Supporting Information

Copper Nanoparticle-Catalyzed Cross-Coupling of Alkyl Halides with Grignard Reagents

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Ⅰ. General Information

Chemicals and Reagents All solvents were dried and distilled according to standard methods before use. Solvents utilized in this work were obtained from Samchun Pure Chemicals (hexanes, ethyl acetate, diethyl ether, dichloromethane, tetrahydrofuran, and acetone).

Copper nanoparticles (5~7 nm, 25~40 nm, and 40~60 nm) were purchased from SkySpring Nanomaterials, Inc. (2935 Westhollow Dr., Houston, TX 77082, USA). Copper(II) oxide nanoparticle were purchased from Aldrich.

Tetrahydrofuran (THF) and toluene were dried over Na/benzophenone and distilled under nitrogen. *n*-Hexane and diethyl ether were used without further purification. Reagents were purchased from Sigma-Aldrich, Alfa Aesar, or TCI and were used as received. 6-Bromo-N,N-diethylhexanamide[1](Table 1, entries 20-21) were prepared according to literature procedures. *Tert*-butylmagnesium chloride (2.0 M solutions in diethyl ether), cyclohexylmagnesium chloride (2.0 M solutions in diethyl ether), *n*-butylmagnesium chloride (2.0 M solutions in THF), methylmagnesium chloride (3.0 M soultions in THF) and phenylmagnesium chloride (2.0 M solutions in THF) were purchased from Aldrich. Reactions were monitored by thin-layer chromatography on 0.25 mm E. Merck silica gel plates (60F-254). The TLC plates were visualized by UV-light (254 nm) and treatment with acidic *p*-anisaldehyde and $KMnO_4$ stain followed by gentle heating. Workup procedures were done in air. Flash column chromatography was carried out on Merck 60 silica gel (230 – 400 mesh).

Physical Methods ^1H and ^{13}C NMR spectra were recorded with Agilent 400-MR DD2 (400 MHz and 100 MHz, respectively) spectrometer. ^1H NMR spectra were taken in $CDCl_3$ and were referenced to residual TMS (0 ppm) and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet). Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.00 ppm). High-Resolution Mass Spectra were obtained at the Korea Basic Science Institute (Daegu, South Korea) on a Jeol JMS 700 high resolution mass spectrometer. GC-MS analyses were performed at NICEM with a Perkin-Elmer Clarus 680GC / 600T with a DB-5MS column (length: 30 m, ID: 0.25 mm, FT: 0.5 μm, Column Program: starting from 40°C, 3 min hold, 10 °C/min to 310°C, 10 min hold). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was obtained at the National Center for Inter-University Facilities (Seoul National University, South Korea) on an OPTIMA 4300DV, Perkin-Elmer (Argon Plasma, 6000 K). The nanoparticles were characterized by high-resolution transmission electron microscopy (JEOL JEM-2100). X-Ray Diffraction (XRD) data were obtained at the Research Institute of Advanced Material (Seoul National University, South

Korea) on a Brucker New D8 Advance.

Ⅱ. Characterization of the catalyst & reused catalysts (HR-TEM and XRD, ICP-AES data)

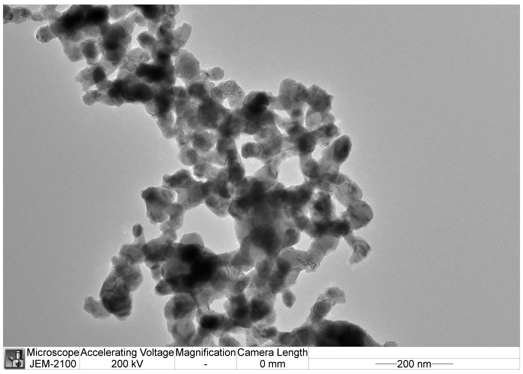


Figure S1. HRTEM images of Cu NPs (new)

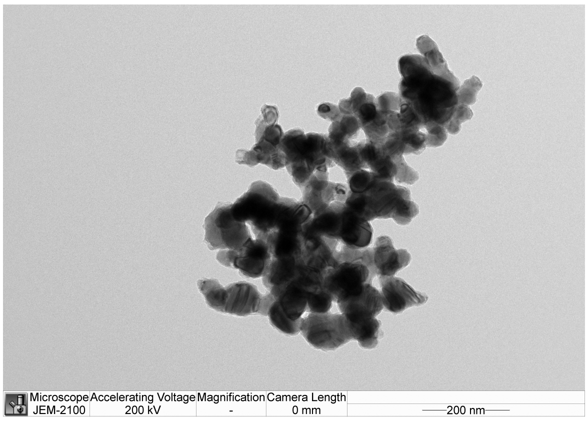


Figure S2. HRTEM images of Cu NP catalyst (after 1st use)

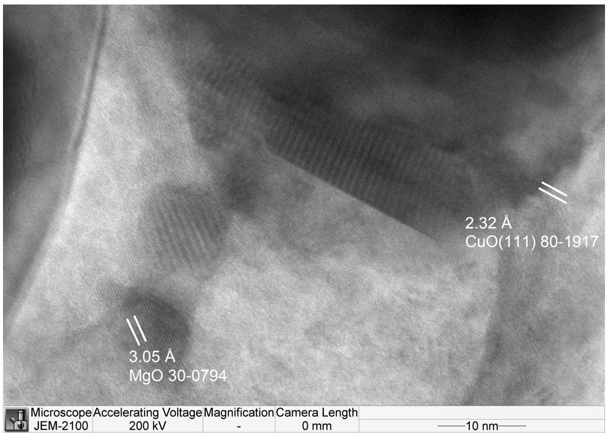


Figure S3. HRTEM images of Cu NP catalyst (after 6th run)

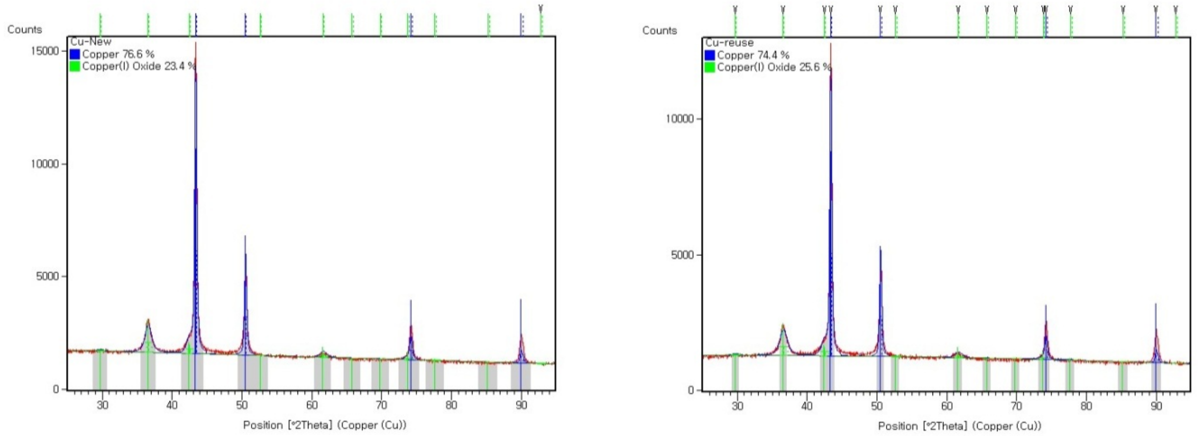


Fig S4. XRD data of Cu NP catalyst (new and 1st reused).

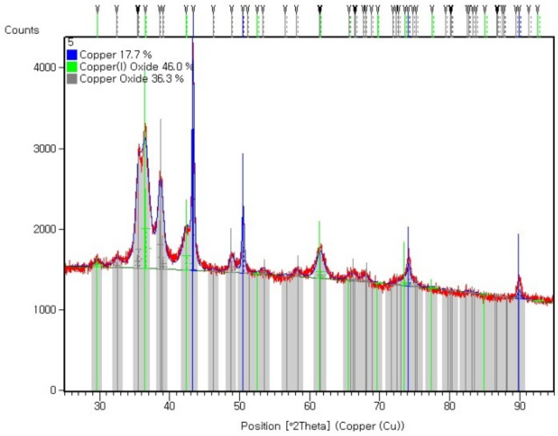
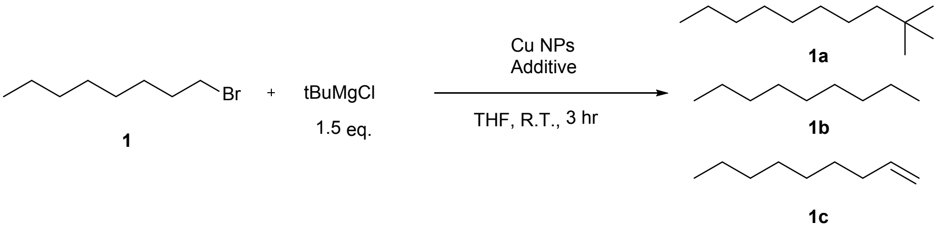


Fig S5. XRD data of Cu NP catalyst (after 5th reuse).

Ⅲ. Screening various reaction conditions and a proposed reaction mechanism

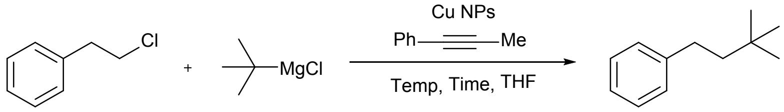
Table S1. Screening the size of the Cu NPs catalyst and additives[a]



Entry	Cat. Size (nm)	Types of Additive	Amounts of Additive (mol %)	Yield (%)[b]		
				1a	**1b**	**1c**
1	X	X	X	No reaction		
2	25-40	Ph—≡—Me	20	>99		
3	40-60	Ph—≡—Me	20	>99		
4	5-7	Ph—≡—Me	20	41	13	22
5	25-40	Ph—≡—Et	20	>99		
6	25-40	Ph—≡—Ph	20	>99		
7[c]	25-40	Ph—≡—H	20	72		
8	25-40	Ph—≡—Me	10	>99		
9	25-40	Ph—≡—Me	40	>99		
10	25-40	Ph—≡—Me	80	>99		

[a] Reaction conditions: **1** (1 mmol), 10 mol% of catalyst, 1 mL of THF. [b] Determined by GC using 1,3,5-trimethyl benzene as an internal standard. [c] 27 % of reactant was recovered.

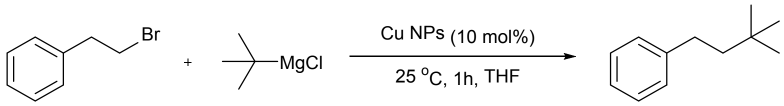
Table S2. Optimization of the cross coupling reaction of 2-chloroethylbenzene with *t*-BuMgCl



Entry	Cat. (mol%)	Additive (mol%)	Grignard (eq.)	Temp (°C)	Time (h)	Yield (%) [a]
1	10	0	1.2	25	1	0
2	10	0	1.2	80	24	13
3	10	10	1.2	40	12	45
4	10	20	1.5	60	12	63
5	10	30	1.5	80	12	61
6	20	20	1.5	60	12	84
7	20	20	1.5	80	6	59
8	20	20	1.5	80	12	96

[a] Determined by GC using 1,3,5-trimethyl benzene as an internal standard.

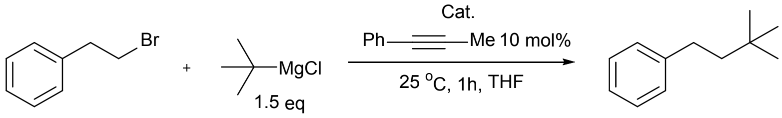
Table S3. Reuse of catalysts.



Entry	Catalyst	Yield[a]
1	1st run	99
2	2nd run	99
3	3rd run	99
4	4th run	99
5	5th run	99
6	6th run	90

[a] Determined by GC using 1,3,5-trimethyl benzene as an internal standard.

Table S4. Screening the Various catalyst.



Entry	Catalyst	Yield (%) [a]
1	Metallic Cu powder	N. R.
2	Metallic CuO powder	N. R.
3	CuO nanoparticle (10 mol%)	84
4	CuCl (0.1 mol%)	trace

[a] Determined by GC using 1,3,5-trimethyl benzene as an internal standard. (N. R. = No reaction)

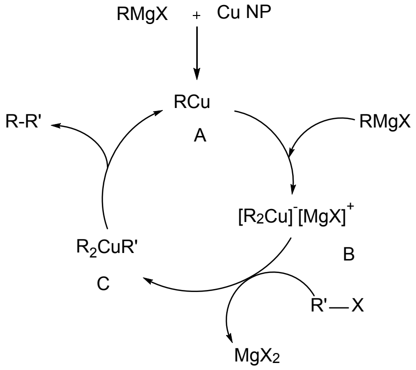
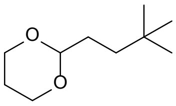


Fig S6. A Proposed reaction mechanism.

V. General Procedure for the entries reported Table 1 from alkyl bromides

Reactions were performed in a schlenk tube equipped with a stirring bar and capped with a rubber septum. The followings were placed in the tube in order: 7 mg (c.a. 10 mol%) of catalyst (in a glove box), 1 mmol of alkyl bromide**,** 20 mol% (24 μL) of 1-phenylpropyne, 1.5 eq. (0.75 mL) of alkyl Grignard reagents and 1 mL of THF. The mixture was stirred at room temperature for 3 h. The reaction mixture was extracted with aqueous NH_4Cl solution and diethyl ether and dried over $MgSO_4$, filtered and finally evaporated under reduced pressure. The mixture was purified by flash chromatography on silica gel (*n*-hexane/diethyl ether) to afford the product. Products that were not isolated by column chromatography were determined by GC analysis using 1,3,5-trimethylbenzene as an internal standard.

Characterization Data for the Isolated Products

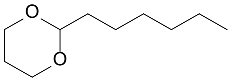


2-(3,3-dimethylbutyl)-1,3-dioxane (table 1, entry 10): colorless liquid, Purified from column with hexane/diethyl ether (5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (t, *J* = 5.2 Hz, 1 H), 4.03 (dd, *J* = 10.8, 5.0 Hz, 2 H), 3.68 (td, *J* = 12.4, 2.4 Hz, 2 H), 2.07 – 1.94 (m, 1 H), 1.54 – 1.47 (m, 2 H), 1.28 – 1.24 (m, 1 H), 1.23 – 1.18 (m, 2 H), 0.80 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 103.0, 66.8, 37.8, 31.5, 30.5, 29.7, 29.1, 25.8, 22.5, 14.0.

HRMS (FAB) calc. for $[C_{10}H_{21}O_2, M+H]^+$ 173.1542, found 173.1543.

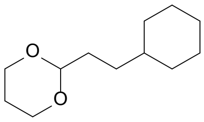


2-hexyl-1,3-dioxane (table 1, entry 12): colorless liquid, Purified from column with hexane/diethyl ether (5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43 (t, *J* = 5.2 Hz, 1 H), 4.05 – 3.99 (m, 2 H), 3.72 – 3.64 (m, 2 H), 2.07 – 1.94 (m, 1 H), 1.54 – 1.48 (m, 2 H), 1.33 – 1.17 (m, 9 H), 0.80 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 102.3, 66.7, 35.1, 31.6, 29.1, 25.8, 23.8, 22.4, 13.9.

HRMS (FAB) calc. for $[C_{10}H_{21}O_2, M+H]^+$ 173.1542, found 173.1539.

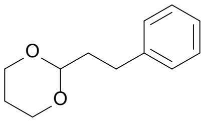


2-(2-cyclohexylethyl)-1,3-dioxane (table 1, entry 11): colorless liquid, Purified from column with hexane/diethyl ether (5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.41 (t, *J* = 5.2 Hz, 1 H), 4.02 (dd, *J* = 10.9, 4.9 Hz, 2 H), 3.68 (td, *J* = 12.3, 2.1 Hz, 2 H), 2.06 – 1.94 (m, 1 H), 1.67 – 1.57 (m, 4 H), 1.55 – 1.49 (m, 2 H), 1.29 – 1.02 (m, 8 H), 0.85 – 0.78 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 102.7, 66.8, 37.4, 33.1, 32.6, 31.4, 26.5, 26.2, 25.8.

HRMS (FAB) calc. for $[C_{12}H_{23}O_2, M+H]^+$ 199.1698, found 199.1696.

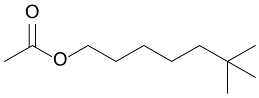


2-phenethyl-1,3-dioxane (table 1, entry 13): colorless liquid, Purified from column with hexane/diethyl ether (5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 4.48 (t, *J* = 5.2 Hz, 1H), 4.11 – 4.05 (m, 2H), 3.74 – 3.67 (m, 2H), 2.71 (dd, *J* = 9.1, 7.0 Hz, 2H), 2.11 – 2.00 (m, 1H), 1.93 – 1.88 (m, 2H), 1.31 – 1.26 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 128.3, 128.2, 125.6, 101.3, 66.7, 36.5, 29.9, 25.7.

HRMS (FAB) calc. for $[C_{12}H_{17}O_2, M+H]^+$ 193.1229, found 193.1225.

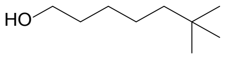


6,6-dimethylheptyl acetate (table 1, entry 14): colorless liquid, Purified from column with hexane/diethyl ether (10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (td, *J* = 6.7, 0.9 Hz, 2 H), 1.97 (d, *J* = 1.2 Hz, 3 H), 1.59 – 1.53 (m, 2 H), 1.27 – 1.19 (m, 4 H), 1.09 – 1.07 (m, 2 H), 0.79 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 64.6, 44.0, 30.2, 29.3, 28.6, 26.8, 24.2, 20.9.

HRMS (EI) calc. for $[C_{11}H_{23}O_2, M+H]^+$ 187.1698, found 187.1770.

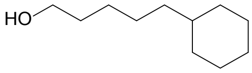


6,6-dimethyl-1-heptanol (table 1, entry 15): colorless liquid, Purified from column with hexane/diethyl ether (3:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 (t, *J* = 6.7 Hz, 2 H), 2.52 (s, 1 H), 1.54 – 1.46 (m, 2 H), 1.29 – 1.15 (m, 4 H), 1.13 – 1.07 (m, 2 H), 0.79 (s, 9 H).

^{13}C NMR (100 MHz, CDl_3) δ 62.7, 44.1, 32.8, 30.2, 29.3, 26.6, 24.3.

HRMS (EI) calc. for $[C_9H_{19}O, M-H]^+$ 143.1436, found 143.1435.

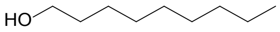


5-cyclohexyl-1-pentanol (table 1, entry 16): colorless liquid, Purified from column with hexane/diethyl ether (3:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (t, *J* = 6.7 Hz, 2 H), 2.50 (s, 1 H), 1.65 – 1.54 (m, 5 H), 1.51 – 1.44 (m, 2 H), 1.26 – 1.21 (m, 4 H), 1.17 – 1.03 (m, 6 H), 0.83 – 0.76 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 62.7, 37.5, 37.4, 33.3, 32.7, 26.7, 26.6, 26.3, 26.0.

HRMS (EI) calc. for $[C_{11}H_{21}O, M-H]^+$ 169.1592, found 169.1590.

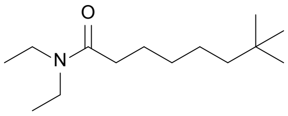


5-cyclohexyl-1-pentanol (table 1, entry 17): colorless liquid, Purified from column with hexane/diethyl ether (3:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (t, *J* = 6.7 Hz, 2 H), 2.41 (s, 1 H), 1.53 – 1.44 (m, 2 H), 1.28 – 1.17 (m, 12 H), 0.81 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 62.7, 32.7, 31.8, 29.5, 29.4, 29.2, 25.7, 22.6, 14.0.

HRMS (EI) calc. for $[C_9H_{19}O, M-H]^+$ 143.1436, found 143.1437.

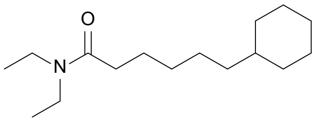


N,N-diethyl-7,7-dimethyloctanamide (table 1, entry 19): colorless liquid, Purified from column with hexane/diethyl ether (4:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (q, *J* = 7.1 Hz, 2 H), 3.17 (q, *J* = 7.2 Hz, 2 H), 2.17 – 2.13 (m, 2 H), 1.56 – 1.48 (m, 2 H), 1.20 – 1.11 (m, 4 H), 1.07 – 1.01 (m, 5 H), 0.97 (t, *J* = 7.1 Hz, 3 H), 0.72 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 43.8, 41.7, 39.8, 32.9, 30.2, 30.0, 29.1, 25.3, 24.1, 14.2, 13.0.

HRMS (FAB) calc. for $[C_{14}H_{30}NO, M+H]^+$ 228.2327, found 228.2329.

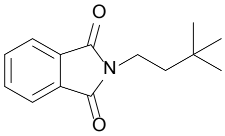


6-cyclohexyl-N,N-diethylhexanamide (table 1, entry 20) : colorless liquid, Purified from column with hexane/diethyl ether (4:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 – 3.17 (m, 2 H), 3.16 – 3.09 (m, 2 H), 2.15 – 2.06 (m, 2 H), 1.57 – 1.38 (m, 7 H), 1.20 – 1.09 (m, 4 H), 1.09 – 0.95 (m, 9 H), 0.93 (td, *J* = 7.1, 2.7 Hz, 3 H), 0.73 – 0.61 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 41.6, 39.6, 37.3, 37.0, 33.1, 32.8, 29.5, 26.4, 26.3, 26.1, 25.2, 14.0, 12.7.

HRMS (FAB) calc. for $[C_{16}H_{32}NO, M+H]^+$ 254.2484, found 254.2485.

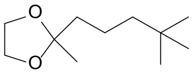


2-(3,3-dimethylbutyl)isoindoline-1,3-dione (table 1, entry 21): pale yellow liquid, Purified from column with hexane/diethyl ether (4:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.5 Hz, 1 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.47 (td, *J* = 7.5, 1.1 Hz, 1 H), 7.39 (td, *J* = 7.4, 0.8 Hz, 1 H), 4.12 – 4.01 (m, 2 H), 3.68 (ddd, *J* = 10.2, 7.9, 6.6 Hz, 1 H), 3.40 – 3.32 (m, 1 H), 0.94 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 148.5, 132.8, 132.4, 129.3, 123.9, 123.5, 105.3, 69.2, 46.21, 39.5, 25.4.

HRMS (FAB) calc. for $[C_{14}H_{18}NO_2, M+H]^+$ 232.1338, found 232.1340.



2-(4,4-dimethylpentyl)-2-methyl-1,3-dioxolane (table 2, entry 7): colorless liquid, eluted, Purified from column with hexane/diethyl ether (15:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (q, *J* = 5.7 Hz, 4 H), 1.52 (dd, *J* = 10.3, 6.0 Hz, 2 H), 1.33 – 1.26 (m, 2 H), 1.25 (s, 3 H), 1.13 – 1.07 (m, 2 H), 0.81 (s, 9 H).

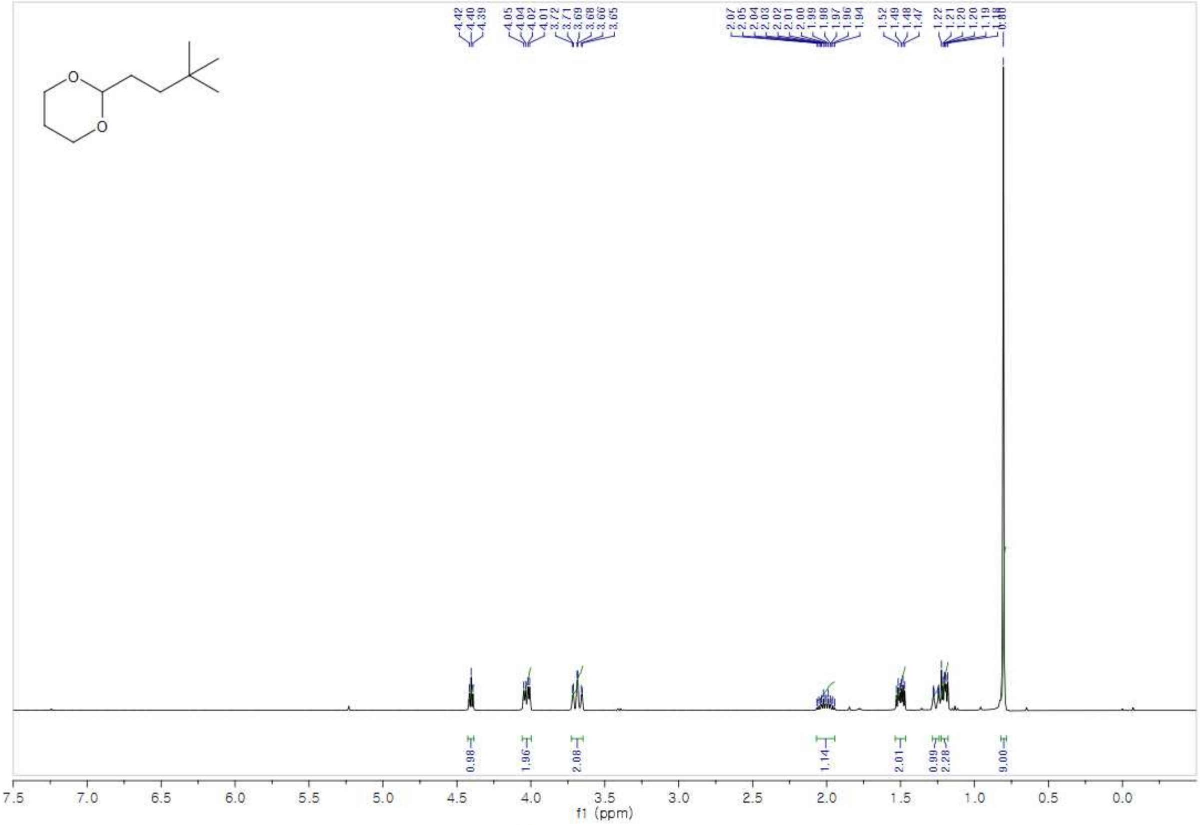
^{13}C NMR (100 MHz, $CDCl_3$) δ 110.1, 64.5, 44.3, 40.1, 30.3, 29.4, 23.7, 19.1.

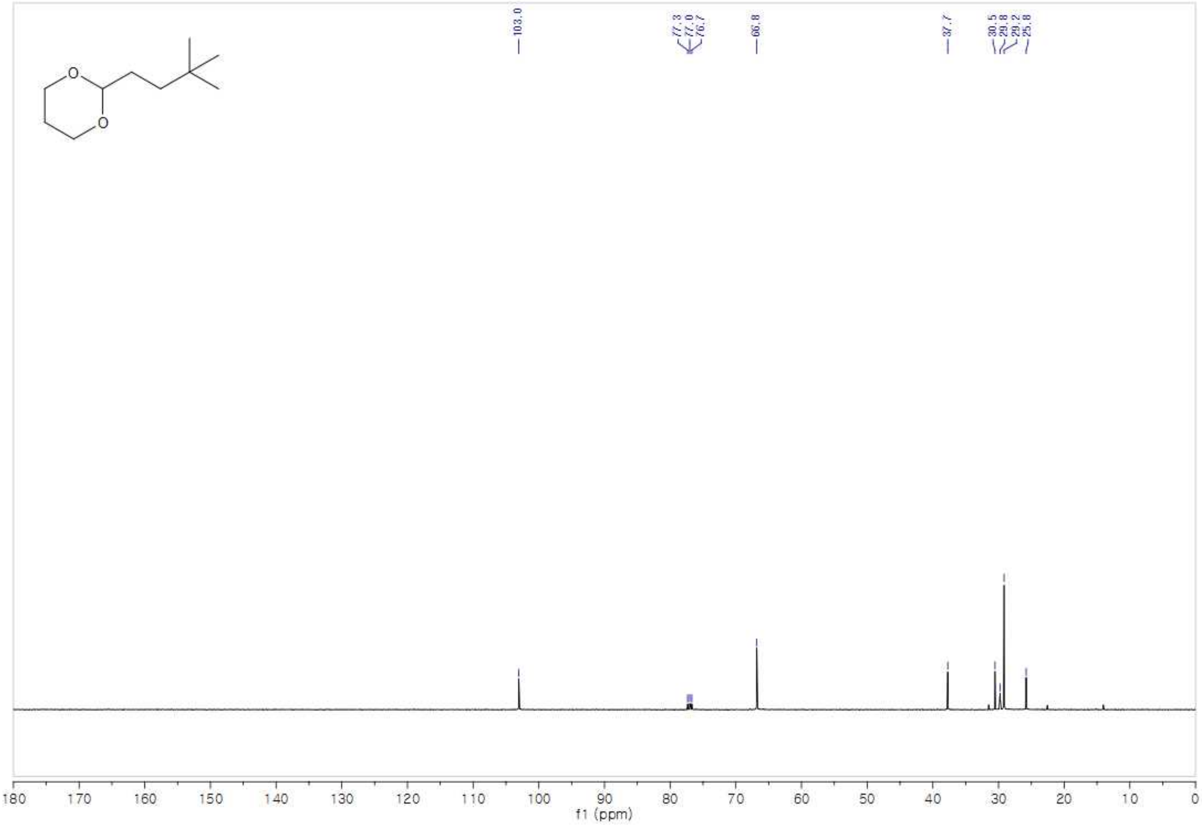
HRMS (FAB) calc. for $[C_{11}H_{23}O_2, M+H]^+$ 187.1698, found 187.1696.

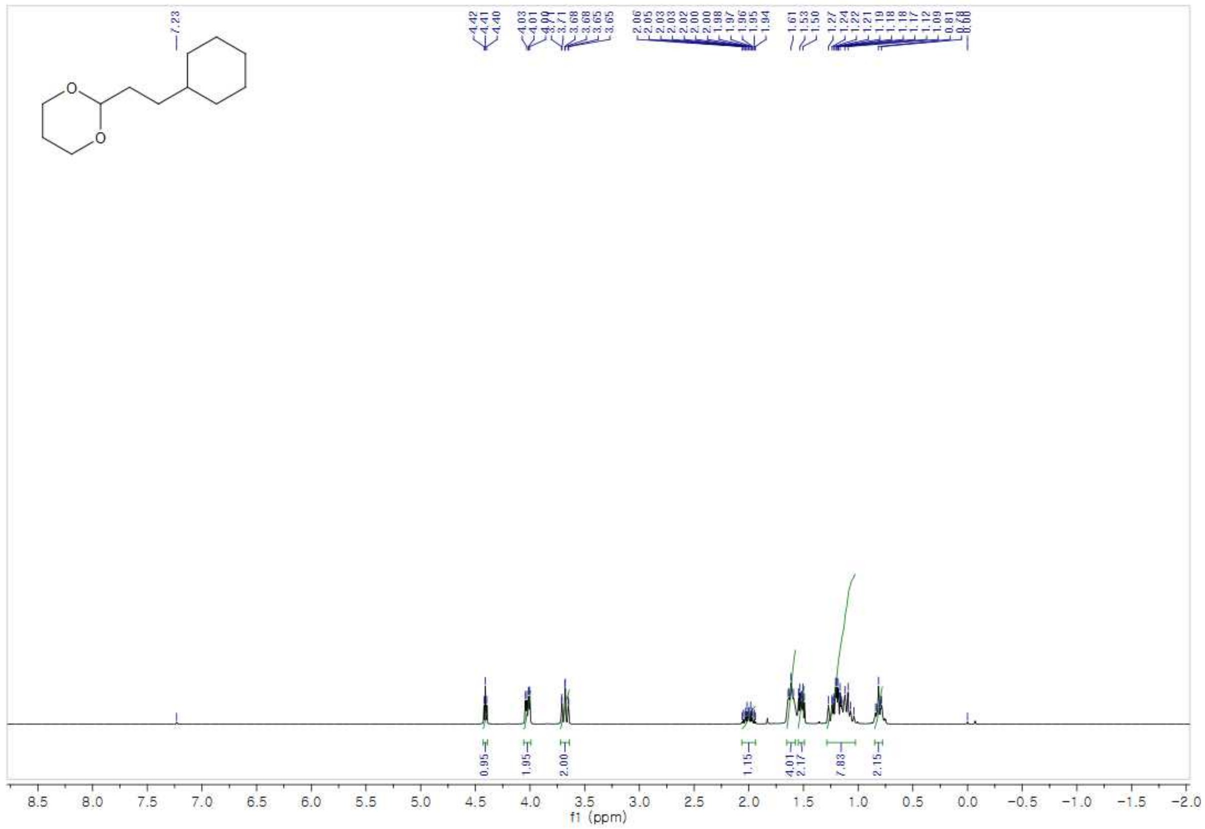
References

1. J. Zhou, G. C. Fu, *J. Am. Chem. Soc.* 2003, **125**, 12527-12530.

Ⅵ. NMR Spectra of Isolated Products



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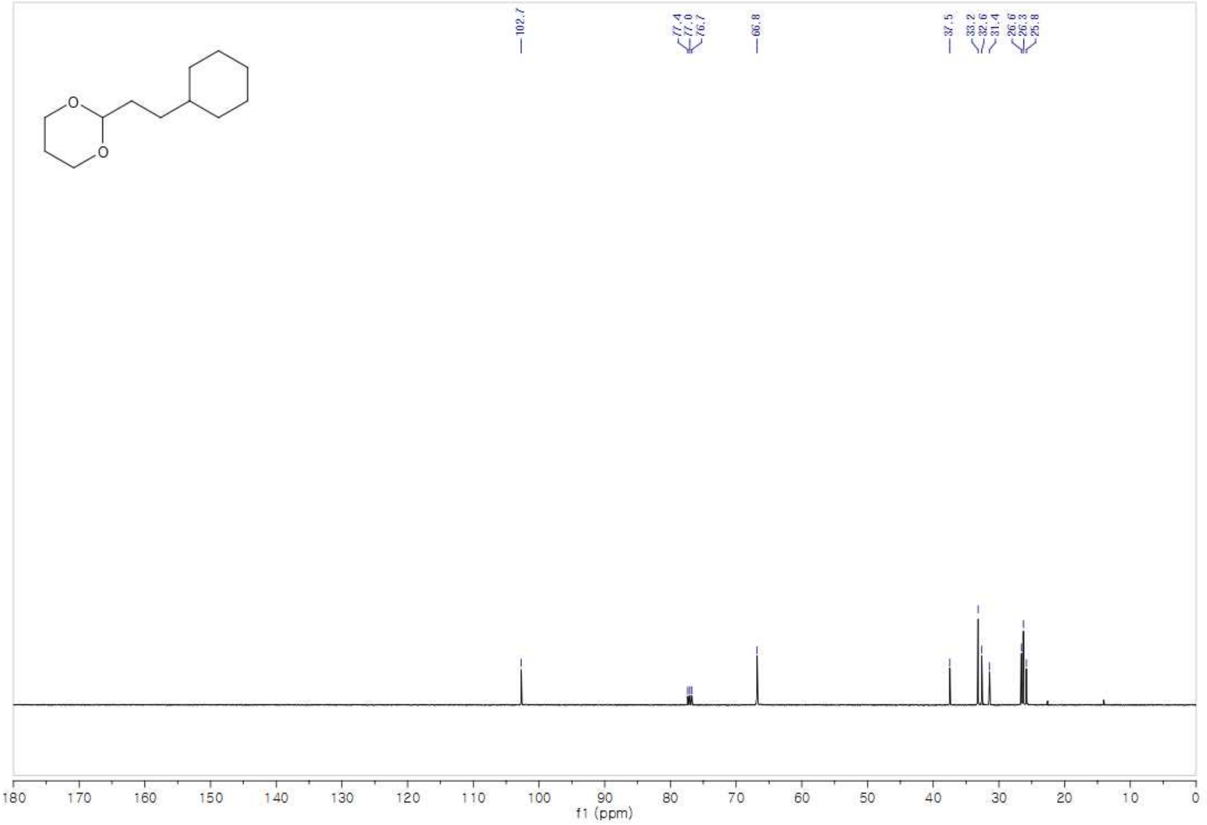
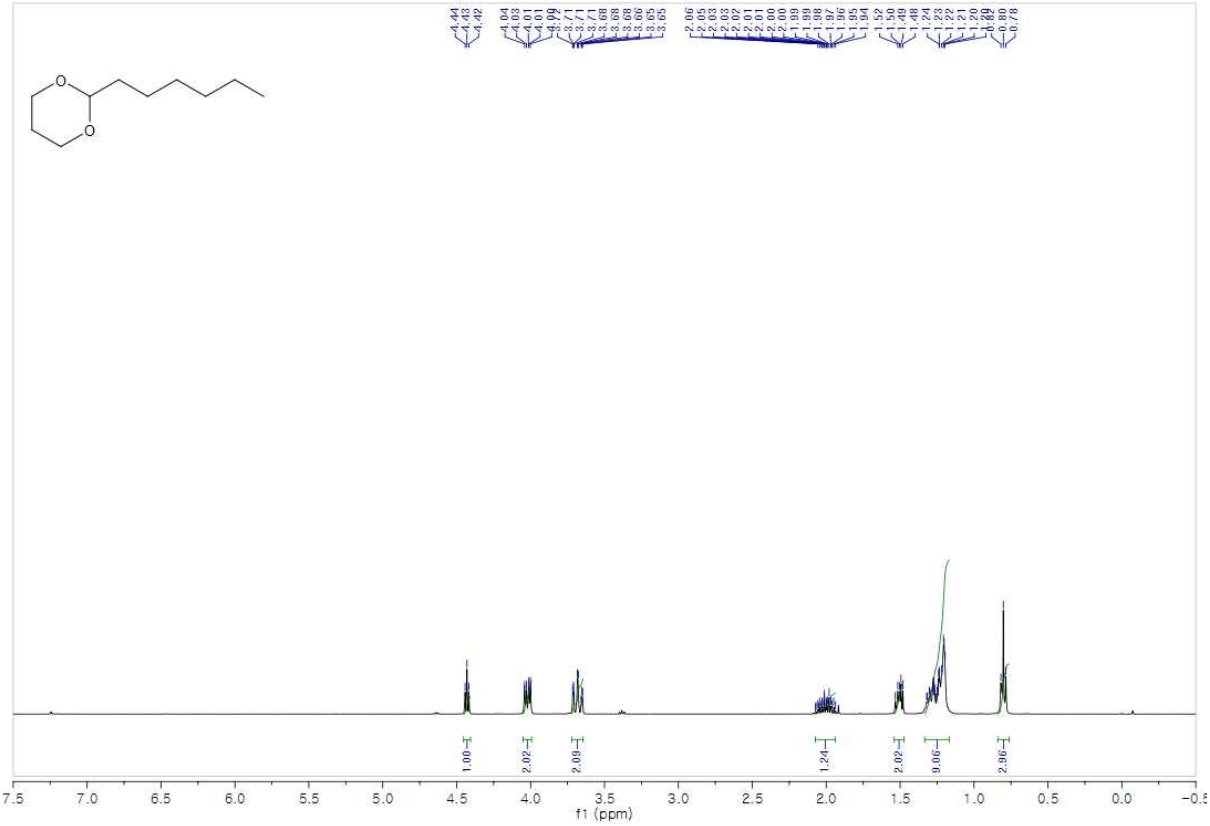
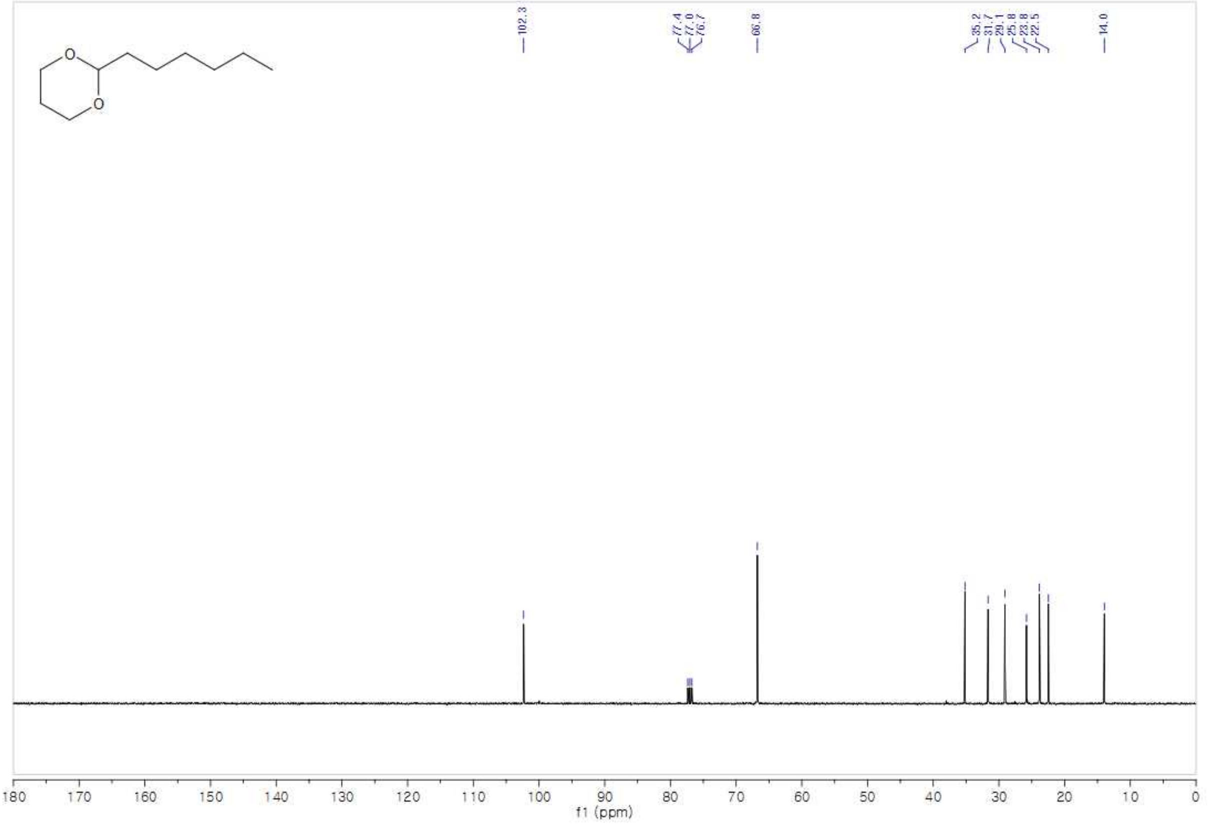
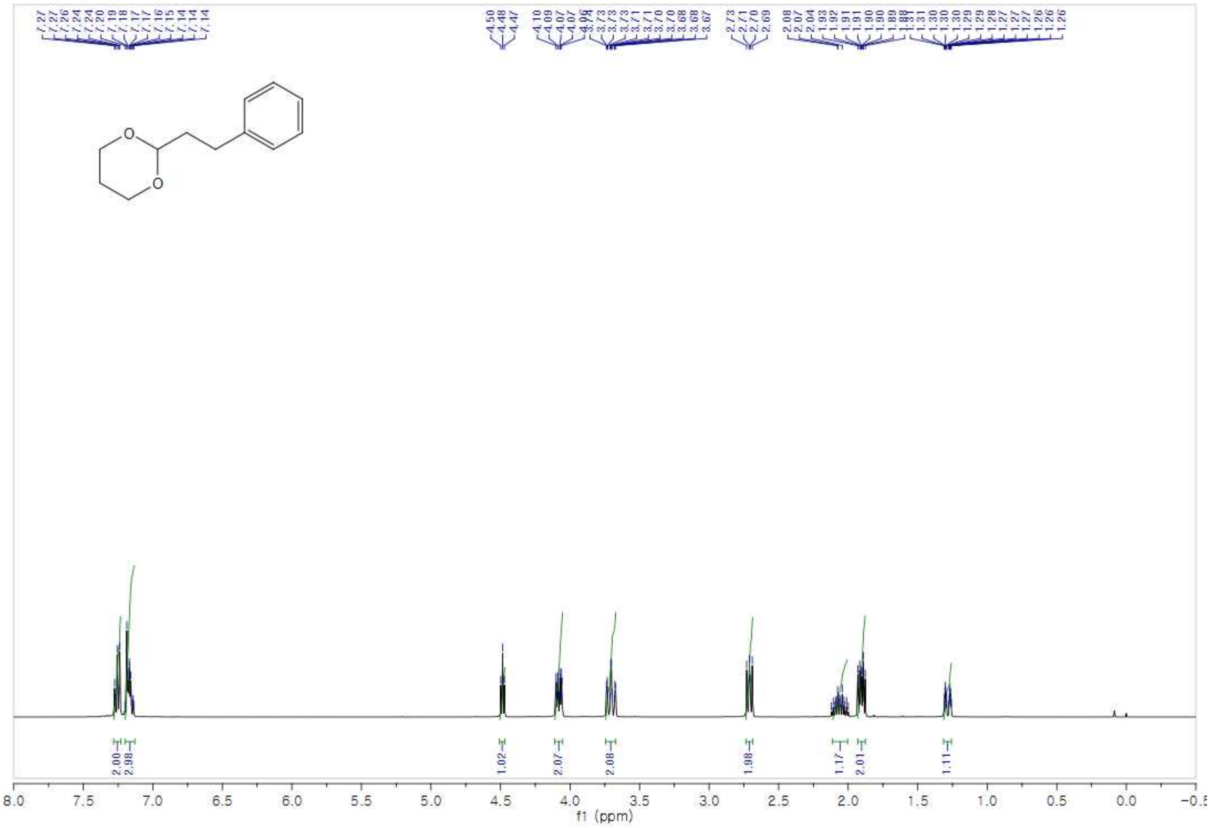
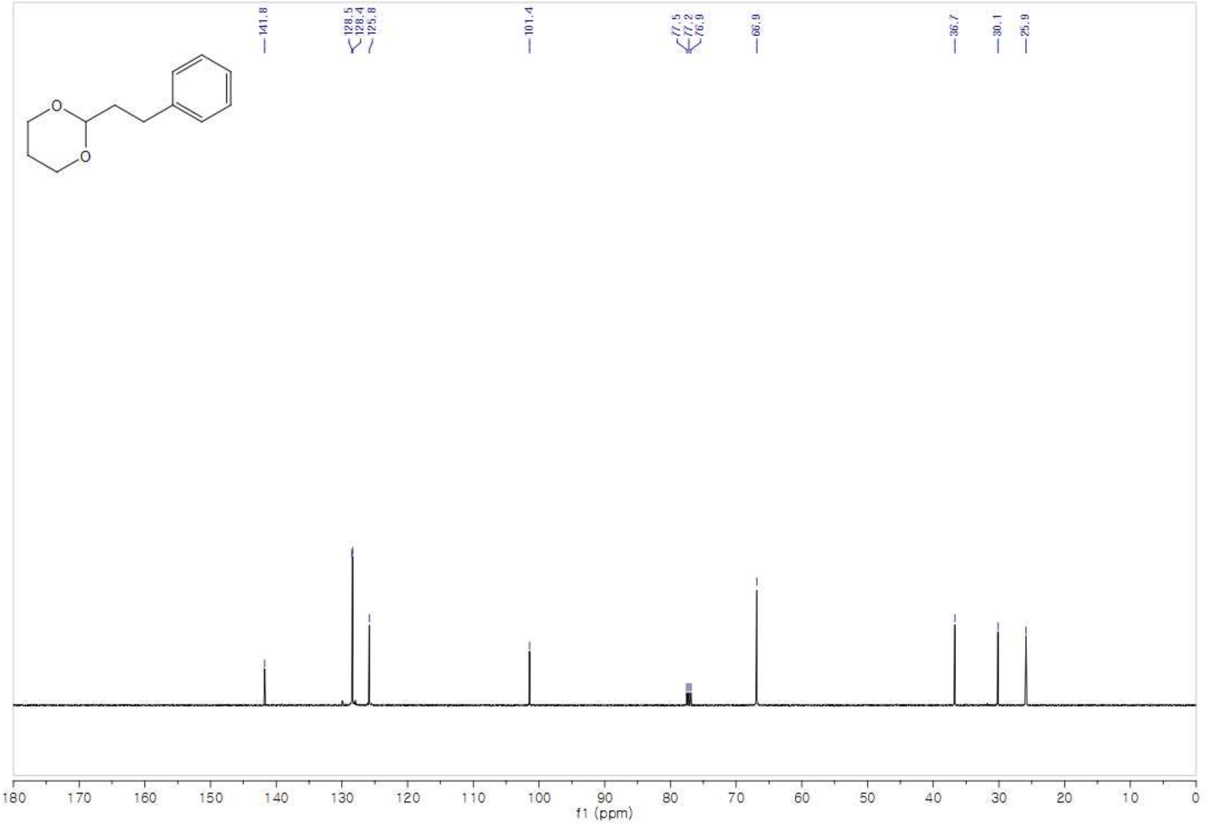
−1.0
−1.5
−2.0
f1 (ppm)

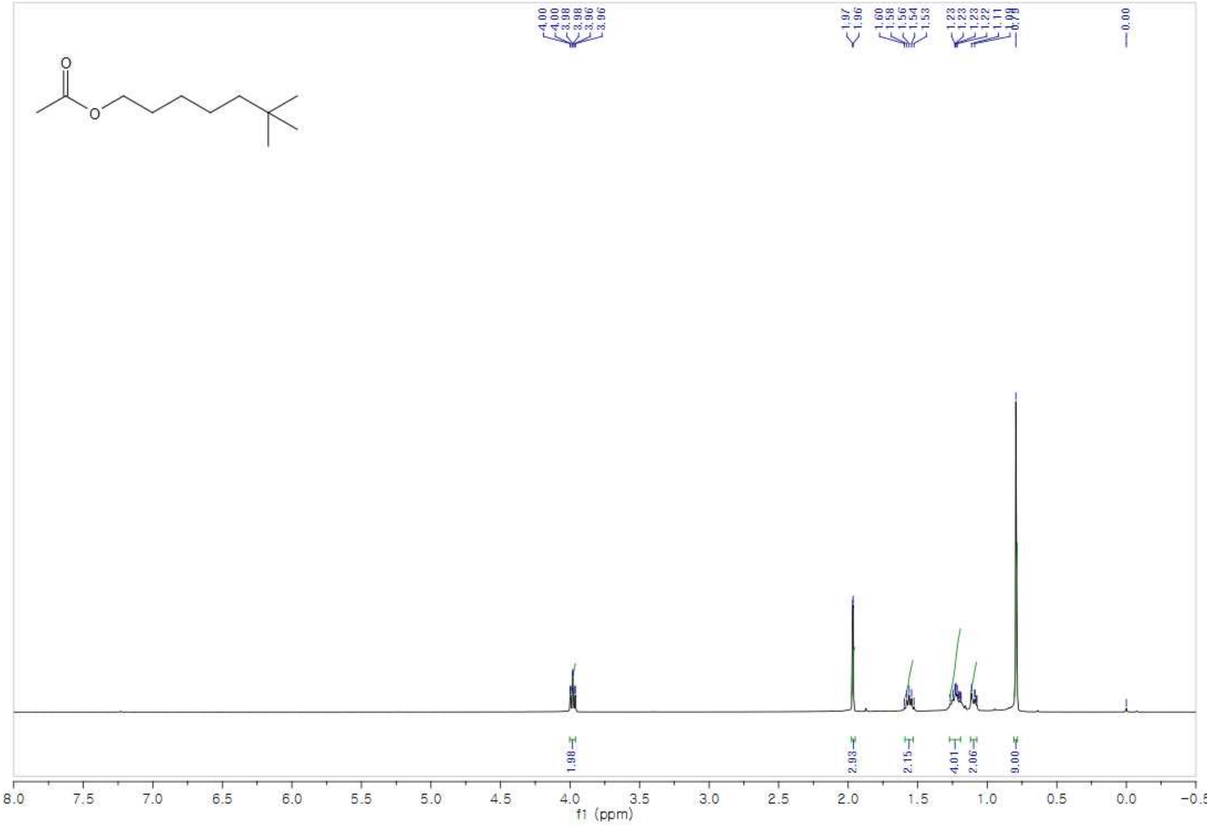

102.7
77.4
77.0
76.7
66.8
37.5
33.2
32.6
31.4
26.6
26.3
25.8
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

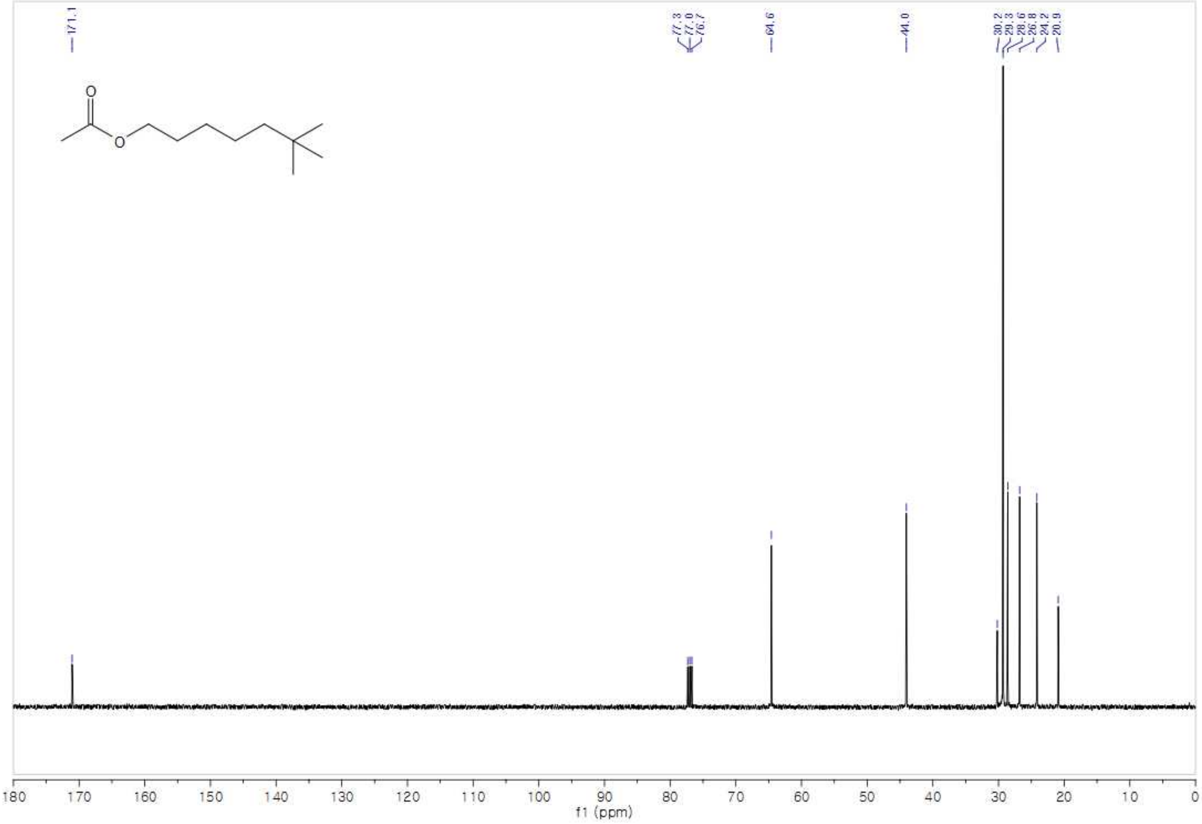

O
O
4.44
4.43
4.42
4.04
4.03
4.01
4.01
4.00
3.72
3.71
3.71
3.71
3.68
3.68
3.68
3.66
3.65
3.65
2.06
2.05
2.03
2.03
2.02
2.01
2.01
2.00
2.00
1.99
1.98
1.98
1.97
1.96
1.95
1.94
1.52
1.50
1.49
1.48
1.24
1.23
1.22
1.21
1.20
1.20
0.82
0.80
0.78
1.00
2.02
2.09
1.24
2.02
9.06
2.96
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

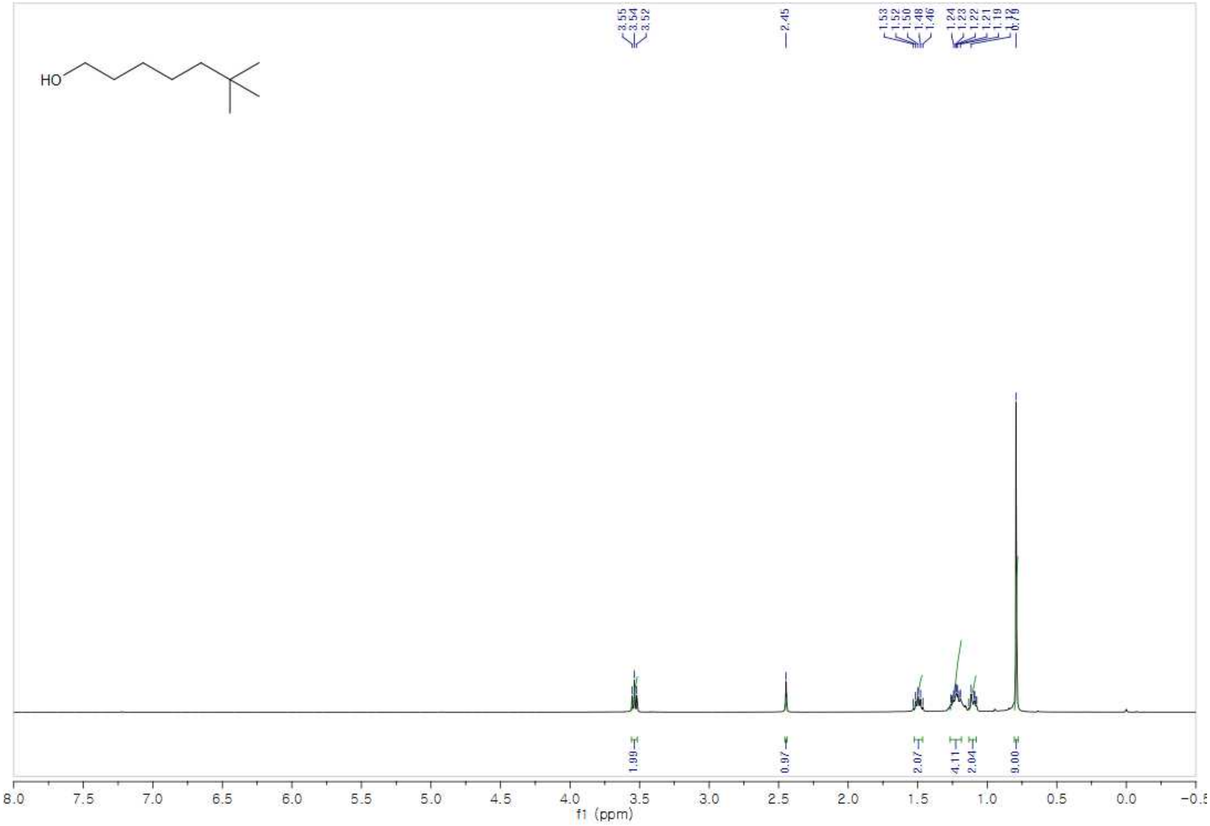

O
O
102.3
77.4
77.0
76.7
66.8
35.2
31.7
29.1
25.8
23.8
22.5
14.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

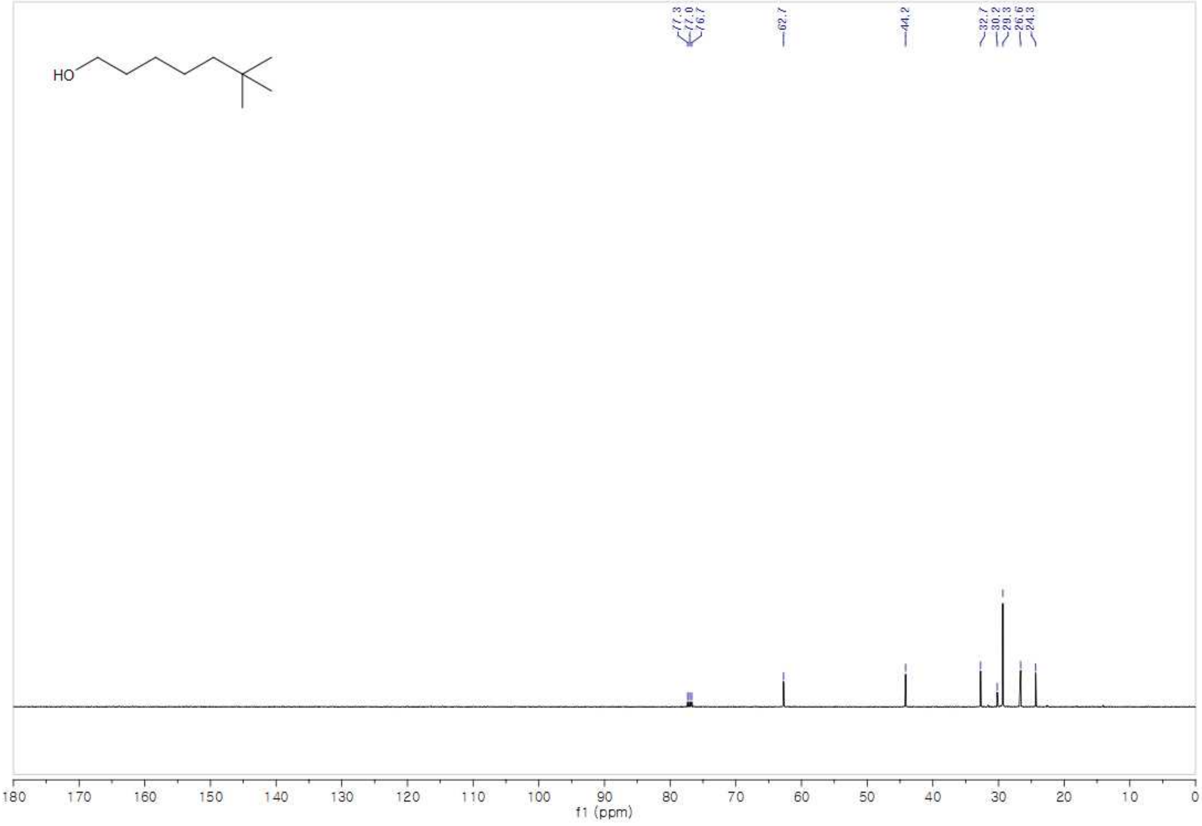

7.27
7.27
7.26
7.24
7.24
7.20
7.19
7.18
7.17
7.17
7.16
7.15
7.14
7.14
7.14
4.50
4.48
4.47
4.10
4.09
4.07
4.07
4.06
3.74
3.73
3.73
3.73
3.71
3.71
3.70
3.70
3.68
3.68
3.67
2.73
2.71
2.70
2.69
2.08
2.07
2.04
1.93
1.92
1.91
1.91
1.90
1.90
1.89
1.88
1.31
1.31
1.30
1.30
1.30
1.29
1.29
1.28
1.27
1.27
1.27
1.26
1.26
O
O
2.00
2.98
1.02
2.07
2.08
1.98
1.17
2.01
1.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

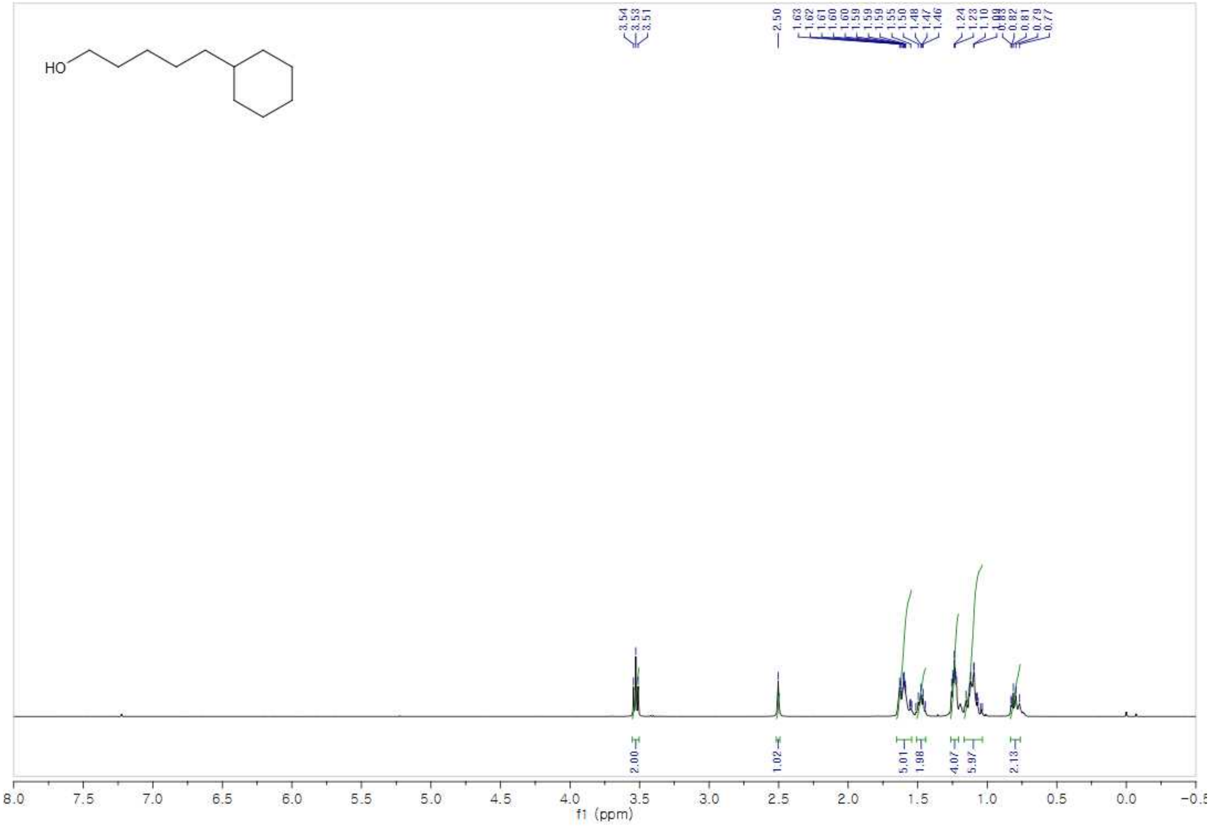

141.8
128.5
128.4
125.8
101.4
77.5
77.2
76.9
66.9
36.7
30.1
25.9
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

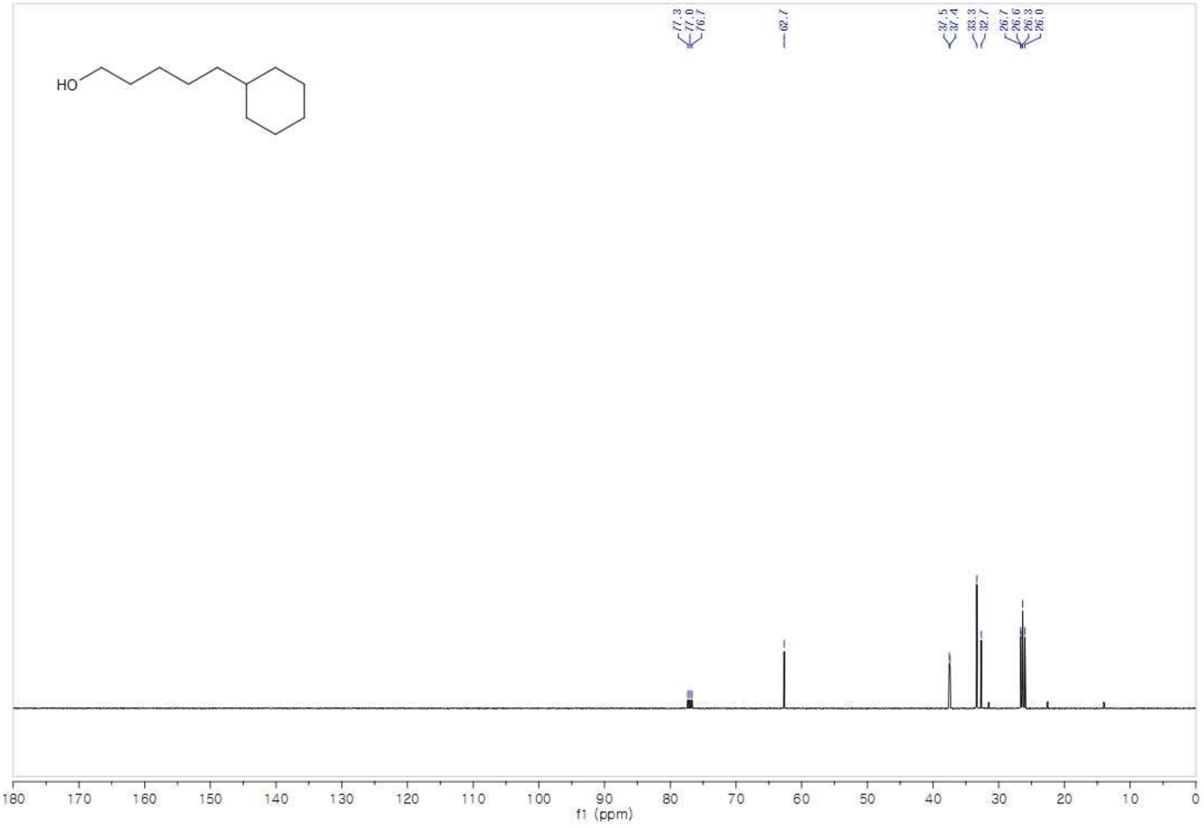

4.00
4.00
3.98
3.98
3.96
3.96
1.97
1.96
1.60
1.58
1.56
1.54
1.53
1.23
1.23
1.23
1.22
1.11
0.79
0.00
O
O
1.98
2.93
2.15
4.01
2.06
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

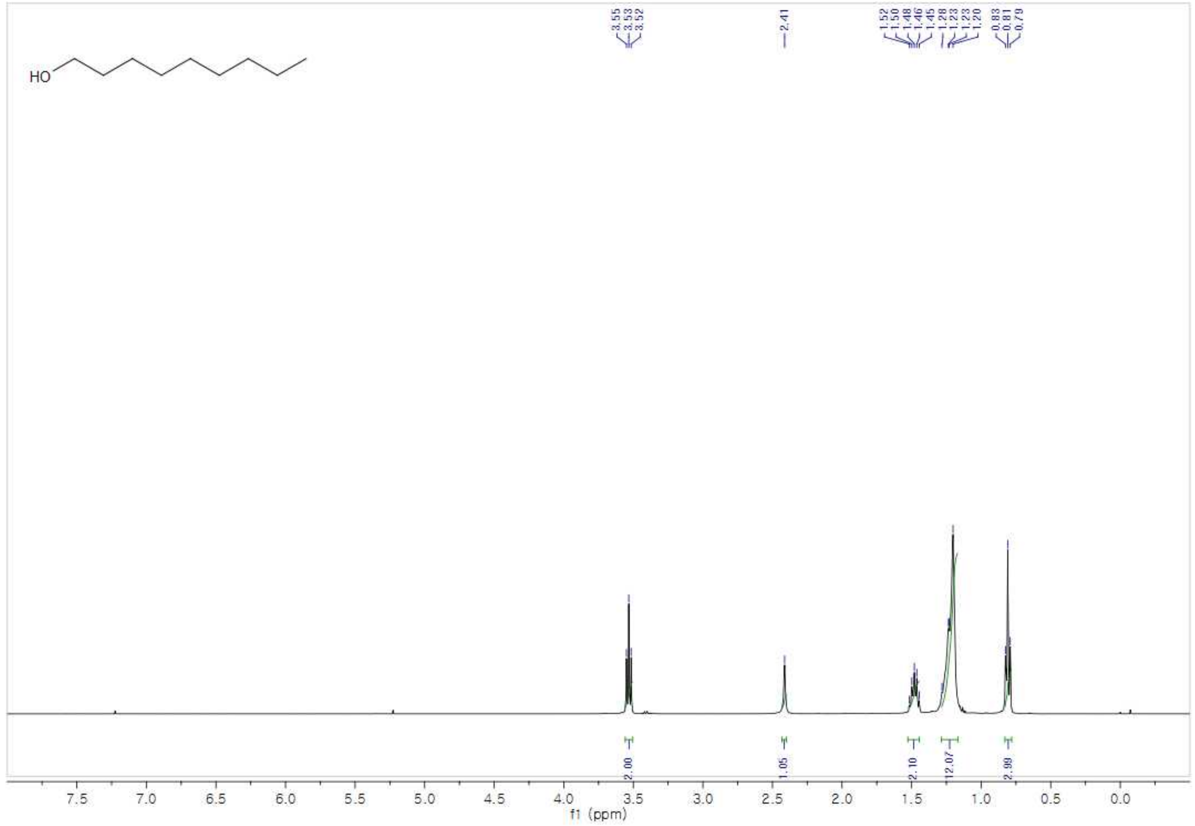

171.1
77.3
77.0
76.7
64.6
44.0
30.2
29.3
28.6
26.8
24.2
20.9
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

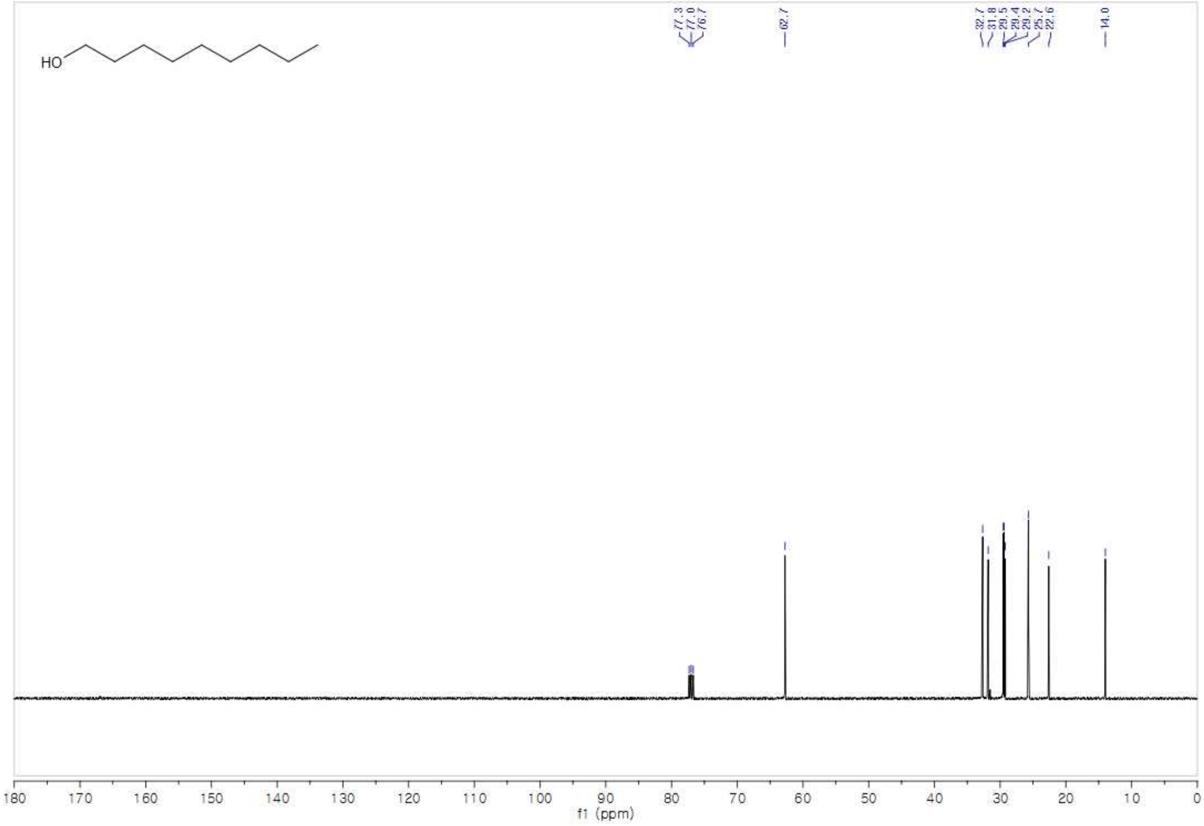

HO
3.55
3.54
3.52
2.45
1.53
1.52
1.50
1.48
1.46
1.24
1.23
1.22
1.21
1.19
1.12
0.79
1.99
0.97
2.07
4.11
2.04
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

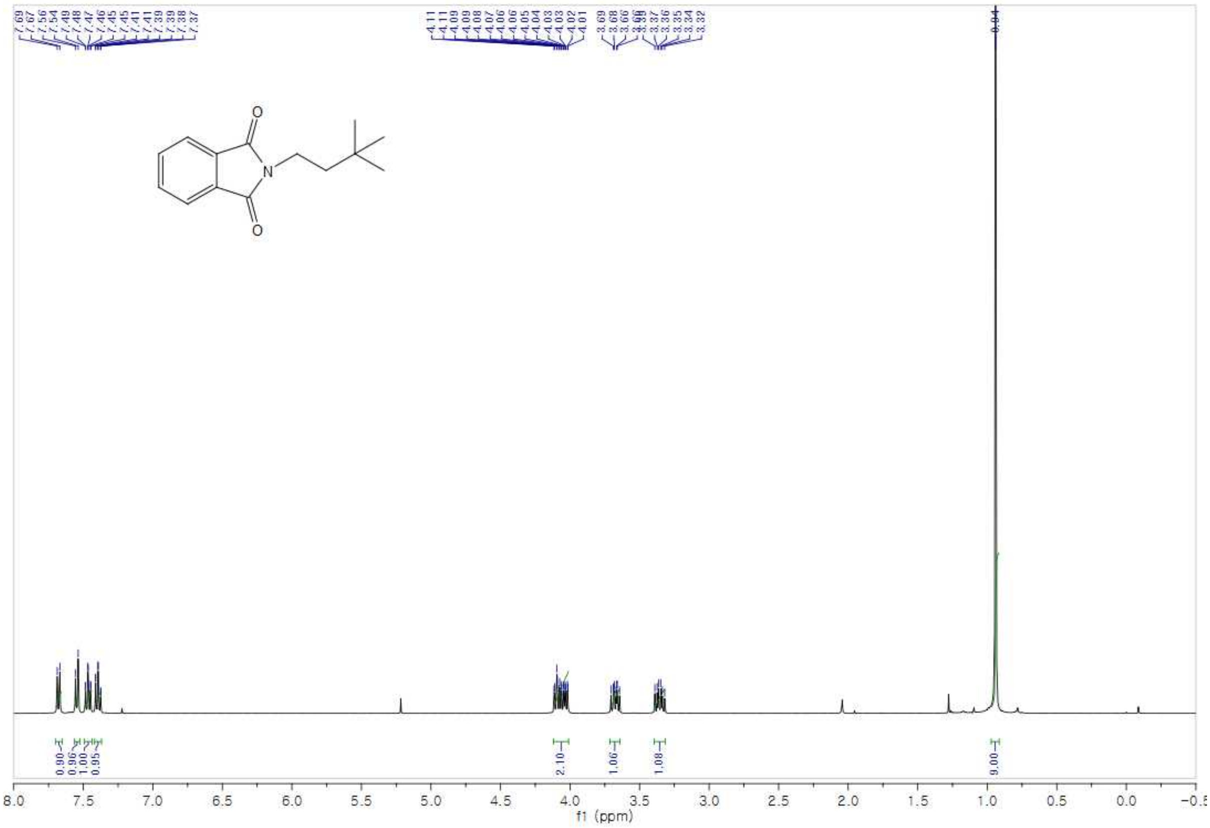

HO
77.3
77.0
76.7
62.7
44.2
32.7
30.2
29.3
26.6
24.3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

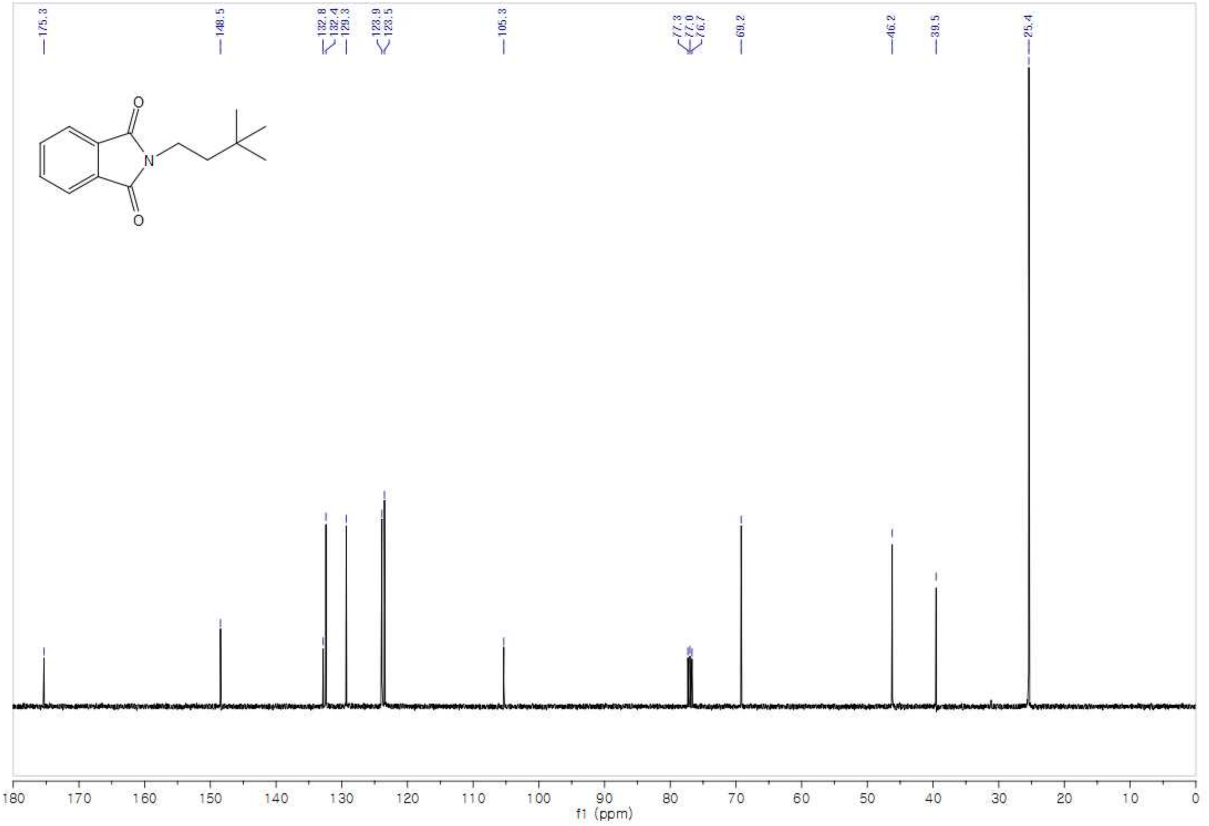

HO
3.54
3.53
3.51
2.50
1.63
1.62
1.61
1.60
1.60
1.59
1.59
1.55
1.50
1.48
1.47
1.46
1.24
1.23
1.10
1.09
0.88
0.82
0.81
0.79
0.77
2.00
1.02
5.01
1.98
4.07
5.97
2.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

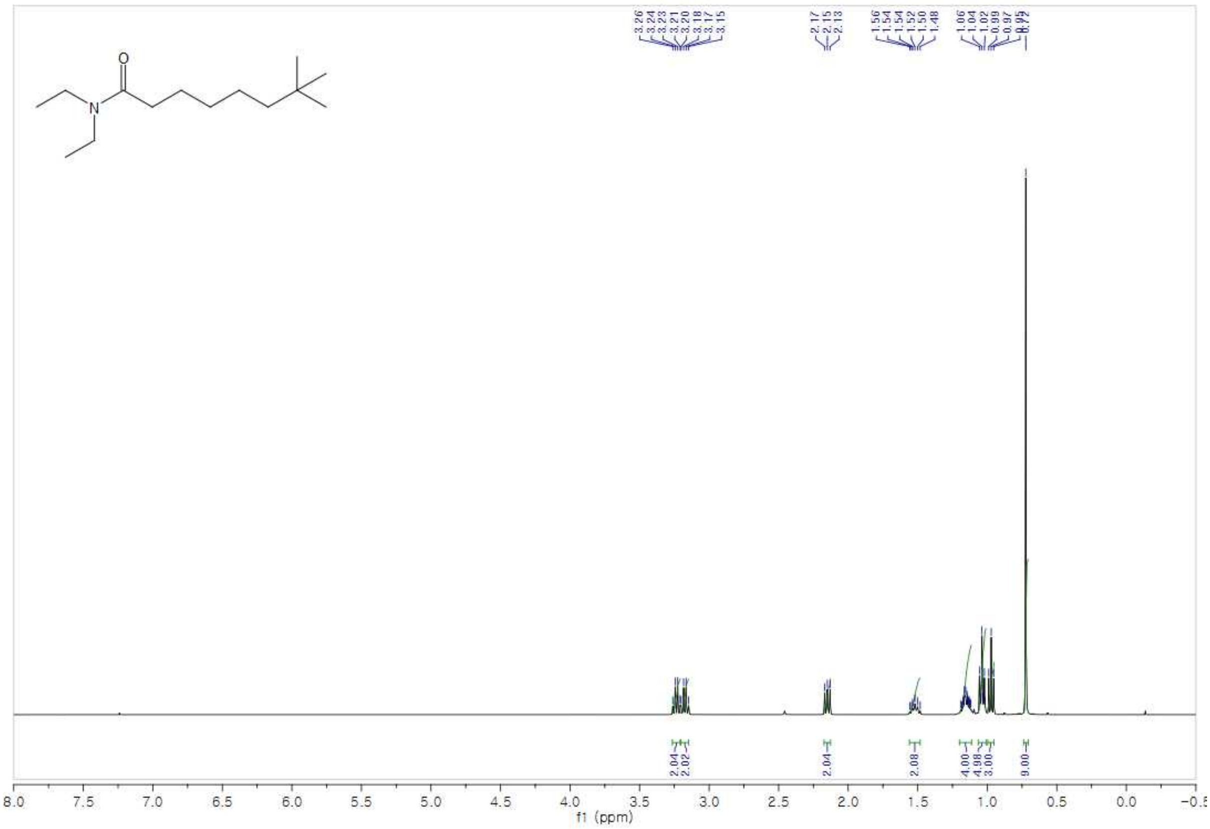

HO
77.3
77.0
76.7
62.7
37.5
37.4
33.3
32.7
26.7
26.6
26.3
26.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

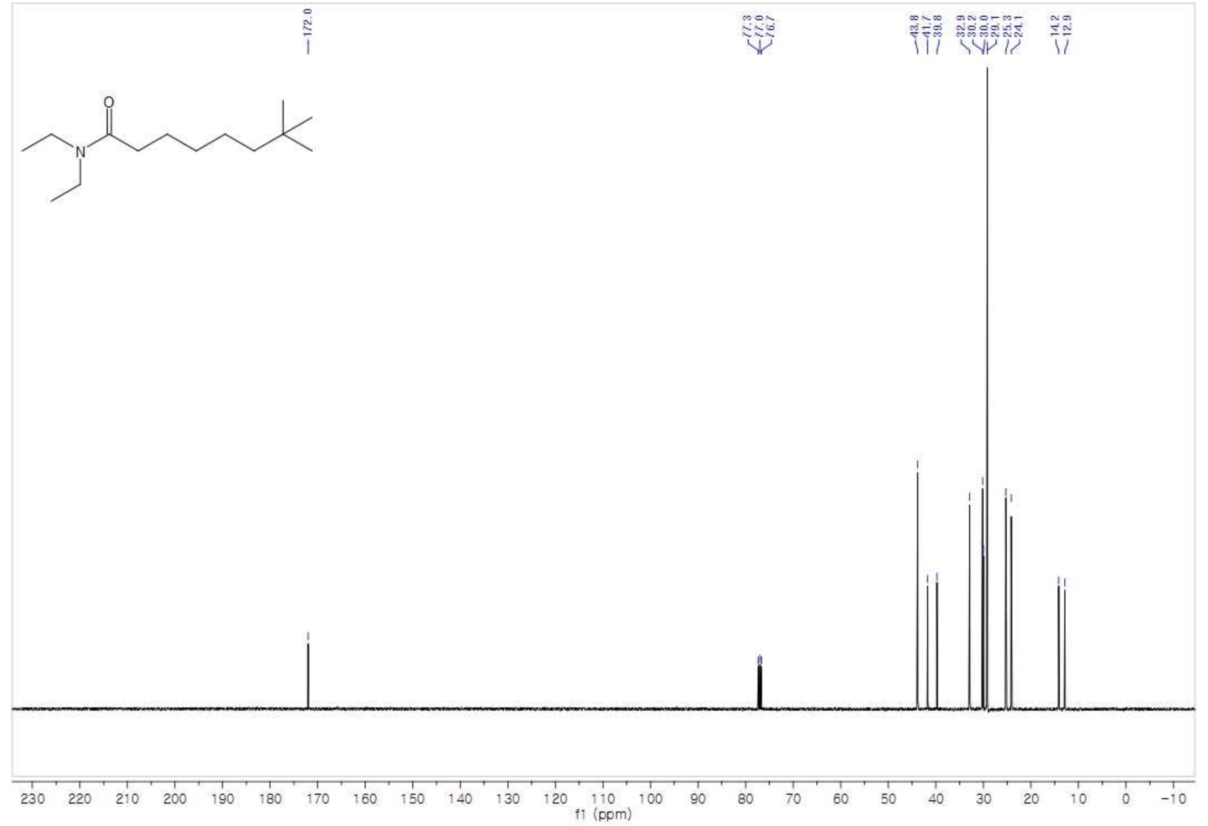

HO
3.55
3.53
3.52
2.41
1.52
1.50
1.48
1.46
1.45
1.28
1.23
1.23
1.20
0.83
0.81
0.79
2.00
1.05
2.10
12.07
2.99
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

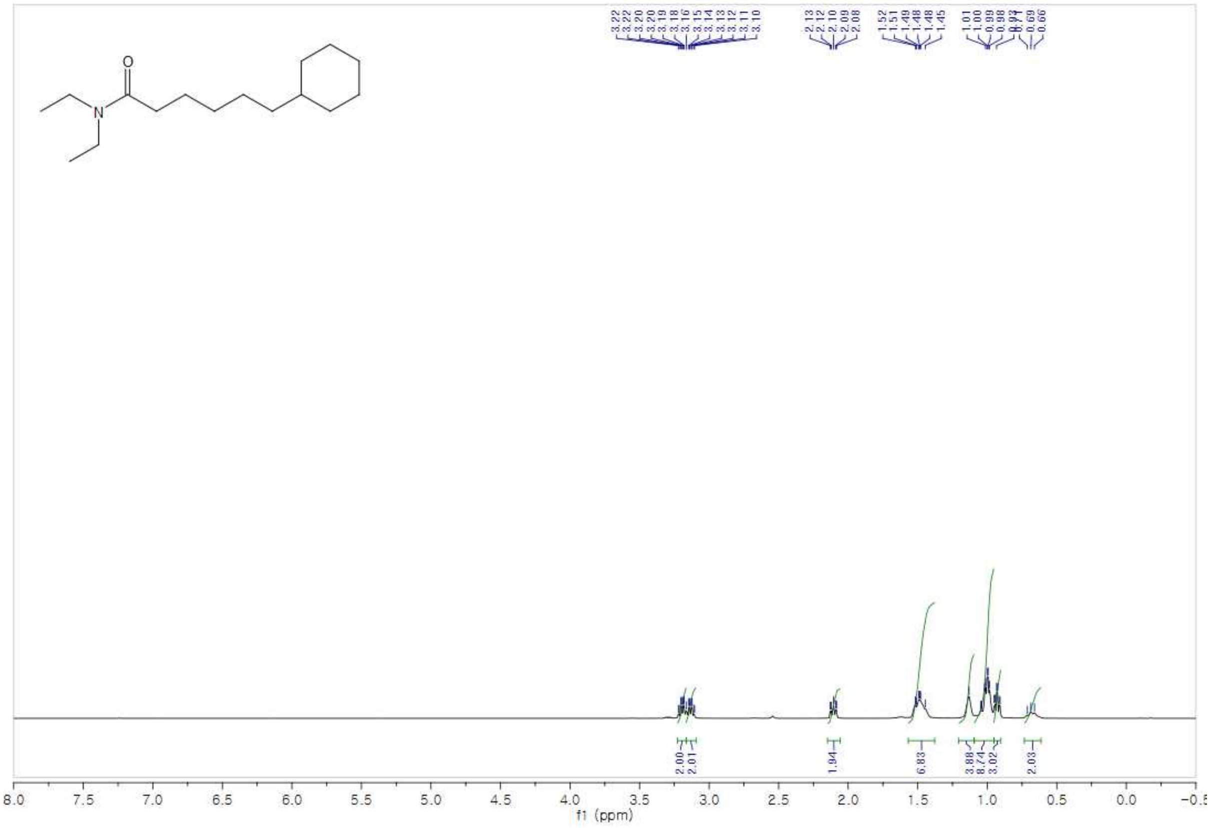

HO
77.3
77.0
76.7
62.7
32.7
31.8
29.5
29.4
29.2
25.7
22.6
14.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

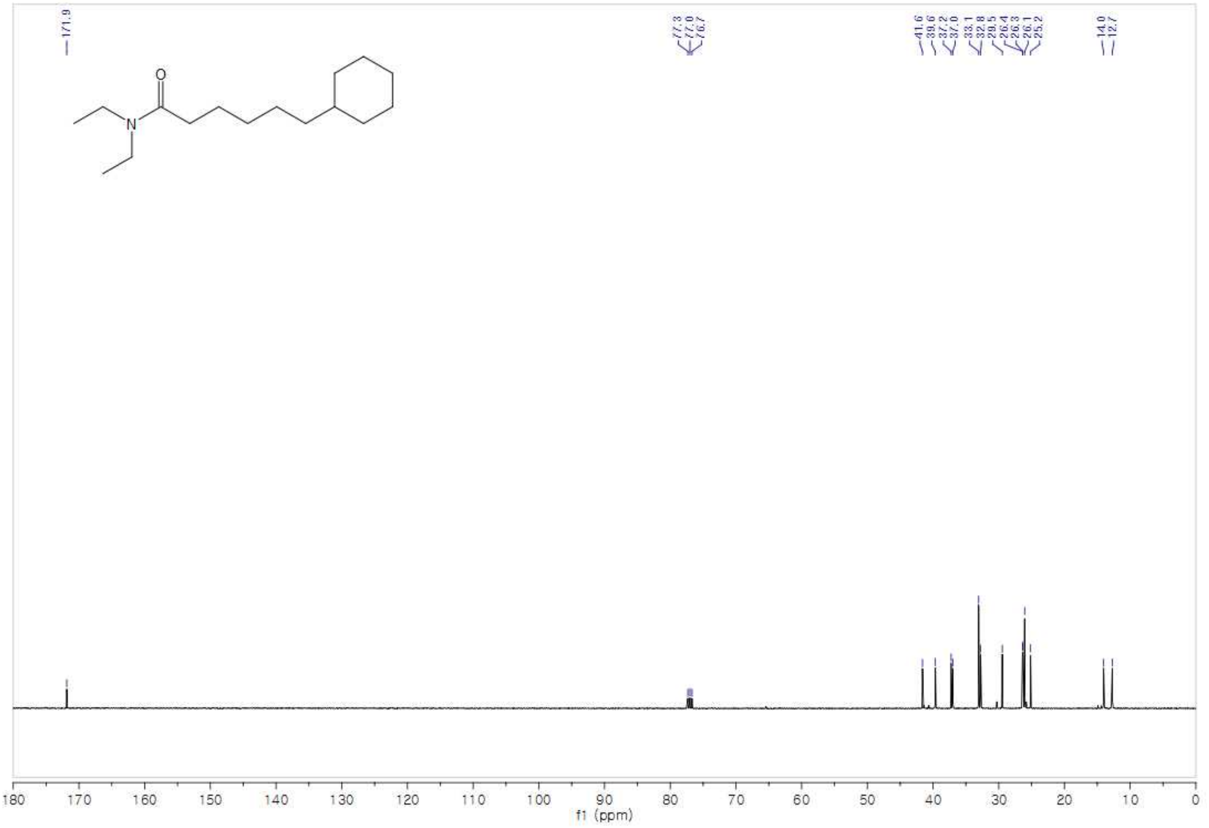

7.69
7.67
7.56
7.54
7.49
7.48
7.47
7.46
7.45
7.41
7.39
7.38
7.37
4.11
4.11
4.09
4.08
4.07
4.06
4.06
4.05
4.04
4.03
4.03
4.02
4.01
3.69
3.68
3.66
3.66
3.39
3.37
3.36
3.35
3.34
3.32
0.94
O
N
O
0.90
0.96
1.00
0.95
2.10
1.06
1.08
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

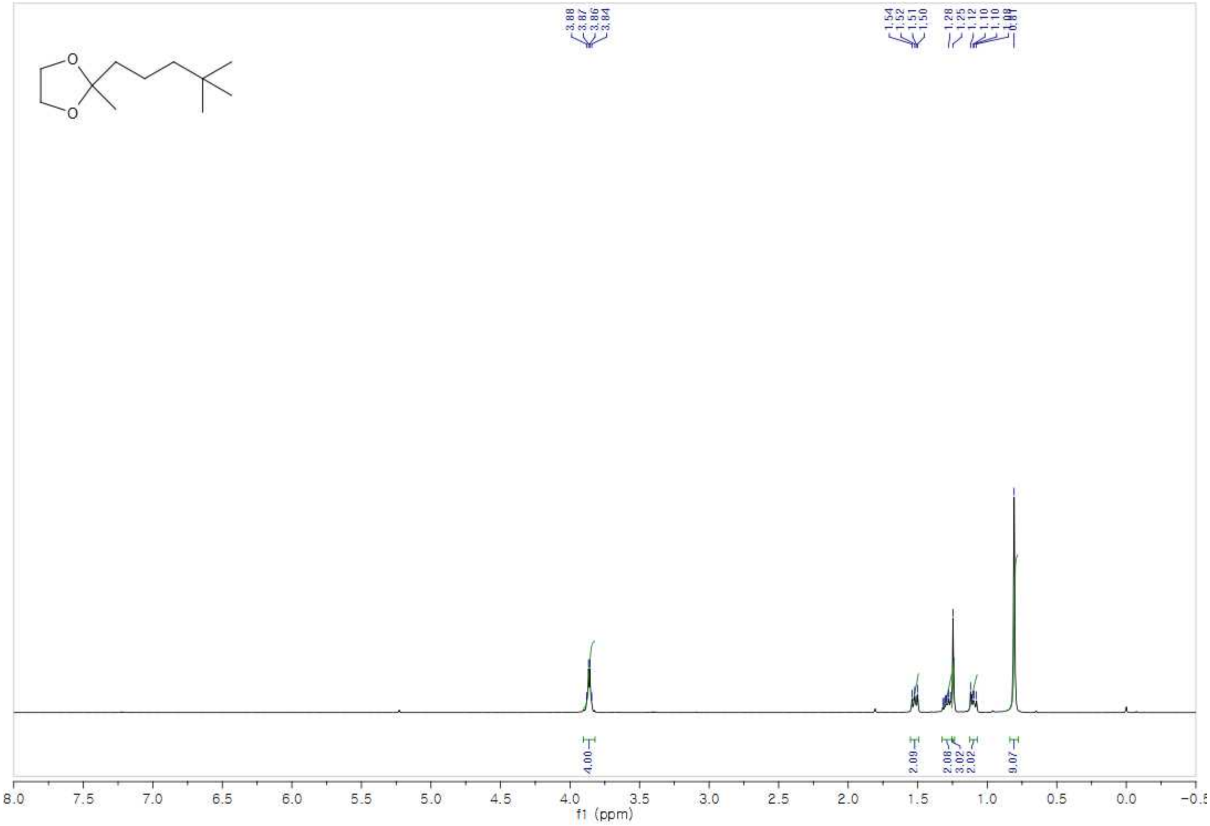

175.3
148.5
132.8
132.4
129.3
123.9
123.5
105.3
77.3
77.0
76.7
69.2
46.2
39.5
25.4
O
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

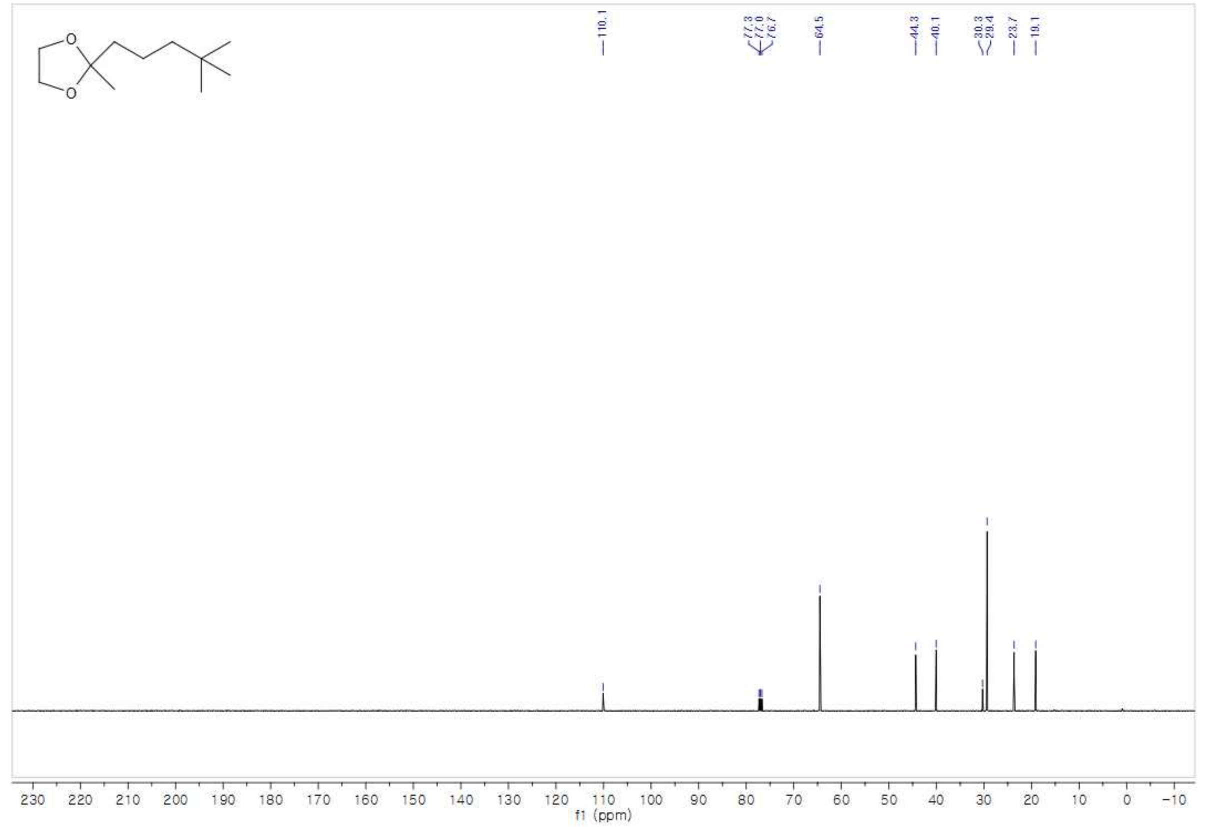

O
N
3.26
3.24
3.23
3.21
3.20
3.18
3.17
3.15
2.17
2.15
2.13
1.56
1.54
1.54
1.52
1.50
1.48
1.06
1.04
1.02
0.99
0.97
0.95
0.72
2.04
2.02
2.04
2.08
4.00
4.98
3.00
9.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


O
N
172.0
77.3
77.0
76.7
43.8
41.7
39.8
32.9
30.2
30.0
29.1
25.3
24.1
14.2
12.9
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


3.22
3.22
3.20
3.20
3.19
3.18
3.16
3.15
3.14
3.13
3.12
3.11
3.10
2.13
2.12
2.10
2.09
2.08
1.52
1.51
1.49
1.48
1.48
1.45
1.01
1.00
0.99
0.98
0.93
0.71
0.69
0.66
O
N
2.00
2.01
1.94
6.83
3.88
8.74
3.02
2.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


171.9
77.3
77.0
76.7
41.6
39.6
37.2
37.0
33.1
32.8
29.5
26.4
26.3
26.1
25.2
14.0
12.7
O
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
3.88
3.87
3.86
3.84
1.54
1.52
1.51
1.50
1.28
1.25
1.12
1.10
1.10
1.08
0.81
4.00
2.09
2.08
3.07
2.02
9.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


O
O
110.1
77.3
77.0
76.7
64.5
44.3
40.1
30.3
29.4
23.7
19.1
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)