

## *Supporting Information*

### Chromium-Catalyzed Linear-Selective Alkylation of Aldehydes with Alkenes

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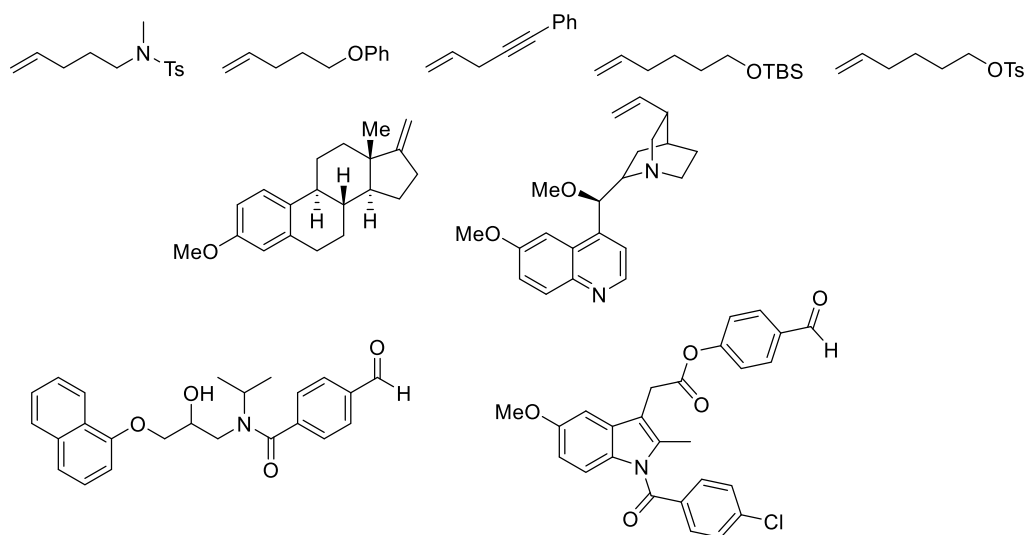
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## 1. General Method

$^1\text{H}$  NMR spectra were recorded on JEOL ECX500 (500 MHz for  $^1\text{H}$  NMR and 125.65 MHz for  $^{13}\text{C}$  NMR), and JEOL ECS400 (400 MHz for  $^1\text{H}$  NMR and 100 MHz for  $^{13}\text{C}$  NMR, and 370 MHz for  $^{19}\text{F}$  NMR) spectrometer. For  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, chemical shifts were reported in the scale relative to  $\text{CDCl}_3$  ( $\delta = 7.26$  for  $^1\text{H}$  NMR and  $\delta = 77.0$  for  $^{13}\text{C}$  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.  $\text{CrCl}_2$  (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

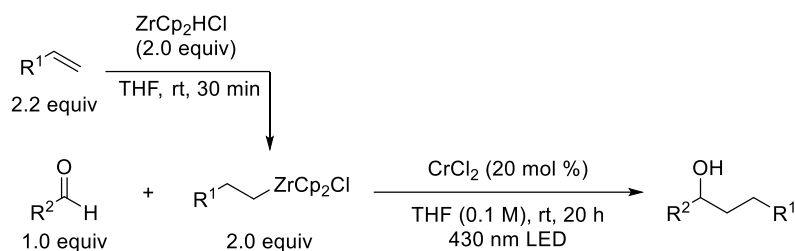
Chiral ligand was prepared according to the reported method.<sup>1</sup>



Above alkenes and aldehydes were prepared according to the reported method.<sup>2-9</sup>

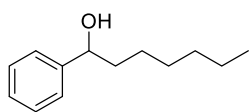
## 3. General Procedure

**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  $\text{ZrCp}_2\text{HCl}$  (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,  $\text{CrCl}_2$  (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  $\text{Et}_2\text{O}$  three times. The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , 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**).

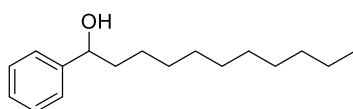


The reaction was conducted using 1-hexene **1a** (55.0  $\mu\text{L}$ , 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11a** as a colorless oil (26.9 mg, 70%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>10</sup>

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

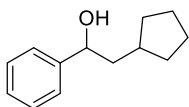


The reaction was conducted using 1-decene (83.4  $\mu\text{L}$ , 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11b** as a colorless oil (31.2 mg, 62%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  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.<sup>11</sup>

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

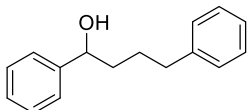


The reaction was conducted using methylenecyclopentane (46.3  $\mu\text{L}$ , 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11c** as a colorless oil (22.2 mg, 58%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  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.<sup>12</sup>

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

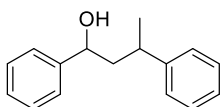


The reaction was conducted using allylbenzene (58.4  $\mu\text{L}$ , 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11d** as a colorless oil (24.1 mg, 53%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>13</sup>

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



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

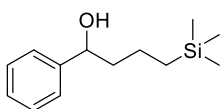


colorless oil (18.0 mg, 40%, 1.3/1 dr).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) major isomer:  $\delta$  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:  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) major isomer:  $\delta$  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:  $\delta$  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.<sup>14</sup>

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

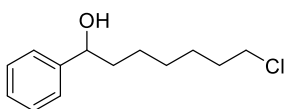


The reaction was conducted using allyltrimethylsilane (69.8  $\mu\text{L}$ , 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11f** as a colorless oil (23.0 mg, 52%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  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.<sup>15</sup>

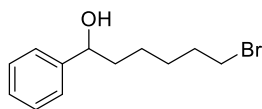
#### 7-chloro-1-phenylheptan-1-ol (**11g**).



The reaction was conducted using 6-chlorohex-1-ene (58.2  $\mu\text{L}$ , 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%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  144.8, 128.4, 127.5, 125.8, 74.6, 45.1, 38.9, 32.5, 28.7, 26.7, 25.6; IR (neat)  $\nu$  3358, 3021, 2932, 2857, 1653, 1451, 1028, 700  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{13}\text{H}_{19}\text{ClONa}$  249.1017; Found 249.1011.

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

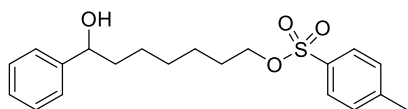


The reaction was conducted using 5-bromopent-1-ene (52.0  $\mu$ L, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11h** as a colorless oil (27.2 mg, 53%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  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.<sup>16</sup>

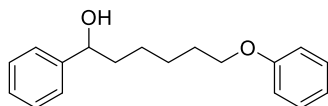
#### 7-hydroxy-7-phenylheptyl 4-methylbenzenesulfonate (**11i**).



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%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  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)  $\nu$  3546, 3412, 3029, 2933, 2857, 1597, 1493, 1453, 1355, 1175, 1097, 1019, 956, 815, 762, 701  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  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**).

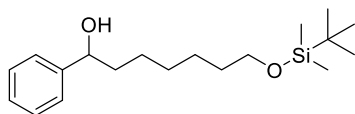


The reaction was conducted using (pent-4-en-1-yloxy)benzene (71.3 mg, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11j** as a colorless oil (36.4 mg, 67%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  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)  $\nu$  3433, 2937, 2859, 1637, 1600, 1496, 1472, 1455, 1300, 1244, 1171, 1031, 754  $\text{cm}^{-1}$ ; HRMS

(ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{18}H_{22}O_2Na$  293.1512; Found 293.1512.

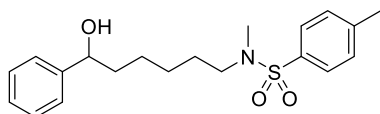
**7-((*tert*-butyldimethylsilyl)oxy)-1-phenylheptan-1-ol (11k).**



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 ( $CDCl_3$ , 500 MHz)  $\delta$  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);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$  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)  $\nu$  3388, 2929, 2856, 1725, 1462, 1254, 1100, 835, 774, 700  $cm^{-1}$ ; HRMS (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{19}H_{34}O_2SiNa$  345.2220; Found 345.2223.

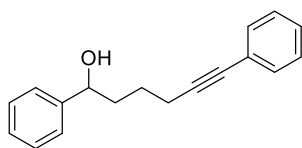
***N*-(6-hydroxy-6-phenylhexyl)-*N*,4-dimethylbenzenesulfonamide (11m).**



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 ( $CDCl_3$ , 400 MHz)  $\delta$  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);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$  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)  $\nu$  3529, 3021, 2934, 2860, 1597, 1492, 1453, 1336, 1159, 1089, 1019, 815, 701  $cm^{-1}$ ; HRMS (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{20}H_{27}NO_3SNa$  384.1604; Found 384.1611.

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

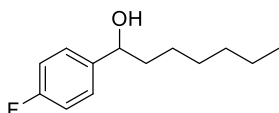


The reaction was conducted using pent-4-en-1-yn-1-ylbenzene (65.4  $\mu$ L, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11n** as a colorless oil (17.8 mg, 36%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>17</sup>

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

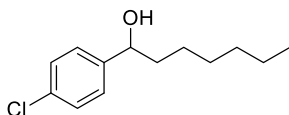


The reaction was conducted using 4-fluorobenzaldehyde (21.0  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11p** as a colorless oil (27.0 mg, 64%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>16</sup>

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

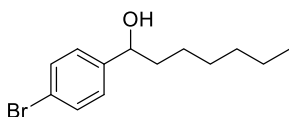


The reaction was conducted using 4-chlorobenzaldehyde (28.1 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11q** as a colorless oil (31.6 mg, 63%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>10</sup>

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



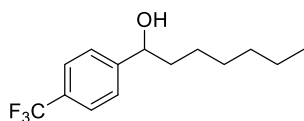
The reaction was conducted using 4-bromobenzaldehyde (37.0 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The

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

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>10</sup>

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

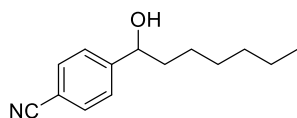


The reaction was conducted using 4-trifluoromethylbenzaldehyde (26.8  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11s** as a colorless oil (25.3 mg, 49%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>16</sup>

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

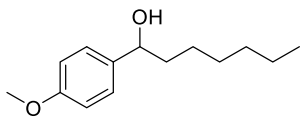


The reaction was conducted using 4-formylbenzonitrile (26.2 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11t** as a colorless oil (16.8 mg, 39%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>16</sup>

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

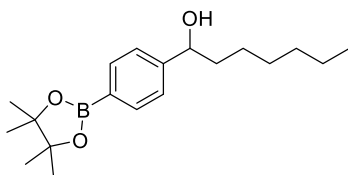


The reaction was conducted using 4-methoxybenzaldehyde (24.3  $\mu$ L, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11u** as a colorless oil (32.6 mg, 73%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>18</sup>

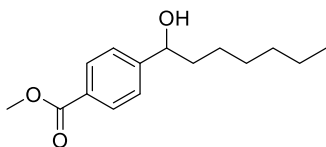
#### 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)heptan-1-ol (**11v**).



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%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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)  $\nu$  3389, 2925, 1641, 1361, 1089, 751  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{19}\text{H}_{31}\text{BO}_3\text{Na}$  341.2258; Found 341.2262.

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



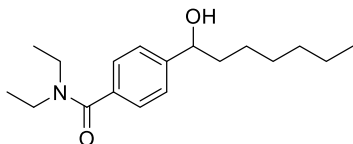
The reaction was conducted using methyl 4-formylbenzoate (32.8 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11w** as a colorless oil (23.2 mg, 46%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>19</sup>

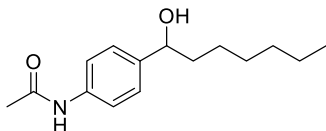
***N,N*-diethyl-4-(1-hydroxyheptyl)benzamide (11x).**



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

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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)  $\nu$  3397, 2930, 1610, 1508, 1430, 1288, 1097, 846  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{18}\text{H}_{29}\text{NO}_2\text{Na}$  314.2091; Found 314.2098.

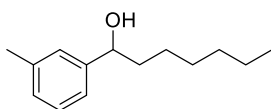
***N*-(4-(1-hydroxyheptyl)phenyl)acetamide (11y).**



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%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  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)  $\nu$  3312, 3126, 3065, 2952, 2927, 2855, 1669, 1604, 1541, 1460, 1411, 1369, 1318, 1269, 1093, 965, 836, 703  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  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).**



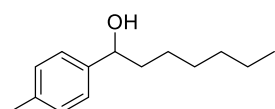
The reaction was conducted using 3-methylbenzaldehyde (23.6  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv) for 20 hours. The

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

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>16</sup>

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

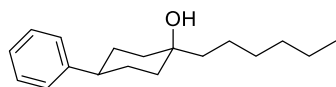


The reaction was conducted using 4-methylbenzaldehyde (23.6  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11aa** as a colorless oil (24.7 mg, 60%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>16</sup>

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

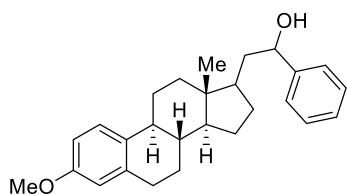


The reaction was conducted using 4-phenylcyclohexan-1-one (34.8 mg, 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11ad** as a colorless oil (12.8 mg, 26%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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)  $\nu$  3434, 2928, 2857, 1493, 1448, 1144, 755, 698  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{18}\text{H}_{28}\text{ONa}$  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**).



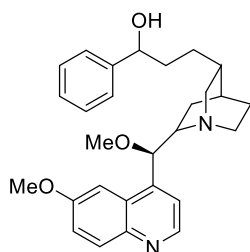


The reaction was conducted using (8*S*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-17-methylene-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene (91.2 mg, 0.26 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford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

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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<sup>-1</sup>; HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>34</sub>O<sub>2</sub>Na 413.2451; Found 413.2441.

Note: In the <sup>13</sup>C 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**).



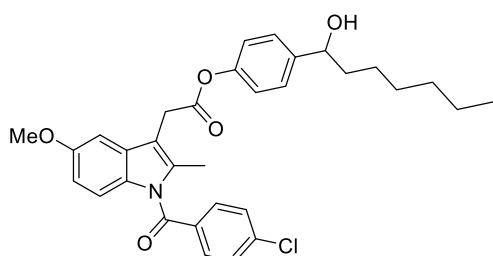
The reaction was conducted using (1*S*,4*S*,5*R*)-2-((*R*)-methoxy(6-methoxyquinolin-4-yl)methyl)-5-vinylquinuclidine (148.8 mg, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (DCM/MeOH) to afford **11ah** as a colorless oil (48.2 mg, 54%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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)  $\nu$  3385, 2926, 2860, 1618, 1508, 1456, 1097, 750  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_3$  447.2642; Found 447.2638.

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

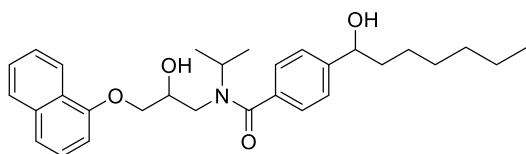
**(S)-4-(1-hydroxyheptyl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (11aj).**



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%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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)  $\nu$  3486, 3391, 2928, 2856, 1752, 1684, 1595, 1477, 1456, 1357, 1321, 1198, 1132, 1068, 1013, 930, 754  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  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).**



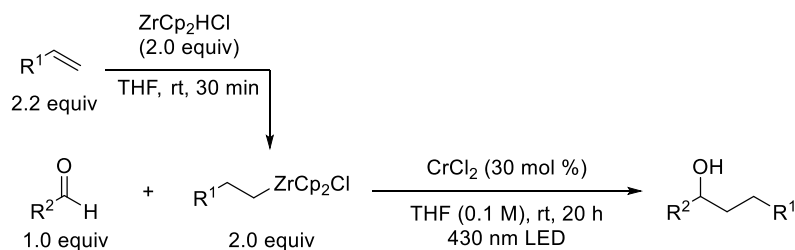
The reaction was conducted using 4-formyl-*N*-(2-hydroxy-3-(naphthalen-1-yloxy)propyl)-*N*-isopropylbenzamide (78.2 mg, 0.2 mmol, 1.0

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%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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)  $\nu$  3404, 2956, 2925, 2851, 1637, 1460, 1095, 956  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{30}\text{H}_{39}\text{NO}_4\text{Na}$  500.2771; Found 500.2768.

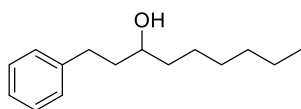
Note: In the  $^{13}\text{C}$  NMR spectra additional signals were observed. These correspond to the pseudoenantiomer forms of the product. In the  $^1\text{H}$  NMR spectra the signals could not be distinguished.

### 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  $\text{ZrCp}_2\text{HCl}$  (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,  $\text{CrCl}_2$  (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  $^\circ\text{C}$ ). After 20 hours, water was added and organic materials were extracted with  $\text{Et}_2\text{O}$  three times. The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , 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**).



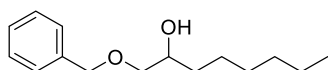
The reaction was conducted using 3-phenylpropanal (26.3  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv) for 20 hours. The crude

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

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  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.<sup>20</sup>

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

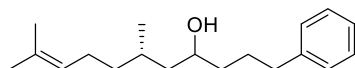


The reaction was conducted using 2-(benzyloxy)acetaldehyde (27.6  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11ac** as a colorless oil (23.8 mg, 50%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  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.<sup>21</sup>

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

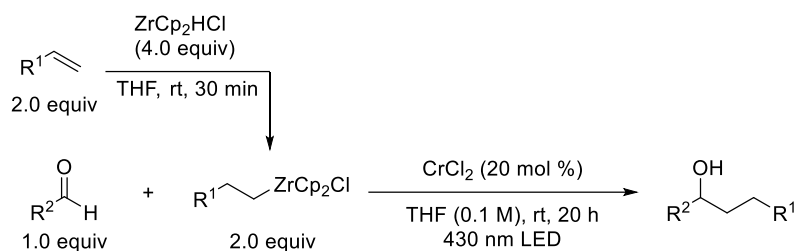


The reaction was conducted using (–)-citronellal (36.3  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11ai** as a colorless oil (24.8 mg, 45%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  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)  $\nu$  3409, 2924, 2860, 1654, 1450, 1377, 1092, 748, 698  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{19}\text{H}_{30}\text{ONa}$  297.2189; Found 297.2176.

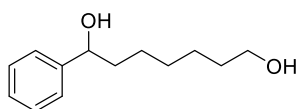
Note: In the  $^{13}\text{C}$  NMR spectra additional signals were observed. These correspond to the pseudoenantiomer forms of the product. In the  $^1\text{H}$  NMR spectra the signals could not be distinguished.

#### 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  $\text{ZrCp}_2\text{HCl}$  (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,  $\text{CrCl}_2$  (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  $\text{Et}_2\text{O}$  three times. The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , 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**).

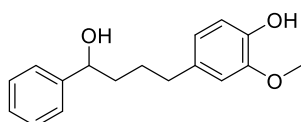


The reaction was conducted using hex-5-en-1-ol (47.1  $\mu\text{L}$ , 0.4 mmol, 2.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/ $\text{EtOAc}$ ) to afford **11l** as a colorless oil (20.9 mg, 51%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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.<sup>22</sup>

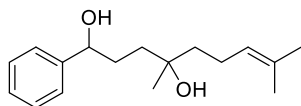
#### 4-(4-hydroxy-4-phenylbutyl)-2-methoxyphenol (**11ae**).



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

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  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)  $\nu$  3406, 2936, 1603, 1514, 1452, 1270, 1152, 1121, 1032, 701  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{20}\text{O}_3\text{Na}$  295.1305; Found 295.1319.

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

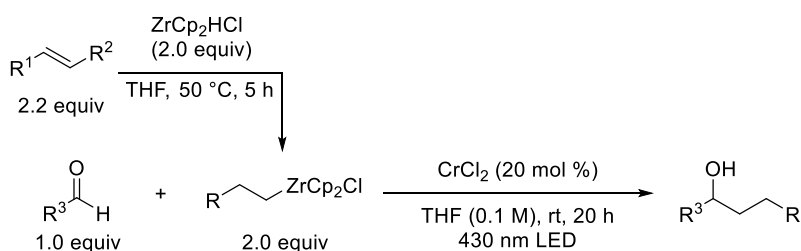


The reaction was conducted using linalool (71.7  $\mu\text{L}$ , 0.4 mmol, 2.0 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11af** as a colorless oil (29.4 mg, 56%, dr mixture).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  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)  $\nu$  3356, 3028, 2965, 2925, 2856, 1647, 1452, 1375, 1057, 914, 700  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{26}\text{O}_2\text{Na}$  285.1825; Found 285.1834.

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

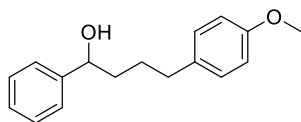
#### Procedure for preparation of **11a**, **11o** with chain walking strategy



Under an argon atmosphere, alkene (0.44 mmol, 2.2 equiv) was added to a solution of  $\text{ZrCp}_2\text{HCl}$  (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,  $\text{CrCl}_2$  (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  $^{\circ}\text{C}$ ). After 20 hours, water was added and

organic materials were extracted with Et<sub>2</sub>O three times. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, 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**).

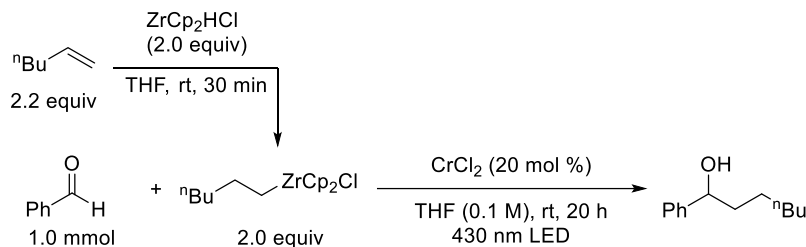


The reaction was conducted using anethole (65.9  $\mu$ L, 0.44 mmol, 2.2 equiv) for 20 hours. The crude material was purified by silica gel flash column chromatography (hexane/EtOAc) to afford **11o** as a colorless oil (31.1 mg, 61%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  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); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  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.<sup>23</sup>

#### 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<sub>2</sub>HCl (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<sub>2</sub> (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<sub>2</sub>O three times. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, 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%).

## Control Experiments

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

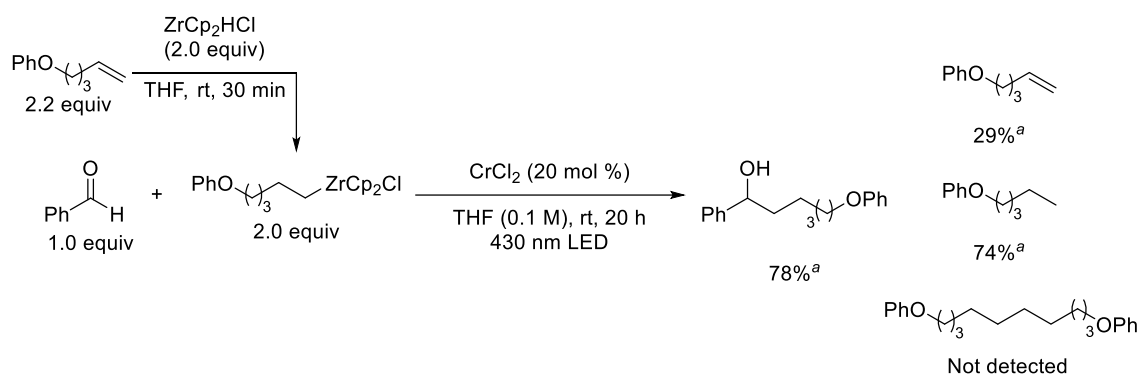
entry	CrCl <sub>2</sub> (mol %)	yield (%) <sup>a</sup>
1	10	26
2	20	75
3	30	82
4	100	82

**Total 98% benzaldehyde was consumed.**



<sup>a</sup>Yield was determined by <sup>1</sup>H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

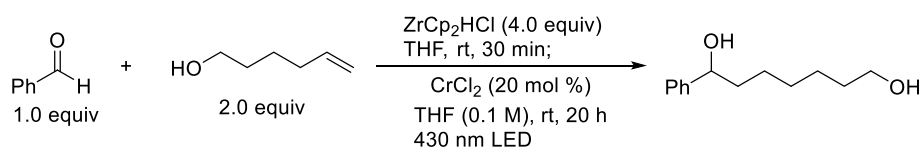
### Mass balance of alkene



**Total 91% alkene was consumed.**

<sup>a</sup>Yield was determined by <sup>1</sup>H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

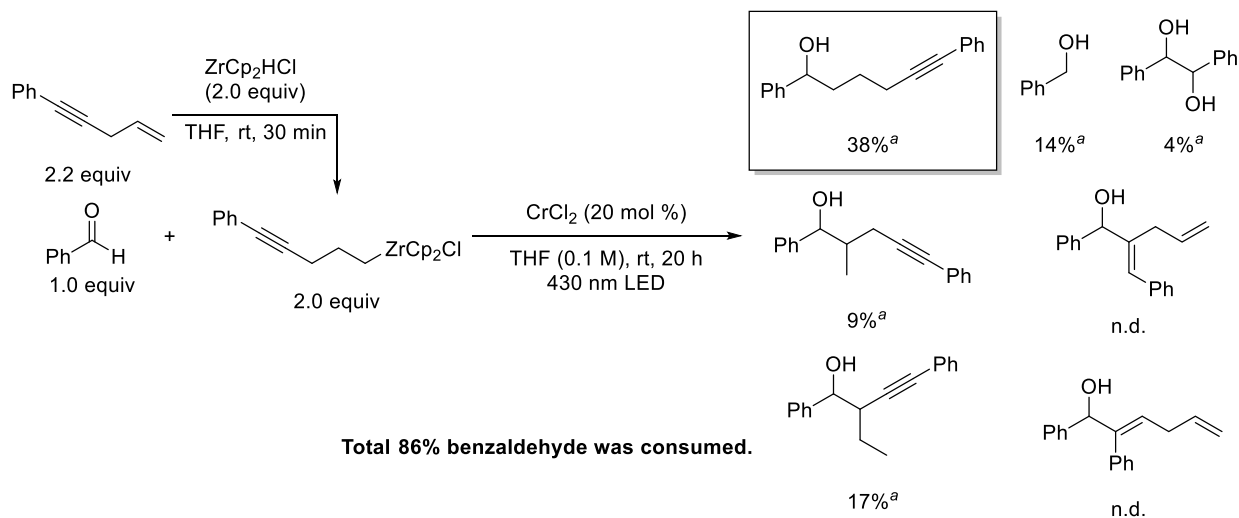
### Comparison with Precedents



entry	deviation from above	yield (%) <sup>a</sup>
1	none	56
2	ZnBr <sub>2</sub> instead of CrCl <sub>2</sub> and 430 nm LED <sup>25</sup>	n.d.
3	AgClO <sub>4</sub> instead of CrCl <sub>2</sub> and 430 nm LED <sup>26</sup>	44

<sup>a</sup>Yield was determined by <sup>1</sup>H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

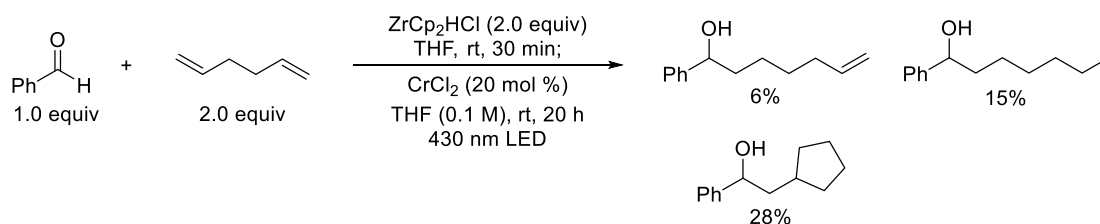
### Chemoselectivity of 11n



**Total 86% benzaldehyde was consumed.**

<sup>a</sup>Yield was determined by <sup>1</sup>H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

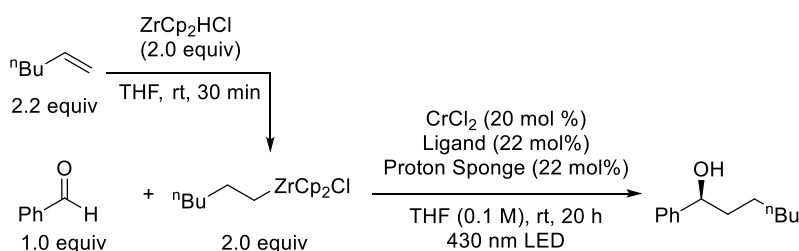
## Mechanism Experiments



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

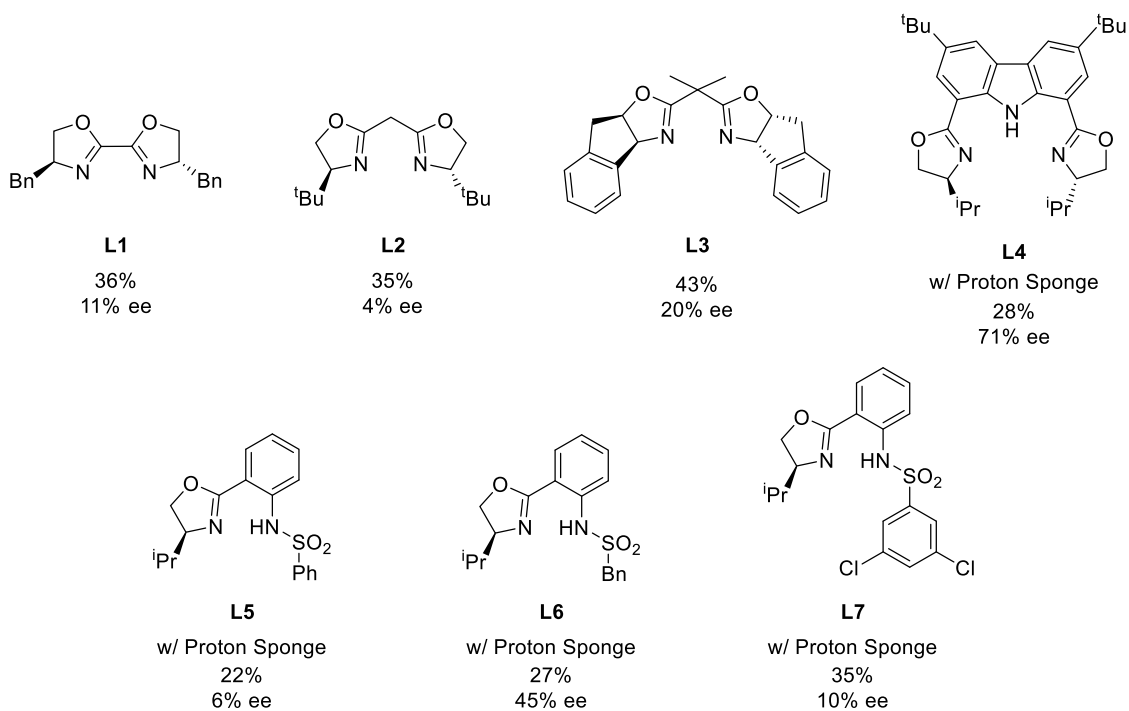
## 5. Catalytic Asymmetric Alkylation of Aldehydes

### Procedure for Catalytic Alkylation Reaction



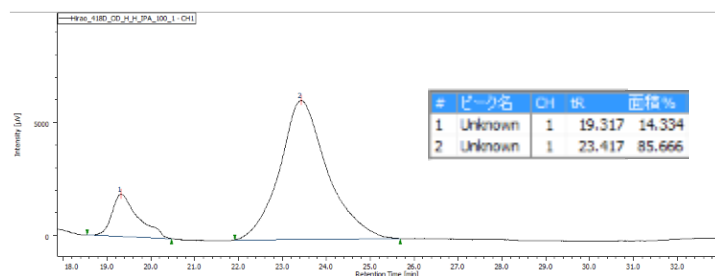
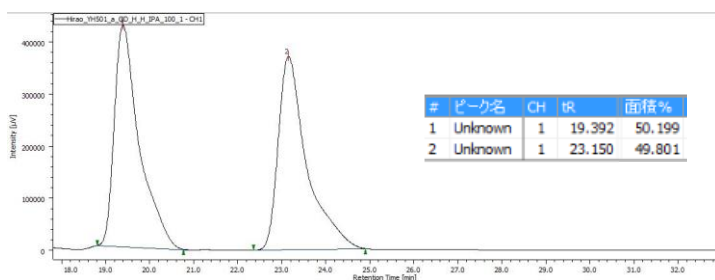
Under an argon atmosphere, alkene (0.22 mmol, 2.2 equiv) was added to a solution of  $\text{ZrCp}_2\text{HCl}$  (51.5 mg, 0.20 mmol, 2.0 equiv) in degassed THF (0.5 mL) in a screw-capped vial, and the mixture was stirred for 30 min at room temperature until a clear yellow solution was obtained. In another screw-capped vial,  $\text{CrCl}_2$  (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  $\text{Et}_2\text{O}$  three times. The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The yield was determined by <sup>1</sup>H 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% ee<sup>27</sup>



## 6. References

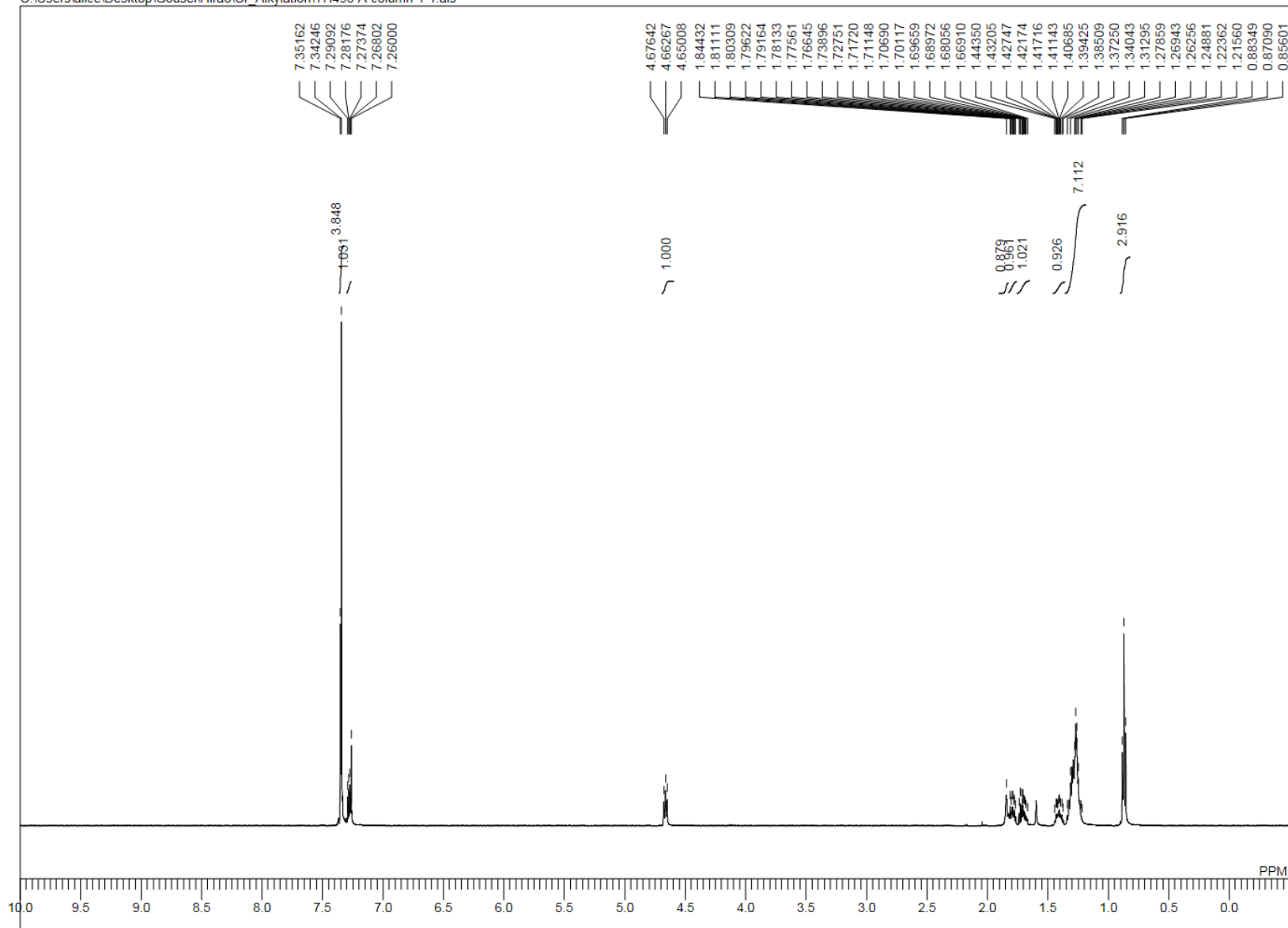
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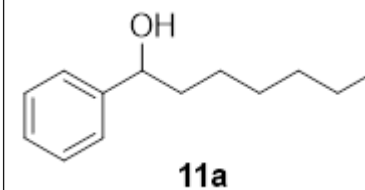
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$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

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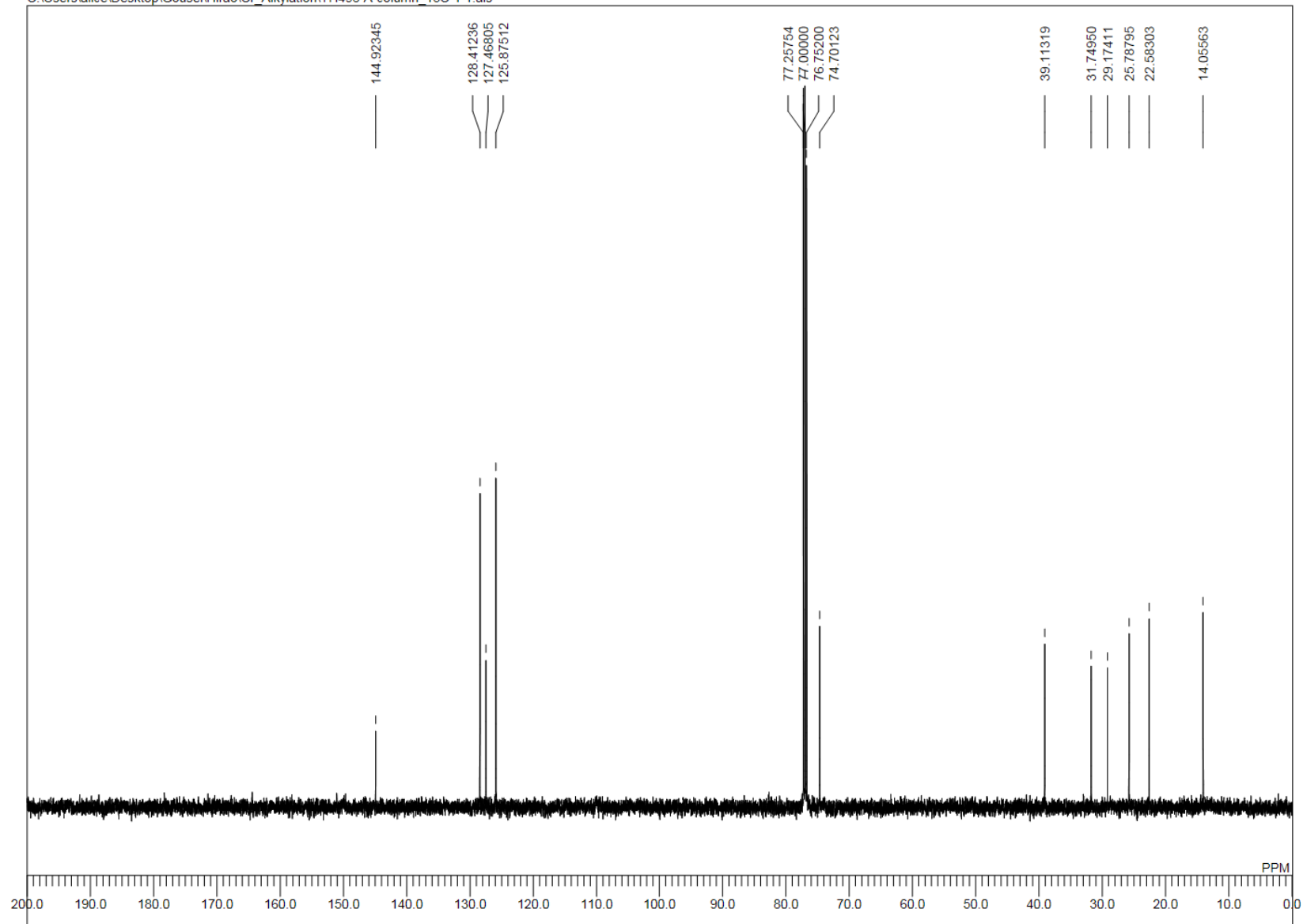


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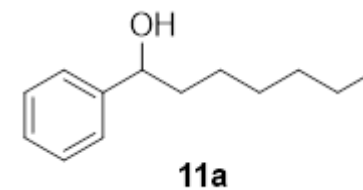


$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

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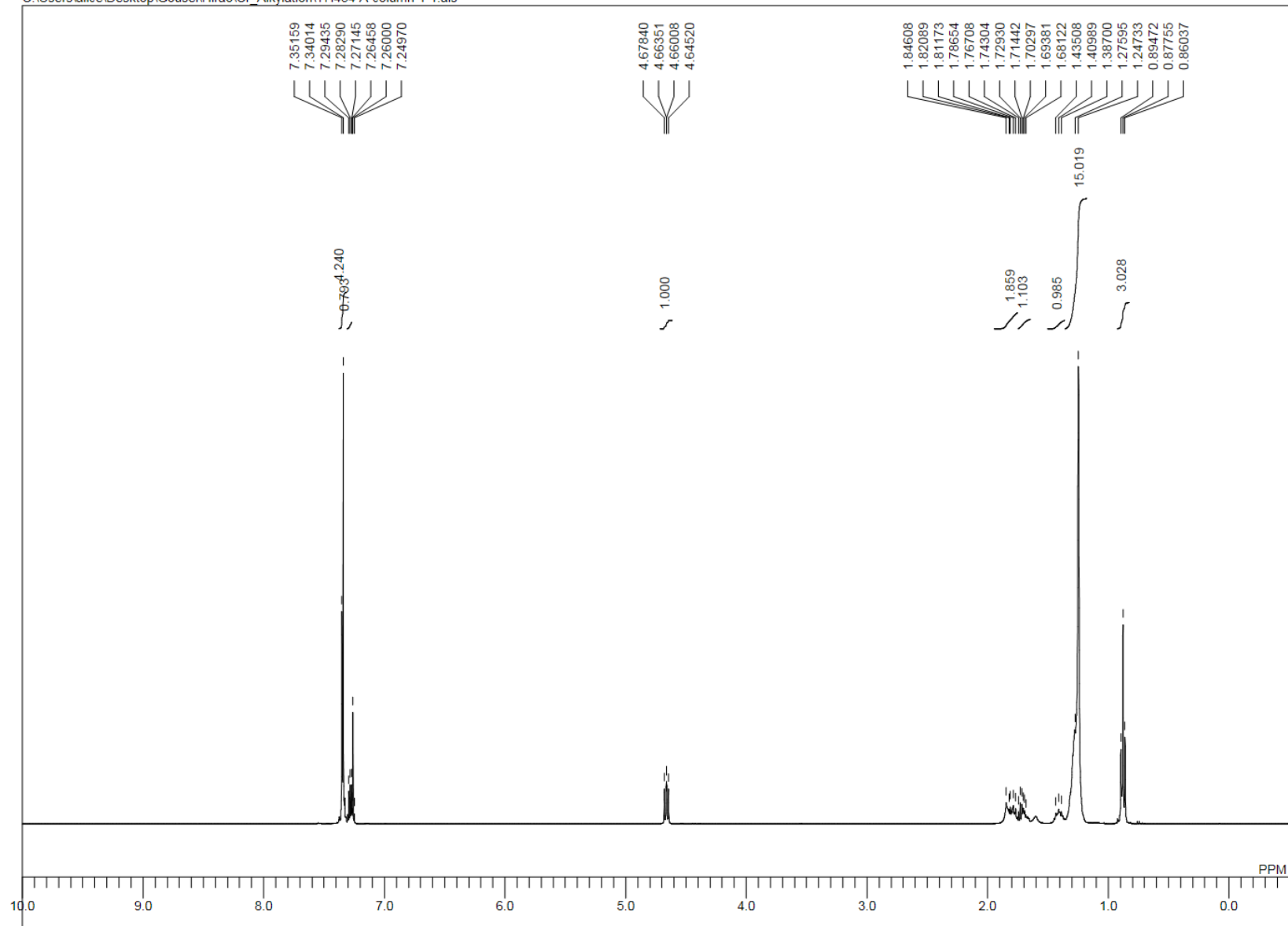


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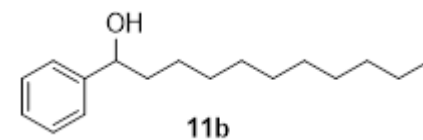


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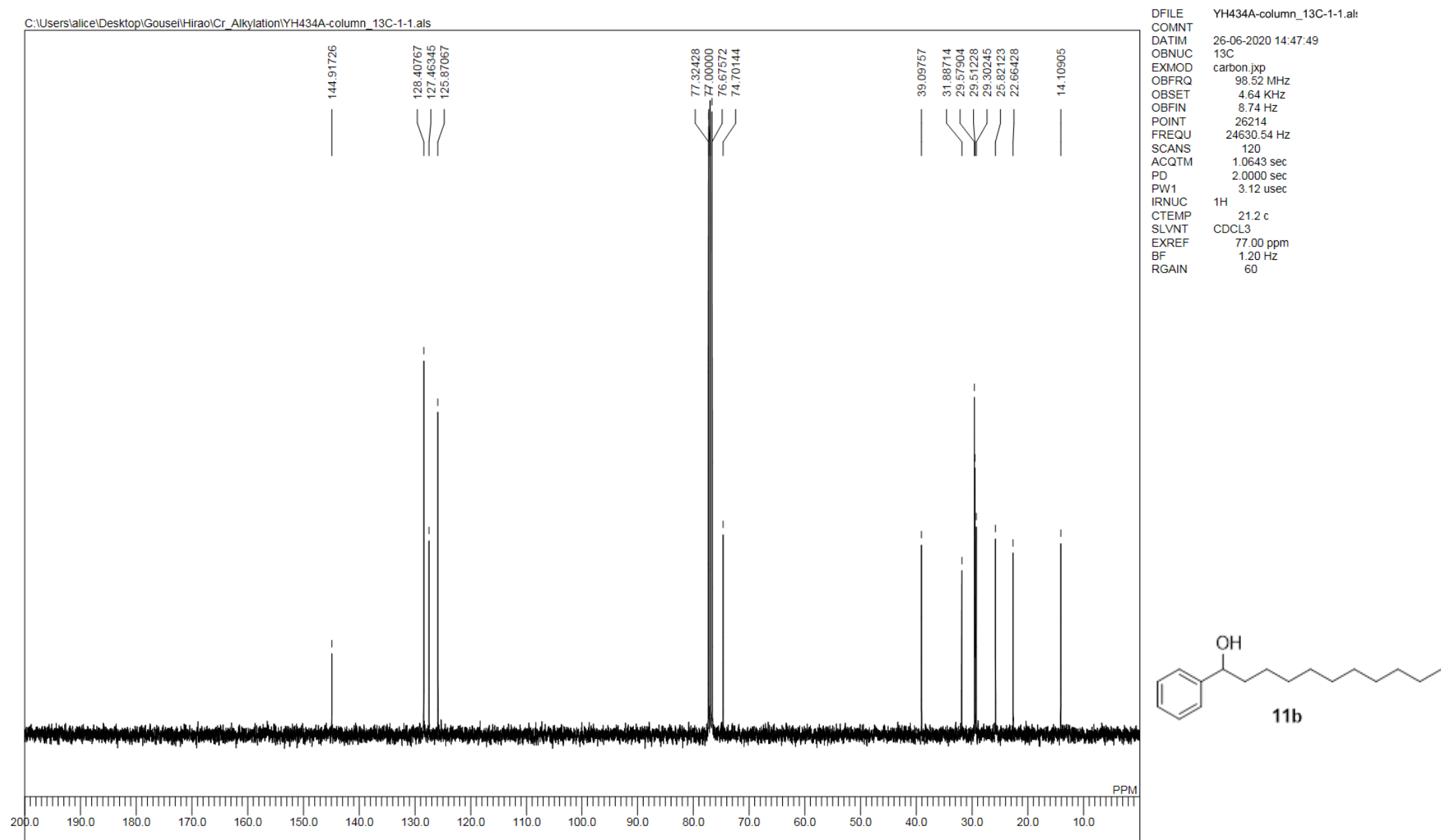


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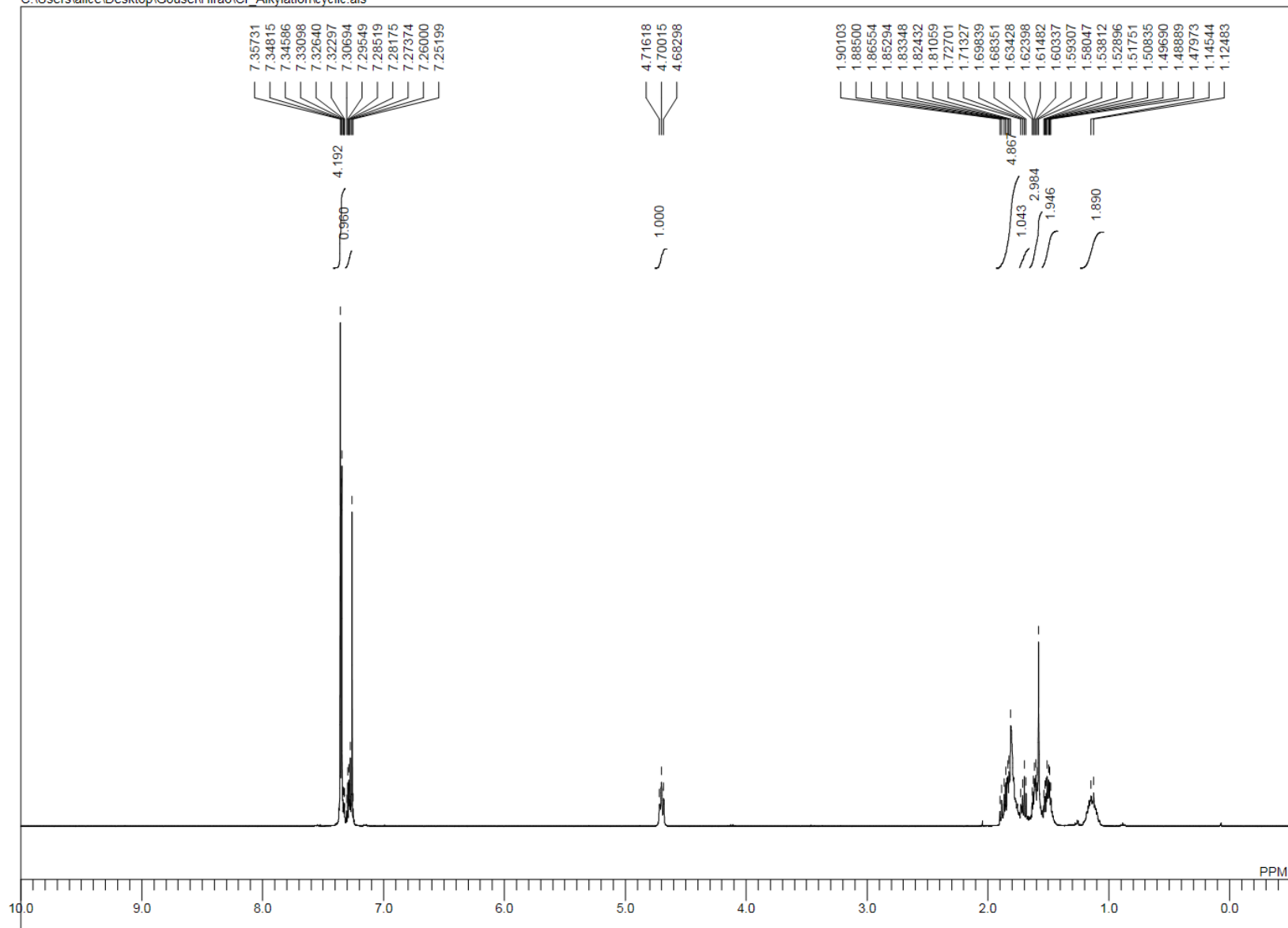


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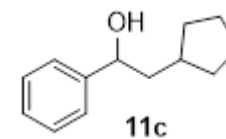


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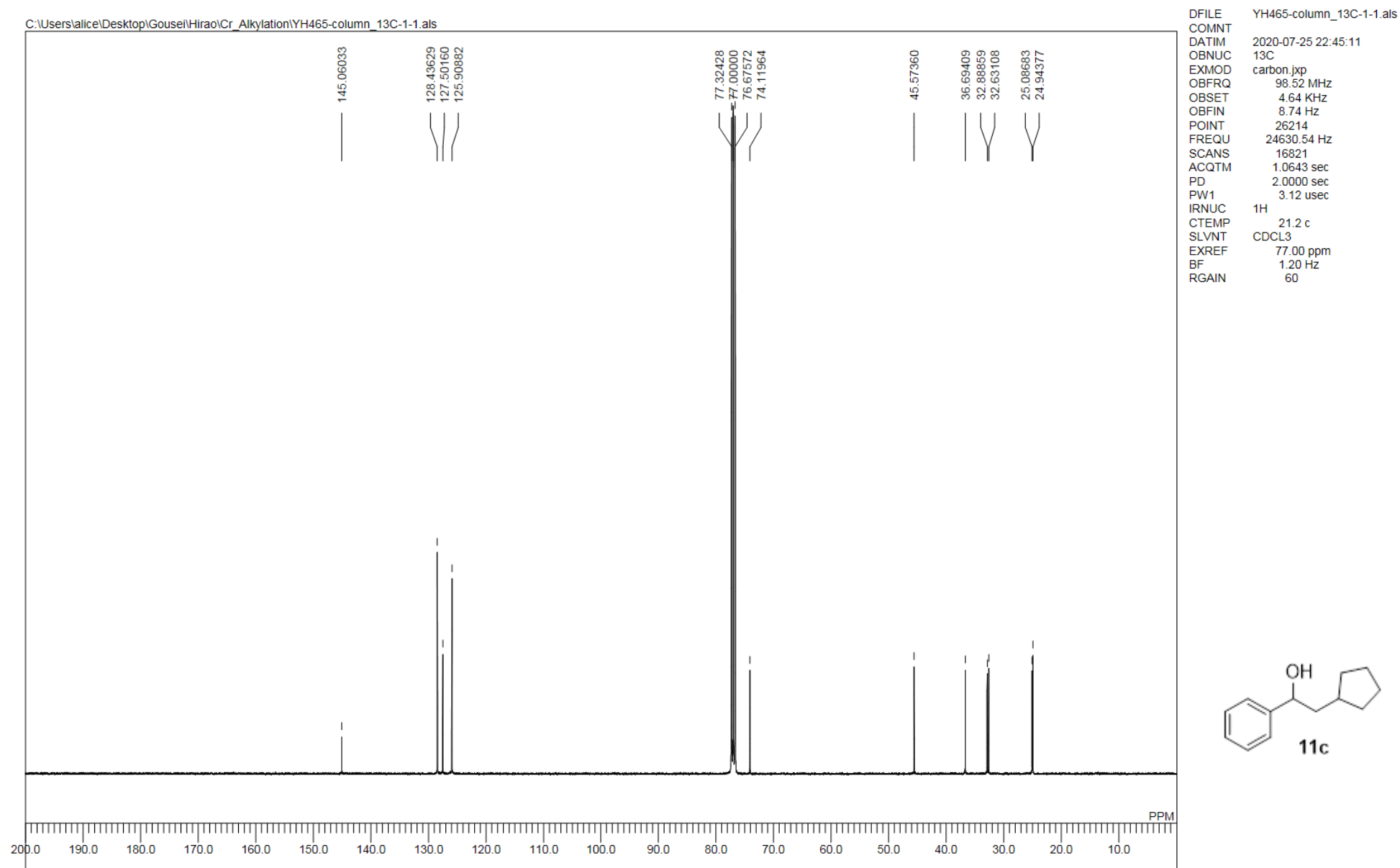
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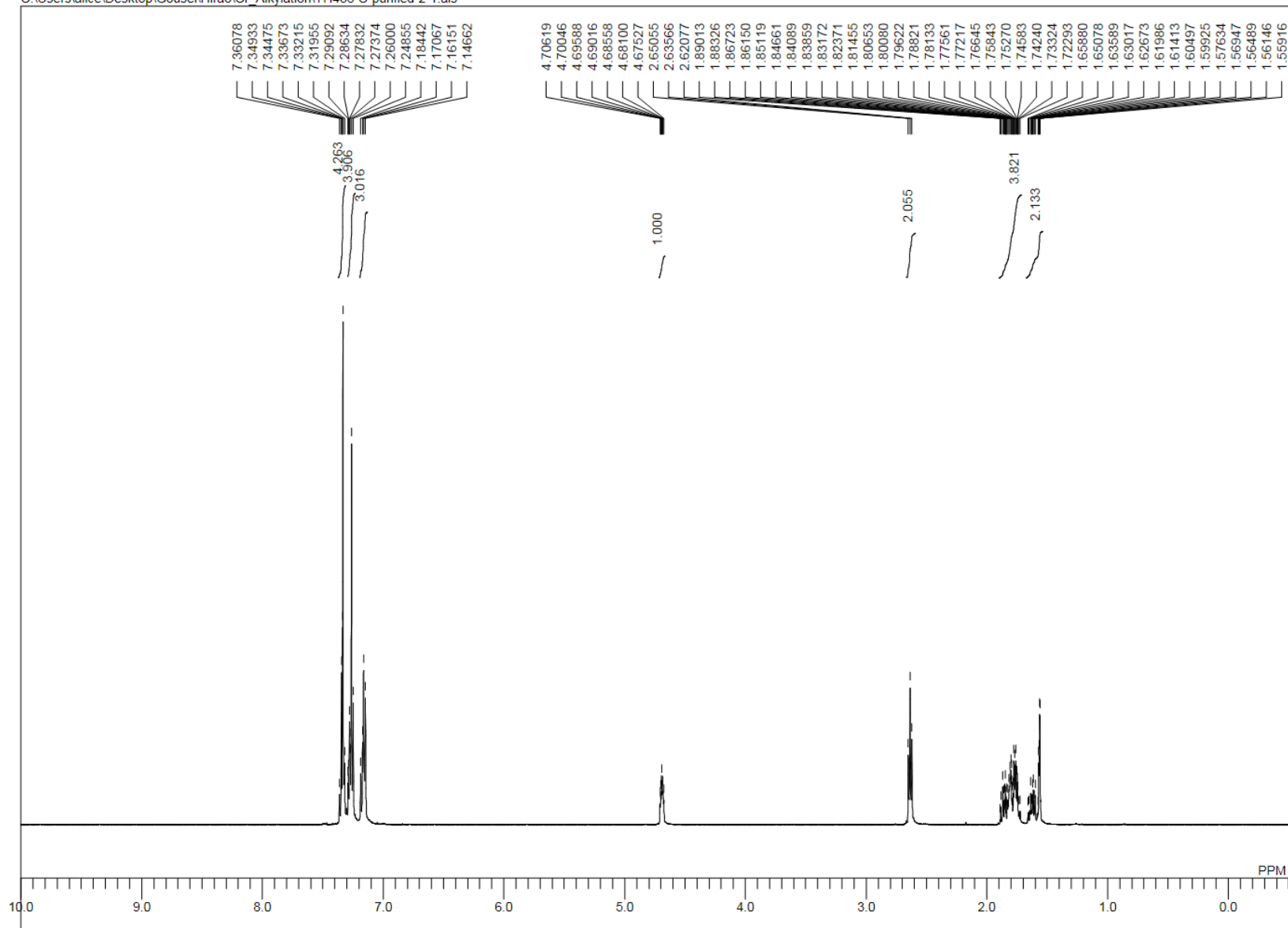


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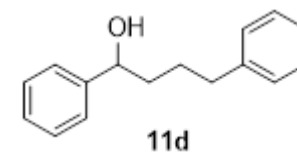


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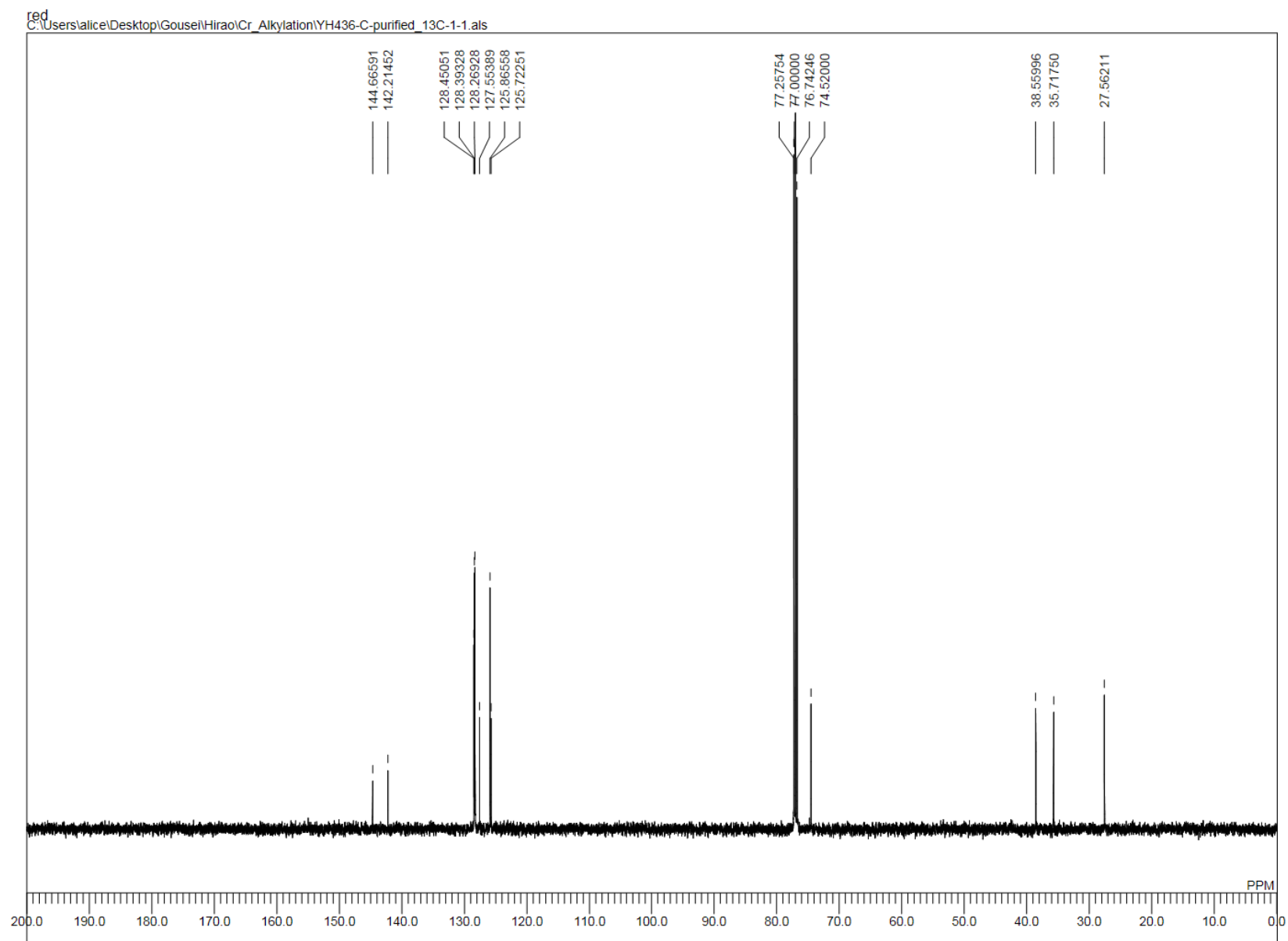
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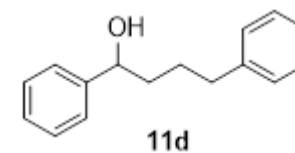
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<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

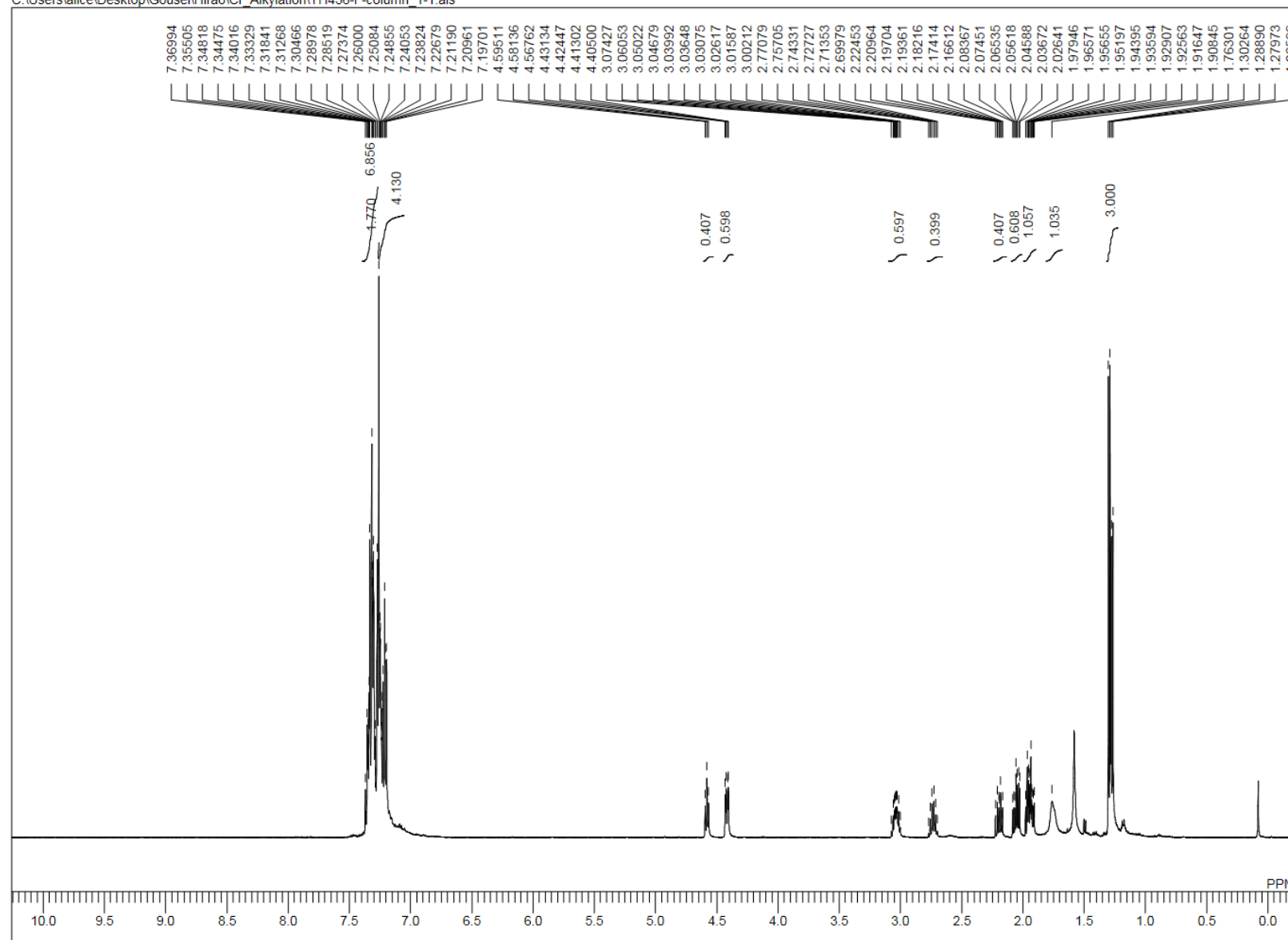


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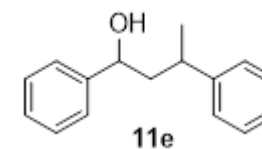


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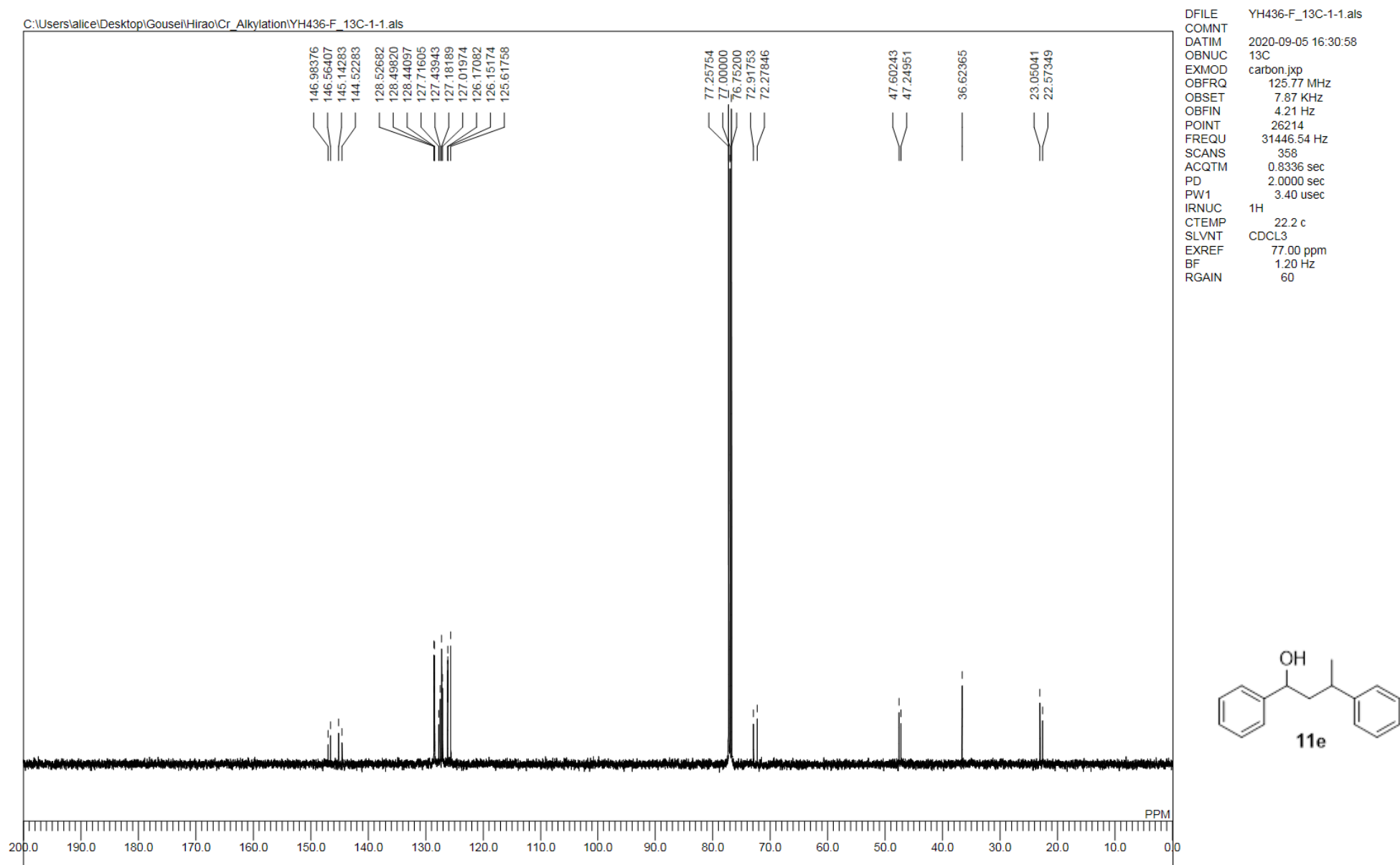
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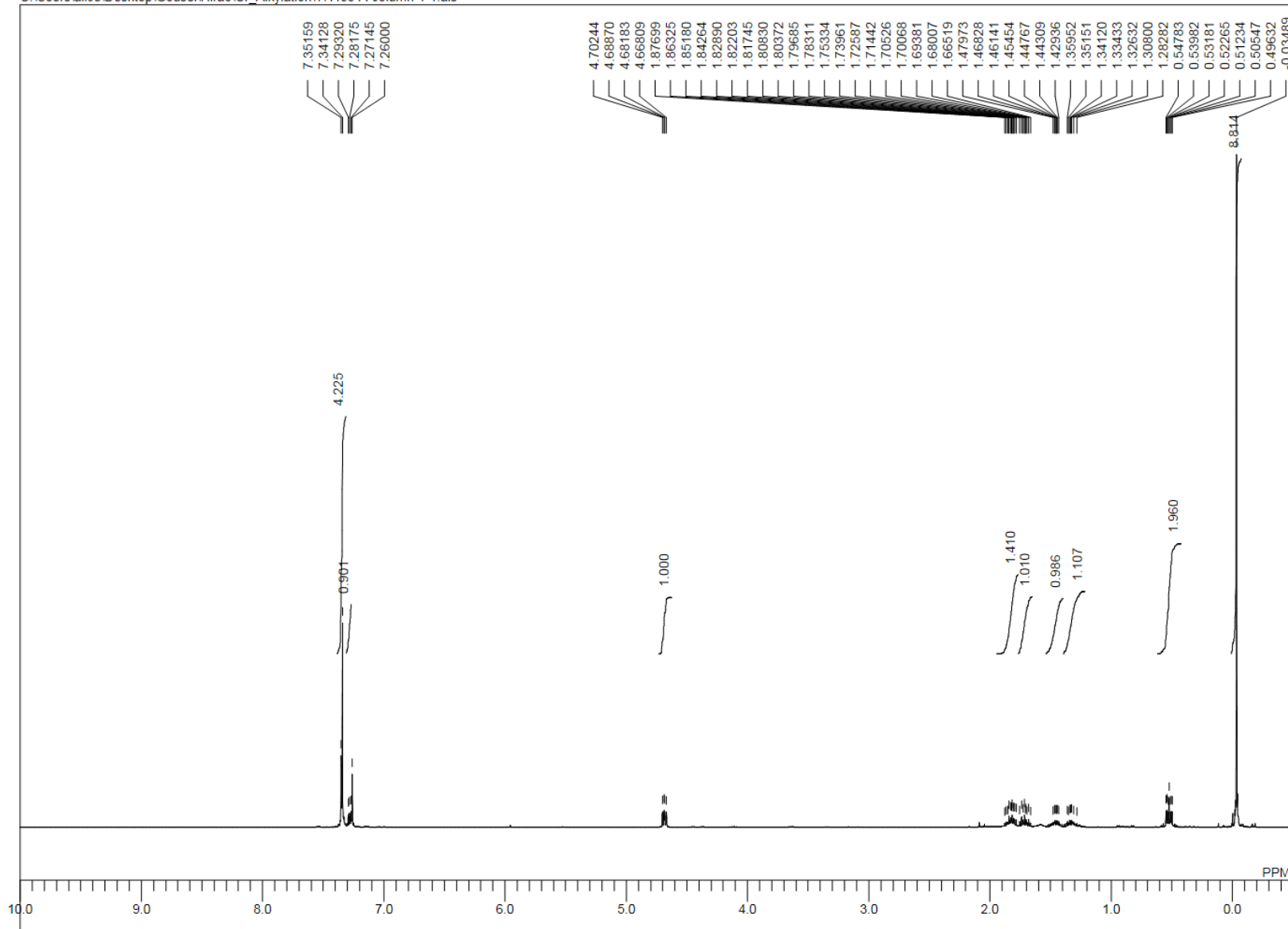


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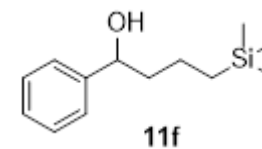


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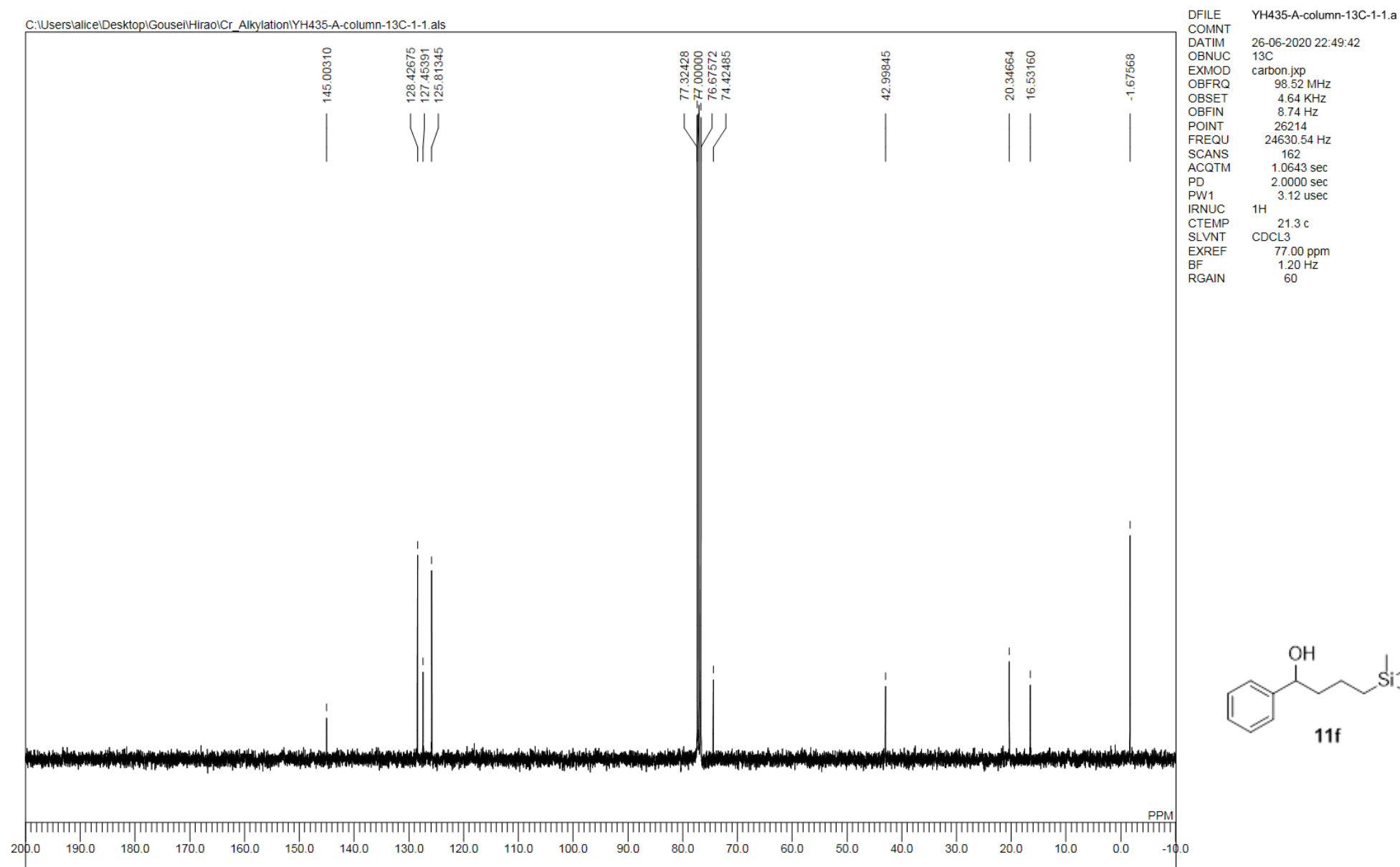


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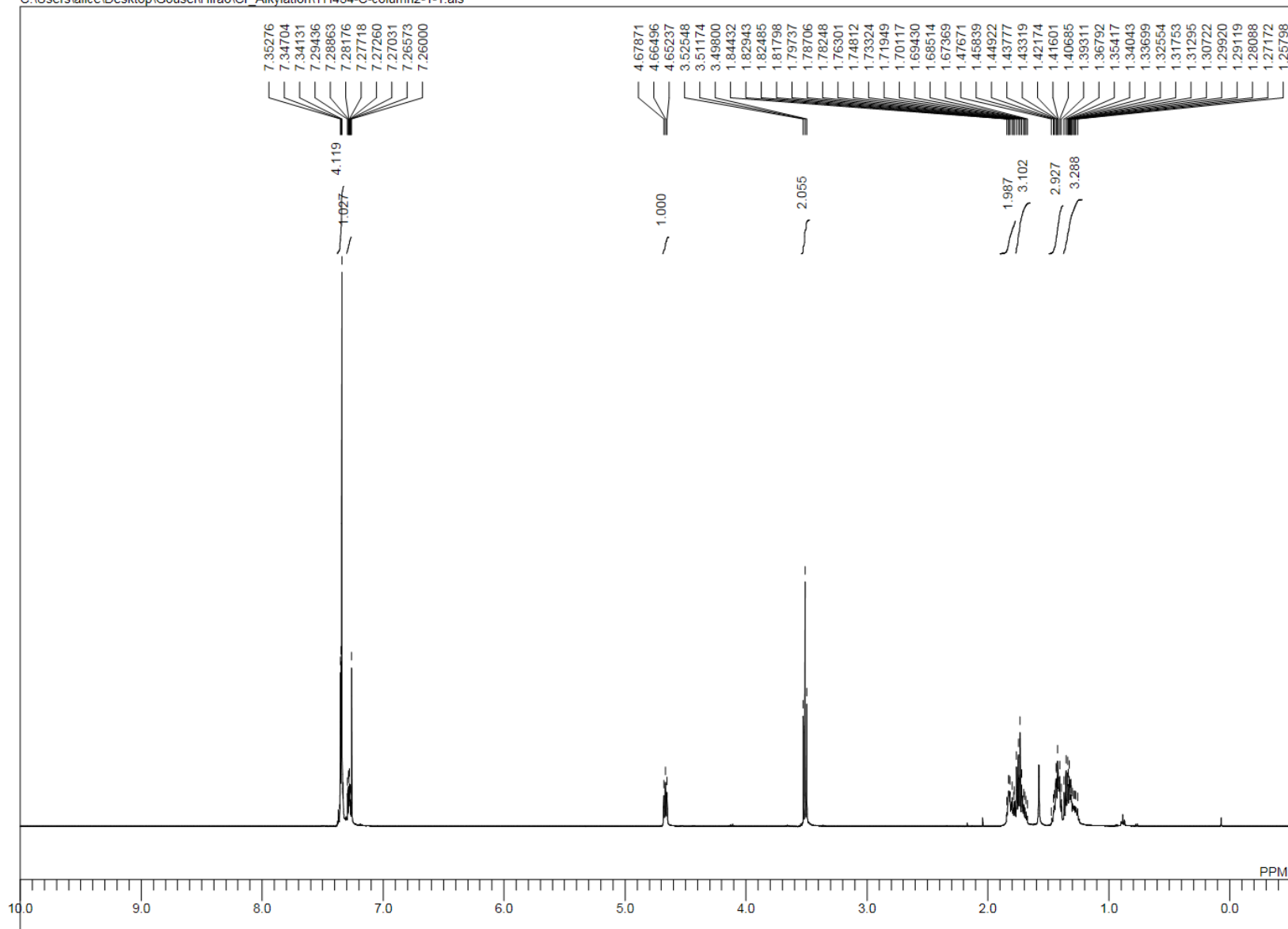


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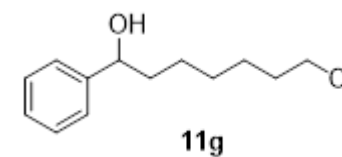


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

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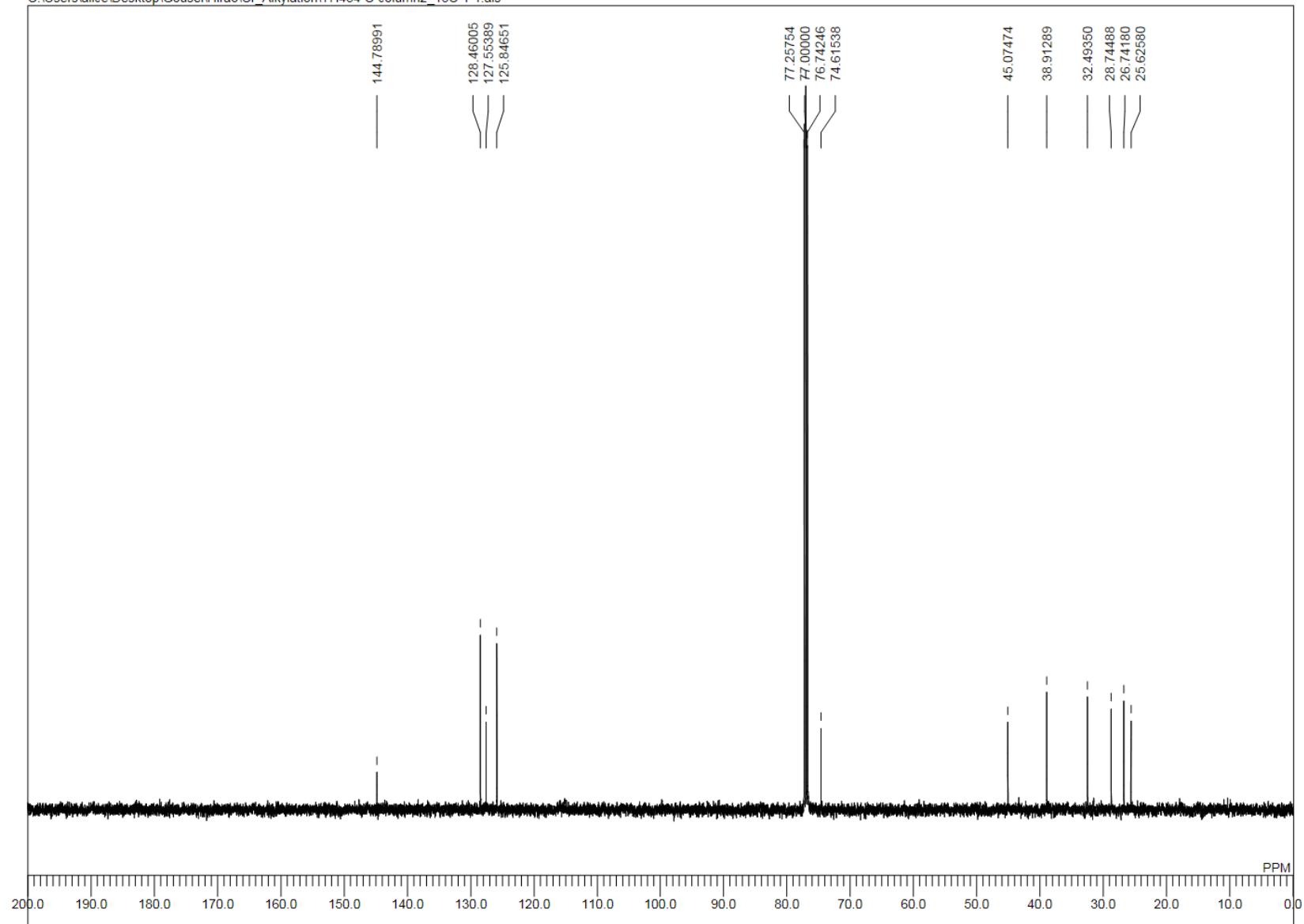


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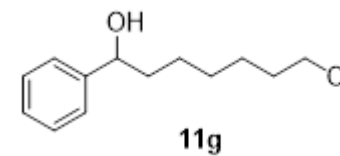


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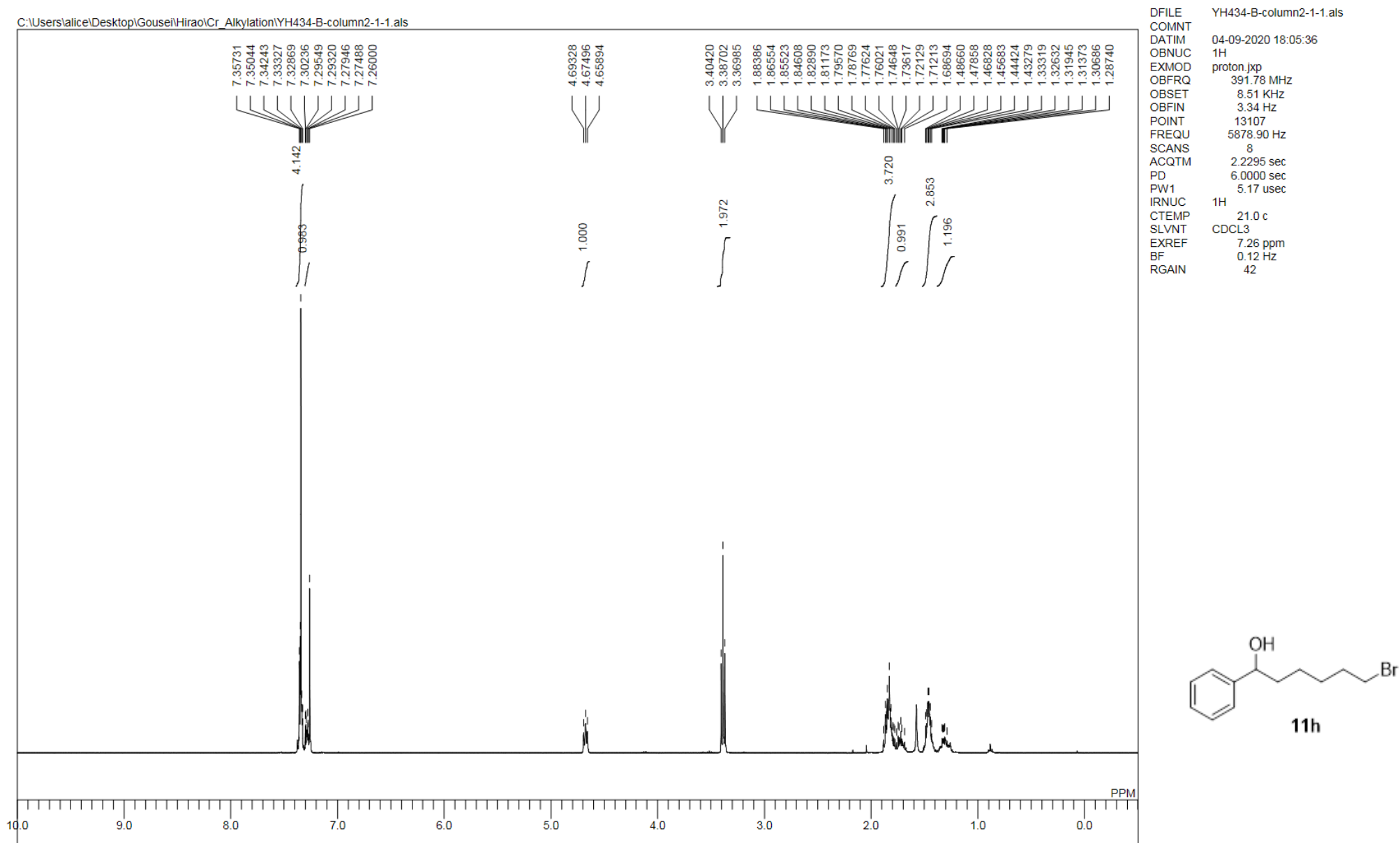
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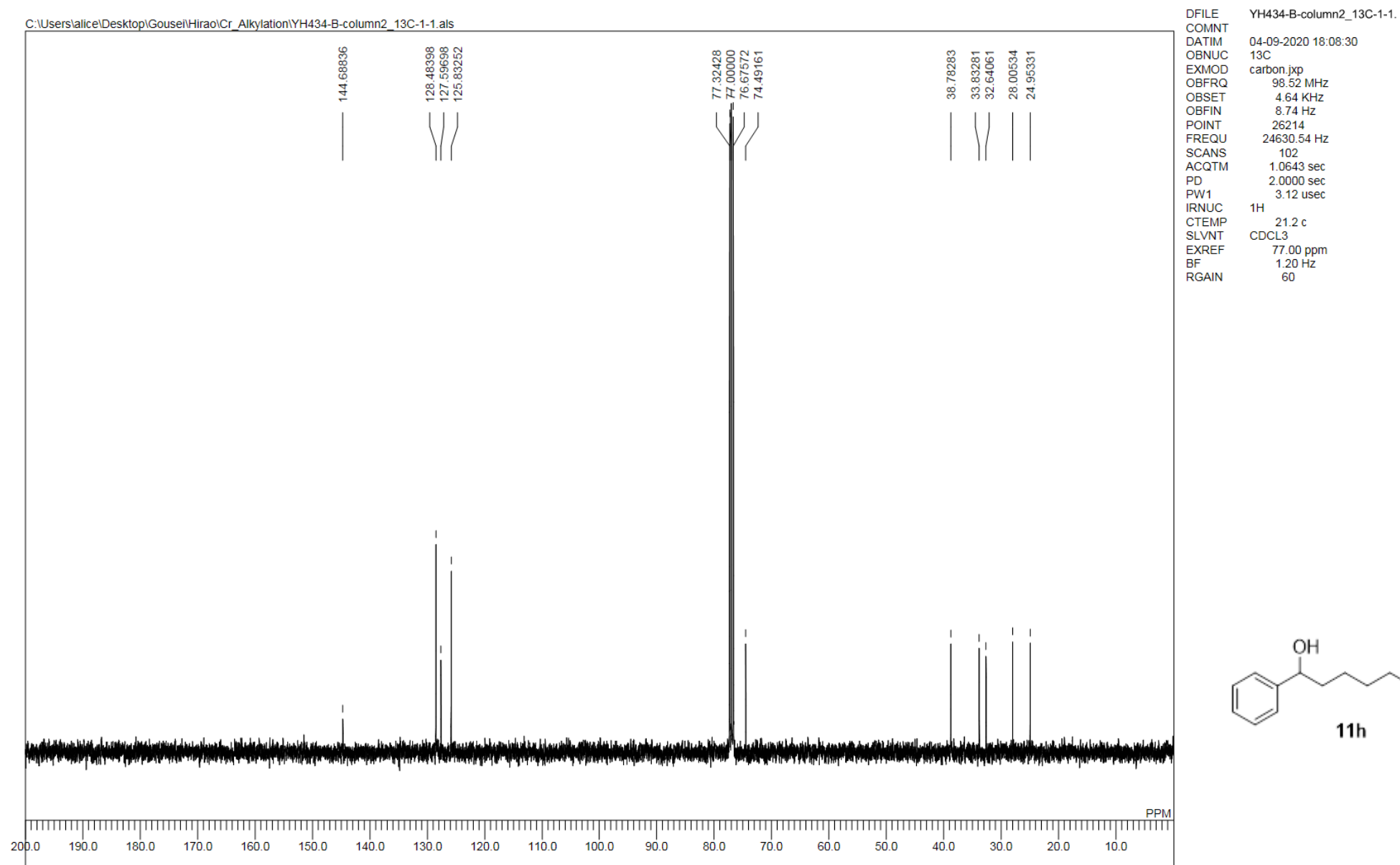
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CTEMP 22.4 c  
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RGAIN 60



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

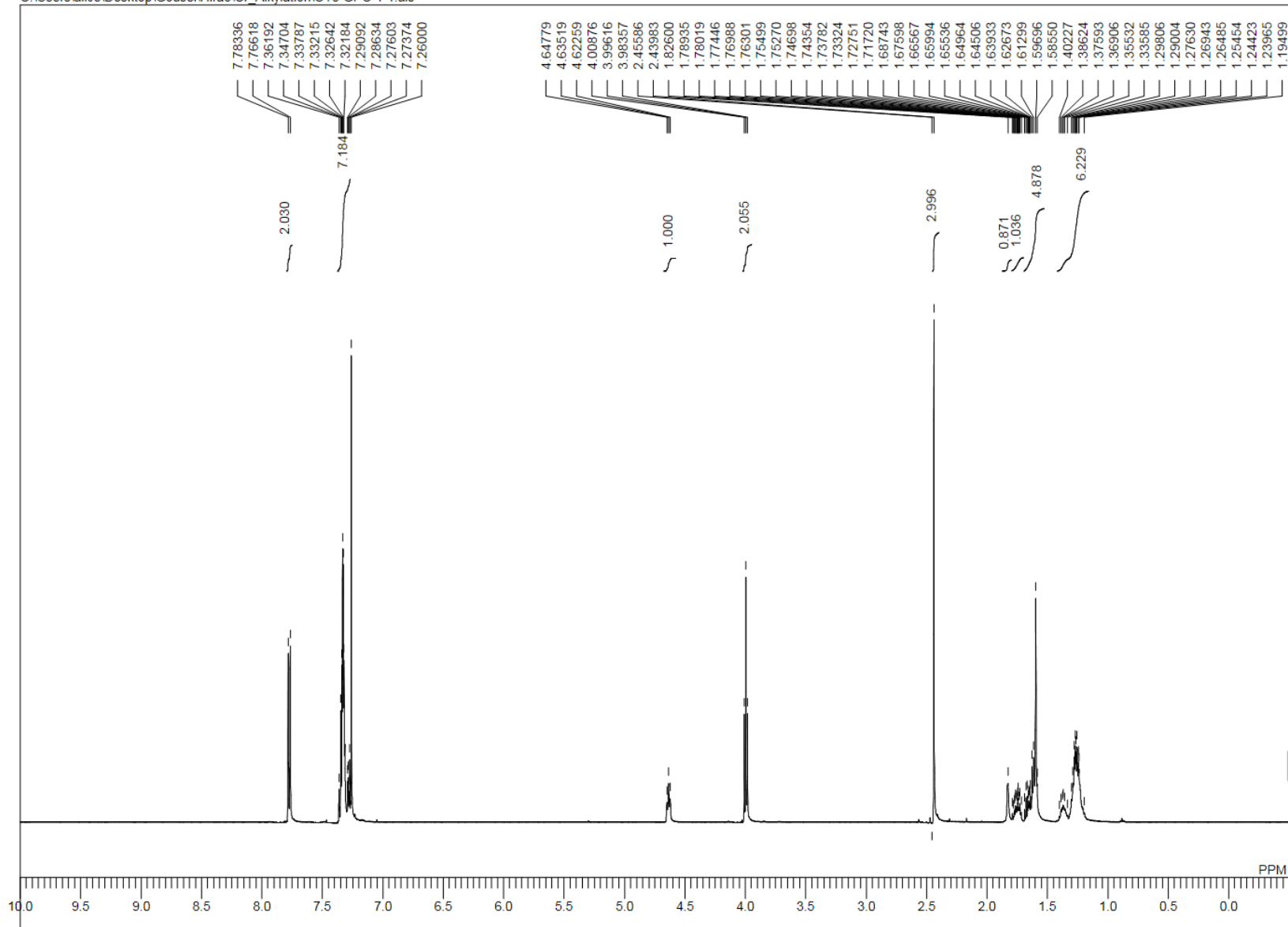


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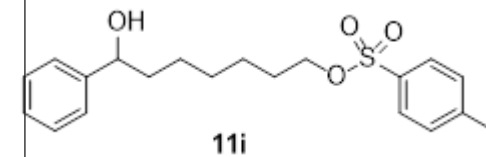


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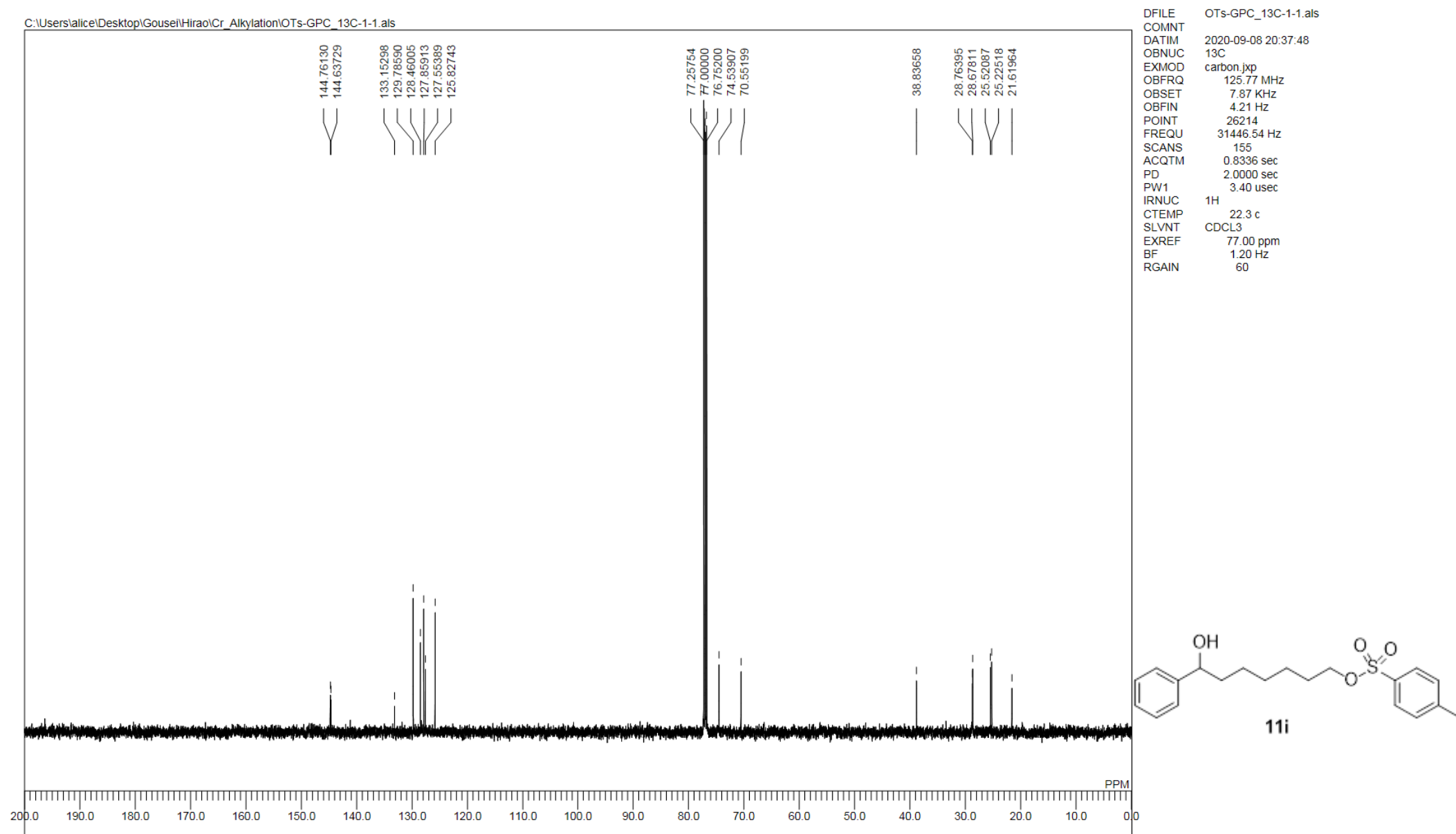
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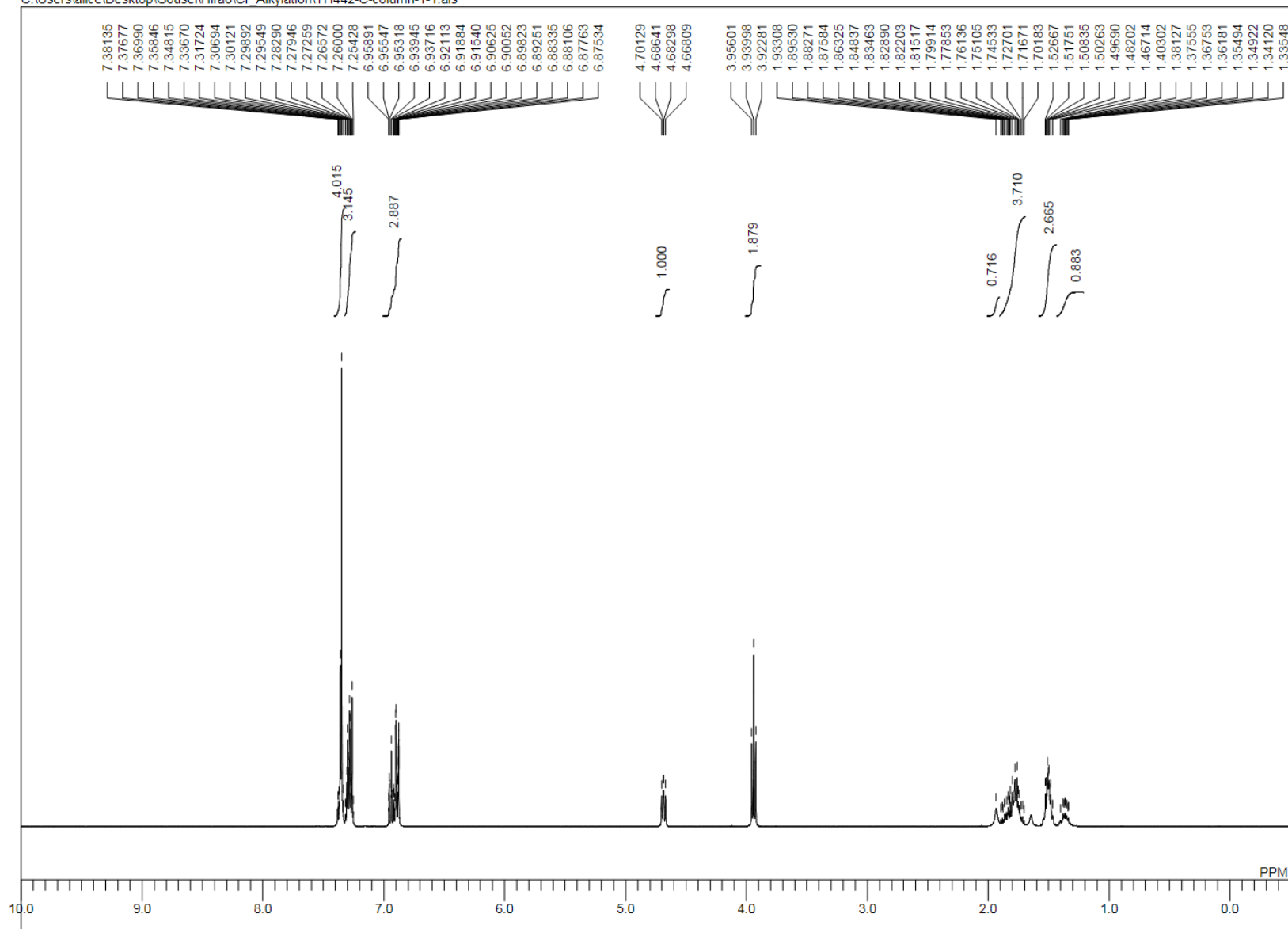


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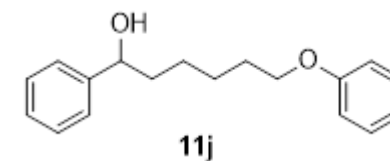


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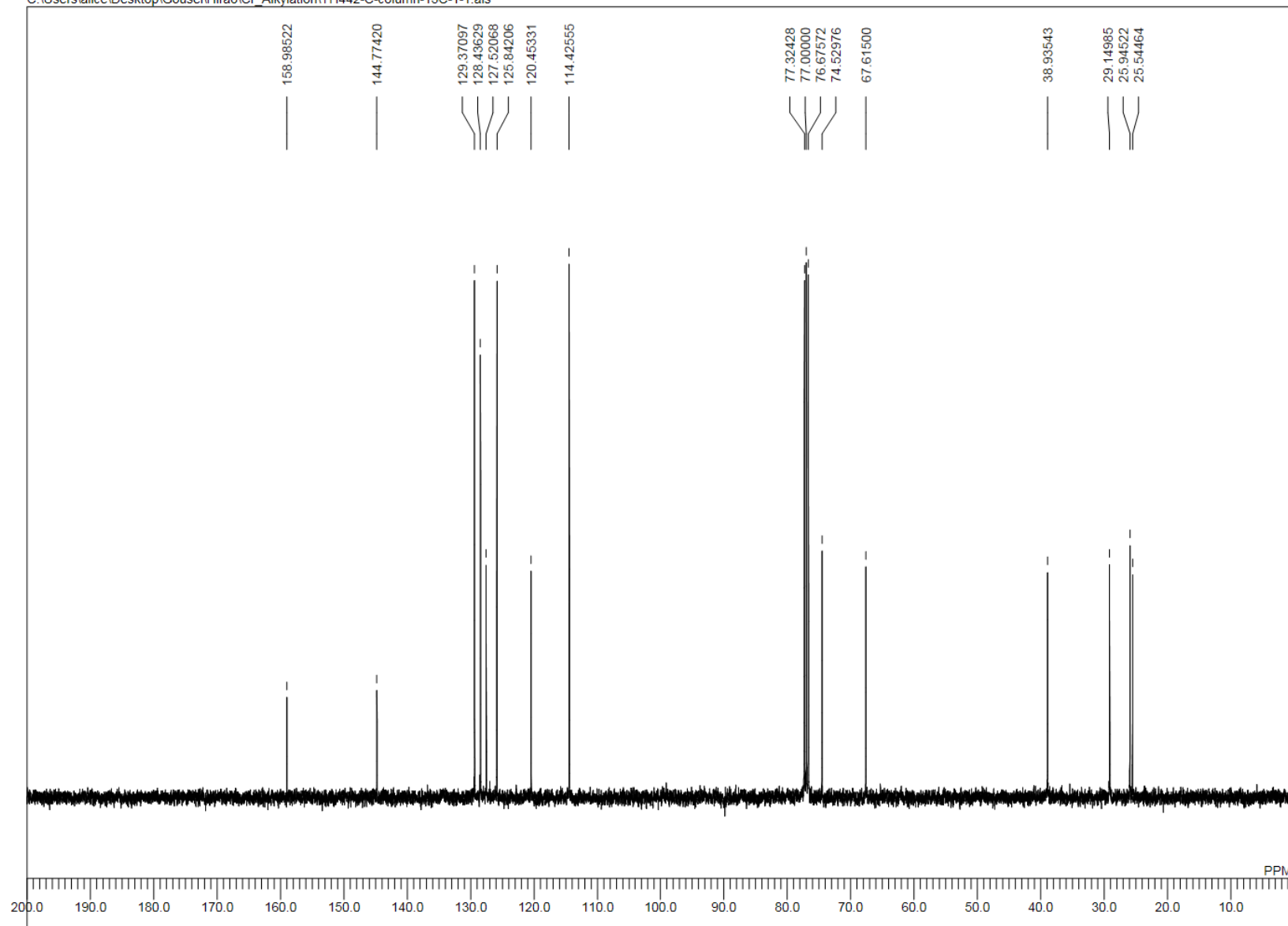
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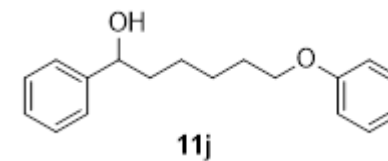


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH442-C-column-13C-1-1.als

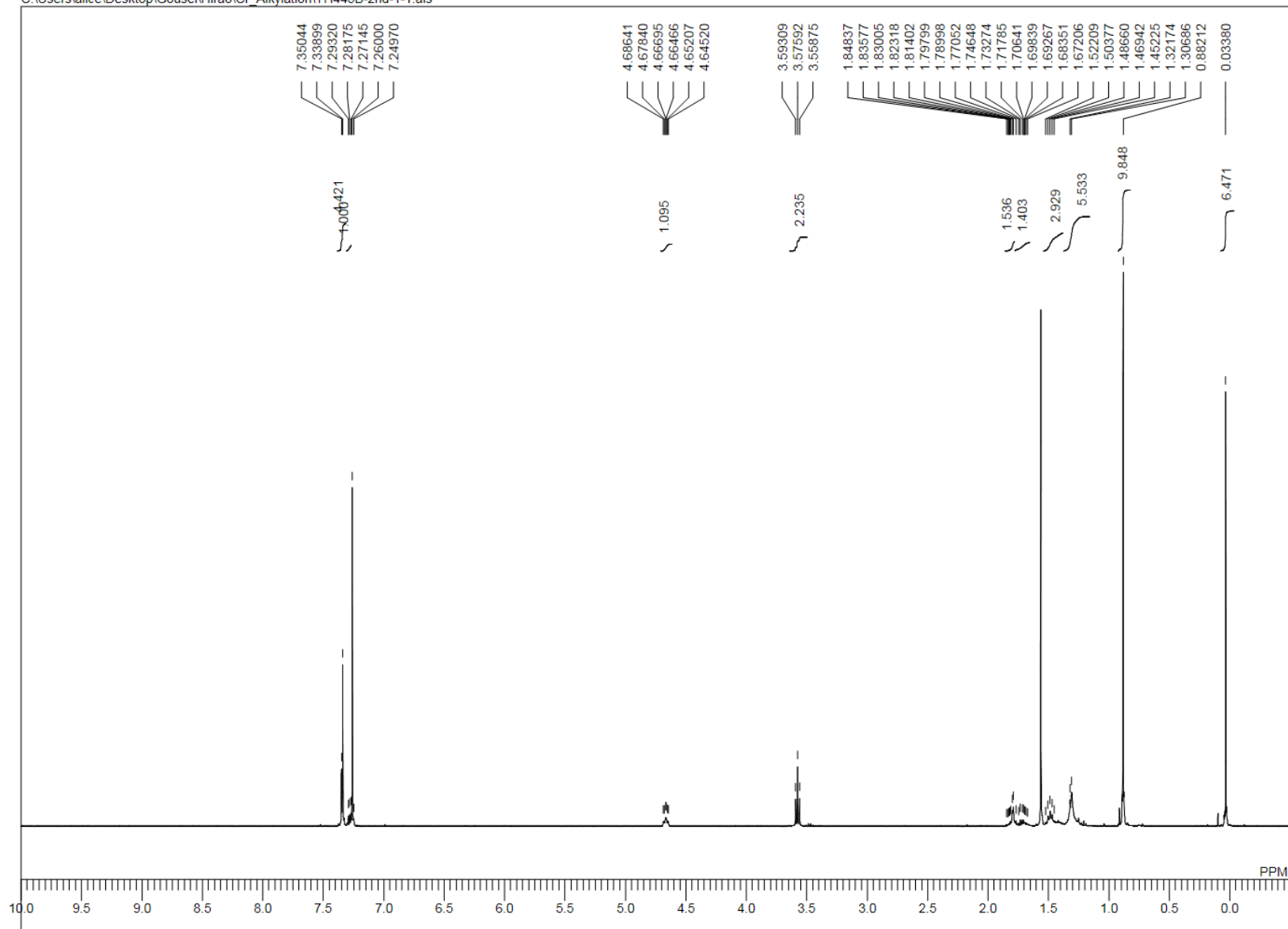


DFILE YH442-C-column-13C-1-1.als  
COMNT  
DATIM 04-07-2020 21:49:46  
OBNUC 13C  
EXMOD carbon.jpg  
OBFRQ 98.52 MHz  
OBSET 4.64 KHz  
OBFIN 8.74 Hz  
POINT 26214  
FREQU 24630.54 Hz  
SCANS 102  
ACQTM 1.0643 sec  
PD 2.0000 sec  
PW1 3.12 usec  
IRNUC 1H  
CTEMP 21.2 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 60

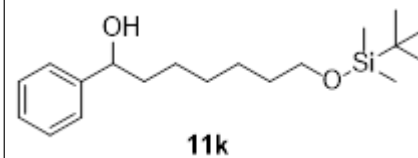


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

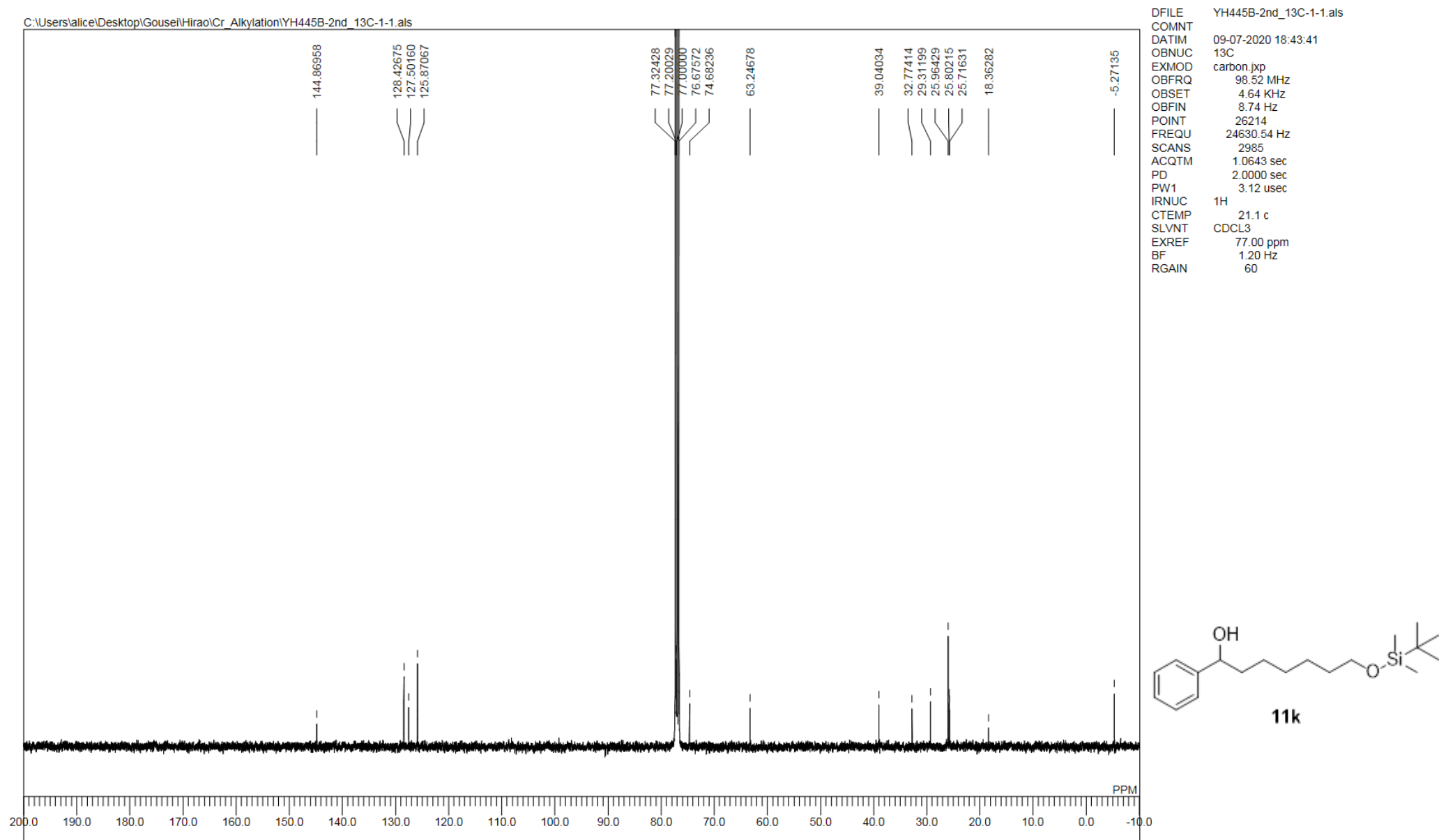
C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH445B-2nd-1-1.als



DFILE YH445B-2nd-1-1.als  
 COMNT  
 DATIM 09-07-2020 18:40:12  
 OBNUC 1H  
 EXMOD proton.jpg  
 OBFRQ 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 21.0 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 50

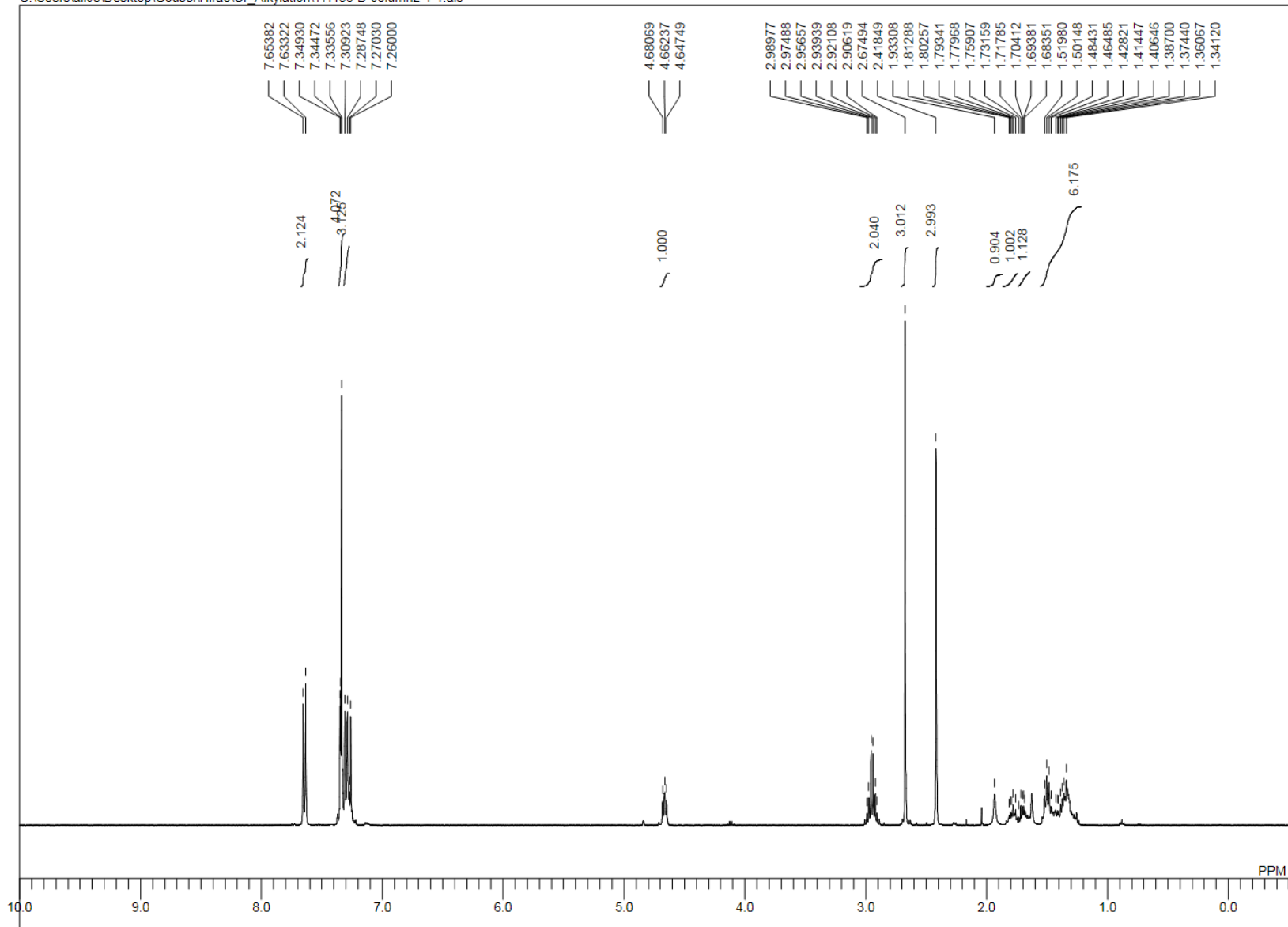


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

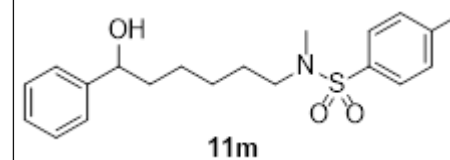


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

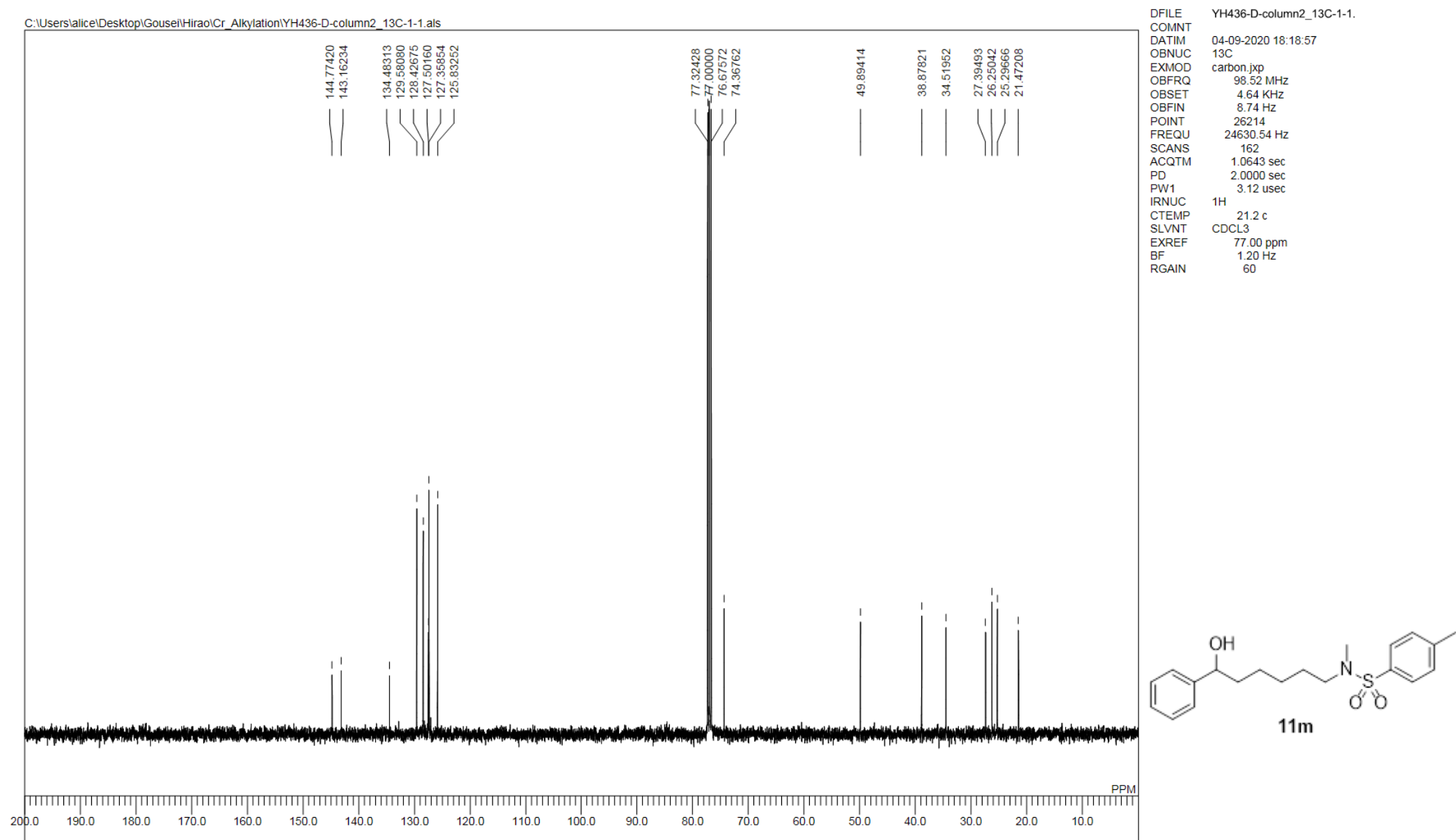
C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH436-D-column2-1-1.als



DFILE YH436-D-column2-1-1.als  
 COMNT  
 DATIM 04-09-2020 18:17:04  
 OBNUC 1H  
 EXMOD proton.jxp  
 OBFRQ 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 20.9 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 36

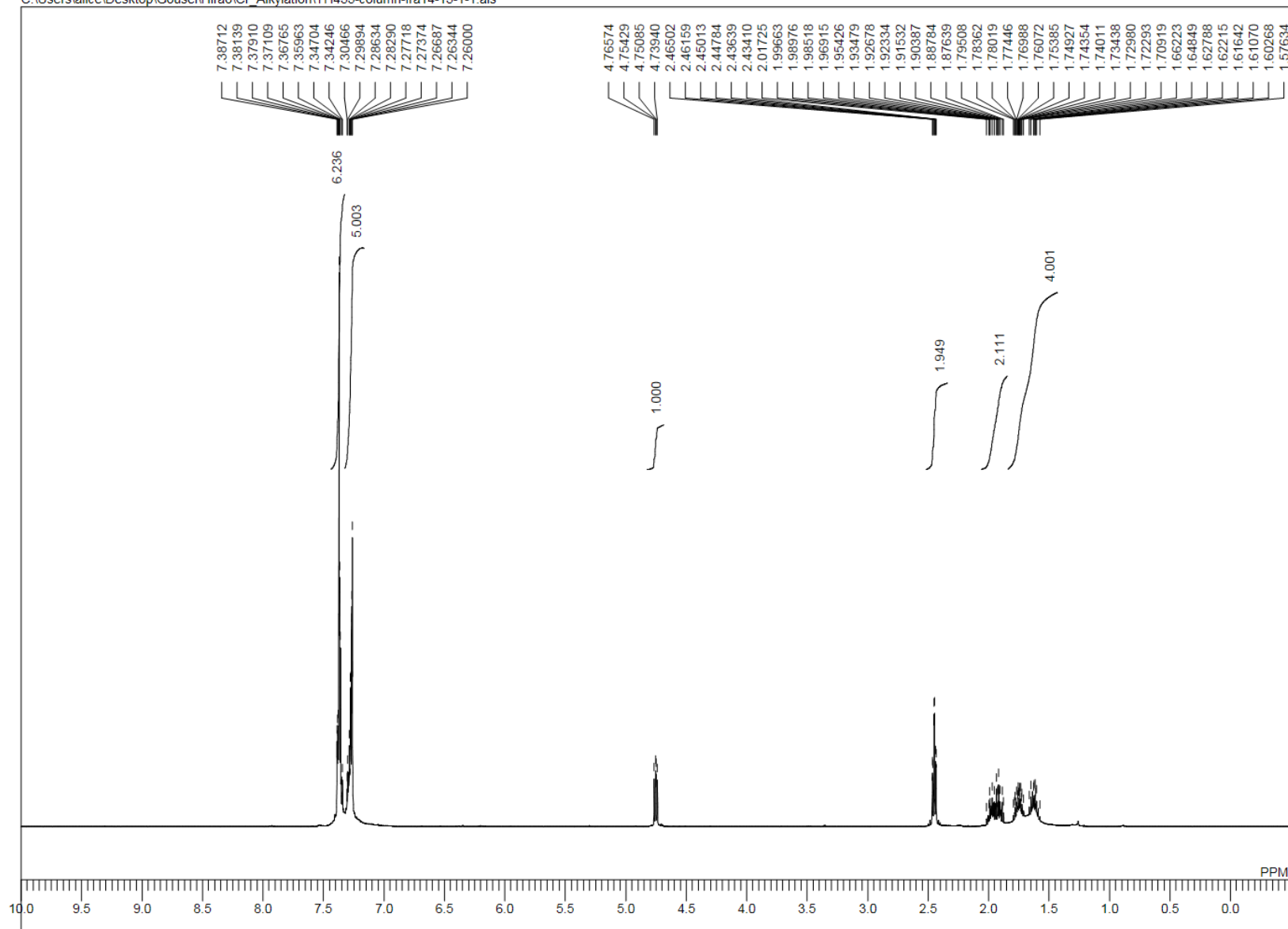


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

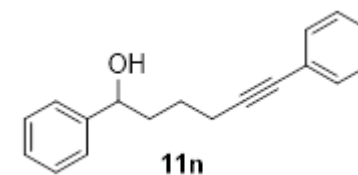


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

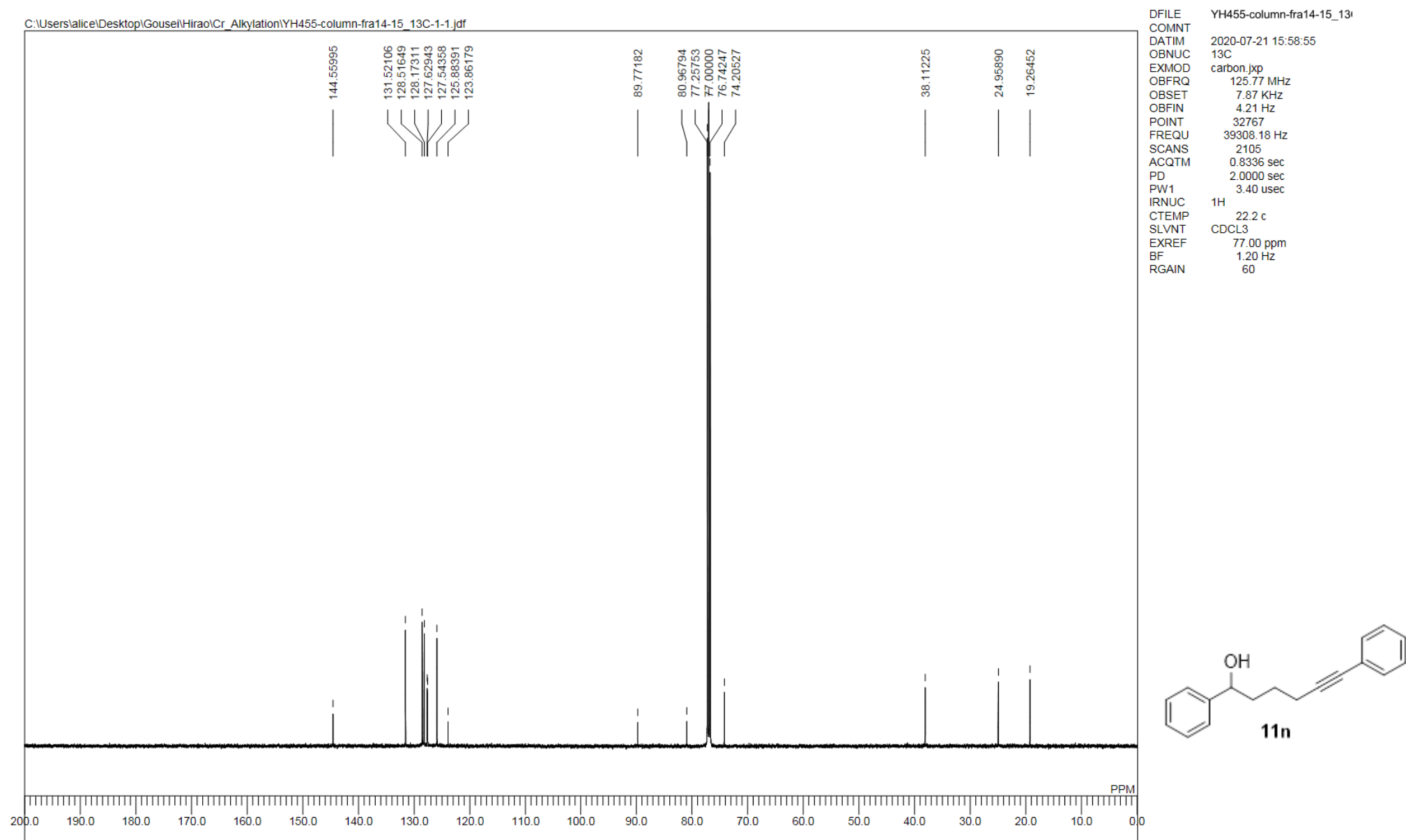
C:\Users\alice\Desktop\Gousei\Hirao\Cr Alkylation\YH455-column-fra14-15-1-1.als



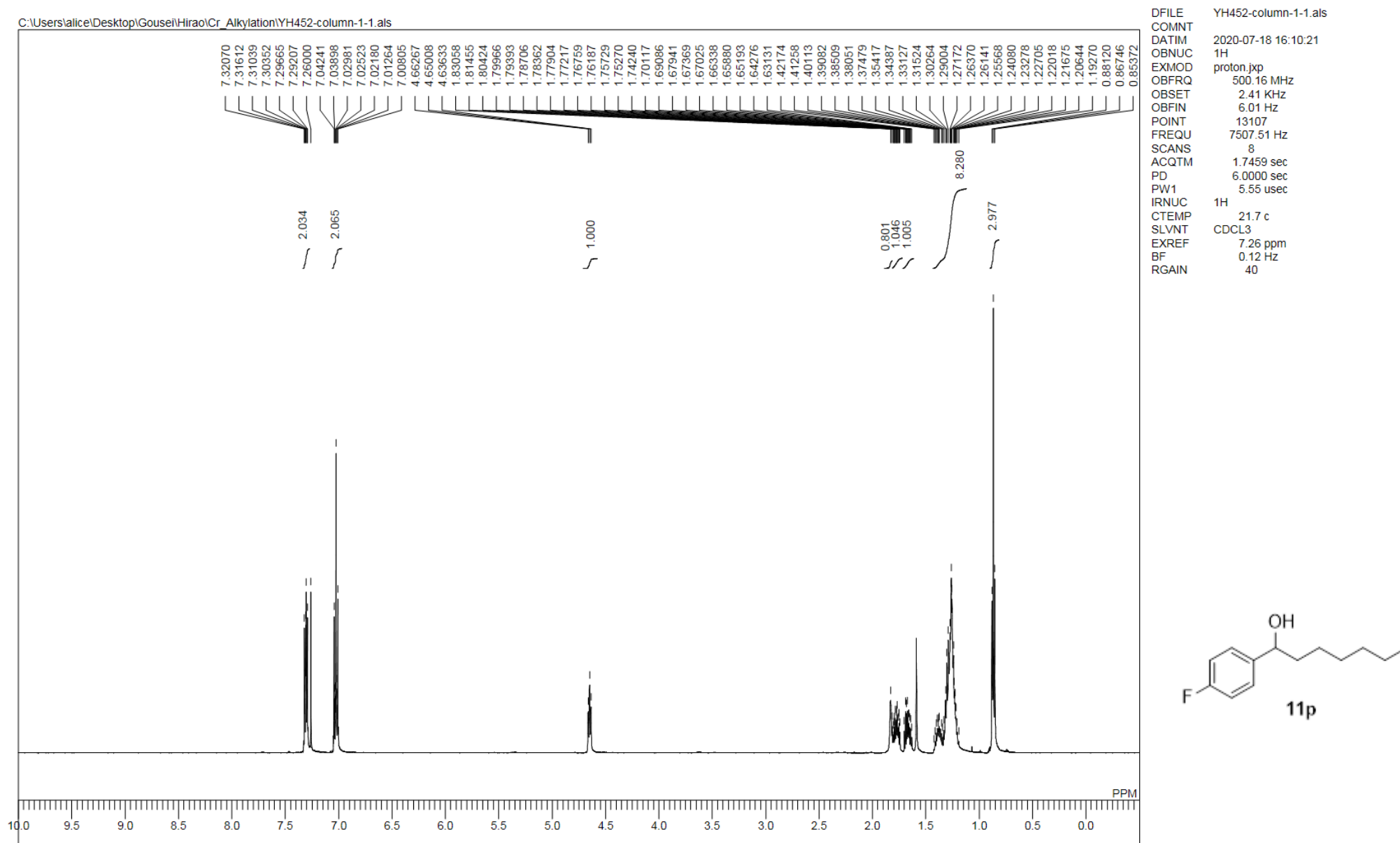
DFILE YH455-column-fra14-15-1-1.  
 COMNT 2020-07-21 15:40:21  
 DATIM 1H  
 OBNUC proton.jpg  
 EXMOD 500.16 MHz  
 OBFRQ 2.41 KHz  
 OBSET 6.01 Hz  
 OBFIN 13107  
 POINT 7507.51 Hz  
 FREQU 8  
 SCANS 1.7459 sec  
 ACQTM 6.0000 sec  
 PD 5.55 usec  
 PW1 1H  
 IRNUC 21.9 c  
 CTMP CDCL3  
 SLVNT 7.26 ppm  
 EXREF 0.12 Hz  
 BF 40  
 RGAIN



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)



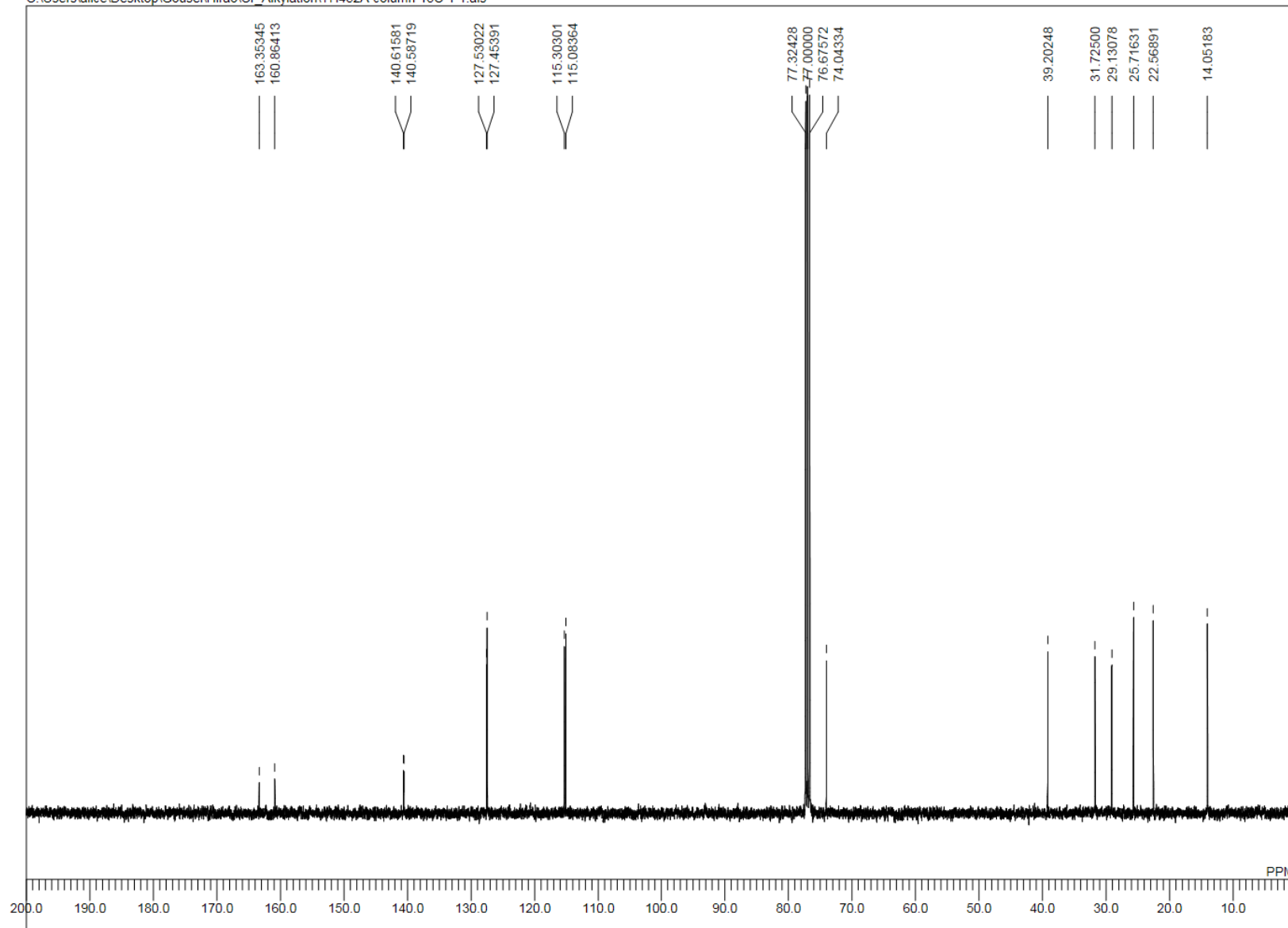
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )





<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH452A-column-13C-1-1.als



DFILE YH452A-column-13C-1-1.als

COMNT 18-07-2020 17:10:58

DATIM 13C

OBNUC carbon.jpg

EXMOD 98.52 MHz

OBFRQ 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 1H

IRNUC 21.0 c

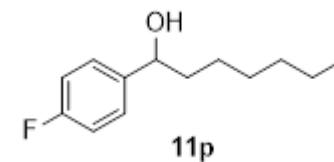
CTEMP CDCL3

SLVNT 77.00 ppm

EXREF 1.20 Hz

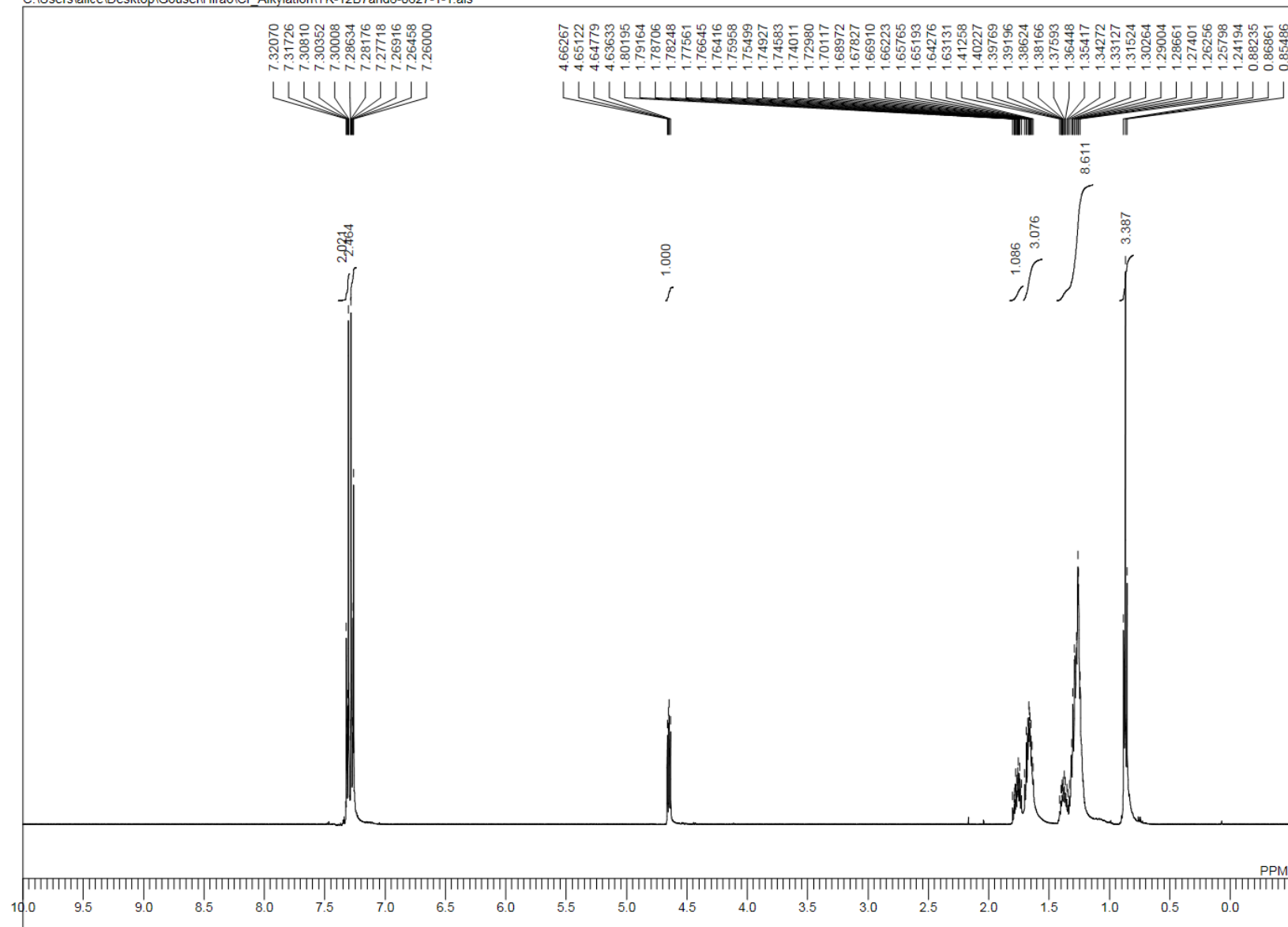
BF 60

RGAIN



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

C:\Users\alice\Desktop\Gousei\Hirao\Cr Alkylation\YK-12B7and8-0627-1-1.als



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

COMNT

DATIM 2020-06-27 12:57:55

OBNUC  $^1\text{H}$

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

IRNUC  $^1\text{H}$

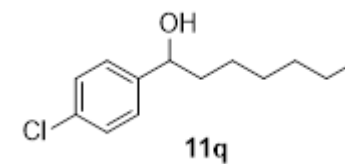
CTEMP 25.0 c

SLVNT  $\text{CDCl}_3$

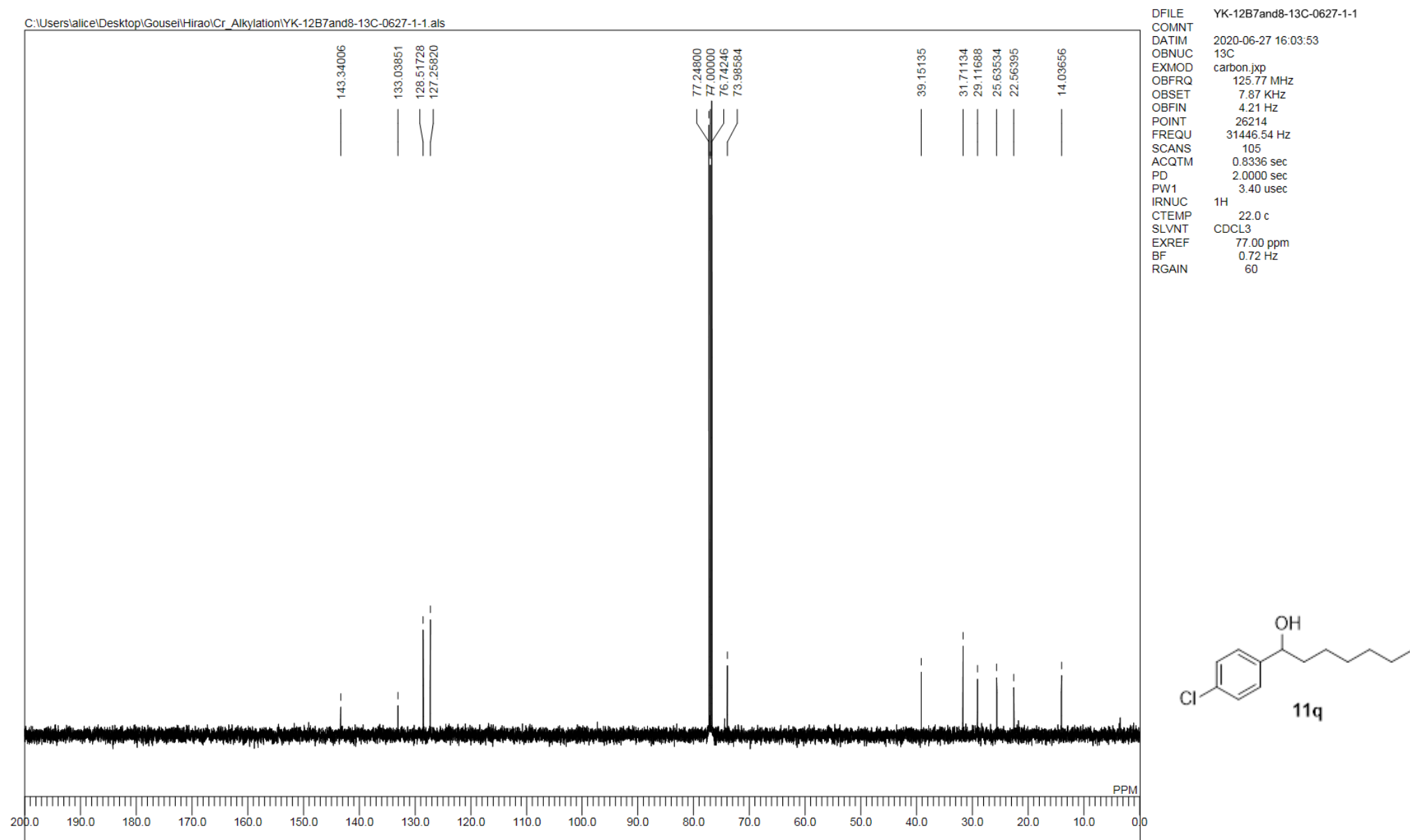
EXREF 7.26 ppm

BF 0.12 Hz

RGAIN 42

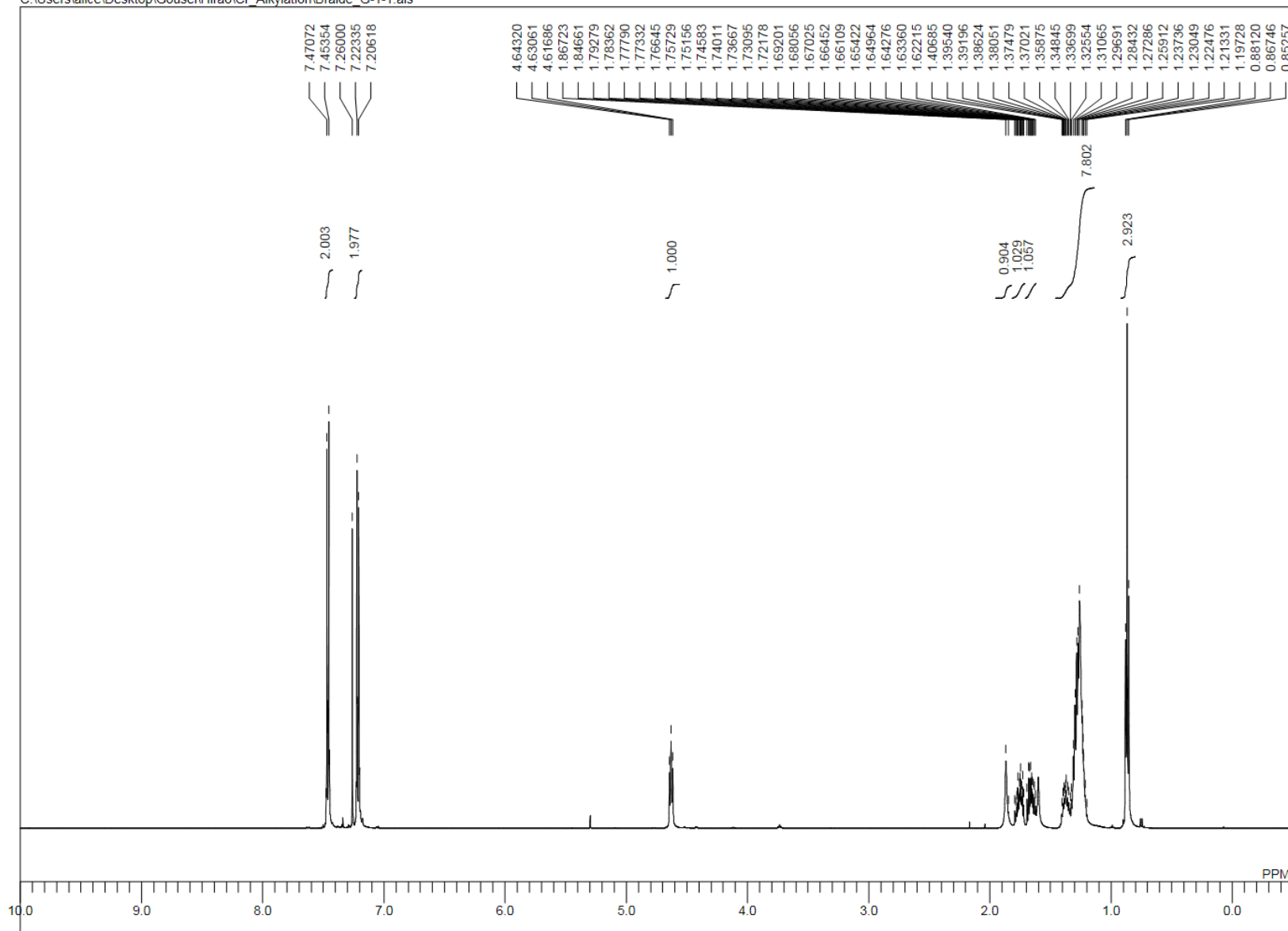


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

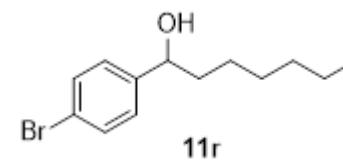


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

C:\Users\alice\Desktop\Gousei\Hirao\Cr Alkylation\Bralde\_G-1-1.als

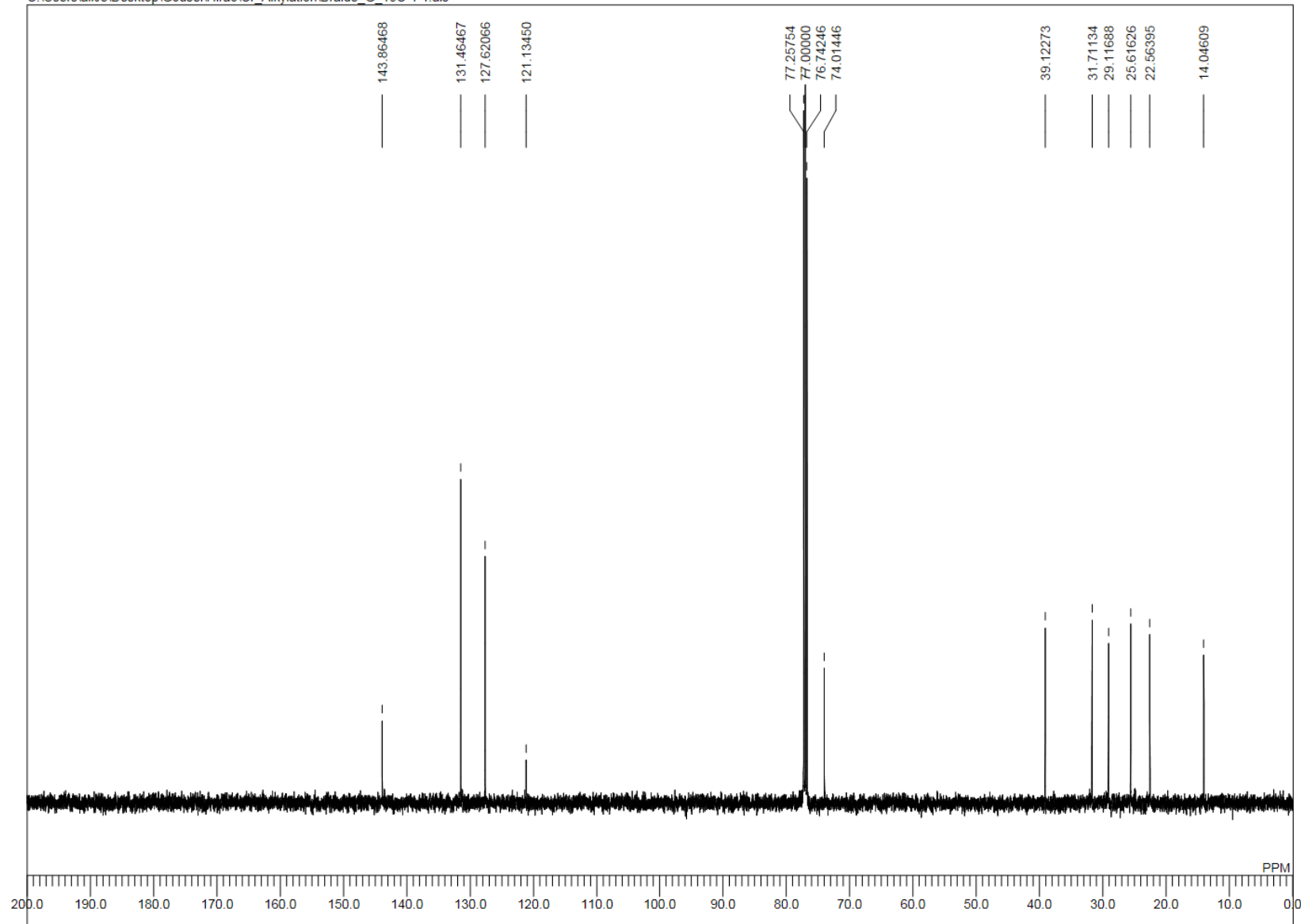


DFILE Bralde\_G-1-1.als  
 COMNT  
 DATIM 2020-09-08 16:14:16  
 OBNUC 1H  
 EXMOD proton.jpg  
 OBFRQ 500.16 MHz  
 OBSET 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 13107  
 FREQU 7507.51 Hz  
 SCANS 8  
 ACQTM 1.7459 sec  
 PD 6.0000 sec  
 PW1 5.55 usec  
 IRNUC 1H  
 CTEMP 21.9 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 40

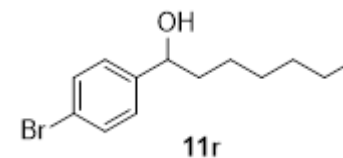


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\Bralde\_G\_13C-1-1.als

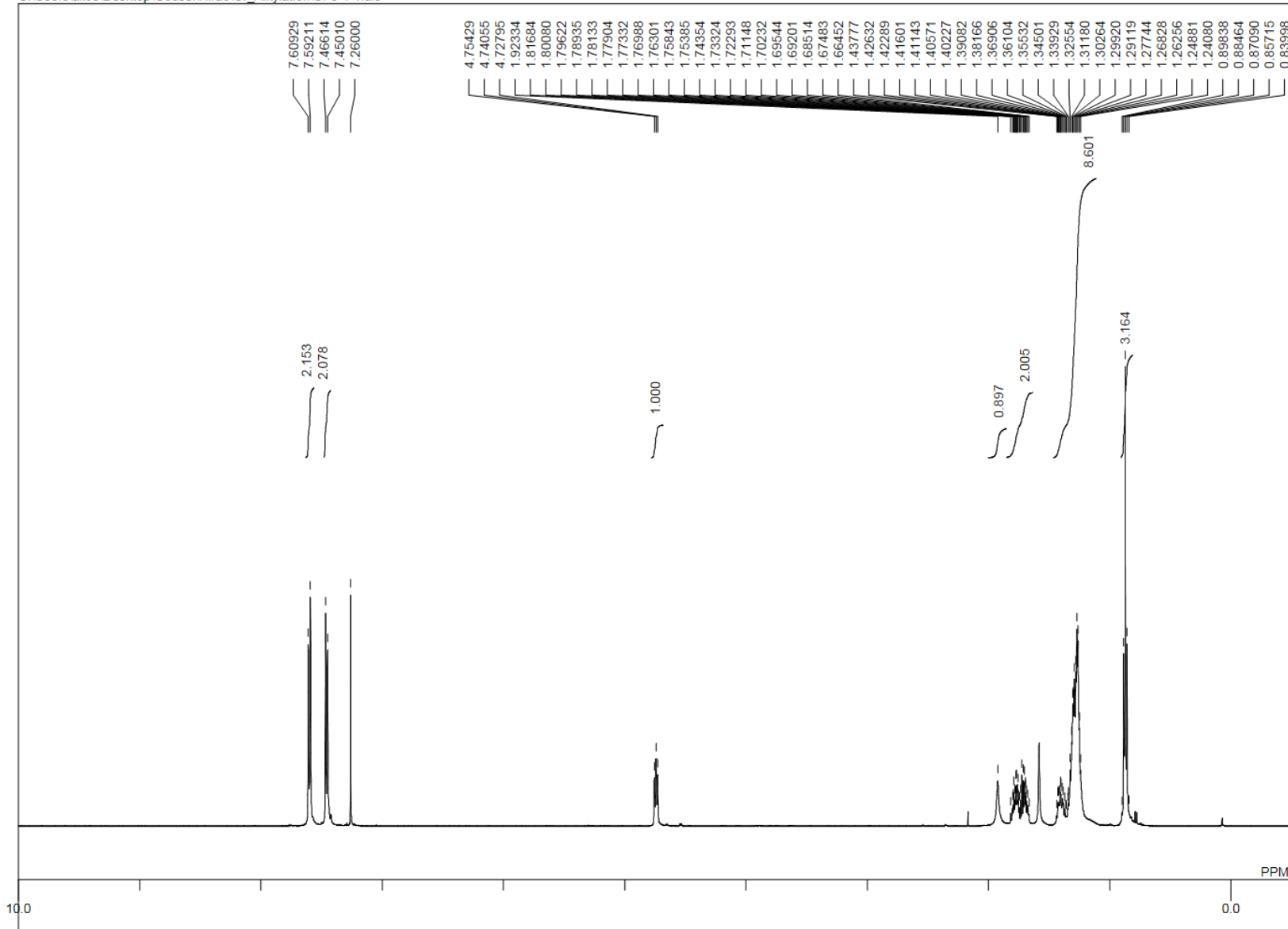


DFILE Bralde\_G\_13C-1-1.als  
COMNT  
DATIM 2020-09-08 16:16:02  
OBNUC 13C  
EXMOD carbon.jpg  
OBFREQ 125.77 MHz  
OBSET 7.87 KHz  
OBFIN 4.21 Hz  
POINT 26214  
FREQU 31446.54 Hz  
SCANS 103  
ACQTM 0.8336 sec  
PD 2.0000 sec  
PW1 3.40 usec  
IRNUC 1H  
CTEMP 22.1 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 60

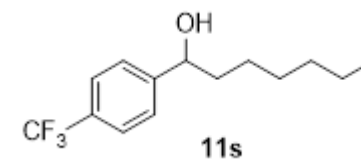


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

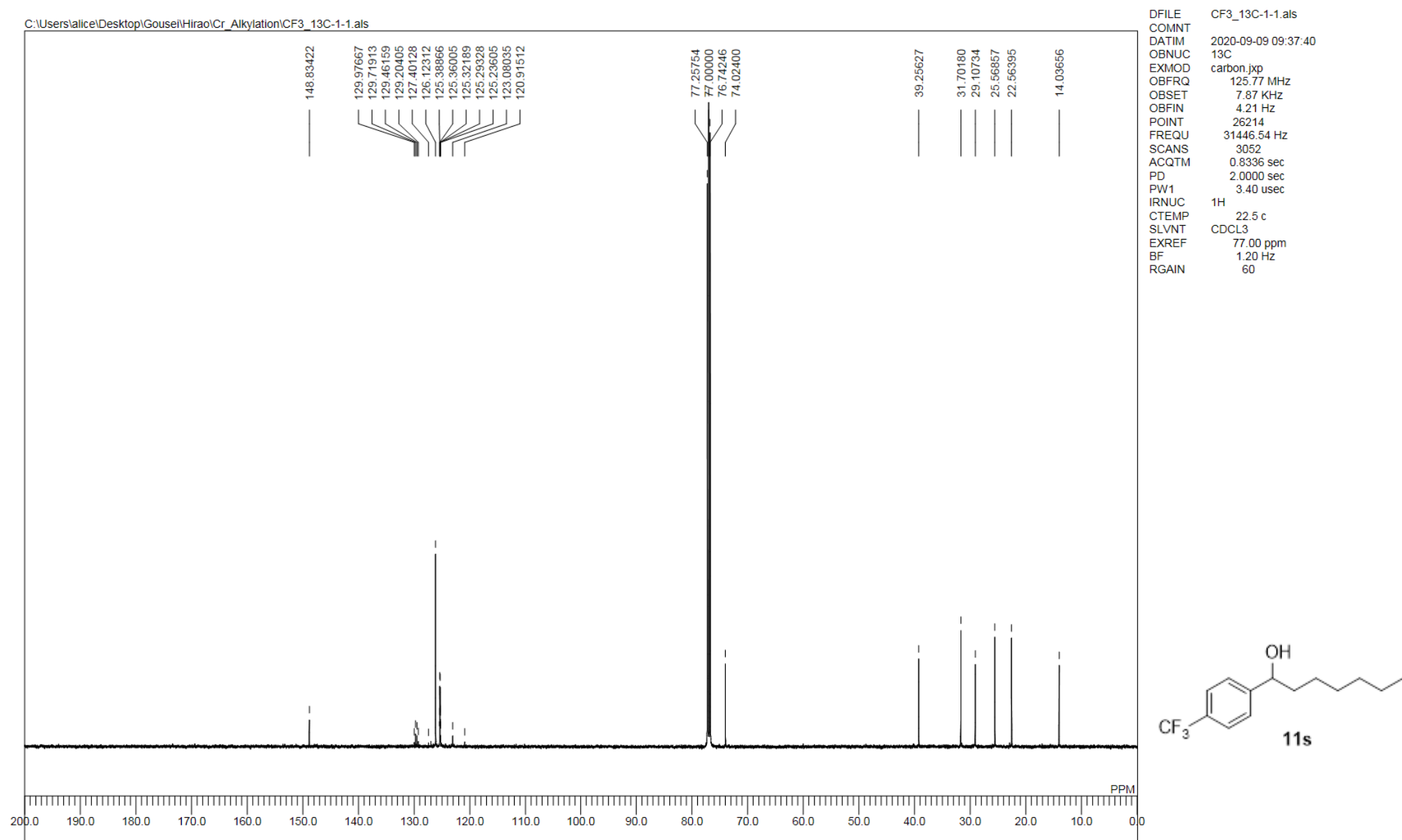
C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\CF3-1-1.als



DFILE CF3-1-1.als  
 COMNT  
 DATIM 2020-09-09 09:35:51  
 OBNUC  $^1\text{H}$   
 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  
 IRNUC  $^1\text{H}$   
 CTEMP 22.2 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 40

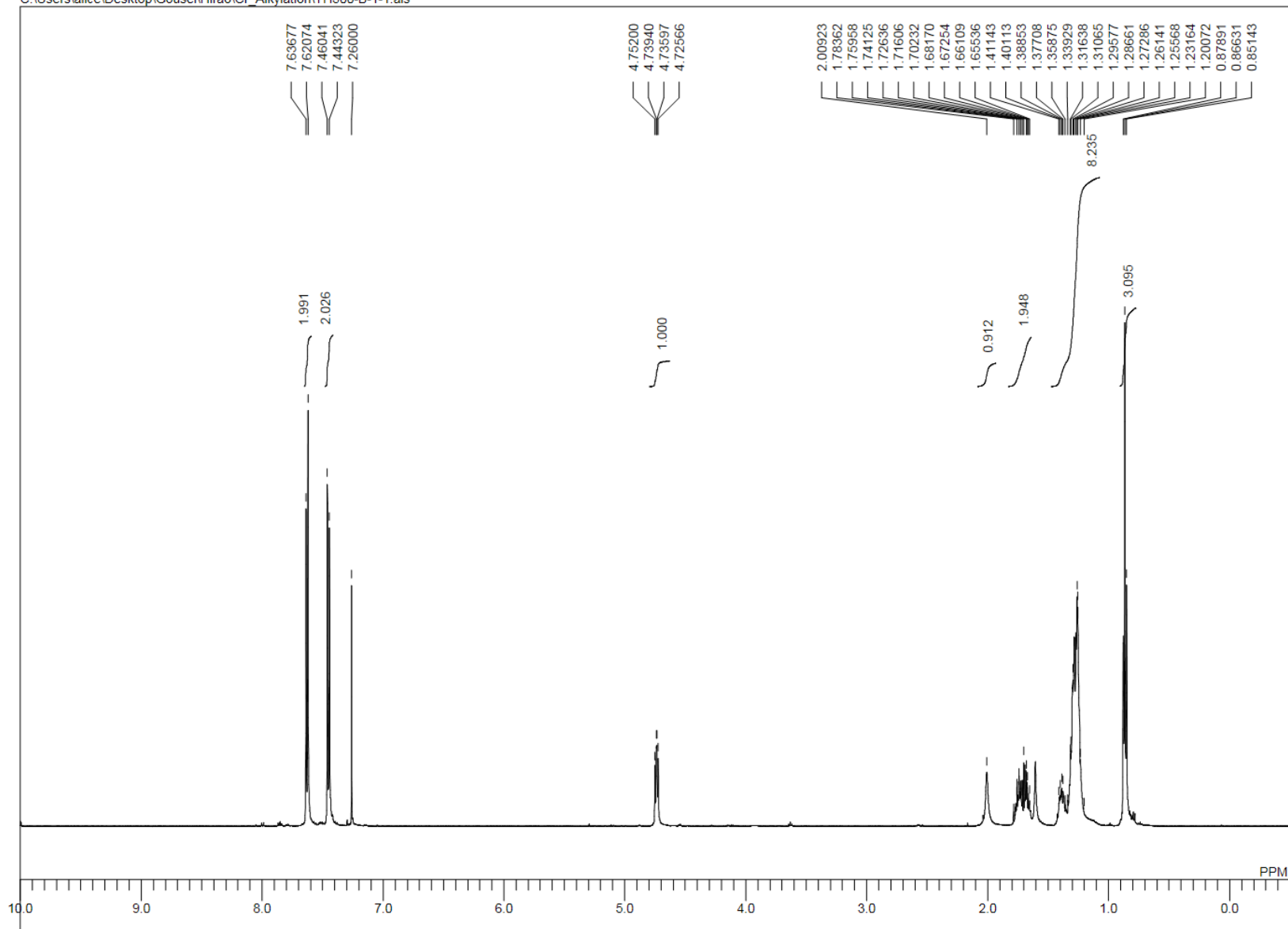


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

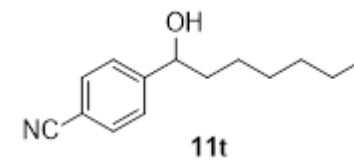


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH500-B-1-1.als



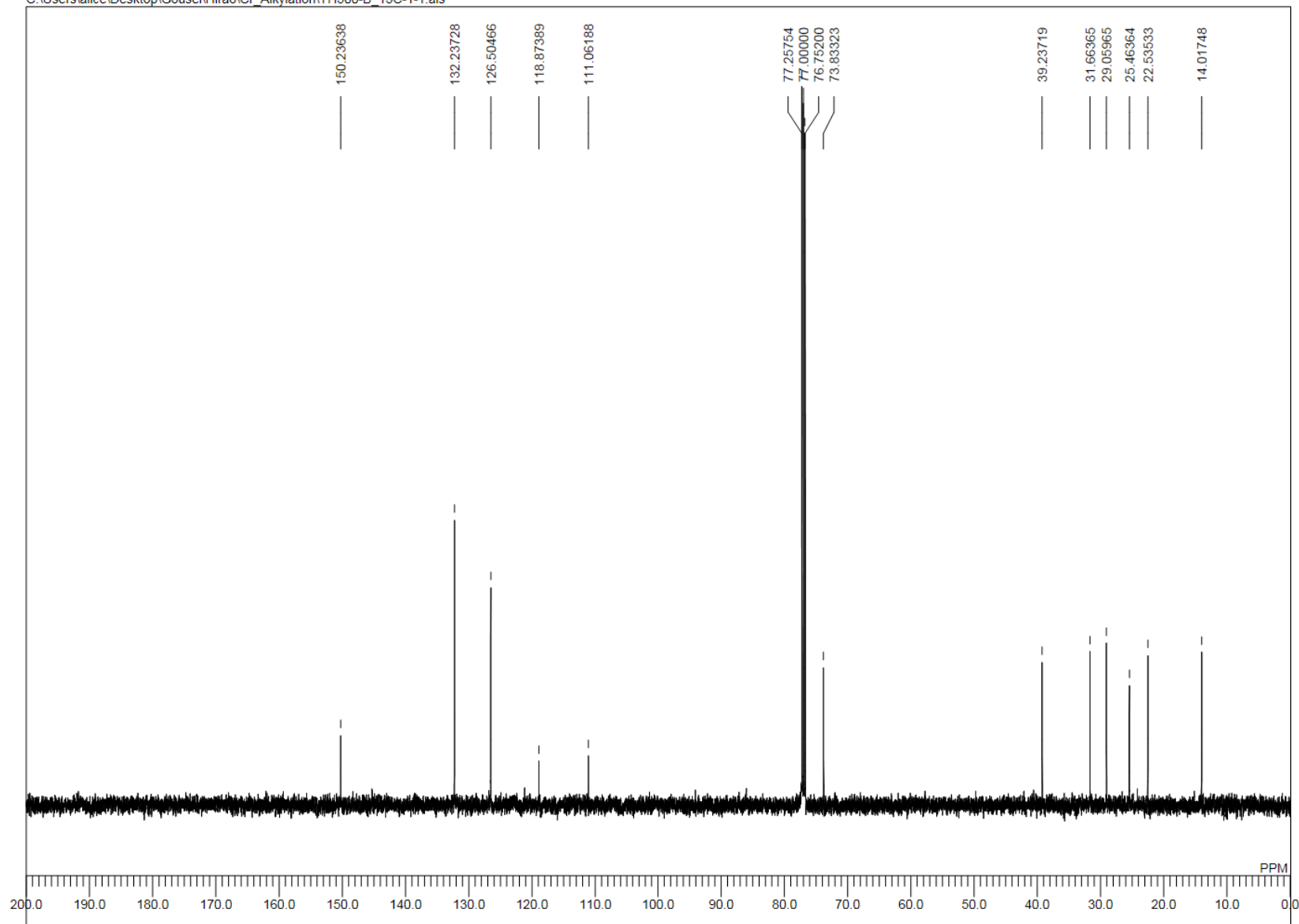
DFILE YH500-B-1-1.als  
COMNT  
DATIM 2020-09-07 10:02:30  
OBNUC 1H  
EXMOD proton.jxp  
OBFRQ 500.16 MHz  
OBSET 2.41 KHz  
OBFIN 6.01 Hz  
POINT 13107  
FREQU 7507.51 Hz  
SCANS 8  
ACQTM 1.7459 sec  
PD 6.0000 sec  
PW1 5.55 usec  
IRNUC 1H  
CTEMP 22.1 c  
SLVNT CDCL3  
EXREF 7.26 ppm  
BF 0.12 Hz  
RGAIN 40



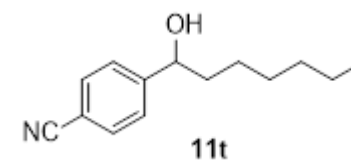


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH500-B\_13C-1-1.als

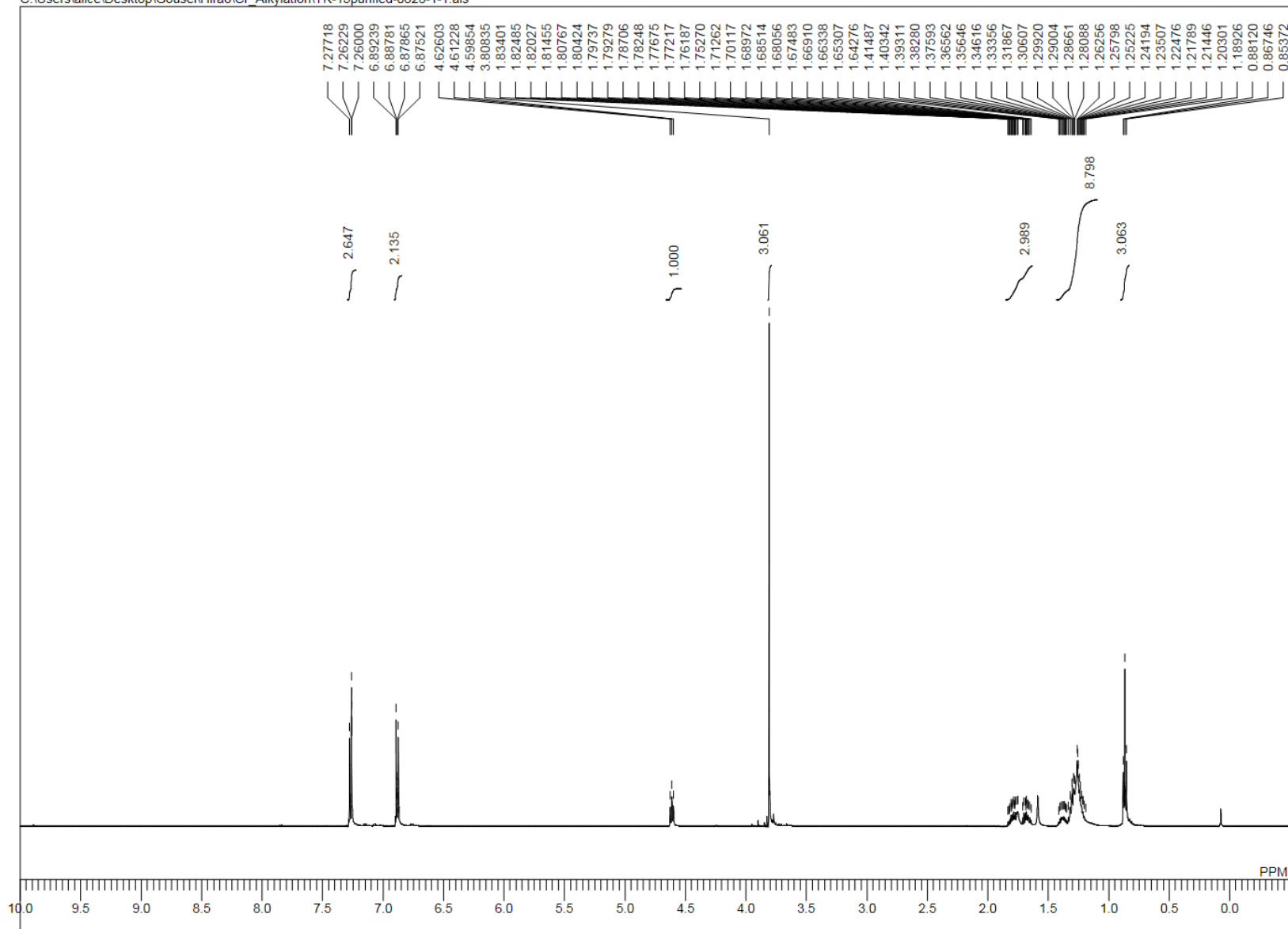


DFILE YH500-B\_13C-1-1.als  
COMNT  
DATIM 2020-09-07 10:04:13  
OBNUC 13C  
EXMOD carbon.jpg  
OBFRQ 125.77 MHz  
OBSET 7.87 KHz  
OBFIN 4.21 Hz  
POINT 26214  
FREQU 31446.54 Hz  
SCANS 103  
ACQTM 0.8336 sec  
PD 2.0000 sec  
PW1 3.40 usec  
IRNUC 1H  
CTEMP 22.4 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 60

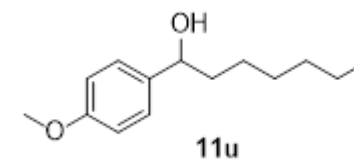


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

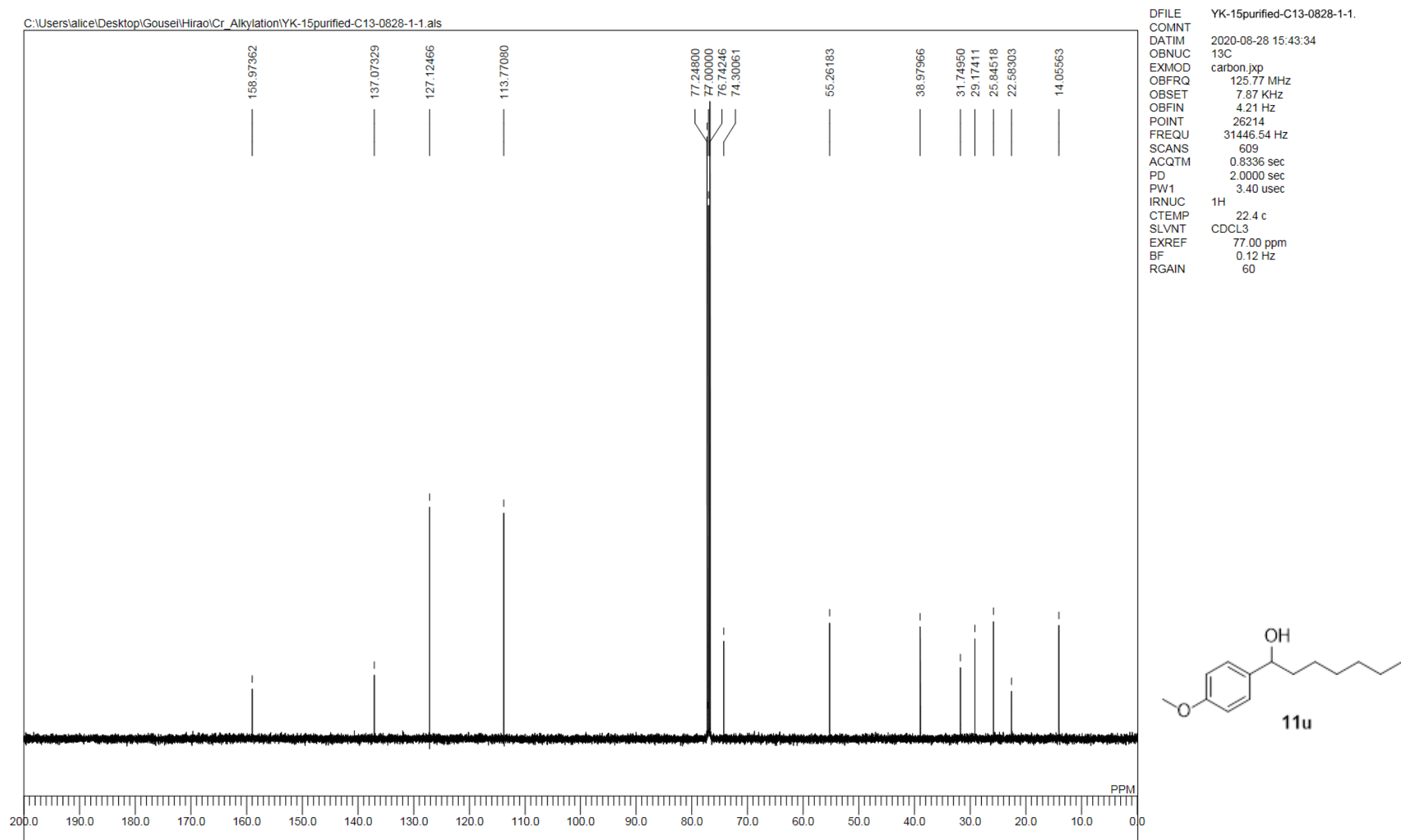
C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YK-15purified-0828-1-1.als



DFILE YK-15purified-0828-1-1.als  
 COMNT  
 DATIM 2020-08-28 13:58:03  
 OBNUC  $^1\text{H}$   
 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  
 IRNUC  $^1\text{H}$   
 CTEMP 21.8 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 42

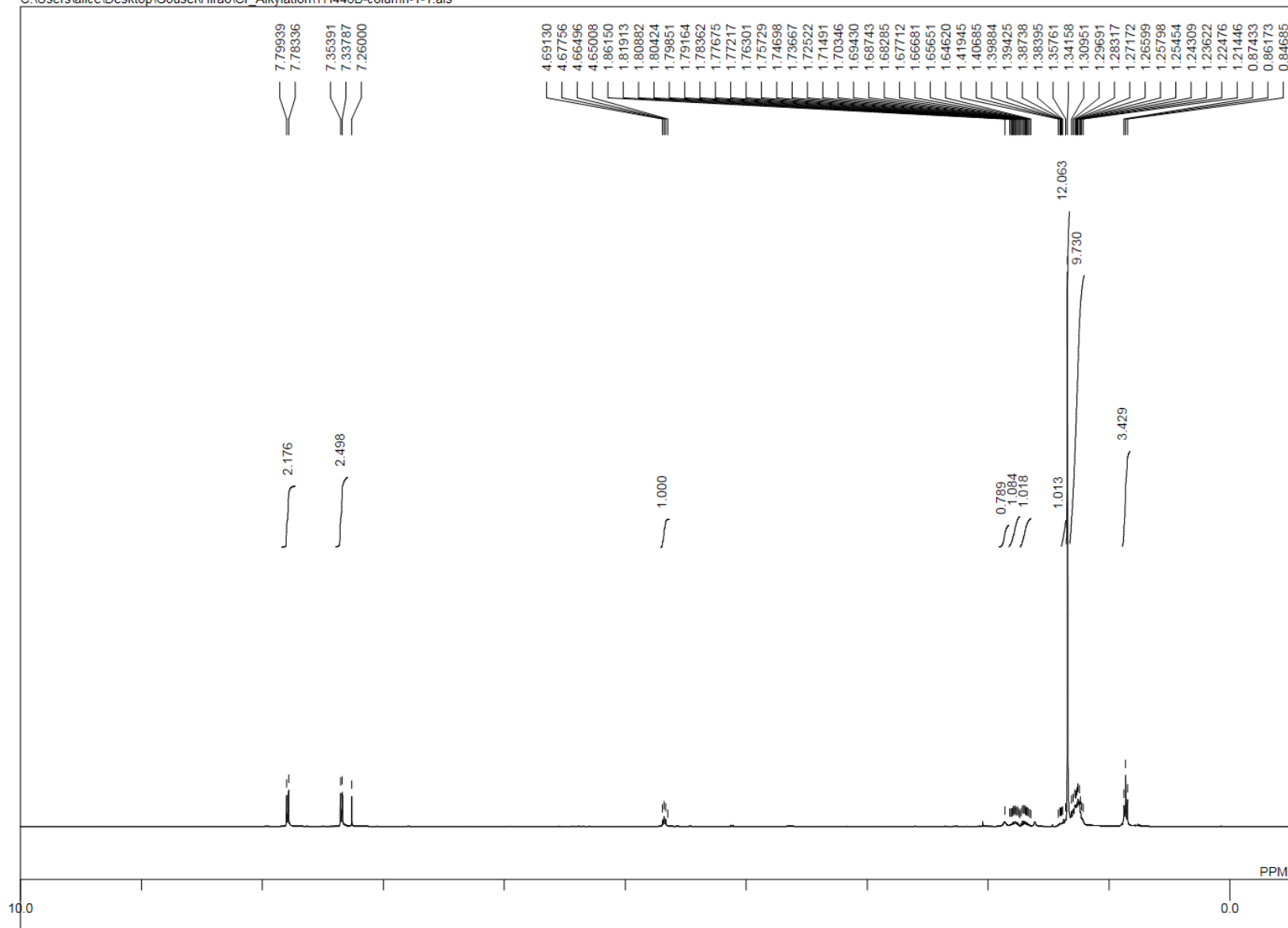


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

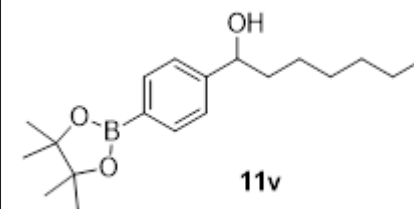


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH448B-column-1-1.als

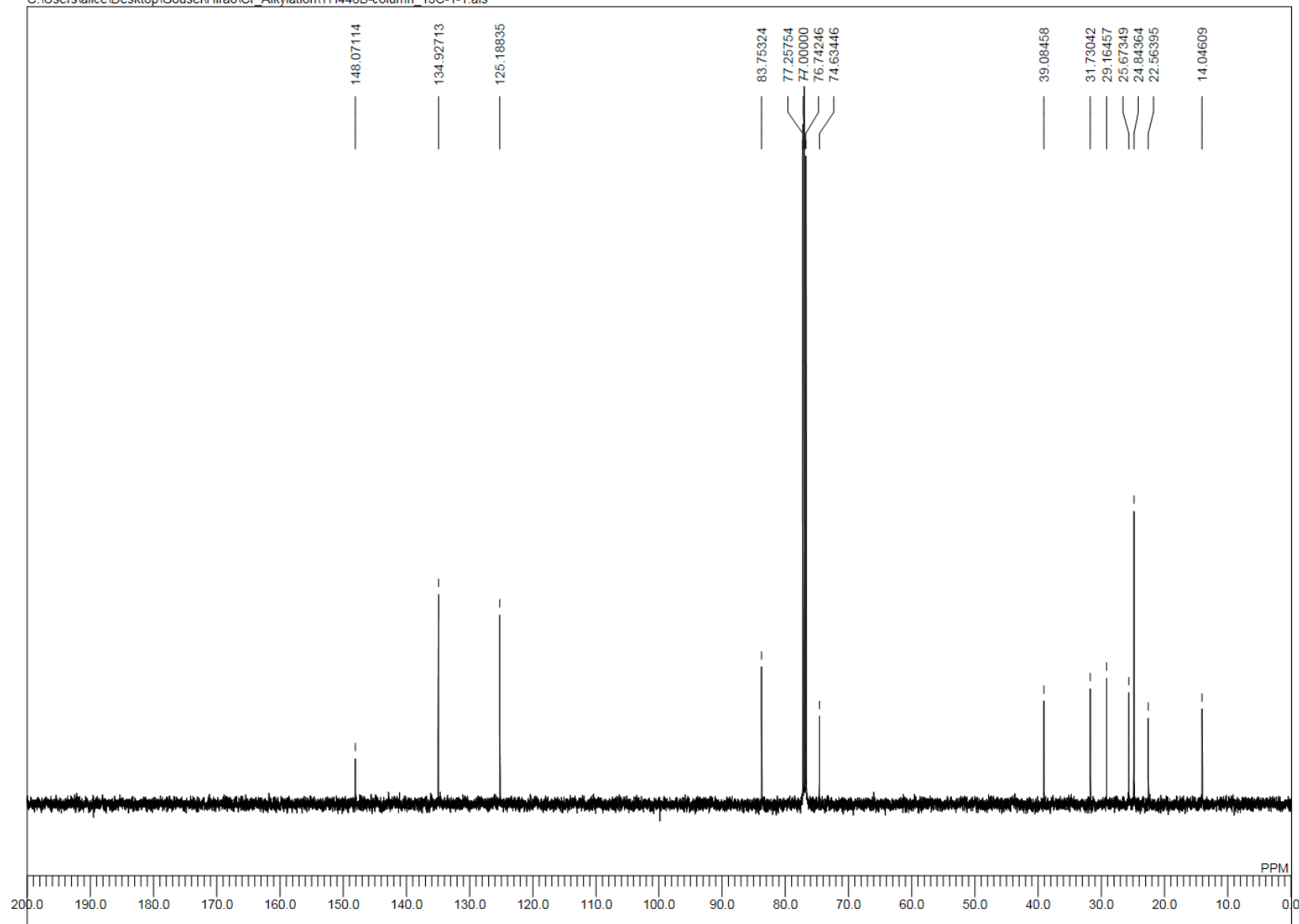


DFILE YH448B-column-1-1.als  
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 OBNUC 1H  
 EXMOD proton.jpg  
 OBFRQ 500.16 MHz  
 OBSET 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 13107  
 FREQU 7507.51 Hz  
 SCANS 8  
 ACQTM 1.7459 sec  
 PD 6.0000 sec  
 PW1 5.55 usec  
 IRNUC 1H  
 CTEMP 21.7 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 40

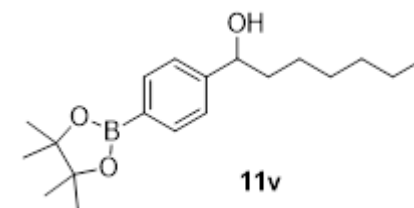


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH448B-column\_13C-1-1.als

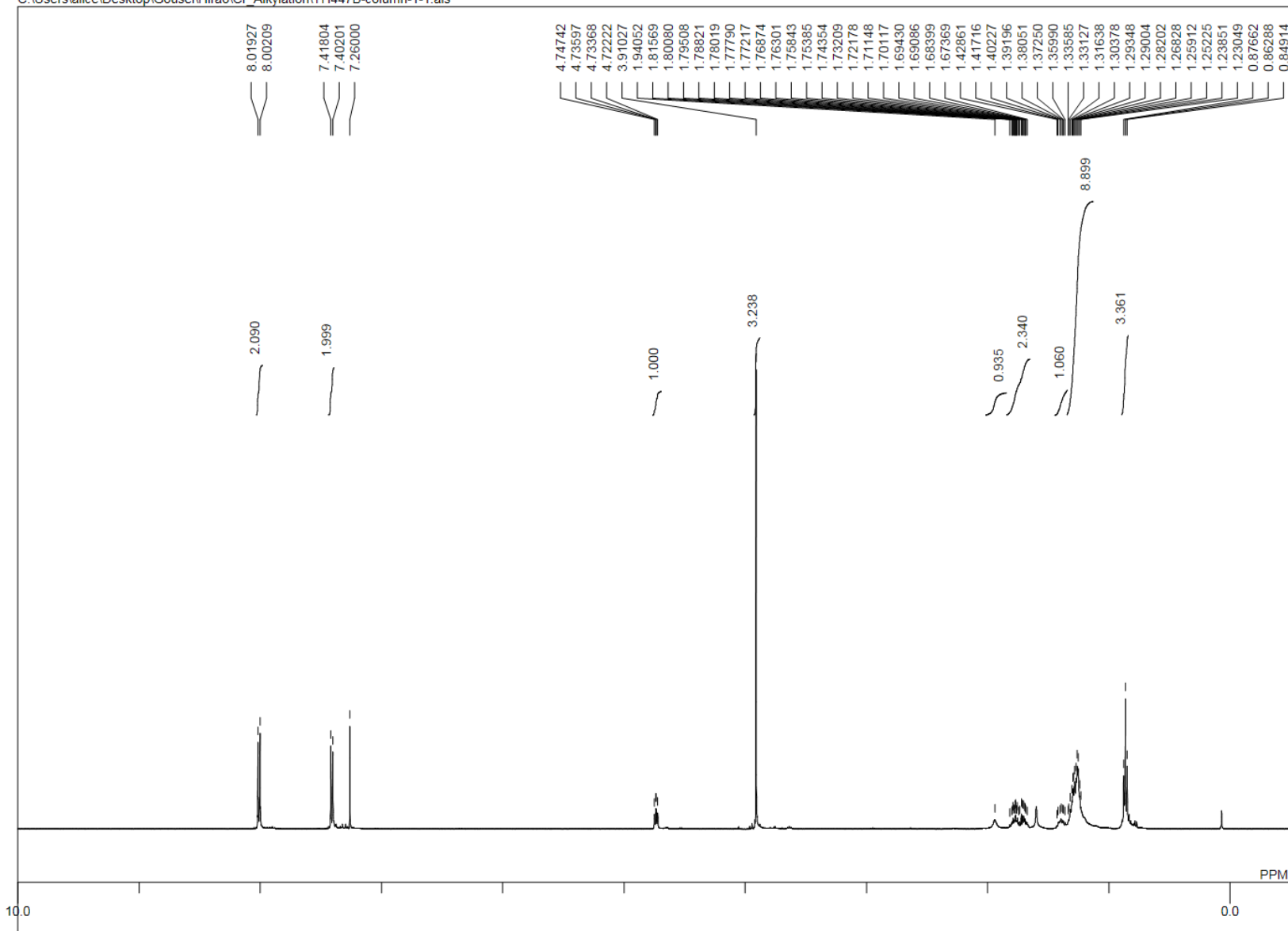


DFILE YH448B-column\_13C-1-1.al  
COMNT  
DATIM 2020-07-16 11:21:44  
OBNUC 13C  
EXMOD carbon.jpg  
OBFRQ 125.77 MHz  
OBSET 7.87 KHz  
OBFIN 4.21 Hz  
POINT 26214  
FREQU 31446.54 Hz  
SCANS 155  
ACQTM 0.8336 sec  
PD 2.0000 sec  
PW1 3.40 usec  
IRNUC 1H  
CTEMP 22.1 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 60

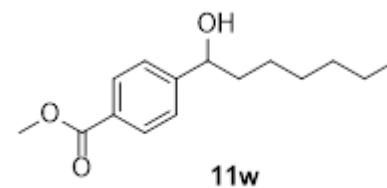


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

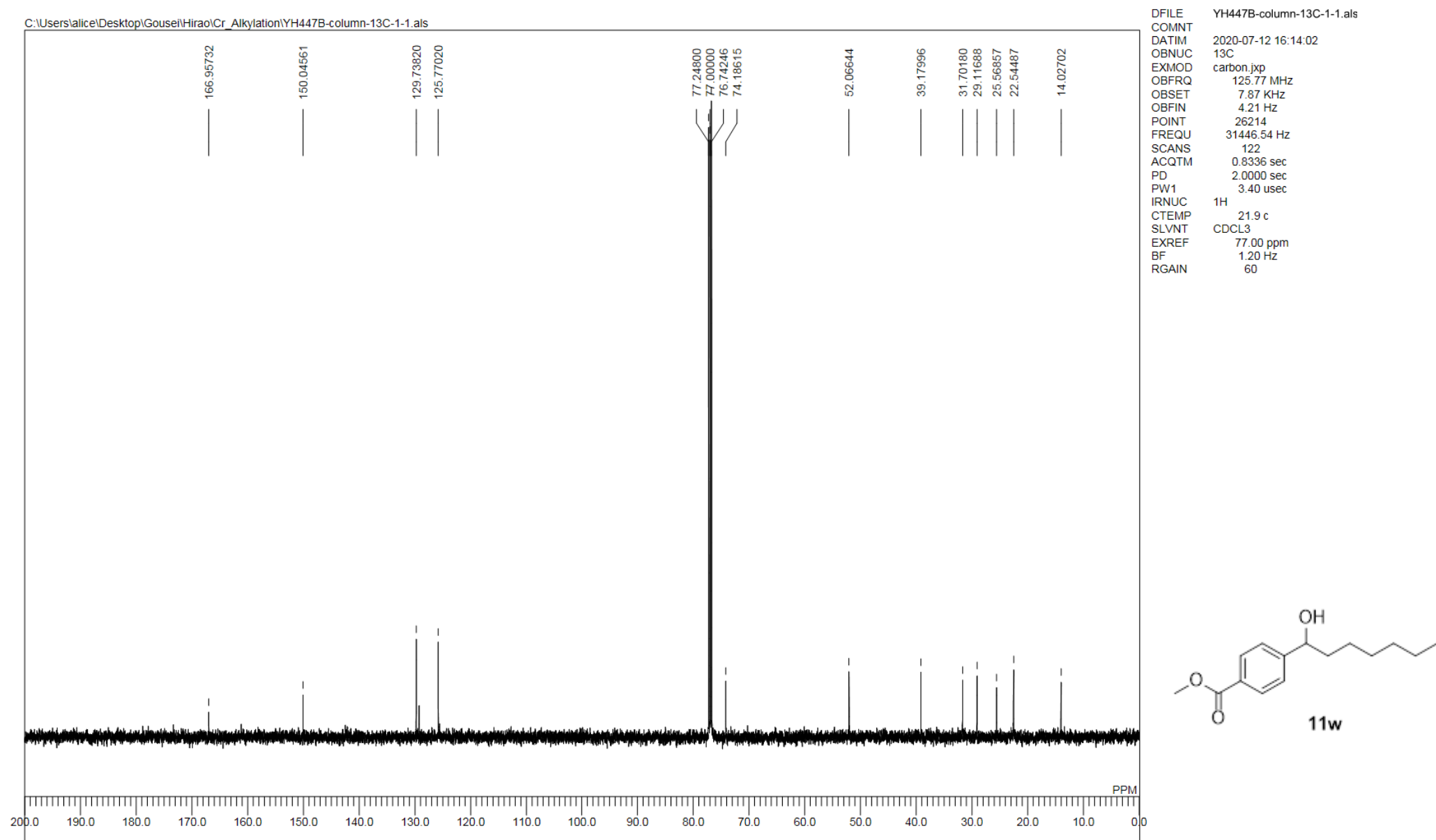
C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH447B-column-1-1.als



DFILE YH447B-column-1-1.als  
 COMNT  
 DATIM 2020-07-12 16:12:13  
 OBNUC  $^1\text{H}$   
 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  
 IRNUC  $^1\text{H}$   
 CTEMP 21.9 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 40

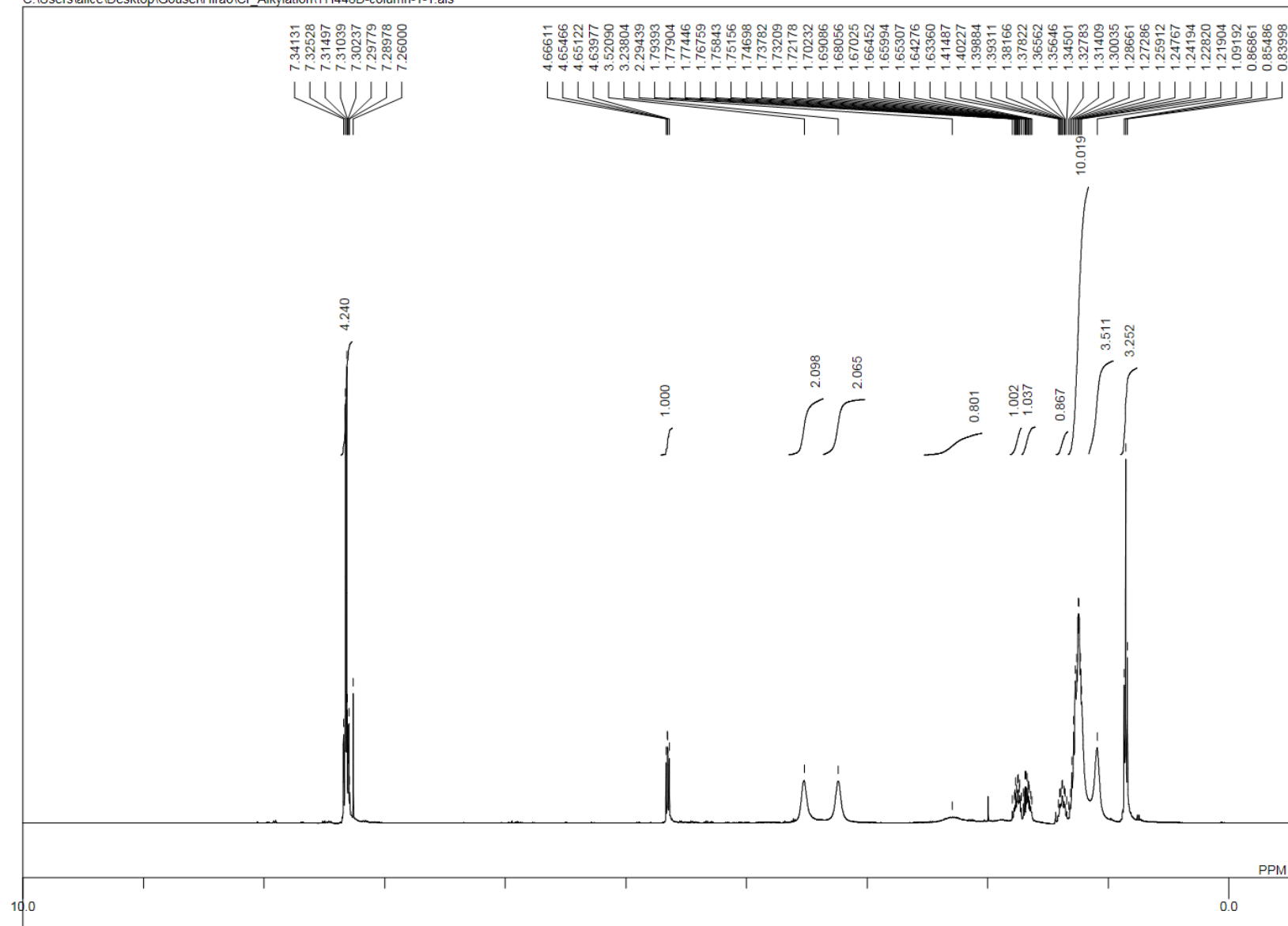


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

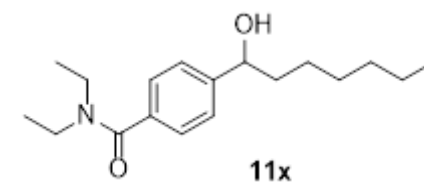


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

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



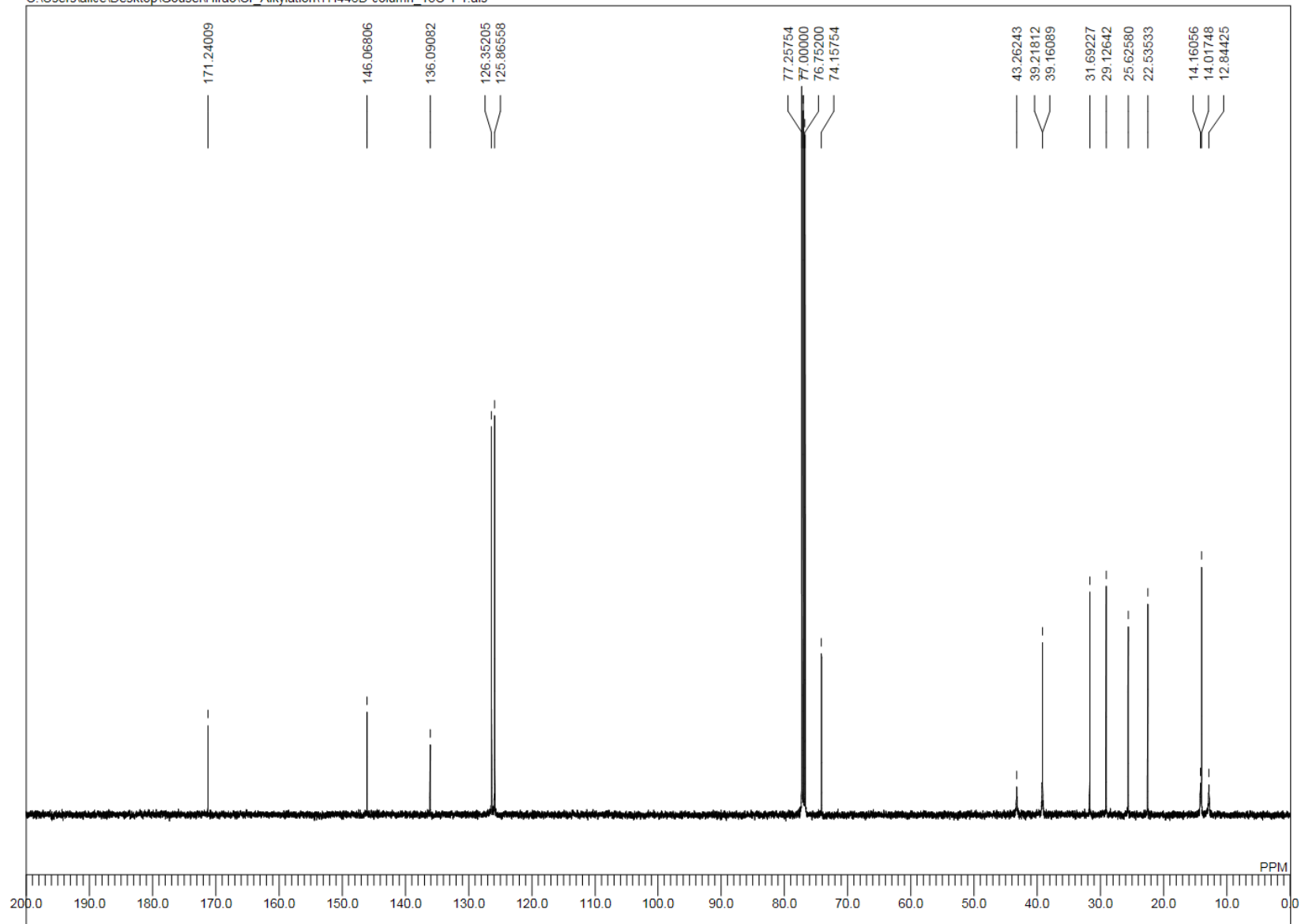
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 COMNT  
 DATIM 2020-07-16 11:35:56  
 OBNUC 1H  
 EXMOD proton.jxp  
 OBFRQ 500.16 MHz  
 OBSET 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 13107  
 FREQU 7507.51 Hz  
 SCANS 8  
 ACQTM 1.7459 sec  
 PD 6.0000 sec  
 PW1 5.55 usec  
 IRNUC 1H  
 CTEMP 21.7 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 38



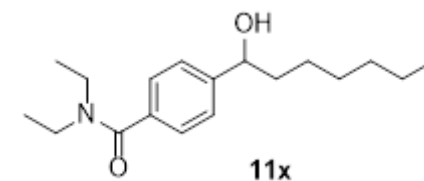


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH448D-column\_13C-1-1.als

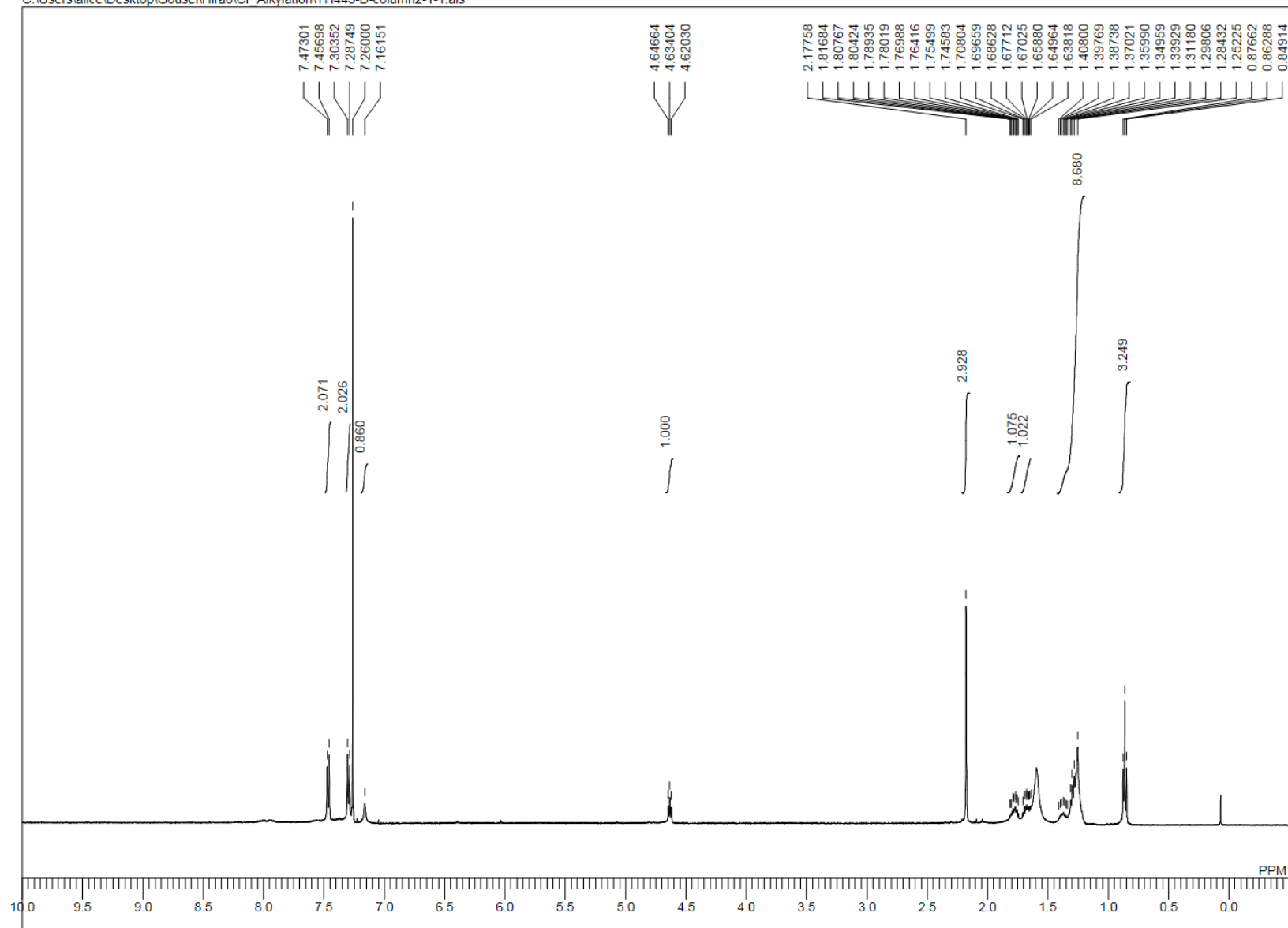


DFILE YH448D-column\_13C-1-1.al  
COMNT  
DATIM 2020-07-16 11:37:45  
OBNUC 13C  
EXMOD carbon.jpg  
OBFREQ 125.77 MHz  
OBSET 7.87 KHz  
OBFIN 4.21 Hz  
POINT 26214  
FREQU 31446.54 Hz  
SCANS 577  
ACQTM 0.8336 sec  
PD 2.0000 sec  
PW1 3.40 usec  
IRNUC 1H  
CTEMP 22.0 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 60

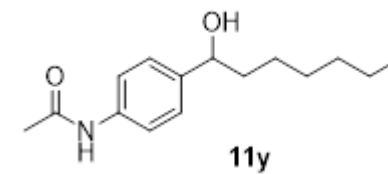


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

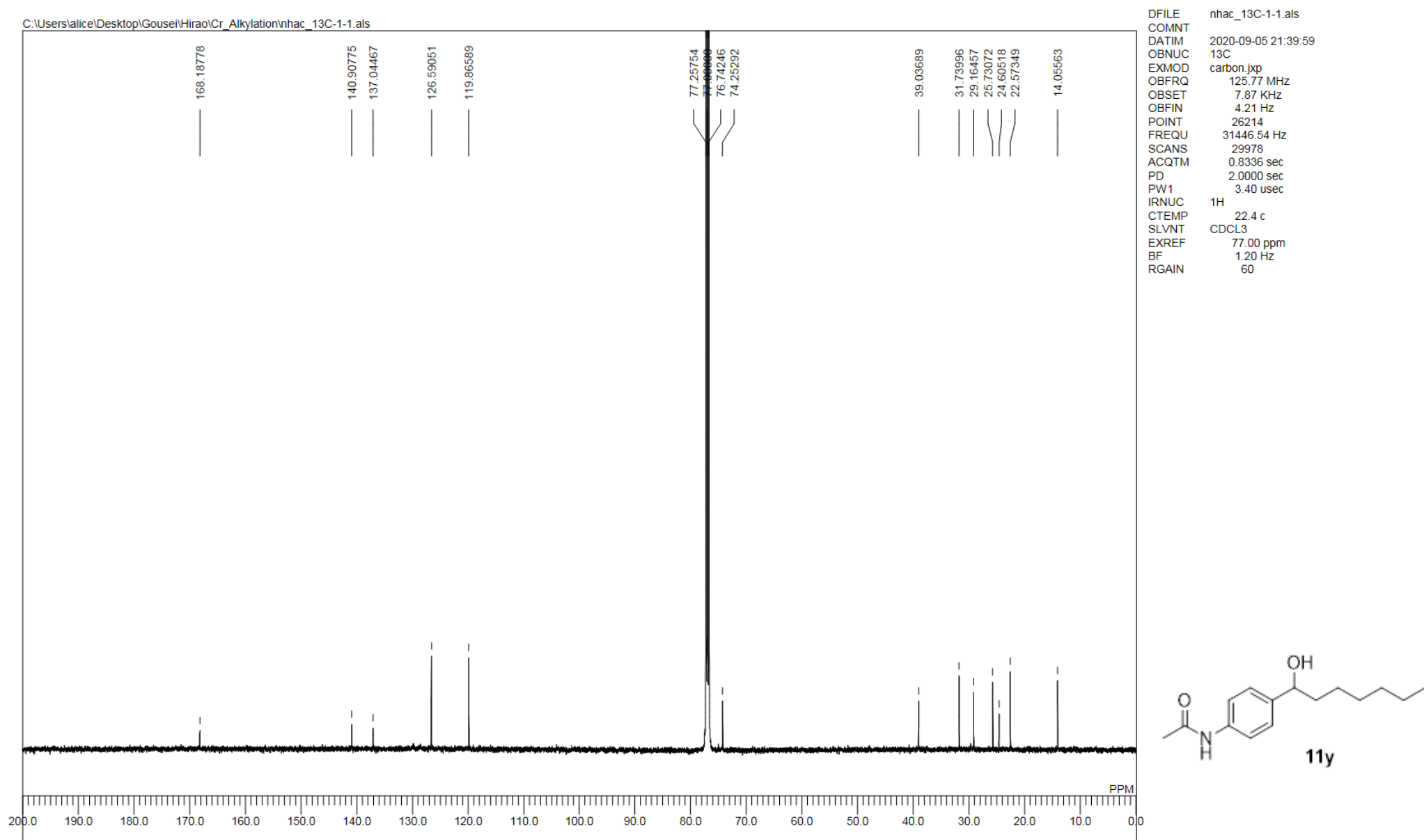
C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH443-D-column2-1-1.als



DFILE YH443-D-column2-1-1.als  
 COMNT  
 DATIM 2020-09-05 15:19:14  
 OBNUC  $^1\text{H}$   
 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  
 IRNUC  $^1\text{H}$   
 CTEMP 22.0 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 42

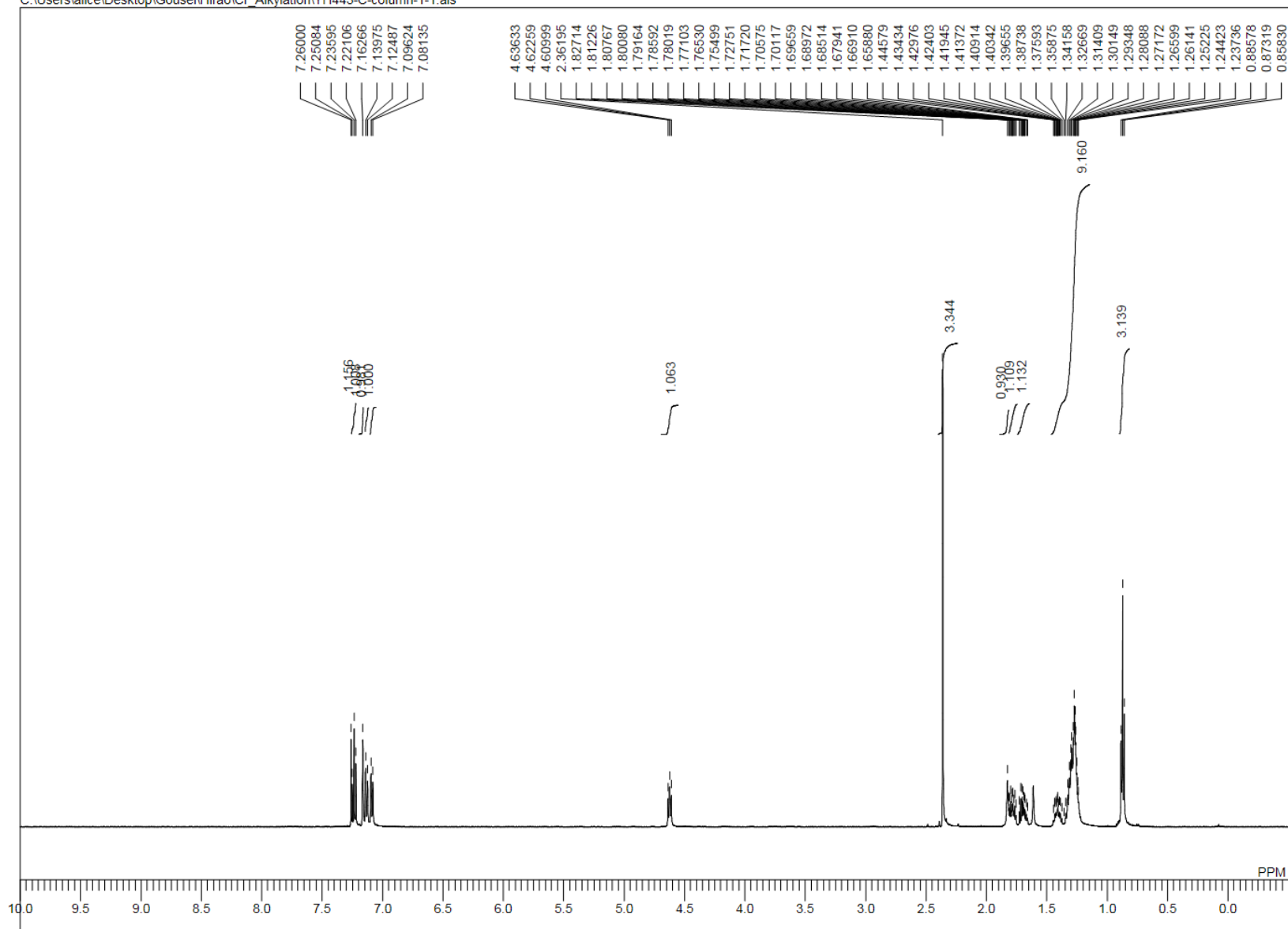


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

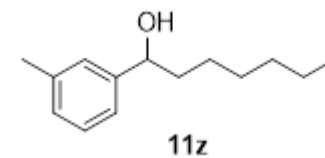


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

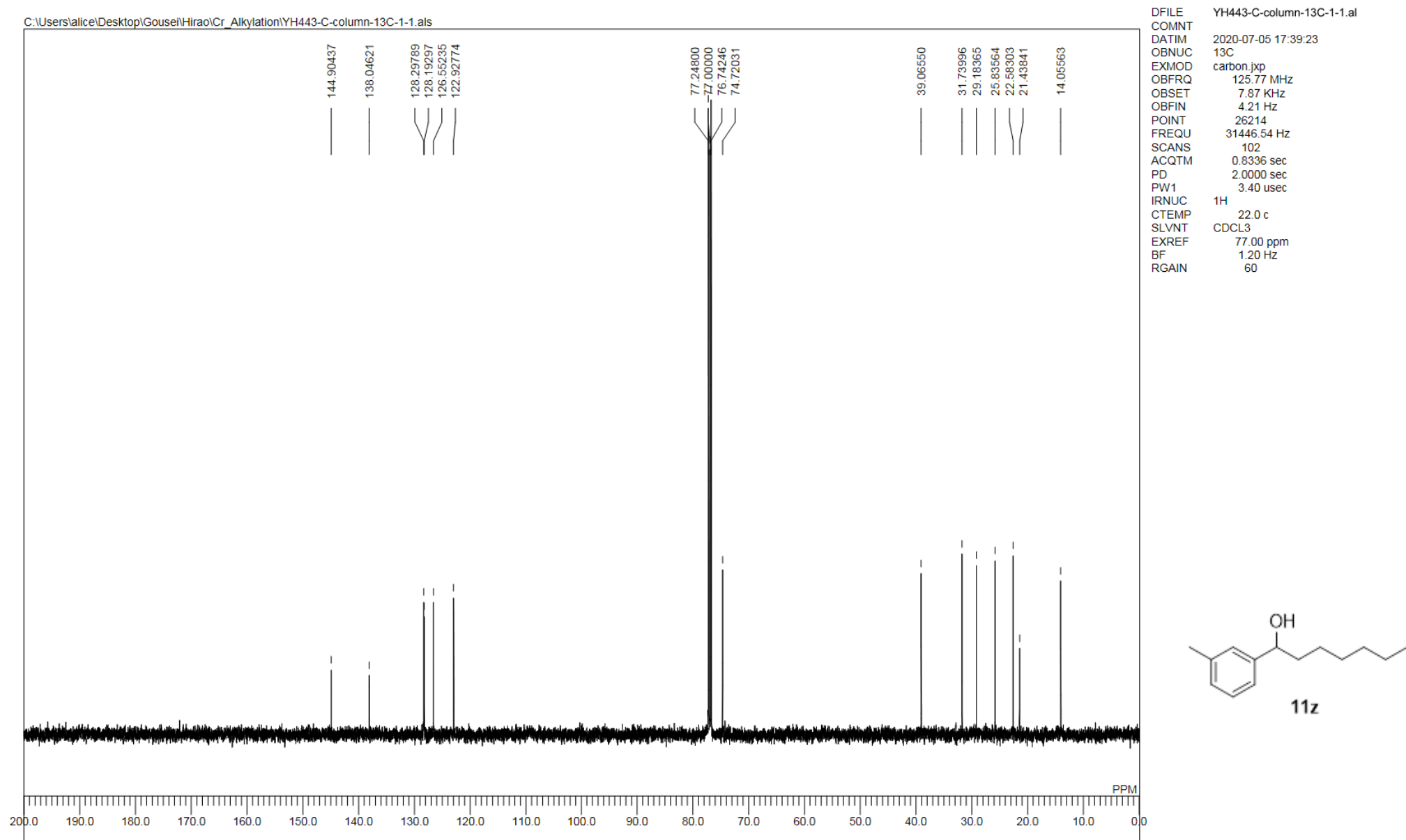
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DFILE YH443-C-column-1-1.als  
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 EXMOD proton.jpg  
 OBFRQ 500.16 MHz  
 OBSET 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 13107  
 FREQU 7507.51 Hz  
 SCANS 8  
 ACQTM 1.7459 sec  
 PD 6.0000 sec  
 PW1 5.55 usec  
 IRNUC 1H  
 CTEMP 21.8 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 40

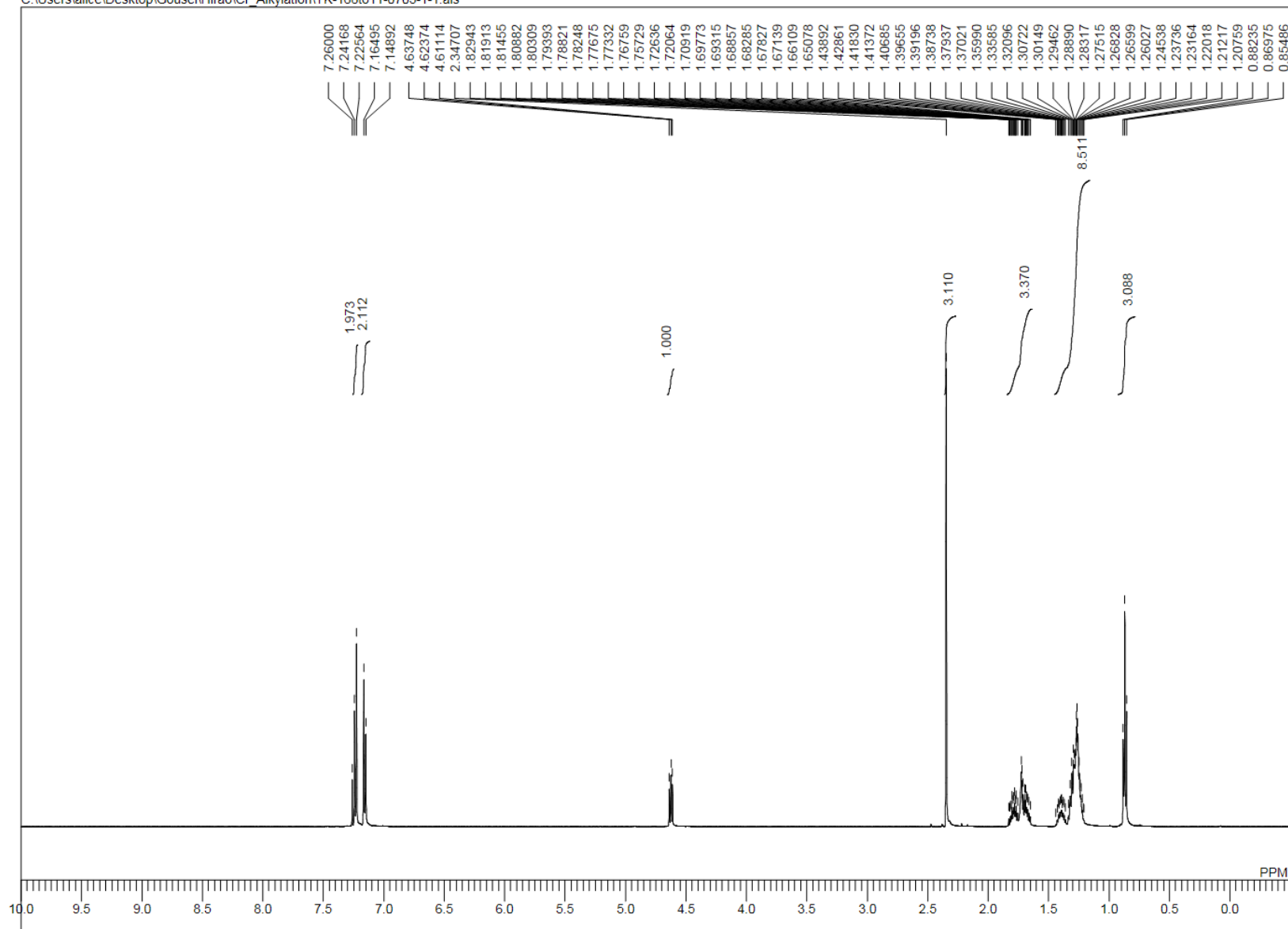


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

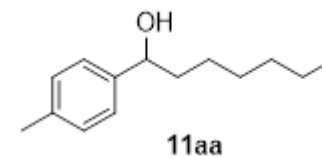


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YK-168to11-0703-1-1.als

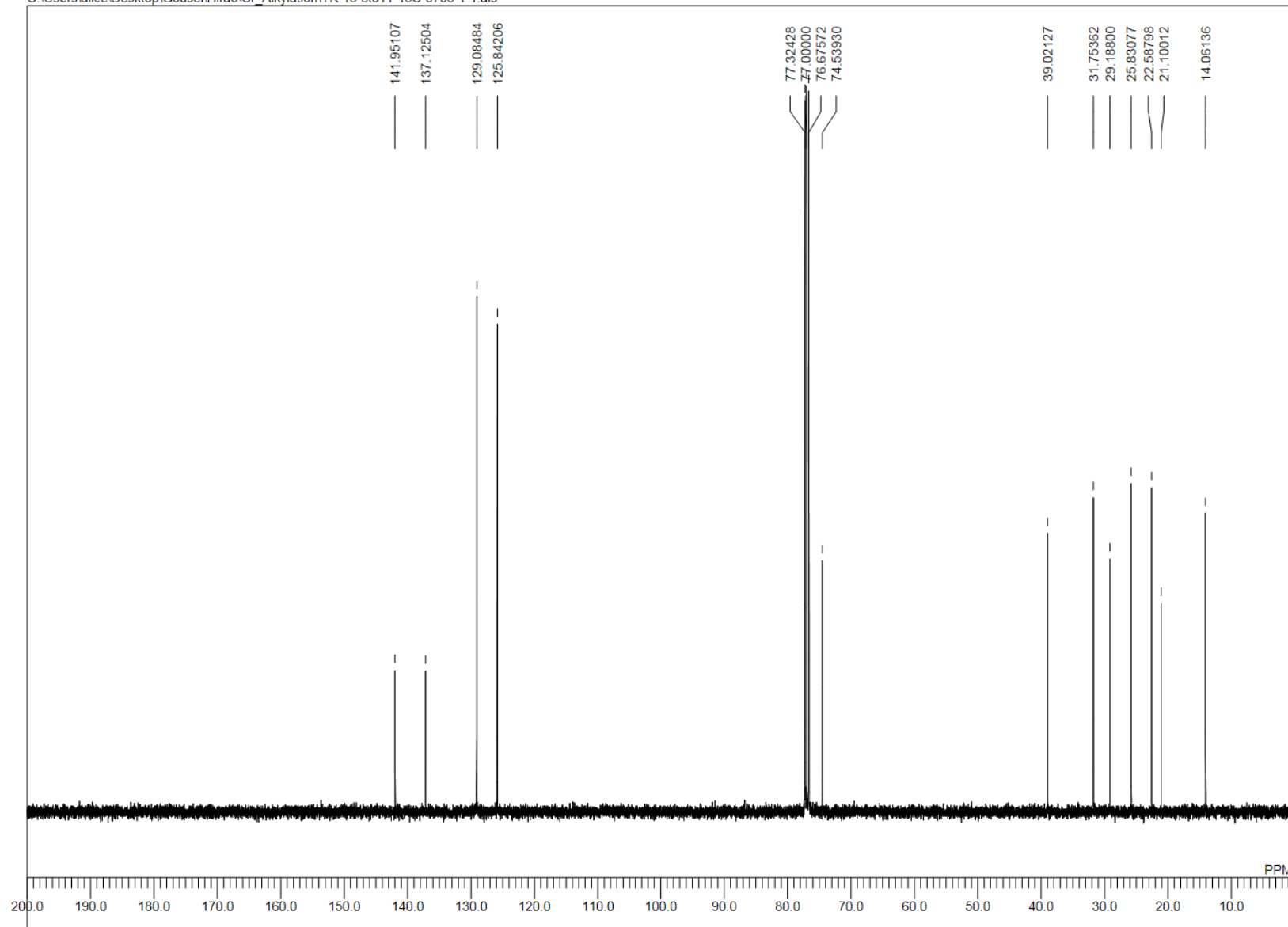


DFILE YK-168to11-0703-1-1.als  
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 DATIM 2020-07-03 14:27:36  
 OBNUC 1H  
 EXMOD proton.jxp  
 OBFRQ 500.16 MHz  
 OBSET 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 13107  
 FREQU 7507.51 Hz  
 SCANS 8  
 ACQTM 1.7459 sec  
 PD 6.0000 sec  
 PW1 5.55 usec  
 IRNUC 1H  
 CTEMP 21.8 c  
 SLVNT CDCL3  
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 40

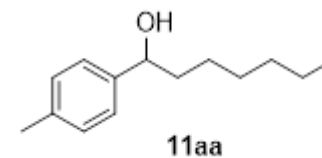


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

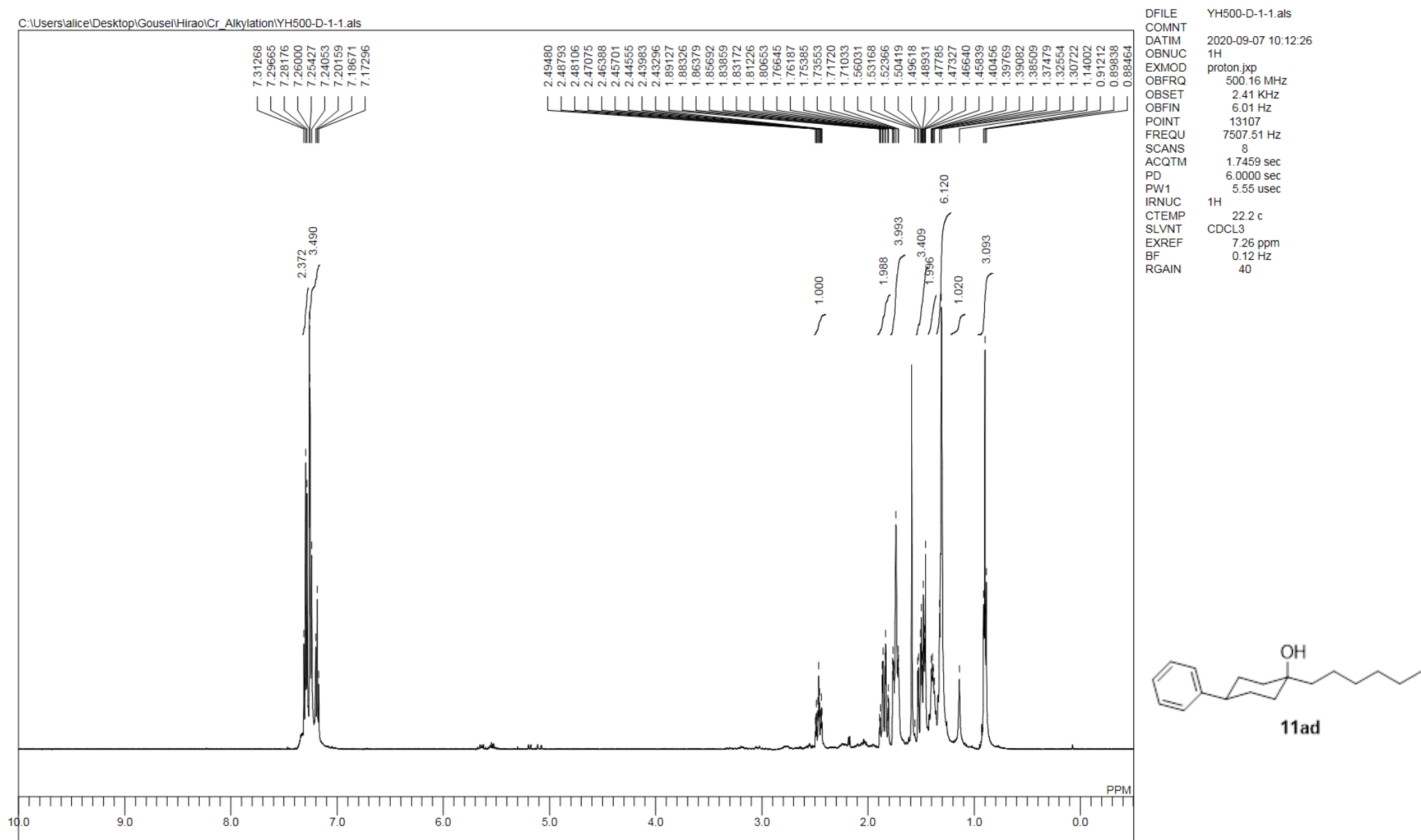
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DFILE YK-16-8to11-13C-0703-1-1.a  
COMNT  
DATIM 03-07-2020 16:53:17  
OBNUC 13C  
EXMOD carbon.jpg  
OBFRQ 98.52 MHz  
OBSET 4.64 KHz  
OBFIN 8.74 Hz  
POINT 26214  
FREQU 24630.54 Hz  
SCANS 340  
ACQTM 1.0643 sec  
PD 2.0000 sec  
PW1 3.12 usec  
IRNUC 1H  
CTEMP 21.1 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 0.52 Hz  
RGAIN 60



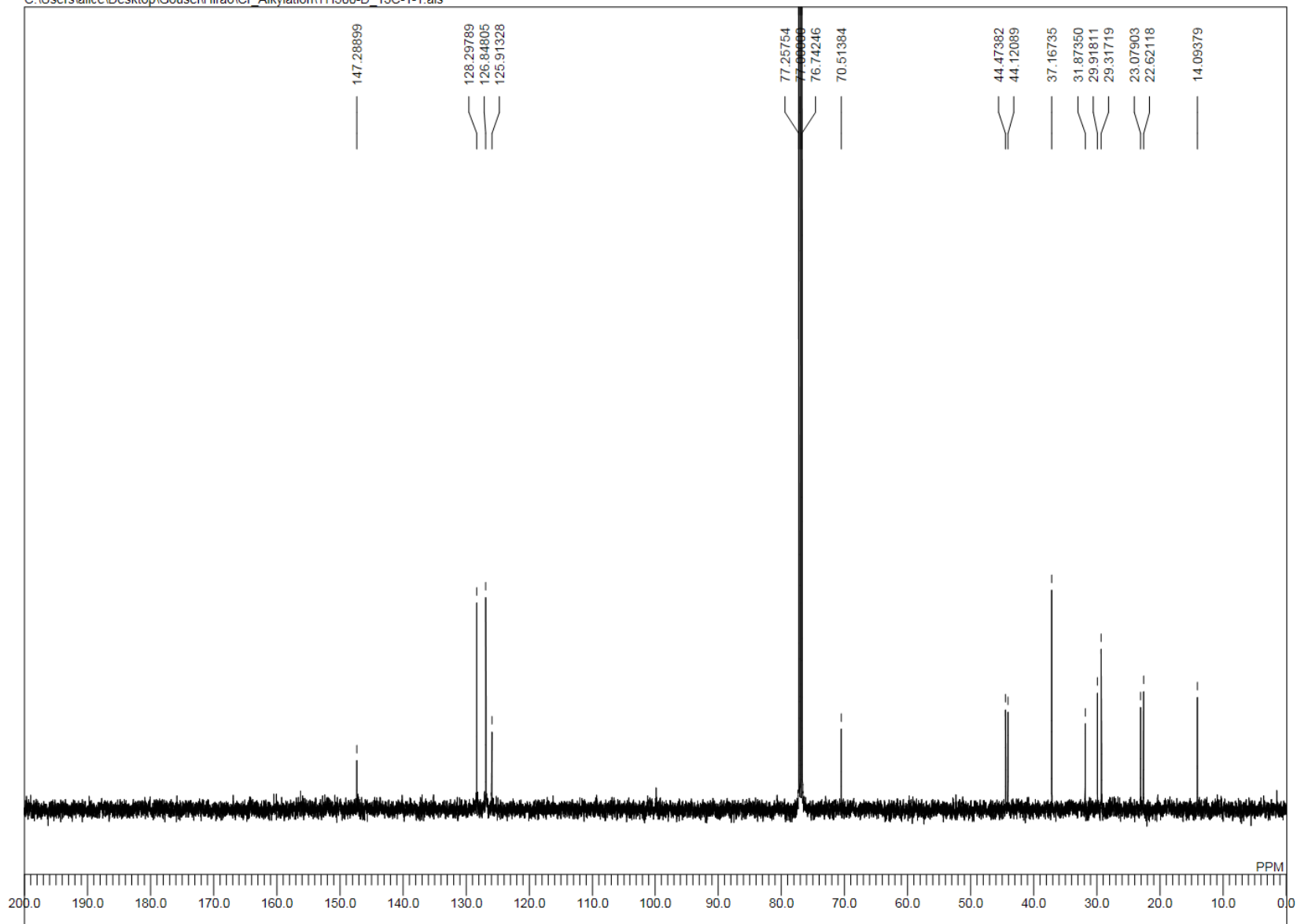
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )



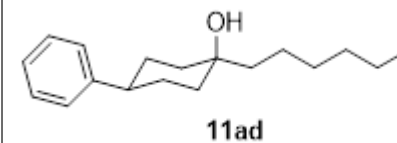


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

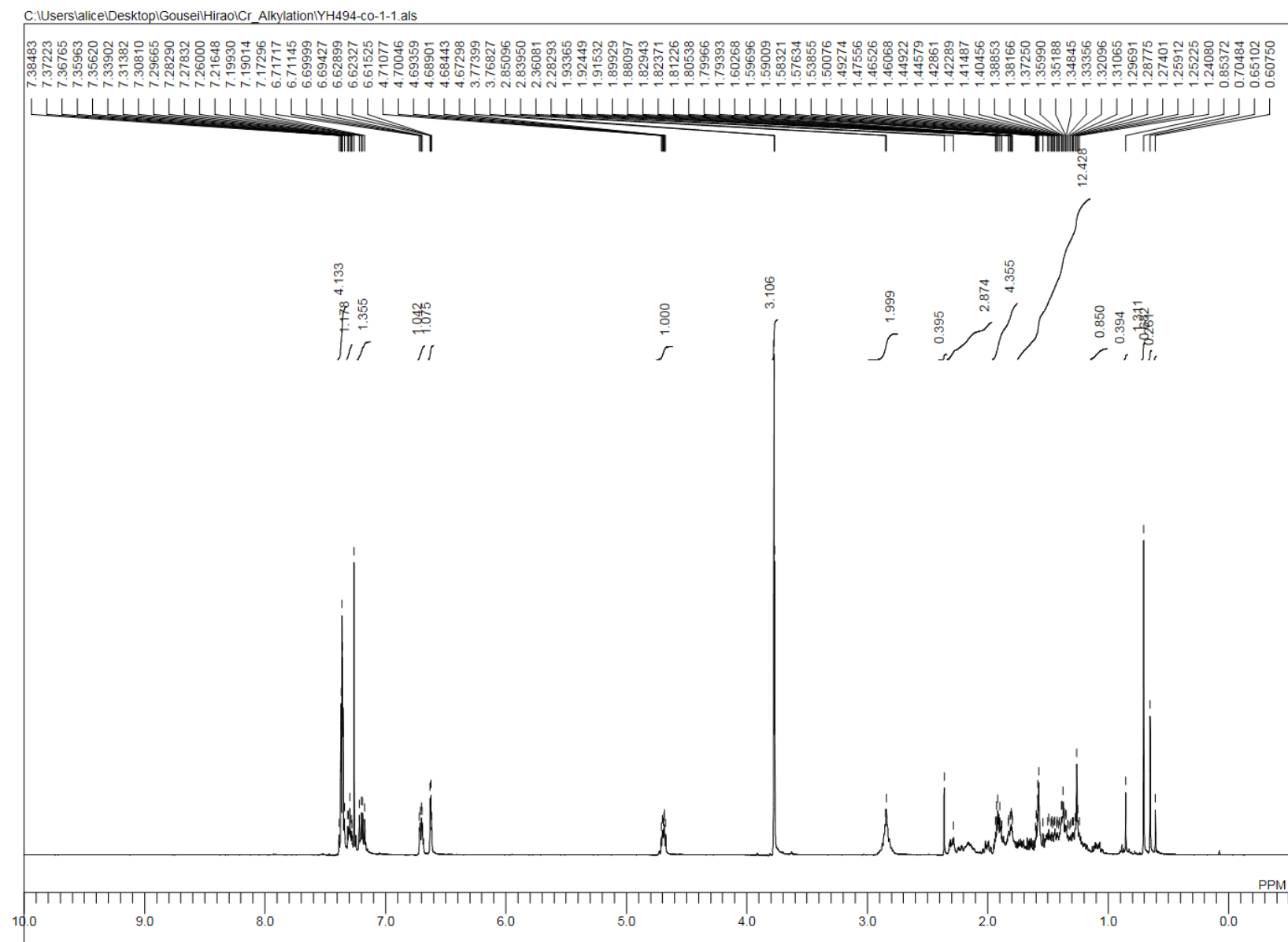
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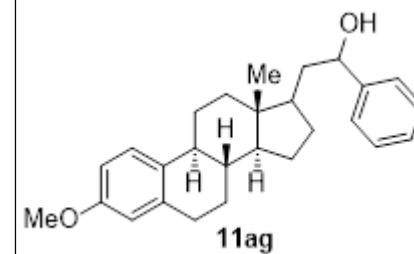
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OBNUC 13C  
EXMOD carbon.jpg  
OBFRQ 125.77 MHz  
OBSET 7.87 KHz  
OBFIN 4.21 Hz  
POINT 26214  
FREQU 31446.54 Hz  
SCANS 203  
ACQTM 0.8336 sec  
PD 2.0000 sec  
PW1 3.40 usec  
IRNUC 1H  
CTEMP 22.5 c  
SLVNT CDCl3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 60



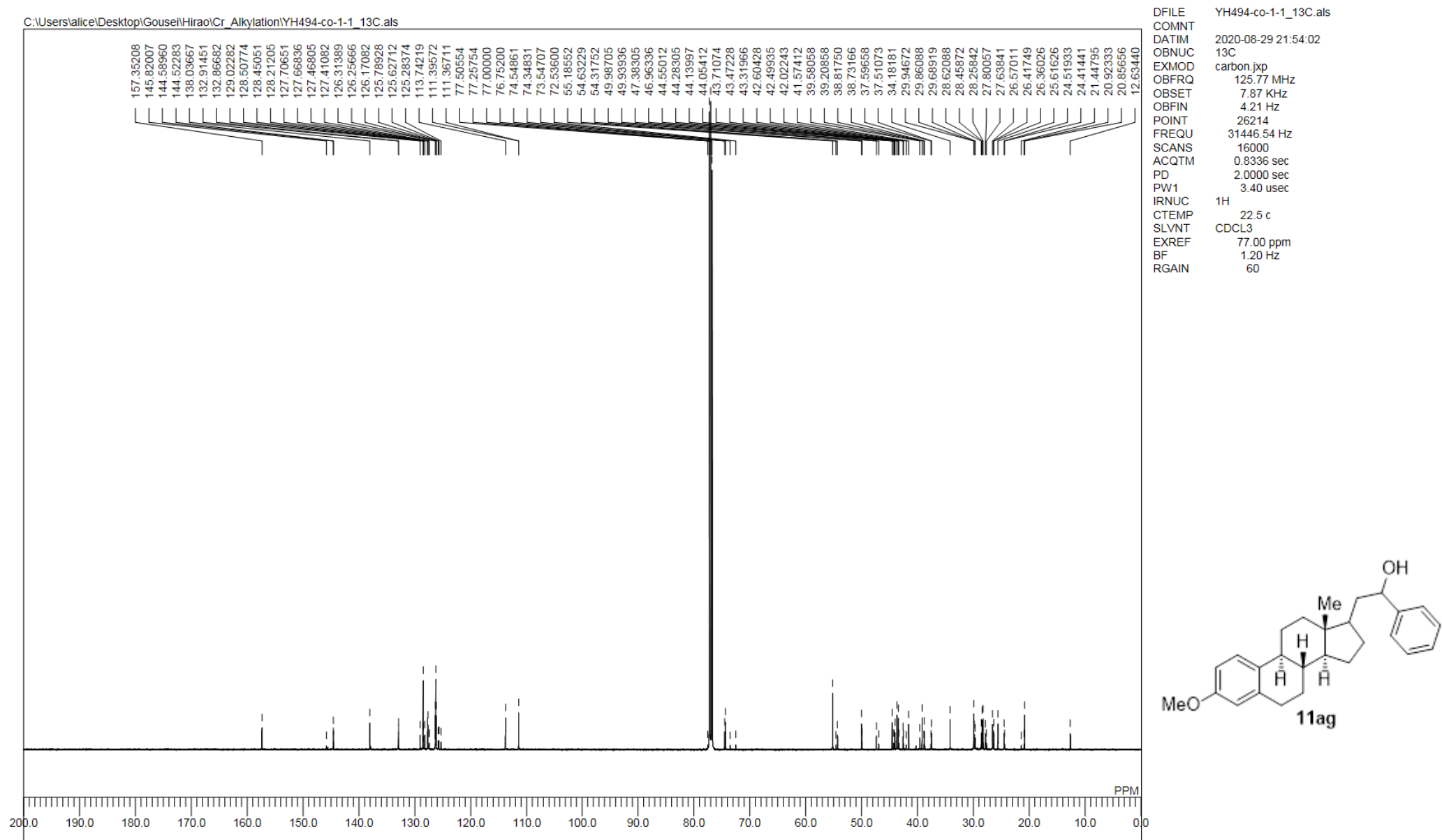
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )



DFILE YH494-co-1-1.als  
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 OBNUC 1H  
 EXMOD proton.jpg  
 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  
 IRNUC 1H  
 CTEMP 21.9 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 40

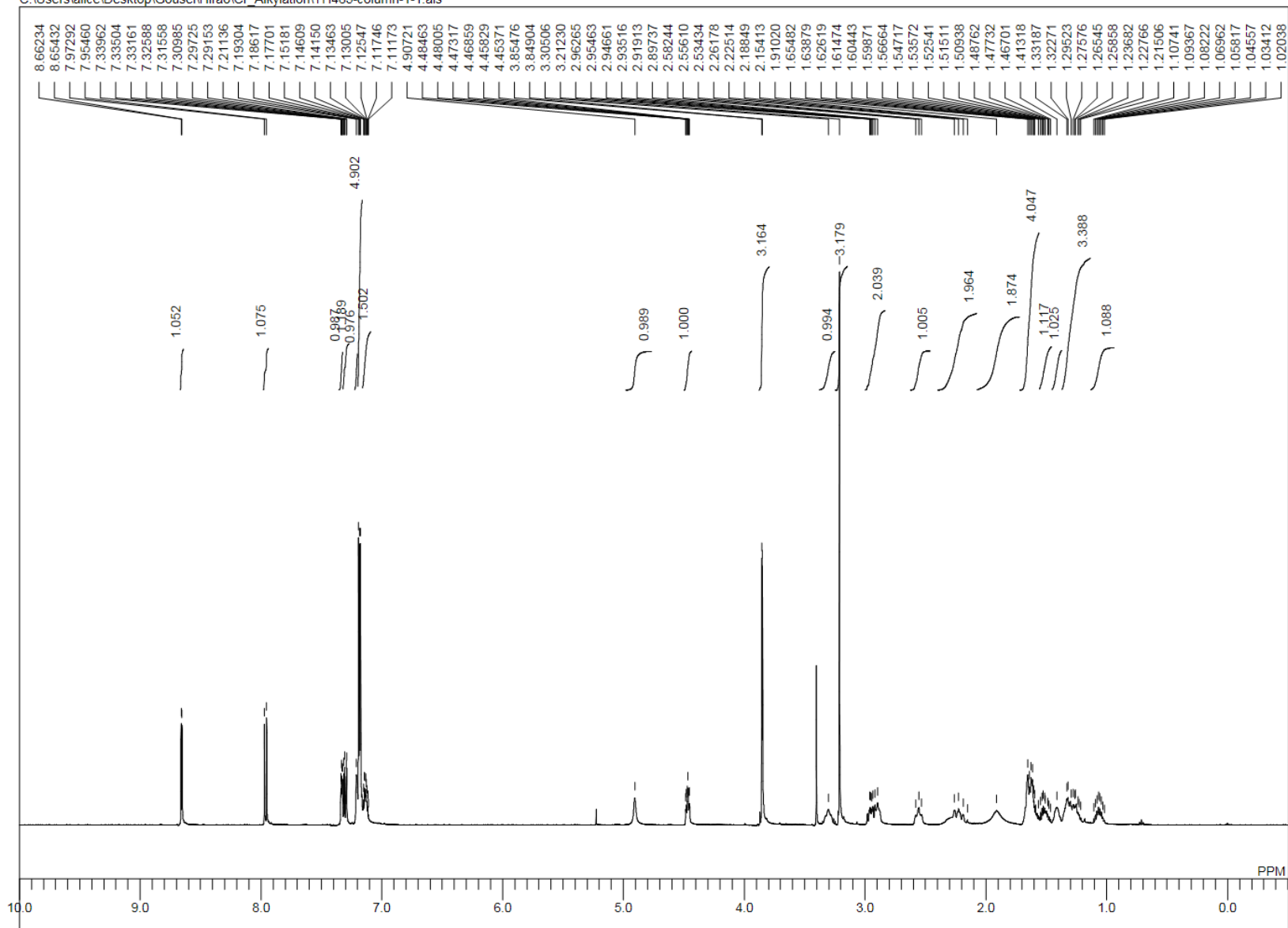


$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

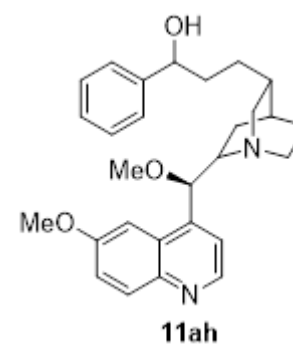


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

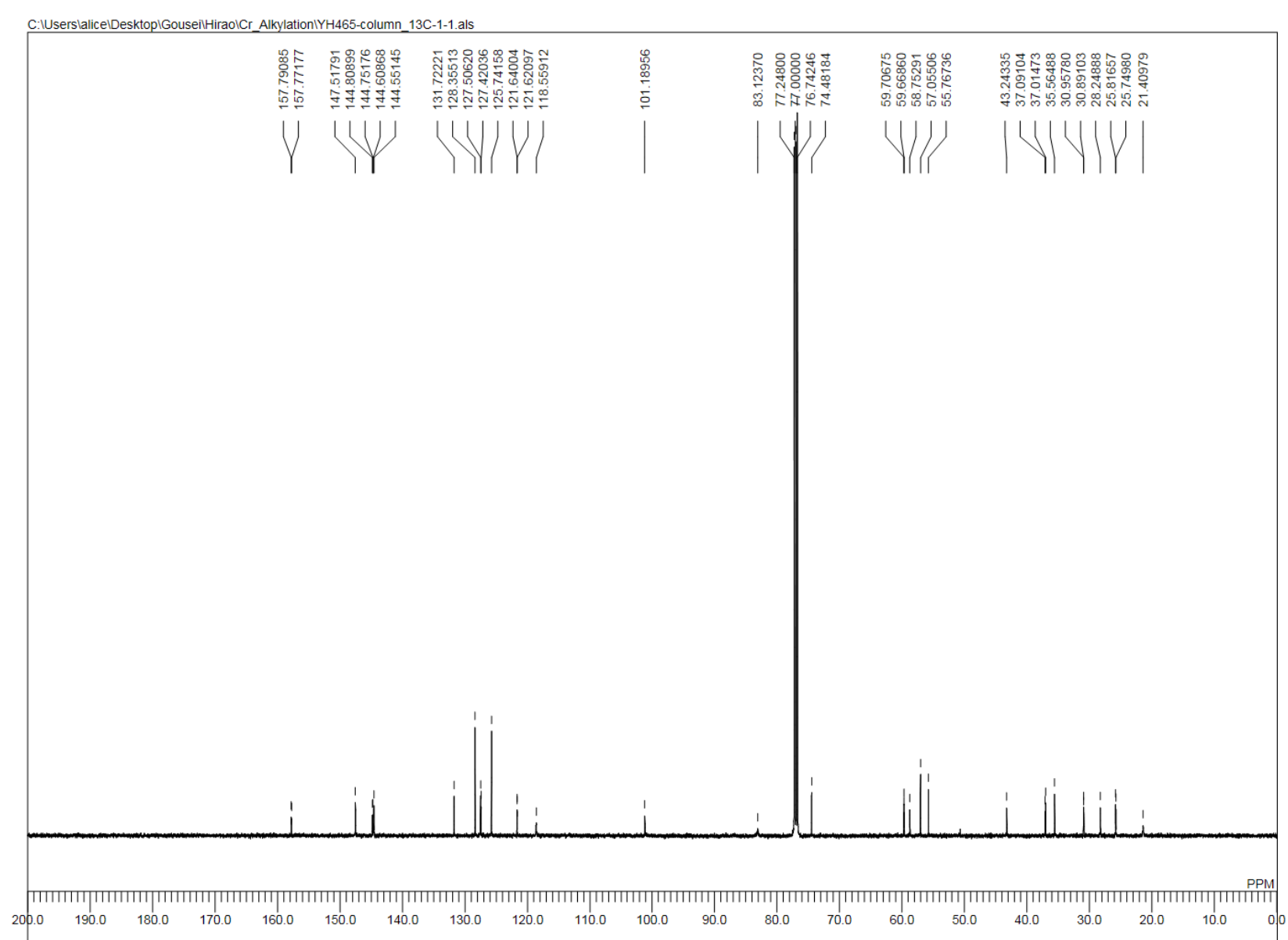
C:\Users\alice\Desktop\Gousei\Hirao\Cr Alkylation\YH465-column-1-1.als



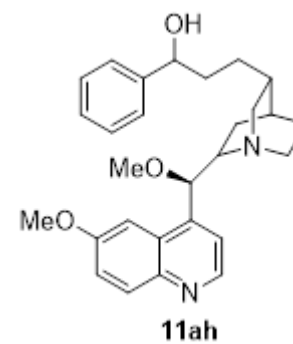
DFILE YH465-column-1-1.als  
 COMNT 2020-07-27 16:33:44  
 DATIM 1H  
 OBNUC proton.jpg  
 EXMOD 500.16 MHz  
 OBFRQ 2.41 KHz  
 OBSET 6.01 Hz  
 OBFIN 13107  
 POINT 7507.51 Hz  
 FREQU 8  
 SCANS 1.7459 sec  
 ACQTM 6.0000 sec  
 PD 5.55 usec  
 PW1 1H  
 IRNUC 21.5 c  
 CTEMP CDCL3  
 SLVNT 0.00 ppm  
 EXREF 0.12 Hz  
 BF 40  
 RGAIN



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

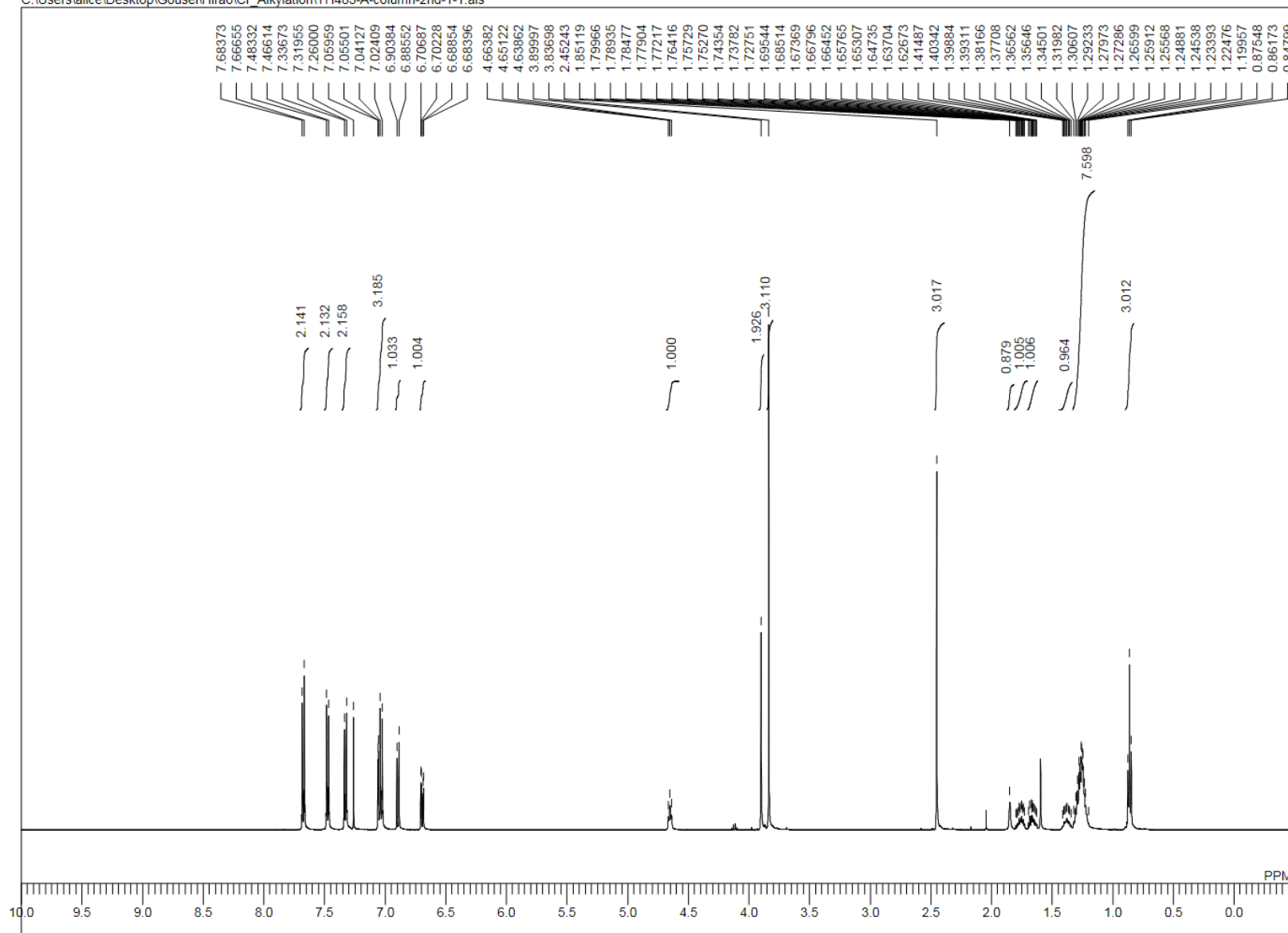


DFILE YH465-column\_13C-1-1.als  
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DATIM 2020-07-27 16:35:33  
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EXMOD carbon.jpg  
OBFRQ 125.77 MHz  
OBSET 7.87 KHz  
OBFIN 4.21 Hz  
POINT 26214  
FREQU 31446.54 Hz  
SCANS 2259  
ACQTM 0.8336 sec  
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

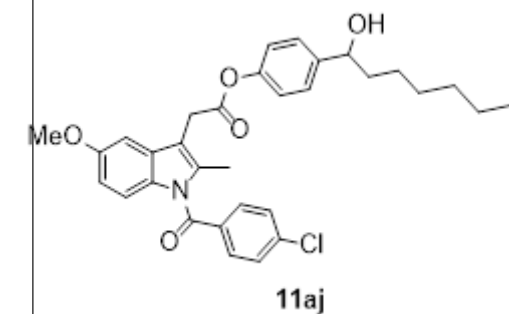


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH483-A-column-2nd-1-1.als

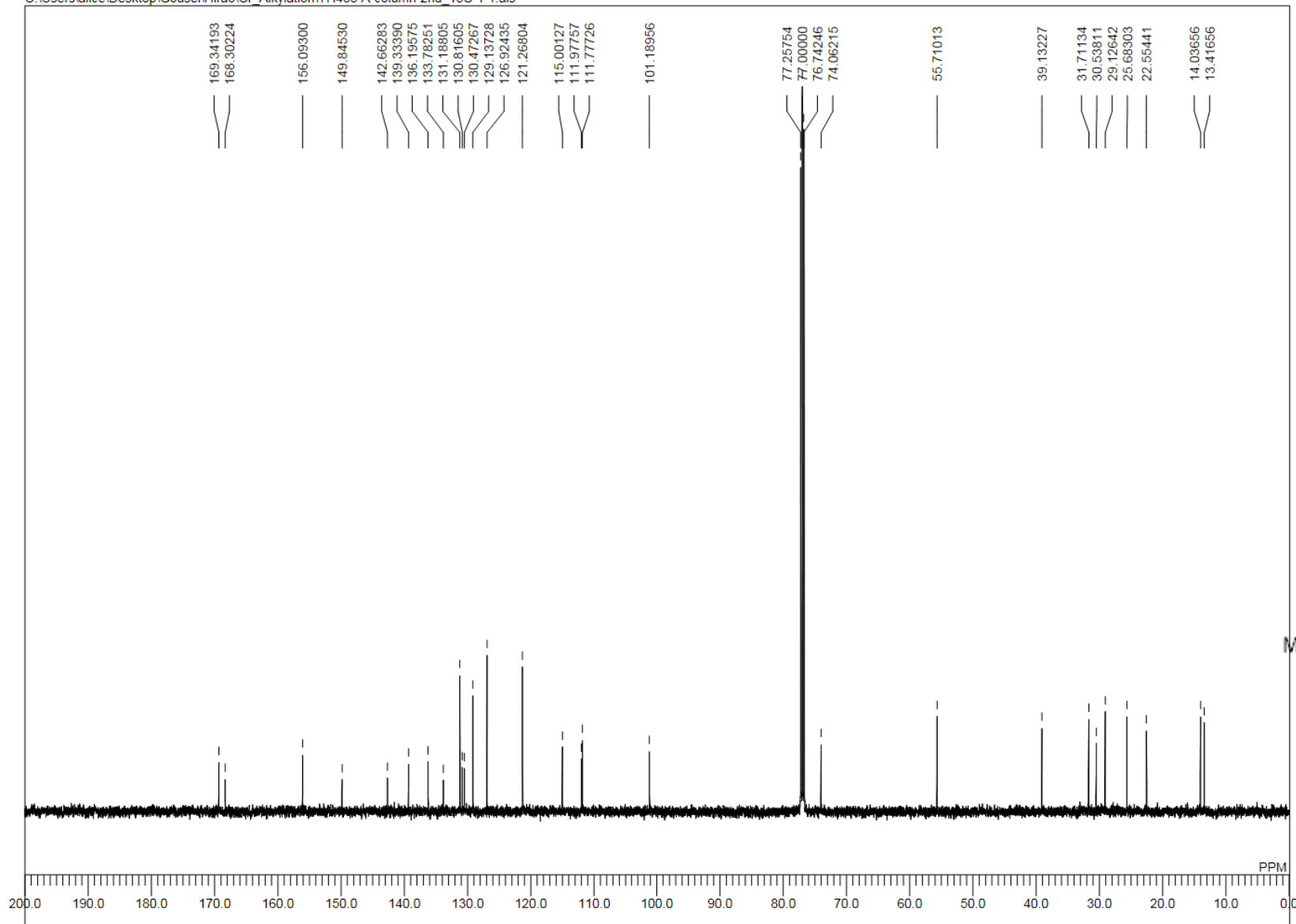


DFILE YH483-A-column-2nd-1-1.al  
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 DATIM 2020-08-08 20:36:59  
 OBNUC 1H  
 EXMOD proton.jpg  
 OBFRQ 500.16 MHz  
 OBSET 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 13107  
 FREQU 7507.51 Hz  
 SCANS 8  
 ACQTM 1.7459 sec  
 PD 6.0000 sec  
 PW1 5.55 usec  
 IRNUC 1H  
 CTEMP 21.7 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 40

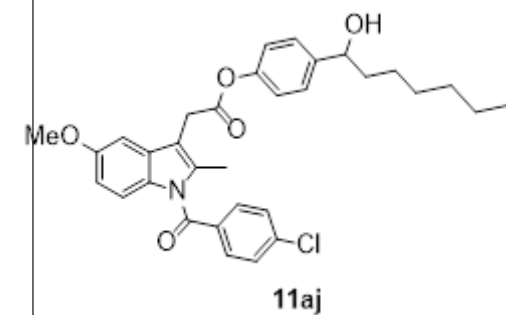


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

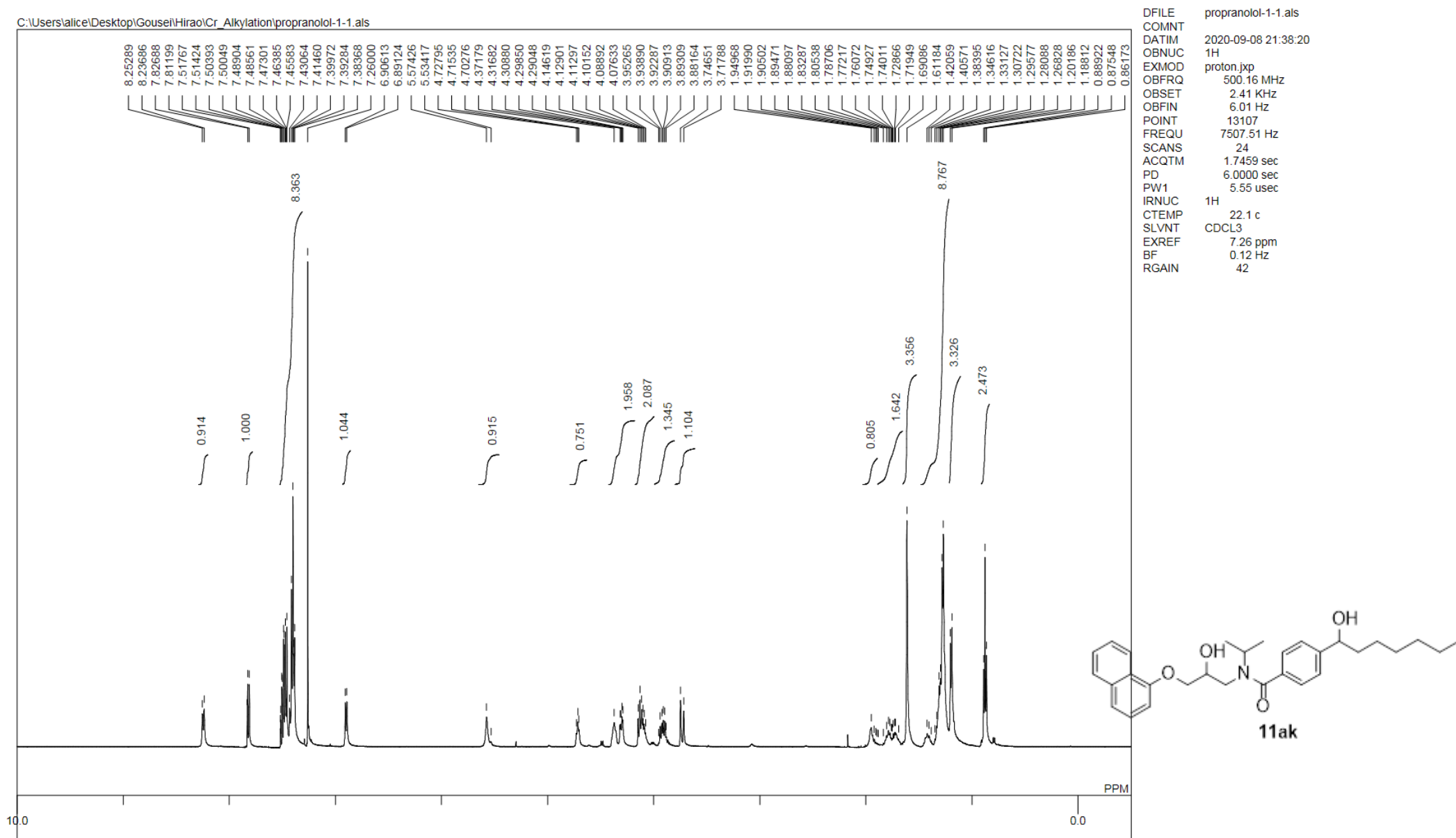
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DFILE YH483-A-column-2nd\_13C-1  
COMNT  
DATIM 2020-08-08 20:39:05  
OBNUC 13C  
EXMOD carbon.jpg  
OBFRQ 125.77 MHz  
OBSET 7.87 KHz  
OBFIN 4.21 Hz  
POINT 26214  
FREQU 31446.54 Hz  
SCANS 267  
ACQTM 0.8336 sec  
PD 2.0000 sec  
PW1 3.40 usec  
IRNUC 1H  
CTEMP 22.1 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 60

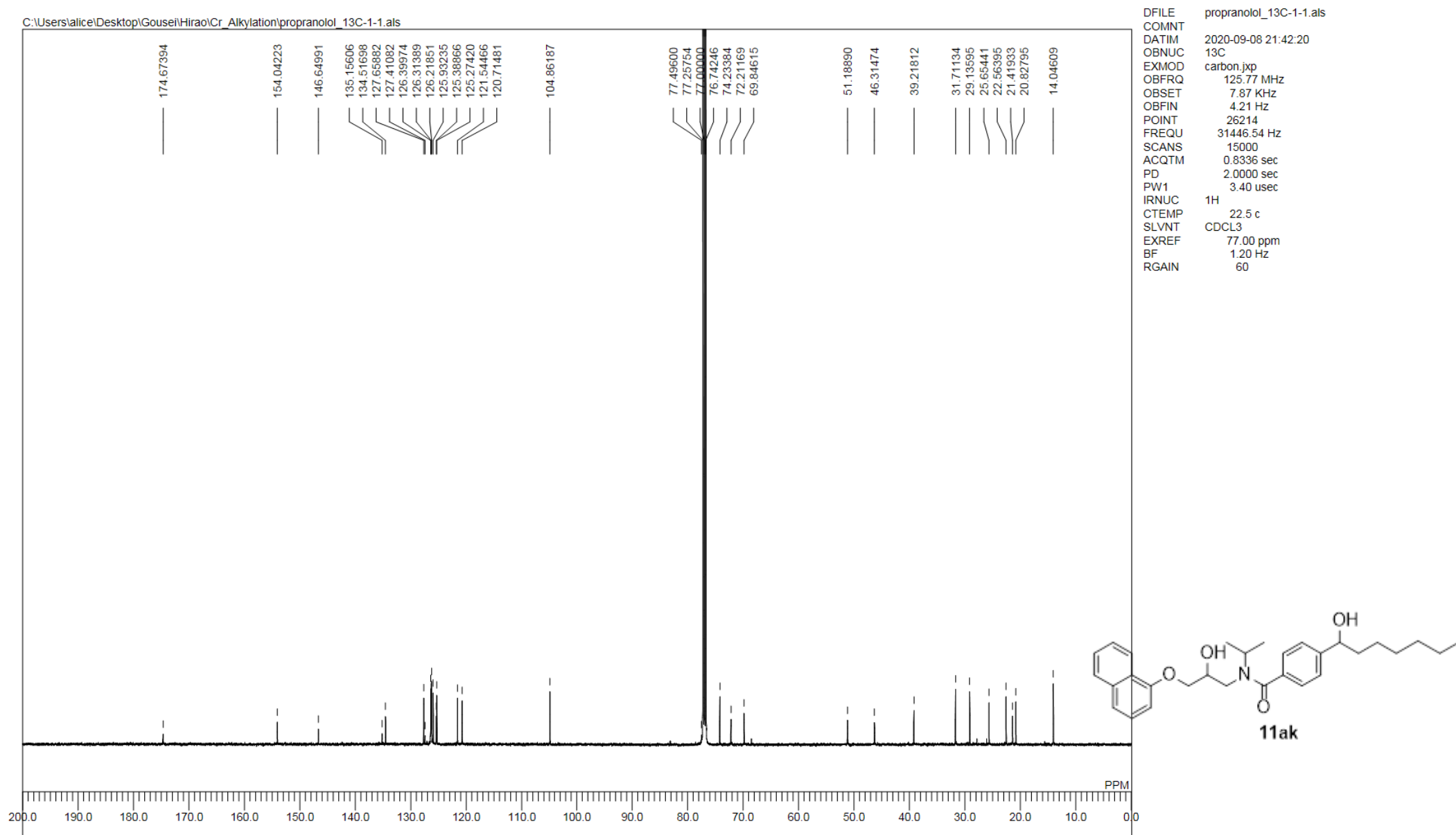


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )



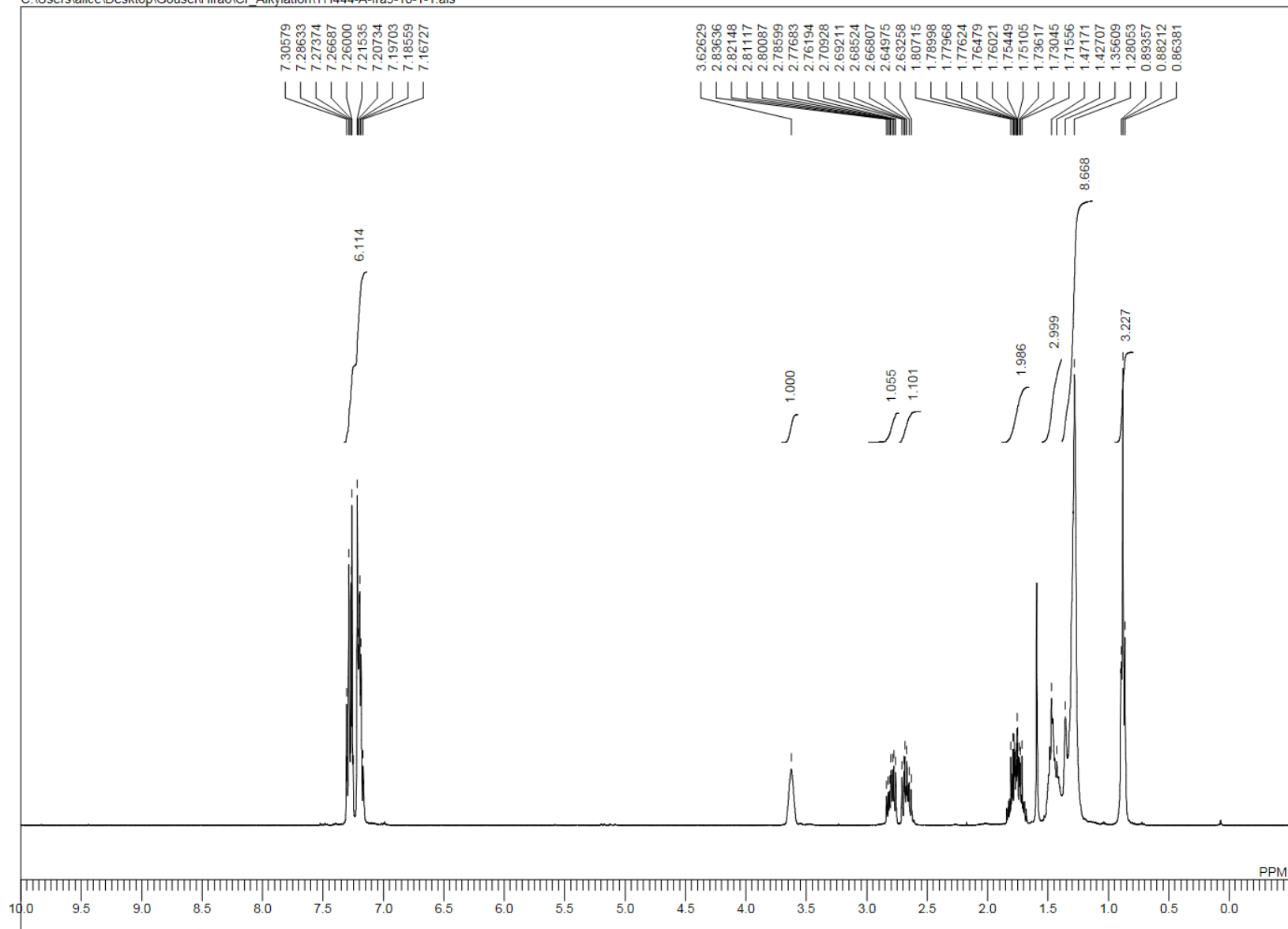


$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

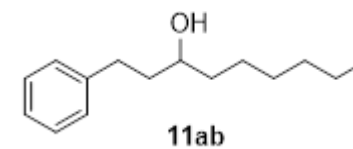


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH444-A-fra9-10-1-1.als

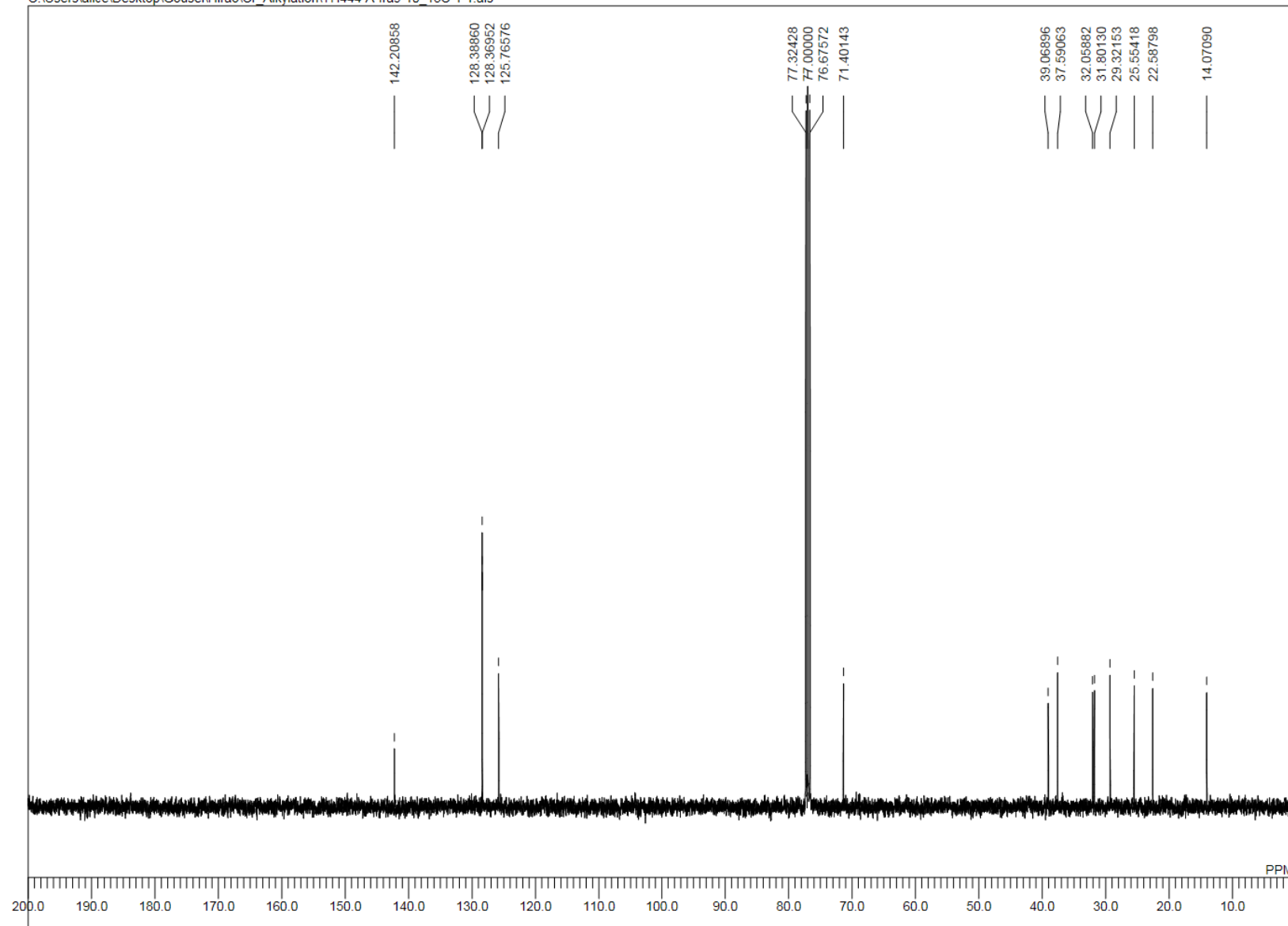


DFILE YH444-A-fra9-10-1-1.als  
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EXMOD proton.jpg  
OBFRQ 391.78 MHz  
OBSET 8.51 KHz  
OBFIN 3.34 Hz  
POINT 13107  
FREQU 5878.90 Hz  
SCANS 8  
ACQTM 2.2295 sec  
PD 6.0000 sec  
PW1 5.17 usec  
IRNUC 1H  
CTEMP 21.0 c  
SLVNT CDCL3  
EXREF 7.26 ppm  
BF 0.12 Hz  
RGAIN 38

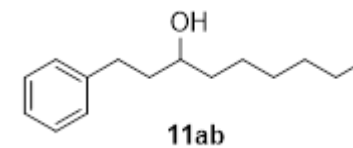


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH444-A-fra9-10\_13C-1-1.als

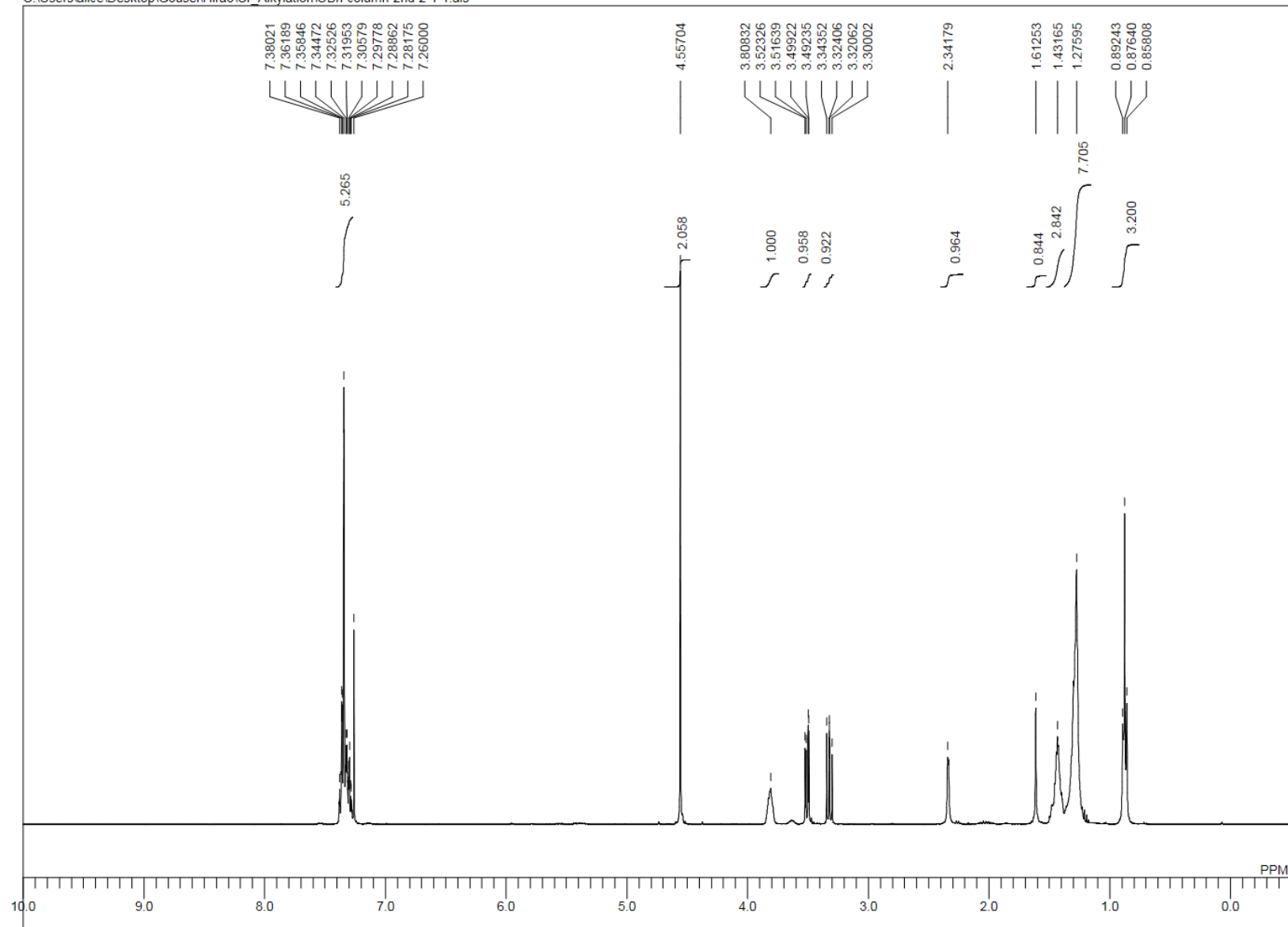


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DATIM 08-07-2020 19:44:35  
OBNUC 13C  
EXMOD carbon.jpg  
OBFRQ 98.52 MHz  
OBSET 4.64 KHz  
OBFIN 8.74 Hz  
POINT 26214  
FREQU 24630.54 Hz  
SCANS 150  
ACQTM 1.0643 sec  
PD 2.0000 sec  
PW1 3.12 usec  
IRNUC 1H  
CTEMP 21.2 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 60

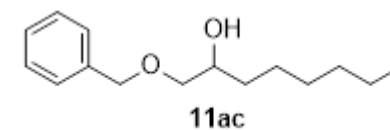


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

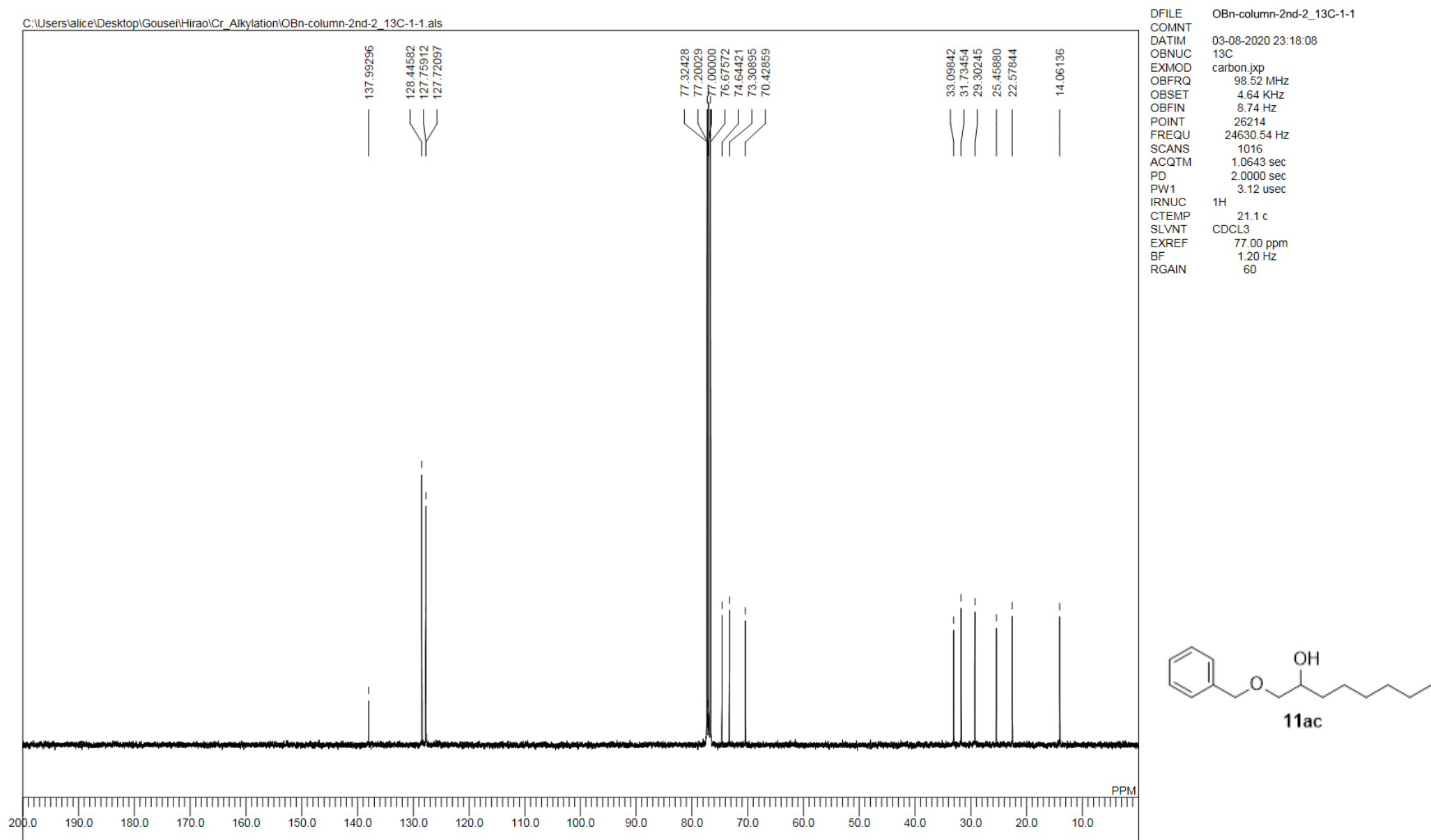
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DFILE OBn-column-2nd-2-1-1.als  
 COMNT  
 DATIM 03-08-2020 23:15:16  
 OBNUC  $^1\text{H}$   
 EXMOD proton.jxp  
 OBFRQ 391.78 MHz  
 OBSET 8.51 KHz  
 OBFIN 3.34 Hz  
 POINT 13107  
 FREQU 5878.90 Hz  
 SCANS 8  
 ACQTM 2.2295 sec  
 PD 6.0000 sec  
 PW1 5.17 usec  
 IRNUC  $^1\text{H}$   
 CTEMP 20.6 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 36

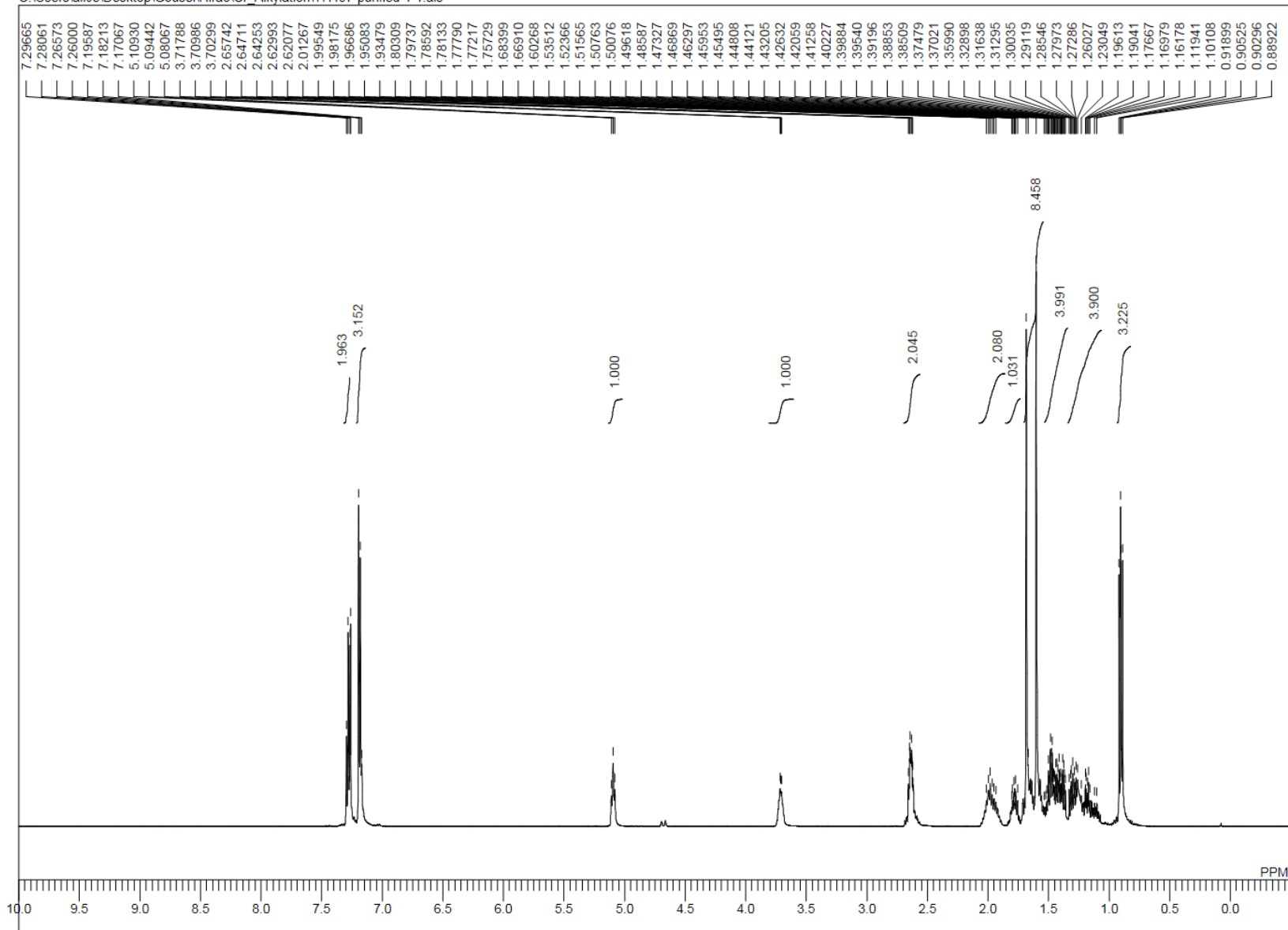


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

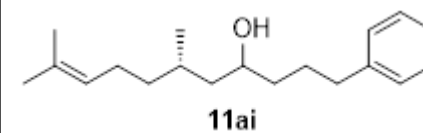


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

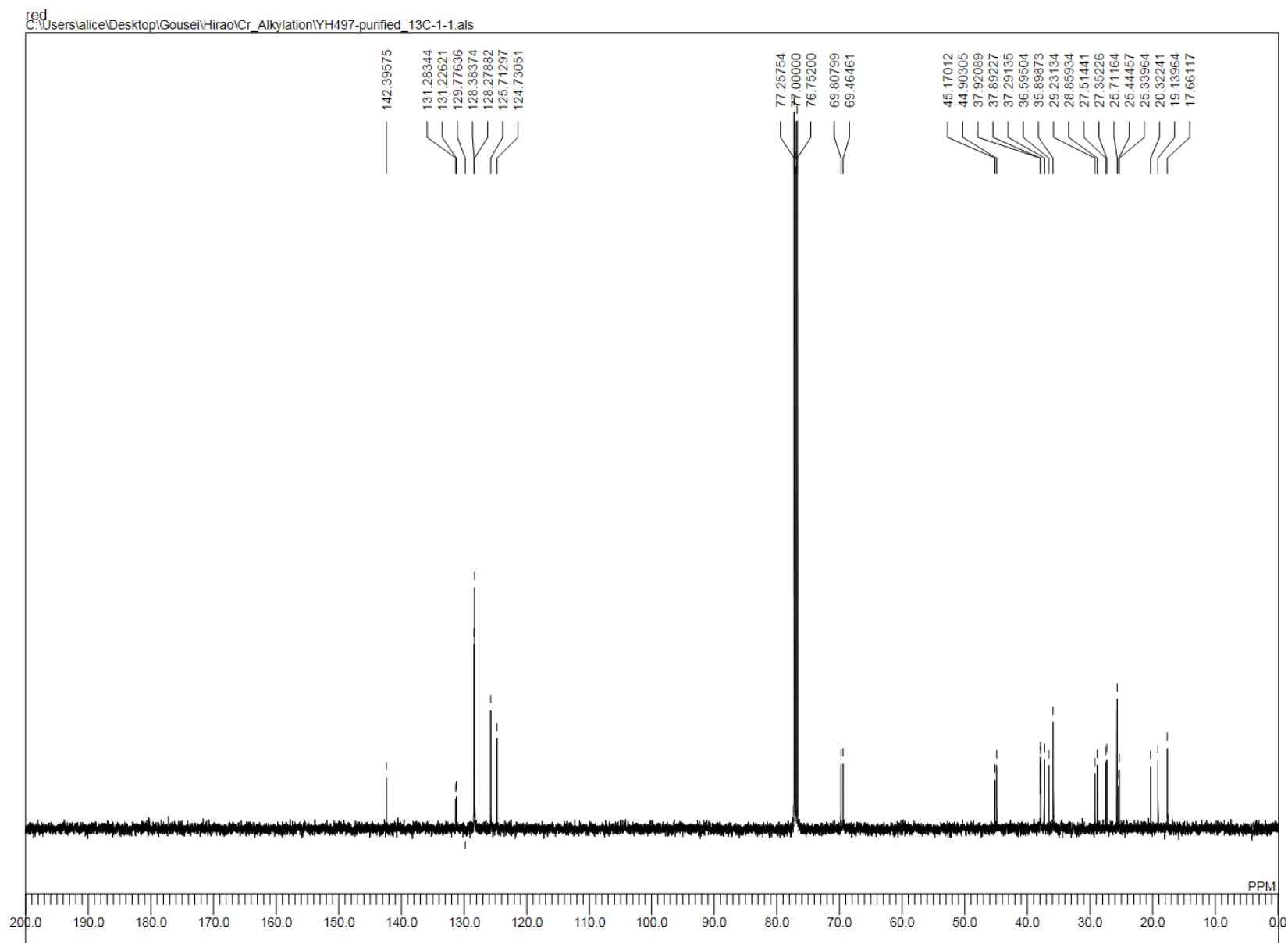
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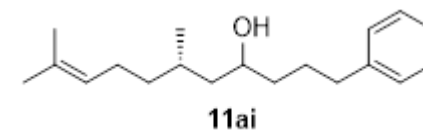
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 COMNT  
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 OBNUC  $^1\text{H}$   
 EXMOD proton.jxp  
 OBFRQ 500.16 MHz  
 OBSET 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 13107  
 FREQU 7507.51 Hz  
 SCANS 8  
 ACQTM 1.7459 sec  
 PD 6.0000 sec  
 PW1 5.55 usec  
 IRNUC  $^1\text{H}$   
 CTEMP 21.7 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 40



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

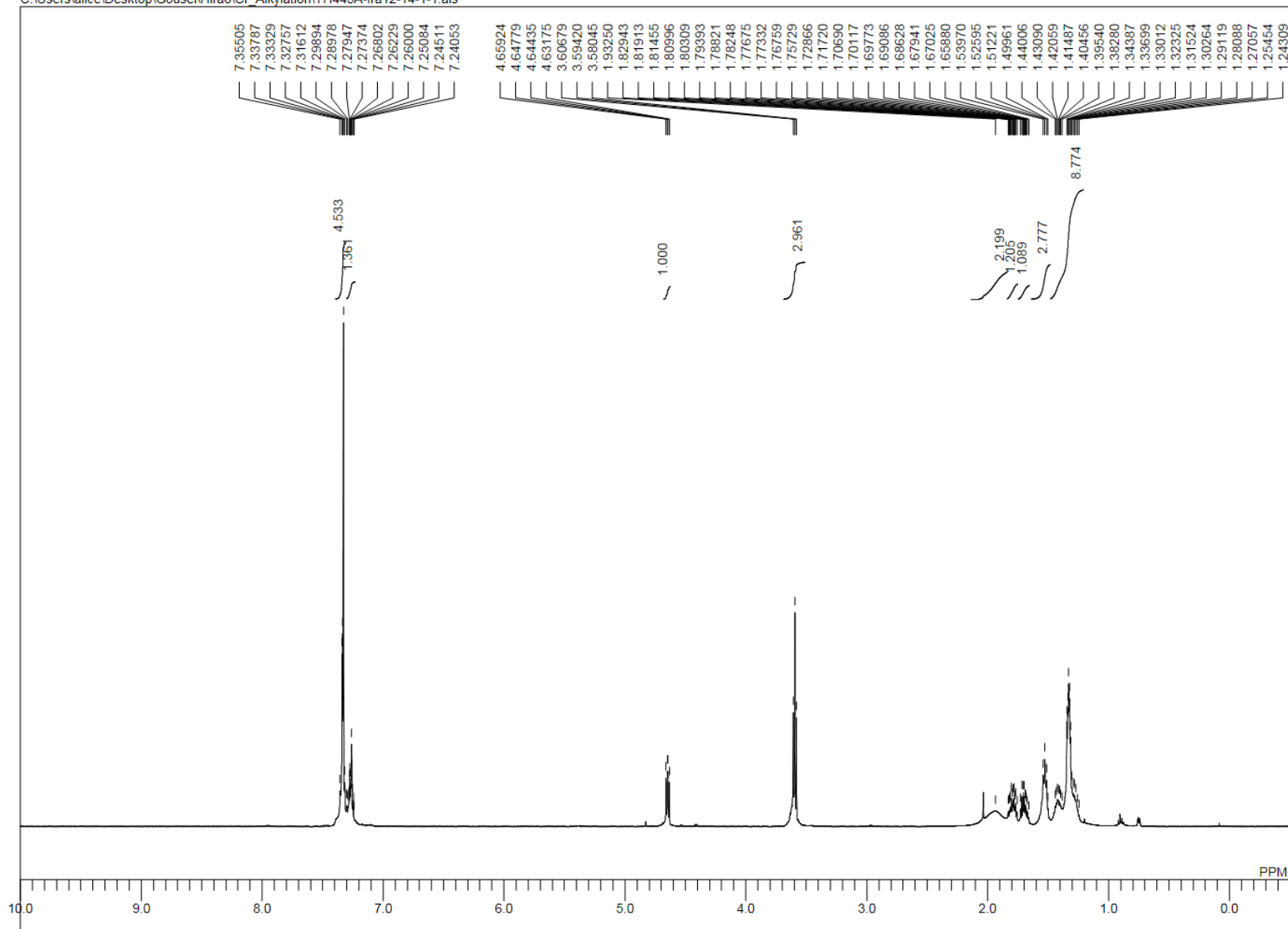


DFILE YH497-purified\_13C-1-1.als  
COMNT red  
DATIM 2020-09-01 18:01:28  
OBNUC 13C  
EXMOD carbon.jpg  
OBFREQ 125.77 MHz  
OBSET 7.87 KHz  
OBFIN 4.21 Hz  
POINT 26214  
FREQU 31446.54 Hz  
SCANS 213  
ACQTM 0.8336 sec  
PD 2.0000 sec  
PW1 3.40 usec  
IRNUC 1H  
CTEMP 22.3 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 60

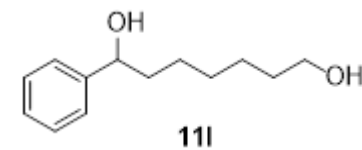


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Alkylation\YH445A-fra12-14-1-1.als

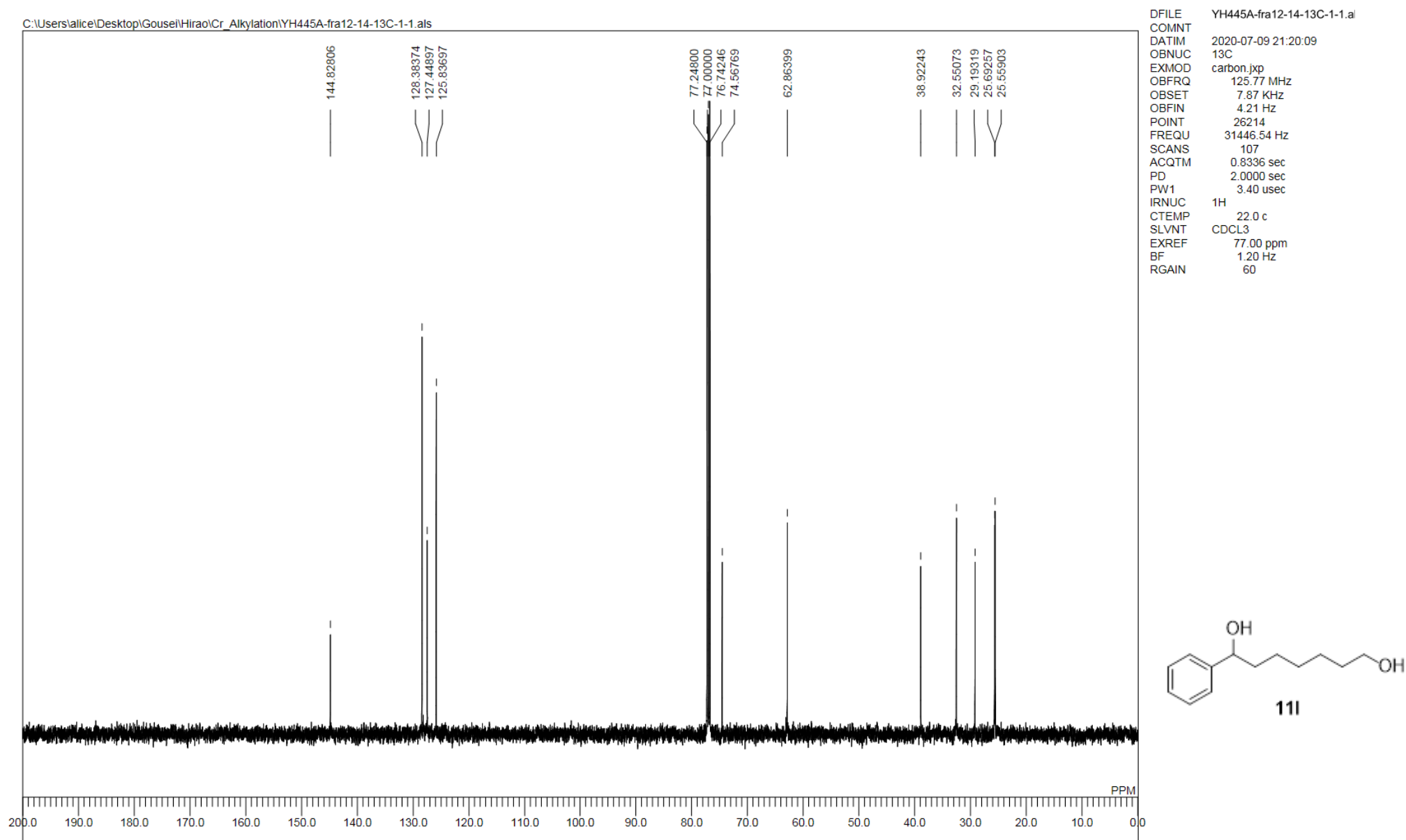


DFILE YH445A-fra12-14-1-1.als  
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 DATIM 2020-07-09 21:18:15  
 OBNUC  $^1\text{H}$   
 EXMOD proton.jxp  
 OBFREQ 500.16 MHz  
 OBSET 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 13107  
 FREQU 7507.51 Hz  
 SCANS 8  
 ACQTM 1.7459 sec  
 PD 6.0000 sec  
 PW1 5.55 usec  
 IRNUC  $^1\text{H}$   
 CTEMP 21.9 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 38



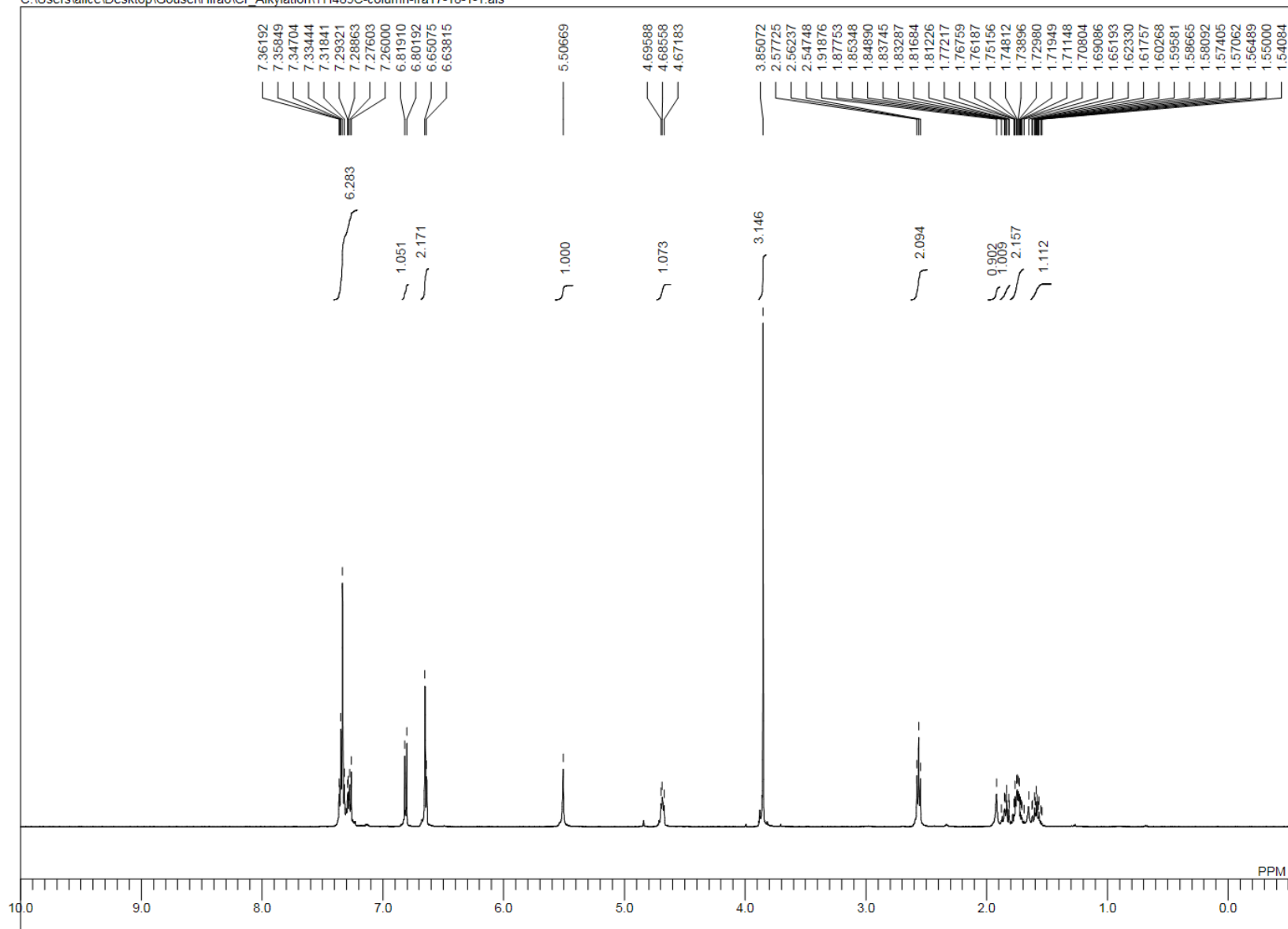


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

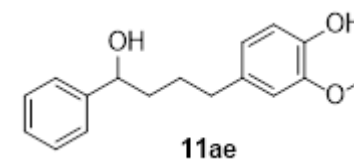


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

C:\Users\alice\Desktop\Gousei\Hirao\Cr\_Akylation\YH489C-column-fra17-18-1-1.als

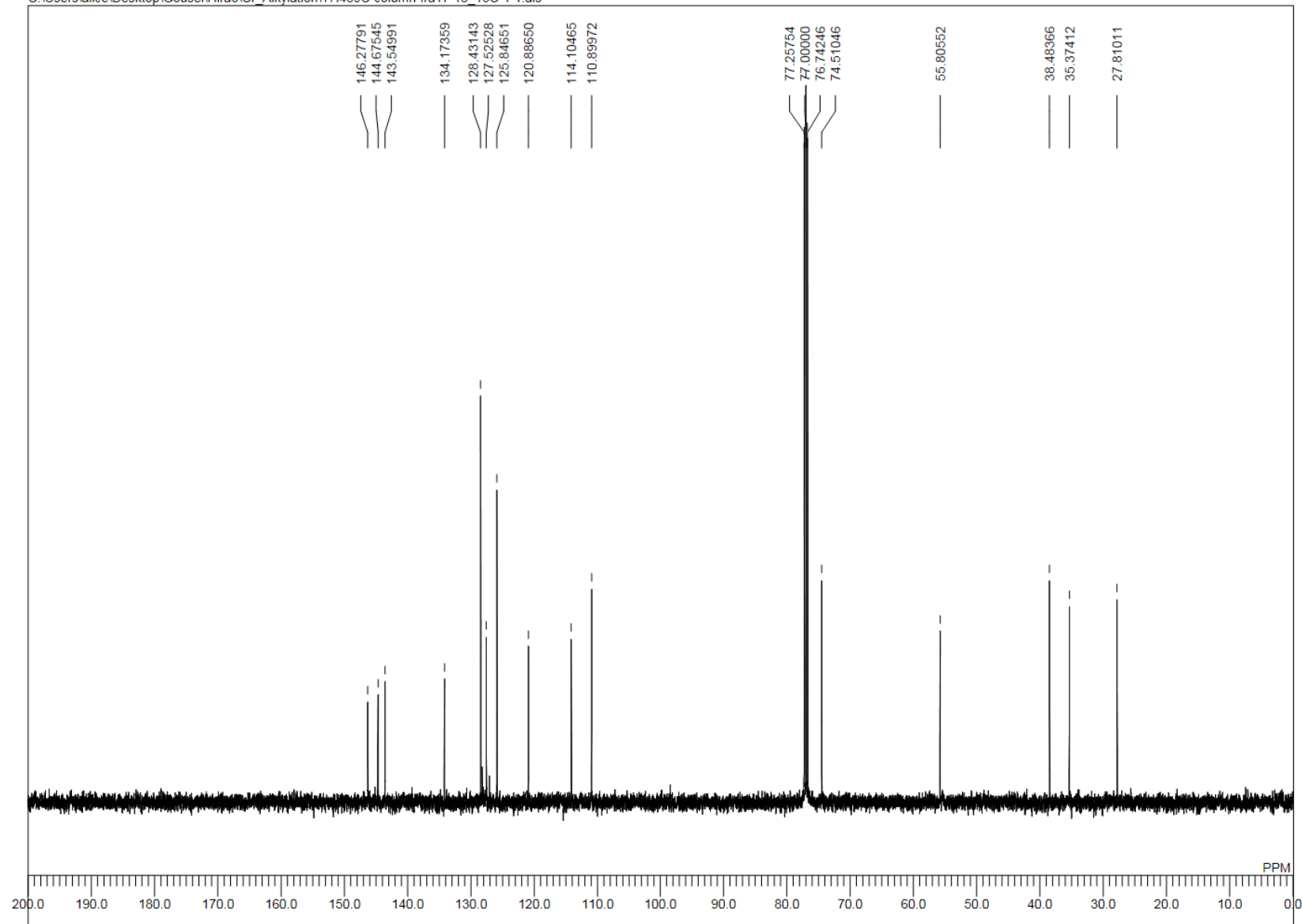


DFILE YH489C-column-fra17-18-1-  
 COMNT  
 DATIM 2020-08-21 10:05:41  
 OBNUC  $^1\text{H}$   
 EXMOD proton.jxp  
 OBFRQ 500.16 MHz  
 OBSET 2.41 KHz  
 OBFIN 6.01 Hz  
 POINT 13107  
 FREQU 7507.51 Hz  
 SCANS 8  
 ACQTM 1.7459 sec  
 PD 6.0000 sec  
 PW1 5.55 usec  
 IRNUC  $^1\text{H}$   
 CTEMP 22.0 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 38

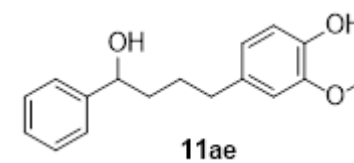


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

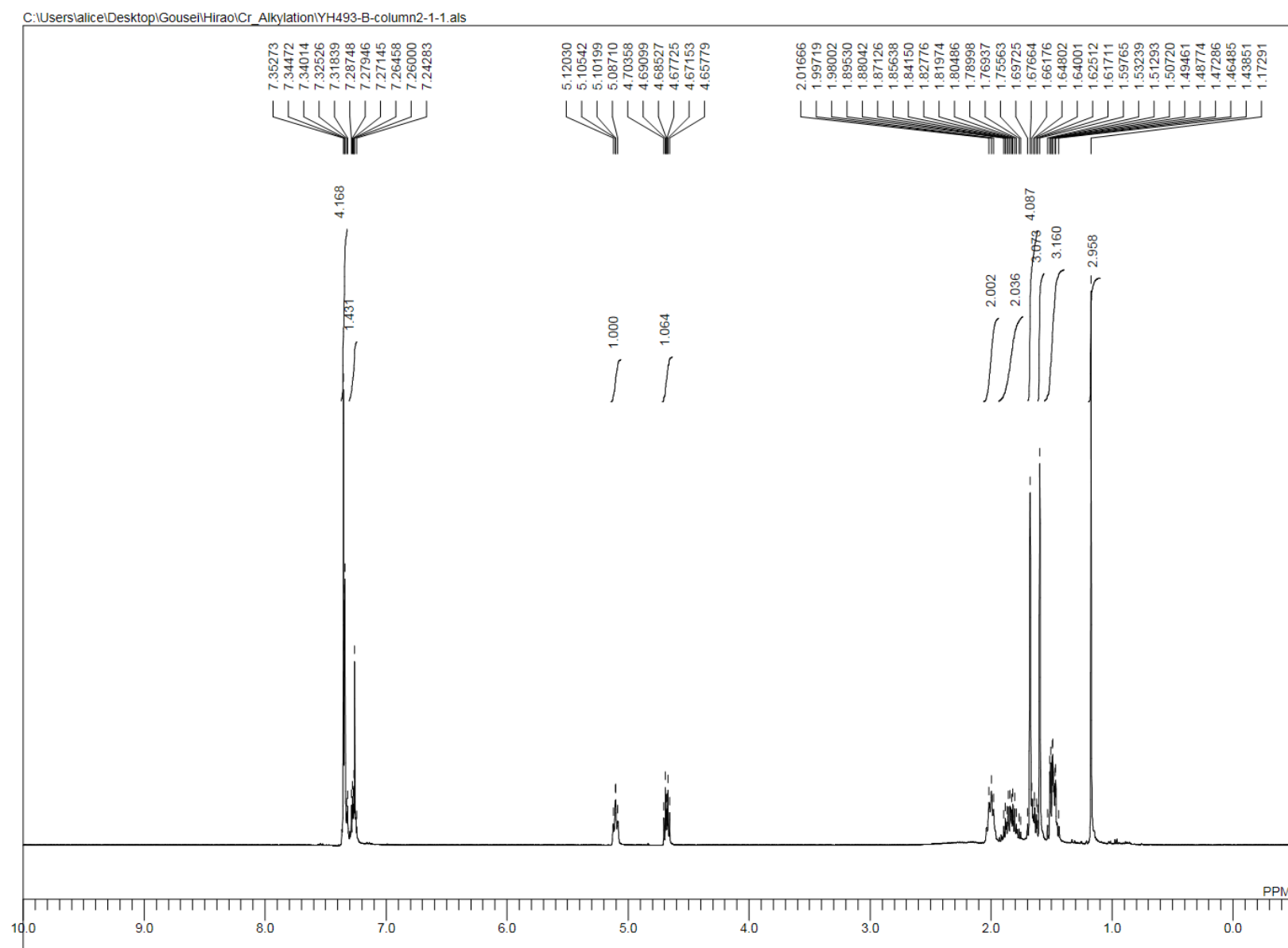
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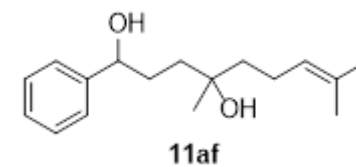
DFILE YH489C-column-fra17-18\_1  
COMNT  
DATIM 2020-08-21 10:07:28  
OBNUC 13C  
EXMOD carbon.jpg  
OBFRQ 125.77 MHz  
OBSET 7.87 KHz  
OBFIN 4.21 Hz  
POINT 26214  
FREQU 31446.54 Hz  
SCANS 104  
ACQTM 0.8336 sec  
PD 2.0000 sec  
PW1 3.40 usec  
IRNUC 1H  
CTEMP 22.2 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 60



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

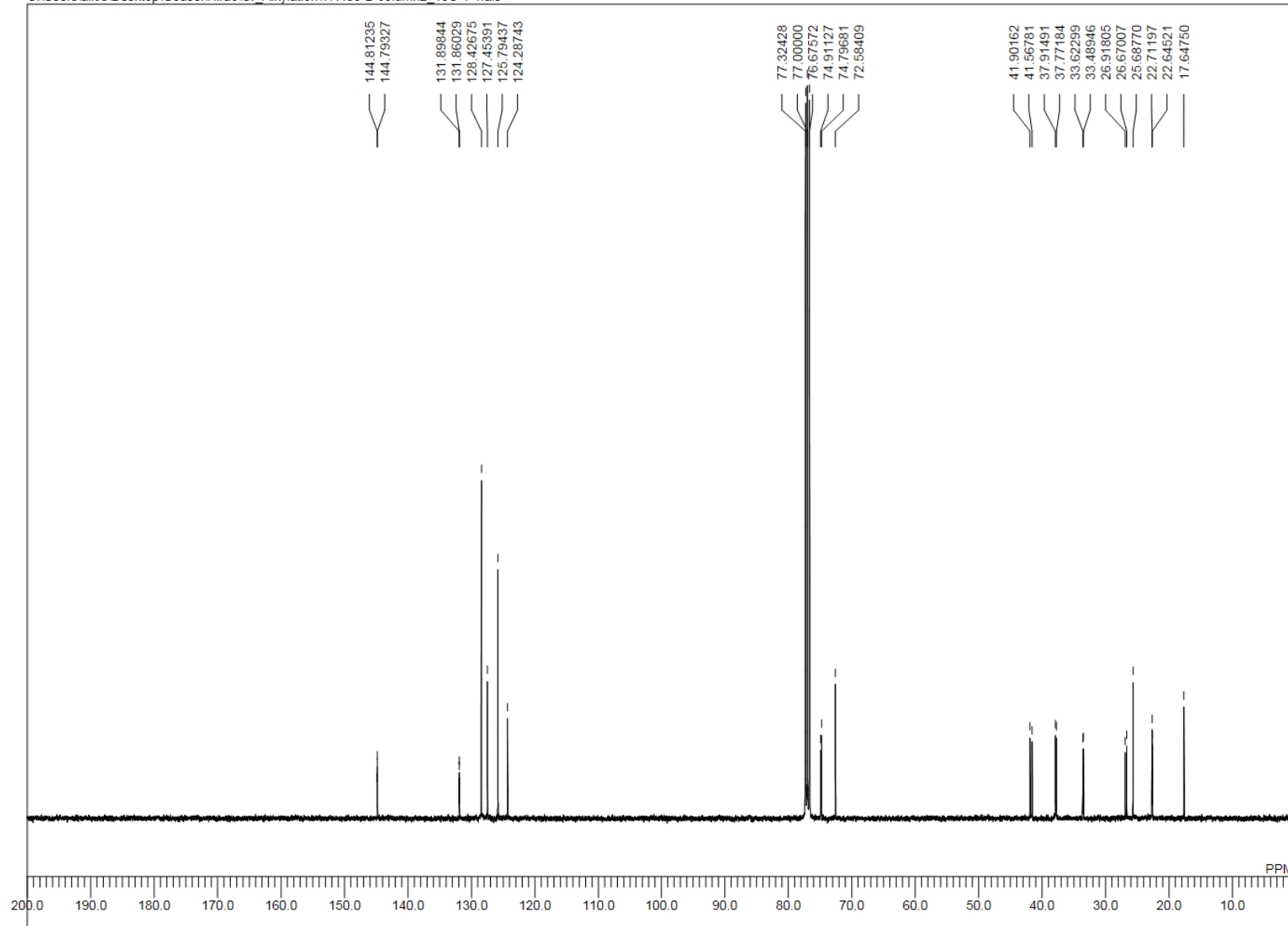


DFILE YH493-B-column2-1-1.als  
 COMNT  
 DATIM 25-08-2020 10:23:15  
 OBNUC  $^1\text{H}$   
 EXMOD proton.jxp  
 OBFRQ 391.78 MHz  
 OBSET 8.51 KHz  
 OBFIN 3.34 Hz  
 POINT 13107  
 FREQU 5878.90 Hz  
 SCANS 8  
 ACQTM 2.2295 sec  
 PD 6.0000 sec  
 PW1 5.17 usec  
 IRNUC  $^1\text{H}$   
 CTEMP 21.0 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 36



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

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DFILE YH493-B-column2\_13C-1-1.

COMNT

DATIM 25-08-2020 10:26:06

OBNUC 13C

EXMOD carbon.jxp

OBFRQ 98.52 MHz

OBSET 4.64 KHz

OBFIN 8.74 Hz

POINT 26214

FREQU 24630.54 Hz

SCANS 1686

ACQTM 1.0643 sec

PD 2.0000 sec

PW1 3.12 usec

IRNUC 1H

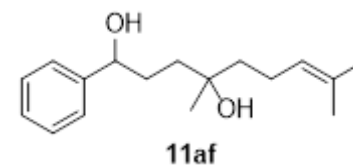
CTEMP 20.8 c

SLVNT CDCL3

EXREF 77.00 ppm

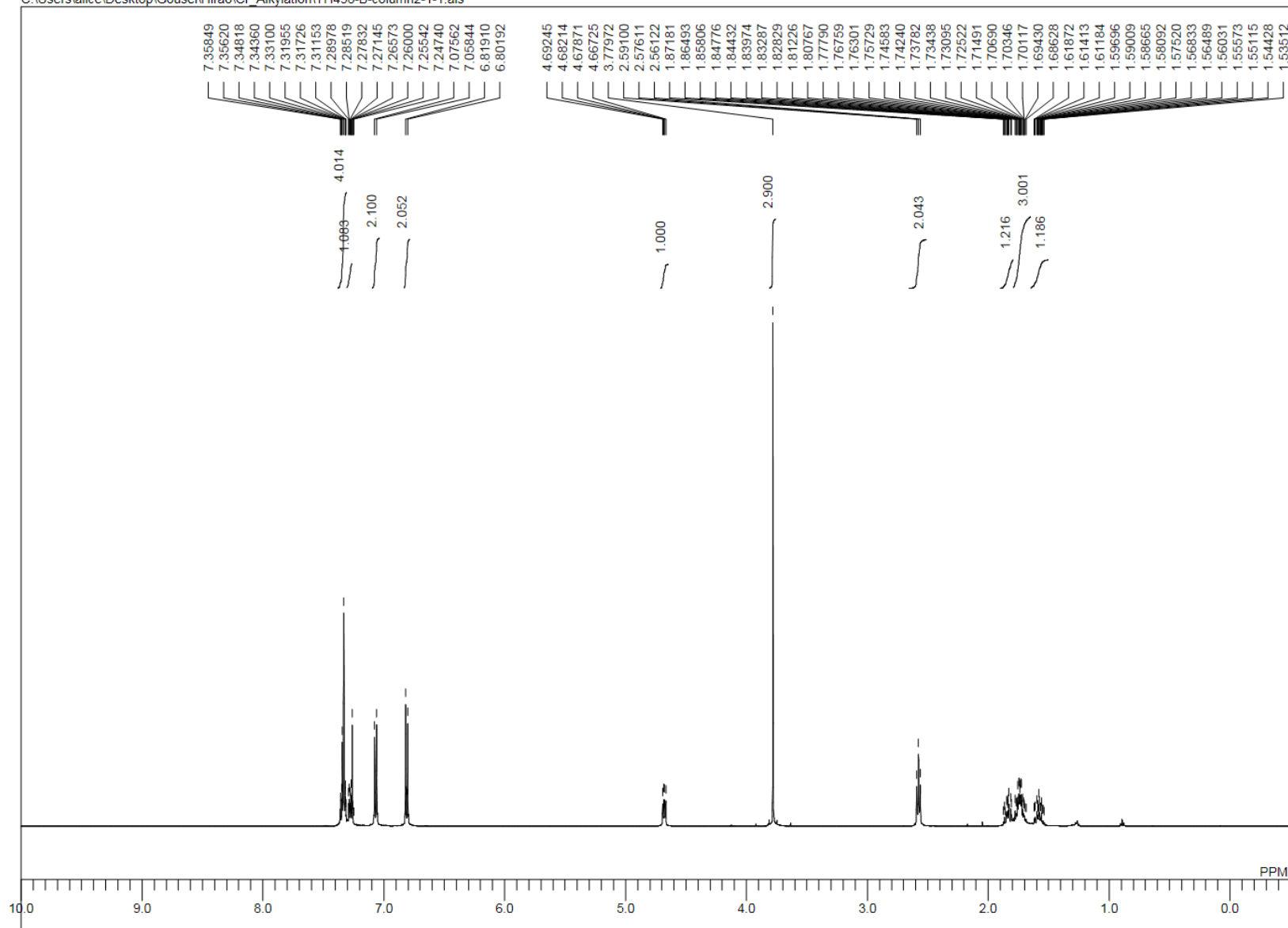
BF 1.20 Hz

RGAIN 60

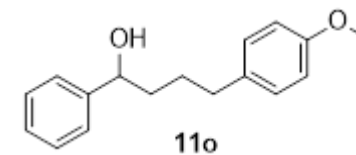


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

C:\Users\alice\Desktop\Gousei\Hirao\Cr Alkylation\YH498-B-column2-1-1.als



DFILE YH498-B-column2-1-1.als  
 COMNT  
 DATIM 2020-09-04 11:59:14  
 OBNUC  $^1\text{H}$   
 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  
 IRNUC  $^1\text{H}$   
 CTEMP 21.9 c  
 SLVNT  $\text{CDCl}_3$   
 EXREF 7.26 ppm  
 BF 0.12 Hz  
 RGAIN 40



$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

