Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information for:

Calcium Tungstate: A Convenient Recoverable Catalyst for Hydrogen Peroxide Oxidation

Catlin M. Williamson, Peter Stonehouse and Keith S. Kyler*

Address: Department of Chemistry, Indiana University of Pennsylvania, Indiana, Pennsylvania, 15707

Keith.kyler@iup.edu

Contents

1. **General Procedure for the Oxidation of Amines:** To 2.2 L of 30% H_2O_2 (12.4 mol) was added 3.4 g (0.12 mol) of $CaWO_4$. The mixture was warmed to 45 ^oC and the solid dissolved to produce a yellow solution. Then was added dropwise over a 30 min period, 1 kg (2.3 mol) of p-toluidine while maintaining the temperature below 50 ^oC. After complete addition, the mixture was warmed to 95 ^oC for about 1 h at which point the yellow color of the aqueous phase disappeared and the colorless $CaWO_4$ precipitated. The mixture was cooled to room temperature, and the organic phase was separated and distilled to af-ford, 1.1 kg (98%) of p-nitrotoluene,(**2**), mp 49-51 ^oC, whose ^{1}H-NMR and IR spectra were consistent with reported data. The aqueous phase was filtered and the $CaWO_4$ (3.4g, >99%+) was recovered.

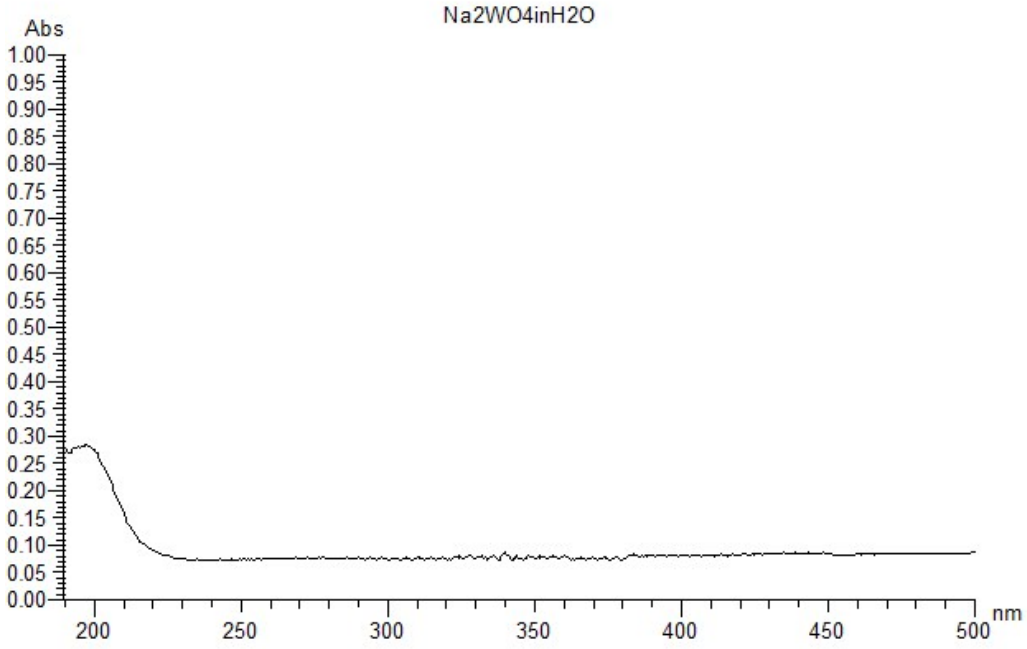
2. **General Procedure for the Oxidation of Alkenes**. To 45.0 mL of 30% H_2O_2 (0.4 mol) and 45 mL of t-butanol was added 0.288 g (1 mmol) of $CaWO_4$. The mixture was warmed to 45 ^oC and the solid dissolved to produce a yellow solution. Then was added 9.4 g (0.10 mol) of norbornene and the mixture was stirred vigorously for 4h at 65 ^oC. The mixture was was then warmed to 95 ^oC for approximately 10 min at which point the yellow color of the aqueous phase disappeared and the colorless $CaWO_4$ precipitated. The mixture was cooled to room temperature, and organic product was extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$, and evaporated to afford 10.55 g (98%) of *exo*-2,3-epoxynorbornane (**5**). ^{1}H-NMR ($CDCl_3$) d 0.92 (2H, d), 1.32 (4H, d), 2.20 (2H, br s) and 3.18 (2H, br s). Decoupled ^{13}C-NMIR ($CDCl_3$) d 24.4, 25.5, 34.2, 51.0. The aqueous phase was filtered and the $CaWO_4$ (0.287g, 99%$^+$) was recovered.

3. **General Procedure for the Oxidation of Alcohols**. To 453 mL of 30% H_2O_2 (4.0 mol) and 400 mL of methanol was added 2.88 g (0.01 mol) of $CaWO_4$. The mixture was warmed to 45 ^oC and the solid dissolved to produce a yellow solution. Then was added 100 g (1.0 mol) of cyclcohexanol and the mixture was stirred vigorously for 20 h at 65 - 70 ^oC. The mixture was was then warmed to 95 ^oC for approximately 1 h at which point the yellow color of the aqueous phase disappeared and the colorless $CaWO_4$ precipitated. The mixture was cooled to room temperature, and organic layer was separated and distilled to afford 95 g (97%) of cyclohexanone, (**6**), bp 152-156 ^oC, lit., 156 ^oC.

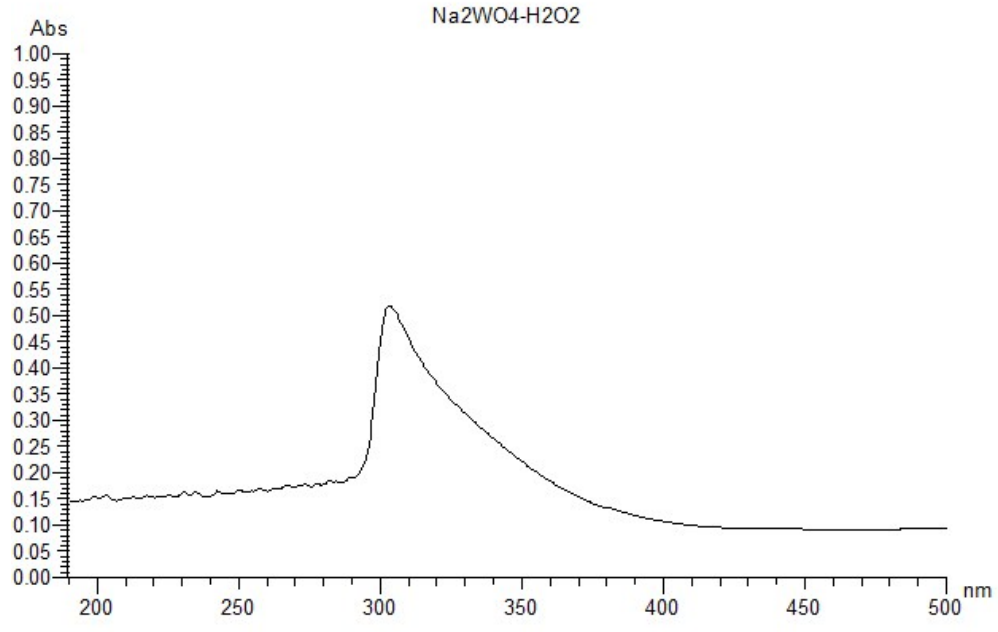
4. **General Procedure for the Oxidation of suflides**. To 22 mL of 30% H_2O_2 (0.20 mol) and 20 mL of t-butanol was added 0.288 g (0.001 mol) of $CaWO_4$. The mixture was warmed to 45 ^oC and the solid dissolved to produce a yellow solution. The mixture was then cooled to 25 ^oC, and was added 15.2 g (0.1 mol) of isopropylphenyl sulfide. The mixture was stirred vigorously for 0.5 h at 25 ^oC. The mixture was was then warmed to 95 ^oC for approximately 1 h at which point the yellow color of the aqueous phase disappeared and the colorless $CaWO_4$ precipitated. The mixture was cooled to room temperature, and 50 mL of ethyl acetate was added then the organic layer was separated and dried over anhydrous $MgSO_4$. Evaporation gave a crude colorless solid which was titurated with cold hexane, filtered, then dried to afford 17.7 g (96%)= of a colorless solid, (**10**). IR (KBr) 3094, 2977, 1305, 1144, and 730 cm^{-1}. GC-MS; 184 (M^+), 142 (78), 78 (100), 51 (22), 43 (36).

5. **UV-Visible Spectra for Tungstate Solutions:** All spectra were recorded at 25 °C on a double-beam Perkin-Elmer Model 552A UV/Vis Spectrophotometer using either water or $H_2O_2(aq)$ as blanks where appropriate. Data were recorded between 500 – 190 nm.

a) 1.0 mM Na_2WO_4 in water

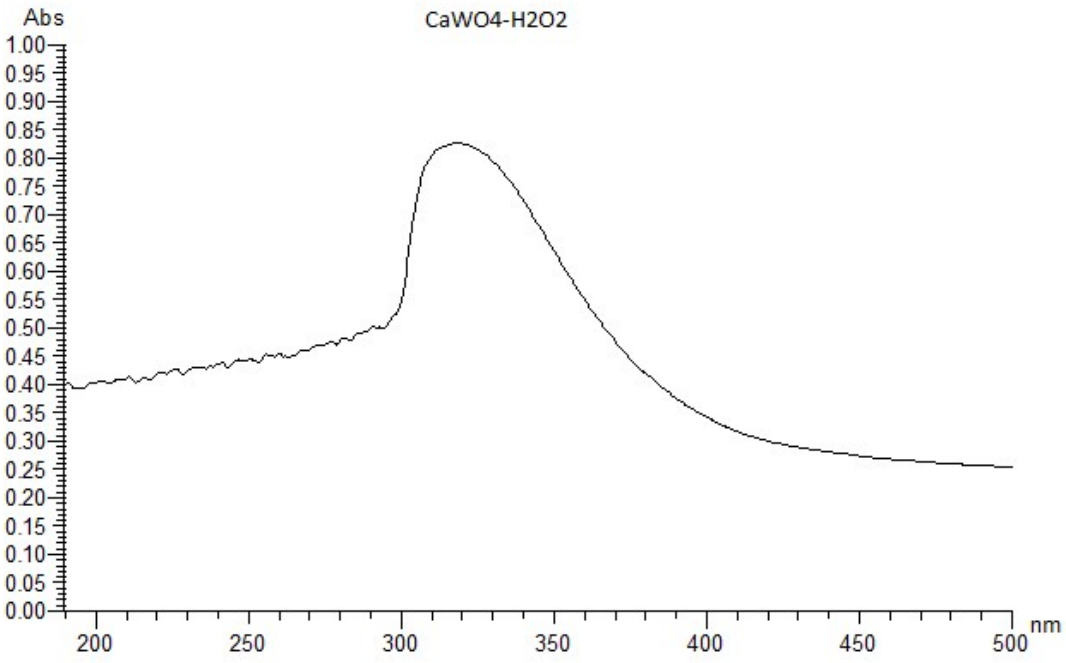


b) 1.0 mM Na_2WO_4 in 8% H_2O_2



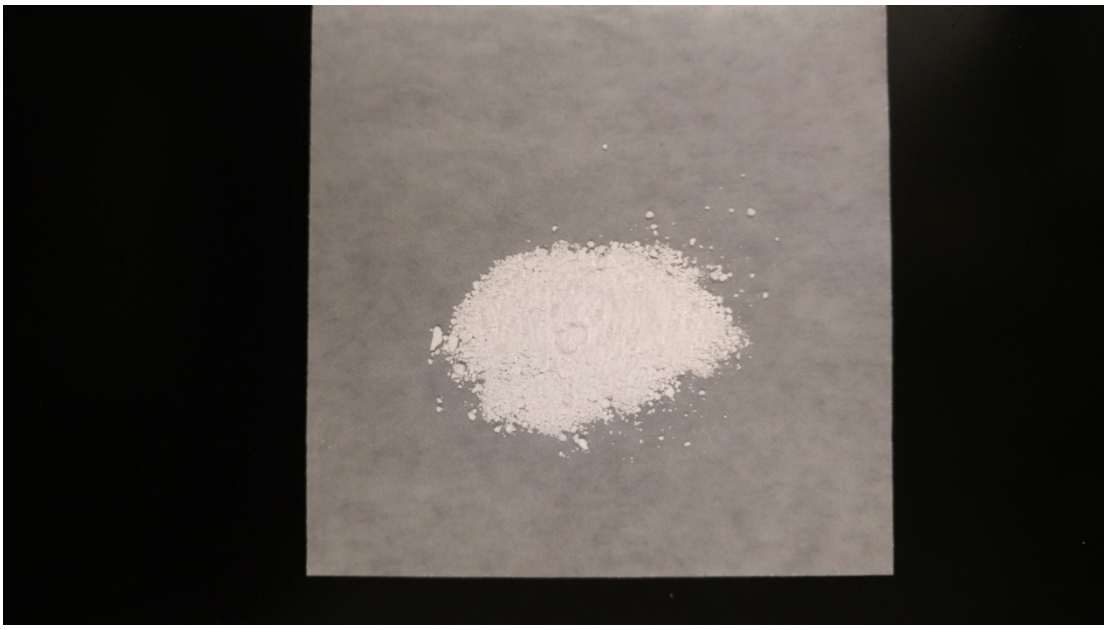
H_2O_2

c) 1.0 mM $CaWO_4$ in 8% H_2O_2

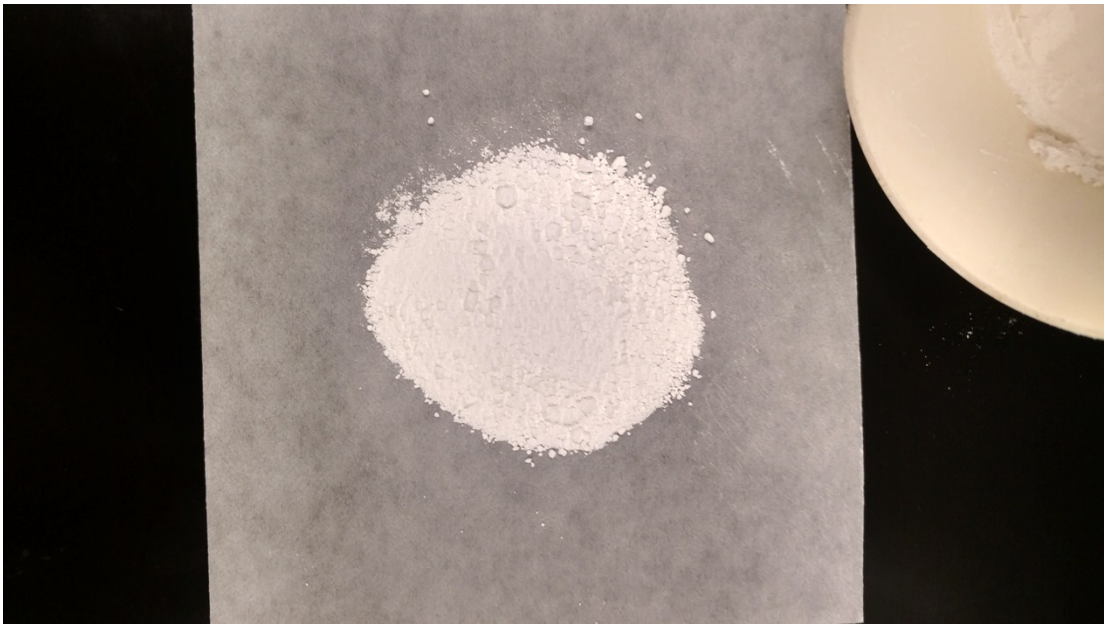


6. Photographs and IR Spectra of CaWO4 before and after Five cycles of Oxidation

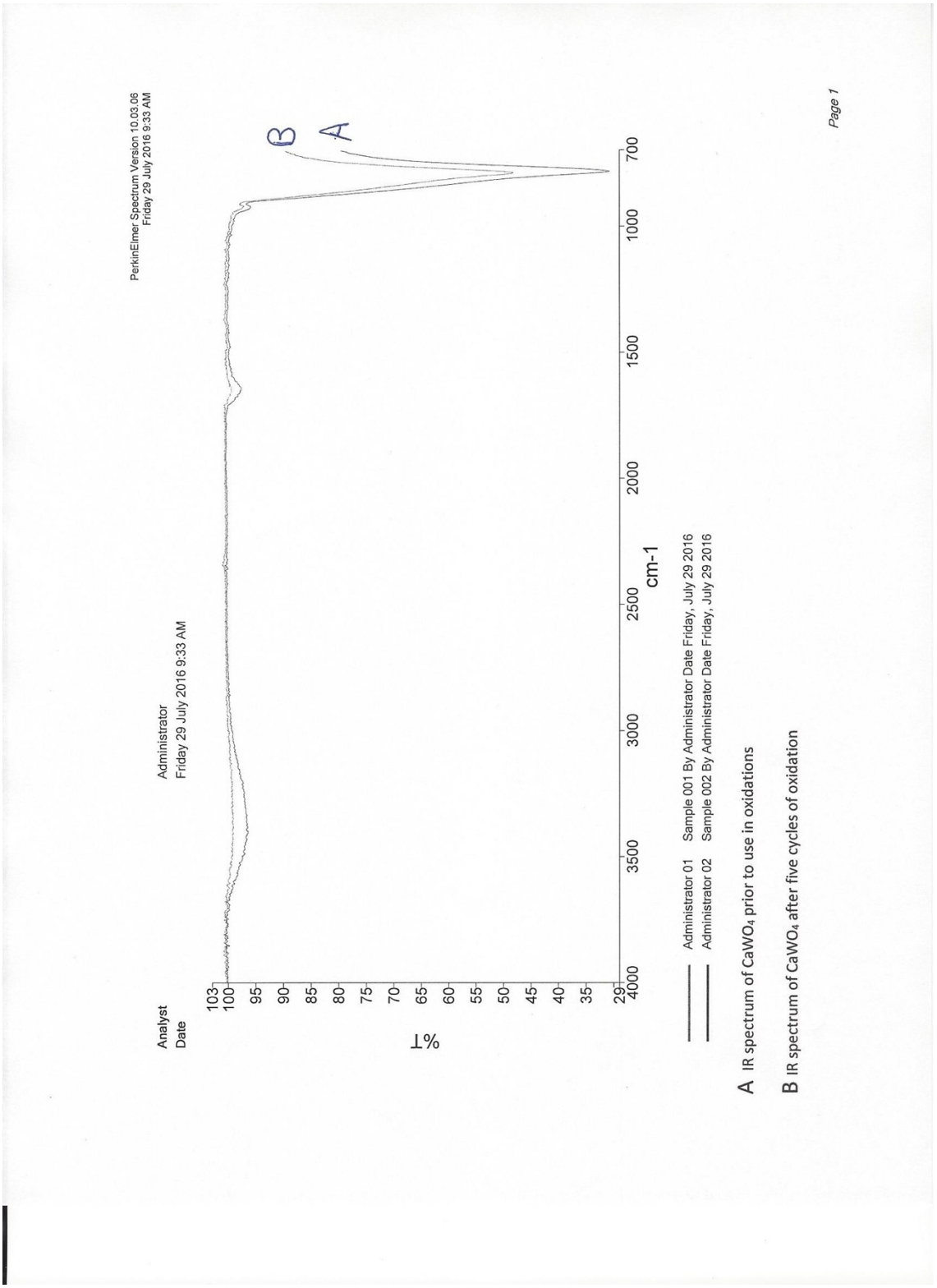
a) $CaWO_4$ prior to oxidations



b) $CaWO_4$ after five cycles of oxidations

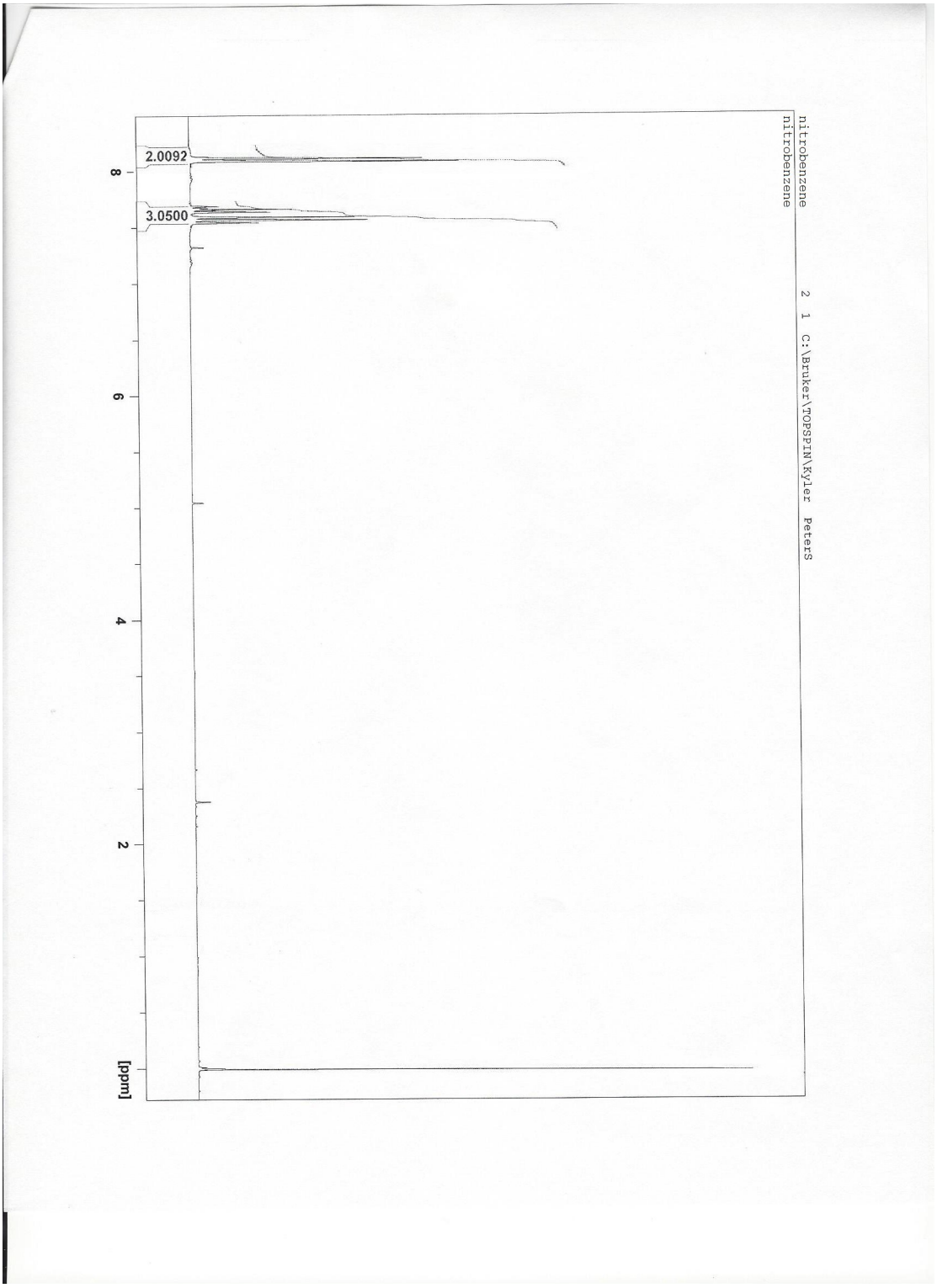


c) Overlay of IR Spectra of $CaWO_4$ before (A) and after (B) five cycles of oxidation

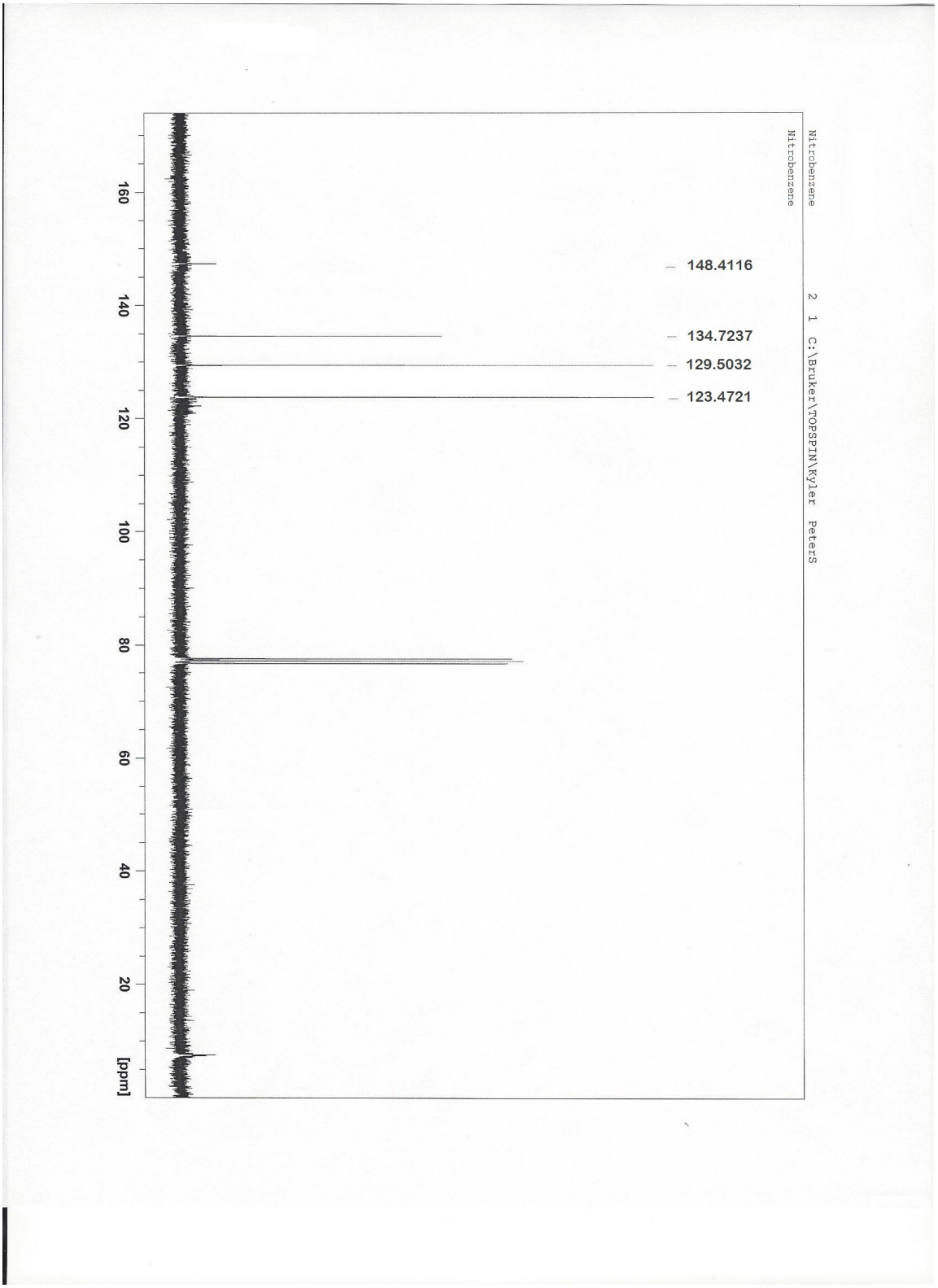


7. All NMR spectra were obtained on a Bruker 300 MHz spectrometer. All Infrared spectra were obtained on a Perkin Elmer Frontier FTIR.

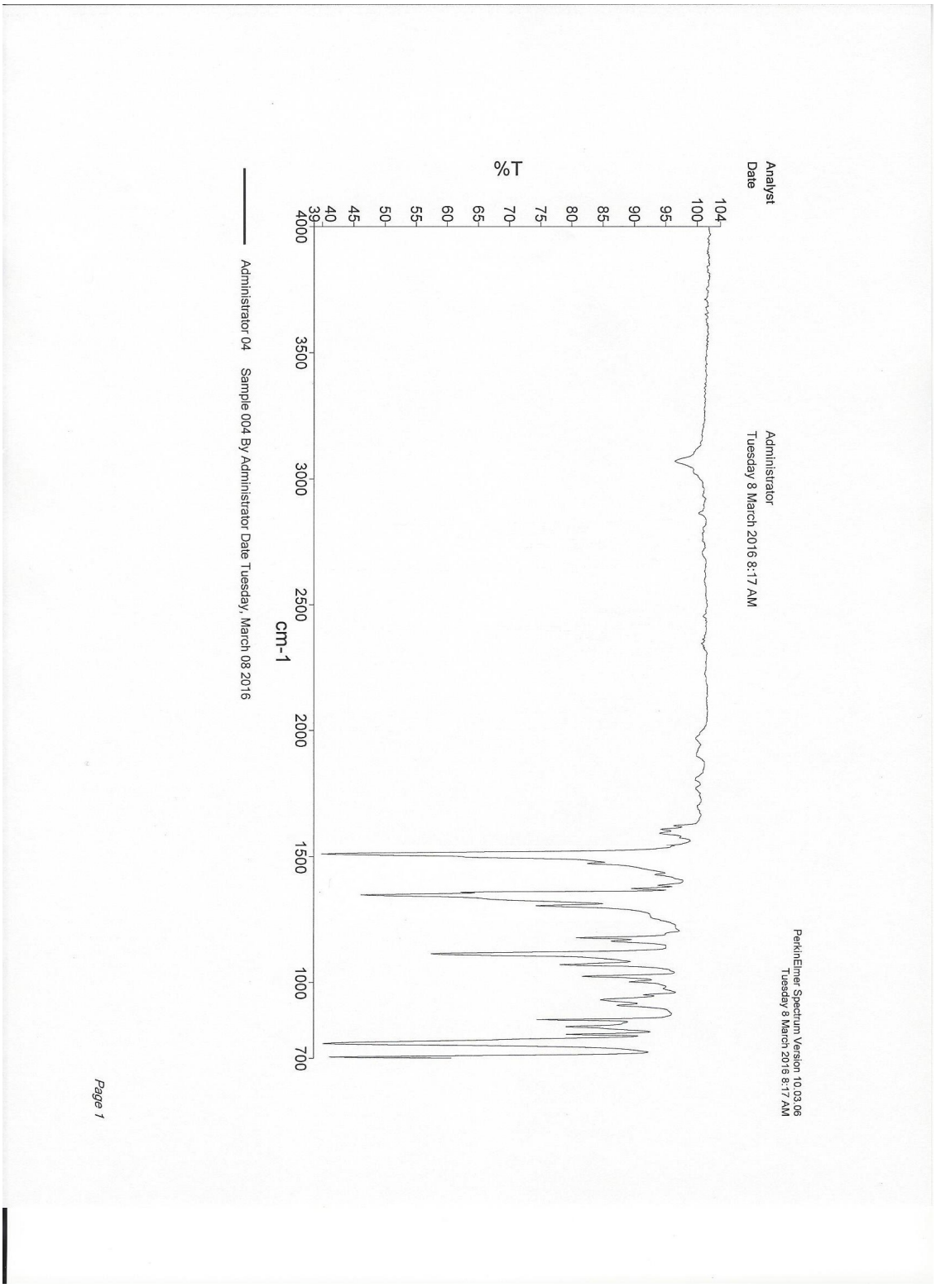
Nitrobenzene: ^{1}H-NMR ($CDCl_3$)



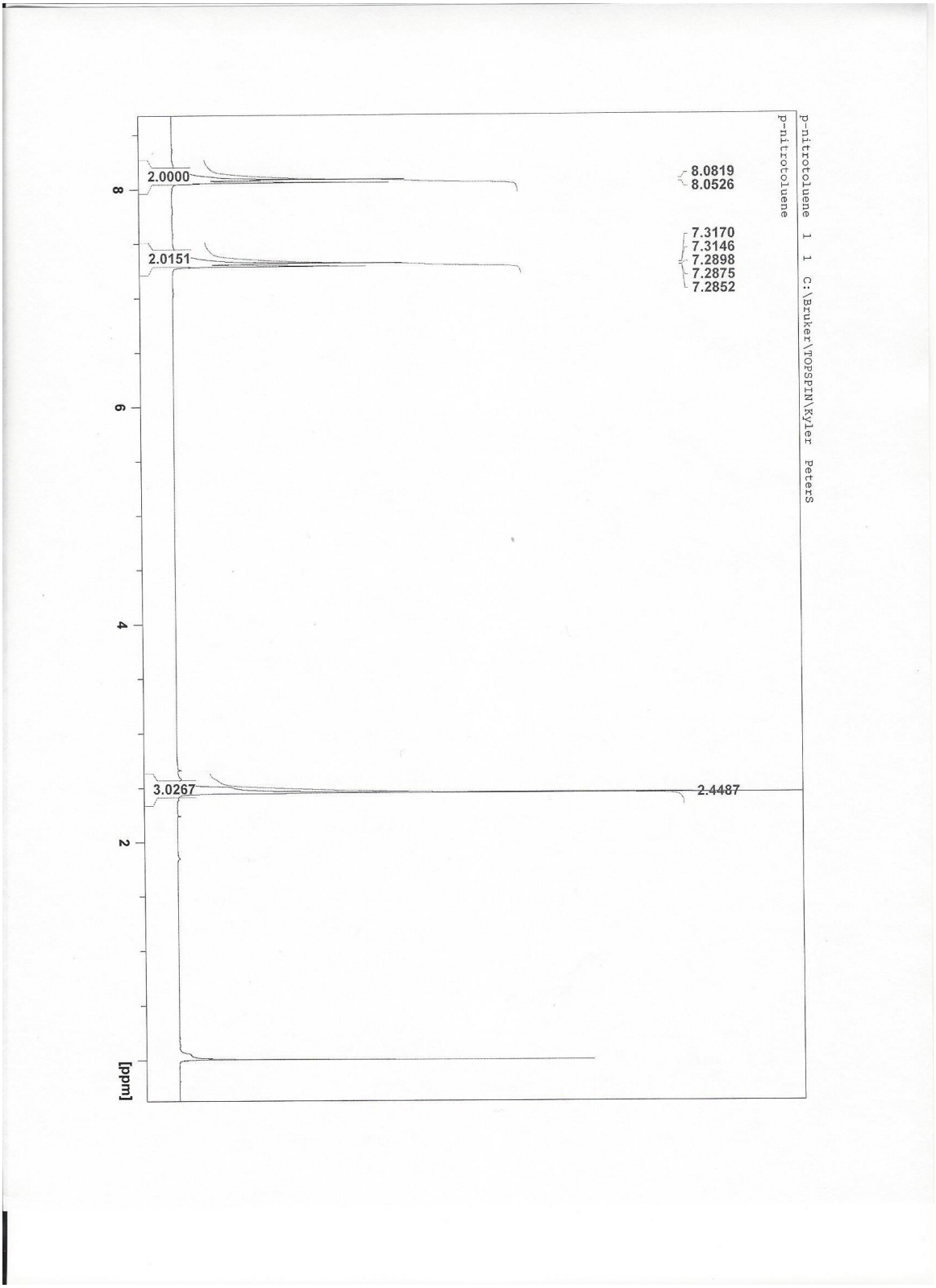
Nitrobenzene: ^{13}C-NMR ($CDCl_3$)



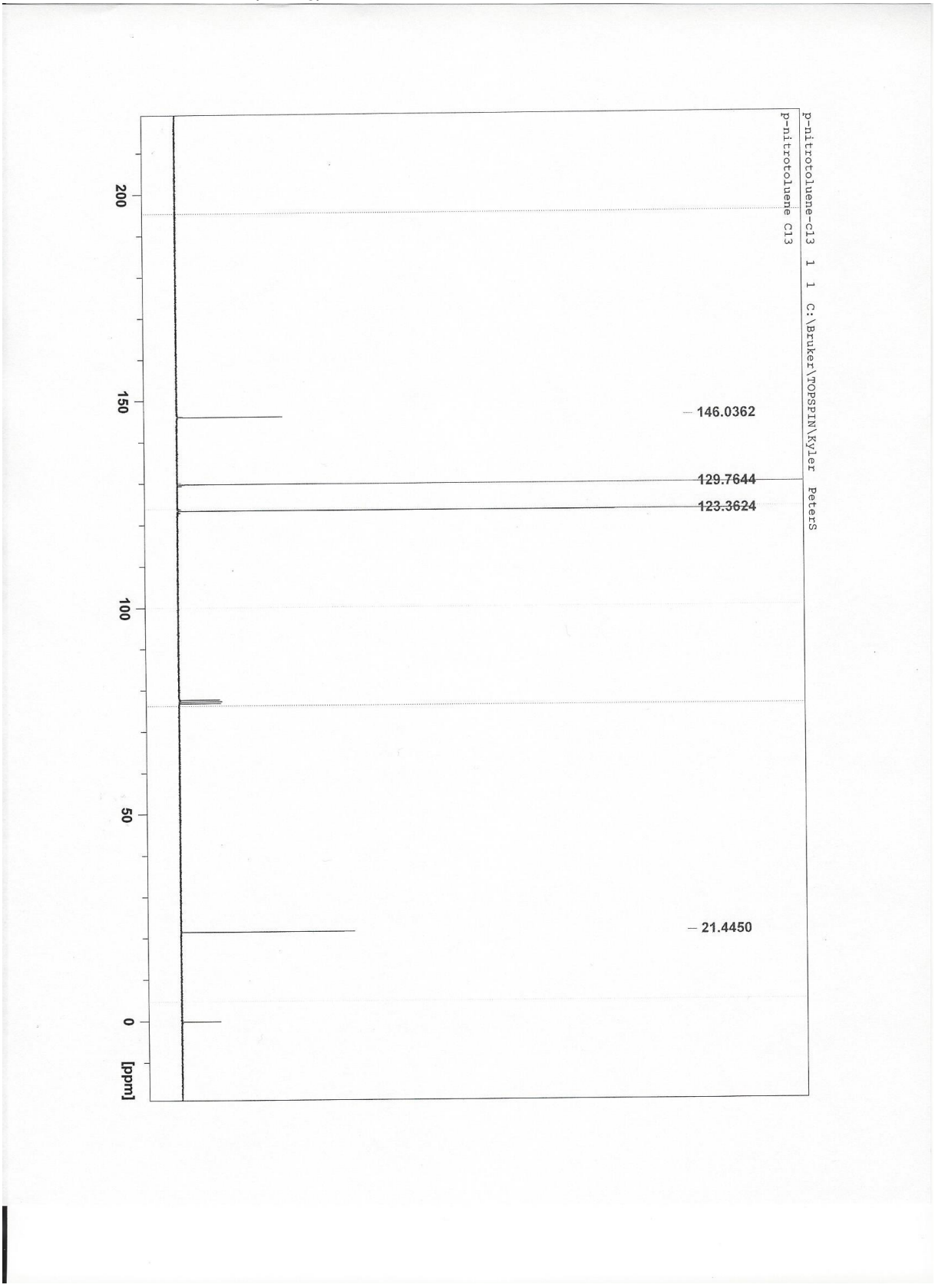
Nitrobenzene: IR



4-nitrotoluene: ^{1}H-NMR ($CDCl_3$)

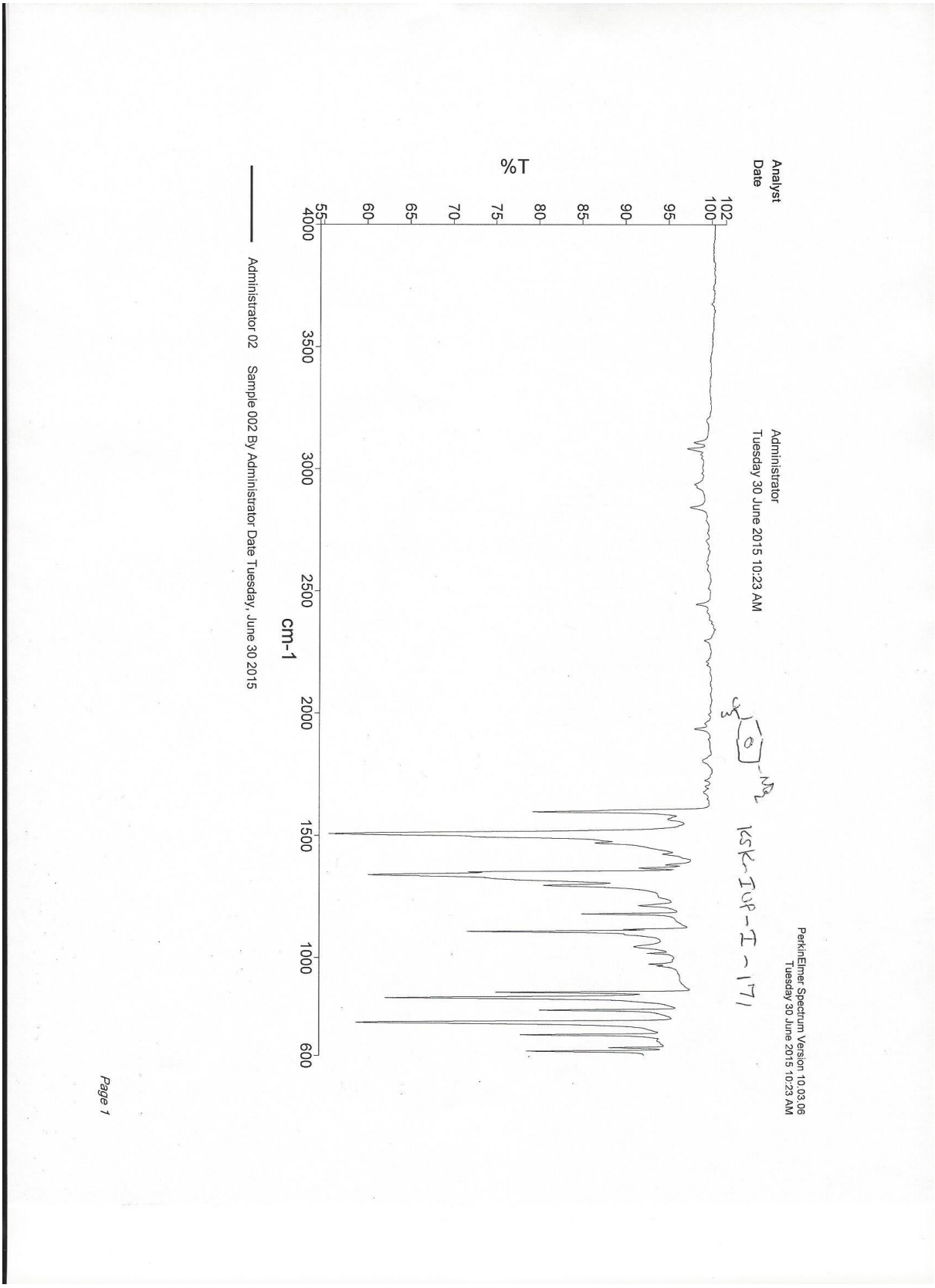


4-nitrotoluene: ^{13}C-NMR ($CDCl_3$)

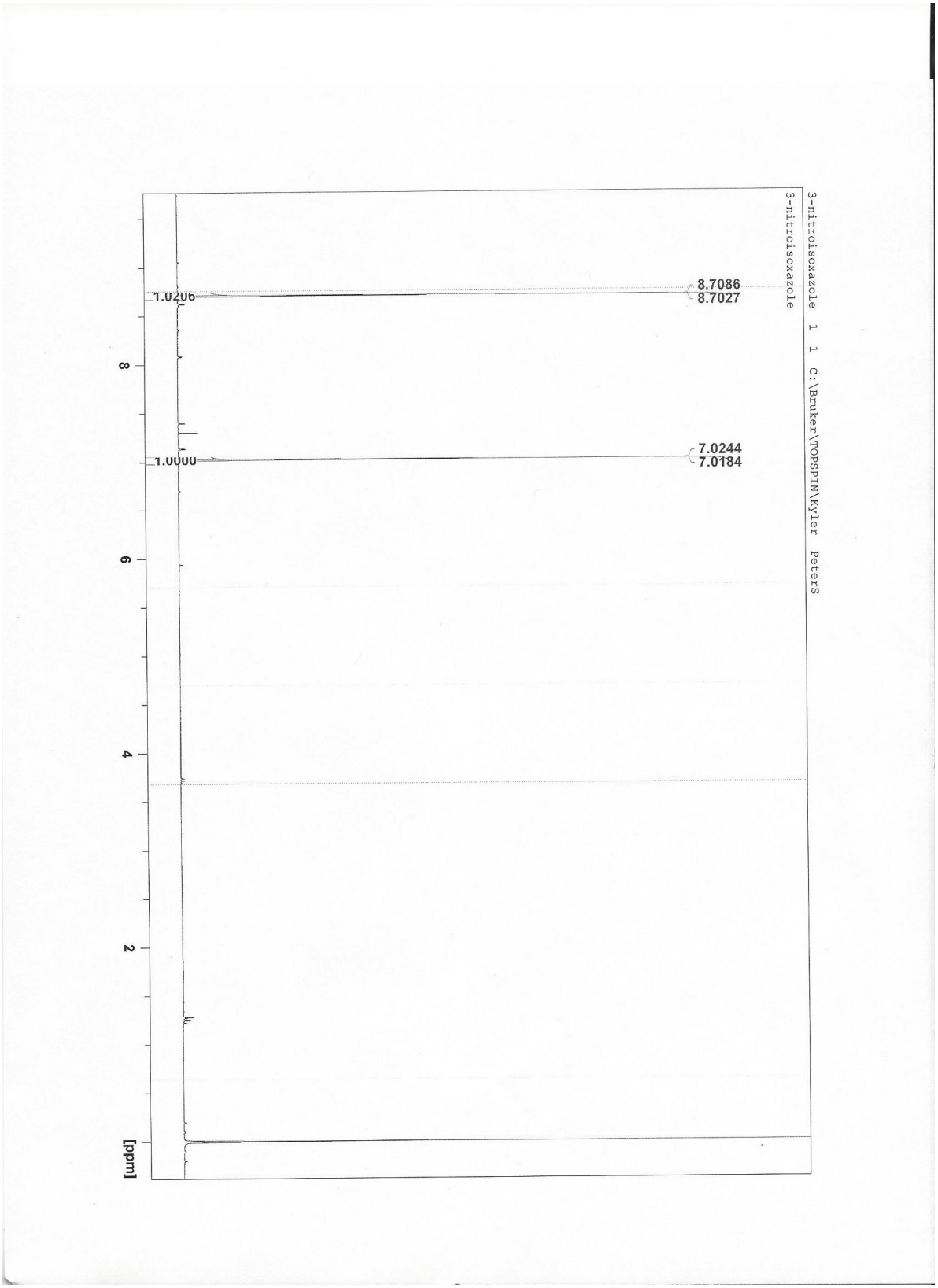


4-

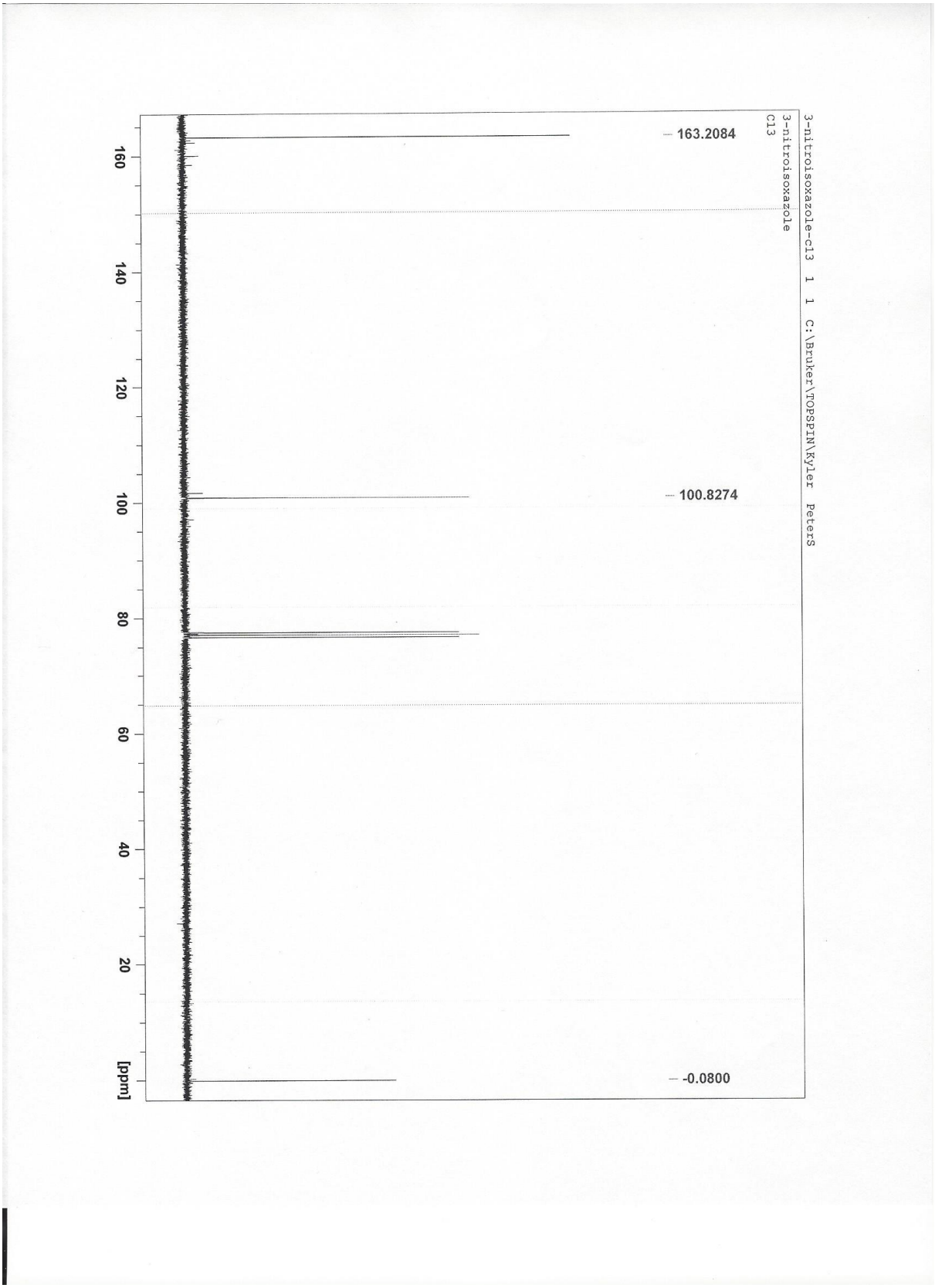
4-nitrotoluene: IR



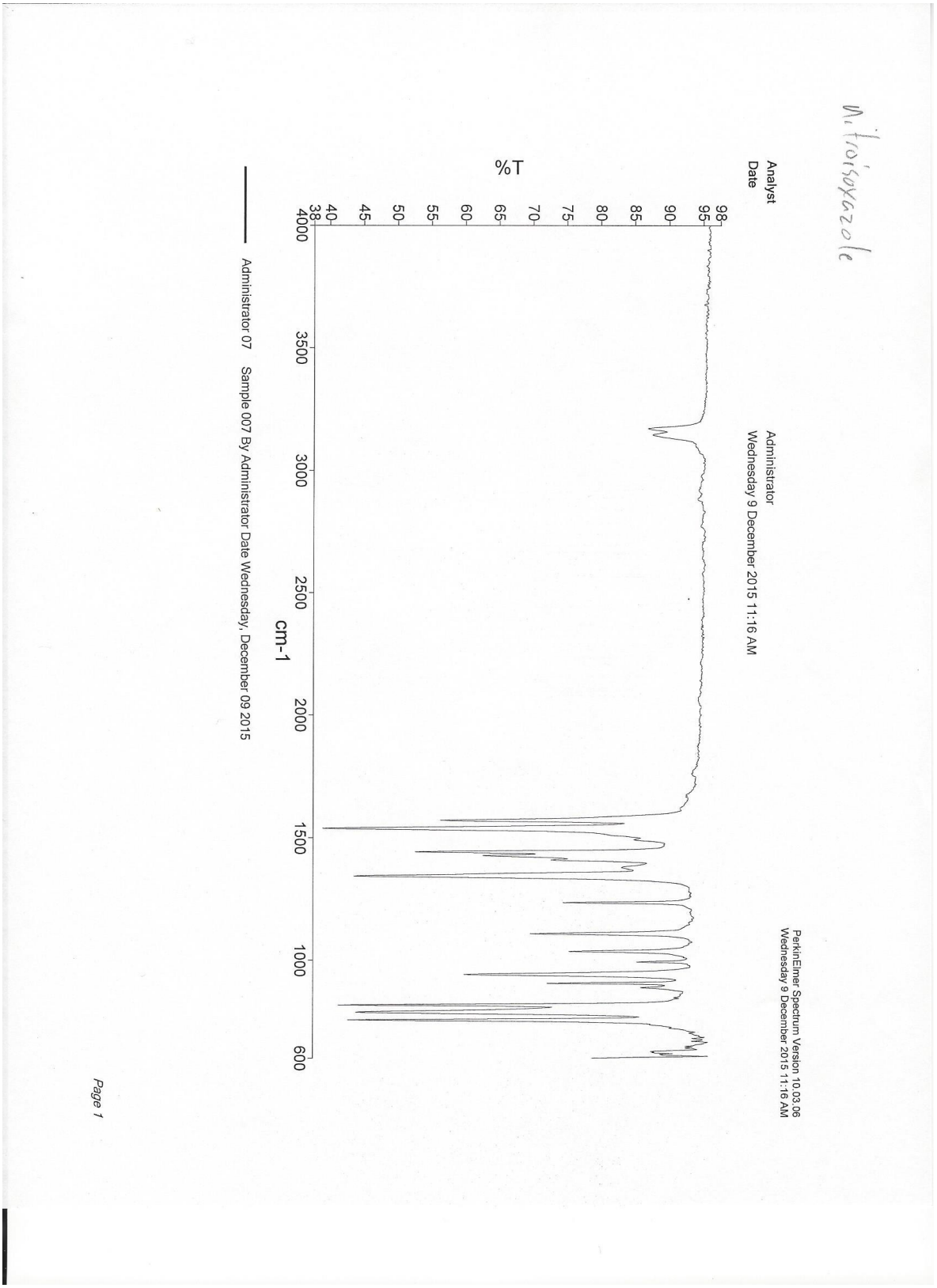
3-nitroisoxazole: ^{1}H-NMR ($CDCl_3$)



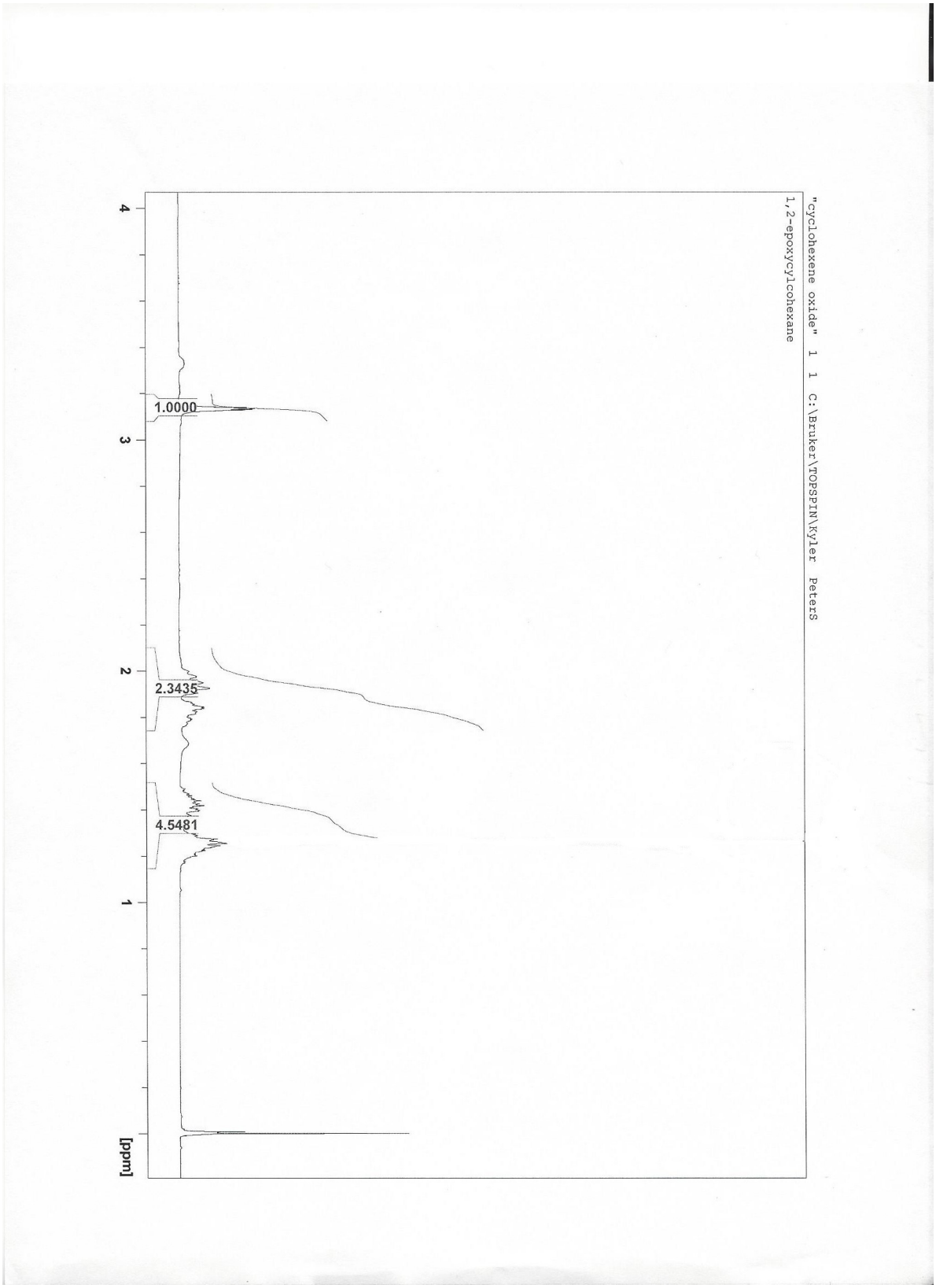
3-nitroisoxazole: ^{13}C-NMR ($CDCl_3$)



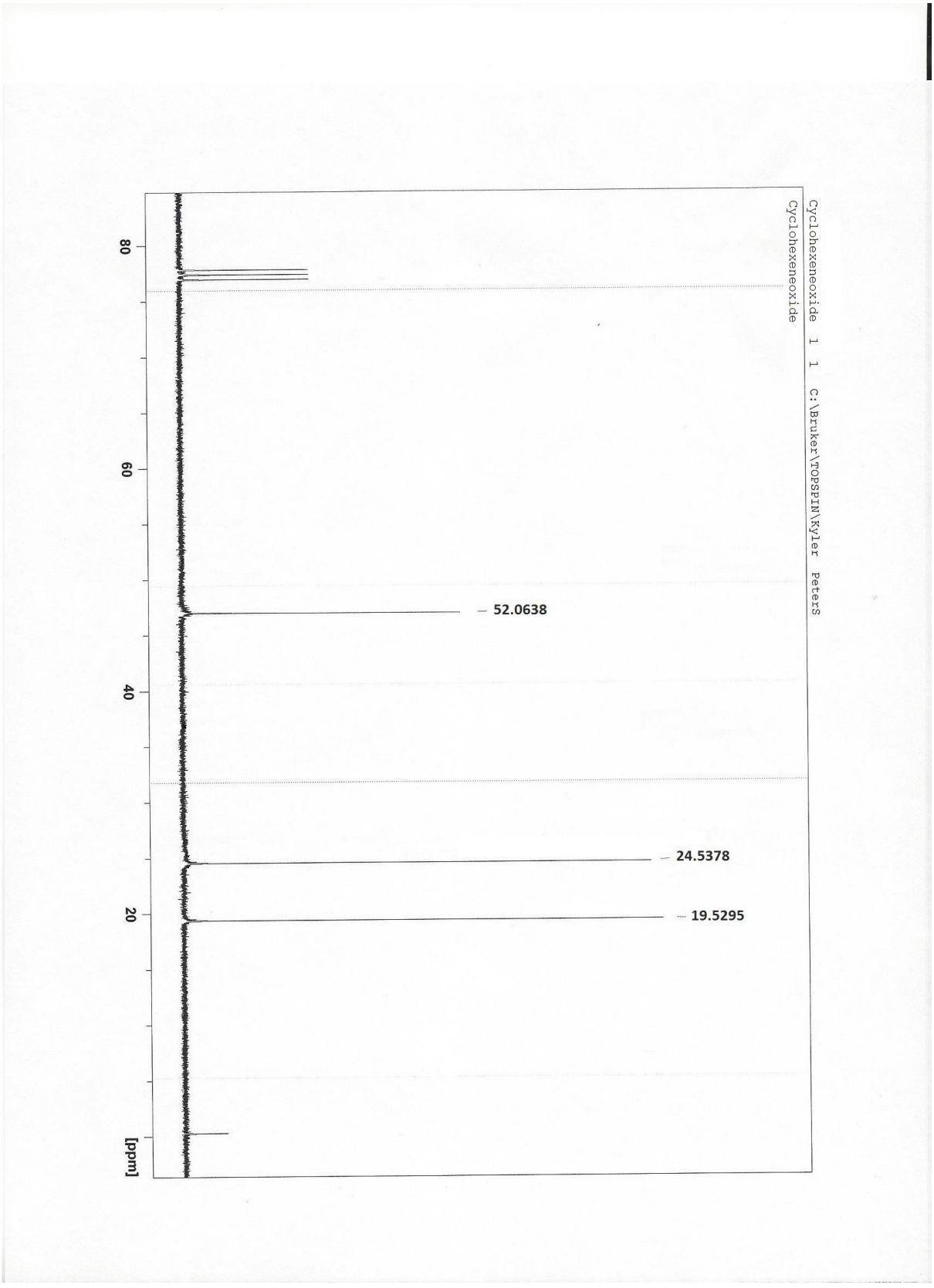
3-nitroisoxazole: IR



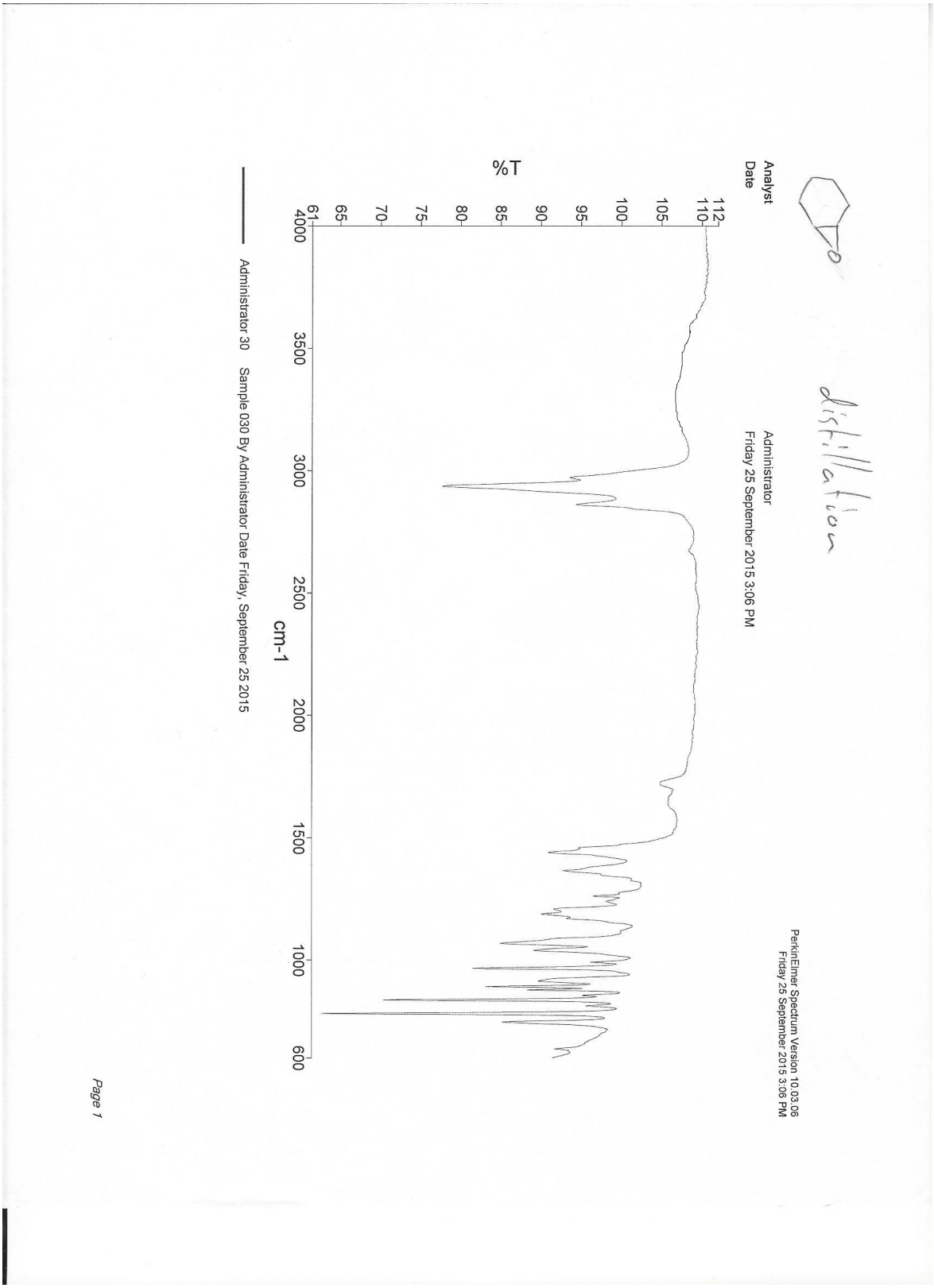
Cyclohexene oxide: ^{1}H-NMR ($CDCl_3$)



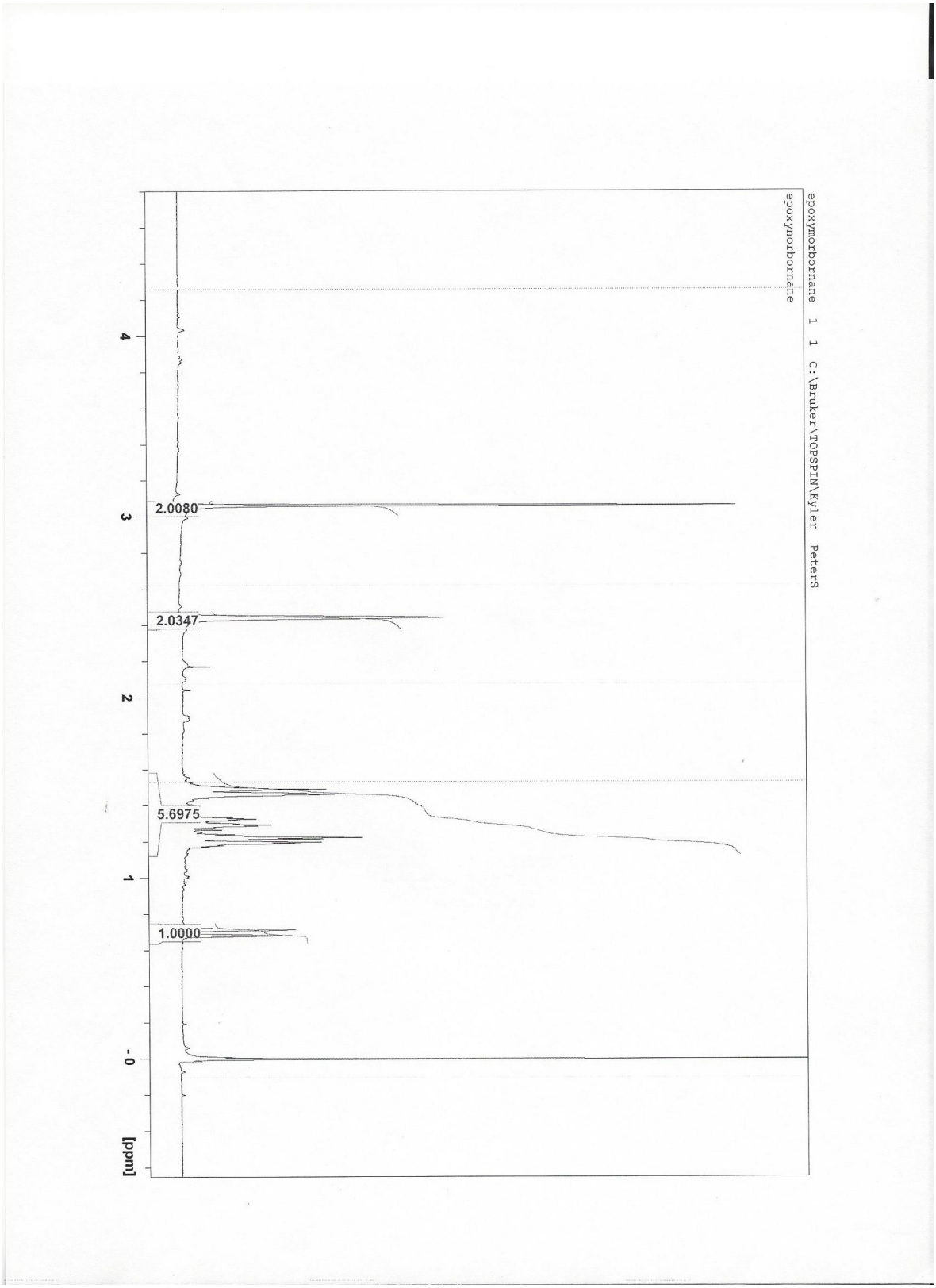
Cyclohexene oxide: ^{13}C-NMR ($CDCl_3$)



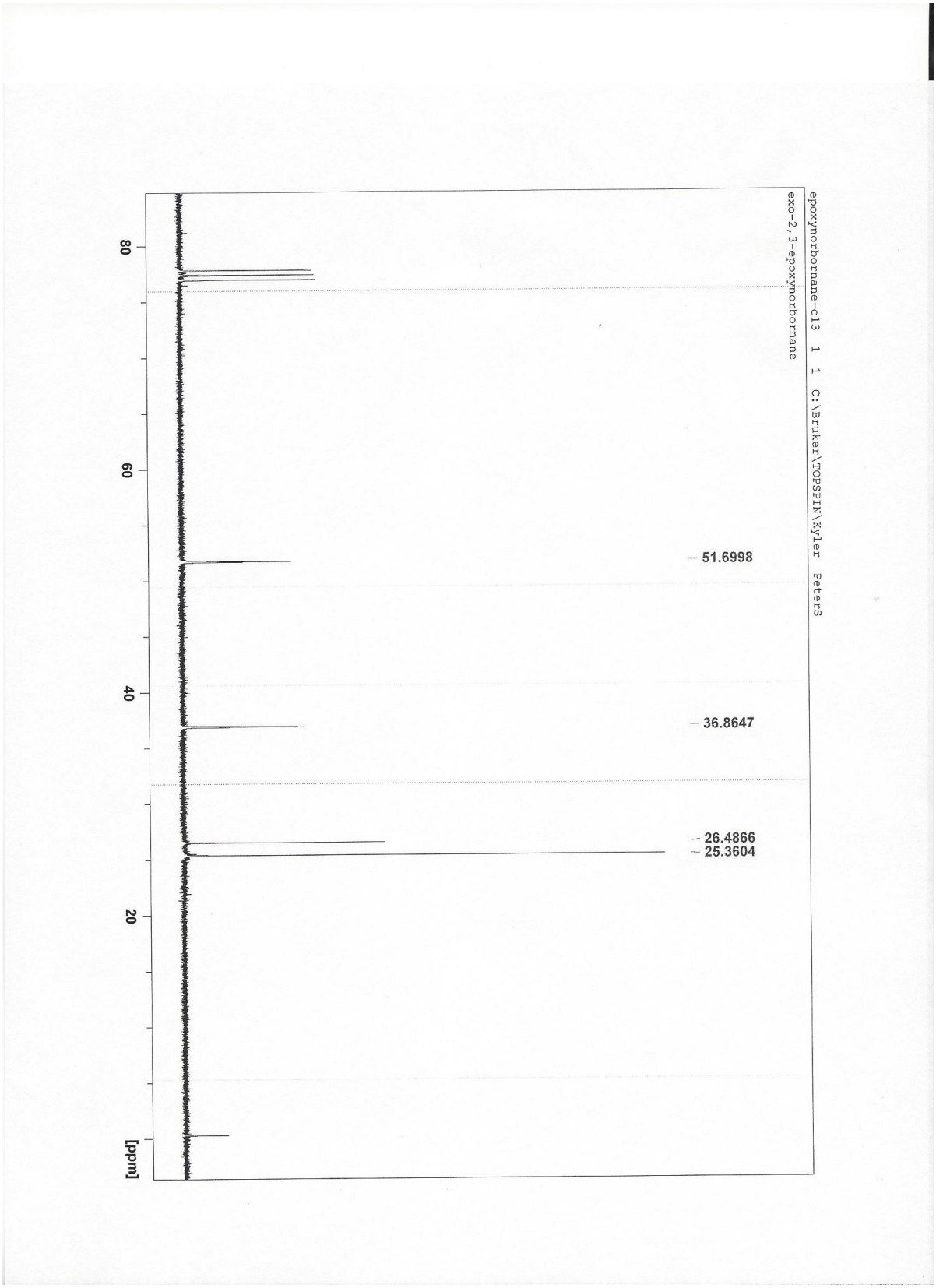
Cyclohexene oxide: IR



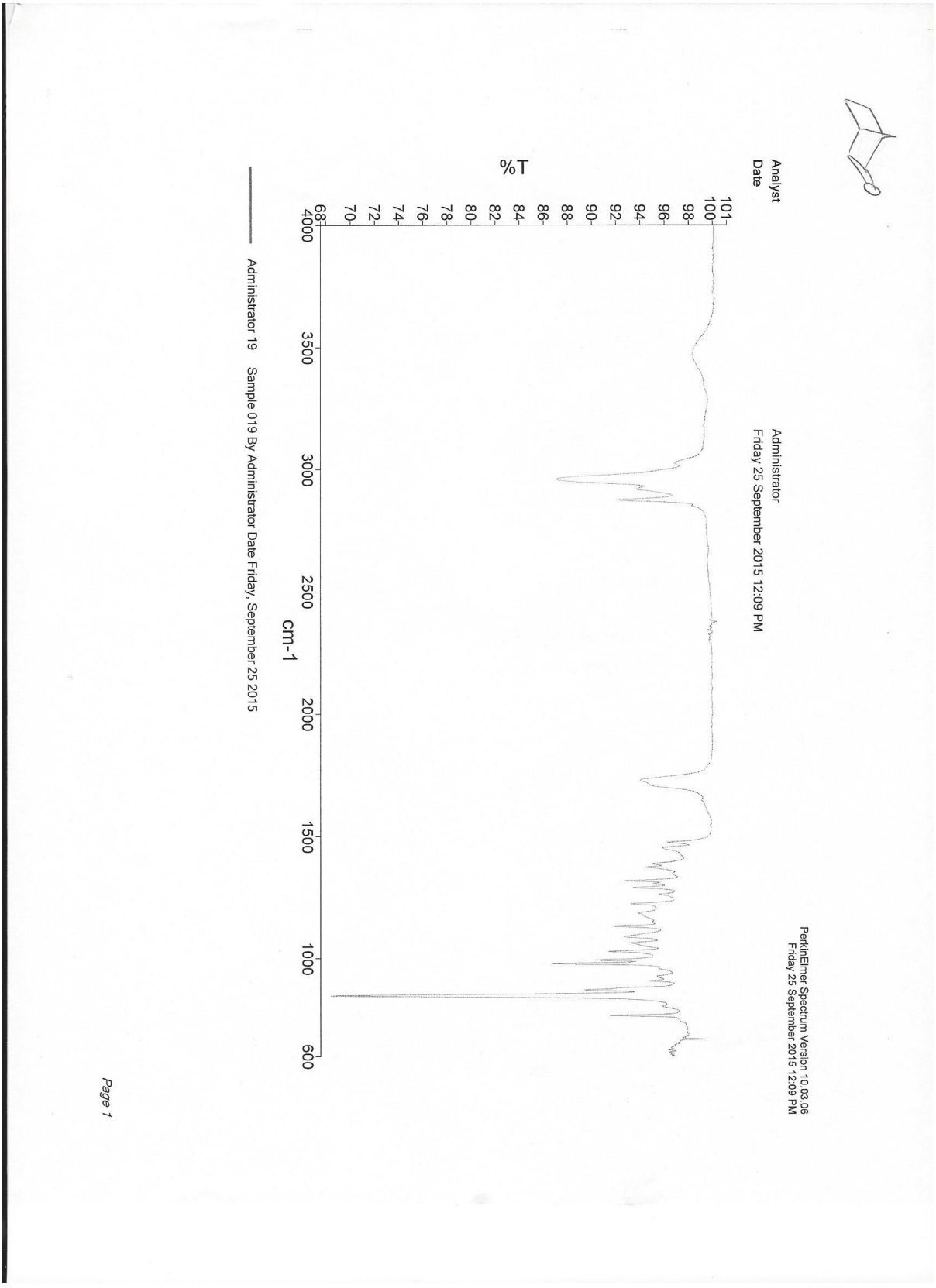
Expoxynorbornane: ^{1}H-NMR ($CDCl_3$)



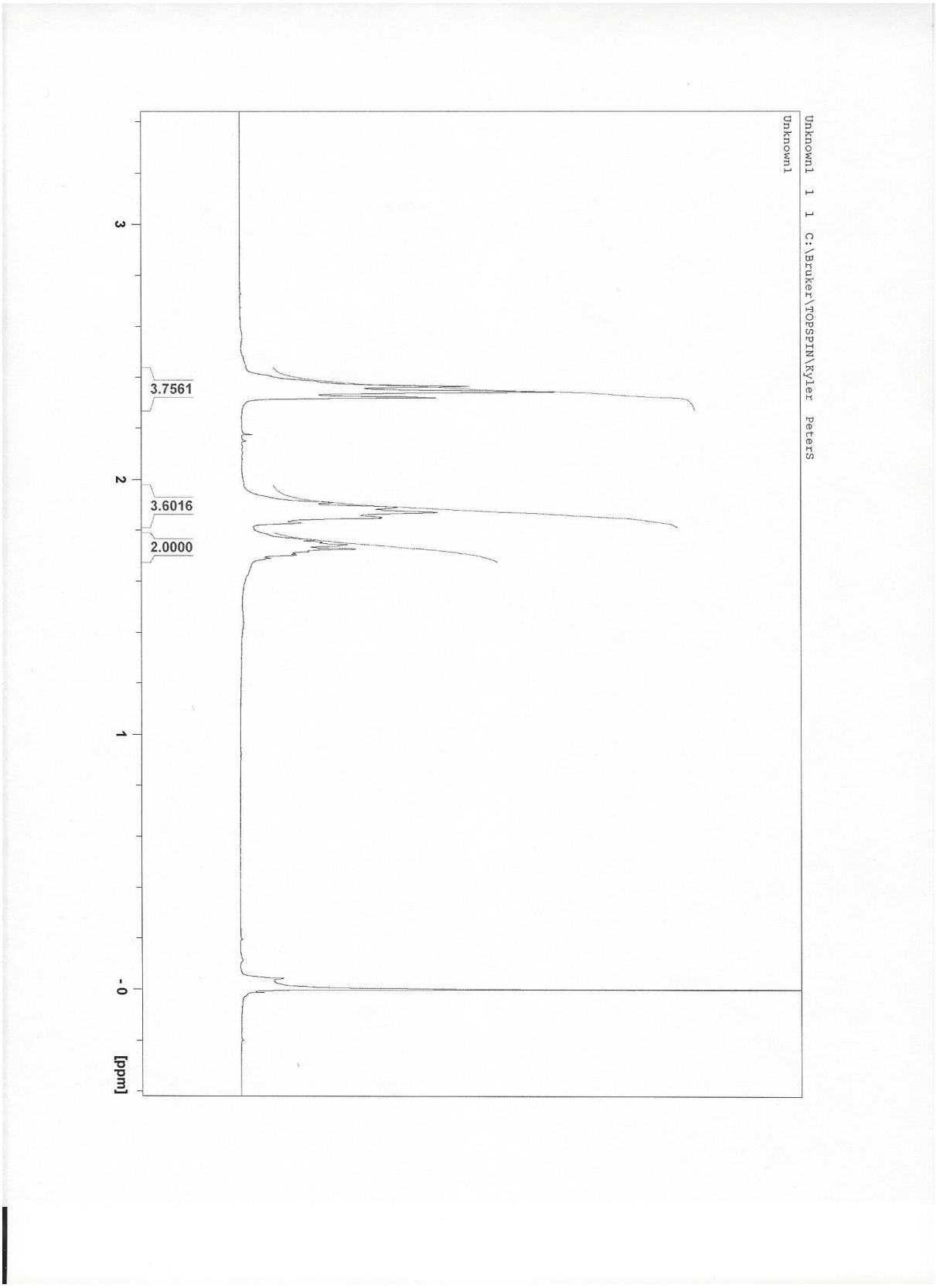
Epoxynorbonane: ^{13}C-NMR ($CDCl_3$)



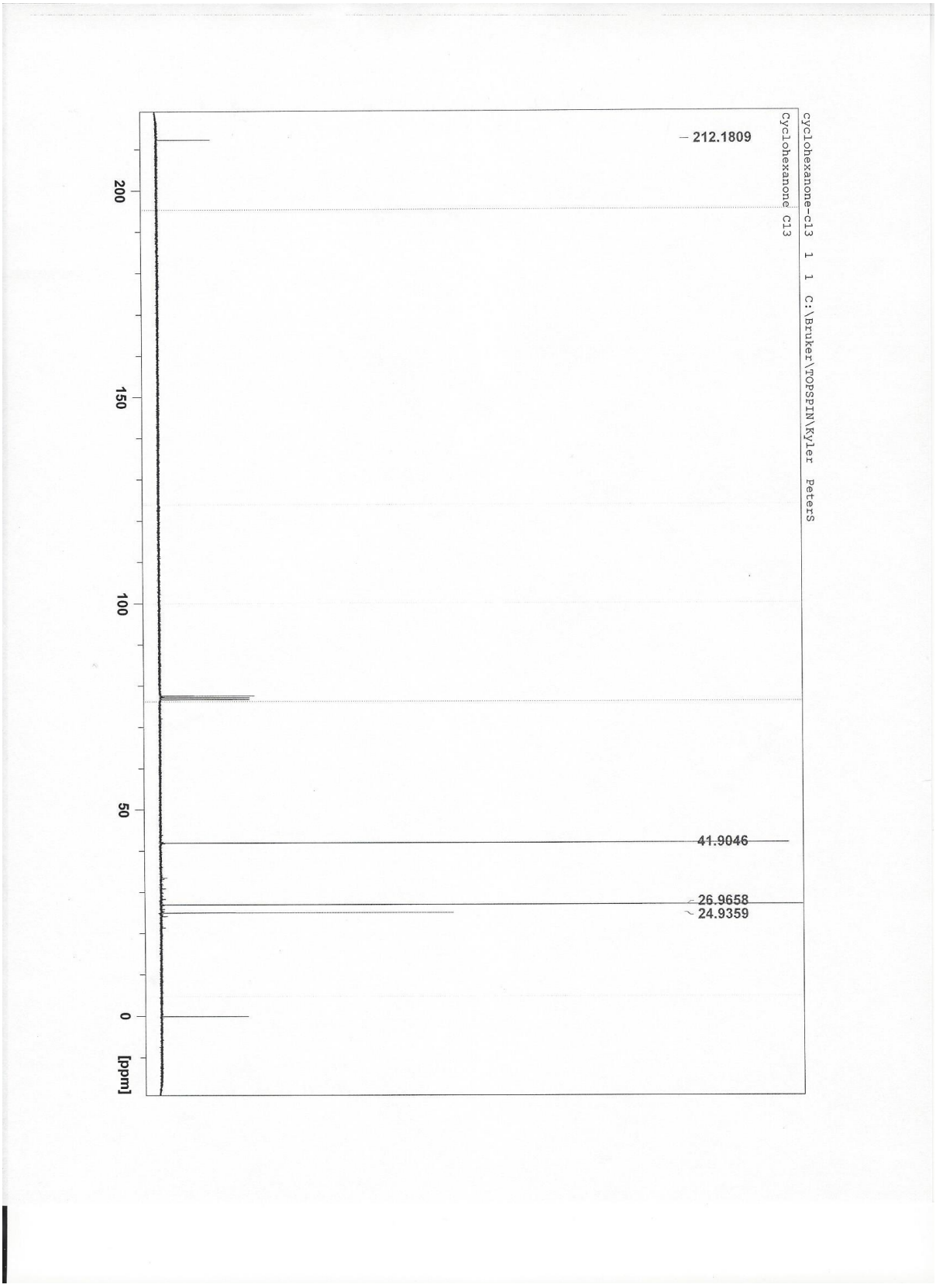
Epoxynorbornane: IR



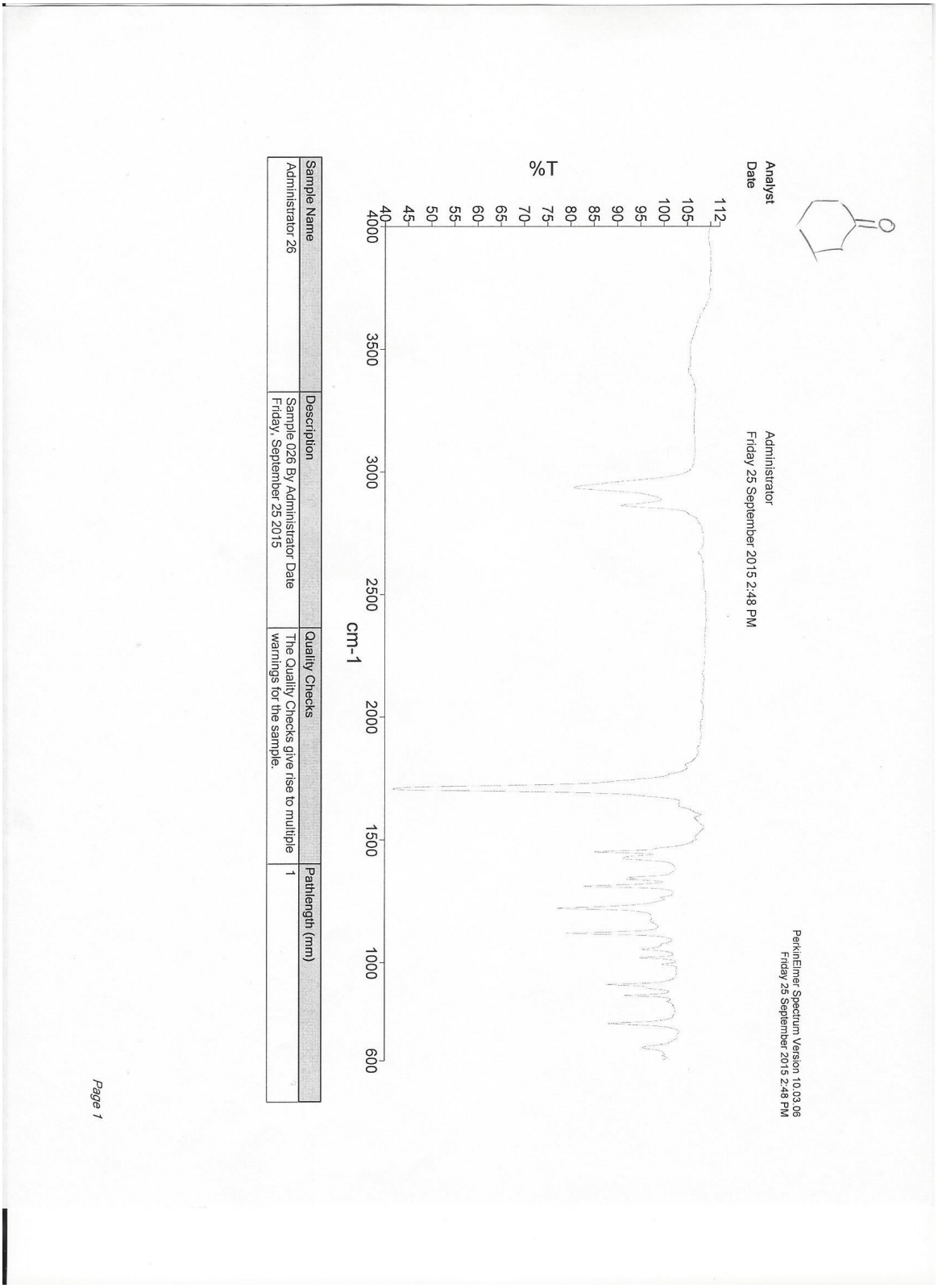
Cyclohexanone: ^{1}H-NMR ($CDCl_3$)



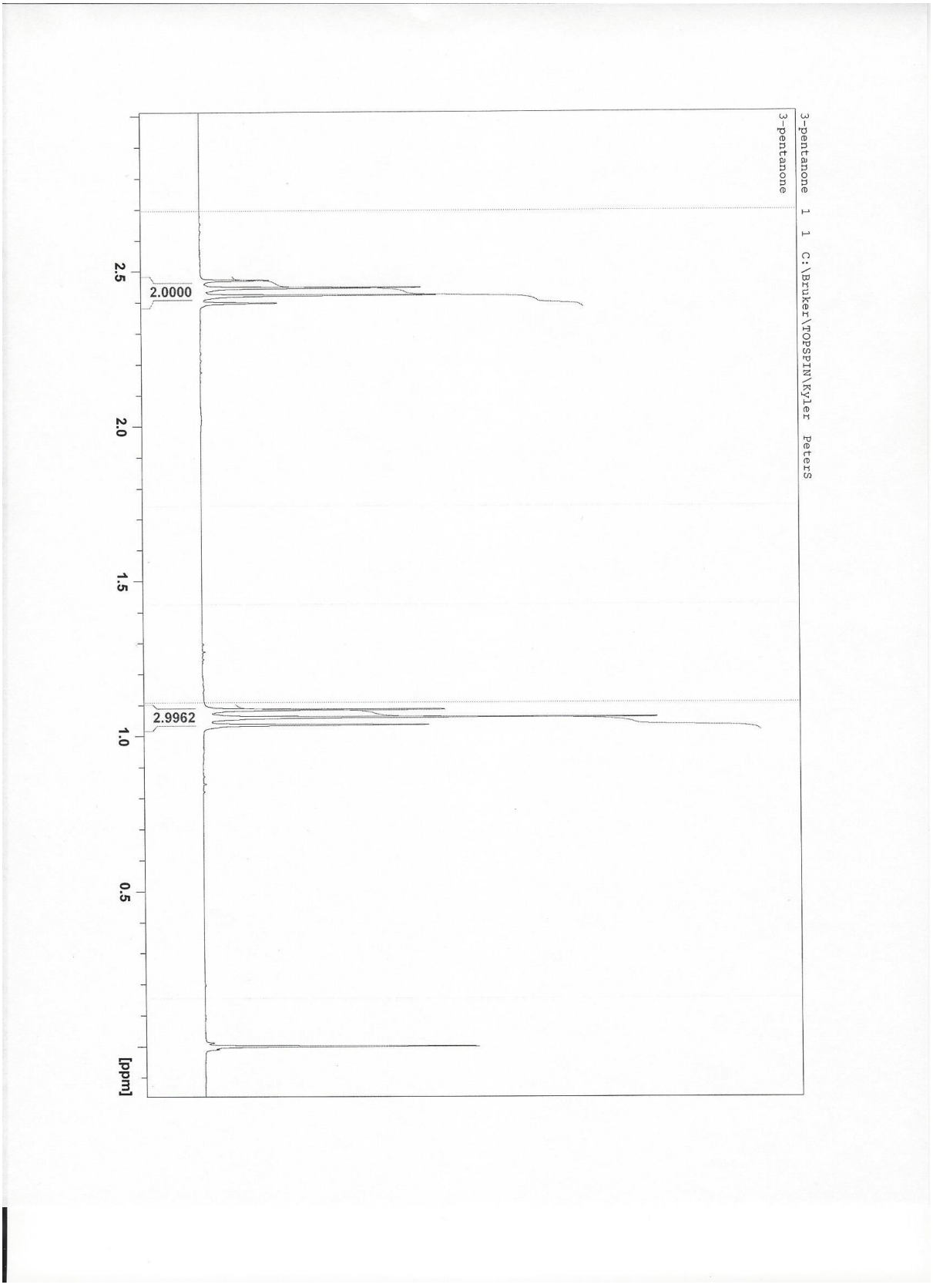
Cyclohexanone: ^{13}C-NMR ($CDCl_3$)



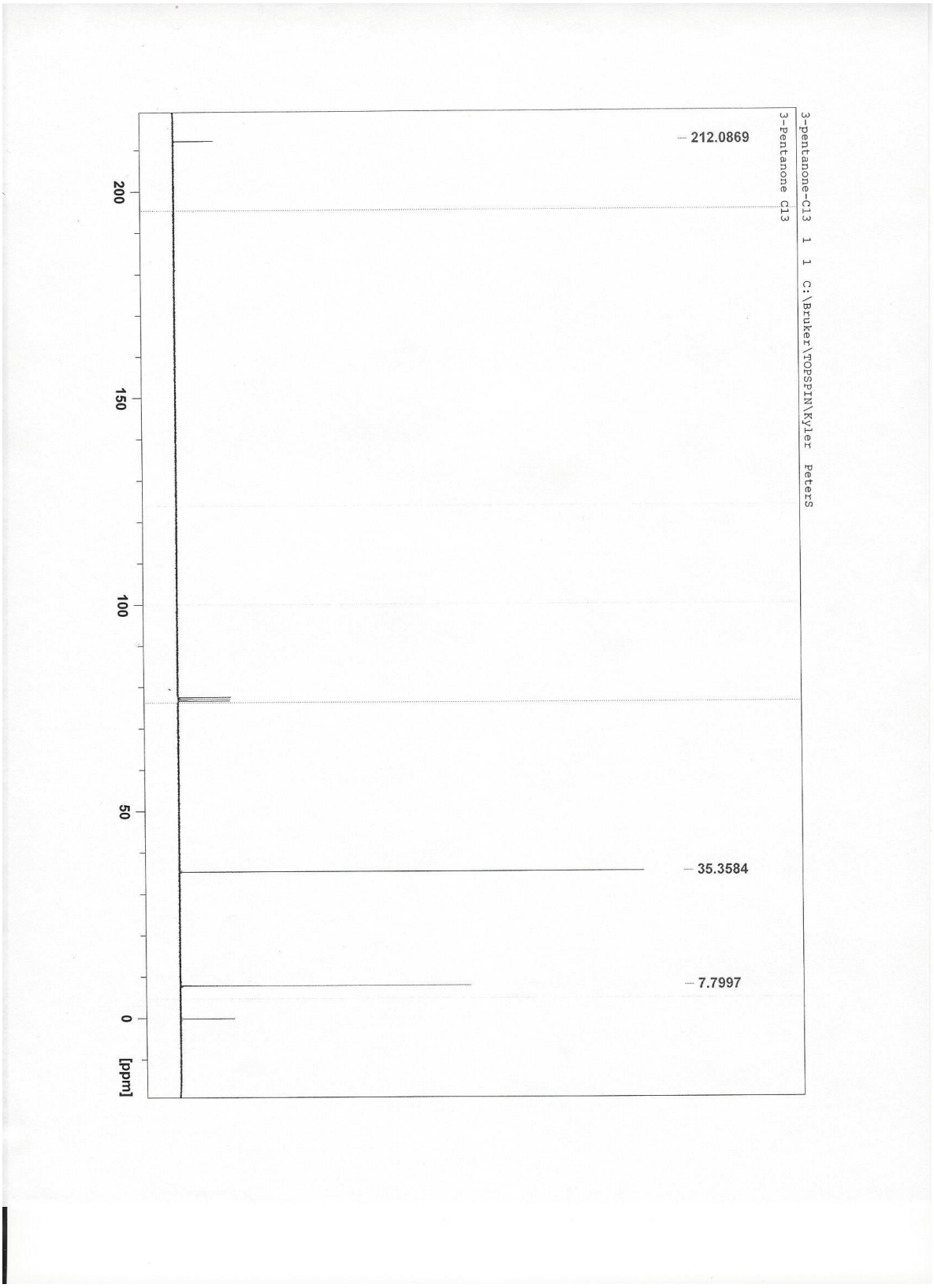
Cyclohexanone: IR



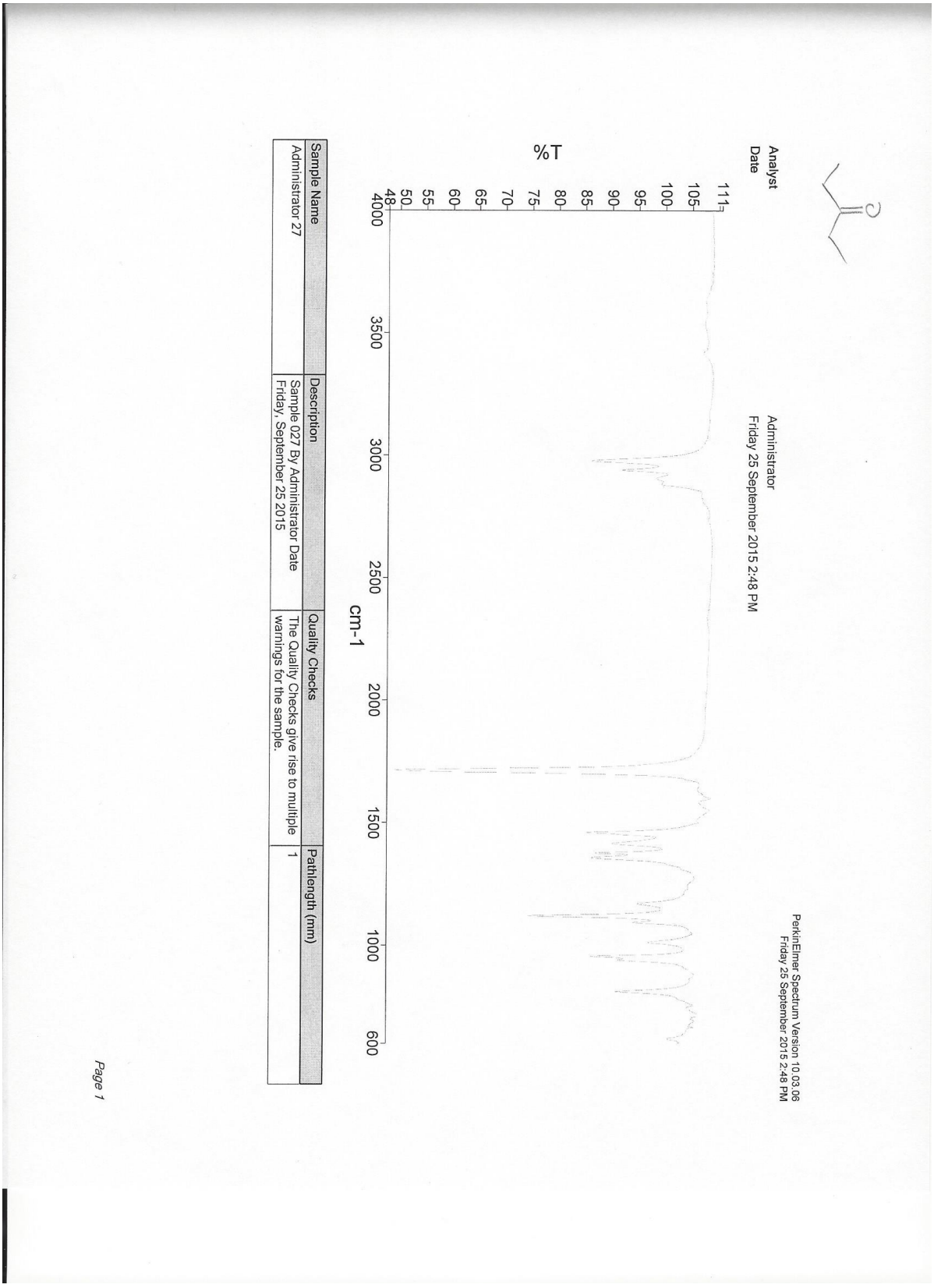
3-pentanone: ^{1}H-NMR ($CDCl_3$)



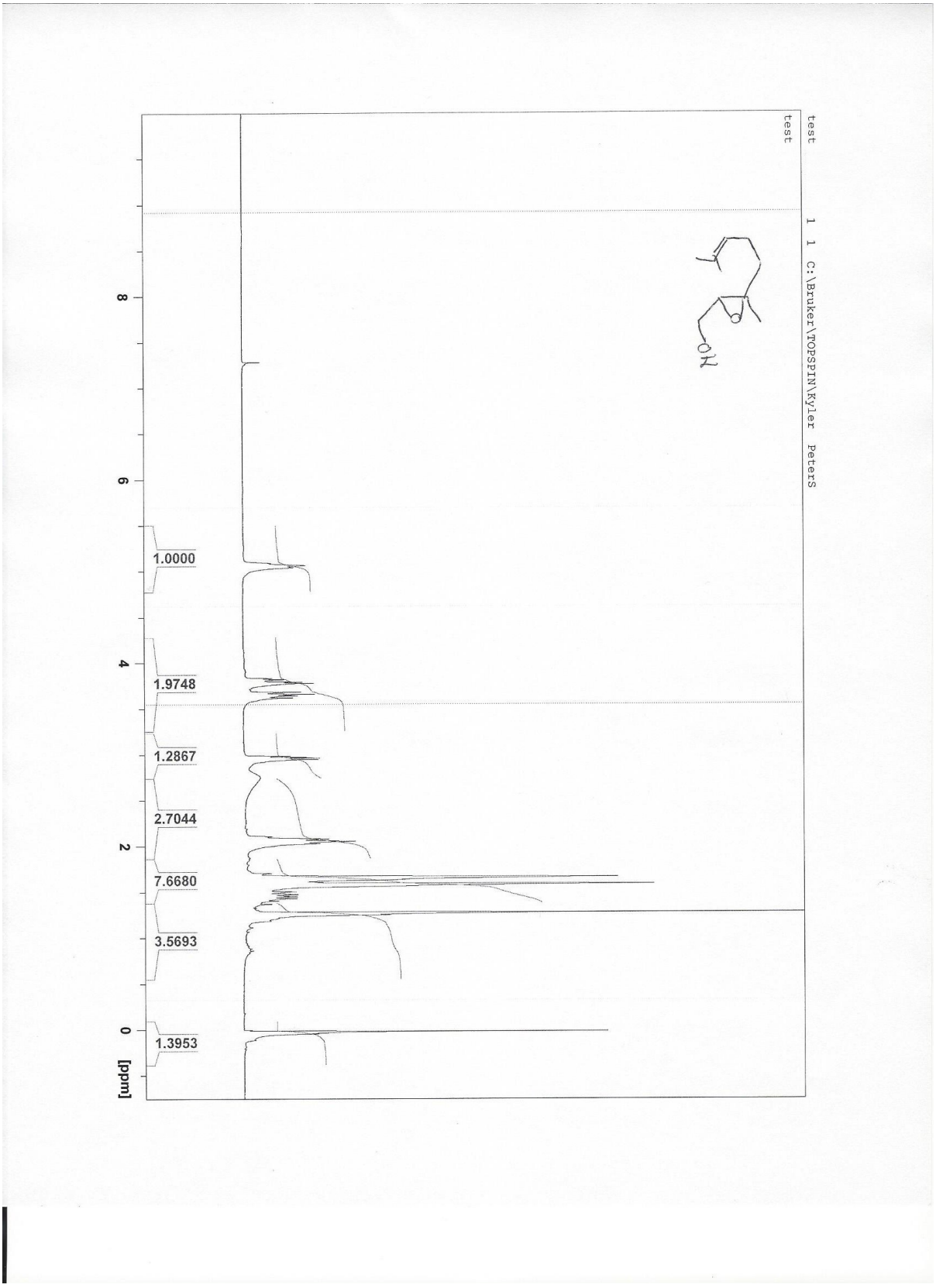
3-pentanone: ^{13}C-NMR ($CDCl_3$)



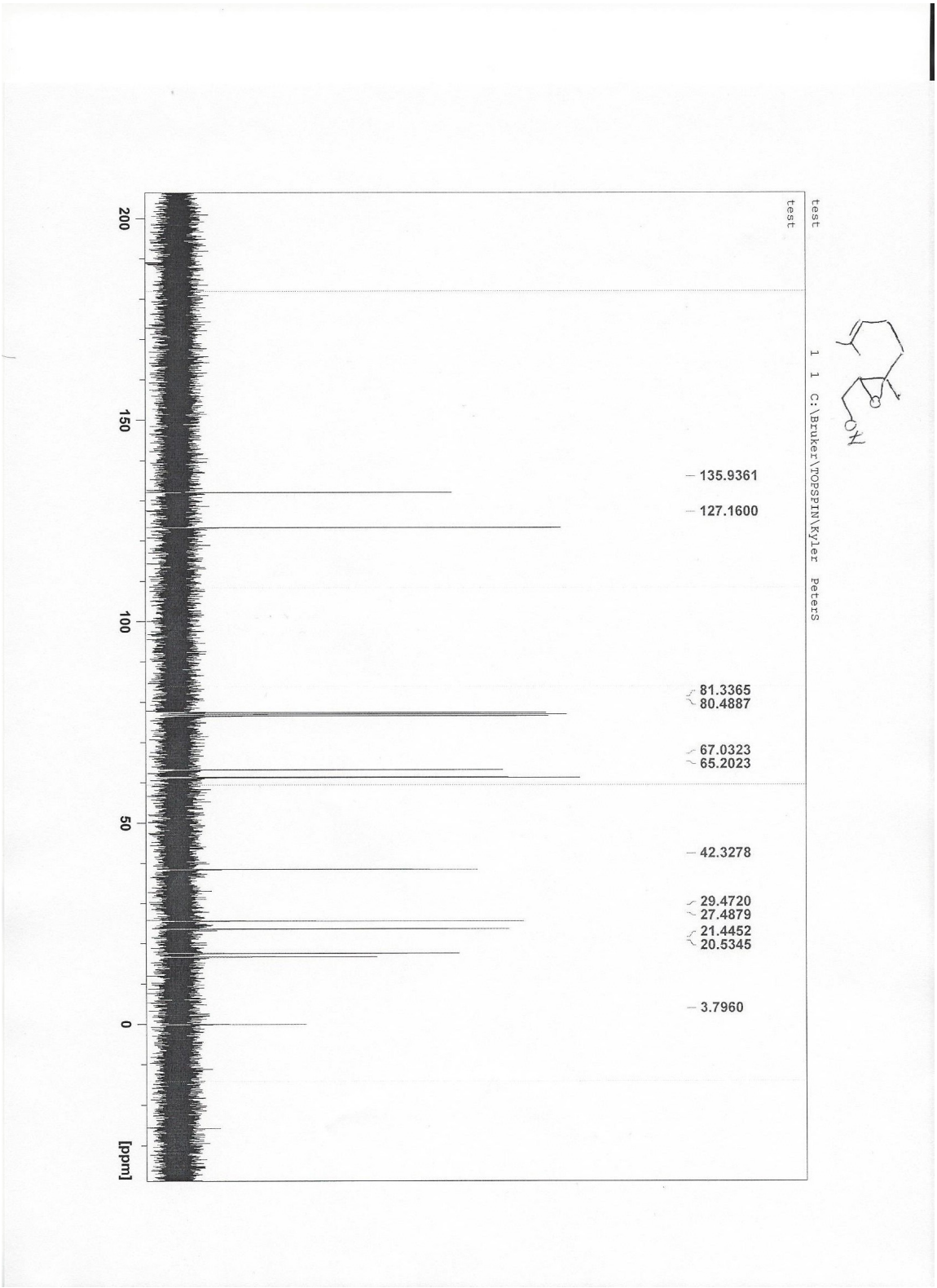
3-pentanone: IR



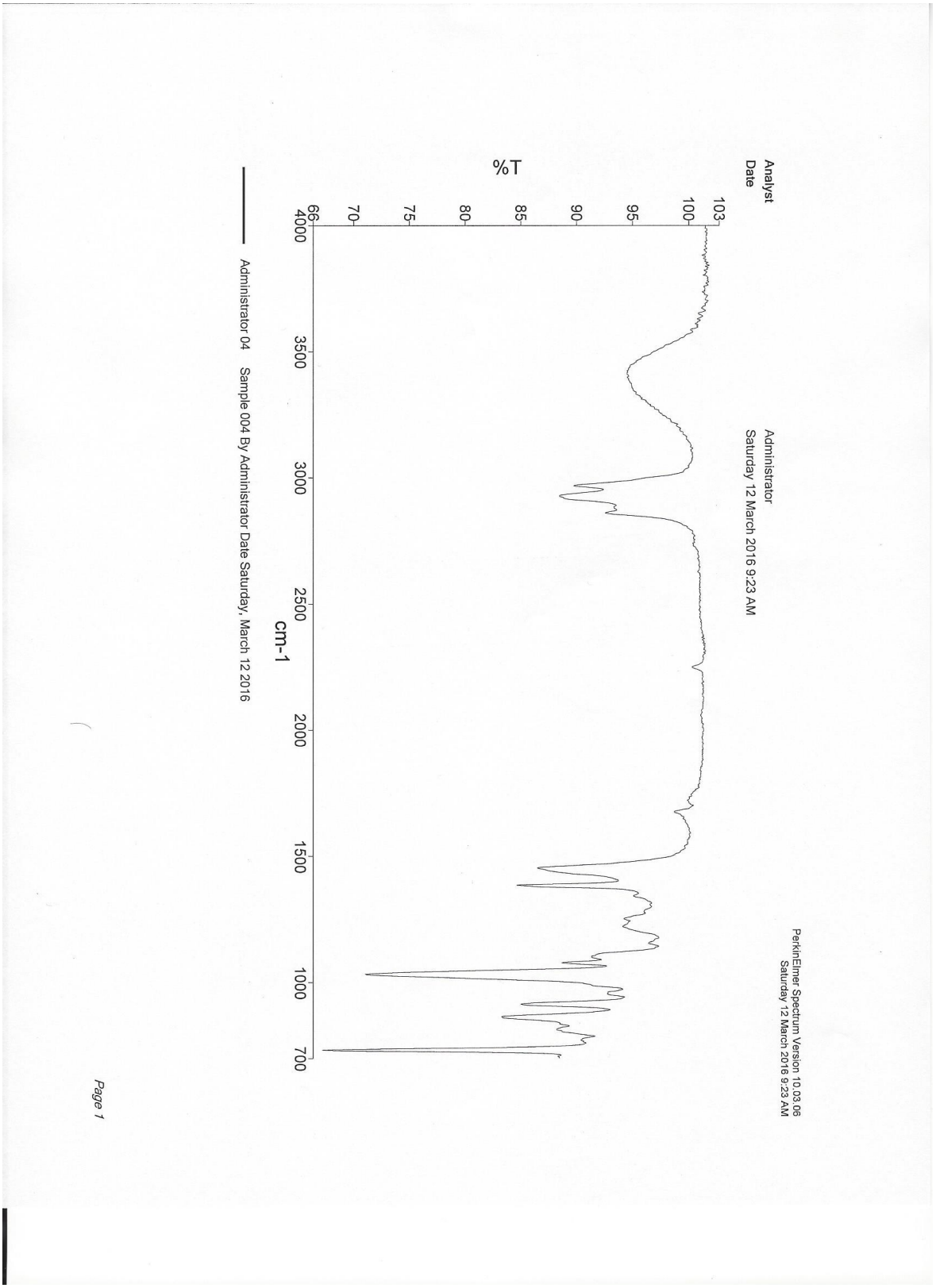
2,3-Epoxygeraniol: ^{1}H-NMR ($CDCl_3$)



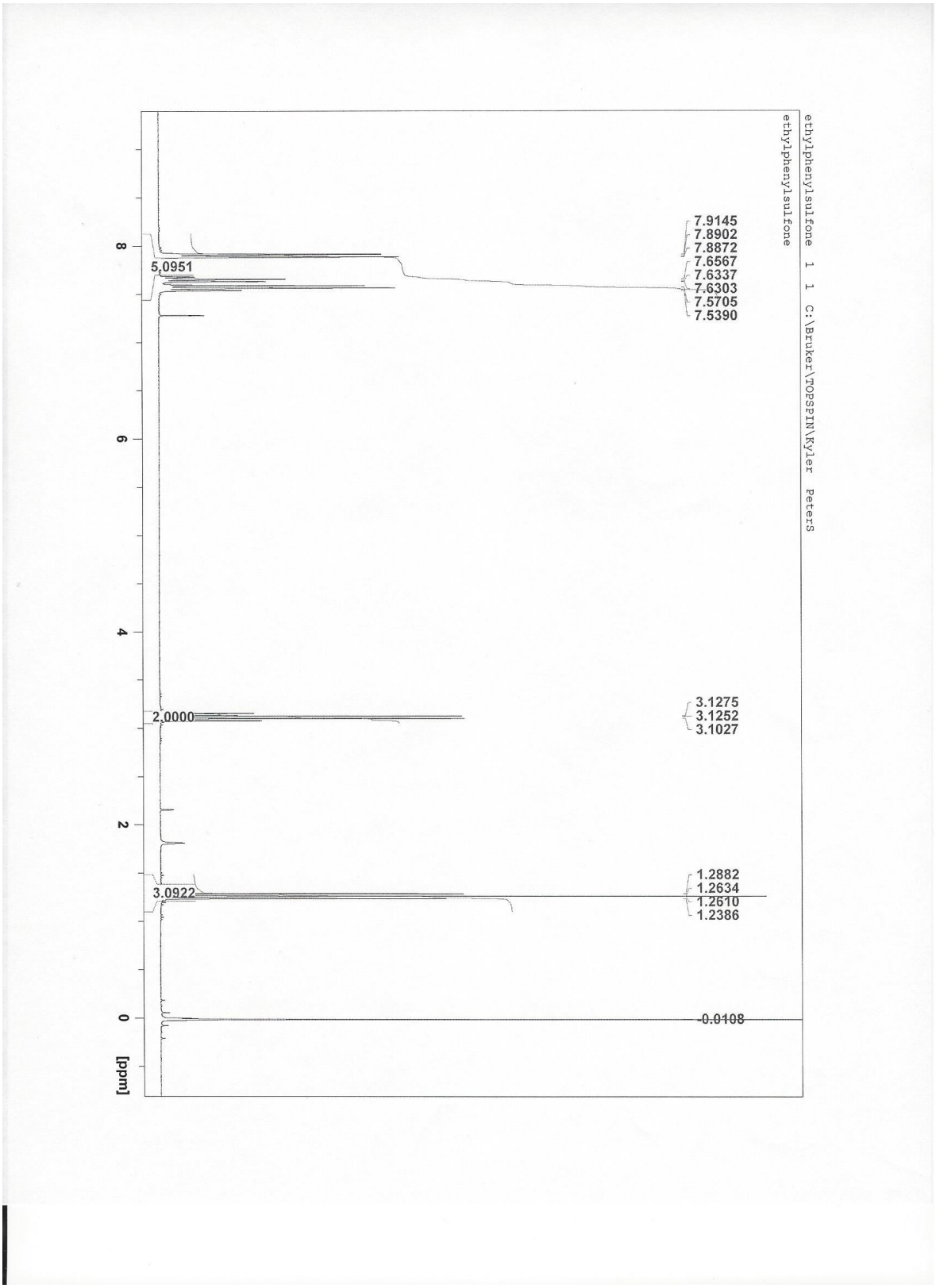
2,3-Epoxygeraniol: ^{13}C-NMR ($CDCl_3$)



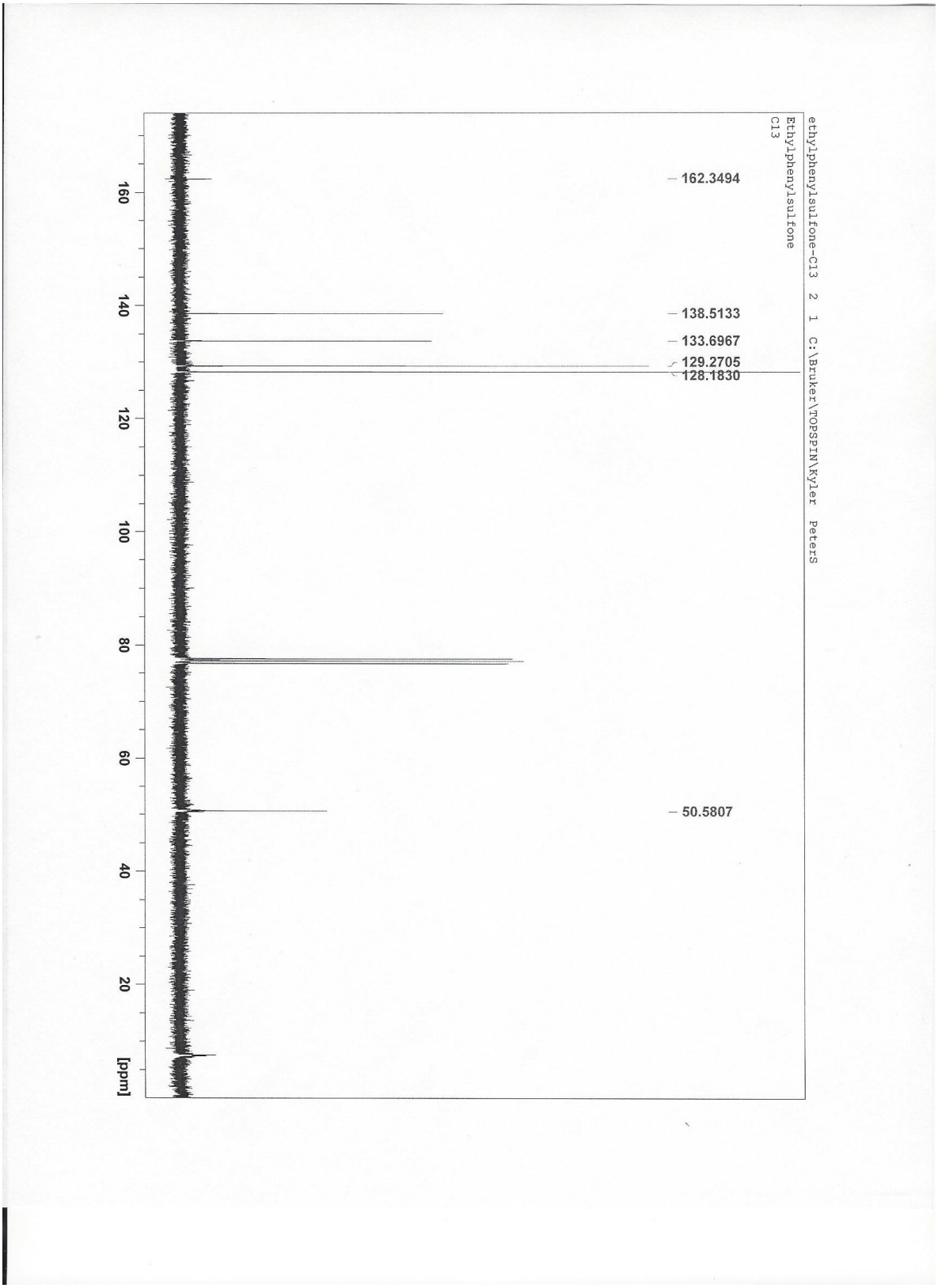
2,3-Epoxygeraniol: IR



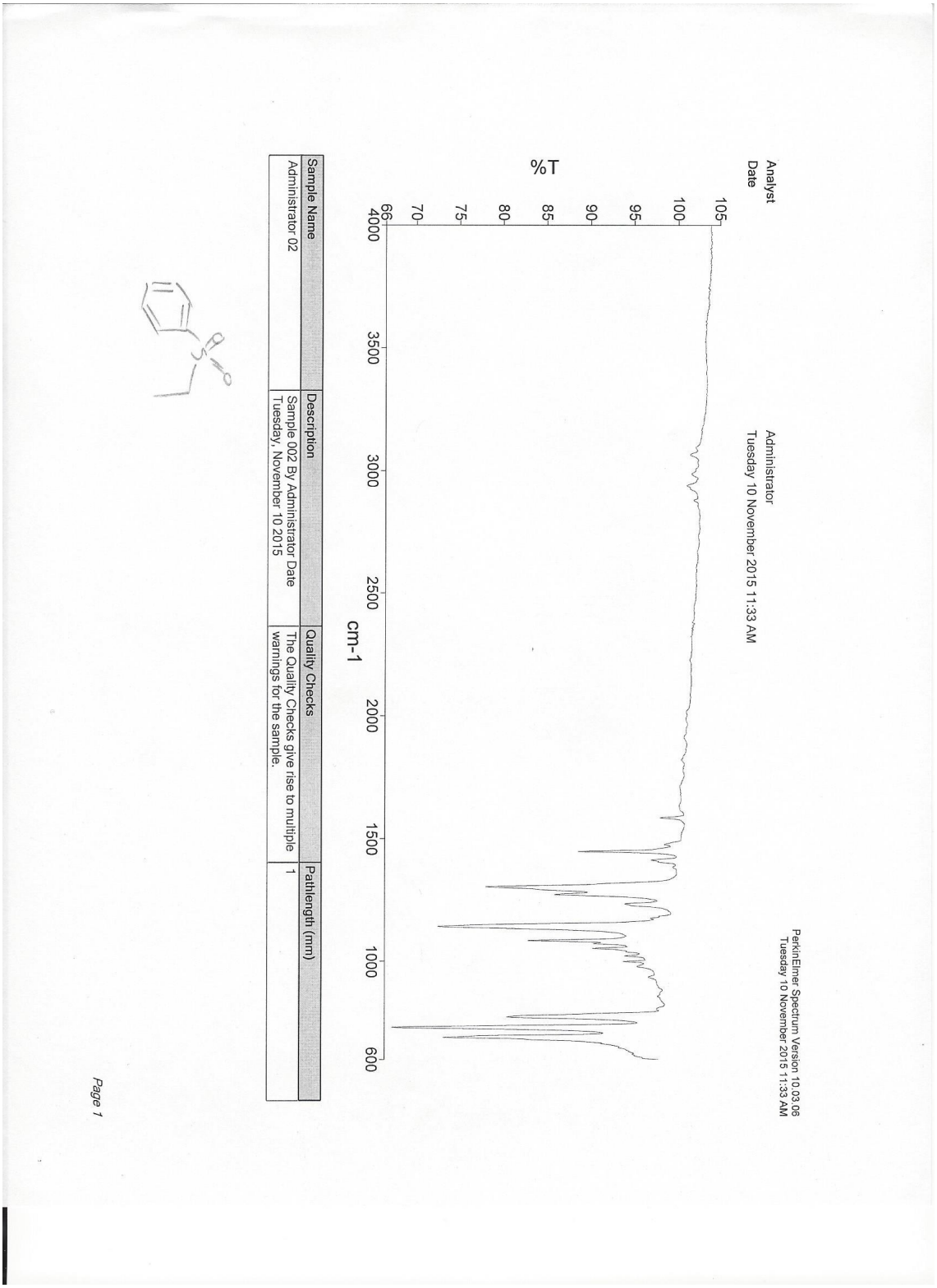
Ethylphenylsulfone: ^{1}H-NMR ($CDCl_3$)



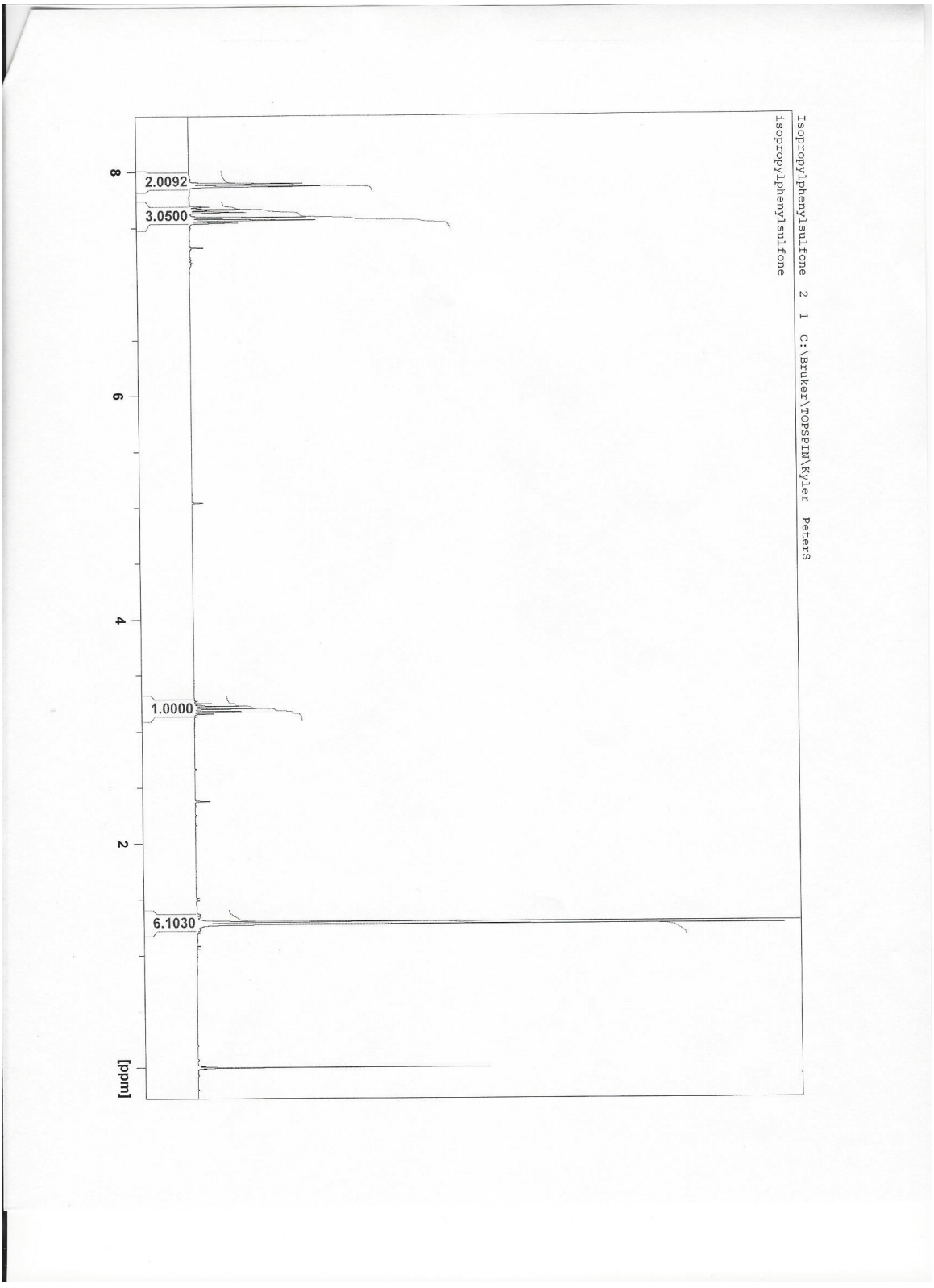
Ethylphenylsulfone: ^{13}C-NMR ($CDCl_3$)



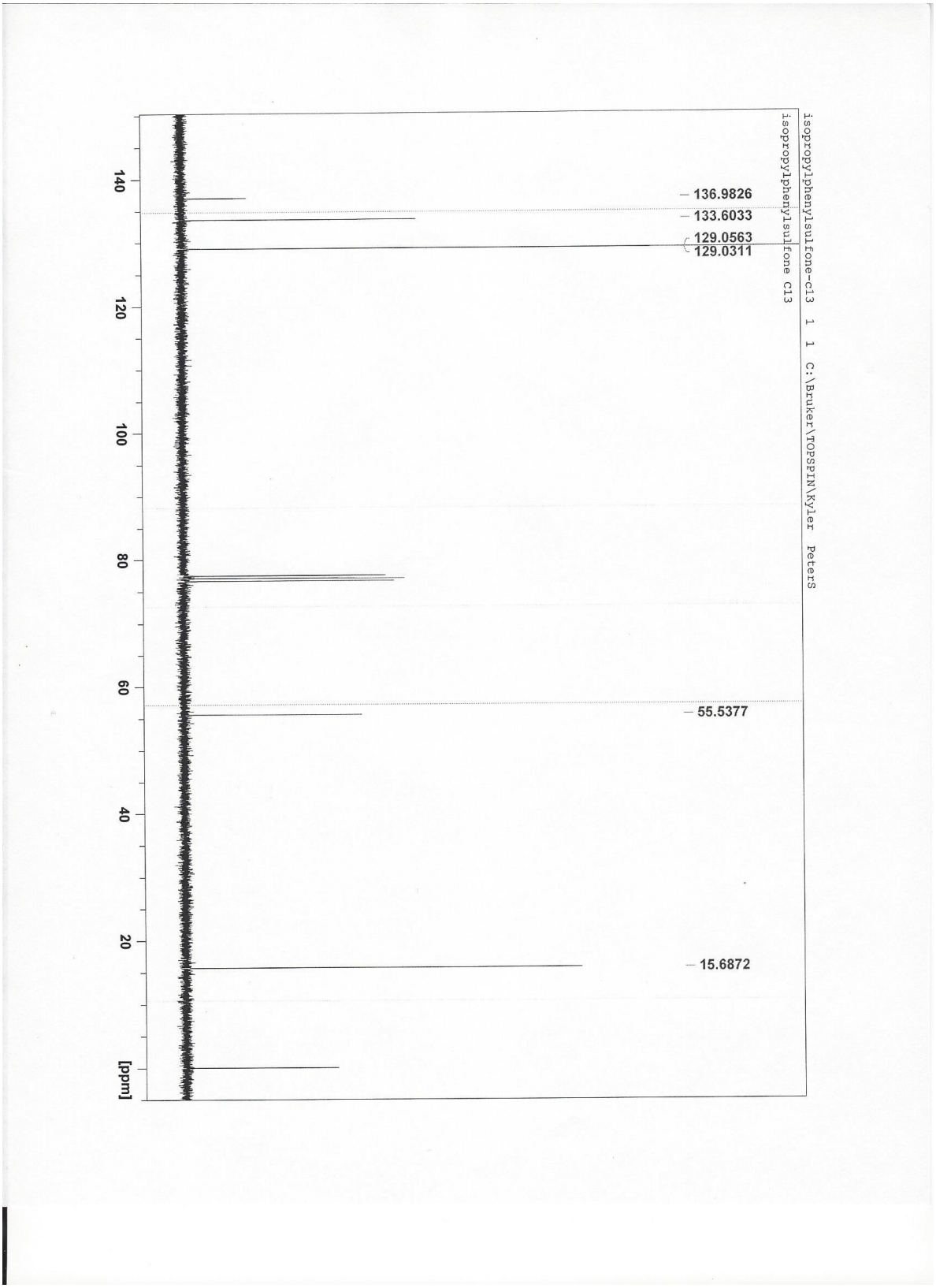
Ethylphenylsulfone: IR



Isopropylphenylsulfone: ^{1}H-NMR ($CDCl_3$)



Isopropylphenylsulfone: ^{13}C-NMR ($CDCl_3$)



Isopropylphenylsulfone: IR