Electronic Supplementary Information

N,N-Dimethylformamide-Stabilized Ruthenium Nanoparticle Catalyst for β-Alkylated Dimer Alcohol Formation via Guerbet Reaction of Primary Alcohols

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Experimental

Materials and Methods

$RuCl_3 \cdot nH_2O$ was purchased from TANAKA Kikinnzoku Kogyo. *N,N*-dimethylformamide (DMF; HPLC grade) was purchased from Fujifilm Wako Pure Chemical Industries Ltd. Unless otherwise stated, all starting alcohols were obtained from commercial suppliers and used without further purification. All work-up and purification procedures were performed with reagent-grade solvents in air.

GLC analyses were performed with a Shimadzu GC-2025 instrument with a flame ionization detector and equipped with a BP-5 column SGE Trajan (0.25 mm i.d. × 30 m). Column flow rate and purge flow rate (N_2) were 0.69 mL/min and 3.0 mL/min, respectively. Temperature program was set to 40 °C for 4 min, and increased the temperature to 280 °C (10 °C/min). Compounds **2a**,[1] **2b**,[2] **2c**,[3] **2d**,[1] **2e**,[4] **2f**,[1] **2g**,[1] **2h**,[1] and **2i**[1] were previously reported; **2j** and **2k** were characterized by ^1H NMR, $^{13}C\{^1H\}$ NMR, and FT-IR spectroscopies, GC-MS, and HRMS. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded with a JEOL JEM-ECZ NMR 400s instrument (^1H 400 MHz, ^{13}C 100 MHz). Signal positions were recorded in parts per million (ppm); the abbreviations s, d, t, q, dd, dt, and m denote singlet, doublet, triplet, quadruplet, doublet of doublets, doublet of triplets, and multiplet, respectively. Chemical shifts were referenced to residual solvent peaks or to tetramethylsilane as an internal standard. FT-IR spectroscopy was performed with a Shimadzu IRAffinity-1 instrument. GC-MS (electron ionization, EI) spectra were acquired with a Shimadzu GCMS-QP2010SE instrument. HRMS was performed with a JEOL JMS-T100GCV(EI) instrument.

Preparation of DMF-stabilized Ru NPs

(i) Preparation of 0.1 M $RuCl_3 \cdot nH_2O$ aqueous solution

$RuCl_3 \cdot nH_2O$ (0.317 g) was dissolved in distilled water (9 mL) and HCl (1 mL, 1.2 M). The solution was allowed to stand at 25 °C overnight.

(ii) Synthesis of DMF-stabilized Ru NPs (1 mM)

DMF (50 mL) was added to a 300 mL three-necked round-bottomed flask. The solution was preheated to 140 °C (±2 °C) and stirred at 1300 to 1500 rpm for 5 min. Then 500 μL of the 0.1 M $RuCl_3 \cdot nH_2O$ aqueous solution prepared by (i) was added to the hot DMF solution. The mixture was stirred (1500 rpm) at 140 °C (±2 °C) for 10 h. The mixture was then cooled to 25 °C.

The solvent of the Ru NPs was evaporated under reduced pressure (80 °C, 30 hPa) in prior to the use in the catalytic reaction.

Characterization of Ru NPs

X-ray photoelectron spectroscopy (XPS)

XPS was performed with a Ulvac PHI 5000 VersaProbe III instrument with an Al X-ray source (Al Kα, 1485 eV). Data were analyzed with CasaXPS software.[5]

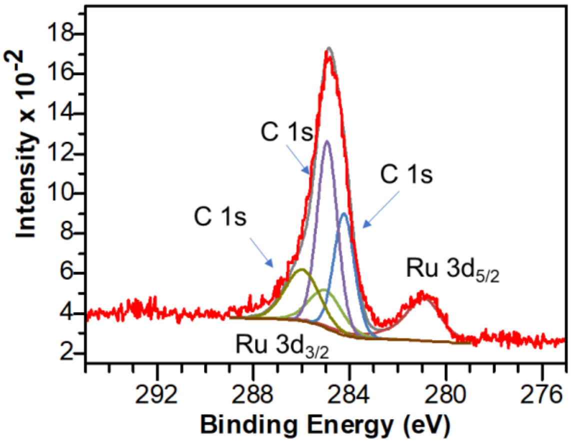


Figure S1. Ru 3d and C1s XPS spectrum of DMF-protected Ru NPs.

X-ray absorption spectroscopy(XAS)

XAS measurements were performed at the BL14B2 beamline of SPring-8, the Japan Synchrotron Radiation Research Institute. A Si(311) double crystal was used as a monochromator. The spectra were recorded at the Ru K edges in transmission mode at 25 °C. First, the Ru NP solution was concentrated (40 mM). Then the condensed sample was sealed in a PTFE cube (diameter 5 mm, length 40 mm) (Barrier Kapton film). The obtained XAFS spectra were analyzed with Athena software version 0.9.26, which is included in the Demeter package.[6]

Thermogravimetric (TG) analysis

TG analysis was performed with a TGA 8000 instrument (PerkinElmer) at a heating rate of 10 °C/min under a nitrogen flow and with an Al sample cup.

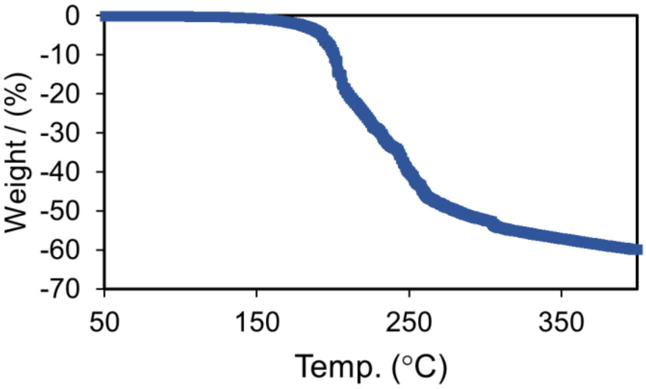


Figure S2. TG profile of DMF-stabilized Ru NPs.

Thermogravimetry-High-Resolution Time-of-Flight Mass Spectrometry (TG-HR-TOFMS)

TG- HR-TOFMS was performed with NETZSCH STA2500 (TG) and JEOL JMS-T2000GC (TOFMS) instruments. The sample (10.3 mg) was placed in an Al sample cup. Before the measurements, the sample furnace was purged with helium. Measurements were performed in a helium atmosphere. The furnace temperature was increased from 60 to 600 °C at a heating rate of 10 °C/min. The emitted compounds were identified with a TOF-MS instrument, which was operated in EI mode at an ionization energy of 70 eV. The mass spectra were recorded from *m*/*z* 10 to 800 a.u. (resolution: 30 000). The temperature of the ion source was held at 200 °C and the temperature of the TOF transfer line was kept at 300 °C.

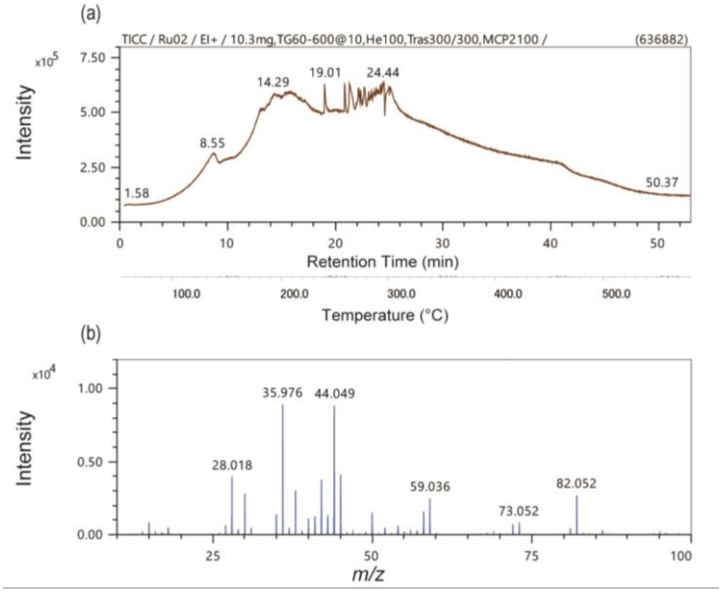


Figure S3 (a) Total ion chromatogram of Ru NPs (b) accumulated mass spectrum of Ru NPs

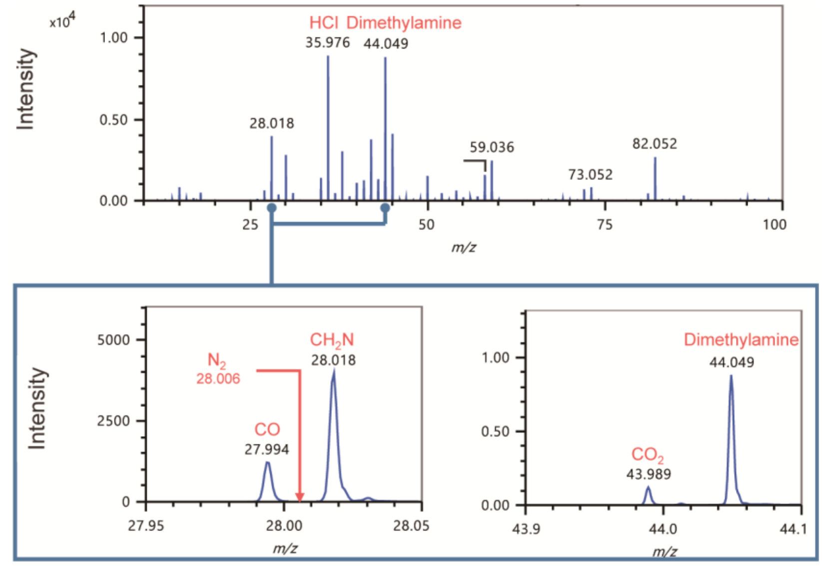


Figure S4. Spectrum assignment of accumulated mass spectrum of Ru NPs.

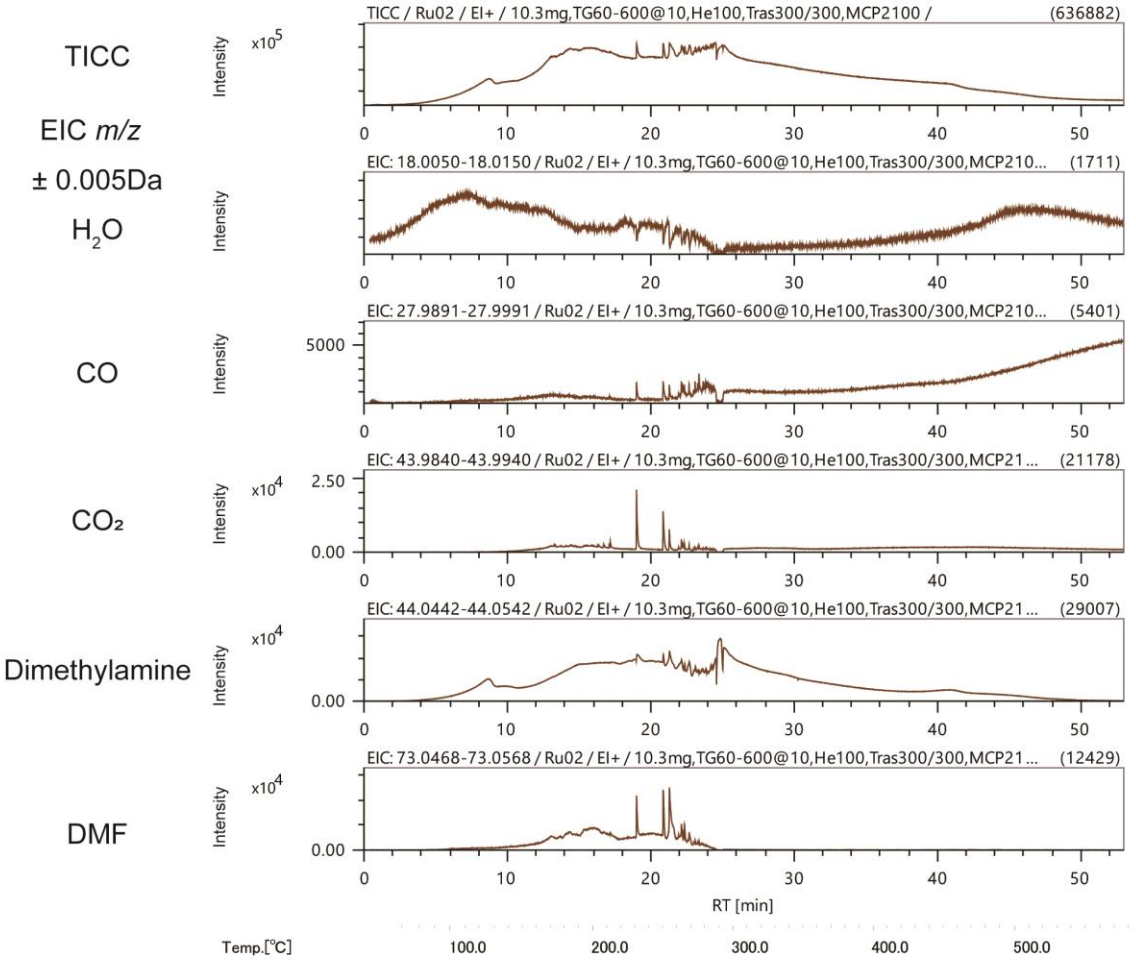
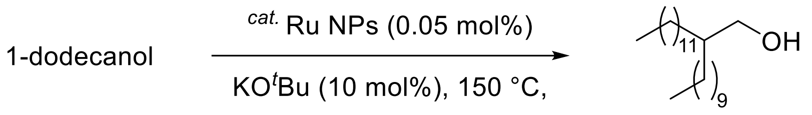


Figure S5. Extracted ion chromatogram of Ru NPs.

Table S1 Optimization of Guerbet reaction



1a **2a**

Entry	Reaction conditions	Conv. (%)	Yield (%)[b] (Selectivity, %)
1	Standard[a]	95	93 (98) [83]
2	DMF (1 mL) instead of neat	10	n.d.
3	Toluene (1 mL) instead of neat	20	n.d.
4	130 °C instead of 150 °C	73	72 (99)
5	20 mol% instead of 10 mol%	80	78 (98)
6	40 mol% instead of 10 mol%	77	34 (44)
7	50 mol% instead of 10 mol%	89	42 (47)

[a]Reaction conditions: 1a (2 mmol) was reacted in the presence of a Ru NPs (0.05 mol%) and base (0.2 mmol) at 150 °C for 24 h. [b]GC yield based on 1a.

Numbers in square brackets show isolated yields. n.d. = not detected by GC. Numbers in parentheses show selectivity of 2a = [Yield (%) 1a]/[Conv. (%) 1a].

General procedure for Guerbet reaction (Table 1, Entry 1)

A 1 mM solution of Ru NPs in DMF (1 mL) was placed in a sealed tube (10 mL). The DMF was evaporated under reduced pressure (80 °C, 30 hPa). 1-Dodecanol (**1a**, 372.7 mg, 2 mmol) and KO^{t}Bu (21 mg, 0.02 mmol) were added, and the mixture was stirred at 150 °C for 24 h. The reaction mixture was cooled to 25 °C, and the product was isolated by silica-gel column chromatography (*n*-hexane:EtOAc = v/v 9:1). Product **2a** was obtained in 83% yield as a colorless oil.

Time course of reaction with DMF-stabilized Ru NPs (Figure 7)

A 1 mM solution of Ru NPs in DMF (1 mL) was placed in a schlenk tube (10 mL). The DMF was evaporated under reduced pressure (80 °C, 30 hPa). 1-Dodecanol (**1a**, 372.7 mg, 2 mmol) and KO^{t}Bu (21 mg, 0.02 mmol) were added, and the mixture was stirred at 150 °C and the yields of the products were determined by GC using *n*-dodecane as an internal standard by sampling the small portion of the reaction mixture.

1g scale Guerbet reaction

A 1 mM solution of Ru NPs in DMF (4.4 mL) was placed in a sealed tube (30 mL). The DMF was evaporated under reduced pressure (80 °C, 30 hPa). 1-Dodecanol (**1a**, 1.64 g, 8.8 mmol) and KO^{t}Bu (99 mg, 0.88 mmol) were added, and the mixture was stirred at 150 °C for 48 h. The reaction mixture was cooled to 25 °C, and the product was isolated by silica-gel column chromatography (*n*-hexane:EtOAc = v/v 9:1). Product **2a** was obtained in 64% (1.02 g) for 24 h and 78% yield (1.22 g) for 48 h, respectively, as a colorless oil.

Catalyst reuse

A mixture of 1-octanol (**1f**, 260.5 mg, 2 mmol), Ru NPs (0.001 mmol), and KO^{t}Bu (22 mg, 0.2 mmol) was stirred at 150 °C for 24 h under Ar in a sealed tube. The substrate conversion and product yield were calculated from the GC peak areas, with *n*-dodecane as an internal standard. Substrates **1f** and product **2f** were removed by vacuum distillation at 130 °C for 1 h under 40 Pa. The mixture was filtered (cotton plug) with 1,2-dichloroethane to remove the base. The recovered catalyst was added to the reaction vessel. The recovered catalyst was used to perform the next catalytic reaction under the same reaction conditions by adding **1f** (260.5 mg, 1 mmol) and KO^{t}Bu (22 mg, 0.2 mmol), and heating at 150 °C for 24 h under Ar.

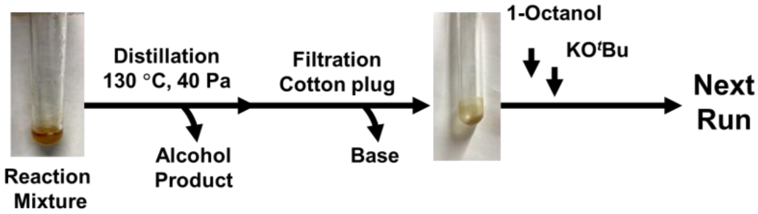


Figure S6. Catalyst reuse procedure.

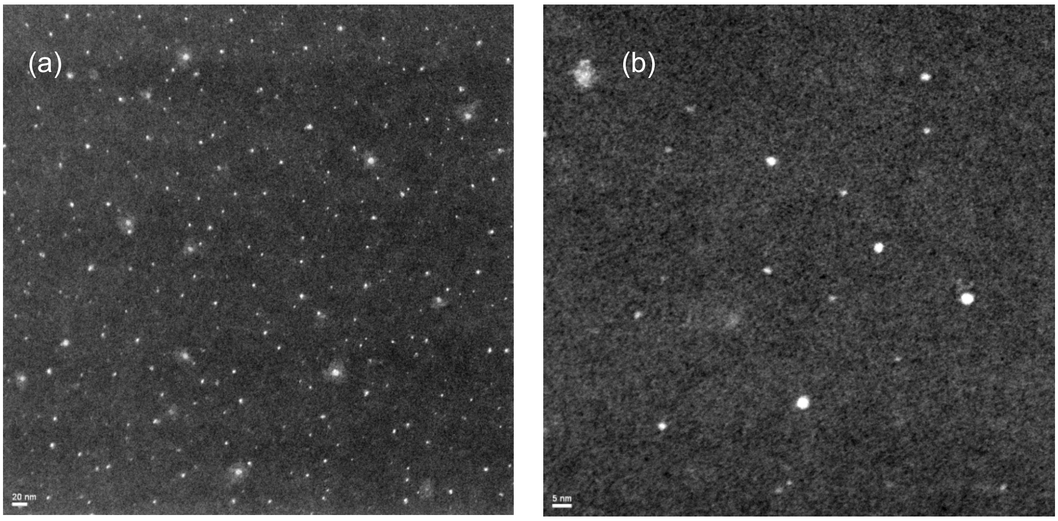


Figure S7. ADF-STEM images of Ru NPs after reaction (a) scale bar 20 nm and (b) scale bar 5 nm.

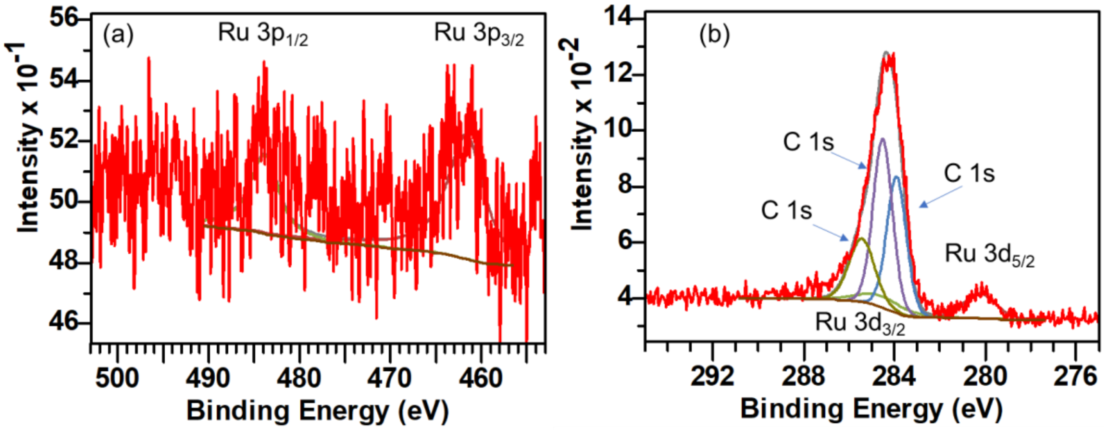
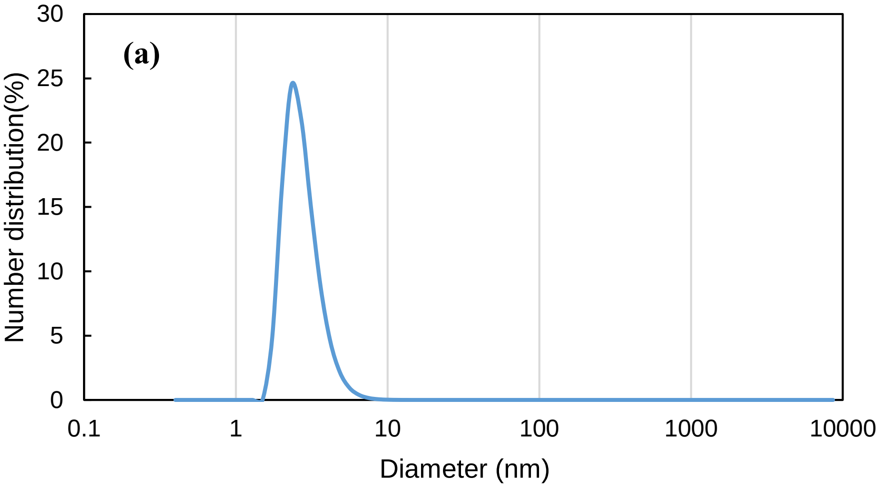


Figure S8. Ru 3p(a), 3d and C1s (b) XPS spectrum after reaction.



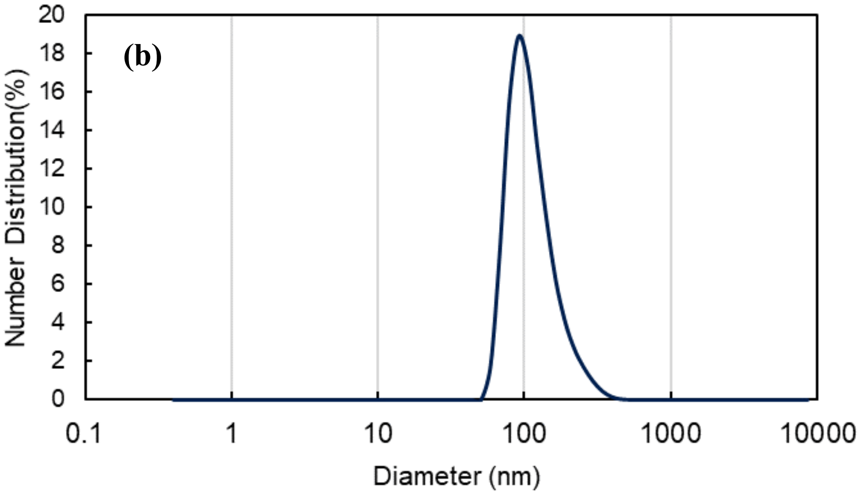


Figure S9. DLS chart of Ru NPs (a) before and (b) after 4th recycling (water, 25 °C, 0.05 mM).

Identification of Products

2a 294.4mg(83%), colorless oil, ^{1}H-NMR (400MHz CDCl$_3$) δ: 3.54 (2H, d, *J* = 5.5 Hz), 1.27-1.25 (42H, m), 0.88 (6H, t, *J* = 6.9 Hz). ^{13}C-NMR (100 MHz CDCl$_3$) δ: 65.75 (CH$_2$), 40.52 (CH), 31.92 (CH$_2$), 30.92 (CH$_2$), 30.06 (CH$_2$), 29.67 (CH$_2$), 29.65 (CH$_2$), 29.63 (CH$_2$), 29.35 (CH$_2$), 29.34 (CH$_2$), 26.88 (CH$_2$), 22.68 (CH$_2$), 14.11 (CH$_3$); GC-MS (EI) m/z (relative intensity) 336 (4) $[M{-}H_2O]^+$ 308(2), 182(5) 111(46), 97(72), 71(77), 57(100), 43(69).

2b 336.2mg(72%), white solid, m.p 37-38 °C ^{1}H-NMR (400 MHz CDCl$_3$) δ: 3.47 (2H, d, *J* = 5.4 Hz), 1.38-1.19 (58H, m), 0.81 (6H, t, *J* = 6.4 Hz); ^{13}C-NMR (100 MHz CDCl$_3$) δ: 65.75 (CH$_2$), 40.53 (CH), 31.93 (CH), 30.93 (CH$_2$), 30.07 (CH$_2$), 29.70 (CH$_2$), 29.66 (CH$_2$), 29.37 (CH$_2$), 26.89 (CH$_2$), 22.69 (CH$_2$), 14.11 (CH$_3$); GC-MS(EI) m/z (relative intensity) 448 (3) $[M{-}H_2O]^+$, 252 (4), 71 (80), 57 (100).

2c 312.2mg(76%), colorless oil ,^{1}H-NMR (400MHz CDCl$_3$) δ: 3.51 (2H, d, *J* = 5.5 Hz), 1.43-1.24 (50H, br m), 0.86 (6H, t, *J* = 6.9 Hz); ^{13}C-NMR (100 MHz CDCl$_3$) δ: 65.74 (CH$_2$), 40.53 (CH), 31.93 (CH$_2$), 30.93 (CH$_2$), 30.07 (CH$_2$), 29.69 (CH$_2$), 29.66 (CH$_2$), 29.36 (CH$_2$), 26.89 (CH$_2$), 22.69 (CH$_2$), 14.11 (CH$_3$); GC-MS(EI) m/z (relative intensity) 392 (3) $[M{-}H_2O]^+$, 97 (66), 57 (100).

2d 223.9mg(75%), colorless oil, ^{1}H-NMR (400 MHz CDCl$_3$) δ: 3.53 (2H, d, *J* = 5.4 Hz), 1.45 (1H, br s), 1.29 (33H, br s), 0.88 (6H, t, *J* = 6.9 Hz);^{13}C-NMR (100 MHz CDCl$_3$) δ: 65.71 (CH$_2$), 40.53 (CH), 31.95 (CH$_2$), 30.93 (CH$_2$), 30.11 (CH$_2$), 29.72 (CH$_2$), 29.69 (CH$_2$), 29.66 (CH$_2$), 29.39 (CH$_2$), 26.91 (CH$_2$), 22.72 (CH$_2$), 14.14 (CH$_3$); GC-MS (EI) m/z (relative intensity) 280 (3) $[M{-}H_2O]^+$, 252 (2) 85 (49), 97 (59), 111 (43) 71 (72), 57 (100), 43(63).

2e 186.6mg(69%), colorless oil, ^{1}H-NMR (400 MHz CDCl$_3$) δ: 3.54 (2H, d, *J* = 5.4 Hz), 1.27 (30H, br), 0.88 (6H, t, *J* = 6.7 Hz); ^{13}C-NMR (100 Hz CDCl$_3$) δ: 65.76 (CH$_2$), 40.56 (CH), 31.93 (CH$_2$), 30.95 (CH$_2$), 30.10 (CH$_2$), 30.07 (CH$_2$), 29.68 (CH$_2$), 29.66 (CH$_2$), 29.37 (CH$_2$), 29.35 (CH$_2$), 26.92 (CH$_2$), 22.71 (CH$_2$), 14.13 (CH$_3$); GC-MS (EI) m/z (relative intensity) 252 (2) $[M{-}H_2O]^+$, 111 (31) 85 (47), 71 (64), 57 (100), 43(63).

2f 179.4mg(74%), colorless oil, ^{1}H-NMR (400MHz CDCl$_3$) δ: 3.54 (2H, d, *J* = 5.4 Hz), 1.42-1.31 (26H, m), 0.88 (6H, t, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz CDCl$_3$) δ: 40.55 (CH$_2$), 31.92 (CH), 31.90 (CH$_2$), 30.95 (CH$_2$), 30.09 (CH$_2$), 29.76 (CH$_2$), 29.63 (CH$_2$), 29.36 (CH$_2$), 26.91 (CH$_2$), 26.88 (CH$_2$), 22.70 (CH$_2$), 14.12 (CH$_3$); GC-MS (EI) m/z (relative intensity) 224 (3) $[M{-}H_2O]^+$, 85 (43), 97 (38), 111 (34) 71 (72), 57 (100), 43(63).

2g 111.8mg(60%), colorless oil, ^{1}H-NMR (400 MHz CDCl$_3$) δ: 3.54 (2H, d, *J* = 5.4 Hz), 1.27 (18H, br), 0.88 (6H, t, *J* = 6.7 Hz); ^{13}C-NMR (100 MHz CDCl$_3$) δ: 65.70 (CH$_2$), 40.50 (CH), 31.85 (CH$_2$), 30.93 (CH$_2$), 30.61 (CH$_2$), 29.72 (CH$_2$), 29.10 (CH$_2$), 26.84 (CH$_2$), 23.08 (CH$_2$), 22.65 (CH$_2$), 14.06 (CH$_3$); GC-MS (EI) m/z (relative intensity) 168 (3) [M−H$_2$O]$^+$, 140(4), 111(23), 71 (49), 57 (100), 43(67).

2h 72.8mg(46%), colorless oil, ^{1}H-NMR (400 MHz CDCl$_3$) δ: 3.54 (2H, d, *J* = 5.5 Hz), 1.49-1.26 (14H, m), 0.92-0.87 (6H, m); ^{13}C-NMR (100 MHz CDCl$_3$) δ: 65.68 (CH$_2$), 40.26 (CH), 33.22 (CH$_2$), 32.26 (CH$_2$), 30.85 (CH$_2$), 26.52 (CH$_2$), 22.64 (CH$_2$), 19.99 (CH$_2$), 14.45 (CH$_3$), 14.07 (CH$_3$); GC-MS (EI) m/z (relative intensity) 140 (3) [M−H$_2$O]$^+$, 71 (67) 57 (67) 43(100).

2i 46.9mg(36%), colorless oil, ^{1}H-NMR (400 MHz CDCl$_3$) δ: 3.55 (2H, d, *J* = 5.1 Hz), 1.46-1.28 (10H, m), 0.92-0.88 (6H, m); ^{13}C-NMR (100 MHz CDCl$_3$) δ: 65.28 (CH$_2$), 41.93 (CH), 30.09 (CH$_2$), 29.09 (CH$_2$), 23.30 (CH$_2$), 23.07 (CH$_2$), 14.08 (CH$_3$), 11.07 (CH$_3$); GC-MS (EI) m/z (relative intensity) 1 (2) [M−H$_2$O]$^+$, 85 (41), 70 (23), 70(23), ++57(100), 43 (91).

2j 197.2mg(74%), colorless oil, ^{1}H-NMR (400 MHz CDCl$_3$) δ: 3.52-3.44 (2H, m), 1.67-1.50 (12H, m), 1.31-1.02 (5H, m), 0.87- 0.80 (4H, m); ^{13}C-NMR (100 MHz CDCl$_3$) δ: 65.91 (CH$_2$), 39.08 (CH$_2$), 37.88 (CH$_2$), 37.63 (CH), 37.27 (CH), 34.99 (CH), 33.78 (CH$_2$), 33.71 (CH$_2$), 33.44 (CH$_2$), 33.41 (CH$_2$), 31.62 (CH$_2$), 26.72 (CH$_2$), 26.67 (CH$_2$), 26.41 (CH$_2$), 26.36 (CH$_2$), 23.94 (CH$_2$); FT-IR(neat) 3307, 2853, 2919, 1447, 1020 cm^{-1}; GC-MS (EI) *m/z* (relative intensity) 248 (9) [M−H$_2$O]$^+$, 96 (100), 83 (62), 55 (85); HRMS(EI) *m/z* [M−H$_2$O]$^+$ calcd for $C_{18}H_{32}$, 248.2504; found, 248.2503.

2k 191.1mg(64%), colorless oil,^{1}H-NMR (400 MHz CDCl$_3$) δ: 3.64-3.51 (2H, m), 1.56-1.49 (2H, m), 1.38-1.08 (20H, m), 0.86-0.84 (18H, m); A mixture of 4 diastereomers, ^{13}C-NMR (100 MHz CDCl$_3$) δ: 64.25 (CH$_2$), 64.17 (CH$_2$), 63.69 (CH$_2$), 63.62 (CH$_2$), 45.82 (CH), 45.75 (CH), 45.72 (CH), 45.59 (CH), 39.33 (CH$_2$), 39.30 (CH$_2$), 39.28 (CH$_2$), 39.27 (CH$_2$), 37.33 (CH$_2$), 37.23 (CH$_2$), 37.22 (CH$_2$), 37.03 (CH$_2$), 35.58 (CH$_2$), 35.52 (CH$_2$), 35.26 (CH$_2$), 35.15 (CH$_2$), 34.50 (CH$_2$), 34.39 (CH$_2$), 34.36 (CH$_2$), 34.21 (CH$_2$), 33.28 (CH), 33.20 (CH), 33.19 (CH), 33.14 (CH), 33.11 (CH), 32.74 (CH), 32.71 (CH), 27.97 (CH), 27.96 (CH), 27.94 (CH), 25.91 (CH), 25.90 (CH$_2$), 25.49 (CH$_2$), 25.46 (CH$_2$), 24.80 (CH$_2$), 24.78 (CH$_2$), 24.75 (CH$_2$), 24.20 (CH$_2$), 24.18 (CH$_2$), 22.72 (CH$_3$), 22.71 (CH$_3$), 22.69 (CH$_3$), 22.60 (CH$_3$), 22.59 (CH$_3$), 19.78 (CH$_3$), 19.71 (CH$_3$), 19.69 (CH$_3$), 19.59 (CH$_3$), 16.21 (CH$_3$), 16.00 (CH$_3$), 15.61 (CH$_3$), 15.49 (CH$_3$); FT-IR(neat) 3278, 2957, 2952, 2867, 1459, 1367, 1045 cm^{-1}; GC-MS (EI) *m/z* (relative intensity) 280 (2) [M−H$_2$O]$^+$ 71 (80) 57 (100) 43(60); HRMS(EI) *m/z* [M−H$_2$O]$^+$ calcd for $C_{20}H_{40}$, 280.3130; found, 280.3128.

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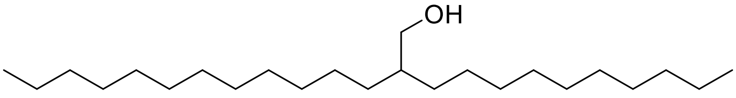
2a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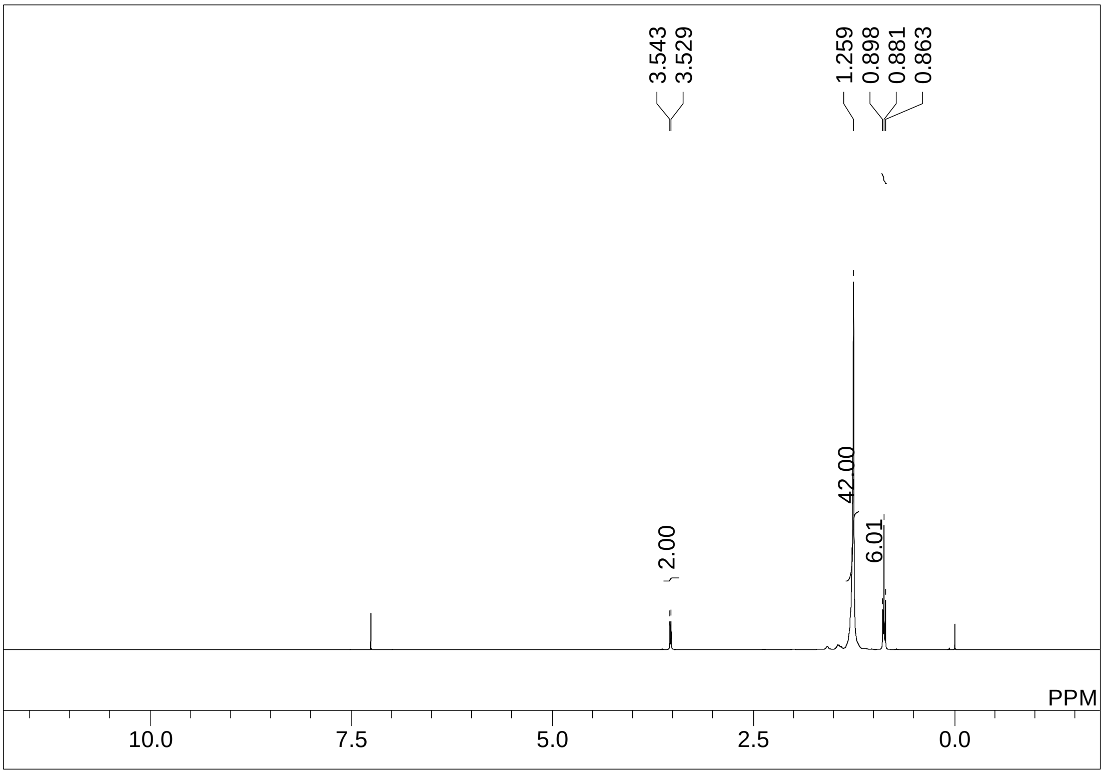
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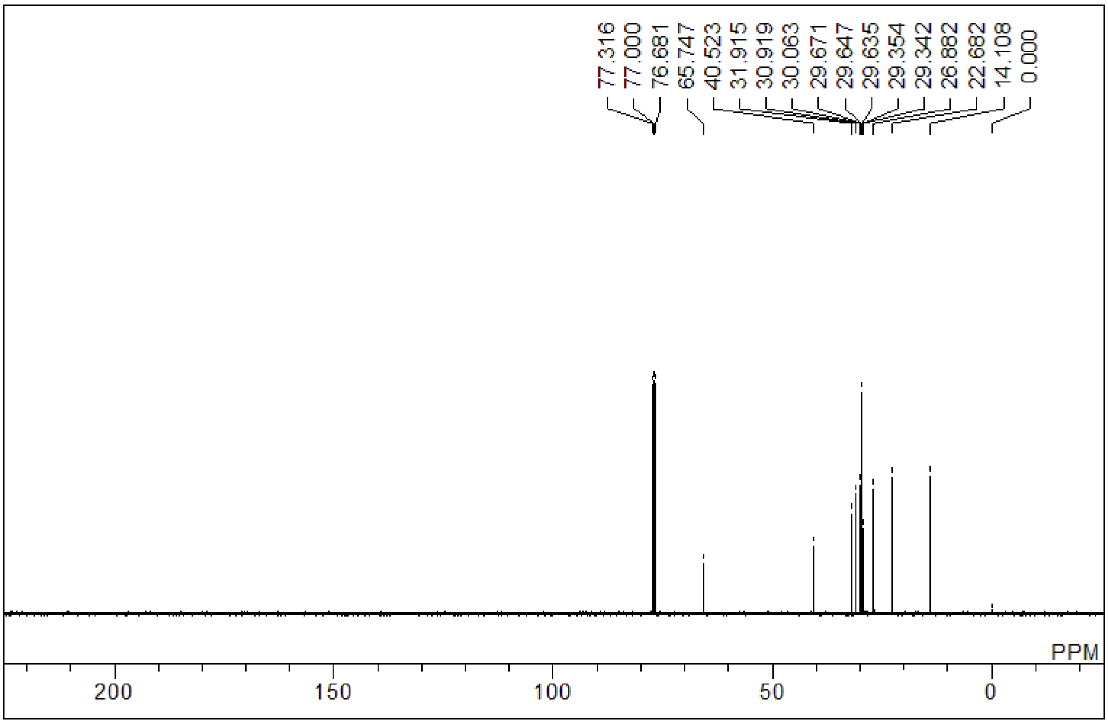
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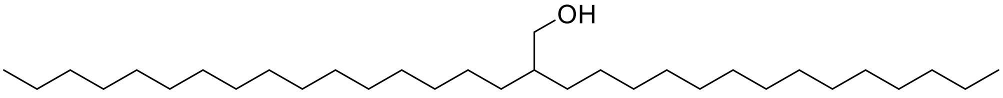
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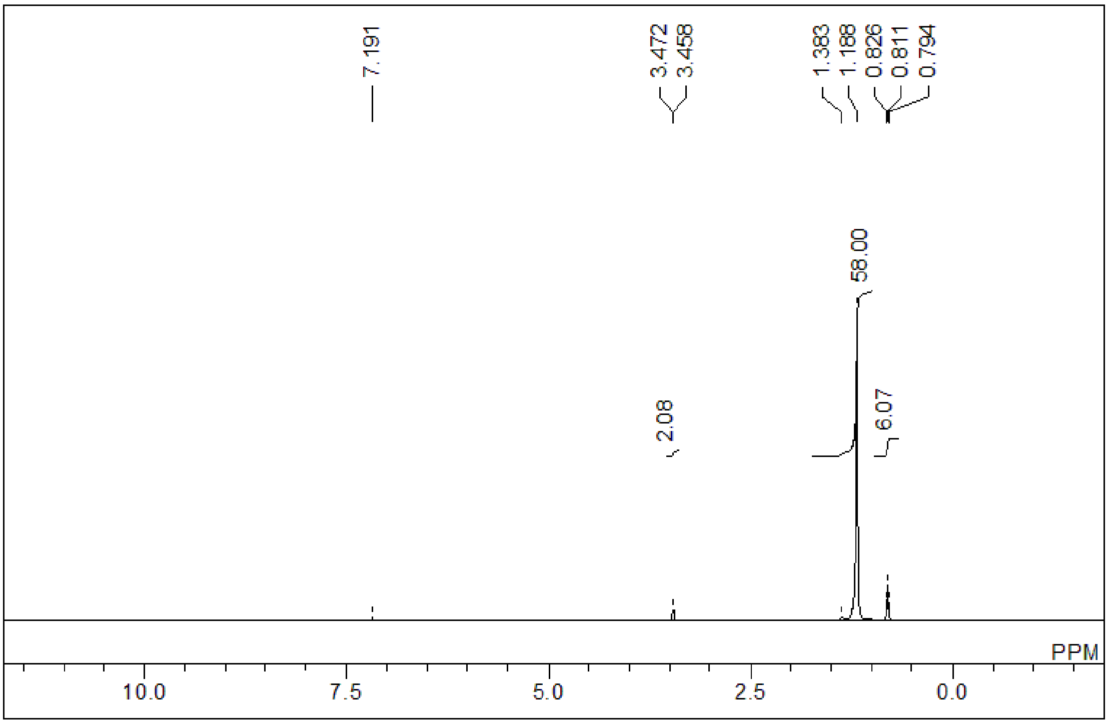
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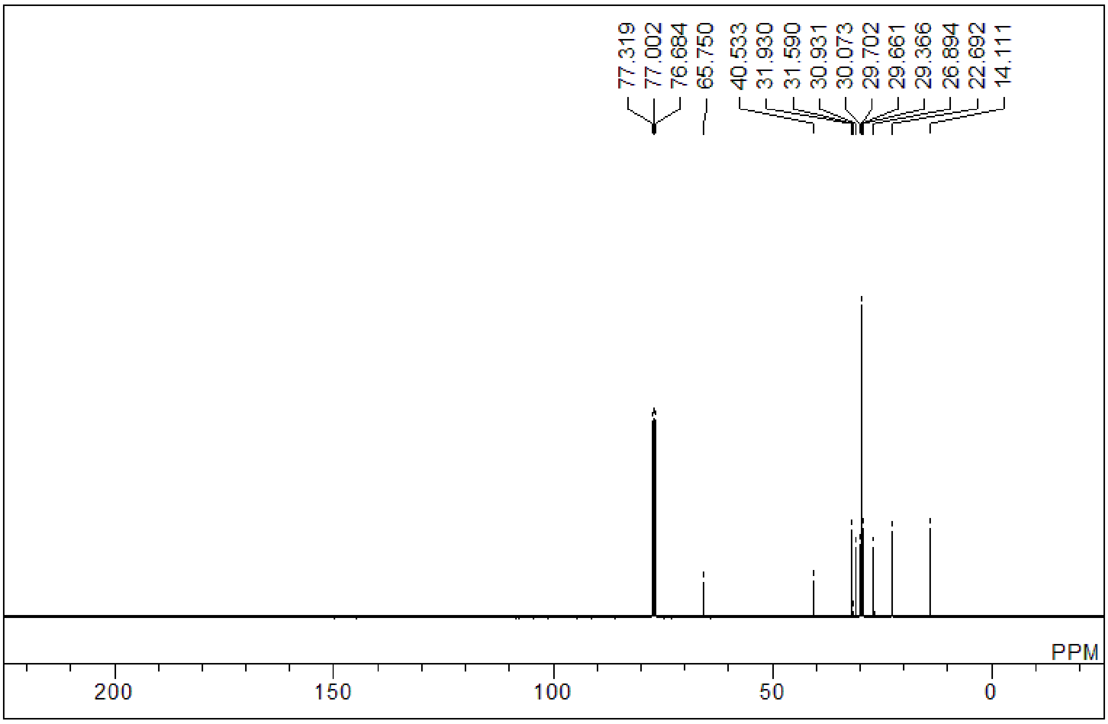
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31.930
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30.931
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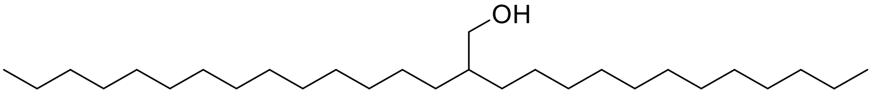
2c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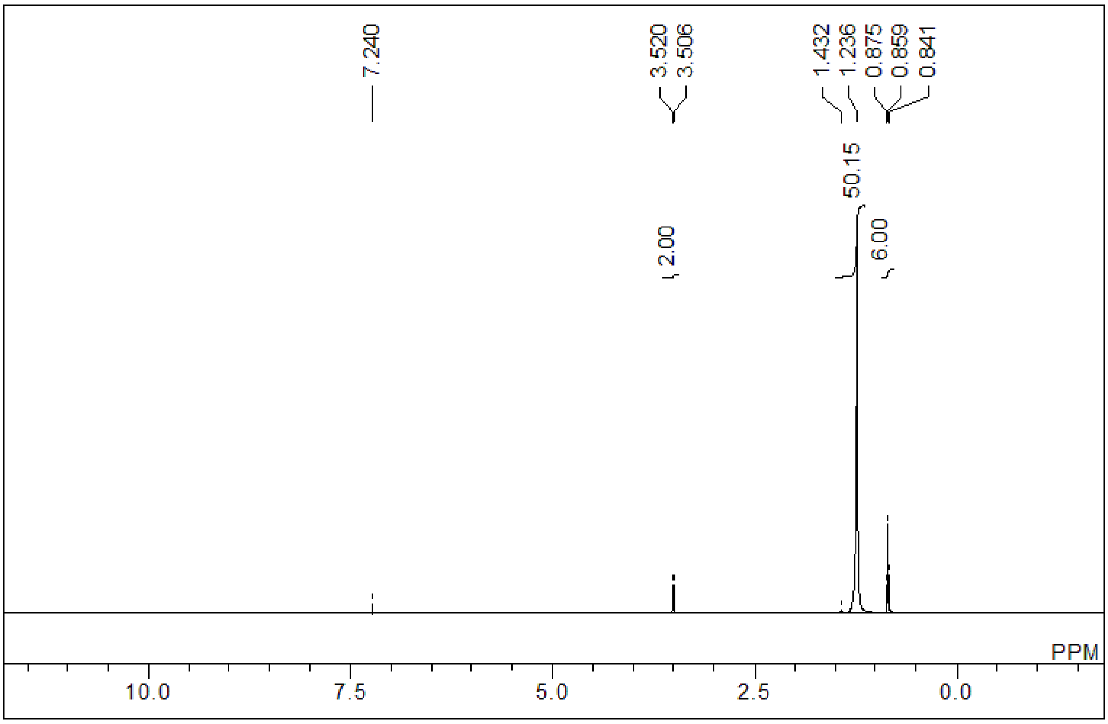
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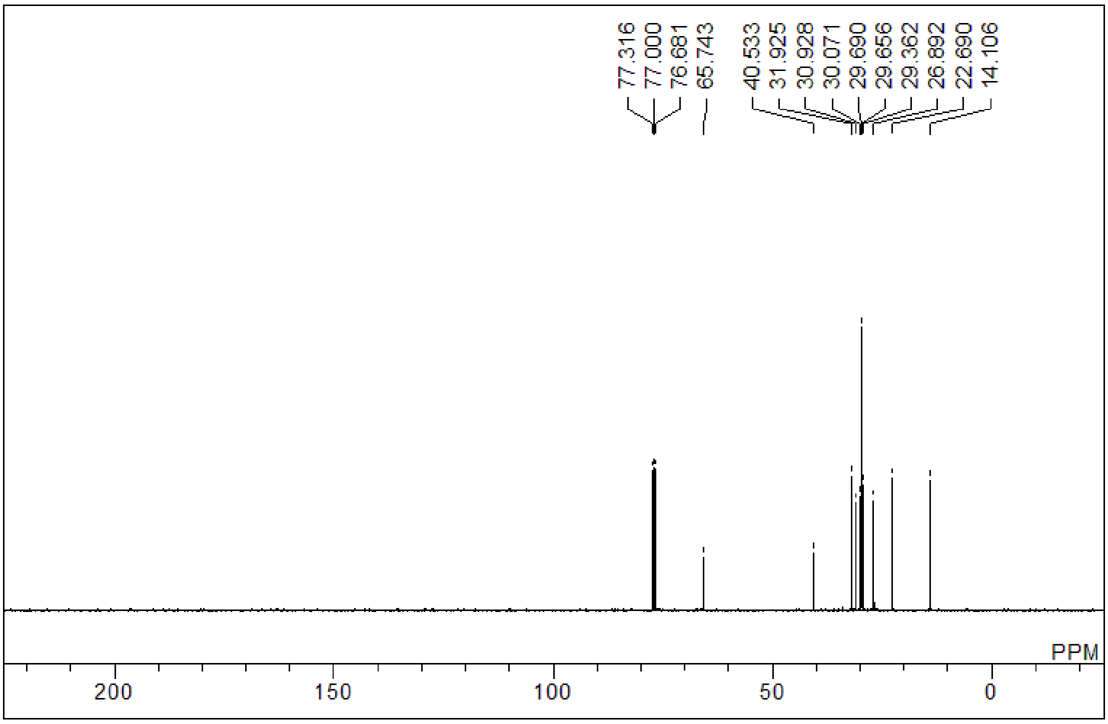
0.0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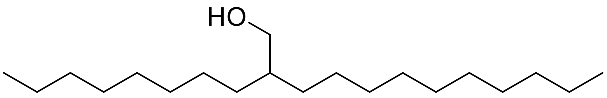
2d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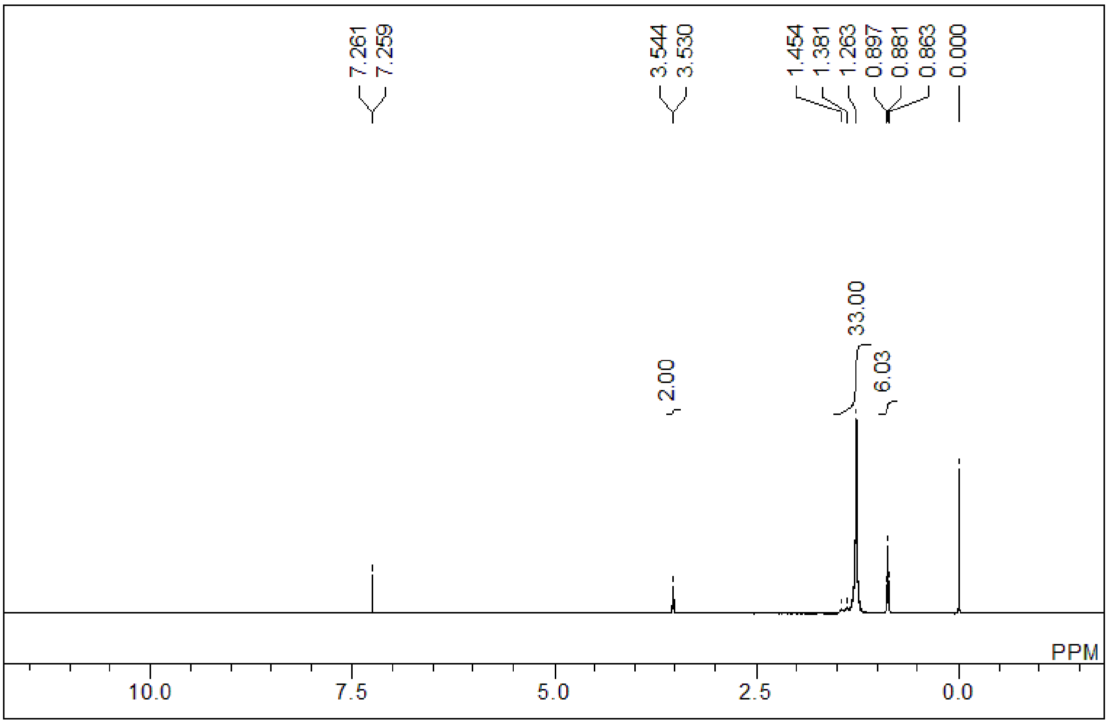
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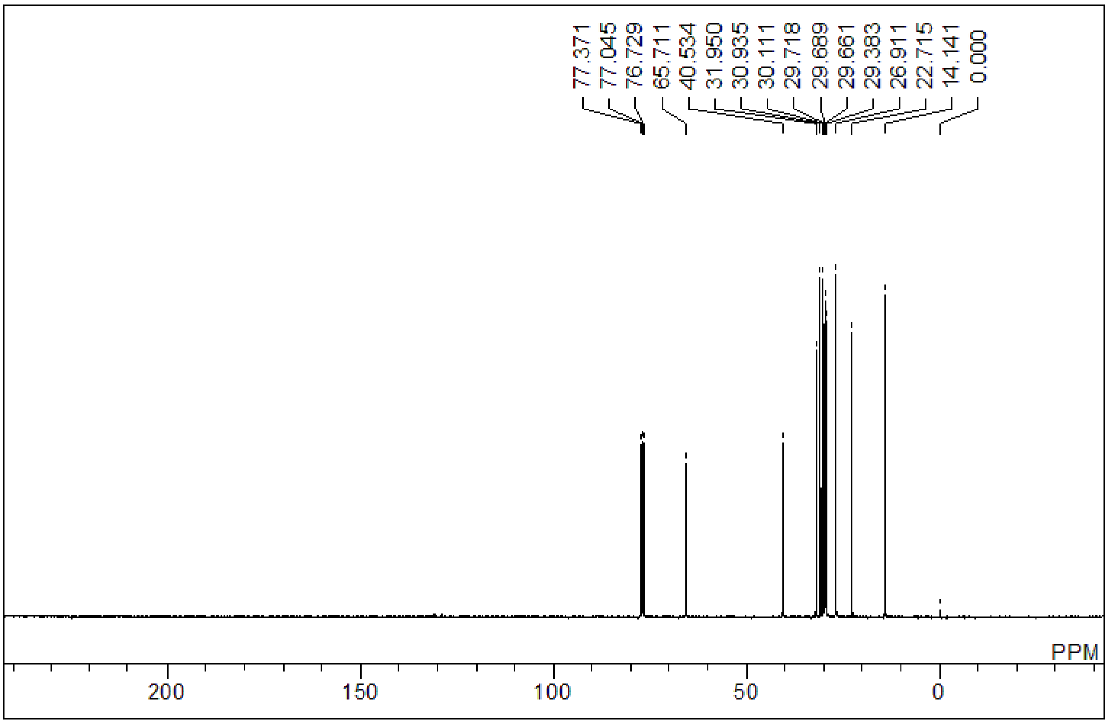
0.0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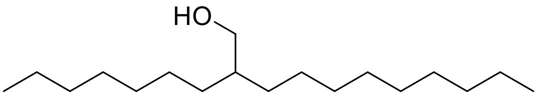
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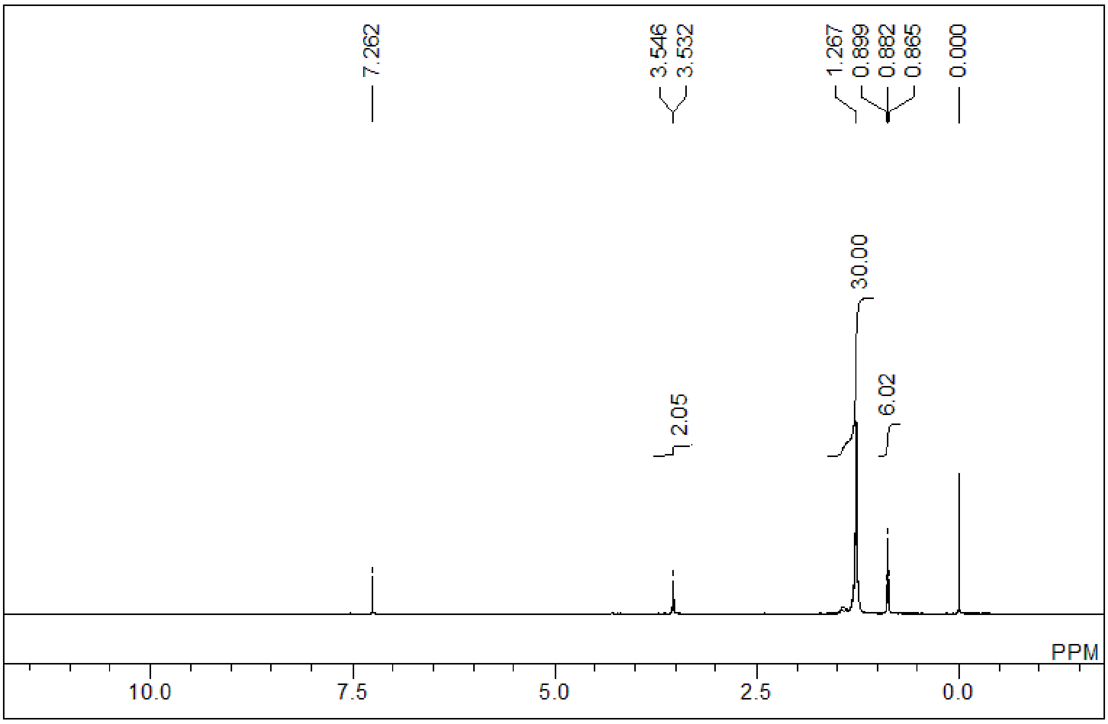
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10.0
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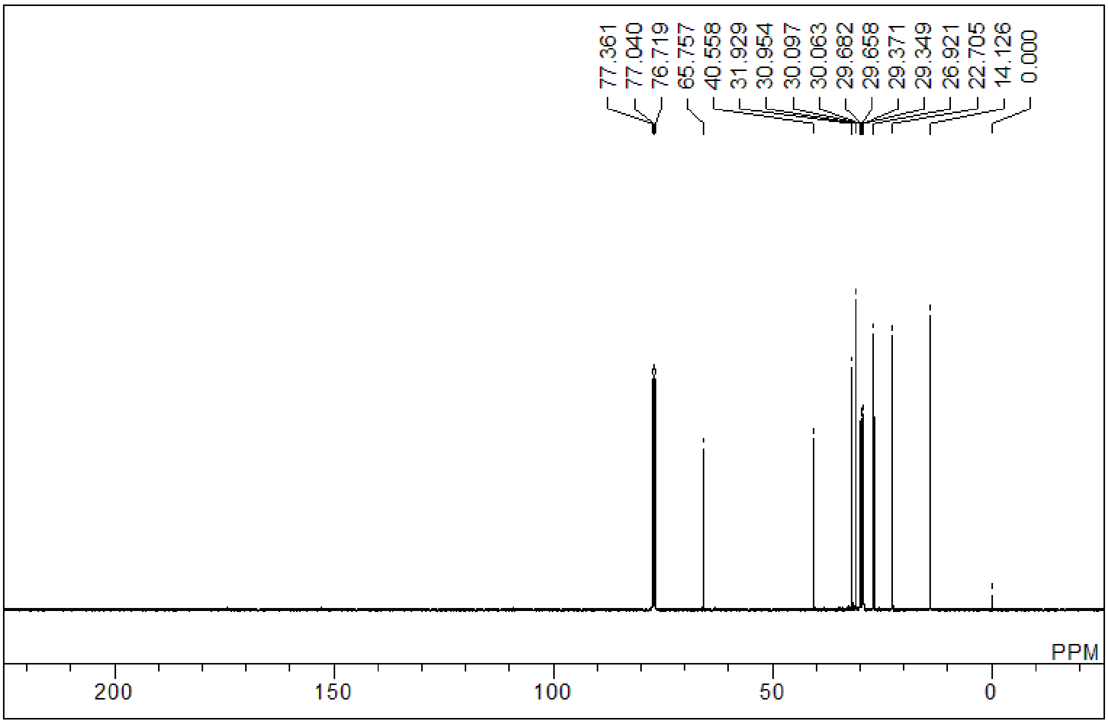
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29.349
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PPM
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150
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50
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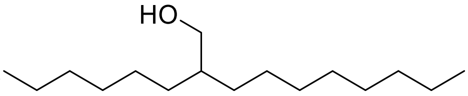

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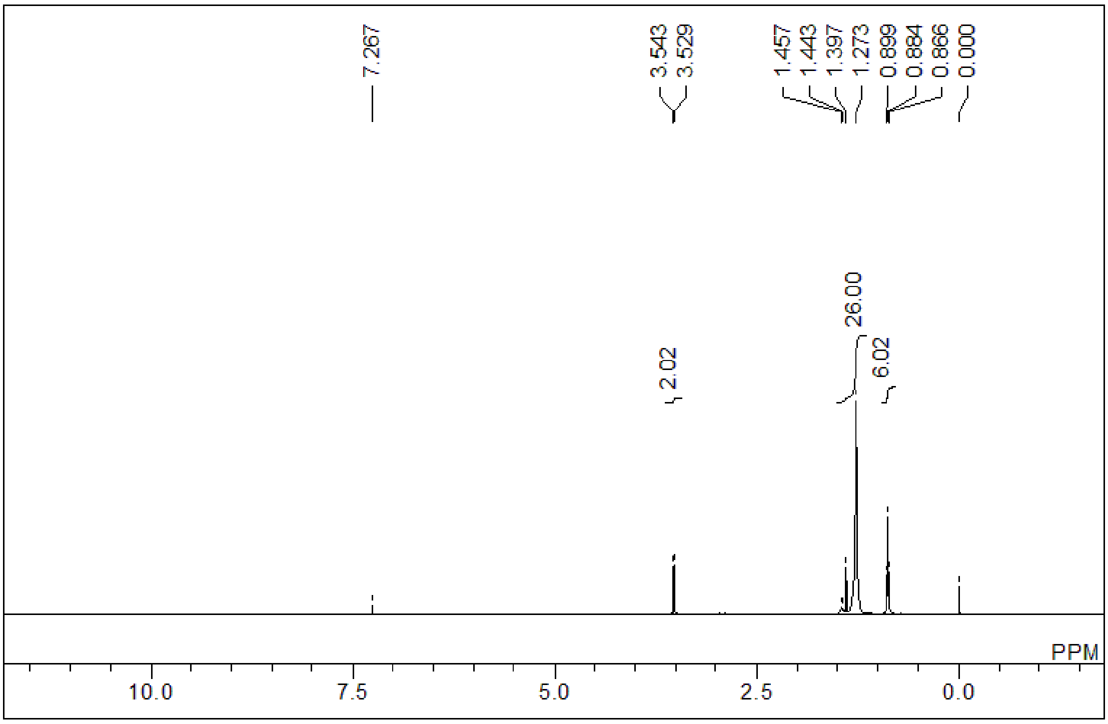
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5.0
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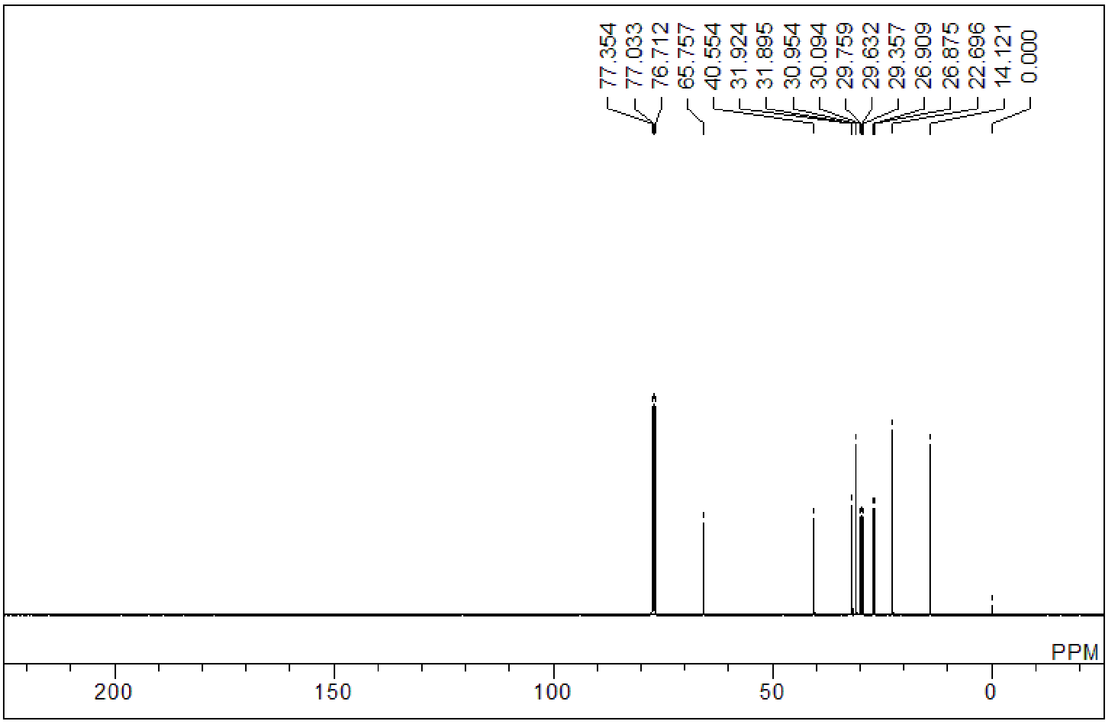
0.0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26.909
26.875
22.696
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PPM
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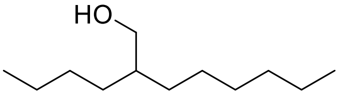
150
100
50
0

2g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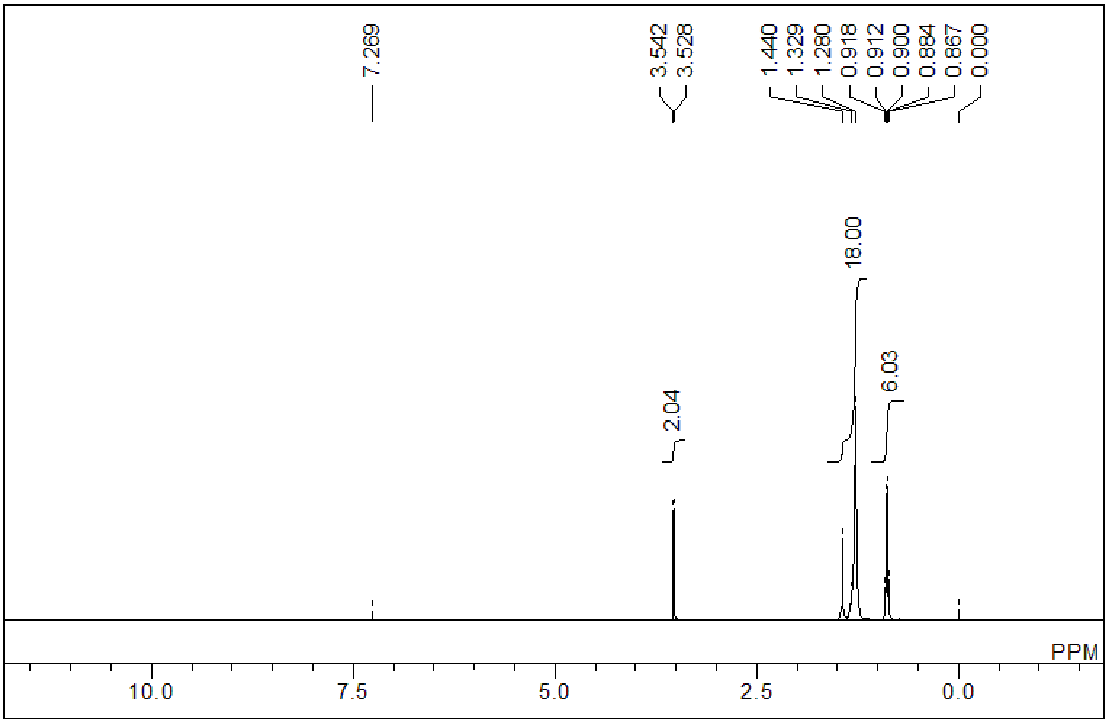
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PPM
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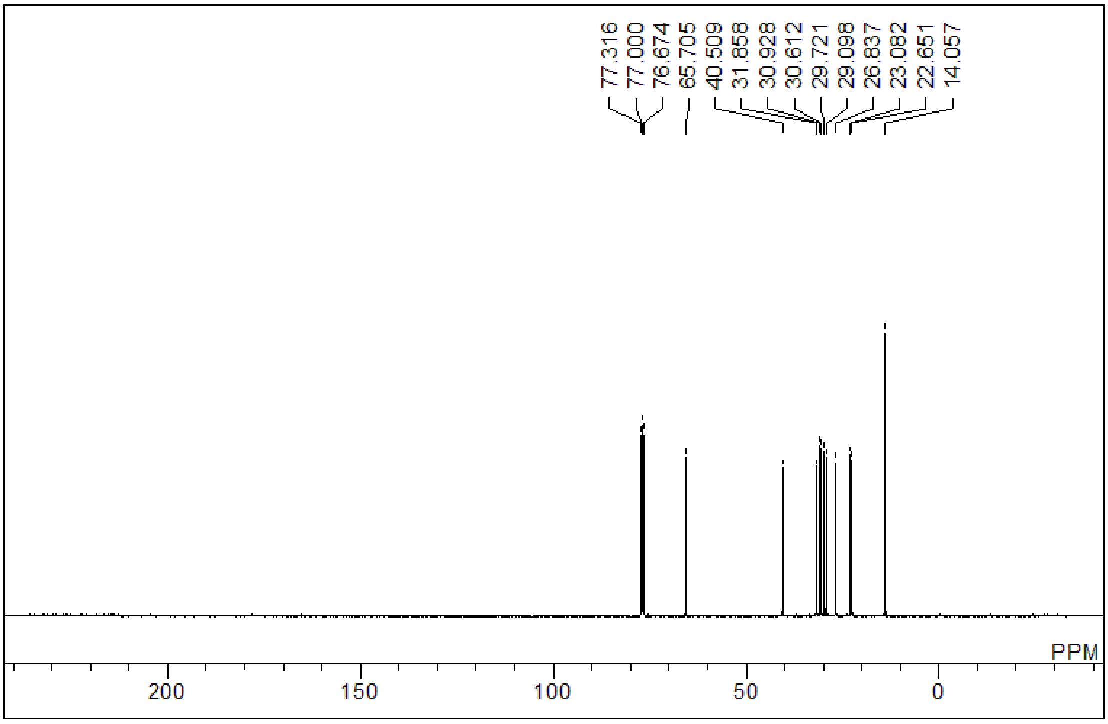
0.0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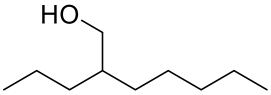
2h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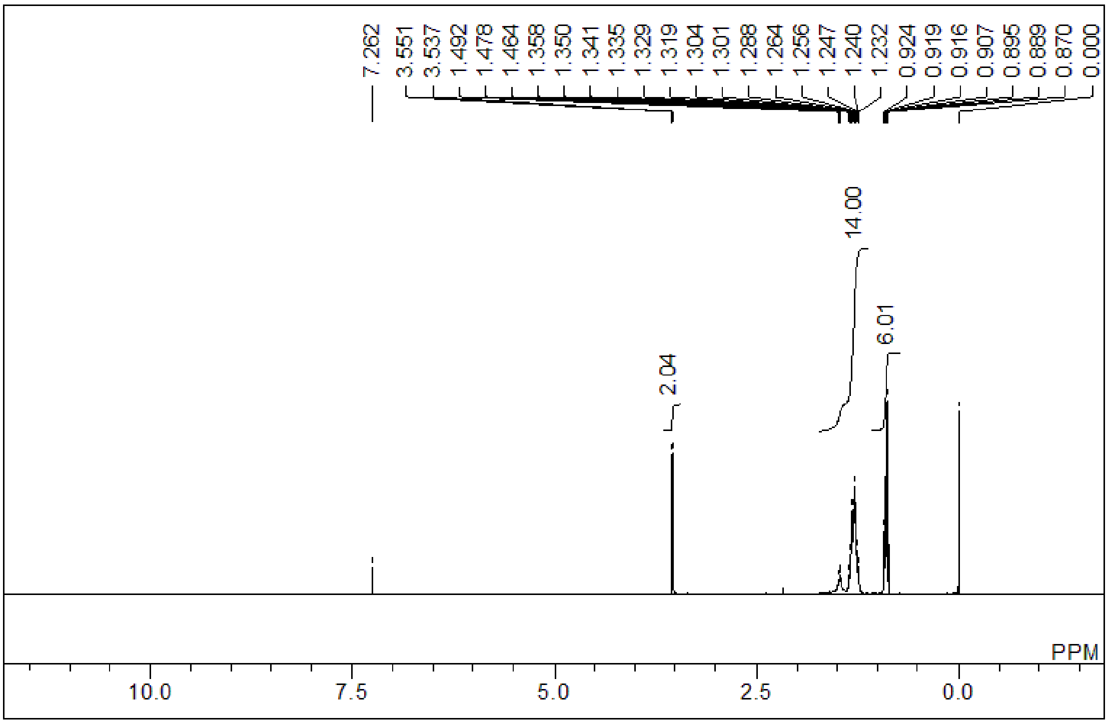
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1.304
1.301
1.288
1.264
1.256
1.247
1.240
1.232
0.924
0.919
0.916
0.907
0.895
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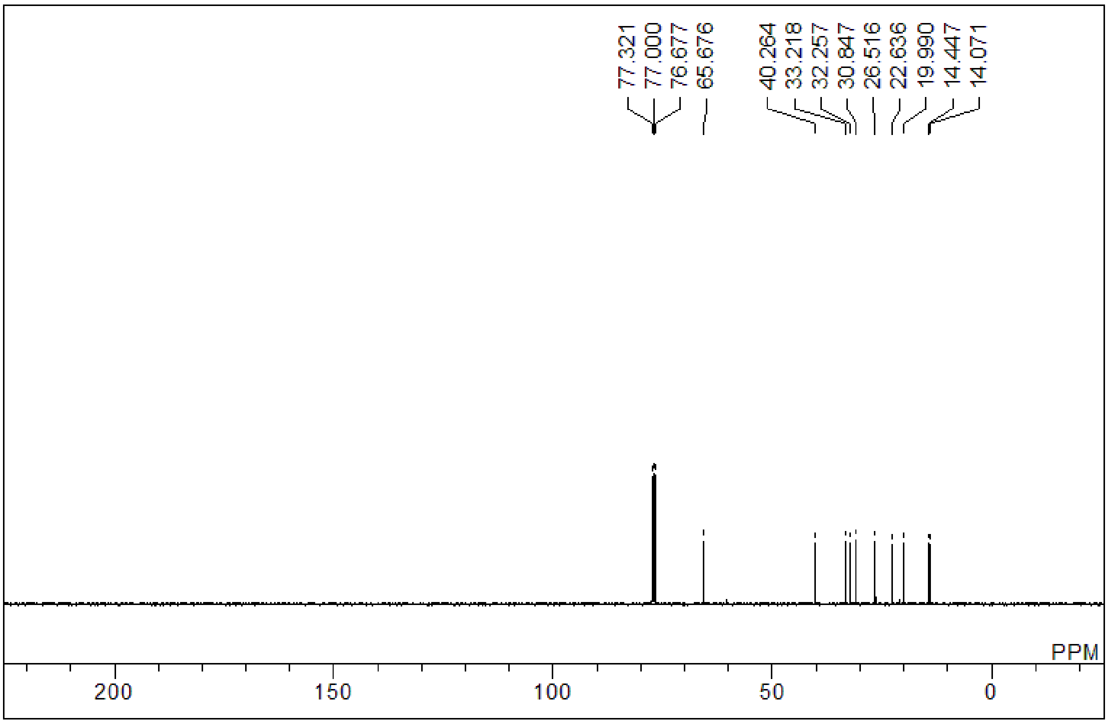
0.0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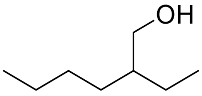
2i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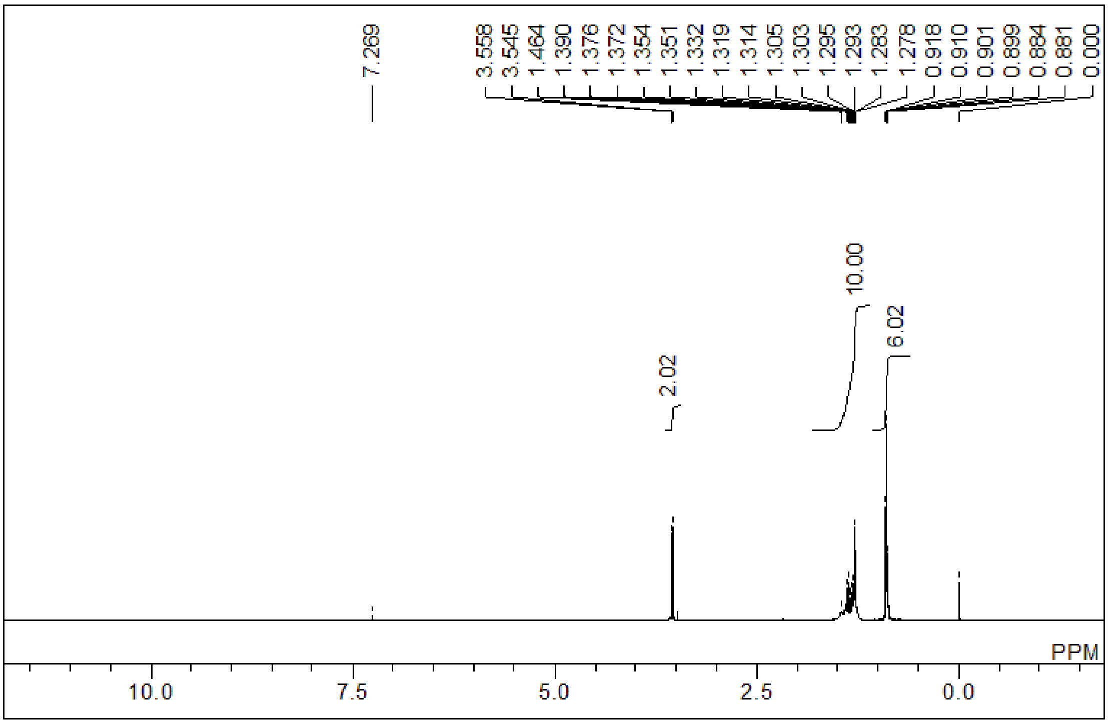
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1.283
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0.910
0.901
0.899
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6.02
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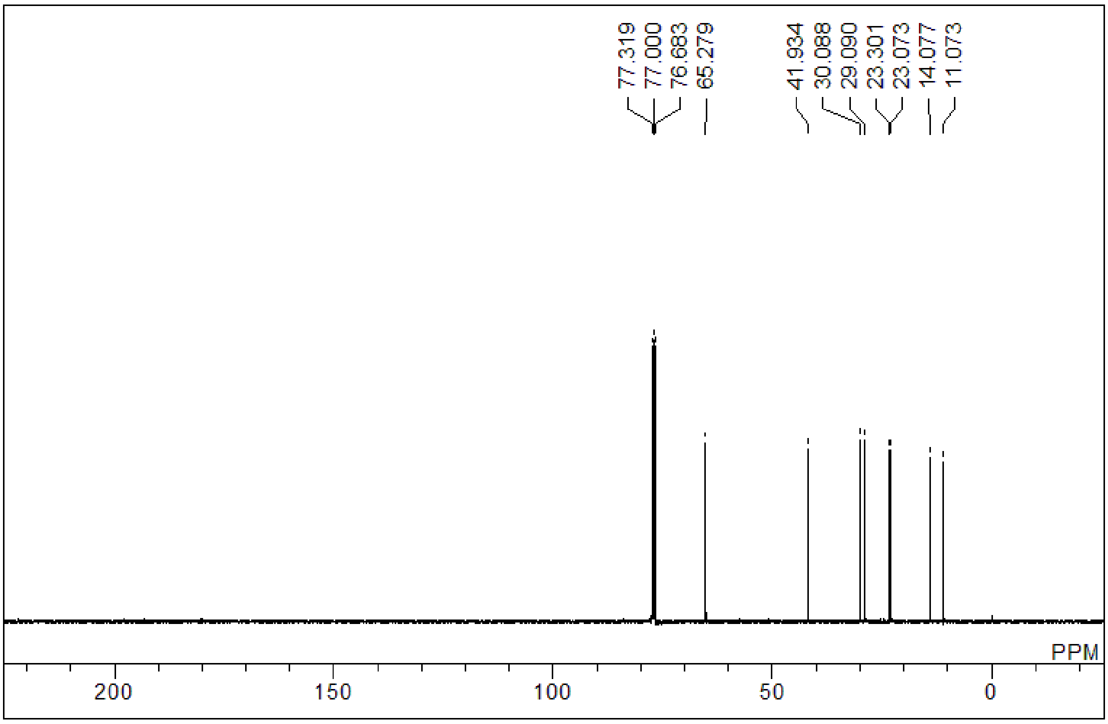
2.5
0.0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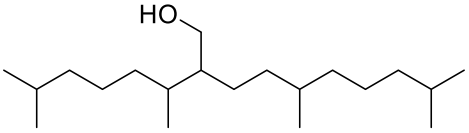

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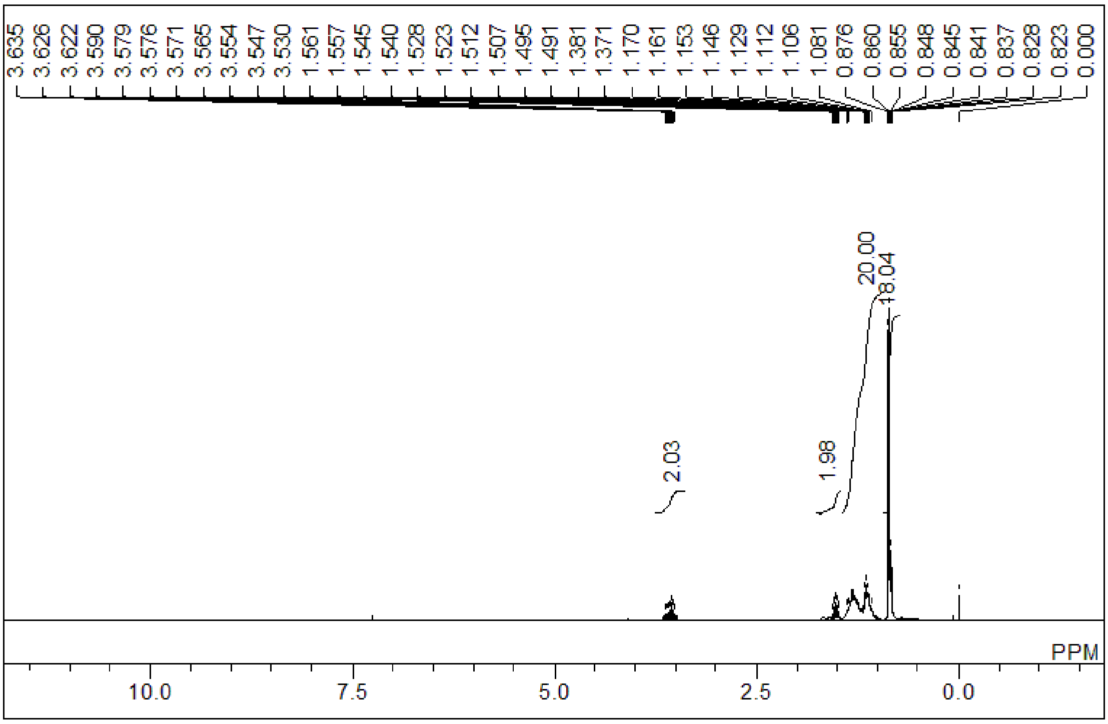
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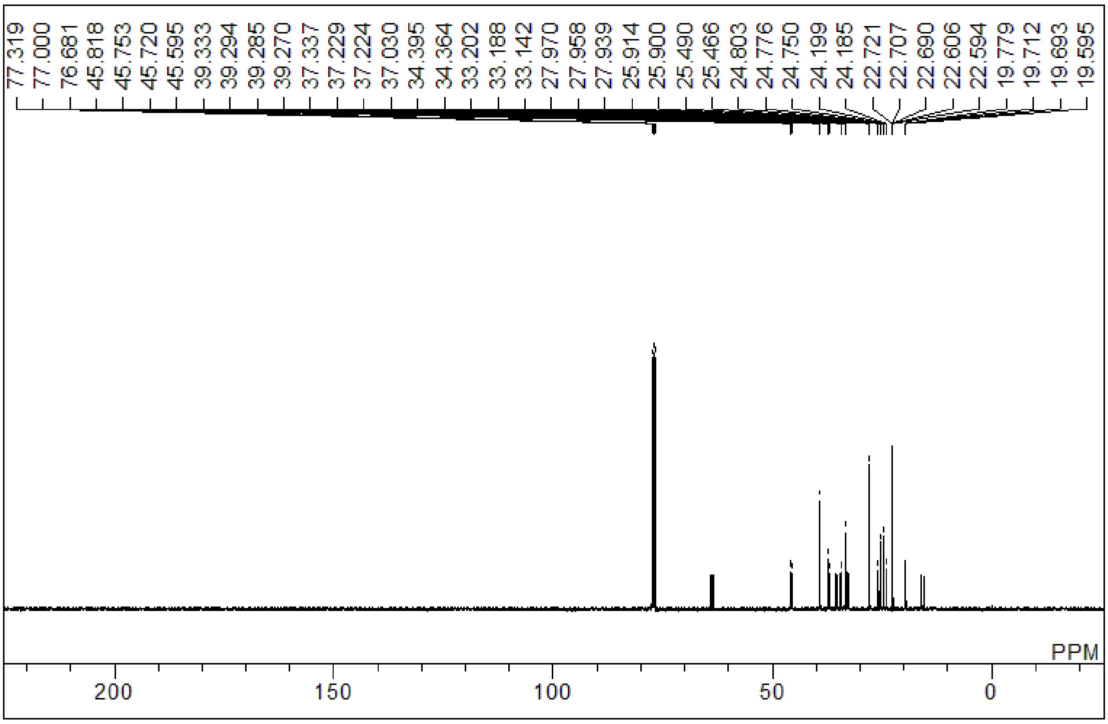
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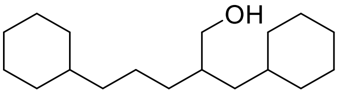
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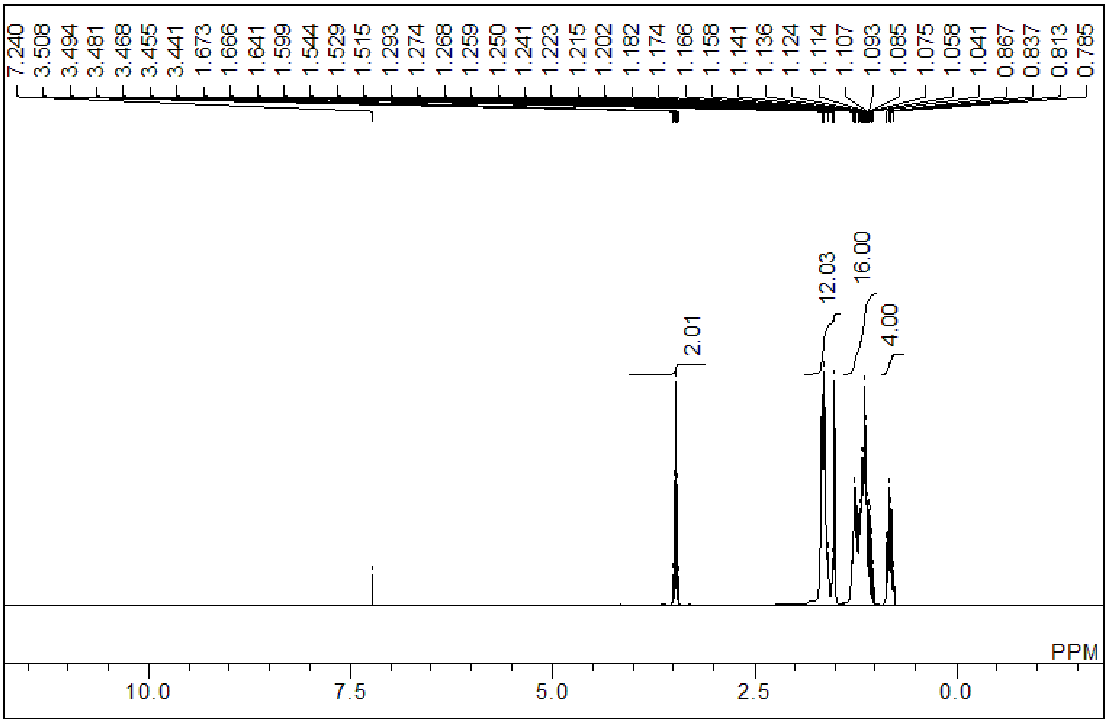
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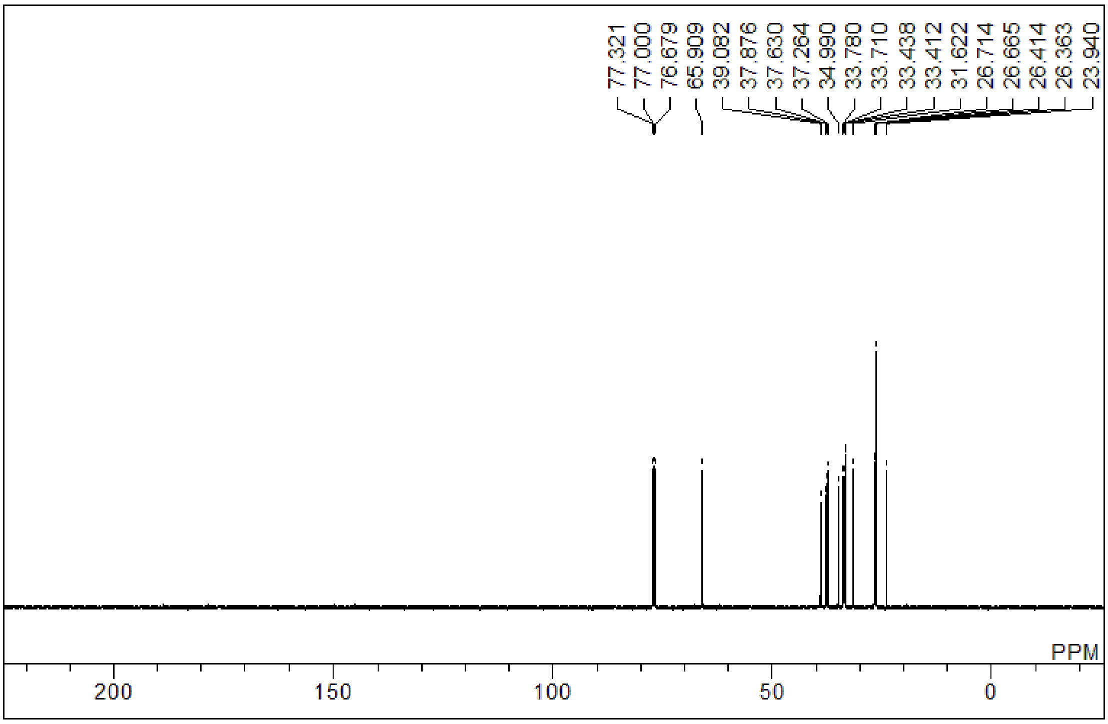
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