Supporting Information

Electrochemical Oxidative Dearomatization of Electron-deficient Phenols Using Br^+/Br^- Catalysis

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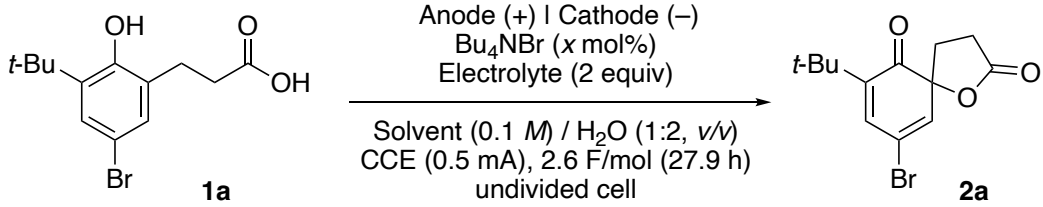
Materials and Methods

Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. ^{1}H NMR spectra were measured on a JEOL ECS-400 (400 MHz) at ambient temperature. Chemical shifts are reported in ppm from Me_4Si resonance (0.00 ppm; $CDCl_3$) as internal standard. Data were recorded as follows: the chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; quin = quintet; sept = septet; m = multiplet; brs = broad singlet), coupling constant (Hz), and integration. ^{13}C NMR spectra were measured on a JEOL ECS-400 (100 MHz) spectrometer at ambient temperature. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$: 77.16 ppm, C_6D_6: 128.06 ppm). Chemical shifts were recorded in ppm from the solvent resonance employed as the external standard ($CFCl_3$ at 0 ppm). High-resolution mass spectral analysis (HRMS) was performed at Chemical Instrument Center, Nagoya University [JEOL JMS-T100TD (DART), Bruker compact (ESI)]. For thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 F_{254} 0.25 mm) were used. The products were purified by column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84).

In experiments that required dry solvents, toluene, benzene, diethyl ether (Et_2O), tetrahydrofuran (THF), and dichloromethane (CH_2Cl_2) were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. as the “anhydrous” and stored over molecular sieves 4A. Other solvents were purchased from Aldrich Chemical Co., Inc., FUJIFILM Wako Pure Chemical Industries, Ltd., or Tokyo Chemical Industry Co., Ltd. and used without further purification. Tetrabutylammonium bromide (Bu_4NBr) and $NaBF_4$ were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. and used without further purification. Other simple chemicals were analytical-grade and obtained commercially and used without further purification.

Additional Information

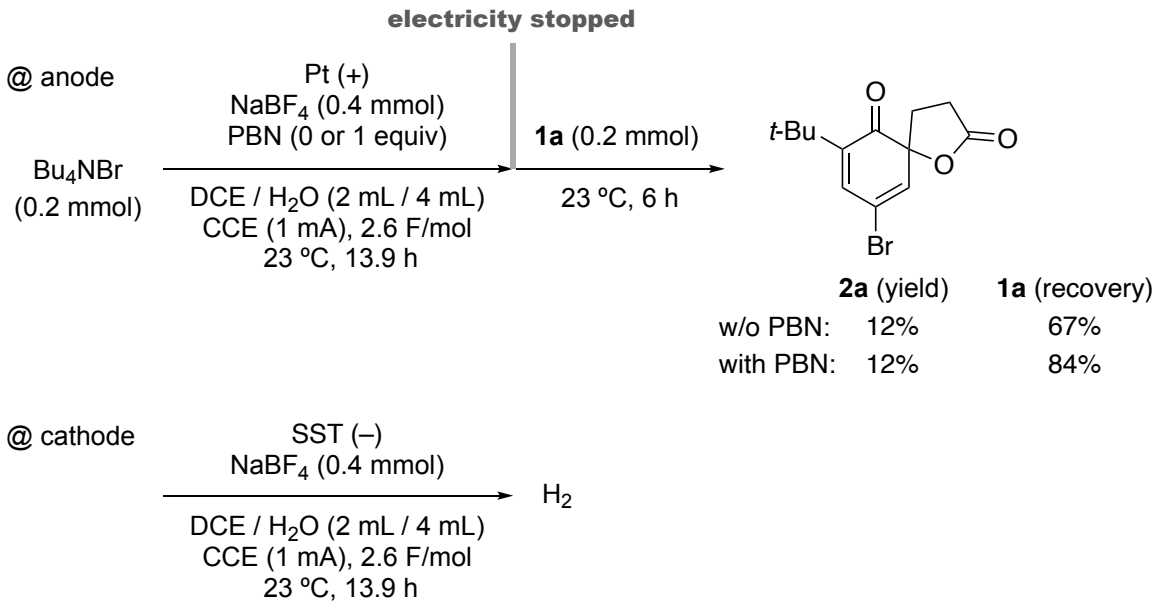
Table S1. Full Data for Electrooxidative Dearomative Spirolactonization of **1a**[a]



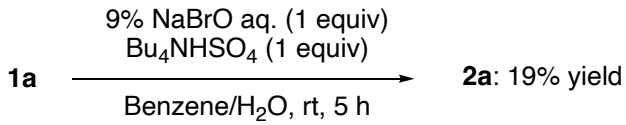
entry	*x* (mol%)	*T* (ºC)	Anode	Cathode	Electrolyte	Solvent	**1a**, Conv. (%)[b]	**2a**, Yield (%)[b]
1	20	25	Pt	SST	$NaBF_4$	DCE	84	72
2[c]	20	25	Pt	SST	$NaBF_4$	DCE	73	60
3	20	5	Pt	SST	$NaBF_4$	DCE	78	71
4	40	5	Pt	SST	$NaBF_4$	DCE	95	92
5	40	5	Pt	SST	$NaBF_4$	CH_2Cl_2	83	78
6	40	5	Pt	SST	$NaBF_4$	$C_6F_5CF_3$	88	83
7	40	5	Pt	SST	$NaBF_4$	CH_3NO_2	18	5
8[d]	40	5	Pt	SST	$NaBF_4$	DCE	94	92 (92)[e]
9	0[f]	25	Pt	SST	$NaBF_4$	DCE	12[g]	<5
10	40	5	Pt	SST	$NaClO_4$	DCE	>95	91
11	40	5	Pt	SST	$NaPF_6$	DCE	>95	92
12	40	5	Pt	SST	$LiClO_4$	DCE	94	87
13	40	5	Pt	Pt	$NaBF_4$	DCE	>95	85
14[h]	20	25	GC	SST	$NaBF_4$	CH_2Cl_2	>95%	36–75[i]
15[h]	20	25	C	SST	$NaBF_4$	CH_2Cl_2	>95%	32
16[h]	10	25	Pt	SST	$NaBF_4$	CH_2Cl_2	>95%	66

[a] Unless otherwise noted, the reactions were carried out using **1a** (0.2 mmol), Bu_4NBr (*x* mol%), and electrolyte (2.0 equiv) under constant-current electrolysis using an anode (10 mm × 10 mm × 0.2 mm) and a cathode (10 mm × 10 mm × 0.15 mm). The distance between electrodes was 10 mm. [b] Determined by ^1H NMR analysis of the crude product using methyl 3,5-dibromobenzoate as an internal standard. [c] $NaHSO_4$ (2.0 equiv) was used as an additive. [d] CCE (1.0 mA); reaction time: 13.9 h. [e] Isolated yield. [f] Bu_4NPF_6 (20 mol%) was used instead of Bu_4NBr. [g] 6-Bromo-8-(*tert*-butyl)chroman-2-one generated by intramolecular dehydration of **1a** was obtained in 9% as the main side product. [h] Electrooxidation was performed using IKA ElectraSyn 2.0. Reaction conditions: $NaBF_4$ (2.5 equiv), CH_2Cl_2/pH 4.4 buffer (1:2.5, *v*/*v*), CCE (0.5 mA). [i] No reproducible results were obtained. GC: Glassy carbon; C: graphite; SST: Stainless steel.

Ex-cell reaction (in the divided cell, ElectraSyn + Pro Divide)



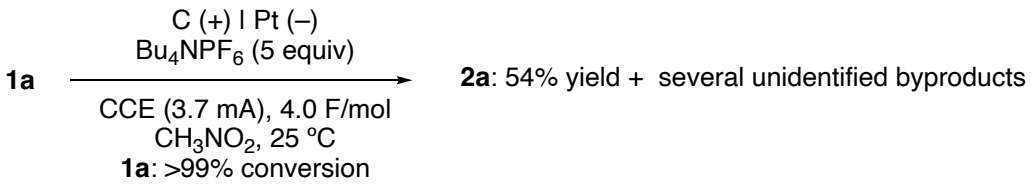
Scheme S1. Control experiment using a divided cell. Initially, we electrochemically oxidized 1 equivalent of Bu_4NBr at the anode, and after 13.9 hours, we stopped the electricity and added substrate **1a** to the reaction mixture. Although the oxidative dearomative spirolactonization proceeded, only 12% of the desired product **2a** was obtained. This result suggests that while Br^+ species were likely generated under electrochemical conditions, they were unstable and decomposed before the substrate was added, which prevented the oxidation reaction from proceeding efficiently. In addition, we conducted the same reaction in the presence of *N*-*tert*-butyl-α-phenylnitrone (PBN), a radical scavenger, which provided the same yield of **2a**, suggesting that a radical mechanism for the oxidative dearomatization is unlikely under these conditions.



Scheme S2. Control experiment using hypobromite as a sole oxidant. The oxidation of **1a** using commercially available 9% aqueous solution of sodium hypobromite in the presence of tetrabutylammonium hydrogen sulfate proceeded to give spirolactone **2a**, suggesting that hypobromite could mediate the present oxidative dearomatization albeit in low yield under stoichiometric conditions.

These control experiments highlight the importance of using a catalytic approach to generate such unstable active species in the reaction system. Catalytic reactions utilizing in situ-generated active species, as opposed to stoichiometric processes, offer improved chemoselectivity and reaction efficiency, which are crucial for achieving the desired transformation. Furthermore, the use of a

biphasic reaction system is particularly advantageous in this context, as it enables the reaction of substrates that might otherwise be incompatible with the electrochemical conditions.



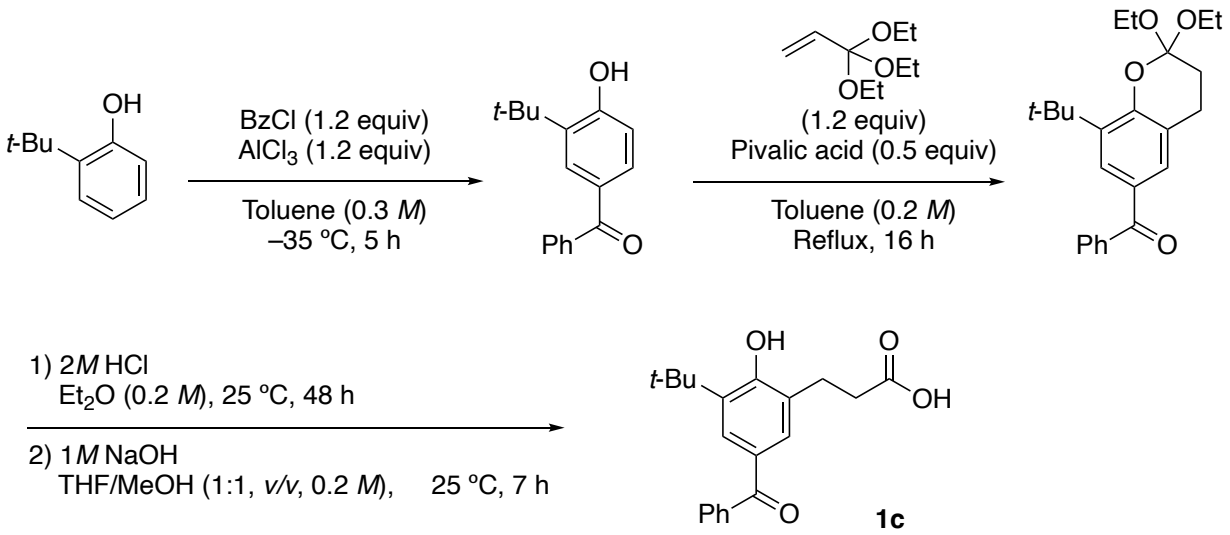
Scheme S3. Direct electrolysis of **1a** under Kalek's conditions (*Synthesis*, 2023, **55**, 4173). Electrooxidation was performed using IKA ElectraSyn 2.0. Although the reaction proceeded and **1a** was completely consumed, the desired product **2a** was obtained in 54% yield, with the remaining material consisting of multiple unidentified compounds. This result clearly demonstrates that direct electrolysis leads to lower selectivity and product yield compared to the indirect electrolysis method using a bromide mediator. It highlights the importance of using a bromide mediator in a biphasic system for achieving chemoselective oxidation, as outlined in our proposed mechanism.

Synthesis and Characterization of Substrates

1a,[1] **1b**,[1] **1d–g**,[1] **1h**,[2] **1i**,[3] **1j**,[1] and **1l**[1] were known compounds and prepared by following the literature procedures.

1m was purchased from Tokyo Chemical Industry Co., Ltd., and used without further purification.

Synthesis of 1c:



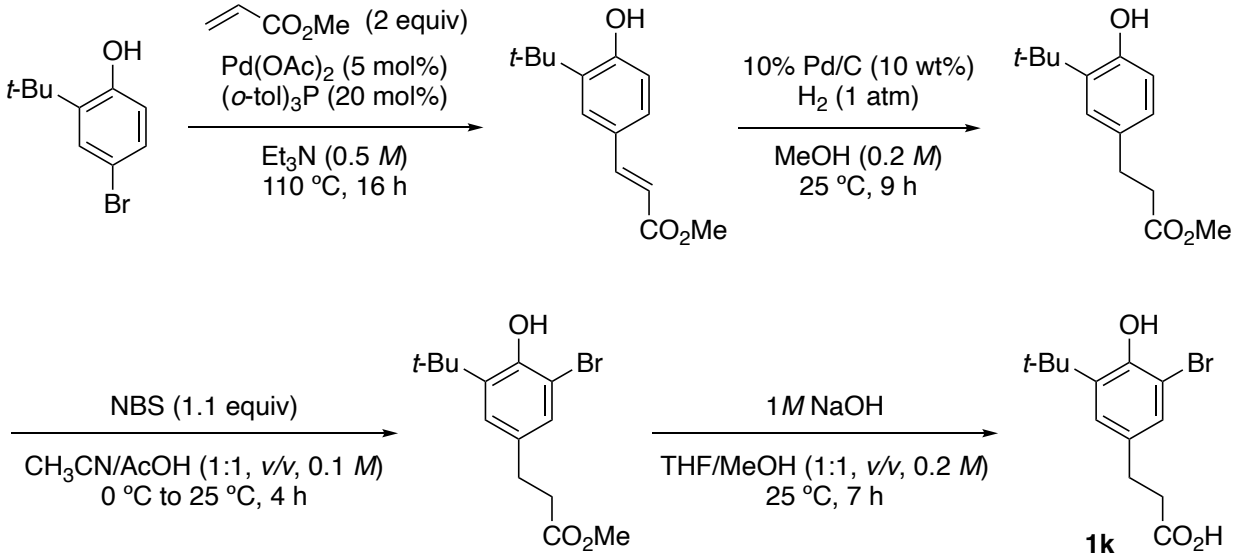
3-(5-benzoyl-3-(*tert*-butyl)-2-hydroxyphenyl)propanoic acid (1c): This step was adopted from the literature and slightly modified.[4] To a stirred solution of anhydrous $AlCl_3$ (FUJIFILM Wako, 5.00 mmol, 0.800 g) in dry toluene (15.0 mL) was added 2-*tert*-butylphenol (TCI, 3.36 mmol, 0.770 g) and stirred at –35 ºC for 1 h. Then, benzoyl chloride (FUJIFILM Wako, 6.00 mmol, 0.691 mL) was added to the flask and the mixture was stirred for 5 h. The reaction was quenched by H_2O (5.00 mL), poured into 1 *M* HCl (15.0 mL), and extracted with EtOAc (three times). The combined organic phase was washed with brine (15.0 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. Reprecipitation of crude mixture from hexane/$CHCl_3$ afforded (3-(*tert*-butyl)-4-hydroxyphenyl)(phenyl)methanone (0.827 g, 3.25 mmol, 65% yield) as a white solid.

To a solution of this phenol and triethyl ortho acrylate[5] (0.906 g, 5.20 mmol) in toluene (16.3 mL) was added pivalic acid (TCI, 0.166 g, 1.63 mmol) and the resulting mixture was refluxed for 16 h. The resulting mixture was poured into 1*M* NaOH (30.0 mL), extracted with Et_2O (twice), and washed with brine. The combined organic layers were dried over anhydrous Na_2SO_4, and solvents were removed in *vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: hexane-EtOAc = 15:1) to give (8-(*tert*-butyl)-2,2-diethoxychroman-6-yl)(phenyl)methanone (0.970 g, 2.54 mmol, 78% yield) as a yellow oil.

This step was adopted from the literature.[1] To a solution of this ortho ester in Et_2O (13.0 mL) was added 2 *M* HCl (6.50 mL) and the resulting mixture was stirred for 48 h at 25 ºC. The resulting

mixture was extracted with Et_2O (twice), and the combined organic layers were washed with brine. The organic layer was dried over anhydrous Na_2SO_4, and solvents were removed in *vacuo*. To a solution of the crude product in THF (6.50 mL) and MeOH (6.50 mL) was added 2*M* NaOH (6.50 mL), and the resulting mixture was stirred for 7 h at 25 ºC. The resulting mixture was poured into 1 *M* HCl, extracted with Et_2O (twice), and washed with brine. The combined organic layers were dried over anhydrous Na_2SO_4, and solvents were removed in *vacuo.* The residue was purified by flash chromatography on silica gel (eluent: hexane–EtOAc = 1:2) to give **1c** (0.406 g, 1.24 mmol) in 49% yield (2 steps) as a white solid. **Mp**: 55.8–63.7 °C (decomposition); **TLC**, R_f = 0.47 (hexane–EtOAc–AcOH = 50:50:1); **IR** (KBr) 3194, 2955, 1707, 1631, 1572 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.93 (br, 1H), 7.75 (d, *J* = 7.3 Hz, 2H), 7.71 (d, *J* = 2.3 Hz, 1H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.52–7.46 (m, 3H), 2.95–2.92 (m, 2H), 2.86–2.83 (m, 2H), 1.41 (s, 9H); **^{13}C NMR** (CD_3OD, 400 MHz) δ 198.3, 178.0, 159.9, 139.8, 138.9, 133.1, 132.5, 130.7, 129.8, 129.3, 129.2, 129.2, 36.0, 35.2, 30.0, 26.1; **HRMS** (ESI+) m/z calcd for $[C_{20}H_{23}O_4+H]^+$ 327.1591, found 327.1579.

Synthesis of 1k:



3-(3-bromo-5-(*tert*-butyl)-4-hydroxyphenyl)propanoic acid (1k): This step was adopted from the literature.[6] To a stirred solution of $Pd(OAc)_2$ (TCI, 0.168 mmol, 0.0377 g) and tris(*o*-tolyl)phosphine (FUJIFILM Wako, 0.68 mmol, 0.0205 g) in Et_3N (6.72 mL) were added 2-*tert*-butyl-4-bromophenol (TCI, 3.36 mmol, 0.770 g) and methyl acrylate (FUJIFILM Wako, 6.72 mmol, 0.602 mL). The reaction mixture was heated to 110 °C (oil bath) under a nitrogen atmosphere for 16 h. The reaction was then cooled to room temperature, poured into 1 *M* HCl (15.0 mL), and extracted with Et_2O (twice). The combined organic phase was washed with brine (15.0 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by flash chromatography on silica gel (eluent: hexane-EtOAc = 4:1) to give methyl (*E*)-3-(3-(*tert*-butyl)-4-hydroxyphenyl)acrylate (0.787 g, 3.36 mmol, >99% yield) as a white solid.

To a solution of this olefin in MeOH (16.8 mL) was added 10% Pd/C (TCI, 78.7 mg). The flask containing the mixture was then evacuated and purged with H_2 three times. After stirring for 9 h at 25 ºC, the mixture was filtered through celite with EtOAc, and the crude product was obtained after removing the solvent *in vacuo*. The residue was purified by flash chromatography on silica gel (eluent: hexane–EtOAc = 4:1) to give methyl 3-(3-(*tert*-butyl)-4-hydroxyphenyl)propanoate (0.794 g, 3.36 mmol, >99% yield) as a colorless oil.

To a solution of this methyl ester in CH_3CN (16.8 mL) and AcOH (16.8 mL) under a nitrogen atmosphere was added *N*-bromosuccinimide (FUJIFILM Wako, 0.658 g, 3.70 mmol) at 0 ºC. After stirring for 4 h at 25 ºC, the resulting mixture was quenched by saturated $Na_2S_2O_3$ (10.0 mL) and diluted with water. The aqueous layers were separated and extracted with Et_2O (twice). The combined organic layers were washed with water, saturated $NaHCO_3$ and brine. The organic layer was dried over anhydrous Na_2SO_4; then, the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (eluent: hexane–EtOAc = 5:1) to give methyl 3-(3-bromo-5-(*tert*-butyl)-4-hydroxyphenyl)propanoate (0.964 g, 3.06 mmol, 91% yield) as a white solid.

To a solution of this methyl ester in THF (7.15 mL) and MeOH (7.15 mL) was added 1 *M* NaOH (7.15 mL), and the resulting mixture was stirred at 25 ºC for 7 h. Then, the resulting mixture was diluted with Et_2O and water. The aqueous layer was separated and poured into Et_2O. To the resulting mixture was added 1 *M* HCl until instantaneous precipitation of a white solid was no longer observed. The precipitated white solids immediately dissolved into the ether phase. The aqueous phase was extracted with Et_2O (twice), and the combined organic layers were washed with distilled water. The combined organic layers were dried over anhydrous Na_2SO_4, and solvents were removed *in vacuo* to give **1k** (0.580 g, 1.93 mmol, 63% yield) as a white solid. **Mp**: 86.9–87.9 °C (decomposition); **TLC**, R_f = 0.50 (Hexane–EtOAc–AcOH = 10:10:1); **IR** (KBr) 3426, 2955, 1693, 1160 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.19 (d, *J* = 2.3 Hz, 1H), 7.04 (d, *J* = 1.8 Hz, 1H), 5.70 (s, 1H), 2.86 (t, *J* = 7.8 Hz, 2H), 2.66–2.62 (m, 2H), 1.38 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 178.8, 149.0, 137.7, 132.7, 129.1, 126.8, 112.2, 35.9, 35.5, 29.9, 29.4; **HRMS** (ESI–) m/z calcd for $[C_{13}H_{17}{}^{79}BrO_3–H]^-$ /$[C_{13}H_{17}{}^{81}BrO_3–H]^-$ 299.0288/301.0269, found 209.0277/301.0257.

Procedures for Electrolysis and Characterization of Products

General for Electrolysis

Electrolysis was carried out using a Pt plate anode (10 mm × 10 mm × 0.2 mm) and an SST cathode (10 mm × 10 mm × 0.15 mm) connected to Pt wire (diameter: 0.50 mm) (Figure S1 (a)). The electrochemical reactions were performed in a 10 mL vial equipped with the two electrodes (the distance between the electrodes: ca. 10 mm) (Figure S1 (b)). The two electrodes were connected to a DC power supply (KIKUSUI PMX350-0.2A) and an ammeter (Colluck PM-128E). The reactions were carried out in a cool bath stirrer (Nissin SWC L-20) (Figure S1 (c) and (d)).

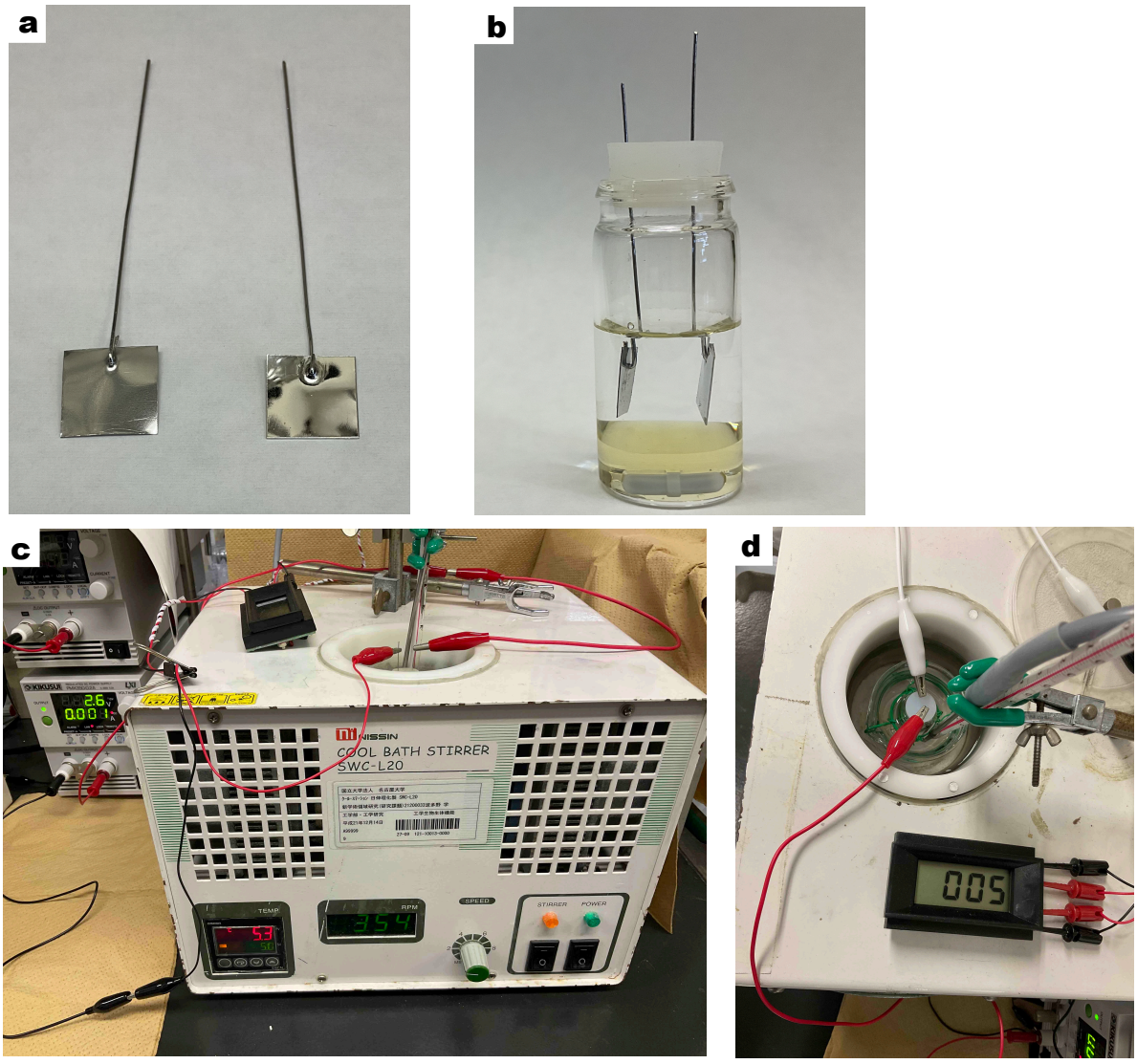
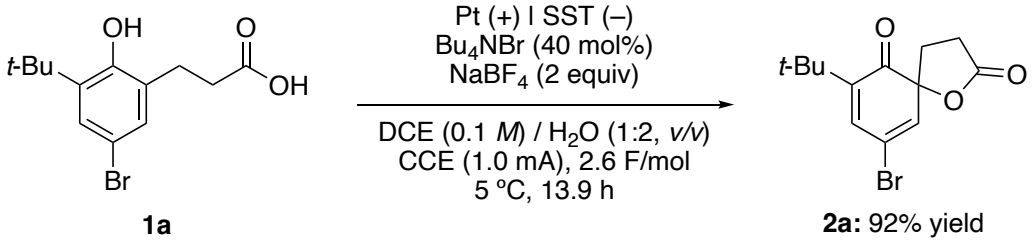


Figure S1. (a) Electrodes (right: Pt, left: SST). (b) A 10 mL vial is equipped with electrodes and charged with the reaction mixture. (c, d) Electrolysis system and reaction in a cool bath stirrer.

Electrooxidative Dearomative Cyclization of Arenol Derivatives

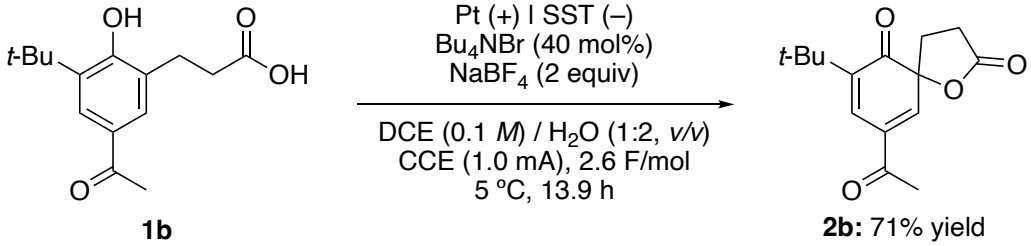


1a **2a:** 92% yield

Representative Example: The electrooxidative spirocyclization was carried out in a 10 ml vial equipped with a Pt plate anode, and a SST plate cathode. A 10 mL vial was charged with a solution of **1a** (0.0602 g, 0.200 mmol) and Bu_4NBr (0.0258 g, 0.0800 mmol, 40 mol%) in dichloroethane (2.00 mL) and a solution of $NaBF_4$ (0.0439 g, 0.400 mmol) in H_2O (4.00 mL). A constant current (1.0 mA, 2.6 F/mol, 13.9 h) was supplied at 5 °C with magnetic stirring (350 rpm). The resulting mixture was extracted with ethyl acetate (5 times). The combined organic phase was dried over Na_2SO_4, and concentrated under reduced pressure (bath temperature: 25 ºC). The residue was purified by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 4:1) to give **2a** (0.0552 g, 0.184 mmol) in 92% yield as a yellow solid.

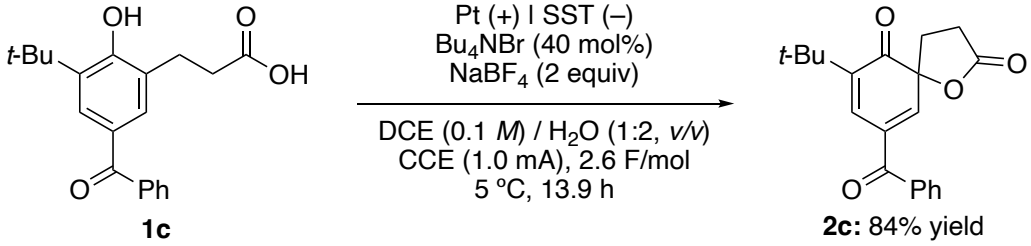
Scale-up (1.00 mmol scale) procedure: The electrooxidative spirocyclization was carried out in a 15 ml vial equipped with a Pt plate anode (10 mm × 15 mm × 0.2 mm), and a SST plate cathode (10 mm × 15 mm × 0.15 mm). A 15 mL vial was charged with a solution of **1a** (0.301 g, 1.00 mmol) and Bu_4NBr (0.129 g, 0.400 mmol, 40 mol%) in dichloroethane (5.00 mL) and a solution of $NaBF_4$ (0.0878 g, 0.800 mmol) in H_2O (8.00 mL). A constant current (1.5 mA, 2.6 F/mol, 46.5 h) was supplied at 5 °C with magnetic stirring (350 rpm). The resulting mixture was extracted with ethyl acetate (5 times). The combined organic phase was dried over Na_2SO_4, and concentrated under reduced pressure (bath temperature: 25 ºC). The residue was purified by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 4:1) to give **2a** (0.298 g, 0.996 mmol) in >99% yield as a yellow solid.

9-Bromo-7-(*tert*-butyl)-1-oxaspiro[4.5]deca-7,9-diene-2,6-dione (2a):[1] **TLC**, R_f = 0.49 (hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz)δ 6.75 (d, J = 2.7 Hz, 1H), 6.54 (d, J = 2.3 Hz, 1H), 2.81–2.72 (m, 1H), 2.55 (m, 1H), 2.42–2.36 (m, 1H), 2.15–2.06 (m, 1H), 1.23 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.5, 175.8, 145.3, 139.4, 136.2, 118.0, 86.1, 34.8, 30.0, 29.0, 25.8.



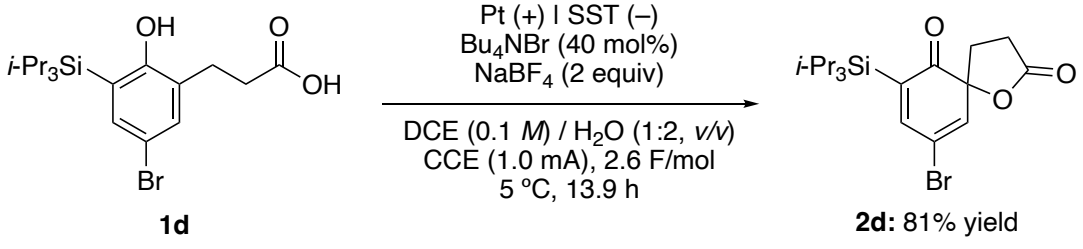
1b **2b:** 71% yield

9-Acetyl-7-(*tert*-butyl)-1-oxaspiro[4.5]deca-7,9-diene-2,6-dione (2b):[1] 0.0372 g, 0.142 mmol, 71% yield. This compound was purified by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 2:1). Yellow solid. **TLC**, R_f = 0.58 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz)δ 7.40 (d, *J* = 2.1 Hz, 1H), 7.10 (d, *J* = 1.8 Hz, 1H), 2.84–2.74 (m, 1H), 2.58 (m, 1H), 2.45 (s, 3H), 2.46–2.39 (m, 3H), 2.20–2.11 (m, 1H), 1.25 (s, 9H); **^{13}C NMR** (C_6D_6, 100 MHz) δ 197.6, 194.3, 175.3, 143.9, 143.5, 133.5, 131.8, 84.7, 34.7, 29.2, 28.9, 25.2, 24.8.



1c **2c:** 84% yield

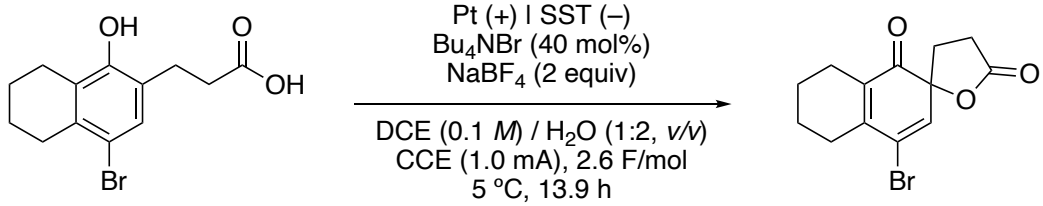
9-Benzoyl-7-(*tert*-butyl)-1-oxaspiro[4.5]deca-7,9-diene-2,6-dione (2c): 0.0543 g, 0.167 mmol, 84% yield. This compound was purified by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 4:1). Yellow solid. **Mp**: 137–143 °C (decomposition); **TLC**, R_f = 0.22 (Hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ7.80–7.77 (m, 2H), 7.65–7.61 (m, 1H), 7.53–7.49 (m, 2H), 7.37 (d, *J* = 2.3 Hz, 1H), 6.79 (d, *J* = 2.3 Hz, 1H), 2.84–2.74 (m, 1H), 2.57–2.41 (m, 2H), 2.15–2.06 (m, 1H), 1.29 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 197.3, 193.5, 175.8, 144.9, 144.1, 135.8, 133.8, 133.5, 133.4, 129.7, 128.9, 85.0, 35.0, 29.8, 29.1, 25.4.



1d **2d:** 81% yield

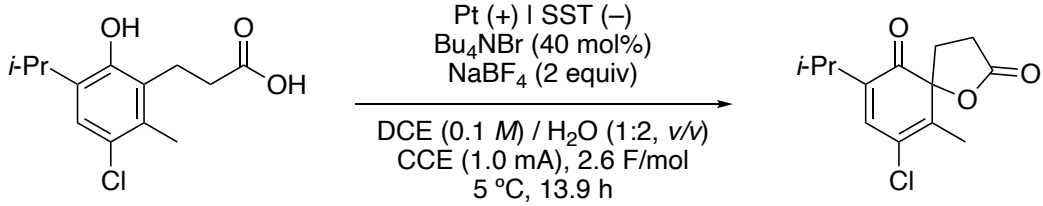
9-Bromo-7-(triisopropylsilyl)-1-oxaspiro[4.5]deca-7,9-diene-2,6-dione (2d):[1] 0.0647 g, 0.162 mmol, 81% yield. This compound was purified by flash column chromatography on silica gel

(KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 4:1). Yellow solid. **TLC**, R_f = 0.62 (Hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.06 (t, *J* = 2.3 Hz, 1H), 6.63 (t, *J* = 2.1 Hz, 1H), 2.78–2.69 (m, 1H), 2.57–2.51 (m, 1H), 2.47–2.42 (m, 1H), 2.20–2.11 (m, 1H), 1.39–1.31 (sept, *J* = 7.3, 3H), 1.06–1.03 (m, 18H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 199.8, 175.6, 153.3, 138.3, 136.7, 118.5, 85.6, 30.4, 25.7, 18.7, 18.7, 11.2.



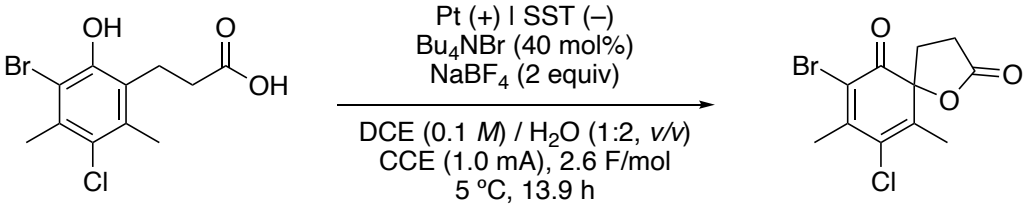
1e **2e:** 81% yield

4'-Bromo-3,4,5',6',7',8'-hexahydro-1'*H*,5*H*-spiro[furan-2,2'-naphthalene]-1',5-dione (2e):[1] 0.0481 g, 0.162 mmol, 81% yield. This compound was purified by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 4:1). Yellow solid. **TLC**, R_f = 0.57 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.62 (s, 1H), 2.94–2.85 (m, 1H), 2.60–2.55 (m, 1H), 2.53–2.24 (m, 5H), 2.19–2.10 (m, 1H), 1.81–1.56 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.6, 176.1, 148.2, 135.8, 131.7, 124.2, 83.5, 31.3, 31.0, 26.4, 22.5, 22.2, 21.0.



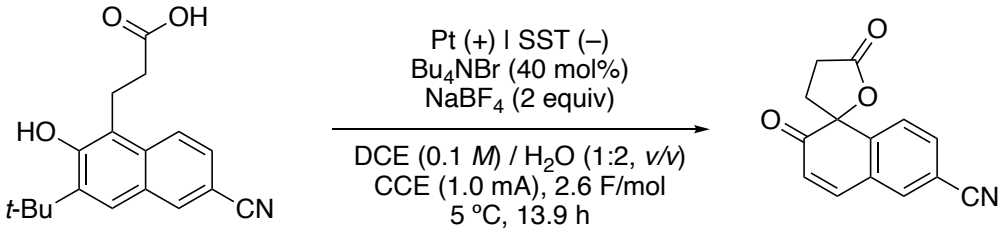
1f **2f:** 92% yield

9-Chloro-7-isopropyl-10-methyl-1-oxaspiro[4.5]deca-7,9-diene-2,6-dione (2f):[1] 0.0472 g, 0.185 mmol, 92% yield. This compound was purified by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 4:1). Yellow solid. **TLC**, R_f = 0.51 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.68 (s, 1H), 2.93–2.86 (m, 1H), 2.82–2.73 (m, 1H), 2.56 (ddd, *J* = 17.9, 9.6, 1.8 Hz), 2.32–2.26 (m, 1H), 2.14–2.05 (m, 1H), 2.00 (s, 3H), 1.10 (d, *J* = 6.9, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 197.5, 176.1, 140.8, 139.3, 138.3, 125.2, 87.6, 29.3, 26.5, 25.7, 21.4, 21.3, 14.8



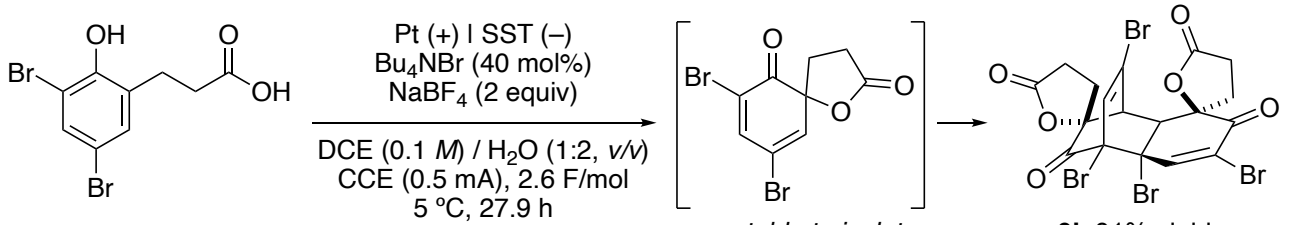
1g **2g:** 93% yield

7-Bromo-9-chloro-8,10-dimethyl-1-oxaspiro[4.5]deca-7,9-diene-2,6-dione (2g):[1] 0.0568 g, 0.186 mmol, 93% yield. This compound was purified by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 4:1). Yellow solid. **TLC**, R_f = 0.58 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.90–2.80 (m, 1H), 2.62–2.57 (m, 1H), 2.49 (s, 3H), 2.39–2.33 (m, 1H), 2.20–2.11 (m, 1H), 2.06 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.9, 175.5, 152.8, 141.7, 127.5, 119.6, 87.0, 30.4, 25.6, 24.2, 15.9.



1h **2h:** 60% yield

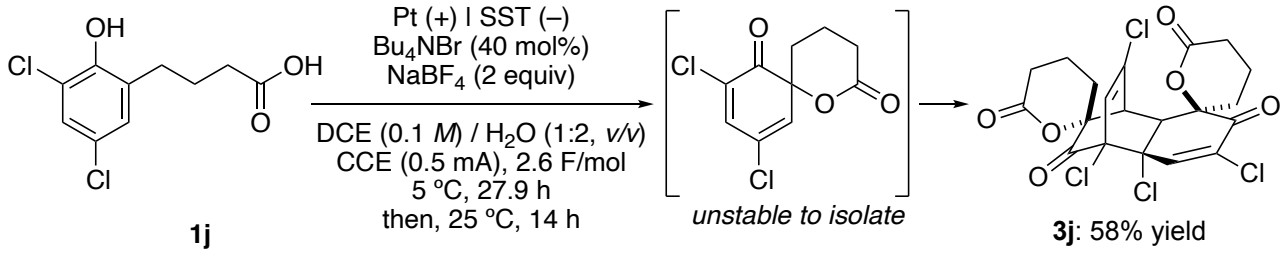
2',5-Dioxo-4,5-dihydro-2'*H*,3*H*-spiro[furan-2,1'-naphthalene]-6'-carbonitrile (2h):[1,2] 0.0289 g, 0.121 mmol, 60% yield. This compound was purified by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 1:1). White solid. **TLC**, R_f = 0.30 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.77 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 1.4 Hz, 1H), 7.49 (d, *J* = 9.6 Hz, 1H), 6.32 (d, *J* = 9.6 Hz, 1H), 2.90–2.80 (m, 1H), 2.73–2.64 (m, 2H), 2.16–2.08 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.0, 175.7, 145.2, 143.6, 134.2, 132.8, 130.4, 126.7, 124.7, 117.5, 113.6, 85.4, 35.6, 26.3.



1i *unstable to isolate* **3i**: 81% yield

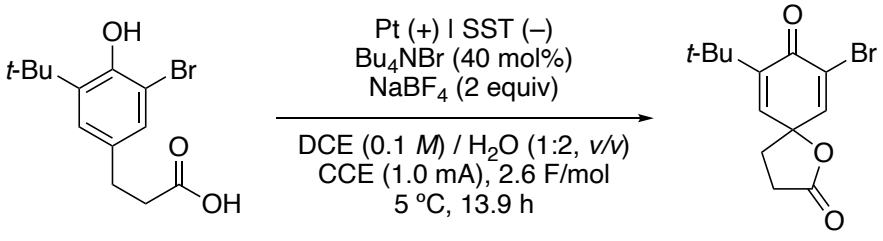
(1'*S*,2*R*,4'*R*,4a'*R*,10'*R*)-2',4',4a',6'-Tetrabromo-1',3,3'',4,4',4a',4'',8a'-octahydro-5*H*,5''*H*,7'*H*-dispiro[furan-2,8'-[1,4]ethanonaphthalene-10',2''-furan]-5,5'',7',9'-tetraone (3i):[1,3] Constant current electrolysis (0.5 mA, 27.9 h). 0.0521 g, 0.0810 mmol, 81% yield. This compound was purified

by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 4:1). Yellow solid. **TLC**, R_f = 0.57 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.33 (s, 1H), 6.53 (d, *J* = 2.7 Hz, 1H), 4.01 (s, 1H), 3.76 (s, 1H), 3.00–2.91 (m, 1H), 2.79–2.52 (m, 5H), 2.47–2.40 (m, 1H), 2.33–2.25 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ193.4, 185.5, 174.3, 173.5, 144.5, 133.3, 124.0, 121.9, 83.4, 80.6, 75.9, 61.0, 54.7, 53.0, 35.0, 30.3, 28.2, 27.0.



1j **3j**: 58% yield

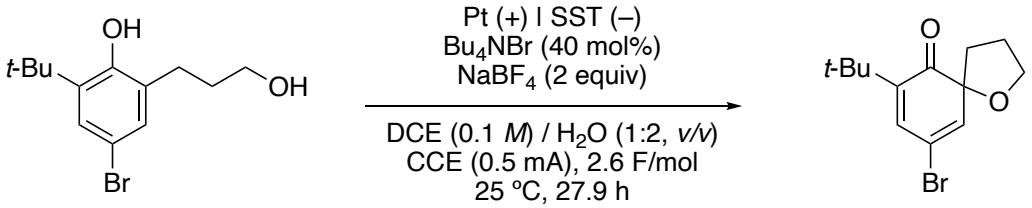
(1'*S*,2*R*,4'*R*,4a'*R*,10'*R*)-2',4',4a',6'-Tetrachloro-1',4,4',4a',4'',5,5'',8a'-octahydro-7'H-dispiro[pyran-2,8'-[1,4]ethanonaphthalene-10',2''-pyran]-6,6'',7',9'(3H,3''H)-tetraone (3j):[1] Constant current electrolysis (0.5 mA, 27.9 h). The reaction mixture was stirring for 14 h at 25 ºC after electrolysis for the completion of (4+2) dimerization. 0.0287 g, 0.0580 mmol, 58% yield. This compound was purified by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 2:1). White solid. **TLC**, R_f = 0.18 (Hexane–EtOAc = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.90 (s, 1H), 6.05 (d, *J* = 2.7 Hz, 1H), 4.03 (s, 1H), 3.87 (t, *J* = 2.3 Hz, 1H), 2.85–2.68 (m, 2H), 2.63–2.50 (m, 3H), 2.21–2.10 (m, 3H), 2.05–1.90 (m, 3H), 1.50–1.43 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 193.1, 187.5, 168.1, 168.0, 138.7, 137.6, 131.5, 128.1, 83.2, 80.2, 79.6, 70.3, 52.0, 50.7, 34.3, 29.4, 29.3, 28.5, 16.6, 16.4.



1k **2k:** >99% yield

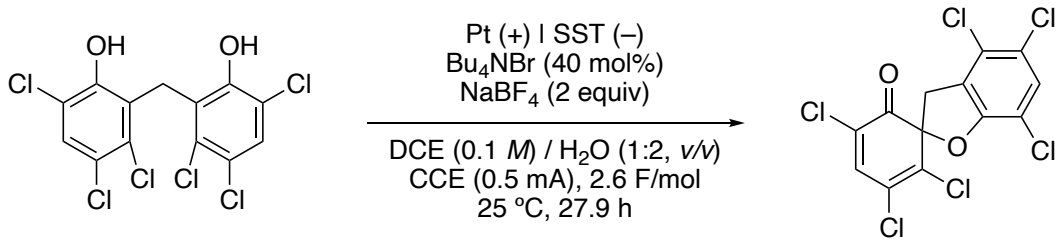
7-Bromo-9-(*tert*-butyl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (2k): 0.0594 g, 0.199 mmol, >99% yield. This compound was purified by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 4:1). Yellow solid. **Mp**: 125–132 °C (decomposition); **TLC**, R_f = 0.32 (Hexane–EtOAc = 4:1); **IR** (KBr) 2960, 1789, 1662, 1173 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.23 (d, *J* = 2.7 Hz, 1H), 6.61 (d, *J* = 3.2 Hz, 1H), 2.80 (t, *J* = 8.2 Hz, 2H), 2.42–2.37 (m, 2H), 1.25 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 177.2, 175.0, 146.1, 144.0,

139.7, 127.7, 80.5, 77.5, 77.1, 76.8, 35.4, 32.4, 29.1, 28.1; **HRMS** (DART+) m/z calcd for $[C_{13}H_{15}{}^{79}BrO_3+H]^+/[C_{13}H_{15}{}^{81}BrO_3+H]^+$ 299.0283/301.0262, found 299.0288/301.0275.



1l **2l:** 47% yield

9-Bromo-7-(*tert*-butyl)-1-oxaspiro[4.5]deca-7,9-dien-6-one (2l):[1] Constant current electrolysis (0.5 mA, 27.9 h) at 25 ºC. 0.0268 g, 0.0940 mmol, 47% yield. This compound was purified by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 3:1). Pale-yellow solid. **TLC**, R_f = 0.45 (Hexane–EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.65 (d, *J* = 2.3 Hz, 1H), 6.49 (d, *J* = 2.7 Hz, 1H), 4.24–4.19 (m, 1H), 4.13–4.07 (m, 1H), 2.21–2.06 (m, 2H), 2.01–1.93 (m, 1H), 1.90–1.84 (m, 1H), 1.21 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 202.0, 145.9, 140.5, 138.4, 115.3, 88.2, 77.5, 77.2, 76.8, 70.9, 35.6, 34.6, 29.2, 24.8.



1m **2m:** 88% yield

2',3',4,5,5',7-Hexachloro-3*H*-spiro[benzofuran-2,1'-cyclohexane]-2',4'-dien-6'-one (2m):[1] Constant current electrolysis (0.5 mA, 27.9 h) at 25 ºC. 0.0713 g, 0.176 mmol, 88% yield. This compound was purified by flash column chromatography on silica gel (KANTO Chemical Co., Inc. 37562-84, eluent: hexane–EtOAc = 4:1). Yellow solid. **TLC**, R_f = 0.58 (Hexane–EtOAc = 2:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.36 (s, 1H), 7.33 (s, 1H), 3.63 (s, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 188.2, 153.7, 140.2, 135.7, 130.5, 129.7, 127.3, 126.1, 126.0, 125.8, 114.1, 88.7, 42.4.

Cyclic Voltammetry

Cyclic Voltammograms (CVs) were recorded on Electrochemical Analyzer (BAS ALS Model 612F). A Pt electrode (diameter: 1.6 mm, BAS), a Ag/Ag+ (Ag wire in 0.01 M $AgNO_3$/0.1 M Bu_4NPF_6/CH_3CN), and a Pt wire electrode were used as working, reference, and counter electrodes, respectively. The working electrode was polished with 5 μm diamond slurry and then with 0.5 μm alumina slurry. After polishing, it was washed with distilled water and acetone. A CH_3CN or CH_3CN/H_2O (v/v =9/1) solution of a sample, including 10 mM of each sample and 0.1 M of Bu_4NPF_6, was prepared as an electrochemical solution. Using the electrodes and the solutions, beaker-typed three-electrode electrochemical cells were constructed and connected with the potentiostat to perform cyclic voltammetry.

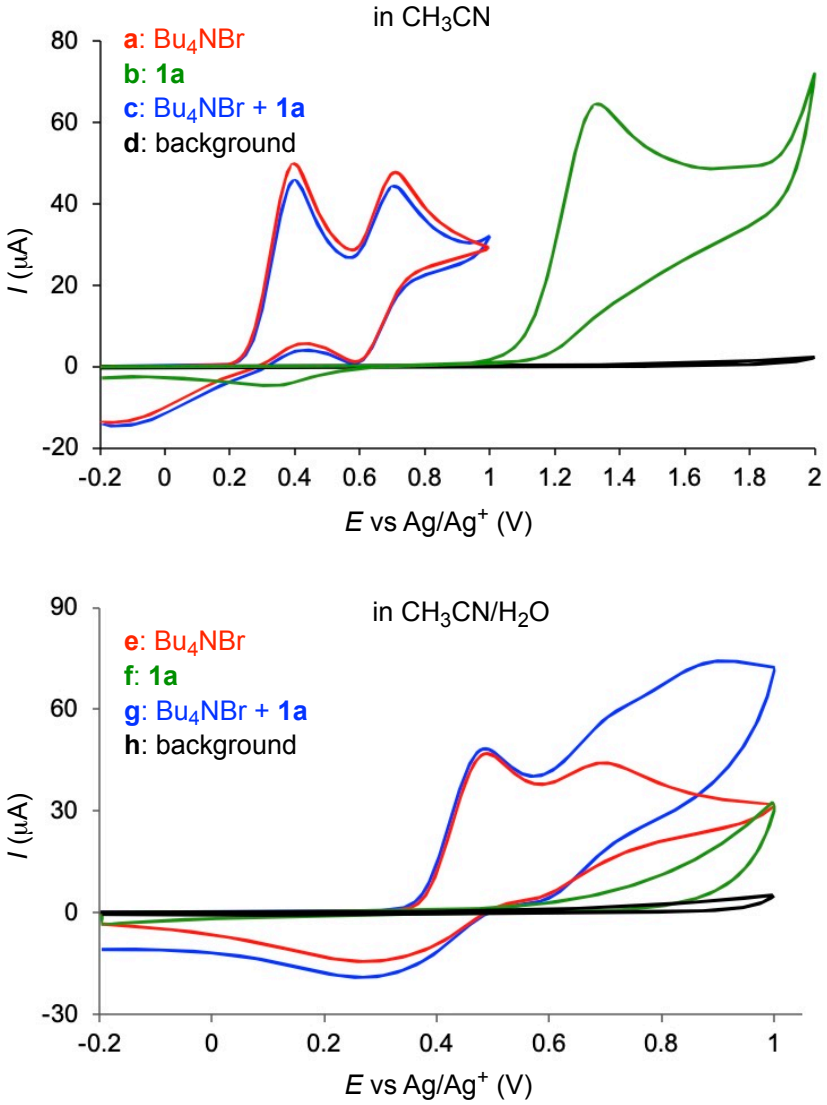


Figure S2. Cyclic voltammograms of Bu_4NBr and **1a** under different conditions. (a–d) CV measurements in CH_3CN: (a) Bu_4NBr (red), (b) **1a** (green), (c) **1a** with Bu_4NBr (blue), and (d) background (black). (e–h) CV measurements in CH_3CN/H_2O (v/v = 9/1): (e) Bu_4NBr (red), (f) **1a** (green), (g) **1a** with Bu_4NBr (blue), and (h) background (black). Scan rate: 100 mV/s.

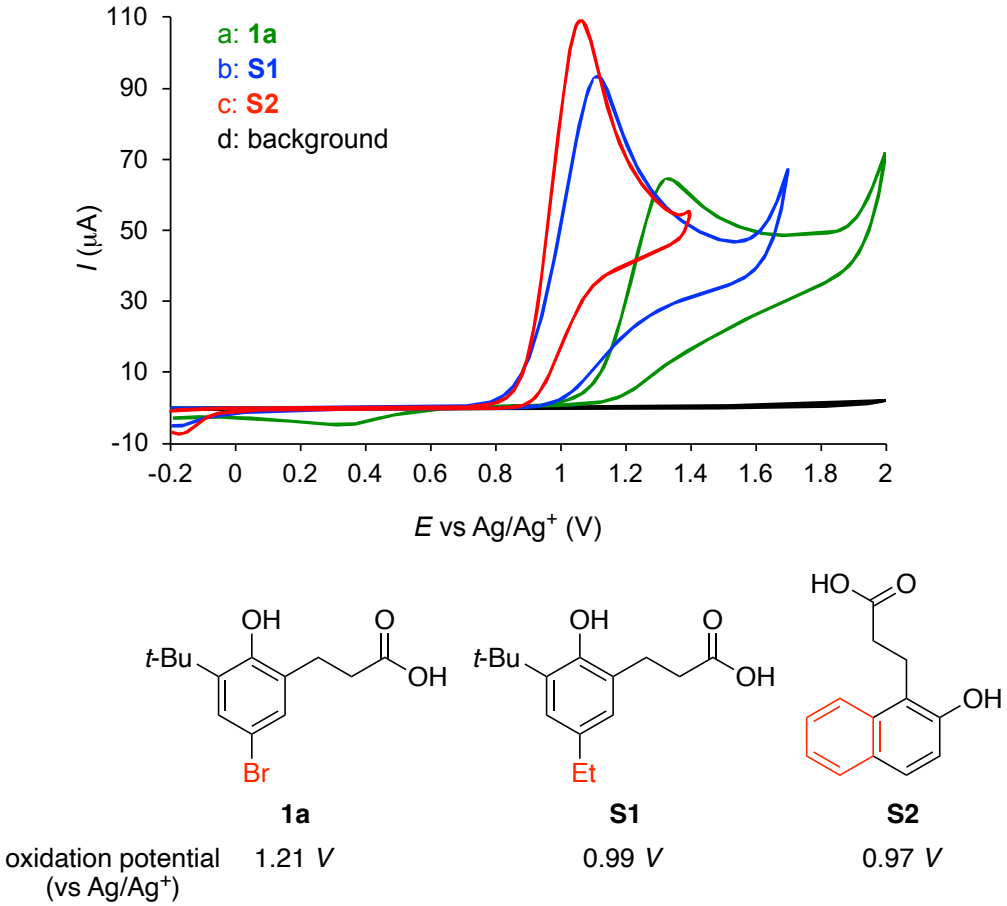


Figure S3. Comparison of CV curves for electron-deficient (**1a**) and electron-rich (**S1** and **S2**) arenols. CV measurements were performed in CH_3CN with a scan rate of 100 mV/s. Traces: (a) **1a** (green), (b) **S1** (blue), (c) **S2** (red), and (d) background.

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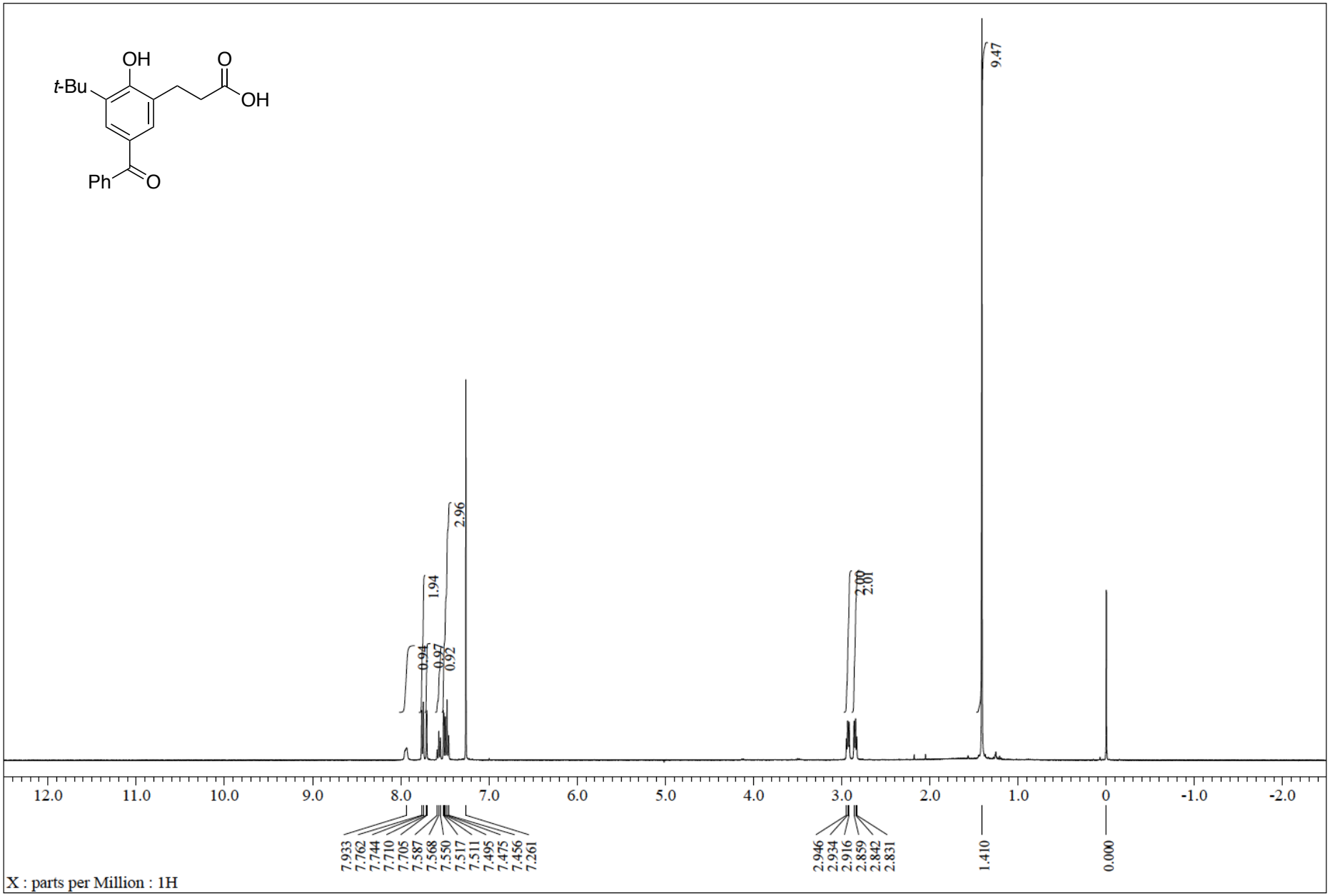
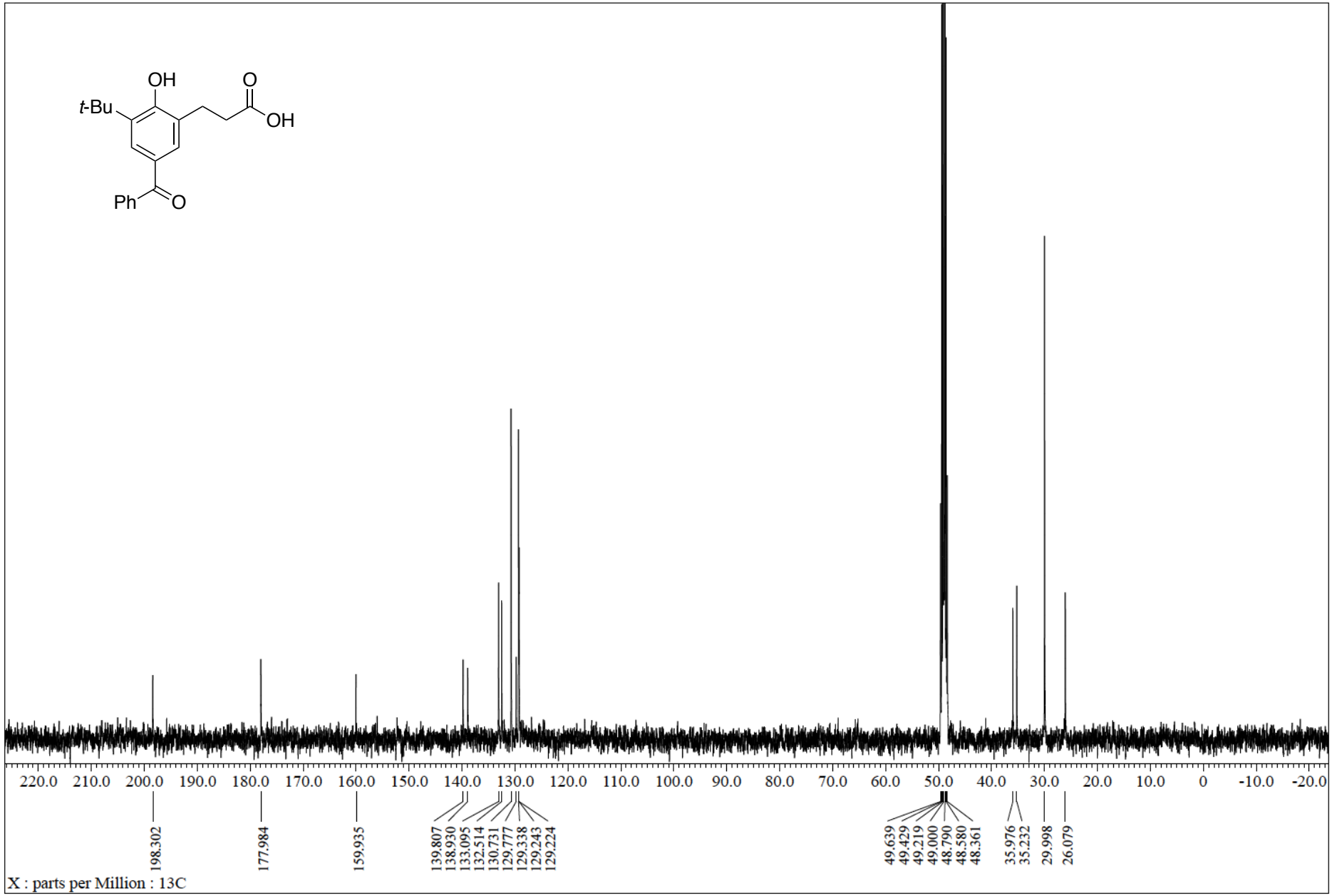
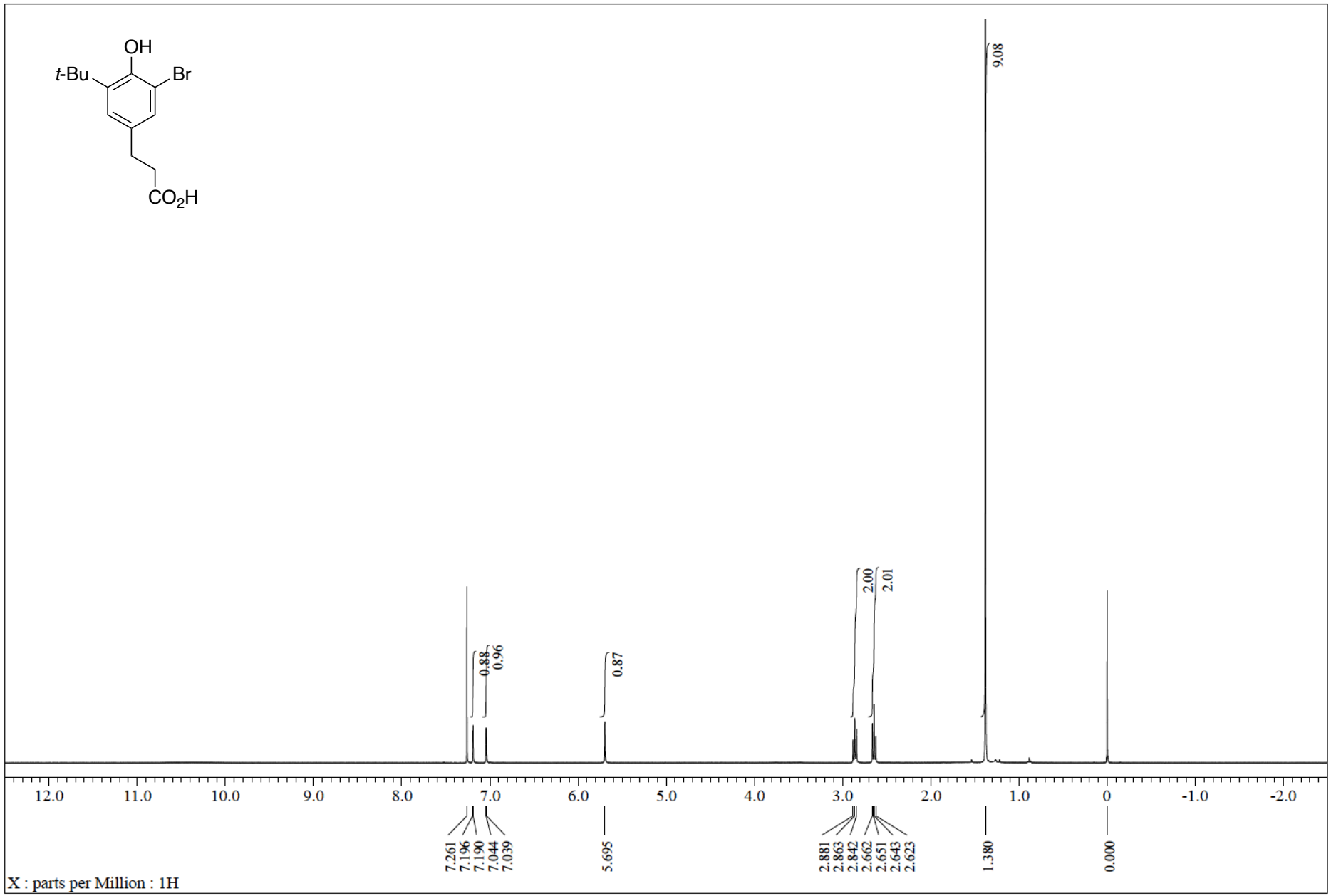
1c, ^{1}H NMR ($CDCl_3$, 400 MHz)



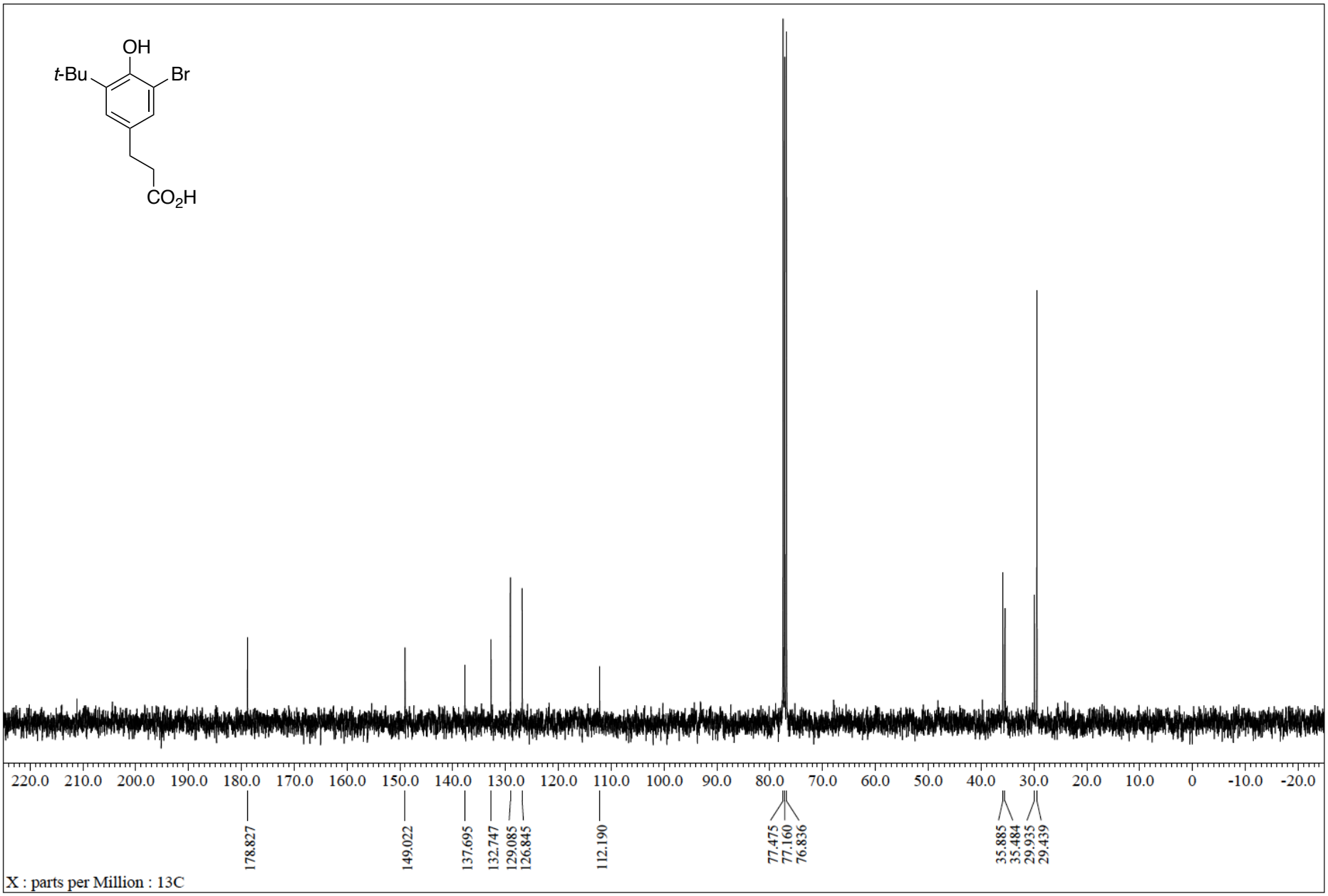
1c, ^{13}C NMR ($CDCl_3$, 100 MHz)



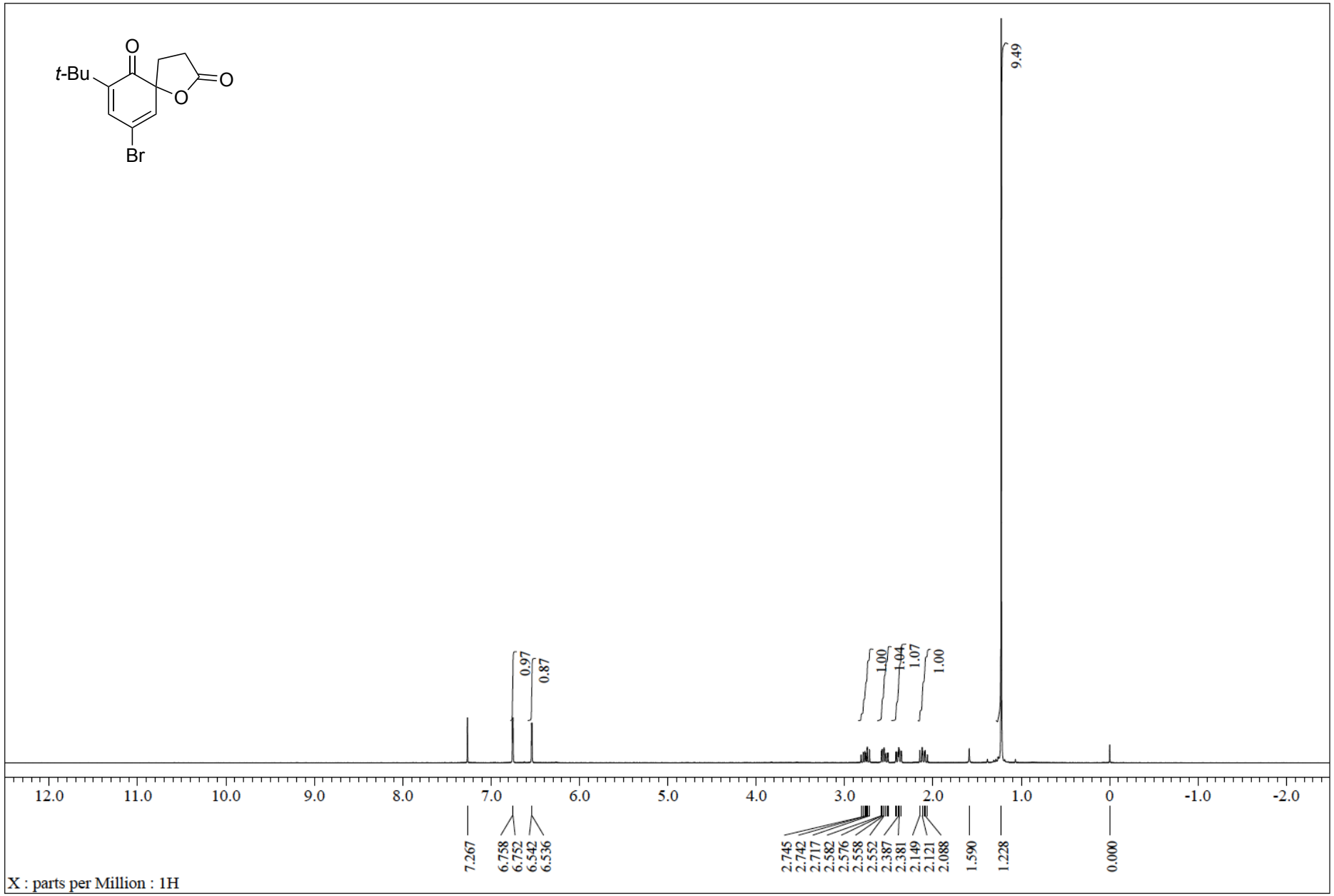
1k, ^{1}H NMR ($CDCl_3$, 400 MHz)



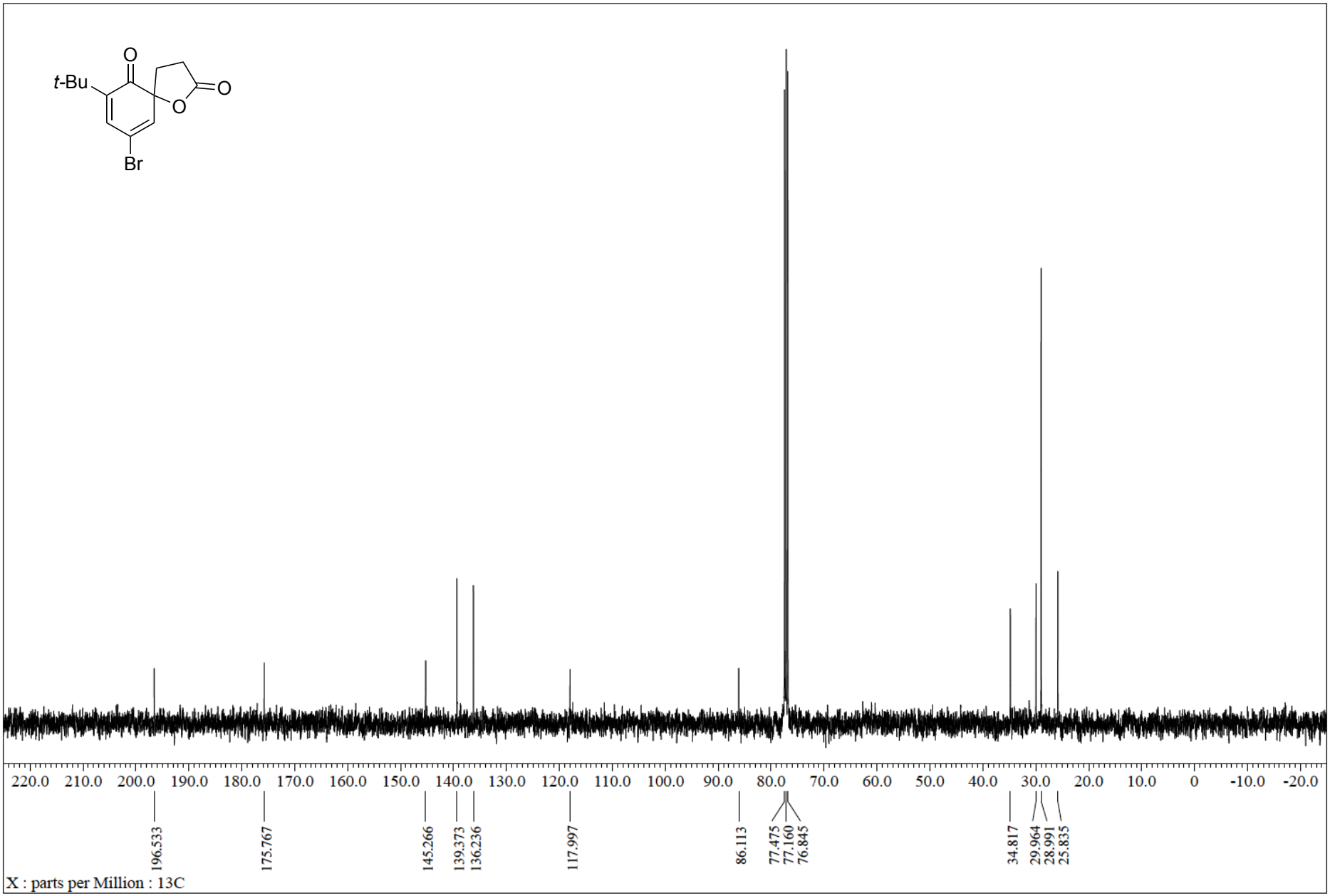
1k, ^{13}C NMR ($CDCl_3$, 100 MHz)



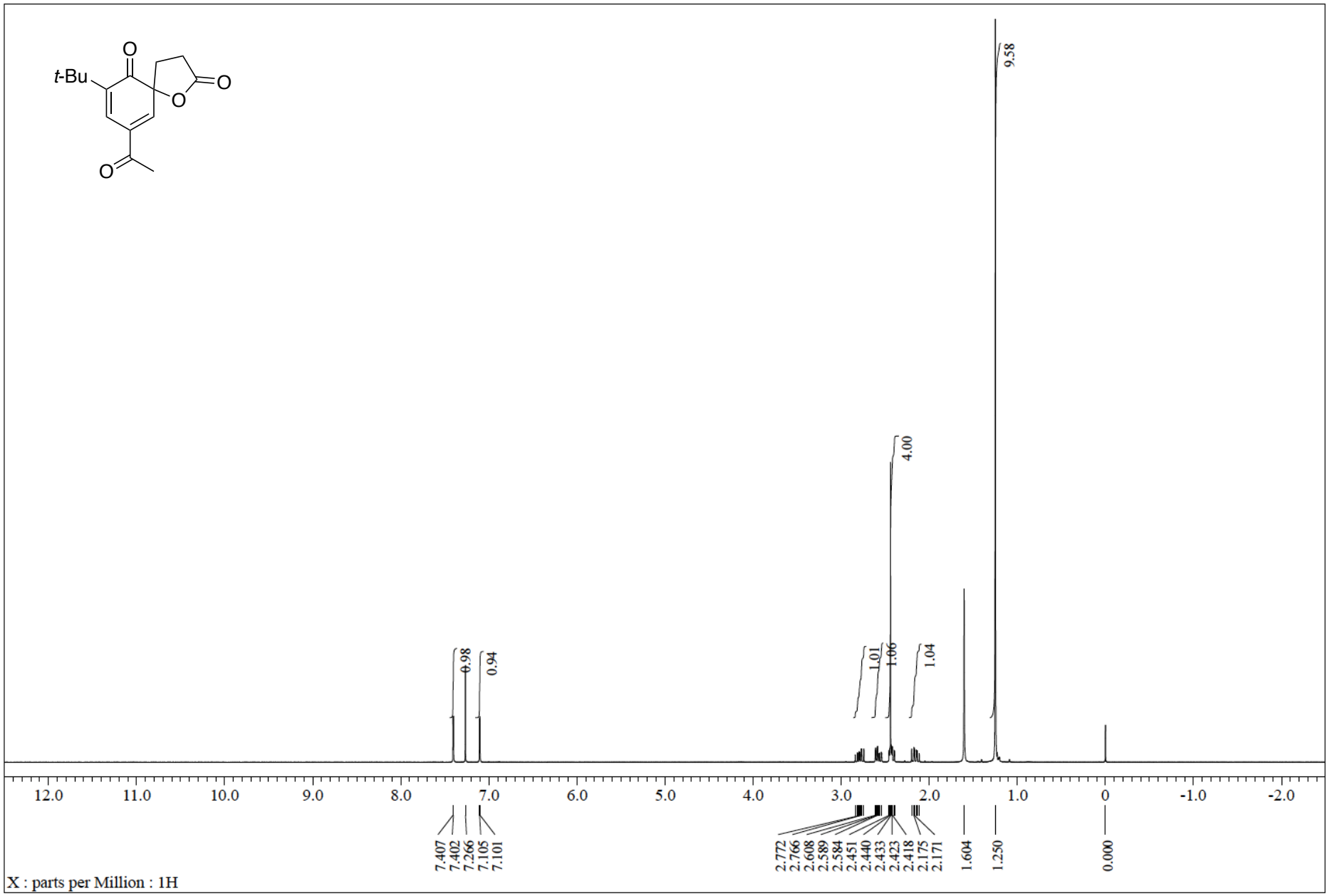
2a, ^{1}H NMR ($CDCl_3$, 400 MHz)



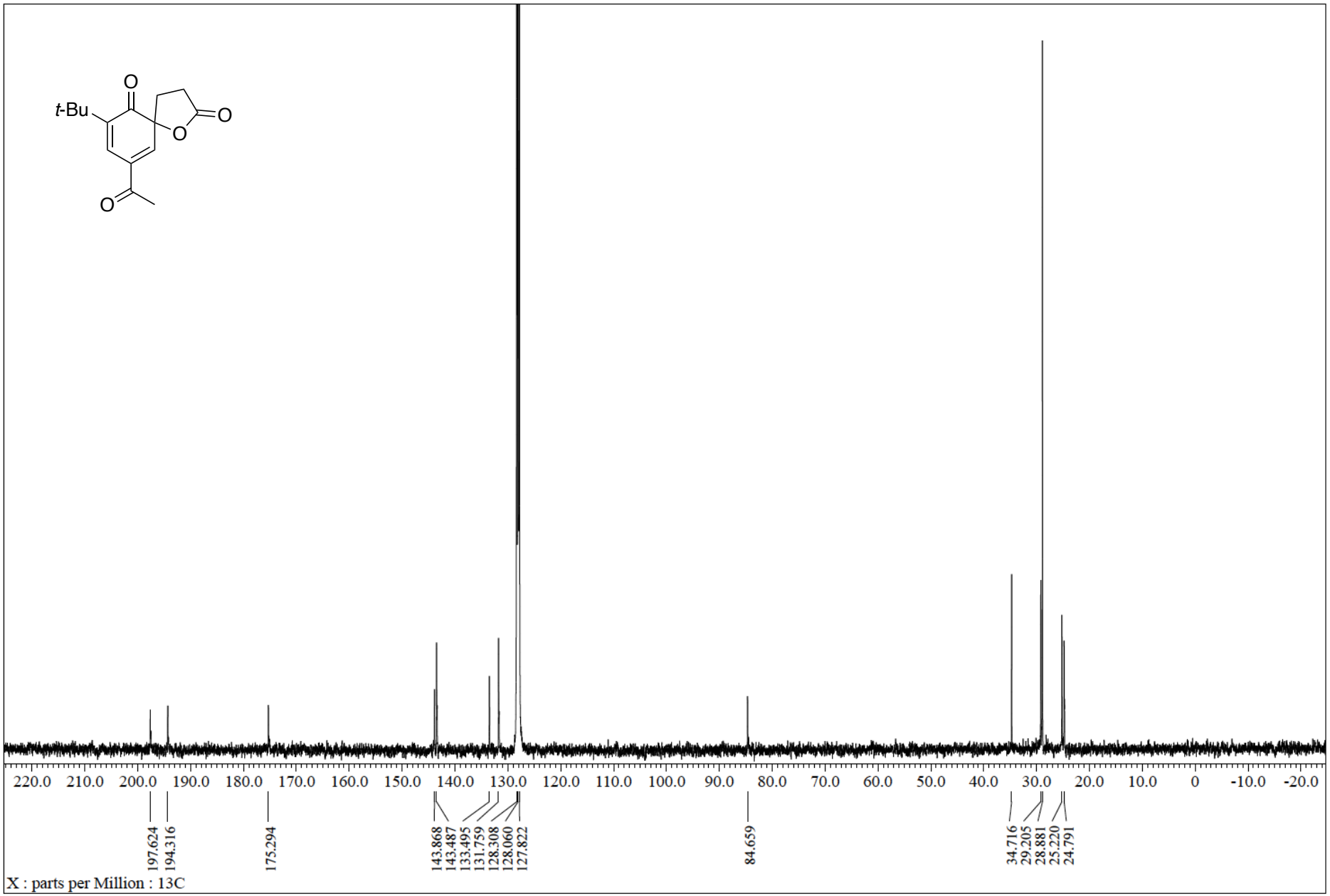
2a, ^{13}C NMR ($CDCl_3$, 100 MHz)



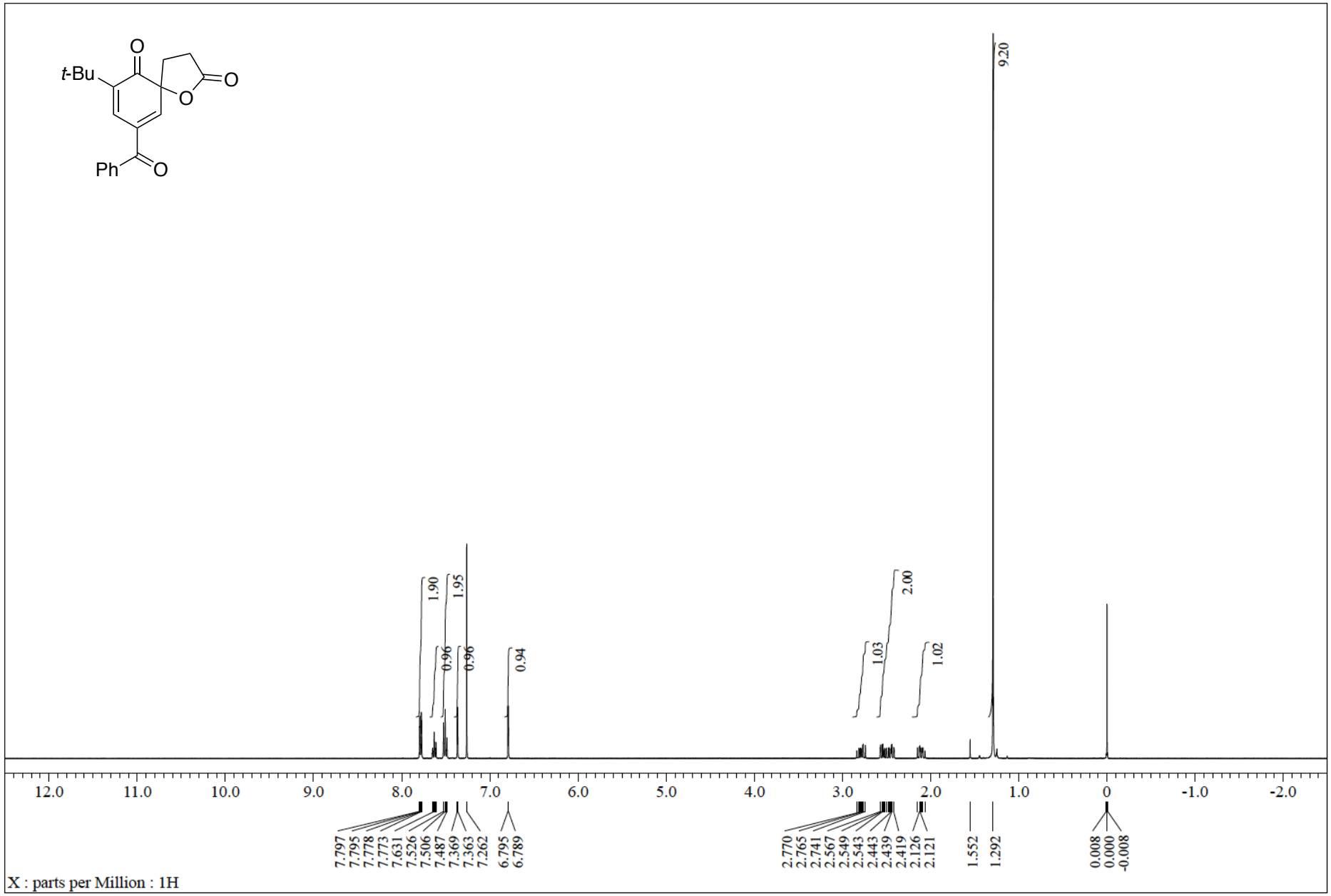
2b, ^{1}H NMR ($CDCl_3$, 400 MHz)



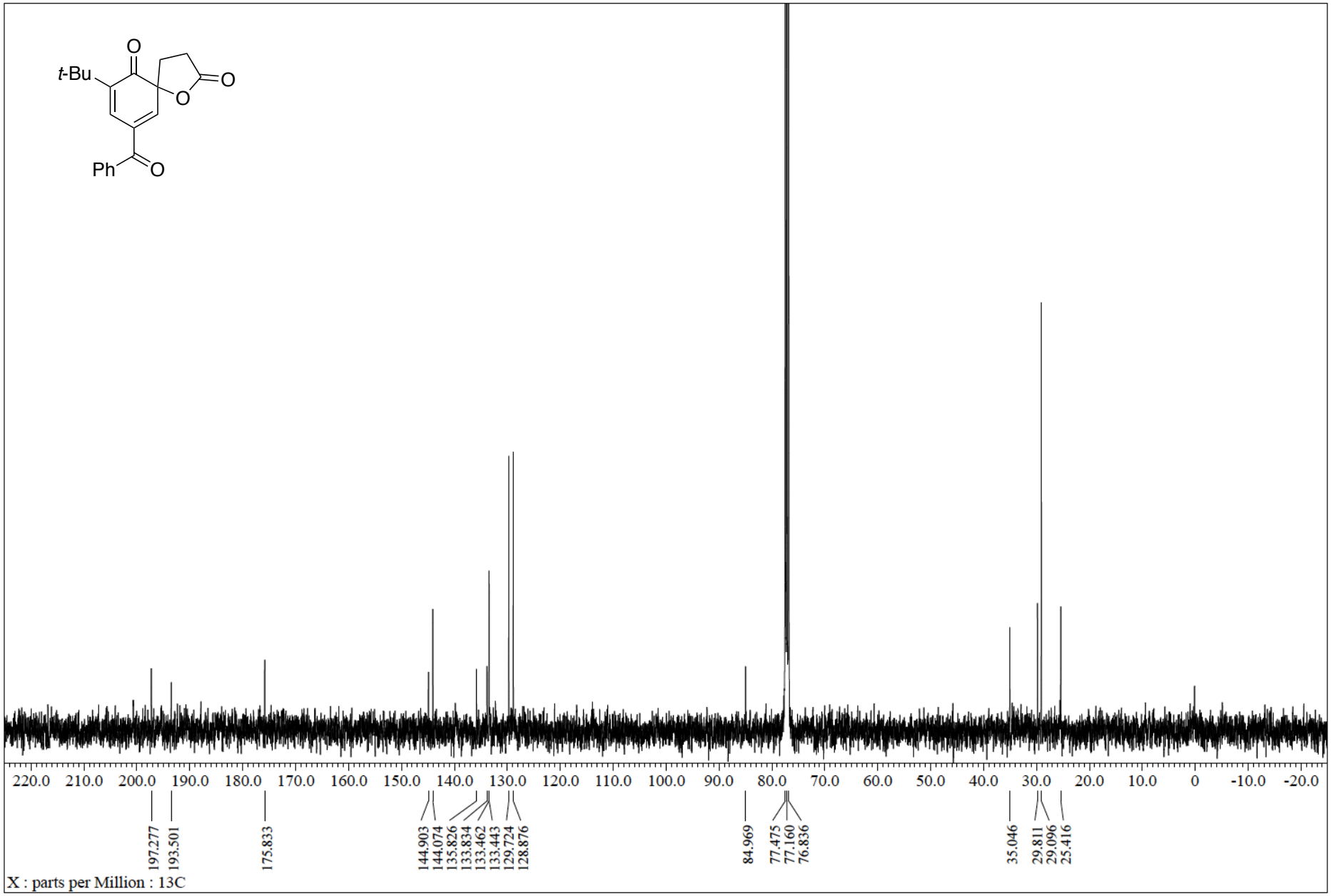
2b, ^{13}C NMR (C_6D_6, 100 MHz)



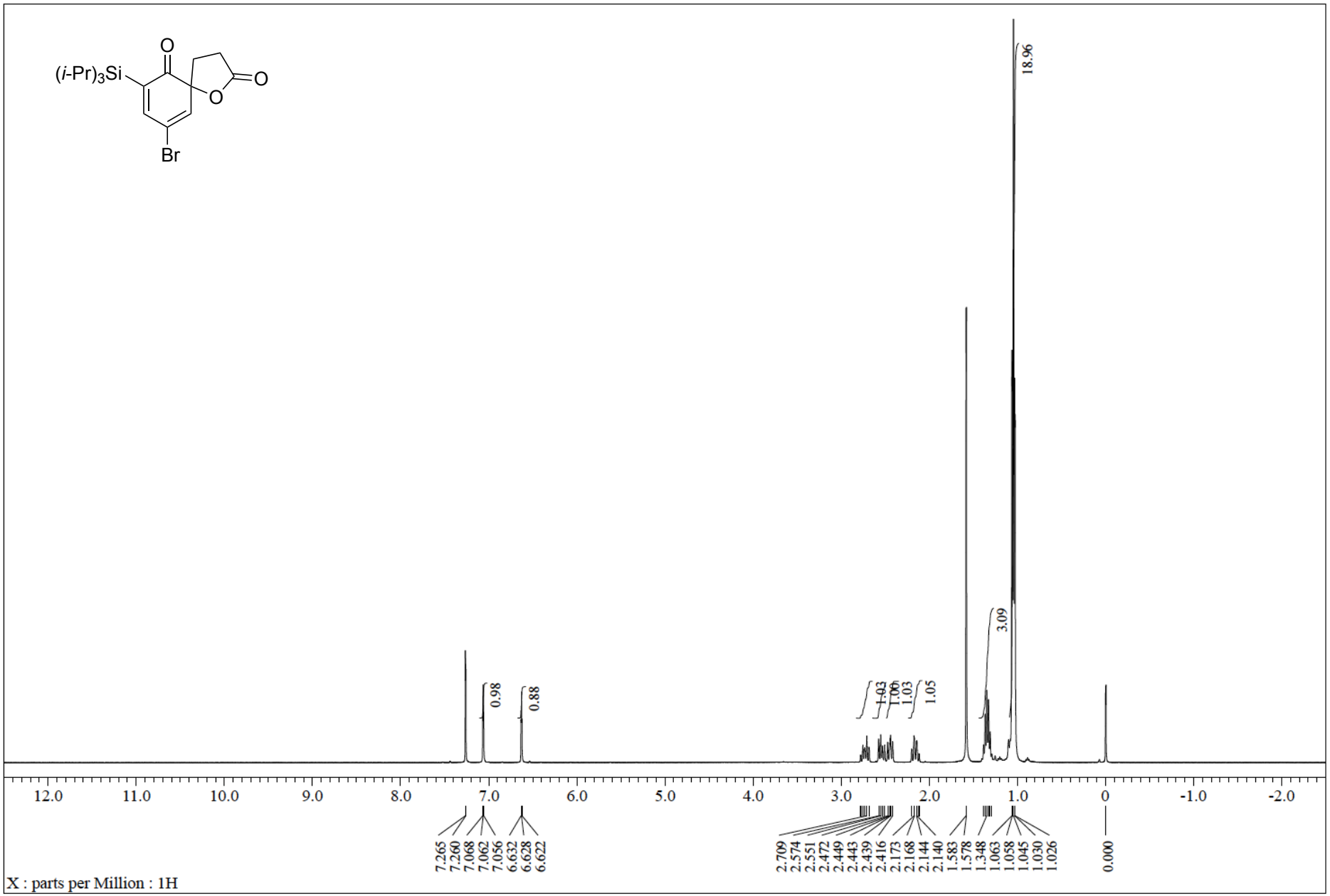
2c, ^{1}H NMR ($CDCl_3$, 400 MHz)



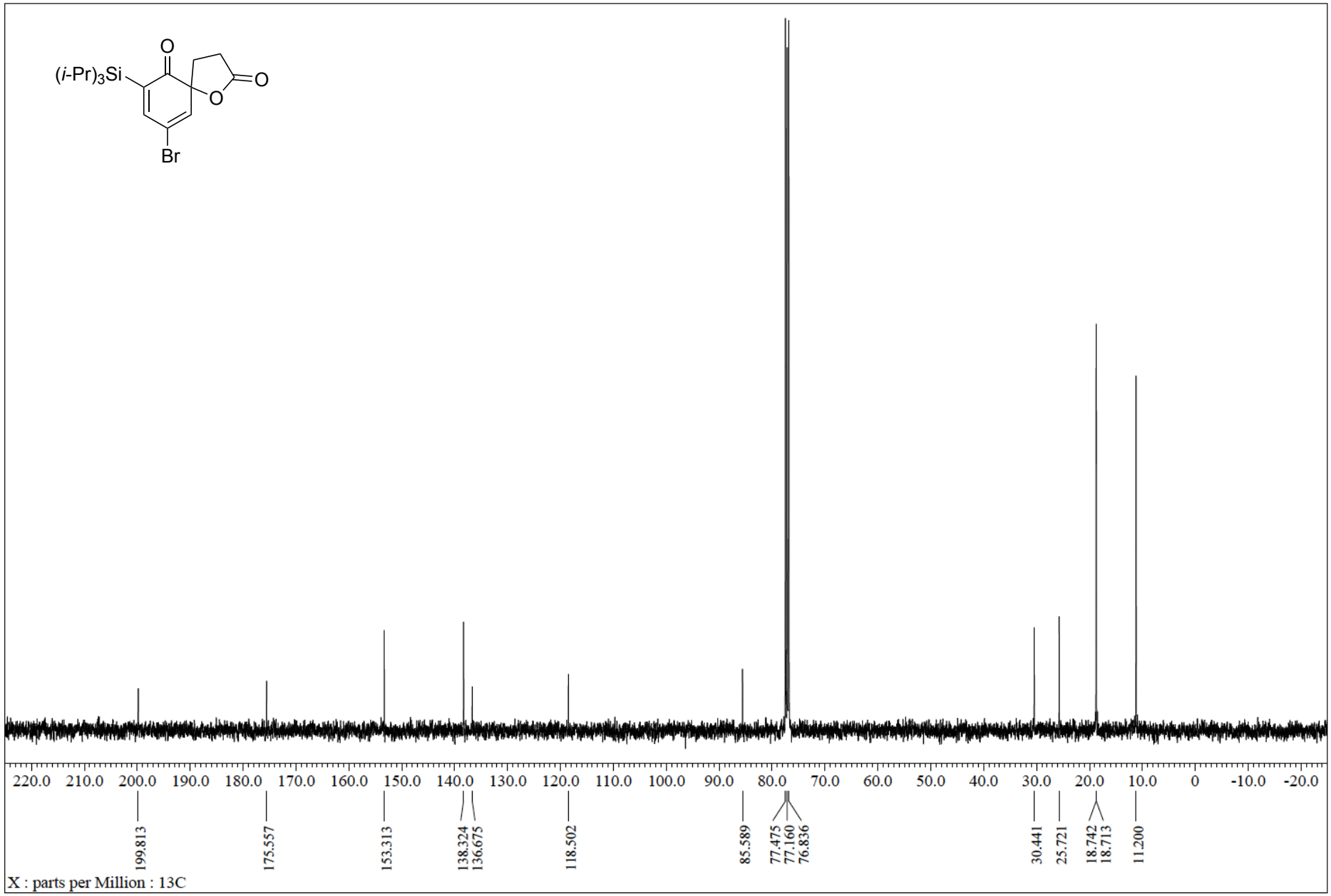
2c, ^{13}C NMR ($CDCl_3$, 100 MHz)



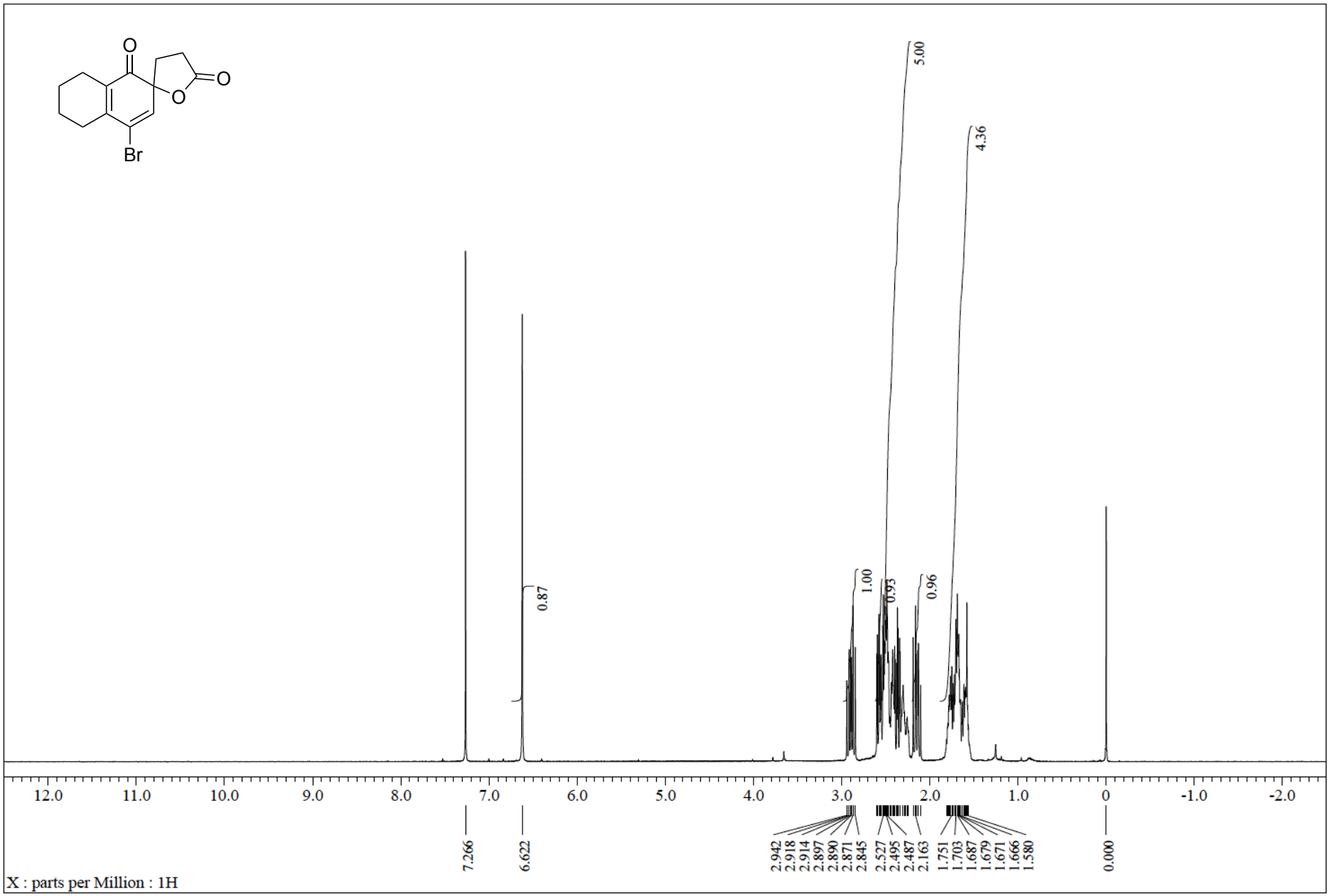
2d, ^{1}H NMR ($CDCl_3$, 400 MHz)



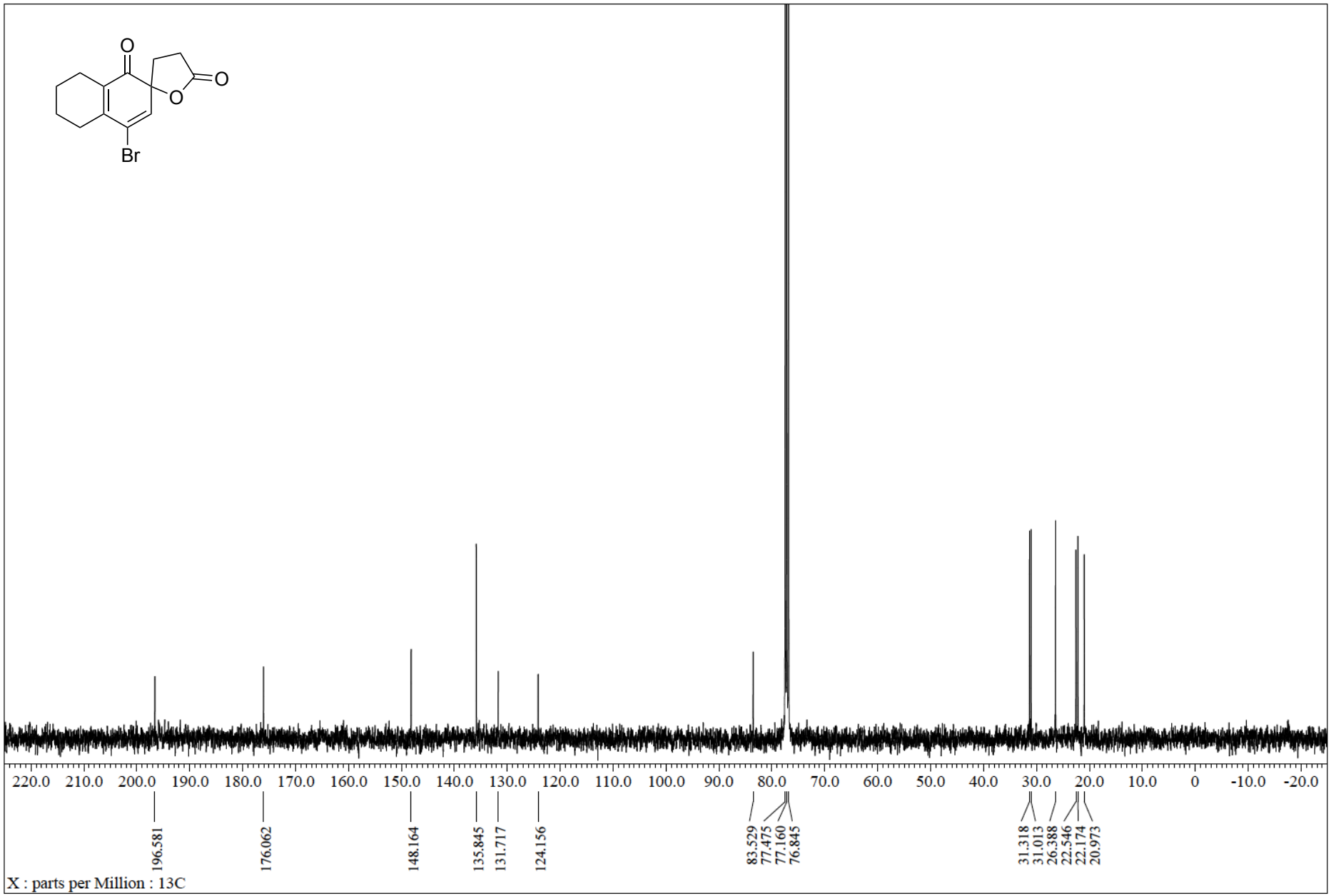
2d, ^{13}C NMR ($CDCl_3$, 100 MHz)



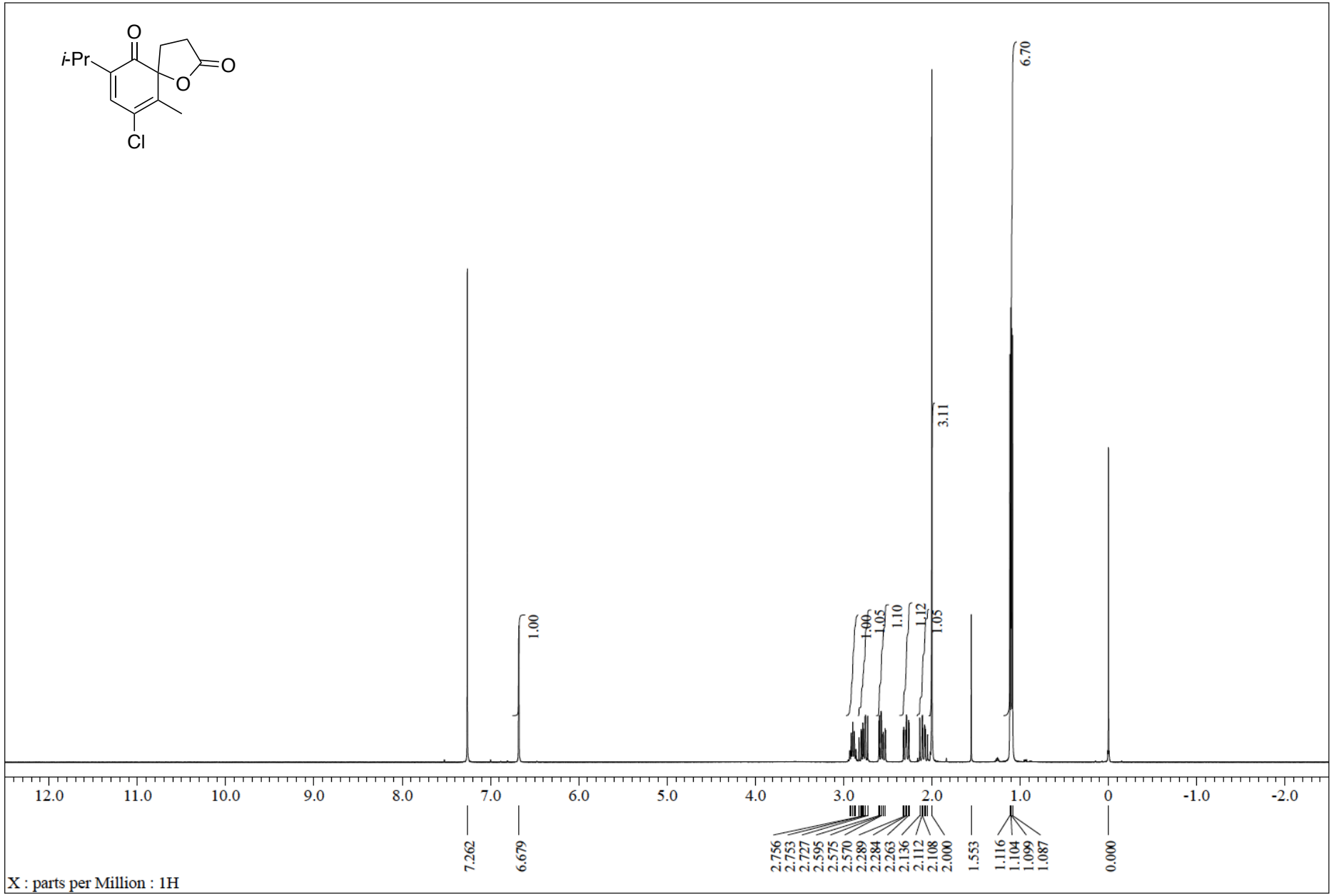
2e, ^{1}H NMR ($CDCl_3$, 400 MHz)



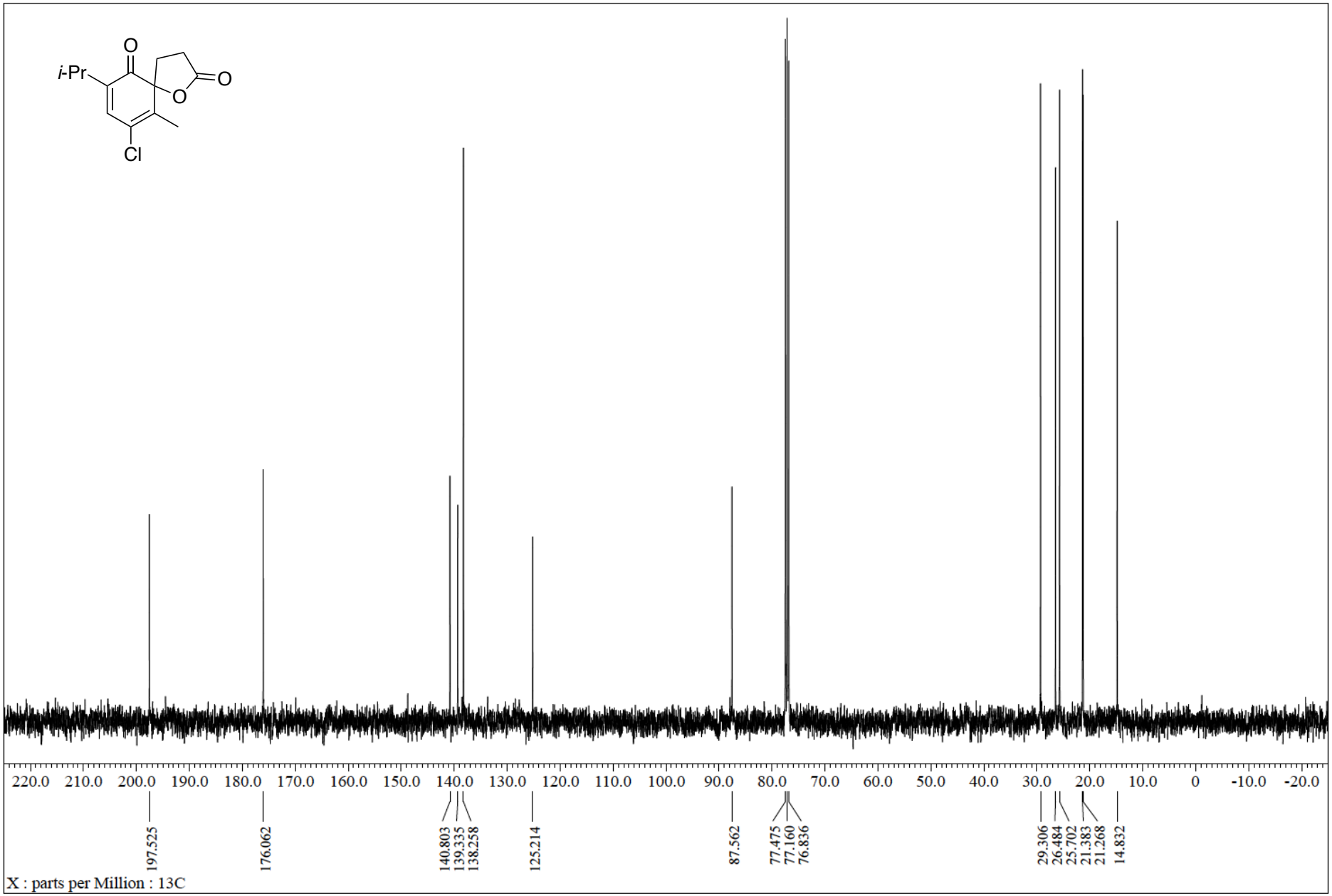
2e, ^{13}C NMR ($CDCl_3$, 100 MHz)



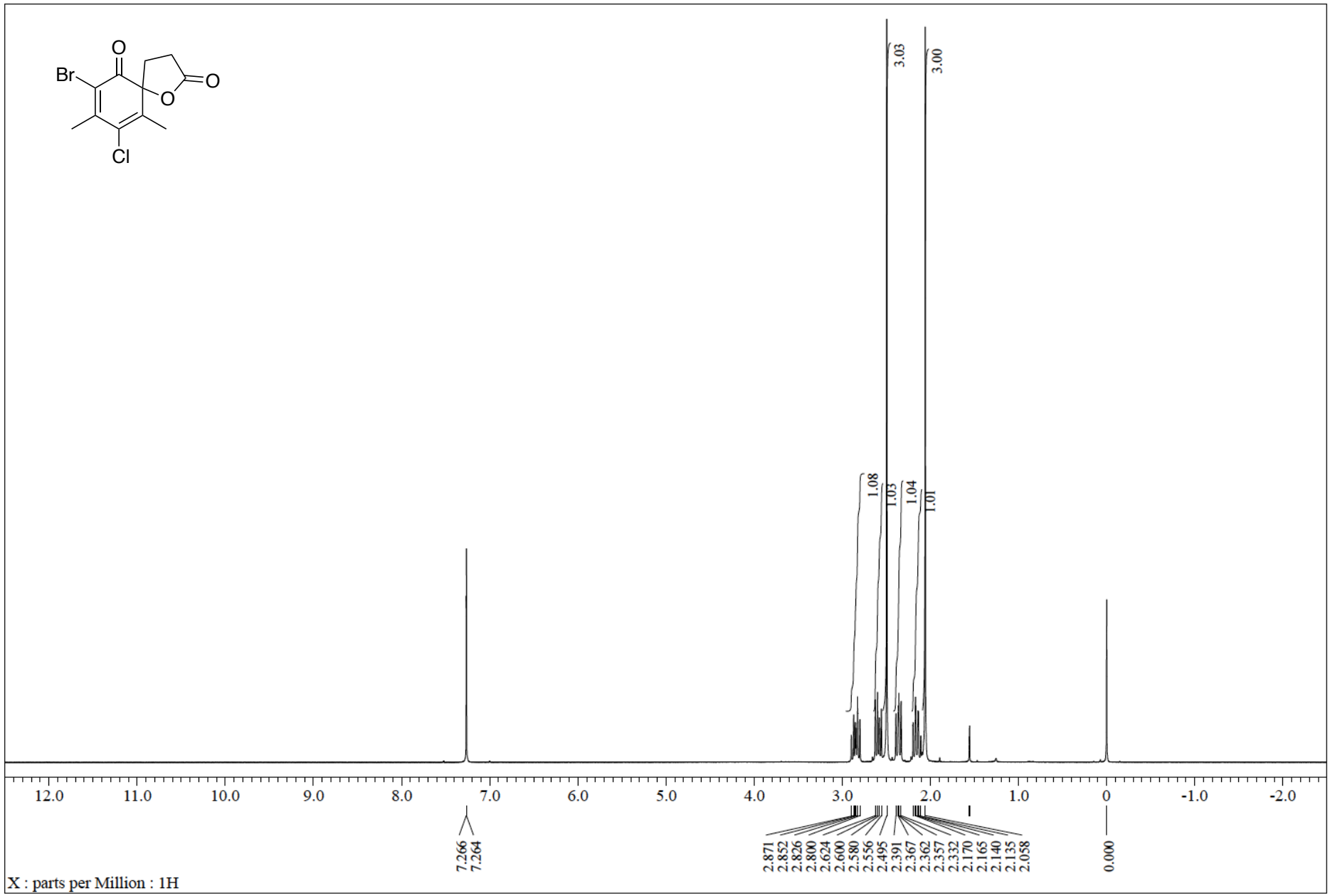
2f, ^{1}H NMR ($CDCl_3$, 400 MHz)



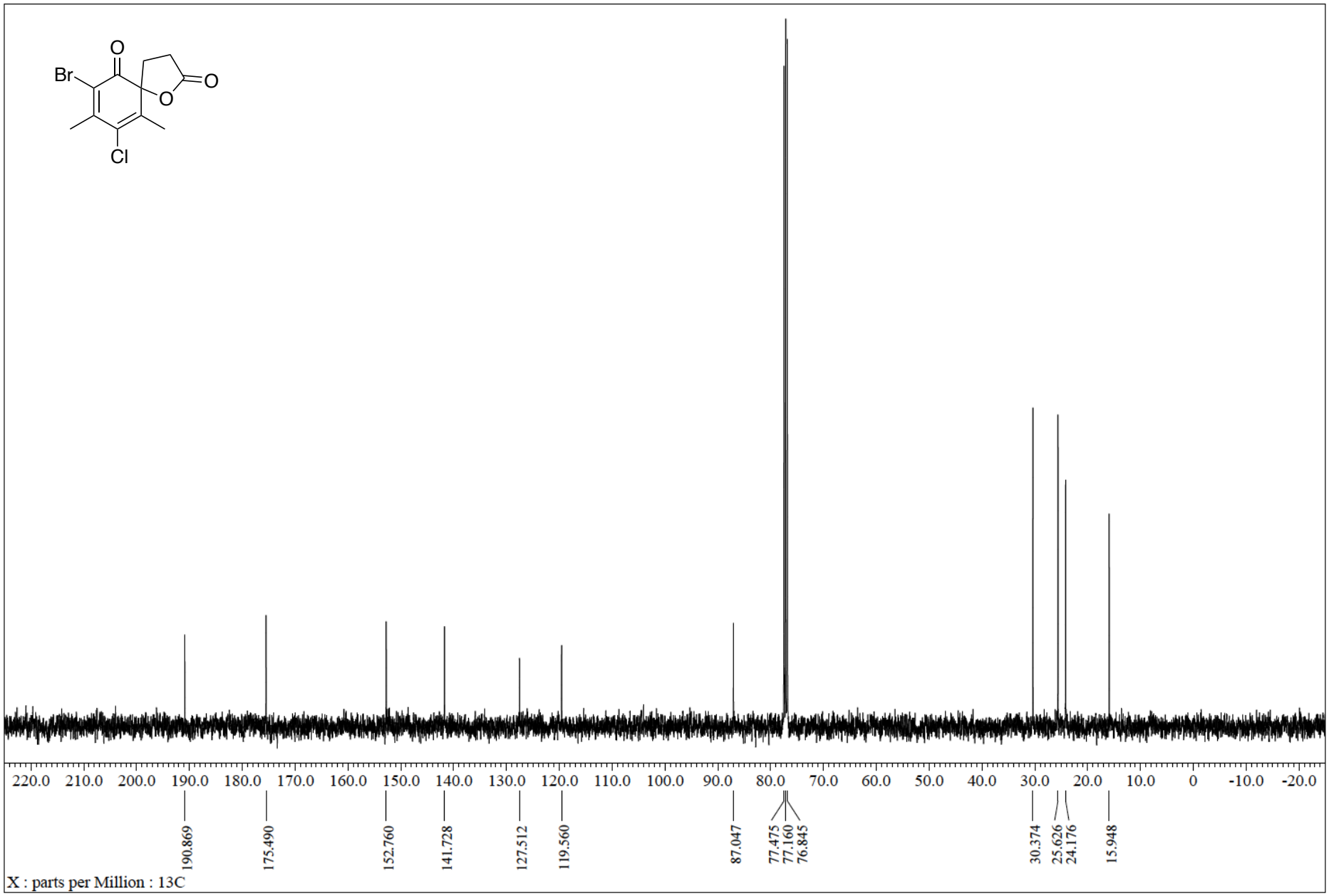
2f, ^{13}C NMR ($CDCl_3$, 100 MHz)



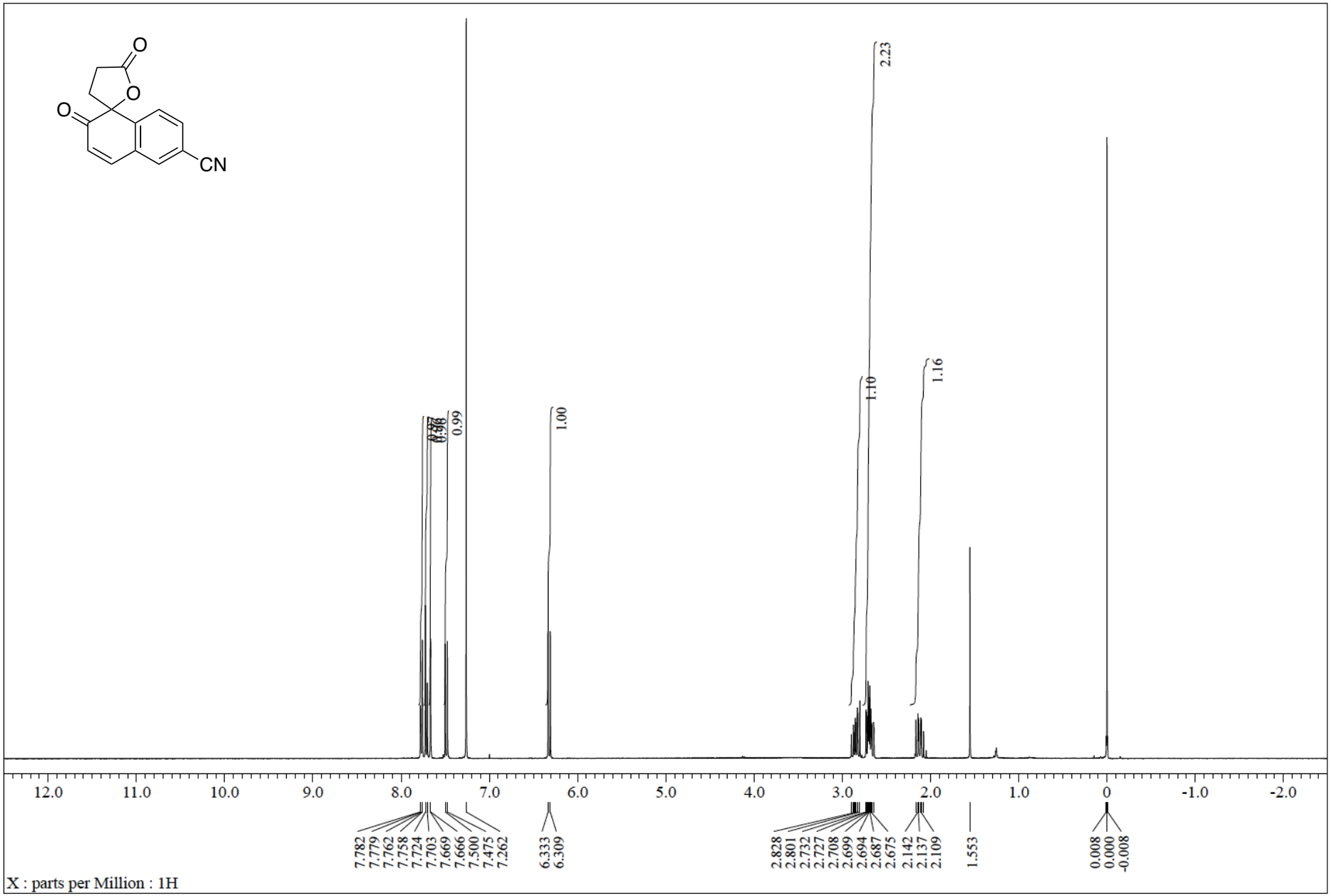
2g, ^{1}H NMR ($CDCl_3$, 400 MHz)



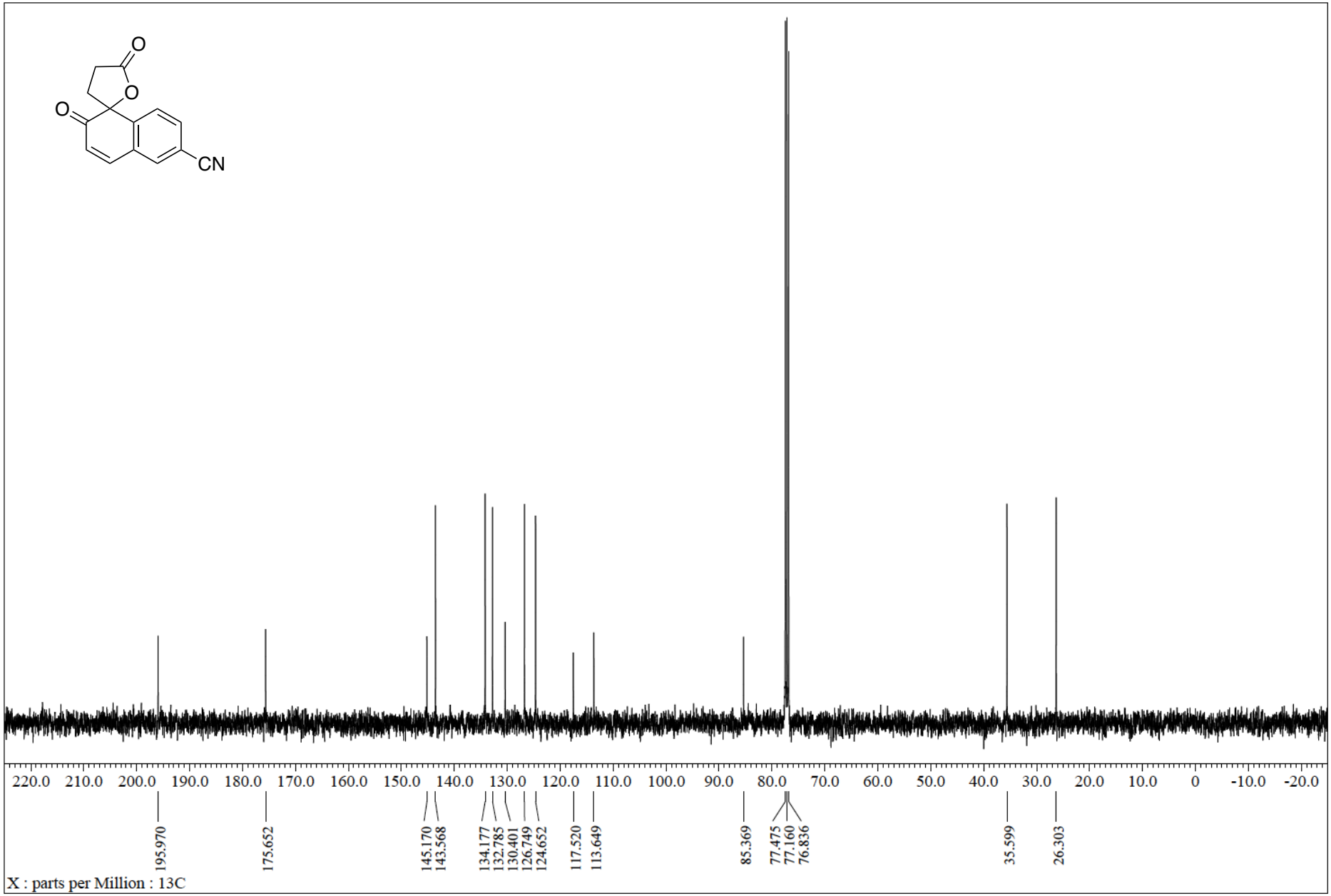
2g, ^{13}C NMR ($CDCl_3$, 100 MHz)



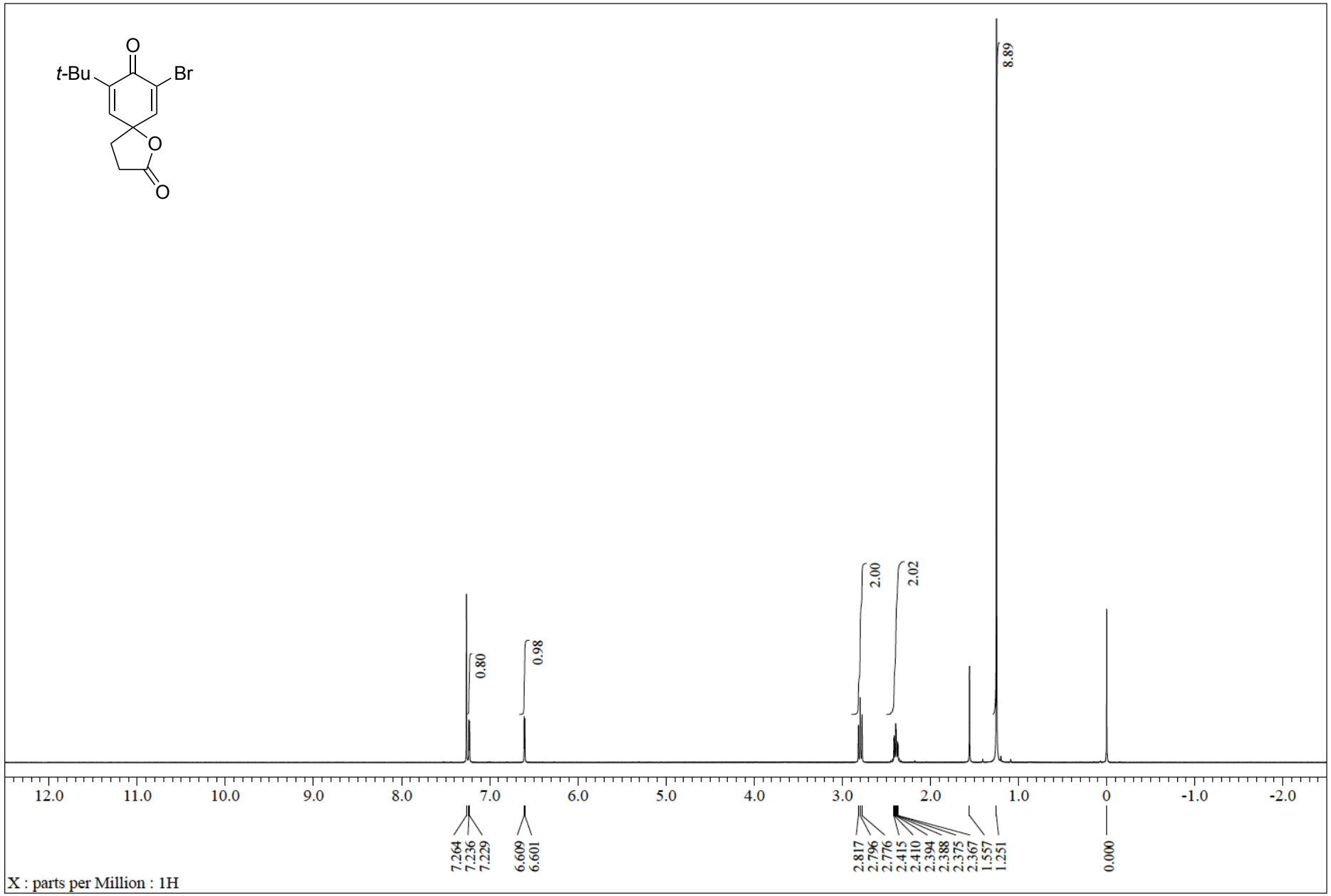
2h, ^{1}H NMR ($CDCl_3$, 400 MHz)



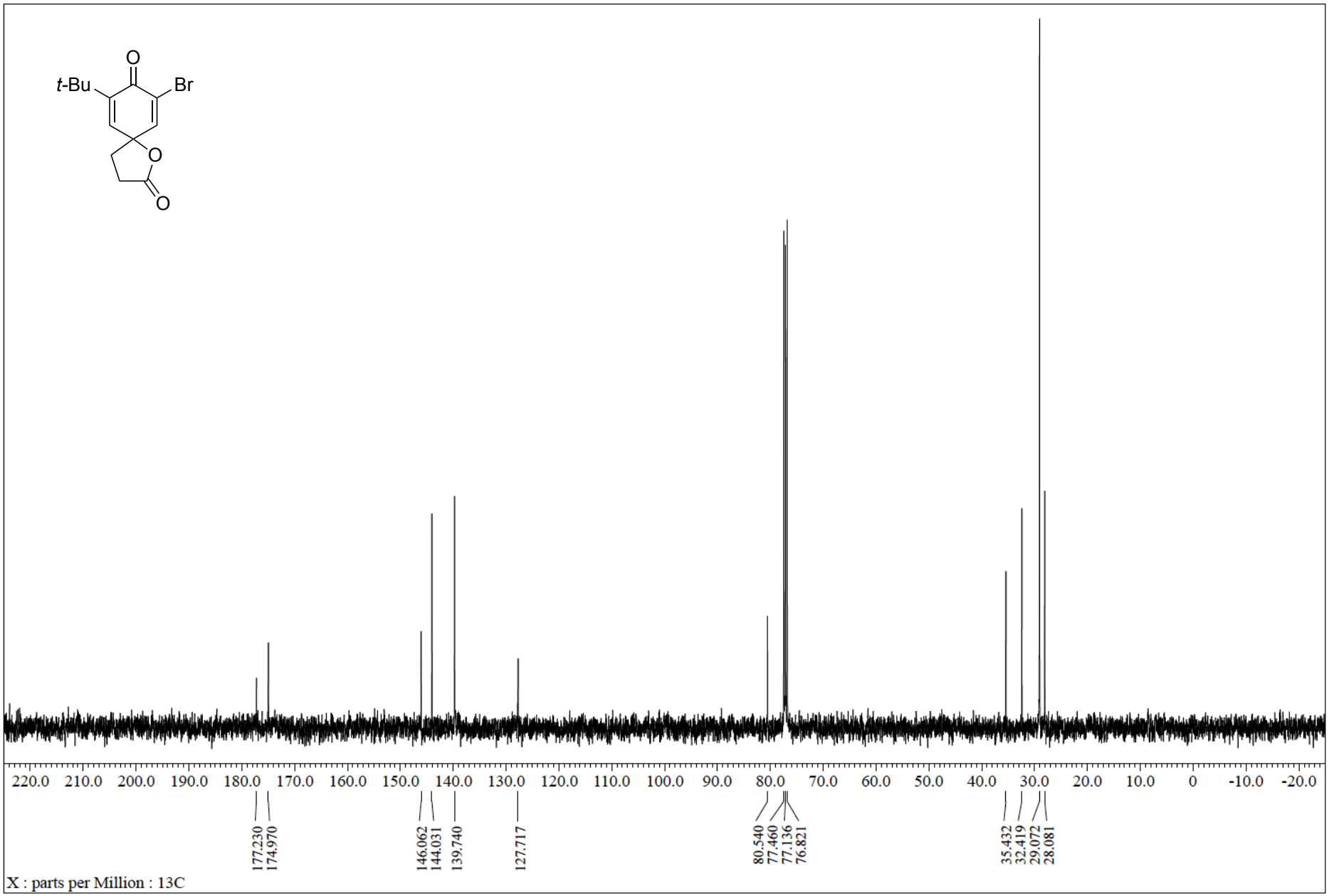
2h, ^{1}H NMR ($CDCl_3$, 400 MHz)



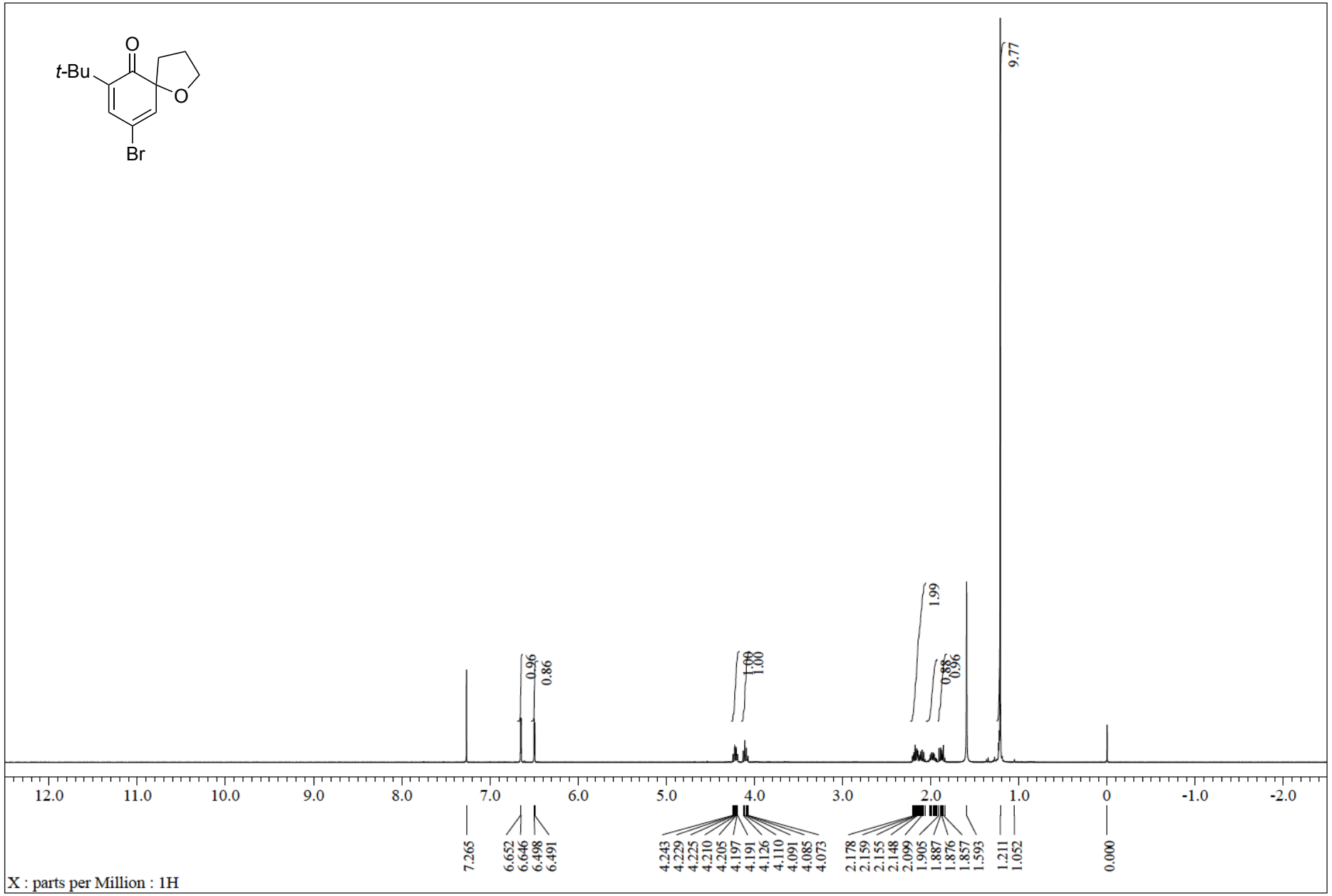
2k, ^{1}H NMR ($CDCl_3$, 400 MHz)



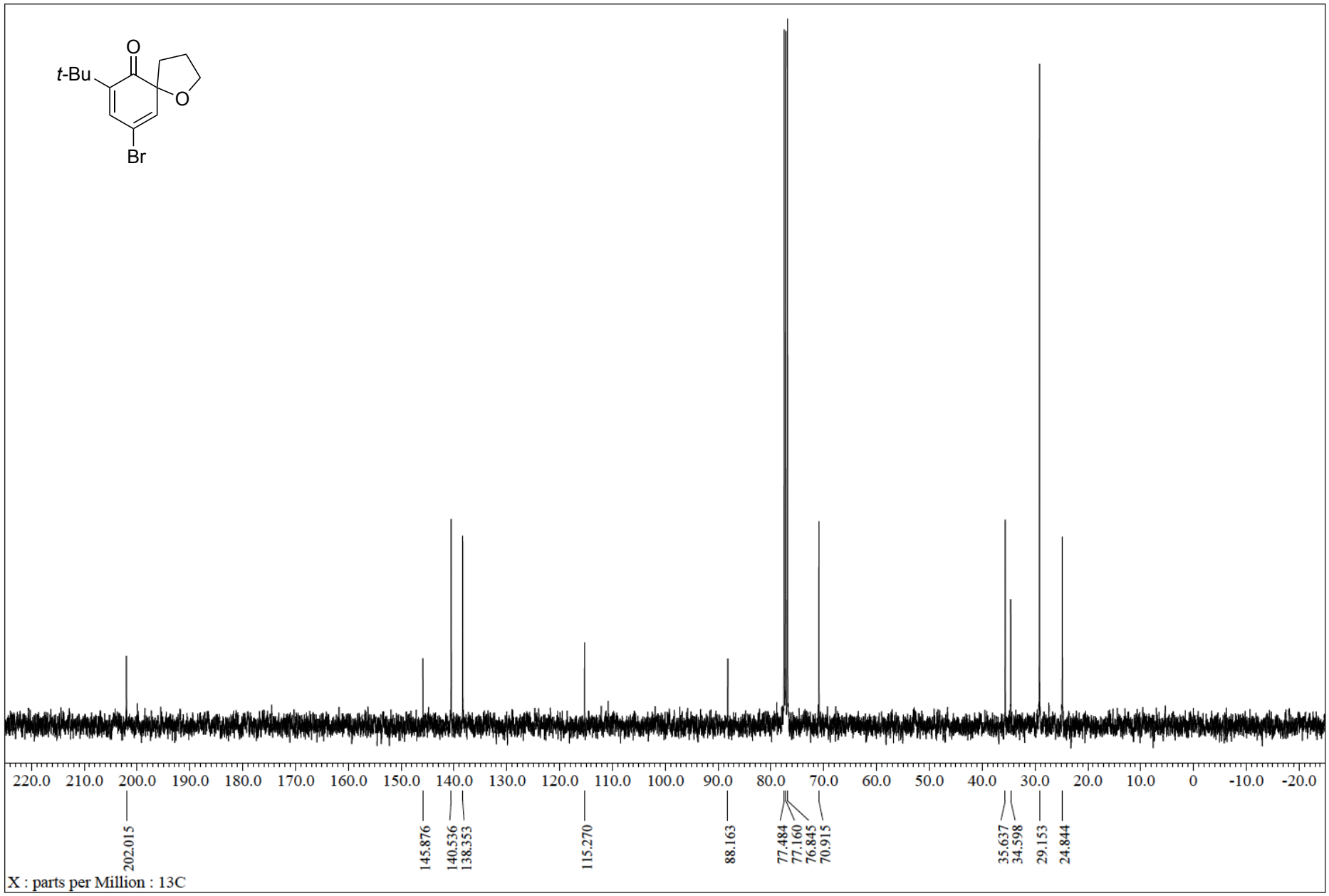
2k, ^{13}C NMR ($CDCl_3$, 100 MHz)



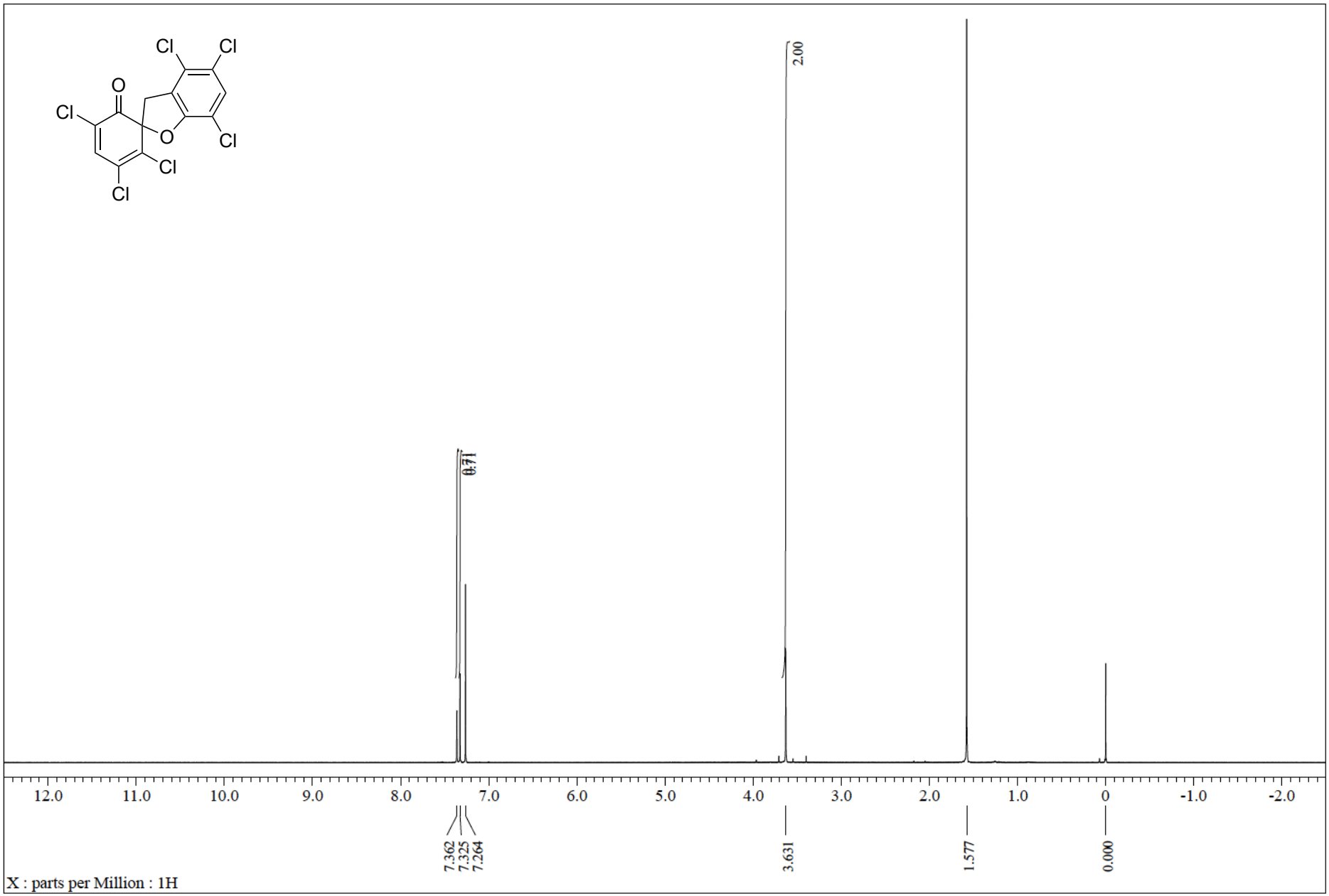
2l, ^{1}H NMR ($CDCl_3$, 400 MHz)



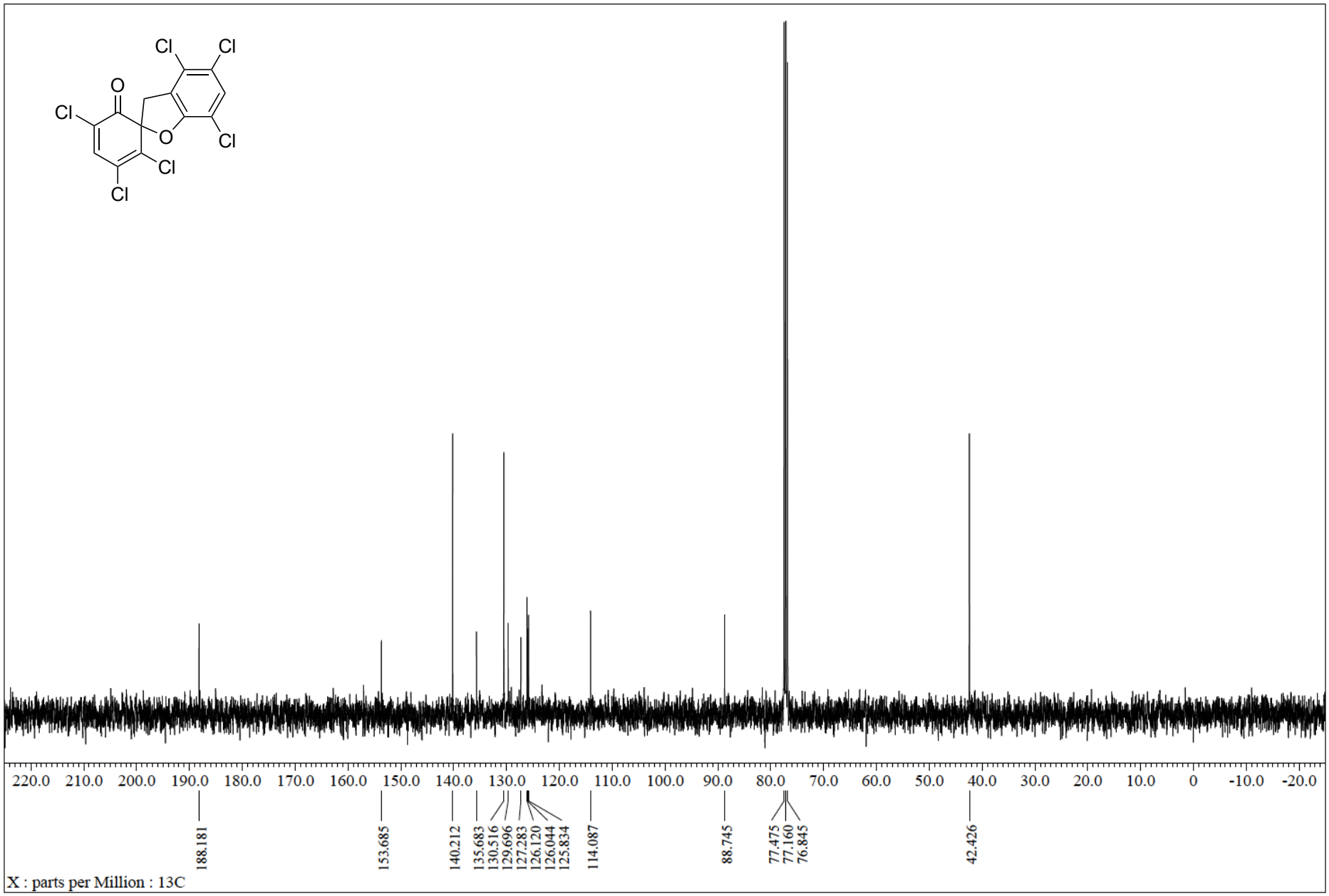
2l, ^{13}C NMR ($CDCl_3$, 100 MHz)



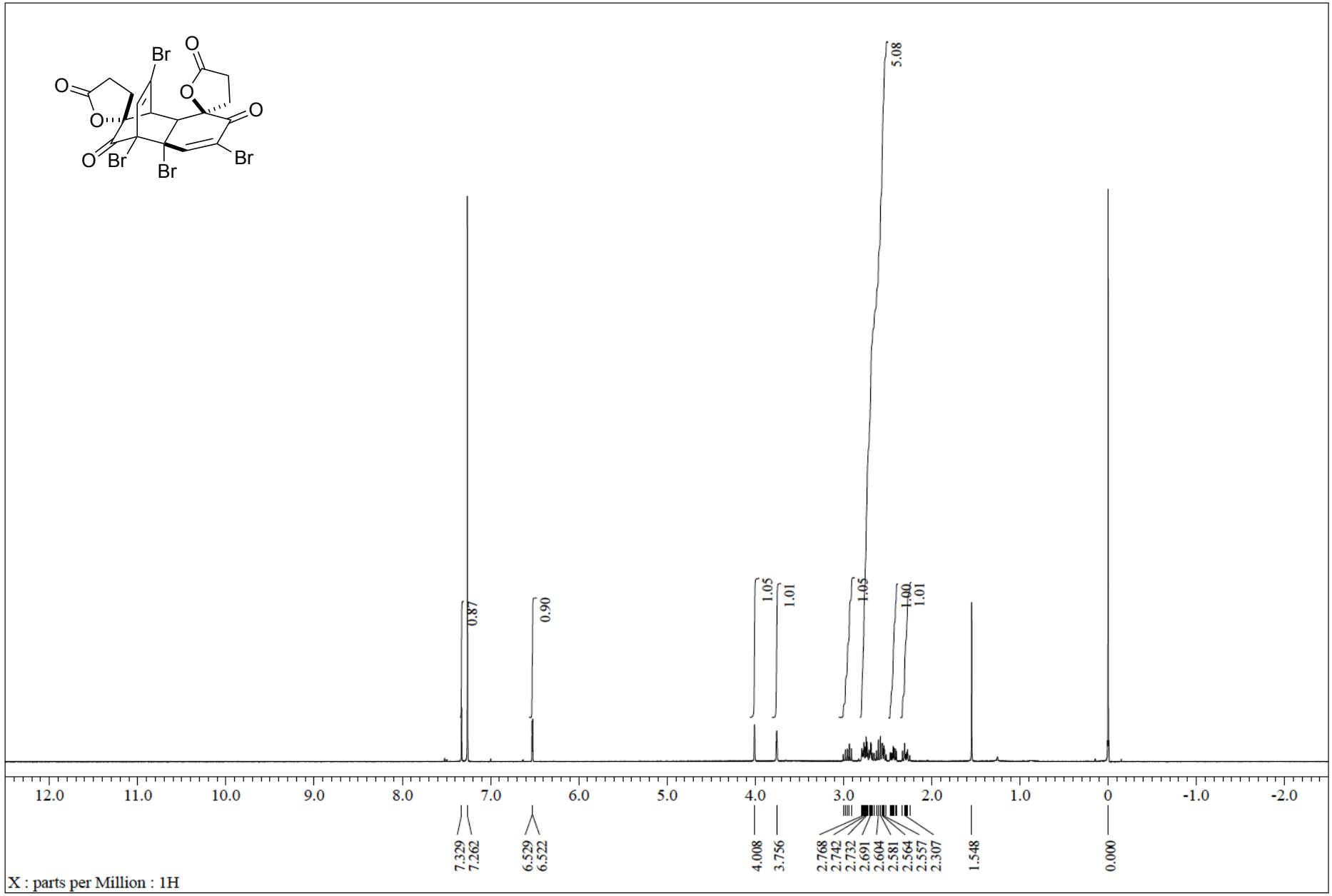
2m, ^{1}H NMR ($CDCl_3$, 400 MHz)



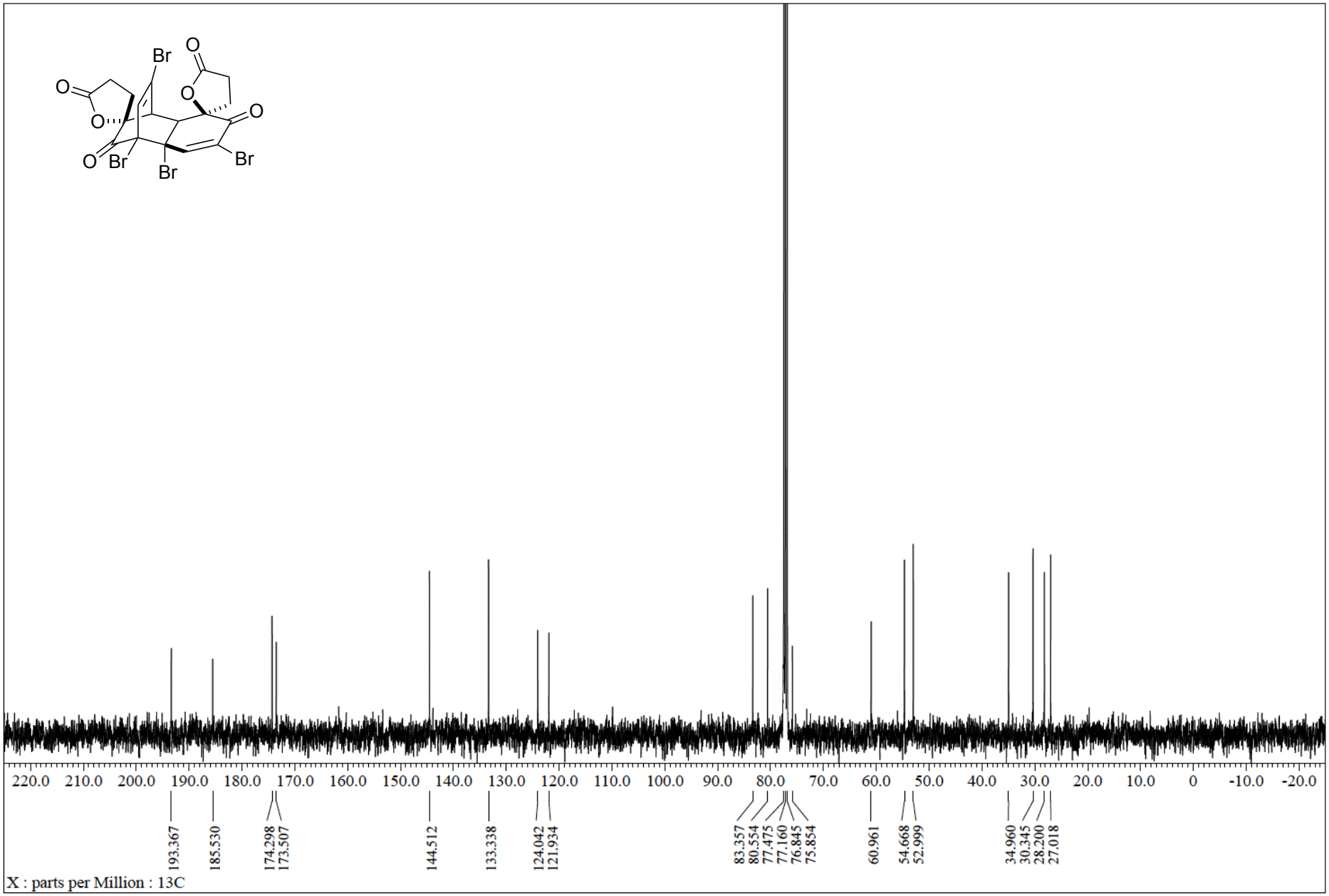
2m, ^{13}C NMR ($CDCl_3$, 100 MHz)



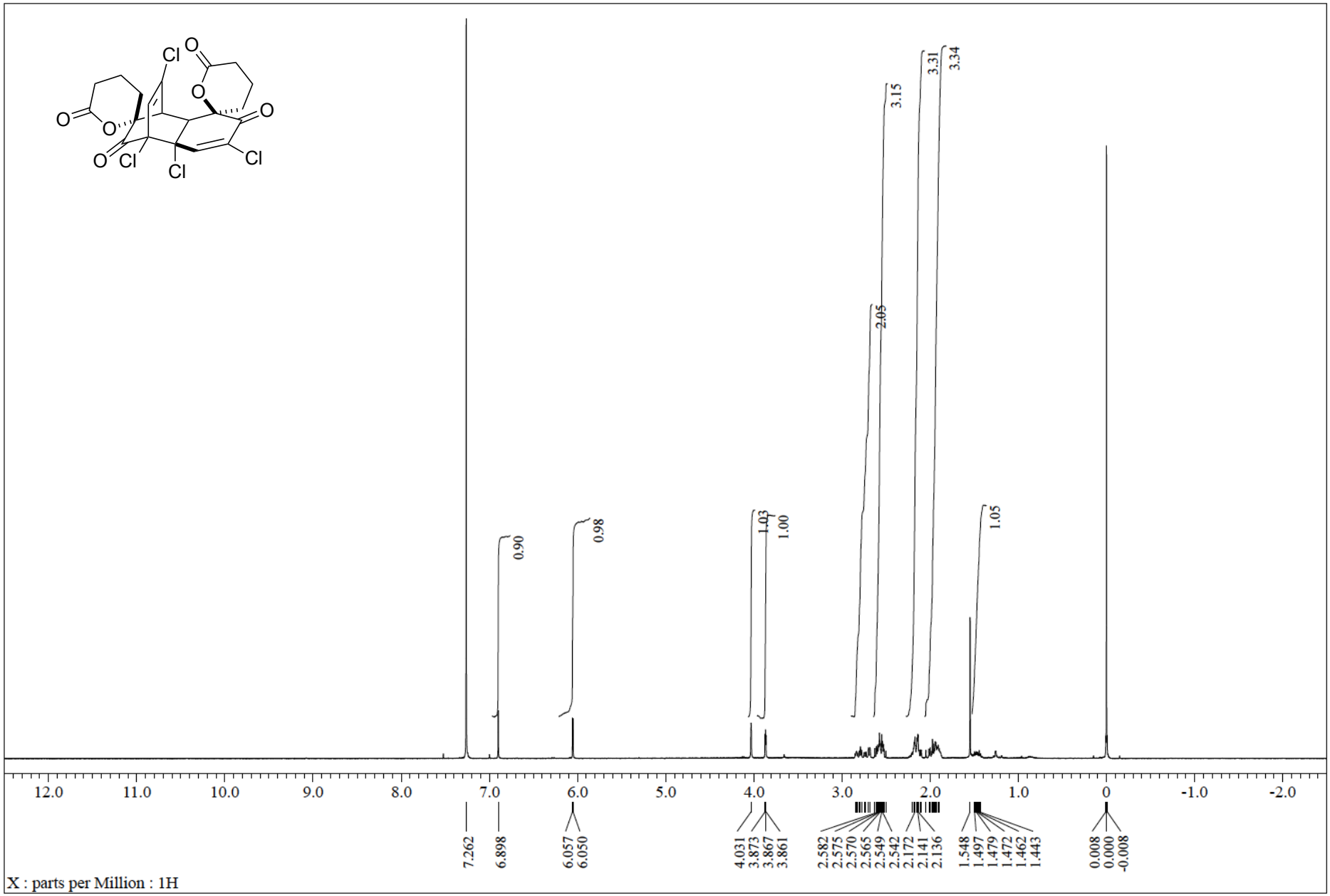
3i, ^{1}H NMR ($CDCl_3$, 400 MHz)



3i, ^{13}C NMR ($CDCl_3$, 100 MHz)



3j, ^{1}H NMR ($CDCl_3$, 400 MHz)



3j, ^{13}C NMR ($CDCl_3$, 100 MHz)