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Supplementary information

The Dual Functional Catalyst for Selective Dicarbamate Synthesis via Oxidative Carbonylation: Enhanced Methoxylation for Suppressing Urea Polymer Formation

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1. General information

1.1. Chemicals

All reagents, cerium(III) nitrate hexahydrate (Alfa Aesar), NaOH (Samchun), palladium(II) nitrate hexahydrate (Alfa Aesar), Al_2O_3 (Strem, gamma-), SiO_2 (Alfa Aesar), TiO_2 (Aldrich), ZrO_2 (Aldrich), 2,4-diaminotoluene (TCI), sodium iodide (Sigma-Aldrich), aniline (Samchun), methyl N-phenyl carbamate (TCI), 2,6-dimethylnaphthalene (Aldrich), 1,3-diphenylurea (Sigma-Aldrich), methylene diphenyl-4,4'-diamine (Sigma-Aldrich), 1,6-hexanediamine (Sigma-Aldrich), 5-amino-1,3,3-trimethylcyclohexanemethylamine (isophorone diamine) (Sigma-Aldrich), methanol (Samchun), ethanol (Samchun), propanol (Samchun), acetone (Samchun), acetone-d6, and dimethylsulfoxide-d6 (CIL), were used without further purification.

1.2. Analytical methods

X-ray diffraction (XRD) data were obtained by Cu Kα radiation with a Rigaku Rotaflex (λ= 1.54059 Å). The data were recorded in a scan range of 10 - 80° with 0.02° step interval. X-ray photoelectron spectroscopy (XPS) (KRATOS, AXIS NOVA) analysis was carried out using monochromatic Al-Kα as an X-ray source. The catalyst surface and structure were analyzed by a transmission electron microscope (TEM) (Talos F200S) at 200kV.

The amount of organic solid in the spent catalysts was determined by a thermogravimetric analysis (TGA) conducted under an air flow from 25 to 900 ℃ (5℃/min). Prior to this analysis, the spent catalyst was washed more than three times with methanol and acetone and then dried in a 60 ℃ oven.

In situ diffuse reflectance infrared transform spectroscopy (DRIFTs) experiments were performed using a Fourier transform infrared (FT-IR) spectrometer (Thermo Fisher Scientific, Nicolet 6700) equipped with a commercial DRIFT cell (PIKE, DiffuseIR) and a mercury cadmium telluride (MCT) detector. The obtained IR spectra were displayed using a common scale. Each IR spectrum was collected in the Kubelka−Munk format by averaging 32 scans with 4 cm^{-1} resolution. Prior to each measurement, the catalyst was pretreated under the same conditions as for the TDC synthesis (400 °C for two hours in 10 % H_2/Ar). After the pretreatment, the temperature was cooled to 50 ℃, then methanol gas was introduced into the catalyst by bubbling N_2 through a methanol saturator kept at 0 ℃ with an ice/water bath.

A gas chromatography (GC) analysis was performed on an Agilent 7890 equipped with a flammable ionization detector and an HP-1 column. High pressure liquid chromatography (HPLC) analysis was carried out on an Agilent Technologies 1260 Infinity II equipped with a diode array detector and an Eclipse XDB-C18 column.

Synthesized dicarbamate compounds are purified *via* flash column chromatography on chromatorex silica gel GS60-40/75 (FUJI SILYSIA chemical). Thin-layer chromatography was carried out on silica gel 60 F254 TLC plates (Merck KGaA). For visualization, a UV lamp having 254 nm and 365 nm wavelength UV light was used.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were taken in a Bruker 400 MHz (Ascend 400). 1H NMR spectra were obtained in Acetone-D6 or dimethyl sulfoxide (DMSO)-D6 and were referenced to residual tetramethylsilane (0 ppm). The NMR spectra were recorded

as follows: multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet), coupling constant (Hz), and integration.

2. Experimental procedures

2.1. Catalysts preparation

2.1.1. Ceria synthesis

10 ml of 5M cerium (III) nitrate hexahydrate solution and 70 ml of 1M sodium hydroxide solution were prepared respectively. The sodium hydroxide solution was then added to the cerium containing solution, after which the mixture was vigorously stirred for 30 minutes. The formed yellowish suspension was transferred into a Teflon vessel, and then the vessel was sealed inside an autoclave. The autoclave was placed in a furnace, where the temperature was raised to 175 ℃ and maintained for 24 hours. After the hydrothermal treatment, the precipitate was separated by centrifugation, followed by washing it three times with deionized water and ethanol, achieved through repeated cycles of centrifugation and resuspension. The prepared precipitate was dried in an oven at 60 ℃ overnight, followed by calcination at 400 ℃ for four hours, and then ground into a powder.

2.1.2. Pd supported catalysts preparation

An appropriate amount of palladium (II) nitrate hexahydrate for a 5 wt% Pd impregnation was dissolved in a mixture solution of 100ml deionized water and 50 ml of ethanol with stirring to ensure complete dissolution. Desired amounts of palladium (II) nitrate hexahydrate, 100 ml of deionized water, and 50 ml of ethanol were added together into a 250 ml beaker to prepare 5 wt.% Pd supported catalysts. After stirring, the desired support (CeO_2, Al_2O_3, SiO_2, ZrO_2) were added to the Pd containing solution and stirring for two hours. The prepared turbid solution was evaporated in a 60 ℃ water bath to form a powder. The residual solid was dried in an oven at 60 ℃ overnight, then calcinated at 300 ℃ under air for three hours. Finally, the calcined powder was reduced at 300 ℃ for two hours in 10 % H_2/Ar (with flow rate 50 ml/min). To verify the reproducibility of the catalyst, TDC synthesis was performed using the catalysts prepared in five different batches. The difference in TDC yields among these catalysts is within 3%, indicating good reproducibility.

2.2. Carbamate synthesis

2.2.1. Dicarbamate synthesis and work up procedures

0.5 mmol of diamine substrate, 30 mol% NaI, Pd catalyst corresponding to 2.8 wt% Pd, and 16 ml of methanol were mixed together in 50 ml glass vessel. The vessel was then placed in an autoclave, which was thoroughly purged with high purity oxygen (99.99 %). After purging with high-purity O_2 three times, the autoclave was pressurized sequentially with 2 bar O_2 and 8 bar CO (a total pressure 10 bar) using individual gas cylinders (99.99% O_2 and 99.5% CO). The CO:O_2 ratio of 4:1 was determined based on the reactions conducted under various CO:O_2 ratios (42% TDC yield at CO:O_2 ratio of 9:1, 50% at 8:2 (4:1), and 26% at 5:5) The reactor was placed in an oil bath and stirred vigorously at 600 rpm. The temperature was raised from room temperature to 135 ℃ and maintained for five hours. After cooling to room temperature, the reactor was carefully depressurized through a vent line, followed by purging the inside of the reactor with Ar gas to remove any remaining CO gas. All procedures were carried out in a well-ventilated fume hood to ensure safety.

2.2.2. Methyl N-phenyl carbamate synthesis

2 mmol of aniline, 30 mol% NaI, Pd catalyst corresponding to 1.4 wt% Pd, and 16 ml of methanol were mixed together in 50 ml glass vessel. The vessel was then placed in an autoclave, which was thoroughly purged with high purity oxygen (99.99 %). After the purging step, the autoclave was pressurized to 2 bar with high purity oxygen, and then filled to a pressure of 10 bar with carbon monoxide gas. The reactor was placed in an oil bath and stirred vigorously at 600 rpm. The temperature was raised from room temperature to 135 ℃ and maintained for one hour. Catalytic conversion and yield were analyzed by GC-FID using 2,6-dimethyl naphthalene(DMN) as an internal standard.

3. Catalyst characterization and carbamate synthesis

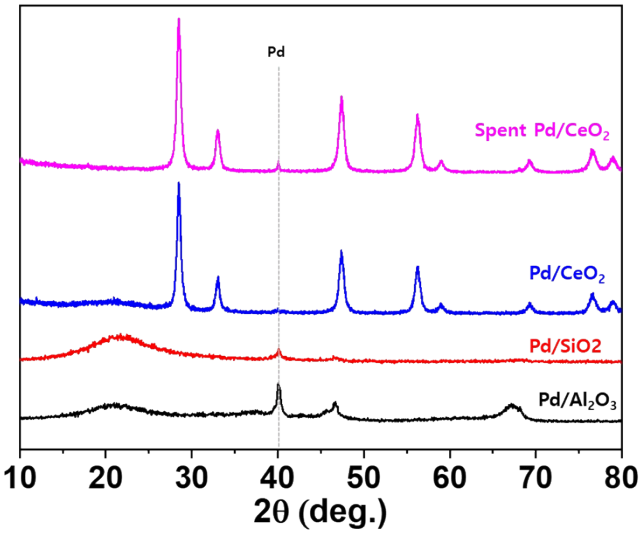


Figure S1. XRD spectra of the Pd catalysts.

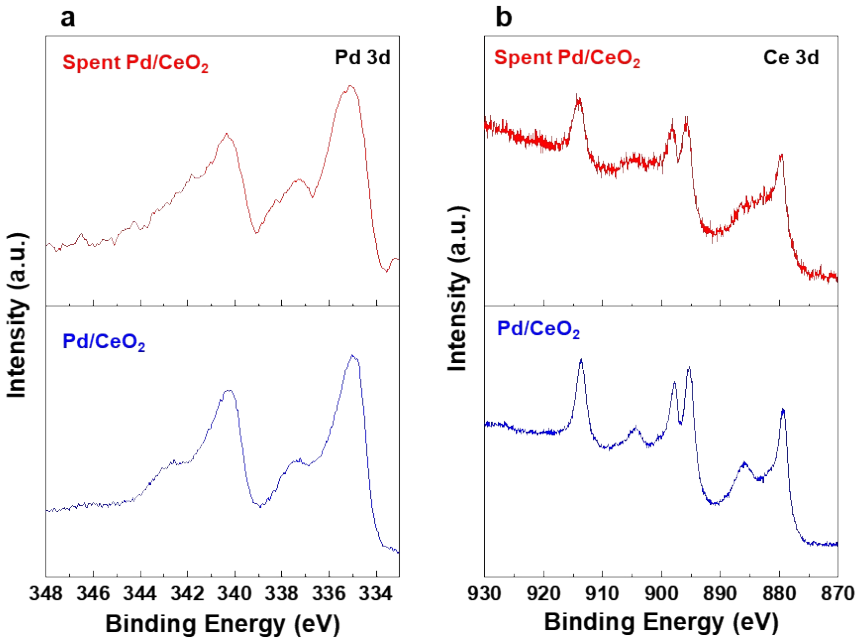


Figure S2. XPS spectra of the Pd/CeO_2 catalysts: (a) Pd 3d, (b) Ce 3d

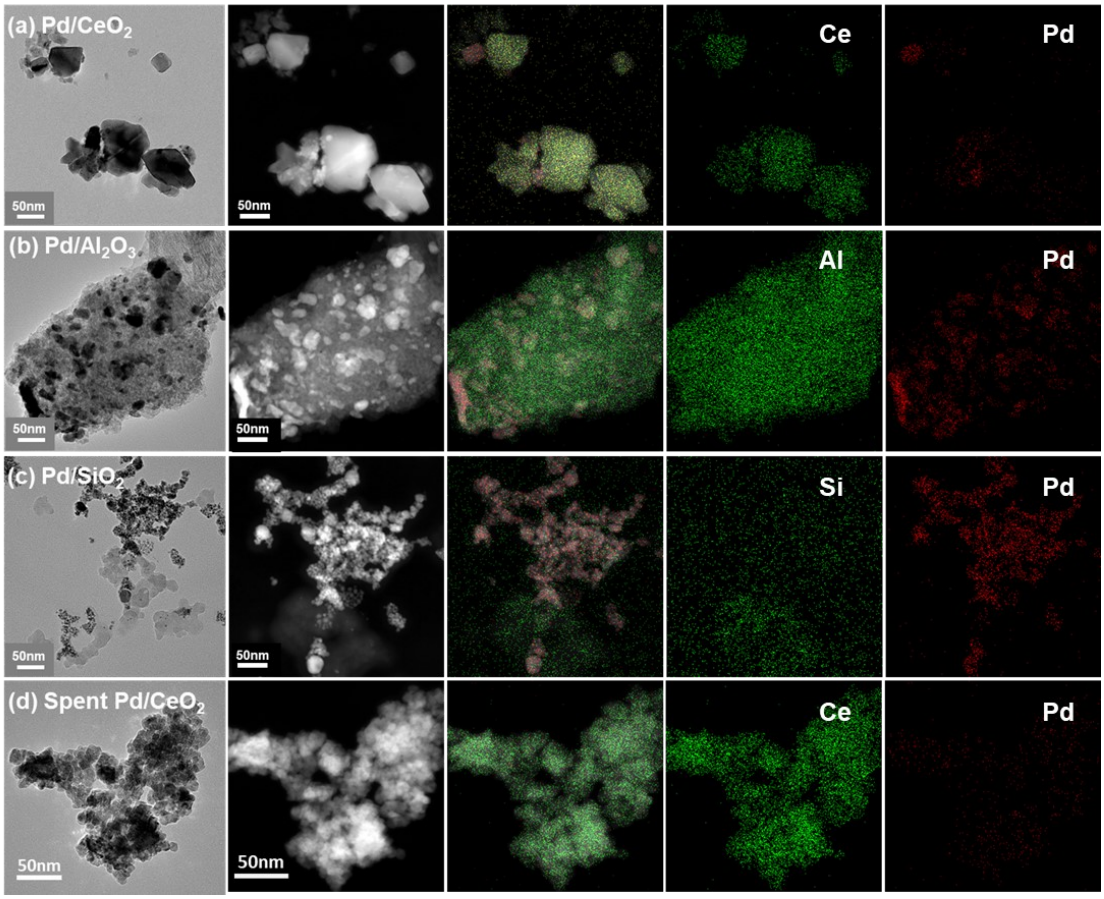


Figure S3. TEM-EDS images of Pd catalysts

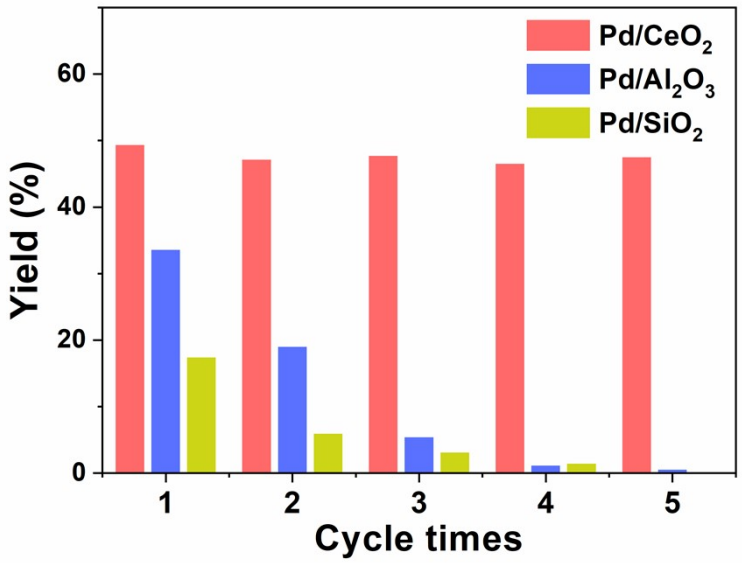


Figure S4. The recycling tests of Pd/CeO_2, Pd/Al_2O_3, and Pd/SiO_2.

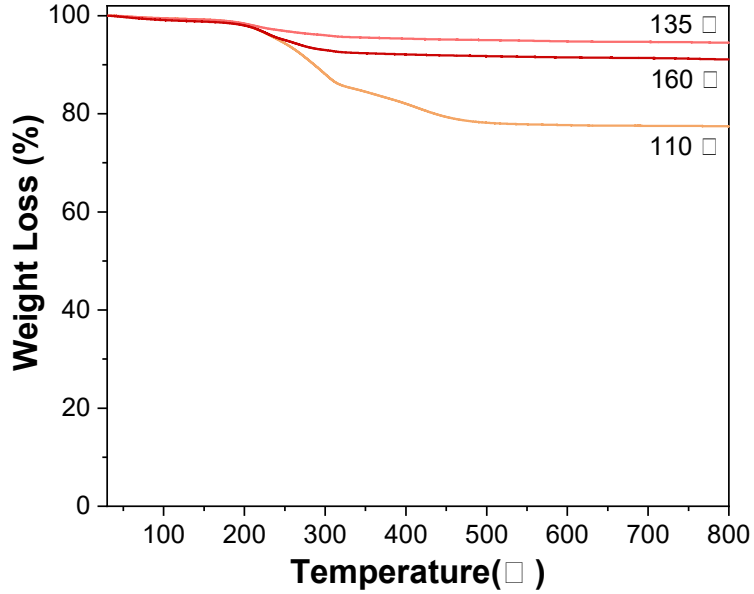
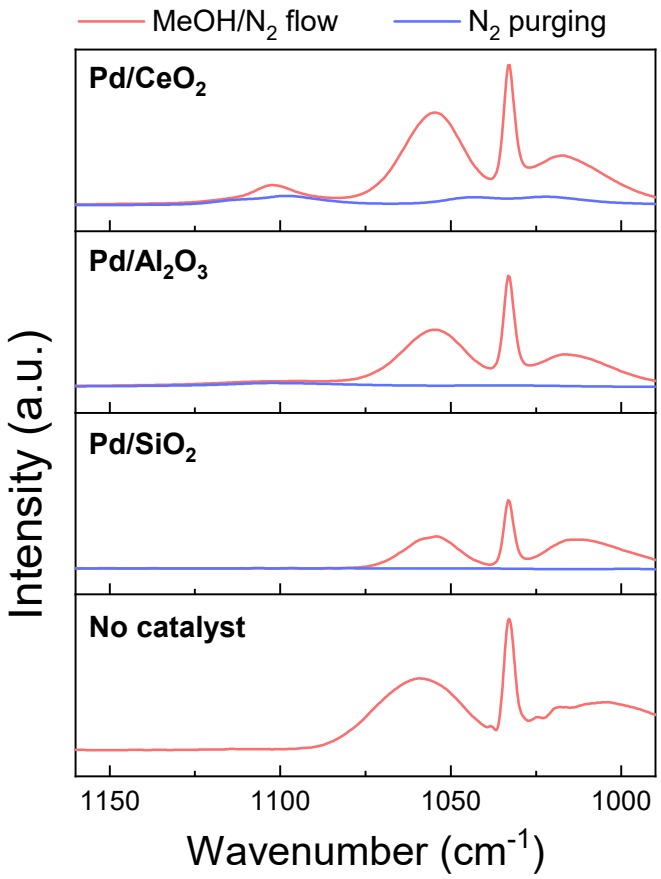


Figure S5. TGA curves of the spent catalysts used at different reaction temperatures.

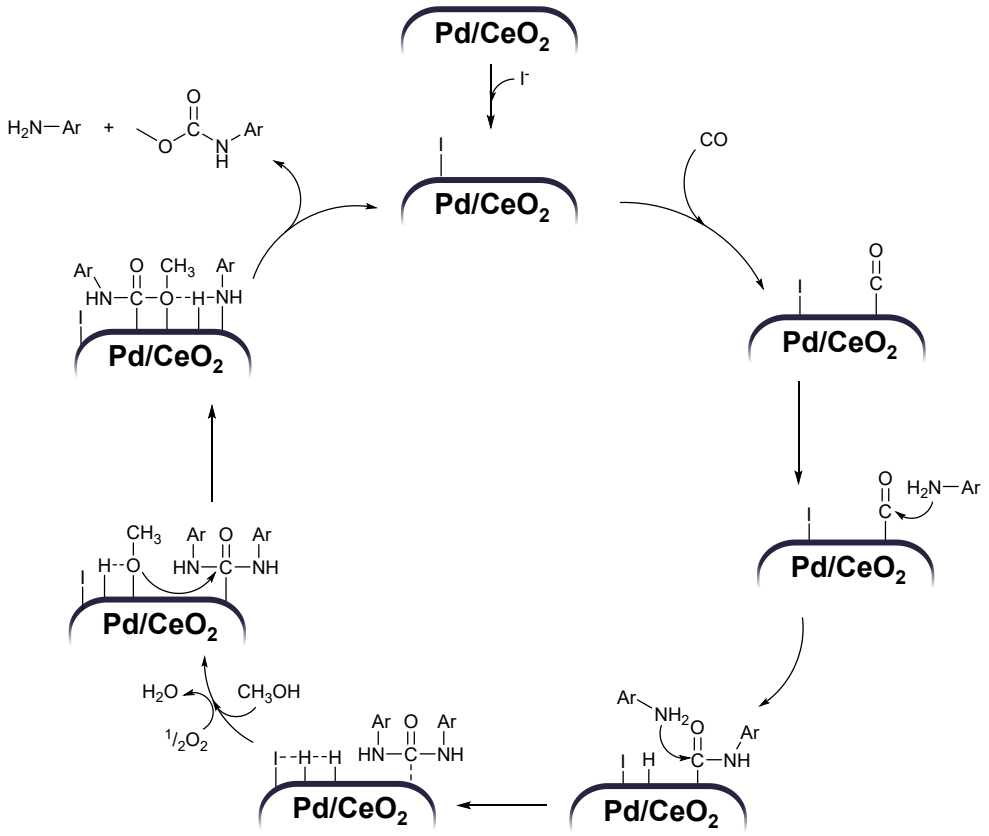
Table S1. TDC synthesis via the oxidative carbonylation of TDA.

Catalyst	NaI (mol%)	TDA conversion (%)	TDC yield (%)
Pd/CeO_2	30	>99	50
Pd/CeO_2	-	0	0
CeO_2	30	0	0

Reaction condition: Pd/CeO_2 catalyst, Pd (2.8 mol%), TDA 0.25 M, NaI (30 mol%), pressure 10 bar, temperature 135 °C, time 5 h.



Figures S6. FT-IR spectra of Pd/CeO_2, Pd/Al_2O_3, and Pd/SiO_2 under gaseous methanol adsorption and desorption.



Scheme S1. Proposed reaction mechanism for the oxidative carbonylation of amine

4. NMR spectra of synthesized products

Dimethyl 2,4-toluenedicarbamate (2,4-TDC): white solid, ^{1}H-NMR (Acetone-d6, 400 MHz) δ: 2.23(s, 3H, C**H**$_3$), 3.68 (s, 3H, OC**H**$_3$), 3.68 (s, 3H, OC**H**$_3$), 7.09(d, 1H, J=8.2 Hz, Ar-**H**), 7.30 (dd, 1H, J=1.83Hz, Ar-**H**), 7.77 (s, 1H, Ar-**H**), 7.78 (s, 1H, N**H**), 8.55 (s, 1H, N**H**). ^{13}C-NMR (Acetone-D6, 400 MHz) δ: 17.03 (CH_3), 51.73 (CH_3O), 51.88 (CH_3O), 113.92 (C-Ar), 115.12 (C-Ar), 124.74 (C-Ar), 130.92 (C-Ar), 137.46 (C-Ar), 138.23 (C-Ar), 154.63 (CO), 155.07 (CO). HR-MS(*m/z*) Calcd for $C_{11}H_{15}N_2O_4[M+H]^{+:}$ 238.1; found: 239.1.

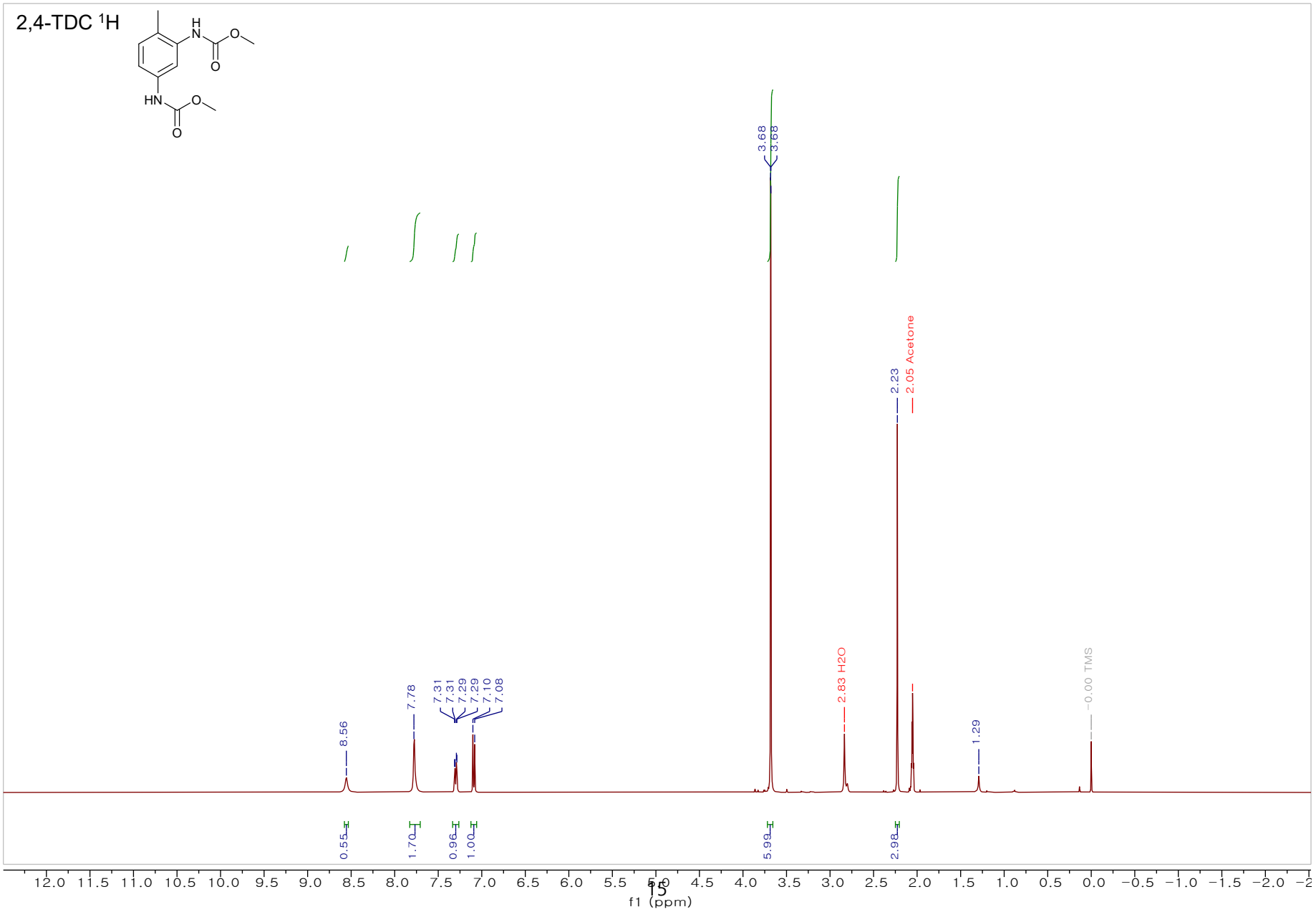
Dimethyl 4,4'-methylenediphenyldicarbamate (4,4'-MDC): slightly yellow solid, ^{1}H-NMR (Acetone-d6, 400 MHz) δ: 3.67 (s, 6H, OC**H**$_3$), 3.88(s, 2H, C**H**$_2$), 7.14 (d, 4H, J=8.5 Hz, Ar-**H**), 7.46 (d, 4H, J=8.6 Hz, Ar-**H**), 8.53 (s, 2H, N**H**). ^{13}C-NMR (Acetone-D6, 400 MHz) δ: 40.19 (CH_2), 51.14 (CH_3O), 118.43 (C-Ar), 129.02 (C-Ar), 135.94 (C-Ar), 137.36 (C-Ar), 154.07 (CO). HR-MS(*m/z*) Calcd for $C_{17}H_{19}N_2O_4[M+H]^{+:}$ 314.13; found: 315.13.

Dimethyl 1,6-Hexylenedicarbamate (1,6-HDC): slightly yellow solid, ^{1}H-NMR (DMSO-d6, 500 MHz) δ: 1.22 (m, 4H, NHCH$_2$CH$_2$C**H**$_2$), 1.36 (m, 4H, NHCH$_2$C**H**$_2$), 2.94 (m, 4H, NHC**H**$_2$), 3.50 (s, 6H, OC**H**$_3$), 7.05 (s, 2H, N**H**). ^{13}C-NMR (DMSO-D6, 400 MHz) δ: 26.39 (CH_2), 29.85 (CH_2), 40.64 (CH_2), 51.56 (CH_3), 157.15 (C=O). HR-MS(*m/z*) Calcd for $C_{10}H_{21}N_2O_4[M+H]^{+:}$ 232.14; found: 233.15.

Diethyl 2,4-toluenedicarbamate: White solid, ^{1}H-NMR (Acetone-d6, 400 MHz) δ: 1.21 – 1.28 (m, 6H, CH$_2$C**H**$_3$), 2.22 (s, 3H, C**H**$_3$), 4.14 (s, 4H, OC**H**$_3$), 7.08 (d, 1H, J=8.2 Hz, Ar-**H**), 7.29 (dd, 1H, J=8.0 Hz, Ar-**H**), 7.71 (s, 1H, Ar-**H**), 7.80 (s, 1H, N**H**), 8.48 (s, 1H, N**H**). ^{13}C-NMR (Acetone-D6, 400 MHz) δ: 14.07 (CH_2CH_3), 16.49 (CH_3), 60.17 (OCH_2), 60.34 (OCH_2), 113.45 (C-Ar), 115.57 (C-Ar), 124.13 (C-Ar), 130.28 (C-Ar), 136.89 (C-Ar), 137.66 (C-Ar), 153.65 (CO), 154.10 (CO). HR-MS(*m/z*) Calcd for $C_{13}H_{19}N_2O_4[M+H]^{+:}$ 266.13; found: 267.13.

Dipropyl 2,4-toluenedicarbamate: slightly yellow solid, ^{1}H-NMR (Acetone-d6, 400 MHz) δ:

0.90 – 0.97 (m, 6H, $CH_2CH_2C\mathbf{H}_3$), 1.65 (m, 4H, $CH_2C\mathbf{H}_3$), 2.22 (s, 3H, $C\mathbf{H}_3$), 4.05 (s, 4H, $OC\mathbf{H}_3$), 7.07 (d, 1H, J=8.3 Hz, Ar-**H**), 7.29 (dd, 1H, J=8.3 Hz, Ar-**H**), 7.73 (s, 1H, Ar-**H**), 7.81 (s, 1H, N**H**), 8.49 (s, 1H, N**H**). ^{13}C-NMR (Acetone-D6, 400 MHz) δ: 9.76 ($CH_2CH_2CH_3$), 16.52 (CH_3), 22.20 (CH_2CH_3), 65.85 (OCH_2), 66.02 (OCH_2), 113.50 (C-Ar), 114.60 (C-Ar), 124.17 (C-Ar), 130.29 (C-Ar), 136.89 (C-Ar), 137.68 (C-Ar), 153.77 (CO), 154.25 (CO). HR-MS(*m/z*) Calcd for $C_{15}H_{23}N_2O_4[M+H]^{+:}$ 294.16; found: 295.17.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0.00 TMS
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7.31
7.31
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7.10
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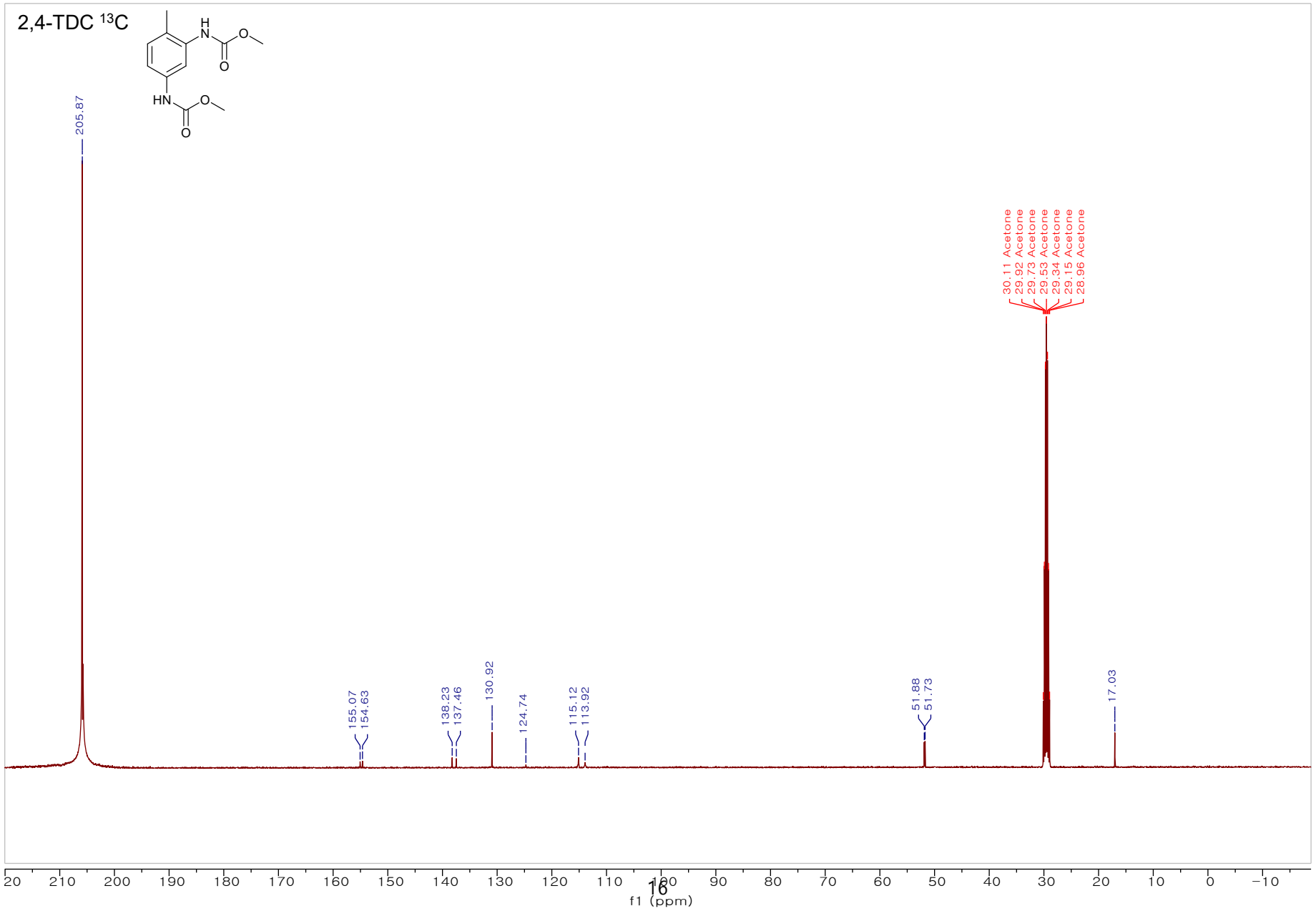
2.98
f1 (ppm)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51.73
30.11 Acetone
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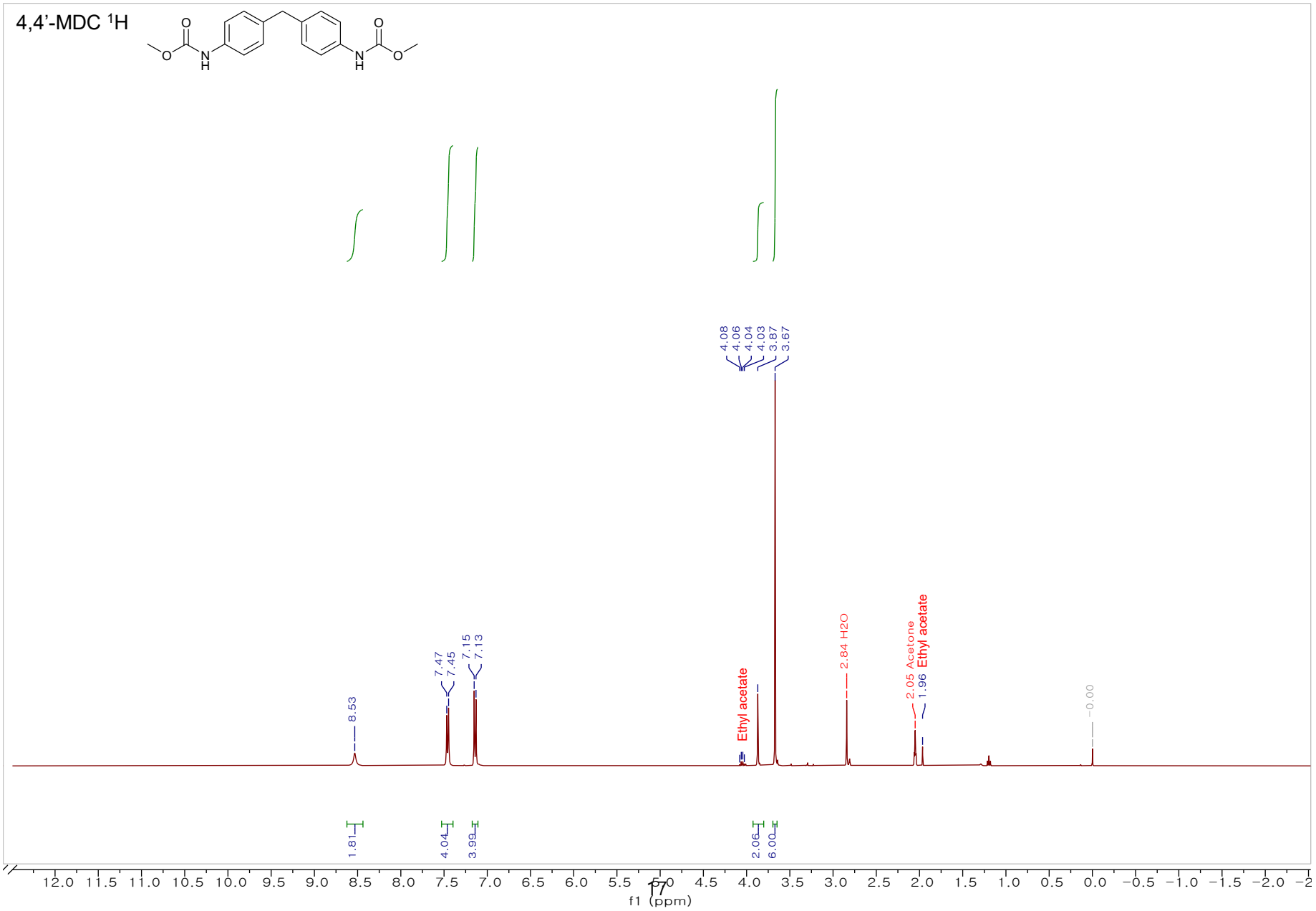
17.03
f1 (ppm)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4.08
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Ethyl acetate
2.84 H2O
2.05 Acetone
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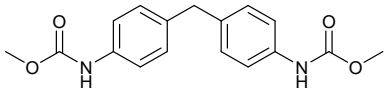
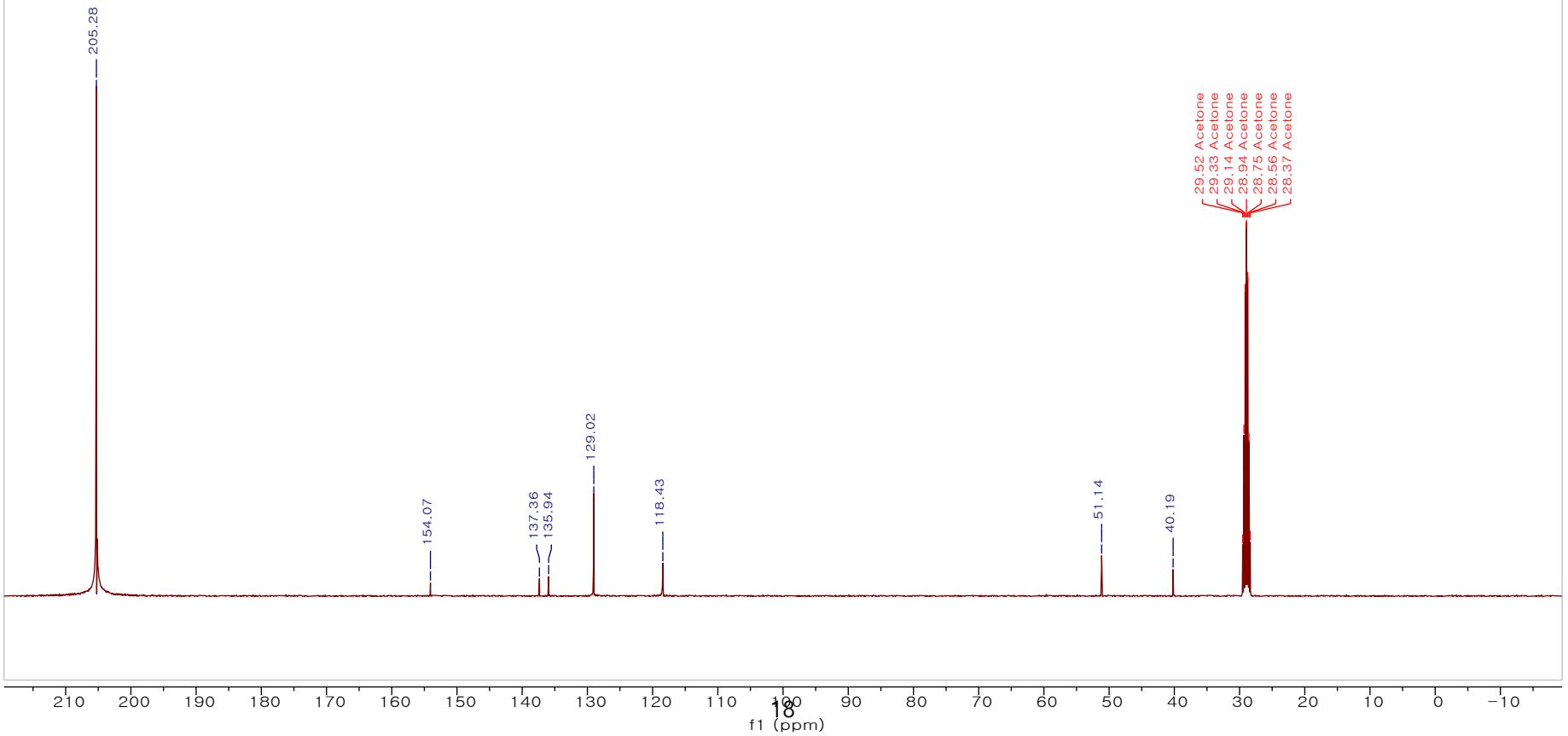
f1 (ppm)

4,4'-MDC ^{13}C

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28.37 Acetone
210
200
190
180
170
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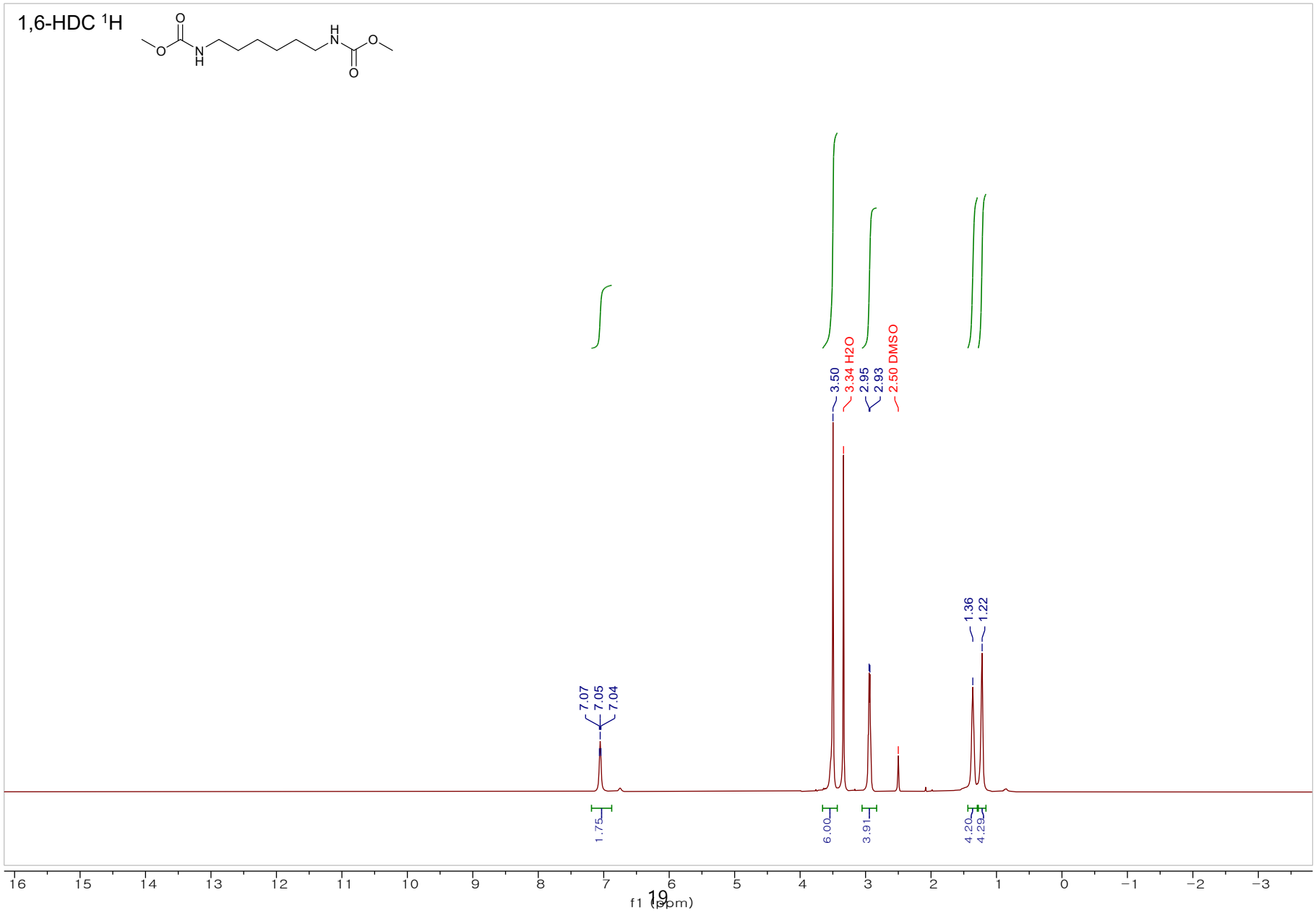
f1 (ppm)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7.04
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1.75
6.00
3.91
4.20
4.29
16
15
14
13
12
11
10
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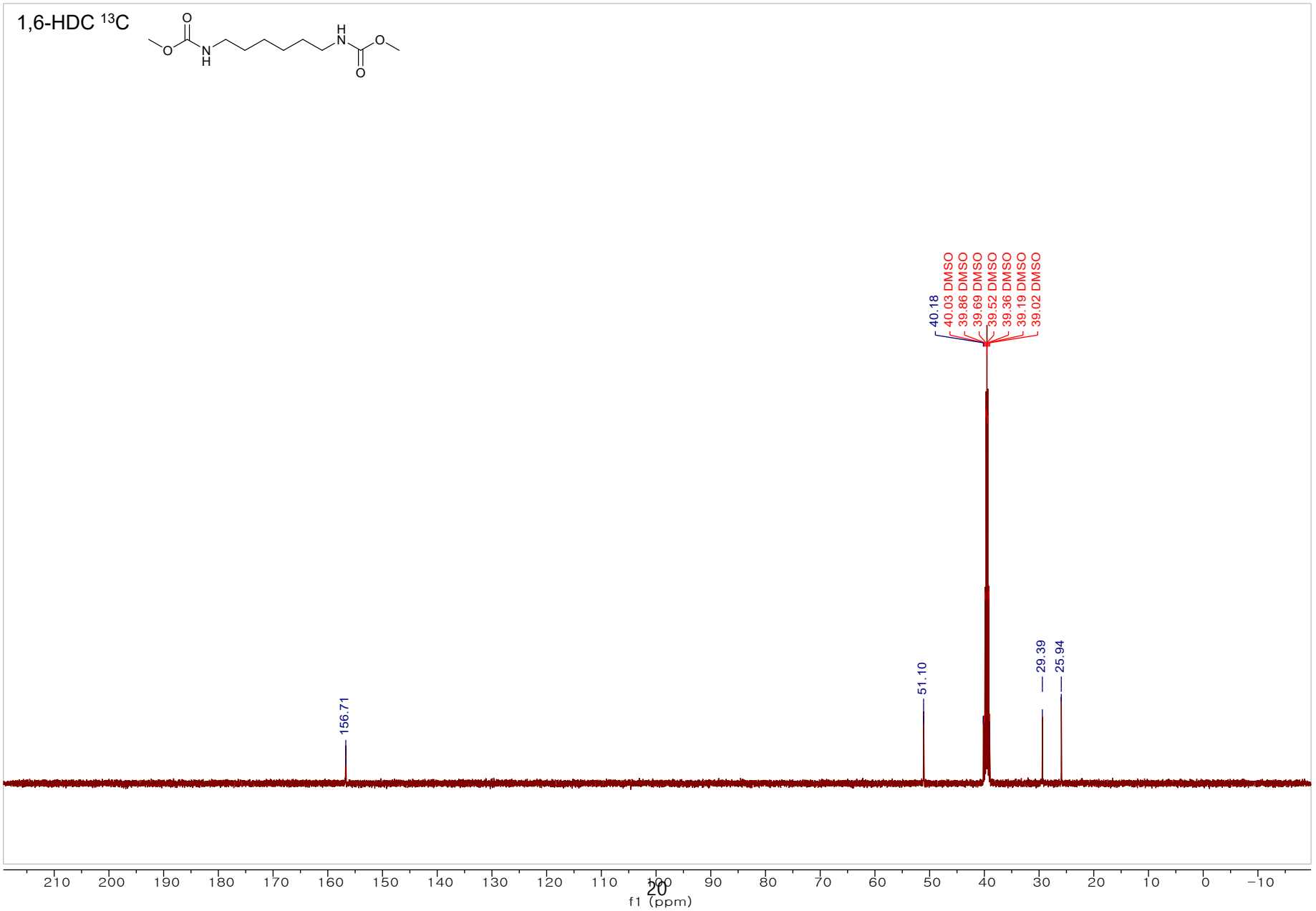
−3
f1 (ppm)

1,6-HDC ^{13}C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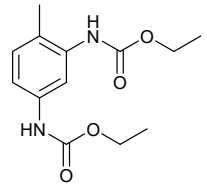
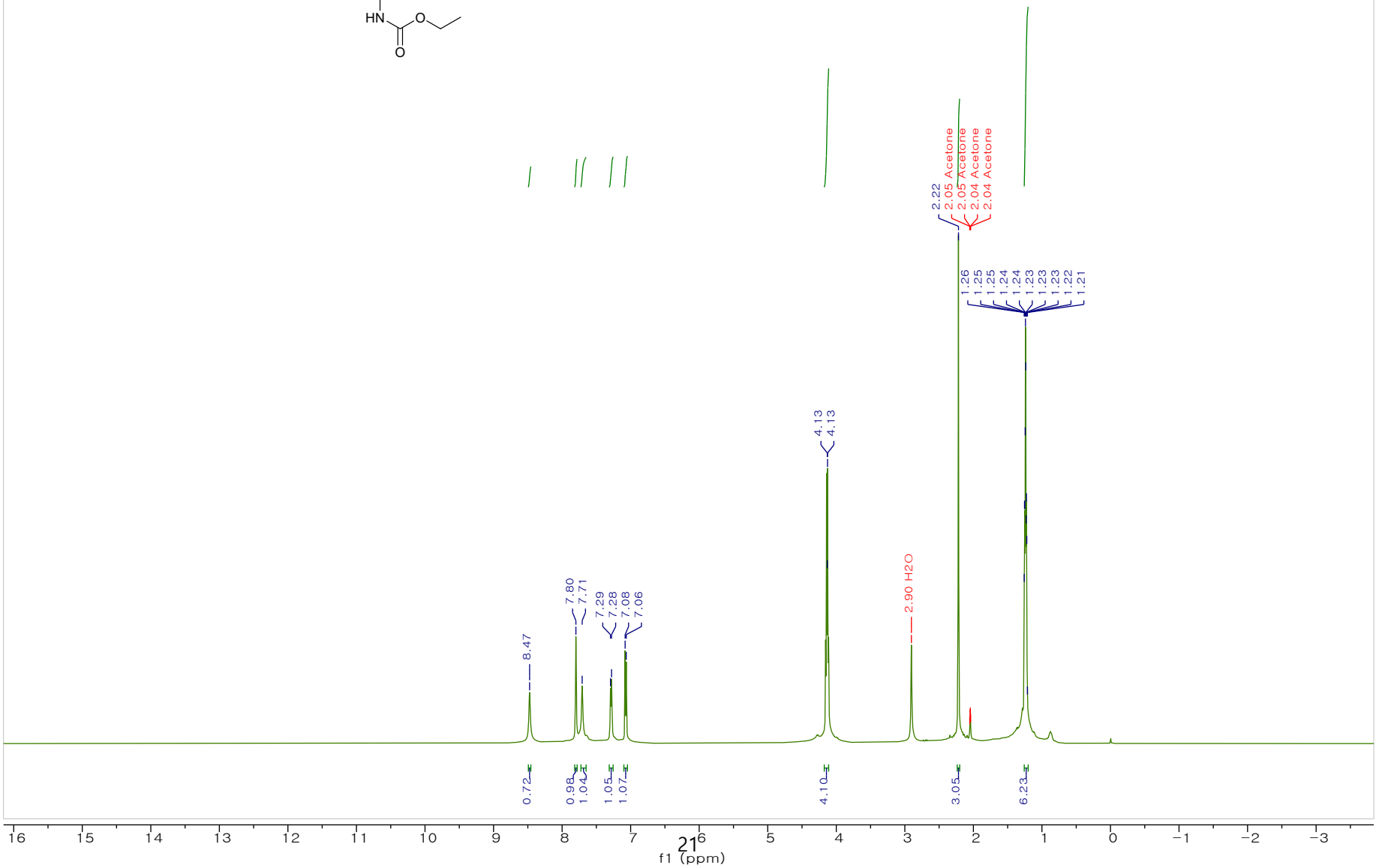
Diethyl 2,4-toluenedicarbamate ^{1}H





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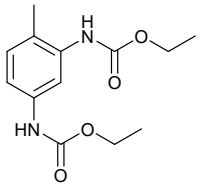

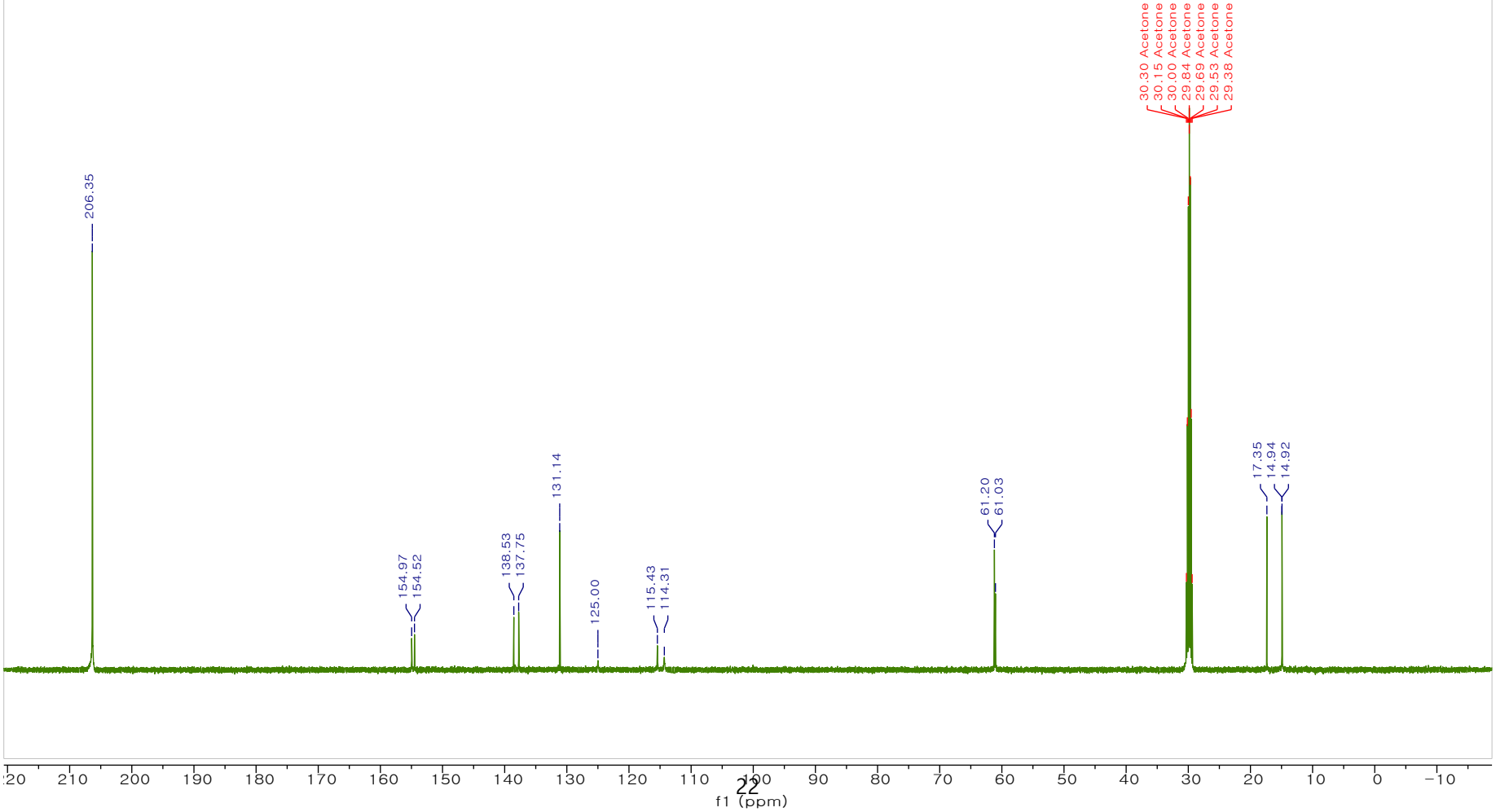

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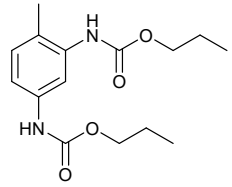
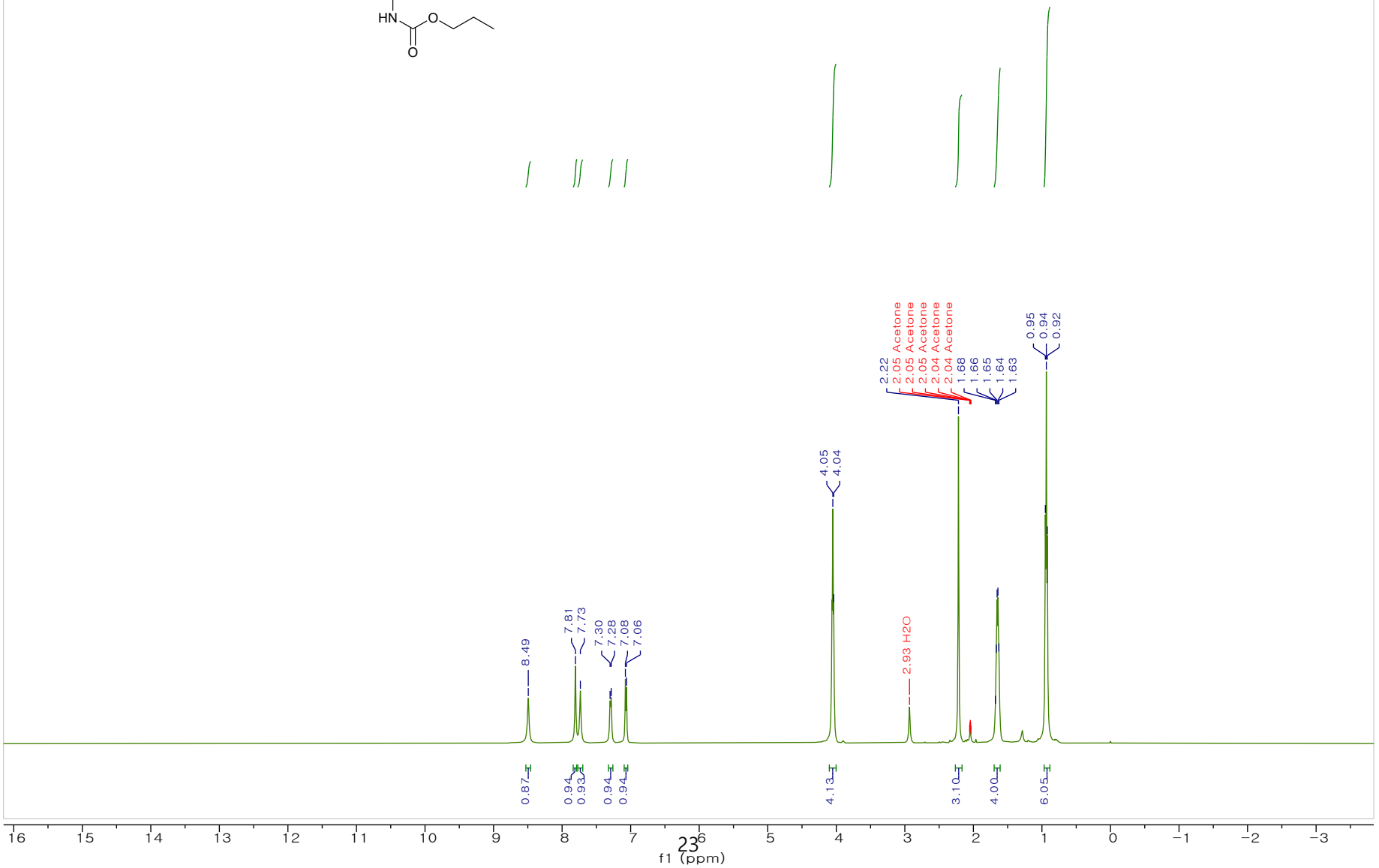
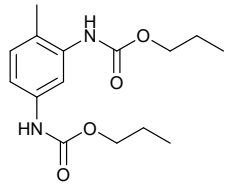
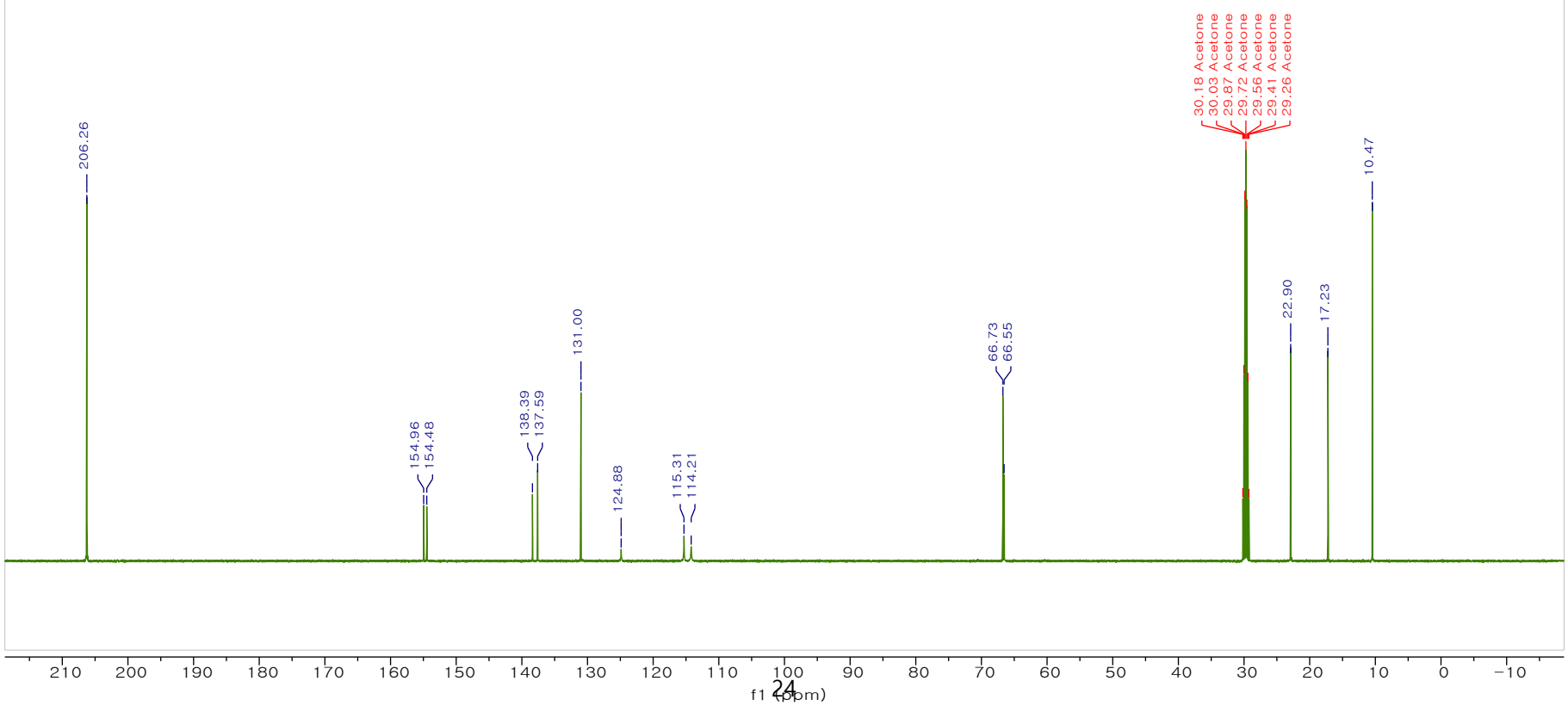




Dipropyl 2,4-toluenedicarbamate ^{13}C





5. References for NMR

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