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Supporting Information

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Palladium-Catalyzed Allylic Substitution at Four-Membered-Ring Systems: Formation of η^1-Allyl Complexes and Electrocyclic Ring Opening**

*Davide Audisio, Gopinadhanpillai Gopakumar, Lan-Gui Xie, Luís G. Alves, Cornelia Wirtz, Ana M. Martins, Walter Thiel, Christophe Farès, and Nuno Maulide**

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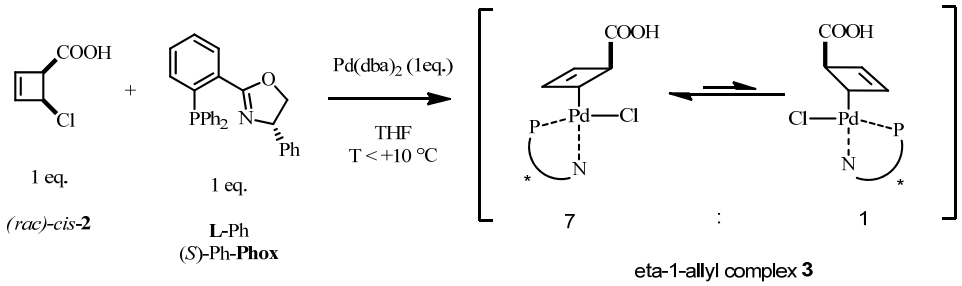
1. General Methods

All reactions were carried out in flame-dried glassware under an atmosphere of argon. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavelengths (ν) are reported in cm^{-1}. Mass spectra were obtained using a Finnigan MAT 8200 (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). Accurate mass determinations were obtained on a Brucker APEX III FT-MS (7 T magnet). All ^{1}H-NMR and ^{13}C-NMR experiments were recorded using Bruker AV-400, AV-500 and AV-600 spectrometers at 300 K. Chemical shifts (δ) are quoted in ppm and coupling constants (*J*) are quoted in Hz. The 7.27, 2.50 and 2.05 ppm resonance of residual $CHCl_3$, D_5H-DMSO and CD_3COCD_2H for proton spectra and 77.16, 39.52, 29.84 ppm resonance of $CDCl_3$, D_6-DMSO and CD_3COCD_3 for carbon spectra were used as internal references. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminum plates coated with keiselgel F_{254} with 0.2 mm thickness. Visualization was achieved by a combination of ultraviolet light (254 nm) and acidic potassium permanganate or anisaldehyde. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.). Bis(dibenzylideneacetone)palladium(0) $Pd(dba)_2$ was purchased from Sigma-Aldrich. (S)-(+)-2-[2-(Diphenylphosphino)phenyl]-4-phenyl-2-oxazoline **L**-Ph was purchased from Sigma-Aldrich or prepared according to the procedure described in the literature.[1] (*rac*)-cis-**2** was prepared according to the procedure described in the literature.[2]

[1] M. R. Krout, J. T. Mohr, B. M. Stoltz *Org. Synth.* **2009**, *86*, 181-193.
[2] D. Audisio, M. Luparia, M. T. Oliveira, D. Klütt, N. Maulide, *Angew. Chem. Int. Ed.* **2012**, *51*, 7314-7317.

2. Synthesis of η_1-allyl complex 3

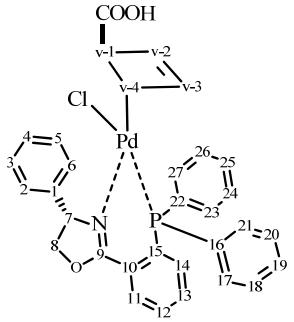


In a flame-dried schlenk flask under Argon atmosphere, $Pd(dba)_2$ (28 mg, 0.049 mmol, 1 equiv.), the **L**-Ph ligand (20 mg, 0.049 mmol, 1 equiv.) and (*rac*)-*cis*-chlorocarboxylic acid-**2** (6.5 mg, 0.049 mmol, 1 equiv.) were added. After three vacuum-Argon cycles, the schlenk is cooled at 0 °C and 1.0 mL THF-$_{d8}$ was added. The solution was stirred at the same temperature 10 minutes. The mixture is then transferred to a schlenk NMR tube and the top is melted with a flame. The mixture was analyzed at 283 K.

When unreacted starting material was still observed in the mixture, the NMR tube was shaken mechanically, avoiding the rise of temperature, to push the reaction to full conversion.

The sample is composed of two diastereoisomers (ratio 1:7). Only the major isomer has been investigated.

η_1-allyl complex 3



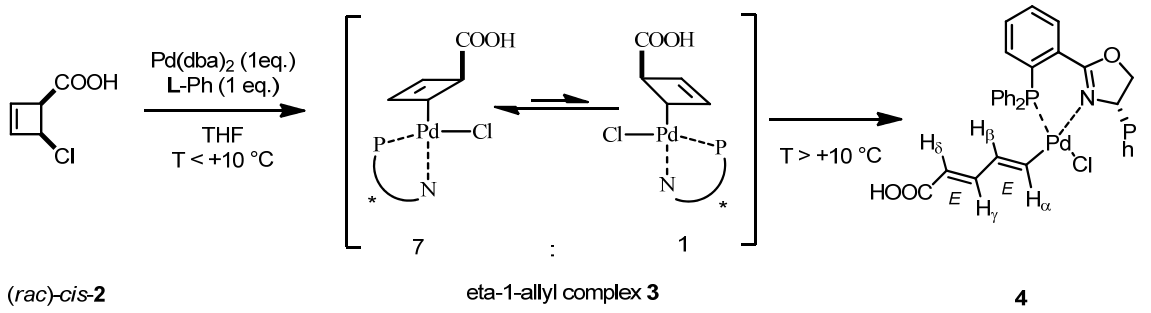
^{31}P-NMR (202 MHz, THF-$_{d8}$): 30.9 (minor isomer), 27.2 (major isomer).

^{1}H-NMR (600 MHz, THF-$_{d8}$): δ 11.00 (bs, 1H), 8.16 (ddd, J = 7.8, 4.0, 1.2 Hz, H_{11}), 7.70 (m, H_{12}), 7.57-7.73 (m, H_{13}, H_{19}, H_{25}), 7.48-7.45 (m, H_{24}, H_{26}), 7.35-7.32 (m, H_{18}, H_{20}), 7.27-7.21 (m, H_{27}, H_{23}, H_4, H_{21}, H_{17}), 7.12-7.09 (m, H_3, H_5), 7.07 (d, J = 7.4 Hz, H_2; H_6), 6. 96 (ddd, J = 10.3, 7.9, 1.0 Hz, H_{14}), 6.25 (dd, J = 10.3, 5.5 Hz, H_7), 5.58 (d, J = 2.7 Hz,

$H_{v\text{-}2}$), 5.08 (t, J = 5.08 Hz, $H_{v\text{-}3}$), 4.81 (dd, J = 10.1, 9.1 Hz, H_{8a}), 4.49 (dd, J = 9.0, 6.5 Hz, H_{8b}), 4.11 (s, $H_{v\text{-}1}$), 3.30 (s, $H_{v\text{-}4}$).

^{13}C-NMR (150 MHz, THF-*d8*): δ 172.3 (COOH), 163.2 (d, *J* = 3.3 Hz, C_9), 147.8 (d, *J* = 6.3 Hz, $C_{v\text{-}3}$), 141 (C_1), 135.4 (d, *J* = 2.3 Hz, C_{14}), 135.3 (d, *J* = 13.6 Hz, C_{17}, C_{21}), 134.3 (d, *J* = 12.1 Hz, C_{23}, C_{27}), 133.6 (d, *J* = 6.9 Hz, C_{13}), 132.9 (d, *J* = 7.4 Hz, C_{11}), 132.4 (d, *J* = 2.0 Hz, C_{12}, C_{19}), 132.3 (d, *J* = 2.3 Hz, C_{25}), 131.6 (d, *J* = 43.2, C_{15}), 130.2 (d, *J* = 11.2 Hz, C_{18}, C_{20}), 130.1 (d, *J* = 11.0, C_{24}, C_{26}), 129.8 (d, *J* = 56 Hz, C_{16}, C_{22}), 129.6 (d, *J* = 20 Hz, C_{10}), 129.5 (C_3, C_5), 129.1 (d, *J* = 7.2 Hz, $C_{v\text{-}2}$), 128.6 (C_4), 128.4 (C_2, C_6), 75.8 (C_8), 69.4 (C_7), 55.7 (d, *J* = 1.9 Hz, $C_{v\text{-}1}$), 46.0 (d, *J* = 4.3 Hz, $C_{v\text{-}4}$).

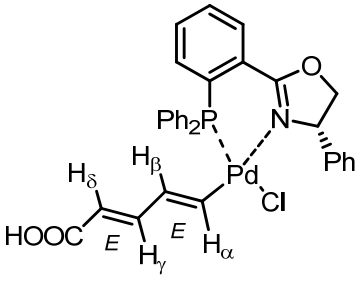
3. Synthesis of (*E,E*)-diene-complex-4



(*rac*)-*cis*-**2** eta-1-allyl complex **3** **4**

In a flame-dried schlenk flask under Argon atmosphere, $Pd(dba)_2$ (345 mg, 0.60 mmol, 1 equiv.), the ligand **L**-Ph ((S)-Phenyl-PHOX 244 mg, 0.60 mmol, 1 equiv.) and the (*rac*)-*cis*-cyclobutene-**2** (79 mg, 0.60 mmol, 1 equiv.) were evacuated three times with Ar and dissolved in THF (15 mL). The mixture was stirred 18h at r.t. then filtered through a 0.2 μm PTFE filter. Purification: SiO_2 was added to the solution and the solvent was evaporated. The powder was added to a short column and eluted with DCM, to remove the dba (dibenzylidenacetone) by-product, then with DCM:EtOH 98:2 to give the Pd-complex. The solution was concentrated in vacuo to give the (*E,E*)-diene-complex-**4** (152 mg, 0.24 mmol, 39 %).

(*E,E*)-diene-complex-4



4

^{31}P = 26.3 ppm

$J_{(H\alpha\text{-}P)}$ = 13.3 Hz

$J_{(H\beta\text{-}P)}$ = 3.6 Hz

R_f 0.36 (DCM/EtOH : 95/5).

^{1}H-NMR (600 MHz, THF-d_8): δ 10.4 (bs, 1H), 8.25 (m, 1H), 7.74 (t, *J* = 7.7. Hz, 1H), 7.61 (t, *J* = 7.7. Hz, 1H), 7.52 (m, 1H), 7.44 (m , 1H), 7.41-7.30 (m, 6H), 7.22-7.19 (m,

2H), 7.17-7.05 (m, 6H), 6.70 (dd, J_1 = 14.8 Hz, J_2 = 13.3 Hz, 1H), 6.54 (dd, J_1 = 10.0 Hz, J_2 = 4.5 Hz, 1H), 6.52 (ddd, J_1 = 15.1 Hz, J_2 = 10.8 Hz, J_3 = 0.3 Hz, 1H), 6.03 (ddd, J_1 = 14.9 Hz, J_2 = 10.9 Hz, J_3 = 3.6 Hz, 1H), 5.09 (d, J = 15.2 Hz, 1H), 4.82 (dd, J_1 = 9.9 Hz, J_2 = 9.1 Hz, 1H), 4.55 (dd, J_1 = 9.0 Hz, J_2 = 4.5 Hz, 1H).

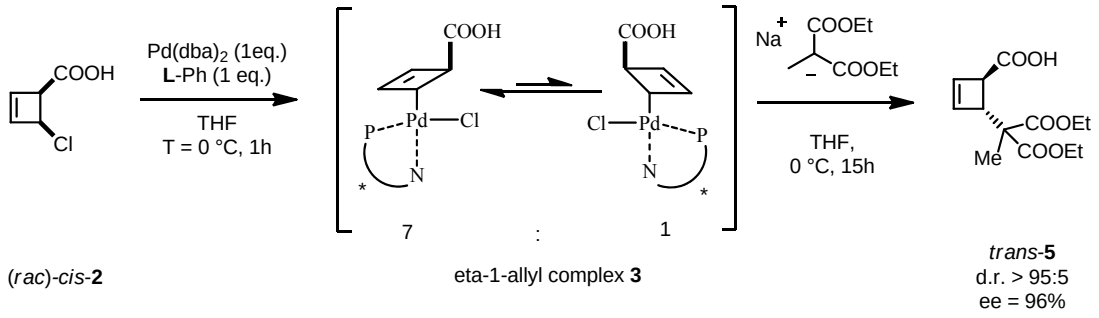
^{13}C-NMR (150 MHz, THF-d_8) δ 168.9, 163.3 (d, J_{C-P} = 5.0 Hz), 161.8, 147.0 (d, J_{C-P} = 3.0 Hz), 142.0, 136.2 (d, J_{C-P} = 3.5 Hz), 135.4 (d, J_{C-P} = 1.0 Hz), 135.3 (d, J_{C-P} = 13.6 Hz, 2C), 134.6 (d, J_{C-P} = 11.1 Hz, 2C), 133.8 (d, J_{C-P} = 6.6 Hz), 133.2 (d, J_{C-P} = 7.6 Hz), 132.6 (d, J_{C-P} = 1.7 Hz), 132.3 (d, J_{C-P} = 2.4 Hz), 131.7 (d, J_{C-P} = 2.3 Hz), 131.2 (d, J_{C-P} = 41.0 Hz), 130.1 (d, J_{C-P} = 11.3 Hz, 2C), 129.9 (d, J_{C-P} = 20.0 Hz), 129.7 (d, J_{C-P} = 56.1 Hz), 129.4 (d, J_{C-P} = 11 Hz, 2C), 129.3 (2C), 129.0 (d, J_{C-P} = 56.1 Hz), 128.4, 128.3 (2C), 113.8, 75.9, 68.9.

^{31}P-NMR (162 MHz, THF-d_8) δ 26.3.

^{15}N-NMR (61 MHz, THF-d_8) δ -190.4.

HRMS (ESI$^+$): exact mass calculated for $[M\text{-}Cl]^+$ ($C_{32}H_{27}{}^{35}Cl_1N_1O_3P_1Pd_1$) requires *m*/*z* 610.0774, found *m*/*z* 610.0772.

Stoichiometric experiment performed with diethyl-(2-methyl)malonate salt



(*rac*)-*cis*-**2**

eta-1-allyl complex **3**

trans-**5**
d.r. > 95:5
ee = 96%

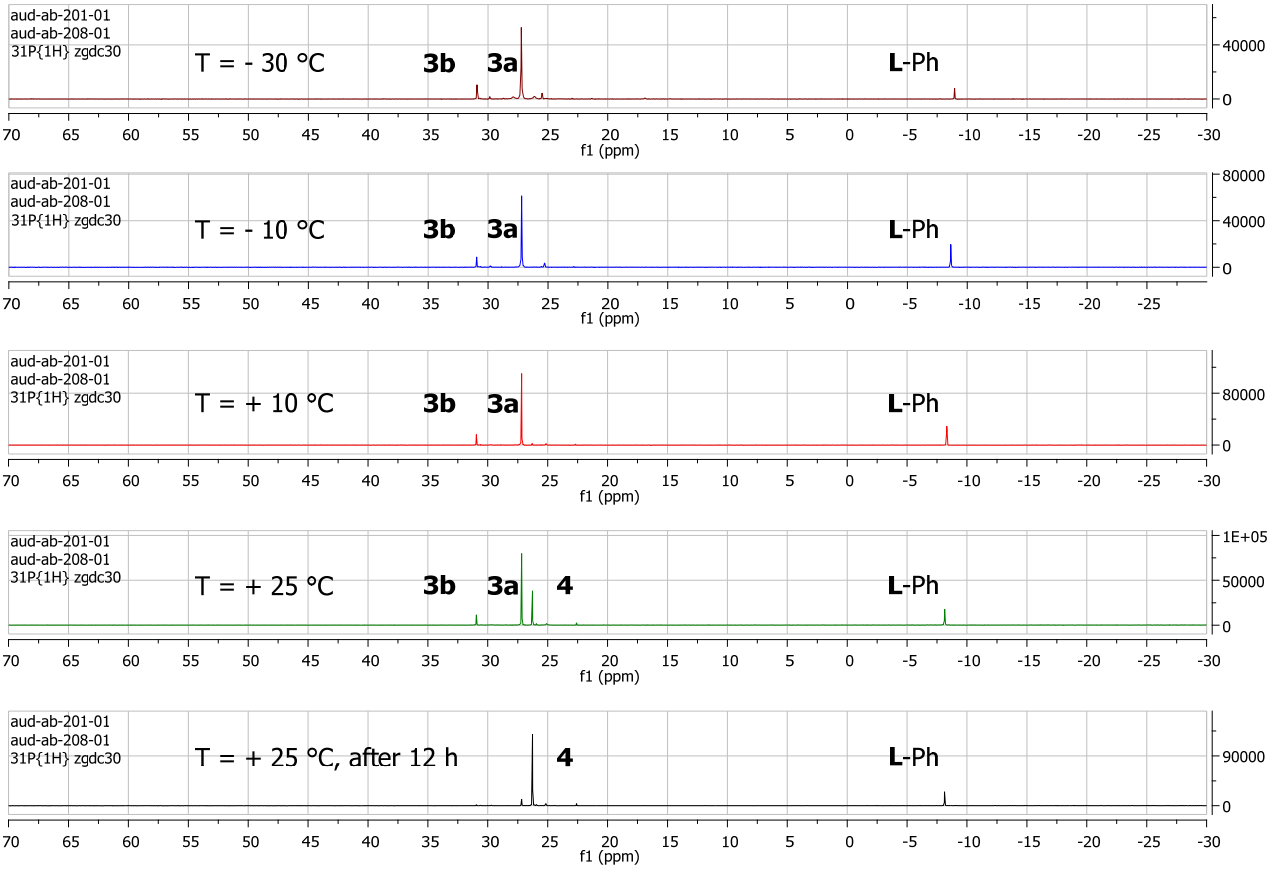
In a schlenk flask (dry and under Argon atmosphere), $Pd(dba)_2$ (28 mg, 0.049 mmol, 1 equiv.), **L**-Ph ((S)-Ph-Phox, 20 mg, 0.049 mmol, 1 equiv.) and (*rac*)-*cis*-chlorocarboxylic acid-**2** (6.5 mg, 0.049 mmol, 1 equiv.) were added. After three vacuum-Argon cycles, the schlenk is cooled at 0 °C and 1.5 mL THF was added. The solution was stirred at the same temperature 60 minutes.

In a second dry flask (under Argon atmosphere), to a suspension of sodium hydride (3.9 mg of 60% dispersion in mineral oil, 0.098 mmol, 2.0 equiv.) in THF (1.0 mL), diethyl methylmalonate (18 μL, 0.108 mmol, 2.2 equiv.) was added dropwise at room temperature and the resulting solution was stirred for 10 min.
The solution of the sodium salt of the malonate is then added dropwise with a syringe to the schlenk containing the palladium/ligand/cyclobutene complex. The mixture was allowed to stir at 0 °C for 15hrs.

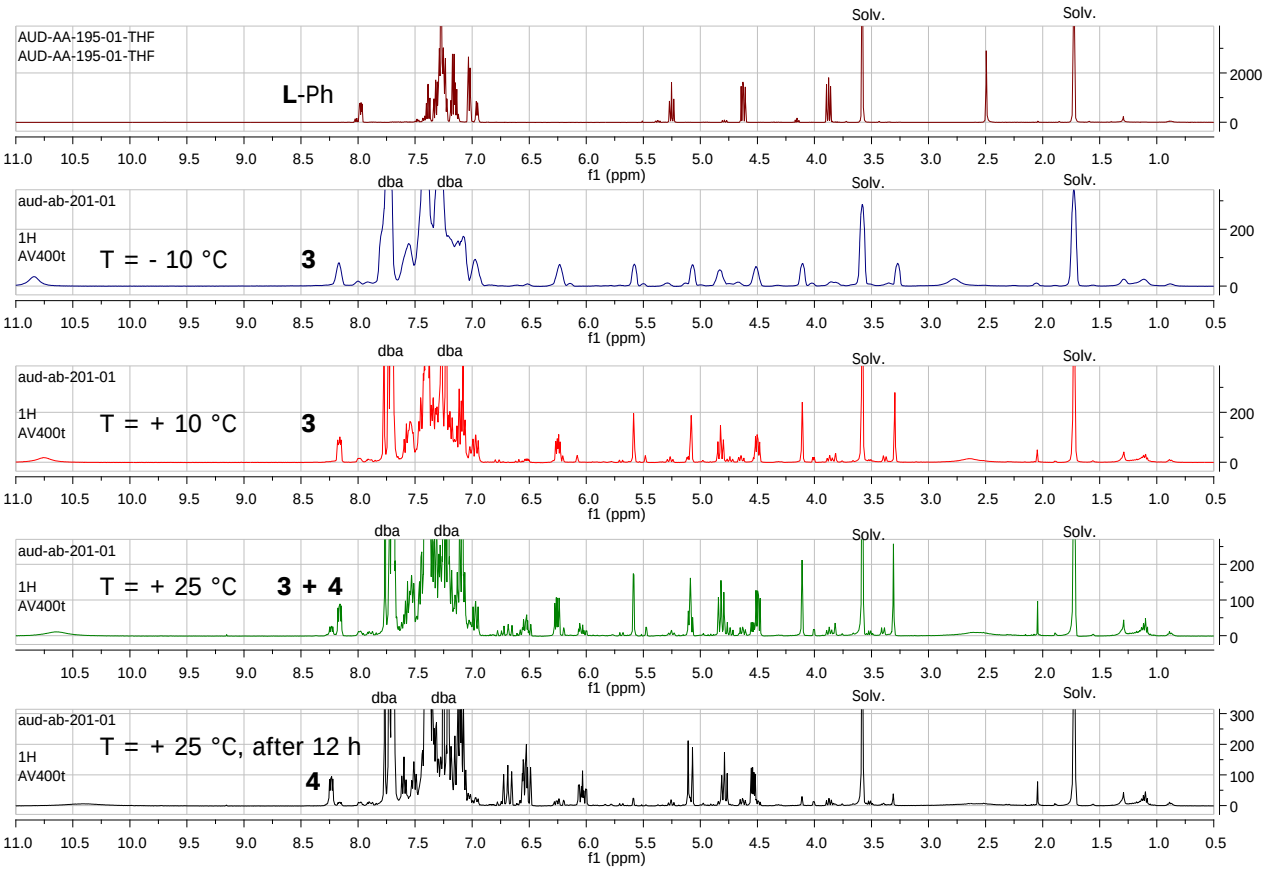
After 15h, the mixture was quenched with $NaHCO_3$ sat. (5 mL) and allowed to warm to room temperature. The aqueous layer was washed with MTBE (3 x 7 mL), slowly acidified with 1.2N HCl (pH ~ 2) and extracted with EtOAc (3 x 7 mL). The combined organic layers were washed with brine (5 mL), dried (Na_2SO_4) and concentrated under reduced pressure to yield the crude cyclobutene carboxylic acid *trans*-**5** (d.r. > 95/5).
For HPLC purposes, to determine the enantiomeric excess, *trans*-**5** was subjected to N-benzylamide formation without further purification according to the following procedure. The crude product was dissolved in CH_2Cl_2 (1.0 mL) and cooled to 0 °C. Benzyl amine (6.0 μL, 0.054 mmol, 1.1 equiv.), HOBt (8.0 mg, 0.054 mmol, 1.1 equiv.) and EDCI (10.5 mg, 0.054 mmol, 1.1 equiv.) were added in this order and the resulting mixture was warmed to room temperature. After being stirred for 16h, CH_2Cl_2 (10 mL) was added and the organic layer was washed successively with aqueous 1N HCl solution (5 mL), brine (5 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (pentane/EtOAc, 7/3) to give pure cyclobutene amide.

Spectroscopic properties in agreement with those reported in the literature.[2] The enantiomeric purity was measured through chiral HPLC for the corresponding N-benzylamide, according to the procedure previously reported.[2] e.e. measured: 96%.

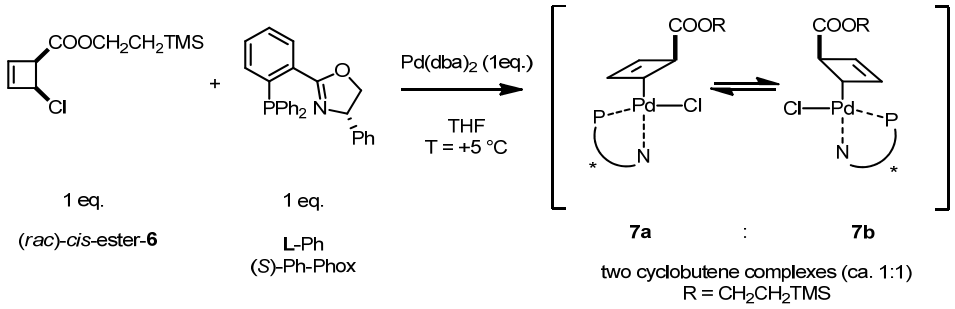
- Temperature resolved ^{31}P-NMR spectra showing the conversion of complex **3a** (major isomer) and **3b** (minor isomer) into the (*E*,*E*)-diene **4**.



- Temperature resolved ^{1}H-NMR spectra showing the conversion of complex **3a** (major isomer) and **3b** (minor isomer) into the (*E*,*E*)-diene **4**.



4. Synthesis of η_1-allyl complex 7a - 7b (with R = CH_2CH_2TMS)

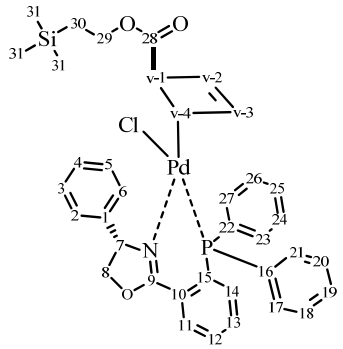


In a schlenk flask (dry and under Argon atmosphere), $Pd(dba)_2$ (28 mg, 0.049 mmol, 1 equiv.), the Ph-Phox ligand (20 mg, 0.049 mmol, 1 equiv.) and (*rac*)-*cis*-chlorocarboxylic ester-**6** (11.5 mg, 0.049 mmol, 1 equiv.) were added. After three vacuum-Argon cycles, the schlank is cooled at 0 °C and 1.0 mL THF-$_{d8}$ was added. The solution was stirred at the same temperature 10 minutes. The mixture is then transferred to a schlenk NMR tube and the top is melted with a flame. The mixture was studied at +5 °C by multinuclear 2D-NMR analysis.

When unreacted starting material was still observed in the mixture, the NMR tube was shaken mechanically, avoiding the rise of temperature, to push the reaction to full conversion.

Two diastereoisomeric species are observed (ratio ca. 1:1).

η_1-allyl complex 7a - 7b (with R = CH_2CH_2TMS)



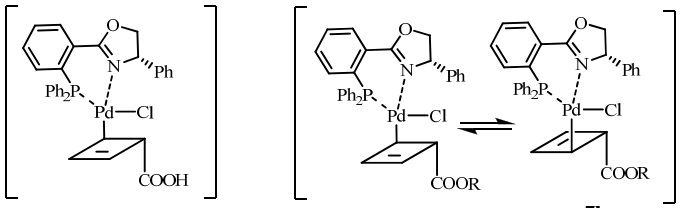
^{1}H-NMR (600 MHz, THF-*d8*): δ 8.14 (m, H_{11}, $H_{\underline{11}}$), 7.68 (m, H_{12}, $H_{\underline{12}}$), 7.55 (t, *J* = 7.5 Hz, C_{13}, $C_{\underline{13}}$), 7.51-7.15 (m, H_4, $H_{\underline{4}}$, H_2, H_6, H_{17}, H_{21}, $H_{\underline{17}}$, $H_{\underline{21}}$, H_{24}, $H_{\underline{24}}$, H_{26}, $H_{\underline{26}}$, H_{19}, $H_{\underline{19}}$, H_{25}, $H_{\underline{25}}$), 7.12 (d, *J* = 7.3 Hz, $H_{\underline{2}}$, $H_{\underline{6}}$), 7.08-7.02 (m, H_3, H_5, $H_{\underline{3}}$, $H_{\underline{5}}$), 6.98-6.92 (m, H_{14}, $H_{\underline{14}}$), 6.65 (dd, *J* = 10.0, 4.6 Hz, H_7), 6.53 (dd, *J* = 10.0, 4.6 Hz, $H_{\underline{7}}$), 6.35 (d, $H_{v\text{-}3}$), 5.58 (d, *J* = 2.4 Hz, $H_{v\text{-}2}$), 5.57-5.56 ($H_{\underline{v\text{-}3}}$, $H_{\underline{v\text{-}2}}$), 4.72 (m, H_{8a}, $H_{\underline{8a}}$), 4.53 (dd, *J* = 9.0, 4.4 Hz, H_{8b}), 4.51 (dd, *J* = 9.0, 4.6 Hz, $H_{\underline{8b}}$), 4.35 (s, $H_{\underline{v\text{-}1}}$), 4.03-3.98 (m, $H_{\underline{29a}}$, $H_{\underline{29b}}$), 3.83 (a, $H_{v\text{-}1}$), 3.76 (m, H_{29a}), 3.72 (m, H_{29b}), 3.39 (d, 8.3 Hz, $H_{\underline{v\text{-}4}}$), 3.22 (d, *J* = 12.9 Hz, $H_{v\text{-}4}$), 0.92-0.90 (m, $H_{\underline{30a}}$, $H_{\underline{30b}}$), 0.72 (m, H_{30a}, H_{30b}), 0.02 (s, 3x $H_{\underline{31}}$), -0.03 (s, 3x H_{31}).
Due to presence of residual dba (dibenzylideneacetone), only a partial assignment of the aromatic region was carried out.

^{13}C-NMR (150 MHz, THF-*d8*): δ 173.8 ($C_{\underline{28}}$), 173.5 (C_{28}), 162.7 (C_9), 162.6 ($C_{\underline{9}}$), 150.3 (d, J = 2.4 Hz, $C_{v\text{-}3}$), 149.3 (d, J = 2.7 Hz, $C_{\underline{v\text{-}3}}$), 142.1 ($C_1$, $C_{\underline{1}}$), 135.6-135.1 (C_{17} C_{21}, C_{14}, C_{17} C_{21}, C_{14}), 134.6-134.3 (C_{23}, C_{27}, $C_{\underline{23}}$, $C_{\underline{27}}$) 133.4 (d, J = 6.4 Hz, C_{13}), 133.3 (d, J = 6.3 Hz, $C_{\underline{13}}$), 132.8 (d, J = 7.3 Hz, C_{11}), 132.1 (C_{12}, $C_{\underline{12}}$), 131.8 (C_{19}, $C_{\underline{19}}$), 131.7 (C_{25}), 131.6 ($C_{\underline{25}}$), 130.5-129.4 (C_{18}, $C_{\underline{18}}$, C_{20}, $C_{\underline{20}}$, C_{24}, $C_{\underline{24}}$, C_{26}, $C_{\underline{26}}$, C_{16}, $C_{\underline{16}}$, C_{22}, $C_{\underline{22}}$, C_{10}, $C_{\underline{10}}$), 129.3 (C_3, C_5, $C_{\underline{3}}$, $C_{\underline{5}}$), 128.5-128.4 (C_2, C_6, $C_{\underline{2}}$, $C_{\underline{6}}$), 128.3 ($C_{\underline{v\text{-}2}}$), 128.2 ($C_4$, $C_{\underline{4}}$), 126.6 ($C_{v\text{-}2}$), 69.2 (C_7), 69.0 ($C_{\underline{7}}$), 61.6 ($C_{\underline{29}}$), 61.4 (C_{29}), 56.7 (d, J = 2.4 Hz, $C_{v\text{-}1}$), 56.5 (d, J = 1.4 Hz, $C_{\underline{v\text{-}1}}$), 44.9 (d, J = 3.7 Hz, $C_{\underline{v\text{-}4}}$), 44.5 (d, J = 3.1 Hz, $C_{v\text{-}4}$), 17.9 (C_{30}), 17.8 ($C_{\underline{30}}$), -1.3 (3x $C_{\underline{31}}$), -1.4 (3x C_{31}).

^{31}P-NMR (202 MHz, THF-$_{d8}$): 30.5, 28.7.

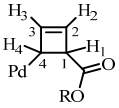
HRMS (ESI$^+$): exact mass calculated for $[M\text{-}Cl]^+$ ($C_{37}H_{39}NO_3{}^{35}ClPPdSi$) requires *m*/*z* 710.1483, found *m*/*z* 710.1477.

For comparison, in the table below, the chemical shifts (reported in ppm) of ^{1}H- and ^{13}C-NMR for the η_1-allyl complexes **3**, **7a** and **7b** are shown.



3 **7a** **7b**

R= CH_2CH_2TMS

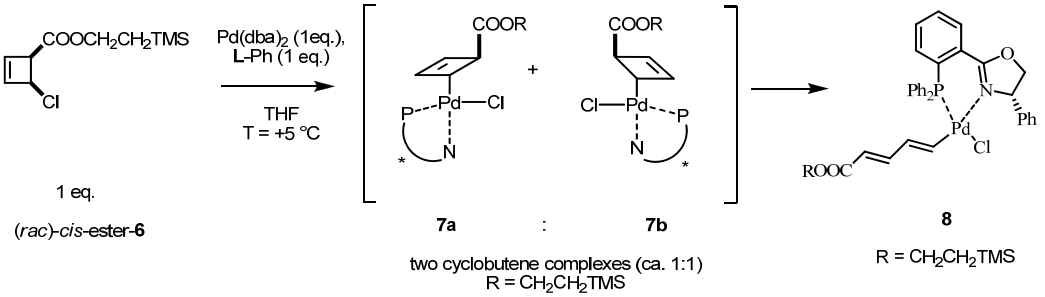


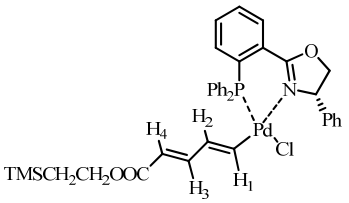
	H_1	H_2	H_3	H_4	C_1	**C_2**	C_3	**C_4**
3	4.11	6.58	5.08	3.30	55.73 (1.9)	129.06 (7.2)	147.86 (6.3)	46.05 (4.3)
7a	3.83	5.58	6.34	3.22	56.68 (2.4)	126.62 (3.6)	150.30 (2.4)	44.50 (3.1)
7b	4.35	5.56	5.57	3.39	56.50 (1.4)	128.39 (-)	149.28 (2.7)	44.94 (3.7)

The chemical shifts (δ) are reported in ppm.
The values between brackets represent the $J_{C\text{-}P}$ (reported in Hz)

5. (*E,E*)-diene-complex-8 (with R = CH_2CH_2TMS)

After standing for 3 hrs at room temperature, the isomeric complexes **7a** and **7b** (prepared according to the previously described procedure) disappear and the corresponding (*E,E*)-diene-**8** is formed.





8

The (*E,E*)-diene-**8** has a very similar ^{1}H-NMR pattern to the (*E,E*)-diene-**4**.

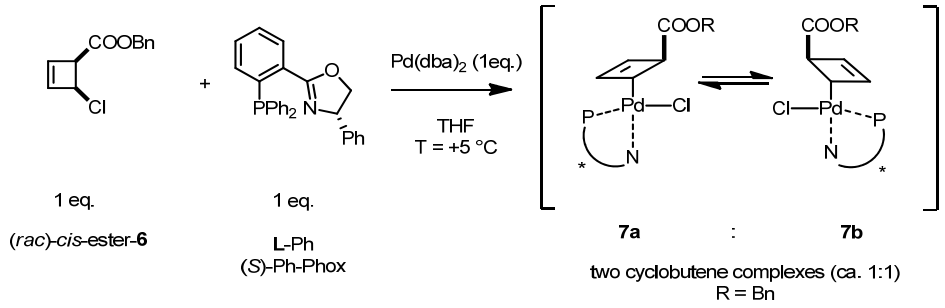
^{1}H-NMR (300 MHz, THF-*d8*): 8.24 (dd, J = 7.2, 4.3 Hz, $1H_{arom.}$), 7.75-7.06 ($18H_{arom.}$ + dba byproduct), 6.71 (dd, J_{PH} = 14.0, J_{HH} = 15.2, H_4), 6.65-6.51 (m, 2H, H_3, $H_{oxazoline}$), 6.04 (ddd, J_{HH} = 14.6, J_{HH} = 11.1, J_{HP} = 3.7 Hz, H_2), 5.11 (d, J = 15.2 Hz, H_1), 4.79 (t, J = 9.4 Hz, $1H_{oxazoline}$), 4.54 (dd, J = 8.9, 4.6 Hz, $1H_{oxazoline}$), 4.06 (t, J = 8.0 Hz, $2H_{CH2CH2TMS}$), 0.91 (t, J = 8.1 Hz, $2H_{CH2CH2TMS}$), 0.01 (s, $9H_{TMS}$).

^{31}P-NMR (121 MHz, THF-*d8*): 26.1.

HRMS (ESI^+): exact mass calculated for $[M-Cl]^+$ ($C_{37}H_{39}NO_3{}^{35}ClPPdSi$) requires *m*/*z* 710.1483, found *m*/*z* 710.1487.

Attempts to further purify intermediate **8** by column chromatography have been unsuccessful.

6. Synthesis of η_1-allyl complex 7a - 7b (with R = Bn)



In a schlenk flask (dry and under Argon atmosphere), $Pd(dba)_2$ (28 mg, 0.049 mmol, 1 equiv.), the Ph-PHOX ligand (20 mg, 0.049 mmol, 1 equiv.) and (*rac*)-*cis*-chlorocarboxylic benzyl ester-**6** (11.0 mg, 0.049 mmol, 1 equiv.) were added. After three vacuum-Argon cycles, the schlenk is cooled to 0 °C and 1.5 mL THF-$_{d8}$ was added. The solution was stirred at the same temperature 10 minutes. The mixture is then transferred to a schlenk NMR tube and the top is melted with a flame. The mixture was studied by NMR at 0 °C.

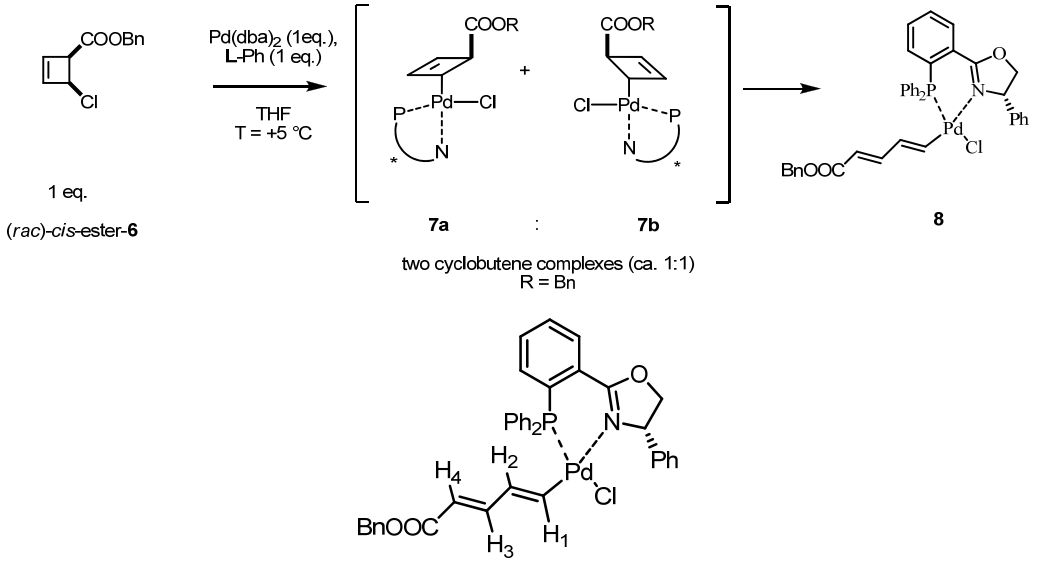
Two diastereisomeric species are observed (ratio ca. 1:1).

^{1}H-NMR (300 MHz, THF-$_{d8}$): δ 8.20-8.07 (m, 2H, $H_{arom.}$), 7.76-6.94 (m, 36$H_{arom.}$ + dba) 6.59 (dd, *J* = 10.1, 5.0 Hz, 2H, $H_{oxazoline}$), 6.30 (s, 1H), 5.58 (s, 3H), 4.97 (m, 2H $_{CH2C5H6}$), 4.74 (m, 4H, 2$H_{oxazoline}$ + 2$H_{CH2C5H6}$), 4.52 (dt, *J* = 9.1, 4.7 Hz, 2H, $H_{oxazoline}$), 4.44 (s, 1H), 3.97 (s, 1H), 3.45 (d, *J* = 8.2 Hz, 1H), 3.27 (d, *J* = 13.0 Hz, 1H).

^{31}P-NMR (121 MHz, THF-$_{d8}$): 33.4, 31.4.

7. (*E,E*)-diene-complex-8 (with R = Bn)

After 5 hrs at room temperature, the isomeric complexes **7a** and **7b** (prepared according to the previously described procedure) disappear and the corresponding (*E,E*)-diene-**8** is formed.

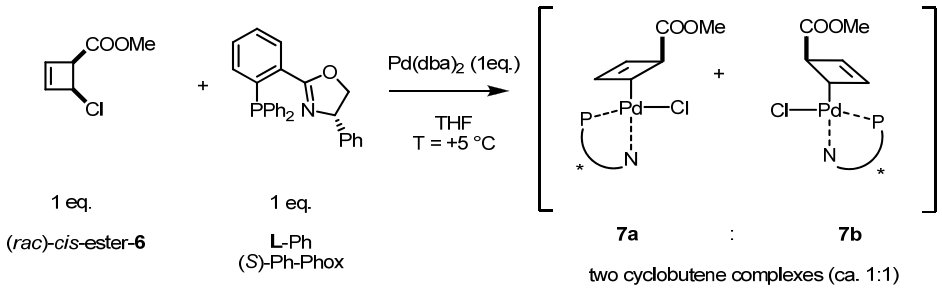


8

^{1}H-NMR (300 MHz, THF-*d8*): δ 8.24 (dd, *J* = 7.7, 4.1 Hz, 1H$_{arom.}$), 7.76-7.04 (m, 18H$_{arom.}$ + dba) 6.85-6.68 (m, 1H, H$_1$), 6.66-6.46 (m, 2H, H$_3$, H$_{oxazoline}$), 6.06 (ddd, *J* = 14.6, 10.9, 3.5 Hz, 1H, H$_2$), 5.18 (d, *J* = 15.0 Hz, 1H, H$_4$), 5.01 (d, *J* = 1.6 Hz, 2H, H$_{CH2C6H5}$), 4.79 (t, *J* = 9.5 Hz, 1H, H$_{oxazoline}$), 4.53 (dd, *J* = 8.9, 4.5 Hz, 1H, H$_{oxazoline}$).

^{31}P-NMR (121 MHz, THF-*d8*): 28.8.

8. Synthesis of η_1-allyl complex 7a - 7b (with R = Me)



In a schlenk flask (dry and under Argon atmosphere), $Pd(dba)_2$ (28 mg, 0.049 mmol, 1 equiv.), the Ph-PHOX ligand (20 mg, 0.049 mmol, 1 equiv.) and (*rac*)-*cis*-chlorocarboxylic methyl ester-**6** (7.2 mg, 0.049 mmol, 1 equiv.) were added. After three vacuum-Argon cycles, the schlenk is cooled at 0 °C and 1.5 mL THF-$_{d8}$ was added. The solution was stirred at the same temperature 10 minutes. The mixture is then transferred to a schlenk NMR tube and the top is melted with a flame. The mixture was studied by NMR at 0 °C.

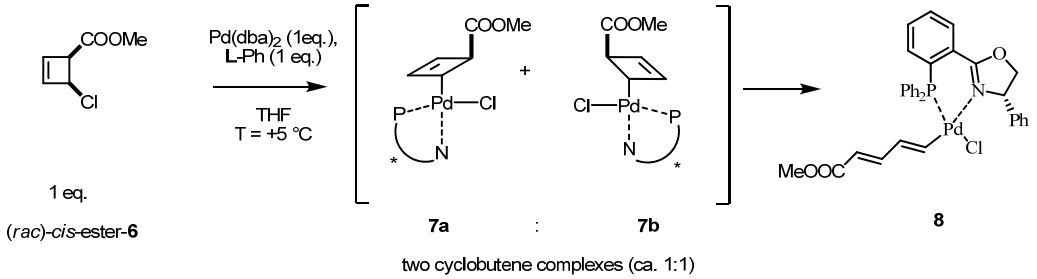
Two diastereisomeric species are observed (ratio ca. 1:1).

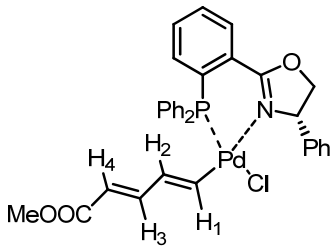
^{1}H NMR (300 MHz, THF) δ 8.22-8.09 (m, 2H), 7.76-6.98 (m, H_{arom} + dba) 6.60-6.53 (m, 2H, $H_{oxazoline}$), 6.34 (s, 1H), 5.63 (s, 1H), 5.56 (s, 2H), 4.74 (t, J = 9.4 Hz, 2H, $H_{oxazoline}$), 4.56-4.48 (m, 2H, $H_{oxazoline}$), 4.36 (s, 1H), 3.81 (s, 1H), 3.44 (s, 3H), 3.34 (d, J = 9.5 Hz, 1H), 3.26-3.22 (m, 4H).

^{31}P-NMR (121 MHz, THF-$_{d8}$): 30.2, 28.6.

9. (*E,E*)-diene-complex-8 (with R = Me)

After 3 hrs at room temperature, the isomeric complexes **7a** and **7b** (prepared according to the previously described procedure) disappear and the corresponding (*E,E*)-diene-**8** is formed.



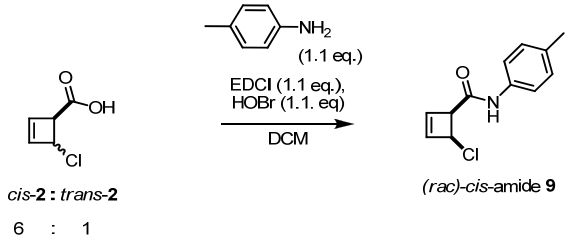


8

^{1}H-NMR (300 MHz, THF-*d8*): δ 8.28-8.17 (m, 1H$_{arom.}$), 7.75-7.68 (m, H$_{arom.}$+dba), 7.60 (t, *J* = 7.6 Hz, 2H), 7.55-7.46 (m, 2H), 7.43-7.07 (m, H$_{arom.}$ + dba), 6.75 (t, *J* = 14.1 Hz, 1H, H$_1$), 6.57-6.52 (m, 2H, H$_3$, H$_{oxazoline}$), 6.05 (t, *J* = 12.8 Hz, 1H, H$_2$), 5.12 (d, *J* = 15.2 Hz, 1H, H$_4$), 4.79 (t, *J* = 9.3 Hz, 1H, H$_{oxazoline}$), 4.54 (dd, *J* = 8.7, 4.3 Hz, 1H, H$_{oxazoline}$), 3.50 (s, 3H).

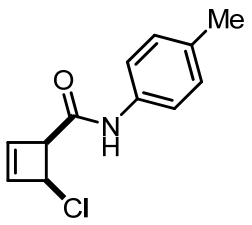
^{31}P-NMR (121 MHz, THF-*d8*): 25.9.

10. Synthesis of (*rac*)-*cis*-amide-9



To a cold (0°C) stirred solution of a crude mixture of *cis*-**2** and *trans*-**2** isomers (6:1 ratio *cis*-**2** / *trans*-**3**, 1.50 mmol, 1.0 equiv.)[2] in dry DCM (15 mL), under Argon, EDCI (315 mg, 1.65 mmol, 1.1 equiv.), HOBt (222 mg, 1.65 mmol, 1.1 equiv.) and *p*-toluidine (178 mg, 1.65 mmol, 1.1 equiv.) were added in this order and the resulting mixture was stirred at room temperature. After 14h, an aqueous solution of $NaHCO_3$ (30 mL) was added and the mixture was extracted successively with DCM (10 mL x 3 times). The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. ^{1}H-NMR analysis of the crude mixture showed that the ratio between *trans*-amide-**9** and *cis*-amide-**9** was 1:4. This crude material was carefully separated by flash column chromatography on silica gel (n-pentane/EtOAc, 8/2 to 6/4) to afford *trans*-amide-**9b** (43 mg, 0.196 mmol, 13 %) as yellow solid, followed by the more polar *cis*-**9b** (172 mg, 0.777 mmol, 52 %) as a yellow solid.

cis-4-chloro-_N_-(_p_-tolyl)cyclobut-2-enecarboxamide (_cis_-amide-9)

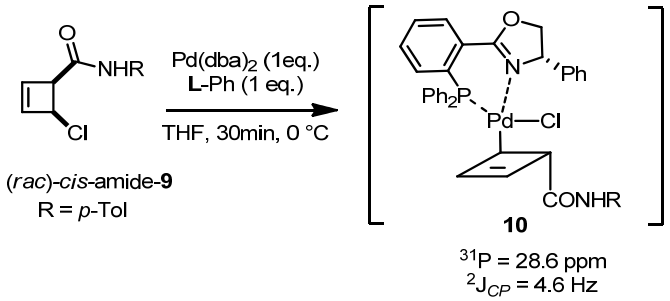


(*rac*)-*cis*-amide-**9**

Yellow solid; R_f 0.34 (*n*-pentane/EtOAc : 7/3); IR (neat) ν_{max} 3296, 3262, 3133, 3082, 1661, 1608, 1543, 1512, 1405, 1356, 1304, 1282, 1250, 1188, 1132, 999, 902, 813, 774,

746; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.15 (bs, 1H), 7.42 (d, *J* = 8.4, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 2.6 Hz, 1H), 6.38 (m, 1H), 5.12 (d, *J* = 4.3, 1H), 4.10 (d, *J* = 4.3 Hz, 1H), 2.30 (d, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 167.4, 142.8, 136.5, 134.8, 134.4, 129.5 (2C), 120.5 (2C), 56.8, 56.6, 20.9; HRMS (ESI^+): exact mass calculated for $[M+Na]^+$ ($C_{12}H_{12}{}^{35}ClNNaO$) requires *m*/*z* 244.0500, found *m*/*z* 244.0501.

11. Procedure for the preparation of crystal of complex 10



In a schlenk flask (dry and under Argon atmosphere), $Pd(dba)_2$ (57.5 mg, 0.1 mmol, 1.0 equiv.), the ligand **L**-Ph (40.75 mg, 0.1 mmol, 1.0 equiv.) and *cis*-chlorocarboxylic amide-**9** (22.17 mg, 0.1 mmol, 1.0 equiv.) were added. After three vacuum-Argon cycles, the solids were cooled at 0 °C. After 5 min., 3.0 mL THF was added. The solution was stirred at 0 °C for 30 min. After removing the solvent under vacuum, DCM (5 mL) was added to dissolve the solid residue. The resulting mixture was then filtered and concentrated carefully to about 1.5 mL volume. 0.5 mL n-pentane was added dropwise. A precipitate of complex **10** containing residual dba as the main impurity was found after 2 days of standing at low temperature (-20 °C). Attempting to recrystallize this precipitate resulted in decomposition. X-ray quality crystals were obtained when a similar procedure was employed but replacing $Pd(dba)_2$ with $Pd(mtdba)_2$ for enhanced removal.

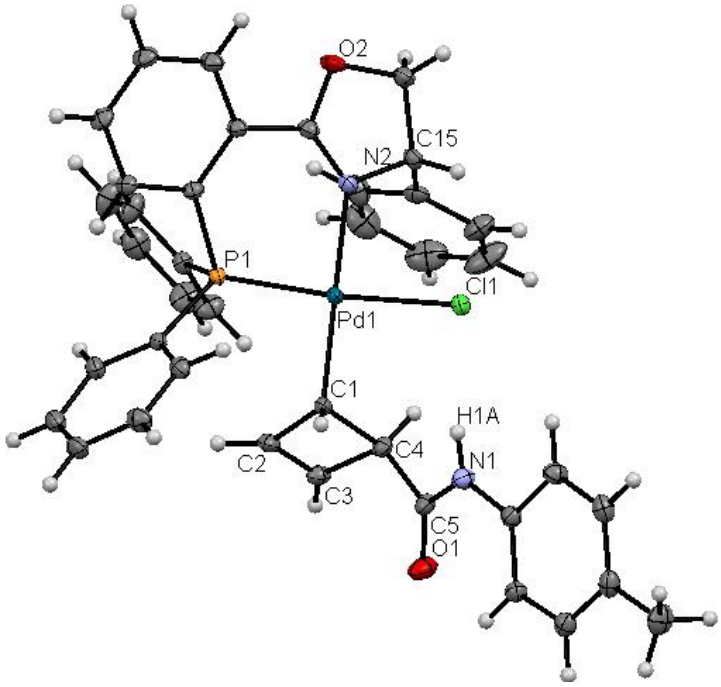
IR (neat): ν_{max} 3240, 3181, 3052, 2170, 1980, 1667, 1635, 1599, 1512, 1481, 1455, 1435, 1403, 1372, 1318, 1264, 1236, 1185, 1142, 1111, 1098, 1047, 997, 946, 886, 862, 840, 821, 751, 727, 694;

^{1}H-NMR (600 MHz, THF-$_{d8}$): δ 10.17 (s, $1H_{N-H}$), 8.18 (m, $1H_{arom.}$), 7.75-6.97 ($22H_{arom.}$ + dba byproduct), 6.42-6.39 (m, 1H, $H_{oxazoline}$), 5.63 (d, J_{HH} = 2.58 Hz, $1H_{C-H}$), 5.11 (s, $1H_{C-H}$), 4.86 (t, J = 9.2 Hz, $1H_{oxazoline}$), 4.54 (dd, J = 9.1, 3.7 Hz, $1H_{oxazoline}$), 4.26 (s, $1H_{C-H}$), 3.29 (s, $1H_{C-H}$), 2.23 (s, $3H_{Me}$);

^{13}C-NMR (150 MHz, THF-$_{d8}$): δ 188.1, 171.3, 163.1, 147.3 (d, J = 5.56 Hz), 143.1, 141.8, 139.2, 136.3, 135.6, 135.5, 135.4 (d, J = 2.2 Hz), 134.2 (d, J = 11.57 Hz), 133.5 (d, J = 6.89 Hz), 133.8 (d, J = 7.71 Hz), 132.8 (d, J = 7.3 Hz), 132.2, 131.9, 131.3, 130.9, 130.1-129.4, 129.1, 128.5, 128.4, 126.4, 118.6, 75.8, 69.1, 58.1, 48.2, 20.9;

^{31}P-NMR (121 MHz, THF-$_{d8}$): δ 28.6. (the complex underwent partial decomposition during the measurement)

HRMS (ESI$^+$): exact mass calculated for $[M\text{-}Cl]^+$ ($C_{39}H_{34}N_2O_2PP$) requires *m*/*z* 699.1405, found *m*/*z* 699.1404.



$Pd(mtdba)_2$ was prepared according to the literature procedure.[3]

3 N. H. Sherden, D. C. Behenna, S. C. Virgil, B. M. Stoltz *Angew. Chem. Int. Ed.* **2009**, *48*, 6840-6843.

12. Crystal data and structure refinement for complex 10.

Identification code	8030sadabs	
Empirical formula	$C_{41}\ H_{38}\ Cl_5\ N_2\ O_2\ P\ Pd$	
Color	yellow	
Formula weight	905.35 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	p 2_1 , (no. 4)	
Unit cell dimensions	a = 9.3374 (11) Å	α= 90°.
	b = 19.234 (2) Å	β= 98.851(2)°.
	c = 10.9480 (13) Å	γ = 90°.
Volume	1942.8(4) $Å^3$	
Z	2	
Density (calculated)	1.548 $Mg \cdot m^{-3}$	
Absorption coefficient	0.902 mm^{-1}	
F(000)	920 e	
Crystal size	0.32 x 0.28 x 0.26 mm^3	
θ range for data collection	2.83 to 31.00°.	
Index ranges	$-13 \le h \le 13$, $-27 \le k \le 27$, $-15 \le l \le 15$	
Reflections collected	55178	
Independent reflections	12209 [R_{int} = 0.0165]	
Reflections with I>2σ(I)	12110	
Completeness to θ = 27.50°	98.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.87172 and 0.83024	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12209 / 1 / 470	
Goodness-of-fit on F^2	1.088	
Final R indices [I>2σ(I)]	R_1 = 0.0445	wR^2 = 0.1401
R indices (all data)	R_1 = 0.0448	wR^2 = 0.1404
Absolute structure parameter	-0.01(2)	
Largest diff. peak and hole	1.440 and -1.933 e · $Å^{-3}$	

Selected bond lengths [Å] and angles [°] for complex 10.

C(1)-C(2)	1.513(5)	C(1)-C(4)
1.599(5)	C(1)-Pd(1)	2.055(3)
C(2)-C(3)	1.335(5)	C(3)-C(4)
1.511(5)	C(4)-C(5)	1.515(5)
C(5)-O(1)	1.235(4)	C(5)-N(1)
1.357(4)	C(6)-C(11)	1.396(5)
C(6)-C(7)	1.415(5)	C(6)-N(1)
1.417(4)	C(7)-C(8)	1.391(5)
C(8)-C(9)	1.399(6)	C(9)-C(10)
1.386(5)	C(9)-C(12)	1.498(5)
C(10)-C(11)	1.399(5)	C(13)-N(2)
1.270(5)	C(13)-O(2)	1.352(4)
C(13)-C(22)	1.483(5)	C(14)-O(2)
1.462(5)	C(14)-C(15)	1.524(5)
C(15)-N(2)	1.504(5)	C(15)-C(16)
1.513(5)	C(16)-C(21)	1.379(6)
C(16)-C(17)	1.396(5)	C(17)-C(18)
1.383(6)	C(18)-C(19)	1.402(9)
C(19)-C(20)	1.391(9)	C(20)-C(21)
1.404(6)	C(22)-C(23)	1.401(4)
C(22)-C(27)	1.417(4)	C(23)-C(24)
1.378(5)	C(24)-C(25)	1.399(5)
C(25)-C(26)	1.396(4)	C(26)-C(27)
1.395(5)	C(27)-P(1)	1.836(3)
C(28)-C(29)	1.399(5)	C(28)-C(33)
1.400(5)	C(28)-P(1)	1.818(3)
C(29)-C(30)	1.387(5)	C(30)-C(31)
1.395(6)	C(31)-C(32)	1.393(6)
C(32)-C(33)	1.384(5)	C(34)-C(35)
1.390(5)	C(34)-C(39)	1.404(5)
C(34)-P(1)	1.828(3)	C(35)-C(36)
1.395(6)	C(36)-C(37)	1.400(7)
C(37)-C(38)	1.378(7)	C(38)-C(39)
1.401(6)	C(40)-Cl(3)	1.741(9)

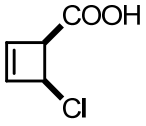
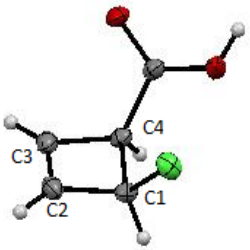
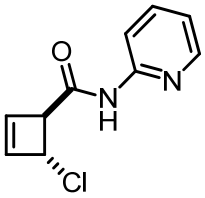
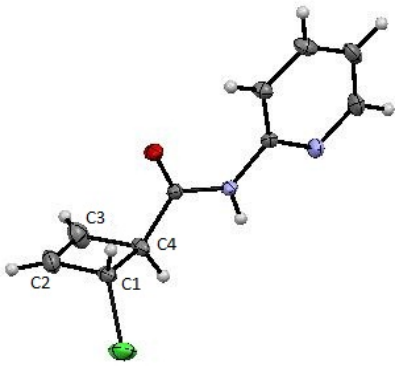
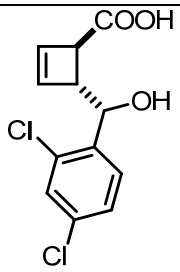
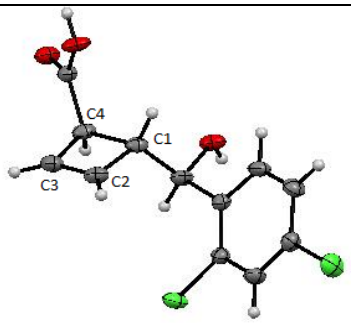
C(40)-Cl(2)	1.763(8)	C(41)-Cl(5)
1.721(8)	C(41)-Cl(4)	1.760(8)
Cl(1)-Pd(1)	2.4200(8)	N(2)-Pd(1)
2.120(2)	P(1)-Pd(1)	2.2108(9)

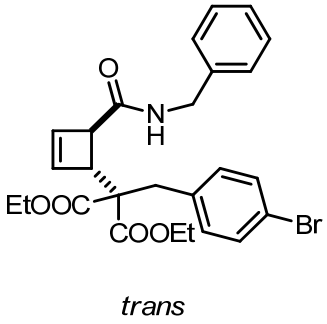
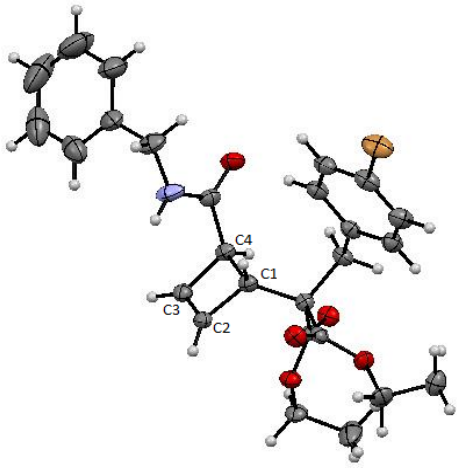
C(2)-C(1)-C(4)	84.7(2)	C(2)-C(1)-Pd(1)
119.0(2)	C(4)-C(1)-Pd(1)	111.5(2)
C(3)-C(2)-C(1)	95.2(3)	C(2)-C(3)-C(4)
94.7(3)	C(3)-C(4)-C(5)	114.9(3)
C(3)-C(4)-C(1)	85.2(2)	C(5)-C(4)-C(1)
114.9(3)	O(1)-C(5)-N(1)	124.7(3)
O(1)-C(5)-C(4)	121.2(3)	N(1)-C(5)-C(4)
114.0(3)	C(11)-C(6)-C(7)	120.1(3)
C(11)-C(6)-N(1)	123.6(3)	C(7)-C(6)-N(1)
116.3(3)	C(8)-C(7)-C(6)	118.2(3)
C(7)-C(8)-C(9)	122.8(3)	C(10)-C(9)-C(8)
117.5(3)	C(10)-C(9)-C(12)	121.1(4)
C(8)-C(9)-C(12)	121.3(4)	C(9)-C(10)-C(11)
121.9(3)	C(6)-C(11)-C(10)	119.4(3)
N(2)-C(13)-O(2)	117.8(3)	N(2)-C(13)-C(22)
127.2(3)	O(2)-C(13)-C(22)	115.0(3)
O(2)-C(14)-C(15)	105.6(3)	N(2)-C(15)-C(16)
111.2(3)	N(2)-C(15)-C(14)	102.4(3)
C(16)-C(15)-C(14)	115.5(3)	C(21)-C(16)-C(17)
119.0(4)	C(21)-C(16)-C(15)	119.5(4)
C(17)-C(16)-C(15)	121.5(4)	C(18)-C(17)-C(16)
120.5(4)	C(17)-C(18)-C(19)	120.4(5)
C(20)-C(19)-C(18)	119.3(4)	C(19)-C(20)-C(21)
119.4(5)	C(16)-C(21)-C(20)	121.2(5)
C(23)-C(22)-C(27)	119.3(3)	C(23)-C(22)-C(13)
118.5(3)	C(27)-C(22)-C(13)	122.2(3)
C(24)-C(23)-C(22)	121.3(3)	C(23)-C(24)-C(25)
119.8(3)	C(26)-C(25)-C(24)	119.6(3)
C(27)-C(26)-C(25)	121.2(3)	C(26)-C(27)-C(22)
118.8(3)	C(26)-C(27)-P(1)	118.8(2)
C(22)-C(27)-P(1)	122.2(2)	C(29)-C(28)-C(33)

120.1(3)	C(29)-C(28)-P(1)	122.6(3)
C(33)-C(28)-P(1)	117.1(2)	C(30)-C(29)-C(28)
119.2(3)	C(29)-C(30)-C(31)	120.6(4)
C(32)-C(31)-C(30)	120.2(3)	C(33)-C(32)-C(31)
119.5(4)	C(32)-C(33)-C(28)	120.4(3)
C(35)-C(34)-C(39)	119.7(3)	C(35)-C(34)-P(1)
118.4(3)	C(39)-C(34)-P(1)	121.9(3)
C(34)-C(35)-C(36)	120.5(4)	C(35)-C(36)-C(37)
119.5(4)	C(38)-C(37)-C(36)	120.4(4)
C(37)-C(38)-C(39)	120.3(4)	C(38)-C(39)-C(34)
119.6(4)	Cl(3)-C(40)-Cl(2)	113.0(5)
Cl(5)-C(41)-Cl(4)	113.5(5)	C(5)-N(1)-C(6)
128.6(3)	C(13)-N(2)-C(15)	108.0(3)
C(13)-N(2)-Pd(1)	133.0(3)	C(15)-N(2)-Pd(1)
118.9(3)	C(13)-O(2)-C(14)	105.8(3)
C(28)-P(1)-C(34)	107.15(15)	C(28)-P(1)-C(27)
103.27(15)	C(34)-P(1)-C(27)	102.49(15)
C(28)-P(1)-Pd(1)	116.55(11)	C(34)-P(1)-Pd(1)
115.60(11)	C(27)-P(1)-Pd(1)	110.19(11)
C(1)-Pd(1)-N(2)	172.81(14)	C(1)-Pd(1)-P(1)
93.68(12)	N(2)-Pd(1)-P(1)	86.28(10)
C(1)-Pd(1)-Cl(1)	91.04(11)	N(2)-Pd(1)-Cl(1)
90.43(10)	P(1)-Pd(1)-Cl(1)	167.88(3)

13. Comparative list of C-C bond distances and selected dihedral angles in cyclobutene carboxylic acids.

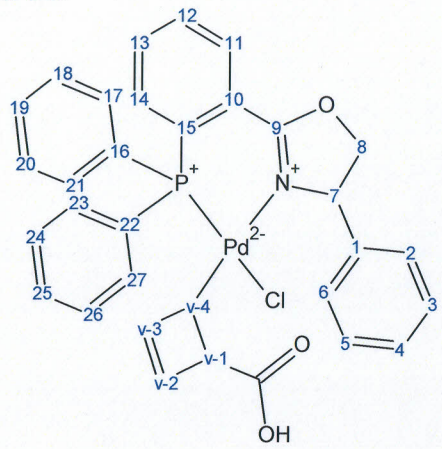
The central C-C [C(1)-C(4)] (Å) bond lengths and the angles [C(2)-C(1)-C(4)] (°) in cyclobutenes derivatives are listed below.

	Cyclobutene derivatives	Crystal structures	Bond lengths of C(1)-(4) [Å]	Angles of C(2)-C(1)-(4) [°]
1	 *cis*		1.574	86.3
2	 *trans*		1.566	97.06
3	 *trans*		1.57	85.61

4	 *trans*		1.585	85.71

H616736

Vorschlag aus NMR:



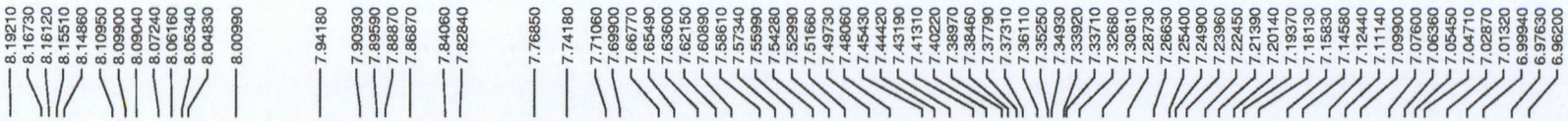
NAME	audab20900
EXPNO	110
PROCNO	1
Date_	20120412
Time	12.46
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	65536
SOLVENT	THF
NS	32
DS	2
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	9
DW	41.600 usec
DE	10.00 usec
TE	283.0 K
D1	1.00000000 sec
TD0	1
==========	CHANNEL f1 ==========
NUC1	1H
P1	8.50 usec
PL1	4.20 dB
PL1W	5.30020905 W
SFO1	600.2242403 MHz
SI	131072
SF	600.2200228 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00
SR	22.81 Hz

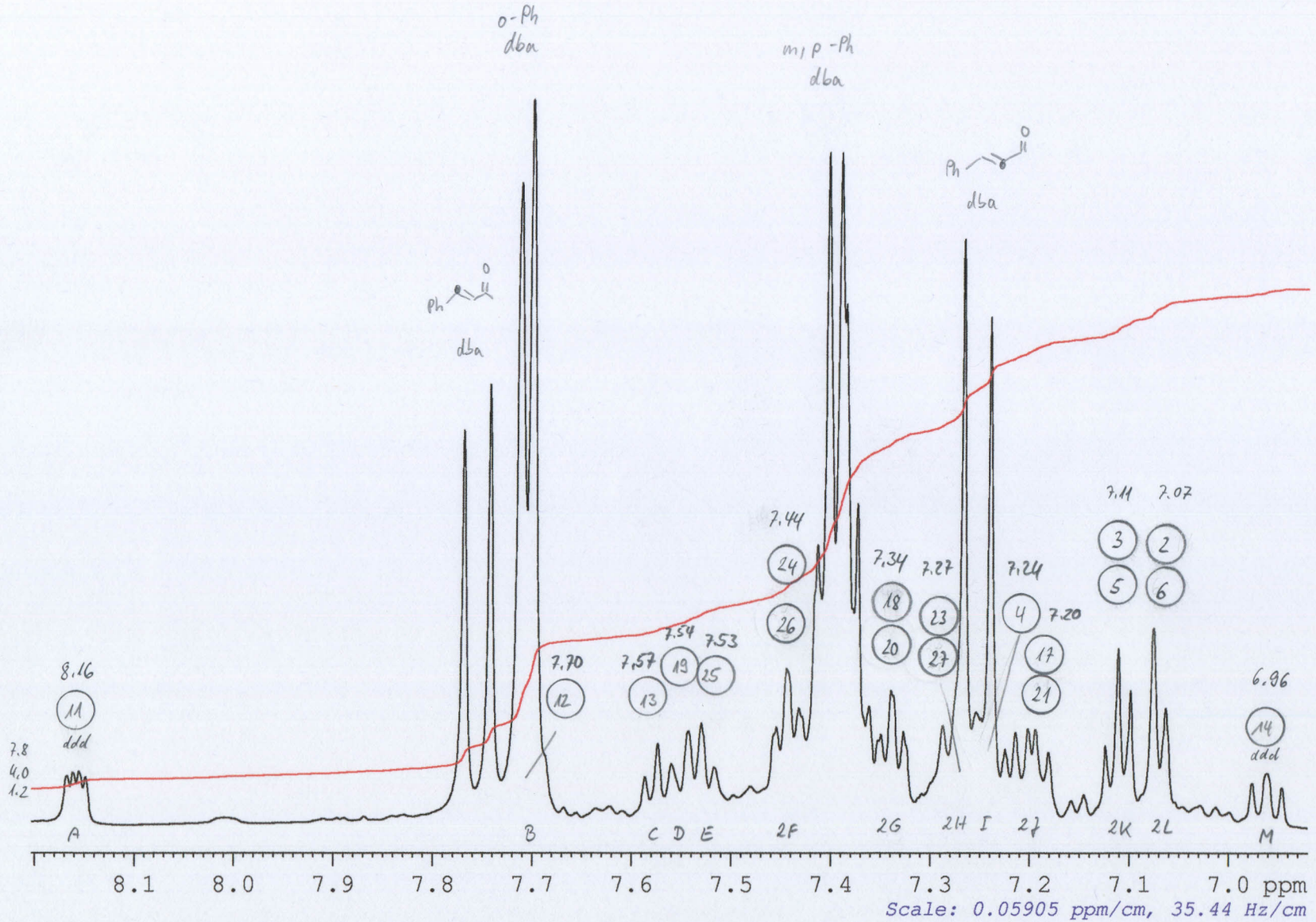
AUD-AB-209-00
283K after shaking

1H

av600

H616736





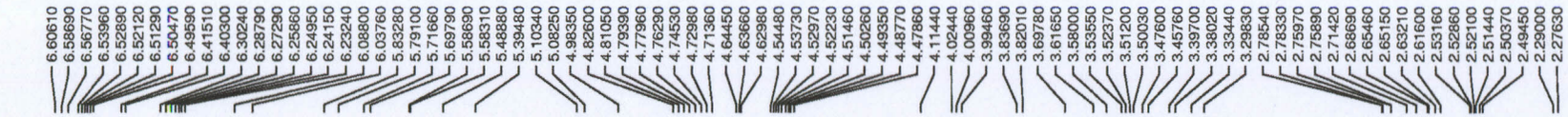
NAME	audab20900
EXPNO	110
PROCNO	1
Date_	20120412
Time	12.48
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	65536
SOLVENT	THF
NS	32
DS	2
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	9
DW	41.600 usec
DE	10.00 usec
TE	283.0 K
D1	1.00000000 sec
TD0	1
==========	CHANNEL f1 ==========
NUC1	1H
P1	8.50 usec
PL1	4.20 dB
PL1W	5.30020905 W
SFO1	600.2242403 MHz
SI	131072
SF	600.2200228 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00
SR	22.81 Hz

AUD-AB-209-00
283K after shaking

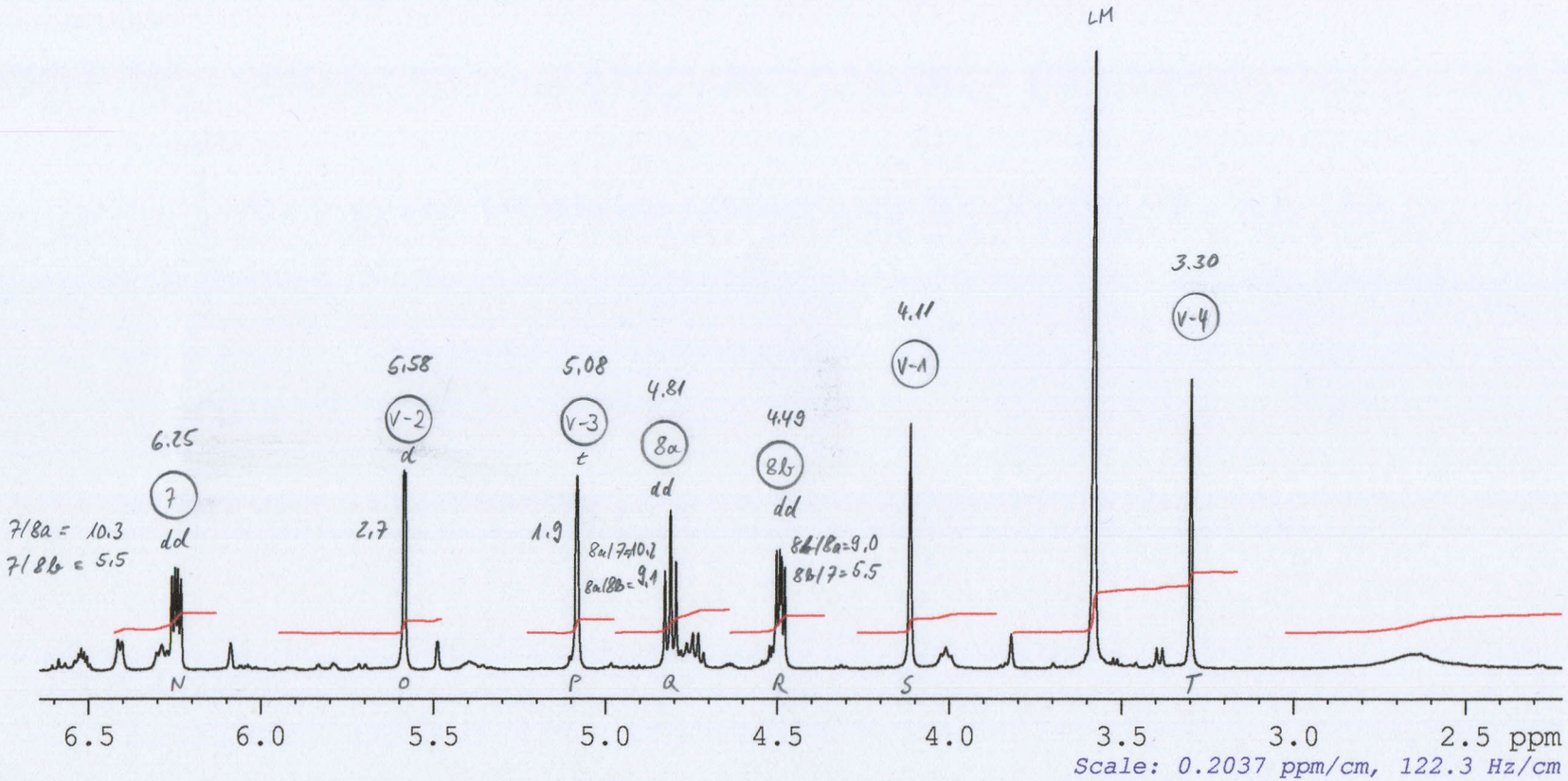
1H

av600

H616736



NAME	audab20900
EXPNO	110
PROCNO	1
Date_	20120412
Time	12.46
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	65536
SOLVENT	THF
NS	32
DS	2
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	9
DW	41.600 usec
DE	10.00 usec
TE	283.0 K
D1	1.00000000 sec
TD0	1
==========	CHANNEL f1 ==========
NUC1	1H
P1	8.50 usec
PL1	4.20 dB
PL1W	5.30020905 W
SFO1	600.2242403 MHz
SI	131072
SF	600.2200228 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00
SR	22.81 Hz

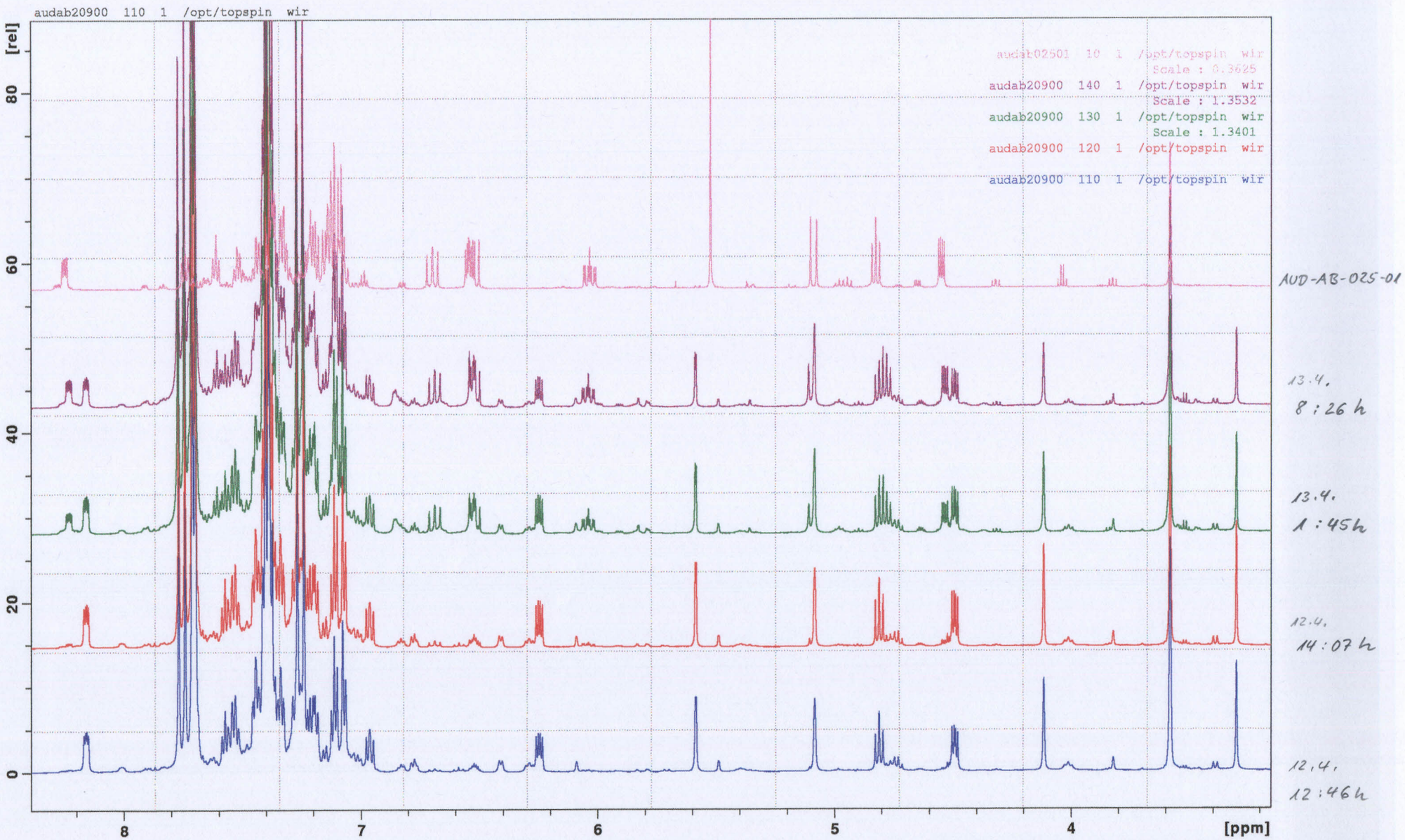


AUD-AB-209-00
283K after shaking

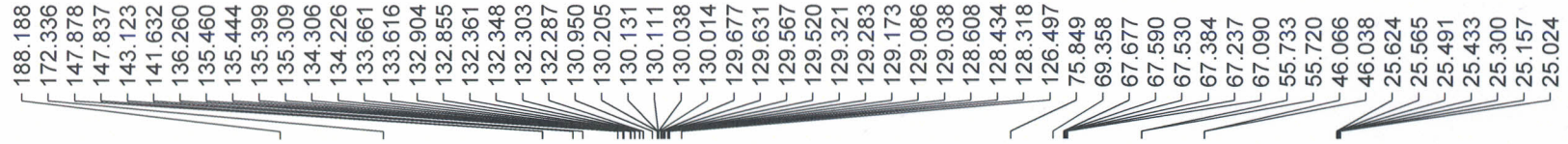
1H

av600

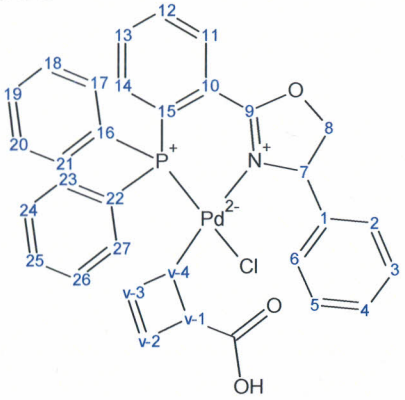
AUD-AB-209-00


audab20900 110 1 /opt/topspin wir
audab02501 10 1 /opt/topspin wir
Scale : 0.3625
audab20900 140 1 /opt/topspin wir
Scale : 1.3532
audab20900 130 1 /opt/topspin wir
Scale : 1.3401
audab20900 120 1 /opt/topspin wir
audab20900 110 1 /opt/topspin wir
[rel]
80
60
40
20
0
8
7
6
5
4
[ppm]
AUD-AB-025-01
13.4.
8:26 h
13.4.
1:45 h
12.4.
14:07 h
12.4.
12:46 h

C616737



Vorschlag aus NMR:



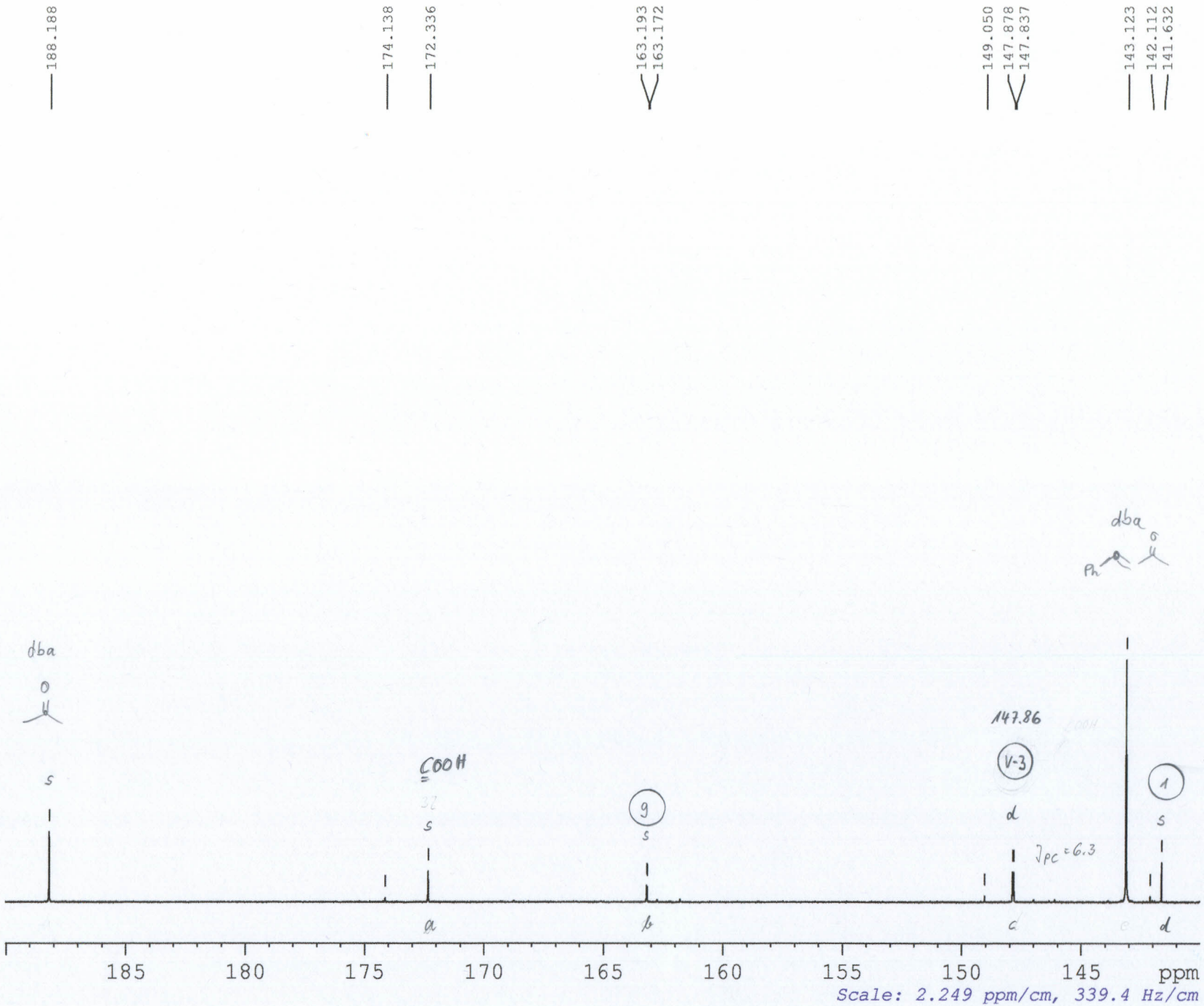
NAME audab20900
EXPNO 111
PROCNO 1
Date_ 20120412
Time 13.21
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 80908
SOLVENT THF
NS 2000
DS 128
SWH 46296.297 Hz
FIDRES 0.572209 Hz
AQ 0.8738564 sec
RG 512
DW 10.800 usec
DE 50.99 usec
TE 283.0 K
D1 0.03000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 -1.00 dB
PL1W 109.73103333 W
SFO1 150.9419956 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz65
NUC2 1H
PCPD2 70.00 usec
PL2 4.20 dB
PL12 22.51 dB
PL2W 5.30020905 W
PL12W 0.07821552 W
SFO2 600.2223000 MHz
SI 131072
SF 150.9252999 MHz
WDW EM
SSB 0
LB 0.80 Hz
GB 0
PC 1.00

AUD-AB-209-00
13C{1H} @ 283K
after shaking

av600



C616737

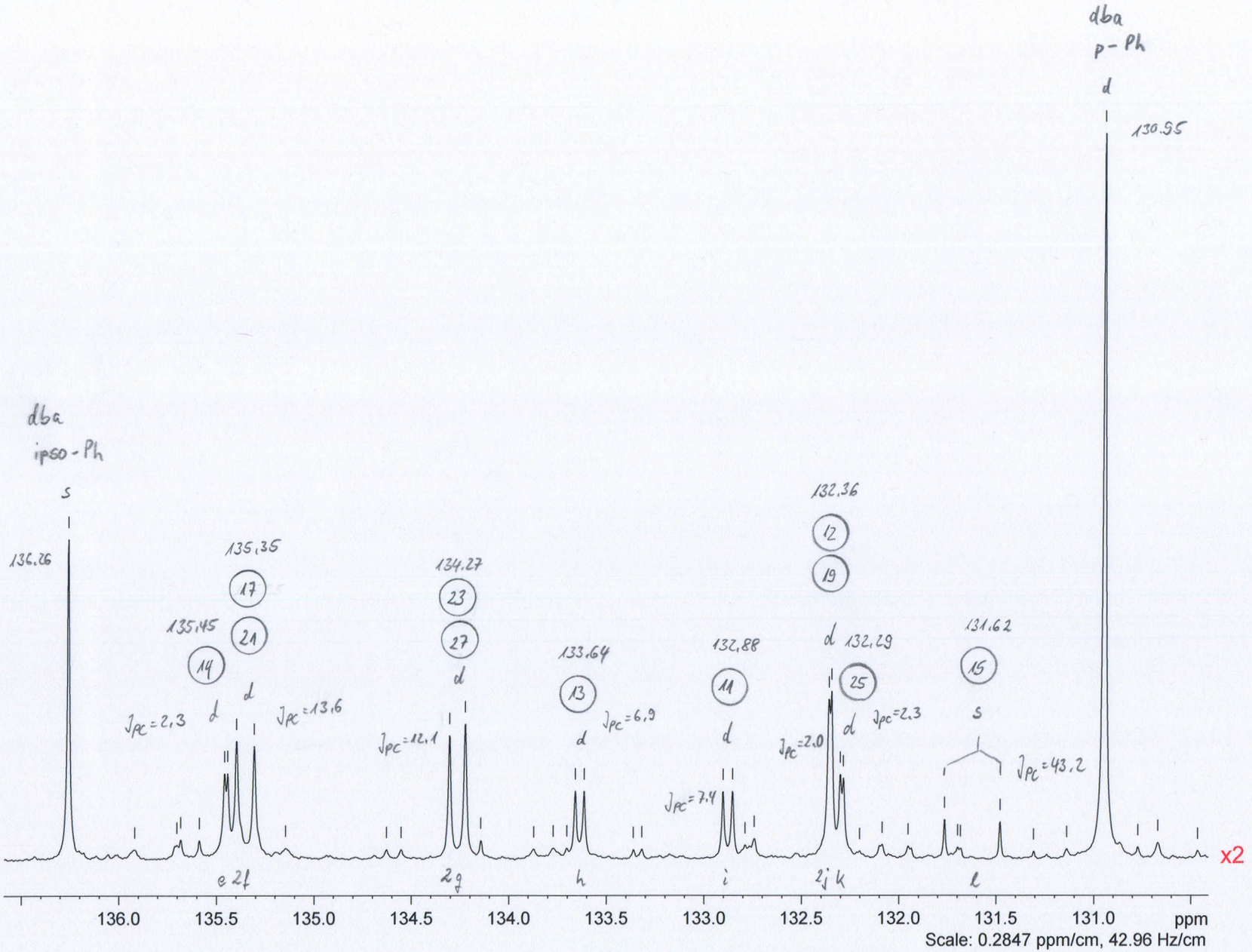
NAME	audab20900	
EXPNO	111	
PROCNO	1	
Date_	20120412	
Time	13.21	
INSTRUM	av600	
PROBHD	5 mm CPTCI 1H-	
PULPROG	zgdc30	
TD	80908	
SOLVENT	THF	
NS	2000	
DS	128	
SWH	46296.297	Hz
FIDRES	0.572209	Hz
AQ	0.8738564	sec
RG	512	
DW	10.800	use
DE	50.99	use
TE	283.0	K
D1	0.03000000	sec
D11	0.03000000	sec
TD0	1	
========== CHANNEL f1 ==========		
NUC1	13C	
P1	11.00	use
PL1	-1.00	dB
PL1W	109.73103333	W
SFO1	150.9419956	MHz
========== CHANNEL f2 ==========		
CPDPRG2	waltz65	
NUC2	1H	
PCPD2	70.00	use
PL2	4.20	dB
PL12	22.51	dB
PL2W	5.30020905	W
PL12W	0.07821552	W
SFO2	600.2223000	MHz
SI	131072	
SF	150.9252999	MHz
WDW	EM	
SSB	0	
LB	0.80	Hz
GB	0	
PC	1.00	
SR	-139.10	Hz

AUD-AB-209-00
13C{1H} @ 283K
after shaking

av600

C616737

136.260
135.918
135.702
135.683
135.588
135.460
135.444
135.399
135.309
135.147
134.629
134.554
134.306
134.226
134.145
133.873
133.773
133.704
133.661
133.616
133.362
133.319
132.904
132.855
132.789
132.742
132.361
132.348
132.303
132.287
132.203
132.087
131.954
131.767
131.699
131.684
131.481
131.308
131.140
130.950
130.774
130.672
130.466



NAME audab20900
EXPNO 111
PROCNO 1
Date_ 20120412
Time 13.21
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 80908
SOLVENT THF
NS 2000
DS 128
SWH 46296.297 Hz
FIDRES 0.572209 Hz
AQ 0.8738564 sec
RG 512
DW 10.800 usec
DE 50.99 usec
TE 283.0 K
D1 0.03000000 sec
D11 0.03000000 sec
TD0 1

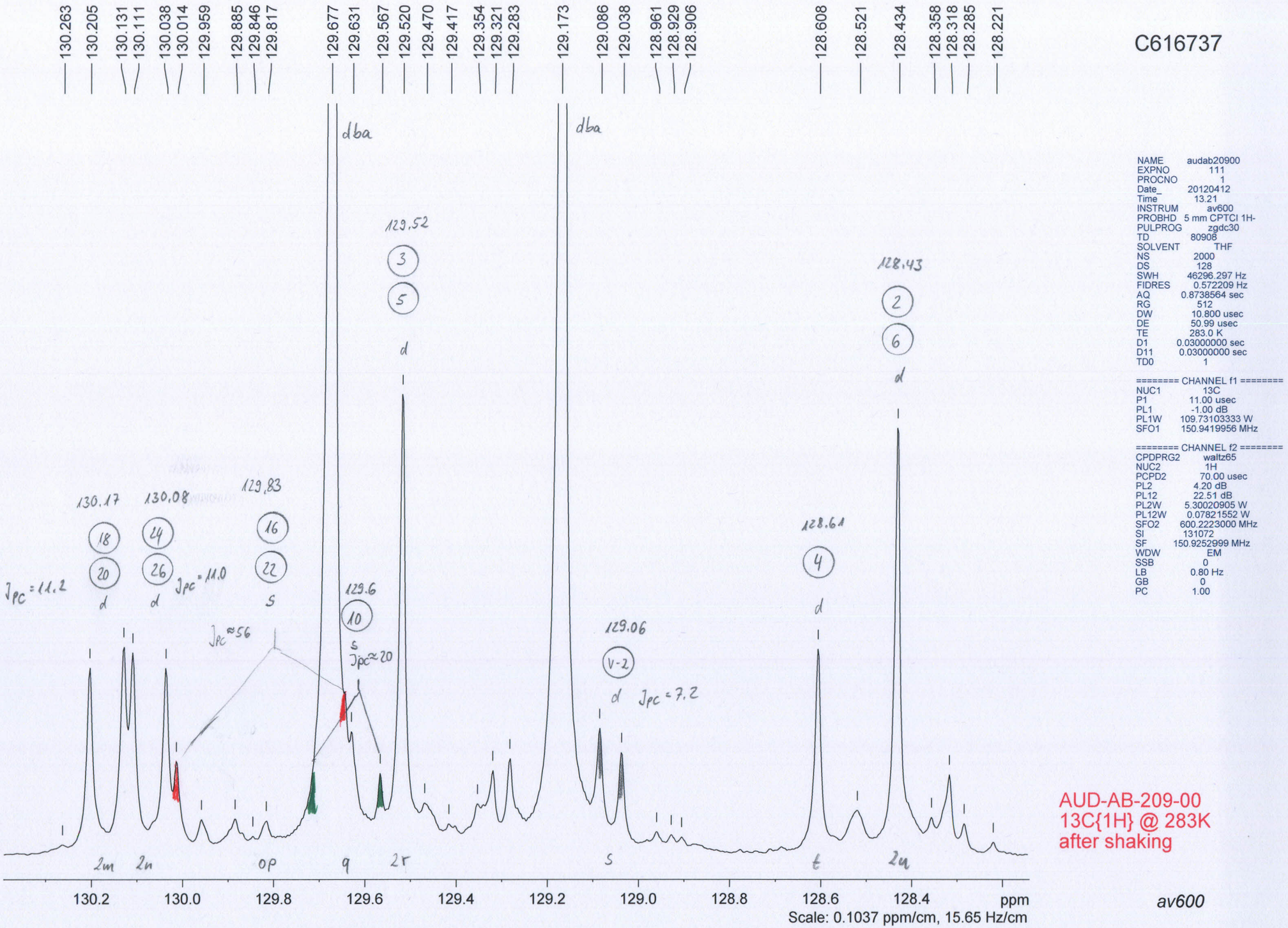
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 -1.00 dB
PL1W 109.73103333 W
SFO1 150.9419956 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz65
NUC2 1H
PCPD2 70.00 usec
PL2 4.20 dB
PL12 22.51 dB
PL2W 5.30020905 W
PL12W 0.07821552 W
SFO2 600.2223000 MHz
SI 131072
SF 150.9252999 MHz
WDW EM
SSB 0
LB 0.80 Hz
GB 0
PC 1.00

AUD-AB-209-00
13C{1H} @ 283K
after shaking

av600

C616737




```
NAME        audab20900
EXPNO           111
PROCNO            1
Date_        20120412
Time            13.21
INSTRUM         av600
PROBHD  5 mm CPTCI 1H-
PULPROG       zgdc30
TD              80908
SOLVENT           THF
NS               2000
DS                128
SWH         46296.297 Hz
FIDRES      0.572209 Hz
AQ          0.8738564 sec
RG                512
DW             10.800 usec
DE             50.99 usec
TE             283.0 K
D1          0.03000000 sec
D11         0.03000000 sec
TD0               1

======== CHANNEL f1 ========
NUC1              13C
P1             11.00 usec
PL1            -1.00 dB
PL1W       109.73103333 W
SFO1       150.9419956 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz65
NUC2              1H
PCPD2          70.00 usec
PL2            4.20 dB
PL12           22.51 dB
PL2W       5.30020905 W
PL12W      0.07821552 W
SFO2       600.2223000 MHz
SI             131072
SF         150.9252999 MHz
WDW               EM
SSB               0
LB             0.80 Hz
GB                0
PC             1.00
```

AUD-AB-209-00
13C{1H} @ 283K
after shaking

av600

C616737

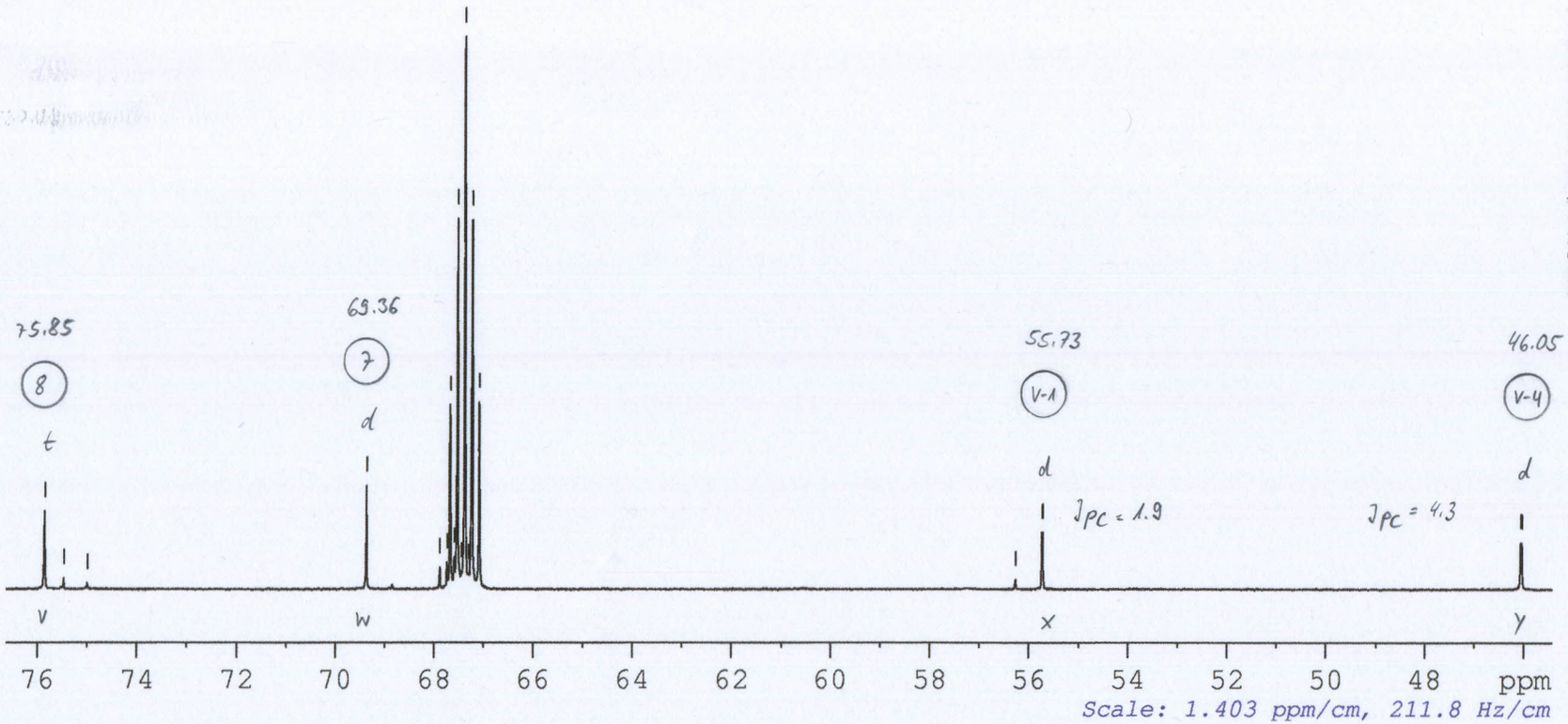
NAME	audab20900
EXPNO	111
PROCNO	1
Date_	20120412
Time	13.21
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zgdc30
TD	80908
SOLVENT	THF
NS	2000
DS	128
SWH	46296.297 Hz
FIDRES	0.572209 Hz
AQ	0.8738564 sec
RG	512
DW	10.800 use
DE	50.99 use
TE	283.0 K
D1	0.03000000 sec
D11	0.03000000 sec
TD0	1
========== CHANNEL f1 ==========	
NUC1	13C
P1	11.00 use
PL1	-1.00 dB
PL1W	109.73103333 W
SFO1	150.9419956 MHz
========== CHANNEL f2 ==========	
CPDPRG2	waltz65
NUC2	1H
PCPD2	70.00 use
PL2	4.20 dB
PL12	22.51 dB
PL2W	5.30020905 W
PL12W	0.07821552 W
SFO2	600.2223000 MHz
SI	131072
SF	150.9252999 MHz
WDW	EM
SSB	0
LB	0.80 Hz
GB	0
PC	1.00
SR	-139.10 Hz

75.849
75.466
74.989

69.358
67.883
67.736
67.677
67.590
67.530
67.447
67.384
67.303
67.237
67.090

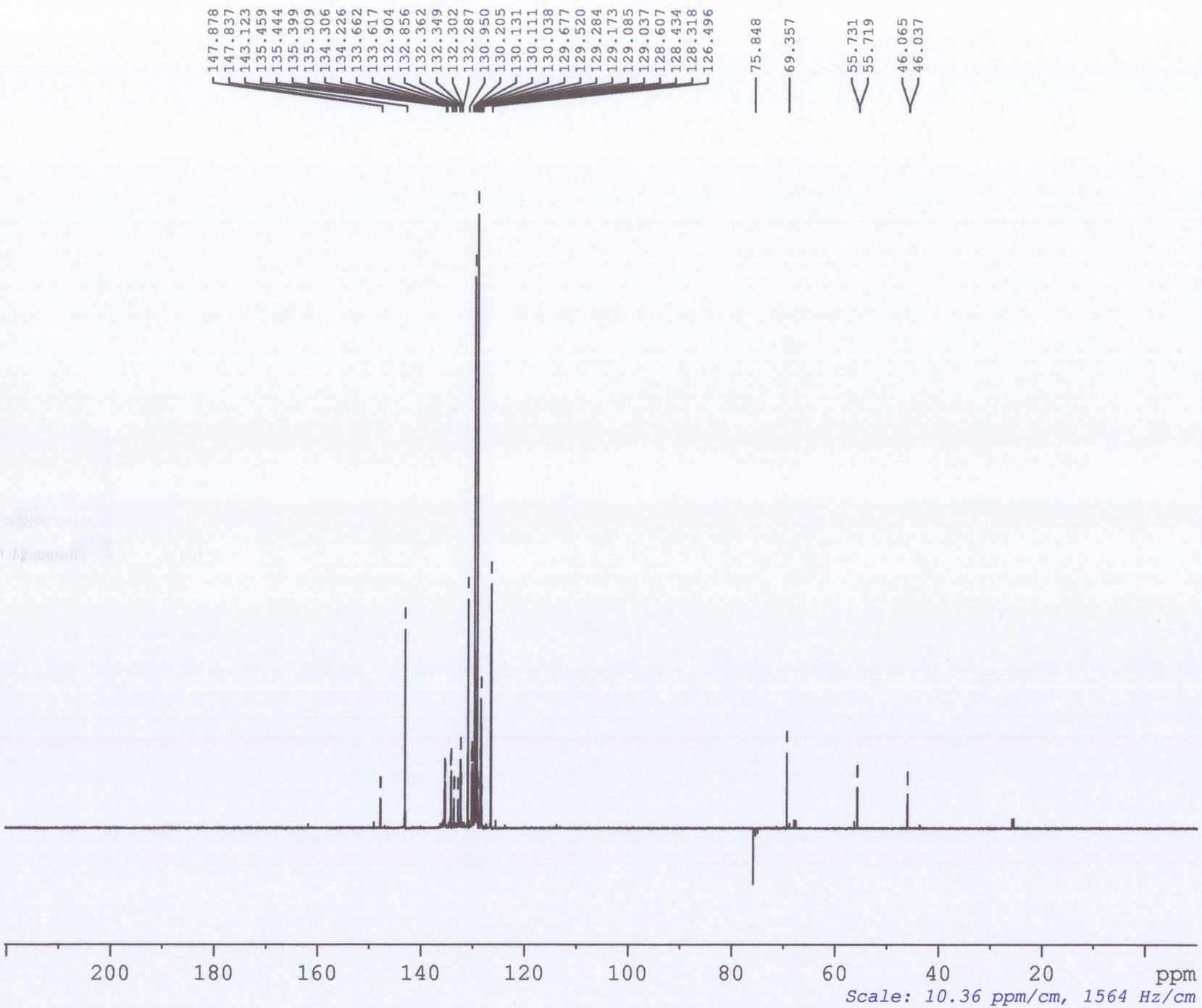
56.266
55.733
55.720

46.066
46.038



AUD-AB-209-00
13C{1H} @ 283K
after shaking

av600



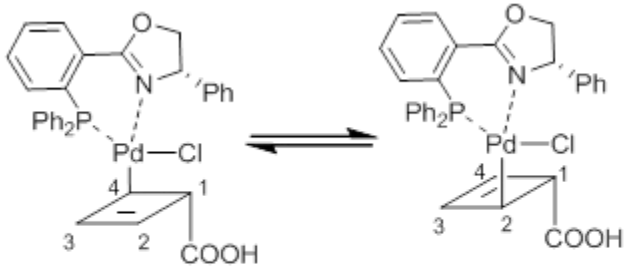
C616738

NAME	audab20900	
EXPNO	112	
PROCNO	1	
Date_	20120412	
Time	13.34	
INSTRUM	av600	
PROBHD	5 mm CPTCI 1H-	
PULPROG	deptsp135	
TD	65536	
SOLVENT	THF	
NS	256	
DS	4	
SWH	36057.691	Hz
FIDRES	0.550197	Hz
AQ	0.9088159	sec
RG	512	
DW	13.867	use
DE	51.34	use
TE	283.0	K
CNST2	145.0000000	
D1	2.00000000	sec
D2	0.00344828	sec
D12	0.00002000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	11.00	use
P12	2000.00	use
PL0	120.00	dB
PL1	-1.00	dB
PL0W	0.00000000	W
PL1W	109.73103333	W
SFO1	150.9405316	MHz
SP2	6.33	dB
SPNAM2	Crp60comp.4	
SPOAL2	0.500	
SPOFFS2	0.00	Hz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
P3	8.50	use
P4	17.00	use
PCPD2	70.00	use
PL2	4.20	dB
PL12	22.51	dB
PL2W	5.30020905	W
PL12W	0.07821552	W
SFO2	600.2223000	MHz
SI	65536	
SF	150.9252999	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.00	

AUD-AB-209-00
dept135 @ 283K
after shaking

av600

aud-ab-201-01
aud-ab-208-01
31P{1H} zgdc30



eta-1-allyl complex **3** (ca. 7:1)

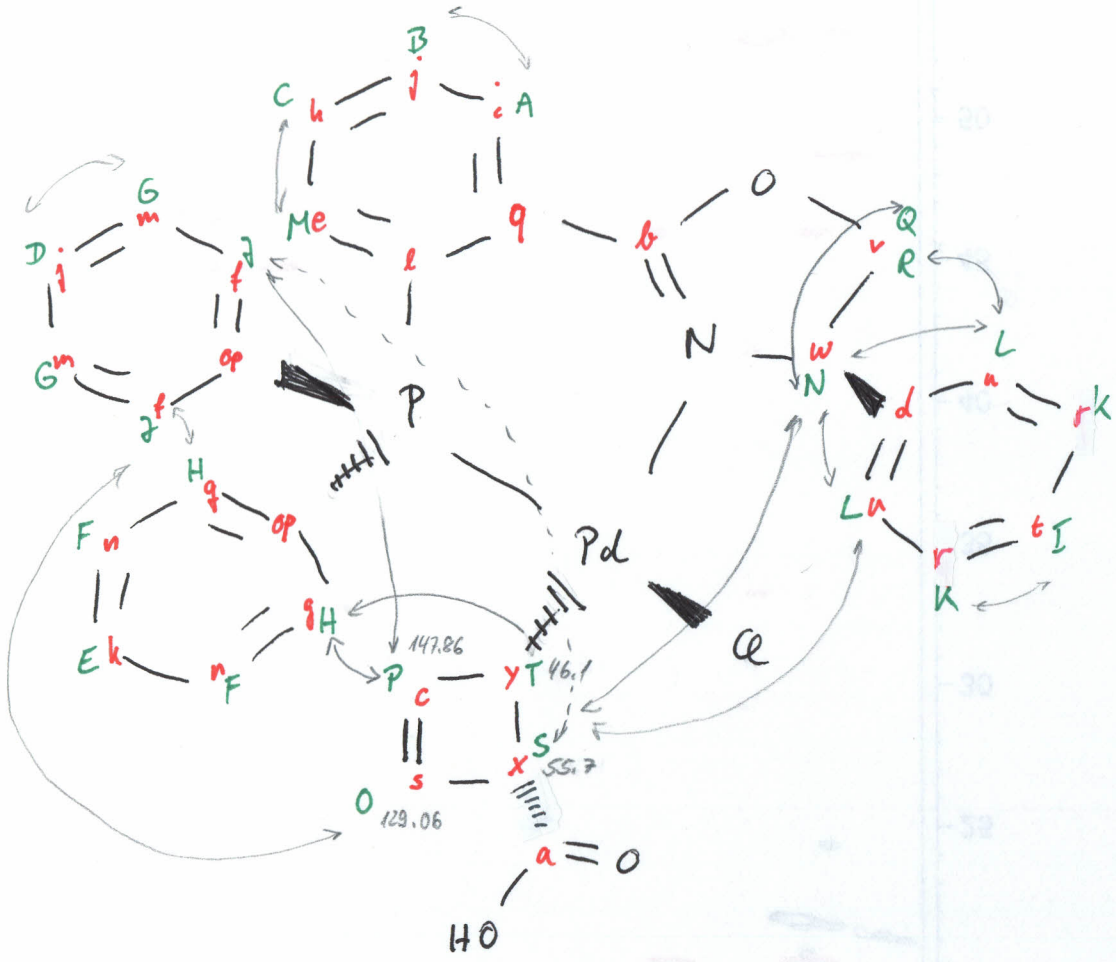
30.95
27.18
1.00
6.95
f1 (ppm)

12/04/2012

AUD - AB - 209 - 00

d_8 - THF

283K !



NOESY ⟷

T ⟷ H

N ⟷ Q S

P ⟷ 2H, 2J

T - S eher trans aus NOESY:

S ⟷ 2(4)C

T ⟷ H(7)

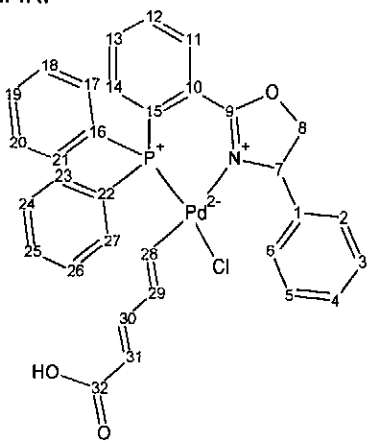
13/04/2012

AUD-AB-209-00

d6-THF 283K!

			HMBC	COSY	HMBC	NOESY
a	(s)	172.34			ST	
b	(s)	163.18			ANR(MQ)	
c	(d)	147.86	P	OS(T)	ST	2H 2J (2F) OT(S) (E)
d	(s)	146.63			2K NQR	
e	(d)	135.45	M	C	B	C 2H 2J
2f	(d)	135.35	2J	2G	D 2G 2J	M 2G (S) P (O)
2g	(d)	134.27	2H	2F	E 2F 2H	2F MT P
h	(d)	133.64	C	BM	A	M
i	(d)	132.88	A	B	C	B
2j	(d)	132.36	BD	AC 2G	A 2J M	A 2G
k	(d)	132.29	E	2F	2H	
l	(s)	131.62			AC	
2m	(d)	130.17	2E	2J D		2J
2n	(d)	130.08	2F	2H E		2H (P)
o	(s)	129.83			2F 2G	
p	(s)	129.83				
q	s	129.6			BM	
2r	(d)	129.52	2K	2L	2K	I
s	(d)	129.06	O	P(S)	(P) ST	PS(T) (2J)
t	(d)	128.61	I	2K	2L	2K
2u	(d)	128.43	2L	2K	N I 2L	(S) R N
v	(t)	75.85	QR	NR NQ		NRA 2L Q (A)
w	(d)	69.36	N	QR	2L R	2L Q S
x	(d)	55.73	S	PT(O)	OPT	(2J 2L) OT (P) (2K) N
y	(d)	46.05	T	PS(O)	OPS	2H PS (O) (2F 2J)

Vorschlag aus NMR:

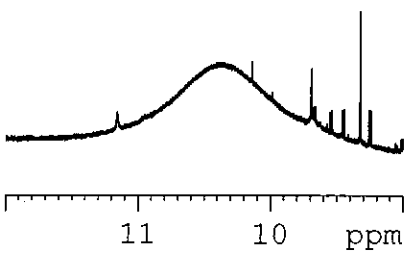


H615630

NAME	audab02501
EXPNO	10
PROCNO	1
Date_	20110810
Time	11.31
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	65536
SOLVENT	THF
NS	32
DS	2
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	9
DW	41.600 usec
DE	10.00 usec
TE	290.5 K
D1	1.00000000 sec
TD0	1

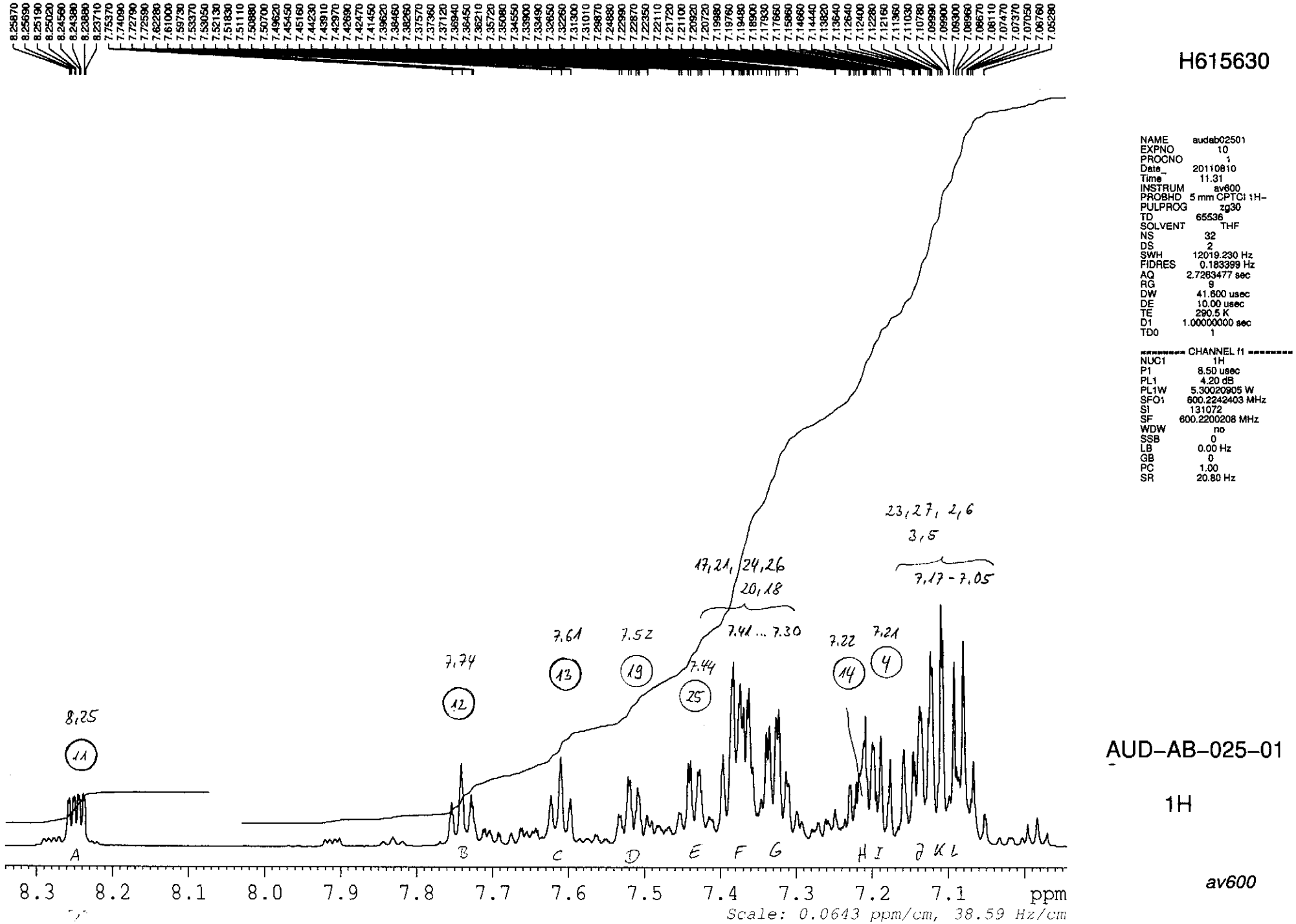
======== CHANNEL f1 ========

NUC1	1H
P1	8.50 usec
PL1	4.20 dB
PL1W	5.30020905 W
SFO1	600.2242403 MHz
SI	131072
SF	600.2200208 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00



AUD-AB-025-01
3mm
1H

av600



H615630

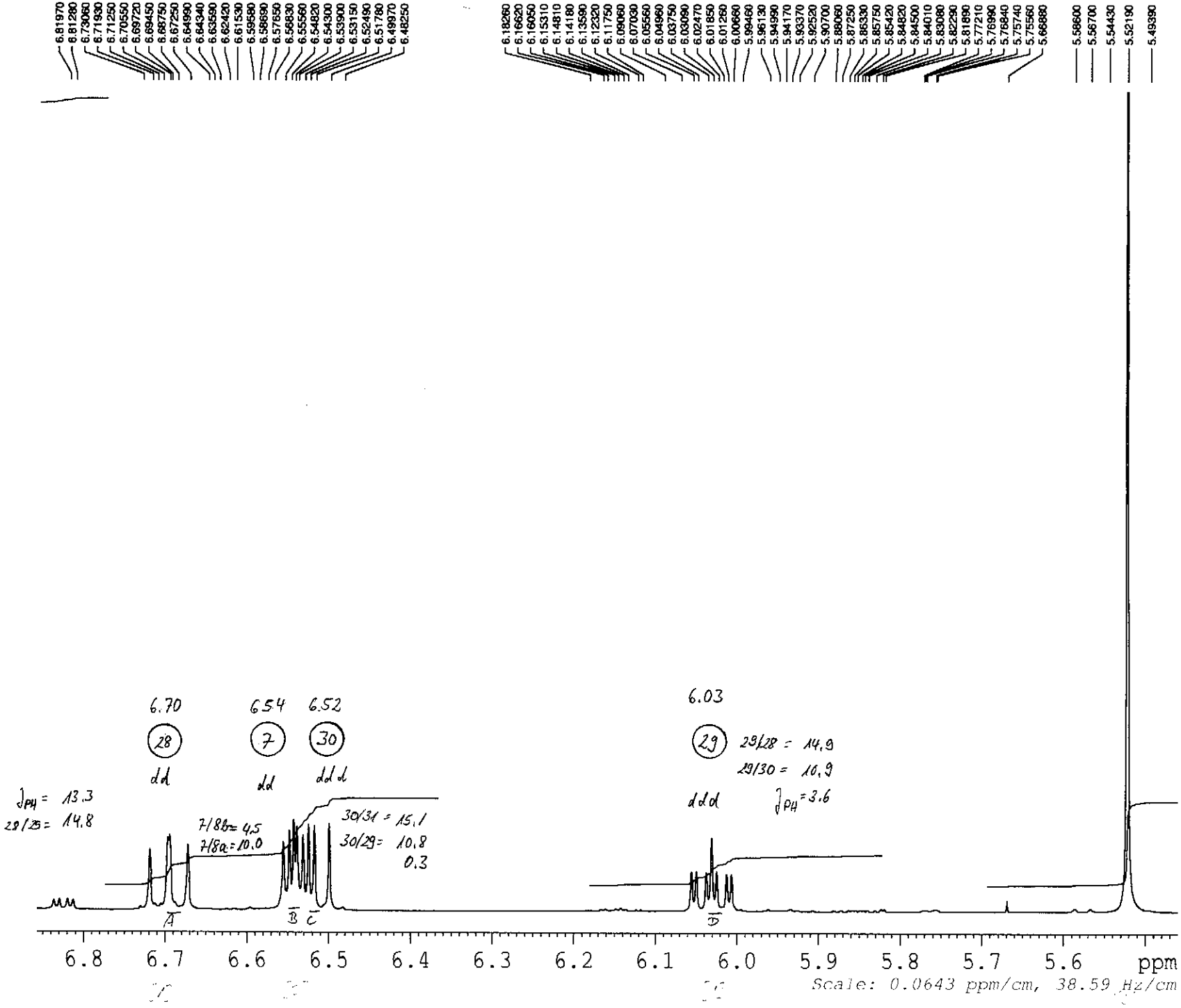
NAME	audab02501
EXPNO	10
PROCNO	1
Date_	20110810
Time	11.31
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	65536
SOLVENT	THF
NS	32
DS	2
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	9
DW	41.600 usec
DE	10.00 usec
TE	290.5 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	8.50 usec
PL1	4.20 dB
PL1W	5.30020905 W
SFO1	600.2242403 MHz
SI	131072
SF	600.2200208 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00
SR	20.80 Hz

AUD-AB-025-01

1H

av600

H615630



NAME	audab02501
EXPNO	10
PROCNO	1
Date_	20110810
Time	11.31
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	65536
SOLVENT	THF
NS	32
DS	2
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	9
DW	41.600 usec
DE	10.00 usec
TE	290.5 K
D1	1.00000000 sec
TD0	1

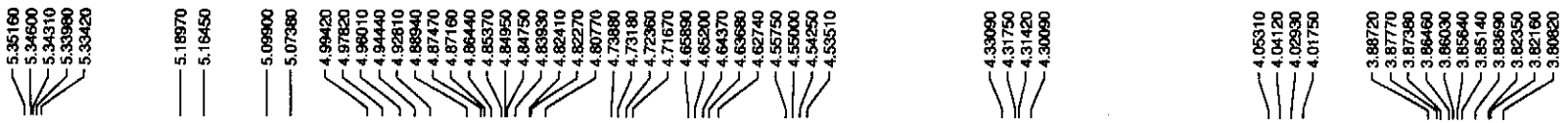
========== CHANNEL f1 ==========

NUC1	1H
P1	8.50 usec
PL1	4.20 dB
PL1W	5.30020905 W
SFO1	600.2242403 MHz
SI	131072
SF	600.2200208 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00
SR	20.80 Hz

AUD–AB–025–01

1H

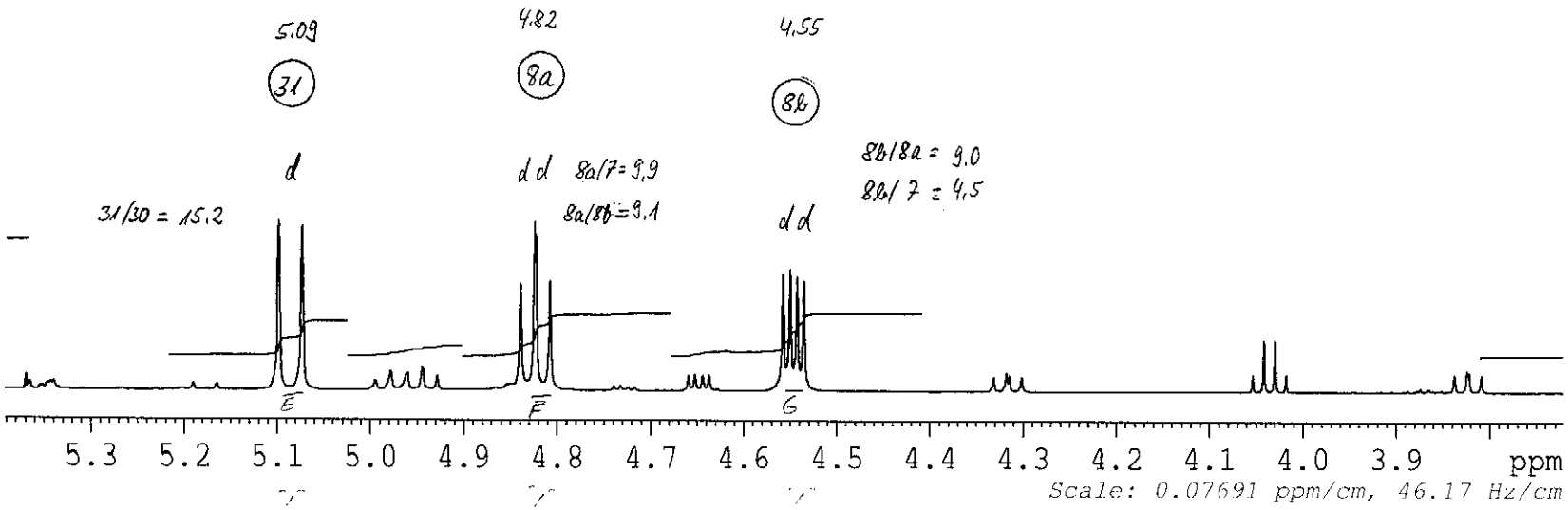
av600



H615630

NAME audab02501
EXPNO 10
PROCNO 1
Date_ 20110610
Time 11.31
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 65536
SOLVENT THF
NS 32
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 9
DW 41.600 usec
DE 10.00 usec
TE 290.5 K
D1 1.00000000 sec
TD0 1

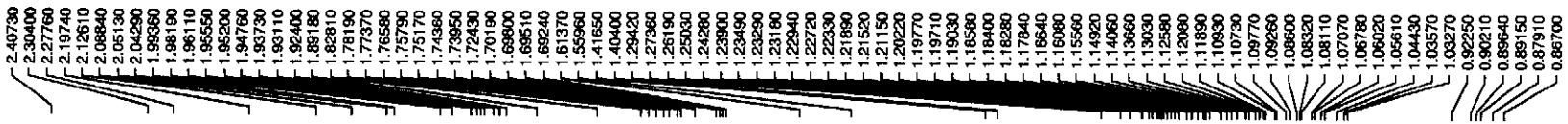
--------- CHANNEL f1 ---------
NUC1 1H
P1 8.50 usec
PL1 4.20 dB
PL1W 5.30020905 W
SFO1 600.2242403 MHz
SI 131072
SF 600.2200208 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
SR 20.80 Hz



AUD-AB-025-01

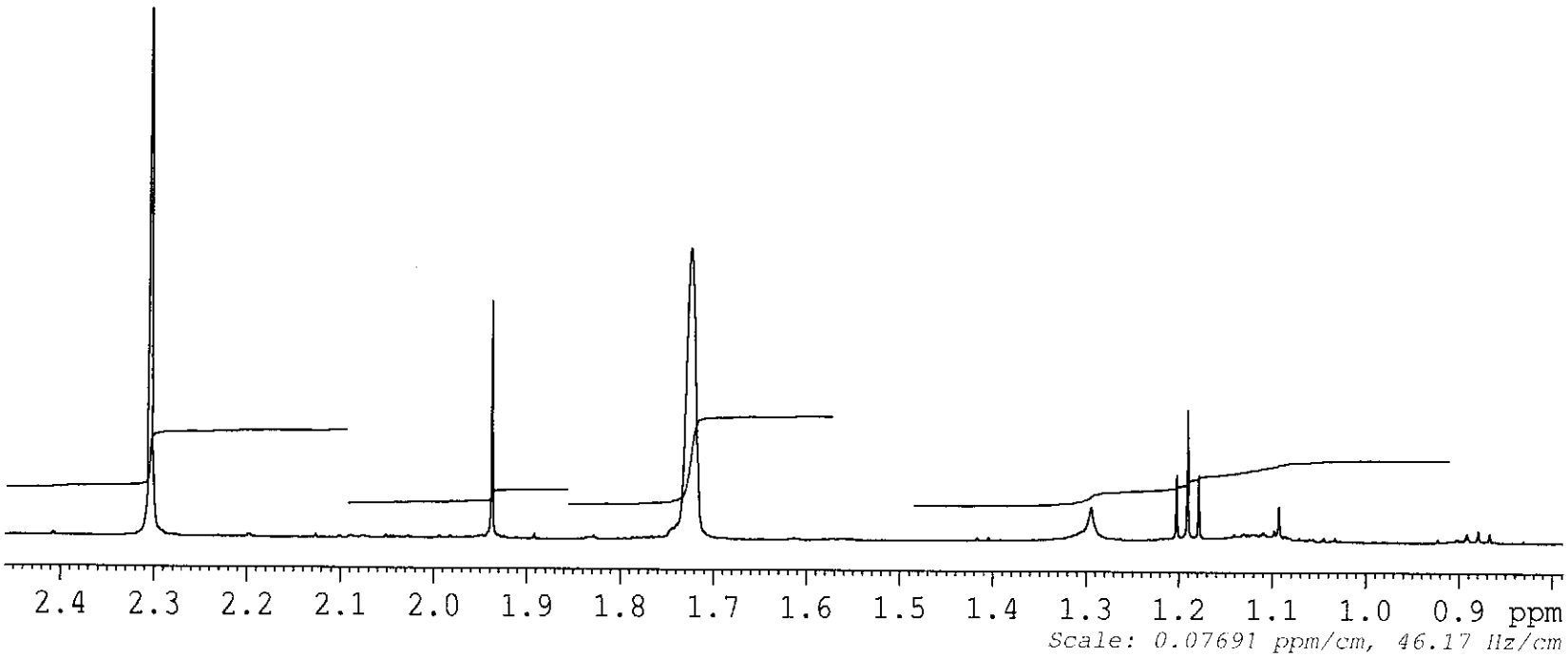
1H

av600



H615630

NAME	audab02501
EXPNO	10
PROCNO	1
Date_	20110810
Time	11.31
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	65536
SOLVENT	THF
NS	32
DS	2
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	9
DW	41.600 usec
DE	10.00 usec
TE	290.5 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	8.50 usec
PL1	4.20 dB
PL1W	5.30020905 W
SFO1	600.2242403 MHz
SI	131072
SF	600.2200208 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00
SR	20.80 Hz



AUD-AB-025-01

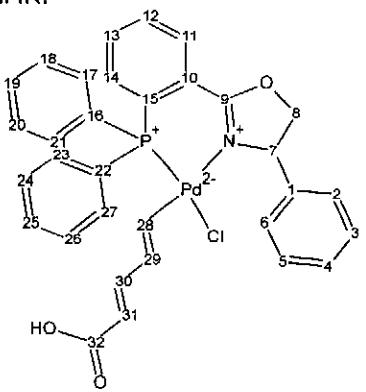
1H

av600

C615631

168.913 163.293 161.829 147.058 147.036 142.038 136.199 136.175 135.449 135.441 135.383 135.293 134.638 134.565 133.797 133.753 133.253 133.202 132.645 132.633 132.315 132.298 131.756 131.740 130.156 130.082 129.968 129.886 129.836 129.662 129.509 129.480 129.423 129.394 129.361 129.167 128.954 128.905 128.791 128.428 128.354 128.233 127.973 126.036 113.825 75.920 68.860 67.687 67.540 67.394 67.247 67.101 54.999 25.572 25.434 25.300 25.167 25.035 21.515

Vorschlag aus NMR:



NAME audab02501
EXPNO 11
PROCNO 1
Date_ 20110810
Time 11.53
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 80906
SOLVENT THF
NS 2000
DS 128
SWH 46296.297 Hz
FIDRES 0.572209 Hz
AQ 0.8738564 sec
RG 512
DW 10.800 usec
DE 50.99 usec
TE 290.5 K
D1 0.03000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 -1.00 dB
PL1W 109.73103333 W
SFO1 150.9419956 MHz

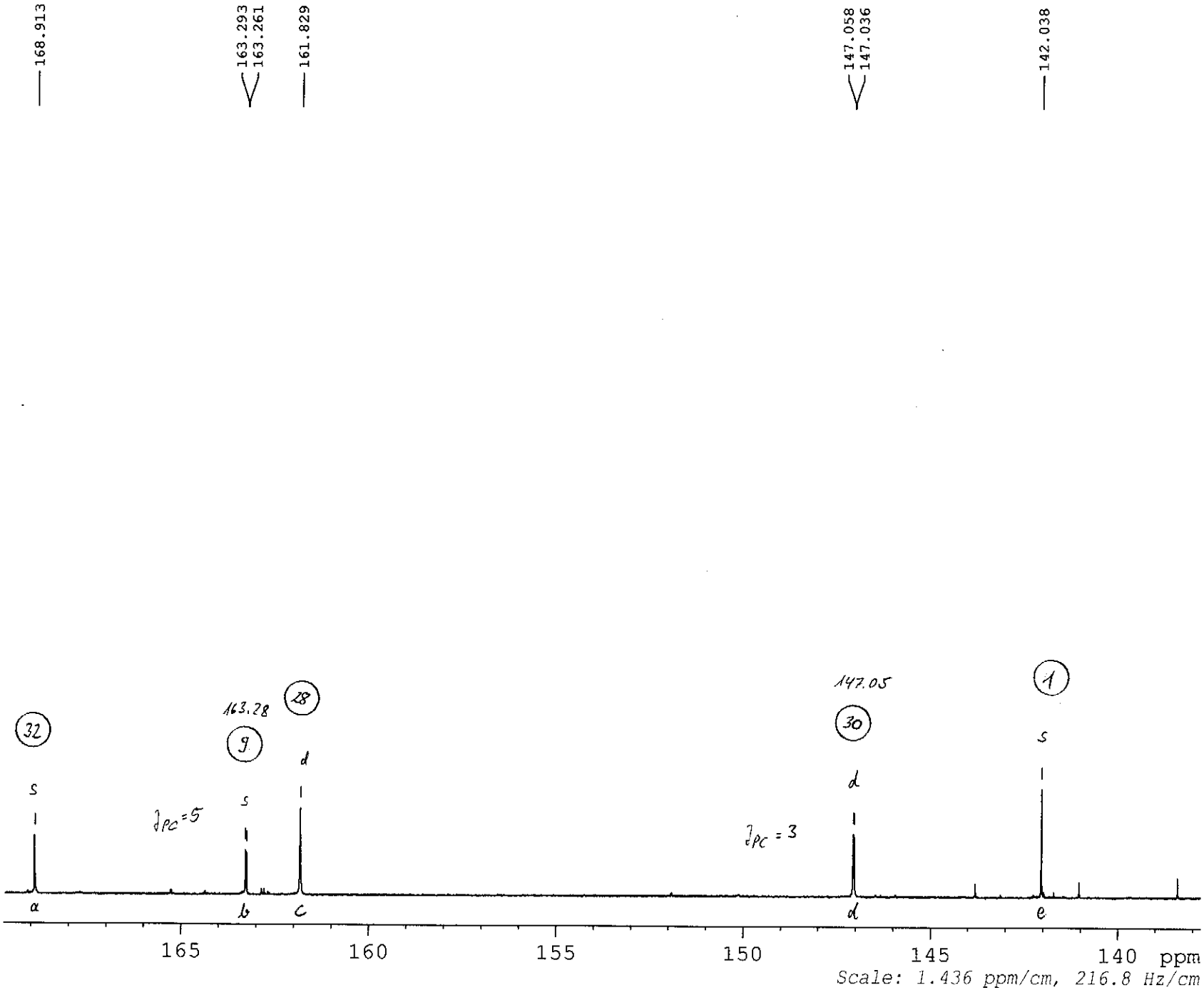
======== CHANNEL f2 ========
CPDPRG2 waltz65
NUC2 1H
PCPD2 70.00 usec
PL2 4.20 dB
PL12 22.51 dB
PL2W 5.30020905 W
PL12W 0.07821552 W
SFO2 600.2223000 MHz
SI 131072
SF 150.9252981 MHz
WDW EM
SSB 0
LB 0.80 Hz
GB 0
PC 1.00

AUD-AB-025-01
13C{1H}

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Scale: 11.51 ppm/cm, 1737 Hz/cm

av600



C615631

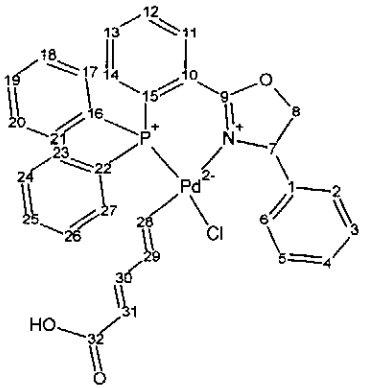
NAME	audab02501	
EXPNO	11	
PROCNO	1	
Date_	20110810	
Time	11.53	
INSTRUM	av600	
PROBHD	5 mm CPTCI 1H-	
PULPROG	zgdc30	
TD	80908	
SOLVENT	THF	
NS	2000	
DS	128	
SWH	46296.297	Hz
FIDRES	0.572209	Hz
AQ	0.8738564	sec
RG	512	
DW	10.800	use
DE	50.99	use
TE	290.5	K
D1	0.03000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	11.00	use
PL1	-1.00	dB
PL1W	109.73103333	W
SFO1	150.9419956	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz65	
NUC2	1H	
PCPD2	70.00	use
PL2	4.20	dB
PL12	22.51	dB
PL2W	5.30020905	W
PL12W	0.07821552	W
SFO2	600.2223000	MHz
SI	131072	
SF	150.9252981	MHz
WDW	EM	
SSB	0	
LB	0.80	Hz
GB	0	
PC	1.00	
SR	-140.93	Hz

AUD-AB-025-01
13C{1H}
av600

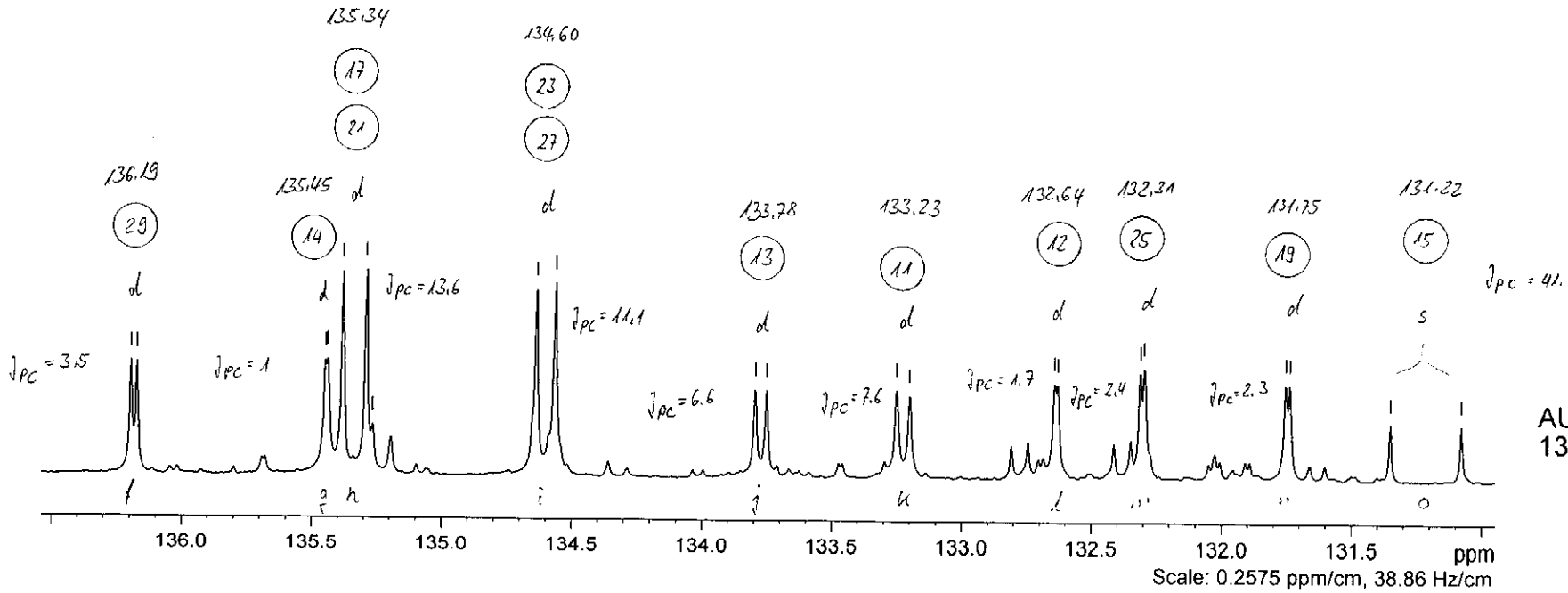
136.199
136.175
135.449
135.441
135.383
135.293
135.268
134.638
134.565
133.797
133.753
133.253
133.202
132.645
132.633
132.315
132.298
131.756
131.740
131.353
131.081

C615631

Vorschlag aus NMR:




```
NAME          audab02501
EXPNO             11
PROCNO             1
Date_          20110810
Time              11.53
INSTRUM           av600
PROBHD  5 mm CPTCI 1H-
PULPROG          zgdc30
TD                80908
SOLVENT             THF
NS                 2000
DS                  128
SWH          46296.297 Hz
FIDRES       0.572209 Hz
AQ           0.8738564 sec
RG                  512
DW           10.800 usec
DE           50.99 usec
TE           290.5 K
D1           0.03000000 sec
D11          0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              13C
P1           11.00 usec
PL1          -1.00 dB
PL1W         109.73103333 W
SFO1         150.9419956 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz65
NUC2              1H
PCPD2        70.00 usec
PL2          4.20 dB
PL12         22.51 dB
PL2W         5.30020905 W
PL12W        0.07821552 W
SFO2         600.2223000 MHz
SI           131072
SF           150.9252981 MHz
WDW              EM
SSB              0
LB           0.80 Hz
GB               0
PC           1.00
```



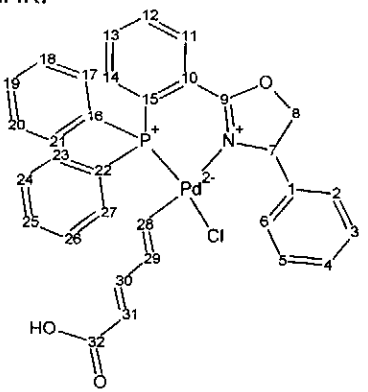
AUD-AB-025-01
13C{1H}

av600

130.156
130.082
129.968
129.886
129.836
129.662
129.509
129.480
129.423
129.394
129.361
129.167
128.954
128.923
128.905
128.791
128.428
128.354
128.233
127.973

C615631

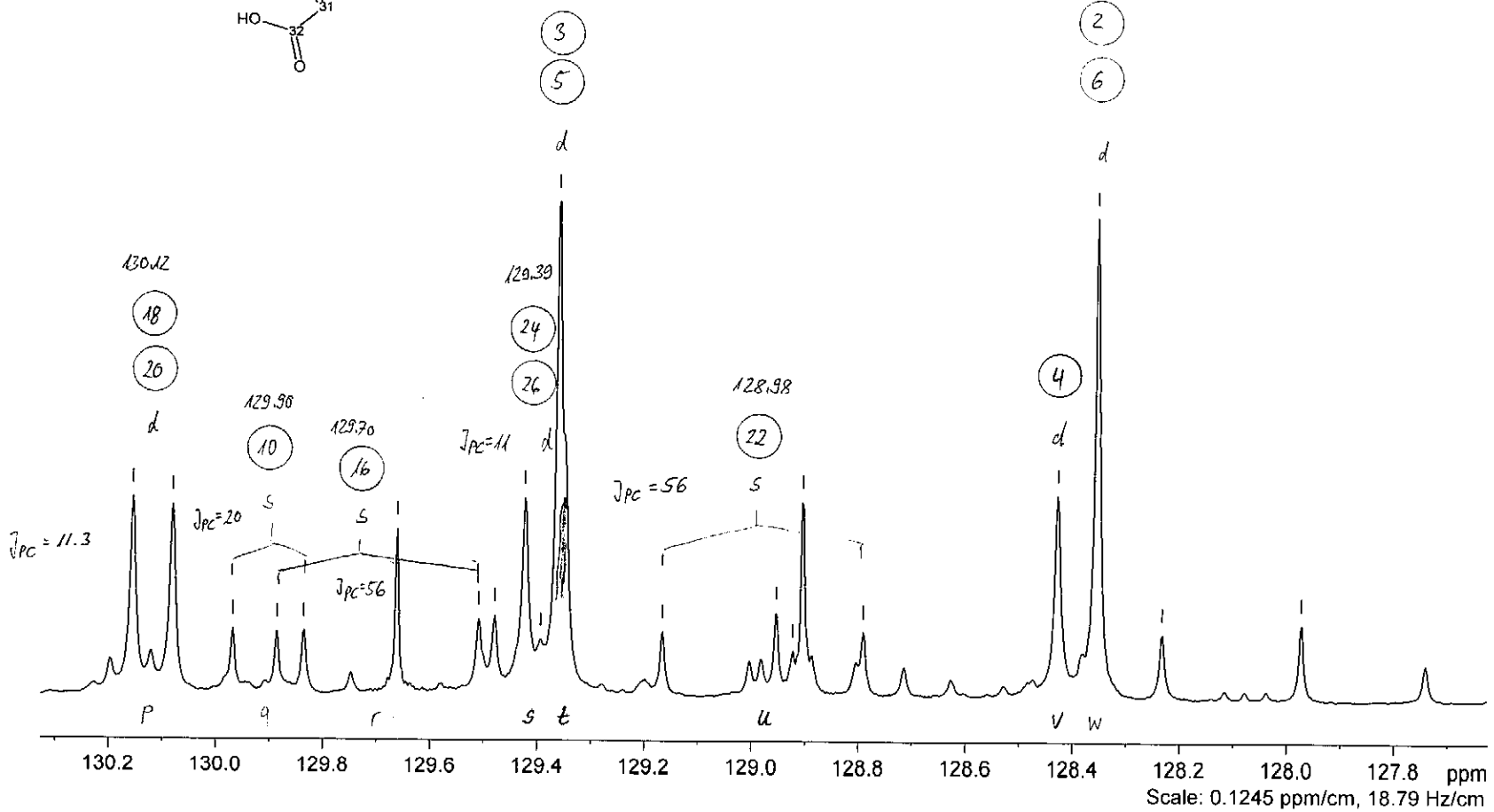
Vorschlag aus NMR:



NAME audab02501
EXPNO 11
PROCNO 1
Date_ 20110810
Time 11.53
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 80908
SOLVENT THF
NS 2000
DS 128
SWH 46296.297 Hz
FIDRES 0.572209 Hz
AQ 0.8738564 sec
RG 512
DW 10.800 usec
DE 50.99 usec
TE 290.5 K
D1 0.03000000 sec
D11 0.03000000 sec
TD0 1

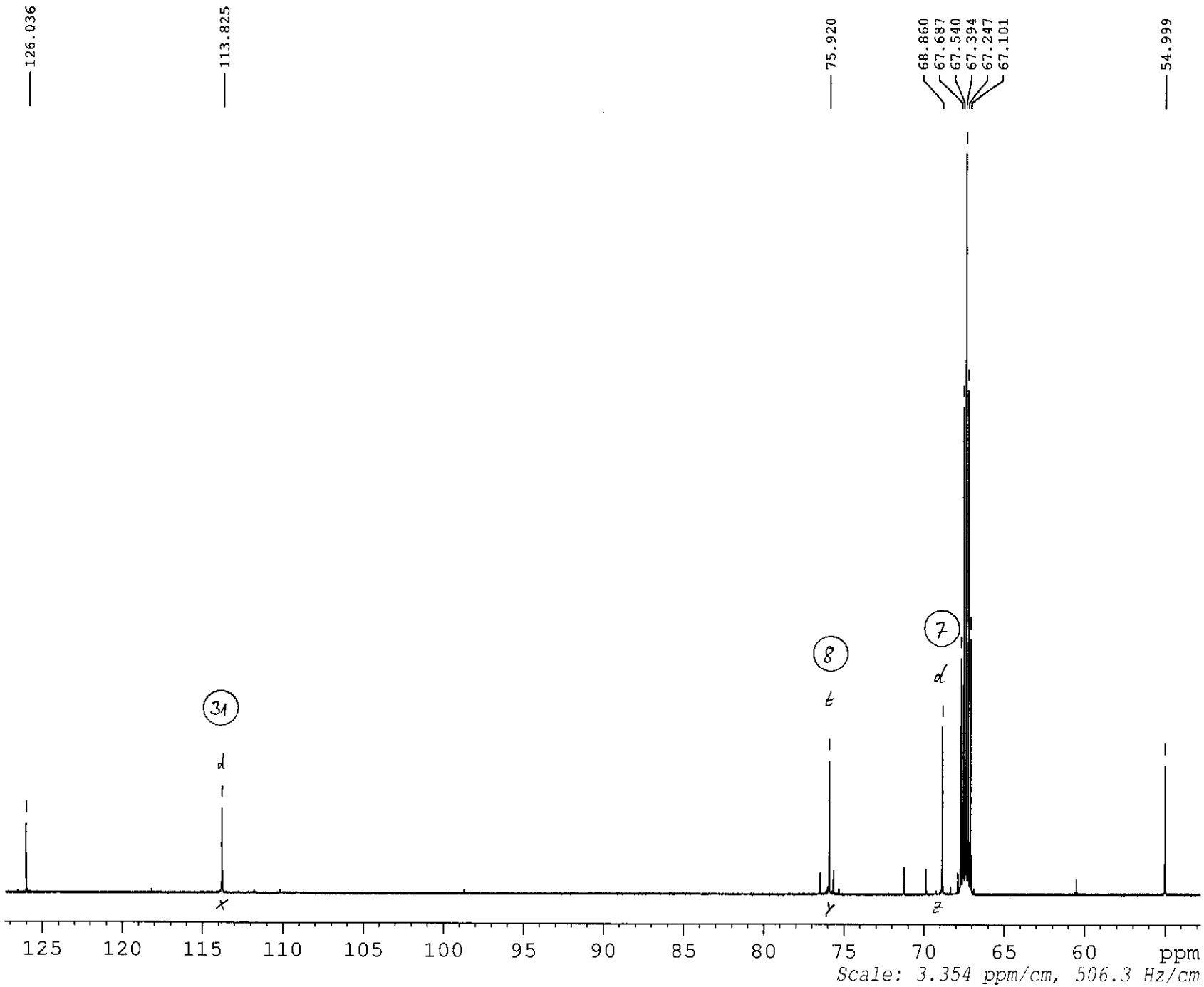
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 -1.00 dB
PL1W 109.73103333 W
SFO1 150.9419956 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz65
NUC2 1H
PCPD2 70.00 usec
PL2 4.20 dB
PL12 22.51 dB
PL2W 5.30020905 W
PL12W 0.07821552 W
SFO2 600.2223000 MHz
SI 131072
SF 150.9252981 MHz
WDW EM
SSB 0
LB 0.80 Hz
GB 0
PC 1.00



AUD-AB-025-01
13C{1H}

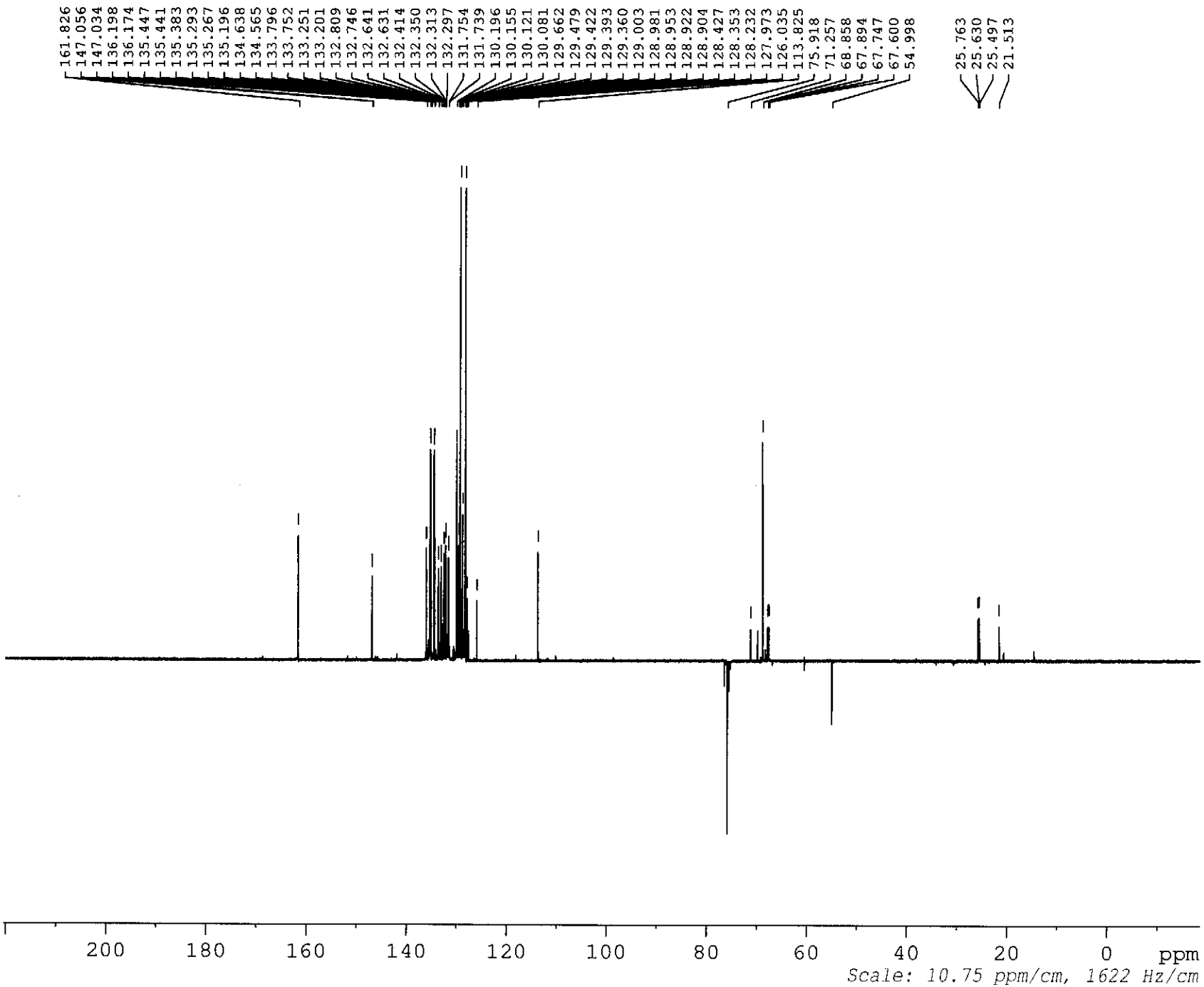
av600



C615631

NAME	audab02501	
EXPNO	11	
PROCNO	1	
Date_	20110810	
Time	11.53	
INSTRUM	av600	
PROBHD	5 mm CPTCI 1H-	
PULPROG	zgdc30	
TD	80908	
SOLVENT	THF	
NS	2000	
DS	128	
SWH	46296.297	Hz
FIDRES	0.572209	Hz
AQ	0.8738564	sec
RG	512	
DW	10.800	use
DE	50.99	use
TE	290.5	K
D1	0.03000000	sec
D11	0.03000000	sec
TD0	1	
-------- CHANNEL f1 -------		
NUC1	13C	
P1	11.00	use
PL1	-1.00	dB
PL1W	109.73103333	W
SFO1	150.9419956	MHz
-------- CHANNEL f2 -------		
CPDPRG2	waltz65	
NUC2	1H	
PCPD2	70.00	use
PL2	4.20	dB
PL12	22.51	dB
PL2W	5.30020905	W
PL12W	0.07821552	W
SFO2	600.2223000	MHz
SI	131072	
SF	150.9252981	MHz
WDW	EM	
SSB	0	
LB	0.80	Hz
GB	0	
PC	1.00	
SR	-140.93	Hz

AUD-AB-025-01
13C{1H}
av600

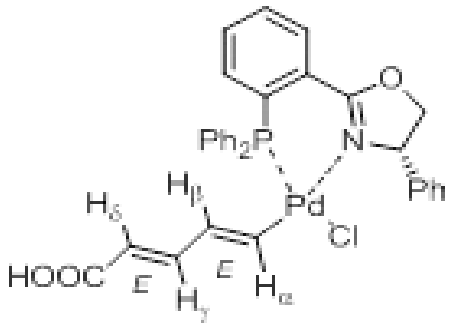


C615632

NAME	audab02501	
EXPNO	12	
PROCNO	1	
Date_	20110810	
Time	12.19	
INSTRUM	av600	
PROBHD	5 mm CPTCI 1H-	
PULPROG	deptsp135	
TD	65536	
SOLVENT	THF	
NS	320	
DS	4	
SWH	36057.691	Hz
FIDRES	0.550197	Hz
AQ	0.9088159	sec
RG	512	
DW	13.867	use
DE	51.34	use
TE	290.5	K
CNST2	145.0000000	
D1	2.00000000	sec
D2	0.00344828	sec
D12	0.00002000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	11.00	use
P12	2000.00	use
PL0	120.00	dB
PL1	-1.00	dB
PL0W	0.00000000	W
PL1W	109.73103333	W
SFO1	150.9405316	MHz
SP2	6.33	dB
SPNAM2	Crp60comp.4	
SPOAL2	0.500	
SPOFFS2	0.00	Hz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
P3	8.50	use
P4	17.00	use
PCPD2	70.00	use
PL2	4.20	dB
PL12	22.51	dB
PL2W	5.30020905	W
PL12W	0.07821552	W
SFO2	600.2223000	MHz
SI	65536	
SF	150.9252981	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.00	

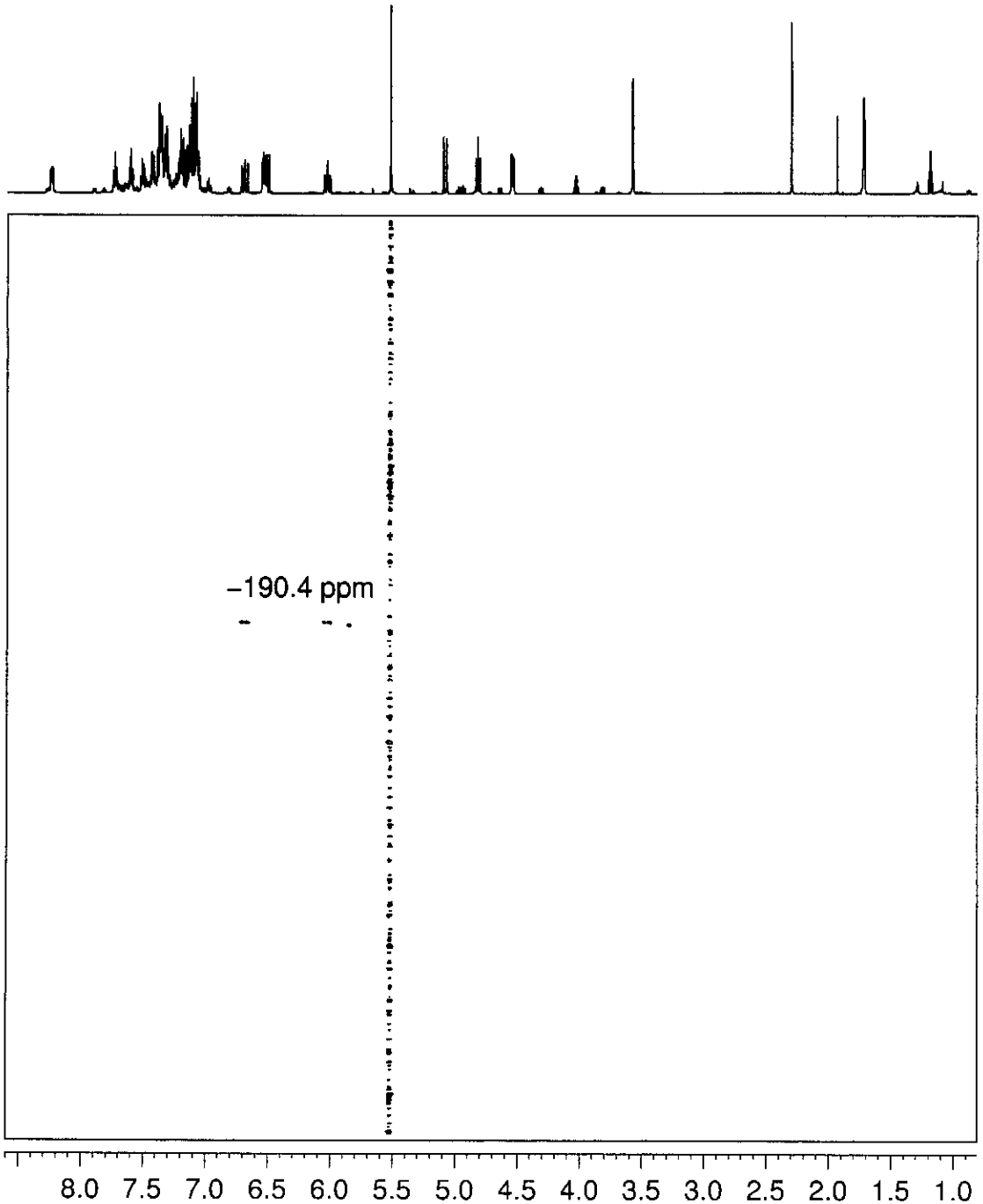
AUD-AB-025-01
dept135
av600

aud-ab-201-01
aud-ab-208-01
31P{1H} zgdc30



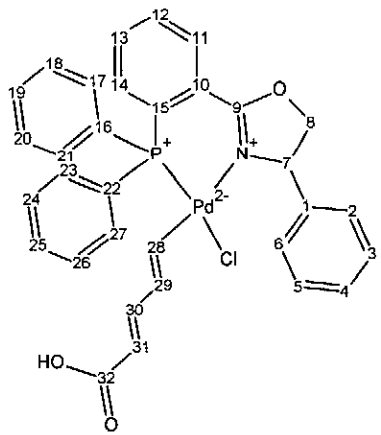
4

N615638



ext. Standard
90% CH3NO2 in CDCl3 = 0 ppm

Vorschlag aus NMR:

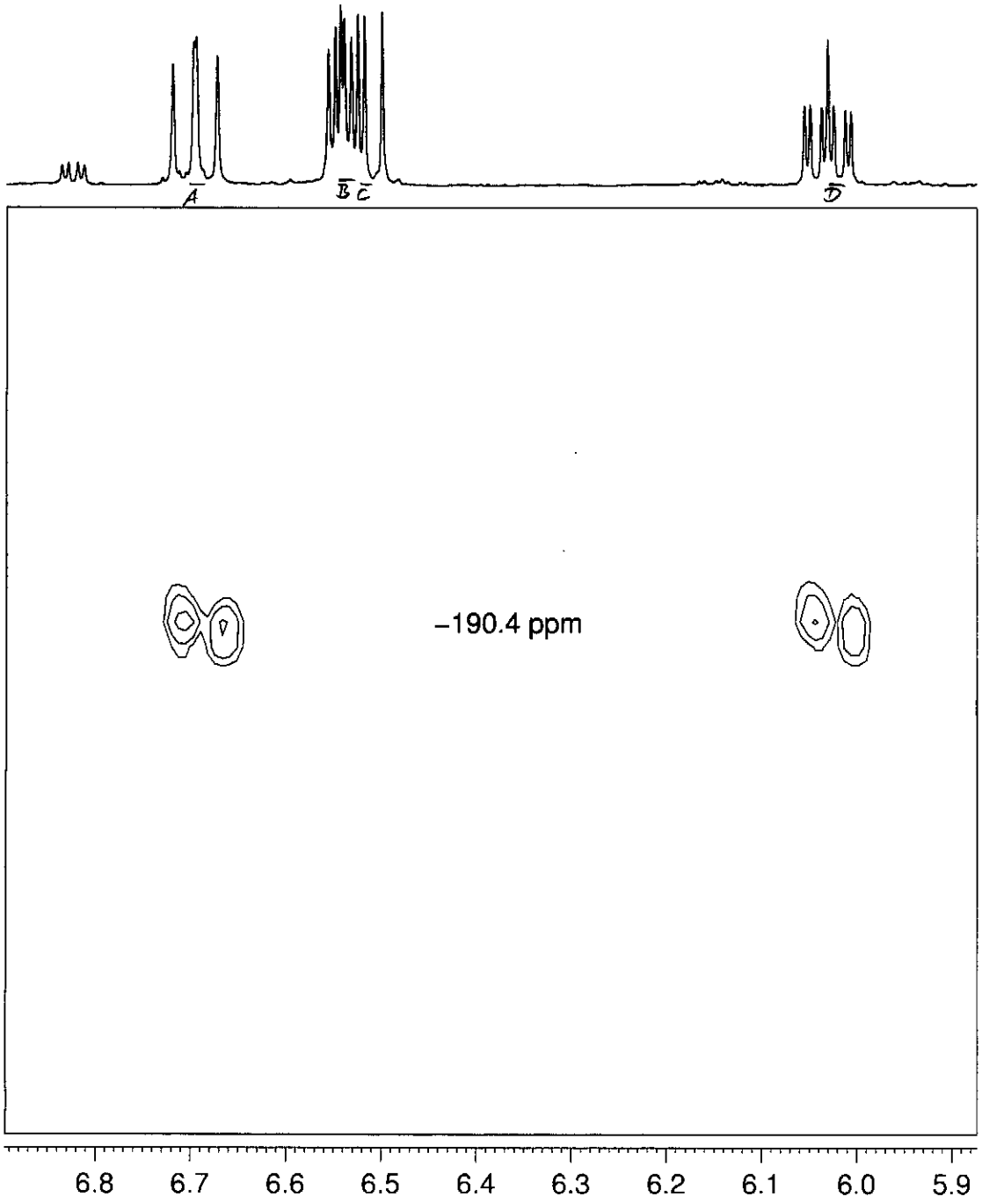


NAME	audab02501
EXPNO	152
PROCNO	1
Date_	20110810
Time	16.39
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	hmbcf3gpndqf_wz
TD	1024
SOLVENT	THF
NS	4
DS	16
SWH	4681.648 Hz
FIDRES	4.571922 Hz
AQ	0.1094132 sec
RG	512
DW	106.800 usec
DE	6.50 usec
TE	290.5 K
CNST13	10.0000000
D0	0.00000300 sec
D1	4.00000000 sec
D6	0.05000000 sec
D16	0.00020000 sec
IN0	0.00001175 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	8.50 usec
P2	17.00 usec
PL1	4.20 dB
PL1W	5.30020905 W
SFO1	600.2228450 MHz
======== CHANNEL f3 ========	
NUC3	15N
P21	34.00 usec
PL3	-3.00 dB
PL3W	121.78649792 W
SFO3	60.8337636 MHz
======= GRADIENT CHANNEL =====	
GPNAM1	SINE.100
GPNAM2	SINE.100
GPNAM3	SINE.100
GPZ1	70.00 %
GPZ2	30.00 %
GPZ3	50.10 %
P16	1000.00 usec
ND0	2
TD	1024
SFO1	60.83376 MHz
FIDRES	41.585579 Hz
SW	700.000 ppm
FnMODE	QF
SI	1024
SF	600.2200208 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.40
SR	20.80 Hz
SI	1024
MC2	QF
SF	60.8428780 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

AUD-AB-025-01
15N via 1H
HMBC nJ(NH)=10 Hz

av600

N615638



ext. Standard
90% CH3NO2 in CDCl3 = 0 ppm

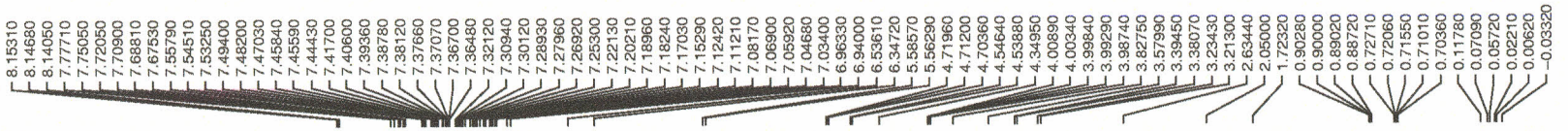
A D

```
NAME        audab02501
EXPNO             152
PROCNO              1
Date_        20110810
Time             16.39
INSTRUM          av600
PROBHD  5 mm CPTCI 1H-
PULPROG  hmbcf3gpndqf_wz
TD                1024
SOLVENT            THF
NS                   4
DS                  16
SWH          4681.648 Hz
FIDRES       4.571922 Hz
AQ           0.1094132 sec
RG                 512
DW           106.800 usec
DE             6.50 usec
TE             290.5 K
CNST13        10.0000000
D0          0.00000300 sec
D1          4.00000000 sec
D6          0.05000000 sec
D16         0.00020000 sec
IN0         0.00001175 sec

======== CHANNEL f1 ========
NUC1               1H
P1              8.50 usec
P2             17.00 usec
PL1             4.20 dB
PL1W        5.30020905 W
SFO1      600.2228450 MHz

======== CHANNEL f3 ========
NUC3              15N
P21            34.00 usec
PL3            -3.00 dB
PL3W       121.78649792 W
SFO3       60.8337536 MHz

====== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPNAM2        SINE.100
GPNAM3        SINE.100
GPZ1           70.00 %
GPZ2           30.00 %
GPZ3           50.10 %
P16          1000.00 usec
ND0                2
TD              1024
SFO1       60.83376 MHz
FIDRES      41.585579 Hz
SW          700.000 ppm
FnMODE             QF
SI              1024
SF       600.2200208 MHz
WDW             QSINE
SSB                2
LB              0.00 Hz
GB                 0
PC              1.40
SR             20.80 Hz
SI              1024
MC2                QF
SF       60.8428780 MHz
WDW             QSINE
SSB                2
LB              0.00 Hz
GB                 0
```

AUD-AB-025-01
15N via 1H
HMBC nJ(NH)=10 Hz

av600

H616833



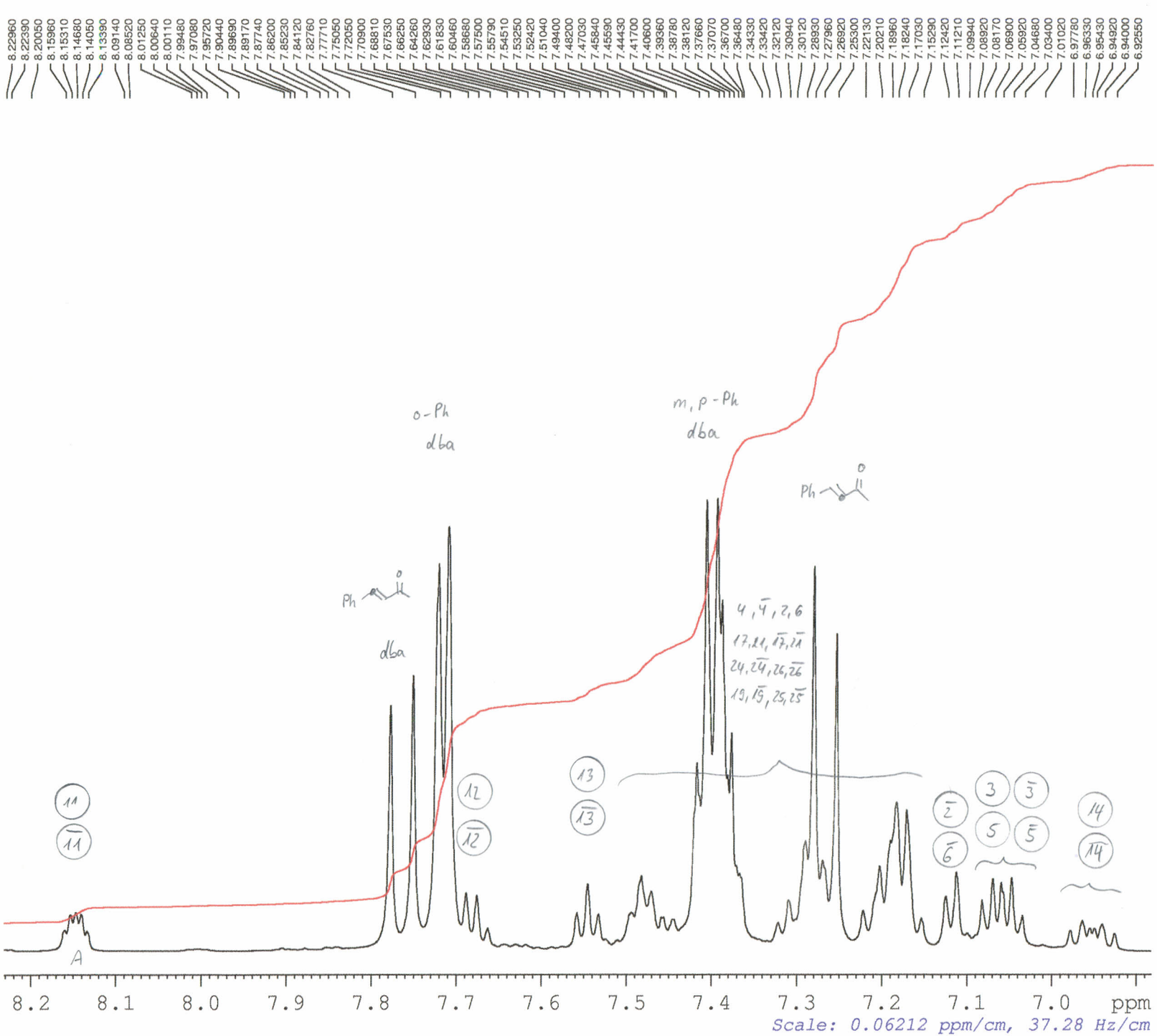
NAME audab231
EXPNO 30
PROCNO 1
Date_ 20120508
Time 10.39
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 65536
SOLVENT THF
NS 32
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 9
DW 41.600 usec
DE 10.00 usec
TE 278.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 8.50 usec
PL1 4.20 dB
PL1W 5.30020905 W
SFO1 600.2242403 MHz
SI 131072
SF 600.2200218 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
SR 21.84 Hz

AUD-AB-231
278K
1H

av600

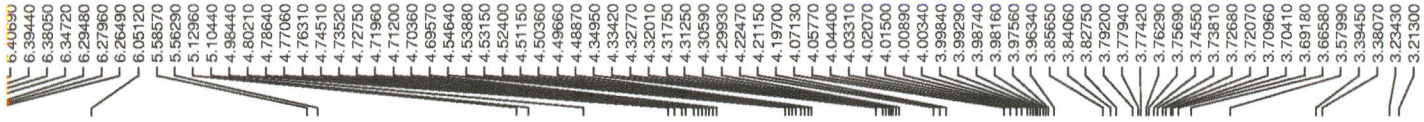
H616833



NAME	audab231
EXPNO	30
PROCNO	1
Date_	20120508
Time	10.39
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	65536
SOLVENT	THF
NS	32
DS	2
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	9
DW	41.600 usec
DE	10.00 usec
TE	278.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	8.50 usec
PL1	4.20 dB
PL1W	5.30020905 W
SFO1	600.2242403 MHz
SI	131072
SF	600.2200218 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00
SR	21.84 Hz

AUD-AB-231
278K
1H

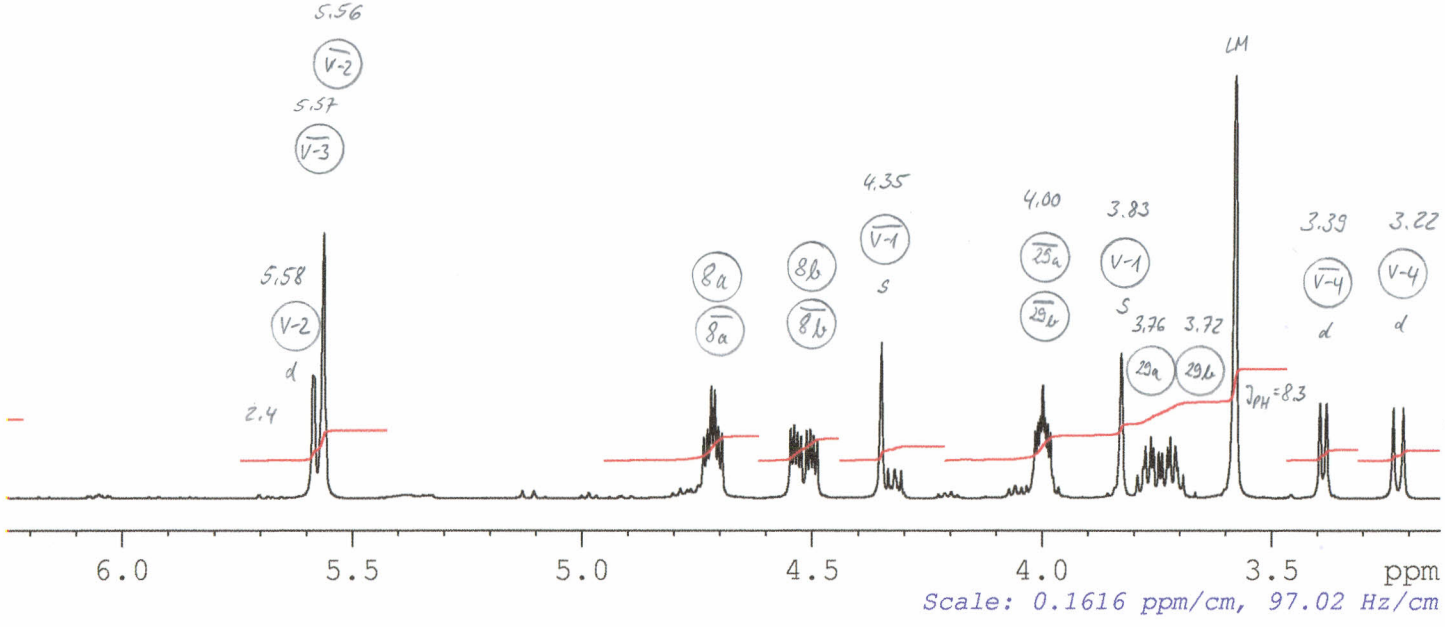
av600



H616833

NAME audab231
EXPNO 30
PROCNO 1
Date_ 20120508
Time 10.39
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 65536
SOLVENT THF
NS 32
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 9
DW 41.600 usec
DE 10.00 usec
TE 278.0 K
D1 1.00000000 sec
TD0 1

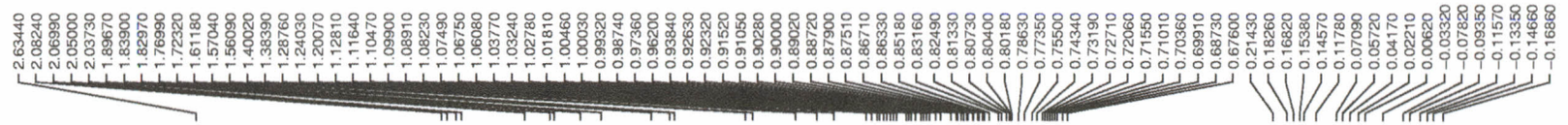
======== CHANNEL f1 ========
NUC1 1H
P1 8.50 usec
PL1 4.20 dB
PL1W 5.30020905 W
SFO1 600.2242403 MHz
SI 131072
SF 600.2200218 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
SR 21.84 Hz

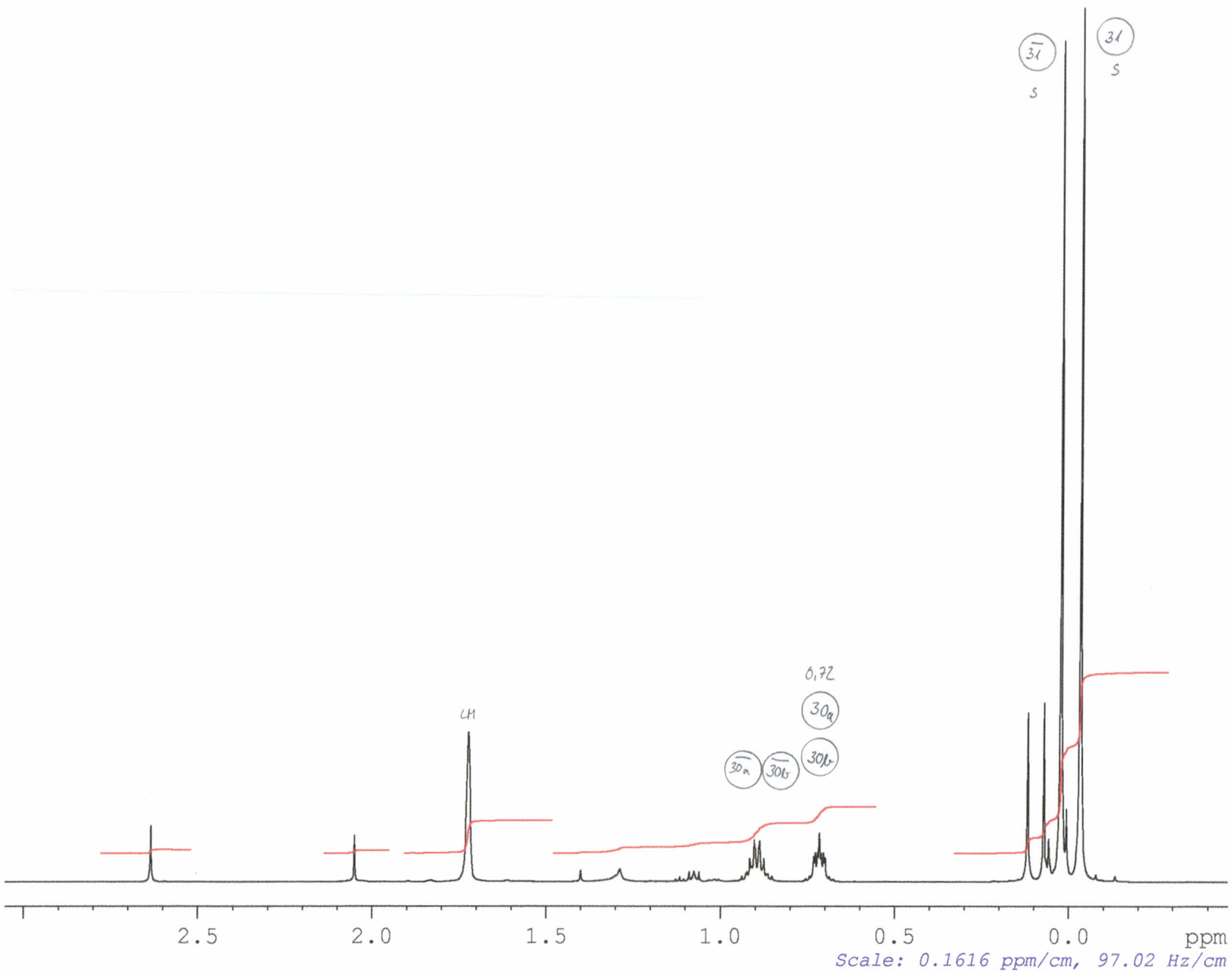


AUD-AB-231
278K
1H

av600

H616833





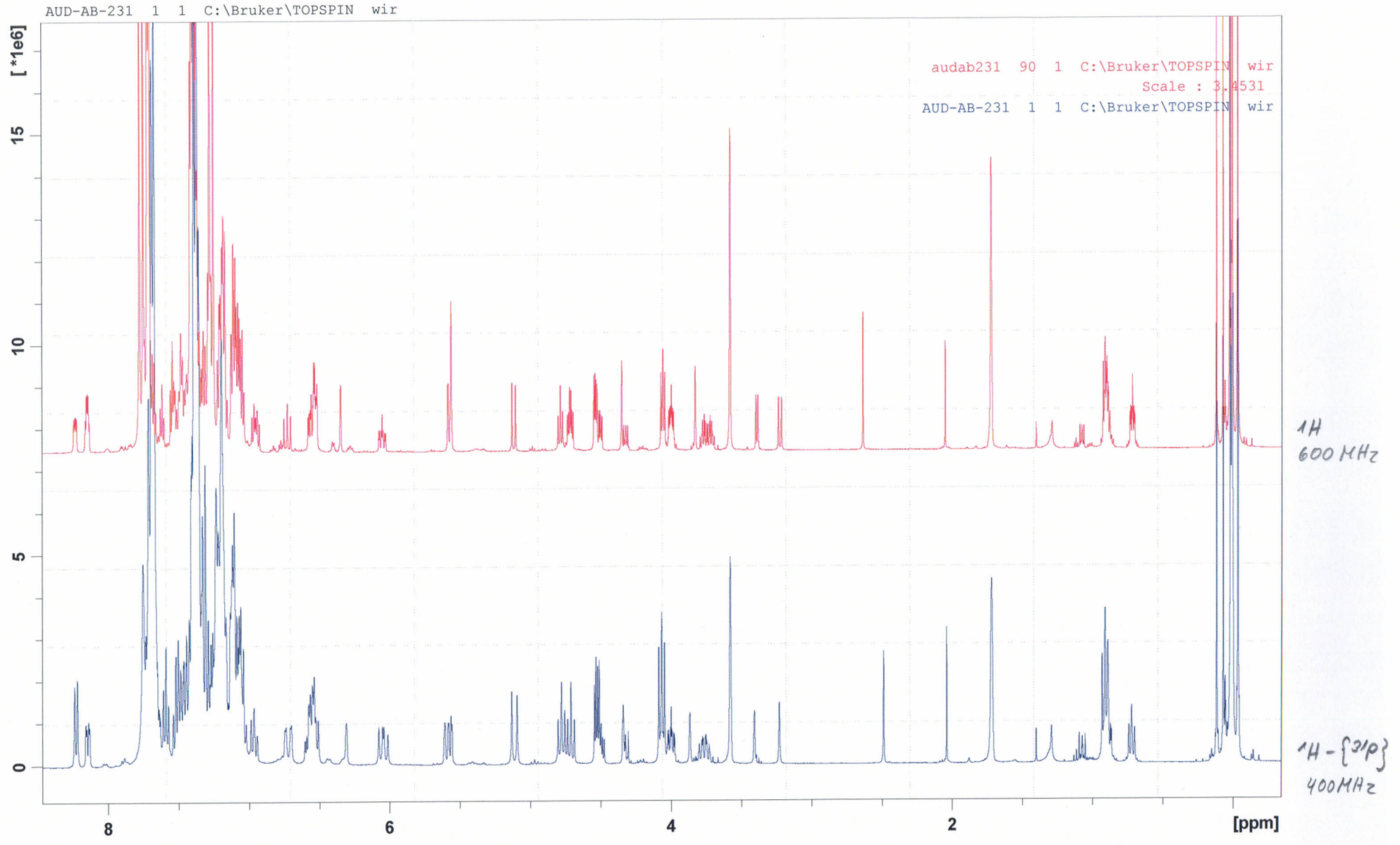
NAME	audab231
EXPNO	30
PROCNO	1
Date_	20120508
Time	10.39
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	65536
SOLVENT	THF
NS	32
DS	2
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	9
DW	41.600 usec
DE	10.00 usec
TE	278.0 K
D1	1.00000000 sec
TD0	1

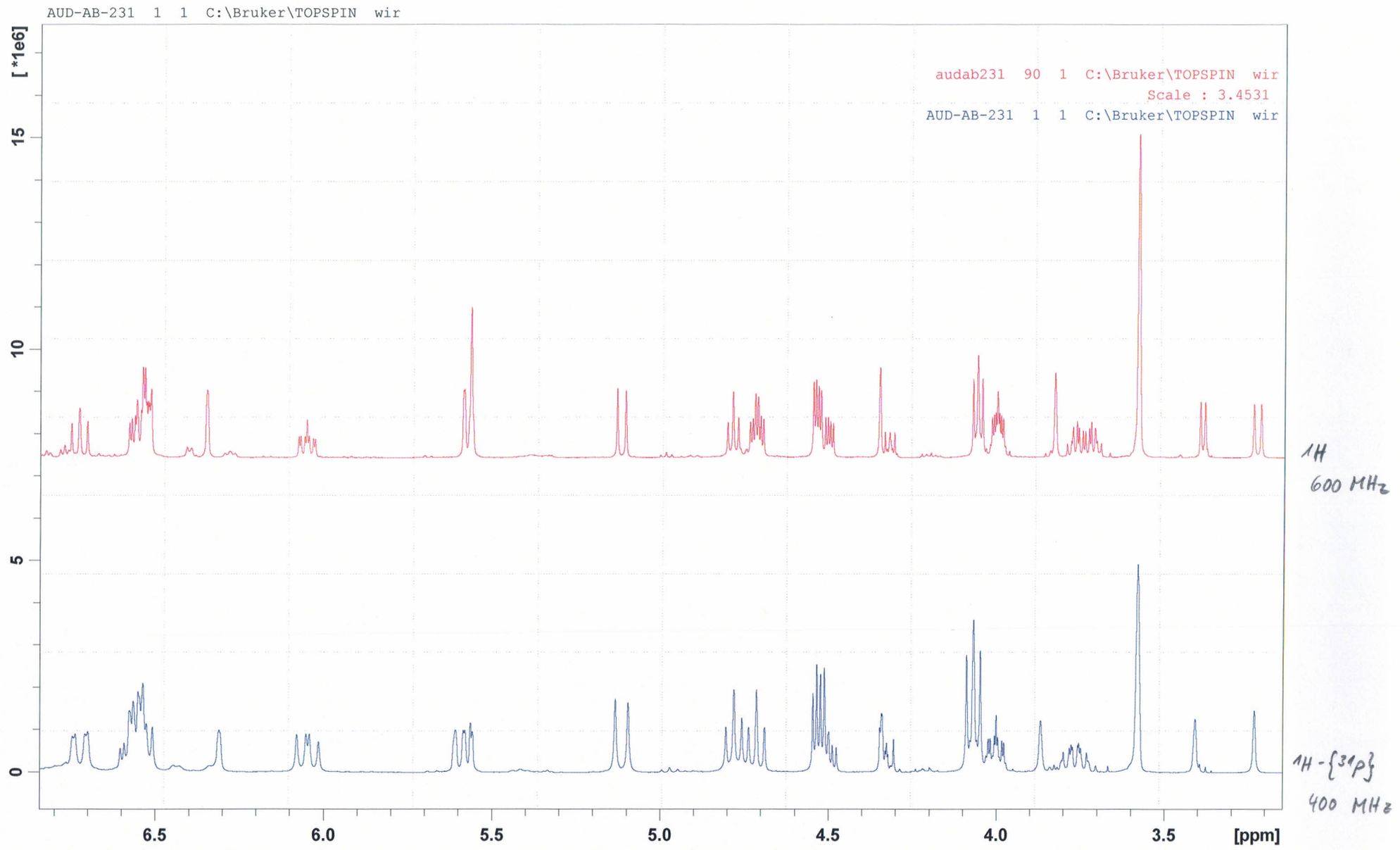
========== CHANNEL f1 ==========

NUC1	1H
P1	8.50 usec
PL1	4.20 dB
PL1W	5.30020905 W
SFO1	600.2242403 MHz
SI	131072
SF	600.2200218 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00
SR	21.84 Hz

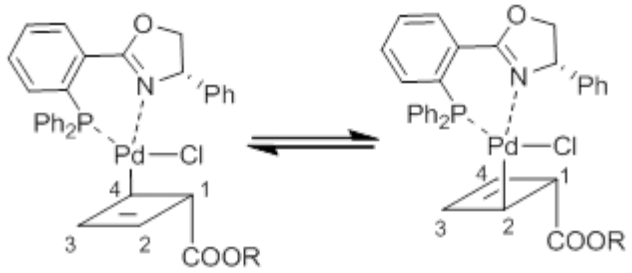
AUD-AB-231
278K
1H

av600


AUD-AB-231 1 1 C:\Bruker\TOPSPIN wir
audab231 90 1 C:\Bruker\TOPSPIN wir
Scale : 3.4531
AUD-AB-231 1 1 C:\Bruker\TOPSPIN wir
[*1e6]
15
10
5
0
8
6
4
2
[ppm]
1H
600 MHz
1H-{31P}
400MHz


AUD-AB-231 1 1 C:\Bruker\TOPSPIN wir
audab231 90 1 C:\Bruker\TOPSPIN wir
Scale : 3.4531
AUD-AB-231 1 1 C:\Bruker\TOPSPIN wir
[*1e6]
15
10
5
0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
[ppm]
1H
600 MHz
1H-{31P}
400 MHz

AUD-AB-227-0 C
AUD-AB-227-0 C



eta-1-allyl complex **7a** and **7b** (ca. 1:1)

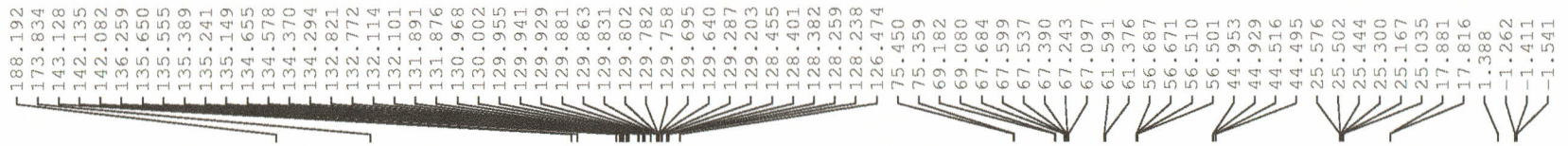
R = CH_2CH_2TMS

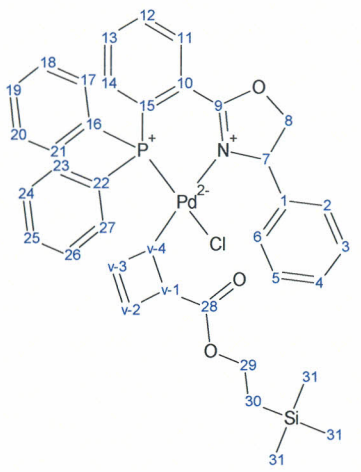
30.61
28.70
26.10
-8.20

7a
7b
(E,E)-diene-**8**
L-Ph

1.05
1.00

f1 (ppm)

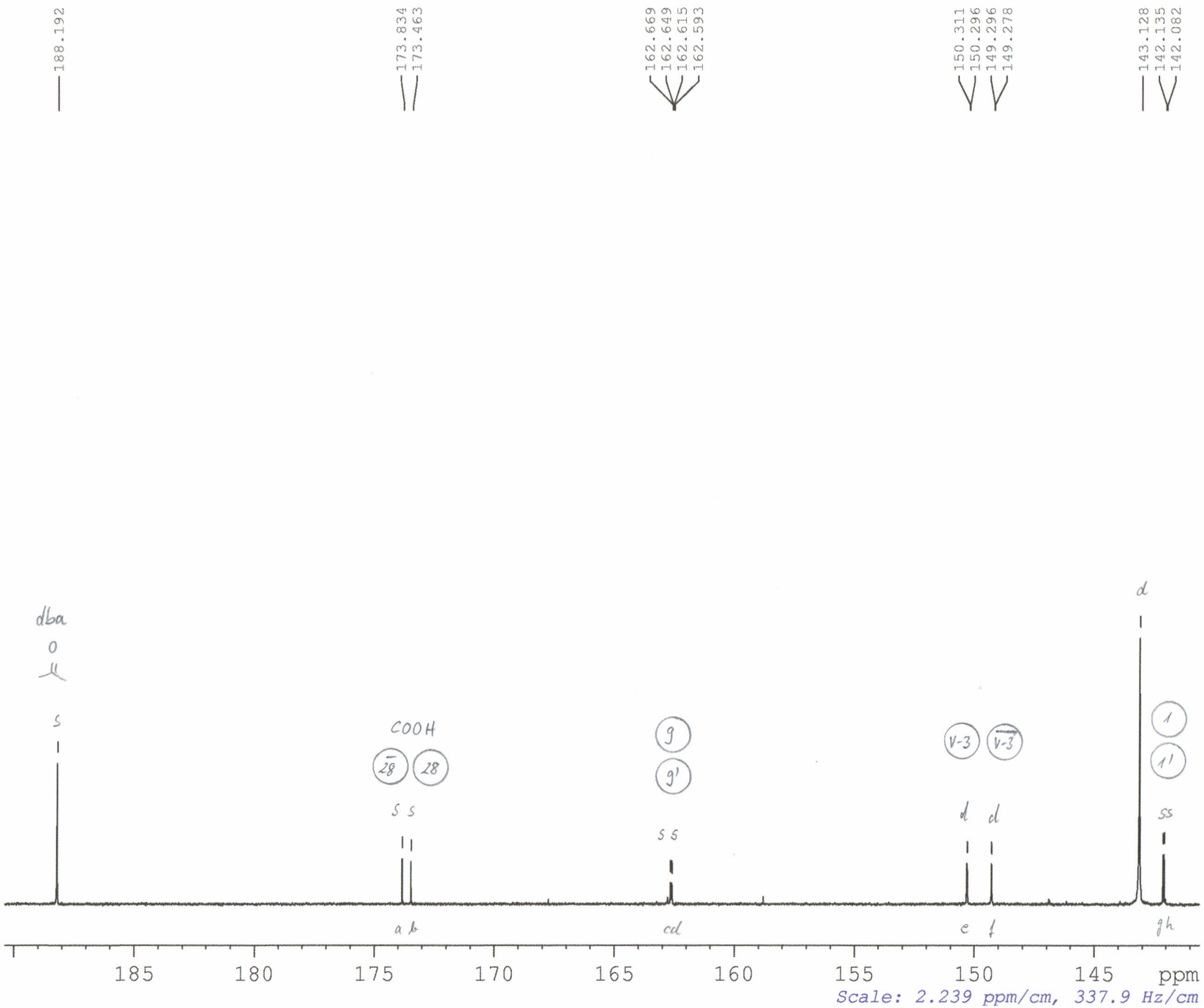




C616834

NAME	audab231
EXPNO	31
PROCNO	1
Date_	20120508
Time	10.47
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zgdc30
TD	80908
SOLVENT	THF
NS	1320
DS	128
SWH	46296.297 Hz
FIDRES	0.572209 Hz
AQ	0.8738564 sec
RG	512
DW	10.800 use
DE	50.99 use
TE	278.0 K
D1	0.03000000 sec
D11	0.03000000 sec
TD0	1
==========	CHANNEL f1 ==========
NUC1	13C
P1	11.00 use
PL1	-1.00 dB
PL1W	109.73103333 W
SFO1	150.9419956 MHz
==========	CHANNEL f2 ==========
CPDPRG2	waltz65
NUC2	1H
PCPD2	70.00 use
PL2	4.20 dB
PL12	22.51 dB
PL2W	5.30020905 W
PL12W	0.07821552 W
SFO2	600.2223000 MHz
SI	131072
SF	150.9252989 MHz
WDW	EM
SSB	0
LB	0.80 Hz
GB	0
PC	1.00
SR	-140.11 Hz

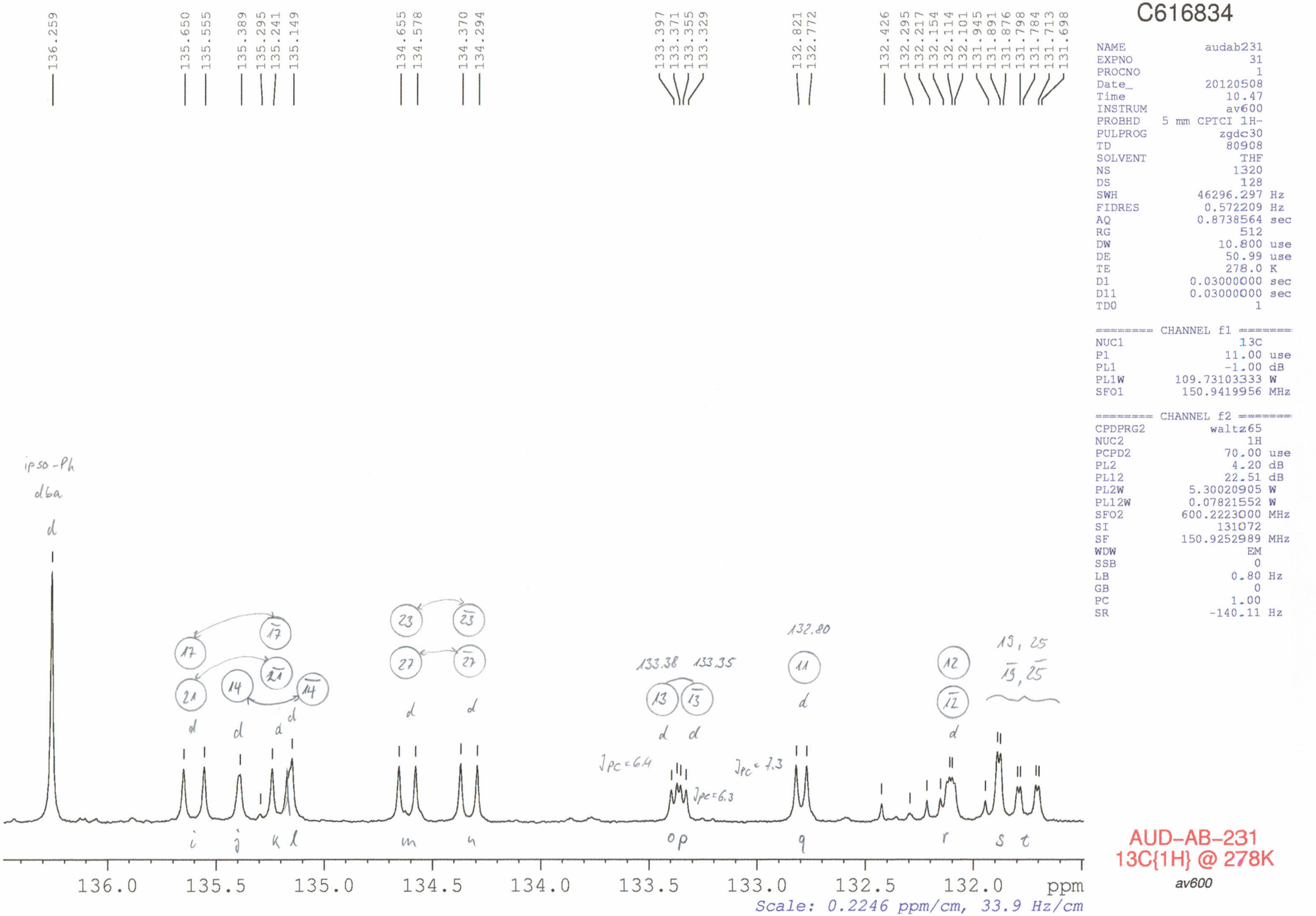
AUD-AB-231
13C{1H} @ 278K
av600



C616834

NAME	audab231	
EXPNO	31	
PROCNO	1	
Date_	20120508	
Time	10.47	
INSTRUM	av600	
PROBHD	5 mm CPTCI 1H-	
PULPROG	zgdc30	
TD	80908	
SOLVENT	THF	
NS	1320	
DS	128	
SWH	46296.297	Hz
FIDRES	0.572209	Hz
AQ	0.8738564	sec
RG	512	
DW	10.800	use
DE	50.99	use
TE	278.0	K
D1	0.03000000	sec
D11	0.03000000	sec
TD0	1	
==========	CHANNEL f1	==========
NUC1	13C	
P1	11.00	use
PL1	-1.00	dB
PL1W	109.73103333	W
SFO1	150.9419956	MHz
==========	CHANNEL f2	==========
CPDPRG2	waltz65	
NUC2	1H	
PCPD2	70.00	use
PL2	4.20	dB
PL12	22.51	dB
PL2W	5.30020905	W
PL12W	0.07821552	W
SFO2	600.2223000	MHz
SI	131072	
SF	150.9252989	MHz
WDW	EM	
SSB	0	
LB	0.80	Hz
GB	0	
PC	1.00	
SR	-140.11	Hz

AUD-AB-231
13C{1H} @ 278K
av600



C616834

NAME	audab231
EXPNO	31
PROCNO	1
Date_	20120508
Time	10.47
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zgdc30
TD	80908
SOLVENT	THF
NS	1320
DS	128
SWH	46296.297 Hz
FIDRES	0.572209 Hz
AQ	0.8738564 sec
RG	512
DW	10.800 use
DE	50.99 use
TE	278.0 K
D1	0.03000000 sec
D11	0.03000000 sec
TD0	1

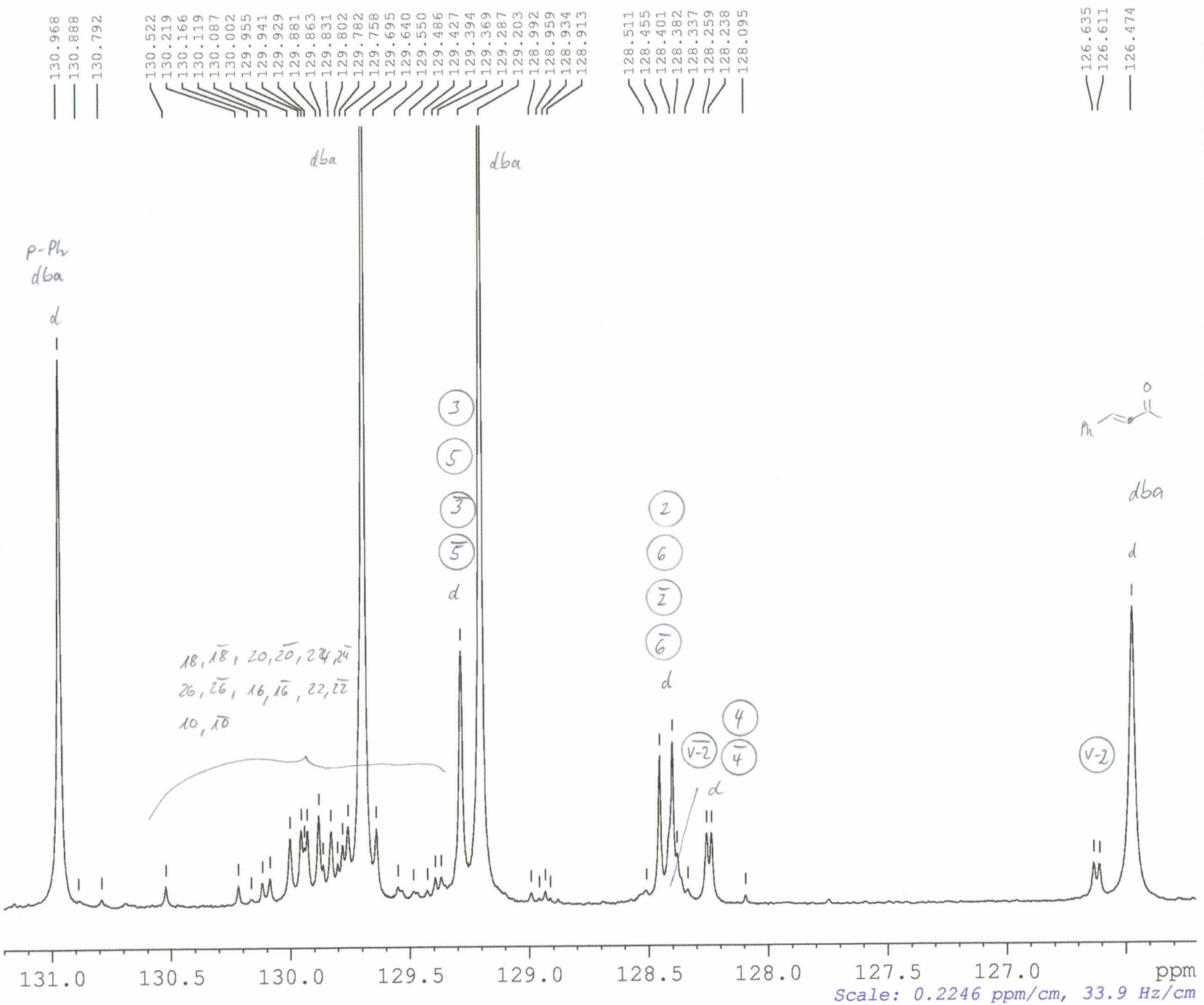
CHANNEL f1

NUC1	13C
P1	11.00 use
PL1	-1.00 dB
PL1W	109.73103333 W
SFO1	150.9419956 MHz

CHANNEL f2

CPDPRG2	waltz65
NUC2	1H
PCPD2	70.00 use
PL2	4.20 dB
PL12	22.51 dB
PL2W	5.30020905 W
PL12W	0.07821552 W
SFO2	600.2223000 MHz
SI	131072
SF	150.9252989 MHz
WDW	EM
SSB	0
LB	0.80 Hz
GB	0
PC	1.00
SR	-140.11 Hz

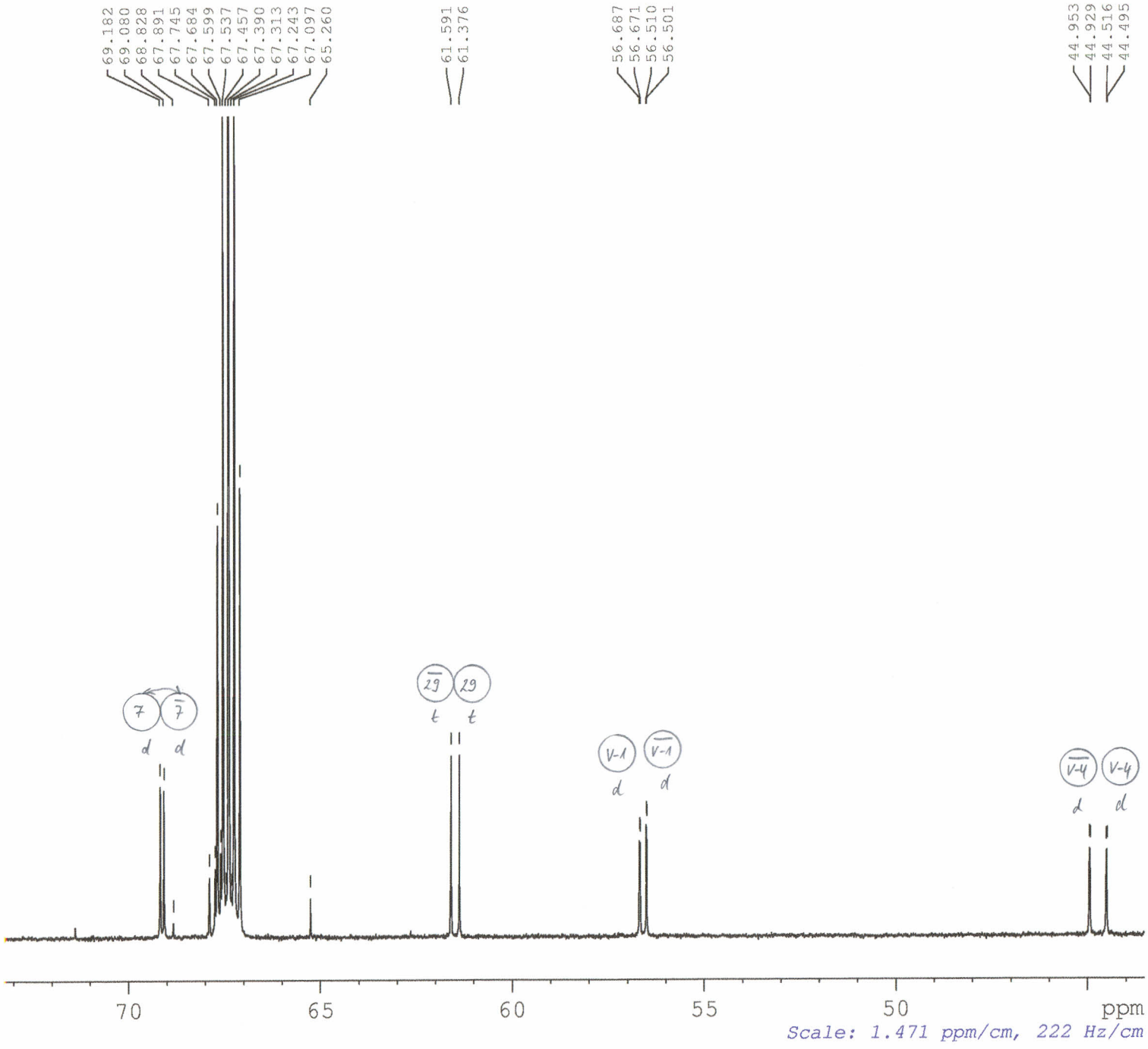
AUD-AB-231
13C{1H} @ 278K
av600



C616834

NAME	audab231
EXPNO	31
PROCNO	1
Date_	20120508
Time	10.47
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zgdc30
TD	80908
SOLVENT	THF
NS	1320
DS	128
SWH	46296.297 Hz
FIDRES	0.572209 Hz
AQ	0.8738564 sec
RG	512
DW	10.800 use
DE	50.99 use
TE	278.0 K
D1	0.03000000 sec
D11	0.03000000 sec
TD0	1
========== CHANNEL f1 ==========	
NUC1	13C
P1	11.00 use
PL1	-1.00 dB
PL1W	109.73103333 W
SFO1	150.9419956 MHz
========== CHANNEL f2 ==========	
CPDPRG2	waltz65
NUC2	1H
PCPD2	70.00 use
PL2	4.20 dB
PL12	22.51 dB
PL2W	5.30020905 W
PL12W	0.07821552 W
SFO2	600.2223000 MHz
SI	131072
SF	150.9252989 MHz
WDW	EM
SSB	0
LB	0.80 Hz
GB	0
PC	1.00
SR	-140.11 Hz

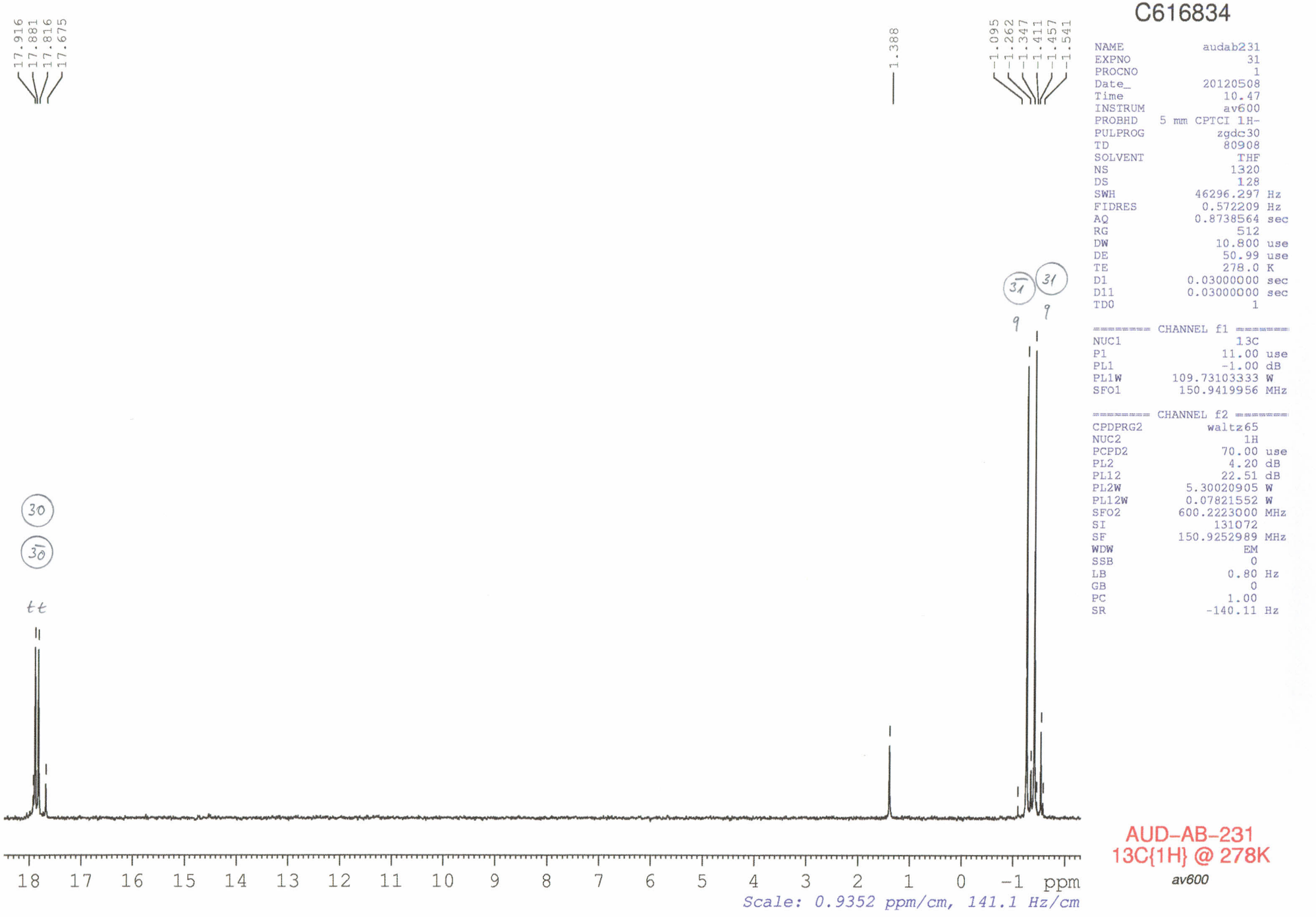
AUD-AB-231
13C{1H} @ 278K
av600



C616834

NAME	audab231	
EXPNO	31	
PROCNO	1	
Date_	20120508	
Time	10.47	
INSTRUM	av600	
PROBHD	5 mm CPTCI 1H-	
PULPROG	zgdc30	
TD	80908	
SOLVENT	THF	
NS	1320	
DS	128	
SWH	46296.297	Hz
FIDRES	0.572209	Hz
AQ	0.8738564	sec
RG	512	
DW	10.800	use
DE	50.99	use
TE	278.0	K
D1	0.03000000	sec
D11	0.03000000	sec
TD0	1	
==========	CHANNEL f1 ==========	
NUC1	13C	
P1	11.00	use
PL1	-1.00	dB
PL1W	109.73103333	W
SFO1	150.9419956	MHz
==========	CHANNEL f2 ==========	
CPDPRG2	waltz65	
NUC2	1H	
PCPD2	70.00	use
PL2	4.20	dB
PL12	22.51	dB
PL2W	5.30020905	W
PL12W	0.07821552	W
SFO2	600.2223000	MHz
SI	131072	
SF	150.9252989	MHz
WDW	EM	
SSB	0	
LB	0.80	Hz
GB	0	
PC	1.00	
SR	-140.11	Hz

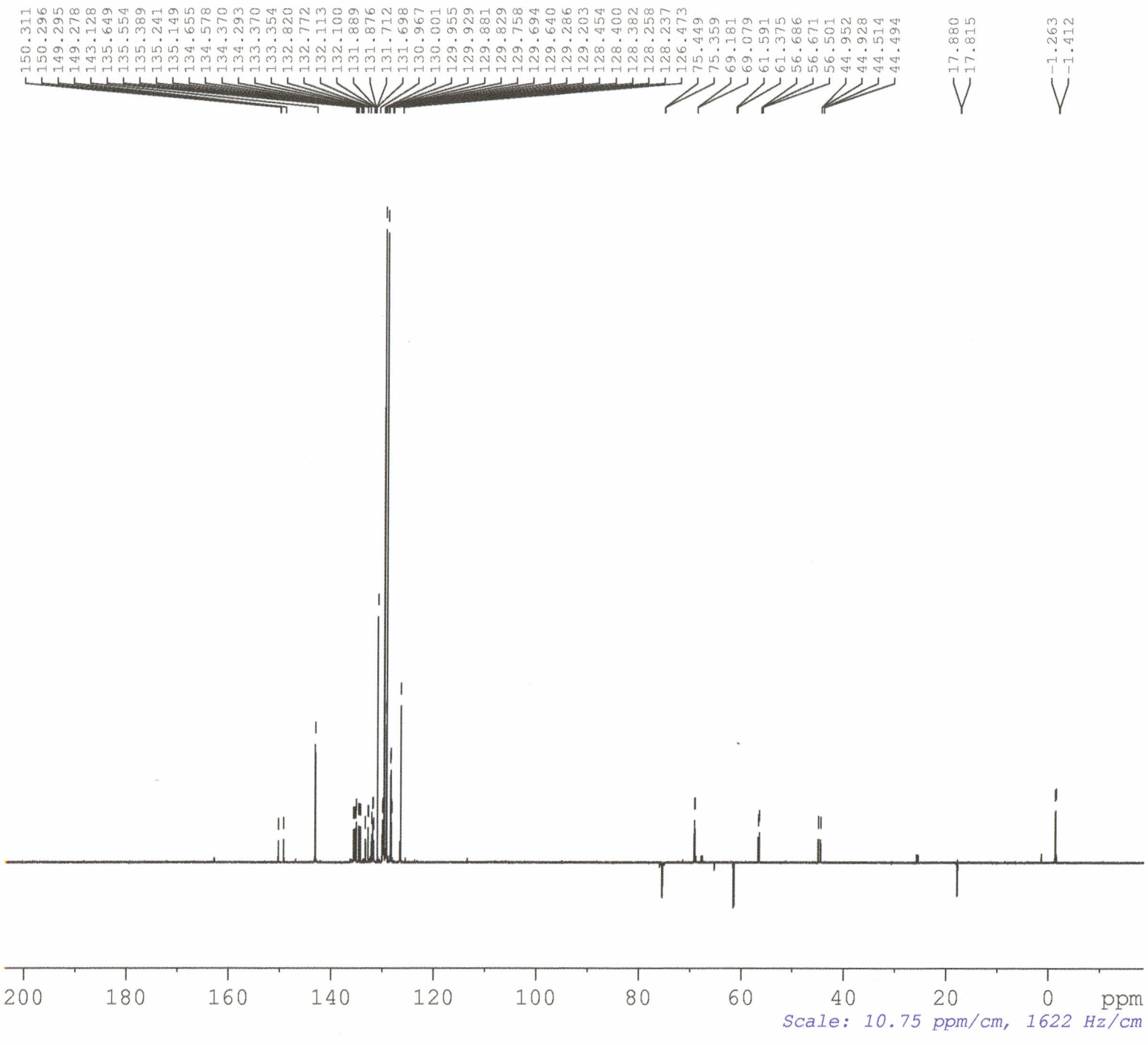
AUD-AB-231
13C{1H} @ 278K
av600



C616834

NAME	audab231
EXPNO	31
PROCNO	1
Date_	20120508
Time	10.47
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	zgdc30
TD	80908
SOLVENT	THF
NS	1320
DS	128
SWH	46296.297 Hz
FIDRES	0.572209 Hz
AQ	0.8738564 sec
RG	512
DW	10.800 use
DE	50.99 use
TE	278.0 K
D1	0.03000000 sec
D11	0.03000000 sec
TD0	1
========== CHANNEL f1 ==========	
NUC1	13C
P1	11.00 use
PL1	-1.00 dB
PL1W	109.73103333 W
SFO1	150.9419956 MHz
========== CHANNEL f2 ==========	
CPDPRG2	waltz65
NUC2	1H
PCPD2	70.00 use
PL2	4.20 dB
PL12	22.51 dB
PL2W	5.30020905 W
PL12W	0.07821552 W
SFO2	600.2223000 MHz
SI	131072
SF	150.9252989 MHz
WDW	EM
SSB	0
LB	0.80 Hz
GB	0
PC	1.00
SR	-140.11 Hz

AUD-AB-231
13C{1H} @ 278K
av600

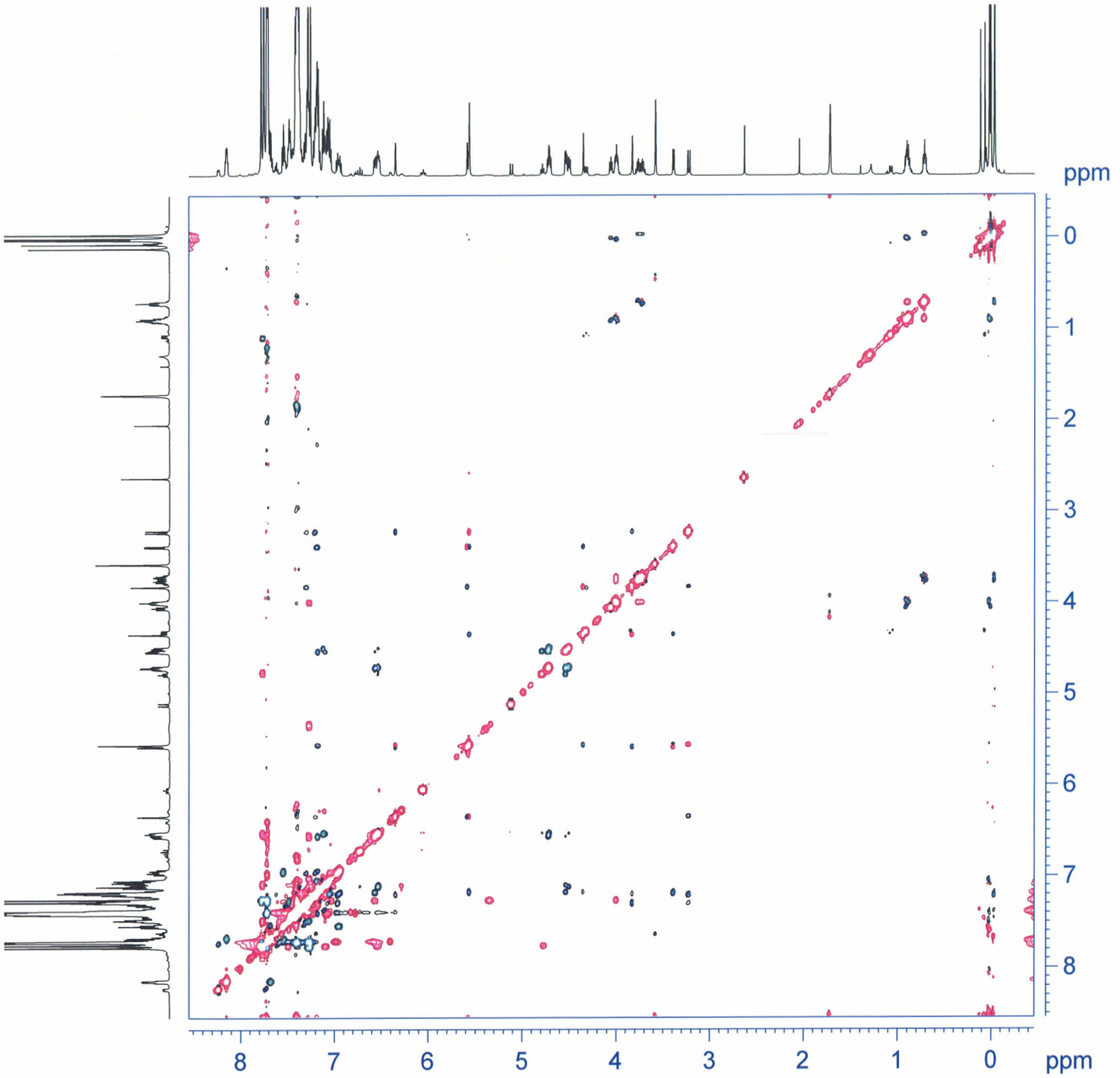


C616835

NAME	audab231	
EXPNO	32	
PROCNO	1	
Date_	20120508	
Time	11.08	
INSTRUM	av600	
PROBHD	5 mm CPTCI 1H-	
PULPROG	deptsp135	
TD	65536	
SOLVENT	THF	
NS	256	
DS	4	
SWH	36057.691	Hz
FIDRES	0.550197	Hz
AQ	0.9088159	sec
RG	512	
DW	13.867	use
DE	51.34	use
TE	278.0	K
CNST2	145.0000000	
D1	2.00000000	sec
D2	0.00344828	sec
D12	0.00002000	sec
TD0	1	
========== CHANNEL f1 ==========		
NUC1	13C	
P1	11.00	use
P12	2000.00	use
PL0	120.00	dB
PL1	-1.00	dB
PL0W	0.00000000	W
PL1W	109.73103333	W
SFO1	150.9405316	MHz
SP2	6.33	dB
SPNAM2	Crp60comp.4	
SPOAL2	0.500	
SPOFFS2	0.00	Hz
========== CHANNEL f2 ==========		
CPDPRG2	waltz16	
NUC2	1H	
P3	8.50	use
P4	17.00	use
PCPD2	70.00	use
PL2	4.20	dB
PL12	22.51	dB
PL2W	5.30020905	W
PL12W	0.07821552	W
SFO2	600.2223000	MHz
SI	65536	
SF	150.9252989	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.00	

AUD-AB-231
dept135 @ 278K
av600

H6168 4Z



NAME	audab231
EXPNO	36
PROCNO	1
Date_	20120508
Time	13.48
INSTRUM	av600
PROBHD	5 mm CPTCI 1H-
PULPROG	noesygpph
TD	1024
SOLVENT	THF
NS	4
DS	16
SWH	5411.255 Hz
FIDRES	5.284429 Hz
AQ	0.0946676 sec
RG	32
DW	92.400 usec
DE	10.00 usec
TE	278.0 K
D0	0.00008158 sec
D1	4.00000000 sec
D8	1.20000005 sec
D16	0.00020000 sec
IN0	0.00018480 sec

======== CHANNEL f1 ========

NUC1	1H
P1	8.50 usec
P2	17.00 usec
PL1	4.20 dB
PL1W	5.30020905 W
SFO1	600.2224440 MHz

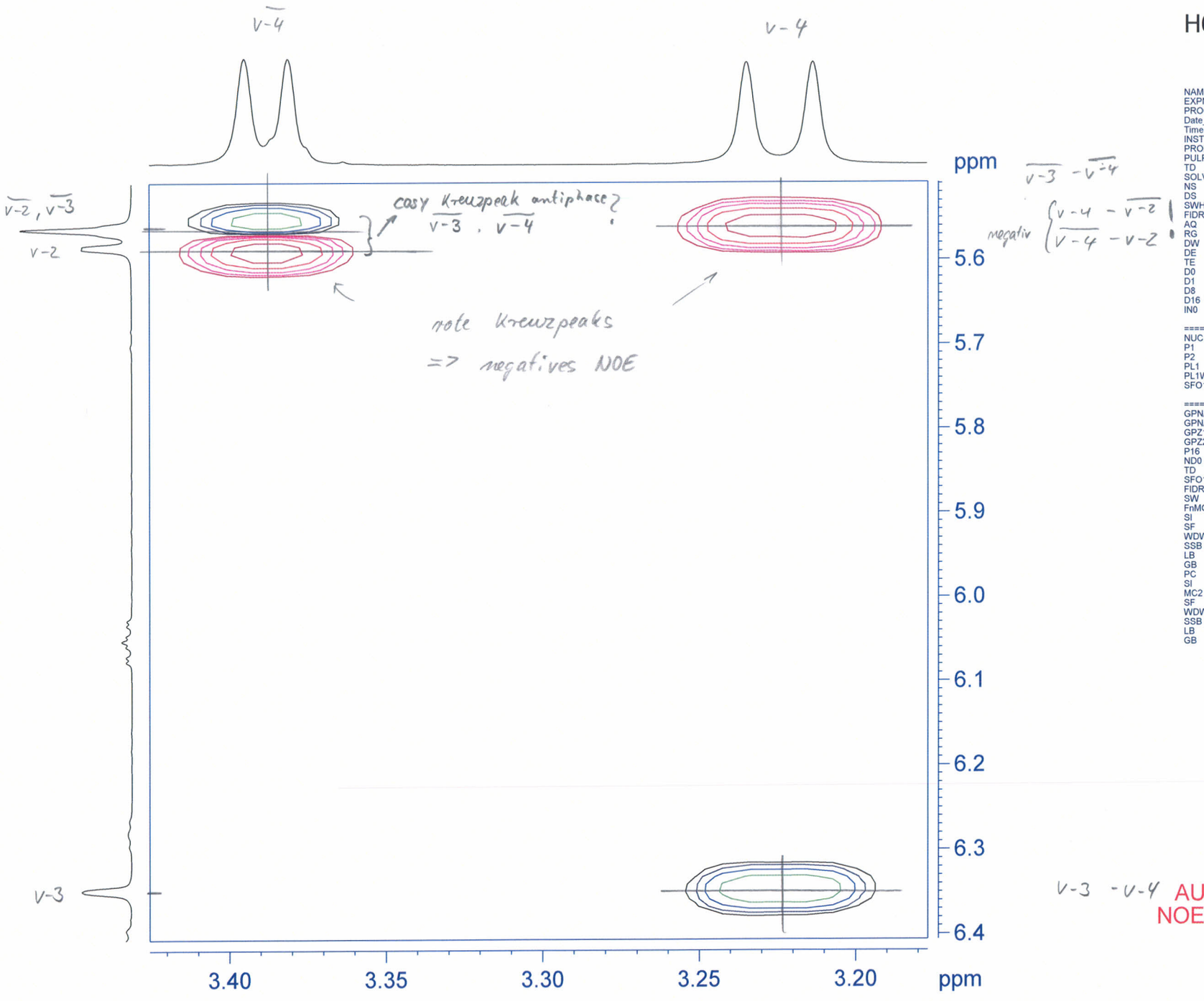
====== GRADIENT CHANNEL =====

GPNAM1	SINE.100
GPNAM2	SINE.100
GPZ1	40.00 %
GPZ2	-40.00 %
P16	1000.00 usec
ND0	1
TD	512
SFO1	600.2224 MHz
FIDRES	10.568839 Hz
SW	9.015 ppm
FnMODE	States-TPPI
SI	1024
SF	600.2200196 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.00
SI	1024
MC2	States-TPPI
SF	600.2200198 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

AUD-AB-231
NOESY @ 278K

av-600

H616842



$\overline{v-3} - \overline{v-4}$

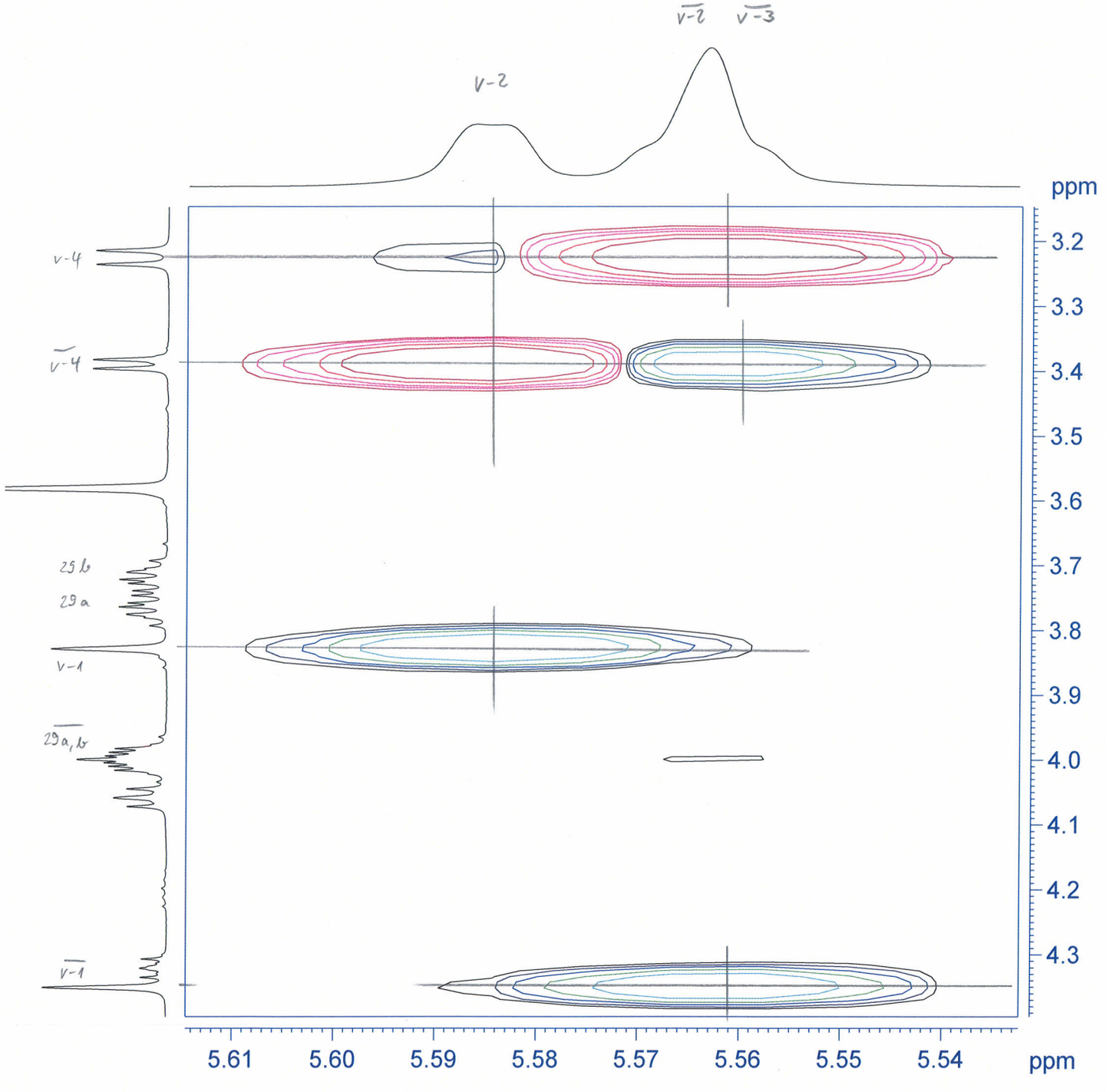
negativ $\begin{cases} v-4 - \overline{v-2} \\ \overline{v-4} - v-2 \end{cases}$

```
NAME         audab231
EXPNO              36
PROCNO              1
Date_        20120508
Time            13.48
INSTRUM          av600
PROBHD  5 mm CPTCI 1H-
PULPROG       noesygpph
TD                1024
SOLVENT            THF
NS                   4
DS                  16
SWH          5411.255 Hz
FIDRES       5.284429 Hz
AQ           0.0946676 sec
RG                  32
DW             92.400 usec
DE             10.00 usec
TE               278.0 K
D0          0.00008158 sec
D1          4.00000000 sec
D8          1.20000005 sec
D16         0.00020000 sec
IN0         0.00018480 sec

======== CHANNEL f1 ========
NUC1               1H
P1              8.50 usec
P2             17.00 usec
PL1             4.20 dB
PL1W       5.30020905 W
SFO1       600.2224440 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPZ1           40.00 %
GPZ2           -40.00 %
P16          1000.00 usec
ND0                 1
TD                512
SFO1       600.2224 MHz
FIDRES     10.568839 Hz
SW           9.015 ppm
FnMODE       States-TPPI
SI                1024
SF         600.2200196 MHz
WDW               QSINE
SSB                 2
LB             0.00 Hz
GB                  0
PC                1.00
SI                1024
MC2          States-TPPI
SF         600.2200198 MHz
WDW               QSINE
SSB                 2
LB             0.00 Hz
GB                  0
```

$v-3 - v-4$ AUD-AB-231
NOESY @ 278K

av-600

H616842



v-4 - v-2
negativ

v-4 - v-2 negativ

v-4 - v-3

v-1 - v-2

v-1 - v-2,v-3

NAME audab231
EXPNO 36
PROCNO 1
Date_ 20120508
Time 13.48
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG noesygpph
TD 1024
SOLVENT THF
NS 4
DS 16
SWH 5411.255 Hz
FIDRES 5.284429 Hz
AQ 0.0946676 sec
RG 32
DW 92.400 usec
DE 10.00 usec
TE 278.0 K
D0 0.00008158 sec
D1 4.00000000 sec
D8 1.20000005 sec
D16 0.00020000 sec
IN0 0.00018480 sec

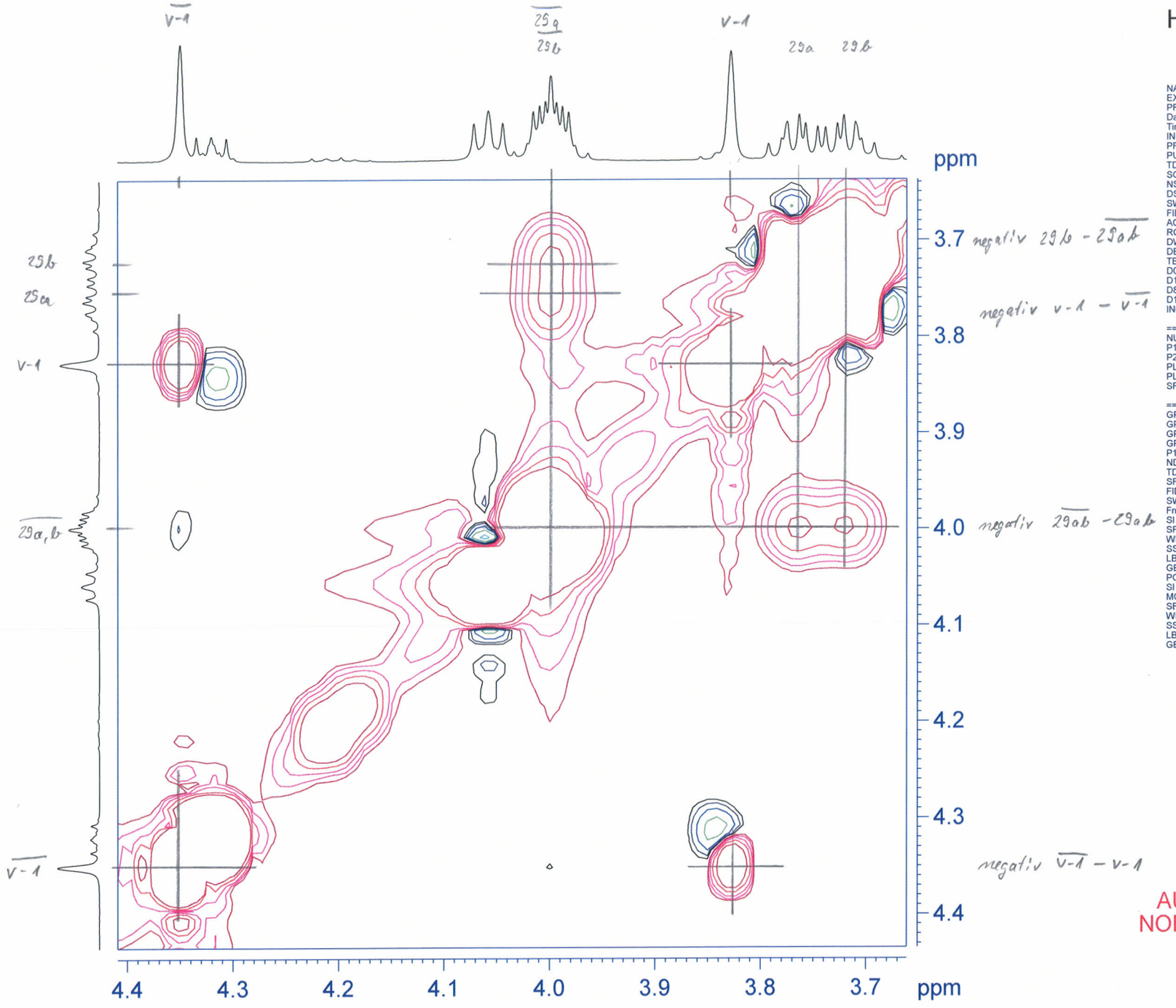
======== CHANNEL f1 ========
NUC1 1H
P1 8.50 usec
P2 17.00 usec
PL1 4.20 dB
PL1W 5.30020905 W
SFO1 600.2224440 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 40.00 %
GPZ2 -40.00 %
P16 1000.00 usec
ND0 1
TD 512
SFO1 600.2224 MHz
FIDRES 10.568839 Hz
SW 9.015 ppm
FnMODE States-TPPI
SI 1024
SF 600.2200196 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
SI 1024
MC2 States-TPPI
SF 600.2200198 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0

AUD-AB-231
NOESY @ 278K

av-600

H616842



negativ 29b - 29ab

negativ v-1 - V-1

negativ 29ab - 29ab

negativ V-1 - v-1

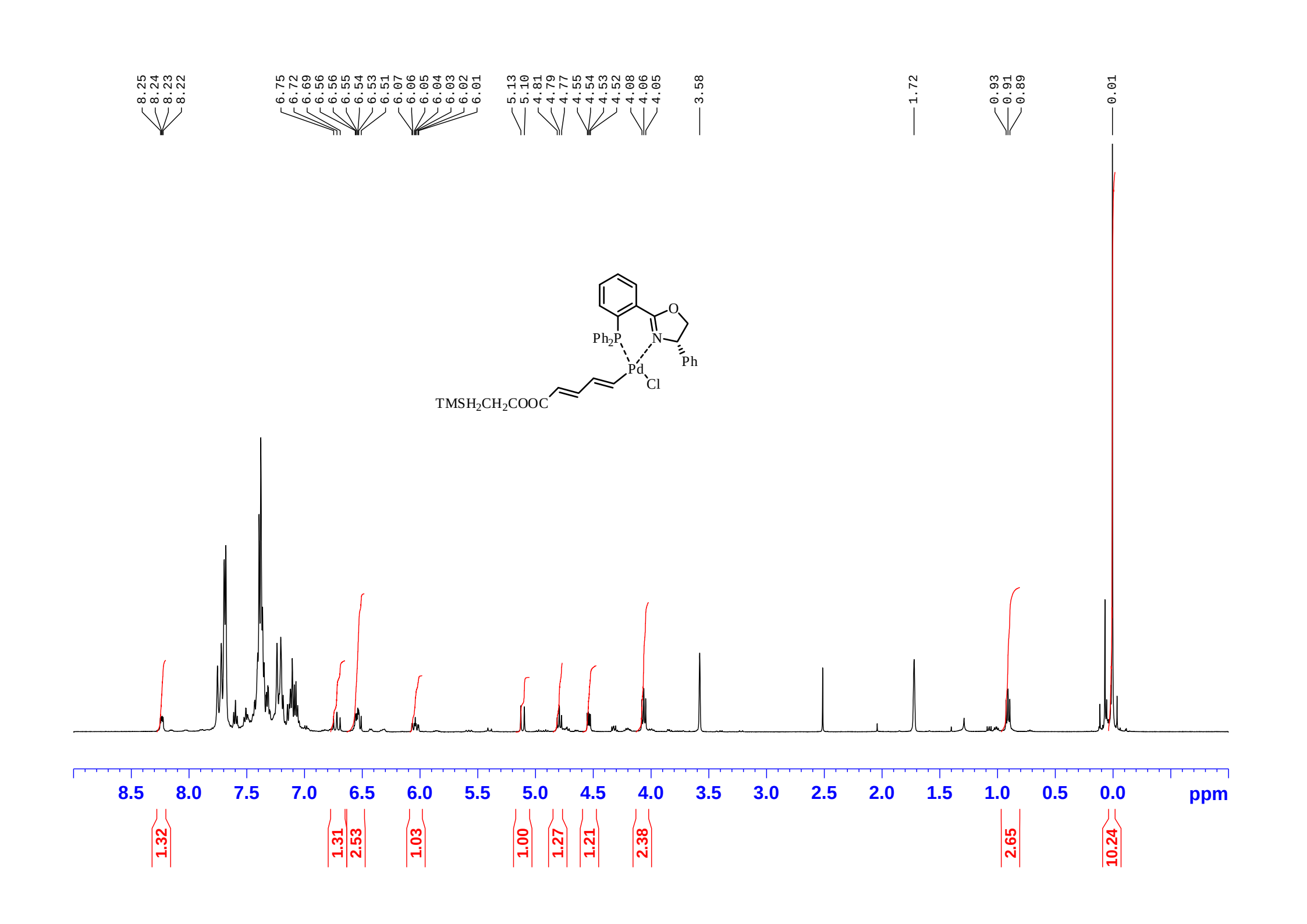
NAME audab231
EXPNO 36
PROCNO 1
Date_ 20120508
Time 13.48
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG noesygpph
TD 1024
SOLVENT THF
NS 4
DS 16
SWH 5411.255 Hz
FIDRES 5.284429 Hz
AQ 0.0946676 sec
RG 32
DW 92.400 usec
DE 10.00 usec
TE 278.0 K
D0 0.00008158 sec
D1 4.00000000 sec
D8 1.20000005 sec
D16 0.00020000 sec
IN0 0.00018480 sec

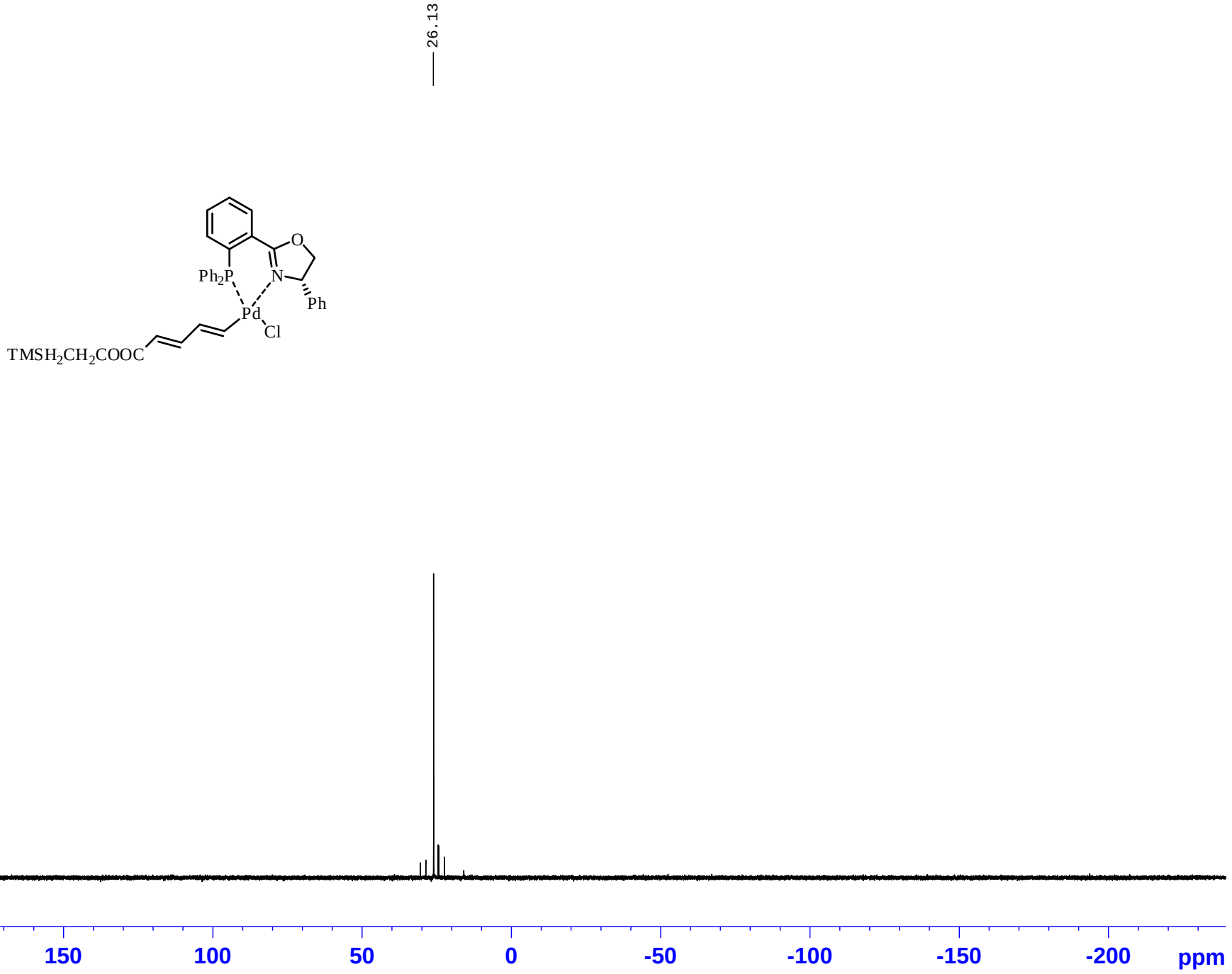
======== CHANNEL f1 ========
NUC1 1H
P1 8.50 usec
P2 17.00 usec
PL1 4.20 dB
PL1W 5.30020905 W
SFO1 600.2224440 MHz

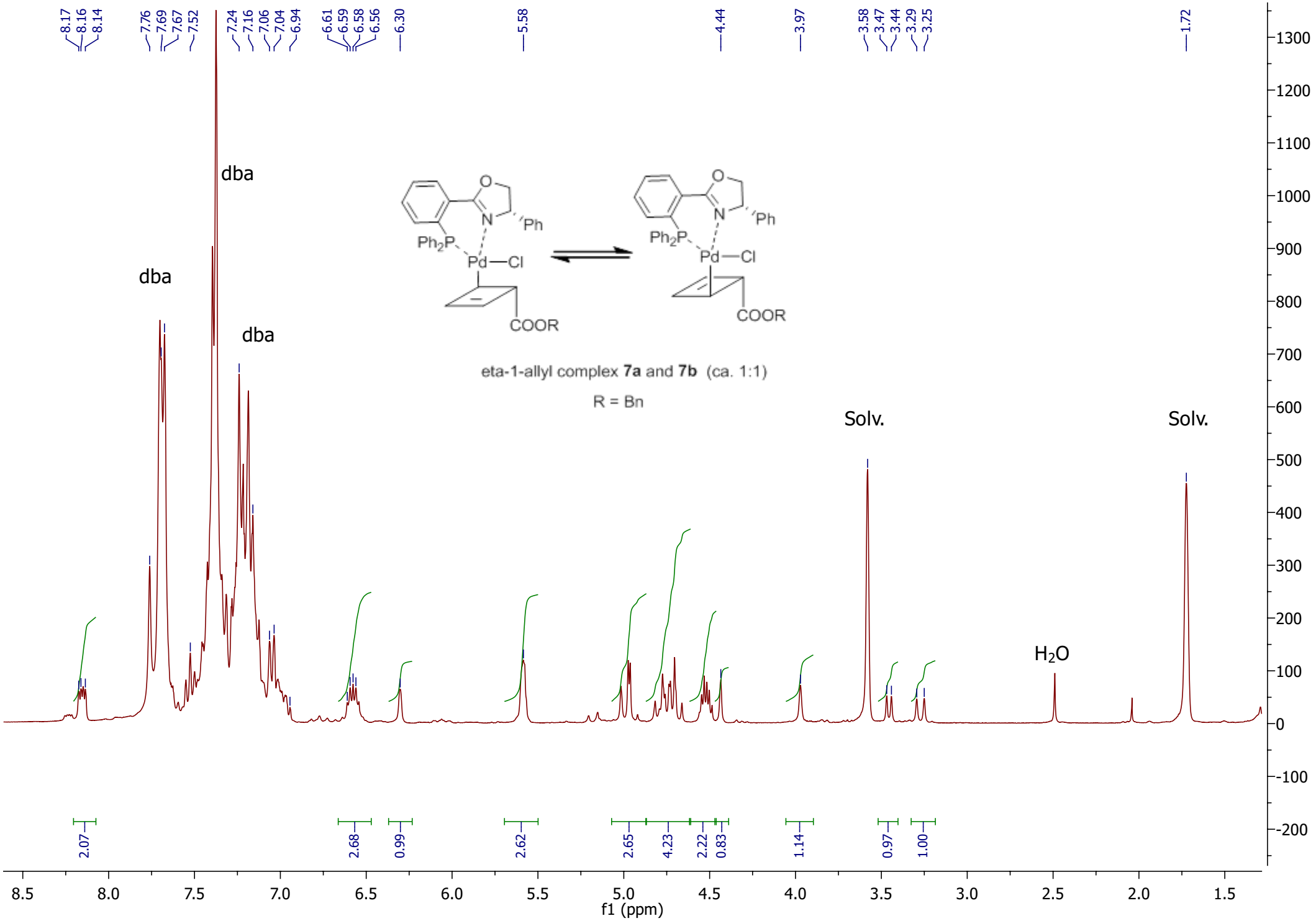
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 40.00 %
GPZ2 -40.00 %
P16 1000.00 usec
ND0 1
TD 512
SFO1 600.2224 MHz
FIDRES 10.568839 Hz
SW 9.015 ppm
FnMODE States-TPPI
SI 1024
SF 600.2200196 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
SI 1024
MC2 States-TPPI
SF 600.2200198 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0

AUD-AB-231
NOESY @ 278K

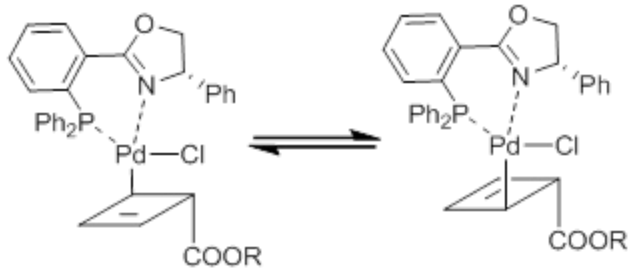
av-600


8.25
8.24
8.23
8.22
6.75
6.72
6.69
6.56
6.56
6.55
6.54
6.53
6.51
6.07
6.06
6.05
6.04
6.03
6.02
6.01
5.13
5.10
4.81
4.79
4.77
4.55
4.54
4.53
4.52
4.08
4.06
4.05
3.58
1.72
0.93
0.91
0.89
0.01
Ph2P
O
N
Ph
Pd
Cl
TMSH2CH2COOC
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.32
1.31
2.53
1.03
1.00
1.27
1.21
2.38
2.65
10.24


26.13
O
Ph2P
N
Ph
Pd
Cl
TMSH2CH2COOC
200
150
100
50
0
-50
-100
-150
-200
ppm


8.17
8.16
8.14
7.76
7.69
7.67
7.52
7.24
7.16
7.06
7.04
6.94
6.61
6.59
6.58
6.56
6.30
5.58
4.44
3.97
3.58
3.47
3.44
3.29
3.25
1.72
dba
dba
dba
Solv.
Solv.
H2O
Ph2P
Pd—Cl
COOR
Ph
N
O
eta-1-allyl complex 7a and 7b (ca. 1:1)
R = Bn
2.07
2.68
0.99
2.62
2.65
4.23
2.22
0.83
1.14
0.97
1.00
f1 (ppm)

ap17027
AUD-AB-216-0Â°C



eta-1-allyl complex **7a** and **7b** (ca. 1:1)

R = Bn

33.42
31.40
28.84

7b

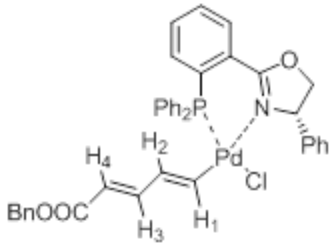
7a

(E,E)-diene-8

1.00
0.92

f1 (ppm)

ap18008
AUD-AB-216-rt 16h



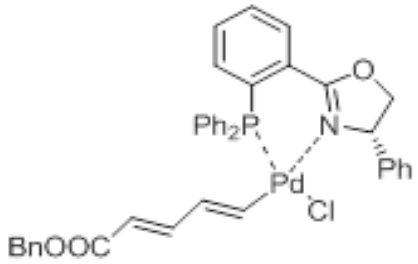
8

dba
dba
dba
Solv.
Solv
H_2O

f1 (ppm)

ap18008
AUD-AB-216-rt 16h

28.80

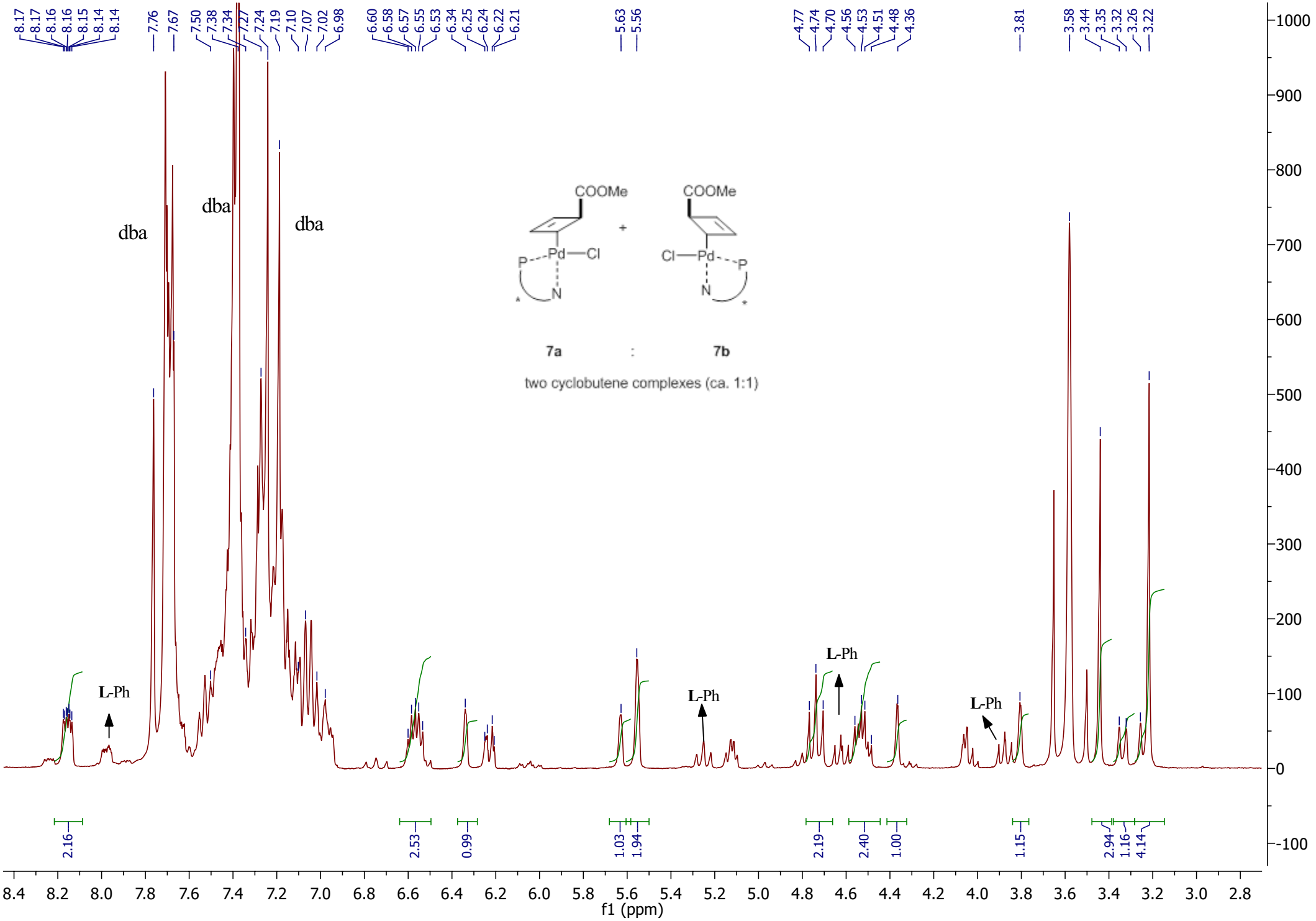


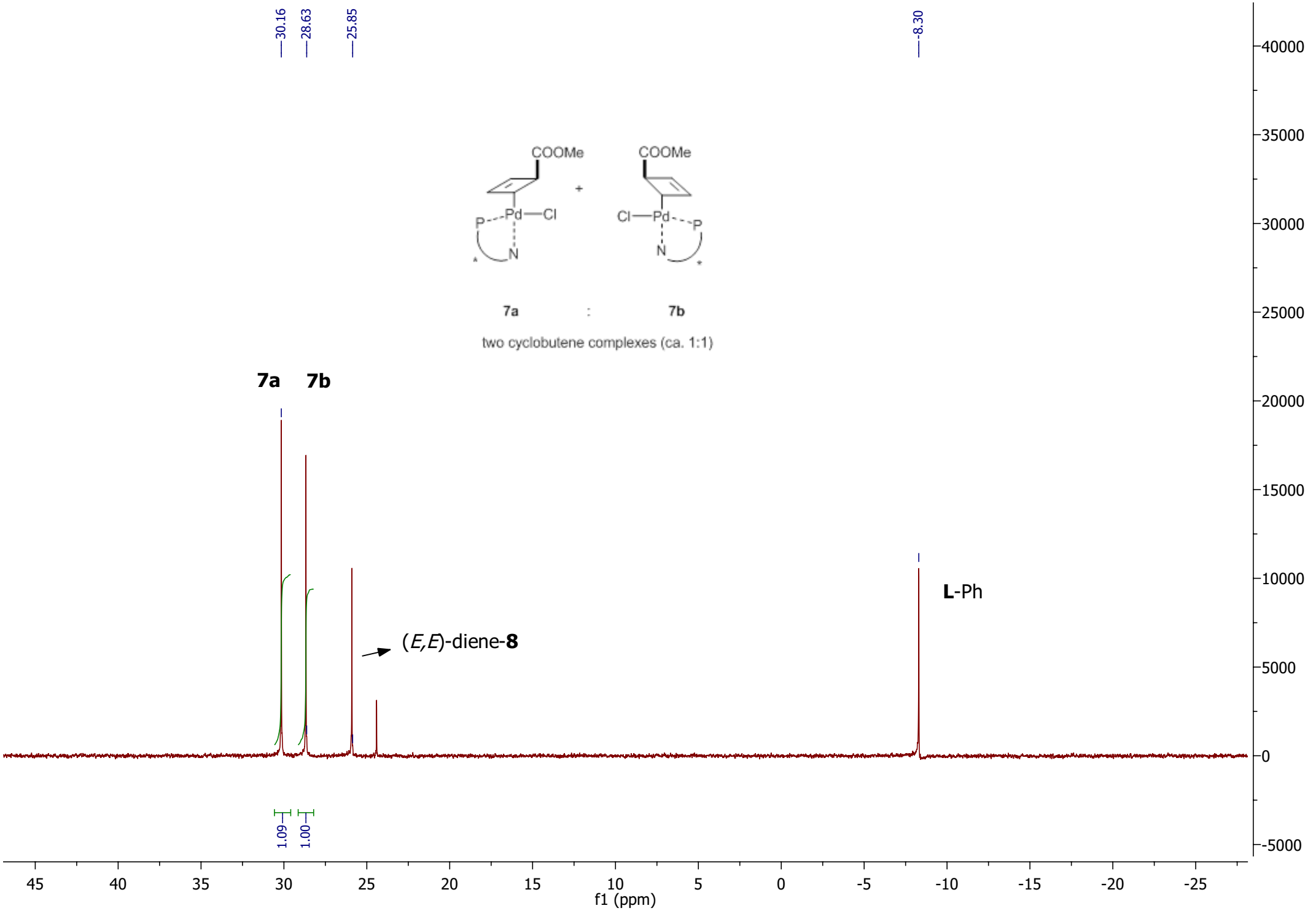
8

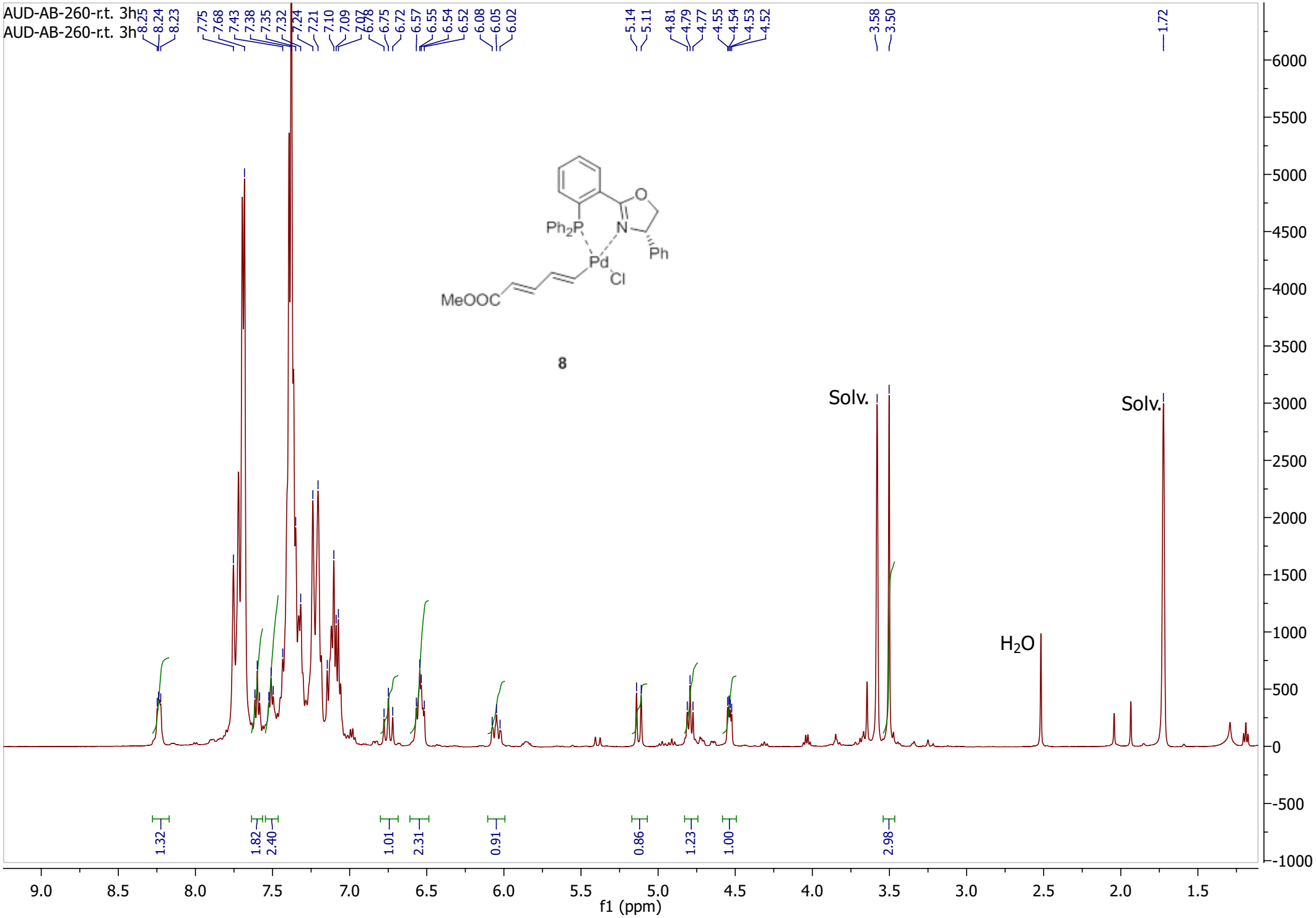
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

f1 (ppm)

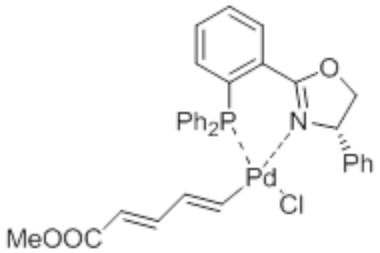

8.17 8.17 8.16 8.16 8.15 8.14 8.14
7.76 7.67 7.50 7.38 7.34 7.27 7.24 7.19 7.10 7.07 7.02 6.98
6.60 6.58 6.57 6.55 6.53 6.34 6.25 6.24 6.22 6.21
5.63 5.56
4.77 4.74 4.70 4.56 4.53 4.51 4.48 4.36
3.81
3.58 3.44 3.35 3.32 3.26 3.22
dba
dba
dba
L-Ph
L-Ph
L-Ph
L-Ph
COOMe
COOMe
P
Pd
Cl
N
Cl
Pd
P
N
7a : 7b
two cyclobutene complexes (ca. 1:1)
2.16
2.53
0.99
1.03
1.94
2.19
2.40
1.00
1.15
2.94
1.16
4.14
1000 900 800 700 600 500 400 300 200 100 0 -100
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8
f1 (ppm)


30.16
28.63
25.85
-8.30
COOMe
COOMe
Pd—Cl
Cl—Pd
P
N
7a : 7b
two cyclobutene complexes (ca. 1:1)
7a 7b
(E,E)-diene-8
L-Ph
1.09
1.00
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

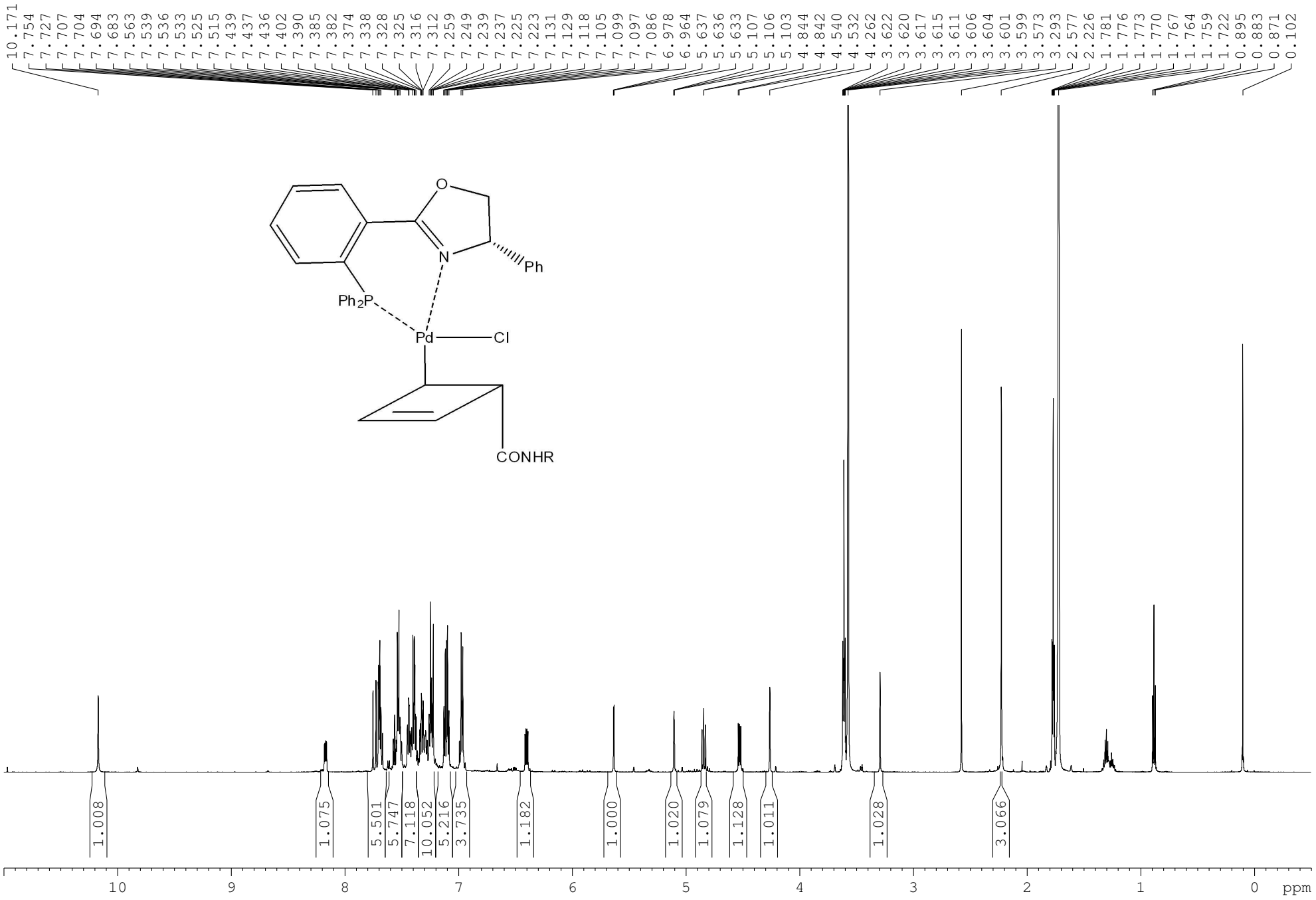

AUD-AB-260-r.t. 3h
AUD-AB-260-r.t. 3h
8.25
8.24
8.23
7.75
7.68
7.43
7.38
7.35
7.32
7.24
7.21
7.10
7.09
7.07
6.78
6.75
6.72
6.57
6.55
6.54
6.52
6.08
6.05
6.02
5.14
5.11
4.81
4.79
4.77
4.55
4.54
4.53
4.52
3.58
3.50
1.72
Ph2P
O
N
Ph
Pd
Cl
MeOOC
8
Solv.
Solv.
H2O
1.32
1.82
2.40
1.01
2.31
0.91
0.86
1.23
1.00
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000

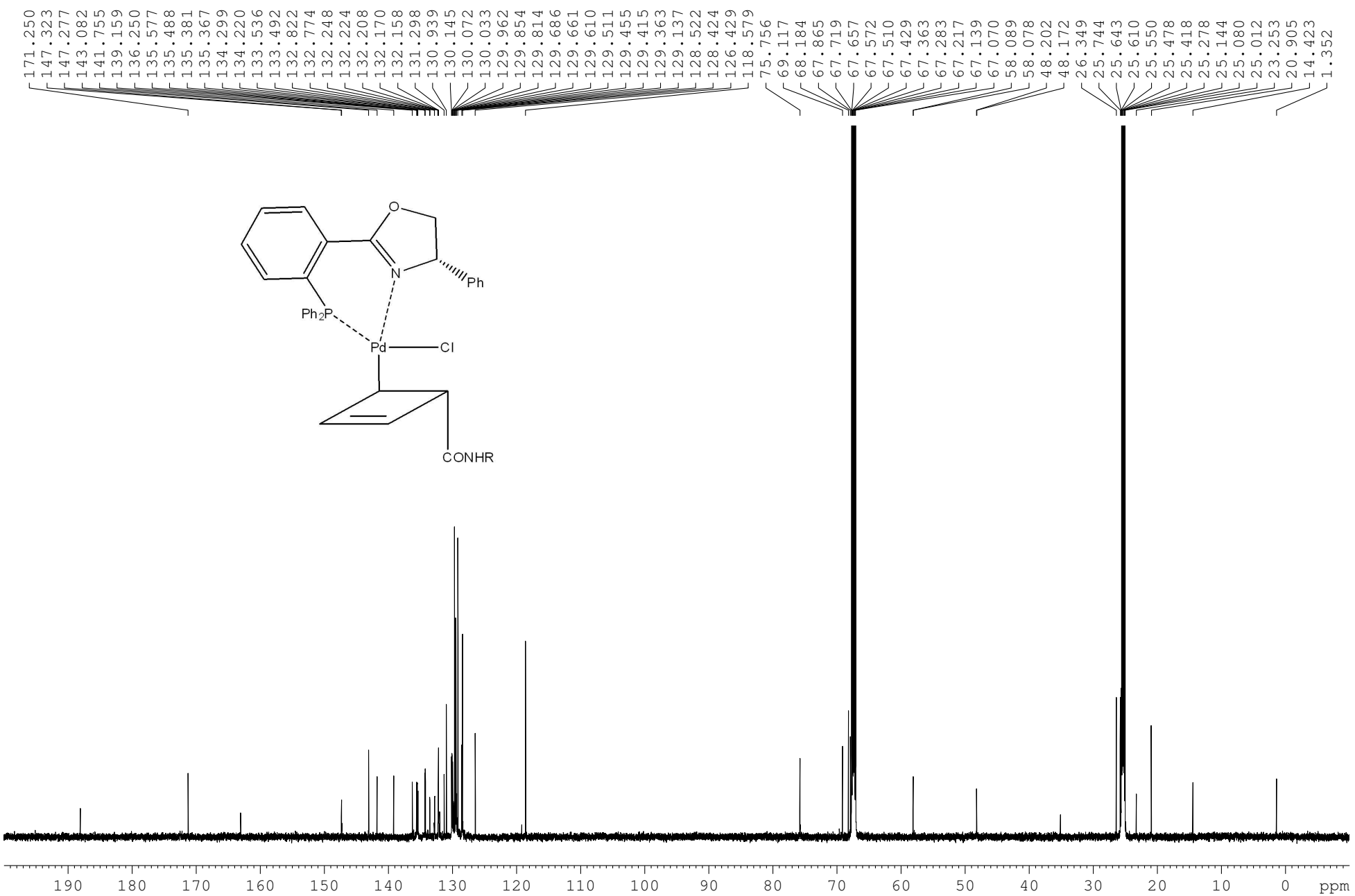
AUD-AB-260-r.t. 3h
AUD-AB-260-r.t. 3h

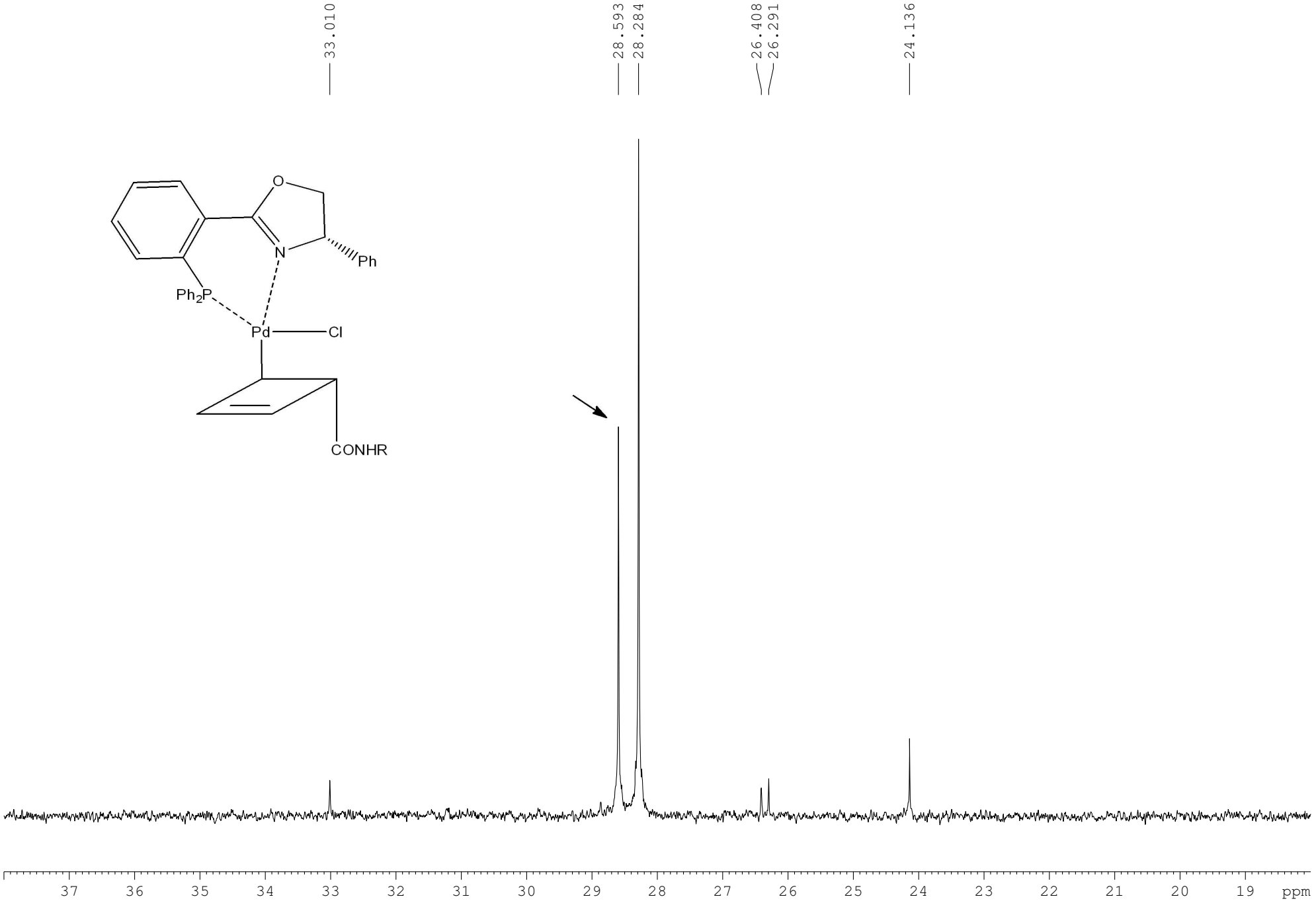
25.90



8


10.171
7.754
7.727
7.707
7.704
7.694
7.683
7.563
7.539
7.536
7.533
7.525
7.515
7.439
7.437
7.436
7.402
7.390
7.385
7.382
7.374
7.338
7.328
7.325
7.316
7.312
7.259
7.249
7.239
7.237
7.225
7.223
7.131
7.129
7.118
7.105
7.099
7.097
7.086
6.978
6.964
5.637
5.636
5.633
5.107
5.106
5.103
4.844
4.842
4.540
4.532
4.262
3.622
3.620
3.617
3.615
3.611
3.606
3.604
3.601
3.599
3.573
3.293
2.577
2.226
1.781
1.776
1.773
1.770
1.767
1.764
1.759
1.722
0.895
0.883
0.871
0.102
O
N
Ph
Ph2P
Pd
Cl
CONHR
1.008
1.075
5.501
5.747
7.118
10.052
5.216
3.735
1.182
1.000
1.020
1.079
1.128
1.011
1.028
3.066
10
9
8
7
6
5
4
3
2
1
0
ppm


171.250
147.323
147.277
143.082
141.755
139.159
136.250
135.577
135.488
135.381
135.367
134.299
134.220
133.536
133.492
132.822
132.774
132.248
132.224
132.208
132.170
132.158
131.298
130.939
130.145
130.072
130.033
129.962
129.854
129.814
129.686
129.661
129.610
129.511
129.455
129.415
129.363
129.137
128.522
128.424
126.429
118.579
75.756
69.117
68.184
67.865
67.719
67.657
67.572
67.510
67.429
67.363
67.283
67.217
67.139
67.070
58.089
58.078
48.202
48.172
26.349
25.744
25.643
25.610
25.550
25.478
25.418
25.278
25.144
25.080
25.012
23.253
20.905
14.423
1.352
O
N
Ph
Ph2P
Pd
Cl
CONHR
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

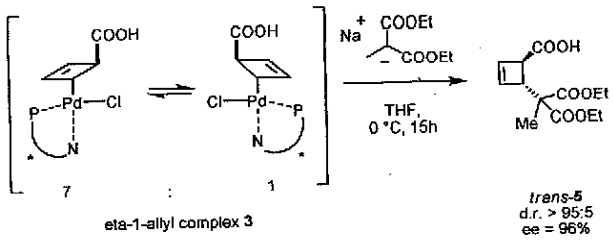

33.010
28.593
28.284
26.408
26.291
24.136
O
N
Ph
Ph2P
Pd
Cl
CONHR
37
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
ppm

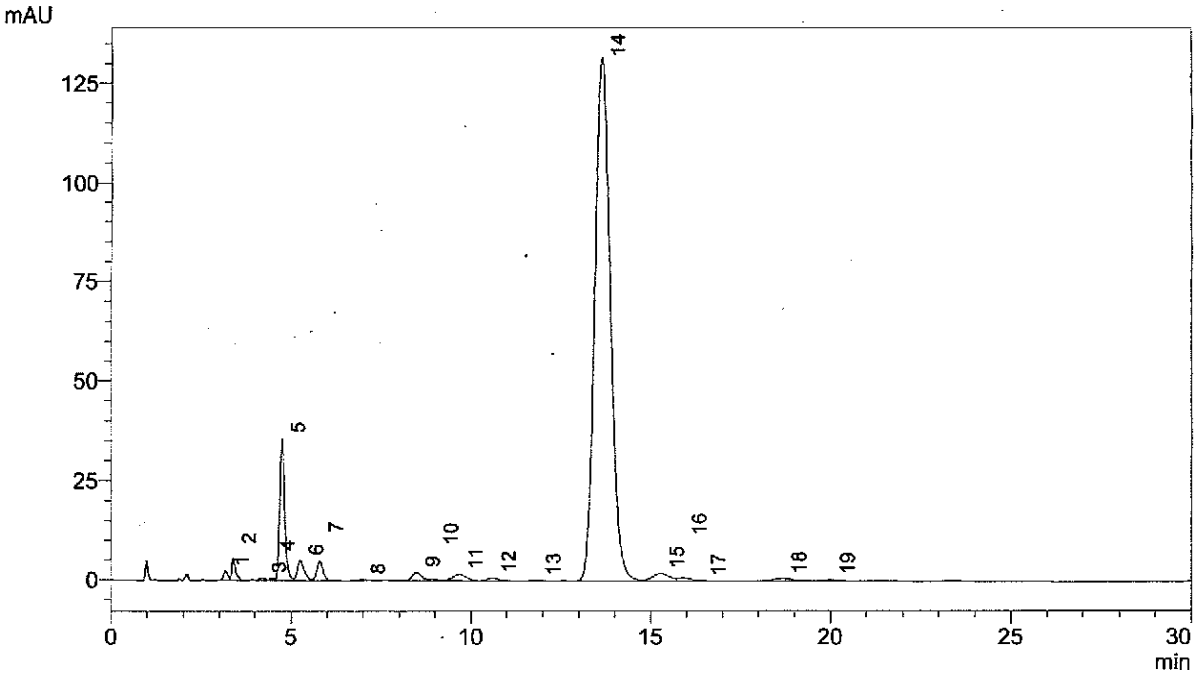
Gerät : UFLC-20-1

Operator : KI
Sample Name : AUD-AB-207-01
Vial # : 1
Injection Volume : 1 uL
Data File Name : AUD-AB-207-01-02.lcd
Method File Name : Audisio.lcm

Data Acquired: 09.05.2012 12:23:31

1 µL AUD-AB-207-01 (in 1 mL 2-Propanol)
150 mm Chiralpak AS-RH, 4.6 mm i.D.
Acetonitril/Wasser = 35:65
1.0 mL/min, 8.1 MPa, 298 K
210 nm





1 210nm,4nm
PDA Ch1 210nm

Peak #	Ret. Time	Area %	Name
1	3.18	0.41	
2	3.39	0.91	
3	4.21	0.15	
4	4.45	0.10	
5	4.75	7.29	
6	5.25	1.47	
7	5.79	1.27	
8	6.96	0.08	
9	8.49	0.85	
10	9:00	0.15	
11	9.68	0.93	
12	10.61	0.35	
13	11.84	0.11	
14	13.66	83.00	1. trans-Enantiomer
15	15.28	1.45	2. trans-Enantiomer
16	15.90	0.52	
17	16.43	0.06	
18	18.68	0.63	
19	20.03	0.25	
Total		100.00	

ee. = 96%

Supporting Information

Computational Part

Palladium-Catalyzed Allylic Substitution at Four Membered Cyclic Systems: Formation of η^1-Allyl Complexes and Electrocyclic Ring Opening

Davide Audisio, Gopinadhanpillai Gopakumar, Lan-Gui Xie, Luis G. Alves, Cornelia Wirtz, Ana M. Martins, Walter Thiel, Christophe Farès and Nuno Maulide*

maulide@kofo.mpg.de

Table of Contents

Computational Methods

Density functional theory (DFT) was applied to study the ring opening reaction catalysed by the palladium complex. Geometry optimizations were carried out using the BP86[1,2] functional in combination with def2-SVP basis sets.[3-5] In the case of palladium, 28 inner-shell core electrons were replaced by an effective core potential (ECP) generated for the neutral atom using quasi-relativistic methods, while the explicitly treated electrons were described by the standard def2-ECP basis set.[6] The resolution-of-identity (RI) approximation[7-9] was applied in conjunction with the appropriate auxiliary basis sets to speed up the calculations. All relevant stationary points were characterized as minima or first-order transition states by evaluating the harmonic vibrational frequencies at the same level (RI-BP86/def2-SVP) that had been applied for geometry optimization.

To check the sensitivity of the computed energy profiles, single-point energies at the optimized RI-BP86/def2-SVP geometries were calculated using the standard B3LYP[1,10,11] hybrid functional and the modern M06 functional,[12] in conjunction with different basis sets, i.e., def2-TZVP[13] and 6-31G*.[14] For the M06 calculations, the palladium was described by the LANL2DZ effective core potential (ECP) and the associated double-ζ basis set. The influence of the solvent environment (THF, dielectric constant ε = 7.426) on the relative energies was investigated through single-point calculations with the conductor-like screening model (COSMO).[15] Empirical Grimme-type dispersion corrections were incorporated at the B3LYP level using the latest parametrization (DFT-D3);[16] the corresponding results are denoted as B3LYP-D.

Zero-point energies (ZPE) were computed from the harmonic vibrational frequencies (RI-BP86/def2-SVP). Relative free energies (ΔG) at standard pressure (1 bar) and 298.15K were determined at the RI-BP86/def2-SVP level. The required thermal and entropic contributions were evaluated within the rigid-rotor harmonic-oscillator approximation.

The DFT computations were performed with TURBOMOLE (version-6.4)[17,18] and Gaussian09.[19]

Survey of Computational Results Presented as Supporting Information

Table S1 summarizes relative energies (with and without considering the zero-point energy corrections) and relative free energies with respect to the energetically lowest-lying complex **7a**. Table S2 lists the single-point results for relative energies evaluated at different levels. Figures S1-S13 show the optimized geometries of the stationary points along the reaction profile and selected values for important bond lengths. The free energy profile (evaluated at 25°C) for ring opening and η^1-η^3-η^1 isomerization is presented in Figure S14, and the shape of highest occupied molecular orbital (HOMO) of **TS$_{ring}$-1** (see below) is illustrated in Figure S15. The following summary of the DFT results for these reactions focuses on the geometries and relative free energies calculated at the BP86/def2-SVP level.

A total of 49 starting geometric configurations were considered for the isomer screening of η^1-complexes, from which we identified the energetically lowest-lying isomer **7a** (Figure S1) and an almost as stable diastereomer **7b** (Figure S2). In both species, the cyclobutene unit contains rather long C-C bonds (1.58 Å) between the carbon atoms bonded to palladium and the ester group. The ring opening reaction in **7a** and **7b** proceeds via the transition states **TS$_{ring}$-1** (Figure S3) and **TS$_{ring}$-2** (Figure S4) and yields the products ***E,E*-(8) [7a]** (Figure S5) and ***E,E*-(8) [7b]** (Figure S6), respectively. The corresponding barriers are computed to be 17.3 and 19.8 kcal/mol, respectively, at the BP86/def2-SVP level. In an attempt to characterize the η^1-η^3-η^1 isomerization pathway, starting from **7a**, the palladium atom was moved along on top of the cyclobutene unit by performing relaxed potential energy surface scans. The transition state **TS-1** at the beginning of the η^1-η^3 isomerization reaction (Figure S7, 14.9 kcal/mol) lies energetically below the ring opening transition state **TS$_{ring}$-1**. The

resulting η^3-isomer **η^3-1** (Figure S8) has a relatively long Pd-N bond (2.23 Å) and lies 10.1 kcal/mol above **7a**. A facile rearrangement via **TS_{int}-1** (Figure S9) with a barrier of 2.1 kcal/mol leads to an intermediate minimum **INT** (Figure S10, 6.9 kcal/mol), in which the Pd-N bond of the ligand unit has been cleaved. In the next step, the palladium-bound chlorine atom adopts a new orientation (facing the forefront) followed by re-coordination of the ruptured Pd-N bond. This rearrangement via transition state **TS_{int}-2** (Figure S11) with a barrier of 5.2 kcal/mol gives rise to the η^3-complex **η^3-2** (Figure S12, 7.7 kcal/mol), which isomerizes via another low-lying transition **TS-2** (Figure S13, 9.8 kcal/mol) to **7b** (Figure S2, 0.8 kcal/mol). Note that all stationary points along the η^1-η^3-η^1 isomerization pathway are of lower energy than the ring opening transition states (see Figure S14), which explains the slow interconversion observed during the EXSY/NOESY experiments.

The single-point energies for the computed reaction profile (Table S2) generally show the same trend as the BP86/def2-SVP gas-phase energies at fully optimized geometries (Table S1). In view of the fact that the actual reaction has been carried out in solution, the BP86/def2-TZVP results from solvent single-point energy calculations should be considered most realistic. They differ from the BP86/def2-SVP relative energies typically by only 1-2 kcal/mol.

References

(1) Becke, A. D. *Phys. Rev. A*, **1988**, *38*, 3098-3100.

(2) Perdew, J. P.; *Phys. Rev. B*, **1986**, *33*, 8822-8824.

(3) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571-2577.

(4) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

(5) Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.

(6) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H.; *Theor. Chim. Acta.* **1990**, *77*, 123-141.

(7) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652-660.

(8) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acc.* **1997**, *97*, 119-124.

(9) Weigend, F. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4285-4291.

(10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

(11) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785-789.

(12) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215-241.

(13) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829-5835.

(14) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257-2261.; Francl, M. M.; Petro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654-3665.

(15) Klamt, A.; Schüürmann, G. *J. Chem. Soc. Perkin Trans. 2* **1993**, *5*, 799-805.

(16) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H.; *J. Chem. Phys.* **2010**, *132*, 154104.

(17) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165-169.

(18) TURBOMOLE V6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, **1989-2007**, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com

(19) Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2010**.

TABLES

Table S1. Relative total energies (with and without ZPE corrections) and free energies (in kcal/mol) with respect to complex **7a** obtained at the BP86/def2-SVP level.

	Stationary points												
	***E,E*-8 [7a]**	**TS_{ring}-1**	**7a**	**TS-1**	**η^3-1**	**TS_{int}-1**	**INT**	**TS_{int}-2**	**η^3-2**	**TS-2**	**7b**	**TS_{ring}-2**	***E,E*-8 [7b]**
Rel. Total Energy	-15.54	19.35	0	17.29	12.47	14.07	10.07	13.92	10.00	10.93	0.78	21.80	-15.03
Rel. Total Energy + ZPE	-15.73	18.09	0	16.43	11.87	13.15	9.35	13.18	9.68	10.37	0.93	20.56	-15.30
Rel. Free Energy	-17.34	17.26	0	14.93	10.14	12.24	6.86	12.09	7.66	9.80	0.84	19.84	-18.66

Table S2. Relative energies (in kcal/mol) with respect to complex **7a** obtained from single-point calculations at different levels of theory (see methodology section).

Method	Stationary points												
	***E,E*-8 [7a]**	**TS_{ring}-1**	**7a**	**TS-1**	**η^3-1**	**TS_{int}-1**	**INT**	**TS_{int}-2**	**η^3-2**	**TS-2**	**7b**	**TS_{ring}-2**	***E,E*-8 [7b]**
B3LYP/def2-TZVP	-20.88	19.24	0	20.24	17.12	16.63[b]	10.04	15.90	13.84	13.87	2.15	22.98	-20.31
B3LYP-D/def2-TZVP	-15.06	23.09	0	24.70	21.44	21.80	16.22	21.18	18.45	18.87	6.92	27.94	-13.03
BP86/def2-TZVP (solvent single-point)	-20.22	16.30	0	15.12	12.04	13.67	8.89	11.99	6.67	9.37	2.37	20.09	-19.59
M06/6-31G*[a]	-6.80	31.20	0	19.61	16.39	15.56[b]	12.14	15.59	14.27	15.16	6.55	34.13	-4.18

[a] Palladium was described by the LANL2DZ effective core potential (ECP) and the associated double-ζ basis set.

[b] The single-point energy of the transition state lies below that of the preceding minimum due to the fact that the geometries were not re-optimized.

Figures

Figure S1. Optimized geometry of η^1 complex, **7a** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (color code: gray balls are carbon; orange ball is phosphorus; red balls are oxygen; green ball is chlorine, blue ball is nitrogen and dark cyan is palladium). Some important bond lengths are also given.

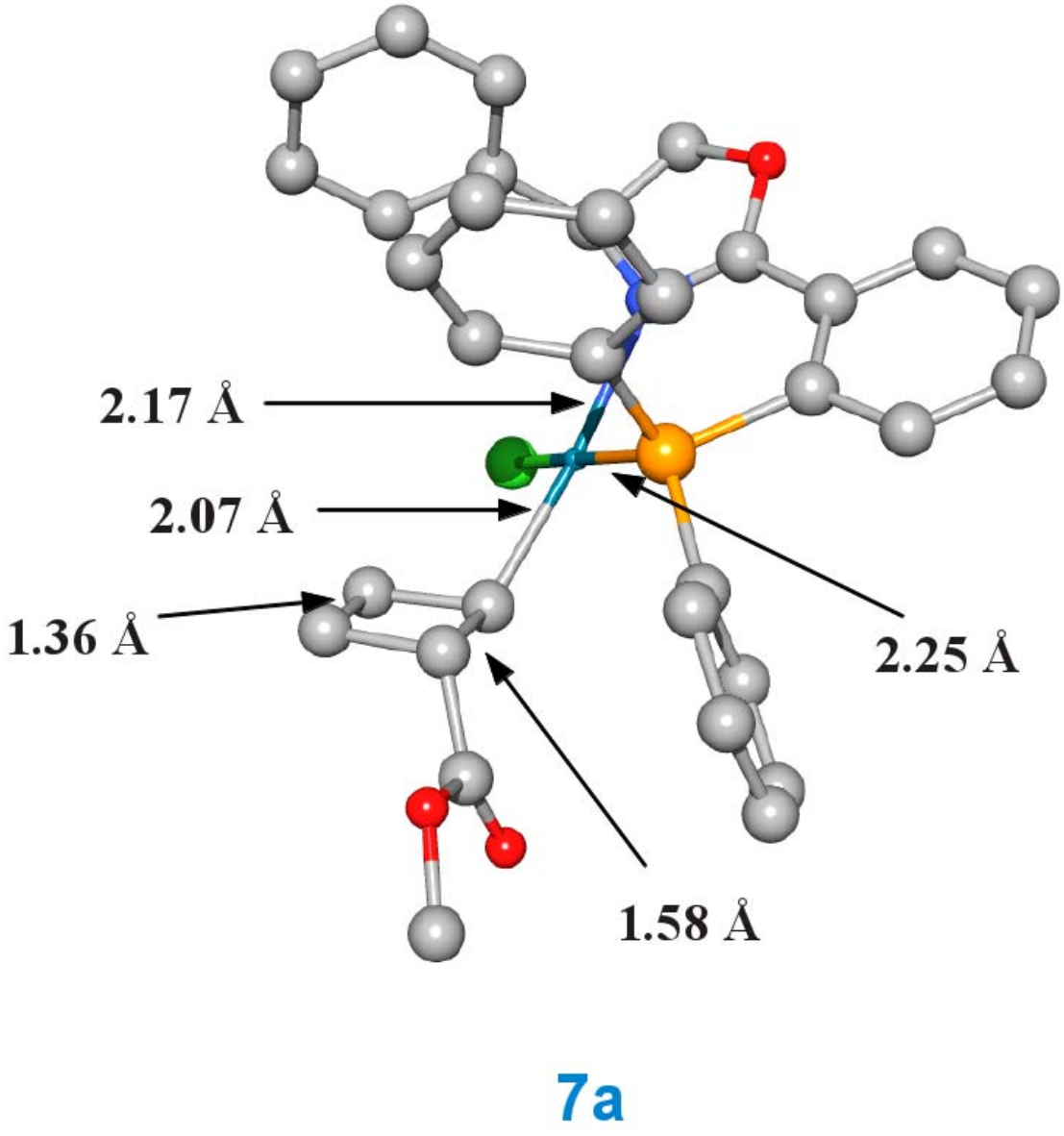


Figure S2. Optimized geometry of η^1 complex, **7b** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (please refer Figure S1 for color code). Some important bond lengths are also given.

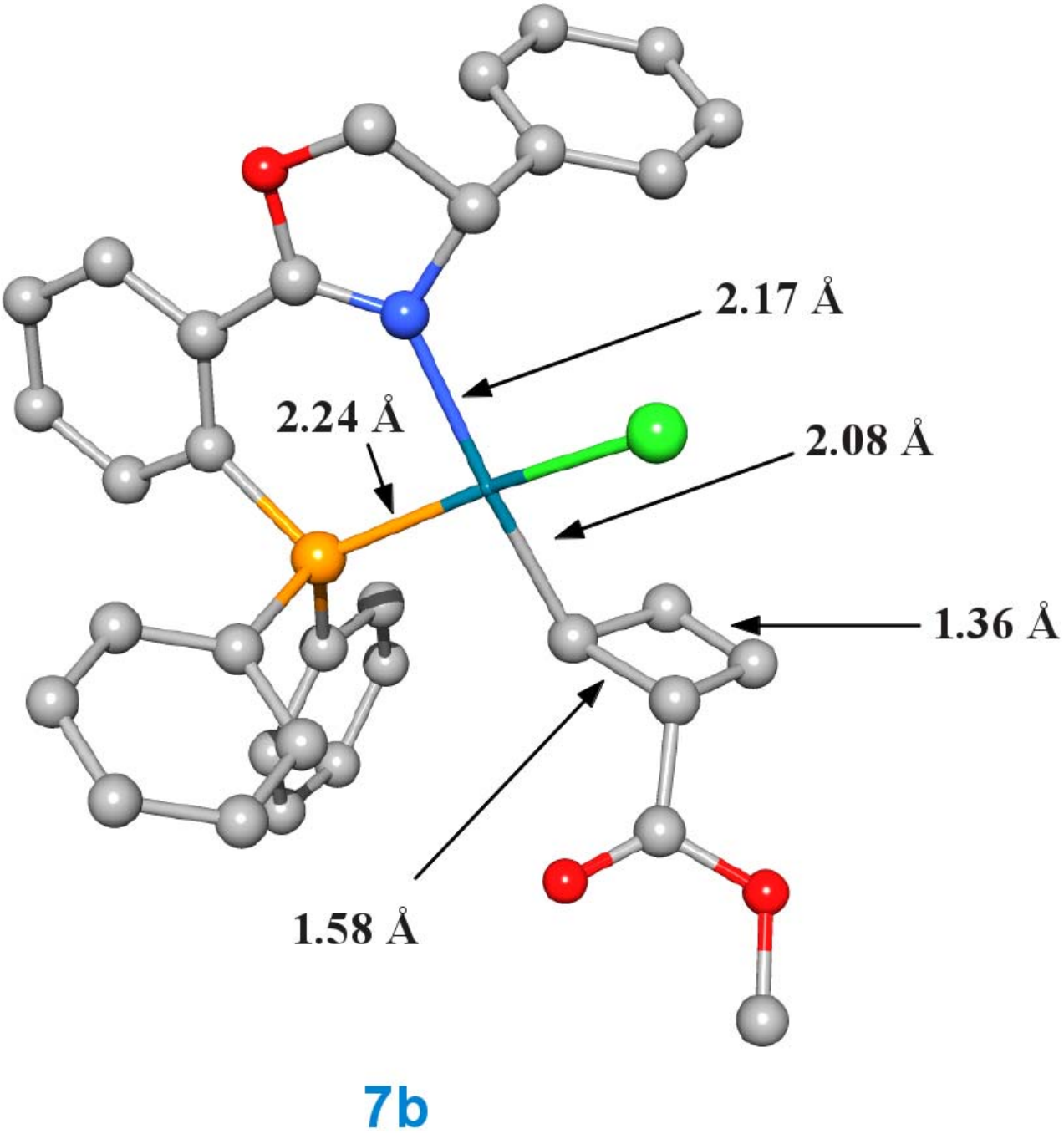
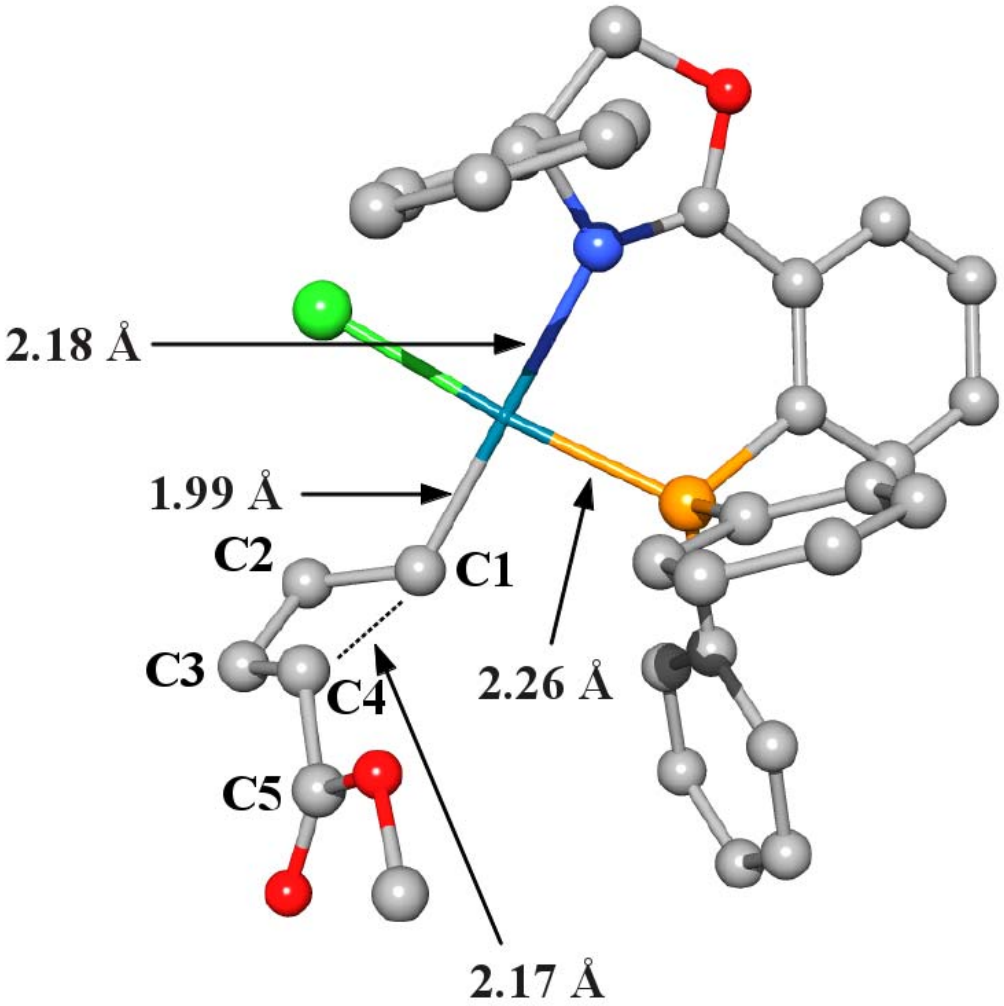
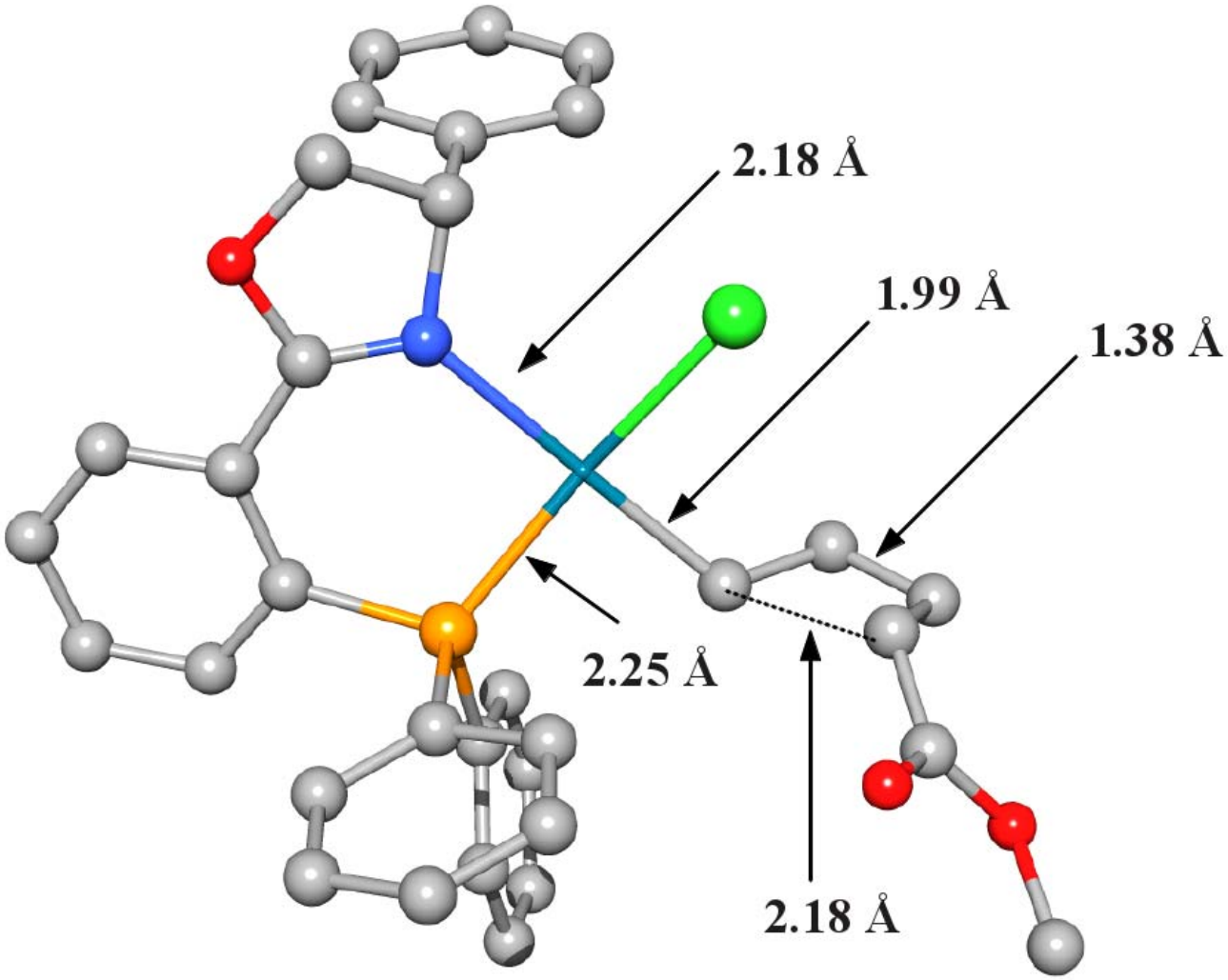


Figure S3. Optimized geometry of $\mathbf{TS_{ring}}$**-1** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (please refer Figure S1 for color code). Some important bond lengths are also given.



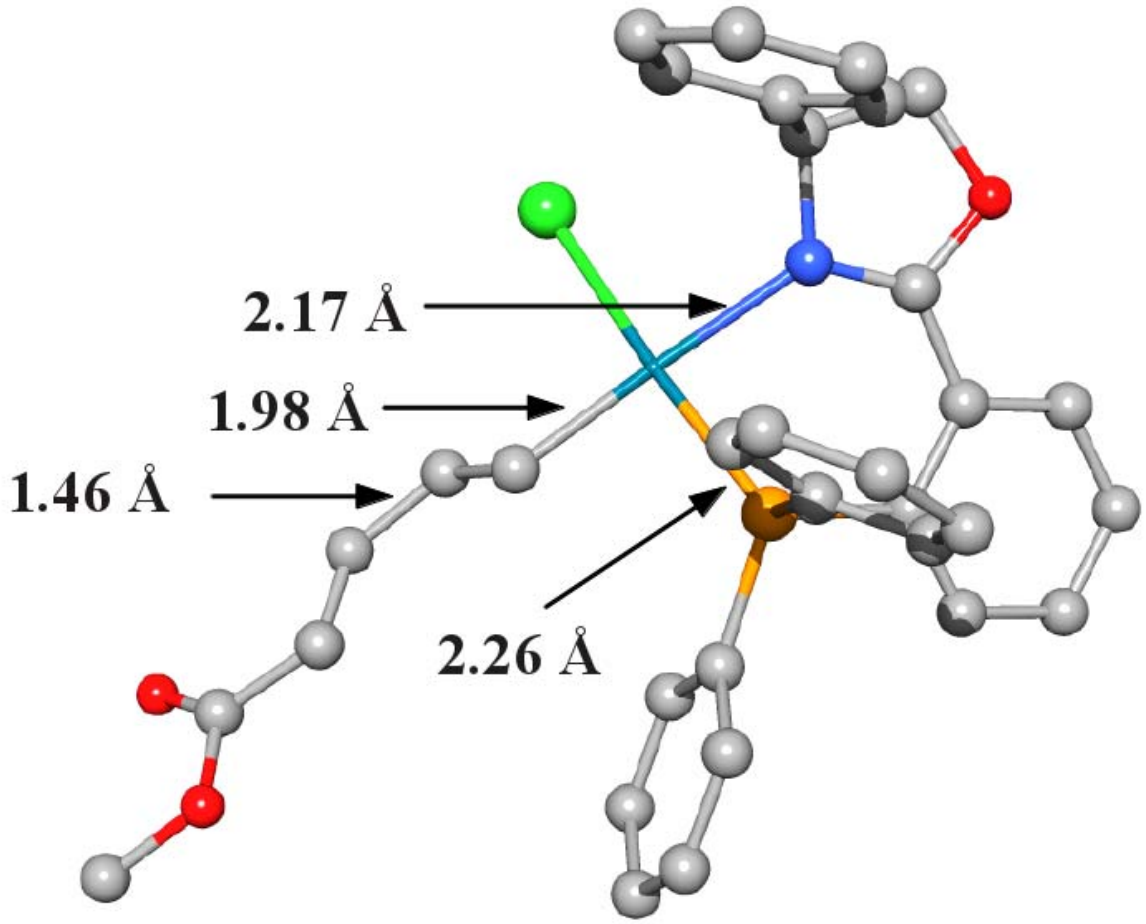
TS_{ring}-1

Figure S4. Optimized geometry of **TS_{ring}-2** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (please refer Figure S1 for color code). Some important bond lengths are also given.



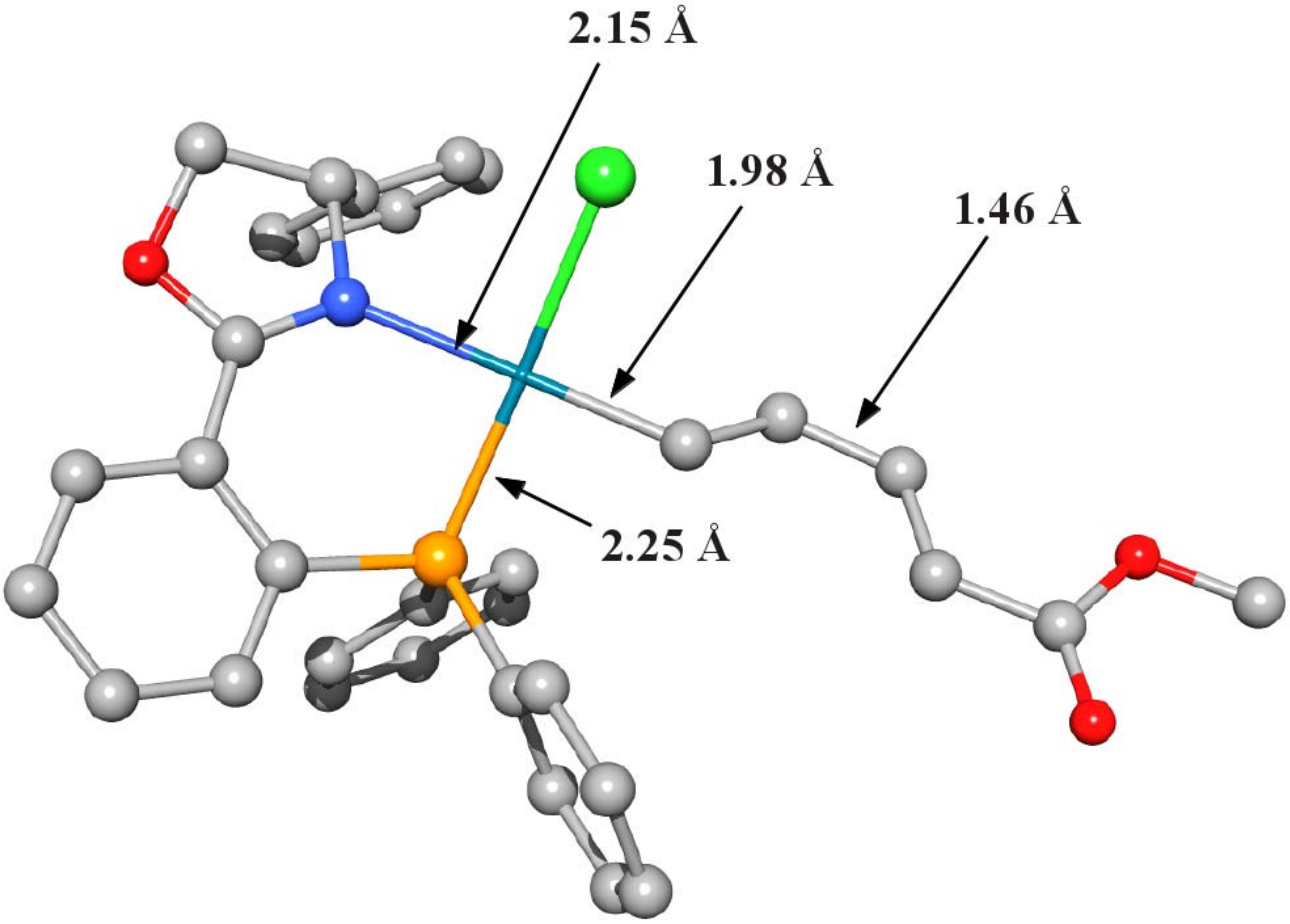
TS_{ring}-2

Figure S5. Optimized geometry of ***E,E*-(8) [7a]** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (please refer Figure S1 for color code). Some important bond lengths are also given.



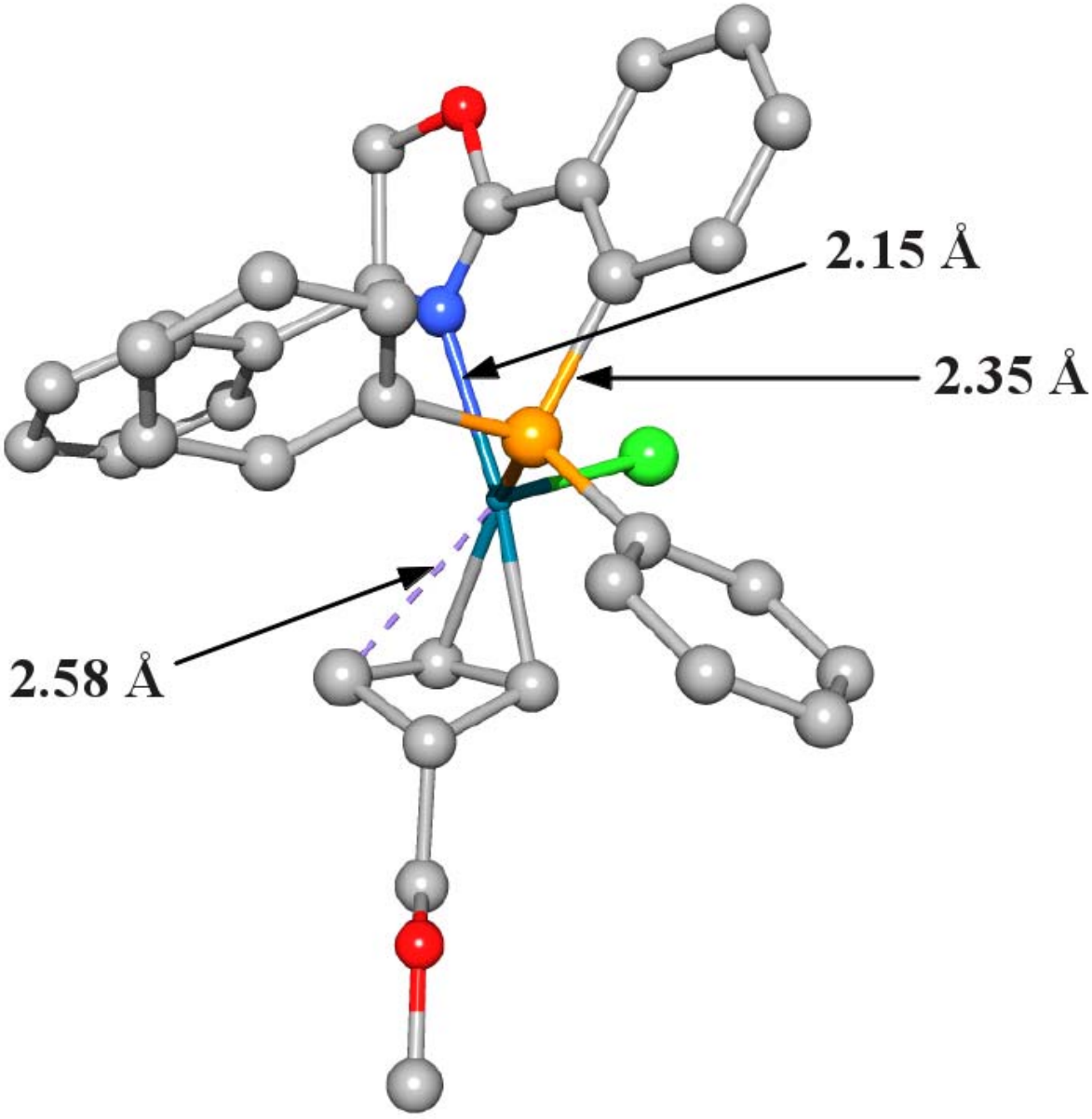
***E,E*-(8) [7a]**

Figure S6. Optimized geometry of ***E,E*-(8) [7b]** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (please refer Figure S1 for color code). Some important bond lengths are also given.



***E,E*-(8) [7b]**

Figure S7. Optimized geometry of **TS-1** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (please refer Figure S1 for color code). Some important bond lengths are also given.



TS-1

Figure S8. Optimized geometry of η^3-**1** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (please refer Figure S1 for color code). Some important bond lengths are also given.

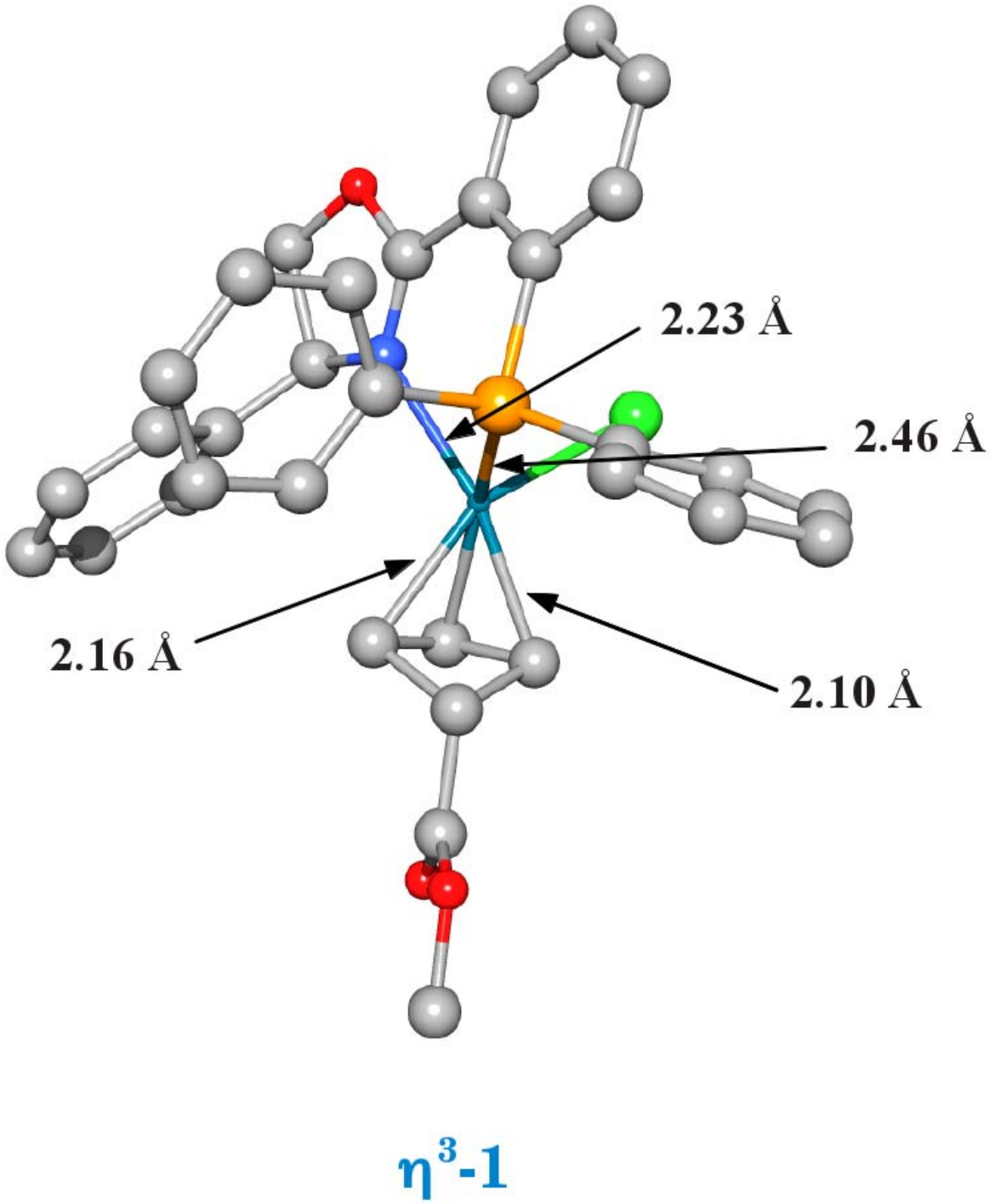


Figure S9. Optimized geometry of **TS_{int}-1** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (please refer Figure S1 for color code). Some important bond lengths are also given.

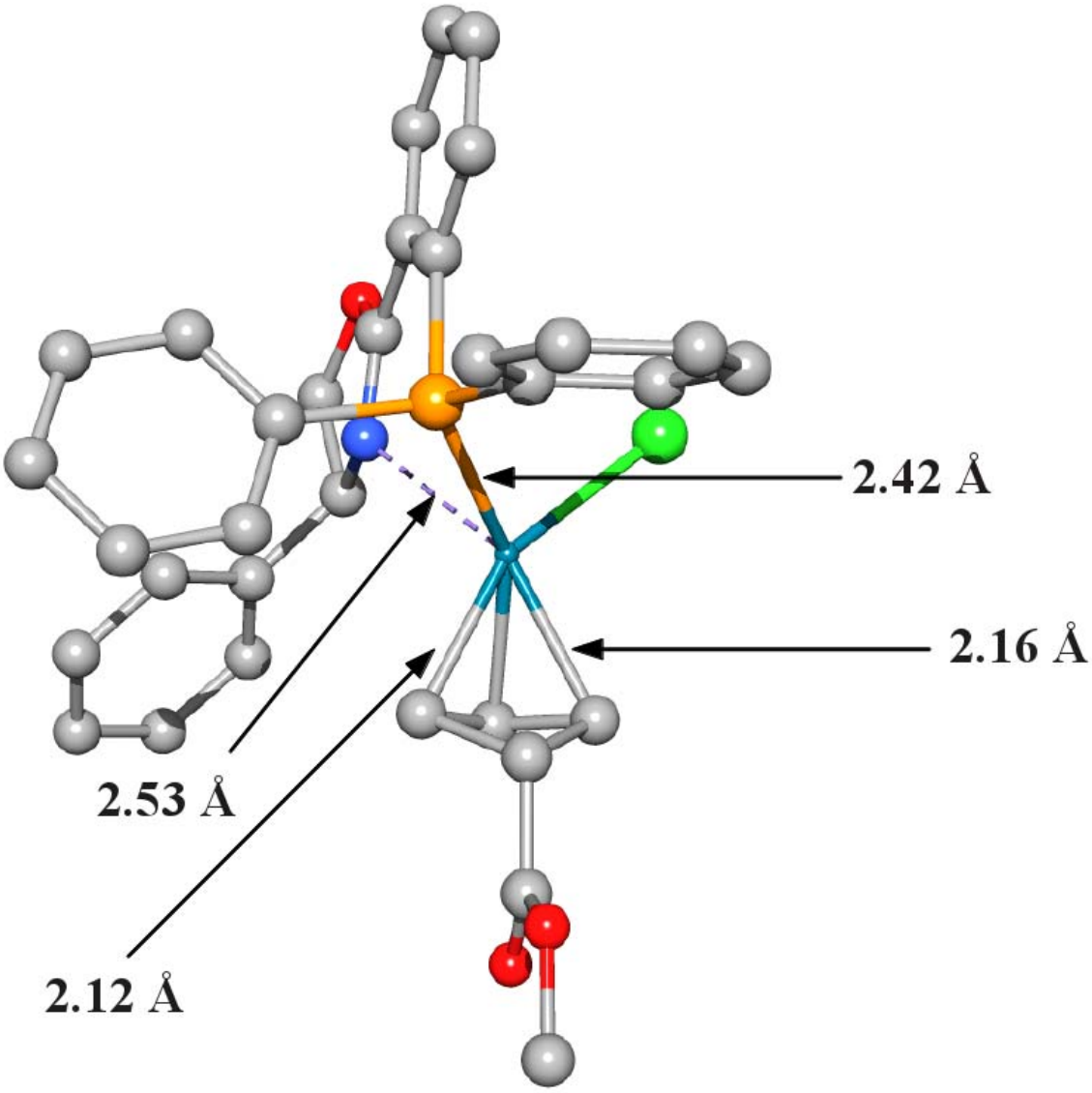
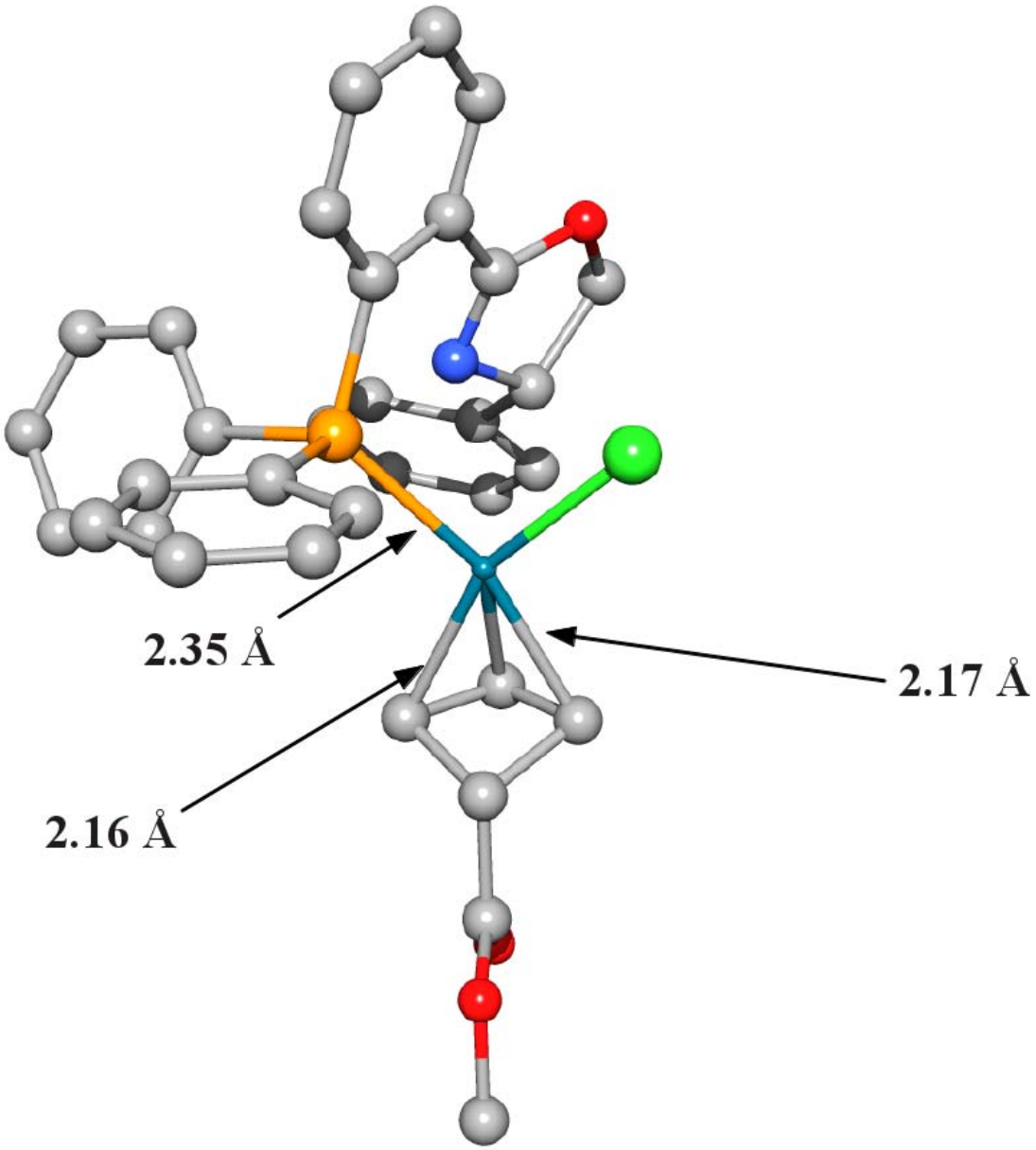
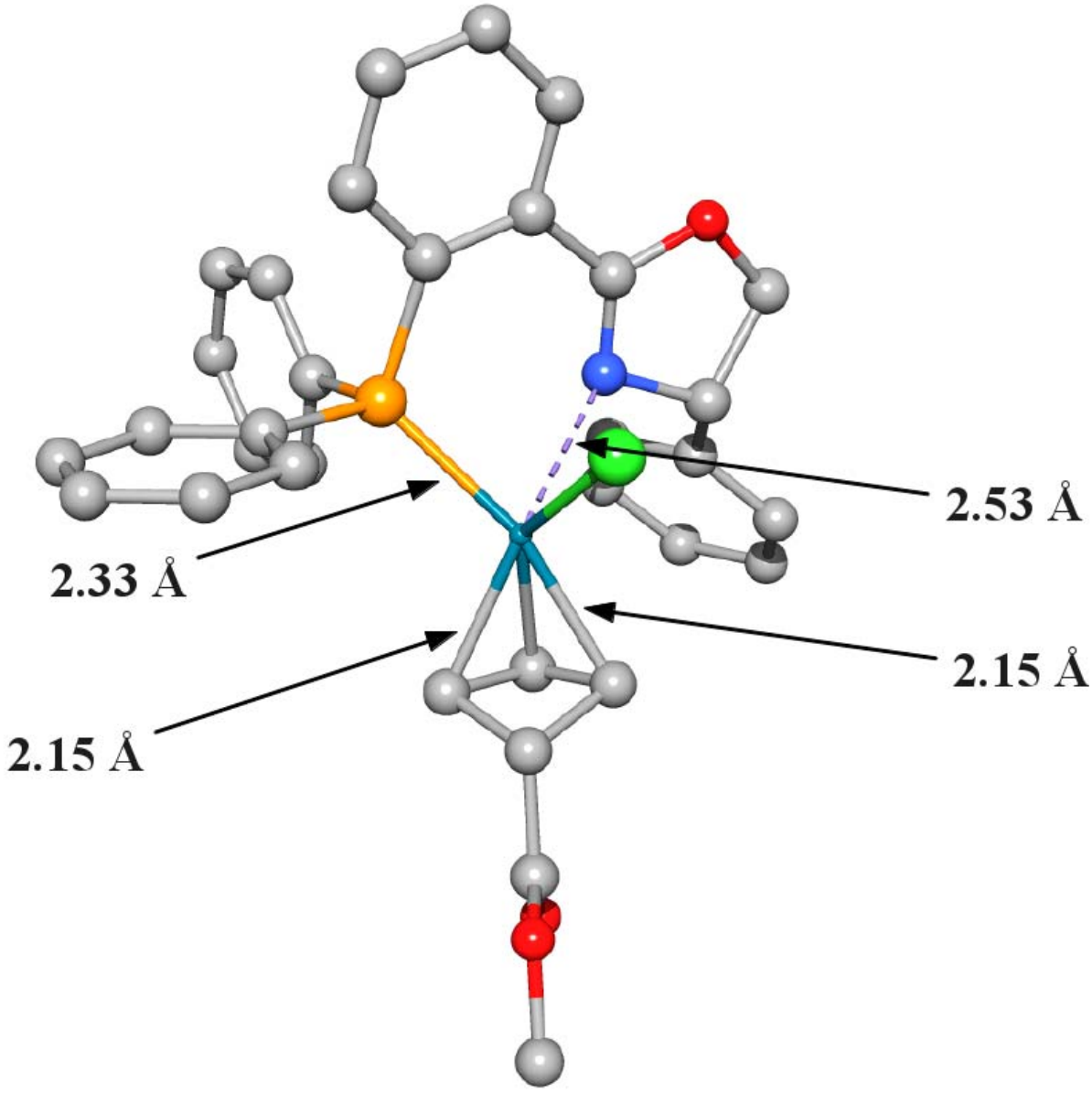


Figure S10. Optimized geometry of **INT** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (please refer Figure S1 for color code). Some important bond lengths are also given.



INT

Figure S11. Optimized geometry of **TS_{int}-2** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (please refer Figure S1 for color code). Some important bond lengths are also given.



TS_{int}-2

Figure S12. Optimized geometry of η^3-**2** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (please refer Figure S1 for color code). Some important bond lengths are also given.

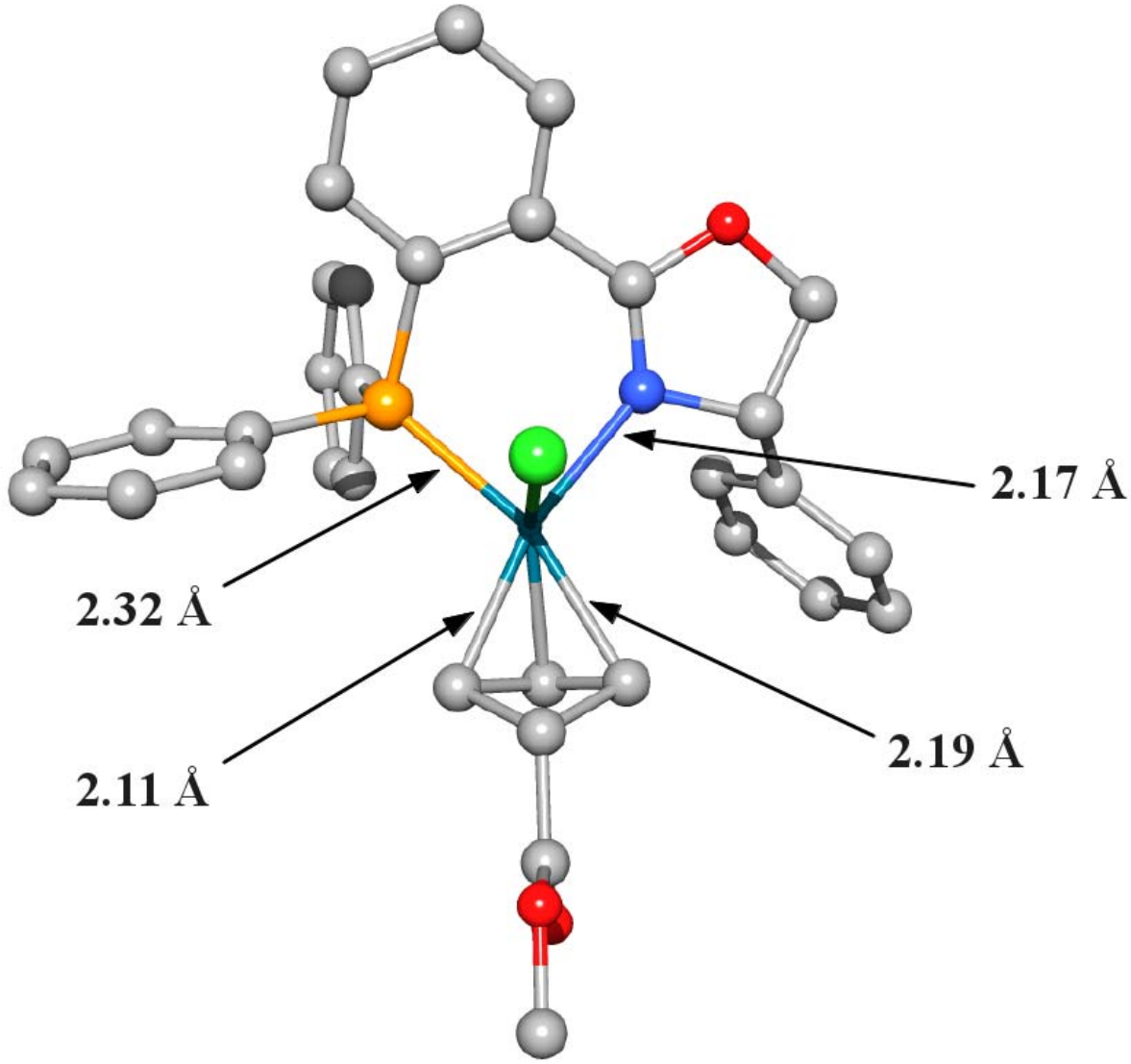


Figure S13. Optimized geometry of **TS-2** at BP86/def2-SVP level. The hydrogen atoms are omitted for clarity (please refer Figure S1 for color code). Some important bond lengths are also given.

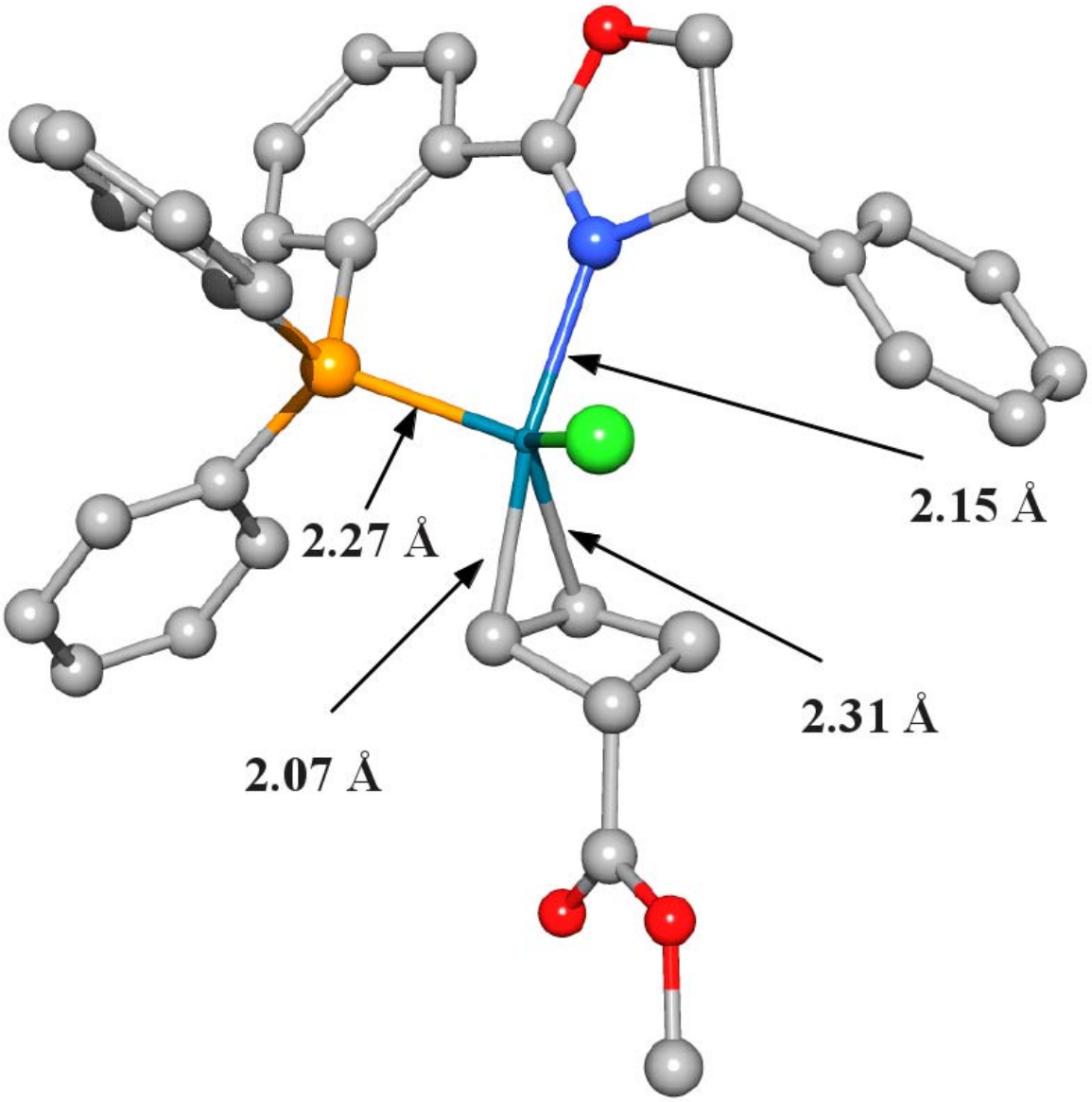


Figure S14. Free energy profile (25°C) for the ring opening and η^1-η^3-η^1 interconversion pathway at BP86/def2-SVP level.

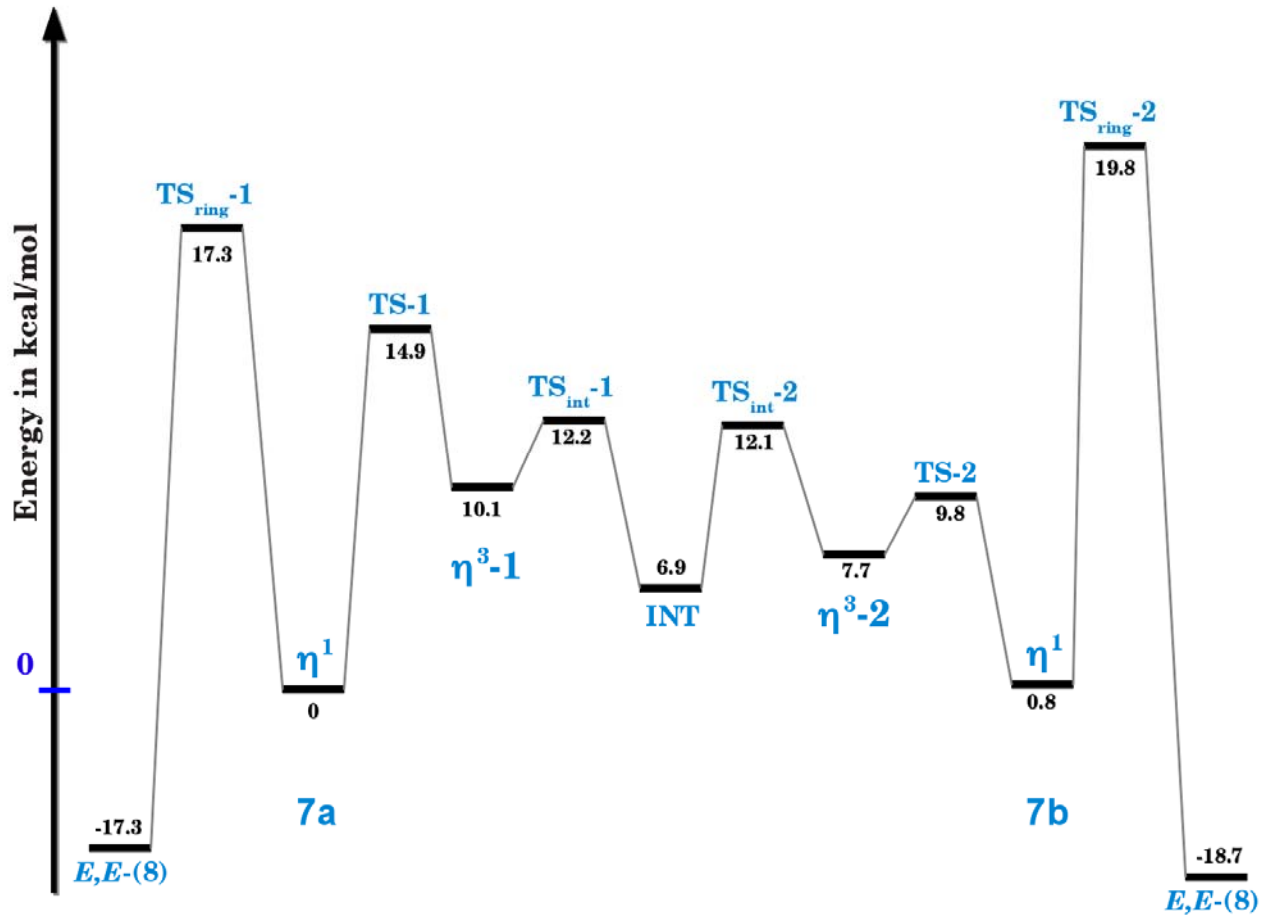
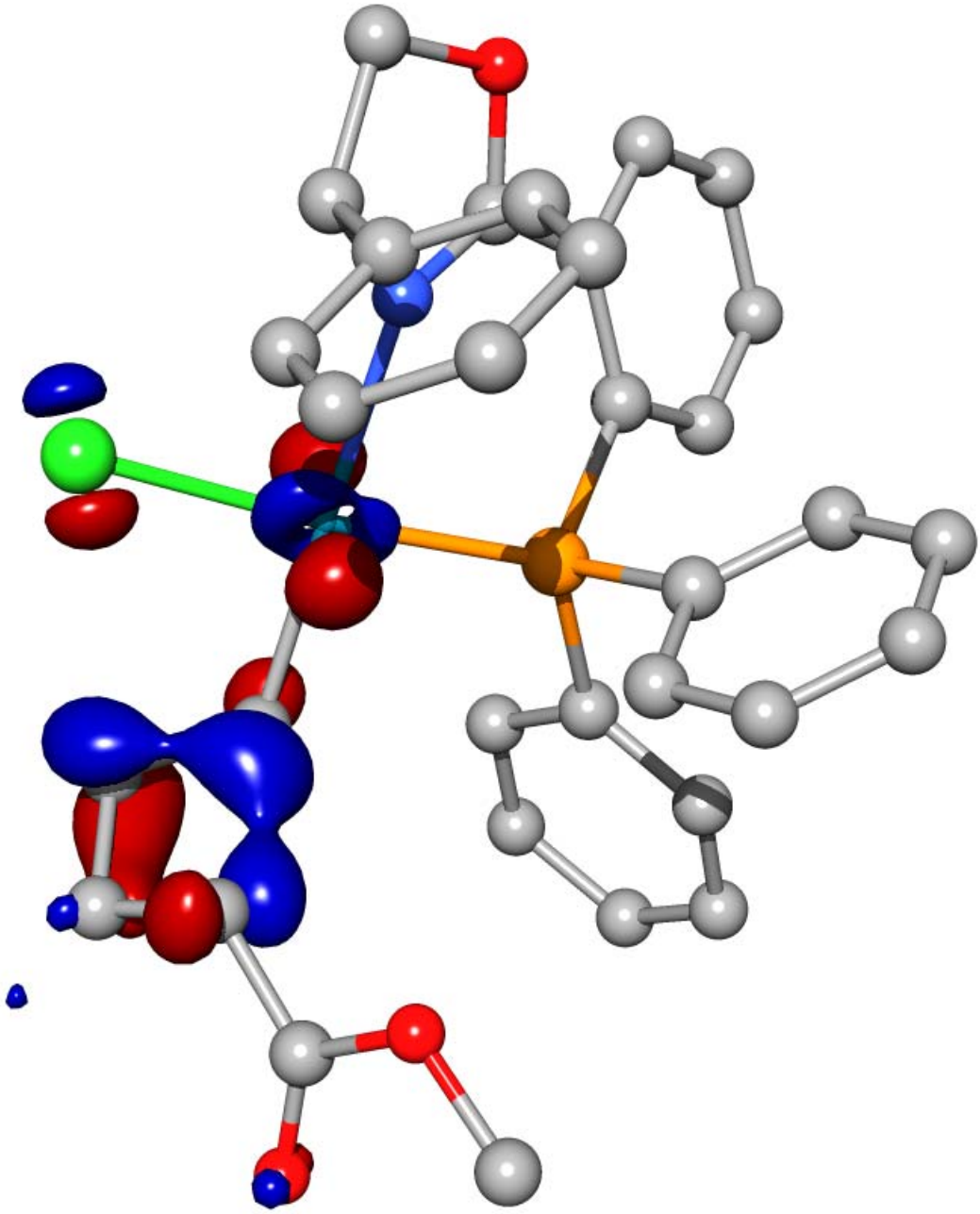


Figure S15. Plot of the highest occupied molecular orbital (HOMO) of the conrotatory ring opening transition state (**TS_{ring}-1**) for complex **7a** at BP86/def2-SVP level.



CARTESIAN COORDINATES OF OPTIMIZED GEOMETRIES (BP86/def2-SVP, Å)

E,E (8) [7a]

69

c	1.7500610987	-0.6054914677	-1.2419457676
c	2.9174512794	-0.6484760525	-4.1188463888
c	-2.5947318232	2.5651749480	0.5570925073
c	-1.3086379958	2.0229525055	0.3420771886
c	-0.1684080909	2.8148634133	0.5982259684
c	-0.3149458539	4.1374286060	1.0462287099
c	-1.5966468790	4.6753094533	1.2515136008
c	-2.7351321960	3.8872615898	1.0102637635
p	-1.0493972121	0.3081594233	-0.2981730710
c	-2.5471050791	-0.6133649933	0.3079744361
c	-2.6194576512	-1.1287297849	1.6376927910
c	-3.7971347148	-1.7857202345	2.0629810627
c	-4.8841134057	-1.9589952267	1.1956598368
c	-4.8090531691	-1.4689788623	-0.1156473710
c	-3.6512881174	-0.7989616525	-0.5477171959
c	-1.5148778827	-1.0227069713	2.6134679943
n	-0.2630967048	-0.7624862392	2.3817269659
c	0.4484991329	-0.7005052352	3.6929085055
c	-0.5898948106	-1.3345894263	4.6440586997
o	-1.8459945111	-1.2593279914	3.9085614018
pd	0.8211963329	-0.6649358964	0.5096445970
cl	2.6993919517	-1.7042807306	1.5044814478
c	0.8711503559	0.7274198395	4.0237900286
c	-0.0440842838	1.6684265891	4.5423920586
c	0.3714176933	2.9743388005	4.8485790343
c	1.7074393931	3.3567460199	4.6356889783
c	2.6210792777	2.4300051792	4.1058141606
c	2.2062687386	1.1233591351	3.7987223202
c	-1.3022327651	0.4377305990	-2.1194753625
c	-1.0233003975	-0.7032350337	-2.9075041472
c	-1.1733333408	-0.6507790002	-4.3015946827
c	-1.5873040964	0.5406742569	-4.9235387949
c	-1.8530047957	1.6799631318	-4.1469639575
c	-1.7111858801	1.6326231937	-2.7489543911
c	3.6351047110	-0.7732282348	-5.3987028364
o	3.3347504968	0.2835847756	-6.2252952415
c	3.9869682199	0.2596000270	-7.4964745352
c	2.4507344151	-1.6238786321	-1.8183835635
c	3.0717498705	-1.5851402750	-3.1379164893
o	4.3973510589	-1.6703665389	-5.7344885266
h	1.3587146570	-1.3239906613	3.5820605508

h	-0.3821849396	-2.4062853228	4.8450517715
h	-0.7189026275	-0.7990100314	5.6025754835
h	-3.8391562934	-2.1708250508	3.0906536943
h	-5.7861015702	-2.4826776456	1.5459551254
h	-5.6519921009	-1.6024664639	-0.8105688529
h	-3.6031798507	-0.4126254952	-1.5761245022
h	-1.9141770542	2.5316667672	-2.1486884722
h	-2.1679694491	2.6178616340	-4.6295488859
h	-1.6909478201	0.5829970784	-6.0185099041
h	-0.9482668008	-1.5420769462	-4.9062071540
h	-0.6699498993	-1.6281229149	-2.4271829633
h	-3.4915412880	1.9537476998	0.3735748158
h	-3.7409612074	4.3023970407	1.1777008008
h	-1.7092420520	5.7106984589	1.6084475355
h	0.5799537180	4.7451835928	1.2469563615
h	0.8354086054	2.3829394404	0.4590065232
h	2.9090225799	0.3963702819	3.3612320110
h	3.6676701443	2.7233715953	3.9308110448
h	2.0351052437	4.3784673889	4.8829648247
h	-0.3523127027	3.6965880343	5.2567649325
h	-1.0962035991	1.3861679234	4.7088123325
h	1.6640459164	0.3506570529	-1.7976122623
h	2.2561384900	0.2240578273	-4.0034155965
h	3.7436738731	-2.4260820406	-3.3883421667
h	2.5984493918	-2.5548465296	-1.2466463940
h	3.6509309365	1.1653225571	-8.0341969585
h	5.0906817431	0.2698431280	-7.3823112031
h	3.7157987134	-0.6501878314	-8.0716202137

TS_{ring}-1

69

c	1.3845885719	-1.5700851807	-1.5854000294
c	3.1110689955	-0.5251588538	-2.3757074288
c	-2.0978321759	2.5345007814	0.0478969978
c	-1.0347103379	1.7211697817	-0.3997740572
c	0.2192105603	2.3070277506	-0.6857680442
c	0.3976517664	3.6902864525	-0.5295041969
c	-0.6617002739	4.4969360287	-0.0793933158
c	-1.9084723089	3.9174961950	0.2085098149
p	-1.2026323876	-0.1047028425	-0.6328409458
c	-2.7637956208	-0.5331955522	0.2881703042
c	-2.7725597460	-0.7960421445	1.6917687426
c	-3.9984691938	-1.0836049726	2.3366283608
c	-5.2016773223	-1.1315509490	1.6213262536
c	-5.1955916697	-0.8846586021	0.2413422965
c	-3.9873360786	-0.5851987784	-0.4106287389
c	-1.5579475240	-0.7895525053	2.5322705200
n	-0.3184711263	-0.8421155071	2.1486215396

c	0.5456076191	-0.7288703205	3.3602787648
c	-0.4713467353	-0.9695769326	4.4977608992
o	-1.7690299957	-0.7467137781	3.8735576037
pd	0.5524990271	-1.2630171085	0.1924317245
cl	2.2848320463	-2.5194846735	1.2272449242
c	1.2752525834	0.6105175312	3.3881425983
c	0.6317895344	1.7949566658	3.8058850311
c	1.3262436814	3.0149353148	3.8251214860
c	2.6719521667	3.0661528505	3.4226522374
c	3.3153904000	1.8936054546	2.9928110321
c	2.6214061785	0.6727365386	2.9723442651
c	-1.6826732805	-0.3120184420	-2.4031894074
c	-1.7428112091	-1.6252574678	-2.9230915411
c	-2.1035833110	-1.8386197112	-4.2616679429
c	-2.3913633989	-0.7452627640	-5.0977575619
c	-2.3189695156	0.5620320348	-4.5903633942
c	-1.9663584394	0.7816410206	-3.2475157813
c	3.2665556821	0.5053641654	-3.4152954896
o	3.0854950722	1.7751928557	-2.9056929380
c	3.1978277765	2.8264241890	-3.8677509344
c	2.3581720658	-2.5887153404	-1.9155113224
c	3.3083805564	-1.9289632242	-2.6637863608
o	3.5088810920	0.3100785189	-4.5994859672
h	1.2968461847	-1.5413942692	3.2850672575
h	-0.4520390485	-2.0154939316	4.8689238318
h	-0.3757659107	-0.2741980625	5.3519737371
h	-3.9866293795	-1.2795136948	3.4171703196
h	-6.1412034215	-1.3662878811	2.1436657700
h	-6.1313109126	-0.9211934288	-0.3370978867
h	-3.9961996446	-0.3865429583	-1.4918425959
h	-1.9097195025	1.8082340117	-2.8560898563
h	-2.5353805262	1.4212305427	-5.2435686826
h	-2.6628090957	-0.9136305437	-6.1512404857
h	-2.1460291411	-2.8644961968	-4.6580004458
h	-1.4948365306	-2.4806616492	-2.2748106293
h	-3.0779445800	2.0892081694	0.2761360376
h	-2.7415308254	4.5438649392	0.5632084162
h	-0.5137439360	5.5800208938	0.0519138836
h	1.3795166645	4.1347483226	-0.7509194201
h	1.0595599521	1.6865188737	-1.0344643434
h	3.1080273093	-0.2475581655	2.6116794484
h	4.3671609941	1.9268881855	2.6692649516
h	3.2180749853	4.0221425692	3.4424899680
h	0.8133481900	3.9310459058	4.1567428263
h	-0.4250002219	1.7729351912	4.1177546990
h	0.8462696649	-1.1396157950	-2.4464144567
h	3.2277231075	-0.1803725028	-1.3369638297
h	4.0398635271	-2.3378075630	-3.3816130713
h	2.3490103915	-3.6282335303	-1.5532270027
h	3.0159507846	3.7703074914	-3.3216477587
h	4.2066651914	2.8418189421	-4.3290703191
h	2.4553197649	2.7072264488	-4.6841719645

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c	0.9834281463	-2.4693479772	-4.6445161038
c	0.6558695887	-1.1521747389	-5.0362510182
c	0.4041953668	-0.8755189663	-6.3965624542
c	0.4604196147	-1.9090731752	-7.3471138248
c	0.7631851763	-3.2216014157	-6.9483586102
c	1.0284496150	-3.4991172155	-5.5960899898
p	0.5617894592	0.1226964594	-3.6999835745
pd	2.1142808911	0.1715354251	-2.0748880931
c	3.6805256334	-0.6370384057	-3.1609685753
c	4.9319133520	0.1820071932	-3.0066696582
c	5.1007336263	0.3791758955	-4.3392199716
c	3.8526460963	-0.4238476963	-4.7168112420
c	4.1598679576	-1.6537041692	-5.5493402011
o	4.4123729525	-2.7700751106	-5.1336073866
c	-1.1325652406	-0.2244655567	-2.9794007110
c	-1.5504492153	0.2865364767	-1.7138152684
c	-2.8663863303	0.0352802109	-1.2585246339
c	-3.7650136236	-0.7245486872	-2.0172788786
c	-3.3548904467	-1.2444367104	-3.2523637767
c	-2.0551569712	-0.9904326733	-3.7225145021
c	-0.6743793325	1.0680241887	-0.8201197665
n	0.6182491346	1.1682752243	-0.8600678707
c	1.0416739677	2.1161407168	0.2114589134
c	-0.2447160762	2.2330968611	1.0589918404
o	-1.2985959460	1.7376239272	0.1852231153
c	1.5696711670	3.4179315905	-0.3831410697
c	0.6989531518	4.4240386383	-0.8530661609
c	1.2100124453	5.6157495049	-1.3917703433
c	2.5992701025	5.8143126627	-1.4707376082
c	3.4726903812	4.8115266789	-1.0169856238
c	2.9624199674	3.6185573476	-0.4789752982
c	0.3113796865	1.7383861488	-4.5716644566
c	1.4058408871	2.6285273155	-4.6301498794
c	1.2804784776	3.8603737794	-5.2928161963
c	0.0613406569	4.2195288082	-5.8910777247
c	-1.0370603129	3.3450583650	-5.8223718747
c	-0.9154781427	2.1098801222	-5.1650232618
cl	3.5323999602	0.0203785250	-0.1443927625
o	4.1797506515	-1.3348569487	-6.8777651680
h	1.8656630293	1.6160373255	0.7600316531
h	-0.2190630719	1.5830912772	1.9583150042
h	-0.5012981362	3.2658132181	1.3589773614
h	-3.1674769012	0.4424938575	-0.2840927291
h	-4.7804571104	-0.9145081794	-1.6385123230
h	-4.0433939301	-1.8513115367	-3.8600667601
h	-1.7507469951	-1.4036181148	-4.6944991425
h	0.1670089513	0.1496118185	-6.7178228553

h	0.2666466309	-1.6834493191	-8.4071379765
h	0.8029584974	-4.0296719279	-7.6950526642
h	1.2926847472	-4.5191491782	-5.2801045105
h	1.2169772067	-2.6833450267	-3.5895200681
h	-1.7852975503	1.4375458095	-5.1069926615
h	-1.9981063787	3.6274523830	-6.2793606627
h	-0.0372264145	5.1885523074	-6.4044588886
h	2.1397917927	4.5468446498	-5.3290409772
h	2.3528587762	2.3569343365	-4.1364010107
h	3.6373633487	2.8140327281	-0.1451457824
h	4.5622159073	4.9574427351	-1.0810109176
h	3.0003390011	6.7515217625	-1.8871235473
h	0.5187537244	6.3938014791	-1.7509360612
h	-0.3925973616	4.2800932309	-0.8043365463
h	3.7392464359	-1.6967232206	-2.8371702001
h	3.0681855758	0.1737207735	-5.2268226453
h	5.8562731854	0.8798406005	-4.9649735248
h	5.4836187907	0.4865193808	-2.1063417791
c	4.5583142468	-2.4013311201	-7.7575261286
h	4.5413089669	-1.9789078096	-8.7785984667
h	5.5730445702	-2.7773319125	-7.5141094121
h	3.8485830636	-3.2497898123	-7.6810979261

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pd	0.4733628928	-0.9034789009	0.1604840303
c	2.7936509072	0.0357587998	-0.4597909040
c	-1.8348708311	1.3672702378	-3.3921903428
c	-1.6334320882	0.2785293960	-2.5174808764
c	-1.6514435092	-1.0381125195	-3.0371459300
c	-1.8991030990	-1.2573999009	-4.3997612223
c	-2.1037563729	-0.1679575254	-5.2665056088
c	-2.0649781266	1.1412795342	-4.7610492909
p	-1.2307841602	0.4465443924	-0.7228940115
cl	0.0807015382	-3.2617761713	0.7419775234
c	-1.1877648798	2.2812447192	-0.4164340648
c	-2.3482677411	3.0869602315	-0.3923672573
c	-2.2482031315	4.4696425190	-0.1665194495
c	-0.9902183574	5.0634634124	0.0379151783
c	0.1675173421	4.2679422090	0.0253639393
c	0.0687622879	2.8831772060	-0.1928016173
c	-2.8170687380	-0.0287026604	0.1249534931
c	-2.8592599706	-0.3437705070	1.5191708406
c	-4.1046227478	-0.6527599809	2.1190063201
c	-5.2872915016	-0.6853022034	1.3711280266

c	-5.2438522738	-0.4065758139	-0.0026427399
c	-4.0207156887	-0.0787838340	-0.6092230800
c	-1.6712887223	-0.4274814350	2.3947183696
n	-0.4131574717	-0.4473505000	2.0640815071
c	0.3809519116	-0.7864573307	3.2666432595
c	-0.6606098893	-0.6355757640	4.4069830423
o	-1.9349699940	-0.5834384598	3.7193657869
c	1.6310916246	0.0543796564	3.4433567312
c	1.5872092095	1.4591496748	3.3186752745
c	2.7416493689	2.2296509012	3.5282209409
c	3.9561159380	1.6063374386	3.8669726629
c	4.0097702795	0.2081325356	3.9887896387
c	2.8537658660	-0.5618747905	3.7751014451
c	1.6977172551	-1.4078836031	-1.4172731207
c	2.6309813791	-1.3428171658	-0.2820899893
c	2.2069752974	-0.0030199168	-1.8860347841
c	3.2959206185	-0.1081436386	-2.9525026831
o	4.2752162598	-0.8295406189	-2.9062256055
o	3.0234240881	0.7161525680	-4.0009165846
c	3.9746256092	0.6773405244	-5.0754219028
h	0.6725464872	-1.8520301475	3.1289043501
h	-0.6794964073	-1.4887638112	5.1109635638
h	-0.5347403587	0.3097437606	4.9760998494
h	-4.1242628202	-0.8904032507	3.1906266296
h	-6.2387506538	-0.9400897936	1.8614911967
h	-6.1621545258	-0.4386694788	-0.6089427649
h	-3.9971307860	0.1431656514	-1.6861775930
h	-1.8091295189	2.3971493156	-3.0061417775
h	-2.2158601864	1.9986179666	-5.4353039500
h	-2.2856600519	-0.3415285238	-6.3384240033
h	-1.9194266589	-2.2865388166	-4.7903204419
h	-1.4623146305	-1.8896693119	-2.3630542947
h	-3.3389462552	2.6311140793	-0.5429107596
h	-3.1598284291	5.0868472342	-0.1472111923
h	-0.9142922686	6.1474771478	0.2150021391
h	1.1547631934	4.7252950205	0.1939850492
h	0.9681364963	2.2472932570	-0.1735195660
h	2.9000463017	-1.6593705866	3.8590760821
h	4.9581457354	-0.2882417683	4.2459614558
h	4.8611699253	2.2110999907	4.0317107574
h	2.6939469694	3.3247914418	3.4247669654
h	0.6426140298	1.9515748335	3.0379095235
h	1.4350619082	-2.2624954166	-2.0611128791
h	1.4571297120	0.7463380382	-2.2037976548
h	3.3655312159	0.8059735536	0.0786171147
h	3.0458309192	-2.0881364767	0.4074323854
h	3.6091438577	1.3919780508	-5.8343202500
h	4.9835876903	0.9711791335	-4.7216620912
h	4.0435033713	-0.3419921471	-5.5061802861

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pd	0.4707460690	-1.0592024155	-0.0690972065
c	2.4276657524	-0.1762215521	-0.3152824636
c	-2.1419363749	1.4125052544	-3.3783970126
c	-1.9012893287	0.2984209549	-2.5462661053
c	-1.9903708608	-1.0082297148	-3.0859338524
c	-2.3369578490	-1.1860569291	-4.4336476433
c	-2.5762666649	-0.0730014370	-5.2606857338
c	-2.4743011234	1.2237885853	-4.7316501465
p	-1.3613231317	0.4264641871	-0.7841170609
cl	-0.9579899724	-3.0358512031	-0.1435090614
c	-1.2615456330	2.2546325588	-0.4713125719
c	-2.3582998421	3.0418831126	-0.0552296172
c	-2.2010971617	4.4197009644	0.1718580276
c	-0.9512268805	5.0316426401	-0.0211844895
c	0.1464897346	4.2571403228	-0.4346540670
c	-0.0050897730	2.8773867256	-0.6468950804
c	-2.8877808730	-0.0480430459	0.1650525845
c	-2.8329306560	-0.4396579568	1.5373719703
c	-4.0366246820	-0.7674065385	2.2083454318
c	-5.2713537195	-0.7385222969	1.5500589123
c	-5.3250667761	-0.3713934228	0.1982832639
c	-4.1425474052	-0.0286768288	-0.4767248533
c	-1.5908383119	-0.5516978282	2.3346710691
n	-0.3516810810	-0.5733871758	1.9405029628
c	0.5084505844	-0.8297545692	3.1127016006
c	-0.4901036182	-0.7424590971	4.3043739456
o	-1.7898298219	-0.6924273233	3.6751380431
c	1.6893109614	0.1178642674	3.2376409120
c	1.5553469404	1.4884620884	2.9330547248
c	2.6382837548	2.3645682612	3.1079814555
c	3.8676637613	1.8838694878	3.5930653304
c	4.0100569099	0.5196971736	3.8954345549
c	2.9268049145	-0.3570167279	3.7154225109
c	1.8421176859	-1.6774092528	-1.5314763241
c	2.4849395745	-1.6227634425	-0.2299439726
c	2.3061026038	-0.2355440020	-1.8654920666
c	3.6604681485	-0.1935095748	-2.5725171695
o	4.6519869552	-0.8225371773	-2.2508789004
o	3.6239095188	0.6555266904	-3.6347471940
c	4.8466775767	0.7625789824	-4.3797346562
h	0.8990639569	-1.8655459153	3.0047316514
h	-0.4586734859	-1.6207290039	4.9770719083
h	-0.3572572714	0.1830518472	4.9024059304
h	-3.9846502779	-1.0668673042	3.2630412809
h	-6.1883014017	-1.0109780931	2.0938934241
h	-6.2864478389	-0.3482073420	-0.3377062691
h	-4.1925638085	0.2581711595	-1.5373207797
h	-2.0695806572	2.4317886227	-2.9697973722
h	-2.6578106695	2.0991914282	-5.3740719400

h	-2.8391231342	-0.2176180843	-6.3202155366
h	-2.4121320141	-2.2051494118	-4.8439526602
h	-1.7870275439	-1.8781440505	-2.4353059393
h	-3.3435490350	2.5752247180	0.0942121084
h	-3.0643270821	5.0192883489	0.5002879015
h	-0.8311263441	6.1117900657	0.1553527293
h	1.1306877287	4.7277333684	-0.5843195031
h	0.8622362924	2.2684571043	-0.9444732344
h	3.0458681547	-1.4288656520	3.9432546639
h	4.9715126949	0.1325907390	4.2663198659
h	4.7163532639	2.5716169757	3.7289072863
h	2.5218591257	3.4306373242	2.8589205255
h	0.6014094871	1.8651120529	2.5325571335
h	1.6059691941	-2.5147512251	-2.2049320565
h	1.5942016014	0.4360678278	-2.3850206073
h	2.8471866133	0.6151478769	0.3251415511
h	2.9380511295	-2.3556111354	0.4483799552
h	4.6486653159	1.4842730180	-5.1921235191
h	5.6730797989	1.1230075465	-3.7343636168
h	5.1407709283	-0.2205807514	-4.7993565637

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pd	0.3212688299	-1.1438714385	-0.4942365343
n	0.7958909170	-0.4624945984	1.8932422674
c	1.6960355990	-0.0597661633	-1.6963478695
c	-3.5763635623	1.5060177749	-1.4872469521
c	-2.9125417813	0.3456246249	-1.0339899246
c	-3.3289164399	-0.9235120291	-1.5028812047
c	-4.4018453359	-1.0212966927	-2.4020986315
c	-5.0574281796	0.1376278005	-2.8556270191
c	-4.6416313615	1.3991153204	-2.3985785947
p	-1.4683189861	0.3571437402	0.1236201182
cl	-0.8768960977	-3.0845088513	0.2628899577
c	-1.0144772872	2.1434228397	0.2774064888
c	-1.1494413724	2.8748610094	1.4767405935
c	-0.7276112533	4.2146923757	1.5457305468
c	-0.1803129363	4.8451880014	0.4170233919
c	-0.0477389990	4.1256800832	-0.7845506888
c	-0.4491354686	2.7833488751	-0.8506065111
c	-2.2409407341	-0.0421524115	1.7655955465
c	-1.4873507702	-0.5131130876	2.8845955488
c	-2.1613373936	-0.8276420465	4.0898136362
c	-3.5476943423	-0.6855283400	4.2083387305
c	-4.2904385453	-0.2226804424	3.1120505429
c	-3.6382905119	0.0880434103	1.9092129672
c	-0.0263798357	-0.7074996698	2.8653852381
c	2.1316692355	-0.9145127493	2.3199479918

c	1.9480974829	-1.1673228642	3.8458155907
o	0.5137490913	-1.2122947324	4.0160425123
c	3.2558085849	0.0508822940	1.9866670098
c	3.0050842605	1.4237974597	1.7904679827
c	4.0643684480	2.3104950762	1.5347729645
c	5.3864957788	1.8382474545	1.4758025689
c	5.6443808598	0.4701285387	1.6668156671
c	4.5849608380	-0.4171234886	1.9162274267
c	1.1978391999	-1.9283167288	-2.3062516381
c	2.2055697852	-1.3985668984	-1.4398834599
c	1.0057046521	-0.5604353733	-3.0058019635
c	1.8983063276	-0.4006442369	-4.2379969575
o	3.0734899567	-0.7094828910	-4.3070131227
o	1.2042802352	0.1532460381	-5.2663854646
c	1.9518503547	0.3563680541	-6.4763719245
h	2.3298961193	-1.8804597146	1.8003222192
h	2.3746784289	-2.1248988255	4.1990987599
h	2.3515645892	-0.3337840422	4.4610551795
h	-1.5678384001	-1.1947329070	4.9374401737
h	-4.0462182370	-0.9390435793	5.1561119748
h	-5.3820761649	-0.1023072734	3.1866675588
h	-4.2331591819	0.4409141794	1.0547264303
h	-3.2621092843	2.4978292120	-1.1284064562
h	-5.1513650026	2.3099918629	-2.7495855823
h	-5.8924932671	0.0568811017	-3.5687752028
h	-4.7223577318	-2.0128119299	-2.7577635737
h	-2.8040745395	-1.8294628084	-1.1498240659
h	-1.5927843058	2.3986132873	2.3641714236
h	-0.8369324259	4.7704086197	2.4900999668
h	0.1428327950	5.8961312938	0.4711489768
h	0.3802905281	4.6111001119	-1.6753493625
h	-0.3260483431	2.2227775197	-1.7904528336
h	4.7930804576	-1.4911593312	2.0527828950
h	6.6760167212	0.0895421178	1.6127728524
h	6.2153313516	2.5340384517	1.2734731990
h	3.8524836952	3.3792676193	1.3758591759
h	1.9667397763	1.7869340057	1.8204637220
h	0.9539503099	-2.9475474312	-2.6397327584
h	-0.0243330116	-0.2260244865	-3.2399605905
h	2.1027405410	0.9349780540	-1.4591096767
h	3.0408982581	-1.8229251027	-0.8691736361
h	1.2502358985	0.8139119535	-7.1962705860
h	2.8166013662	1.0268569804	-6.2985568983
h	2.3355330014	-0.6066285699	-6.8690241351

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pd	0.1162042796	-0.9845403176	-0.9383919082
n	0.8230986666	-0.1245378924	1.9753394914

c	1.1987108978	0.1536954981	-2.4141387209
c	-3.5513351806	1.7922074192	-1.2932756392
c	-2.8918493153	0.5831379407	-0.9860738301
c	-3.3575008996	-0.6240996768	-1.5598281190
c	-4.4640076252	-0.6142420763	-2.4229756297
c	-5.1109262472	0.5951925697	-2.7336373307
c	-4.6526871733	1.7959775502	-2.1676111216
p	-1.4062561392	0.4592573201	0.1272122628
cl	-0.8427729639	-2.9141868989	0.0546796178
c	-0.9274022981	2.2236059646	0.4106710683
c	-0.9797691054	2.8247407107	1.6850518366
c	-0.5778032551	4.1602050803	1.8585187619
c	-0.1253659697	4.9133534489	0.7628773624
c	-0.0750698561	4.3232216196	-0.5117577990
c	-0.4674066189	2.9870479871	-0.6851569302
c	-2.1764863235	-0.0675098347	1.7440071746
c	-1.4303017522	-0.6387736975	2.8154292260
c	-2.0992200069	-1.0943255593	3.9737234772
c	-3.4868766028	-0.9668669685	4.1038226381
c	-4.2249978305	-0.3827568989	3.0641878241
c	-3.5736949676	0.0507806486	1.8982903731
c	0.0337186857	-0.7710372739	2.7653363408
c	2.1695383043	-0.6809120562	2.1800350699
c	2.0218175571	-1.4949606345	3.5022820964
o	0.5914960247	-1.6596222176	3.6415982837
c	3.2877428088	0.3444424215	2.2089367933
c	3.0225454458	1.7126030424	2.4154707123
c	4.0767377782	2.6386869199	2.4863710229
c	5.4082698300	2.2104912860	2.3544379161
c	5.6813918766	0.8484317998	2.1410378450
c	4.6276297181	-0.0763426114	2.0649864569
c	1.5541634499	-1.8530862227	-2.3155486434
c	2.1199611984	-0.6878132902	-1.7025175301
c	0.9199710273	-0.9853951980	-3.4387643176
c	1.8244667646	-0.8903005525	-4.6700160582
o	3.0151350318	-0.6389505672	-4.6540169963
o	1.1190467311	-1.1293713380	-5.8042559389
c	1.8765425228	-1.0786396289	-7.0245343490
h	2.3584119316	-1.3836925800	1.3348055847
h	2.4888843947	-2.4971656383	3.4732786478
h	2.4040588027	-0.9335161141	4.3831778958
h	-1.5006031937	-1.5513836994	4.7736900523
h	-3.9896550811	-1.3243393891	5.0151944124
h	-5.3167406938	-0.2706686827	3.1490424343
h	-4.1730878522	0.4813275081	1.0841553275
h	-3.2069212636	2.7376862223	-0.8484956249
h	-5.1562669156	2.7462888082	-2.4039812258
h	-5.9731762151	0.6014673008	-3.4184118862
h	-4.8191366002	-1.5600643763	-2.8606246861
h	-2.8485506210	-1.5720598005	-1.3129730135
h	-1.3374040655	2.2472032092	2.5498961292
h	-0.6240143278	4.6153340173	2.8601946341
h	0.1866962963	5.9600557594	0.9007529023
h	0.2761085928	4.9054177260	-1.3776073734
h	-0.4288641836	2.5336358746	-1.6872218524

h	4.8492568468	-1.1416963167	1.8867155155
h	6.7209810358	0.5045011734	2.0261246723
h	6.2330537326	2.9376587885	2.4100052275
h	3.8541492366	3.7059481371	2.6413381632
h	1.9765924210	2.0426181225	2.5006127569
h	1.8251141440	-2.9179209072	-2.3020358469
h	-0.1229521953	-1.1880680494	-3.7535925842
h	1.1666844886	1.2438065055	-2.5504984817
h	2.9315002749	-0.4999063417	-0.9865934671
h	1.1617498783	-1.2981098706	-7.8371569228
h	2.3287491163	-0.0764963136	-7.1664665697
h	2.6927077801	-1.8289034674	-7.0130135818

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cl	-0.8940265972	-2.7180496059	-0.3208976854
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c	0.3677369996	-0.6691632994	-2.9042473183
c	-0.7808431453	0.9231029116	-2.3998010855
c	4.6461032836	-0.6412168971	-1.6190850217
c	3.8055449412	-0.3392593260	-0.5273543594
c	3.8398438562	0.9592511598	0.0205923719
c	4.7025309222	1.9327352865	-0.5098618501
c	5.5437999359	1.6208361960	-1.5917969478
c	5.5128450648	0.3299781954	-2.1461311943
c	2.9206649519	-1.4196759005	0.0674768011
n	1.7212914461	-0.9162840903	0.7557784315
c	1.5922471150	-1.5860856894	1.8556228831
o	2.5891047664	-2.4704204967	2.1582388685
c	3.6196424313	-2.2785680826	1.1624294615
c	0.4759380458	-1.5380199779	2.8206616714
c	-0.6932900375	-0.7385071544	2.6451821771
c	-1.7074410866	-0.8118231491	3.6215334148
c	-1.5875250088	-1.6367427738	4.7518206612
c	-0.4354178314	-2.4151680693	4.9248871426
c	0.5819285193	-2.3632887485	3.9647395815
p	-0.9364918136	0.4069776146	1.1974514664
c	-0.1953072143	1.9969593718	1.8024151041
c	-0.0493158876	2.3056666443	3.1726471517
c	0.5067358344	3.5340046717	3.5686200996
c	0.9200632393	4.4684623419	2.6042263643
c	0.7811082795	4.1679135704	1.2383575250
c	0.2359177412	2.9365560027	0.8407817256
c	0.6344089292	0.6866793890	-2.4698200538
c	-1.0782581155	-0.2848550883	-3.3276747958
c	-1.1724398975	0.1234767498	-4.7990526859
o	-2.2355979324	-0.4729594040	-5.3972549938
c	-2.4157500543	-0.1646995069	-6.7883514378
c	-2.7593736310	0.7181200110	1.2002357456

c	-3.3466857852	1.9246758010	1.6348356752
c	-4.7393596719	2.1014409388	1.5482127895
c	-5.5506520738	1.0761828892	1.0359331410
c	-4.9668964102	-0.1284846031	0.6020057308
c	-3.5774355598	-0.3097811965	0.6722035812
o	-0.4096691584	0.8769940526	-5.3767680093
h	2.5625469358	-2.0770452467	-0.7578741605
h	3.9567115638	-3.2714494110	0.8101871098
h	4.4718488402	-1.7438073377	1.6344542280
h	1.4837565399	-2.9787884034	4.0805326928
h	-0.3285439260	-3.0701845911	5.8027396434
h	-2.4016887673	-1.6685918131	5.4921531391
h	-2.6215194168	-0.2144447402	3.4911986626
h	-2.7169181399	2.7309135531	2.0404506852
h	-5.1899380239	3.0480251394	1.8851018880
h	-6.6408025560	1.2166570958	0.9703265183
h	-5.5989187228	-0.9333770445	0.1958733054
h	-3.1089756609	-1.2460858651	0.3187473013
h	-0.3685733161	1.5818475435	3.9374108891
h	0.6185810345	3.7603675249	4.6404120443
h	1.3556552094	5.4297343119	2.9177523333
h	1.1083448084	4.8916158889	0.4760259930
h	0.1501266216	2.6897909876	-0.2282365682
h	4.6157604761	-1.6477390780	-2.0677457560
h	6.1606650354	0.0800808685	-3.0005542968
h	6.2179973071	2.3852600400	-2.0077183927
h	4.7141570866	2.9446551823	-0.0759706520
h	3.1668361372	1.2044019386	0.8562085435
h	1.0153927482	-1.4719000198	-3.2850471918
h	-1.9072777277	-0.9689083487	-3.0637363320
h	-1.3814519067	1.8260240437	-2.2102772106
h	1.5373518981	1.2910544121	-2.3143455332
h	-3.3070650280	-0.7300009087	-7.1138782345
h	-2.5729492181	0.9230614556	-6.9349695177
h	-1.5278669202	-0.4689159604	-7.3784726403

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cl	-1.1438630999	-2.4808882785	-0.4844250738
pd	0.0451698859	-0.2091303216	-0.7138420495
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c	-0.9501620786	0.7666852477	-2.2920361982
c	4.5030258628	-0.7014406733	-1.8345787285
c	3.6922284221	-0.4233362950	-0.7153170797
c	3.7343813472	0.8651688967	-0.1444302098
c	4.5740594096	1.8535419677	-0.6829980573
c	5.3847668167	1.5661535794	-1.7949320153
c	5.3473112612	0.2852849449	-2.3702374128

c	2.8455732643	-1.5274348974	-0.1058086349
n	1.6014213287	-1.0601947165	0.5370881839
c	1.5054612096	-1.6197659151	1.7072277816
o	2.5573789978	-2.3995489869	2.0778986861
c	3.5613501677	-2.2934118437	1.0441226311
c	0.4002304739	-1.5673714484	2.6883907420
c	-0.7180628755	-0.6850743390	2.6095453630
c	-1.7124568527	-0.7645007525	3.6043110463
c	-1.6258057240	-1.6825204132	4.6630533865
c	-0.5220040187	-2.5418644054	4.7459057336
c	0.4788653948	-2.4785389542	3.7696321377
p	-0.9124310218	0.5698883548	1.2559747243
c	-0.2102940859	2.1162967314	1.9997205044
c	0.1456509794	2.2403050778	3.3599986753
c	0.6978050882	3.4397082669	3.8436066343
c	0.8920479739	4.5296672135	2.9797600317
c	0.5407503123	4.4144664928	1.6224902407
c	0.0054277490	3.2133569248	1.1336811115
c	0.4715686160	1.0564444296	-2.3668371655
c	-0.7927411456	-0.4587631622	-3.2361279542
c	-1.0162364149	-0.0966644324	-4.7023385650
o	-1.8475139856	-0.9904391671	-5.2995019812
c	-2.1322373097	-0.7388607415	-6.6832583569
c	-2.7322291762	0.8805247426	1.1906547684
c	-3.3326548770	2.0449804710	1.7160108277
c	-4.7207394238	2.2351561477	1.5976861961
c	-5.5139351213	1.2657308143	0.9624337946
c	-4.9157702720	0.1046228696	0.4399596423
c	-3.5299609224	-0.0929423693	0.5429109408
o	-0.5333656860	0.8599792596	-5.2836371821
h	2.5405858058	-2.2298359309	-0.9124732063
h	3.8877406463	-3.3135969983	0.7662636562
h	4.4246402225	-1.7289247335	1.4540520219
h	1.3404098345	-3.1566218072	3.8217310111
h	-0.4398864468	-3.2706629733	5.5663139245
h	-2.4261202218	-1.7241234736	5.4177476265
h	-2.5853364791	-0.0978546692	3.5406922954
h	-2.7175355153	2.8077964859	2.2168339313
h	-5.1817944400	3.1477332047	2.0065599384
h	-6.6010186319	1.4164506026	0.8718524386
h	-5.5334177764	-0.6568756853	-0.0611806248
h	-3.0488711162	-0.9998298169	0.1268514093
h	-0.0083447860	1.3958699985	4.0478796904
h	0.9751375557	3.5207860401	4.9061236917
h	1.3221250287	5.4683285903	3.3617471096
h	0.6943439153	5.2625105297	0.9374515379
h	-0.2451802516	3.1180355900	0.0654366578
h	4.4688534229	-1.7016880679	-2.2968568232
h	5.9722485167	0.0543579520	-3.2465982665
h	6.0405374383	2.3429184125	-2.2171893990
h	4.5915400356	2.8578060509	-0.2321678077
h	3.0885258688	1.0964792236	0.7164272568
h	1.5862118466	-0.8308416274	-3.1514045030
h	-1.3218196703	-1.3913672818	-2.9593708673
h	-1.8296531931	1.4106989971	-2.1331140026

h	1.1017036703	1.9487427188	-2.2634074224
h	-2.8172194215	-1.5430432984	-7.0061906366
h	-2.6105619695	0.2527758736	-6.8155503292
h	-1.2031989537	-0.7563042992	-7.2882881528

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pd	-0.1148603515	-0.1715016099	-0.5684743390
c	-1.1016361280	0.8950259917	-2.8935407919
c	-0.1656791799	-2.6949634793	1.9673586235
c	-0.1796917103	-1.4600835522	2.6491351574
c	-0.0157701496	-1.4308610208	4.0533667019
c	0.1437151415	-2.6273563845	4.7686572381
c	0.1465995904	-3.8593355914	4.0889952017
c	-0.0049475794	-3.8892227463	2.6937457293
p	-0.4133297623	0.0986678043	1.6705816930
c	-2.0124644695	0.7943337147	2.2658298925
c	-2.3771435826	2.1037282049	1.8689748307
c	-3.6320392901	2.6292199023	2.2102678329
c	-4.5523257811	1.8481163737	2.9316607185
c	-4.2076526248	0.5404262001	3.3099856626
c	-2.9465276828	0.0137801502	2.9818565471
c	-1.3589953296	1.4512331922	-1.6452850718
c	-2.0442445843	0.2335957693	-1.1830445832
c	-2.0571616443	-0.2860766154	-2.6622224988
c	-3.4022130756	-0.0709010299	-3.3446498717
o	-4.1907831100	0.8272377004	-3.1040939194
cl	0.1304022485	-2.4883654678	-1.5999197325
n	2.0034926493	-0.1400743337	-0.1908157630
c	2.9371622897	-0.8056246878	-1.1447607080
c	4.2400426590	-0.8923740107	-0.3166767986
o	4.0248997859	0.0156082786	0.8002213615
c	2.6958267786	0.3001330888	0.8182227599
c	3.0383441193	-0.0252858527	-2.4508632505
c	2.3815893055	-0.5094628696	-3.6005931215
c	2.4730262419	0.1896797797	-4.8162793553
c	3.2088523737	1.3841351885	-4.8938938535
c	3.8526693868	1.8818091738	-3.7472620766
c	3.7676430135	1.1804357883	-2.5340159139
c	2.2408122447	1.1380856579	1.9478796028
c	0.8855594876	1.2111536281	2.3941855209
c	0.5726819672	2.0998080285	3.4456337050
c	1.5572573188	2.8920392184	4.0564534746
c	2.8923613367	2.7953921968	3.6353649020
c	3.2272108241	1.9196741012	2.5959418425
o	-3.6267568794	-1.0282110751	-4.2837626772
c	-4.8671280472	-0.9152569681	-4.9953701322

h	2.4997467085	-1.8030098909	-1.3635938661
h	4.4114937119	-1.9047842190	0.1042334687
h	5.1451360625	-0.5643727051	-0.8613774147
h	4.2682603462	1.8363044796	2.2556809715
h	3.6753631045	3.4021022639	4.1144052846
h	1.2781791523	3.5746323293	4.8738252395
h	-0.4662070907	2.1662115416	3.8004529735
h	-0.0102293618	-0.4707080255	4.5922627506
h	0.2706435301	-2.5974498268	5.8619645378
h	0.2743985258	-4.7971449189	4.6519064739
h	0.0071884281	-4.8488016098	2.1541226942
h	-0.2549855013	-2.7234085494	0.8647404129
h	-1.6693578108	2.7184423601	1.2909075814
h	-3.8974503862	3.6512511815	1.8994947620
h	-5.5409428710	2.2567492777	3.1906096458
h	-4.9254639955	-0.0806297934	3.8677816875
h	-2.6881402304	-1.0118240711	3.2832782054
h	1.7788487901	-1.4287369328	-3.5169176376
h	1.9628747771	-0.2030074378	-5.7097986777
h	3.2805344626	1.9299641288	-5.8475014853
h	4.4263135251	2.8202282132	-3.7987796291
h	4.2754345145	1.5823635269	-1.6420271112
h	-0.5449091833	1.2281362251	-3.7815064308
h	-1.6745704011	-1.3097638856	-2.8435763363
h	-2.8809039509	0.1463630325	-0.4699240818
h	-1.1623115759	2.4393186080	-1.2059761425
h	-4.8982046775	-1.7701528425	-5.6944137008
h	-5.7286085011	-0.9550632040	-4.2984511014
h	-4.9197369452	0.0414985589	-5.5539050448

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pd	0.2316236616	-0.3229772197	-0.9143422867
c	-2.5601963433	-0.0418374347	-3.4135876817
c	-1.6684971781	-2.2654018401	1.5876086868
c	-0.7122544732	-1.3816927394	2.1407251551
c	-0.0830702166	-1.7217017811	3.3589124565
c	-0.4073054303	-2.9220137965	4.0139193388
c	-1.3666948748	-3.7892557463	3.4680505154
c	-1.9971647853	-3.4538211153	2.2578199285
p	-0.3035131960	0.1694800639	1.2049166406
c	-1.7123944793	1.3205030073	1.5436534149
c	-1.7031550937	2.5704476111	0.8841866354
c	-2.7392267538	3.4911730187	1.0987676878
c	-3.8043663655	3.1669037993	1.9586823209
c	-3.8265611163	1.9202692197	2.6042825633
c	-2.7839337104	0.9981402764	2.4015812529
c	-1.9604727671	0.8225107439	-2.5561505265

c	-1.7682617915	-0.2046905109	-1.4656251424
c	-2.4017715831	-1.2336700400	-2.4807936989
c	-3.6132793651	-2.0077287660	-2.0280257106
o	-3.7905436228	-2.4684379469	-0.9085274711
cl	0.7512587058	-1.5203370175	-2.9292103425
n	2.3448792547	-0.1518232354	-0.4326637921
c	3.4071827262	-0.4068791346	-1.4636422387
c	4.5835243472	-0.8427827370	-0.5799821817
o	4.2971524482	-0.2140786706	0.7017851346
c	2.9597674697	0.0496433738	0.6975744238
c	3.6552715919	0.8596984506	-2.2852204971
c	3.0664469278	0.9979900617	-3.5591400574
c	3.2888507102	2.1549505021	-4.3246000440
c	4.0952992665	3.1921040405	-3.8277826175
c	4.6783852735	3.0678283865	-2.5551420850
c	4.4595143089	1.9112321320	-1.7899089503
c	2.4455517327	0.6611434616	1.9413263465
c	1.0674950555	0.8975887388	2.2214027396
c	0.7290754539	1.6290617898	3.3803413018
c	1.7080788099	2.1018382445	4.2670092677
c	3.0612266928	1.8314647039	4.0131025590
c	3.4211418111	1.1181938675	2.8645393148
o	-4.5088665348	-2.1808244630	-3.0365073437
c	-5.6695282756	-2.9574640862	-2.7109735495
h	3.0397012111	-1.2107277633	-2.1312678928
h	4.6103768721	-1.9415905983	-0.4196999489
h	5.5728290709	-0.4906898745	-0.9239866981
h	4.4786728794	0.9191211298	2.6481433984
h	3.8415286620	2.1825376131	4.7050234339
h	1.4079667356	2.6693077100	5.1609835946
h	-0.3314849550	1.8206406448	3.5986990008
h	0.6689456666	-1.0544075268	3.8038562937
h	0.0975810568	-3.1775818516	4.9585360548
h	-1.6188754223	-4.7291837126	3.9832312018
h	-2.7491094818	-4.1222390696	1.8120053146
h	-2.1754418833	-2.0505183178	0.6328808744
h	-0.8809513621	2.8152901069	0.1926281343
h	-2.7215145672	4.4633116853	0.5826239479
h	-4.6228652335	3.8855353268	2.1180517219
h	-4.6623319392	1.6572912816	3.2707651684
h	-2.8077864872	0.0217958368	2.9079001173
h	2.4091091418	0.1945492337	-3.9278884002
h	2.8235019489	2.2450160573	-5.3184853157
h	4.2684136855	4.0977649213	-4.4296995843
h	5.3096940009	3.8763015398	-2.1546036078
h	4.9213116283	1.8342719516	-0.7929720361
h	-2.9945404280	0.0472617172	-4.4210232727
h	-1.6339672453	-1.9564366550	-2.8433720808
h	-2.4141165837	-0.0464642511	-0.5777695871
h	-1.6952556841	1.8892044989	-2.6200144905
h	-6.2865568533	-2.9845105702	-3.6270211864
h	-5.3872737533	-3.9861925104	-2.4075687781
h	-6.2365630411	-2.4947070574	-1.8780722866

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c	-2.9936060245	-0.0957403222	-2.7623787855
c	-1.4483036253	0.7939877561	-1.5148536204
c	3.0332044258	-0.7780924362	3.3921623188
c	2.1278437886	-0.6084155238	2.3144665851
c	0.9477063266	0.1654633841	2.5219569006
c	0.7630032344	0.7974965470	3.7701661448
c	1.6878479936	0.6486631550	4.8149743668
c	2.8188783669	-0.1595184524	4.6289890516
c	2.5517021432	-1.1693528160	1.0127217511
n	2.1392466862	-0.8598925827	-0.1841229510
c	3.1636721526	-1.3899170004	-1.1470596754
c	3.8427229060	-2.4696134473	-0.2938277861
o	3.6142848186	-2.0164591634	1.0727898368
pd	0.2415879291	-0.0382439356	-0.8684417504
cl	0.5816427417	-0.8651381636	-3.0807803126
c	4.0814921609	-0.2558113459	-1.6053229477
c	3.8392653639	0.3882825081	-2.8364741578
c	4.6699148054	1.4356783183	-3.2673292076
c	5.7495685417	1.8584036151	-2.4750087351
c	5.9938760445	1.2283214077	-1.2431170096
c	5.1659577291	0.1800599510	-0.8115264806
p	-0.4086813935	0.2638794618	1.2631542187
c	-1.2934496305	1.8254920701	1.7041231136
c	-0.7056068790	3.0461626521	1.3018220892
c	-1.3318727885	4.2638231761	1.6039354917
c	-2.5587202402	4.2752260707	2.2923388730
c	-3.1559563453	3.0646884413	2.6777961542
c	-2.5266297321	1.8406578283	2.3878887415
c	-4.3358081851	-0.6052379985	-2.4345187378
o	-5.3259840932	0.2845541439	-2.7664083863
c	-6.6583627519	-0.1503794500	-2.4868587614
c	-1.5545375594	-1.1040665699	1.7728908456
c	-2.4120423173	-1.6567157273	0.7951469323
c	-3.3308998439	-2.6606893205	1.1398594377
c	-3.3869793275	-3.1408680228	2.4585854067
c	-2.5251614819	-2.6091537914	3.4336001202
c	-1.6150754797	-1.5930004427	3.0974509591
c	-1.5308406884	1.6033852848	-2.7081335549
c	-2.6941213603	1.1972326452	-3.3313347769
o	-4.5803924525	-1.6816388528	-1.8948746340
h	2.6206645426	-1.7983797224	-2.0217146392
h	3.3615335770	-3.4645233370	-0.4037324997
h	4.9328766580	-2.5625365586	-0.4485078737
h	3.9306139392	-1.3892823950	3.2301895256
h	3.5458992946	-0.3002942627	5.4429869775
h	1.5138568466	1.1559624781	5.7760624236
h	-0.1337068206	1.4146663430	3.9289566716

h	-0.9465863561	-1.1903015973	3.8725660310
h	-2.5573928705	-2.9879065883	4.4670160202
h	-4.0998530632	-3.9356297128	2.7280165583
h	-3.9946878373	-3.0494500474	0.3536545284
h	-2.3720055457	-1.3127464849	-0.2481050146
h	0.2406246715	3.0369206518	0.7374030584
h	-0.8665127080	5.2099404878	1.2878529118
h	-3.0543279918	5.2316845771	2.5188826088
h	-4.1218120194	3.0677179209	3.2059312925
h	-3.0000253814	0.8946271881	2.6908773111
h	2.9726357114	0.0715163160	-3.4388193897
h	4.4680168074	1.9262772667	-4.2322069522
h	6.4002096385	2.6793317447	-2.8145276270
h	6.8364467014	1.5533685570	-0.6129286288
h	5.3714844626	-0.2979393415	0.1592684630
h	-3.3063525577	1.7353301688	-4.0749010327
h	-2.2294637115	-0.8850972582	-2.8527661570
h	-2.2653296747	0.9374058145	-0.7875463926
h	-0.7606899514	2.3078514882	-3.0617904282
h	-7.3249143123	0.6725800186	-2.8036621410
h	-6.9053653532	-1.0777290997	-3.0445117174
h	-6.7931772621	-0.3583088563	-1.4051774260

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c	-4.5525824369	-1.1077105976	-1.5362397318
c	-1.5165302211	-1.2016907334	-0.9275675226
c	3.3553637454	-0.7464329051	3.6036520047
c	2.5075979333	-0.5229516043	2.4919245294
c	1.1593559077	-0.1109503145	2.7159452259
c	0.7200210590	0.0538990477	4.0465440350
c	1.5721031197	-0.1757428557	5.1390651662
c	2.8962238749	-0.5782360988	4.9155054863
c	3.0990340710	-0.7286136886	1.1533602729
n	2.4976439183	-0.8213536898	0.0052241585
c	3.5479985144	-0.8972829524	-1.0569030515
c	4.7990246366	-1.2502593250	-0.2290399666
o	4.4531926107	-0.8438548576	1.1266784394
pd	0.4102650307	-1.0206101554	-0.4901522939
cl	0.9320748949	-2.3871873482	-2.3521551549
c	3.6218495711	0.4082487942	-1.8434963477
c	2.9918364487	0.4954314207	-3.1023875140
c	3.0532943276	1.6849993414	-3.8468542924
c	3.7384307518	2.8024893293	-3.3414082436
c	4.3578048468	2.7280383016	-2.0818419597
c	4.2985664780	1.5391295352	-1.3371836073
p	-0.0414202915	0.2256040525	1.3338728043
c	0.0890747285	2.0440003788	1.0323814228

c	-0.3972728220	2.5336537509	-0.2008953170
c	-0.3559908953	3.9091164122	-0.4772291137
c	0.1844298326	4.8031654258	0.4631998477
c	0.6811120254	4.3190717798	1.6849455256
c	0.6327358669	2.9447384171	1.9729902394
c	-5.9739464377	-1.2040378892	-1.9050433951
o	-6.1899115151	-1.1214792697	-3.2575449819
c	-7.5580638526	-1.2059934499	-3.6590990762
c	-1.6811992169	-0.0023370366	2.1495869491
c	-2.5815356226	1.0619458332	2.3583427505
c	-3.8390111669	0.8177176895	2.9382992567
c	-4.2048913145	-0.4843448752	3.3138362783
c	-3.3110871696	-1.5501678943	3.1051067088
c	-2.0590644682	-1.3144323035	2.5187454070
c	-2.0958914767	-0.8667127785	-2.1155554816
c	-3.5224148875	-0.9507922783	-2.4185478322
o	-6.8913406568	-1.3399605949	-1.1041474760
h	3.2450608715	-1.7132938155	-1.7428647628
h	5.0022622509	-2.3416518364	-0.2115661994
h	5.7149148126	-0.7088277943	-0.5288336836
h	4.3895015950	-1.0641237263	3.4154929414
h	3.5742054297	-0.7669552870	5.7613358627
h	1.1934401160	-0.0404859440	6.1635763436
h	-0.3190207926	0.3629052100	4.2322727123
h	-1.3701191401	-2.1557241710	2.3386920264
h	-3.5971172585	-2.5748468376	3.3871517485
h	-5.1933446535	-0.6729927773	3.7593979090
h	-4.5387731929	1.6535965096	3.0908447053
h	-2.3046648808	2.0848774891	2.0631299799
h	-0.8033800529	1.8279136382	-0.9427944757
h	-0.7391759572	4.2818601295	-1.4392381977
h	0.2247542435	5.8804991131	0.2402987610
h	1.1118914562	5.0148892290	2.4213251412
h	1.0251649130	2.5754670720	2.9323868060
h	2.4338311502	-0.3778342271	-3.4769428122
h	2.5610896558	1.7367740807	-4.8303472003
h	3.7892219427	3.7332897186	-3.9273403295
h	4.8916334181	3.6012865232	-1.6759165457
h	4.7846867387	1.4990987756	-0.3490417325
h	-3.7937364313	-0.8646020235	-3.4847849679
h	-4.3803135987	-1.1642645995	-0.4501854516
h	-2.1614511930	-1.6030331237	-0.1209913819
h	-1.4510908419	-0.5405829652	-2.9491099661
h	-7.5616827775	-1.1233671991	-4.7614677056
h	-8.0100860047	-2.1700561618	-3.3466060047
h	-8.1607214540	-0.3883021729	-3.2119626585