Supporting Information

Hypoiodite-catalyzed oxidative homocoupling of arenols and tandem oxidation/cross-coupling of hydroquinones with arenes

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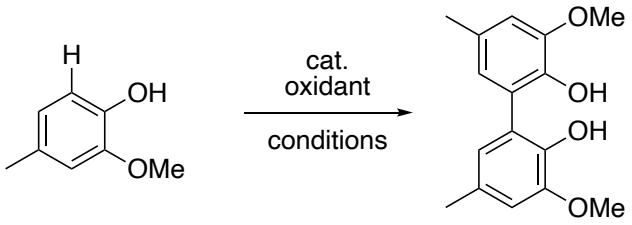
Materials and Methods

Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. ^{1}H NMR spectra were measured on a Varian INOVA-500 (500 MHz) or a JEOL ECS-400 (400 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on a Varian INOVA-500 (125 MHz) or a JEOL ECS-400 (100 MHz) spectrometers. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.00 ppm). For thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 F_{254} 0.25 mm or silica gel 60 NH_2 F_{254}s 0.20 mm) were used. The products were purified by column chromatography on silica gel (E. Merck Art. 9385). High-resolution mass spectral analysis (HRMS) was performed at Chemical Instrument Center, Nagoya University [JEOL JMS-700 (FAB)]. HRMS were obtained by fast atom bombardment (FAB) using a double-focusing magnetic sector mass spectrometer.

In experiments that required dry solvents, toluene, diethyl ether (Et_2O), tetrahydrofuran (THF), dichloromethane, were purchased from FUJIFILM Wako as the “anhydrous” and stored over 4A molecular sieves. Other solvents were purchased from Aldrich Chemical Co., Inc. or FUJIFILM Wako and used without further purification. Tetrabutylammonium iodide (Bu_4NI) was purchased from Tokyo Chemical Industry (TCI) and used without further purification. 30-wt% Aqueous hydrogen peroxide and anhydrous TBHP (5.5 *M* decane solution) were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. and Aldrich Chemical Co., Inc., respectively, and used without further purification. Lithium tetrakis(pentafluorophenyl)borate ethyl etherate was purchased from Aldrich Chemical Co., Inc. and used without further purification. Other simple chemicals were analytical-grade and obtained commercially and used without further purification.

Optimization of Reaction Conditions and Control Experiments

Table S1. Oxidative Homocoupling of 1a to 2a

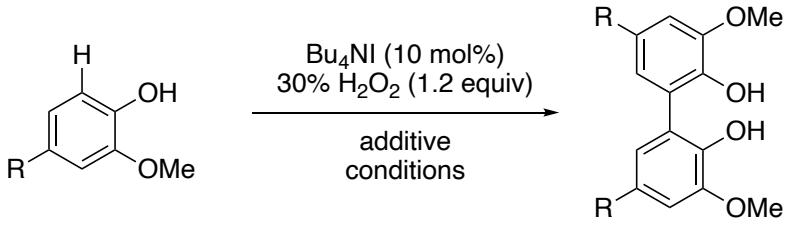


1a **2a**

entry	cat. (mol%)	oxidant (equiv)	additive (equiv)	solvent (*M*)	time (h)	**2a**, yield (%)[a]
1	Bu_4NI (10)	30% H_2O_2 (1.2)	–	EtOAc (0.2)	3 (24)	40 (40)
2	Bu_4NI (10)	30% H_2O_2 (2)	–	EtOAc (0.2)	3	30
3	Bu_4NI (20)	30% H_2O_2 (1.2)	–	EtOAc (0.2)	24	40
4	Bu_4NI (10+10[b])	30% H_2O_2 (1+1[b])	–	EtOAc (0.2)	6	<5 *(messy)*
5	Bu_4NI (10)	TBHP (1.2)	–	EtOAc (0.2)	24	20
6	Oct_4NI (10)	30% H_2O_2 (1.2)	–	EtOAc (0.2)	24	42
7	Bu_4PI (10)	30% H_2O_2 (1.2)	–	EtOAc (0.2)	24	44
8	NH_4I (10)	30% H_2O_2 (1.2)	–	EtOAc (0.2)	24	28
9	KI (10)	30% H_2O_2 (1.2)	–	EtOAc (0.2)	24	40
10	Bu_4NI (10)	30% H_2O_2 (1.2)	–	CH_3CN (0.2)	24	22
11	Bu_4NI (10)	30% H_2O_2 (1.2)	–	THF (0.2)	24	29
12	Bu_4NI (10)	30% H_2O_2 (1.2)	–	Toluene (0.2)	24	30
13	Bu_4NI (10)	30% H_2O_2 (1.2)	–	DMF (0.2)	24	<5
14	Bu_4NI (10)	30% H_2O_2 (1.2)	–	CH_3NO_2 (0.2)	24	<5
15	Bu_4NI (10)	30% H_2O_2 (1.2)	–	H_2O (0.2)	24	<5 *(messy)*
16	Bu_4NI (10)	30% H_2O_2 (1.2)	$B(OH)_3$ (0.1)	EtOAc (0.2)	24	38
17	Bu_4NI (10)	30% H_2O_2 (1.2)	4-$CF_3C_6H_4B(OH)_2$ (0.1)	EtOAc (0.2)	24	34
18	Bu_4NI (10)	30% H_2O_2 (1.2)	*i*-Pr_2NEt (0.1)	EtOAc (0.2)	24	23
19	Bu_4NI (10)	30% H_2O_2 (1.2)	K_2CO_3 (0.25)	EtOAc (0.2)	24	72
20	Bu_4NI (10)	30% H_2O_2 (1.2)	K_2CO_3 in H_2O (1 *M*) (1)	EtOAc (0.2)	24	26
21	Bu_4NI (10)	30% H_2O_2 (1.2)	K_2CO_3 (0.5)	EtOAc (0.2)	9	78
22	Bu_4NI (10)	30% H_2O_2 (1.2)	K_2CO_3 (1)	EtOAc (0.2)	1.5	90
23	Bu_4NI (10)	30% H_2O_2 (1.2)	K_2CO_3 (1)	EtOAc (0.1)	4	>95 (87)[c]
24	Bu_4NI (10)	30% H_2O_2 (1.2)	K_2CO_3 (1) + 18-C-6 (1)	EtOAc (0.1)	24	20
25	Bu_4NI (10)	30% H_2O_2 (1.2)	Na_2CO_3 (1)	EtOAc (0.1)	5	>95 (73)[c]
26	Bu_4NI (10)	30% H_2O_2 (1.2)	Cs_2CO_3 (1)	EtOAc (0.1)	4	<5
27	Bu_4NI (10)	30% H_2O_2 (1.2)	$CaCO_3$ (1)	EtOAc (0.1)	6	20
28	Bu_4NI (10)	30% H_2O_2 (1.2)	$KHCO_3$ (1)	EtOAc (0.1)	24	45
29	Bu_4NI (10)	30% H_2O_2 (1.2)	KOAc (1)	EtOAc (0.1)	24	49
30	Bu_4NI (10)	TBHP (1.2)	K_2CO_3 (0.25)	EtOAc (0.2)	24	47[c]
31	–	30% H_2O_2 (1.2)	K_2CO_3 (1)	EtOAc (0.1)	24	<5
32	Bu_4NI (10)	–	K_2CO_3 (1)	EtOAc (0.1)	24	<5

[a] Determined by ^1H NMR analysis. [b] Additional Bu_4NI and 30% H_2O_2 was added after 3 h. [c] Isolated yield.

Table S2. Oxidative Homocoupling of 2-Methoxyphenols 1b–d

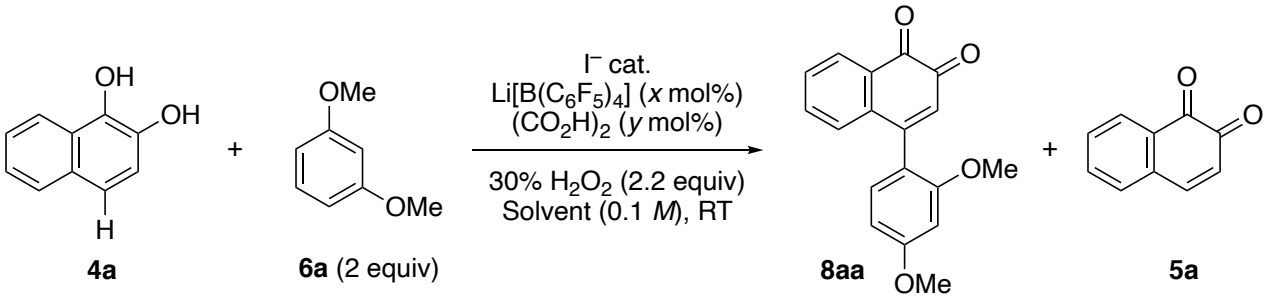


1 **2**

entry	R (**1**)	additive (equiv)	conditions	time (h)	**2**, yield (%)[a]
1	*n*-Pr (**1b**)	–	EtOAc (0.2 *M*), rt	24	46
2	*n*-Pr (**1b**)	Na_2CO_3 (1)	EtOAc (0.2 *M*), rt	24	91[b]
3	Allyl (**1c**)	–	EtOAc (0.2 *M*), 50 °C	10	26
4	Allyl (**1c**)	K_2CO_3 (1)	EtOAc (0.2 *M*), 50 °C	10	49
5	Allyl (**1c**)	K_2CO_3 (1)	EtOAc (0.1 *M*), rt	24	44
6	Allyl (**1c**)	Na_2CO_3 (1)	EtOAc (0.2 *M*), 50 °C	3	45
7	Allyl (**1c**)	Na_2CO_3 (1)	EtOAc (0.2 *M*), rt	6	68[b]
8	CH_2OMe (**1d**)	–	EtOAc (0.2 *M*), rt	21	12
9	CH_2OMe (**1d**)	K_2CO_3 (1)	EtOAc (0.2 *M*), 50 °C	6	26
10	CH_2OMe (**1d**)	Na_2CO_3 (1)	EtOAc (0.2 *M*), 50 °C	6	34
11	CH_2OMe (**1d**)	–	$(CH_3O)_2CO$ (0.2 *M*), 50 °C	6	45
12	CH_2OMe (**1d**)	Na_2CO_3 (2)	$(CH_3O)_2CO$ (0.2 *M*), 50 °C	6	60 (42)[b]
13[c]	CH_2OMe (**1d**)	Na_2CO_3 (2)	$(CH_3O)_2CO$ (0.1 *M*), 50 °C	6	71[b]

[a] ^{1}H NMR analysis. [b] Isolated yield. [c] 30% H_2O_2 (2x0.6 equiv) was added as two portions at 0 h and 3 h.

Table S3. Tandem Oxidation/Cross-coupling of 4a with 6a

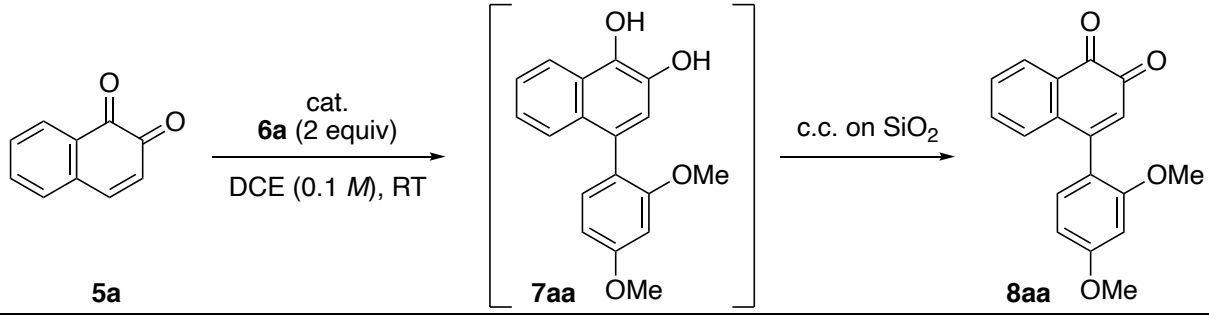


4a **6a** (2 equiv) **8aa** **5a**

entry	I^- (mol%)	*x* (mol%)	*y* (mol%)	solvent	time (h)	**8aa**, yield (%)[a]	**5a**, yield (%)[a]
1	–	5	10	DCE	3	0	0
2	Bu_4NI (10)	–	–	DCE	24	0	85
3	Bu_4NI (10)	–	10	DCE	24	0	85
4	Bu_4NI (10)	–	10[c]	DCE	24	0	85
5	Bu_4NI (10)	10[d]	–	DCE	24	0	85
6	Bu_4NI (5)	5	10	DCE	2	71	<1
7	Bu_4NI (5)	5	10	Toluene	2.5	55	<1
8	Bu_4NI (5)	5	10	EtOAc	2.5	16	11
9	NaI (10)	1	10	DCE	2.5	63	5
10	KI (10)	1	10	DCE	2	67	10
11	CaI_2 (5)	1	10	DCE	1	86 (80)[b]	<1
12	CaI_2 (5)	1	5	DCE	1.5	74	<1
13	CaI_2 (5)	1	20	DCE	1	76	<1
14[e]	CaI_2 (5)	–	10	DCE	5	78	<1
15[e]	CaI_2 (5)	–	–	DCE	5	0	85

[a] Determined by ^{1}H NMR analysis. [b] Isolated yield. [c] TsOH instead of $(CO_2H)_2$. [d] $Sc(OTf)_3$ instead of Li^+ salt. [e] Since no coupling reaction with **6a** proceeded in the absence of oxalic acid (entry 15), we believed that an active LBA catalysts might be generated from Ca^{2+} and oxalic acid in entry 14 to mediate the 1,4-addition reaction.

Table S4. Tandem Coupling of 5a with 6a

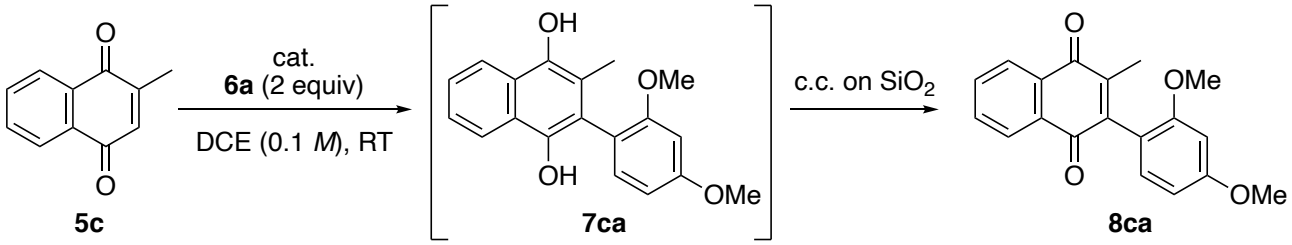


5a **7aa** **8aa**

entry	cat. (mol%)	time (h)	**8aa**, yield (%)[a]
1	–	24	0
2	$(CO_2H)_2$ (10)	24	0
3	$Li[B(C_6F_5)_4]$ (10)	24	0
4	$Li[B(C_6F_5)_4]$ (1) + $(CO_2H)_2$ (10)	2	82 (77)[b]
5	CaI_2 (5) + $(CO_2H)_2$ (10)	27	78
6	NaI (5) + $(CO_2H)_2$ (10)	24	0
7	CaI_2 (5)	24	0

[a] Determined by ^{1}H NMR analysis. [b] Isolated yield.

Table S5. Tandem Coupling of 5c with 6a

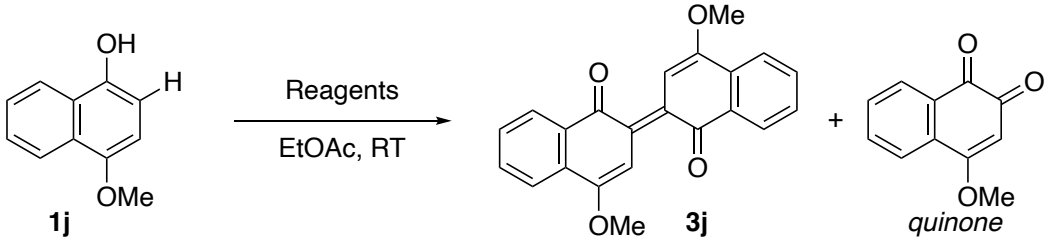


5c **7ca** **8ca**

entry	cat. (mol%)	time (h)	**8aa**, yield (%)[a]
1	–	24	0
2	$(CO_2H)_2$ (10)	24	0
3	$Li[B(C_6F_5)_4]$ (10)	24	0
4	$Li[B(C_6F_5)_4]$ (1) + $(CO_2H)_2$ (10)	2	83 (79)[b]
5	CaI_2 (5) + $(CO_2H)_2$ (10)	24	0

[a] Determined by ^{1}H NMR analysis. [b] Isolated yield.

Table S6. Investigation of Catalytic Active Species



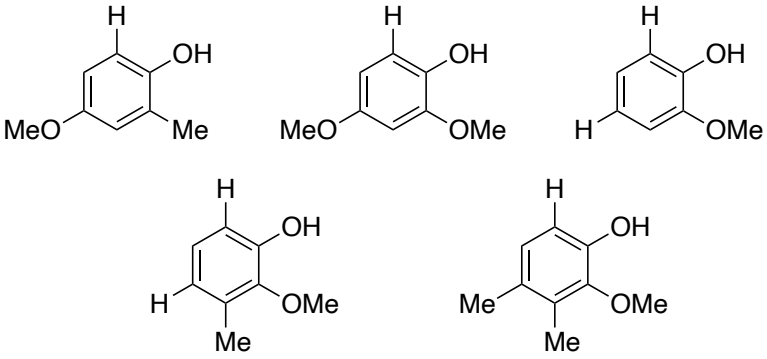
1j **3j** *quinone*

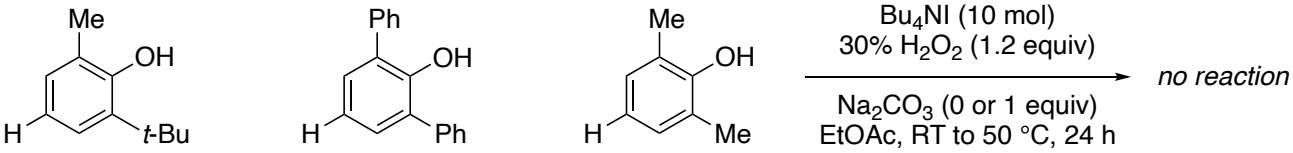
entry	reagents (equiv)	time (h)	**3j**, yield (%)[a]
1	Bu_4NI (0.1) + 30% H_2O_2 (1.2)	1	99 (93)[b]
2	I_2 (1)	24	<1
3[c]	I_2 (1) + KOH (2)	3	99
4[d]	$NaIO_4$ (1)	3	70 (quinone: 25)
5	Bu_4NBr (0.1) + 30% H_2O_2 (1.2)	24	<1
6	Bu_4NCl (0.1) + 30% H_2O_2 (1.2)	24	<1

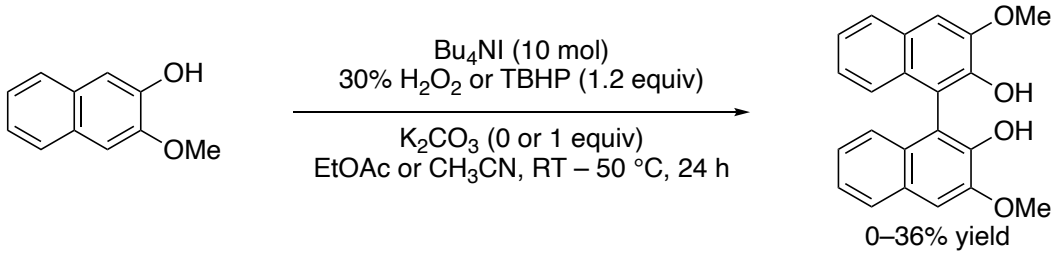
[a] Determined by ^{1}H NMR analysis. [b] Isolated yield. [c] Hypoiodite species might be generated *in situ*.[1] [d] Although oxidation of **1j** proceeded using $NaIO_4$ to give **3j** along with quinone in 25% yield, no quinone formation was observed under the catalytic conditions in entry 1. As in our previous studies on hypoiodite-catalyzed oxidative α-C–O coupling of carbonyl compounds,[2] these results suggest that periodate (+7) was partially decomposed during reaction period to the low valent iodine (+1) species and then catalytic oxidation proceeded with high valent iodine (+7) species as a stoichiometric co-oxidant for re-generation of low valent iodine species (–1 to +1).

Scheme S1. Unsuccessful Examples for Biaryl Coupling

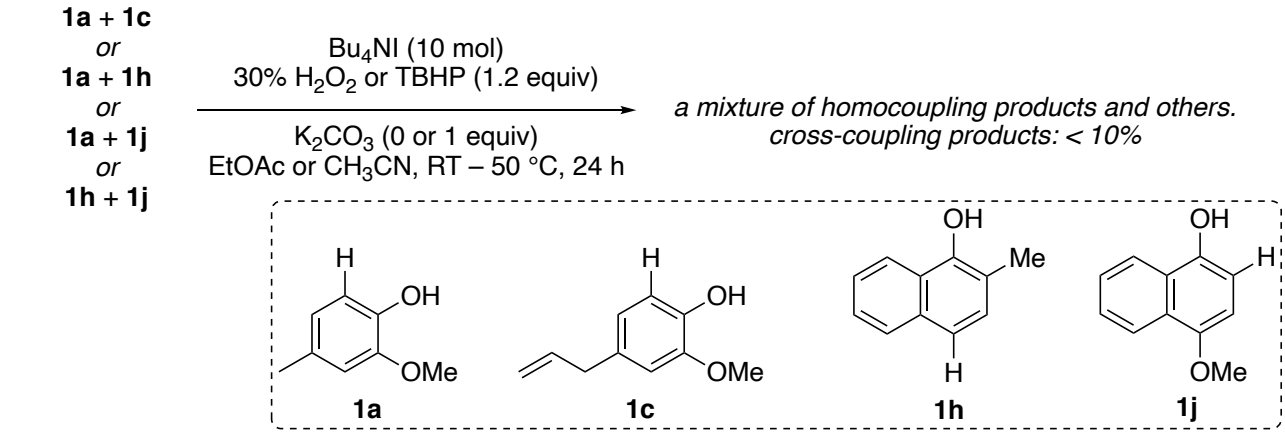
homocoupling



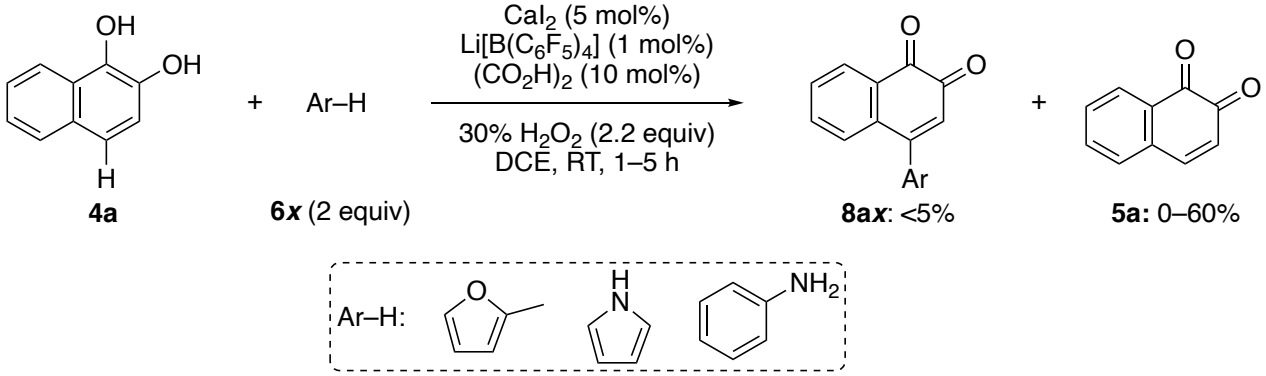




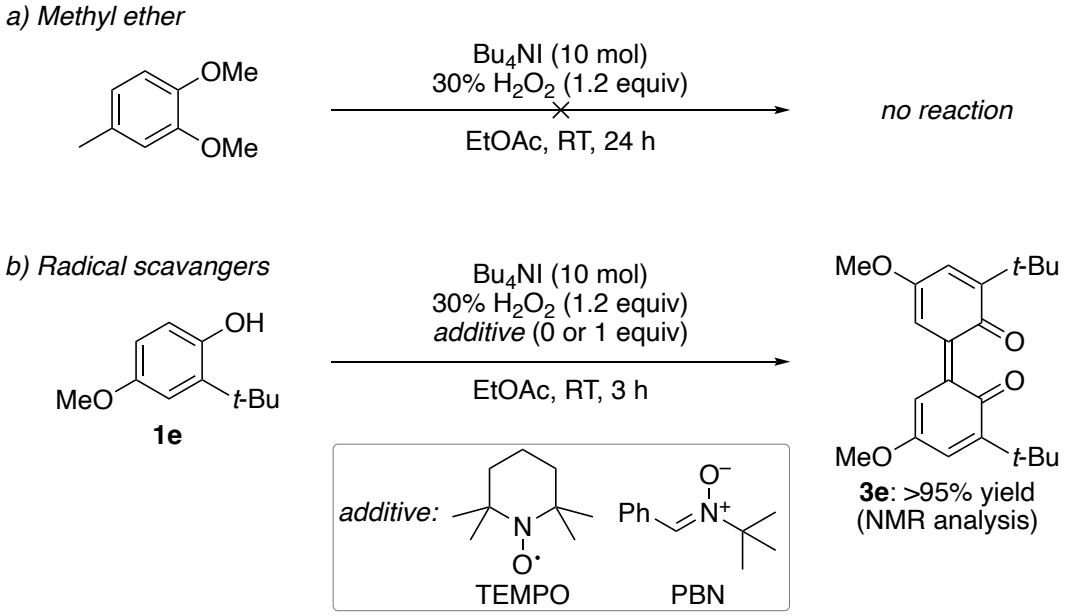
cross-coupling



tandem coupling

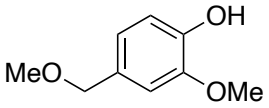


Scheme S2. Control Experiments

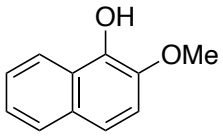


Synthesis and Characterization of Substrates

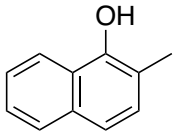
Compounds **1a**–**1c**, **1e**, **1f**, **1j**, **4a**, **4b**, **5a**–**e** and **6a**–**h** are commercially available and used without further purification. Compounds **1d**, **1g**–**1i**, **1k**–**1n** were prepared by standard methods following the literature.



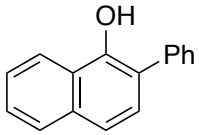
2-Methoxy-4-(methoxymethyl)phenol (1d):[3] Colorless oil. **TLC**, R_f = 0.35 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.37 (s, 3H), 3.90 (s, 3H), 4.38 (s, 2H), 5.60 (s, 1H), 6.81–6.83 (m, 1H), 6.87–6.89 (m, 2H).



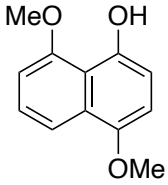
2-Methoxy-1-naphthol (1g):[4] Pale yellow solid. **TLC**, R_f = 0.49 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 4.01 (s, 3H), 6.00 (brs, 1H), 7.26 (d, J = 8.7 Hz, 1H), 7.34–7.47 (m, 3H), 7.75 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 8.7 Hz, 1H).



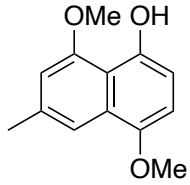
2-Methyl-1-naphthol (1h):[5] Red solid. **TLC**, R_f = 0.58 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.42 (s, 3H), 5.06 (s, 1H), 7.24 (d, J = 8.7 Hz, 1H), 7.37–7.49 (m, 3H), 7.78 (d, J = 8.2 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H).



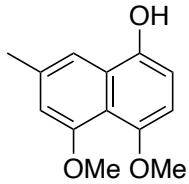
2-Phenyl-1-naphthol (1i):[6] Pale yellow solid. **TLC**, R_f = 0.36 (hexane–EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.84 (s, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.42–7.58 (m, 8H), 7.82–7.84 (m, 1 H), 8.28–8.31 (m, 1H).



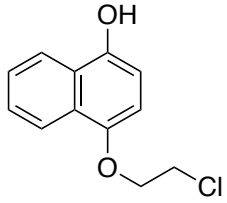
4,8-Dimethoxy-1-naphthol (1k):[7,8] White solid. **TLC**, R_f = 0.25 (hexane–EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.94 (s, 3H), 4.06 (s, 3H), 6.78 (s, 2H), 6.85 (d, J = 7.8 Hz, 1H), 7.34 (t, J = 8.2 Hz, 1H), 7.85 (d, J = 8.7 Hz, 1H), 8.95 (s, 1H).



4,8-Dimethoxy-6-methyl-1-naphthol (1l):[9] White solid. **TLC**, R_f = 0.25 (hexane–EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.48 (s, 3H), 3.93 (s, 3H), 4.04 (s, 3H), 6.67–6.75 (m, 3H), 7.63 (s, 1H), 8.88 (s, 1H).

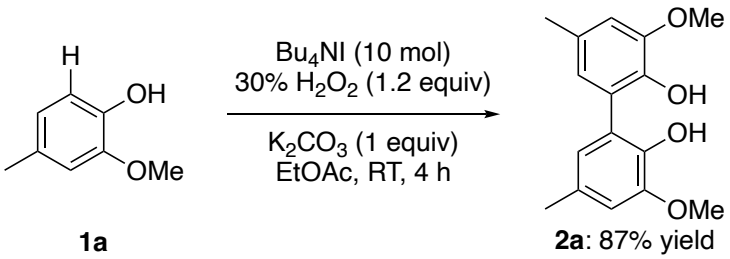


4,5-Dimethoxy-7-methyl-1-naphthol (1m):[9a,10] Tan solid. **TLC**, R_f = 0.33 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.50 (s, 3H), 3.90 (s, 3H), 3.97 (s, 3H), 5.00 (s, 1H), 6.63–6.74 (m, 3H), 7.53 (s, 1H).



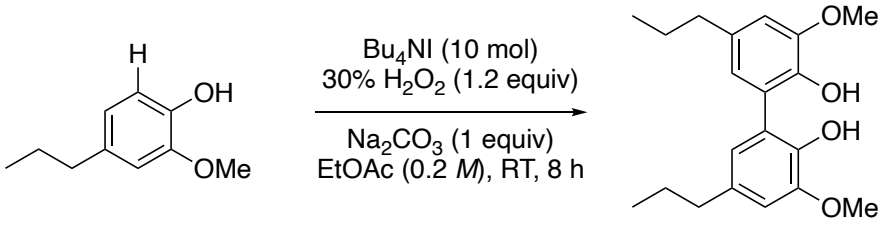
4-(2-Chloroethoxy)-1-naphthol (1n):[7] Purple solid. **TLC**, R_f = 0.37 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.93 (t, J = 5.5 Hz, 2H), 4.36 (t, J = 5.5 Hz, 2H), 4.93 (s, 1H), 6.67 (d, J = 8.3 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 7.51–7.56 (m, 2H), 8.12–8.14 (m, 1H), 8.26–8.28 (m, 1H).

Representative Procedures for Oxidative Homocoupling of Arenols and Characterization of Products



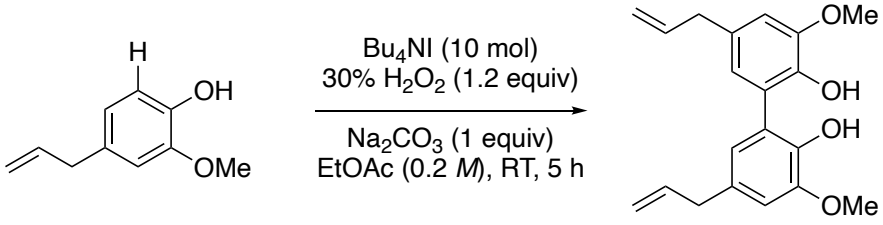
1a **2a**: 87% yield

3,3'-Dimethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol (2a):[11] To a stirring solution of **1a** (0.691 g, 0.500 mmol) and Bu_4NI (0.0185 g, 0.0500 mmol, 10 mol%) in ethyl acetate (5.00 mL) were added potassium carbonate (0.0691 g, 0.500 mmol, 1 equiv) and 30% aqueous hydrogen peroxide (0.0620 mL, 0.600 mmol, 1.2 equiv) at room temperature. The reaction was monitored by TLC analysis. Upon the completion of the reaction (4 h), the resulting mixture was poured into saturated aqueous $NaHSO_3$ solution (ca. 5 mL). To the resulting mixture was added a saturated aqueous NH_4Cl solution (ca. 10 mL), and the aqueous layers were extracted with EtOAc (3 times). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 1:1) to give analytically pure **2a** (0.0595 g, 0.217 mmol, 87% yield). White solid. **TLC**, R_f = 0.44 (hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.33 (s, 6H), 3.92 (s, 6H), 5.98 (s, 2H), 6.72–6.73 (m, 4H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 21.1, 56.0, 111.2, 123.3, 124.3, 129.6, 140.2, 147.0.



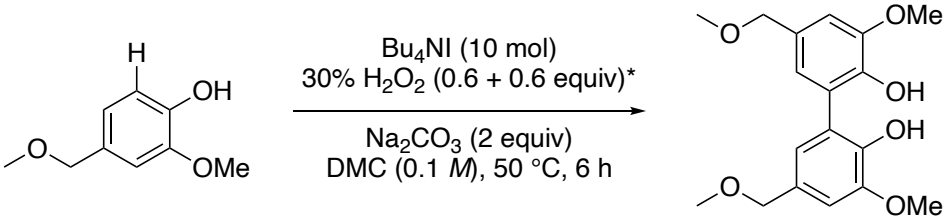
1b **2b**: 91% yield

3,3'-Dimethoxy-5,5'-dipropyl-[1,1'-biphenyl]-2,2'-diol (2b):[12] 1.00 mmol scale, 0.151 g, 0.457 mmol, 91% yield. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 1:1) to give analytically pure **2b**. White solid. **TLC**, R_f = 0.50 (hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.96 (t, J = 7.4 Hz, 6H), 1.60–1.70 (m, 4H), 2.56 (t, J = 7.4 Hz, 4H), 3.92 (s, 6H), 6.04 (s, 2H), 6.72–6.74 (m, 4H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 13.9, 24.8, 37.8, 56.0, 110.5, 122.9, 124.4, 134.7, 140.4, 147.1.



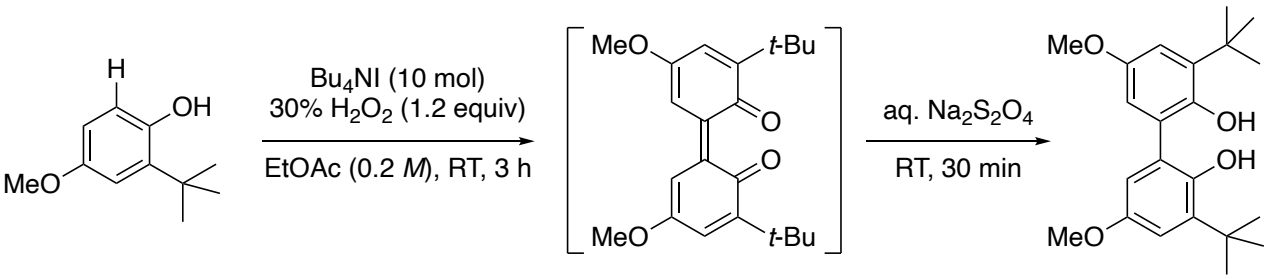
1c **2c**: 68% yield

5,5'-Diallyl-3,3'-dimethoxy-[1,1'-biphenyl]-2,2'-diol (2c):[12a, 13] 0.300 mmol scale, 0.0334 g, 0.102 mmol, 68% yield. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 10:1 to 1:1) to give analytically pure **2c**. White solid. **TLC**, R_f = 0.44 (hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.36 (d, *J* = 6.9 Hz, 4H), 3.91 (s, 6H), 5.05–5.14 (m, 4H), 5.93–6.02 (m, 2H), 6.02 (s, 2H), 6.72–6.76 (m, 4H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 40.0, 56.0, 110.6, 115.7, 123.1, 124.3, 131.9, 137.6, 140.8, 147.2.



1d **2d**: 71% yield

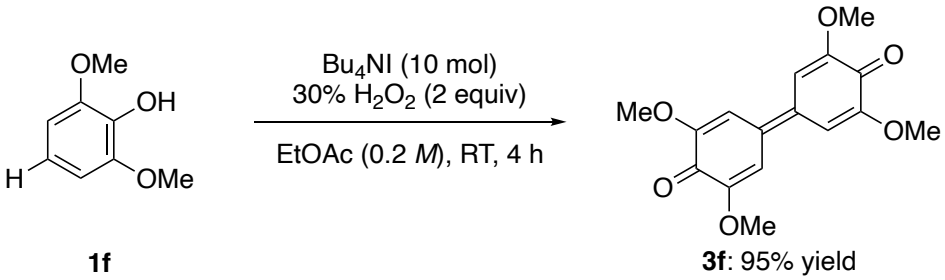
3,3'-Dimethoxy-5,5'-bis(methoxymethyl)-[1,1'-biphenyl]-2,2'-diol (2d): Two portions of 30% H_2O_2 (0.6 equiv) were added at 0 h and 3 h. 0.500 mmol scale, 0.0594 g, 0.178 mmol, 71% yield. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 1:1) to give analytically pure **2d**. White solid. **TLC**, R_f = 0.15 (hexane–EtOAc = 10:1 to 1:1); **IR** ($CHCl_3$) 3600–3200, 2934, 1597, 1460, 1272 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.39 (s, 6H), 3.94 (s, 6H), 4.42 (s, 4H), 6.14 (s, 2H), 6.89–6.93 (m, 4H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 56.1, 58.0, 74.7, 109.8, 122.9, 123.9, 130.0, 142.2, 147.3; **HRMS** (FAB) *m*/*z* calcd for $[C_{18}H_{22}O_6]^+$ 334.1411, found 334.1418.



1e **3e** *not isolated (unstable)* **2e**: 95% yield

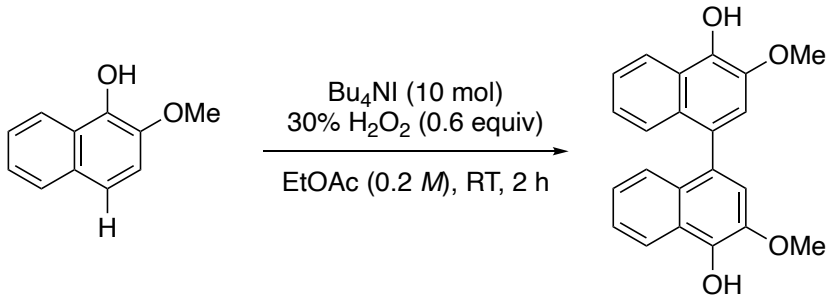
3,3'-Di-*tert*-butyl-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diol (2e):[14] To a stirring solution of **1e** (0.901 g, 0.500 mmol) and Bu_4NI (0.0185 g, 0.0500 mmol, 10 mol%) in ethyl acetate (2.50 mL) was added 30% aqueous hydrogen peroxide (0.0620 mL, 0.600 mmol, 1.2 equiv) at room temperature. The reaction was monitored by TLC analysis. Upon the completion of the reaction (3 h), to the resulting mixture was added a saturated aqueous $Na_2S_2O_4$ solution (ca. 10 mL), and the resulting mixture was

stirred at room temperature for 30 minutes. To the resulting mixture was added a saturated aqueous NH_4Cl solution (ca. 20 mL), and the aqueous layers were extracted with EtOAc (3 times). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 1:1) to give analytically pure **2e** (0.0851 g, 0.237 mmol, 95% yield). Brown solid. **TLC**, R_f = 0.68 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.43 (s, 18H), 3.78 (s, 6H), 5.00 (s, 2H), 6.63 (d, *J* = 3.2 Hz, 2H), 6.96 (d, *J* = 3.2 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 29.5, 35.2, 55.7, 111.7, 115.2, 123.1, 138.9, 145.9, 153.1.



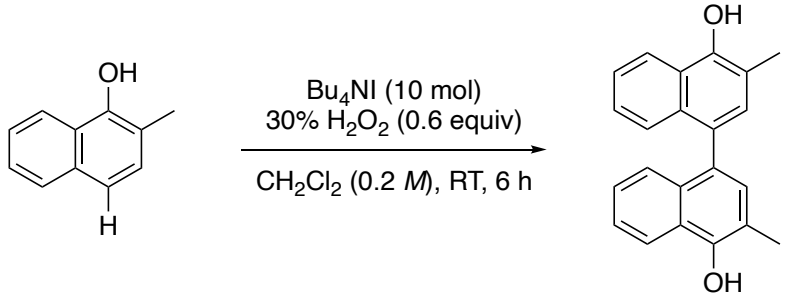
1f **3f**: 95% yield

3,3',5,5'-Tetramethoxy-[1,1'-bi(cyclohexylidene)]-2,2',5,5'-tetraene-4,4'-dione (3f):[15] 0.500 mmol scale, 0.0726 g, 0.239 mmol, 95% yield. Upon the completion of the reaction, the solids were filtered on a Büchner funnel and washed with hexane. The solids were dried under vacuum to give analytically pure **3f**. Purple solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.98 (s, 12H), 6.91 (s, 4H).



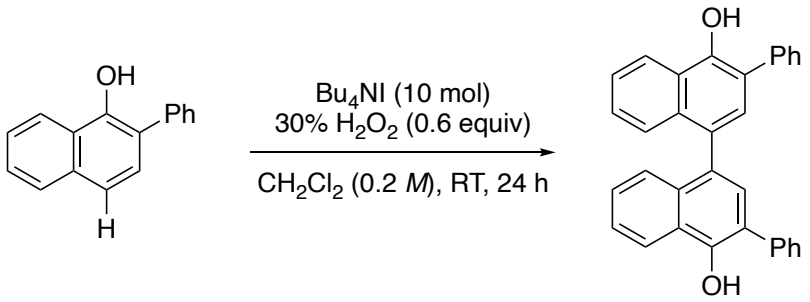
1g **2g**: 95% yield

3,3'-Dimethoxy-[1,1'-binaphthalene]-4,4'-diol (2g):[16] 0.300 mmol scale, 0.0491 g, 0.142 mmol, 95% yield. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 1:1) to give analytically pure **2g**. Light purple solid. **TLC**, R_f = 0.32 (hexane–EtOAc = 2:1); **IR** (film) 3550–3200, 2942, 1624, 1596, 1466, 1337 cm^{-1}; **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 3.91 (s, 6H), 7.10–7.15 (m, 4H), 7.35–7.40 (m, 4H), 8.18 (d, *J* = 8.4 Hz, 2H), 9.38 (s, 2H); **^{13}C NMR** (DMSO-d_6, 400 MHz) δ 57.1, 117.3, 121.6, 124.0, 124.7, 125.1, 125.8, 128.6, 128.9, 139.6, 141.5; **HRMS** (FAB) *m*/*z* calcd for $[C_{22}H_{18}O_4]^+$ 346.1200, found 346.1207.



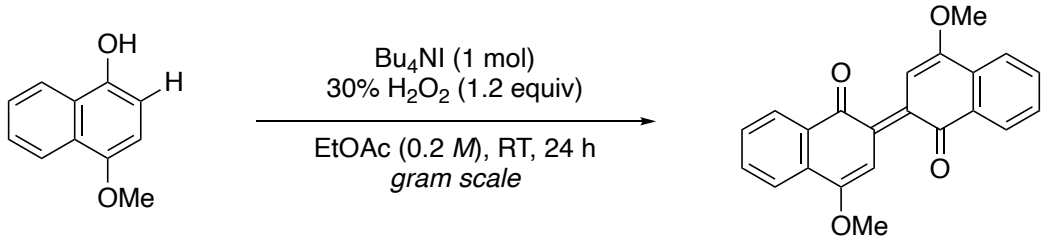
1h **2h**: 75% yield

3,3'-Dimethyl-[1,1'-binaphthalene]-4,4'-diol (2h):[17] 0.300 mmol scale, 0.0353 g, 0.112 mmol, 75% yield. [*cf*: in EtOAc, 30% yield]. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 10:1 to 1:1) to give analytically pure **2h**. Red solid. **TLC**, R_f = 0.47 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.46 (s, 6H), 5.14 (s, 2H), 7.24–7.26 (m, 4H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.46–7.48 (m, 2H), 8.22 (d, *J* = 8.2 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 15.7, 115.7, 121.0, 124.1, 125.1, 125.4, 126.6, 130.7, 131.1, 132.8, 148.2.



1i **2i**: 77% yield

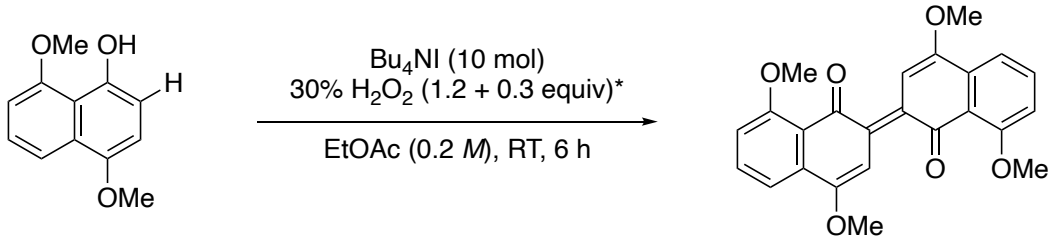
3,3'-Diphenyl-[1,1'-binaphthalene]-4,4'-diol (2i):[18] 0.300 mmol scale, 0.0506 g, 0.115 mmol, 77% yield. [*cf*: in EtOAc, no clean reaction and no data]. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 10:1 to 1:1) to give analytically pure **2i**. Purple solid. **TLC**, R_f = 0.58 (hexane–EtOAc = 2:1); **IR** (film) 3600–3200, 1578, 1498, 1375, 1224 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.96 (s, 2H), 7.33–7.37 (m, 2H), 7.40–7.44 (m, 4H), 7.49–7.55 (m, 8H), 7.58–7.60 (m, 4H), 8.40 (d, *J* = 8.2 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 120.8, 122.5, 124.3, 125.4, 126.4, 126.5, 127.9, 129.3, 129.6, 129.7, 130.6, 133.6, 137.2, 147.4; **HRMS** (FAB+) *m*/*z* calcd for $[C_{32}H_{22}O_2+H]^+$ 439.1693, found 439.1689.



1j **3j**: 93% yield
Russig's blue

(*E*)-4,4'-Dimethoxy-1*H*,1'*H*-[2,2'-binaphthalenylidene]-1,1'-dione (3j):[19] To a stirring solution of **1j** (1.74 g, 10.0 mmol) and Bu_4NI (0.0369 g, 0.100 mmol, 1 mol%) in ethyl acetate (50.0 mL) was

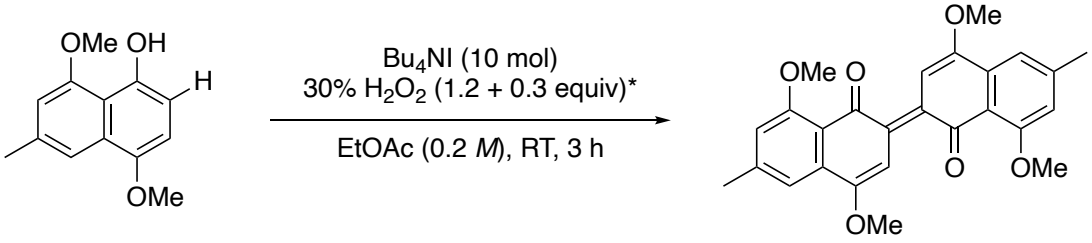
added 30% aqueous hydrogen peroxide (1.23 mL, 12.0 mmol, 1.2 equiv) at room temperature. The reaction was monitored by TLC analysis. Upon the completion of the reaction (24 h), the solids were filtered on a Büchner funnel and washed with hexane. The solids were dried under vacuum to give analytically pure **3j** (1.61 g, 4.67 mmol, 93% yield). [*cf*: Bu_4NI (10 mol%) on 0.5 mmol scale reaction, 1 h, >99% yield (^{1}H NMR analysis)]. Purple solid. **TLC**, R_f = 0.61 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 4.08 (s, 6H), 7.47–7.50 (m, 2H), 7.60–7.64 (m, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 8.17 (d, *J* = 8.2 Hz, 2H), 8.42 (s, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 55.9, 103.1, 121.9, 127.6, 129.0, 131.5, 131.7, 131.8, 133.1, 157.3, 189.3.



1k

3k: 98% yield
synthetic precursor of 3,3'-bijuglone

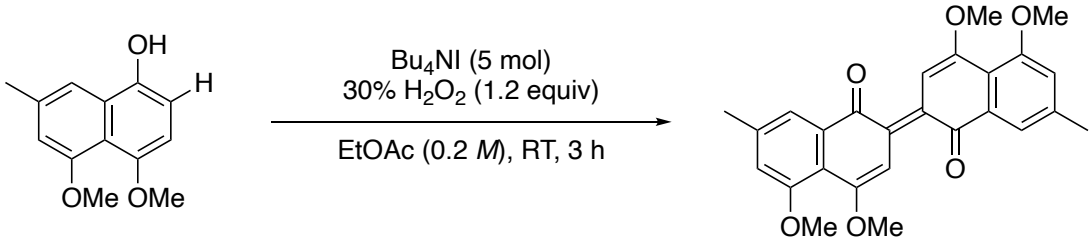
(*E*)-4,4',8,8'-Tetramethoxy-1*H*,1'*H*-[2,2'-binaphthalenylidene]-1,1'-dione (3k):[19, 20] 0.200 mmol scale, 0.0398 g, 0.0984 mmol, 98% yield. Additional 30% H_2O_2 (0.5 equiv) was added at 4 h. The crude was purified by a short column chromatography on silica gel (eluent: CH_2Cl_2 only) to give analytically pure **3k**. Purple solid. **TLC**, R_f = 0.17 (hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.99 (s, 6H), 4.01 (s, 6H), 7.00 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.50–7.54 (m, 2H), 7.92 (s, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 56.0, 56.3, 102.3, 112.4, 114.6, 120.6, 133.3, 133.9, 134.5, 155.4, 159.9, 189.5.



1l

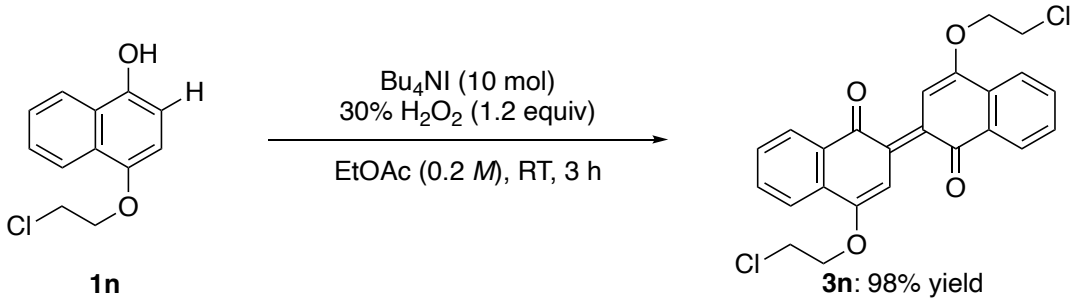
3l: 96% yield
synthetic precursor of mamegakinone

(*E*)-4,4',8,8'-Tetramethoxy-6,6'-dimethyl-1*H*,1'*H*-[2,2'-binaphthalenylidene]-1,1'-dione (3l):[9] 0.500 mmol scale, 0.0726 g, 0.239 mmol, 96% yield. Additional 30% H_2O_2 (0.3 equiv) was added at 1.5 h. The crude was purified by a short column chromatography on silica gel (eluent: CH_2Cl_2 only) to give analytically pure **3l**. Purple solid. **TLC**, R_f = 0.17 (hexane–EtOAc = 1:1); **IR** ($CHCl_3$) 3003, 1587, 1458, 1387, 1235 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.42 (s, 6H), 3.97 (s, 6H), 4.00 (s, 6H), 6.80 (s, 2H), 7.23 (s, 2H), 7.97 (s, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 22.3, 55.8, 56.2, 102.5, 113.1, 115.1, 118.4, 133.3, 134.9, 144.9, 155.4, 160.1, 189.2; **HRMS** (FAB+) *m*/*z* calcd for $[C_{26}H_{24}O_6+H]^+$ 433.1646, found 433.1650.



1m **3m**: 98% yield
synthetic precursor of biramentaceone

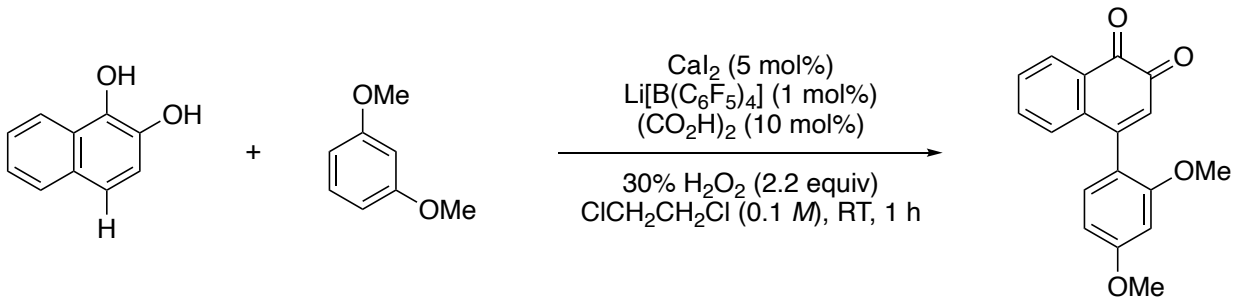
(*E*)-4,4',5,5'-Tetramethoxy-7,7'-dimethyl-1*H*,1'*H*-[2,2'-binaphthalenylidene]-1,1'-dione (3m):[21] 0.2 mmol scale, 0.0425 g, 0.0982 mmol, 98% yield. The crude was purified by a short column chromatography on silica gel (eluent: CH_2Cl_2 only) to give analytically pure **3m**. Purple solid. **TLC**, R_f = 0.28 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.43 (s, 6H), 3.92 (s, 6H), 4.05 (s, 6H), 6.97 (s, 2H), 7.70 (s, 2H), 8.37 (s, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 21.7, 56.1, 56.8, 103.2, 117.9, 118.1, 121.7, 130.3, 133.6, 140.3, 156.1, 159.5, 188.9.



1n **3n**: 98% yield

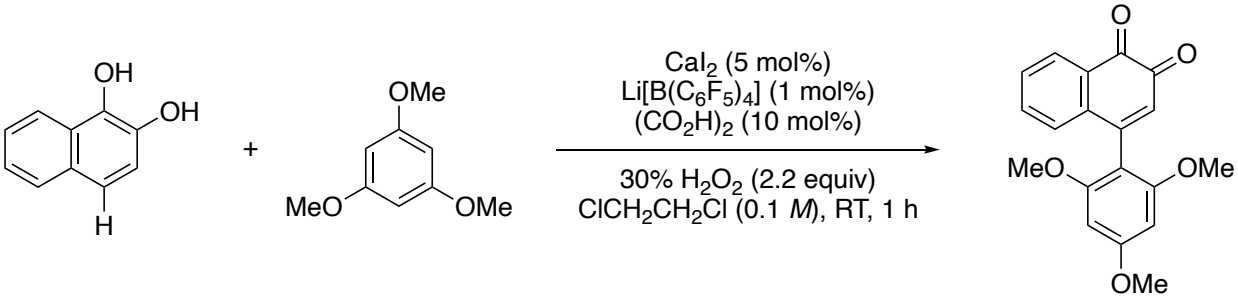
(*E*)-4,4'-bis(2-chloroethoxy)-1*H*,1'*H*-[2,2'-binaphthalenylidene]-1,1'-dione (3n):[7b, 22] 0.500 mmol scale, 0.108 g, 0.244 mmol, 98% yield. Product was isolated from the reaction mixture by a direct short column chromatography on silica gel (eluent: CH_2Cl_2 only). Purple solid. **TLC**, R_f = 0.44 (hexane–EtOAc = 2:1); **IR** ($CHCl_3$) 2964, 1586, 1560, 1271 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 4.00 (t, *J* = 5.2 Hz, 4H), 4.52 (t, *J* = 5.2 Hz, 4H), 7.49–7.52 (m, 2H), 7.63–7.67 (m, 2H), 7.86 (d, *J* = 7.8 Hz, 2H), 8.15 (d, *J* = 7.8 Hz, 2H), 8.37 (s, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 41.8, 68.2, 103.7, 122.1, 127.6, 129.2, 131.3, 131.4, 131.9, 133.3, 156.1, 189.1; **HRMS** (FAB+) *m*/*z* calcd for $[C_{24}H_{18}{}^{35}Cl_2O_4+H]^+$/$[C_{24}H_{18}{}^{35}Cl^{37}ClO_4+H]^+$/$[C_{24}H_{19}{}^{37}Cl_2O_4+H]^+$ 441.0655/443.0626/445.0596, found 441.0656/443.0623/443.0601.

Representative Procedures for Tandem Oxidation/Cross-coupling of Hydroquinones and Characterization of Products



4a **6a** (2 equiv) **8aa**: 80% yield

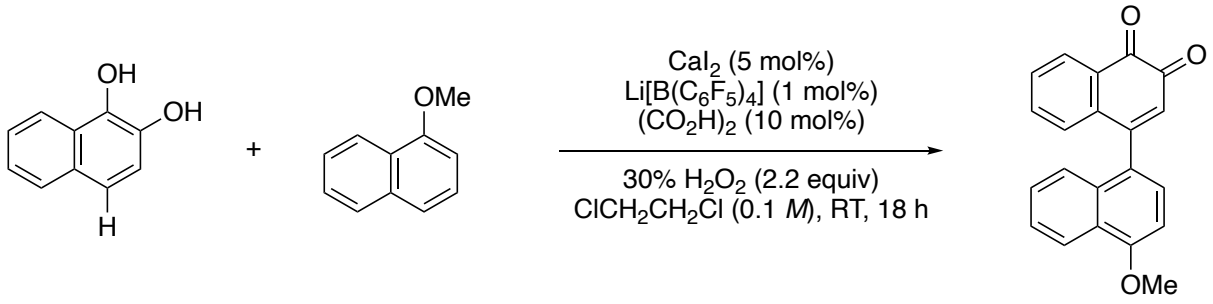
4-(2,4-Dimethoxyphenyl)naphthalene-1,2-dione (8aa): To a stirring mixture of **4a** (0.0320 g, 0.200 mmol), **6a** (0.0553 g, 0.400 mmol, 2 equiv), calcium iodide (0.00300 g, 0.0100 mmol, 5 mol%), oxalic acid (0.00180 g, 0.0200 mmol, 10 mol%) and $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$ (0.00180 g, 0.00200 mmol, 1 mol%) in dichloroethane (2.00 mL) was added 30% aqueous hydrogen peroxide (0.0449 mL, 0.440 mmol, 2.2 equiv) at room temperature. The reaction was monitored by TLC analysis. Upon the completion of the reaction (1 h), the resulting mixture was poured into saturated aqueous $Na_2S_2O_3$ (ca. 5 mL), and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 4:1 to 1:1) to give analytically pure **8aa** (0.0468 g, 0.159 mmol, 80% yield). Red solid. **TLC**, R_f = 0.30 (hexane–EtOAc = 2:1); **IR** ($CHCl_3$) 3009, 1665, 1607, 1504, 1287 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.74 (s, 3H), 3.89 (s, 3H), 6.39 (s, 1H), 6.59–6.63 (m, 2H), 7.06–7.08 (m, 1H), 7.18 (d, J = 8.3 Hz, 1H), 7.45–7.55 (m, 2H), 8.14–8.16 (m, 1H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 55.4, 55.5, 98.9, 104.8, 118.3, 128.3, 129.4, 129.8, 130.3, 130.4, 131.3, 135.0, 135.6, 155.3, 157.7, 162.2, 179.9, 180.8; **HRMS** (FAB+) *m*/*z* calcd for $[C_{18}H_{14}O_4+H]^+$ 295.0965, found 295.0962.



4a **6b** (2 equiv) **8ab**: 79% yield

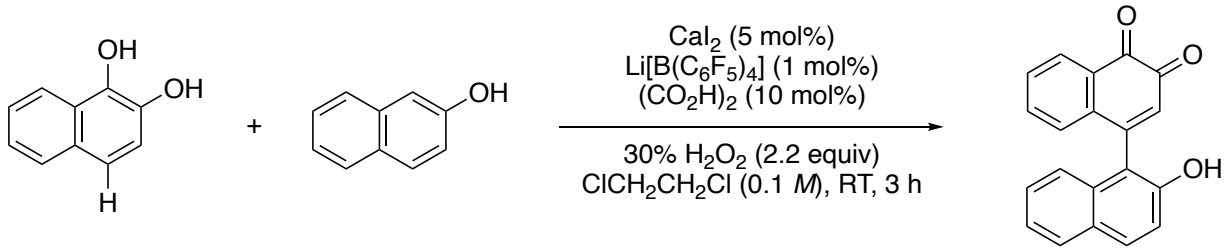
4-(2,4,6-Trimethoxyphenyl)naphthalene-1,2-dione (8ab):[23] 0.200 mmol scale, 0.0514 g, 0.158 mmol, 79% yield. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 4:1 to 1:1) to give analytically pure **8ab**. Red solid. **TLC**, R_f = 0.50 (hexane–EtOAc = 2:1); **IR** ($CHCl_3$) 2940, 1655, 1610, 1585, 1454 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.72 (s, 6H), 3.90 (s, 3H), 6.24 (s, 2H), 6.36 (s, 1H), 6.99 (d, J = 7.4 Hz, 1H), 7.43–7.51 (m, 2H), 8.14 (dd, J =

1.8, 7.4 Hz 1H) ; **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 55.5, 55.8, 90.6, 106.3, 128.5, 129.6, 130.0, 131.4, 135.2, 136.0, 151.7, 158.3, 162.3, 180.1, 180.8; **HRMS** (FAB+) *m*/*z* calcd for $[C_{18}H_{17}O_5+H]^+$ 325.1071, found 325.1074.



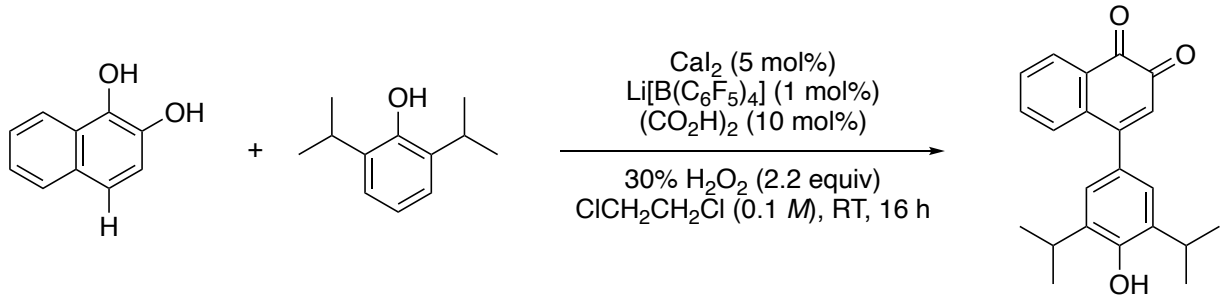
4a **6c** (2 equiv) **8ac**: 60% yield

4'-Methoxy-[1,1'-binaphthalene]-3,4-dione (8ac):[24] 0.200 mmol scale, 0.0376 g, 0.120 mmol, 60% yield. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 4:1 to 1:1) to give analytically pure **8ac**. Red solid. **TLC**, R_f = 0.57 (hexane–EtOAc = 1:1); **IR** ($CHCl_3$) 3066, 2938, 1656, 1583 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 4.09 (s, 3H), 6.54 (s, 1H), 6.89–6.93 (m, 2H), 7.39–7.55 (m, 5H), 7.64 (d, *J* = 6.7 Hz, 1H), 8.21–8.23 (m, 1H), 8.38 (d, *J* = 6.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 55.7, 103.2, 122.6, 125.4, 125.6, 125.9, 126.3, 126.4, 127.3, 129.0, 130.2, 130.2, 130.7, 131.3, 131.9, 135.4, 136.2, 156.6, 157.0, 179.6, 180.8; **HRMS** (FAB+) *m*/*z* calcd for $[C_{21}H_{14}O_3+H]^+$ 315.1016, found 315.1019.



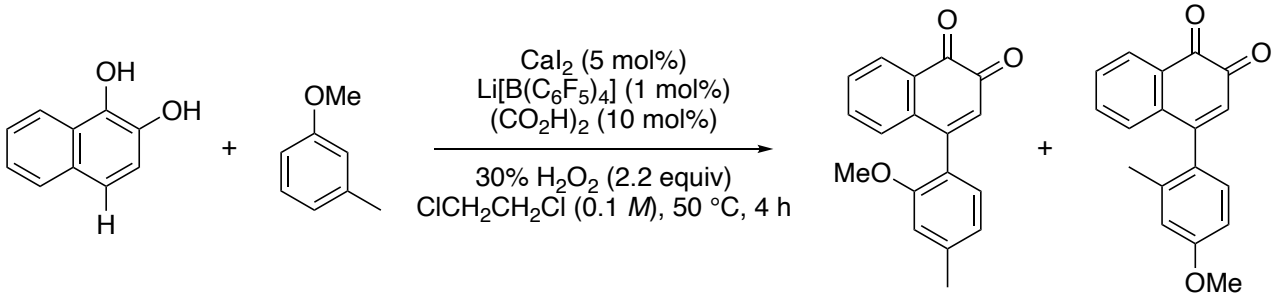
4a **6d** (2 equiv) **8ad**: 90% yield

2'-Hydroxy-[1,1'-binaphthalene]-3,4-dione (8ad):[25] 1.00 mmol scale, 0.271 g, 0.902 mmol, 90% yield. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 4:1 to 1:1) to give analytically pure **8ad**. Brown solid. **TLC**, R_f = 0.24 (hexane–EtOAc = 2:1); **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 6.36 (s, 1H), 6.71 (d, *J* = 6.8 Hz, 1H), 7.29–7.37 (m, 3H), 7.49–7.57 (m, 2H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 9.2 Hz, 1H), 8.08 (dd, *J* =, 1.8, 7.3 Hz, 1H), 9.86 (s, 1H); **^{13}C NMR** (DMSO-d_6, 400 MHz) δ 115.5, 118.4, 123.2, 124.2, 126.9, 127.8, 128.1, 128.3, 128.9, 130.4, 130.5, 132.1, 132.5, 135.2, 135.5, 151.7, 151.8, 179.0, 179.9.



4a **6e** (2 equiv) **8ae**: 38% yield

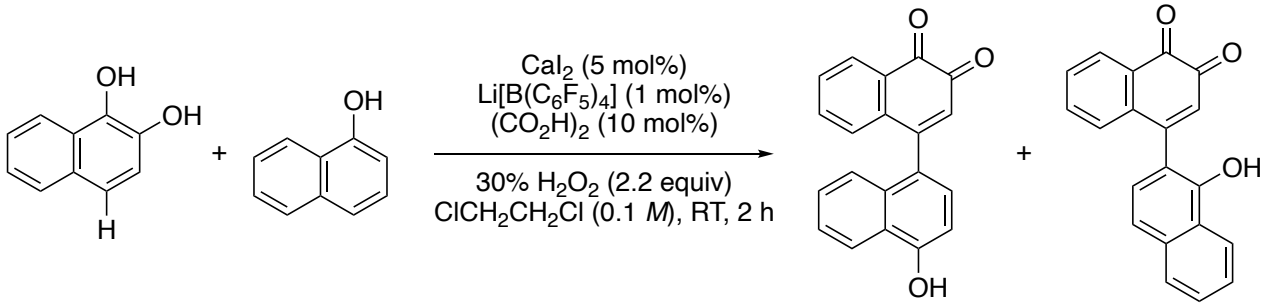
4-(4-Hydroxy-3,5-diisopropylphenyl)naphthalene-1,2-dione (8ae): 0.500 mmol scale, 0.0630 g, 0.188 mmol, 38% yield. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 10:1 to 1:1) to give analytically pure **8ae**. Red solid. **TLC**, R_f = 0.43 (hexane–EtOAc = 2:1); **IR** ($CHCl_3$) 3475, 2962, 1655, 1586, 1467 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.31 (d, J = 6.9 Hz, 12H), 3.18–3.26 (m, 2H), 5.10 (s, 1H), 6.45 (s, 1H), 6.15 (s, 2H), 7.44 (d, J = 7.3 Hz, 1H), 7.52–7.63 (m, 2H), 8.21 (dd, J = 7.8, 1.4 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 22.7, 27.1, 123.9, 126.8, 128.6, 129.7, 130.5, 130.6, 131.8, 134.2, 135.0, 135.4, 151.8, 158.0, 180.0, 180.6; **HRMS** (FAB+) *m/z* calcd for $[C_{22}H_{22}O_3+H]^+$ 335.1642, found 335.1645.



4a **6f** (2 equiv) **8af** **8af'**

8af + **8af'** (r.s. ~1:1): 30% yield inseparable mixture

4-(2-Methoxy-4-methylphenyl)naphthalene-1,2-dione (8af) and 4-(2-Methyl-4-methoxyphenyl)naphthalene-1,2-dione (8af'): 0.200 mmol scale, 0.0189 g, 0.0679 mmol, 34% yield (**8af** + **8af'**). The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 10:1 to 1:1) to give **8af** and **8af'** (ca. 1:1) as an inseparable mixture. Red solid. **TLC**, R_f = 0.38 (hexane–EtOAc = 2:1); **IR** ($CHCl_3$) 2919, 1657, 1609, 1586 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz for **8af** and **8af'**) δ 2.20 (s, 3H), 2.45 (s, 3H), 3.75 (s, 3H), 3.87 (s, 3H), 6.35 (s, 1H), 6.39 (s, 1H), 6.85–7.06 (m, 6H), 7.14 (s, 1H), 7.15 (s, 1H), 7.45–7.57 (m, 4H), 8.14–8.20 (m, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz for **8af** and **8af'**) δ 20.2, 21.8, 55.3, 55.4, 111.4, 111.9, 116.2, 121.6, 122.6, 128.0, 128.1, 128.4, 129.3, 129.4, 129.4, 129.8, 130.2, 130.3, 130.7, 131.2, 131.3, 135.0, 135.3, 135.4, 135.6, 136.9, 141.5, 155.6, 156.3, 157.4, 160.1, 179.5, 179.7, 180.6, 180.7; **HRMS** (FAB+) *m/z* calcd for $[C_{17}H_{15}O_3+H]^+$ 279.1016, found 279.1016.

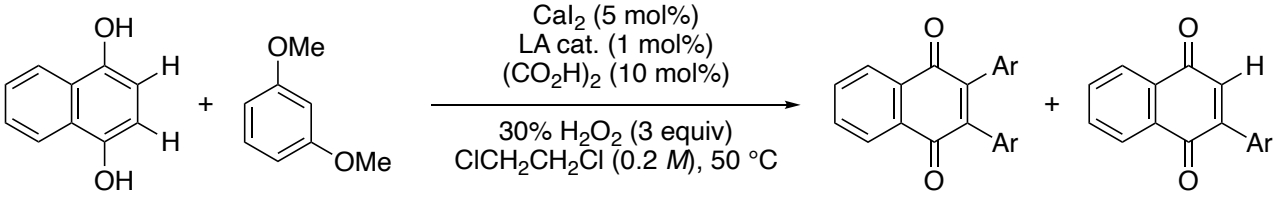


4a **6g** (2 equiv) **8ag**: 59% **8ag'**: 20%

The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 4:1 to 1:1) to give **8ag** (high polar) and **8ag'** (less polar) as separable regiomers.

4'-Hydroxy-[1,1'-binaphthalene]-3,4-dione (8ag):[26] 1.00 mmol scale, 0.178 g, 0.593 mmol, 59% yield. Including some minor impurities and ethyl acetate used for column chromatography. Black solid. **TLC**, R_f = 0.17 (hexane–EtOAc = 2:1); **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 6.38 (s, 1H), 6.73 (d, J = 7.3 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.40–7.56 (m, 4H), 7.76 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 7.2 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H), 10.60 (s, 1H); **^{13}C NMR** (DMSO-d_6, 400 MHz) δ 107.6, 122.5, 124.5, 124.9, 125.1, 125.8, 126.8, 126.9, 128.9, 129.11, 129.14, 130.4, 131.9, 132.1, 134.9, 136.1, 154.3, 154.8, 178.8, 180.0.

1'-Hydroxy-[1,2'-binaphthalene]-3,4-dione (8ag'):[26] 1.00 mmol scale, 0.0590 g, 0.196 mmol, 20% yield. Including some minor impurities and ethyl acetate used for column chromatography. Brown solid. **TLC**, R_f = 0.36 (hexane–EtOAc = 2:1); **^{1}H NMR** (CDCl3, 400 MHz) δ 5.83 (s, 1H), 6.60 (s, 1H), 7.23–7.28 (m, 1H), 7.53–7.78 (m, 5H), 7.94 (d, J = 7.8 Hz, 1H), 8.20 (d, J = 7.4 Hz, 1H), 8.28 (d, J = 7.8 Hz, 1H), 8.38–8.45 (m, 1H); **^{13}C NMR** (DMSO-d_6, 400 MHz) δ 117.5, 119.5, 122.6, 125.0, 125.7, 126.7, 127.1, 127.7, 128.9, 129.0, 129.4, 130.5, 131.9, 134.6, 135.2, 135.3, 149.4, 153.3, 179.2, 180.0.



4b

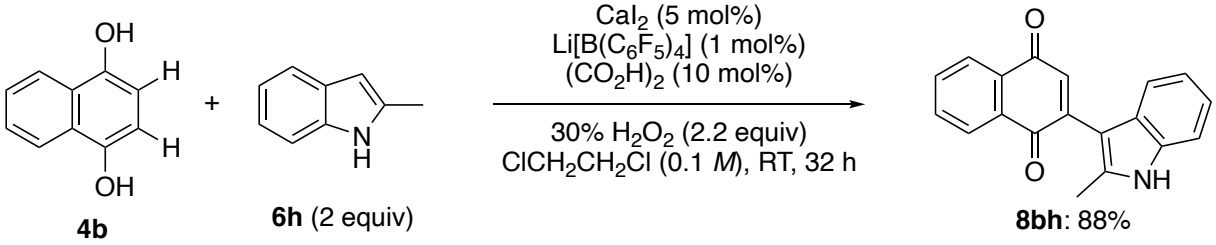
6a (*x* equiv)	LA cat.	time (h)	**8ba**	**8ba'**
2	$Li[B(C_6F_5)_4]$	21[a]	10%	30%
2	$Ca[B(C_6F_5)_4]_2$	25[a]	42%	27%
4	$Li[B(C_6F_5)_4]$	8	31%	56%
4	$Ca[B(C_6F_5)_4]_2$	8	84%	6%

[a] 30% H_2O_2 (2.2 equiv), DCE (0.1 *M*), RT Ar = 2,4-$(MeO)_2C_6H_3$

2,3-Bis(2,4-dimethoxyphenyl)naphthalene-1,4-dione (8ba): To a stirring mixture of **4b** (0.0320 g, 0.200 mmol), **6a** (0.111 g, 0.800 mmol, 4 equiv), calcium iodide (0.00300 g, 0.0100 mmol, 5 mol%), oxalic acid (0.00180 g, 0.0200 mmol, 10 mol%) and $Ca[B(C_6F_5)_4]_2$[27] (0.00410 g, 0.00200 mmol, 1

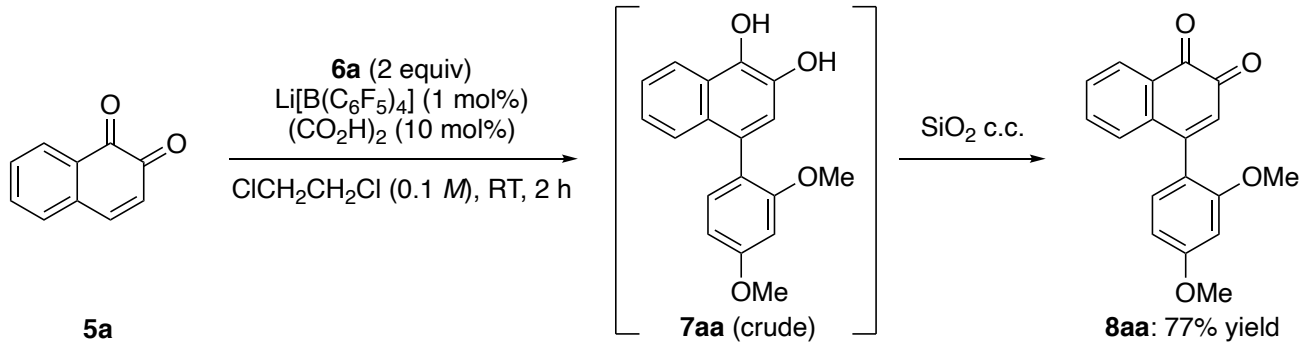
mol%) in dichloroethane (1.00 mL) was added 30% aqueous hydrogen peroxide (0.0600 mL, 0.600 mmol, 3 equiv) at room temperature. The reaction was monitored by TLC analysis. Upon the completion of the reaction (8 h), the resulting mixture was poured into saturated aqueous $Na_2S_2O_3$ (ca. 5 mL), and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 4:1 to 1:1) to give analytically pure **8ba** (0.0723 g, 0.168 mmol, 84% yield). Red solid. **TLC**, R_f = 0.23 (hexane–EtOAc = 2:1); **IR** ($CHCl_3$) 3005, 2938, 2836 1664, 1610, 1502, 1463, 1292, 1263, 1209, 1159, 1034 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz for *two rotamers*) δ 3.56 (s, 1.2H), 3.73 (s, 1.8H), 3.76 (s, 1.8H), 3.78 (s, 1.2H), 6.29–6.42 (m, 4H), 6.75 (d, *J* = 8.2 Hz, 1.2H), 6.87 (d, *J* = 8.2 Hz, 0.8H), 7.72–7.75 (m, 2H), 8.14–8.17 (m, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz for *two rotamers*) δ 55.19, 55.23*, 55.25, 55.55.5*, 98.2, 98.4*, 103.7*, 104.4, 116.0*, 116.5, 126.4*, 126.5, 130.2, 131.5*, 132.5, 132.6*, 133.3 (2C), 144.4*, 145.7, 157.9*, 158.0, 161.0 (2C), 184.0, 184.3*; **HRMS** (FAB+) *m/z* calcd for $[C_{26}H_{22}O_6+H]^+$ 431.1489, found 431.1491.

2-(2,4-Dimethoxyphenyl)naphthalene-1,4-dione (8ba'):[28] Red solid. **TLC**, R_f = 0.41 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.78 (s, 3H), 3.86 (s, 3H), 6.55–6.59 (m, 2H), 7.04 (s, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.73–7.78 (m, 2H), 8.09–8.16 (m, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 55.5, 55.7, 99.0, 104.6, 115.8, 125.9, 126.9, 131.6, 132.1, 132.7, 133.5, 133.6, 136.2, 147.4, 158.6, 162.3, 184.0, 185.4.



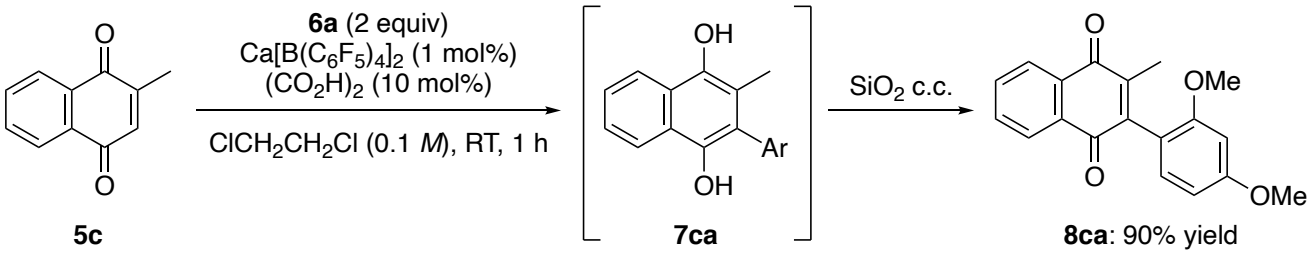
2-(2-Methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (8bh):[29] 1.00 mmol scale, 0.251 g, 0.875 mmol, 88% yield. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 4:1 to 1:1) to give analytically pure **8bh**. Purple solid. **TLC**, R_f = 0.31 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.46 (s, 3H), 7.10 (s, 1H), 7.13–7.21 (m, 2H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.75–7.81 (m, 2H), 8.14–8.21 (m, 2H), 8.32 (brs, 1H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 13.9, 107.3, 110.6, 119.3, 120.9, 122.2, 125.9, 127.0, 127.7, 132.2, 132.7, 133.5, 133.7, 134.7, 135.4, 137.0, 144.4, 184.6, 185.3.

Representative Procedures for Tandem Coupling of Quinones and Characterization of Products



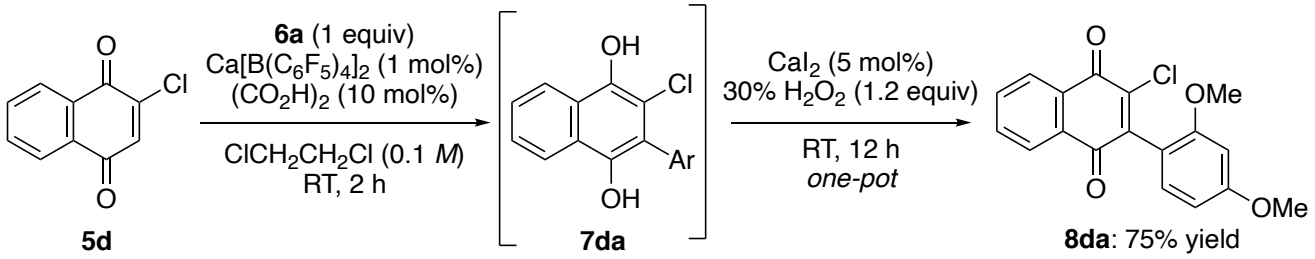
5a **7aa** (crude) **8aa**: 77% yield

To a stirring mixture of **5a** (0.0316 g, 0.200 mmol) and **6a** (0.0553 g, 0.400 mmol, 2 equiv) in dichloroethane (2.00 mL) were added oxalic acid (0.00180 g, 0.0200 mmol, 10 mol%) and $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$ (0.00180 g, 0.00200 mmol, 1 mol%) at room temperature. The reaction was monitored by TLC analysis. Upon the completion of the reaction (2 h), the resulting mixture was poured into saturated aqueous $NaHCO_3$ (ca. 5 mL), and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 4:1 to 1:1) to give analytically pure **8aa** (0.0454 g, 0.154 mmol, 77% yield). ^{1}H NMR analysis of the crude revealed the formation of both aryl hydroquinone **7aa** and arylquinone **8aa**. **7aa** was fully converted to **8aa** by air oxidation during column chromatography.

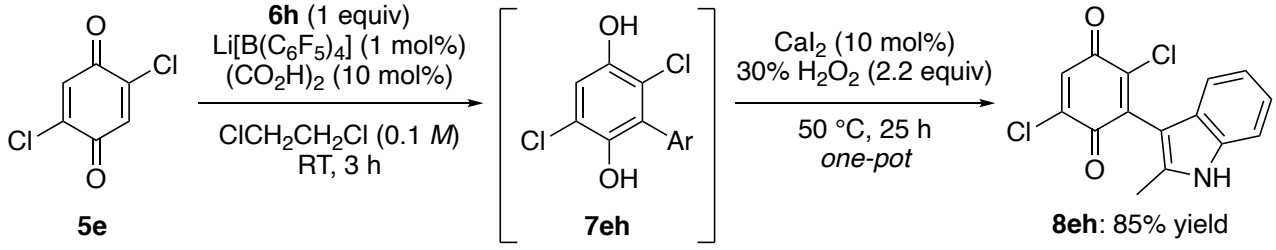


5c **7ca** **8ca**: 90% yield

2-(2,4-Dimethoxyphenyl)-3-methylnaphthalene-1,4-dione (8ca): 0.200 mmol scale, 0.0555 g, 0.180 mmol, 90% yield. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 4:1 to 1:1) to give analytically pure **8ca**. Orange solid. **TLC**, R_f = 0.46 (hexane–EtOAc = 2:1); **IR** ($CHCl_3$) 2938, 1661, 1614, 1506, 1294 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.03 (s, 1H), 3.74 (s, 3H), 3.86 (s, 3H), 6.56–6.60 (m, 2H), 7.00 (d, J = 8.2 Hz, 1H), 7.69–7.74 (m, 2H), 8.08–8.16 (m, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 14.5, 55.4, 55.5, 98.7, 104.4, 115.4, 126.1, 126.5, 130.9, 132.2, 132.3, 133.2, 133.4, 143.9, 145.2, 157.7, 161.4, 183.8, 185.7; **HRMS** (FAB+) *m*/*z* calcd for $[C_{19}H_{16}O_4+H]^+$ 309.1121, found 309.1123.



2-Chloro-3-(2,4-dimethoxyphenyl)naphthalene-1,4-dione (8da): To a stirring mixture of **5d** (0.0963 g, 0.500 mmol) and **6a** (0.0692 g, 0.500 mmol, 1 equiv) in dichloroethane (5.00 mL) were added oxalic acid (0.00450 g, 0.0500 mmol, 10 mol%) and $Ca[B(C_6F_5)_4]_2$[27] (0.0103 g, 0.00500 mmol, 1 mol%) at room temperature. The reaction was monitored by TLC analysis. Upon the completion of the 1,4-addition reaction (2 h), to the resulting mixture were added CaI_2 (0.00750 g, 0.0250 mmol, 5 mol%) and 30% aqueous hydrogen peroxide (0.0562 mL, 0.550 mmol, 1.2 equiv) at room temperature. After stirring for 12 h at room temperature, the resulting mixture was poured into saturated aqueous $Na_2S_2O_3$ (ca. 5 mL), and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, then the solvents were removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 4:1 to 1:1) to give analytically pure **8aa** (0.123 g, 0.375 mmol, 75% yield). Orange solid. **TLC**, R_f = 0.50 (hexane–EtOAc = 2:1); **IR** ($CHCl_3$) 2939, 1680, 1611, 1505 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.76 (s, 3H), 3.88 (s, 3H), 6.57–6.63 (m, 2H), 7.12 (d, J = 8.7 Hz, 1H), 7.76–7.80 (m, 2H), 8.14–8.16 (m, 1H), 8.21–8.24 (m, 1H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 55.4, 55.6, 98.8, 104.6, 114.1, 127.1, 127.2, 131.0, 131.5, 132.0, 133.8, 134.2, 143.8, 144.7, 157.9, 162.1, 178.2, 181.7; **HRMS** (FAB+) *m*/*z* calcd for $[C_{18}H_{13}ClO_4+H]^+$ 329.0575, found 329.0579.



2,5-Dichloro-3-(2-methyl-1*H*-indol-3-yl)cyclohexa-2,5-diene-1,4-dione (8eh):[29b,30] 0.200 mmol scale, 0.0529 g, 0.169 mmol, 85% yield. The crude was purified by flash column chromatography on silica gel (eluent: hexane–EtOAc = 4:1 to 1:1) to give analytically pure **8ea**. Purple solid. **TLC**, R_f = 0.38 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 7.11–7.34 (m, 5H), 8.34 (brs, 1H); **^{13}C NMR** ($CDCl_3$, 400 MHz) δ 13.9, 104.9, 110.8, 119.8, 120.6, 122.1, 126.7, 133.2, 135.2, 136.9, 139.4, 140.0, 144.5, 176.7, 178.0.

Experimental Procedures for Mechanistic Studies

Control Experiments to Probe Active Species (Table S6)

To a solution of **1j** (0.0871 g, 0.500 mmol) in EtOAc (2.50 mL) was added iodine (0.127 g, 0.500 mmol) or iodine (0.127 g, 0.500 mmol) with KOH (0.561 g, 1.00 mmol) or sodium periodate (0.107 g, 0.500 mmol) or Bu_4NBr (0.0161 g, 0.05 mmol) with 30% H_2O_2 (0.0613 mL, 0.600 mmol) or Bu_4NCl (0.0139 g, 0.05 mmol) with 30% H_2O_2 (0.0613 mL, 0.600 mmol) room temperature. The reaction was monitored by TLC analysis and ^1H NMR analysis, and results were reported in Table S2.

Radical Trapping Experiments (Scheme S2)

To a stirring solution of **1e** (0.901 g, 0.500 mmol), Bu_4NI (0.0185 g, 0.0500 mmol, 10 mol%) and TEMPO (0.0781 g, 0.500 mmol, 1 equiv) or PBN (0.0886 g, 0.500 mmol, 1 equiv) in ethyl acetate (2.50 mL) was added 30% aqueous hydrogen peroxide (0.0620 mL, 0.600 mmol, 1.2 equiv) at room temperature. The reaction was monitored by TLC analysis and ^1H NMR analysis, and results were reported in Scheme S2.

References

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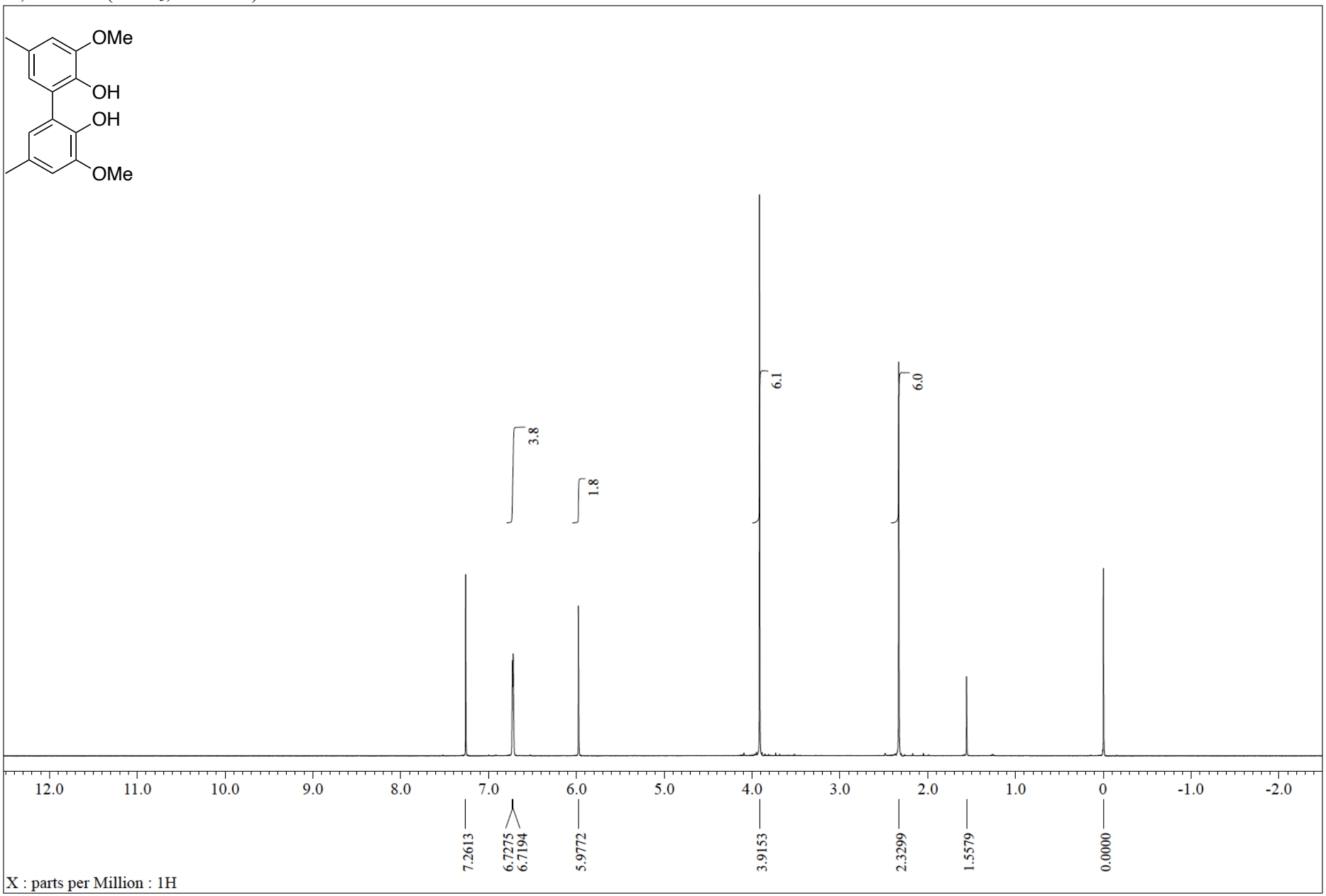
2a, ^{1}H NMR ($CDCl_3$, 400 MHz)



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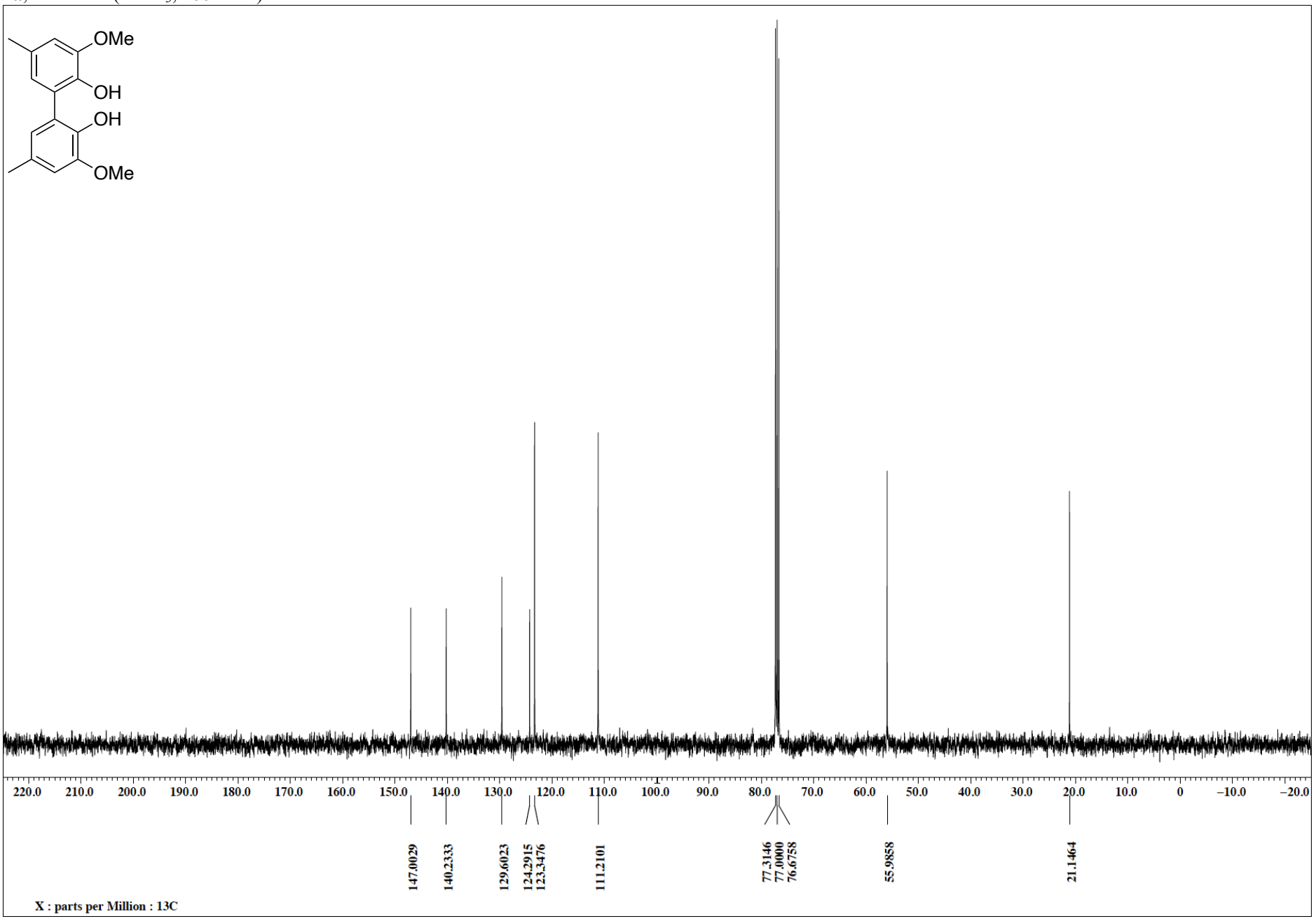

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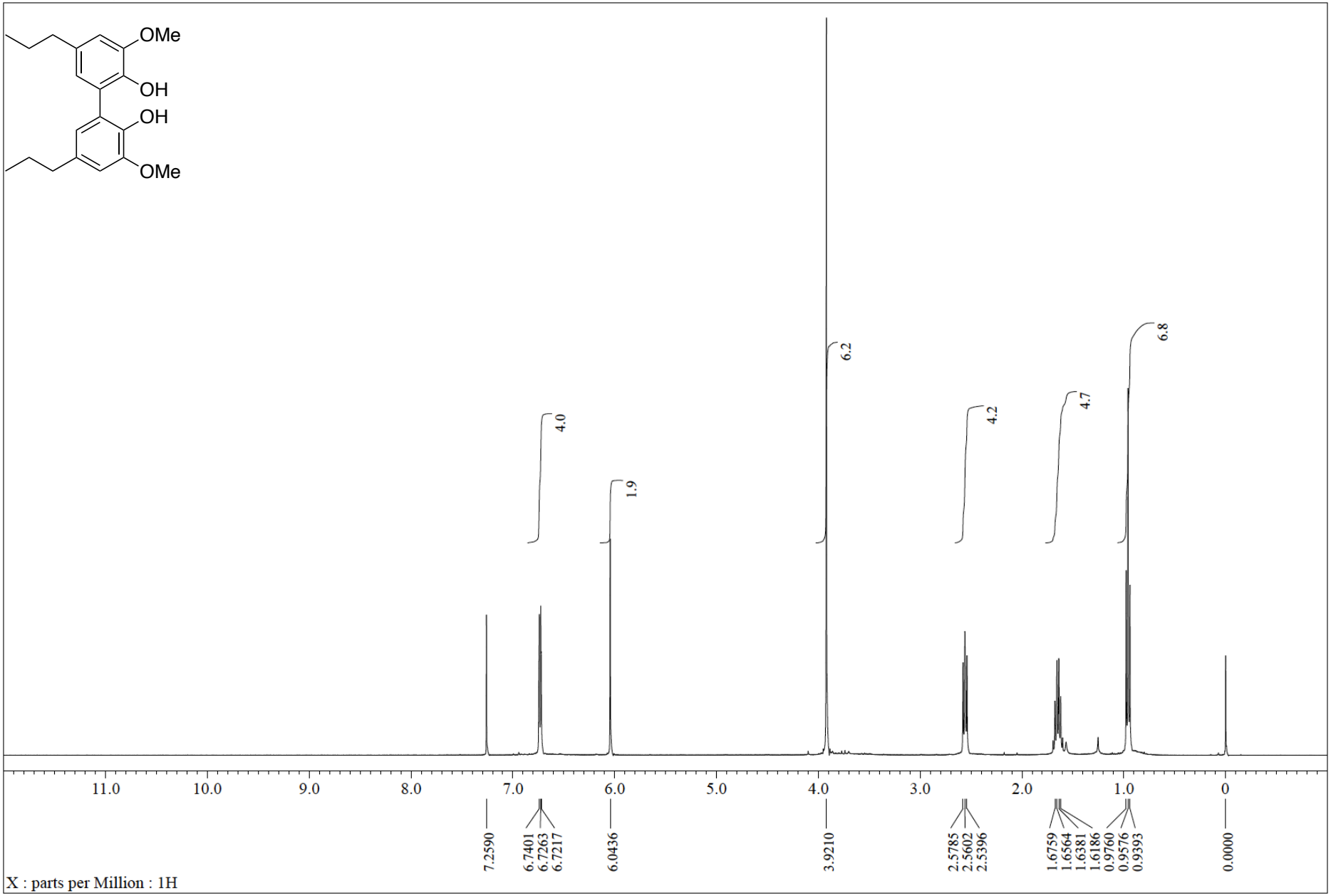

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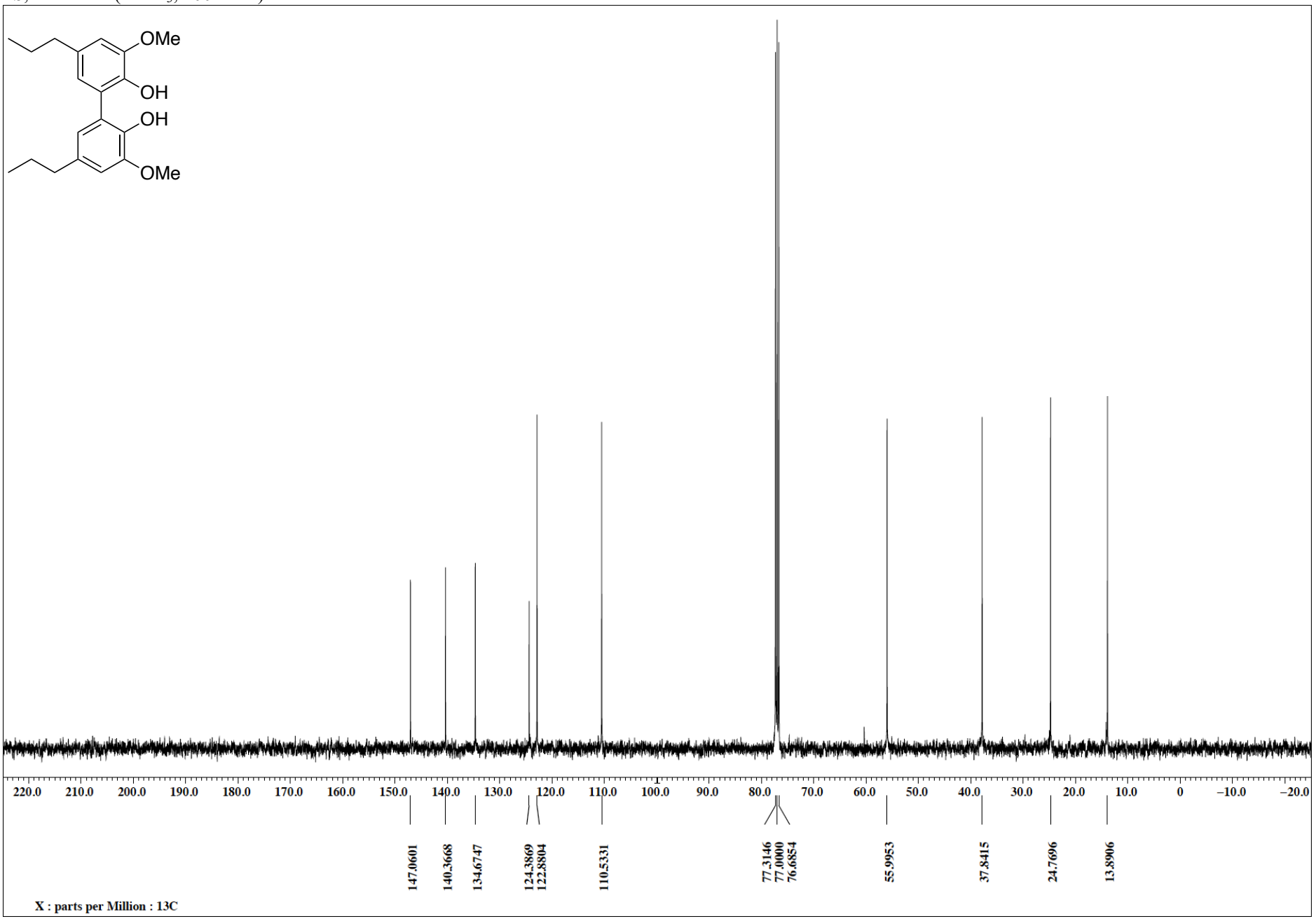

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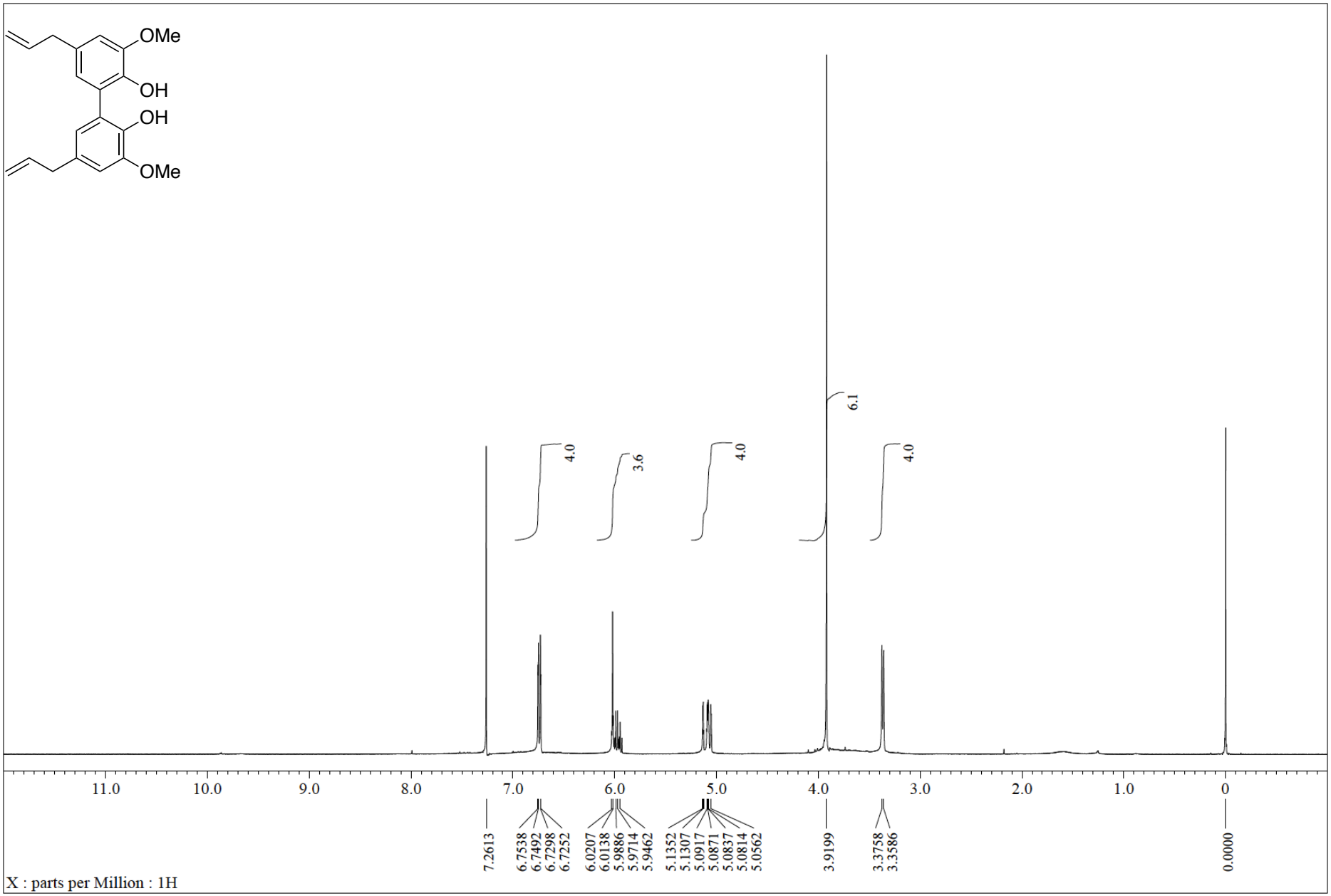

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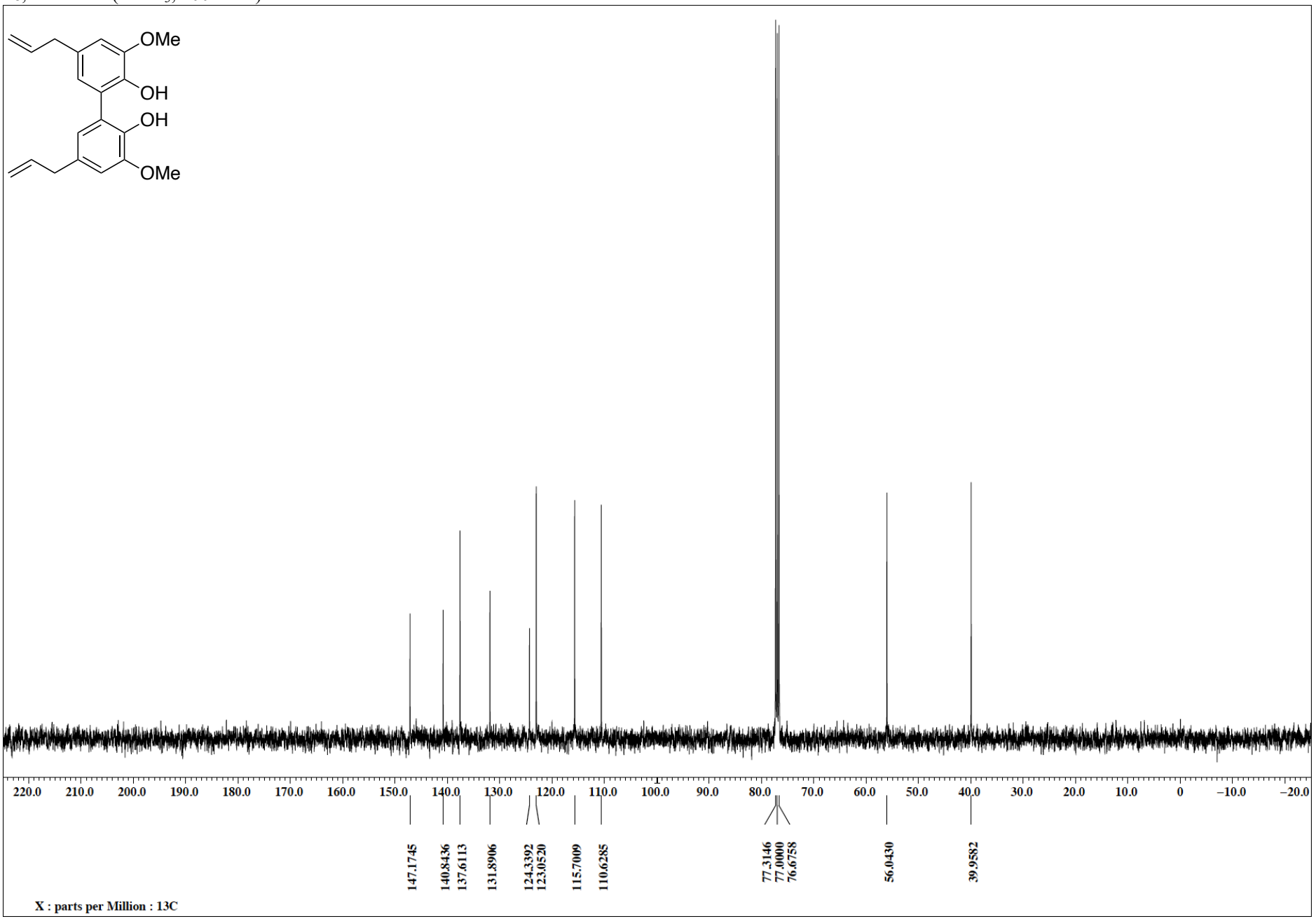

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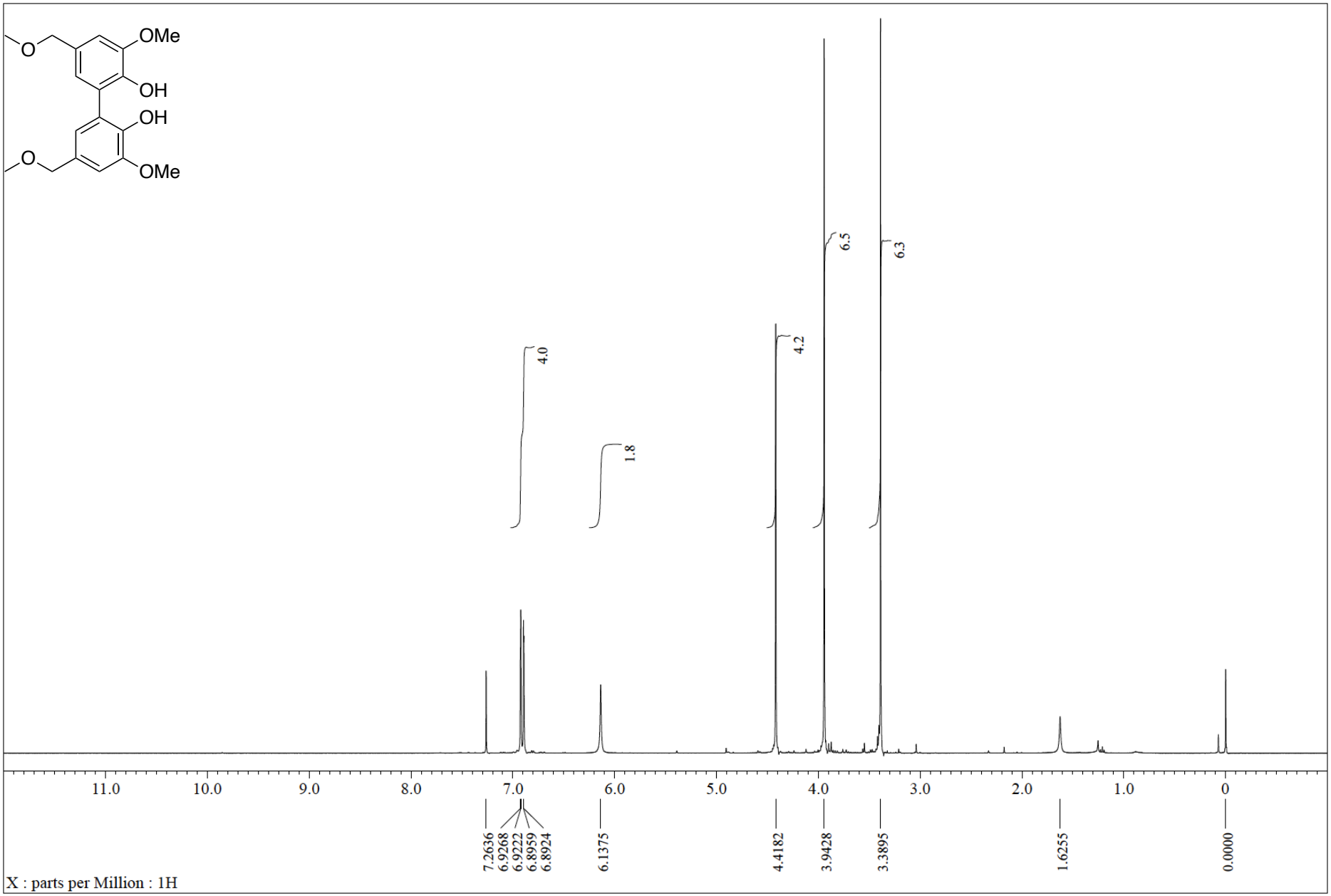

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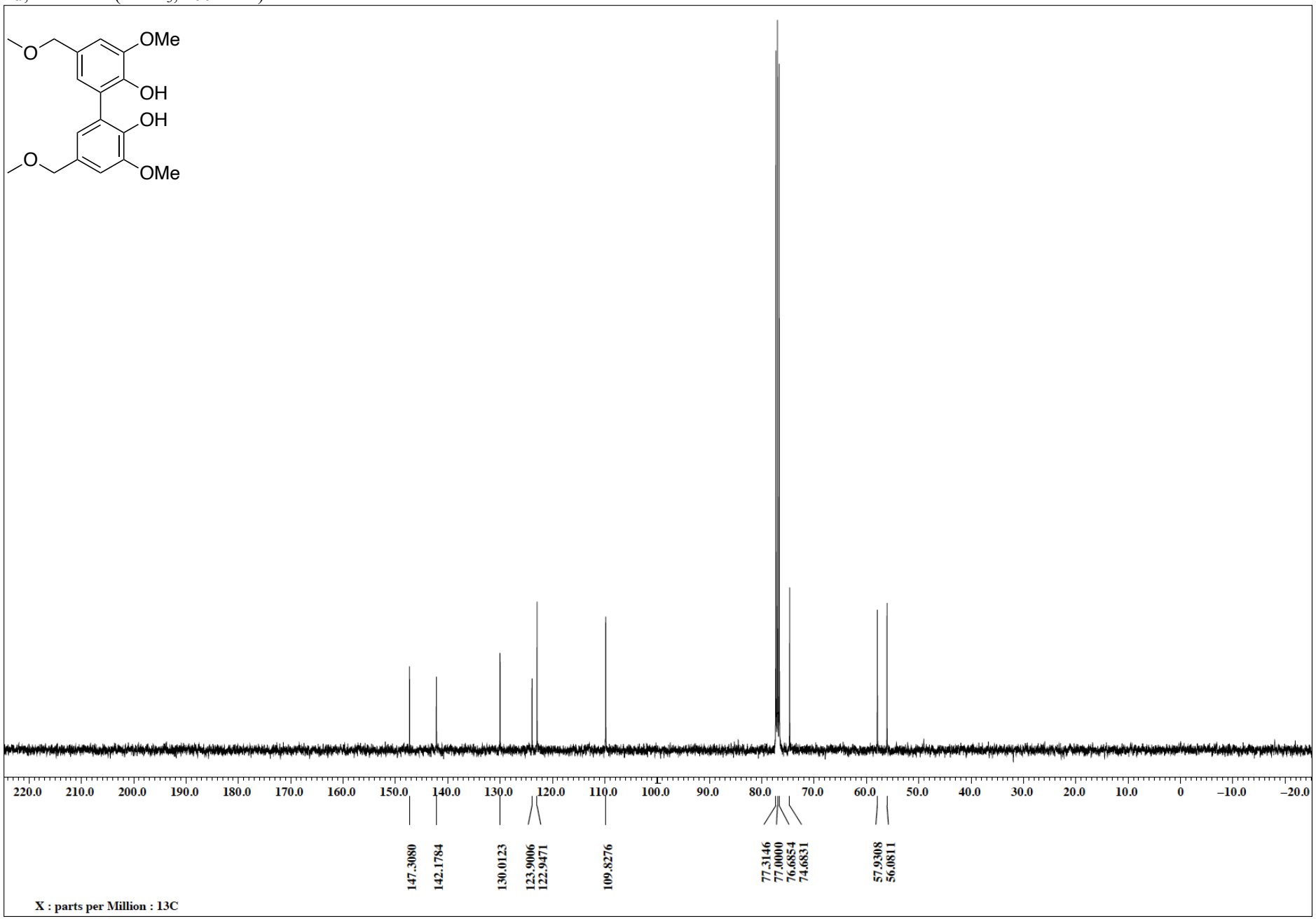

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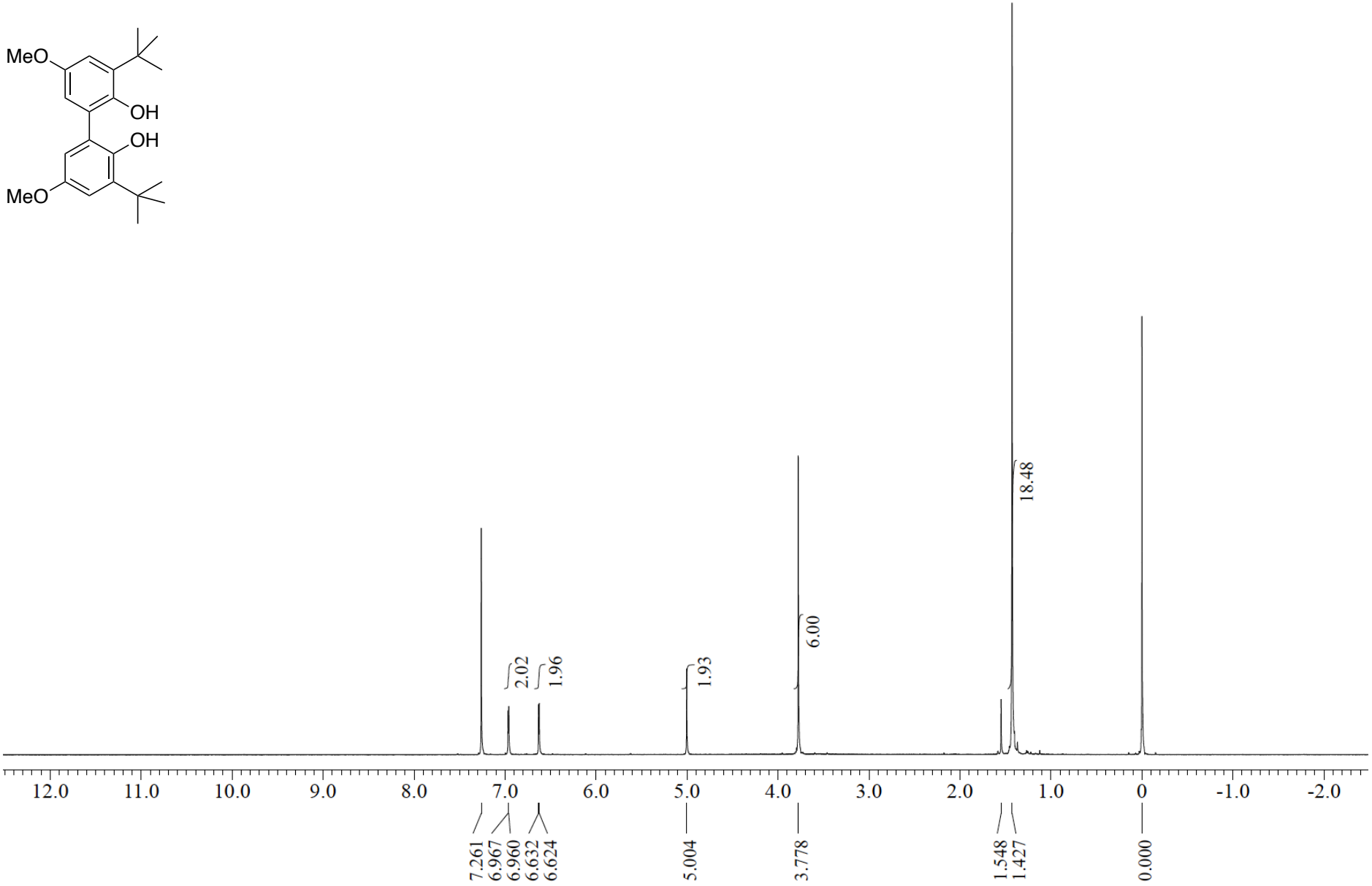

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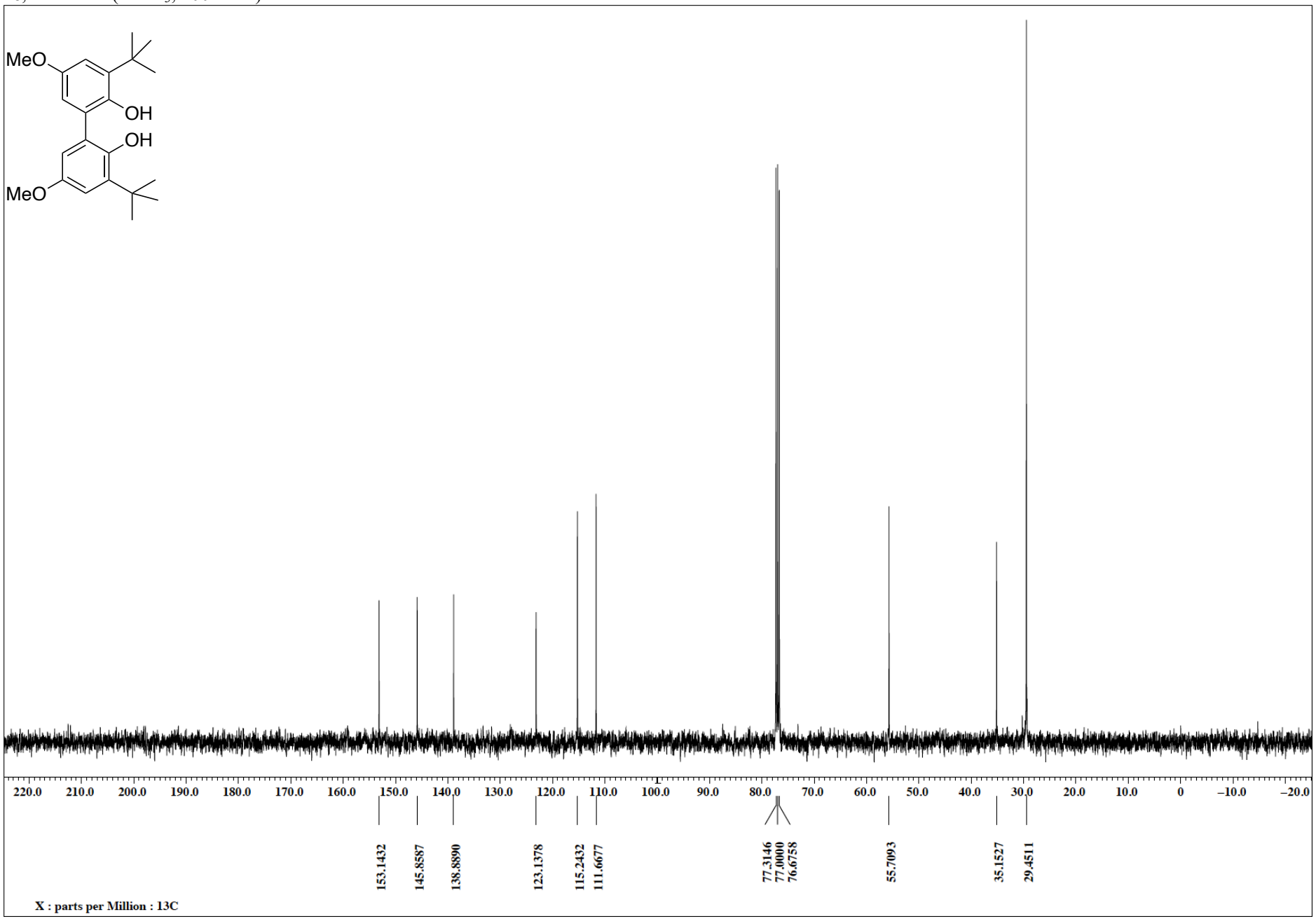

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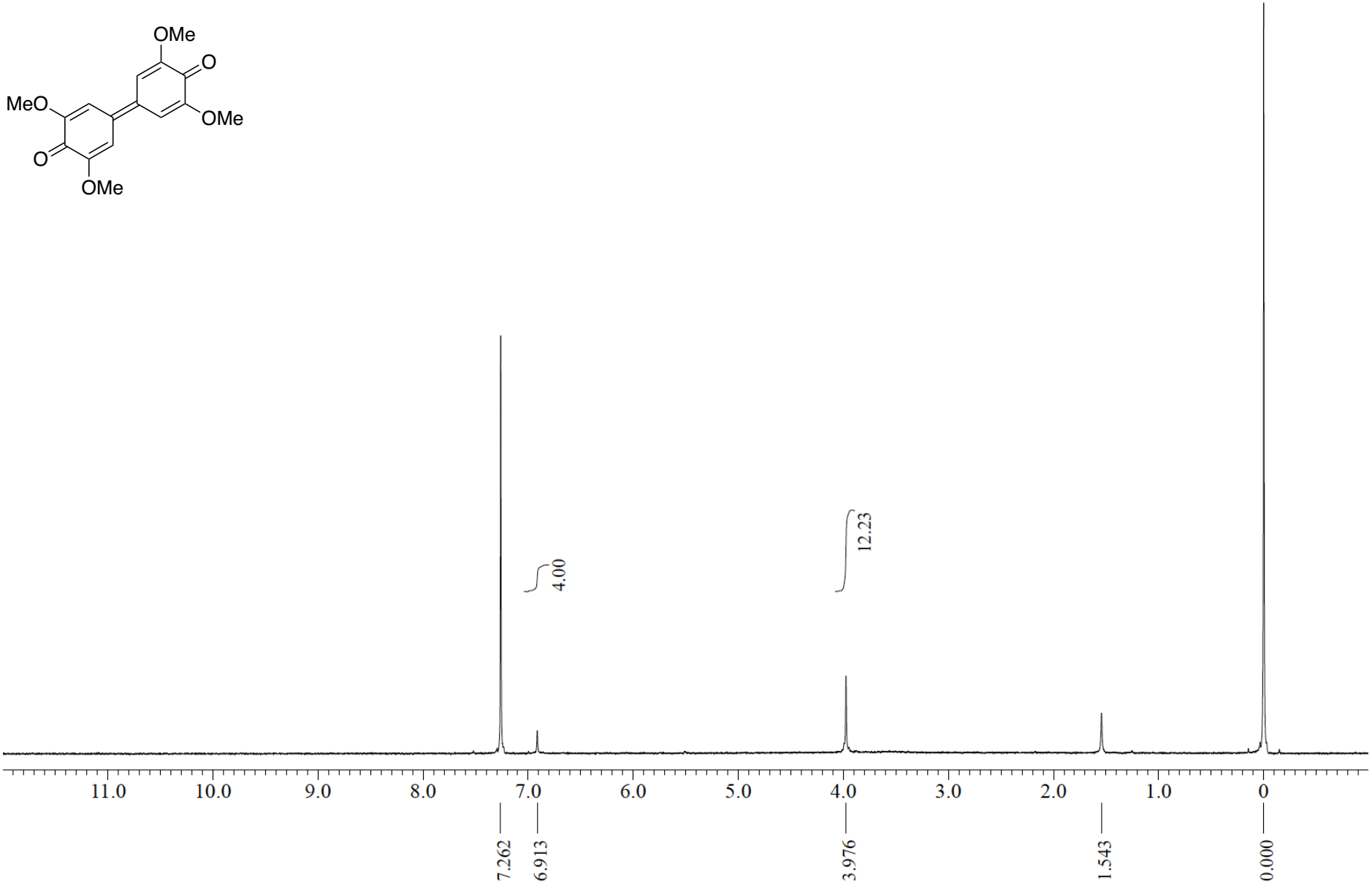

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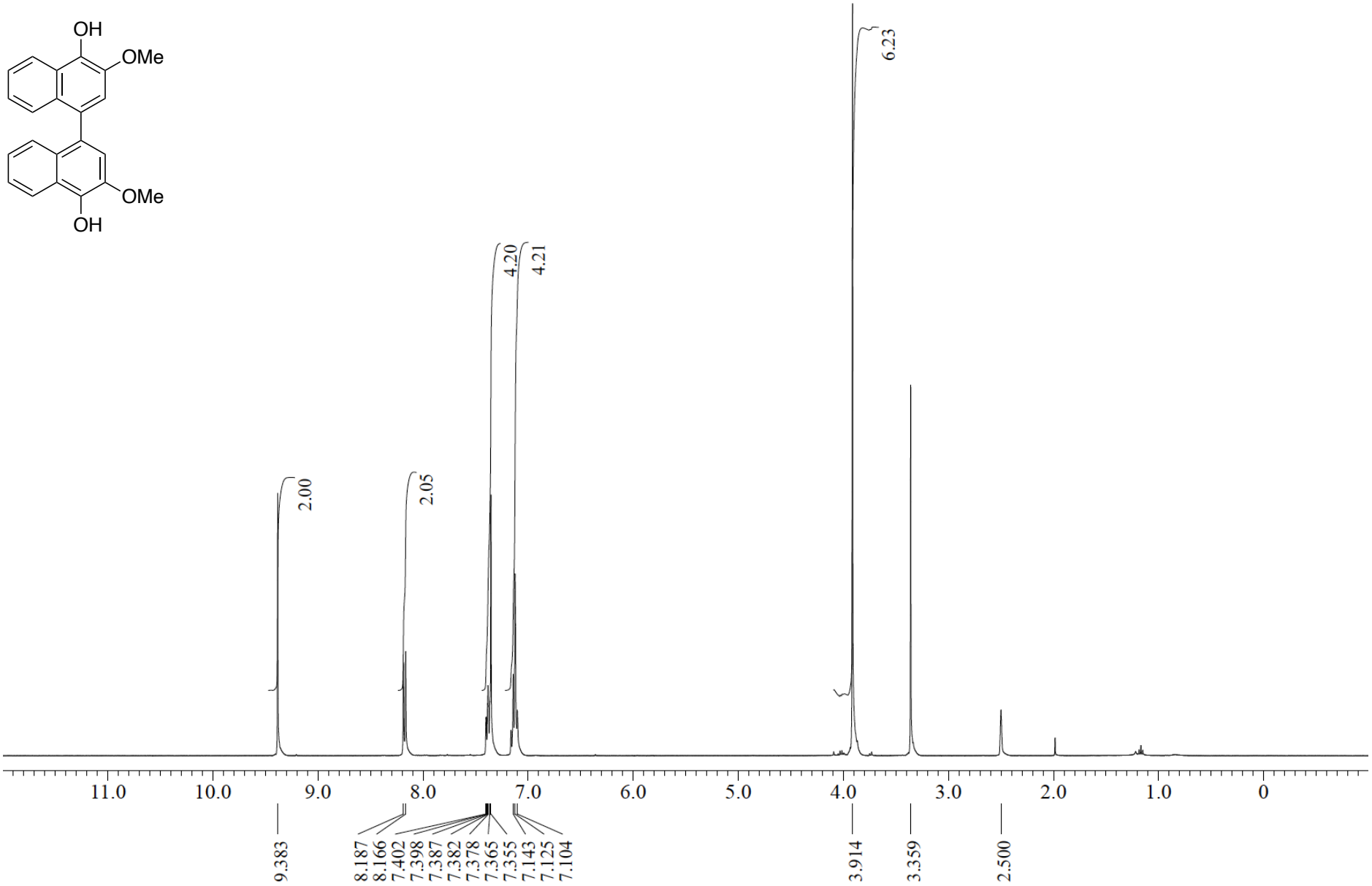

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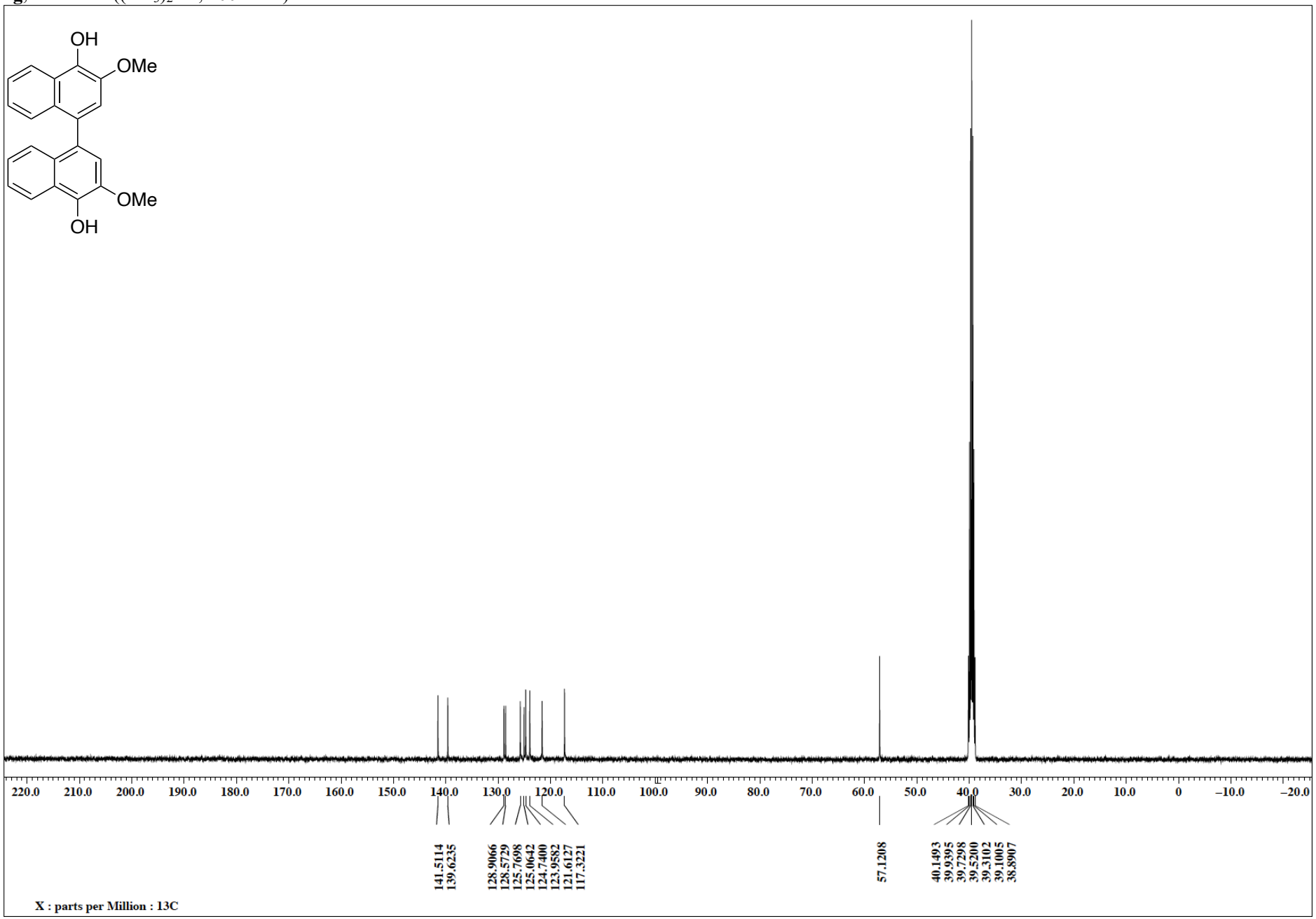

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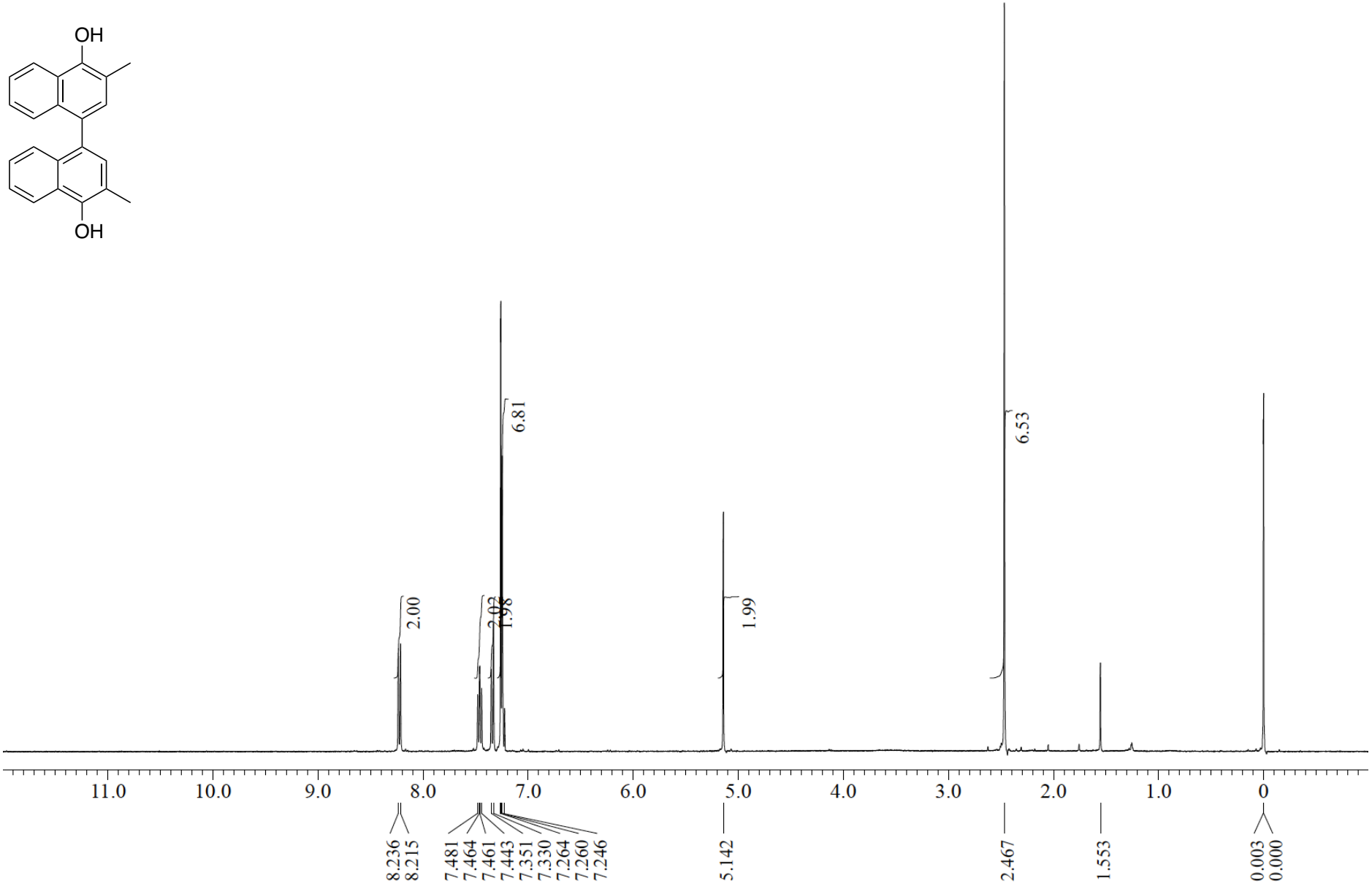

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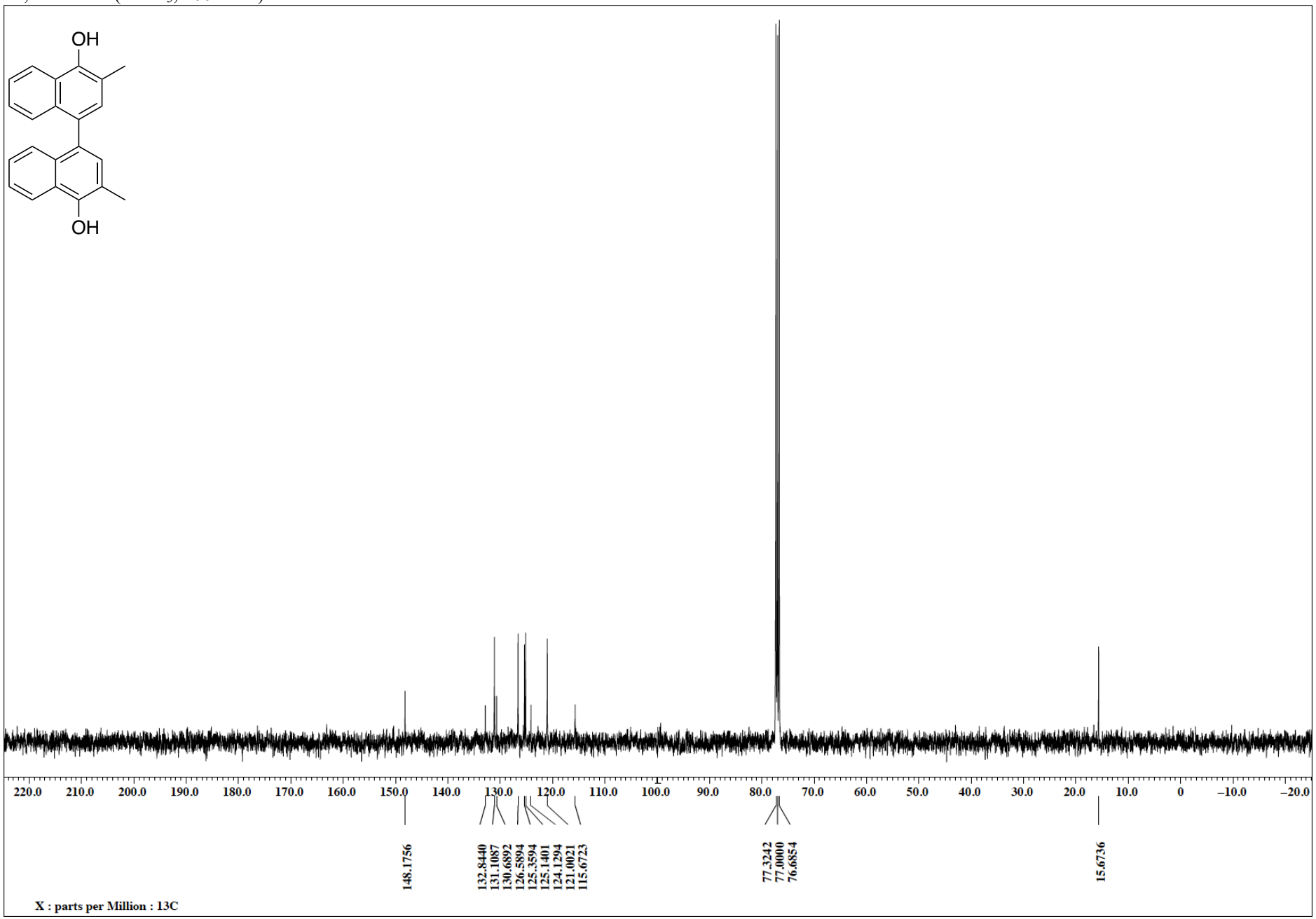

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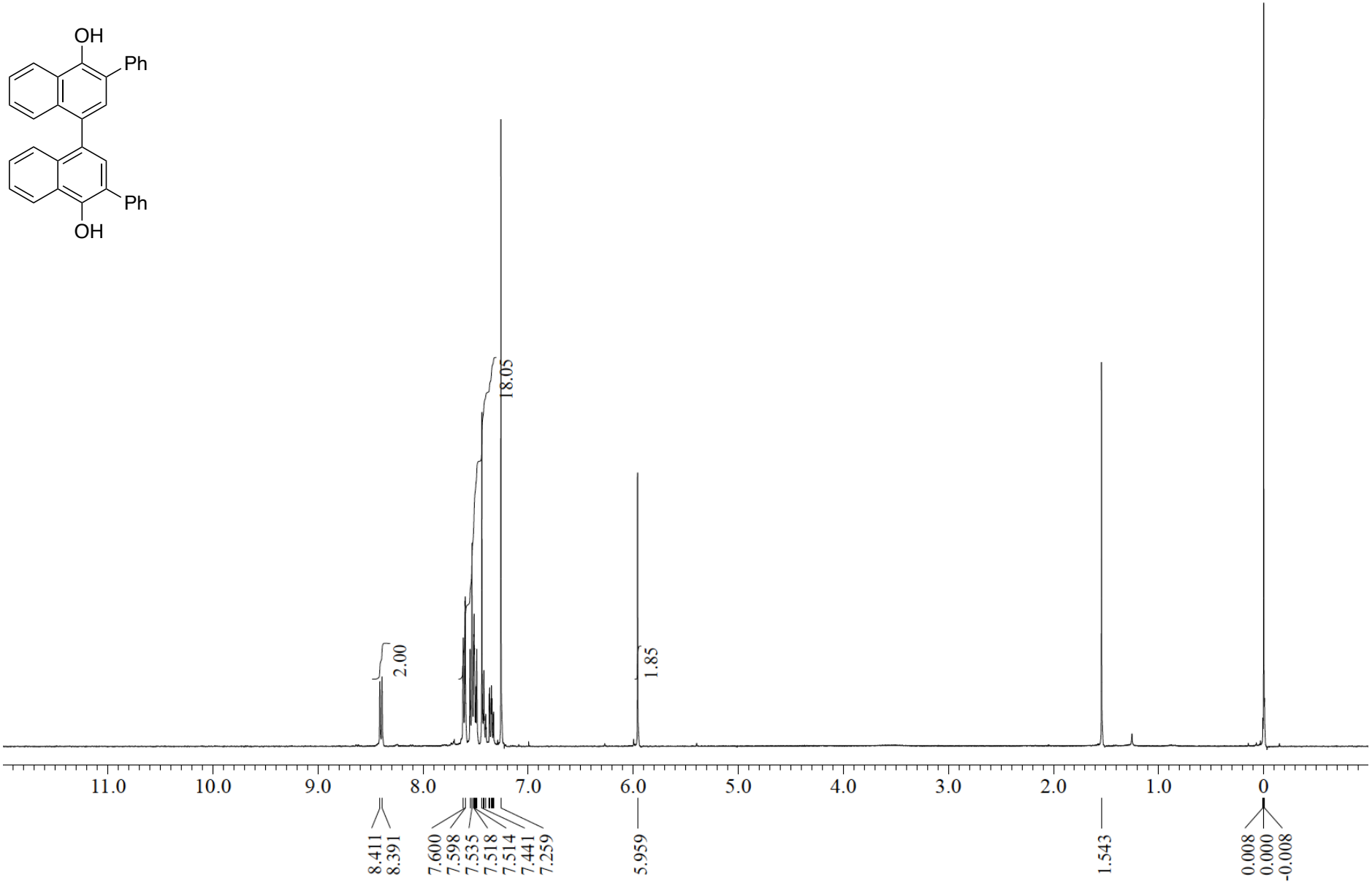

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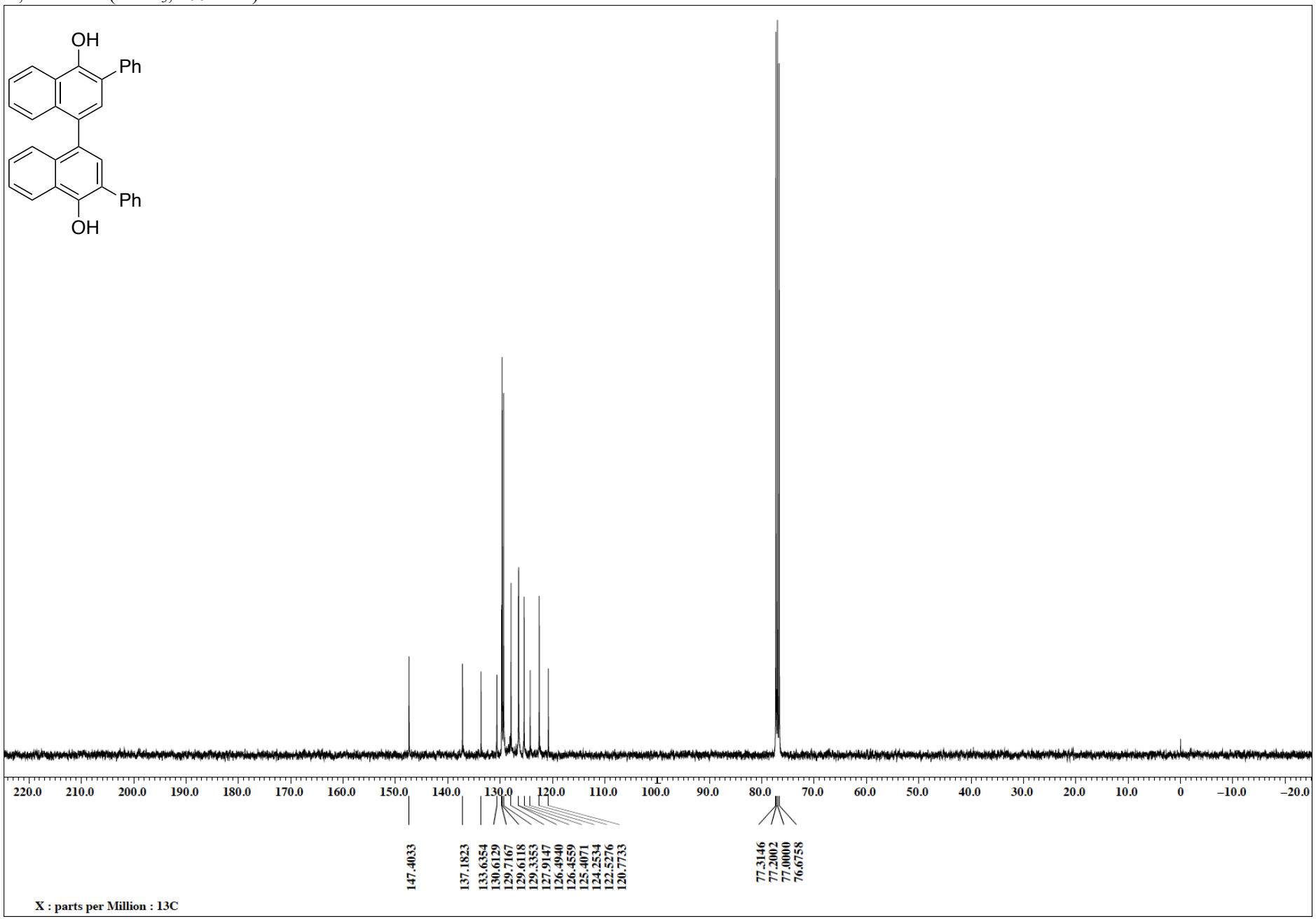

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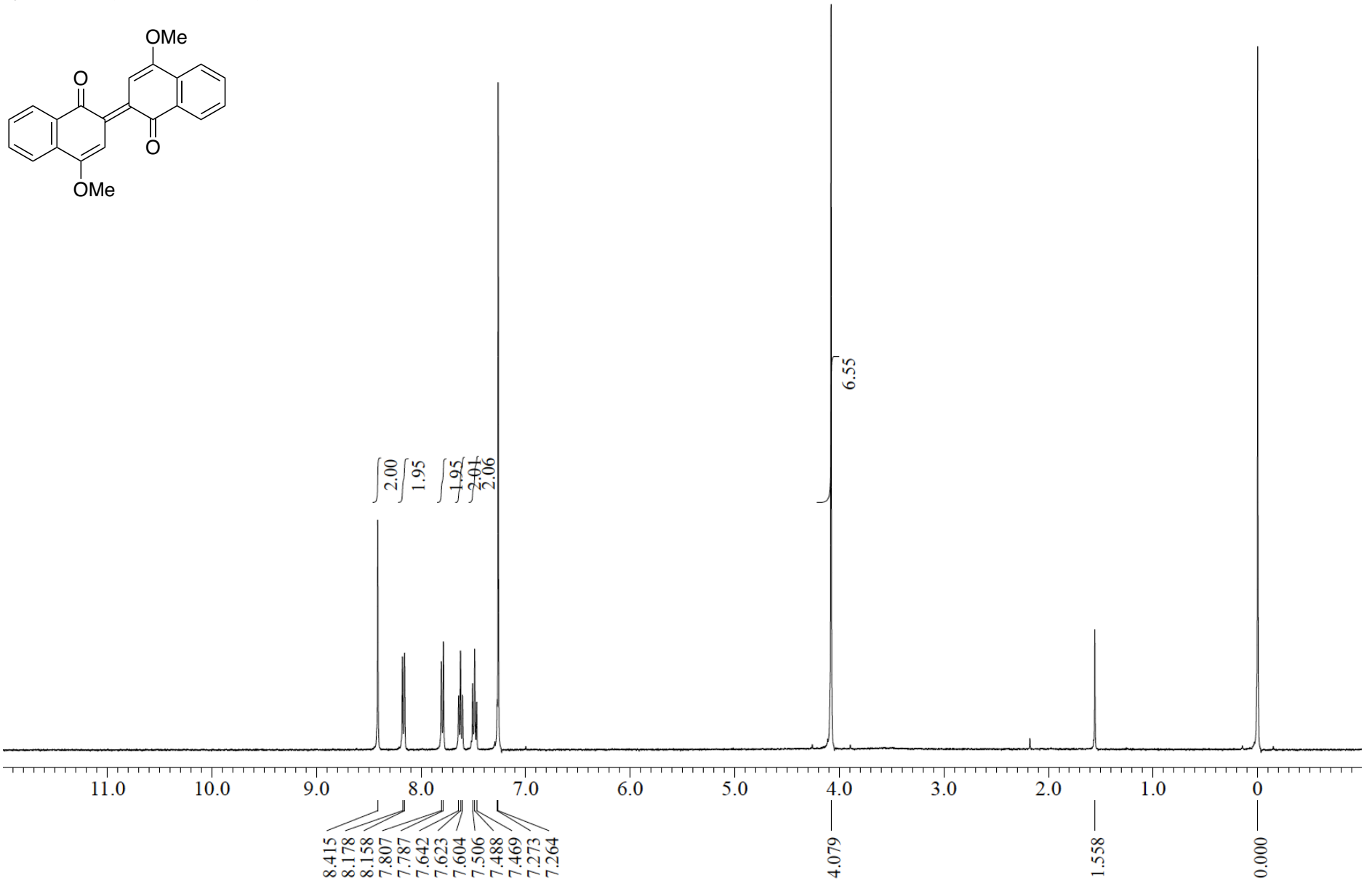

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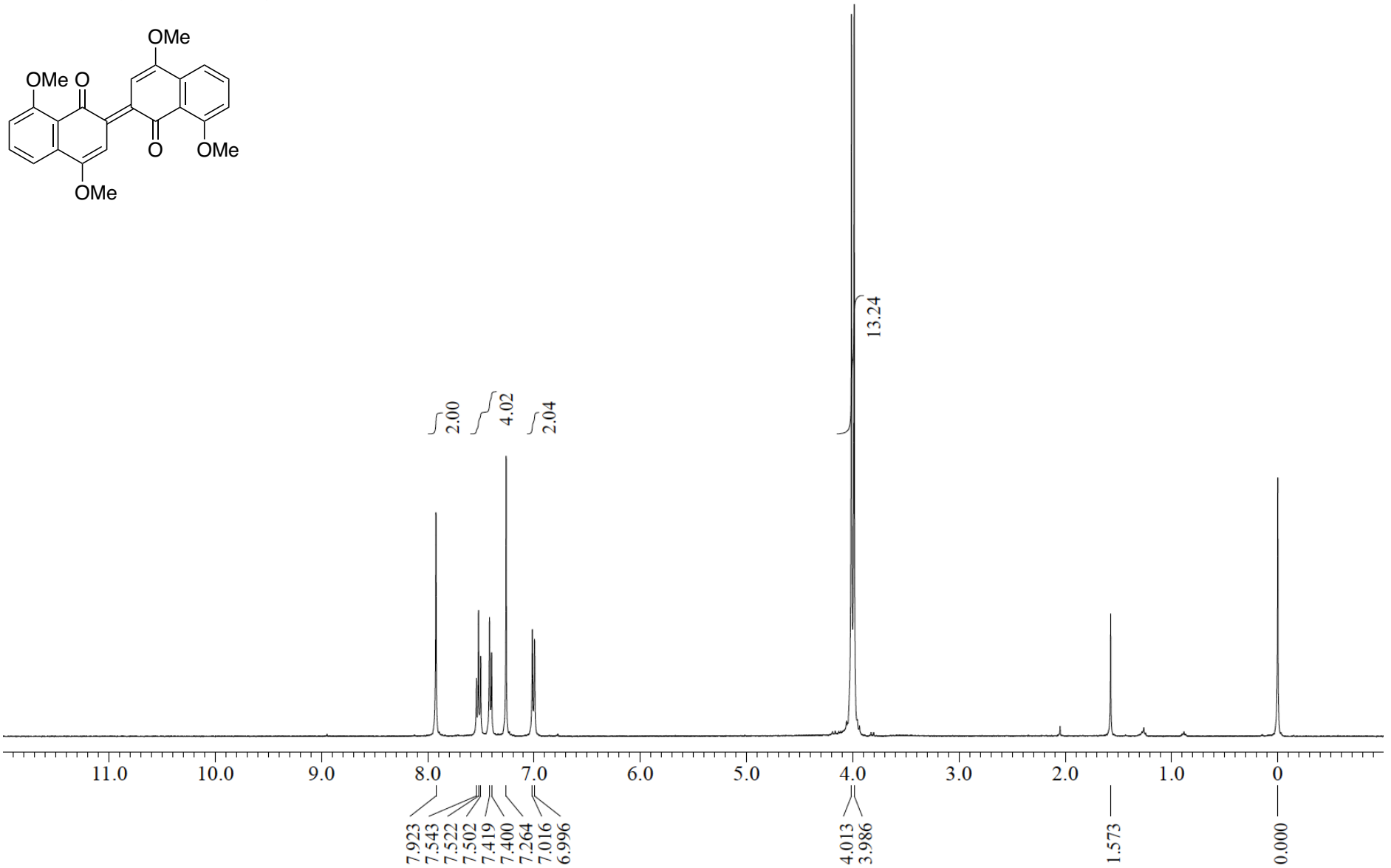

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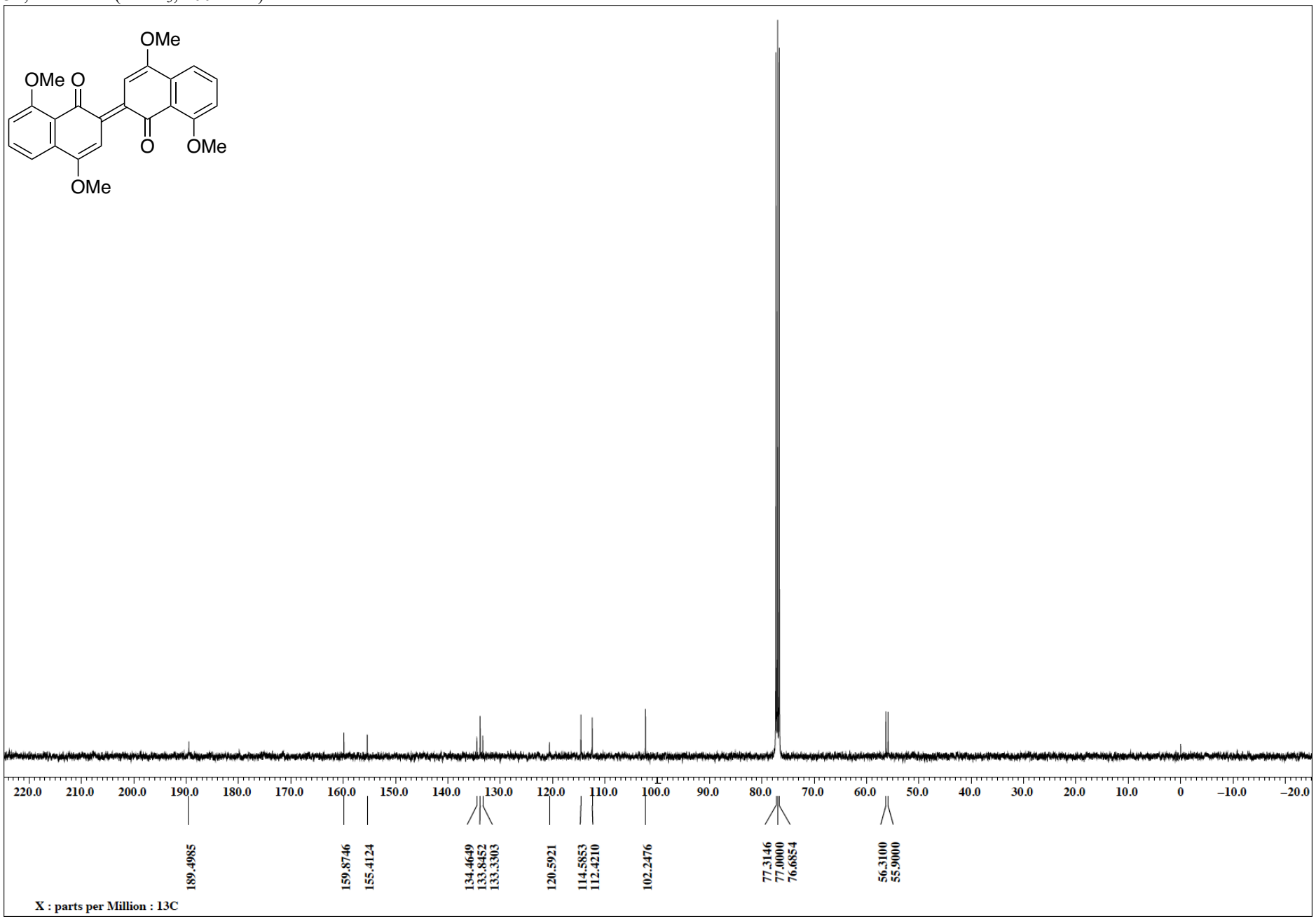

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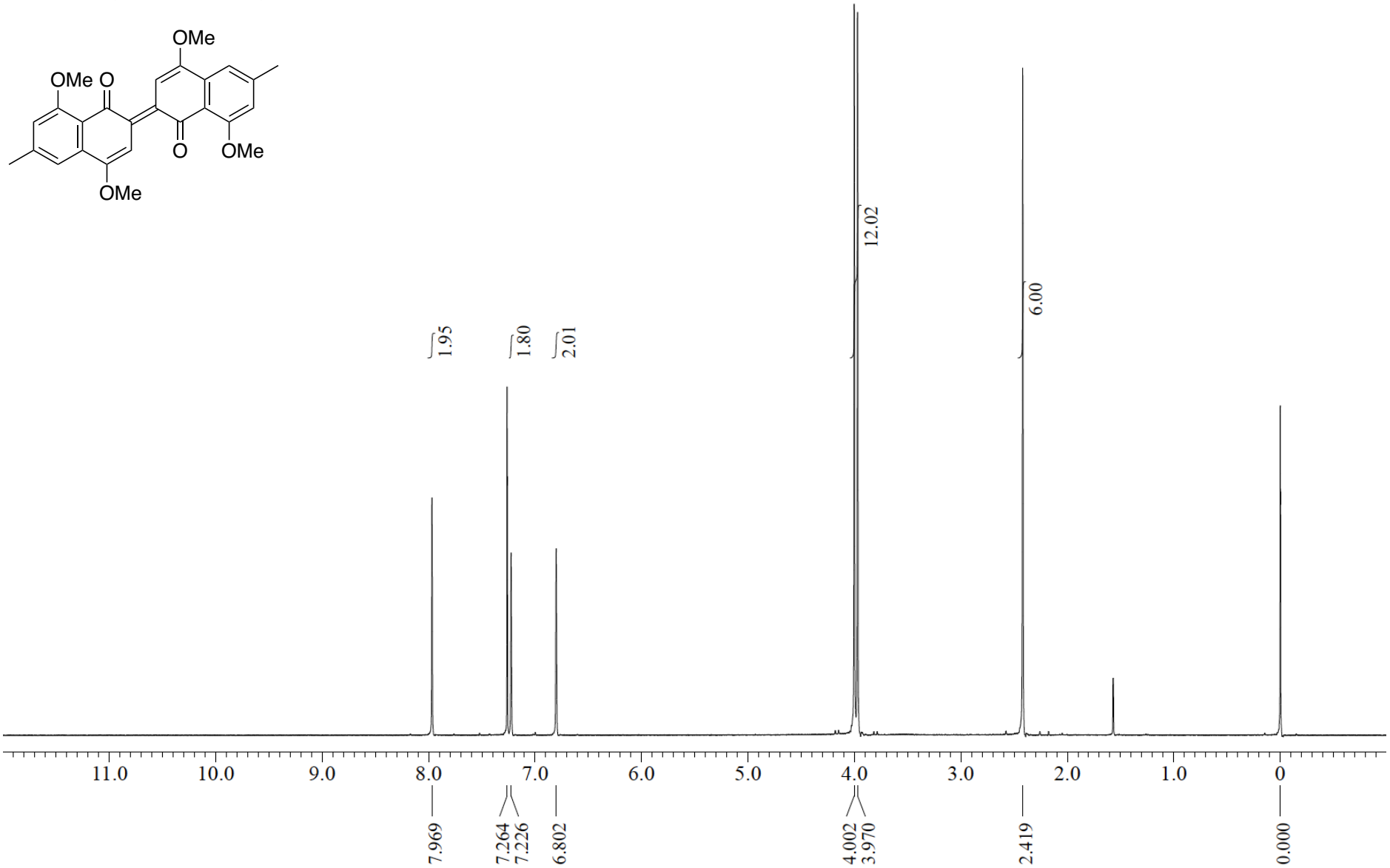

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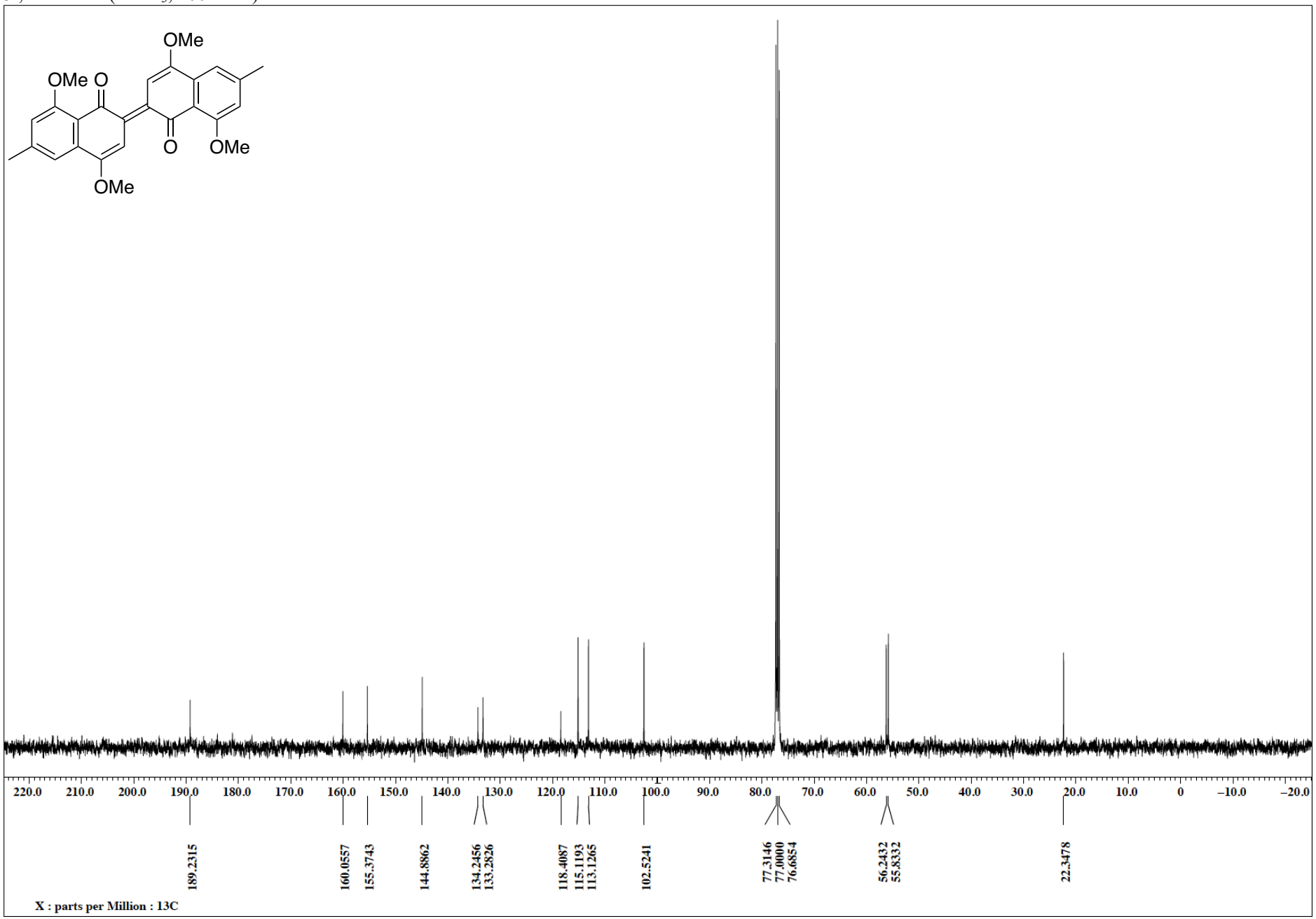

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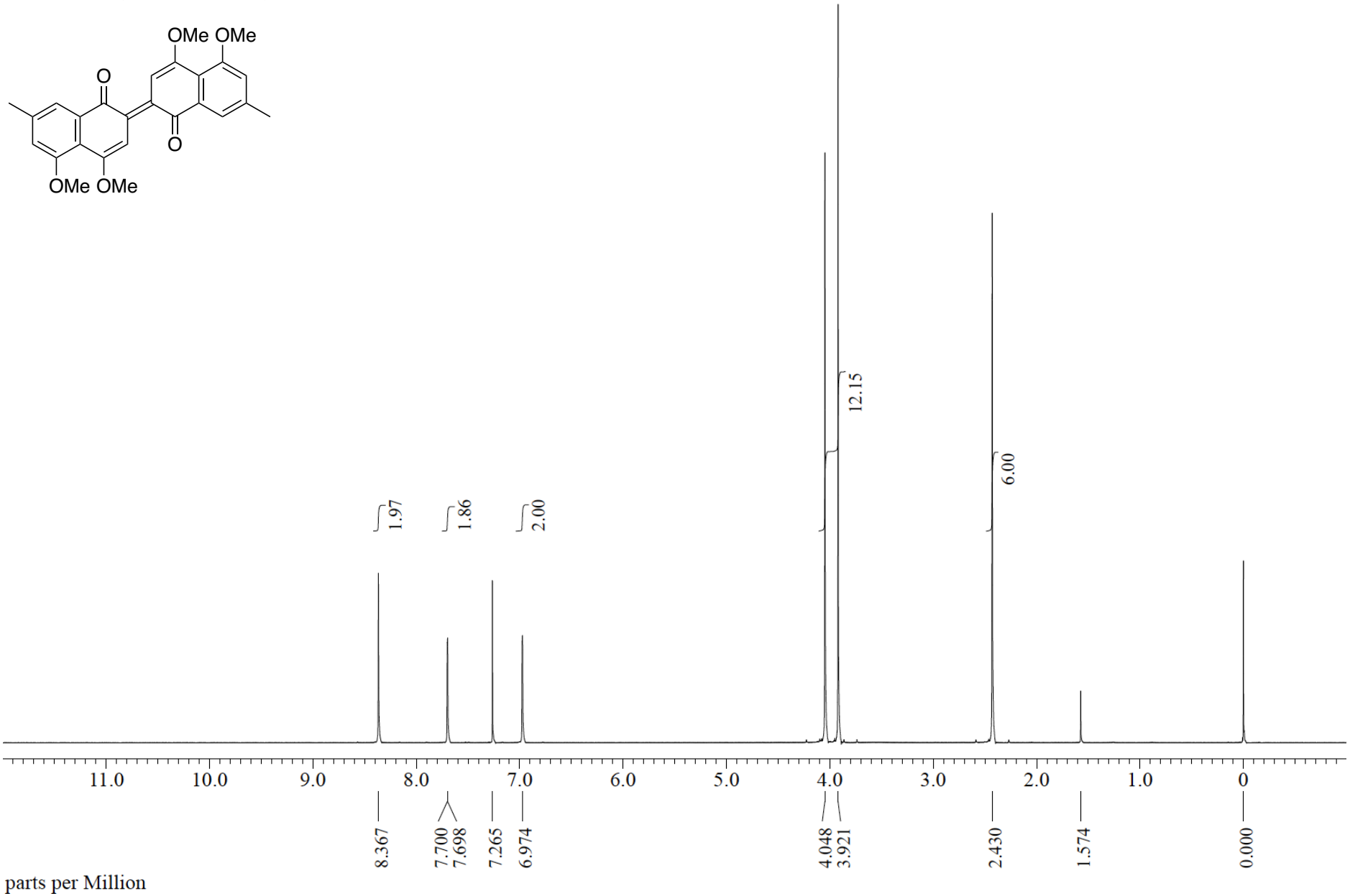

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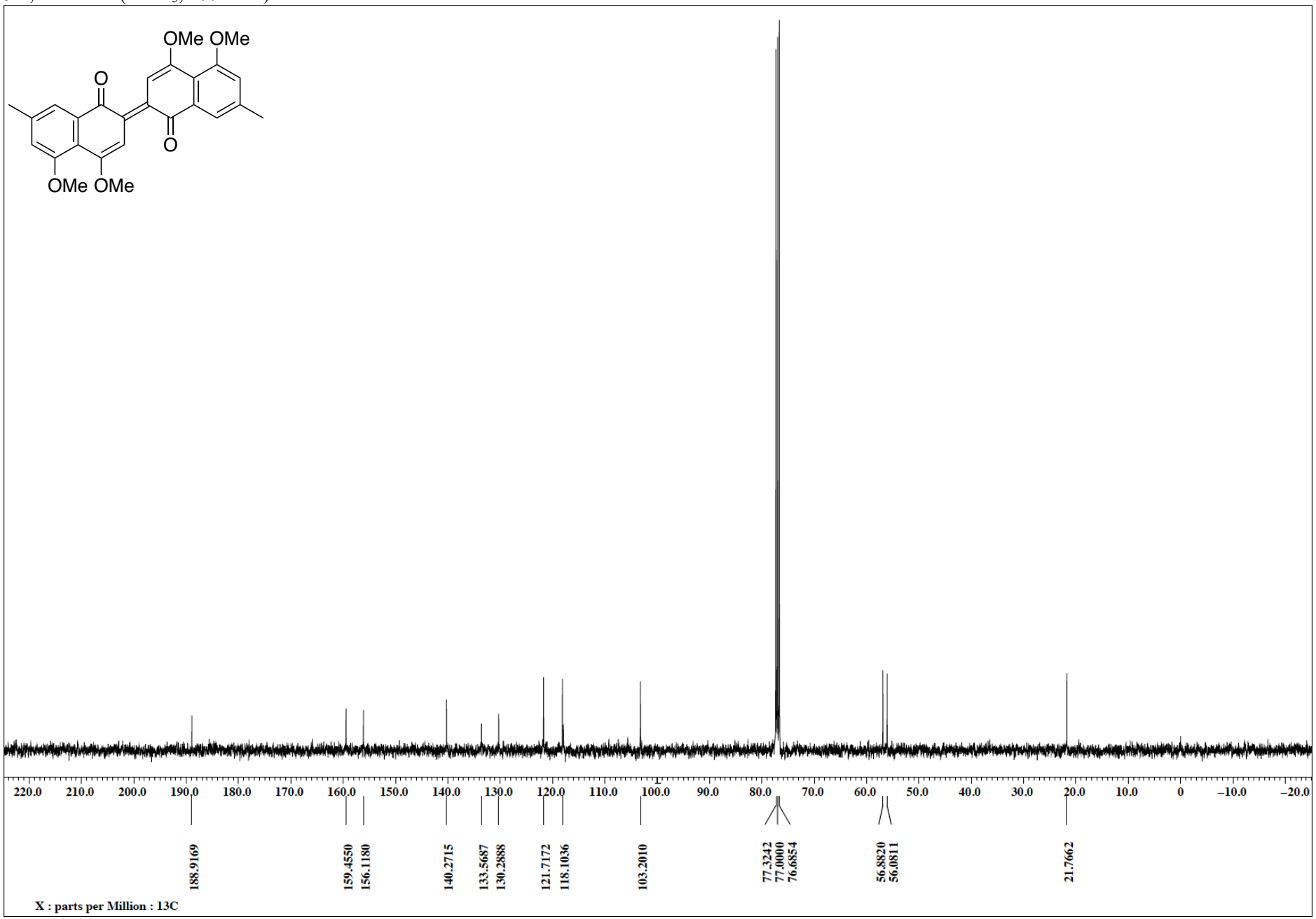

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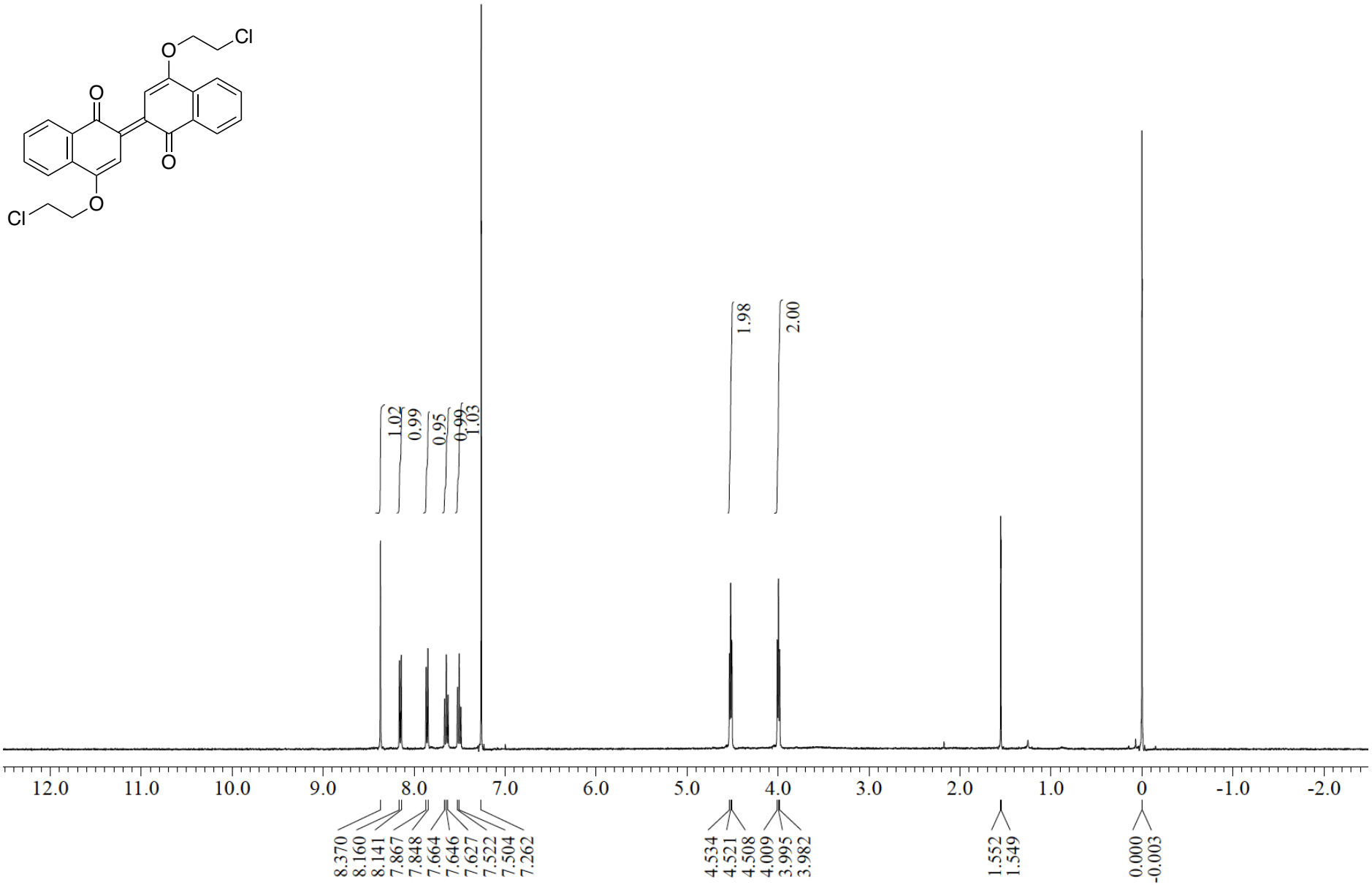

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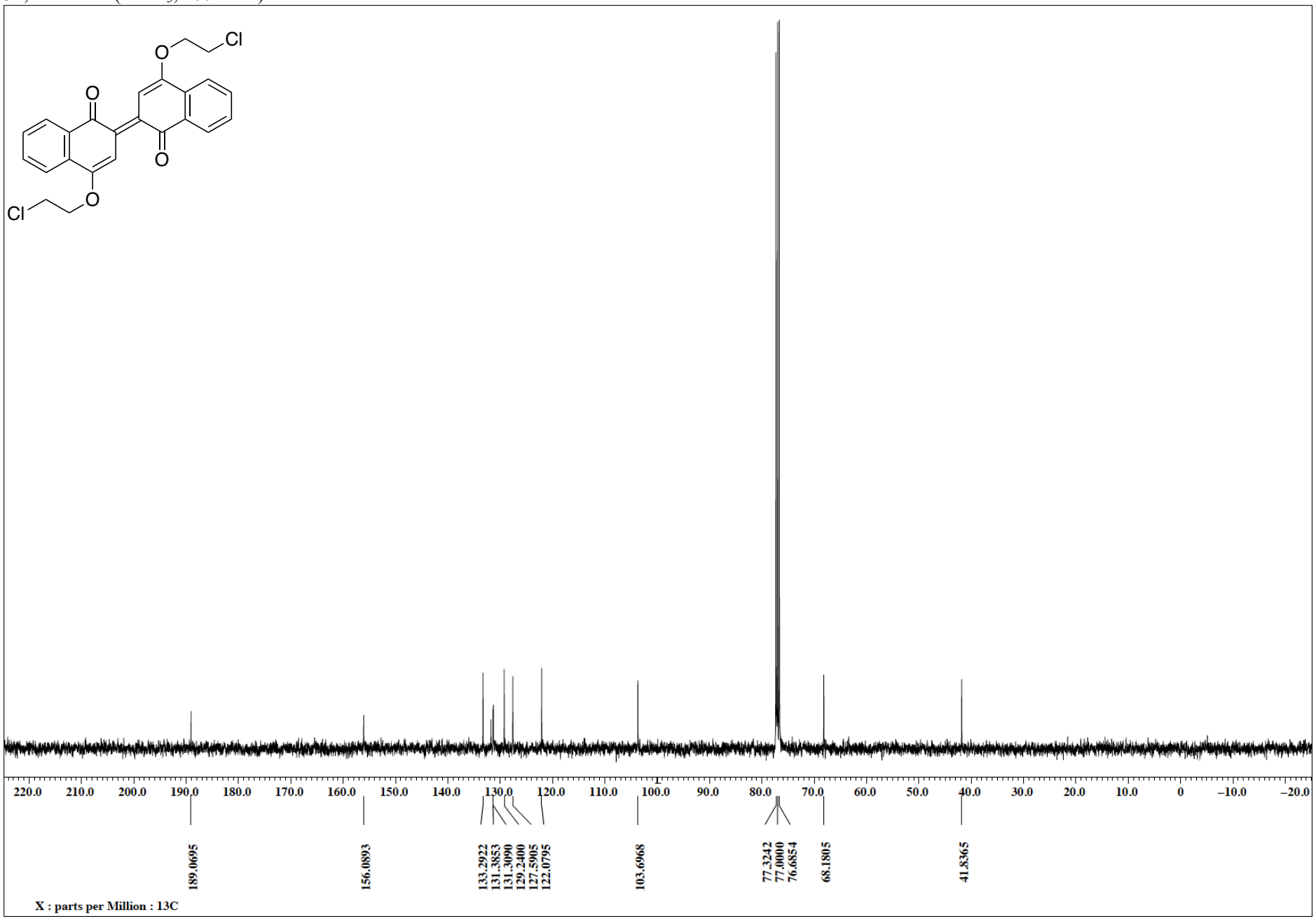

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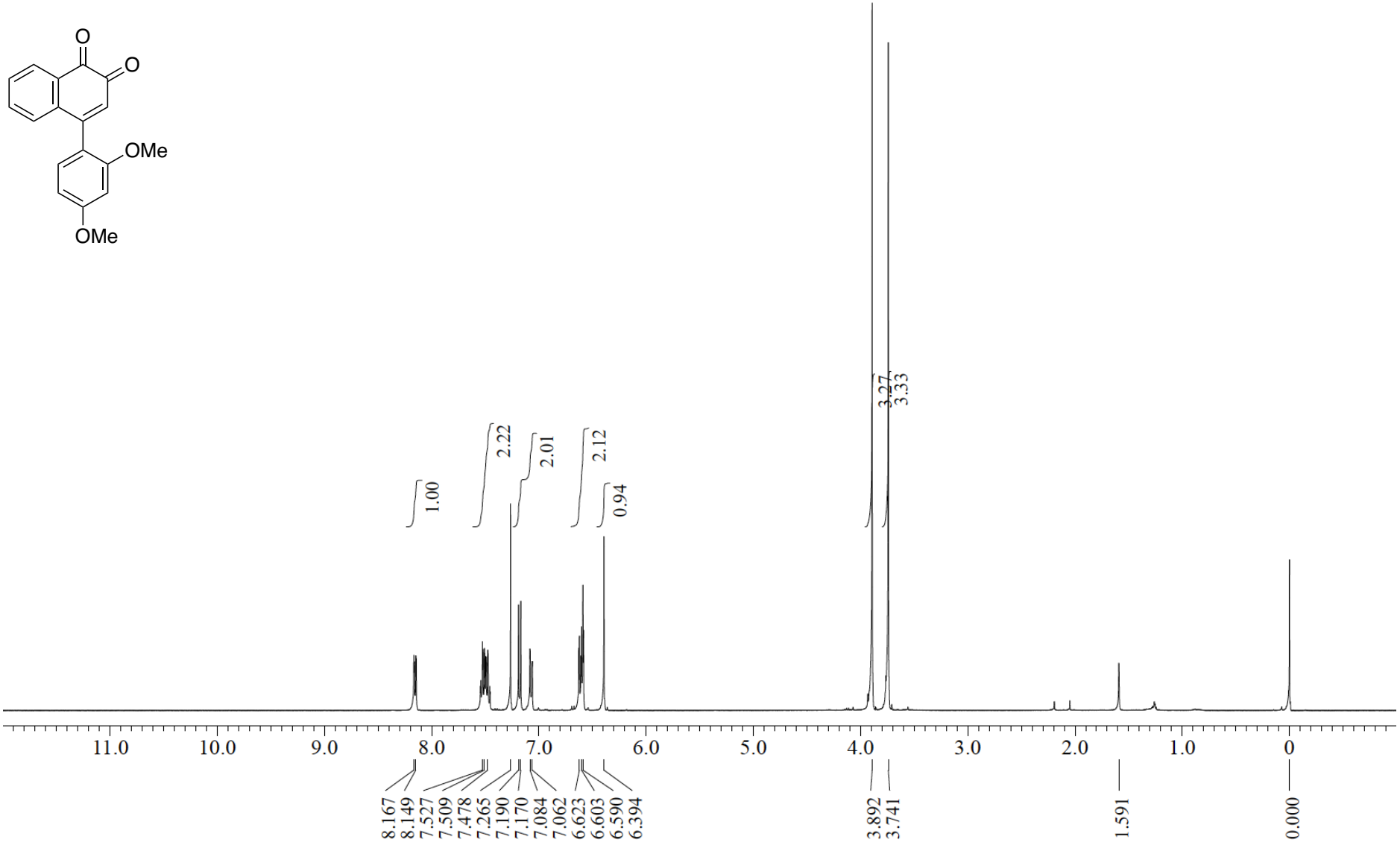

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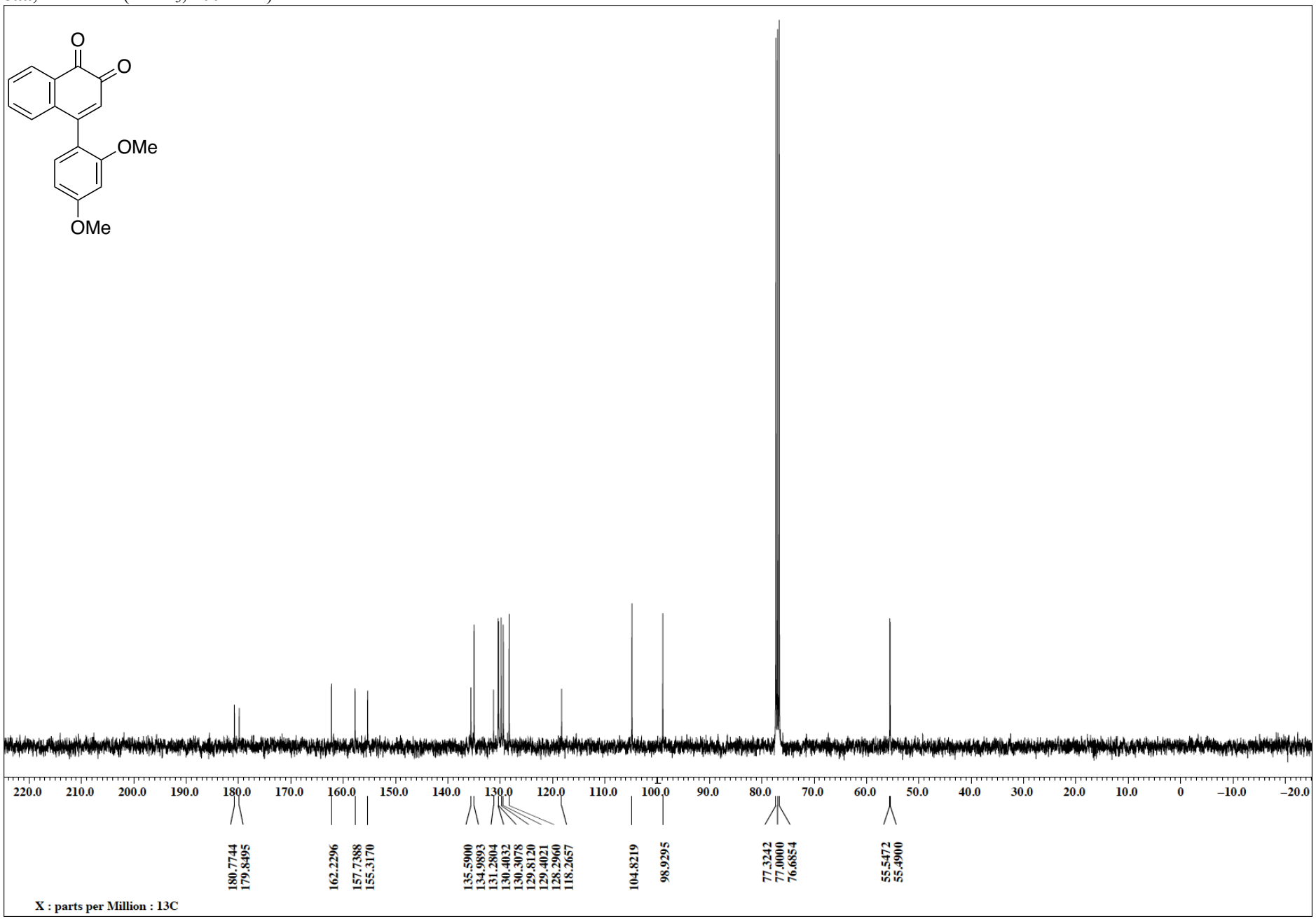

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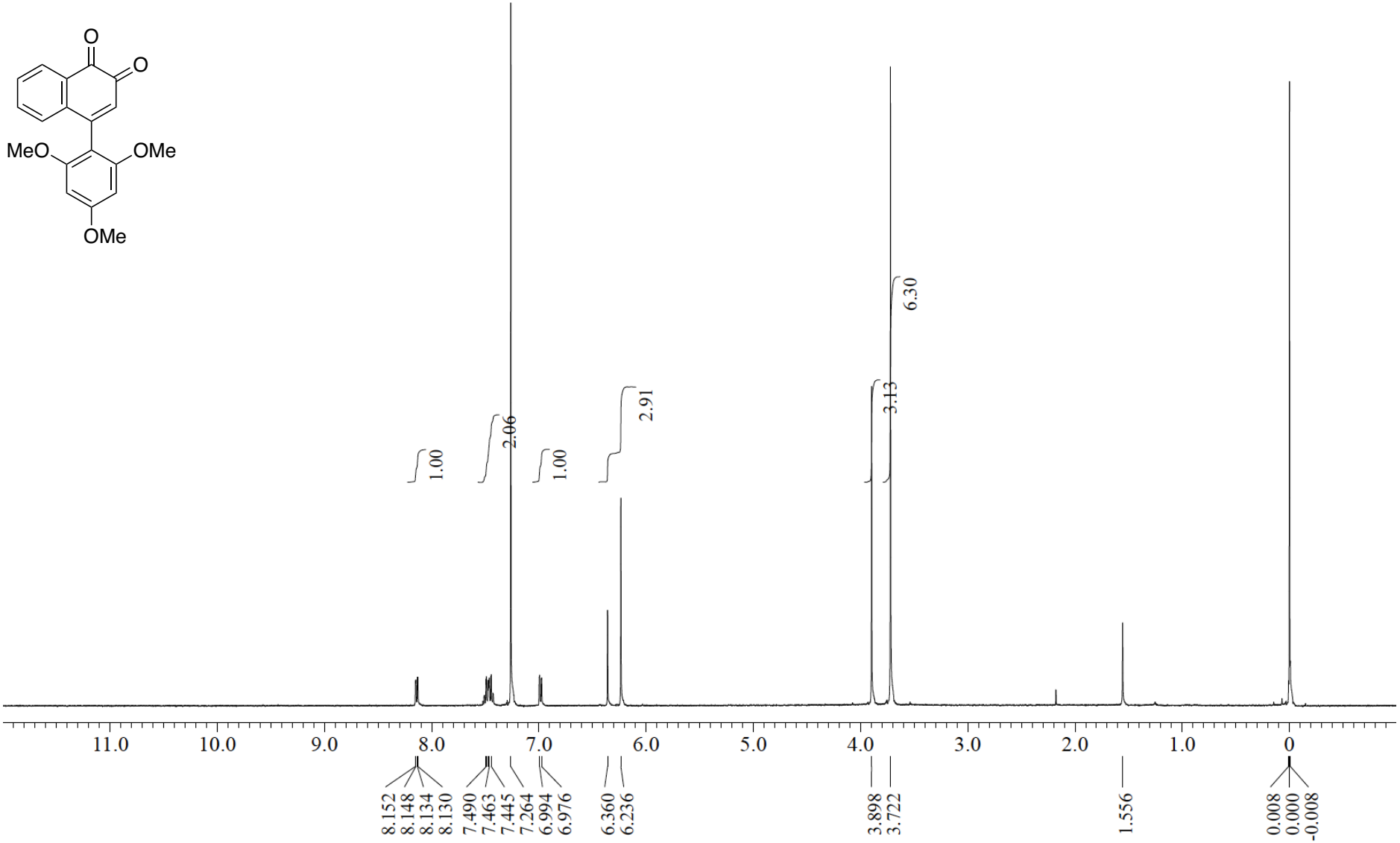

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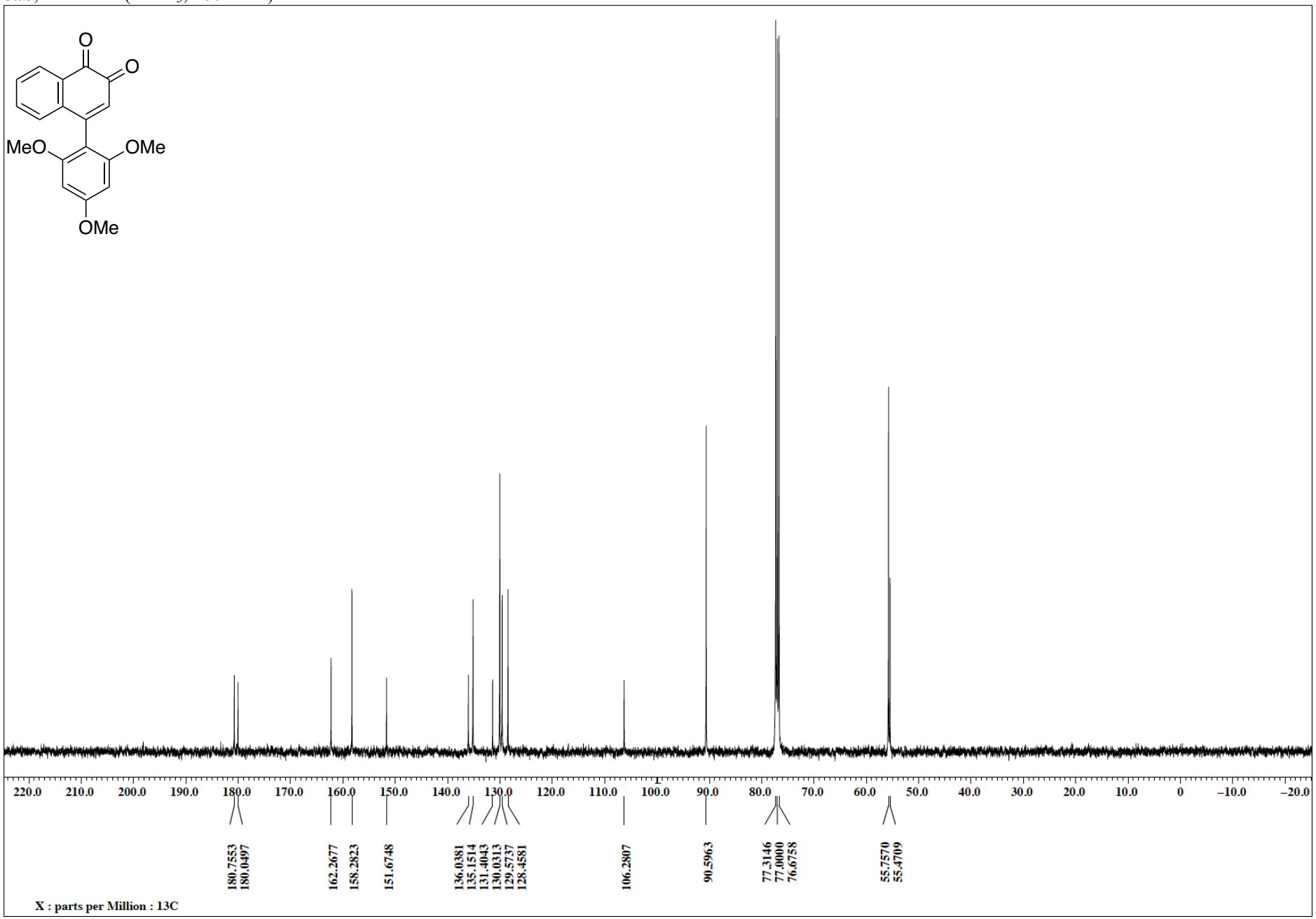

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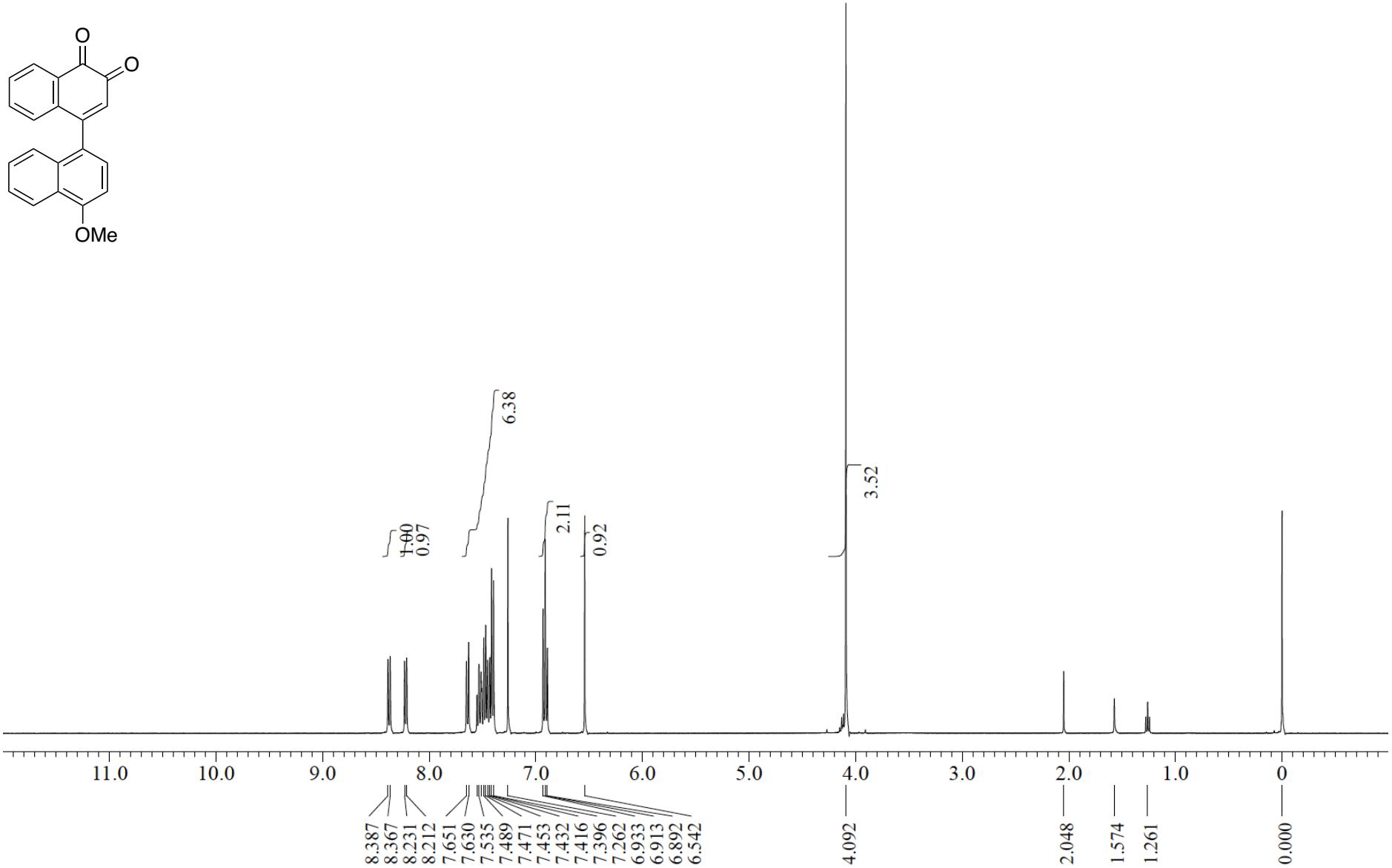

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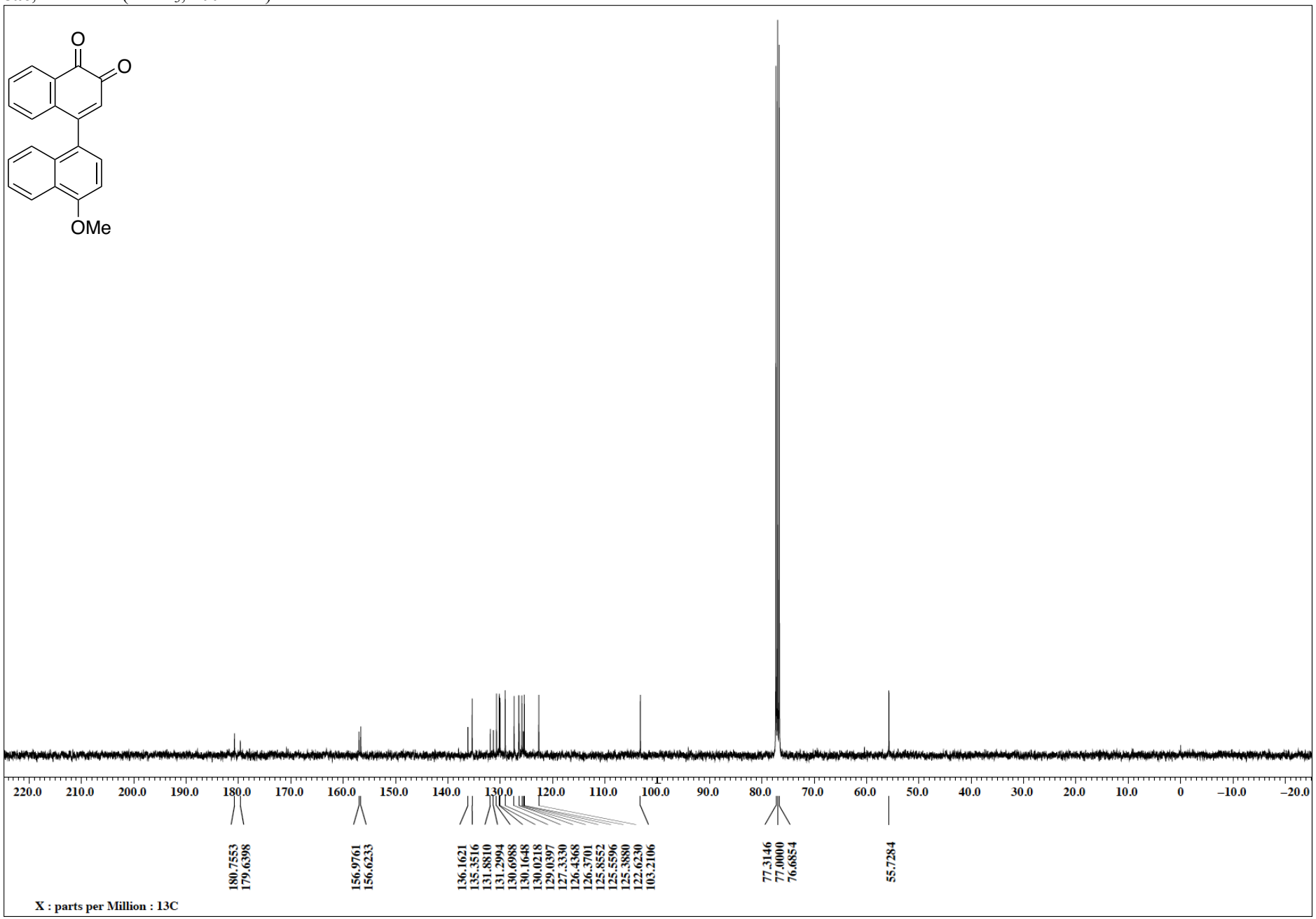

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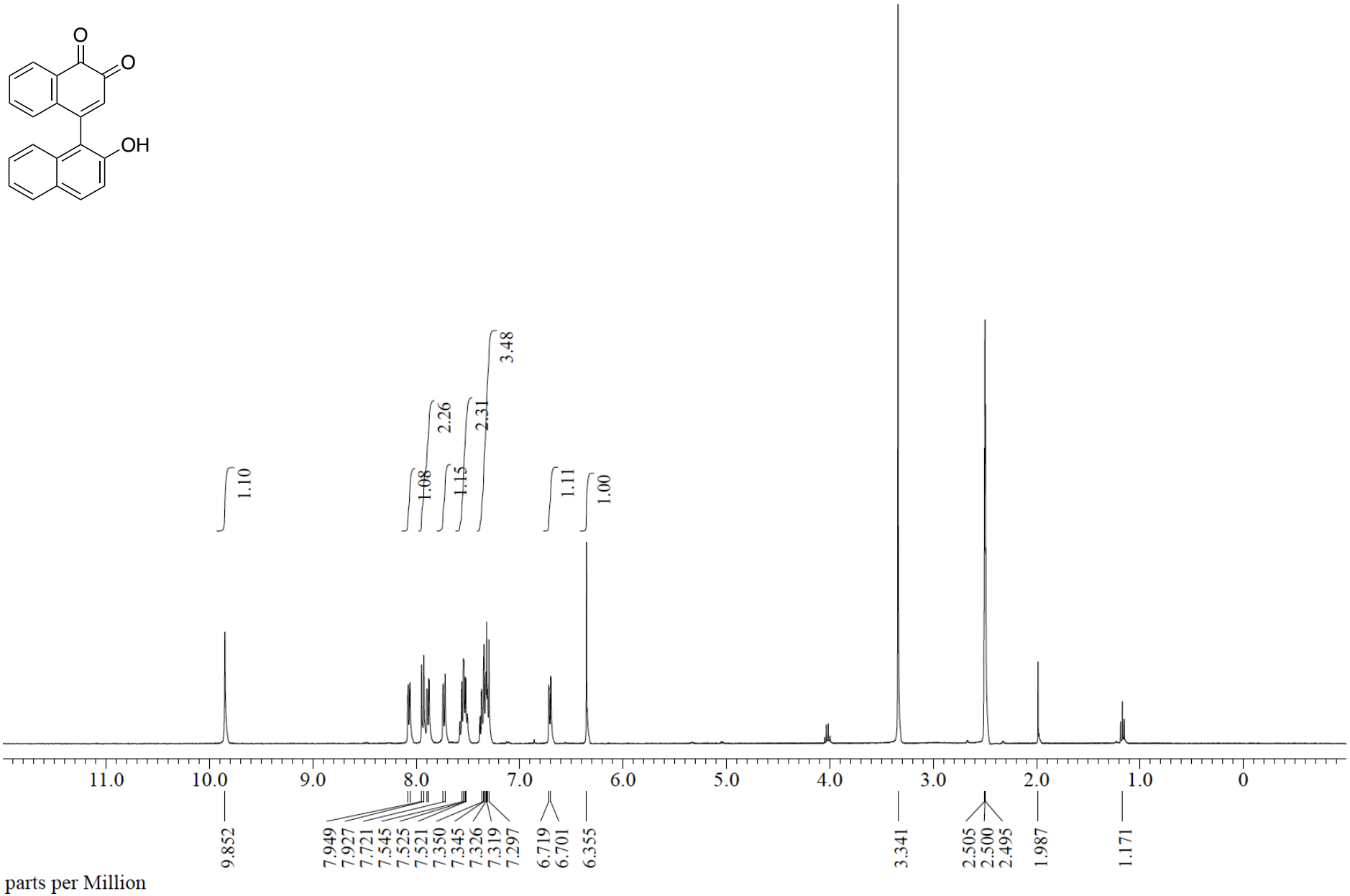

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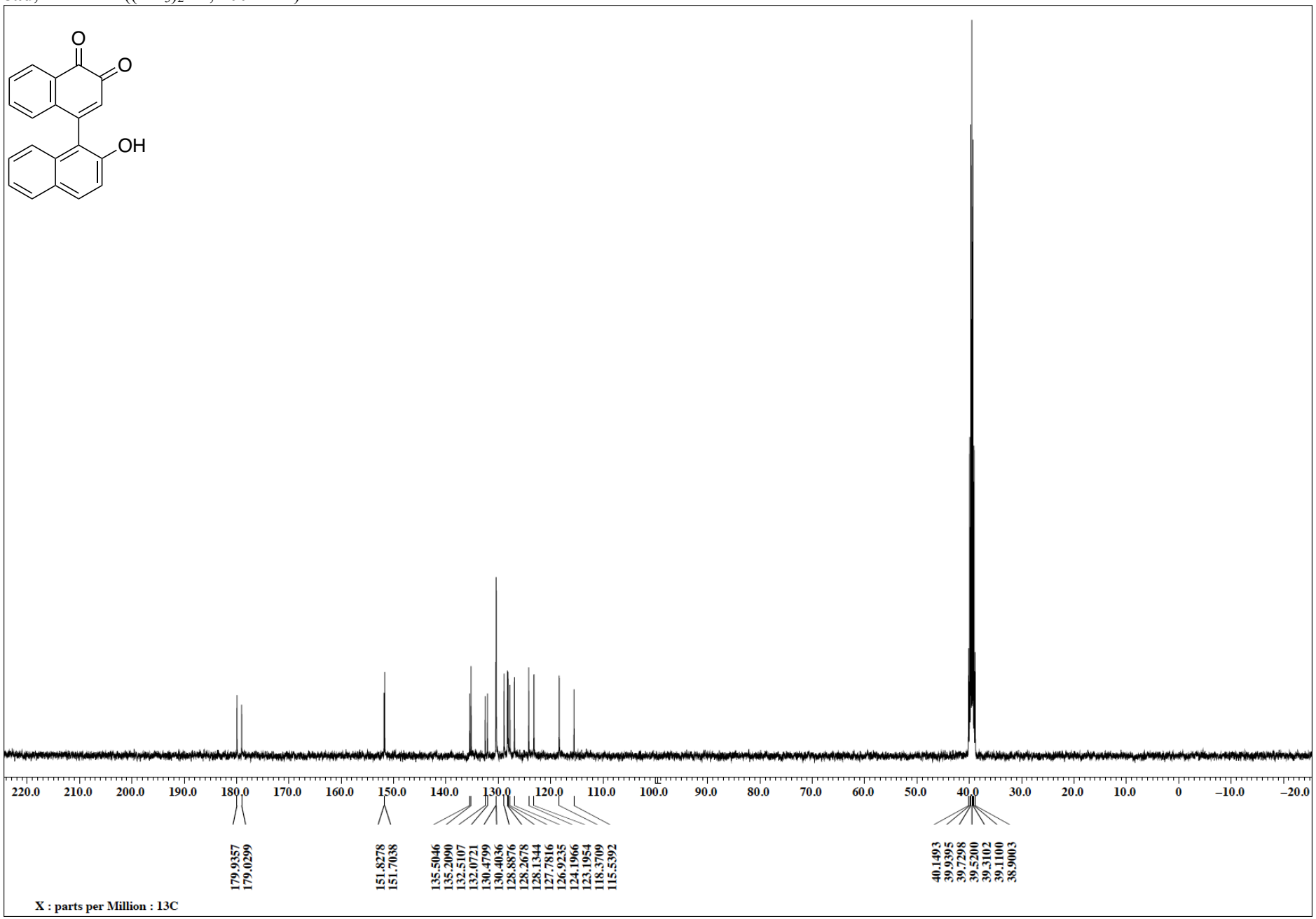

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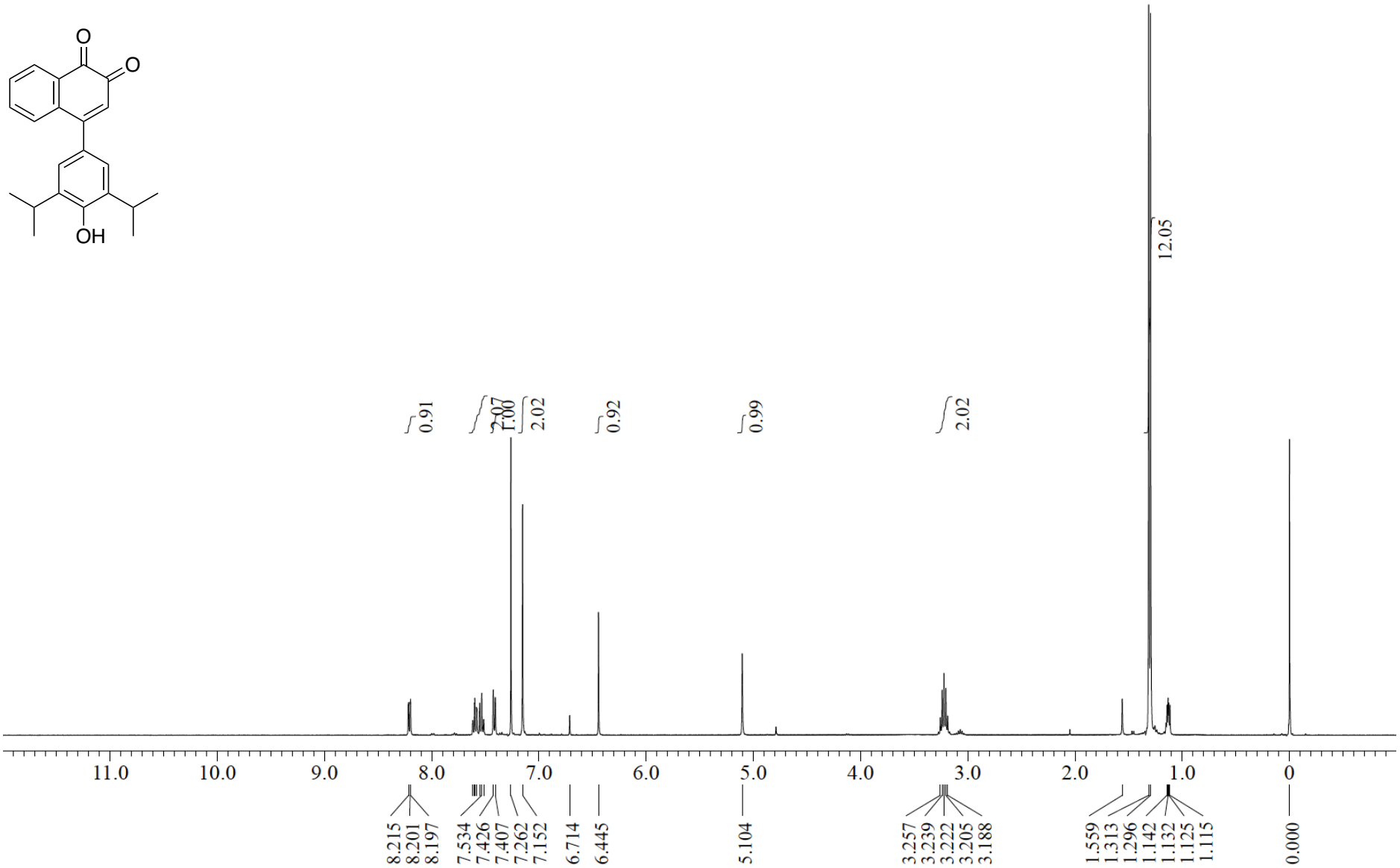

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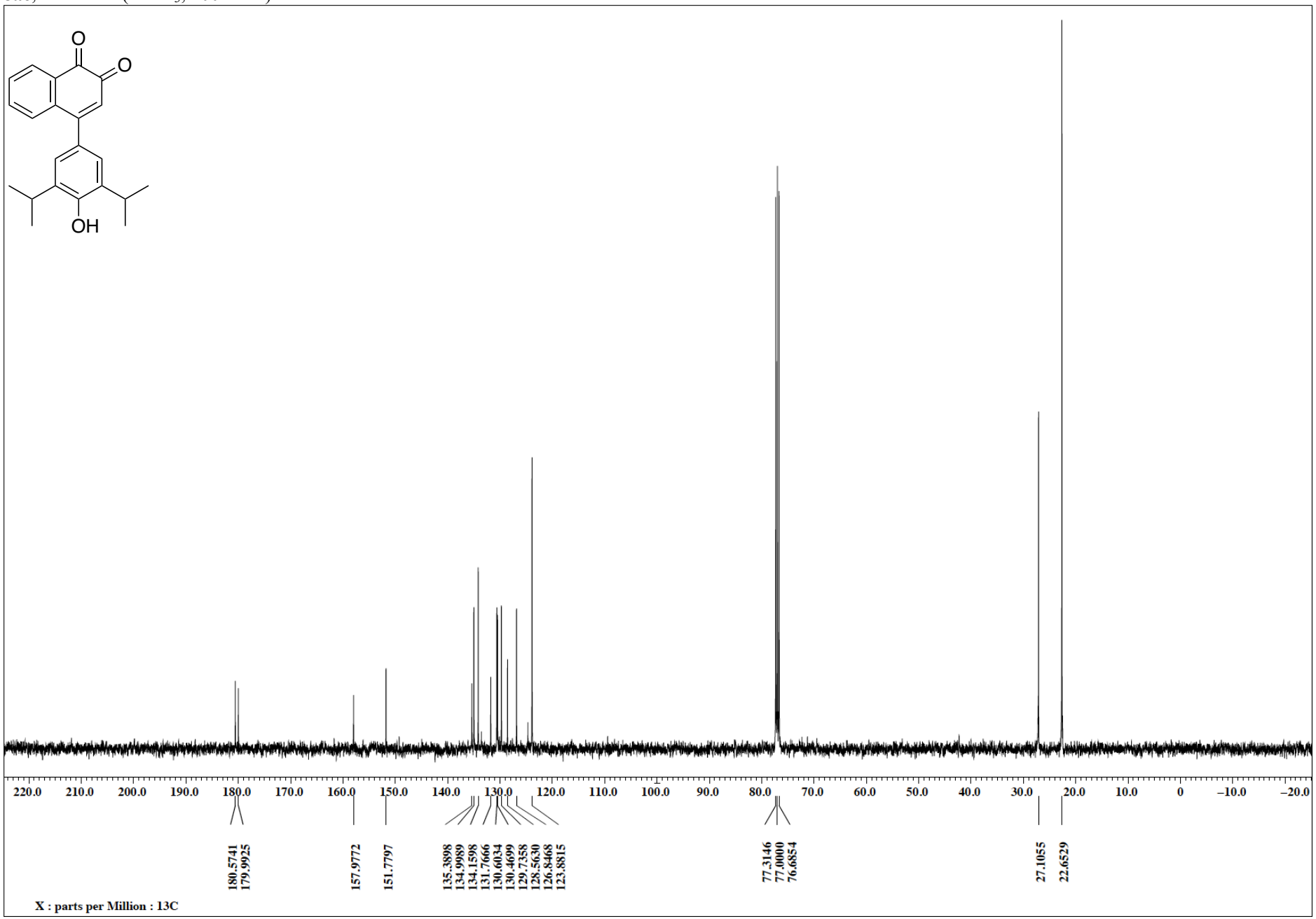

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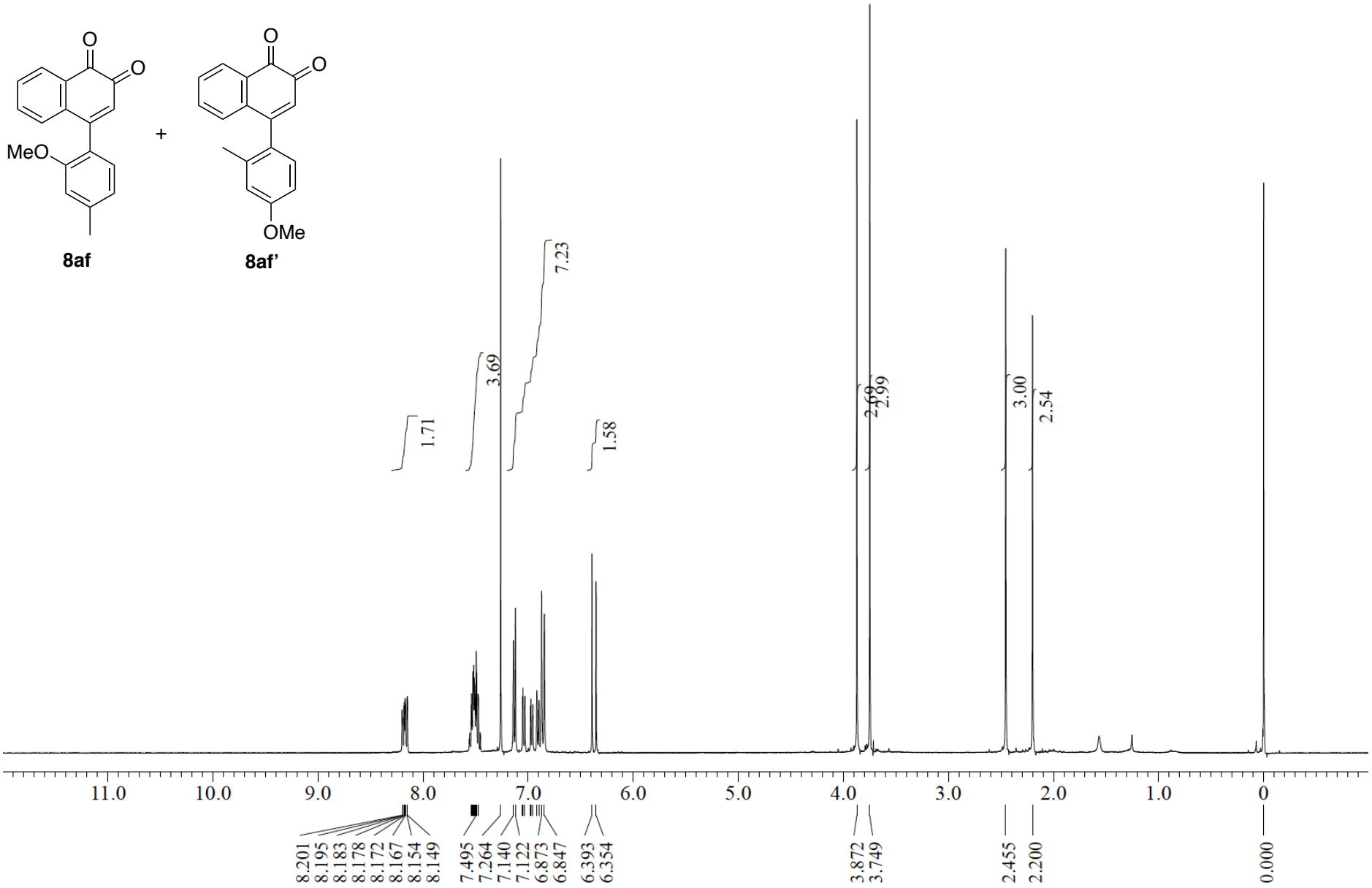

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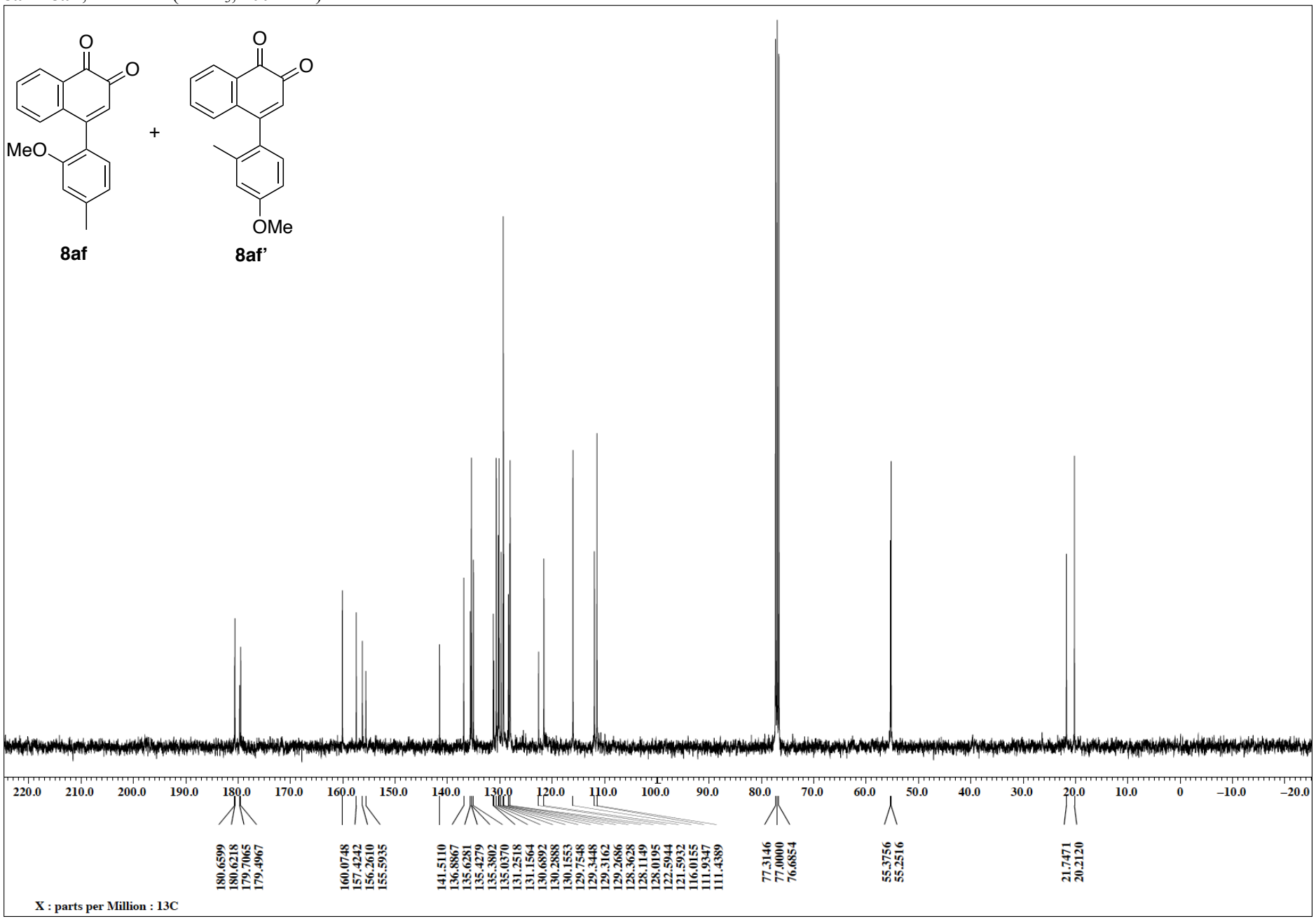

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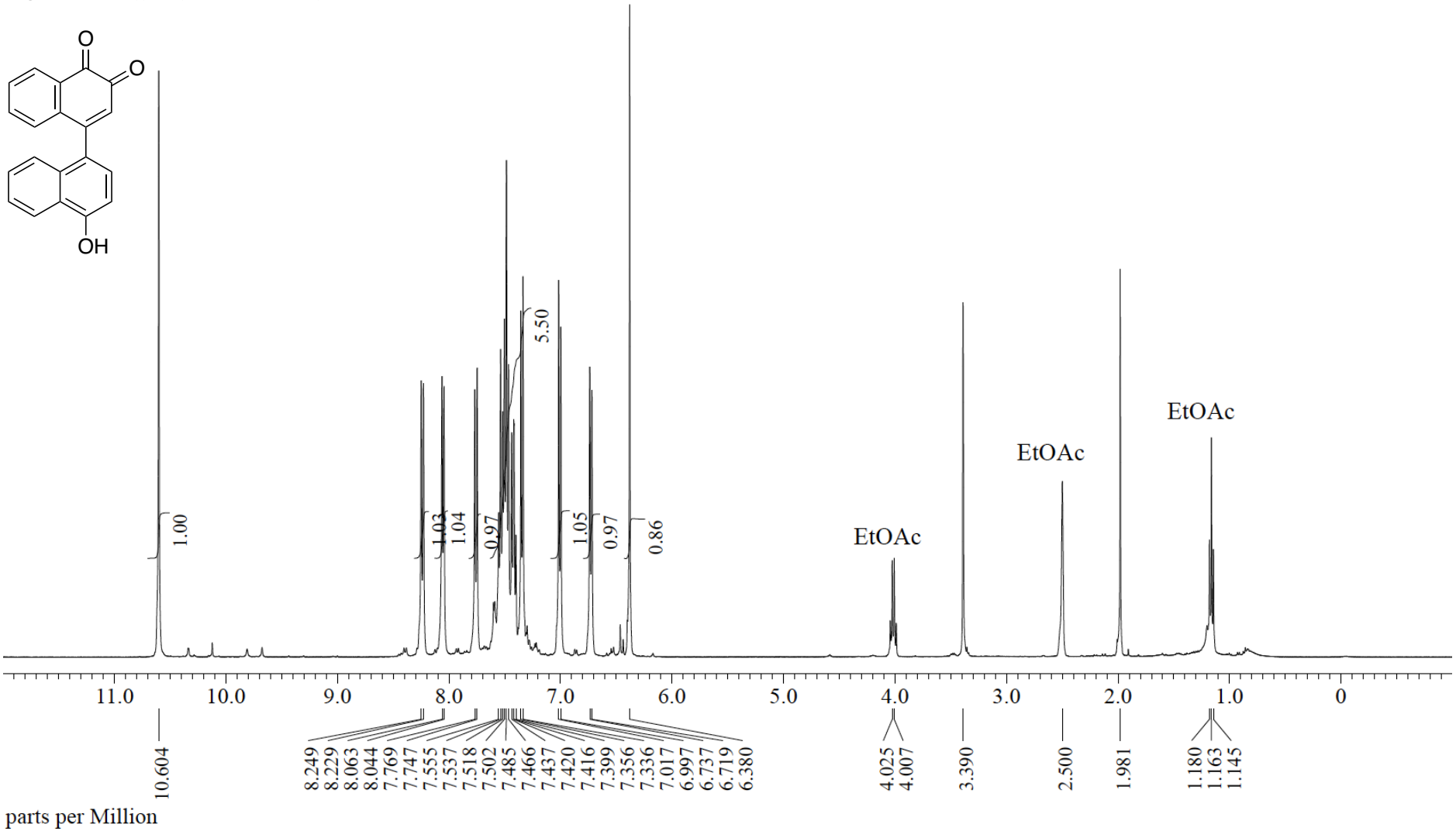

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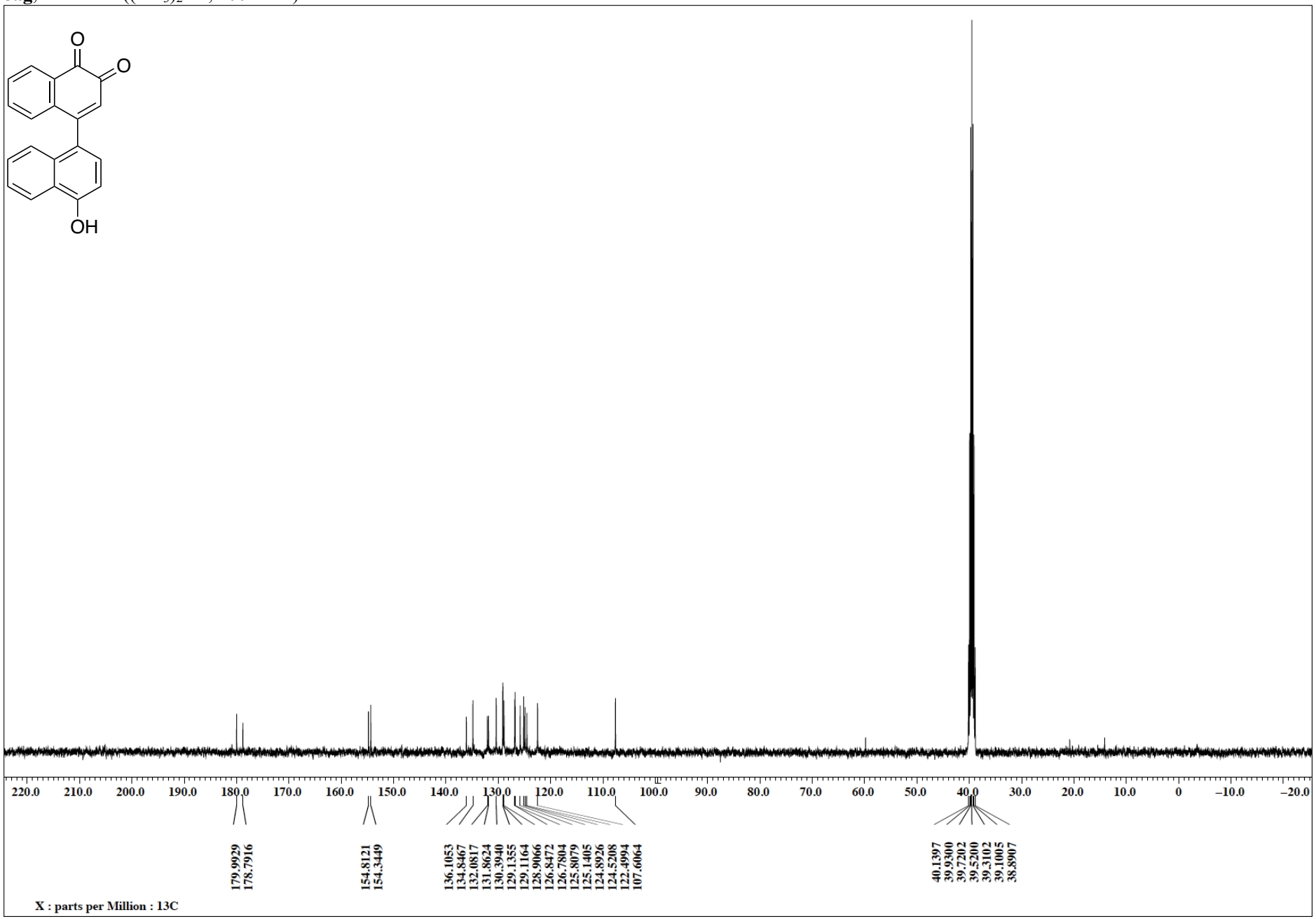
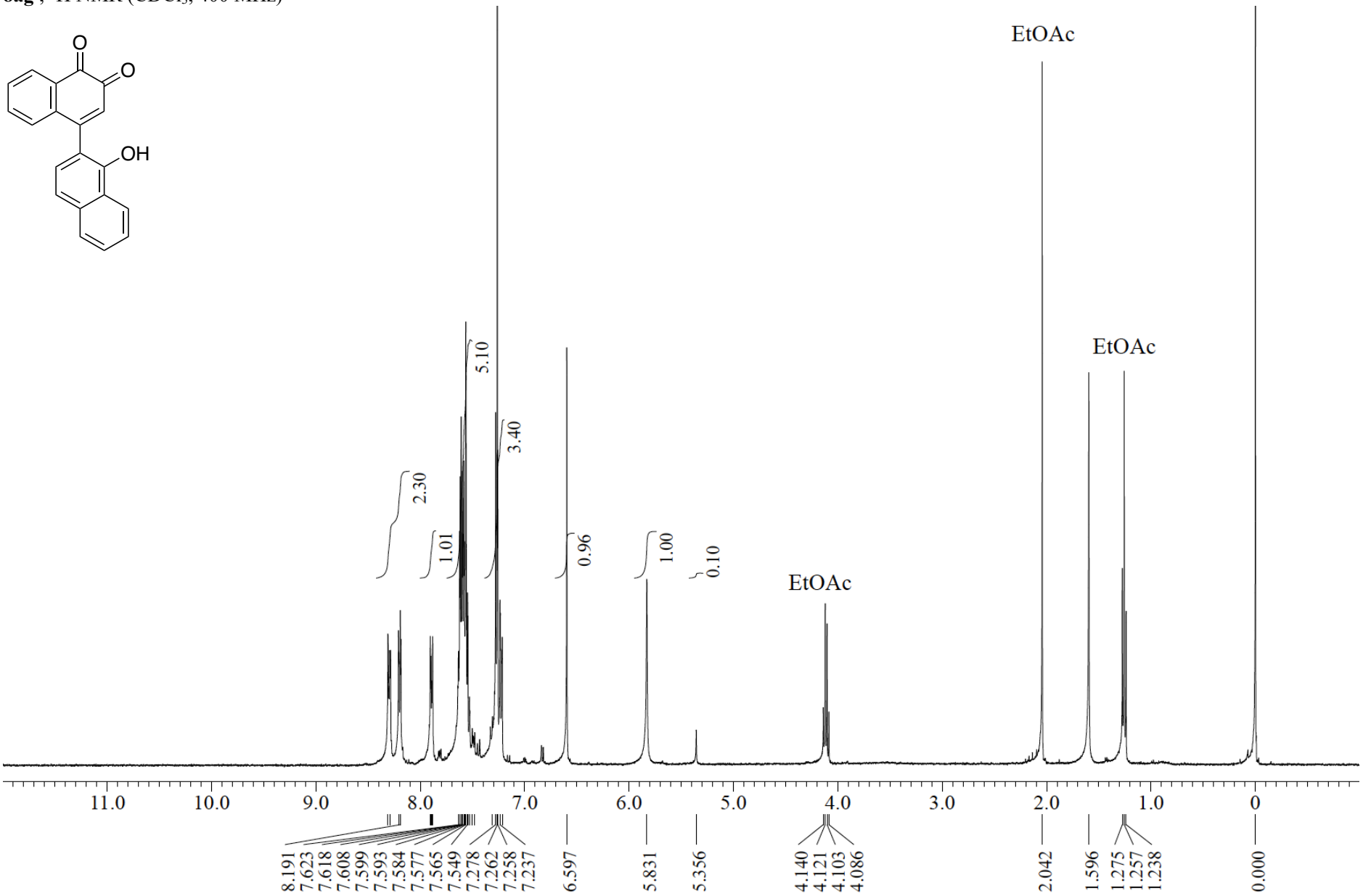
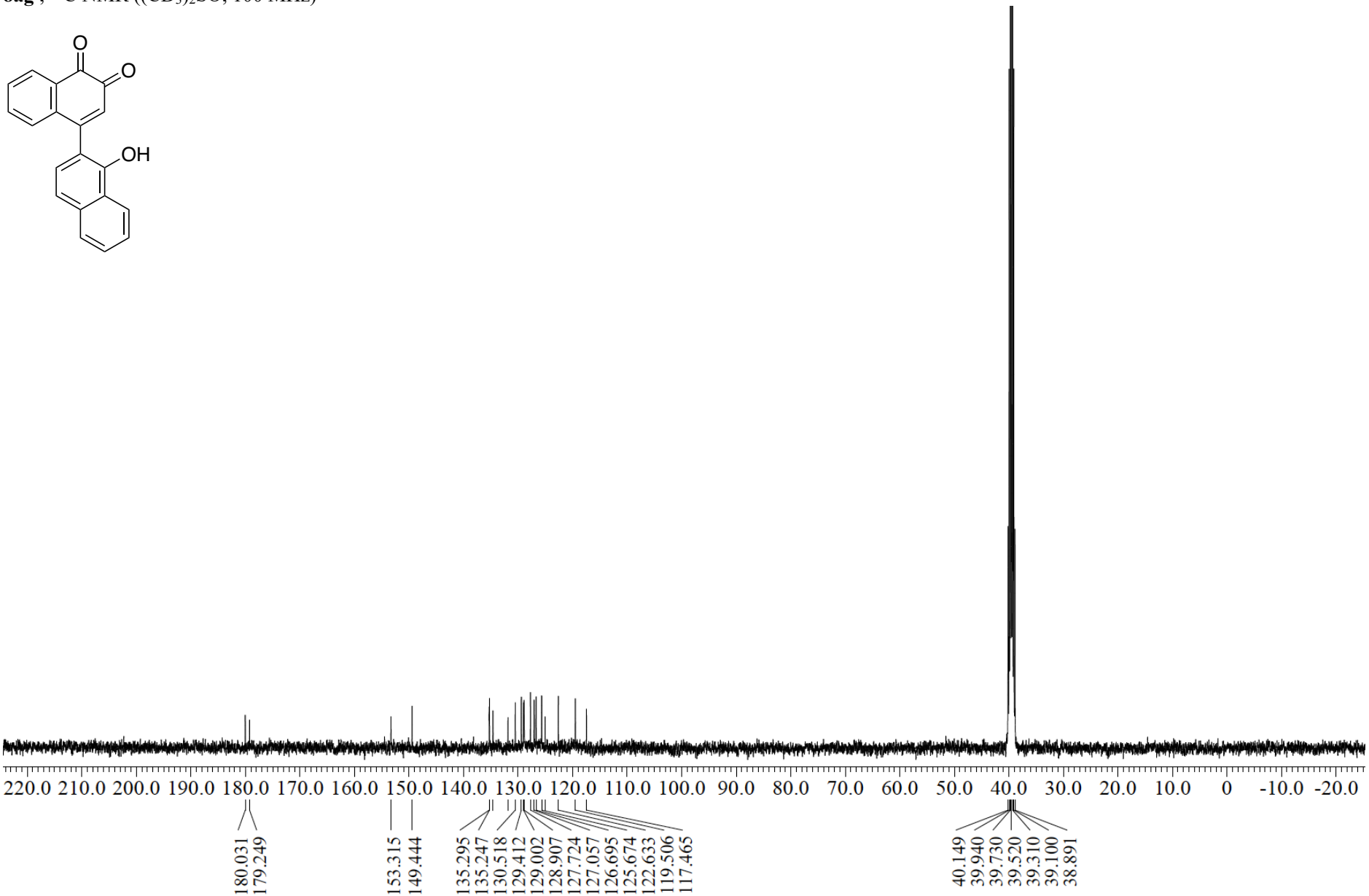


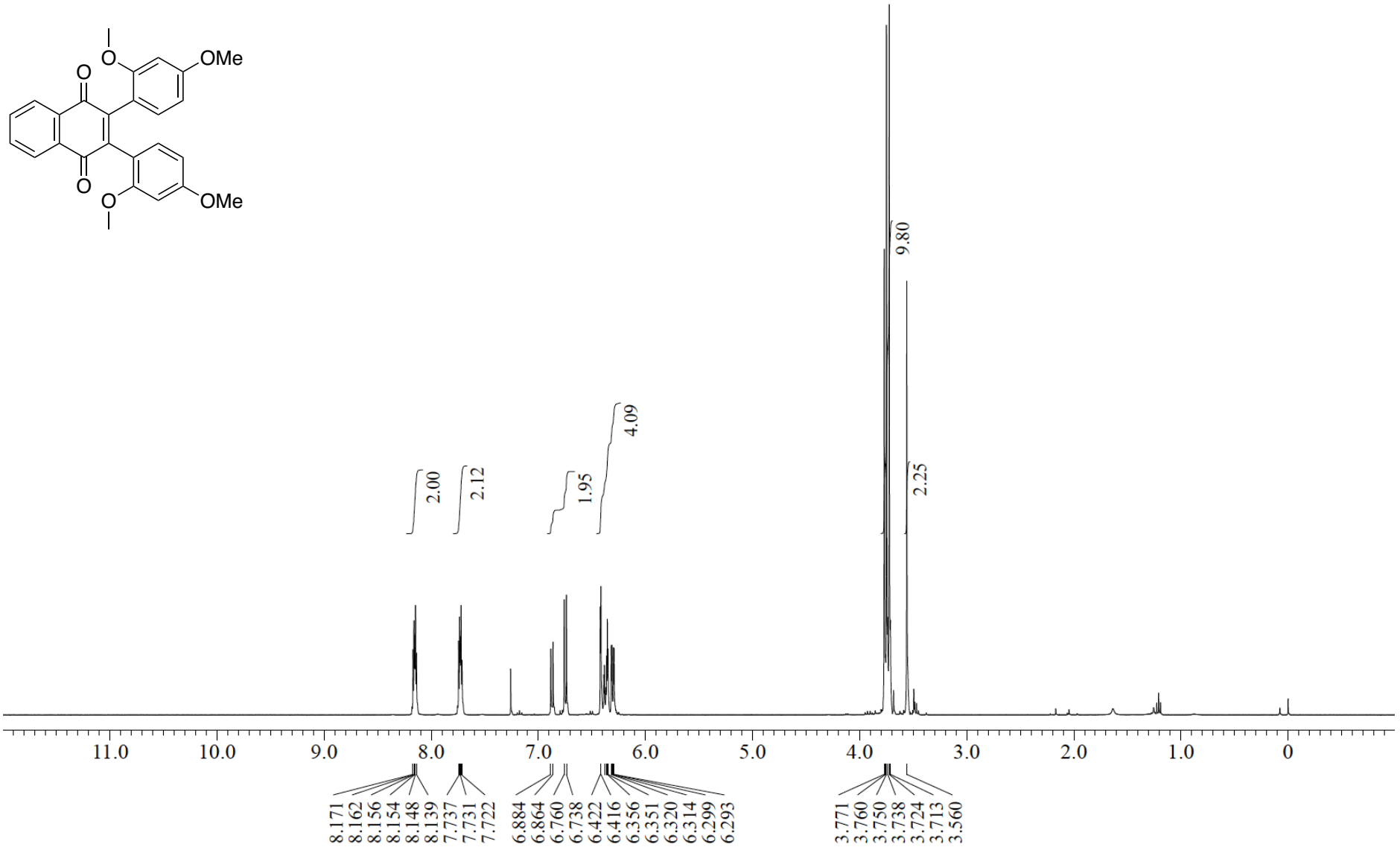
8ag', ^{1}H NMR ($CDCl_3$, 400 MHz)



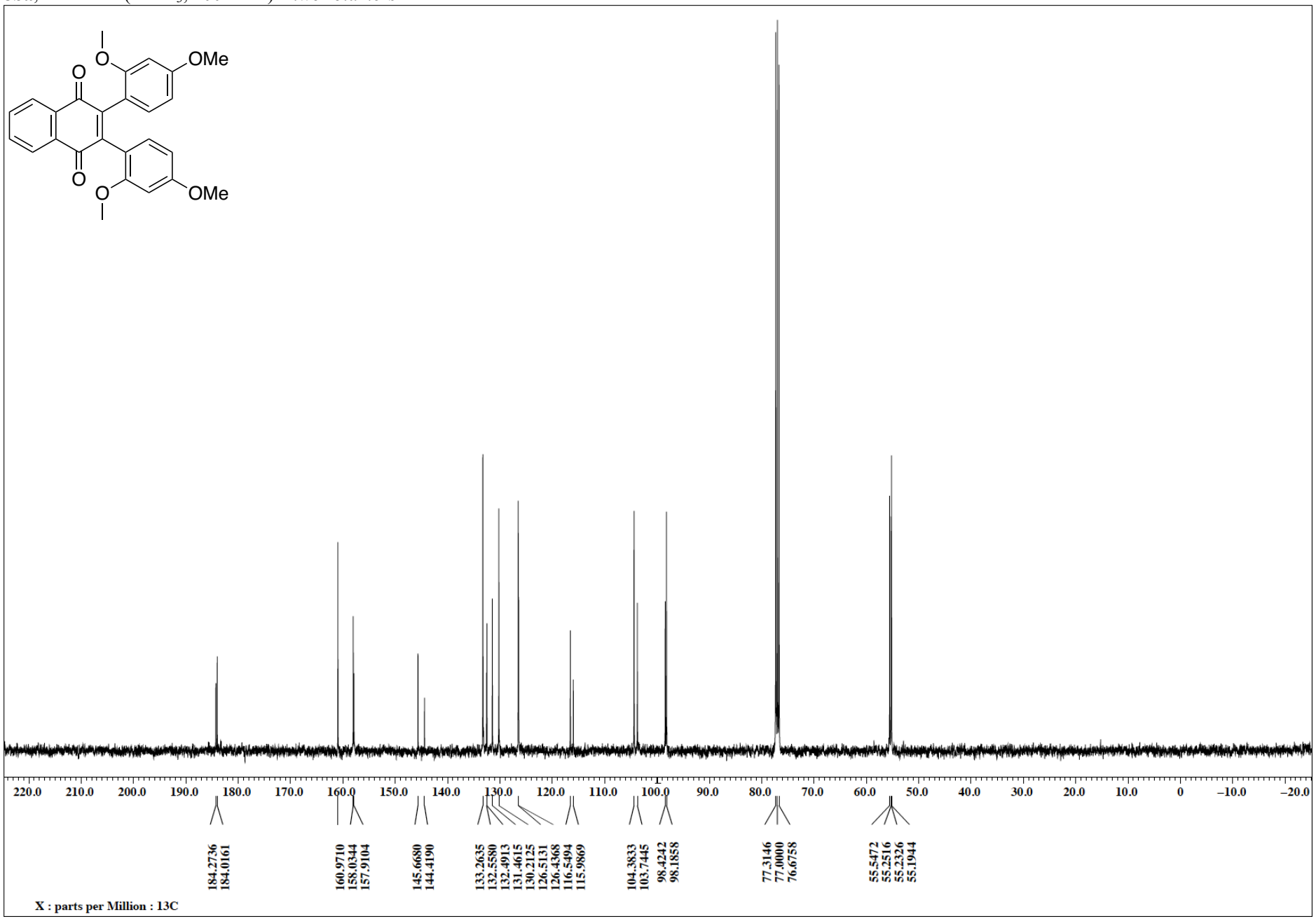
8ag', ^{13}C NMR ($(CD_3)_2SO$, 100 MHz)



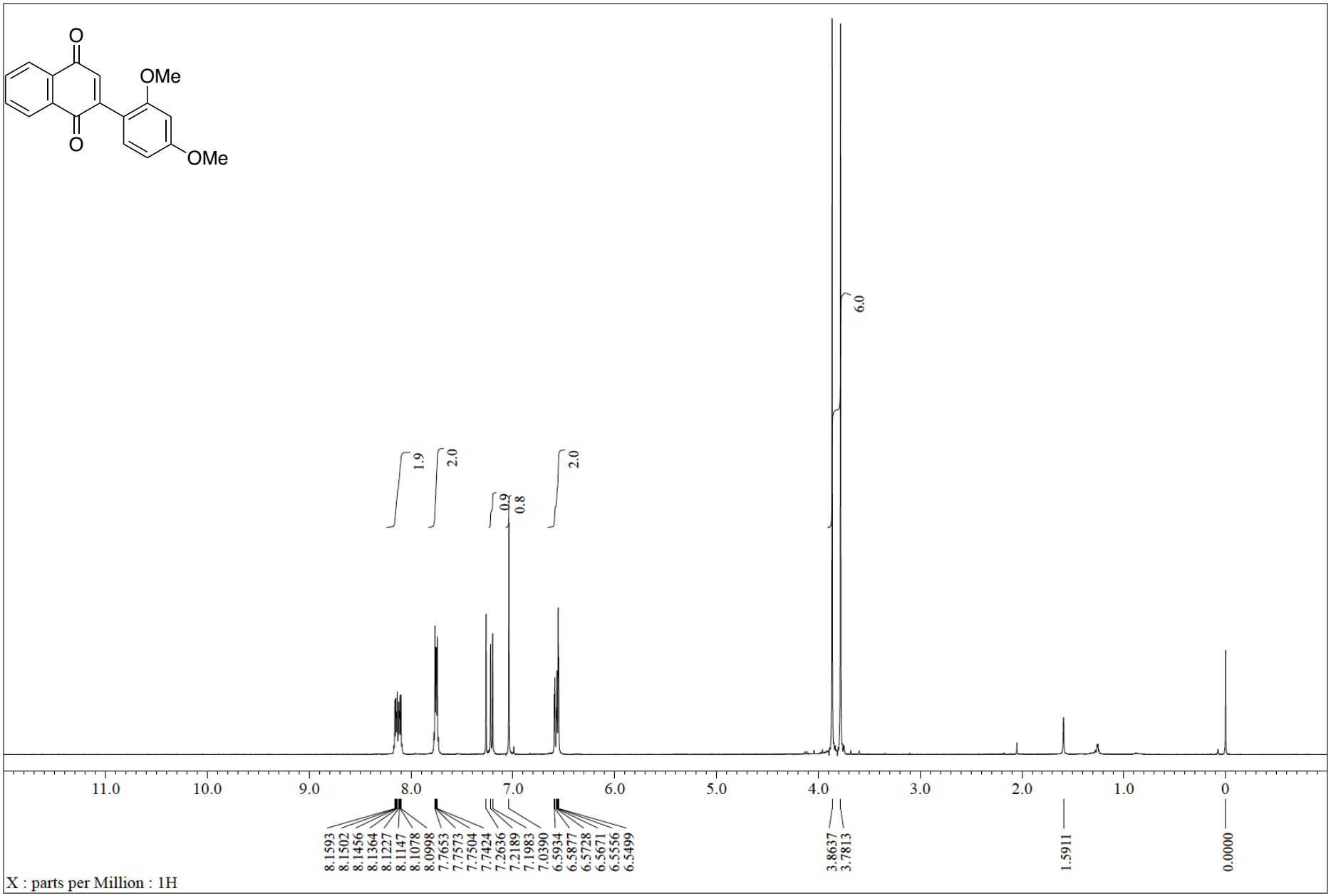
8ba, ^{1}H NMR ($CDCl_3$, 400 MHz) *two rotamers*



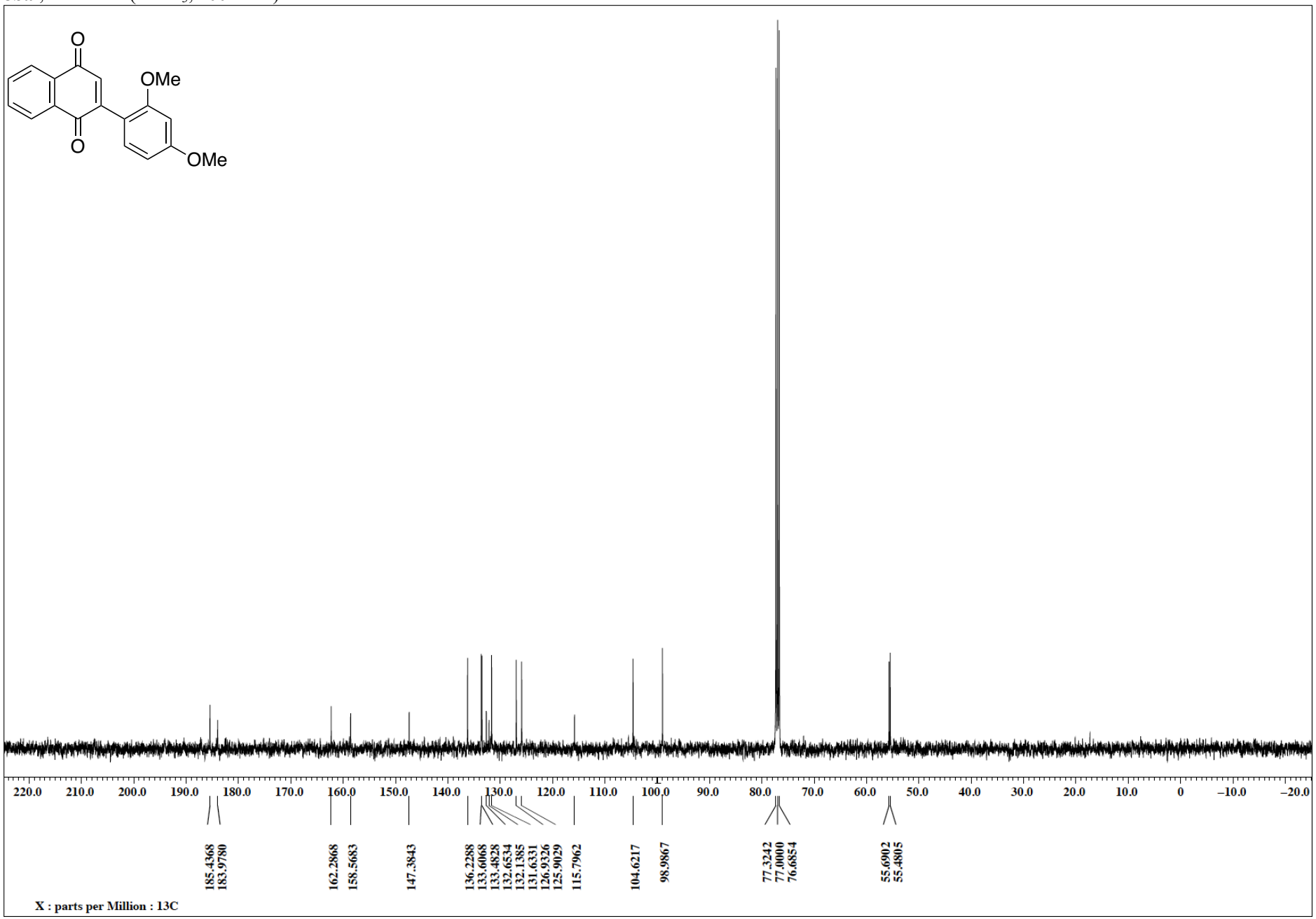
8ba, ^{13}C NMR ($CDCl_3$, 100 MHz) *two rotamers*



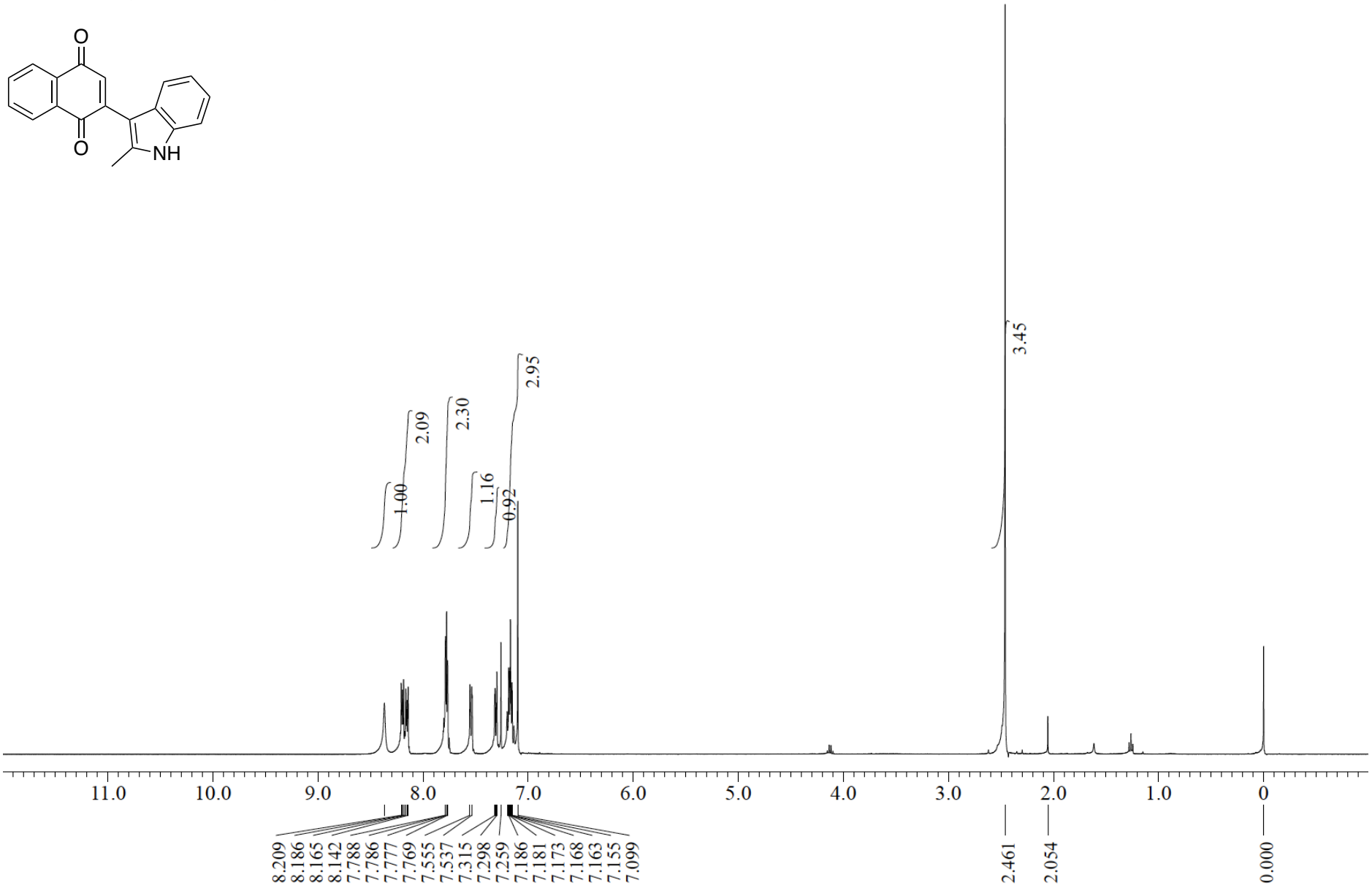
8ba', ^{1}H NMR ($CDCl_3$, 400 MHz)



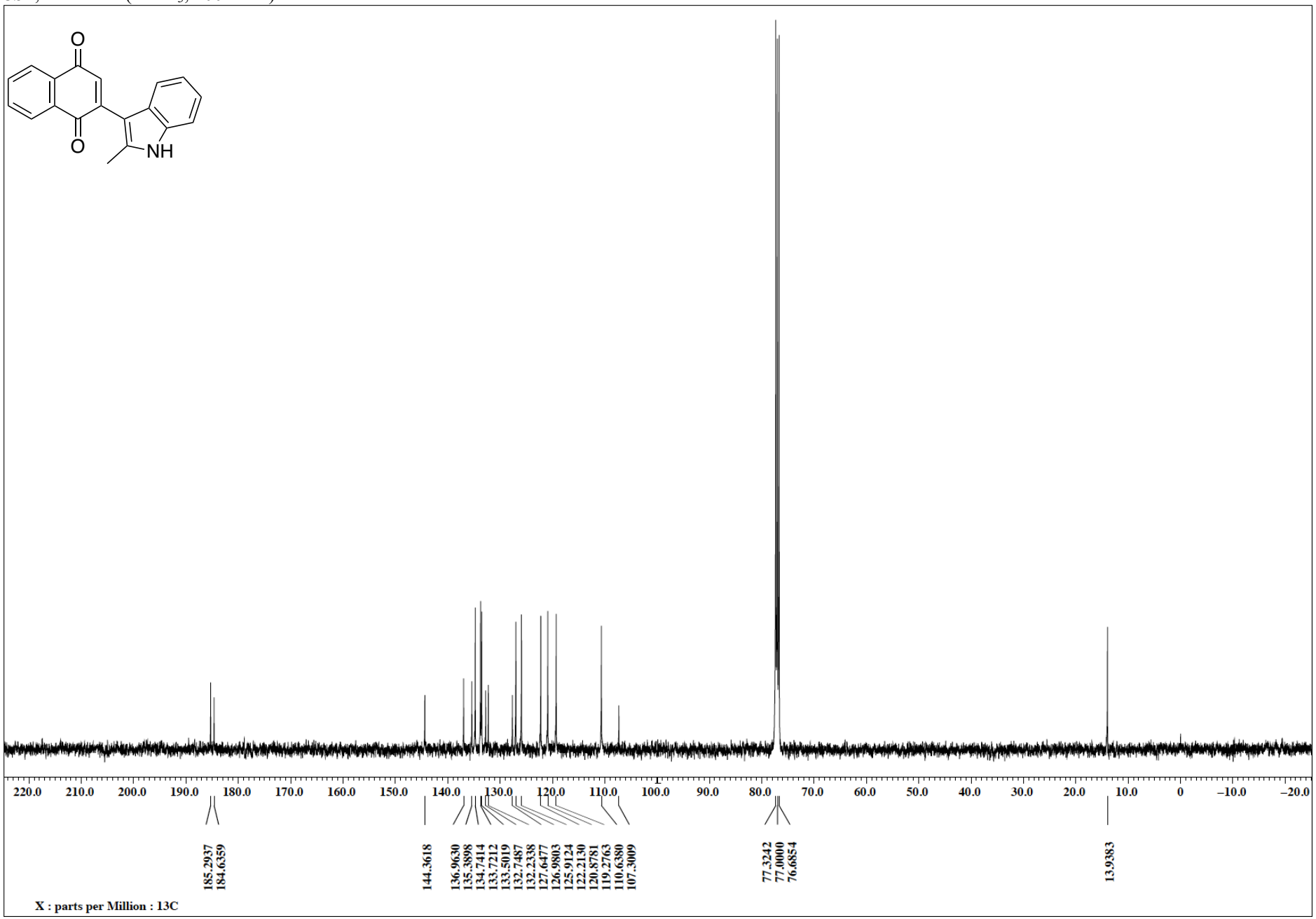
8ba', ^{13}C NMR ($CDCl_3$, 100 MHz)



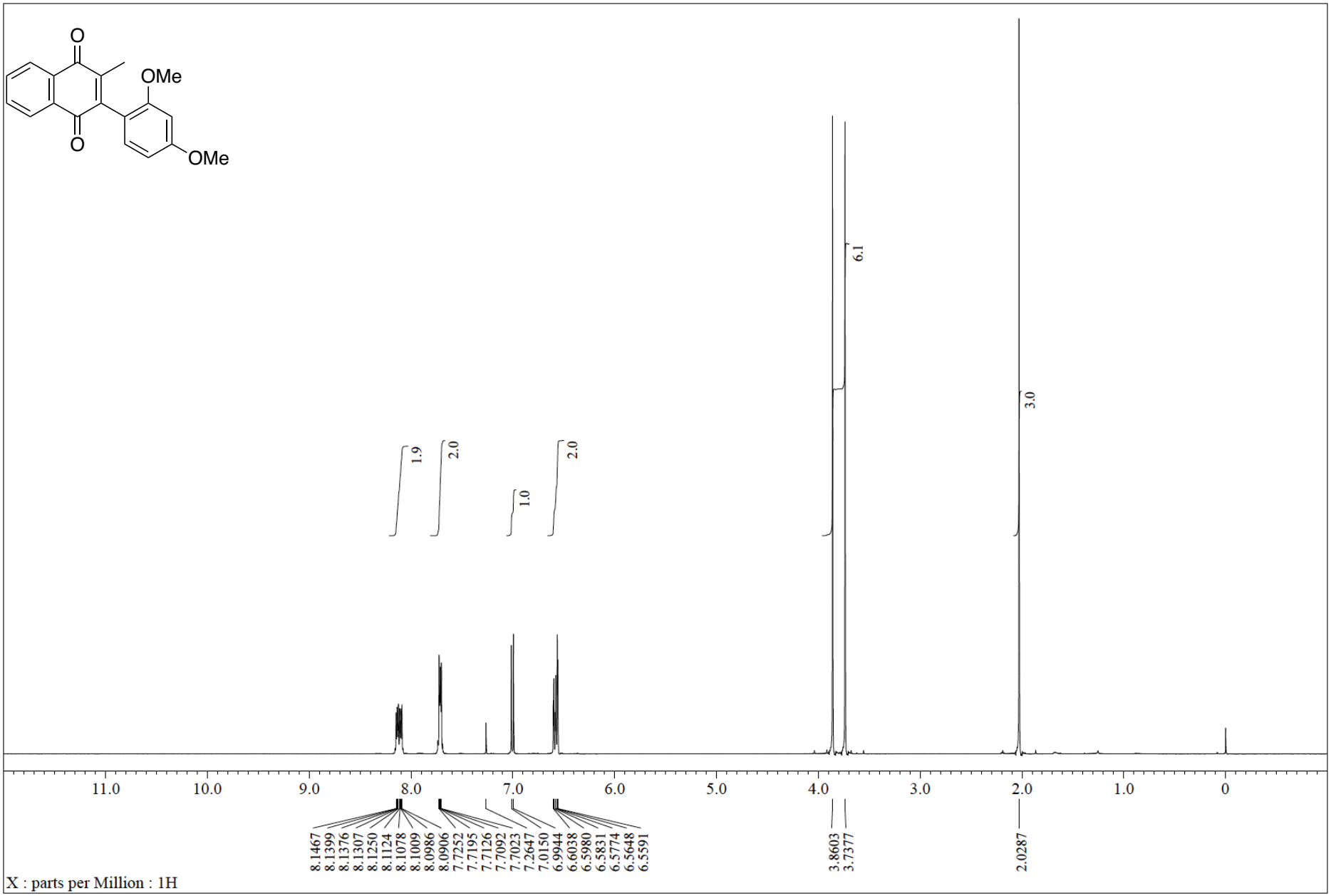
8bh, ^{1}H NMR ($CDCl_3$, 400 MHz)



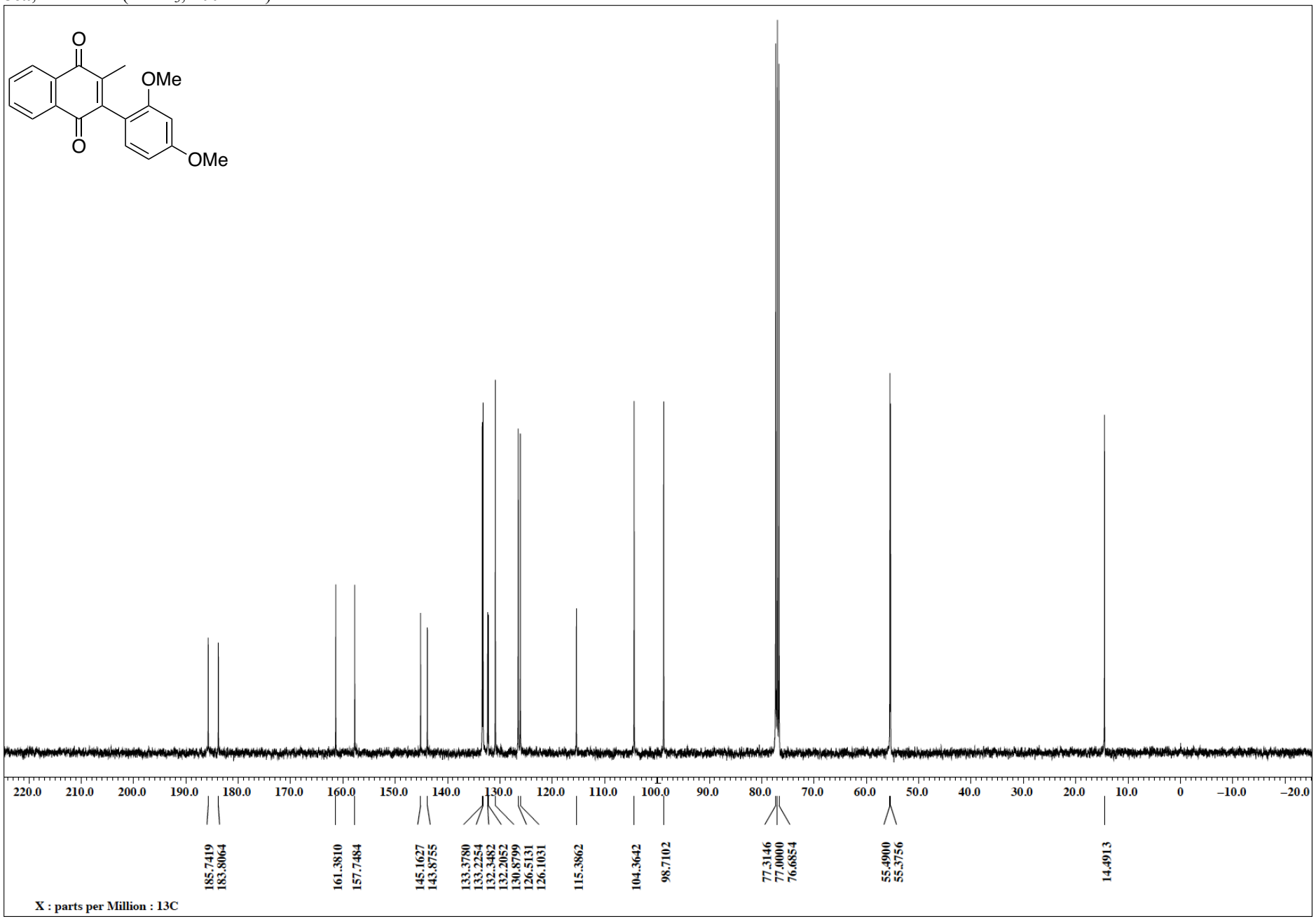
8bh, ^{13}C NMR ($CDCl_3$, 100 MHz)



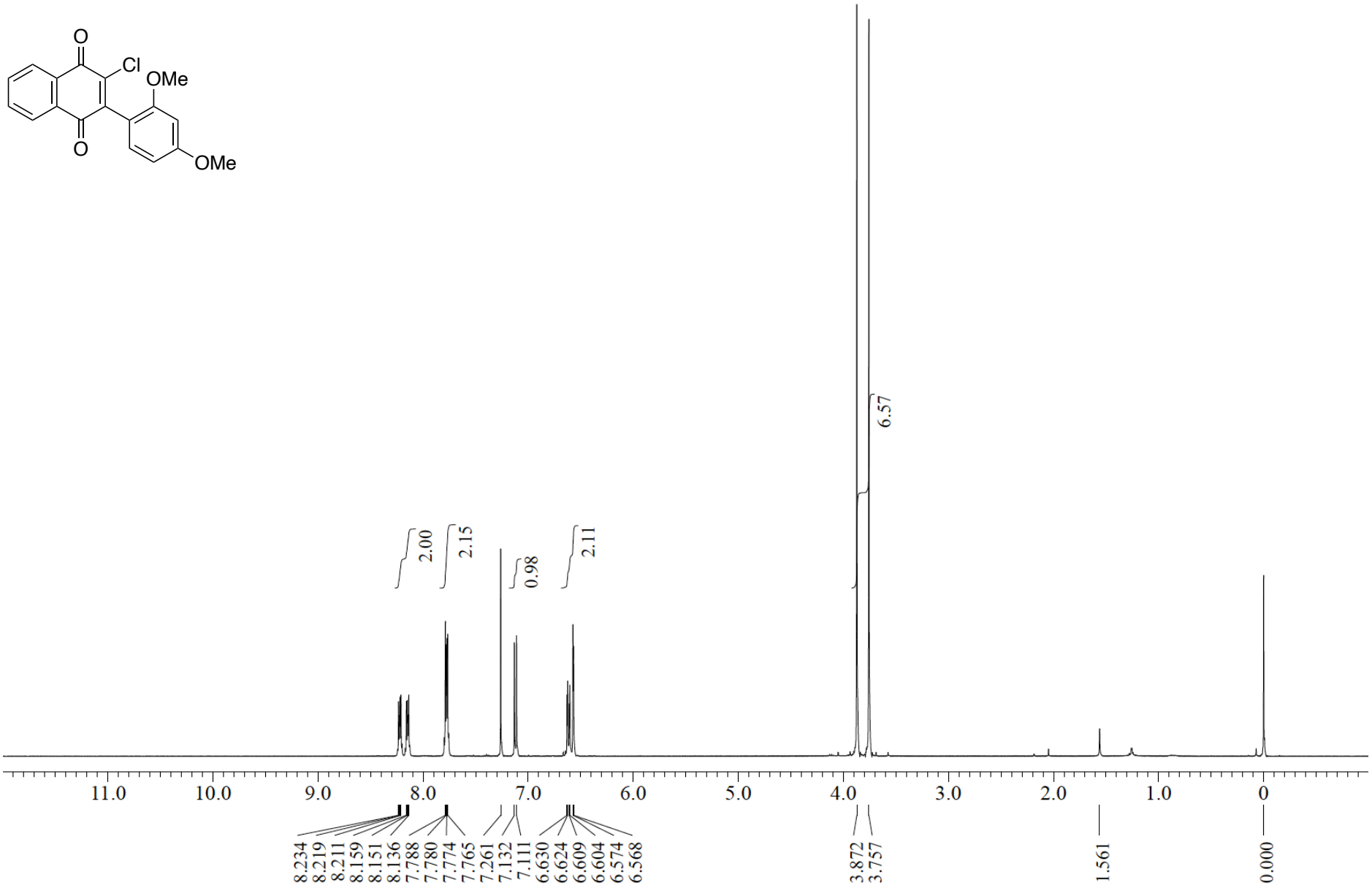
8ca, ^{1}H NMR ($CDCl_3$, 400 MHz)



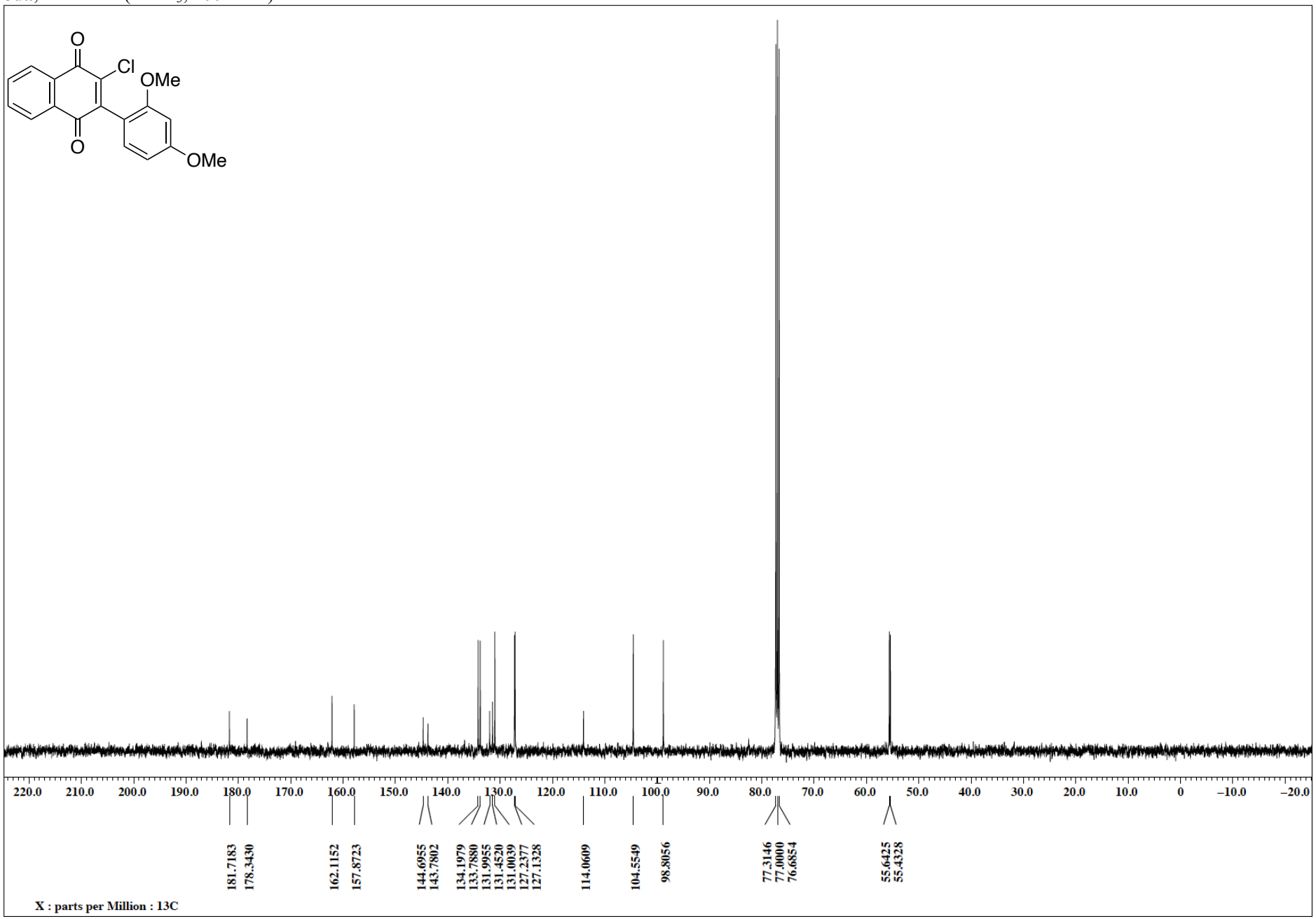
8ca, ^{13}C NMR ($CDCl_3$, 100 MHz)



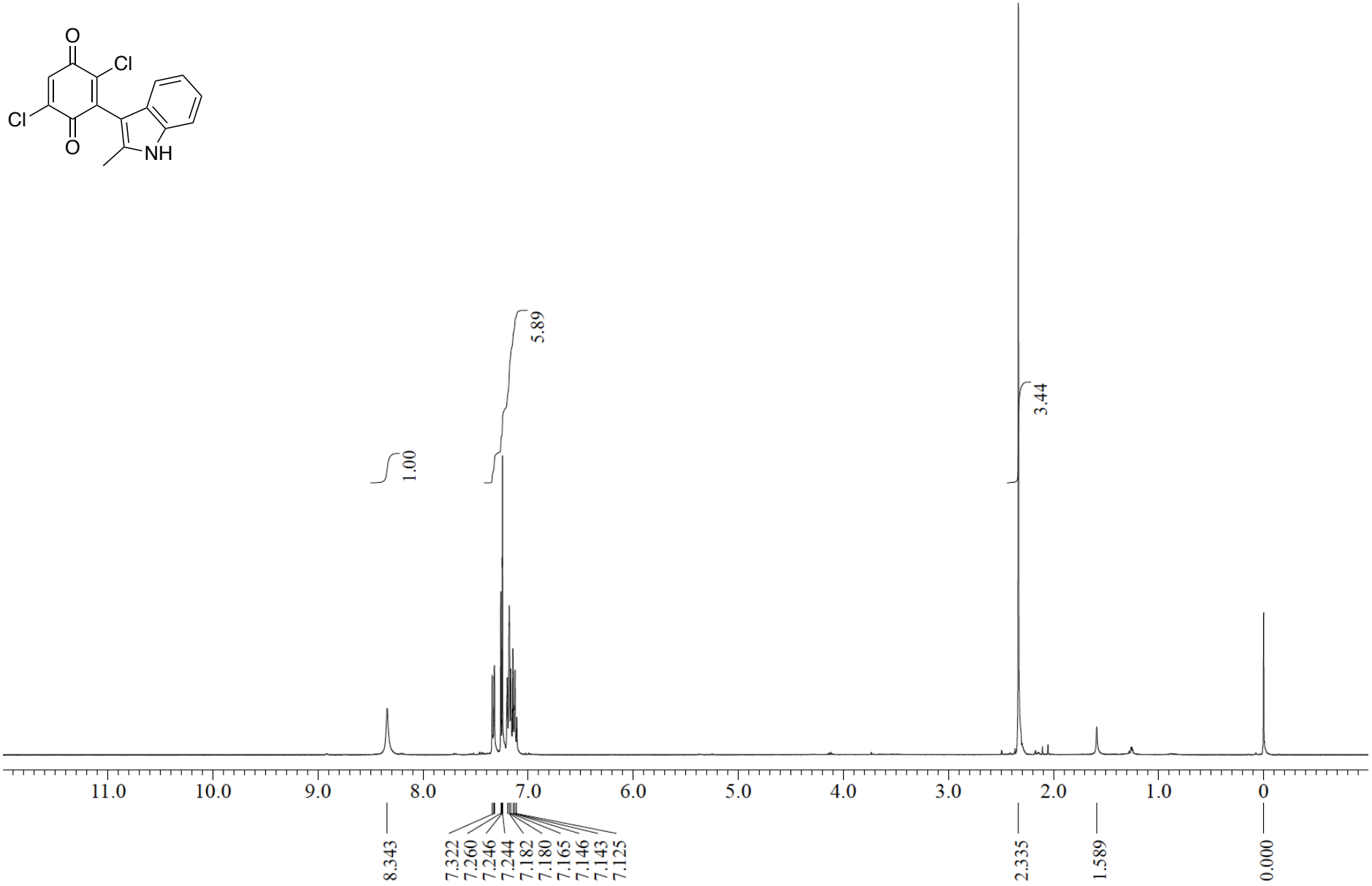
8da, ^{1}H NMR ($CDCl_3$, 400 MHz)



8da, ^{13}C NMR ($CDCl_3$, 100 MHz)



8eh, ^{1}H NMR ($CDCl_3$, 400 MHz)



8eh, ^{13}C NMR ($CDCl_3$, 100 MHz)