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**Supporting Information**

# Selective rearrangement of terminal epoxides into methylketones catalysed by a nucleophilic rhodium-NHC-pincer complex

Eva Jürgens,[a] Barbara Wucher,[a] Frank Rominger,[b] Karl W. Törnroos,[c] Doris Kunz[a]*

[a] Institut für Anorganische Chemie, Eberhard Karls Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen (Germany)

[b] Institut für Organische Chemie, Heidelberg University Im Neuenheimer Feld 250, D-69120 Heidelberg (Germany)

[c] Department of Chemistry, University of Bergen, Allégaten 41, 5007 Bergen (Norway)

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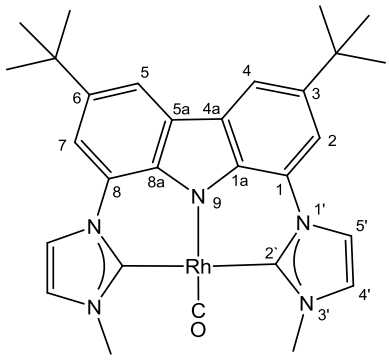
# 1. Experimental procedures and analytical data

**General Procedures.** Unless otherwise noted, all reactions were carried out under an argon atmosphere in dried and degassed solvents using Schlenk techniques. Acetonitrile and thf were purchased from Sigma Aldrich, dried, and degassed using an MBraun SPS-800 solvent purification system. All lithium and sodium salts used were obtained from commercial suppliers, dried in vacuum and used without further purification. Epoxides were obtained from commercial suppliers and degassed under vacuum prior to use. The rhodium complex **1** was synthesised according to the literature procedure.[1] $^{1}$H and $^{13}$C NMR spectra were recorded using a Bruker ARX 250 and AVANCE II +400 spectrometer. $^{1}$H and $^{13}$C chemical shifts are reported in ppm and calibrated to TMS on the basis of the residual solvent proton signal as an internal standard (1.73 ppm, thf-$d_8$; 1.94 ppm, $CD_3CN$; 5.32 ppm, dichloromethane-$d_2$). Assignment of peaks was made using 2D NMR correlation spectra. IR spectra were recorded on a Bruker Vertex70 instrument. The mass spectrum was recorded on a Thermo Finnigan TSQ 70.

**Synthesis of rhodium complex 1**:




**1**

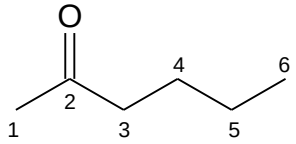
We already reported the synthesis of this compound.[1] Additional $^{1}$H NMR data of compound **1** in thf-$d_8$ and $C_6D_6$:

$^{1}$H NMR (thf-$d_8$, 400.11 MHz): $\delta$ = 1.55 (s, 18H, t-Bu), 4.20 (s, 6H, $NCH_3$), 7.45 (d, $^{3}J$ = 2.0 Hz, 2H, H-4´), 7.82 (d, $^{4}J$ = 1.8 Hz, 2H, H-2/7), 8.16 (d, $^{4}J$ = 1.8 Hz, 2H, H-4/5), 8.23 (d, $^{3}J$ = 2.0 Hz, 2H, H-5´).

$^{1}$H NMR (benzene-$d_6$, 400.14 MHz): $\delta$ = 1.56 (s, 18H, t-Bu), 3.74 (s, 6H, $NCH_3$), 6.14 (d, $^{3}J$ = 1.6 Hz, 2H, H-4´), 7.31 (d, $^{3}J$ = 1.6 Hz, 2H, H-5´), 7.63 (d, $^{4}J$ = 2.0 Hz, 2H, H-2/7), 8.49 (d, $^{4}J$ = 2.0 Hz, 2H, H-4/5).

$^{13}$C{$^{1}$H}NMR (benzene-$d_6$, 100.61 MHz): $\delta$ = 32.5 ($C(CH_3)_3$), 35.0 ($C(CH_3)_3$), 40.3 (N-$CH_3$), 110.9 (C2/7), 114.7 (C4/5), 115.7 (C5´), 122.7 (C4´), 125.4 (C1/8), 129.3 (C4a/5a), 37.3 (C1a/8a), 139.2 (C3/6), 182.5 (d, $^{1}J_{RhC}$ = 45.9 Hz, C2´), 199.8 (d, $^{1}J_{RhC}$ = 71.4 Hz, CO).

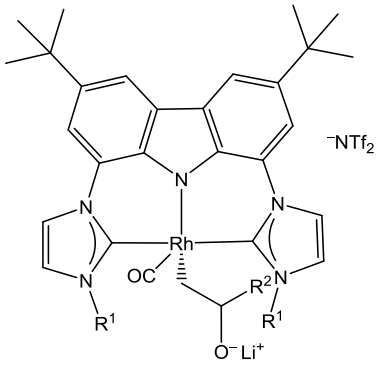
**General Procedure for the Meinwald rearrangement with rhodium complex 1**:




Rh(bimca)CO[1] **1** (2 mg, 4 μmol, 10 mol%) and lithium bis(trifluoromethanesulfonimide) (1 mg, 10 mol%) were placed into a J. Young NMR tube and 1,3,5-trimethoxybenzene as internal standard and benzene (0.5 mL) were added. At last dried 1,2-epoxyhexane (4.2 µL, 35 μmol) was added and the reaction mixture was heated to 60 °C and monitored via $^1$H NMR spectroscopy during the time given.

$^1$H NMR (benzene-$d_6$, 400.11 MHz): $\delta$ = 0.77 (t, $^3J$ = 7.4 Hz, 3H, H-6), 1.08 (ps sext, $^3J$ = 7.5 Hz, 2H, H-5), 1.34 (ps quint, $^3J$ = 7.7 Hz, 2H, H-4), 1.64 (s, 3H, H-1), 1.87 (t, $^3J$ = 7.3 Hz, 2H, H-3).

**Synthesis of rhodium complex 2**:




**2**

In the glove box, 10 mg **1** (18.5 µmol) and lithium bis(trifluoromethanesulfonimide) (5 mg, 1 eq) were dissolved in 0.5 mL benzene-$d_6$ in a J. Young NMR tube. Propylene oxide (1.5 µL, 1.2 eq) was added to the reaction mixture, which was allowed to react at room temperature for 10 minutes. The resulting species **2** ($R^1$, $R^2$ = $CH_3$) was characterised by NMR and IR spectroscopy in solution.

$^1$H NMR (benzene-$d_6$, 400.14 MHz): δ = 1.04 (d,$^3J$ = 5.8 Hz, 3H, $CH_3$), 1.35 and 1.52 (each s br, each 9H, t-Bu), 3.56–3.63 (m, 1H, CH), 3.69 and 3.85 (each s br, each 3H, $NCH_3$), 6.32 and 6.49 (each s br, each 1H, H-4', H-9'), 7.11 and 7.45 (each s br, each 1H, H-Carb), 7.16 (from 2D) and 7.49 (each s br, each 1H, H-5', H-10'), 7.86 and 8.07 (each s br, each 1H, H-Carb). The signal at 7.16 ppm is covered by the solvent signal and was assigned via 2D spectra ($^1$H$^1$H-COSY, $^1$H$^{13}$C-HMBC, $^1$H$^{13}$C-HSQC) as well as the signal for the $CH_2$-group that is covered by the t-Bu-group (1.52 ppm) signals.

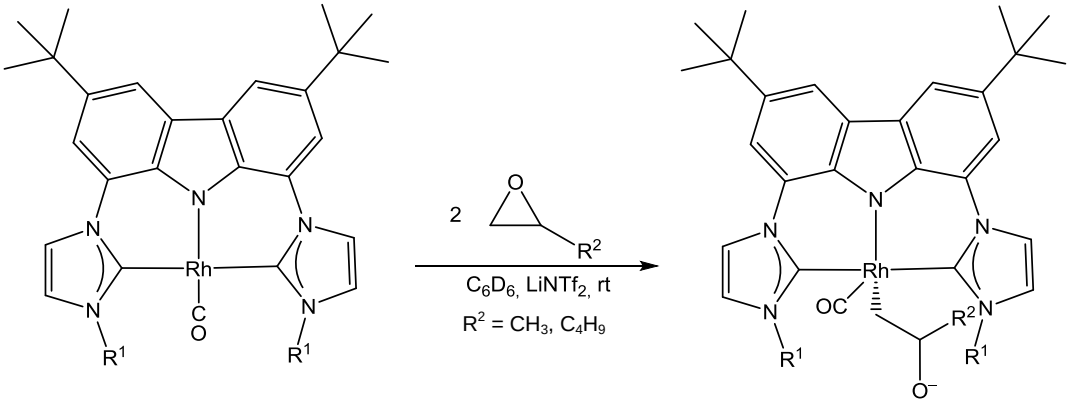
$^1$H NMR (toluene-$d_8$, 400.14 MHz): δ = 1.04 (d,$^3J$ = 5.8 Hz, 3H, $CH_3$), 1.31 and 1.51 (each s br, each 9H, t-Bu), 1.37–1.44 (s br, 2H, $CH_2$) 3.56–3.63 (m, 1H, CH), 3.65 and 3.82 (each s br, each 3H, $NCH_3$), 6.26 and 6.49 (each s br, each 1H, H-4', H-9'), 7.09 and 7.40 (each s br,

each 1H, H-Carb), 7.15 and 7.52 (each s br, each 1H, H-5', H-10'), 7.74 and 7.95 (each s br, each 1H, H-Carb).

$^{13}C\{^{1}H\}$ NMR (benzene-$d_6$, 400.14 MHz): δ = 19.1 ($CH_3$), 23.2 (d br, $^{1}J_{RhC}$ = 23.0 Hz, $CH_2$), 32.0 and 32.2 ($C(CH_3)_3$), 34.4 and 34.6 ($C(CH_3)_3$), 38.7 and 39.0 ($NCH_3$), 80.5 (s br, CH), 109.6 and 109.9 (CCarb), 114.2 and 114.5 (CCarb), 115.2 and 116.6 (C5´, C10´), 118.5 and 121.7 (C1, C8), 123.4 and 123.7 (C4a, C5a), 124.5 and 124.7 (C4´, C9´), 135.5 (C1a, C8a), 138.2 (C3, C6), 174.1 and 174.5, (each d, each $^{1}J_{RhC}$ = 56.0 Hz, C2´, C7´), 207.1 (d, $^{1}J_{RhC}$ = 46.2 Hz, CO).

$\tilde{\nu}$ (benzene-$d_6$, $cm^{-1}$) = 2046 (vw br, Rh-CO), 1716 (w, acetone), 1645 (w), 1588 (w).
(Formation of complex **2** was confirmed by NMR spectroscopy prior to the IR-measurement. Therefore benzene-$d_6$ was used as a solvent.)

**In situ generation of type 2 complexes by reaction of 1a/b and epoxides in benzene-$d_6$:**




**1**
$R^1$ = $CH_3$ (**a**), $C_2H_5$ (**b**)

**2a/b** ($R^1$ = $CH_3$, $R^2$ = $CH_3$ (**a**), $C_4H_9$ (**b**))
**2c/d** ($R^1$ = $C_2H_5$, $R^2$ = $CH_3$ (**c**), $C_4H_9$ (**d**))

Other unsymmetrical complexes of type **2** can be generated at room temperature by reacting Rh(I) complexes **1a** and **1b** with 2 eq of epoxide and 2 eq of $LiNTf_2$ in benzene-$d_6$. Reaction of complexes [Rh(bimca)(CO)] (**1a**) or [Rh(bimca$^{Et}$)(CO)] (**1b**) with propylene oxide and 1,2-epoxyhexane lead clearly to the respective complexes of type **2**, but the amount depends on the steric demand of both reaction partners. Complex **1a** ($R^1$ = $CH_3$) reacts with both epoxides at room temperature completely to **2a/b**, while **1b** ($R^2$ = $C_2H_5$) leads to a mixture of **1b** and **2c/d.**

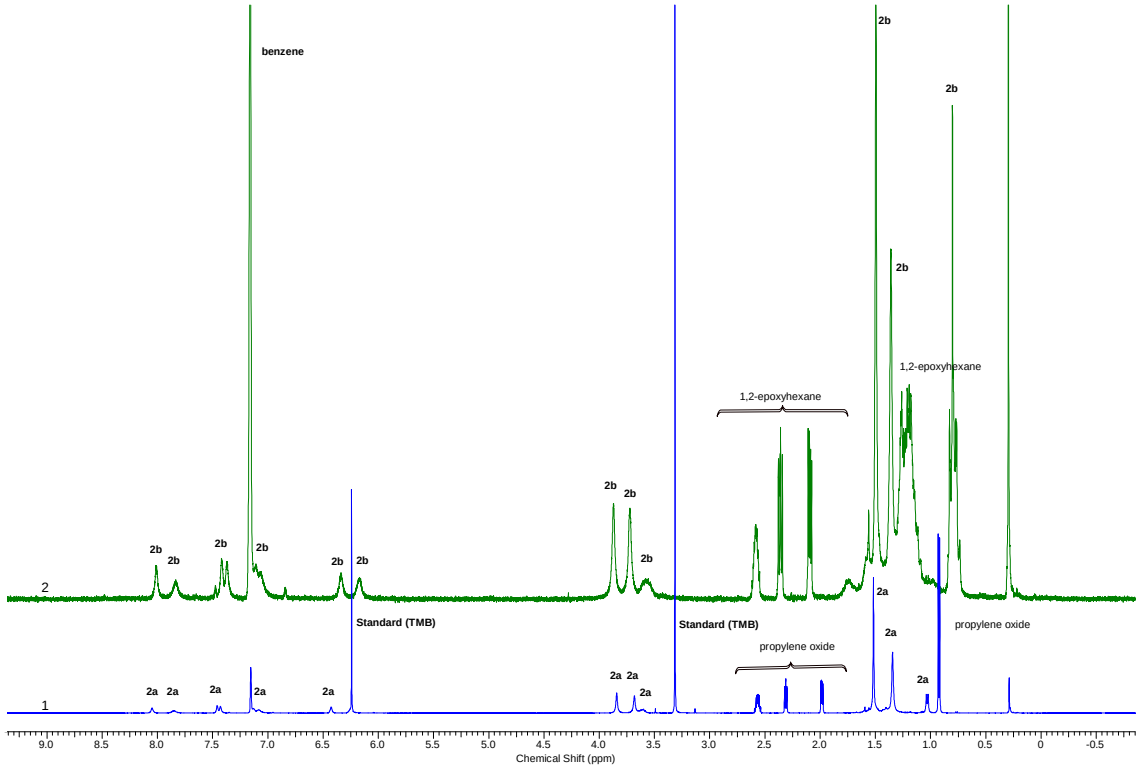



**Figure 1.** Complete conversion of **1a** and propylene oxide (1, blue) or 1,2-epoxyhexane (2, green) at room temperature to complexes **2a** and **2b.**

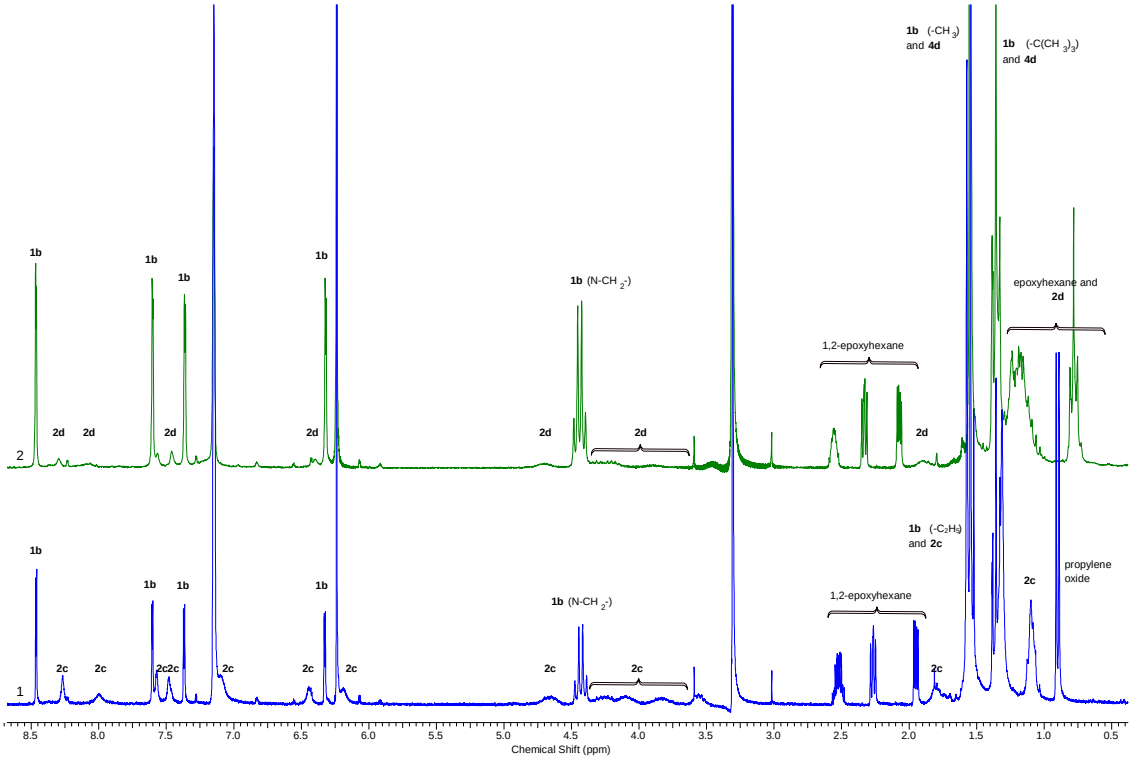



**Figure 2.** Reaction of **1b** with propylene oxide (1, blue) and 1,2-epoxyhexane (2, green) at room temperature led to the analogue complexes **2c** and **2d**. In this case the conversion of **1b** is incomplete and led to a ratio of **1b**:**2c = 4:3** or **2d** (**1b**:**2d = 8:1**).

After full conversion of the epoxide the starting complexes **1a/b** are recovered (by NMR spectroscopy).

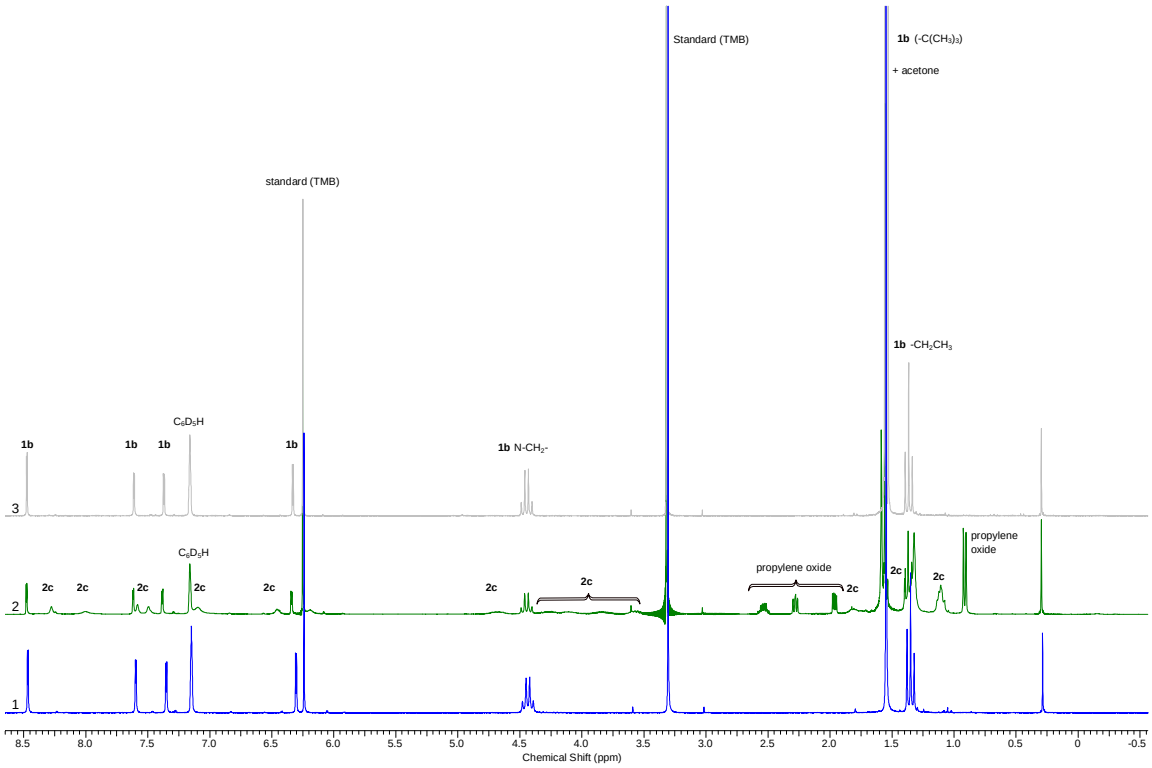
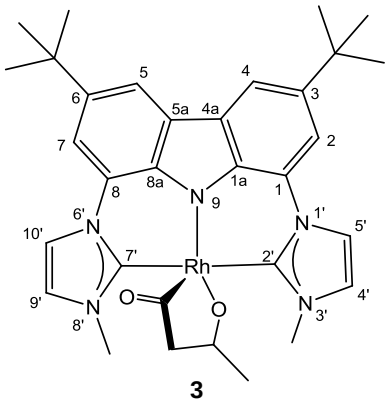



**Figure 3.** Monitoring the reaction of **1b** with propylene oxide in benzene-$d_6$; spectrum 1 (blue): before addition of propylene oxide, spectrum 2 (green): after addition of 2 eq propylene oxide, and spectrum 3 (grey): after 16 h at room temperature (full conversion of the epoxide to acetone and recovery of complex **1b**).

## Synthesis of rhodium complex 3:




**3**

*Route 1:*

In the glove box, 15 mg of **1** (26 µmol) were dissolved in 0.5 mL tetrahydrofurane-$d_8$ with propylene oxide (2 µL, 1 eq) and lithium chloride (1 mg, 1 eq) in a J. Young NMR tube. The reaction mixture was allowed to react at room temperature for 4 days, after which the complete formation of **3** was observed. Slow decomposition during workup prevents further analysis.

$^{1}$H NMR (thf-$d_8$, 400.14 MHz): δ = 1.16 (d, $^{3}J$ = 6.2 Hz, 3H, $CH_3$), 1.50 and 1.51 (each s, each 9H, t-Bu), 1.65–1.75 (m, 2H, $CH_2$), 3.55–3.66 (m, 1H, CH), 3.98 and 3.99 (each s, each 3H, $NCH_3$), 7.21 and 7.22 (each d, each $^{3}J$ = 2.1 Hz, each 1H, H-4´, H-9´), 7.61 and 7.64 (each d, each $^{4}J$ = 1.5 Hz, each 1H, H-4, H-5), 7.99 and 8.00 (each d, each $^{4}J$ = 1.5 Hz, each 1H, H-2, H-7), 8.18 and 8.19 (each d, each $^{3}J$ = 2.1 Hz, each 1H, H-5´, H-10´).

$^{13}$C{$^{1}$H} NMR (thf-$d_8$,100.61 MHz): δ = 22.3 ($CH_3$), 26.1 (d, $^{2}J_{RhC}$ = 30.0 Hz, $CH_2$), 32.9 and 32.9 (C($CH_3$)$_3$), 35.5 (2x $C$($CH_3$)$_3$), 39.5 and 39.8 ($NCH_3$), 79.4 (CH), 109.5 and 109.7 (C4, C5), 114.3 and 114.5 (C2, C7), 117.6 and 117.8 (C5´, C10´), 124.6 and 124.8 (C4´, C9´), 125.7 and 126.3 (C4a, C5a), 127.6 and 127.5 (C1, C8), 136.9 and 137.0 (C1a, C8a), 136.9 and 137.0 (C3, C6) 180.5 and 181.0 (each d, each $^{1}J_{RhC}$ = 41.0 Hz, C2´, C7´), 229.4 (d, $^{1}J_{RhC}$ = 43.3 Hz, $C_{Acyl}$).

MS (FAB$^+$): m/z = 628.3 (1 %) [M+H]$^+$, 642.3 (100 %) [M-$C_3H_6O_2$]$^+$.

*Route 2:*

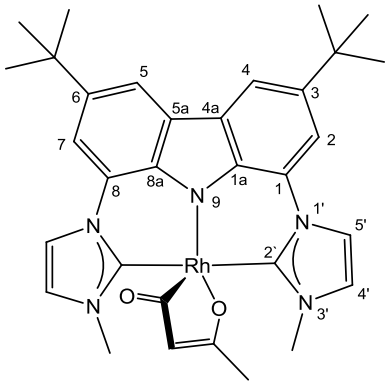
In the glove box, 15 mg of **1** (26 µmol) were dissolved in 0.5 mL acetontirile-$d_3$ with propylene oxide (2 µL, 1 eq) and lithium chloride (1 mg, 1 eq) in a J. Young NMR tube. The reaction mixture was allowed to react at room temperature for 24 h at 60 °C, after which the complete formation of the new species **3** was observed. Slow decomposition during workup prevents further analysis.

$^{1}$H NMR ($CD_3CN$, 400.14 MHz): δ = 1.14 (d, $^{3}J$ = 6.1 Hz, 3H, H-15), 1.51 (s, 18H, t-Bu), 1.56–1.63, 1.64–1.73 (each m, each 1H, $CH_2$), 3.55–3.66 (m, 1H, CH), 3.95 and 3.95 (each s, each 3H, $NCH_3$), 7.23 and 7.24 (each d, each $^{3}J$ = 2.2 Hz, each 1H, H-4´), 7.68 and 7.70 (each d, each $^{4}J$ = 1.5 Hz, each 1H, H-4, H-5), 8.07 and 8.08 (each d, each $^{4}J$ = 1.5 Hz, each 1H, H-2, H-7), 8.18 and 8.20 (each d, each $^{3}J$ = 2.1 Hz, each 1H, H-5´).

$^{13}$C{$^{1}$H} NMR ($CD_3CN$, 100.61 MHz): δ = 22.4 ($CH_3$), 26.6 (d, $^{2}J_{RhC}$ = 36.7 Hz, $CH_2$), 30.0 and 32.9 (C($CH_3$)$_3$), 36.0 (2x $C$($CH_3$)$_3$), 40.0 and 40.3 ($NCH_3$), 80.0 (CH), 110.8 (C4, C5), 115.0 and 115.3 (C2, C7), 125.7 and 126.0 (C4´, C9´), 126.2 and 126.7 (C4a, C5a), 127.2 and 127.4 (C1, C8), 136.0 and 136.6 (C1a, C8a), 139.0 (C3, C6) 179.6 and 179.8 (each d, each $^{3}J_{RhC}$ = 40.7 Hz, C2´, C7´), 228.8 ($C_{Acyl}$, no coupling detected due to low intensity). Signals for C5´ and C10´ could not be detected due to overlap with the signal for $CD_3CN$.

MS (FAB$^+$): m/z = 628.3 (1 %) [M+H]$^+$, 642.3 (100 %) [M-$C_3H_6O_2$]$^+$.

**Synthesis of rhodium complex 4a:**



**4a**

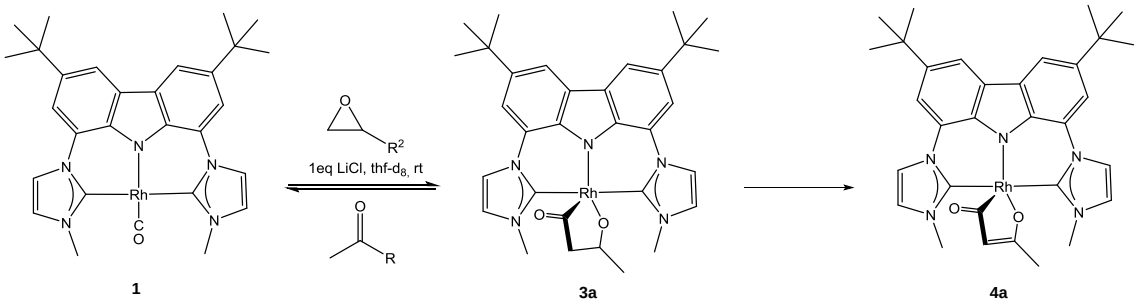
In the glove box, 15 mg **1** (26 µmol) were dissolved in 0.5 mL thf-$d_8$ with propylene oxide (2 µL, 1 eq) and lithium chloride (1 mg, 1 eq) in a J. Young NMR tube. The reaction mixture was allowed to react at 80 °C for 4 days, after which the formation of yellow precipitate was observed. The solvent was removed and the yellow residue dissolved in $CD_2Cl_2$ and characterised NMR spectroscopically.

$^1$H NMR ($CD_2Cl_2$, 400.14 MHz): δ = 1.55 (s, 18H, t-Bu), 2.01 (br s, 3H, $CH_3$), 3.96 (s br, 1H, CH), 4.18 (s, 6H, $NCH_3$), 7.17 (d, $^3J$ = 1.7 Hz, 2H, H-4´), 7.65 (d, $^4J$ = 1.3 Hz, 2H, H-2/7), 8.03 (d, $^3J$ = 1.7 Hz, 2H, H-5´), 8.14 (d, $^4J$ = 1.3 Hz, 2H, H-4/5).

$^{13}$C{$^1$H} NMR (thf-$d_8$, 100.61 MHz): δ = 21.0 ($CH_3$), 31.9 (C($CH_3$)$_3$), 34.7 ($C$($CH_3$)$_3$), 38.7 ($NCH_3$), 93.6 (CH), 110.8 (C4´), 114.7 (C2/7), 116.3 (C5´), 125.3 (C4/5), 127.6 (C4a/5a), 135.0 (C1a/8a), 137.2 (C1/8), 139.3 (C3/6), 174.6 (d, $^1J_{RhC}$ = 112.6 Hz, C2´), 189.8 (d, $^2J_{RhC}$ = 89.0 Hz, CORh), the $C_{Acyl}$ signal could not be detected.

**The equilibrium between Rh-catalyst 1 and complex 3a in thf-$d_8$:**

*Experiment whether species **3a** is able to release acetone and such reacts back to catalyst **1** or complex **3a** gets only deactivated by dehydrogenation to **4a** (Figures 4-7).*




**1** **3a** **4a**

Complex **1** was dissolved with a catalytic amount of LiCl and propylene oxide in thf-$d_8$ (Figure 4). After 20 h at room temperature a mixture of **1** and **3a** (2:1) and a small amount of Rh complex **4a** was obtained. Upon evaporation of the solvent and redissolving the residue in thf-$d_8$, the ratio of complexes **1** to **3a** remained unchanged, but all organic components were removed (Figure 5). After 1 day at room temperature acetone was generated and the $^1$H NMR spectrum shows complex **1** as the only organometallic species (Figure 6). The thf-$d_8$ and all volatiles were evaporated again and the residue dissolved in dichloromethane-$d_2$ (as

the solubility of **4a** is much better in $CD_2Cl_2$). The $^1H$ NMR spectrum gives evidence for the formation of **4a** (Figure 7).

Thus we could demonstrate that some amount of complex **3a** releases acetone under regeneration of **1** as well as it can be dehydrogenated to complex **4a**.

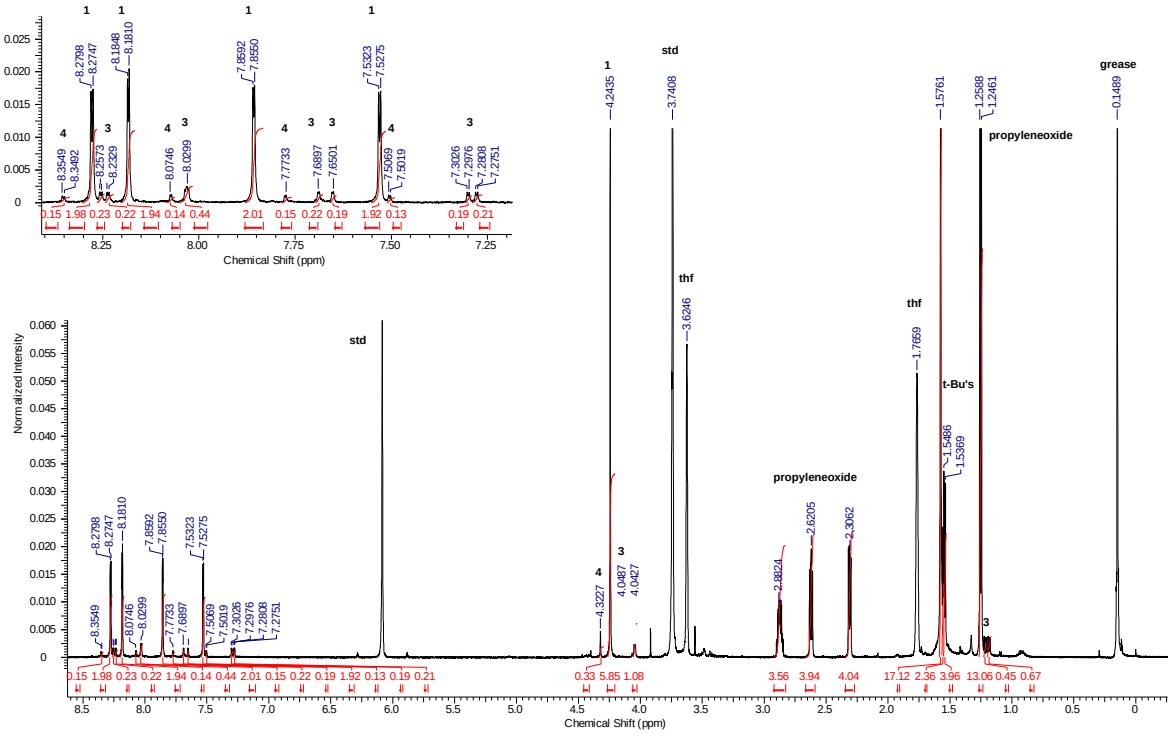



**Figure 4.** $^1H$ NMR spectrum recorded directly after the addition of propylene oxide (std = 1,3,5-trimethoxybenzene).

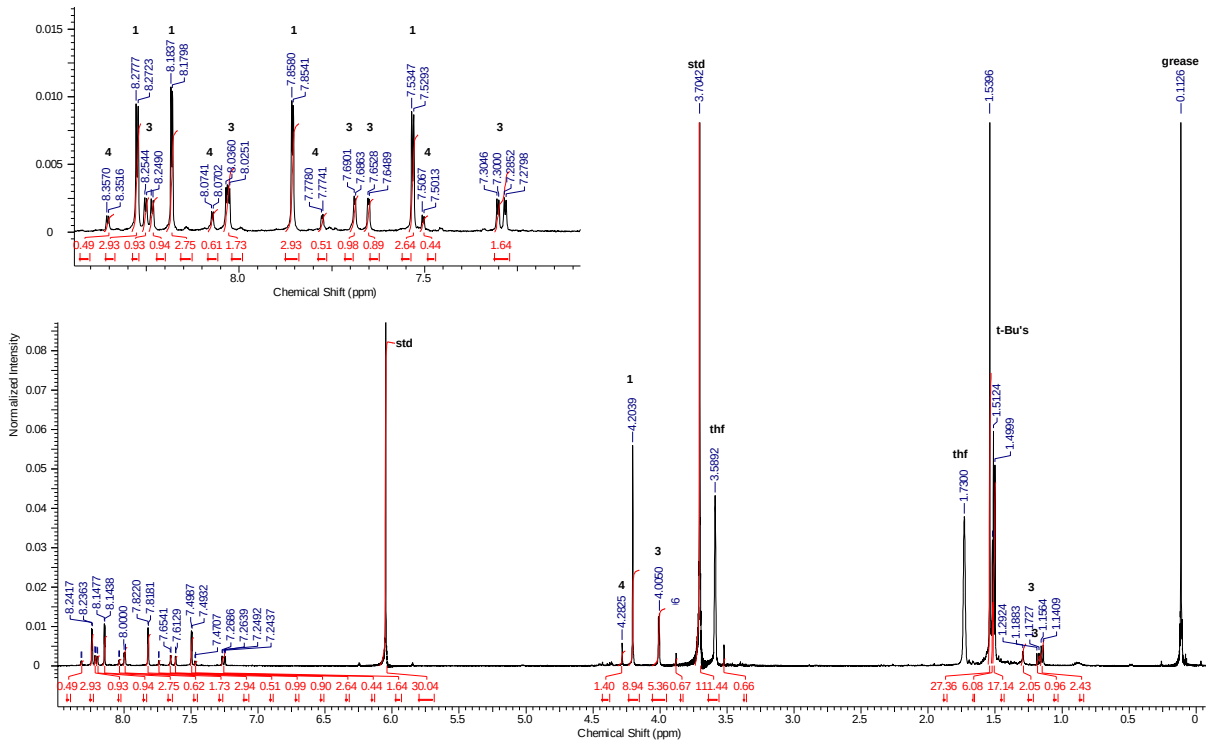



**Figure 5.** $^1H$ NMR spectrum after removing all volatiles in vacuo and redissolving the residue in thf-$d_8$ (std = 1,3,5-trimethoxybenzene).

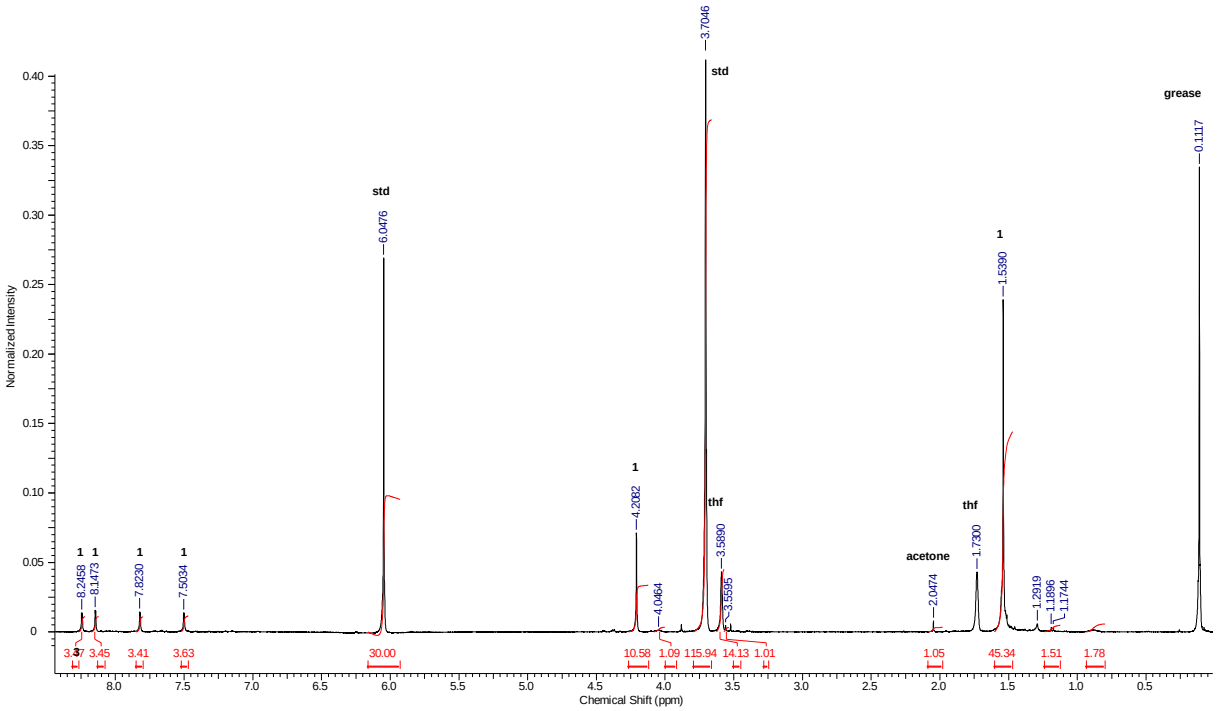



**Figure 6.** After 1 day at room temperature only species **1** can be detected and some acetone is produced (std = 1,3,5-trimethoxybenzene).

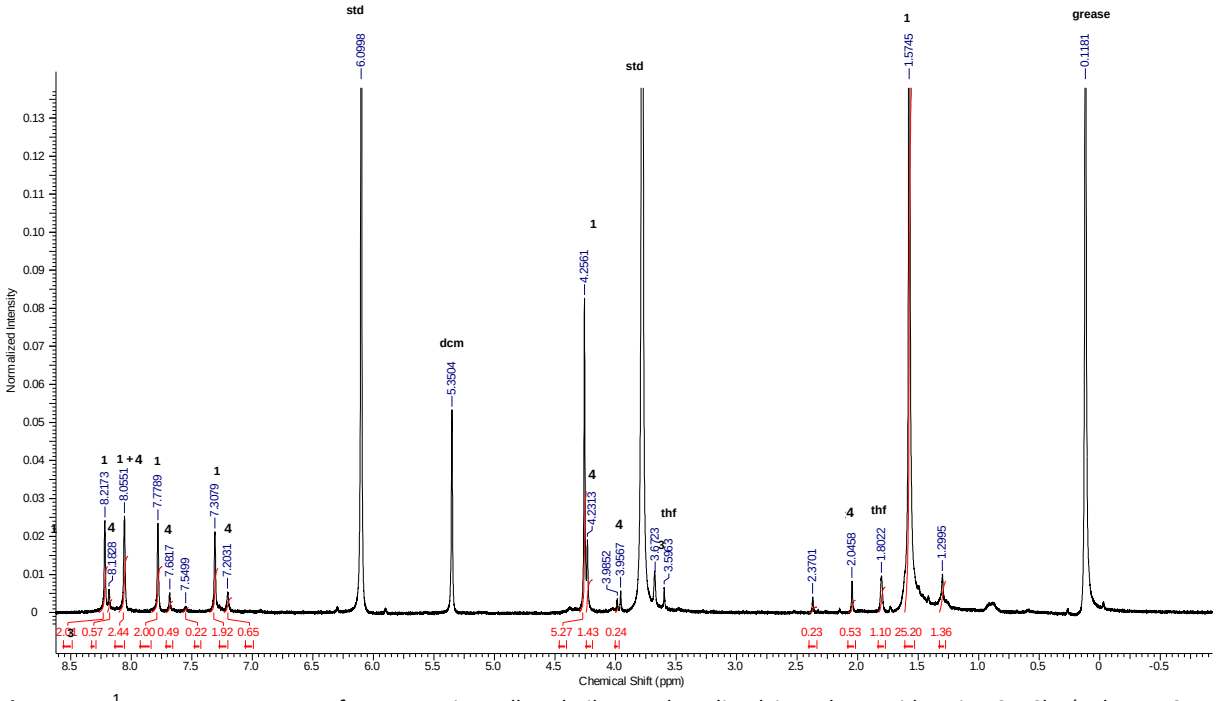
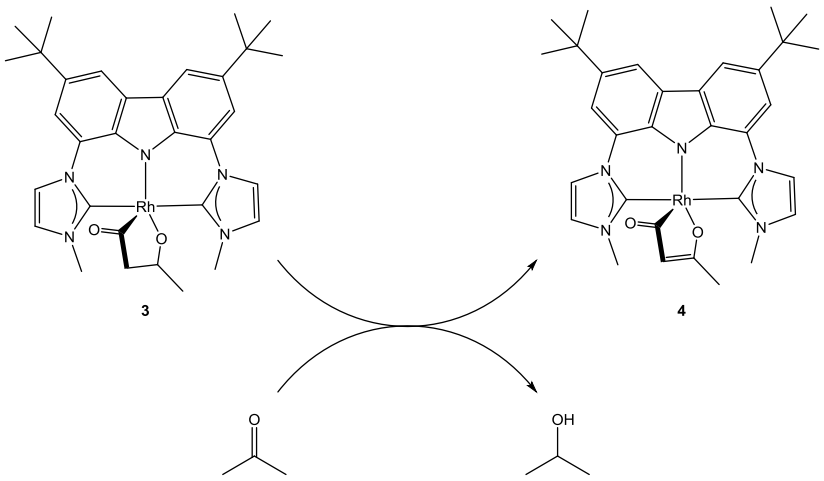



**Figure 7.** $^{1}$H NMR spectrum after removing all volatiles and redissolving the residue in $CD_2Cl_2$ (std = 1,3,5-trimethoxybenzene).

**Dehydrogenation of complex 3 to the deactivation product 4:**




Dehydrogenation of complex **3** to complex **4** is accompanied by hydrogenation of the acetone (which is formed during the catalysis) to isopropanol (Figure 8).

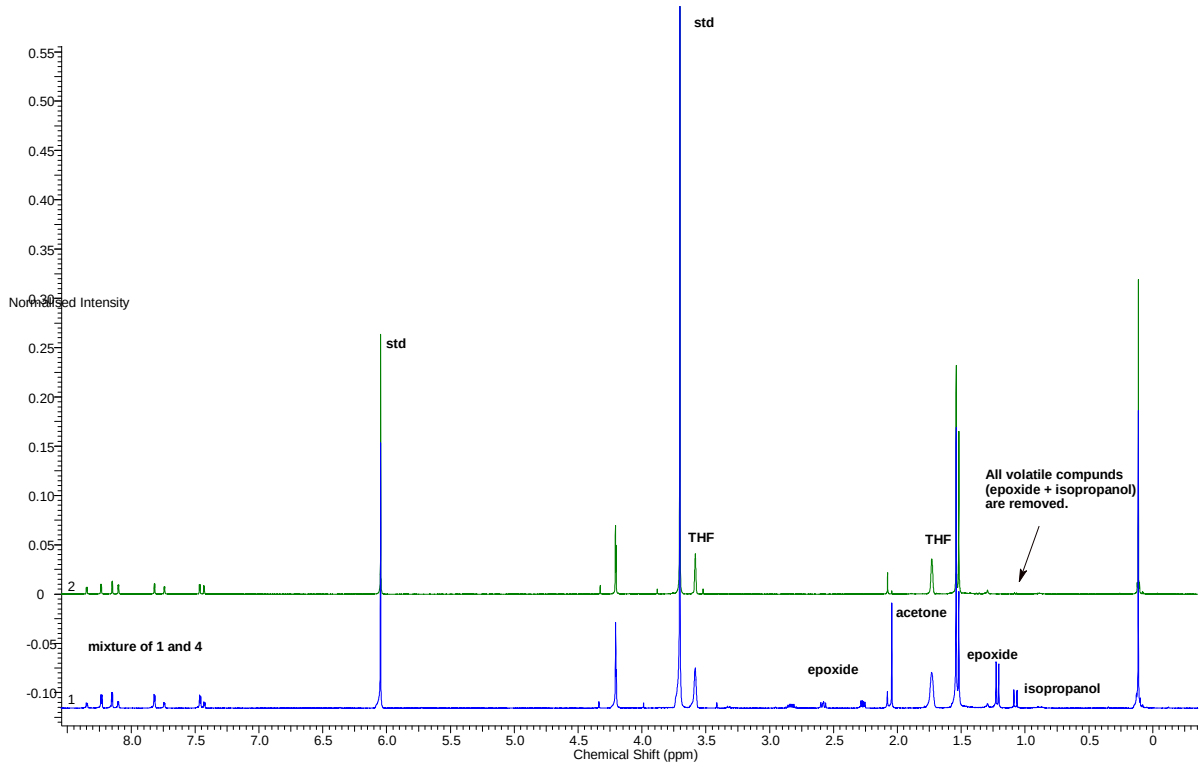



**Figure 8.** After evaporation of all volatile compounds the signal at 1.08 ppm (isopropanol) is missing (std = 1,3,5-trimethoxybenzene).

**The equilibrium between 1 and 3 in benzene:**

Experiment, if complex **3** (generated in thf-$d_8$) also released acetone upon dissolving in benzene-$d_6$. Two independent experiments were carried out.

*Experiment 1*: Complex **1** was dissolved with a catalytic amount of LiCl and propylene oxide in thf-$d_8$. After 16 h at 60 °C a mixture of complexes **1**:**3** (1:1) and Rh complex **4** was obtained. Upon evaporation of the solvent and redissolving the residue in thf-$d_8$ the ratio of **1** to **3** remained constant, but all volatile components were removed. The thf-$d_8$ is again removed and the residue dissolved in benzene-$d_6$. The $^1$H NMR spectrum shows **1** as the major organometallic species. As the acetone signal is covered by the *t*-Bu signal in benzene-$d_6$, a few drops of dmso-$d_6$ were added to shift the acetone peak (Figure 11). The outcome of this experiment gives evidence for the backward reaction of **3** into the catalytic cycle also in benzene.

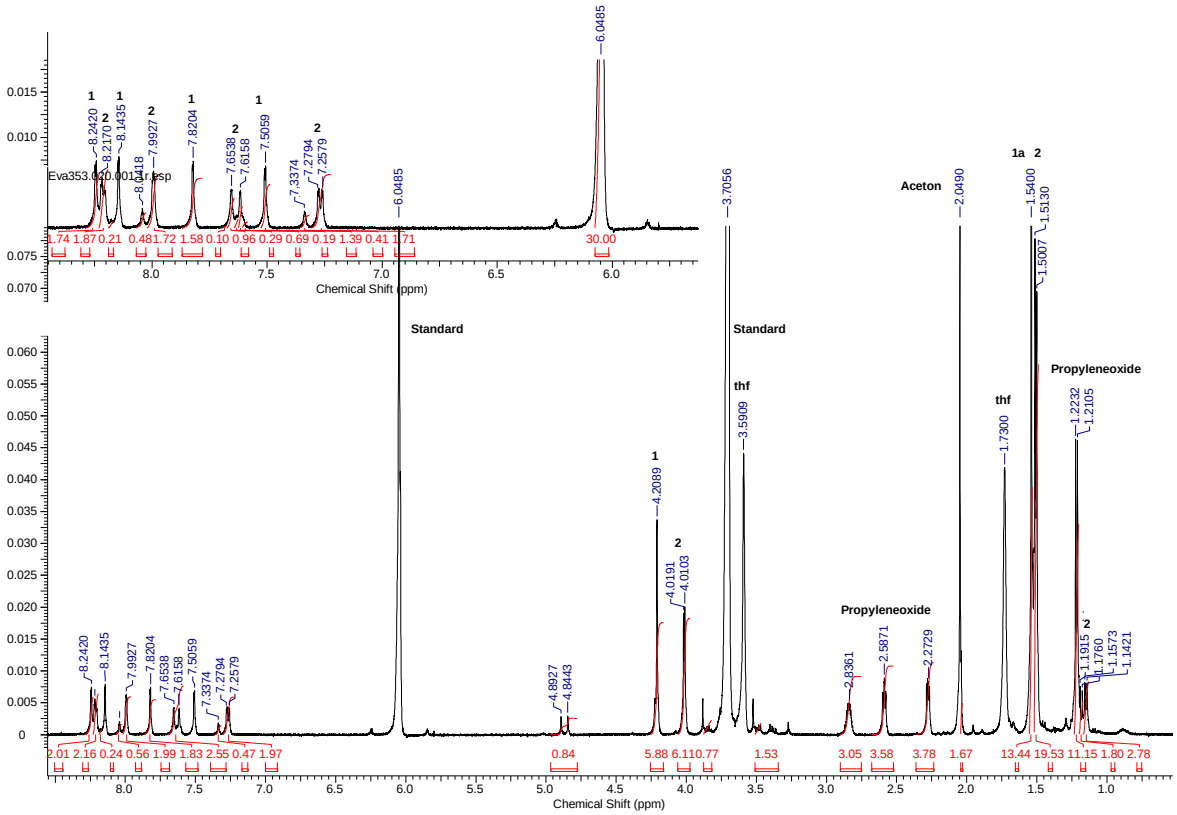



**Figure 9.** Reaction of catalyst **1** with propylene oxide at 60 °C; after 16 h at room temperature a 1:1 mixture of complexes **1**:**3** was obtained (Standard = 1,3,5-trimethoxybenzene).

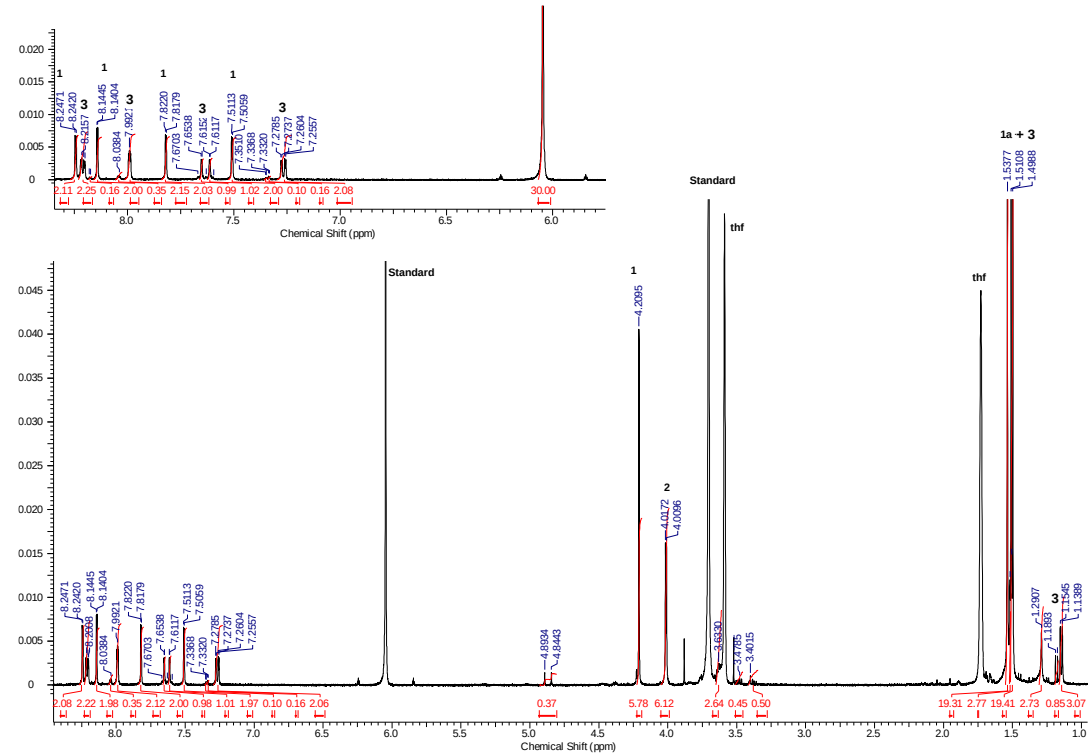



**Figure 10.** Reaction mixture after removing all volatiles and dissolving the residue in thf-$d_8$ (Standard = 1,3,5-trimethoxybenzene).

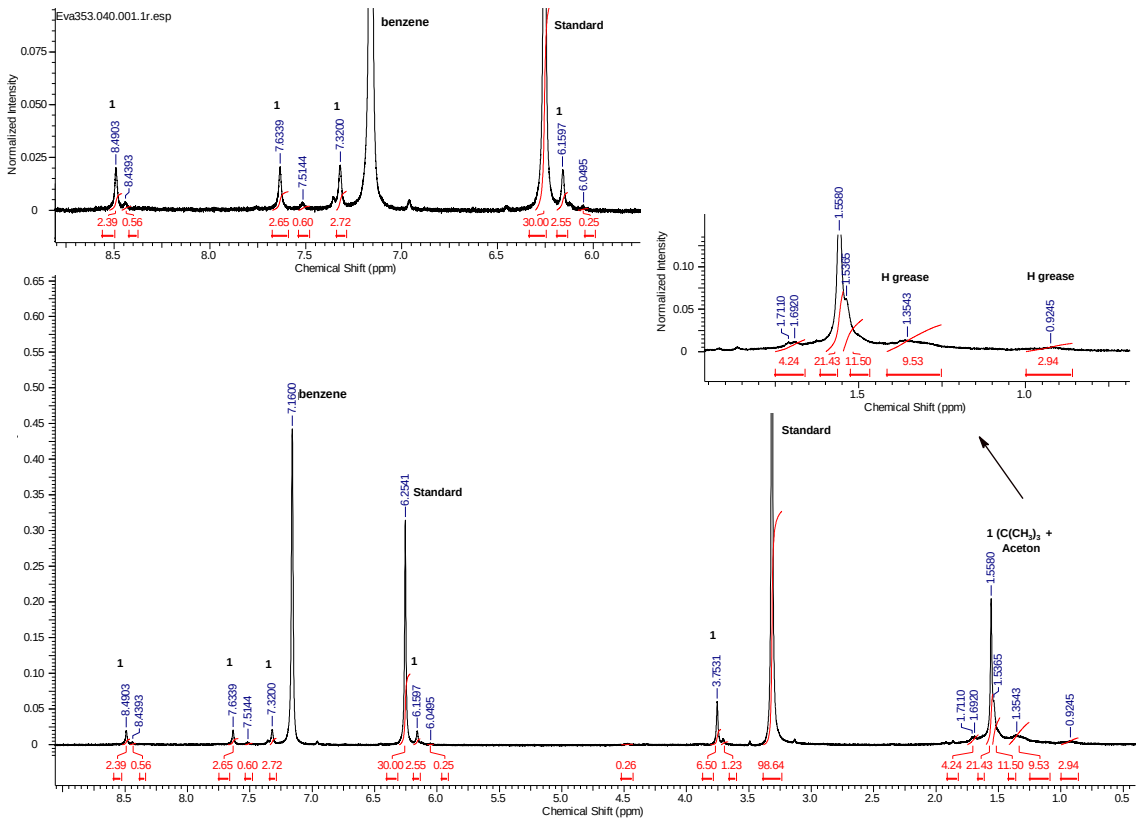



**Figure 11.** The reaction mixture after removing all volatiles and dissolving of the residue in benzene-$d_6$ (Standard = 1,3,5-trimethoxybenzene).

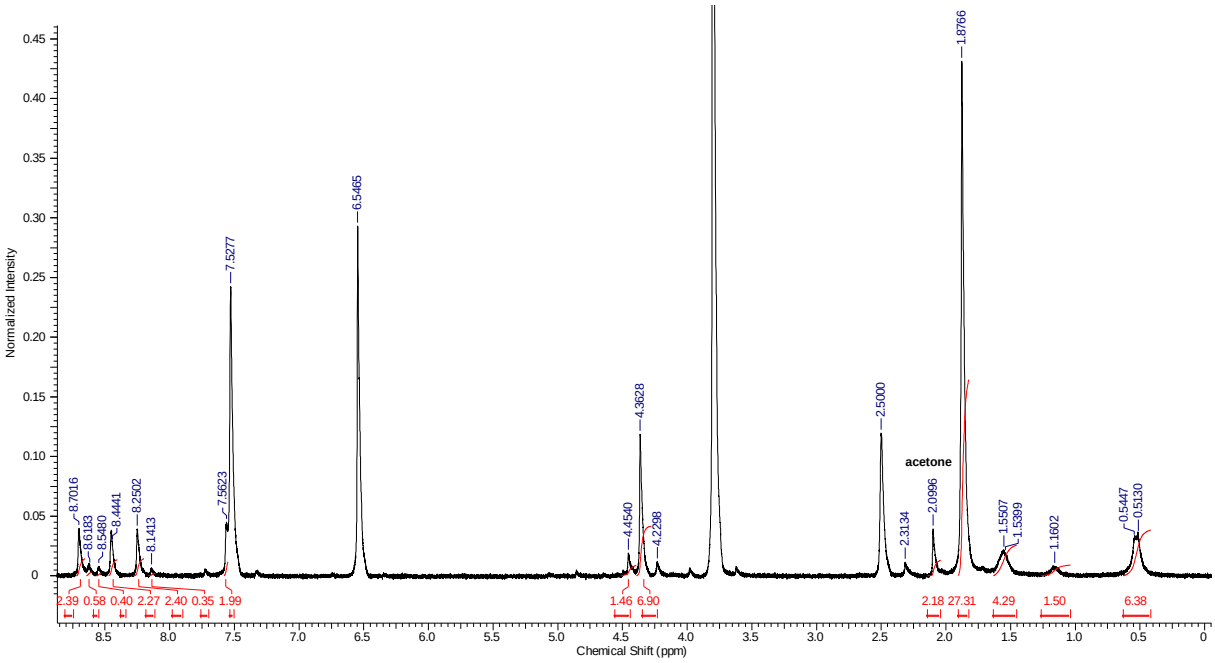



**Figure 12.** Addition of dmso-$d_6$ to the solution shifts the acetone signal so that it is not covered by the *t*-Bu signal.

*Experiment 2*: Complex **1** is dissolved with a catalytic amount of LiCl and propylene oxide in thf-$d_8$. After 16 h at r.t. a mixture of complexes **1**:**3a** = 1.3:1 was obtained. Upon evaporation of all volatile compounds and dissolving the residue in thf-$d_8$ the ratio of **1**:**3a** remained constant. All volatiles were removed again in vacuo and the residue was dissolved in benzene-$d_6$. The $^1$H NMR spectrum of the suspension clearly shows complex **1** as the only organometallic species. Heating the sample for 1 h at 60 °C led to formation of a new Rh complex. Upon removal of benzene-$d_6$ in vacuo and dissolving the residue in $CD_2Cl_2$ this species was identified as complex **4a** which could have formed from precipitated **3a** by dehydrogenation.

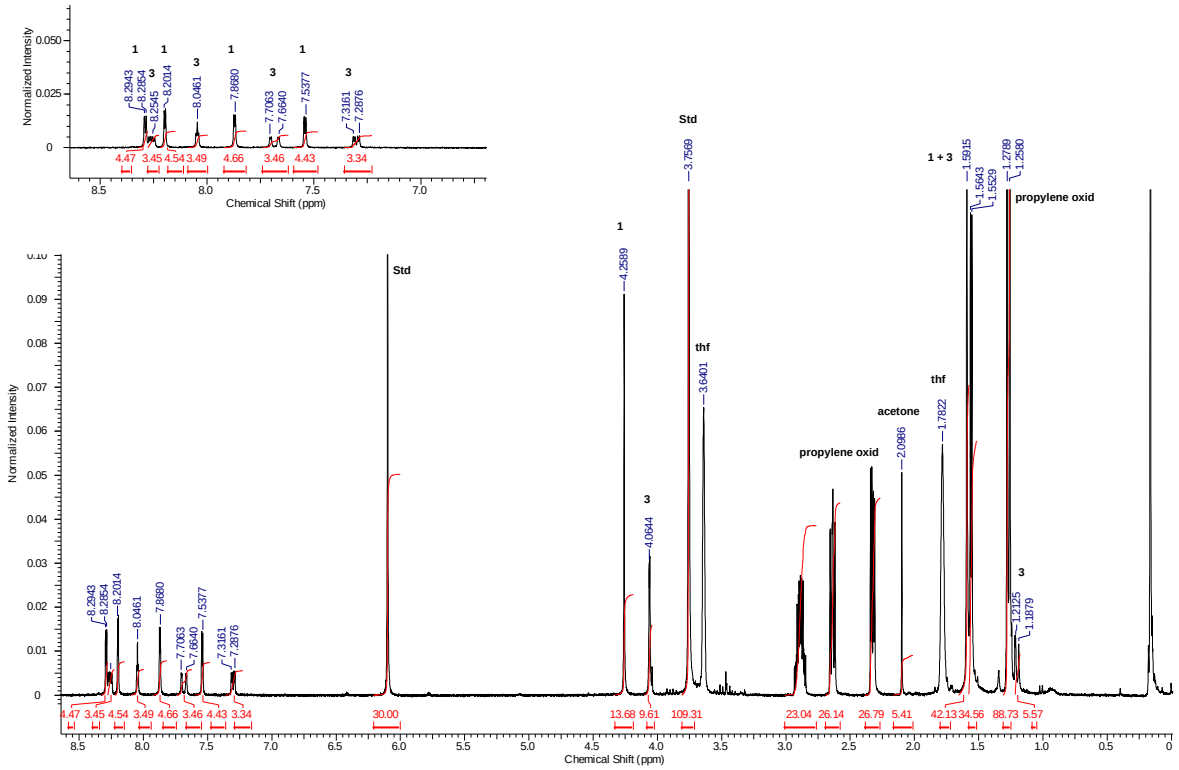



**Figure 13.** $^1$H NMR spectrum after 16 h at room temperature in thf-$d_8$ (std = 1,3,5-trimethoxybenzene).

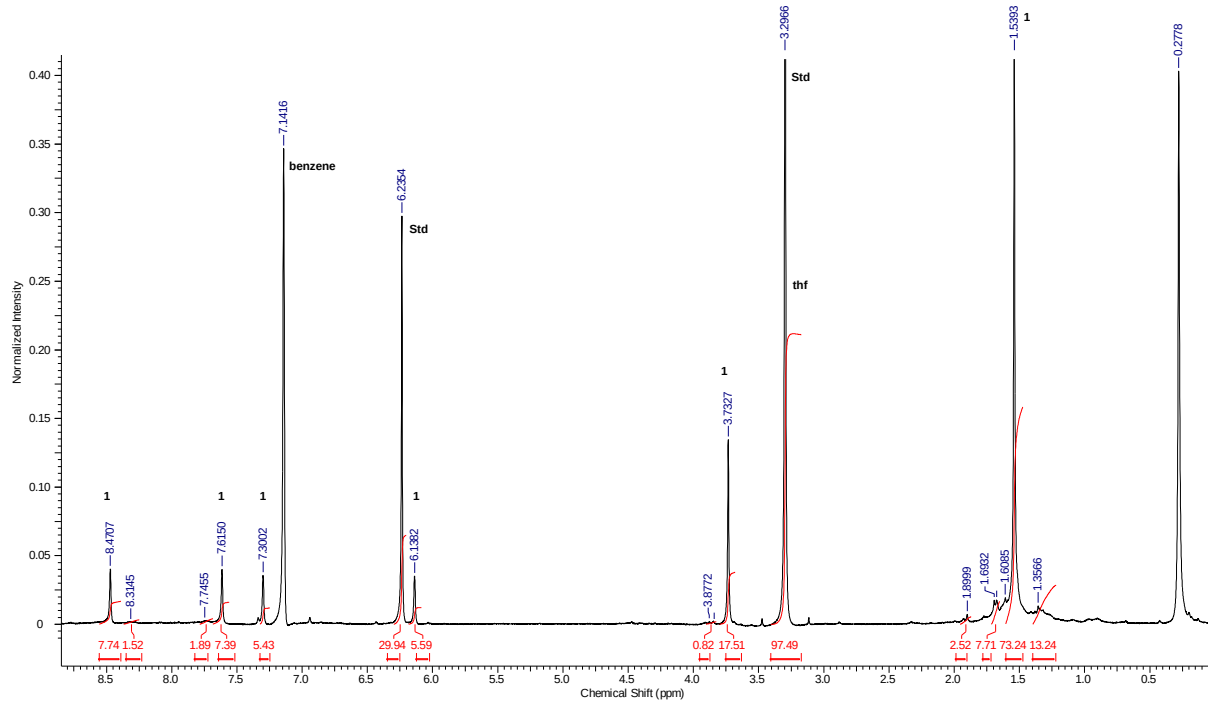



**Figure 14.** $^{1}$H NMR spectrum after removing all volatiles in vacuo and dissolving the residue in benzene-$d_6$ (std = 1,3,5-trimethoxybenzene).

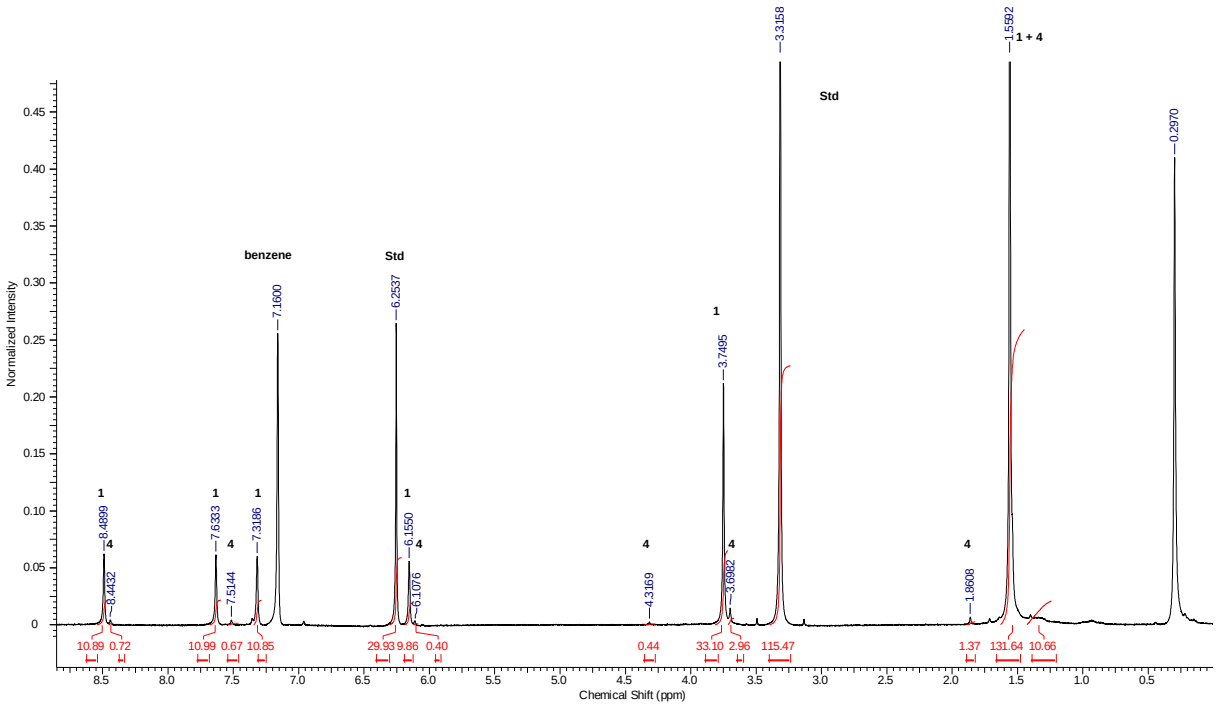



**Figure 15.** After heating the suspension for 1 h at 60 °C, the dehydrogenated rhodium species **4** can be detected in the $^{1}$H NMR spectrum (std = 1,3,5-trimethoxybenzene).

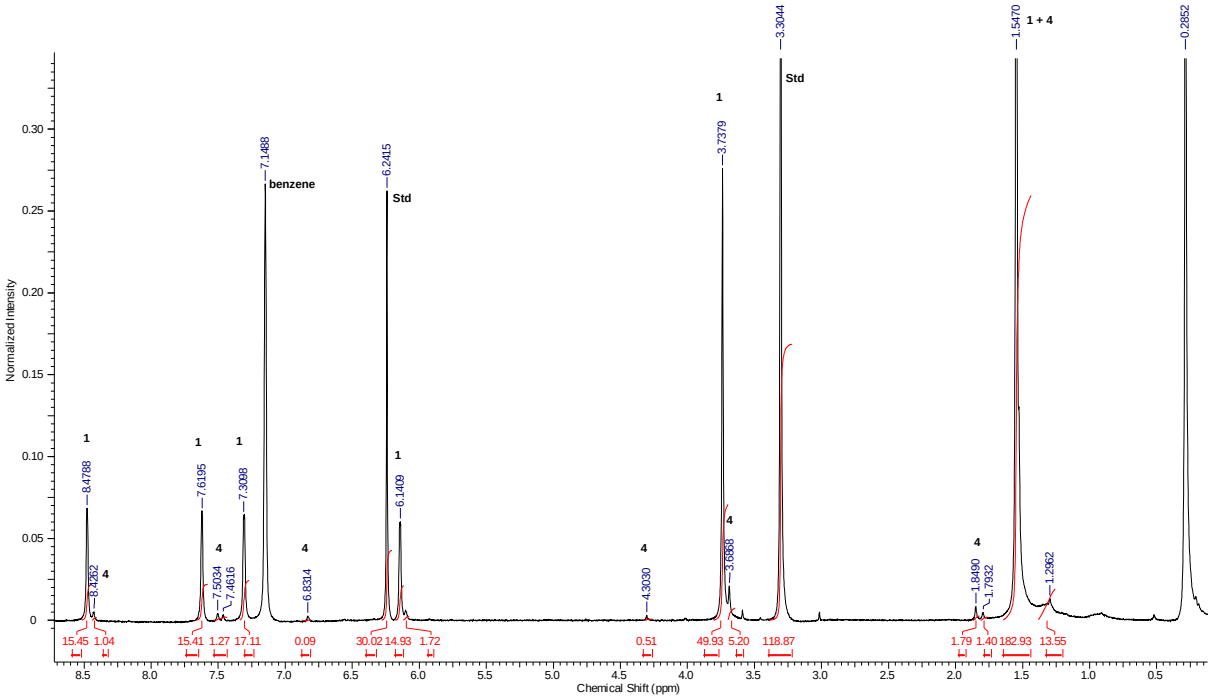



**Figure 16.** $^{1}$H NMR spectrum after removing all volatiles in vacuo and dissolving the residue again in benzene-$d_6$ (std = 1,3,5-trimethoxybenzene).

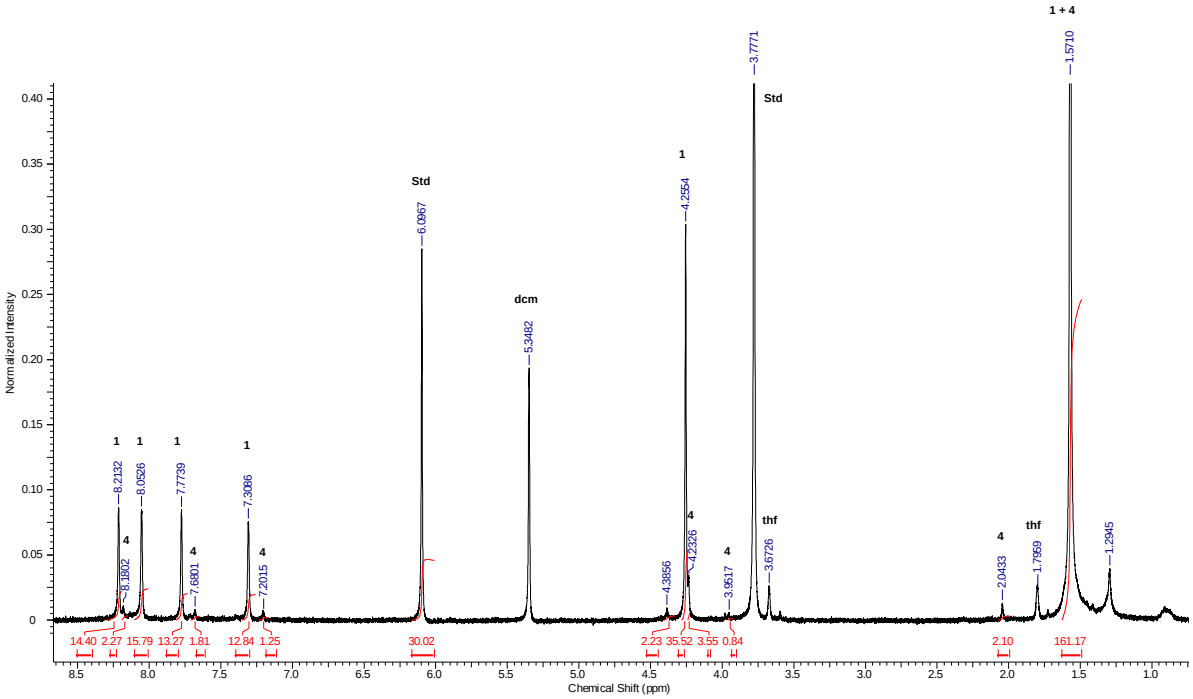
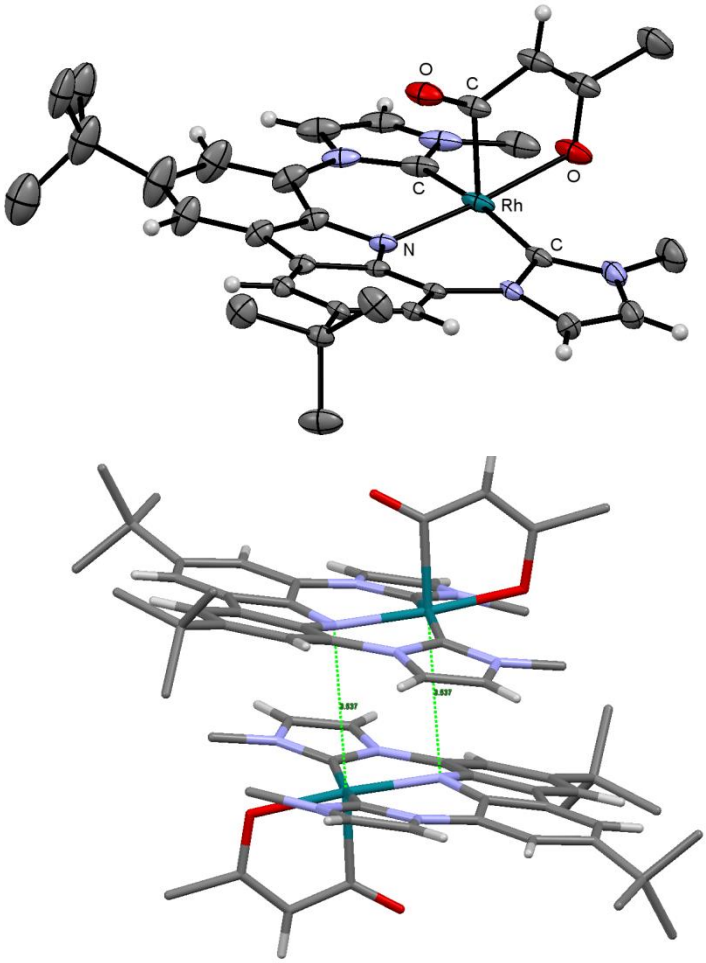



**Figure 17.** $^{1}$H NMR spectrum after removing benzene-$d_6$ and dissolving the residue in dichloromethane-$d_2$ to verify complex **4** by its chemical shift (std = 1,3,5-trimethoxybenzene).

## 2. Crystallographic details for compounds 4a and 4b

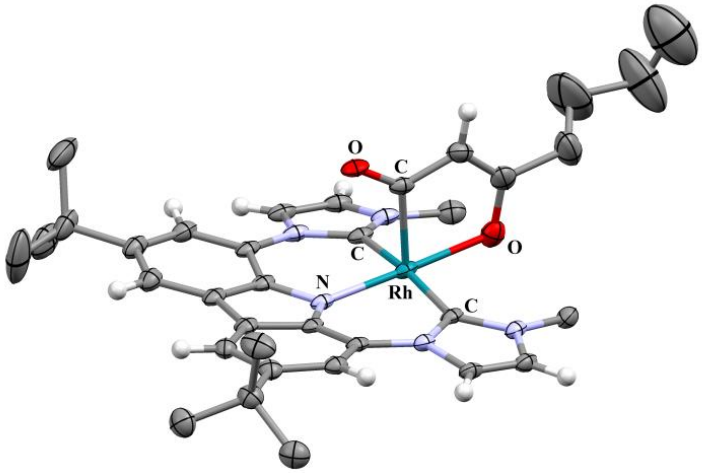
**Crystallographic Data**. Data collection was carried out on a Bruker APEX Duo CCD (**4b**) with an Incoatec IμS Microsource with a Quazar MX mirror, or a Bruker APEX CCD (**4a**) diffractometer, using Mo $K_\alpha$ radiation (λ = 0.71073 Å) and a graphite monochromator in both cases. Corrections for absorption effects were applied using SADABS.[2] All structures were solved by direct methods using SHELXS and refined using SHELXL.[3] Further details of the refinement and crystallographic data are given in the respective CIF-files. CCDC 1018408 (compound **4a**) and 1018409 (compound **4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Crystal structure of complex 4a**:
In the glove box, 15 mg **1** (26 μmol) were dissolved in 0.5 mL thf-$d_8$ with propylene oxide (2 μL, 1 eq) and lithium chloride (1 mg, 1 eq) in a J. Young NMR tube. The reaction mixture was allowed to react at 80 °C for 4 days. Single crystals suitable for X-ray diffraction were obtained from a saturated solution of the reaction mixture at room temperature. The structure contains three thf solvent molecules, two of which are disordered.



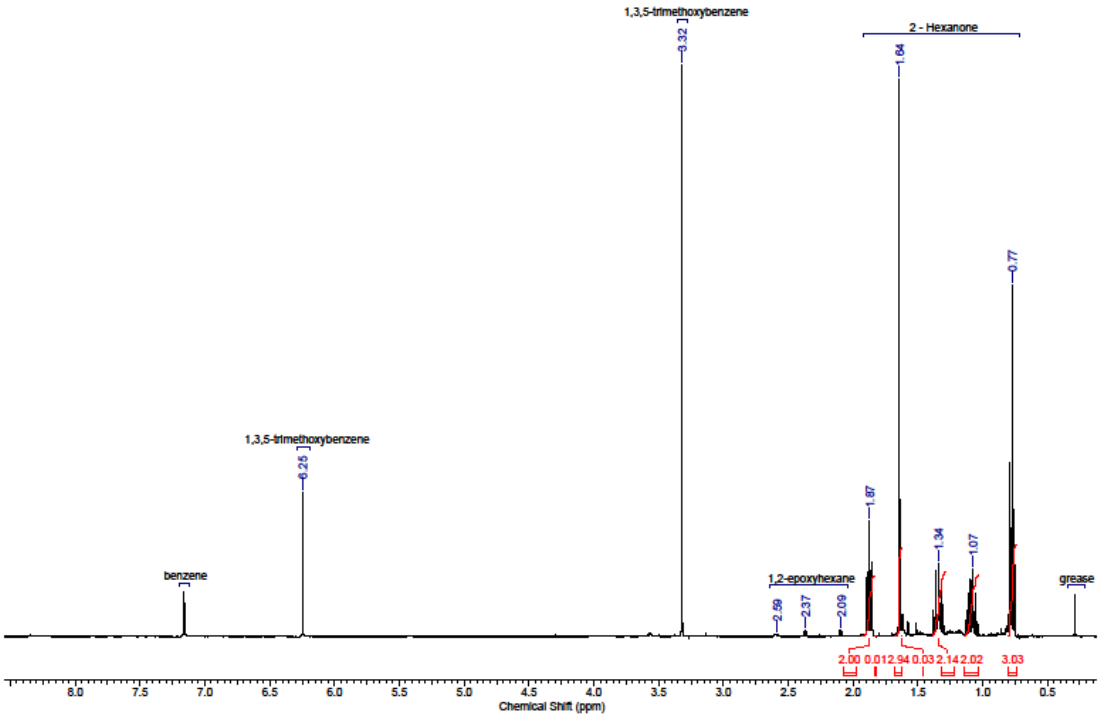
**Crystal structure of complex 4b:**

Rh(bimca)CO[1] **1** (2 mg, 4 μmol, 10 mol%) and lithium bis(trifluoromethanesulfonimide) (1 mg, 10 mol%) were placed into a J. Young NMR tube and 1,3,5-trimethoxybenzene as internal standard and benzene (0.5 mL) were added. At last dried 1,2-epoxyhexane (4.2 µL, 35 μmol) was added and the reaction mixture was heated to 60 °C. Single crystals from pentane/thf, suitable for X-ray diffraction were obtained from a saturated solution of the reaction mixture upon cooling to room temperature. The structure contains a region with heavily disordered solvent molecules. These could be identified from the shape to be a pentane and a thf molecule. The two add up to 144 electrons. The Squeeze procedure[4] in programme package PLATON[5] reports the equivalent of 167 electrons per asymmetric unit, in total 344 electrons. One ordered thf solvent molecule is included in the reported structure. The alkyl product suffers from disorder in all three unique molecules. The current model still suffers from large displacement parameters, in particular at the terminal end of the alkyl product; also the C-C-distances in those regions suffer from large variations.

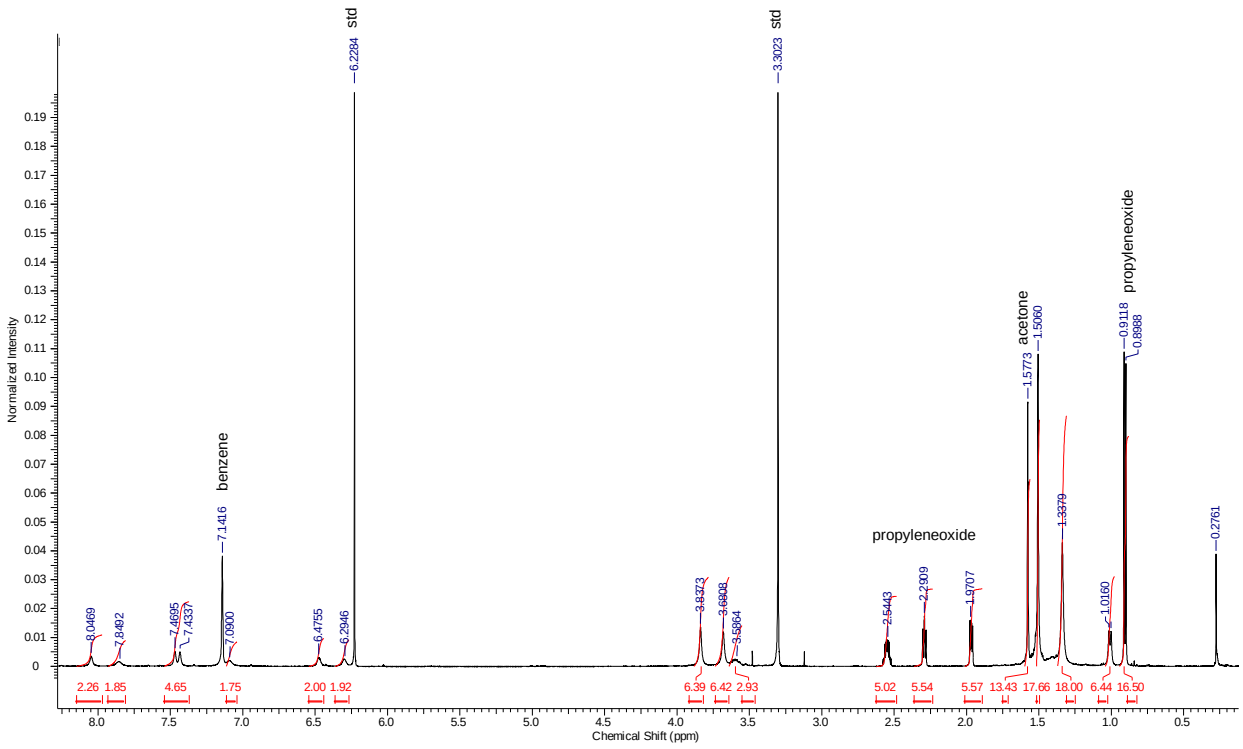


## 3. $^{1}H$ and $^{13}C$ NMR spectra of the new compounds

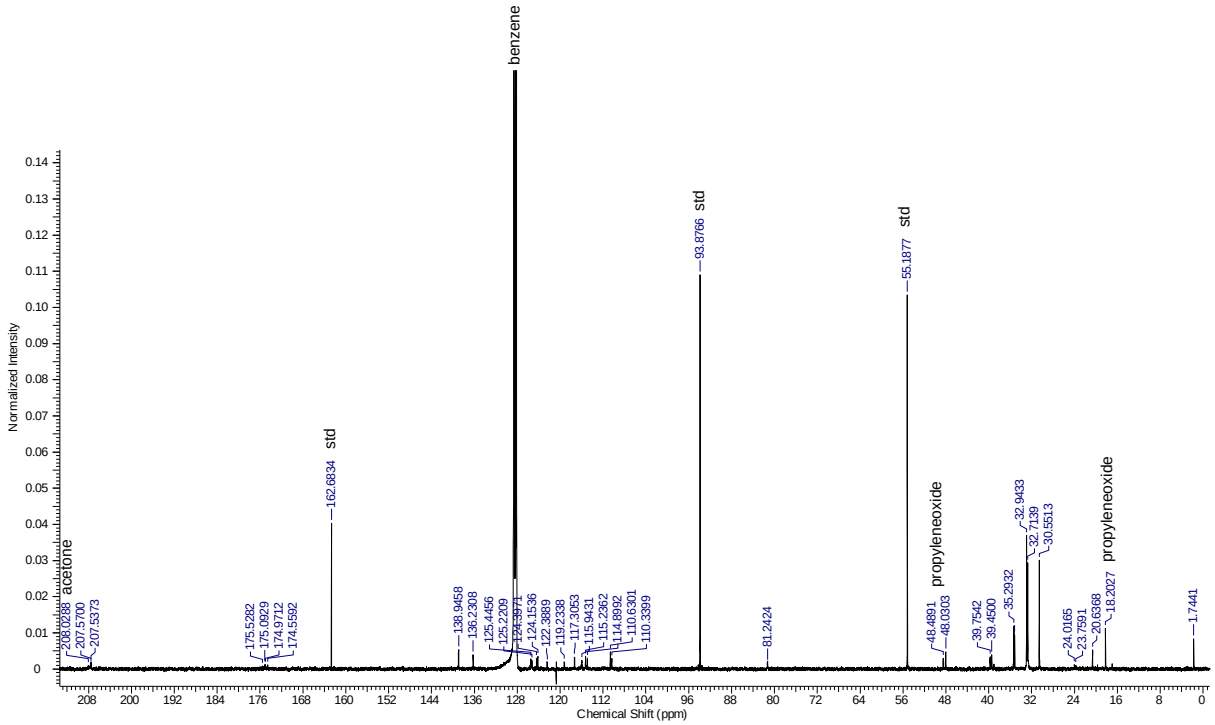
Exemplary $^{1}H$ NMR spectrum for a Meinwald rearrangement (100 min, 60 °C, 30 mol% $LiNTf_2$, 10 mol% **1**, benzene)



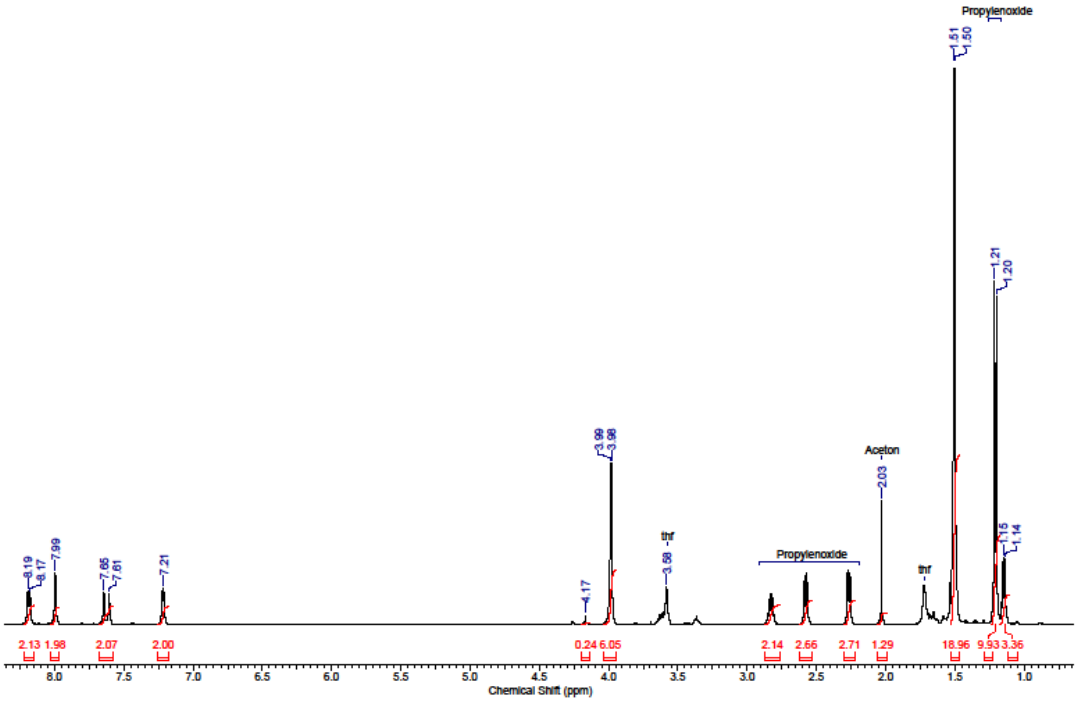

$^{1}H$ NMR spectrum of **2** in benzene-$d_6$:



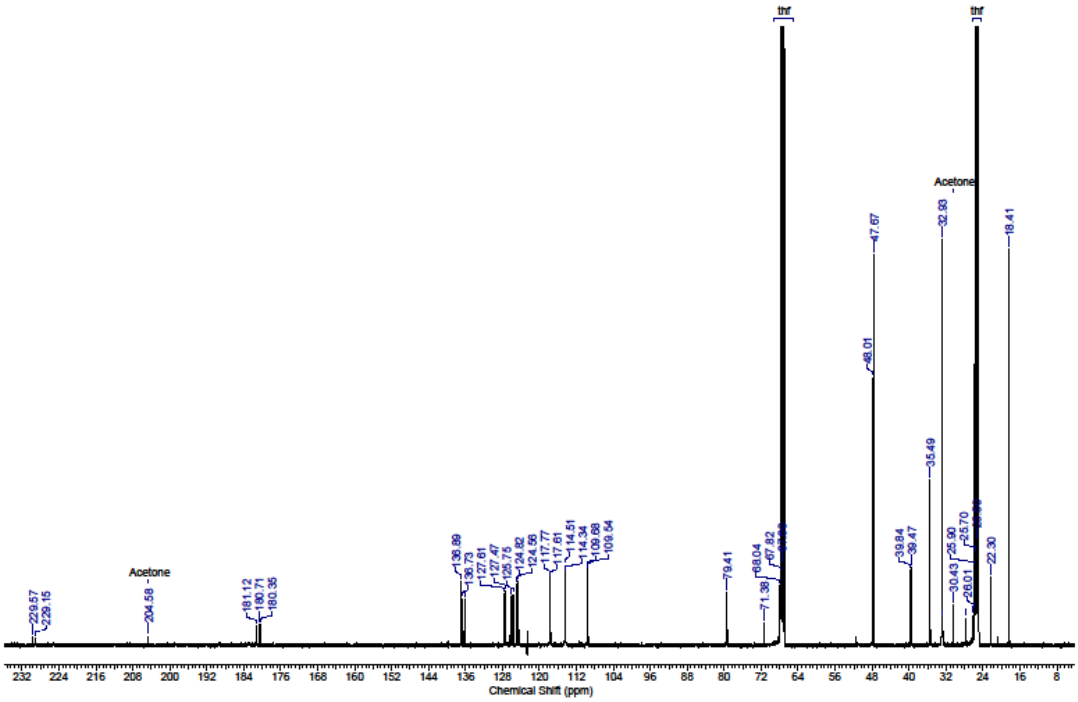
$^{13}C\{^{1}H\}$ NMR spectrum of **2** in benzene-$d_6$:



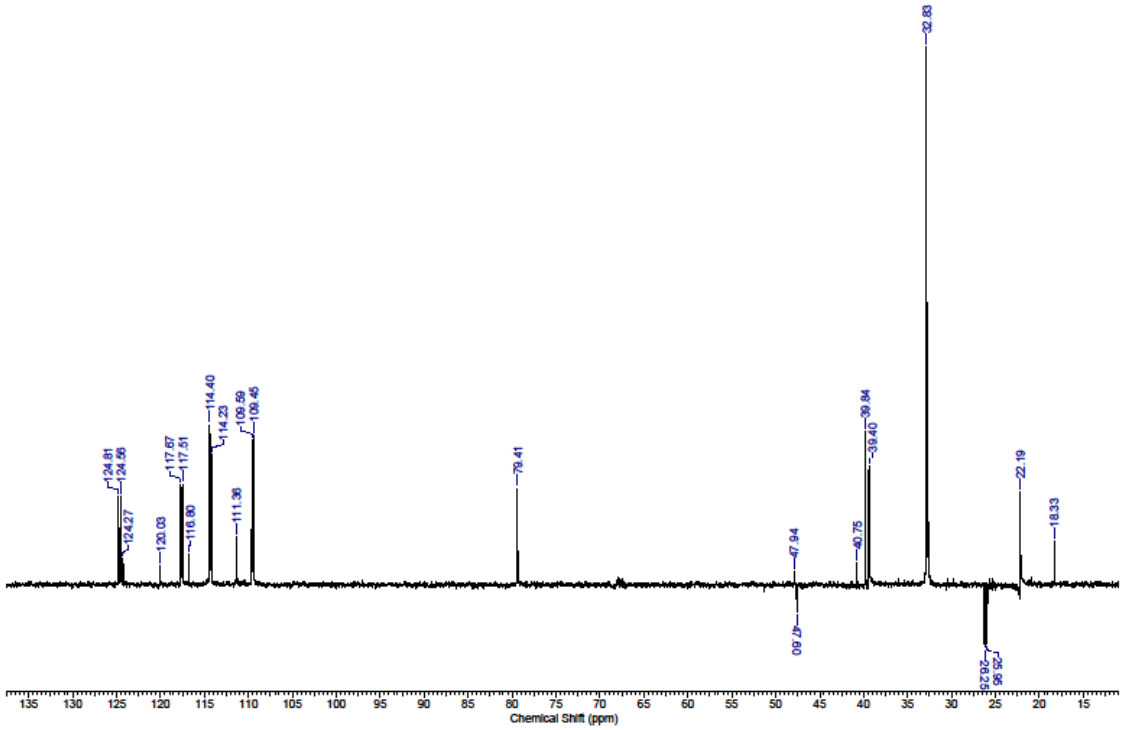

$^{1}H$ NMR spectrum of **3a** in thf-$d_8$:



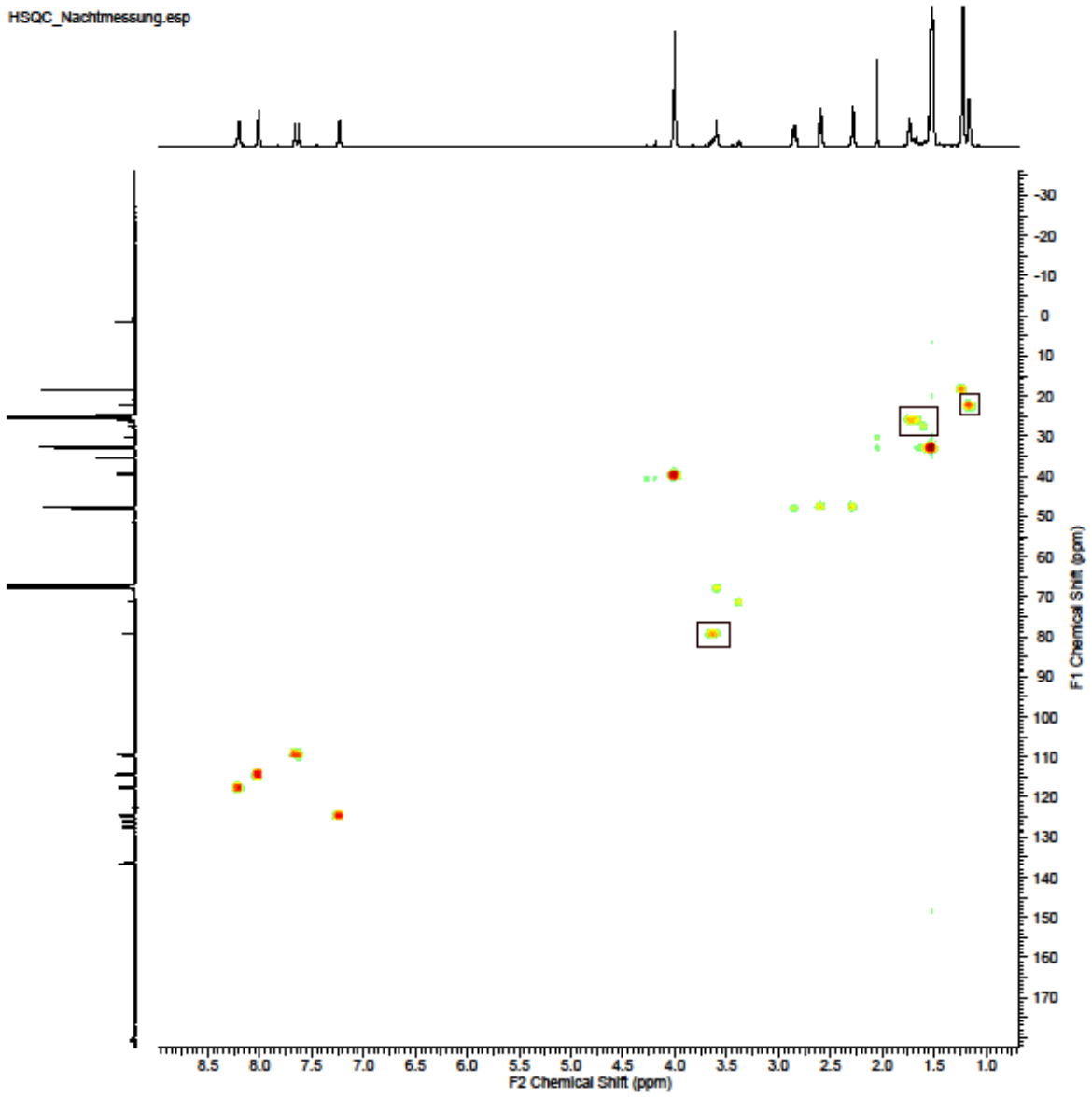
$^{13}C\{^{1}H\}$ NMR spectrum of **3a** in thf-$d_8$:



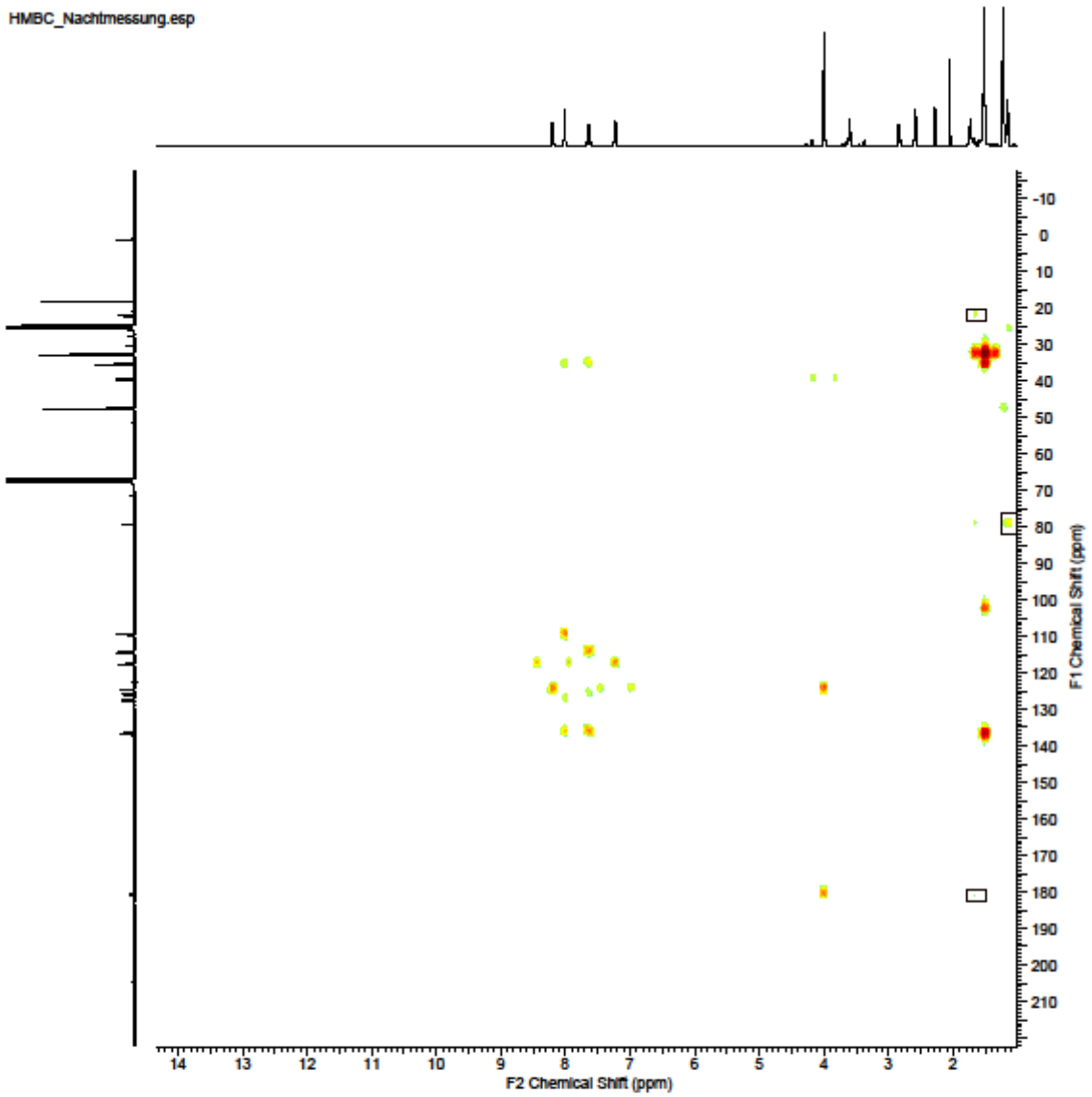

$^{13}C$-DEPT-135 NMR spectrum of **3a** in thf-$d_8$:



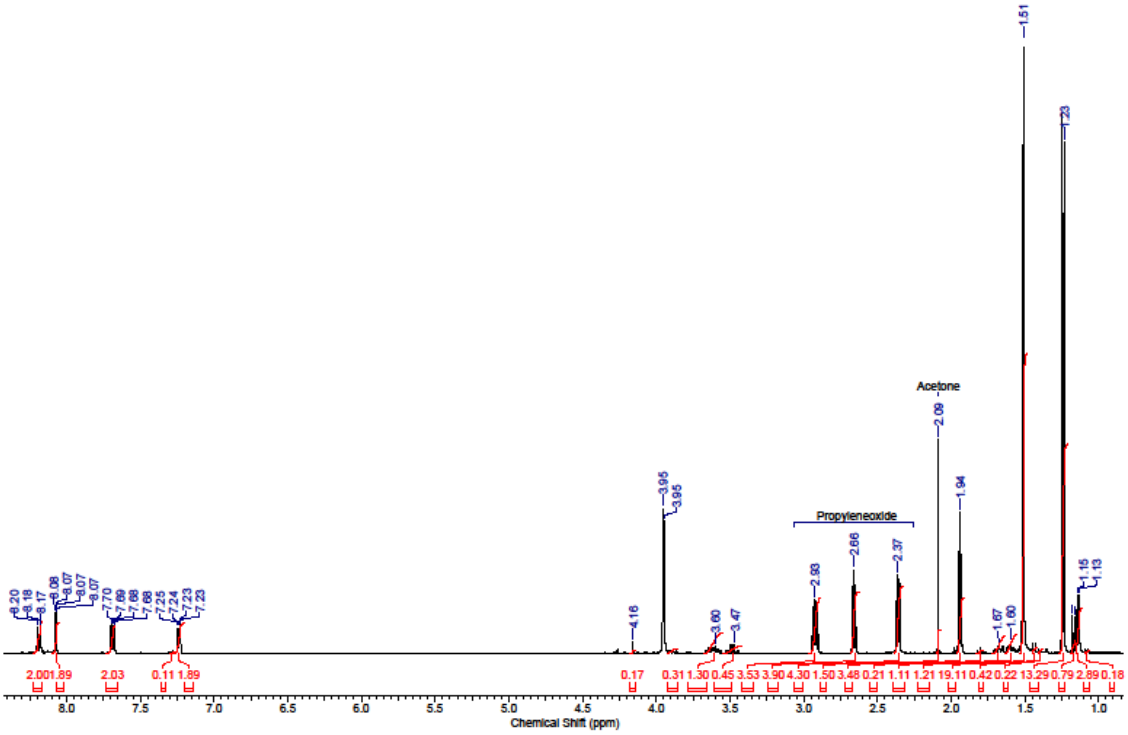
$^{1}H^{13}C$-HSQC NMR spectrum of **3a** in thf-$d_8$:



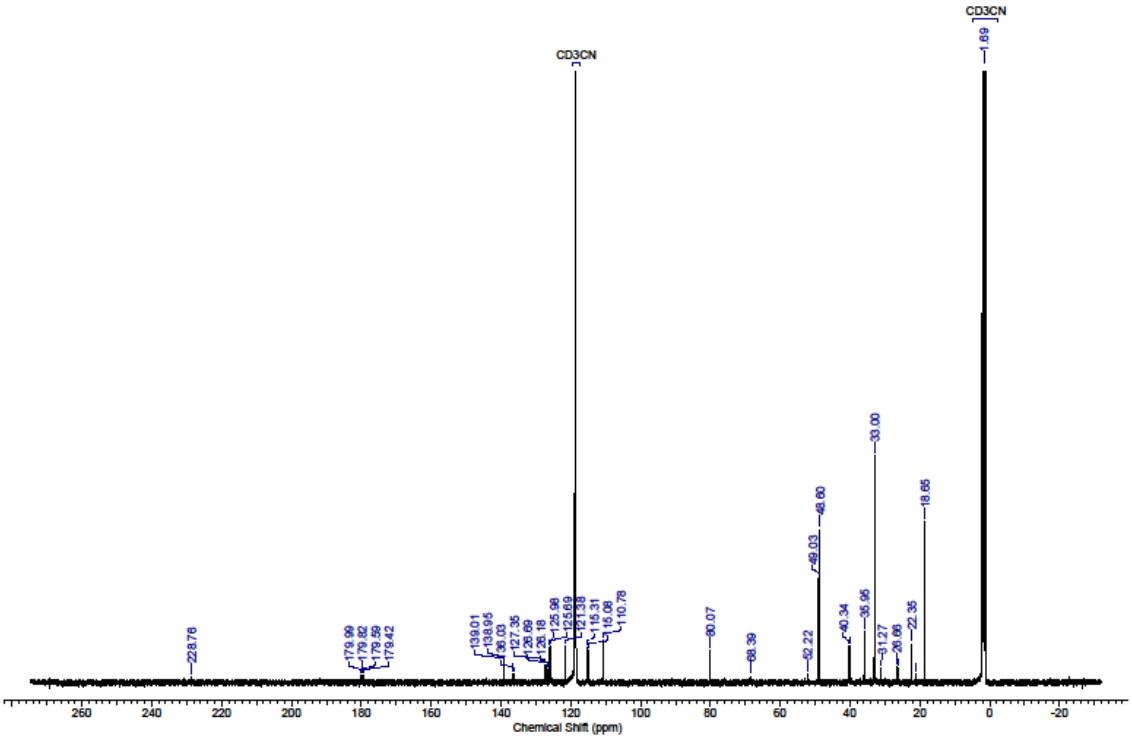
$^{1}H^{13}C$-HMBC NMR spectrum of **3a** in thf-$d_8$:



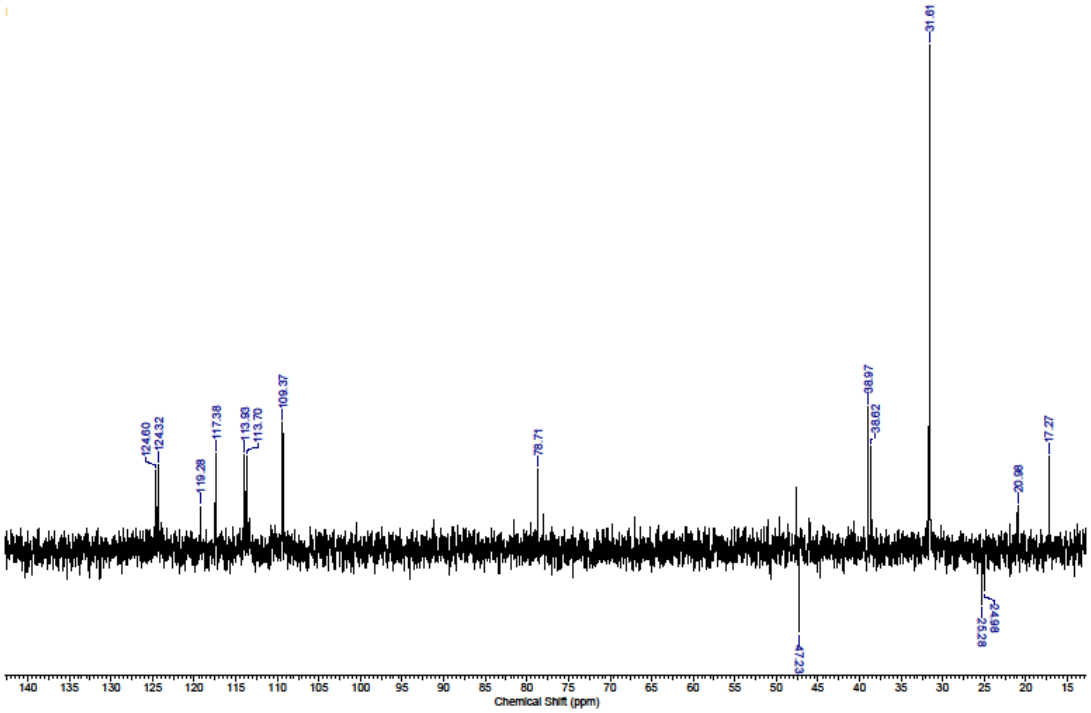
$^{1}$H NMR spectrum of **3a** in $CD_3CN$:



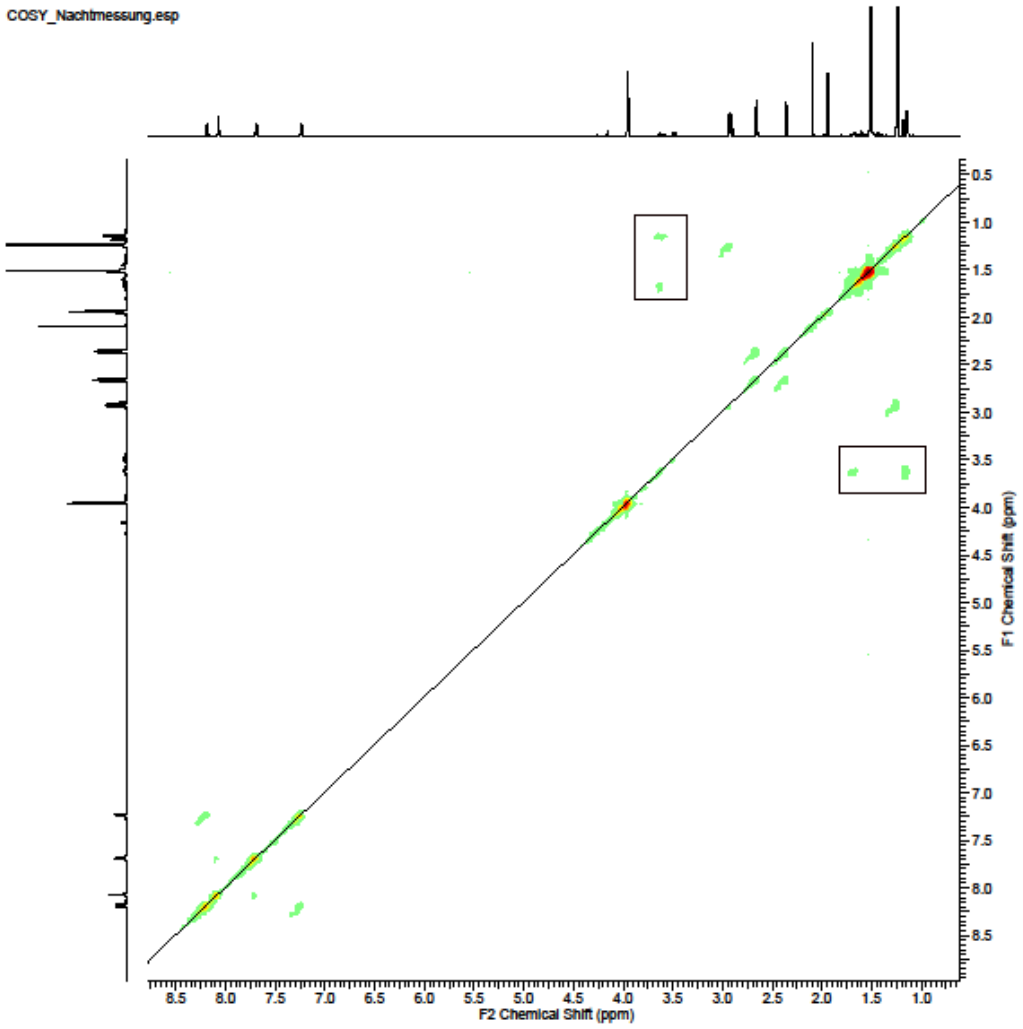

$^{13}C\{^{1}H\}$ NMR spectrum of **3a** in $CD_3CN$:



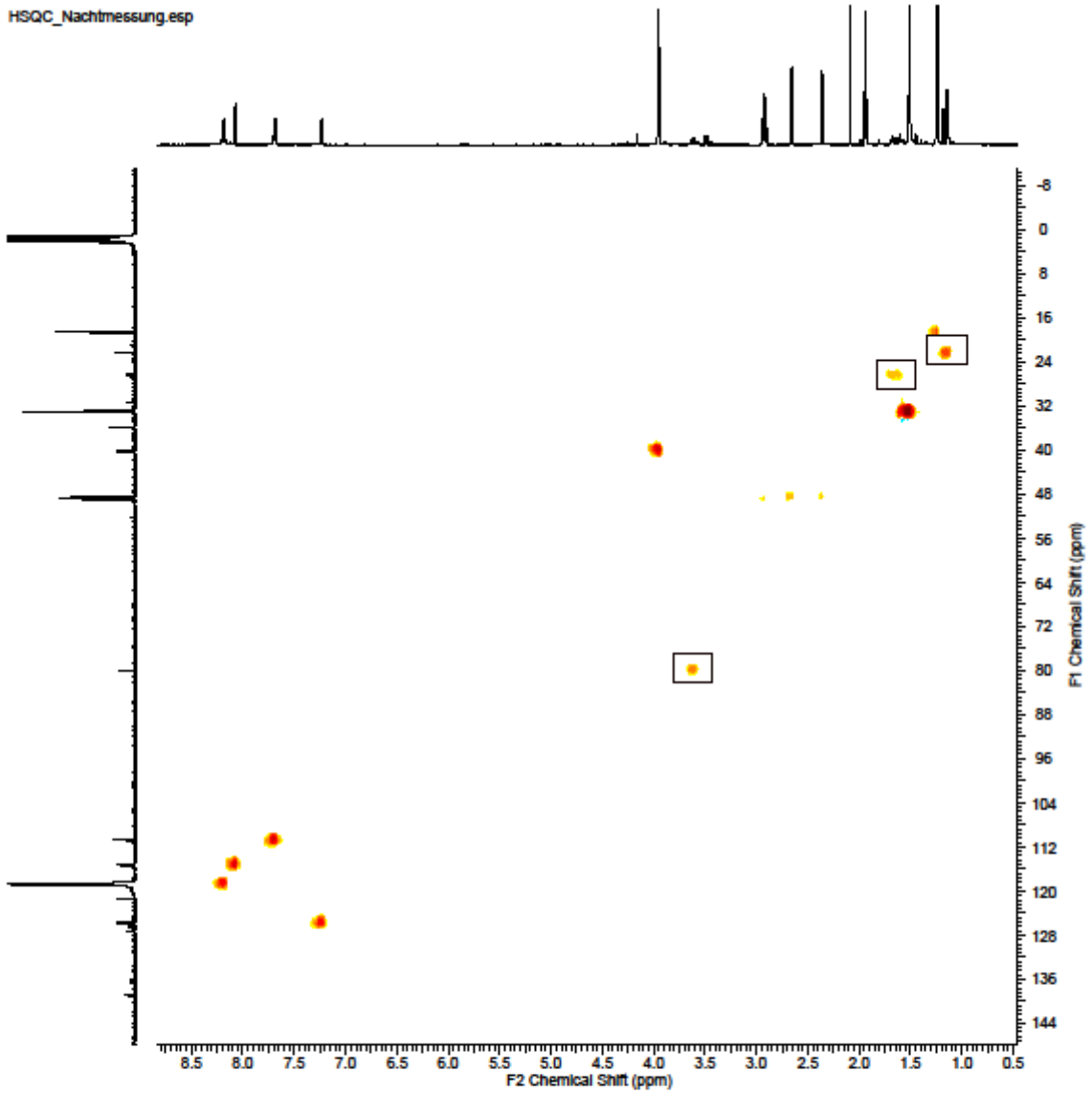
$^{13}$C-DEPT-135 NMR spectrum of **3a** in $CD_3CN$:



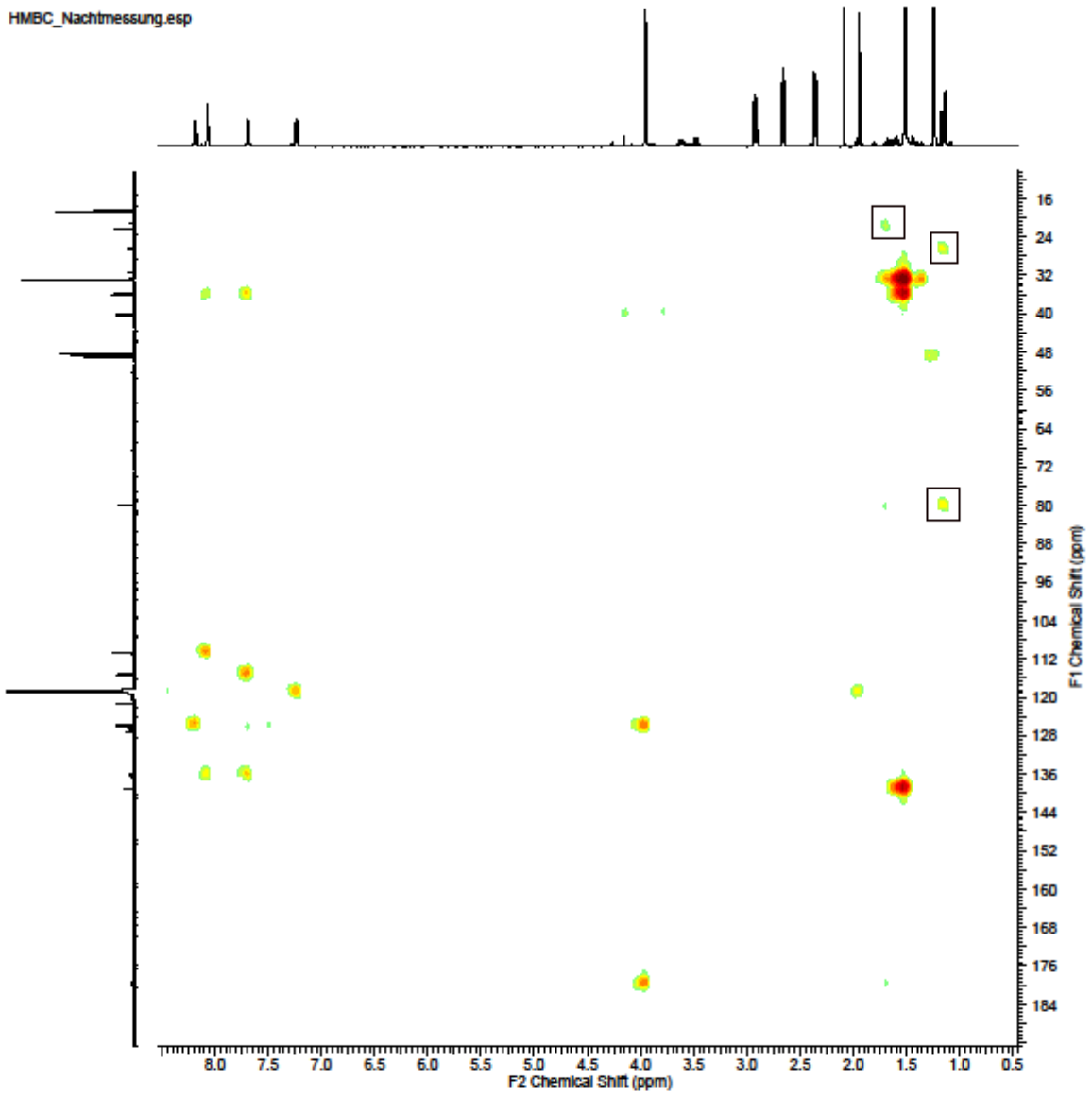

$^{1}$H$^{1}$H-COSY NMR spectrum of **3a** in $CD_3CN$:



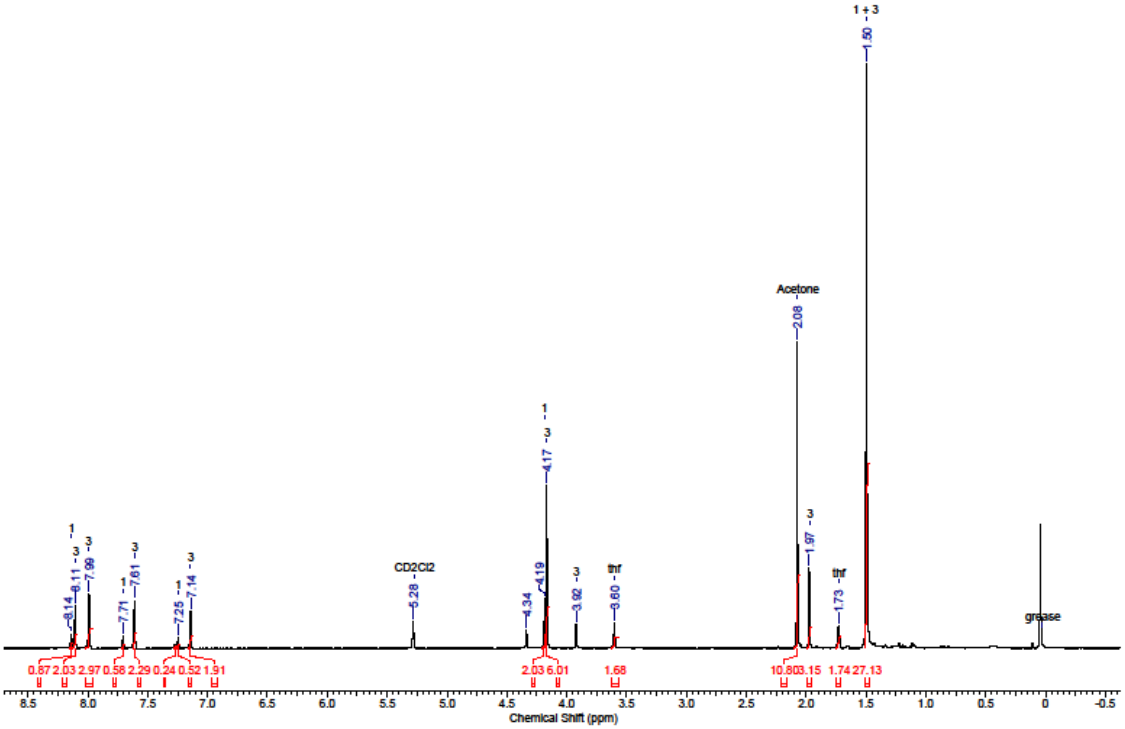
$^{1}H^{13}C$-HSQC NMR spectrum of **3a** in $CD_3CN$:



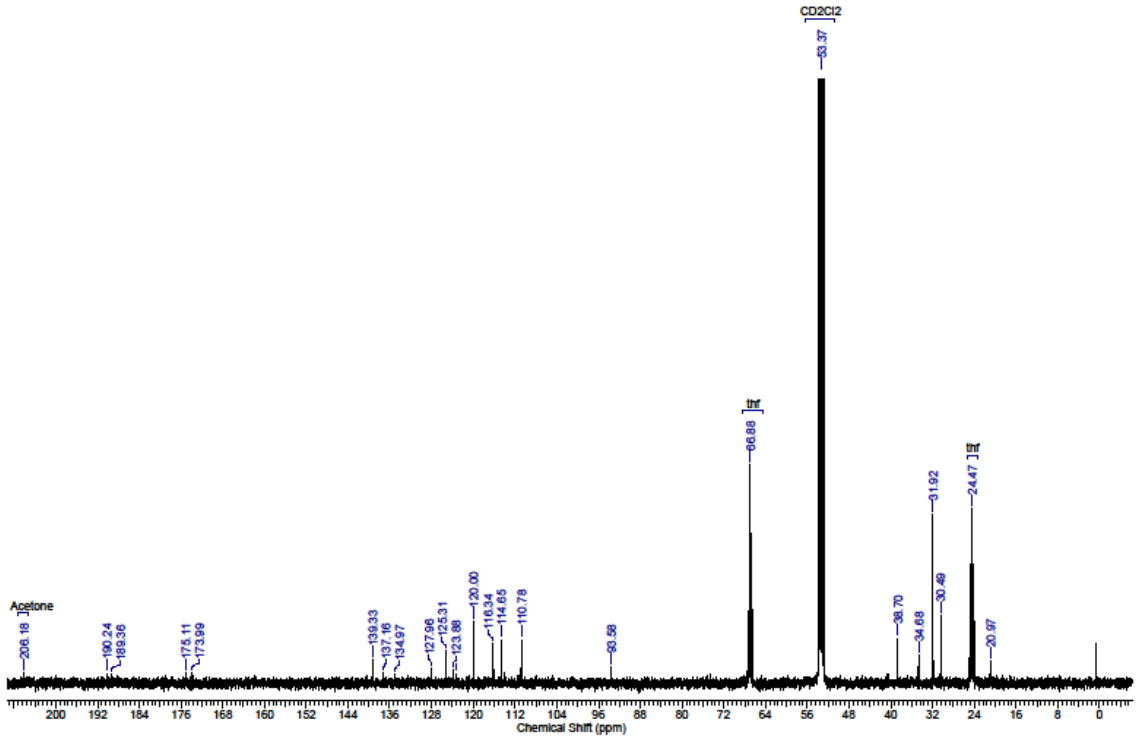
$^{1}H^{13}C$-HMBC NMR spectrum of **3a** in $CD_3CN$:



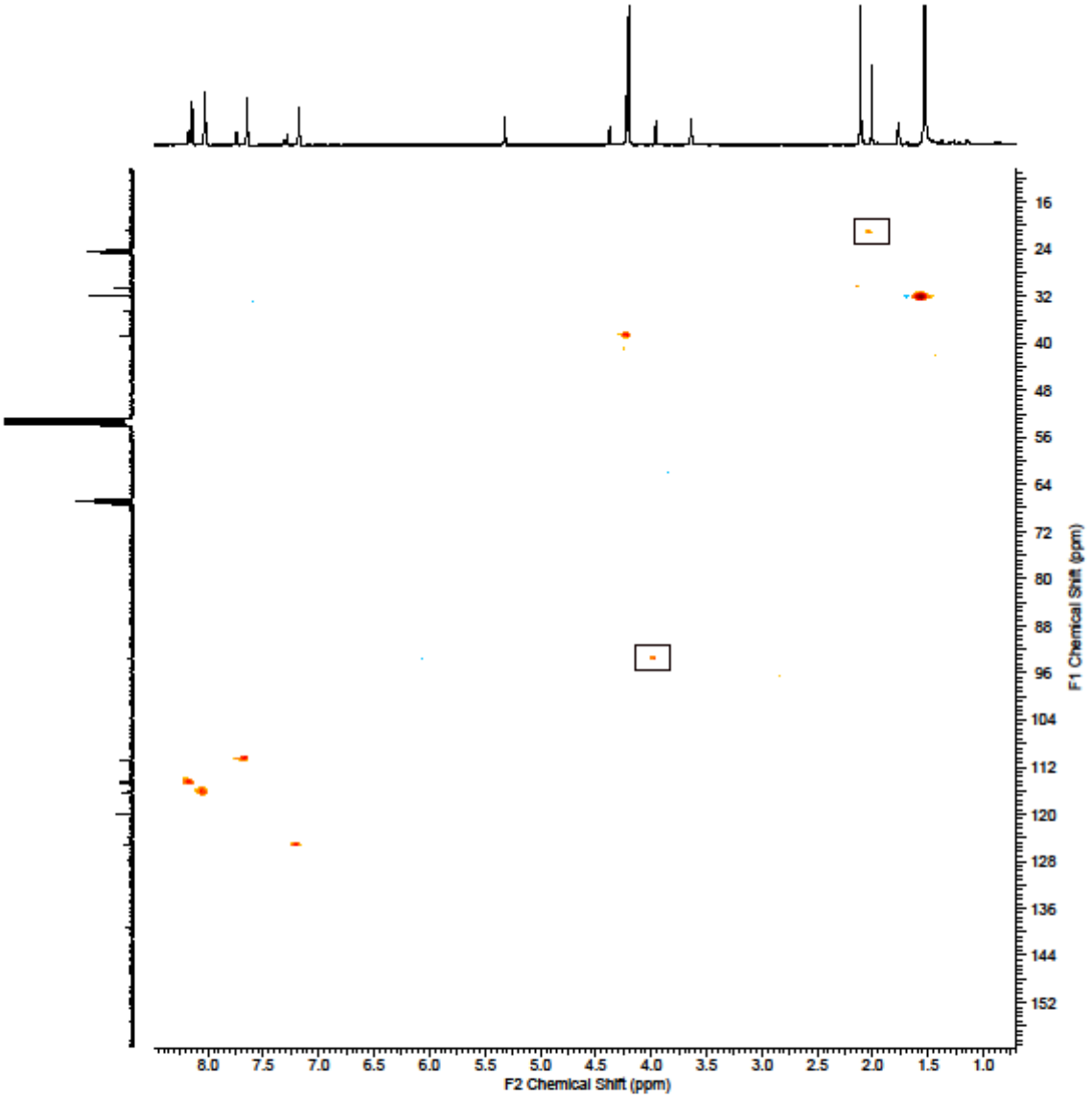
$^{1}$H NMR spectrum of **4a** in $CD_2Cl_2$:



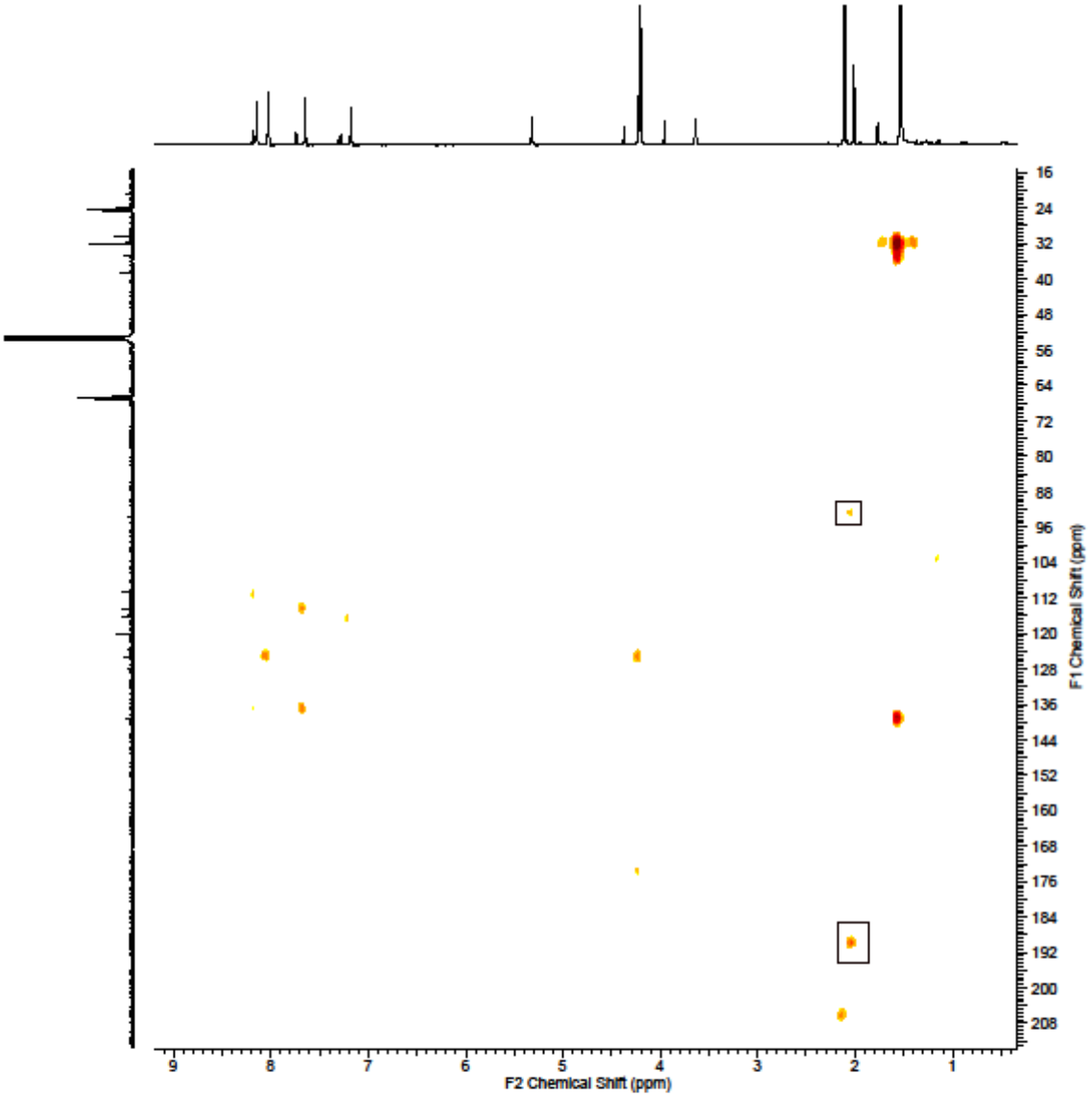

$^{13}$C{$^{1}$H} NMR spectrum of **4a** in $CD_2Cl_2$:



$^{1}H^{13}C$-HSQC NMR spectrum of **4a** in $CD_2Cl_2$

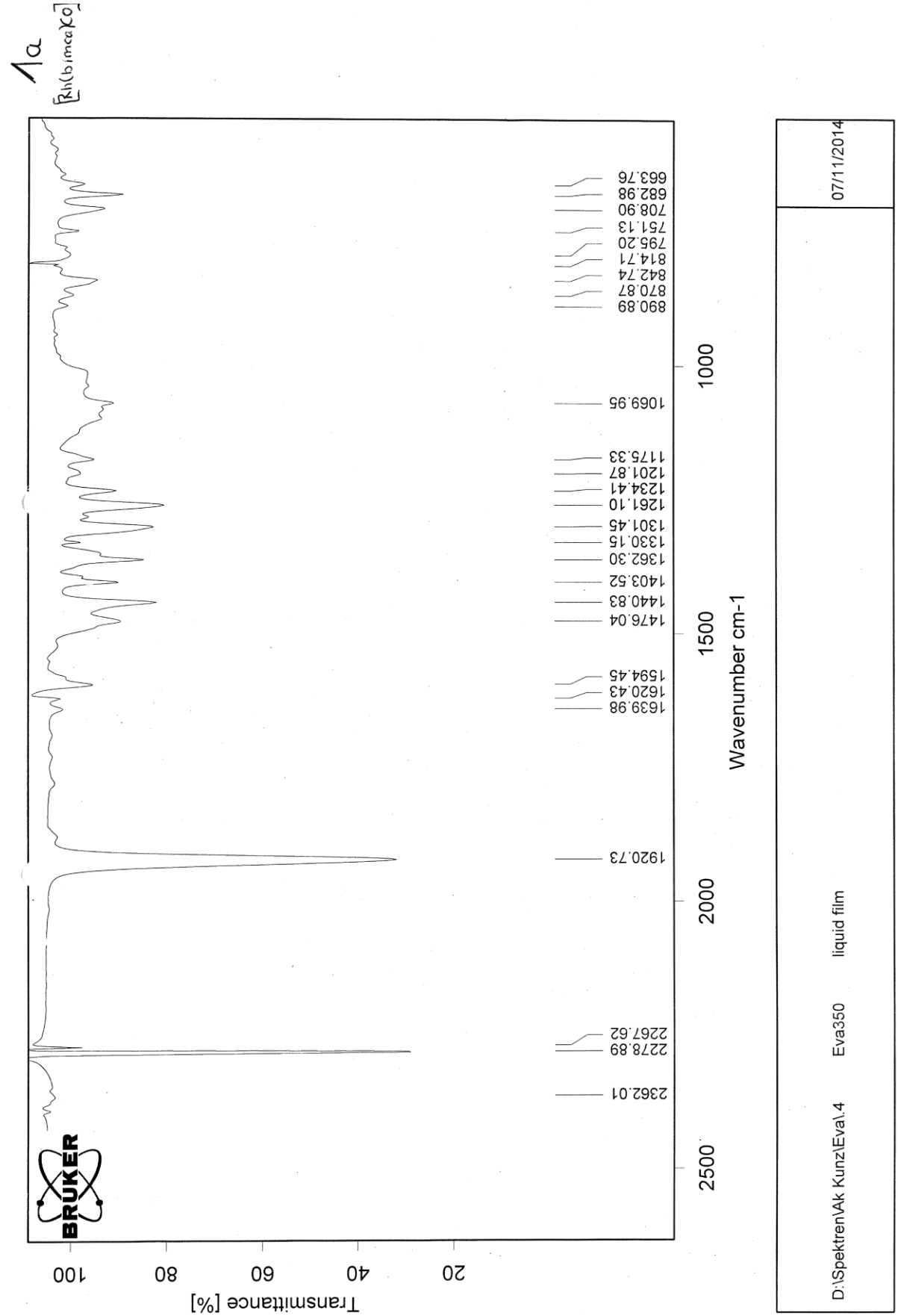


$^{1}H^{13}C$-HMBC NMR spectrum of **4a** in $CD_2Cl_2$

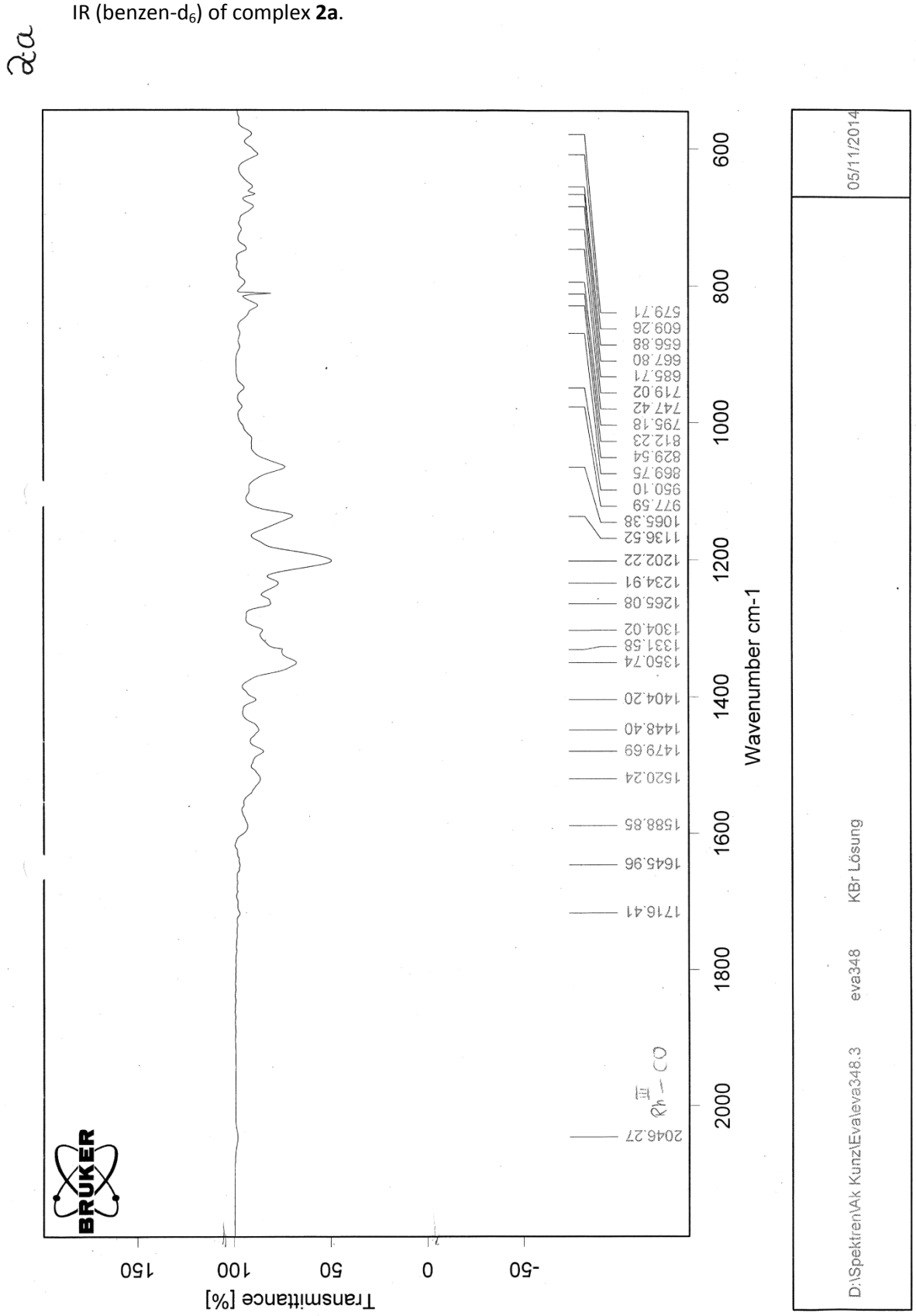


## 4. IR spectra of 1 and 2a

IR spectrum (benzene-$d_6$) of complex **1**.

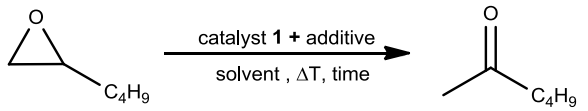


IR (benzen-$d_6$) of complex **2a**.



## 5. Catalytic epoxide rearrangement: optimisation of the reaction conditions regarding additive and solvent

**Table 1** Optimisation of the reaction conditions: additive and solvent.[a]




| Entry | Additive | Solvent | T [°C] | Time [h] | Yield[b,c] [%] |
|---|---|---|---|---|---|
| 1 | LiCl | thf-$d_8$ | 60 | 24 | 4 |
| 2 | NaCl | thf-$d_8$ | 60 | 24 | 2 |
| 3 | LiCl | $CD_2Cl_2$ | 60 | 24 | 0[d] |
| 4 | LiCl | $CD_3CN$ | 60 | 24 | 0[d] |
| 5 | $NaBF_4$ | thf-$d_8$ | 60 | 24 | 13 |
| 6 | $NaBPh_4$ | thf-$d_8$ | 60 | 24 | 45 |
| 7 | $NaBPh_4$ | $C_6D_6$ | 60 | 24 | 61 |
| 8 | $LiB(C_6F_5)_3$ | $C_6D_6$ | 60 | 24 | 90 |
| 9 | $LiNTf_2$ | $C_6D_6$ | 60 | 24 | >99 |

[a] Reaction conditions: **1** (10 mol%), additive (10 mol%), all reactions were carried out in a *J. Young* NMR tube with 1,2-epoxyhexane (35 µmol) as substrate and 0.5 mL solvent. [b] The ketone was observed as the sole reaction product. [c] The yield was determined by $^1$H NMR using 1,3,5-trimethoxybenzene as internal standard. [d] Catalyst deactivation due to organometallic side products.[6]

## 6. References


[1] M. Moser, B. Wucher, F. Rominger, D. Kunz, *Organometallics* **2007**, *26*, 1024–1030.

[2] G. M. Sheldrick, SADABS 2012/1; University of Göttingen, Göttingen, Germany, **2012**.

[3] a) G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122; b) C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* **2011**, *44*, 1281−1284.

[4] SQUEEZE routine: van der Sluis, P.; Spek, A. L. *Acta Cryst.* **1990**, *A46*, 194-201.

[5] PLATON: Spek, A. L. *J. Appl. Cryst.,* **2003**, *36*, 7-13.

[6] In dichloromethane oxidative addition (trans) of the solvent to complex 1 is observed which leads to [Rh(bimca)Cl($CH_2Cl$)(CO)]. M. Moser, *PhD thesis*, Heidelberg University, 2007.