Supplementary Information (SI) for ChemComm.

Enhancing Selectivity of Cleavage β-O-4 Bond for Lignin Depolymerization via Sacrificial Anode

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Contents

1 General information

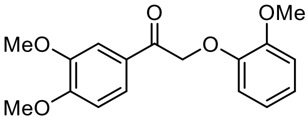
Unless otherwise noted, chemicals were purchased from Energy-Chemical company and used without further purification. The wasted woods were obtained from local plant. The extraction and oxidation of lignin are based on the methods described in literature.[1-3] The instrument for electrolysis is four-display galvanostat (HSPY-120-1, Hanshengpuyuan Instruments). Cyclic voltammograms were screened on an electrochemical workstation (CS Studio5, Correst Instruments). All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz, which relative to tetramethylsilane $CDCl_3$ (0 ppm for 1H, 77.00 ppm for 13C), respectively. Short-range ^{13}C-^{1}H correlation (HSQC) NMR spectra were recorded on 400 MHz Bruker spectrometer using DMSO-d_6 as solvent. Normal HSQC experiments were conducted as following parameters: acquired from 9 to 0 ppm in F2 (1H) using 1864 data points (acquisition time of 200 ms), 160 to 0 ppm in F1(^{13}C) using 512 increments (F1 acquisition time of 11.3 ms) of 16 scans with a 1 s interscan delay, total acquisition time of 168 min; the d24 delay was set to 1.72 ms (approximately 1/4 J). Aluminum sheet, magnesium sheet, iron sheet are purchased from the Internet, the purity is 99.9%. Carbon sheet and other electrode materials purchased from Gaoss Union (Tianjin) Photoelectric Technology Co., Ltd. All working electrodes are polished and cleaned with ethanol before use.

2 Synthesis of lignin model substrates:

2.1 General procedure for the synthesis of keto aryl ethers

2-Bromo-1-(3,4-dimethoxyphenyl)ethanone (2.6 g, 10.0 mmol), anhydrous K_2CO_3 (1.4 g, 10.1 mmol) and the corresponding phenol derivative (10.2 mmol) were dissolved in acetone (30 mL). The reaction mixture was stirred at room temperature overnight. The reaction mixture was filtered and concentrated under reduced pressure to afford the crude product, which was purified by flash chromatography on silica gel or recrystallization to give target product.

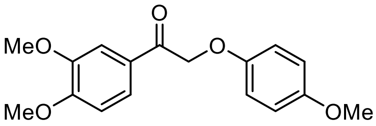
1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (1a)[4]:



^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.68 (dd, J = 8.4, 1.9 Hz, 1H), 7.60 (d, J= 1.9 Hz 1H), 6.98 - 6.89(m, 3H), 6.85 - 6.84 (m, 2H), 5.29 (s, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ =193.40, 153.92, 149.82, 149.31, 147.68, 127.96, 122.88, 122.46, 120.92, 114.79, 112.26, 110.56, 110.23, 72.14, 56.22, 56.12, 56.01.

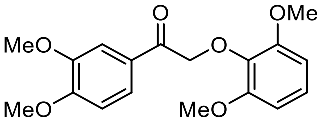
1-(3,4-dimethoxyphenyl)-2-(4-methoxyphenoxy)ethan-1-one (1b)[5]:



^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.65 (dd, J = 8.4, 2.0 Hz, 1H), 7.58 - 7.56 (m, 1H), 6.91 -6.88(m, 3H), 6.83 - 6.81 (m, 2H), 5.17 (s, 2H), 3.95 (s, 3H), 3.93 (s, 3H) 3.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.64, 154.53, 153.97, 152.40, 149.36, 127.93, 122.93, 116.06, 114.80, 110.47, 110.23, 71.79, 56.22, 56.13, 55.79.

2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethan-1-one (1c)[4]:



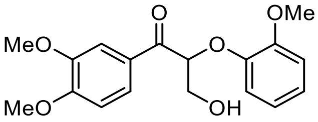
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 8.4, 1.7 Hz, 1H), 7.65 (d, J = 1.7 Hz, 1H), 7.00 (t, J = 8.4 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.58 (d, J = 8.4 Hz, 2H), 5.14 (s, 2H), 3.94 (s, 6H), 3.81 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.82, 153.49, 153.34, 149.09, 136.76, 128.48, 124.15, 123.14, 110.77, 110.13, 105.44, 75.37, 56.18, 56.15, 56.13.

2.2 Procedure for the preparation of 1d

1a (2.6 g, 8.7 mmol, 1.0 eq.), paraformaldehyde (0.32 g, 10.4 mmol, 1.2 eq.) and anhydrous K_2CO_3 (0.06 g, 0.43 mmol, 0.05 eq.) were dissolved in dry DMSO (20 mL). The mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was quenched with distilled water (20 mL) and extracted ethyl acetate (30 mL x 2). The organic layer was washed with saturated brine (20 mL) and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1:1) to obtain the desired product 1d (2.3 g, 7 mmol, 81%) as a white solid.

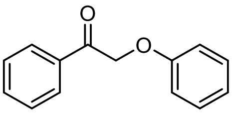
1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one (1d)[4]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 8.5, 2.0 Hz, 1H), 7.60(d, J = 2.0 Hz, 1H), 6.99 - 6.95 (m, 1H), 6.93 - 6.80 (m, 4H), 5.41 (t, J = 5.1 Hz 1H), 4.07 (d, J = 5.1 Hz 2H), 3.93 (s, 3H), 3.90 (s, 3H), 3.84 (s, 3H), 3.43(br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.07, 154.02, 150.25, 149.26, 146.97, 128.08, 123.67, 123.44, 121.24, 117.83, 112.34, 111.01, 110.20, 84.30, 63.79, 56.18, 56.04, 55.87.

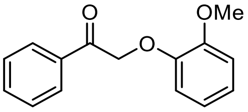
2-phenoxy-1-phenylethan-1-one (1e)[6]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 - 7.99 (d, 2H), 7.62 - 7.59 (m, 1H), 7.51 - 7.47 (m, 2H), 7.30 - 7.26 (m, 2H), 7.00 - 6.93 (m, 3H), 5.26 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.64, 158.07, 134.66, 133.94, 129.65, 128.90, 128.21, 121.73, 114.89, 70.86.

2-(2-methoxyphenoxy)-1-phenylethan-1-one (1f)[6]:



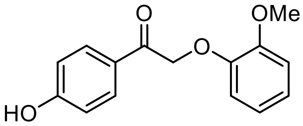
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 - 8.00 (m, 2H), 7.64 - 7.57 (m, 1H), 7.55 - 7.46 (m, 2H), 7.01 - 6.88 (m, 2H), 6.88 - 6.83 (m, 2H), 5.34 (s, 2H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.64, 149.89, 147.60, 134.72, 133.82, 128.85, 128.16, 122.58, 120.87, 115.02, 112.31, 77.12, 72.21, 56.00.

2.3 Procedure for the preparation of 1g:

Synthesis method according to literature[7]

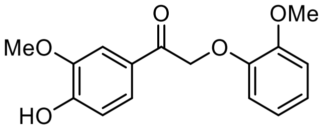
1-(4-hydroxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (1g)[6]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.62 (m, 1H), 7.06 - 7.04 (m, 1H), 6.93 - 6.88 (m, 3H),6.84 - 6.79(m, 2H) 5.25 (s, 2H), 3.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.39, 157.67, 149.76, 147.71, 147.38, 146.28, 127.78, 122.12, 120.81, 114.40, 113.70, 111.73, 109.73, 63.44, 55.83

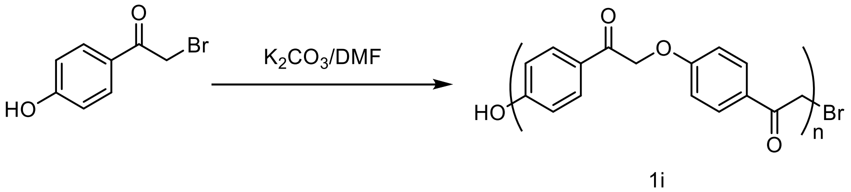
1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (1h)[6]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 - 7.61 (m, 1H), 7.57 - 7.55 (m, 1H), 6.99 - 6.78 (m, 5H), 5.25 (s, 2H), 3.90 (s, 3H), 3.72 (s, 3H).

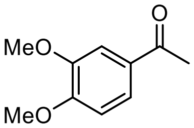
^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.43, 158.09, 152.91, 149.95, 147.86, 146.37, 127.94, 122.13, 121.04, 114.74, 114.02, 112.15, 109.78, 63.78, 55.96

2.4 Procedure for the preparation of 1i[8]



4-hydroxyacetophenone (1.64 g, 13.2 mmol) and anhydrous K_2CO_3 (3.31 g, 24 mmol) were added to N, N-dimethylformamide solution (20 mL) at room temperature, and the reaction mixture was stirred at room temperature for 24 h. After the reaction was over, 20 mL of ice water was poured into the reaction mixture. Pour out the liquid, then wash with deionized water and saturated sodium chloride solution, wash with ethanol, completely filter out the solid, and dry to obtain the polymerization model reactants of lignin.

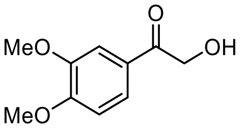
3 Analytical data of products



1-(3,4-dimethoxyphenyl)ethan-1-one (2a)[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 - 7.55 (dd, J = 8.4, 2.1 Hz, 1H), 7.51 - 7.50 (d, J = 2.1 Hz, 1H), 6.88 - 6.86 (d, J = 8.4 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 2.55 (s, 3H).

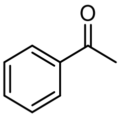
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.92, 153.30, 148.99, 130.49, 123.36, 110.02, 109.94, 56.12, 26.29.



1-(3,4-dimethoxyphenyl)-2-hydroxyethan-1-one (2b)[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 - 7.53 (dd, J = 8.4, 1.6 Hz, 1H), 7.47 - 7.47 (d, J = 1.4 Hz 1H), 6.86 - 6.84 (d, J = 8.4 Hz, 1H), 3.98 -3.96 (t, J = 5.4 Hz, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 3.16 - 3.13 (t, *J* = 5.4 Hz,2H), 2.98 (s, 1H).

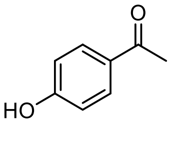
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.99, 153.54, 148.97, 129.85, 122.98, 109.98, 109.79, 58.22, 56.06, 55.93, 39.88.



Acetophenone (2c)[6]:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 - 7.90 (m, 2H), 7.56 - 7.53 (m, 1H), 7.46 - 7.42 (m, 2H), 2.59 (s, 3H).

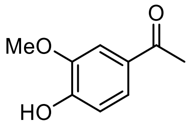
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.21, 137.07, 133.13, 128.58, 128.31, 26.64.



1-(4-hydroxyphenyl)ethan-1-one (2d)[4]:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (br, 1H), 7.92 - 7.90 (d, J = 8.7 Hz, 2H), 6.98 - 6.95 (d, J = 8.7 Hz, 2H), 2.59 (s, 3H).

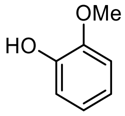
^{13}C NMR (101 MHz, CDCl$_3$) δ 199.24, 161.85, 131.39, 129.28, 115.69, 26.37.



1-(4-hydroxy-3-methoxyphenyl)ethan-1-one (2e)[4]:

^{1}H NMR (400 MHz, CDCl$_3$)δ 7.53 (d, *J* = 4.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.09 (s, 1H), 3.95 (s, 3H), 2.56 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 150.49 , 146.71 , 130.35 , 124.11 , 113.86 , 109.81 , 77.12 , 56.19 , 26.30 .

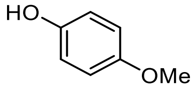


2-methoxyphenol (3a)[4]:

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.01 - 6.98 (m, 1H), 6.94 - 6.89 (m, 3H), 5.88 (br, 1H), 3.89(s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 146.60, 145.62, 121.42, 120.16, 114.59, 110.77, 55.81.

NMR data are consistent with those previously reported in the literature

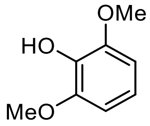


4-methoxyphenol (3b)[5]:

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.81 - 6.76 (m, 4H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 153.86, 149.49, 116.11, 114.90, 55.87.

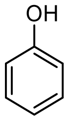
NMR data are consistent with those previously reported in the literature



2,6-dimethoxyphenol (3c)[4]:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.83 - 6.78 (t, J = 8.3 Hz, 1H), 6.60 - 6.58 (d, J = 8.3 Hz, 3H), 5.56 (br, 1H), 3.89 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 147.28, 134.84, 119.14, 104.90, 56.32.



Phenol (3d)[6]:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 - 7.24 (m, 2H), 6.96 - 6.93 (t, *J* = 7.4 Hz, 1H), 6.86 - 6.84 (m, 2H), 5.41 (br, 1H).

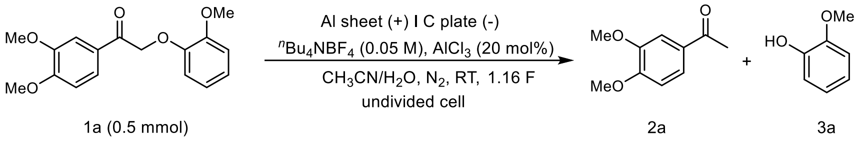
^{13}C NMR (101 MHz, CDCl$_3$) δ 155.53, 129.76, 120.84, 115.39.

4 Cleavage of C_{β}-O-4 bond of Lignin models

4.1 General procedure for the reaction of 1a under various conditions

To an oven-dried undivided three-necked bottle (25 mL) equipped with a stir-bar, lignin model compound 1a (0.5 mmol) and electrolyte (0.5 mmol) were added. After equipping with aluminium sheet (25 mm × 15 mm), iron sheet (25 mm × 15 mm), magnesium sheet (25 mm × 15 mm) as anode, and carbon plate (25 mm × 15 mm), carbon cloth (25 mm × 15 mm), carbon foam (25 mm × 15 mm) or graphite rod (Φ = 5 mm) as cathode, the reaction bottle was allowed to be vacuumed and purged with nitrogen for three times. Then, the corresponding solvent (CH3CN/H2O = 9/1, 10 mL) was injected by syringe. The electrodes were submerged in the solution. Finally, the reaction mixture was stirred for 75 – 110 mins at a constant current of 17 – 25 mA at room temperature. The yields of product 2a and 3a were obtained by GC analysis with biphenyl as the internal standard. Results were shown in Table 1 in the manuscript.

Table S1: The influence of aluminium salt.



Entry	Variation from the standard conditions	Yield (%)	
		2a	3a
1	no current	n.r.	n.r.
2	C plate as anode	24 (21)	10 (9)

To an oven-dried undivided three-necked bottle (25 mL) equipped with a stir-bar, lignin model compound 1a (0.5 mmol), ^{n}Bu$_4$NBF$_4$ (0.5 mmol) and AlCl$_3$ (20 mol%) were added. After equipping with carbon plate (25 mm × 15mm) or aluminium sheet (25 mm × 15 mm) as anode, and carbon plate (25 mm × 15 mm) as cathode, the reaction bottle was allowed to be vacuumed and purged with nitrogen for three times. Then, the corresponding solvent (CH$_3$CN/H$_2$O = 9/1, 10 mL) was injected by syringe. The electrodes were submerged in the solution. Finally, the reaction mixture was stirred for 110 mins at a constant current of 0 - 17 mA at room temperature. The yields of product 2a and 3a were obtained by GC analysis with biphenyl as the internal standard.

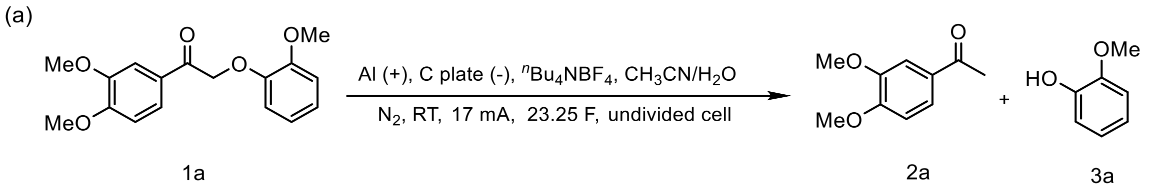
4.2 Standard procedure for the reaction of 1

To an oven-dried undivided three-necked bottle (25 mL) equipped with a stir-bar, lignin model compound 1 (0.5 mmol) and ^{n}Bu$_4$NBF$_4$ (0.5 mmol) were added. Then the bottle was equipped with aluminium sheet as anode (25 mm × 15 mm) and carbon plate as cathode (25 mm × 15 mm), and allowed to be vacuumed and purged with nitrogen for three times. After that, CH$_3$CN (9.0 mL) and H$_2$O (1.0 mL) were injected by syringe. The electrodes were submerged in the solution. The reaction mixture was stirred at a constant current of 17 mA at room temperature for 110 minutes, after which the reaction was stopped.

Namely, 1.16 F electricity was passed through the reaction, and TLC monitoring showed a full conversion of substrates was just achieved. The yields of products were obtained by GC analysis with biphenyl as the internal standard. Pure products were obtained through flash column chromatography on silica gel using a petroleum: ethyl acetate ratio of 5:1. Results were shown in Table 2 in the manuscript.

4.3 Standard procedure for the gram reaction of 1a

As shown in Table S1, continuous flow reaction was conducted with our customized device. The dosage of 1a and electrolyte were 10 mmol, 180 mL of CH_3CN and 20 mL of H_2O were used as the solvent. the anode (54 mm x 24 mm x 5 mm) was prepared from waste aluminum cans and carbon plate were used as cathodic electrode respectively. The reaction solution reacts or 2200, 150, 190, 220 mins under a constant current of 17 or 250 mA. Otherwise noted, the reaction was performed at room temperature.



Entry	Variation from the standard conditions	Cov.(%)	Yield (%)	
			2a	3a
1	17 mA, 23.25 F	63	62	61
2	250 mA, 23.25 F	70	30	44
3	250 mA, 27.97 F	85	69	80
4	250 mA, 29.53 F	93	57	70

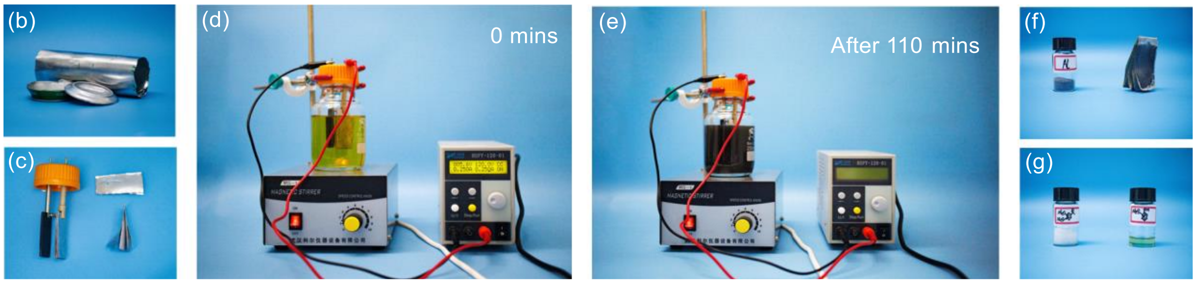


Fig. S1 (a) Gram reaction of 1a (b) Discarded aluminium can (c) Anodes were prepared from waste aluminium cans (d) At the beginning of reaction (e) After the reaction (f) Recycled aluminium and anodes (g) Separated product

4.4 Calculation of Faradic efficiency (FE)

$$FE = \left(\frac{m \times n \times F}{I \times t}\right) \times 100\%$$

FE = Faradaic Efficiency

m = Molar amount of products, mol

n = transferred electron numbers per molecule

F = Faraday's constant, 96485 C mol^{-1}

I = current value, A

t = reaction time, s

5 Mechanistic investigation

5.1 General procedures for cyclic voltammetry test

Cyclic voltammetry was performed in a three-electrode cell under nitrogen at room temperature. Glassy carbon disk electrode (0.19625 cm^{-2}, Φ = 3 mm), platinum wire and Ag/AgCl electrode were selected as the working, counter and reference electrode, respectively. Ag/AgCl electrode was submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. Subsequently, the substrate 1a/2a/3a, and solvents (MeCN/H_2O = 9/1 mL) containing 0.05 M ^{n}Bu$_4$NBF$_4$ were added into the electrochemical cell. All the substrates were measured at the concentration of 0.05 M. The scan rate was set as 0.05 V s^{-1} and test was ranged from [-3,0]

Results were shown in Fig. S2 blow.

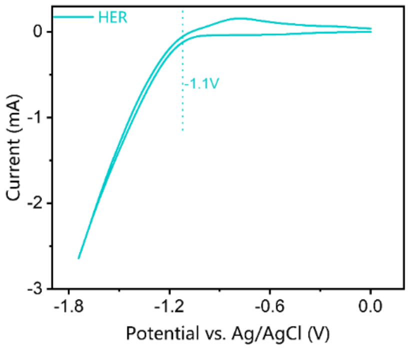
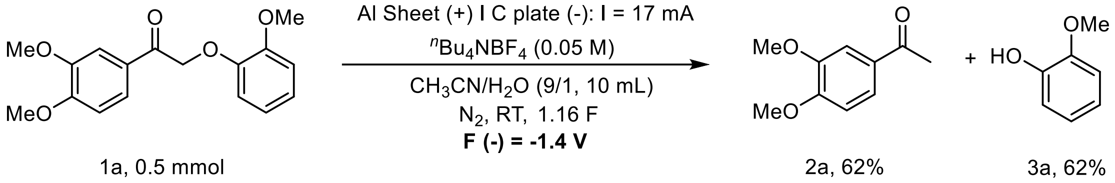
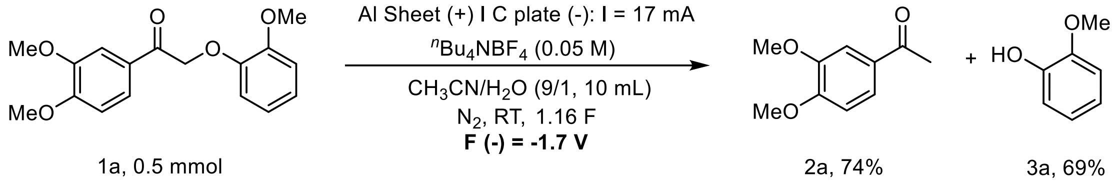


Fig. S2: CV spectra of HER at a scan rate of 50 mV s^{-1}.

5.2 Constant potential reaction procedures of 1a





Constant potential experiment was conducted as following: 1a (0.5 mmol) and ^{n}Bu$_4$NBF$_4$ (0.5 mmol) were mixed with CH_3CN/H_2O (9 mL/1 mL) under N_2 atmosphere in a three-electrode cell, which was equipped with carbon plate, nickel foam and Ag/AgCl electrode as anode, cathode and reference electrode, respectively. Plenty of ^{n}Bu$_4$NBF$_4$ was added in order to enhanced the conductivity of the electrolytic system.

Upon the completion of the electrolysis at constant potential of -1.7 V or -1.4 V for 126 mins or 180 mins at room temperature, yields of products was determined by GC analysis with biphenyl as the internal standard.

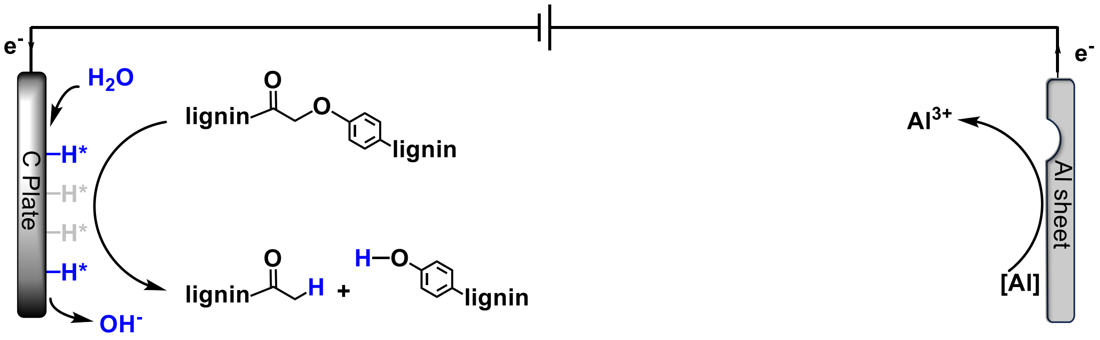


Fig. S3: A proposed catalytic mechanism of cleavage β-O-4 lignin model compounds.

6 Extraction, oxidation and depolymerization of lignin

6.1 Extraction of native lignin

Wasted poplar wood sawdust was dried at 333 K for 24 h before extraction. 60 g of wood sawdust, along with 400 mL of dioxane and 40 mL of 2 mol L^{-1} HCl aqueous solution, were mixed in a flask. The mixture was then heated to reflux under nitrogen atmosphere for 2 hours at 110 °C. Afterward, the mixture was filtered and rinsed with dioxane, and concentrated to yield a brown liquid-gel. Then the concentrated liquid was dissolved in a solution composed of acetone and water in a 9:1 ratio, amounting to 250 mL. Crude lignin was obtained through precipitation by adding this solution to 500 mL of water. The resulting crude lignin was dissolved in a solution of acetone and methanol in a 9:1 ratio again. The lignin was then regenerated by precipitation in 500 mL of diethyl ether, followed by filtration and vacuum drying at 60 °C to give a purified lignin

6.2 Oxidized poplar wood

Firstly, 400 mg of purified poplar lignin and 80 mg of 2,3-dichloro-5,6-dicyano-1,4benzoquinone (DDQ) were added into a 25 mL three-necked flask. Then, 2-methoxyethanol (2.4 mL) and 1,2-dimethoxyethane (3.6 mL) were injected to the flask via a syringe. Subsequently, ultrasound the mixtures until solid materials completely dissolved. Finally, 80 µL of ^{t}BuONO was transferred into the flask, and the resulting mixture was allowed to be stirred for 14 hours under an oxygen atmosphere at 80 °C. After that, the solvent was evaporated as much as possible. The oxidized lignin was precipitated after adding an appropriate amount of anhydrous ether and washing by ether for three times.

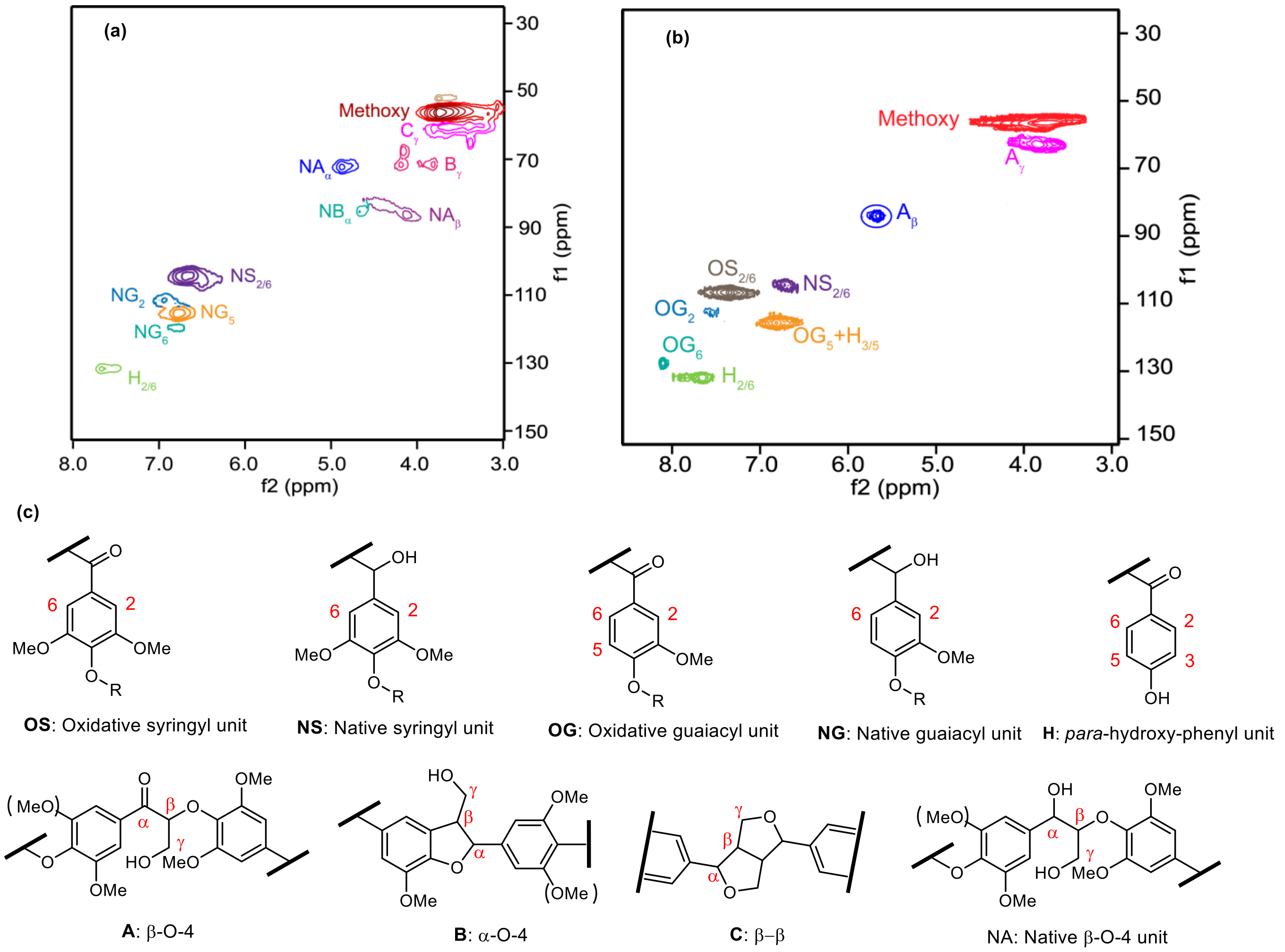


Fig. S4: HSQC spectrum of (a) native poplar lignin, (b) oxidized poplar lignin.

To an oven-dried undivided three-necked bottle (25 mL) equipped with a stir-bar, the oxidized poplar lignin (50.0 mg), ^{n}Bu$_4$NBF$_4$ (0.5 mmol) were added. Then the bottle was equipped with aluminium sheet as anode (25 mm × 15 mm) and carbon plate as cathode (25 mm × 15 mm), and allowed to be vacuumed and purged with nitrogen for three times. After that, CH_3CN (9.0 mL) and H_2O (1.0 mL) was injected via syringe. The electrodes were submerged in the solution. The reaction mixture was stirred and reacted at a constant current of 75 mA at 80 ℃ for 110 mins, after which the reaction was stopped. The yields of products with low-molecular weight were obtained by GC analysis with biphenyl as internal standard.

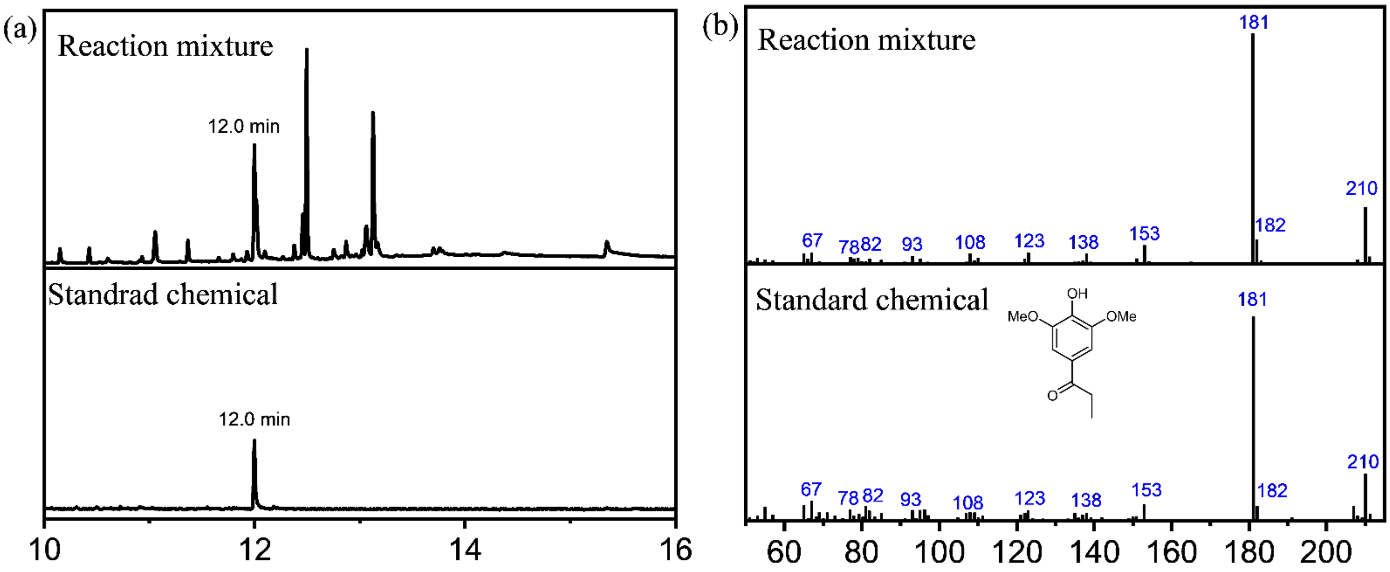
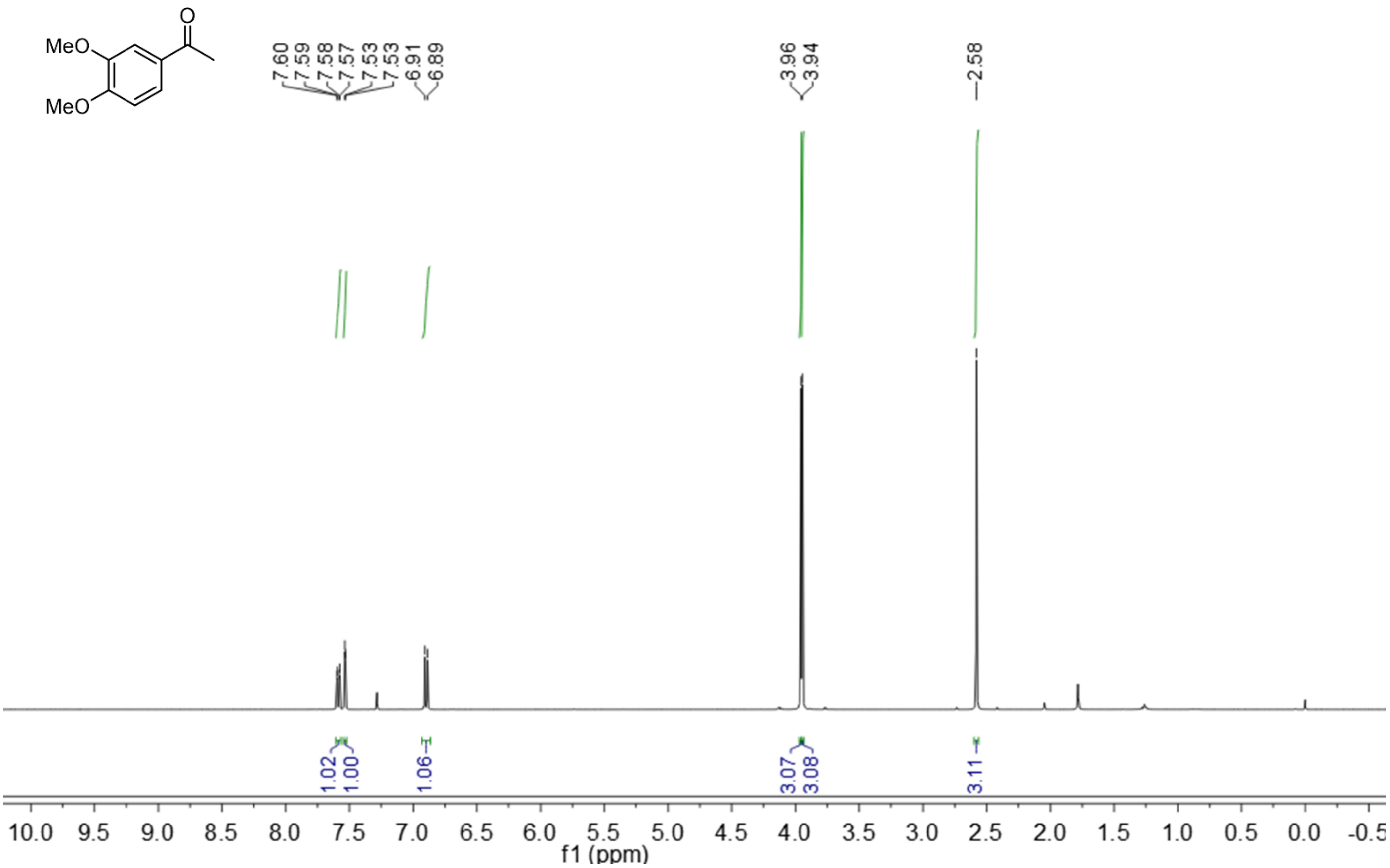


Fig. S5: Identification of product of oxidized poplar lignin depolymerization and mass spectrum of 3j.[9]

7 NMR spectra



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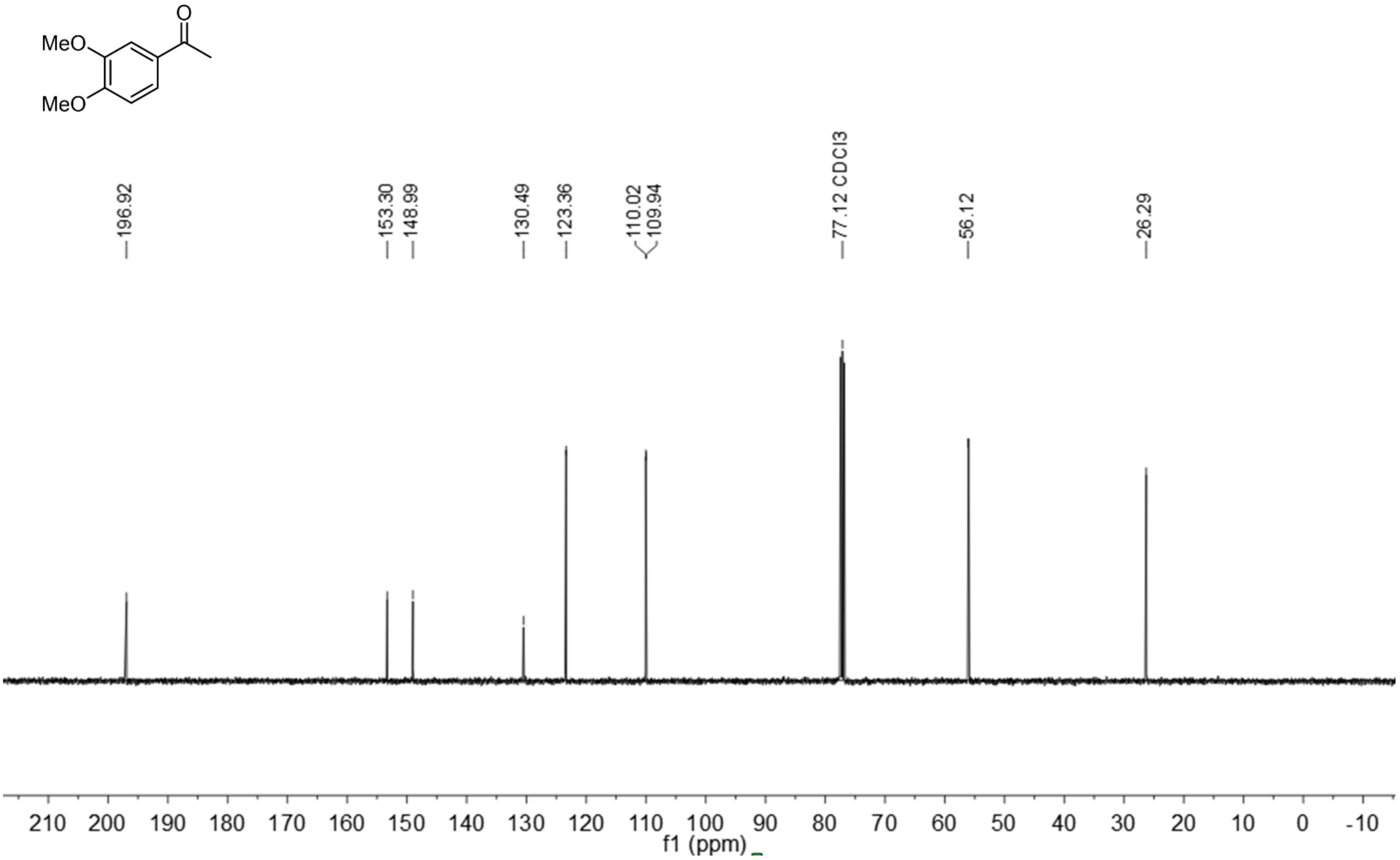

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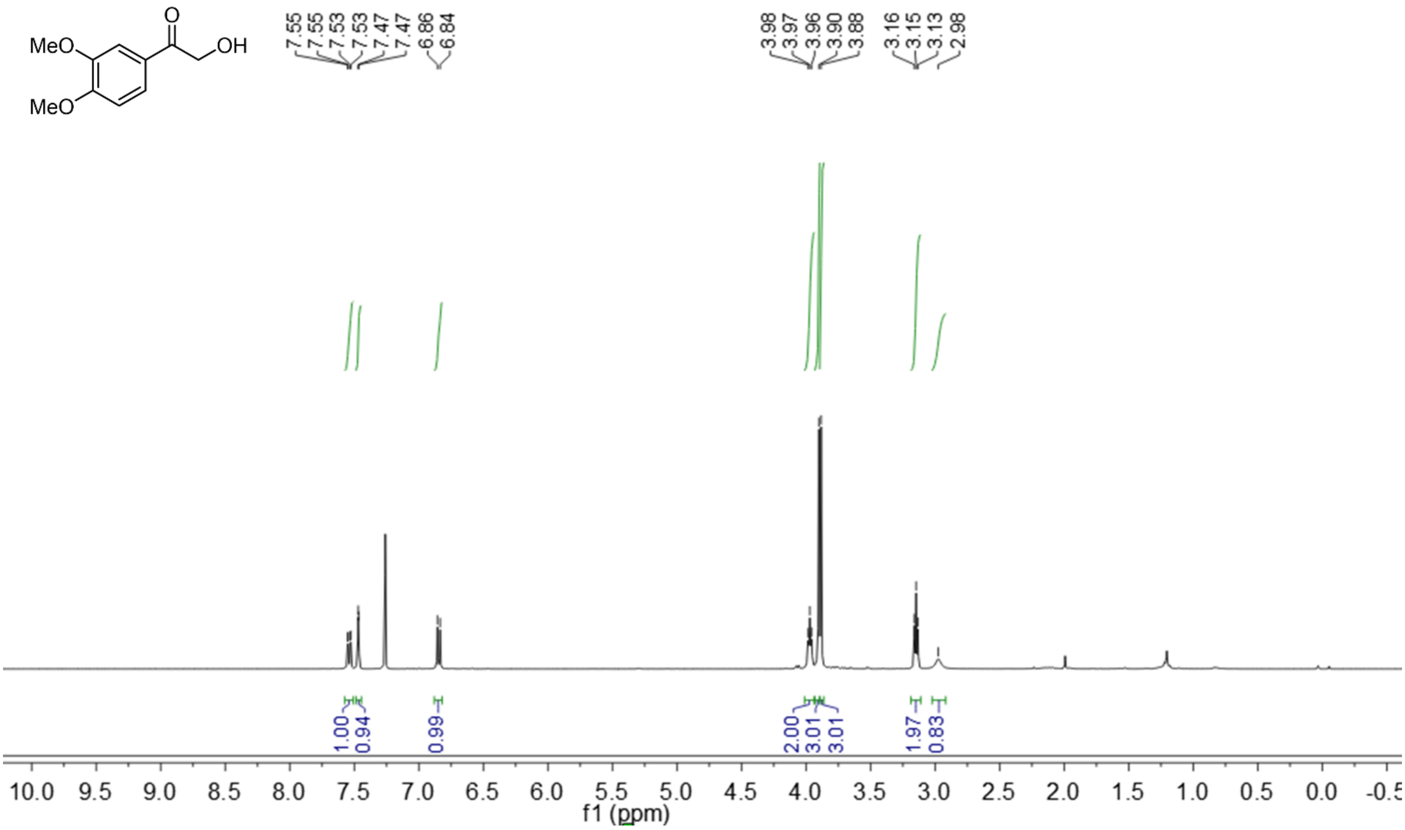

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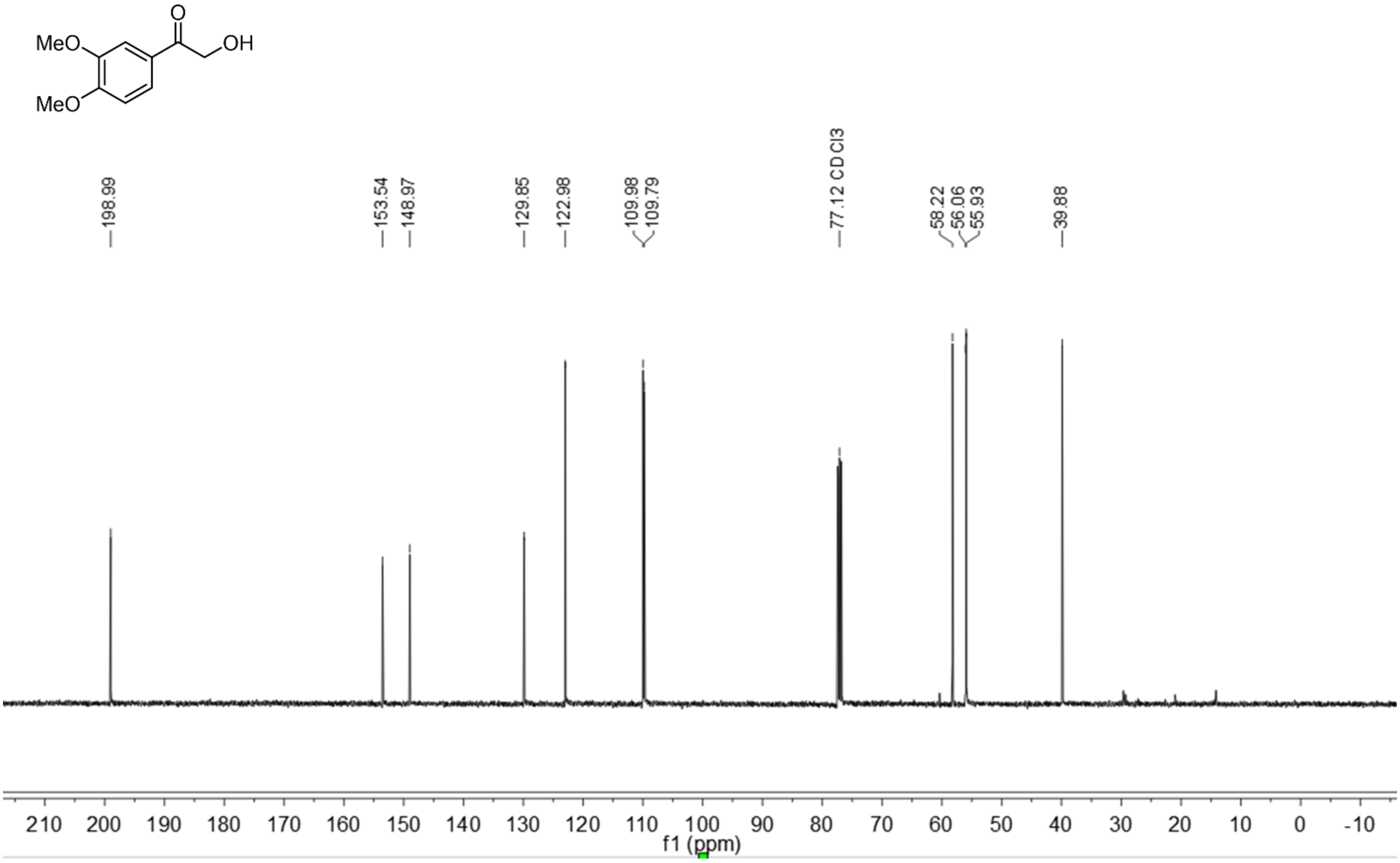

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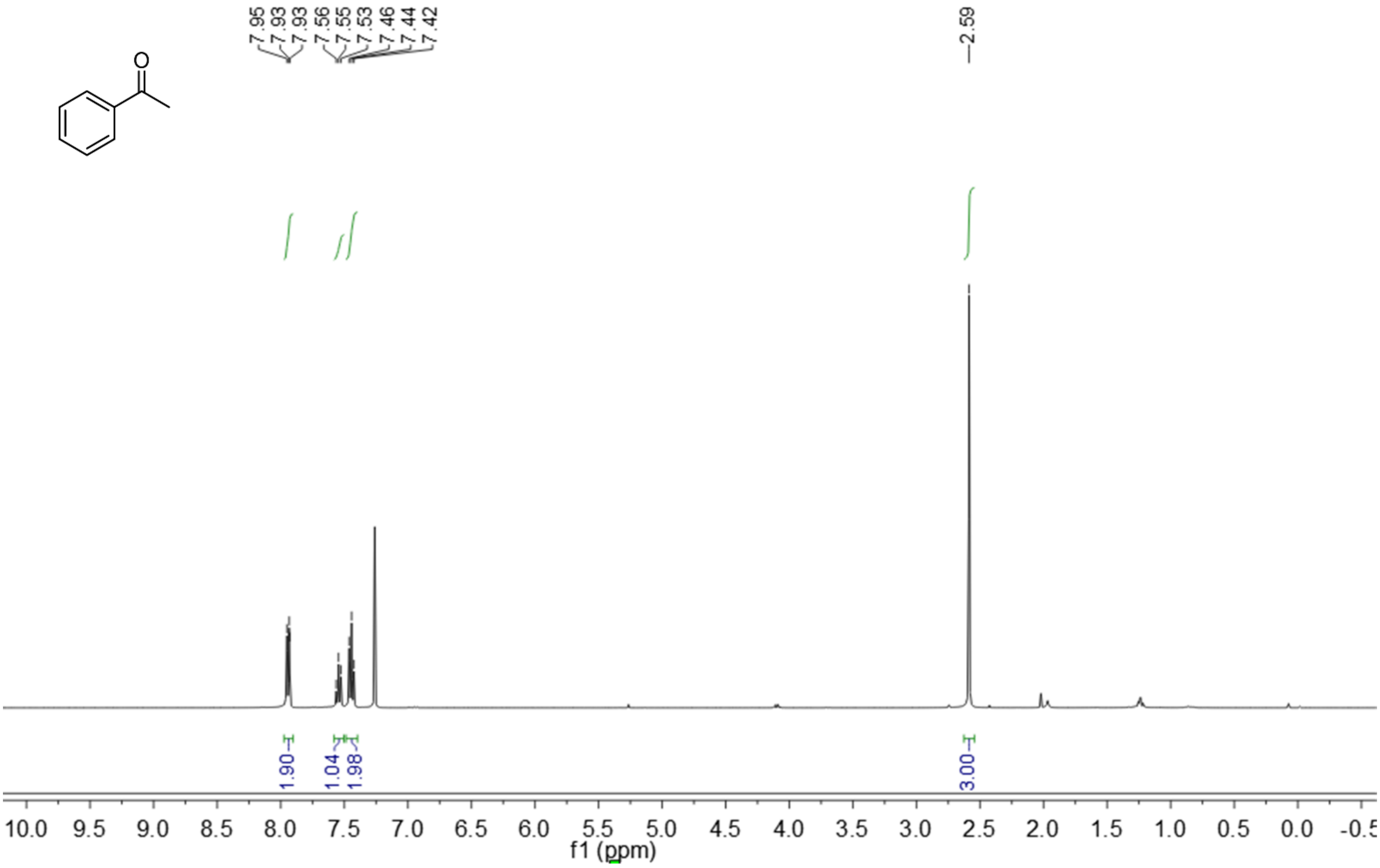

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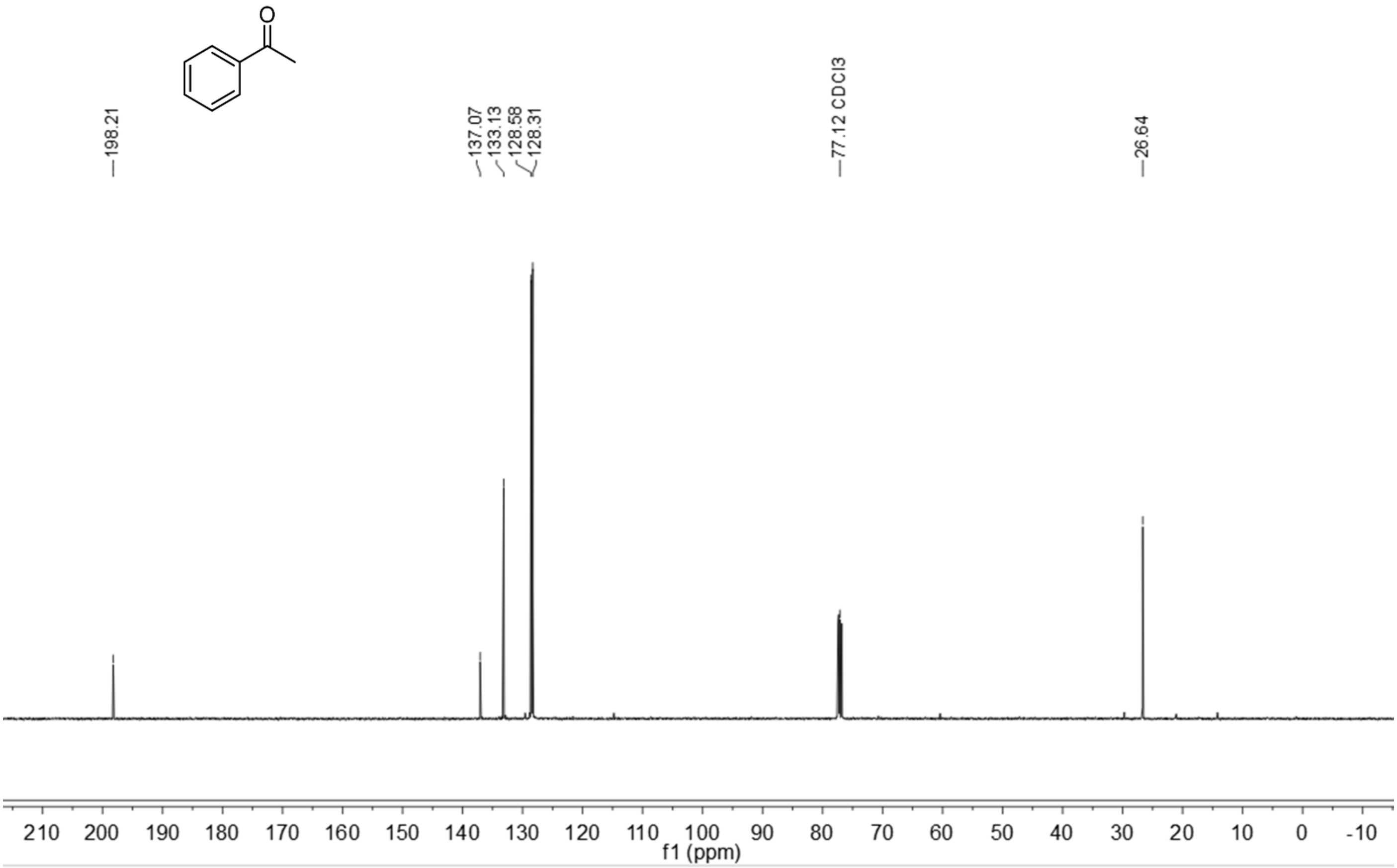

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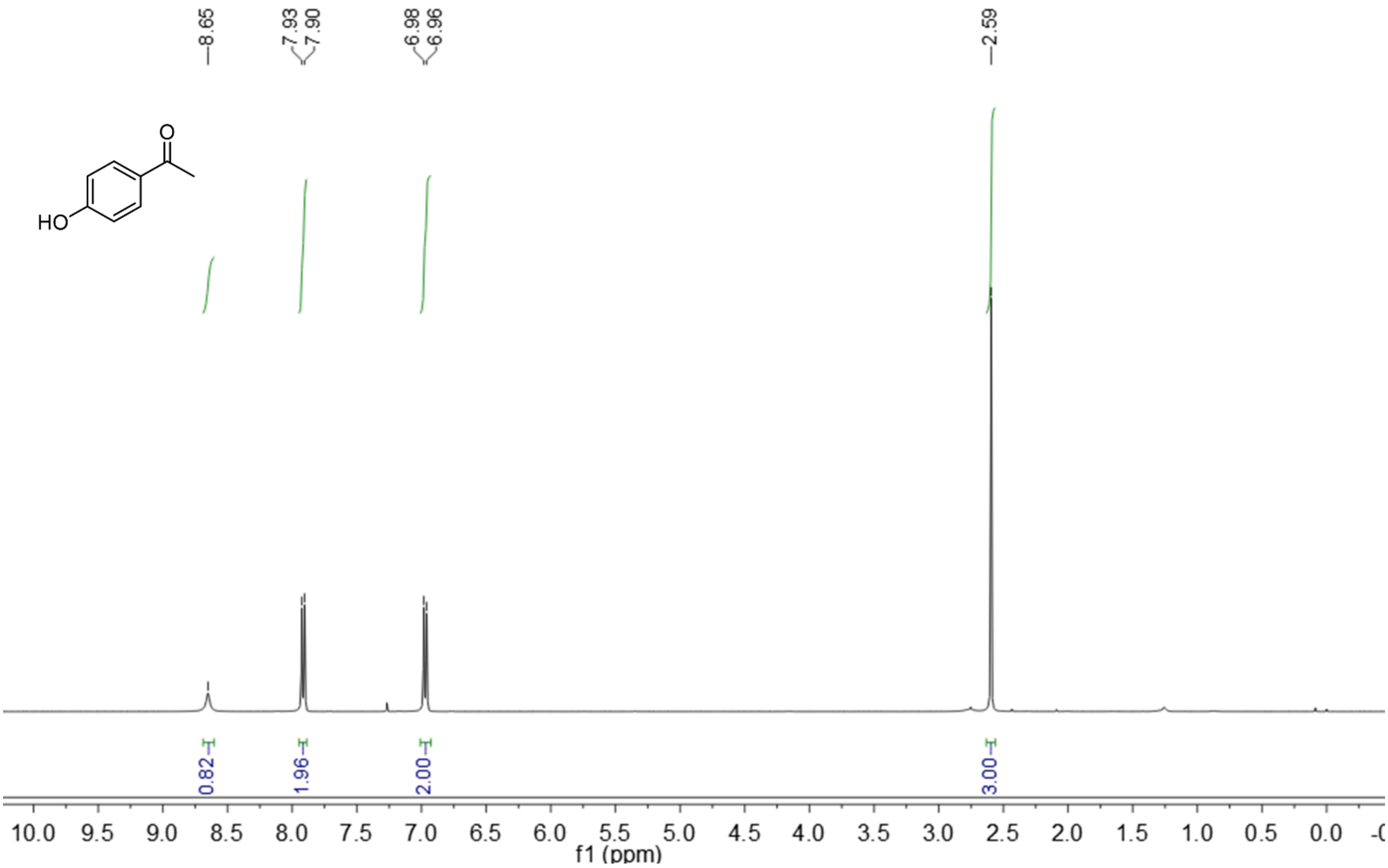

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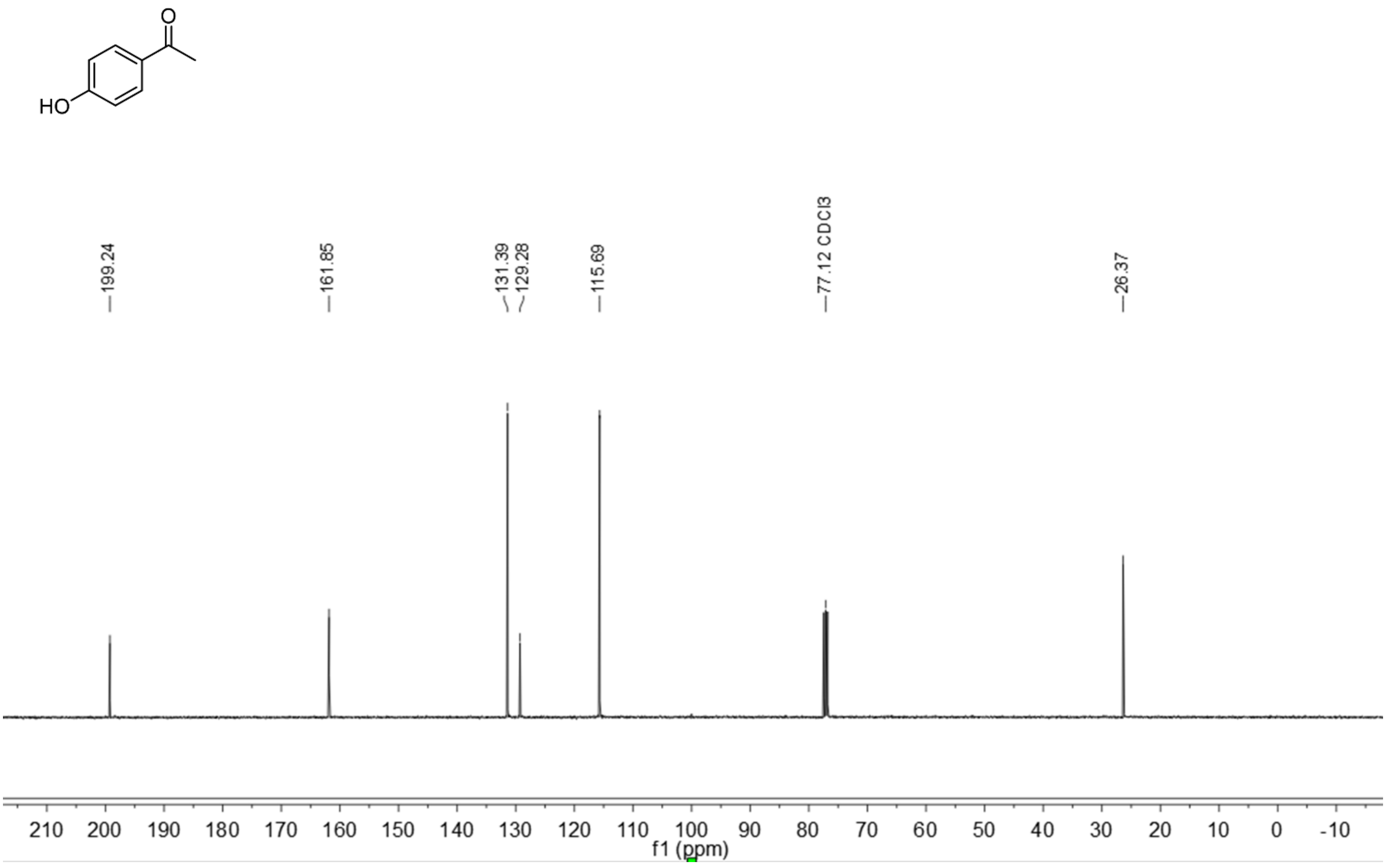

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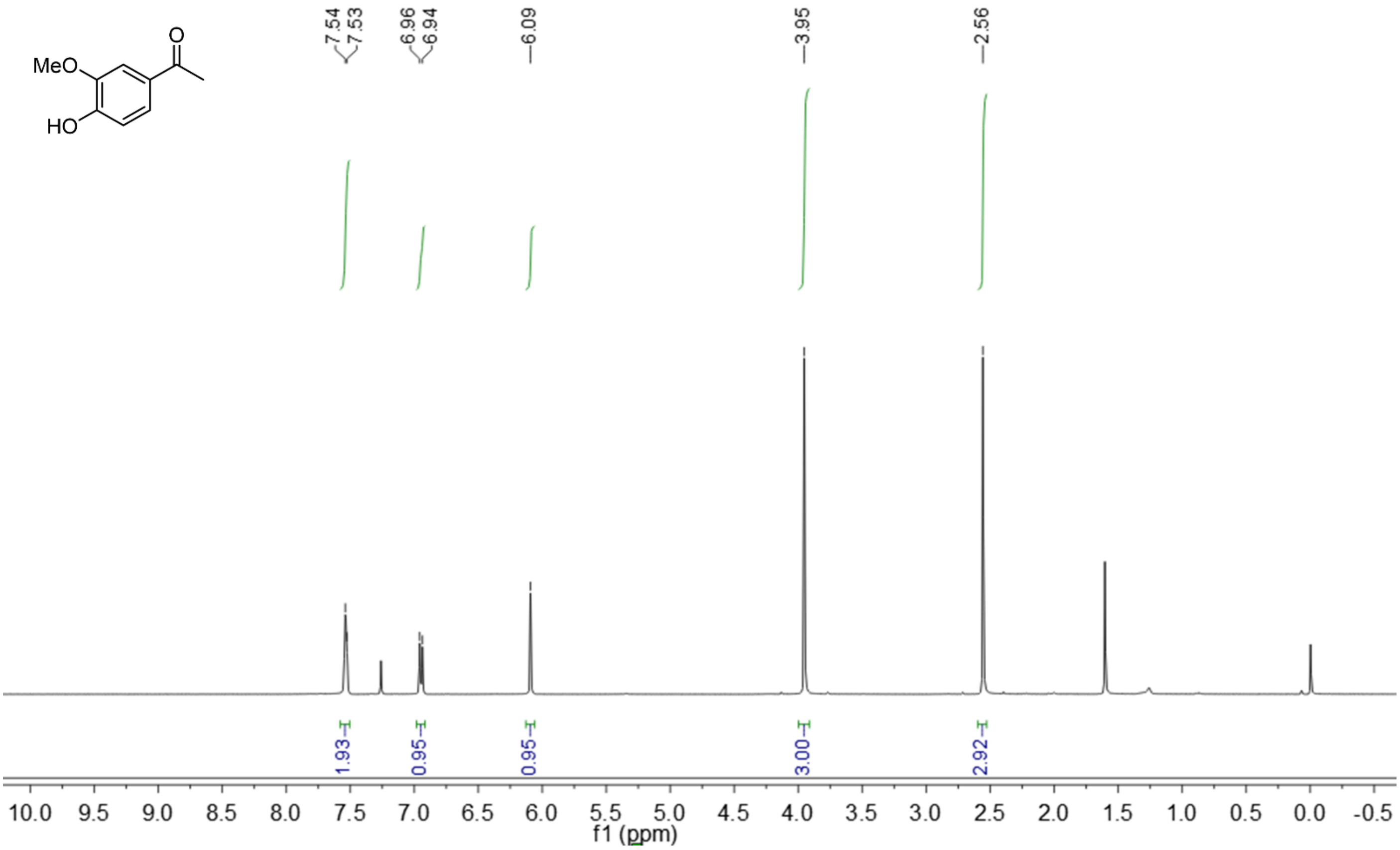

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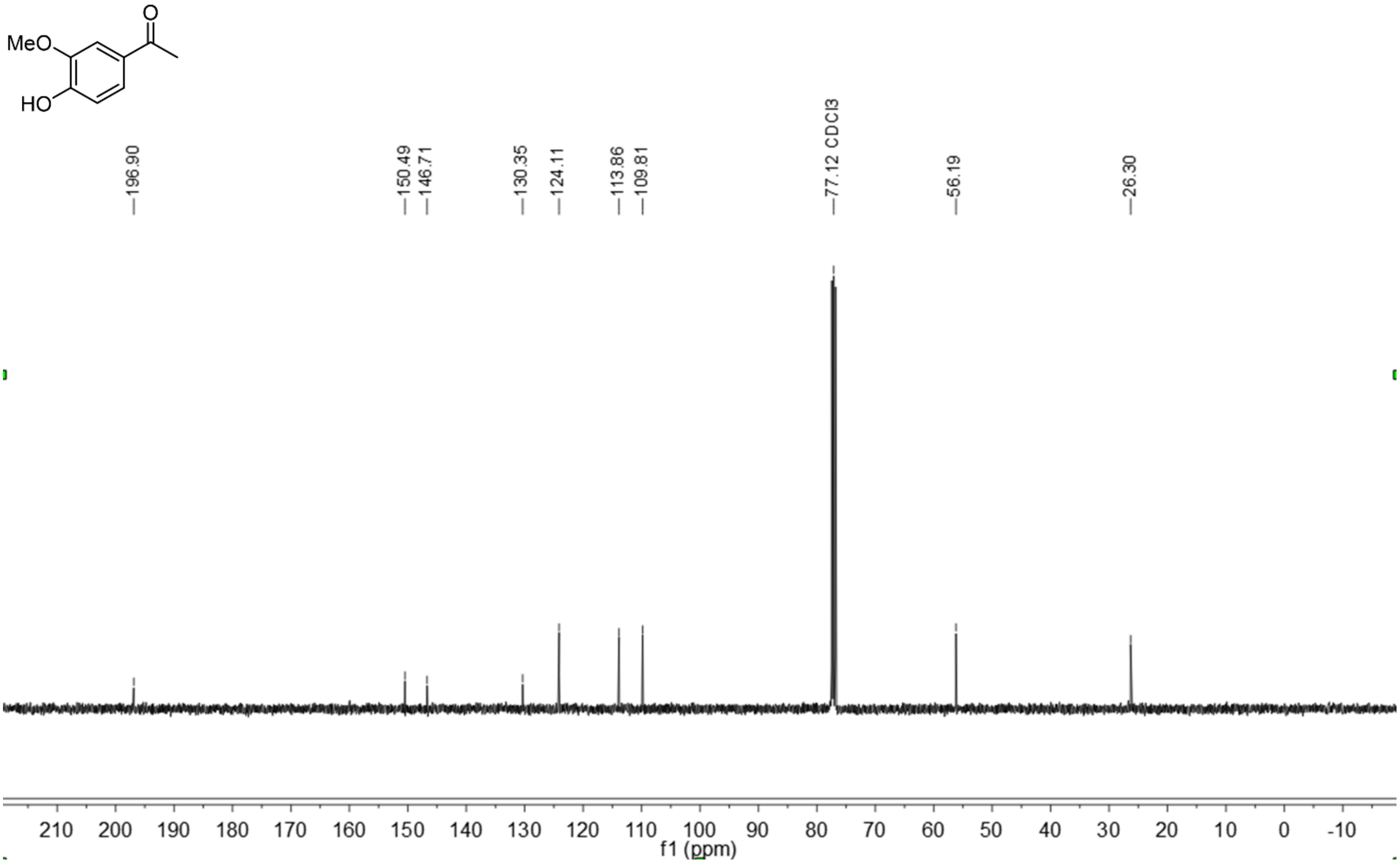

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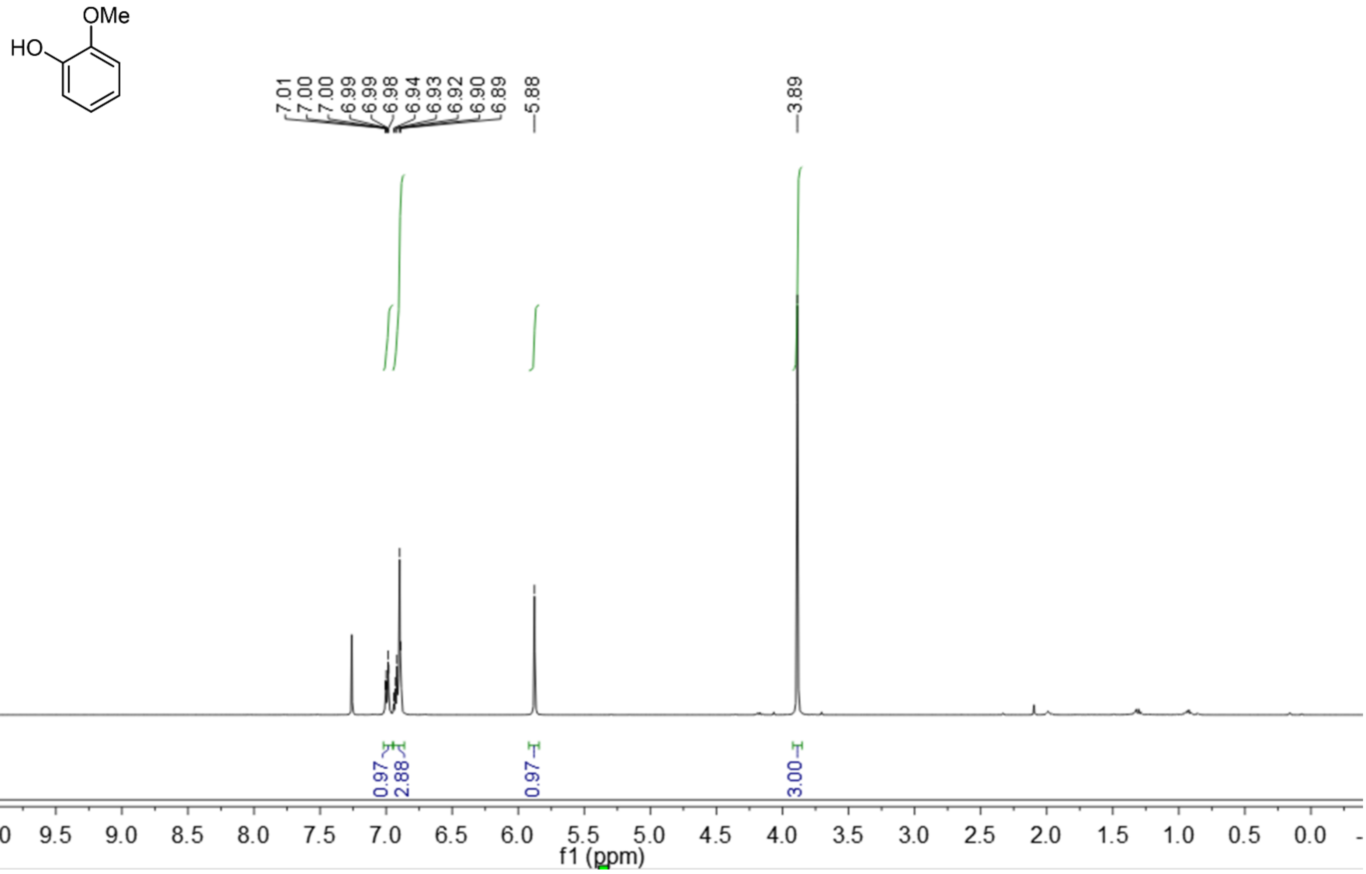

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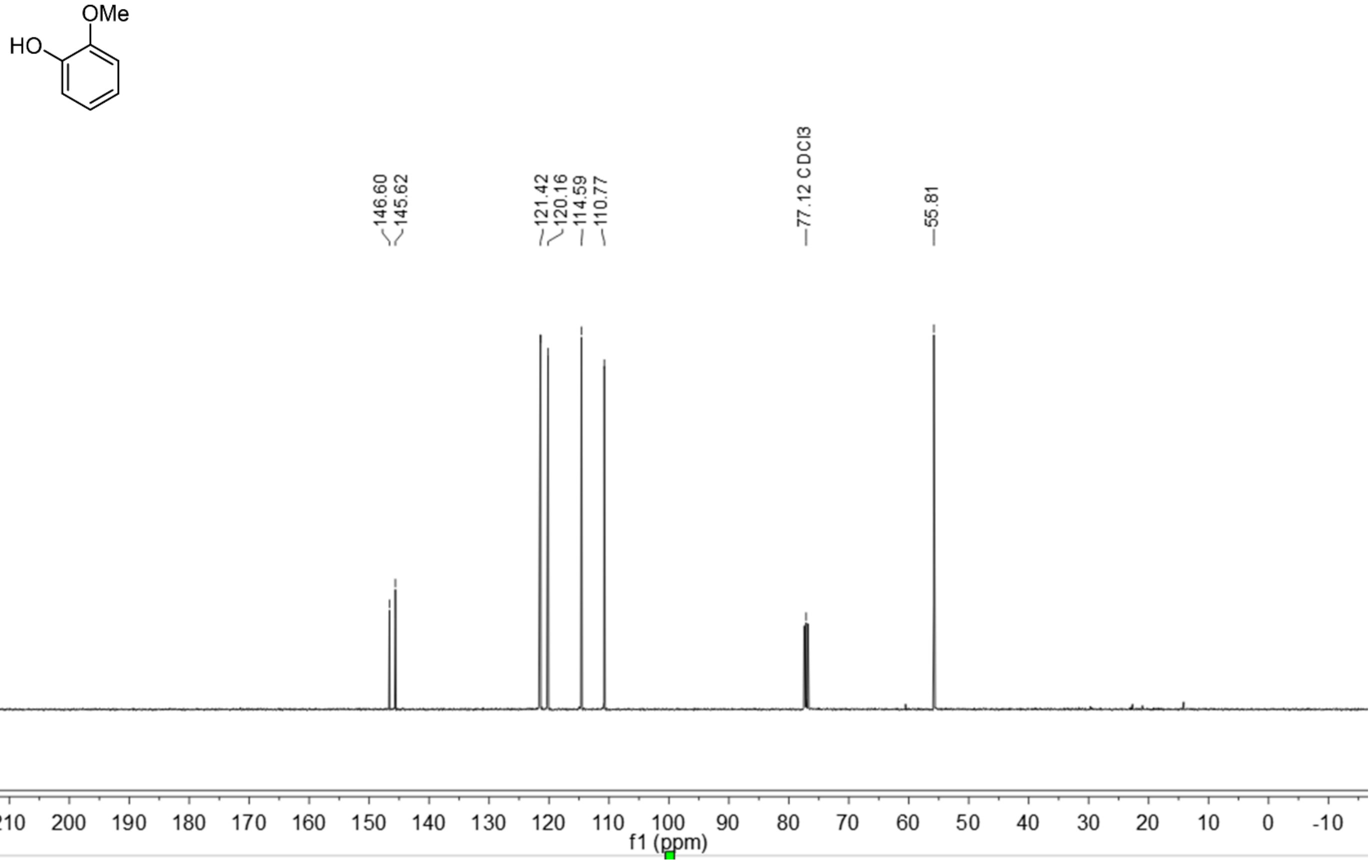

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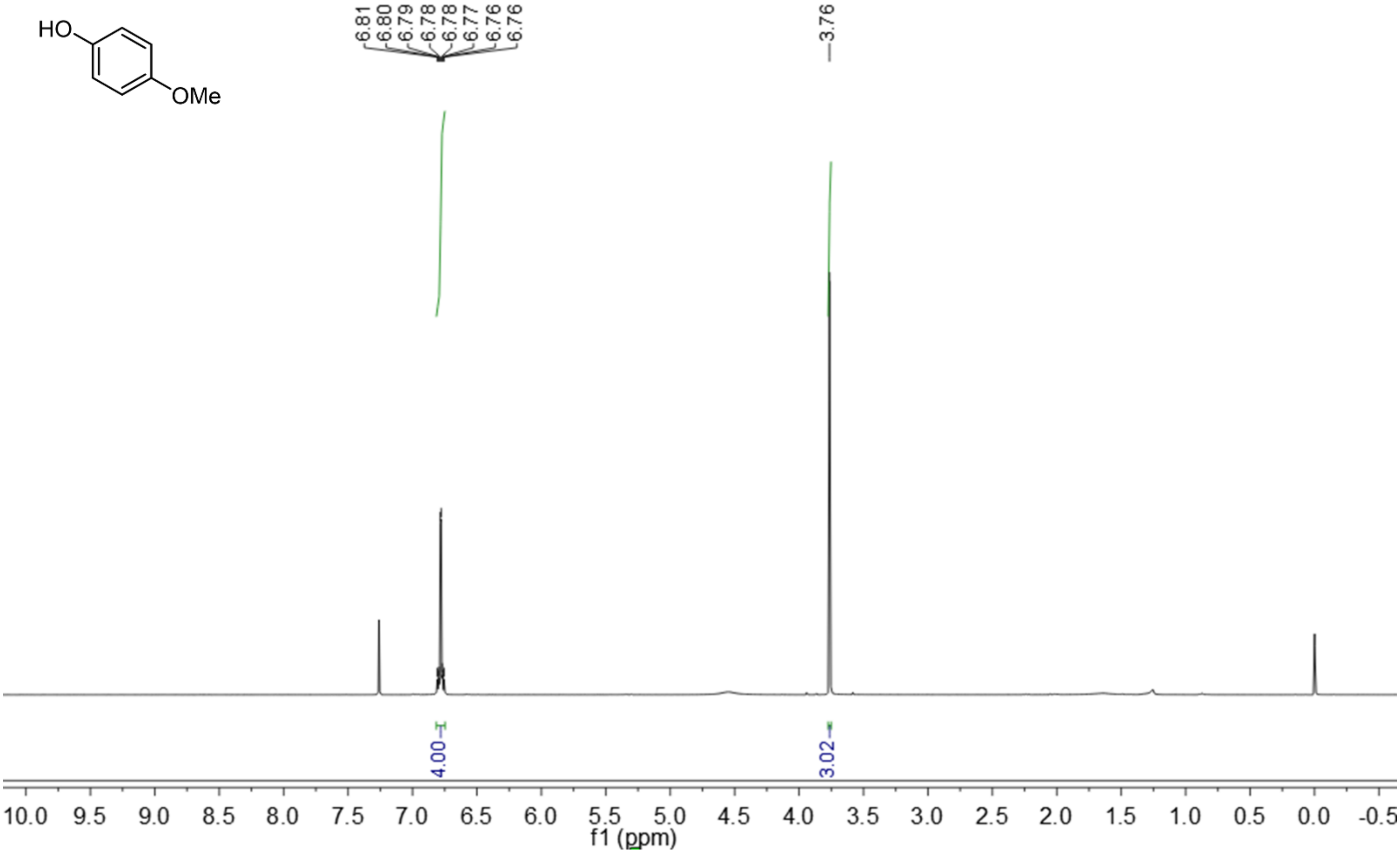

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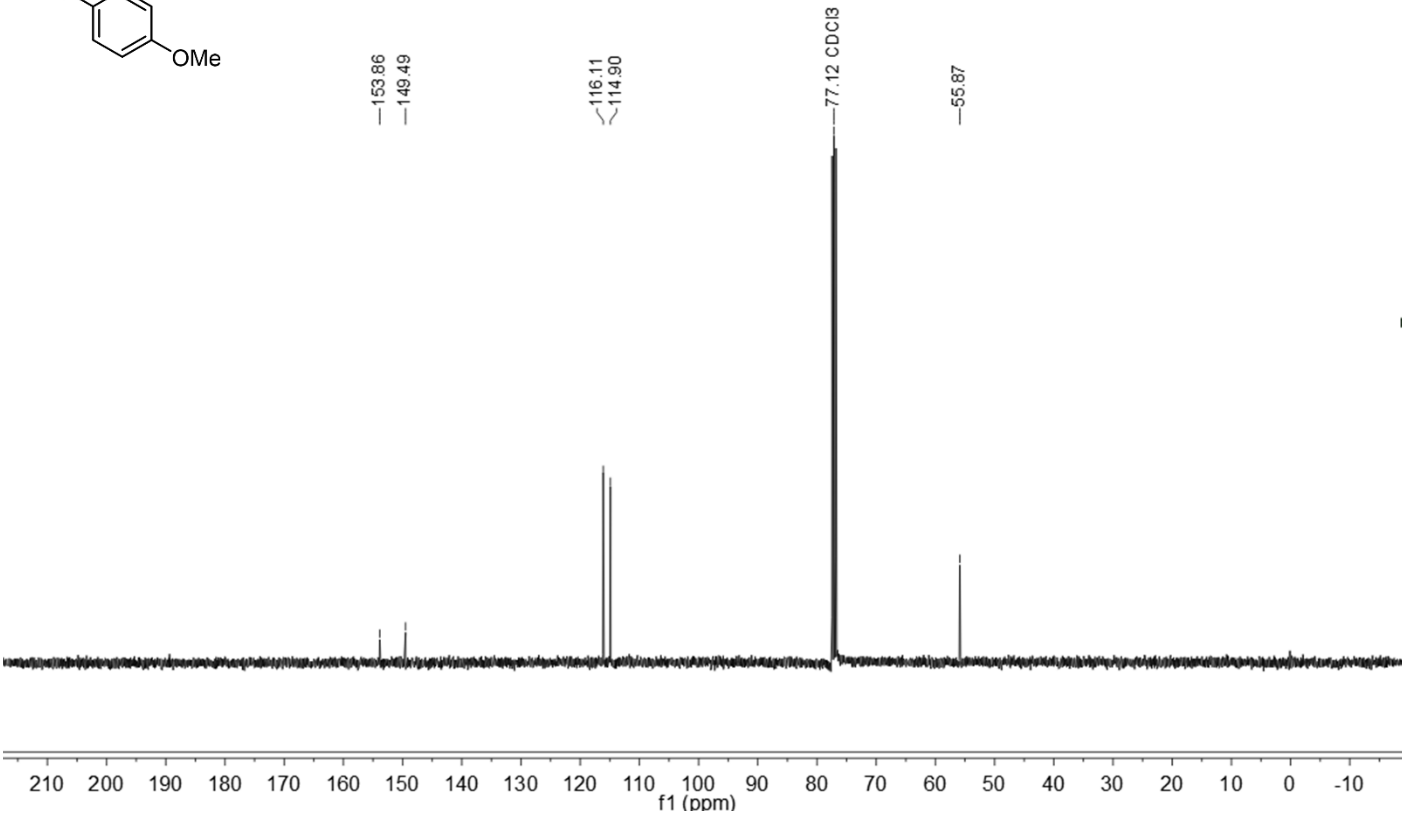

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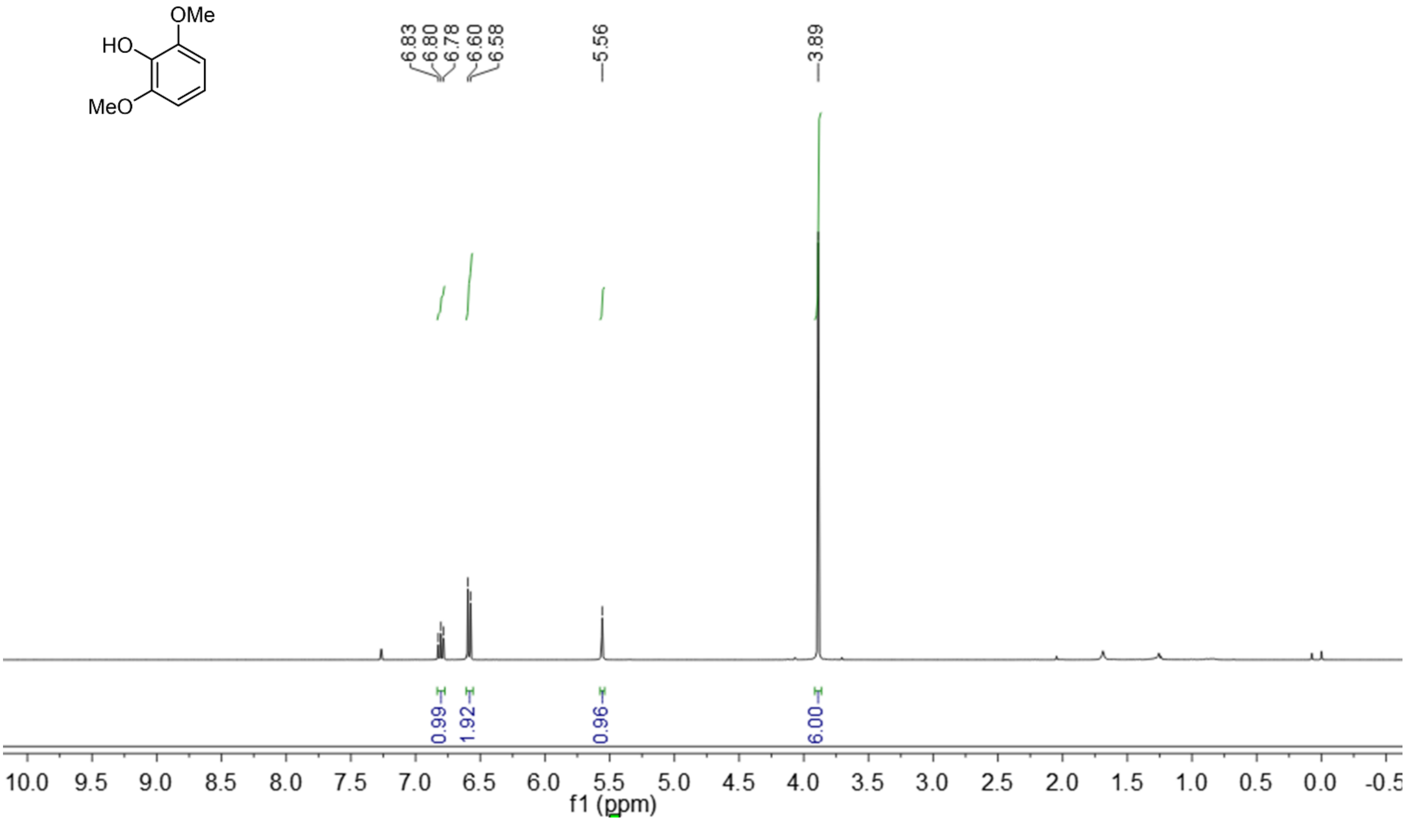

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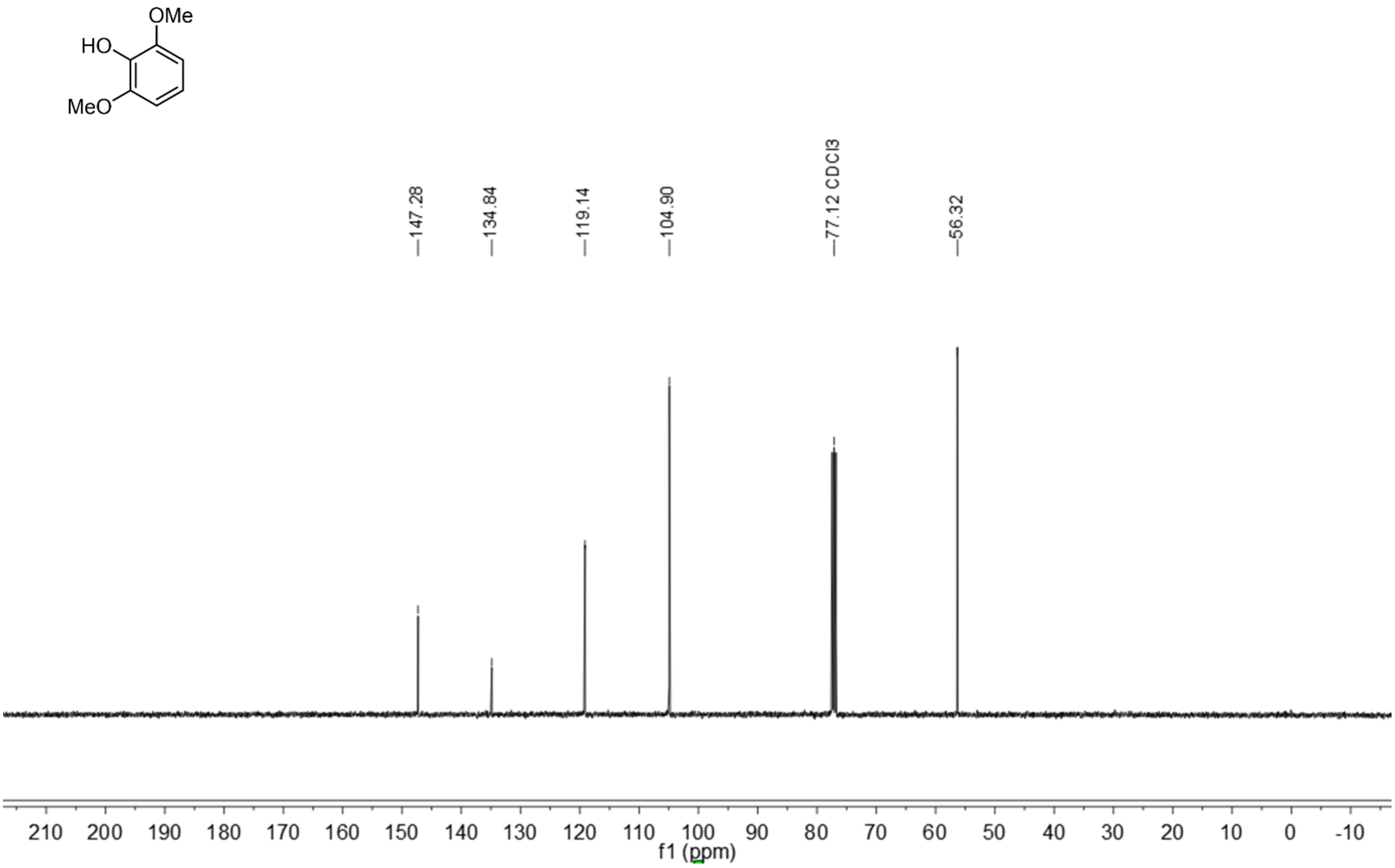

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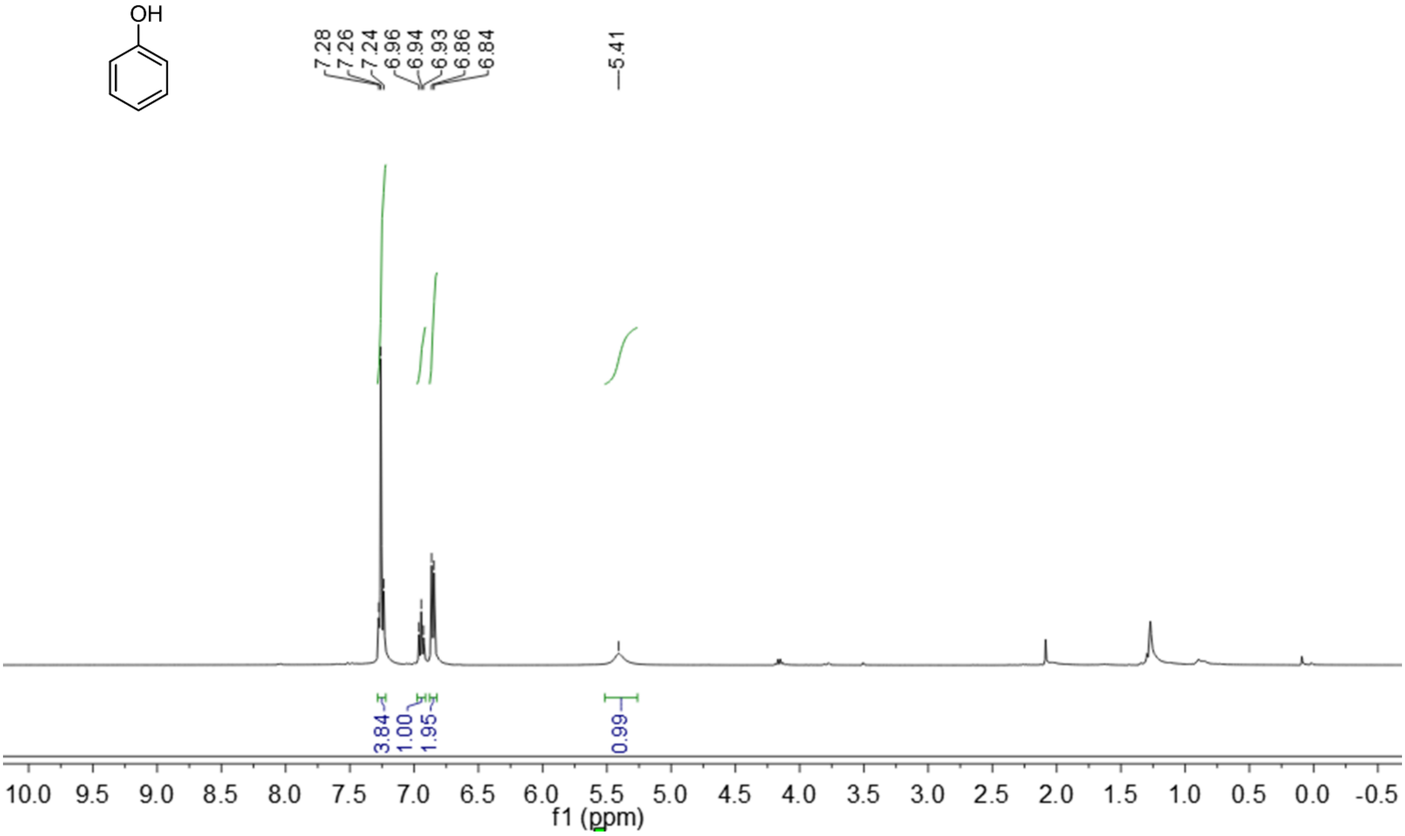

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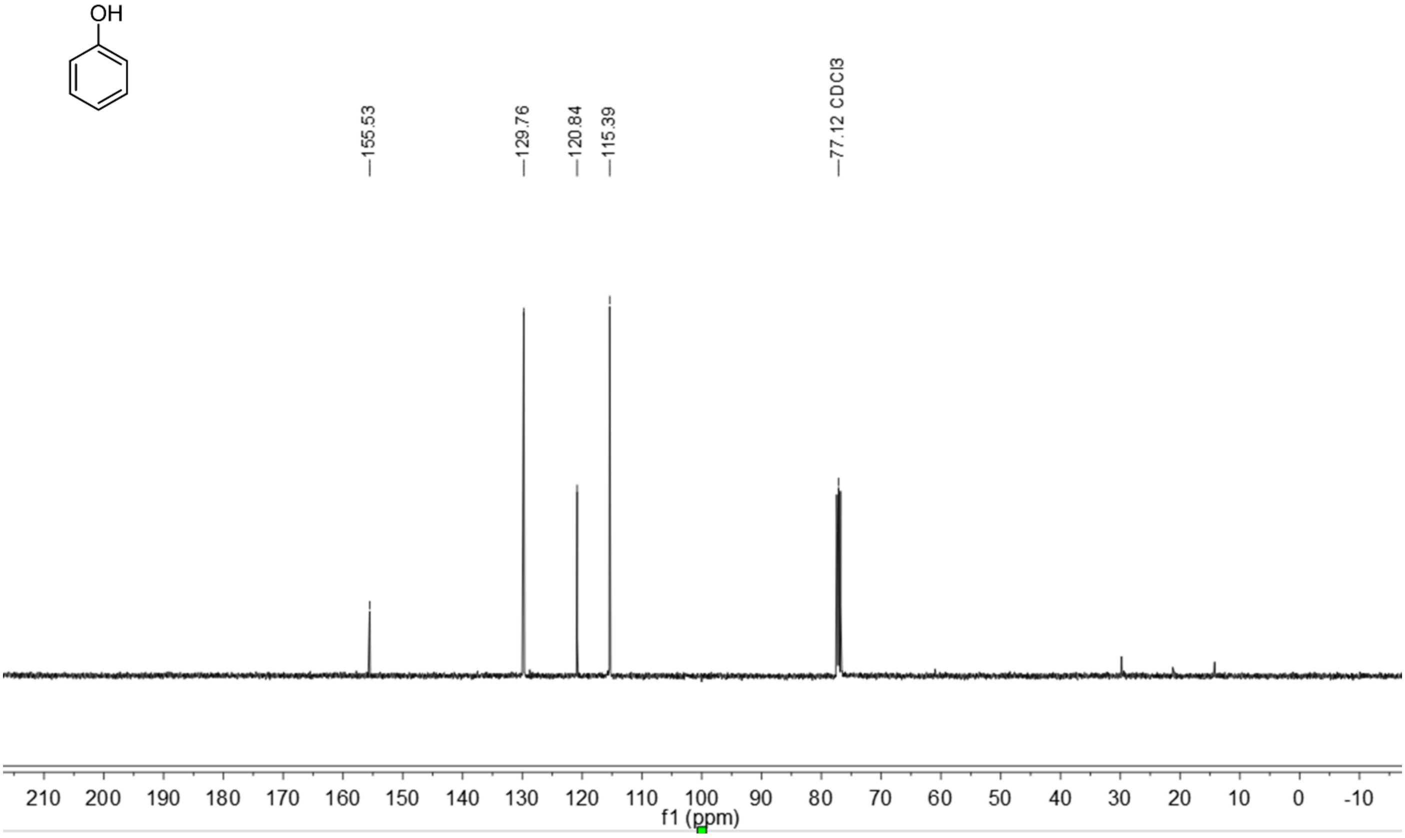

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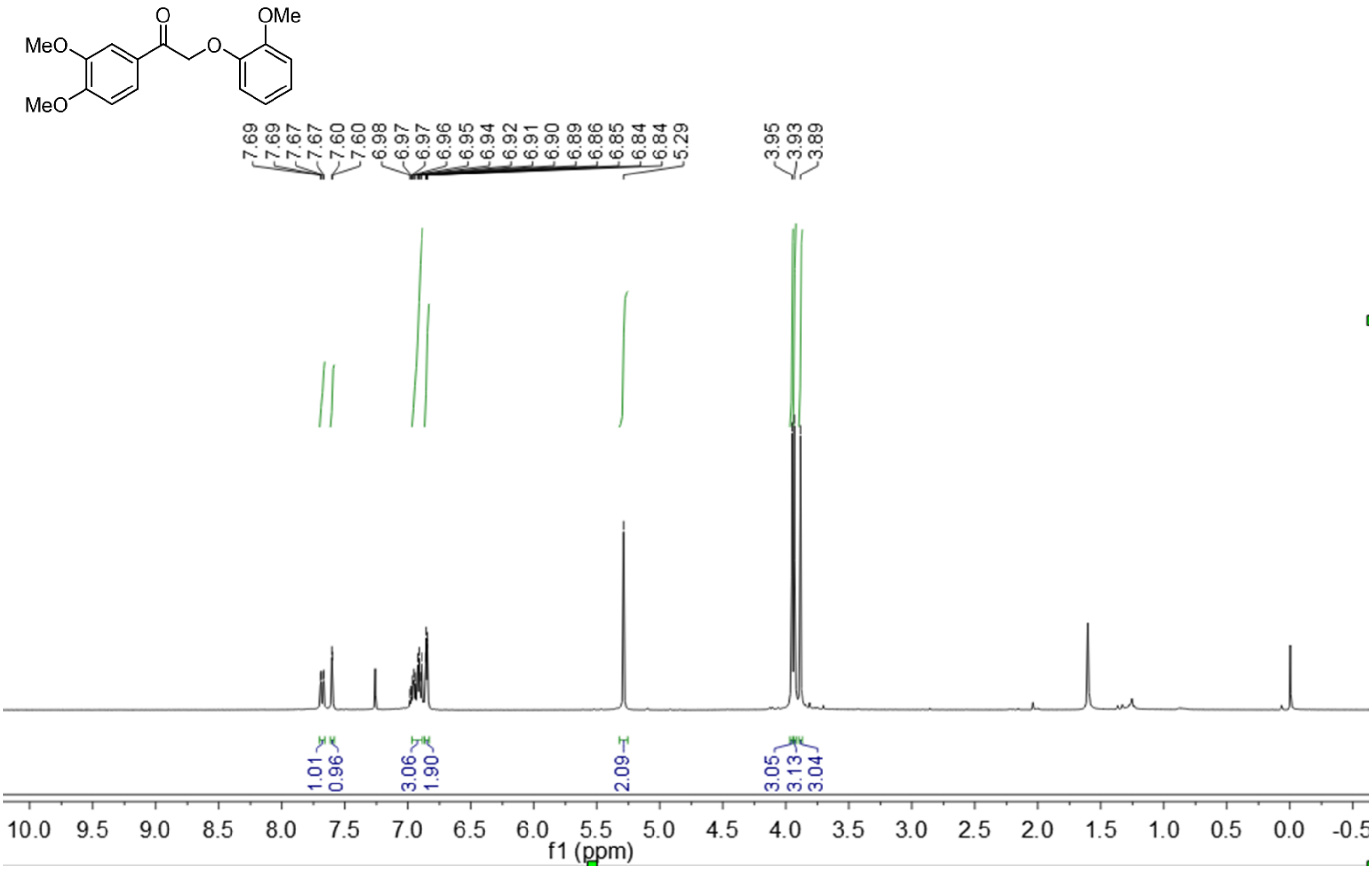

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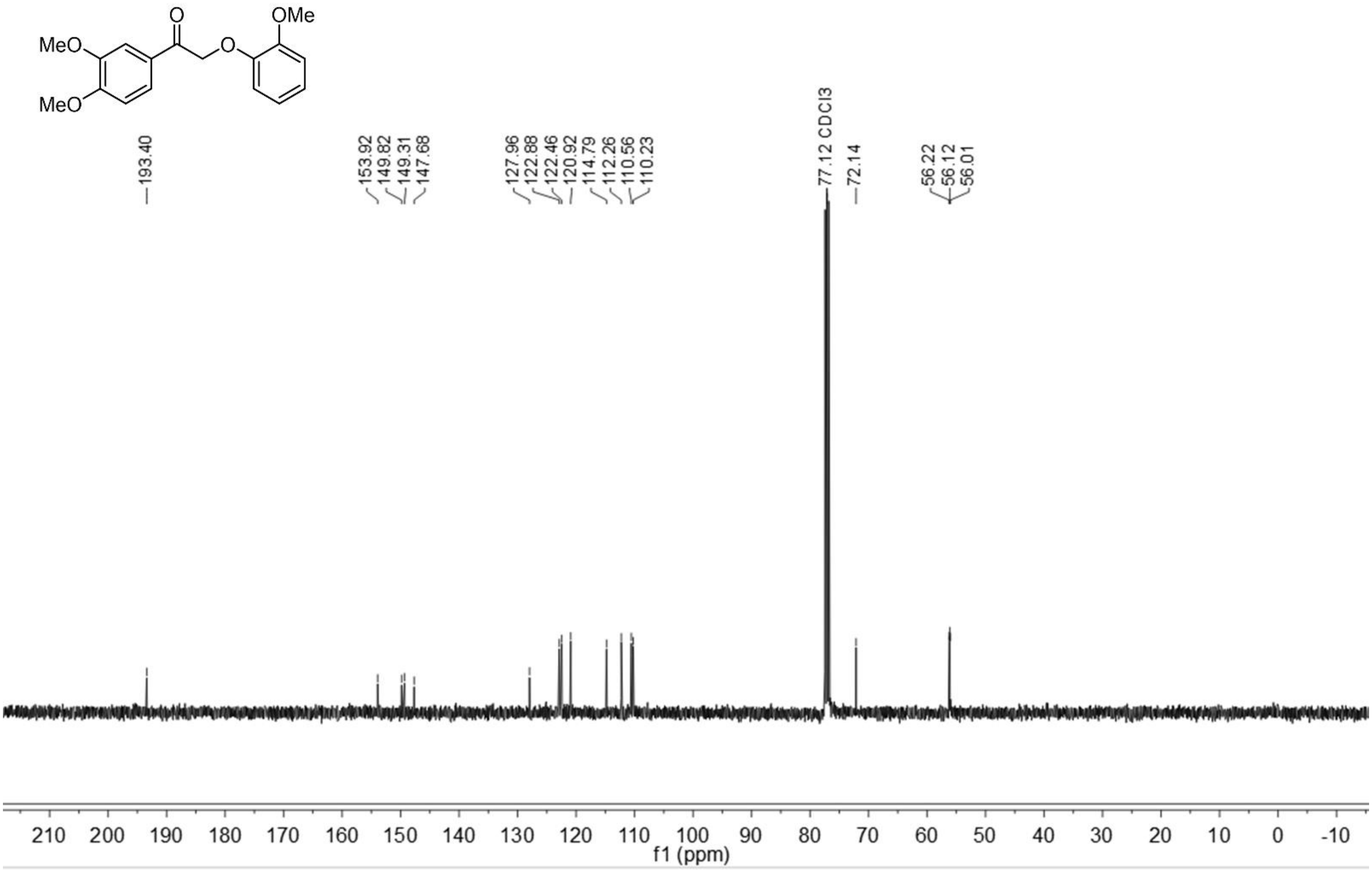

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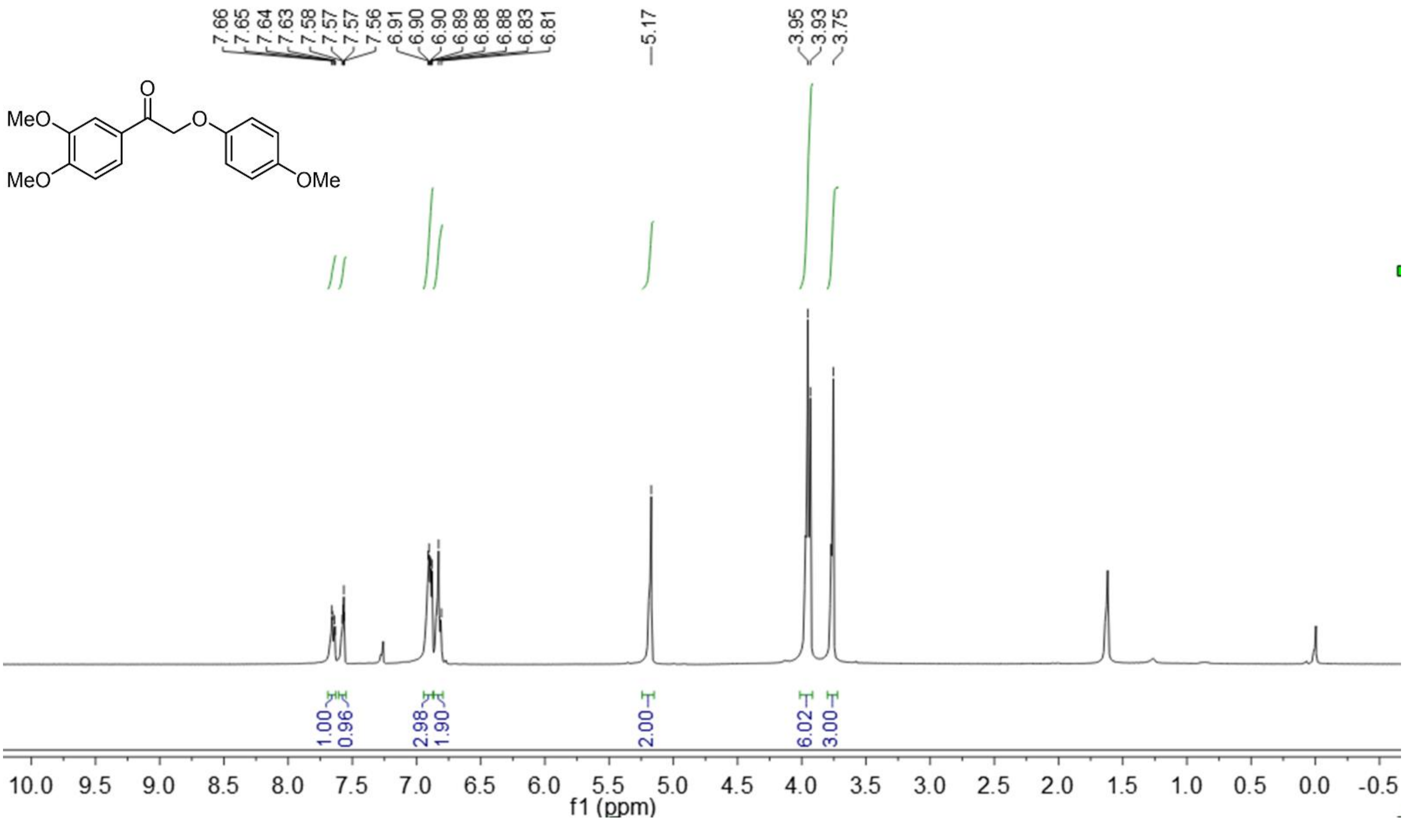

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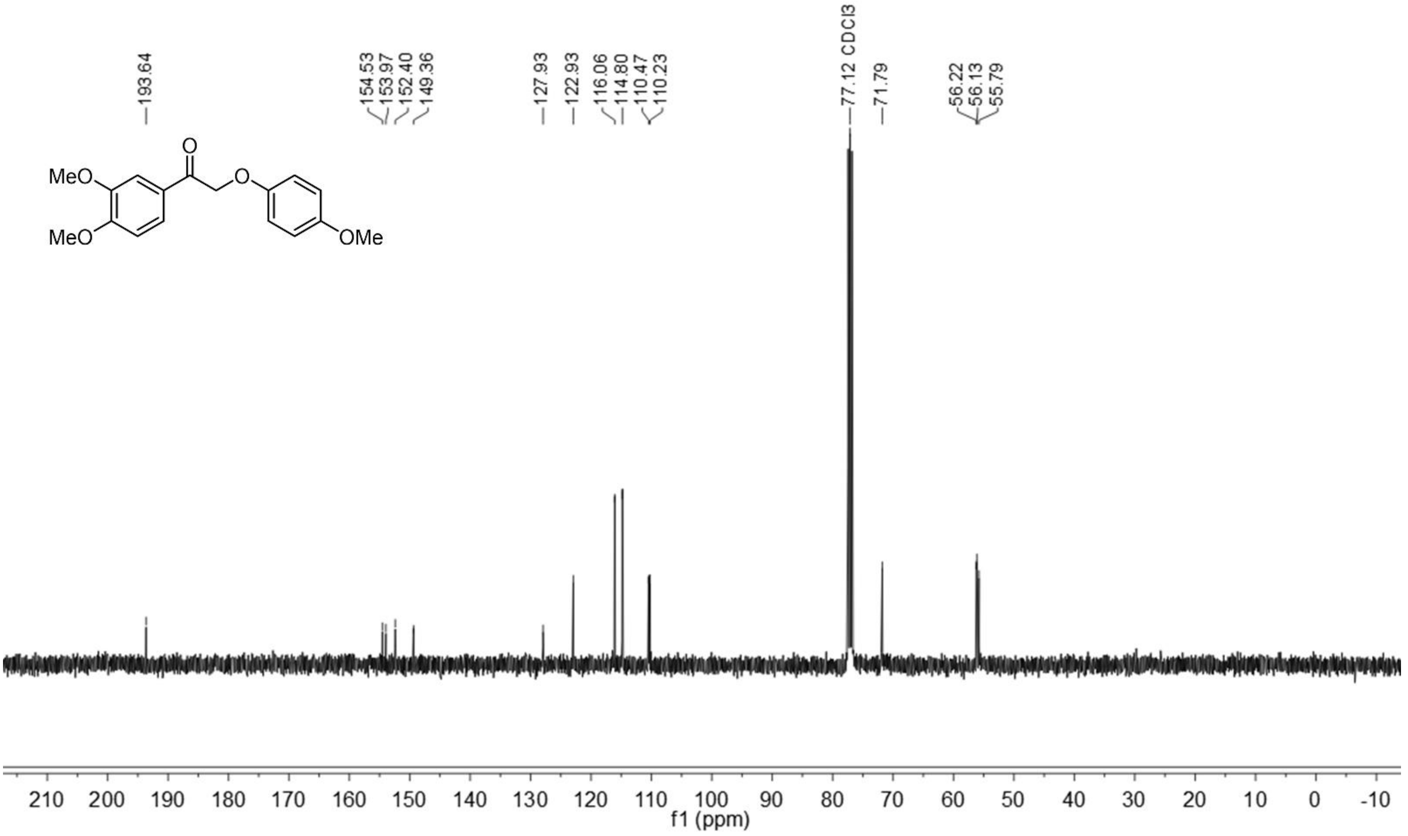

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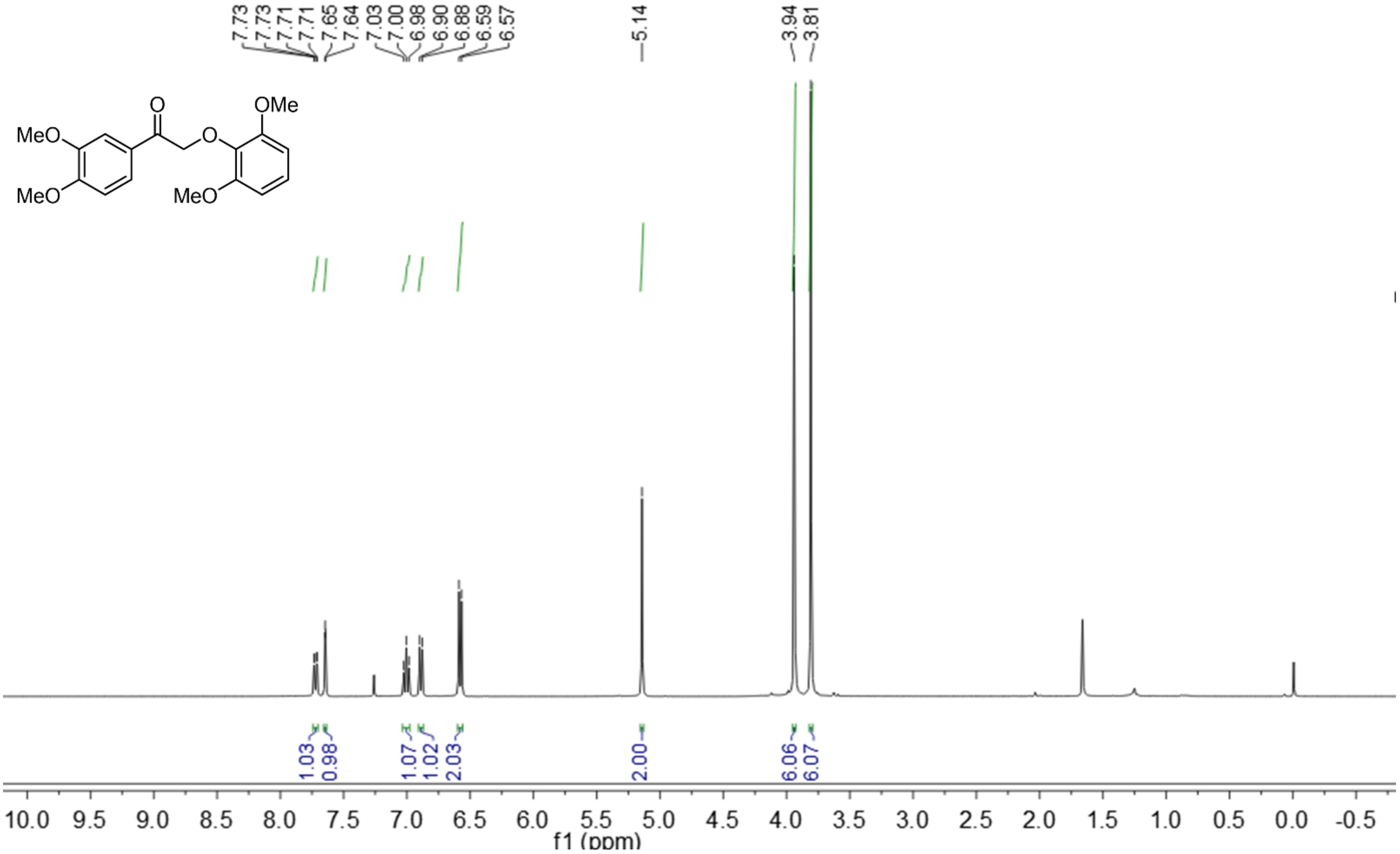

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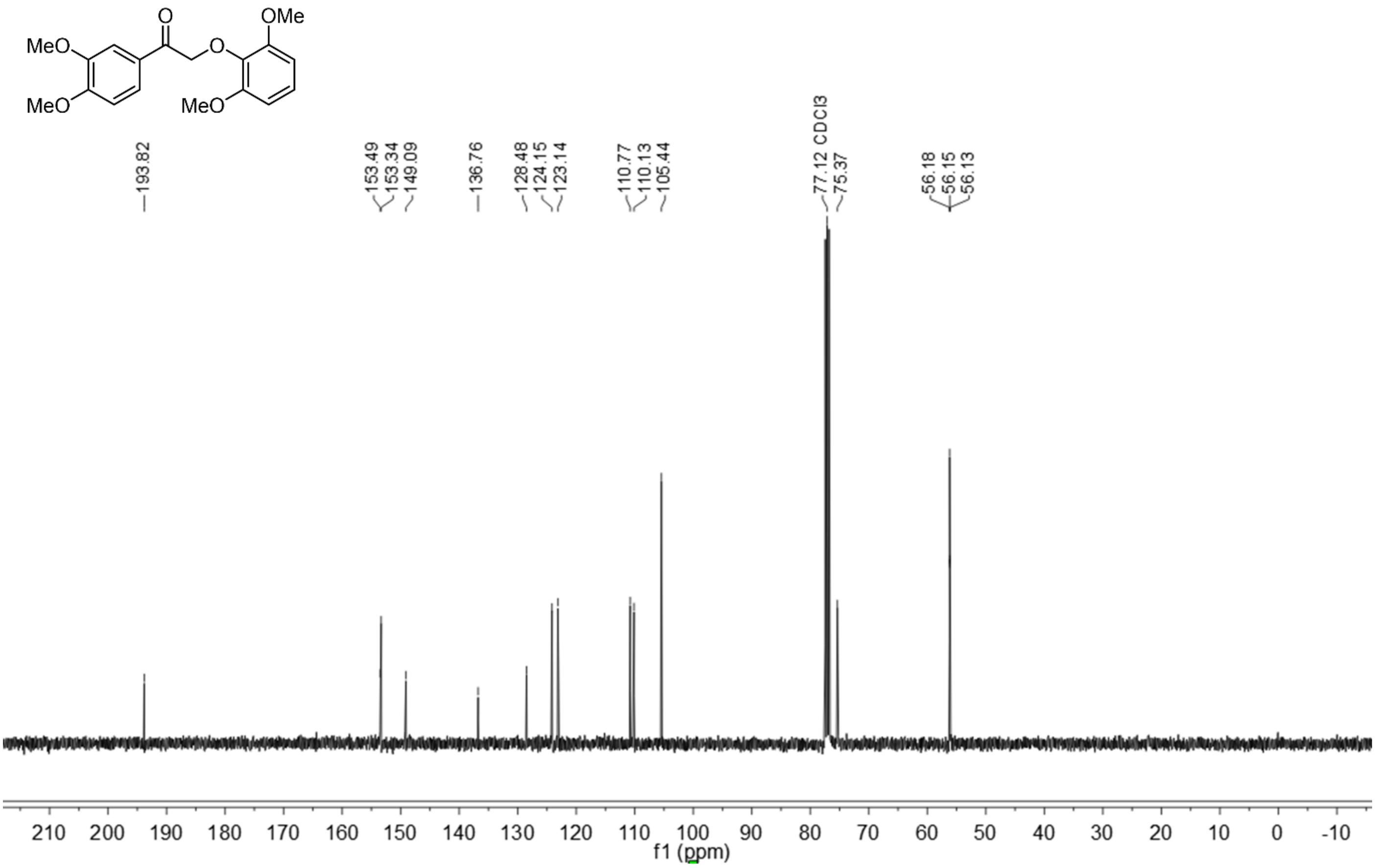

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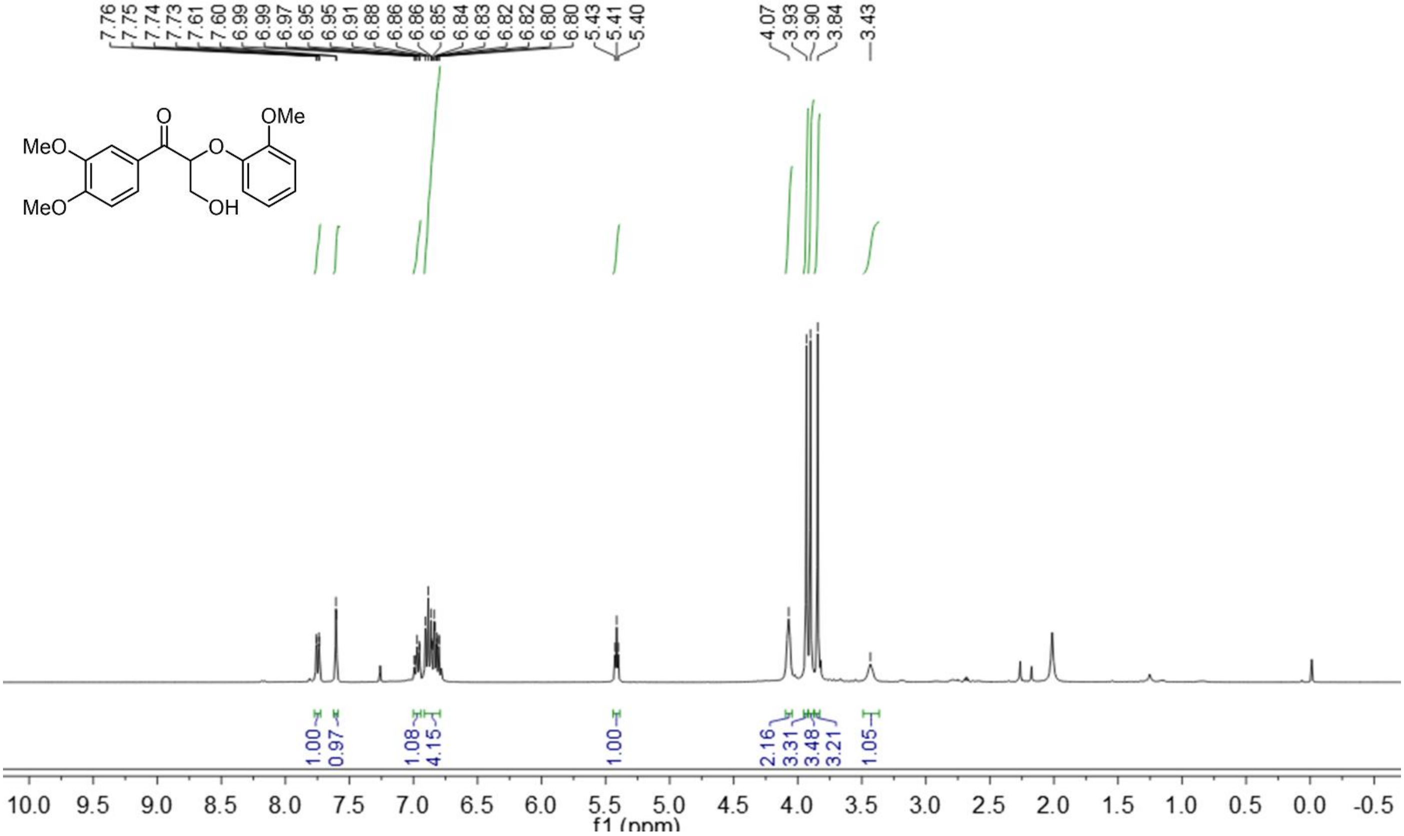

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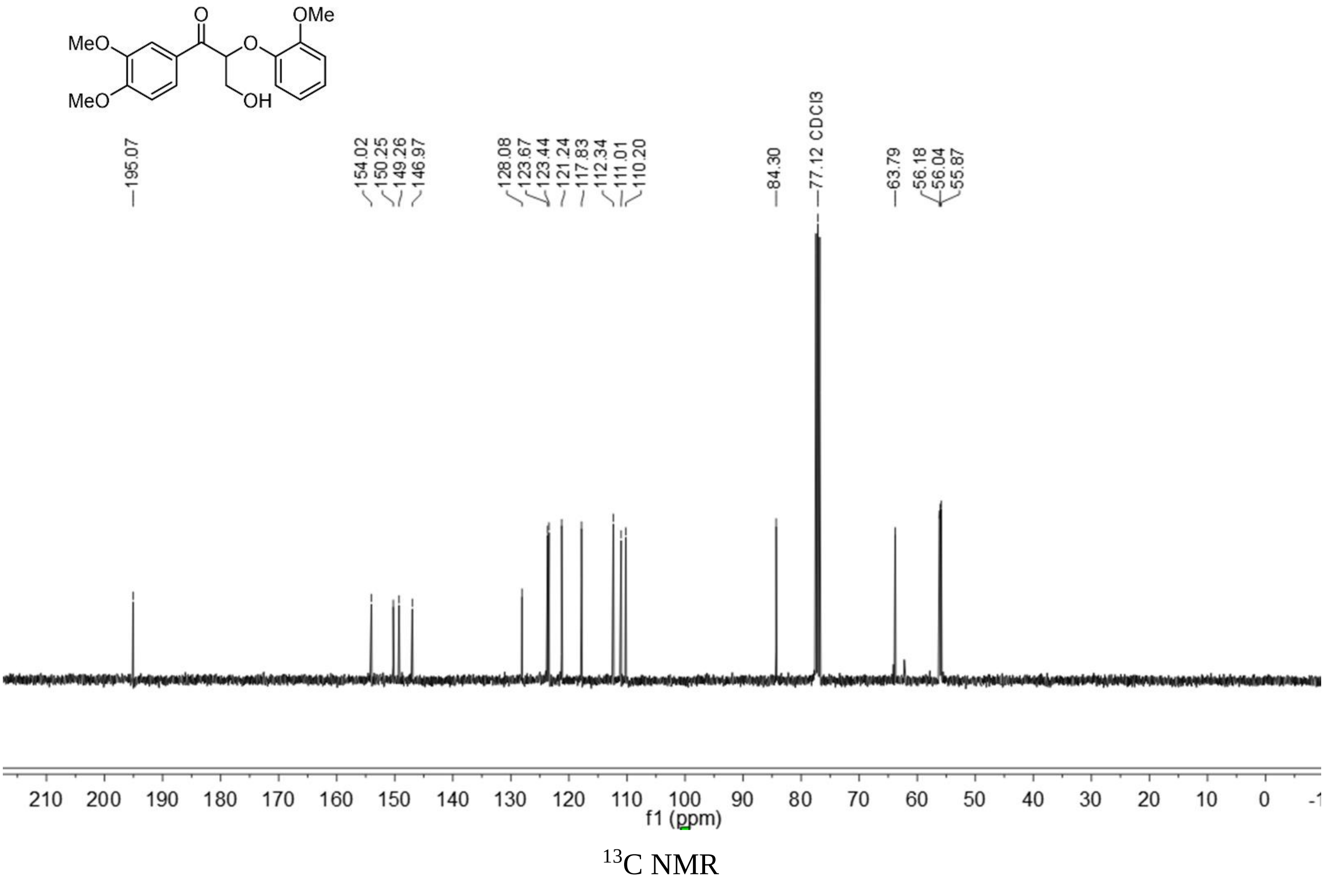

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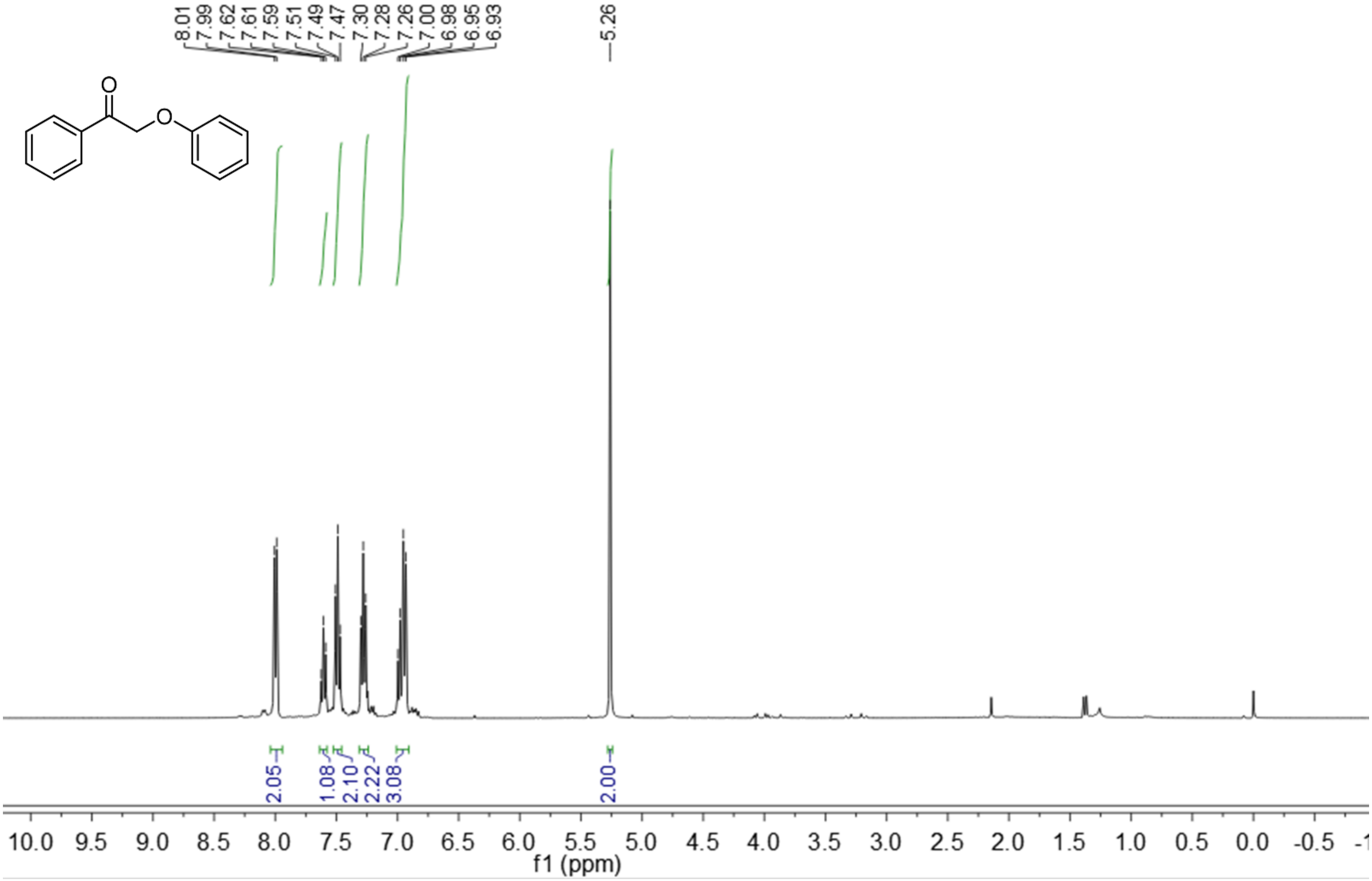

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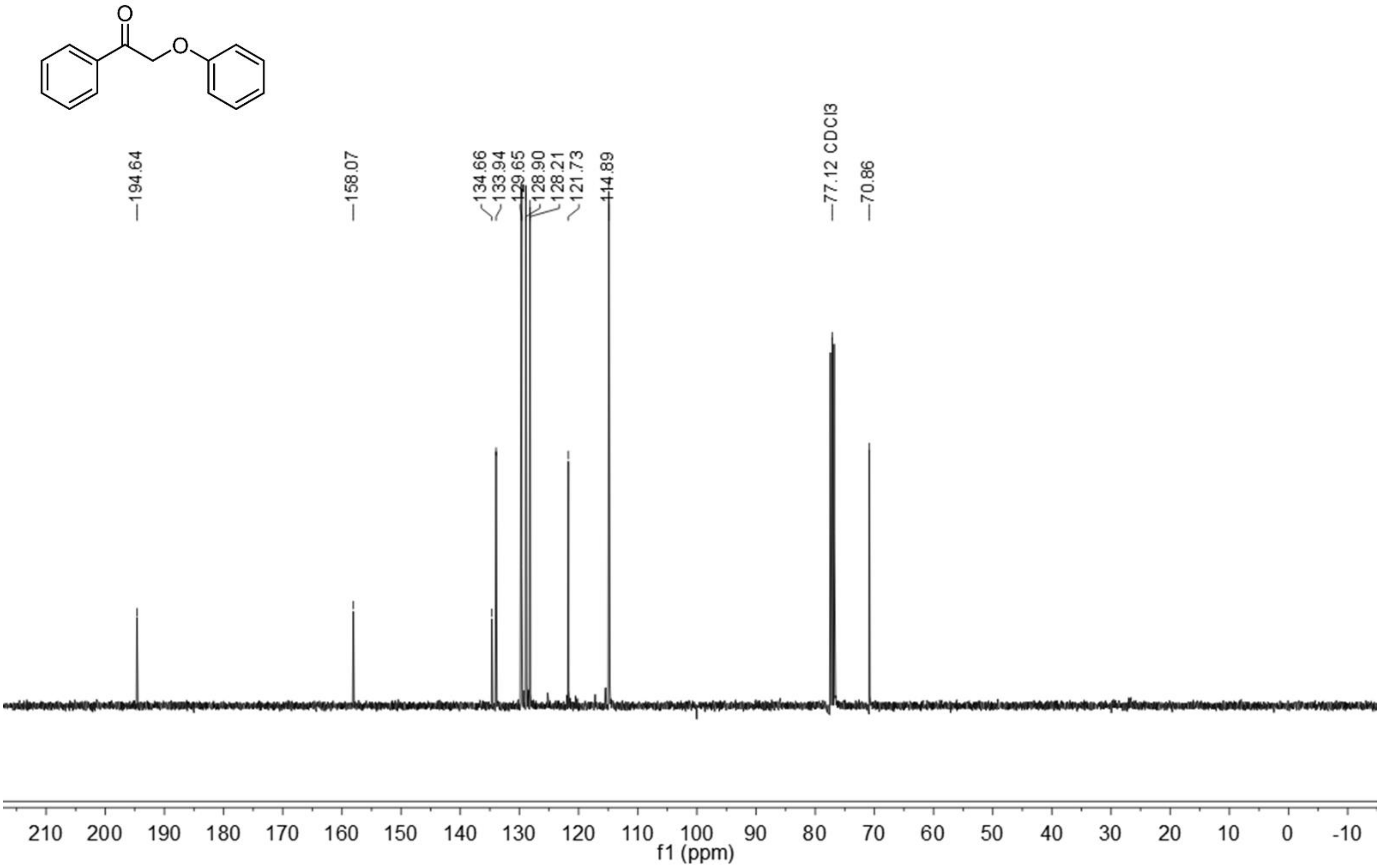

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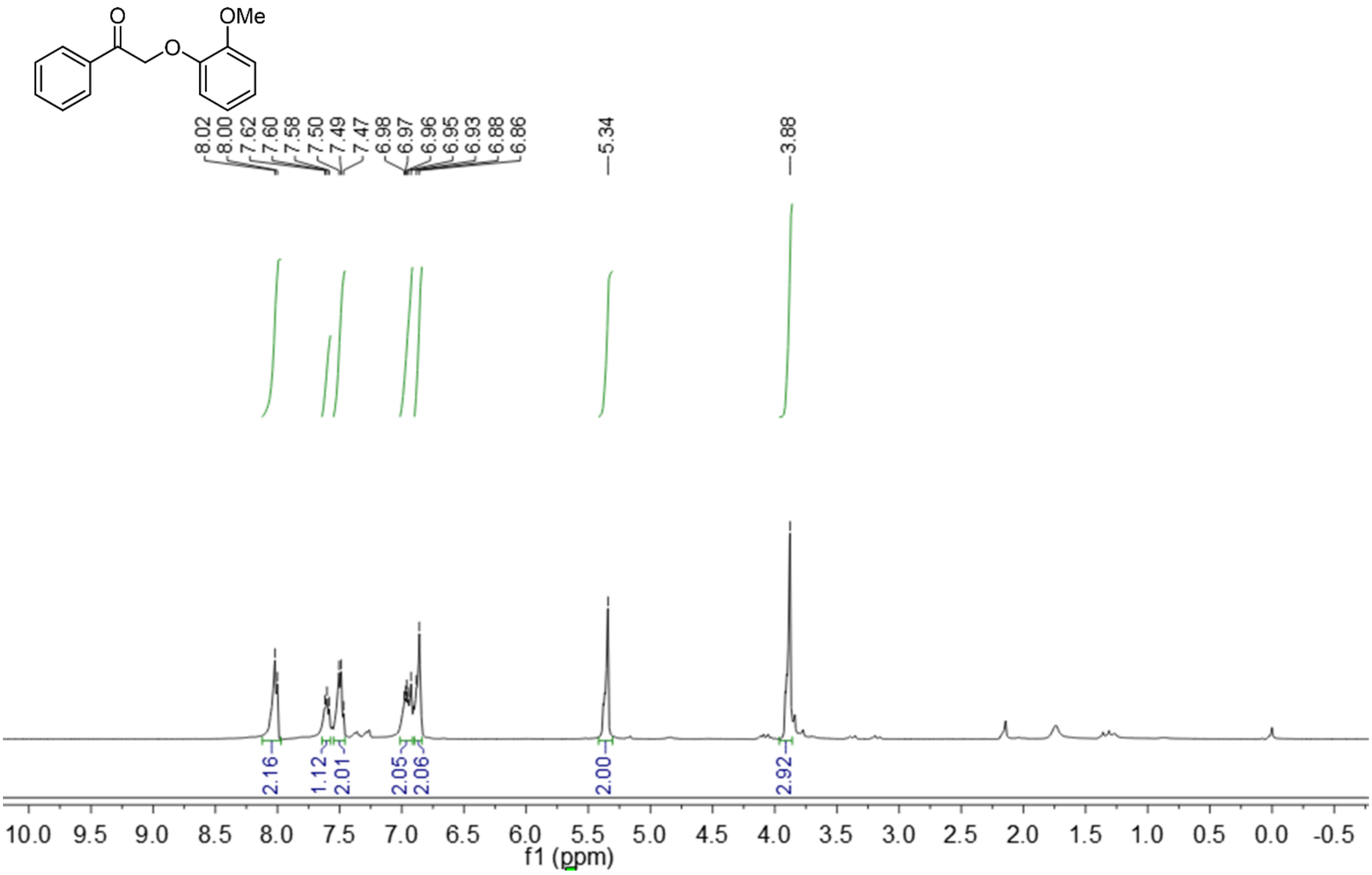

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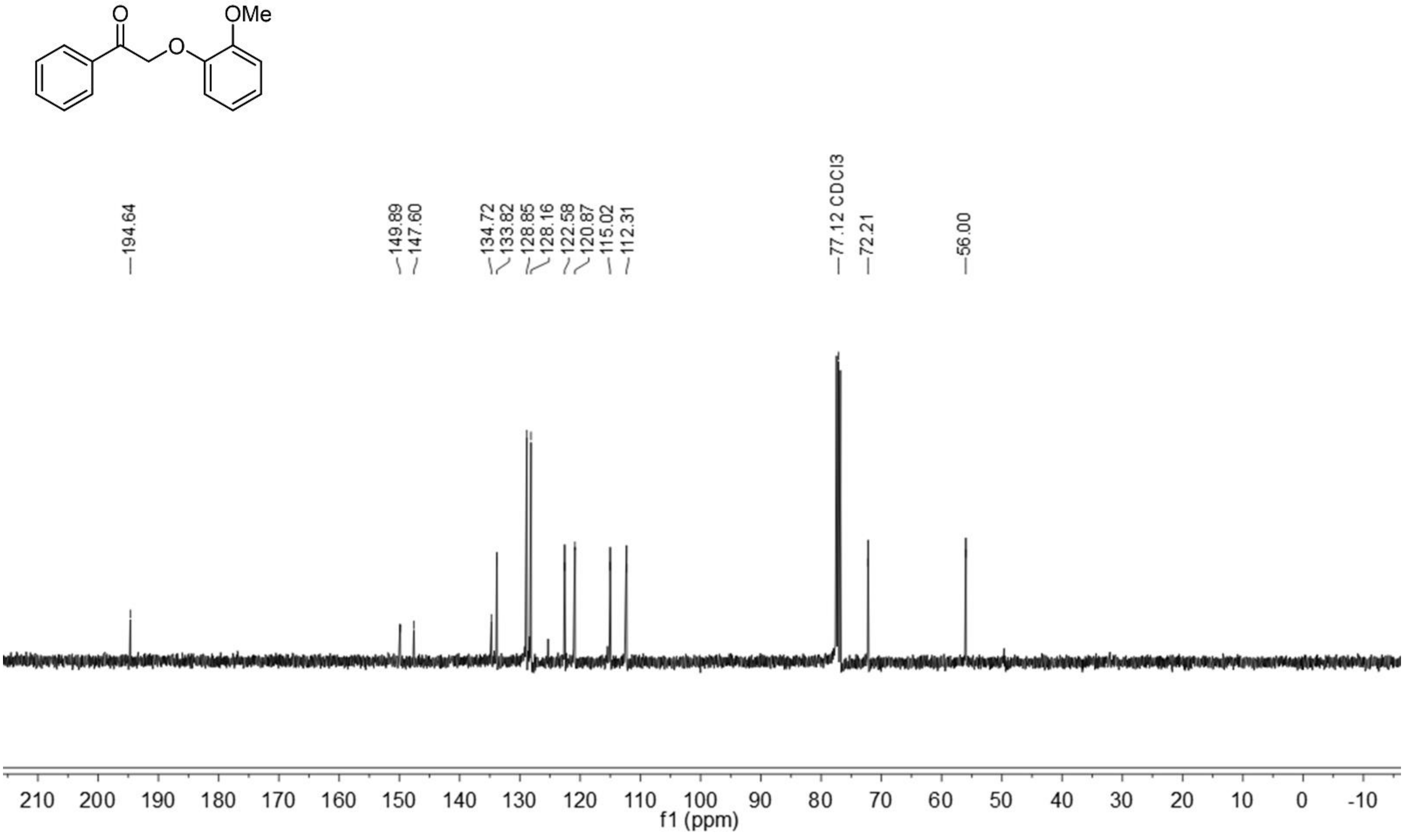

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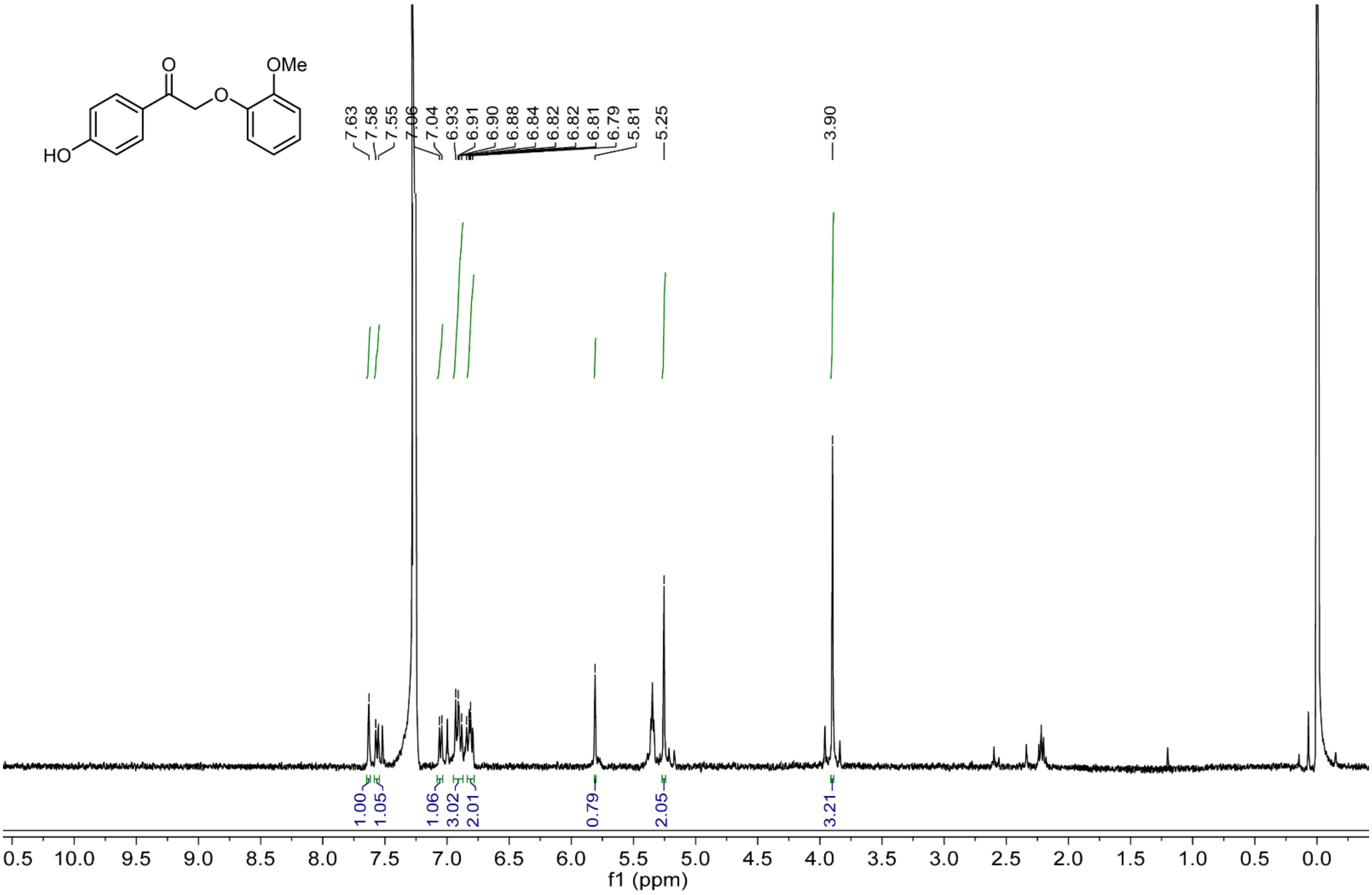

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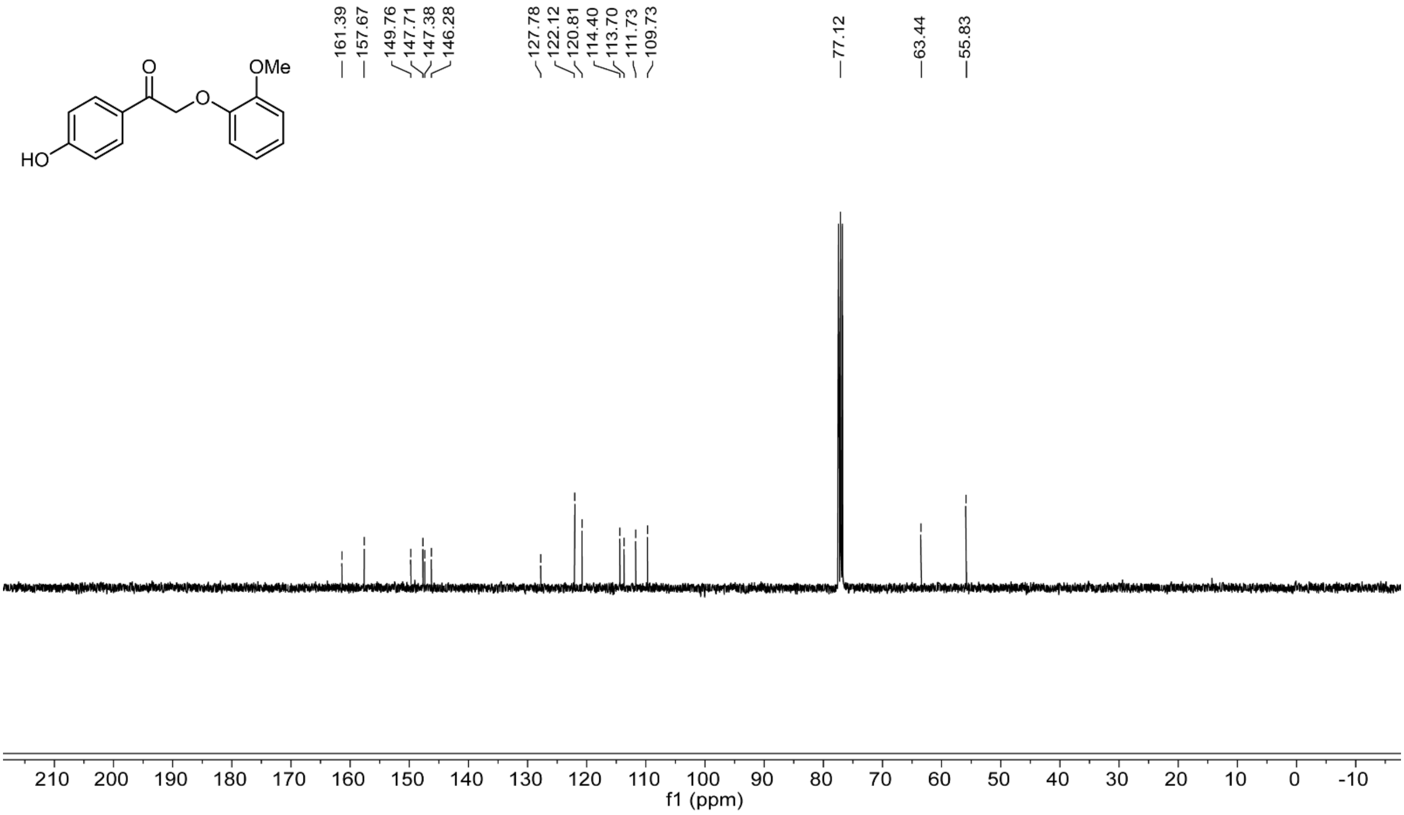

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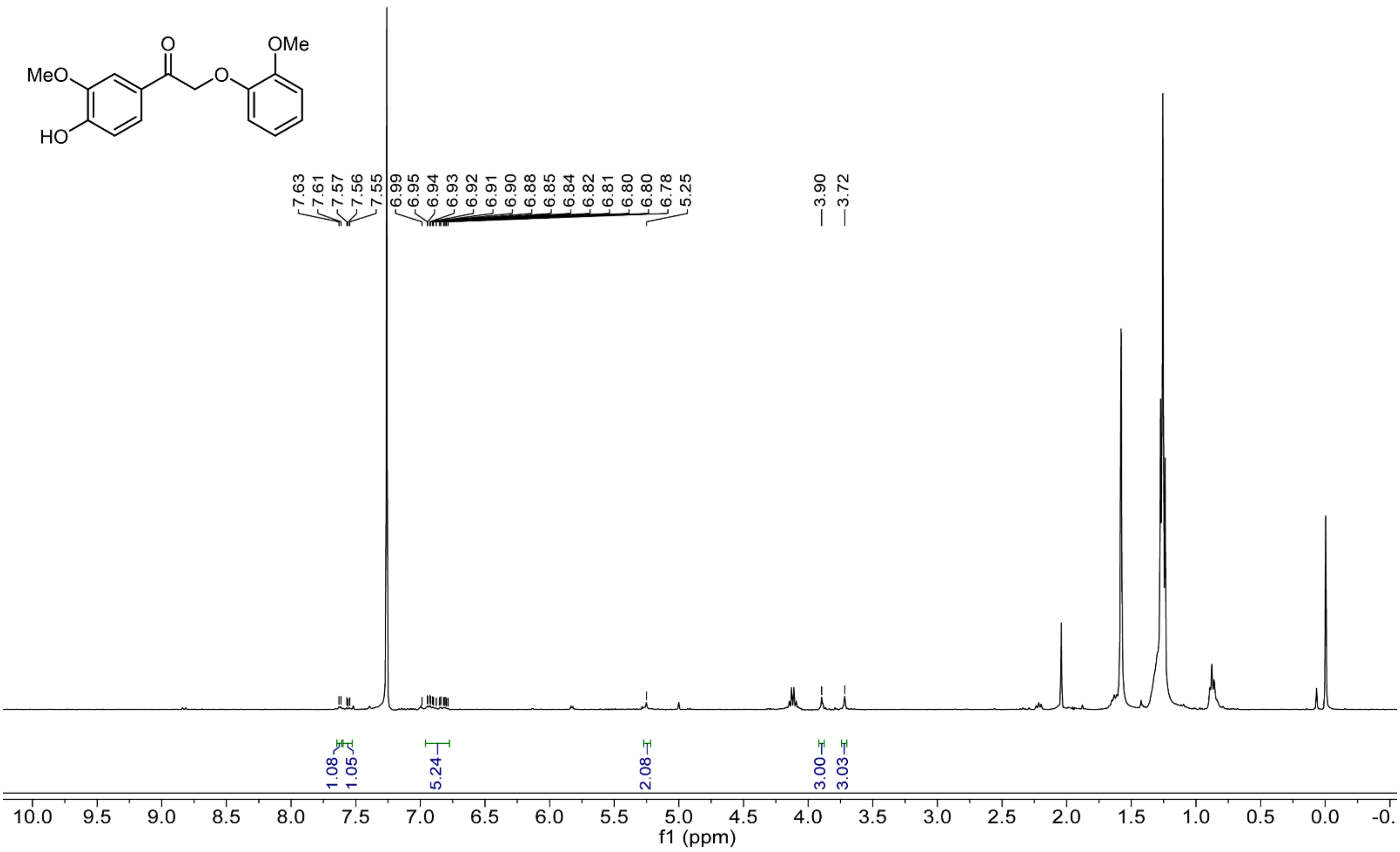

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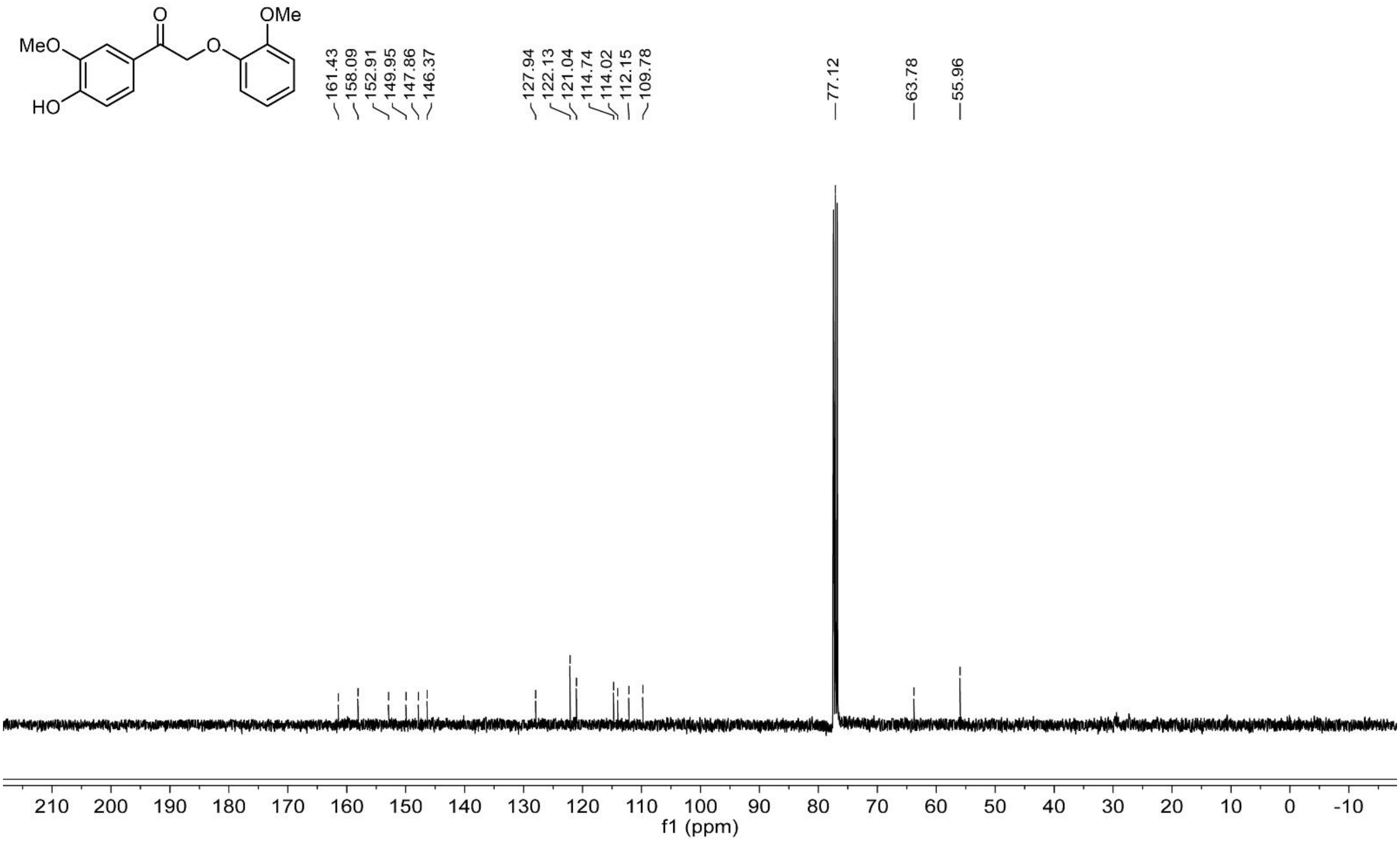

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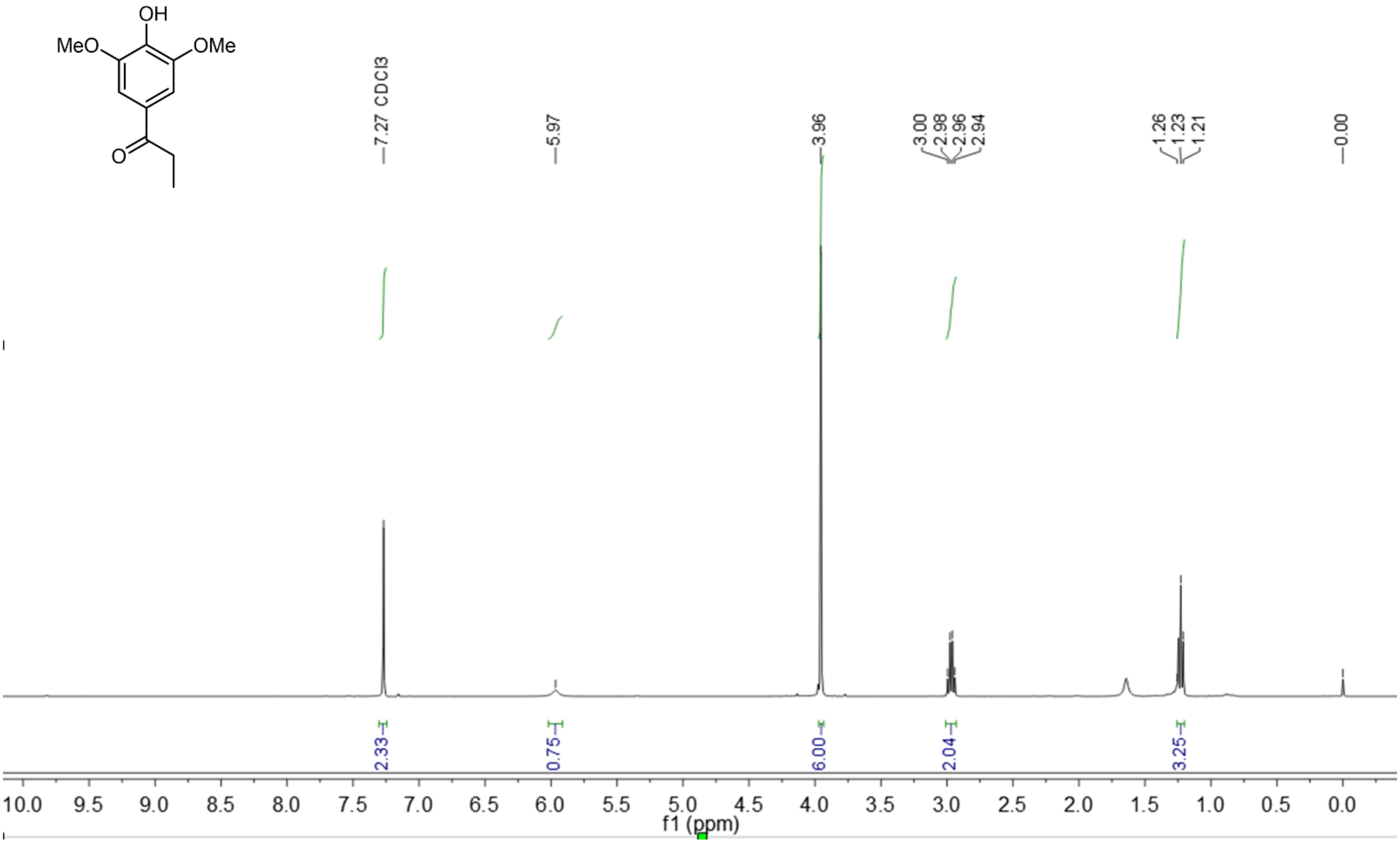

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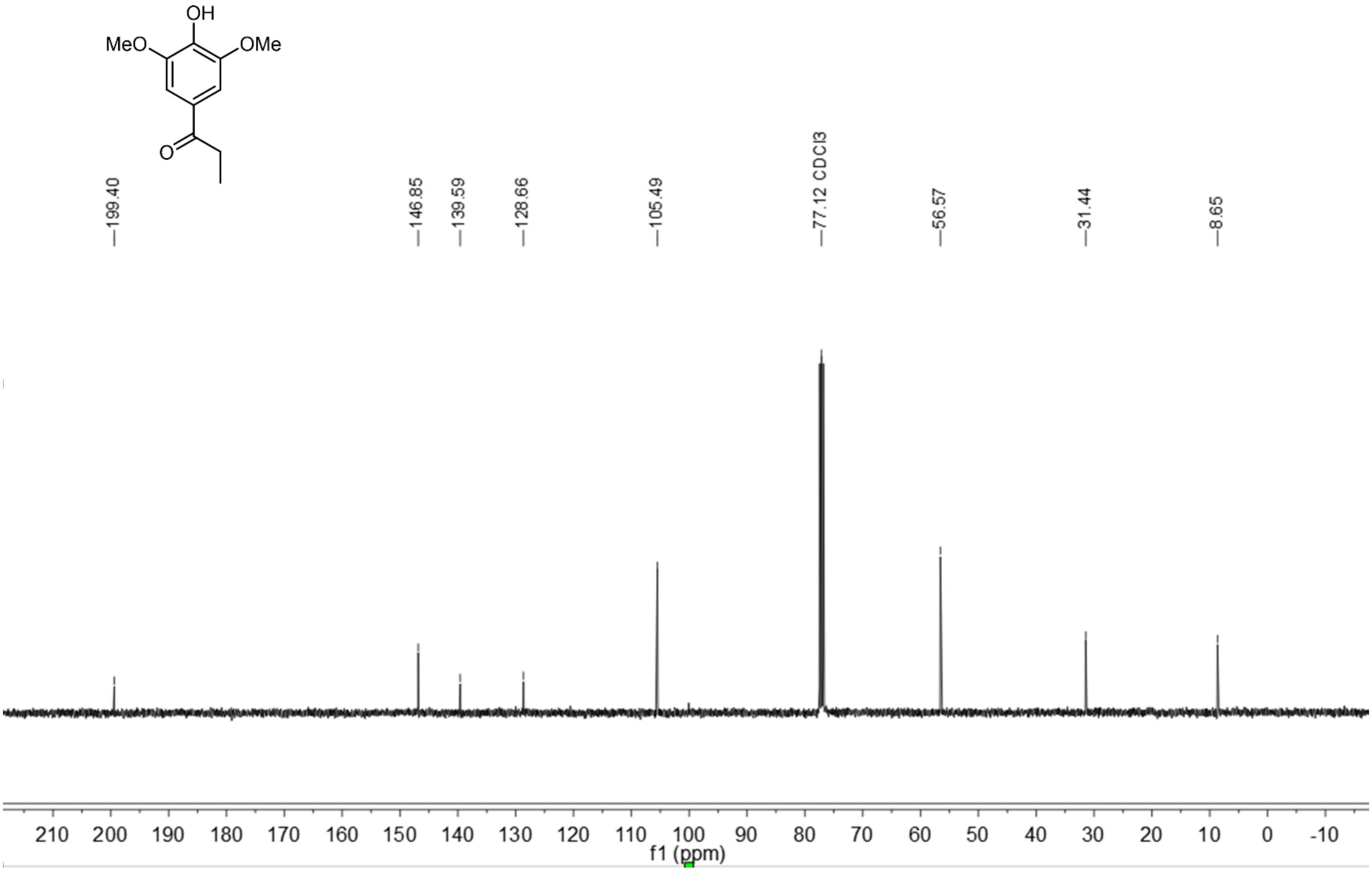

^{13}C NMR

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