Supplementary Information

Photocatalytic Shono-Type Oxidation of *N*-Alkylamides with Hydrogen Evolution

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1. General Methods and Materials

General Methods

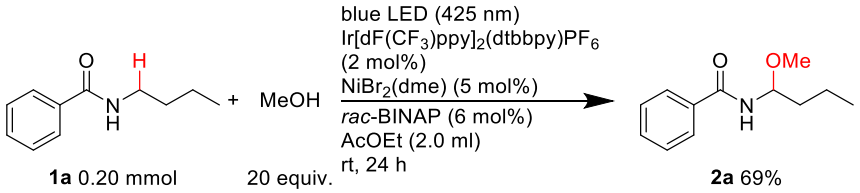
All reactions were carried out under a nitrogen atmosphere using flame-dried glassware. Photoreactions were carried out with blue LEDs (HepatoChem, EvoluChem 425 PF, HCK1012-01-012, 18 W). Gas chromatography of gas phase was measured on SHIMADZU GAS CHROMATOGRAPH GC-2014s equipped with a TCD detector using argon as the carrier gas. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECZ400S/L1 (^{1}H at 400 MHz, ^{13}C at 101 MHz) spectrometer and JEOL JNM-ECZ500R/S1 (^{1}H at 500 MHz). NMR data were obtained in $CDCl_3$ or CD_3CN. Chemical shifts are recorded in δ ppm referenced to a residual $CDCl_3$ (δ = 7.26 for ^{1}H, δ = 77.0 for ^{13}C) or CD_3CN (δ = 1.94 for ^{1}H, δ = 1.32 for ^{13}C), respectively. IR measurements were performed on FTIR SHIMADZU Affinity-1S spectrometer fitted with a Pike Technologies MIRacle Single Reflection ATR adapter. High-resolution mass spectra were recorded on Thermo Fisher Scientific Exactive Plus (ESI). Flash column chromatography was performed with Hi-Flash™ Column Silica gel 40 μm 60 Å (Yamazen), Hi-Flash™ Premium Column Silica gel 30 μm 60 Å (Yamazen) or diol-silica gel CHROMATOREX DIOL MB100-40/75 (FUJISILYSIA).

Materials

N-Butylbenzamide (**1a**),[1] *N*-butyl-4-methoxybenzamide (**1b**),[1] *N*-butyl-4-(trifluoromethyl)benzamide (**1c**),[1] *N*-butyl-3-(trifluoromethyl)benzamide (**1e**),[1] *N*-(5-hydroxypentan-1-yl)acetamide[2] and methyl 2,6-bis(benzamido)hexanoate (**1o**)[1] were prepared according to the previously reported methods. Other chemicals were purchased from commercial suppliers and used as received unless described below.

2. C–H Methoxylation of *N*-Alkylamides

2-1. A Typical Procedure



To a Schlenk tube (internal volume: 9.4 mL) containing Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.7 mg, 0.004 mmol, 2 mol%), *rac*-BINAP (7.8 mg, 0.013 mmol, 6 mol%) and *N*-butylbenzamide (**1a**) (35.7 mg, 0.20 mmol.) were added $NiBr_2$(dme) (3.1 mg, 0.010 mmol, 5 mol%), dehydrated methanol (128.4 mg, 4.0 mmol, 20 equiv.) and dehydrated ethyl acetate (2.0 mL) under nitrogen atmosphere. The tube was capped with rubber septa, and the reaction mixture was stirred under blue light irradiation, with being cooled by a fan (Figure S1). After 24 hours, the reaction mixture was passed through a short column of Florisil® with ethyl acetate as an eluent. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography with silica gel (10% AcOEt/Hexane) to give *N*-acyl-*N*,*O*-acetal **2a** (28.6 mg, 0.14 mmol, 69%) as a white solid.

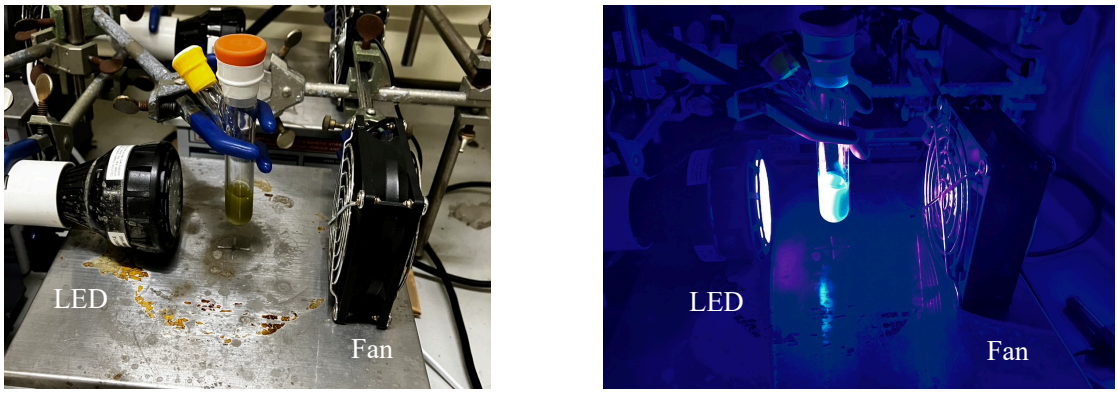
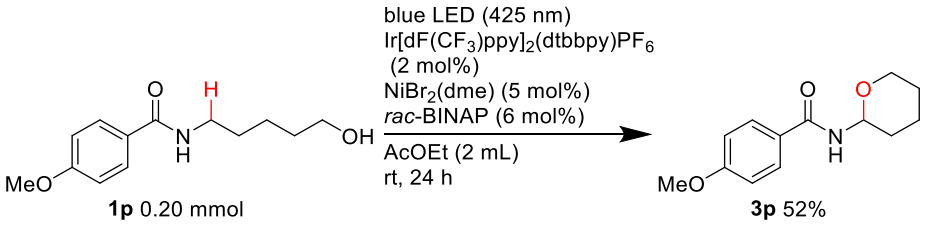


Figure S1. Photos of the Reaction Vessel (left: light off, right: light on)

Caution: *The present reaction evolves gaseous hydrogen, increasing the internal pressure. The reaction must be performed using a vessel equipped with a pressure-relief mechanism or a pressure-resistant vessel. In our experiment, rubber septa were used to safely vent excess pressure in case of excessive pressure buildup.*

2-2. Intramolecular Cyclization



To a Schlenk tube (internal volume: 9.4 mL) containing $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.9 mg, 0.004 mmol, 2 mol%), *rac*-BINAP (7.3 mg, 0.012 mmol, 6 mol%) and *N*-(5-hydroxypentan-1-yl)-4-methoxybenzamide (**1p**) (47.2 mg, 0.20 mmol, 1.0 equiv.) were added $NiBr_2(dme)$ (3.2 mg, 0.010 mmol, 5 mol%) and dehydrated ethyl acetate (2.0 mL) under nitrogen atmosphere. The tube was capped with rubber septa, and the reaction mixture was stirred under blue light irradiation, with being cooled by a fan. After 24 hours, the septum was removed, and the reaction mixture was passed through a short column of Florisil® with ethyl acetate as an eluent. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography with silica gel (gradient from 79 to 100% AcOEt/Hexane) to give **3p** (24.3 mg, 0.103 mmol, 52%) as a white solid.

2-3. Quantification of Evolved Hydrogen Gas

The amount of H_2 was quantified using GC equipped with a TCD detector. GC conditions are as follows: [column temp.: 60 °C | injector temp.: 100 °C | detector temp.: 200 °C | GC column: SHINWA CHEMICAL INDUSTRIES LTD., Shincarbon-ST 50-80 (length: 6.0 m, inner diameter: 3.00 mm) | Carrier gas: argon]. The calibration curve prepared using standard H_2 gas (purity: 99.9%, purchased from Kyoto Teisan Co. Ltd.) is shown in Figure S2.

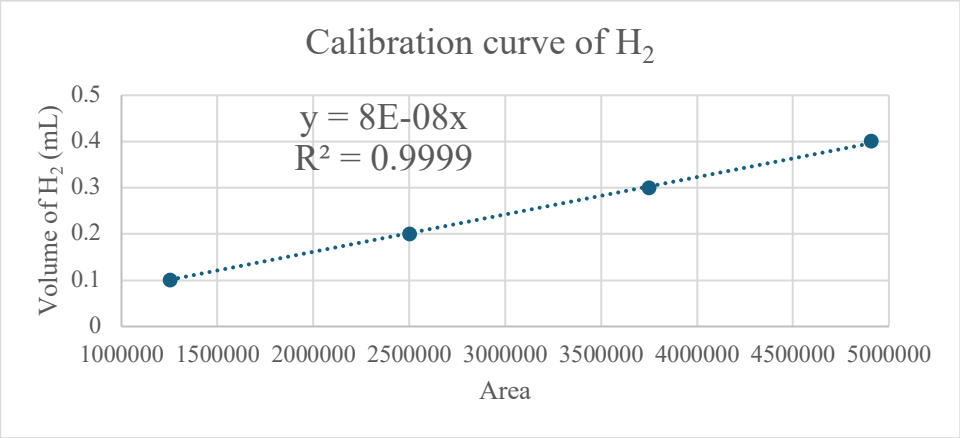


Figure S2. Calibration Curve of H_2

The C–H methoxylation of *N*-butylbenzamide **1a** was performed according to the typical procedure. After completion of the reaction, the gas phase in the headspace of the reaction vessel was analyzed. A gas-tight syringe was used to take a sample (0.20 mL) from the vessel, which was then injected into the GC. The uncorrected amount of H_2 [$x(H_2)$] was calculated according to the following equation, where A is an area of peak of detected H_2 in the GC chromatogram, f is a factor determined by a calibration curve, and V is an internal volume of the gas phase of the reaction vessel.

$$x(H_2) = A \times f \times \frac{V}{0.20} \times \frac{1}{22.4}$$

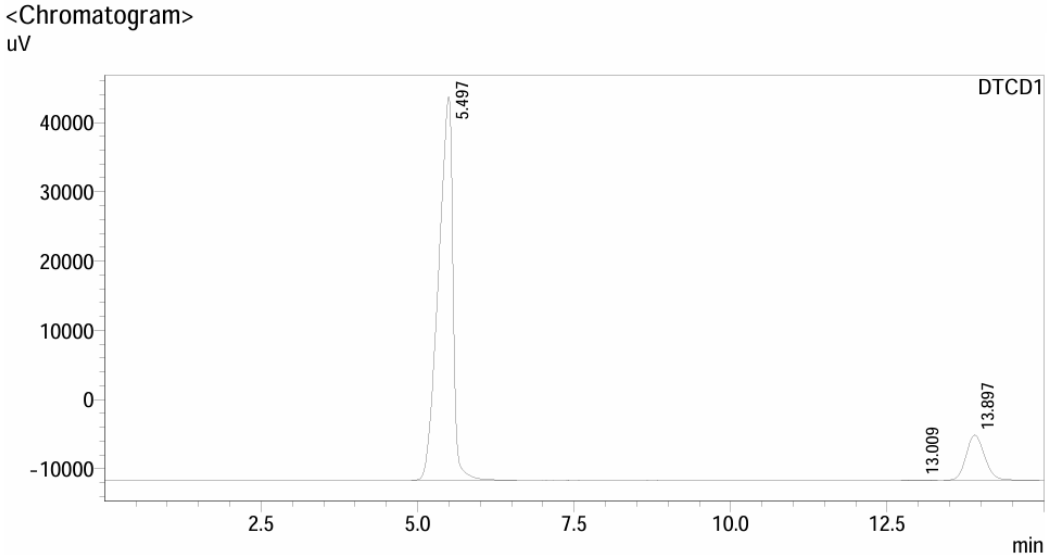
Subsequently, the calculated value is corrected to account for the increase in internal pressure. The relationship between $x(H_2)$ and actual value $x'(H_2)$ is represented by the following equation:

$$x(H_2) = x'(H_2) \times \frac{V}{V + 22.4 \times x'(H_2)}$$

This can be rearranged to derive the following equation:

$$x'(H_2) = x(H_2) \times \frac{V}{V - 22.4 \times x(H_2)}$$

Considering the vessel's internal volume of 9.4 mL and 2.0 mL of solvent used, we assumed internal volume of the gas phase (V) to be 7.4 mL. The factor (f) was 8×10^{-8} according to the calibration curve, and the area (A) was 888037. Upon substituting these values into the equation, the amount of H_2 was determined to be 0.18 mmol, indicating the yield was almost quantitative.



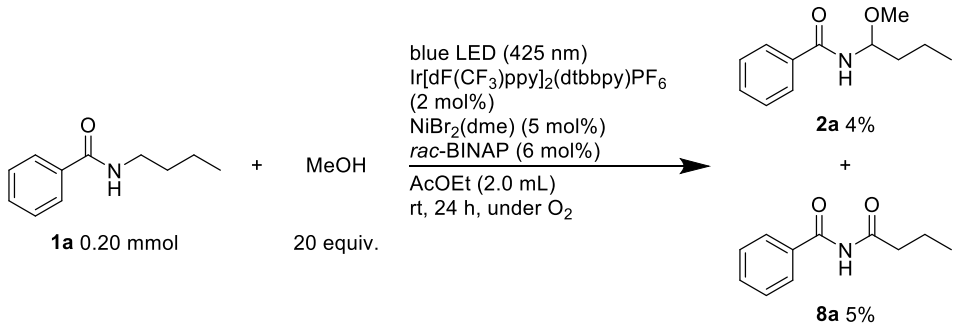
<Peak Reports>
DTCD1

Peak#	Retention Time	Area
1	5.497	888037
2	13.009	463
3	13.897	132754

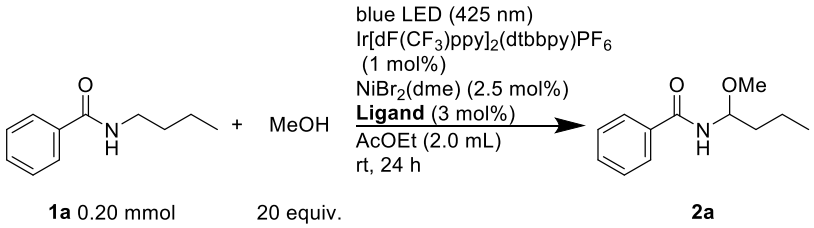
Figure S3. Gas Chromatogram

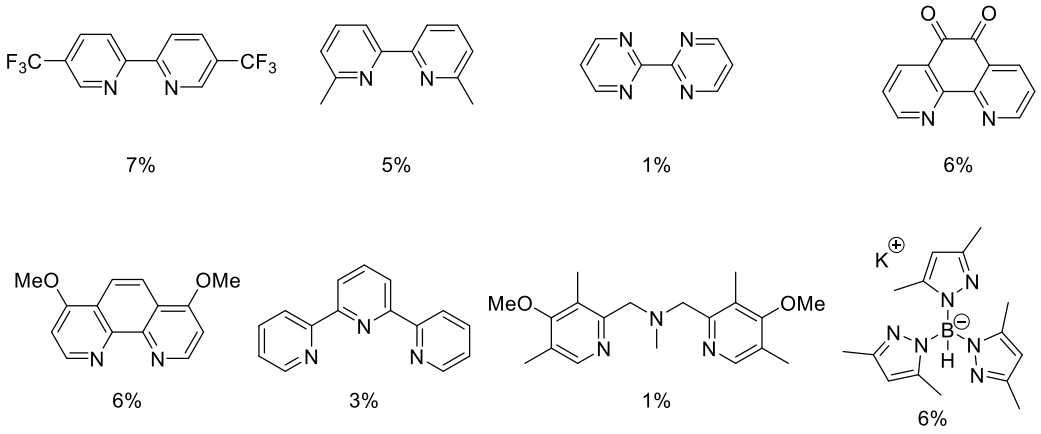
2-4. Reaction under Oxygen Atmosphere

Reaction **1a** was performed in an oxygen atmosphere, with all other conditions kept as described in Section 2-1. A ^{1}H NMR analysis of the reaction mixture showed the formation of **2a** (4%) and imide **8a** (5%) along with recovery of **1a** (89%). ^{1}H NMR spectrum of **8a** was confirmed in previous literature.[3]



2-5. Screening of Ligands





NMR yields of **2a**

Figure S4. Screening of Heteroaryl Ligands

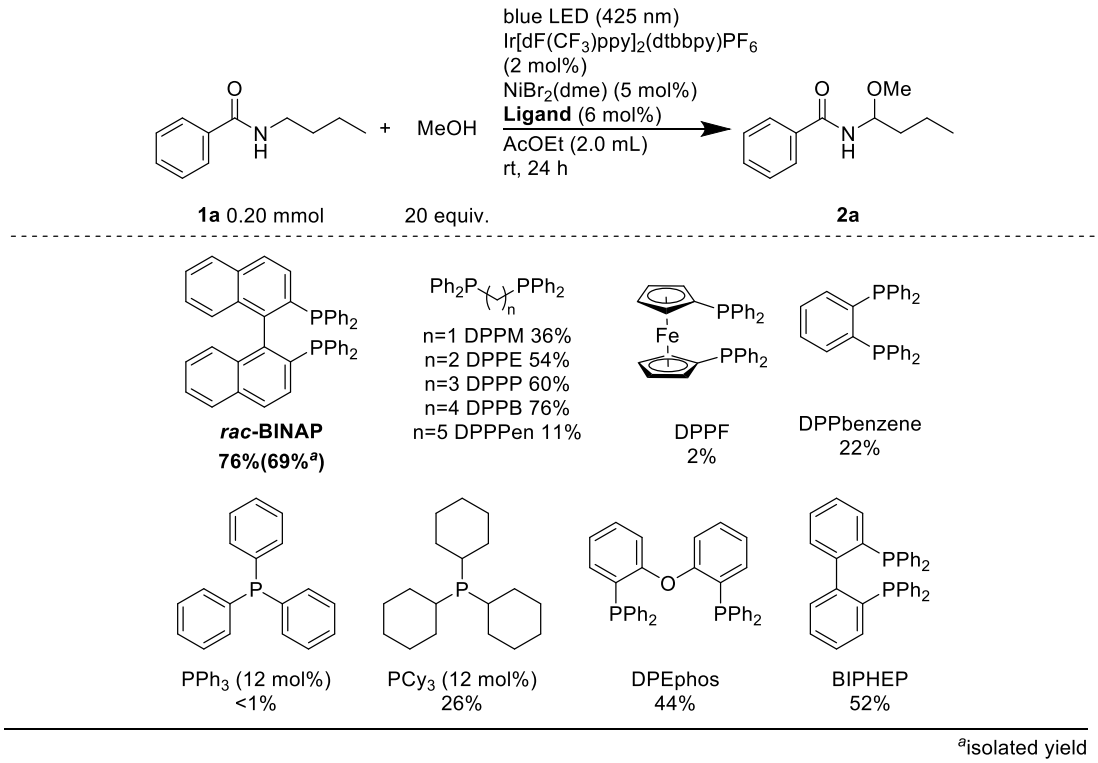
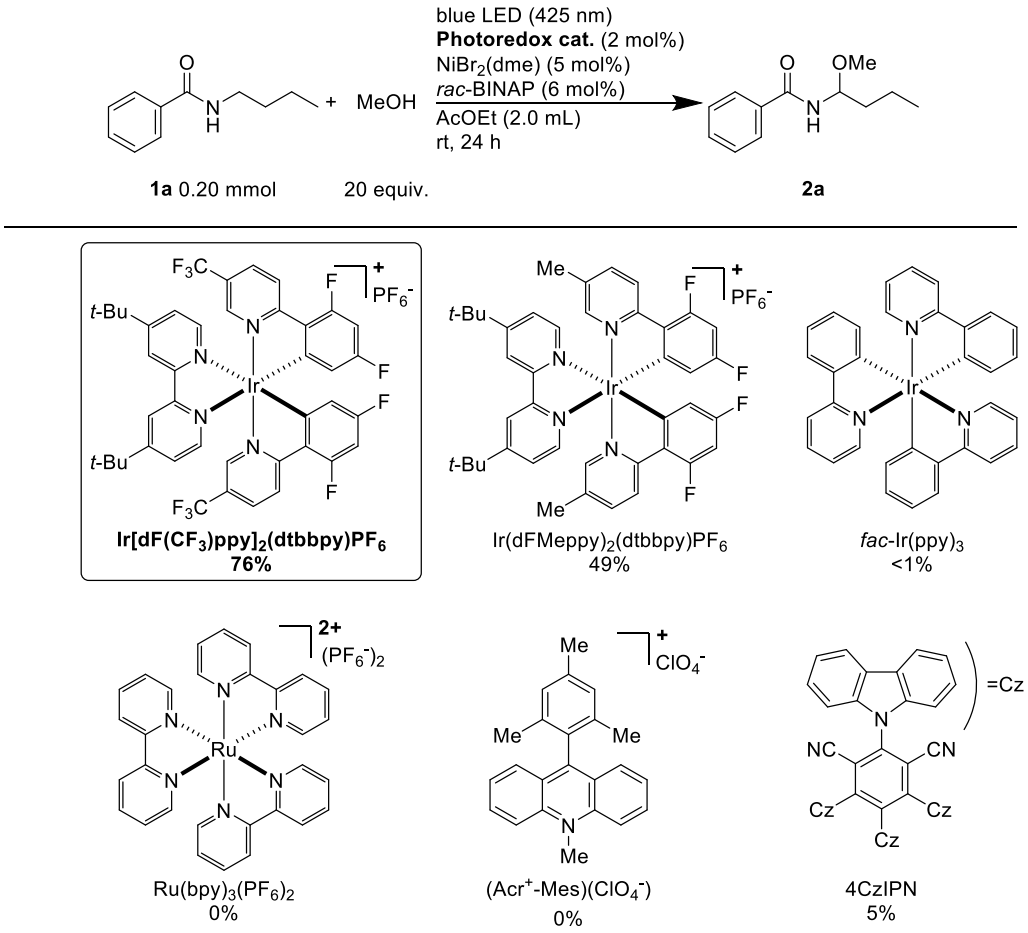


Figure S5. Screening of Phosphine Ligands

2-6. Screening of Photocatalysts



NMR yields of **2a**

Figure S6. Screening of Photocatalysts

2-7. Screening of the Methanol Amount

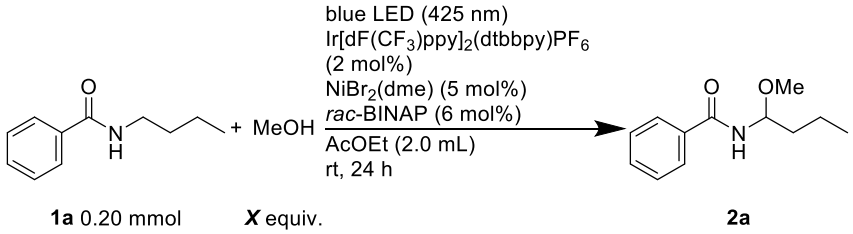
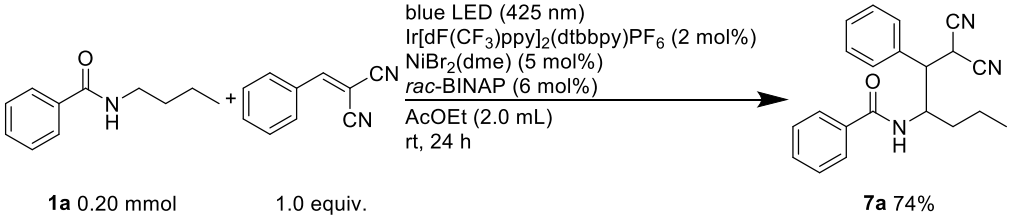


Table S1. Screening of the Methanol Amount

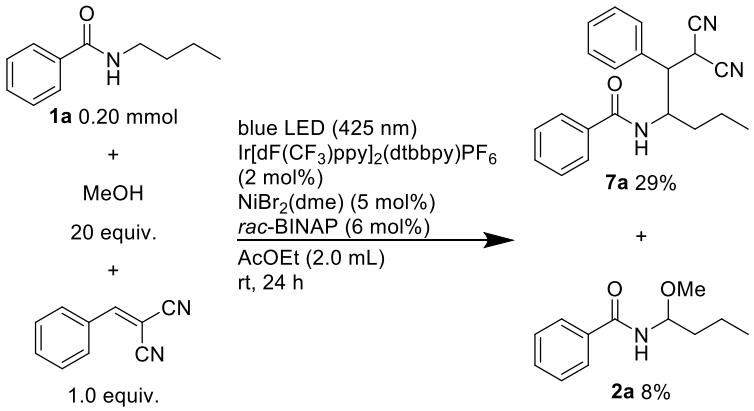
Entry	***X***	NMR yields of **2a**
1	1.0	20
2	5.0	43
3	10	40
4	**20**	**76**
5	30	72

[a]Reaction conditions: **1a** (0.20 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.004 mmol, 2 mol%), $NiBr_2$(dme) (0.010 mmol, 5 mol%), *rac*-BINAP (0.012 mmol, 6 mol%), AcOEt (2.0 mL), 24 h, rt, blue LED irradiation (λ= 425 nm).

2-8. Radical Trapping Experiments

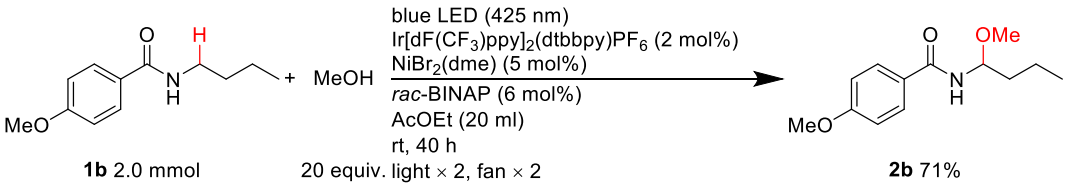


To a 5 mL Schlenk tube containing $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.8 mg, 0.004 mmol, 2 mol%), *rac*-BINAP (7.5 mg, 0.012 mmol, 6 mol%), benzalmalononitrile (30.5 mg, 0.20 mmol, 1.0 equiv.) and *N*-butylbenzamide (34.9 mg, 0.20 mmol, 1.0 equiv.) was added $NiBr_2(dme)$ (3.0 mg, 0.010 mmol, 5 mol%) and dehydrated ethyl acetate (2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred under blue light irradiation, with being cooled by a fan. After 24 hours, the septum was removed, and the reaction mixture was passed through a short column of Florisil® with ethyl acetate as an eluent. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography with silica gel (gradient from 0% to 30% AcOEt/Hexane) to give *N*-(1,1-dicyano-2-phenylhexan-3-yl)benzamide (**7a**) (49.3 mg, 0.15 mmol, 74%) as a white solid.



To a 5 mL Schlenk tube containing $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 2 mol%), *rac*-BINAP (7.3 mg, 0.012 mmol, 6 mol%), benzalmalononitrile (31.1 mg, 0.20 mmol, 1.0 equiv.) and *N*-butylbenzamide (35.0 mg, 0.20 mmol, 1.0 equiv.) was added $NiBr_2(dme)$ (3.2 mg, 0.010 mmol, 5 mol%), dehydrated methanol (128.0 mg, 4.0 mmol, 20 equiv.) and dehydrated ethyl acetate (2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred under blue light irradiation, with being cooled by a fan. After 24 hours, the septum was removed, and the reaction mixture was passed through a short column of Florisil® with ethyl acetate as an eluent. After removal of the solvent under reduced pressure, the NMR yields of **7a** and **2a** were 29% and 8% yield, respectively, determined using 1,1,2,2-tetrachloroethane as an internal standard.

2-9. 2 mmol Scale Reaction



Following the typical procedure (section 2-1), the reaction was performed with *N*-butyl-4-methoxybenzamide (**1b**) (441.29 mg, 2.0 mmol). A large Schrenk tube (internal volume: 94 mL) equipped with an oil bubbler was employed as the reaction vessel. The crude mixture was purified by silica gel flash column chromatography (10% AcOEt/Hexane) to afford *N*-(1-methoxybutan-1-yl)-4-methoxybenzamide (**2b**) (336.1 mg, 1.42 mmol, 71%) as a white solid.

2-10. Cyclic Voltammogram

Oxidation potentials of *n*-Bu_4NBr, *rac*-BINAP, and $NiBr_2$(dme) were measured by cyclic voltammetry. Cyclic voltammetry was measured on an ALS electrochemical analyzer model 612E by using a glassy carbon working electrode, a Pt counter electrode, and Ag/Ag^+ electrode. A sample (0.01 mmol) and *n*-Bu_4NBF_4 (1 mmol) were placed in 20 mL cell and dissolved in 10 mL AcOEt (*rac*-BINAP and $NiBr_2$(dme) were not dissolved completely). The solution was degassed by purging N_2 gas prior to the measurements. The voltammograms were taken at room temperature under an N_2 atmosphere.

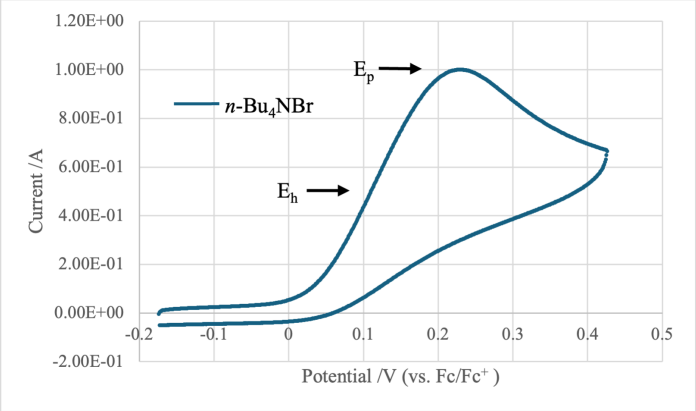


Figure S7. Cyclic voltammogram of *n*-Bu_4NBr in AcOEt.

Scan rate: 0.1 V/s

E_p = 0.23 V (vs. Fc/Fc^+)

$E_{ox} \fallingdotseq E_h$ = 0.11 V (vs. Fc/Fc^+)

Ferrocene was used as the internal standard.

As an estimate of the oxidation potential, we used the half-peak potential E_h (the potential at half the current in E_p).[4]

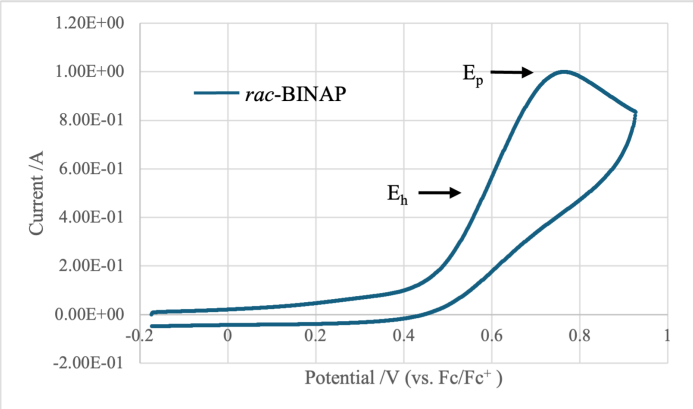


Figure S8. Cyclic voltammogram of *rac*-BINAP in AcOEt.

Scan rate: 0.1 V/s

E_p = 0.76 V (vs. Fc/Fc^+)

$E_{ox} \fallingdotseq E_h$ = 0.58 V (vs. Fc/Fc^+)

Ferrocene was used as the internal standard.

As an estimate of the oxidation potential, we used the half-peak potential E_h (the potential at half the current in E_p).[4]

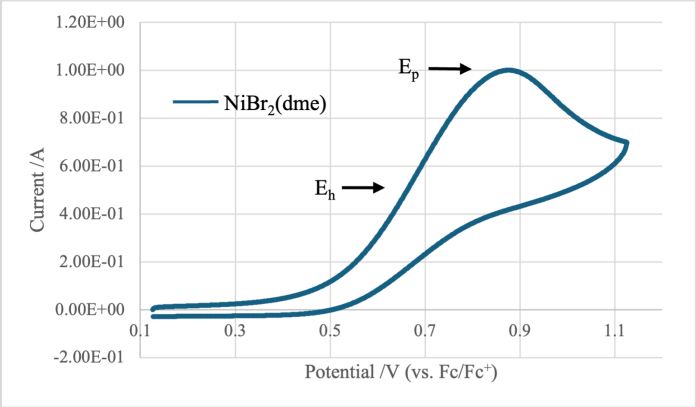


Figure S9. Cyclic voltammogram of $NiBr_2$(dme) in AcOEt.

Scan rate: 0.1 V/s

E_p = 0.88 V (vs. Fc/Fc^+)

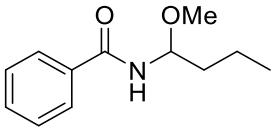
$E_{ox} \fallingdotseq E_h$ = 0.66 V (vs. Fc/Fc^+)

Ferrocene was used as the internal standard.

As an estimate of the oxidation potential, we used the half-peak potential E_h (the potential at half the current in E_p).[4]

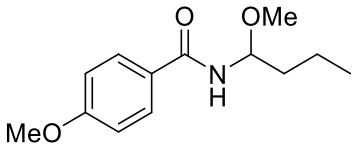
2-11. Spectral Data of Products

N-(1-Methoxybutan-1-yl)benzamide (**2a**)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82-7.79 (m, 2H), 7.52 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.46-7.42 (m, 2H), 6.39 (d, *J* = 9.2 Hz, 1H), 5.35 (dt, *J* = 9.6, 6.4 Hz, 1H), 3.40 (s, 3H), 1.80-1.71 (m, 1H), 1.66-1.57 (m. 1H), 1.51-1.37 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 133.9, 131.8, 128.6, 126.9, 81.4, 55.9, 37.7, 18.2, 13.8; HRMS (ESI^+) m/z: $[M+Na]^+$ calcd for $C_{12}H_{17}NNaO_2$, 230.1152; found, 230.1150. IR (neat): 3263, 2938, 1638, 1533, 698 cm^{-1}.

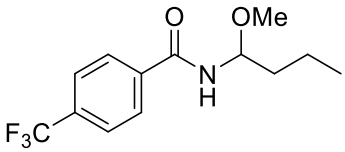
N-(1-Methoxybutan-1-yl)-4-methoxybenzamide (**2b**)



Following the typical procedure, the reaction was performed using *N*-butyl-4-methoxybenzamide (**1b**) as a substrate. The crude mixture was purified by silica gel flash column chromatography (8% AcOEt/Hexane) to afford *N*-(1-methoxybutan-1-yl)-4-methoxybenzamide (**2b**) (36.8 mg, 0.16 mmol, 78%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.8Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.32 (d, *J* = 9.2 Hz, 1H), 5.33 (dt, *J* = 9.6, 6.0 Hz, 1H), 3.84 (s, 3H), 3.38 (s, 3H), 1.78-1.69 (m, 1H), 1.64-1.55 (m, 1H), 1.51-1.36 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 162.4, 128.8, 126.1, 113.7, 81.4, 55.9, 55.4, 37.7, 18.2, 13.7; HRMS (ESI^+) m/z: $[M+Na]^+$ calcd for $C_{13}H_{19}NNaO_3$, 260.1257; found, 260.1252. IR (neat): 3254, 2959, 1634, 1504, 1250, 1182, 851, 689 cm^{-1}.

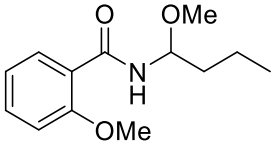
N-(1-Methoxybutan-1-yl)-4-(trifluoromethyl)benzamide (**2c**)



Following the typical procedure, the reaction was performed using *N*-butyl-4-(trifluoromethyl)benzamide (**1c**) as a substrate. The crude mixture was purified by silica gel flash column chromatography (gradient from 0% to 13% AcOEt/Hexane) to afford *N*-(1-methoxybutan-1-yl)-4-(trifluoromethyl)benzamide (**2c**) (31.9 mg, 0.12 mmol, 58%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 9.2 Hz, 1H), 5.34 (dt, *J* = 9.6, 6.0 Hz, 1H), 3.40 (s, 3H), 1.80-1.71 (m, 1H), 1.67-1.58 (m, 1H), 1.53-1.36 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 137.3, 133.5 (q, *J* = 32.6 Hz), 127.5, 125.7 (q, *J* = 3.8 Hz), 123.5 (q, *J* = 271.2 Hz), 81.8, 56.1, 37.6, 18.2, 13.7; HRMS (ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{13}H_{16}F_3NNaO_2$, 298.1025; found, 298.1022. IR (neat): 3283, 2986, 1645, 1506, 1327, 1123, 856, 683 cm^{-1}.

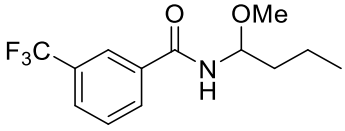
N-(1-Methoxybutan-1-yl)-2-methoxybenzamide (**2d**)



Following the typical procedure, the reaction was performed using *N*-butyl-2-methoxybenzamide (**1d**) as a substrate. The crude mixture was purified by silica gel flash column chromatography (gradient from 0% to 32% AcOEt/Hexane) to afford *N*-(1-methoxybutan-1-yl)-2-methoxybenzamide (**2d**) (30.2 mg, 0.13 mmol, 64%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.46 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.09 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 5.40 (dt, *J* = 9.2, 6.0 Hz, 1H), 3.96 (s, 3H), 3.40 (s, 3H), 1.79-1.58 (m, 2H), 1.52-1.39 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 157.4, 132.9, 132.3, 121.2, 120.9, 111.2, 81.0, 55.8, 55.7, 37.6, 17.9, 13.7; HRMS (ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{13}H_{19}NNaO_3$, 260.1257; found, 260.1255; IR (neat): 3387, 2959, 1651, 1520, 1236, 754 cm^{-1}.

N-(1-Methoxybutan-1-yl)-3-(trifluoromethyl)benzamide (**2e**)

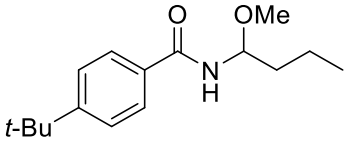


Following the typical procedure, the reaction was performed using *N*-butyl-3-(trifluoromethyl)benzamide (**1e**) as a substrate. The crude mixture was purified by silica gel flash column chromatography (gradient from 0% to 10% AcOEt/Hexane) to afford *N*-(1-methoxybutan-1-yl)- 3-(trifluoromethyl)benzamide (**2e**) (29.8 mg, 0.11 mmol, 54%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.47 (d, *J* = 9.2 Hz, 1H), 5.35 (dt, *J* = 9.2, 6.4 Hz, 1H), 3.41 (s, 3H), 1.81-1.72 (m, 1H), 1.67-1.59 (m, 1H), 1.53-1.36 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 134.8, 131.2 (q, *J* = 32.6 Hz), 130.2, 129.3, 128.4 (q, *J* = 3.9 Hz), 124.0 (q, *J* = 2.9 Hz), 123.6 (q, *J* = 271.2 Hz), 81.8, 56.1, 37.7, 18.2, 13.7; HRMS (ESI$^+$) m/z: $[M+Na]^+$

calcd for $C_{13}H_{16}F_3NNaO_2$, 298.1025; found, 298.1022; IR (neat): 3298, 2936, 1643, 1533, 1327, 1123, 696 cm^{-1}.

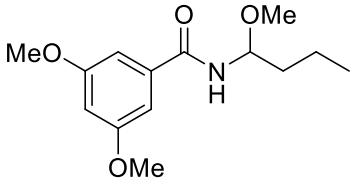
N-(1-Methoxybutan-1-yl)-4-*tert*-butylbenzamide (**2f**)



Following the typical procedure, the reaction was performed using *N*-butyl-4-*tert*-butylbenzamide (**1f**) as a substrate. The crude mixture was purified by silica gel flash column chromatography (10% AcOEt/Hexane) to afford *N*-(1-methoxybutan-1-yl)-4-*tert*-butylbenzamide (**2f**) (36.9 mg, 0.14 mmol, 70%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 6.35 (d, *J* = 9.6 Hz, 1H), 5.35 (dt, *J* = 9.6, 6.4 Hz, 1H), 3.39 (s, 3H), 1.79-1.71 (m, 1H), 1.65-1.56 (m, 1H), 1.51-1.39 (m, 2H), 1.33 (s, 9H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 155.4, 131.0, 126.8, 125.5, 81.3, 55.9, 37.7, 34.9, 31.1, 18.2, 13.8; HRMS (ESI^+) m/z: $[M+Na]^+$ calcd for $C_{16}H_{25}NNaO_2$, 286.1778; found, 286.1777. IR (neat): 3306, 2959, 1641, 1499, 851 cm^{-1}.

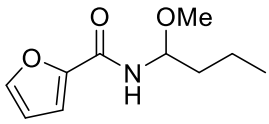
N-(1-Methoxybutan-1-yl)-3,5-dimethoxybenzamide (**2g**)



Following the typical procedure, the reaction was performed using *N*-butyl-3,5-dimethoxybenzamide (**1g**) as a substrate. The crude mixture was purified by silica gel flash column chromatography (gradient from 8% to 10% AcOEt/Hexane) to afford *N*-(1-methoxybutan-1-yl)-3,5-dimethoxybenzamide (**2g**) (34.5 mg, 0.13 mmol, 65%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.91 (d, *J* = 2.4 Hz, 2H), 6.58 (t, *J* =2.4 Hz, 1H), 6.32 (d, *J* = 9.6 Hz, 1H), 5.32 (dt, *J* = 9.6, 6.4 Hz, 1H), 3.81 (s, 6H), 3.39 (s, 3H), 1.78-1.69 (m, 1H), 1.64-1.55 (m, 1H), 1.53-1.34 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 160.9, 136.2, 104.9, 103.7, 81.5, 55.9, 55.5, 37.6, 18.2, 13.7; HRMS (ESI^+) m/z: $[M+Na]^+$ calcd for $C_{14}H_{21}NNaO_4$, 290.1363; found, 290.1360. IR (neat): 3256, 2928, 1601, 1533, 1159, 856 cm^{-1}.

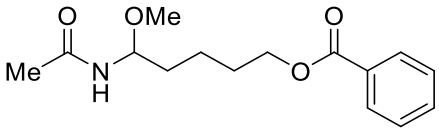
N-(1-Methoxybutan-1-yl)-2-furamide (**2h**)



Following the typical procedure, the reaction was performed using *N*-butyl-2-furamide (**1h**) as a substrate. The crude mixture was purified by silica gel flash column chromatography (10% AcOEt/Hexane) to afford *N*-(1-Methoxybutan-1-yl)-2-furamide (**2h**) (13.9 mg, 0.070 mmol, 35%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, *J* = 2.0, 0.8 Hz, 1H), 7.15 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.52 (dd, *J* = 3.6, 2.0 Hz, 1H), 6.46 (d, *J* = 9.6 Hz, 1H), 5.28 (dt, *J* = 10.0, 6.0 Hz, 1H), 3.38 (s, 3H),1.79-1.70 (m, 1H), 1.65-1.56 (m, 1H), 1.50-1.37 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 147.4, 144.1, 115.0, 112.3, 80.6, 55.9, 37.7, 18.1, 13.7; HRMS (ESI^+) m/z: $[M+Na]^+$ calcd for $C_{10}H_{15}NNaO_3$, 220.0944; found, 220.0946; IR (neat): 3298, 2959, 1651, 1514, 1074, 752 cm^{-1}.

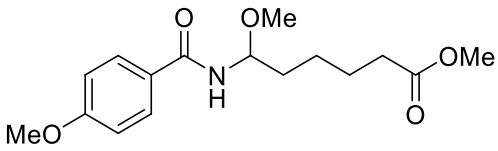
5-Acetamido-5-methoxypentan-1-yl benzoate (**2i**)



Following the typical procedure, the reaction was performed using 5-acetamidopentan-1-yl benzoate (**2i**) as a substrate. The crude mixture was purified by silica gel flash column chromatography (gradient from 90% to 100% AcOEt/Hexane) to afford 5-acetamido-5-methoxypentan-1-yl benzoate (**2i**) (24.7 mg, 0.088 mmol, 44%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04-8.01 (m, 2H), 7.55 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.45-7.41 (m, 2H), 5.76 (d, *J* = 9.6 Hz, 1H), 5.12 (dt, *J* = 9.6, 6.0 Hz, 1H), 4.36-4.26 (m, 2H), 3.33 (s, 3H), 2.01 (s, 3H), 1.86-1.67 (m, 3H), 1.64-1.44 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 166.6, 132.9, 130.2, 129.5, 128.3, 80.8, 64.5, 55.8, 35.0, 28.3, 23.4, 21.4; HRMS (ESI^+) m/z: $[M+Na]^+$ calcd for $C_{15}H_{21}NNaO_4$, 302.1363; found, 302.1360; IR (neat): 3321, 2953, 1717, 1653, 1271, 708 cm^{-1}.

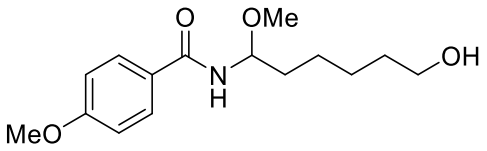
Methyl 6-methoxy-6-(4-methoxybenzamido)hexanoate (**2j'**)



Following the typical procedure, the reaction was performed using 6-(4-methoxybenzamido)hexanoic acid (**1j**) as a substrate. After irradiation of blue light, saturated

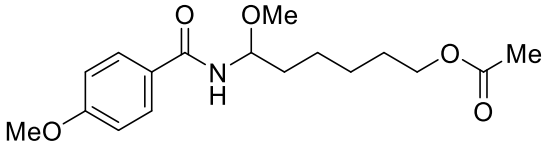
NH_4Cl aq. (10 mL) was added to the reaction mixture. The mixture was then extracted with dichloromethane (3 × 10 mL) and the combined organic phase was dried over Na_2SO_4. The solvent was removed under reduced pressure, followed by addition of methanol (6.0 mL), diethyl ether (6.0 mL) and trimethylsilyldiazomethane (0.6 M in *n*-hexane) (0.66 mL, 0.40 mmol, 2.0 equiv. to **1j**). The mixture was stirred at room temperature for 10 min, followed by adding acetic acid (0.5 mL). After removal solvent under reduced pressure, the crude mixture was purified by silica gel flash column chromatography (gradient from 30% to 40% AcOEt/Hexane) to afford methyl 6-methoxy-6-(4-methoxybenzamido)hexanoate (**2j'**) (35.2 mg, 0.11 mmol, 57%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 9.2 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.33 (d, *J* = 9.6 Hz, 1H), 5.31 (dt, *J* = 9.6, 6.4 Hz, 1H), 3.84 (s, 3H), 3.63 (s, 3H), 3.37 (s, 3H), 2.30 (t, *J* = 7.2 Hz, 2H), 1.80-1.71 (m, 1H), 1.68-1.59 (m, 3H), 1.52-1.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.9, 166.9, 162.4, 128.8, 126.0, 113.7, 81.4, 55.9, 55.4, 51.5, 35.3, 33.8, 24.5, 24.4; HRMS (ESI^+) m/z: $[M+Na]^+$ calcd for $C_{16}H_{23}NNaO_5$, 332.1468; found, 332.1465; IR (neat): 3308, 2949, 1639, 1169, 837, 687 cm^{-1}.

N-(6-Hydroxy-1-methoxyhexan-1-yl)-4-methoxybenzamide (**2k**)



Following the typical procedure, the reaction was performed using *N*-(6-hydroxyhexan-1-yl)-4-methoxybenzamide (**1k**) as a substrate. The crude mixture was purified by flash column chromatography with diol silica gel (60% AcOEt/Hexane) to afford *N*-(6-hydroxy-1-methoxyhexan-1-yl)-4-methoxybenzamide (**2k**) (21.7 mg, 0.077 mmol, 39%) as a pale yellow oil. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.80 (d, *J* = 9.2 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 9.2 Hz, 2H), 5.22 (dt, *J* = 9.6, 6.4 Hz, 1H), 3.83 (s, 3H), 3.46 (dt, *J* = 6.4, 5.6 Hz, 2H), 3.27 (s, 3H), 2.56 (t, *J* = 5.6 Hz, 1H), 1.80-1.70 (m, 1H), 1.68-1.59 (m, 1H), 1.50-1.29 (m, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ = 167.8, 163.3, 130.1, 127.4, 114.5, 82.4, 62.4, 56.1, 55.5, 35.7, 33.4, 26.3, 25.7; HRMS (ESI^+) m/z: $[M+Na]^+$ calcd for $C_{15}H_{23}NNaO_4$, 304.1519; found, 304.1518; IR (neat): 3300, 2934, 1638, 1605, 1501, 1252, 1028, 843 cm^{-1}.

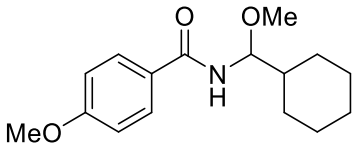
6-Methoxy-6-(4-methoxybenzamido)hexan-1-yl acetate (**2l**)



Following the typical procedure, the reaction was performed using 6-(4-methoxybenzamido)hexan-1-yl acetate (**1l**) as a substrate. The crude mixture was purified by silica gel flash column chromatography (gradient from 35% to 50% AcOEt/Hexane) to afford 6-methoxy-6-(4-methoxybenzamido)hexan-1-yl acetate (**2l**) (40.8 mg, 0.13 mmol, 63%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 9.6 Hz, 1H), 5.31 (dt, *J* = 9.6, 6.4 Hz, 1H), 4.02 (t, *J* = 6.4 Hz, 2H), 3.84 (s, 3H), 3.37 (s, 3H), 2.01 (s, 3H), 1.80-1.71 (m, 1H), 1.67-1.57 (m, 3H), 1.52-1.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 166.9, 162.4, 128.8, 126.0, 113.8, 81.4, 64.3, 55.9, 55.4, 35.6, 28.4, 25.6, 24.5, 20.9; HRMS (ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{17}H_{25}NNaO_5$, 346.1625; found, 346.1621; IR (neat): 3335, 2940, 1736, 1605, 1501, 1248, 845 cm^{-1}.

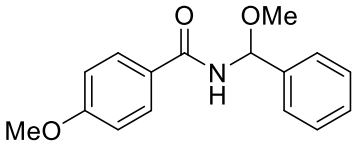
N-(Cyclohexyl(methoxy)methyl)-4-methoxybenzamide (**2m**)



Following the typical procedure, the reaction was performed using *N*-(cyclohexylmethyl)-4-methoxybenzamide (**1m**) as a substrate. The crude mixture was purified by silica gel flash column chromatography (gradient from 0% to 10% AcOEt/Hexane) to afford *N*-(cyclohexyl(methoxy)methyl)-4-methoxybenzamide (**2m**) (19.4 mg, 0.070 mmol, 35%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.21 (d, *J* = 9.6 Hz, 1H), 5.09 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.85 (s, 3H), 3.38 (s, 3H), 1.89 (d, *J* = 12.4 Hz, 1H), 1.76-1.73 (m, 3H), 1.67-1.53 (m, 2H), 1.28-1.05 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 162.4, 128.8, 126.2, 113.8, 85.1, 56.1, 55.4, 42.9, 28.3, 27.9, 26.3, 25.8, 25.7; HRMS (ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{16}H_{23}NNaO_3$, 300.1570; found, 300.1567; IR (neat): 3273, 2916, 2849, 1630, 1252, 1032, 841 cm^{-1}.

4-Methoxy-*N*-(methoxy(phenyl)methyl)benzamide (**2n**)

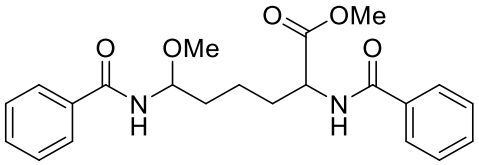


Following the typical procedure, the reaction was performed using *N*-benzyl-4-methoxybenzamide (**1n**) as a substrate. After irradiation of blue light, saturated $NaHCO_3$ aq. (10

mL) was added. The mixture was extracted with dichloromethane (3 × 10 mL), and the combined organic phase was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude mixture was purified by flash column chromatography with silica gel (gradient from 0% to 25% AcOEt/Hexane) to afford methyl 4-methoxy-*N*-(methoxy(phenyl)methyl)benzamide (**2n**) (29.6 mg, 0.11 mmol, 55%) as a white solid.

^{1}H NMR (400 MHz, CD_3CN): δ = 7.82 (d, *J* = 8.8 Hz, 2H), 7.50-7.47 (m, 2H), 7.43-7.31 (m, 4H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.29 (d, *J* = 9.2 Hz, 1H), 3.83 (s, 3H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ = 167.7, 163.5, 141.0, 130.3, 129.3, 129.1, 127.2, 127.1, 114.6, 82.9, 56.2, 56.1; HRMS (ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{16}H_{17}NNaO_3$, 294.1101; found, 294.1091; IR (neat): 3262, 2940, 1634, 1256, 1074, 845, 683 cm^{-1}.

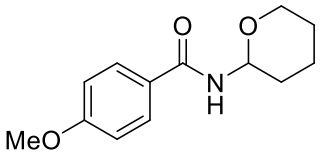
Methyl 2,6-bis(benzamido)-6-methoxyhexanoate (**2o**)



Following the typical procedure, the reaction was performed using methyl 2,6-bis(benzamido)hexanoate (**1o**) as a substrate. The crude mixture was purified by silica gel flash column chromatography (gradient from 40% to 45% AcOEt/Hexane) to afford methyl 2,6-bis(benzamido)-6-methoxyhexanoate (**2o**) (40.5 mg, 0.10 mmol, 51%) as a white solid.

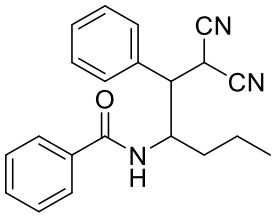
^{1}H NMR (500 MHz, CD_3CN): (diastereomer mixture, d.r. = 52 : 48) δ = 7.82-7.77 (m, major 4H, minor 4H), 7.56-7.51 (m, major 2H, minor 2H), 7.48-7.41 (m, major 4H, minor 4H), 7.24-7.21 (m, major 1H, minor 1H), 7.14 (d, *J* = 9.5 Hz, major 1H, minor 1H), 5.28-5.23 (m, major 1H, minor 1H), 4.57-4.53 (m, major 1H, minor 1H), 3.674 (s, major 3H), 3.665 (s, minor, 3H), 3.30 (s, major 3H), 3.29 (s, minor 3H), 1.98-1.64 (m, major 4H, minor 4H), 1.55-1.46 (m, major 2H, minor 2H); ^{13}C NMR (100 MHz, CD_3CN): δ = 173.8, 173.7, 168.6, 168.4, 168.2, 168.1, 135.25, 135.18, 134.95, 134.89, 132.5, 129.41, 129.374, 129.368, 128.233, 128.228, 128.18, 128.17, 82.33, 82.31, 55.69, 55.68, 53.8, 53.7, 52.73, 52.70, 35.1, 35.0, 31.7, 31.6, 22.22, 22.17, Four peaks of the phenyl carbons overlapped at 132.5 ppm and two peaks of the phenyl carbons overlapped at 129.4 ppm, determined by quantitative ^{13}C NMR; HRMS (ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{22}H_{26}N_2NaO_5$, 421.1734; found, 421.1726; IR (neat): 3312, 2951, 1638, 1522, 712 cm^{-1}.

4-Methoxy-*N*-(tetrahydropyran-2-yl)benzamide (**3p**)



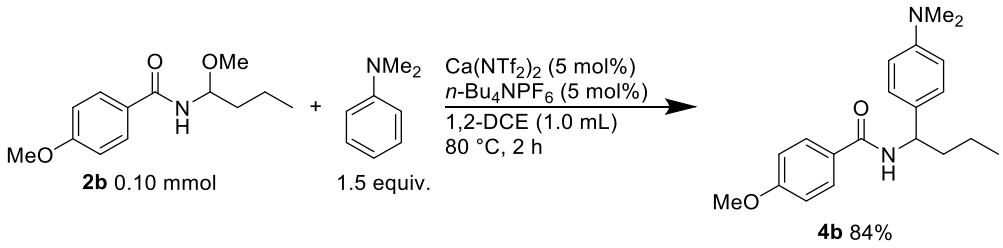
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 9.2 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 1H), 5.29 (ddd, *J* = 9.8, 9.8, 2.0 Hz, 1H), 4.04-3.98 (m, 1H), 3.83 (s, 3H), 3.68-3.62 (m, 1H), 1.95-1.85 (m, 2H), 1.71-1.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 162.3, 128.9, 126.2, 113.7, 78.3, 67.5, 55.3, 31.7, 25.1, 22.9; HRMS (ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{13}H_{17}NNaO_3$, 258.1101; found, 258.1102; IR (neat): 3321, 2995, 1609 cm^{-1}.

N-(1,1-dicyano-2-phenylhexan-3-yl)benzamide (**7a**)



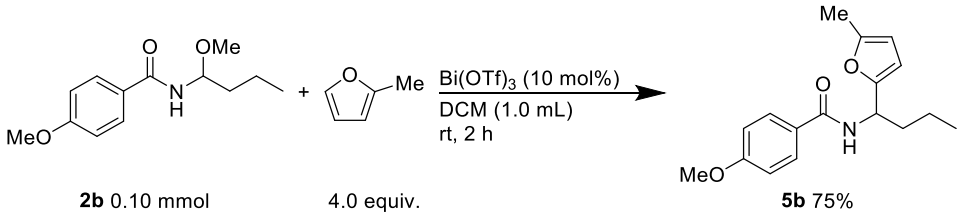
^{1}H NMR (400 MHz, $CDCl_3$): (diastereomer mixture, d.r. = 44 : 56) δ = 7.84-7.82 (m, minor, 2H), 7.71-7.68 (m, major, 2H), 7.57-7.53 (m, major 1H, minor 1H), 7.48-7.39 (m, major 5H, minor 7H), 7.22-7.18 (m, major 2H), 6.46 (d, *J* = 8.4 Hz, minor 1H), 5.69 (d, *J* = 8.4 Hz, major 1H), 4.77-4.70 (m, major 1H), 4.64-4.56 (m, minor 1H), 4.53 (d, *J* = 10.8 Hz, major 1H), 4.36 (d, *J* = 6.0 Hz, minor 1H), 3.53 (dd, *J* = 10.8, 2.4 Hz, major 1H), 3.47 (dd, *J* = 10.4, 6.4 Hz, minor 1H), 1.63-1.20 (m, major 4H, minor 4H), 0.94 (t, *J* = 7.2 Hz, major 3H), 0.80 (t, *J* = 7.2 Hz, minor 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (diastereomeric mixture, d.r. = 44 : 56) δ = 168.6, 168.3, 135.4, 133.4, 133.2, 133.1, 132.2, 132.1, 129.5, 129.2, 128.84, 128.77, 128.7, 128.4, 127.1, 126.80, 113.0, 112.8, 112.1, 111.9, 52.5, 51.7, 51.6, 50.4, 35.8, 34.5, 27.4, 26.8, 19.4, 19.1, 13.6, 13.5. Three peaks of the phenyl carbons overlapped at 129.2 ppm, determined by quantitative ^{13}C NMR; HRMS (ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{21}H_{21}N_3NaO$, 354.1577; found, 354.1573; IR (neat): 3250, 2963, 2897, 1636, 698 cm^{-1}.

3. Synthetic Application of *N*-Acyl-*N*,*O*-Acetals[5,6,7]



Calcium(II) bis(trifluoromethanesulfonyl)imide (3.2 mg, 0.005 mmol, 5 mol%), tetrabutylammonium hexafluorophosphate (2.1 mg, 0.005 mmol, 5 mol%) and **2b** (23.9 mg, 0.10 mmol, 1 equiv.) were placed in a 5 mL Schlenk tube. The tube was capped with a rubber septum and purged with argon. To the tube, *N*,*N*-dimethylaniline (18.9 μL, 0.15 mmol, 1.5 equiv.) and dehydrated 1,2-dichloroethane (1.0 mL) were added. The resulting mixture was stirred at room temperature for 2 hours. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography with silica gel (25% AcOEt/Hexane) to afford *N*-(1-(4-(dimethylamino)phenyl)butan-1-yl)-4-methoxybenzamide (**4b**) (27.4 g, 0.084 mmol, 84%) as a white solid.

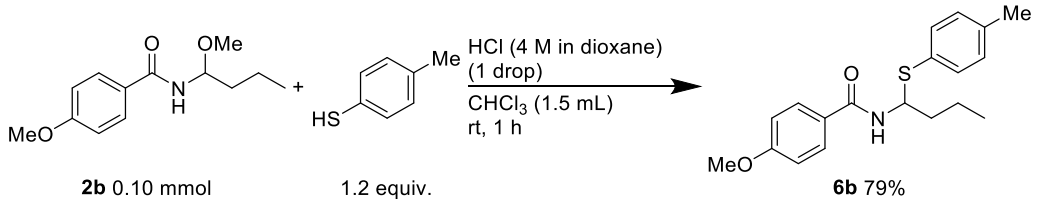
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.21 (d, *J* = 8.4 Hz, 1H), 5.09 (dt, *J* = 7.6, 7.6 Hz, 1H), 3.82 (s, 3H), 2.93 (s, 6H), 1.98-1.78 (m, 2H), 1.44-1.26 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 161.9, 149.8, 130.1, 128.6, 127.5, 127.1, 113.5, 112.6, 55.3, 53.0, 40.6, 38.1, 19.6, 13.9; HRMS (ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{20}H_{26}N_2NaO_2$, 349.1886; found, 349.1879; IR (neat): 3296, 2930, 2365, 1632, 1252, 843, 812 cm^{-1}.



Bismuth(III) trifluoromethanesulfonate (6.6 mg, 0.010 mmol, 10 mol%) and **2b** (24.4 mg, 0.10 mmol, 1 equiv.) were placed in a 5 mL Schlenk tube. The tube was capped with a rubber septum and purged with argon. To the tube, 2-methylfuran (36.1 μL, 0.40 mmol, 4.0 equiv.) and dehydrated dichloromethane (1.0 mL) were added. The resulting mixture was stirred at room temperature. After 2 hours, the septum was removed, and the reaction mixture was passed through a short column of Celite with dichloromethane as an eluent. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography with silica gel (gradient from 12% to 30% AcOEt/Hexane) to give 4-methoxy-*N*-(1-(5-methylfuran-2-yl)butan-

1-yl)benzamide (**5b**) (21.6 mg, 0.075 mmol, 75%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.25 (d, *J* = 8.8 Hz, 1H), 6.09 (d, *J* = 2.8 Hz, 1H), 5.88 (dq, *J* = 3.2, 0.8 Hz, 1H), 5.23 (dt, *J* = 8.4, 8.4 Hz, 1H), 3.84 (s, 3H), 2.27 (d, *J* = 0.8 Hz, 3H), 1.93-1.79 (m, 2H), 1.44-1.29 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 162.1, 152.7, 151.4, 128.7, 126.8, 113.6, 107.0, 106.0, 55.4, 47.4, 36.4, 19.3, 13.8, 13.6; HRMS (ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{17}H_{21}NNaO_3$, 310.1414; found, 310.1408; IR (neat): 3281, 2957, 2359, 1624, 1022, 845, 781 cm^{-1}.



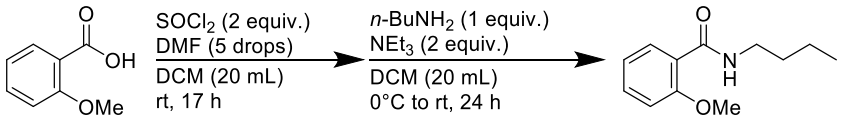
2b 0.10 mmol 1.2 equiv. **6b** 79%

Amide **2b** (24.2 mg, 0.10 mmol, 1.0 equiv.) and *p*-toluenethiol (15.3 mg, 0.12 mmol, 1.2 equiv.) were dissolved using dehydrated chloroform (1.5 mL) in a 4 mL vial under nitrogen atmosphere. Hydrogen chloride (4 M in 1,4-dioxane) (1 drop) was then added, and the mixture was stirred at room temperature for 1 hour. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography with silica gel (gradient from 8 to 27% AcOEt/Hexane) to afford 4-methoxy-*N*-(1-(*p*-tolylthio)butan-1-yl)benzamide (**6b**) (26.0 g, 0.079 mmol, 79%) as a white solid.

^{1}H NMR (400 MHz, CD_3CN): δ = 7.66 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.13-7.08 (m, 3H), 6.92 (d, *J* = 9.2 Hz, 2H), 5.50 (ddd, *J* = 9.6, 8.0, 6.4 Hz, 1H), 3.81 (s, 3H), 2.27 (s, 3H), 1.86-1.76 (m, 2H), 1.45 (ddq, *J* = 7.6, 7.6, 7.6 Hz, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ = 166.6, 163.2, 138.9, 134.8, 130.48, 130.47, 129.9, 127.4, 114.5, 58.4, 56.1, 38.3, 21.1, 20.5, 13.8; HRMS (ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{19}H_{23}NNaO_2S$, 352.1342; found, 353.1335; IR (neat): 3292, 2957, 1628, 1501, 1256, 1179, 810 cm^{-1}.

4. Preparation of Substrates

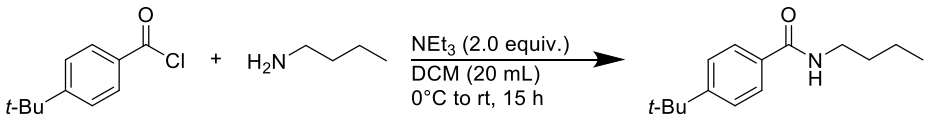
N-Butyl-2-methoxybenzamide (**1d**)



10 mmol **1d** 90%

o-Anisic acid (1.51 g, 10 mmol, 1.0 equiv.) was placed in a 50 mL two-necked flask. The flask was capped with a rubber septum and purged with argon. To the flask dehydrated dichloromethane (20 mL), thionyl chloride (1.45 mL, 20 mmol, 2.0 equiv.), and dimethylformamide (5 drops) were added. The resulting mixture was stirred at room temperature. After 17 hours, the reaction mixture was concentrated under reduced pressure. To the residue was added dehydrated dichloromethane (20 mL), *n*-butylamine (713 mg, 10 mmol, 1.0 equiv.), and triethylamine (2.77 mL, 20 mmol, 2.0 equiv.) at 0 ℃ under argon atmosphere. The mixture was stirred and warmed to room temperature. After 24 hours, the reaction mixture was diluted with water (40 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic phase was washed with saturated NH_4Cl aq. (3 × 40 mL) and brine (40 mL), and then dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography with silica gel (gradient from 10 to 31% AcOEt/Hexane) to afford *N*-butyl-2-methoxybenzamide (**1d**) (1.87 g, 8.98 mmol, 90%) as a brown oil. Spectral data were matched with previous literature.[8]

N-Butyl-4-*tert*-butylbenzamide (**1f**) (Procedure A)

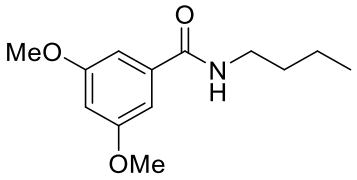


10 mmol 1.5 equiv. **1f** 89%

A 50 mL two-necked flask was capped with a rubber septum and purged with argon. To the flask *n*-butylamine (1.48 mL, 15 mmol, 1.5 equiv.), triethylamine (2.77 mL, 20 mmol, 2.0 equiv.) and dehydrated dichloromethane (20 mL) were added. Then, 4-*tert*-butylbenzoyl chloride (1.97 g, 10 mmol, 1.0 equiv.) was slowly added to the reaction mixture at 0°C. The mixture was stirred and warmed to room temperature. After 15 hours, the reaction mixture was diluted with water (40 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic phase was washed with saturated NH_4Cl aq. (3 × 40 mL) and brine (40 mL), and then dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography with silica gel (gradient from 5 to 26% AcOEt/Hexane) to afford *N*-butyl-4-*tert*-

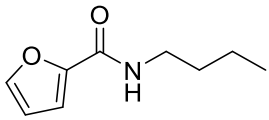
butylbenzamide (**1f**) (2.07 g, 8.87 mmol, 89%) as a white solid. Spectral data were matched with previous literature.[9]

N-Butyl-3,5-dimethoxybenzamide (**1g**)



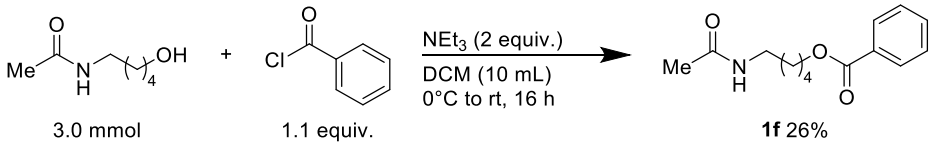
Following procedure A, 3,5-dimehoxybenzoyl chloride (2.03 g, 10 mmol, 1.0 equiv.) and *n*-butylamine (1.48 mL, 15 mmol, 1.5 equiv.) were used. The resulting crude mixture was purified by flash column chromatography with silica gel (gradient from 13 to 34% AcOEt/Hexane) to afford *N*-butyl-3,5-dimethoxybenzamide (**1g**) (2.05 g, 8.64 mmol, 86%) as a white solid. Spectral data were matched with previous literature.[10]

N-Butyl-2-furamide (**1h**)



Following procedure A, 2-furoyl chloride (395 mg, 3.0 mmol, 1.0 equiv.) and *n*-butylamine (0.44 mL, 4.5 mmol, 1.5 equiv.) were used. The resulting crude mixture was purified by flash column chromatography with silica gel (17% AcOEt/Hexane) to afford *N*-butyl-2-furamide (**1g**) (392 mg, 2.34 mmol, 78%) as a pale yellow oil. Spectral data were matched with previous literature.[11]

5-(Acetamido)pentan-1-yl benzoate (**1i**)

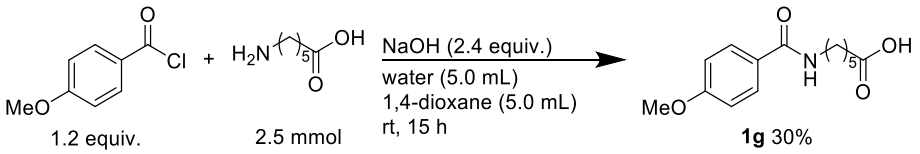


N-(5-hydroxypentan-1-yl)acetamide (430 mg, 3.0 mmol, 1.0 equiv.) was placed in a 50 mL two-necked flask. The flask was capped with a rubber septum and purged with argon. To the flask dehydrated dichloromethane (20 mL) and triethylamine (0.83 mL, 6.0 mmol, 2.0 equiv.) were added at 0 °C. Benzoyl chloride (0.38 mL, 3.3 mmol, 1.1 equiv.) was slowly added to the reaction mixture at 0°C. The mixture was stirred and warmed to room temperature. After 16 hours, the reaction mixture was diluted with water (40 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic phase was washed with saturated NH_4Cl aq. (3 × 40 mL) and brine (40

mL), and then dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography with silica gel (gradient from 31 to 90% AcOEt/Hexane) to afford 5-(acetamido)pentan-1-yl benzoate (**1i**) (192 mg, 0.77 mmol, 26%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05-8.02 (m, 2H), 7.56 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.44 (dd, *J* = 8.0, 8.0Hz, 2H), 5.50 (brs, 1H), 4.33 (t, *J* = 6.4 Hz, 2H), 3.27 (dt, *J* = 6.4, 6.4 Hz, 2H), 1.97 (s, 3H), 1.80 (tt, *J* = 7.0, 7.0 Hz, 2H), 1.62-1.54 (m, 2H), 1.52-1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 166.7, 132.9, 130.3, 129.5, 128.3, 64.6, 39.5, 29.2, 28.4, 23.4, 23.3; HRMS (ESI^+) m/z: $[M+Na]^+$ calcd for $C_{14}H_{19}NNaO_3$, 272.1257; found, 272.1257; IR (neat): 3291, 2943, 1709, 1265, 708 cm^{-1};

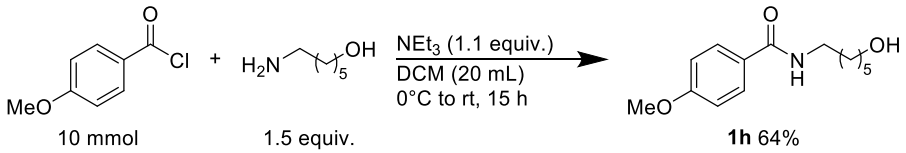
6-(4-Methoxybenzamido)hexanoic acid (**1j**)



6-Aminohexanoic acid (330 mg, 2.5 mmol, 1.0 equiv.) and sodium hydroxide (265 mg, 6.0 mmol, 2.4 equiv.) were placed in a 50 mL two-necked flask. The flask was capped with a rubber septum and purged with argon. To the flask dehydrated 1,4-dioxane (5.0 mL) and water (5.0 mL) were added. 4-Methoxybenzoyl chloride (513 mg, 3.0 mmol, 1.2 equiv.) was slowly added, and the mixture was stirred at room temperature for 15 hours. Brine (50 mL) was then added, and the mixture was washed with diethyl ether (3 × 10 mL). Conc. HCl (1 mL) was added to the aqueous layer, and the resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic phase was washed with brine (40 mL), and then dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography with silica gel (gradient from 70 to 100% AcOEt/$CHCl_3$) to afford 6-(4-methoxybenzamido)hexanoic acid (**1j**) (196 mg, 0.74 mmol, 30%) as a white solid.

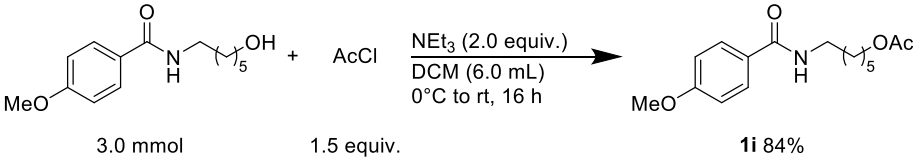
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.13 (t, *J* = 4.6 Hz, 1H), 3.84 (s, 3H), 3.45 (dt, *J* = 6.0, 6.0 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.73-1.60 (m, 4H), 1.48-1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.3, 167.2, 162.1, 128.6, 126.8, 113.7, 55.4, 39.7, 33.7, 29.3, 26.3, 24.2; HRMS (ESI^+) m/z: $[M+Na]^+$ calcd for $C_{14}H_{19}NNaO_4$, 288.1206; found, 288.1204; IR (neat): 3348, 1695, 1634, 1504, 1250, 853 cm^{-1};

N-(6-Hydroxyhexan-1-yl)-4-methoxybenzamide (**1k**)



A 50 mL two-necked flask was capped with a rubber septum and purged with argon. To the flask 6-amino-1-hexanol (1.74 g, 10 mmol, 1.5 equiv.), triethylamine (1.48 mL, 10.7 mmol, 1.1 equiv.) and dehydrated dichloromethane (20 mL) were added. 4-Methoxybenzoyl chloride (1.77 g, 10 mmol, 1.0 equiv.) was slowly added to the reaction mixture at 0 °C. The mixture was stirred and warmed to room temperature. After 15 hours, the reaction mixture was diluted with water (40 mL) and extracted with dichloromethane (3 × 40 mL). The combined organic phase was washed with saturated NH_4Cl aq. (3 × 40 mL) and brine (40 mL), and then dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography with silica gel (97% AcOEt/Hexane) to afford *N*-(6-hydroxyhexan-1-yl)-4-methoxybenzamide (**1k**) (1.61 g, 6.40 mmol, 64%) as a white solid. Spectral data were matched with previous literature.[12]

6-(4-Methoxybenzamido)hexan-1-yl acetate (**1l**)

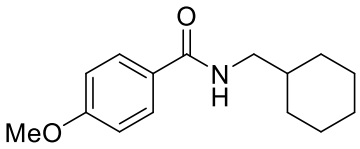


N-(6-Hydroxyhexan-1-yl)-4-methoxybenzamide (751 mg, 3.0 mmol, 1.0 equiv.) was placed in a 50 mL two-necked flask. The flask was capped with a rubber septum and purged with argon. To the flask triethylamine (0.83 mL, 6.0 mmol, 2.0 equiv.) and dehydrated dichloromethane (6.0 mL) were added. Acetyl chloride (0.32 mL, 4.5 mmol, 1.5 equiv.) was then slowly added to the reaction mixture at 0°C. The mixture was stirred and warmed o room temperature. After 16 hours, the reaction mixture was diluted with water (40 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic phase was washed with saturated NH_4Cl aq. (3 × 40 mL) and brine (40 mL), and then dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography with silica gel (54% AcOEt/Hexane) to afford 6-(4-methoxybenzamido)hexan-1-yl acetate (**1l**) (737 mg, 2.51 mmol, 84%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 9.2 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.04 (brs, 1H), 4.06 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 3.44 (td, *J* = 6.8, 5.6 Hz, 2H), 2.04 (s, 3H), 1.68-1.60 (m, 4H), 1.45-1.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3, 167.0, 162.0, 128.6, 127.0, 113.7,

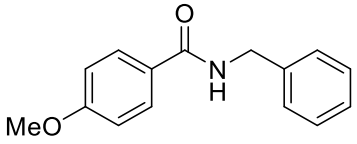
64.4, 55.4, 39.8, 29.6, 28.5, 26.5, 25.6, 21.0; HRMS (ESI$^+$) m/z: [M+Na]$^+$ calcd for $C_{16}H_{23}NNaO_4$, 316.1519; found, 316.1518; IR (neat): 3304, 2936, 1724, 1607, 1256, 768 cm^{-1}.

N-(Cyclohexylmethyl)-4-methoxybenzamide (**1m**)



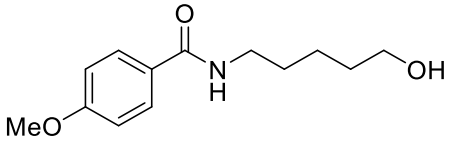
Following procedure A, 4-mehoxybenzoyl chloride (342 mg, 2.0 mmol, 1.0 equiv.) and cyclohexylmethylamine (0.39 mL, 3.0 mmol, 1.5 equiv.) were used. The resulting crude mixture was purified by flash column chromatography with silica gel (gradient from 12 to 36% AcOEt/Hexane) to afford *N*-(Cyclohexylmethyl)-4-methoxybenzamide (**1m**) (467 mg, 1.89 mmol, 94%) as a white solid. Spectral data were matched with previous literature.[13]

N-Benzyl-4-methoxybenzamide (**1n**)



Following procedure A, 4-mehoxybenzoyl chloride (1.71 g, 10 mmol, 1.0 equiv.) and benzylamine (1.64 mL, 15 mmol, 1.5 equiv.) were used. The resulting crude mixture was purified by flash column chromatography with silica gel (gradient from 23 to 44% AcOEt/Hexane) to afford *N*-benzyl-4-methoxybenzamide (**1n**) (2.26 g, 9.39 mmol, 94%) as a white solid. Spectral data were matched with previous literature.[14]

N-(5-Hydroxypentan-1-yl)-4-methoxybenzamide (**1p**)



Following procedure A, 4-mehoxybenzoyl chloride (866 mg, 5 mmol, 1.0 equiv.) and 5-amino-1-pentanol (772 mg, 7.5 mmol, 1.5 equiv.) were used. The resulting crude mixture was purified by flash column chromatography with silica gel (100% AcOEt) to afford *N*-(5-Hydroxypentan-1-yl)-4-methoxybenzamide (**1p**) (1.01 g, 4.26 mmol, 85%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 9.2 Hz, 2H), 6.12 (brs, 1H), 3.84 (s, 3H), 3.67 (t, *J* = 6.0 Hz, 2H), 3.46 (td, *J* = 7.2, 6.0 Hz, 2H), 1.68-1.59 (m, 4H), 1.51-1.43

(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 162.0, 128.6, 126.9, 113.7, 62.7, 55.4, 39.8, 32.2, 29.5, 23.1; HRMS (ESI^+) m/z: $[M+Na]^+$ calcd for $C_{13}H_{19}NNaO_3$, 260.1257; found, 260.1259; IR (neat): 3503, 3325, 1609, 1252, 839 cm^{-1}.

5. References

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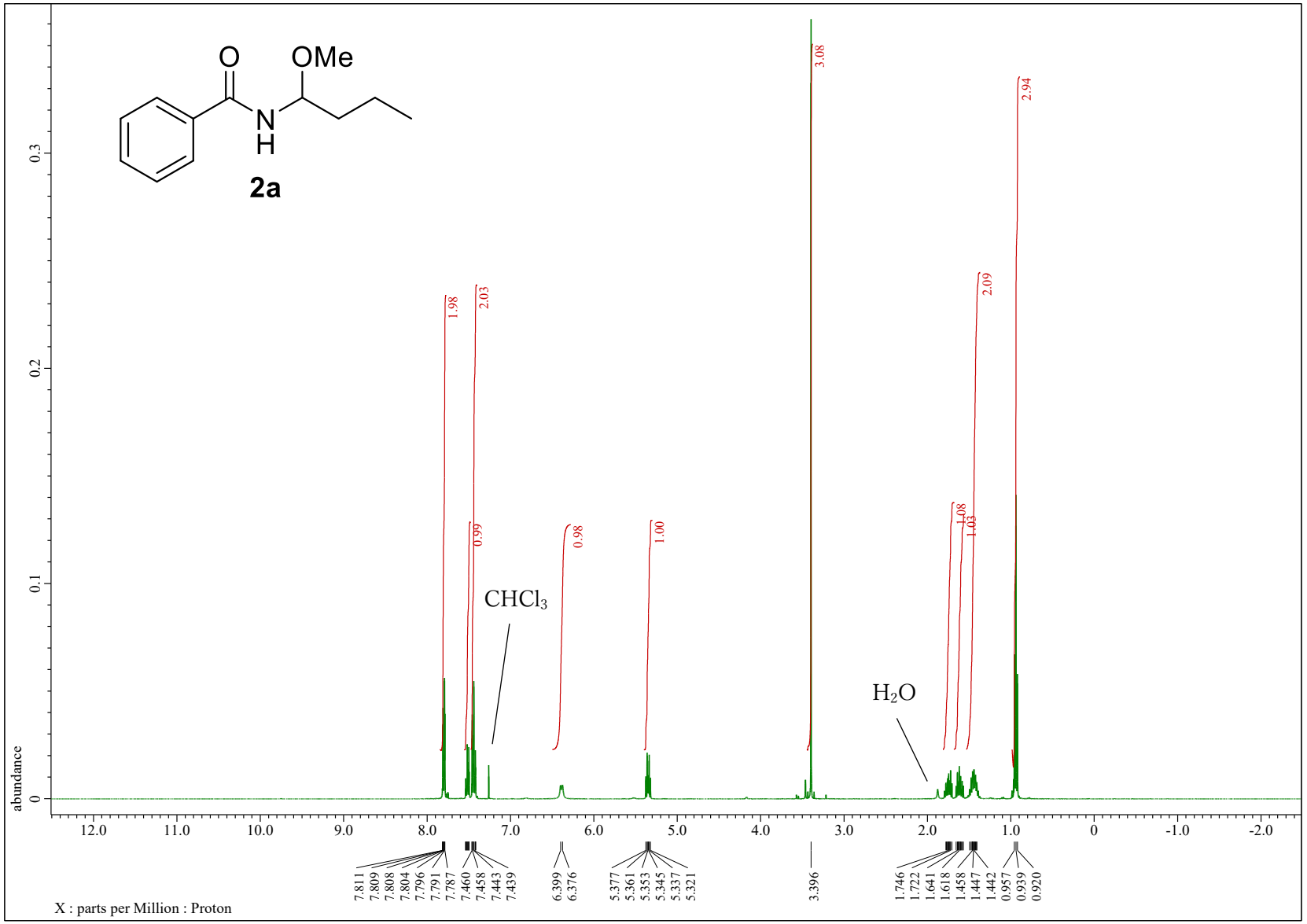
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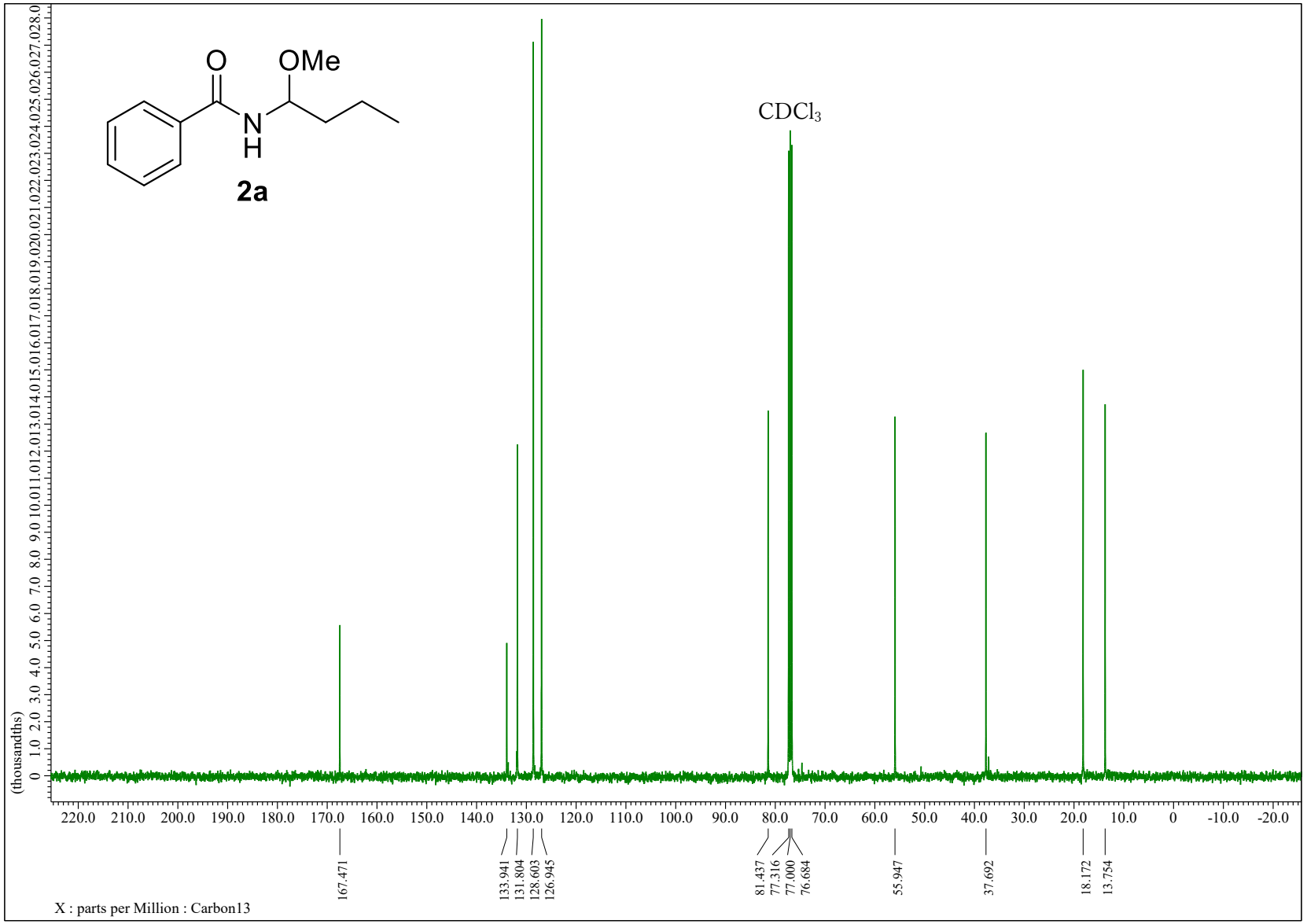
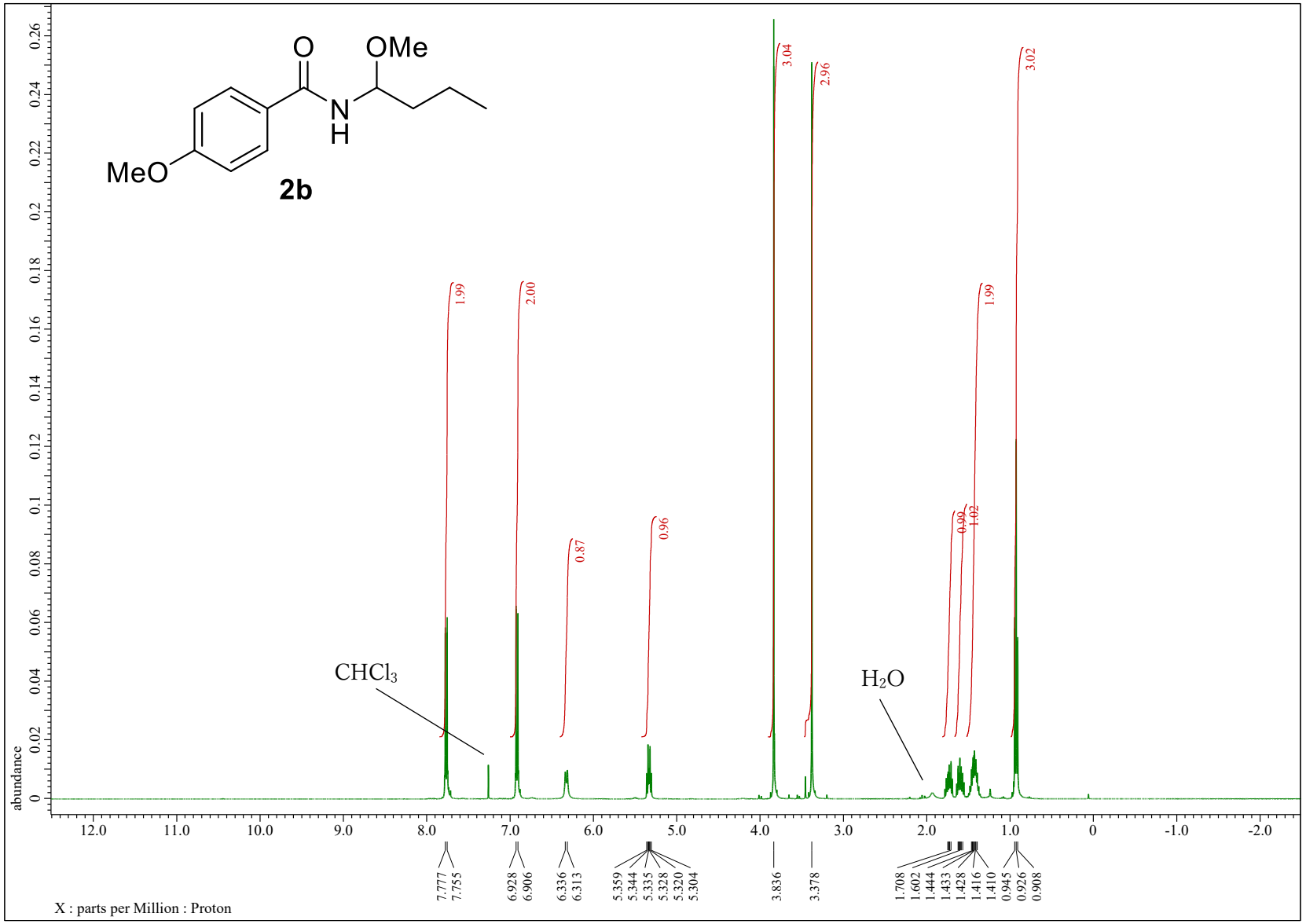
OMe
N
H
2a
abundance
0.3
0.2
0.1
0
1.98
2.03
0.99
0.98
1.00
3.08
2.94
2.09
1.08
1.03
CHCl3
H2O
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.811
7.809
7.808
7.804
7.796
7.791
7.787
7.460
7.458
7.443
7.439
6.399
6.376
5.377
5.361
5.353
5.345
5.337
5.321
3.396
1.746
1.722
1.641
1.618
1.458
1.447
1.442
0.957
0.939
0.920
X : parts per Million : Proton


O
OMe
N
H
2a
CDCl3
(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0 24.0 25.0 26.0 27.0 28.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.471
133.941
131.804
128.603
126.945
81.437
77.316
77.000
76.684
55.947
37.692
18.172
13.754
X : parts per Million : Carbon13


O
OMe
N
H
MeO
2b
CHCl3
H2O
abundance
X : parts per Million : Proton
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2.00
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0.96
3.04
2.96
0.99
1.02
1.99
3.02
7.777
7.755
6.928
6.906
6.336
6.313
5.359
5.344
5.335
5.328
5.320
5.304
3.836
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1.602
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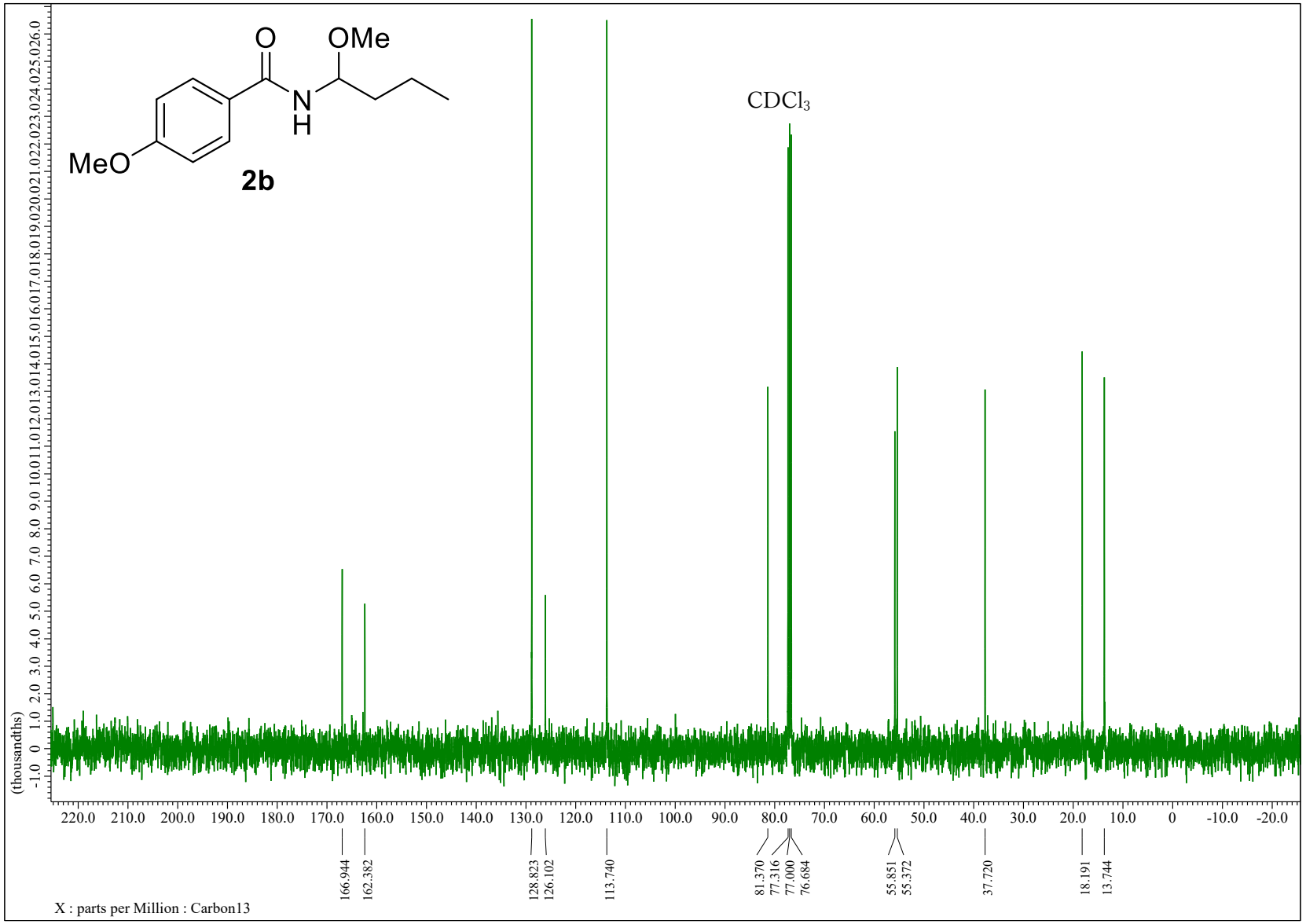
1.433
1.428
1.416
1.410
0.945
0.926
0.908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N
H
MeO
2b
CDCl3
(thousandths)
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77.000
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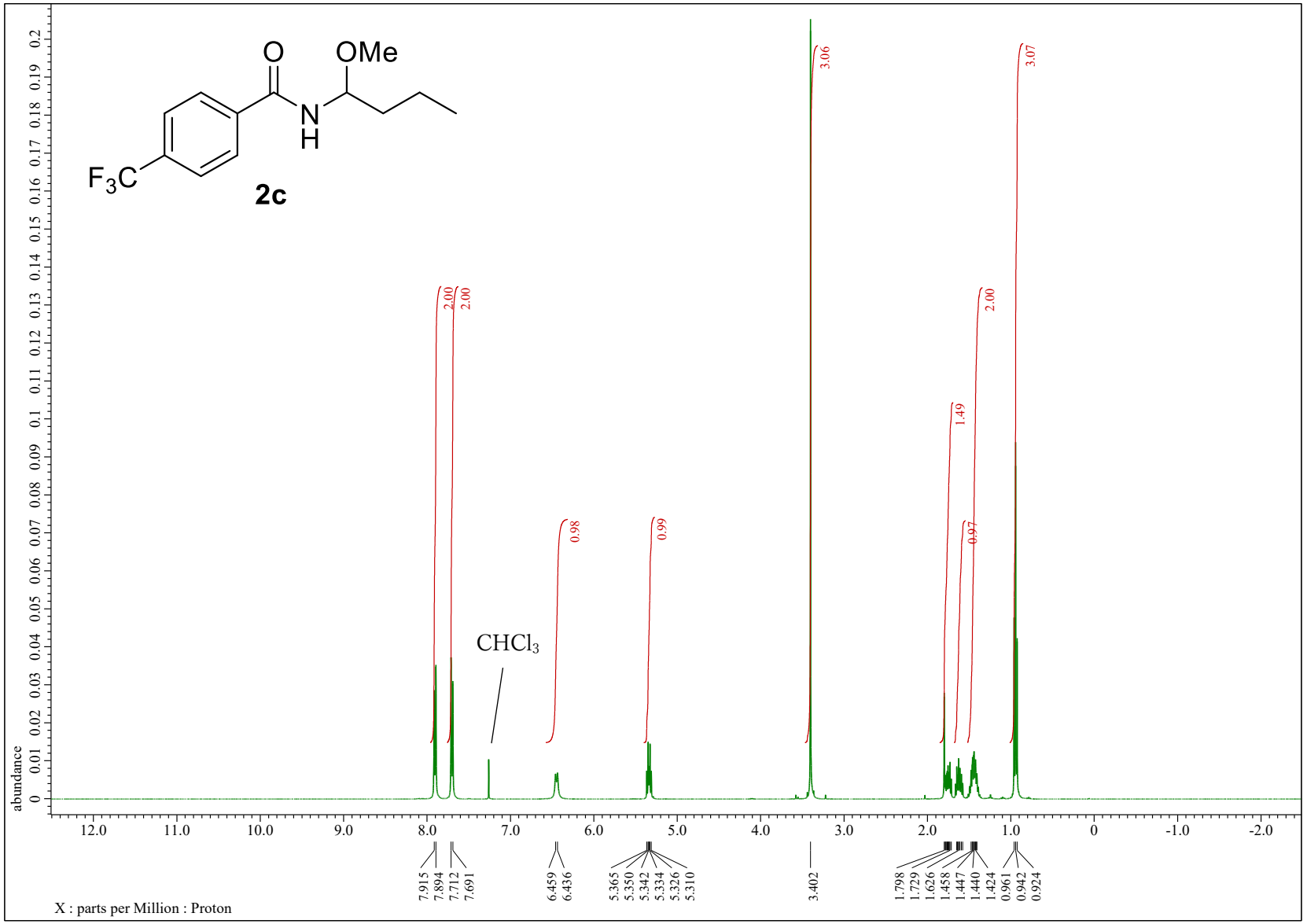
55.372
37.720
18.191
13.744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N
H
F3C
2c
abundance
CHCl3
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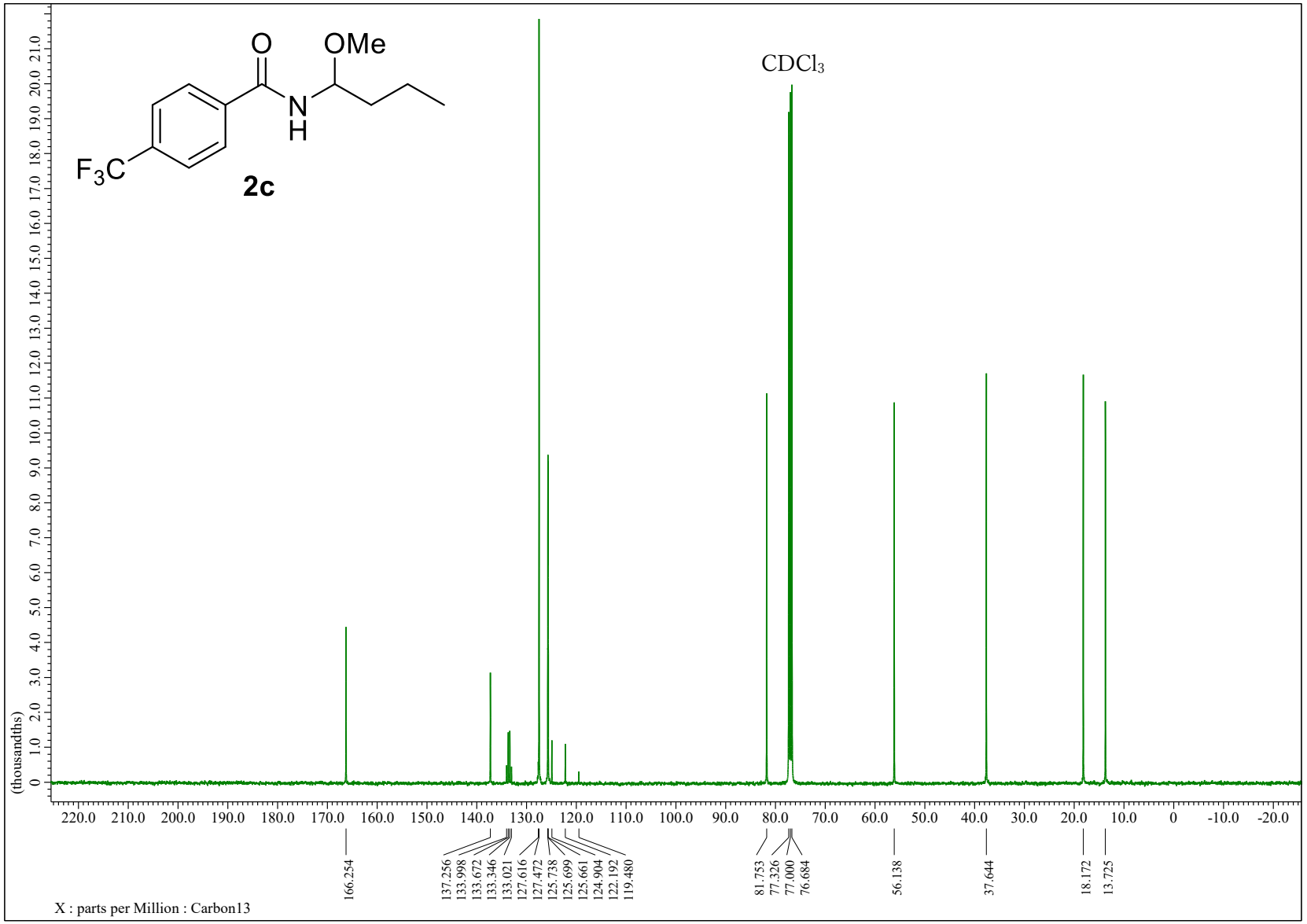
2.00
0.98
0.99
3.06
1.49
0.97
2.00
3.07
7.915
7.894
7.712
7.691
6.459
6.436
5.365
5.350
5.342
5.334
5.326
5.310
3.402
1.798
1.729
1.626
1.458
1.447
1.440
1.424
0.961
0.942
0.924
X : parts per Million : Proton


O
OMe
N
H
F3C
2c
CDCl3
(thousandths)
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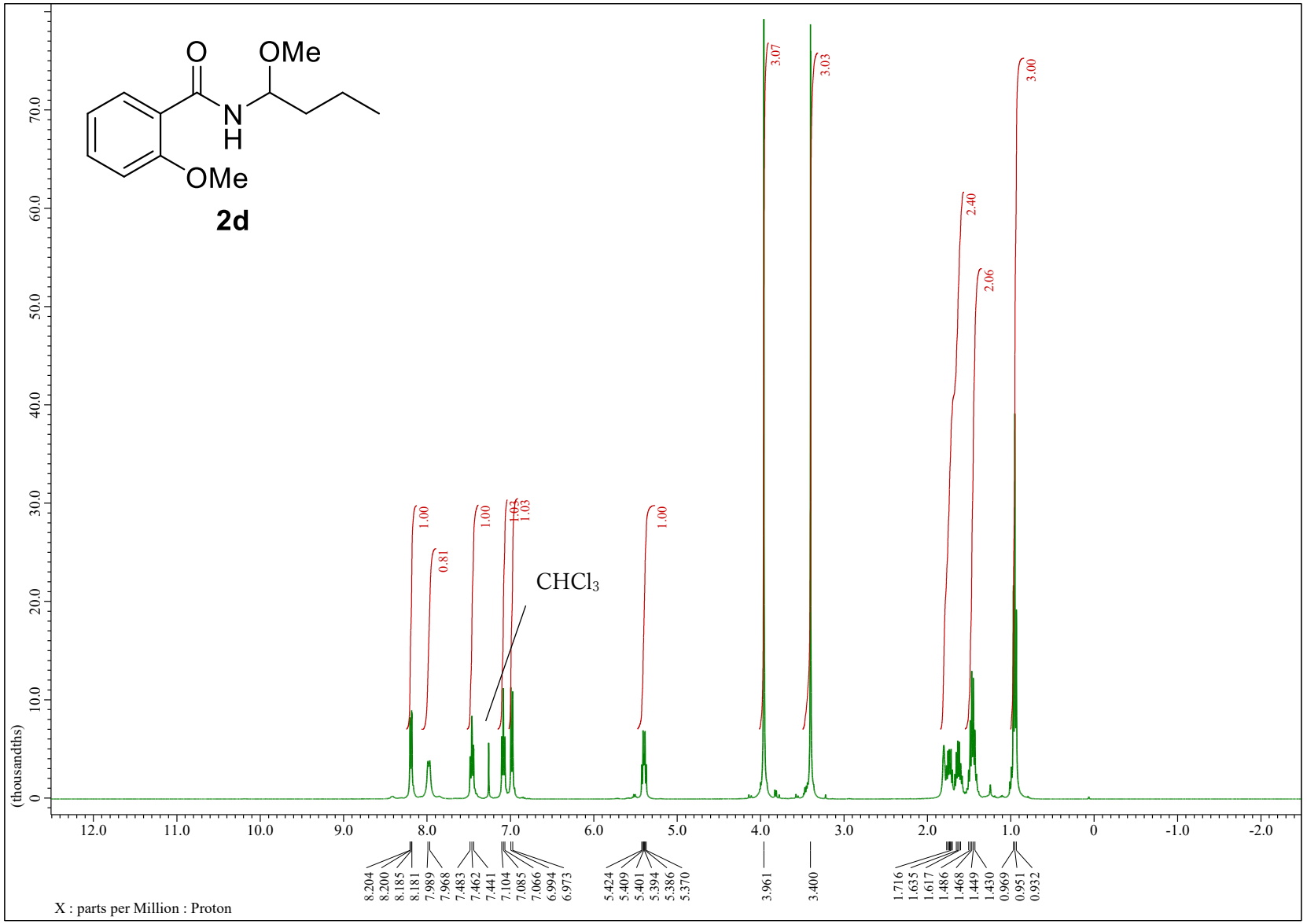
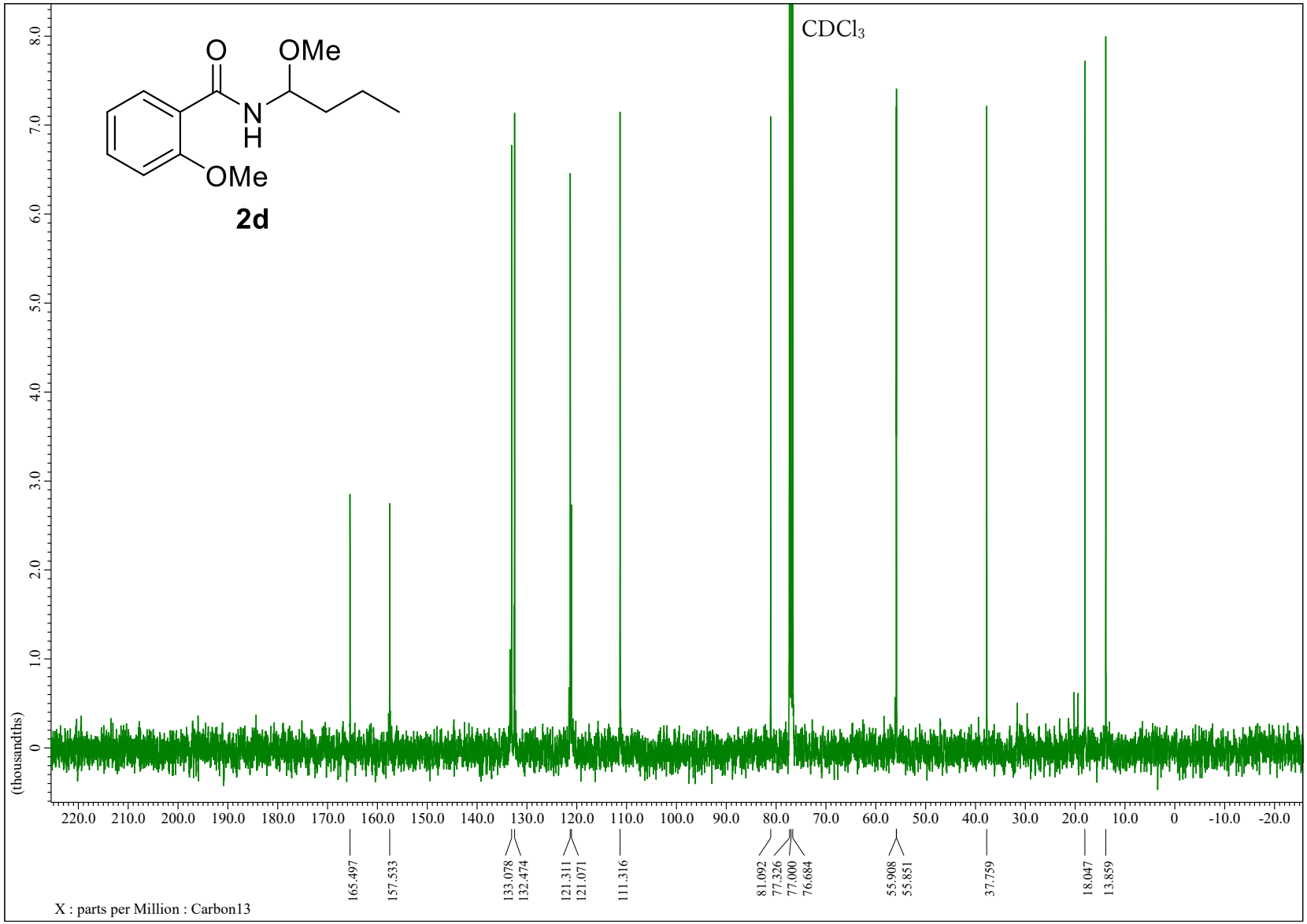
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
166.254
137.256
133.998
133.672
133.346
133.021
127.616
127.472
125.738
125.699
125.661
124.904
122.192
119.480
81.753
77.326
77.000
76.684
56.138
37.644
18.172
13.725
X : parts per Million : Carbon13


O
OMe
N
H
OMe
2d
3.07
3.03
3.00
2.40
2.06
1.00
0.81
1.00
1.00
1.03
1.00
CHCl3
(thousandths)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.204
8.200
8.185
8.181
7.989
7.968
7.483
7.462
7.441
7.104
7.085
7.066
6.994
6.973
5.424
5.409
5.401
5.394
5.386
5.370
3.961
3.400
1.716
1.635
1.617
1.486
1.468
1.449
1.430
0.969
0.951
0.932
X : parts per Million : Proton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OMe
N
H
OMe
2d
CDCl3
(thousandths)
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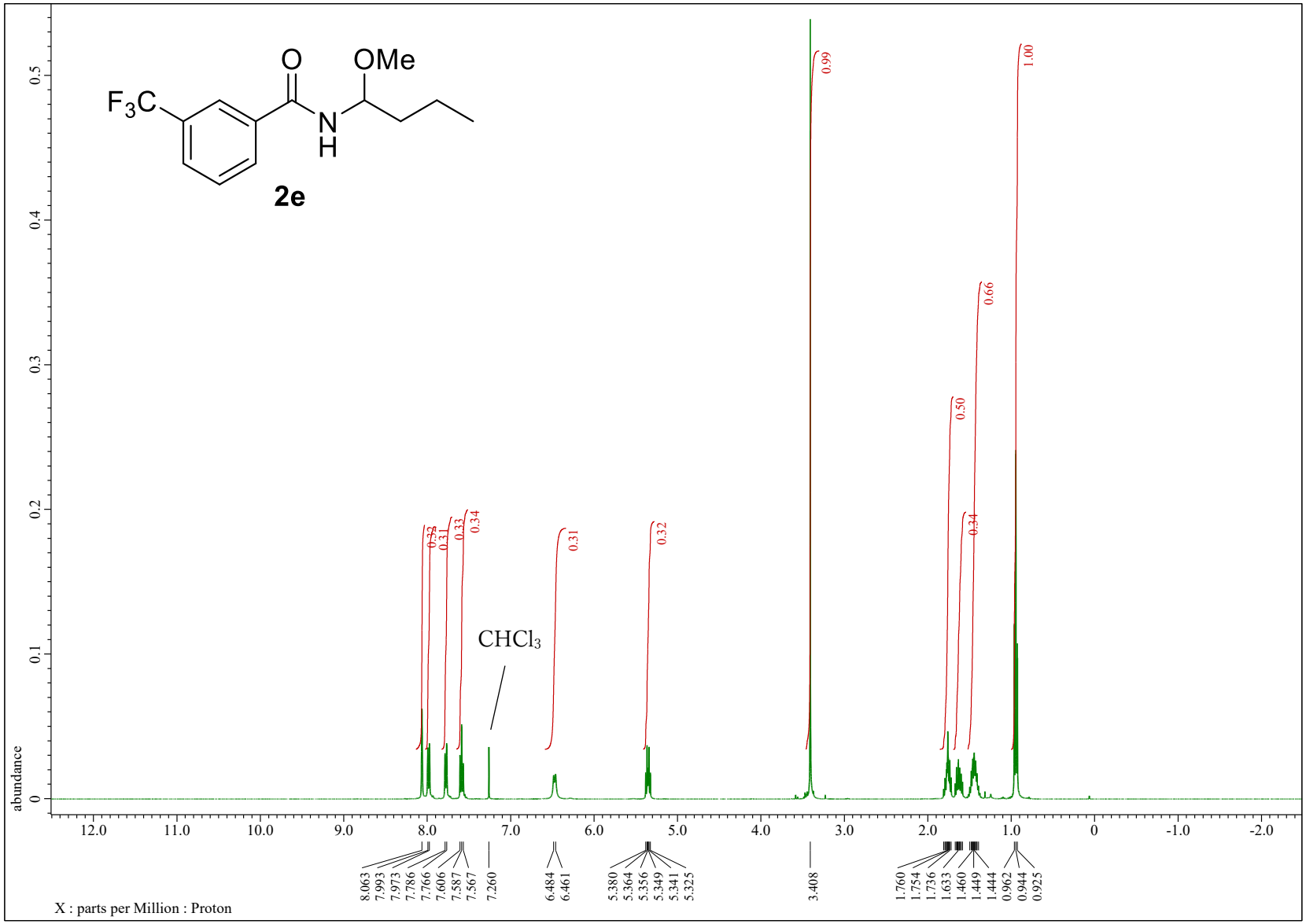
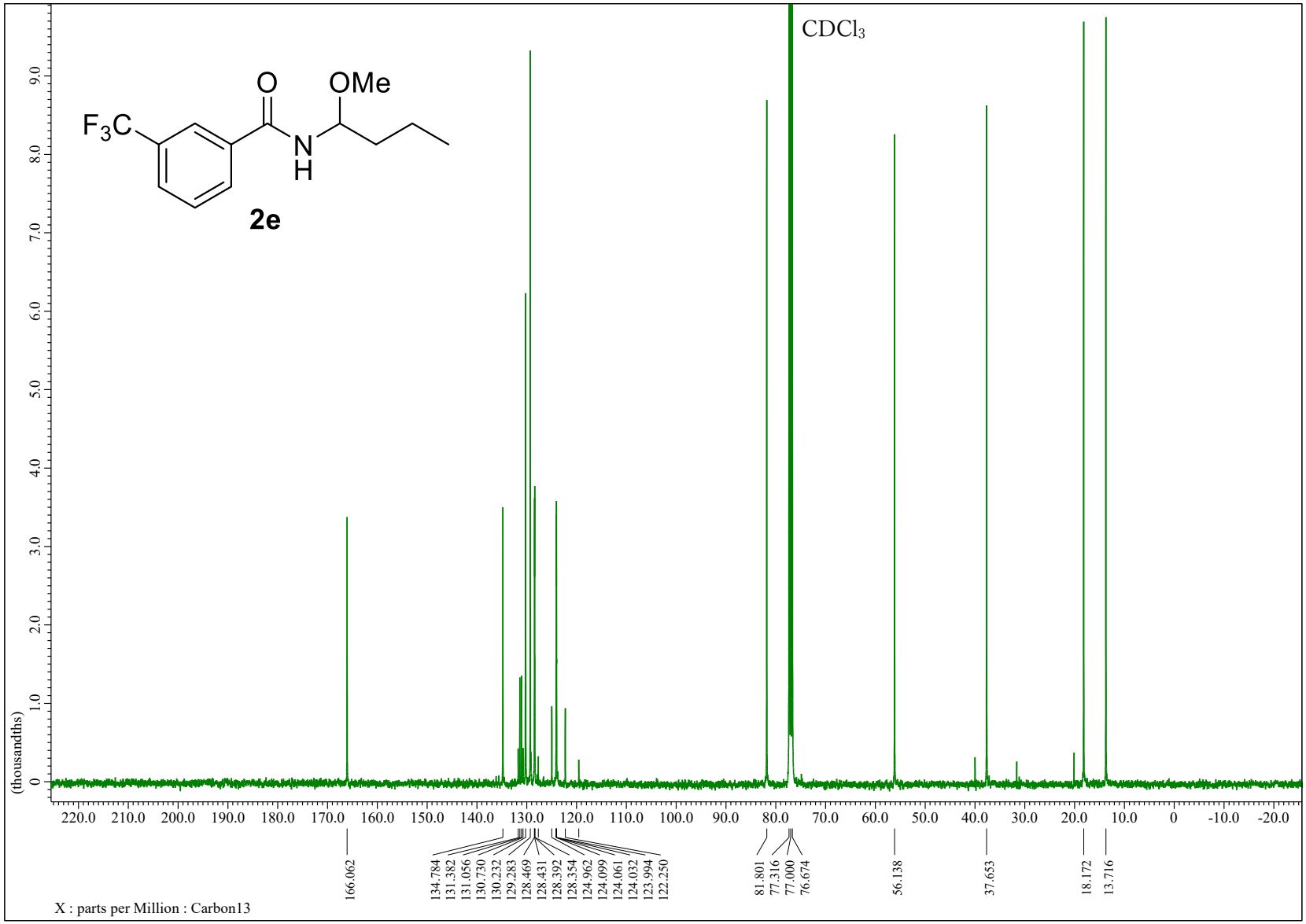
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
165.497
157.533
133.078
132.474
121.311
121.071
111.316
81.092
77.326
77.000
76.684
55.908
55.851
37.759
18.047
13.859
X : parts per Million : Carbon13


O
OMe
F3C
N
H
2e
CHCl3
abundance
X : parts per Million : Proton
0.99
1.00
0.66
0.50
0.34
0.31
0.32
0.33
8.063
7.993
7.973
7.786
7.766
7.606
7.587
7.567
7.260
6.484
6.461
5.380
5.364
5.356
5.349
5.341
5.325
3.408
1.760
1.754
1.736
1.633
1.460
1.449
1.444
0.962
0.944
0.925


CDCl3
O
OMe
F3C
N
H
2e
(thousandths)
X : parts per Million : Carbon13
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134.784
131.382
131.056
130.730
130.232
129.283
128.469
128.431
128.392
128.354
124.962
124.099
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123.994
122.250
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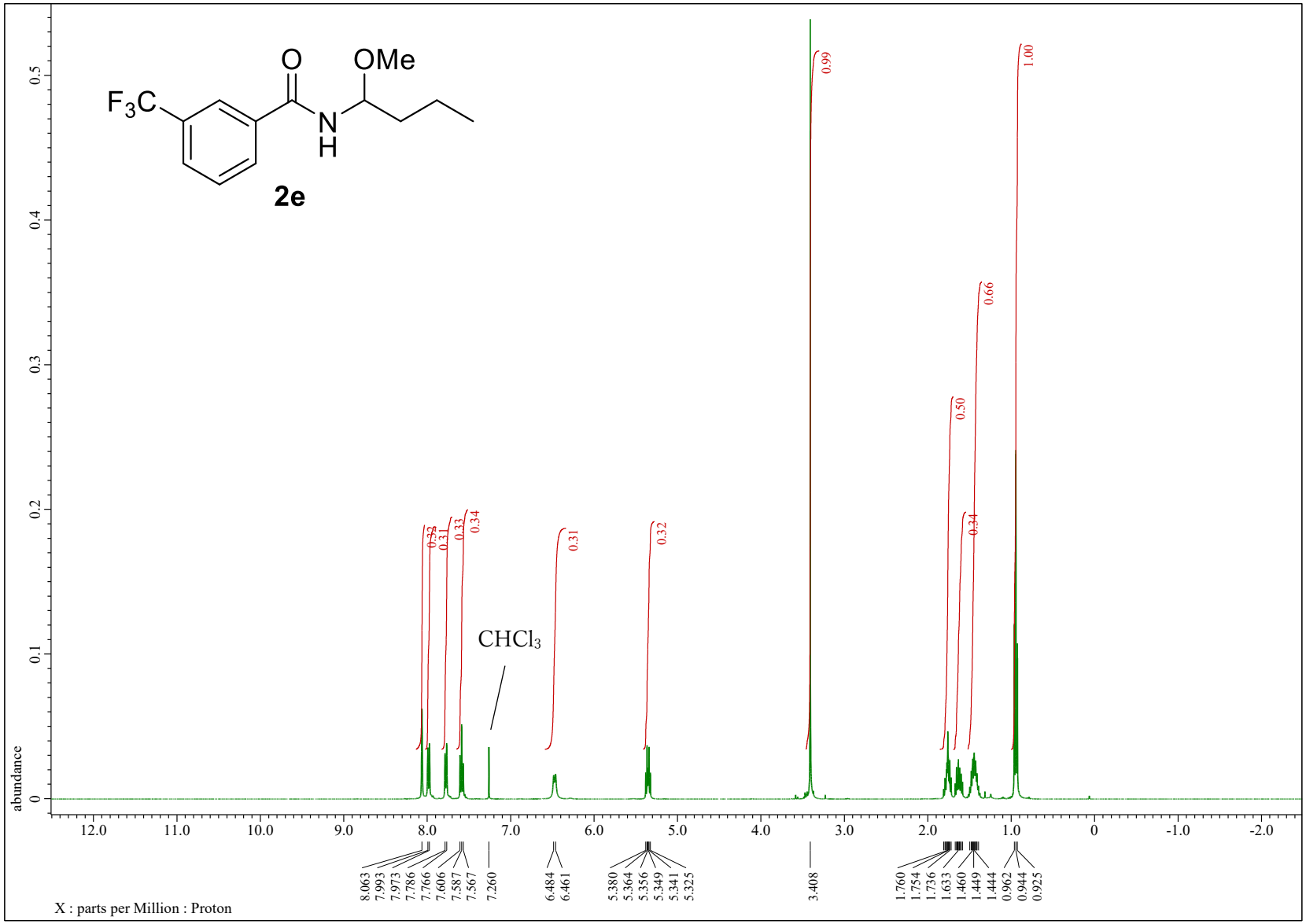
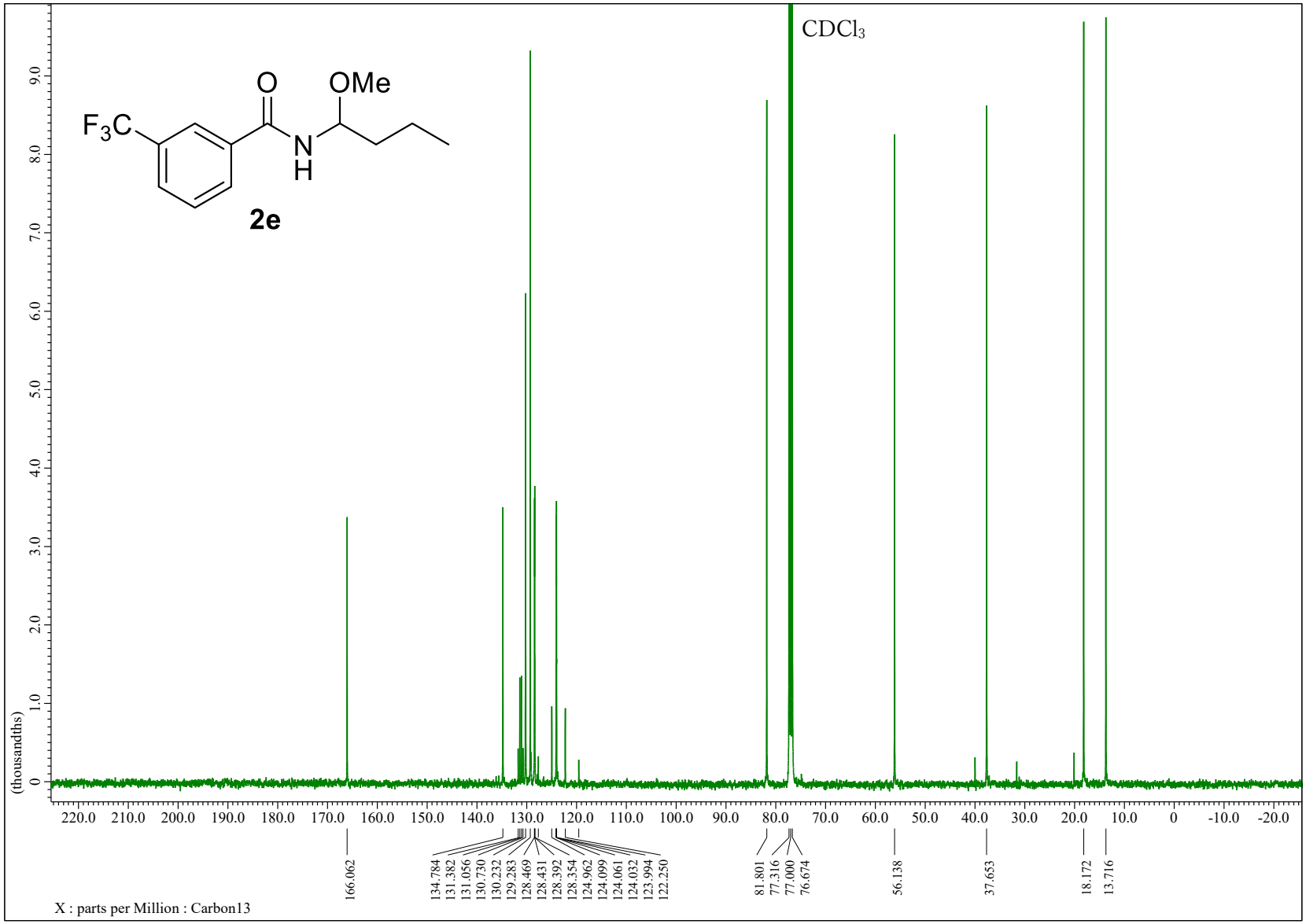
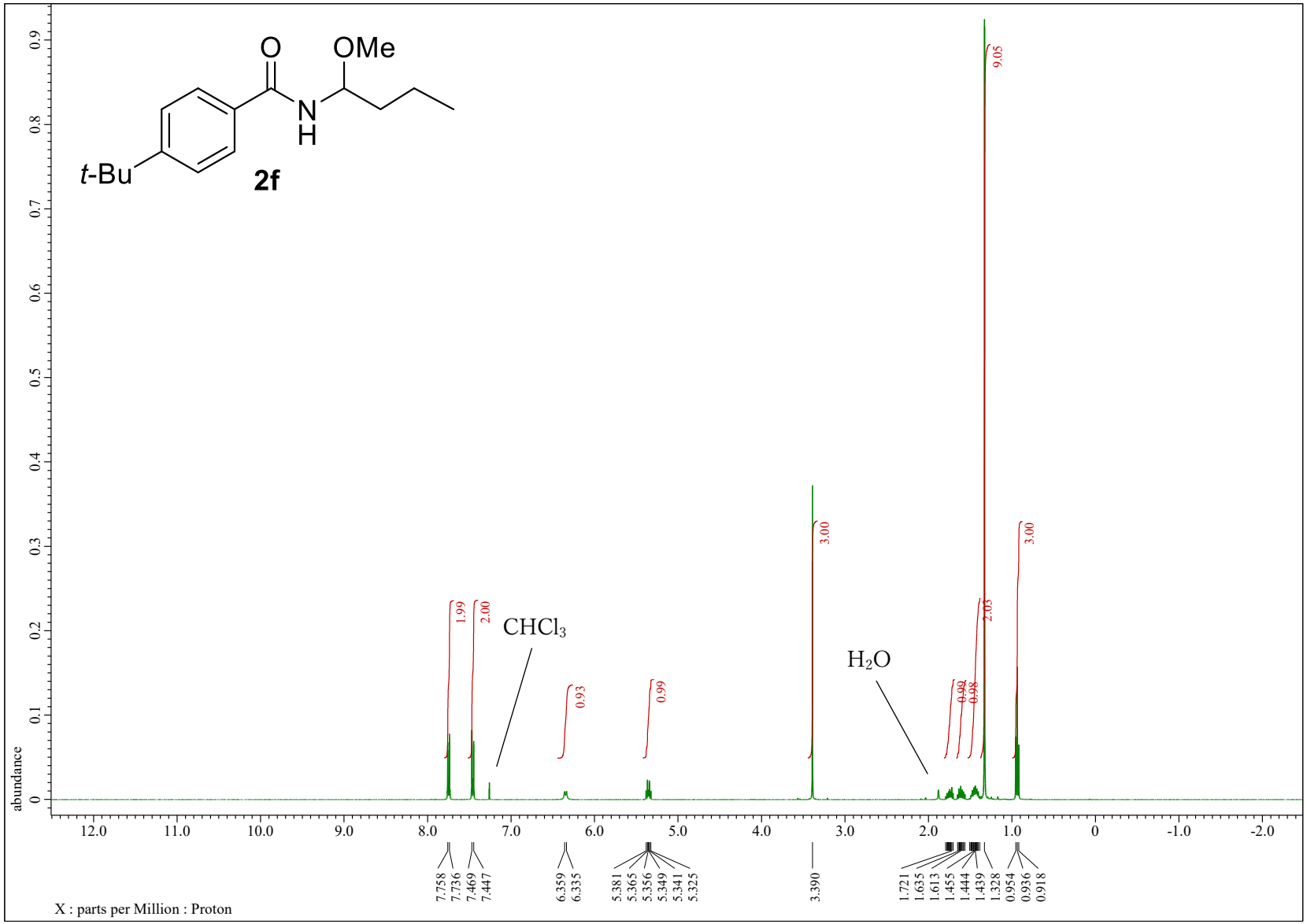
77.000
76.674
56.138
37.653
18.172
13.716


O
OMe
F3C
N
H
2e
CHCl3
abundance
X : parts per Million : Proton
0.99
1.00
0.66
0.50
0.34
0.31
0.32
0.33
8.063
7.993
7.973
7.786
7.766
7.606
7.587
7.567
7.260
6.484
6.461
5.380
5.364
5.356
5.349
5.341
5.325
3.408
1.760
1.754
1.736
1.633
1.460
1.449
1.444
0.962
0.944
0.925


CDCl3
O
OMe
F3C
N
H
2e
(thousandths)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
166.062
134.784
131.382
131.056
130.730
130.232
129.283
128.469
128.431
128.392
128.354
124.962
124.099
124.061
124.032
123.994
122.250
81.801
77.316
77.000
76.674
56.138
37.653
18.172
13.716
X : parts per Million : Carbon13


O
OMe
N
H
t-Bu
2f
9.05
3.00
3.00
2.05
1.99
2.00
0.93
0.99
0.99
0.98
CHCl3
H2O
abundance
X : parts per Million : Proton
7.758
7.736
7.469
7.447
6.359
6.335
5.381
5.365
5.356
5.349
5.341
5.325
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1.635
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1.444
1.439
1.328
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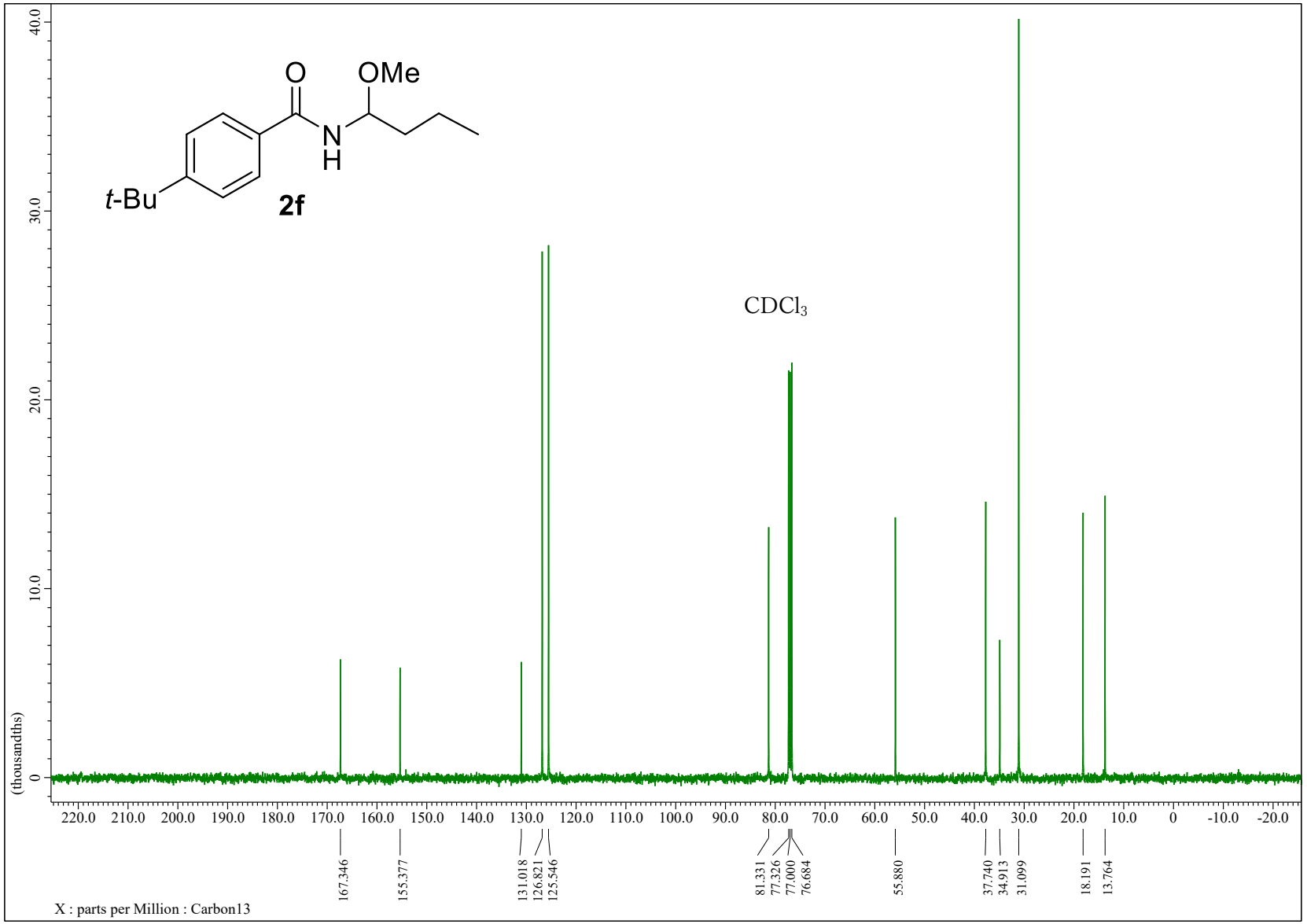
0.936
0.918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OMe
N
H
t-Bu
2f
CDCl3
(thousandths)
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30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.346
155.377
131.018
126.821
125.546
81.331
77.326
77.000
76.684
55.880
37.740
34.913
31.099
18.191
13.764
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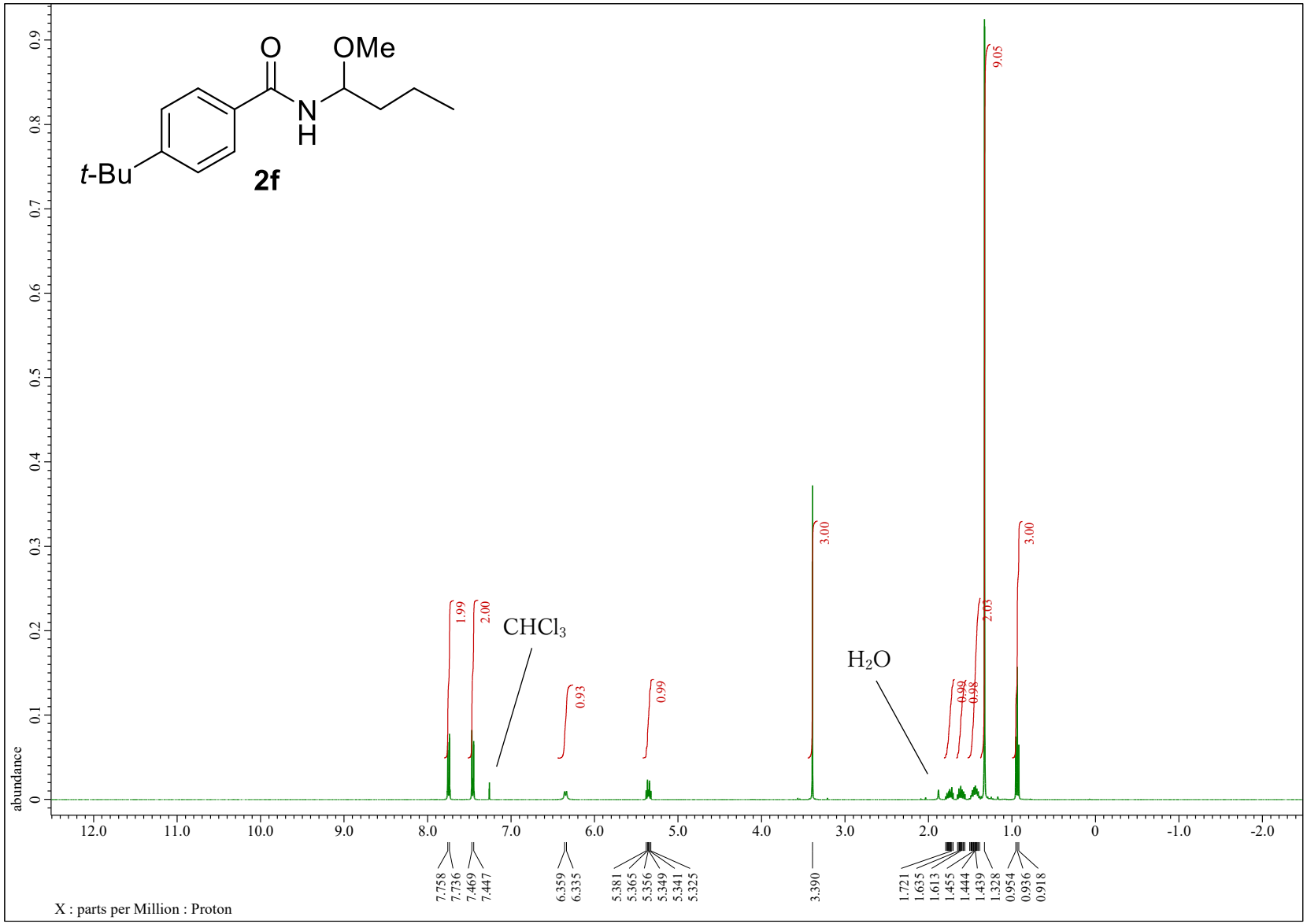
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OMe
N
H
t-Bu
2f
9.05
3.00
3.00
2.05
1.99
2.00
0.93
0.99
0.99
0.98
CHCl3
H2O
abundance
X : parts per Million : Proton
7.758
7.736
7.469
7.447
6.359
6.335
5.381
5.365
5.356
5.349
5.341
5.325
3.390
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1.328
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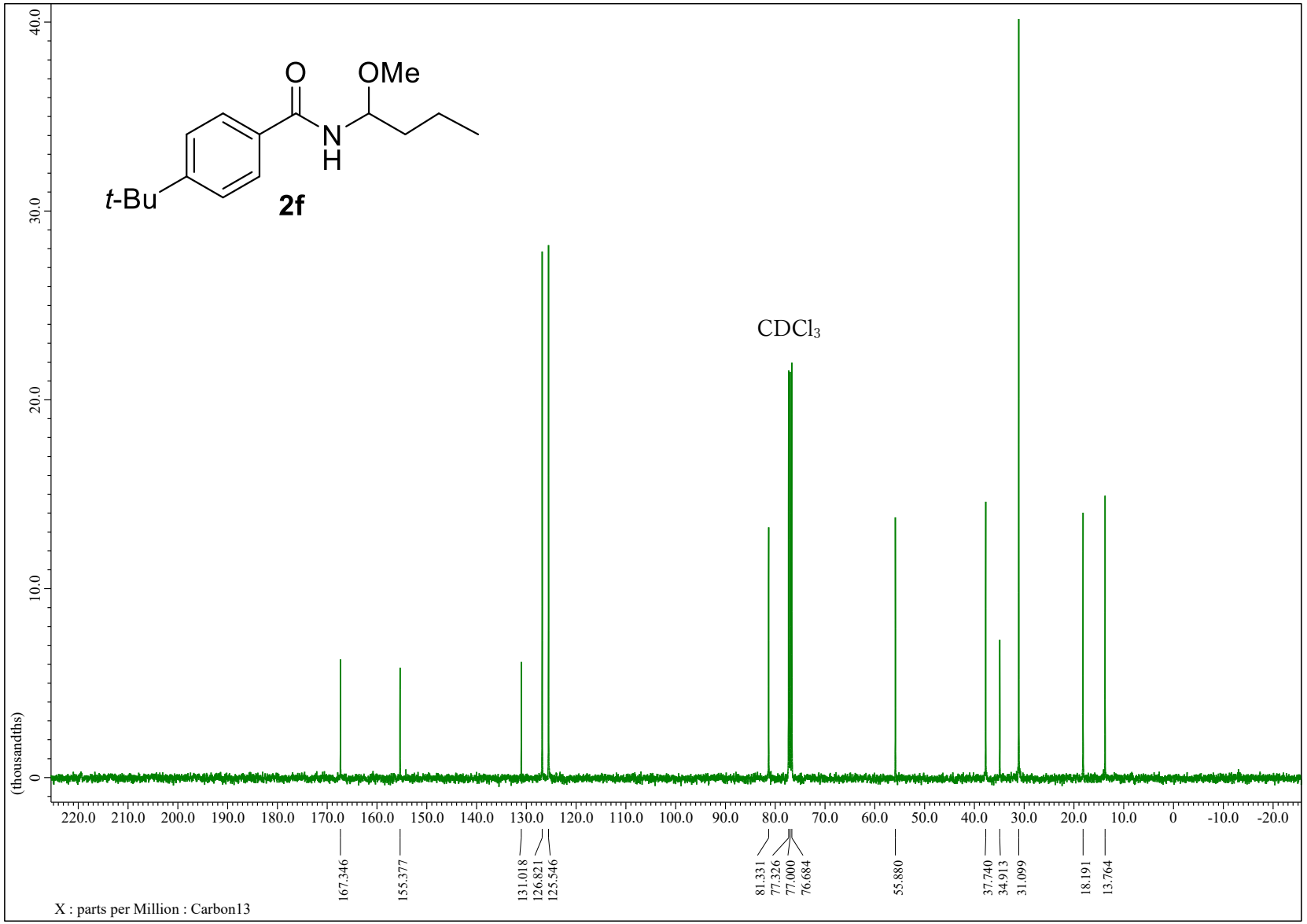
0.936
0.918


O
OMe
N
H
t-Bu
2f
CDCl3
(thousandths)
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.346
155.377
131.018
126.821
125.546
81.331
77.326
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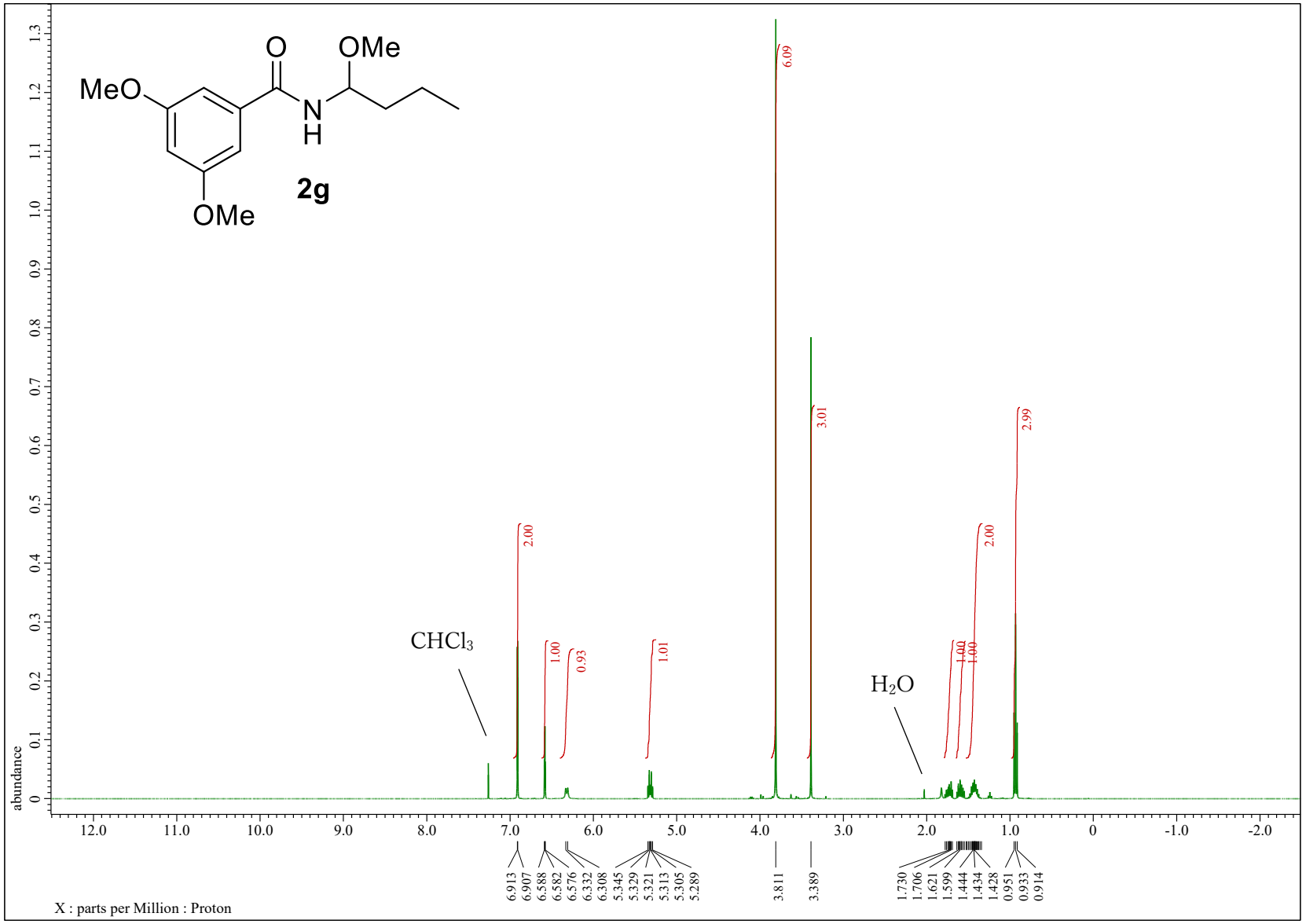
76.684
55.880
37.740
34.913
31.099
18.191
13.764
X : parts per Million : Carbon13


MeO
O
OMe
N
H
OMe
2g
CHCl3
H2O
6.09
3.01
2.99
2.00
2.00
1.00
0.93
1.01
1.00
1.00
abundance
X : parts per Million : Proton
6.913
6.907
6.588
6.582
6.576
6.332
6.308
5.345
5.329
5.321
5.313
5.305
5.289
3.811
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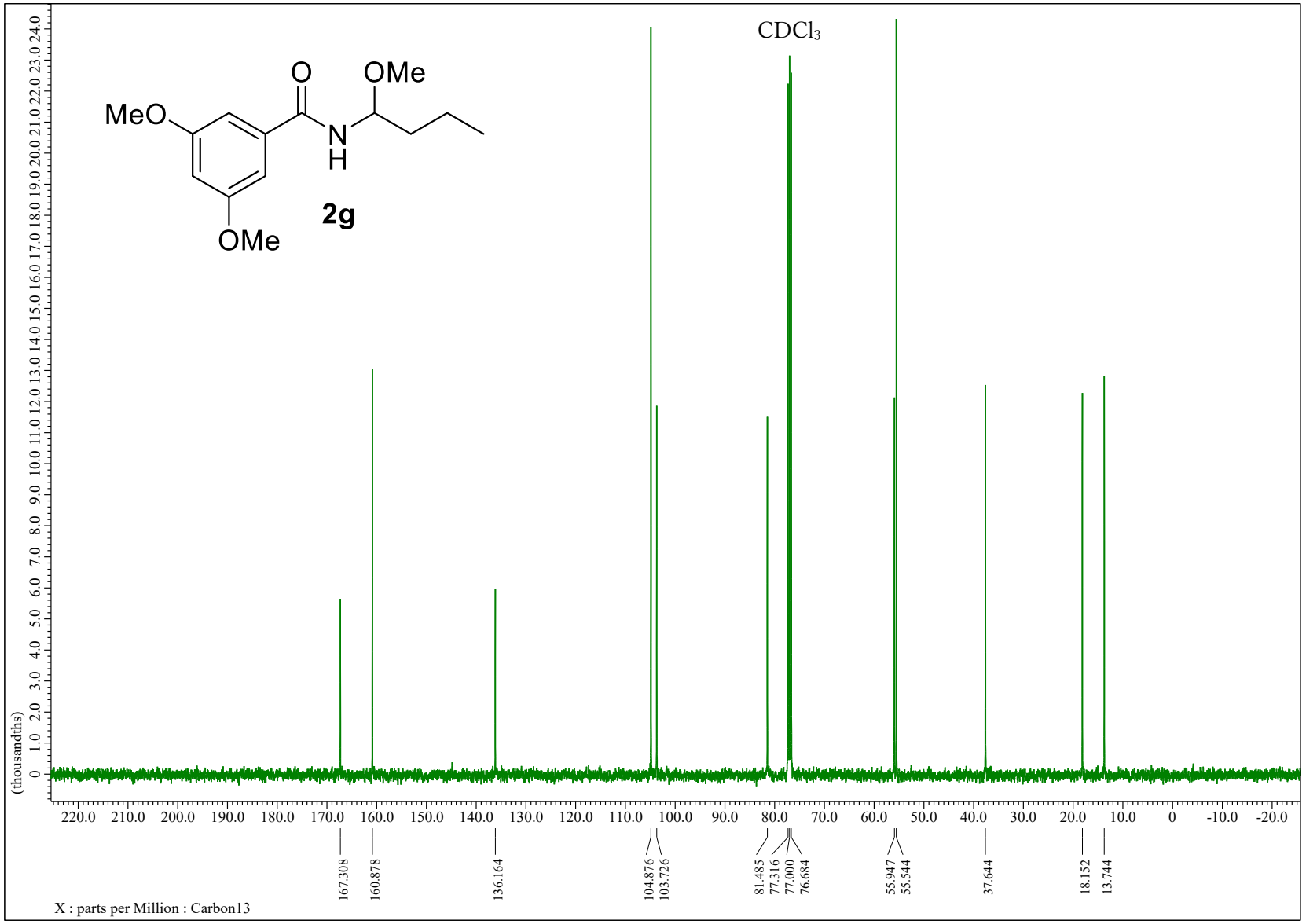
CDCl3
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OMe
MeO
N
H
OMe
2g
(thousandths)
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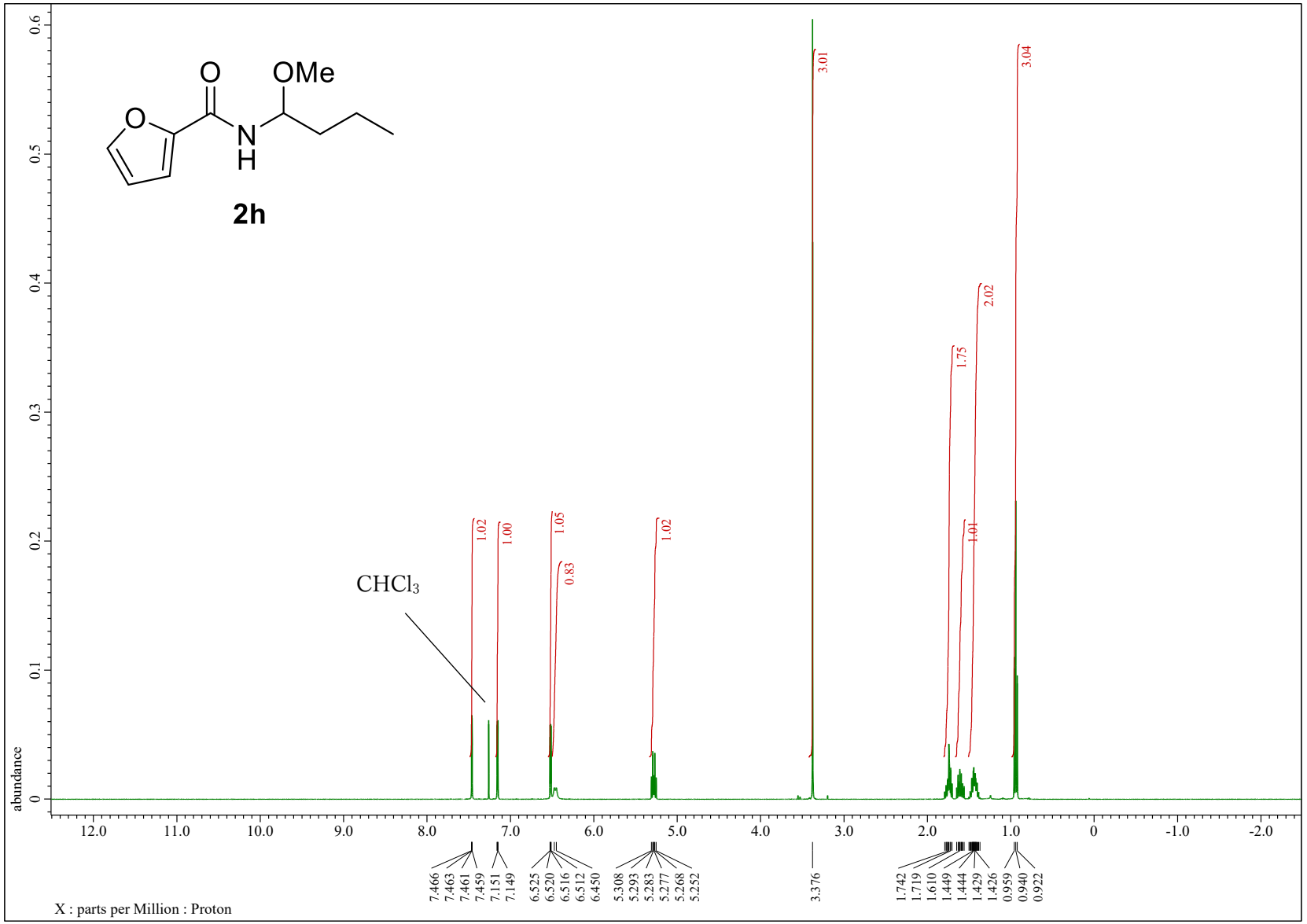
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.308
160.878
136.164
104.876
103.726
81.485
77.316
77.000
76.684
55.947
55.544
37.644
18.152
13.744
X : parts per Million : Carbon13


O
OMe
N
H
O
2h
CHCl3
abundance
X : parts per Million : Proton
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1.05
0.83
1.02
3.01
3.04
1.75
2.02
1.01
7.466
7.463
7.461
7.459
7.151
7.149
6.525
6.520
6.516
6.512
6.450
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5.283
5.277
5.268
5.252
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1.719
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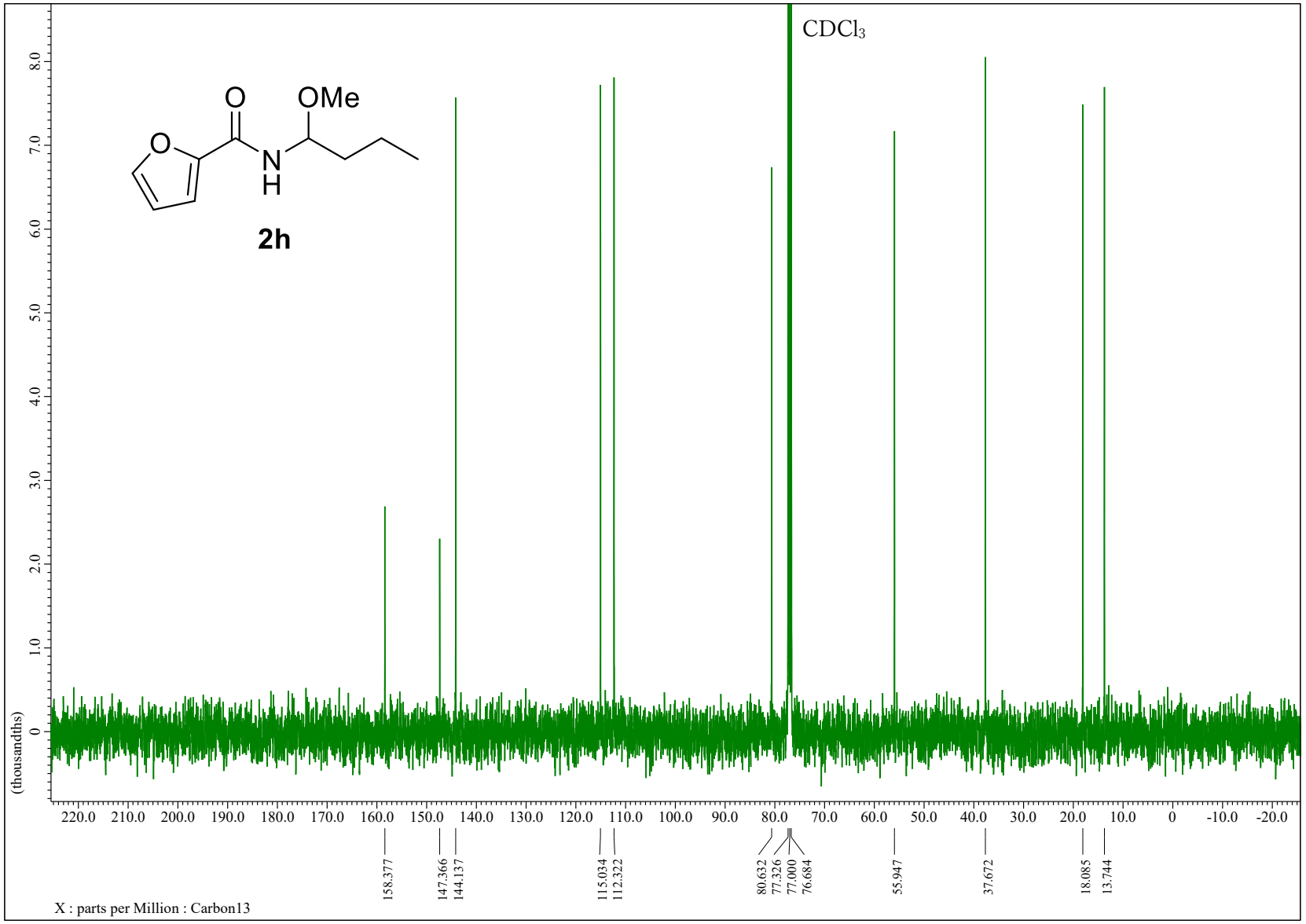
0.940
0.922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OMe
O
N
H
2h
(thousandths)
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7.0
6.0
5.0
4.0
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1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
158.377
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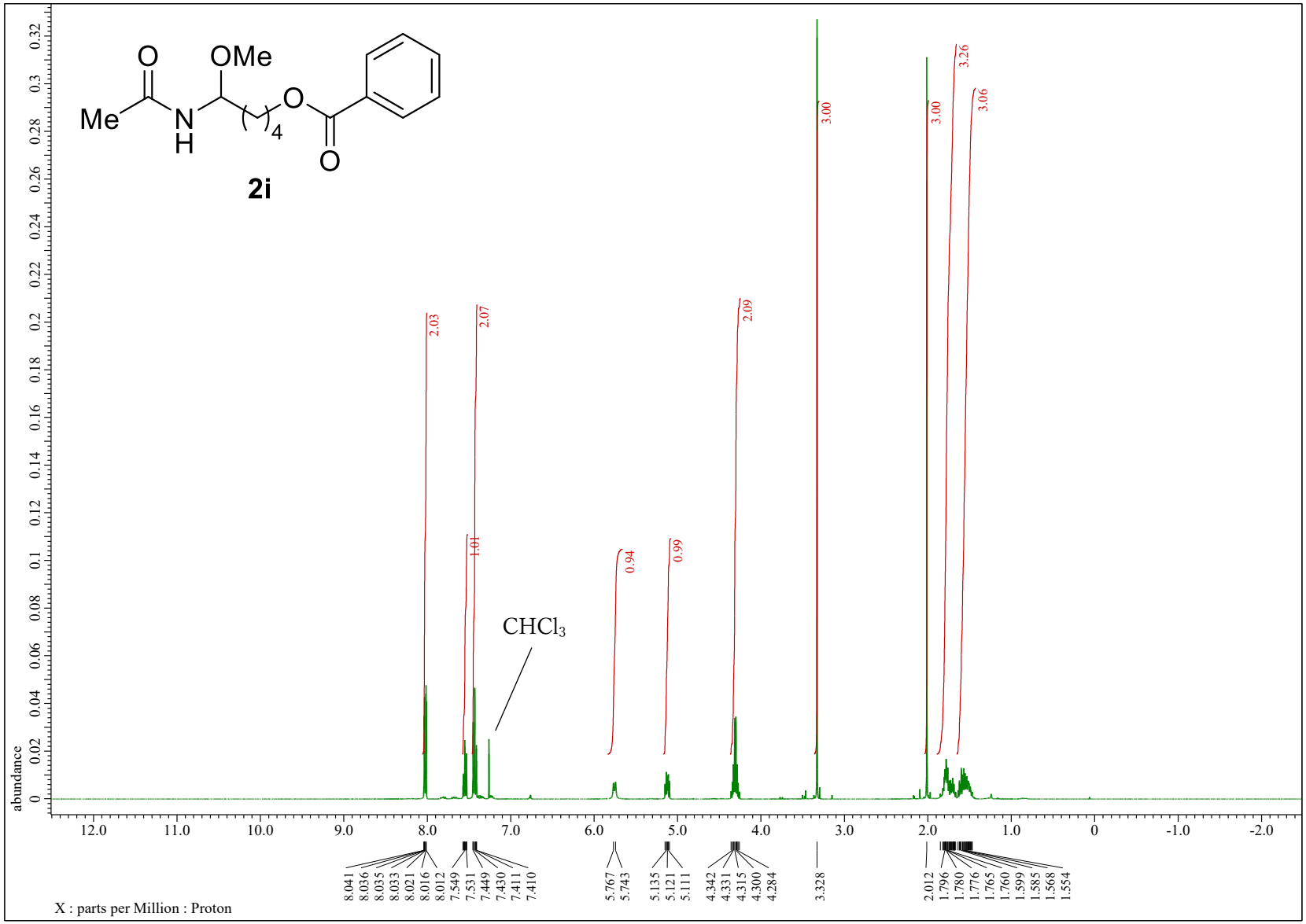
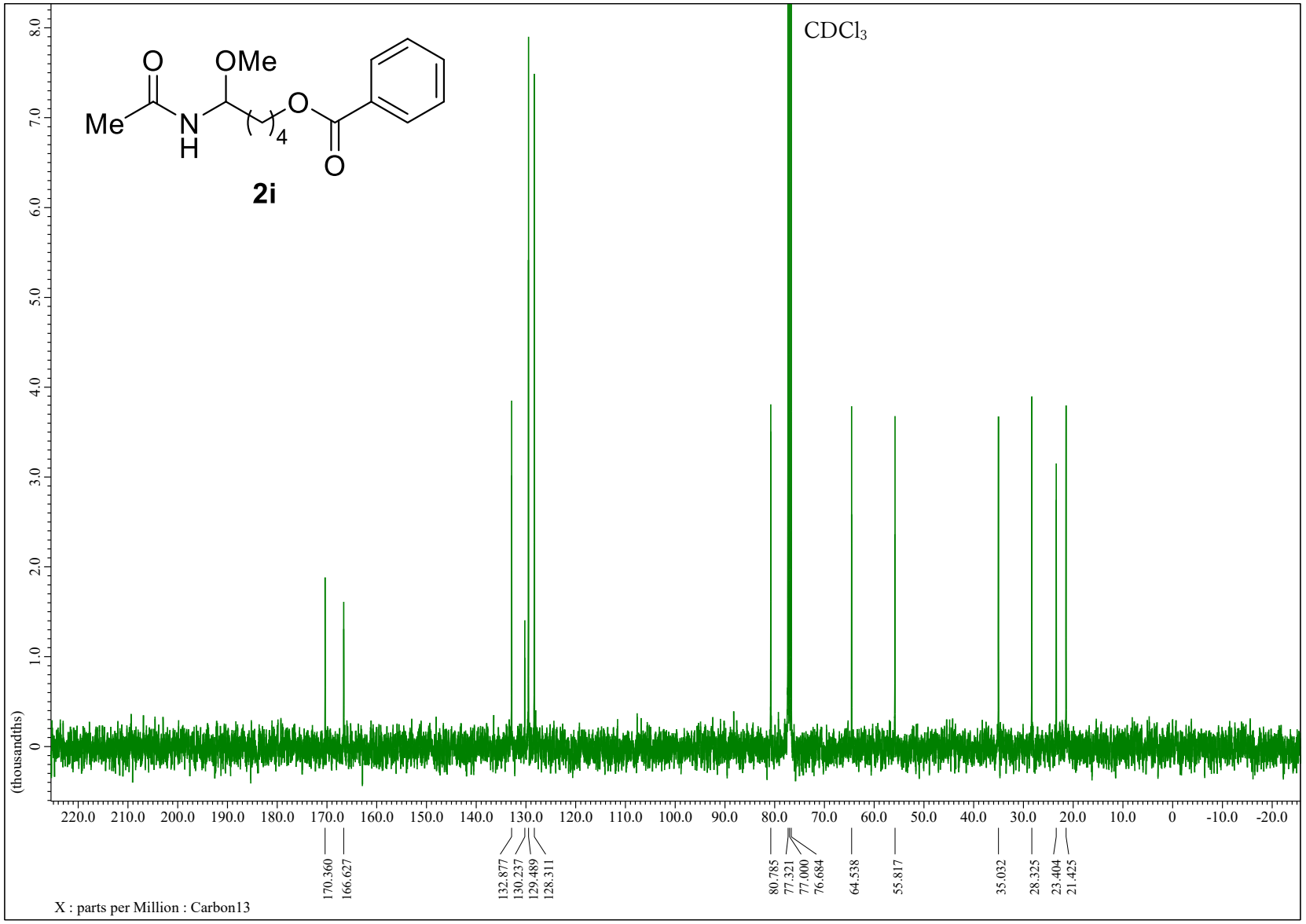
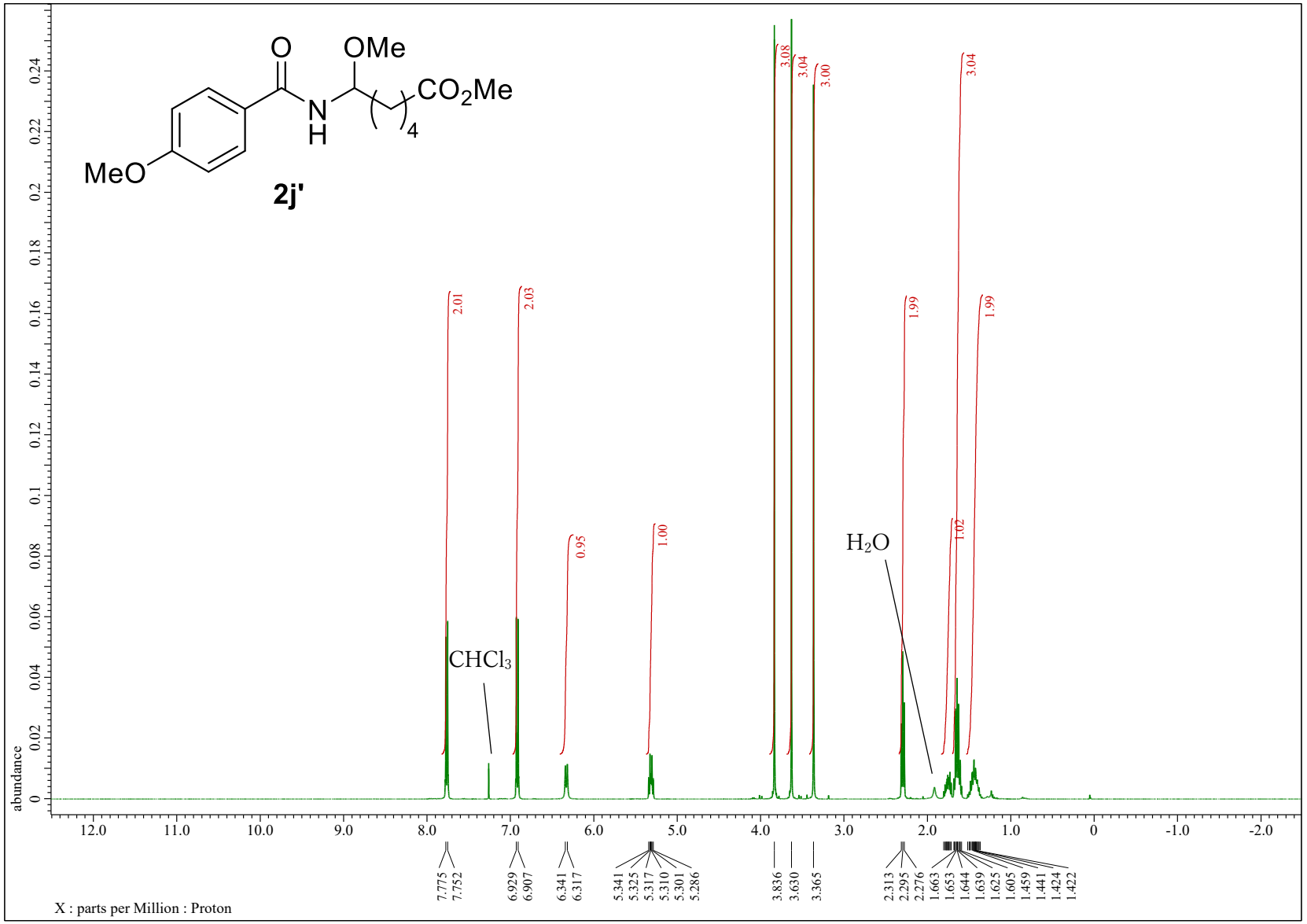
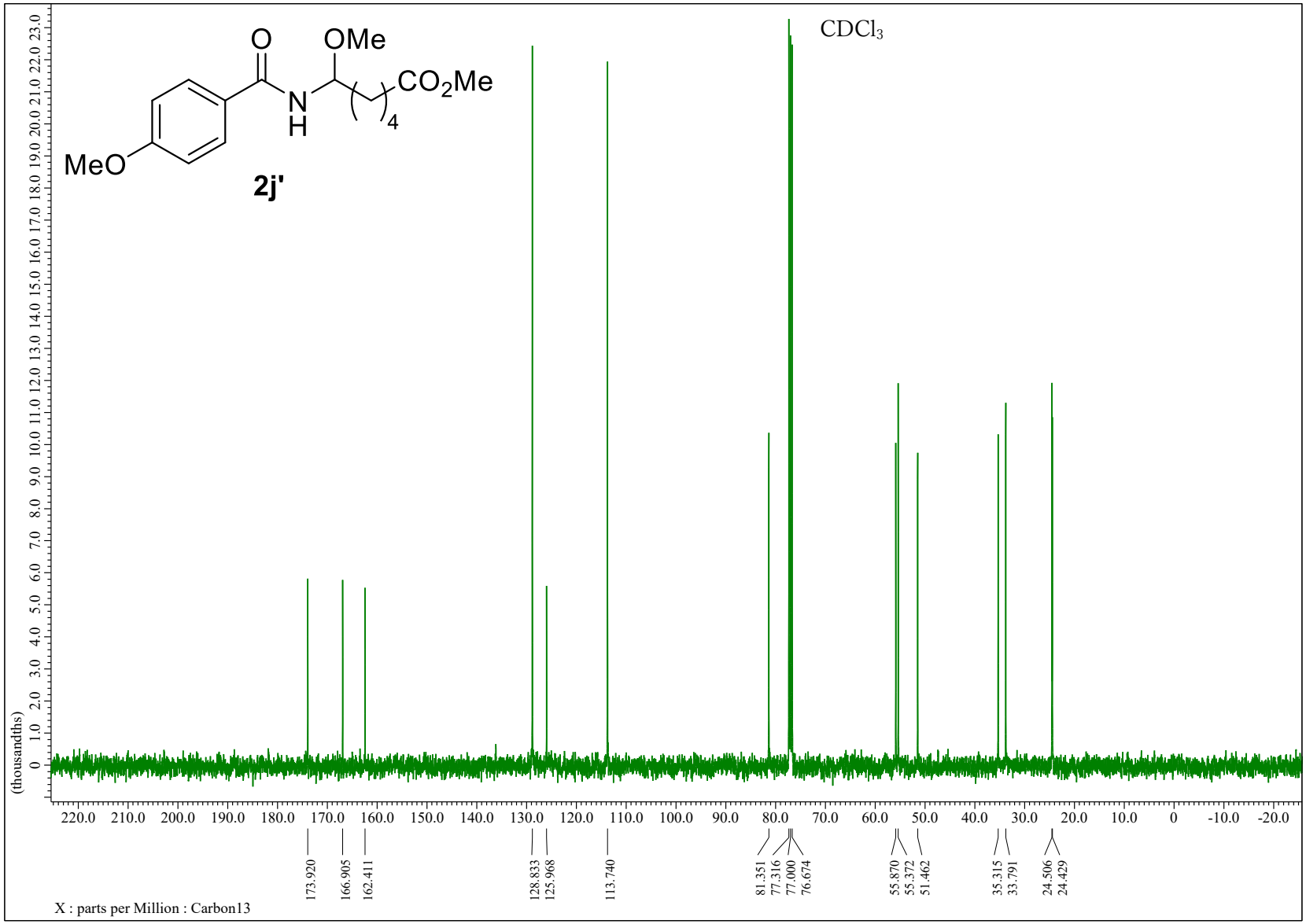
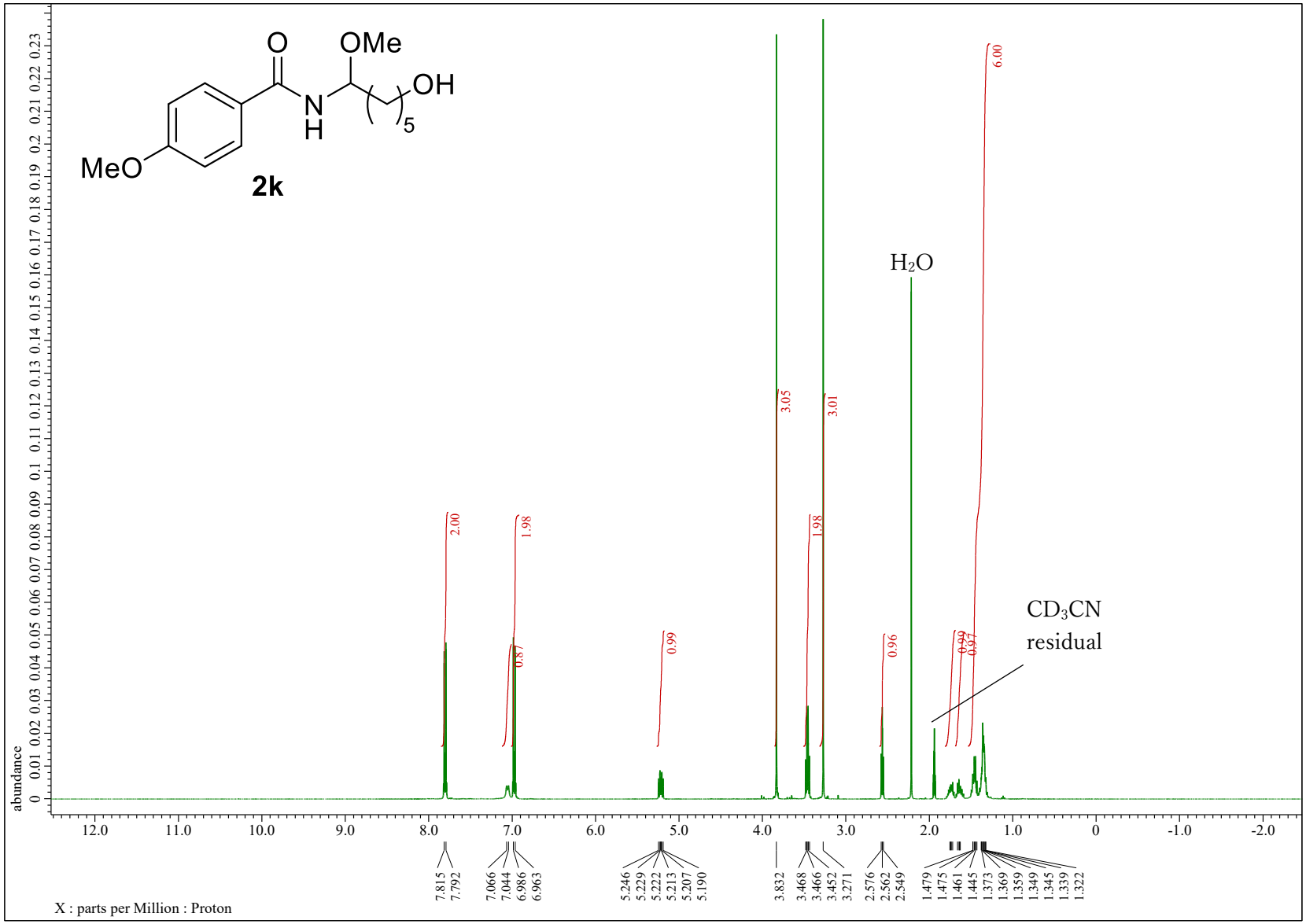
144.137
115.034
112.322
80.632
77.326
77.000
76.684
55.947
37.672
18.085
13.744
X : parts per Million : Carbon13

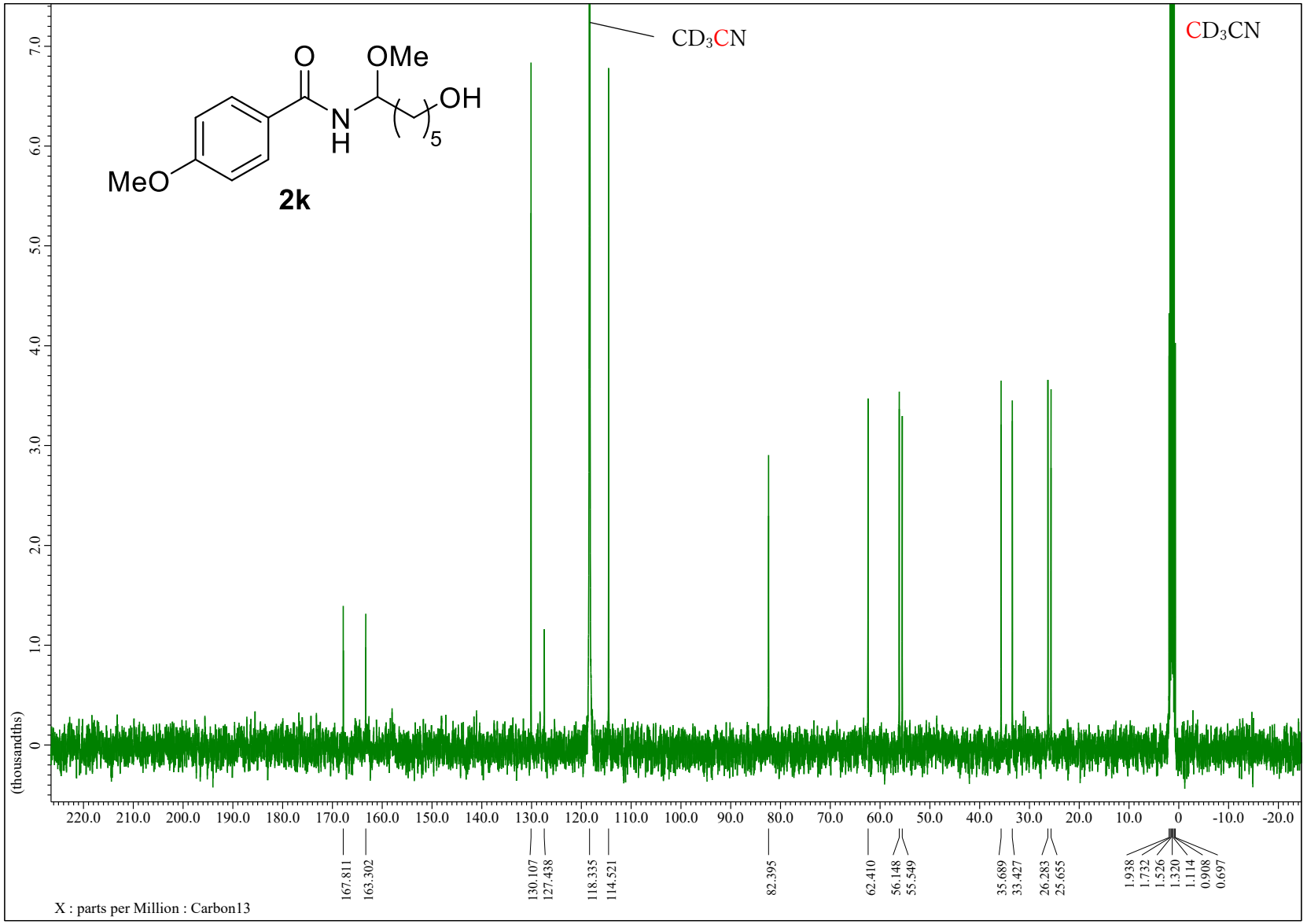

O
OMe
Me
N
H
O
4
O
2i
2.03
2.07
1.01
0.94
0.99
2.09
3.00
3.00
3.26
3.06
CHCl3
abundance
X : parts per Million : Proton
8.041
8.036
8.035
8.033
8.021
8.016
8.012
7.549
7.531
7.449
7.430
7.411
7.410
5.767
5.743
5.135
5.121
5.111
4.342
4.331
4.315
4.300
4.284
3.328
2.012
1.796
1.780
1.776
1.765
1.760
1.599
1.585
1.568
1.554

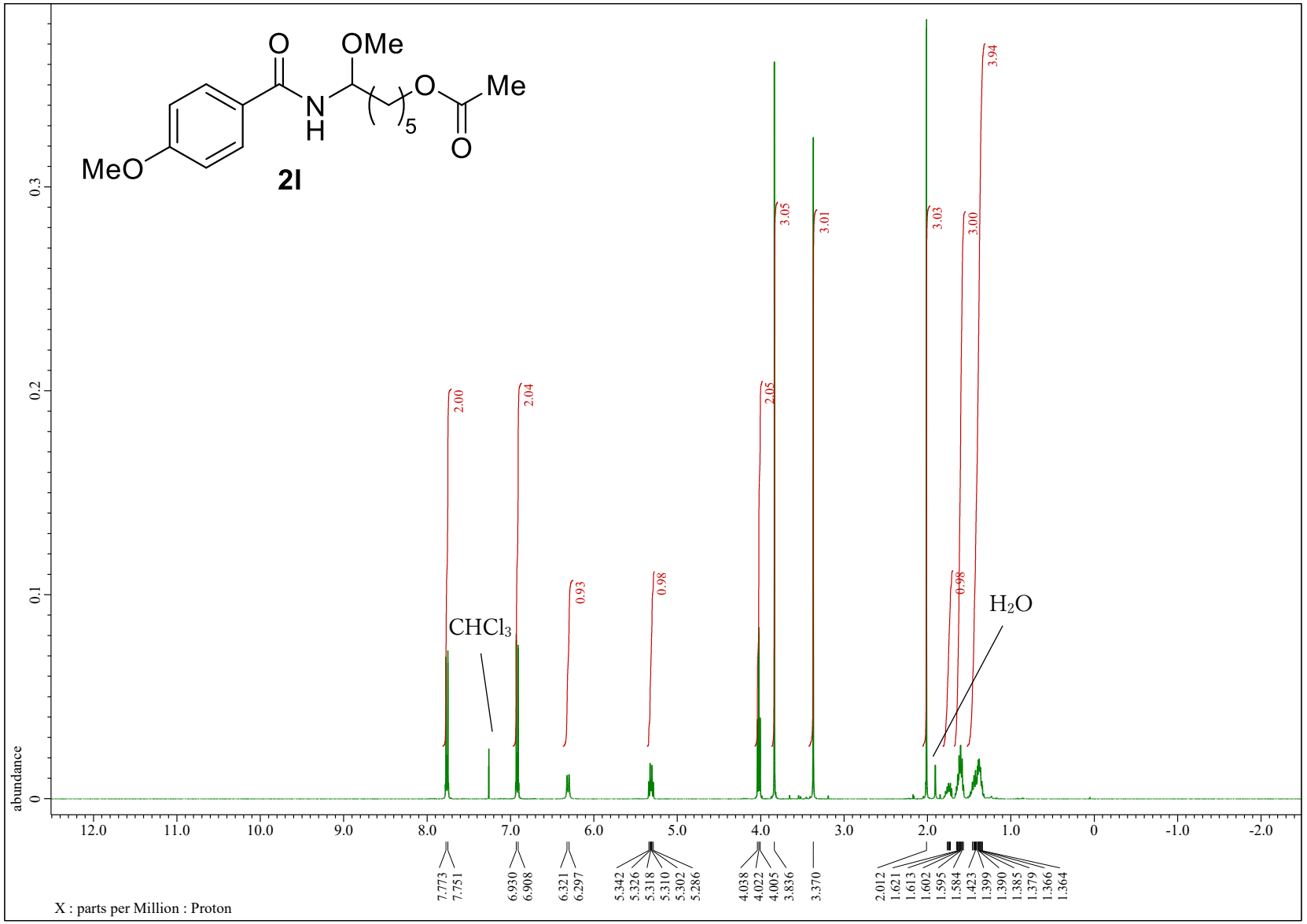

O
OMe
Me
N
H
O
4
O
2i
CDCl3
(thousandths)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
170.360
166.627
132.877
130.237
129.489
128.311
80.785
77.321
77.000
76.684
64.538
55.817
35.032
28.325
23.404
21.425
X : parts per Million : Carbon13

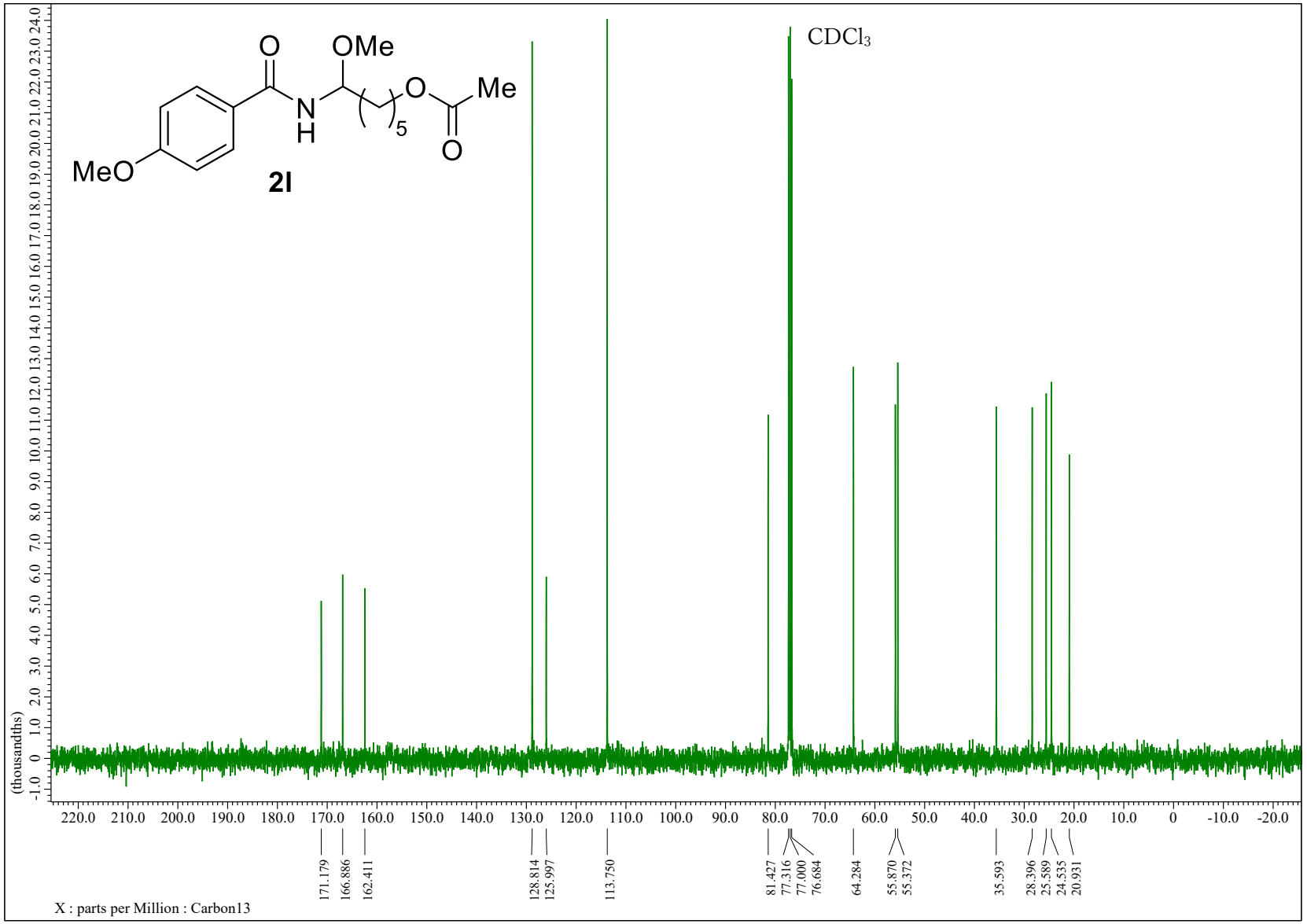

O
OMe
N
H
CO2Me
4
MeO
2j'
abundance
CHCl3
H2O
2.01
2.03
0.95
1.00
3.08
3.04
3.00
1.99
1.02
3.04
1.99
7.775
7.752
6.929
6.907
6.341
6.317
5.341
5.325
5.317
5.310
5.301
5.286
3.836
3.630
3.365
2.313
2.295
2.276
1.663
1.653
1.644
1.639
1.625
1.605
1.459
1.441
1.424
1.422
X : parts per Million : Proton

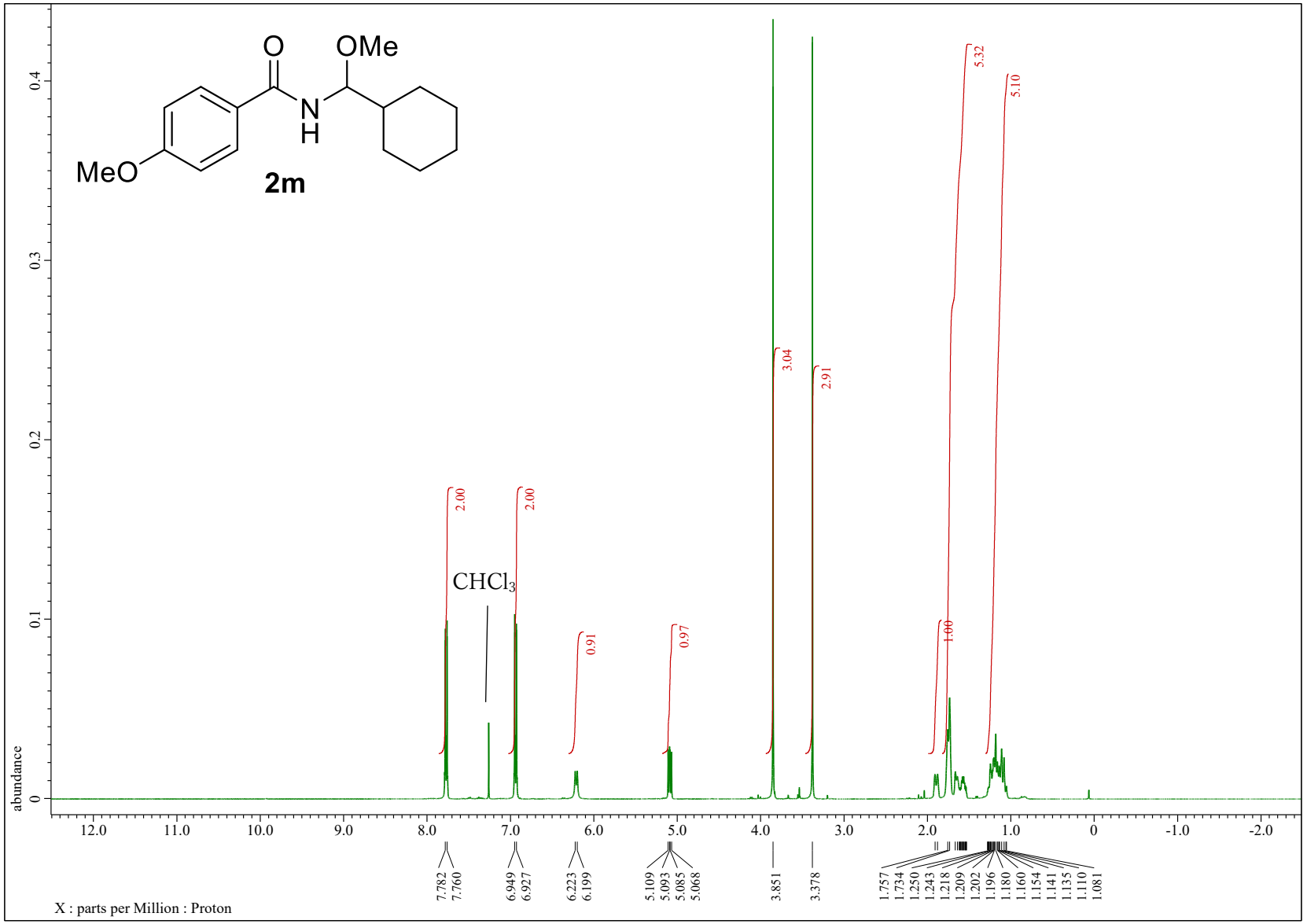

O
OMe
N
H
CO2Me
4
MeO
2j'
CDCl3
(thousandths)
23.0 22.0 21.0 20.0 19.0 18.0 17.0 16.0 15.0 14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
173.920
166.905
162.411
128.833
125.968
113.740
81.351
77.316
77.000
76.674
55.870
55.372
51.462
35.315
33.791
24.506
24.429
X : parts per Million : Carbon13

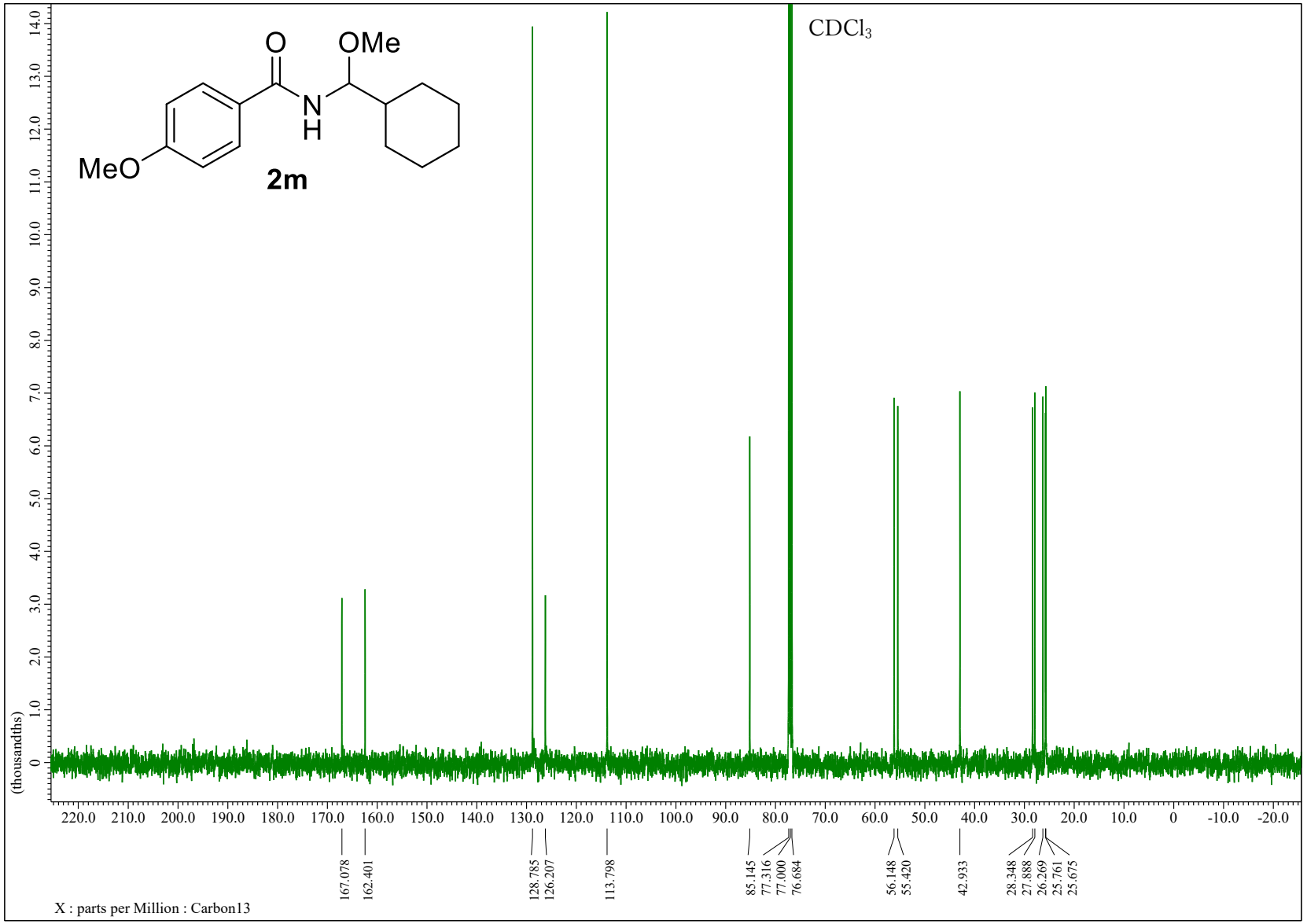

O
OMe
N
H
OH
5
MeO
2k
H2O
CD3CN
residual
abundance
X : parts per Million : Proton
2.00
1.98
0.87
0.99
3.05
1.98
3.01
0.96
0.99
0.97
6.00
7.815
7.792
7.066
7.044
6.986
6.963
5.246
5.229
5.222
5.213
5.207
5.190
3.832
3.468
3.466
3.452
3.271
2.576
2.562
2.549
1.479
1.475
1.461
1.445
1.373
1.369
1.359
1.349
1.345
1.339
1.322

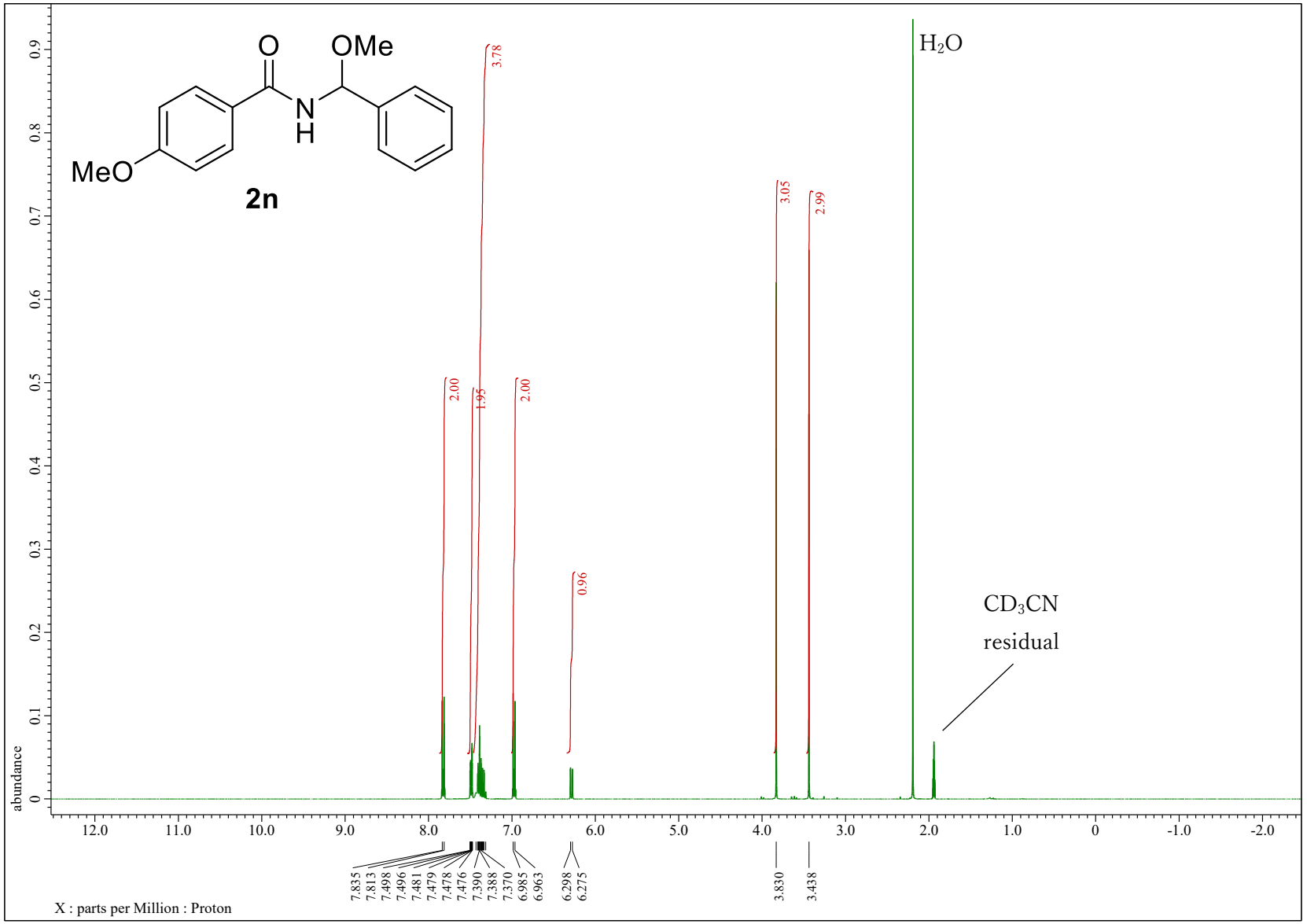

CD3CN
CD3CN
O
OMe
N
H
OH
5
MeO
2k
(thousandths)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.811
163.302
130.107
127.438
118.335
114.521
82.395
62.410
56.148
55.549
35.689
33.427
26.283
25.655
1.938
1.732
1.526
1.320
1.114
0.908
0.697
X : parts per Million : Carbon13

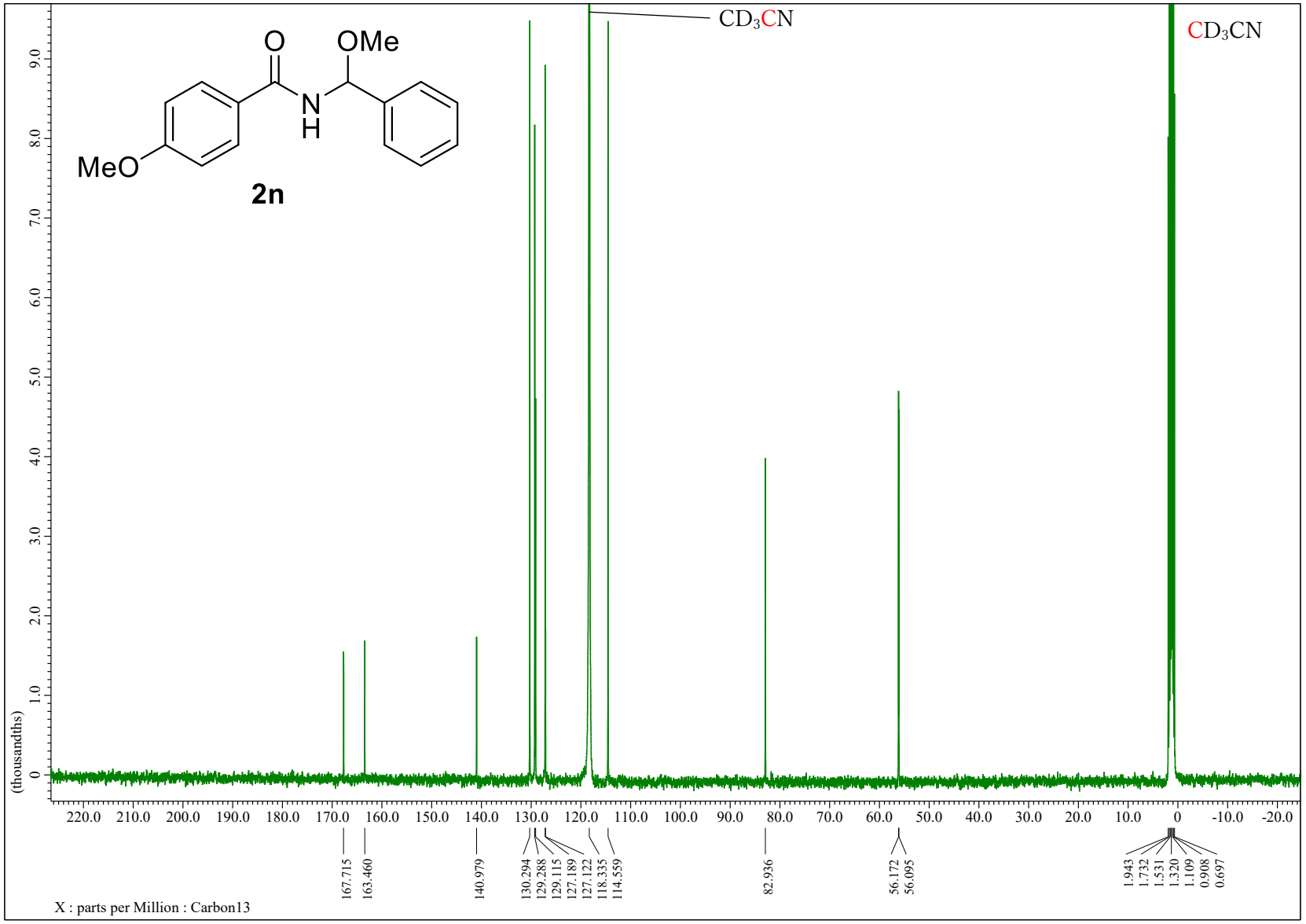

O
OMe
N
H
O
Me
5
O
MeO
2l
abundance
0
0.1
0.2
0.3
2.00
2.04
0.93
0.98
2.05
3.05
3.01
3.03
3.00
0.98
3.94
CHCl3
H2O
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.773
7.751
6.930
6.908
6.321
6.297
5.342
5.326
5.318
5.310
5.302
5.286
4.038
4.022
4.005
3.836
3.370
2.012
1.621
1.613
1.602
1.595
1.584
1.423
1.399
1.390
1.385
1.379
1.366
1.364
X : parts per Million : Proton

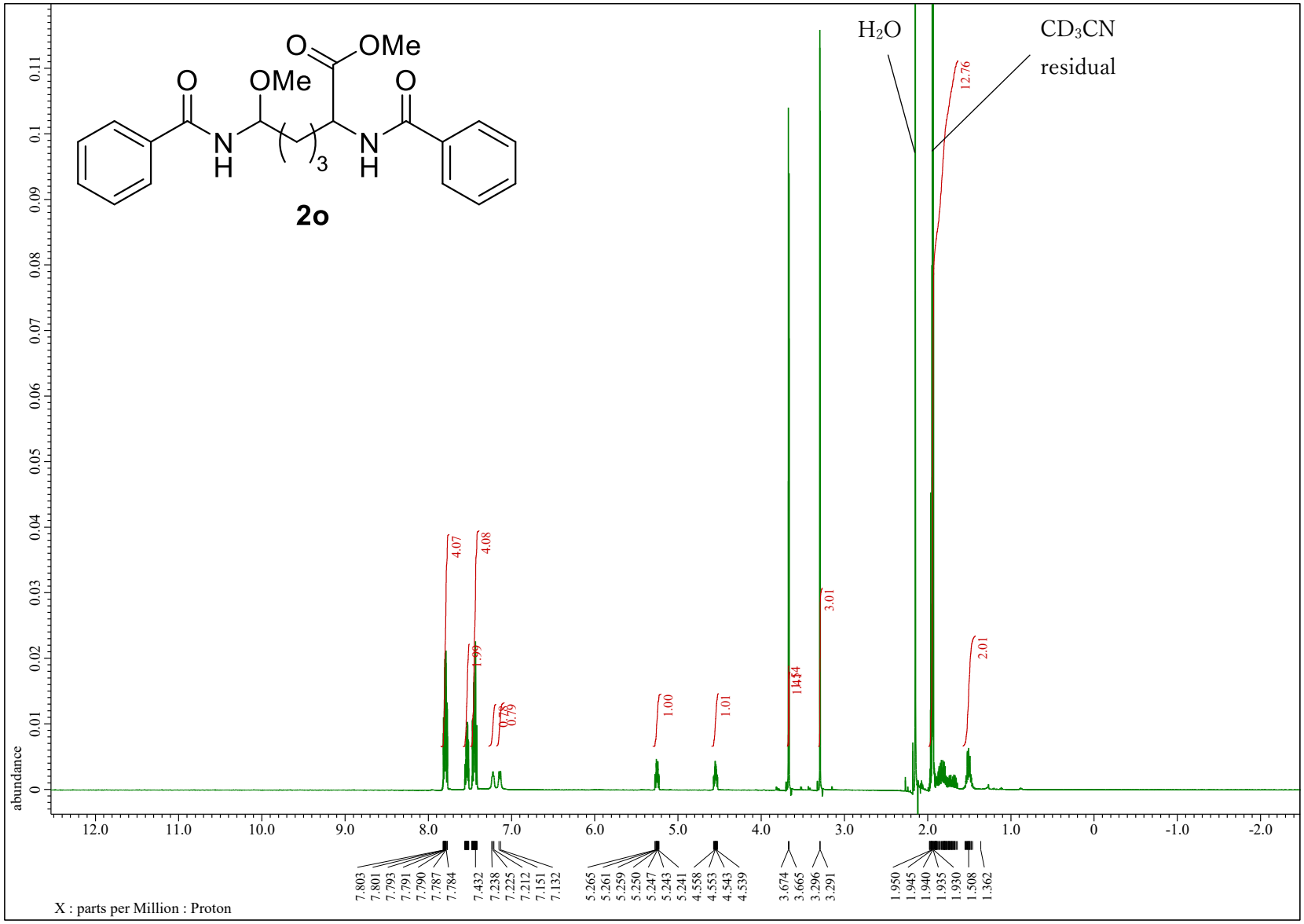

O
OMe
N
H
5
O
Me
O
MeO
2l
CDCl3
(thousandths)
X : parts per Million : Carbon13
171.179
166.886
162.411
128.814
125.997
113.750
81.427
77.316
77.000
76.684
64.284
55.870
55.372
35.593
28.396
25.589
24.535
20.931

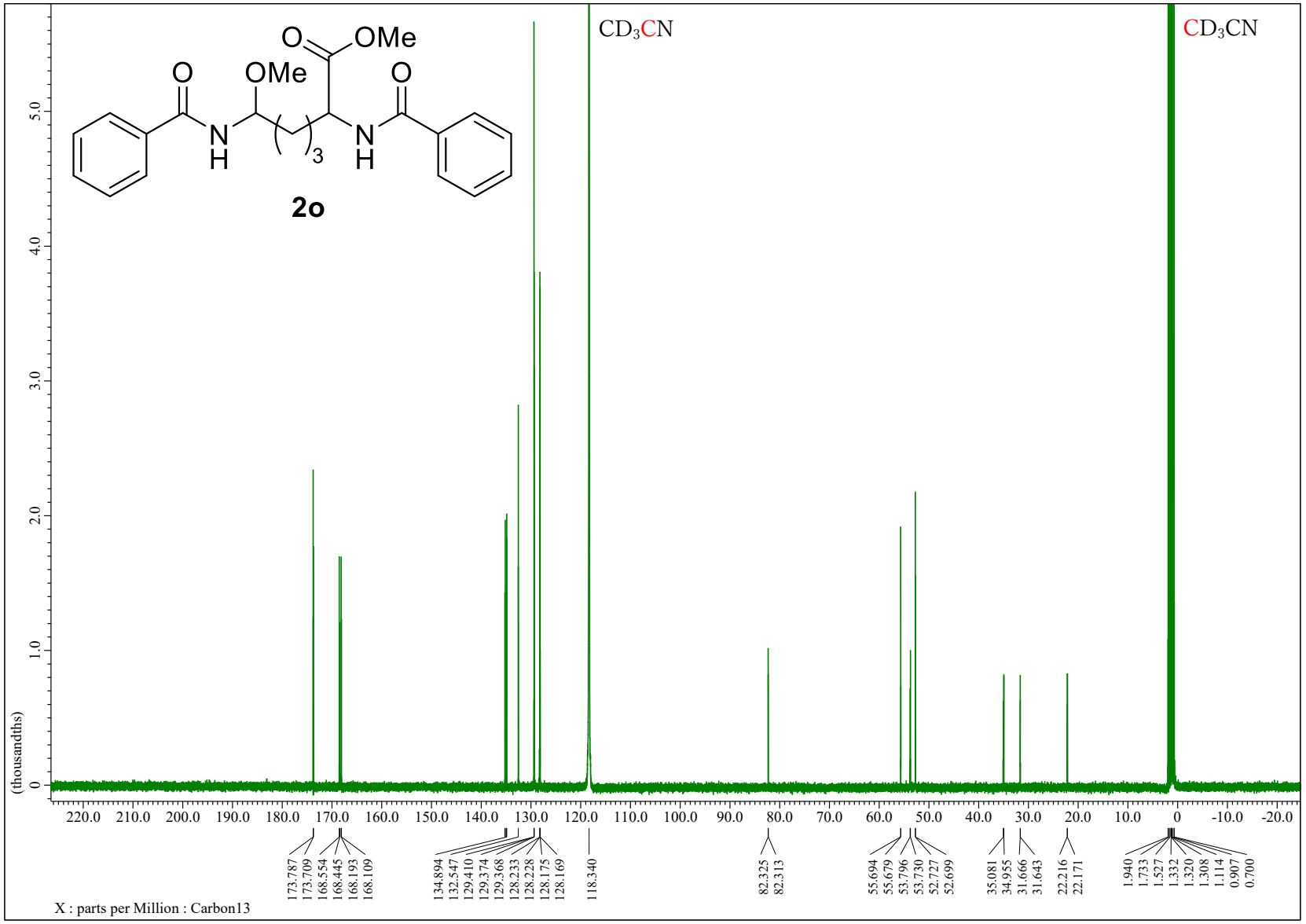

O
OMe
N
H
MeO
2m
abundance
0.4
0.3
0.2
0.1
0
2.00
2.00
0.91
0.97
3.04
2.91
1.00
5.32
5.10
CHCl3
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.782
7.760
6.949
6.927
6.223
6.199
5.109
5.093
5.085
5.068
3.851
3.378
1.757
1.734
1.250
1.243
1.218
1.209
1.202
1.196
1.180
1.160
1.154
1.141
1.135
1.110
1.081
X : parts per Million : Proton

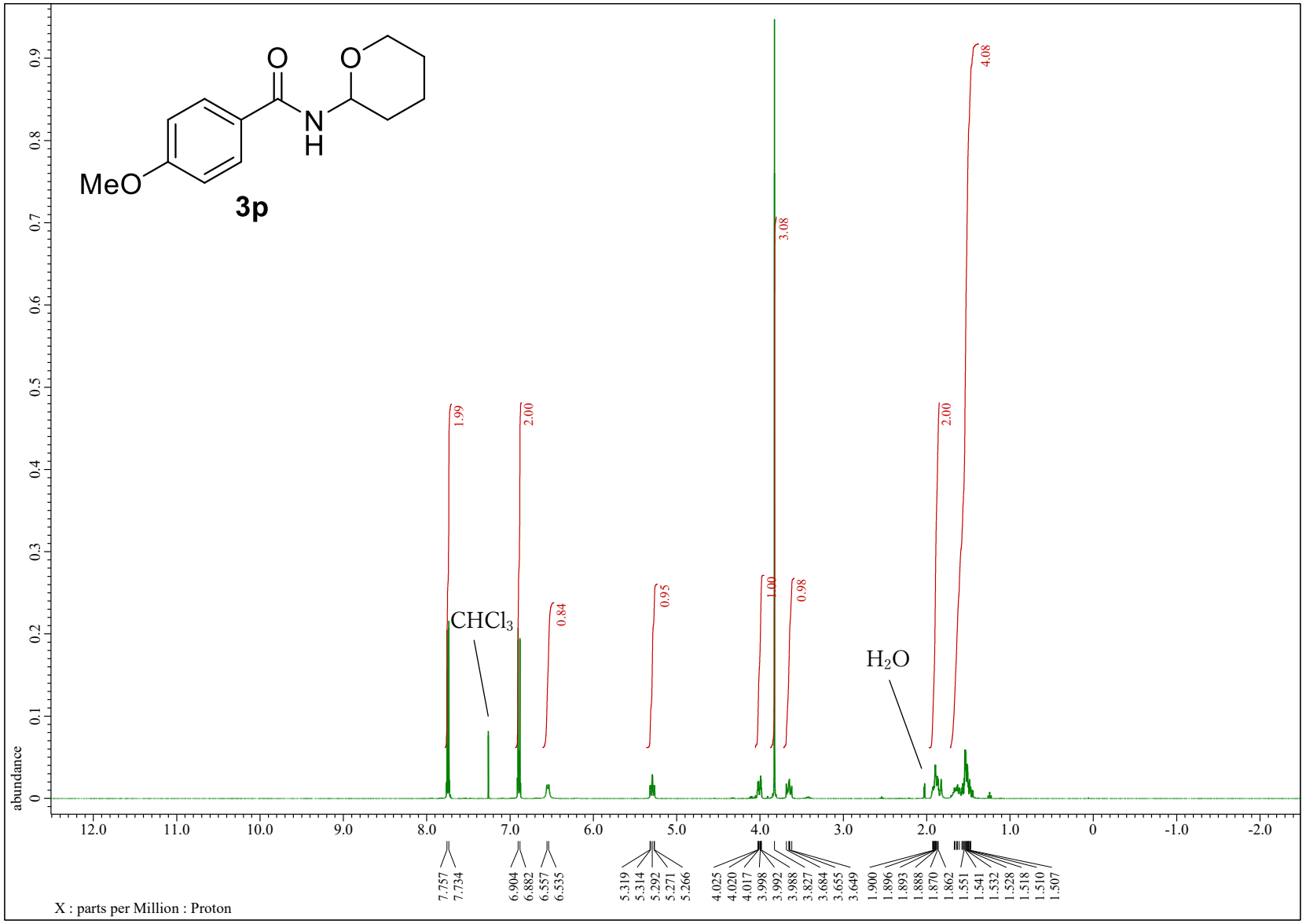

O
OMe
N
H
MeO
2m
CDCl3
(thousandths)
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
167.078
162.401
128.785
126.207
113.798
85.145
77.316
77.000
76.684
56.148
55.420
42.933
28.348
27.888
26.269
25.761
25.675
X : parts per Million : Carbon13

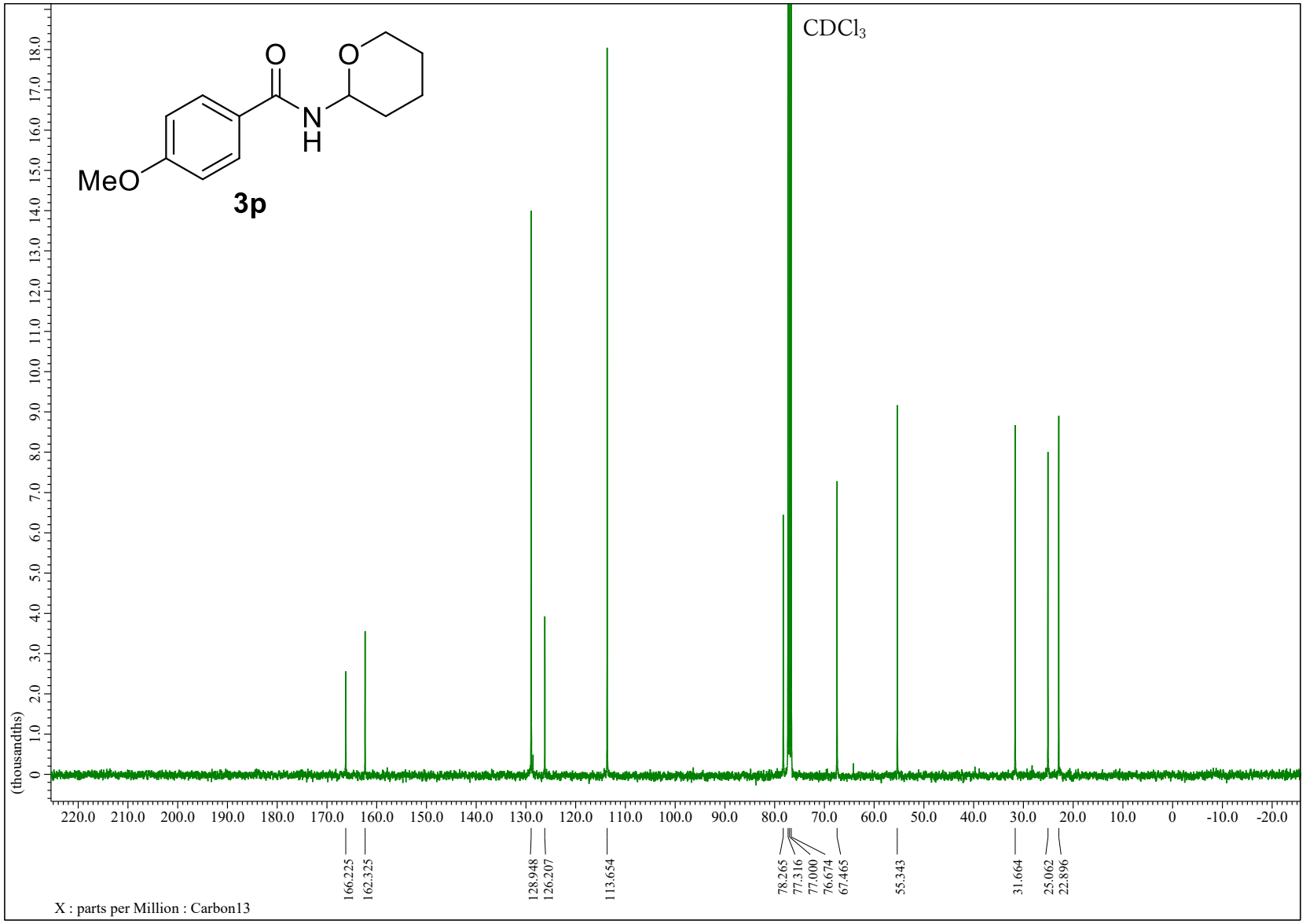

O
OMe
N
H
MeO
2n
3.78
3.05
2.99
2.00
1.95
2.00
0.96
H2O
CD3CN
residual
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.835
7.813
7.498
7.496
7.481
7.479
7.478
7.476
7.390
7.388
7.370
6.985
6.963
6.298
6.275
3.830
3.438
X : parts per Million : Proton

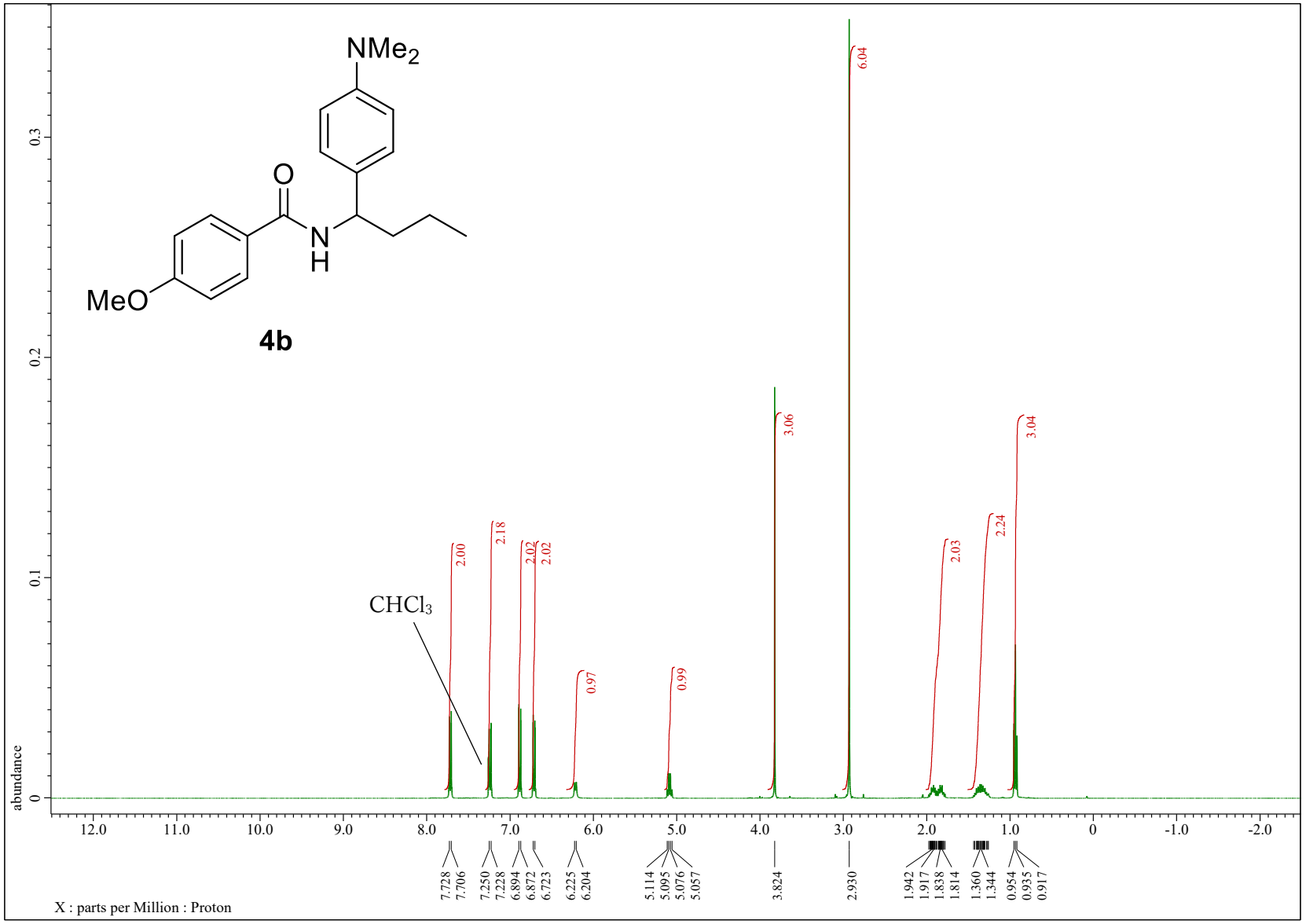

O
OMe
N
H
MeO
2n
CD3CN
CD3CN
(thousandths)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.715
163.460
140.979
130.294
129.288
129.115
127.189
127.122
118.335
114.559
82.936
56.172
56.095
1.943
1.732
1.531
1.320
1.109
0.908
0.697
X : parts per Million : Carbon13

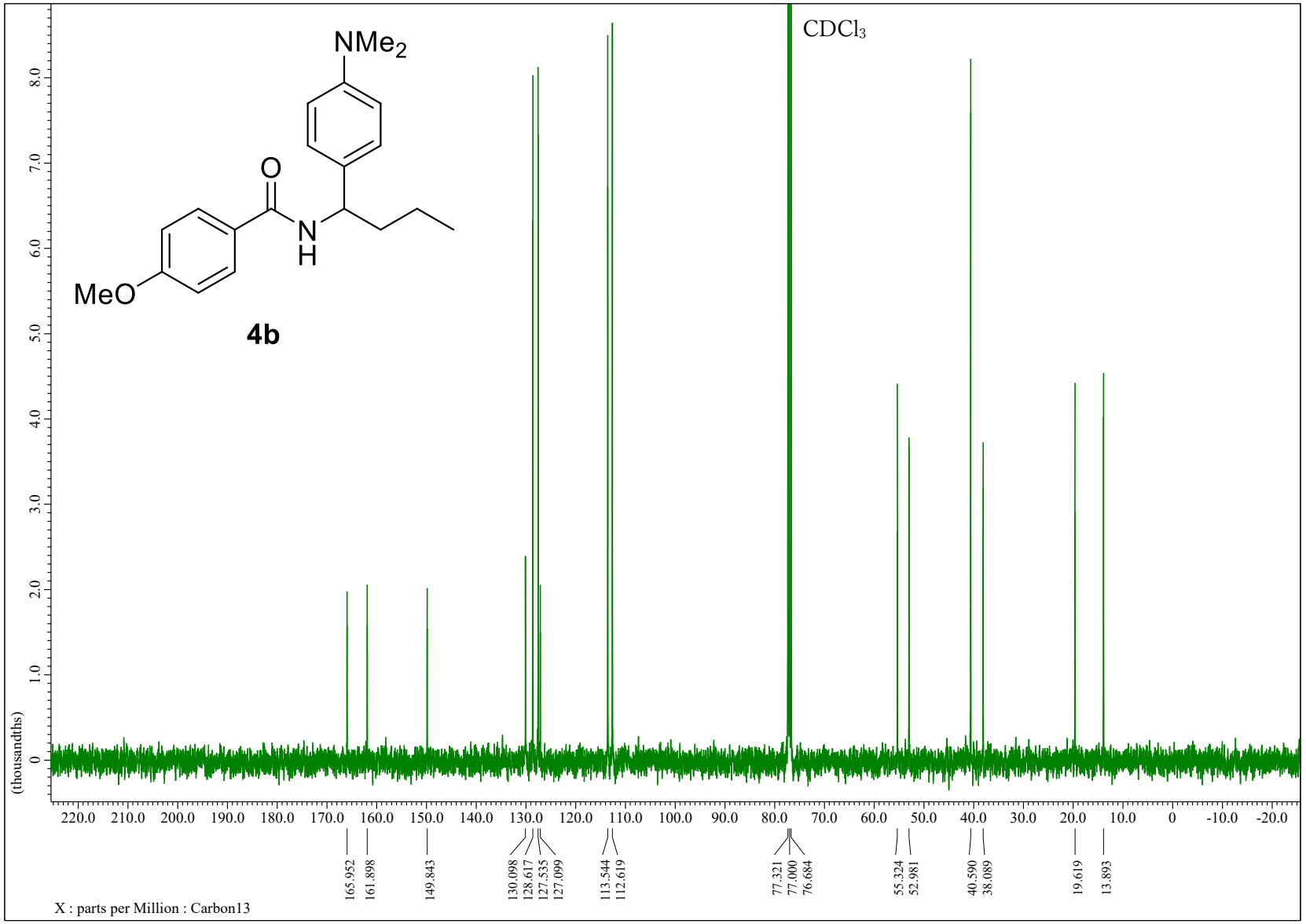

O
OMe
O
OMe
O
N
H
3
N
H
2o
H2O
CD3CN
residual
12.76
4.07
4.08
1.99
0.76
0.79
1.00
1.01
1.44
1.54
3.01
2.01
abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.803
7.801
7.793
7.791
7.790
7.787
7.784
7.432
7.238
7.225
7.212
7.151
7.132
5.265
5.261
5.259
5.250
5.247
5.243
5.241
4.558
4.553
4.543
4.539
3.674
3.665
3.296
3.291
1.950
1.945
1.940
1.935
1.930
1.508
1.362
X : parts per Million : Proton

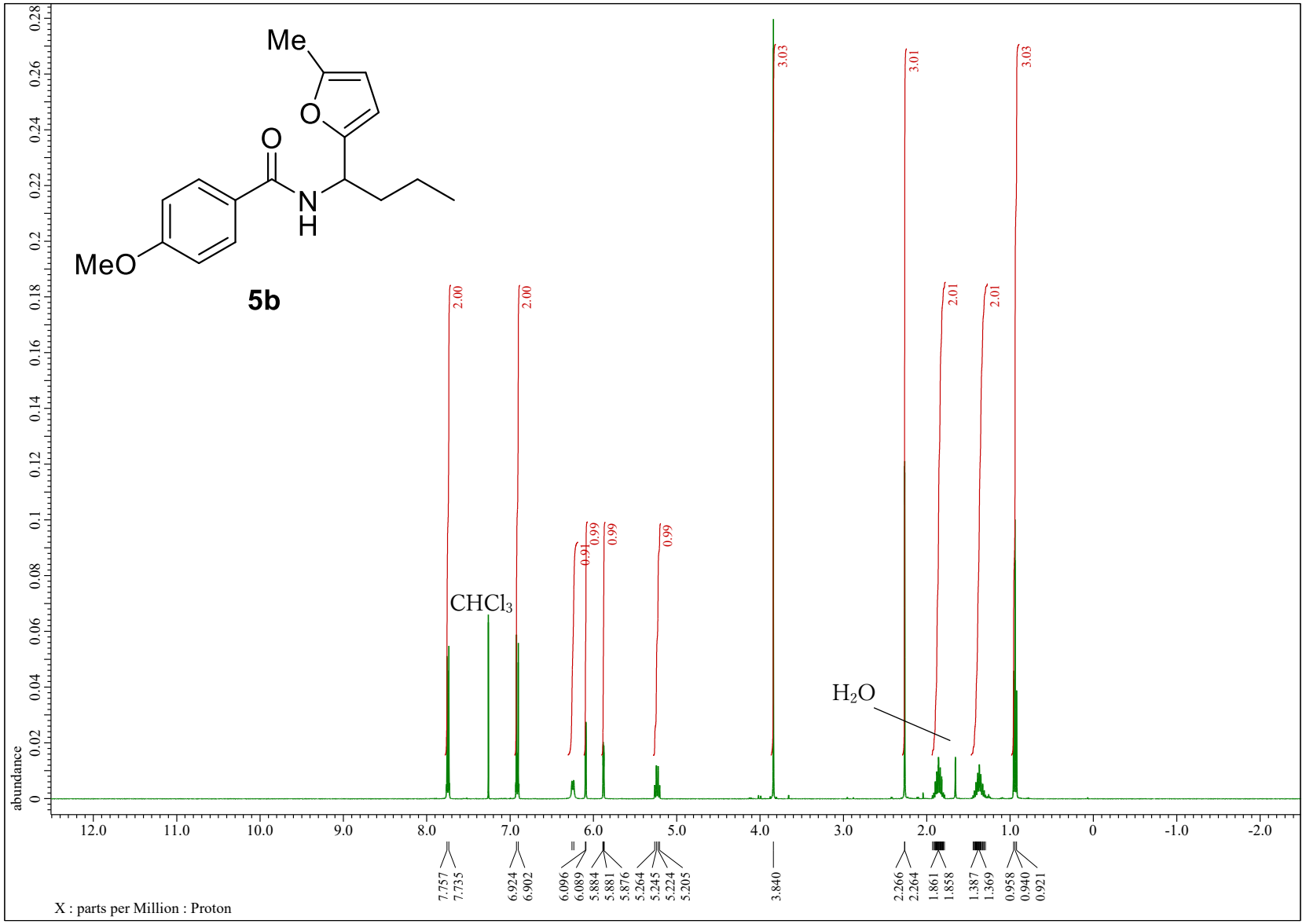

O
OMe
O
OMe
O
N
H
3
N
H
2o
CD3CN
CD3CN
(thousandths)
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
173.787
173.709
168.554
168.445
168.193
168.109
134.894
132.547
129.410
129.374
129.368
128.233
128.228
128.175
128.169
118.340
82.325
82.313
55.694
55.679
53.796
53.730
52.727
52.699
35.081
34.955
31.666
31.643
22.216
22.171
1.940
1.733
1.527
1.332
1.320
1.308
1.114
0.907
0.700
X : parts per Million : Carbon13

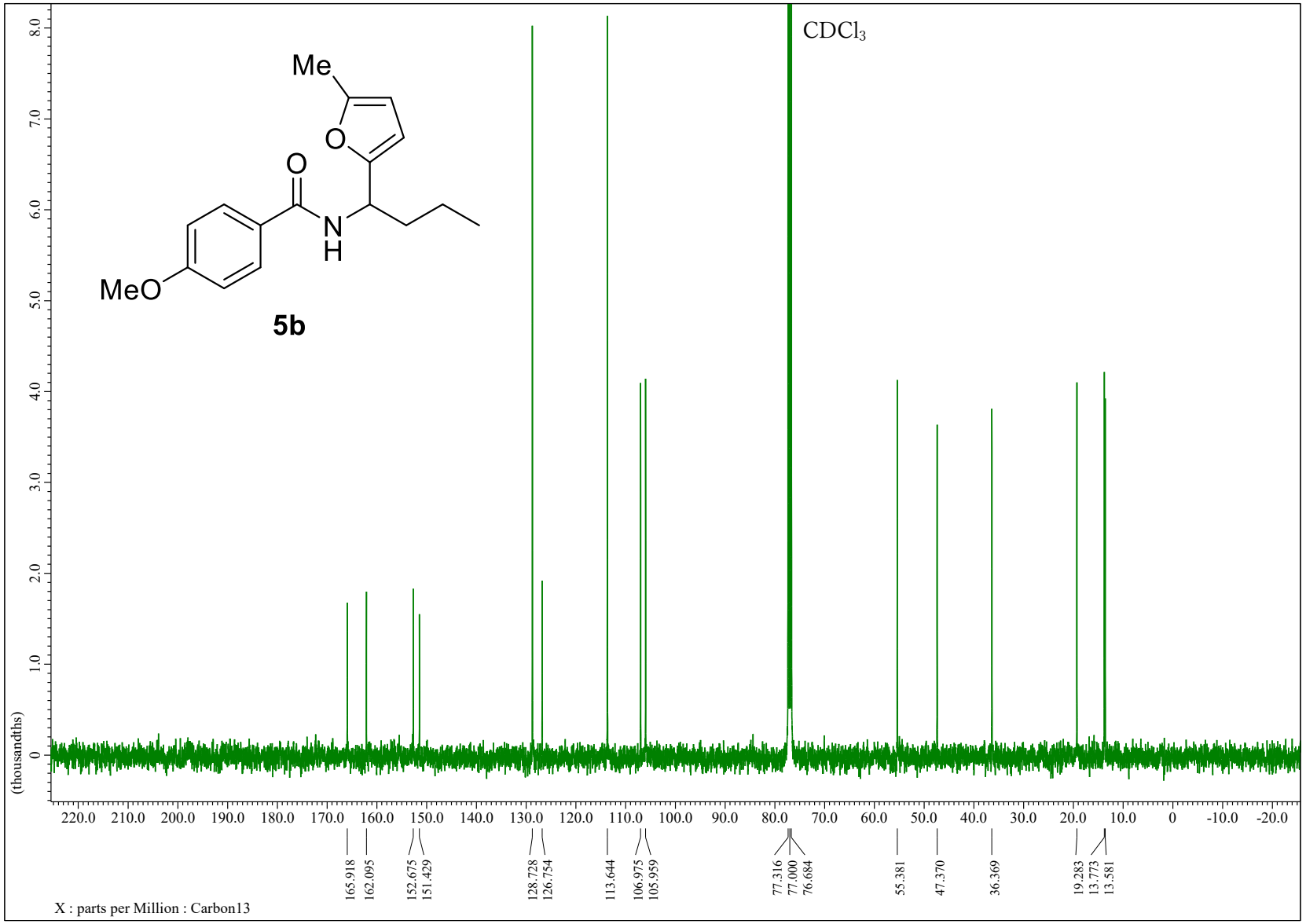

O
O
N
H
MeO
3p
abundance
CHCl3
H2O
1.99
2.00
0.84
0.95
1.00
0.98
3.08
2.00
4.08
X : parts per Million : Proton

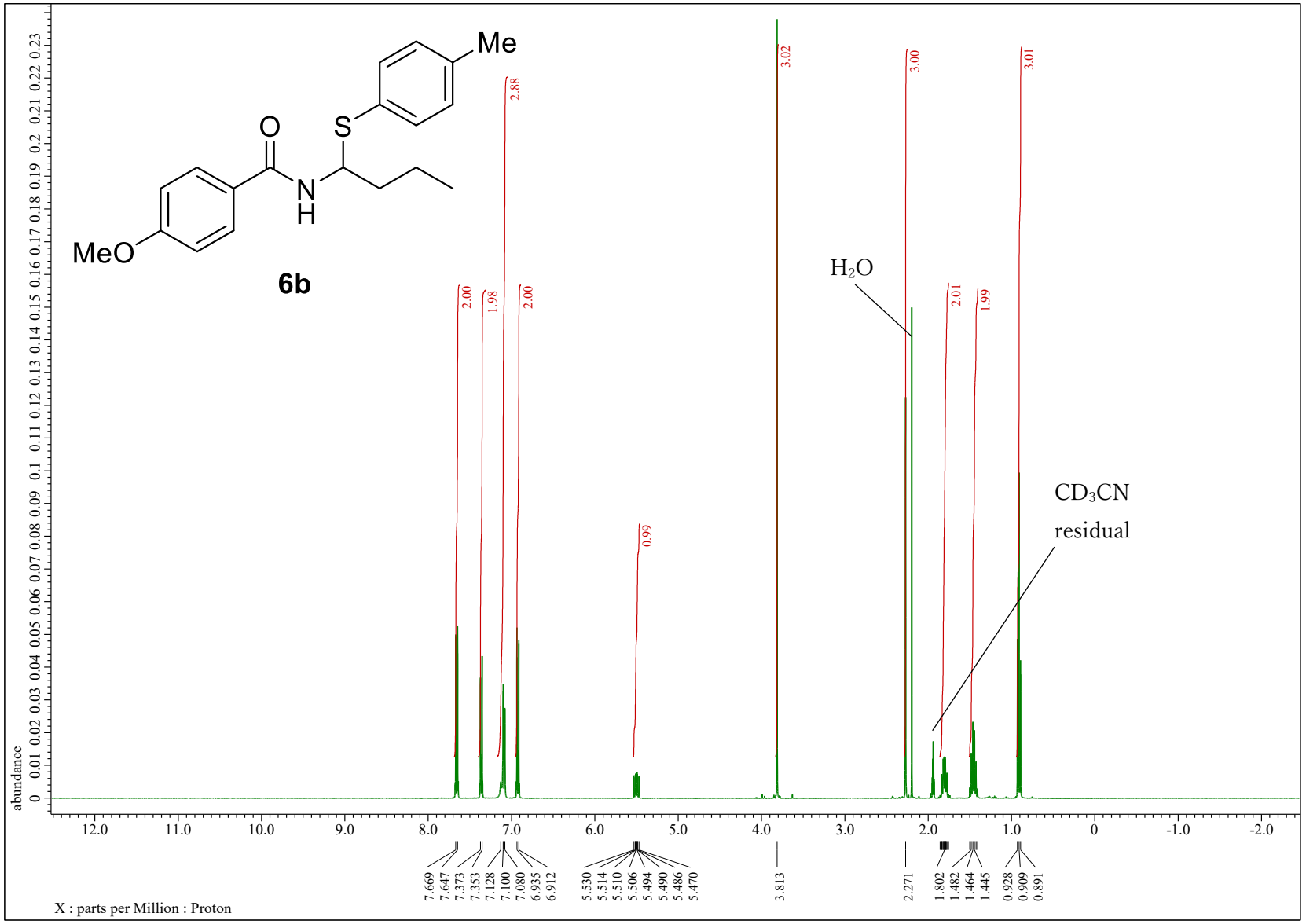

CDCl3
MeO
3p
(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
166.225
162.325
128.948
126.207
113.654
78.265
77.316
77.000
76.674
67.465
55.343
31.664
25.062
22.896
X : parts per Million : Carbon13

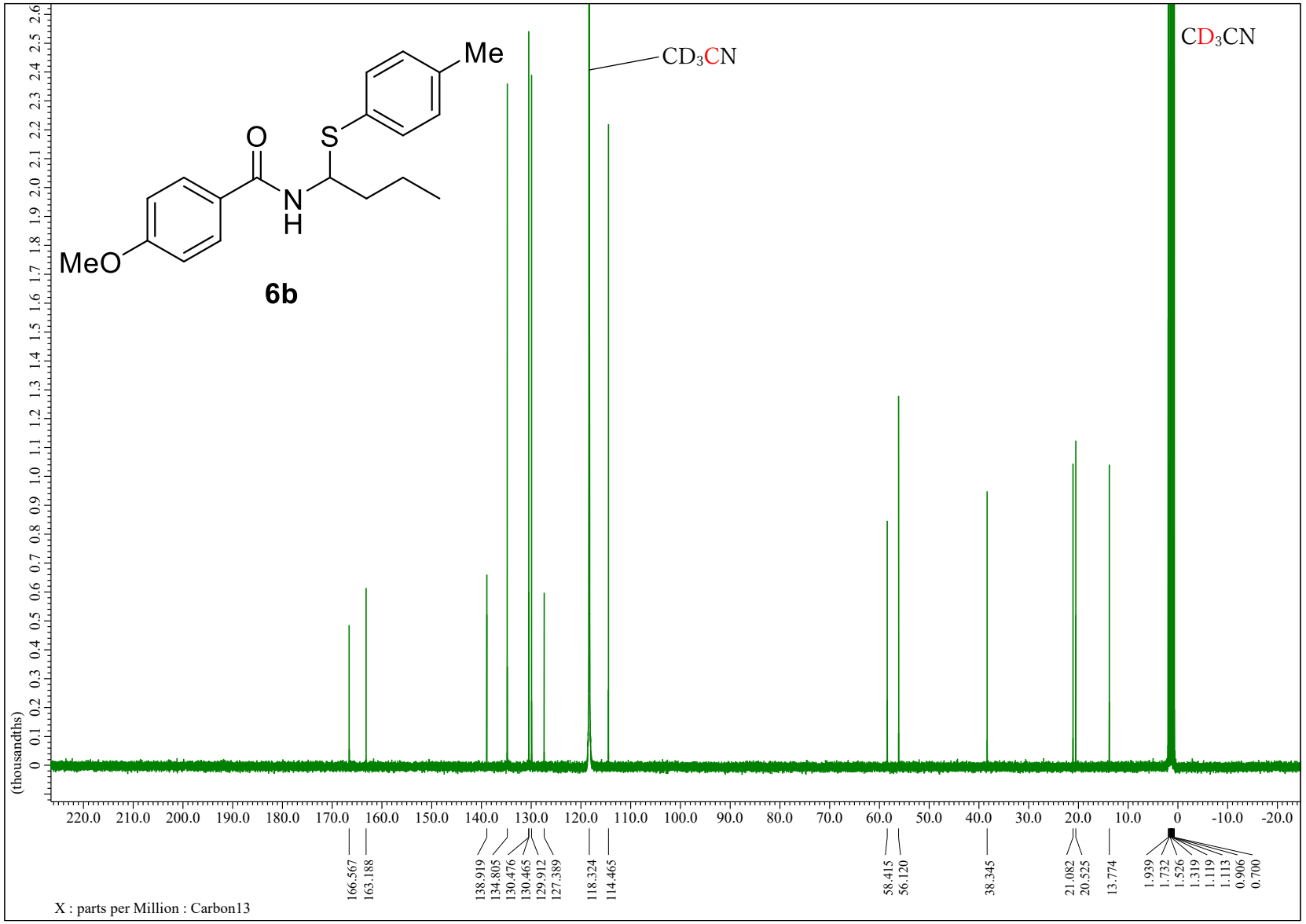

NMe2
O
N
H
MeO
4b
CHCl3
6.04
3.06
3.04
2.18
2.24
2.00
2.02
2.02
2.03
0.97
0.99
abundance
X : parts per Million : Proton
7.728
7.706
7.250
7.228
6.894
6.872
6.723
6.225
6.204
5.114
5.095
5.076
5.057
3.824
2.930
1.942
1.917
1.838
1.814
1.360
1.344
0.954
0.935
0.917

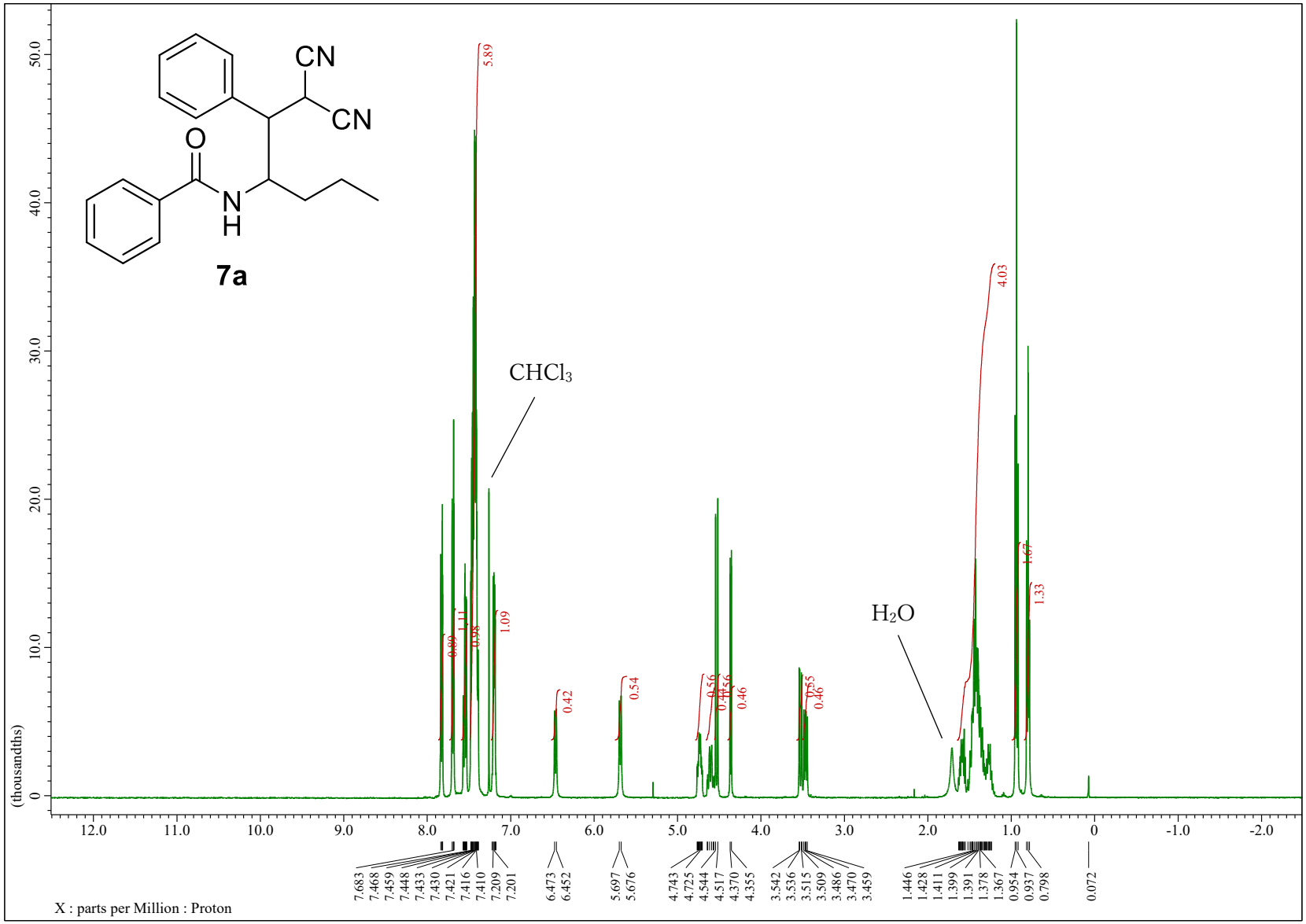

NMe2
O
N
H
MeO
4b
CDCl3
(thousandths)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
165.952
161.898
149.843
130.098
128.617
127.535
127.099
113.544
112.619
77.321
77.000
76.684
55.324
52.981
40.590
38.089
19.619
13.893
X : parts per Million : Carbon13

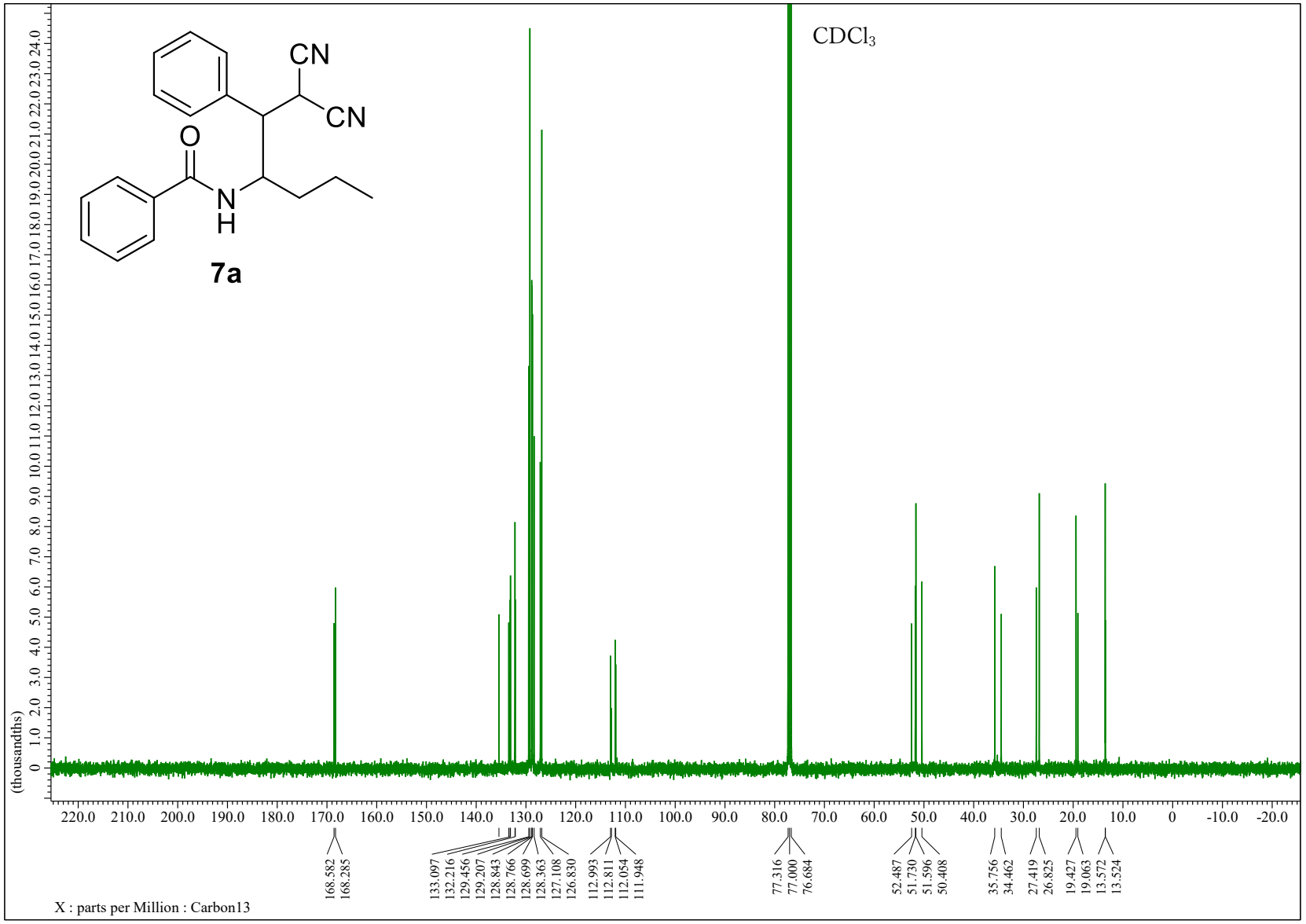

Me
O
O
N
H
MeO
5b
abundance
CHCl3
H2O
2.00
2.00
0.91
0.99
0.99
0.99
3.03
3.01
2.01
2.01
3.03
7.757
7.735
6.924
6.902
6.096
6.089
5.884
5.881
5.876
5.264
5.245
5.224
5.205
3.840
2.266
2.264
1.861
1.858
1.387
1.369
0.958
0.940
0.921
X : parts per Million : Proton

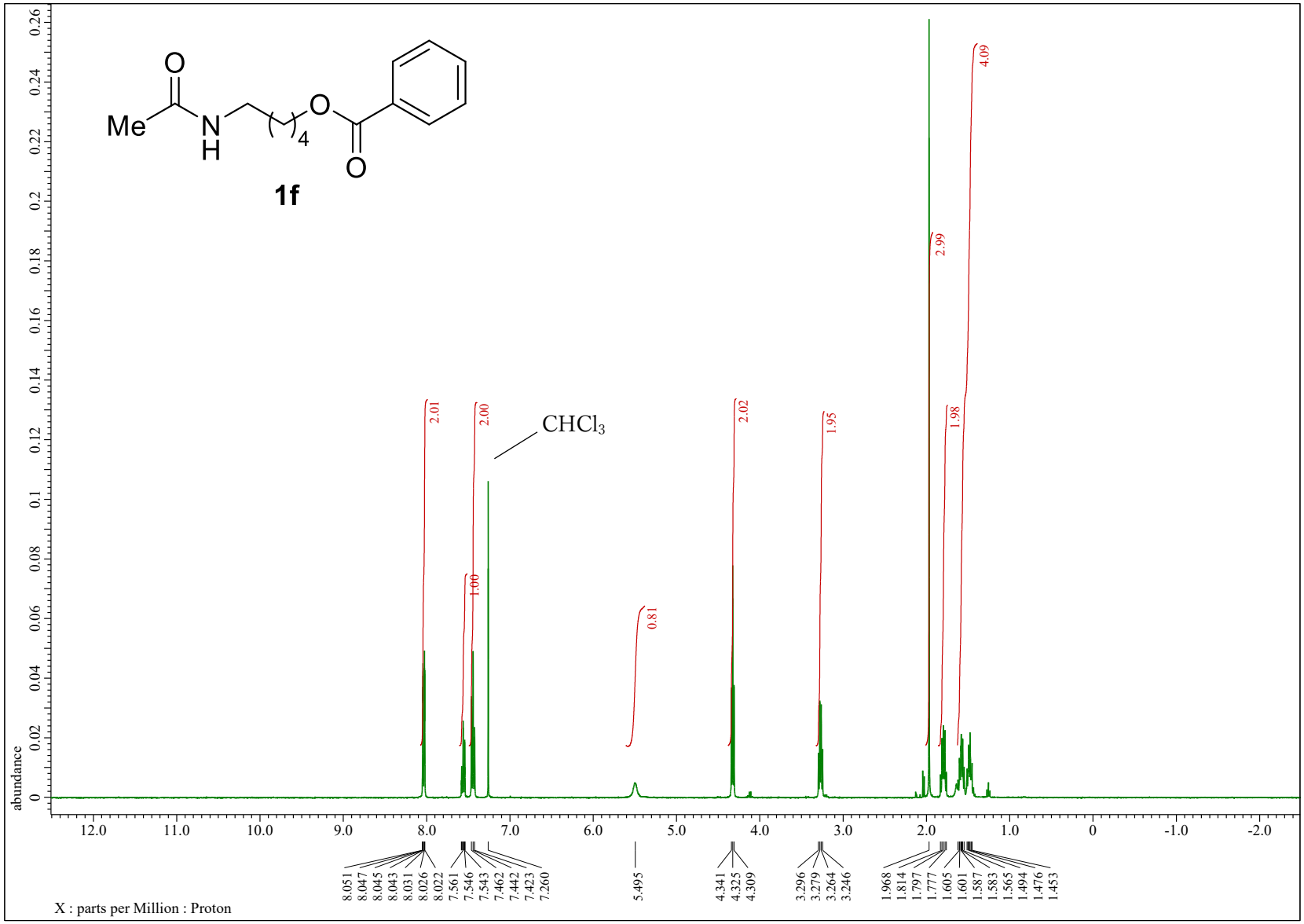

Me
O
O
N
H
MeO
5b
CDCl3
(thousandths)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
165.918
162.095
152.675
151.429
128.728
126.754
113.644
106.975
105.959
77.316
77.000
76.684
55.381
47.370
36.369
19.283
13.773
13.581
X : parts per Million : Carbon13

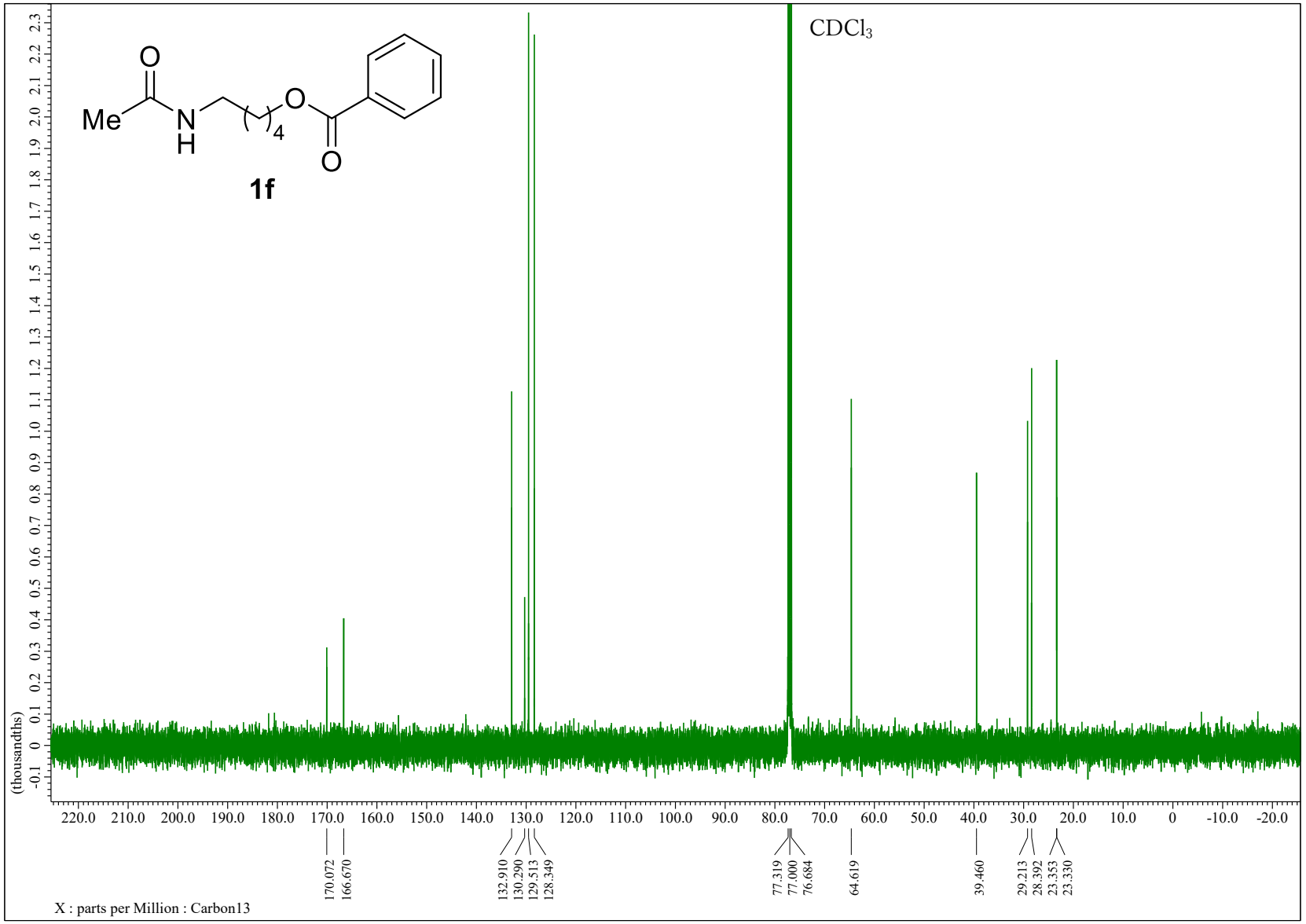

Me
O
S
N
H
MeO
6b
H2O
CD3CN
residual
abundance
X : parts per Million : Proton
2.00
1.98
2.00
2.88
0.99
3.02
3.00
2.01
1.99
3.01
7.669
7.647
7.373
7.353
7.128
7.100
7.080
6.935
6.912
5.530
5.514
5.510
5.506
5.494
5.490
5.486
5.470
3.813
2.271
1.802
1.482
1.464
1.445
0.928
0.909
0.891

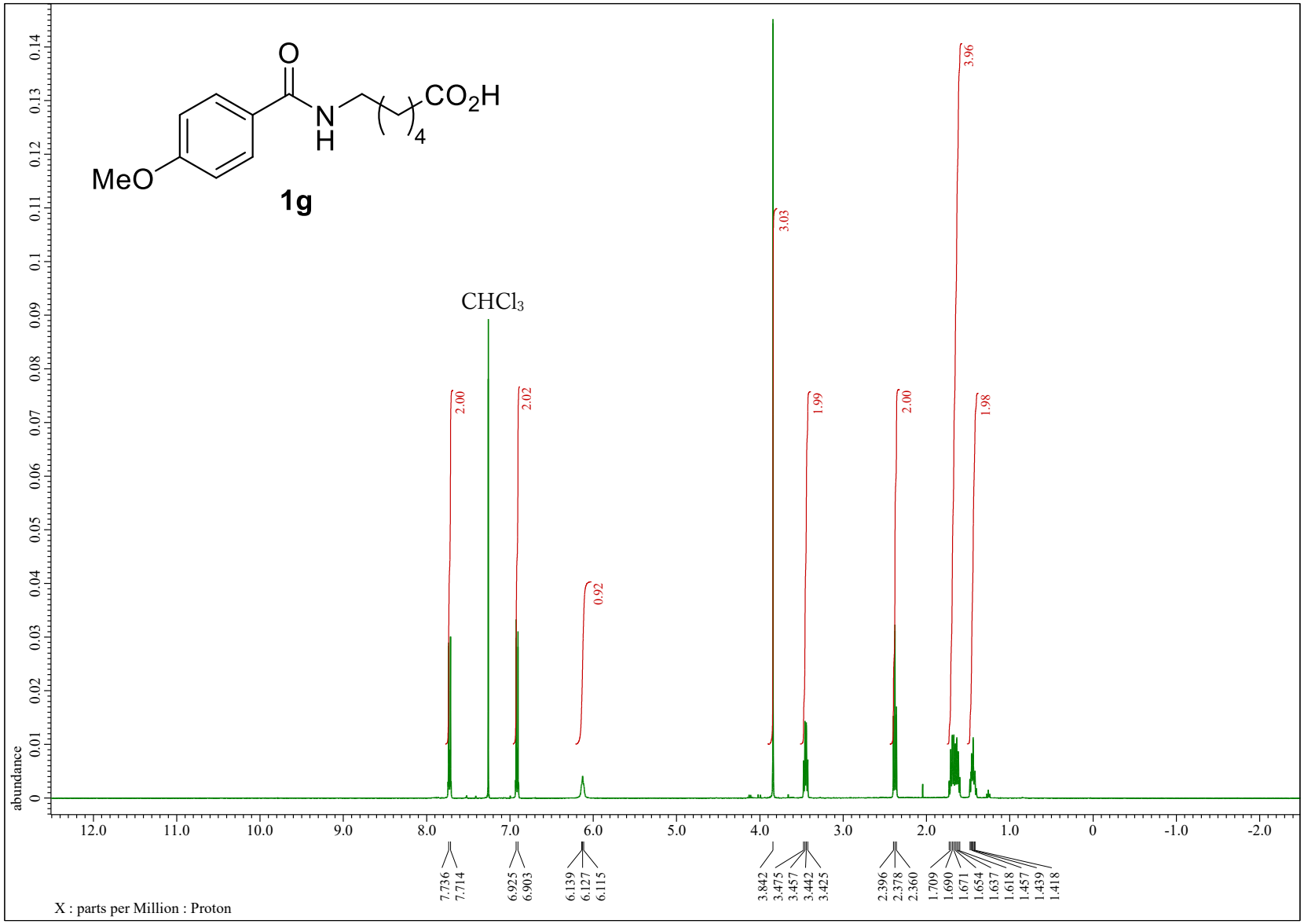

Me
O
S
N
H
MeO
6b
CD3CN
CD3CN
(thousandths)
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
166.567
163.188
138.919
134.805
130.476
130.465
129.912
127.389
118.324
114.465
58.415
56.120
38.345
21.082
20.525
13.774
1.939
1.732
1.526
1.319
1.119
1.113
0.906
0.700
X : parts per Million : Carbon13

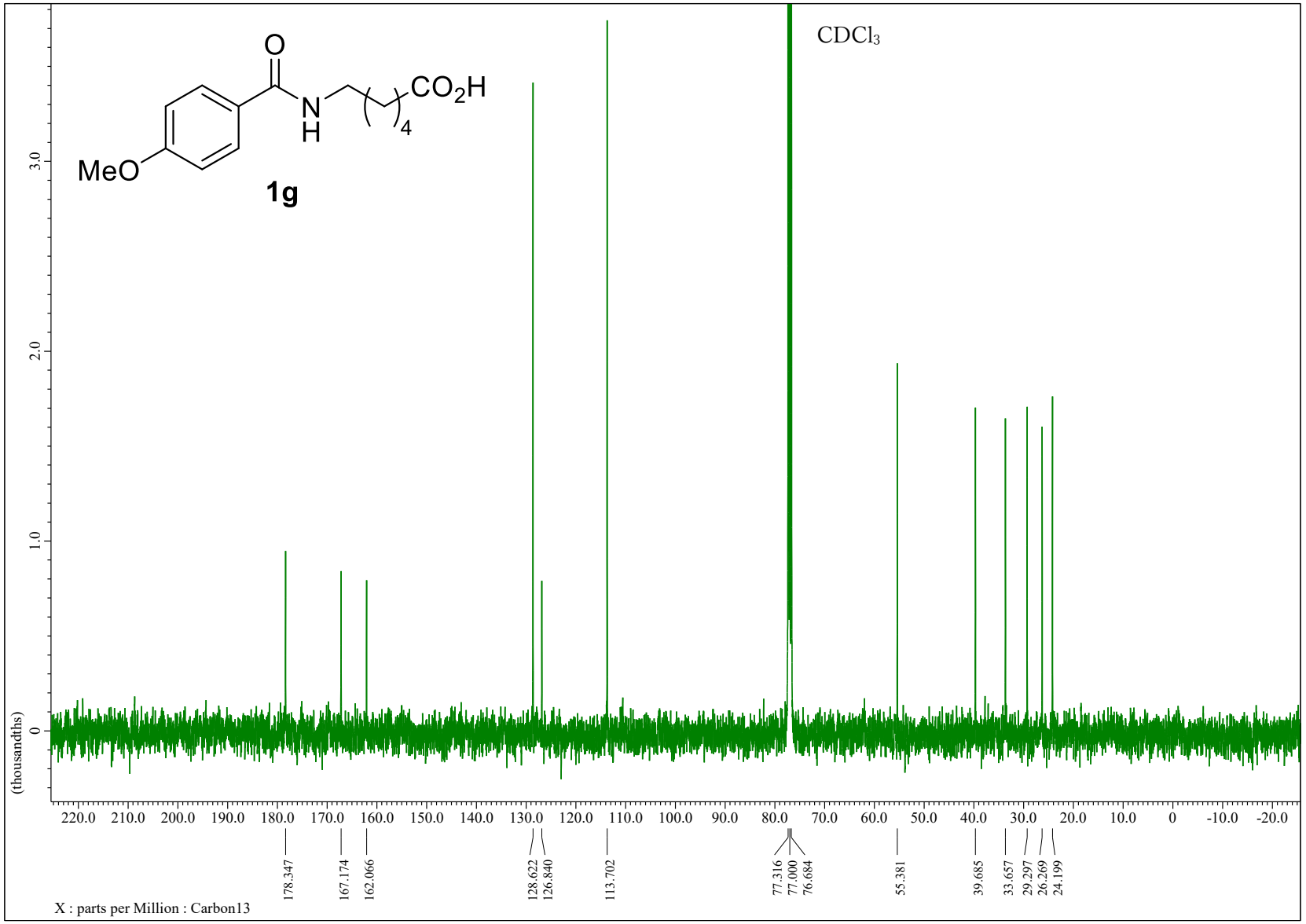

CN
CN
O
N
H
7a
CHCl3
H2O
5.89
4.03
1.09
1.11
0.98
0.89
0.42
0.54
0.46
1.67
1.33
(thousandths)
X : parts per Million : Proton

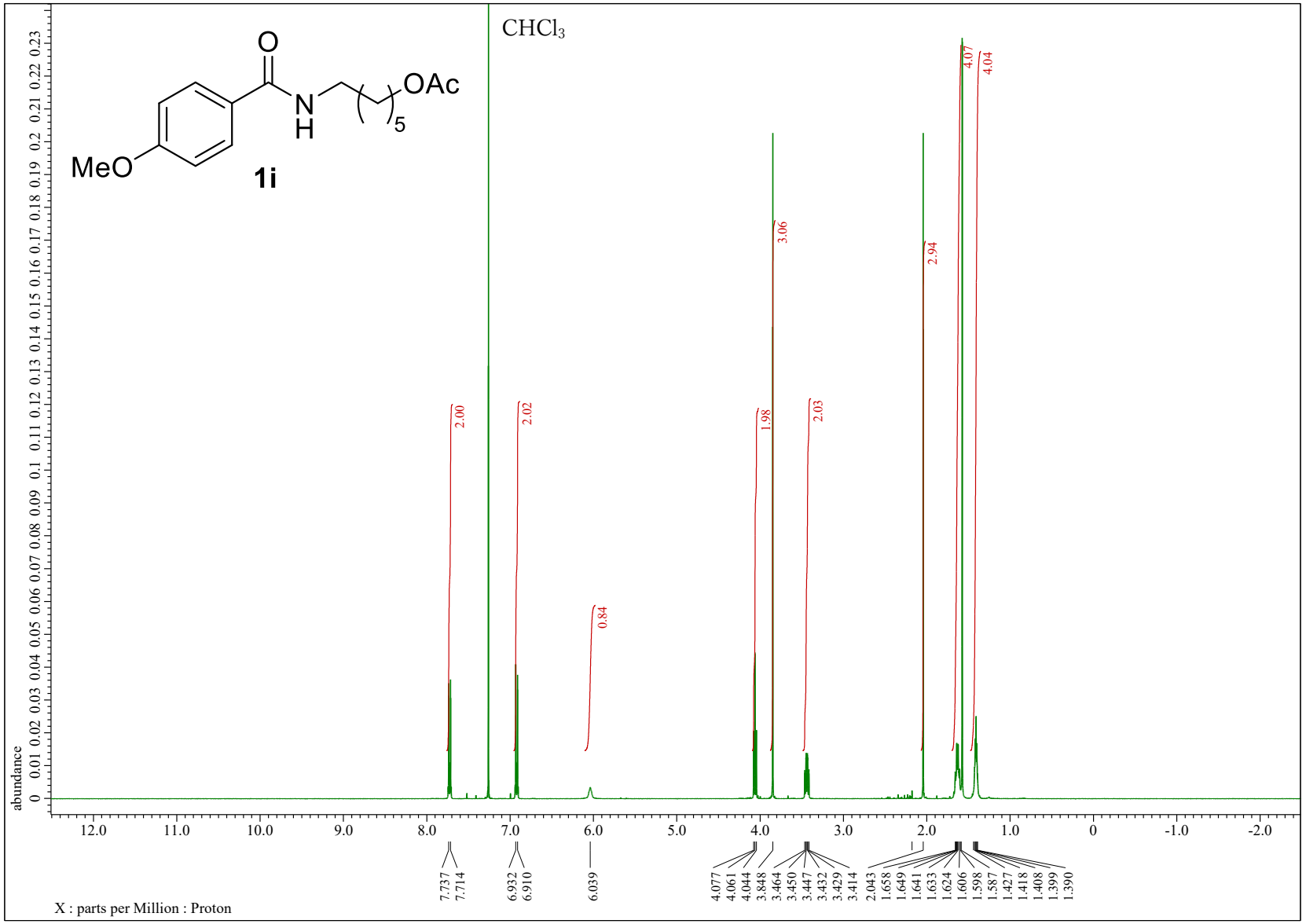

CN
CN
O
N
H
7a
CDCl3
(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0 24.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
168.582
168.285
133.097
132.216
129.456
129.207
128.843
128.766
128.699
128.363
127.108
126.830
112.993
112.811
112.054
111.948
77.316
77.000
76.684
52.487
51.730
51.596
50.408
35.756
34.462
27.419
26.825
19.427
19.063
13.572
13.524
X : parts per Million : Carbon13

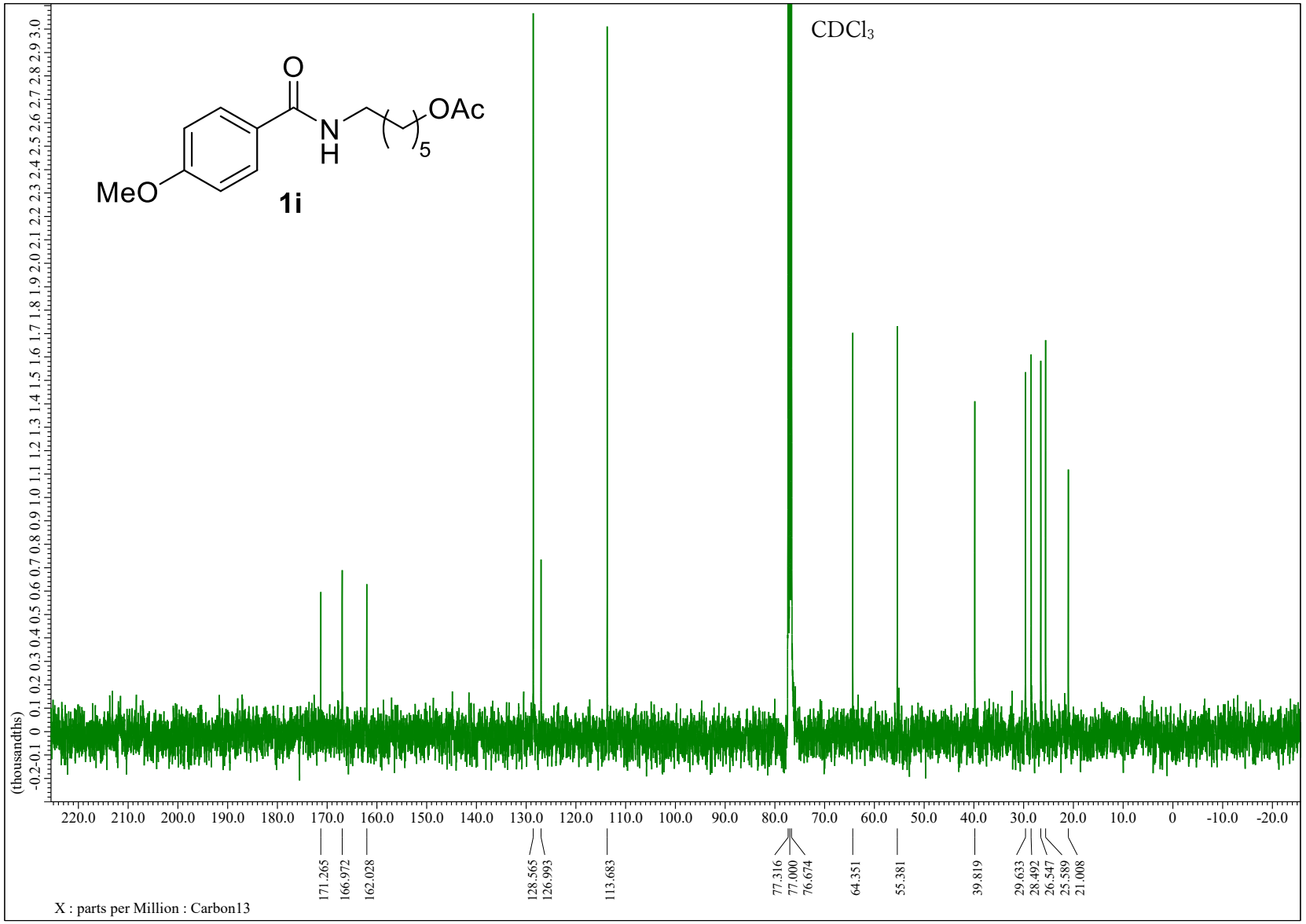

O
Me
N
H
O
4
O
1f
abundance
2.01
2.00
CHCl3
1.00
0.81
2.02
1.95
2.99
1.98
4.09
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.051
8.047
8.045
8.043
8.031
8.026
8.022
7.561
7.546
7.543
7.462
7.442
7.423
7.260
5.495
4.341
4.325
4.309
3.296
3.279
3.264
3.246
1.968
1.814
1.797
1.777
1.605
1.601
1.587
1.583
1.565
1.494
1.476
1.453
X : parts per Million : Proton

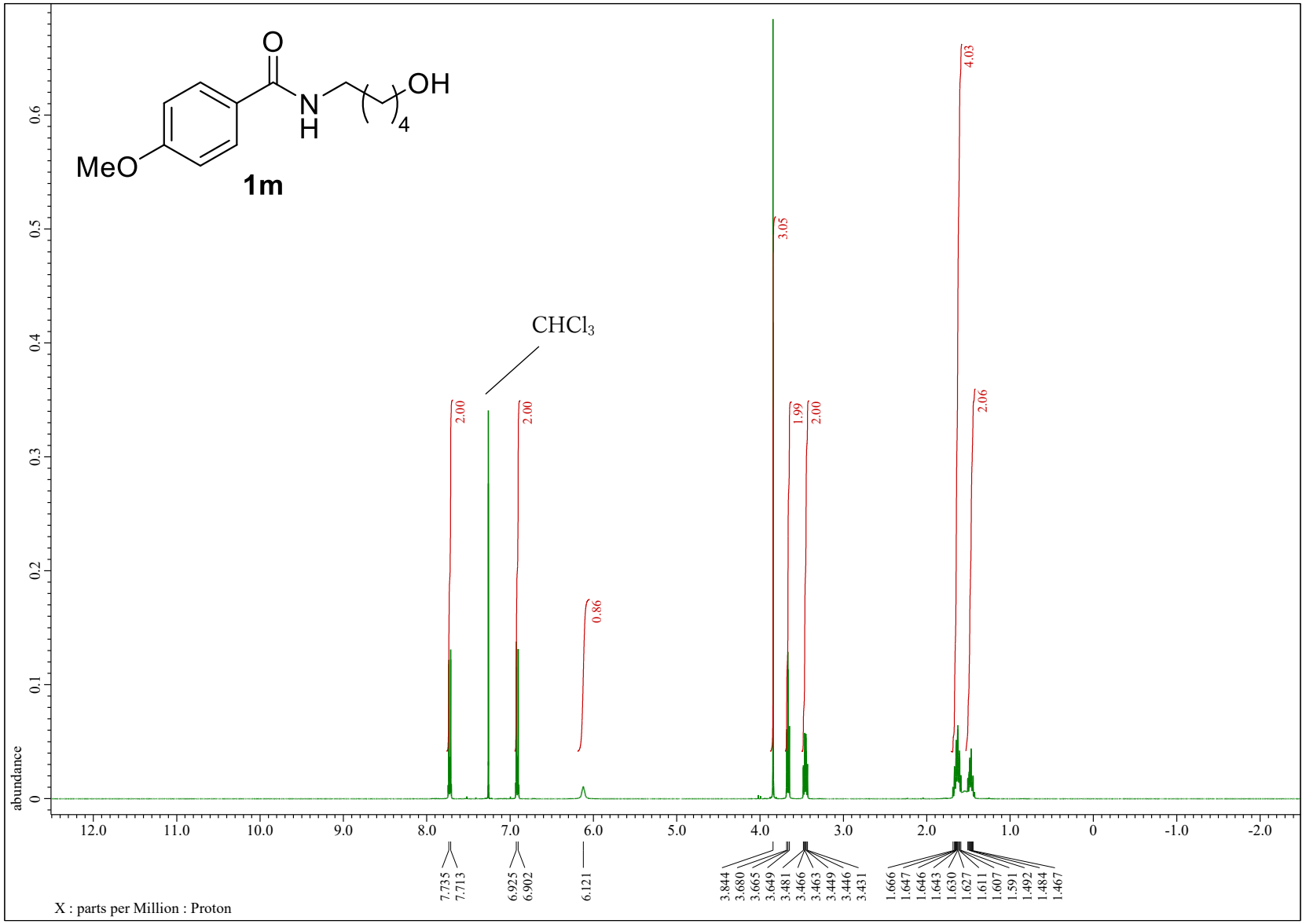

CDCl3
1f
(thousandths)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
170.072
166.670
132.910
130.290
129.513
128.349
77.319
77.000
76.684
64.619
39.460
29.213
28.392
23.353
23.330
X : parts per Million : Carbon13

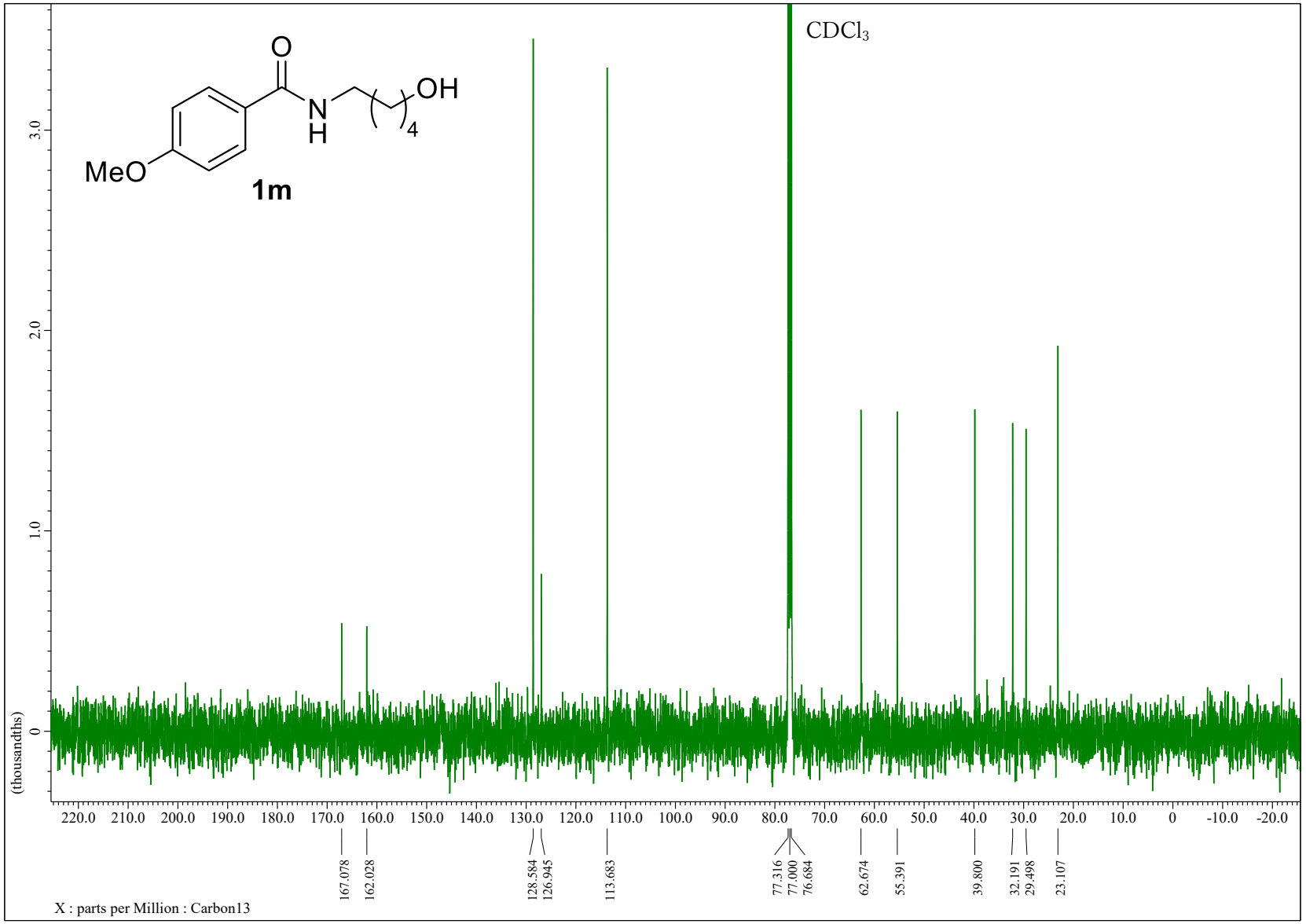

O
N
H
CO2H
4
MeO
1g
CHCl3
3.96
3.03
2.00
2.02
1.99
2.00
1.98
0.92
abundance
X : parts per Million : Proton
7.736
7.714
6.925
6.903
6.139
6.127
6.115
3.842
3.475
3.457
3.442
3.425
2.396
2.378
2.360
1.709
1.690
1.671
1.654
1.637
1.618
1.457
1.439
1.418


O
N
H
CO2H
4
MeO
1g
CDCl3
(thousandths)
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
178.347
167.174
162.066
128.622
126.840
113.702
77.316
77.000
76.684
55.381
39.685
33.657
29.297
26.269
24.199
X : parts per Million : Carbon13


O
N
H
OAc
5
MeO
1i
CHCl3
2.00
2.02
0.84
1.98
2.03
3.06
2.94
4.07
4.04
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.737
7.714
6.932
6.910
6.039
4.077
4.061
4.044
3.848
3.464
3.450
3.447
3.432
3.429
3.414
2.043
1.658
1.649
1.641
1.633
1.624
1.606
1.598
1.587
1.427
1.418
1.408
1.399
1.390
X : parts per Million : Proton


CDCl3
O
N
H
OAc
5
MeO
1i
(thousandths)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
171.265
166.972
162.028
128.565
126.993
113.683
77.316
77.000
76.674
64.351
55.381
39.819
29.633
28.492
26.547
25.589
21.008
X : parts per Million : Carbon13


O
N
H
OH
4
MeO
1m
CHCl3
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
2.00
2.00
0.86
3.05
1.99
2.00
4.03
2.06
7.735
7.713
6.925
6.902
6.121
3.844
3.680
3.665
3.649
3.481
3.466
3.463
3.449
3.446
3.431
1.666
1.647
1.646
1.643
1.630
1.627
1.611
1.607
1.591
1.492
1.484
1.467
X : parts per Million : Proton


O
N
H
OH
4
MeO
1m
CDCl3
(thousandths)
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.078
162.028
128.584
126.945
113.683
77.316
77.000
76.684
62.674
55.391
39.800
32.191
29.498
23.107
X : parts per Million : Carbon13