Supporting Information

# Identifying high-performance catalytic conditions for the carbon dioxide reduction to dimethoxymethane by multivariate modelling

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# Contents

# 1 Materials and Methods

## 1.1 Preliminary Remarks

### 1.1.1 General Procedures

Air and moisture sensitive syntheses were carried out within an argon atmosphere under exclusion of air and moisture. The argon gas was dried by silica gel and molecular sieve (4 Å). All glassware was flame-dried prior to use and standard Schlenk techniques were applied. The given yields refer to isolated and purified products.

### 1.1.2 Solvents and Reagents

Toluene was dried in a MB SPS-800 system and stored under nitrogen. All other anhydrous solvents used were bought and directly used or stored under exclusion of air and moisture. Degassing was accomplished by at least three Freeze-Pump-Thaw cycles. The anhydrous and degassed solvents were stored under argon over molecular sieve (3 Å). Argon gas (Ar 5.0), hydrogen gas ($H_2$ 5.0) and carbon dioxide gas ($CO_2$ 4.5) were purchased from Air Liquide Deutschland GmbH. Argon gas was purified as described above, whereas hydrogen gas and carbon dioxide gas were used without further purification. All other solvents and chemicals were purchased from manufacturing and trading companies (abcr GmbH, Acros Organics b.v.b.a., Sigma-Aldrich Co. LLC., Strem Chemicals Inc. and TCI Europe N.V.) and stored according to the respective instructions. Isolated compounds were stored under argon and, if needed, at 5 or -20 °C.

## 1.2 Analytical Methods

### 1.2.1 NMR Spectroscopy

NMR spectra were recorded on a 400 MHz Bruker Avance III HD spectrometer and a 400 MHz Bruker Avance III HD spectrometer with a CryoProbe Prodigy. NMR spectra of air and moisture sensitive compounds were measured using J. Young NMR tubes. The solvent residual signals were used for internal calibration.[1] Chemical shifts $\delta$ are reported in ppm and coupling constants $J$ in Hz. The different multiplicities are defined by s (singlet), d (doublet) and m (multiplet) or by combinations of these. In few cases, the peak shape is specified by b (broad) in addition to the description of the multiplicity. The assignments in $^{13}$C NMR and $^{31}$P NMR spectra refer to proton decoupled experiments. The assignment of all signals was realized by two-dimensional NMR spectroscopy ($^{1}$H-$^{1}$H-COSY, $^{1}$H-$^{13}$C-HSQC-ME and $^{1}$H-$^{13}$C-HMBC experiments). Atom numbering for NMR assignments is not based on IUPAC nomenclature.

For the quantification experiments, $^{1}$H NMR spectra were obtained with a pulse width of 3.6 µs (30° flip angle), an acquisition time of 4.1 s and a delay time of 1.0 s or a pulse width of 5.0 µs (30° flip angle), an acquisition time of 5.1 s and a delay time of 1.0 s.

### 1.2.2 Mass Spectrometry

Mass spectrometric measurements were performed on a Thermo Finnigan LTQ Ultra FT-ICR mass spectrometer. The mode (positive / negative) of the experiment, the solvent used to dissolve the sample and the method of injection together with potential solvents are listed. The *m/z* value of the most abundant or characteristic peak is given in comparison to the calculated *m/z* value. In case of characteristic peaks, the abundance is given in percent. If isotopic patterns are pronounced, the most intensive peak is indicated. Molecular ions are abbreviated as *M*.

[1] G. R. Fulmer et al., *Organometallics*, 2010, **29**, 2176–2179.

### 1.2.3 Vibrational Spectroscopy

IR spectra were recorded on a Thermo Scientific Nicolet 700 ATR-FT-IR spectrometer using the purified products without further modification. The background transmission was measured before the sample measurement and subtracted. Wave numbers $\tilde{\nu}$ are given in $cm^{-1}$.

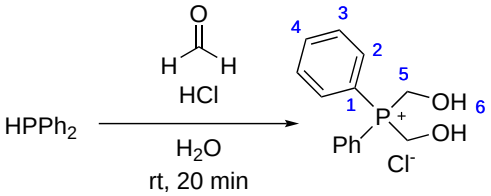
### 1.2.4 Elemental Analysis

Elemental analyses were performed using a Elementar vario EL or a Elementar vario MICRO cube instrument.

# 2 Synthetic Procedures

## 2.1 Synthesis of the Ligand Precursor

### 2.1.1 Bis(hydroxymethyl)diphenylphosphonium chloride SI-2




**SI-1** **SI-2**

Compound **SI-2** is literature known[2] and was synthesized according to a reported procedure.[3]

Diphenylphosphine **SI-1** (9.31 g, 8.70 mL, 50.0 mmol, 1.00 eq.) was stirred with degassed hydrochloric acid (37 *wt*%, 7.04 mL, 85.0 mmol, 1.70 eq.) and degassed aqueous formaldehyde solution (37 *wt*%, 14.5 mL, 195 mmol, 3.90 eq.) for 20 min at room temperature. The volatile compounds were removed *in vacuo*. Precipitation was induced by addition of acetone (5 mL). The resulting colorless solid was filtered and washed with cold $Et_2O$ ($3 \cdot 10$ mL). The product **SI-2** (12.9 g, 45.6 mmol, 91 %) was isolated as a colorless solid.

[2] J. Fawcett, P. A. T. Hoye, R. D. W. Kemmitt, D. J. Law and D. R. Russell, *J. Chem. Soc., Dalton Trans.* 1993, 2563–2568.
[3] A. Phanopoulos, N. J. Brown, A. J. P. White, N. J. Long and P. W. Miller, *Inorg. Chem.* 2014, **53**, 3742–3752.

**$^{1}$H NMR ($CDCl_3$, 400 MHz, 298 K)**:

$\delta$ = 5.06 (s, 4H, $H^5$), 7.62-7.67 (m, 4H, $H^3$), 7.77-7.83 (m, 6H, $H^{2,4}$).

**$^{13}$C{$^{1}$H} NMR ($CDCl_3$, 101 MHz, 298 K)**:

$\delta$ = 54.7 (d, $^{1}J_{C\text{-}P}$ = 55.9 Hz, 2C, $C^5$), 116.2 (d, $^{1}J_{C\text{-}P}$ = 73.2 Hz, 2C, $C^1$), 130.4 (d, $^{3}J_{C\text{-}P}$ = 10.8 Hz, 4C, $C^3$), 133.4 (d, $^{2}J_{C\text{-}P}$ = 8.5 Hz, 4C, $C^2$), 135.3 (d, $^{4}J_{C\text{-}P}$ = 3.1 Hz, 2C, $C^4$).

**$^{31}$P{$^{1}$H} NMR ($CDCl_3$, 162 MHz, 298 K)**:

$\delta$ = 13.39 (s, 1P).

**HR-MS ($ESI^+$, $CHCl_3$, FIA: ACN/$H_2O$)**:

$[M\text{-}CH_2O\text{-}Cl]^+$ : $C_{13}H_{14}OP^+$ calculated *m/z* 217.0777

found *m/z* 217.0776

**IR (FT-ATR)**:

$\tilde{\nu}$ = 3161, 3094, 3065, 3021, 2929, 2887, 2877, 2821, 2607, 1588, 1489, 1437, 1418, 1311, 1288, 1238, 1210, 1191, 1118, 1112, 1059, 1051, 934, 891, 844, 752, 740, 688.

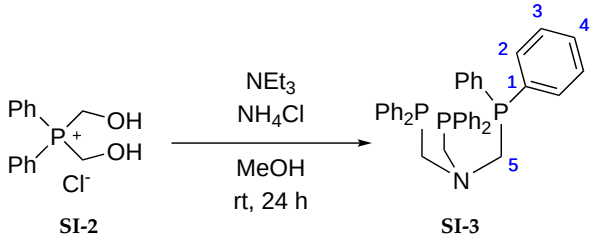
**EA (vario MICRO)**:

$C_{14}H_{16}ClO_2P$ calculated [%] C 59.48; H 5.70

found [%] C 58.72; H 5.69

## 2.2 Synthesis of the Ligand

### 2.2.1 *N*-triphos$^{Ph}$ SI-3




**SI-2** **SI-3**

Compound **SI-3** is literature known[4] and was synthesized according to a reported procedure.[5]

Bis(hydroxymethyl)diphenylphosphonium chloride **SI-2** (6.68 g, 23.6 mmol, 1.00 eq.) was dissolved in anhydrous degassed MeOH (25 mL) and anhydrous degassed $NEt_3$ (6.55 mL, 47.3 mmol, 2.00 eq.) was added. The solution was stirred for 1 h at room temperature. A solution of $NH_4Cl$ (417 mg, 7.80 mmol, 0.33 eq.) in anhydrous degassed MeOH (25 mL) and additional anhydrous degassed $NEt_3$ (6.55 mL, 47.3 mmol, 2.00 eq.) was added. The reaction mixture was stirred for 24 h at room temperature. The colorless precipitate was filtered and washed with anhydrous degassed MeOH ($4 \cdot 15$ mL). The product **SI-3** (4.30 g, 7.03 mmol, 89 %) was isolated as a colorless solid.

**$^1$H NMR ($CDCl_3$, 400 MHz, 298 K)**:
$\delta$ = 3.79 (d, $^2J_{H\text{-}P}$ = 3.6 Hz, 6H, $H^5$), 7.18-7.29 (m, 18H, $H^{2/3,4}$), 7.33-7.39 (m, 12H, $H^{2/3}$).

**$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz, 298 K)**:
$\delta$ = 59.9-60.2 (m, 3C, $C^5$), 128.4 (d, $^{2/3}J_{C\text{-}P}$ = 6.9 Hz, 12C, $C^{2/3}$), 128.6 (s, 6C, $C^4$), 133.3 (d, $^{2/3}J_{C\text{-}P}$ = 18.2 Hz, 12C, $C^{2/3}$), 137.9 (d, $^1J_{C\text{-}P}$ = 12.2 Hz, 6C, $C^1$).

**$^{31}$P{$^1$H} NMR ($CDCl_3$, 162 MHz, 298 K)**:
$\delta$ = -28.96 (s, 3P).

[4] G. Märkl and G. Y. Jin, *Tetrahedron Lett.* 1981, **22**, 1105–1108.
[5] J. Lloret Fillol, A. Kruckenberg, P. Scherl, H. Wadepohl and L. H. Gade, *Chem. Eur. J.* 2011, **17**, 14047–14062.

**HR-MS (ESI$^+$, $CHCl_3$, FIA: ACN/$H_2O$)**:

$[M+O_2\text{-}PPh_2]^+ : C_{27}H_{26}NO_2P_2^+$ calculated *m/z* 458.1433

found *m/z* 458.1431

**IR (FT-ATR)**:

$\tilde{\nu}$ = 3067, 3048, 3014, 2998, 2927, 2903, 2843, 2802, 2789, 2779, 1952, 1885, 1876, 1583, 1568, 1478, 1429, 1419, 1383, 1298, 1276, 1230, 1211, 1178, 1097, 1073, 1067, 1052, 1025, 934, 883, 868, 863, 757, 745, 739, 691.

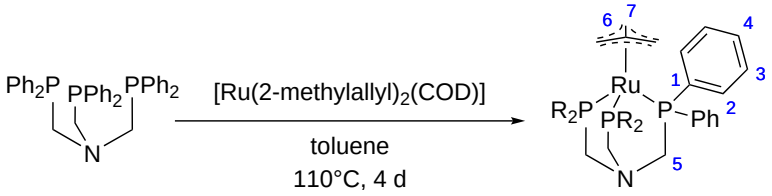
**EA (vario MICRO)**:

$C_{39}H_{36}NP_3$ calculated [%] C 76.59; H 5.93; N 2.29

found [%] C 75.64; H 5.96; N 2.31

## 2.3 Synthesis of the Complex

### 2.3.1 [Ru(*N*-triphos$^{Ph}$)(tmm)] SI-4




**SI-3** **SI-4**

Compound **SI-4** is literature known and was synthesized according to a reported procedure.[3]

*N*-triphos$^{Ph}$ **SI-3** (4.30 g, 7.03 mmol, 1.00 eq.) and [Ru(2-methylallyl)$_2$(COD)] (2.25 g, 7.03 mmol, 1.00 eq.) were dissolved in anhydrous degassed toluene (50 mL). The solution was stirred for 4 d at 110 °C. The volatile compounds were removed *in vacuo* by half inducing precipitation. The supernatant solution was removed using a filter cannula. The solid was washed with anhydrous degassed toluene (1 · 15 mL, 2 · 7.5 mL). The product **SI-4** (3.36 g, 4.38 mmol, 62 %) was isolated as an off-white solid.

**$^1$H NMR ($CDCl_3$, 400 MHz, 298 K)**:
$\delta$ = 1.68 (s, 6H, $H^7$), 3.86 (s, 6H, $H^5$), 6.88-6.99 (m, 24H, $H^{2,3}$), 7.04-7.10 (m, 6H, $H^4$).

**$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz, 298 K)**:
$\delta$ = 43.9-44.2 (m, 3C, $C^7$), 53.8-54.2 (m, 3C, $C^5$), 105.5 (bs, 1C, $C^6$), 127.5-127.6 (m, 12C, $C^{2/3}$), 127.7 (s, 6C, $C^4$), 132.5-132.7 (m, 12C, $C^{2/3}$), 141.1-141.5 (m, 6C, $C^1$).

**$^{31}$P{$^1$H} NMR ($CDCl_3$, 162 MHz, 298 K)**:
$\delta$ = 18.42 (s, 3P).

**HR-MS ($ESI^+$, $CHCl_3$, FIA: ACN/$H_2O$)**:
$[M+H]^+ : C_{43}H_{43}NP_3Ru^+$ calculated *m/z* 768.1646
found *m/z* 768.1655

**IR (FT-ATR)**:
$\tilde{\nu}$ = 3070, 3050, 3032, 2986, 2881, 2804, 2789, 2779, 1972, 1872, 1804, 1585, 1572, 1480, 1432, 1411, 1385, 1317, 1299, 1271, 1180, 1091, 1083, 1070, 996, 934, 894, 861, 853, 842, 736, 695.

**EA (vario EL)**:

| | | |
|---|---|---|
| $C_{43}H_{42}NP_3Ru$ | calculated [%] | C 67.35; H 5.52; N 1.83 |
| | found [%] | C 67.35; H 5.47; N 1.88 |

# 3 Multivariate Modeling

All calculations were done using the statistical software R.[6] Random forest modeling was performed with the R-package 'randomForest'.[7,8] Experimental designs were calculated with the D-optimal criterion of the function optFederov() in the R-package 'AlgDesign'.[9] Optimization was achieved with the augmented Lagrange method from the R-package 'Rsolnp'.[10] Graphics were produced with the R-package 'lattice'.[11,12]

The whole optimization process can be divided into three major steps, namely experimental data analysis, DoE1 and DoE2. Each of the two steps DoE1 and DoE2 can be further divided into three sub-steps comprising design creation, OLS modeling and constrained optimization.

All steps of the project can be reproduced with the data file 'all.data.xlsx' and the R-script 'all.R.code.r'. No special R knowledge is required to run the code and for reproducing the results of the individual steps. With some basic R-knowledge, it should be easily possible to adapt the code to the needs of other projects. All additional packages (libraries) that have to be added to the standard user library are mentioned within the R-script 'all.R.code.r'.

[6] R Core Team, *R: A Language and Environment for Statistical Computing*, https://www.R-project.org, 2017.
[7] A. Liaw and M. Wiener, *R News*, 2002, **2**, 18–22.
[8] L. Breiman, A. Cutler, A. Liaw and M. Wiener, *randomForest: Breiman and Cutler's Random Forests for Classification and Regression*, https://CRAN.R-project.org/package=randomForest, 2018.
[9] B. Wheeler, *AlgDesign: Algorithmic Experimental Design*, https://CRAN.R-project.org/package=AlgDesign, 2014.
[10] A. Ghalanos and S. Theussl, *Rsolnp: General Non-linear Optimization Using Augmented Lagrange Multiplier Method*, https://CRAN.R-project.org/package=Rsolnp, 2015.
[11] D. Sarkar, *Lattice*, Springer-Verlag, New York, 2008.
[12] D. Sarkar, *lattice: Trellis Graphics for R*, https://CRAN.R-project.org/package=lattice, 2018.

These packages have to be downloaded prior to the calculations (namely 'lattice',[11,12] 'randomForest',[7,8] 'pals',[13] 'viridis',[14] 'readxl',[15] 'AlgDesign',[9] 'MASS',[16] 'Rsolnp'[10]).
To calculate the different steps of the optimization process, the user has to run the individual steps in the given order. Therefore, the respective code framed by the descriptions given below has to be marked and run.

**Important:** The user has to make sure to put the R-script 'all.R.code.r' in the folder 'R-code' with the path C:\R-code\and to put the data file 'all.data.xlsx' in the subfolder 'data' with the path C:\R-code\data\. If a different location for the folder was chosen, the path in line #5 of the R-script has to be adjusted accordingly.

Referring to the R-code and the comments used therein, the different steps can be characterized:

1. **Experimental data analysis:** The code, starting in line #1 to entry 'End 1', reads the experimental data of dimension 144 x 10 from the Excel sheet 'historical.data', performs random forest modeling and visualizes the modeling results of the major response ton.dmm as scatter and trellis plots.

2. **DoE1**

   a) The code, starting at entry 'Start 2a' to entry 'End 2a', augments the set of nine candidates with ton.dmm>400 by another six d-optimal candidate points and reports the results to the console along with the condition number of the augmented design.

   b) The code, starting at entry 'Start 2b' to entry 'End 2b', analyzes the data with stepwise ordinary least squares (stepOLS) using the Bayesian Information Criterion (BIC) for model building. Modeling results for the major response, ton.dmm, are reported similar to those obtained for experimental data analysis (plot observed ton.dmm versus predicted ton.dmm and response surface trellis plots).

[13] K. Wright, *pals: Color Palettes, Colormaps, and Tools to Evaluate Them*, https://CRAN.R-project.org/package=pals, 2018.
[14] S. Garnier, *viridis: Default Color Maps from 'matplotlib'*, https://CRAN.R-project.org/package=viridis, 2018.
[15] H. Wickham et al., *readxl: Read Excel Files*, https://CRAN.R-project.org/package=readxl, 2019.
[16] B. Ripley et al., *MASS: Support Functions and Datasets for Venables and Ripley's MASS*, https://CRAN.R-project.org/package=MASS, 2018.

c) The code, starting at entry 'Start 2c' to entry 'End 2c', maximizes ton.dmm under relaxed hypercubical constraints, here at step size of 10, 20, 30 % and reports the results to the console. The values reported for ton.dmm and ton.mf are OLS-based expectations against which experimental results can be compared.

3. **DoE2**

a) The code, starting at entry 'Start 3a' to entry 'End 3a', creates a small, d-optimal design comprising the factors T (80-100), p.H2 (80-100), p.CO2 (15-25) and t.H (16-20) aiming at the linear effects of the four process parameters. The design is reported to the console together with its condition number.

b) With the code, starting at entry 'Start 3b' to entry 'End 3b', DoE2 results are modeled with stepOLS and modeling results are reported similar to 2b.

c) The code, starting at entry 'Start 3c' to entry 'End 3c', follows the same rationale as 2c, however with modified step size of 0, 25 and 50 %.

The simplified parameter designations used here do not correspond with the designations used in the text or the remaining SI that have been optimized for legibility. Nevertheless, the parameter designation is unambiguous. For the sake of clarity, the use of units in the mathematical approach has been omitted.

# 4 Experimental Data

The data obtained from a comprehensive screening of the catalysis process parameters temperature, partial pressure of $H_2$ and $CO_2$, time, additive as well as catalyst and additive loading were used for the multivariate analysis approach.[17] The complete data is given in Supplementary Table 1. While the TON values given here were rounded, for the multivariate analysis the exact values were taken, which were calculated with the values and formulas given in the original literature.[17] For the sake of the statistical evaluation, significant digits were not taken into account in the SI, while the values given in the manuscript were rounded to three decimal places for the substance quantities and the reaction volume.

The entries 142-144 of Supplementary Table 1 refer to an additional triple experiment that was performed to investigate the dependency of catalyst deactivation on concentration effects. This triple was added to the experimental data mentioned above to account for the effect of different reaction volumes in the statistical analysis.

[17] M. Siebert, M. Seibicke, A. F. Siegle, S. Kräh and O. Trapp, *J. Am. Chem. Soc.* 2019, **141**, 334–341.

**Supplementary Table 1:** Overview of the experimental data from a previous publication of our group used for the random forest algorithm.[17]

| | | Catalysis Process Parameters | | | | | | | Responses | |
|---|---|---|---|---|---|---|---|---|---|---|
| | entry | $T$ | $p_{H2}$ | $p_{CO2}$ | $t$ | additive | $n_{cat}$ | $n_{add}$ | $V_{MeOH}$ | TON | |
| | | (°C) | (bar) | (bar) | (h) | | (µmol) | (µmol) | (mL) | DMM | MF |
| Temperature | 1 | 20 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 4 | 49 |
| | 2 | 20 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 7 | 46 |
| | 3 | 20 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 13 | 59 |
| | 4 | 70 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 154 | 165 |
| | 5 | 70 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 156 | 163 |
| | 6 | 70 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 181 | 156 |
| | 7 | 80 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 269 | 108 |
| | 8 | 80 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 289 | 115 |
| | 9 | 80 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 319 | 114 |
| | 10 | 85 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 314 | 96 |
| | 11 | 85 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 329 | 91 |
| | 12 | 85 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 329 | 92 |
| | 13 | 90 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 296 | 80 |
| | 14 | 90 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 313 | 88 |
| | 15 | 90 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 320 | 88 |
| | 16 | 95 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 263 | 69 |
| | 17 | 95 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 271 | 76 |
| | 18 | 95 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 280 | 74 |
| | 19 | 100 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 201 | 70 |
| | 20 | 100 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 205 | 59 |

Continued on next page. . .

**Supplementary Table 1:** Overview of the experimental data from a previous publication of our group used for the random forest algorithm.[17] (continued)

| | | Catalysis Process Parameters | | | | | | | | Responses | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | entry | $T$ | $p_{H2}$ | $p_{CO2}$ | $t$ | additive | $n_{cat}$ | $n_{add}$ | $V_{MeOH}$ | TON | |
| | | (°C) | (bar) | (bar) | (h) | | (µmol) | (µmol) | (mL) | DMM | MF |
| | 21 | 100 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 219 | 69 |
| | 22 | 110 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 111 | 48 |
| | 23 | 110 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 118 | 51 |
| | 24 | 110 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 129 | 58 |
| | 25 | 120 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 47 | 41 |
| | 26 | 120 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 60 | 43 |
| | 27 | 120 | 60 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 61 | 42 |
| | 28 | 90 | 40 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 241 | 67 |
| | 29 | 90 | 40 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 243 | 70 |
| | 30 | 90 | 40 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 266 | 70 |
| | 31 | 90 | 50 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 254 | 76 |
| | 32 | 90 | 50 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 289 | 80 |
| | 33 | 90 | 50 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 293 | 72 |
| | 34 | 90 | 70 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 291 | 87 |
| | 35 | 90 | 70 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 332 | 80 |
| | 36 | 90 | 70 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 334 | 81 |
| | 37 | 90 | 80 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 292 | 77 |
| | 38 | 90 | 80 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 333 | 86 |
| | 39 | 90 | 80 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 352 | 85 |
| | 40 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 348 | 91 |

$H_2$ pressure

Continued on next page. . .

**Supplementary Table 1:** Overview of the experimental data from a previous publication of our group used for the random forest algorithm.[17] (continued)

| | | Catalysis Process Parameters | | | | | | | | Responses | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | entry | $T$ | $p_{H2}$ | $p_{CO2}$ | $t$ | additive | $n_{cat}$ | $n_{add}$ | $V_{MeOH}$ | TON | |
| | | (°C) | (bar) | (bar) | (h) | | (µmol) | (µmol) | (mL) | DMM | MF |
| $CO_2$ pressure | 41 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 358 | 85 |
| | 42 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 383 | 102 |
| | 43 | 90 | 100 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 303 | 82 |
| | 44 | 90 | 100 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 336 | 93 |
| | 45 | 90 | 100 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 357 | 84 |
| | 46 | 90 | 90 | 5 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 86 | 8 |
| | 47 | 90 | 90 | 5 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 87 | 8 |
| | 48 | 90 | 90 | 5 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 118 | 9 |
| | 49 | 90 | 90 | 10 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 202 | 34 |
| | 50 | 90 | 90 | 10 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 214 | 38 |
| | 51 | 90 | 90 | 10 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 222 | 34 |
| | 52 | 90 | 90 | 15 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 272 | 65 |
| | 53 | 90 | 90 | 15 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 322 | 71 |
| | 54 | 90 | 90 | 15 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 347 | 69 |
| | 55 | 90 | 90 | 25 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 341 | 109 |
| | 56 | 90 | 90 | 25 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 358 | 94 |
| | 57 | 90 | 90 | 25 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 383 | 100 |
| | 58 | 90 | 90 | 30 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 317 | 101 |
| | 59 | 90 | 90 | 30 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 320 | 113 |
| | 60 | 90 | 90 | 30 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 349 | 111 |

Continued on next page. . .

**Supplementary Table 1:** Overview of the experimental data from a previous publication of our group used for the random forest algorithm.[17] (continued)

| | | Catalysis Process Parameters | | | | | | | Responses | |
|---|---|---|---|---|---|---|---|---|---|---|
| | entry | $T$ | $p_{H2}$ | $p_{CO2}$ | $t$ | additive | $n_{cat}$ | $n_{add}$ | $V_{MeOH}$ | TON | |
| | | (°C) | (bar) | (bar) | (h) | | (µmol) | (µmol) | (mL) | DMM | MF |
| | 61 | 90 | 90 | 40 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 259 | 120 |
| | 62 | 90 | 90 | 40 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 278 | 116 |
| | 63 | 90 | 90 | 40 | 18 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 287 | 116 |
| | 64 | 90 | 90 | 5 | 1 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 20 | 36 |
| | 65 | 90 | 90 | 5 | 1 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 21 | 36 |
| | 66 | 90 | 90 | 5 | 1 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 21 | 32 |
| | 67 | 90 | 90 | 5 | 6 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 95 | 13 |
| | 68 | 90 | 90 | 5 | 6 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 95 | 14 |
| | 69 | 90 | 90 | 5 | 6 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 102 | 20 |
| | 70 | 90 | 90 | 5 | 12 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 91 | 11 |
| | 71 | 90 | 90 | 5 | 12 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 97 | 11 |
| | 72 | 90 | 90 | 5 | 12 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 130 | 18 |
| | 73 | 90 | 90 | 5 | 24 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 69 | 7 |
| | 74 | 90 | 90 | 5 | 24 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 93 | 8 |
| | 75 | 90 | 90 | 5 | 24 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 94 | 5 |
| | 76 | 90 | 90 | 5 | 48 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 30 | 3 |
| | 77 | 90 | 90 | 5 | 48 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 38 | 4 |
| | 78 | 90 | 90 | 5 | 48 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 57 | 5 |
| | 79 | 90 | 90 | 5 | 72 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 12 | 1 |
| Time at 5 bar $CO_2$ | 80 | 90 | 90 | 5 | 72 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 15 | 2 |

Continued on next page. . .

**Supplementary Table 1:** Overview of the experimental data from a previous publication of our group used for the random forest algorithm.[17] (continued)

| | | Catalysis Process Parameters | | | | | | | Responses | |
|---|---|---|---|---|---|---|---|---|---|---|
| | entry | $T$ | $p_{H2}$ | $p_{CO2}$ | $t$ | additive | $n_{cat}$ | $n_{add}$ | $V_{MeOH}$ | TON | |
| | | (°C) | (bar) | (bar) | (h) | | (µmol) | (µmol) | (mL) | DMM | MF |
| Time at 20 bar $CO_2$ | 81 | 90 | 90 | 5 | 72 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 33 | 5 |
| | 82 | 90 | 90 | 5 | 168 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 3 | 0 |
| | 83 | 90 | 90 | 5 | 168 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 3 | 0 |
| | 84 | 90 | 90 | 5 | 168 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 5 | 0 |
| | 85 | 90 | 90 | 20 | 1 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 15 | 71 |
| | 86 | 90 | 90 | 20 | 1 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 17 | 56 |
| | 87 | 90 | 90 | 20 | 1 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 17 | 60 |
| | 88 | 90 | 90 | 20 | 6 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 157 | 61 |
| | 89 | 90 | 90 | 20 | 6 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 158 | 61 |
| | 90 | 90 | 90 | 20 | 6 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 163 | 66 |
| | 91 | 90 | 90 | 20 | 12 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 217 | 74 |
| | 92 | 90 | 90 | 20 | 12 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 223 | 75 |
| | 93 | 90 | 90 | 20 | 12 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 305 | 101 |
| | 94 | 90 | 90 | 20 | 24 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 295 | 75 |
| | 95 | 90 | 90 | 20 | 24 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 326 | 78 |
| | 96 | 90 | 90 | 20 | 24 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 330 | 79 |
| | 97 | 90 | 90 | 20 | 48 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 271 | 56 |
| | 98 | 90 | 90 | 20 | 48 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 303 | 65 |
| | 99 | 90 | 90 | 20 | 48 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 306 | 61 |
| | 100 | 90 | 90 | 20 | 72 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 229 | 56 |

Continued on next page. . .

**Supplementary Table 1:** Overview of the experimental data from a previous publication of our group used for the random forest algorithm.[17] (continued)

| | | Catalysis Process Parameters | | | | | | | | Responses | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | entry | $T$ | $p_{H2}$ | $p_{CO2}$ | $t$ | additive | $n_{cat}$ | $n_{add}$ | $V_{MeOH}$ | TON | |
| | | (°C) | (bar) | (bar) | (h) | | (µmol) | (µmol) | (mL) | DMM | MF |
| Catalyst loading | 101 | 90 | 90 | 20 | 72 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 238 | 54 |
| | 102 | 90 | 90 | 20 | 72 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 262 | 55 |
| | 103 | 90 | 90 | 20 | 168 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 168 | 44 |
| | 104 | 90 | 90 | 20 | 168 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 172 | 48 |
| | 105 | 90 | 90 | 20 | 168 | $Al(OTf)_3$ | 1.5 | 6.25 | 0.5 | 191 | 48 |
| | 106 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.1875 | 0.78125 | 0.5 | 669 | 1375 |
| | 107 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.1875 | 0.78125 | 0.5 | 670 | 1115 |
| | 108 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.1875 | 0.78125 | 0.5 | 846 | 1377 |
| | 109 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 1.5625 | 0.5 | 725 | 521 |
| | 110 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 1.5625 | 0.5 | 785 | 527 |
| | 111 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 1.5625 | 0.5 | 849 | 552 |
| | 112 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 3.125 | 0.5 | 443 | 159 |
| | 113 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 3.125 | 0.5 | 510 | 240 |
| | 114 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 3.125 | 0.5 | 630 | 219 |
| | 115 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 2.25 | 9.375 | 0.5 | 180 | 44 |
| | 116 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 2.25 | 9.375 | 0.5 | 203 | 50 |
| | 117 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 2.25 | 9.375 | 0.5 | 219 | 46 |
| | 118 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 3.0 | 12.5 | 0.5 | 117 | 35 |
| | 119 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 3.0 | 12.5 | 0.5 | 119 | 31 |
| | 120 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 3.0 | 12.5 | 0.5 | 131 | 32 |

Continued on next page. . .

**Supplementary Table 1:** Overview of the experimental data from a previous publication of our group used for the random forest algorithm.[17] (continued)

| | entry | Catalysis Process Parameters | | | | | | | | Responses | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $T$ | $p_{H2}$ | $p_{CO2}$ | $t$ | additive | $n_{cat}$ | $n_{add}$ | $V_{MeOH}$ | TON | |
| | | (°C) | (bar) | (bar) | (h) | | (µmol) | (µmol) | (mL) | DMM | MF |
| Additive loading | 121 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 0.9375 | 0.5 | 345 | 633 |
| | 122 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 0.9375 | 0.5 | 467 | 642 |
| | 123 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 0.9375 | 0.5 | 527 | 676 |
| | 124 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 1.25 | 0.5 | 455 | 476 |
| | 125 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 1.25 | 0.5 | 456 | 468 |
| | 126 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 1.25 | 0.5 | 683 | 588 |
| | 127 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 1.875 | 0.5 | 644 | 371 |
| | 128 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 1.875 | 0.5 | 705 | 366 |
| | 129 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 1.875 | 0.5 | 745 | 507 |
| | 130 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 2.1875 | 0.5 | 648 | 387 |
| | 131 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 2.1875 | 0.5 | 712 | 392 |
| | 132 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 2.1875 | 0.5 | 906 | 559 |
| | 133 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 2.5 | 0.5 | 699 | 327 |
| | 134 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 2.5 | 0.5 | 755 | 470 |
| | 135 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 2.5 | 0.5 | 789 | 535 |
| Background | 136 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.0 | 0.0 | 0.5 | 0 | 6 |
| | 137 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.0 | 0.0 | 0.5 | 1 | 2 |
| | 138 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 0.0 | 0.5 | 0 | 8 |
| | 139 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 1.5 | 0.0 | 0.5 | 1 | 11 |
| | 140 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.0 | 6.25 | 0.5 | 0 | 5 |

Continued on next page...

**Supplementary Table 1:** Overview of the experimental data from a previous publication of our group used for the random forest algorithm.[17] (continued)

| | | Catalysis Process Parameters | | | | | | | | Responses | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | entry | $T$ | $p_{H2}$ | $p_{CO2}$ | $t$ | additive | $n_{cat}$ | $n_{add}$ | $V_{MeOH}$ | TON | |
| | | (°C) | (bar) | (bar) | (h) | | (µmol) | (µmol) | (mL) | DMM | MF |
| Volume | 141 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.0 | 6.25 | 0.5 | 1 | 5 |
| | 142 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 1.5625 | 0.25 | 604 | 204 |
| | 143 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 1.5625 | 0.25 | 616 | 188 |
| | 144 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.375 | 1.5625 | 0.25 | 631 | 195 |

# 5 Catalytic Investigations

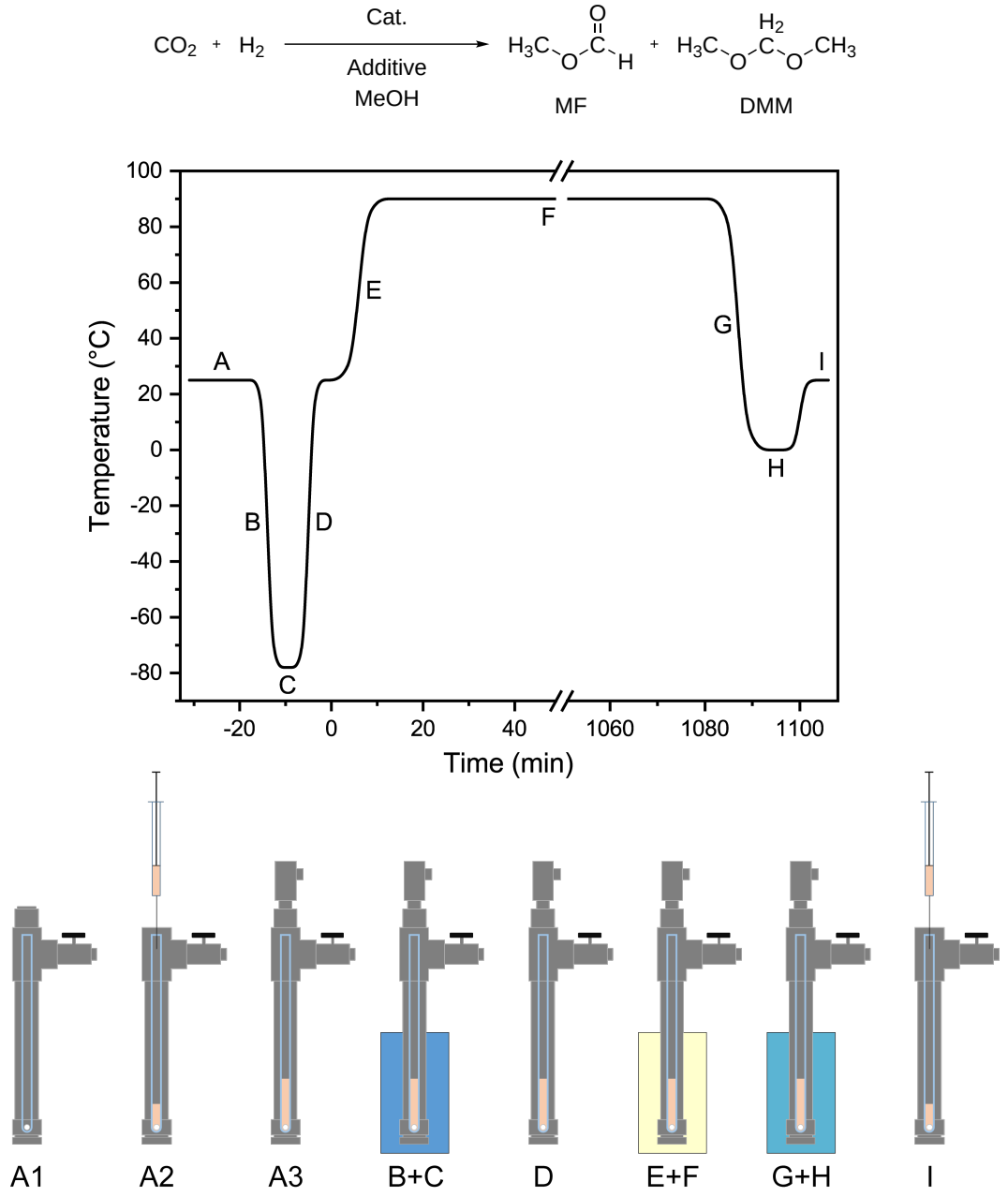
## 5.1 General Procedure for Hydrogenation Reactions

All catalyses and the corresponding analyses were performed three times following a procedure previously reported by our group.[17]

The catalyses were performed in stainless steel high-pressure autoclaves (10 mL total volume) using an NMR tube as inset and a small stirring bar for mixing. The catalyst and the additive were suspended in a Schlenk tube in MeOH and the mixture was stirred for 1 h. The autoclave was evacuated and flushed with nitrogen three times before the respective amount of reaction mixture was transferred into the NMR tube inset. The carbon dioxide gas line was purged with $CO_2$ and the hydrogen gas line was purged with $H_2$ at least seven times. After the autoclave was pressurized with $CO_2$, the $CO_2$ was deposited by cooling the autoclave to -78 °C for 5 min. Then, the autoclave was further pressurized with $H_2$. The closed autoclave was allowed to warm to room temperature for 10 min. The reaction mixture was stirred at the mentioned temperature for the defined time. The autoclaves were cooled to 0 °C for 15 min before the gas was discharged. The TONs of the catalyses were determined by $^1$H NMR spectroscopy. A sample of 50 µL of the reaction mixture and 35 µL mesitylene as internal standard were dissolved in 450 µL DCM-$d_2$.[17]

With the experimental setup tailor-made for the optimized conditions, the catalysis was performed twice. The new autoclave (35 mL total volume) enabled better mixing of the catalysis mixture and enhanced the mass transfer within the catalytic reaction. For this autoclave, the cool-down time at -78 °C was extended to 10 min and the warm-up time at room temperature as well as the cool-down time at 0 °C to 20 min.

The catalysis was also performed in the absence of a catalyst, a co-catalyst or both to demonstrate the need of the catalytic system for the formation of DMM and MF. In all cases, no significant conversions for both of these compounds were observed.




**Supplementary Figure 1:** Exemplary timeline of an experimental procedure regarding every step and the respective temperature at which it was performed together with a schematic drawing of the experimental setup.

A1: A glass inset is placed in the autoclave and the autoclave is closed. Evacuation of the autoclave and flushing with nitrogen at 25 °C.

A2: Opening of the autoclave and transfer of the reaction mixture into the glass inset in a nitrogen gas counter-flow at 25 °C.

A3: Installing of the proportional relief valve in a nitrogen gas counter-flow at 25 °C. Afterwards, the autoclave is pressurized with $CO_2$.

B: Cooling of the autoclave to -78 °C using an acetone / dry-ice bath.

C: The autoclave is kept at -78 °C for 5 min in order to deposit $CO_2$. Afterwards, the autoclave is pressurized with $H_2$.

D: Warming of the autoclave to 25 °C for 10 min.

E: Heating of the autoclave to the respective temperature (90 °C in the example) using a preheated oil bath. The temperature of the oil bath is stable within ± 0.1 °C after the autoclave is tempered at the desired temperature.

F: The autoclave is kept at constant temperature over the course of the reaction (18 h in the example).

G: Cooling of the autoclave to 0 °C using an ice bath.

H: The autoclave is kept at 0 °C for 15 min.

I: The autoclave is vented carefully and a sample is taken for quantification at 25 °C.

The TONs for DMM and MF were calculated using equations 5.2 and 5.4 and the peaks at 4.57 - 4.58 and 3.73 - 3.77 ppm, respectively.

$$TON_{DMM} = \frac{\frac{V_{cat}}{V_{sample}} \cdot \frac{Int_{DMM}}{x_{Proton,DMM}} \cdot \frac{x_{Proton,mes}}{Int_{mes}} \cdot \frac{\rho_{mes} \cdot V_{mes}}{M_{mes}}}{n_{cat}} \tag{5.1}$$

$$TON_{DMM} = 2.5160\,\frac{\mu mol}{\mu L} \cdot \frac{V_{cat} \cdot Int_{DMM}}{n_{cat}} \tag{5.2}$$

$$TON_{MF} = \frac{\frac{V_{cat}}{V_{sample}} \cdot \frac{Int_{MF}}{x_{Proton,MF}} \cdot \frac{x_{Proton,mes}}{Int_{mes}} \cdot \frac{\rho_{mes} \cdot V_{mes}}{M_{mes}}}{n_{cat}} \tag{5.3}$$

$$TON_{MF} = 1.6773\,\frac{\mu mol}{\mu L} \cdot \frac{V_{cat} \cdot Int_{MF}}{n_{cat}} \tag{5.4}$$

where:

$TON_{DMM}$ = Turnover number for DMM
$TON_{MF}$ = Turnover number for MF
$V_{cat}$ = Volume of catalysis solution
$V_{sample}$ = Volume of sample taken for NMR analysis
$Int_{DMM}$ = Integral of the methylene group of DMM
$Int_{MF}$ = Integral of the methyl group of MF
$x_{Proton,DMM}$ = Number of integrated protons of DMM (here: 2)
$x_{Proton,MF}$ = Number of integrated protons of MF (here: 3)
$Int_{mes}$ = Integral of the aromatic protons of mesitylene (set manually to 3)
$x_{Proton,mes}$ = Number of integrated protons of mesitylene (here: 3)
$\rho_{mes}$ = Density of mesitylene at 25 °C (0.864 g $mL^{-1}$)
$V_{mes}$ = Volume of mesitylene used as internal standard (here: 35 µL)
$M_{mes}$ = Molar mass of mesitylene (120.19 g $mol^{-1}$)
$n_{cat}$ = Amount of catalyst in catalysis solution

The sample standard deviation mentioned for each mean value was calculated using equation 5.5.

$$SD = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \overline{x})^2}{N-1}} \tag{5.5}$$

where:

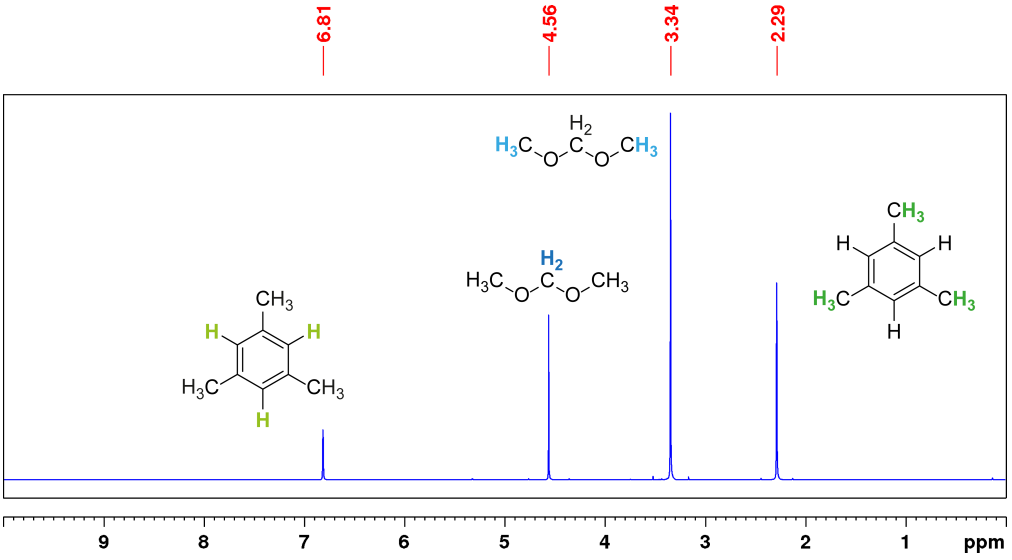
$SD$ = Standard Deviation
$i$ = Number of experiment
$N$ = Total number of observations in the sample
$x_i$ = Observed values of the sample item
$\overline{x}$ = Mean value of the observations

The average TONs for DMM and MF as well as the ratios and their average values in Chapter 5 were calculated using the exact values obtained by the given integrals of DMM and MF and equations 5.2 and 5.4, respectively. Therefore, these values might vary slightly compared to the average of the rounded values. The sample standard deviations were calculated using the exact values of the TONs and the ratios.

The respective values for the amount of DMM and MF formed in the reactions without any catalyst were calculated using the given integrals of DMM and MF and equations 5.2 and 5.4, respectively, except that only the counter was calculated and the denominator was neglected. The average amounts of DMM and MF as well as the ratios and their average values were calculated using the exact values.

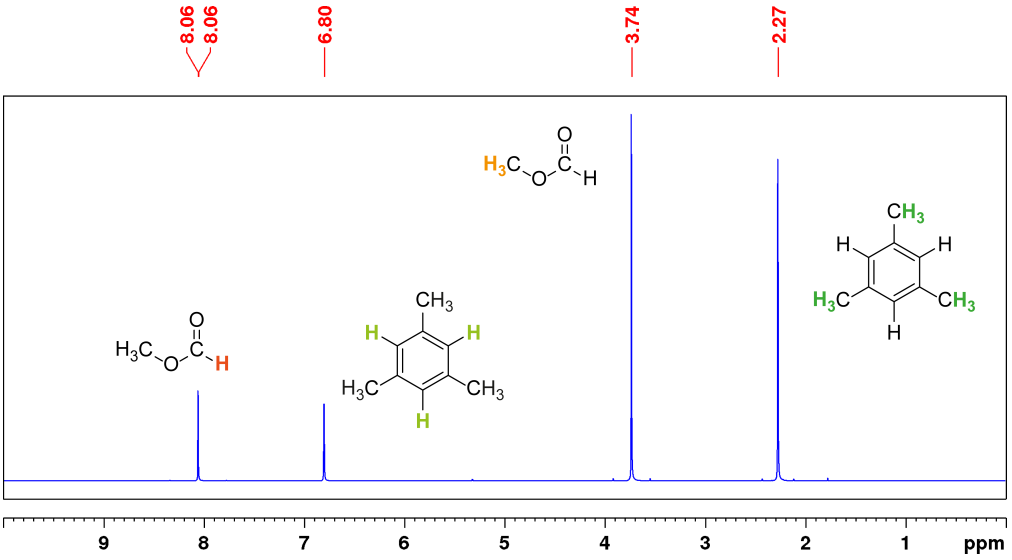
## 5.2 References

### NMR Spectra of DMM[17]



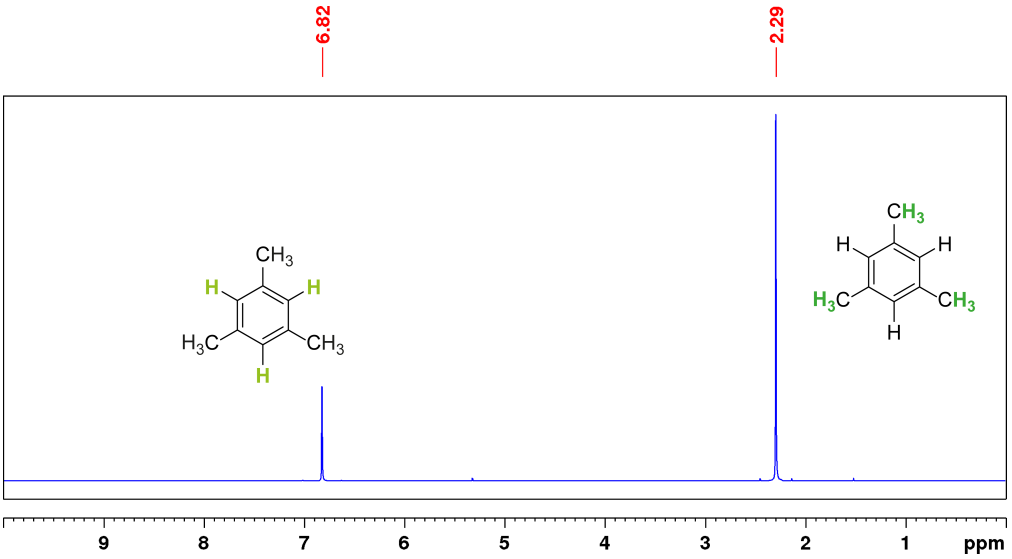

**Supplementary Figure 2:** NMR spectra of 50 µL DMM and 35 µL mesitylene in 450 µL DCM-$d_2$.

### NMR Spectra of MF[17]




**Supplementary Figure 3:** NMR spectra of 50 µL MF and 35 µL mesitylene in 450 µL DCM-$d_2$.

## NMR Spectra of Mesitylene[17]




**Supplementary Figure 4:** NMR spectra of 35 µL mesitylene in 450 µL DCM-$d_2$.

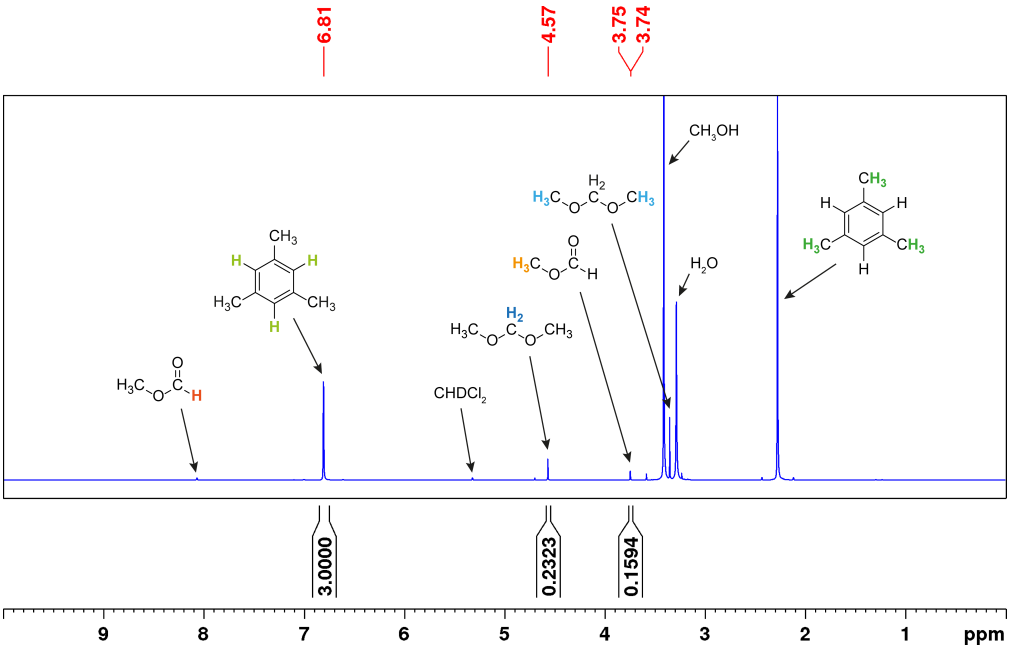
## 5.3 First DoE

### 5.3.1 First Triple

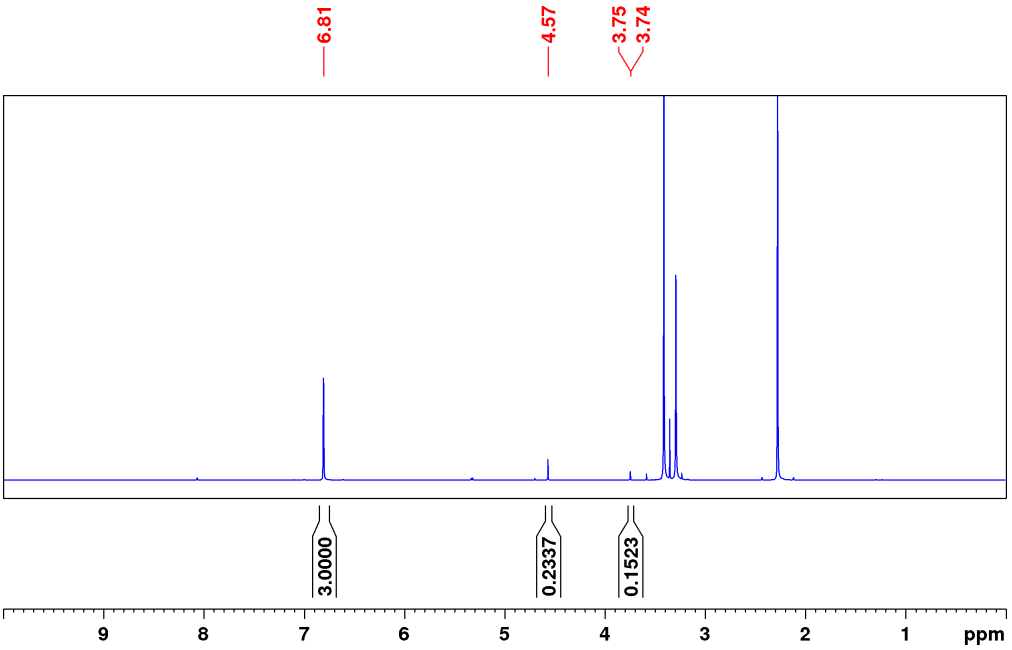
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.75\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 0.78125\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = $Al(OTf)_3$ |
| $t = 18\,h$ | $V_{MeOH} = 0.25\,mL$ |

**Supplementary Table 2:** Catalysis results of the first triple.

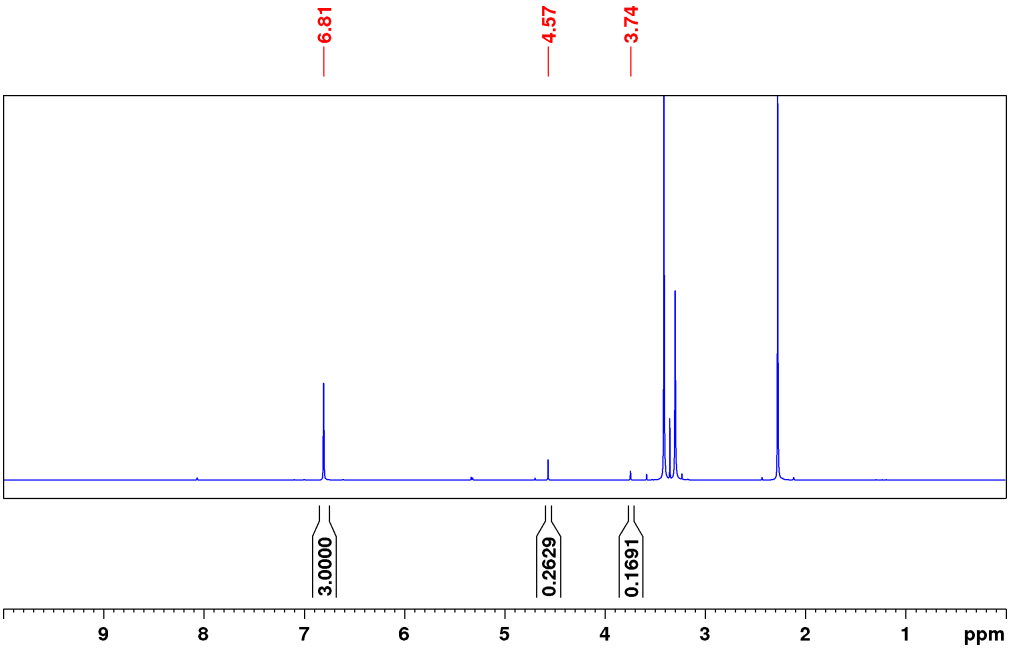
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.2323 | 195 | 0.1594 | 89 | 2.19 |
| Experiment 2 | 0.2337 | 196 | 0.1523 | 85 | 2.30 |
| Experiment 3 | 0.2629 | 220 | 0.1691 | 95 | 2.33 |
| Average | - | 204(14) | - | 90(5) | 2.27(0.08) |




**Supplementary Figure 5:** Experiment 1.




**Supplementary Figure 6:** Experiment 2.



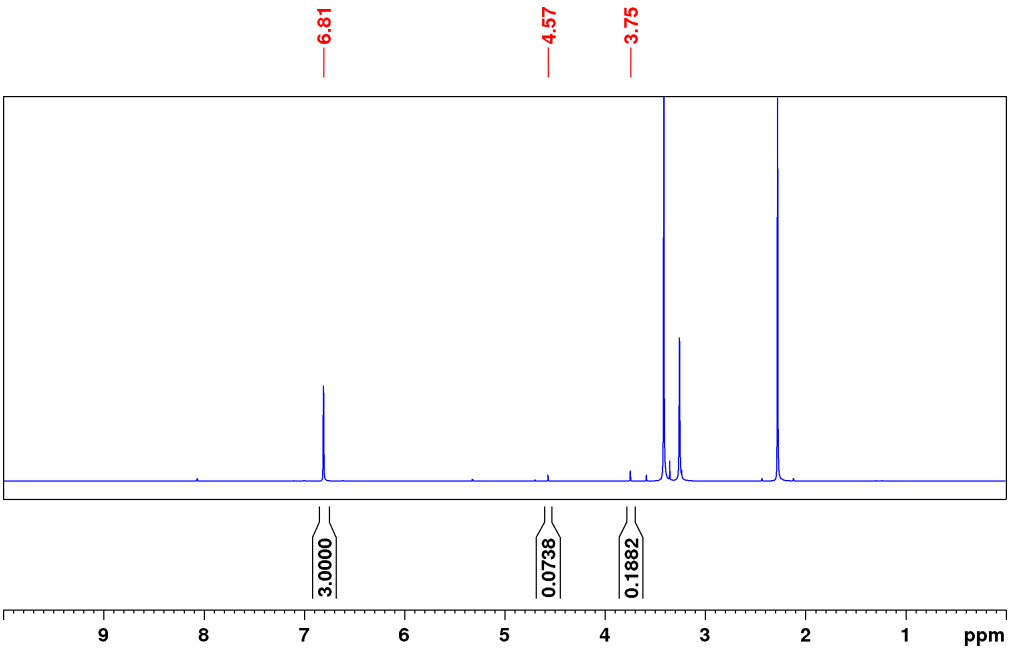

**Supplementary Figure 7:** Experiment 3.

### 5.3.2 Second Triple

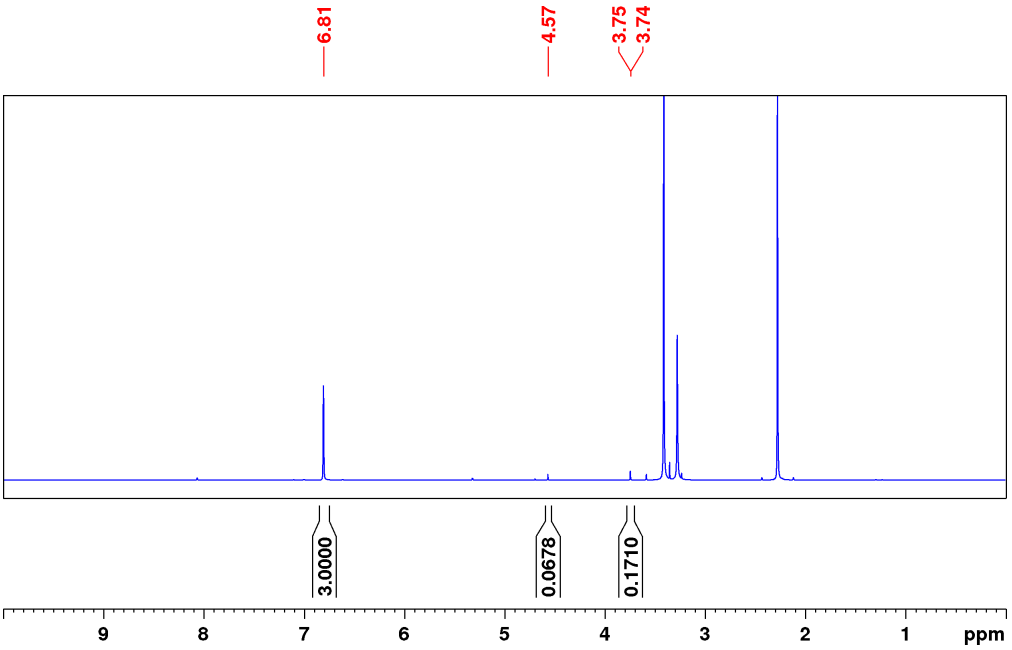
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.75\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 0.78125\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = $Al(OTf)_3$ |
| $t = 18\,h$ | $V_{MeOH} = 0.5\,mL$ |

**Supplementary Table 3:** Catalysis results of the second triple.

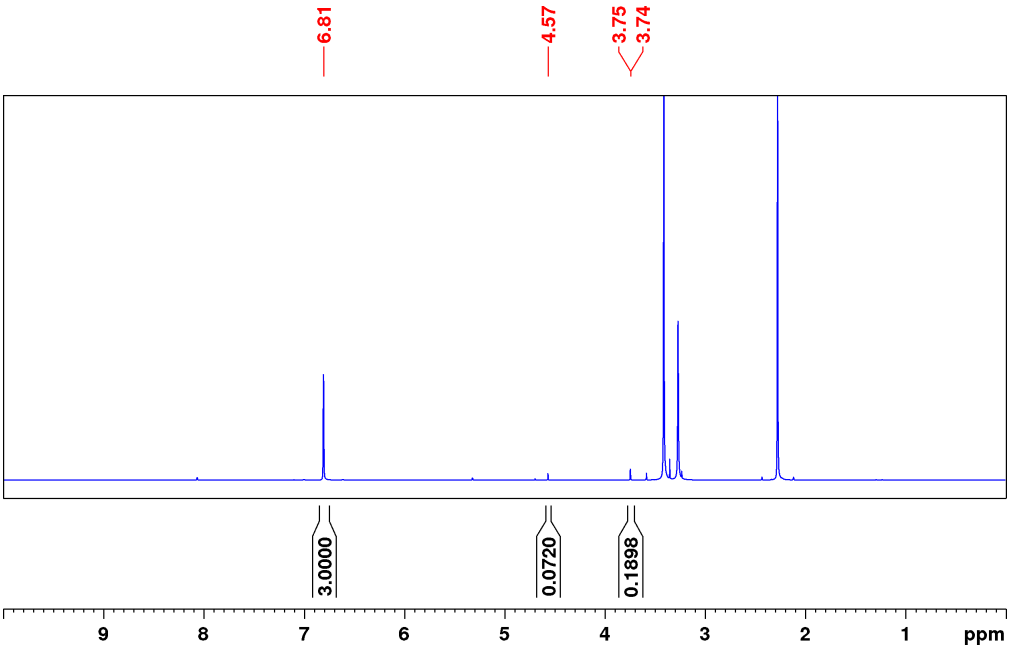
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.0738 | 124 | 0.1882 | 210 | 0.59 |
| Experiment 2 | 0.0678 | 114 | 0.1710 | 191 | 0.59 |
| Experiment 3 | 0.0720 | 121 | 0.1898 | 212 | 0.57 |
| Average | - | 119(5) | - | 205(12) | 0.58(0.01) |




**Supplementary Figure 8:** Experiment 1.




**Supplementary Figure 9:** Experiment 2.



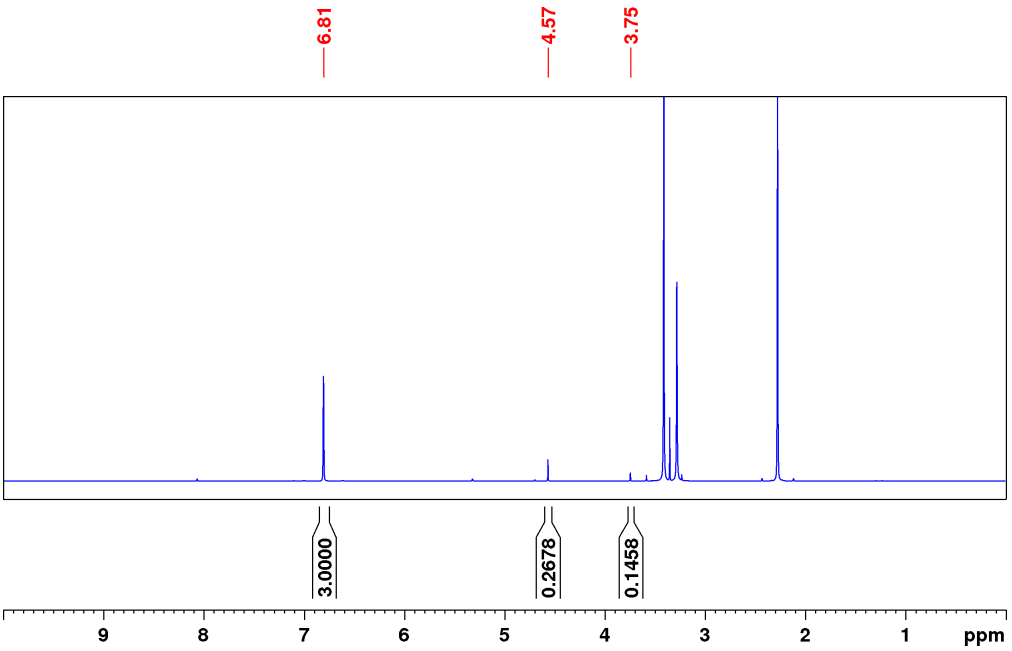

**Supplementary Figure 10:** Experiment 3.

### 5.3.3 Third Triple

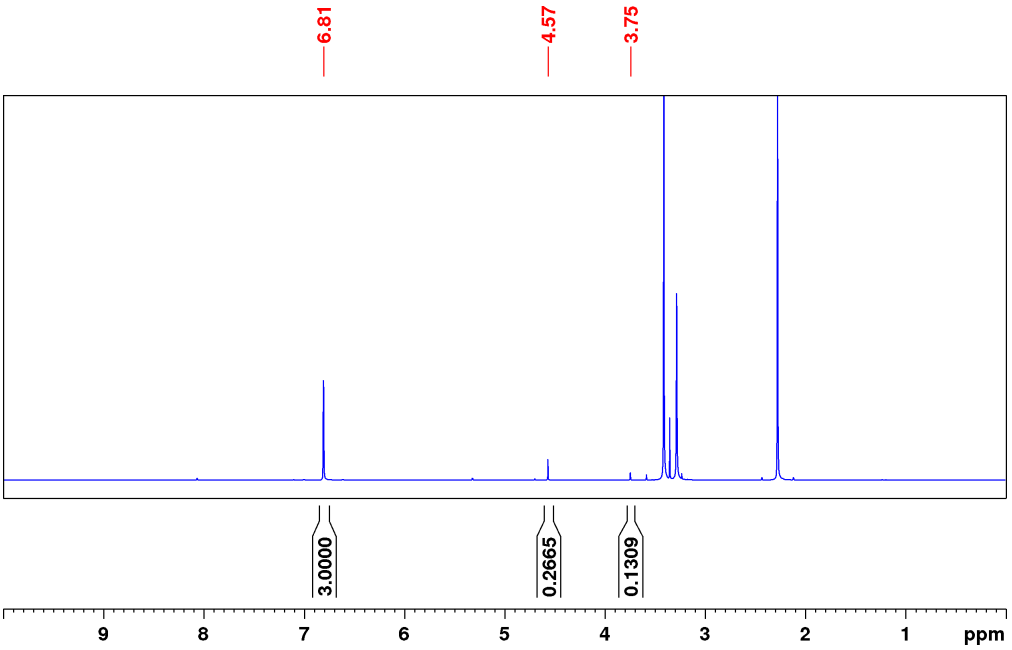
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.75\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 1.953125\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = $Al(OTf)_3$ |
| $t = 18\,h$ | $V_{MeOH} = 0.375\,mL$ |

**Supplementary Table 4:** Catalysis results of the third triple.

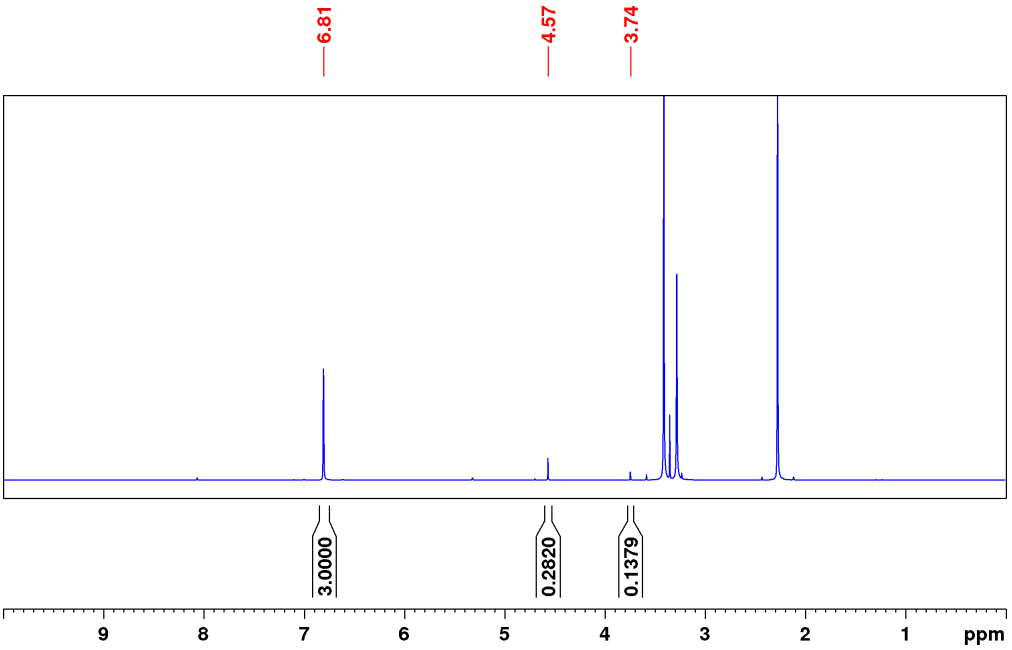
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.2678 | 337 | 0.1458 | 122 | 2.76 |
| Experiment 2 | 0.2665 | 335 | 0.1309 | 110 | 3.05 |
| Experiment 3 | 0.2820 | 355 | 0.1379 | 116 | 3.07 |
| Average | - | 342(11) | - | 116(6) | 2.96(0.18) |




**Supplementary Figure 11:** Experiment 1.




**Supplementary Figure 12:** Experiment 2.



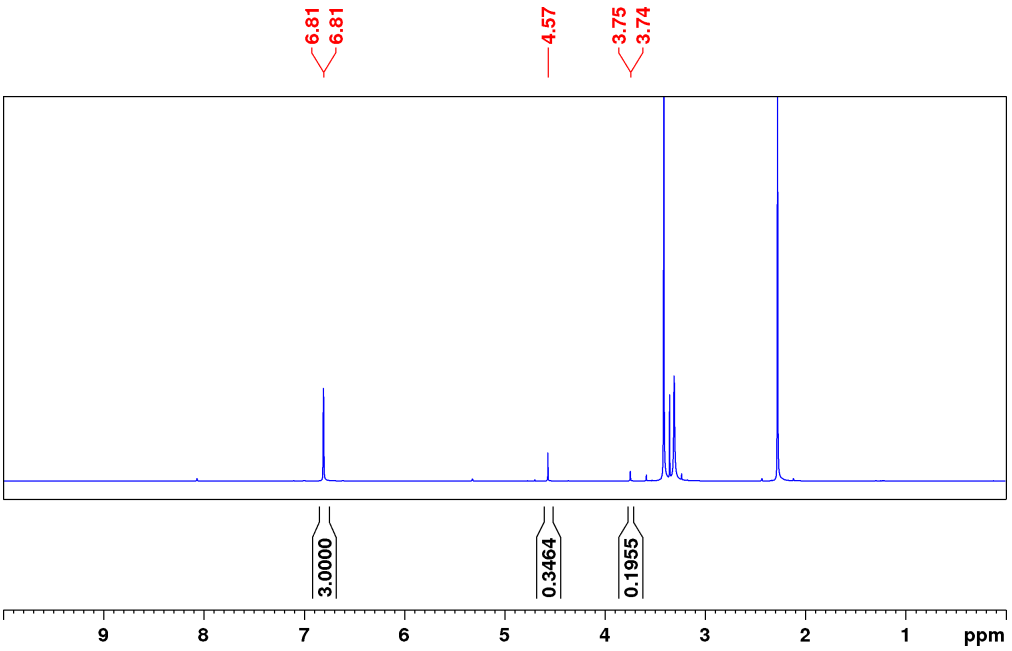

**Supplementary Figure 13:** Experiment 3.

### 5.3.4 Fourth Triple

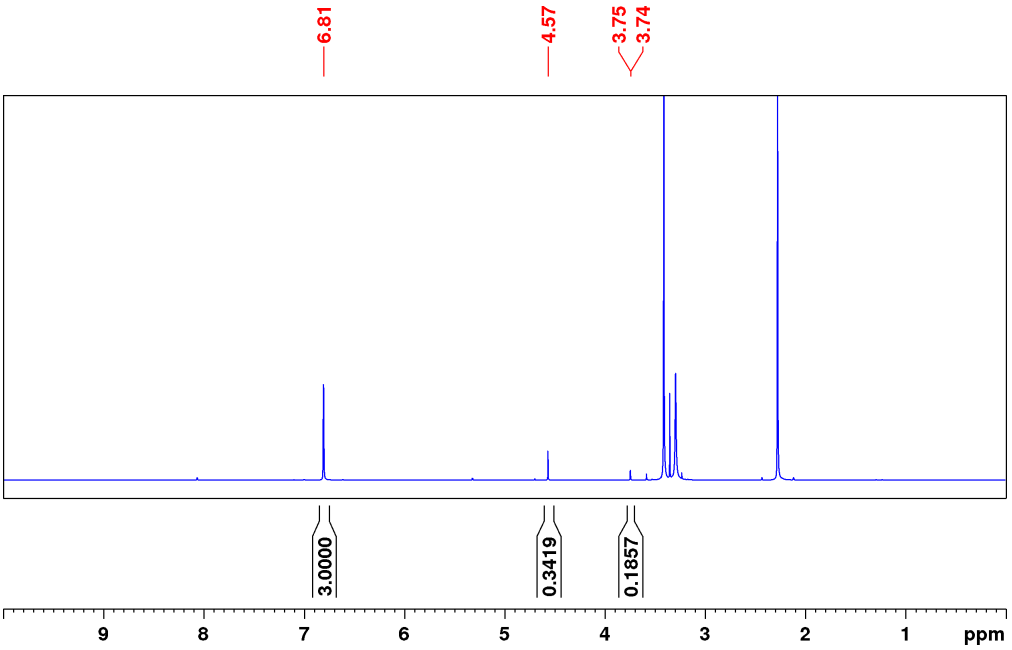
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.1875\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 3.125\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = $Al(OTf)_3$ |
| $t = 18\,h$ | $V_{MeOH} = 0.25\,mL$ |

**Supplementary Table 5:** Catalysis results of the fourth triple.

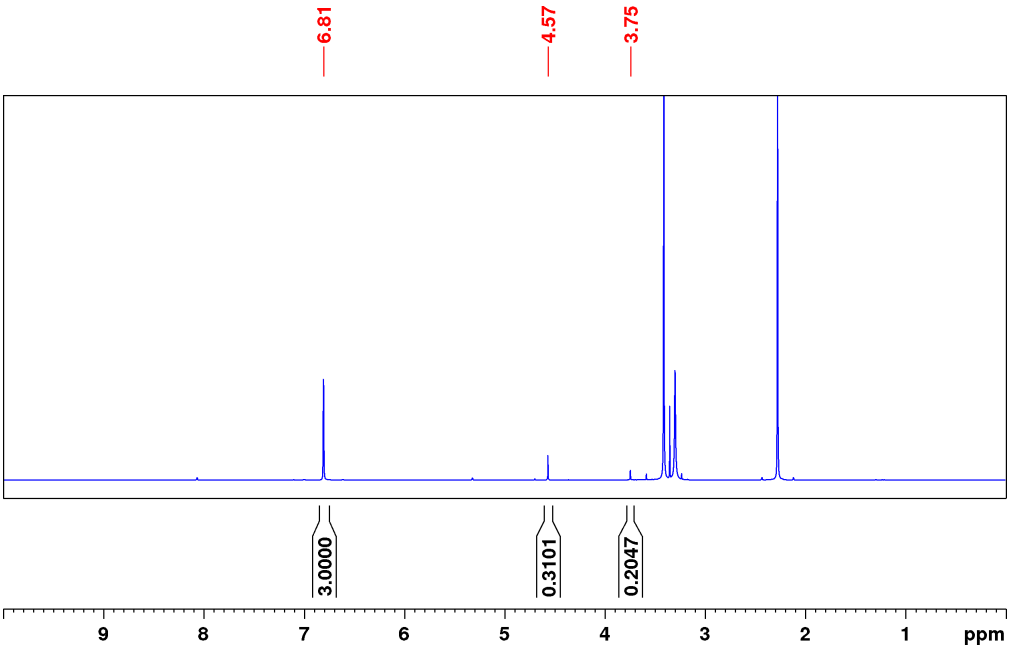
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.3464 | 1162 | 0.1955 | 437 | 2.66 |
| Experiment 2 | 0.3419 | 1147 | 0.1857 | 415 | 2.76 |
| Experiment 3 | 0.3101 | 1040 | 0.2047 | 458 | 2.27 |
| Average | - | 1116(66) | - | 437(21) | 2.56(0.26) |




**Supplementary Figure 14:** Experiment 1.




**Supplementary Figure 15:** Experiment 2.



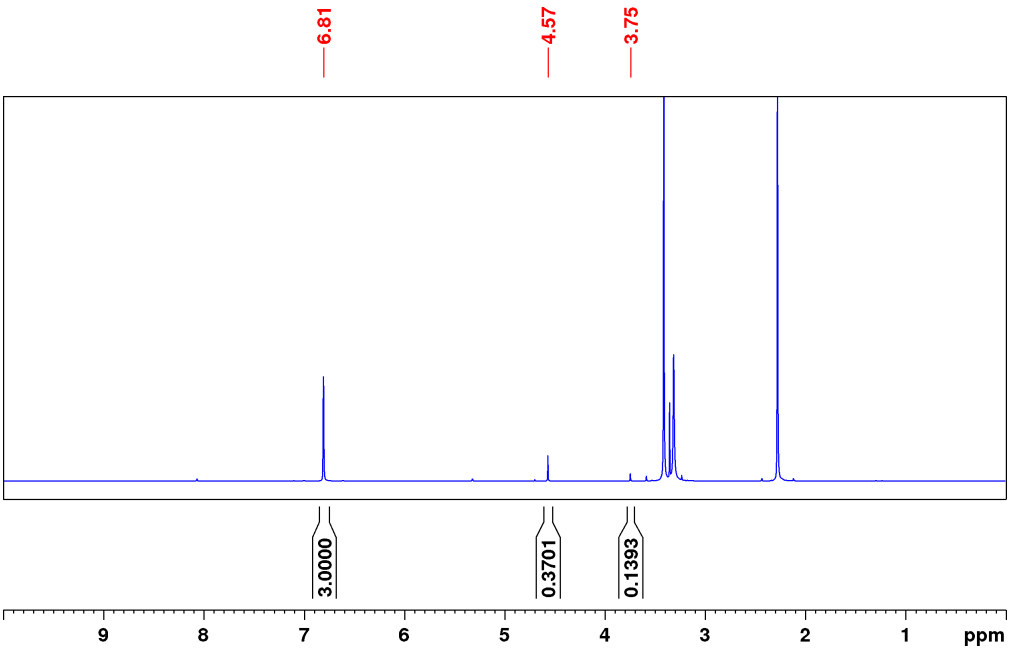

**Supplementary Figure 16:** Experiment 3.

### 5.3.5 Fifth Triple

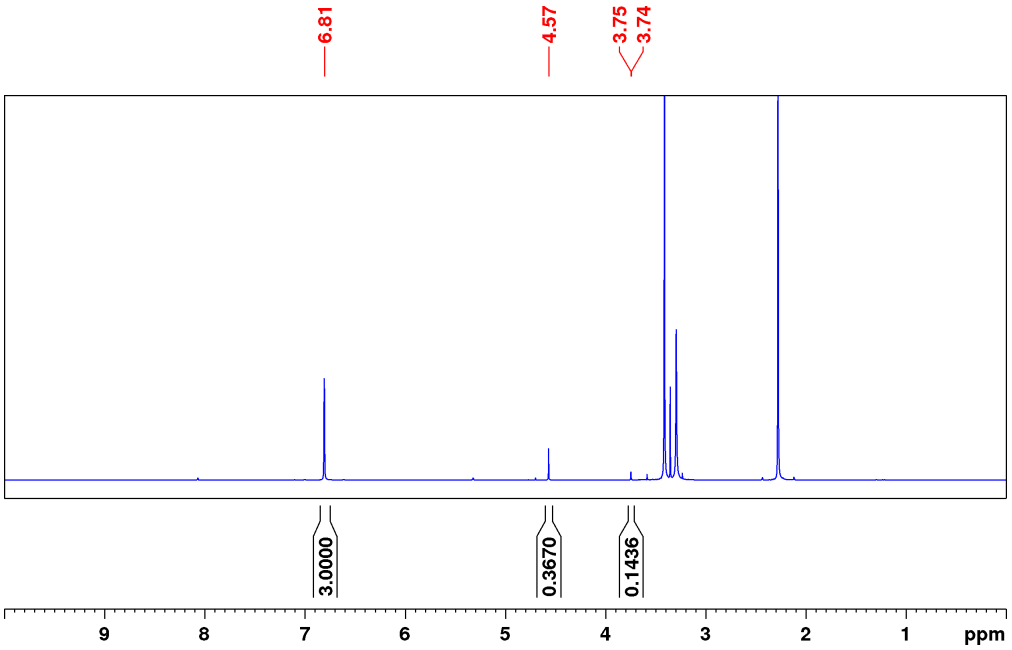
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.75\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 3.125\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = $Al(OTf)_3$ |
| $t = 18\,h$ | $V_{MeOH} = 0.25\,mL$ |

**Supplementary Table 6:** Catalysis results of the fifth triple.

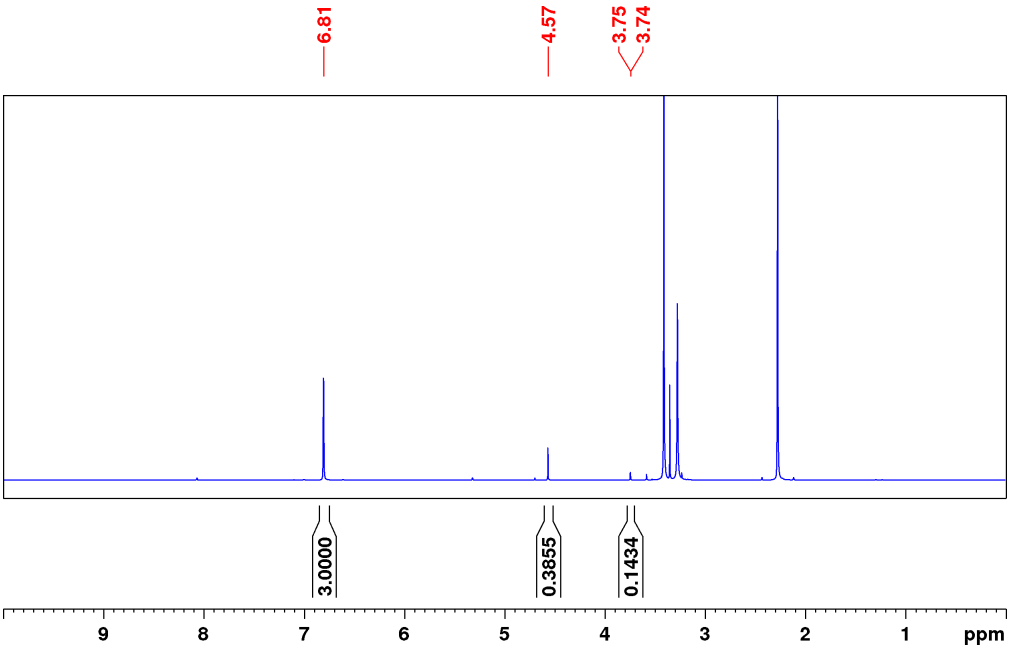
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.3701 | 310 | 0.1393 | 78 | 3.99 |
| Experiment 2 | 0.3670 | 308 | 0.1436 | 80 | 3.83 |
| Experiment 3 | 0.3855 | 323 | 0.1434 | 80 | 4.03 |
| Average | - | 314(8) | - | 79(1) | 3.95(0.10) |




**Supplementary Figure 17:** Experiment 1.




**Supplementary Figure 18:** Experiment 2.



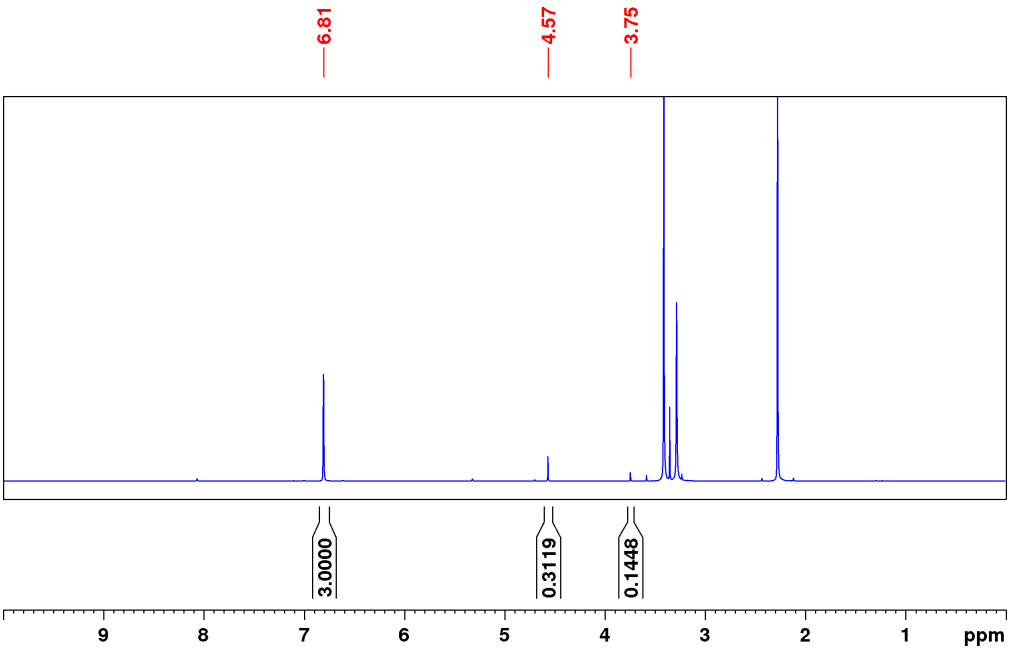

**Supplementary Figure 19:** Experiment 3.

### 5.3.6 Sixth Triple

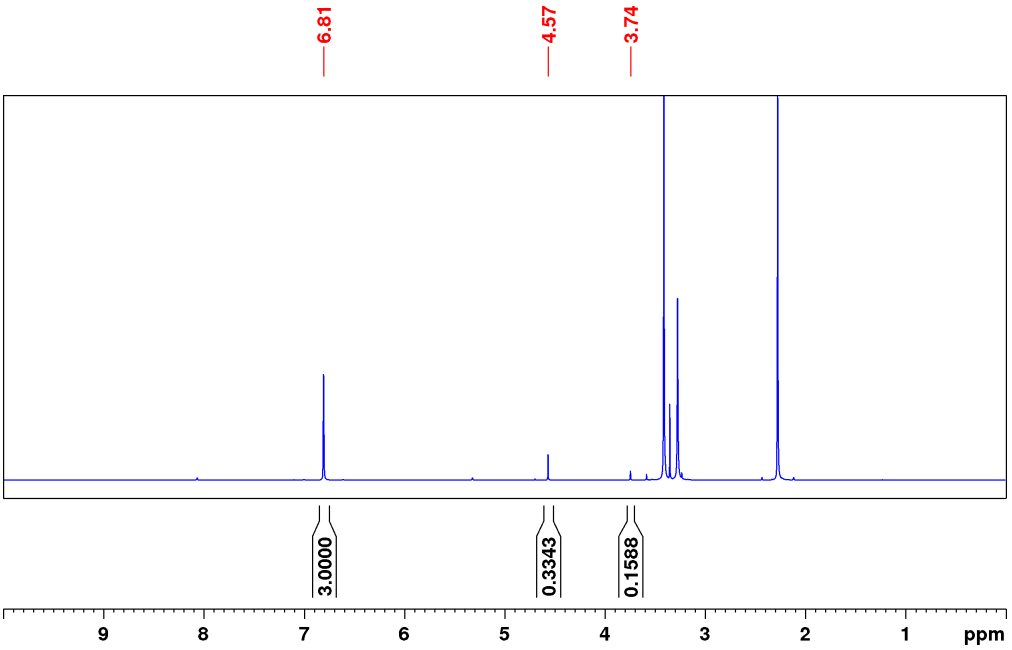
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.46875\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 3.125\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = $Al(OTf)_3$ |
| $t = 18\,h$ | $V_{MeOH} = 0.375\,mL$ |

**Supplementary Table 7:** Catalysis results of the sixth triple.

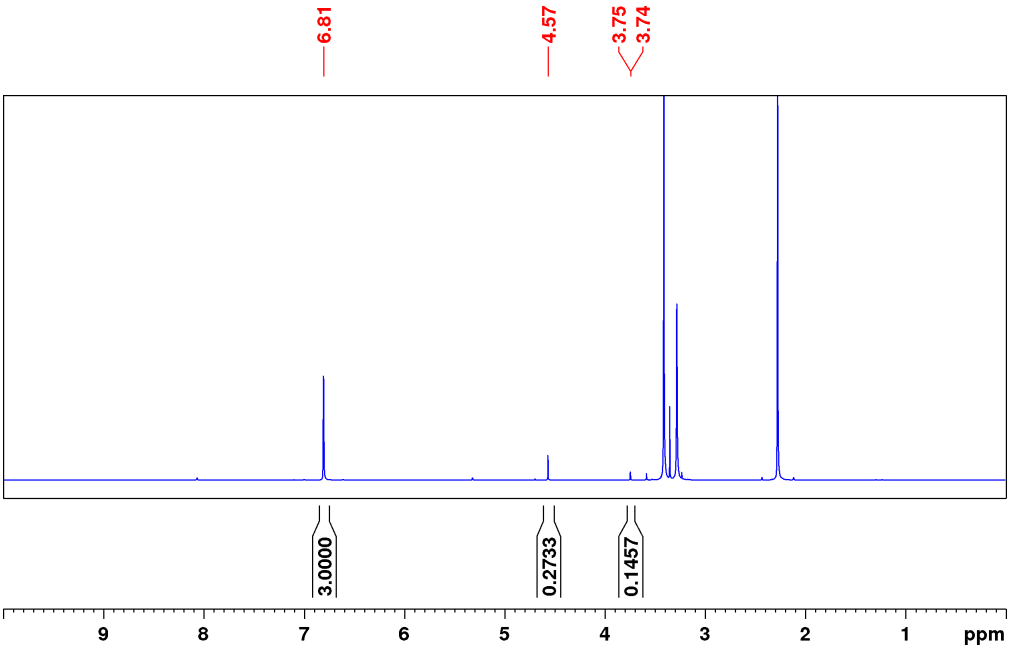
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.3119 | 628 | 0.1448 | 194 | 3.23 |
| Experiment 2 | 0.3343 | 673 | 0.1588 | 213 | 3.16 |
| Experiment 3 | 0.2733 | 550 | 0.1457 | 195 | 2.81 |
| Average | - | 617(62) | - | 201(11) | 3.07(0.22) |




**Supplementary Figure 20:** Experiment 1.




**Supplementary Figure 21:** Experiment 2.




**Supplementary Figure 22:** Experiment 3.

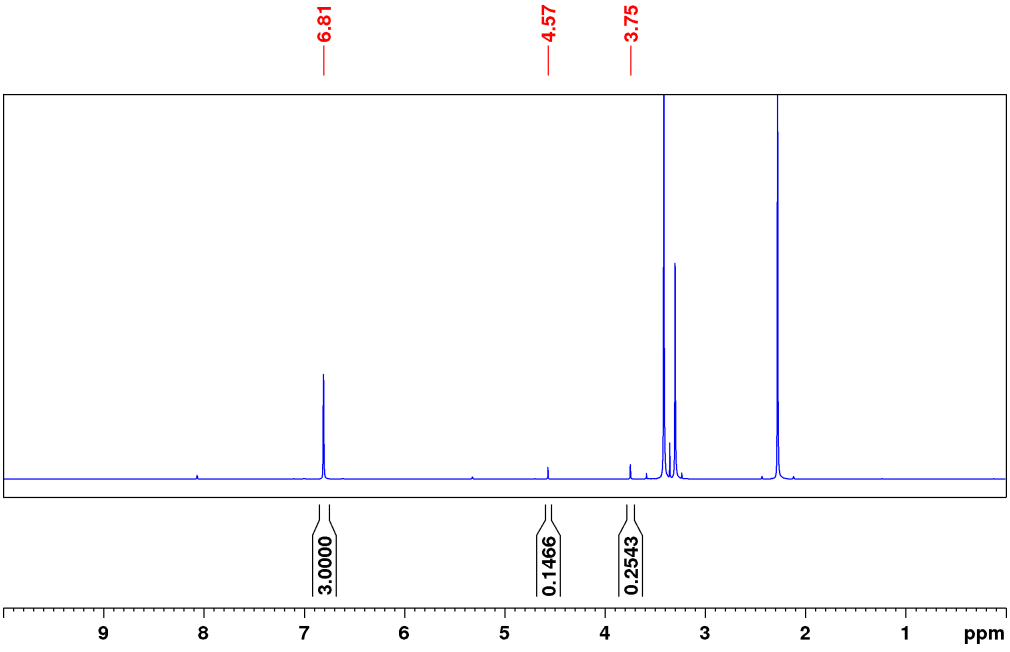
## 5.4 First Relaxation

### 5.4.1 10 % Relaxation

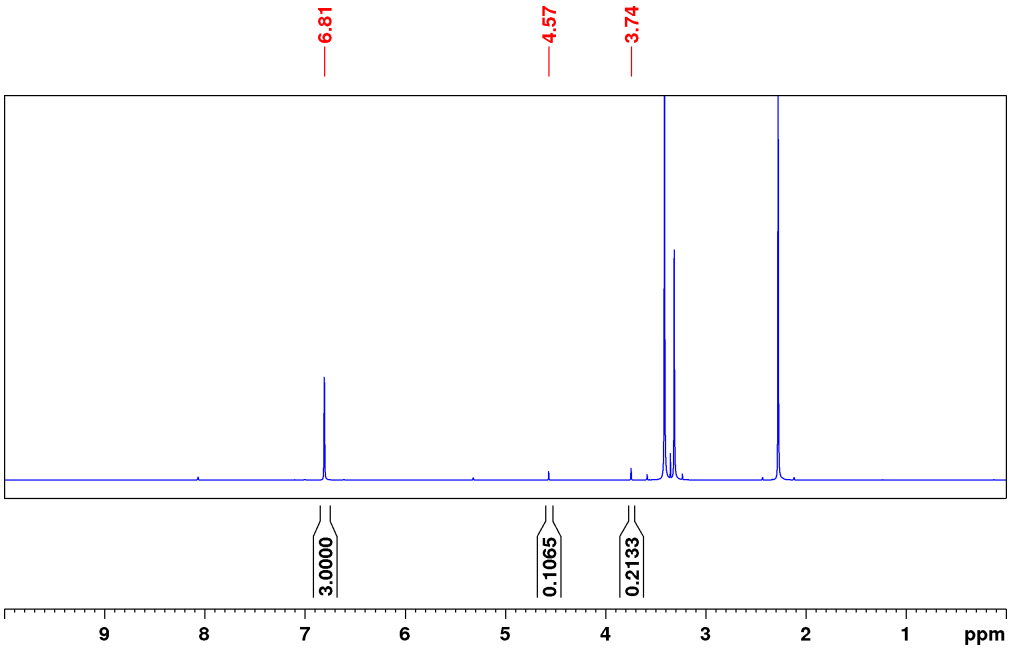
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.1313\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 3.3594\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = $Al(OTf)_3$ |
| $t = 18\,h$ | $V_{MeOH} = 0.525\,mL$ |

**Supplementary Table 8:** Catalysis results of the 10 % relaxation trials.

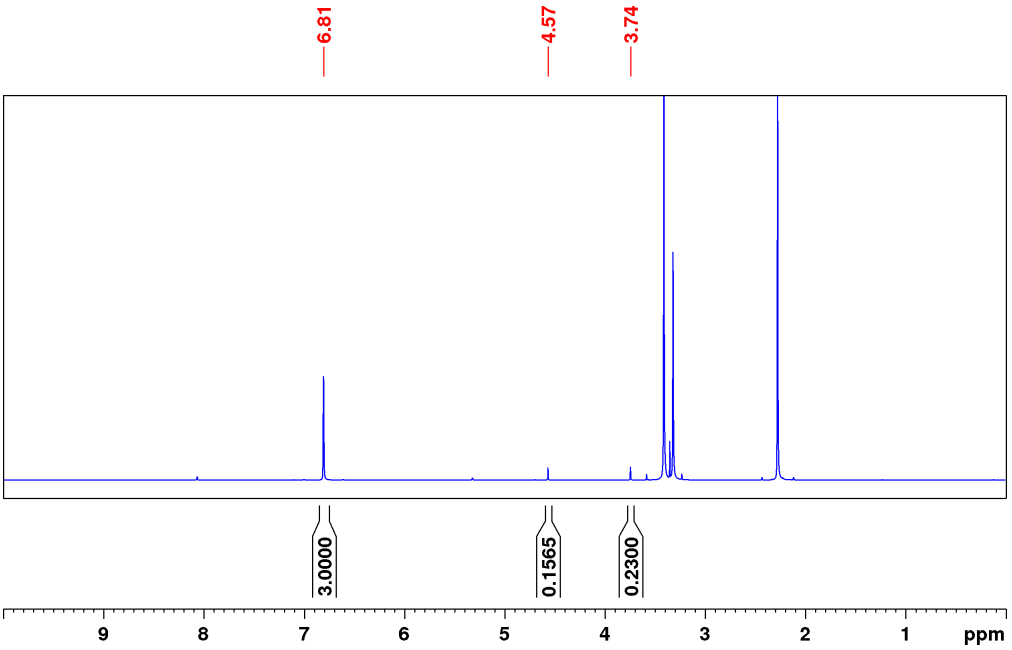
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.1466 | 1475 | 0.2543 | 1706 | 0.86 |
| Experiment 2 | 0.1065 | 1071 | 0.2133 | 1431 | 0.75 |
| Experiment 3 | 0.1565 | 1574 | 0.2300 | 1543 | 1.02 |
| Average | - | 1374(266) | - | 1560(138) | 0.88(0.14) |




**Supplementary Figure 23:** Experiment 1.




**Supplementary Figure 24:** Experiment 2.



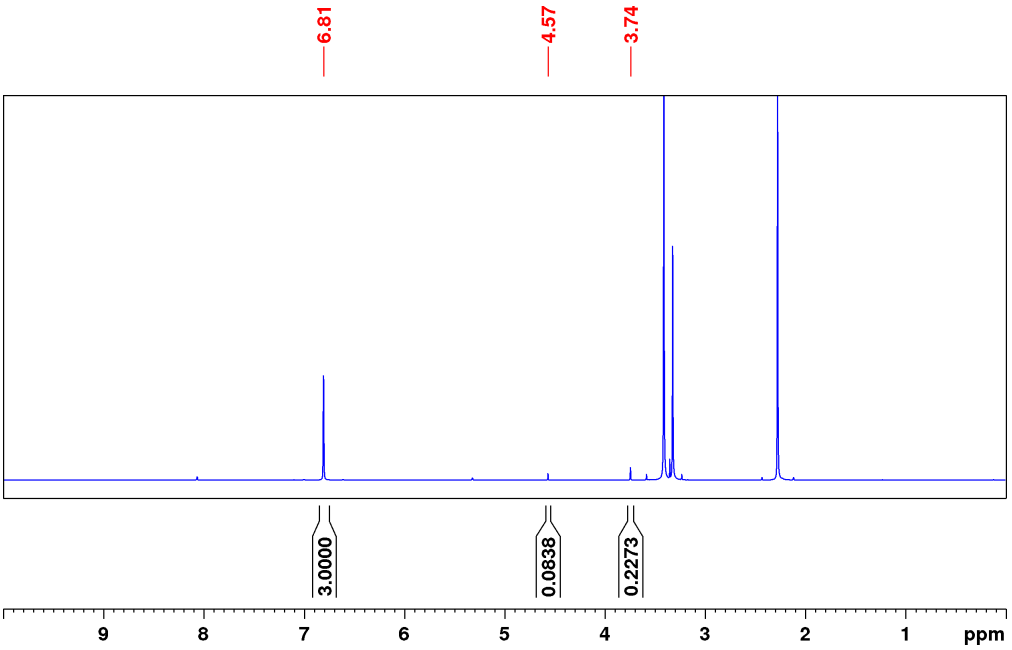

**Supplementary Figure 25:** Experiment 3.

### 5.4.2 20 % Relaxation

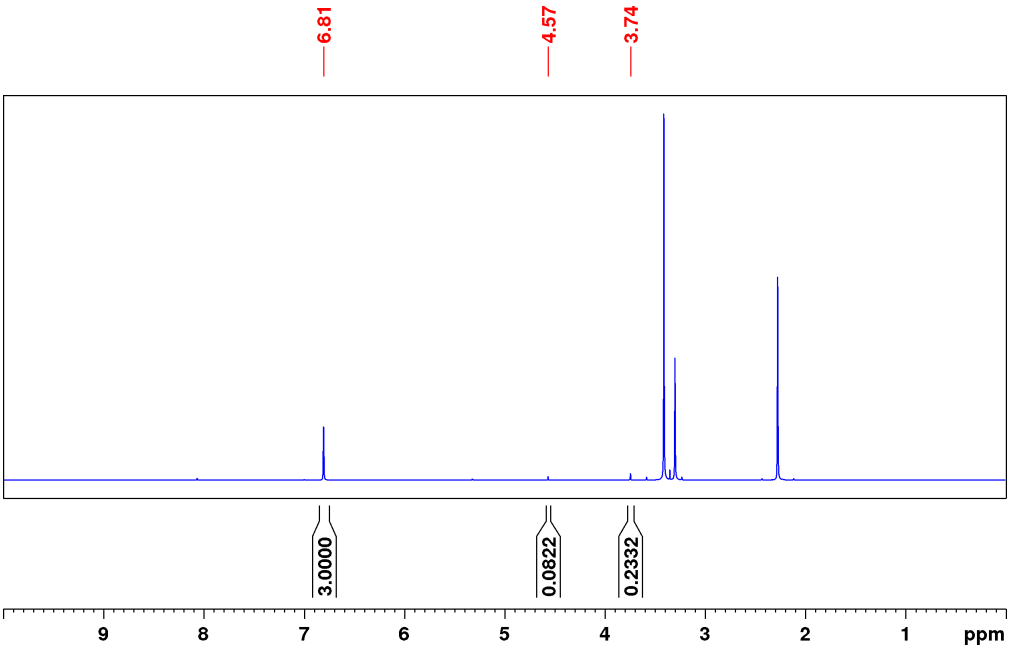
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.075\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 3.576\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = $Al(OTf)_3$ |
| $t = 18\,h$ | $V_{MeOH} = 0.55\,mL$ |

**Supplementary Table 9:** Catalysis results of the 20 % relaxation trials.

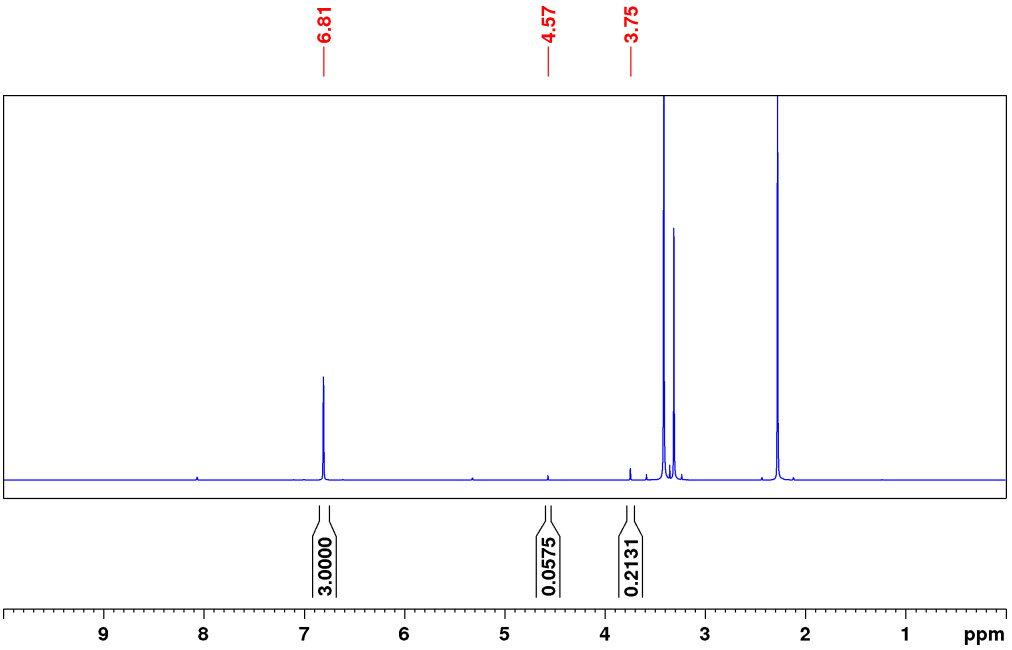
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.0838 | 1546 | 0.2273 | 2796 | 0.55 |
| Experiment 2 | 0.0822 | 1517 | 0.2332 | 2868 | 0.53 |
| Experiment 3 | 0.0575 | 1061 | 0.2131 | 2621 | 0.40 |
| Average | - | 1375(272) | - | 2762(127) | 0.50(0.08) |




**Supplementary Figure 26:** Experiment 1.




**Supplementary Figure 27:** Experiment 2.



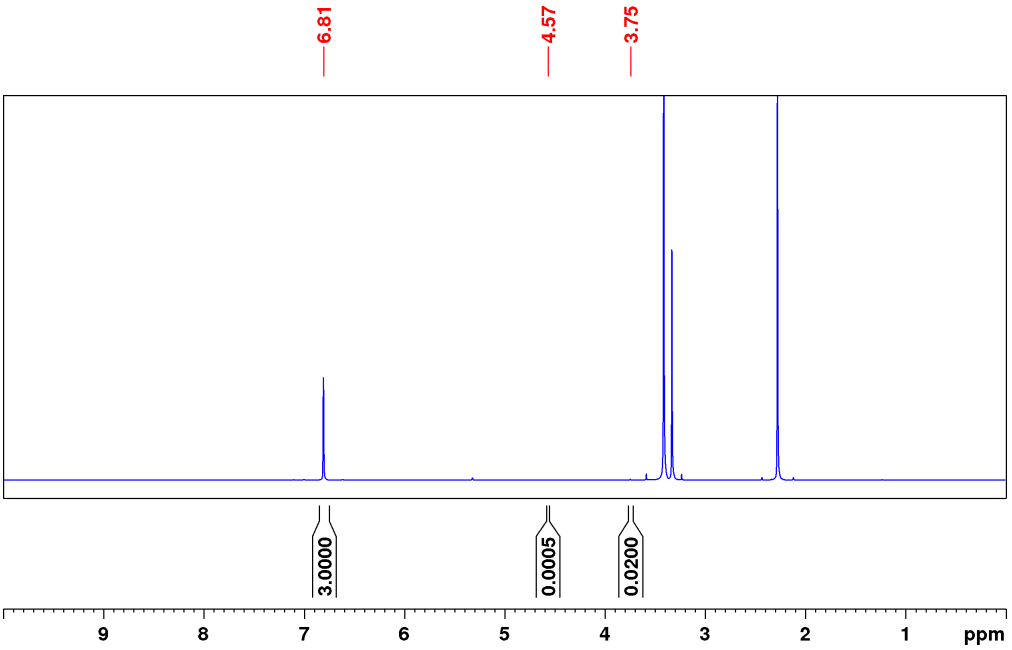

**Supplementary Figure 28:** Experiment 3.

### 5.4.3 30 % Relaxation

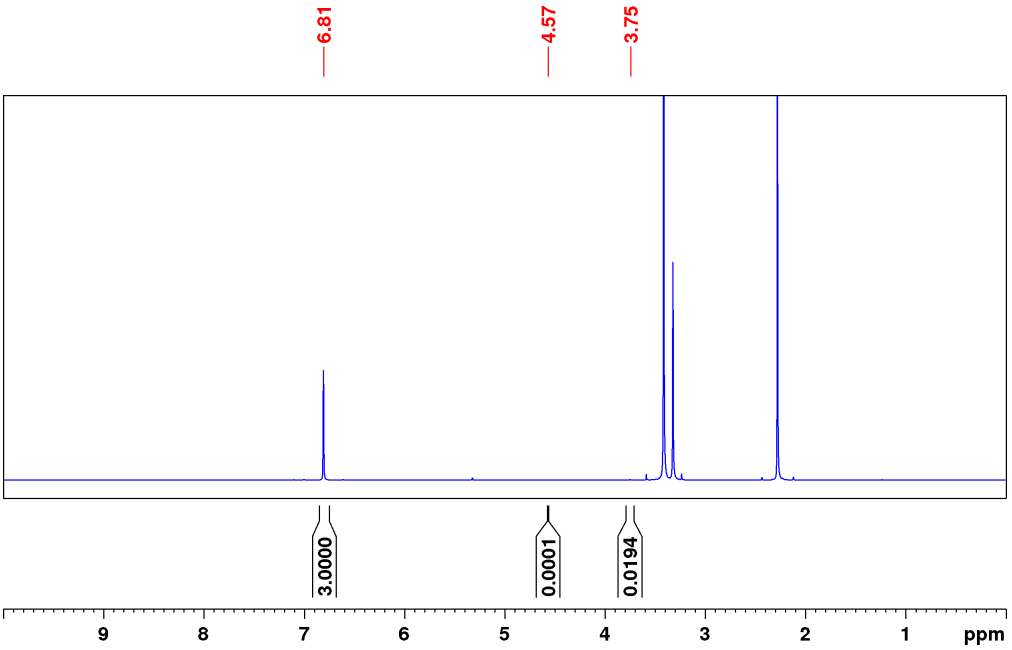
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.0188\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 3.6594\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = $Al(OTf)_3$ |
| $t = 18\,h$ | $V_{MeOH} = 0.575\,mL$ |

**Supplementary Table 10:** Catalysis results of the 30 % relaxation trials.

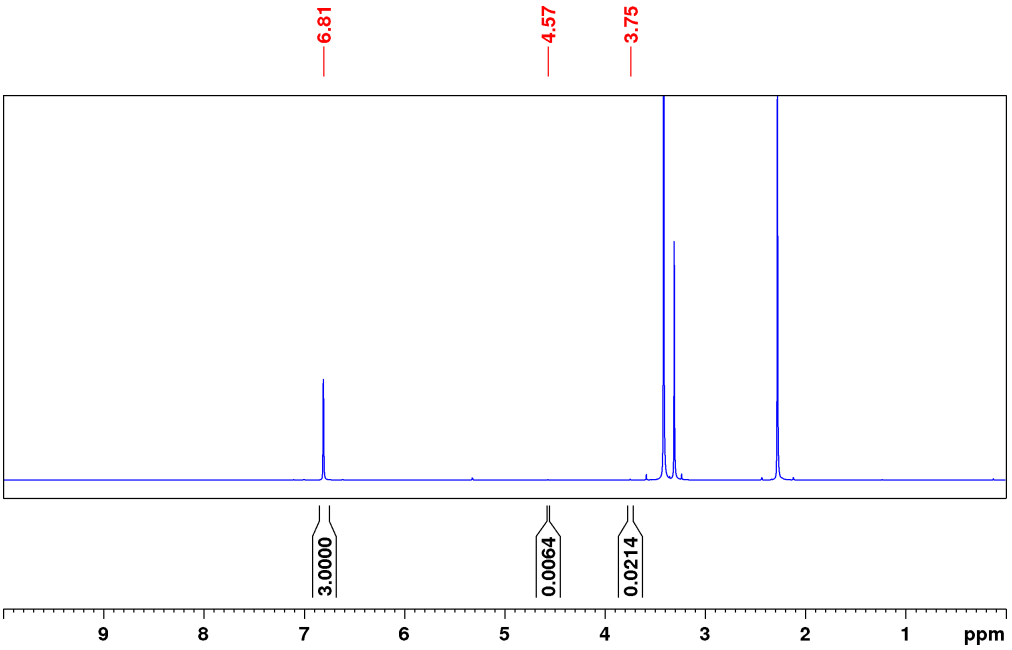
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.0005 | 38 | 0.0200 | 1026 | 0.04 |
| Experiment 2 | 0.0001 | 8 | 0.0194 | 995 | 0.01 |
| Experiment 3 | 0.0064 | 492 | 0.0214 | 1098 | 0.45 |
| Average | - | 180(271) | - | 1040(53) | 0.16(0.25) |




**Supplementary Figure 29:** Experiment 1.




**Supplementary Figure 30:** Experiment 2.




**Supplementary Figure 31:** Experiment 3.

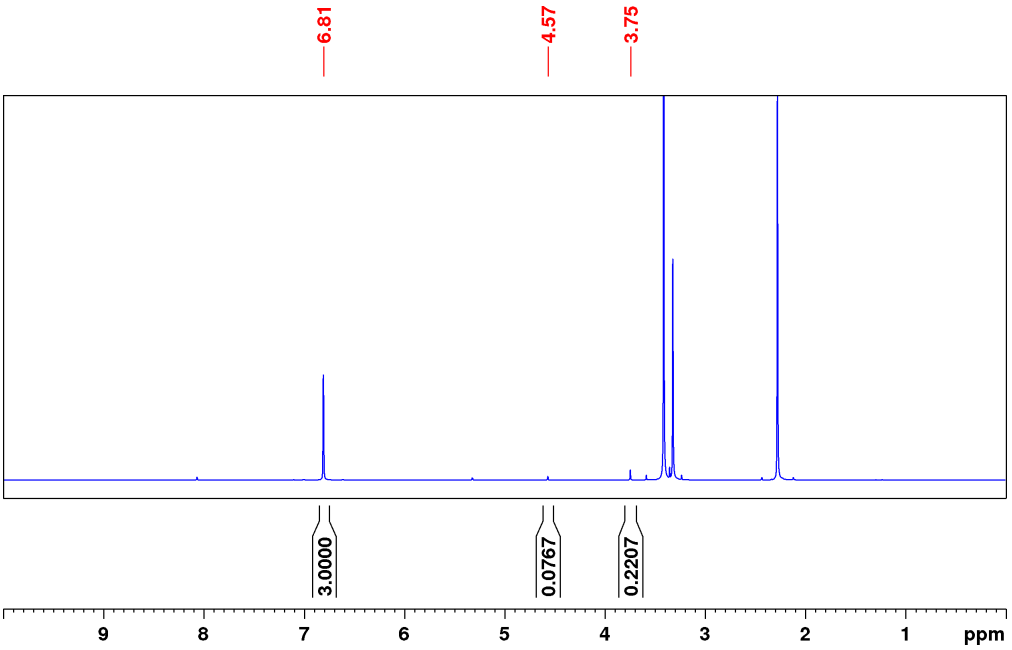
## 5.5 Second DoE

### 5.5.1 Replication: Best Hit First Relaxation

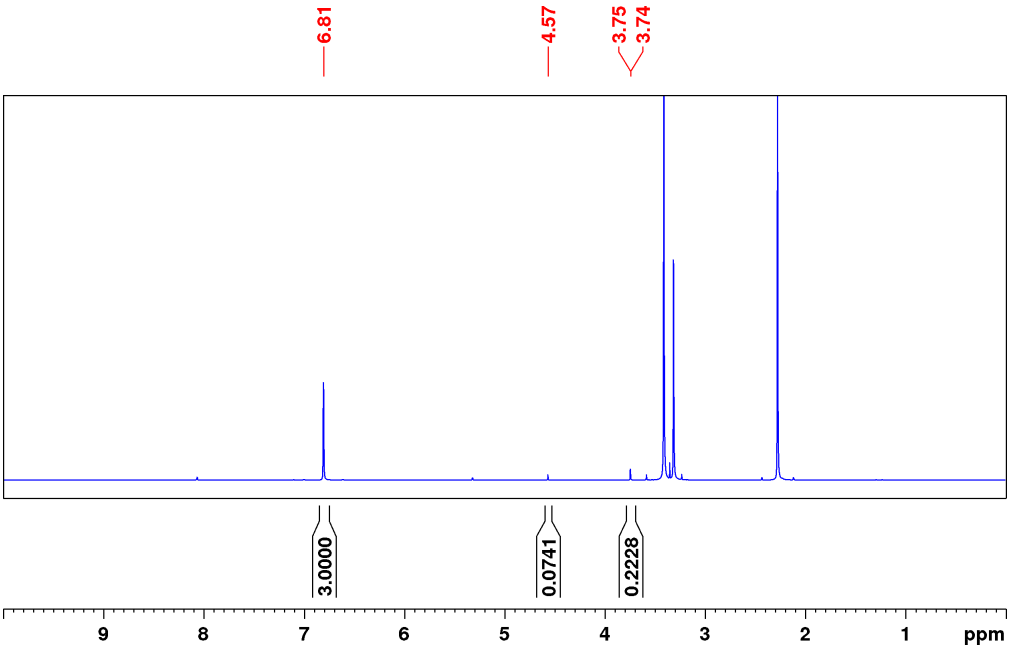
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.075\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 3.576\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = $Al(OTf)_3$ |
| $t = 18\,h$ | $V_{MeOH} = 0.55\,mL$ |

**Supplementary Table 11:** Catalysis results of the replication study.

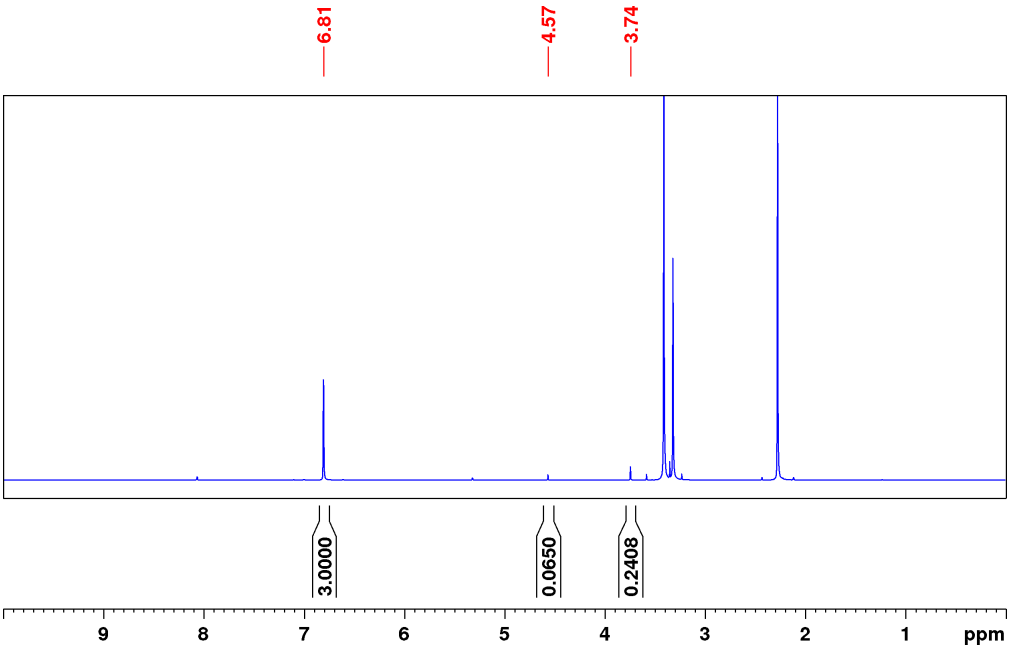
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.0767 | 1415 | 0.2207 | 2715 | 0.52 |
| Experiment 2 | 0.0741 | 1367 | 0.2228 | 2741 | 0.50 |
| Experiment 3 | 0.0650 | 1199 | 0.2408 | 2962 | 0.40 |
| Average | - | 1327(113) | - | 2806(136) | 0.48(0.06) |




**Supplementary Figure 32:** Experiment 1.




**Supplementary Figure 33:** Experiment 2.



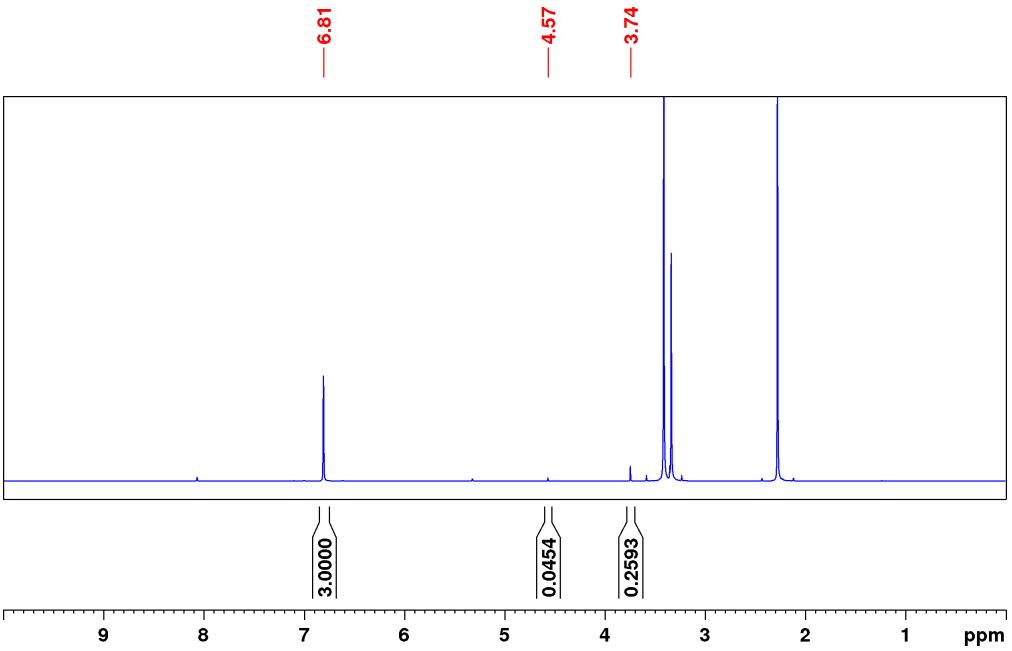

**Supplementary Figure 34:** Experiment 3.

### 5.5.2 First Triple

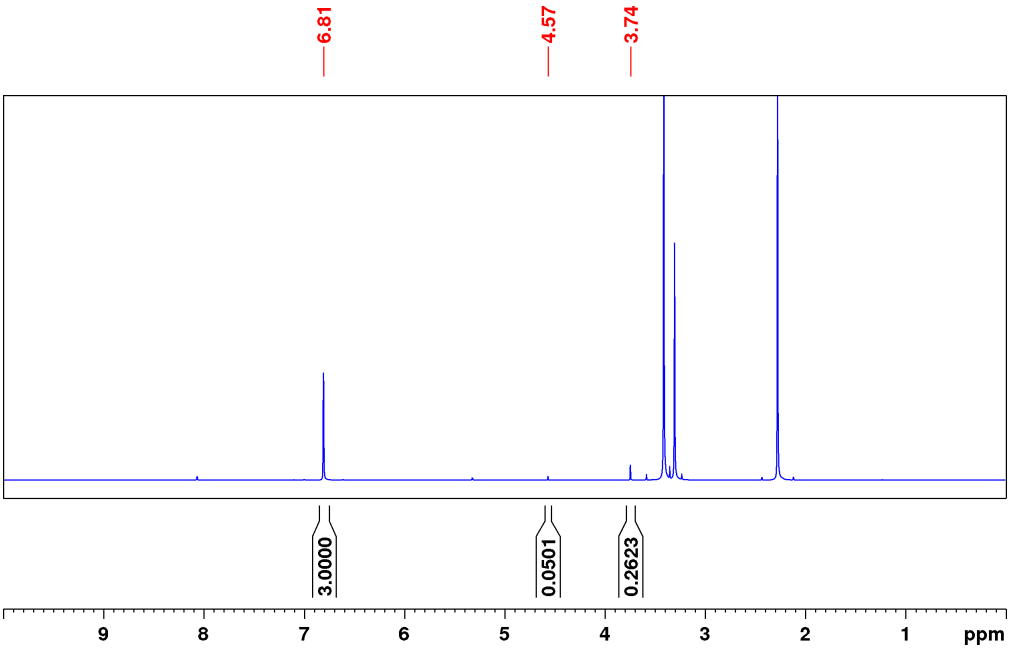
| | |
|---|---|
| $T = 80\,°C$ | $n_{cat} = 0.075\,\mu mol$ |
| $p_{H2} = 100\,bar$ | $n_{add} = 3.576\,\mu mol$ |
| $p_{CO2} = 25\,bar$ | add = $Al(OTf)_3$ |
| $t = 20\,h$ | $V_{MeOH} = 0.55\,mL$ |

**Supplementary Table 12:** Catalysis results of the first triple.

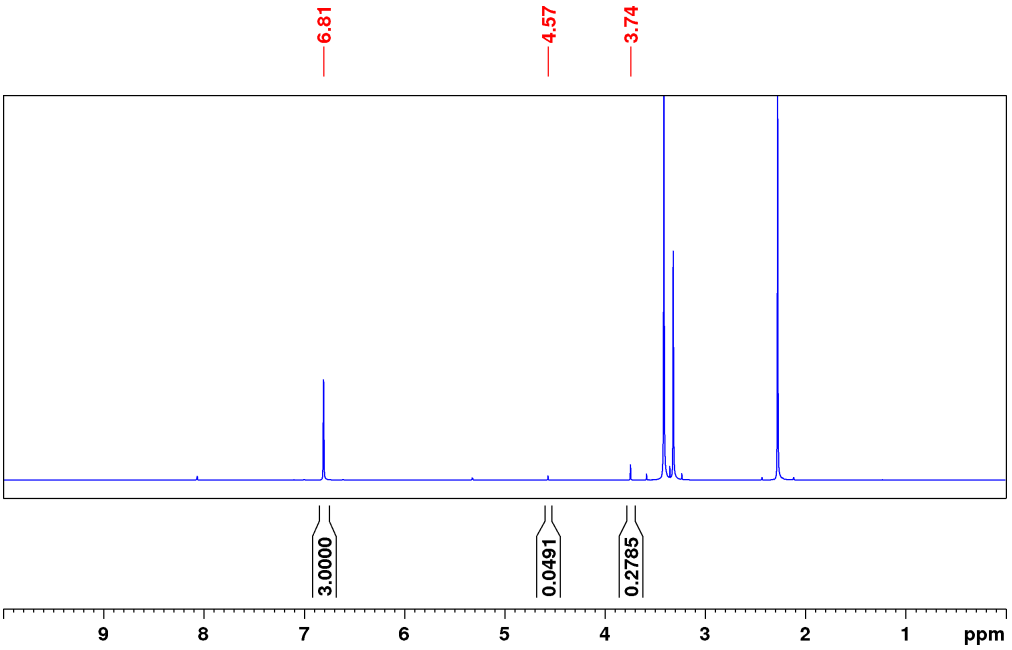
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.0454 | 838 | 0.2593 | 3190 | 0.26 |
| Experiment 2 | 0.0501 | 924 | 0.2623 | 3226 | 0.29 |
| Experiment 3 | 0.0491 | 906 | 0.2785 | 3426 | 0.26 |
| Average | - | 889(46) | - | 3281(127) | 0.27(0.01) |




**Supplementary Figure 35:** Experiment 1.




**Supplementary Figure 36:** Experiment 2.



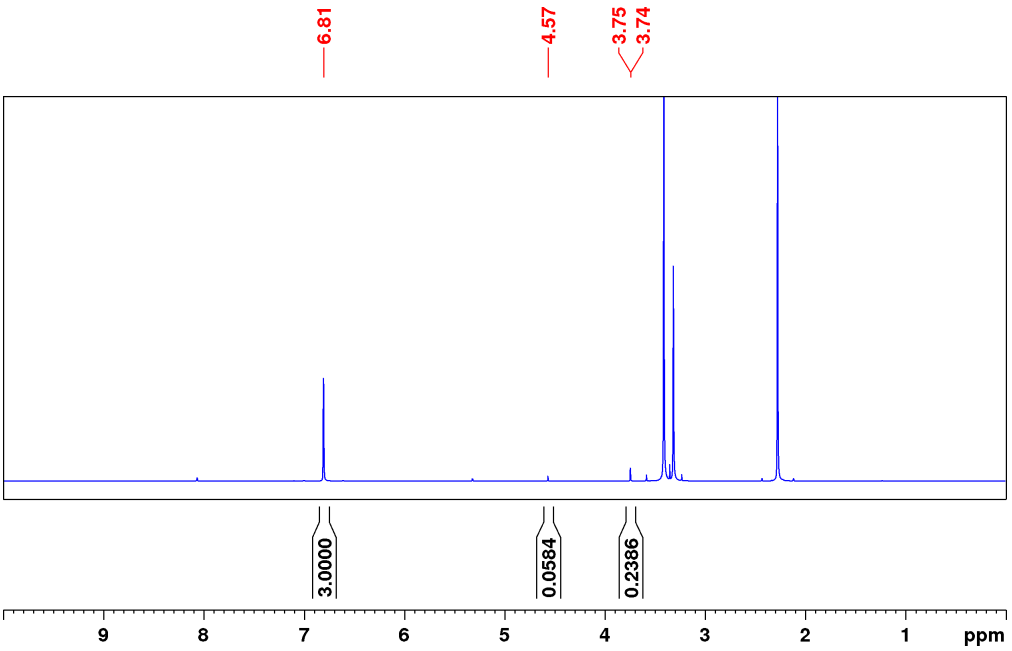

**Supplementary Figure 37:** Experiment 3.

### 5.5.3 Second Triple

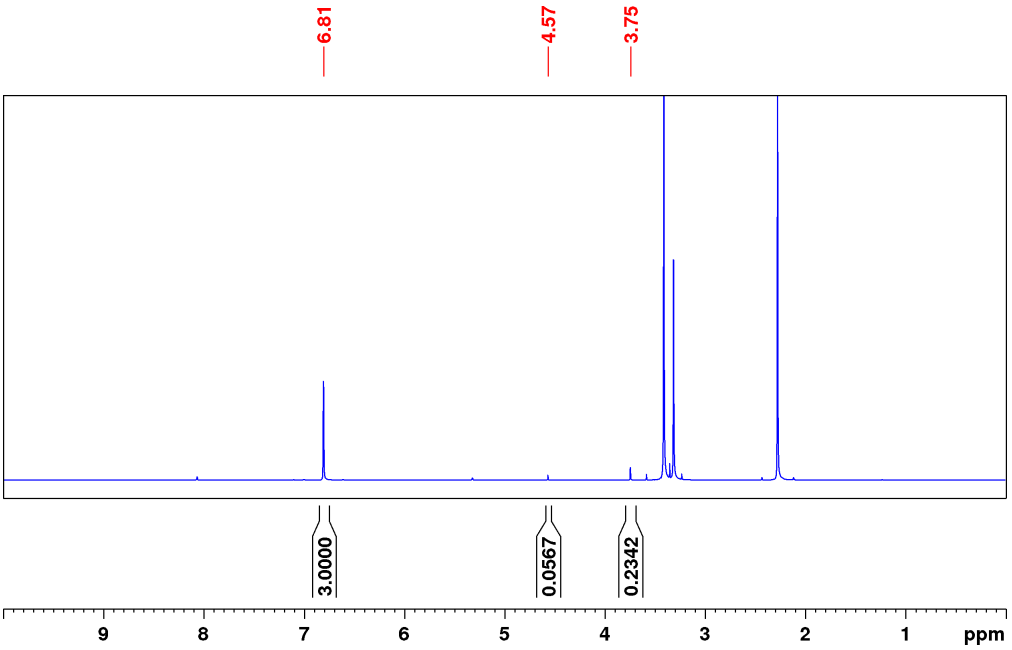
| | |
|---|---|
| $T = 100\,°C$ | $n_{cat} = 0.075\,\mu mol$ |
| $p_{H2} = 80\,bar$ | $n_{add} = 3.576\,\mu mol$ |
| $p_{CO2} = 25\,bar$ | add = $Al(OTf)_3$ |
| $t = 20\,h$ | $V_{MeOH} = 0.55\,mL$ |

**Supplementary Table 13:** Catalysis results of the second triple.

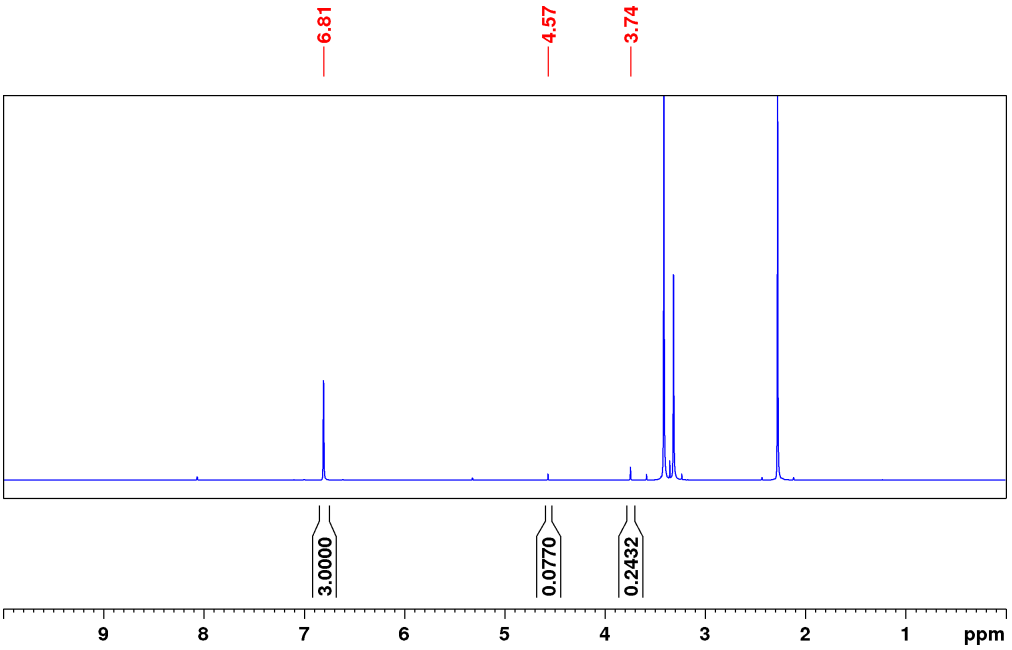
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.0584 | 1078 | 0.2386 | 2935 | 0.37 |
| Experiment 2 | 0.0567 | 1046 | 0.2342 | 2881 | 0.36 |
| Experiment 3 | 0.0770 | 1421 | 0.2432 | 2991 | 0.47 |
| Average | - | 1181(208) | - | 2936(55) | 0.40(0.06) |




**Supplementary Figure 38:** Experiment 1.




**Supplementary Figure 39:** Experiment 2.



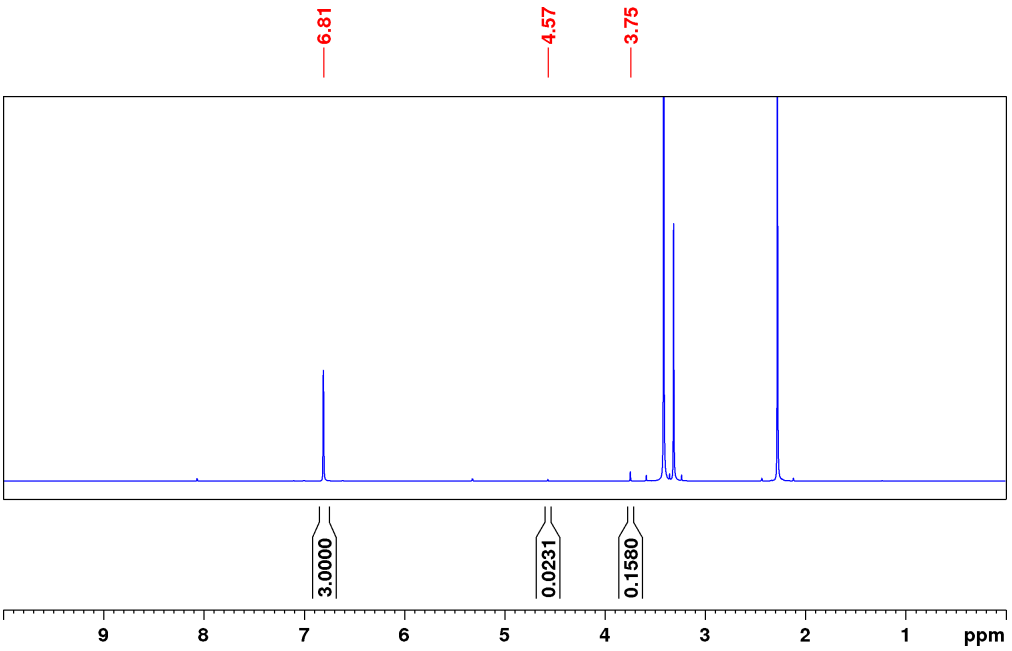

**Supplementary Figure 40:** Experiment 3.

### 5.5.4 Third Triple

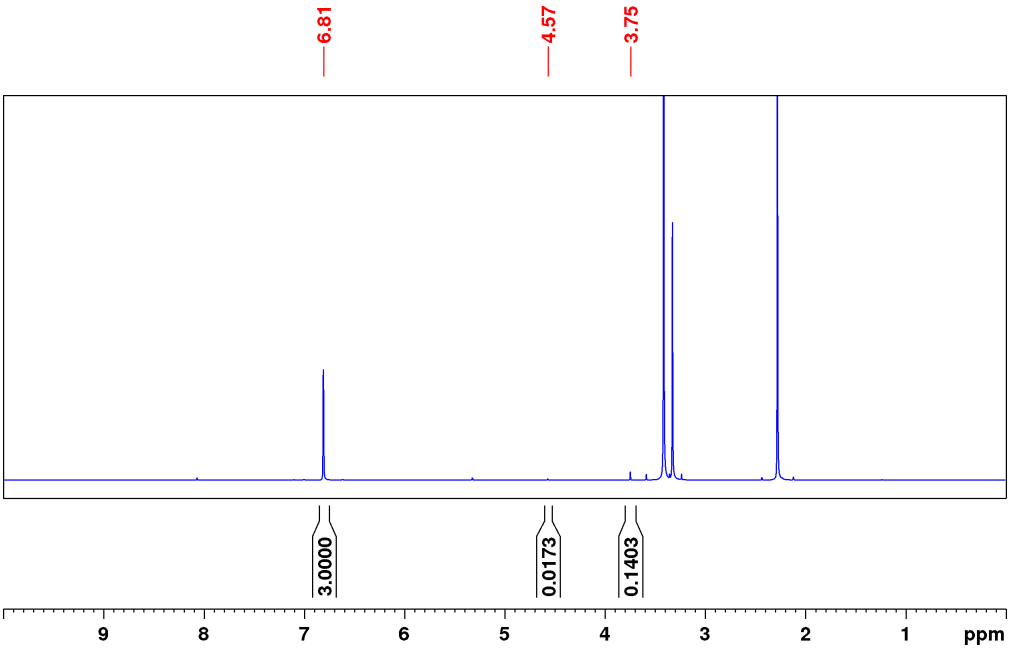
| | |
|---|---|
| $T = 80\,°C$ | $n_{cat} = 0.075\,\mu mol$ |
| $p_{H2} = 80\,bar$ | $n_{add} = 3.576\,\mu mol$ |
| $p_{CO2} = 15\,bar$ | add = $Al(OTf)_3$ |
| $t = 16\,h$ | $V_{MeOH} = 0.55\,mL$ |

**Supplementary Table 14:** Catalysis results of the third triple.

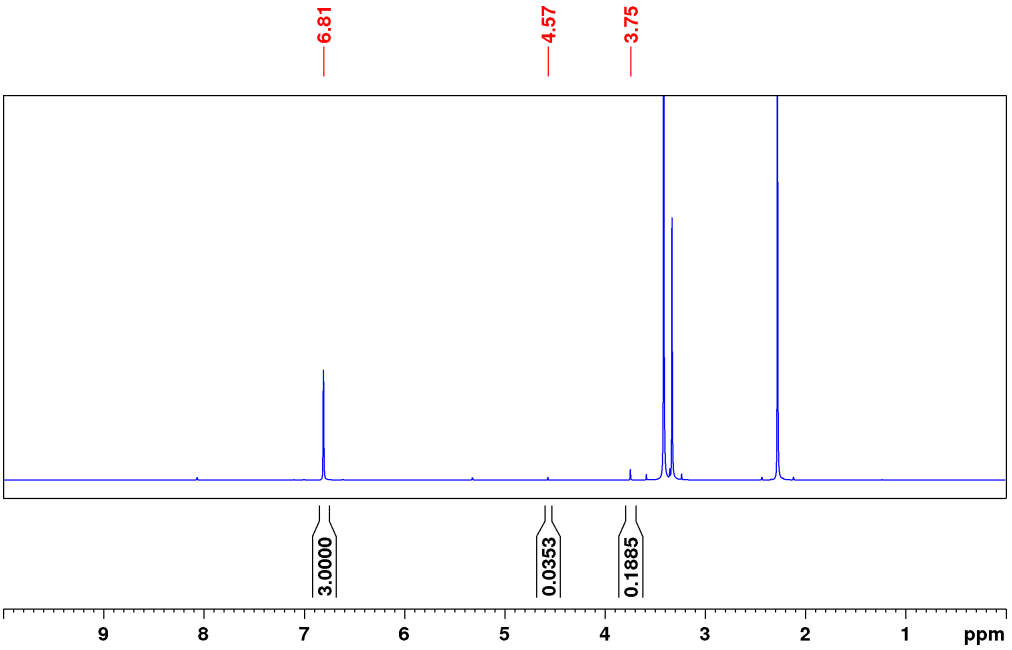
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.0231 | 426 | 0.1580 | 1943 | 0.22 |
| Experiment 2 | 0.0173 | 319 | 0.1403 | 1726 | 0.18 |
| Experiment 3 | 0.0353 | 651 | 0.1885 | 2319 | 0.28 |
| Average | - | 466(170) | - | 1996(300) | 0.23(0.05) |




**Supplementary Figure 41:** Experiment 1.




**Supplementary Figure 42:** Experiment 2.



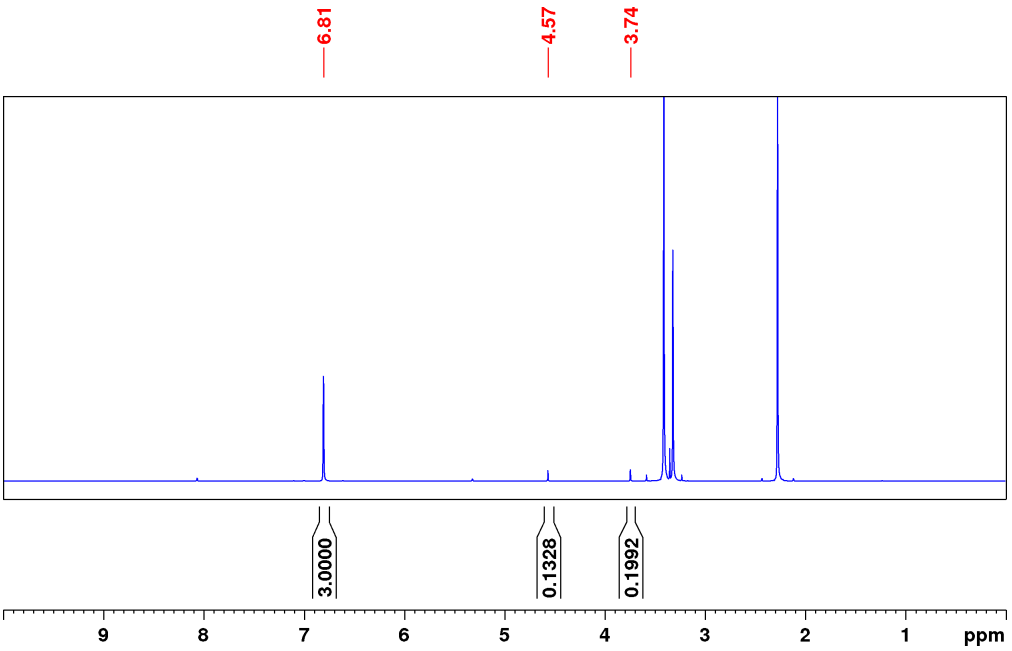

**Supplementary Figure 43:** Experiment 3.

### 5.5.5 Fourth Triple

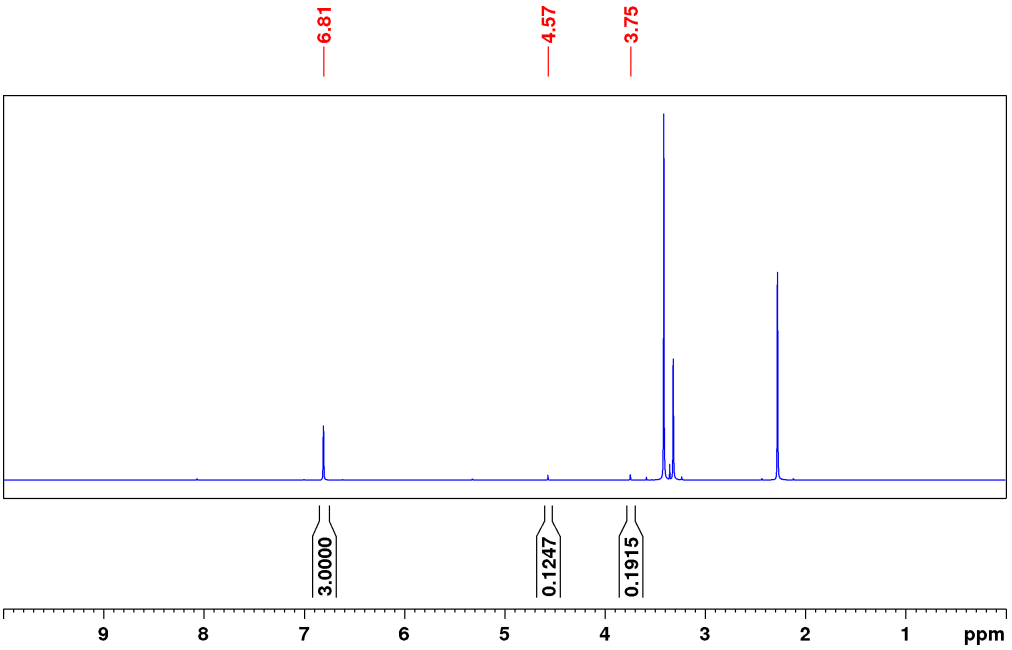
| | |
|---|---|
| $T = 100\,°C$ | $n_{cat} = 0.075\,\mu mol$ |
| $p_{H2} = 100\,bar$ | $n_{add} = 3.576\,\mu mol$ |
| $p_{CO2} = 15\,bar$ | add = $Al(OTf)_3$ |
| $t = 20\,h$ | $V_{MeOH} = 0.55\,mL$ |

**Supplementary Table 15:** Catalysis results of the fourth triple.

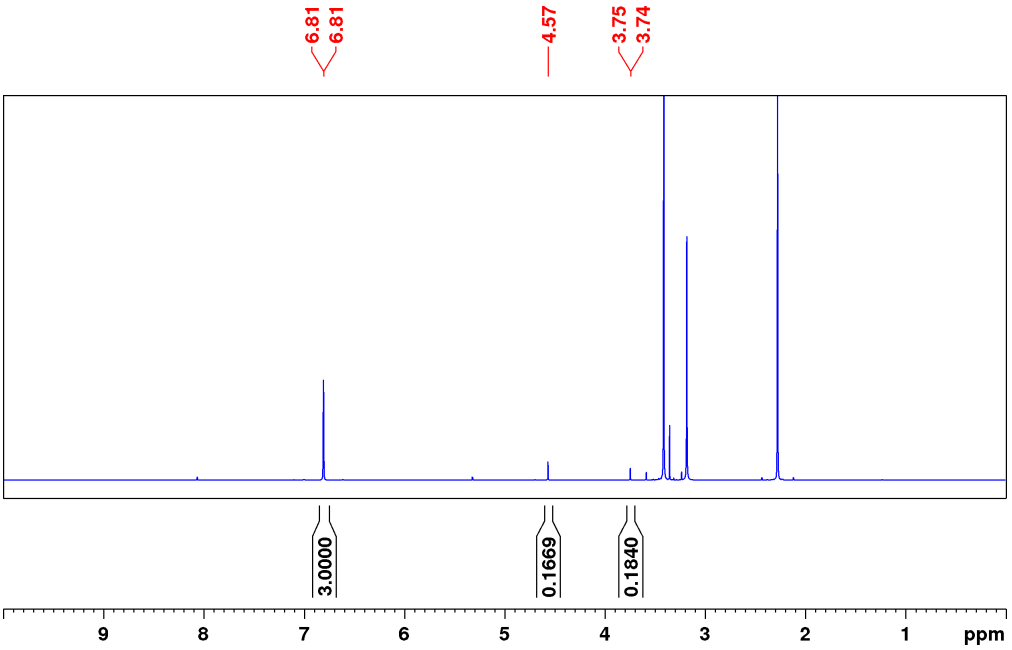
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.1328 | 2450 | 0.1992 | 2450 | 1.00 |
| Experiment 2 | 0.1247 | 2301 | 0.1915 | 2356 | 0.98 |
| Experiment 3 | 0.1669 | 3079 | 0.1840 | 2263 | 1.36 |
| Average | - | 2610(413) | - | 2356(93) | 1.11(0.22) |




**Supplementary Figure 44:** Experiment 1.




**Supplementary Figure 45:** Experiment 2.



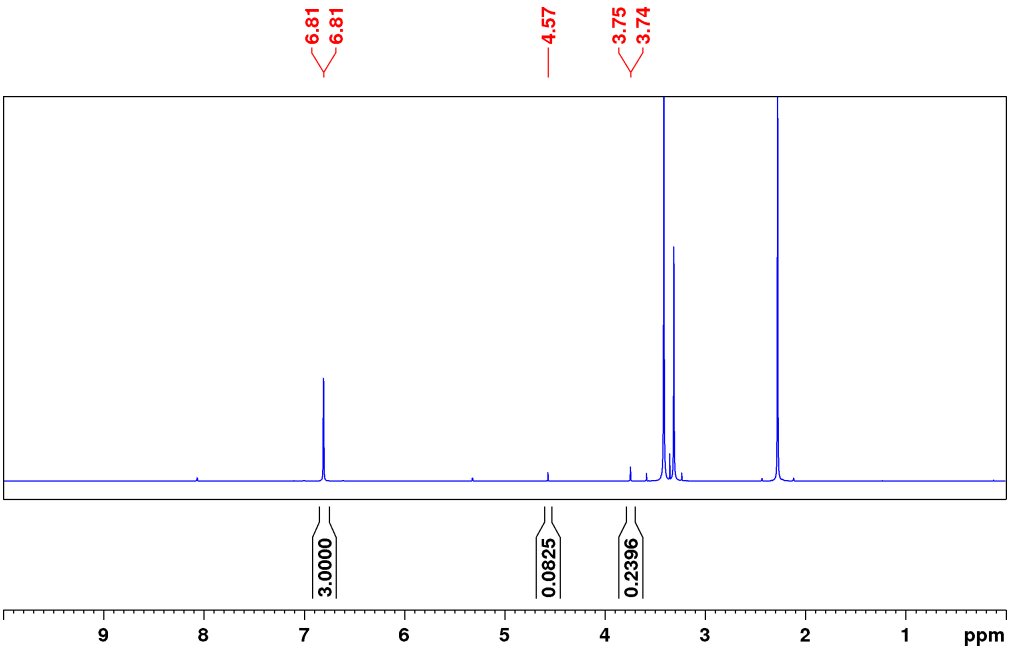

**Supplementary Figure 46:** Experiment 3.

### 5.5.6 Fifth Triple

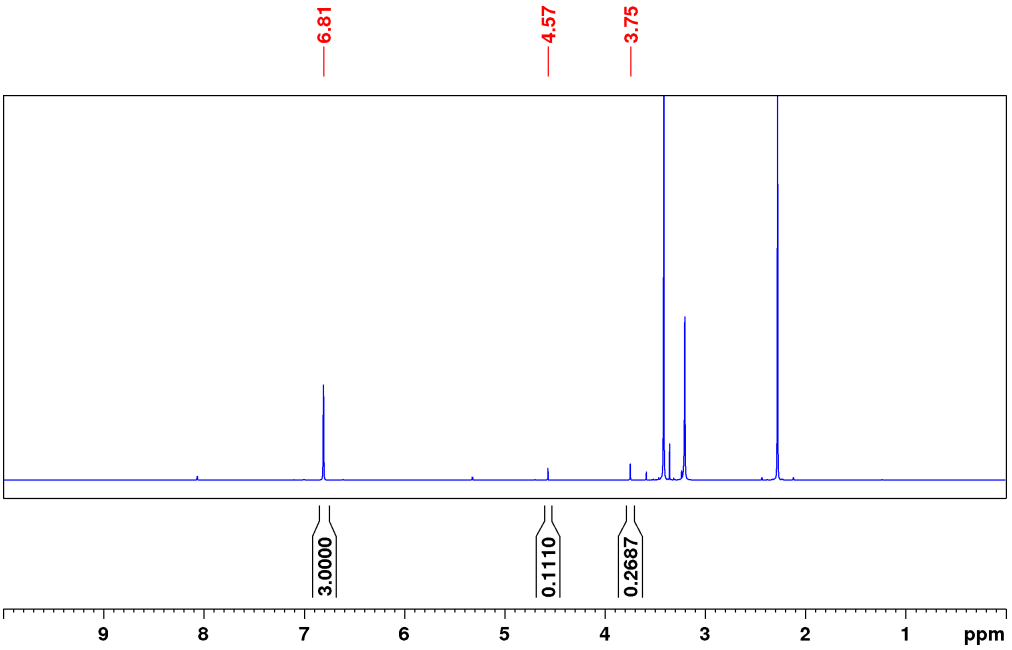
| | |
|---|---|
| $T = 100\,°C$ | $n_{cat} = 0.075\,\mu mol$ |
| $p_{H2} = 100\,bar$ | $n_{add} = 3.576\,\mu mol$ |
| $p_{CO2} = 25\,bar$ | add = $Al(OTf)_3$ |
| $t = 16\,h$ | $V_{MeOH} = 0.55\,mL$ |

**Supplementary Table 16:** Catalysis results of the fifth triple.

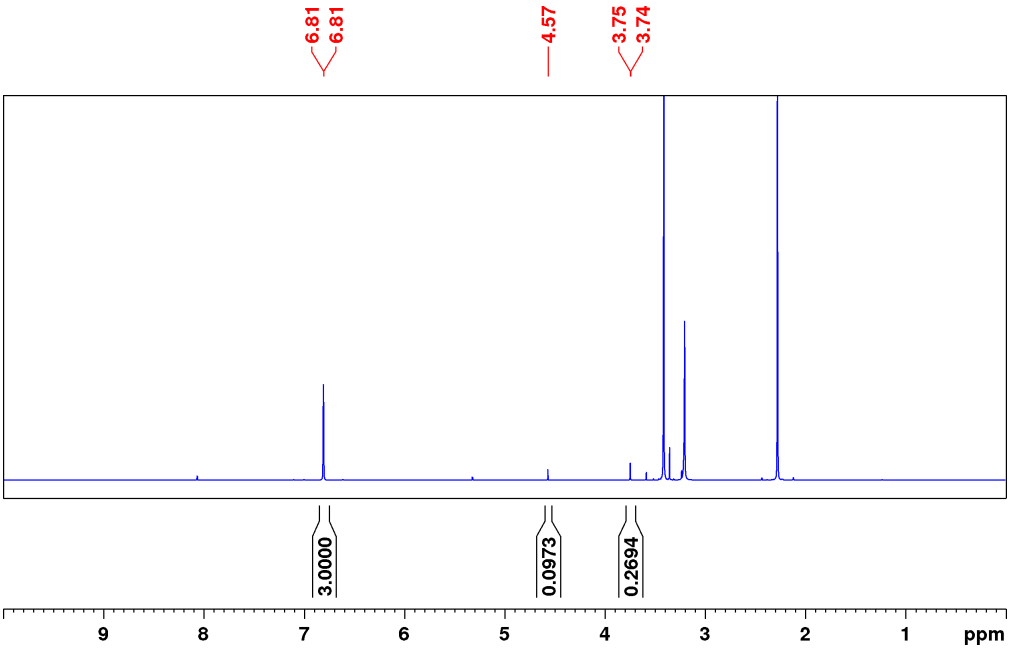
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.0825 | 1522 | 0.2396 | 2947 | 0.52 |
| Experiment 2 | 0.1110 | 2048 | 0.2687 | 3305 | 0.62 |
| Experiment 3 | 0.0973 | 1795 | 0.2694 | 3314 | 0.54 |
| Average | - | 1788(263) | - | 3189(209) | 0.56(0.05) |




**Supplementary Figure 47:** Experiment 1.




**Supplementary Figure 48:** Experiment 2.



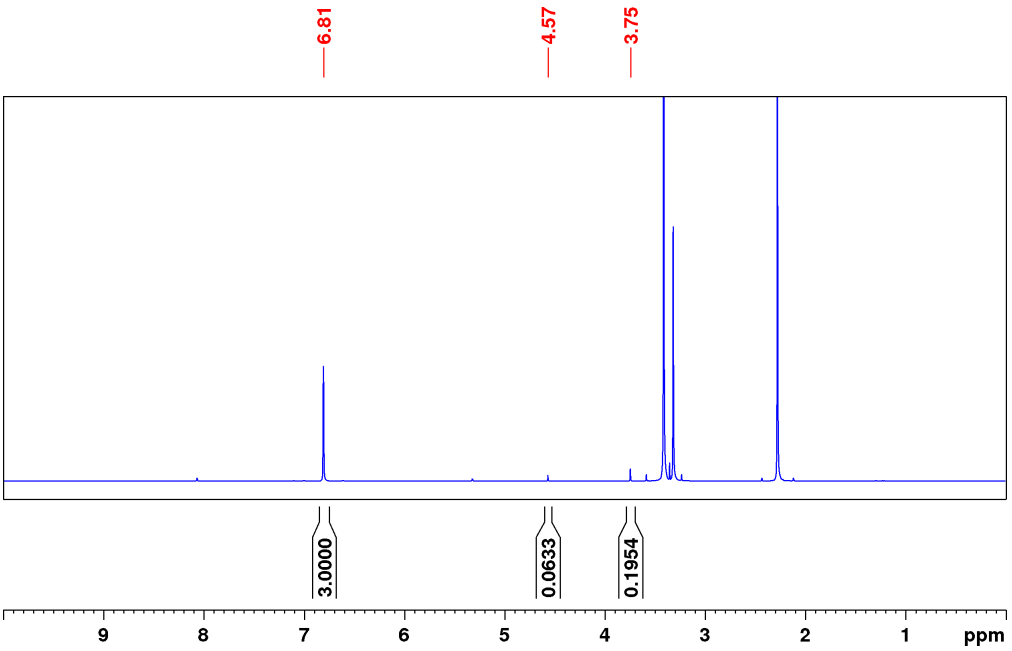

**Supplementary Figure 49:** Experiment 3.

### 5.5.7 Replication: Best Hit First Relaxation

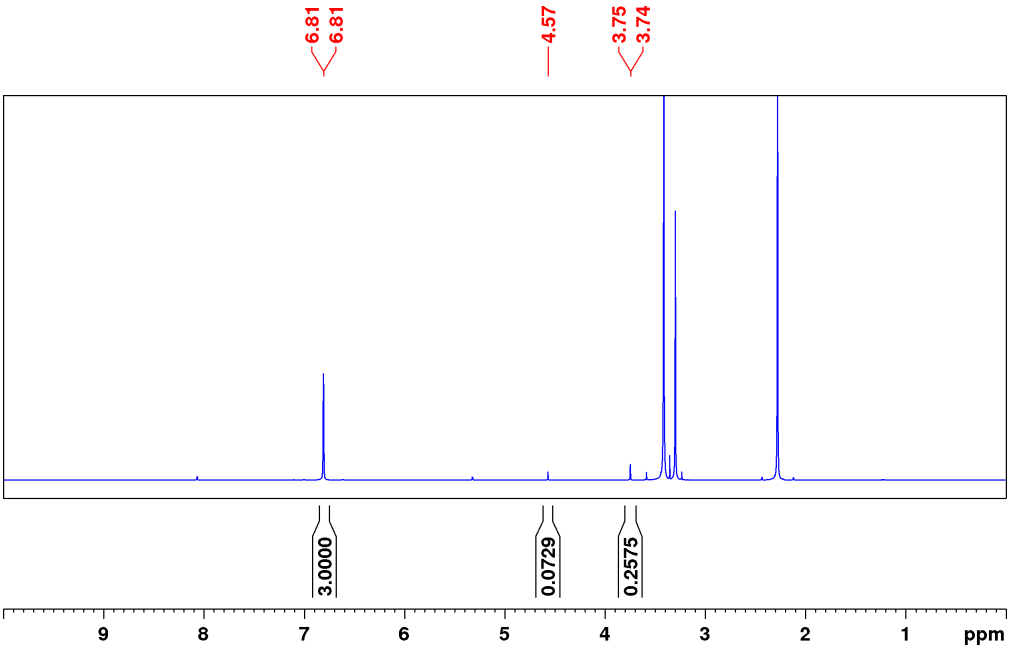
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.075\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 3.576\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = $Al(OTf)_3$ |
| $t = 18\,h$ | $V_{MeOH} = 0.55\,mL$ |

**Supplementary Table 17:** Catalysis results of the replication study.

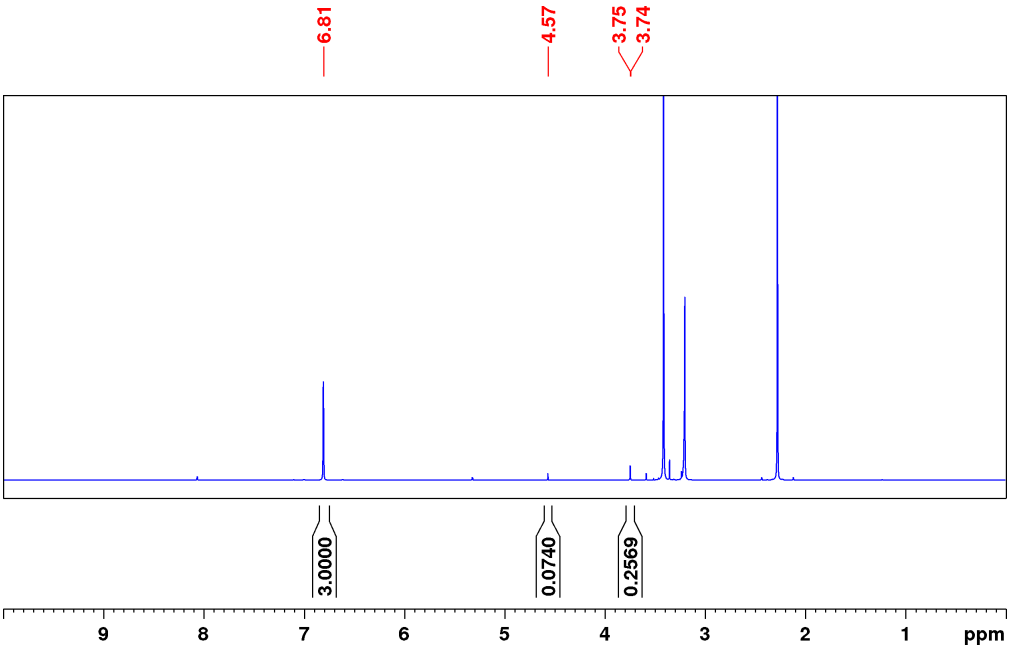
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.0633 | 1168 | 0.1954 | 2404 | 0.49 |
| Experiment 2 | 0.0729 | 1345 | 0.2575 | 3167 | 0.42 |
| Experiment 3 | 0.0740 | 1365 | 0.2569 | 3160 | 0.43 |
| Average | - | 1293(109) | - | 2910(439) | 0.45(0.03) |




**Supplementary Figure 50:** Experiment 1.




**Supplementary Figure 51:** Experiment 2.




**Supplementary Figure 52:** Experiment 3.

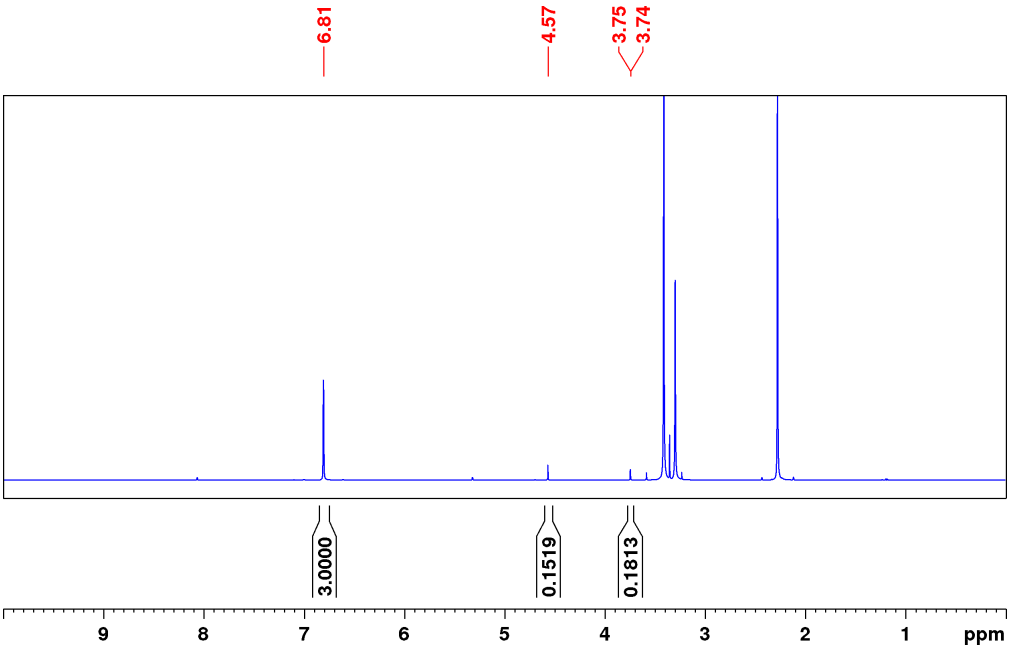
## 5.6 Second Relaxation

### 5.6.1 Replication: Best Hit Second DoE

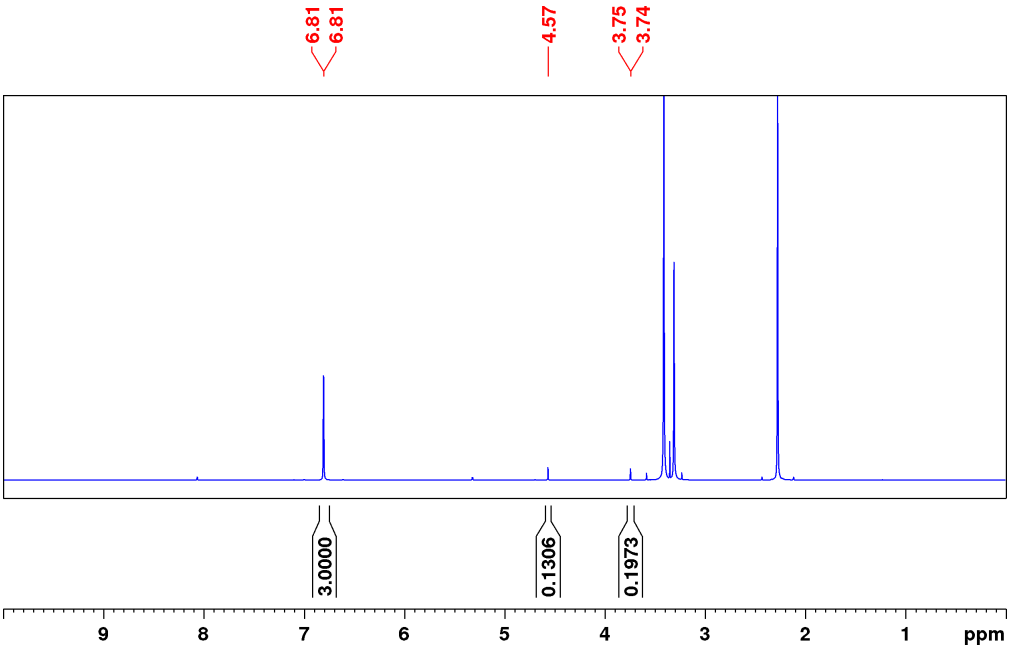
| | |
|---|---|
| $T = 100\,°C$ | $n_{cat} = 0.075\,\mu mol$ |
| $p_{H2} = 100\,bar$ | $n_{add} = 3.576\,\mu mol$ |
| $p_{CO2} = 15\,bar$ | add = $Al(OTf)_3$ |
| $t = 20\,h$ | $V_{MeOH} = 0.55\,mL$ |

**Supplementary Table 18:** Catalysis results of the replication study.

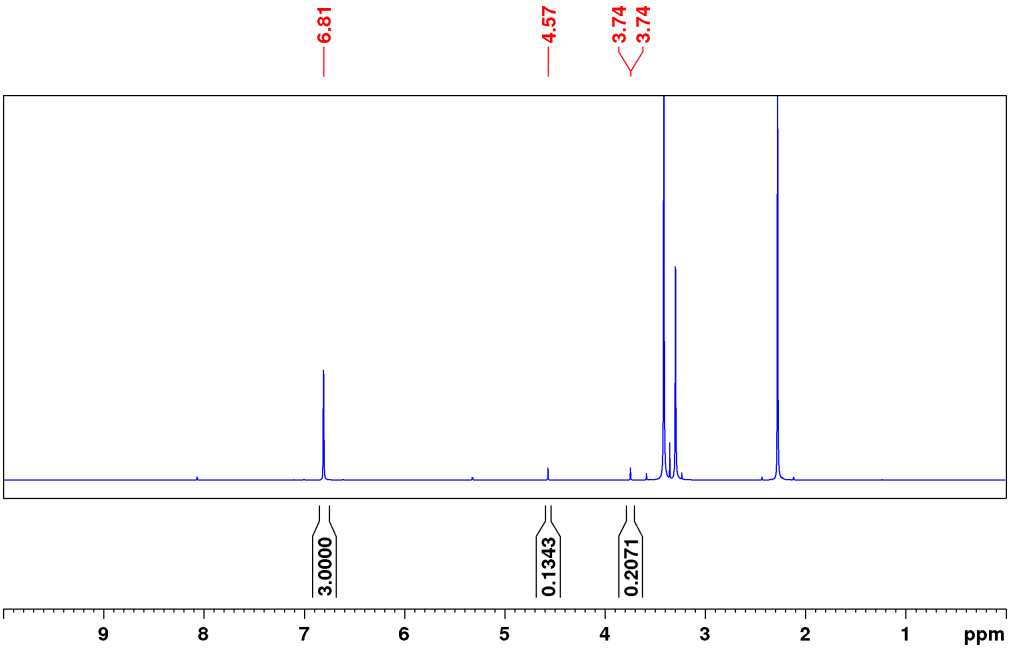
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.1519 | 2803 | 0.1813 | 2230 | 1.26 |
| Experiment 2 | 0.1306 | 2410 | 0.1973 | 2427 | 0.99 |
| Experiment 3 | 0.1343 | 2478 | 0.2071 | 2547 | 0.97 |
| Average | - | 2563(210) | - | 2401(160) | 1.07(0.16) |




**Supplementary Figure 53:** Experiment 1.




**Supplementary Figure 54:** Experiment 2.



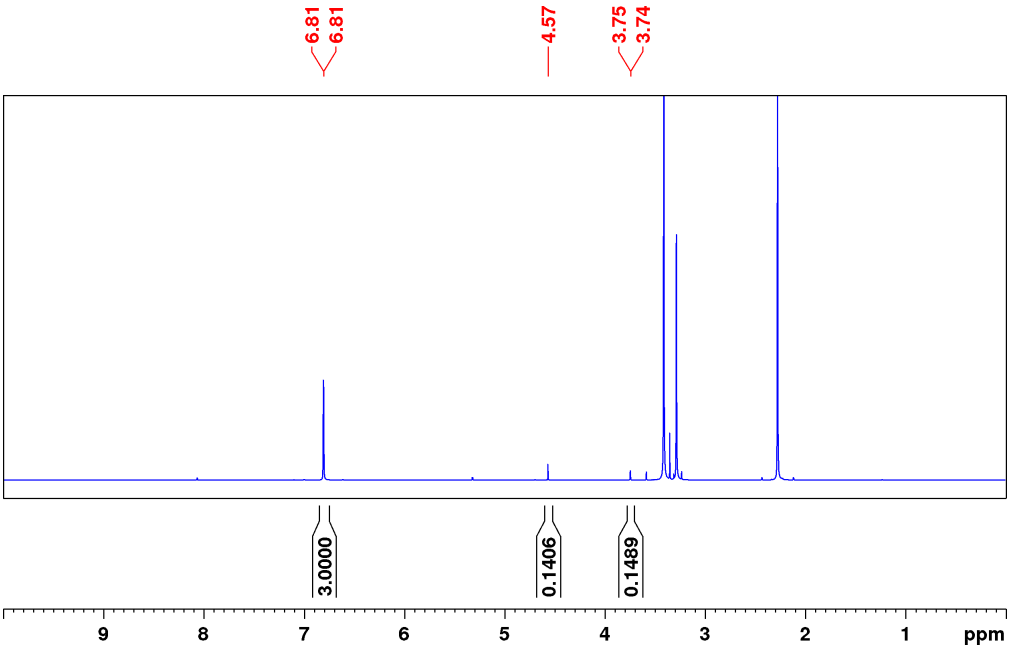

**Supplementary Figure 55:** Experiment 3.

### 5.6.2 25 % Relaxation

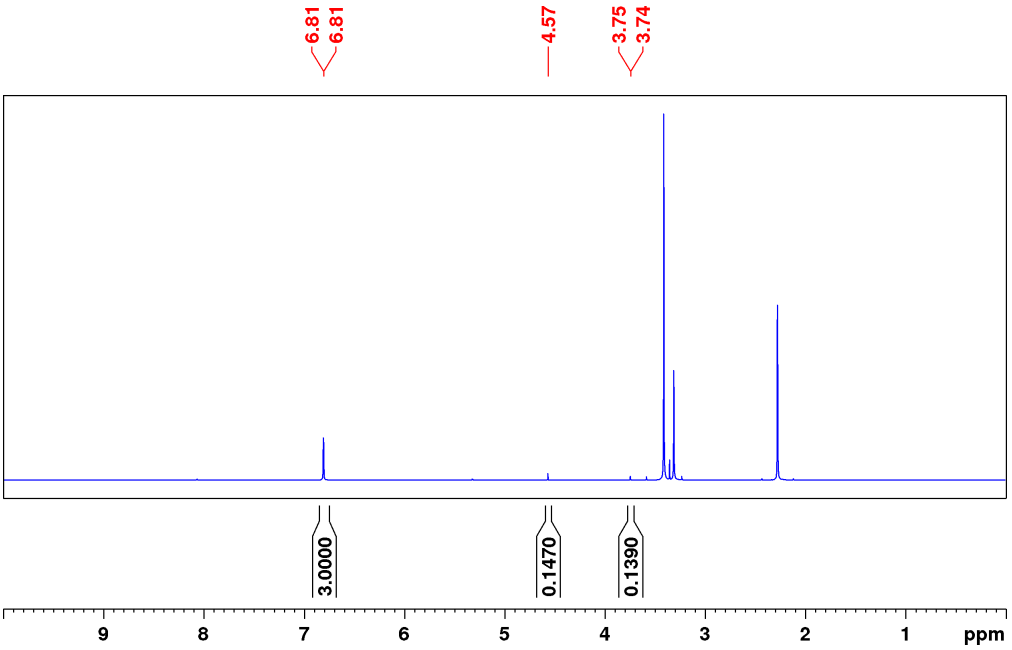
| | |
|---|---|
| $T = 105\,°C$ | $n_{cat} = 0.075\,\mu mol$ |
| $p_{H2} = 105\,bar$ | $n_{add} = 3.576\,\mu mol$ |
| $p_{CO2} = 12.5\,bar$ | add = $Al(OTf)_3$ |
| $t = 21\,h$ | $V_{MeOH} = 0.55\,mL$ |

**Supplementary Table 19:** Catalysis results of the 25 % relaxation trials.

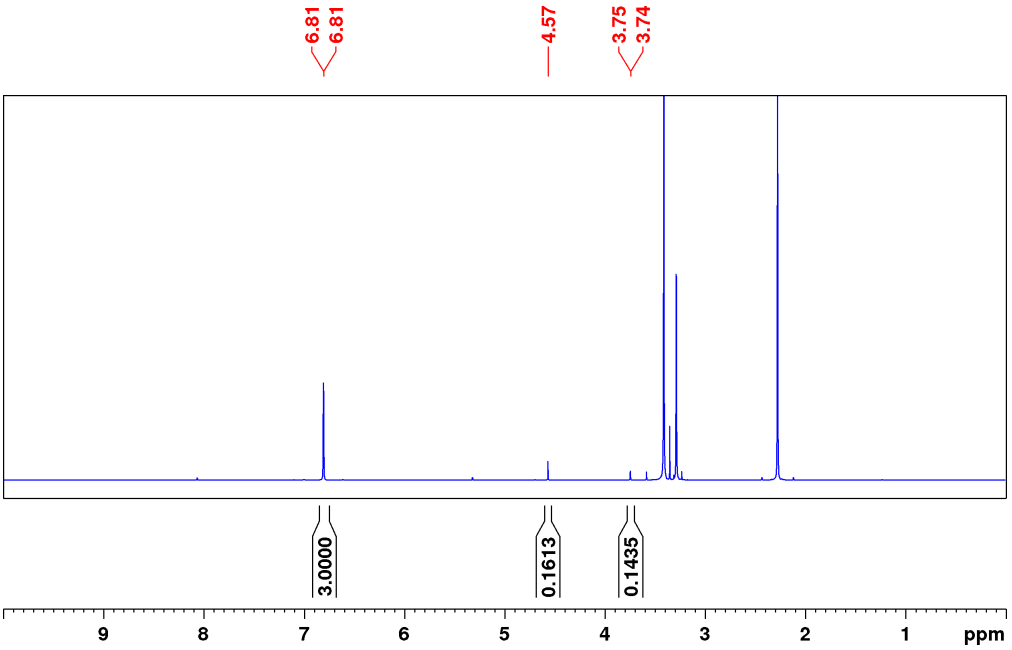
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.1406 | 2594 | 0.1489 | 1832 | 1.42 |
| Experiment 2 | 0.1470 | 2712 | 0.1390 | 1710 | 1.59 |
| Experiment 3 | 0.1613 | 2976 | 0.1435 | 1765 | 1.69 |
| Average | - | 2761(196) | - | 1769(61) | 1.56(0.14) |




**Supplementary Figure 56:** Experiment 1.




**Supplementary Figure 57:** Experiment 2.



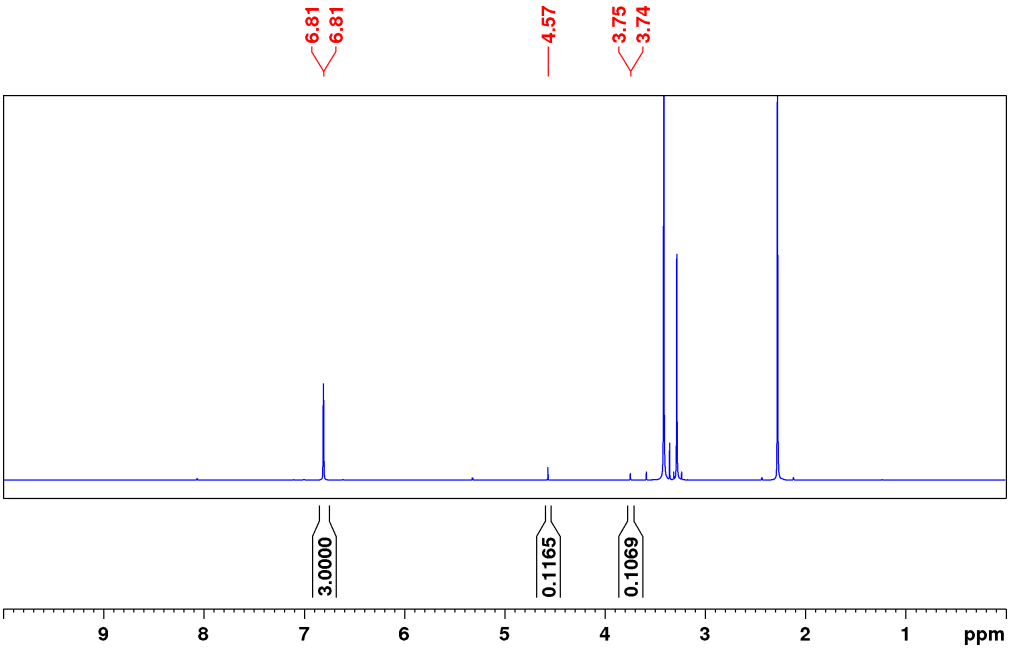

**Supplementary Figure 58:** Experiment 3.

### 5.6.3 50 % Relaxation

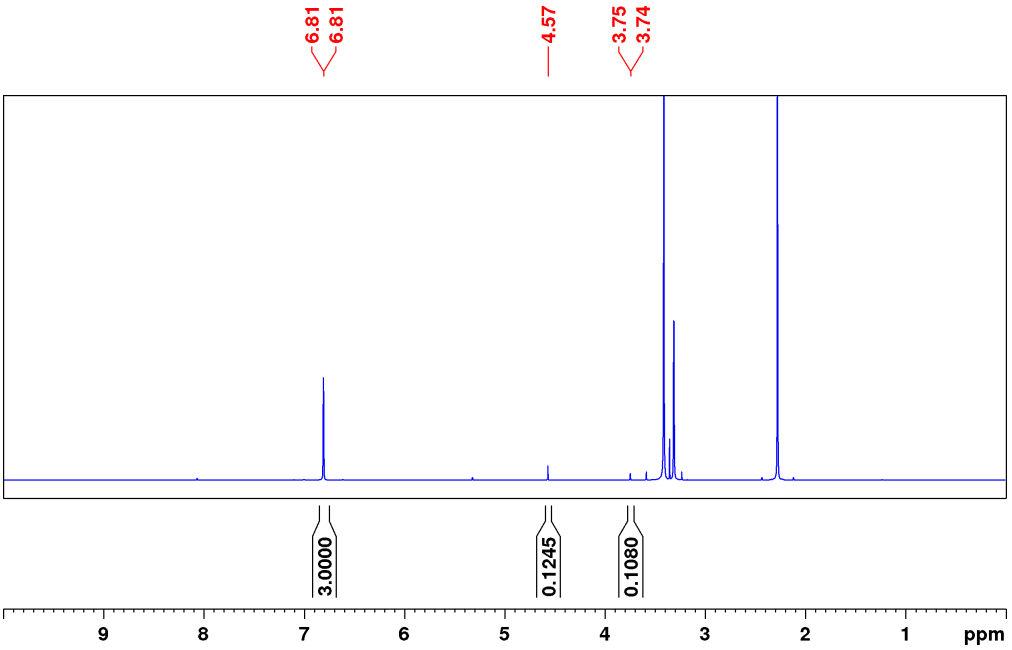
| | |
|---|---|
| $T = 110\,°C$ | $n_{cat} = 0.075\,\mu mol$ |
| $p_{H2} = 110\,bar$ | $n_{add} = 3.576\,\mu mol$ |
| $p_{CO2} = 10\,bar$ | add = $Al(OTf)_3$ |
| $t = 22\,h$ | $V_{MeOH} = 0.55\,mL$ |

**Supplementary Table 20:** Catalysis results of the 50 % relaxation trials.

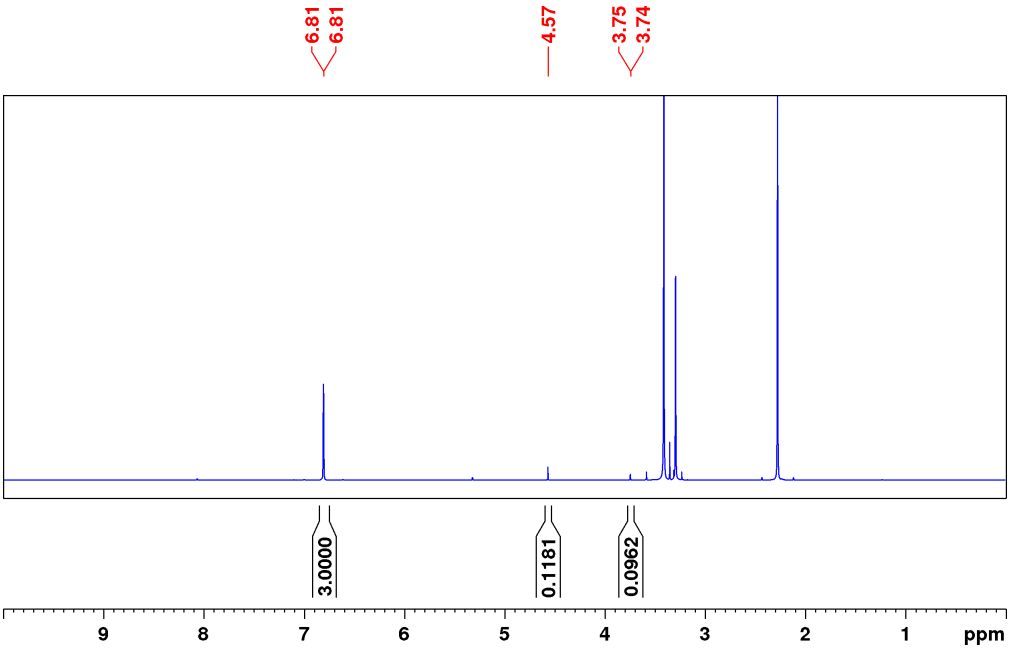
| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.1165 | 2150 | 0.1069 | 1315 | 1.63 |
| Experiment 2 | 0.1245 | 2297 | 0.1080 | 1328 | 1.73 |
| Experiment 3 | 0.1181 | 2179 | 0.0962 | 1183 | 1.84 |
| Average | - | 2209(78) | - | 1276(80) | 1.74(0.10) |




**Supplementary Figure 59:** Experiment 1.




**Supplementary Figure 60:** Experiment 2.



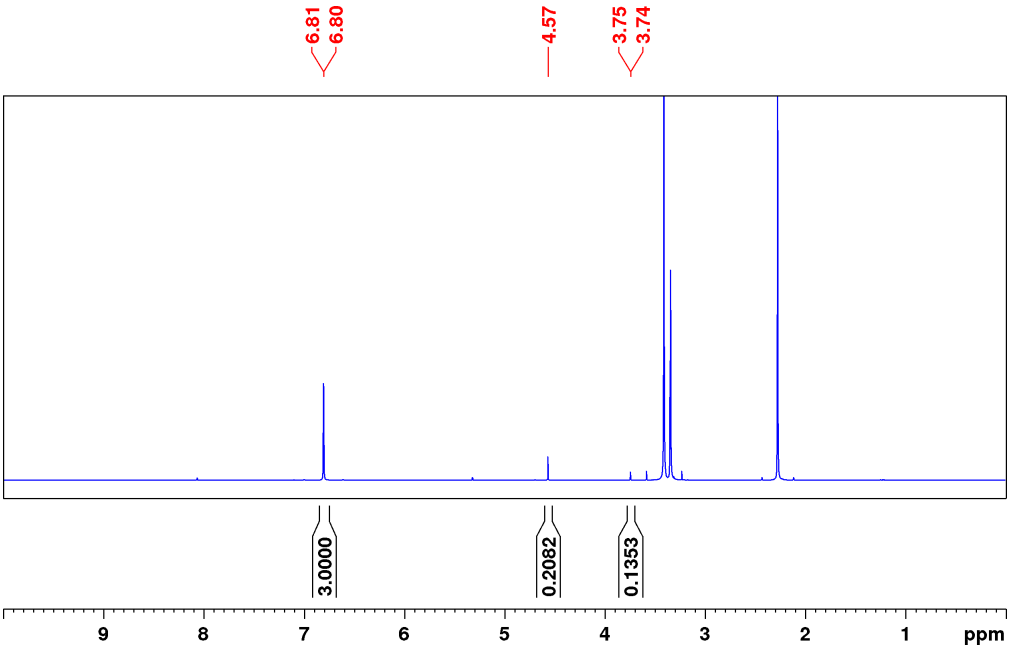

**Supplementary Figure 61:** Experiment 3.

## 5.7 Upscale Reactions

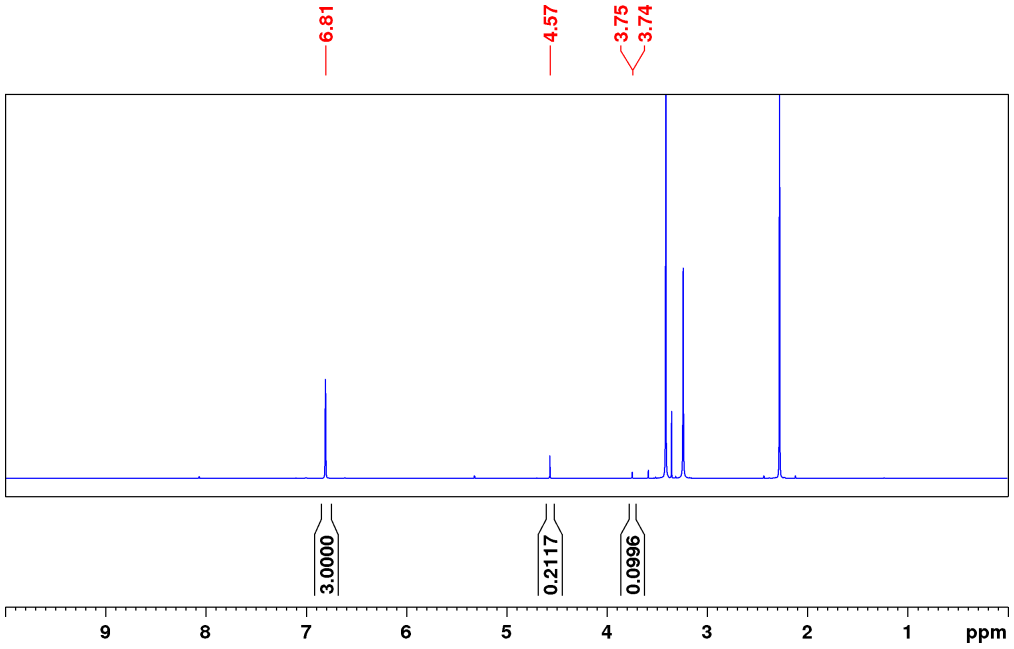
| | |
|---|---|
| $T = 100\,°C$ | $n_{cat} = 0.75\,\mu mol$ |
| $p_{H2} = 100\,bar$ | $n_{add} = 35.76\,\mu mol$ |
| $p_{CO2} = 15\,bar$ | add = $Al(OTf)_3$ |
| $t = 20\,h$ | $V_{MeOH} = 5.5\,mL$ |

**Supplementary Table 21:** Catalysis results of the upscale reactions.

| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.2082 | 3841 | 0.1353 | 1664 | 2.31 |
| Experiment 2 | 0.2117 | 3906 | 0.0996 | 1225 | 3.19 |
| Average | - | 3874(46) | - | 1445(311) | 2.75(0.62) |




**Supplementary Figure 62:** Experiment 1.




**Supplementary Figure 63:** Experiment 2.

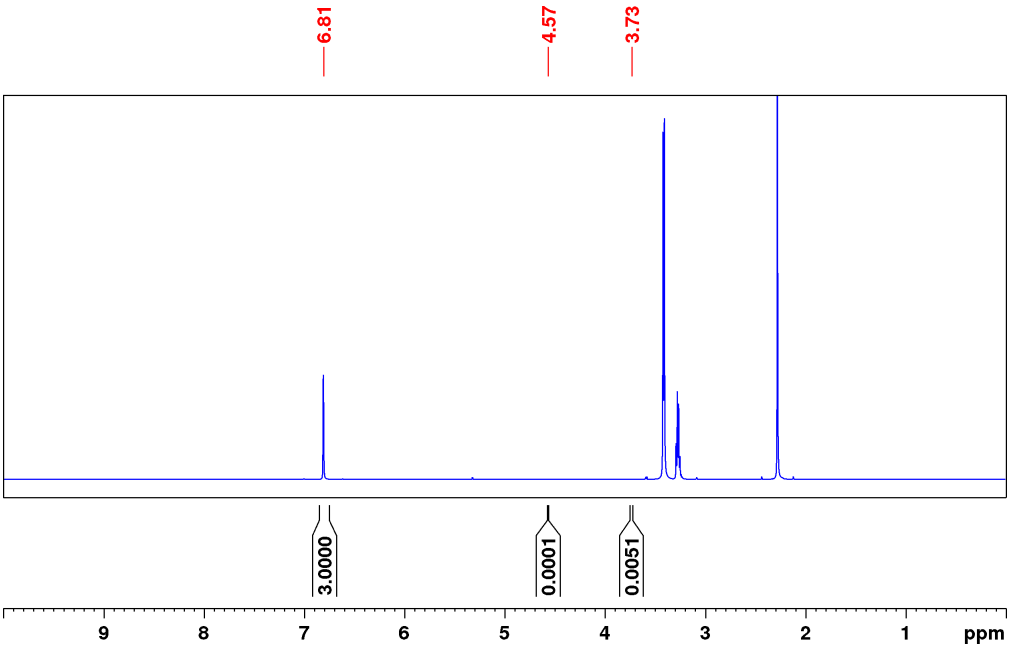
## 5.8 Background Measurements

### Run without Catalyst and Co-Catalyst[17]

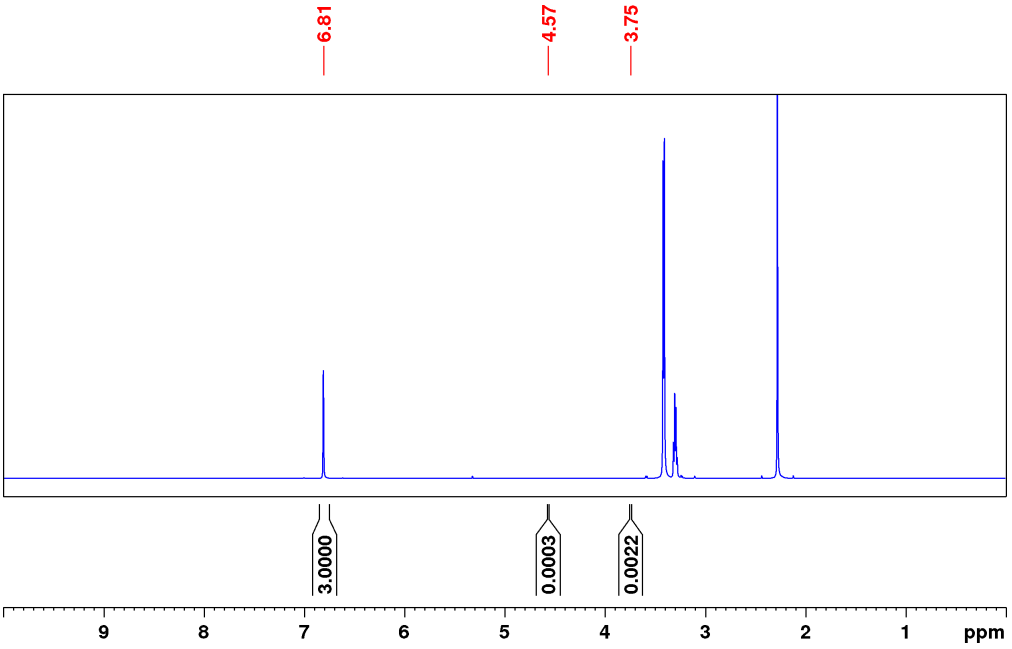
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.00\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 0.00\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = none |
| $t = 18\,h$ | $V_{MeOH} = 0.5\,mL$ |

**Supplementary Table 22:** Run without catalyst and co-catalyst.

| | $Integral_{DMM}$ | $n_{DMM}$ (µmol) | $Integral_{MF}$ | $n_{MF}$ (µmol) | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.0001 | 0.13 | 0.0051 | 4.28 | 0.03 |
| Experiment 2 | 0.0003 | 0.38 | 0.0022 | 1.85 | 0.20 |
| Average | - | 0.25(0.18) | - | 3.06(1.72) | 0.12(0.12) |




**Supplementary Figure 64:** Experiment 1.



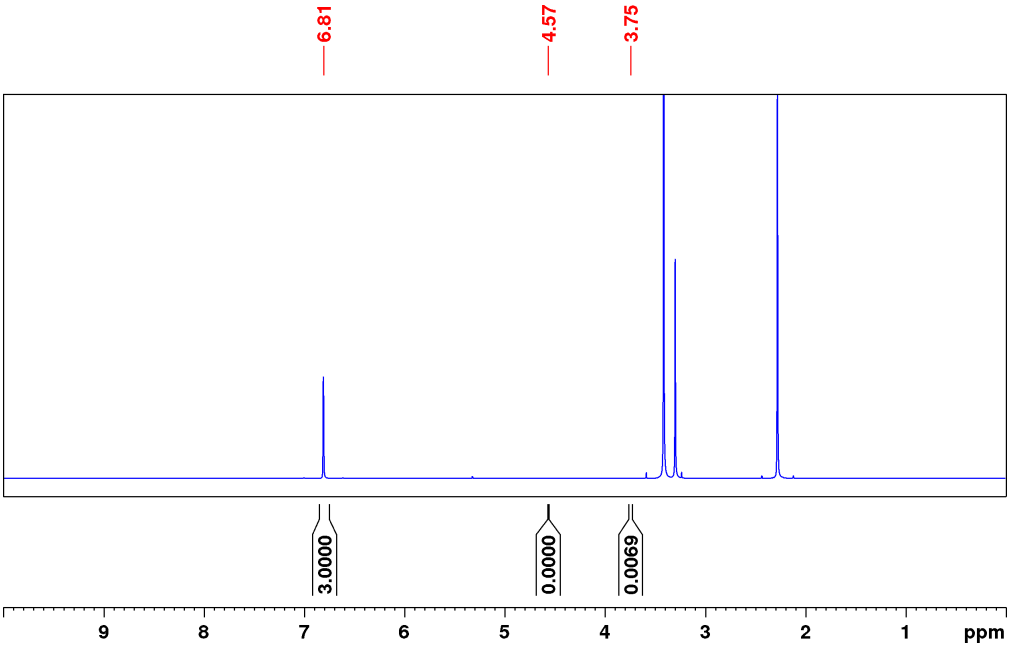

**Supplementary Figure 65:** Experiment 2.

### Run without Co-Catalyst[17]

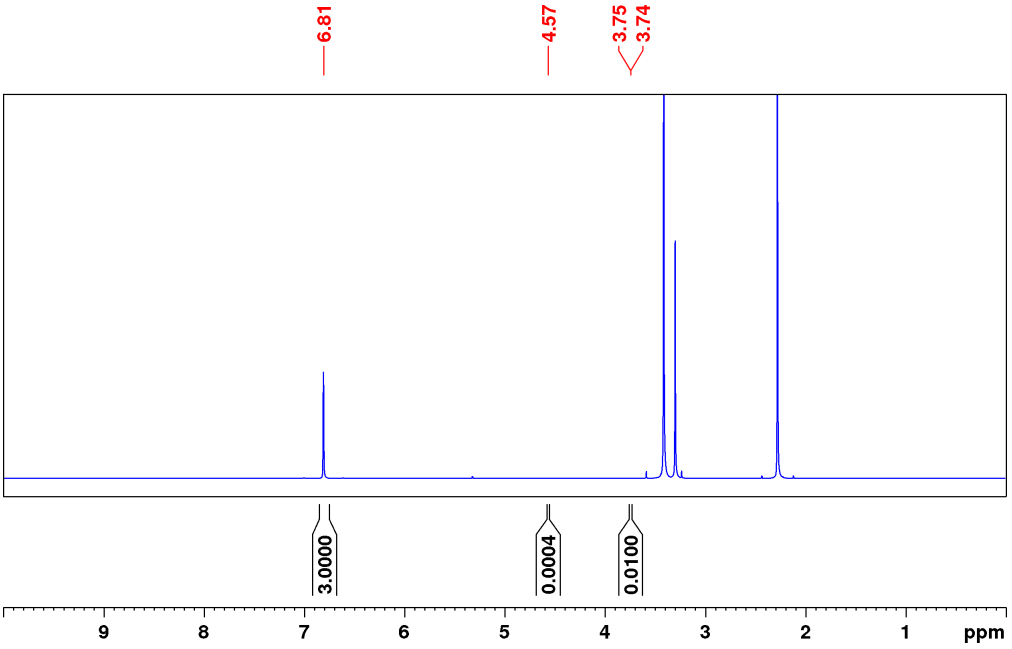
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 1.50\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 0.00\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = none |
| $t = 18\,h$ | $V_{MeOH} = 0.5\,mL$ |

**Supplementary Table 23:** Run without co-catalyst.

| | $Integral_{DMM}$ | $TON_{DMM}$ | $Integral_{MF}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.0000 | 0 | 0.0069 | 4 | 0.00 |
| Experiment 2 | 0.0004 | 0 | 0.0100 | 6 | 0.06 |
| Average | - | 0(0) | - | 5(1) | 0.03(0.04) |




**Supplementary Figure 66:** Experiment 1.



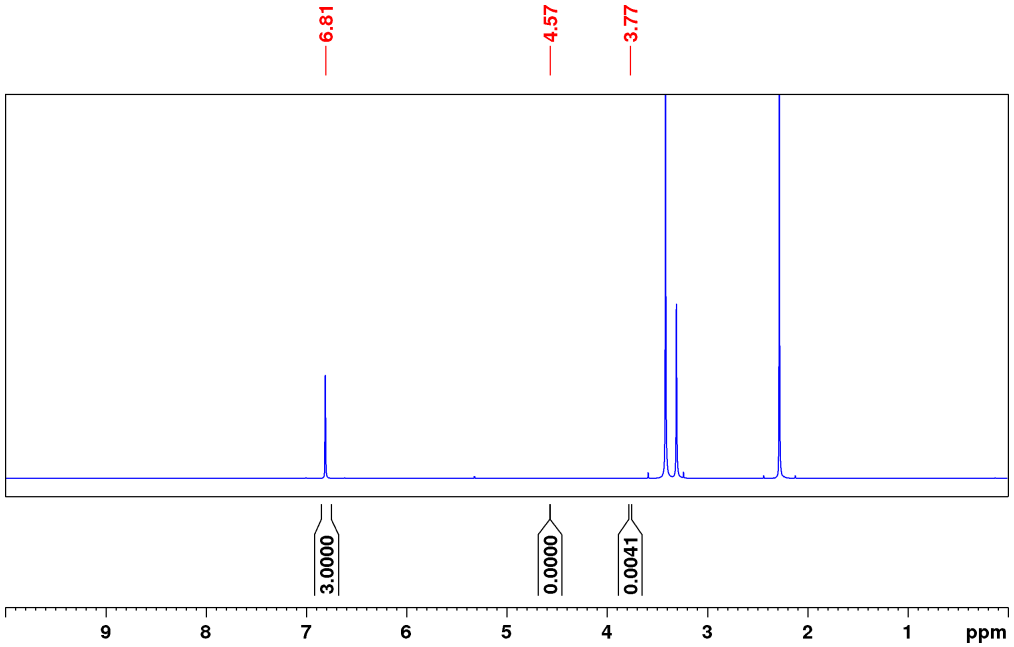

**Supplementary Figure 67:** Experiment 2.

### Run without Catalyst[17]

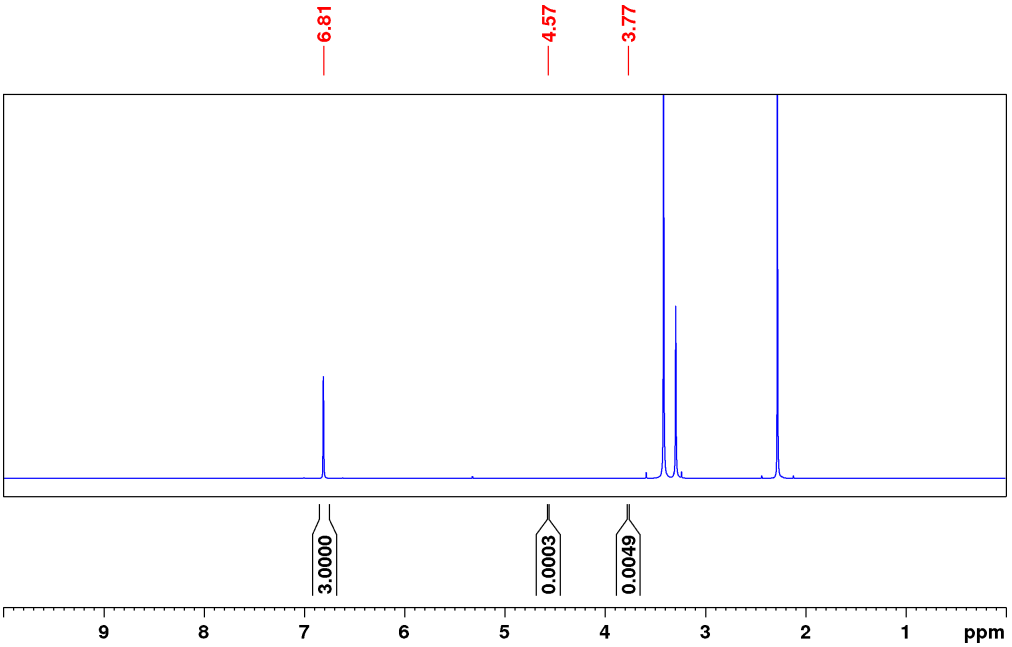
| | |
|---|---|
| $T = 90\,°C$ | $n_{cat} = 0.00\,\mu mol$ |
| $p_{H2} = 90\,bar$ | $n_{add} = 6.25\,\mu mol$ |
| $p_{CO2} = 20\,bar$ | add = $Al(OTf)_3$ |
| $t = 18\,h$ | $V_{MeOH} = 0.5\,mL$ |

**Supplementary Table 24:** Run without catalyst.

| | $Integral_{DMM}$ | $n_{DMM}$ (µmol) | $Integral_{MF}$ | $n_{MF}$ (µmol) | Ratio |
|---|---|---|---|---|---|
| Experiment 1 | 0.0000 | 0.00 | 0.0041 | 3.44 | 0.00 |
| Experiment 2 | 0.0003 | 0.38 | 0.0049 | 4.11 | 0.09 |
| Average | - | 0.19(0.27) | - | 3.77(0.47) | 0.05(0.06) |




**Supplementary Figure 68:** Experiment 1.




**Supplementary Figure 69:** Experiment 2.

## 5.9 Overview of Catalysis Results

All catalysis results from the first DoE (Section 5.3), the first relaxation (Section 5.4), the second DoE (Section 5.5), the second relaxation (Section 5.6) and the reactions performed in the tailor-made experimental setup (Section 5.7) are given in Supplementary Table 25.

**Supplementary Table 25:** Overview of the catalysis results.

| | entry | Catalysis Process Parameters | | | | | | | | Responses | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $T$ | $p_{H2}$ | $p_{CO2}$ | $t$ | additive | $n_{cat}$ | $n_{add}$ | $V_{MeOH}$ | TON | |
| | | (°C) | (bar) | (bar) | (h) | | (µmol) | (µmol) | (mL) | DMM | MF |
| First DoE | 1 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 0.78125 | 0.25 | 195 | 89 |
| | 2 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 0.78125 | 0.25 | 196 | 85 |
| | 3 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 0.78125 | 0.25 | 220 | 95 |
| | 4 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 0.78125 | 0.5 | 124 | 210 |
| | 5 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 0.78125 | 0.5 | 114 | 191 |
| | 6 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 0.78125 | 0.5 | 121 | 212 |
| | 7 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 1.953125 | 0.375 | 337 | 122 |
| | 8 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 1.953125 | 0.375 | 335 | 110 |
| | 9 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 1.953125 | 0.375 | 355 | 116 |
| | 10 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.1875 | 3.125 | 0.25 | 1162 | 437 |
| | 11 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.1875 | 3.125 | 0.25 | 1147 | 415 |
| | 12 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.1875 | 3.125 | 0.25 | 1040 | 458 |
| | 13 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 3.125 | 0.25 | 310 | 78 |
| | 14 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 3.125 | 0.25 | 308 | 80 |
| | 15 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.75 | 3.125 | 0.25 | 323 | 80 |
| | 16 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.46875 | 3.125 | 0.375 | 628 | 194 |
| | 17 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.46875 | 3.125 | 0.375 | 673 | 213 |
| | 18 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.46875 | 3.125 | 0.375 | 550 | 195 |
| | 19 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.1313 | 3.3594 | 0.525 | 1475 | 1706 |
| | 20 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.1313 | 3.3594 | 0.525 | 1071 | 1431 |

Continued on next page. . .

**Supplementary Table 25:** Overview of the catalysis results. (continued)

| | entry | Catalysis Process Parameters | | | | | | | | Responses | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $T$ | $p_{H2}$ | $p_{CO2}$ | $t$ | additive | $n_{cat}$ | $n_{add}$ | $V_{MeOH}$ | TON | |
| | | (°C) | (bar) | (bar) | (h) | | (µmol) | (µmol) | (mL) | DMM | MF |
| First relaxation | 21 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.1313 | 3.3594 | 0.525 | 1574 | 1543 |
| | 22 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1546 | 2796 |
| | 23 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1517 | 2868 |
| | 24 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1061 | 2621 |
| | 25 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.0188 | 3.6594 | 0.575 | 38 | 1026 |
| | 26 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.0188 | 3.6594 | 0.575 | 8 | 995 |
| | 27 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.0188 | 3.6594 | 0.575 | 492 | 1098 |
| Second DoE | 28 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1415 | 2715 |
| | 29 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1367 | 2741 |
| | 30 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1199 | 2962 |
| | 31 | 80 | 100 | 25 | 20 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 838 | 3190 |
| | 32 | 80 | 100 | 25 | 20 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 924 | 3226 |
| | 33 | 80 | 100 | 25 | 20 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 906 | 3426 |
| | 34 | 100 | 80 | 25 | 20 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1078 | 2935 |
| | 35 | 100 | 80 | 25 | 20 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1046 | 2881 |
| | 36 | 100 | 80 | 25 | 20 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1421 | 2991 |
| | 37 | 80 | 80 | 15 | 16 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 426 | 1943 |
| | 38 | 80 | 80 | 15 | 16 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 319 | 1726 |
| | 39 | 80 | 80 | 15 | 16 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 651 | 2319 |
| | 40 | 100 | 100 | 15 | 20 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 2450 | 2450 |

Continued on next page. . .

**Supplementary Table 25:** Overview of the catalysis results. (continued)

| | entry | Catalysis Process Parameters | | | | | | | | Responses | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $T$ | $p_{H2}$ | $p_{CO2}$ | $t$ | additive | $n_{cat}$ | $n_{add}$ | $V_{MeOH}$ | TON | |
| | | (°C) | (bar) | (bar) | (h) | | (µmol) | (µmol) | (mL) | DMM | MF |
| Second relaxation | 41 | 100 | 100 | 15 | 20 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 2301 | 2356 |
| | 42 | 100 | 100 | 15 | 20 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 3079 | 2263 |
| | 43 | 100 | 100 | 25 | 16 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1522 | 2947 |
| | 44 | 100 | 100 | 25 | 16 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 2048 | 3305 |
| | 45 | 100 | 100 | 25 | 16 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1795 | 3314 |
| | 46 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1168 | 2404 |
| | 47 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1345 | 3167 |
| | 48 | 90 | 90 | 20 | 18 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 1365 | 3160 |
| | 49 | 100 | 100 | 15 | 20 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 2803 | 2230 |
| | 50 | 100 | 100 | 15 | 20 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 2410 | 2427 |
| | 51 | 100 | 100 | 15 | 20 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 2478 | 2547 |
| | 52 | 105 | 105 | 12.5 | 21 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 2594 | 1832 |
| | 53 | 105 | 105 | 12.5 | 21 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 2712 | 1710 |
| | 54 | 105 | 105 | 12.5 | 21 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 2976 | 1765 |
| | 55 | 110 | 110 | 10 | 22 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 2150 | 1315 |
| | 56 | 110 | 110 | 10 | 22 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 2297 | 1328 |
| | 57 | 110 | 110 | 10 | 22 | $Al(OTf)_3$ | 0.075 | 3.576 | 0.55 | 2179 | 1183 |
| Upscale | 58 | 100 | 100 | 15 | 20 | $Al(OTf)_3$ | 0.75 | 35.76 | 5.5 | 3841 | 1664 |
| | 59 | 100 | 100 | 15 | 20 | $Al(OTf)_3$ | 0.75 | 35.76 | 5.5 | 3906 | 1225 |

# 6 Additional Information

## 6.1 Simple Spearman Rank Correlation Analysis

Supplementary Table 26 lists the simple Spearman rank correlation analysis between SD($TON_{DMM}$), SD($TON_{MF}$) and the process parameters $X_i$.

**Supplementary Table 26:** Simple Spearman rank correlation analysis.

| SD | $T$ | $p_{H2}$ | $p_{CO2}$ | $t$ | $n_{cat}$ | $n_{add}$ | $V$ |
|---|---|---|---|---|---|---|---|
| $TON_{DMM}$ | 0.33 | 0.04 | -0.09 | 0.01 | -0.76 | 0.64 | 0.73 |
| $TON_{MF}$ | -0.06 | 0.09 | 0.02 | -0.17 | -0.73 | 0.47 | 0.74 |

## 6.2 Replication Error

Supplementary Table 27 (summary of Supplementary Table 11 and Supplementary Table 17) lists the six replication experiments of the best hit of the first relaxation shown in Supplementary Table 28 (see Supplementary Table 9).
Supplementary Table 29 (see Supplementary Table 18) lists the three replication experiments of the best hit of the second DoE shown in Supplementary Table 30 (see Supplementary Table 15).
The comparison of Supplementary Table 27 and Supplementary Table 28 as well as of Supplementary Table 29 and Supplementary Table 30 illustrates the low replication error and thus the good repeatability of the catalytic reaction and the reliability of the system.

**Supplementary Table 27:** Replication study of the best hit of the first relaxation.

| | $TON_{DMM}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|
| Experiment 1.1 | 1415 | 2715 | 0.52 |
| Experiment 1.2 | 1367 | 2741 | 0.50 |
| Experiment 1.3 | 1199 | 2962 | 0.40 |
| Average | 1327(113) | 2806(136) | 0.48(0.06) |
| Experiment 2.1 | 1168 | 2404 | 0.49 |
| Experiment 2.2 | 1345 | 3167 | 0.42 |
| Experiment 2.3 | 1365 | 3160 | 0.43 |
| Average | 1293(109) | 2910(439) | 0.45(0.03) |
| Overall Average | 1310(101) | 2858(296) | 0.46(0.05) |

**Supplementary Table 28:** Catalysis results of the 20 % relaxation trials of the first relaxation.

| | $TON_{DMM}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|
| Experiment 1 | 1546 | 2796 | 0.55 |
| Experiment 2 | 1517 | 2868 | 0.53 |
| Experiment 3 | 1061 | 2621 | 0.40 |
| Average | 1375(272) | 2762(127) | 0.50(0.08) |

**Supplementary Table 29:** Replication study of the best hit of the second DoE.

| | $TON_{DMM}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|
| Experiment 1 | 2803 | 2230 | 1.26 |
| Experiment 2 | 2410 | 2427 | 0.99 |
| Experiment 3 | 2478 | 2547 | 0.97 |
| Average | 2563(210) | 2401(160) | 1.07(0.16) |

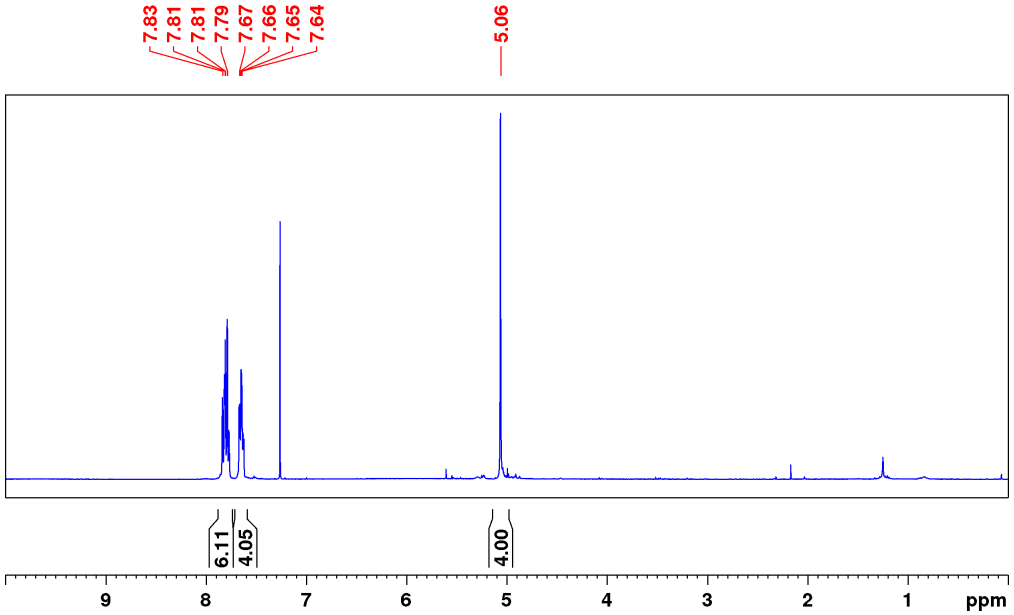
**Supplementary Table 30:** Catalysis results of the fourth triple of the second DoE.

| | $TON_{DMM}$ | $TON_{MF}$ | Ratio |
|---|---|---|---|
| Experiment 1 | 2450 | 2450 | 1.00 |
| Experiment 2 | 2301 | 2356 | 0.98 |
| Experiment 3 | 3079 | 2263 | 1.36 |
| Average | 2610(413) | 2356(93) | 1.11(0.22) |

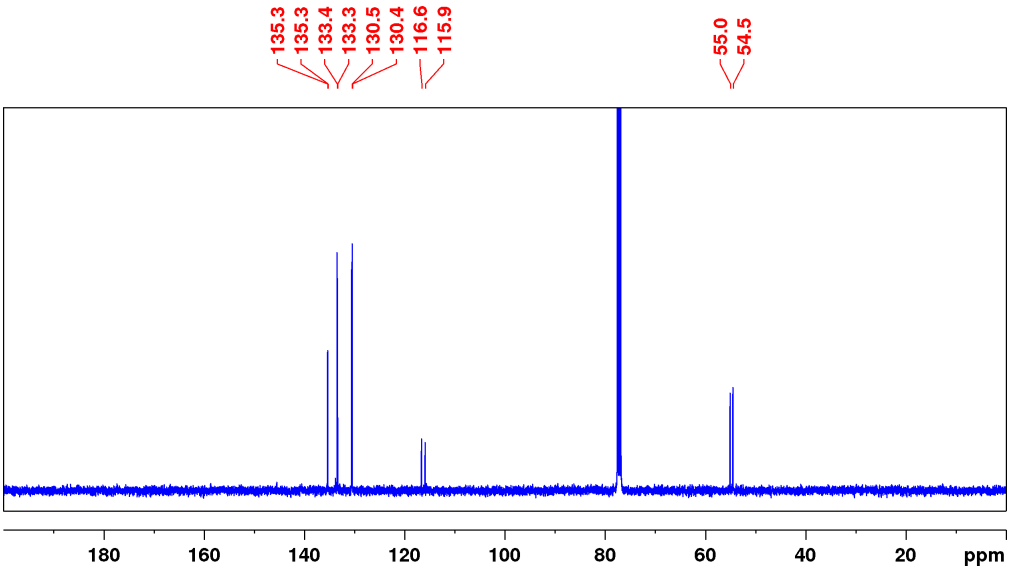
# 7 Appendix

## 7.1 NMR Spectra of the Ligand Precursor

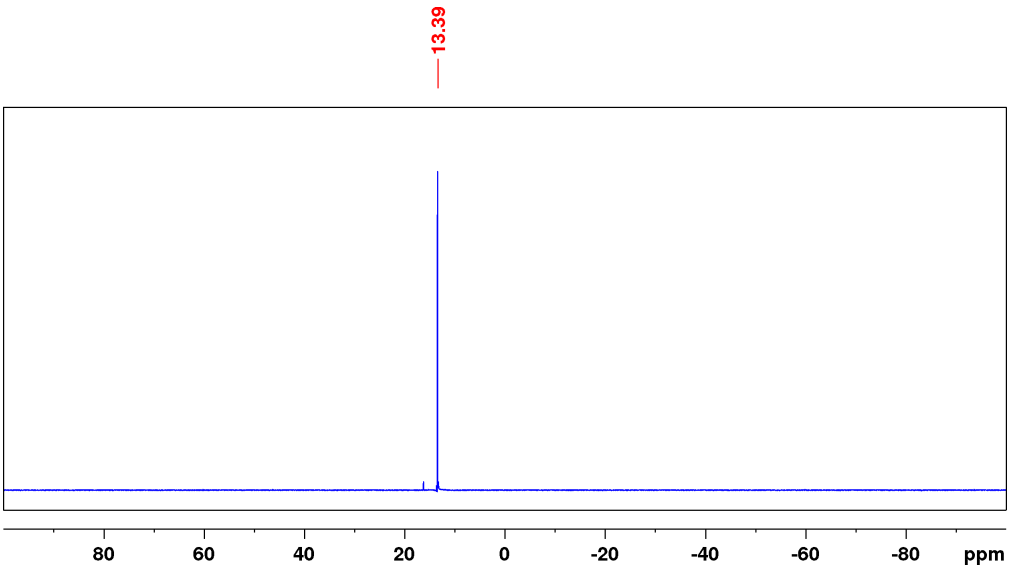
### 7.1.1 Bis(hydroxymethyl)diphenylphosphonium chloride SI-2




**Supplementary Figure 70:** $^{1}$H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of compound **SI-2**.



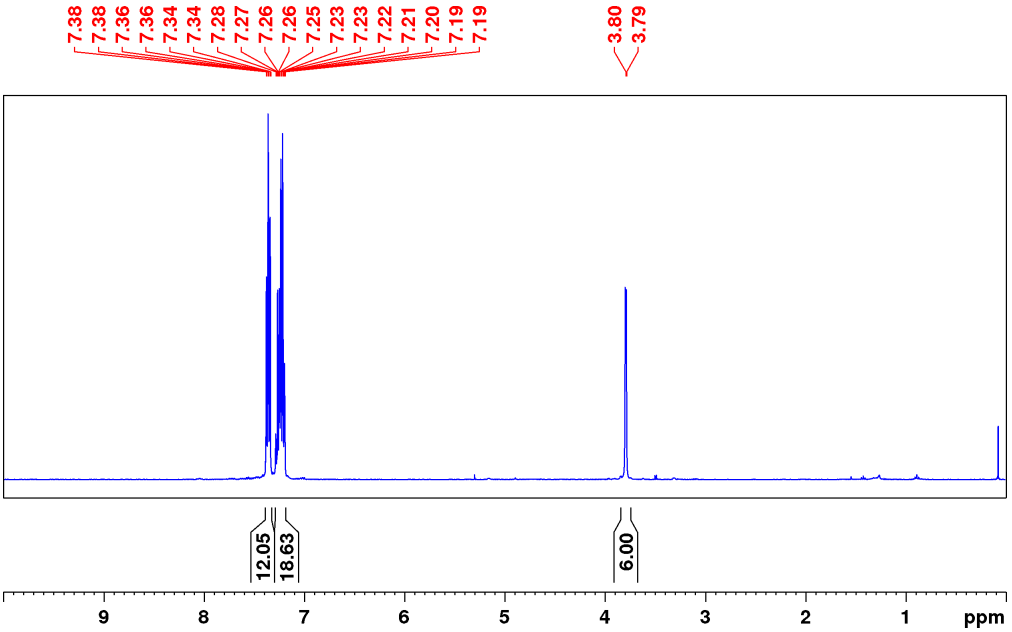

**Supplementary Figure 71:** $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz, 298 K) spectrum of compound **SI-2**.



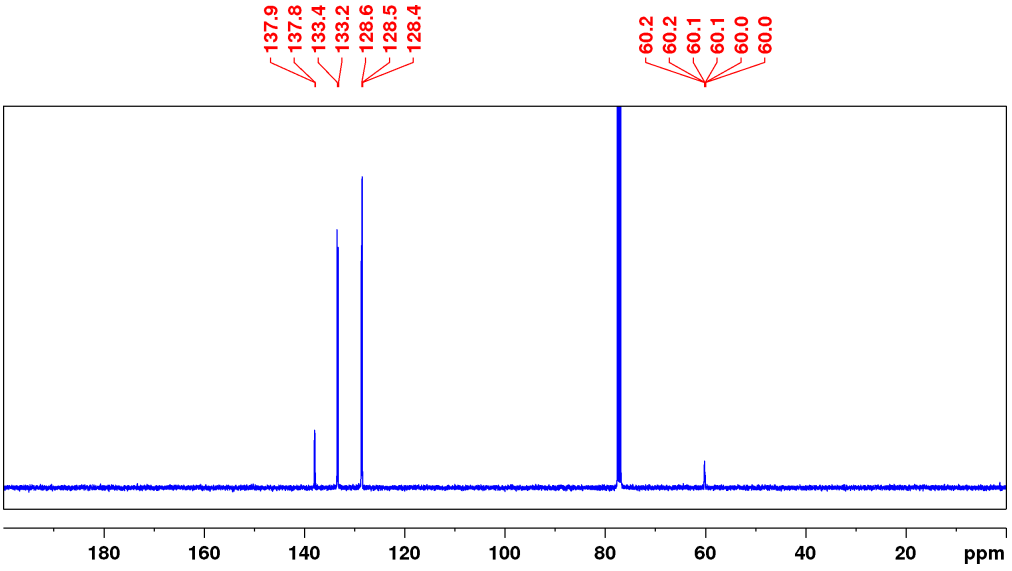

**Supplementary Figure 72:** $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz, 298 K) spectrum of compound **SI-2**.

## 7.2 NMR Spectra of the Ligand

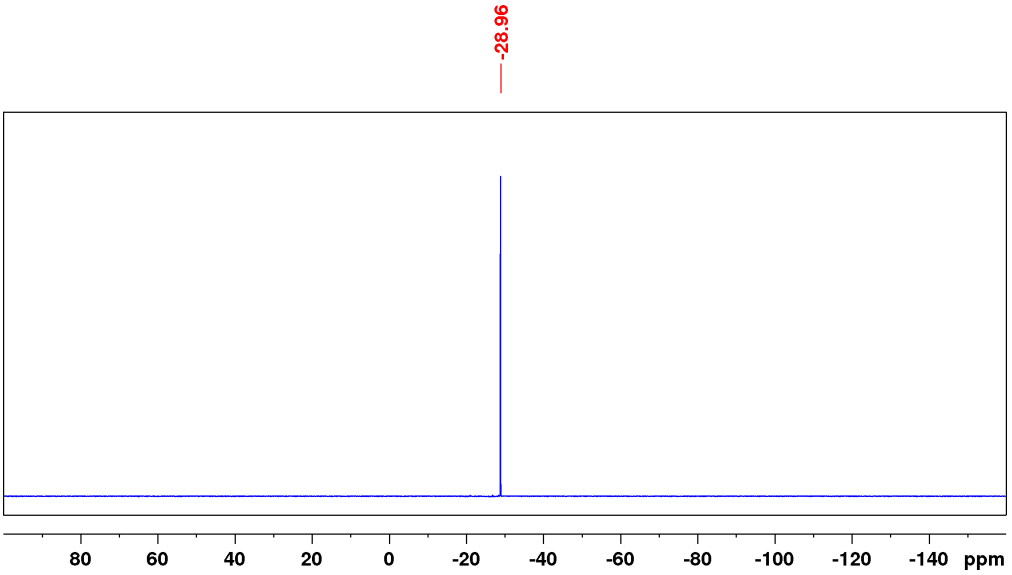
### 7.2.1 *N*-triphos$^{Ph}$ SI-3




**Supplementary Figure 73:** $^{1}$H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of compound **SI-3**.



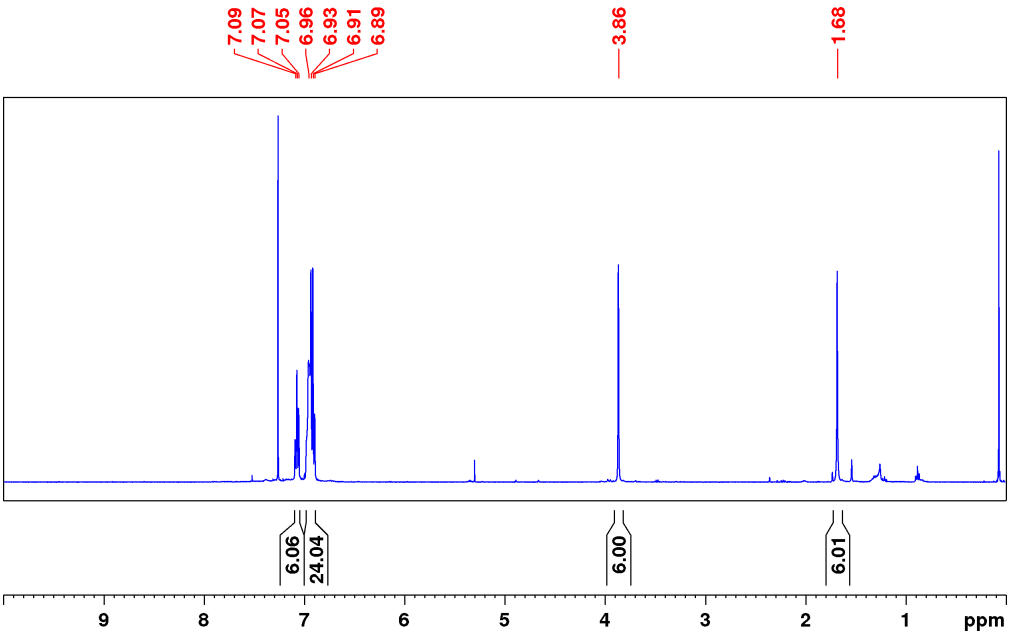

**Supplementary Figure 74:** $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz, 298 K) spectrum of compound **SI-3**.



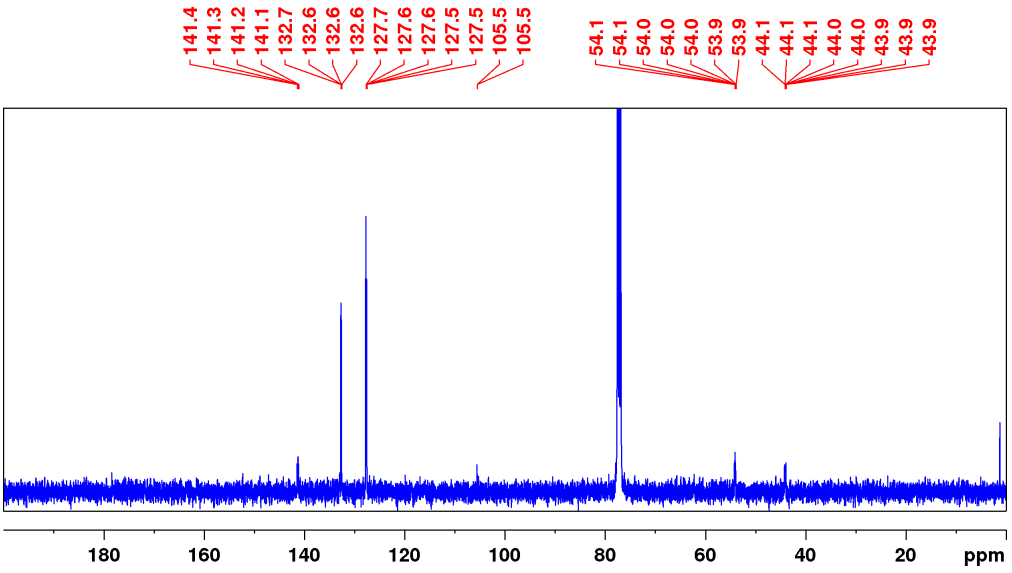

**Supplementary Figure 75:** $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz, 298 K) spectrum of compound **SI-3**.

## 7.3 NMR Spectra of the Complex

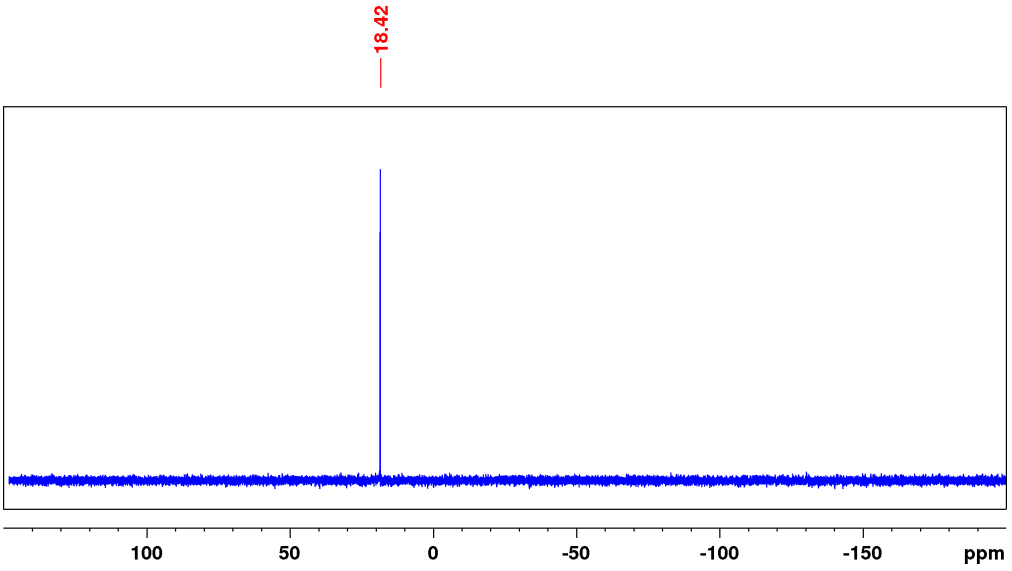
### 7.3.1 [Ru(*N*-triphos$^{Ph}$)(tmm)] SI-4




**Supplementary Figure 76:** $^{1}$H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of compound **SI-4**.




**Supplementary Figure 77:** $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz, 298 K) spectrum of compound **SI-4**.




**Supplementary Figure 78:** $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz, 298 K) spectrum of compound **SI-4**.

# List of Abbreviations

| Abbreviation | Full Name |
|---|---|
| add | Additive |
| ACN | Acetonitrile |
| ATR | Attenuated Total Reflection |
| b | Broad |
| BIC | Bayesian Information Criterion |
| cat | Catalyst |
| COSY | Correlation Spectroscopy |
| d | Doublet |
| DCM | Dichloromethane |
| DMM | Dimethoxymethane |
| DoE | Design of Experiments |
| EA | Elemental Analysis |
| ESI | Electrospray Ionization |
| Et | Ethyl |
| eq. | Equivalents |
| FIA | Flow Injection Analysis |
| FT | Fourier Transformation |
| FT-ICR | Fourier Transform Ion Cyclotron Resonance |
| HMBC | Heteronuclear Multiple-Bond Correlation |
| HR | High Resolution |
| HSQC-ME | Heteronuclear Single-Quantum Correlation Multiplicity-edited |
| IR | Infrared |
| IUPAC | International Union of Pure and Applied Chemistry |
| LTQ | Linear Ion Trap Quadrupole |

| Abbreviation | Full Name |
|---|---|
| m | Multiplet |
| *m/z* | Mass-to-charge ratio |
| M | Molecular ion |
| Me | Methyl |
| mes | Mesitylene |
| MF | Methyl Formate |
| MS | Mass Spectrometry |
| *n* | *normal* |
| NMR | Nuclear Magnetic Resonance |
| OLS | Ordinary Least Squares |
| Ph | Phenyl |
| ppm | Part Per Million |
| rt | Room temperature |
| s | Singlet |
| SI | Supporting Information |
| SPS | Solvent Purification System |
| THF | Tetrahydrofuran |
| tmm | Trimethylenemethane dianion |
| TON | Turnover Number |
| triphos | 1,1,1-Tris(diphenylphosphinomethyl)ethane |

# Bibliography


1. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.
2. J. Fawcett, P. A. T. Hoye, R. D. W. Kemmitt, D. J. Law and D. R. Russell, *J. Chem. Soc., Dalton Trans.* 1993, 2563–2568.
3. A. Phanopoulos, N. J. Brown, A. J. P. White, N. J. Long and P. W. Miller, *Inorg. Chem.* 2014, **53**, 3742–3752.
4. G. Märkl and G. Y. Jin, *Tetrahedron Lett.* 1981, **22**, 1105–1108.
5. J. Lloret Fillol, A. Kruckenberg, P. Scherl, H. Wadepohl and L. H. Gade, *Chem. Eur. J.* 2011, **17**, 14047–14062.
6. R Core Team, *R: A Language and Environment for Statistical Computing*, `https://www.R-project.org`, 2017.
7. A. Liaw and M. Wiener, *R News*, 2002, **2**, 18–22.
8. L. Breiman, A. Cutler, A. Liaw and M. Wiener, *randomForest: Breiman and Cutler's Random Forests for Classification and Regression*, `https://CRAN.R-project.org/package=randomForest`, 2018.
9. B. Wheeler, *AlgDesign: Algorithmic Experimental Design*, `https://CRAN.R-project.org/package=AlgDesign`, 2014.
10. A. Ghalanos and S. Theussl, *Rsolnp: General Non-linear Optimization Using Augmented Lagrange Multiplier Method*, `https://CRAN.R-project.org/package=Rsolnp`, 2015.
11. D. Sarkar, *Lattice*, Springer-Verlag, New York, 2008.
12. D. Sarkar, *lattice: Trellis Graphics for R*, `https://CRAN.R-project.org/package=lattice`, 2018.

13. K. Wright, *pals: Color Palettes, Colormaps, and Tools to Evaluate Them*, https://CRAN.R-project.org/package=pals, 2018.

14. S. Garnier, *viridis: Default Color Maps from 'matplotlib'*, https://CRAN.R-project.org/package=viridis, 2018.

15. H. Wickham, J. Bryan, RStudio, M. Kalicinski, K. Valery, C. Leitienne, B. Colbert, D. Hoerl and E. Miller, *readxl: Read Excel Files*, https://CRAN.R-project.org/package=readxl, 2019.

16. B. Ripley, B. Venables, D. M. Bates, K. Hornik, A. Gebhardt and D. Firth, *MASS: Support Functions and Datasets for Venables and Ripley's MASS*, https://CRAN.R-project.org/package=MASS, 2018.

17. M. Siebert, M. Seibicke, A. F. Siegle, S. Kräh and O. Trapp, *J. Am. Chem. Soc.* 2019, **141**, 334–341.