

Supporting Information for the Paper

Catalytic Antioxidants – Regenerable Tellurium Analogues of Vitamin E

Vijay P. Singh, Jia-fei Poon and Lars Engman*

Uppsala University, Department of Chemistry – BMC, Box 576, SE-751 23 Uppsala,
Sweden

p S2-S7 Experimental section

p S8 -S22 ^1H , ^{13}C and ^{125}Te NMR spectra for compounds prepared

Experimental Section

(+)- δ -Tocopherol $\geq 90\%$ was purchased and used as received. ^1H and ^{13}C NMR spectra were recorded on 300 MHz (^1H : 300 MHz; ^{13}C : 75 MHz) and 400 MHz (^1H : 399.97 MHz; ^{13}C : 100.58 MHz) spectrometers, using the residual solvent peaks of CDCl_3 (^1H : δ 7.26; ^{13}C : δ 77.0) as an indirect reference to TMS. ^{125}Te NMR spectra were recorded on 400 MHz (^{125}Te : 126.2 MHz) using Ph_2Te_2 as an external standard. Flash column chromatography was performed using silica gel (0.04-0.06 mm). The high resolution mass spectra (HRMS) were obtained using a time of flight instrument equipped with electrospray ionization. Tetrahydrofuran was dried in a solvent purification system by passing it through an activated alumina column before use. Di-*n*-octyl ditelluride¹ was prepared according to literature methods.

5-Bromo- δ -tocopherol (5a). To a solution of δ -Tocopherol (3.50 g, 8.69 mmol) in dichloromethane (50 mL) was added dropwise Bu_4NBr_3 (4.19 g, 8.69 mmol) in dichloromethane (10 mL). After stirring for 1 h, the solution was evaporated and the residue was purified by column chromatography (pentane/diethyl ether = 98:2) to give the title compound as a light red, dense liquid (4.10 g, 98%). ^1H and ^{13}C NMR data were in accord with reported data in the literature.²

THP-protected 5-bromo- δ -tocopherol (5b). To a solution of 5-bromo- δ -tocopherol (4.0 g, 8.31 mmol) and 3,4-dihydro-2*H*-pyran (3.03 mL, 33.2 mmol) was added 1 drop of conc. HCl at room temperature. After stirring for two days, the solution was quenched with a saturated sodium hydrogen carbonate solution (10 mL) and extracted

with dichloromethane (10 mL x 3). The organic phase was dried over sodium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 99:1) to give the title compound as a yellow oil. Yield: 4.35 g (93%). ^1H NMR (CDCl_3): δ 6.88 (s, 1H), 5.33 (quartet, $J = 4.0$ Hz, 1H), 4.01 (m, 1H), 3.61 (d, $J = 11.3$ Hz, 1H), 2.72 (t, $J = 7.0$ Hz, 2H), 2.12 (s, 3H), 0.85-1.99 (several peaks, 44H). ^{13}C NMR (CDCl_3): δ 147.9, 147.8, 146.1 (2C) 125.8, 121.3, 117.8 (2C), 113.0 (2C), 97.9, 97.8, 75.5, 61.9 (2C), 39.7, 39.6, 39.4, 37.4 (2C), 32.8, 32.7 (2C), 31.4, 31.3, 30.4, 28.0, 25.4, 24.8, 24.4, 24.2, 23.8, 23.7, 22.7, 22.6, 21.0, 19.7, 19.6, 18.6, 16.2. HRMS (TOF MS ES^+) m/z calcd for $\text{C}_{32}\text{H}_{53}\text{O}_3\text{Br}$ $[\text{M}+\text{Na}]^+$: 587.3076. Found: 587.3105.

THP-protected 5-(*n*-octyltelluro)- δ -tocopherol (6a). To a solution of THP-protected 5-bromo- δ -tocopherol **5b** (2.50 g, 4.41 mmol) in anhydrous THF (30 mL) was added *tert*-BuLi ((1.7 M, 5.20 mL, 8.82 mmol)) under nitrogen at -78°C . The solution was stirred for 1.5 h at -78°C before the addition of dioctyl ditelluride (3.19 g, 6.62 mmol). After stirring at ambient temperature for overnight, the solution was quenched with a saturated ammonium chloride solution (40 mL) and extracted with ether (50 mL x 3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography using pentane/diethyl ether = 98:2 as eluent to give the title compound as a light brown viscous oil (1.60 g, 50%). ^1H NMR (CDCl_3): δ 6.84 (s, 1H), 5.34 (quintet, $J = 3.2$ Hz, 1H), 4.00 (t, $J = 10.2$ Hz, 1H), 3.61 (m, 1H), 2.80-2.91 (several peaks, 5H), 2.17 (s, 3H), 1.03-2.11 (several peaks, 43H), 0.84-0.90 (several peaks, 15H). ^{13}C NMR (CDCl_3): 151.8, 151.7, 147.2, 147.1, 127.9, 126.5, 115.5,

115.4, 104.9, 104.8, 97.6, 97.5, 75.2, 61.9, 40.0, 39.8, 39.4, 37.5, 37.4, 37.3, 32.8, 32.7, 32.4 (2C), 31.9, 31.8, 30.8, 29.7, 29.2, 28.9, 27.9, 25.4, 24.8, 24.4, 24.0, 23.9, 22.7, 22.6, 21.0, 19.7, 19.6, 19.0, 16.5, 14.1, 7.8. ^{125}Te NMR (CDCl_3) δ 201.0, 201.4. HRMS (TOF MS ES^+) m/z calcd for $\text{C}_{40}\text{H}_{70}\text{O}_3\text{Te}$ $[\text{M}+\text{Na}]^+$: 751.4285. Found: 751.4322.

5-(*n*-Octyltelluro)- δ -tocopherol (6b). To a solution of compound **6a** (0.80 g, 1.10 mmol) in dichloromethane (25 mL) was added trifluoroacetic acid (0.063 g, 0.042 mL, 0.55 mmol) at room temperature. After stirring for 2.5 h, the solution was quenched with a saturated NaHCO_3 solution (10 mL) and extracted with dichloromethane (10 mL x 3). The organic layer was dried over sodium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/diethyl ether = 99.7: 0.3) to give the title compound as a pale yellow liquid (0.450 g, 64%). $[\alpha]_{\text{D}}^{21} = +15.5^\circ$ ($c = 0.04$, CHCl_3). ^1H NMR (CDCl_3): δ 6.82 (s, 1H), 6.10 (s, 1H), 2.85 (sextet, $J = 3.6$ Hz, 2H), 2.59 (t, $J = 7.2$ Hz, 2H), 2.18 (s, 3H), 1.75-1.83 (several peaks, 2H), 1.66 (quintet, $J = 6.8$ Hz, 2H), 0.84-1.57 (several peaks, 49H). ^{13}C NMR (CDCl_3): δ 150.9, 145.6, 130.6, 125.9, 112.9, 102.5, 75.1, 39.7, 39.4, 37.5 (2C), 37.4, 37.3, 32.8, 32.7, 32.5, 31.8 (2C), 31.7, 29.8, 29.1, 28.8, 28.0, 24.8, 24.5, 23.9, 22.7, 22.6, 21.0, 19.7, 19.6, 16.4, 14.1, 9.0. ^{125}Te NMR (CDCl_3) δ -5.9. HRMS (TOF MS ES^+) m/z calcd for $\text{C}_{35}\text{H}_{62}\text{O}_2\text{Te}$ $[\text{M}-\text{H}]^+$: 643.3734; found: 643.3697.

THP-protected β -Tocopherol. THP-protected 5-bromo- δ -tocopherol **5b** (3.40 g, 6.00 mmol) in THF (60 mL) was lithiated with *tert*-BuLi (1.7 M, 7.0 mL, 12.00 mmol) following the procedure for **6a**. Then, instead of dioctyl ditelluride, methyl iodide

(0.56 g, 9.00 mmol) was added. After stirring and workup as described for **6a**, the mixture was purified by column chromatography (pentane/ethyl acetate = 98.5:1.5) to give the title compound as a pale yellow oil (2.71 g, 90%). ¹H NMR (CDCl₃): δ 6.79 (s, 1H), 5.23 (m, 1H), 3.98 (m, 1H), 3.60 (m, 1H), 2.61 (t, *J* = 6.0 Hz, 2H), 1.05-2.14 (several peaks, 38H), 0.84-0.92 (several peaks, 12H). ¹³C NMR (CDCl₃): δ. 147.4, 146.9, 123.4, 123.2, 120.1, 116.2, 116.1, 97.7 (2C), 74.5, 62.2, 39.9, 39.8, 39.4, 37.4, 37.3, 32.8, 32.7, 31.8, 28.0, 25.4, 24.8, 24.4, 24.0, 23.9, 22.7, 22.6, 22.3, 21.0, 20.8, 19.7, 19.6, 19.2, 16.2, 14.0, 11.3.

β-Tocopherol. To a solution of THP-protected β-tocopherol (1.8 g, 3.59 mmol) in dichloromethane/methanol (40 mL, 1:1) was added *p*-toluenesulfonic acid monohydrate (112.5 mg, 0.59 mmol) at room temperature. After stirring for overnight, the solution was quenched with a saturated NaHCO₃ solution (40 mL) and extracted with dichloromethane (50 mL x 3). The organic layer was dried over sodium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 98:2) to give the title compound as a pale yellow liquid (1.29 g, 86%). As determined by ¹H and ¹³C NMR, the material was identical to a sample of β-tocopherol prepared according to literature methods.³

7-Bromo-β-tocopherol (7a). β-Tocopherol (2.192 g, 5.26 mmol) in dichloromethane (60 mL) and Bu₄NBr₃ (2.52 g) in dichloromethane (120 mL) were reacted as described for the preparation of compound **5a**. The residue was purified by flash column chromatography (pentane/ethyl acetate = 99:1) to give the title compound as a colourless liquid (2.17 g, 83%). As determined by ¹H and ¹³C NMR, the material was

identical to a sample of 7-bromo- β -tocopherol prepared according to literature methods.²

7-(*n*-Octyltelluro)- β -tocopherol (7b). To a solution of 7-bromo- β -tocopherol **7a** (0.74 g, 1.50 mmol) in anhydrous THF (15 mL) was added *tert*-BuLi (1.7 M, 2.64 mL, 4.5 mmol) under nitrogen at -78 °C. The solution was stirred for 1.5 h at -78 °C before the addition of dioctyl ditelluride (1.09 g, 2.25 mmol). After stirring at ambient temperature for overnight, the solution was quenched with a saturated ammonium chloride solution (25 mL) and extracted with ether (40 mL x 3). The residue was purified by column chromatography (pentane/ethyl acetate = 99:1) to give the title compound as a yellow oil (0.29 g, 30%). $[\alpha]_D^{21} = -10.6^\circ$ ($c = 0.014$, CHCl₃). ¹H NMR (CDCl₃): δ 6.30 (s, 1H), 2.67 (t, $J = 6.8$ Hz, 2H), 2.61 (t, $J = 8.0$ Hz, 2H), 2.48 (s, 3H), 2.18 (s, 3H), 0.84-1.82 (several peaks, 53H). ¹³C NMR (CDCl₃): δ . 148.4, 144.7, 129.6, 123.1, 117.5, 105.8, 74.9, 39.7, 39.4, 37.4, 37.3, 34.1, 32.8, 32.7, 31.8 (2C), 31.6, 31.5, 29.1, 28.8, 28.0, 24.8, 24.4, 23.8, 22.7, 22.6, 22.3, 22.2, 21.0, 20.9, 19.7, 19.6, 14.1, 12.8, 9.3. ¹²⁵Te NMR (CDCl₃) δ 27.4. Anal. Calcd for C₃₆H₆₄O₂Te: C, 65.86; H, 9.83. Found: C, 65.80; H, 9.80.

HPLC Peroxidation Assay. The experimental setup for recording inhibition times (T_{inh}) and inhibited rates of peroxidation (R_{inh}) during azo-initiated peroxidation of linoleic acid in a two-phase system was recently described.⁴ The values reported in Table 1 for reactions performed in the presence of NAC and in the absence of NAC are means \pm SD based on triplicates. We have found that R_{inh} and T_{inh} values show slight variations depending on the amount of linoleic acid hydroperoxide which is

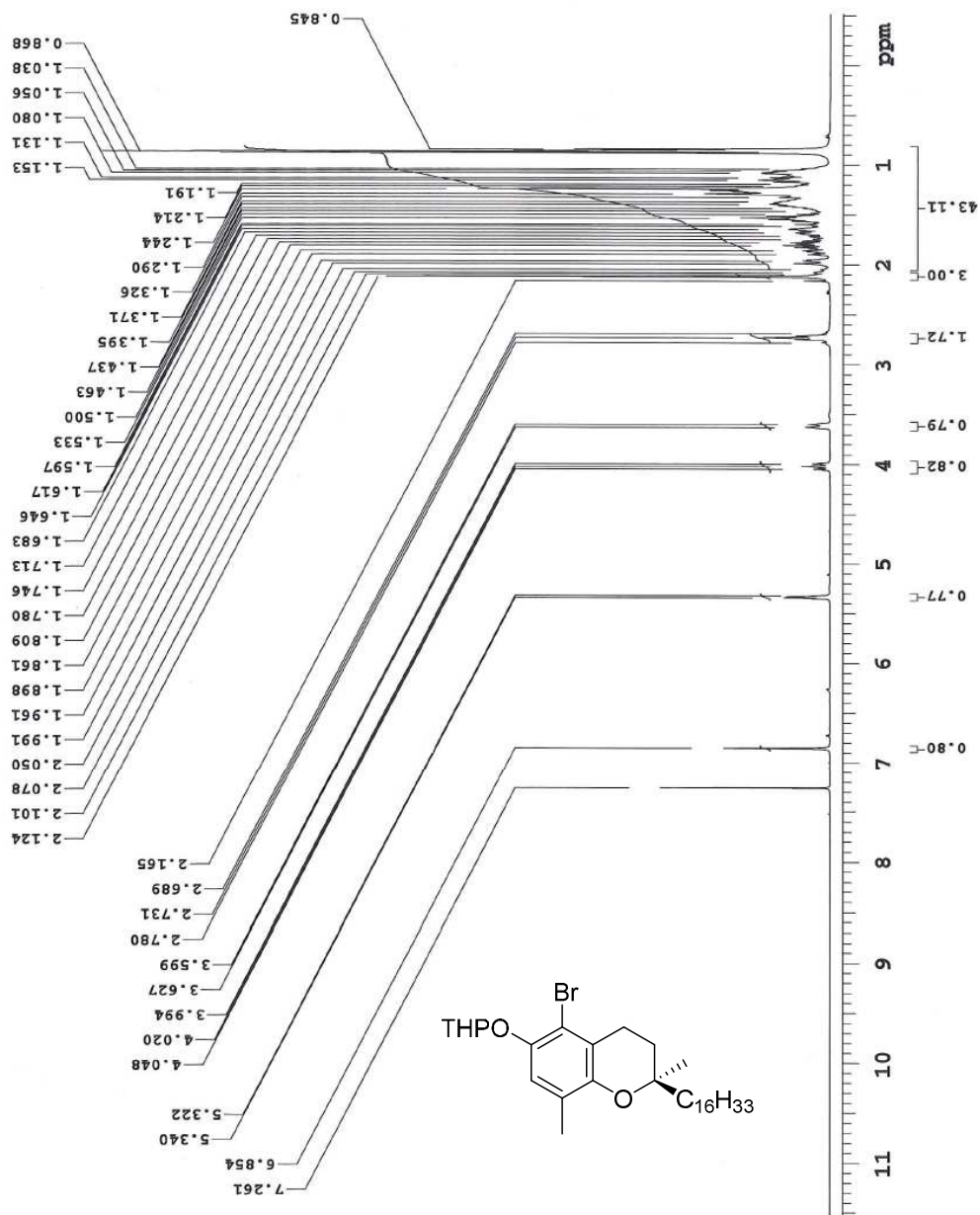
always present in commercial samples as an impurity, and which increases upon storage. We have therefore standardized the procedure by adding small amounts of older, peroxidised linoleic acid to samples of fresh one until the final concentration of hydroperoxide is ca 175 μM at the beginning of an experiment.

Thiol Peroxidase Activity: The GPx-like activities of novel organotellurium compounds prepared were determined by UV-spectroscopy following the protocol by Tomoda⁵ with slight modifications. The test mixture contained PhSH (1 mM) and catalyst (0.01 mM) at 21 °C and the reaction was initiated by addition of H₂O₂ (3.75 mM). Initial reaction rates were based on the formation of diphenyl disulfide (PhSSPh) as assessed by UV-spectroscopy at 305 nm. The initial reduction rate was determined at least 3-4 times and calculated from the first 10 seconds of reaction by using 1.24 mM⁻¹cm⁻¹ as the extinction coefficient for PhSSPh.

References

1. Li, Y.; Silverton, L. C.; Haasch, R.; Tong, Y. Y. *Langmuir* **2008**, *24*, 7048–7053.
2. Patel, A.; Böhmendorfer, S.; Hofinger, A.; Netscher, T.; Rosenau, T. *Eur. J. Org. Chem.* **2009**, 4873-4881.
3. Netscher, T.; Mazzini, F.; Jestin, R. *Eur. J. Org. Chem.* **2007**, 1176-1183.
4. Shanks, D.; Amorati, R.; Fumo, M. G.; Pedulli, G. F.; Valgimigli, L.; Engman, L. *J. Org. Chem.* **2006**, *71*, 1033-1038.
5. Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1994**, *116*, 2557-2561.

¹H NMR spectrum of **5b**



SAMPLE: VPS-401H

VPS-401H

ErrorLog:
auto_20130830_01 loc:12
(day)
Findz0 failed - low S/N

Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #12, Operator: palsingh
File: VPS-401H_PROTON_01
VNMRS-400 "MR400"

PULSE SEQUENCE

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
15 repetitions

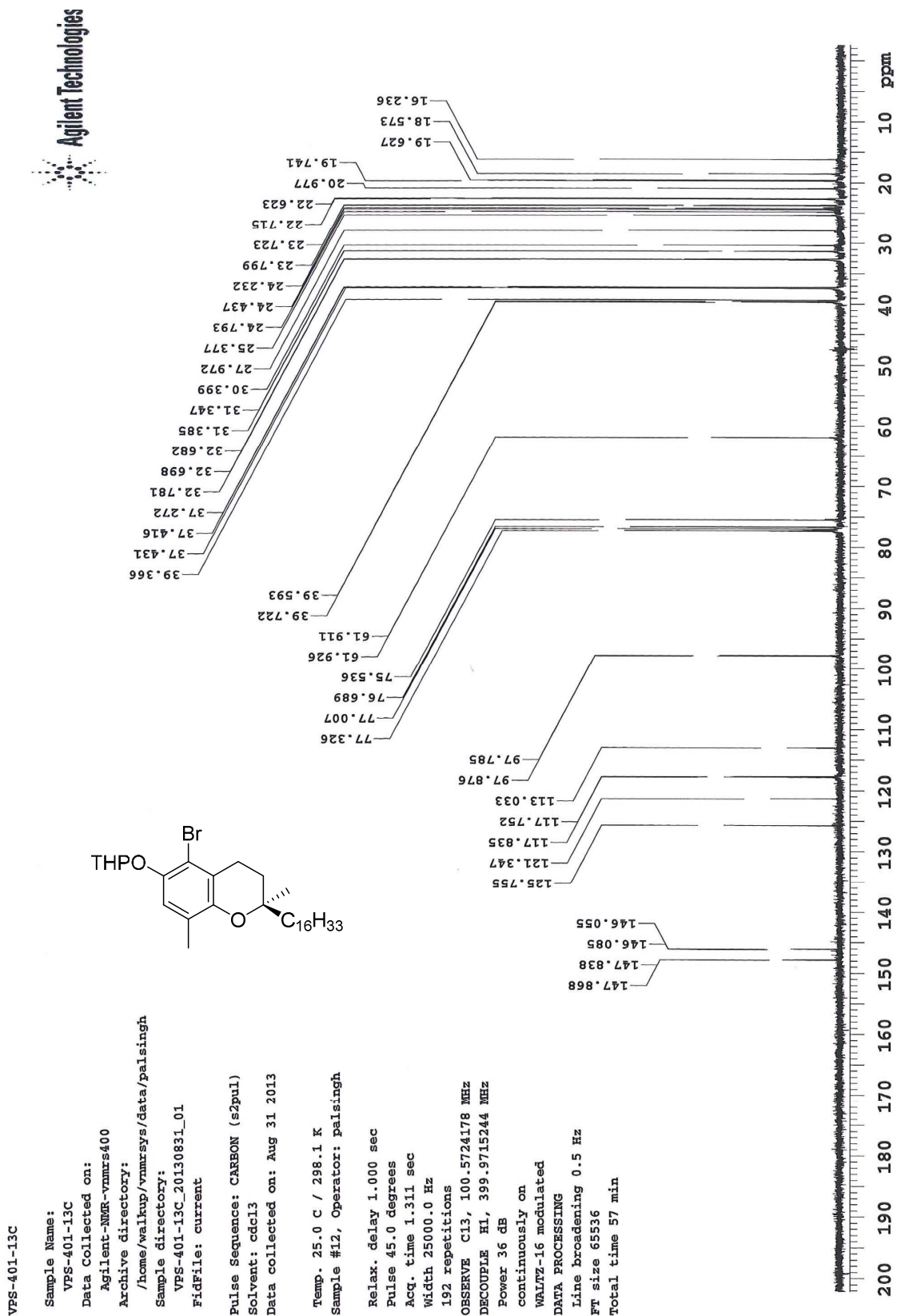
OBSERVE H1, 399.9695233

DATA PROCESSING

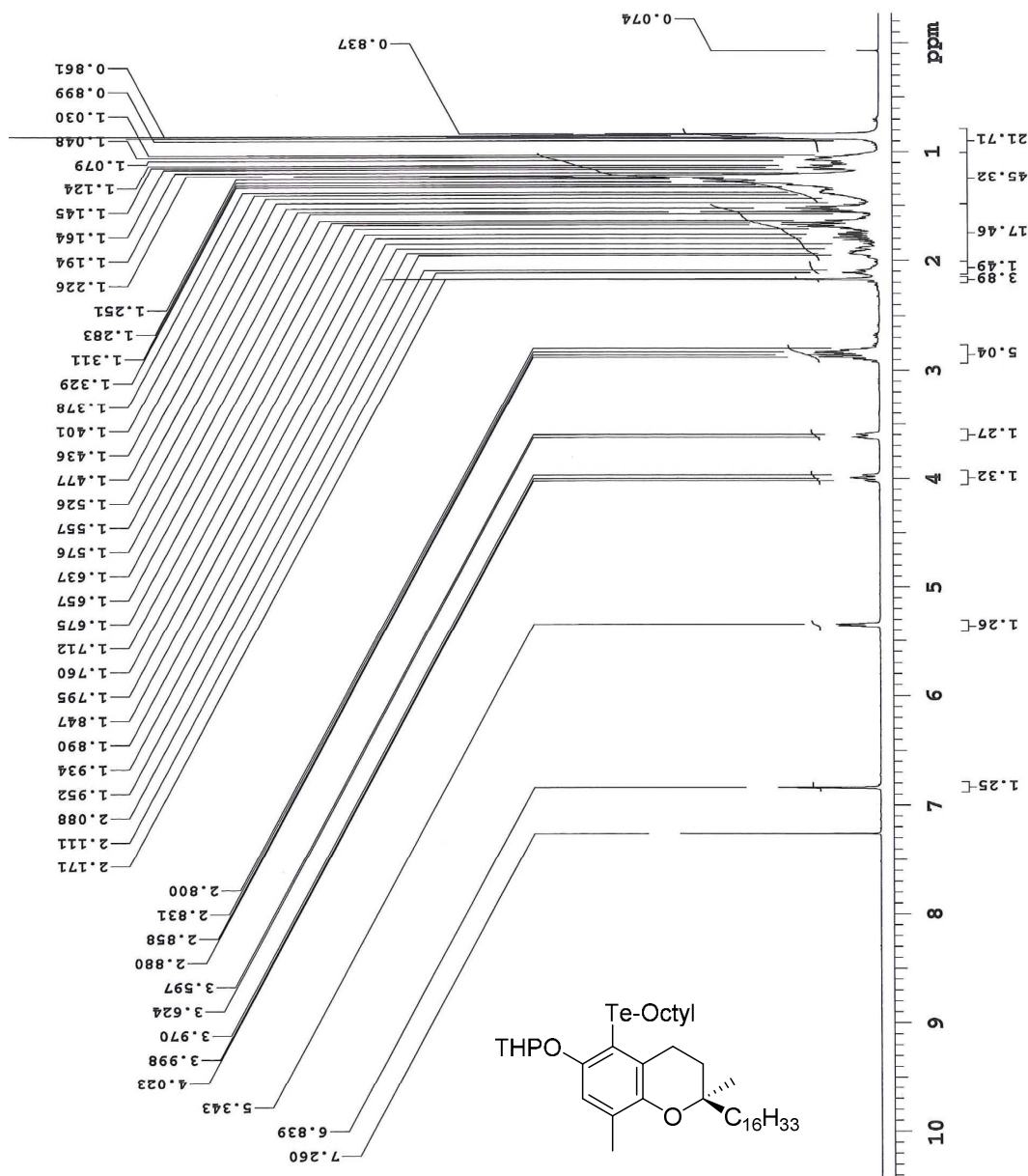
Ft size 32768
Total time 1 minute

Archive dir: /home/valkup/vnmrsvs/data/palsingh Sample: VPS-401H_20130831_01 File: VPS-401H_PROTON_01

¹³C NMR spectrum of **5b**



¹H NMR spectrum of **6a**



SAMPLE: VPS-408-1H

VPS-408-1H

ErrorLog:

auto_20130827_01 loc:1

(night)

Findz0 failed - low S/N

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

Sample #1, Operator: palsingh

File: VPS-408-1H_PROTON_01

VNMR5-400 "MR400"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.556 sec

Width 6410.3 Hz

20 repetitions

OBSERVE H1, 399.9695238

DATA PROCESSING

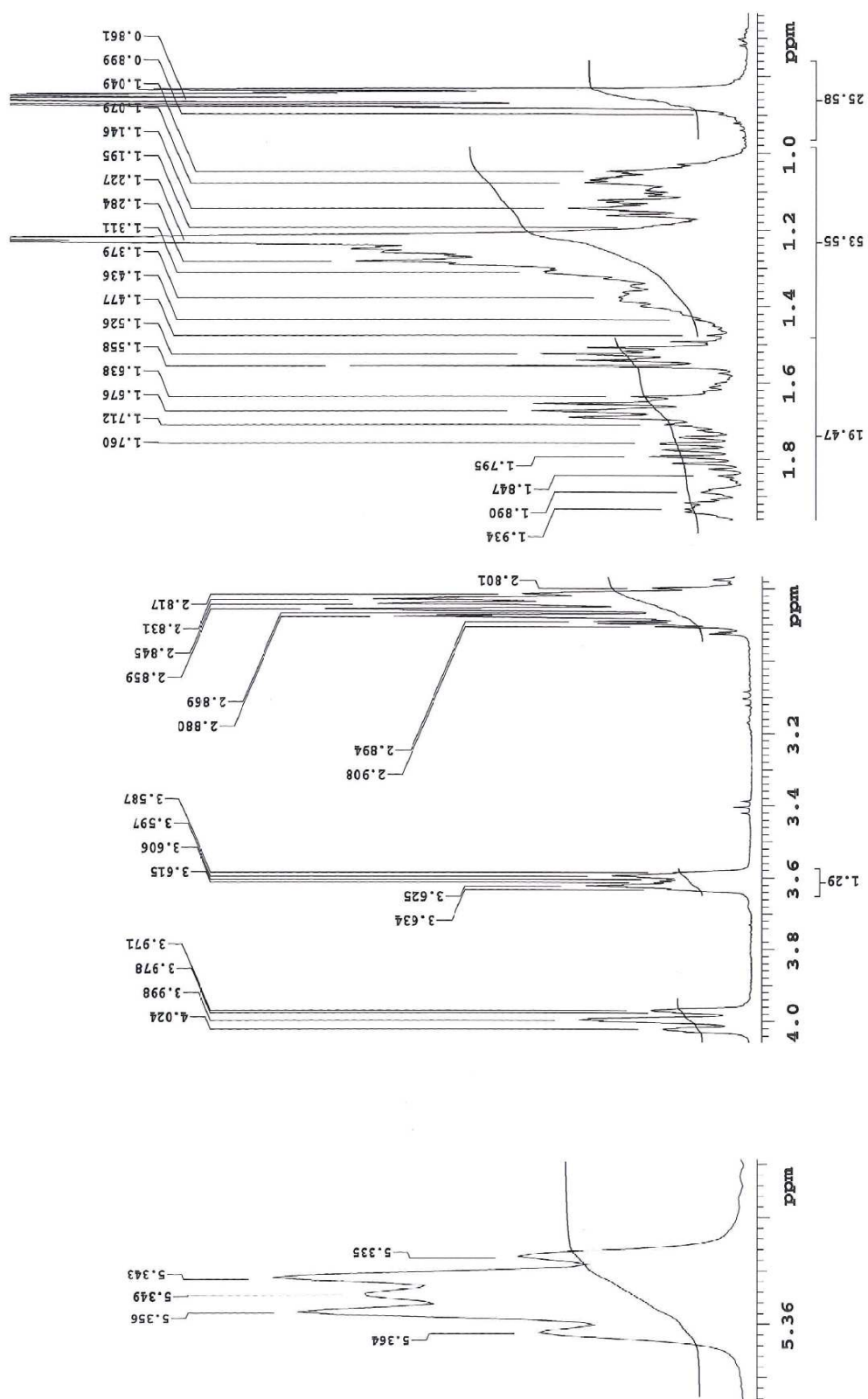
Ft size 32768

Total time 1 minute

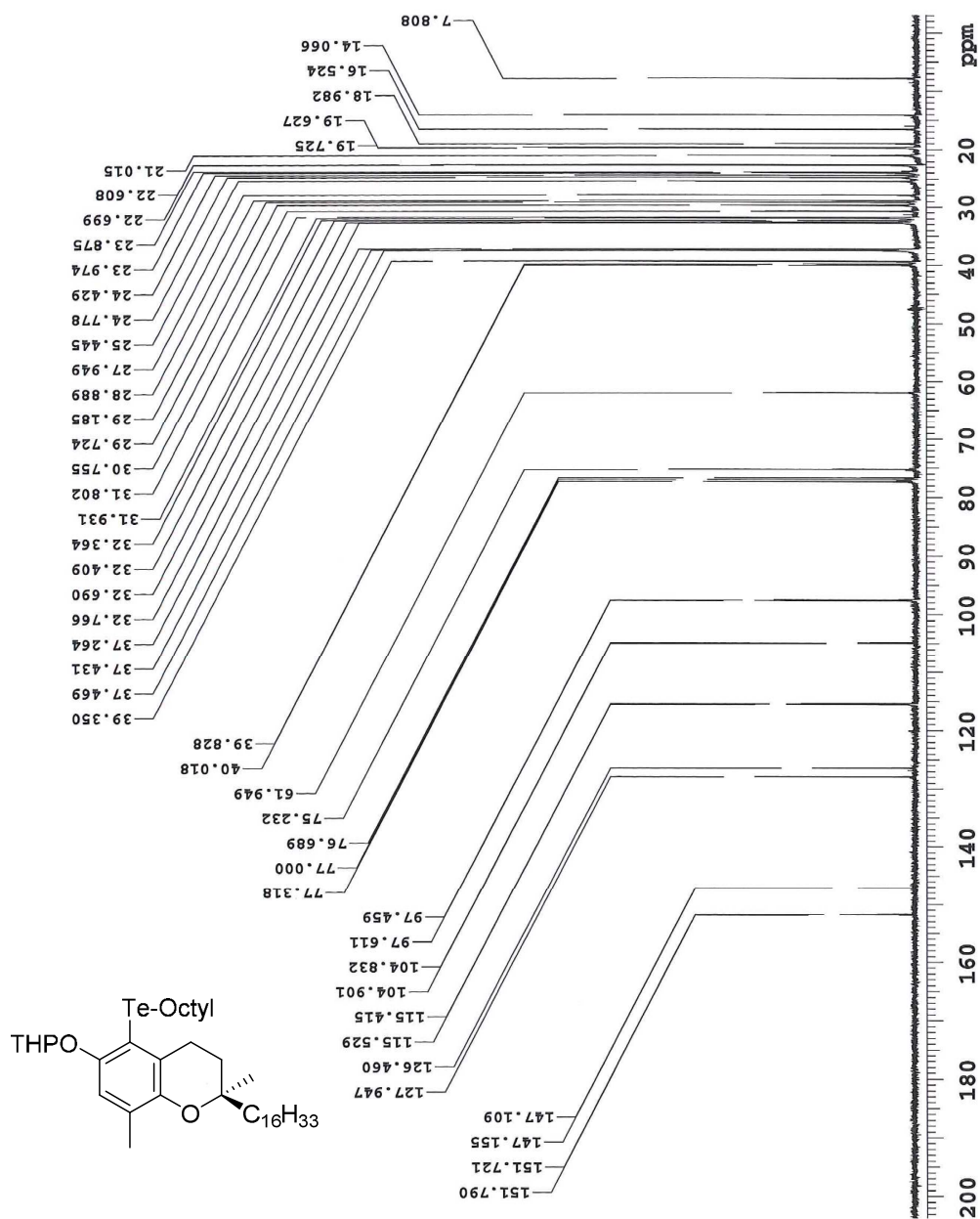
Archive dir: /home/walshup/vnmrsys/data/palsingh

Sample: VPS-408-1H_20130827_01 File: VPS-408-1H_PROTON_01

Expanded version of ^1H NMR spectrum of **6a**



¹³C NMR spectrum of **6a**



SAMPLE: VPS-408-13C

VPS-408-13C

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

Sample #1, Operator: palsingh

File: current

VNMR-400 "MR400"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.311 sec

Width 25000.0 Hz

320 repetitions

OBSERVE C13, 100.5724201

DECOUPLE H1, 399.9715244

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

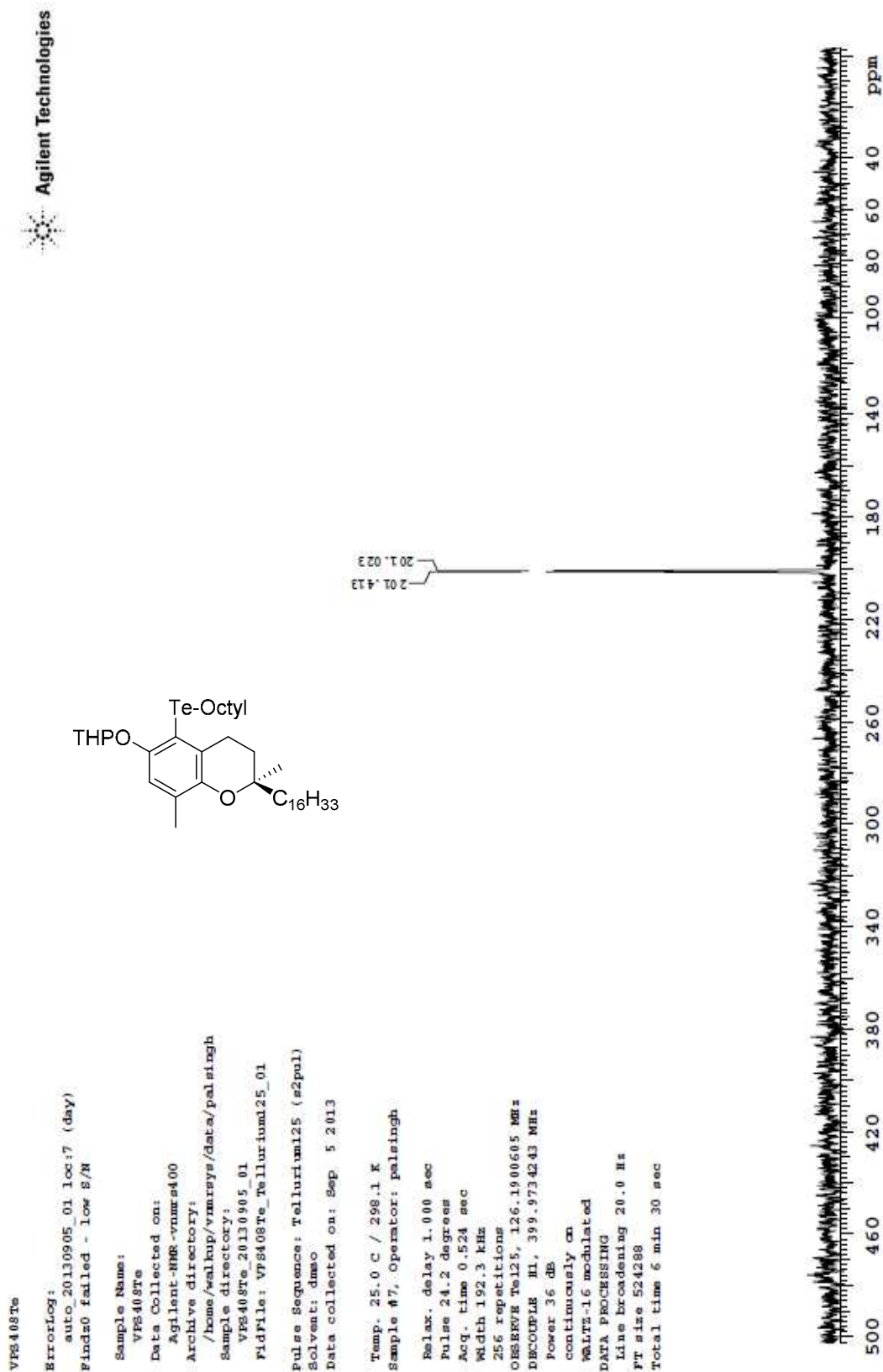
Line broadening 1.0 Hz

FT size 65536

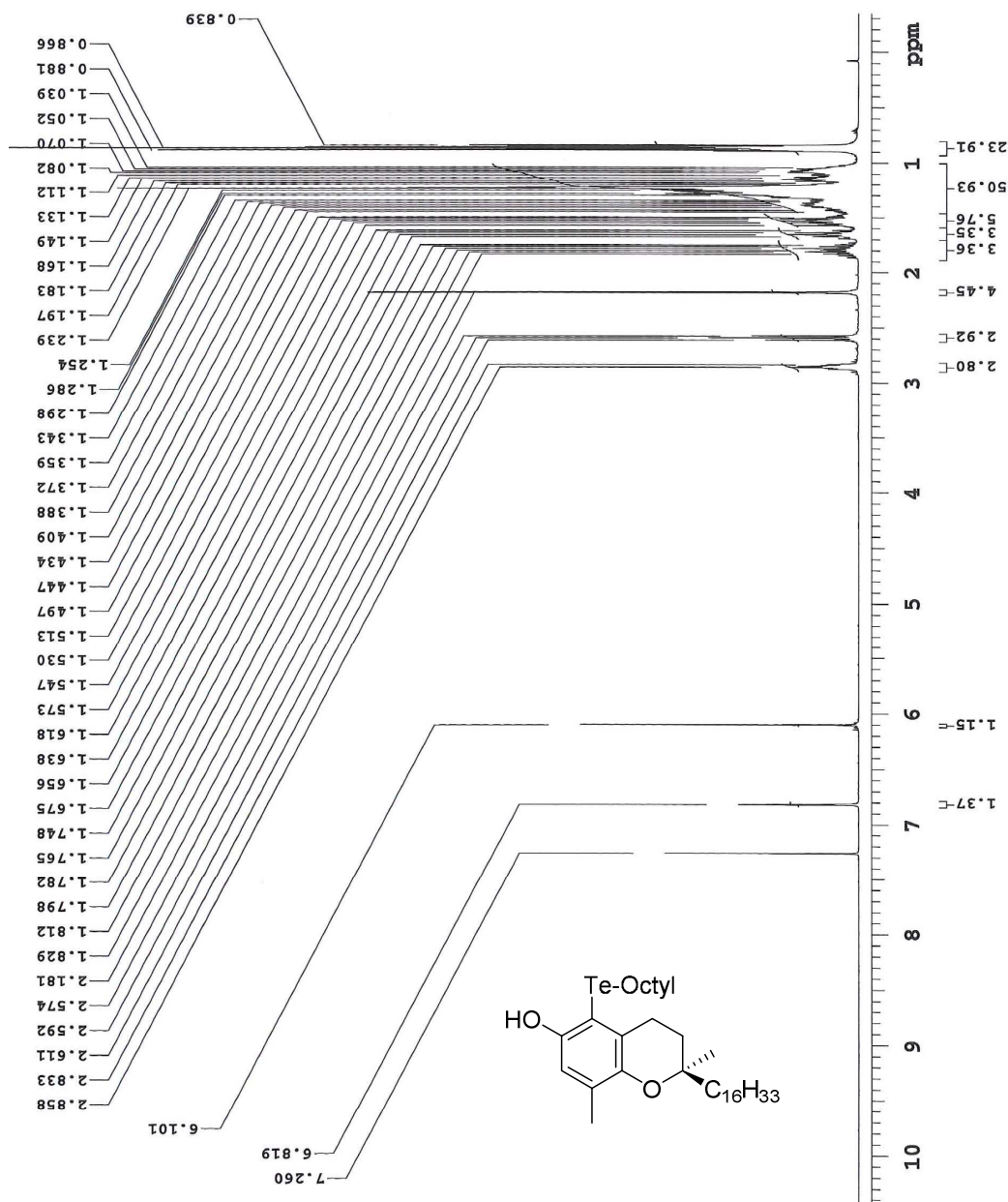
Total time 12 minutes

Archive dir: /home/walkup/vnmrsys/data/palsingh Sample: VPS-408-13C_20130827_01 File: current

^{125}Te NMR spectrum of **6a**



¹H NMR spectrum of **6b**



SAMPLE: VPS-415-1H

VPS-415-1H

ErrorLog:

auto_20130827_01 loc:1
(night)

Findz0 failed - low S/N

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

Sample #1, Operator: palsingh

File: VPS-415-1H_PROTON_01

VNMR5-400 "MR400"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.556 sec

Width 6410.3 Hz

15 repetitions

OBSERVE H1, 399.9695236

DATA PROCESSING

Ft size 32768

Total time 1 minute

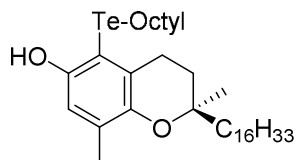
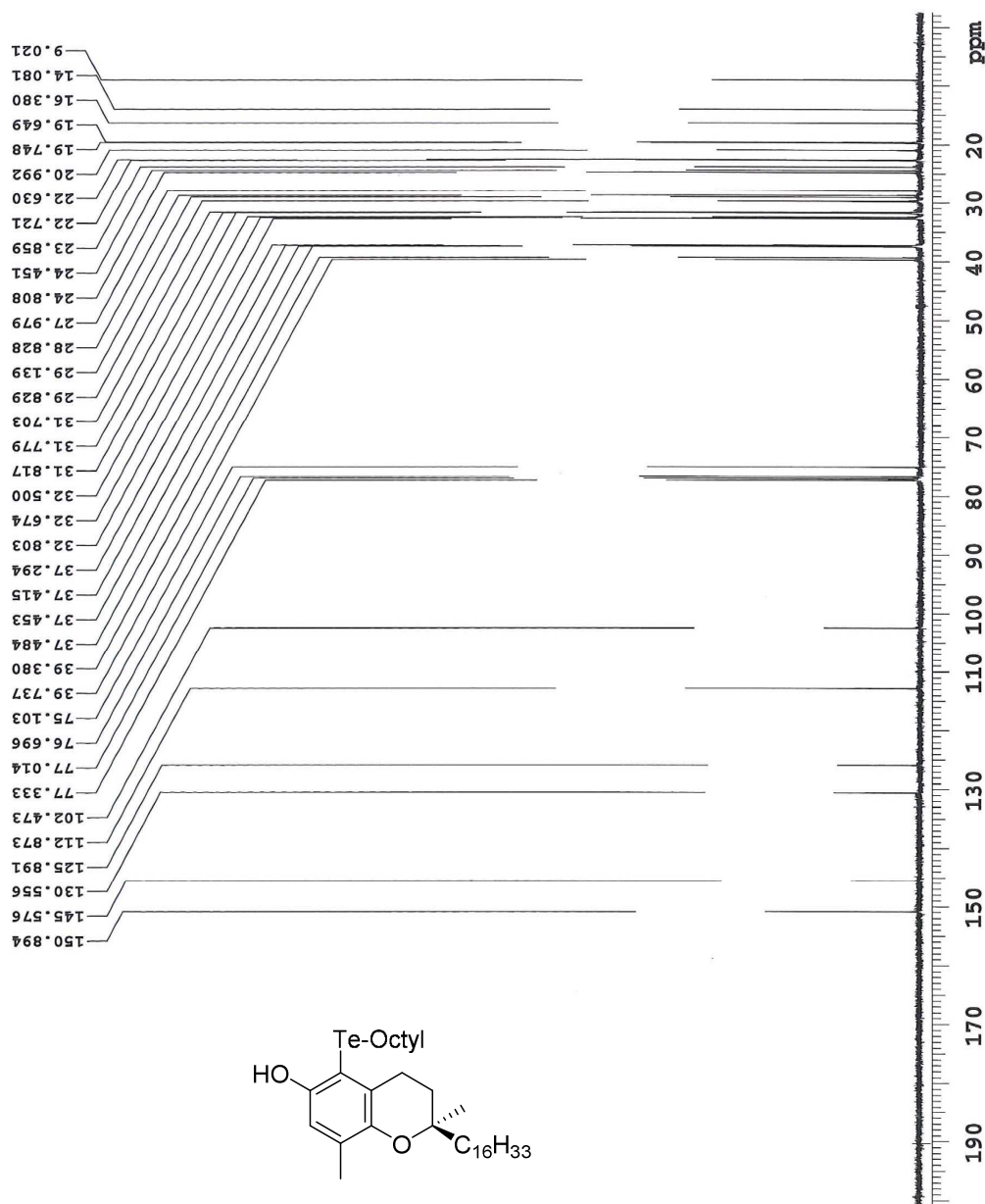
Archive dir: /home/walkup/vnmrsys/data/palsingh

Sample: VPS-415-1H_20130827_01 File: VPS-415-1H_PROTON_01

¹H NMR Spectrum (Top): This spectrum shows the chemical shifts of compound 1 in CDCl₃. The x-axis represents the chemical shift in ppm, ranging from 0.8 to 1.9. The spectrum displays several sharp peaks, with integration curves overlaid. The chemical shift values (ppm) are listed on the right side of the spectrum: 0.816, 0.866, 1.019, 1.051, 1.082, 1.112, 1.133, 1.149, 1.168, 1.197, 1.238, 1.286, 1.343, 1.371, 1.388, 1.409, 1.434, 1.480, 1.497, 1.513, 1.530, 1.546, 1.573, 1.618, 1.637, and 1.656. The integration curve shows a series of steps, indicating the relative areas under the peaks.

¹H NMR Spectrum (Bottom): This spectrum shows the chemical shifts of compound 1 in DMSO-d₆. The x-axis represents the chemical shift in ppm, ranging from 2.5 to 2.9. The spectrum displays several sharp peaks, with integration curves overlaid. The chemical shift values (ppm) are listed on the right side of the spectrum: 2.574, 2.592, 2.611, 2.64, 2.67, 2.72, 2.78, 2.80, 2.88, 2.92, 2.95, 2.97, 2.99, 3.01, 3.03, 3.05, 3.07, 3.09, 3.11, 3.13, 3.15, 3.17, 3.19, 3.21, 3.23, 3.25, 3.27, 3.29, 3.31, 3.33, 3.35, 3.37, 3.39, 3.41, 3.43, 3.45, 3.47, 3.49, 3.51, 3.53, 3.55, 3.57, 3.59, 3.61, 3.63, 3.65, 3.67, 3.69, 3.71, 3.73, 3.75, 3.77, 3.79, 3.81, 3.83, 3.85, 3.87, 3.89, 3.91, 3.93, 3.95, 3.97, 3.99, 4.01, 4.03, 4.05, 4.07, 4.09, 4.11, 4.13, 4.15, 4.17, 4.19, 4.21, 4.23, 4.25, 4.27, 4.29, 4.31, 4.33, 4.35, 4.37, 4.39, 4.41, 4.43, 4.45, 4.47, 4.49, 4.51, 4.53, 4.55, 4.57, 4.59, 4.61, 4.63, 4.65, 4.67, 4.69, 4.71, 4.73, 4.75, 4.77, 4.79, 4.81, 4.83, 4.85, 4.87, 4.89, 4.91, 4.93, 4.95, 4.97, 4.99, 5.01, 5.03, 5.05, 5.07, 5.09, 5.11, 5.13, 5.15, 5.17, 5.19, 5.21, 5.23, 5.25, 5.27, 5.29, 5.31, 5.33, 5.35, 5.37, 5.39, 5.41, 5.43, 5.45, 5.47, 5.49, 5.51, 5.53, 5.55, 5.57, 5.59, 5.61, 5.63, 5.65, 5.67, 5.69, 5.71, 5.73, 5.75, 5.77, 5.79, 5.81, 5.83, 5.85, 5.87, 5.89, 5.91, 5.93, 5.95, 5.97, 5.99, 6.01, 6.03, 6.05, 6.07, 6.09, 6.11, 6.13, 6.15, 6.17, 6.19, 6.21, 6.23, 6.25, 6.27, 6.29, 6.31, 6.33, 6.35, 6.37, 6.39, 6.41, 6.43, 6.45, 6.47, 6.49, 6.51, 6.53, 6.55, 6.57, 6.59, 6.61, 6.63, 6.65, 6.67, 6.69, 6.71, 6.73, 6.75, 6.77, 6.79, 6.81, 6.83, 6.85, 6.87, 6.89, 6.91, 6.93, 6.95, 6.97, 6.99, 7.01, 7.03, 7.05, 7.07, 7.09, 7.11, 7.13, 7.15, 7.17, 7.19, 7.21, 7.23, 7.25, 7.27, 7.29, 7.31, 7.33, 7.35, 7.37, 7.39, 7.41, 7.43, 7.45, 7.47, 7.49, 7.51, 7.53, 7.55, 7.57, 7.59, 7.61, 7.63, 7.65, 7.67, 7.69, 7.71, 7.73, 7.75, 7.77, 7.79, 7.81, 7.83, 7.85, 7.87, 7.89, 7.91, 7.93, 7.95, 7.97, 7.99, 8.01, 8.03, 8.05, 8.07, 8.09, 8.11, 8.13, 8.15, 8.17, 8.19, 8.21, 8.23, 8.25, 8.27, 8.29, 8.31, 8.33, 8.35, 8.37, 8.39, 8.41, 8.43, 8.45, 8.47, 8.49, 8.51, 8.53, 8.55, 8.57, 8.59, 8.61, 8.63, 8.65, 8.67, 8.69, 8.71, 8.73, 8.75, 8.77, 8.79, 8.81, 8.83, 8.85, 8.87, 8.89, 8.91, 8.93, 8.95, 8.97, 8.99, 9.01, 9.03, 9.05, 9.07, 9.09, 9.11, 9.13, 9.15, 9.17, 9.19, 9.21, 9.23, 9.25, 9.27, 9.29, 9.31, 9.33, 9.35, 9.37, 9.39, 9.41, 9.43, 9.45, 9.47, 9.49, 9.51, 9.53, 9.55, 9.57, 9.59, 9.61, 9.63, 9.65, 9.67, 9.69, 9.71, 9.73, 9.75, 9.77, 9.79, 9.81, 9.83, 9.85, 9.87, 9.89, 9.91, 9.93, 9.95, 9.97, 9.99, 10.01, 10.03, 10.05, 10.07, 10.09, 10.11, 10.13, 10.15, 10.17, 10.19, 10.21, 10.23, 10.25, 10.27, 10.29, 10.31, 10.33, 10.35, 10.37, 10.39, 10.41, 10.43, 10.45, 10.47, 10.49, 10.51, 10.53, 10.55, 10.57, 10.59, 10.61, 10.63, 10.65, 10.67, 10.69, 10.71, 10.73, 10.75, 10.77, 10.79, 10.81, 10.83, 10.85, 10.87, 10.89, 10.91, 10.93, 10.95, 10.97, 10.99, 11.01, 11.03, 11.05, 11.07, 11.09, 11.11, 11.13, 11.15, 11.17, 11.19, 11.21, 11.23, 11.25, 11.27, 11.29, 11.31, 11.33, 11.35, 11.37, 11.39, 11.41, 11.43, 11.45, 11.47, 11.49, 11.51, 11.53, 11.55, 11.57, 11.59, 11.61, 11.63, 11.65, 11.67, 11.69, 11.71, 11.73, 11.75, 11.77, 11.79, 11.81, 11.83, 11.85, 11.87, 11.89, 11.91, 11.93, 11.95, 11.97, 11.99, 12.01, 12.03, 12.05, 12.07, 12.09, 12.11, 12.13, 12.15, 12.17, 12.19, 12.21, 12.23, 12.25, 12.27, 12.29, 12.31, 12.33, 12.35, 12.37, 12.39, 12.41, 12.43, 12.45, 12.47, 12.49, 12.51, 12.53, 12.55, 12.57, 12.59, 12.61, 12.63, 12.65, 12.67, 12.69, 12.71, 12.73, 12.75, 12.77, 12.79, 12.81, 12.83, 12.85, 12.87, 12.89, 12.91, 12.93, 12.95, 12.97, 12.99, 13.01, 13.03, 13.05, 13.07, 13.09, 13.11, 13.13, 13.15, 13.17, 13.19, 13.21, 13.23, 13.25, 13.27, 13.29, 13.31, 13.33, 13.35, 13.37, 13.39, 13.41, 13.43, 13.45, 13.47, 13.49, 13.51, 13.53, 13.55, 13.57, 13.59, 13.61, 13.63, 13.65, 13.67, 13.69, 13.71, 13.73, 13.75, 13.77, 13.79, 13.81, 13.83, 13.85, 13.87, 13.89, 13.91, 13.93, 13.95, 13.97, 13.99, 14.01, 14.03, 14.05, 14.07, 14.09, 1

¹³C NMR spectrum of **6b**



SAMPLE: VPS-415-13C

VPS-415-13C

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #1, Operator: palsingh
File: VPS-415-13C CARBON_01
VNMR-400 "MR400"

PULSE SEQUENCE

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
1200 repetitions

OBSERVE C13, 100.5724164

DECOUPLE H1, 399.9715244

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

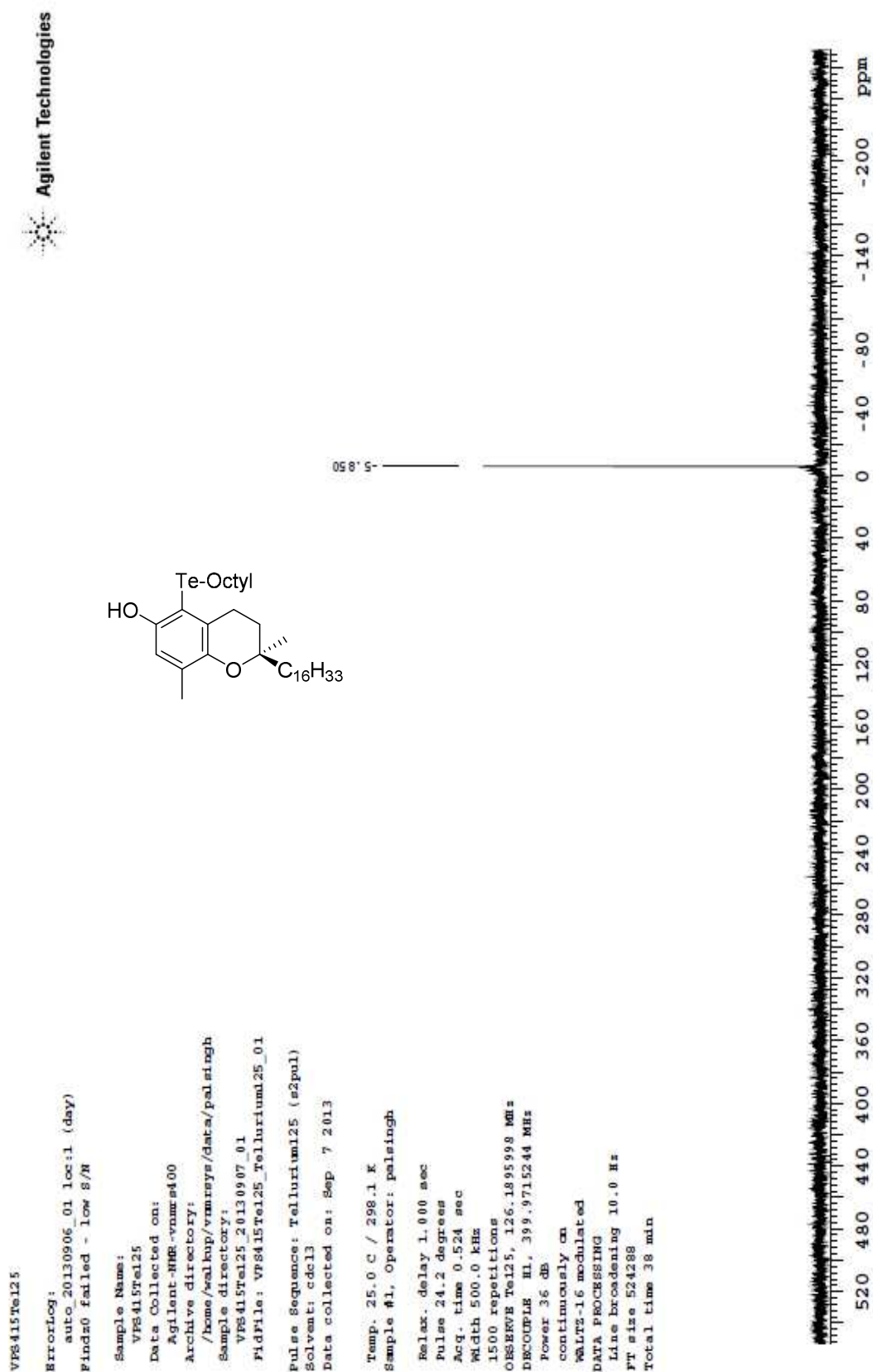
Line broadening 0.5 Hz

FT size 65536

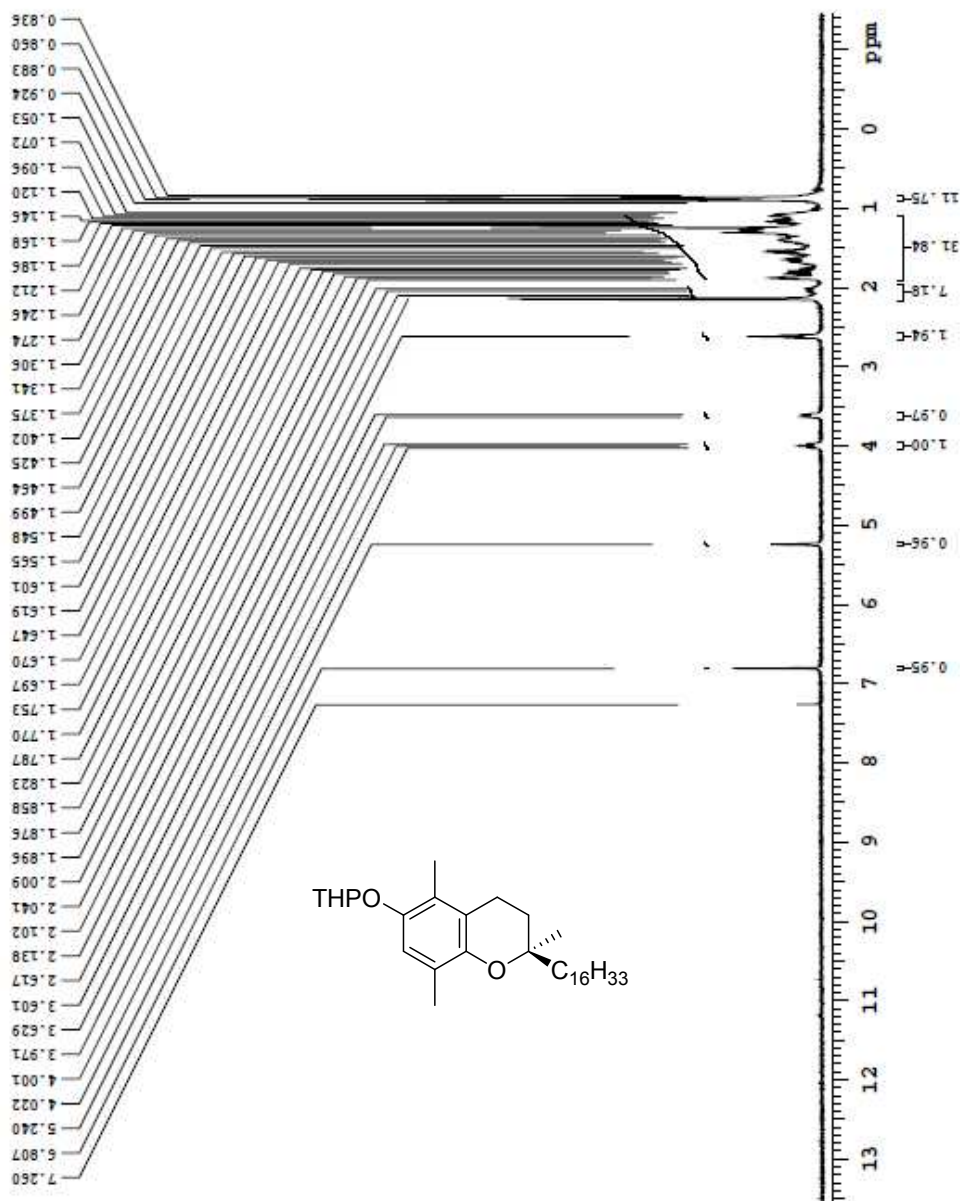
Total time 46 minutes

Archive dir: /home/walkup/vnmrsys/data/palsingh Sample: VPS-415-13C_20130827_01 File: VPS-415-13C CARBON_01

^{125}Te NMR spectrum of **6b**



¹H NMR spectrum of THP-protected β-Tocopherol



Agilent Technologies

STANDARD 1H OBSERVE

Solvent: CDCl₃
Temp: 25.0 C / 298.1 K
Operator: jiafei
File: JP220-1R-3
UNITYplus-400 "ME400"

PULSE SEQUENCE

Pulse 39.6 degrees
Acq. time 3.744 sec
Width 6000.6 Hz
Single scan

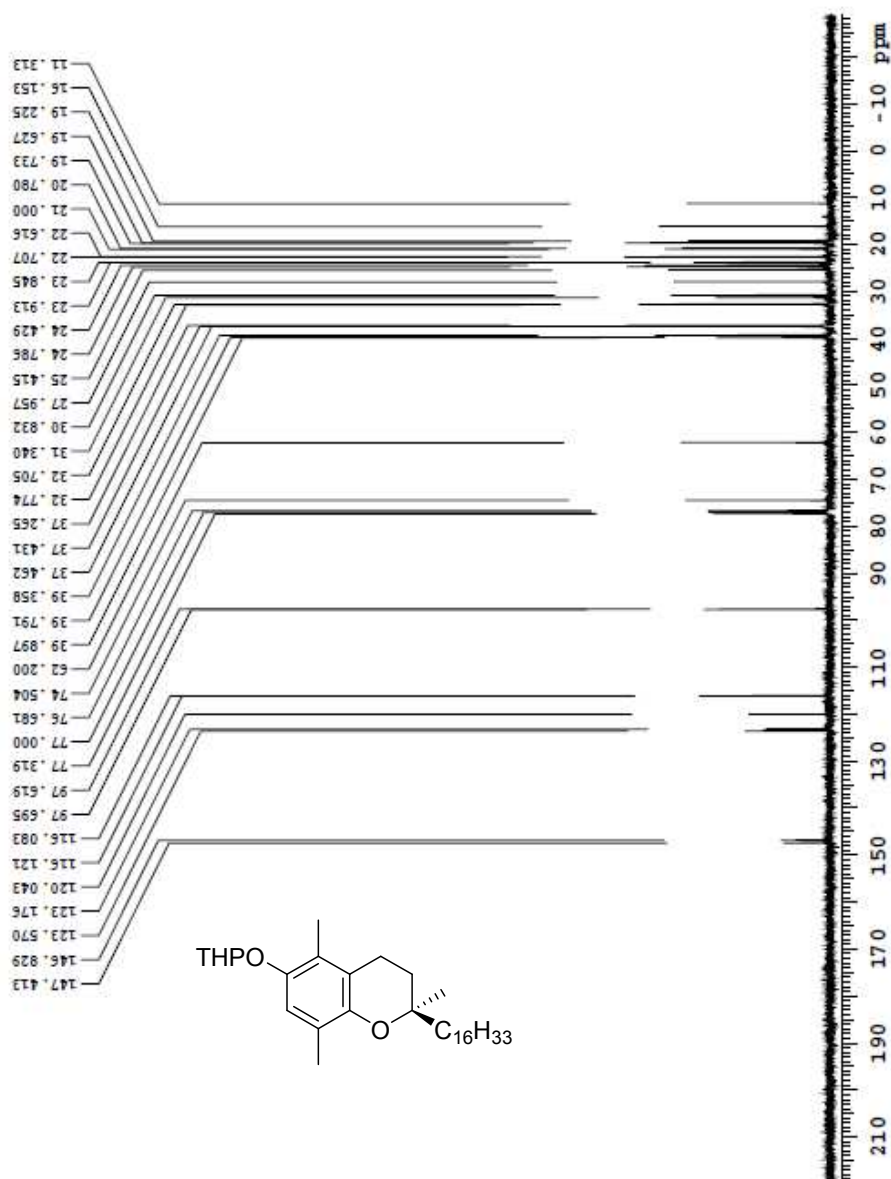
OBSERVE H1, 399.968221

DATA PROCESSING

line broadening 0.2 Hz
FT size 65536
Total time 1 minute

Archive dir: File: JP220-1R-3

^{13}C NMR spectrum of THP-protected β -Tocopherol



^{13}C OBSERVE

Solvent: CDCl₃
Temp. 25.0 C / 298.1 K
Operator: jiafei
File: JP220-13C-2
UNITYplus-400 "164.00"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 68.1 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
480 repetitions

OBSERVE C13, 100.5720931
DECOUPLE H1, 399.976393
Power 49 dB
continuously on
WALTZ-16 modulated
Single precision data

DATA PROCESSING
Line broadening 1.0 Hz
Ft size 65536
Total time 17 minutes

Archive dir: File: JP220-13C-2



Agilent Technologies

SAMPLE: JP280

```
ErrorLog:
  auto_20130905_01 loc:1
  (night)
  Fmdr0 failed - low S/N

  Solvent: cdcl3
  Temp. 25.0 C / 298.1 K
  Sample #1, operator: jiafei
  File: J280_PROTON_01
  VNMR-400 "MR400"
```

PULSE SEQUENCE

Relax. delay	1.000 sec
Pulse	45.0 degrees
Acq. time	2.556 sec
Width	640.3 Hz
	16 repetitions

OBSERVE H1, 399.9695238

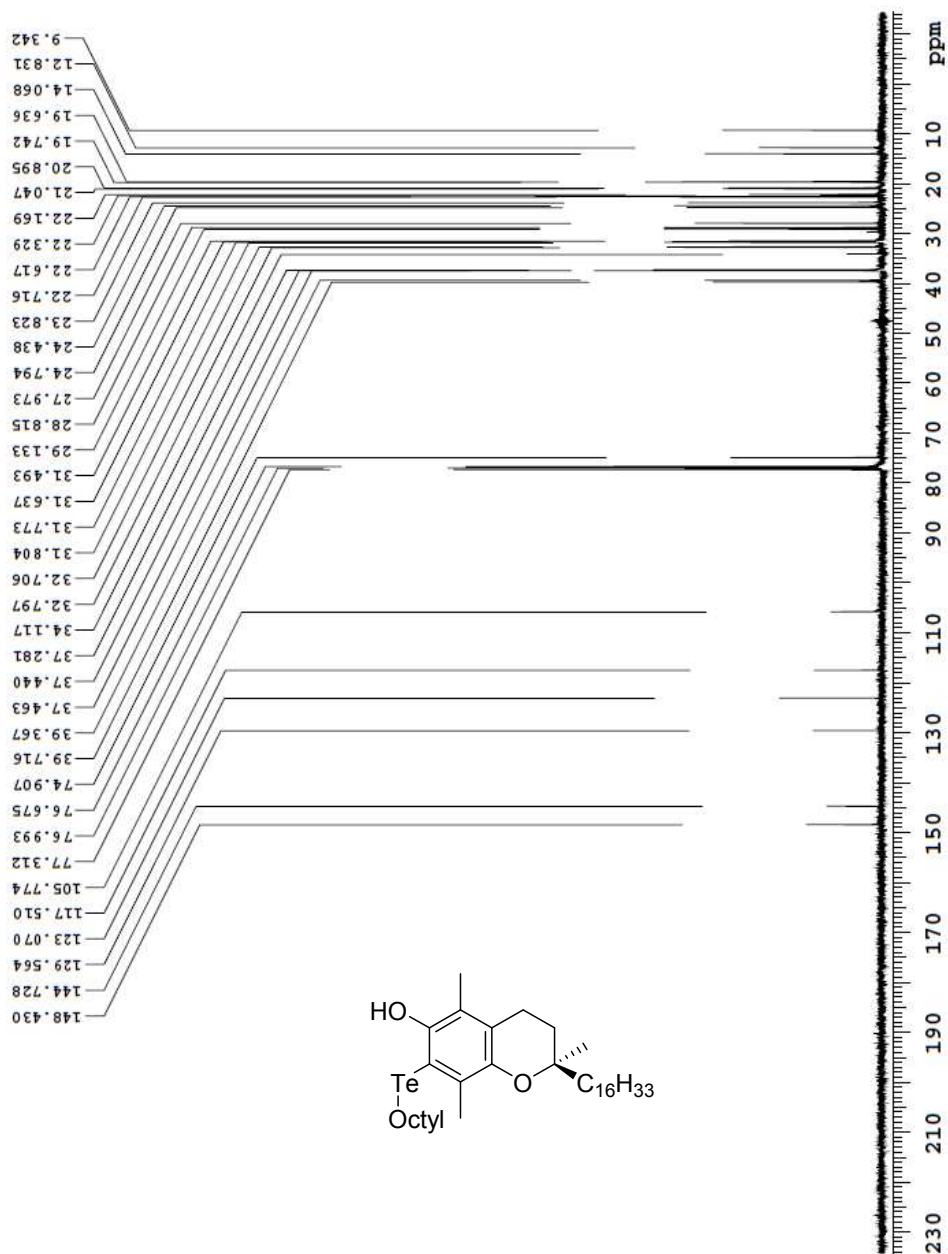
DATA PROCESSING

FT size 32768

Total time 1 minute

Archive dir: /home/walkup/vnmrsys/data/jiafei	Sample: JP280_20130905_01	File: JP280_PROTON_01
---	---------------------------	-----------------------

^{13}C NMR spectrum of **7b**



SAMPLE: JP280

ErrorLog:
auto_20130905_01 loc:1
(night)
Findr0 failed - low S/N

Solvent: cdcl3
Temp: 25.0 C / 298.1 K
Sample #1, Operator: jiafei
File: JP280 CARBON_01
VNMR-400 "MR400"

PULSE SEQUENCE

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
1536 repetitions

OBSERVE C13, 100.5724170
DECOUPLE H1, 399.9715244
Power 36 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz
FT size 65536
Total time 59 minutes

Archive dir: /home/walkup/vnmrSYS/data/jiafei

Sample: JP280_20130905_01 File: JP280 CARBON_01

^{125}Te NMR spectrum of **7b**

