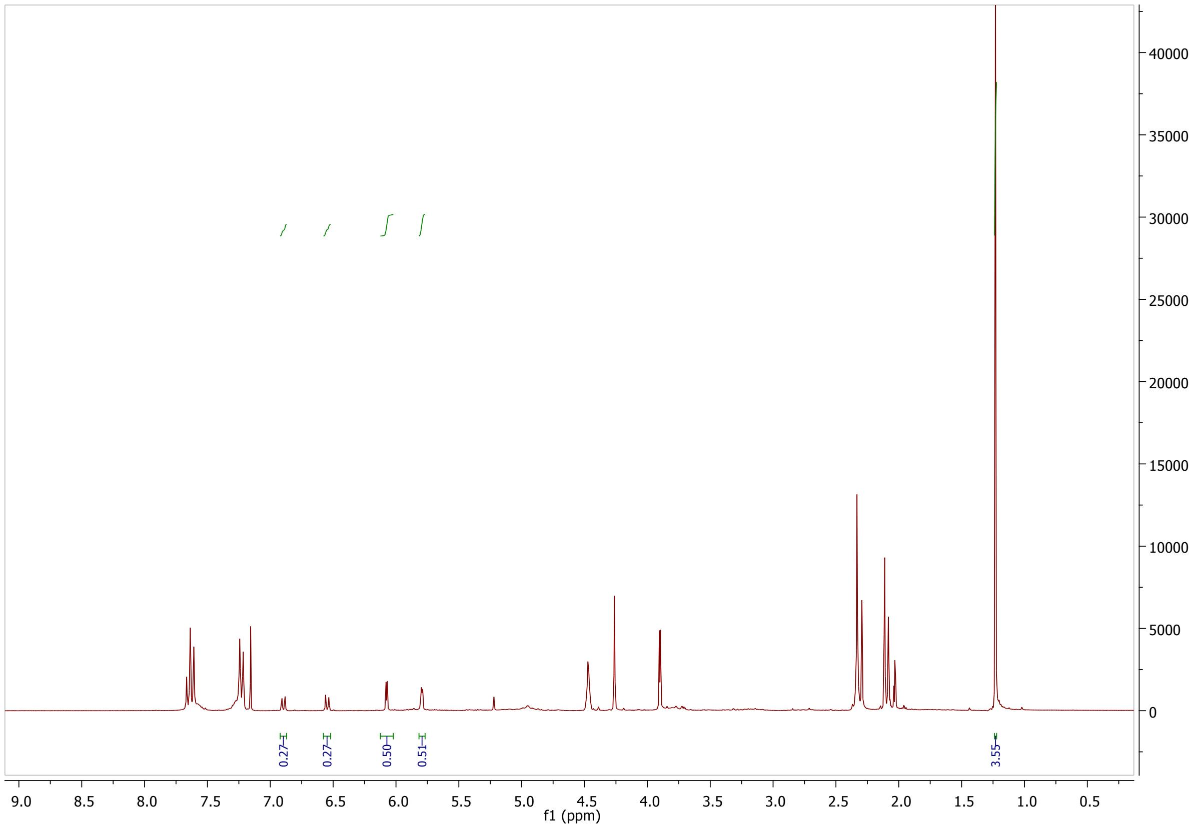


7.3 Catalyst: 3. Catalyst loading: 0,001 mol%.

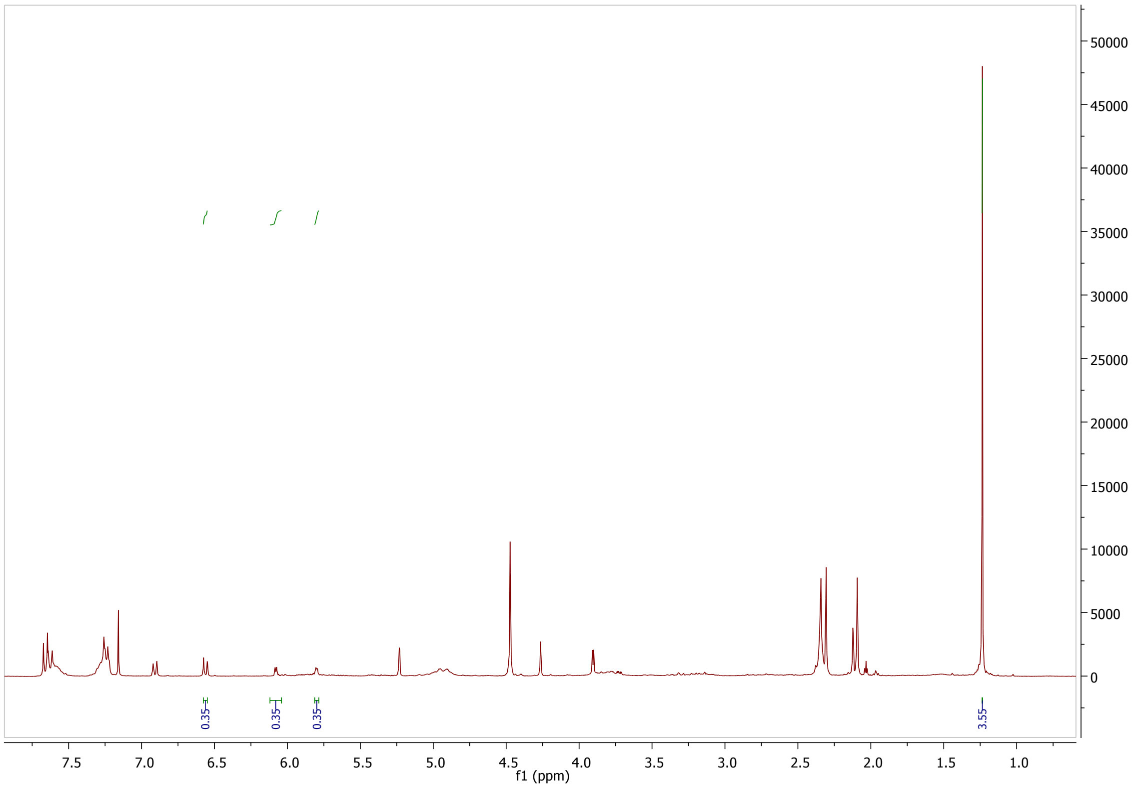
Time: 0 h, Conversion 0%



Time: 20 h, Conversion 50%, yield 27%



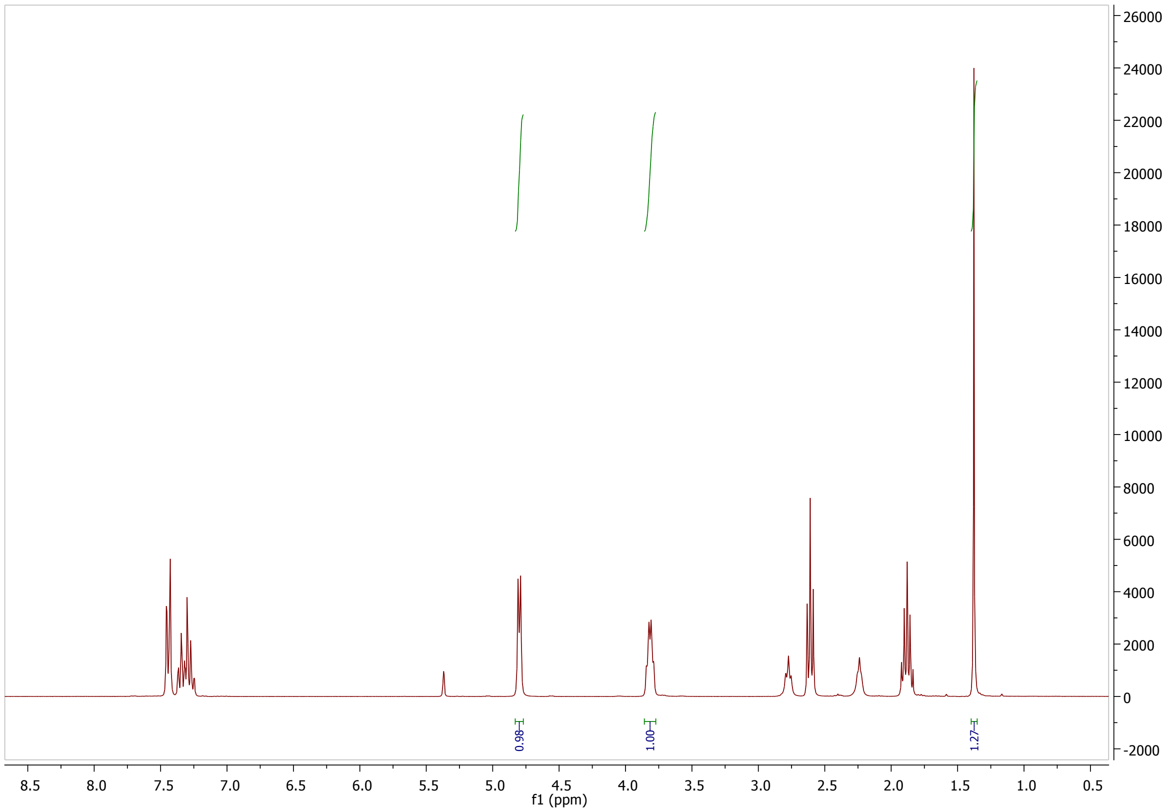
Time: 40 h, Conversion 65%, yield 35%



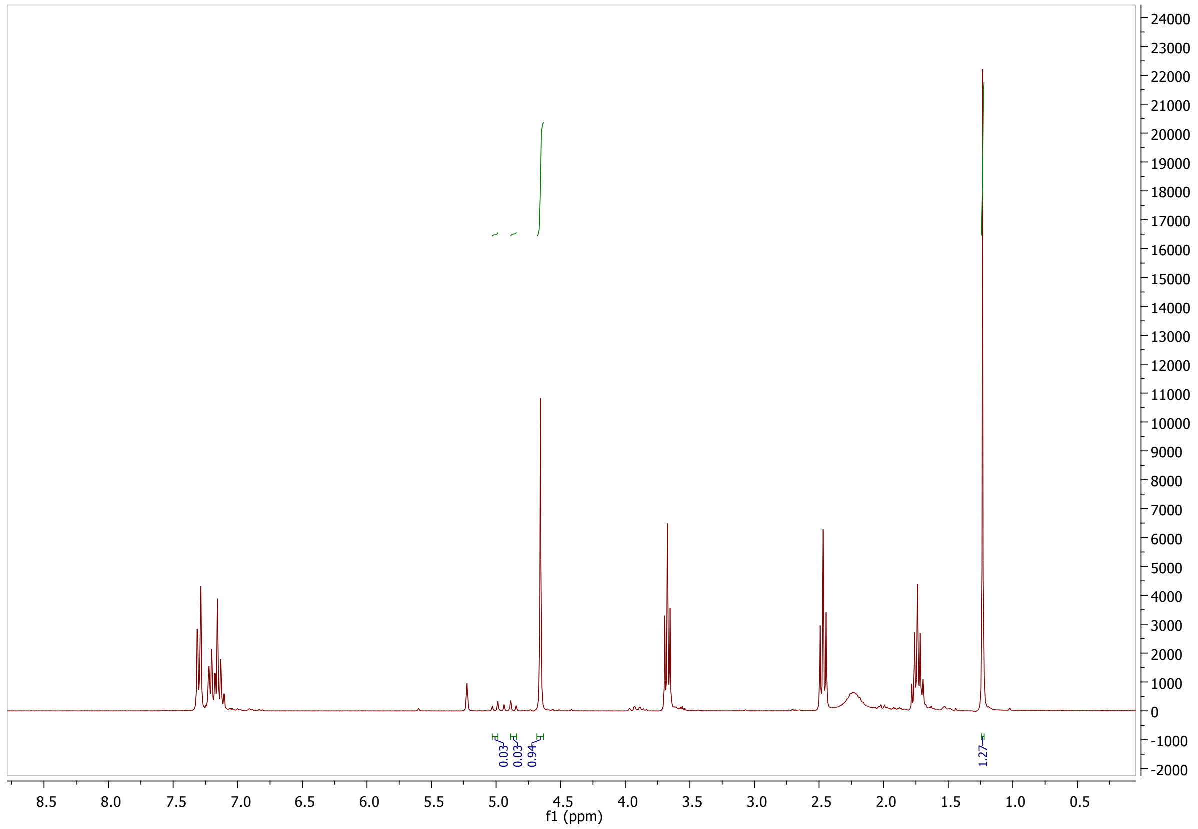
8. Catalysts Rate of Conversion of Substrate 9. NMR Spectra Catalytic Conversions

8.1 Catalyst: 1. Catalyst loading: 0,0001 mol%.

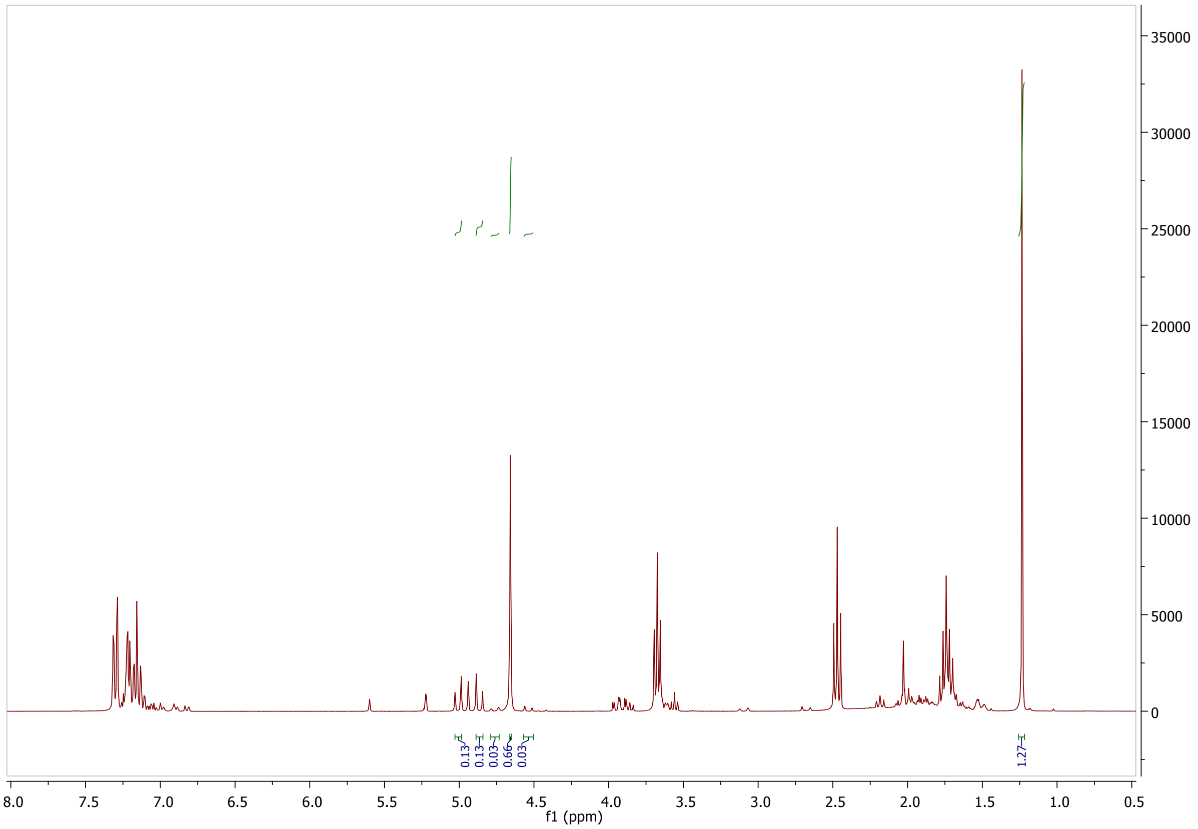
Time: 0 h, Conversion 0%



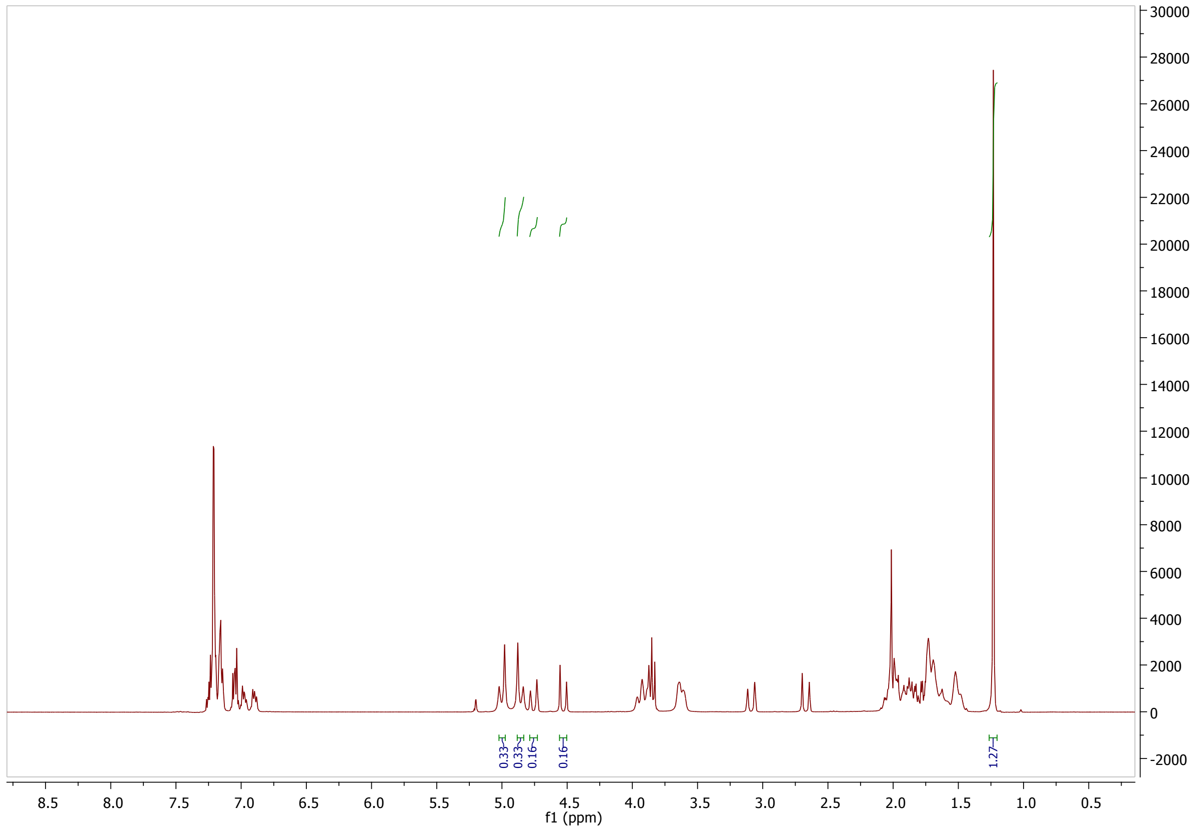
Time: 6 h, Conversion 6%



Time: 20 h, Conversion 34%

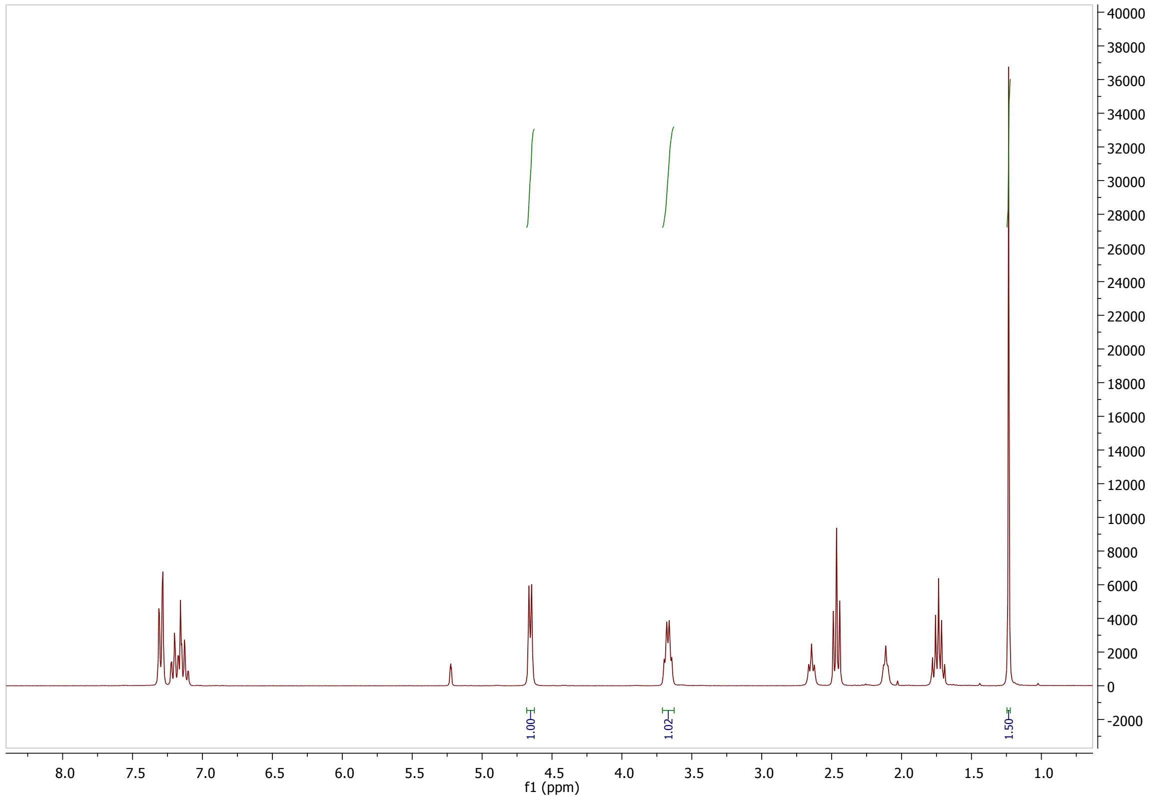


Time: 40 h, Conversion 100%

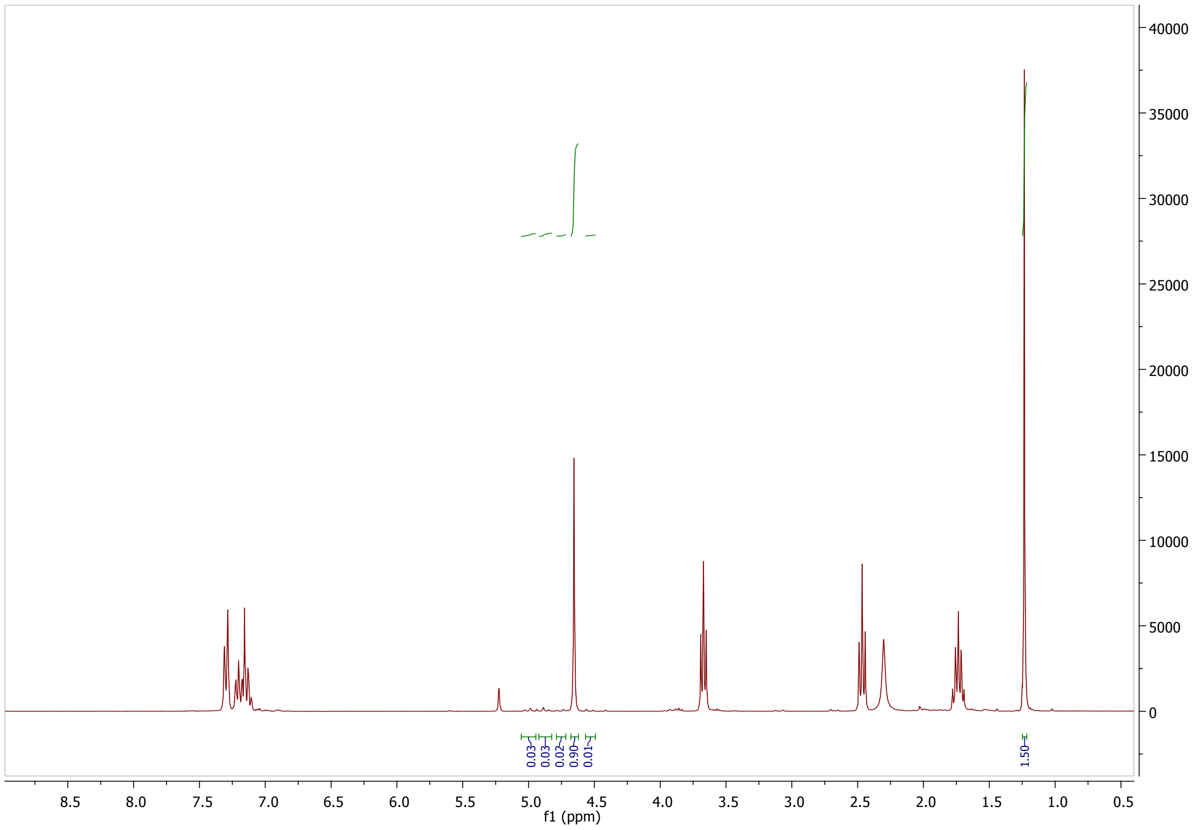


8.2 Catalyst: 2. Catalyst loading: 0,0001 mol%.

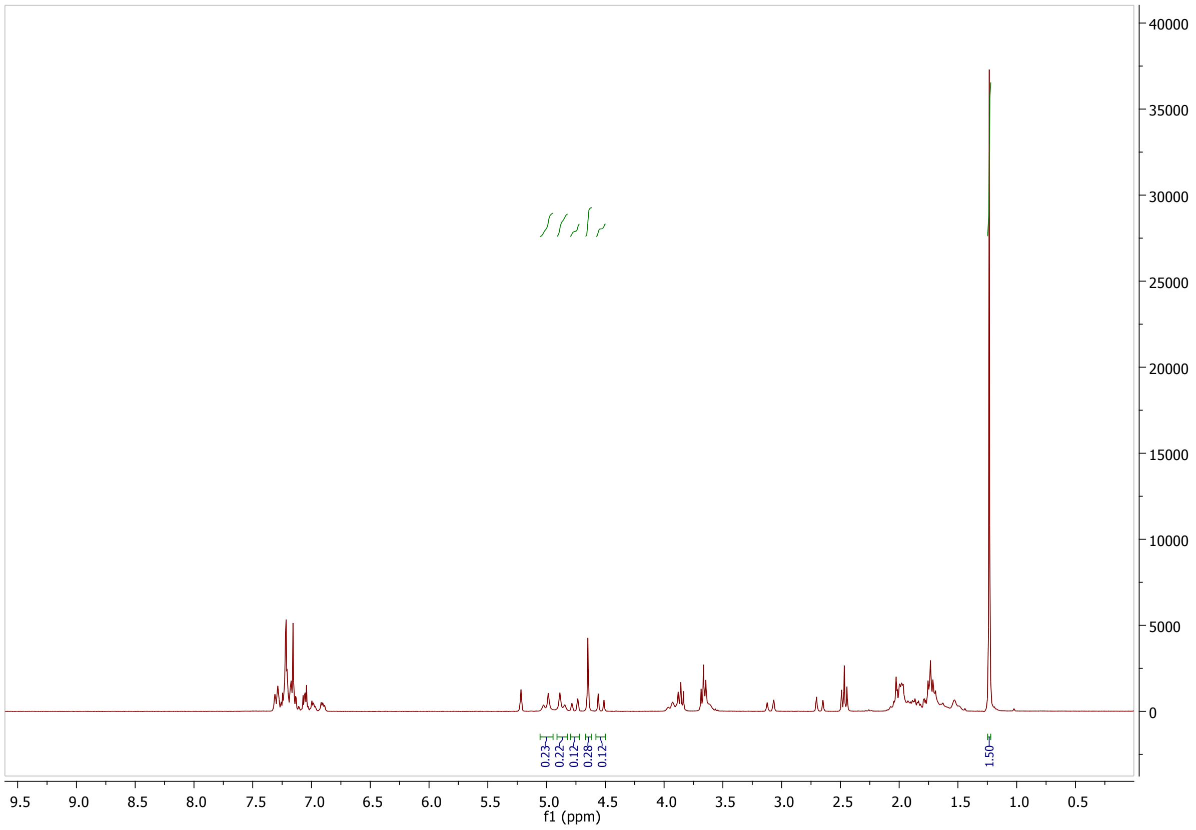
Time: 0 h, Conversion 0%



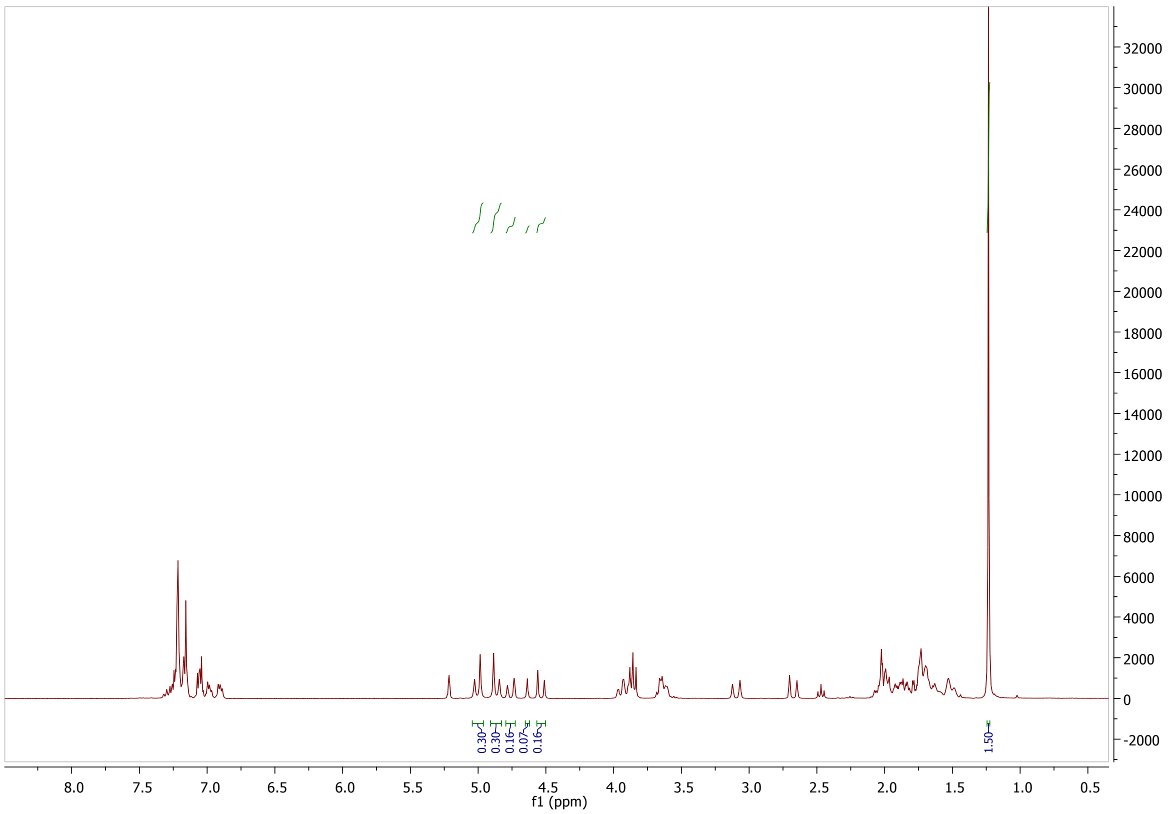
Time: 6 h, Conversion 10%



Time: 25 h, Conversion 72%

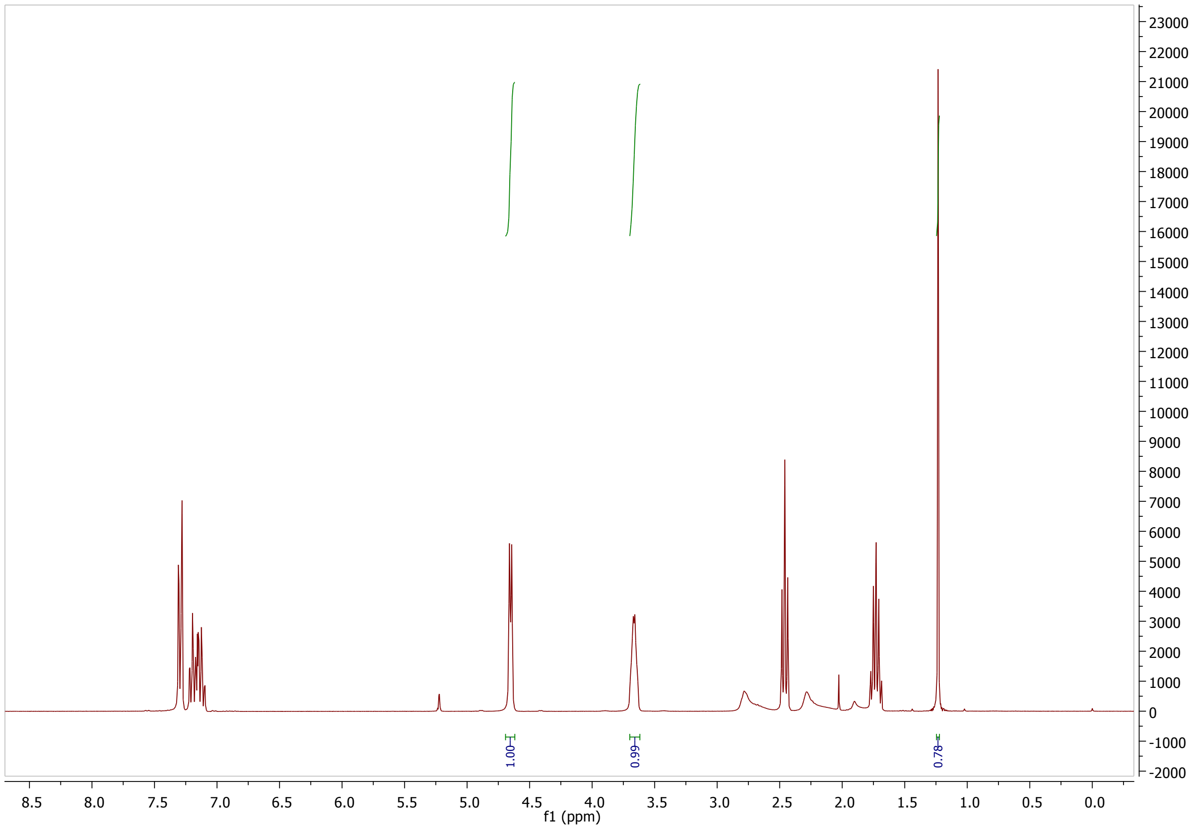


Time: 40 h, Conversion 100%

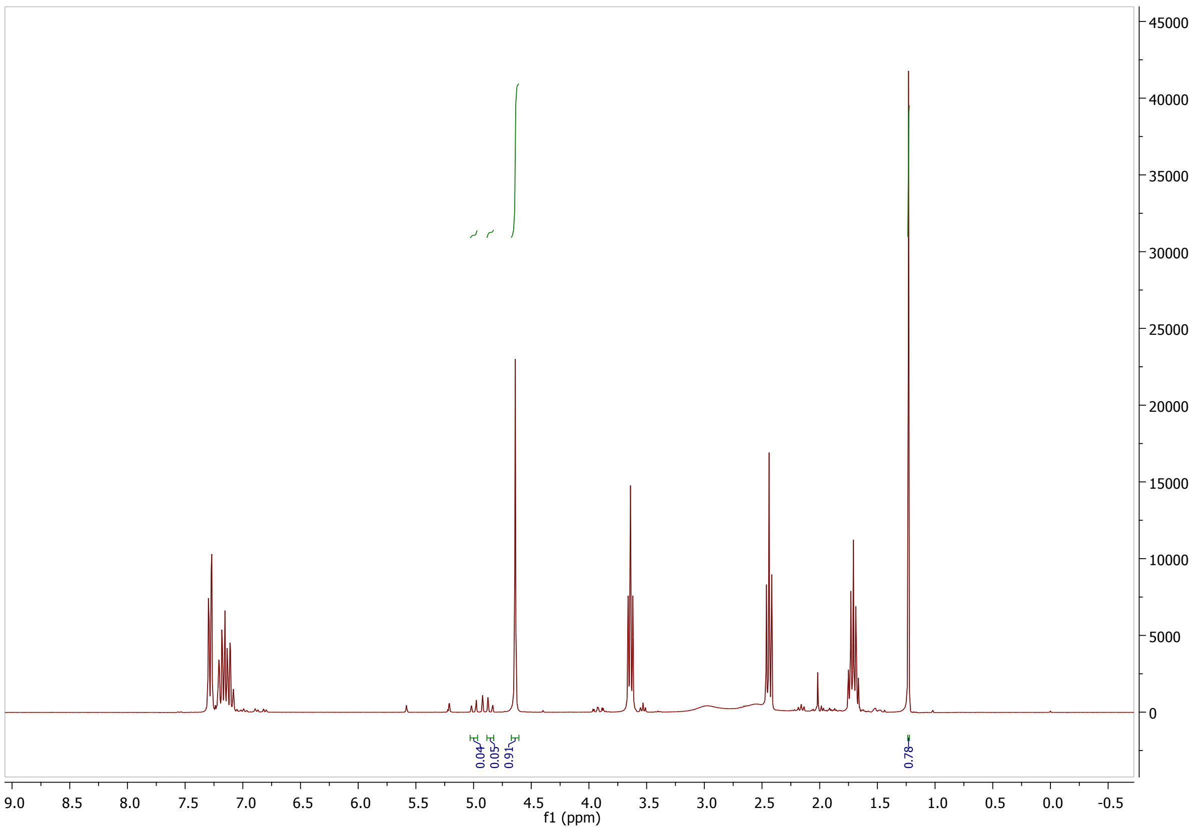


8.3 Catalyst: 3. Catalyst loading: 0,0001 mol%.

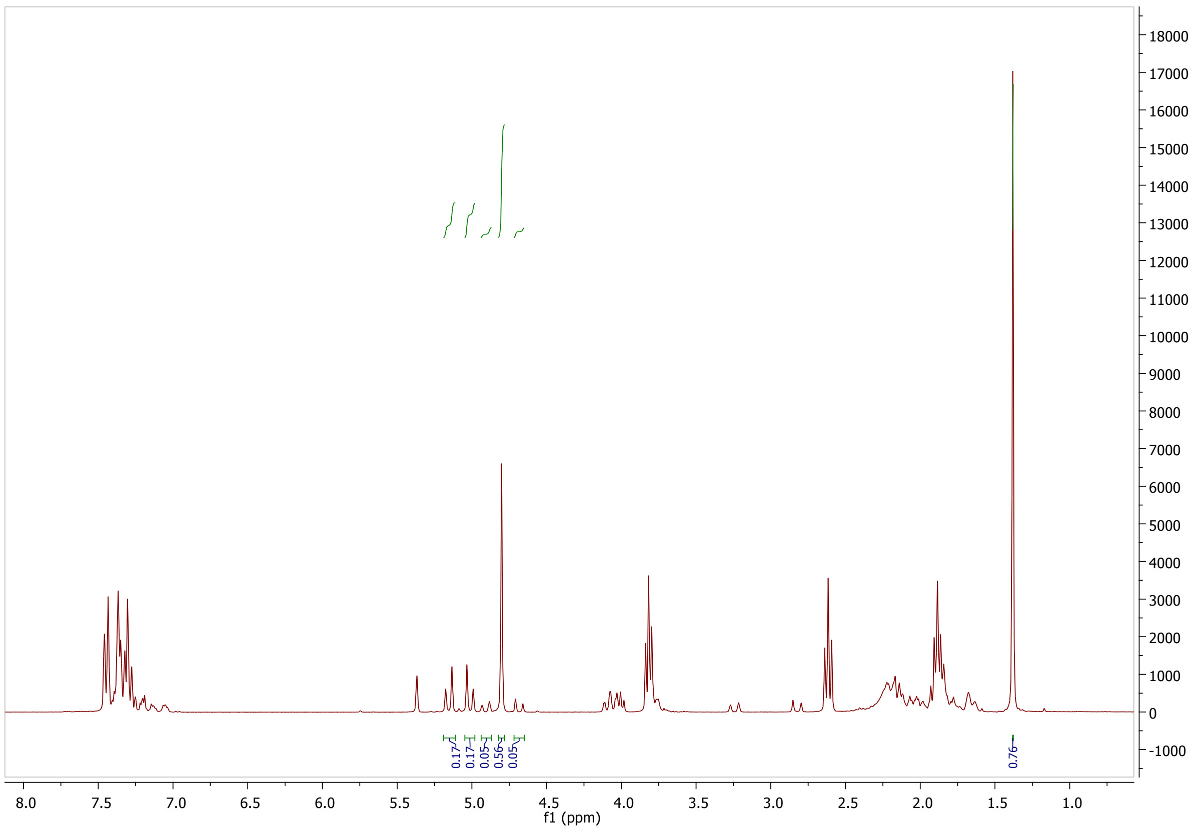
Time: 0 h, Conversion 0%



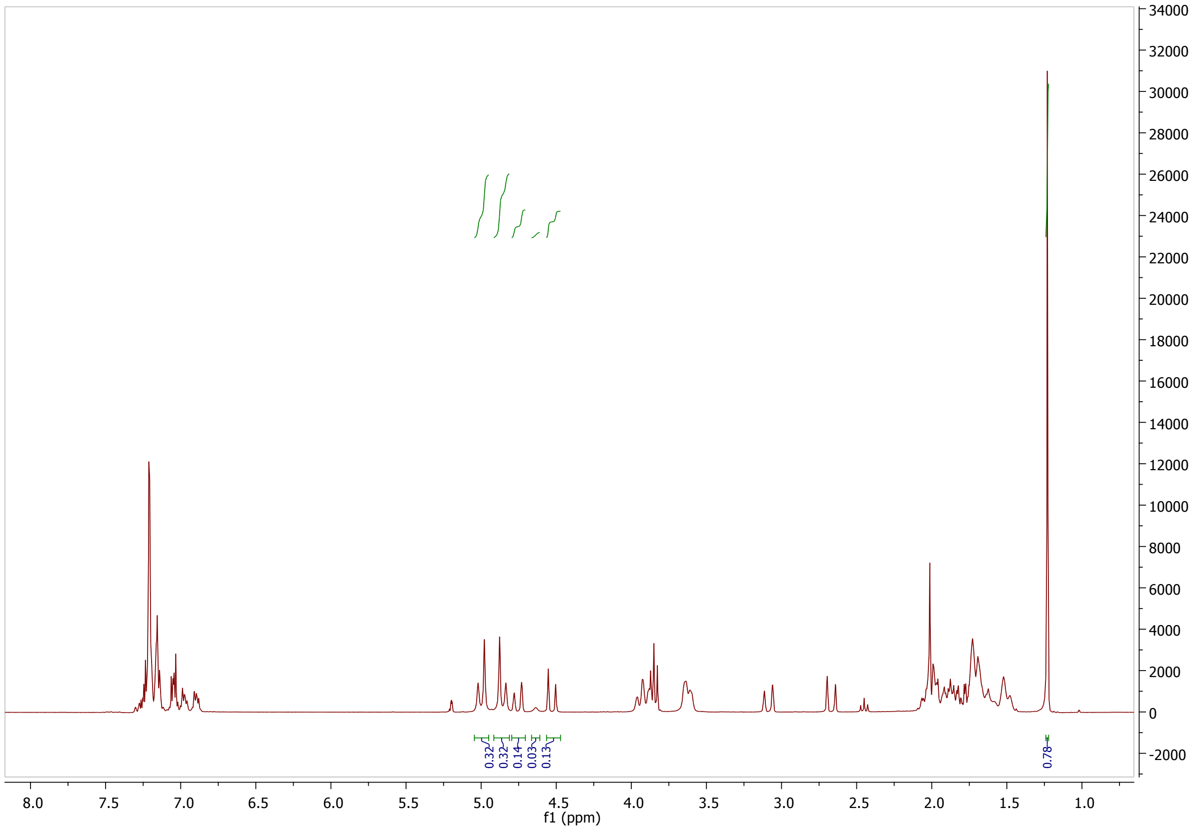
Time: 6 h, Conversion 9%



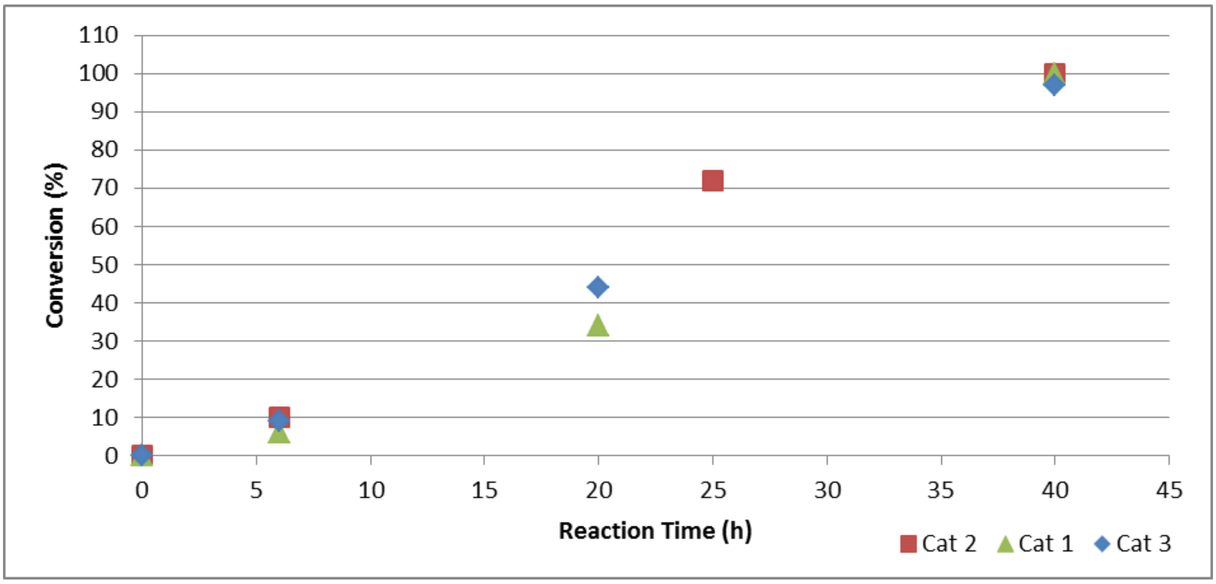
Time: 20 h, Conversion 44%



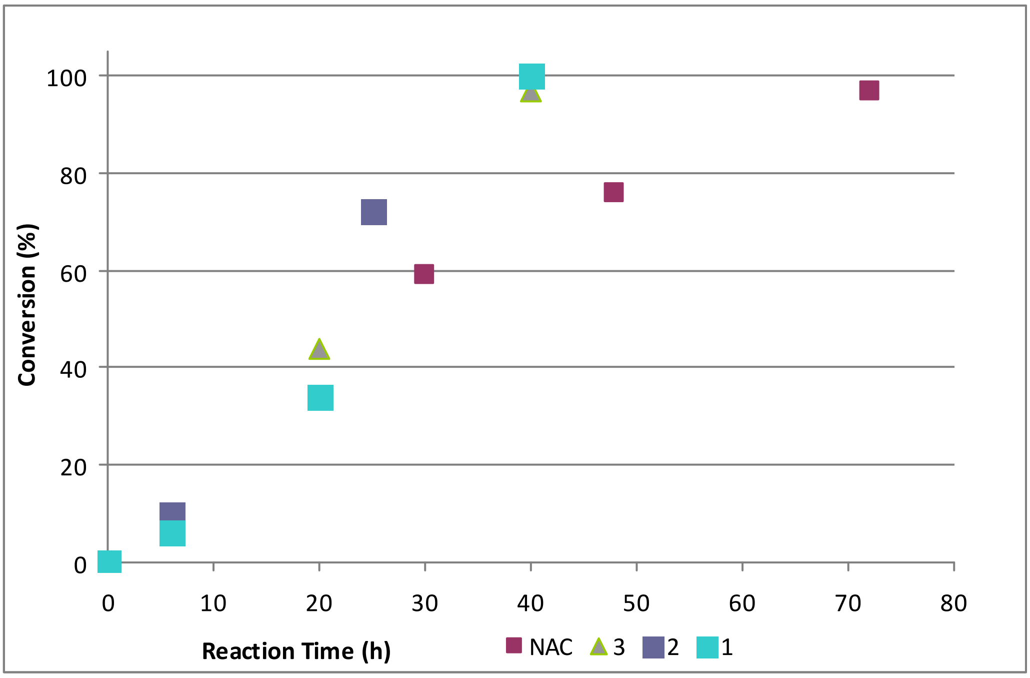
Time: 40 h, Conversion 97%



9. Comparison of the Conversion of Substrate 9 using Catalyst 1-3 at 0.0001 mol% Catalyst Loading



10. Comparison of the Conversion of Substrate 9 using the NAC catalyst and catalysts 1-3 at 0.0001 mol% Catalyst Loading



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