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Supporting Information

Cobalt-Catalysed Hydroformylation of Epoxides in the Presence of Phosphine Oxides

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Summary

General Remarks

Air- and moisture-sensitive syntheses were performed under argon atmosphere. All chemicals were purchased from Aldrich, TCI, Alfa, Fluka, Acros or Strem and were used without further purification, unless otherwise mentioned. The solvents were collected from an SPS machine and used without any further purification. Anisole, dimethyl carbonate (DMC), and diethyl carbonate (DEC) were purchased in a Sure/Seal™ bottle and used without special treatment.

Thin layer chromatography (TLC) was performed on aluminium-backed hand-cut silica plates (5 × 10 cm, pre-coated TLC sheets ALUGRAM® Xtra SIL G/UV_{254}). If necessary, Phosphomolybdic acid (20 wt% in 100 mL ethanol) or potassium permanganate (1.5 g of $KMnO_4$, 10 g K_2CO_3, and 1.25 mL 10% NaOH in 200mL water) were used as developing stains. Column chromatography was done using silica (0.035-0.070 mm, silica gel 60, Fluka Chemika). All the products were isolated by silica gel column chromatography using (50 % pentane/ethyl acetate) mixtures as eluent.

NMR-spectra were recorded on Bruker AV 300 and 400 spectrometers. Chemicals shifts (δ) are reported in ppm downfield of tetramethylsilane. NMR spectra were treated and interpreted using MestReNova (version 14.0.1-23559). All NMR data are expressed as chemical shift in parts per million (ppm). The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra ($CDCl_3$: δH = 7.26 ppm, δC = 77.12 ppm). Coupling constants (J) are quoted in Hz. The multiplicity of each signal is designed as follows: s (singlet), d (doublet), t (triplet), b (broad), m (multiplet). All measurements were carried out at room temperature unless otherwise stated.

GC analysis was performed on an Agilent 7890A chromatograph with a 29 m HP5 column by GC-FID. EI (Electron impact) mass spectra were recorded on a MAT 95XP spectrometer (70 eV, Thermo ELECTRON CORPORATION).

General procedure for the hydroformylation of epoxides

In a typical experiment, the reactions were performed in 10 mL glass vial containing a stirring bar that was sequentially charged with $Co_2(CO)_8$ (0.5-1 mol%), ligand or promoter (2-20 mol%), and solvent (4 mL) in the glove box. The vials were

closed using a rubber septum/phenolic cap, and then removed from glove box. Substrates (2 mmol) were added under argon atmosphere, then the vials were pierced with a syringe needle and set on a metal plate inside a Parr 4560 series reactor (300 mL). The reactor was closed and flushed three times with syngas. After the last release, the autoclave was pressurized with syngas (40 bar) and then heated to 70 °C for 24 h in an aluminium block. At the end of the reaction, the autoclave was placed into an ice bath to cool down and stop the reaction. Finally, the pressure was released, and the reactor flushed with N_2 and opened. The reaction mixture was analysed by GC using isooctane as internal standard.

General procedure for the hydrogenation of β-hydroxyaldehydes

After the hydroformylation reaction, the vials were opened and charged with 10.6 mg of Pd/C (10% Pd in charcoal). Afterward, the reaction vials were pierced with a syringe needle and set in a metal plate inside a Parr 4560 series reactor (300 mL). The reactor was closed, and the gas line was purged with N_2 (about 20 bar). This was carried out two times before the same procedure was done three times with H_2 (about 20 bar). After the last release, the autoclave was pressurized with 40 bar of H_2 and then heated to 70 °C for 24 h inside an aluminium block. At the end of the reaction, the autoclave was placed into an ice bath to cool down and stop the reaction. Pure products were obtained by silica gel column chromatography (using 50% pentane/ethyl acetate as eluent) to give the corresponding products as isolated yields. Spectroscopic data for the products are presented in the ESI.

General procedure for kinetic measurements

In a typical run, a solution was prepared in a Schlenk under inert atmosphere (glove box) containing $Co_2(CO)_8$ (1 mol%), **P2** (2 mol%), substrate (10 mmol), in the toluene (20 mL). Then, the solution was transferred into a reactor under an inert atmosphere. The reactor was pressurized with 40 bar (CO: H_2 = 1:1) and heated using an aluminium block to the desired temperature. The reaction solution was periodically sampled from the reactor through a valved dip tube without depressurization. At the end of the reaction, the reactor was placed into an ice bath to cool down and stop the

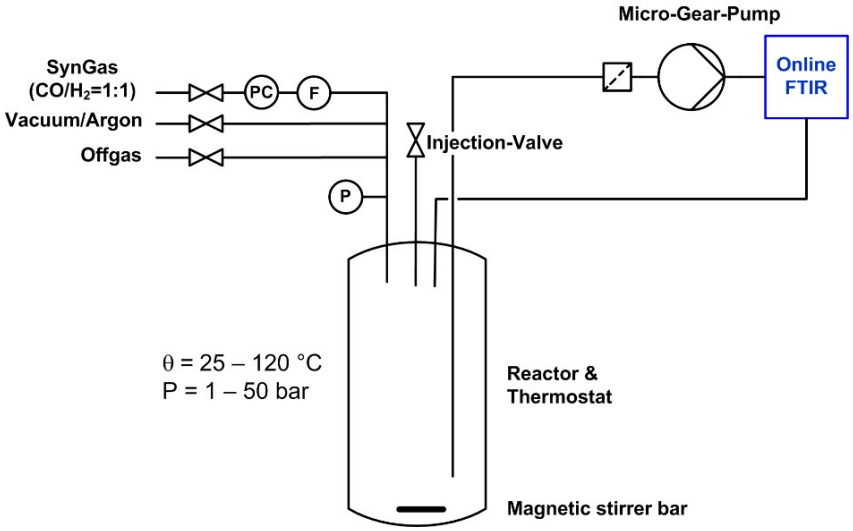
reaction. Finally, the pressure was released, and the reactor flushed with N_2 and opened. The samples were analysed by gas chromatography. Conversion and selectivity were calculated using isooctane as internal standard.

General procedure HP-FTIR spectroscopic measurements

Prior to the *in situ* FTIR experiments, background spectra of the solvent toluene have been recorded at experimental conditions (identical temperature and pressure). Hydroformylation reactions for *in situ* infrared spectroscopic monitoring were conducted in a HP-FTIR apparatus consisting of a 25 mL stainless steel cylinder (miniature cylinder, Swagelok) with a magnetic stirrer bar connected to a pressurizable and heatable transmission flow-through infrared spectroscopic cell. A schematic illustration of the entire set-up is given in **Scheme S1**. The liquid reaction solution was circulated between the reactor and the IR cell by a micro gear pump (mzr-7255, HNP Mikrosysteme GmbH, Parchim, Germany). The micro gear pump was set to 600 rpm (displacement volume = 48 µL).

The *in situ* transmission IR cell was placed in the regulated heating device, fixed in the optical pathway of modified a Bruker Matrix FTIR spectrometer with a MCT-A detector. As a window material, CaF_2 (Korth Kristalle GmbH, Kiel, Germany) was used. The optical path length was 0.2 mm, adjusted with a spacer element placed between the IR windows. FTIR spectra have been recorded between 3950 and 900 cm^{-1} with a spectral resolution of 2 cm^{-1}. For each individual FTIR spectrum ten scans were collected (double-sided, forward−backward).

The preparations of catalyst solutions and the transfer of liquids were carried out under argon atmosphere using standard Schlenk techniques.



Scheme S1. Scheme of the HP FTIR-reactor system used for the in situ spectroscopic investigations within this study.

IR-Experiment 1: $Co_2(CO)_8$/P2 in the presence of 1a at 80 °C, 40 bar of synthesis gas (CO/H_2)

A solution of $Co_2(CO)_8$ (0.04 mmol), tricyclohexylphosphine oxide **P2** (0.16 mmol) and 1,2-expoxybute **1a** (8 mmol) was prepared in toluene (16 mL). The solution was transferred with the help of a syringe into the IR apparatus which was pre-heated to 80 °C. The solution was circulated between the reactor and IR cell with the micro gear pump. The hydroformylation reaction was started by introducing 40 bar of synthesis gas (CO/H_2) and the *in situ* FTIR monitoring simultaneously initiated.

IR-Experiment 2: $Co_2(CO)_8$ in the presence of 1a at 80 °C, 40 bar S of synthesis gas (CO/H_2)

A solution of $Co_2(CO)_8$ (0.04 mmol) and 1,2-expoxybute (8 mmol) was prepared in toluene (16 mL). All other steps described above were applied here as well.

IR-Experiment 3: $Co_2(CO)_8$ at 80 °C, 40 bar SG

A solution of $Co_2(CO)_8$ (0.04 mmol) was prepared in toluene (16 mL). All other steps described above were applied here as well.

IR-Experiment 4: $Co_2(CO)_8$/P2 at 80 °C, 40 bar of synthesis gas (CO/H_2)

A solution of $Co_2(CO)_8$ (0.04 mmol) and tricyclohexylphosphine oxide **P2** (0.16 mmol) was prepared in toluene (16 mL). All other steps described above were applied here as well.

Chemometric treatment of spectroscopic data

Baseline corrections and succeeding decomposition of IR-spectra series have been performed by tools within the Facpack chemometric analysis software tool developed by the group of Prof. K. Neymeyr and Dr. M. Sawall from the University of Rostock and the Leibniz-Institute for Catalysis. For the extraction of pure component spectra and concentration profiles, the peak group analysis (PGA) tool was used.[1]

Tables and figures

Table S1. Effect of the metal precursor in the hydroformylation of **1a**.[a]

Entry	Metal source	Conversion[b] (%)	Selectivity[b] (%)	
			1d	Others
1	$Co_2(CO)_8$	81	77	23
2	$Co(acac)_2$	0	0	0
3	$Co(acac)_3$	0	0	0
4	$Co(OAc)_2$	0	0	0
5	$Co(NO_3)_2\ 6H_2O$	0	0	0
6	$Rh(CO)_2acac$	0	0	0
7	$Ir(CO)_2acac$	0	0	0
8	$Pd(dba)_2$	0	0	0
9	$Pd(OAc)_2$	0	0	0
10	$Fe_3(CO)_{12}$	0	0	0

11	$Mn_2(CO)_8$	0	0	0

[a] Reaction conditions: **1a** (2 mmol), metal source (1 mol% based on the metal content), **P2** (2 mol% based on the metal content), toluene (4 mL), 70 °C, gas phase – CO/H_2 (1:1) 40 bar, 24 h. [b] Determined by GC analysis using isooctane as internal standard.

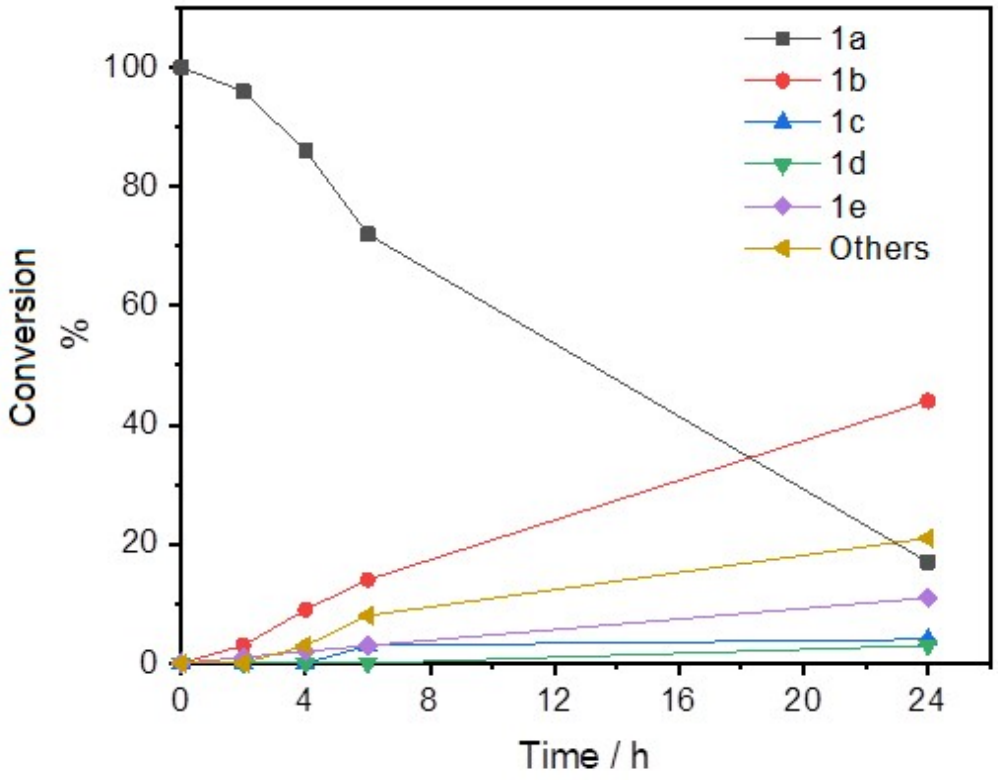


Figure S1. Kinetic curves for the cobalt-catalysed hydroformylation of **1a**. Reaction conditions: **1a** (10 mmol), $Co_2(CO)_8$ (1 mol%), **P2** (2 mol%), toluene (20 mL), 70 °C, gas phase – CO/H_2 (1:1) 40 bar. [b] Conversions were determined by GC analysis using isooctane as internal standard.

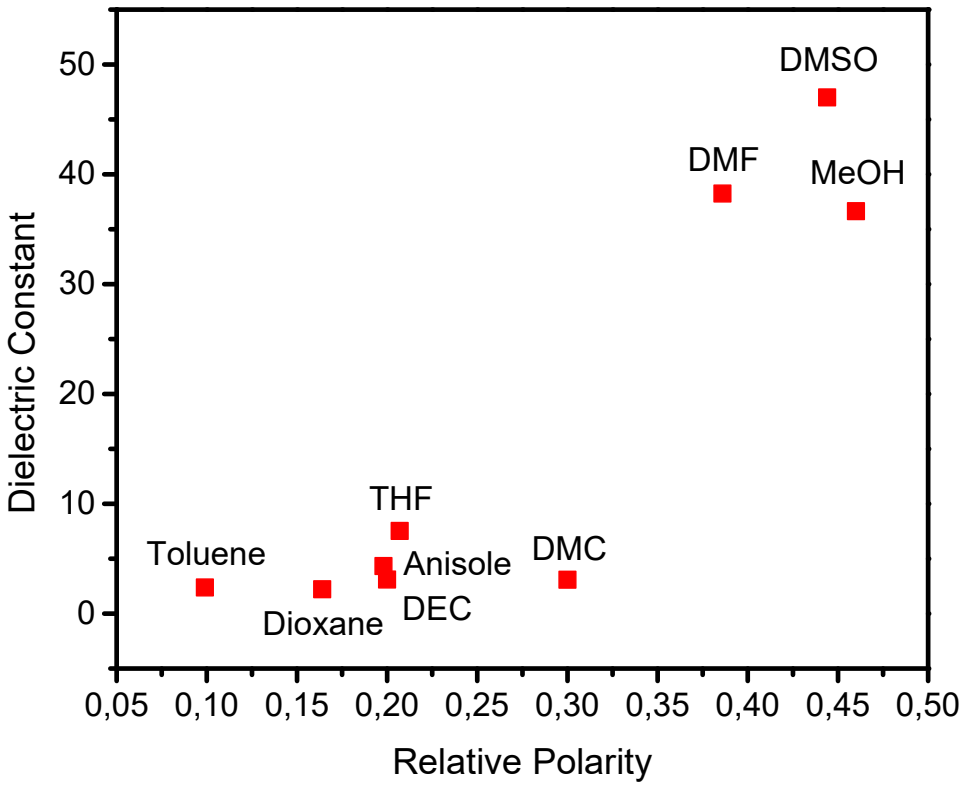
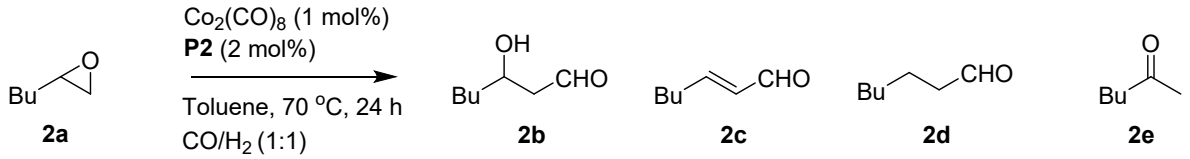


Figure S2. Solvent effect: dielectric constant vs. relative polarity.

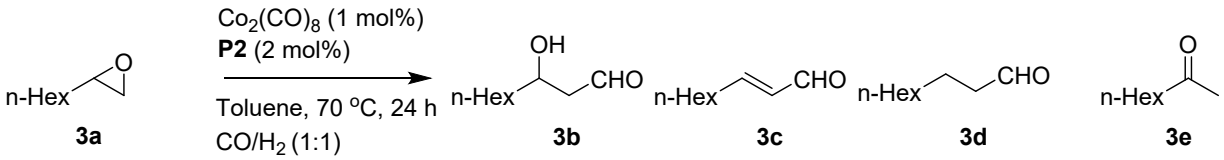
Table S2. Hydroformylation of the substrate **2a** under optimized conditions.



Entry	Conversion[b](%)	Selectivity[b] (%)				
		2b	**2c**	**2d**	**2e**	Others[b]
1	>99	51	13	10	17	9

[a] Reaction conditions: **2a** (2 mmol), $Co_2(CO)_8$ (1 mol%), **P2** (2.0 mol%), toluene (4 mL), 70 °C, gas phase – CO/H_2 (1:1) 40 bar, 24 h. [b] Determined by GC analysis using isooctane as internal standard. [b] mainly aldehyde **2f**.

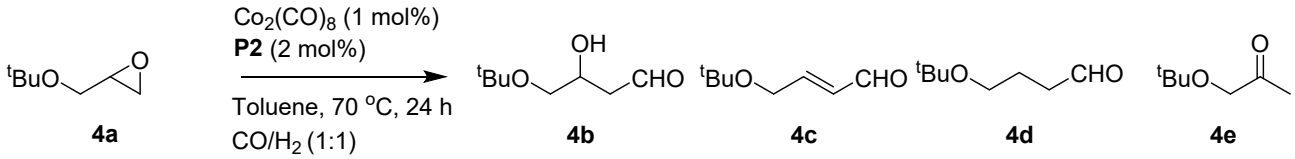
Table S3. Hydroformylation of the substrate **3a** under optimized conditions.



Entry	Conversion[b](%)	Selectivity[b] (%)				
		3b	**3c**	**3d**	**3e**	Others[b]
1	>99	55	13	2	19	11

[a] Reaction conditions: **3a** (2 mmol), $Co_2(CO)_8$ (1 mol%), **P2** (2.0 mol%), toluene (4 mL), 70 °C, gas phase – CO/H_2 (1:1) 40 bar, 24 h. [b] Determined by GC analysis using isooctane as internal standard. [b] mainly aldehyde 3**f**.

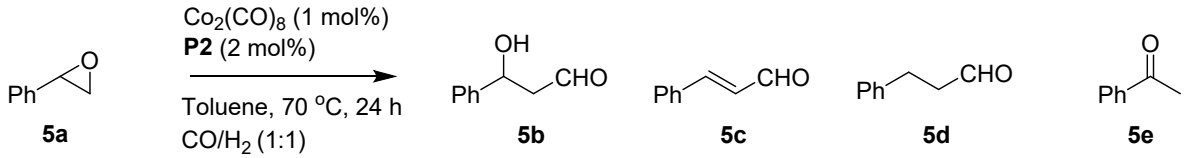
Table S4. Hydroformylation of the substrate **4a** under optimized conditions.



Entry	Conversion[b](%)	Selectivity[b] (%)				
		4b	**4c**	**4d**	**4e**	Others[b]
1	>99	44	5	10	25	16

[a] Reaction conditions: **4a** (2 mmol), $Co_2(CO)_8$ (1 mol%), **P2** (2.0 mol%), toluene (4 mL), 70 °C, gas phase – CO/H_2 (1:1) 40 bar, 24 h. [b] Determined by GC analysis using isooctane as internal standard. [b] mainly aldehyde **4f**.

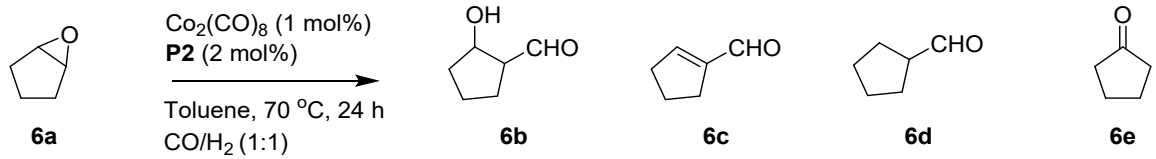
Table S5. Hydroformylation of the substrate **5a** under optimized conditions.



Entry	Conversion[b](%)	Selectivity[b] (%)				
		5b	**5c**	**5d**	**5e**	Others[b]
1	85	1	6	8	53	32

[a] Reaction conditions: **5a** (2 mmol), $Co_2(CO)_8$ (1 mol%), **P2** (2.0 mol%), toluene (4 mL), 70 °C, gas phase – CO/H_2 (1:1) 40 bar, 24 h. [b] Determined by GC analysis using isooctane as internal standard. [b] mainly aldehyde 5**f**.

Table S6. Hydroformylation of the substrate **6a** under optimized conditions.

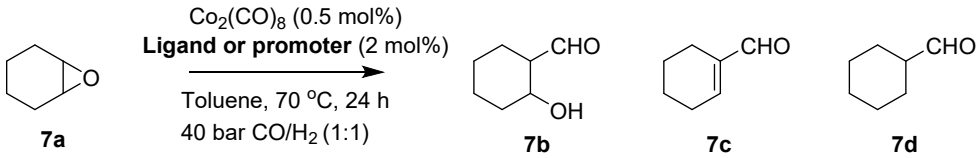


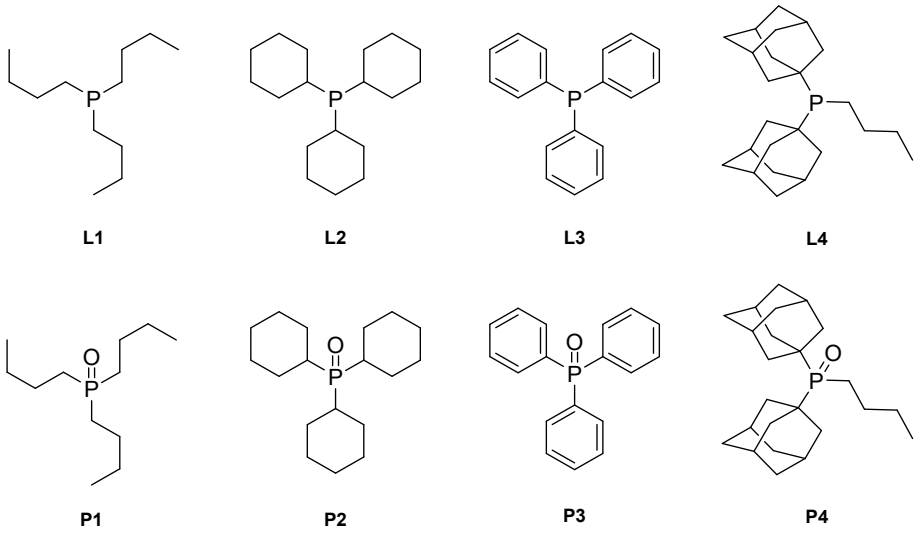
6a **6b** **6c** **6d** **6e**

Entry	Conversion[b](%)	Selectivity[b] (%)				
		6b	**6c**	**6d**	**6e**	Others
1	>99	74	20	1	3	2

[a] Reaction conditions: **6a** (2 mmol), $Co_2(CO)_8$ (1 mol%), **P2** (2.0 mol%), toluene (4 mL), 70 °C, gas phase – CO/H_2 (1:1) 40 bar, 24 h. [b] Determined by GC analysis using isooctane as internal standard.

Table S7. Effect of the ligand/promoter ratio in the hydroformylation of **7a**.[a]

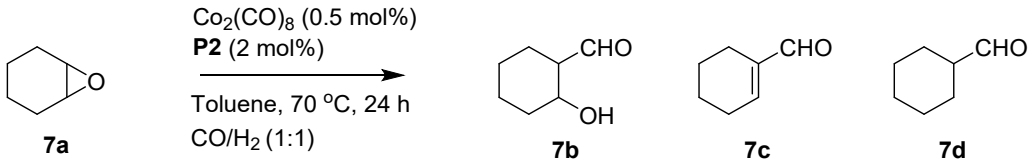




Entry	Ligand or promoter	Conversion[b] (%)	Selectivity[b] (%)			
			7b	**7c**	**7d**	Others
1	-	10	81	5	3	11
2	L1	0	0	0	0	0
3	L2	3	0	0	32	68
4	L3	0	0	0	0	0
5	L4	12	95	1	2	2
6	P1	60	79	6	1	14
7	P2	>99	80	5	2	13
8	P3	24	88	4	2	6
9	P4	68	82	4	2	12

[a] Reaction conditions: **7a** (2 mmol), $Co_2(CO)_8$ (0.5 mol%), ligand or promoter (2.0 mol%), toluene (4 mL), 70 °C, gas phase – CO/H_2 (1:1) 40 bar, 24 h. [b] Determined by GC analysis using isooctane as internal standard.

Table S8. Effect of the temperature in the hydroformylation of **7a**.[a]



7a **7b** **7c** **7d**

Entry	Temperature (°C)	Conversion[b] (%)	Selectivity[b] (%)			
			7b	**7c**	**7d**	Others
1	100	>99	24	27	45	4
2	90	>99	41	15	39	5
3	70	>99	80	5	2	13
4	60	56	85	4	2	9

[a] Reaction conditions: **7a** (2 mmol), $Co_2(CO)_8$ (0.5 mol%), **P2** (2.0 mol%), toluene (4 mL), gas phase – CO/H_2 (1:1) 40 bar, 24 h. [b] Determined by GC analysis using isooctane as internal standard.

Scope limitations

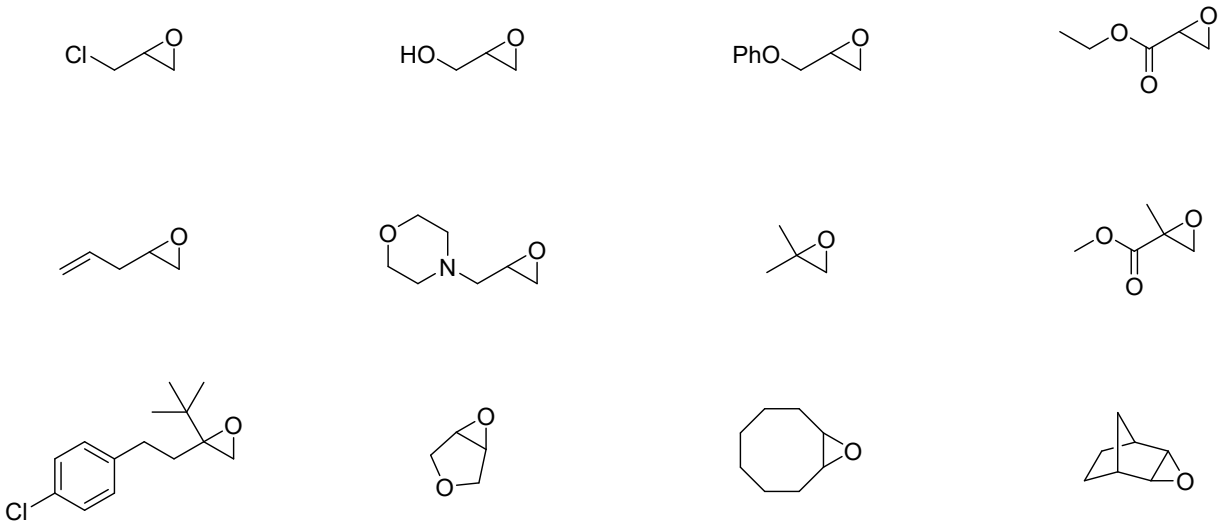


Figure S3. Scope limitations: the substrates which showed low conversions or selectivity towards hydroformylation of epoxides under the standard conditions. Reaction conditions: substrate (2 mmol), $Co_2(CO)_8$ (0.5 mol%), **P2** (2.0 mol%), toluene (4 mL), gas phase – CO/H_2 (1:1) 40 bar, 24 h.

Results from IR-Experiment 3

Collected FTIR-spectra measured during the treatment of the precatalyst $Co_2(CO)_8$ (0.04 mmol) dissolved in toluene at 80 °C and 40 bar synthesis gas are shown in **Figure S3**. Pure component spectra and corresponding concentration profiles obtained by the chemometric analysis using the peak group analysis (PGA) tool are given in **Figure S4**.

The formation of the hydride complex $HCo(CO)_4$ is much slower compared the system with added trihexylphosphine oxide **P2** (see Exp. 4) and did not reached quasi-stationarity even after 1000 min.

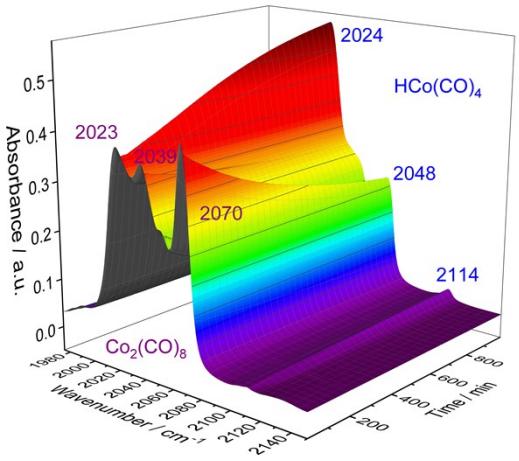


Figure S4. HP FTIR-spectra registered during the treatment of the precatalyst $Co_2(CO)_8$ at 80 °C and $p(CO/H_2)$ = 40 bar in toluene as a solvent. Further reaction conditions: $n(Co_2(CO)_8)$ = 0.04 mmol, vol.(toluene) = 16 mL.

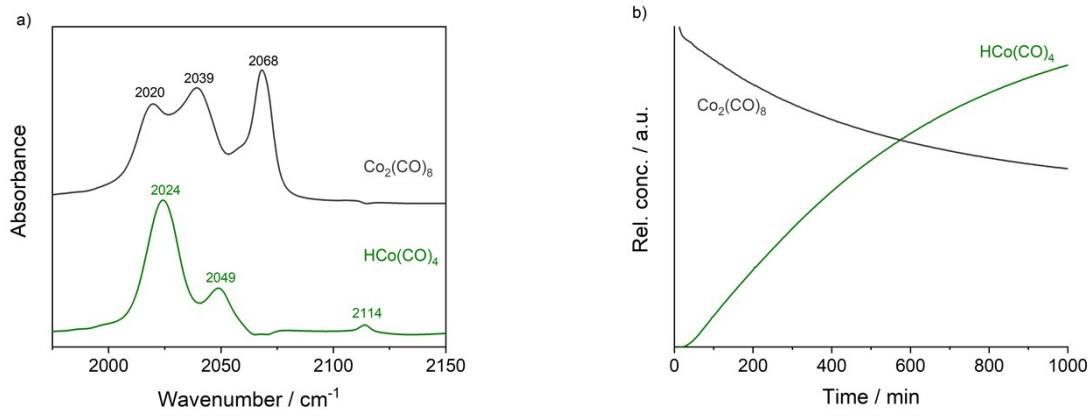


Figure S5. Pure component spectra and relative concentration profiles extracted from the IR-spectra series collected during IR-experiment 3 via peak group analysis tool. Reaction conditions: 80 °C, p(CO/H_2) = 40 bar, n($Co_2(CO)_8$) = 0.04 mmol, vol.(toluene) = 16 mL.

Results from IR-Experiment 4

In **Figure S6** the series of FTIR-spectra measured during the treatment of the precatalyst $Co_2(CO)_8$ (0.04 mmol) in the presence tricyclohexylphosphineoxide **P2** (0.16 mmol) at 80 °C and 40 bar synthesis gas in toluene. Results from the chemometric analysis to extract pure component spectra and corresponding relative concentration profiles using the peak group analysis (PGA) tool are given in **Figure S7**.

The data shows that the formation of the cobalt hydride complex $HCo(CO)_4$ has reached quasi-stationarity after ca. 150 min. At the reaction start due to partial disproportionation of $Co_2(CO)_8$ in the presence of **P2**, only a certain fraction of the amount of cobalt is present in form of dissolvable $Co_2(CO)_8$.

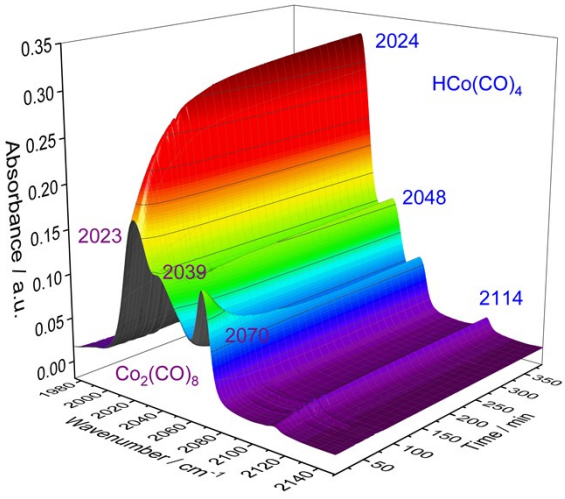


Figure S6. HP FTIR-spectra series collected during the treatment of $Co_2(CO)_8$ in the presence of **P2** at 80 °C and p(CO/H_2) = 40 bar in toluene as a solvent. Further reaction conditions: n($Co_2(CO)_8$) = 0.04 mmol, n(**P2**) = 0.16 mmol, vol.(toluene) = 16 mL.

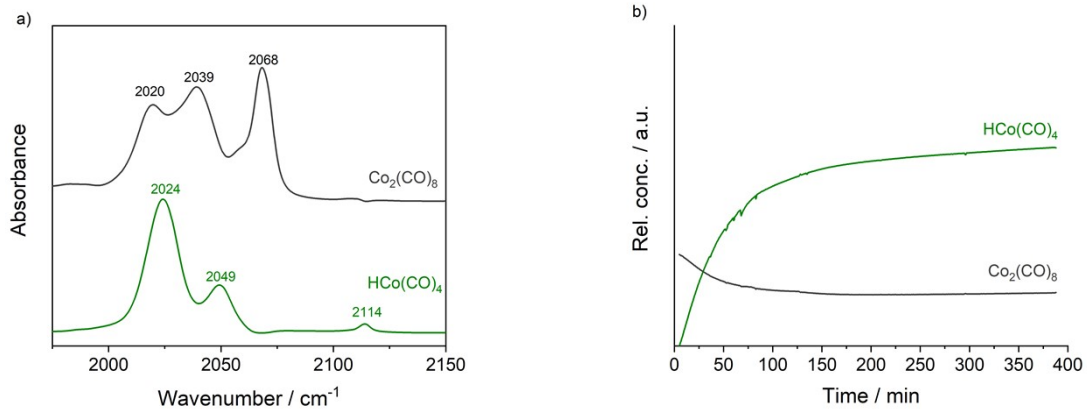
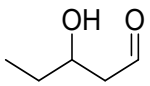


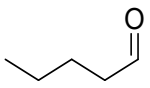
Figure S7. Pure component spectra and relative concentration profiles extracted from the IR-spectra series collected during IR-experiment 4 via peak group analysis tool. Reaction conditions: 80 °C, p(CO/H_2) = 40 bar, n($Co_2(CO)_8$) = 0.04 mmol, n(**P2**) = 0.16 mmol, vol.(toluene) = 16 mL.

Products identification and characterization



1b

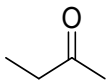
3-hydroxypentanal (**1b**): MS (70 eV, EI): m/z (%) 102 (M^+, 4), 101 (73), 84 (1), 83 (7), 59 (100), 58 (31), 56 (8).



1d

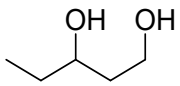
Pentanal (**1d**): Colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.78 (t, *J* = 1.9 Hz, 1H), 2.44 (m, 2H), 1.70 – 1.54 (m, 2H), 1.45 – 1.29 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75

MHz, $CDCl_3$) δ 203.11, 43.74, 24.27, 22.40, 13.91. MS (70 eV, EI): m/z (%) 86 (M^+, 4), 85 (2), 71 (6), 58 (100), 57 (73), 55 (14), 53 (6).



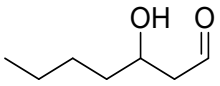
1e

butan-2-one (**1e**): MS (70 eV, EI): m/z (%) 72 (M^+, 100), 71 (4), 58 (1), 57 (25), 53 (2), 50 (3).



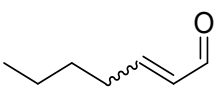
1g

Pentane-1,3-diol (**1g**): Colourless oil. R_f: 0.28 (50% Ethyl acetate/Pentane) – Stain: 20 wt% Phosphomolybdic acid in ethanol. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.93 – 3.63 (m, 3H), 3.31 (br s, 1H), 3.20 (br s, 1H), 2.02 – 1.51 (m, 2H), 1.55 – 1.41 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.47, 61.63, 37.85, 30.59, 9.93. The analytical data for this compound were in excellent agreement with the reported data.[2]



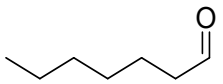
2b

3-hydroxyheptanal (**2b**): MS (70 eV, EI): m/z (%) 129 (M^+-H, 1), 112 (4), 88 (12), 87 (15), 84 (58), 83 (32), 73 (100), 69 (97), 89 (58), 55 (51).



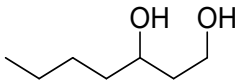
2c

Hept-2-enal (**2c**): MS (70 eV, EI): m/z (%) 112 (M^+, 3), 97 (13), 92 (26), 91 (48), 84 (23), 83 (100), 70 (42), 69 (45), 68 (38), 57 (60), 56(50), 55 (80), 53 (16).



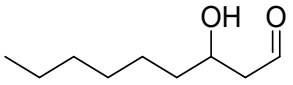
2d

Heptanal (**2d**): MS (70 eV, EI): m/z (%) 114 (M^+, 2), 96 (18), 91 (18), 86 (23), 81 (31), 71 (31), 70 (700), 68 (20), 57 (47), 55 (54).



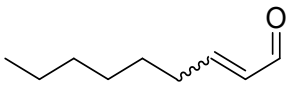
2g

Heptane-1,3-diol (**2g**): Colourless oil. Rf: 0.23 (50% Ethyl acetate/Pentane) – Stain: 20 wt% Phosphomolybdic acid in ethanol. ^{1}H NMR (300 MHz, Chloroform-d) δ 4.11 – 3.49 (m, 3H), 2.30 (bs, 2H), 1.73 – 1.55 (m, 2H), 1.48 – 1.37 (m, 2H), 1.34 – 1.21 (m, 4H), 0.84 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 72.61, 62.13, 38.41, 37.71, 27.83, 22.82, 14.19. MS (70 eV, EI): m/z (%) 132 (M^+, 1), 114 (5), 101 (5), 87 (14), 85 (44), 75 (100), 72 (10), 69 (41), 58 (23), 57 (72), 55 (13).



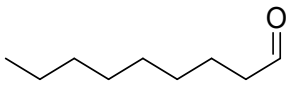
3b

3-hydroxynonanal (**3b**): MS (70 eV, EI): m/z (%) m/z (%) 158 (M^+,1), 140 (1), 112 (17), 97 (32), 96 (22), 83 (45), 81 (24), 70 (87), 69 (37), 57 (41), 55 (100).



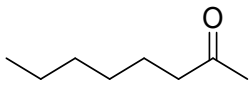
3c

Non-2-enal (**3c**): MS (70 eV, EI): m/z (%) 140 (M^+, 1), 139 (1), 122 (7), 111 (17), 107 (10), 97 (28), 96 (41), 94 (11), 93 (24), 84 (45), 83 (91), 79 (16), 70 (100), 69 (65), 55 (94).



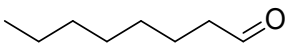
3d

3-hydroxynonanal (**3d**): MS (70 eV, EI): m/z (%) 142 (M^+,1), 141 (1), 114 (13), 99 (10), 96 (31), 95 (35), 82 (40), 81 (33), 70 (44), 69 (67), 68 (35), 57 (100), 55 (51).



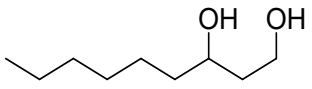
3e

Octan-2-one (**3e**): MS (70 eV, EI): 128 (M^+, 12), 113 (7), 85 (11), 71 (23). 59 (18), 58 (100), 55 (7).



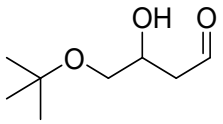
3f

Octanal (**3f**): MS (70 eV, EI): 128 (M^+, 3), 127 (1), 110 (15), 100 (25), 95 (19), 85 (35), 84 (100), 82 (47) 81 (47), 72 (17), 71 (21), 68 (41), 67 (36), 58 (23), 57 (100), 56 (93), 55 (79), 54 (12).



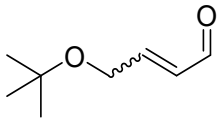
3g

Nonane-1,3-diol (**3g**): Colourless oil. Rf: 0.23 (50% Ethyl acetate/Pentane) – Stain: 20 wt% Phosphomolybdic acid in ethanol. ^{1}H NMR (400 MHz, Chloroform-d) δ 3.94 – 3.76 (m, 3H), 2.18 (br s, 2H), 1.79 – 1.60 (m, 3H), 1.55 – 1.38 (m, 3H), 1.37 – 1.21 (m, 6H), 0.89 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 72.62, 62.12, 38.41, 38.02, 31.95, 29.42, 25.62, 22.74, 14.22. MS (70 eV, EI): m/z (%) 159 (M^+-H, 1), 142 (2), 115 (8), 113 (33), 99 (5), 97 (25), 96 (10), 85 (14), 81 (13), 75 (100), 70 (23), 69 (10), 57 (49), 55 (39). The analytical data for this compound were in excellent agreement with the reported data.[3]



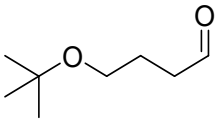
4b

4-(tert-butoxy)-3-hydroxybutanal (**4b**): MS (70 eV, EI): m/z (%) 145 (M^+-CH_3, 1), 142 (1), 130 (3), 127 (5), 116 (5), 103 (5), 87 (34), 75 (10), 74 (12), 73 (11), 69 (14), 59 (20) , 57 (100). The analytical data for this compound were in excellent agreement with the reported data.



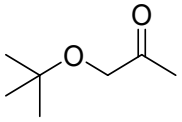
4c

4-(tert-butoxy)but-2-enal (**4c**): MS (70 eV, EI): m/z (%) 142 (M^+, 1), 128 (8), 127 (87), 86 (38), 69 (81), 68 (6), 59 (44), 57 (100). The analytical data for this compound were in excellent agreement with the reported data.



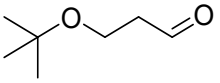
4d

4-(tert-butoxy)butanal (**4d**): MS (70 eV, EI): m/z (%) 144 (M^+, 4), 143 (51), 101 (74), 99 (10), 85 (37), 73 (13), 59 (11), 57 (100).



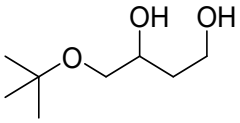
4e

1-(tert-butoxy)propan-2-one (**4e**): MS (70 eV, EI): m/z (%) 130 (M^+, 2), 115 (5), 100 (14), 87 (10), 57 (100).



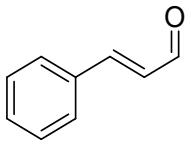
4f

3-(tert-butoxy)propanal (**4f**): MS (70 eV, EI): m/z (%) 129 (M^+-H, 2), 100 (15), 91 (7), 87 (32), 71 (100), 59 (29), 59 (29), 57 (66).



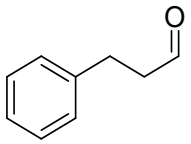
4g

4-(tert-butoxy)butane-1,3-diol (**4g**): Colourless oil; R_f: 0.20 (50% Ethyl acetate/Pentane) – Stain: 20 wt% Phosphomolybdic acid in ethanol. ^{1}H NMR (300 MHz, Chloroform-d) δ 3.95 – 3.82 (m, 1H), 3.77 (t, *J* = 5.5 Hz, 2H), 3.33 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.23 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.18 (s, 2H), 1.75 – 1.60 (m, 2H), 1.16 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.45, 70.40, 65.94, 60.72, 35.30, 27.57. MS (70 eV, EI): m/z (%) 147 (M^+-CH_3, 2), 117 (1), 105 (3), 89 (10), 88 (10), 87 (11), 75 (55), 71 (17), 59 (26), 57 (100). The analytical data for this compound were in excellent agreement with the reported data.[4]



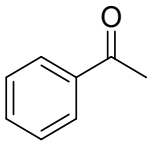
5c

Cinnamaldehyde (**5c**): MS (70 eV, EI): 132 (M^+, 54), 104 (54), 103 (100), 78 (11), 77 (37), 51 (13).



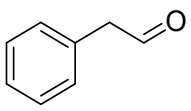
5d

3-phenylpropanal (**5d**): MS (70 eV, EI): m/z (%) 134 (M^+, 13), 105 (100), 103 (14), 79 (17), 77 (17).



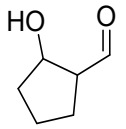
5e

Acetophenone (**5e**): MS (70 eV, EI): m/z (%) 120 (49), 119 (52), 105 (34), 91 (100), 89 (62), 77 (28), 65 (15), 63 (16).



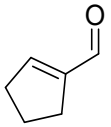
5f

2-phenylacetaldehyde (**5f**): MS (70 eV, EI): 120 (M^+, 25), 92 (25), 91 (100), 65 (15).



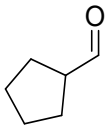
6b

2-hydroxycyclopentane-1-carbaldehyde (**6b**): mixture of diasteroisomers, shorter GC retention time: MS (70 eV, EI): m/z (%) 114 (M^+, 1), 96 (16), 95 (9), 85 (3), 70 (100), 67 (71), 58 (24), 57 (74), 55 (11). Longer GC retention time: MS (70 eV, EI): m/z (%) 96 (M^+-H_2O, 20), 95 (8), 85 (2), 70 (100), 67 (33), 58 (26), 57 (67), 55 (10).



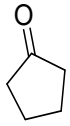
6c

Cyclopent-1-ene-1-carbaldehyde (**6c**): MS (70 eV, EI): m/z (%) 96 (M^+, 67), 95 (34), 67 (100), 65 (22), 53 (7).



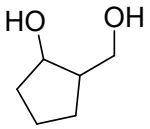
6d

Cyclopentanecarbaldehyde (**6d**): MS (70 eV, EI): m/z (%) 98 (M^+, 37), 97 (4), 92 (30), 91 (46), 80 (9), 70 (13), 69 (100), 67 (17), 57 (53).



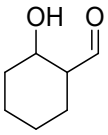
6e

Cyclopentanone (**6e**): MS (70 eV, EI): m/z (%) 84 (M^+, 68), 83 (3), 56 (32), 55 (100).



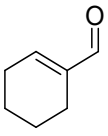
6g

2-(hydroxymethyl)cyclopentan-1-ol (**6g**): Colourless oil; R_f: 0.13 (50% Ethyl acetate/Pentane) – Stain: 20 wt% Phosphomolybdic acid in ethanol. Mixture of diasteroisomers (shorter GC retention time): MS (70 eV, EI): m/z (%) 98 (M^+-H_2O, 29), 97 (17), 83 (39), 80 (100), 79 (18), 70 (46), 69 (40), 67 (19), 54 (96), 55 (58). Longer GC retention time: MS (70 eV, EI): m/z (%) 115 (M^+-H, 1), 98 (28), 97 (23), 83 (39), 80 (100), 79 (21), 70 (49), 69 (39), 68 (47), 67 (30), 54 (80). The analytical data for this compound were in excellent agreement with the reported data.[5]



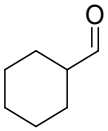
7b

2-hydroxycyclohexane-1-carbaldehyde (**7b**): MS (70 eV, EI): m/z (%) 128 (M^+, 4), 127 (1), 110 (60), 109 (10), 95 (24), 92 (11), 84 (10), 83 (23), 82 (95), 81 (85), 79 (39), 77 (10), 71 (14), 67 (100), 66 (28), 57 (90), 55 (32), 54 (34), 53 (20).



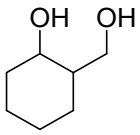
7c

Cyclohex-1-ene-1-carbaldehyde (**7c**): MS (70 eV, EI): m/z (%). 110 (M^+, 98), 109 (11), 95 (39), 81 (100), 79 (72), 77 (21), 67 (25), 54 (13), 53 (29), 51 (13).



7d

Cyclohexanecarbaldehyde (**7d**): MS (70 eV, EI): m/z (%) 112 (M^+,10), 111 (1), 94 (28), 83 (65), 81 (9), 79 (18), 70 (22), 68 (35), 67 (8), 57 (10), 56 (11), 55 (100).



7g

2-(hydroxymethyl)cyclohexan-1-ol (**7g**): Colourless oil; R_f: 0.20 (50% Ethyl acetate/Pentane) – Stain: 20 wt% Phosphomolybdic acid in ethanol. ^{1}H NMR (300 MHz, Chloroform-d) δ 4.23 (br s, 2H), 3.69 – 3.50 (m, 2H), 3.50 – 3.35 (m, 1H), 1.90 (dtd, J = 9.4, 3.3, 1.6 Hz, 1H), 1.77 – 1.38 (m, 4H), 1.34 – 1.01 (m, 3H), 0.87 (qd, J = 12.1, 3.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 75.81, 68.05, 45.89, 35.09, 27.24, 25.06, 24.43. MS (70 eV, EI): m/z (%) 129 (M^+-H, 1), 112 (32), 97 (29), 94 (65), 84 (28), 83 (34), 81 (27), 79 (76), 70 (33), 68 (100), 67 (41), 57 (45), 55 (46), 53 (13). The analytical data for this compound were in excellent agreement with the reported data.[5]

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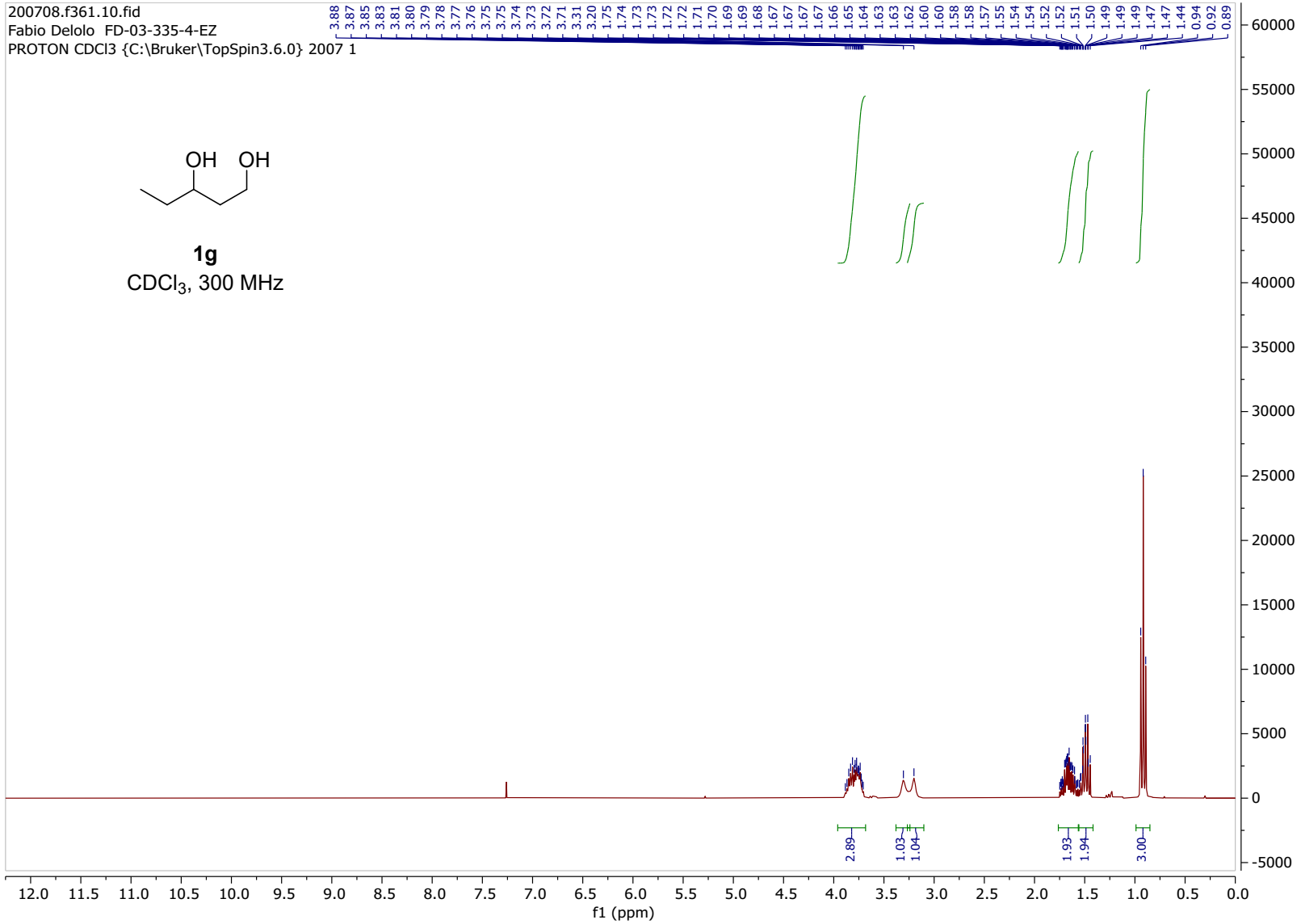
1. (a) https://www.math.uni-rostock.de/facpack/; (b) M. Sawall, C. Kubis, E. Barsch, D. Selent, A. Börner, K. Neymeyr, *J. Iran Chem. Soc.* **2016**, *13*, 191-205.
2. J. Kim, K. A. De Castro, M. Lim and H. Rhee, *Tetrahedron*, 2010, **66**, 3995-4001.
3. T. Cohen, I. H. Jeong, B. Mudryk, M. Bhupathy, M. M. A. Awad, *J. Org. Chem.*, 1990, **55** (5), 1528–1536.
4. D. Seebach, M. Eberle, *Synthesis*, 1986; **1986** (1), 37-40.
5. M. Lenze and E. B. Bauer, *Chemical Communications*, 2013, 49, 5889-5891.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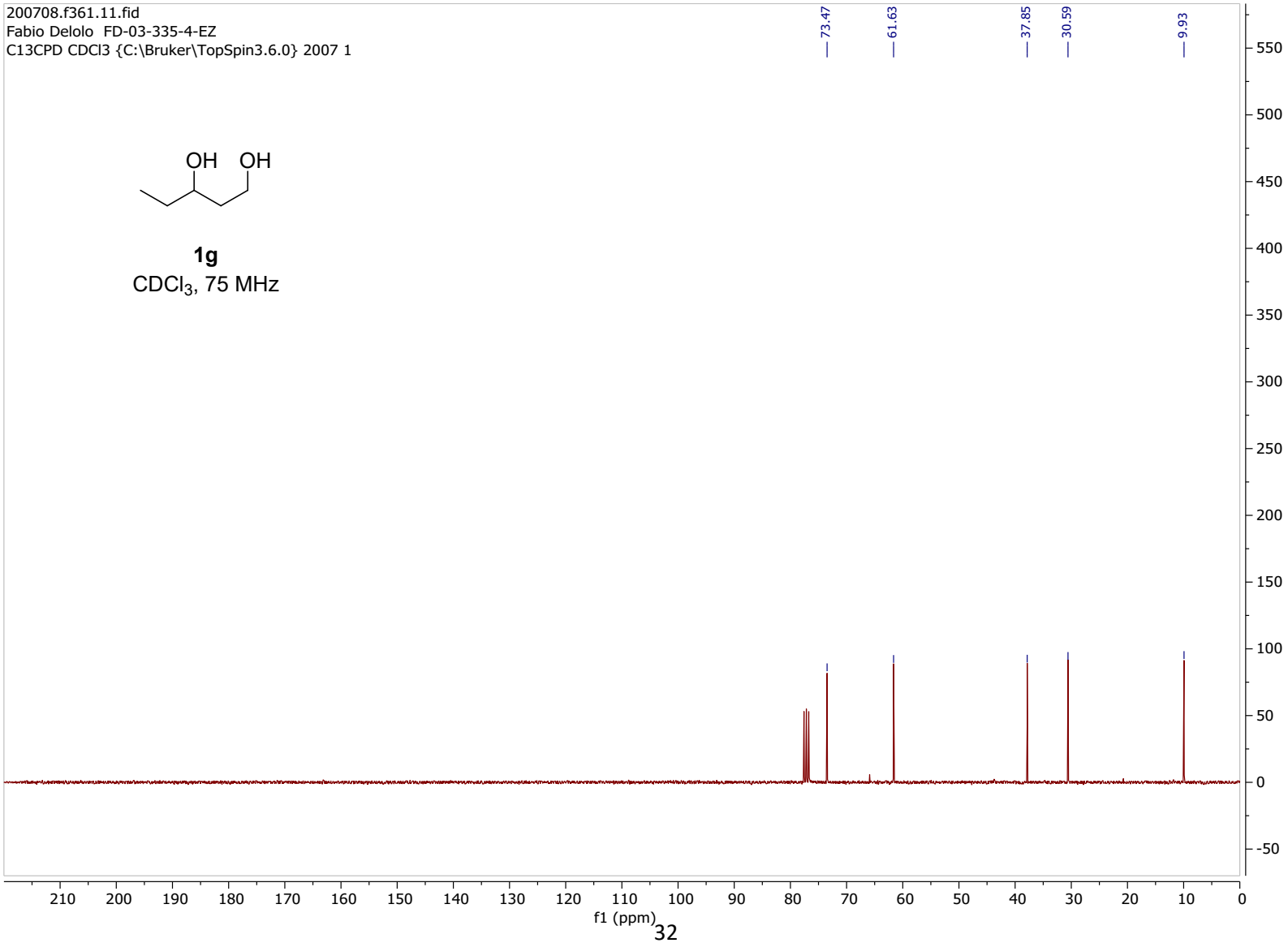
1g
CDCl3, 300 MHz
f1 (ppm)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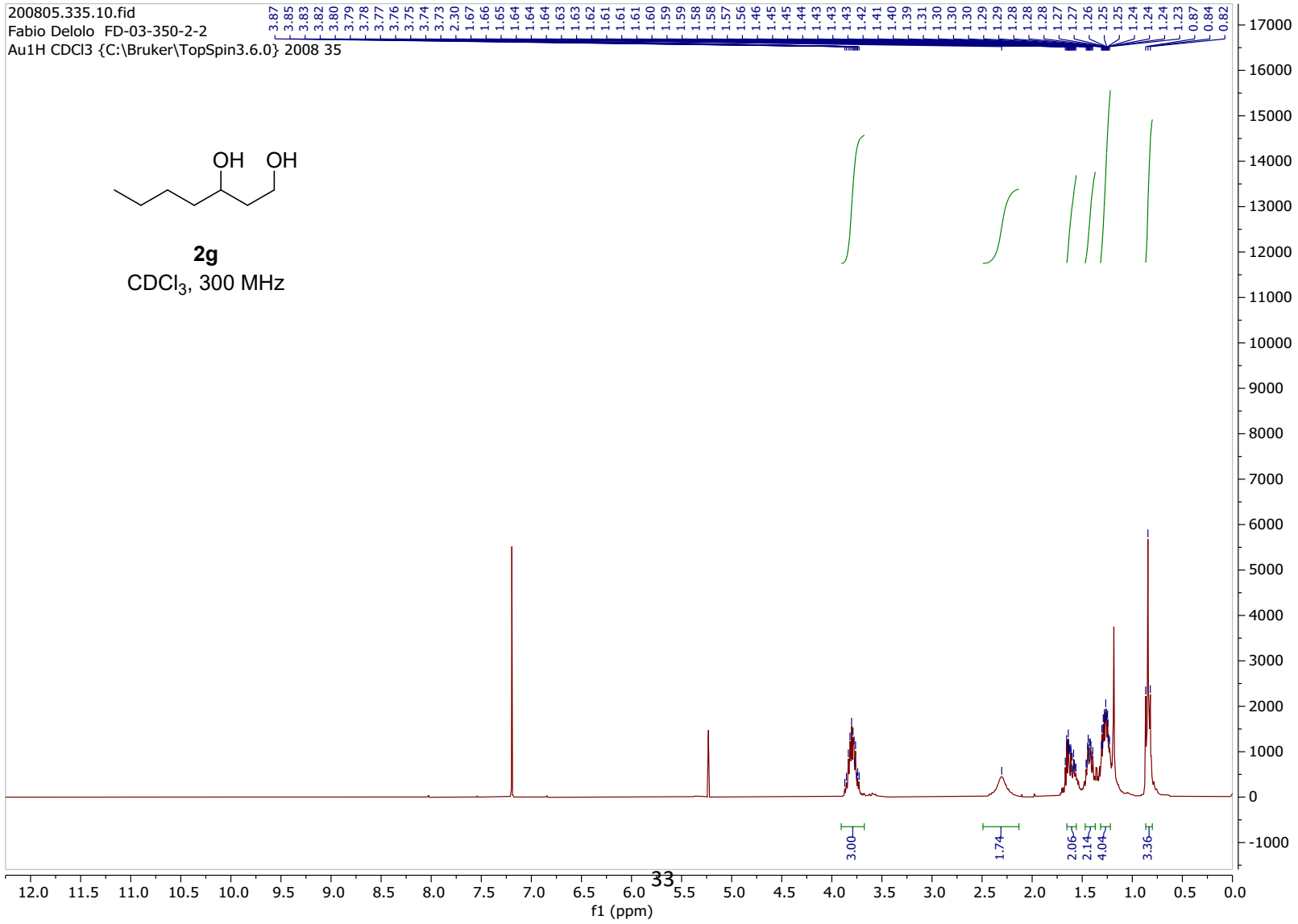
61.63
37.85
30.59
9.93
OH
OH
1g
CDCl3, 75 MHz
f1 (ppm)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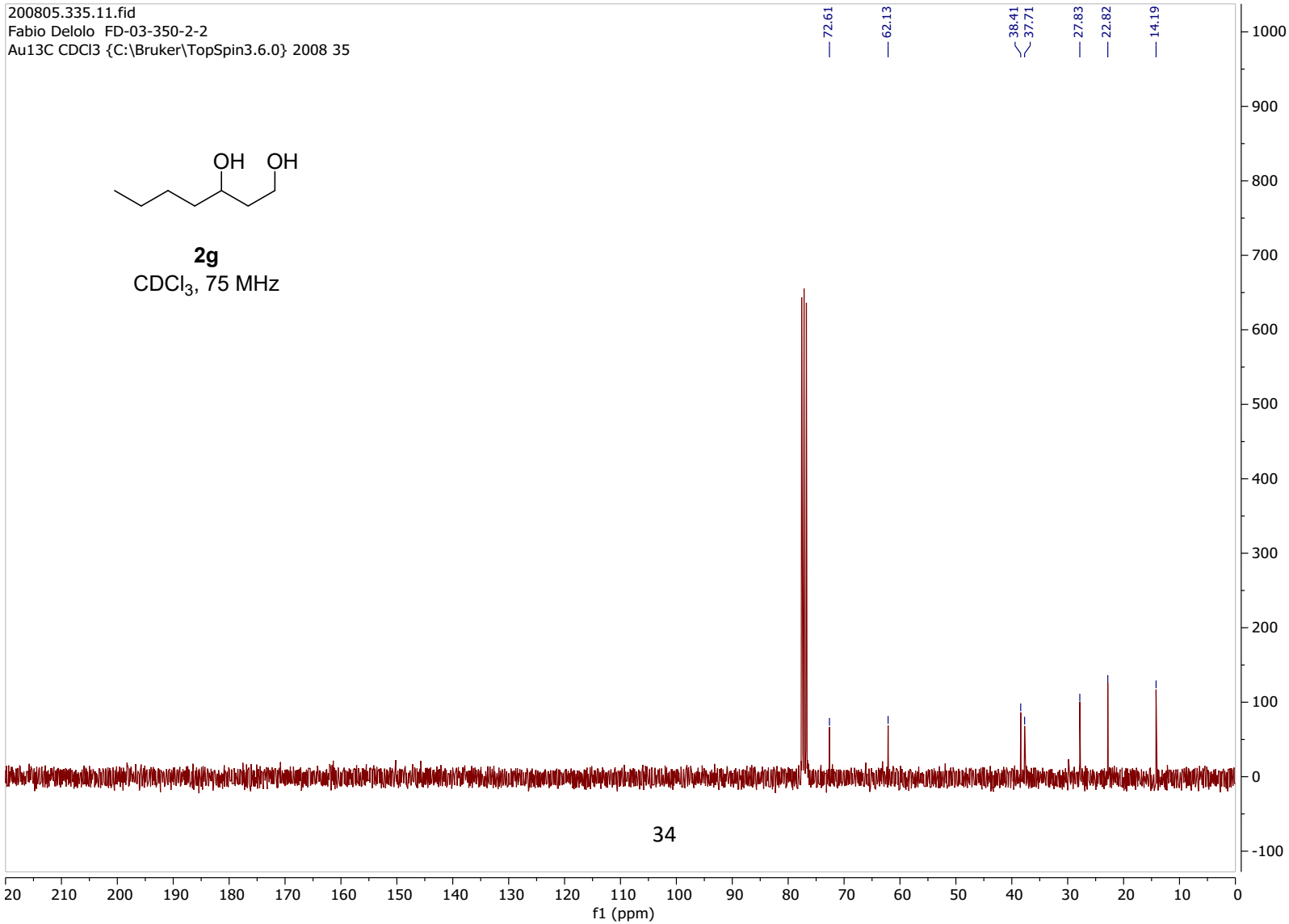
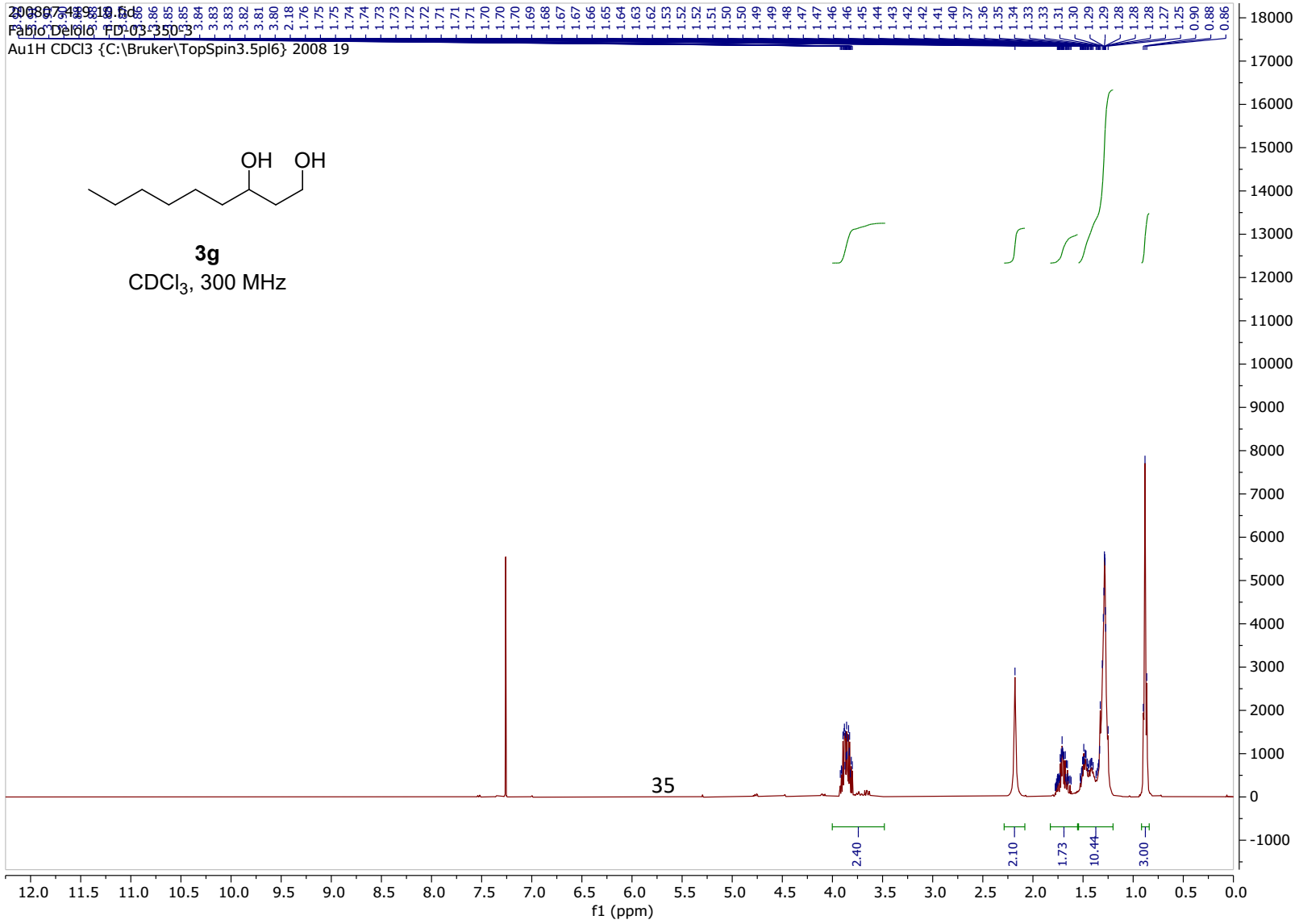
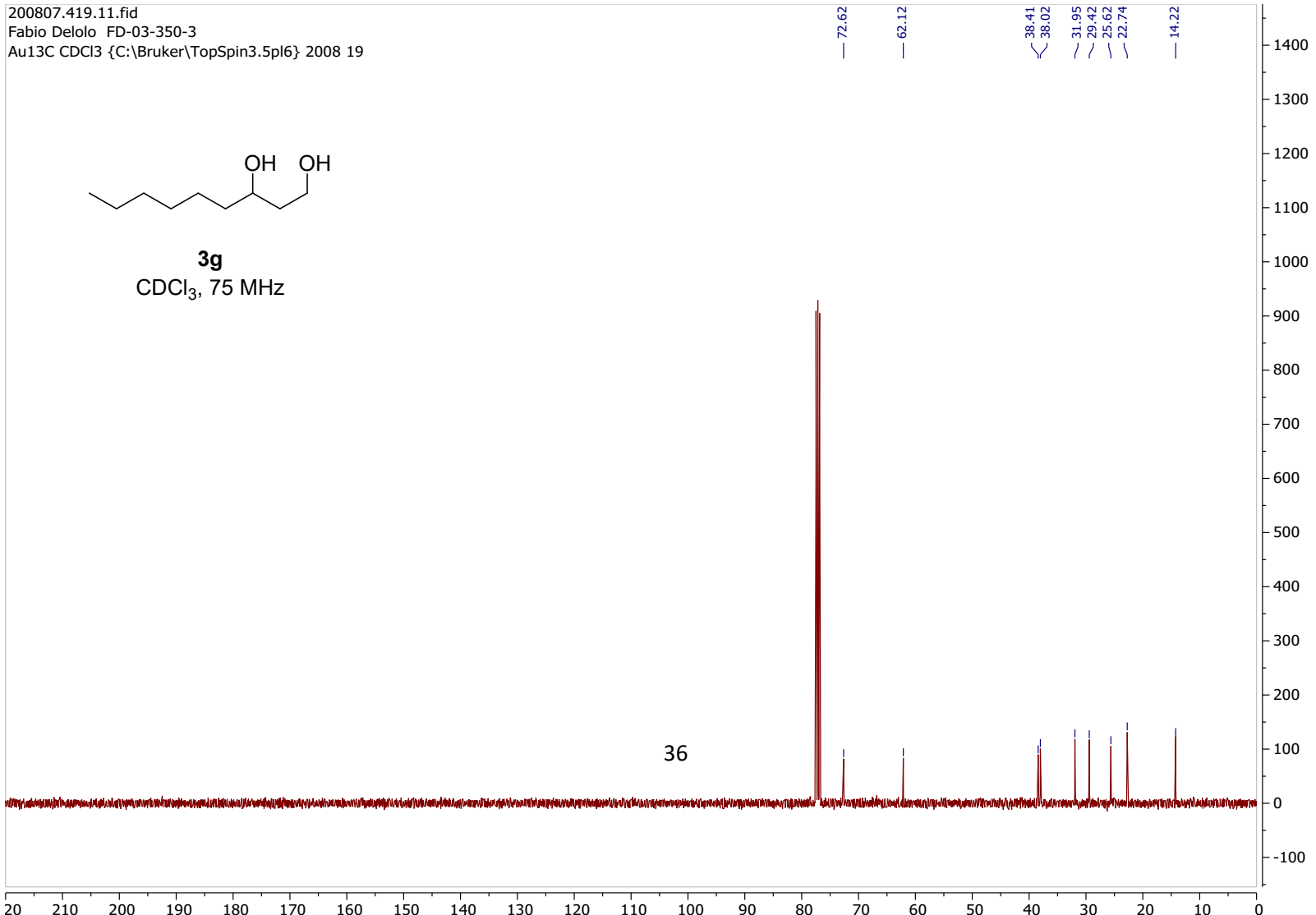
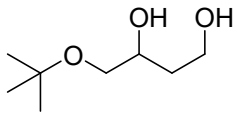
1.74
2.06
2.14
4.04
3.36
f1 (ppm)


200805.335.11.fid
Fabio Delolo FD-03-350-2-2
Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 35
72.61
62.13
38.41
37.71
27.83
22.82
14.19
OH
OH
2g
CDCl3, 75 MHz
34
f1 (ppm)


Fabio Delolo FD-03-350-3
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 2008 19
OH
OH
3g
CDCl3, 300 MHz
35
2.40
2.10
1.73
10.44
3.00
f1 (ppm)


200807.419.11.fid
Fabio Delolo FD-03-350-3
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 2008 19
72.62
62.12
38.41
38.02
31.95
29.42
25.62
22.74
14.22
OH
OH
3g
CDCl3, 75 MHz
36

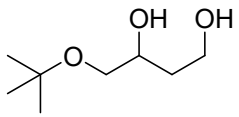
200828.f332.10.fid
Fabio Delolo, FD-03-360-1
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 32



4g

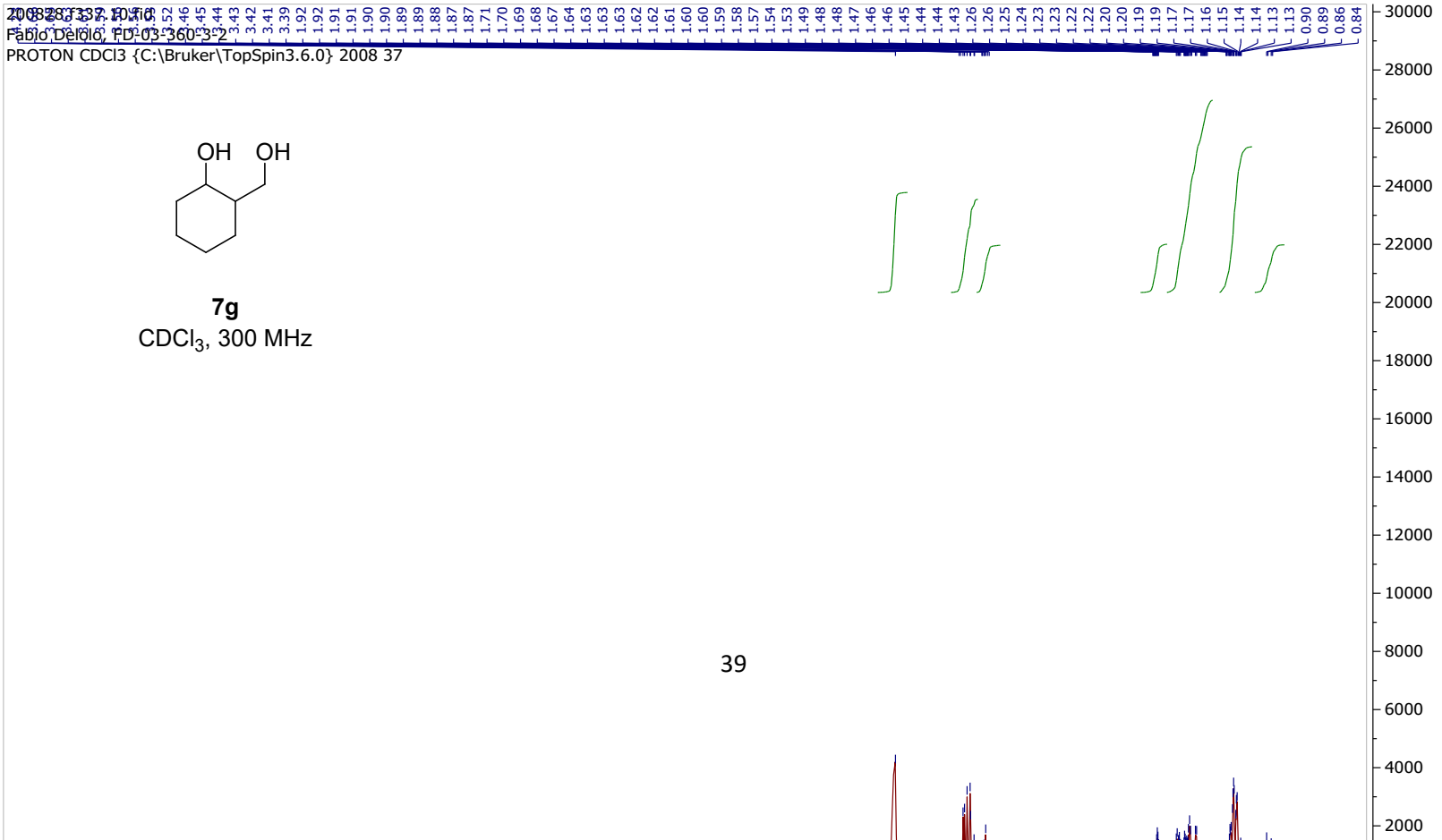
$CDCl_3$, 300 MHz

200828.f332.11.fid
Fabio Delolo, FD-03-360-1
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 32



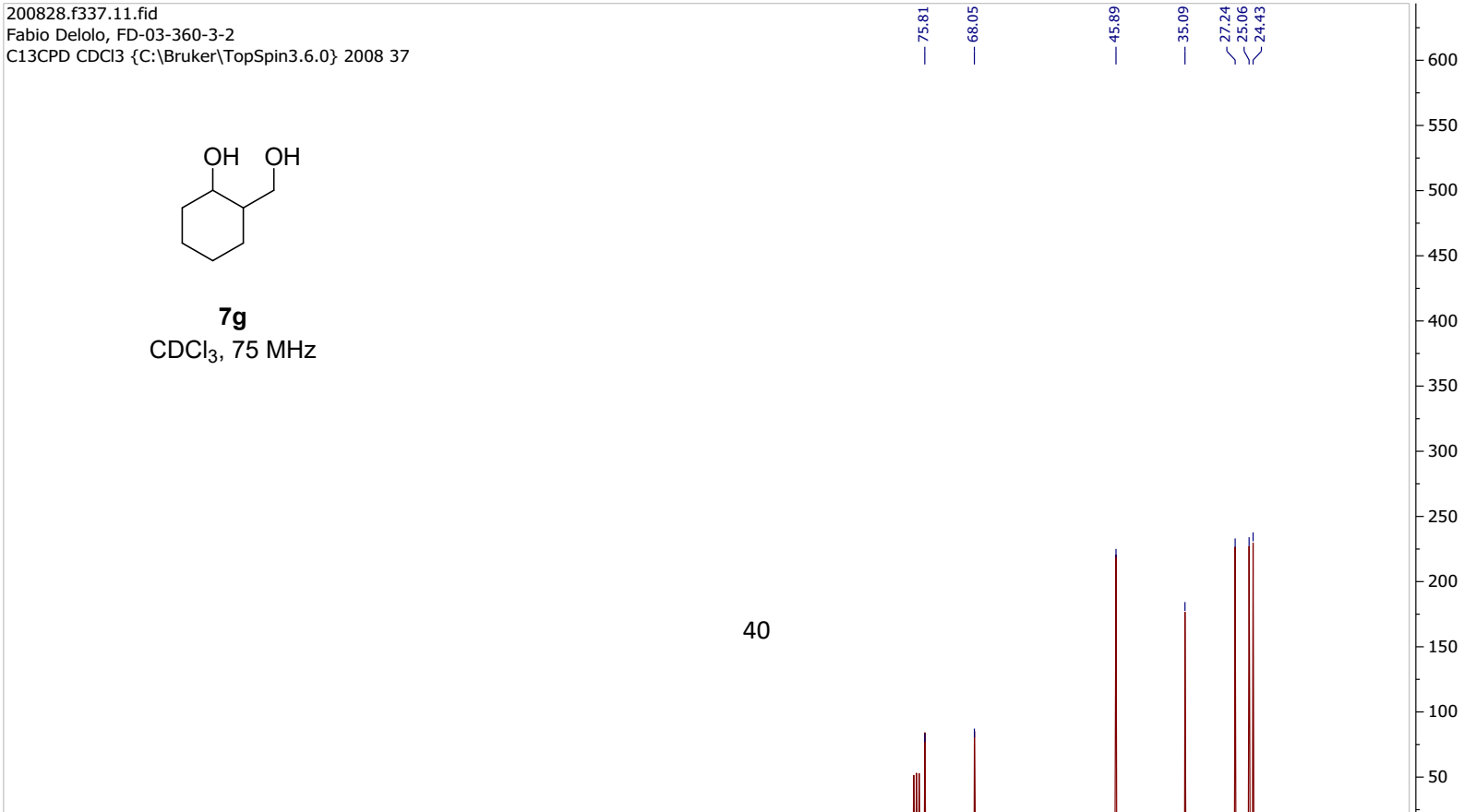
4g

$CDCl_3$, 75 MHz



7g

$CDCl_3$, 300 MHz


200828.f337.11.fid
Fabio Delolo, FD-03-360-3-2
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2008 37
75.81
68.05
45.89
35.09
27.24
25.06
24.43
OH
OH
7g
CDCl3, 75 MHz
600
550
500
450
400
350
300
250
200
150
100
50