

Supporting Information

Chromium-Catalyzed Linear-Selective Alkylation of Aldehydes with Alkenes

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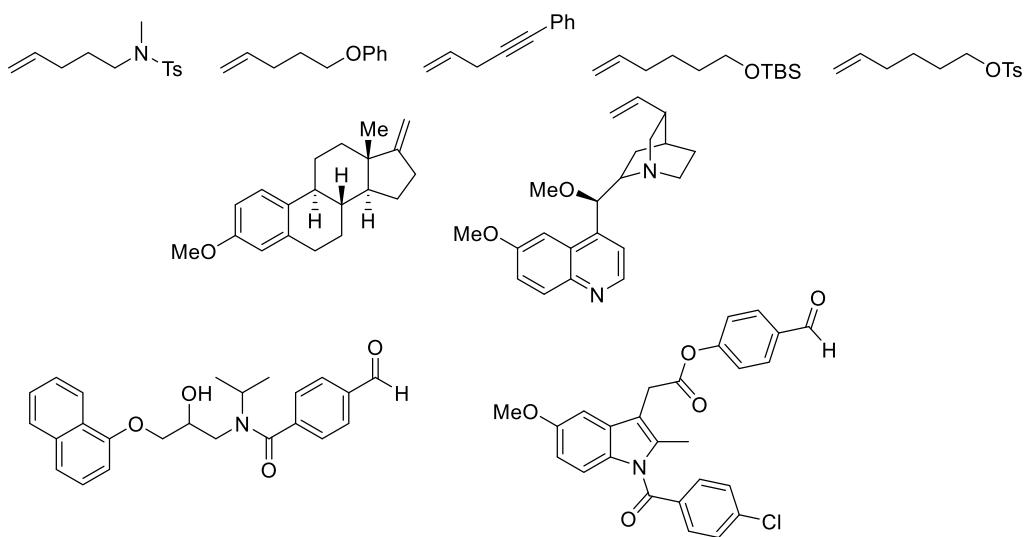
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1. General Method

¹H NMR spectra were recorded on JEOL ECX500 (500 MHz for ¹H NMR and 125.65 MHz for ¹³C NMR), and JEOL ECS400 (400 MHz for ¹H NMR and 100 MHz for ¹³C NMR, and 370 MHz for ¹⁹F NMR) spectrometer. For ¹H NMR and ¹³C NMR, chemical shifts were reported in the scale relative to CDCl₃ (δ = 7.26 for ¹H NMR and δ = 77.0 for ¹³C NMR) used as an internal reference. Electrospray ionization (ESI)-mass spectra were measured on a JEOL JMS-T100LC AccuTOF spectrometer for HRMS. Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. The enantiomeric excess (ee) was determined by HPLC analysis (JASCO HPLC systems; pump: PU-986; detector: UV-2075, measured at 210 nm or 254 nm; column: CHIRALPAK OD-H). Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM), Biotage Isolera One and Biotage SNAP Ultra, or Yamazen Smart Flash and Universal Column Premium. All non-commercially available compounds were prepared and characterized as described in Section 2 of this SI. Commercially-available alkenes and aldehydes were purchased and used without further purification. CrCl₂ (anhydrous, 99.9%-Cr) was purchased from Strem Chemicals, Inc. and used as received. Other reagents were purchased from Aldrich, Tokyo Chemical Industry Co., Ltd. (TCI), Kanto Chemical Co., Inc., and Wako Pure Chemical Industries, Ltd., and were used as received. A Valore VBP-L24-C2 with 38W LED lamp (VBL-SE150-BBB (430)) was used as the 430 nm light source.

2. Preparation of Substrates

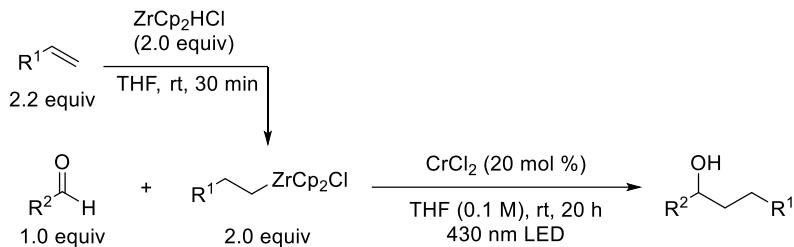
Chiral ligand was prepared according to the reported method.¹



Above alkenes and aldehydes were prepared according to the reported method.²⁻⁹

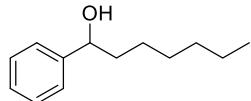
3. General Procedure

Procedure for preparation of 11a-11k, 11m-11n, 11p-11aa, 11ad, 11ag, 11ah, 11aj, 11ak



Under an argon atmosphere, alkene (0.44 mmol, 2.2 equiv) was added to a solution of ZrCp_2HCl (103.1 mg, 0.40 mmol, 2.0 equiv) in degassed THF (0.5 mL) in a screw-capped vial, and the mixture was stirred for 30 min at room temperature until a clear yellow solution was obtained. In another screw-capped vial, CrCl_2 (4.9 mg, 0.04 mmol, 20 mol %) was dissolved in degassed THF (1.5 mL). Then, the yellow alkyl zirconium solution was added dropwise to this reaction vial. Aldehyde (0.20 mmol, 1 equiv) was added to the reaction mixture. The vial was subjected to 430 nm LED irradiation by a Valore VBP-L24-C2 with 38W LED lamp (VBL-SE150-BBB (430)) under temperature control (ca. 27-29 °C). After 20 hours, water was added and organic materials were extracted with Et_2O three times. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with EtOAc and hexane to afford the desired product.

1-phenylheptan-1-ol (11a).

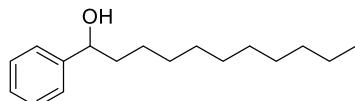


The reaction was conducted using 1-hexene **1a** (55.0 μL , 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/ EtOAc) to afford **11a** as a colorless oil (26.9 mg, 70%).

^1H NMR (CDCl_3 , 500 MHz) δ 7.46-7.24 (m, 5H), 4.66 (dd, J = 6.3, 6.3 Hz, 1H), 2.76 (s, 1H), 1.95-1.65 (m, 2H), 1.48-1.25 (m, 8H), 0.95 (t, J = 7.1 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 145.1, 128.4, 127.4, 126.0, 74.6, 39.2, 31.9, 29.3, 25.8, 22.7, 14.1.

All the spectroscopic data matches with the previously reported data.¹⁰

1-phenylundecan-1-ol (11b).

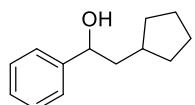


The reaction was conducted using 1-decene (83.4 μL , 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/ EtOAc) to afford **11b** as a colorless oil (31.2 mg, 62%).

¹H NMR (CDCl₃, 400 MHz) δ 7.39-7.21 (m, 5H), 4.66 (dd, *J* = 7.2, 5.8 Hz, 1H), 1.84-1.61 (m, 2H), 1.44-1.37 (m, 1H), 1.37-1.17 (m, 15H), 0.88 (t, *J* = 6.7 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 144.9, 128.4, 127.5, 125.9, 74.7, 39.1, 31.9, 29.6, 29.5, 29.5, 29.5, 29.3, 25.8, 22.7, 14.1

All the spectroscopic data matches with the previously reported data.¹¹

2-cyclopentyl-1-phenylethan-1-ol (11c).

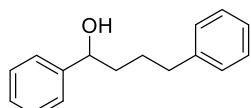


The reaction was conducted using methylenecyclopentane (46.3 μL, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11c** as a colorless oil (22.2 mg, 58%).

¹H NMR (CDCl₃, 400 MHz) δ 7.36-7.24 (m, 5H), 4.70 (dd, *J* = 6.7, 6.7 Hz, 1H), 1.90-1.73 (m, 5H), 1.73-1.55 (m, 2H), 1.54-1.44 (m, 2H), 1.21-1.06 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 145.1, 128.4, 127.5, 125.9, 74.1, 45.5, 36.7, 32.9, 32.6, 25.1, 24.9.

All the spectroscopic data matches with the previously reported data.¹²

1,4-diphenylbutan-1-ol (11d).

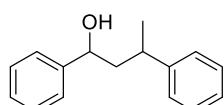


The reaction was conducted using allylbenzene (58.4 μL, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11d** as a colorless oil (24.1 mg, 53%).

¹H NMR (CDCl₃, 500 MHz) δ 7.38-7.25 (m, 4H), 7.25-7.21 (m, 3H), 7.20-7.12 (m, 3H), 4.69 (dd, *J* = 7.4, 7.4 Hz, 1H), 2.64 (t, *J* = 7.4 Hz, 2H), 1.90-1.69 (m, 3H), 1.68-1.50 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 144.7, 142.2, 128.4, 128.4, 128.3, 127.6, 125.9, 125.7, 74.5, 38.6, 35.7, 27.6.

All the spectroscopic data matches with the previously reported data.¹³

1,3-diphenylbutan-1-ol (11e).



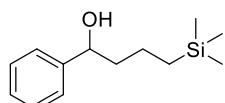
The reaction was conducted using 2-phenyl-1-propene (57.1 μL, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11e** as a

colorless oil (18.0 mg, 40%, 1.3/1 dr).

¹H NMR (CDCl₃, 500 MHz) major isomer: δ 7.40–7.16 (m, 10H), 4.42 (dd, J = 9.7, 3.4 Hz, 1H), 3.09–2.95 (m, 1H), 2.10–2.00 (m, 1H), 1.99–1.88 (m, 1H), 1.76 (brs, 1H), 1.29 (d, J = 6.9 Hz, 3H); minor isomer: δ 7.40–7.16 (m, 10H), 4.58 (dd, J = 6.9, 6.9 Hz, 1H), 2.79–2.68 (m, 1H), 2.24–2.14 (m, 1H), 1.99–1.88 (m, 1H), 1.76 (brs, 1H), 1.27 (d, J = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) major isomer: δ 146.6, 145.1, 128.5, 128.4, 127.4, 127.2, 126.2, 125.6, 72.3, 47.6, 36.6, 23.1; minor isomer: δ 147.0, 144.5, 128.5, 128.4, 127.7, 127.0, 126.2, 125.6, 72.9, 47.2, 36.6, 22.6.

All the spectroscopic data matches with the previously reported data.¹⁴

1-phenyl-4-(trimethylsilyl)butan-1-ol (11f).

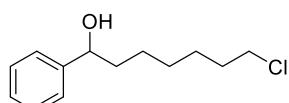


The reaction was conducted using allyltrimethylsilane (69.8 μ L, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11f** as a colorless oil (23.0 mg, 52%).

¹H NMR (CDCl₃, 400 MHz) δ 7.35–7.31 (m, 4H), 7.30–7.24 (m, 1H), 4.68 (dd, J = 8.1, 5.4 Hz, 1H), 1.90–1.64 (m, 2H), 1.49–1.40 (m, 1H), 1.39–1.25 (m, 1H), 0.55–0.46 (m, 2H), –0.03 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz) δ 145.0, 128.4, 127.5, 125.8, 74.4, 43.0, 20.3, 16.5, –1.7.

All the spectroscopic data matches with the previously reported data.¹⁵

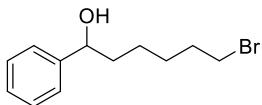
7-chloro-1-phenylheptan-1-ol (11g).



The reaction was conducted using 6-chlorohex-1-ene (58.2 μ L, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11g** as a colorless oil (27.1 mg, 60%).

¹H NMR (CDCl₃, 400 MHz) δ 7.38–7.25 (m, 5H), 4.66 (dd, J = 6.3, 6.3 Hz, 1H), 3.51 (t, J = 6.7 Hz, 2H), 1.90–1.58 (m, 5H), 1.50–1.20 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz) δ 144.8, 128.4, 127.5, 125.8, 74.6, 45.1, 38.9, 32.5, 28.7, 26.7, 25.6; IR (neat) ν 3358, 3021, 2932, 2857, 1653, 1451, 1028, 700 cm^{-1} ; HRMS (ESI) m/z : [M+Na]⁺ Calcd for C₁₃H₁₉ClONa 249.1017; Found 249.1011.

6-bromo-1-phenylhexan-1-ol (11h).

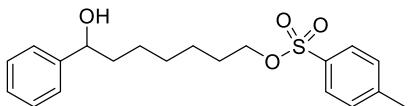


The reaction was conducted using 5-bromopent-1-ene (52.0 μ L, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11h** as a colorless oil (27.2 mg, 53%).

^1H NMR (CDCl_3 , 400 MHz) δ 7.38-7.25 (m, 5H), 4.67 (dd, J = 7.4, 5.8 Hz, 1H), 3.39 (t, J = 7.2 Hz, 2H), 1.9-1.58 (m, 4H), 1.50-1.40 (m, 3H), 1.35-1.17 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 144.7, 128.5, 127.6, 125.8, 74.5, 38.8, 33.8, 32.6, 28.0, 24.9.

All the spectroscopic data matches with the previously reported data.¹⁶

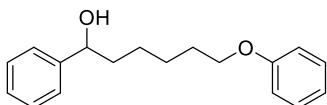
7-hydroxy-7-phenylheptyl 4-methylbenzenesulfonate (11i).



The reaction was conducted using hex-5-en-1-yl 4-methylbenzenesulfonate (111.8 mg, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11i** as a colorless oil (43.9 mg, 61%).

^1H NMR (CDCl_3 , 400 MHz) δ 7.77 (d, J = 8.5 Hz, 2H), 7.36-7.26 (m, 7H), 4.64 (dd, J = 6.3, 6.3 Hz, 1H), 3.99 (t, J = 6.3 Hz, 2H), 2.44 (s, 3H), 1.82 (brs, 1H), 1.80-1.56 (m, 4H), 1.42-1.18 (m, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 144.8, 144.6, 133.1, 129.8, 128.5, 127.9, 127.5, 125.8, 74.5, 70.6, 38.8, 28.8, 28.7, 25.5, 25.2, 21.6; IR (neat) ν 3546, 3412, 3029, 2933, 2857, 1597, 1493, 1453, 1355, 1175, 1097, 1019, 956, 815, 762, 701 cm^{-1} ; HRMS (ESI) m/z : [M+Na]⁺ Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_4\text{SNa}$ 385.1444; Found 385.1447.

6-phenoxy-1-phenylhexan-1-ol (11j).

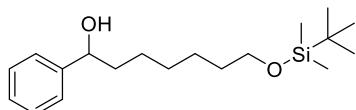


The reaction was conducted using (pent-4-en-1-yloxy)benzene (71.3 mg, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11j** as a colorless oil (36.4 mg, 67%).

^1H NMR (CDCl_3 , 400 MHz) δ 7.36-7.35 (m, 4H), 7.31-7.26 (m, 3H), 6.96-6.87 (m, 3H), 4.68 (dd, J = 7.2, 5.8 Hz, 1H), 3.94 (t, J = 6.3 Hz, 2H), 1.93-1.68 (m, 5H), 1.53-1.46 (m, 3H), 1.39-1.33 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.0, 144.8, 129.4, 128.4, 127.5, 125.8, 120.5, 114.4, 74.5, 67.6, 38.9, 29.2, 25.9, 25.5; IR (neat) ν 3433, 2937, 2859, 1637, 1600, 1496, 1472, 1455, 1300, 1244, 1171, 1031, 754 cm^{-1} ; HRMS

(ESI) m/z : [M+Na]⁺ Calcd for C₁₈H₂₂O₂Na 293.1512; Found 293.1512.

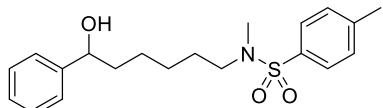
7-((*tert*-butyldimethylsilyl)oxy)-1-phenylheptan-1-ol (11k).



The reaction was conducted using *tert*-butyl(hex-5-en-1-yloxy)dimethylsilane (94.2 mg, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11k** as a colorless oil (32.6 mg, 51%).

¹H NMR (CDCl₃, 500 MHz) δ 7.35-7.24 (m, 5H), 4.66 (dd, J = 7.1, 5.1 Hz, 1H), 3.58 (t, J = 6.3 Hz, 2H), 1.80-1.70 (m, 2H), 1.52-1.47 (m, 3H), 1.34-1.26 (5H), 0.88 (s, 9H), 0.03 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 144.9, 128.4, 127.5, 125.9, 77.3, 74.7, 39.0, 32.8, 29.3, 26.0, 25.8, 25.7, 18.4, -5.3; IR (neat) ν 3388, 2929, 2856, 1725, 1462, 1254, 1100, 835, 774, 700 cm⁻¹; HRMS (ESI) m/z : [M+Na]⁺ Calcd for C₁₉H₃₄O₂SiNa 345.2220; Found 345.2223.

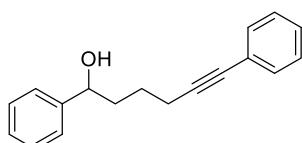
N-(6-hydroxy-6-phenylhexyl)-N,4-dimethylbenzenesulfonamide (11m).



The reaction was conducted using *N*,4-dimethyl-*N*-(pent-4-en-1-yl)benzenesulfonamide (111.4 mg, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11m** as a colorless oil (52.2 mg, 72%).

¹H NMR (CDCl₃, 400 MHz) δ 7.64 (d, J = 8.1 Hz, 2H), 7.36-7.26 (m, 7H), 4.66 (dd, J = 7.2, 5.8 Hz, 1H), 3.02-2.88 (m, 2H), 2.68 (s, 3H), 2.42 (s, 3H), 1.93 (brs, 1H), 1.87-1.63 (m, 2H), 1.57-1.18 (m, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 144.8, 143.2, 134.5, 129.6, 128.4, 127.5, 127.4, 125.8, 74.4, 49.9, 38.9, 34.5, 27.4, 26.3, 25.3, 21.5; IR (neat) ν 3529, 3021, 2934, 2860, 1597, 1492, 1453, 1336, 1159, 1089, 1019, 815, 701 cm⁻¹; HRMS (ESI) m/z : [M+Na]⁺ Calcd for C₂₀H₂₇NO₃SiNa 384.1604; Found 384.1611.

1,6-diphenylhex-5-yn-1-ol (11n).

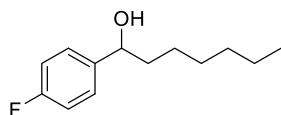


The reaction was conducted using pent-4-en-1-yn-1-ylbenzene (65.4 μ L, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11n** as a colorless oil (17.8 mg, 36%).

¹H NMR (CDCl₃, 500 MHz) δ 7.39-7.32 (m, 6H), 7.30-7.25 (m, 4H), 4.75 (dd, *J* = 7.2, 5.7 Hz, 1H), 2.44 (t, *J* = 6.9 Hz, 2H), 2.03-1.86 (m, 2H), 1.80-1.48 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 144.6, 131.5, 128.5, 128.2, 127.6, 127.5, 125.9, 123.9, 89.8, 81.0, 74.2, 38.1, 25.0, 19.3.

All the spectroscopic data matches with the previously reported data.¹⁷

1-(4-fluorophenyl)heptan-1-ol (11p).

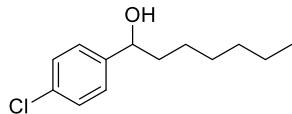


The reaction was conducted using 4-fluorobenzaldehyde (21.0 µL, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11p** as a colorless oil (27.0 mg, 64%).

¹H NMR (CDCl₃, 500 MHz) δ 7.30-7.28 (m, 2H), 7.05-7.00 (m, 2H), 4.65 (dd, *J* = 6.3, 6.3 Hz, 1H), 1.84-1.60 (m, 3H), 1.45-1.19 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 162.1 (d, *J* = 245.2 Hz), 140.6 (d, *J* = 3.6 Hz), 127.5 (d, *J* = 7.2 Hz), 115.2 (d, *J* = 20.4 Hz), 74.0, 39.2, 31.7, 29.1, 25.7, 22.5, 14.0.

All the spectroscopic data matches with the previously reported data.¹⁶

1-(4-chlorophenyl)heptan-1-ol (11q).

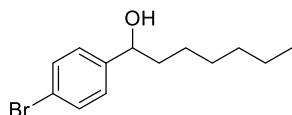


The reaction was conducted using 4-chlorobenzaldehyde (28.1 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11q** as a colorless oil (31.6 mg, 63%).

¹H NMR (CDCl₃, 500 MHz) δ 7.35-7.22 (m, 4H), 4.65 (dd, *J* = 7.4, 5.7 Hz, 1H), 1.82-1.58 (m, 2H), 1.44-1.18 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 143.5, 133.2, 128.7, 127.4, 74.1, 39.3, 31.9, 29.3, 25.8, 22.7, 14.2.

All the spectroscopic data matches with the previously reported data.¹⁰

1-(4-bromophenyl)heptan-1-ol (11r).



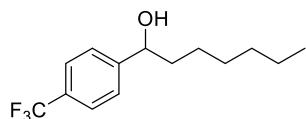
The reaction was conducted using 4-bromobenzaldehyde (37.0 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The

crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11r** as a colorless oil (31.0 mg, 57%).

¹H NMR (CDCl₃, 500 MHz) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 4.63 (dd, *J* = 6.9, 6.9 Hz, 1H), 1.87 (brs, 1H), 1.82–1.58 (m, 2H), 1.42–1.18 (m, 8H), 0.87 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 143.9, 131.5, 127.6, 121.1, 74.0, 39.1, 31.7, 29.1, 25.6, 22.6, 14.0.

All the spectroscopic data matches with the previously reported data.¹⁰

1-(4-(trifluoromethyl)phenyl)heptan-1-ol (11s).

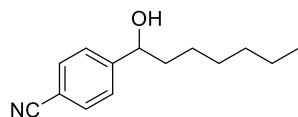


The reaction was conducted using 4-trifluoromethylbenzaldehyde (26.8 μL, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11s** as a colorless oil (25.3 mg, 49%).

¹H NMR (CDCl₃, 500 MHz) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 4.74 (dd, *J* = 6.9, 6.9 Hz, 1H), 1.94 (brs, 1H), 1.82–1.60 (m, 2H), 1.46–1.15 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 148.8, 129.6 (q, *J* = 32.4 Hz), 126.1, 125.3 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.8 Hz), 74.0, 39.2, 31.7, 29.1, 25.6, 22.5, 14.0.

All the spectroscopic data matches with the previously reported data.¹⁶

4-(1-hydroxyheptyl)benzonitrile (11t).

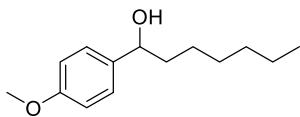


The reaction was conducted using 4-formylbenzonitrile (26.2 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11t** as a colorless oil (16.8 mg, 39%).

¹H NMR (CDCl₃, 500 MHz) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 4.74 (dd, *J* = 6.9, 5.7 Hz, 1H), 2.01 (brs, 1H), 1.82–1.58 (m, 2H), 1.46–1.18 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 150.2, 132.2, 126.5, 118.9, 111.1, 73.8, 39.2, 31.7, 29.1, 25.5, 22.5, 14.0.

All the spectroscopic data matches with the previously reported data.¹⁶

1-(4-methoxyphenyl)heptan-1-ol (11u).

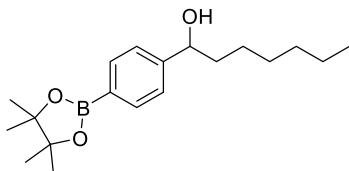


The reaction was conducted using 4-methoxybenzaldehyde (24.3 μ L, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11u** as a colorless oil (32.6 mg, 73%).

^1H NMR (CDCl_3 , 400 MHz) δ 7.26 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.60 (dd, J = 6.7, 6.7 Hz, 1H), 3.80 (s, 3H), 1.86-1.56 (m, 3H), 1.45-1.15 (m, 8H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 159.0, 137.1, 127.1, 113.8, 74.3, 55.3, 39.0, 31.8, 29.2, 25.8, 22.6, 14.0.

All the spectroscopic data matches with the previously reported data.¹⁸

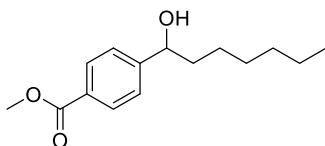
1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)heptan-1-ol (11v).



The reaction was conducted using 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (46.4 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11v** as a colorless oil (36.5 mg, 57%).

^1H NMR (CDCl_3 , 500 MHz) δ 7.79 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.68 (dd, J = 6.9, 6.9 Hz, 1H), 1.92-1.82 (brs, 1H) 1.82-1.64 (m, 2H), 1.34 (s, 12H), 1.30-1.20 (m, 8H), 1.15-1.00 (m, 3H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 148.1, 134.9, 125.2, 83.8, 74.6, 39.1, 31.7, 29.2, 25.7, 24.8, 22.6, 14.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.; IR (neat) ν 3389, 2925, 1641, 1361, 1089, 751 cm^{-1} ; HRMS (ESI) m/z : [M+Na]⁺ Calcd for $\text{C}_{19}\text{H}_{31}\text{BO}_3\text{Na}$ 341.2258; Found 341.2262.

methyl 4-(1-hydroxyheptyl)benzoate (11w).



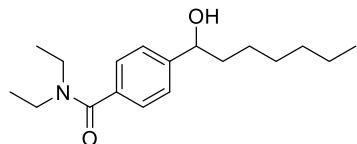
The reaction was conducted using methyl 4-formylbenzoate (32.8 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11w** as a colorless oil (23.2 mg, 46%).

^1H NMR (CDCl_3 , 500 MHz) δ 8.01 (d, J = 6.9 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 4.74 (dd, J = 6.9, 5.7 Hz, 1H), 3.91 (s, 3H), 1.94 (s, 1H), 1.82-1.64 (m, 2H), 1.45-1.35 (m, 1H), 1.31-1.18 (m, 7H), 0.87 (t, J = 6.9 Hz,

3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 166.9, 150.0, 129.7, 129.2, 125.8, 74.2, 52.1, 39.2, 31.7, 29.1, 25.6, 22.5, 14.0.

All the spectroscopic data matches with the previously reported data.¹⁹

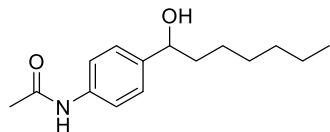
***N,N*-diethyl-4-(1-hydroxyheptyl)benzamide (11x).**



The reaction was conducted using *N,N*-diethyl-4-formylbenzamide (38.0 μL , 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11x** as a colorless oil (42.0 mg, 72%).

^1H NMR (CDCl_3 , 500 MHz) δ 7.36-7.27 (m, 4H), 4.66 (dd, J = 7.4, 5.7 Hz, 1H), 3.52 (brs, 2H), 3.24 (brs, 2H), 1.80-1.58 (m, 2H), 1.45-1.32 (m, 1H), 1.30-1.15 (m, 10H), 1.15-1.00 (m, 3H), 0.85 (t, J = 6.9 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 171.2, 146.1, 136.1, 126.4, 125.9, 74.2, 43.3, 39.2, 39.2, 31.7, 29.1, 25.6, 22.5, 14.2, 14.0, 12.8; IR (neat) ν 3397, 2930, 1610, 1508, 1430, 1288, 1097, 846 cm^{-1} ; HRMS (ESI) m/z : [M+Na]⁺ Calcd for $\text{C}_{18}\text{H}_{29}\text{NO}_2\text{Na}$ 314.2091; Found 314.2098.

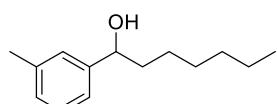
***N*-(4-(1-hydroxyheptyl)phenyl)acetamide (11y).**



The reaction was conducted using *N*-(4-formylphenyl)acetamide (32.6 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11y** as a colorless oil (20.4 mg, 41%).

^1H NMR (CDCl_3 , 400 MHz) δ 7.46 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.63 (dd, J = 6.3, 6.3 Hz, 1H), 2.18 (s, 3H), 1.86-1.58 (m, 2H), 1.50-1.18 (m, 8H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 168.2, 140.9, 137.0, 126.6, 119.9, 74.3, 39.0, 31.7, 29.2, 25.7, 24.6, 22.6, 14.1; IR (neat) ν 3312, 3126, 3065, 2952, 2927, 2855, 1669, 1604, 1541, 1460, 1411, 1369, 1318, 1269, 1093, 965, 836, 703 cm^{-1} ; HRMS (ESI) m/z : [M+Na]⁺ Calcd for $\text{C}_{15}\text{H}_{23}\text{NO}_2\text{Na}$ 272.1621; Found 272.1624.

1-(*m*-tolyl)heptan-1-ol (11z).



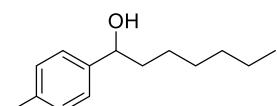
The reaction was conducted using 3-methylbenzaldehyde (23.6 μL , 0.2 mmol, 1.0 equiv) for 20 hours. The

crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11z** as a colorless oil (24.8 mg, 60%).

¹H NMR (CDCl₃, 500 MHz) δ 7.30-7.05 (m, 4H), 4.64 (dd, *J* = 6.9, 6.9 Hz, 1H), 2.35 (s, 3H), 1.85-1.76 (m, 2H), 1.76-1.66 (m, 1H), 1.45-1.20 (m, 8H), 0.87 (t, *J* = 6.3 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 144.9, 138.0, 128.3, 128.2, 126.6, 122.9, 74.7, 39.1, 31.7, 29.2, 25.8, 22.6, 21.4, 14.1.

All the spectroscopic data matches with the previously reported data.¹⁶

1-(*p*-tolyl)heptan-1-ol (11aa**).**

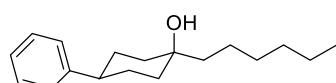


The reaction was conducted using 4-methylbenzaldehyde (23.6 μL, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11aa** as a colorless oil (24.7 mg, 60%).

¹H NMR (CDCl₃, 500 MHz) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.62 (dd, *J* = 6.9, 6.9 Hz, 1H), 2.34 (s, 3H), 1.80-1.60 (m, 2H), 1.45-1.28 (m, 8H), 0.86 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 142.0, 137.1, 129.1, 125.8, 74.5, 39.0, 31.7, 29.2, 25.8, 22.6, 21.1, 14.1.

All the spectroscopic data matches with the previously reported data.¹⁶

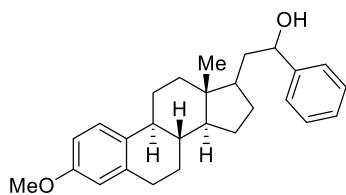
1-hexyl-4-phenylcyclohexan-1-ol (11ad**).**



The reaction was conducted using 4-phenylcyclohexan-1-one (34.8 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11ad** as a colorless oil (12.8 mg, 26%).

¹H NMR (CDCl₃, 500 MHz) δ 7.32-7.14 (m, 5H), 2.46 (tt, *J* = 12.0, 3.4 Hz, 1H), 1.92-1.79 (m, 2H), 1.79-1.66 (m, 4H), 1.55-1.21 (m, 11H), 1.14 (s, 1H), 0.90 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 147.3, 128.3, 126.8, 125.9, 70.5, 44.5, 44.1, 37.2, 31.9, 29.9, 29.3, 23.1, 22.6, 14.1; IR (neat) ν 3434, 2928, 2857, 1493, 1448, 1144, 755, 698 cm⁻¹; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₈H₂₈ONa 283.2032; Found 283.2030.

2-((8*S*,9*S*,13*R*,14*S*)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)-1-phenylethan-1-ol (11ag**).**

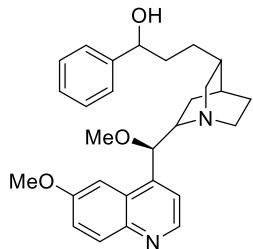


The reaction was conducted using (8S,9S,13S,14S)-3-methoxy-13-methyl-17-methylene-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene (91.2 mg, 0.26 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11ag** as a colorless oil (24.5 mg, 52%, inseparable mixture of diastereomers A:B:C:D=4.8:2.9:1.3:1).

¹H NMR (CDCl₃, 500 MHz) δ 7.38-7.32 (m, 4H, A+B+C+D), 7.32-7.25 (m, 1H, A+B+C+D), 7.24-7.15 (m, 1H, A+B+C+D), 6.73-6.66 (m, 1H, A+B+C+D), 6.64-6.59 (m, 1H, A+B+C+D), 4.73-4.64 (m, 1H, A+B+C+D), 3.78-3.75 (m, 3H, A+B+C+D), 2.95-2.75 (m, 2H, A+B+C+D), 2.35-1.96 (m, 3H, A+B+C+D), 1.95-1.77 (m, 4H, A+B+C+D), 1.70-1.00 (m, 12H, A+B+C+D), 0.85 (s, 3H, C), 0.70 (s, 3H, A), 0.65 (s, 3H, B), 0.61 (s, 3H, D); ¹³C NMR (CDCl₃, 125 MHz) δ 157.4, 145.8, 144.6, 144.5, 138.0, 132.9, 129.0, 128.5, 128.2, 127.7, 127.5, 127.4, 126.3, 126.2, 125.8, 125.6, 125.3, 113.7, 111.4, 74.5, 74.3, 73.5, 72.5, 55.2, 54.6, 54.3, 50.0, 49.9, 47.4, 47.0, 44.6, 44.3, 44.1, 43.7, 43.5, 43.3, 42.6, 42.5, 42.0, 41.6, 39.6, 39.2, 38.8, 38.7, 37.6, 37.5, 34.2, 29.9, 29.7, 28.6, 28.5, 28.3, 27.8, 27.6, 26.6, 26.4, 25.6, 24.5, 24.4, 21.4, 20.9, 12.6; IR (neat) ν 3378, 2929, 2864, 1608, 1498, 1451, 1254, 1100, 1039, 701 cm⁻¹; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₇H₃₄O₂Na 413.2451; Found 413.2441.

Note: In the ¹³C NMR spectra additional signals were observed. These correspond to the pseudoenantiomer forms of the product.

3-((1*S*,3*R*,4*S*)-6-((*R*)-methoxy(6-methoxyquinolin-4-yl)methyl)quinuclidin-3-yl)-1-phenylpropan-1-ol (11ah).



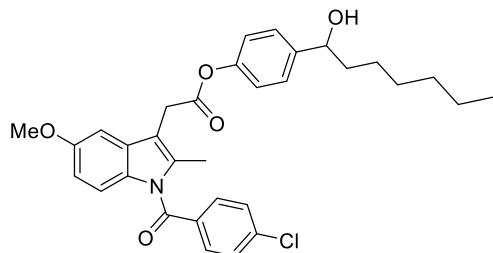
The reaction was conducted using (1*S*,4*S*,5*R*)-2-((*R*)-methoxy(6-methoxyquinolin-4-yl)methyl)-5-vinylquinuclidine (148.8 mg, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (DCM/MeOH) to afford **11ah** as a colorless oil (48.2 mg, 54%).

¹H NMR (CDCl₃, 500 MHz) δ 8.66 (d, *J* = 4.0 Hz, 1H), 7.96 (d, *J* = 9.2 Hz, 1H), 7.36-7.28 (m, 2H),

7.23-7.10 (m, 6H), 4.94-4.86 (m, 1H), 4.50-4.42 (m, 1H), 3.86-3.82 (m, 3H), 3.36-3.24 (m, 1H), 3.21 (s, 3H), 3.00-2.82 (m, 2H), 2.62-2.48 (m, 1H), 2.24-2.09 (m, 1H), 2.20-1.72 (m, 2H), 1.70-1.45 (m, 4H), 1.45-1.37 (m, 1H), 1.37-1.20 (m, 3H), 1.12-1.00 (m, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 157.8, 147.5, 144.8, 144.6, 131.7, 128.4, 127.5, 127.4, 125.7, 121.6, 118.6, 101.2, 83.1, 74.5, 59.7, 58.8, 55.8, 43.2, 37.1, 37.0, 35.6, 31.0, 30.9, 28.2, 25.8, 21.4; IR (neat) ν 3385, 2926, 2860, 1618, 1508, 1456, 1097, 750 cm^{-1} ; HRMS (ESI) m/z : [M+H] $^+$ Calcd for $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_3$ 447.2642; Found 447.2638.

Note: In the ^{13}C NMR spectra additional signals were observed. These correspond to the pseudoenantiomer forms of the product. In the ^1H NMR spectra the signals could not be distinguished.

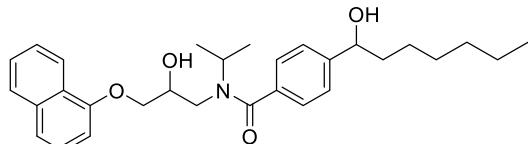
(S)-4-(1-hydroxyheptyl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (11aj).



The reaction was conducted using 4-formylphenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (92.2 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11aj** as a colorless oil (73.2 mg, 67%).

^1H NMR (CDCl_3 , 500 MHz) δ 7.67 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.07-7.00 (m, 3H), 6.89 (d, J = 9.2 Hz, 1H), 6.70 (dd, J = 9.2, 2.3 Hz, 1H), 4.65 (dd, J = 6.3, 6.3 Hz, 1H), 3.90 (s, 2H), 3.84 (s, 3H), 2.45 (s, 3H), 1.85 (brs, 1H), 1.81-1.61 (m, 2H), 1.42-1.17 (m, 8H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 169.3, 168.3, 156.1, 149.8, 142.7, 139.3, 136.2, 133.8, 131.2, 130.8, 130.4, 129.1, 126.9, 121.3, 115.0, 112.0, 111.8, 101.2, 74.1, 55.7, 39.1, 31.7, 30.5, 29.1, 25.7, 22.6, 14.0, 13.4; IR (neat) ν 3486, 3391, 2928, 2856, 1752, 1684, 1595, 1477, 1456, 1357, 1321, 1198, 1132, 1068, 1013, 930, 754 cm^{-1} ; HRMS (ESI) m/z : [M+Na] $^+$ Calcd for $\text{C}_{32}\text{H}_{34}\text{ClNO}_5\text{Na}$ 570.2018; Found 570.2019.

N-(2-hydroxy-3-(naphthalen-1-yloxy)propyl)-4-(1-hydroxyheptyl)-N-isopropylbenzamide (11ak).



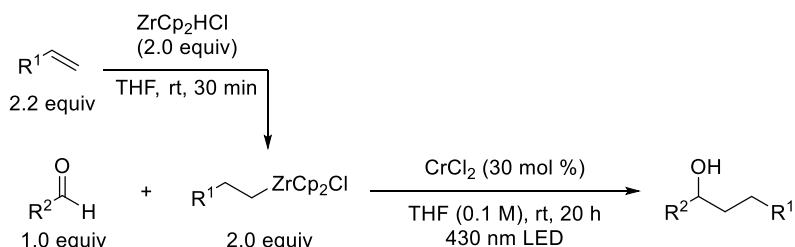
The reaction was conducted using 4-formyl-N-(2-hydroxy-3-(naphthalen-1-yloxy)propyl)-N-isopropylbenzamide (78.2 mg, 0.2 mmol, 1.0

equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11ak** as a colorless oil (47.4 mg, 50%).

¹H NMR (CDCl₃, 500 MHz) δ 8.24 (d, *J* = 7.4 Hz, 1H), 7.82 (d, *J* = 6.9 Hz, 1H), 7.52-7.35 (8H, m), 6.89 (d, *J* = 7.4 Hz, 1H), 5.58 (brs, 1H), 4.72 (dd, *J* = 6.3, 6.3 Hz, 3H), 4.43-4.26 (m, 2H), 4.15-4.02 (m, 2H), 3.95-3.86 (m, 1H), 3.78-3.69 (m, 1H), 1.92 (brs, 1H), 1.84-1.65 (m, 2H), 1.45-1.13 (m, 14H), 0.88 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 174.7, 154.0, 146.6, 135.2, 134.5, 127.7, 127.4, 126.4, 126.3, 126.2, 125.9, 125.4, 125.3, 121.5, 120.7, 104.9, 74.2, 72.2, 69.8, 51.2, 46.3, 39.2, 31.7, 29.1, 25.7, 22.6, 21.4, 20.8, 14.0; IR (neat) ν 3404, 2956, 2925, 2851, 1637, 1460, 1095, 956 cm⁻¹; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₀H₃₉NO₄Na 500.2771; Found 500.2768.

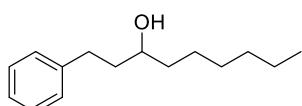
Note: In the ¹³C NMR spectra additional signals were observed. These correspond to the pseudoenantiomer forms of the product. In the ¹H NMR spectra the signals could not be distinguished.

Procedure for aliphatic aldehydes of **11ab**, **11ac**, **11ai**



Under an argon atmosphere, alkene (0.44 mmol, 2.2 equiv) was added to a solution of ZrCp₂HCl (103.1 mg, 0.40 mmol, 2.0 equiv) in degassed THF (0.5 mL) in a screw-capped vial, and the mixture was stirred for 30 min at room temperature until a clear yellow solution was obtained. In another screw-capped vial, CrCl₂ (7.3 mg, 0.06 mmol, 30 mol %) was dissolved in degassed THF (1.5 mL). Then, the yellow alkyl zirconium solution was added dropwise to this reaction vial. Aldehyde (0.20 mmol, 1 equiv) was added to the reaction mixture. The vial was subjected to 430 nm LED irradiation by a Valore VBP-L24-C2 with 38W LED lamp (VBL-SE150-BBB (430)) under temperature control (ca. 27-29 °C). After 20 hours, water was added and organic materials were extracted with Et₂O three times. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to afford the desired product.

1-phenylnonan-3-ol (**11ab**).



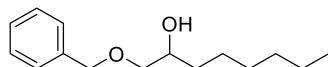
The reaction was conducted using 3-phenylpropanal (26.3 μL, 0.2 mmol, 1.0 equiv) for 20 hours. The crude

material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11ab** as a colorless oil (23.4 mg, 53%).

¹H NMR (CDCl₃, 400 MHz) δ 7.32-7.15 (m, 5H), 3.62 (m, 1H), 2.85-2.60 (m, 2H), 1.85-1.67 (m, 2H), 1.52-1.20 (m, 11H), 0.88 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 142.2, 128.4, 128.4, 125.8, 71.4, 39.1, 37.6, 32.1, 31.8, 29.3, 25.6, 22.6, 14.1.

All the spectroscopic data matches with the previously reported data.²⁰

1-(benzyloxy)octan-2-ol (11ac).

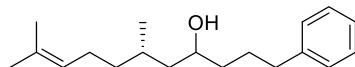


The reaction was conducted using 2-(benzyloxy)acetaldehyde (27.6 μL, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11ac** as a colorless oil (23.8 mg, 50%).

¹H NMR (CDCl₃, 400 MHz) δ 7.40-7.27 (m, 5H), 4.56 (s, 2H), 3.81 (m, 1H), 3.53-3.48 (m, 1H), 3.35-3.29 (m, 1H), 2.34 (brs, 1H), 1.51-1.20 (m, 10H), 0.88 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 138.0, 128.4, 127.8, 127.7, 74.6, 73.3, 70.4, 33.1, 31.7, 29.3, 25.5, 22.6, 14.1.

All the spectroscopic data matches with the previously reported data.²¹

(6*S*)-6,10-dimethyl-1-phenylundec-9-en-4-ol (11ai).

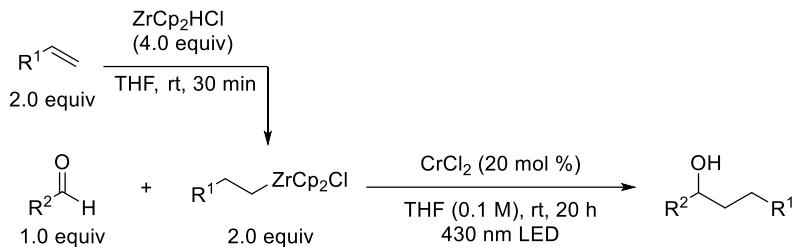


The reaction was conducted using (−)-citronellal (36.3 μL, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11ai** as a colorless oil (24.8 mg, 45%).

¹H NMR (CDCl₃, 500 MHz) δ 7.31-7.23 (m, 2H), 7.20-7.14 (m, 3H), 5.09 (t, *J* = 6.9 Hz, 1H), 3.76-3.64 (m, 1H), 2.67-2.56 (m, 2H), 2.08-1.86 (m, 2H), 1.84-1.72 (m, 1H), 1.71-1.52 (m, 8H), 1.52-1.05 (m, 7H), 0.93-0.86 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 142.4, 131.3, 131.2, 128.4, 128.3, 125.7, 124.7, 69.8, 69.5, 45.2, 44.9, 37.9, 37.3, 36.6, 35.9, 29.2, 28.9, 27.5, 27.4, 25.7, 25.4, 25.3, 20.3, 19.1, 17.7; IR (neat) ν 3409, 2924, 2860, 1654, 1450, 1377, 1092, 748, 698 cm^{−1}; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₃₀ONa 297.2189; Found 297.2176.

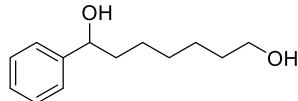
Note: In the ¹³C NMR spectra additional signals were observed. These correspond to the pseudoenantiomer forms of the product. In the ¹H NMR spectra the signals could not be distinguished.

Procedure for preparation of 11l, 11ae, 11af which have free hydroxyl groups



Under an argon atmosphere, alkene (0.40 mmol, 2.0 equiv) was added to a solution of ZrCp_2HCl (206.2 mg, 0.80 mmol, 4.0 equiv) in degassed THF (0.5 mL) in a screw-capped vial, and the mixture was stirred for 30 min at room temperature until a clear yellow solution was obtained. In another screw-capped vial, CrCl_2 (4.9 mg, 0.04 mmol, 20 mol %) was dissolved in degassed THF (1.5 mL). Then, the yellow alkyl zirconium solution was added dropwise to this reaction vial. Aldehyde (0.20 mmol, 1 equiv) was added to the reaction mixture. The vial was subjected to 430 nm LED irradiation by a Valore VBP-L24-C2 with 38W LED lamp (VBL-SE150-BBB (430)) under temperature control (ca. 27-29 °C). After 20 hours, water was added and organic materials were extracted with Et_2O three times. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to afford the desired product.

1-phenylheptane-1,7-diol (11l).

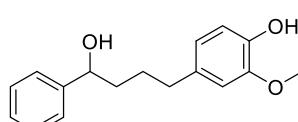


The reaction was conducted using hex-5-en-1-ol (47.1 μL , 0.4 mmol, 2.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11l** as a colorless oil (20.9 mg, 51%).

^1H NMR (CDCl_3 , 500 MHz) δ 7.35-7.28 (m, 5H), 4.64 (dd, J = 7.4, 5.7 Hz, 1H), 3.61 (t, J = 6.3 Hz, 2H), 1.86-1.76 (m, 1H), 1.75-1.65 (1H), 1.60-1.25 (m, 8H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 144.8, 128.4, 127.4, 125.8, 74.6, 62.9, 38.9, 32.6, 29.2, 25.7, 25.6.

All the spectroscopic data matches with the previously reported data.²²

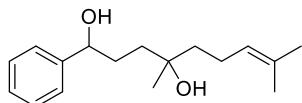
4-(4-hydroxy-4-phenylbutyl)-2-methoxyphenol (11ae).



The reaction was conducted using eugenol (61.4 μL , 0.4 mmol, 2.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11ae** as a colorless oil (39.0 mg, 72%).

¹H NMR (CDCl₃, 500 MHz) δ 7.38-7.24 (m, 5H), 6.81 (d, *J* = 8.6 Hz, 1H), 6.66-6.62 (m, 2H), 5.51 (s, 1H), 4.69 (dd, *J* = 6.9, 6.9 Hz, 1H), 3.86 (s, 3H), 2.56 (t, *J* = 7.4 Hz, 2H), 1.92 (s, 1H), 1.84-1.64 (m, 3H), 1.62-1.55 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 146.3, 144.7, 143.5, 134.2, 128.4, 127.5, 125.8, 120.9, 114.1, 110.9, 74.5, 55.8, 38.5, 35.4, 27.8; IR (neat) ν 3406, 2936, 1603, 1514, 1452, 1270, 1152, 1121, 1032, 701 cm⁻¹; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₂₀O₃Na 295.1305; Found 295.1319.

4,8-dimethyl-1-phenylnon-7-ene-1,4-diol (11af).

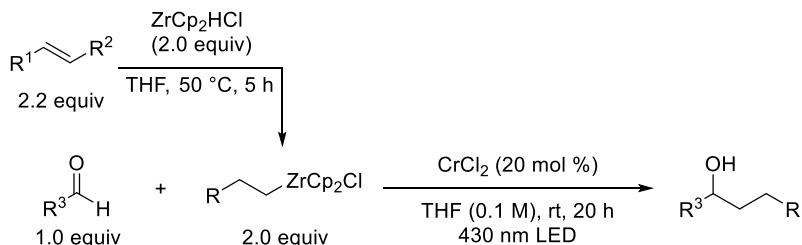


The reaction was conducted using linalool (71.7 μL, 0.4 mmol, 2.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11af** as a colorless oil (29.4 mg, 56%, dr mixture).

¹H NMR (CDCl₃, 400 MHz) δ 7.38-7.25 (m, 5H), 5.14-5.06 (m, 1H), 4.68 (m, 1H), 2.07-1.94 (m, 2H), 1.93-1.72 (m, 2H), 1.70-1.61 (m, 4H), 1.60 (s, 3H), 1.90-1.58 (m, 5H), 1.54-1.40 (m, 3H), 1.17 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 144.8, 131.9, 128.4, 127.5, 125.8, 124.3, 74.9, 74.8, 72.6, 41.9, 41.6, 37.9, 37.8, 33.6, 33.5, 26.9, 26.7, 25.7, 22.7, 22.6, 17.6; IR (neat) ν 3356, 3028, 2965, 2925, 2856, 1647, 1452, 1375, 1057, 914, 700 cm⁻¹; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₂₆O₂Na 285.1825; Found 285.1834.

Note: In the ¹³C NMR spectra additional signals were observed. These correspond to the pseudoenantiomer forms of the product. In the ¹H NMR spectra the signals could not be distinguished.

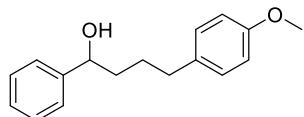
Procedure for preparation of 11a, 11o with chain walking strategy



Under an argon atmosphere, alkene (0.44 mmol, 2.2 equiv) was added to a solution of ZrCp₂HCl (103.1 mg, 0.40 mmol, 2.0 equiv) in degassed THF (0.5 mL) in a screw-capped vial, and the mixture was stirred for 30 min at room temperature until a clear yellow solution was obtained. In another screw-capped vial, CrCl₂ (4.9 mg, 0.04 mmol, 20 mol %) was dissolved in degassed THF (1.5 mL). Then, the yellow alkyl zirconium solution was added dropwise to this reaction vial. Aldehyde (0.20 mmol, 1 equiv) was added to the reaction mixture. The vial was subjected to 430 nm LED irradiation by a Valore VBP-L24-C2 with 38W LED lamp (VBL-SE150-BBB (430)) under temperature control (ca. 27-29 °C). After 20 hours, water was added and

organic materials were extracted with Et_2O three times. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to afford the desired product.

4-(4-methoxyphenyl)-1-phenylbutan-1-ol (11o).

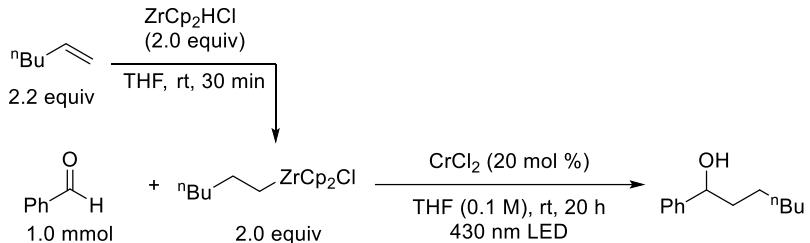


The reaction was conducted using anethole (65.9 μL , 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/ EtOAc) to afford **11o** as a colorless oil (31.1 mg, 61%).

^1H NMR (CDCl_3 , 500 MHz) δ 7.37-7.30 (m, 4H), 7.30-7.25 (m, 1H), 7.06 (d, J = 8.6 Hz, 1H), 6.81 (d, J = 8.6 Hz, 1H), 4.68 (dd, J = 7.4, 5.2 Hz, 1H), 3.78 (s, 3H), 2.58 (t, J = 7.4 Hz, 2H), 1.88-1.64 (m, 4H), 1.63-1.51 (m, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 157.7, 144.7, 134.3, 129.3, 128.4, 127.5, 125.9, 113.7, 74.5, 55.2, 38.5, 34.8, 27.8.

All the spectroscopic data matches with the previously reported data.²³

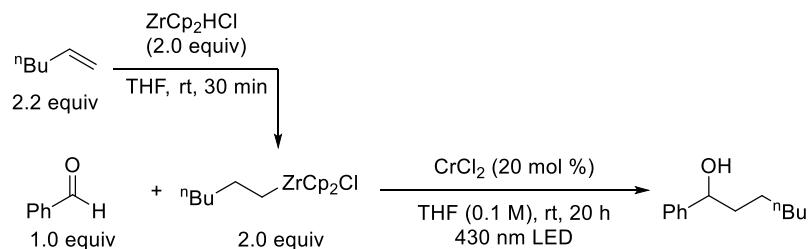
Experimental Procedure for the Large-Scale Reaction



Under an argon atmosphere, 1-hexene (2.2 mmol, 2.2 equiv) was added to a solution of ZrCp_2HCl (515 mg, 2.0 mmol, 2.0 equiv) in degassed THF (2.5 mL) in a screw-capped vial, and the mixture was stirred for 30 min at room temperature until a clear yellow solution was obtained. In another screw-capped vial, CrCl_2 (24.6 mg, 0.2 mmol, 20 mol %) was dissolved in degassed THF (7.5 mL). Then, the yellow alkyl zirconium solution was added dropwise to this reaction vial. Benzaldehyde (1.0 mmol, 1 equiv) was added to the reaction mixture. The vial was subjected to 430 nm LED irradiation by a Valore VBP-L24-C2 with 38W LED lamp (VBL-SE150-BBB (430)) under temperature control (ca. 27-29 °C). After 20 hours, water was added and organic materials were extracted with Et_2O three times. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography with EtOAc and hexane to afford **11a** as a colorless oil (130.5 mg, 68%).

4. Reaction Profiles

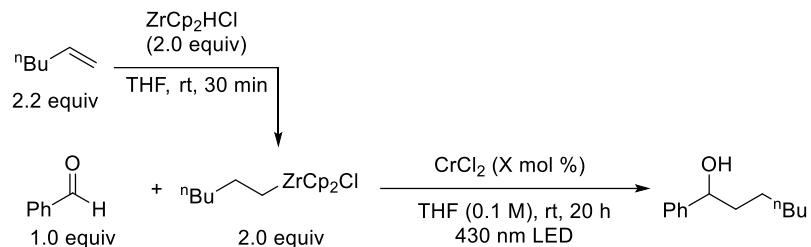
Control Experiments



entry	deviation from above	yield (%) ^a
1	none	75
2	CrCl ₃ instead of CrCl ₂	43
3	DCM instead of THF	0
4	THF/DMF 1:1 instead of THF ²⁴	50
5	THF/DMSO 1:1 instead of THF ²⁴	29
6	without CrCl ₂	13
7	without 430 nm LED	13
8	without CrCl ₂ and 430 nm LED	0

^aYield was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

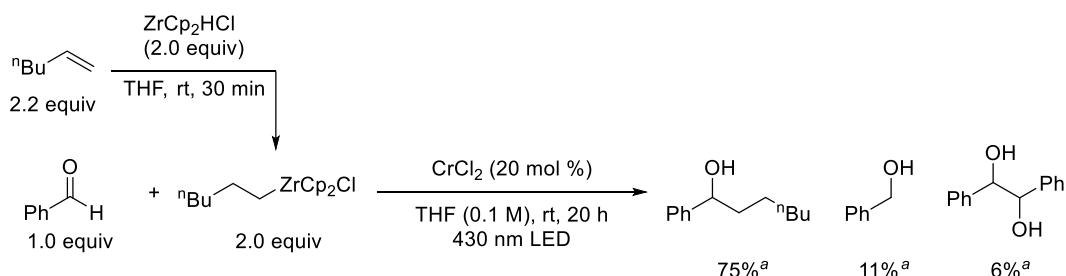
Amount of Cr Source



entry	CrCl ₂ (mol %)	yield (%) ^a
1	10	26
2	20	75
3	30	82
4	100	82

^aYield was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

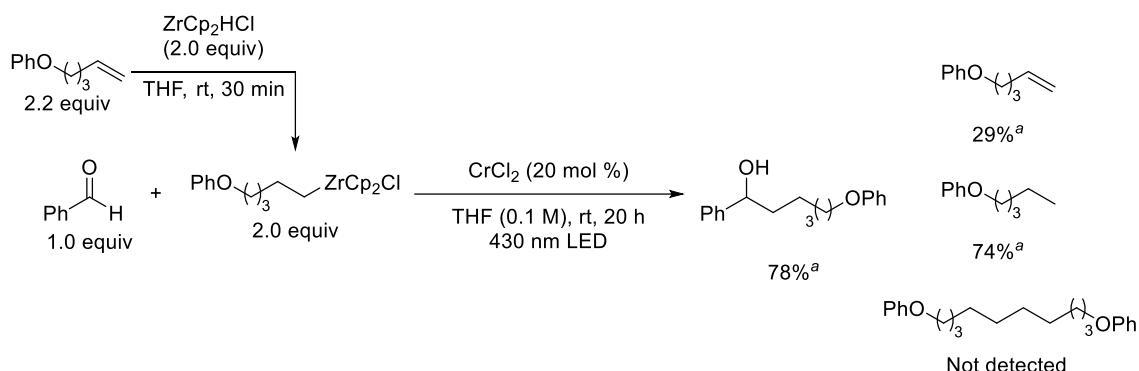
Mass balance of aldehyde



Total 98% benzaldehyde was consumed.

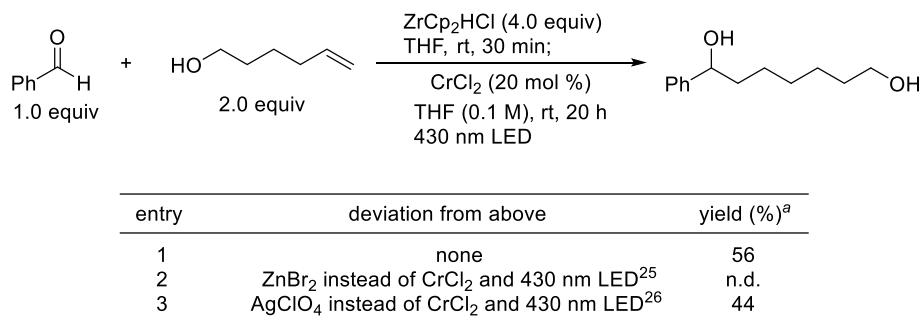
^aYield was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Mass balance of alkene



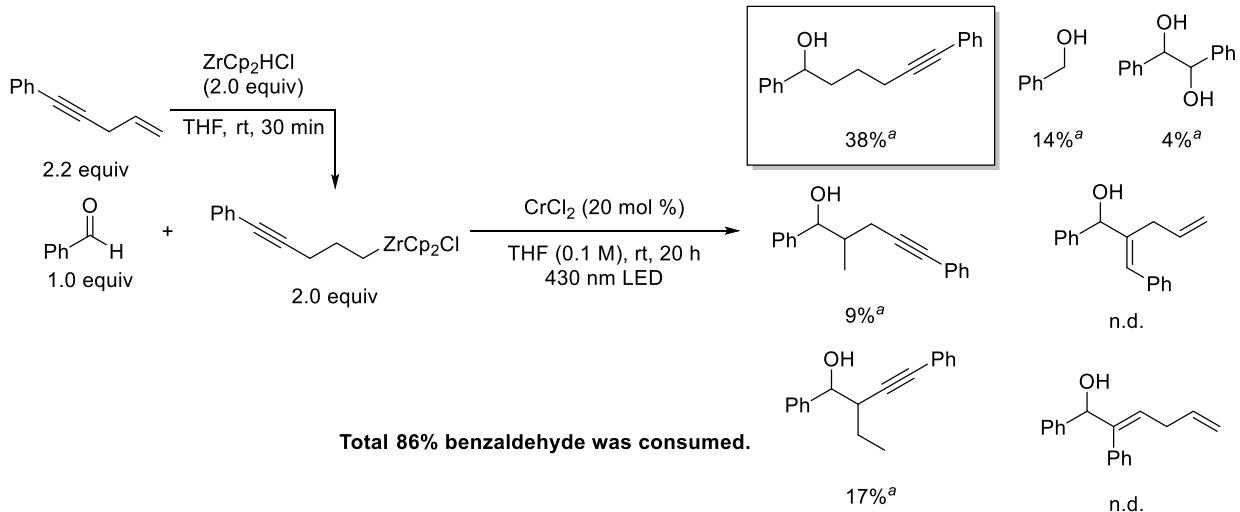
^aYield was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Comparison with Precedents



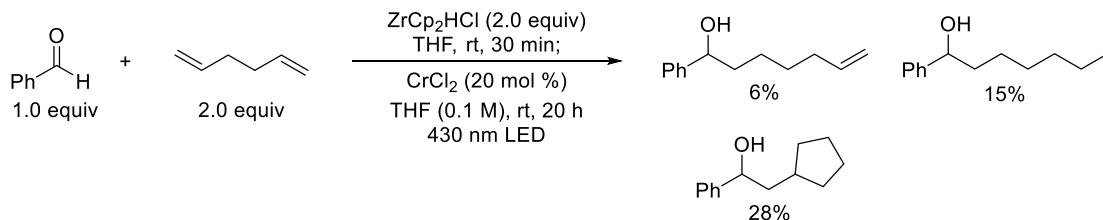
^aYield was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Chemoselectivity of 11n



^aYield was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

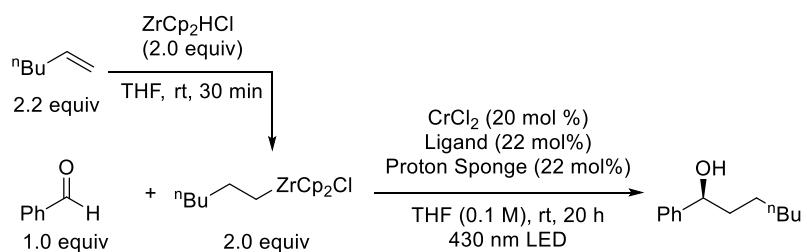
Mechanism Experiments



When 1,5-hexadiene was used as alkene substrate, cyclized product was obtained in 28% yield. This result indicated the generation of alkyl radical.

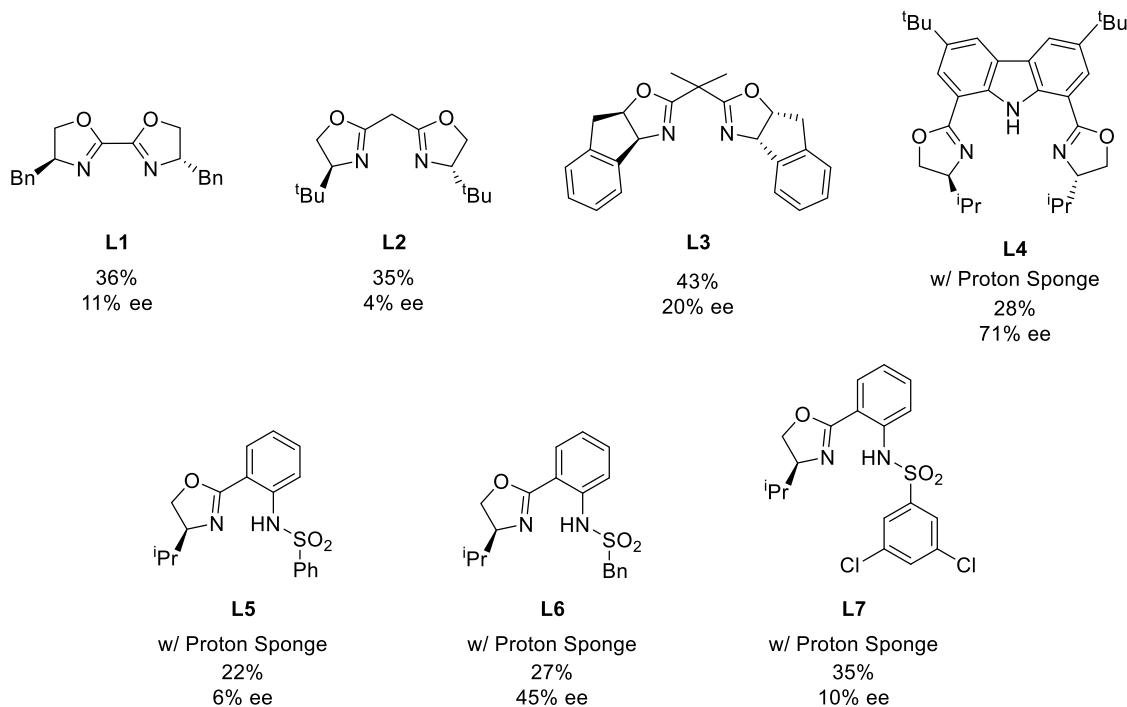
5. Catalytic Asymmetric Alkylation of Aldehydes

Procedure for Catalytic Alkylation Reaction



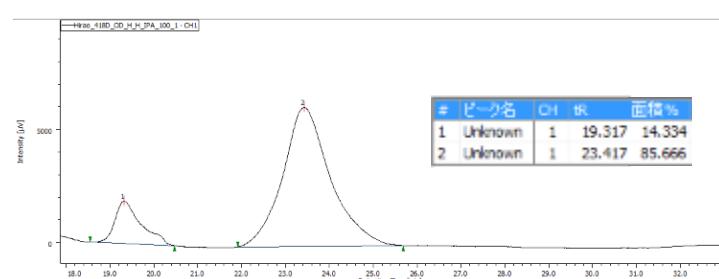
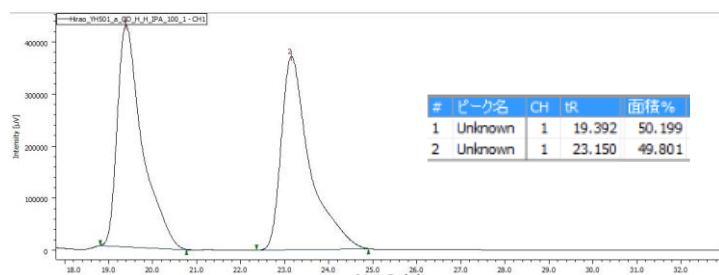
Under an argon atmosphere, alkene (0.22 mmol, 2.2 equiv) was added to a solution of ZrCp_2HCl (51.5 mg, 0.20 mmol, 2.0 equiv) in degassed THF (0.5 mL) in a screw-capped vial, and the mixture was stirred for 30 min at room temperature until a clear yellow solution was obtained. In another screw-capped vial, CrCl_2 (2.5 mg, 0.02 mmol, 20 mol%), ligand (11.0 mg, 0.022 mmol, 22 mol%) and Proton Sponge (4.7 mg, 0.022 mmol, 22 mol%) were reacted in degassed THF (0.5 mL) for 1 hour. Then, the yellow alkyl zirconium solution was added dropwise to this reaction vial. Aldehyde (0.10 mmol, 1 equiv) was added to the reaction mixture. The vial was subjected to 430 nm LED irradiation by a Valore VBP-L24-C2 with 38W LED lamp (VBL-SE150-BBB (430)) under temperature control (ca. 27-29 °C). After 20 hours, water was added and organic materials were extracted with Et_2O three times. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The yield was determined by ¹H NMR analysis using 1,1,2,2-tetrachloroethane as internal standard. The enantiomeric excess was determined by chiral HPLC analysis (chiral column: CHIRALPAK OD-H; solvent: hexane/2-propanol = 100/1; flow rate: 1.0 mL/min; detection: at 210 nm): t_R = 19.4 min (minor) and 23.2 min (major)

Ligand Screening



With L4

The enantiomeric excess was determined by chiral HPLC analysis (chiral column: CHIRALPAK OD-H; solvent: hexane/2-propanol = 100/1; flow rate: 1.0 mL/min; detection: at 210 nm): t_R = 19.4 min (minor) and 23.2 min (major) 71% ee²⁷



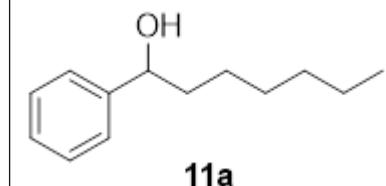
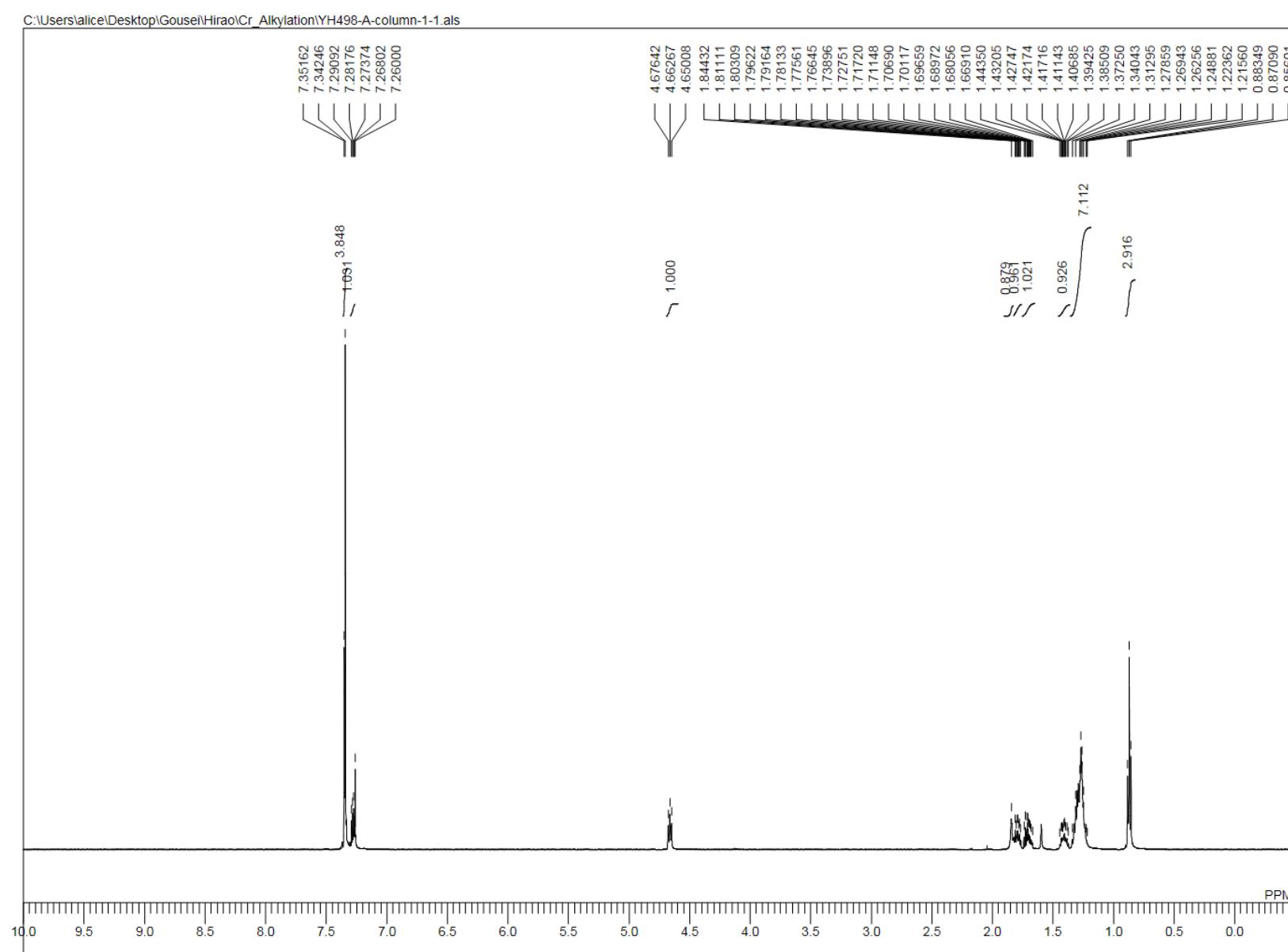
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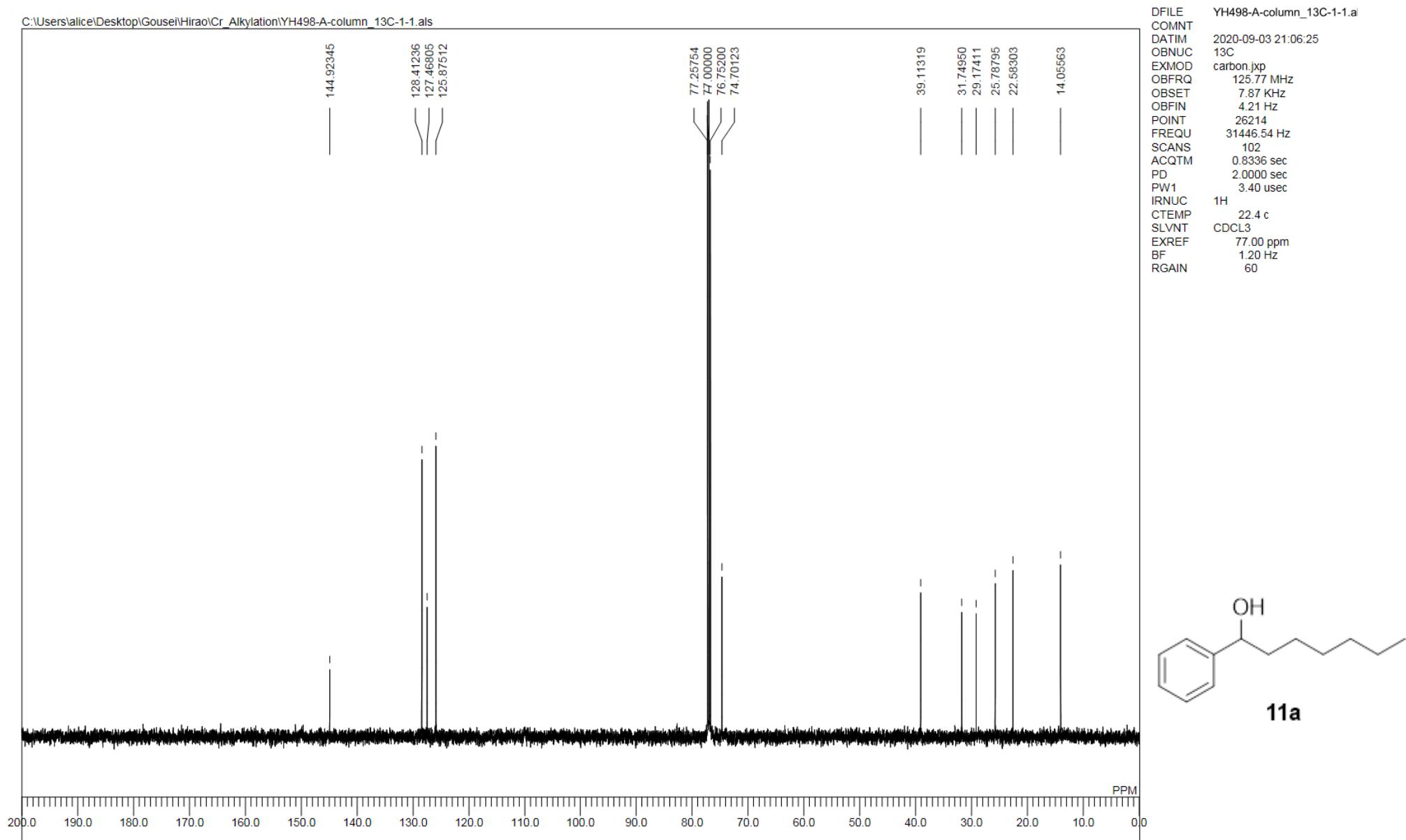
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¹H NMR (500 MHz, CDCl₃)

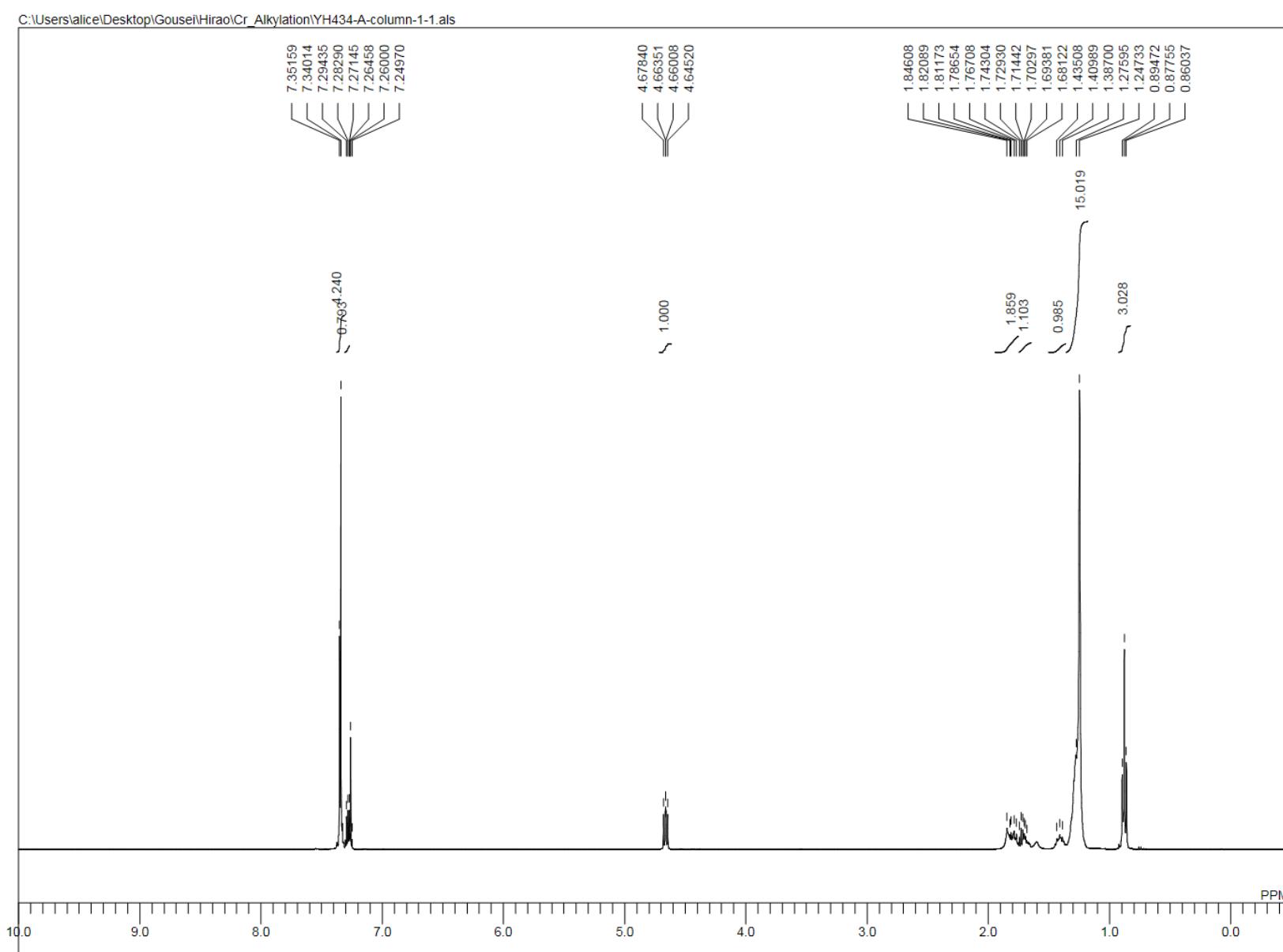


11a

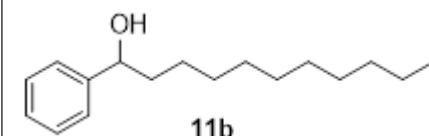
¹³C NMR (125 MHz, CDCl₃)



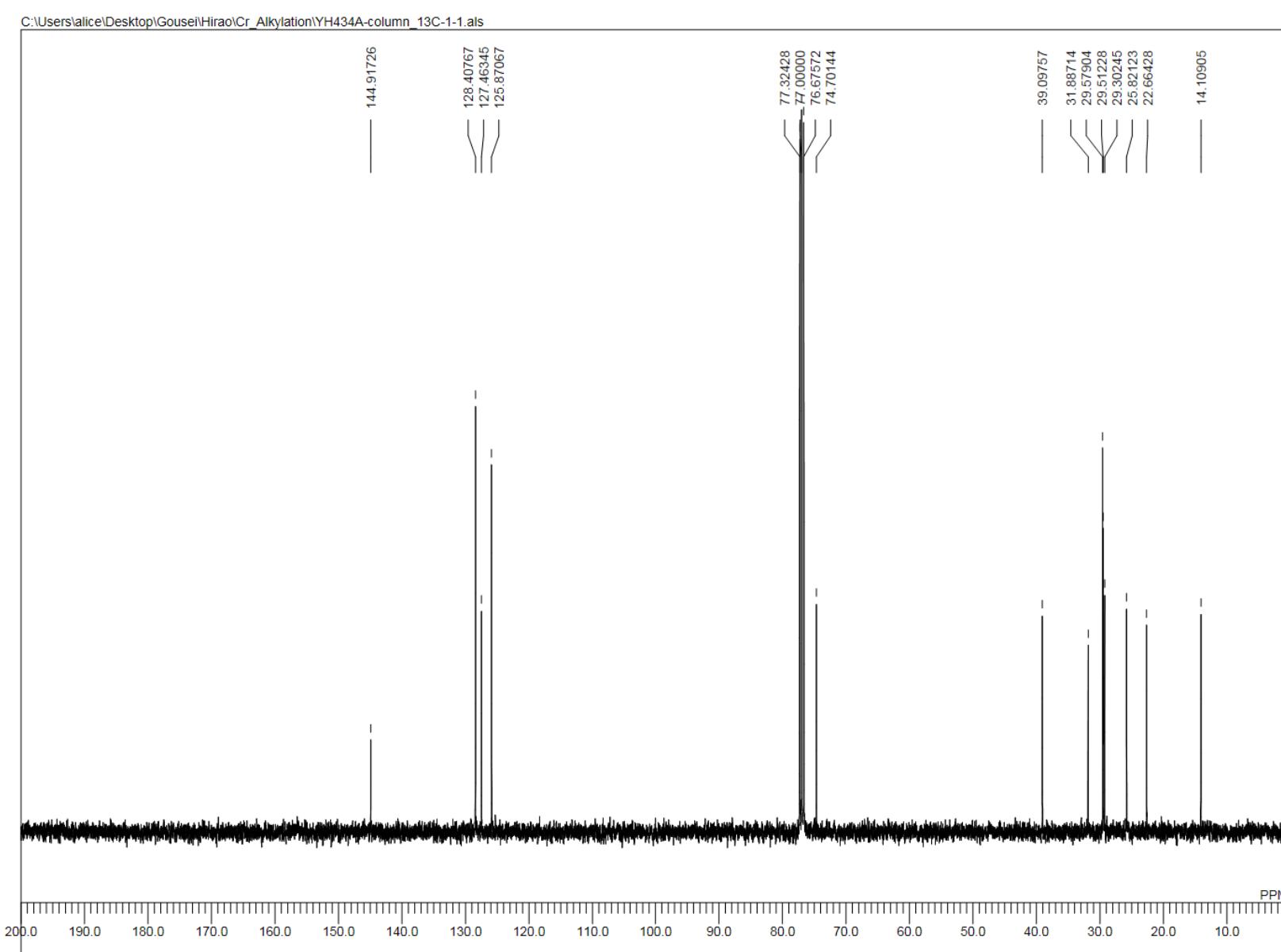
¹H NMR (400 MHz, CDCl₃)



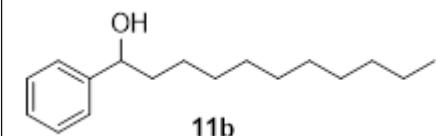
YH434-A-column-1-1.als
26-06-2020 14:34:50
1H
proton.jxp
391.78 MHz
8.51 kHz
3.34 Hz
13107
5878.90 Hz
8
2.2295 sec
6.0000 sec
5.17 usec
1H
21.0 c
CDCl₃
7.26 ppm
0.12 Hz
34



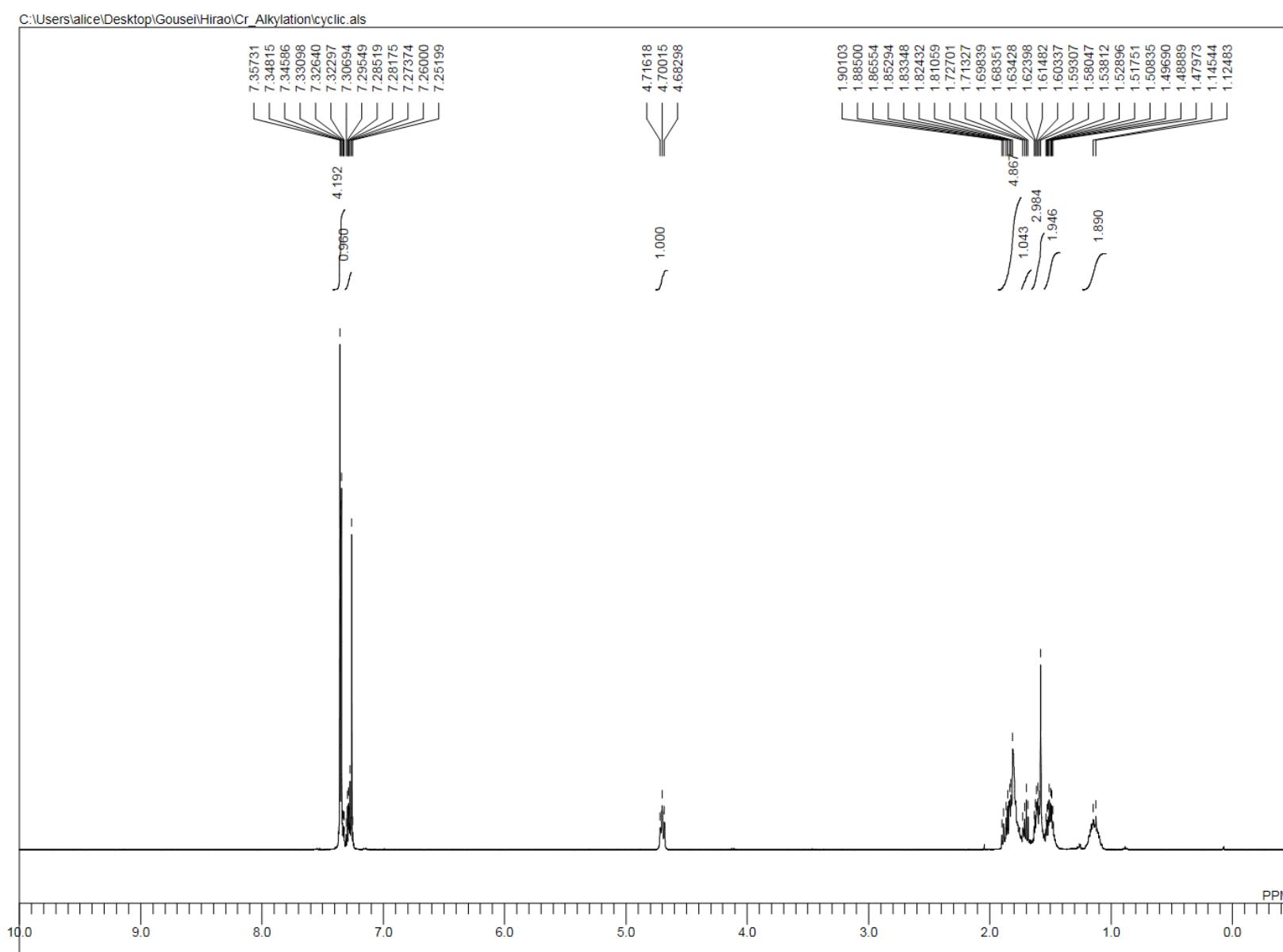
¹³C NMR (100 MHz, CDCl₃)



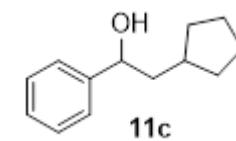
YH434A-column_13C-1-1.ak
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFREQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
13C
26-06-2020 14:47:49
carbon.jxp
98.52 MHz
4.64 KHz
8.74 Hz
26214
24630.54 Hz
120
1.0643 sec
2.0000 sec
3.12 usec
1H
21.2 c
CDCL₃
77.00 ppm
1.20 Hz
60



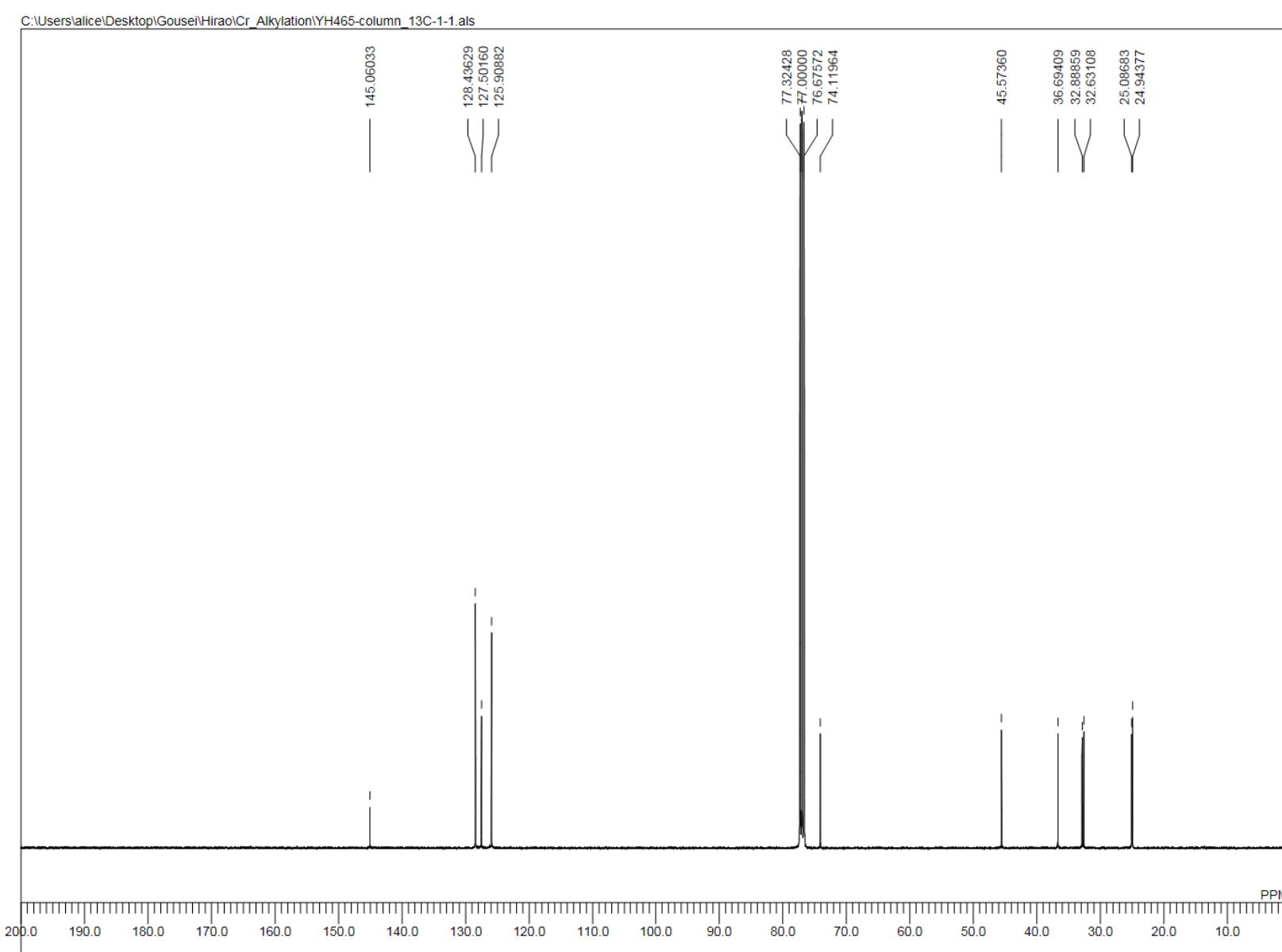
¹H NMR (400 MHz, CDCl₃)



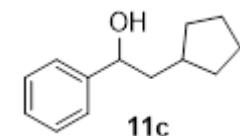
DFILE cyclic.als
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DATIM 1H
OBNUC proton.jxp
EXMOD 391.78 MHz
OBFREQ 8.51 KHz
OBSET 3.34 Hz
OBFIN 13107
POINT 5878.90 Hz
FREQU 8
SCANS 2.2295 sec
ACQTM 6.0000 sec
PD 5.17 usec
PW1 1H
IRNUC 21.1 c
CTEMP CDCl₃
SLVNT 7.26 ppm
EXREF 0.12 Hz
BF 42
RGAIN



¹³C NMR (100 MHz, CDCl₃)

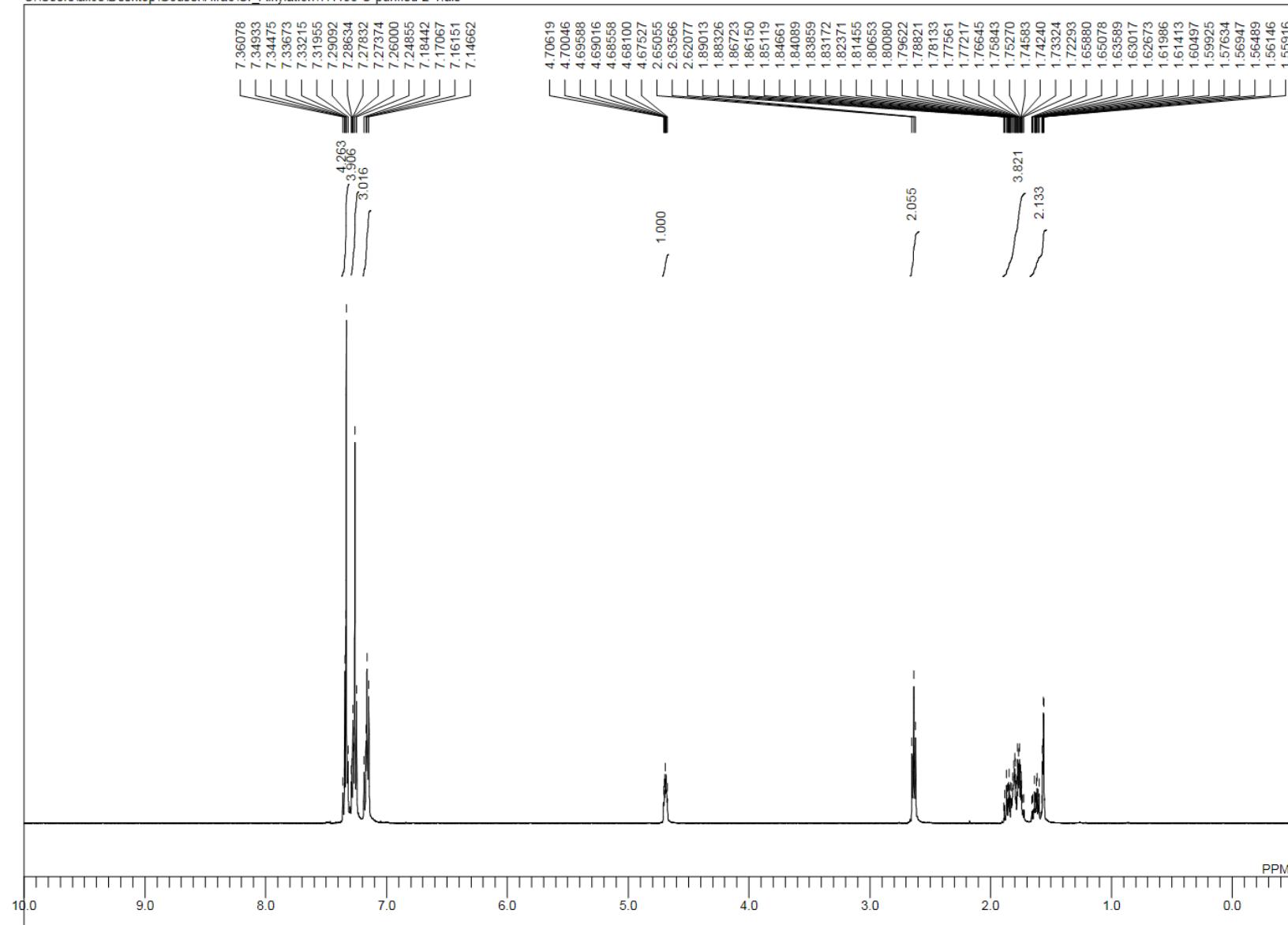


DFILE YH465-column_13C-1-1.als
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OBNUC 13C
EXMOD carbon.jxp
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OBSET 4.64 kHz
OBFIN 8.74 Hz
POINT 26214
FREQU 24630.54 Hz
SCANS 16821
ACQTM 1.0643 sec
PD 2.0000 sec
PW1 3.12 usec
IRNUC 1H
CTEMP 21.2 c
SLVNT CDCl₃
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60

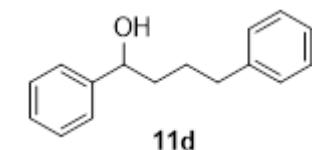


¹H NMR (500 MHz, CDCl₃)

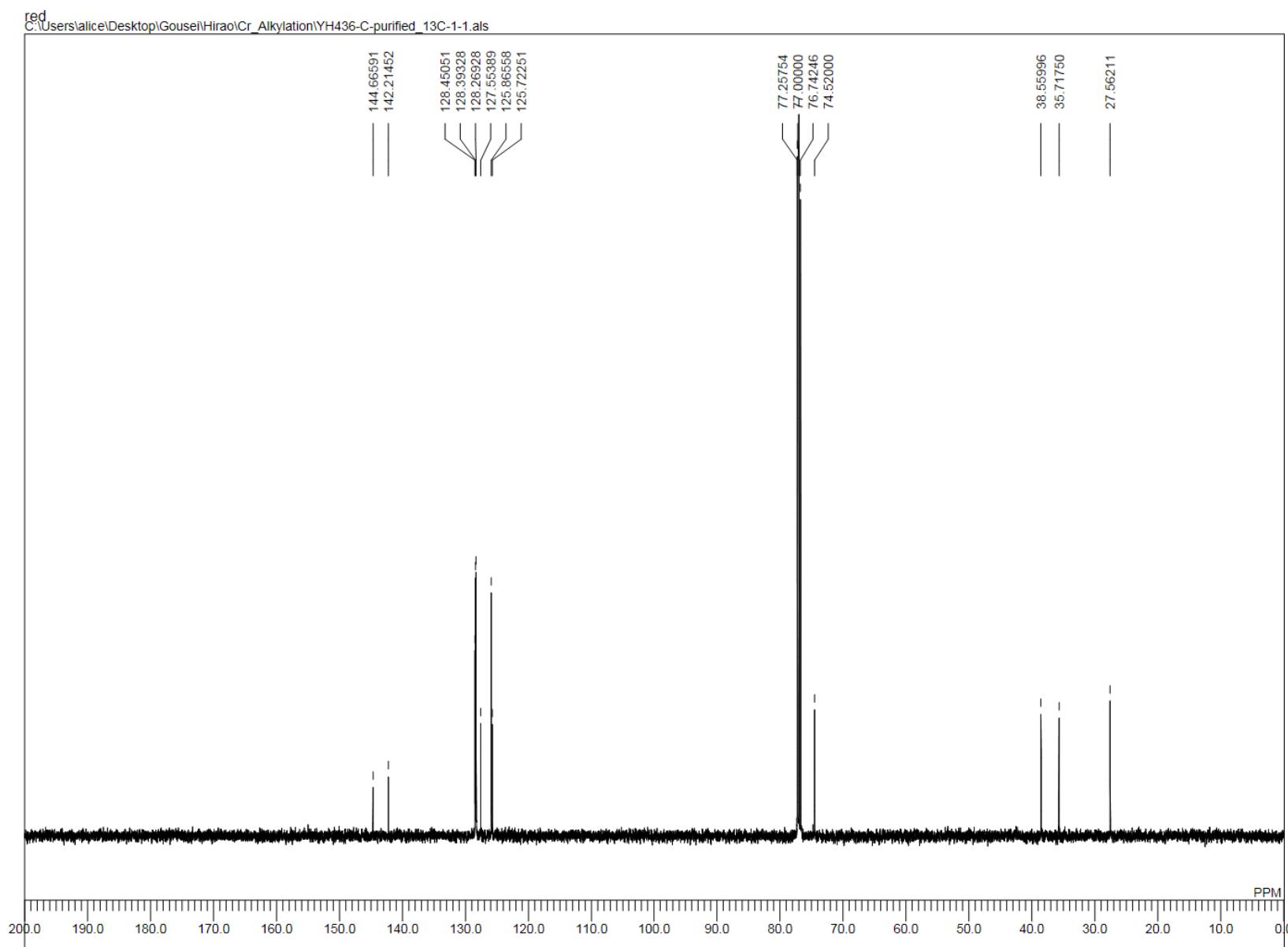
C:\Users\alice\Desktop\Gousei\Hirao\Cr_Aalkylation\YH436-C-purified-2-1.als



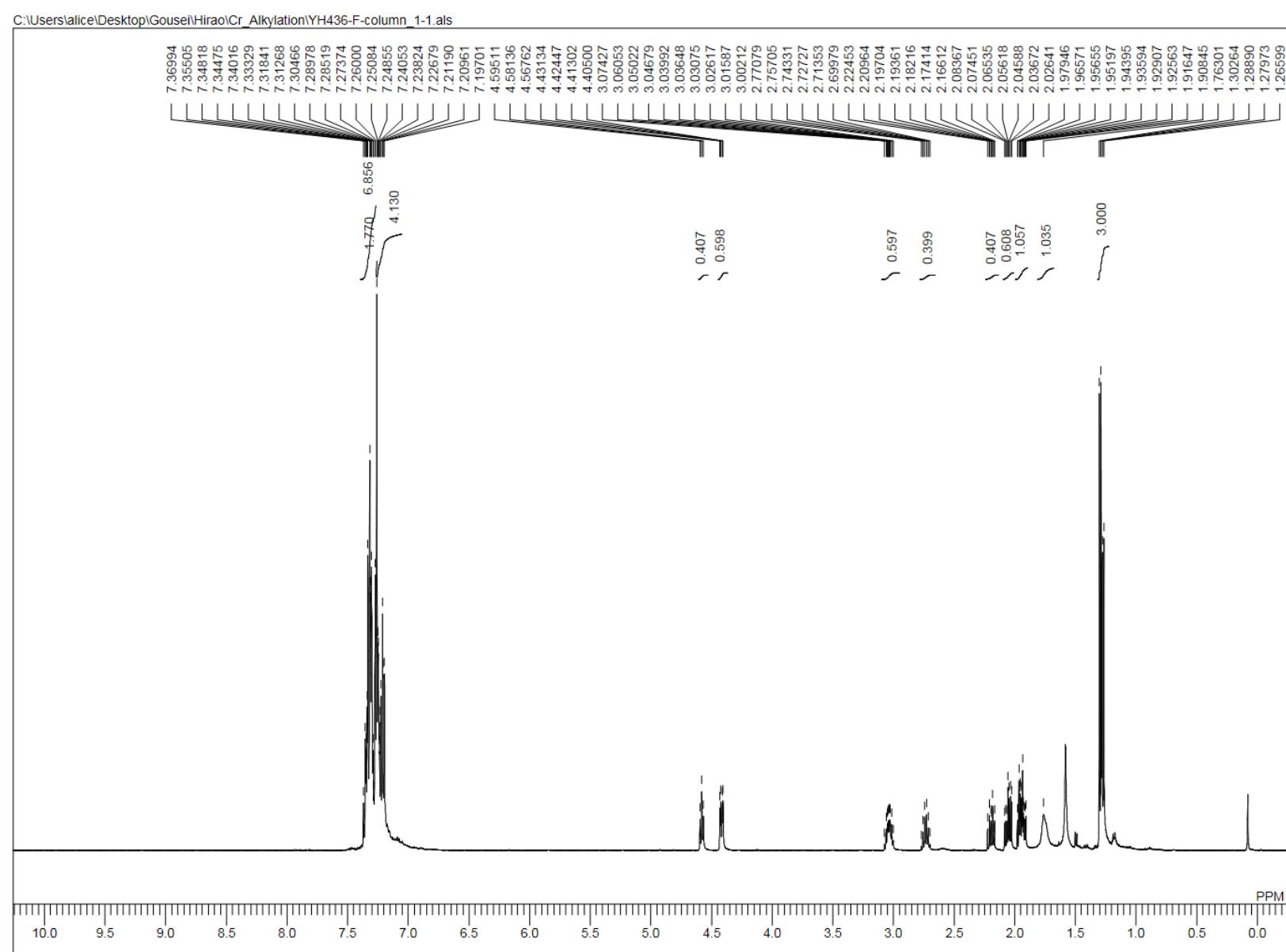
YH436-C-purified-2-1.als
DFILE
COMNT
DATIM
OBNUC
EXMOD
proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 kHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 6.0000 sec
PW1 5.55 usec
1H
IRNUC 22.0 c
CTEMP CDCl₃
SLVNT 7.26 ppm
EXREF BF 0.12 Hz
RGAIN 42



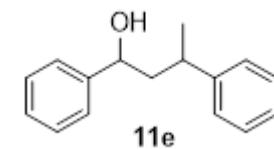
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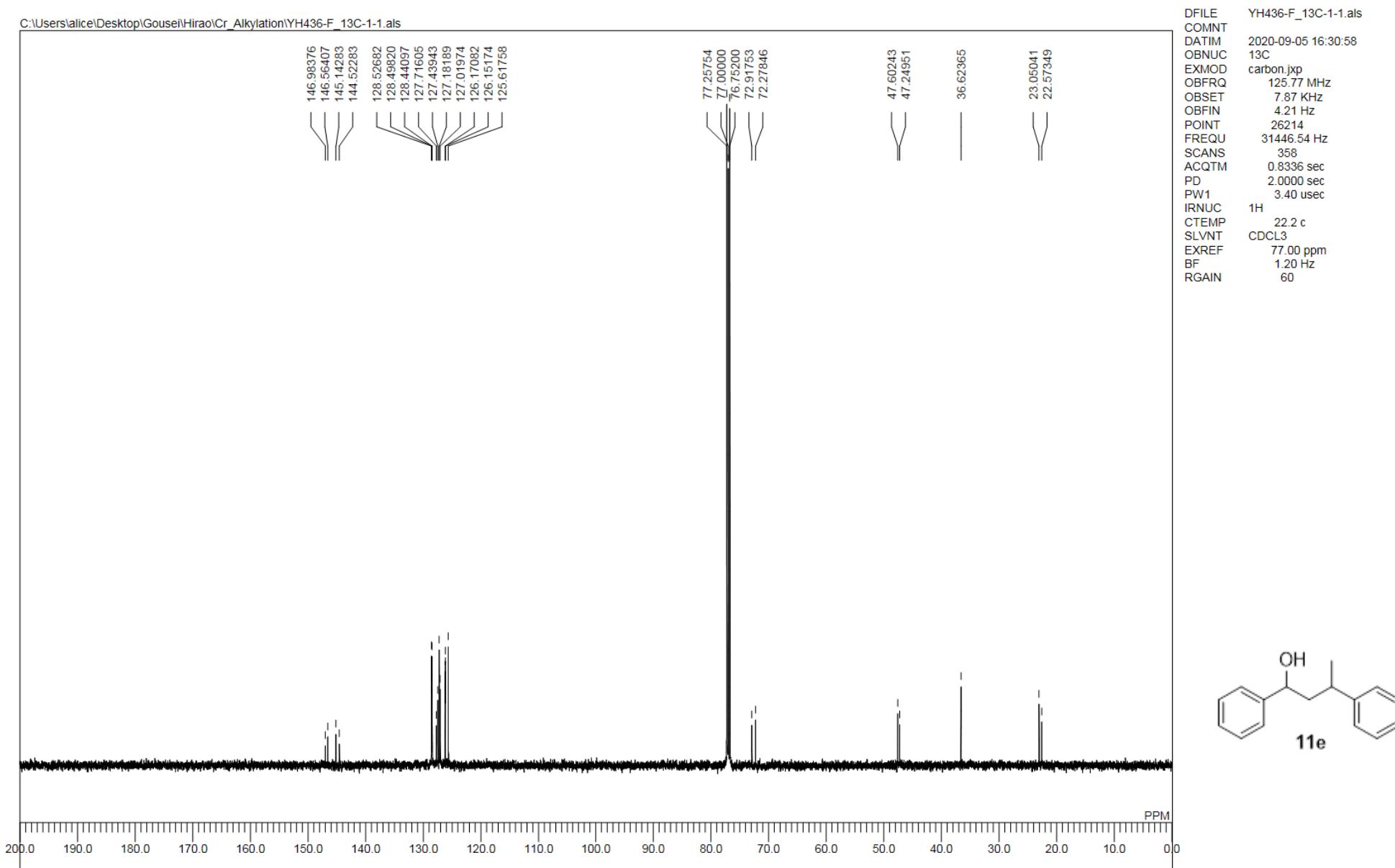
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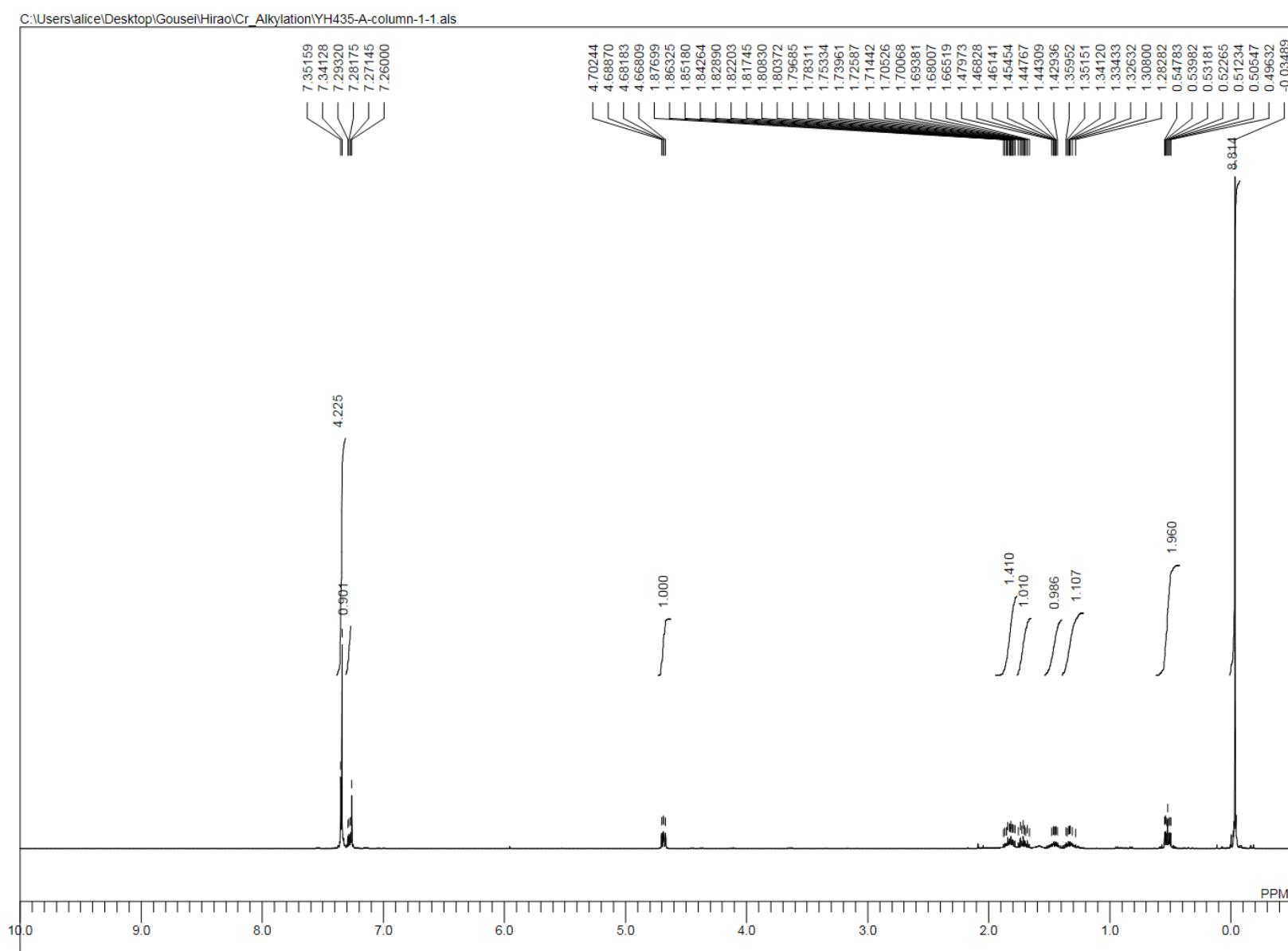
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 2020-09-05 16:29:13
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 proton.jxp
 500.16 MHz
 2.41 kHz
 6.01 Hz
 13107
 7507.51 Hz
 8
 1.7459 sec
 6.0000 sec
 5.55 usec
 1H
 21.9 c
 CDCl₃
 7.26 ppm
 0.12 Hz
 40



¹³C NMR (125 MHz, CDCl₃)



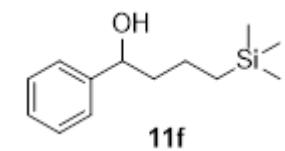
¹H NMR (400 MHz, CDCl₃)



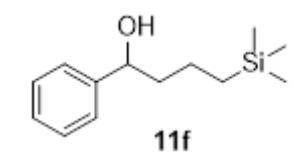
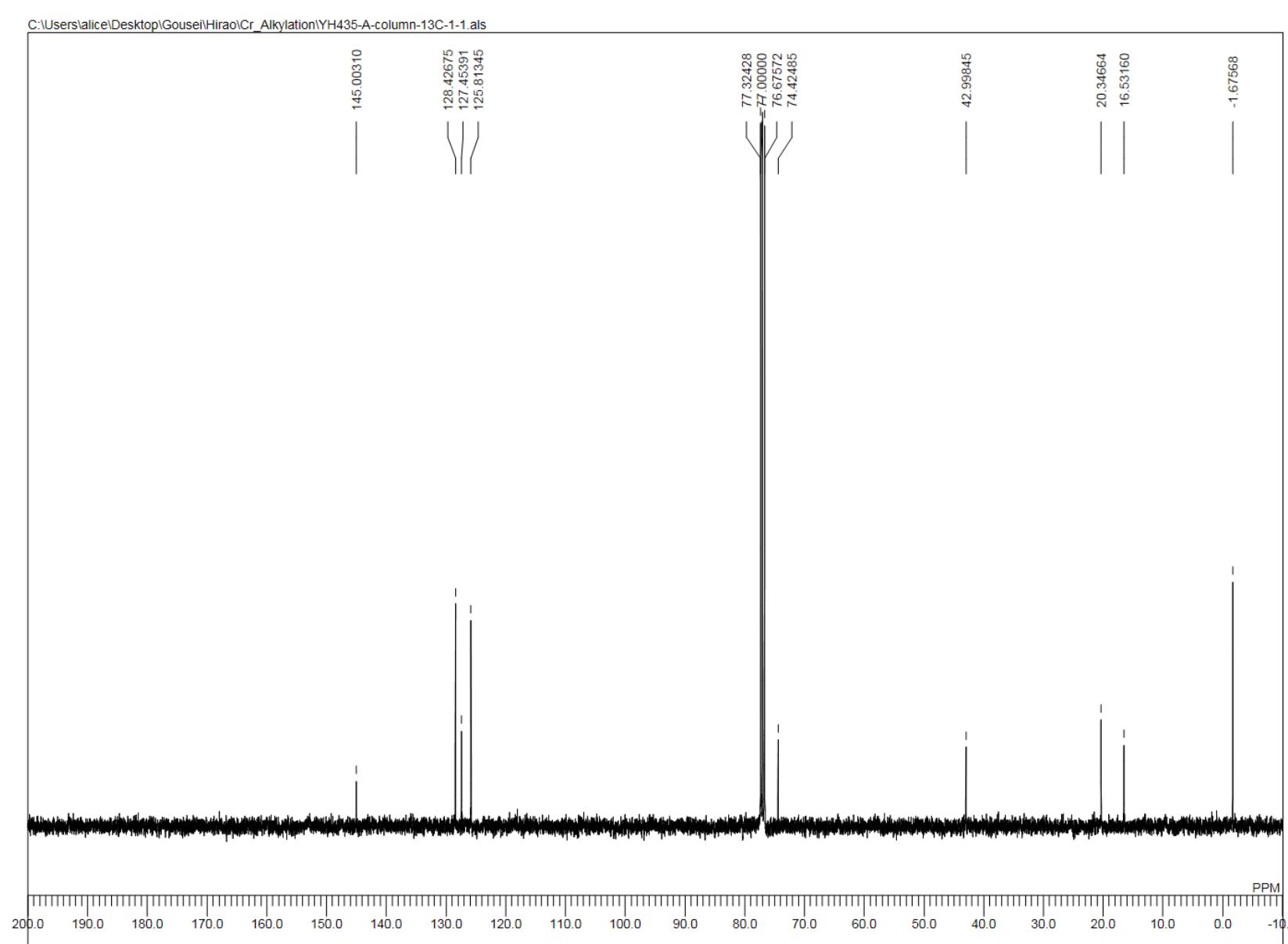
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EXMOD proton.jxp
OBFREQ 391.78 MHz
OBSET 8.51 kHz
OBFIN 3.34 Hz
POINT 13107
FREQU 5878.90 Hz
SCANS 8
ACQTM 2.2295 sec
PD 6.0000 sec
PW1 5.17 usec
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 38

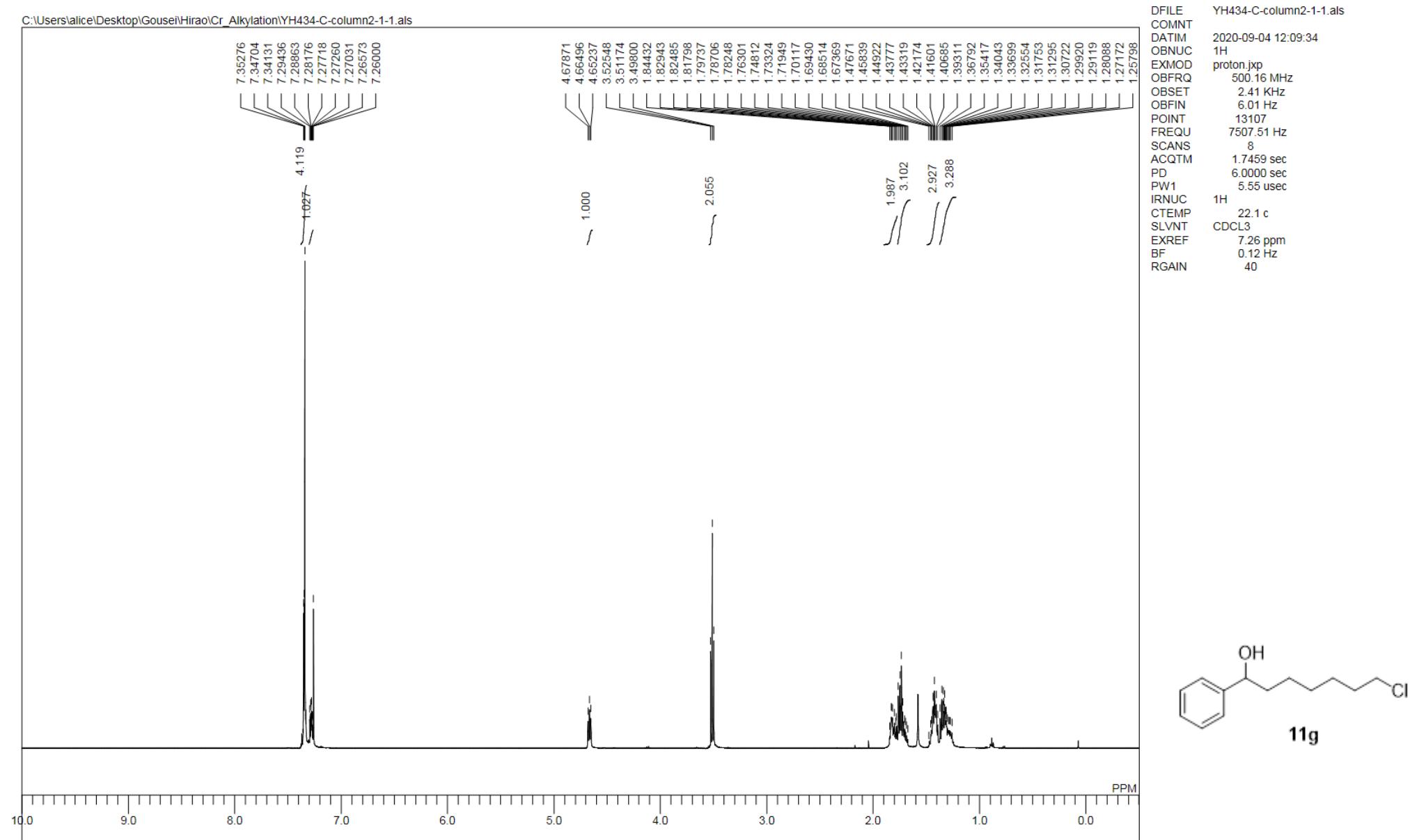
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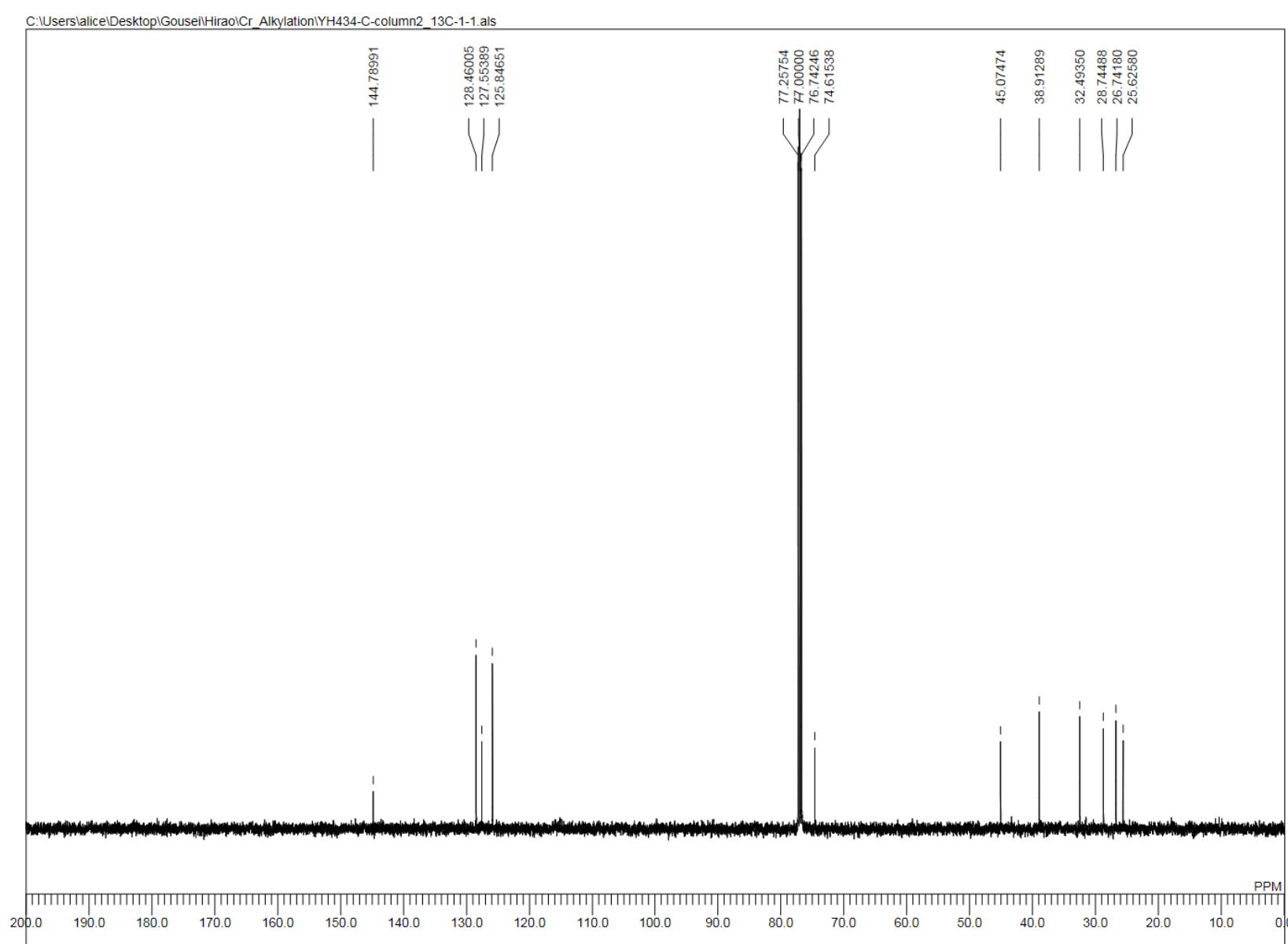
¹³C NMR (100 MHz, CDCl₃)



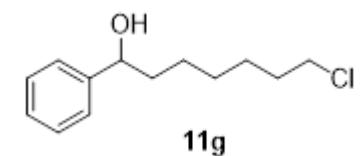
¹H NMR (500 MHz, CDCl₃)



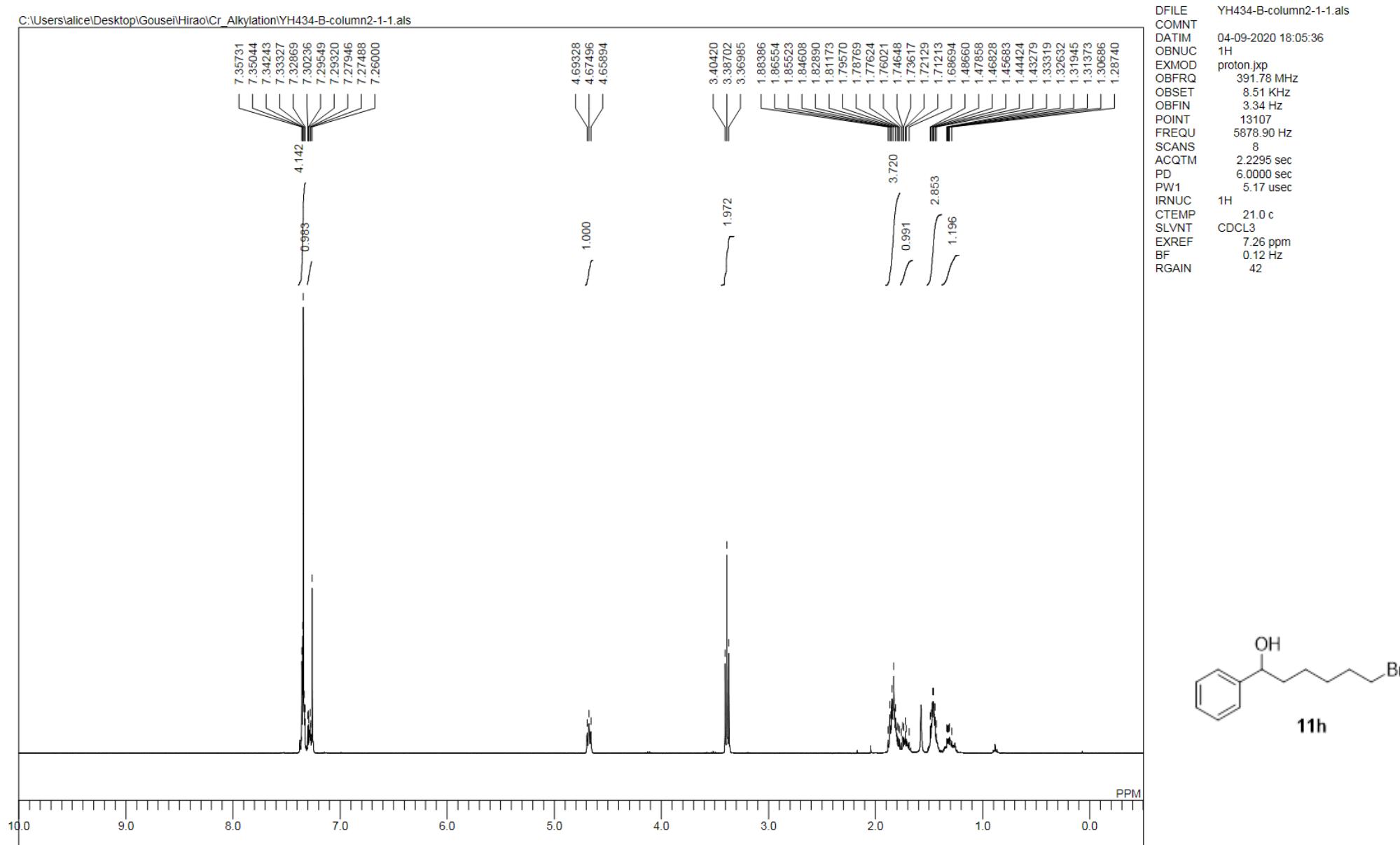
¹³C NMR (125 MHz, CDCl₃)



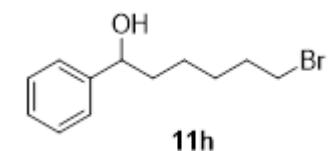
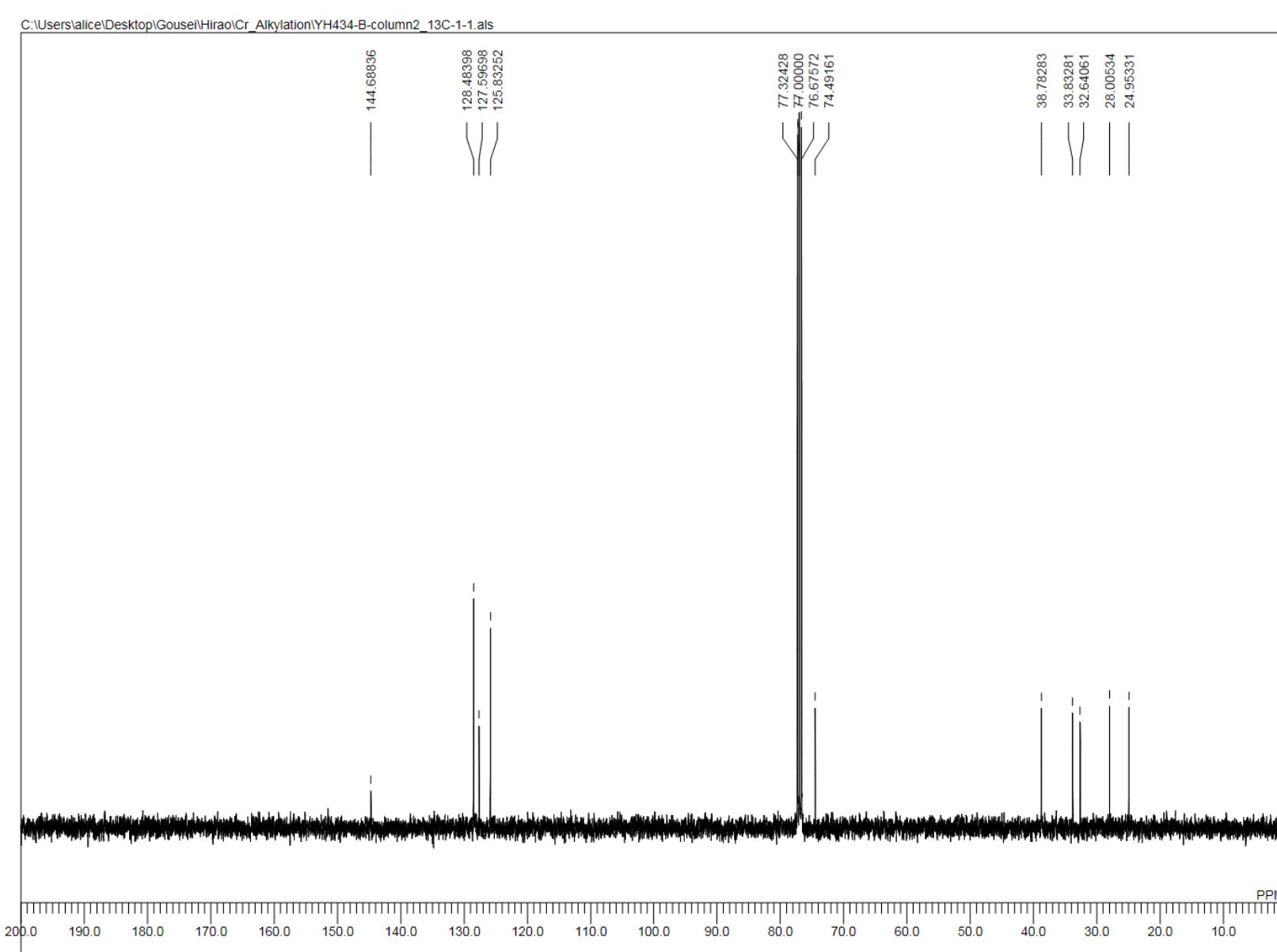
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DFILE
COMNT
DATIM
OBNUC
EXMOD
carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 172
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCl₃
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60



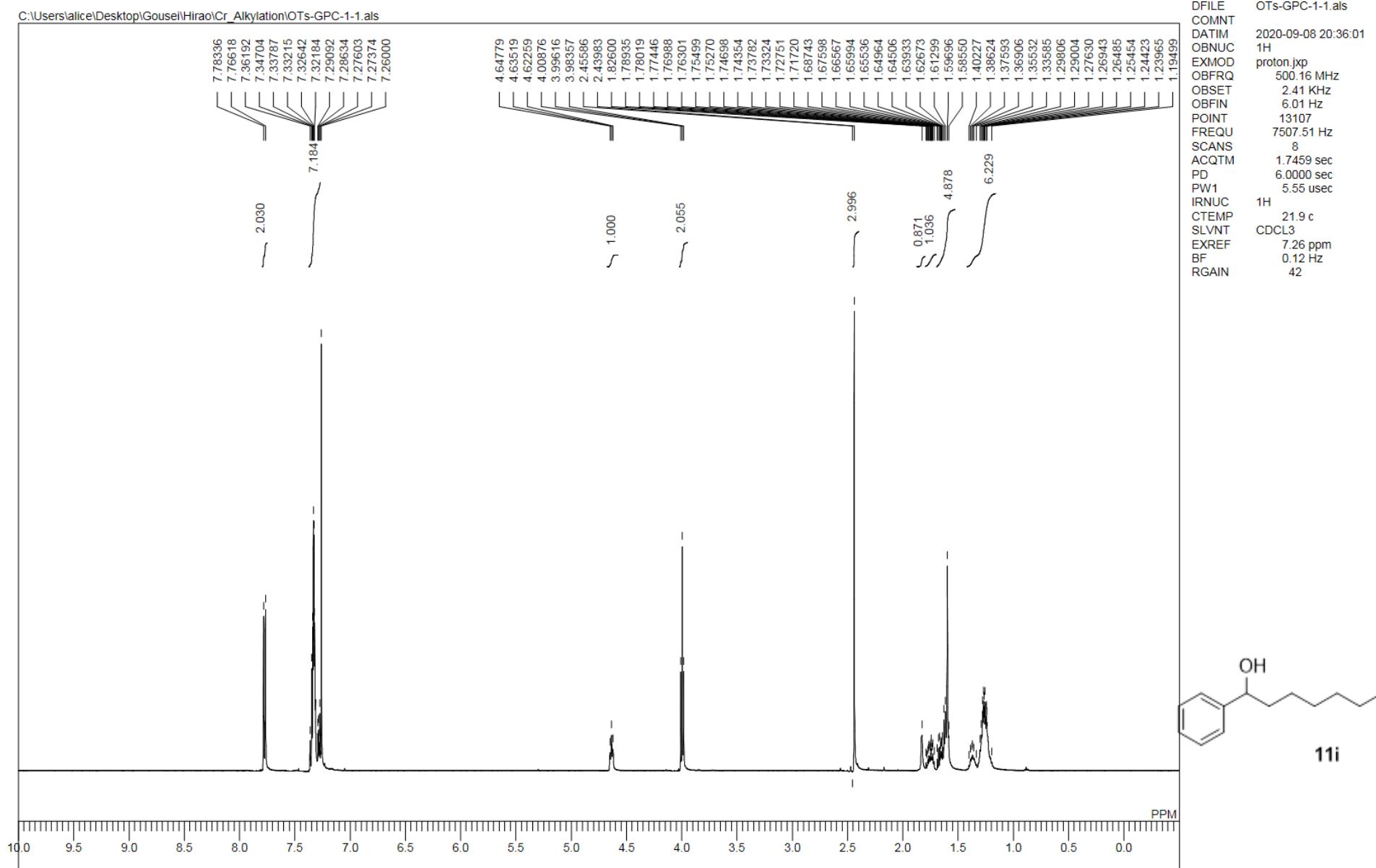
¹H NMR (400 MHz, CDCl₃)



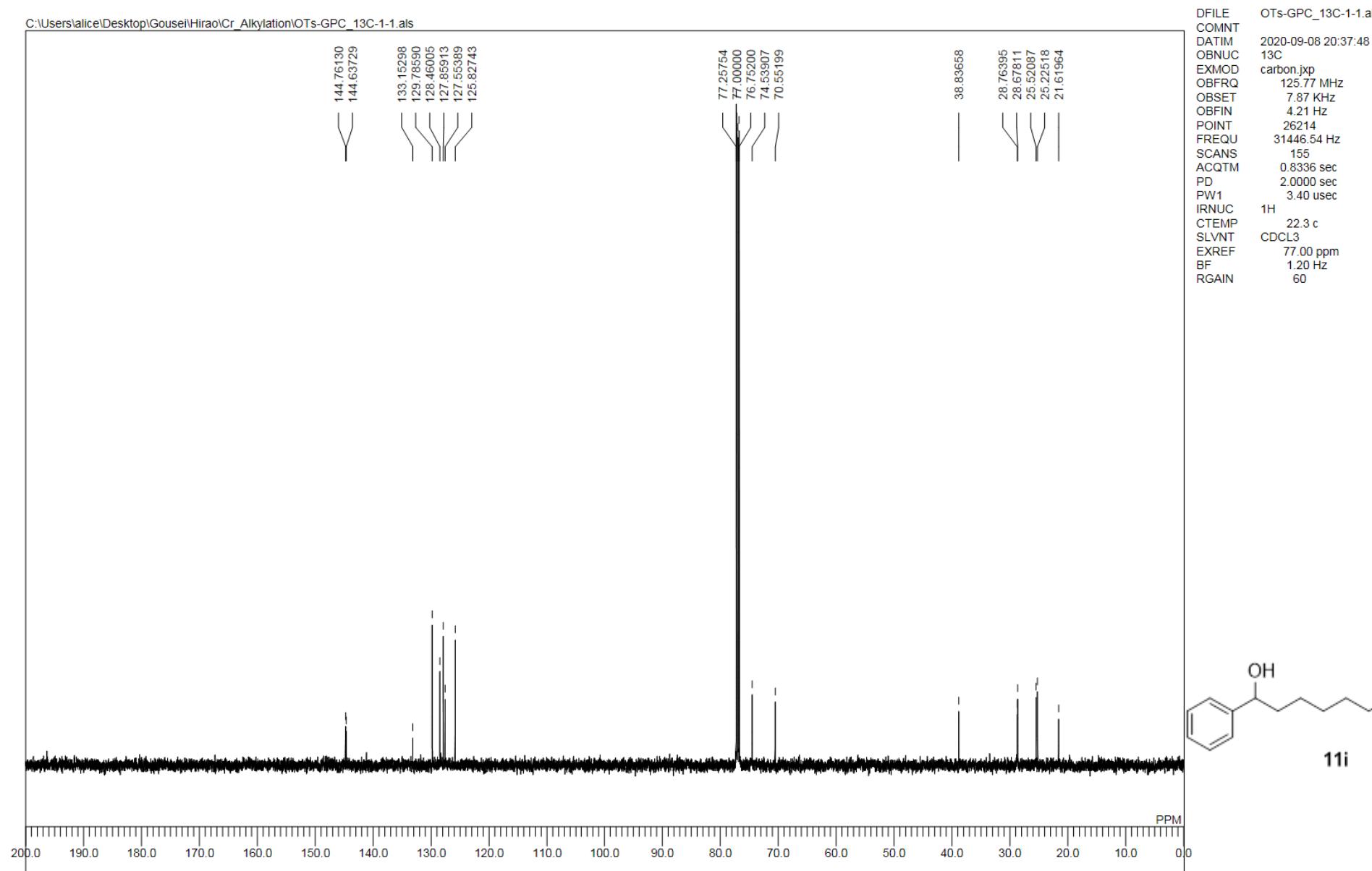
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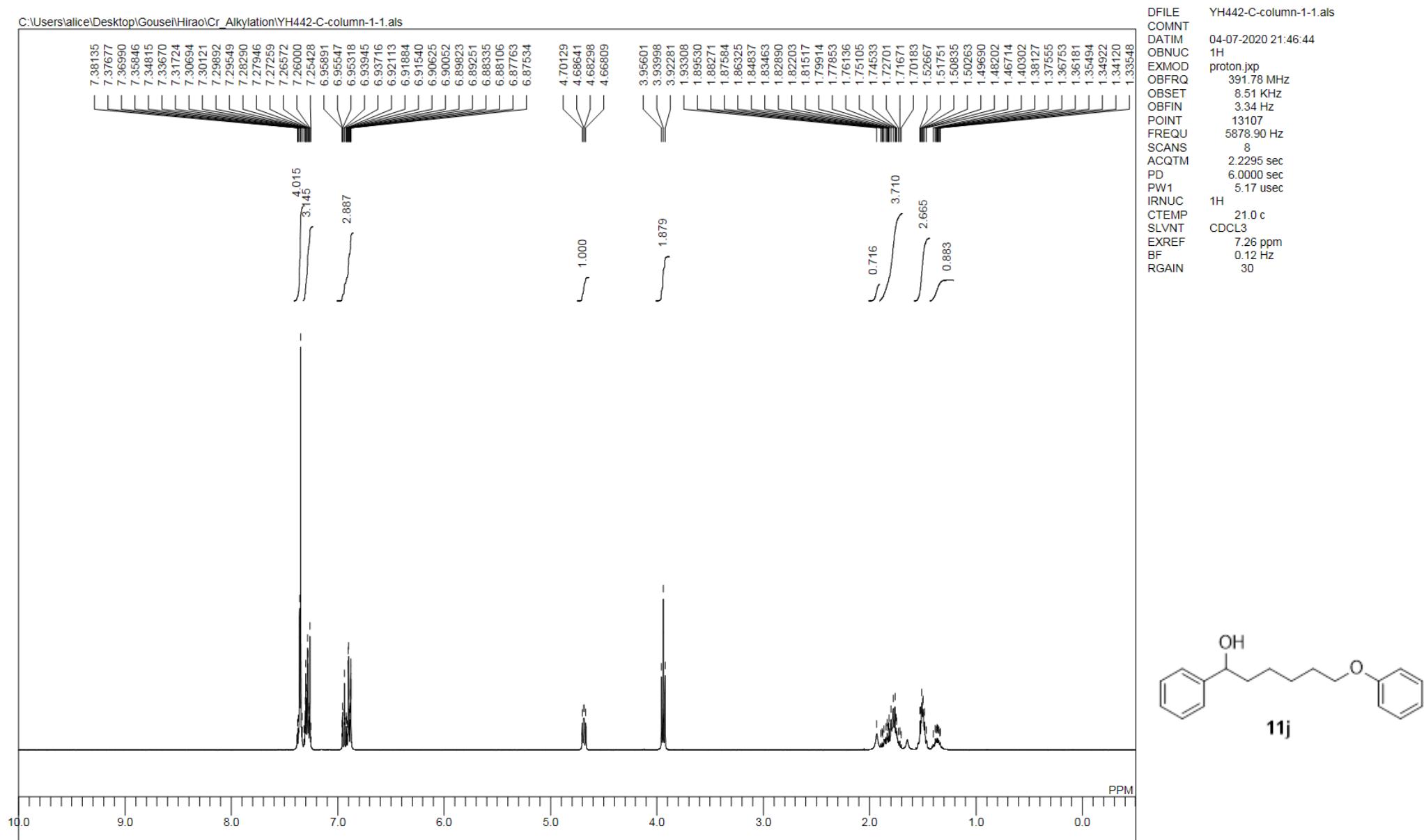
¹H NMR (500 MHz, CDCl₃)



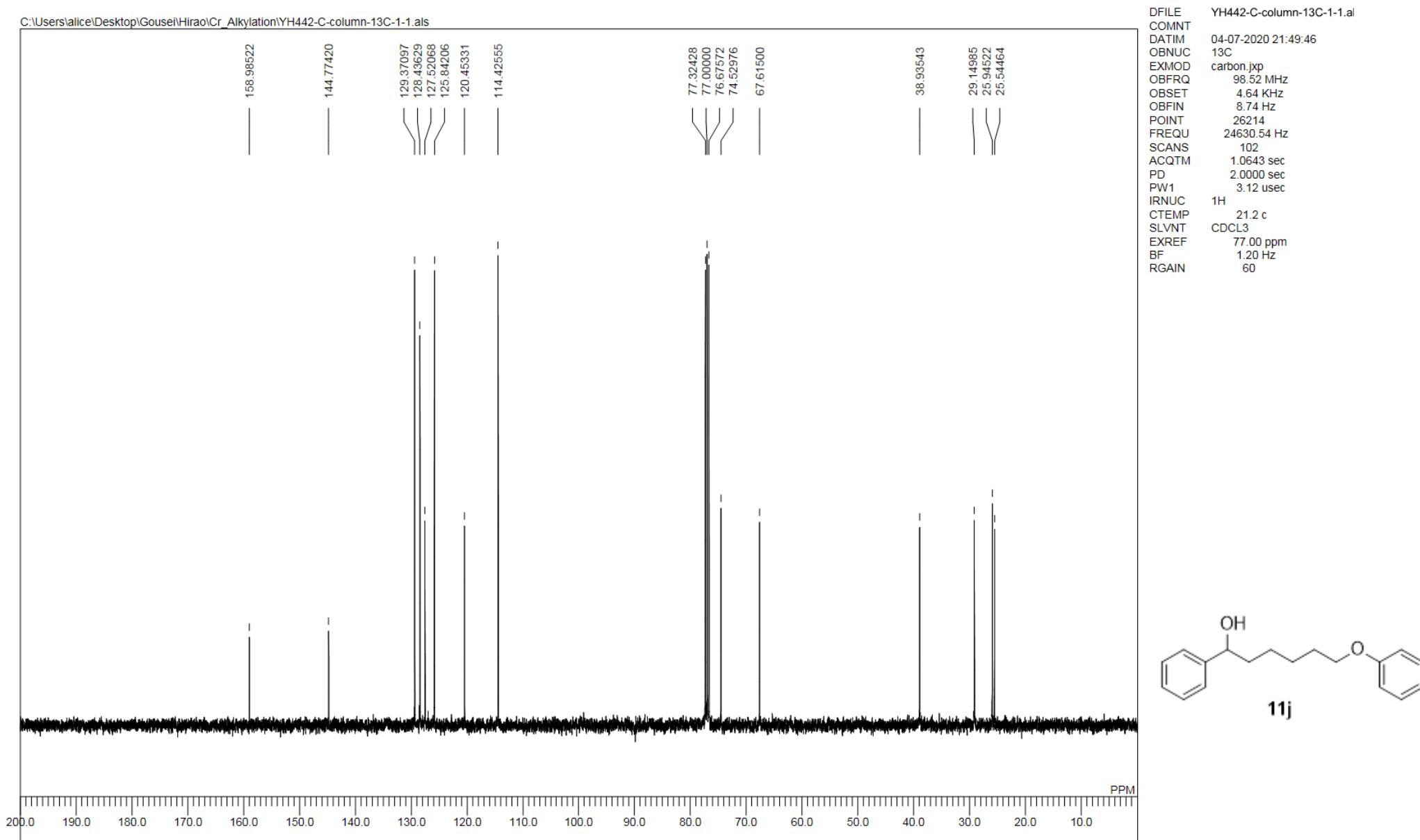
¹³C NMR (125 MHz, CDCl₃)



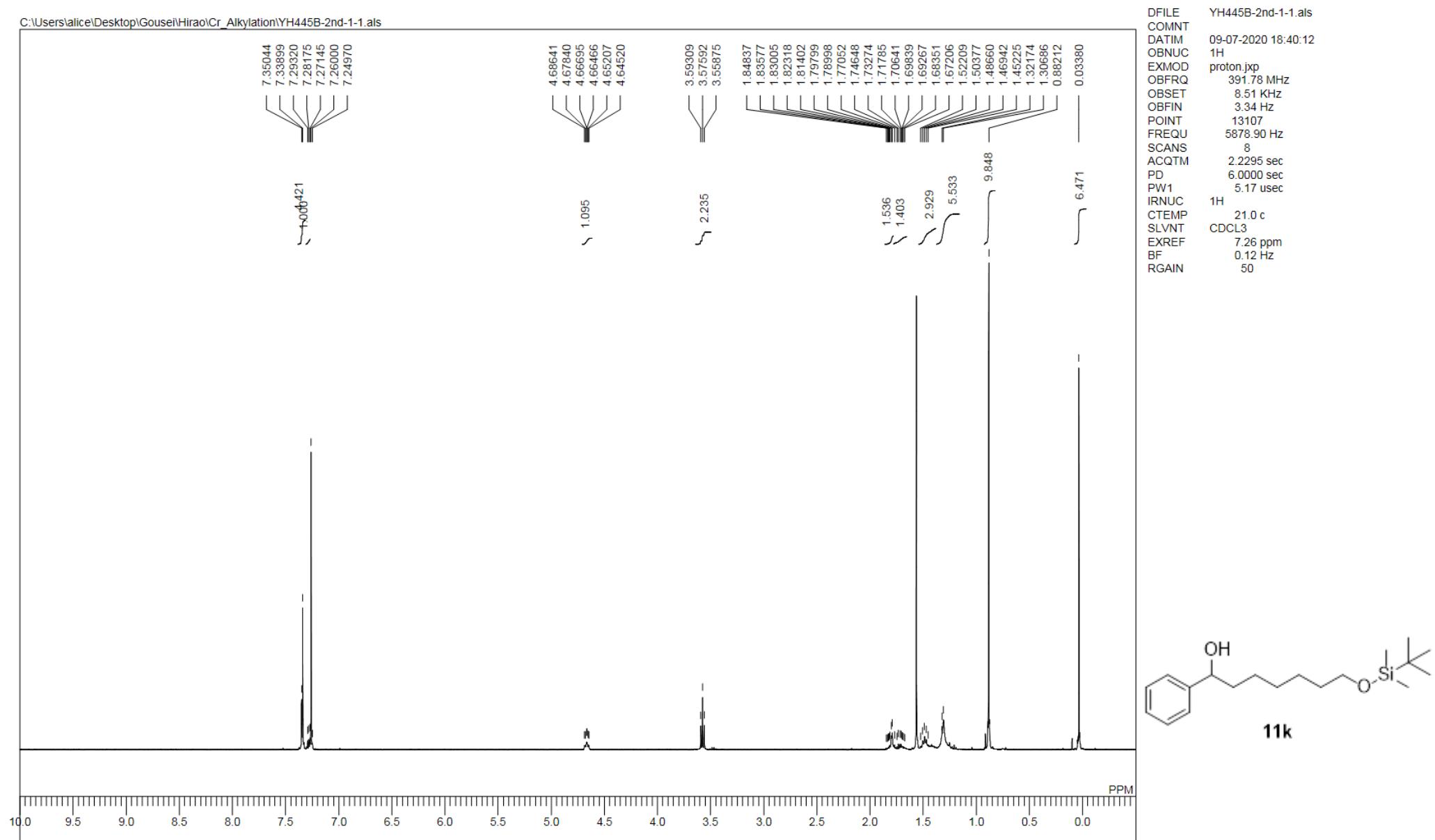
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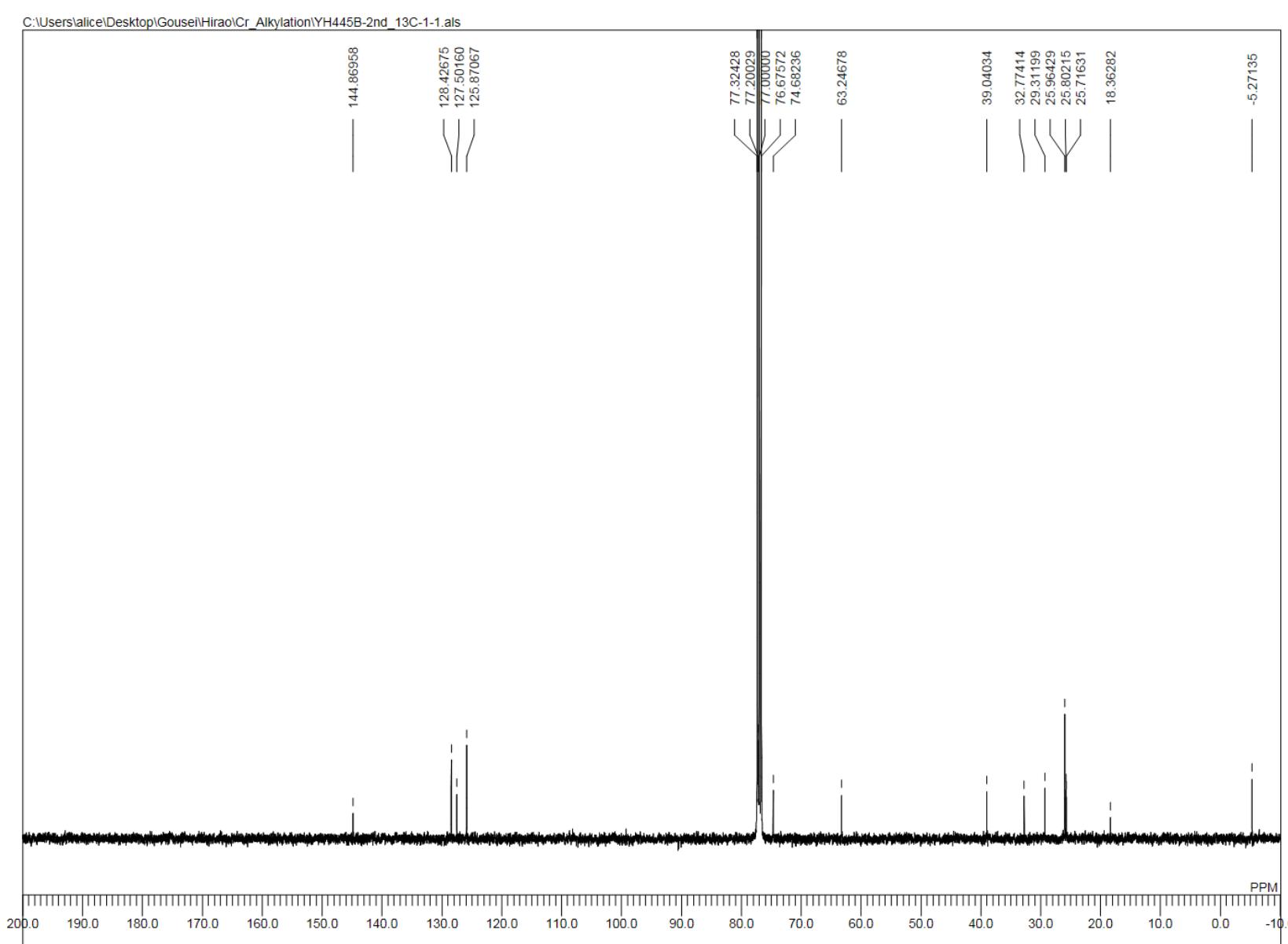
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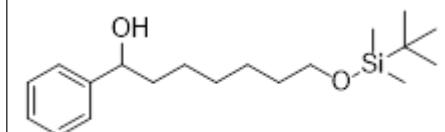
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¹³C NMR (100 MHz, CDCl₃)

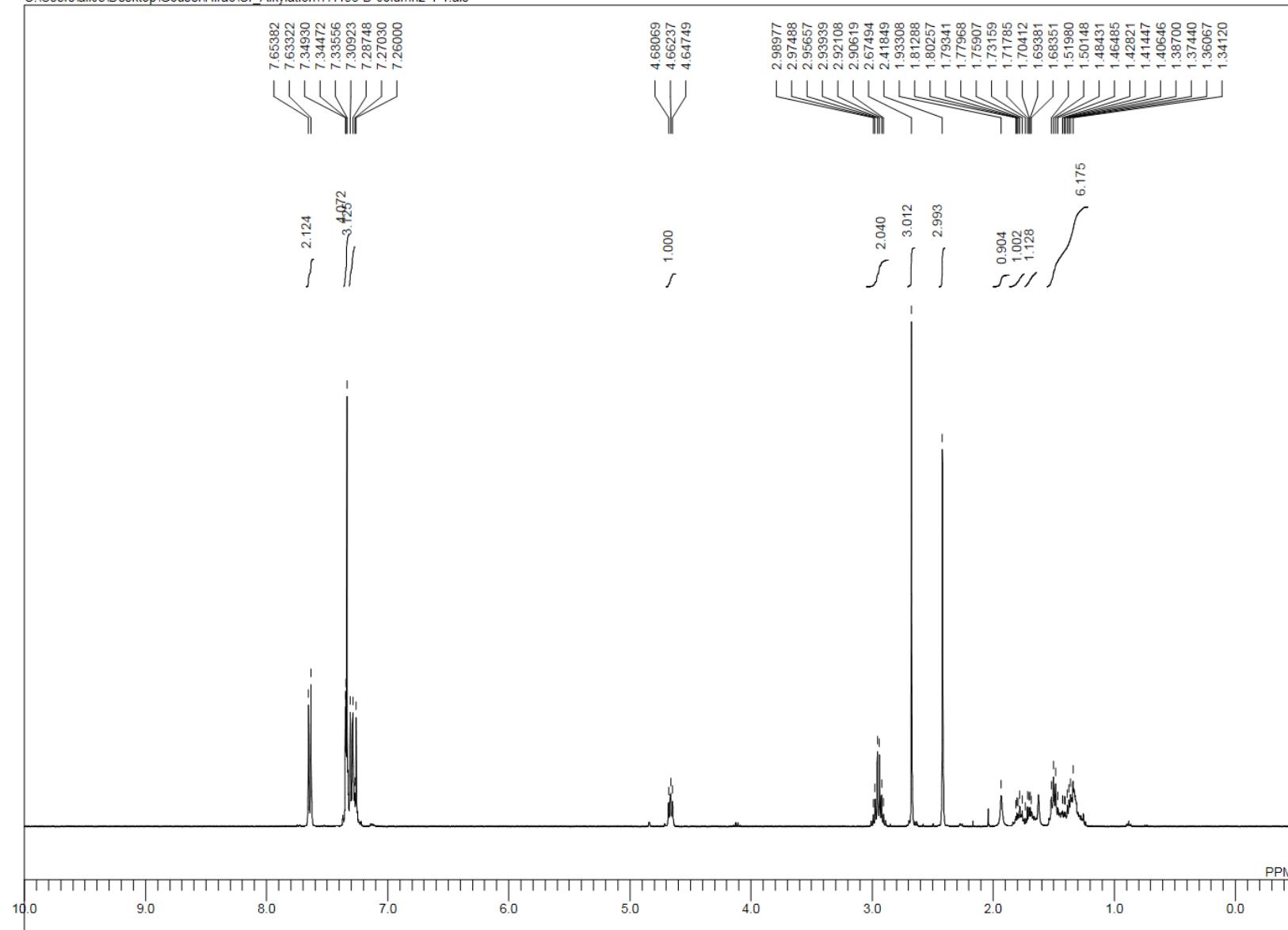


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DATIM 13C
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EXMOD 98.52 MHz
OBFRQ 4.64 KHz
OBSET 8.74 Hz
OBFIN 26214
POINT 24630.54 Hz
FREQU 2985
SCANS 1.0643 sec
ACQTM 2.0000 sec
PD 3.12 usec
PW1 1H
IRNUC 21.1 c
CTEMP CDCl₃
SLVNT 77.00 ppm
EXREF 1.20 Hz
BF 60
RGAIN



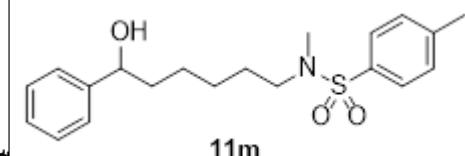
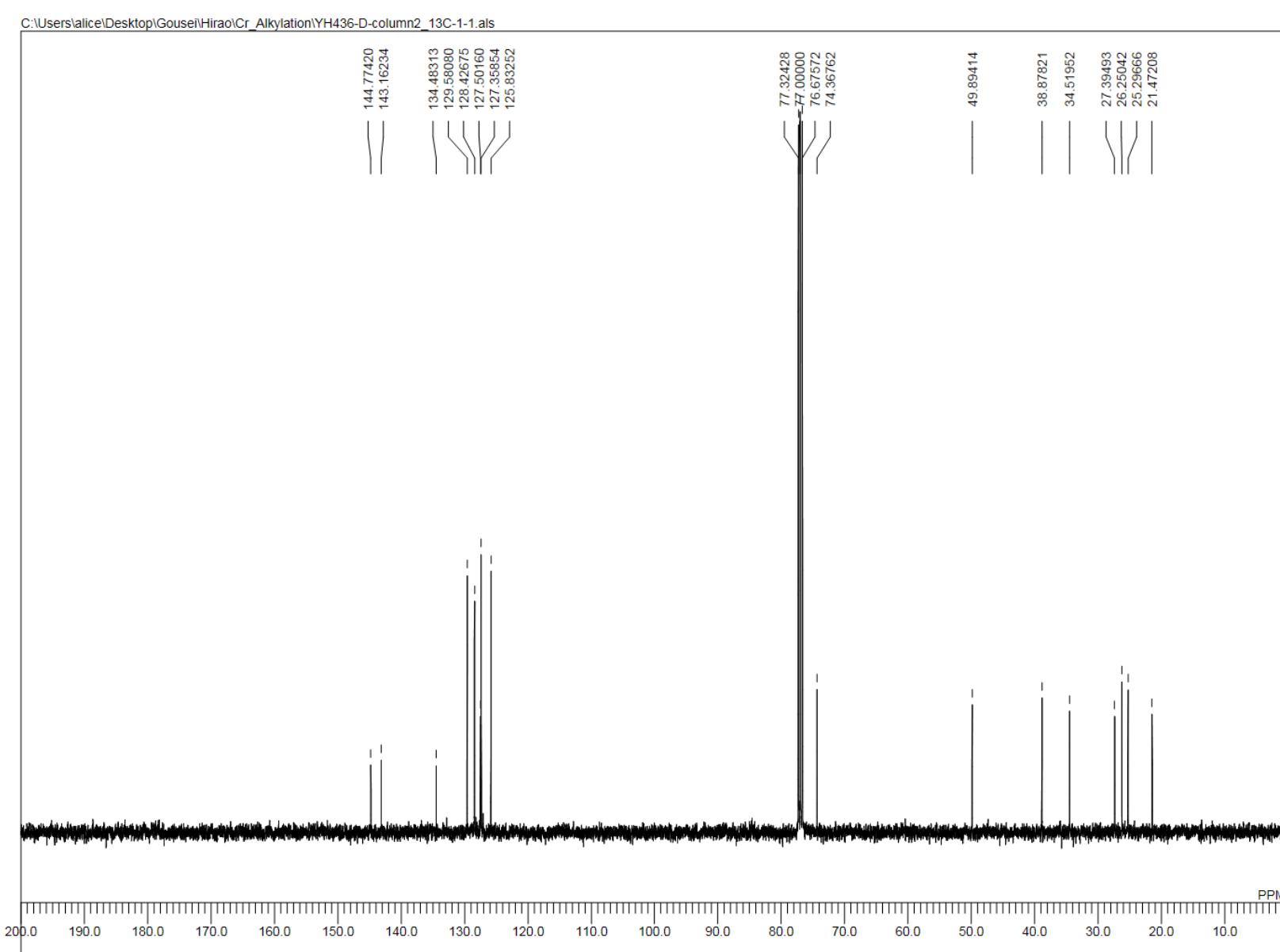
¹H NMR (400 MHz, CDCl₃)

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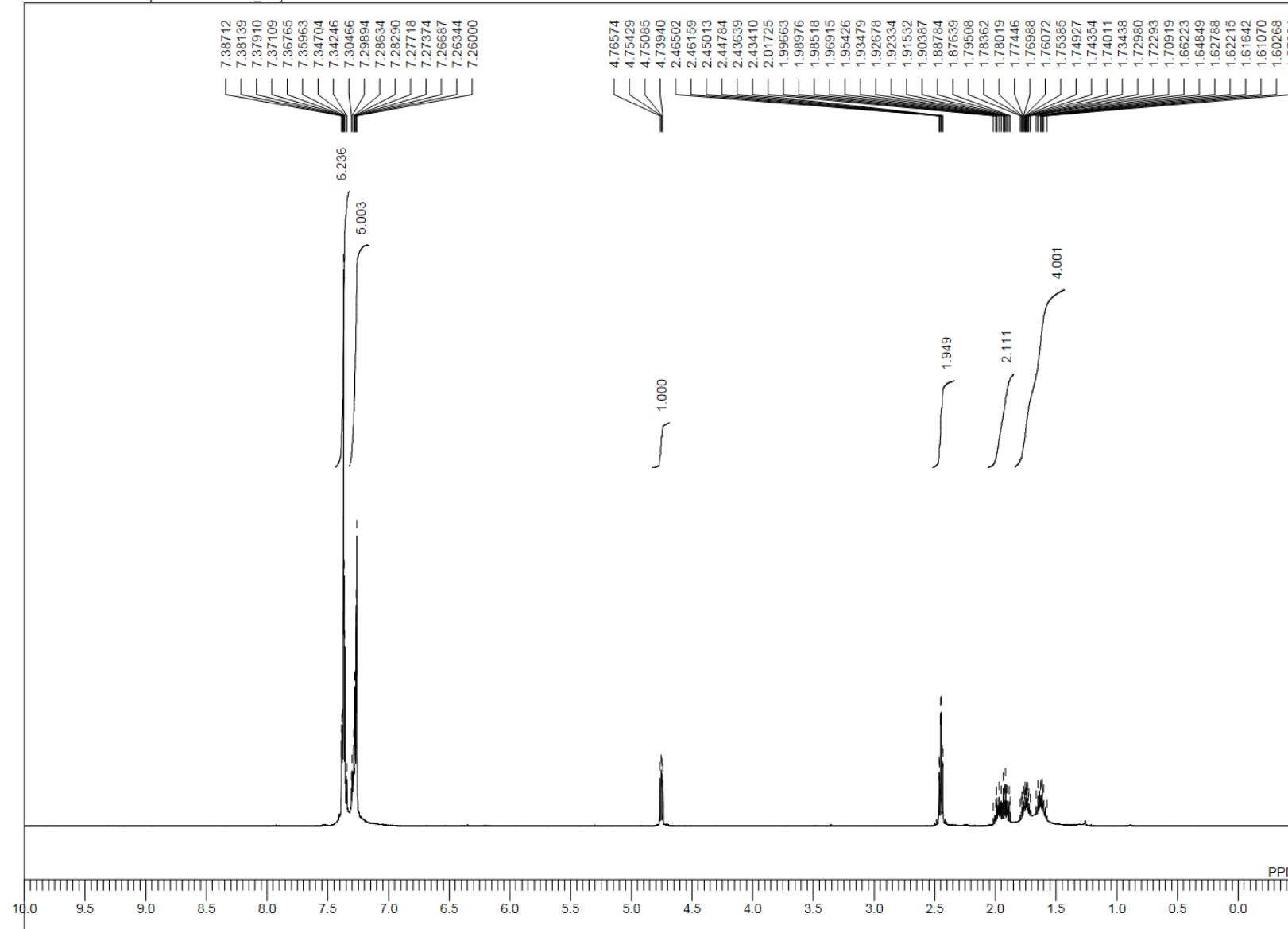
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 04-09-2020 18:17:04
 1H
 proton.jxp
 391.78 MHz
 8.51 kHz
 3.34 Hz
 13107
 5878.90 Hz
 8
 2.2295 sec
 6.0000 sec
 5.17 usec
 1H
 20.9 c
 CDCl₃
 7.26 ppm
 0.12 Hz
 36

¹³C NMR (100 MHz, CDCl₃)



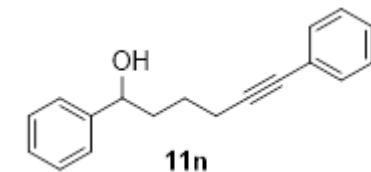
¹H NMR (500 MHz, CDCl₃)

C:\Users\alice\Desktop\Gousei\Hirao\Cr_Alylation\YH455-column-fra14-15-1-1.als

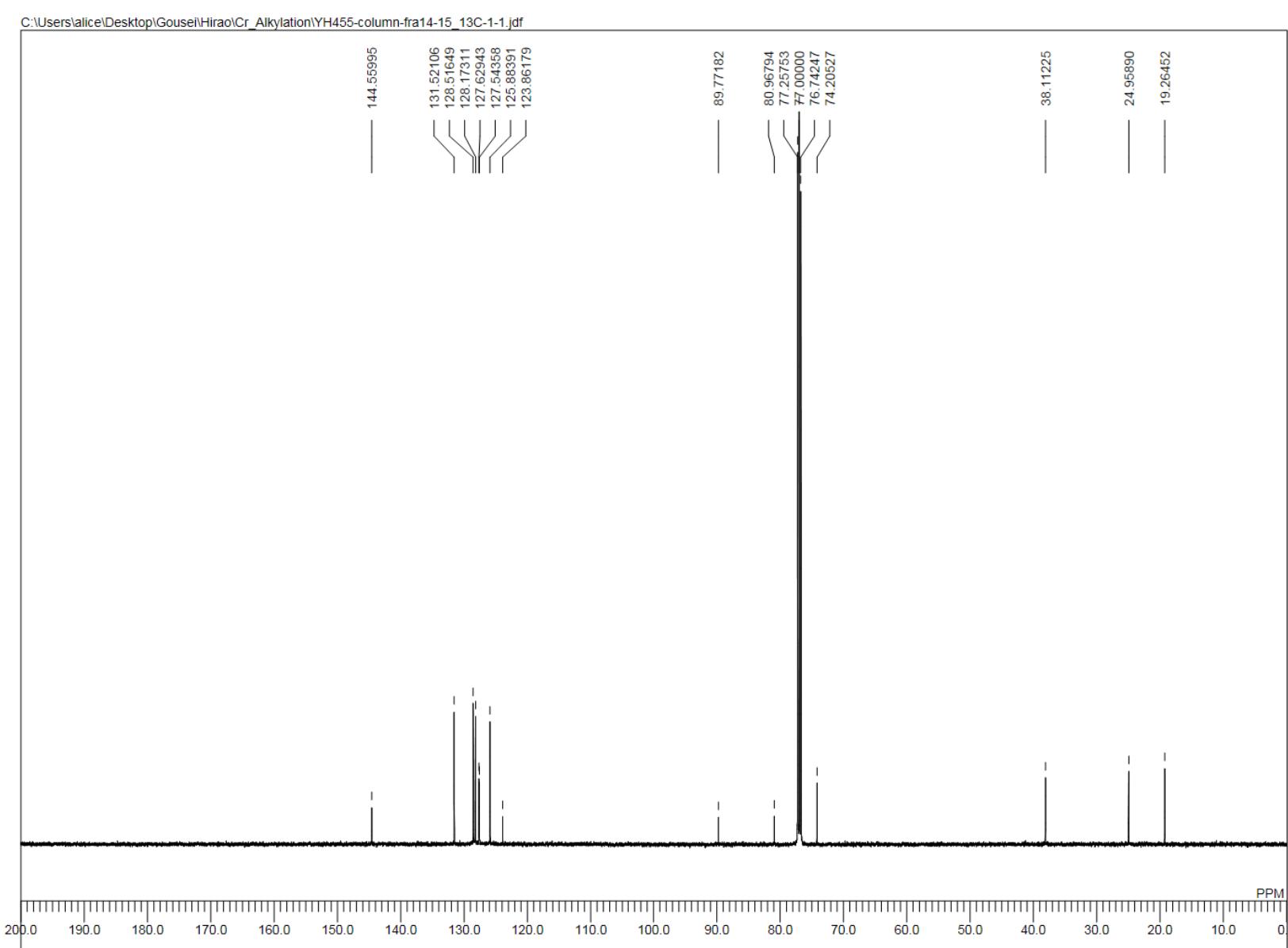


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 DATIM
 OBNUC
 EXMOD
 OBFREQ
 OBSET
 OBFIN
 POINT
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 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

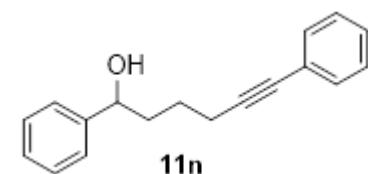
2020-07-21 15:40:21
 1H
 proton.jxp
 500.16 MHz
 2.41 kHz
 6.01 Hz
 13107
 7507.51 Hz
 8
 1.7459 sec
 6.0000 sec
 5.55 usec
 1H
 21.9 c
 CDCl₃
 7.26 ppm
 0.12 Hz
 40



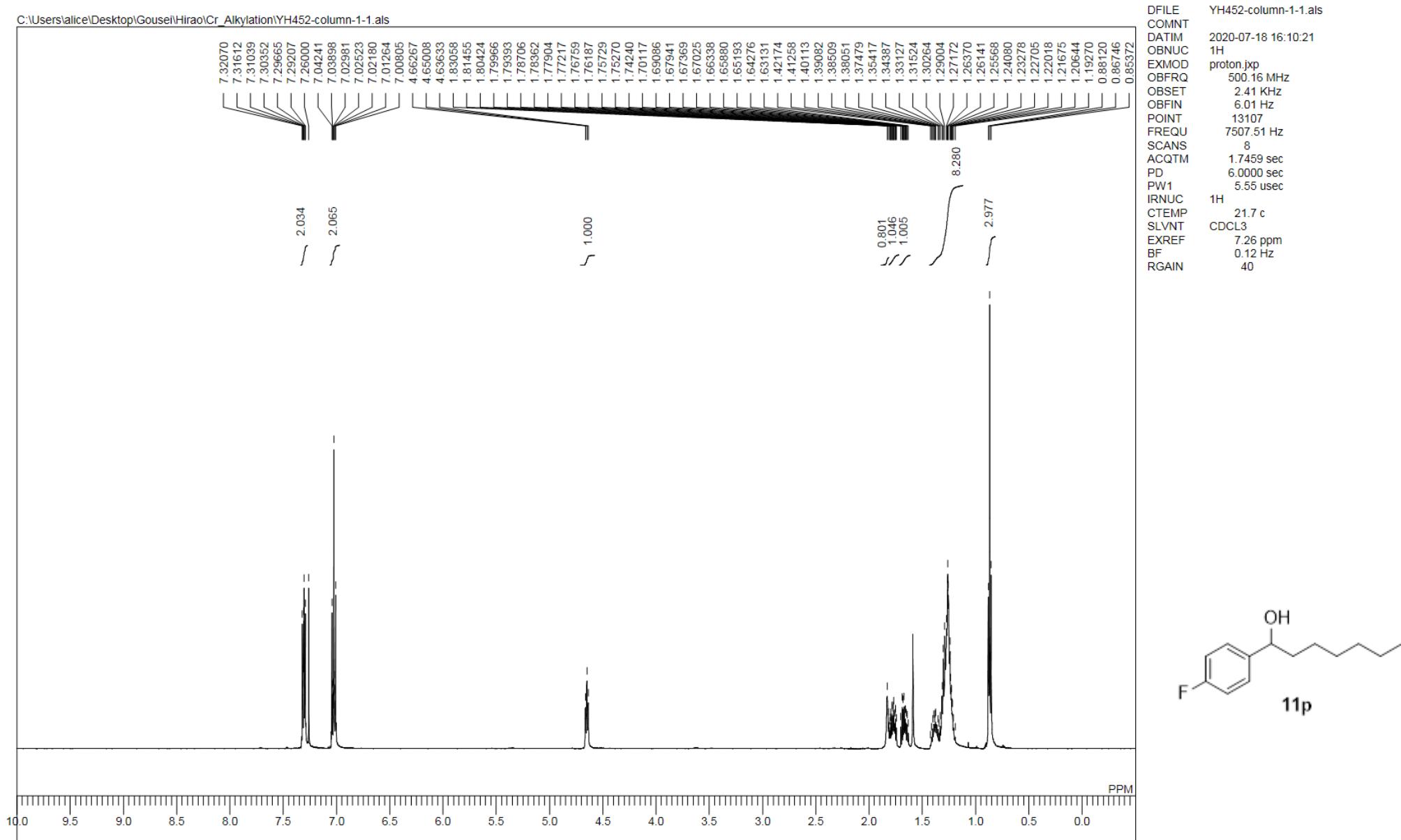
¹³C NMR (125 MHz, CDCl₃)



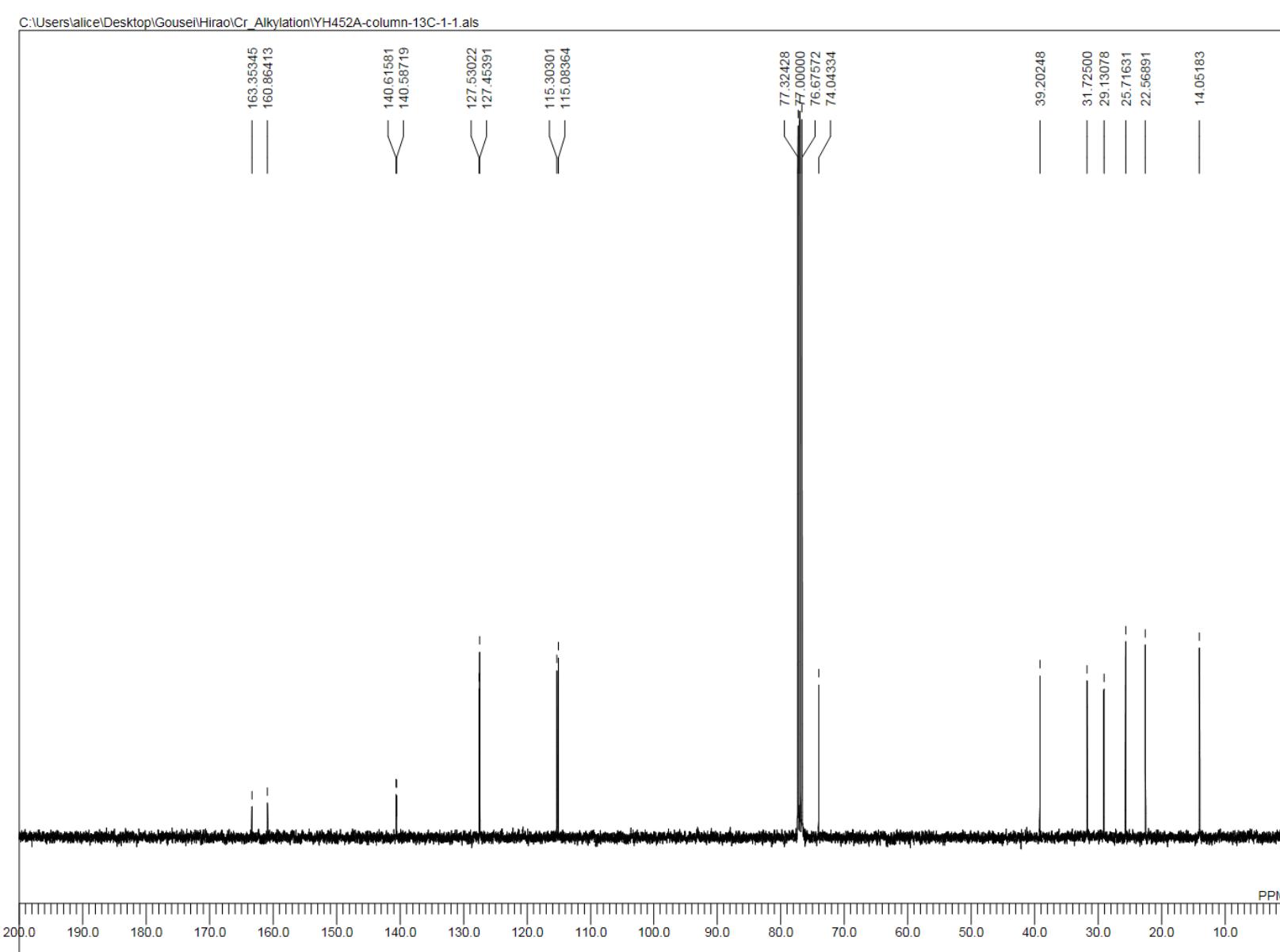
YH455-column-fra14-15_13C
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DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
2020-07-21 15:58:55
13C
carbon.jxp
125.77 MHz
7.87 KHz
4.21 Hz
32767
39308.18 Hz
2105
0.8336 sec
2.0000 sec
3.40 usec
1H
22.2 c
CDCL₃
77.00 ppm
1.20 Hz
60



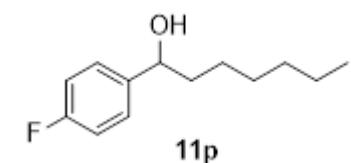
¹H NMR (500 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)

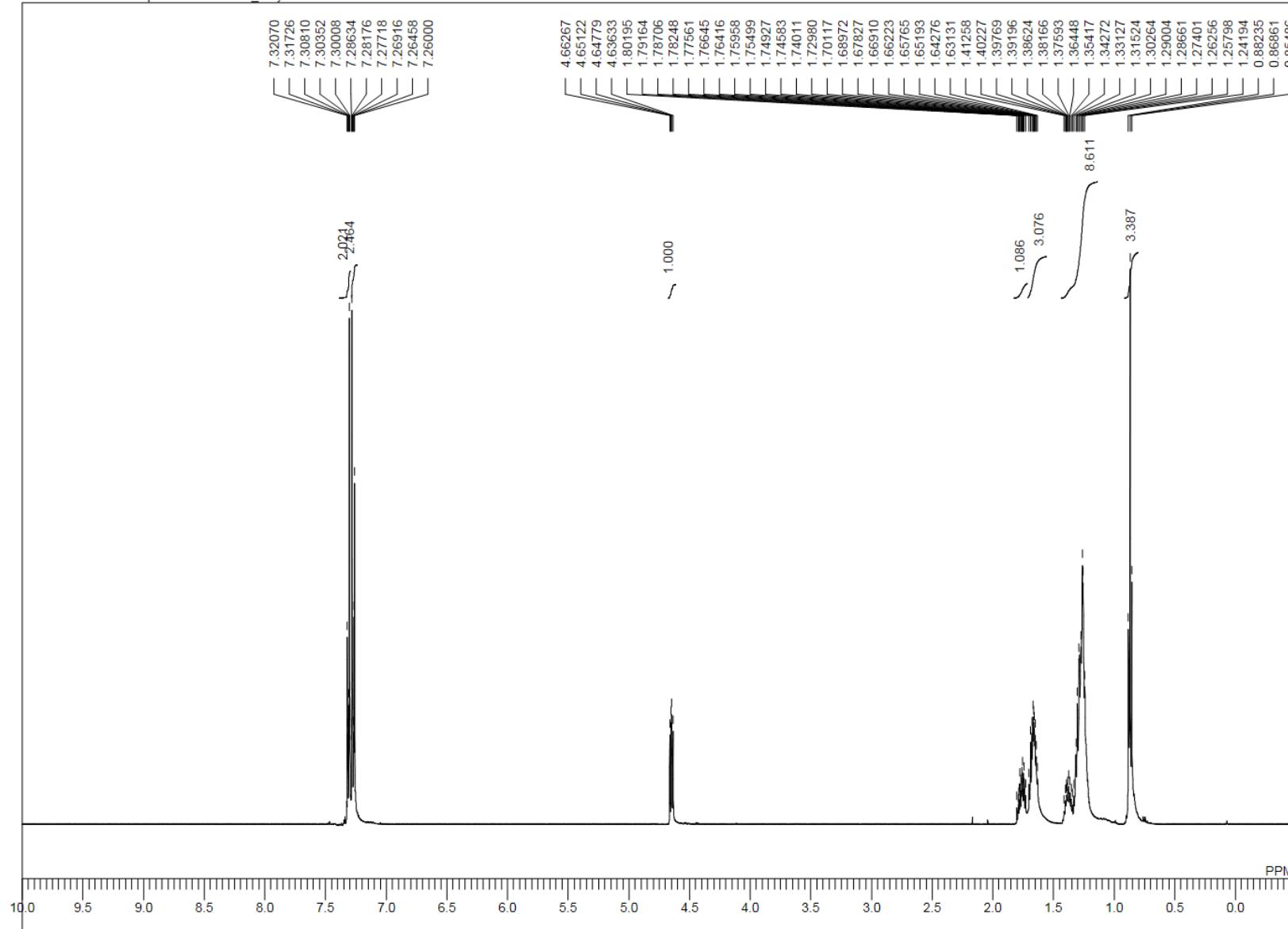


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COMNT
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13C
OBNUC carbon.jxp
EXMOD 98.52 MHz
OBFRFQ 4.64 KHz
OBSET 8.74 Hz
OBFIN 26214
POINT 24630.54 Hz
FREQU 302
SCANS 1.0643 sec
ACQTM 2.0000 sec
PD 3.12 usec
PW1
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCl₃
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60



¹H NMR (500 MHz, CDCl₃)

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DFILE

YK-12B7and8-0627-1-1.als

2020-06-27 12:57:55

1H

proton.jpx

500.16 MHz

2.41 KHz

6.01 Hz

POINT

13107

FREQU

7507.51 Hz

SCANS

8

ACQTM

1.7459 sec

PD

6.0000 sec

PW1

5.55 usec

1H

25.0 c

IRNUC

CDCl₃

CTEMP

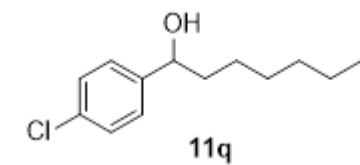
7.26 ppm

SLVNT

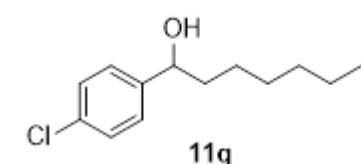
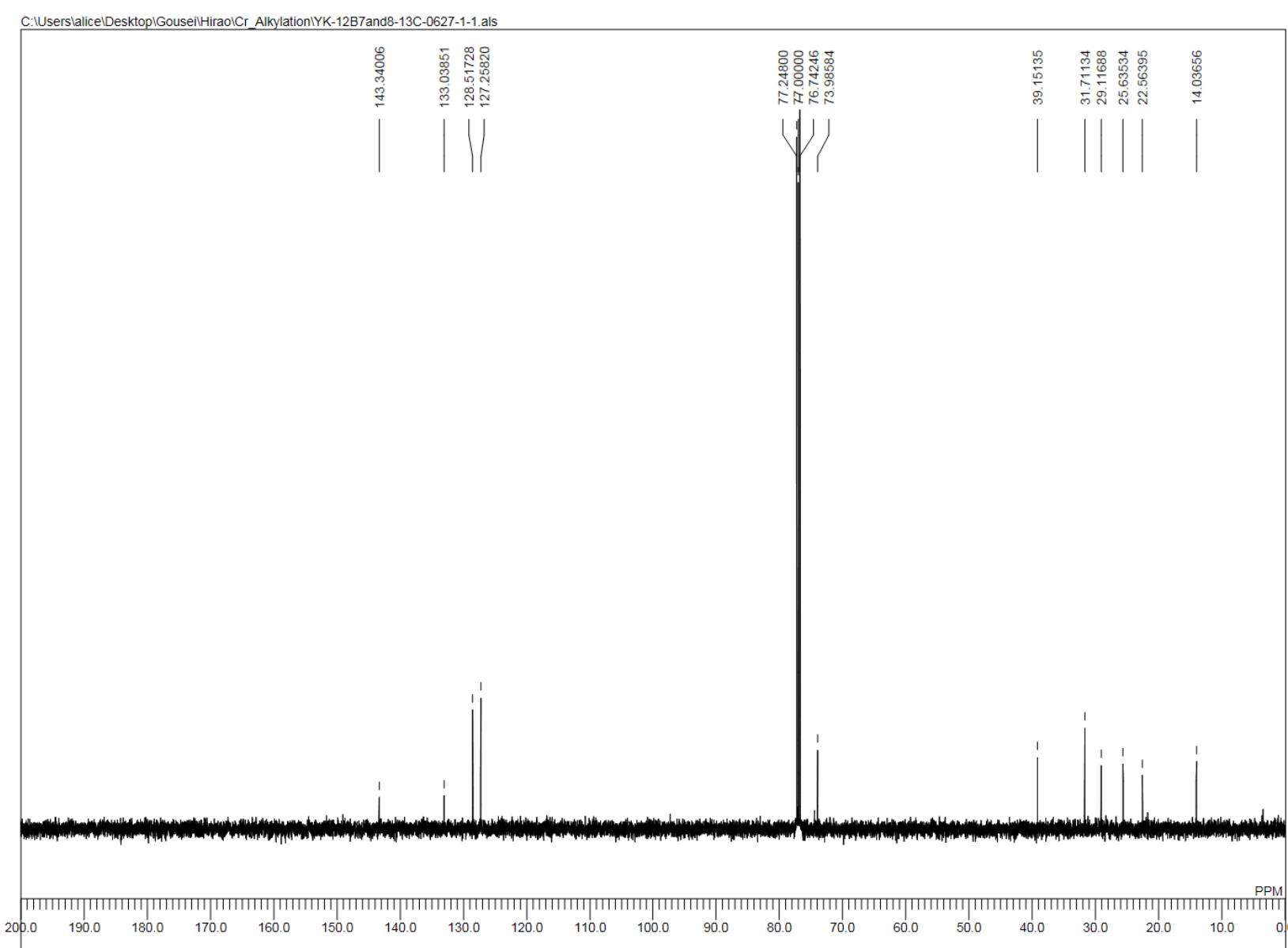
0.12 Hz

EXREF

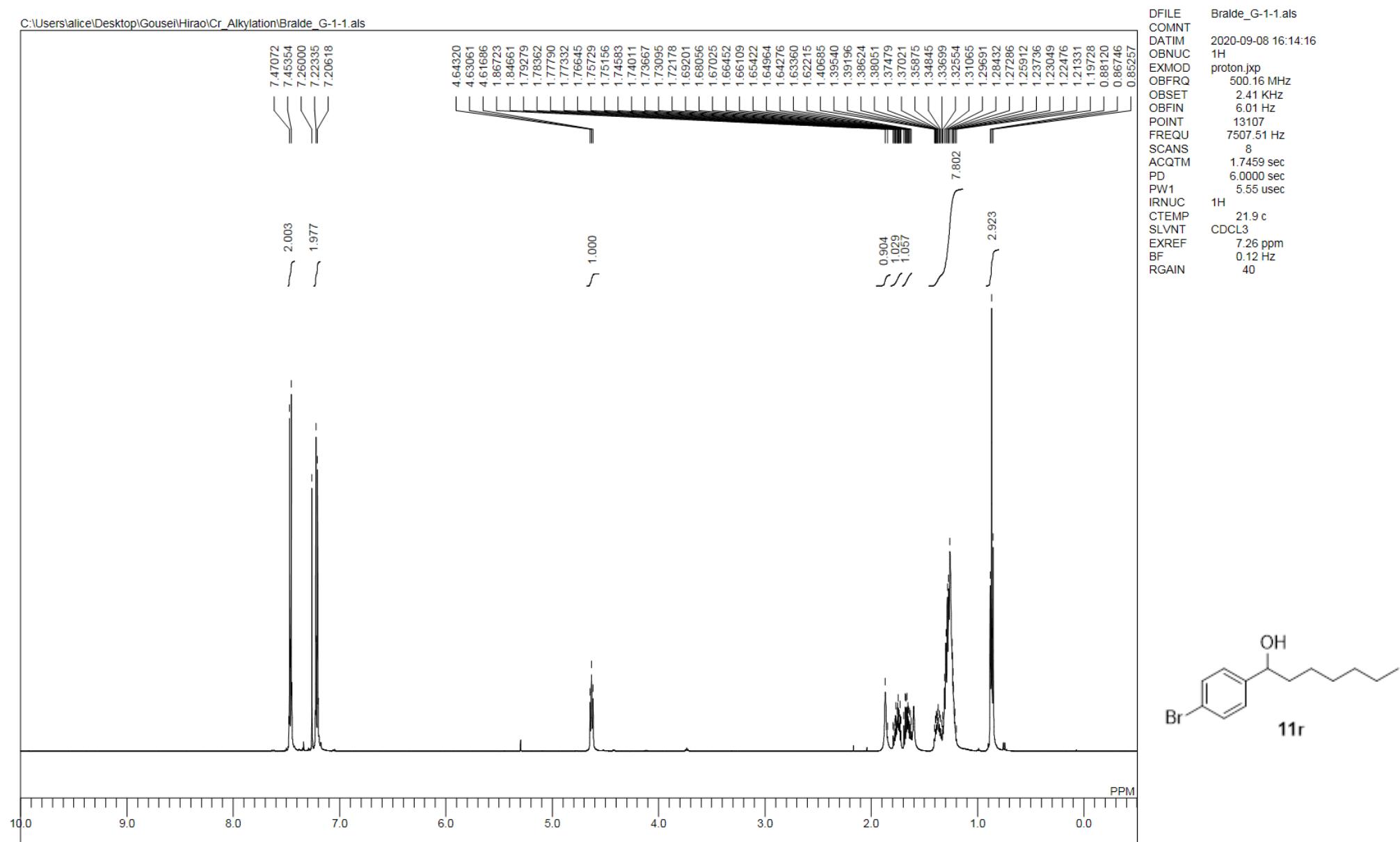
42



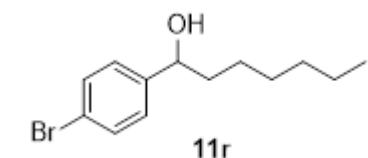
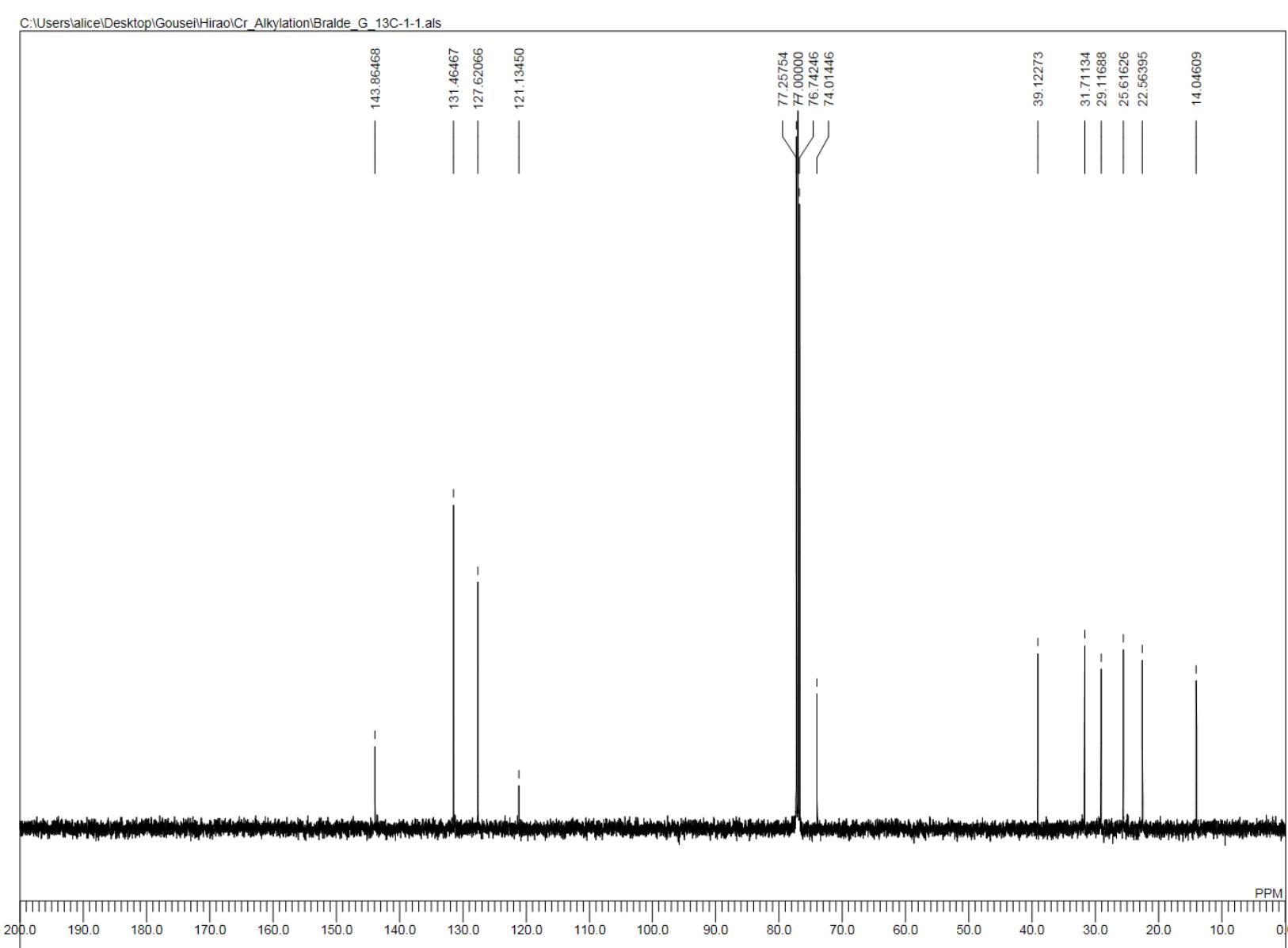
¹³C NMR (125 MHz, CDCl₃)



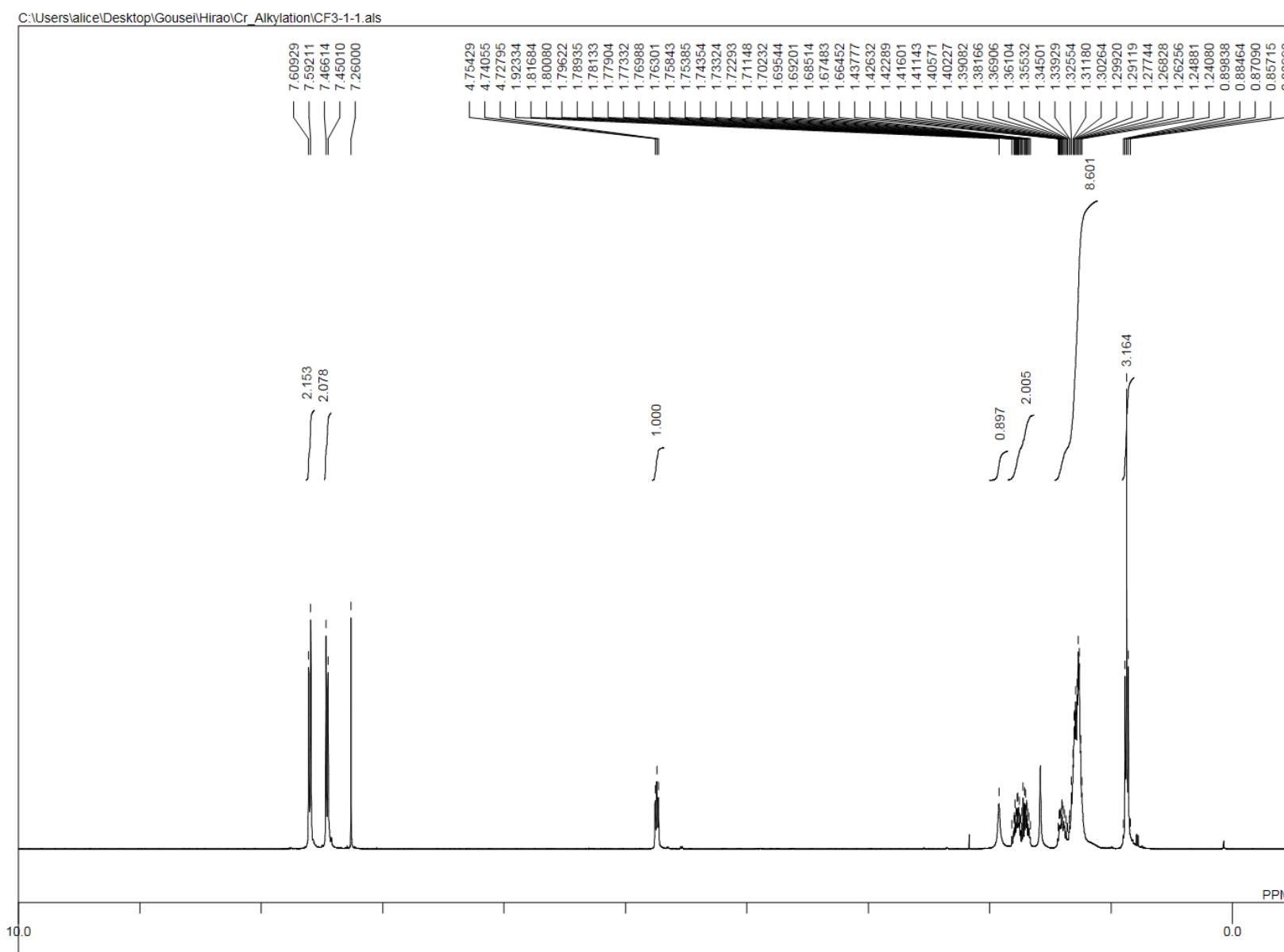
¹H NMR (500 MHz, CDCl₃)



¹³C NMR (125 MHz, CDCl₃)

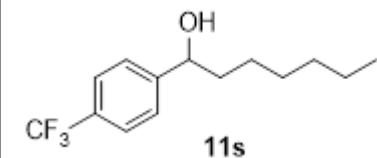


¹H NMR (500 MHz, CDCl₃)

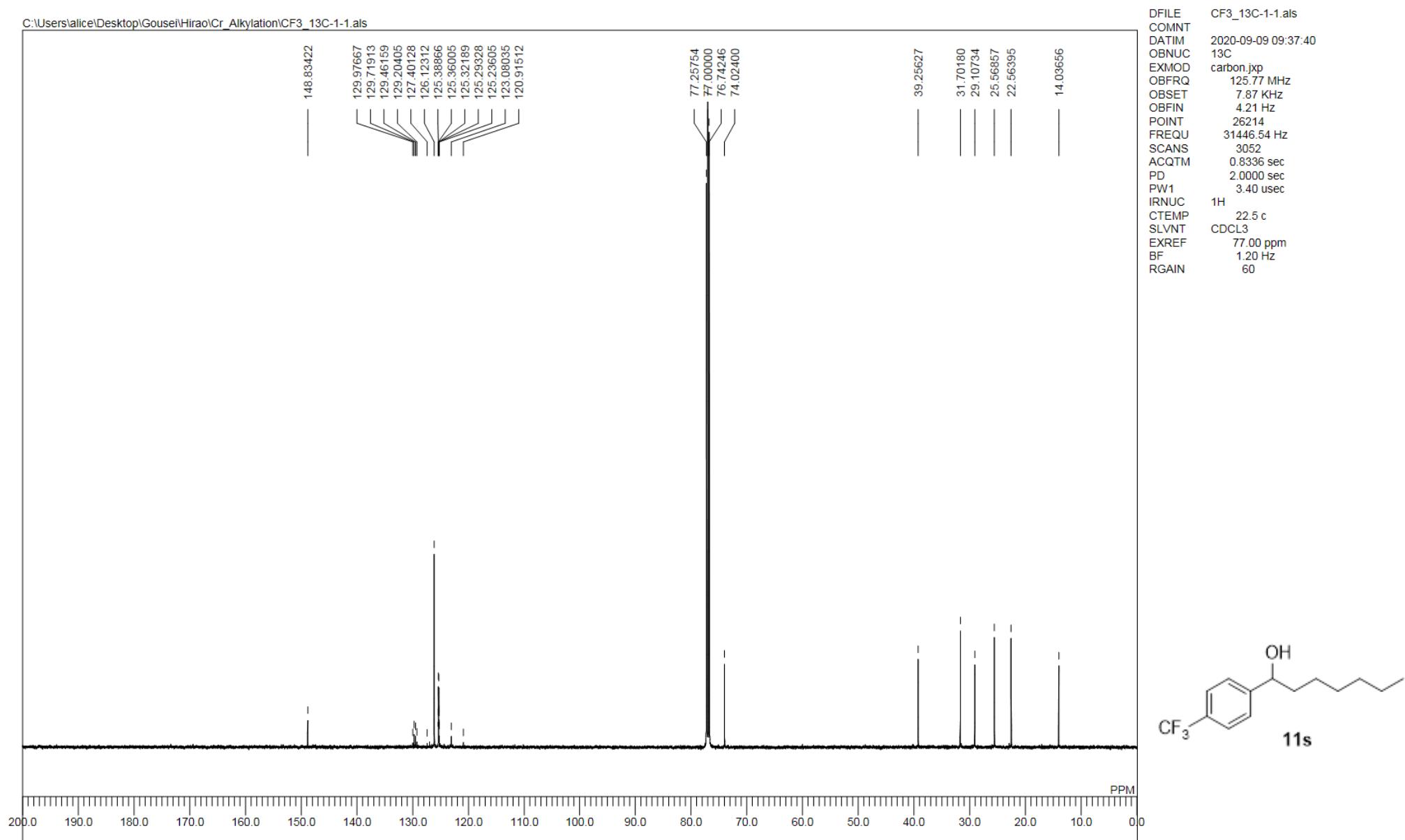


CF3-1-1.als
 DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFREQ
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
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 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

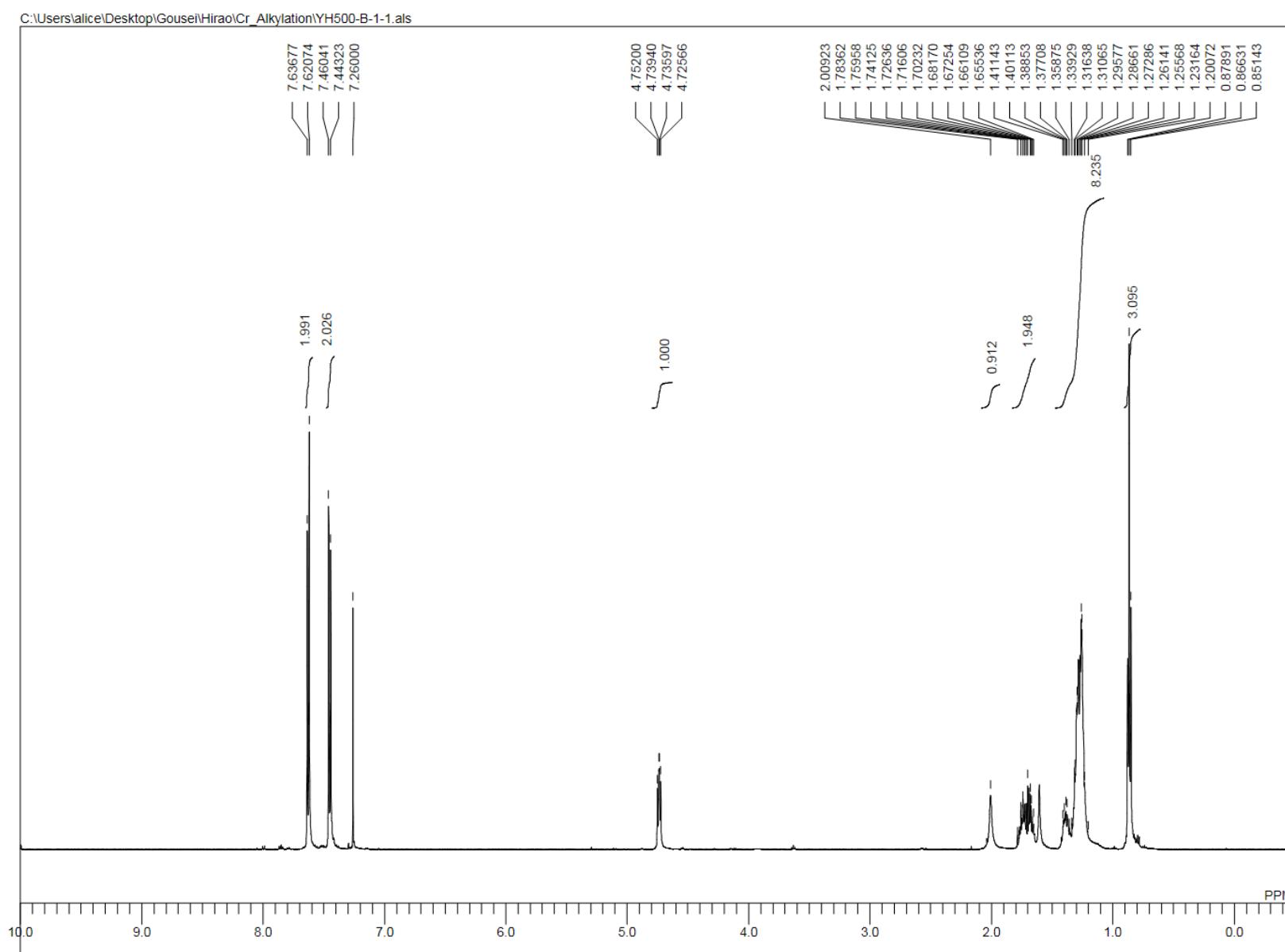
2020-09-09 09:35:51
 1H
 proton.jxp
 500.16 MHz
 2.41 KHz
 6.01 Hz
 13107
 7507.51 Hz
 8
 1.7459 sec
 6.0000 sec
 5.55 usec
 1H
 22.2 c
 CDCl₃
 7.26 ppm
 0.12 Hz
 40



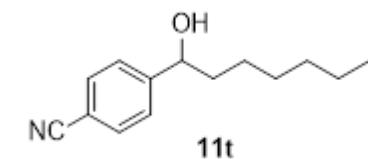
¹³C NMR (125 MHz, CDCl₃)



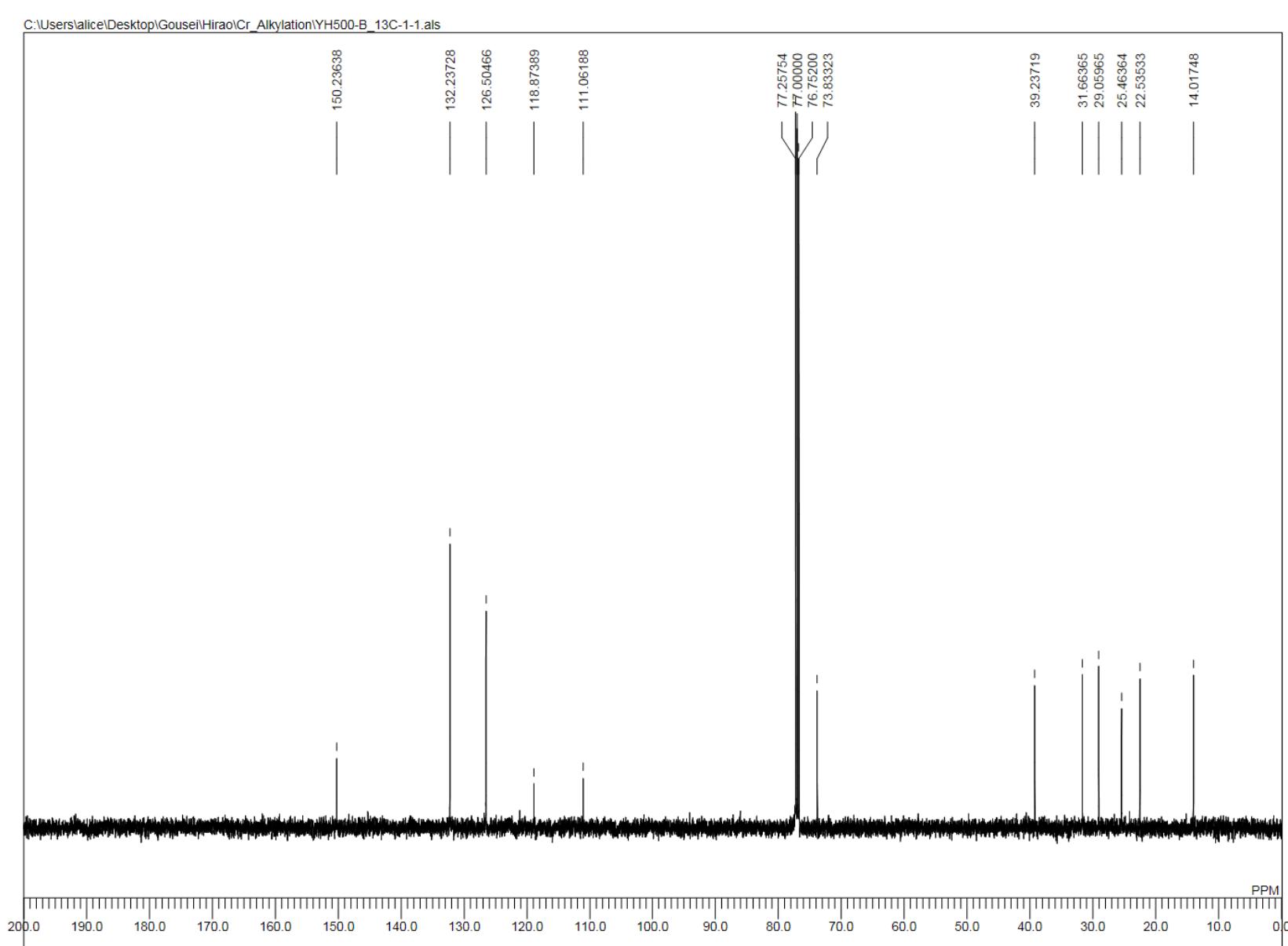
¹H NMR (500 MHz, CDCl₃)



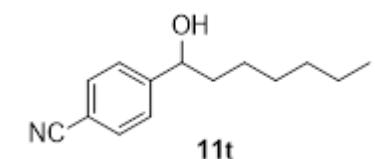
YH500-B-1-1.als
2020-09-07 10:02:30
1H
proton.jxp
500.16 MHz
2.41 KHz
6.01 Hz
13107
7507.51 Hz
8
1.7459 sec
6.0000 sec
5.55 usec
1H
22.1 c
CDCl₃
7.26 ppm
0.12 Hz
40



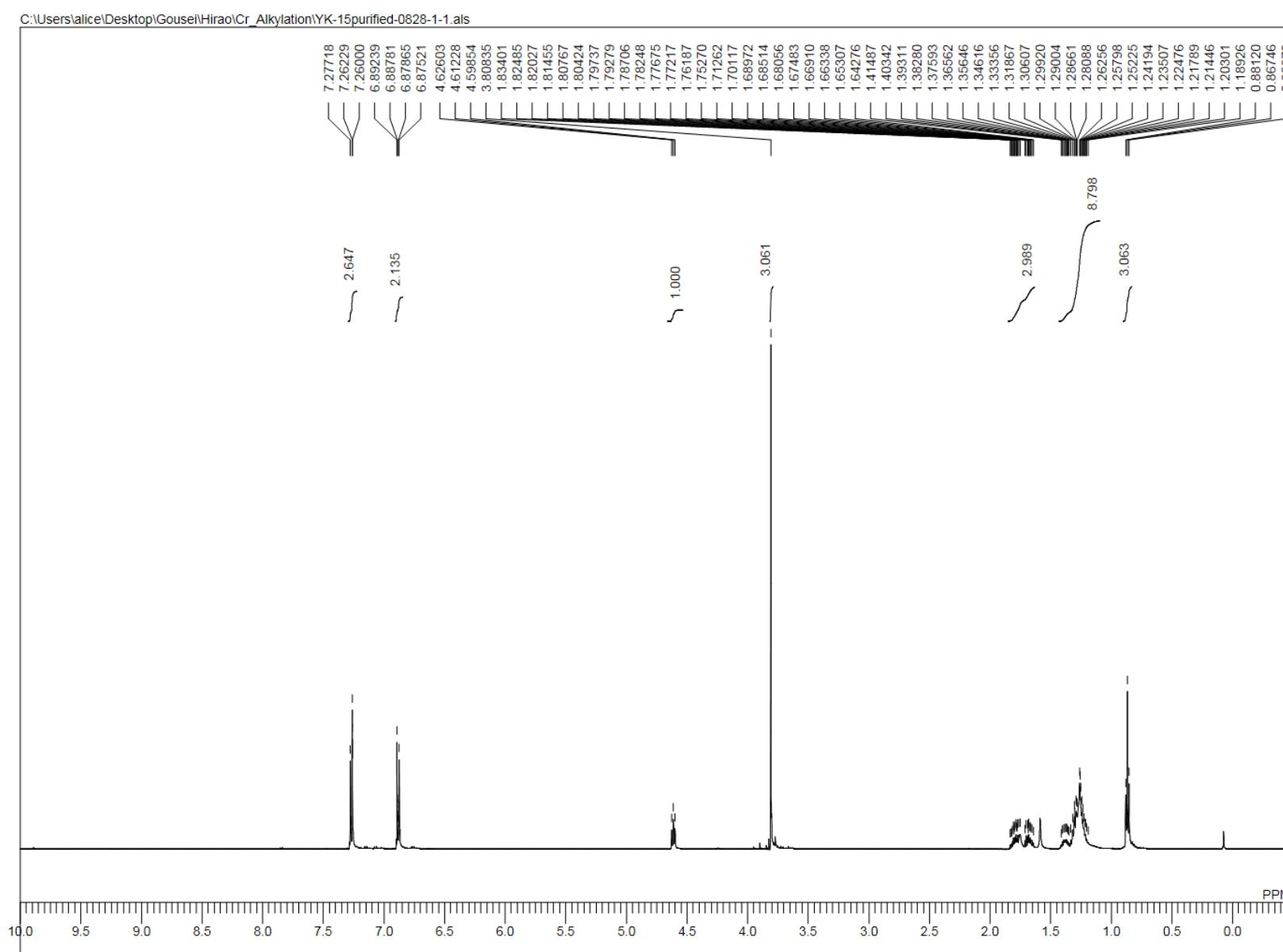
¹³C NMR (125 MHz, CDCl₃)



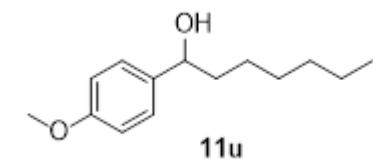
DFILE YH500-B_13C-1-1.als
COMNT
DATIM 2020-09-07 10:04:13
13C
OBNUC carbon.jxp
EXMOD 125.77 MHz
OBFREQ 7.87 kHz
OBSET 4.21 Hz
OBFIN 26214
POINT 31446.54 Hz
FREQU 0.8336 sec
SCANS 103
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCl₃
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60



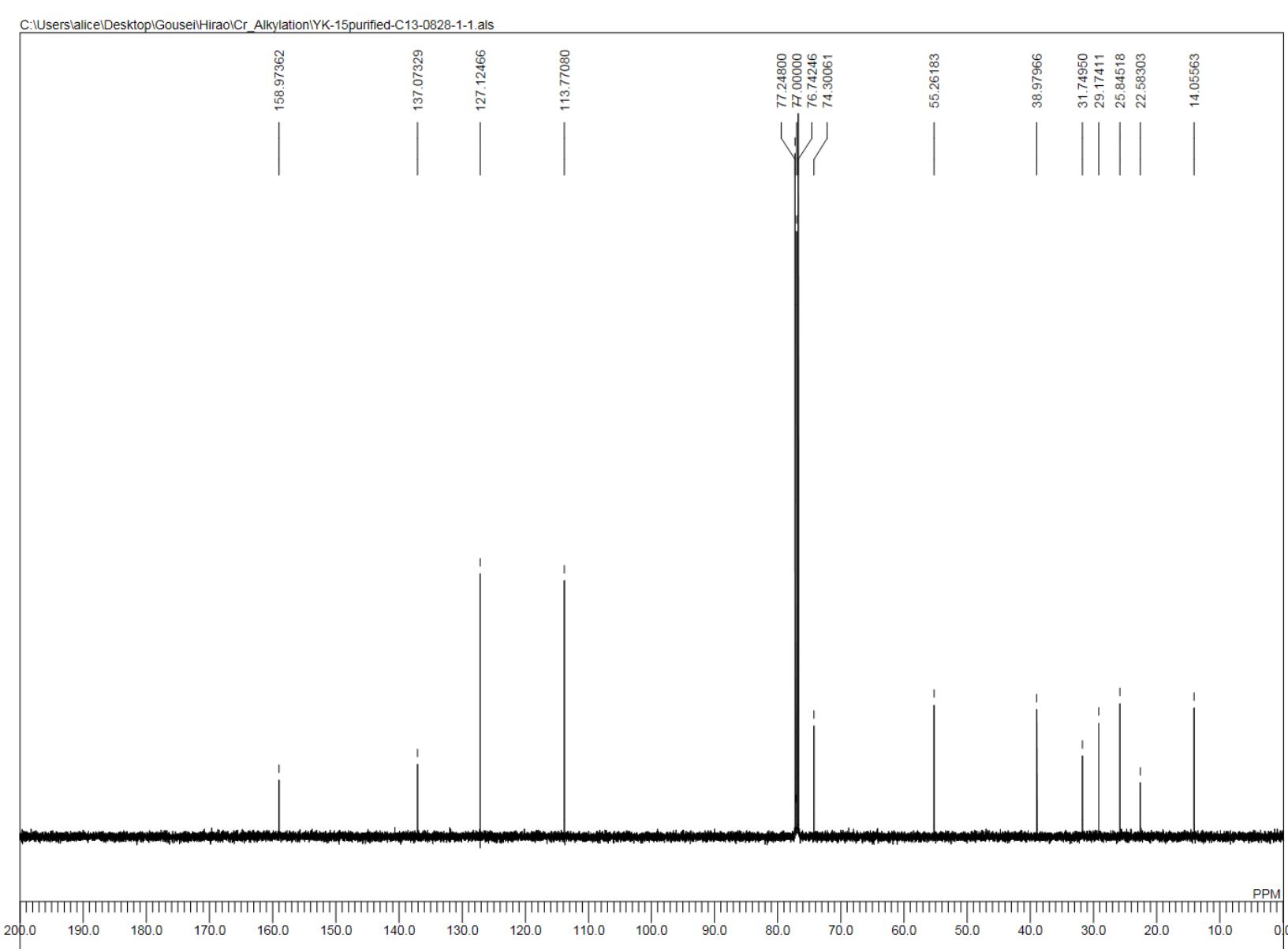
¹H NMR (500 MHz, CDCl₃)



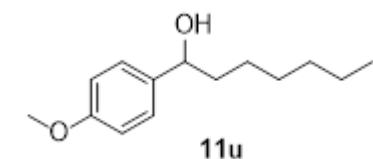
YK-15purified-0828-1-1.als
 2020-08-28 13:58:03
 1H
 proton.jxp
 500.16 MHz
 2.41 KHz
 6.01 Hz
 13107
 7507.51 Hz
 8
 1.7459 sec
 6.0000 sec
 5.55 usec
 1H
 21.8 c
 CDCl₃
 7.26 ppm
 0.12 Hz
 42



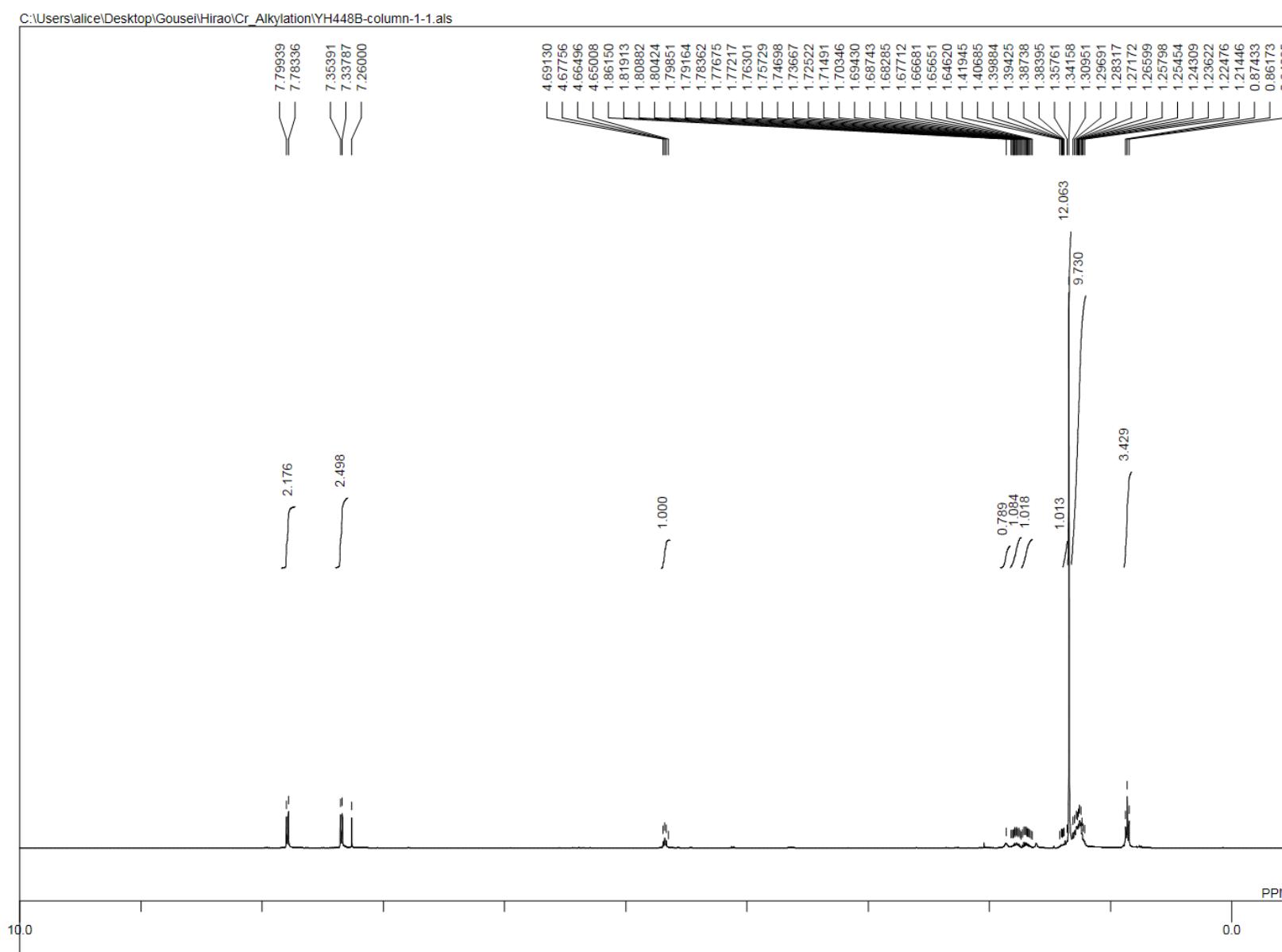
¹³C NMR (125 MHz, CDCl₃)



DFILE YK-15purified-C13-0828-1-1.
COMNT
DATIM 2020-08-28 15:43:34
DBNUC 13C
EXMOD carbon.jxp
OBFREQ 125.77 MHz
OBSET 7.87 kHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 609
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCl₃
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

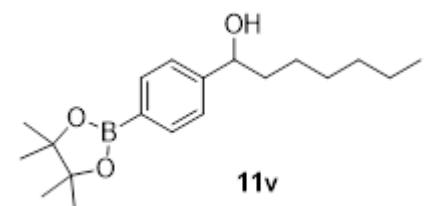


¹H NMR (500 MHz, CDCl₃)

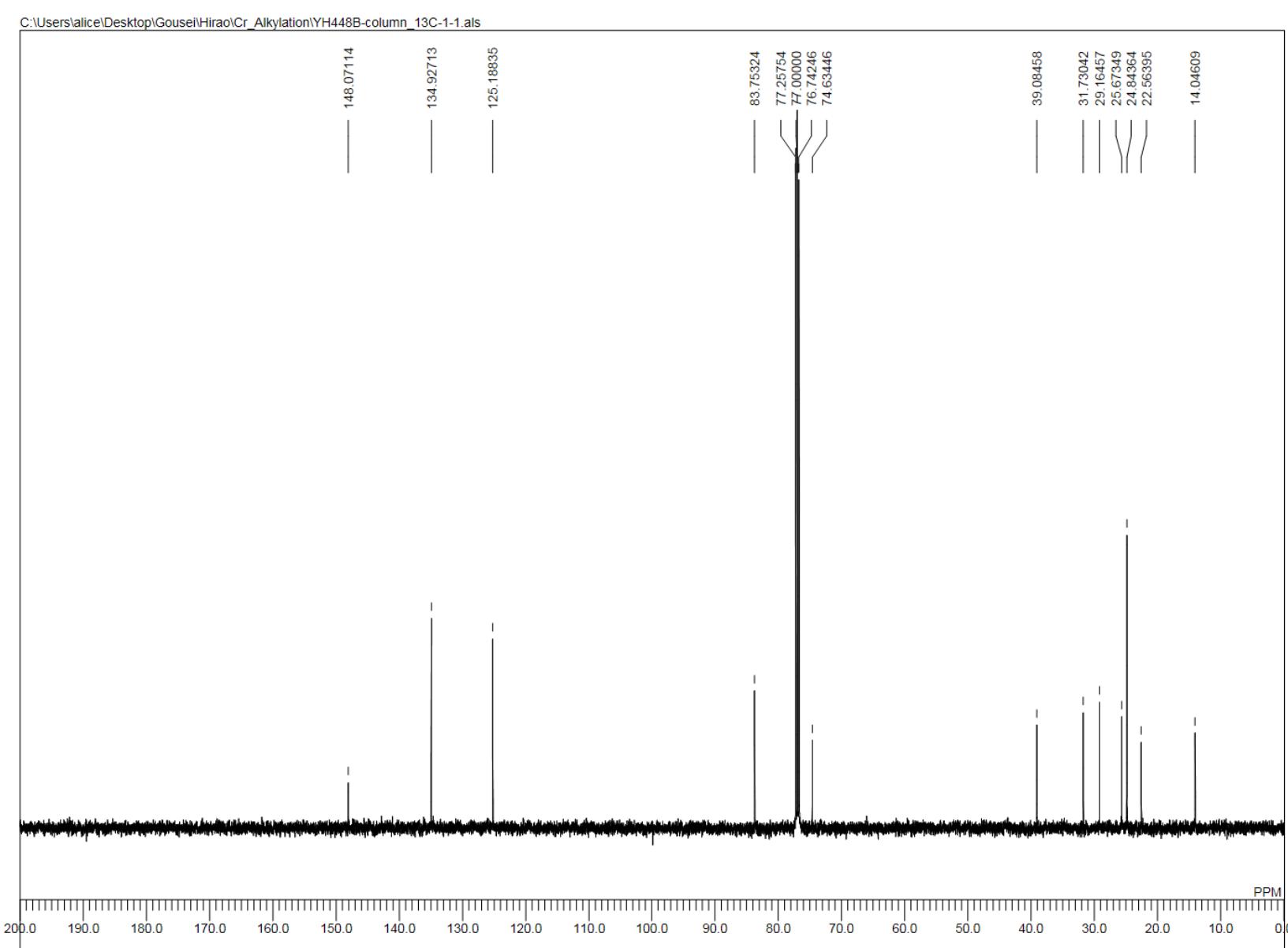


YH448B-column-1-1.als
 DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFREQ
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

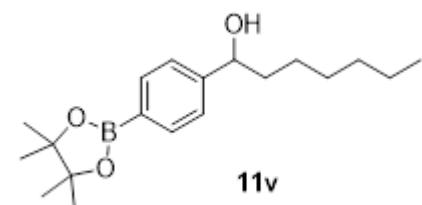
2020-07-16 11:19:55
 1H
 proton.jxp
 500.16 MHz
 2.41 kHz
 6.01 Hz
 13107
 7507.51 Hz
 8
 1.7459 sec
 6.0000 sec
 5.55 usec
 1H
 21.7 c
 CDCl₃
 7.26 ppm
 0.12 Hz
 40



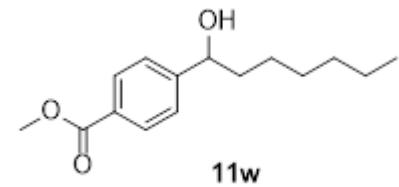
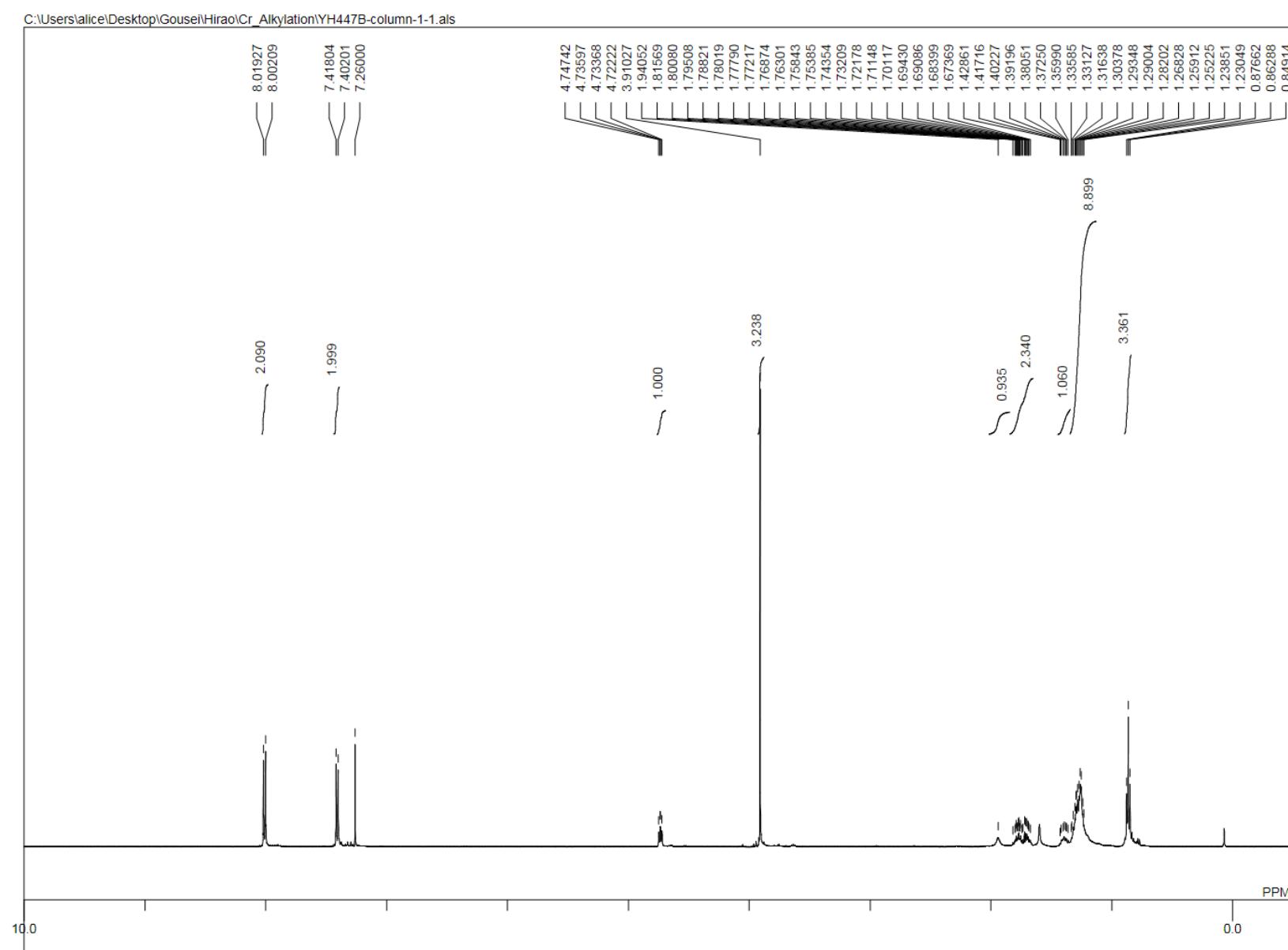
¹³C NMR (125 MHz, CDCl₃)



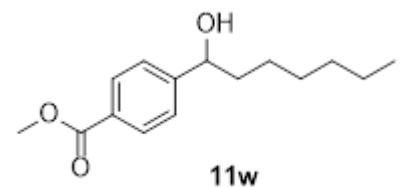
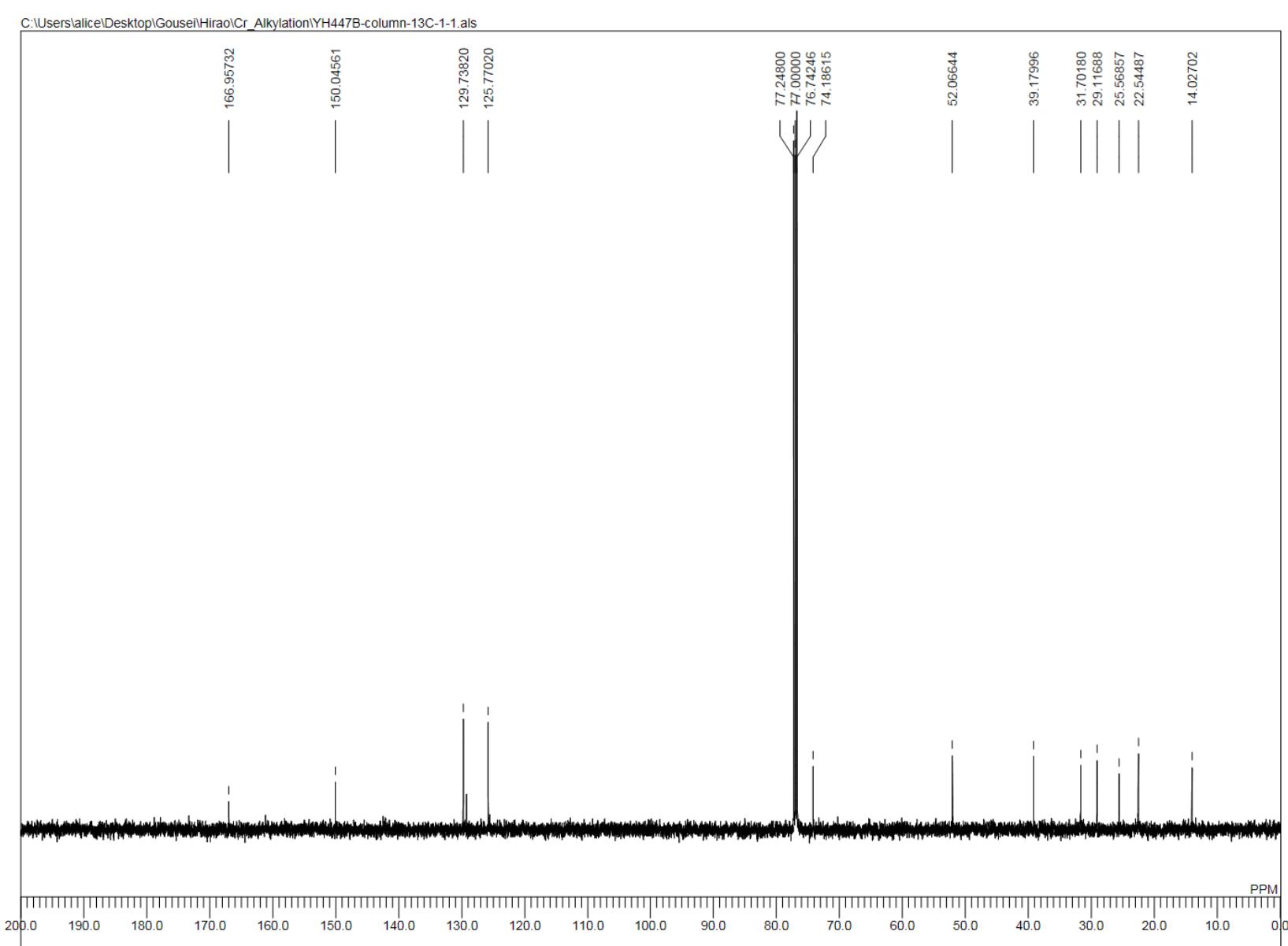
DFILE YH448B-column_13C-1-1.al
COMNT
DATIM 2020-07-16 11:21:44
OBNUC ¹³C
EXMOD carbon.jxp
OBFREQ 125.77 MHz
OBSET 7.87 kHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 155
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC ^{1H}
CTEMP 22.1 c
SLVNT CDCl₃
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60



¹H NMR (500 MHz, CDCl₃)

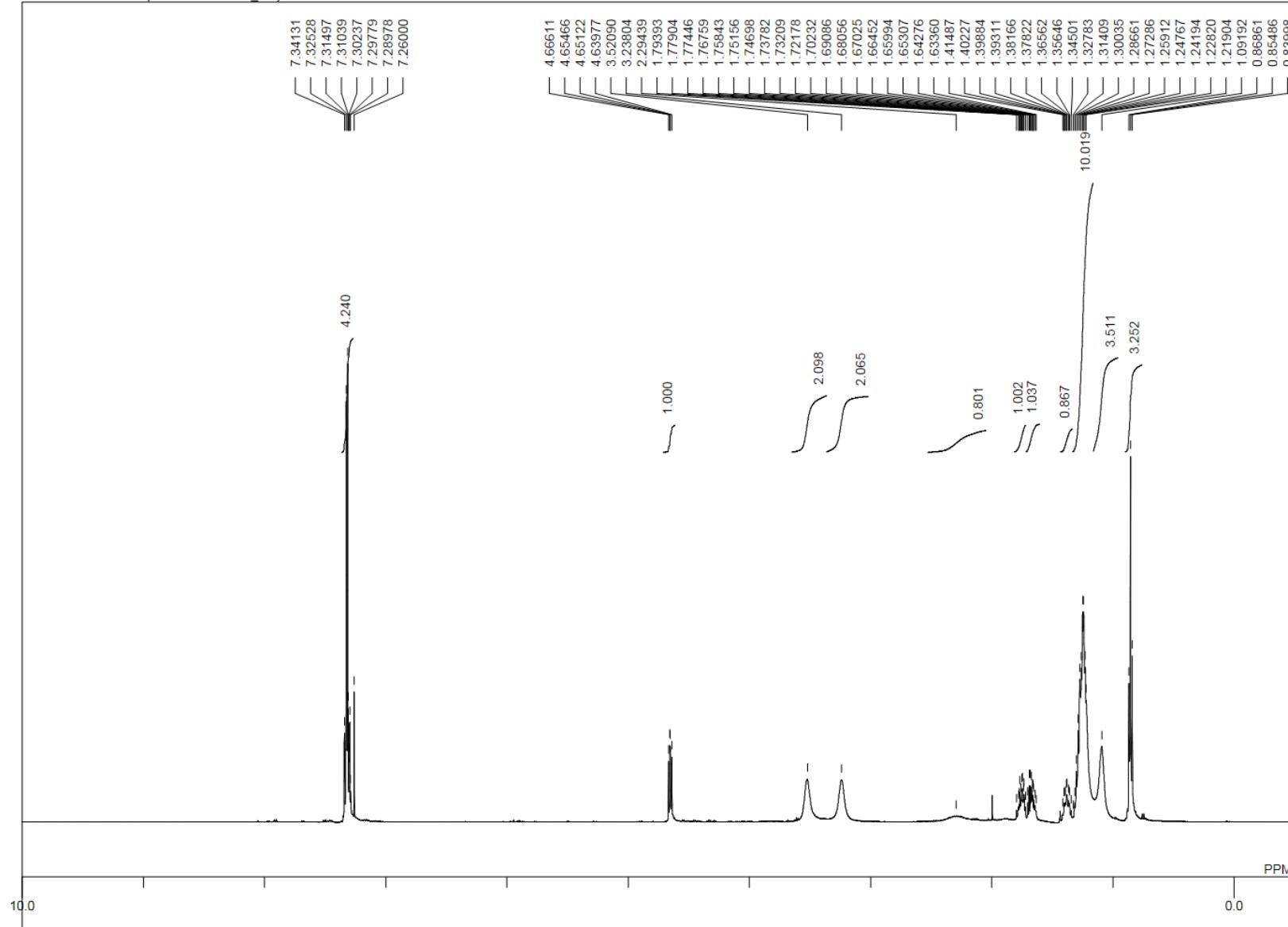


¹³C NMR (125 MHz, CDCl₃)

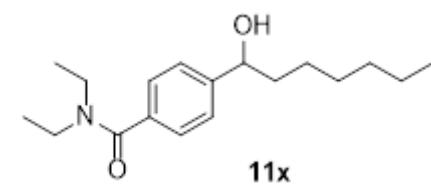


¹H NMR (500 MHz, CDCl₃)

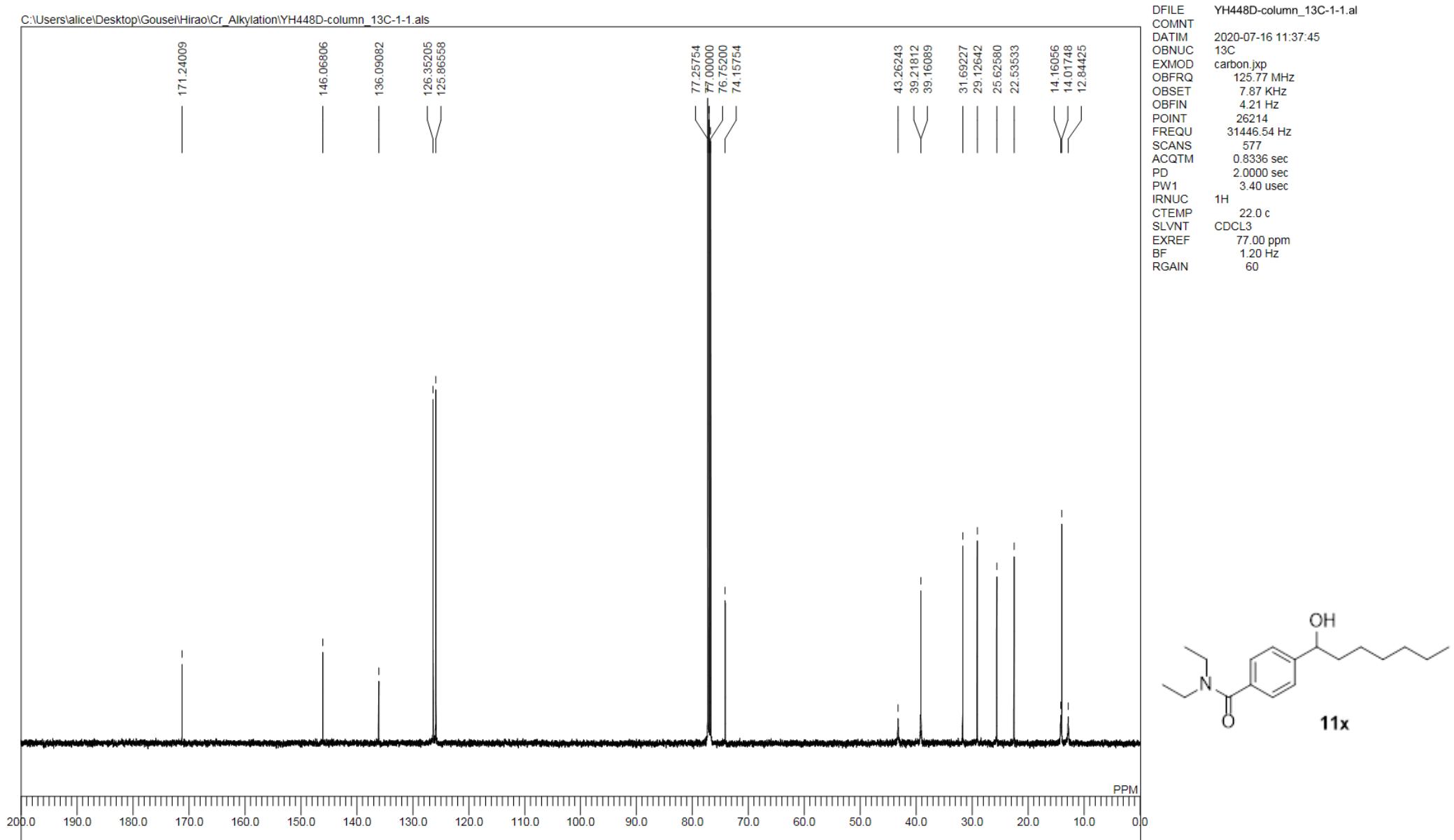
C:\Users\alice\Desktop\Gousei\Hirao\Cr_Aalkylation\YH448D-column-1-1.als



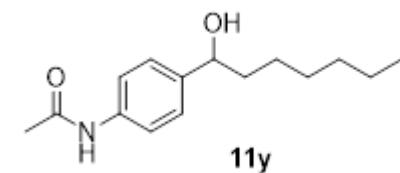
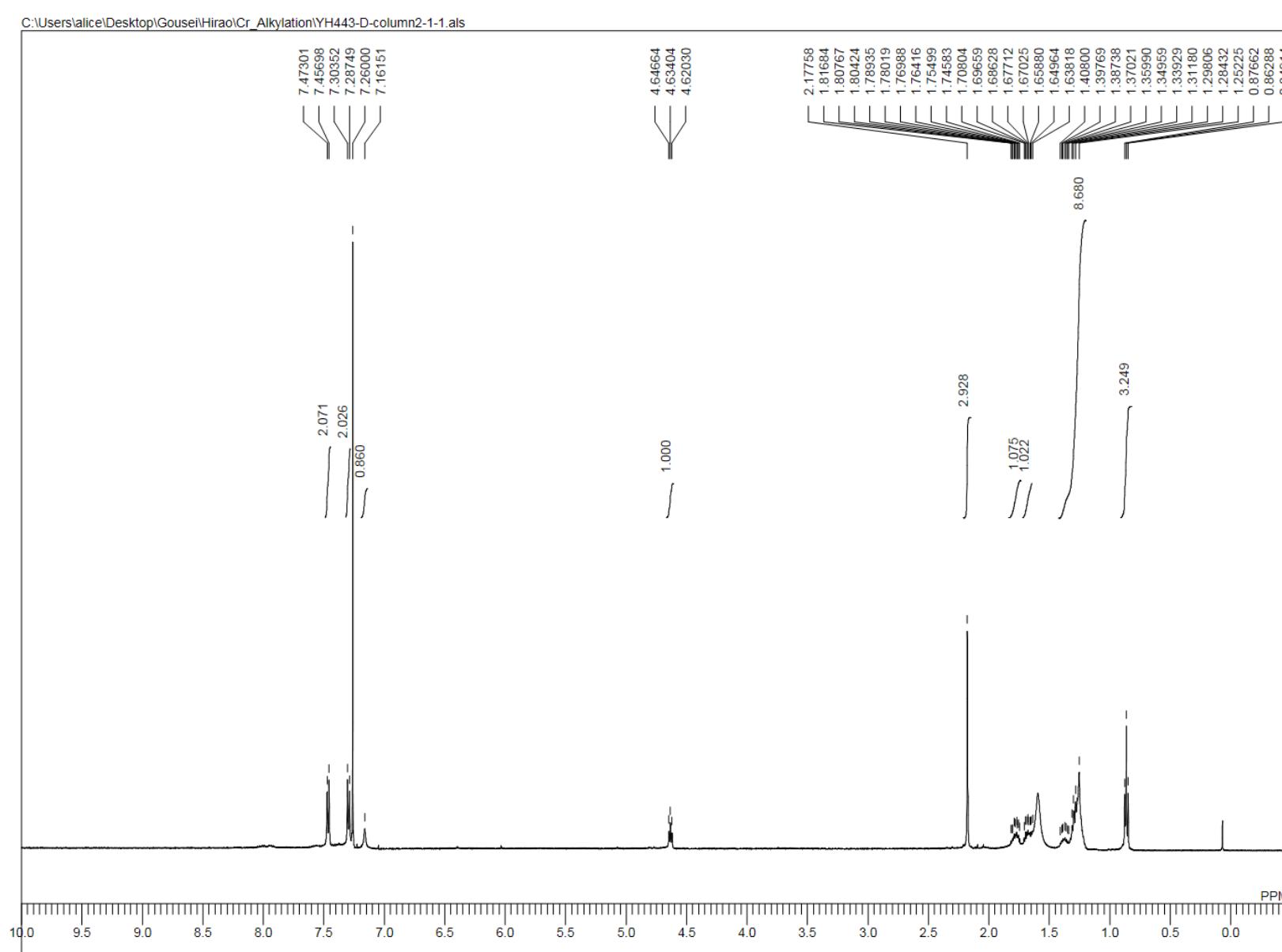
YH448D-column-1-1.als
 DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRQ
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN
 2020-07-16 11:35:56
 1H
 proton.jpx
 500.16 MHz
 2.41 KHz
 6.01 Hz
 13107
 7507.51 Hz
 8
 1.7459 sec
 6.0000 sec
 5.55 usec
 1H
 21.7 c
 CDCl₃
 7.26 ppm
 0.12 Hz
 38



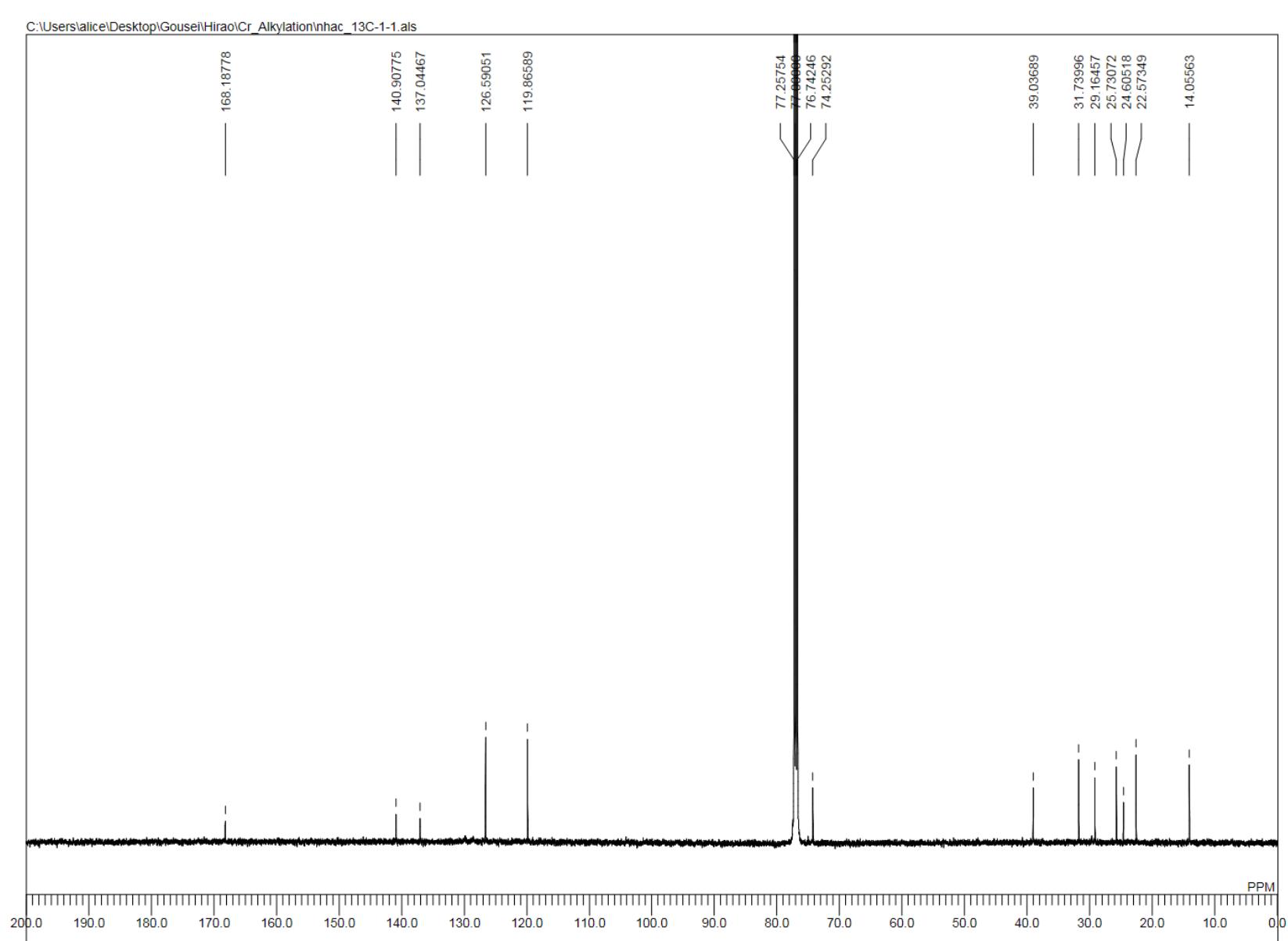
¹³C NMR (125 MHz, CDCl₃)



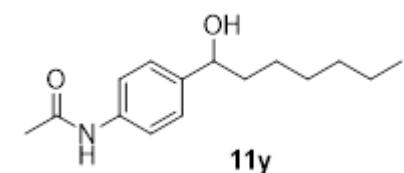
¹H NMR (500 MHz, CDCl₃)



¹³C NMR (125 MHz, CDCl₃)

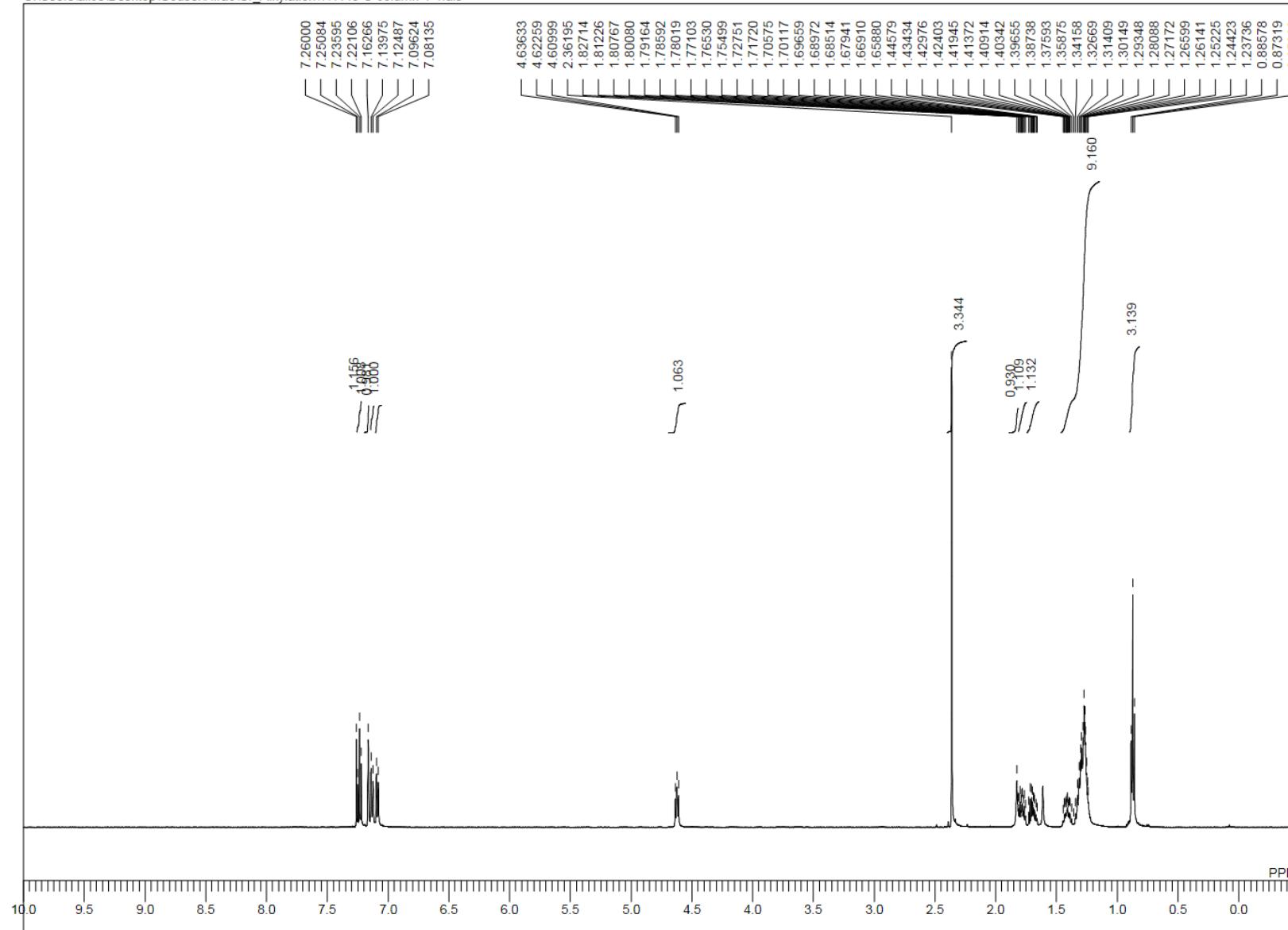


DFILE nhac_13C-1-1.als
COMNT 2020-09-05 21:39:59
DATIM 13C
OBNUC carbon.jxp
EXMOD 125.77 MHz
OBFREQ 7.87 kHz
OBSET 4.21 Hz
OBFIN 26214
POINT 31446.54 Hz
FREQU 29978
SCANS 0.8336 sec
ACQTM 2.0000 sec
PD 3.40 usec
PW1 1H
IRNUC 22.4 c
CTEMP CDCl₃
SLVNT 77.00 ppm
EXREF 1.20 Hz
BF RGAIN 60

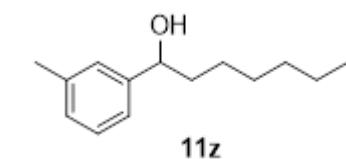


¹H NMR (500 MHz, CDCl₃)

C:\Users\alice\Desktop\Gousei\Hirao\Cr_Aalkylation\YH443-C-column-1-1.als

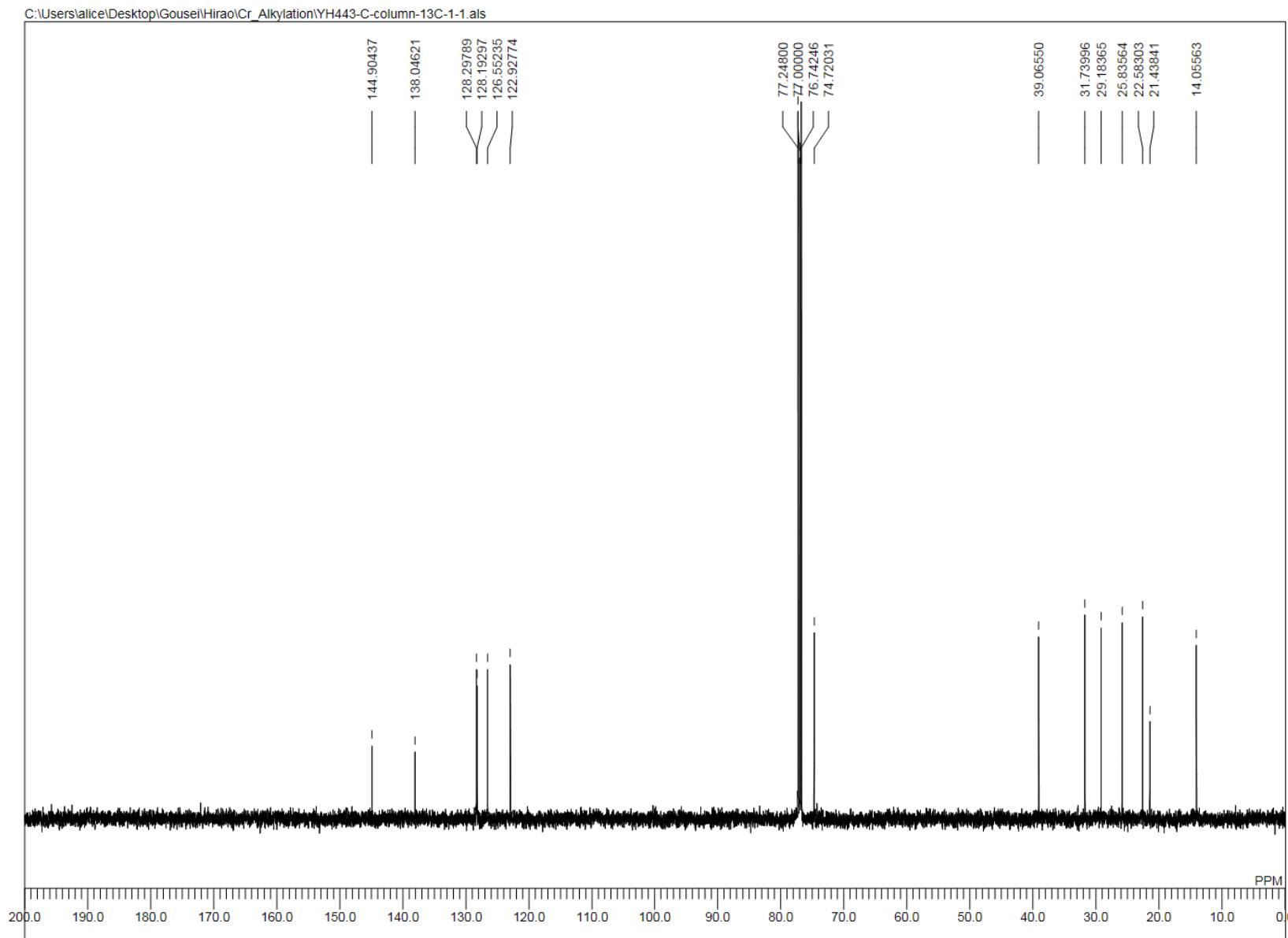


YH443-C-column-1-1.als
 DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 proton.jpx
 OBFRQ 500.16 MHz
 OBSET 2.41 kHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.51 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 6.0000 sec
 PW1 5.55 usec
 1H
 IRNUC 21.8 c
 CTEMP CDCl₃
 SLVNT 7.26 ppm
 EXREF BF 0.12 Hz
 RGAIN 40

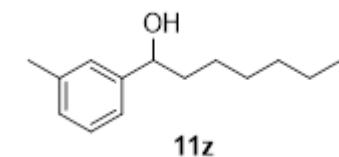


¹³C NMR (125 MHz, CDCl₃)

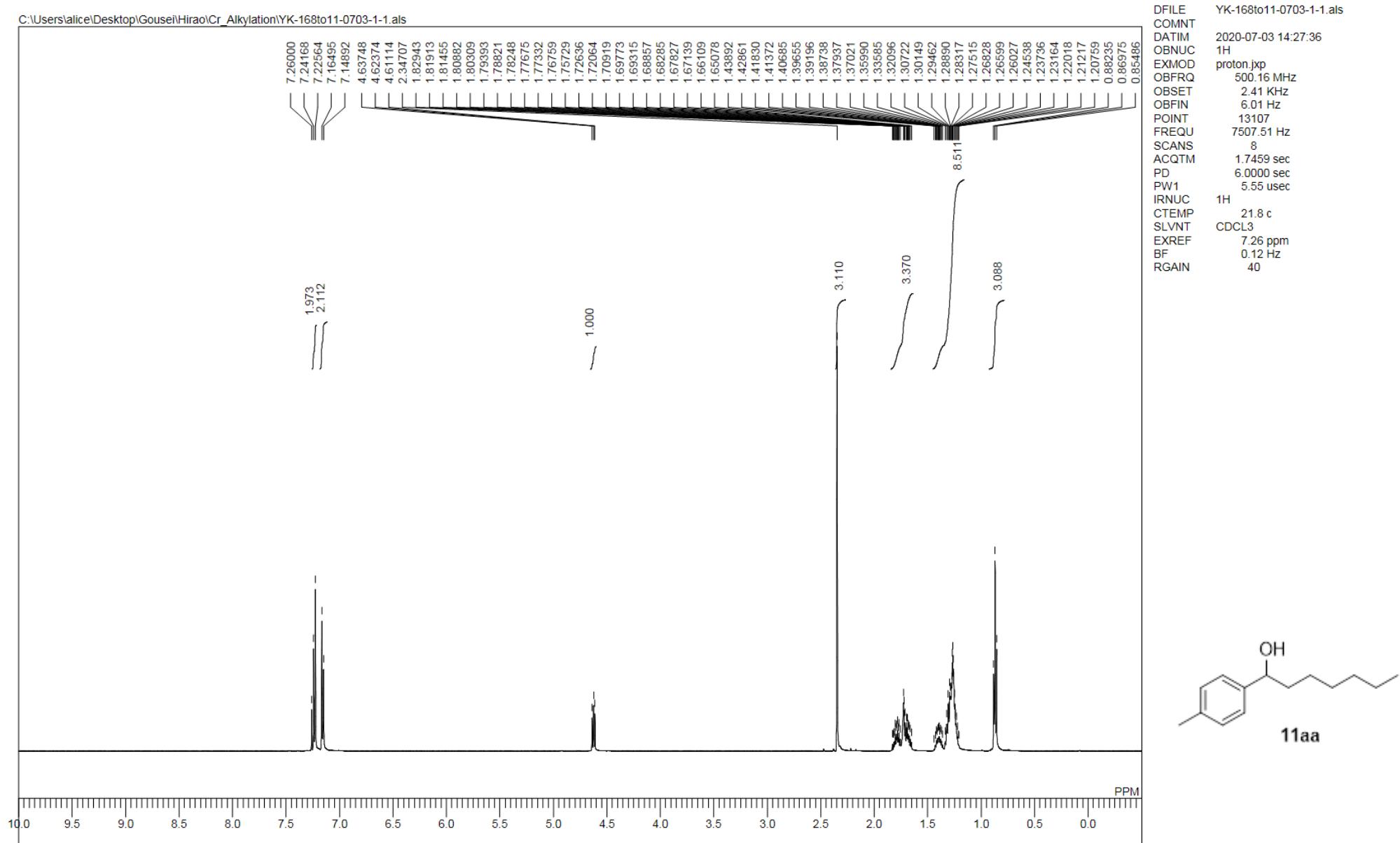
C:\Users\alice\Desktop\Gousei\Hirao\Cr_Alylation\YH443-C-column-13C-1-1.als



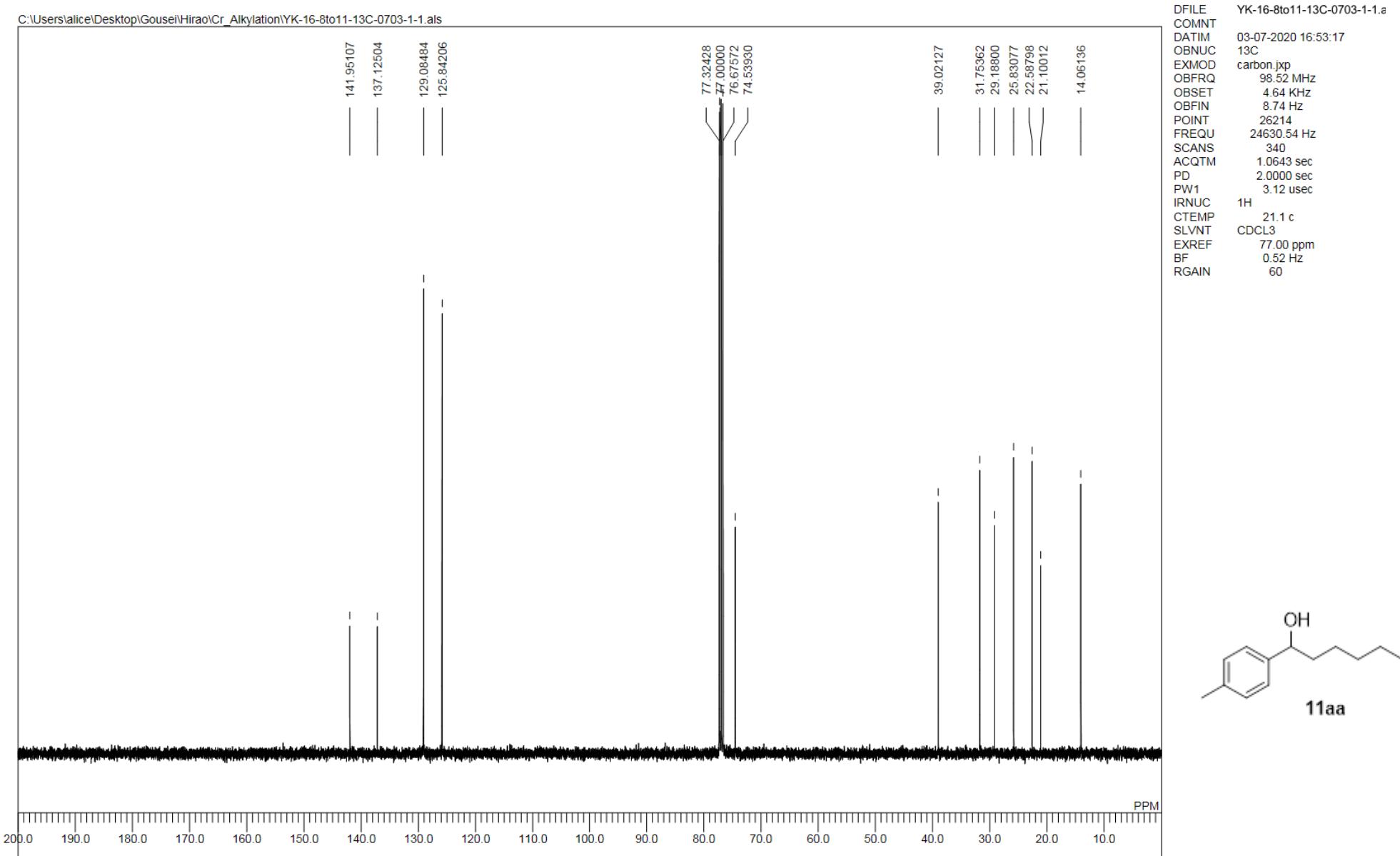
DFILE YH443-C-column-13C-1-1.al
COMNT
DATIM 2020-07-05 17:39:23
OBNUC 13C
EXMOD carbon.jp
OBFRQ 125.77 MHz
OBSET 7.87 kHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 102
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 22.0 c
SLVNT CDCl₃
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60



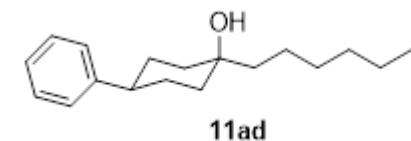
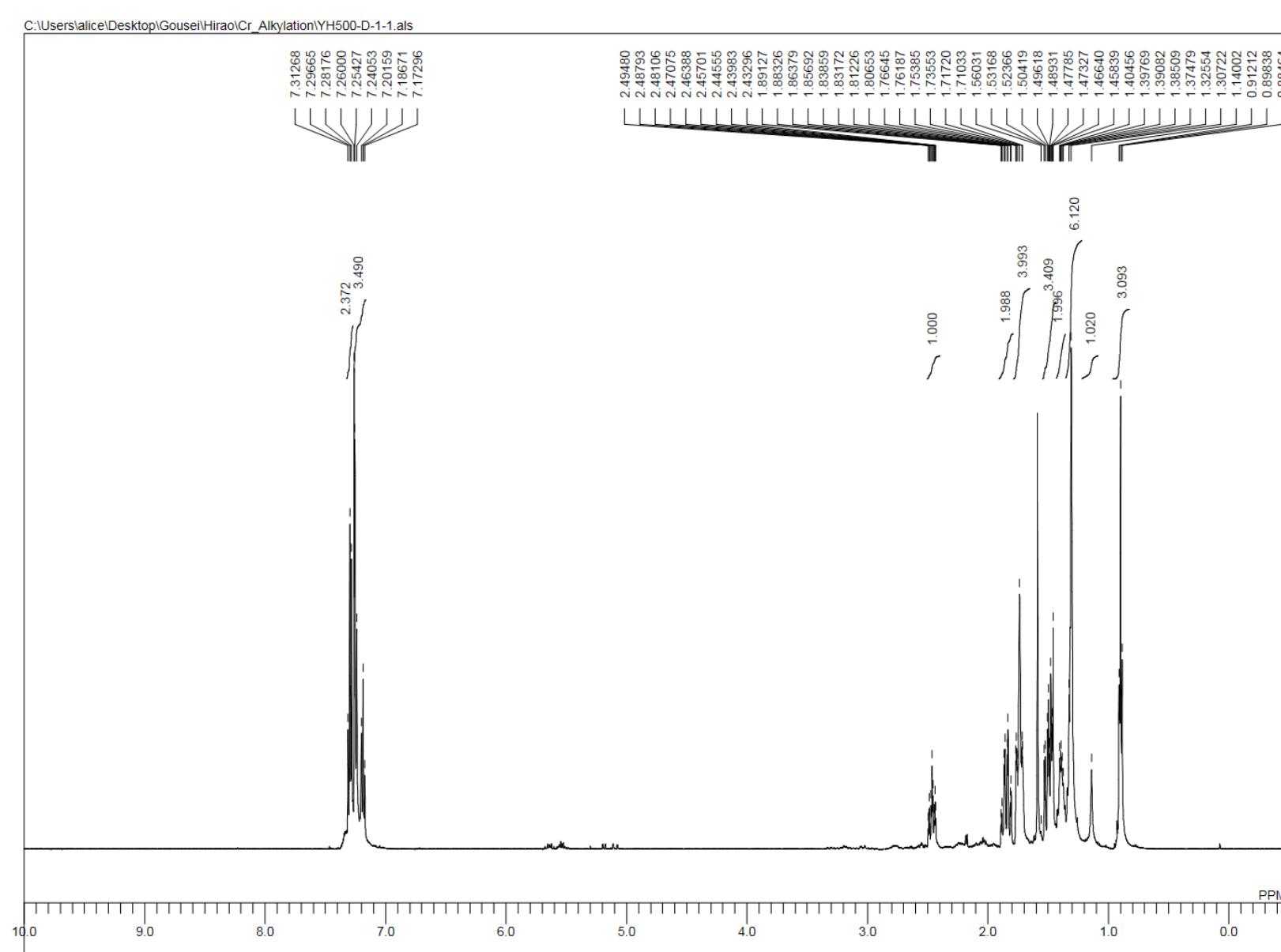
¹H NMR (500 MHz, CDCl₃)



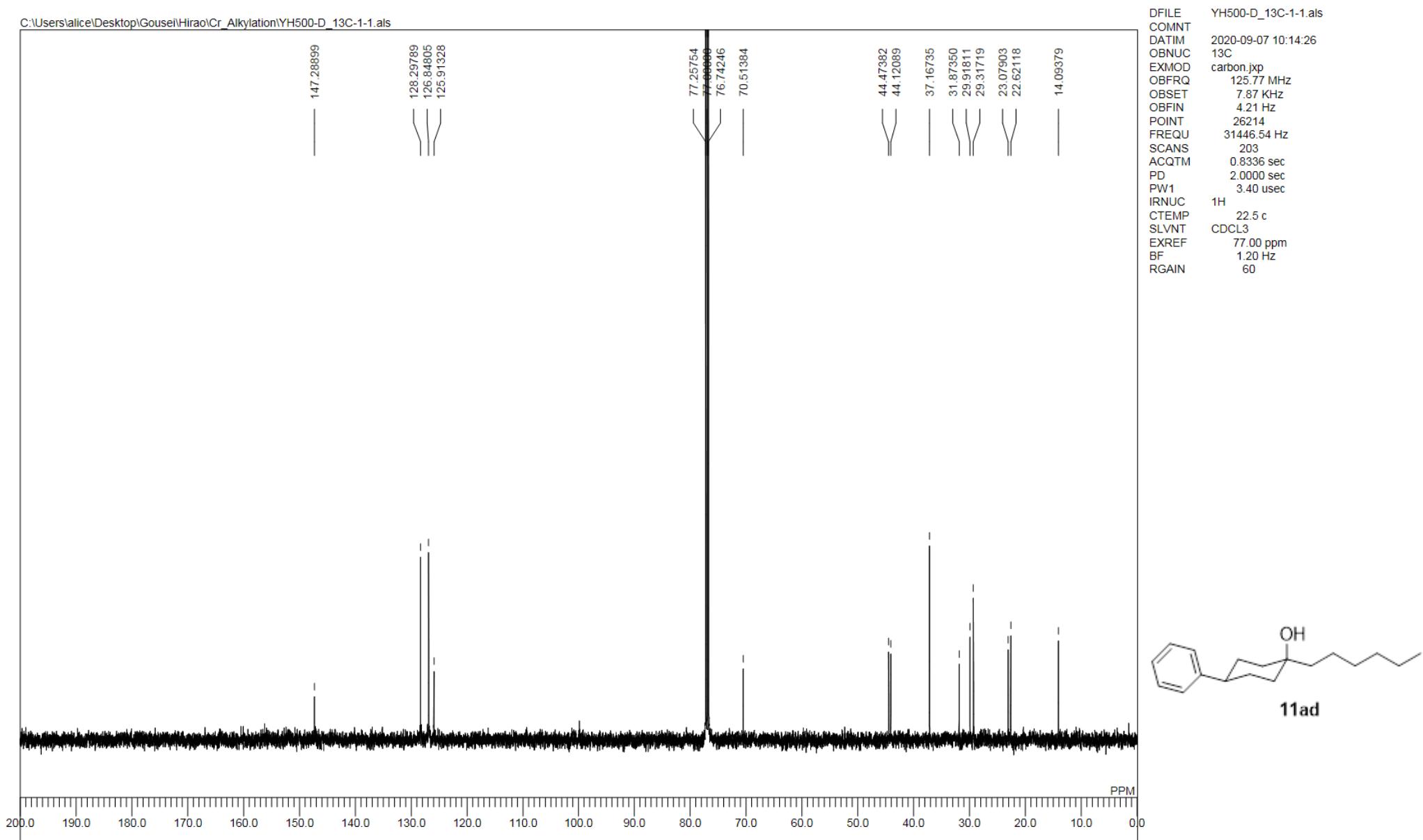
¹³C NMR (100 MHz, CDCl₃)



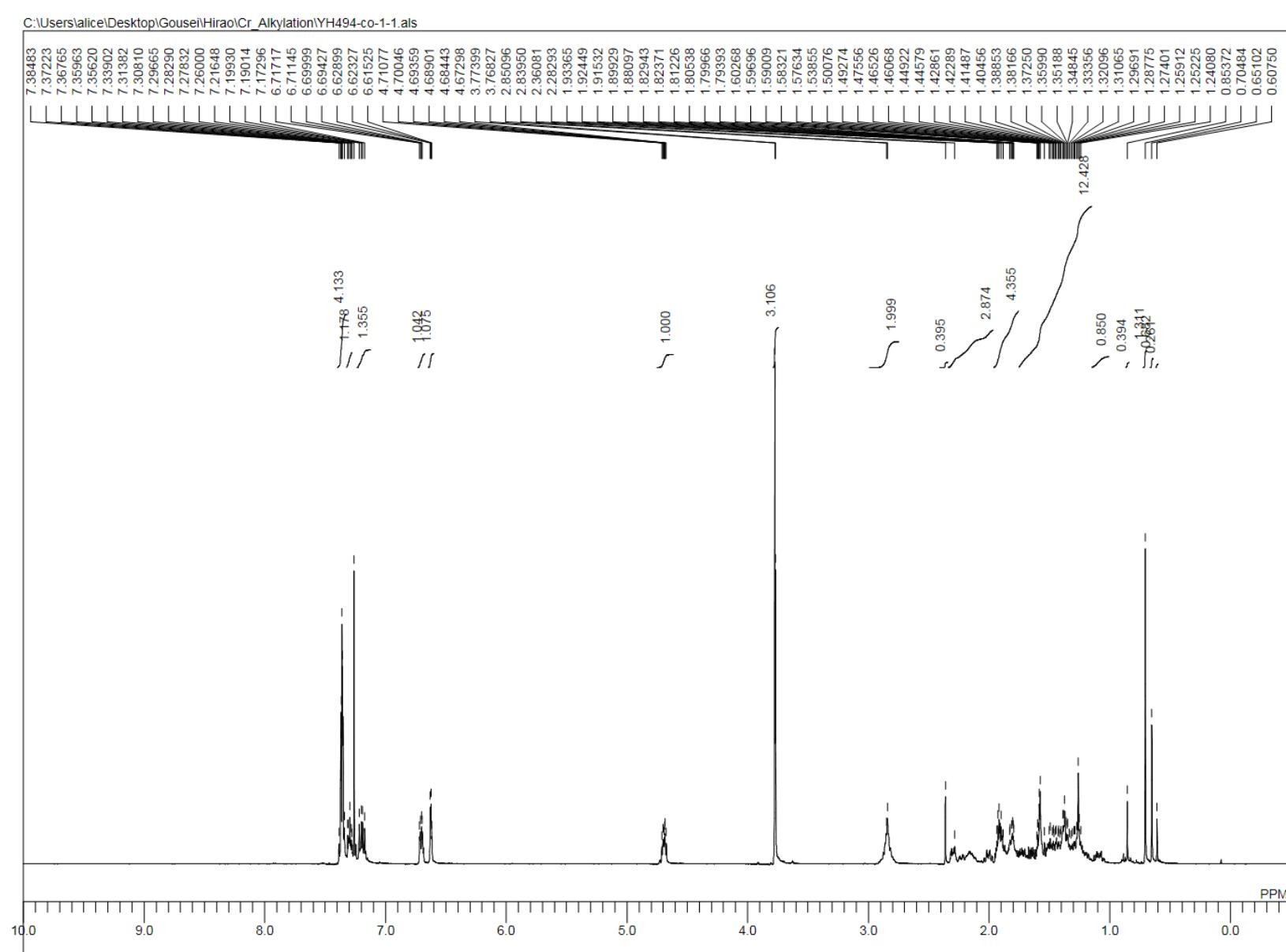
¹H NMR (500 MHz, CDCl₃)



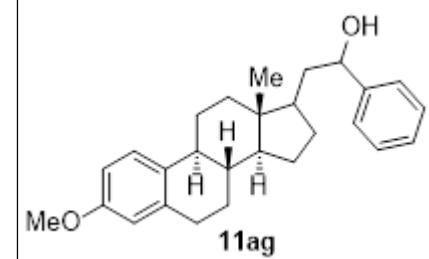
¹³C NMR (125 MHz, CDCl₃)



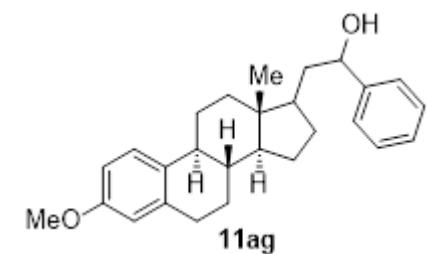
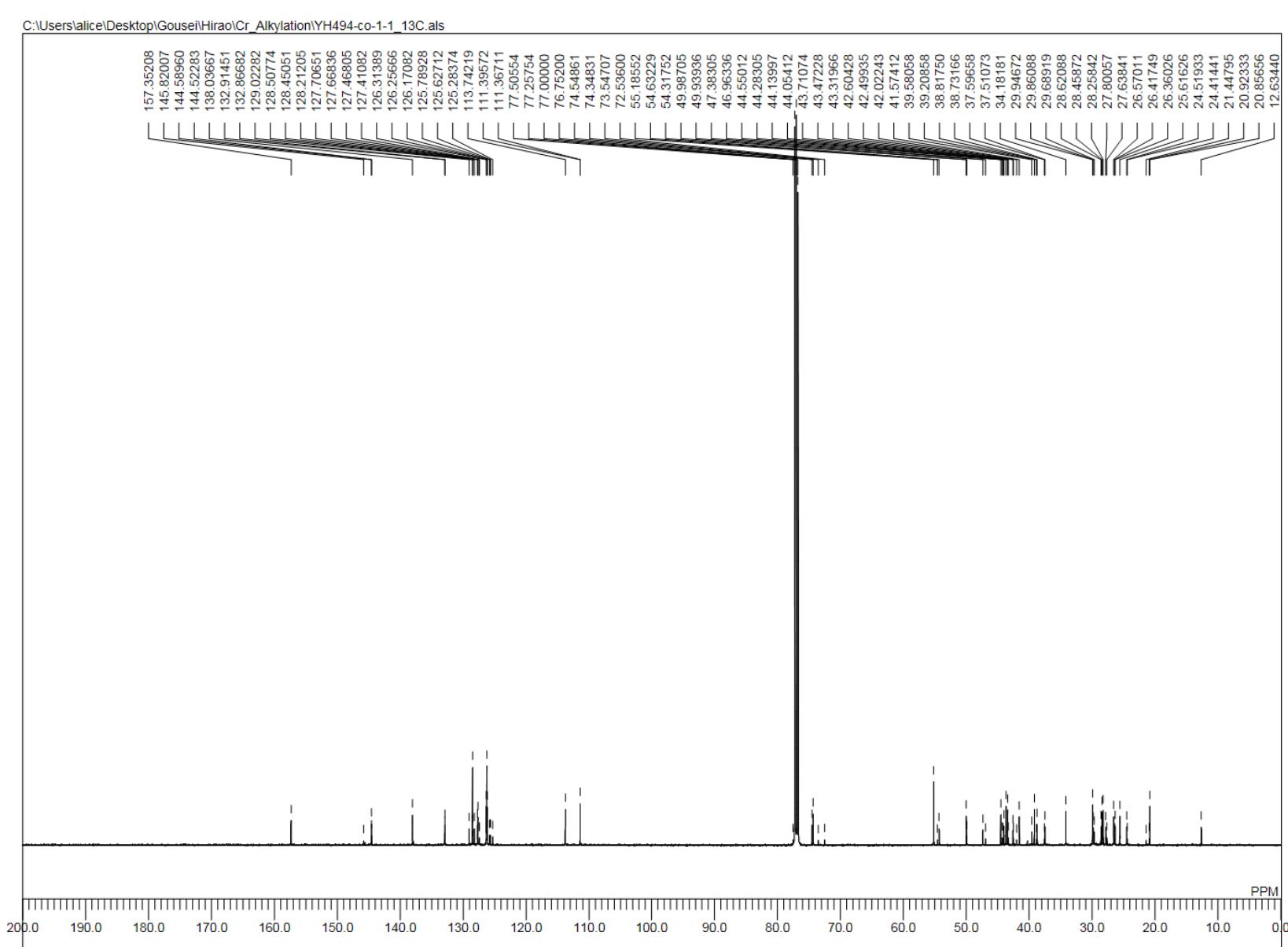
¹H NMR (500 MHz, CDCl₃)



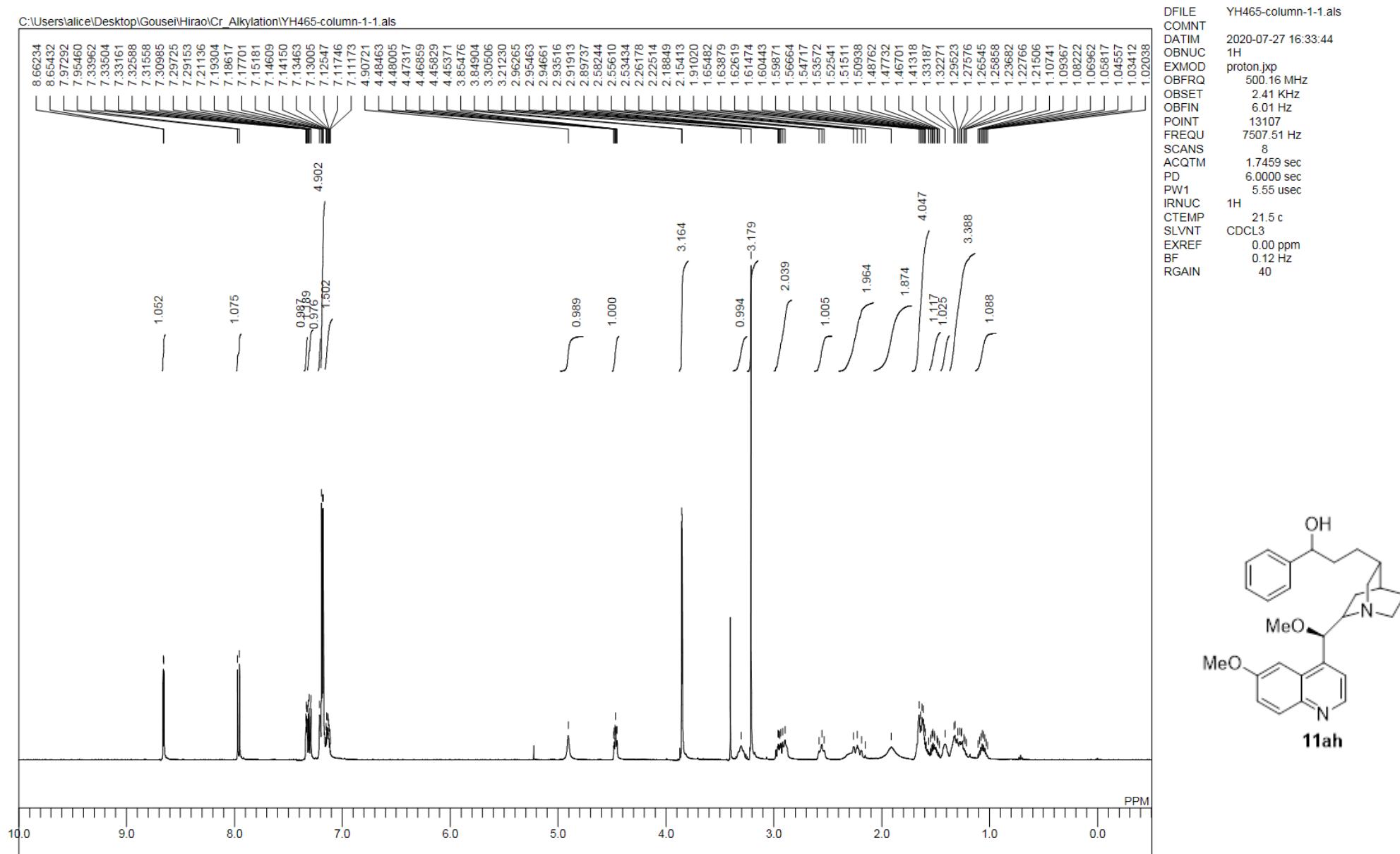
DFILE YH494-co-1-1.als
 COMNT
 DATIM 2020-08-28 19:55:20
 OBNUC 1H
 EXMOD proton.jxp
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.51 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 6.0000 sec
 PW1 5.55 usec
 1H 21.9 c
 CTEMP CDCl₃
 SLVNT 7.26 ppm
 EXREF 0.12 Hz
 RGAIN 40



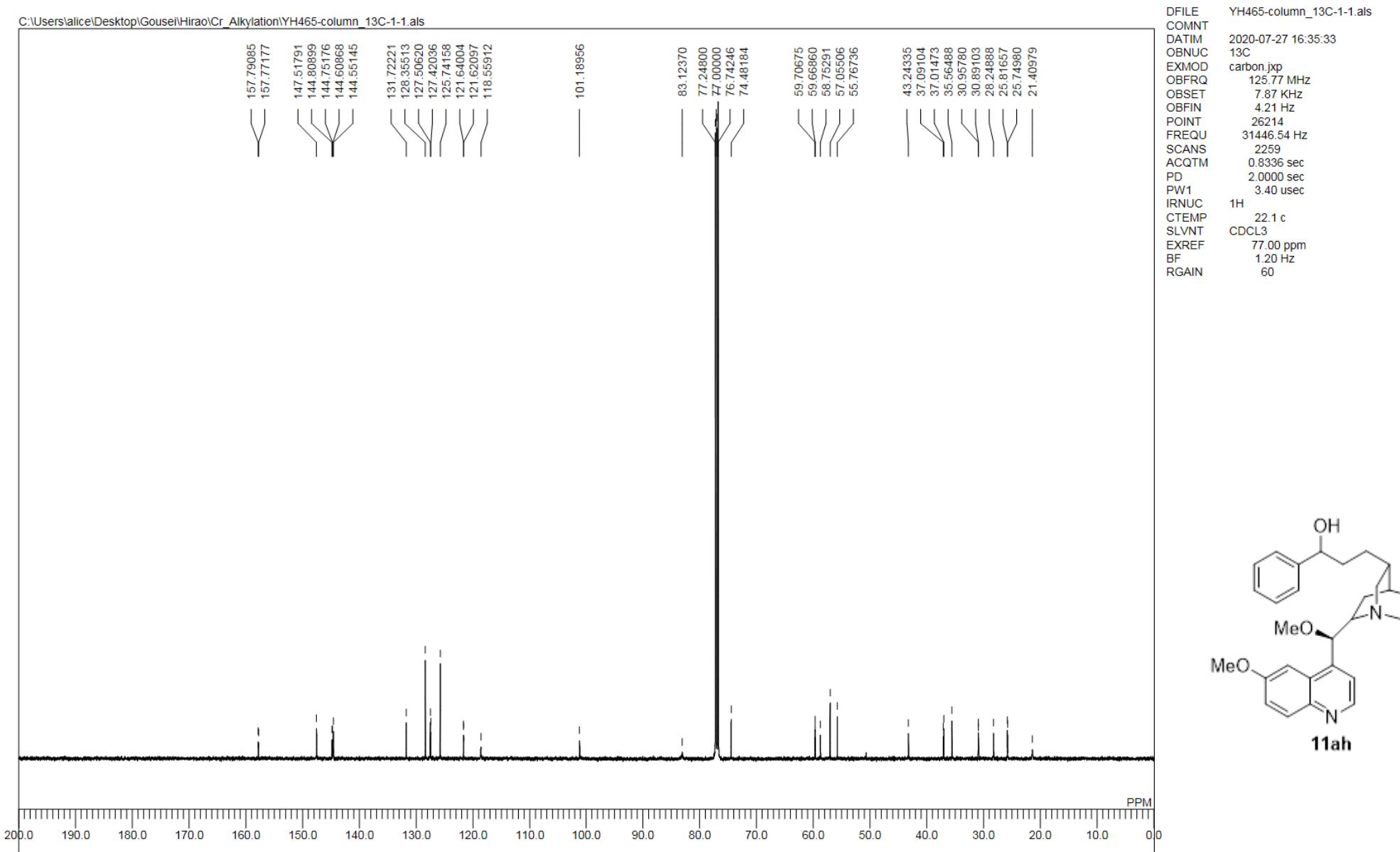
¹³C NMR (125 MHz, CDCl₃)



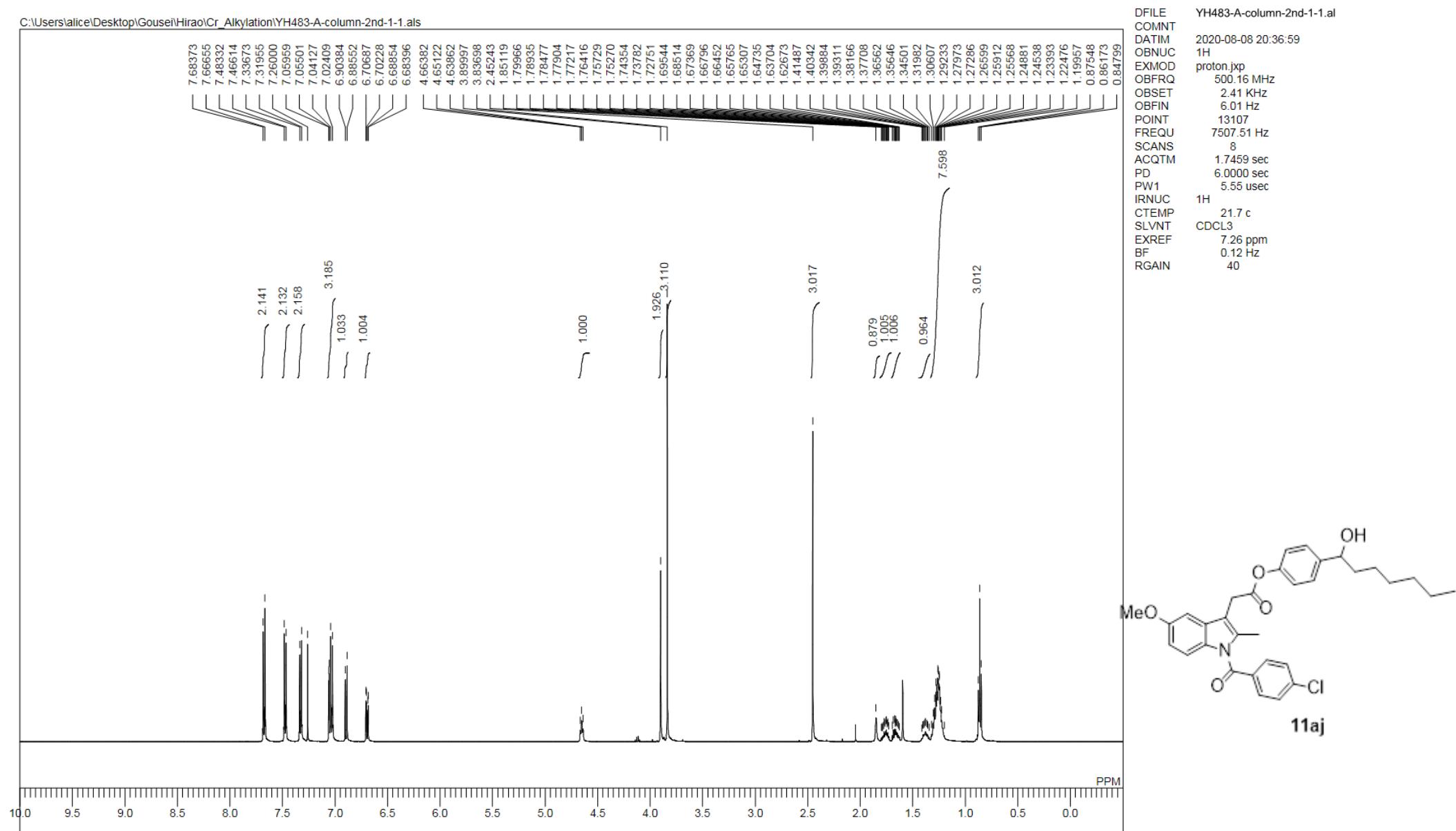
¹H NMR (500 MHz, CDCl₃)



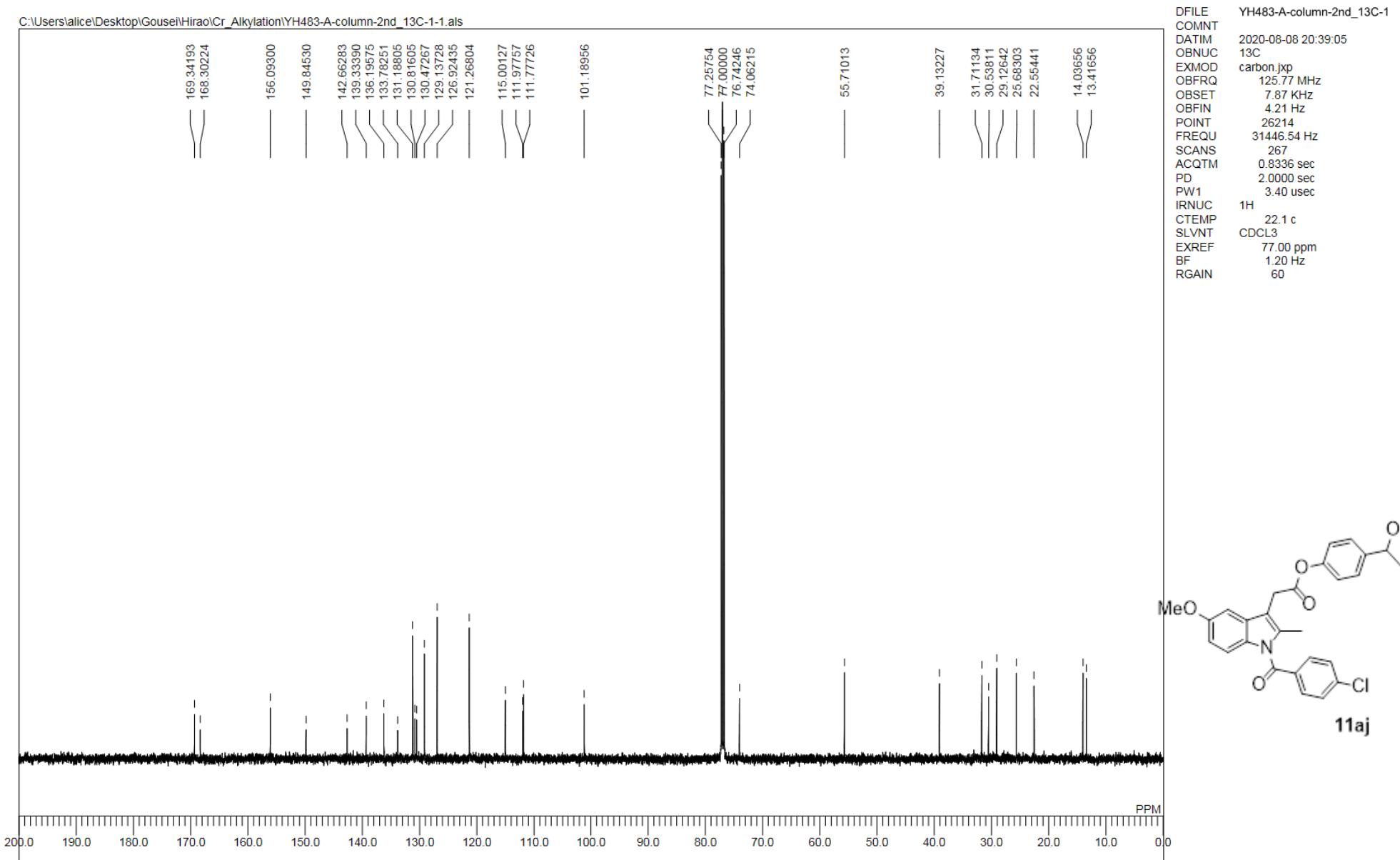
¹³C NMR (125 MHz, CDCl₃)



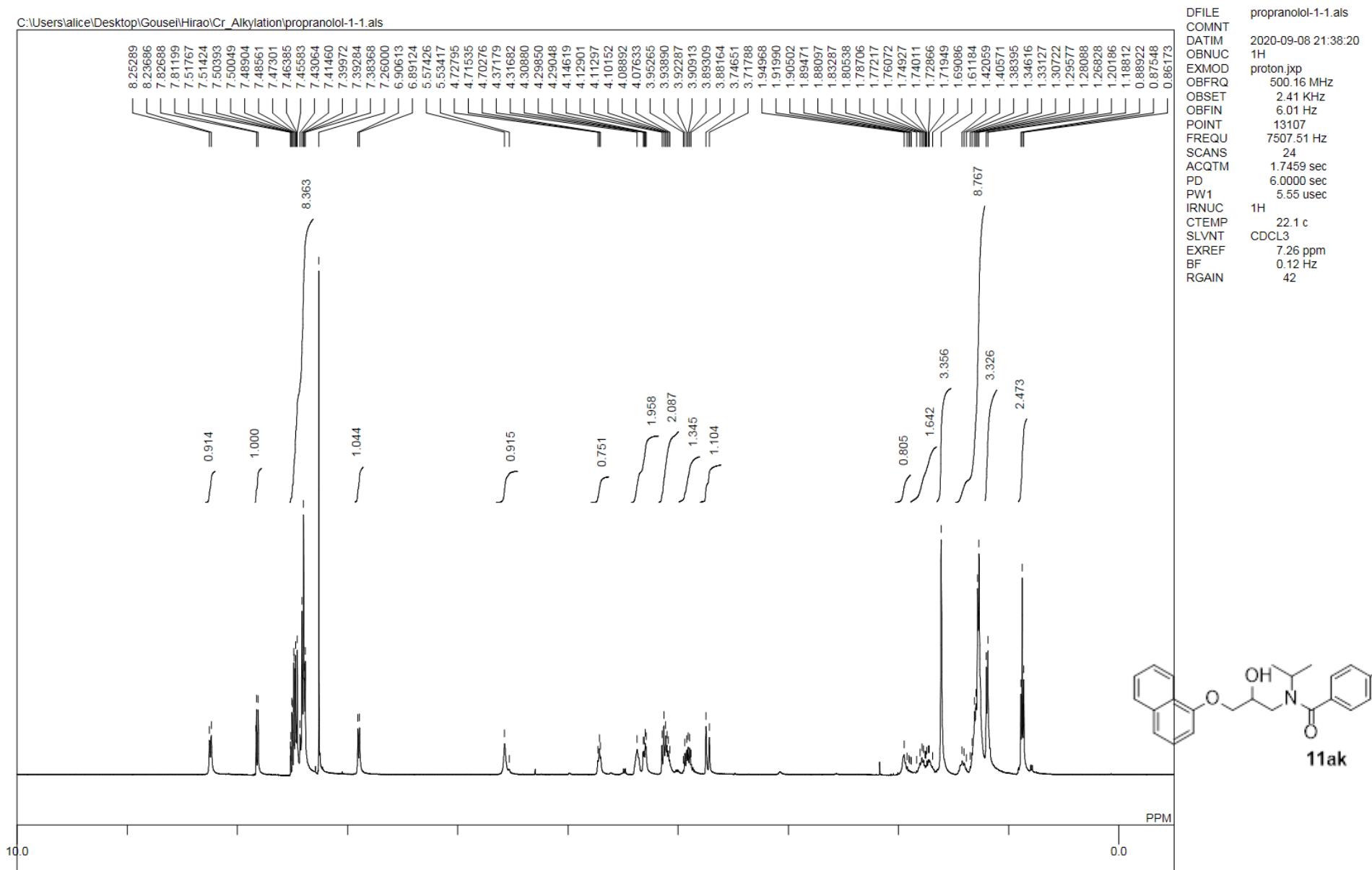
¹H NMR (500 MHz, CDCl₃)



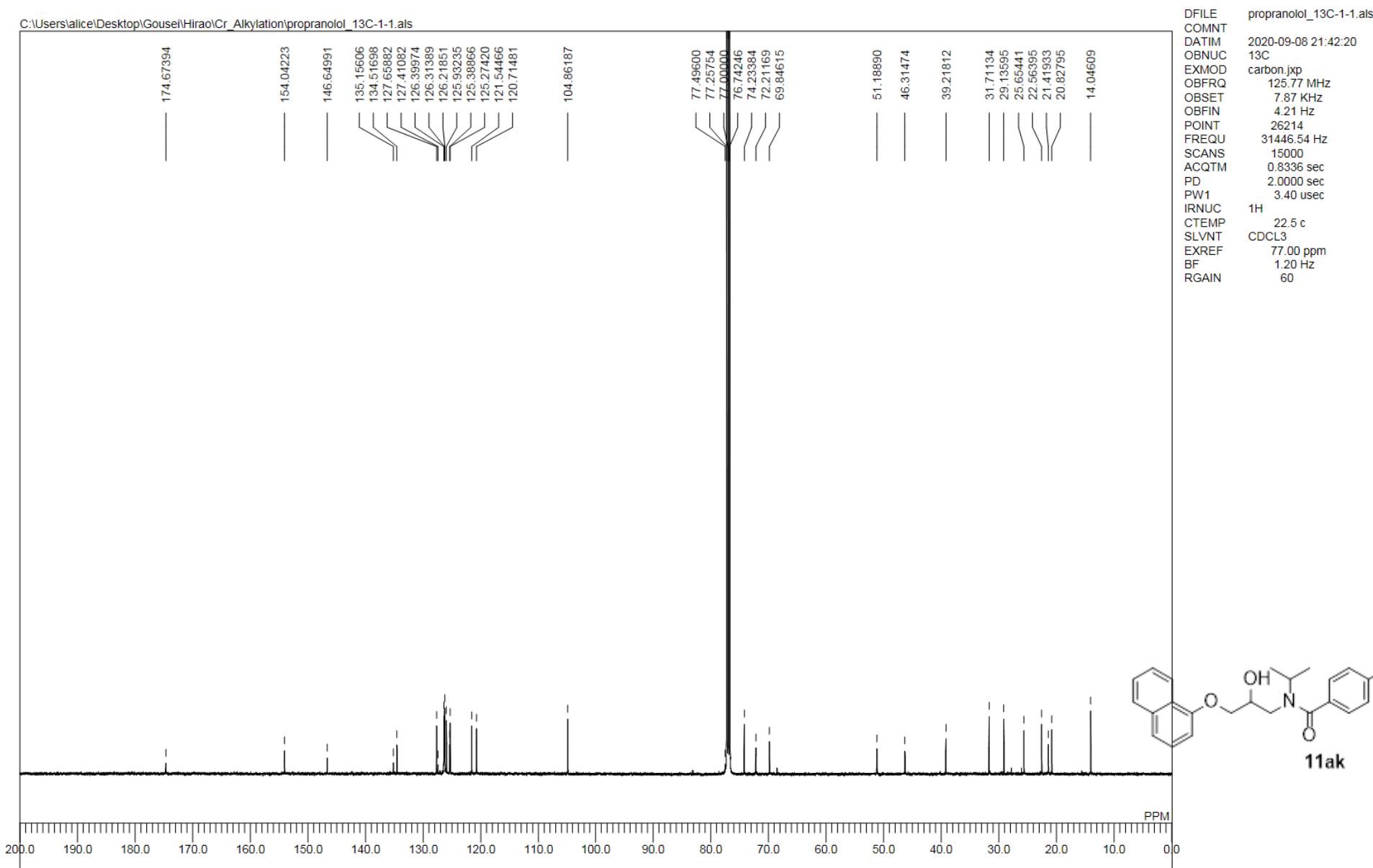
¹³C NMR (125 MHz, CDCl₃)



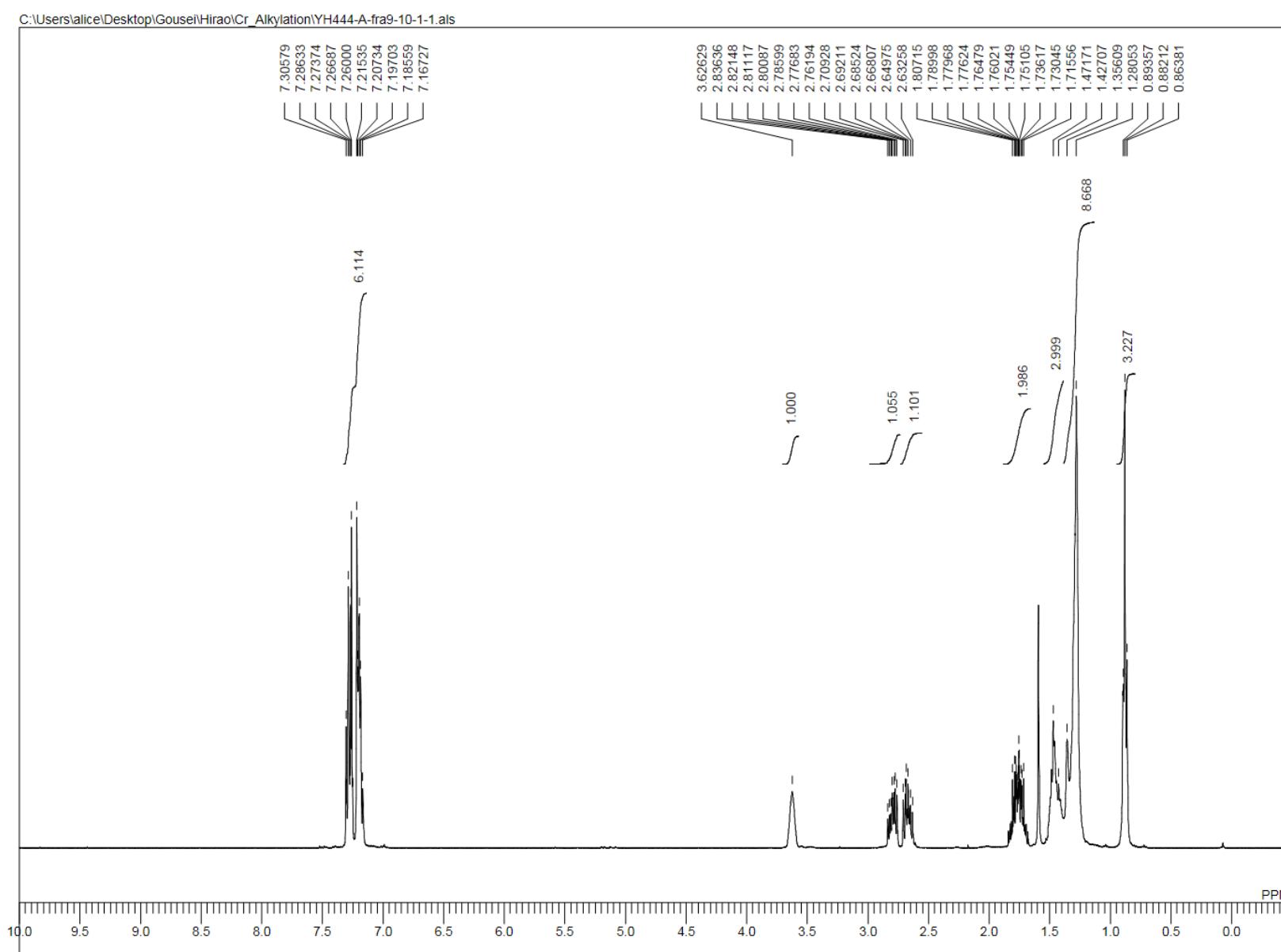
¹H NMR (500 MHz, CDCl₃)



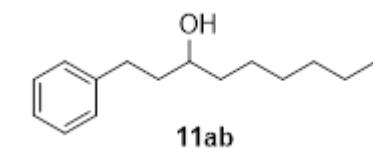
¹³C NMR (125 MHz, CDCl₃)



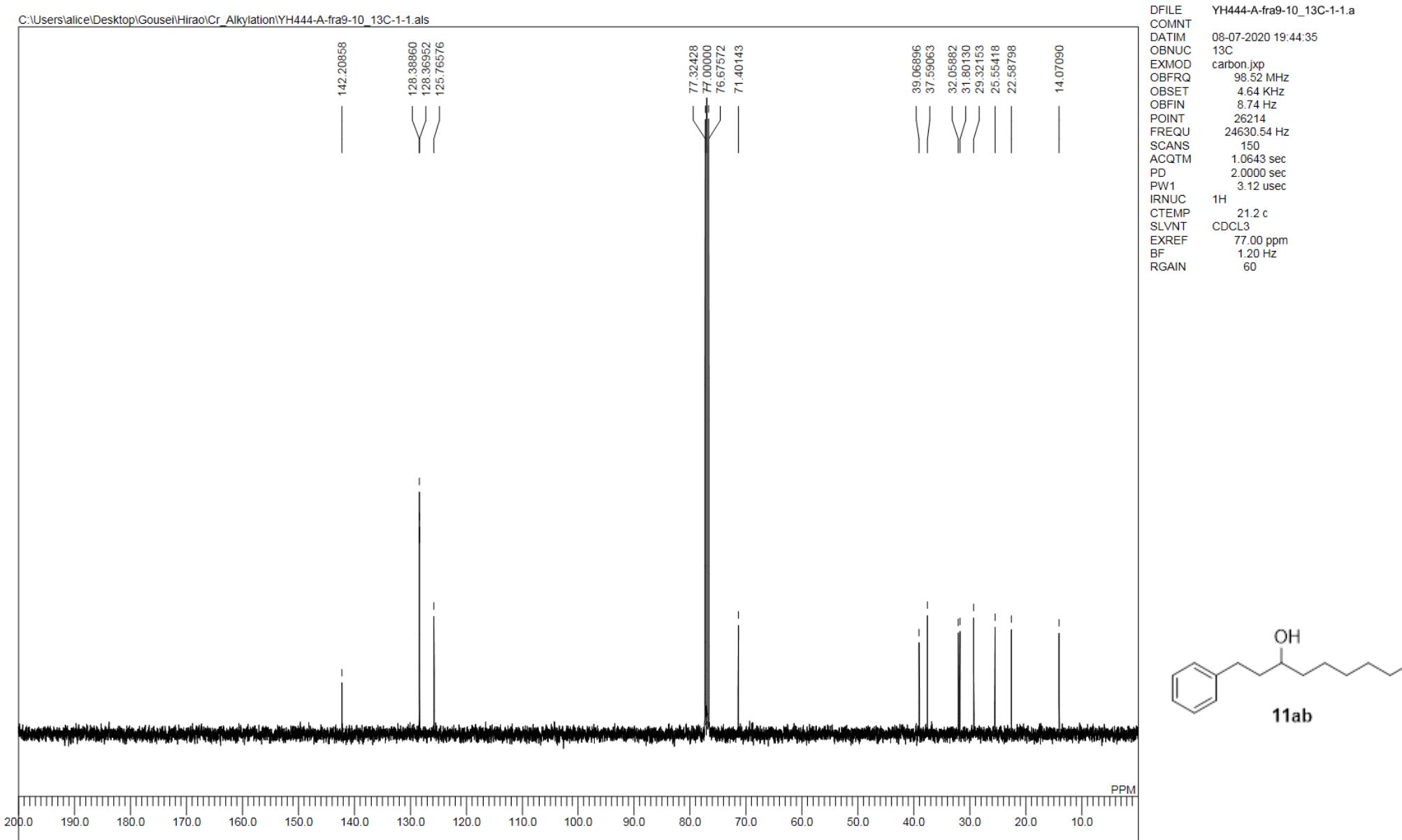
¹H NMR (400 MHz, CDCl₃)



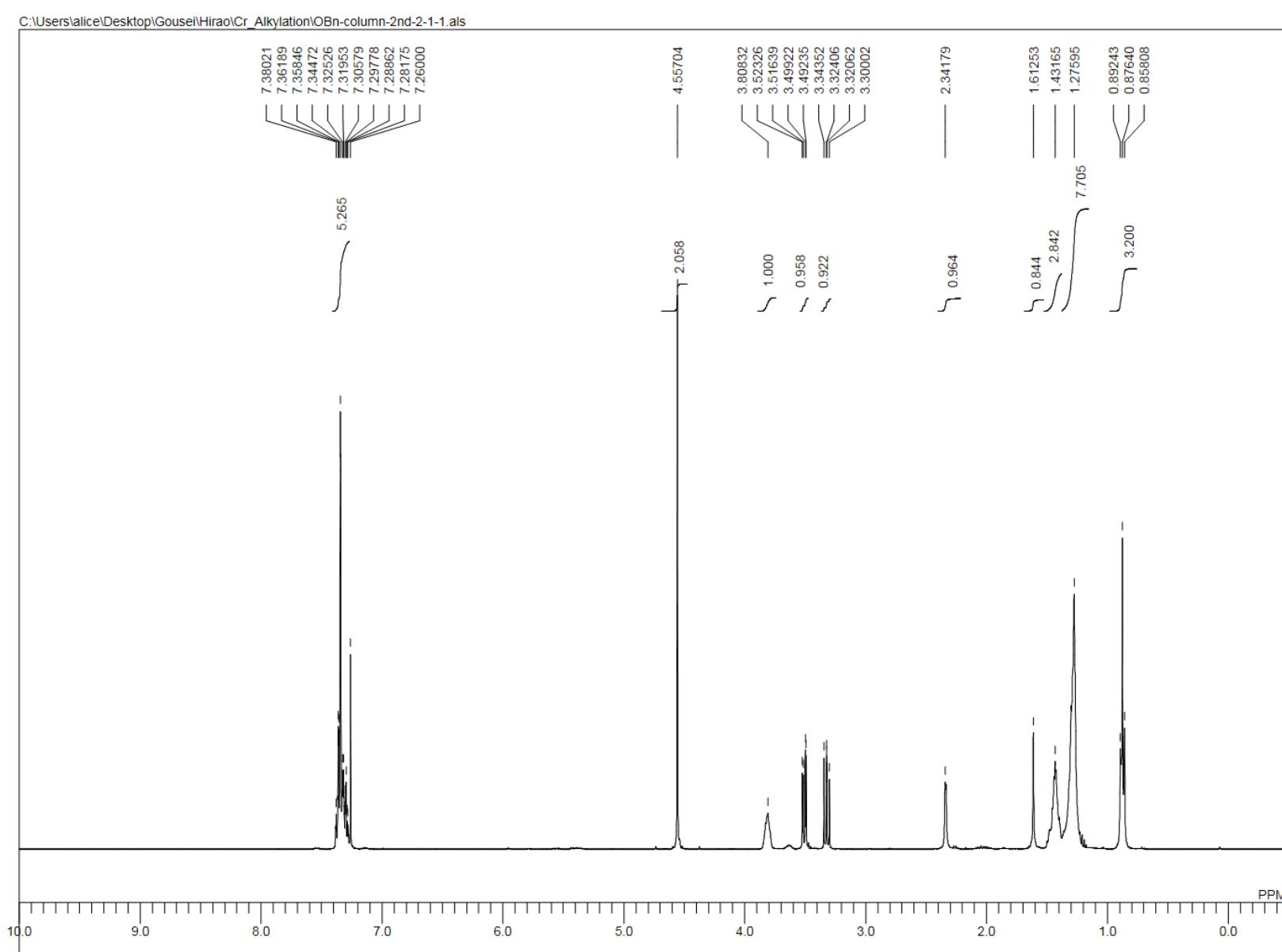
YH444-A-fra9-10-1-1.als
 DFILE 08-07-2020 19:42:29
 COMNT 1H
 DATIM proton.jxp
 OBNUC 391.78 MHz
 EXMOD 8.51 KHz
 OBFRQ 3.34 Hz
 OBSET 13107
 OBFIN 5878.90 Hz
 POINT 8
 FREQU 2.2295 sec
 SCANS 6.0000 sec
 PW1 5.17 usec
 IRNUC 1H
 CTEMP 21.0 c
 SLVNT CDCl₃
 EXREF 7.26 ppm
 BF 0.12 Hz
 RGAIN 38



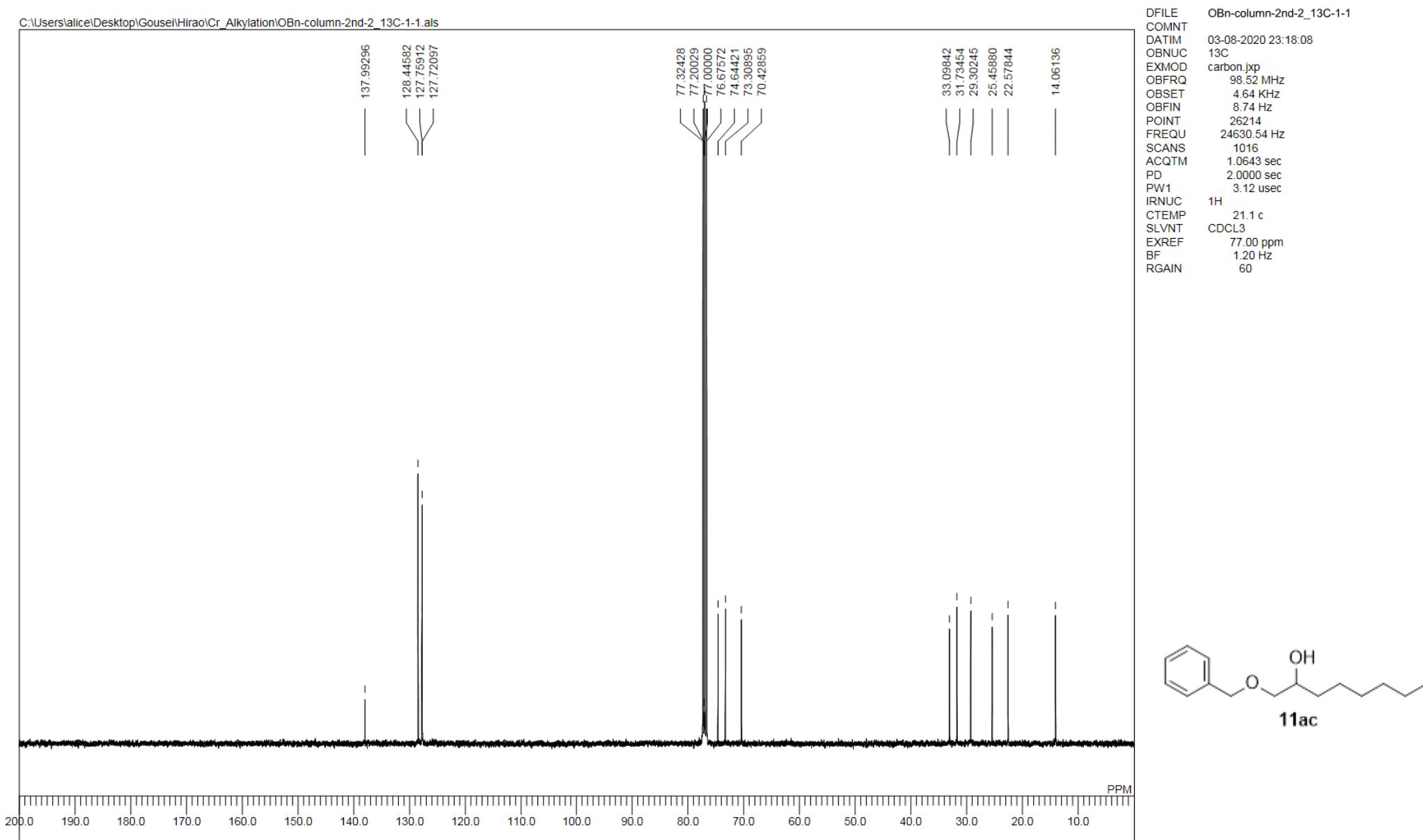
¹³C NMR (100 MHz, CDCl₃)



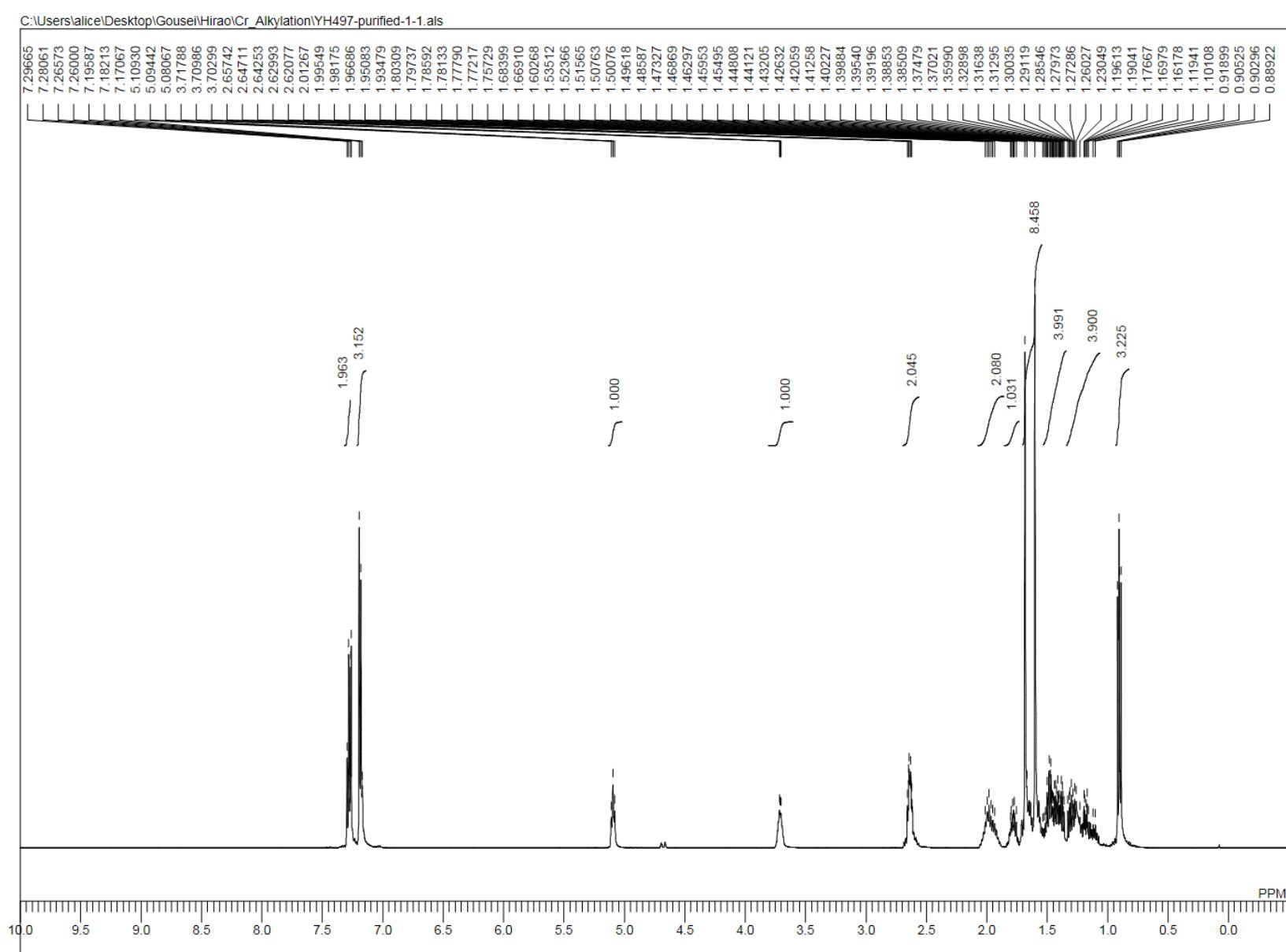
¹H NMR (400 MHz, CDCl₃)



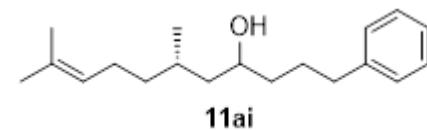
¹³C NMR (100 MHz, CDCl₃)



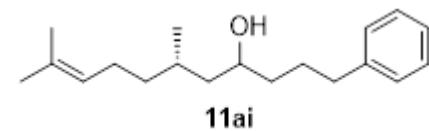
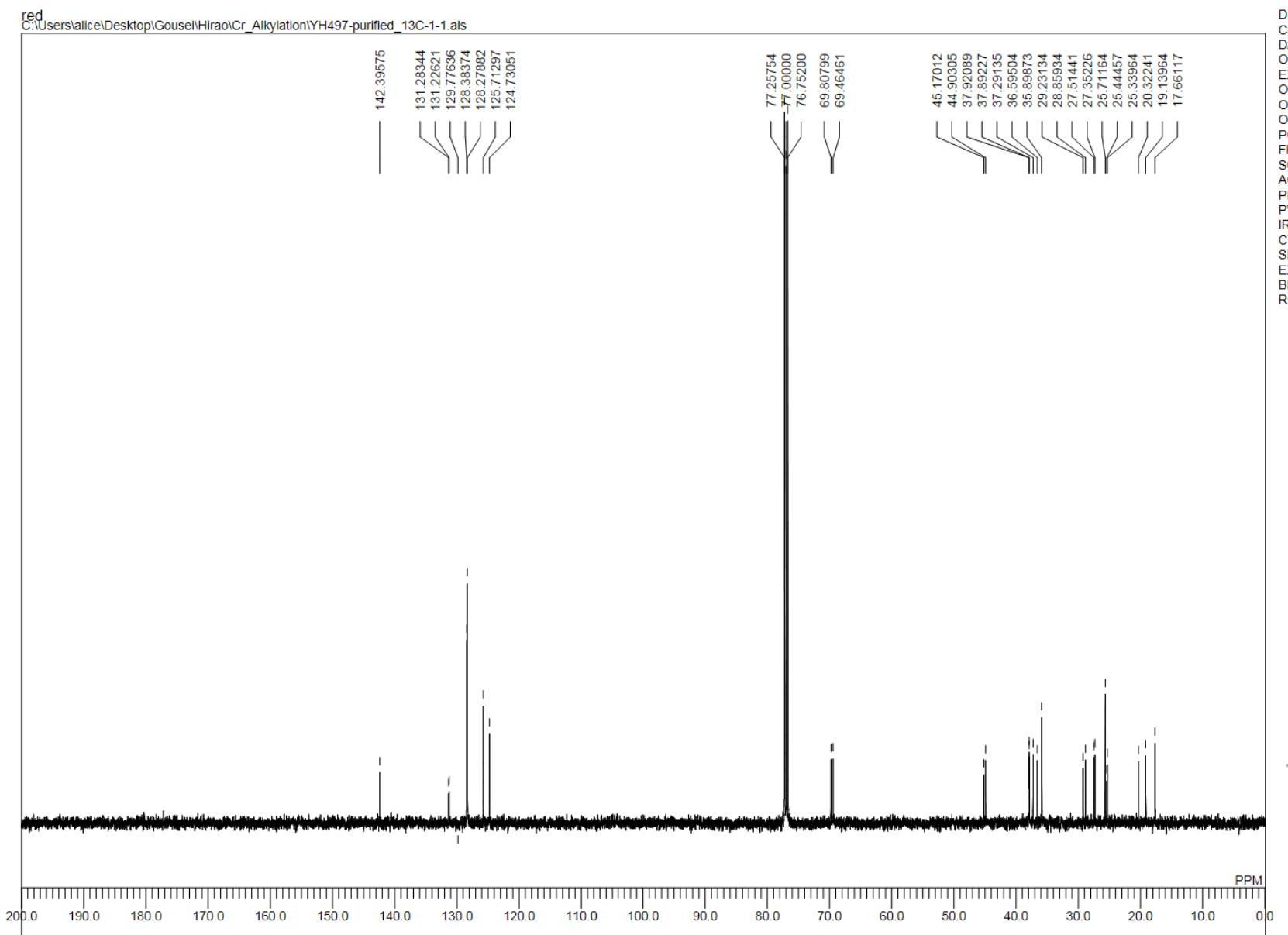
¹H NMR (500 MHz, CDCl₃)



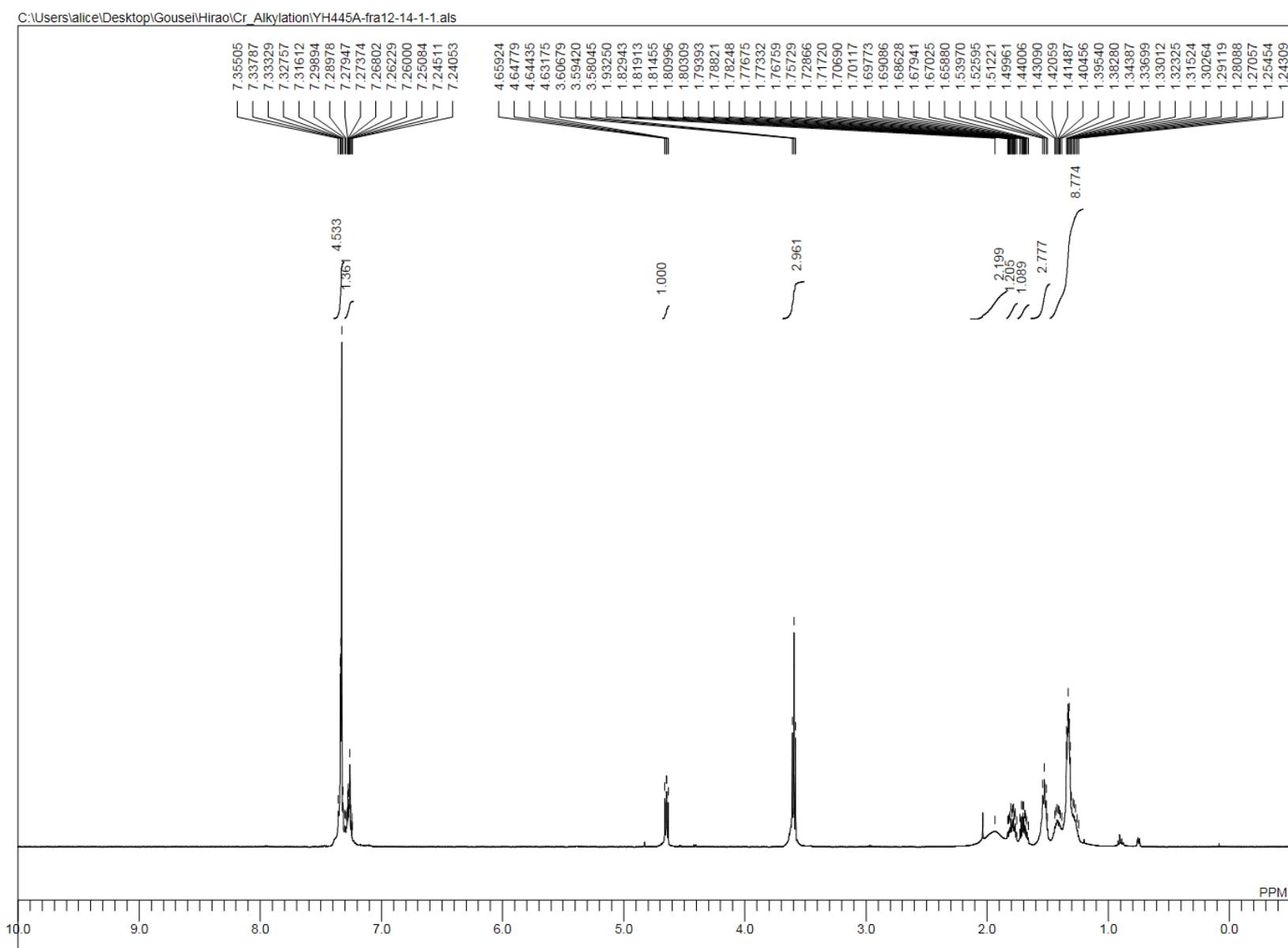
YH497-purified-1-1.als
2020-09-01 17:59:40
1H
proton.jxp
500.16 MHz
2.41 KHz
6.01 Hz
13107
7507.51 Hz
8
1.7459 sec
6.0000 sec
5.55 usec
1H
21.7 c
CDCl₃
7.26 ppm
0.12 Hz
40



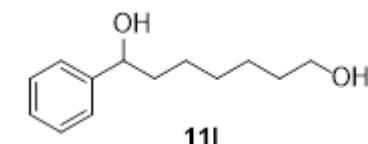
¹³C NMR (125 MHz, CDCl₃)



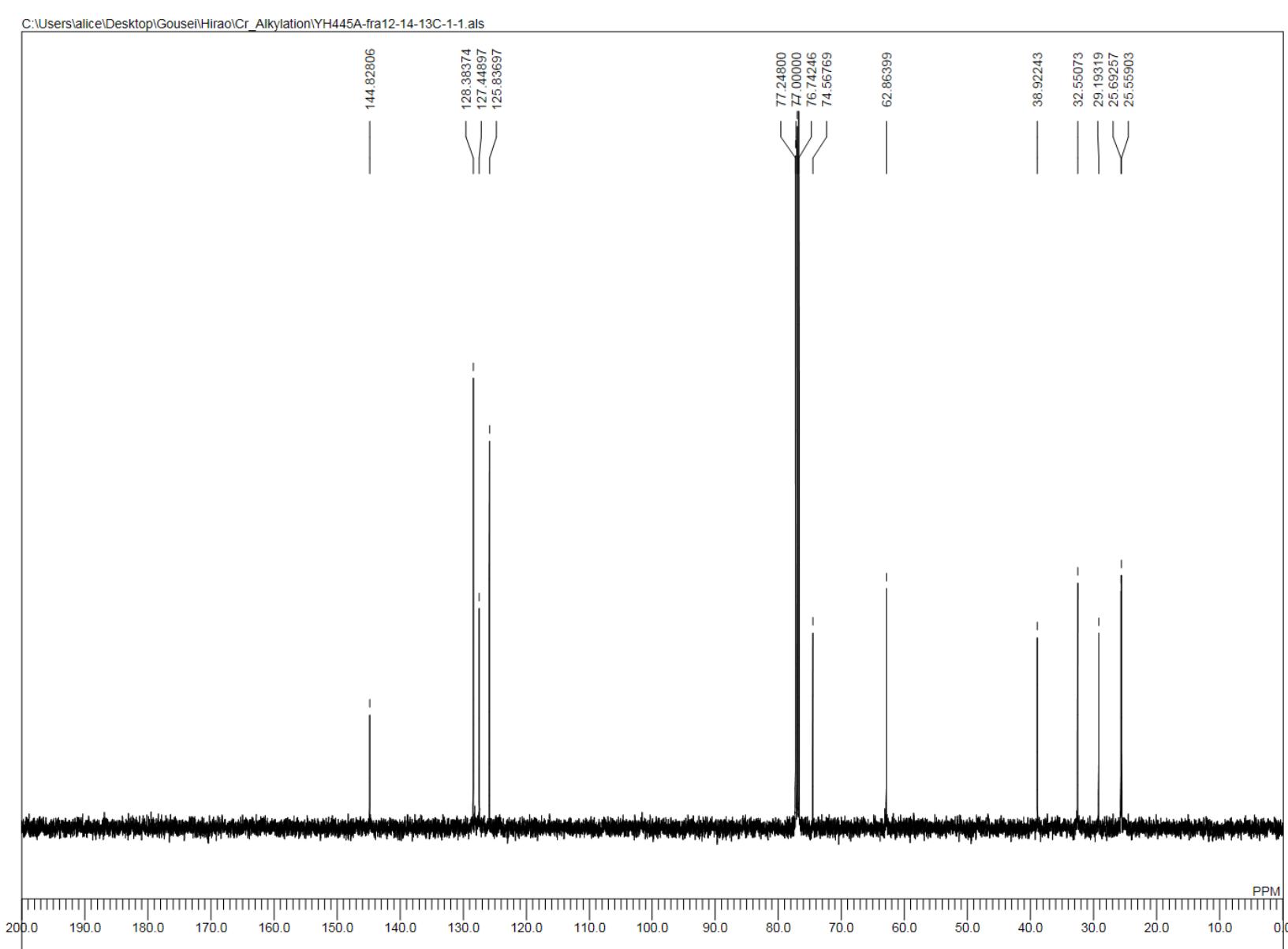
¹H NMR (500 MHz, CDCl₃)



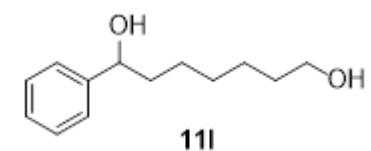
YH445A-fra12-14-1-1.als
 2020-07-09 21:18:15
 1H
 proton.jpx
 500.16 MHz
 2.41 kHz
 6.01 Hz
 13107
 7507.51 Hz
 8
 1.7459 sec
 6.0000 sec
 5.55 usec
 1H
 21.9 c
 CDCl₃
 7.26 ppm
 0.12 Hz
 38



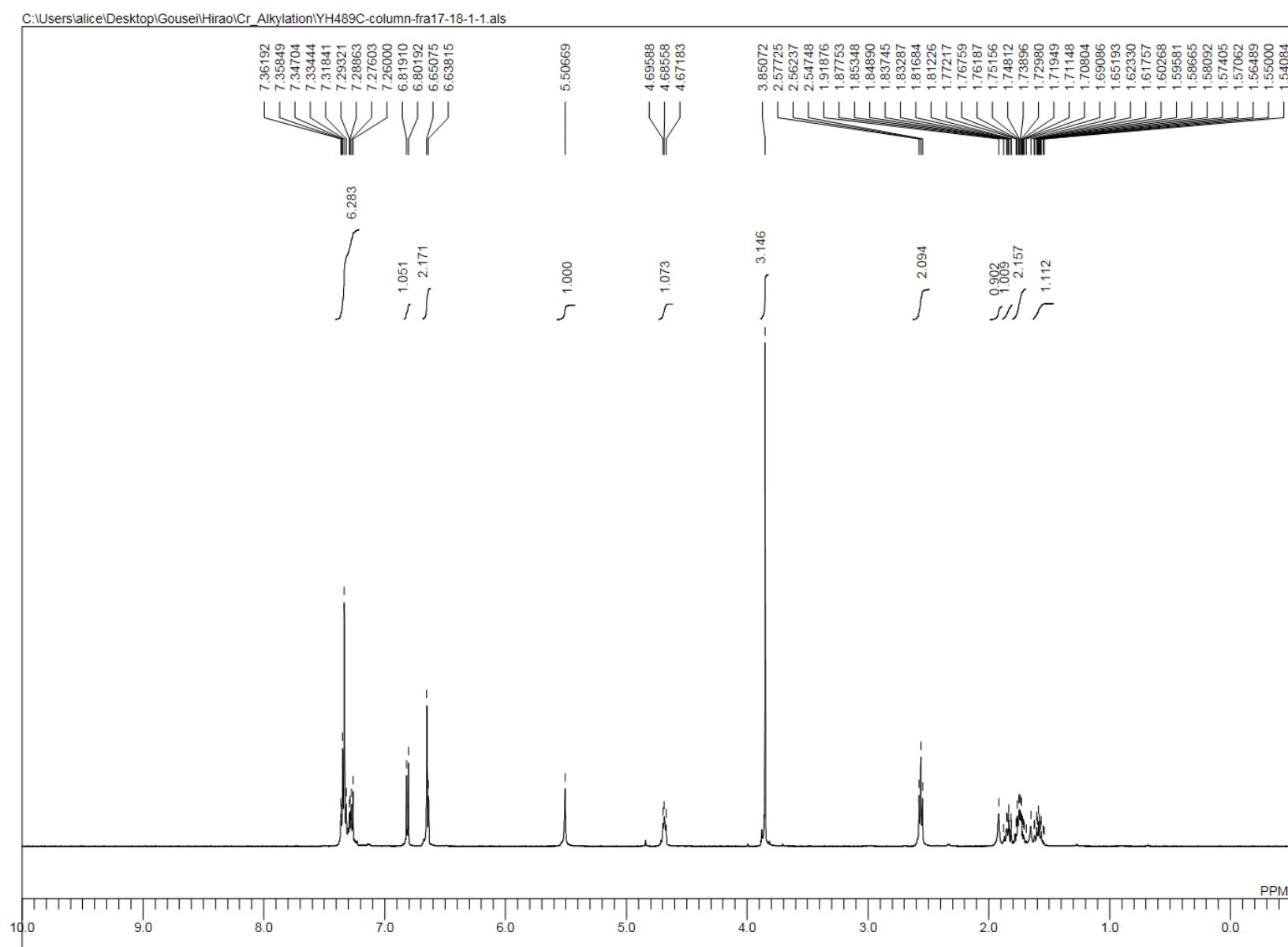
¹³C NMR (125 MHz, CDCl₃)



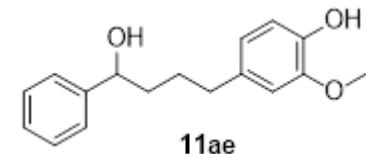
DFILE YH445A-fra12-14-13C-1-1.a
COMNT
DATIM 2020-07-09 21:20:09
13C
OBNUC carbon.jxp
EXMOD 125.77 MHz
OBFREQ 7.87 kHz
OBSET 4.21 Hz
OBFIN 26214
POINT 31446.54 Hz
FREQU 107
SCANS 0.8336 sec
ACQTM 2.0000 sec
PD 3.40 usec
PW1
IRNUC 1H
CTEMP 22.0 c
SLVNT CDCl₃
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60



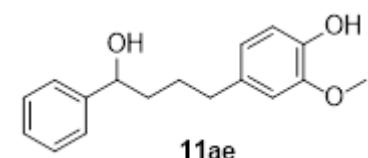
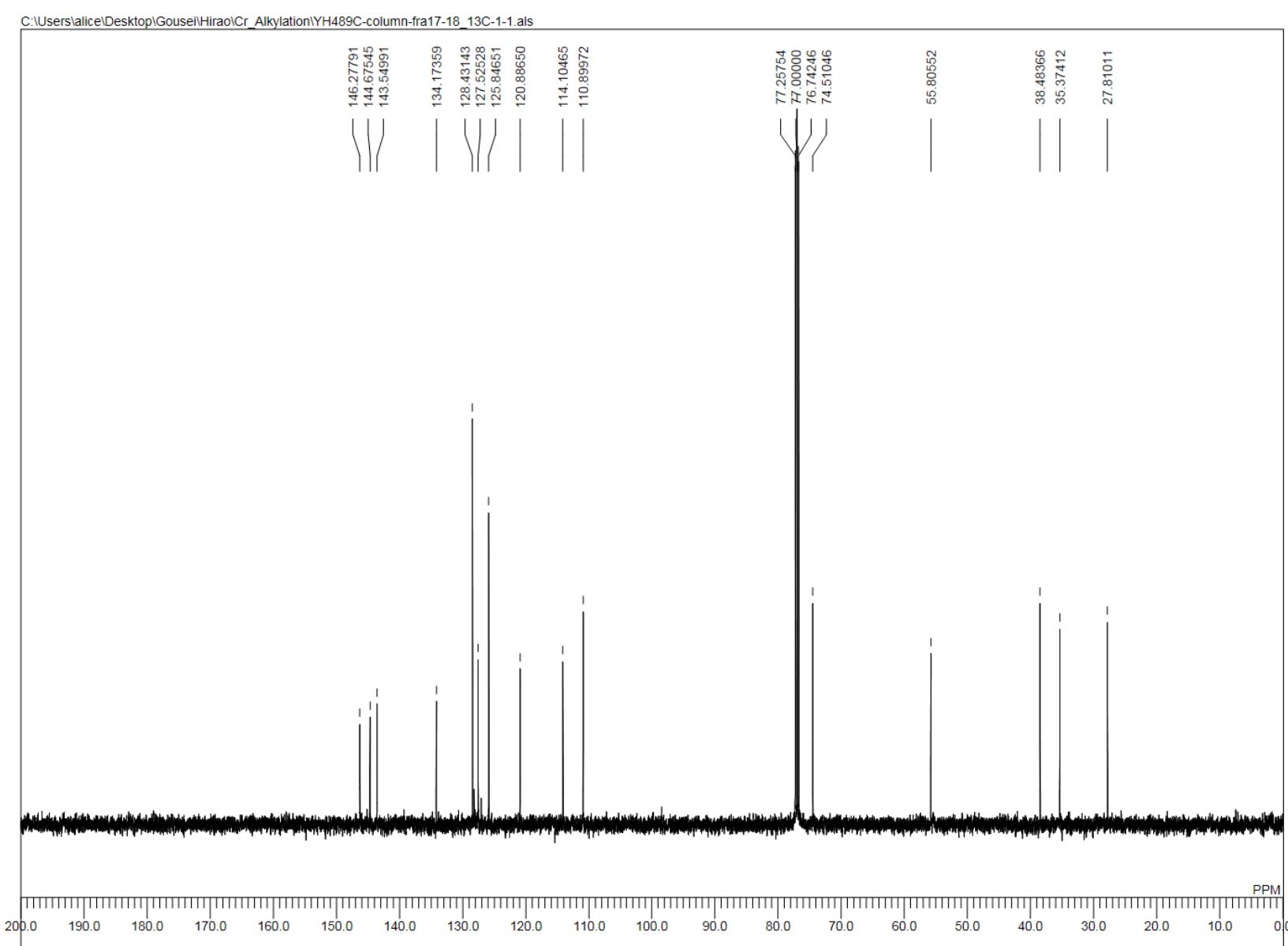
¹H NMR (500 MHz, CDCl₃)



YH489C-column-fra17-18-1-1
2020-08-21 10:05:41
1H
proton.jxp
500.16 MHz
2.41 kHz
6.01 Hz
13107
7507.51 Hz
8
1.7459 sec
6.0000 sec
5.55 usec
1H
22.0 c
CDCl₃
7.26 ppm
0.12 Hz
38

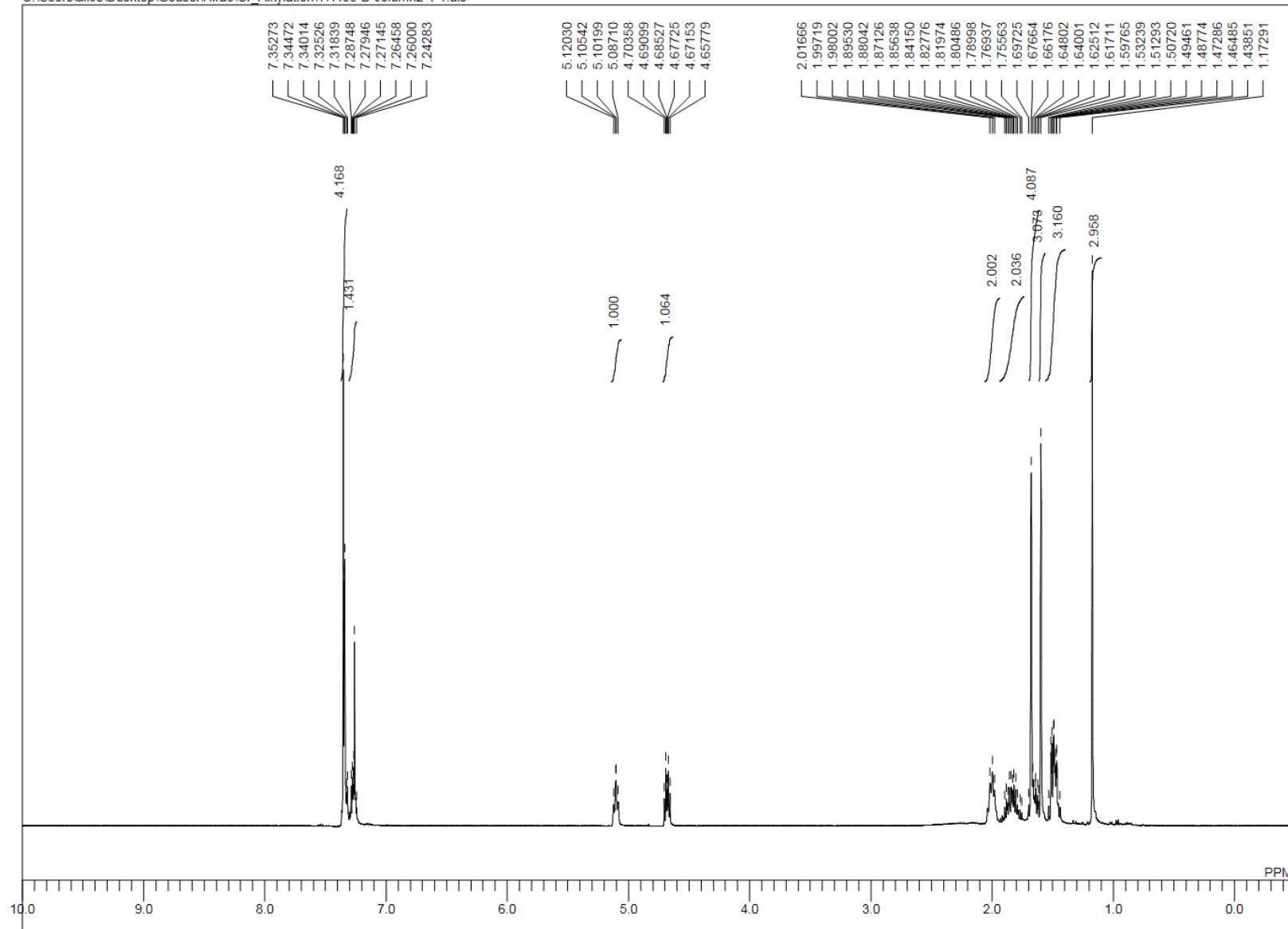


¹³C NMR (125 MHz, CDCl₃)

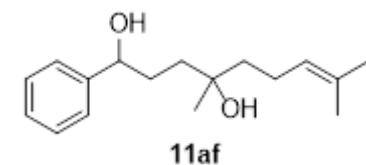


¹H NMR (400 MHz, CDCl₃)

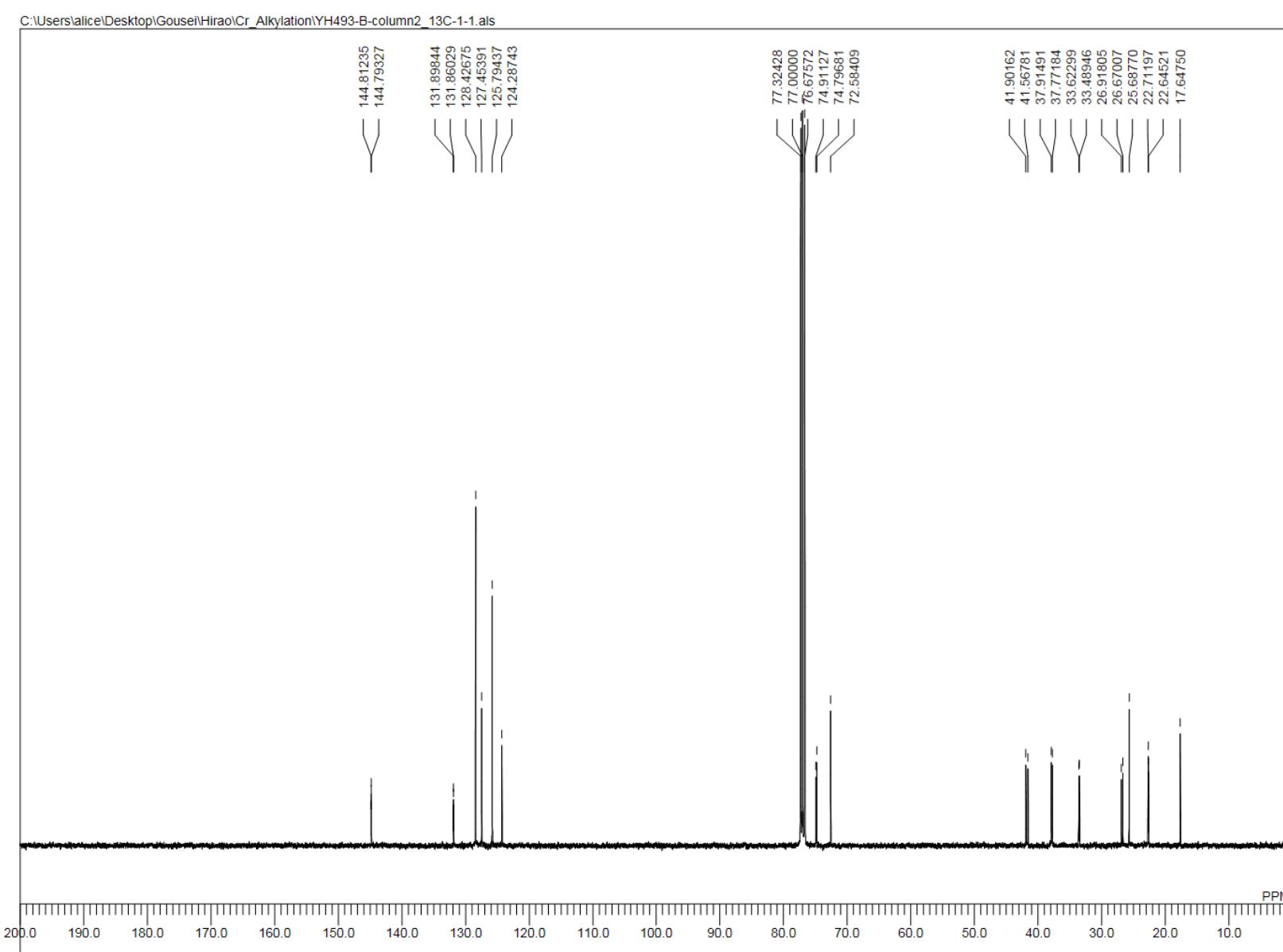
C:\Users\alice\Desktop\Gousei\Hirao\Cr_Aalkylation\YH493-B-column2-1-1.als



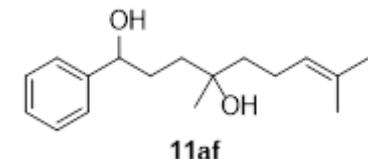
YH493-B-column2-1-1.als
25-08-2020 10:23:15
1H
proton jxp
391.78 MHz
8.51 KHz
3.34 Hz
13107
5878.90 Hz
8
2.2295 sec
6.0000 sec
5.17 usec
1H
21.0 c
CDCl₃
7.26 ppm
0.12 Hz
36



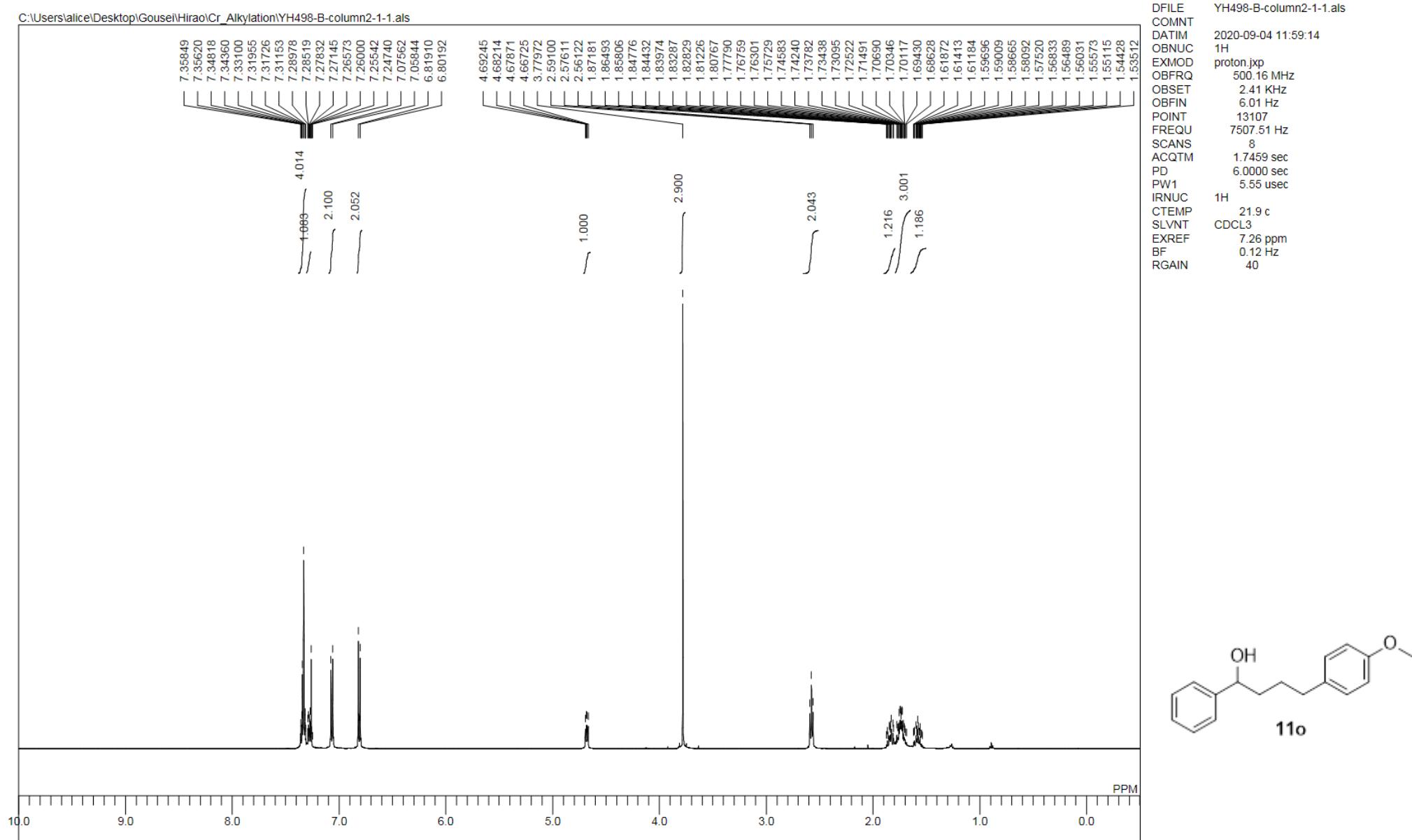
¹³C NMR (100 MHz, CDCl₃)



YH493-B-column2_13C-1-1..
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
13C
carbon.jxp
25-08-2020 10:26:06
98.52 MHz
4.64 KHz
8.74 Hz
26214
24630.54 Hz
1666
1.0643 sec
2.0000 sec
3.12 usec
1H
20.8 c
CDCl₃
77.00 ppm
1.20 Hz
60



¹H NMR (500 MHz, CDCl₃)



¹³C NMR (125 MHz, CDCl₃)

