Supplementary Material

Formation of methyl acrylate from CO_2 and ethylene via methylation of nickelalactones

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Experimental Section

Instrumentation and Materials

All manipulations were carried out using Schlenk techniques under an atmosphere of argon. Methylene chloride (CD_2Cl_2-d^2) and THF-d^8 were obtained from *Deutero*. Methyl iodide was obtained from *Aldrich* (*extra pure* 99%). Methylene chloride and Methyl iodide were distilled over P_2O_5 prior to use. THF was refluxed and distilled over Potassium prior to use.
ESI-mass-spectral analysis was performed on a *Varian* LCMS 500 spectrometer.
NMR-spectra were recorded on a *Bruker* ARX-300 spectrometer. All spectra were referenced to TMS or deuterated solvent as an internal standard.[1] For the assignment of the NMR signals of methyl acrylate, propionic acid and methyl propionate reference spectra were recorded under analogue conditions.
In-situ IR-measurements were carried out on Mettler-Toledo system under argon atmosphere.

Complex **1** and complex **2** were prepared according to literature procedures.[2 - 4]

Reactions

General procedure for methylation of complex 1

Complex **1** (100 mg, 184 μmol) is dissolved together with the methylation agent in CD_2Cl_2 (0.6 ml). After that the solution is stirred at rt or 40 °C, respectively and finally stopped by hydrolysis with 1.0 ml HCl (32%). The resulting mixture is shaked for 2 h and afterwards the phases are separated.

For NMR-spectroscopic characterizations chloroform (14.8 μl, 21.9 mg, 184 μmol, 1 eq.) was added to the organic phase as internal standard.

For the recording of the mass-spectrum the methyl acrylate is hydrolyzed with $NaOH_{aq}$ (2 N, 0.5 ml) for 6 h at rt and extracted into the aqueous phase. Prior to mass-analysis the aqueous phase was separated and adjusted to pH~10.

Data of the kinetic measurements

Yields of methyl acrylate

solvent	reactant	time	temperature	yield* [%] methyl acrylate
CD_2Cl_2	MeI, 10 eq	15 min	40 °C	13
CD_2Cl_2	MeI, 10 eq	1.5 h	40 °C	17
CD_2Cl_2	MeI, 10 eq	20 h	40 °C	21
CD_2Cl_2	MeI, 10 eq	2 d	40 °C	21

** detected via NMR-spectroscopy ($CHCl_3$-Standard)*

Decomposition of complex 1

Complex **1** (100 mg, 184 μmol) is dissolved in CD_2Cl_2 (0.6 ml), stirred at rt for 2 d and finally stopped by hydrolysis with 1.0 ml HCl (32%). The resulting mixture is shaked for 2 h and afterwards the phases are separated and quantified by NMR. This gave a yield of propionic acid of 30% which indicate that 70% of the complex decomposed.

For the recording of the mass-spectrum the methyl acrylate is hydrolyzed with $NaOH_{aq}$ (2 N, 0.5 ml) for 6 h at rt and extracted into the aqueous phase. Prior to mass-analysis the aqueous phase was separated and adjusted to pH~10.

To verify the occurrence of CO_2 we used the analogue procedure with slowly passing argon gas over the solution and bubbling the gas stream through a solution of $Ba(OH)_2$ in water which gave white $BaCO_3$.

To quantify this decomposition with the help of the mass balance complex **1** (300 mg, 552 μmol) is added in a flask and tared under argon atmosphere. Then the complex is dissolved in absolute CH_2Cl_2 (0.6 ml) and stirred at rt for 2 d. After that all volatile parts of the reaction solution are removed under reduced pressure. Then the flask is put under argon to reweight the remaining mass. This resulted in a weight loss of 25 mg.

$M(C_2H_4 + CO_2)$ = 72,06 g/mol → 25 mg 347 μmol 63 mol-%

This indicates that 63 mol-% of the complex liberated ethylene and CO_2 which is in the same magnitude as the value from the NMR-spectroscopic quantification (see above).

Reaction of complex 1 with LiI

Complex **1** (100 mg, 184 μmol) is dissolved together with LiI (73.9 mg, 550 μmol, 3 eq) in CD_2Cl_2 (0.6 ml). After that the solution is stirred at rt and after 5 d stopped by hydrolysation with 1.0 ml HCl (32%). The resulting mixture is shaked for 2 h and afterwards the phases are separated.

For NMR-spectroscopical characterization chloroforme (14.8 μl, 21.9 mg, 184 μmol, 1 eq.) was added to the organic phase as internal standard.

For the recording of the mass-spectrum the acrlyic acid is extracted with $NaOH_{aq}$ (2 N, 0.5 ml). Prior to mass-analysis the aqueous phase was separated and adjusted to pH~10.

Reaction of complex 1 with HI

In a 10 ml schlenk flask complex 1 (100 mg, 184 μmol) is dissolved in CD_2Cl_2 (0.6 ml) and stirred under an atmosphere of anhydrous HI at rt. Anhydrous HI was prepared according to literature procedure.[5, 6]

The reaction solution is stirred for 6 d in this atmosphere and finally stopped by hydrolysis with 1.0 ml HCl (32%). The resulting mixture is shaked for 2 h and afterwards the phases are separated.

For NMR-spectroscopical characterization chloroforme (14.8 μl, 21.9 mg, 184 μmol, 1 eq.) was added to the organic phase as internal standard.

For the recording of the mass-spectrum the acrlyic acid is extracted with $NaOH_{aq}$ (2 N, 0.5 ml). Prior to mass-analysis the aqueous phase was separated and adjusted to pH~10.

Methylation of complex 2

Complex **2** (7 mg, 11.8 μmol) and MeI (0.24 mmol, 20 eq, 15 μl) were dissolved in 0,4 ml CD_2Cl_2 and 0.2 ml THF-d^8 in a screw cap NMR-glas under argon atmosphere. The solution was kept at ambient temperature during the experiment.

Synthesis of 3-iodo methyl propionate

A solution of 3-iod propionic acid (6.0 g, 30 mmol) in CH_3OH (300 ml) and concentrated aqueous HCl (10 drops) was stirred for 3 h at 60 °C. The solution was concentrated by rotary evaporation, and the resulting oil was diluted in Et_2O (250 mL), then washed with saturated $NaHCO_3$ (3 x 150 ml) and brine (150 ml). The organic phase was dried over Na_2SO_4, concentrated by rotary evaporation and distilled under reduced pressure to afford the desired methyl ester as colorless oil (4.8 g, 22 mmol, 73%).
^{1}H-NMR (300 MHz, $CDCl_3$): 2.96 (2H, *t*, $^3J_{HH}$=7.5 Hz), 3.31 (2H, *t*, $^3J_{HH}$=7.5 Hz), 3.71 (3H, s); ^{13}C-NMR (75 MHz, $CDCl_3$): -3.7, 38.6, 52.3, 171.8; IR: 2951 (CH), 1733 (CO), 1436, 1211, 1155; EA: ber.: C 22.5; H 3.3; gef.: C 22.5; H 3.2.

Reaction of Ni(0) with 3-iodo methyl propionate

Bis(1,5-cyclooctadiene)Ni(0) (125 mg, 0.46 mmol,1 eq.) and DPPP (190 mg, 0.46 mmol, 1 eq) were suspended in THF-d^8 (0.5 ml). 3-iodo methyl propionate (98.4 mg, 0.46 mmol, 1 eq) was added to the orange suspension and heated to 40 °C for 24 h. The reaction was stopped by hydrolysis with 1.0 ml HCl (32%). Afterwards dichloromethane-d^2 (0.5 ml) was added and resulting mixture is shaked for 2 h and afterwards the phases are separated.

References

[1] H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.***1997**, *62*, 7512-7515.

[2] R. Fischer, B. Nestler, H. Schütz, *Z. anorg. allg. Chem.*, **1989**, *577*, 111 - 114.

[3] J. Langer, D. Walther, R. Fischer, H. Görls, *J. Organomet. Chem.*, **2004**, *689*, 2952 - 2962.

[4] R. Fischer, J. Langer, A. Malassa, D. Walther, H. Goerls and G. Vaughan, *Chem. Commun.* **2006**, 2510-2512.

[5] M. Miyamoto, M. Sawamoto, T. Higashimura, *Makromolecules* **1984**, 17, 265 - 268.

[6] G. Volet, C. Amiel, L. Auvray, *Makromolecules* **2003**, 36, 3327 - 3336.

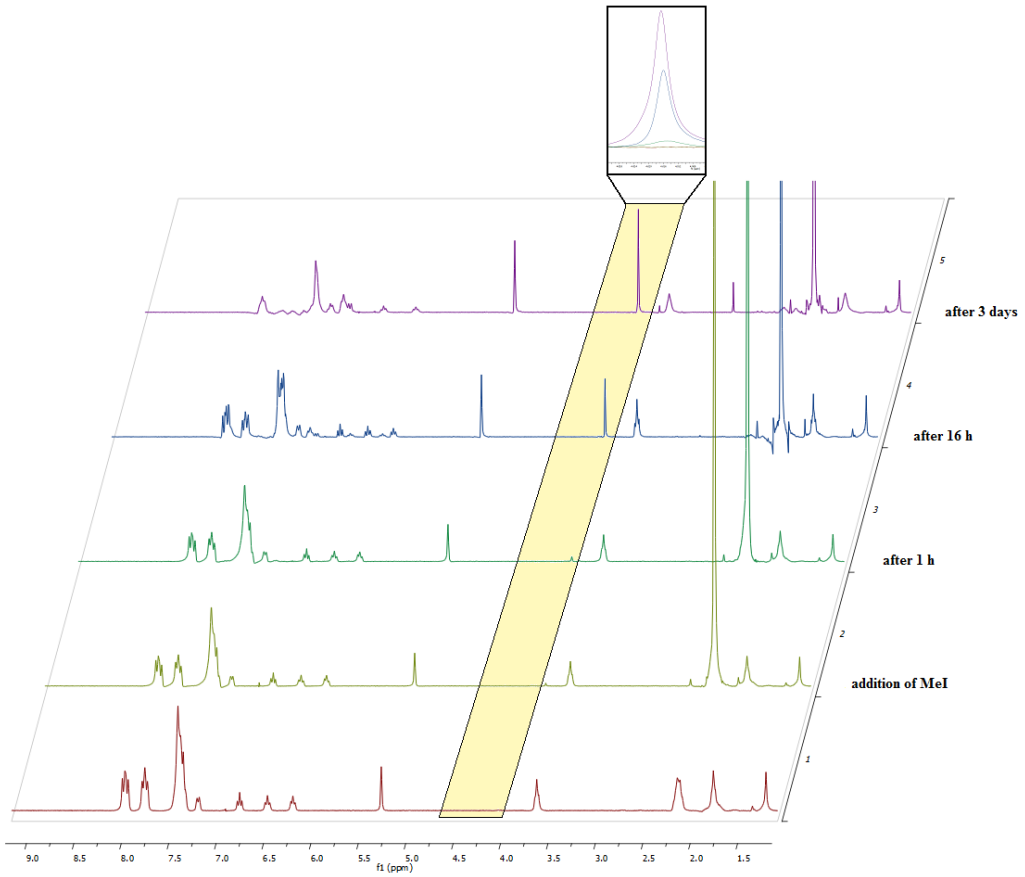

Fig. 1: ^{1}H-NMR-spectroscopic study of the methylation of nickelalactone **2**

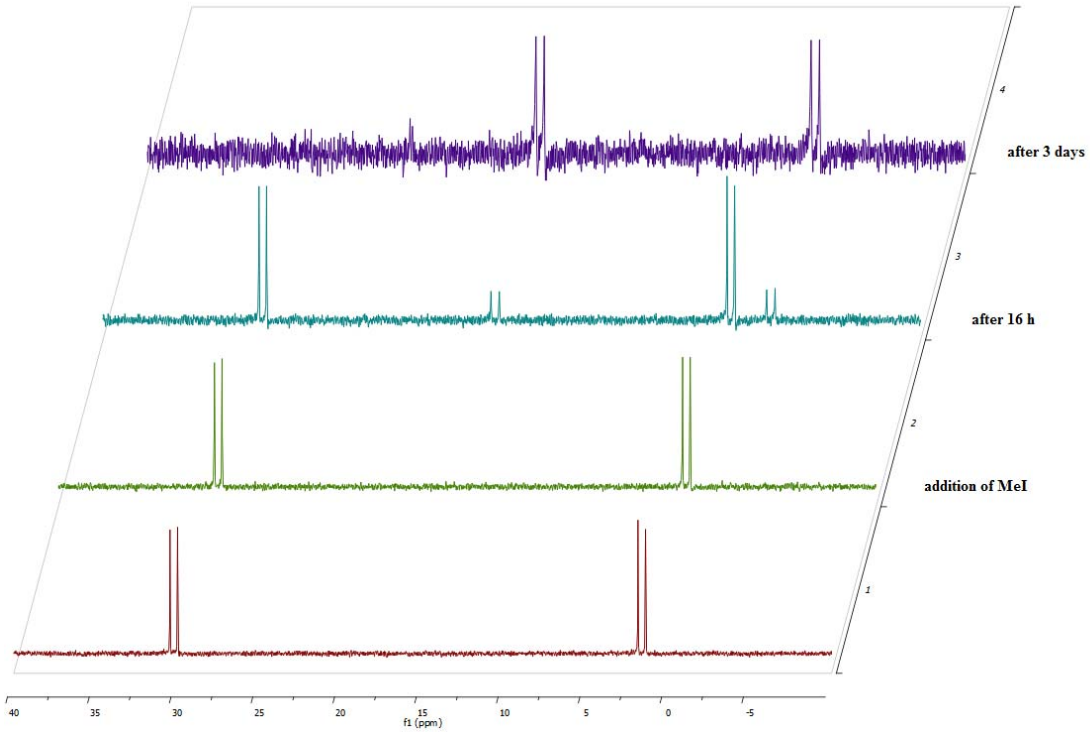

Fig. 2: ^{31}P –NMR-spectroscopic study of the methylation of nickelalactone **2**

Appendix

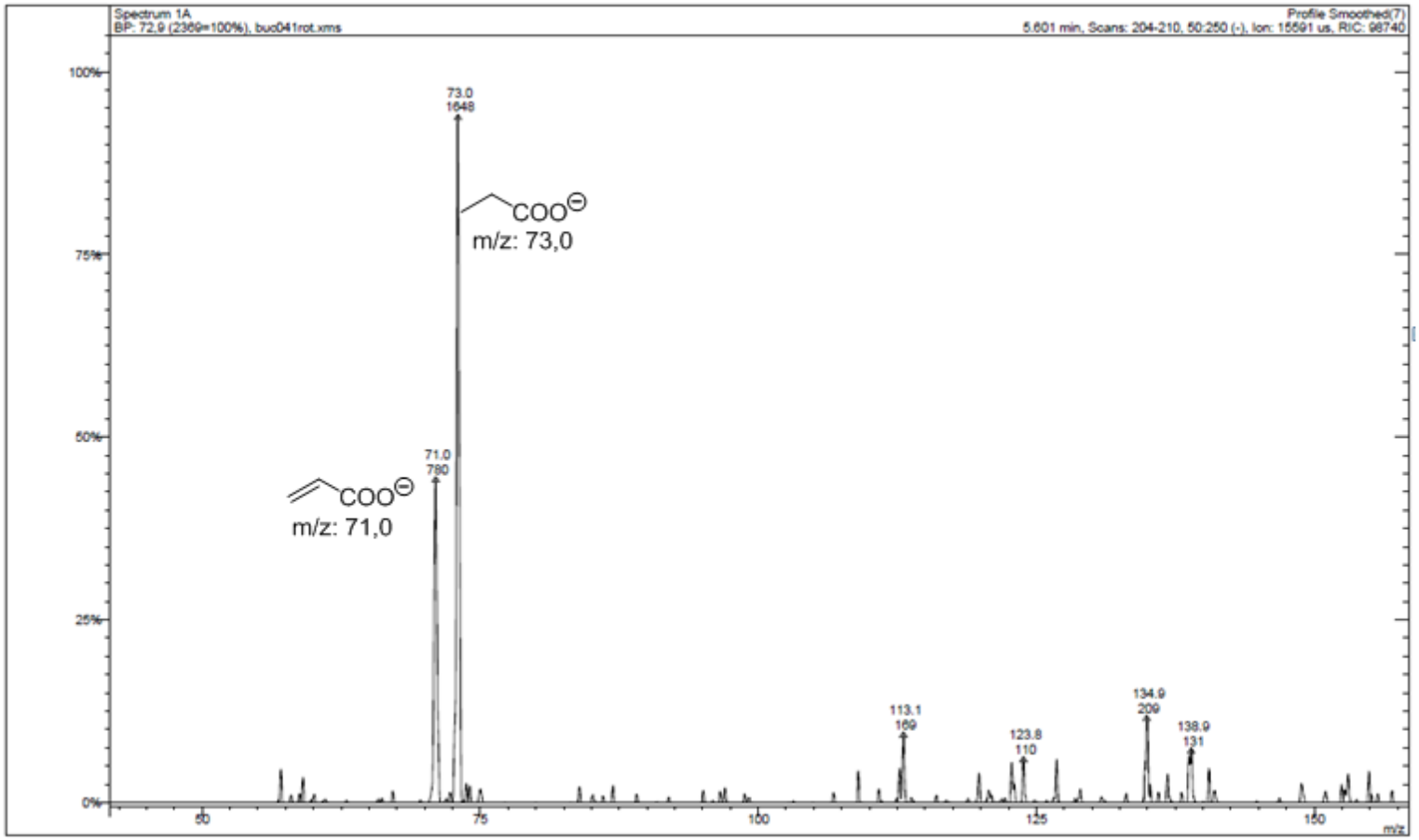

Fig. 3: ESI-mass-spectrum, methylation of complex **1** (2 eq MeI, rt, 2d)

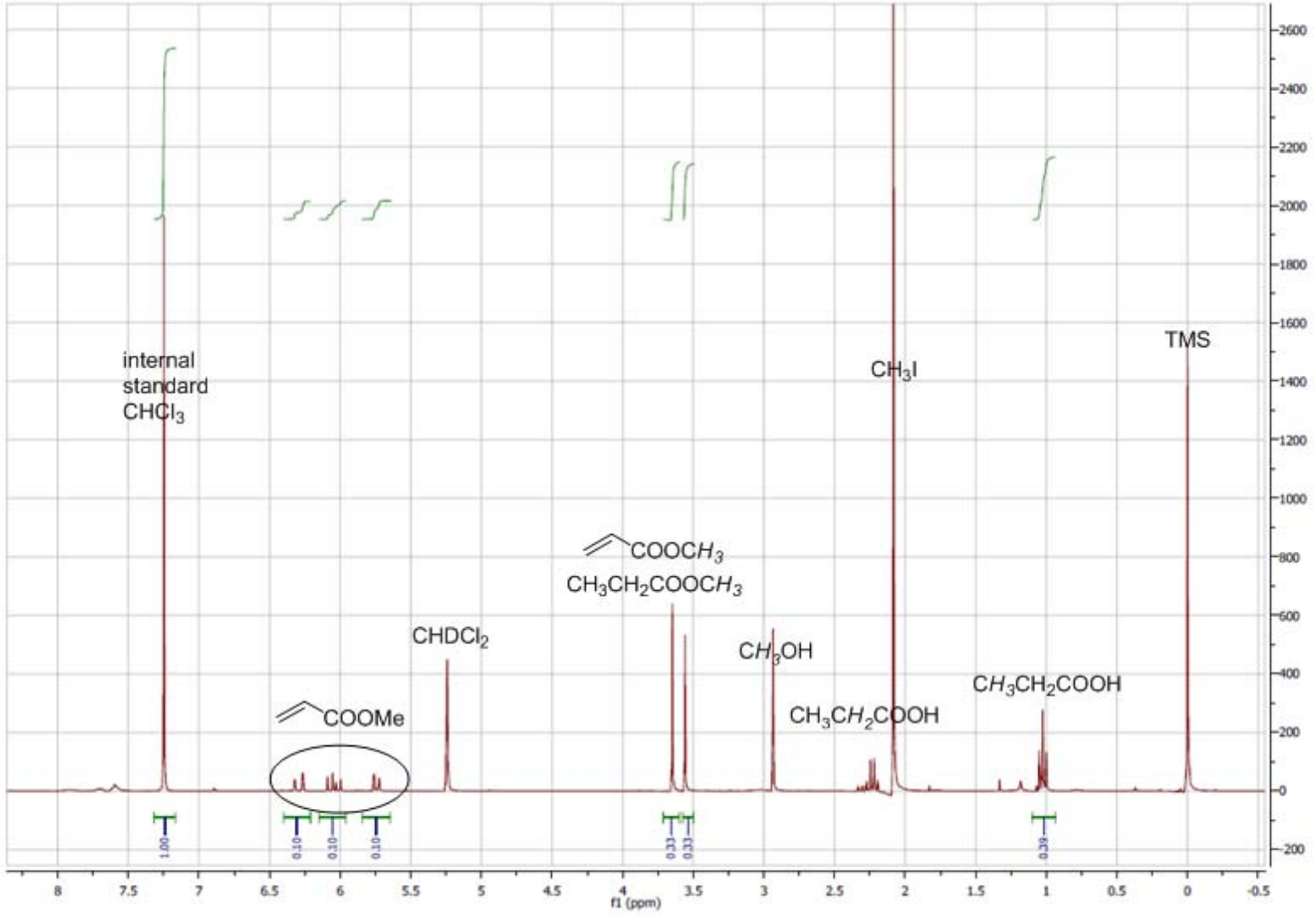

Fig. 4: ^{1}H-NMR-spectrum, methylation of complex **1** (2 eq MeI, rt, 2d, CD_2Cl_2)

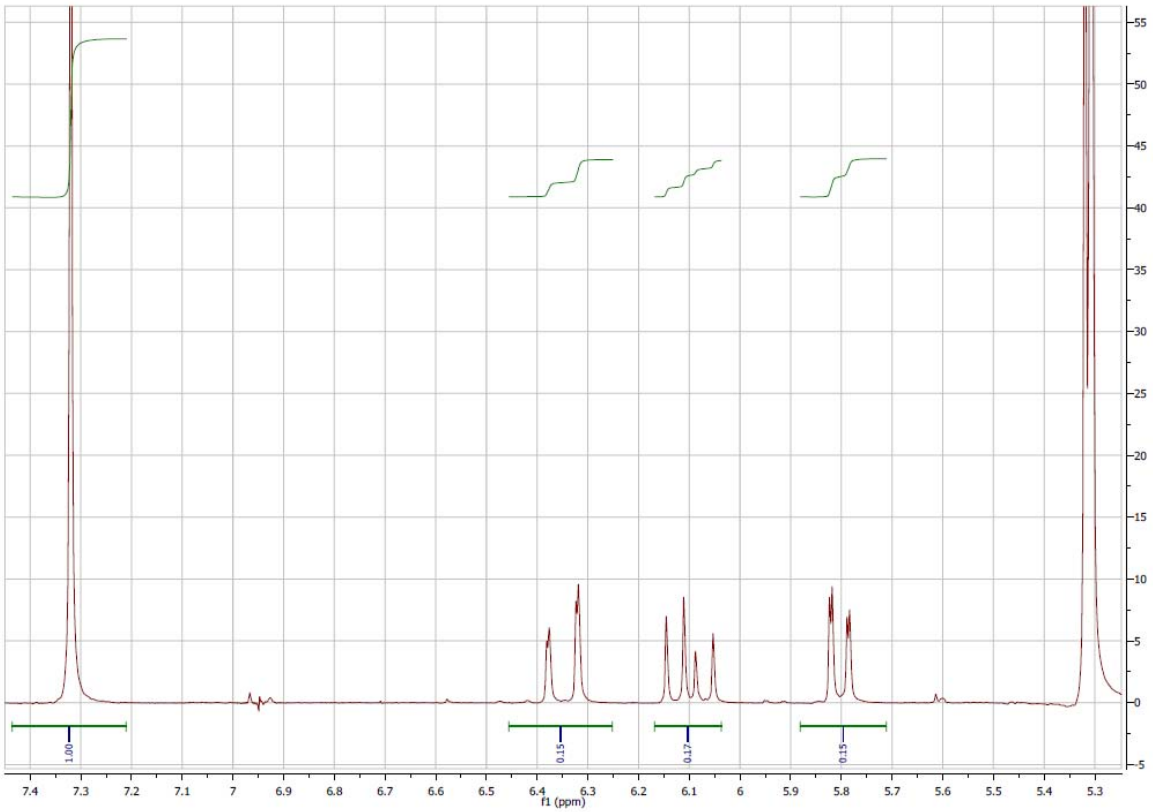

Fig. 5: ^{1}H-NMR-spectrum, methylation of complex **1** (10 eq MeI, rt, 2d, CD_2Cl_2)

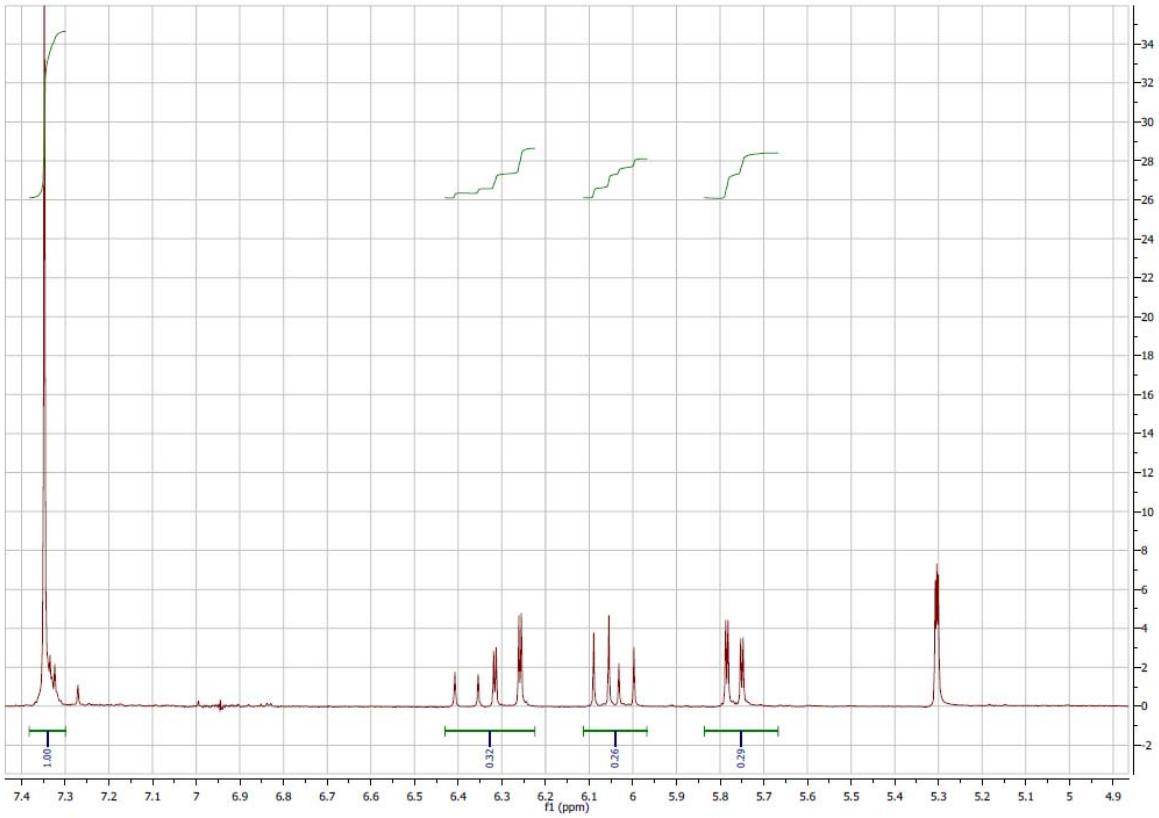

Fig. 6: ^{1}H-NMR-spectrum, methylation of complex **1** (100 eq MeI, rt, 2d, CD_2Cl_2)

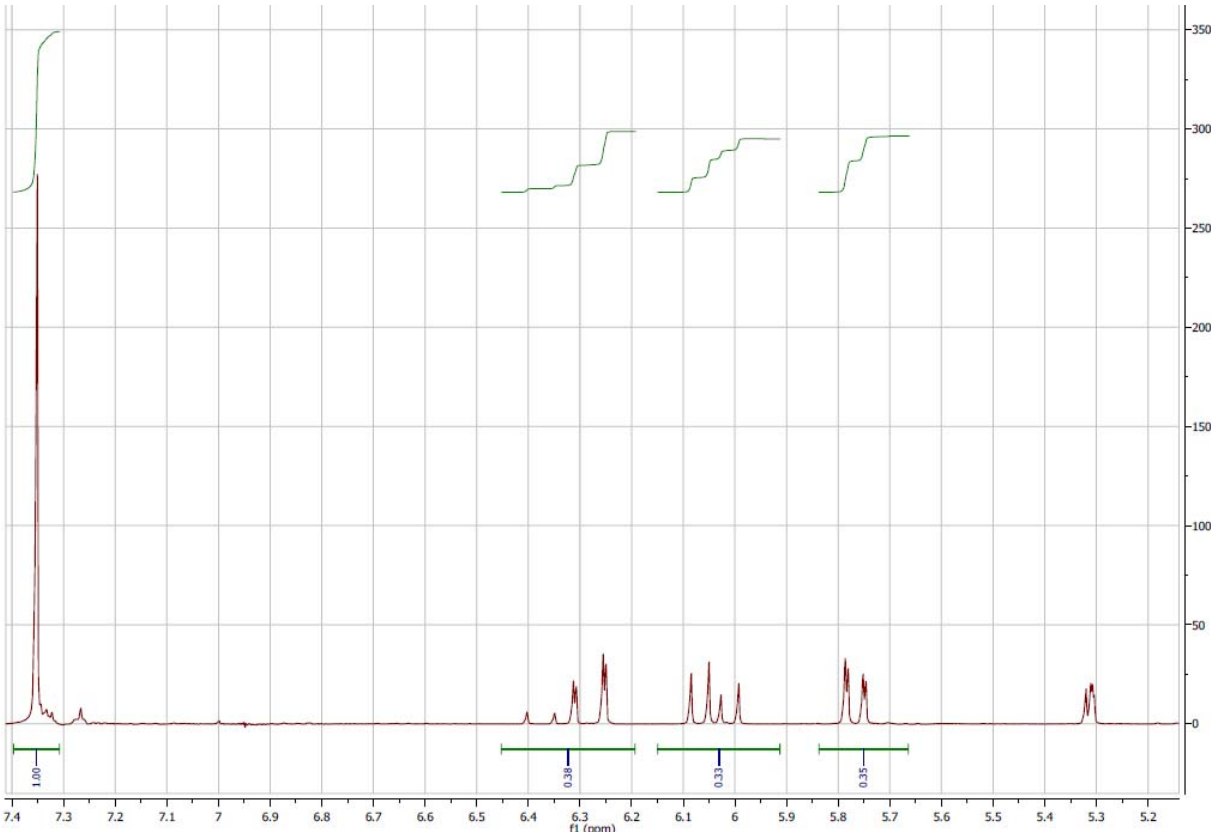

Fig. 7: ^{1}H-NMR-spectrum, methylation of complex **1** (neat MeI, rt, 2d, CD_2Cl_2)

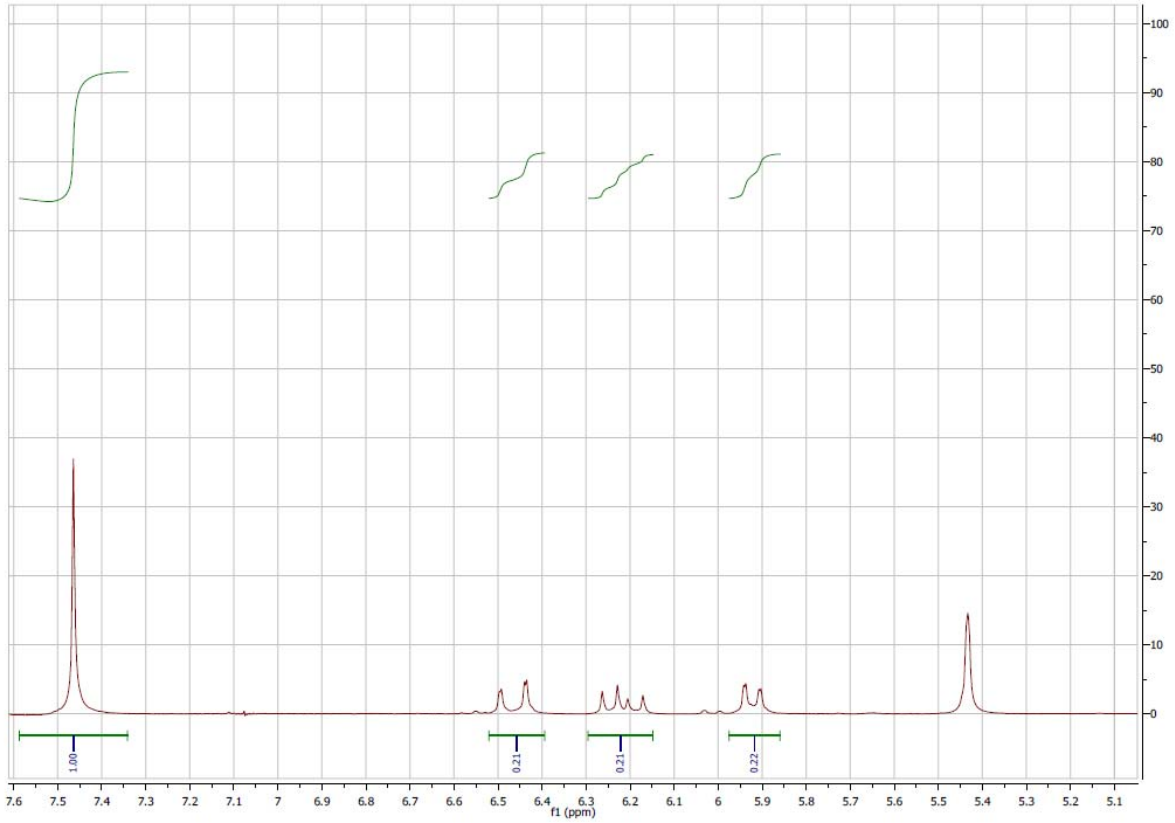

Fig. 8: ^{1}H-NMR-spectrum, methylation of complex **1** (10 eq MeI, reflux, 2d, CD_2Cl_2)

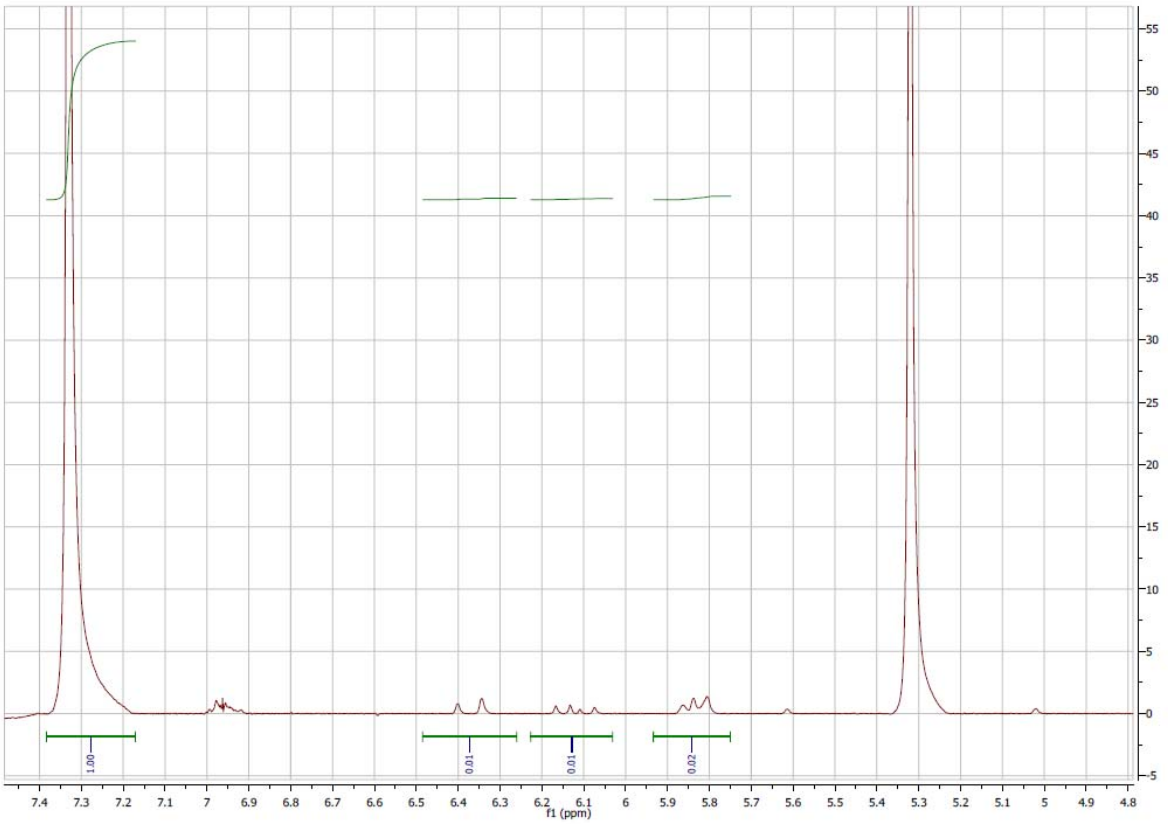

Fig. 9: ^{1}H-NMR-spectrum, methylation of complex **1** (3 eq $(CH3)_4OBF_4$, reflux, 2d, CD_2Cl_2)

Kinetic study

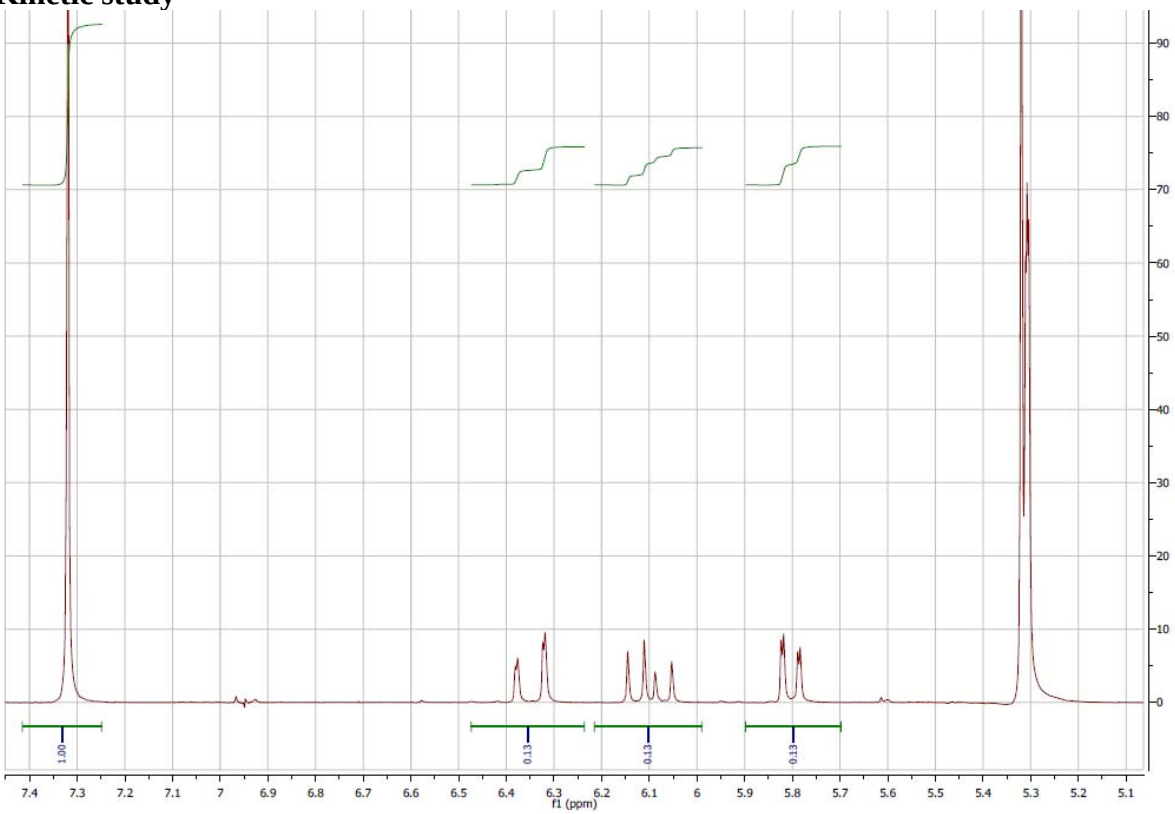

Fig. 10: NMR-spectrum, methylation of complex **1** (10 eq MeI, reflux, 15 min, CD_2Cl_2)

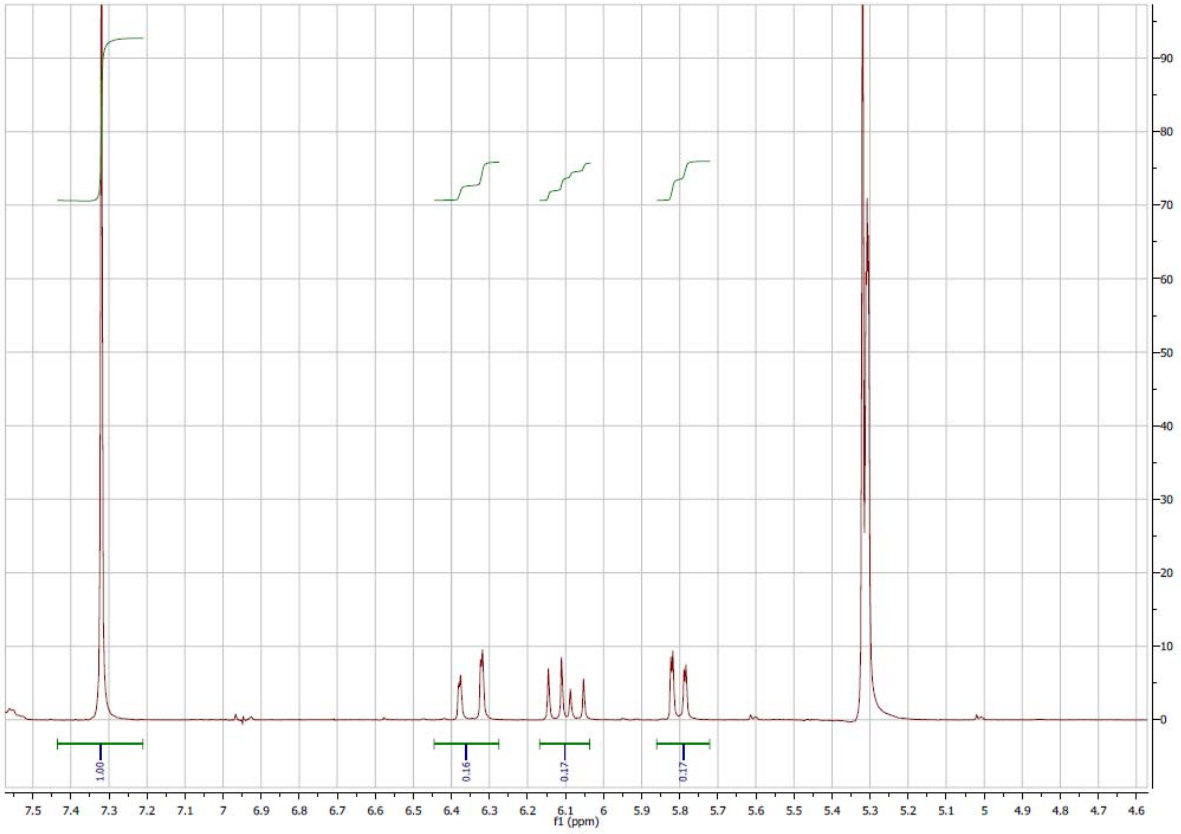

Fig. 11: ^{1}H-NMR-spectrum, methylation of complex **1** (10 eq MeI, reflux, 1.5 h, CD_2Cl_2)

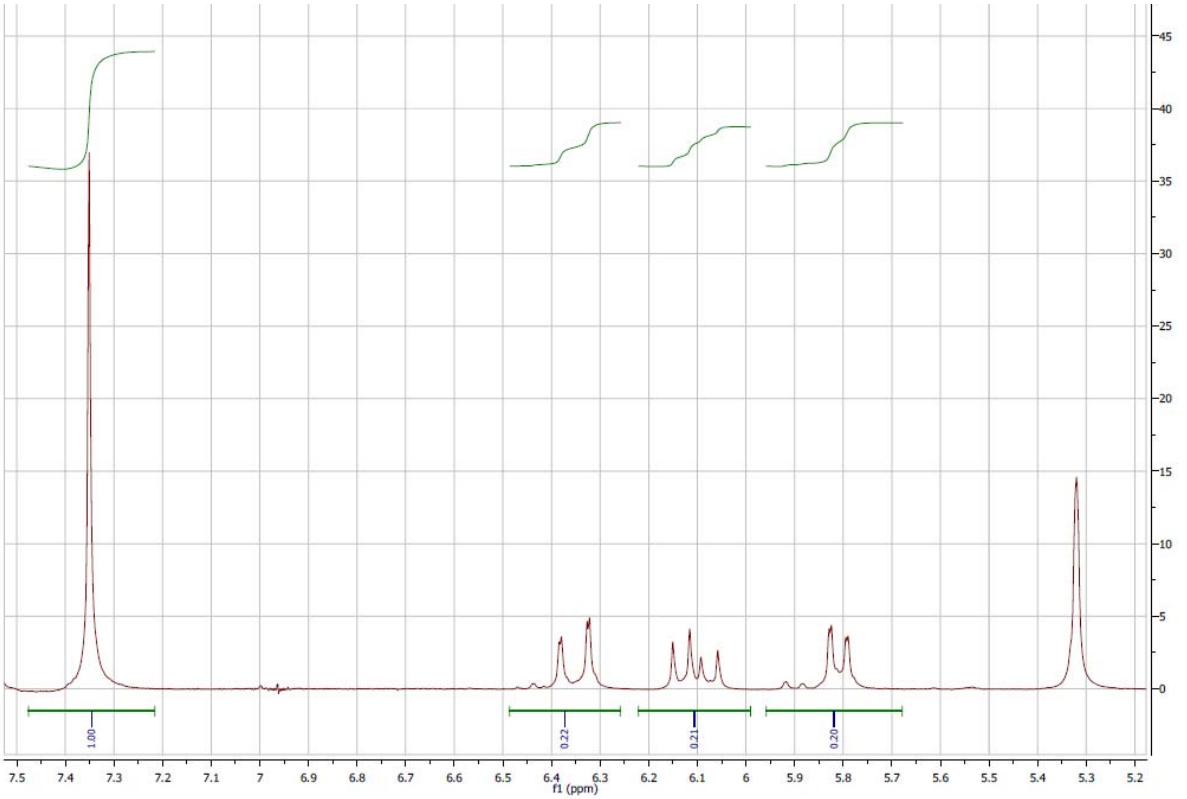

Fig. 12: ^{1}H-NMR-spectrum, methylation of complex **1** (10 eq MeI, reflux, 20 h, CD_2Cl_2)

Decomposition of nickelalactone 1 (CD_2Cl_2, 48 h, rt)

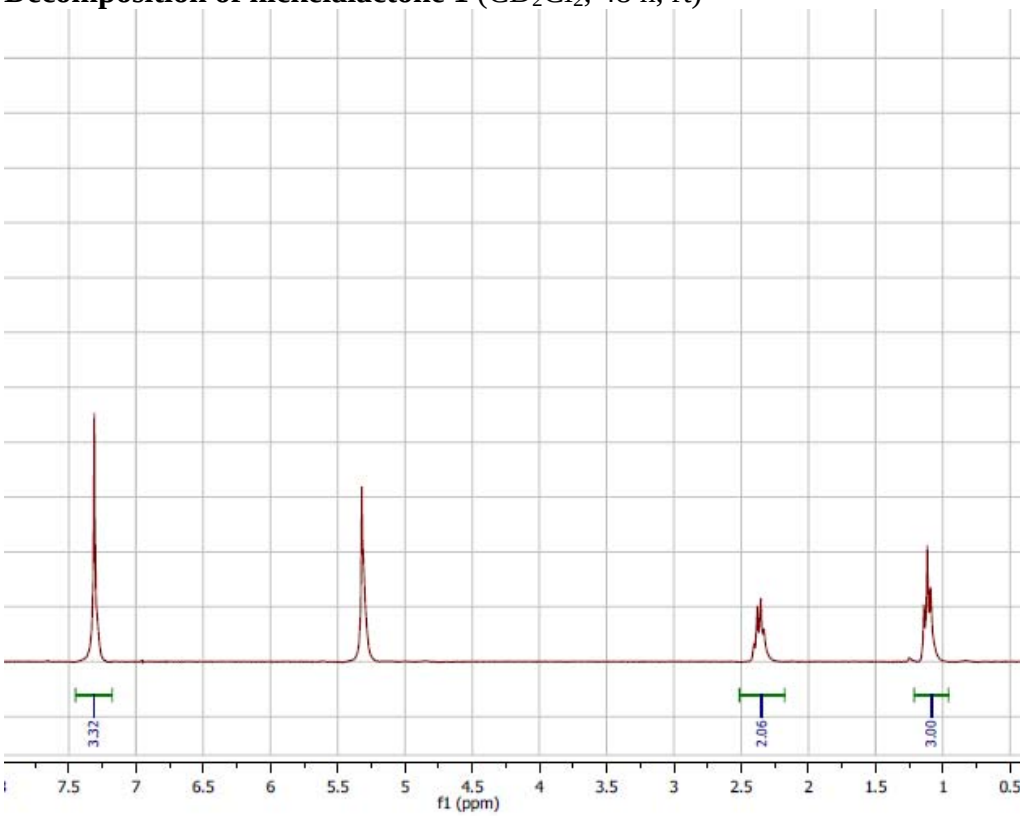

Fig. 13: ^{1}H-NMR-spectrum, decomposition of complex **1** (rt, 2d, CD_2Cl_2)

Reaction of complex 1 with HI

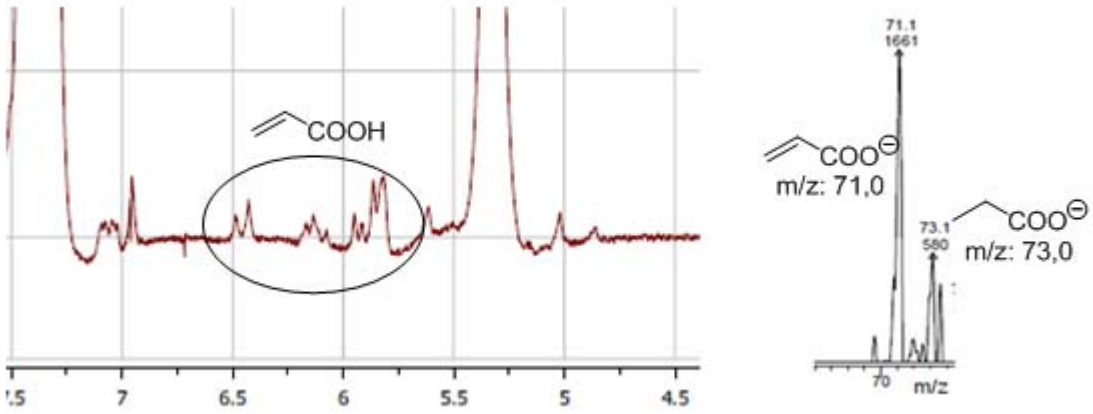

Fig. 14: NMR-spektroscopic (left) and massenspectrometric (right) proof for acrylic acid after stirring complex **1** in an atmosphere of anhydrous HI (CD_2Cl_2, 6 d, rt)

Reaction of nickelalactone 1 with LiI

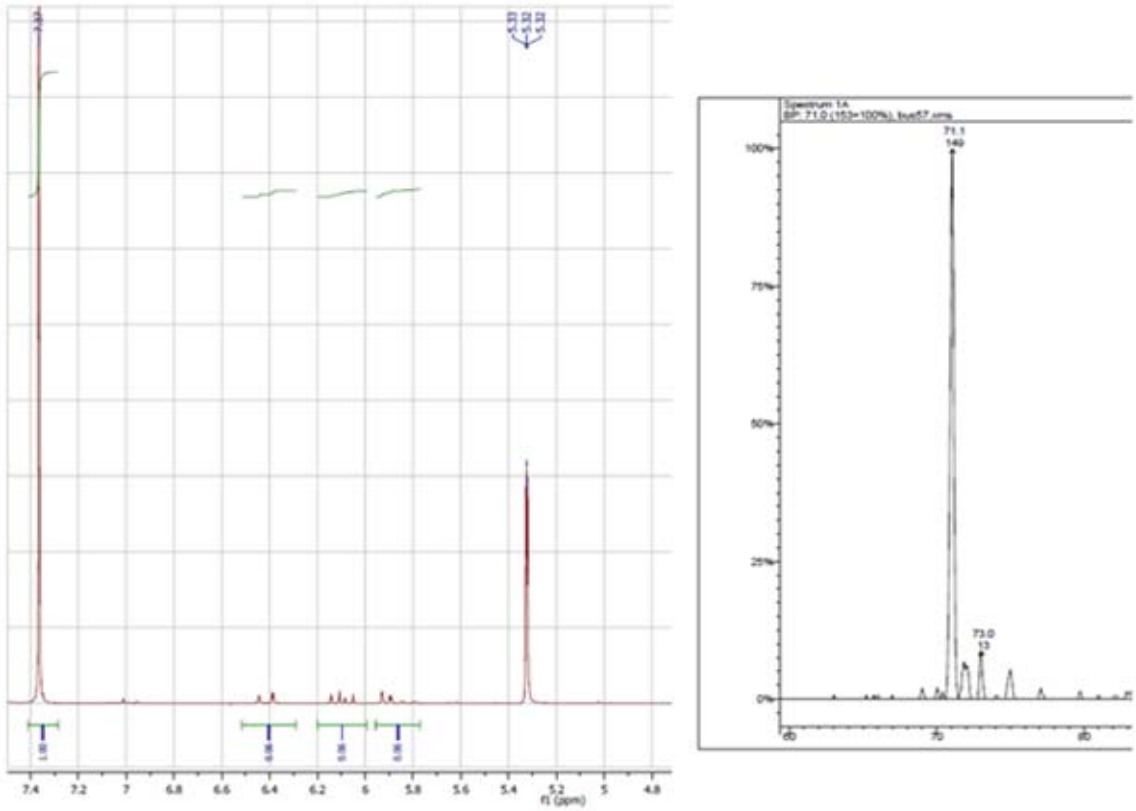

Fig. 15: ^{1}H-NMR-spectrum, (3 eq LiI, rt, 5d, CD_2Cl_2), ESI-mass-spectrum, (3 eq LiI, rt, 5d, CD_2Cl_2)

Reaction of Ni(0) with 3-iodo methyl propionate

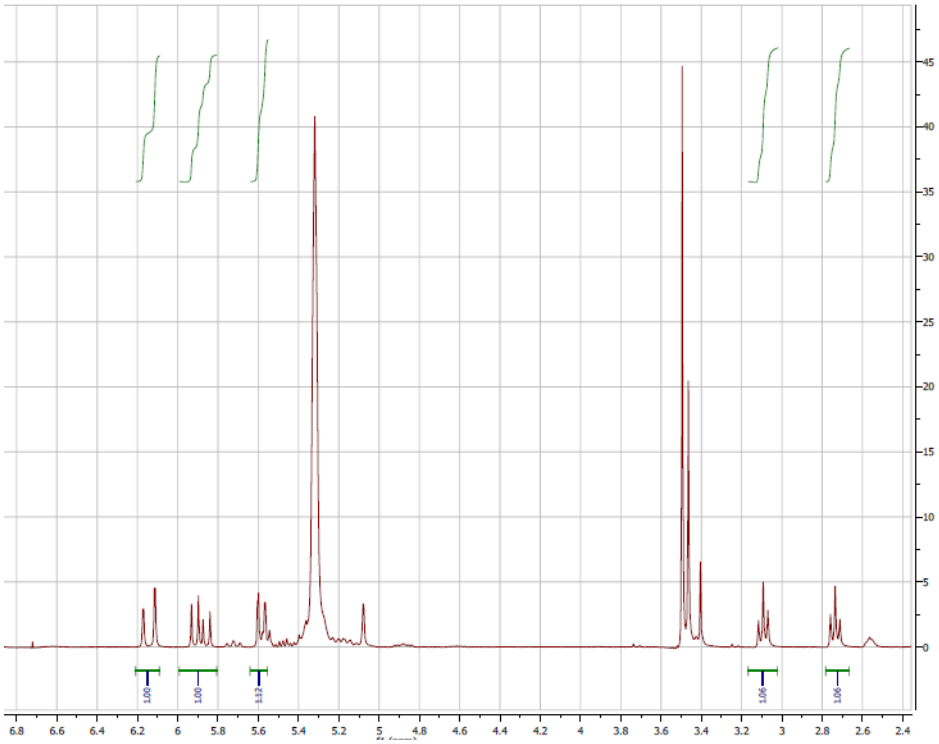

Fig. 16: Reaction of Ni(0) with 3-iodo methyl propionate