Supporting Information

Base-free oxidation of alcohols enabled by nickel(II)-catalyzed transfer dehydrogenation

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Table of Content

1. General information

Unless otherwise noted, all reactions were carried out in oven dried glassware. Anhydrous solvents were purified according to the procedures outlined in "Purification of Laboratory Chemicals"[1]. Commercially available chemicals were used without further purification.

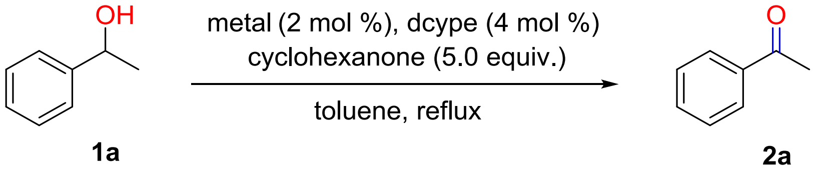
All NMR spectra were acquired on a Bruker 600 MHz or a JEOL ECZ 400 MHz NMR spectrometer. ^{1}H NMR chemical shifts were recorded relative to TMS (δ 0.00) or residual protonated solvents ($CDCl_3$; δ 7.26). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), hept (heptet) and m (multiplet). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as J values in Hz. ^{13}C NMR spectra were obtained at 100 MHz or at 150 MHz, respectively, using the instruments noted above. Chemical shifts were recorded relative to the solvent resonance ($CDCl_3$: δ 77.16). ^{19}F NMR spectra were recorded at 376 MHz or at 565 MHz on the spectrometers noted above without any external standard. Evidence of purity for new compounds was obtained through these spectroscopic studies (see below for copies of the individual spectra), as well as through mass spectrometric analyses; the latter yielded data consistent with the proposed structures in all cases.

TLC analyses were performed on pre-coated, glass-backed silica gel plates and visualized with a UV light. Flash chromatography was performed using Qingdao Haiyang silica gel (200-300 mesh). The GC internal standards tetralin was degassed and dried over activated 4 Å molecular sieves before use. GC analyses were performed on a Shimadzu GC 2020 instrument equipped with an Agilent J&W GC column DB-5MS-UI. GC/MS analyses were conducted on a Shimadzu GC Mass-QP 2020 single quadruple GC/MS instrument with an Agilent J & W GC column DB-5MS-UI. High resolution mass spectra (HRMS) were recorded on a Bruker SolariX spectrometer.

2. Condition optimization

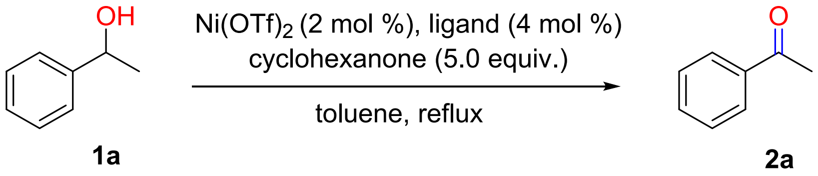
General procedure: A 10-mL Schlenk tube containing a magnetic stir bar was charged with 1-phenylethanol (12 mg, 0.1 mmol), $Ni(OTf)_2$ (1 mg, 0.002 mmol), dcype (2 mg, 0.004 mmol), cyclohexanone (49 mg, 0.5 mmol), the GC standard tetralin (10 μL), and 0.5 mL of toluene. Note: dcype = 1,2-bis(dicyclohexylphosphino)ethane. The reaction mixture was stirred under reflux overnight (ca. 12 h). Water (1 mL) was added to quench the reaction. Then, the reaction mixture was diluted with ethyl acetate (2 mL). After stirring for 30 minutes, aliquots of the upper layer reaction mixture were passed through a short plug of silica gel, which was washed with ethyl acetate. The filtrate was subjected to GC analysis to determine the conversion of the alcohol, as well as the yield of the product.

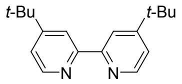
Table S1. Effect of nickel salts



entry	metal	conversion of **1a** (%)	**2a** yield (%)
1	$Ni(OTf)_2$	100	99
2	NiI_2	3	1
3	$NiBr_2·DME$	2	1
4	$NiBr_2$	3	0
5	$NiCl_2·DME$	5	1
6	$NiCl_2·6H_2O$	0	0
7	$NiCl_2$	1	<1
8	$Ni(acac)_2$	13	7
9	$Ni(COD)_2$	7	1
10	$Ni(PPh_3)_4$	6	1

Table S2. Effect of ligands

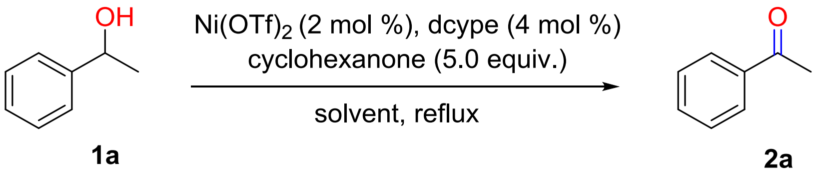


entry	ligand	conversion of **1a** (%)	**2a** yield (%)
1	dcype	100	99
2	dcypp	95	93
3	PCy_3	85	trace
4	$P^tBu_3 \cdot HBF_4$	85	1
5	P(2-fury)$_2$	29	0
6	DPPE	12	1
7	DPPP	31	1
8	DPPF	88	45
9	1,10-phenanthroline	8	2
10		7	trace
11	none	15	0

dcype: 1,2-bis(dicyclohexylphosphino)ethane; dcypp: 1,2-bis(dicyclohexylphosphino)propane.

As for the reaction of PCy_3, the major by-product was the aldol condensation of acetophenone, which was confirmed by GC and GC-Mass analysis. Additionally, no desired product was detected in the absence of ligand; rather, the reaction gave rise to the aldol condensation by-product.

Table S3. Effect of solvents

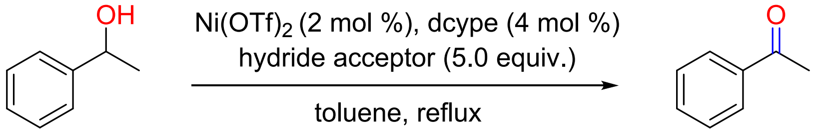


entry[a]	solvent	conversion of **1a** (%)	**2a** yield (%)
1	toluene	100	99
2	DMF	100	96

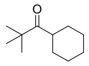
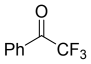
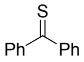
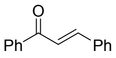
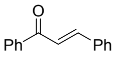
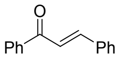
3	DMA	98	98
4	DMSO	92	89
5	CH_3CN	98	98
6	1,4-dioxane	92	90
7	diglyme	97	96
8	THF	29	22
9	$CHCl_3$	12	5
10	DCM	3	<1

[a] The reaction temperatures for the reactions run in CH_3CN, THF, $CHCl_3$ and dichloromethane were those of their corresponding boiling points. Other reactions were run at 110 °C.

Table S4. Studies involving the hydride acceptor

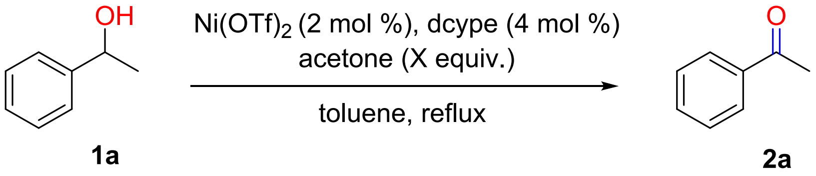


1a **2a**

entry	hydride acceptor	conversion of **1a** (%)	**2a** yield (%)
1	cyclohexanone	100	99
2	acetone	86	85
3	1,1,1-trifluoroacetone	18	10
4		10	2
5		92	91
6		1	<1
7		6	4
8[a]		14	4
9[b]		46	38

[a] 10.0 equiv. of chalcone was used under otherwise identical conditions. [b] 20.0 equiv. of chalcone was used.

Table S5. Studies on the acetone as the hydride acceptor

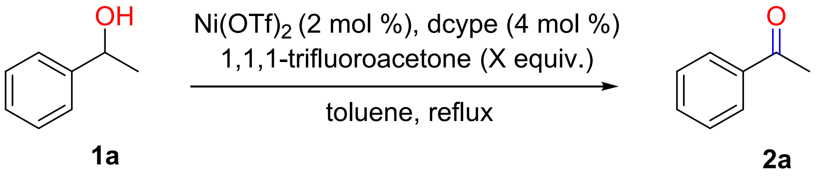


entry	acetone	conversion of **1a** (%)	**2a** yield (%)
1	5.0 equiv.	86	85
2	10.0 equiv.	95	91
3	20.0 equiv.	99	96
4	50.0 equiv.	100	99
5	100 equiv.	100	99
6	acetone as solvent	100	99
7[a]	acetone as solvent	87	85
8[b]	acetone as solvent	55	42

[a] The temperature of oil bath was kept at 80 °C. [b] The temperature of oil bath was kept at 60 °C.

**It should be noted that almost quantitative yield was detected by GC when pure acetone was used both as the solvent and the hydride acceptor at 120 °C (entry 6).

Table S6. Studies involving the use of 1,1,1-trifluoroacetone as the hydride acceptor

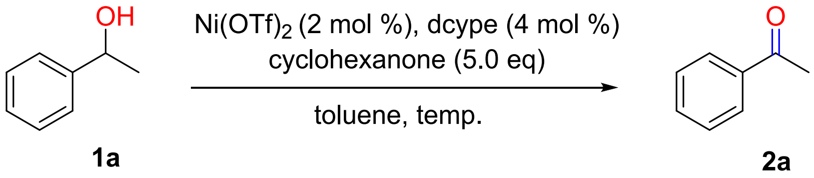


entry	trifluoroacetone (X equiv.)	conversion of **1a** (%)	**2a** yield (%)
1	5.0 equiv.	18	10
2	10.0 equiv.	77	70
3	20.0 equiv.	100	99
4	50.0 equiv.	100	99

**We attribute the initial "detrimental effect" of 1,1,1-trifluoroacetone to its relatively low boiling point (22 °C) and its volatility. In fact when the reaction was run with the oil bath kept at 120 °C (i.e., with stirring under reflux), the bulk of the 1,1,1-trifluoroacetone was found in the vapor layer.

It was thus not an efficient hydride acceptor. Consistent with this rationale, the yield increased when an excess of trifluoroacetone was employed.

Table S7. Effect of temperature

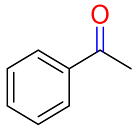


entry	temp. (°C)	conversion of **1a** (%)	**2a** yield (%)
1	25	0	0
2	60	0	0
3	80	15	13
4	110	100	99

3. Preparation of products

General procedure: A 10-mL Schlenk tube containing a magnetic stir bar was charged with the secondary alcohol of interest (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), 1,2-bis(dicyclohexylphosphino)ethane (dcype) (0.012 mmol), cyclohexanone (1.5 mmol), and 1.5 mL of toluene. The reaction mixture was stirred under reflux overnight (*ca.* 12 h). The volatiles were then evaporated off under reduced pressure and the residue purified by flash chromatography over silica gel using ethyl acetate (EA)/petroleum ether as the eluent to give the product. Details of reactions giving specific ketones now follow.

Note: As the boiling point of products **2af**, **2ag**, **2ah**, **2aj** are relatively low yields were determined relative to an external standard. The formation of the products was also confirmed via GC-MS analysis.



Acetophenone (2a) [98-86-2][2]

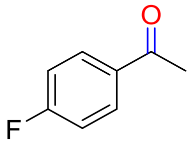
According to the general procedure, reaction of 1-phenylethanol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol), and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (34 mg, 94% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

**As a demonstration, this reaction was performed on a 0.3 mmol scale using 20.0 equiv. of acetone as the hydride acceptor. Under these conditions an almost quantitative yield was obtained as inferred from a GC analysis.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (d, J = 7.8 Hz, 2H), 7.58 – 7.55 (m, 1H), 7.47 (t, J = 7.1 Hz, 2H), 2.61 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 198.3, 137.2, 133.2, 128.7, 128.4, 26.7.

GC-MS: Calcd for C_8H_8O: 120.1; found: 120.0.



1-(4-Fluorophenyl)ethan-1-one (2b) [403-42-9][2]

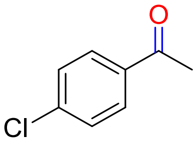
According to the general procedure, the reaction of 1-(4-fluorophenyl)ethan-1-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (26 mg, 64% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 8.01 – 7.97 (m, 2H), 7.16 – 7.12 (m, 2H), 2.59 (s, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 196.6, 165.9 (d, J = 254.8 Hz), 133.7, 131.1 (d, J = 9.2 Hz), 115.8 (d, J = 22.0 Hz),, 26.6.

^{19}F {^{1}H} NMR (565 MHz, CDCl$_3$): δ -105.4.

GC-MS: Calcd for C_8H_7FO: 138.0; found: 138.0.



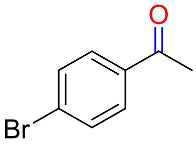
1-(4-Chlorophenyl)ethan-1-one (2c) [99-91-2][2]

According to the general procedure, the reaction of 1-(4-chlorophenyl)ethan-1-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (42 mg, 90% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.90 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 2.59 (s, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 196.9, 139.7, 135.6, 129.8, 129.0, 26.7.

GC-MS: Calcd for C_8H_7ClO: 154.0; found: 154.0.



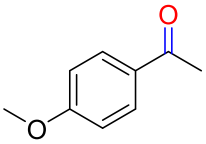
1-(4-Bromophenyl)ethan-1-one (2d) [99-90-1][3]

According to the general procedure, the reaction of 1-(4-bromophenyl)ethan-1-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (50 mg, 84% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.82 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 2.59 (s, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 197.1, 136.0, 132.0, 130.0, 128.4, 26.7.

GC-MS: Calcd for C_8H_7BrO: 198.0; found: 198.0.



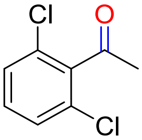
1-(4-Methoxyphenyl)ethan-1-one (2e) [100-06-1][4]

According to the general procedure, the reaction of 1-(4-methoxyphenyl)ethan-1-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (44 mg, 98% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.95 – 7.93 (m, 2H), 6.95 – 6.92 (m, 2H), 3.87 (s, 3H), 2.56 (s, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 196.9, 163.6, 130.7, 130.5, 113.8, 55.6, 26.5.

GC-MS: Calcd for $C_9H_{10}O_2$: 150.1; found: 150.0.



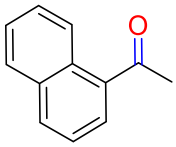
1-(2,6-Dichlorophenyl)ethan-1-one (2f) [2040-05-3][5]

According to the general procedure, the reaction of 1-(2,6-dichlorophenyl)ethan-1-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (42 mg, 74% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.52 (t, *J* = 3.0 Hz, 1H), 7.36 (d, *J* = 1.5 Hz, 1H), 2.64 (s, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 199.1, 140.4, 133.3, 132.04, 132.01, 129.7, 129.5, 30.7.

GC-MS: Calcd for $C_8H_6Cl_2O$: 188.0; found: 188.0.



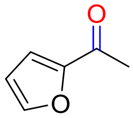
1-(Naphthalen-1-yl)ethan-1-one (2g) [941-98-0][6]

According to the general procedure, the reaction of 1-(naphthalen-1-yl)ethan-1-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (39 mg, 76% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 8.74 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.95 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.59 (m, 1H), 7.55 – 7.49 (m, 2H), 2.75 (s, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 202.0, 135.6, 134.1, 133.2, 130.3, 128.8, 128.6, 128.2, 126.6, 126.2, 124.5, 30.1.

GC-MS: Calcd for $C_{12}H_{10}O$: 170.1; found: 170.0.



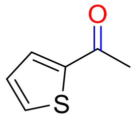
1-(Furan-2-yl)ethan-1-one (2h) [1192-62-7][7]

According to the general procedure, the reaction of 1-(furan-2-yl)ethan-1-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (32 mg, 98% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.59 (dd, J = 1.6, 0.7 Hz, 1H), 7.19 (dd, J = 3.5, 0.6 Hz, 1H), 6.54 – 6.54 (m, 1H), 2.48 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 186.9, 153.0, 146.5, 117.3, 112.3, 26.1.

GC-MS: Calcd for $C_6H_6O_2$: 110.0; found: 110.0.



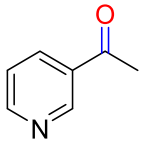
1-(Thiophen-2-yl)ethan-1-one (2i) [88-15-3][7]

According to the general procedure, the reaction of 1-(thiophen-2-yl)ethan-1-ol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (36 mg, 95% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (dd, J = 3.8, 1.1 Hz, 1H), 7.64 (dd, J = 4.9, 1.1 Hz, 1H), 7.14 – 7.13 (m, 1H), 2.57 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 190.8, 144.6, 133.9, 132.6, 128.2, 27.0.

GC-MS: Calcd for C_6H_6OS: 126.0; found: 126.0.



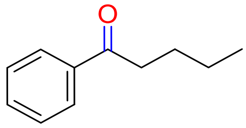
1-(Pyridin-3-yl)ethan-1-one (2j) [350-03-8][2]

According to the general procedure, the reaction of 1-(pyridin-3-yl)ethan-1-ol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in DMA (1.5 mL) with stirring at 110 °C for 12 h, afforded the title compound as a yellow oil (30 mg, 83% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 20:1 to 10:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 9.18 (d, *J* = 2.3 Hz, 1H), 8.79 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.24 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.43 (dd, *J* = 7.9, 4.8 Hz, 1H), 2.65 (s, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 196.9, 153.7, 150.1, 135.6, 132.5, 123.8, 26.9.

GC-MS: Calcd for C_7H_7NO: 121.1; found: 121.0.



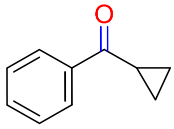
1-Phenylpentan-1-one (2k) [1009-14-9][8]

According to the general procedure, the reaction of 1-phenylpentan-1-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring at 110 °C for 12 h, afforded the title compound as a yellow oil (48 mg, 99% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.98 – 7.97 (m, 1H), 7.96 – 7.95 (m, 1H), 7.58 – 7.53 (m, 1H), 7.48 – 7.44 (m, 2H), 2.97 (t, *J* = 7.4 Hz, 2H), 1.76 – 1.69 (m, 2H), 1.46 – 1.37 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 200.8, 137.2, 133.0, 128.7, 128.2, 38.5, 26.6, 22.6, 14.1.

GC-MS: Calcd for $C_{11}H_{14}O$: 162.1; found: 162.0.



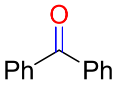
Cyclopropyl(phenyl)methanone (2l) [3481-02-5][2]

According to the general procedure, the reaction of cyclopropyl(phenyl)methanol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless crystal (43 mg, 98% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 2.70 – 2.66 (m, 1H), 1.26 – 1.23 (m, 2H), 1.06 – 1.03 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 200.8, 138.2, 132.9, 128.6, 128.2, 17.3, 11.8.

GC-MS: Calcd for $C_{10}H_{10}O$: 146.1; found: 146.0.



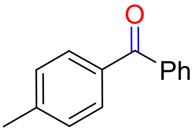
Benzophenone (2m) [119-61-9][2]

According to the general procedure, the reaction of diphenylmethanol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless crystal (54 mg, 99% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.79 (m, 4H), 7.61 – 7.56 (m, 2H), 7.48 (t, J = 7.6 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 137.7, 132.6, 130.2, 128.4.

GC-MS: Calcd for $C_{13}H_{10}O$: 182.1; found: 182.0.



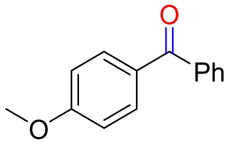
Phenyl(*p*-tolyl)methanone (2n) [134-84-9][9]

According to the general procedure, the reaction of phenyl(*p*-tolyl)methanol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (57 mg, 97% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, $CDCl_3$): 7.79 – 7.77 (m, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.59 – 7.56 (m, 1H), 7.48 – 7.46 (m, 2H), 7.28 (d, J = 7.9 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): 196.6, 143.4, 138.1, 135.0, 132.3, 130.4, 130.1, 129.1, 128.3, 21.8.

GC-MS: Calcd for $C_{14}H_{12}O$: 196.1; found: 196.0.



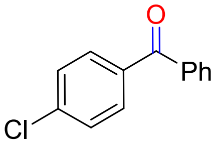
(4-Methoxyphenyl)(phenyl)methanone (2o) [611-94-9][10]

According to the general procedure, the reaction of (4-methoxyphenyl)(phenyl)methanol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (62 mg, 98% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.83 (d, J = 8.8 Hz, 2H), 7.76 – 7.75 (m, 2H), 7.58 – 7.55 (m, 1H), 7.47 (t, J = 7.7 Hz, 2H), 6.98 – 6.95 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 195.7, 163.4, 138.4, 132.7, 132.0, 130.3, 129.9, 128.3, 113.7, 55.6.

GC-MS: Calcd for $C_{14}H_{12}O_2$: 212.1; found: 212.0.



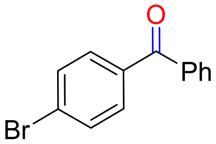
(4-Chlorophenyl)(phenyl)methanone (2p) [134-85-0][7]

According to the general procedure, the reaction of (4-chlorophenyl)(phenyl)methanol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (64 mg, 99% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.78 – 7.75 (m, 4H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 195.7, 139.1, 137.4, 136.0, 132.8, 131.6, 130.1, 128.8, 128.6.

GC-MS: Calcd for $C_{13}H_9ClO$: 216.0; found: 216.0.



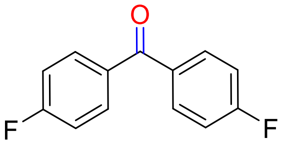
(4-Bromophenyl)(phenyl)methanone (2q) [90-90-4][11]

According to the general procedure, the reaction of (4-bromophenyl)(phenyl)methanol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (73 mg, 93% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, $CDCl_3$): 7.78 (d, J = 7.0 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 195.8, 137.3, 136.5, 132.8, 131.8, 131.7, 130.1, 128.6, 127.7.

GC-MS: Calcd for $C_{13}H_9BrO$: 260.0; found: 260.0.



Bis(4-fluorophenyl)methanone (2r) [345-92-6][10]

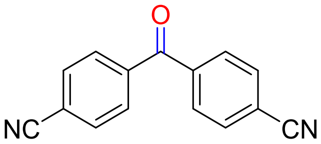
According to the general procedure, the reaction of bis(4-fluorophenyl)methanol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (61 mg, 93% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, $CDCl_3$): 7.82 (dd, J = 8.7, 5.4 Hz, 4H),, 7.17 (t, J = 8.6 Hz, 4H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 194.0, 165.6 (d, J = 254.6 Hz), 133.9 (d, J = 3.1 Hz), 132.7 (d, J = 9.2 Hz), 115.71 (d, J = 21.9 Hz).

^{19}F {^{1}H} NMR (565 MHz, $CDCl_3$): δ -105.8.

GC-MS: Calcd for $C_{13}H_8F_2O$: 218.1; found: 218.0.



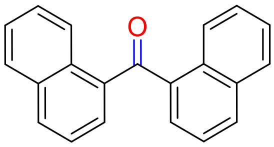
4,4'-Carbonyldibenzonitrile (2s) [32446-66-5][12]

According to the general procedure, the reaction of 4,4'-(hydroxymethylene)dibenzonitrile (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in DMF (1.5 mL) with stirring at 110 °C for 12 h, afforded the title compound as a white solid (41 mg, 59% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 10:1 to 6:1 as the eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.87 (m, 4H), 7.84 – 7.82 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 193.6, 139.9, 132.6, 130.4, 117.8, 116.7.

GC-MS: Calcd for $C_{15}H_8N_2O$: 232.1; found: 232.0.



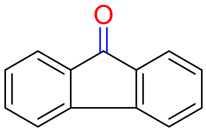
Di(naphthalen-1-yl)methanone (2t) [605-78-7][12]

According to the general procedure, the reaction of di(naphthalen-1-yl)methanol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (81 mg, 96% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 – 8.54 (m, 2H), 8.03 (d, J = 8.2 Hz, 2H), 7.97 – 7.93 (m, 2H), 7.62 – 7.56 (m, 6H), 7.46 – 7.42 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 137.3, 134.0, 132.7, 131.3, 130.6, 128.6, 128.0, 126.7, 126.0, 124.5.

GC-MS: Calcd for $C_{21}H_{14}O$: 282.1; found: 282.0.



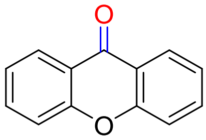
9*H*-Fluoren-9-one (2u) [486-25-9][7]

According to the general procedure, the reaction of 9*H*-fluoren-9-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a yellow solid (53 mg, 98% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.66 (d, J = 7.3 Hz, 2H), 7.54 – 7.47 (m, 4H), 7.31 – 7.26 (m, 2H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 194.1, 144.6, 134.8, 134.3, 129.2, 124.5, 120.4.

GC-MS: Calcd for $C_{13}H_8O$: 180.1; found: 180.0.



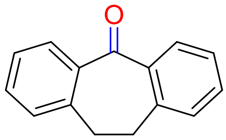
9*H*-Xanthen-9-one (2v) [90-47-1][10]

According to the general procedure, the reaction of 9*H*-xanthen-9-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (48 mg, 81% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.35 (dd, J = 7.9, 1.4 Hz, 2H), 7.75 – 7.72 (m, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 177.4, 156.3, 135.0, 126.9, 124.1, 122.0, 118.1.

GC-MS: Calcd for $C_{13}H_8O_2$: 196.1; found: 196.0.



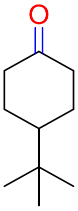
10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-one (2w) [51529-12-5][13]

According to the general procedure, the reaction of dibenzosuberol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (59 mg, 95% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 8.01 (d, J = 7.8 Hz, 2H), 7.44 – 7.42 (m, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 7.5 Hz, 2H), 3.21 (s, 4H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 195.8, 142.1, 138.8, 132.5, 130.7, 129.4, 126.8, 35.1.

GC-MS: Calcd for $C_{15}H_{12}O$: 208.1; found: 208.0.



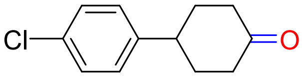
4-(*tert*-Butyl)cyclohexan-1-one (2x) [98-53-3][14]

According to the general procedure, the reaction of 4-(*tert*-butyl)cyclohexan-1-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless crystal (41 mg, 89% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 30:1 to 15:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 2.42 – 2.38 (m, 2H), 2.35 – 2.29 (m, 2H), 2.11 – 2.07 (m, 2H), 1.52 – 1.41 (m, 3H), 0.92 (s, 9H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 212.8, 46.9, 41.5, 32.6, 27.8.

GC-MS: Calcd for $C_{10}H_{18}O$: 154.1; found: 154.0.



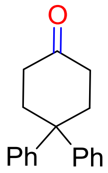
4-(4-Chlorophenyl)cyclohexan-1-one (2y) [14472-80-1][15]

According to the general procedure, the reaction of 4-(4-chlorophenyl)cyclohexan-1-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (33 mg, 53% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.04 – 2.98 (m, 1H), 2.52 – 2.49 (m, 4H), 2.21 – 2.18 (m, 2H), 1.95 – 1.87 (m, 2H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 210.8, 143.4, 132.4, 128.9, 128.2, 42.3, 41.4, 34.0.

GC-MS: Calcd for $C_{12}H_{13}ClO$: 208.1; found: 208.0.



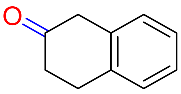
4,4-Diphenylcyclohexan-1-one (2z) [4528-68-1][16]

According to the general procedure, the reaction of 4,4-diphenylcyclohexan-1-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (69 mg, 92% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.33 – 7.32 (m, 8H), 7.24 – 7.19 (m, 2H), 2.67 (t, *J* = 6.6 Hz, 4H), 2.45 (t, *J* = 6.6 Hz, 4H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 211.2, 145.9, 128.8, 126.9, 126.5, 45.7, 38.8, 36.5.

GC-MS: Calcd for $C_{18}H_{18}O$: 250.1; found: 250.0.



3,4-Dihydronaphthalen-2(1*H*)-one (2aa) [530-93-8][17]

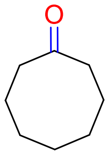
According to the general procedure, the reaction of 1,2,3,4-tetrahydronaphthalen-2-ol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a yellow oil (36 mg, 82% yield).

Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 20:1 as the eluent.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 – 7.20 (m, 3H), 7.14 – 7.12 (m, 1H), 3.59 (s, 2H), 3.06 (t, *J* = 6.7 Hz, 2H), 2.55 (t, *J* = 6.7 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 210.8, 136.8, 133.4, 128.3, 127.7, 127.03, 126.96, 45.2, 38.3, 28.5.

GC-MS: Calcd for $C_{10}H_{10}O$: 146.1; found: 146.0.



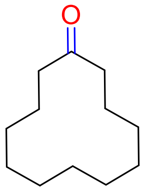
Cyclooctenone (2ab) [502-49-8][18]

According to the general procedure, the reaction of cyclooctanol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless crystal (28 mg, 75% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 80:1 to 60:1 as the eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 – 2.40 (m, 6H), 1.90 – 1.86 (m, 4H), 1.57 – 1.53 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 218.6, 42.0, 27.2, 25.7, 24.8.

GC-MS: Calcd for $C_8H_{14}O$: 126.1; found: 126.0.



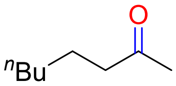
Cyclododecanone (2ac) [830-13-7][4]

According to the general procedure, the reaction of cyclododecanol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (48 mg, 87% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 80:1 to 60:1 as the eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 – 2.45 (m, 4H), 1.75 – 1.68 (m, 4H), 1.31 – 1.25 (m, 14H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.1, 40.5, 24.9, 24.7, 24.4, 22.7, 22.5.

GC-MS: Calcd for $C_{12}H_{22}O$: 182.2; found: 182.0.



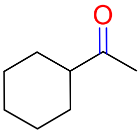
2-Octanone (2ad) [111-13-7][19]

According to the general procedure, the reaction of cyclododecanol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (35 mg, 91% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 60:1 to 30:1 as the eluent.

^1H NMR (400 MHz, $CDCl_3$): δ 2.42 (t, J = 7.5 Hz, 2H), 2.14 (s, 3H), 1.59 – 1.53 (m, 2H), 1.33 – 1.23 (m, 6H), 0.90 – 0.86 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.7, 44.0, 31.7, 30.0, 29.0, 24.0, 22.6, 14.2.

GC-MS: Calcd for $C_8H_{16}O$: 128.1; found: 128.1.



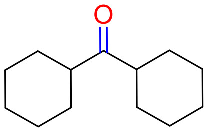
1-Cyclohexylethan-1-one (2ae) [823-76-7][2]

According to the general procedure, the reaction of cyclododecanol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (37 mg, 99% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 60:1 to 20:1 as the eluent.

^1H NMR (400 MHz, $CDCl_3$): 2.34 – 2.27 (m, 1H), 2.10 (s, 3H), 1.87 – 1.82 (m, 2H), 1.78 – 1.73 (m, 2H), 1.67 – 1.62 (m, 1H), 1.35 – 1.19 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.6, 51.6, 28.5, 28.0, 26.0, 25.8.

GC-MS: Calcd for $C_8H_{14}O$: 126.1; found: 126.0.



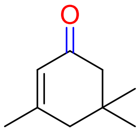
Dicyclohexylmethanone (2ai) [119-60-8][20]

According to the general procedure, the reaction of dicyclohexylmethanol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (28 mg, 48% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 30:1 to 15:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 2.50 – 2.46 (m, 2H), 1.80 – 1.75 (m, 8H), 1.68 – 1.65 (m, 2H), 1.36 – 1.16 (m, 10H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 217.3, 49.3, 28.7, 26.0, 25.9.

GC-MS: Calcd for $C_{13}H_{22}O$: 194.2; found: 194.0.



3,5,5-Trimethylcyclohex-2-en-1-one (2ak) [78-59-1][2]

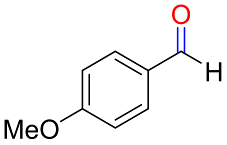
According to the general procedure, the reaction of 3,5,5-trimethylcyclohex-2-en-1-ol (12 mmol), Ni(OTf)$_2$ (0.24 mmol), dcype (0.48 mmol) and cyclohexanone (60 mmol) in dioxane (60 mL) with stirring under reflux for 12 h, afforded the title compound as a colorless oil (1.1 g, 66% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 10:1 to 5:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 5.89 (s, 1H), 2.20 (s, 2H), 2.17 (s, 2H), 1.94 (s, 3H), 1.04 (s, 6H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 200.0, 160.4, 125.6, 50.9, 45.4, 33.6, 28.4, 24.6.

GC-MS: Calcd for $C_9H_{14}O$: 138.1; found: 138.0.

The formation and the yields of **2al** and **2am** were determined by GC using standard samples as the reference, and further confirmed by GC-MS analyses.



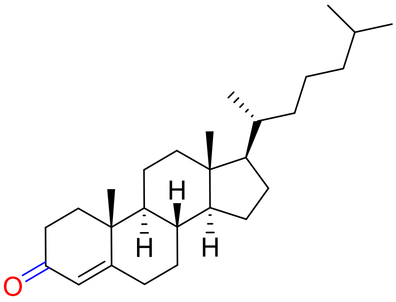
4-Methoxybenzaldehyde (2an) [123-11-5][21]

According to the general procedure, the reaction of cyclododecanol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a light yellow oil (20 mg, 50% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 40:1 to 10:1 as the eluent.

^{1}H NMR (600 MHz, $CDCl_3$): 9.82 (s, 1H), 7.79 – 7.76 (m, 2H), 6.95 – 6.93 (m, 2H), 3.83 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 190.9, 164.6, 132.0, 130.0, 114.3, 55.6.

GC-MS: Calcd for $C_8H_8O_2$: 136.1; found: 136.0.



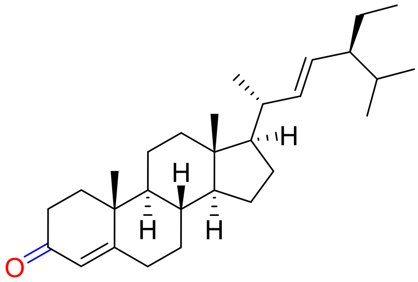
Cholest-4-en-3-one (2ao) [601-57-0][2]

According to the general procedure, the reaction of sterol derivative (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in DMSO (1.5 mL) with stirring at 110 °C for 12 h, afforded the title compound as a white solid (99 mg, 87% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 20:1 to 10:1 as the eluent.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.72 (s, 1H), 2.45 – 2.31 (m, 3H), 2.28 – 2.25 (m, 1H), 2.05 – 2.01 (m, 2H), 1.86 – 1.82 (m, 2H), 1.72 – 1.67 (m, 2H), 1.63 – 1.58 (m, 1H), 1.55 – 1.48 (m, 3H), 1.46 – 1.24 (m, 6H), 1.18 (s, 3H), 1.16 – 1.07 (m, 6H), 1.00 – 0.97 (m, 3H), 0.91 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 2.7 Hz, 3H), 0.86 (d, J = 2.7 Hz, 3H), 0.71 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 199.8, 171.9, 123.9, 56.2, 56.0, 54.0, 42.5, 39.8, 39.6, 38.7, 36.3, 35.9, 35.82, 35.75, 34.1, 33.1, 32.2, 28.3, 28.1, 24.3, 24.0, 23.0, 22.7, 21.2, 18.8, 17.5, 12.1.

HRMS (ESI): Calcd for $C_{27}H_{44}O$ $[M+H]^+$: 385.3465; found: 385.3469.



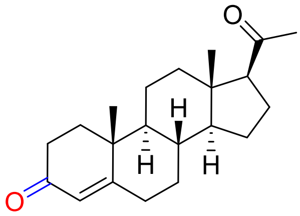
Stigmasta-4,22-dien-3-one (2ap) [20817-72-5][22]

According to the general procedure, the reaction of (8*S*,9S,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,5*S*,*E*)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol (0.3 mmol), $Ni(OTf)_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (77 mg, 63% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 20:1 to 10:1 as the eluent.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.72 (s, 1H), 5.15 (dd, J = 15.1, 8.7 Hz, 1H), 5.02 (dd, J = 15.1, 8.7 Hz, 1H), 2.45 – 2.32 (m, 3H), 2.28 – 2.24 (m, 1H), 2.08 – 2.00 (m, 3H), 1.86 – 1.82 (m, 1H), 1.75 – 1.66 (m, 3H), 1.61 – 1.50 (m, 5H), 1.47 – 1.39 (m, 2H), 1.33 – 1.25 (m, 2H), 1.18 (s, 3H), 1.17 – 1.04 (m, 4H), 1.02 (d, J = 6.6 Hz, 3H), 0.95 – 0.89 (m, 1H), 0.85 (d, J = 6.2 Hz, 3H), 0.82 – 0.80 (t, J = 7.5 Hz, 6H), 0.73 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 199.8, 171.8, 138.3, 129.6, 123.9, 56.1, 56.0, 54.0, 51.4, 42.4, 40.6, 39.7, 38.8, 35.83, 35.75, 34.1, 33.1, 32.2, 32.0, 29.0, 25.5, 24.4, 21.3, 21.23, 21.15, 19.1, 17.5, 12.4, 12.3.

HRMS (ESI): Calcd for $C_{29}H_{46}O$ $[M+H]^+$: 411.3621; found: 411.3629.



Progesterone (2aq) [57-83-0][2]

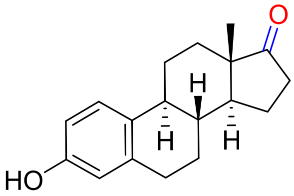
According to the general procedure, the reaction of 1-((8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-3-hydroxy-10,13-

dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)ethan-1-one (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in DMSO (1.5 mL) with stirring at 110 °C for 12 h, afforded the title compound as a white solid (81 mg, 86% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 10:1 to 5:1 as the eluent.

^{1}H NMR (400 MHz, CDCl$_3$): δ 5.74 (s, 1H), 2.55 – 2.52 (m, 1H), 2.46 – 2.27 (m, 4H), 2.22 – 2.16 (m, 1H), 2.13 (s, 3H), 2.08 – 2.02 (m, 2H), 1.89 – 1.85 (m, 1H), 1.74 – 1.63 (m, 5H), 1.59 – 1.53 (m, 1H), 1.50 – 1.42 (m, 2H), 1.31 – 1.25 (m, 1H), 1.19 (s, 3H), 1.18 – 1.15 (m, 1H), 1.10 – 0.96 (m, 2H), 0.67 (s, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 209.4, 199.6, 171.0, 124.1, 63.6, 56.1, 53.8, 44.0, 38.8, 38.7, 35.8, 35.7, 34.1, 32.9, 32.1, 31.6, 24.5, 23.0, 21.1, 17.5, 13.5.

GC-MS: Calcd for $C_{21}H_{30}O_2$: 314.2; found: 314.0.



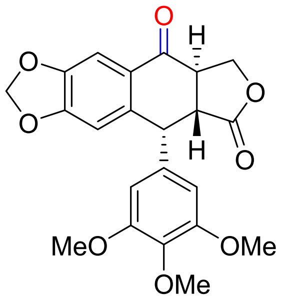
Estrone (2ar) [53-16-7][23]

According to the general procedure, the reaction of estradiol (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in toluene (1.5 mL) with stirring under reflux for 12 h, afforded the title compound as a white solid (68 mg, 84% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 30:1 to 15:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.15 (d, J = 8.4 Hz, 1H), 6.64 (dd, J = 8.4, 2.7 Hz, 1H), 6.59 (d, J = 2.5 Hz, 1H), 4.85 (s, 1H), 2.89 – 2.86 (m, 2H), 2.53 – 2.48 (m, 1H), 2.40 – 2.37 (m, 1H), 2.26 – 2.22 (m, 1H), 2.18 – 2.12 (m, 1H), 2.08 – 2.03 (m, 1H), 2.02 – 1.94 (m, 2H), 1.61 – 1.40 (m, 6H), 0.91 (s, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 221.3, 153.7, 138.2, 132.3, 126.7, 115.4, 113.0, 50.6, 48.2, 44.1, 38.5, 36.0, 31.7, 29.6, 26.6, 26.1, 21.7, 14.0.

GC-MS: Calcd for $C_{18}H_{22}O_2$: 270.2; found: 270.0.



Podophyllotone (2as) [477-49-6][24]

According to the general procedure, the reaction of podophyllotoxin (0.3 mmol), Ni(OTf)$_2$ (0.006 mmol), dcype (0.012 mmol) and cyclohexanone (1.5 mmol) in DMA (1.5 mL) with stirring at 110 °C for 12 h, afforded the title compound as a white solid (57 mg, 46% yield). Purification conditions: Flash column chromatography over silica gel using petroleum ether/EA 20:1 to 10:1 as the eluent.

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.56 (s, 1H), 6.70 (s, 1H), 6.39 (s, 2H), 6.09 (d, J = 12.3 Hz, 2H), 4.85 (d, J = 4.3 Hz, 1H), 4.58 – 4.55 (m, 1H), 4.38 – 4.34 (m, 1H), 3.82 (s, 3H), 3.75 (s, 6H), 3.55 – 3.49 (m, 1H), 3.30 – 3.26 (m, 1H).

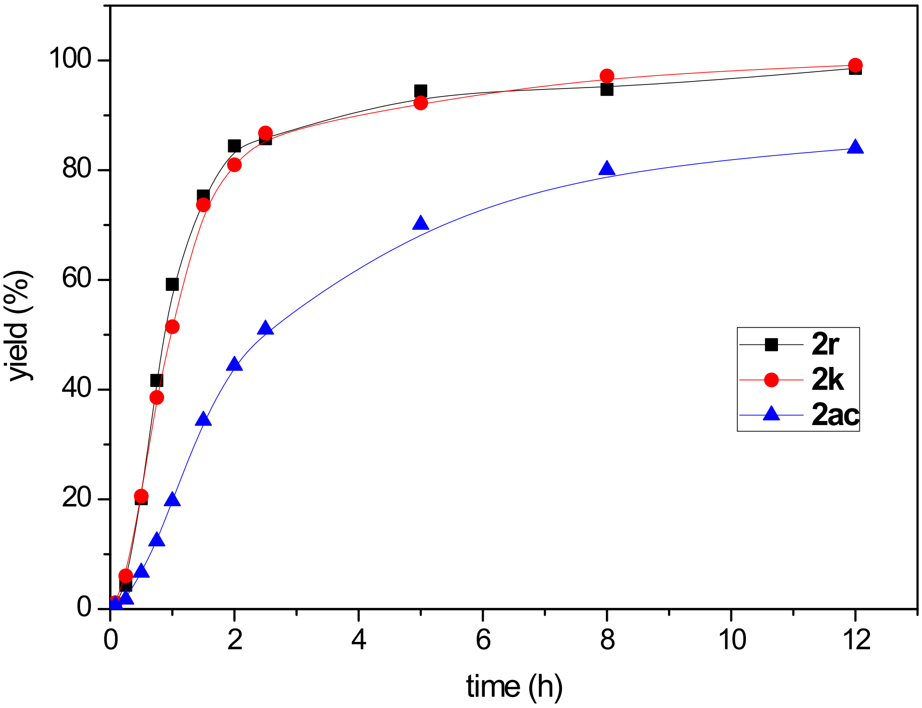
^{13}C NMR (150 MHz, CDCl$_3$): δ 192.6, 173.2, 153.2, 148.2, 141.6, 137.8, 132.2, 128.3, 109.8, 107.8, 106.2, 102.5, 67.1, 60.8, 56.4, 46.8, 44.8, 43.6.

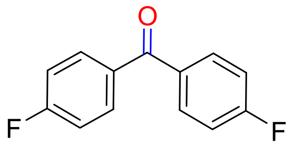
HRMS (ESI): Calcd for $C_{22}H_{20}O_8$ [M+H]$^+$: 413.1231; found: 413.1234.

4. Mechanistic studies:

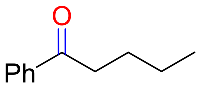
(a) Reaction kinetics for three representative alcohols

Typical procedure: in an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with Ni(OTf)$_2$ (1.4 mg, 0.004 mmol), dcype (3.4 mg, 0.008 mmol), and 1.0 mL of toluene. After stirring at room temperature for 5 minutes, alcohol (0.2 mmol), cyclohexanone (98 mg, 1.0 mmol), and GC standard dodecane (20 μL) were then added sequentially. The tube was capped tightly and the reaction mixture was heated on an oil bath maintained at 120 ^{o}C. At intervals, aliquots of the reaction mixture were taken in the glove box and passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC analysis for determination of the conversion of alcohol and to allow calibrated quantification of the GC yields of the associated ketone products.

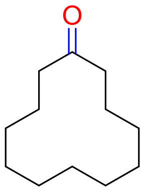




2r



2k

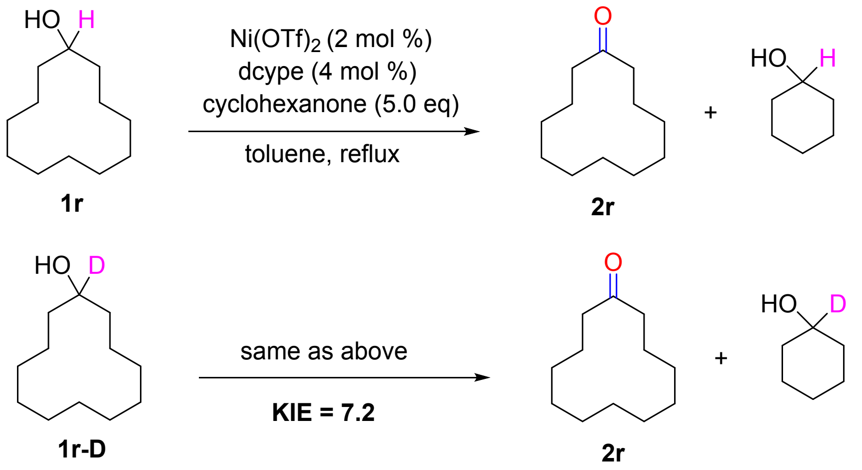


2ac

Figure S1. Plot of yield vs. time for the reaction of **1ac**, **1k** and **1r**.

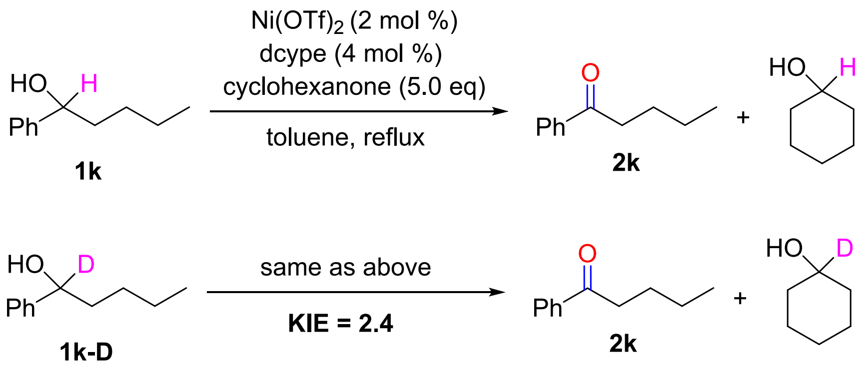
(b) Kinetic isotope experiments (KIE) carried out in parallel in two separate vessels

Typical procedure: In an argon-filled glove box, A 10-mL Schlenk tube containing a magnetic stir bar was charged with the alcohol of interest (0.2 mmol), Ni(OTf)$_2$ (1.4 mg, 0.004 mmol), dcype (3.4 mg, 0.008 mmol), cyclohexanone (98 mg, 1.0 mmol), the GC standard dedecane (20 μL), and 1.0 mL of toluene. A separate tube was charged in exactly the same way except that the corresponding deuterated alcohol (0.2 mmol) was added instead. The two tubes were capped tightly and the reactions were heated on an oil bath pre-heated at 120 °C. At 15 min, aliquots of the reaction mixtures were passed through a short plug of silica gel with ethyl acetate washings. The filtrates were subjected to GC analysis so as to determine the extent of conversion of alcohol and to allow calibrated quantification of the GC yields of the associated ketone products.



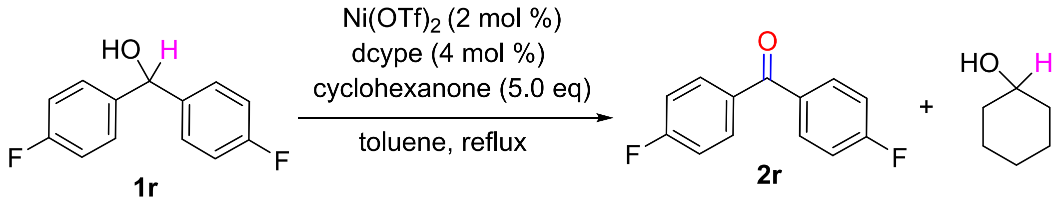
product	0.25 h	0.75 h
non-labeled product (%)	1.63	6.14
d-labeled product (%)	0.23	0.86

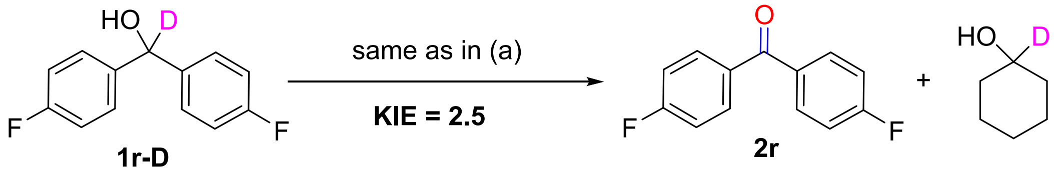
The initial KIE value at 0.25 h was calculated to be 7.2.



product	yield (%)
non-labeled product	6.0
d-labeled product	2.5

The initial KIE value at 0.25 h was calculated to be 2.4.





product	yield (%)
non-labeled product	4.3
d-labeled product	1.7

The initial KIE value at 0.25 h was calculated to be 2.5.

5. Supplemental references

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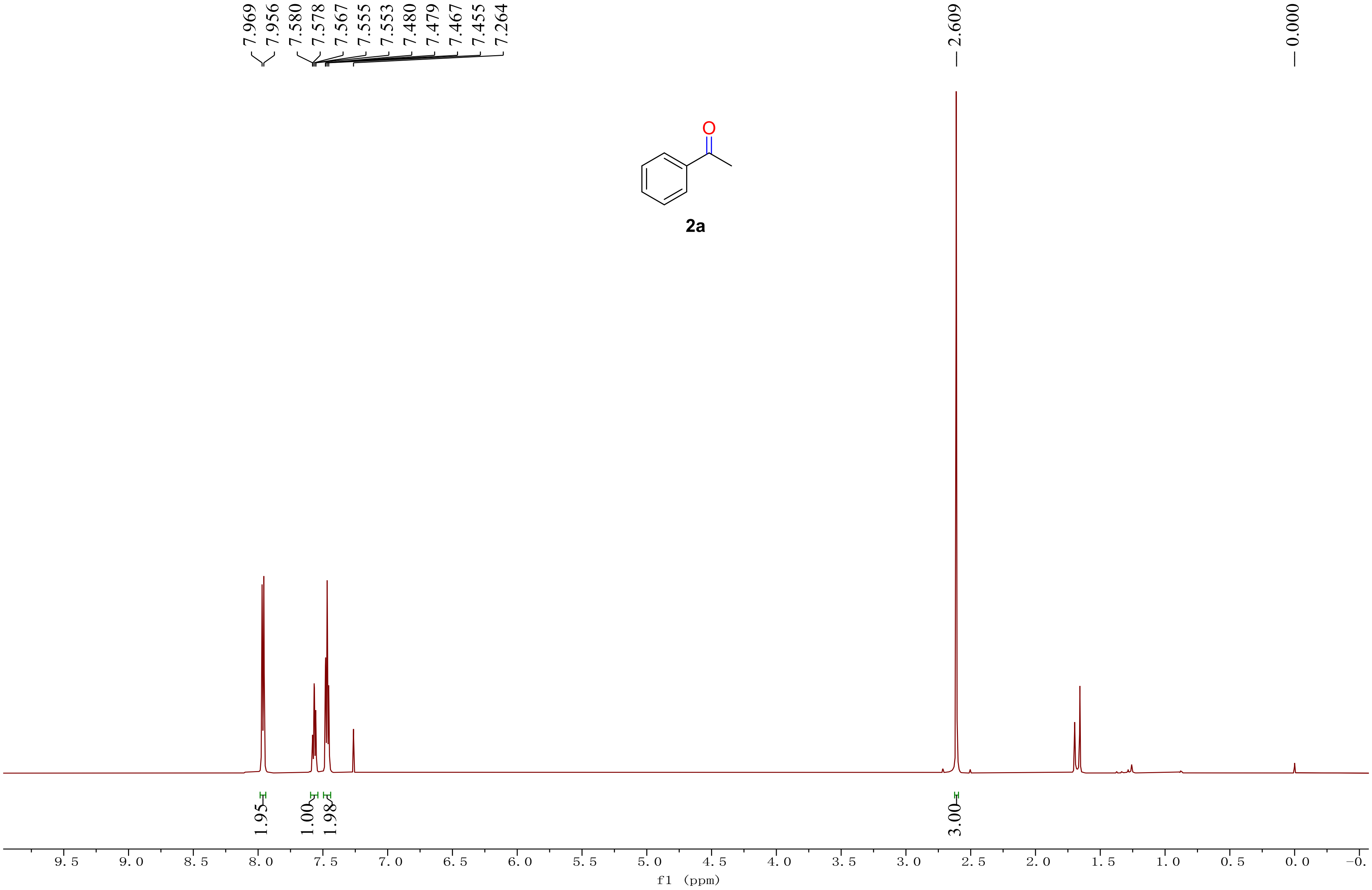
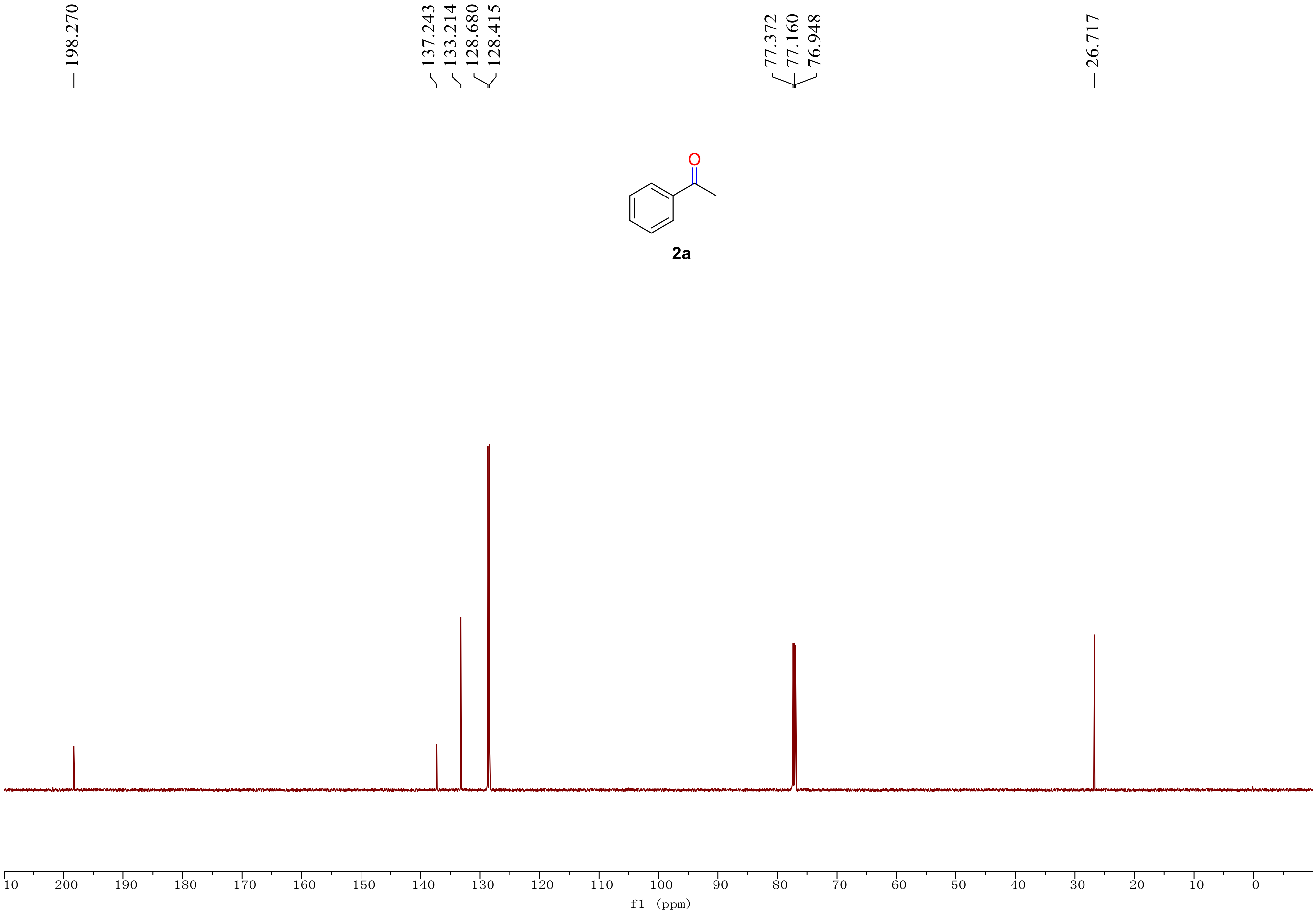
6. NMR Spectra



2a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133.214
128.680
128.415
77.372
77.160
76.948
26.717
O
2a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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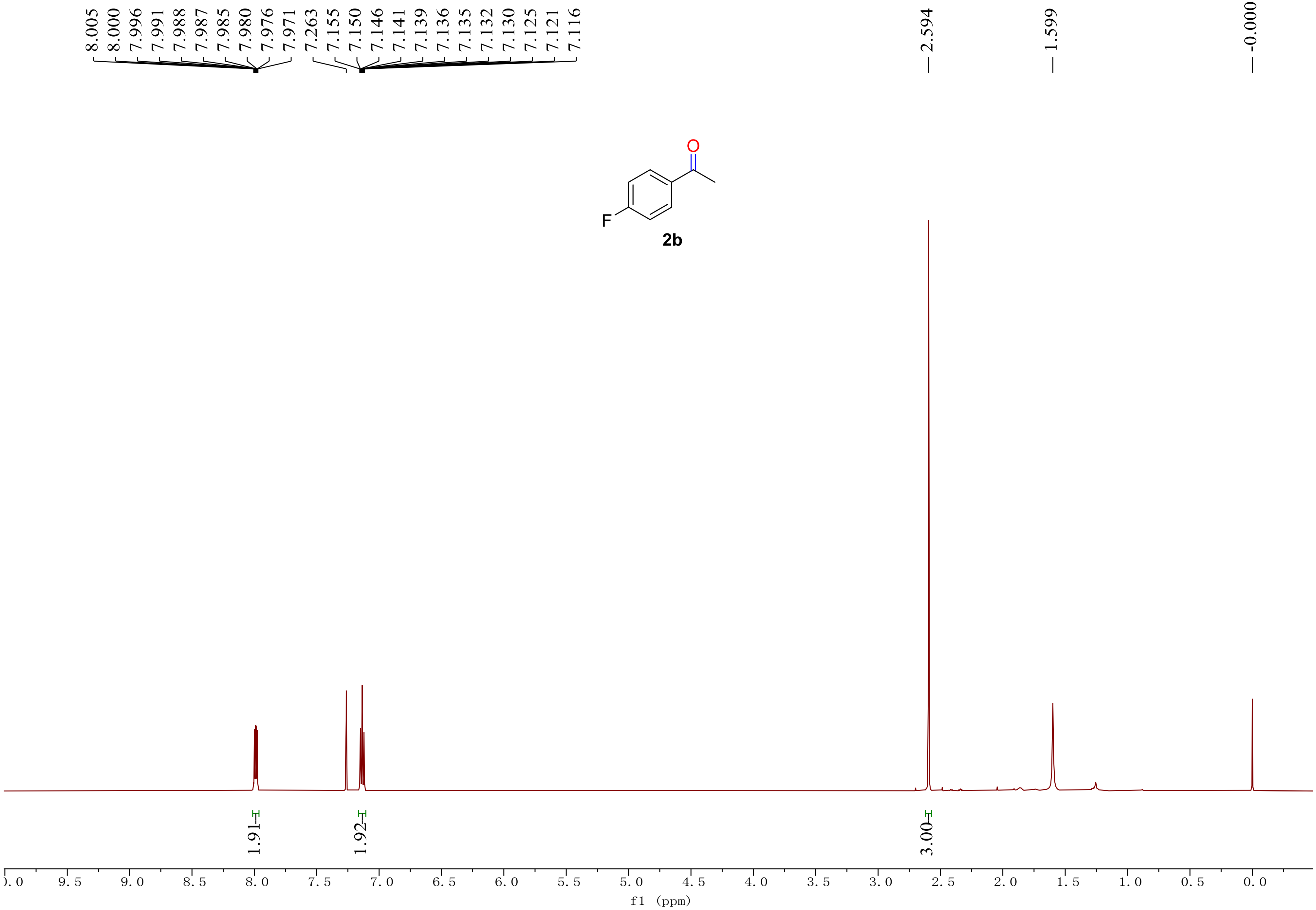
f1 (ppm)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8.000
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7.988
7.987
7.985
7.980
7.976
7.971
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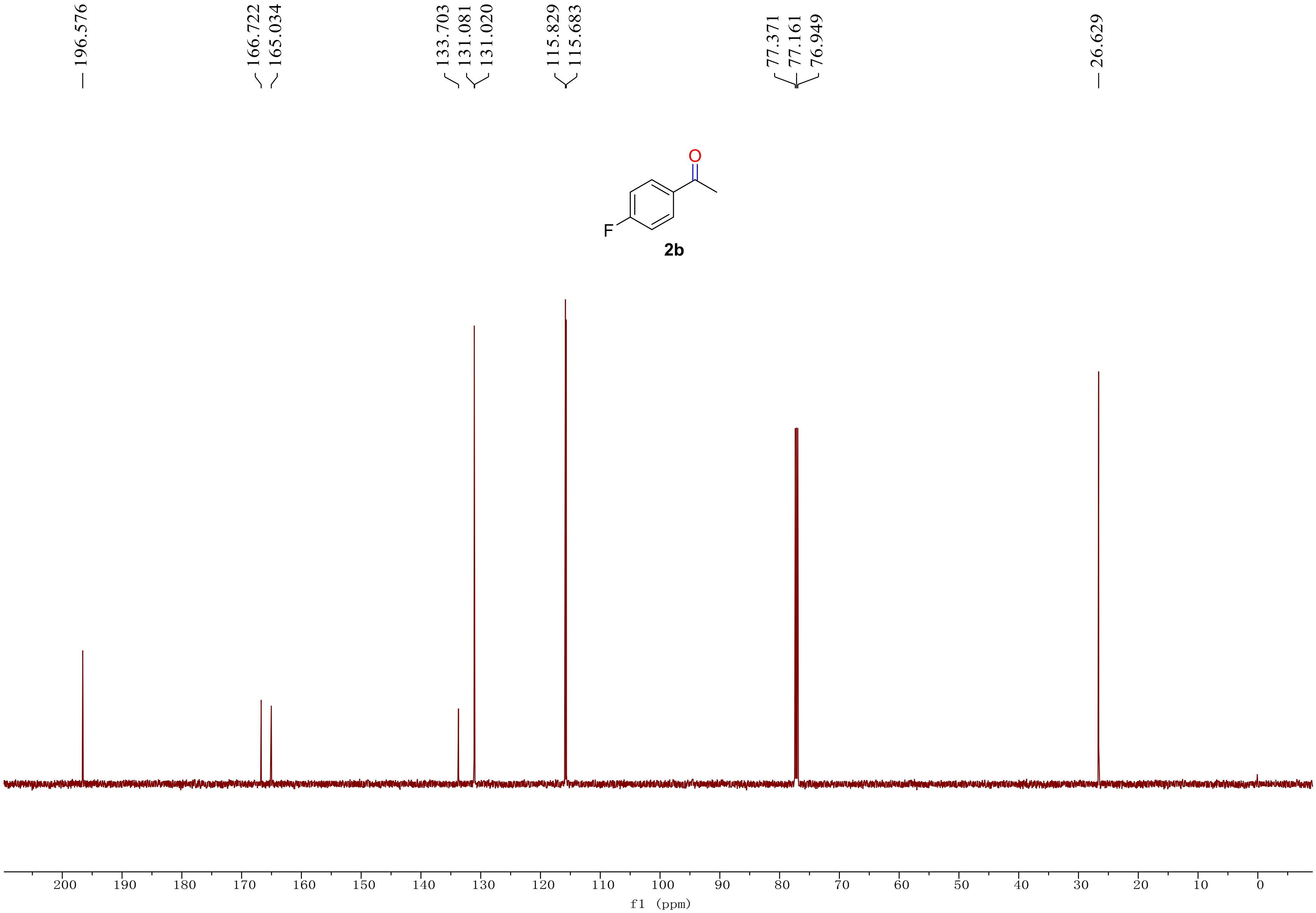
7.155
7.150
7.146
7.141
7.139
7.136
7.135
7.132
7.130
7.125
7.121
7.116
2.594
1.599
-0.000
O
F
1.91
1.92
3.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2b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131.020
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115.683
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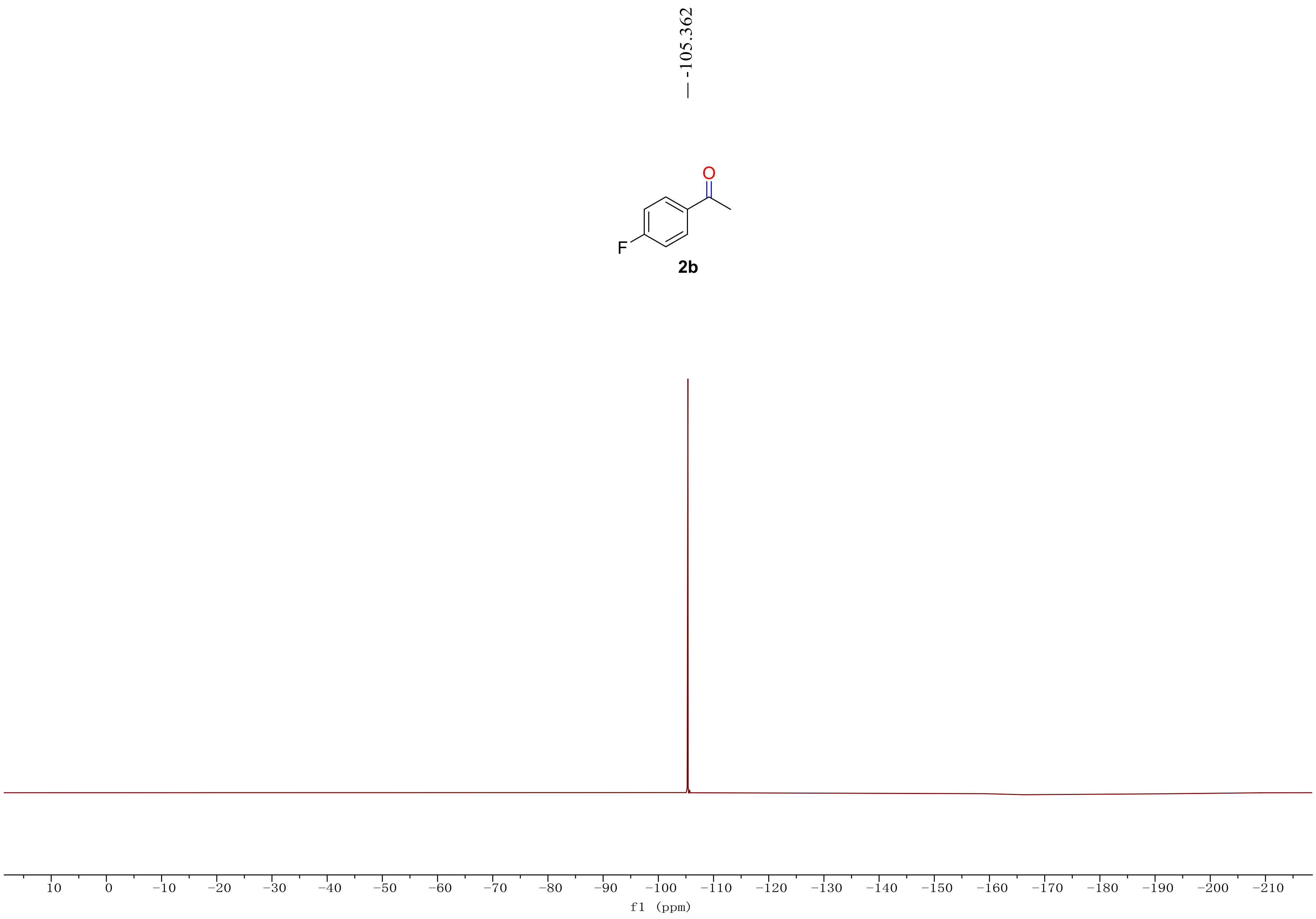
77.161
76.949
26.629
O
F
2b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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F
2b
10
0
−10
−20
−30
−40
−50
−60
−70
−80
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−100
−110
−120
−130
−140
−150
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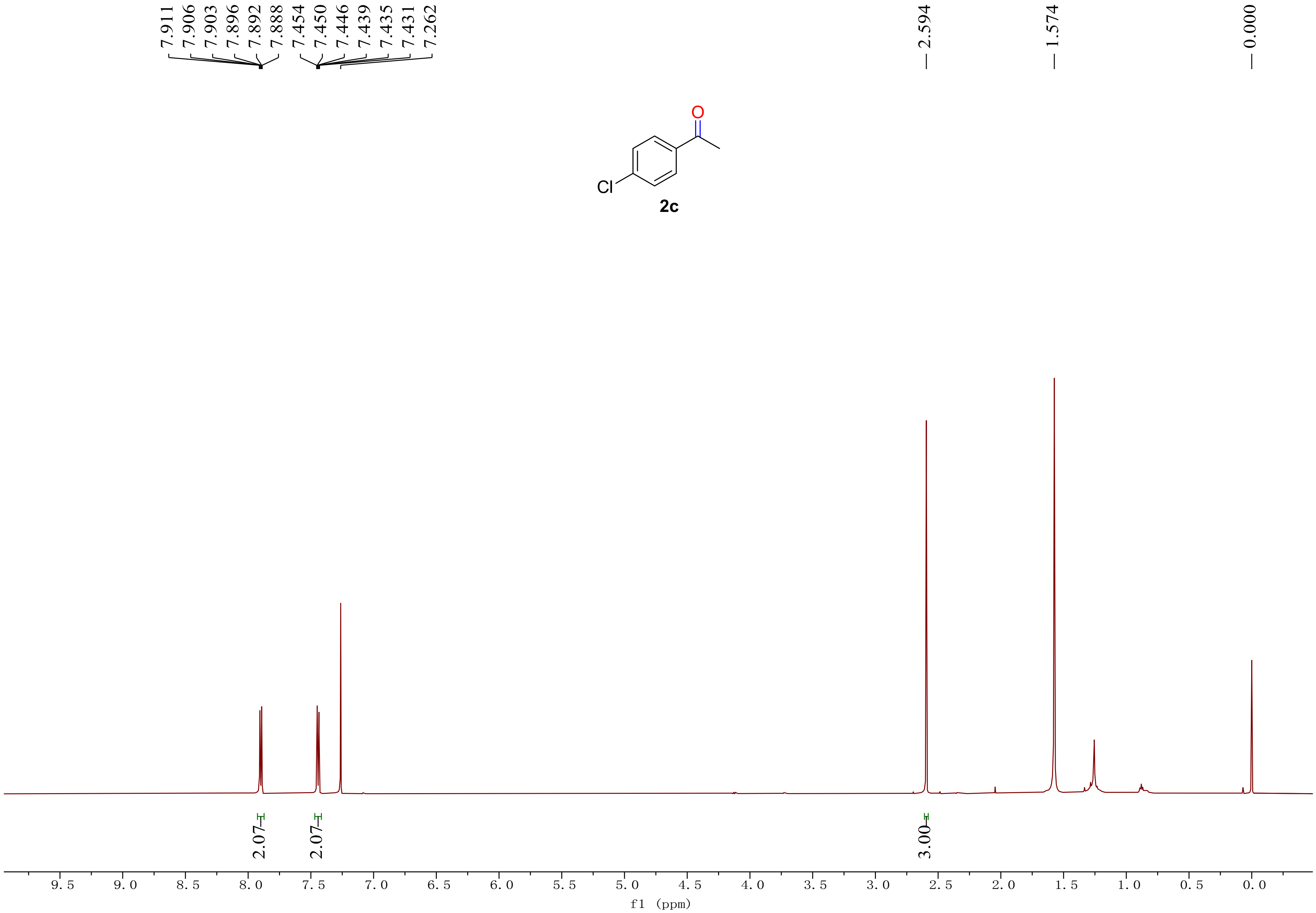
−170
−180
−190
−200
−210
f1 (ppm)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7.450
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7.439
7.435
7.431
7.262
2.594
1.574
0.000
O
Cl
2c
2.07
2.07
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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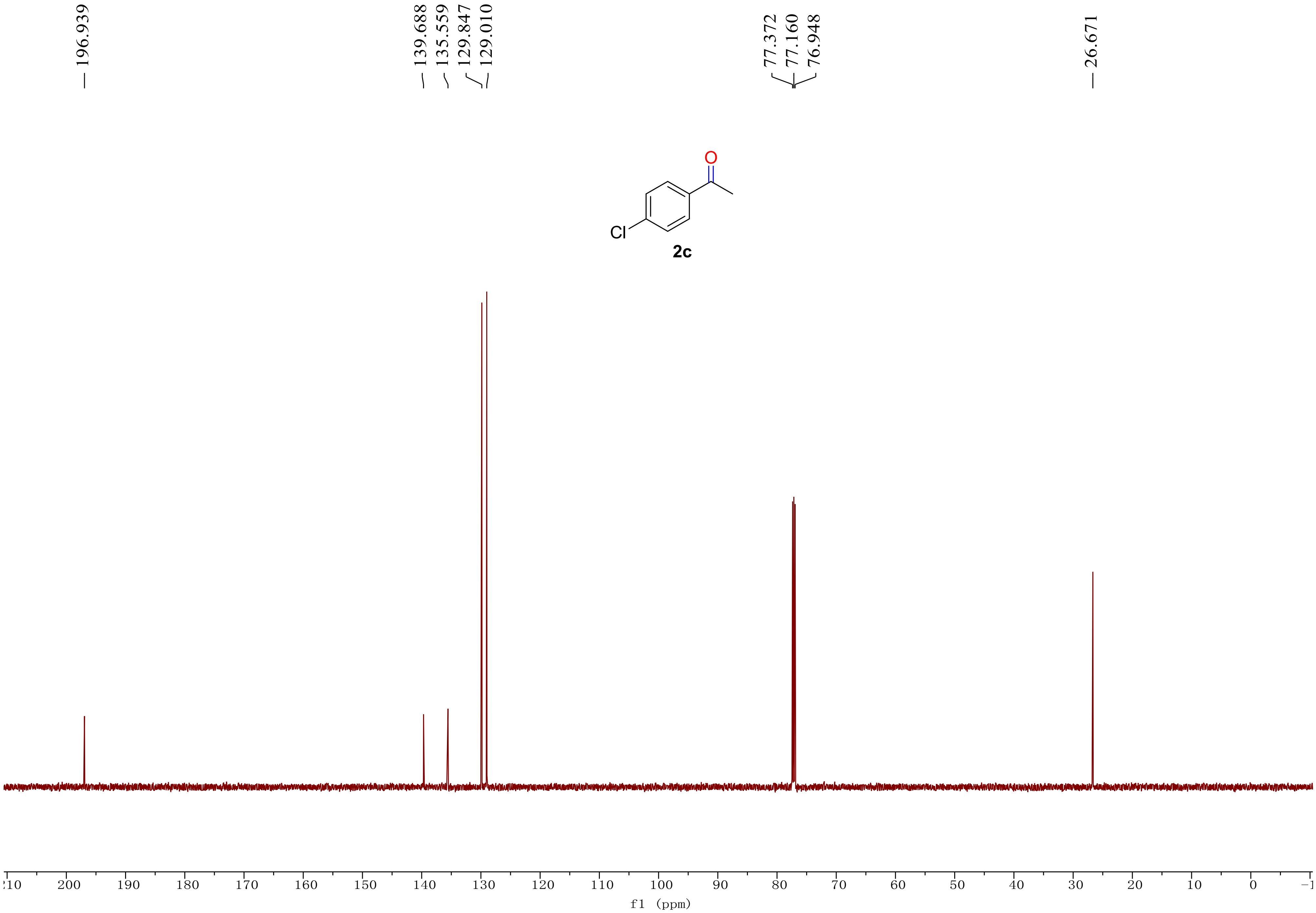
0.0
f1 (ppm)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76.948
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Cl
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200
190
180
170
160
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140
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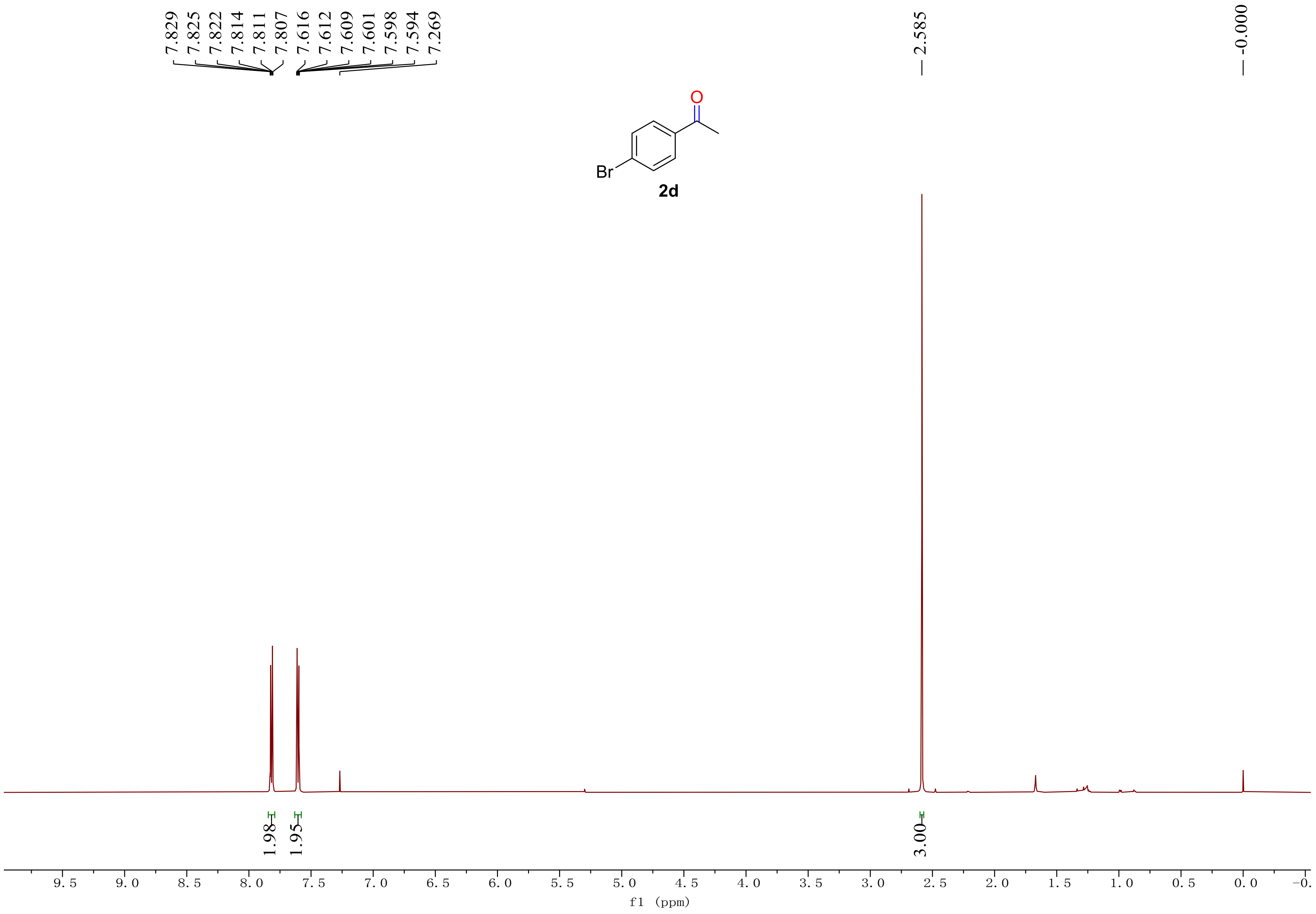
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

2c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7.601
7.598
7.594
7.269
2.585
-0.000
O
Br
2d
1.98
1.95
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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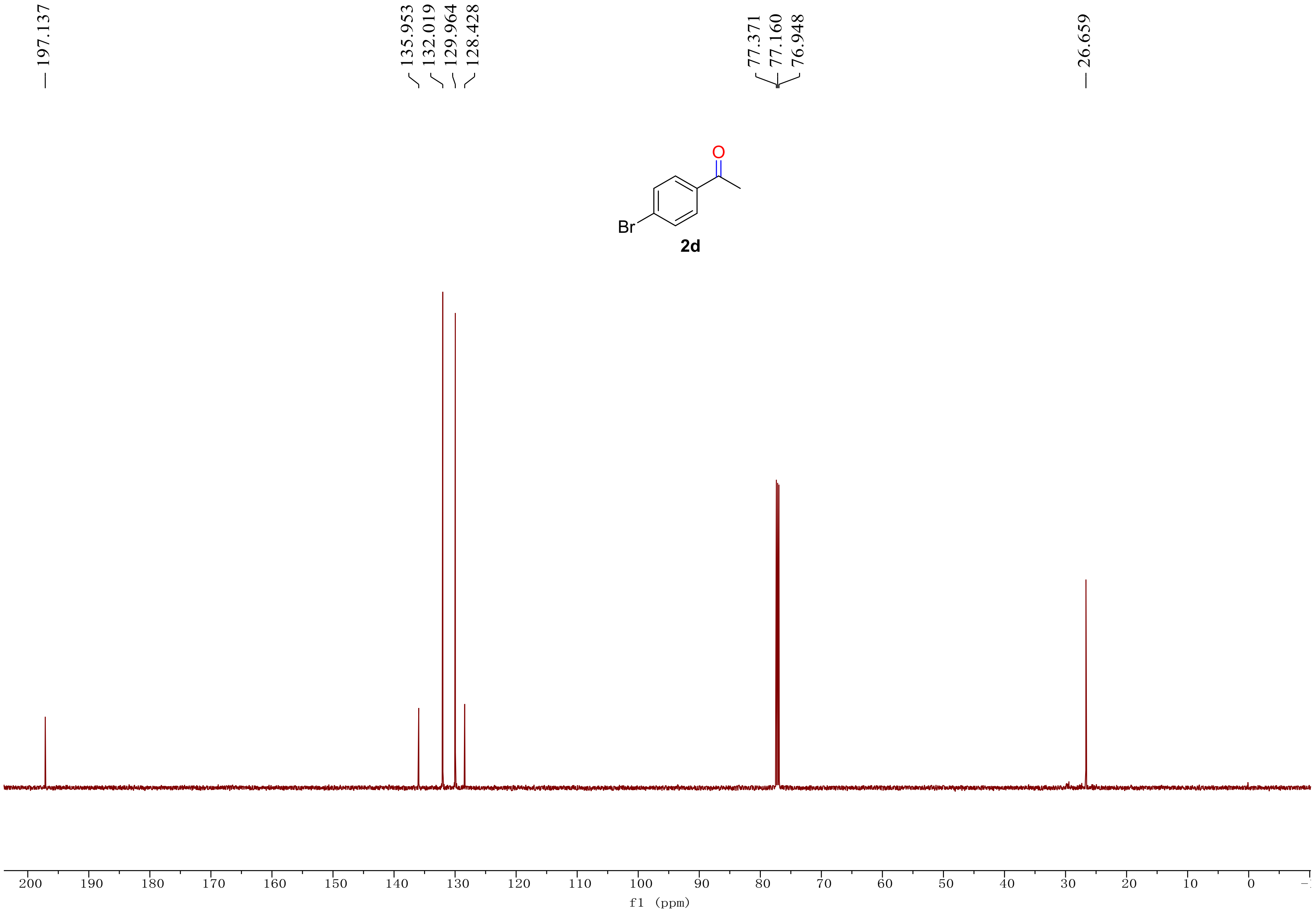
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)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128.428
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76.948
26.659
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Br
2d
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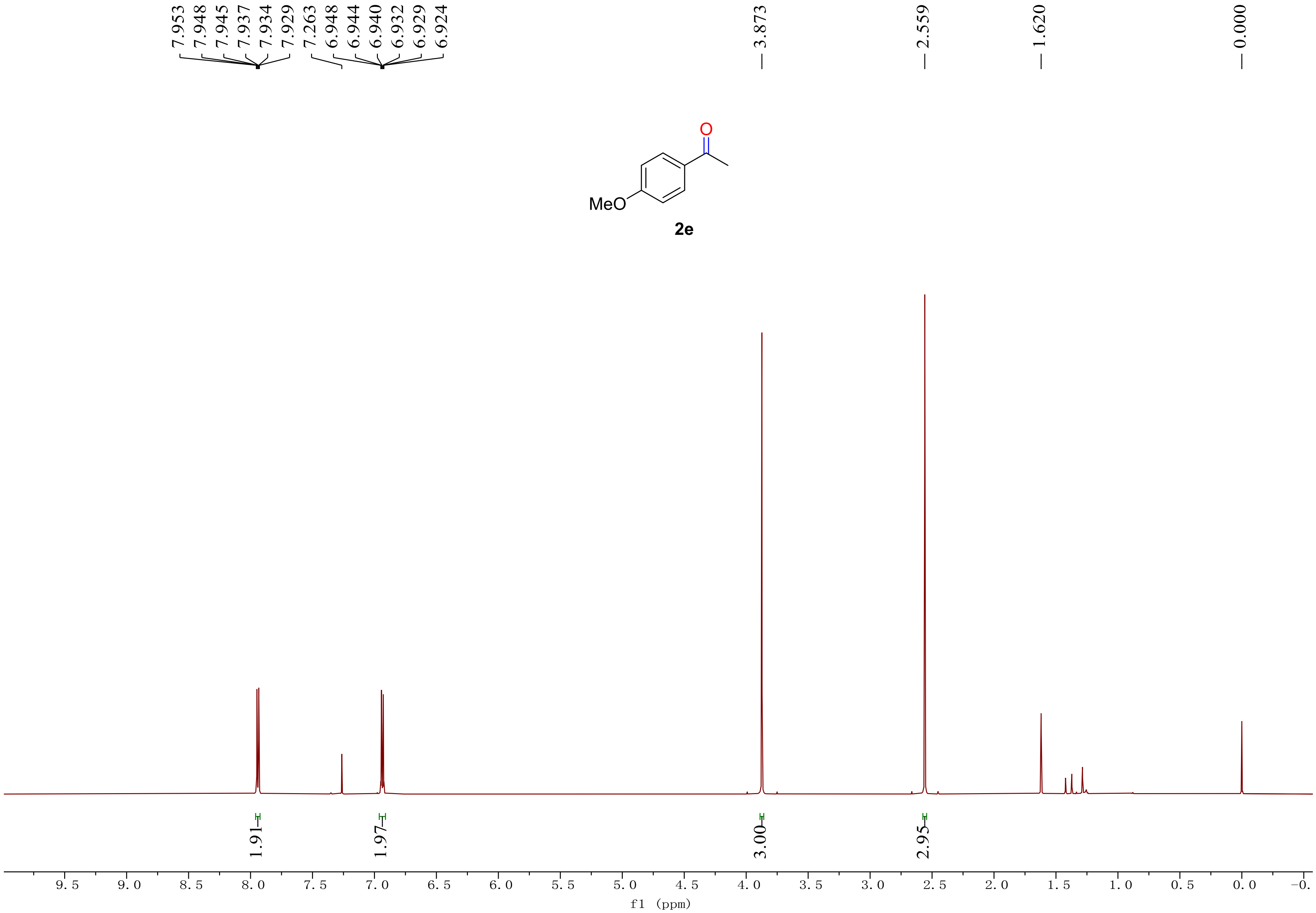
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.929
6.924
3.873
2.559
1.620
0.000
O
MeO
2e
1.91
1.97
3.00
2.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
2.5
2.0
1.5
1.0
0.5
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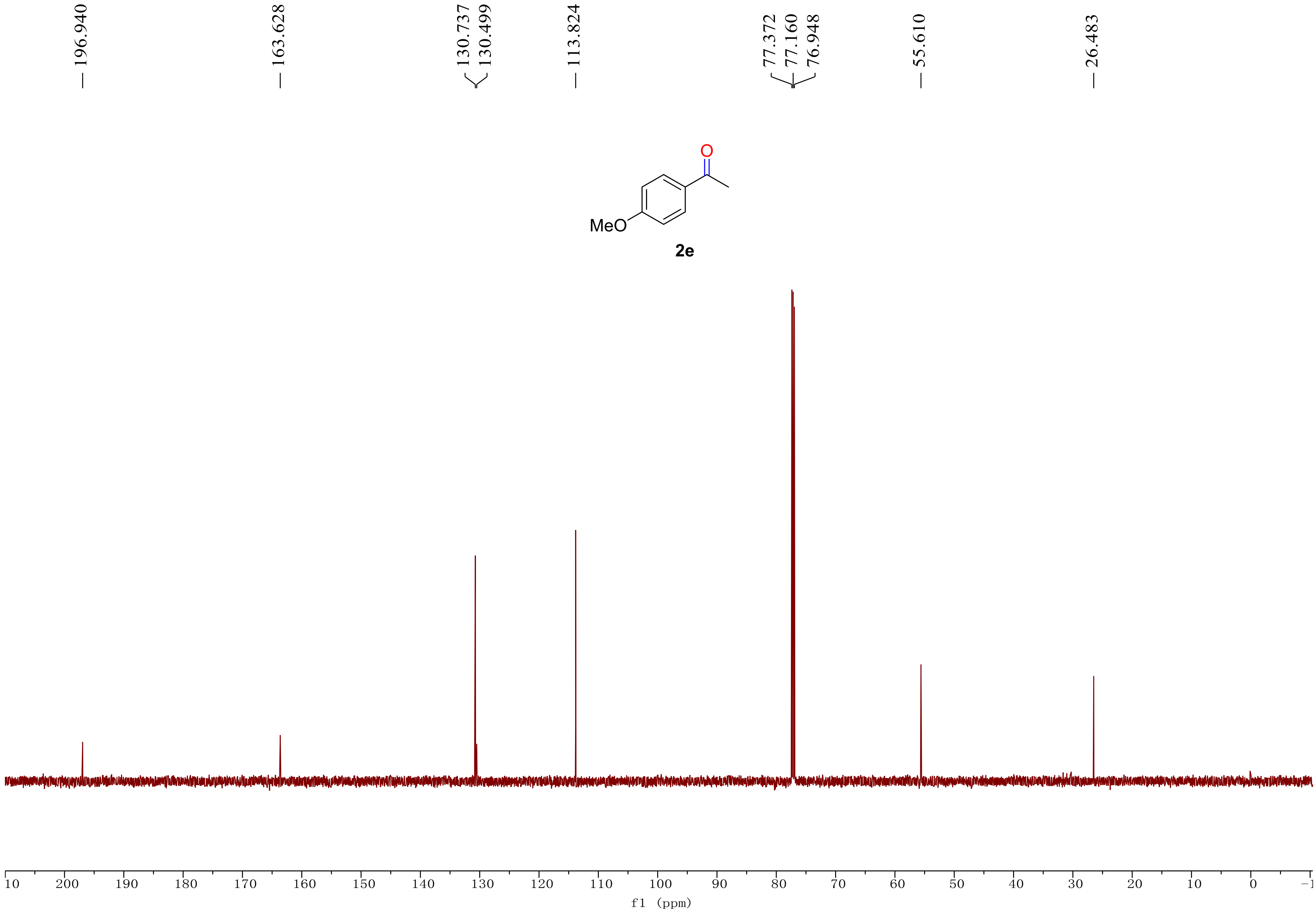
-0.
f1 (ppm)


2e

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77.160
76.948
55.610
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MeO
O
10
200
190
180
170
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150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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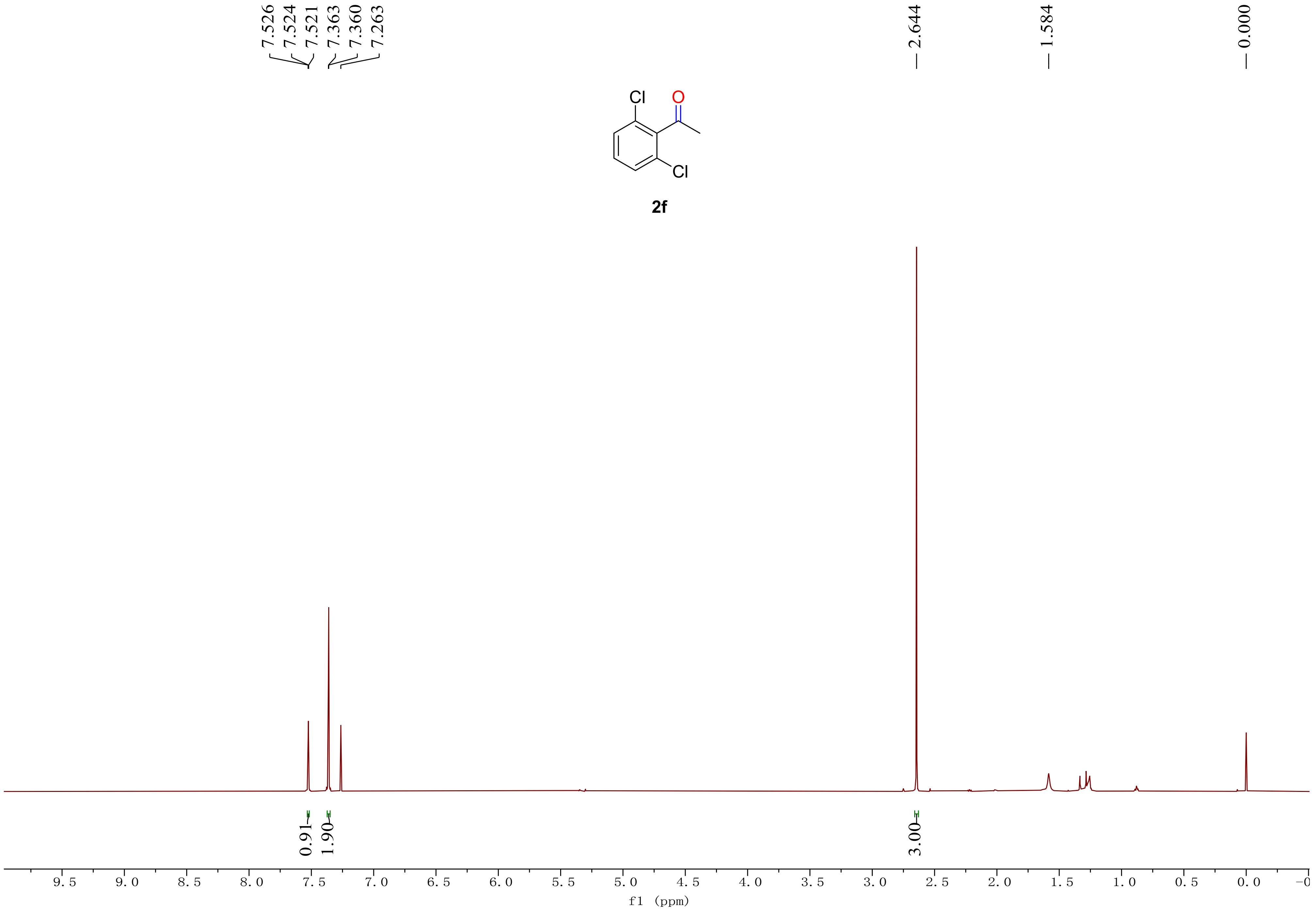
−1
f1 (ppm)



2f

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7.360
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1.584
0.000
Cl
O
Cl
0.91
1.90
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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5.5
5.0
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3.0
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1.0
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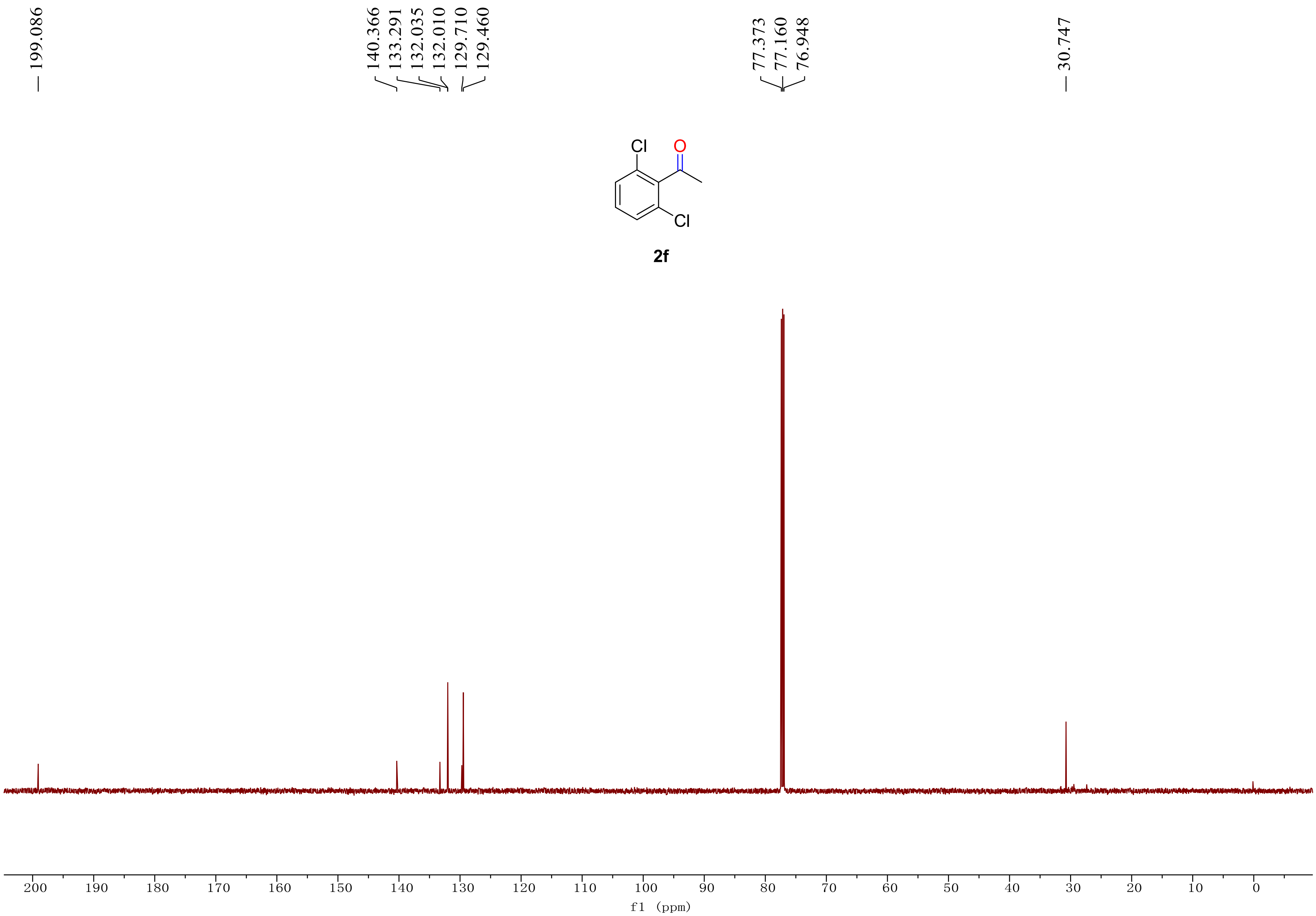
f1 (ppm)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Cl
2f
200
190
180
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150
140
130
120
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100
90
80
70
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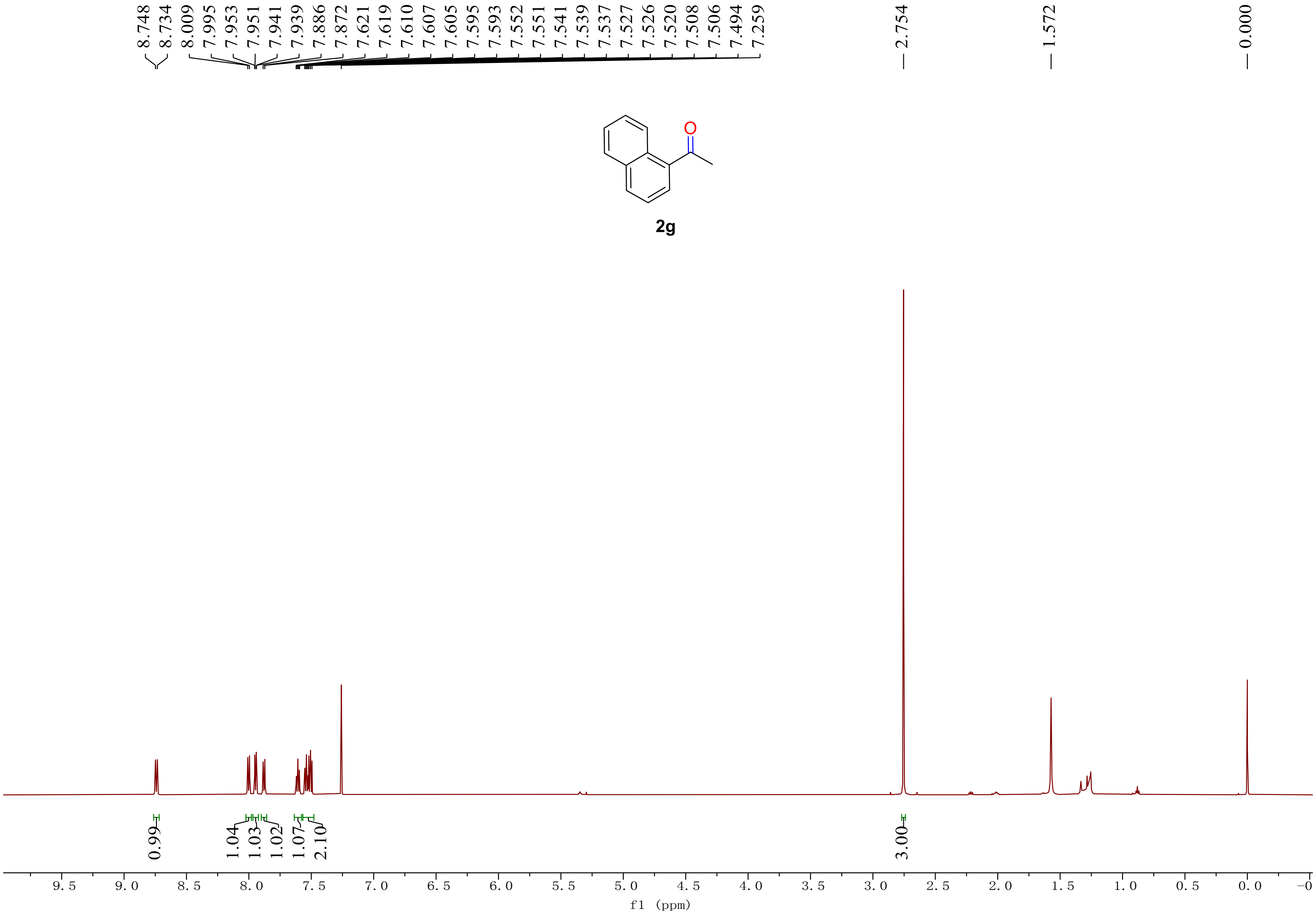
50
40
30
20
10
0
f1 (ppm)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7.619
7.610
7.607
7.605
7.595
7.593
7.552
7.551
7.541
7.539
7.537
7.527
7.526
7.520
7.508
7.506
7.494
7.259
2.754
1.572
0.000
O
2g
0.99
1.04
1.03
1.02
1.07
2.10
3.00
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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3.0
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1.0
0.5
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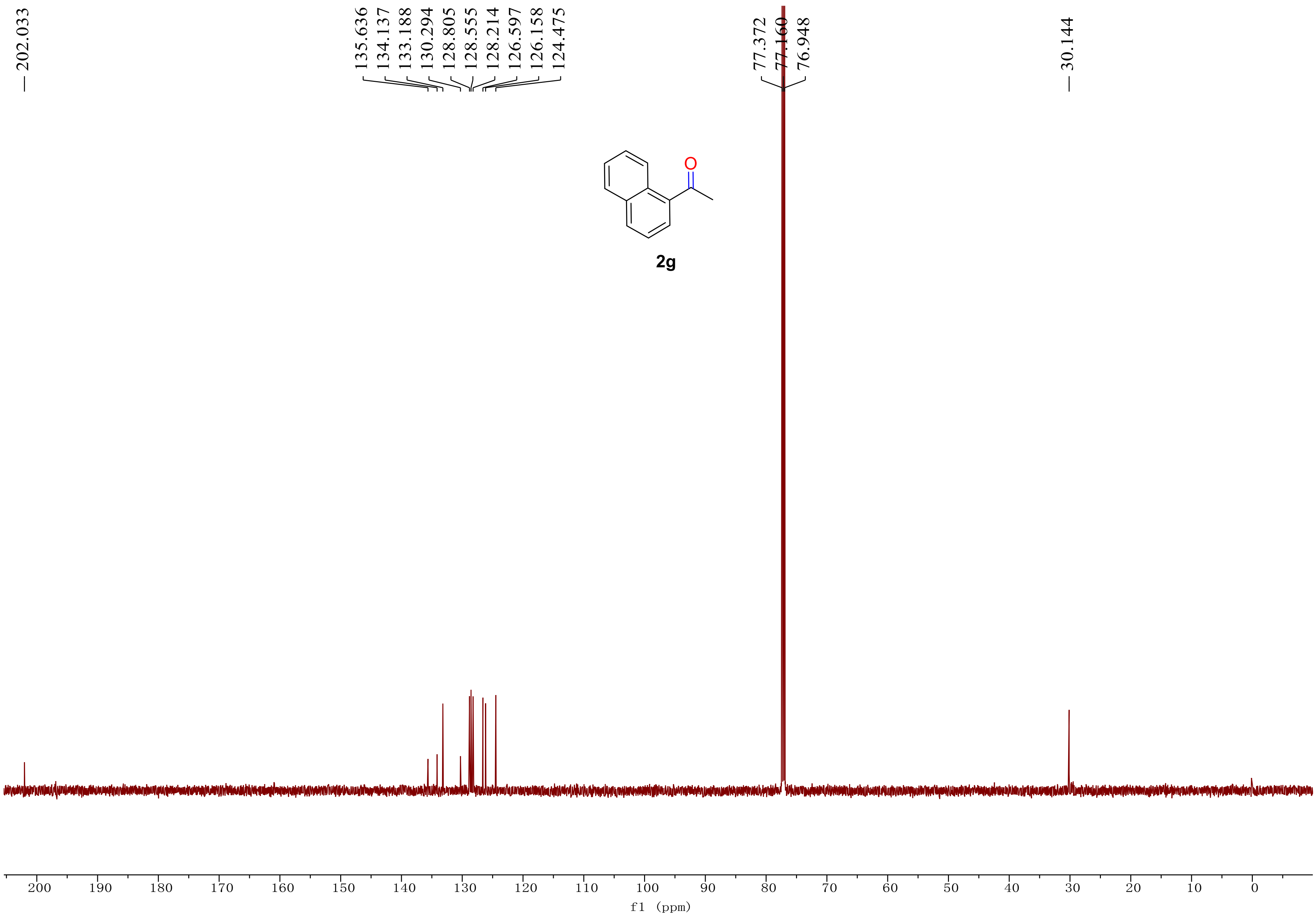
f1 (ppm)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77.160
76.948
30.144
O
200
190
180
170
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30
20
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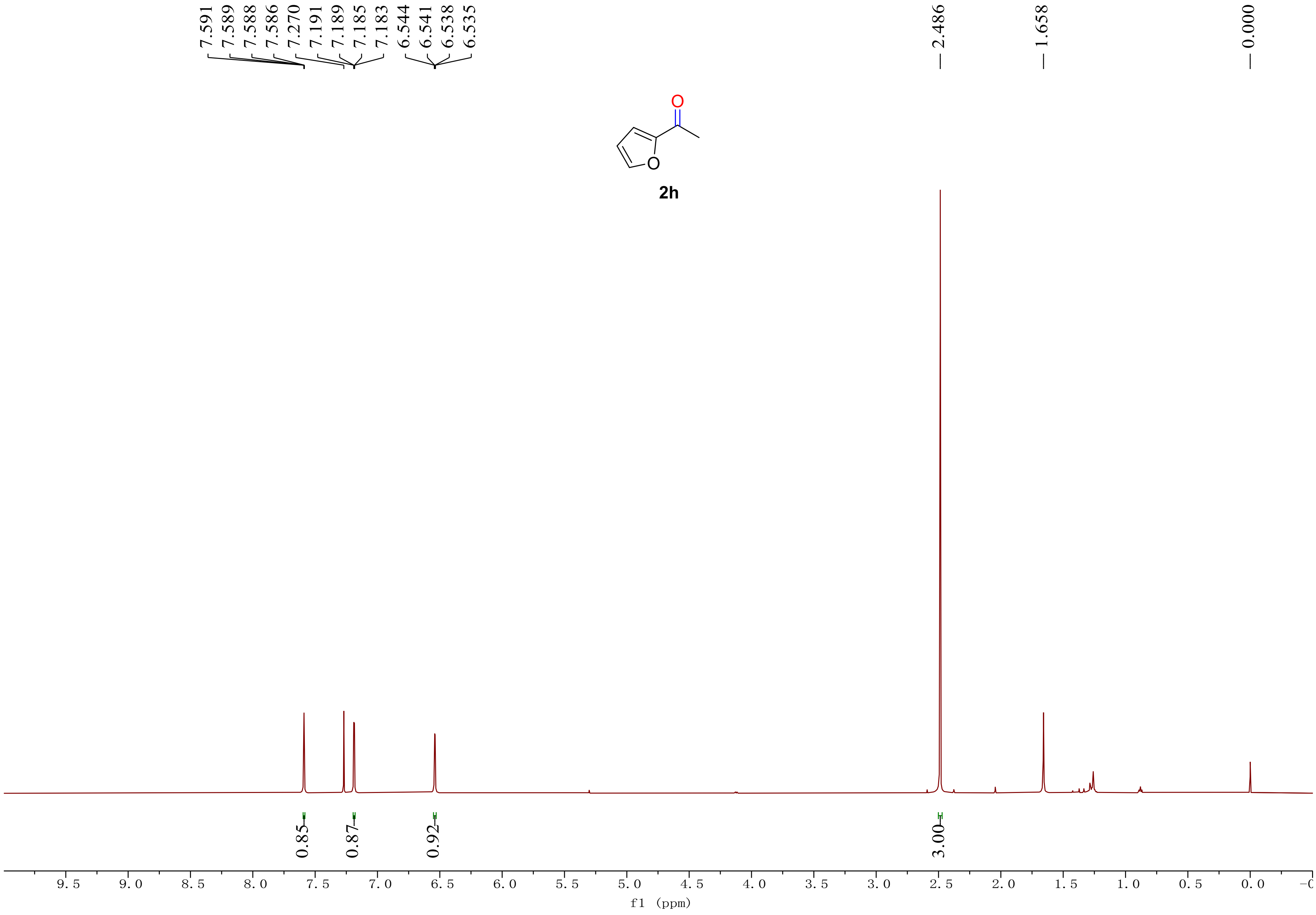
0
f1 (ppm)

2g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6.535
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O
2h
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0.87
0.92
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8.0
7.5
7.0
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6.0
5.5
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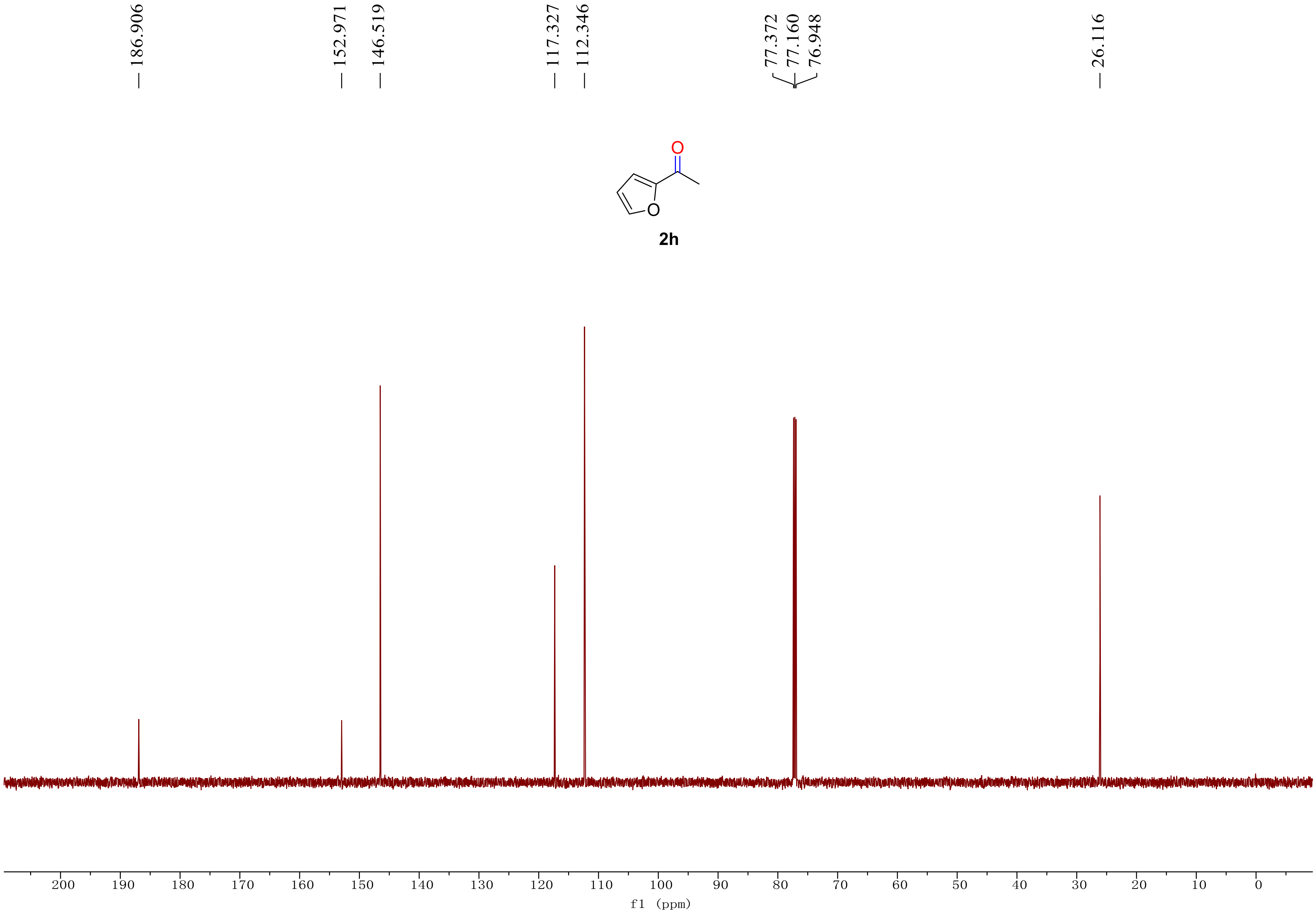
1.5
1.0
0.5
0.0
f1 (ppm)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76.948
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O
2h
200
190
180
170
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150
140
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90
80
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50
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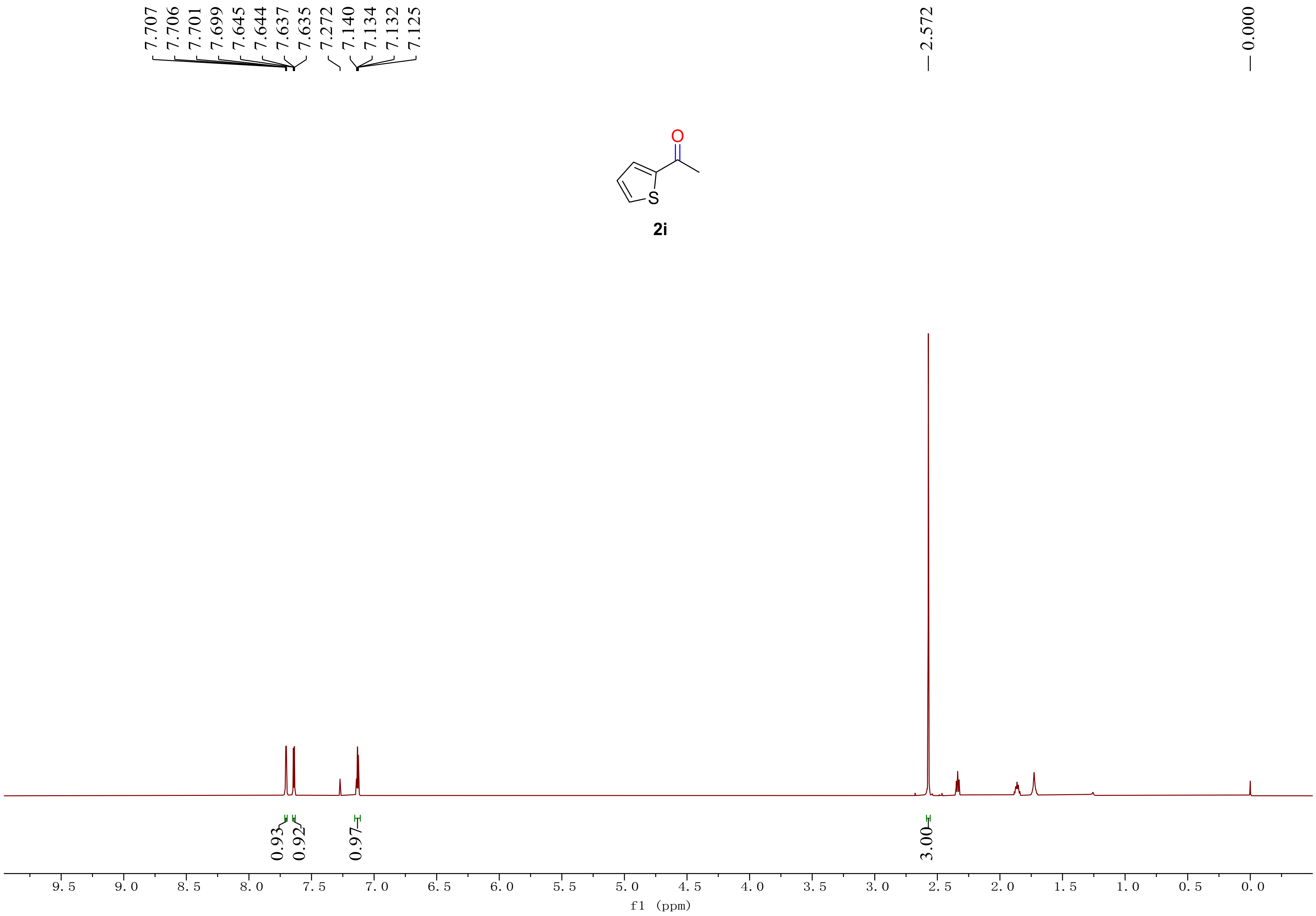
f1 (ppm)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7.125
2.572
0.000
O
S
2i
0.93
0.92
0.97
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
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2.5
2.0
1.5
1.0
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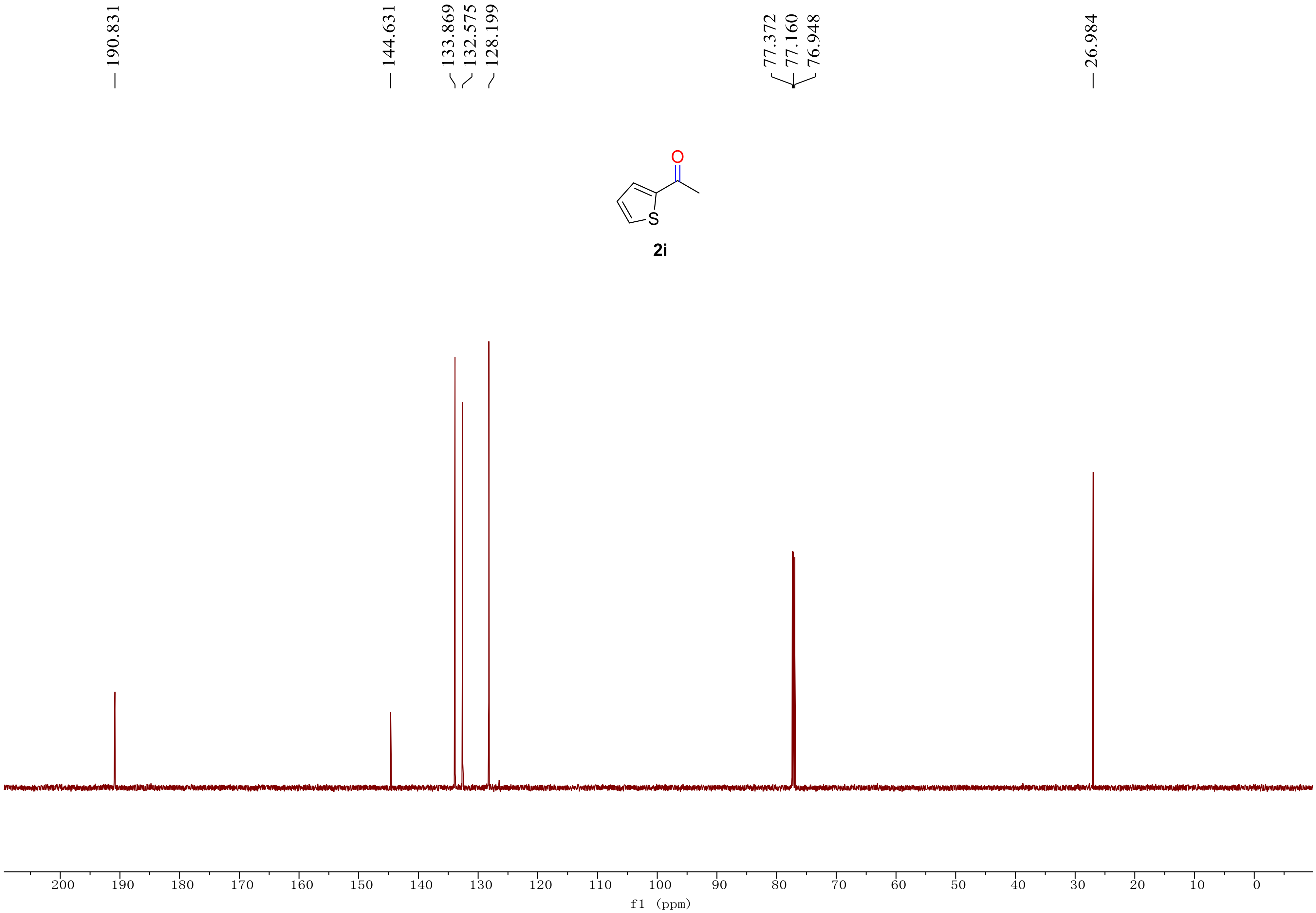
f1 (ppm)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S
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190
180
170
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100
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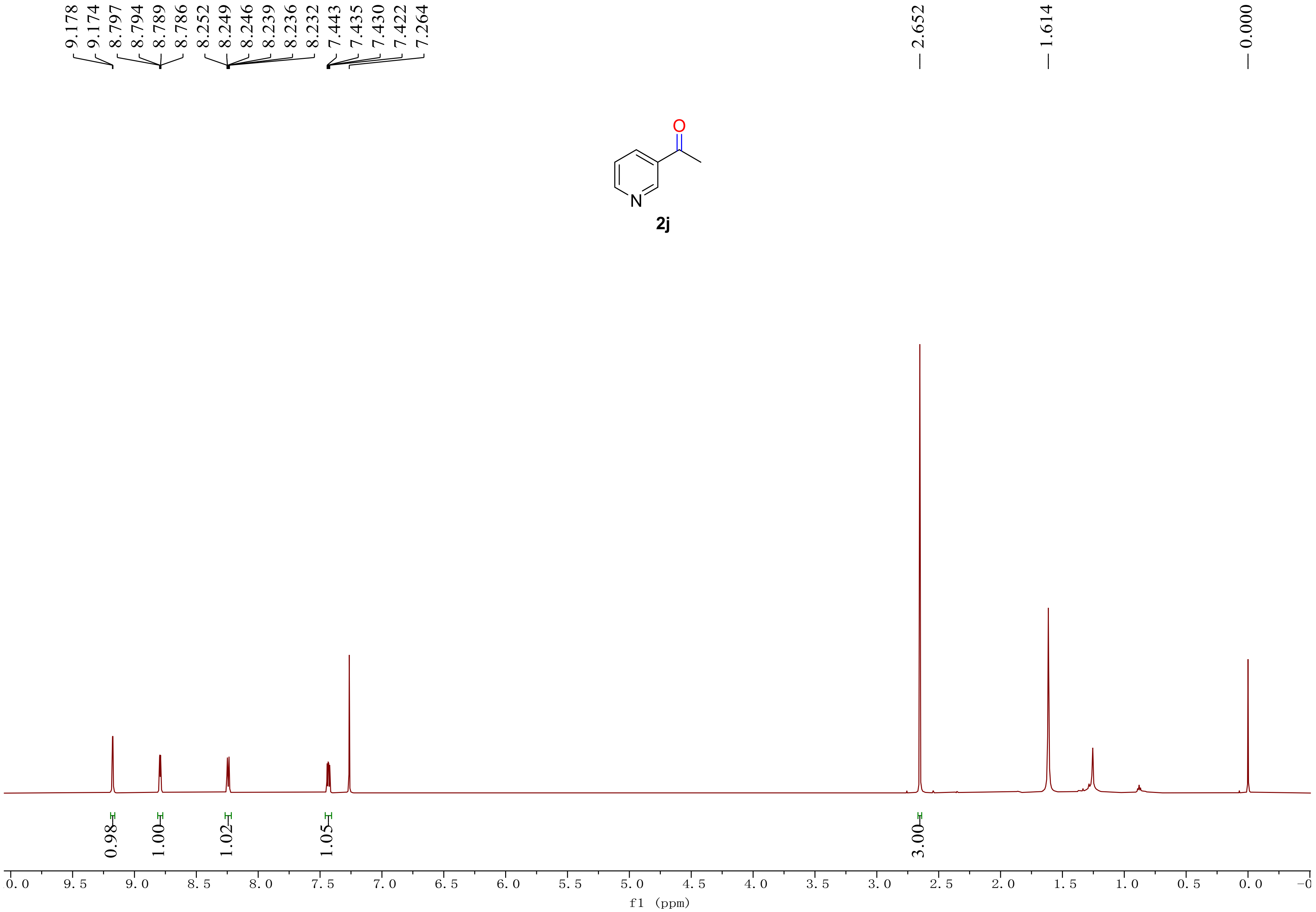
60
50
40
30
20
10
0
f1 (ppm)

2i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7.443
7.435
7.430
7.422
7.264
2.652
1.614
0.000
O
N
2j
0.98
1.00
1.02
1.05
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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1.5
1.0
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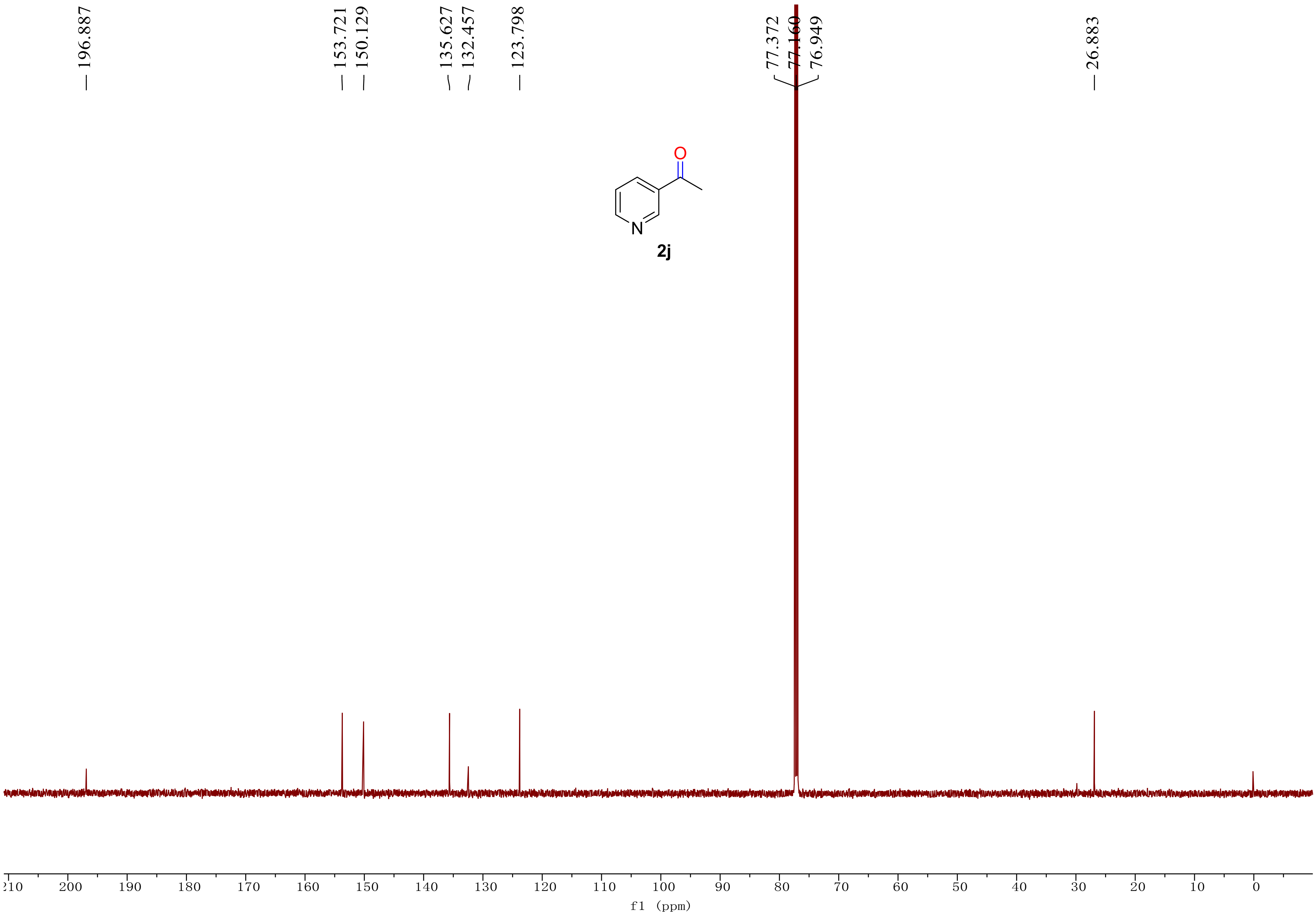
f1 (ppm)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26.883
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200
190
180
170
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130
120
110
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90
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50
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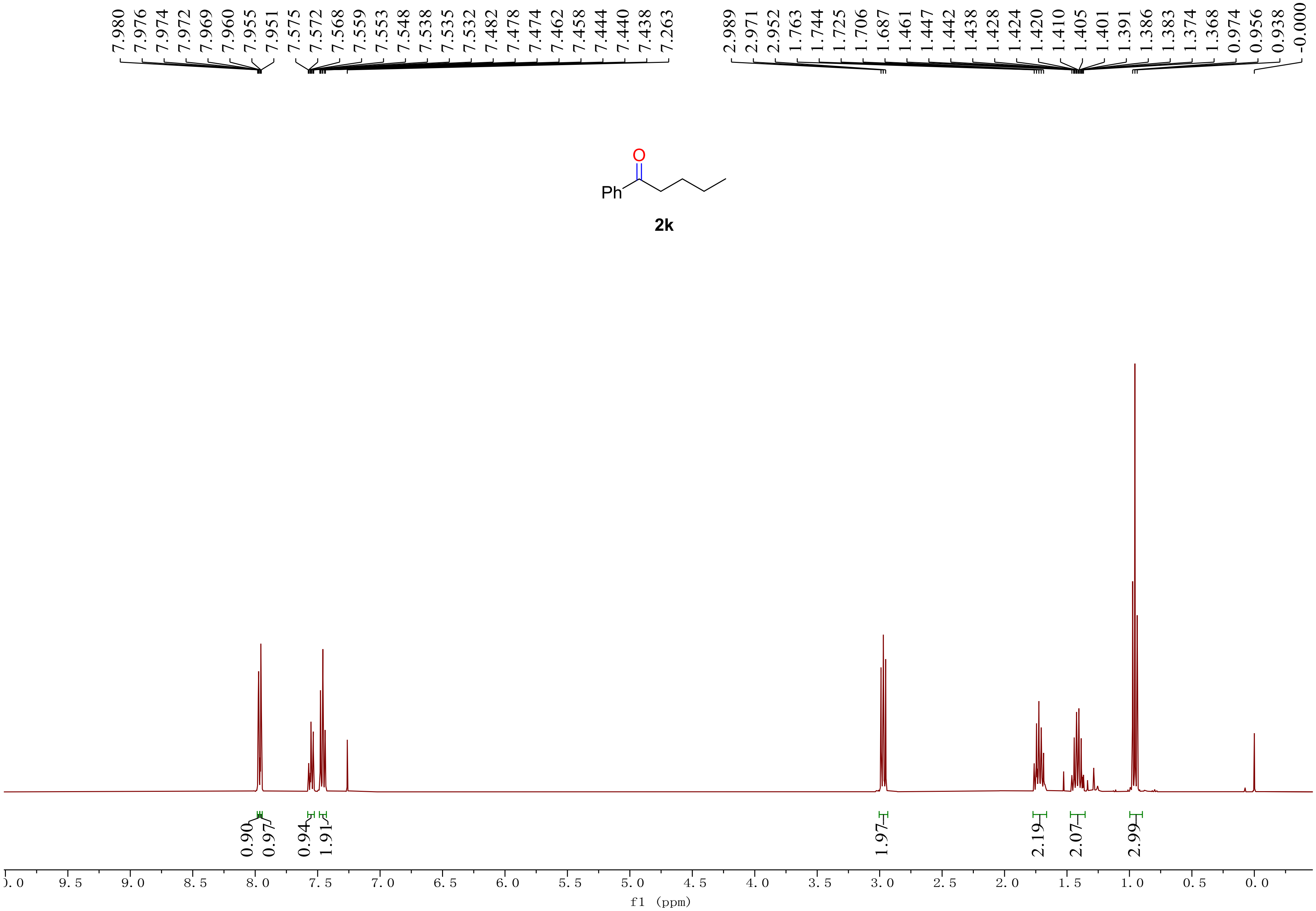
20
10
0
f1 (ppm)



2k

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7.960
7.955
7.951
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7.568
7.559
7.553
7.548
7.538
7.535
7.532
7.482
7.478
7.474
7.462
7.458
7.444
7.440
7.438
7.263
2.989
2.971
2.952
1.763
1.744
1.725
1.706
1.687
1.461
1.447
1.442
1.438
1.428
1.424
1.420
1.410
1.405
1.401
1.391
1.386
1.383
1.374
1.368
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0.938
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O
Ph
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2.19
2.07
2.99
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6.0
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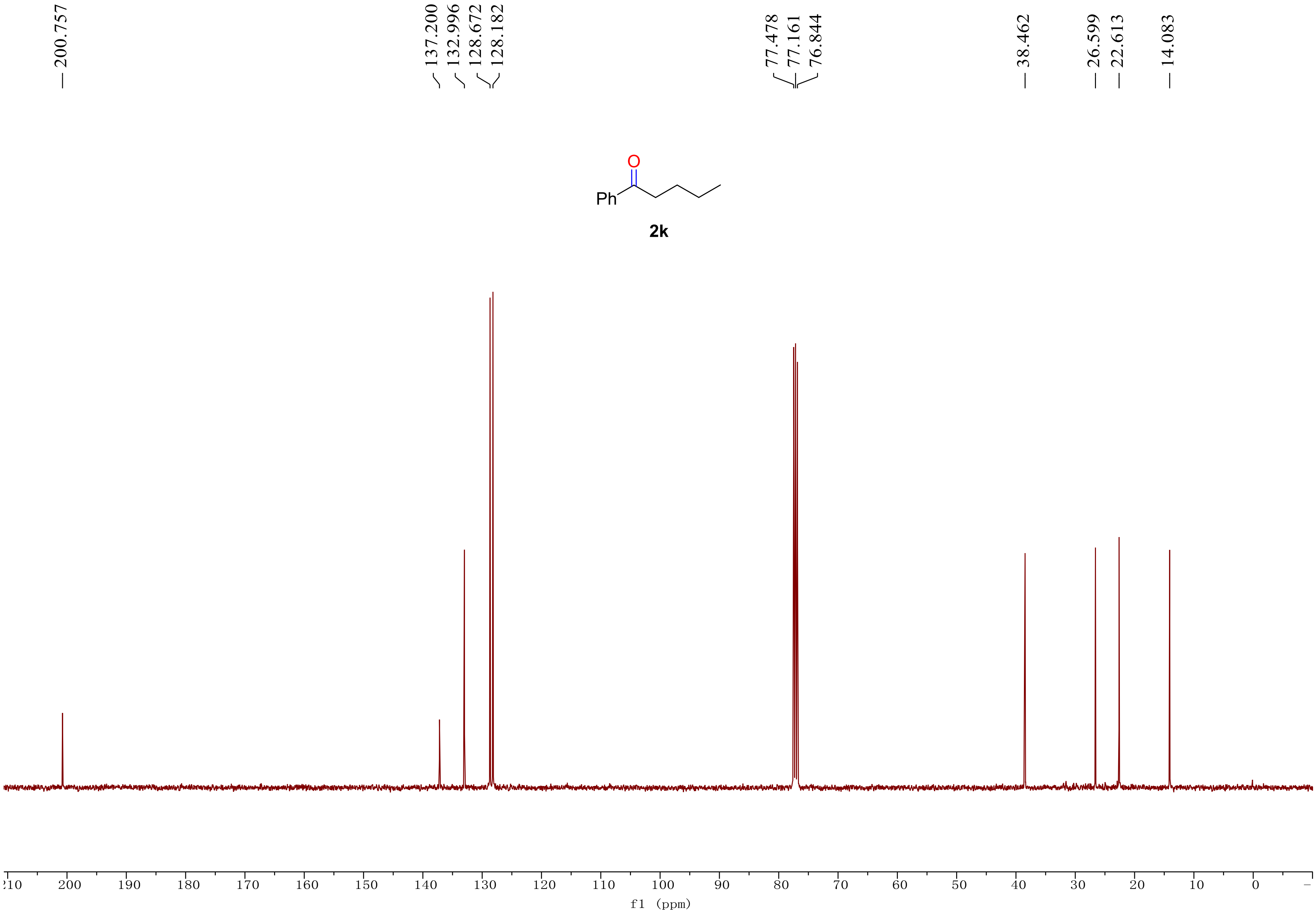
f1 (ppm)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O
Ph
210
200
190
180
170
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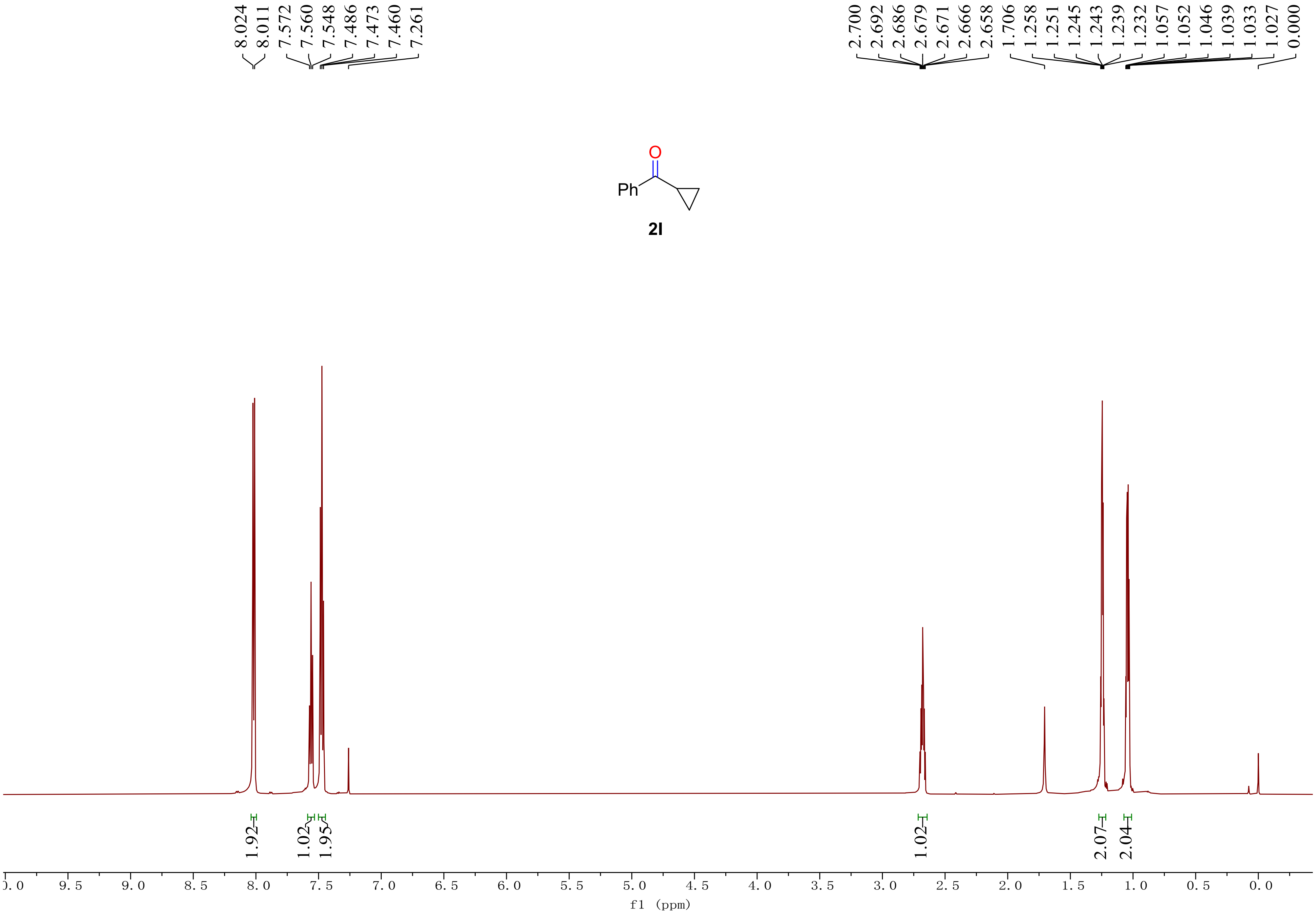
30
20
10
0
f1 (ppm)

2k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2.679
2.671
2.666
2.658
1.706
1.258
1.251
1.245
1.243
1.239
1.232
1.057
1.052
1.046
1.039
1.033
1.027
0.000
O
Ph
1.92
1.02
1.95
1.02
2.07
2.04
). 0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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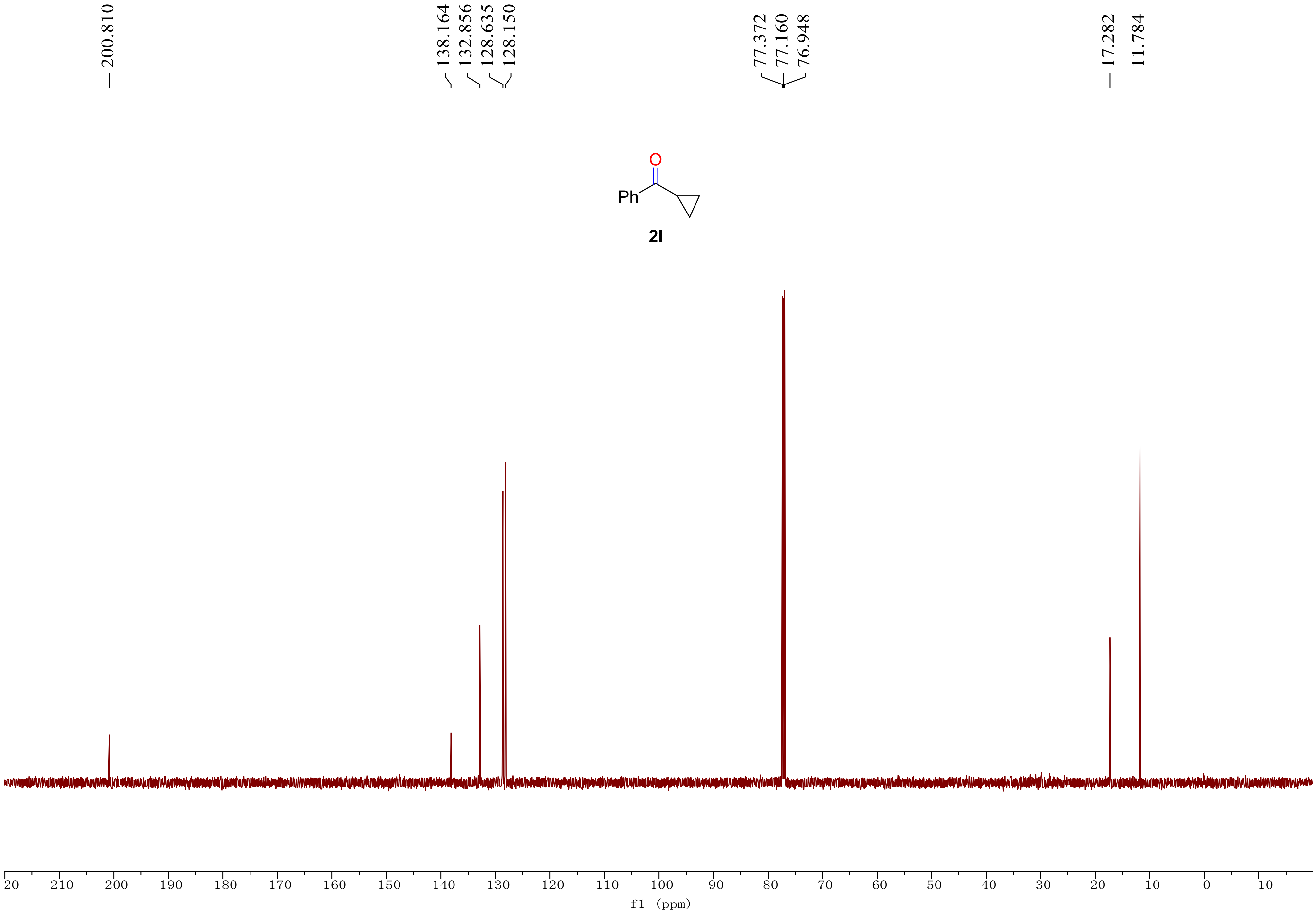
1.5
1.0
0.5
0.0
f1 (ppm)

2l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128.635
128.150
77.372
77.160
76.948
17.282
11.784
O
Ph
2l
20
210
200
190
180
170
160
150
140
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120
110
100
90
80
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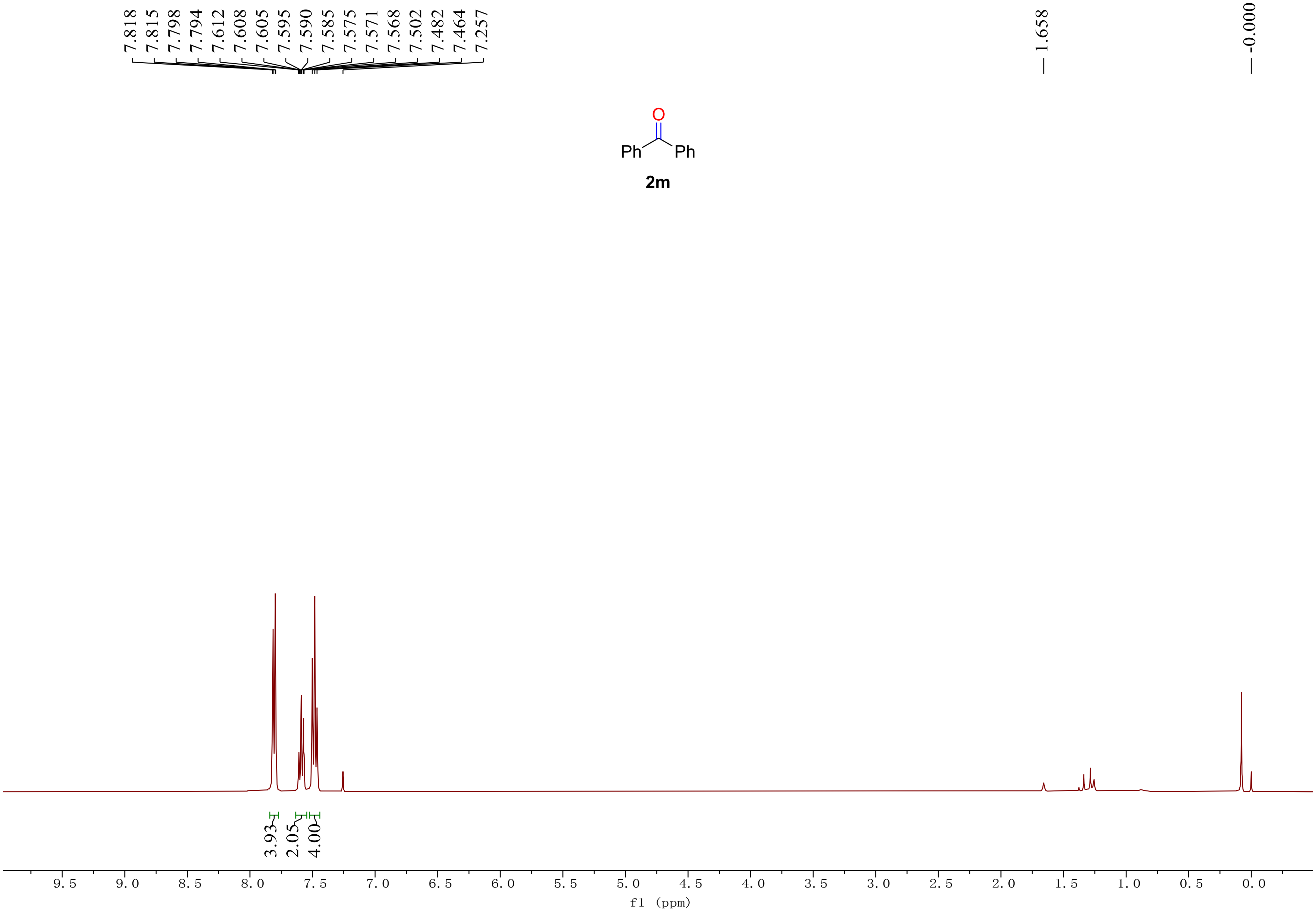
60
50
40
30
20
10
0
−10
f1 (ppm)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7.798
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7.605
7.595
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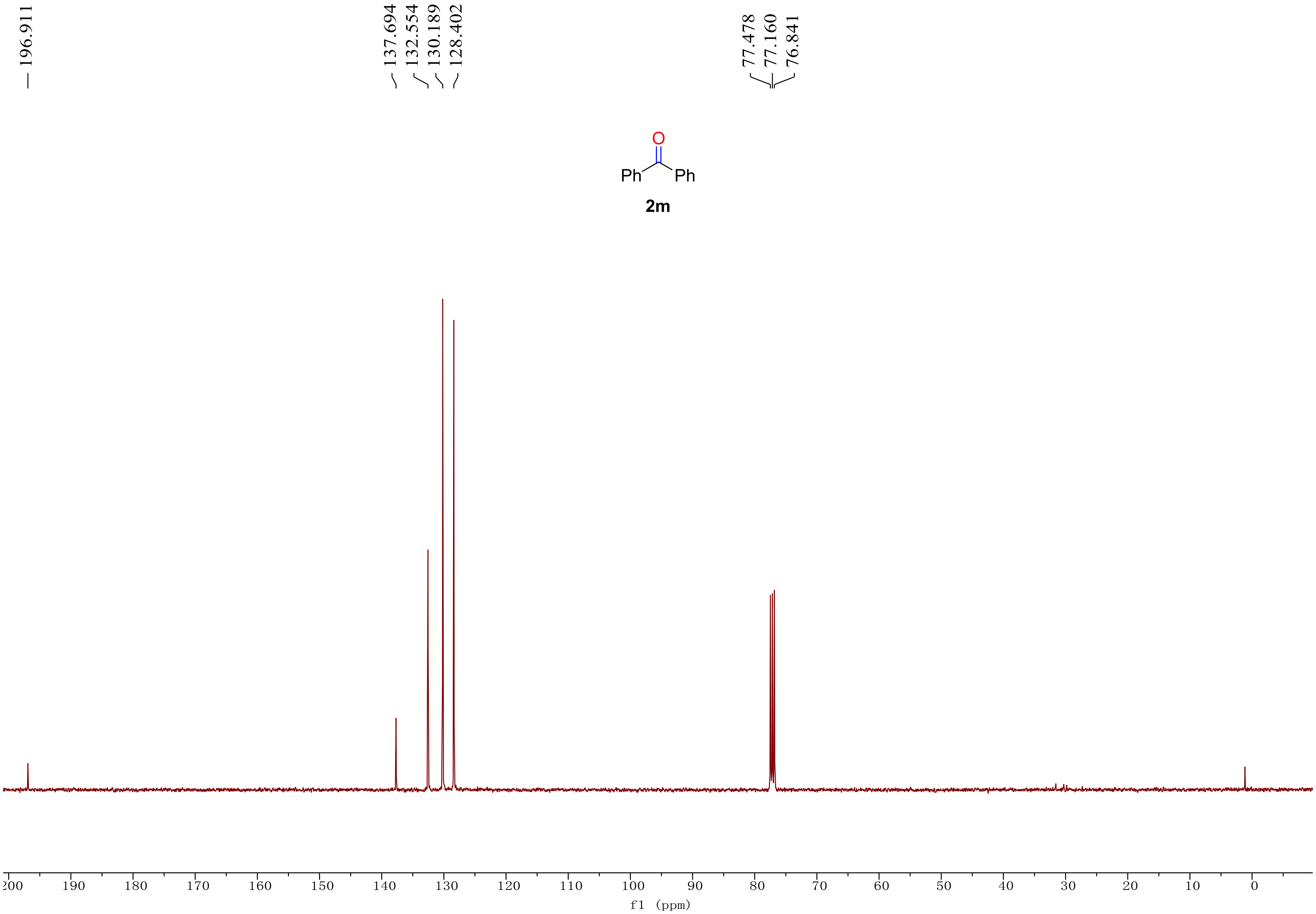
7.585
7.575
7.571
7.568
7.502
7.482
7.464
7.257
1.658
-0.000
O
Ph
Ph
2m
3.93
2.05
4.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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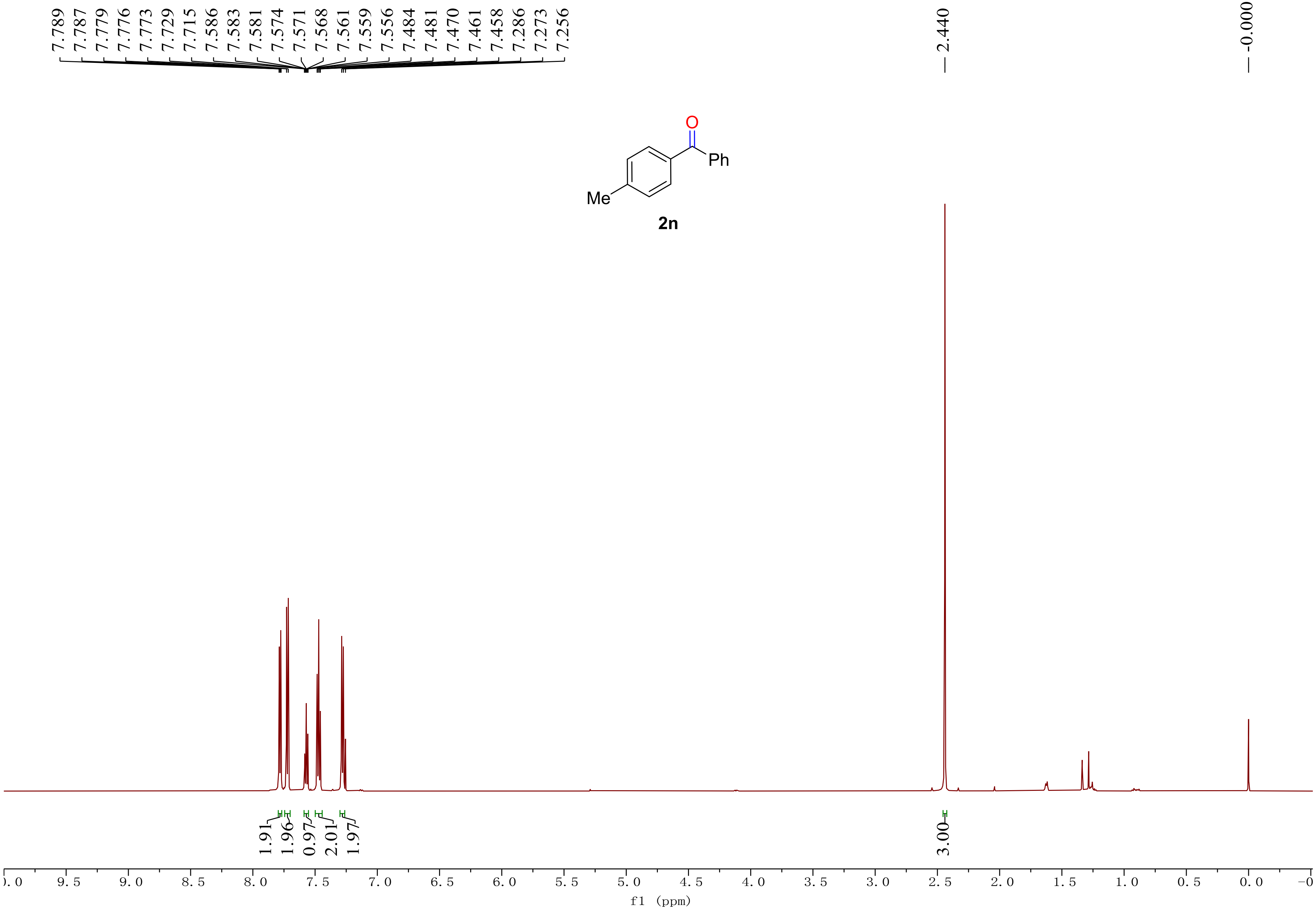
137.694
132.554
130.189
128.402
77.478
77.160
76.841
O
Ph
Ph
2m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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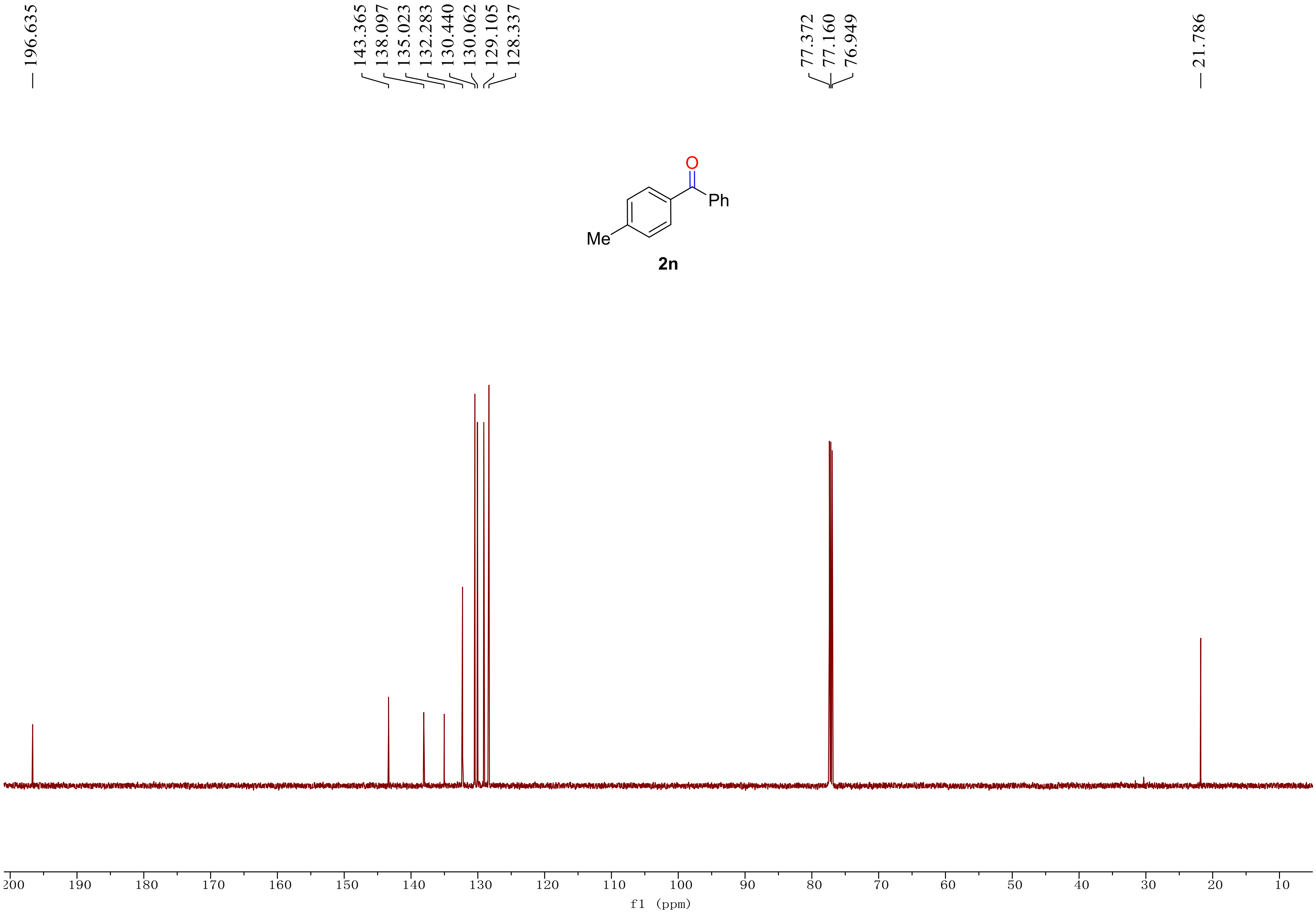
7.787
7.779
7.776
7.773
7.729
7.715
7.586
7.583
7.581
7.574
7.571
7.568
7.561
7.559
7.556
7.484
7.481
7.470
7.461
7.458
7.286
7.273
7.256
2.440
-0.000
O
Ph
Me
2n
1.91
1.96
0.97
2.01
1.97
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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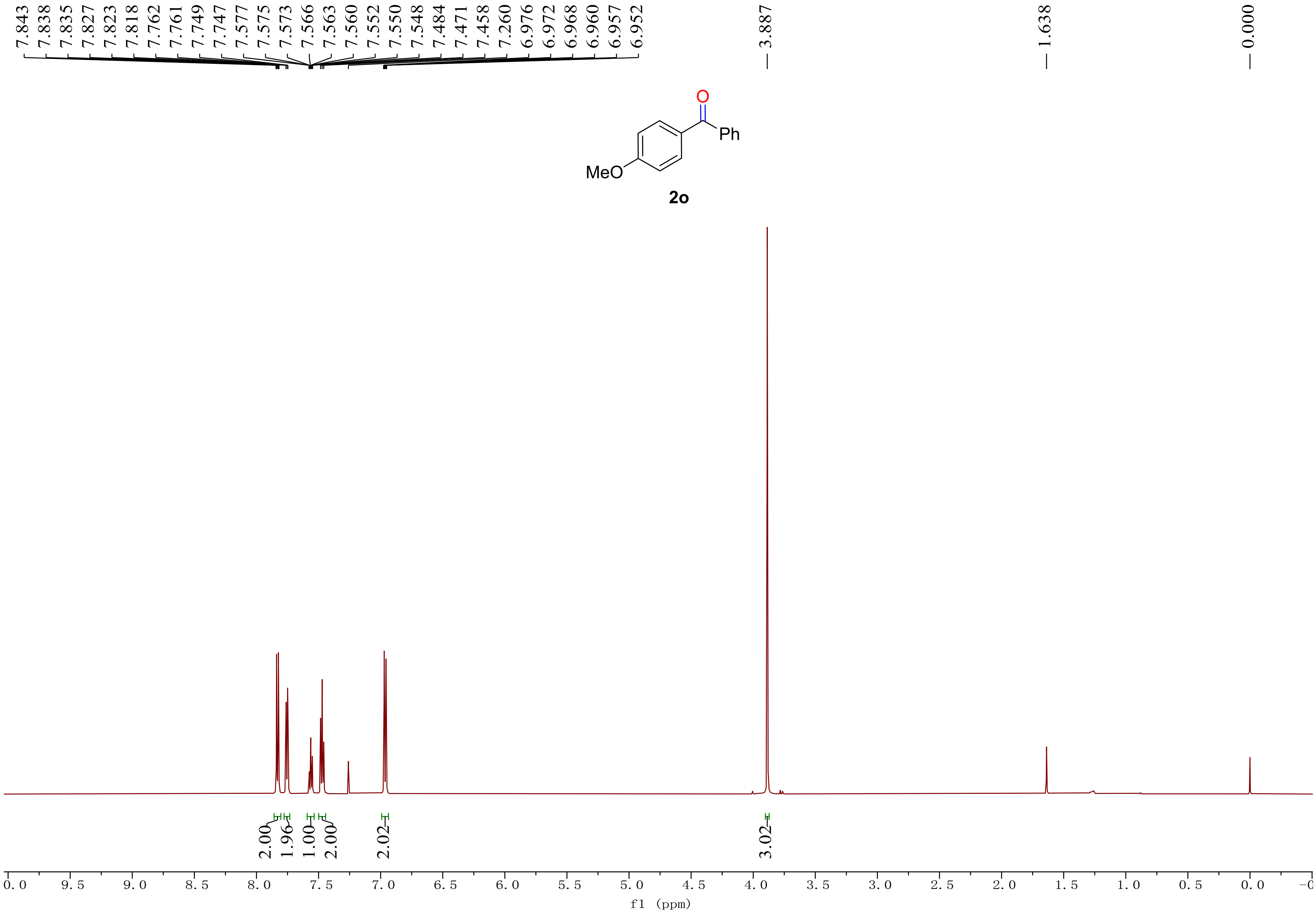
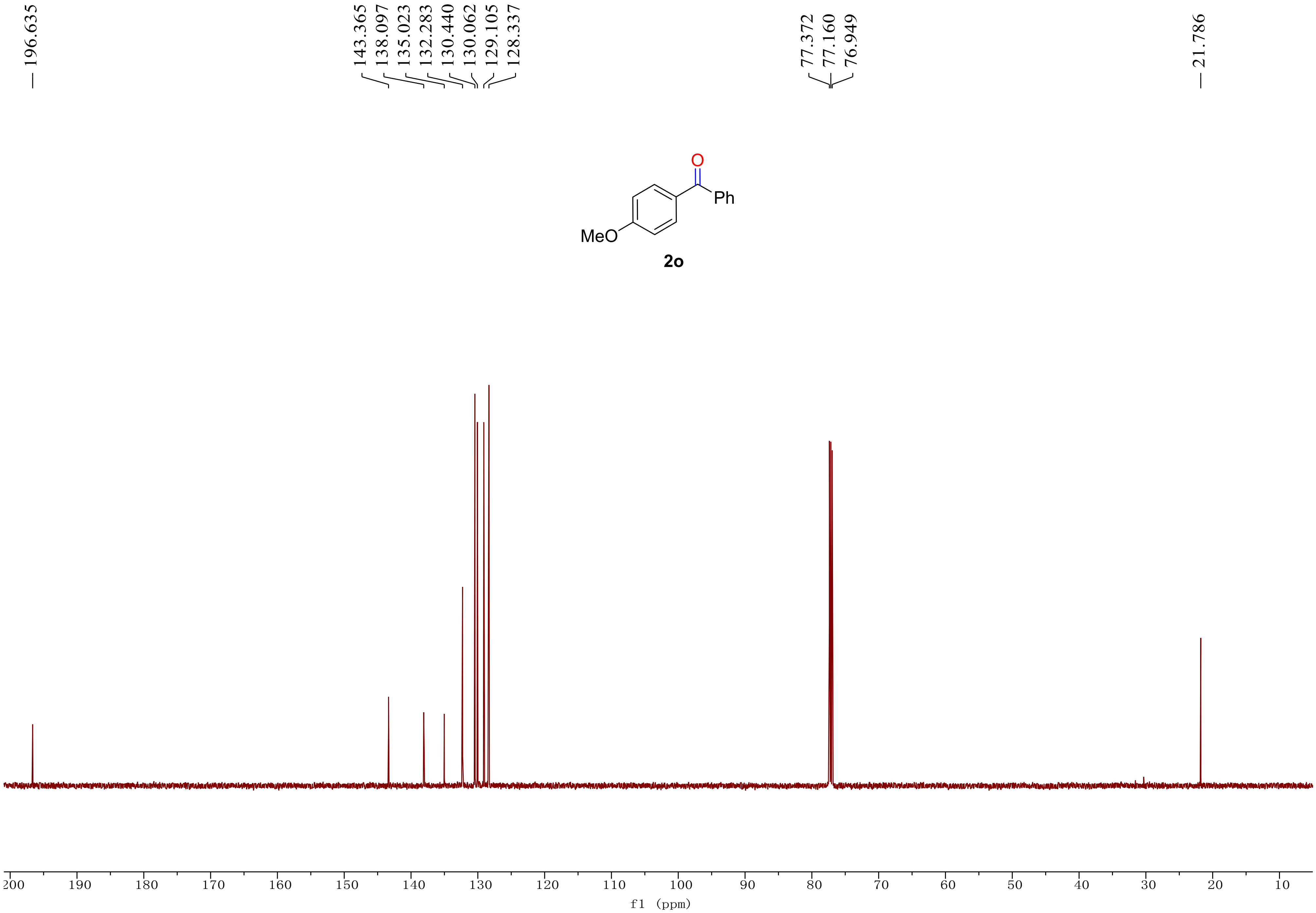
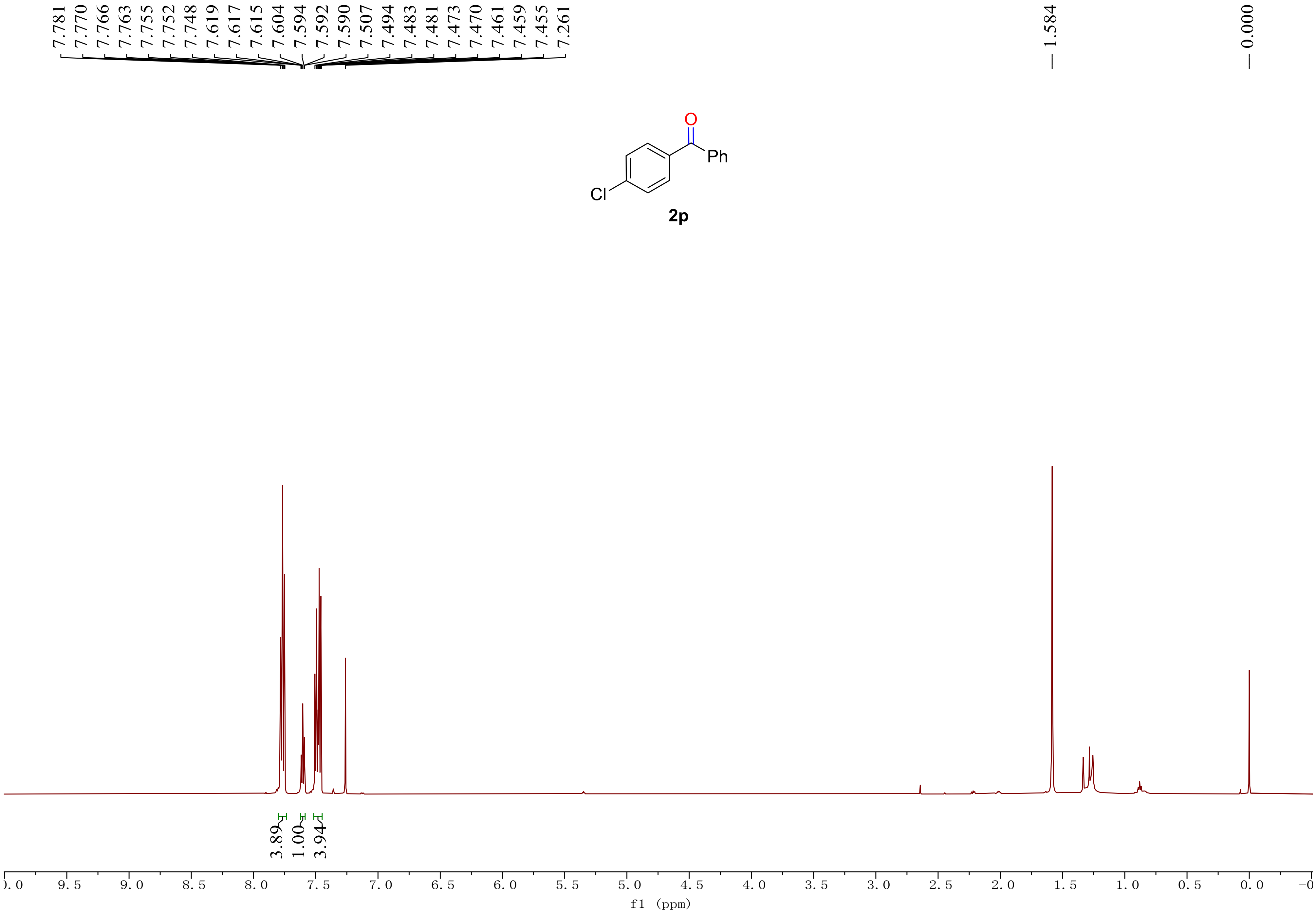
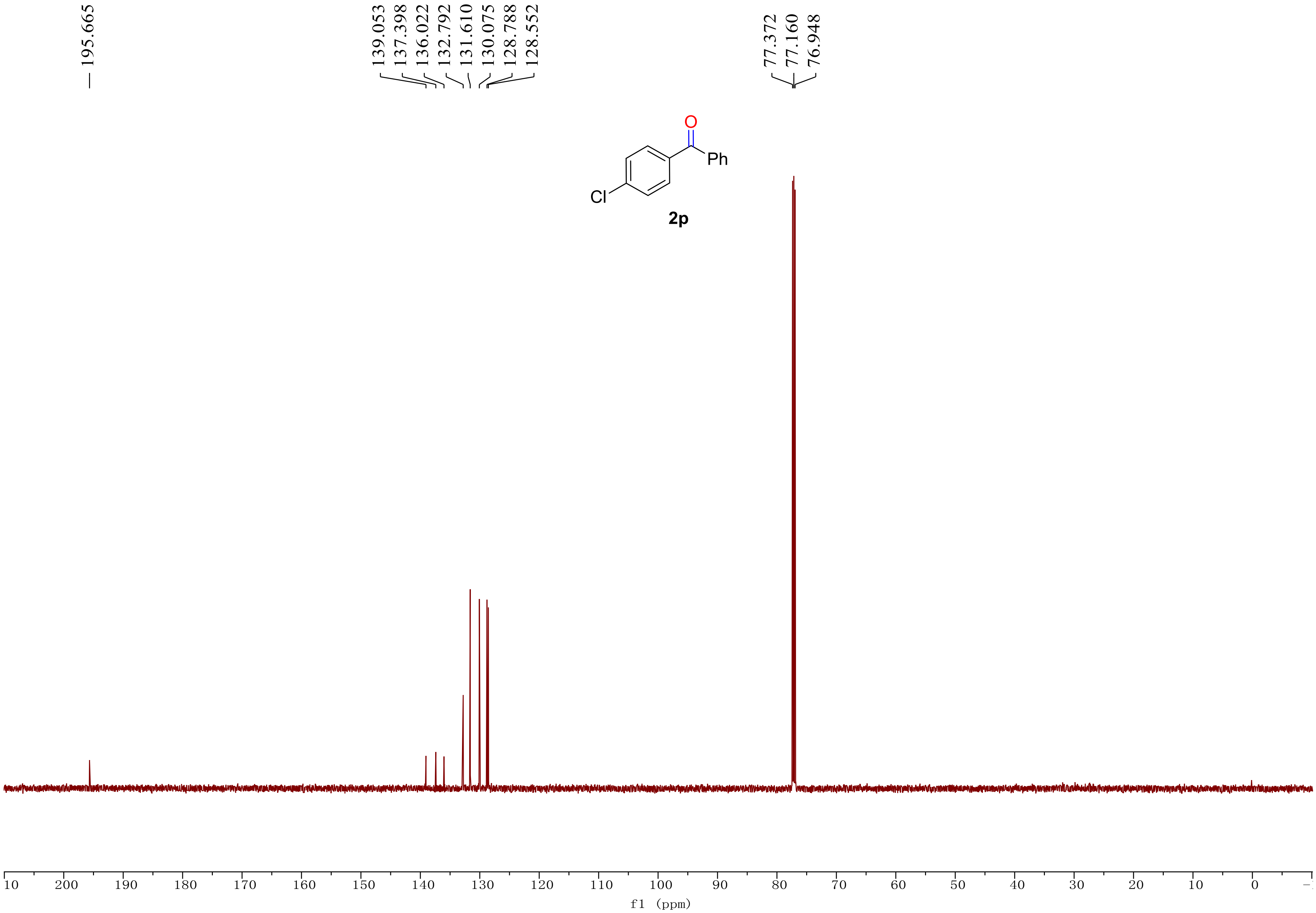
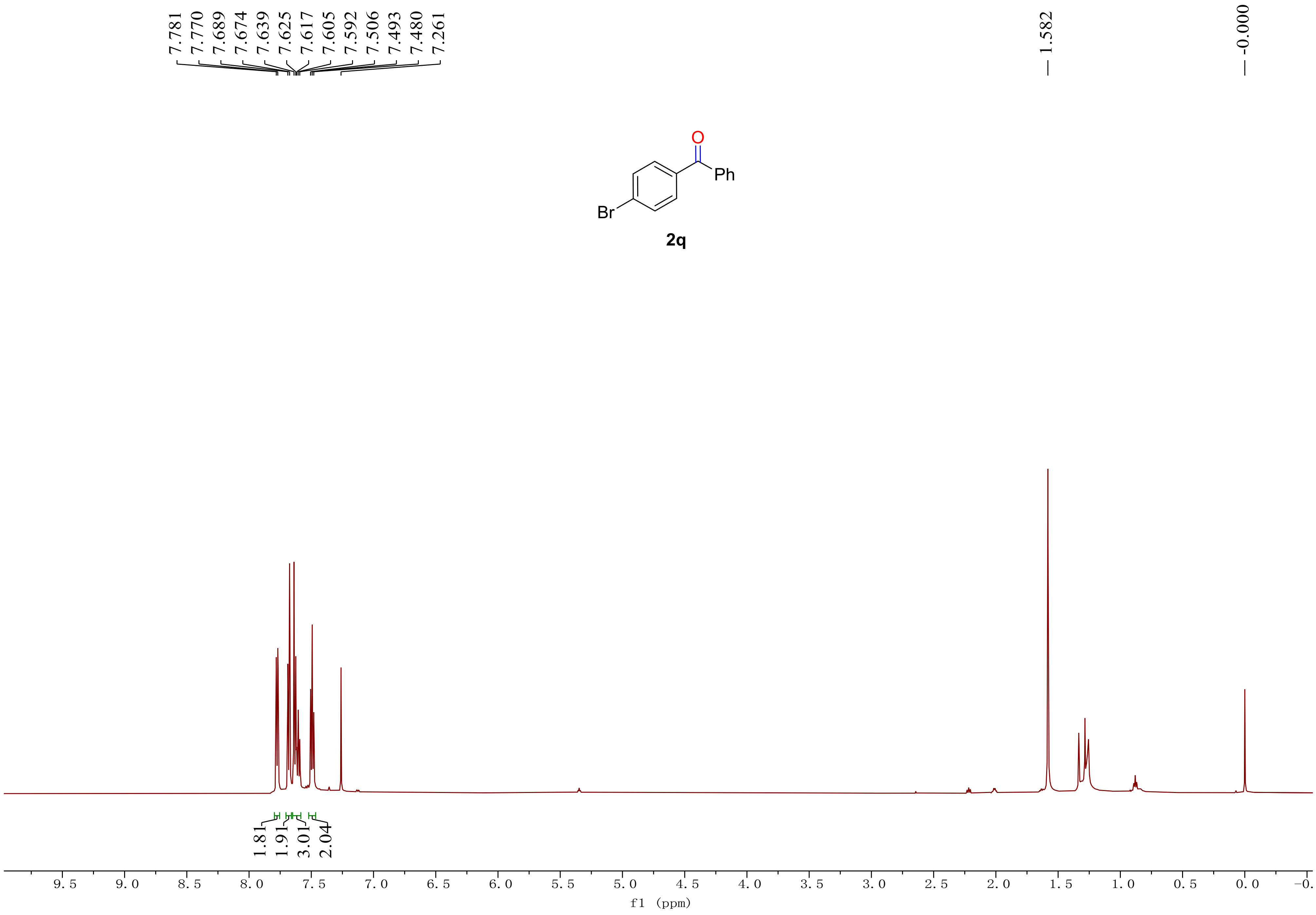
143.365
138.097
135.023
132.283
130.440
130.062
129.105
128.337
77.372
77.160
76.949
21.786
O
Ph
Me
2n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.843
7.838
7.835
7.827
7.823
7.818
7.762
7.761
7.749
7.747
7.577
7.575
7.573
7.566
7.563
7.560
7.552
7.550
7.548
7.484
7.471
7.458
7.260
6.976
6.972
6.968
6.960
6.957
6.952
3.887
1.638
0.000
O
Ph
MeO
2o
2.00
1.96
1.00
2.00
2.02
3.02
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

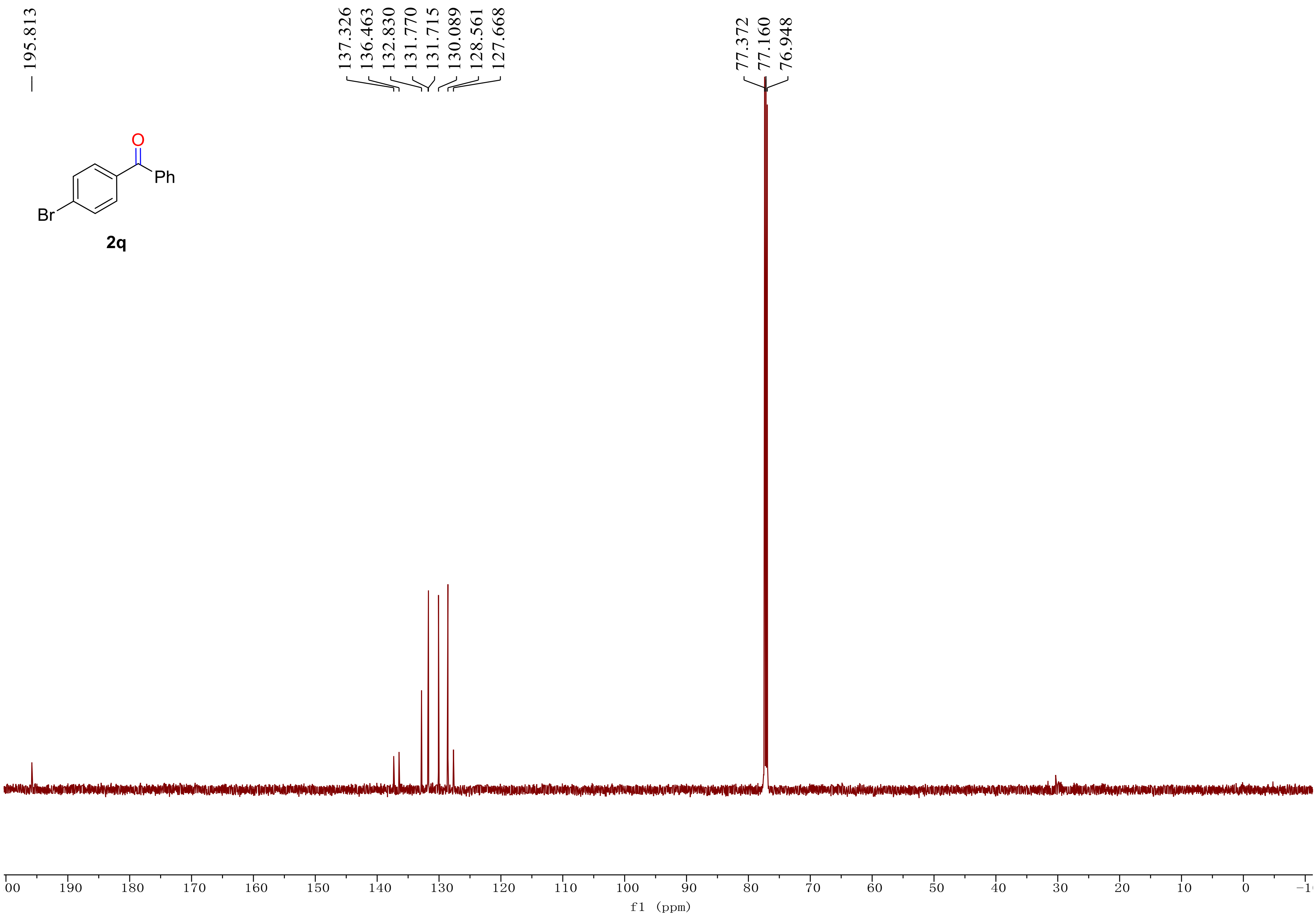

196.635
143.365
138.097
135.023
132.283
130.440
130.062
129.105
128.337
77.372
77.160
76.949
21.786
O
Ph
MeO
2o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

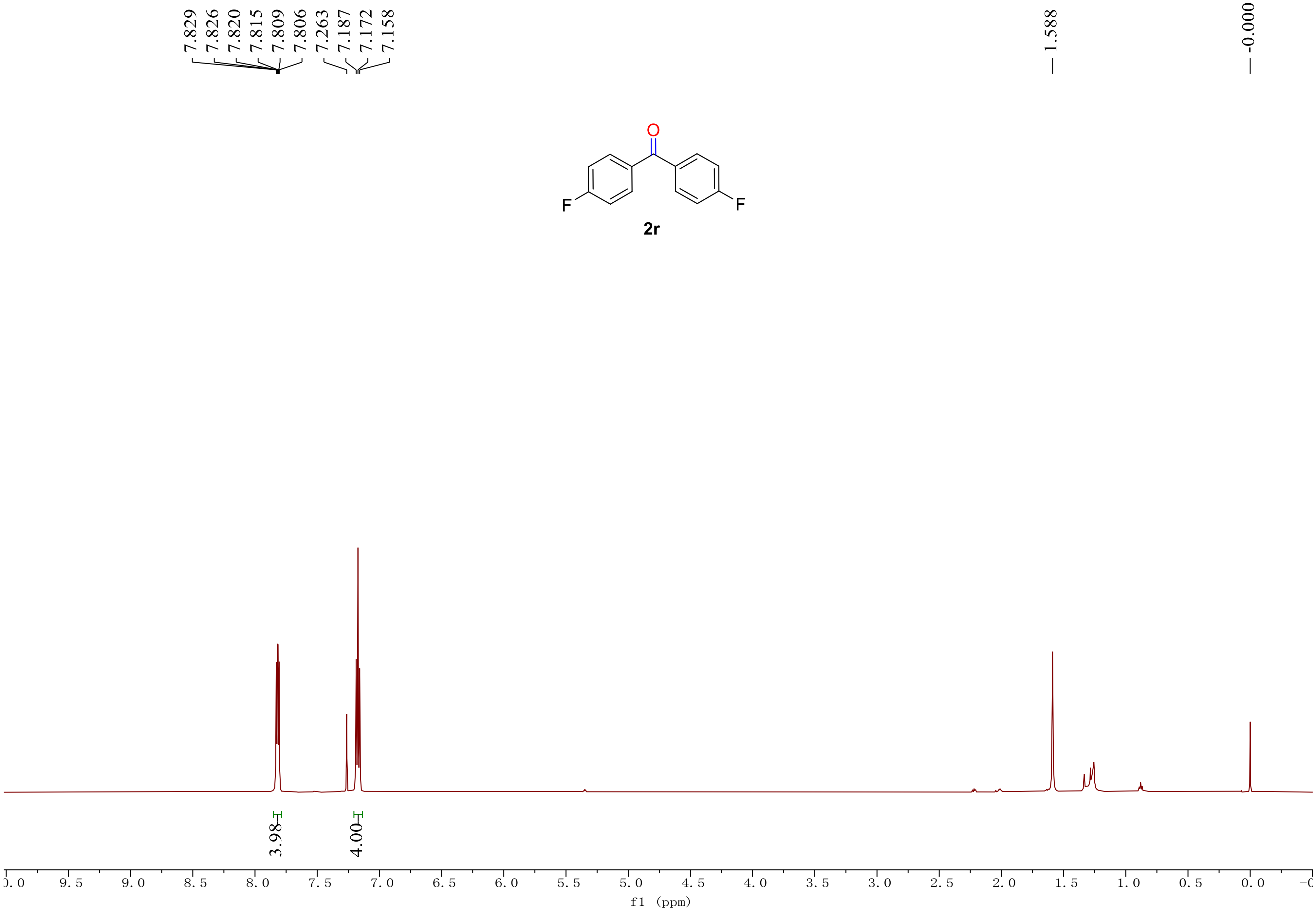

7.781
7.770
7.766
7.763
7.755
7.752
7.748
7.619
7.617
7.615
7.604
7.594
7.592
7.590
7.507
7.494
7.483
7.481
7.473
7.470
7.461
7.459
7.455
7.261
1.584
0.000
O
Ph
Cl
2p
3.89
1.00
3.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

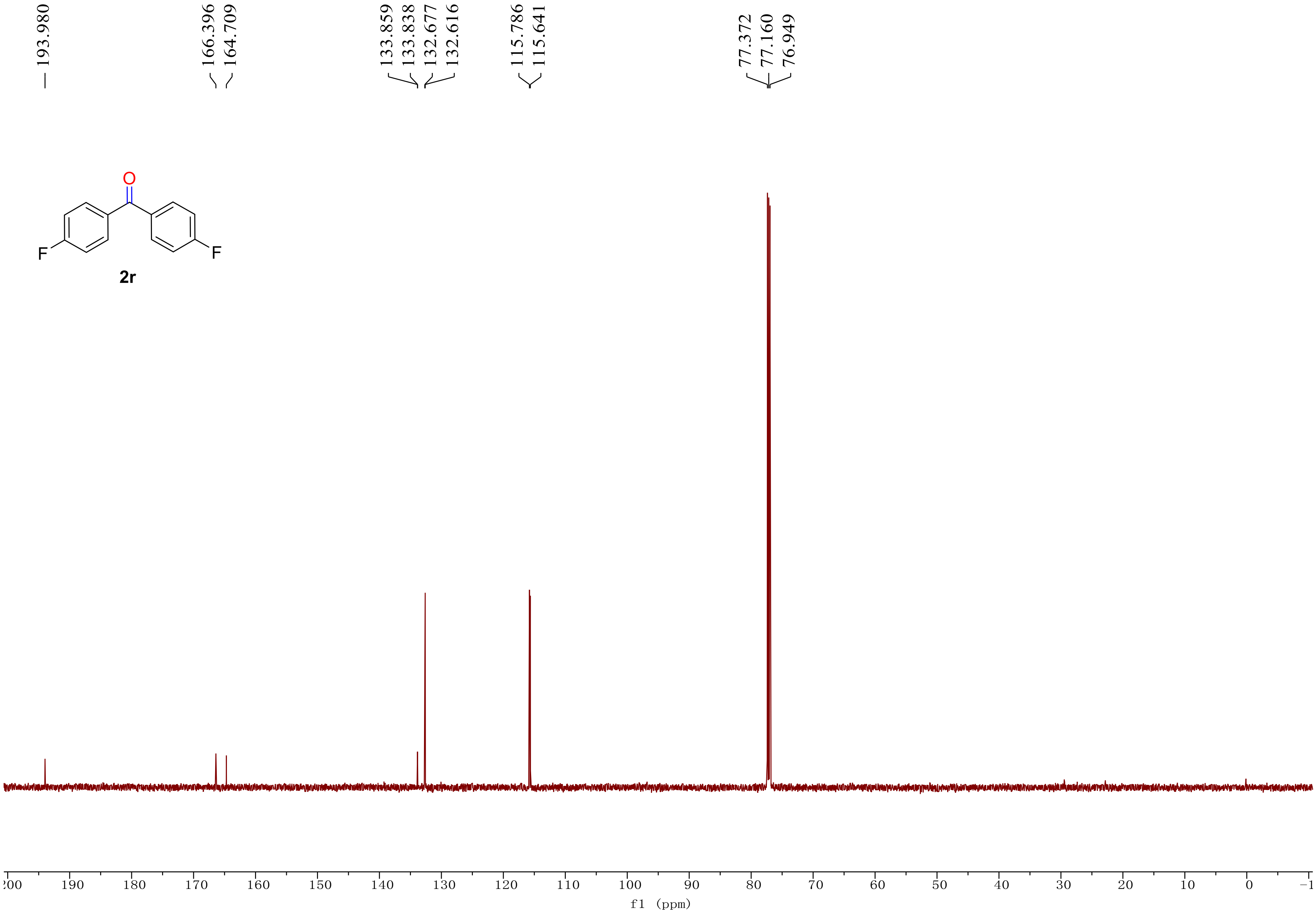

195.665
139.053
137.398
136.022
132.792
131.610
130.075
128.788
128.552
77.372
77.160
76.948
O
Ph
Cl
2p
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

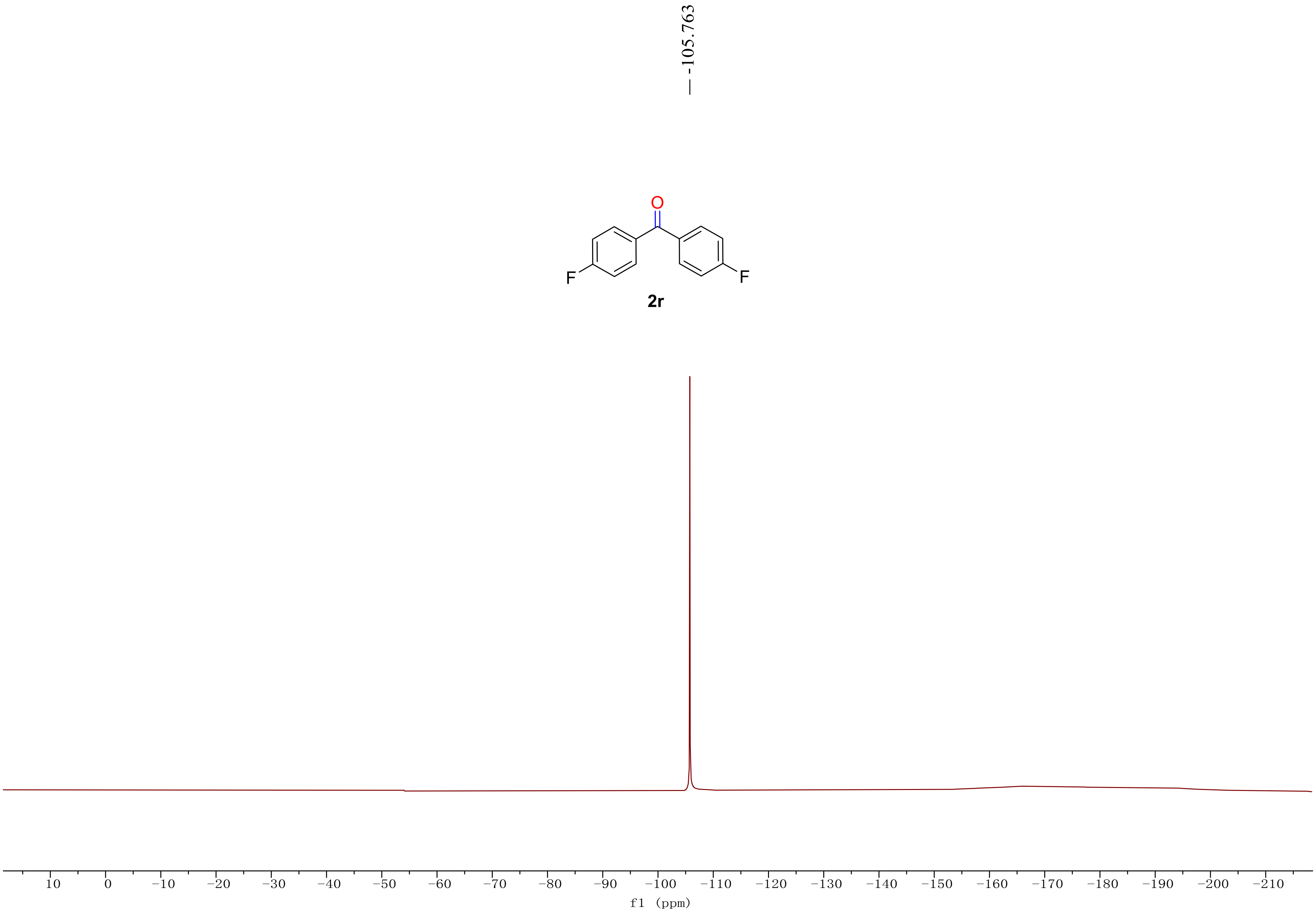

7.781
7.770
7.689
7.674
7.639
7.625
7.617
7.605
7.592
7.506
7.493
7.480
7.261
1.582
-0.000
O
Ph
Br
1.81
1.91
3.01
2.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

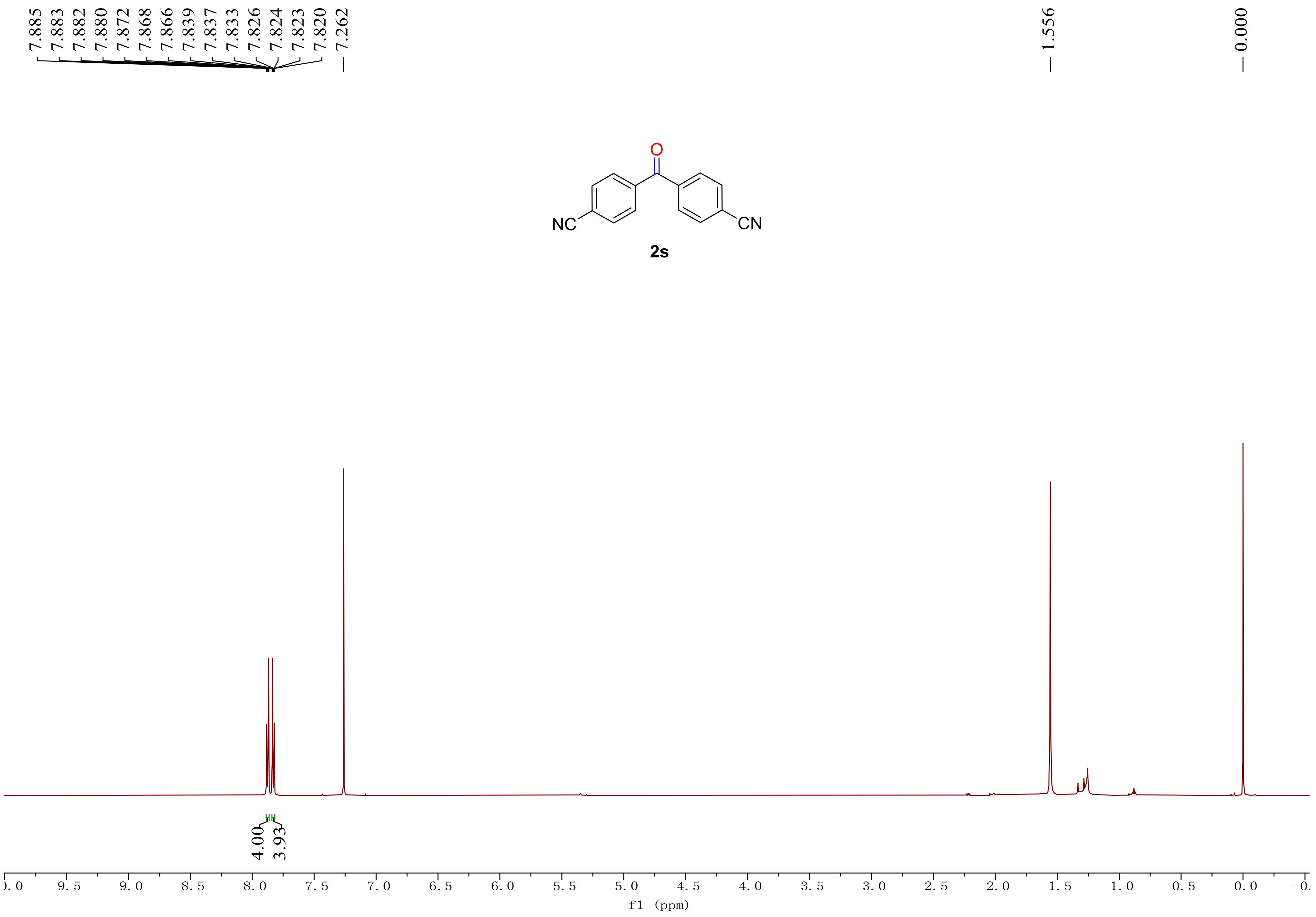
2q

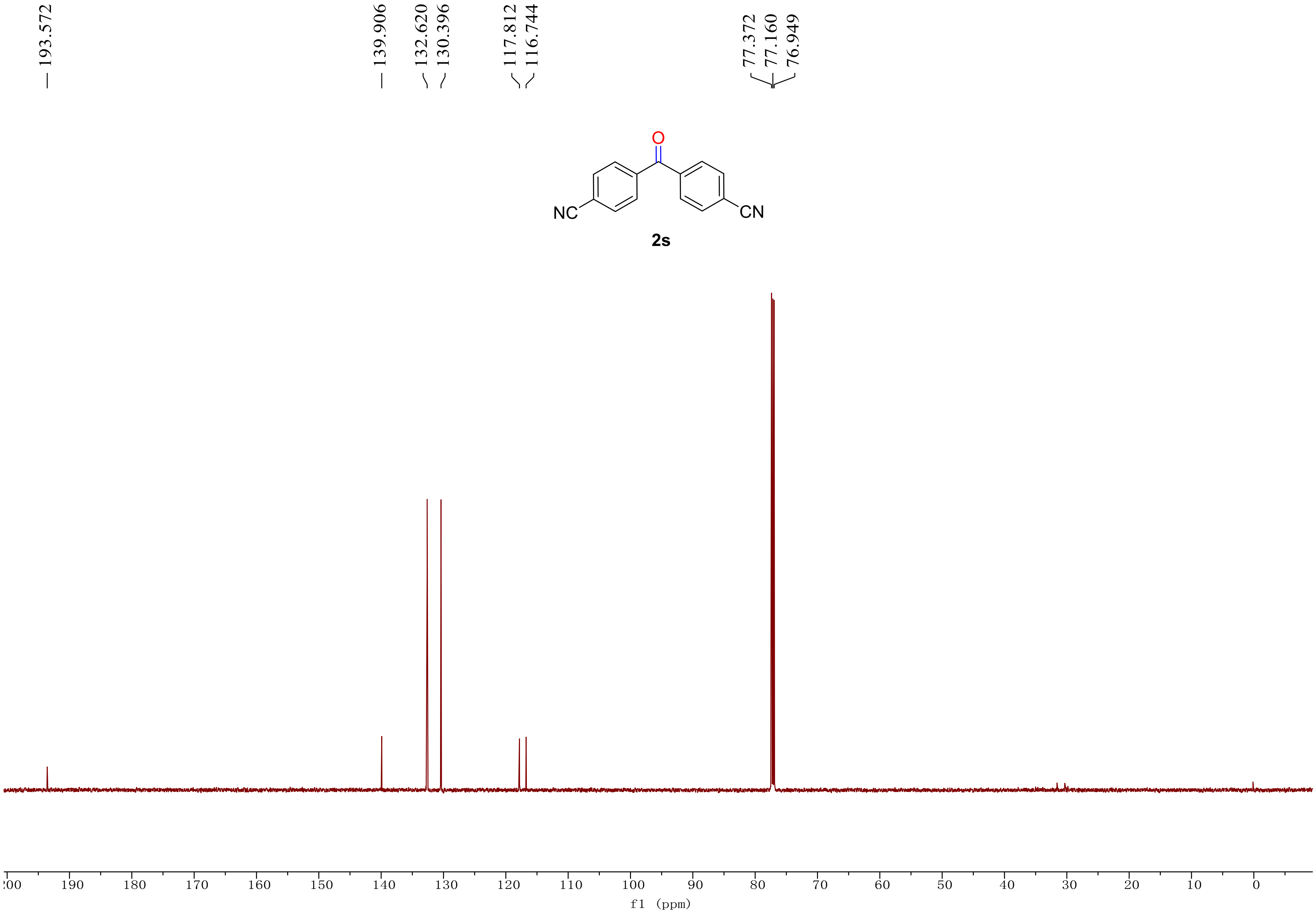

195.813
137.326
136.463
132.830
131.770
131.715
130.089
128.561
127.668
77.372
77.160
76.948
O
Ph
Br
2q
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)


7.829
7.826
7.820
7.815
7.809
7.806
7.263
7.187
7.172
7.158
1.588
-0.000
O
F
F
2r
3.98
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

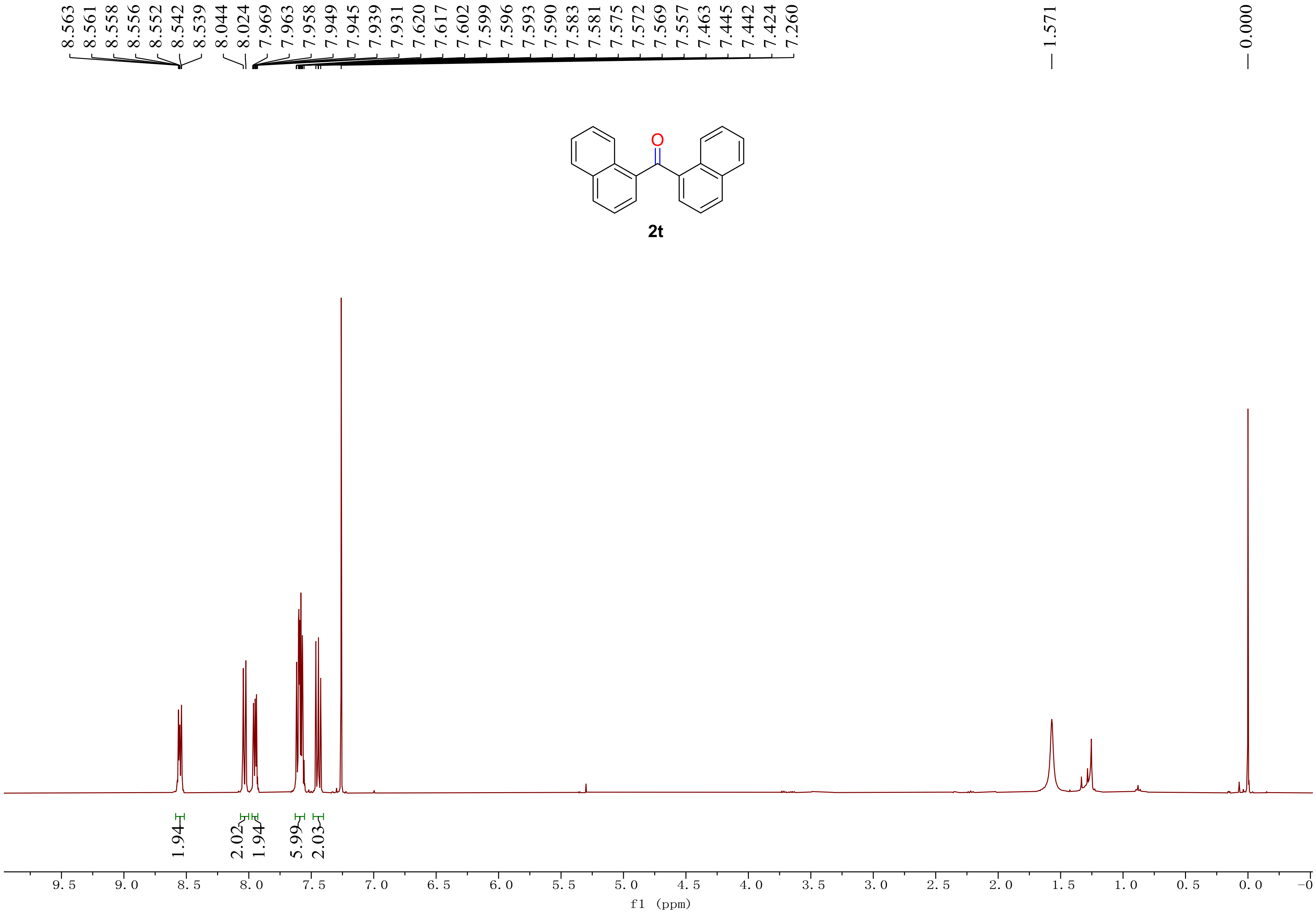

193.980
166.396
164.709
133.859
133.838
132.677
132.616
115.786
115.641
77.372
77.160
76.949
O
F
F
2r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)


-105.763
O
F
F
2r
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)


7.885
7.883
7.882
7.880
7.872
7.868
7.866
7.839
7.837
7.833
7.826
7.824
7.823
7.820
7.262
1.556
0.000
O
NC
CN
2s
4.00
3.93
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.
f1 (ppm)

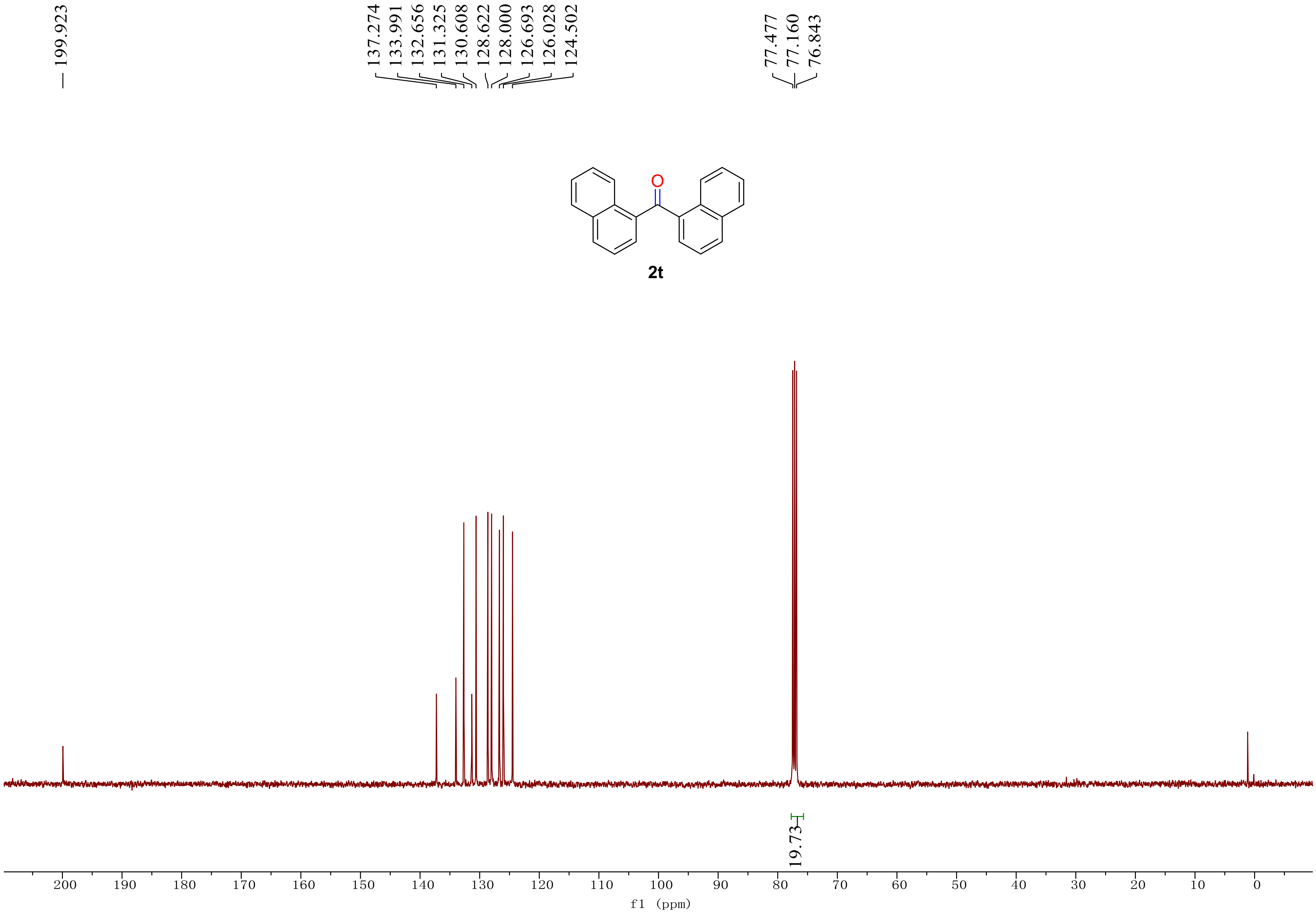


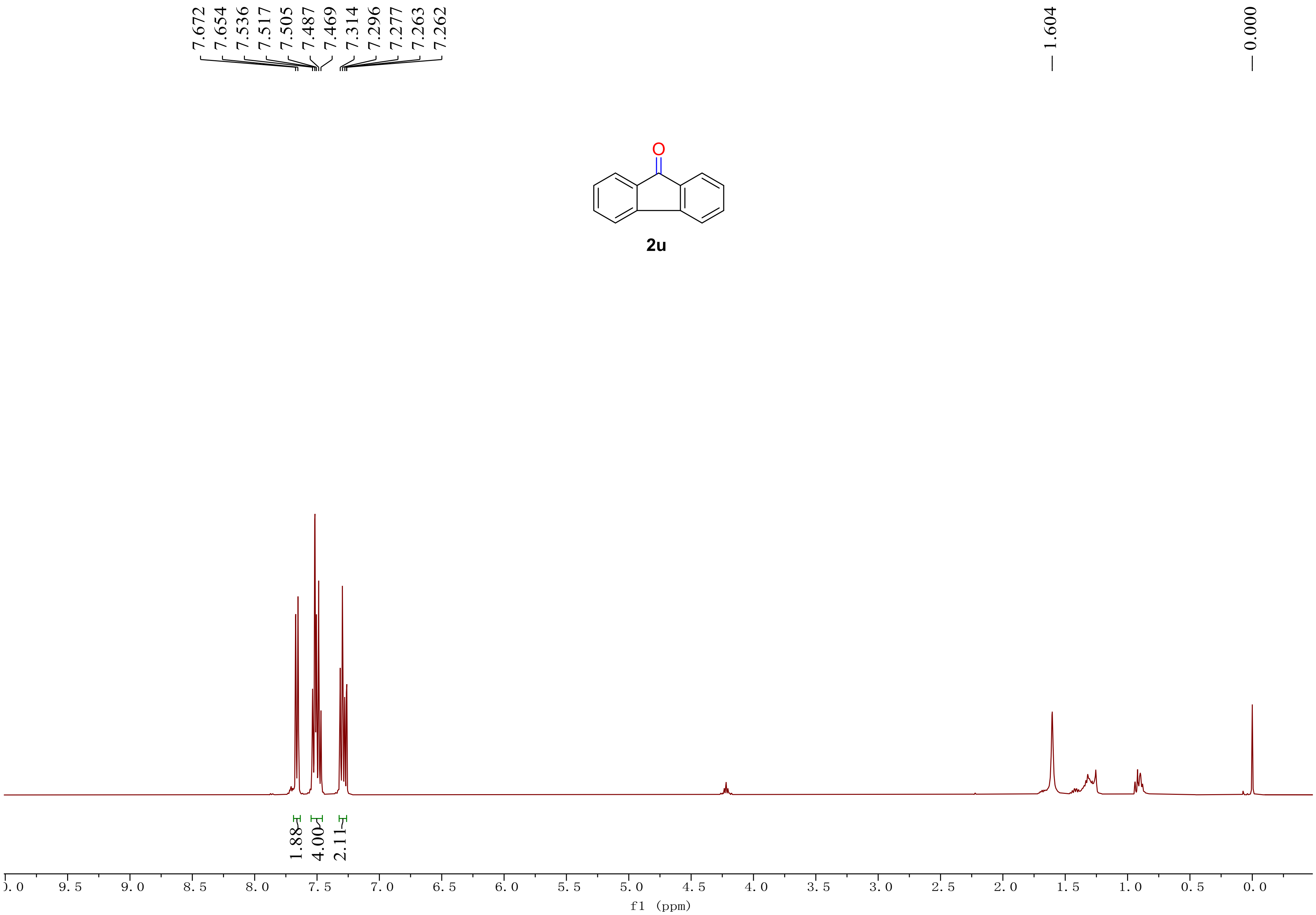
193.572
139.906
132.620
130.396
117.812
116.744
77.372
77.160
76.949
O
NC
CN
2s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



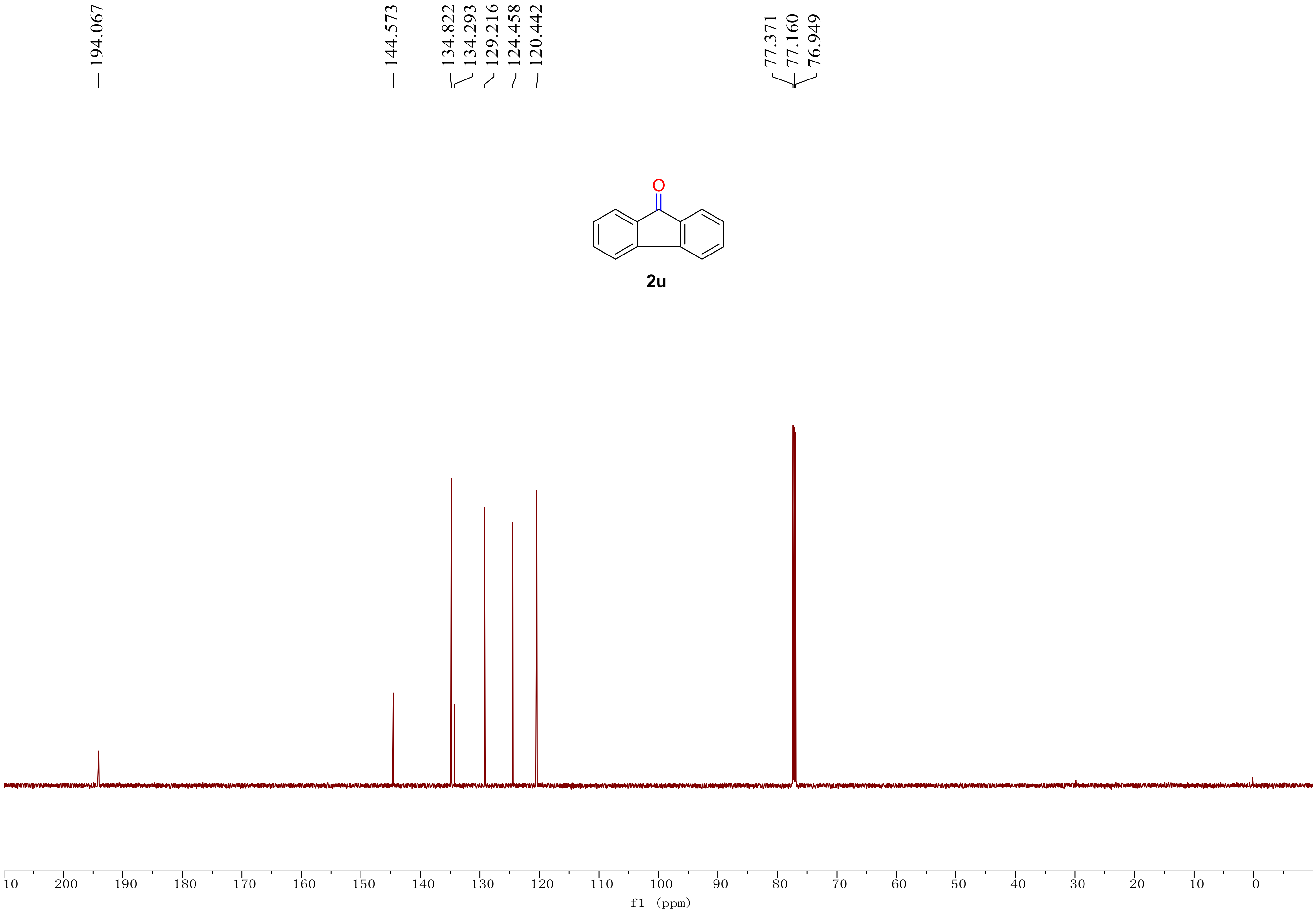
2t

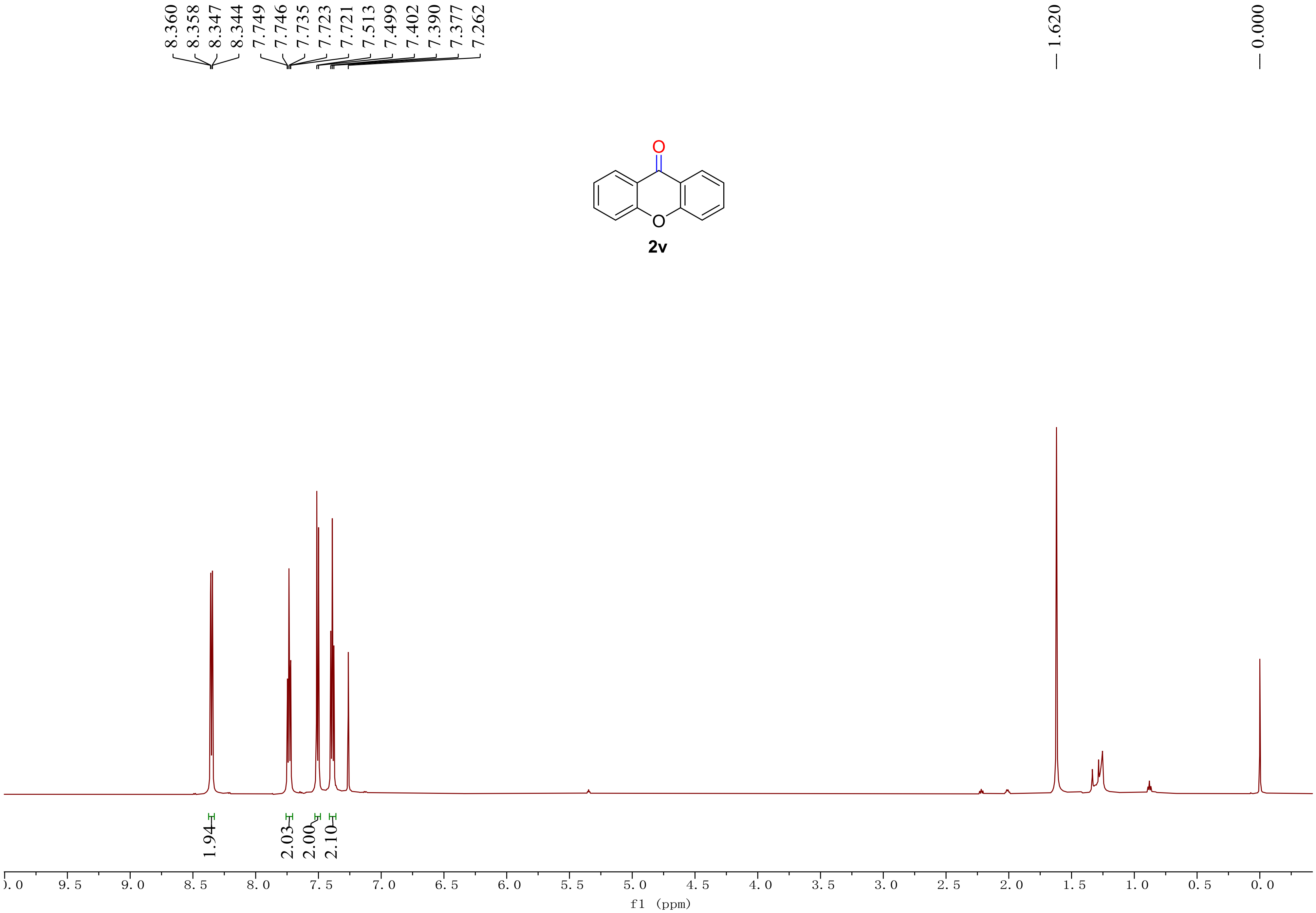
8.563
8.561
8.558
8.556
8.552
8.542
8.539
8.044
8.024
7.969
7.963
7.958
7.949
7.945
7.939
7.931
7.620
7.617
7.602
7.599
7.596
7.593
7.590
7.583
7.581
7.575
7.572
7.569
7.557
7.463
7.445
7.442
7.424
7.260
1.571
0.000
O
1.94
2.02
1.94
5.99
2.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

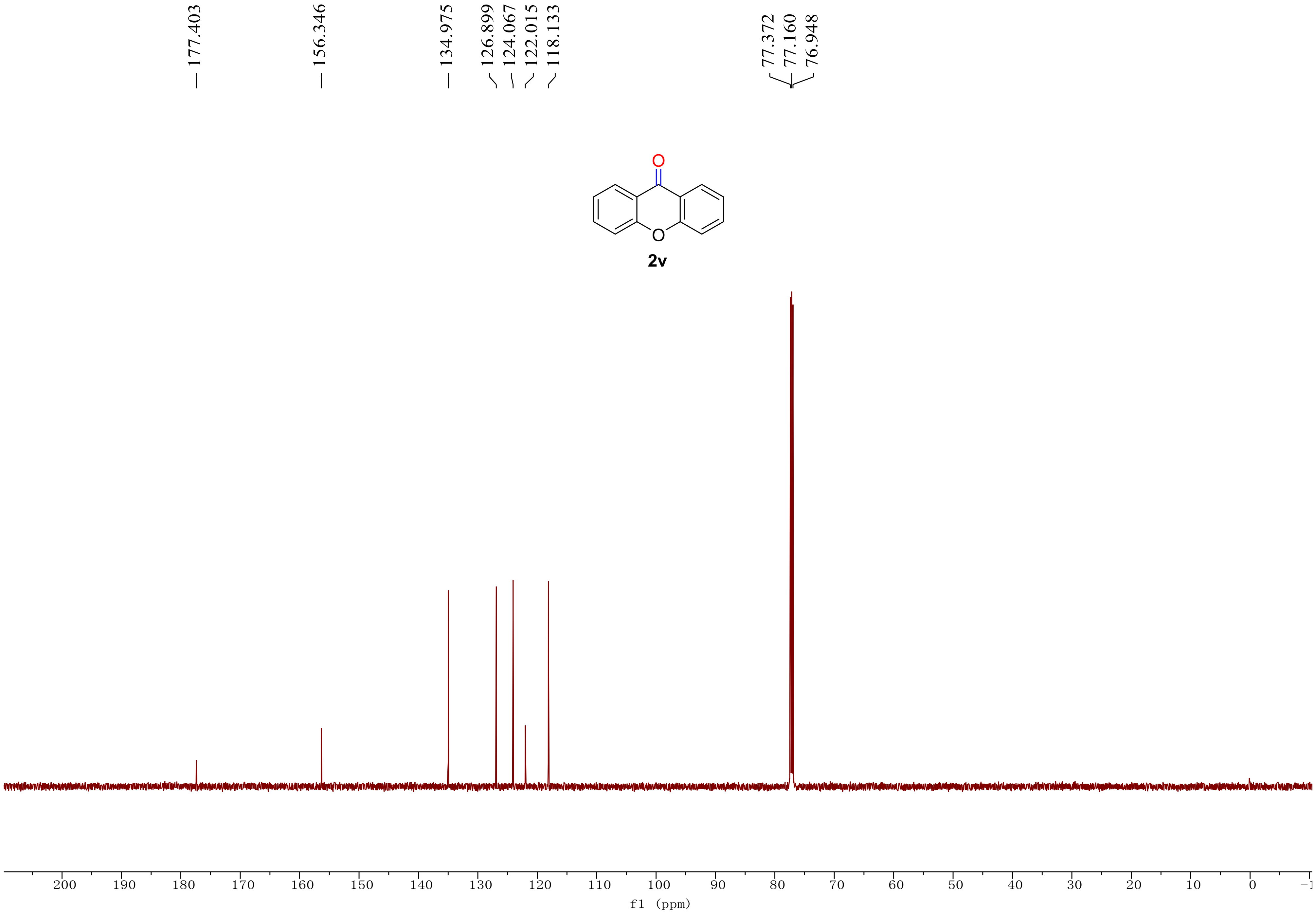

199.923
137.274
133.991
132.656
131.325
130.608
128.622
128.000
126.693
126.028
124.502
77.477
77.160
76.843
O
2t
19.73
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

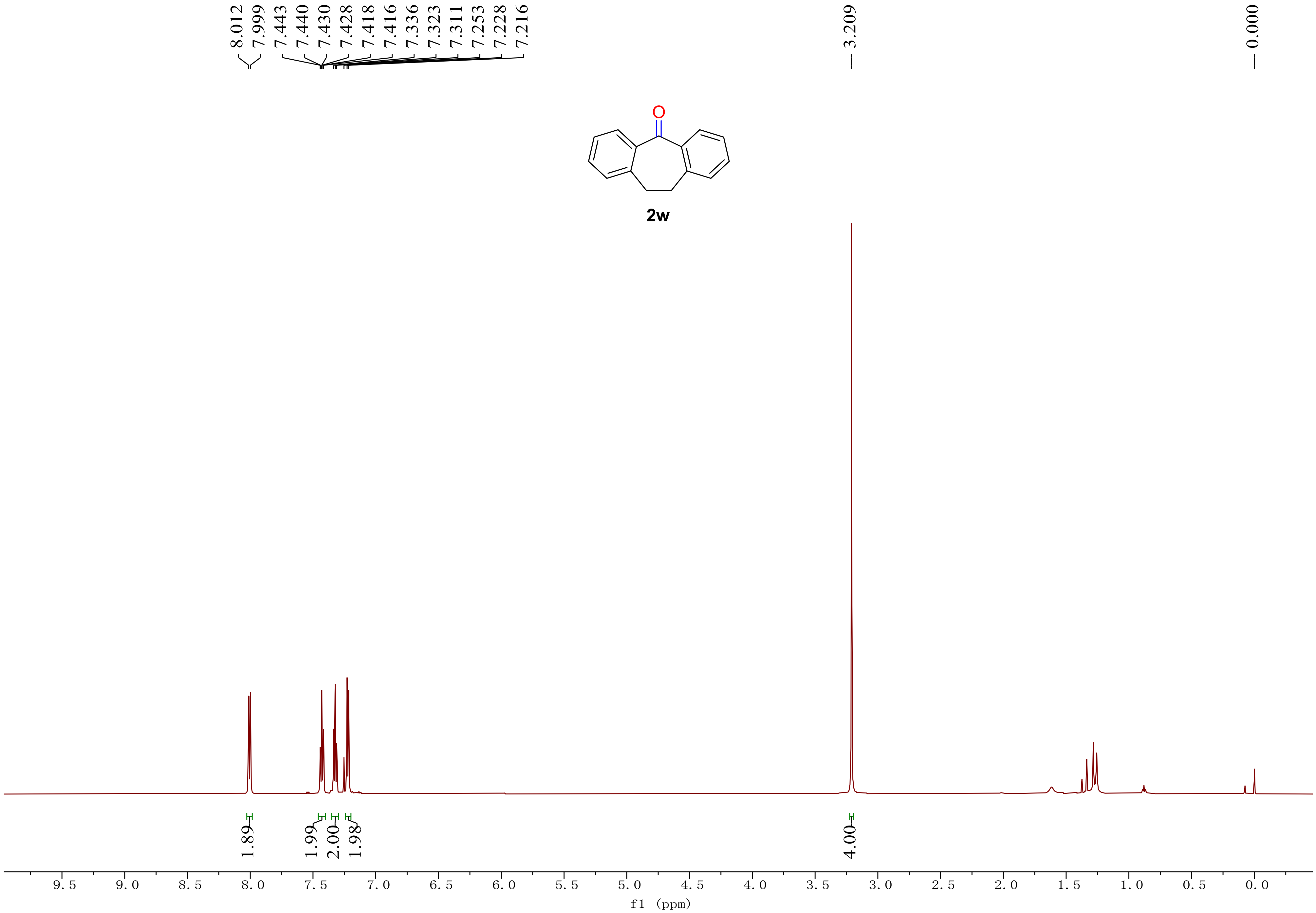

7.672
7.654
7.536
7.517
7.505
7.487
7.469
7.314
7.296
7.277
7.263
7.262
1.604
0.000
O
1.88
4.00
2.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2u

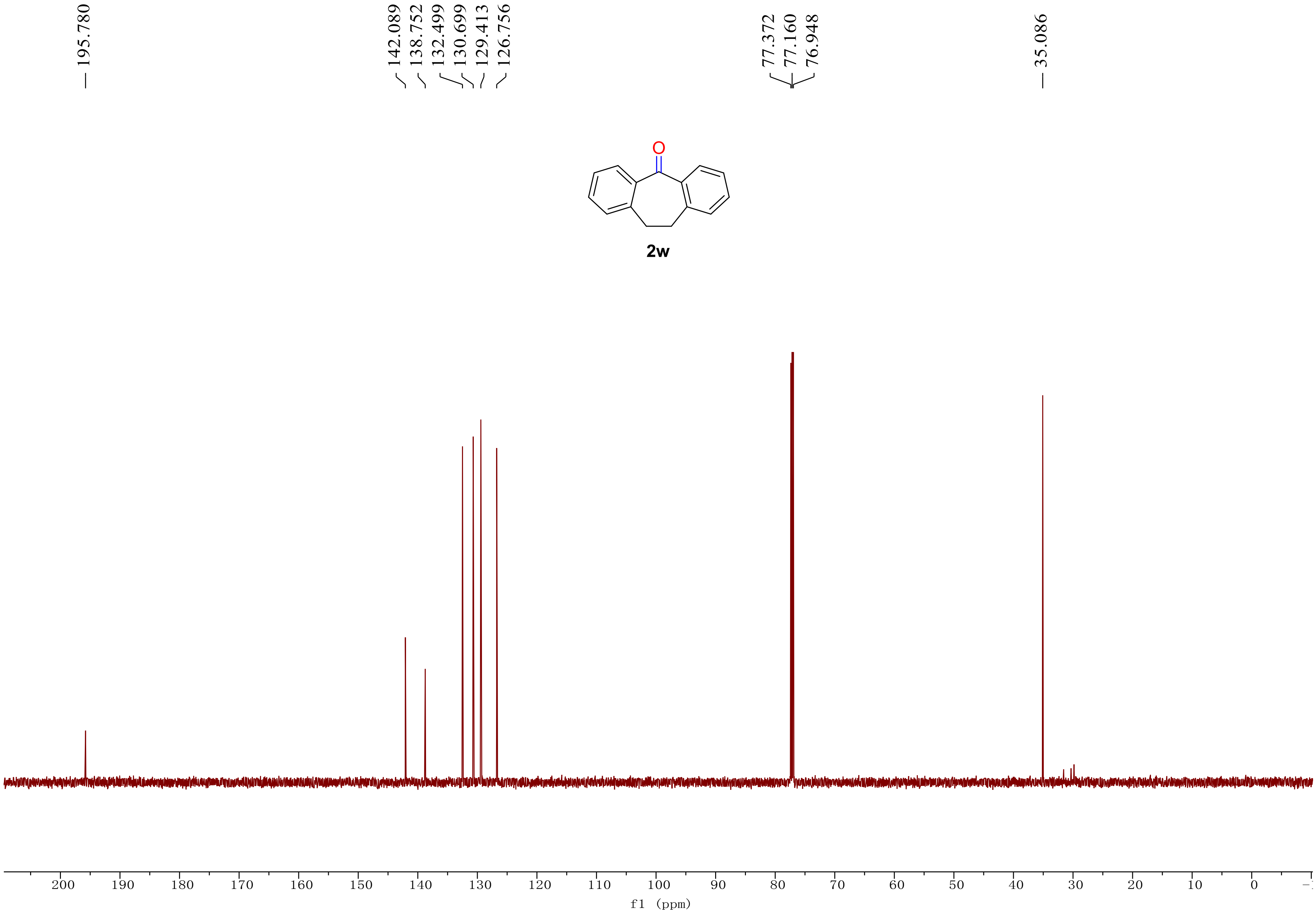

194.067
144.573
134.822
134.293
129.216
124.458
120.442
77.371
77.160
76.949
O
2u
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

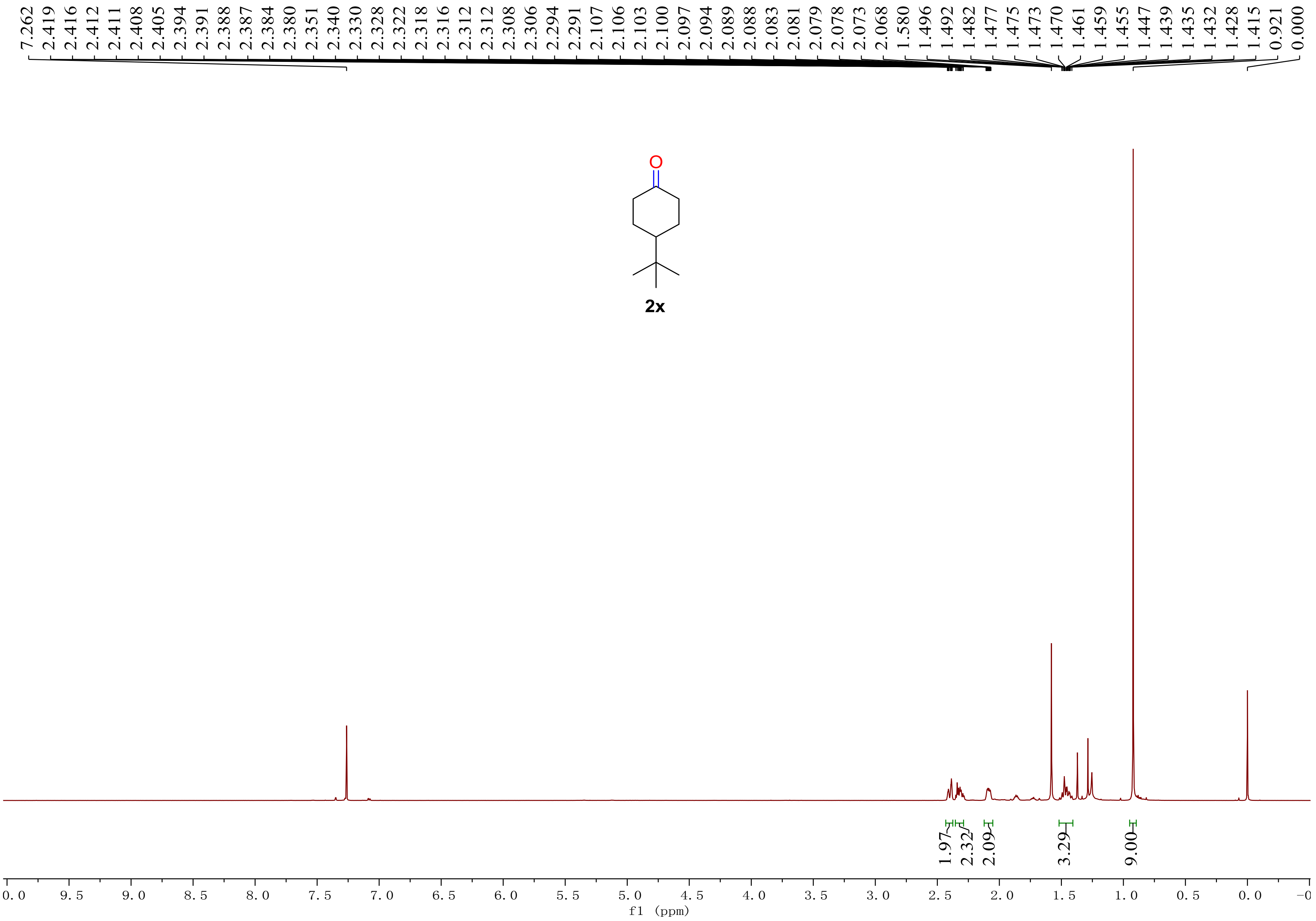

8.360
8.358
8.347
8.344
7.749
7.746
7.735
7.723
7.721
7.513
7.499
7.402
7.390
7.377
7.262
1.620
0.000
O
O
2v
1.94
2.03
2.00
2.10
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

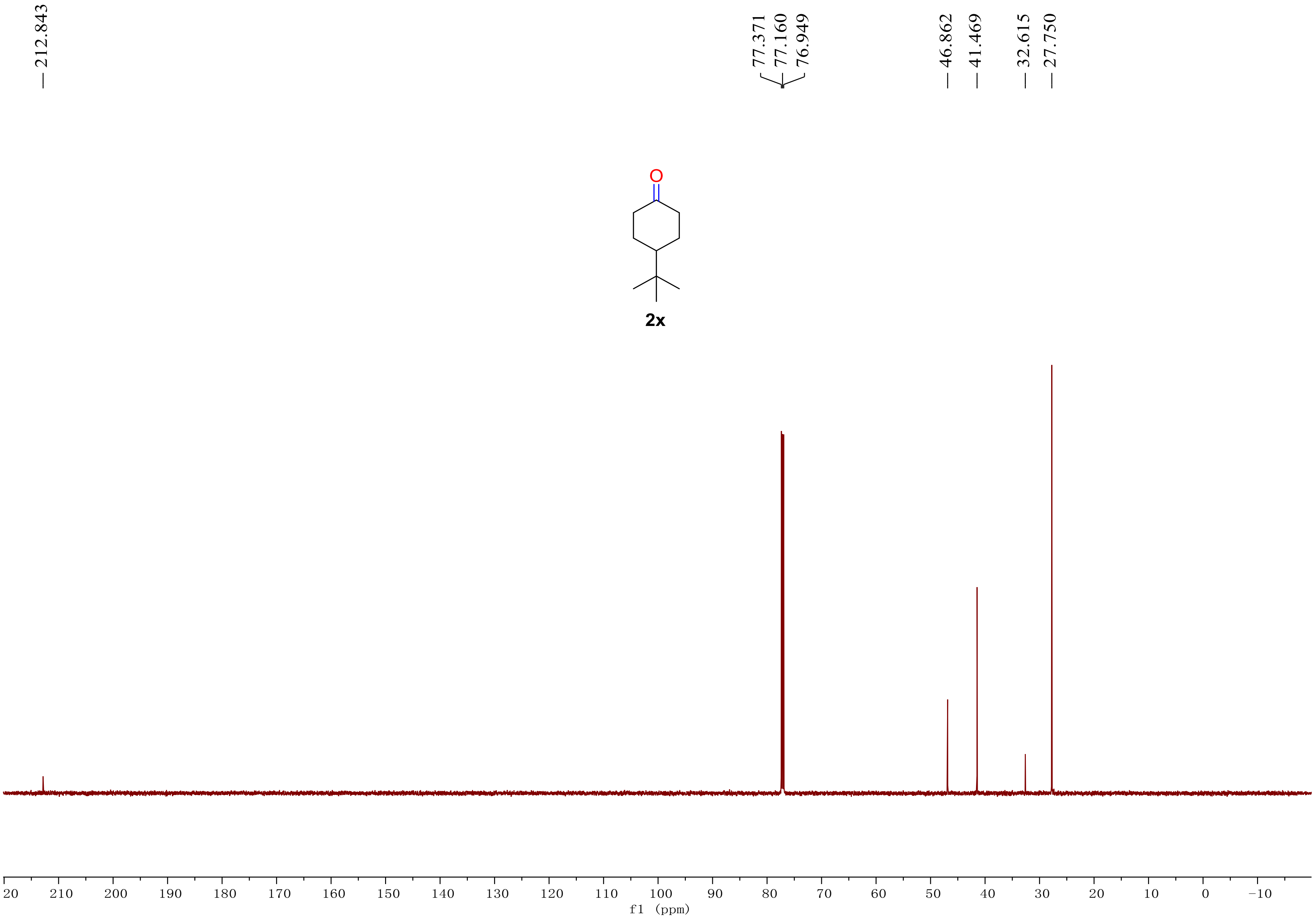

177.403
156.346
134.975
126.899
124.067
122.015
118.133
77.372
77.160
76.948
O
O
2v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)


8.012
7.999
7.443
7.440
7.430
7.428
7.418
7.416
7.336
7.323
7.311
7.253
7.228
7.216
3.209
0.000
O
1.89
1.99
2.00
1.98
4.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

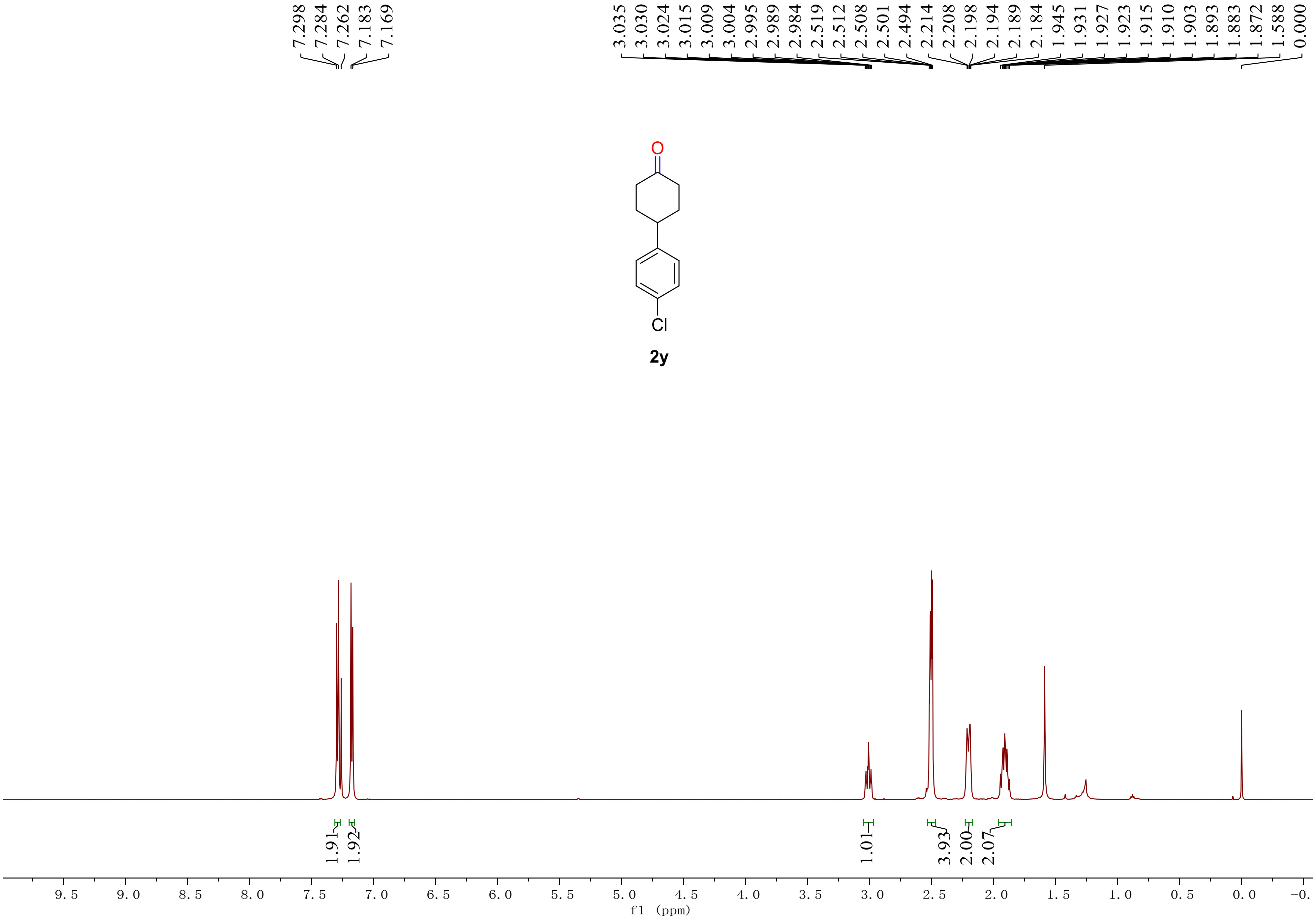
2w


195.780
142.089
138.752
132.499
130.699
129.413
126.756
77.372
77.160
76.948
35.086
O
2w
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.262
2.419
2.416
2.412
2.411
2.408
2.405
2.394
2.391
2.388
2.387
2.384
2.380
2.351
2.340
2.330
2.328
2.322
2.318
2.316
2.312
2.312
2.308
2.306
2.294
2.291
2.107
2.106
2.103
2.100
2.097
2.094
2.089
2.088
2.083
2.081
2.079
2.078
2.073
2.068
1.580
1.496
1.492
1.482
1.477
1.475
1.473
1.470
1.461
1.459
1.455
1.447
1.439
1.435
1.432
1.428
1.415
0.921
0.000
O
2x
1.97
2.32
2.09
3.29
9.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

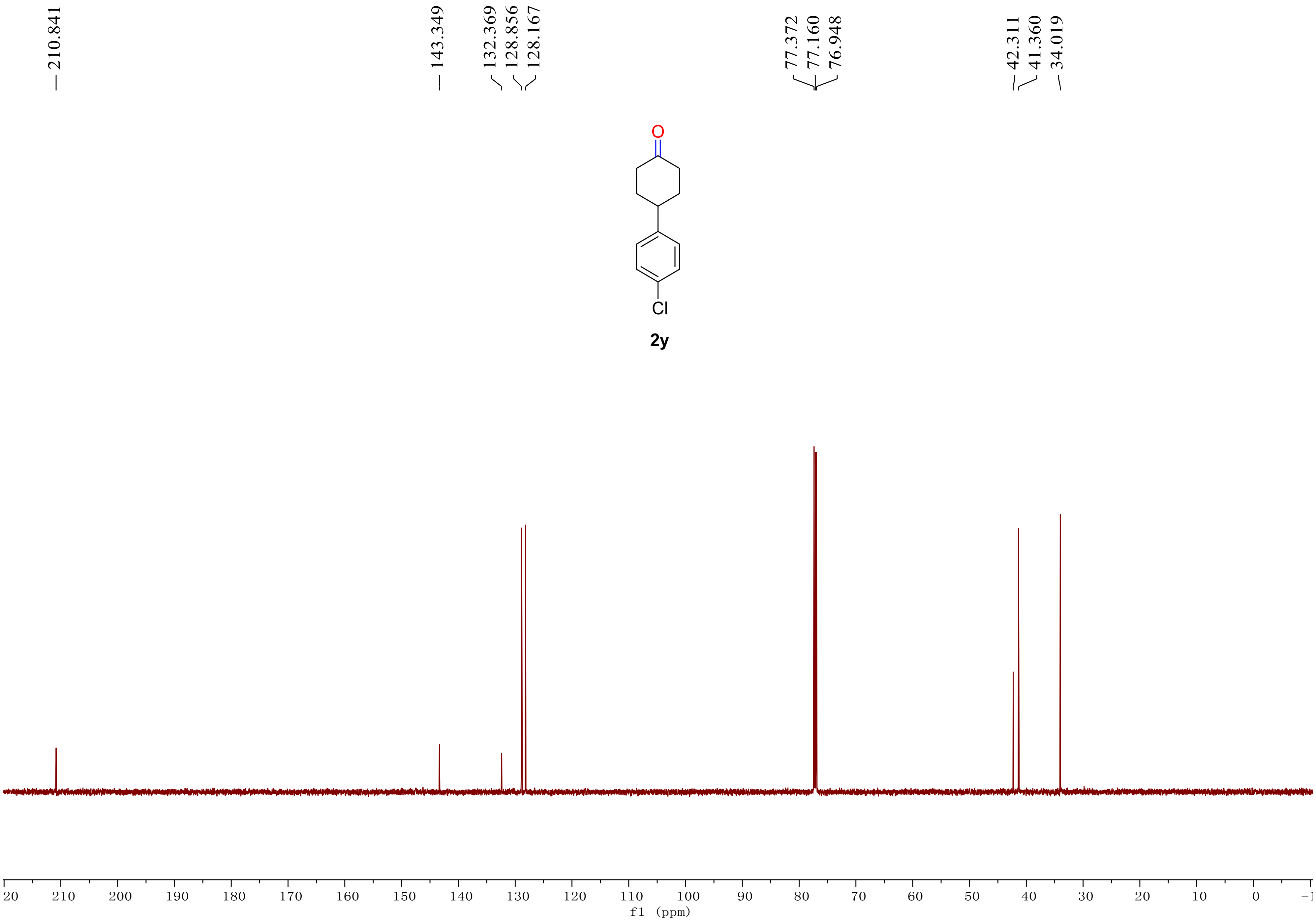


212.843
77.371
77.160
76.949
46.862
41.469
32.615
27.750
O
2x
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

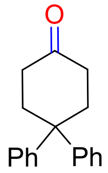


2y

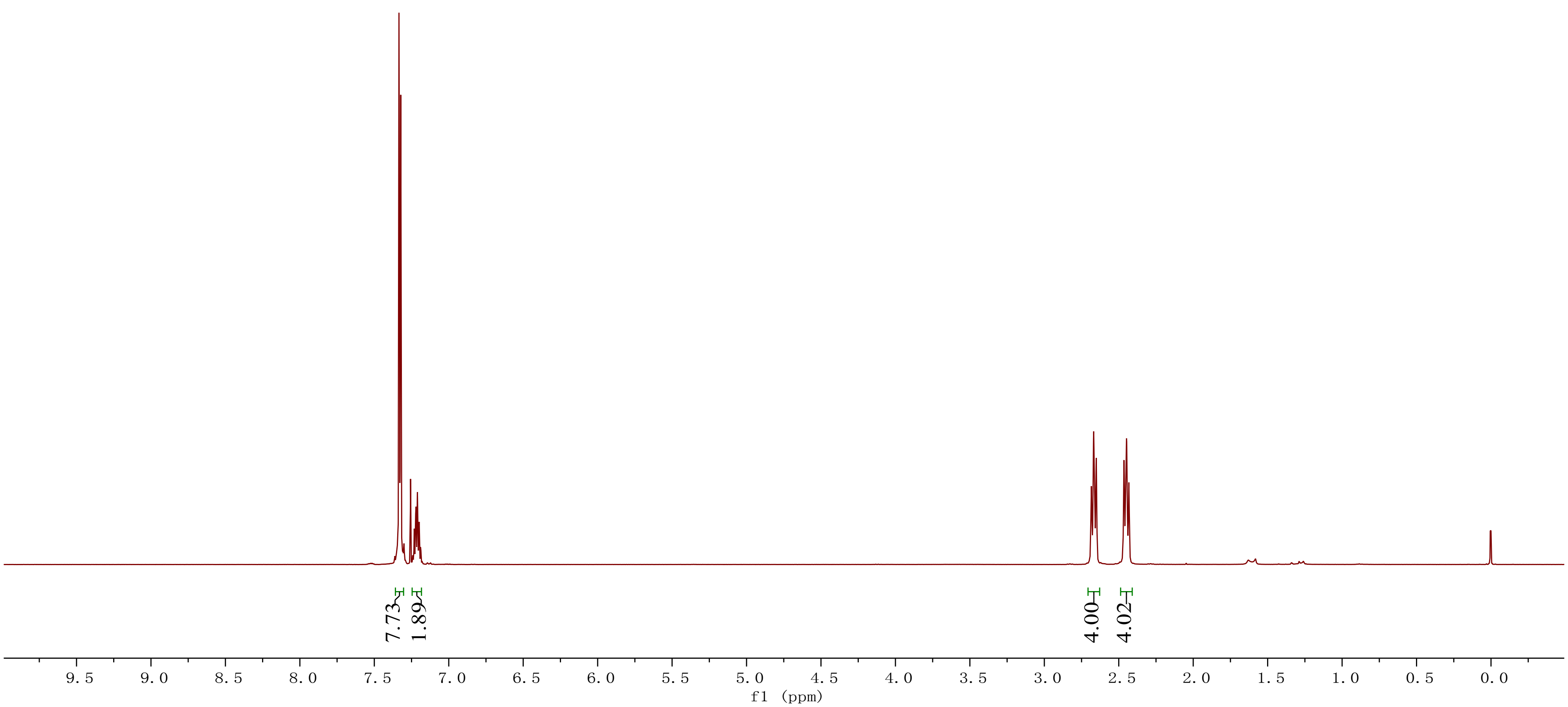
7.298
7.284
7.262
7.183
7.169
3.035
3.030
3.024
3.015
3.009
3.004
2.995
2.989
2.984
2.519
2.512
2.508
2.501
2.494
2.214
2.208
2.198
2.194
2.189
2.184
1.945
1.931
1.927
1.923
1.915
1.910
1.903
1.893
1.883
1.872
1.588
0.000
O
Cl
1.91
1.92
1.01
3.93
2.00
2.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


210.841
143.349
132.369
128.856
128.167
77.372
77.160
76.948
42.311
41.360
34.019
O
Cl
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

2y



2z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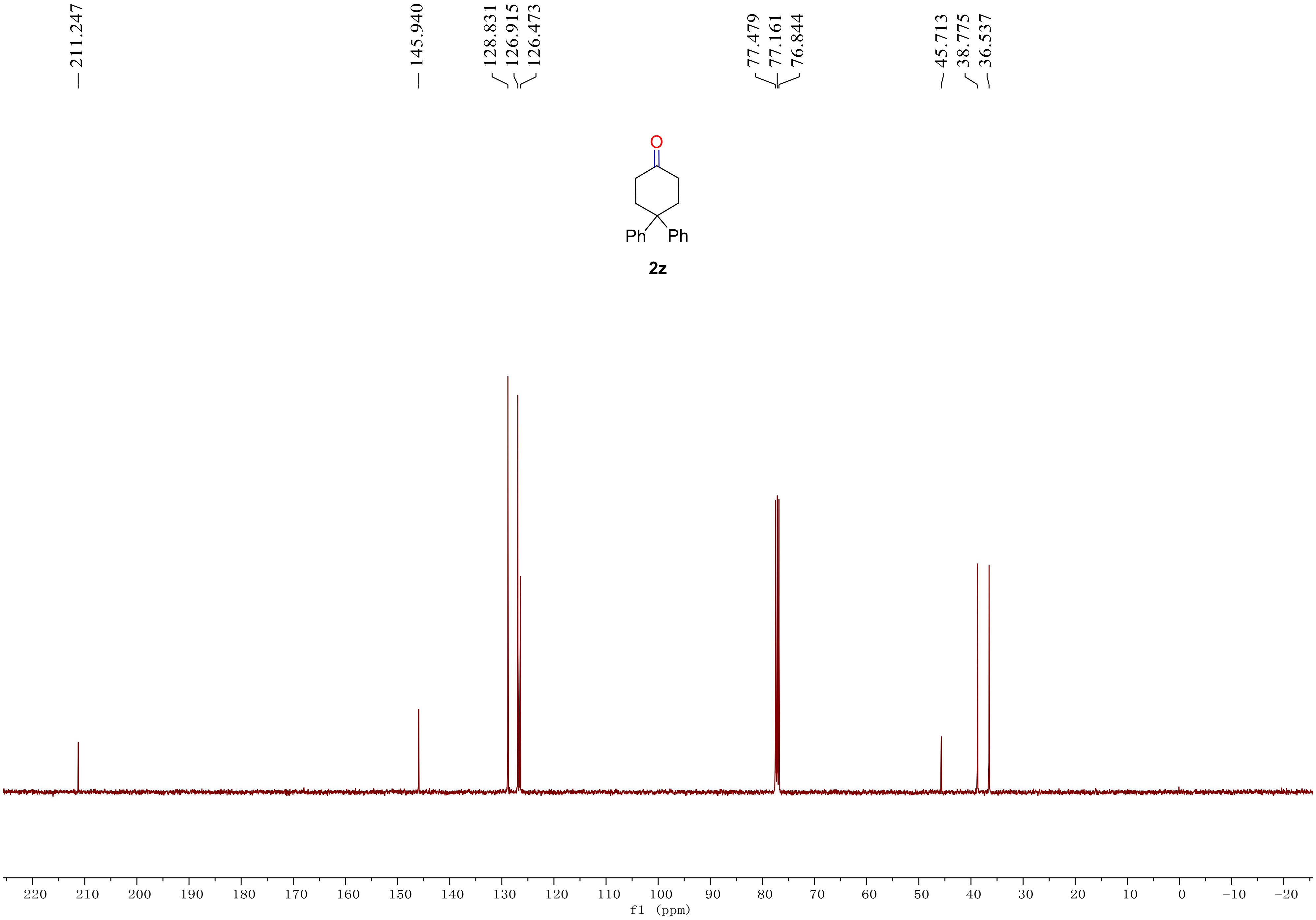
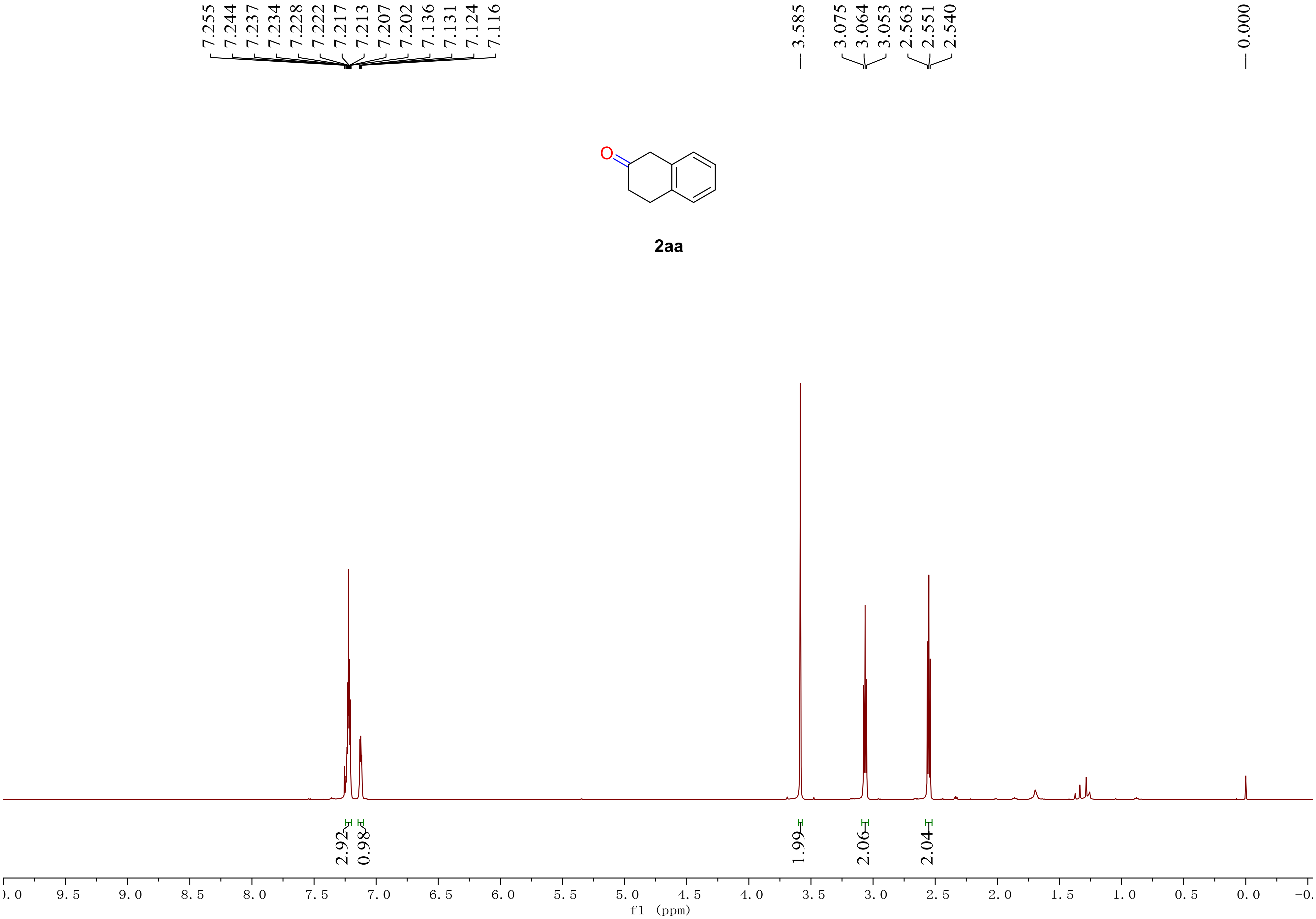
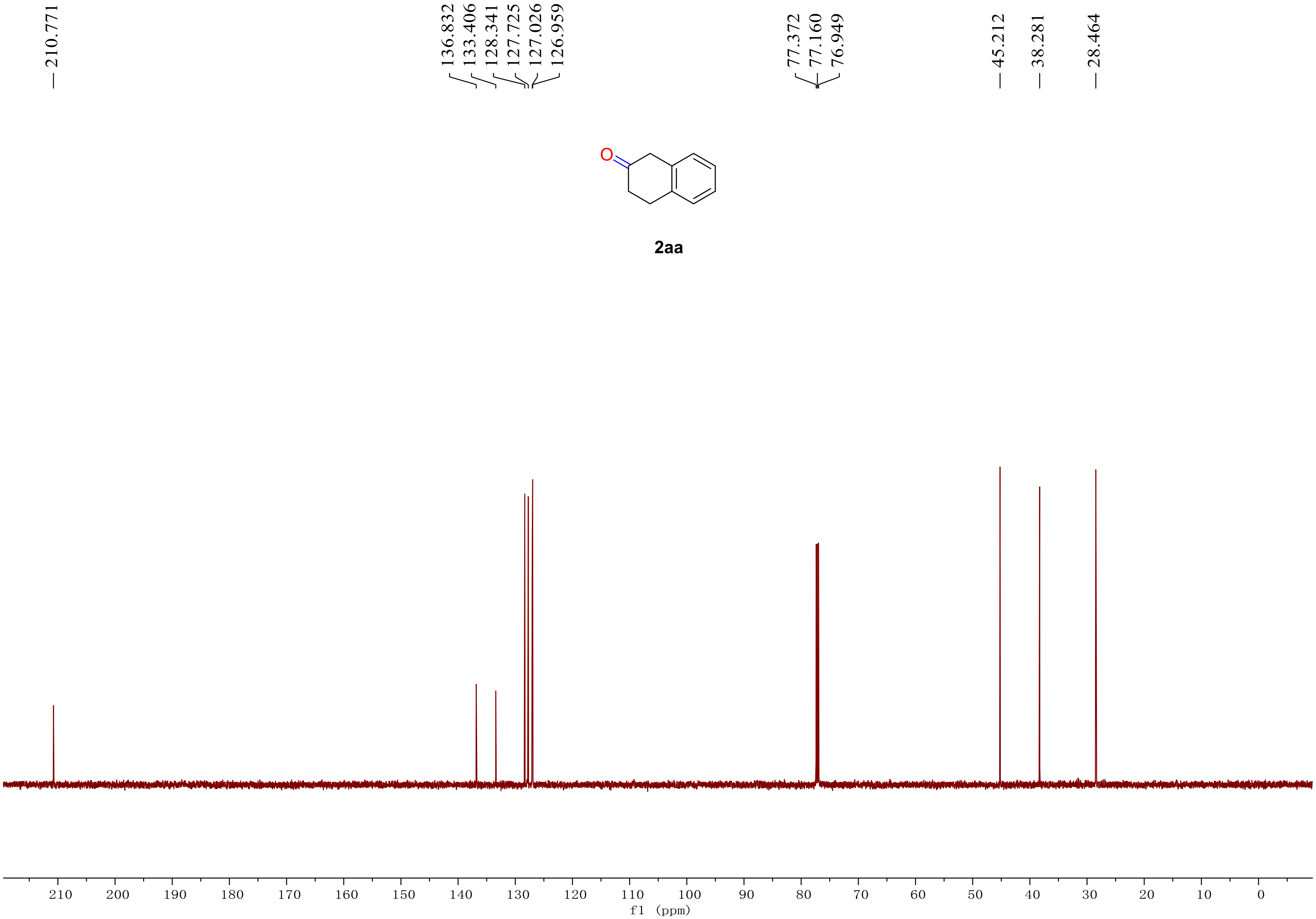
7.322
7.257
7.242
7.232
7.230
7.224
7.222
7.220
7.214
7.211
7.208
7.201
7.198
7.196
7.190
7.187
2.684
2.668
2.651
2.465
2.448
2.432
0.000
7.73
1.89
4.00
4.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


211.247
145.940
128.831
126.915
126.473
77.479
77.161
76.844
45.713
38.775
36.537
O
Ph
Ph
2z
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)



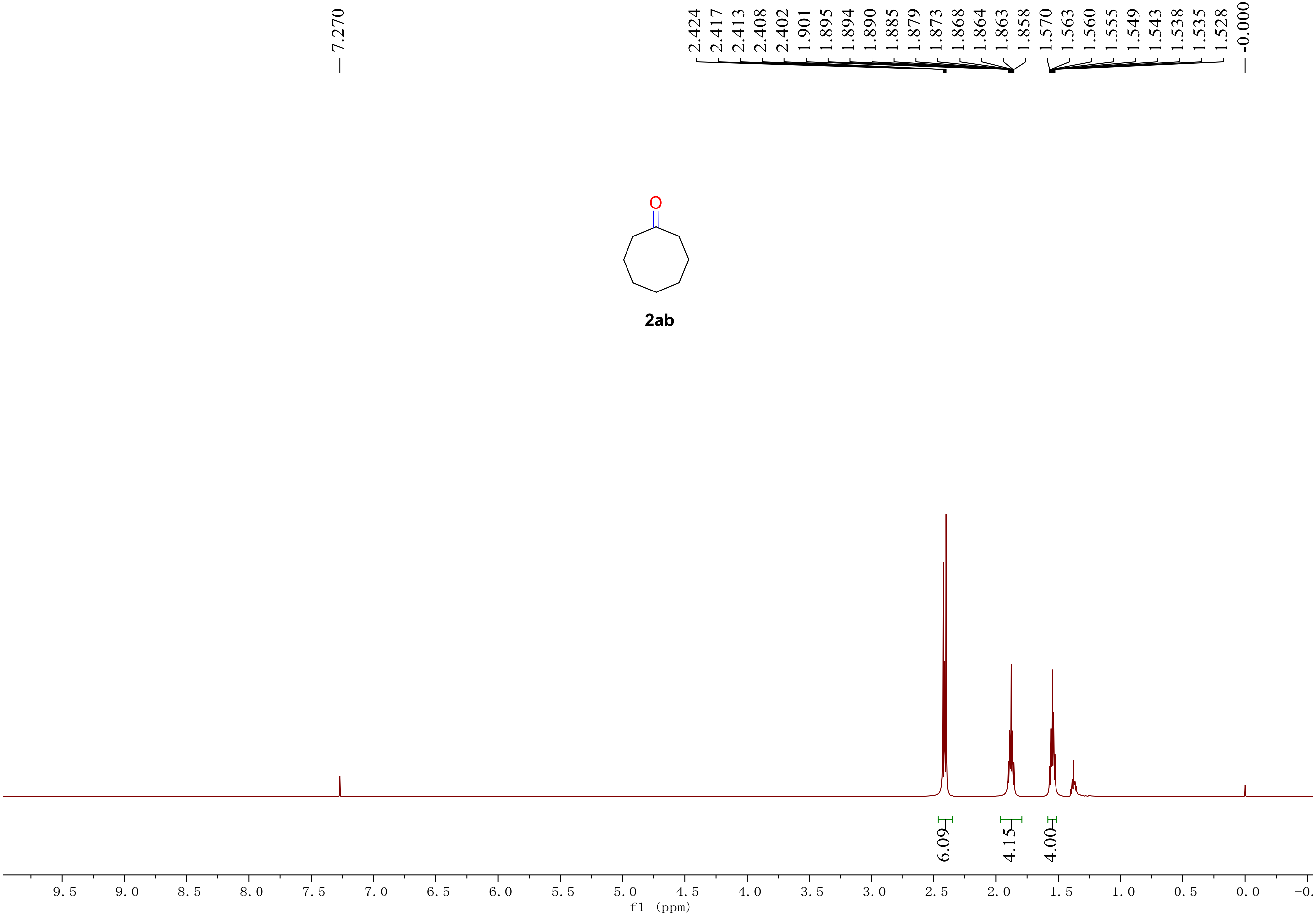
2aa

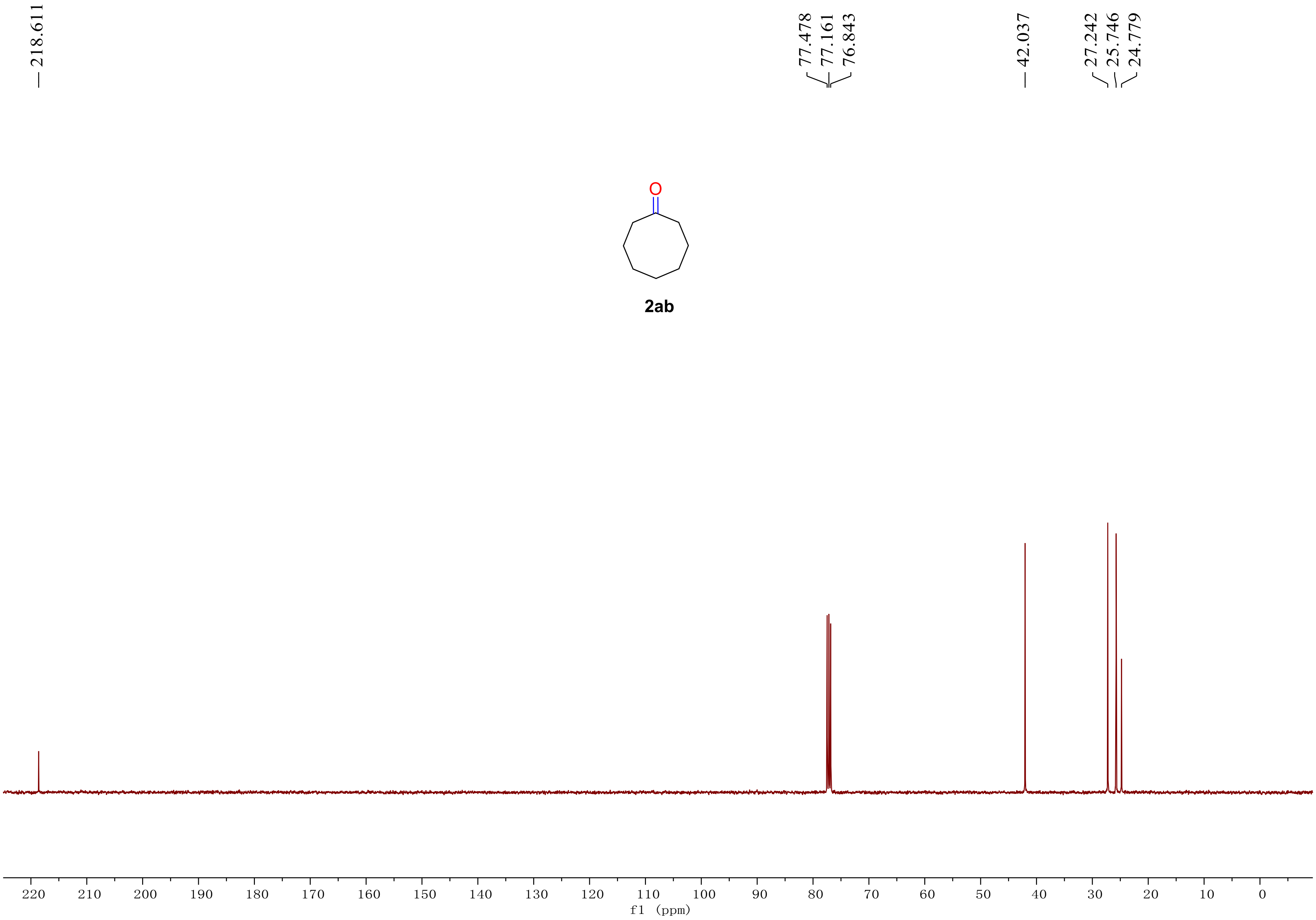
7.255
7.244
7.237
7.234
7.228
7.222
7.217
7.213
7.207
7.202
7.136
7.131
7.124
7.116
3.585
3.075
3.064
3.053
2.563
2.551
2.540
0.000
O
2.92
0.98
1.99
2.06
2.04
). 0
9. 5
9. 0
8. 5
8. 0
7. 5
7. 0
6. 5
6. 0
5. 5
5. 0
4. 5
4. 0
3. 5
3. 0
2. 5
2. 0
1. 5
1. 0
0. 5
0. 0
-0.
f1 (ppm)

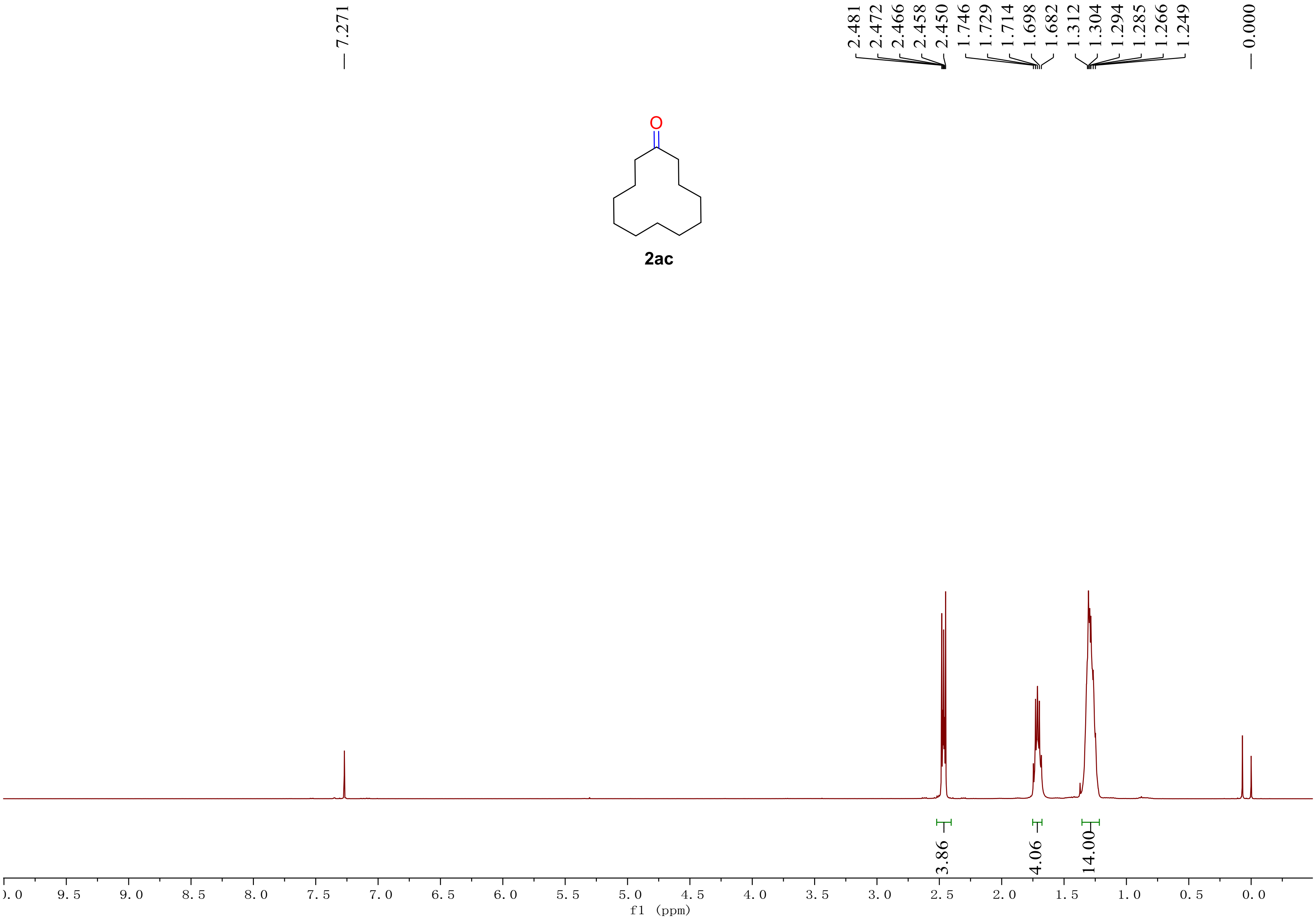


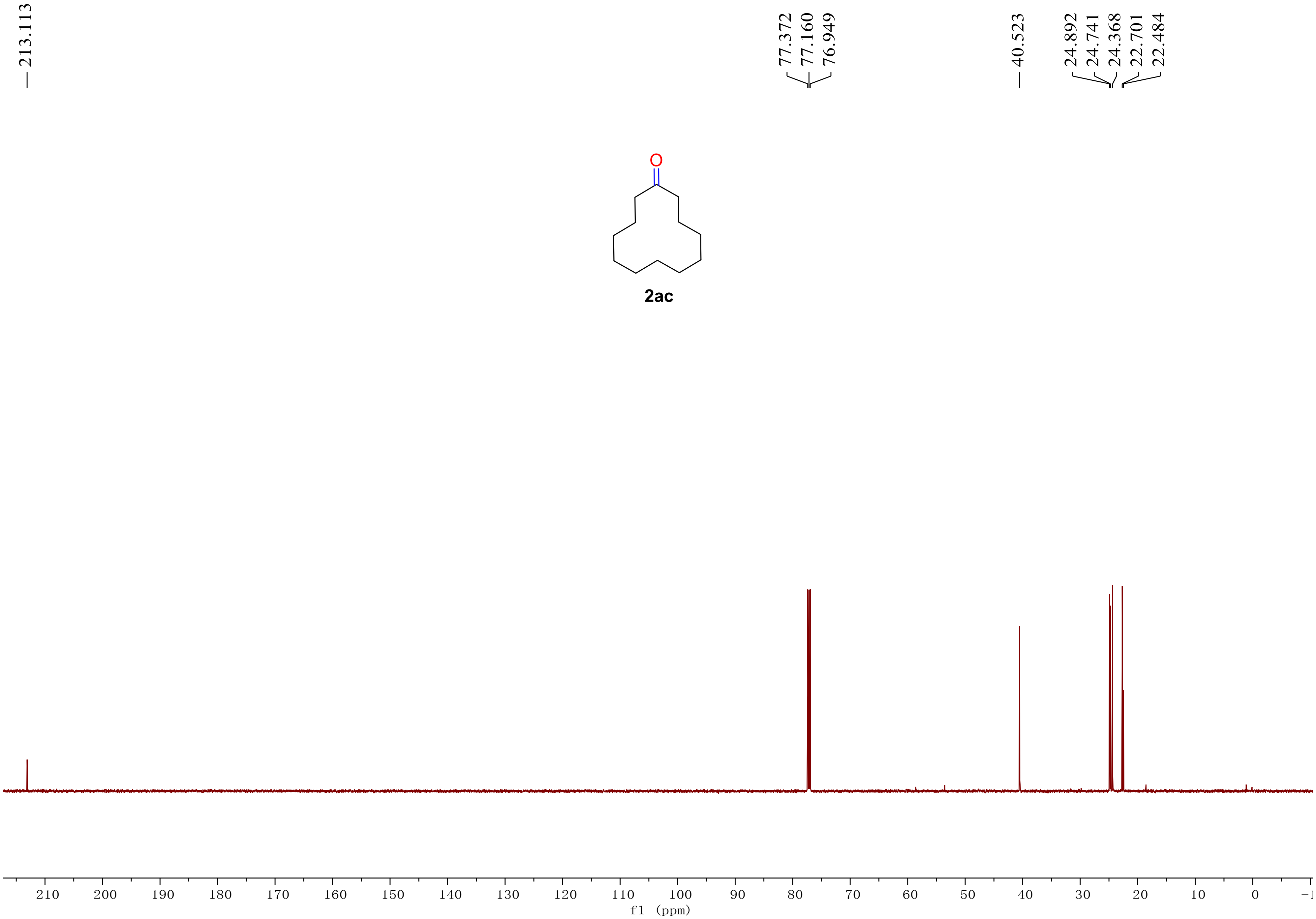
2aa

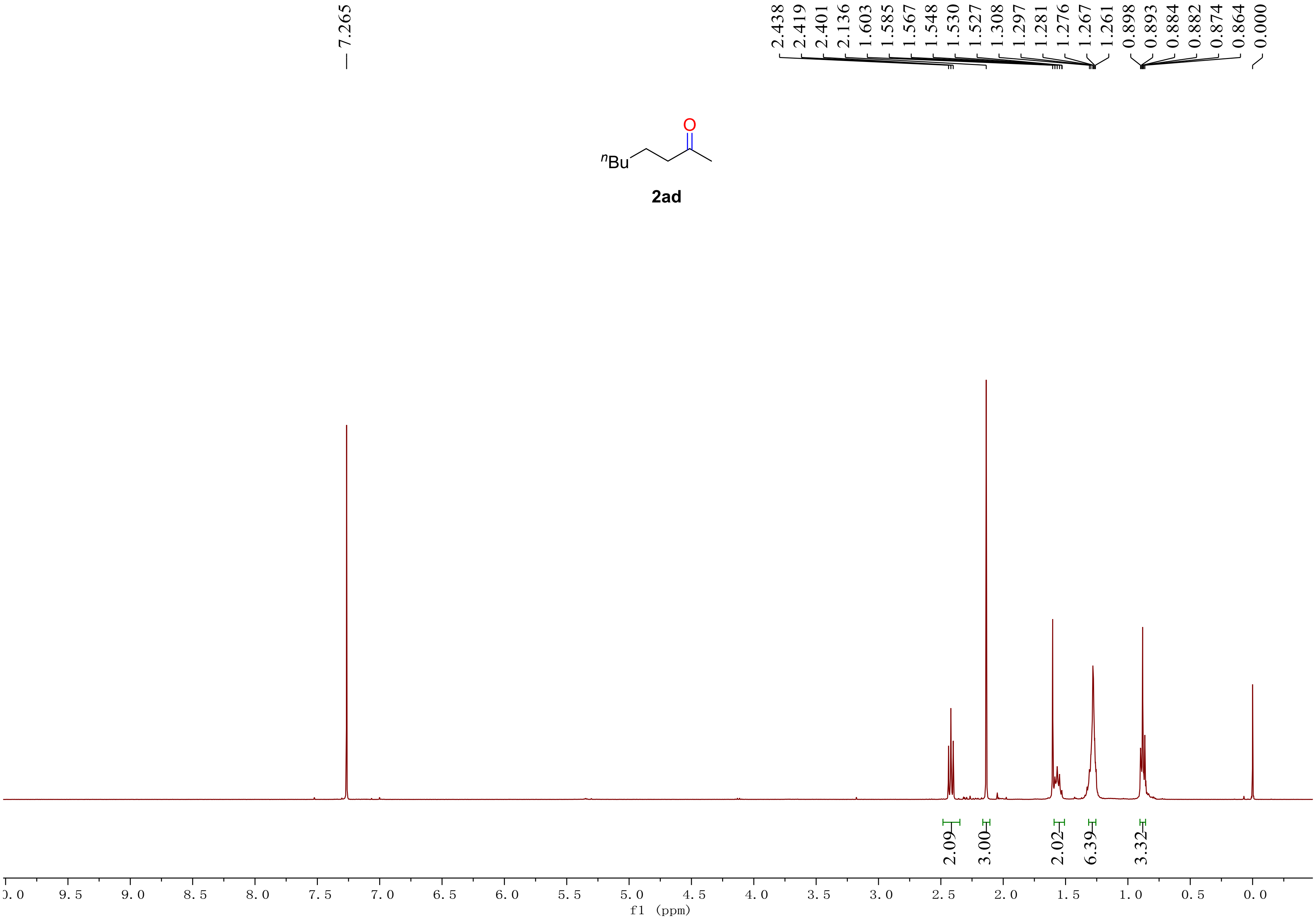
210.771
136.832
133.406
128.341
127.725
127.026
126.959
77.372
77.160
76.949
45.212
38.281
28.464
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.270
2.424
2.417
2.413
2.408
2.402
1.901
1.895
1.894
1.890
1.885
1.879
1.873
1.868
1.864
1.863
1.858
1.570
1.563
1.560
1.555
1.549
1.543
1.538
1.535
1.528
-0.000
O
2ab
6.09
4.15
4.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


218.611
77.478
77.161
76.843
42.037
27.242
25.746
24.779
O
2ab
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

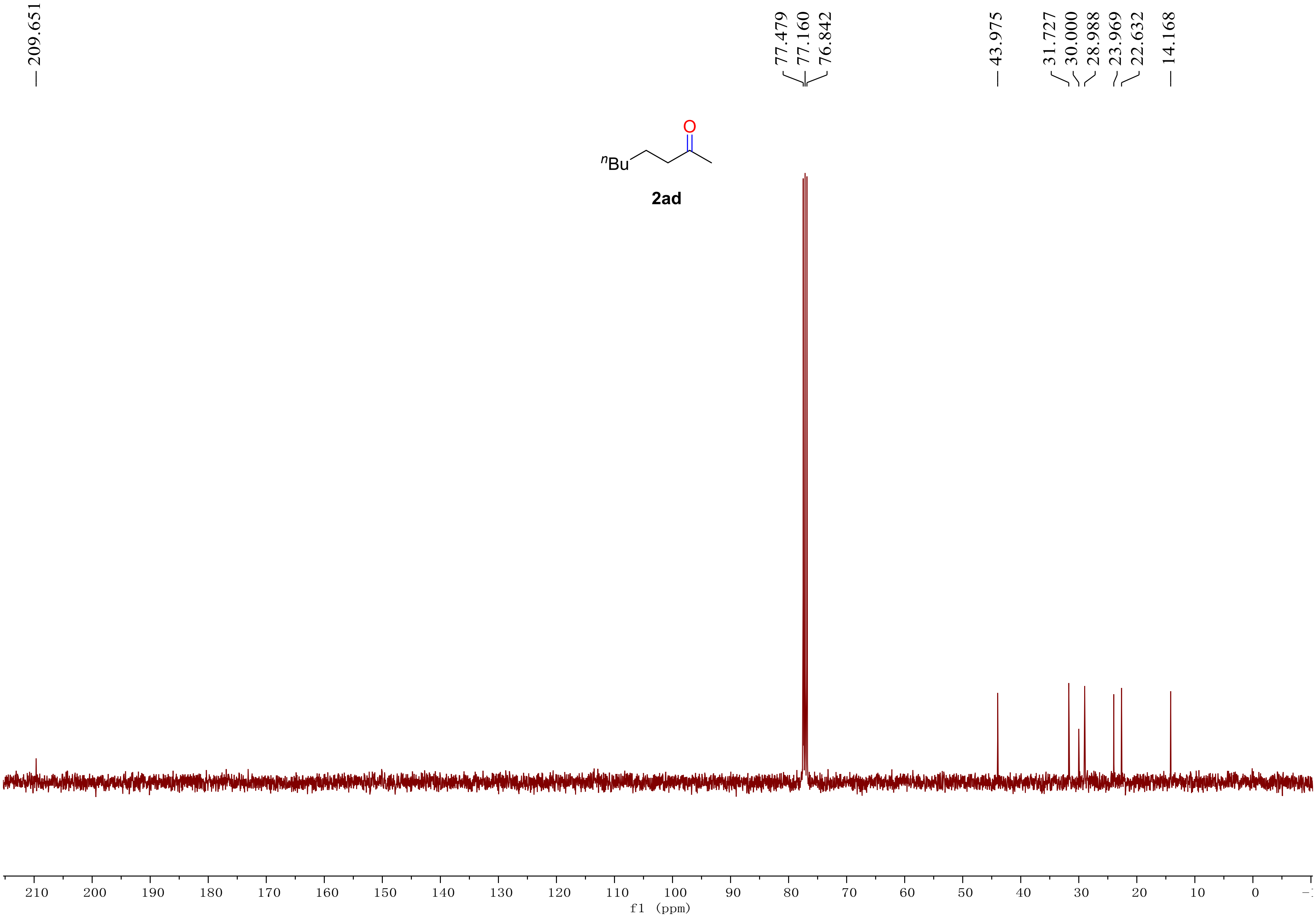

7.271
2.481
2.472
2.466
2.458
2.450
1.746
1.729
1.714
1.698
1.682
1.312
1.304
1.294
1.285
1.266
1.249
0.000
O
2ac
3.86
4.06
14.00
). 0
9. 5
9. 0
8. 5
8. 0
7. 5
7. 0
6. 5
6. 0
5. 5
5. 0
4. 5
4. 0
3. 5
3. 0
2. 5
2. 0
1. 5
1. 0
0. 5
0. 0
f1 (ppm)

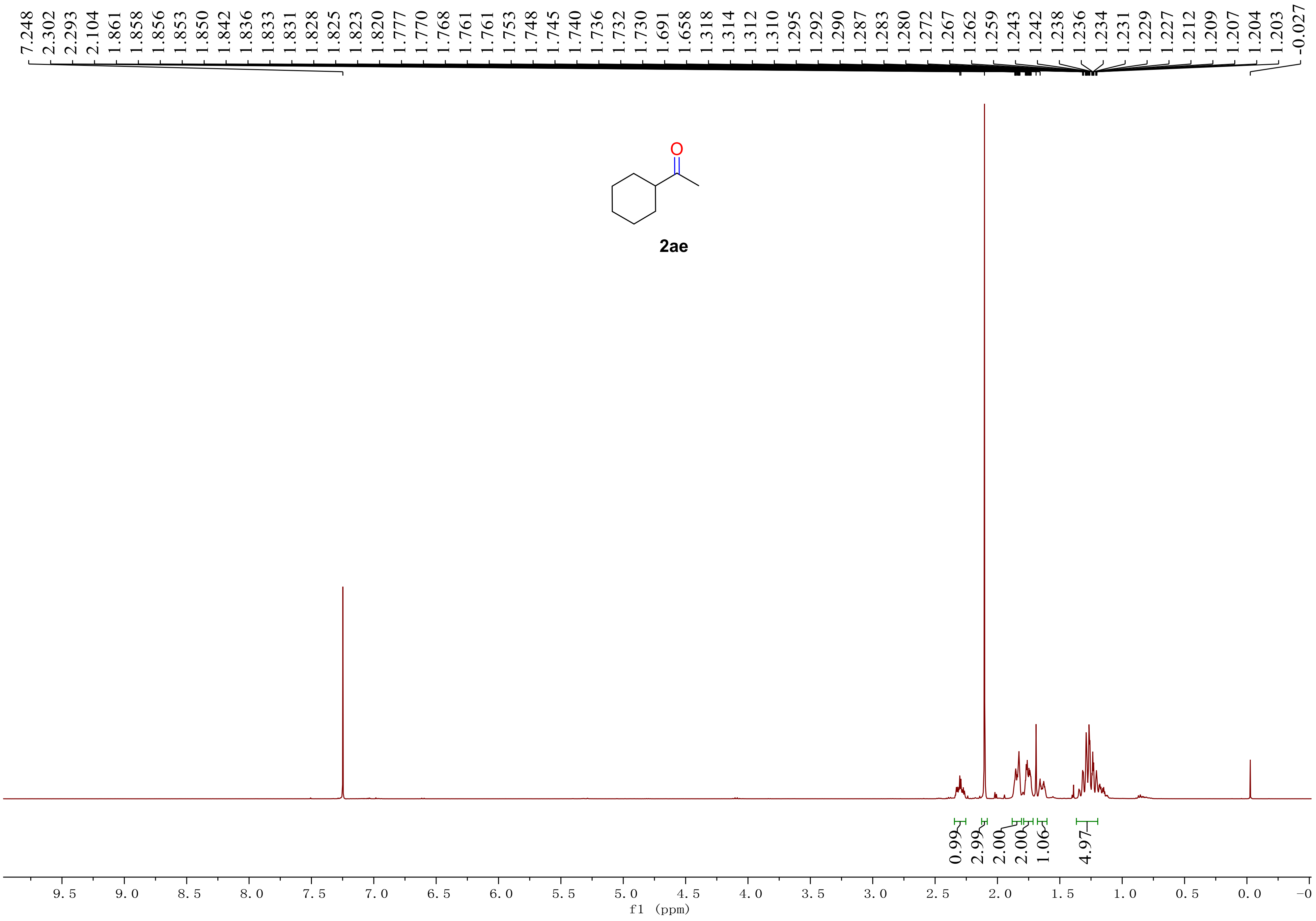

213.113
77.372
77.160
76.949
40.523
24.892
24.741
24.368
22.701
22.484
O
2ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

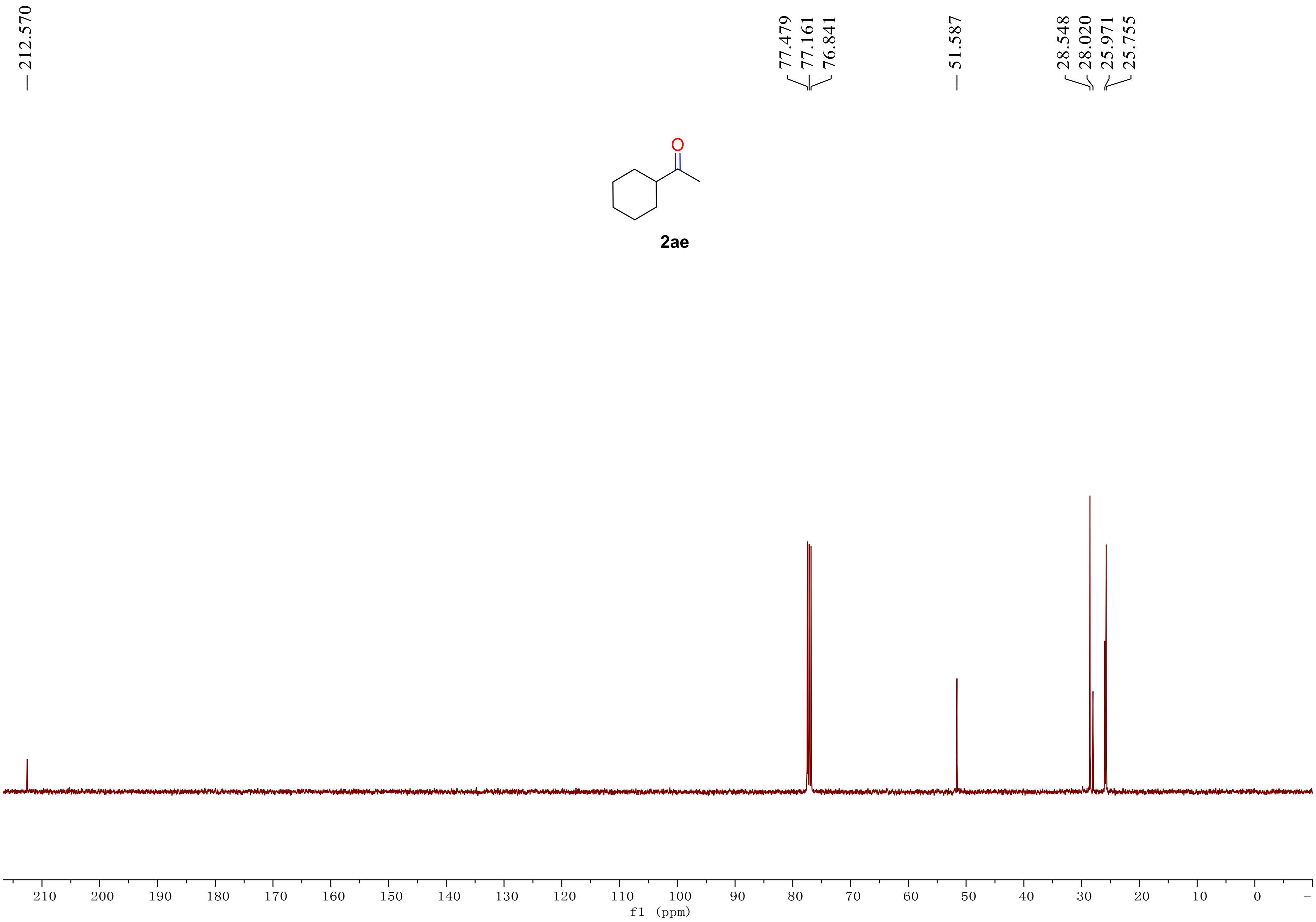


2ad

7.265
2.438
2.419
2.401
2.136
1.603
1.585
1.567
1.548
1.530
1.527
1.308
1.297
1.281
1.276
1.267
1.261
0.898
0.893
0.884
0.882
0.874
0.864
0.000
O
nBu
2.09
3.00
2.02
6.39
3.32
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

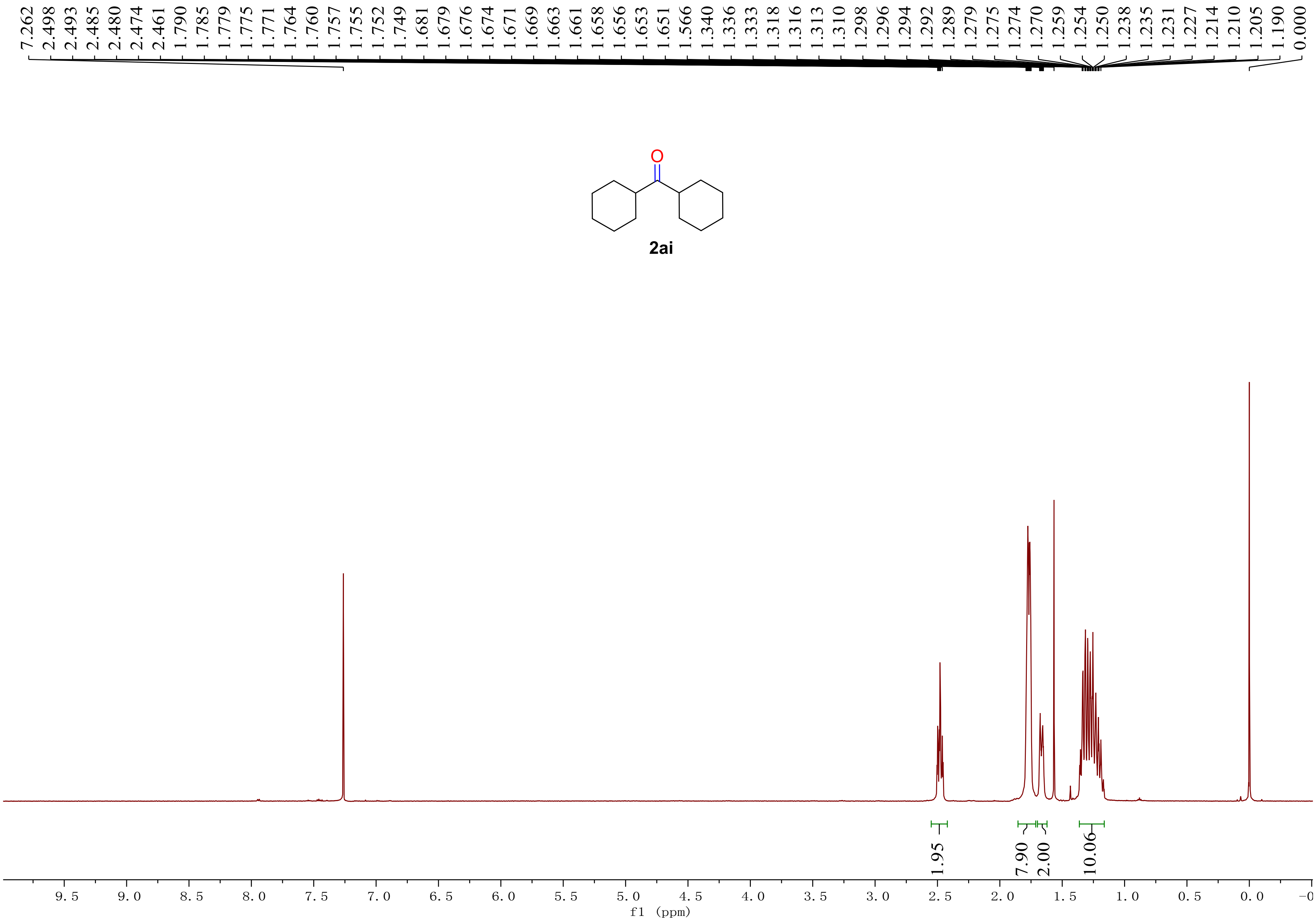

2ad
209.651
77.479
77.160
76.842
43.975
31.727
30.000
28.988
23.969
22.632
14.168
O
nBu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

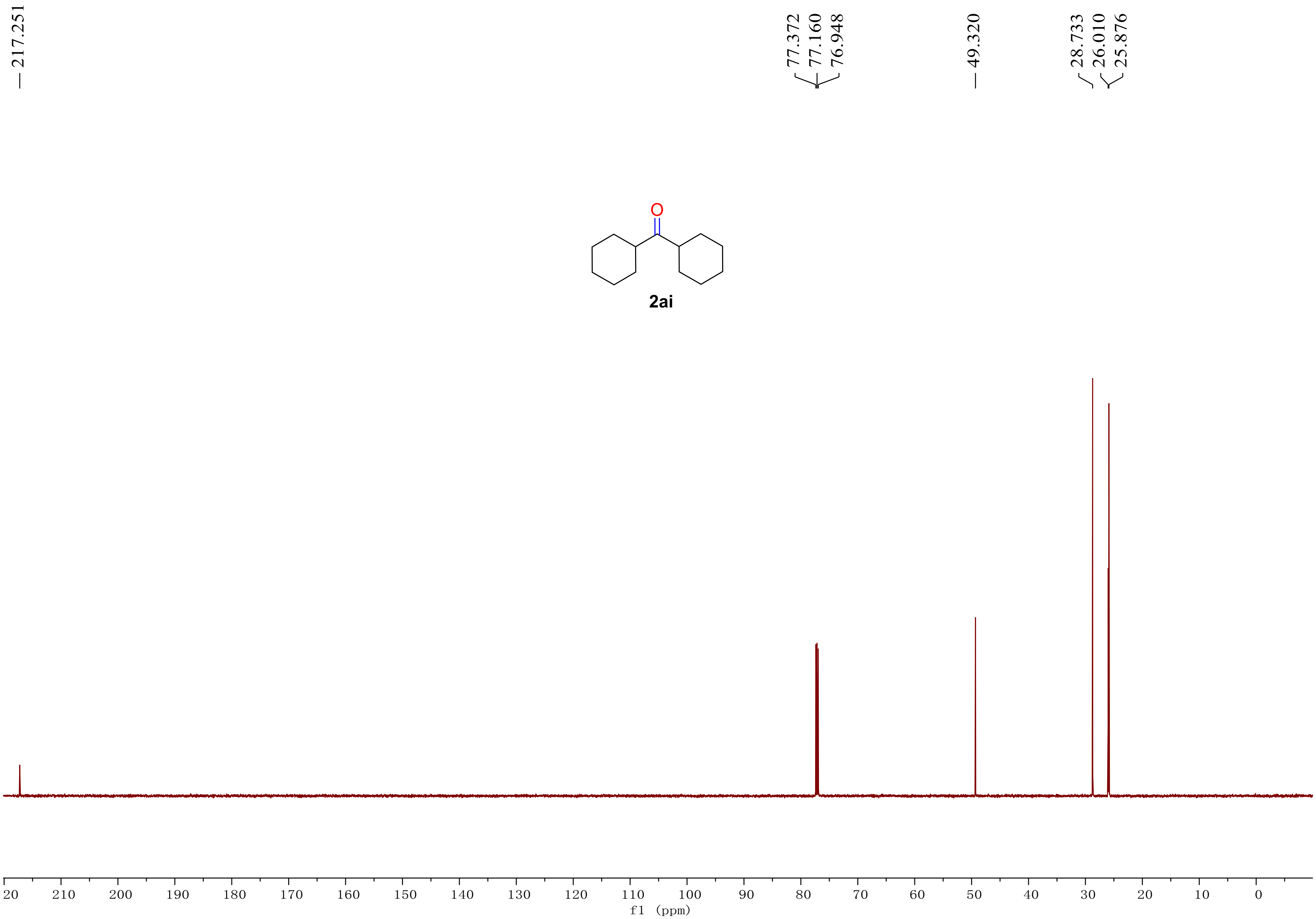

7.248
2.302
2.293
2.104
1.861
1.858
1.856
1.853
1.850
1.842
1.836
1.833
1.831
1.828
1.825
1.823
1.820
1.777
1.770
1.768
1.761
1.761
1.753
1.748
1.745
1.740
1.736
1.732
1.730
1.691
1.658
1.318
1.314
1.312
1.310
1.295
1.292
1.290
1.287
1.283
1.280
1.272
1.267
1.262
1.259
1.243
1.242
1.238
1.236
1.234
1.231
1.229
1.227
1.212
1.209
1.207
1.204
1.203
-0.027
O
2ae
0.99
2.99
2.00
2.00
1.06
4.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

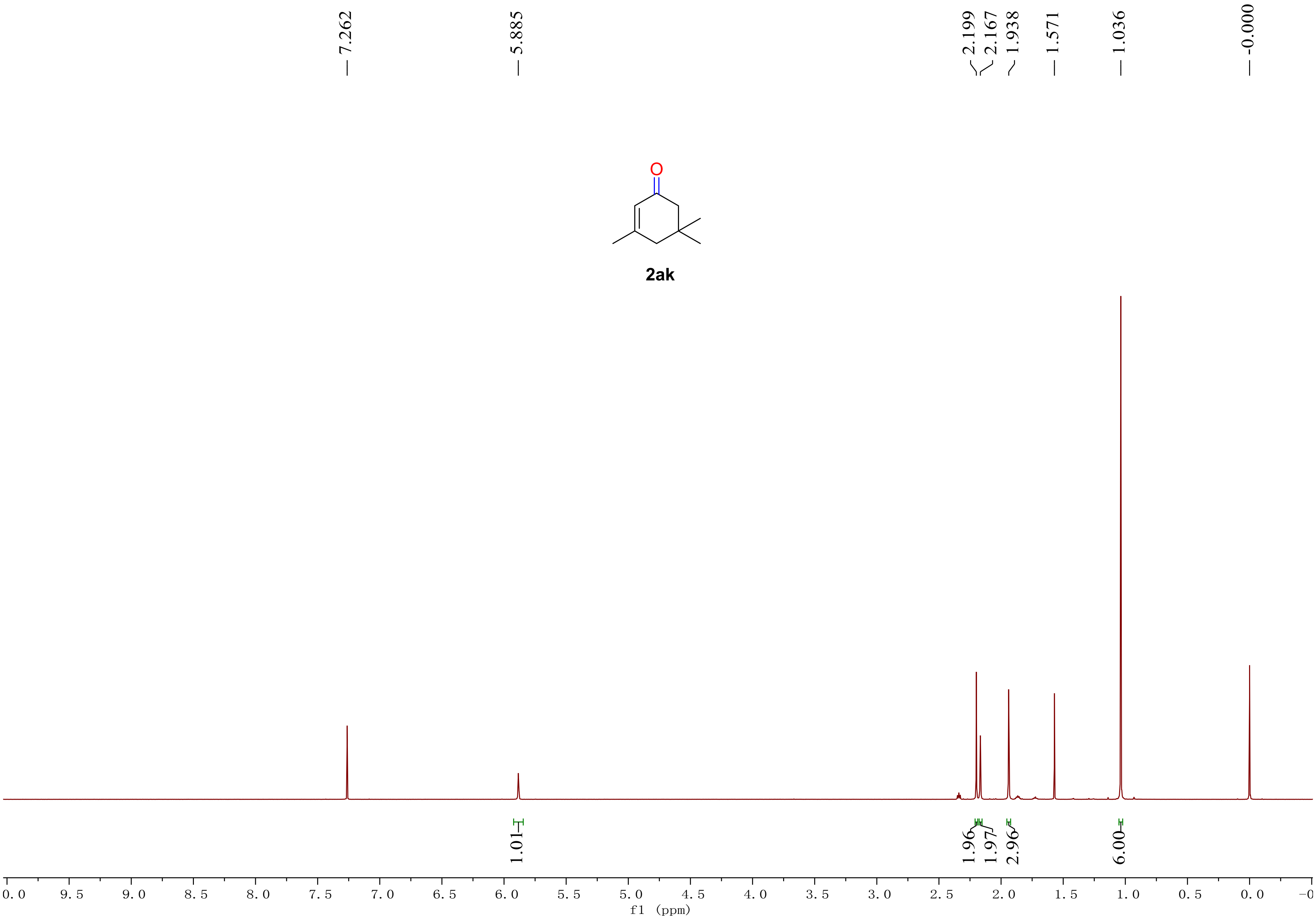


2ae

212.570
77.479
77.161
76.841
51.587
28.548
28.020
25.971
25.755
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

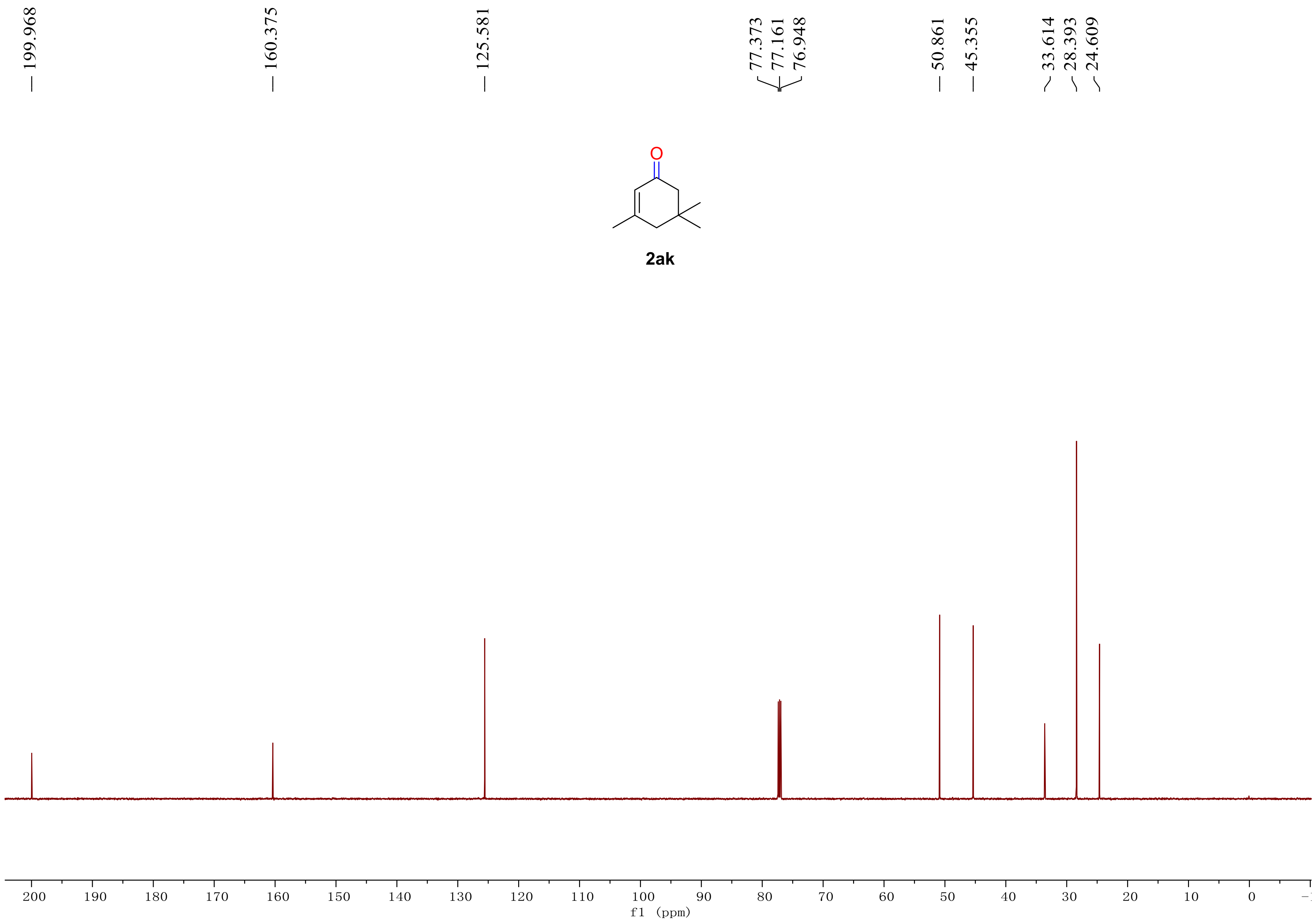

7.262
2.498
2.493
2.485
2.480
2.474
2.461
1.790
1.785
1.779
1.775
1.771
1.764
1.760
1.757
1.755
1.752
1.749
1.681
1.679
1.676
1.674
1.671
1.669
1.663
1.661
1.658
1.656
1.653
1.651
1.566
1.340
1.336
1.333
1.318
1.316
1.313
1.310
1.298
1.296
1.294
1.292
1.289
1.279
1.275
1.274
1.270
1.259
1.254
1.250
1.238
1.235
1.231
1.227
1.214
1.210
1.205
1.190
0.000
O
2ai
1.95
7.90
2.00
10.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


217.251
77.372
77.160
76.948
49.320
28.733
26.010
25.876
O
2ai
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



2ak

7.262
5.885
2.199
2.167
1.938
1.571
1.036
-0.000
O
1.01
1.96
1.97
2.96
6.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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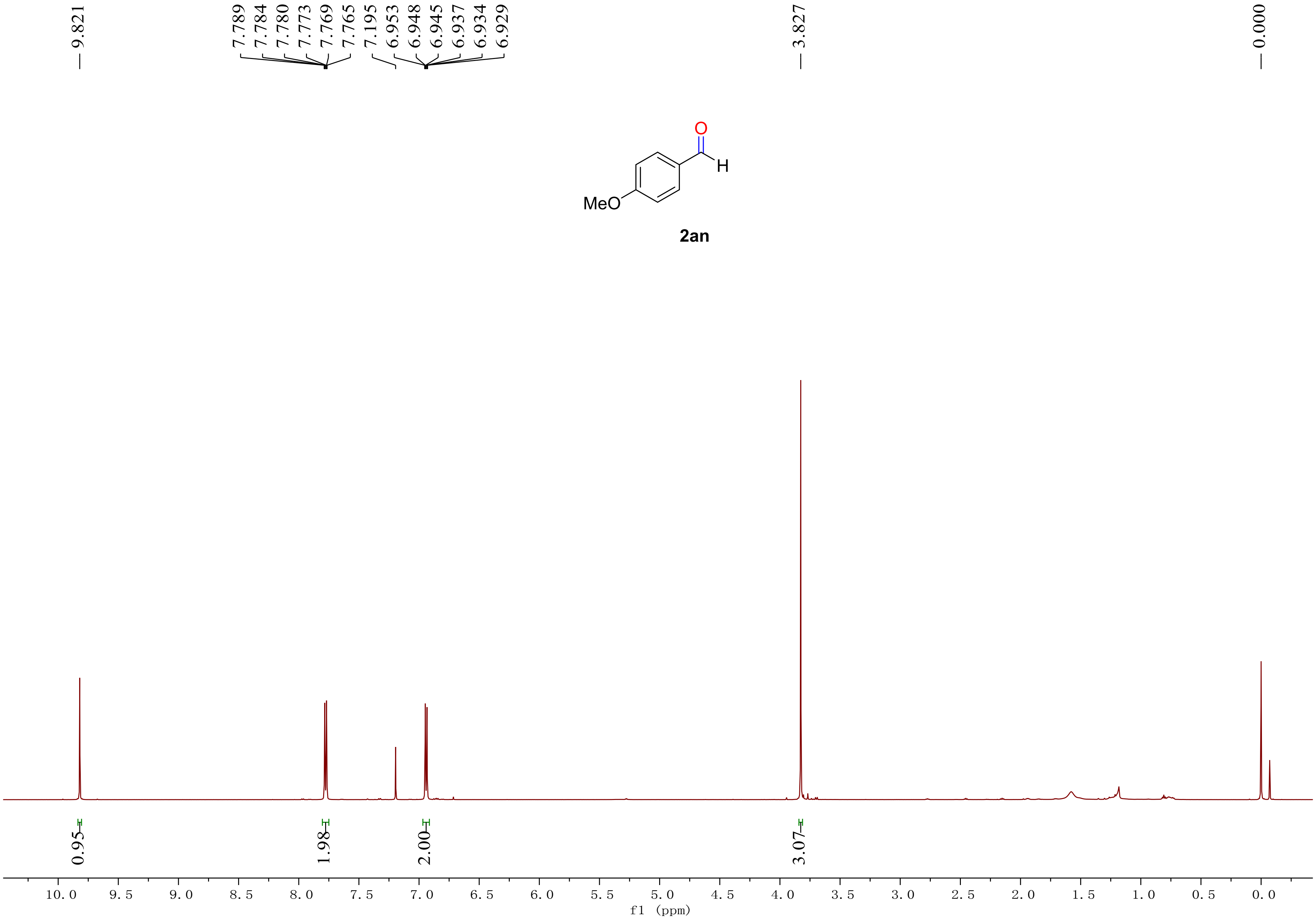
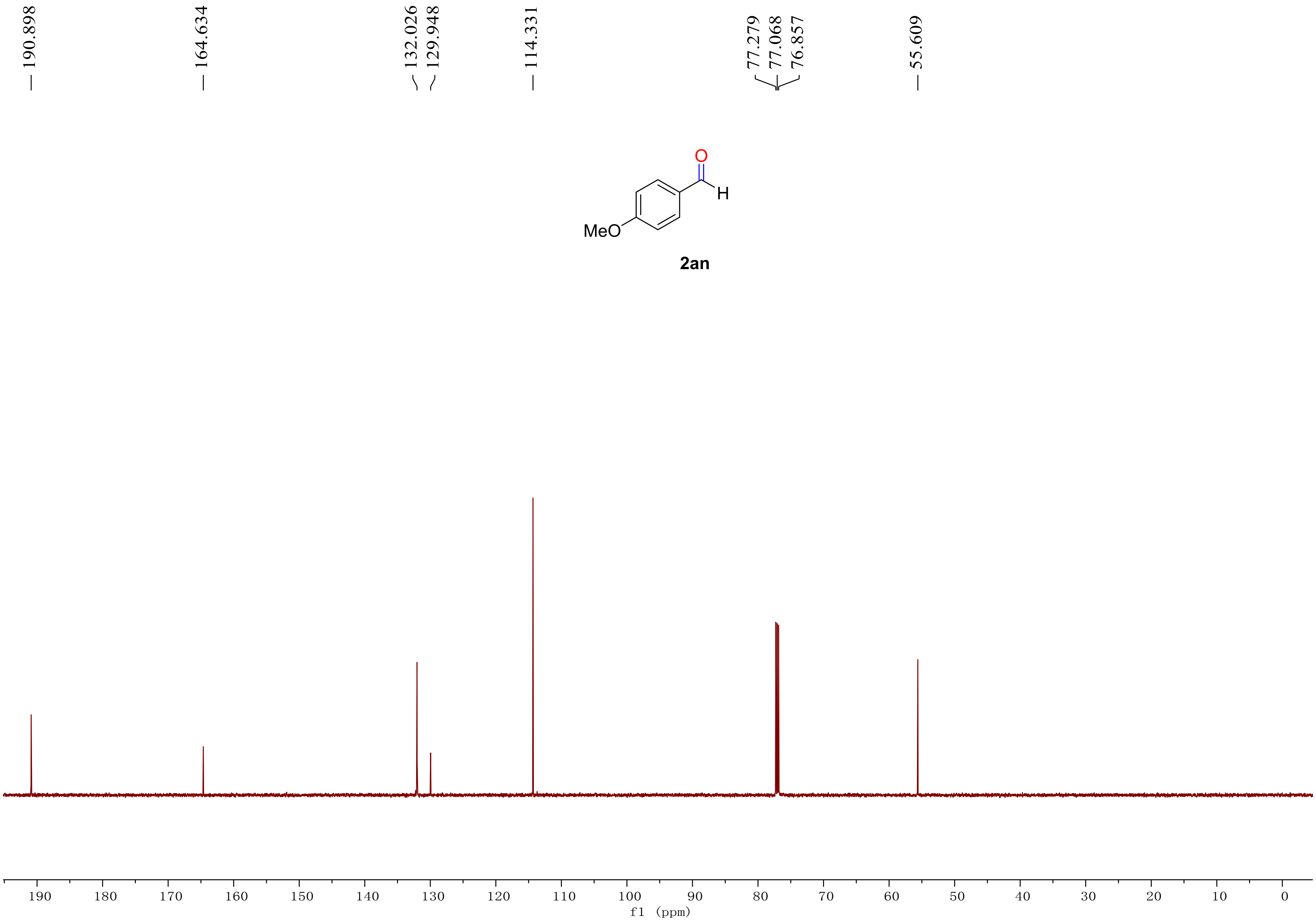
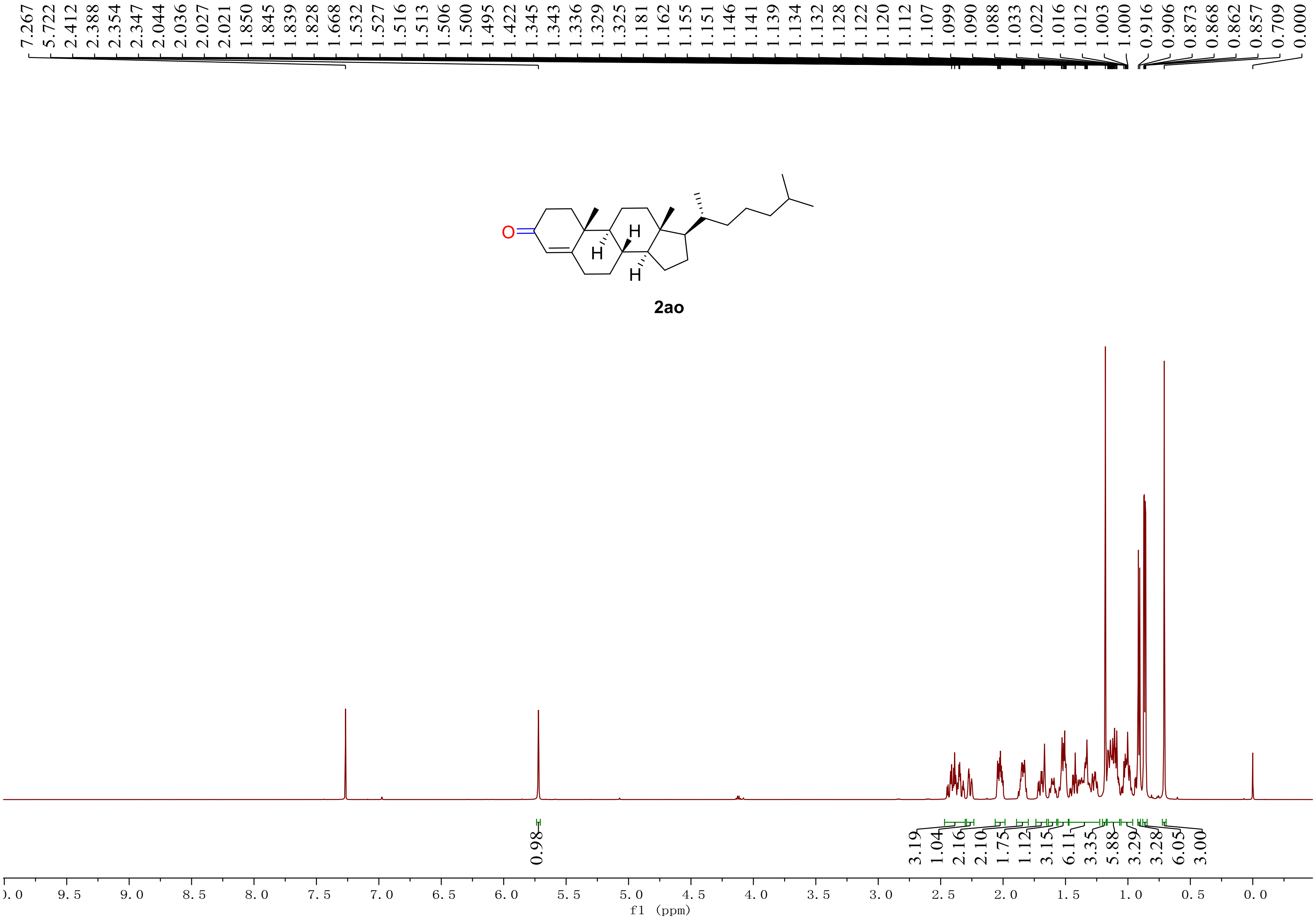
160.375
125.581
77.373
77.161
76.948
50.861
45.355
33.614
28.393
24.609
O
2ak
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

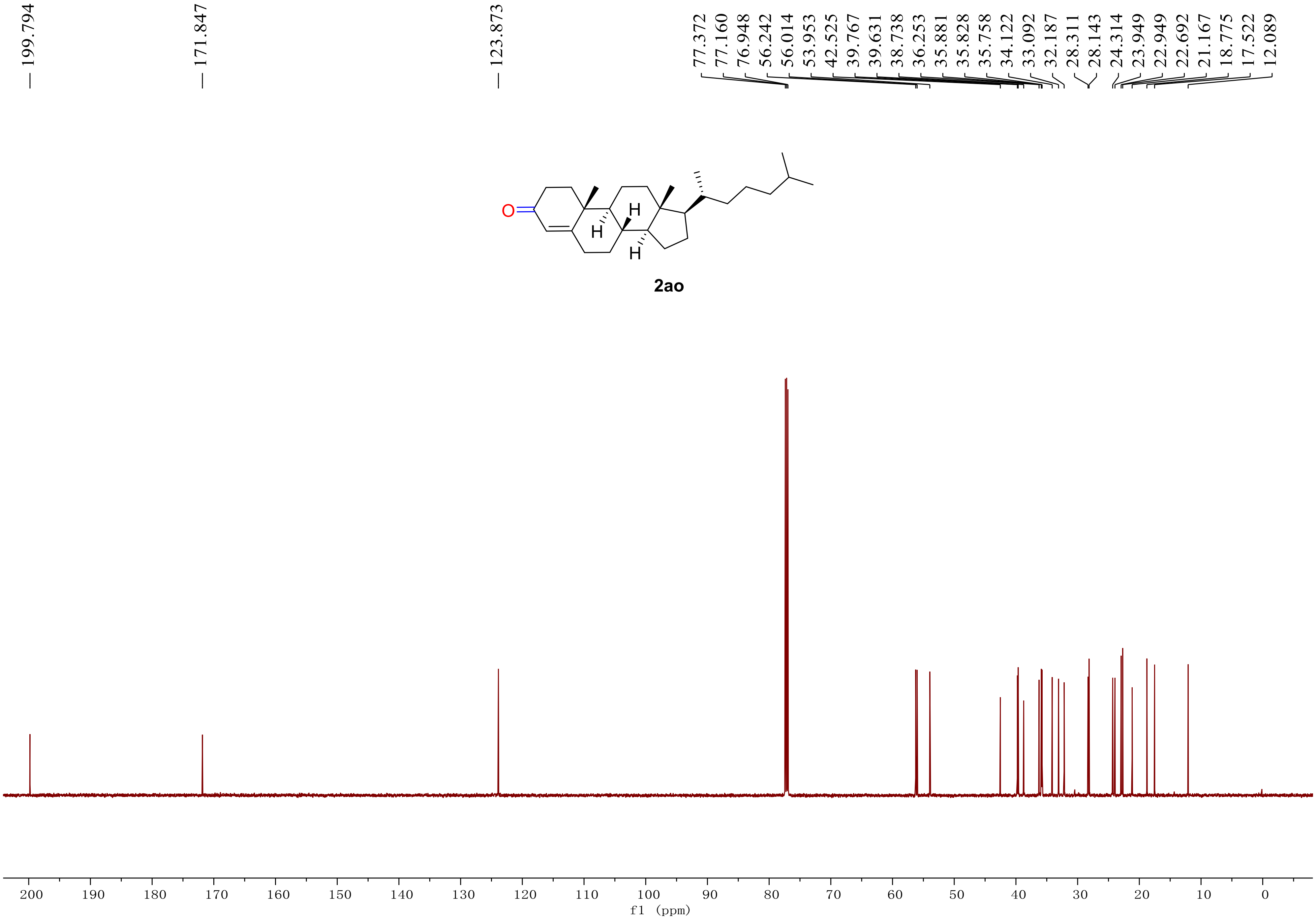

9.821
7.789
7.784
7.780
7.773
7.769
7.765
7.195
6.953
6.948
6.945
6.937
6.934
6.929
3.827
0.000
O
H
MeO
0.95
1.98
2.00
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2an


190.898
164.634
132.026
129.948
114.331
77.279
77.068
76.857
55.609
O
H
MeO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2an


7.267
5.722
2.412
2.388
2.354
2.347
2.044
2.036
2.027
2.021
1.850
1.845
1.839
1.828
1.668
1.532
1.527
1.516
1.513
1.506
1.500
1.495
1.422
1.345
1.343
1.336
1.329
1.325
1.181
1.162
1.155
1.151
1.146
1.141
1.139
1.134
1.132
1.128
1.122
1.120
1.112
1.107
1.099
1.090
1.088
1.033
1.022
1.016
1.012
1.003
1.000
0.916
0.906
0.873
0.868
0.862
0.857
0.709
0.000
O
H
H
H
2ao
0.98
3.19
1.04
2.16
2.10
1.75
1.12
3.15
6.11
3.35
5.88
3.29
3.28
6.05
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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123.873
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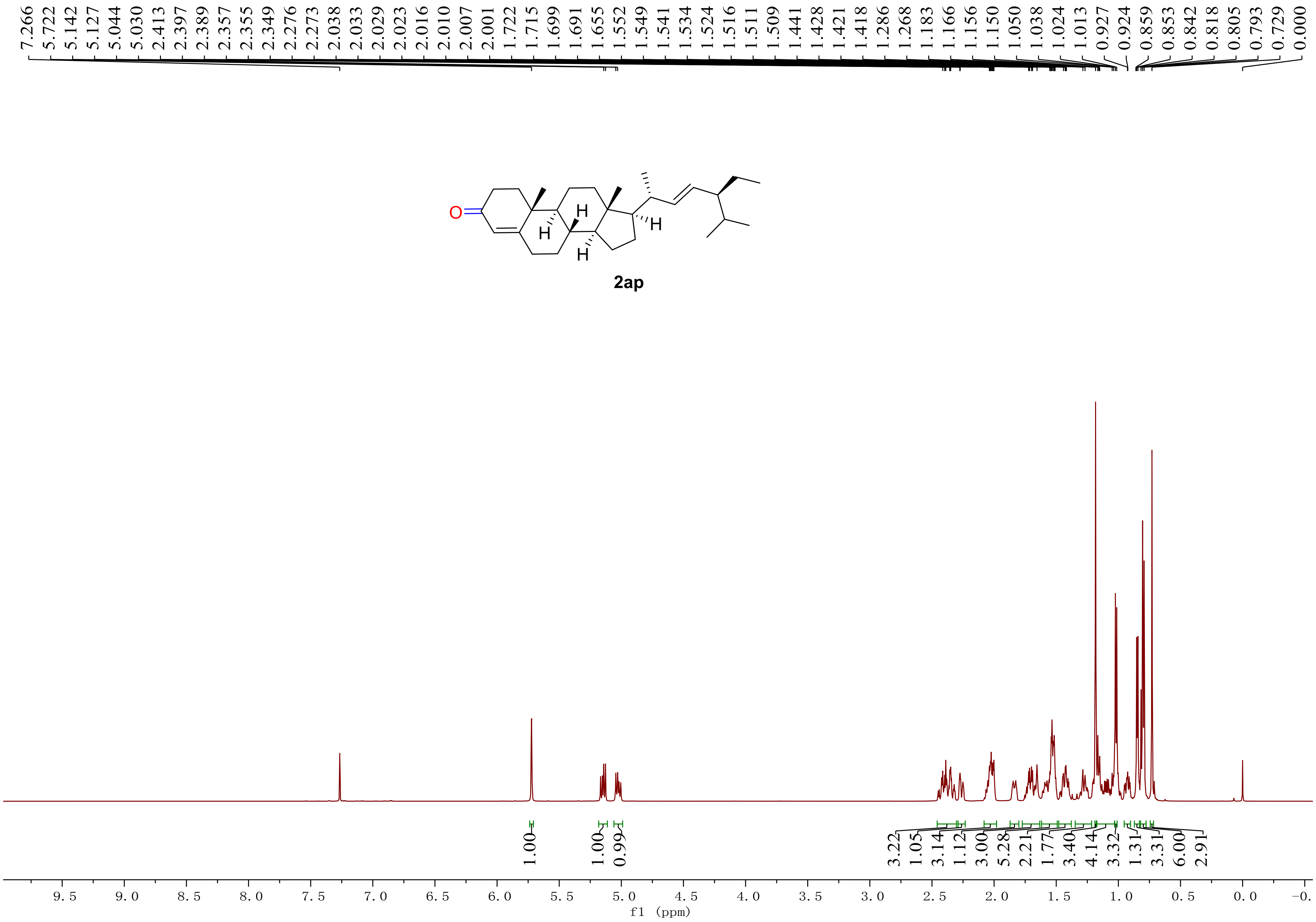
77.160
76.948
56.242
56.014
53.953
42.525
39.767
39.631
38.738
36.253
35.881
35.828
35.758
34.122
33.092
32.187
28.311
28.143
24.314
23.949
22.949
22.692
21.167
18.775
17.522
12.089
O
H
H
H
2ao
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
H
H
H
H

2ap

7.266
5.722
5.142
5.127
5.044
5.030
2.413
2.397
2.389
2.357
2.355
2.349
2.276
2.273
2.038
2.033
2.029
2.023
2.016
2.010
2.007
2.001
1.722
1.715
1.699
1.691
1.655
1.552
1.549
1.541
1.534
1.524
1.516
1.511
1.509
1.441
1.428
1.421
1.418
1.286
1.268
1.183
1.166
1.156
1.150
1.050
1.038
1.024
1.013
0.927
0.924
0.859
0.853
0.842
0.818
0.805
0.793
0.729
0.000
1.00
1.00
0.99
3.22
1.05
3.14
1.12
3.00
5.28
2.21
1.77
3.40
4.14
3.32
1.31
3.31
6.00
2.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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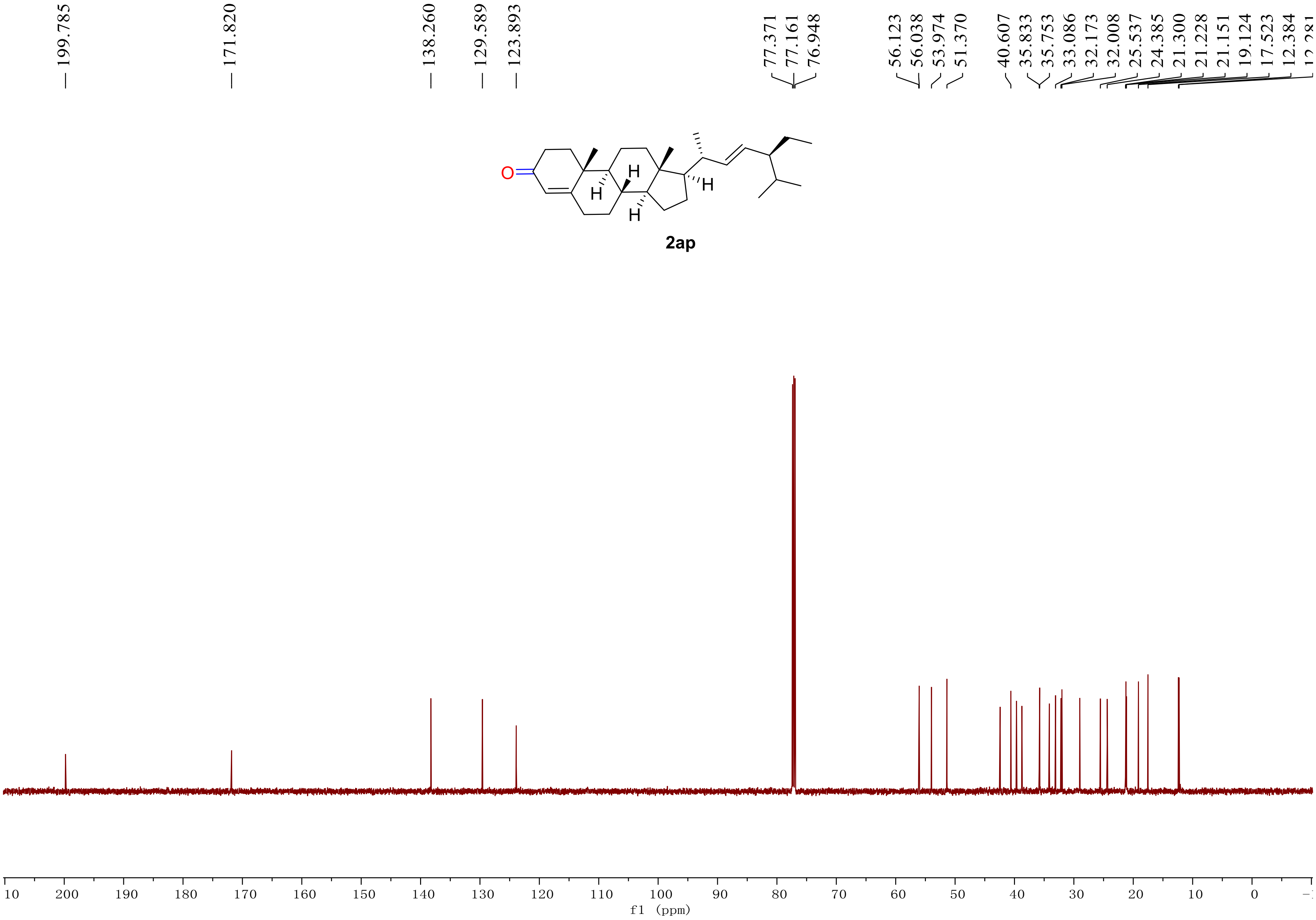
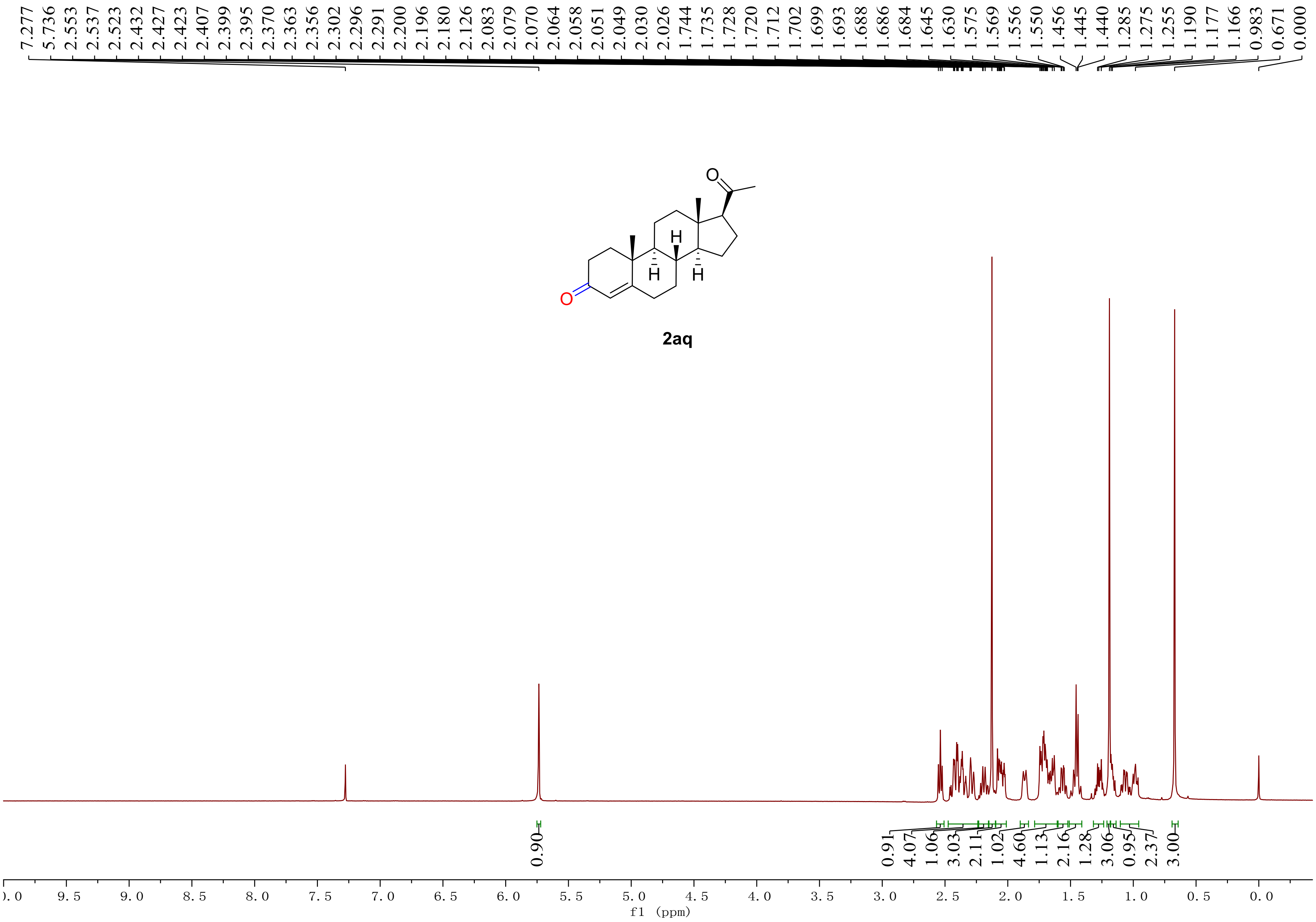
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)



2ap

199.785
171.820
138.260
129.589
123.893
77.371
77.161
76.948
56.123
56.038
53.974
51.370
40.607
35.833
35.753
33.086
32.173
32.008
25.537
24.385
21.300
21.228
21.151
19.124
17.523
12.384
O
H
H
H
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.277
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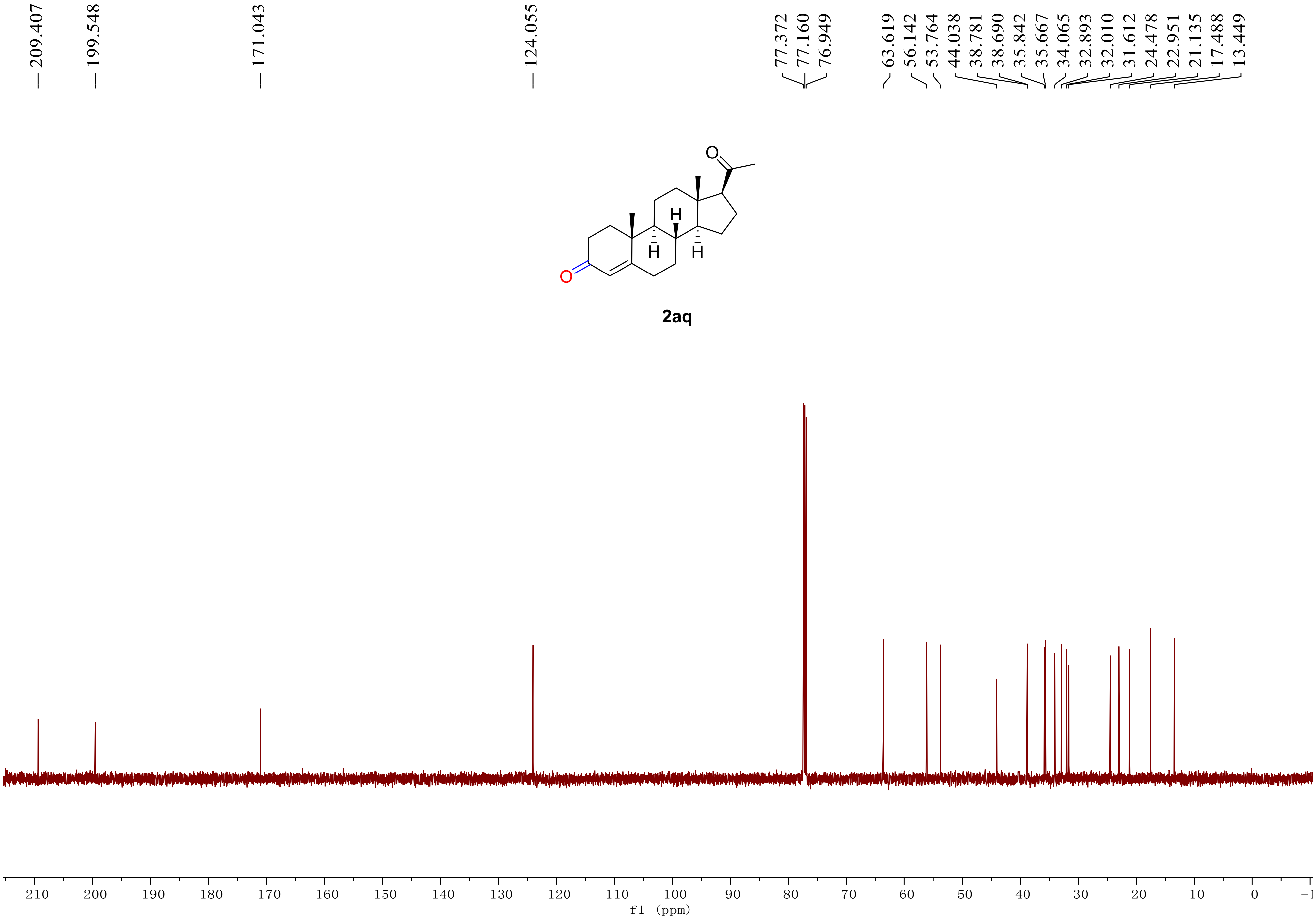
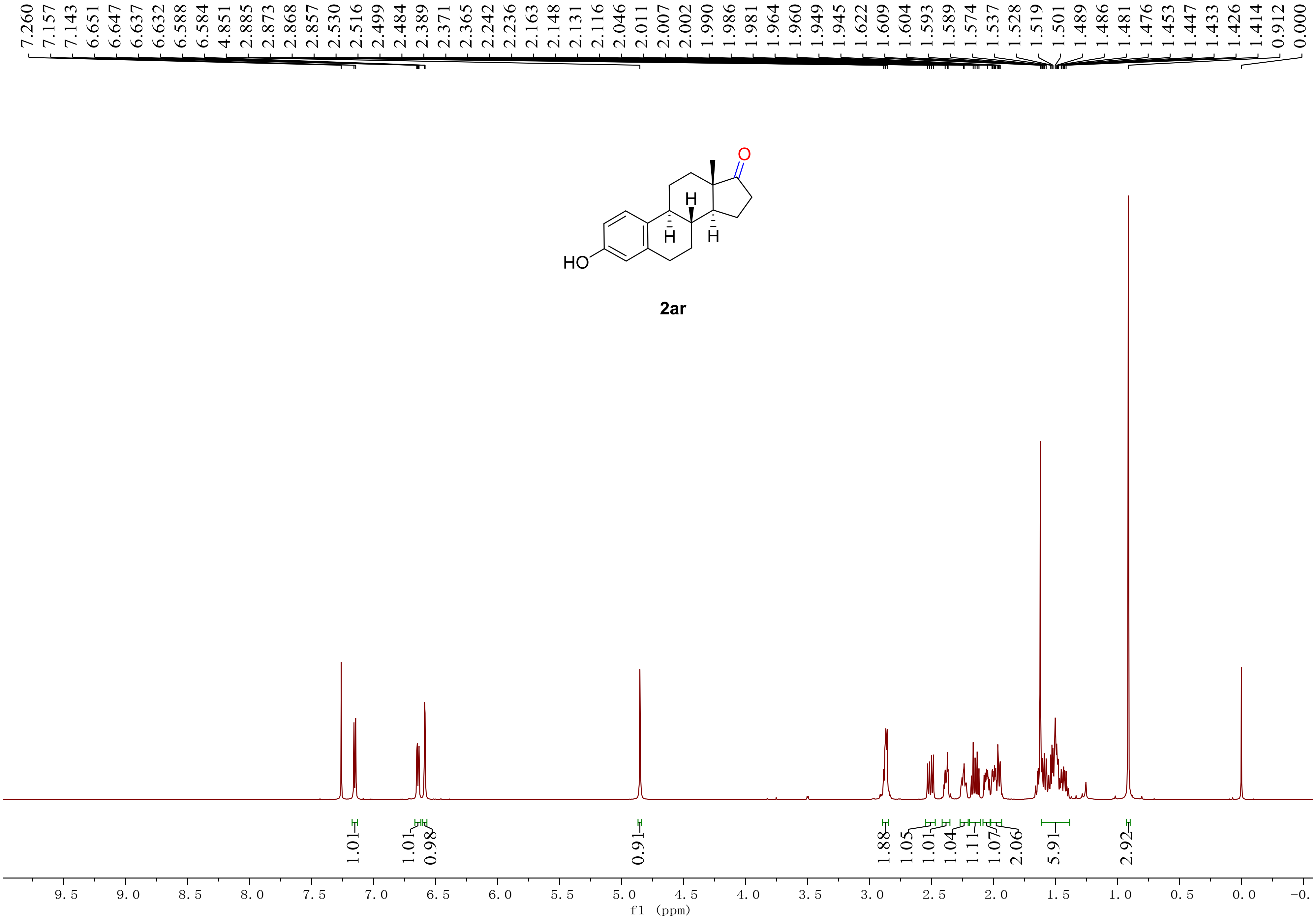
2.553
2.537
2.523
2.432
2.427
2.423
2.407
2.399
2.395
2.370
2.363
2.356
2.302
2.296
2.291
2.200
2.196
2.180
2.126
2.083
2.079
2.070
2.064
2.058
2.051
2.049
2.030
2.026
1.744
1.735
1.728
1.720
1.712
1.702
1.699
1.693
1.688
1.686
1.684
1.645
1.630
1.575
1.569
1.556
1.550
1.456
1.445
1.440
1.285
1.275
1.255
1.190
1.177
1.166
0.983
0.671
0.000
O
O
H
H
H
0.90
0.91
4.07
1.06
3.03
2.11
1.02
4.60
1.13
2.16
1.28
3.06
0.95
2.37
3.00
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2aq



2aq

209.407
199.548
171.043
124.055
77.372
77.160
76.949
63.619
56.142
53.764
44.038
38.781
38.690
35.842
35.667
34.065
32.893
32.010
31.612
24.478
22.951
21.135
17.488
13.449
O
O
H
H
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.157
7.143
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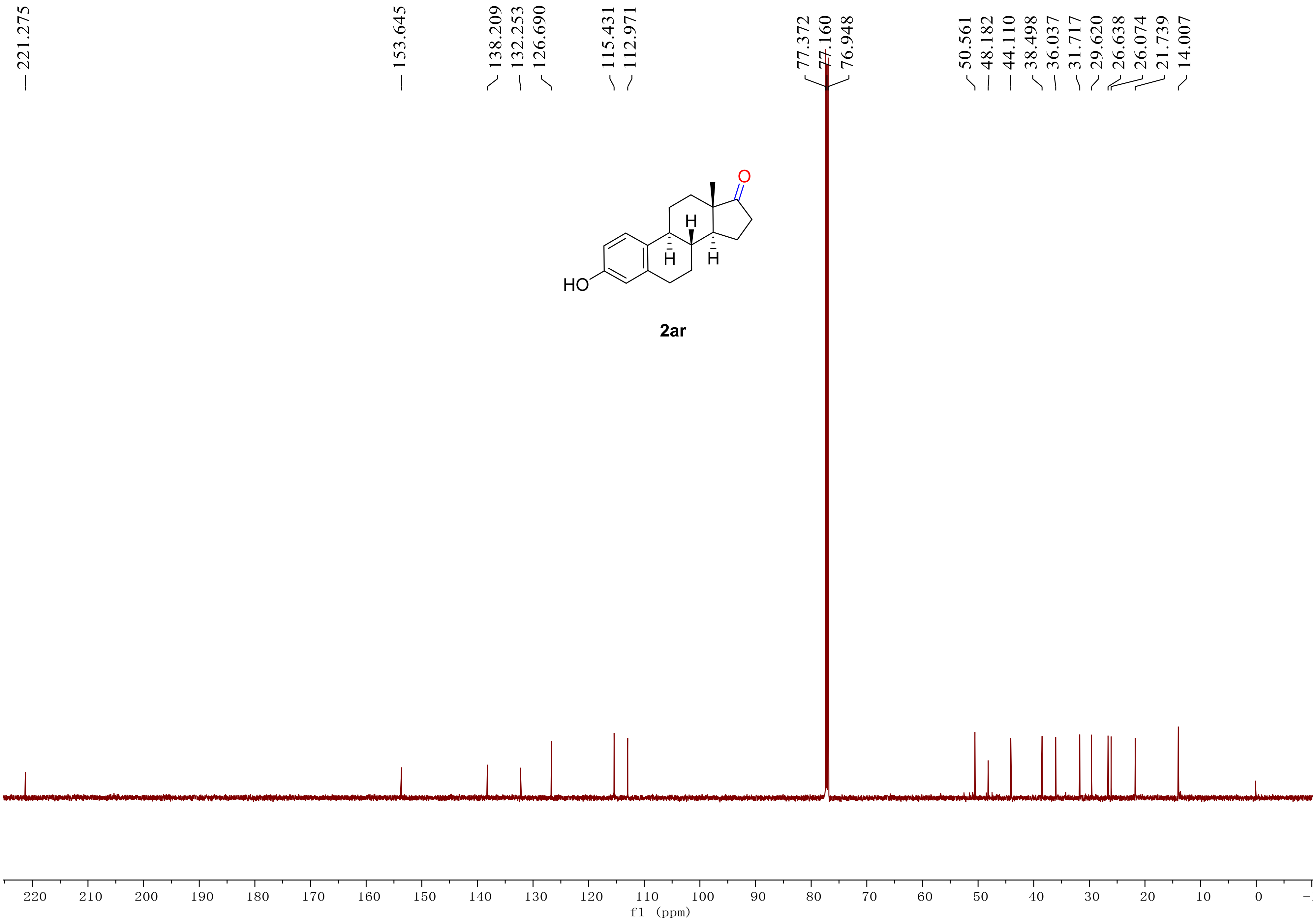
6.647
6.637
6.632
6.588
6.584
4.851
2.885
2.873
2.868
2.857
2.530
2.516
2.499
2.484
2.389
2.371
2.365
2.242
2.236
2.163
2.148
2.131
2.116
2.046
2.011
2.007
2.002
1.990
1.986
1.981
1.964
1.960
1.949
1.945
1.622
1.609
1.604
1.593
1.589
1.574
1.537
1.528
1.519
1.501
1.489
1.486
1.481
1.476
1.453
1.447
1.433
1.426
1.414
0.912
0.000
O
H
HO
H
H
1.01
1.01
0.98
0.91
1.88
1.05
1.01
1.04
1.11
1.07
2.06
5.91
2.92
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

2ar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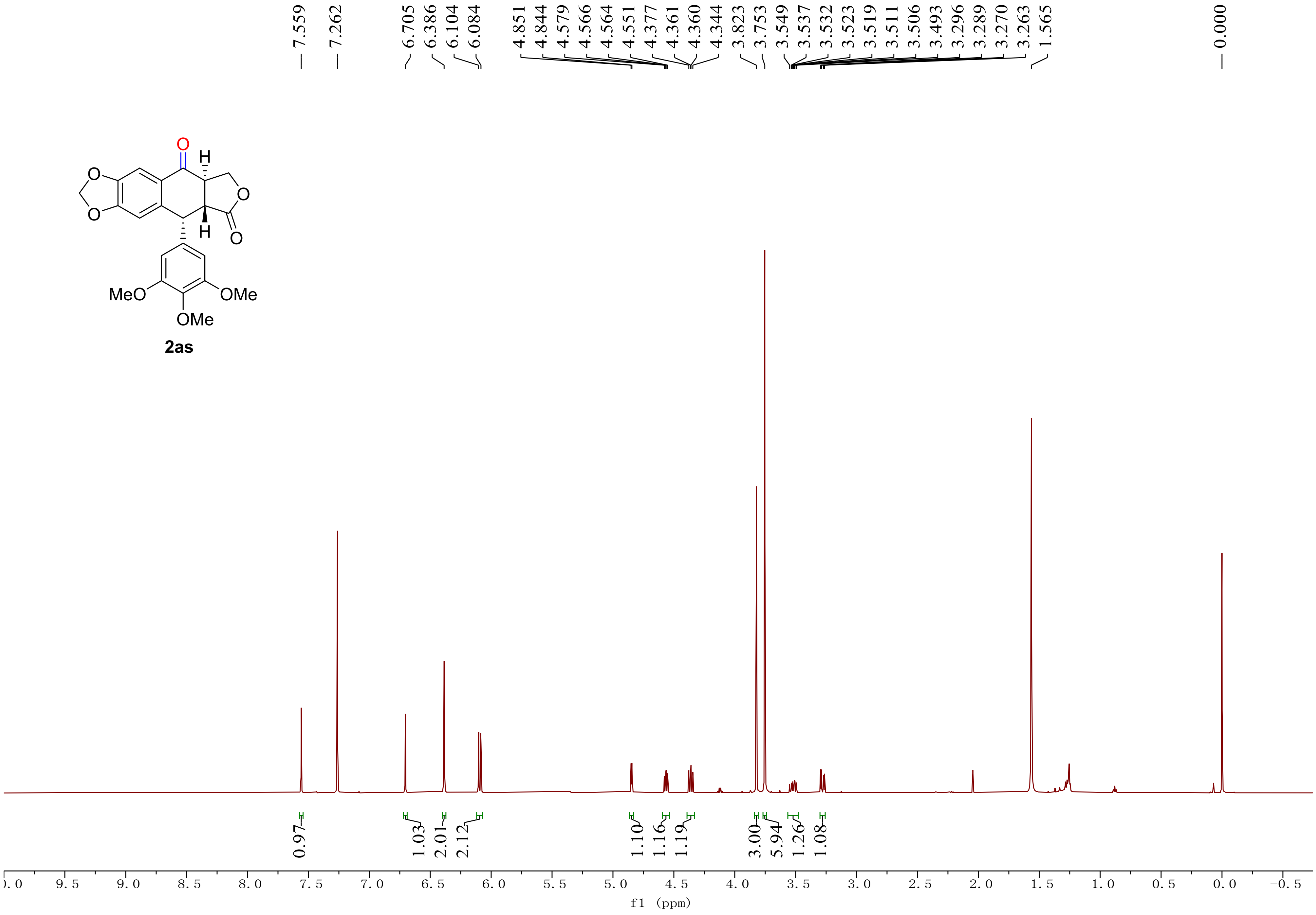
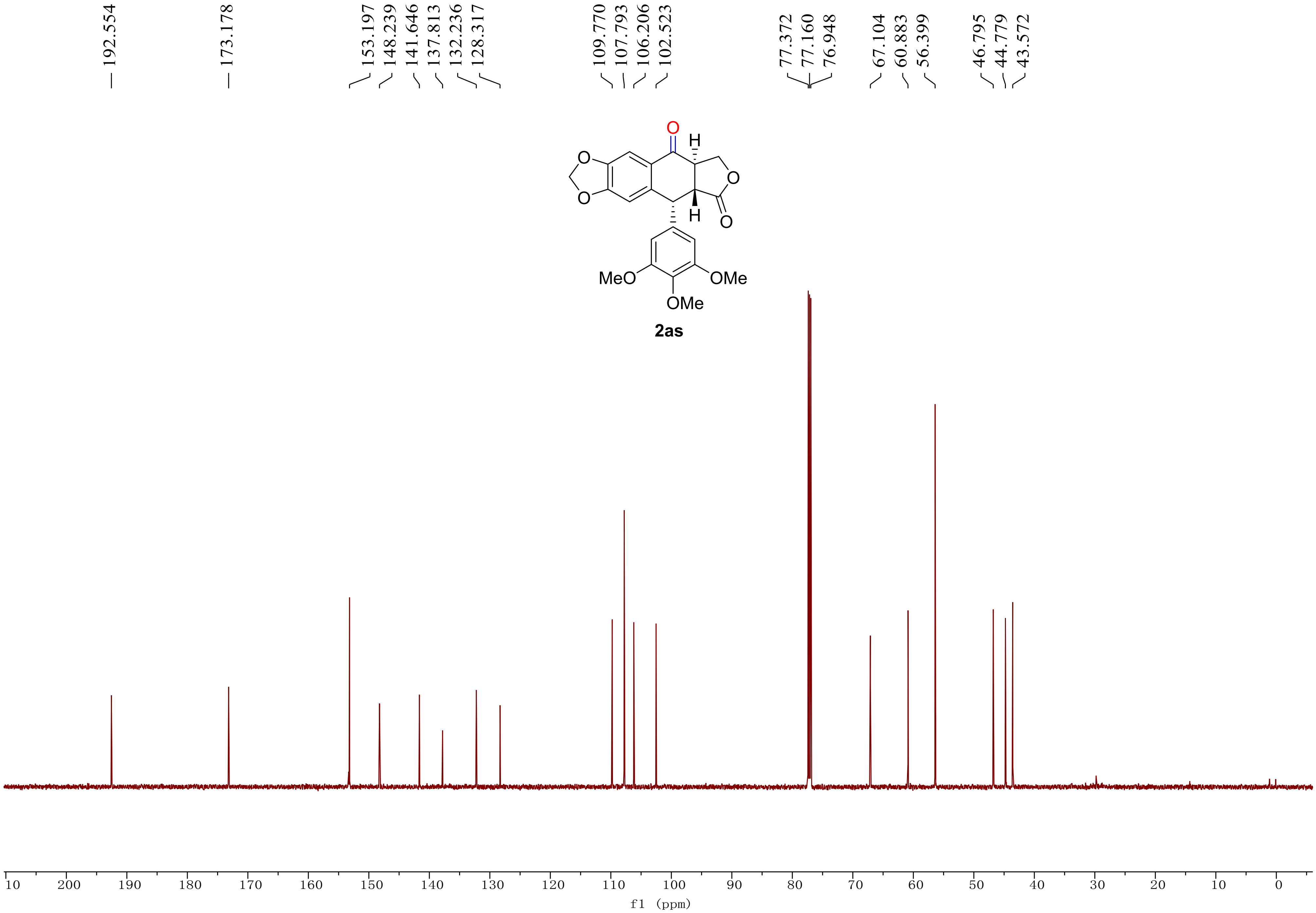
153.645
138.209
132.253
126.690
115.431
112.971
77.372
77.160
76.948
50.561
48.182
44.110
38.498
36.037
31.717
29.620
26.638
26.074
21.739
14.007
HO
H
H
H
O
2ar
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



7.559
7.262
6.705
6.386
6.104
6.084
4.851
4.844
4.579
4.566
4.564
4.551
4.377
4.361
4.360
4.344
3.823
3.753
3.549
3.537
3.532
3.523
3.519
3.511
3.506
3.493
3.296
3.289
3.270
3.263
1.565
0.000
O
H
O
O
O
O
H
MeO
OMe
OMe
0.97
1.03
2.01
2.12
1.10
1.16
1.19
3.00
5.94
1.26
1.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

2as


192.554
173.178
153.197
148.239
141.646
137.813
132.236
128.317
109.770
107.793
106.206
102.523
77.372
77.160
76.948
67.104
60.883
56.399
46.795
44.779
43.572
O
H
O
O
O
H
O
MeO
OMe
OMe
2as
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)