Supplementary Materials for

Synthesis of catechols from cyclohexanones via acid-regulated dual oxidative transformations with TEMPO

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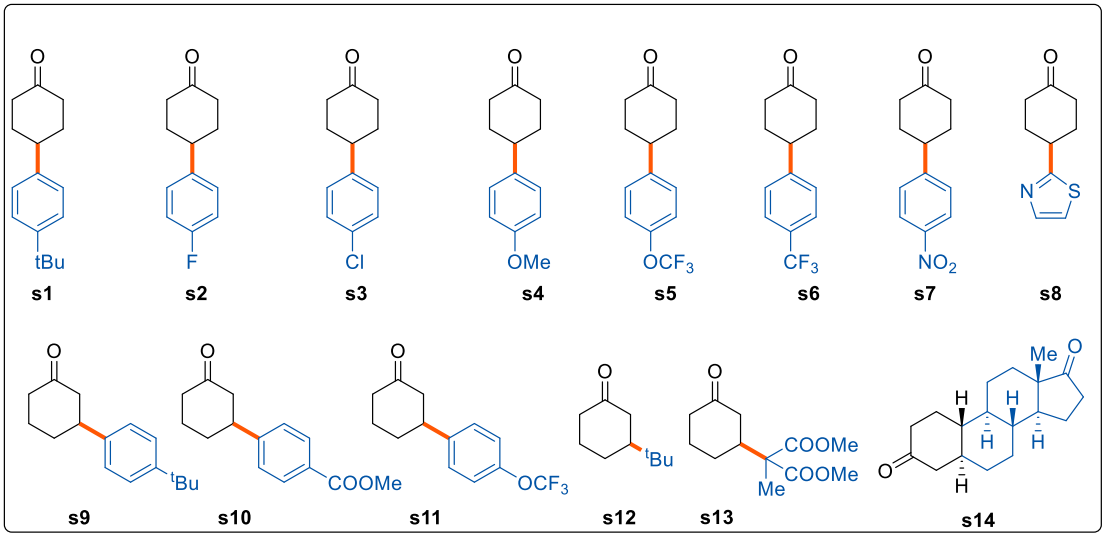
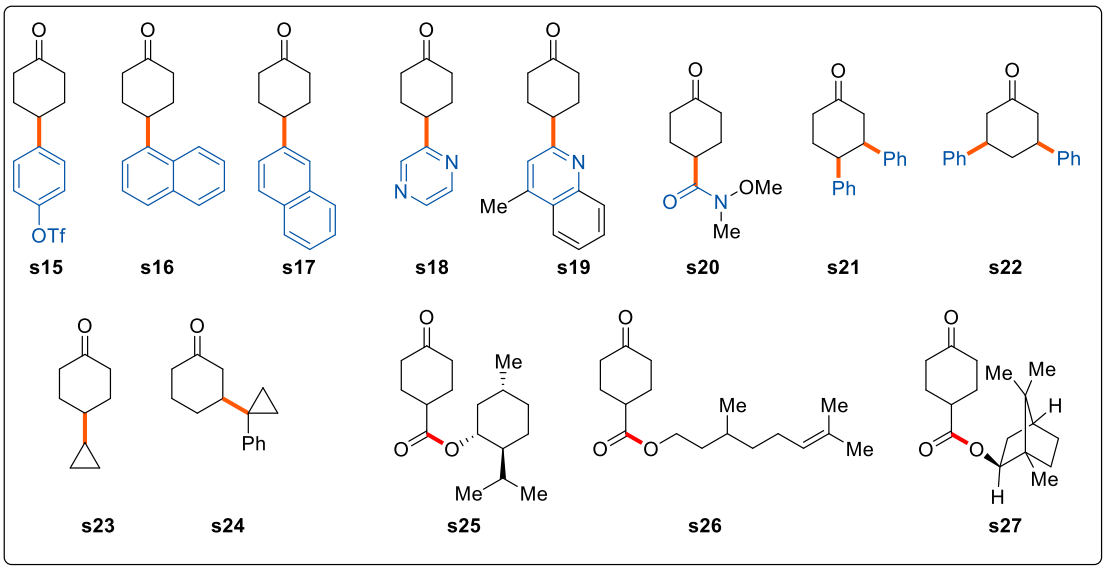
1. General Information

All reactions were conducted under an atmosphere of nitrogen with dry solvents. Unless otherwise noted, chemical reagents were purchased from commercial supplies (Accela, Acros Organics, Adamas-beta®, Alfa Aesar, Aladdin, Bidepharmatech Energy Chemical, TCI Chemicals, Innochem, J&K Chemicals, Laajoo, Leyan, Sigma-Aldrich, Sinocompound, and 3A Chemicals) and used directly without further purification. Dioxane and toluene were distilled from metal Na and stored under nitrogen atmosphere. HPLC data were recorded on Waters Acquity UPLC H-Class. Flash chromatography was performed with Sepaflash columns produced by Santai Technologies. NMR spectra were recorded on a Bruker AVANCE 400, JEOL ECZ400S 400M spectrometer (^{1}H NMR: 400 MHz, ^{13}C NMR: 101 MHz, ^{19}F NMR: 376 MHz) using $CDCl_3$ and DMSO-d_6 as solutions. The chemical shift δ was calibrated using tetramethylsilane (TMS) (0 ppm) for ^{1}H NMR and residual undeuterated solvent ($CDCl_3$ 77.0 ppm and DMSO-d_6 40.00 ppm) for ^{13}C NMR. HRMS (High Resolution Mass Spectra) were performed by the Shanghai Institute of Organic Chemistry, Chinese Academic of Sciences (Instrument Themo Fisher Scientific LTQFTICR-MS, Operated Mode: ESI Positive, Negative or DART Positive; Waters Micromass GCT Premier, Operated Mode: EI positive).

Materials:



For preparations see *Angew. Chem. Int. Ed.* **2022**, 61, e202203365



For preparations see *Sci. Adv.* **2024**, 10, eadn7656

Preparation procedures of substrates **s1-s27** were disclosed in previous literature[1,2].

Substrate **s1-s3, s5**, **s6**, **s16**, **s17** were synthesized via the reductive cross coupling reactions from cyclohexanone-4-carboxylic NHPI ester and corresponding aryl iodides. Substrate **s4** was synthesized via the methylation of 4-(4-hydroxyphenyl)cyclohexanone. Substrate **s7** was synthesized via the nitration of 4-phenylcyclohexanone. Substrate **s8**, **s18** and **s19** was synthesized through multiple step reactions from 4,4,5,5-tetramethyl-2-(1,4-dioxaspiro[4.5]dec-7-en-8-yl)-1,3,2-dioxaborolane and corresponding (hetero)aryl halides. Substrate **s9-s11** were synthesized *via* the conjugate addition reaction from cyclohexenone and

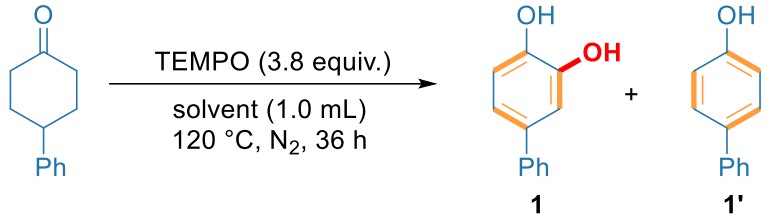
corresponding aryl boronic acids. Substrate **s12** was synthesized *via* the conjugate addition reaction from cyclohexenone and *tert*-butyl magnesium bromide. Substrate **s13** was synthesized *via* the base mediated 1,4-conjugate addition reaction between cyclohexenone and dimethyl methylmalonate. Substrate **s14** was synthesized via the palladium catalyzed hydrogenation of Bolandione.

Substrate **s15** was synthesized from the 4-(4-hydroxyphenyl)cyclohexanone and trifluoromethanesulfonic anhydride. Substrate **s16** was synthesized from lepidine and cyclohexanone-4-carboxylic NHPI ester. Substrate **s20** was synthesized from the condensation between 4-oxocyclohexanecarboxylic acid and *N*,*O*-dimethylhydroxylamine hydrochloride. Substrate **s21** was synthesized from a 2-step reaction between 2-phenylacetophenone and methyl vinyl ketone. Substrate **s22** was synthesized from multiple step reactions between chalcone and ethyl acetoacetate. Substrate **s23** was synthesized from multiple step reactions between 1,4-dioxaspiro[4.5]decan-8-ol and cyclopropyl magnesium bromide. Substrate **s24** was synthesized from reactions between cyclohexenone and 1-phenylcyclopropane-1-carboxylic acid under photocatalysis. Substrate **s25-s27** was synthesized from in situ generated 4-oxocyclohexane-1-carbonyl chloride from 4-oxocyclohexanecarboxylic acid with corresponding natural alcohols.

2. General Procedures

2.1 Optimization of reaction parameters

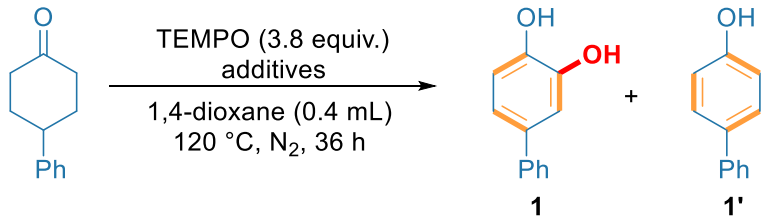
Table S1. Screening of solvents[a]



entry	solvent	yield of **1** (%)[b]	yield of **1'** (%)[b]
1	Toluene	20	25
2	PhCl	23	20
3	DMF	N.D.	N.D.
4	DMSO	N.D.	N.D.
5	DMA	N.D.	N.D.
6	NMP	N.D.	N.D.
7	THF	25	24
8	1,4-dioxane	26	33
9	MeCN	N.D.	N.D.
10	DME	19	22
11	$^{n}Bu_2O$	20	22

[a]All reactions were performed on a 0.20 mmol scale. [b]Yield was determined by UPLC analysis with benzyl benzoate as an internal standard.

Table S2. Screening of additves[a]

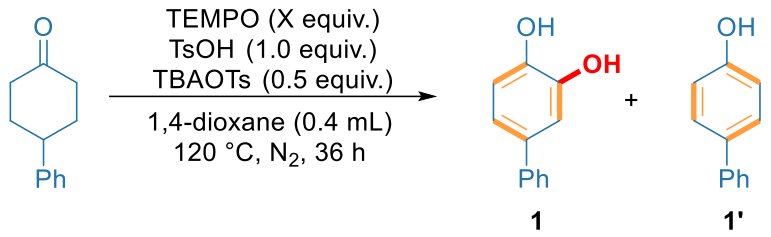


1 **1'**

entry	solvent	yield of **1** (%)[b]	yield of **1'** (%)[b]
1	none	26	33
2	TsOH (0.1 equiv.)	49	16
3	TsOH (0.2 equiv.)	56	12
4	TsOH (0.5 equiv.)	67	7
5	TsOH (1.0 equiv.)	76	5
6	TsOH (1.0 equiv.)+ NBu_4OTs (0.5 equiv.)	86(**82**[c])	trace

[a]All reactions were performed on a 0.20 mmol scale. [b]Yield was determined by UPLC analysis with benzyl benzoate as an internal standard.

Table S3. Screening of oxidant loading[a]

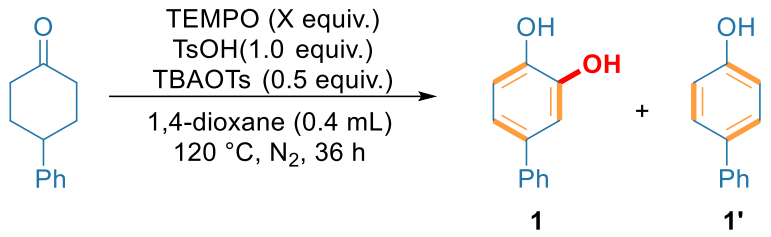


1 **1'**

entry	Oxidant loading	yield of **1** (%)[b]	yield of **1'** (%)[b]
1	TEMPO (1.0 equiv.)	17	13
2	TEMPO (2.0 equiv.)	30	16
3	TEMPO (3.0 equiv.)	51	5
4	TEMPO (3.5 equiv.)	82	trace
5	TEMPO (4.0 equiv.)	80	trace
6[c]	TEMPO (3.8 equiv.)	71	2
7[d]	TEMPO (3.8 equiv.)	N.D.	N.D.
8[c]	TEMPO (0.5 equiv.)	N.D.	N.D.
9[d]	TEMPO (0.5 equiv.)	N.D.	N.D.

[a]All reactions were performed on a 0.20 mmol scale. [b]Yield was determined by UPLC analysis with benzyl benzoate as an internal standard. [c]The reaction was carried out under air atmosphere. [d]The reaction was carried out under oxygen atmosphere.

Table S4. Screening of reaction temperature[a]

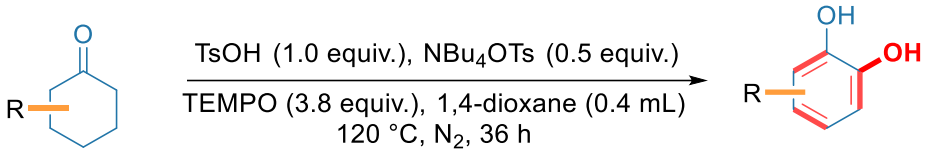


1 **1'**

entry	Oxidant loading	yield of **1** (%)[b]	yield of **1'** (%)[b]
1	100 °C	57	3
2	110 °C	66	2
3	130 °C	57	trace
4	140 °C	54	trace
5	150 °C	45	trace
6	160 °C	42	trace

[a]All reactions were performed on a 0.20 mmol scale. [b]Yield was determined by UPLC analysis with benzyl benzoate as an internal standard.

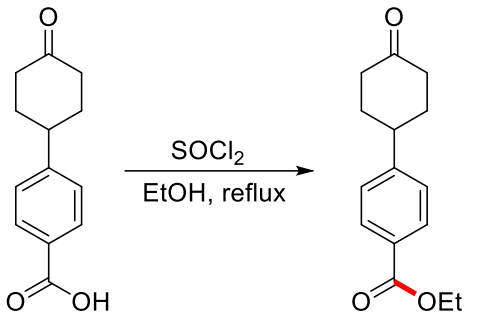
2.2 General procedure for dehydrogenative syntheses of catechols



In a nitrogen-filled glovebox, the 35 mL pressure tube equipped with a stir bar was charged with cyclic ketone (0.20 mmol)， *p*-toluenesulfonic acid (34.4 mg, 0.20 mmol), tetrabutylammonium *p*-toluenesulfonate (41.3 mg, 0.10 mmol) and TEMPO (120.0 mg, 0.76 mmol), then dioxane (0.4 mL) was added to the pressure tube via syringe. Later, the vial was capped with a screw cap fitted with a PTFE-faced silicone septum, removed from the glove box, and stirred at 120 °C for 36 hours with a speed of 300 round per minute (rpm). After the reaction was finished, the mixture was filtered through a short plug of silica gel and washed with 10 mL of ethyl acetate. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel to provide the corresponding product.

3. Typical procedure for preparing substituted cyclohexanones

3.1 4-Aryl substituted cyclohexanones



s28

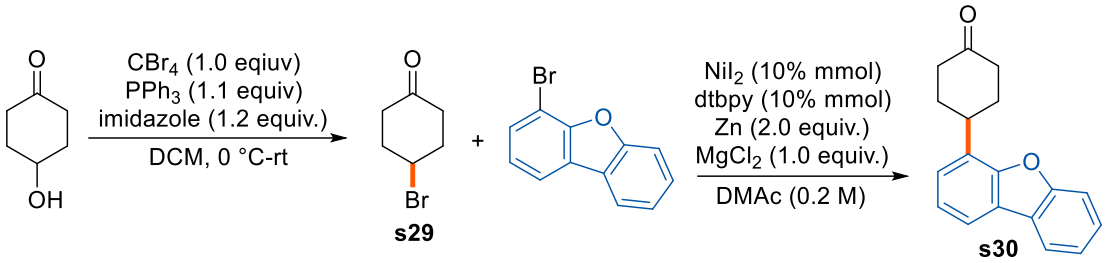
To a 100 mL round-bottom flask equipped with a Teflon-coated magnetic stir-bar was added 4-(4-oxocyclohexyl)benzoic acid (2.18 g, 10 mmol) and dry EtOH (20 mL). To this mixture was dropwise added thionyl chloride ($SOCl_2$) (0.64 g, 6.0 mmol) via syringe, then the solution was allowed to heated to the refluxed temperature and stirred overnight. After the reaction was finished and cooled to room temperature, the solvent was carefully removed under reduced pressure, and purified by flash chromatography on silica gel (eluent = PE/EA = 95:5) to obtain the ester product **s28** as yellow solid.

Ethyl 4-(4-oxocyclohexyl)benzoate (s28)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 4.34 (t, *J* = 7.1 Hz, 2H), 3.08 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.56 – 2.49 (m, 4H), 2.22 – 2.17 (m, 2H), 1.99 – 1.88 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.44, 166.25, 149.84, 129.75, 128.75, 126.57, 60.72, 42.58, 41.02, 33.48, 14.18.

3.2 4-Heteroaryl substituted cyclohexanones



Step 1: To a 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir-bar was added 4-hydroxycyclohexanone (2.28 g, 20.0 mmol), PPh_3 (5.76 g, 22 mmol) and imidazole (1.63 g, 24 mmol). Then anhydrous dichloromethane (200 mL) was added and the reaction was cooled down to 0 °C. To this mixture was portion-wisely added carbon tetrabromide (CBr_4) (6.10 g, 24 mmol), and the reaction mixture was allowed to warm to room temperature and stirred 24 hours. After the reaction was judged complete by TLC, the reaction mixture was filtrated and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 95:5) to obtain the deoxygenative brominated product **s29** as colorless oil.

4-Bromocyclohexan-1-one (s29)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (p, *J* = 4.4 Hz, 1H), 2.79 – 2.70 (m, 2H), 2.40 – 2.29 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.73, 49.17, 38.43, 35.65.

Step 2: According to the literature[3], in a nitrogen-filled glovebox, to a 250 mL round-bottom flask containing a Teflon-coated magnetic stir-bar was added 4-bromocyclohexanone (1.77 g, 10.0 mmol), NiI_2 (0.31 g, 1.0 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy) (0.27 g, 1.0 mmol), Zn dust (1.30 g, 20.0 mmol) and $MgCl_2$ (0.95 g, 10.0 mmol). Then DMAc (50 mL) was added via syringe through the rubber septum and the resulting mixture was stirred at room temperature for 24 hours. After reaction was finished, the reaction mixture was filtrated and concentrated under reduced pressure. Ethyl acetate (100 mL) was added and the reaction mixture was

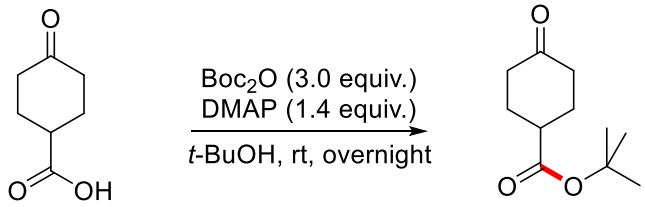
washed with water twice in funnel. The organic phases were collected and dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash chromatography on silica gel (eluent = petroleum ether/DCM = 95:5) to obtain product **s30** as white solid.

4-(Dibenzo[*b*,*d*]furan-4-yl)cyclohexan-1-one (s30)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.28 (m, 2H), 3.66 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.68 – 2.54 (m, 4H), 2.40 – 2.34 (m, 2H), 2.26 – 2.15 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 211.23, 155.85, 153.93, 128.76, 127.13, 124.34, 124.31, 124.15, 122.98, 122.71, 120.68, 118.76, 111.60, 41.42, 37.39, 32.33.

3.3 4-Non-aromatic substituted cyclohexanones



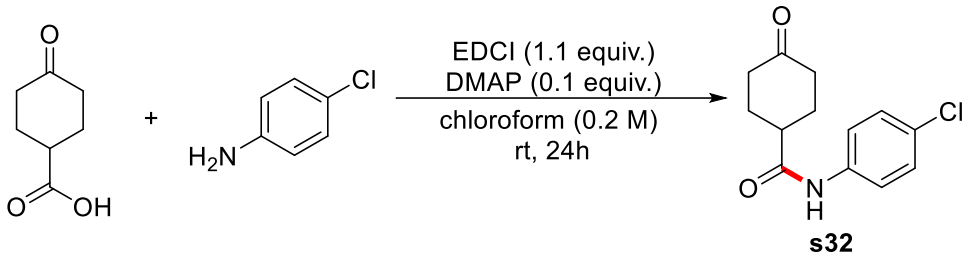
s31

According to the literature[4], to a 100 mL round-bottom flask equipped with a Teflon-coated magnetic stir-bar was added 4-oxocyclohexanecarboxylic acid (1.42 g, 10 mmol), 4-dimethylaminopyridine (DMAP) (1.71 g, 14.0 mmol) and *t*-BuOH (20 mL). To this mixture was carefully dropwise added di-*tert*-butyl dicarbonate (Boc_2O) (6.54 g, 30.0 mmol), then the solution was stirred at room temperature overnight. After the reaction was finished, the solvent was carefully removed under reduced pressure, and purified by flash chromatography on silica gel (eluent = PE/EA = 10:1) to obtain the product *tert*-butyl 4-oxocyclohexane-1-carboxylate (**s31**) as colorless solid.

***tert*-Butyl 4-oxocyclohexane-1-carboxylate (s31)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 – 2.62 (m, 1H), 2.49 – 2.43 (m, 2H), 2.38 – 2.29 (m, 2H), 2.19 – 2.12 (m, 2H), 2.03 – 1.94 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.49, 173.46, 80.69, 41.51, 39.69, 28.54, 27.98.



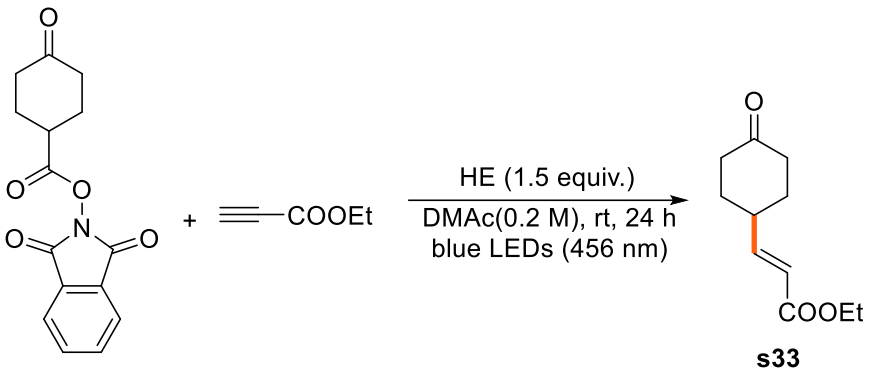
s32

According to the literature[5], to a 250 mL round-bottom flask equipped with a Teflon-coated magnetic stir-bar was added 4-oxocyclohexane-1-carboxylic acid (1.56g, 11.0 mmol), 4-chloroaniline (1.27 g, 10.0 mmol) and DMAP (0.12 g, 1.0 mmol.). Then *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDCI) (2.09 g, 11.0 mmol) and chloroform 50 mL was added, and the mixture was stirred at room temperature for 24 hours. After the reaction was judged complete by TLC, the reaction solvent was carefully removed under reduced pressure. Then 50 mL ethyl acetate was added to the reaction mixture before it was washed with 1N aqueous HCl solution twice, brine once. The organic layer was collected and concentrated under reduced pressure and purified by flash chromatography on silica gel (eluent = PE/EA = 1:1) to obtain the amide product (**s32**) as colorless solid.

***N*-(4-chlorophenyl)-4-oxocyclohexane-1-carboxamide (s32)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 2.69 (tt, *J* = 10.4, 3.8 Hz, 1H), 2.61 – 2.55 (m, 2H), 2.42 – 2.34 (m, 2H), 2.28 – 2.23 (m, 2H), 2.16 – 2.06 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.49, 173.46, 80.69, 41.51, 39.69, 28.54, 27.98.



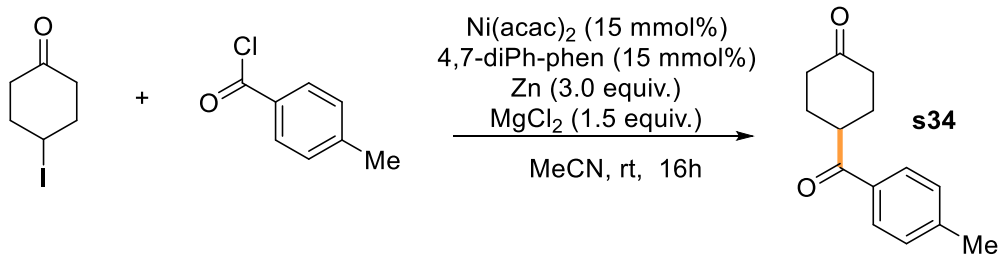
s33

According to the literature[6], in a nitrogen-filled glovebox to a 250 mL round-bottom flask containing a Teflon-coated magnetic stir-bar was added cyclohexanone-4-carboxylic NHPI ester (4.31 g, 15.0 mmol), ethyl propiolate (0.98 g, 10.0 mmol), diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (HE) (3.80 g, 15.0 mmol), then DMAc 50 mL was added via syringe through the rubber septum. The reaction mixture was stirred under irradiation with blue LEDs (456 nm, distance app. 3.0 cm from the bulb), maintained at approximately room temperature by a desk fan in the air-conditioned room of 25 °C. After 24 h, the reaction solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent = petroleum ether/EtOAc = 9:1) to obtain the ethyl (*E*)-3-(4-oxocyclohexyl)acrylate (**s33**) as colorless oil.

Ethyl (*E*)-3-(4-oxocyclohexyl)acrylate (s33)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (dd, *J* = 15.8, 6.7 Hz, 1H), 5.89 (dd, *J* = 15.8, 1.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.69 – 2.60 (m, 1H), 2.49 – 2.37 (m, 4H), 2.17 – 2.11 (m, 2H), 1.69 (qd, *J* = 11.5, 5.7 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.27, 166.43, 150.52, 120.71, 60.35, 40.12, 38.24, 31.22, 14.16.



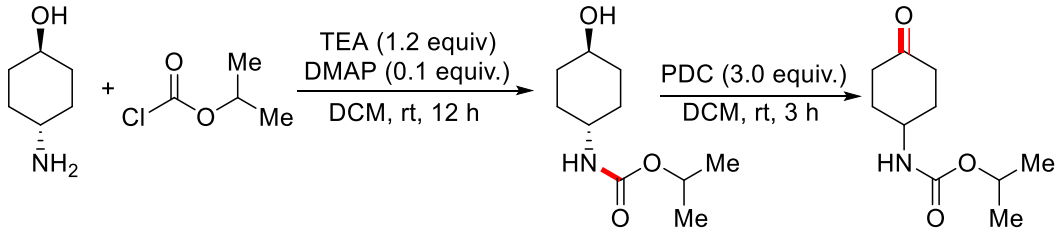
s34

According to the literature[7,8], in a nitrogen-filled glovebox, to a 250 mL round-bottom flask containing a Teflon-coated magnetic stir-bar was added 4-iodocyclohexan-1-one (1.12 g, 5.0 mmol), $Ni(acac)_2$ (0.19 g, 0.75 mmol), bathophenanthroline (4,7-diPh-phen) (0.25 g, 0.75 mmol), Zn dust (0.98 g, 7.5 mmol), $MgCl_2$ (1.43 g, 7.5 mmol) and MeCN (50 mL). The *p*-toluoyl chloride was dropwise added via syringe through the rubber septum and the reaction mixture was stirred at room temperature for 16 hours. After reaction was finished, the reaction mixture was filtrated and concentrated in under reduced pressure, and the residue was purified by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 9:1) to obtain ketone (**s34**) as white solid.

4-(4-Methylbenzoyl)cyclohexan-1-one (s34)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 3.71 (tt, *J* = 10.1, 3.8 Hz, 1H), 2.55 (dt, *J* = 14.3, 4.6 Hz, 2H), 2.50 – 2.42 (m, 5H), 2.26 – 2.18 (m, 2H), 2.10 – 2.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.21, 201.39, 144.10, 133.09, 129.39, 128.27, 42.48, 39.84, 28.77, 21.54.



s35 **s36**

Step 1: To a 100 mL round-bottom flask equipped with a Teflon-coated magnetic stir-bar was added *trans*-4-aminocyclohexanol (3.45 g, 30.0 mmol), trimethylamine (3.54 g, 35.0 mmol) and DMAP (0.36 g, 3.0 mmol), then dry DCM 100 mL was added and the reaction was cooled down to 0 °C. To this mixture was dropwise added isopropyl chloroformate (4.27 g, 35.0 mmol) over 10 min via syringe through the rubber septum. After this time, the solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with water (50 mL) and washed twice with 1M HCl (50 mL), once with saturated Na_2CO_3 (aq). Then the

organic phase was dried over Na_2SO_4 and concentrated to deliver isopropyl amide **s35** as pure white solid without further purification.

Isopropyl (4-hydroxycyclohexyl)carbamate (s35)

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.90 – 4.87 (m, 1H), 4.52 (brs, 1H), 3.62 – 3.57 (m, 1H), 3.46 (brs, 1H), 2.08 – 1.96 (m, 6H), 1.42 – 1.35 (m, 2H), 1.22 – 1.15 (m, 7H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.51, 69.62, 67.81, 49.02, 33.80, 31.06, 22.09.

Step 2: To a 100 mL round-bottom flask equipped with a Teflon-coated magnetic stir-bar was added **s35** (1.39 g, 10.0 mmol), then dry DCM 50 mL was added. To this mixture was portion-wisely added pyridinium dichromate (PDC) (8.91 g, 30.0 mmol), then the suspension was stirred at room temperature for 3 hours. After reaction was finished, the crude mixture was filtered through a Celite plug, and the filtrate was concentrated under reduced pressure to obtain the oxidized product **s36** as white solid without any further purification.

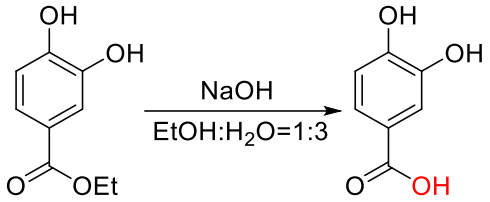
Isopropyl (4-oxocyclohexyl)carbamate (s36)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.93 (p, *J* = 6.4 Hz, 1H), 4.65 (d, *J* = 7.5 Hz, 1H), 3.98 (brs, 1H), 2.50 – 2.39 (m, 4H), 2.28 – 2.24 (m, 2H), 1.75 – 1.65 (m, 2H), 1.25 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.69, 155.50, 68.23, 47.73, 38.93, 32.21, 22.11.

4 Synthetic Applications

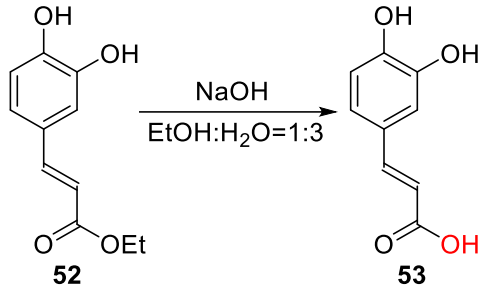
4.1 Synthesis of protocatechuic acid



50 **51**

A round bottom flask equipped with a Teflon-coated magnetic stir-bar was charged with **50** (36.4 mg, 0.2 mmol) and NaOH (80.0 mg, 2.0 mmol). Then solvent EtOH: H_2O (1.5 mL: 4.5 mL) was added to the flask via syringe. Then reaction mixture was stirred at room temperature for 3 hours. After the reaction was finished, the reaction mixture was dropwise acidified with HCl (1 M) to pH 2, during which white precipitation emerged. The mixture was filtrated and washed with water twice, yielding the protocatechuic acid **51** in quantitative yield as white solid.

4.2 Synthesis of caffeic acid

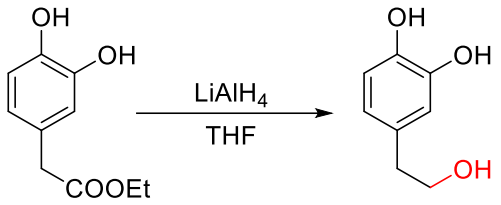


52 **53**

A round bottom flask equipped with a Teflon-coated magnetic stir-bar was charged with **52** (36.4 mg, 0.2 mmol) and NaOH (80.0 mg, 2.0 mmol). Then solvent EtOH: H_2O (1.5 mL: 4.5 mL) was added to the flask via syringe. Then the reaction mixture was stirred at room temperature for 3 hours. After the reaction was finished, the reaction mixture was dropwise acidified with HCl (1 M) to pH 2, then the reaction mixture was extracted with EA twice. Then the combined organic layer was dried

with anhydrous $NaSO_4$, followed by evaporation under reduced pressure to remove the solvent. The residue was purified by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 4:1) to obtain the caffeic acid **53** in 89 % yield (32.0 mg, brown solid).

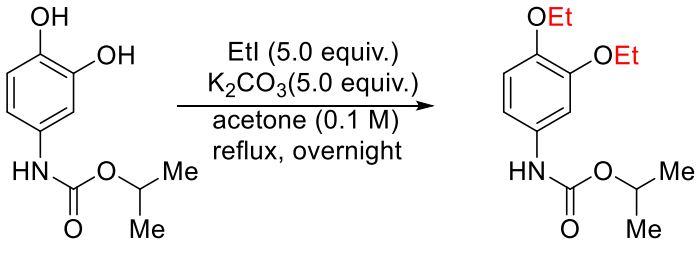
4.3 Synthesis of hydroxytyrosol



54 **55**

According to the literature[9], to a 25 mL round-bottom flask equipped with a Teflon-coated magnetic stir-bar was added **54** (39.2 mg, 0.2 mmol), then dry THF 2.0 mL was added to the flask via syringe. To this mixture was added lithium aluminum hydride ($LiAlH_4$) (38.0 mg, 1.0 mmol), then the suspension was stirred at room temperature for 12 hours. After reaction was finished, the crude mixture was acidified with HCl (1 M) to pH 2, and the reaction mixture was concentrated under reduced pressure, yielding the hydroxytyrosol **55** in quantitative yield as colorless oil.

4.4 Synthesis of diethofencarb



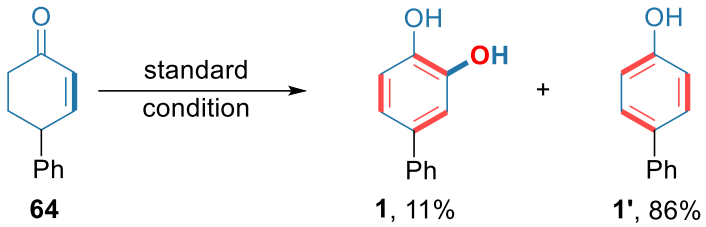
58 **59**

To a pressure tube charged with **58** (42.2 mg, 0.2 mmol) and K_2CO_3 (138.0 mg, 1.0 mmol) in acetone (2.0 mL) was added iodoethane (155 mg, 1.0 mmol), then the reaction was heated at 65 °C overnight. After the reaction was finished, the mixture

was concentrated under reduced pressure and purified by flash chromatography on silica gel (eluent = petroleum ether: ethyl acetate = 10:1) to obtain the diethofencarb **59** in 80 % yield (42.7 mg, white solid).

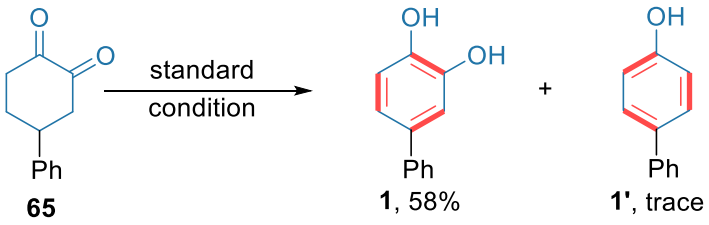
5 Mechanistic Studies

5.1 Validate cyclohexenone as the possible reaction intermediate



In a nitrogen-filled glovebox, the 35 mL pressure tube equipped with a stir bar was charged with 2,3-dihydro-[1,1'-biphenyl]-4(1*H*)-one (34.2 mg, 0.20 mmol)，*p*-toluenesulfonic acid (34.4 mg, 0.20 mmol), tetrabutylammonium *p*-toluenesulfonate (41.3 mg, 0.10 mmol) and TEMPO (120.0 mg, 0.76 mmol), then dioxane (0.4 mL) was added to the pressure tube via syringe. Later, the vial was capped with a screw cap fitted with a PTFE-faced silicone septum, removed from the glove box, and stirred at 120 °C for 36 hours with a speed of 300 rpm. After the reaction was finished, the mixture was filtered through a short plug of silica gel and washed with 10 mL of ethyl acetate. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel to provide **1** and **1'** in 11% and 86% yield, respectively.

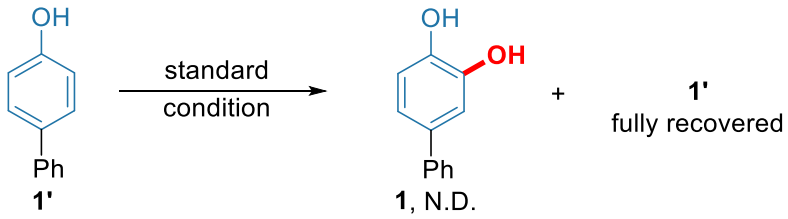
5.2 Validate cyclohexanedione as the possible reaction intermediate



In a nitrogen-filled glovebox, the 35 mL pressure tube equipped with a stir bar was charged with 4-phenylcyclohexane-1,2-dione (37.6 mg, 0.20 mmol), *p*-toluenesulfonic acid (34.4 mg, 0.20 mmol), tetrabutylammonium *p*-toluenesulfonate (41.3 mg, 0.10 mmol) and TEMPO (120.0 mg, 0.76 mmol), then dioxane (0.4 mL) was added to the pressure tube via syringe. Later, the vial was capped with a screw cap fitted with a PTFE-faced silicone septum, removed from the glove box, and

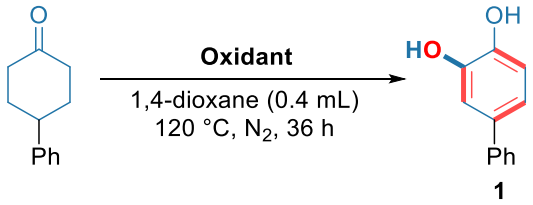
stirred at 120 °C for 36 hours with a speed of 300 rpm. After the reaction was finished, the mixture was filtered through a short plug of silica gel and washed with 10 mL of ethyl acetate. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel to provide **1** exclusively in 58% yield.

5.3 Validate phenol as the possible reaction intermediate



In a nitrogen-filled glovebox, the 35 mL pressure tube equipped with a stir bar was charged with 4-phenylphenol (34.0 mg, 0.20 mmol)，*p*-toluenesulfonic acid (34.4 mg, 0.20 mmol), tetrabutylammonium *p*-toluenesulfonate (41.3 mg, 0.10 mmol) and TEMPO (120.0 mg, 0.76 mmol), then dioxane (0.4 mL) was added to the pressure tube via syringe. Later, the vial was capped with a screw cap fitted with a PTFE-faced silicone septum, removed from the glove box, and stirred at 120 °C for 36 hours with a speed of 300 rpm. After the reaction was finished, the mixture was filtered through a short plug of silica gel and washed with 10 mL of ethyl acetate. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel to provide **1'** in 95% isolated yield.

5.4 Excluding oxoammonium salt as the possible reaction oxidant

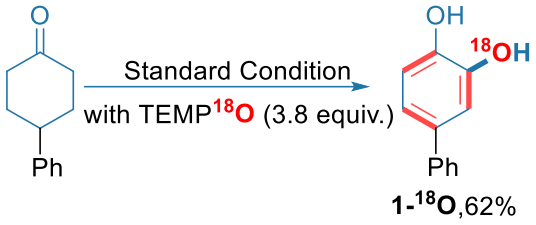


Oxidant	
= 2.8 eq TEMPO + 1.0 eq $TEMPO^+BF_4^-$,	**37%**
= 1.8 eq TEMPO + 1.0 eq $TEMPO^+BF_4^-$,	**5%**
= 3.8 eq $TEMPO^+BF_4^-$,	**N.D**

In a nitrogen-filled glovebox, the 35 mL pressure tube equipped with a stir bar was

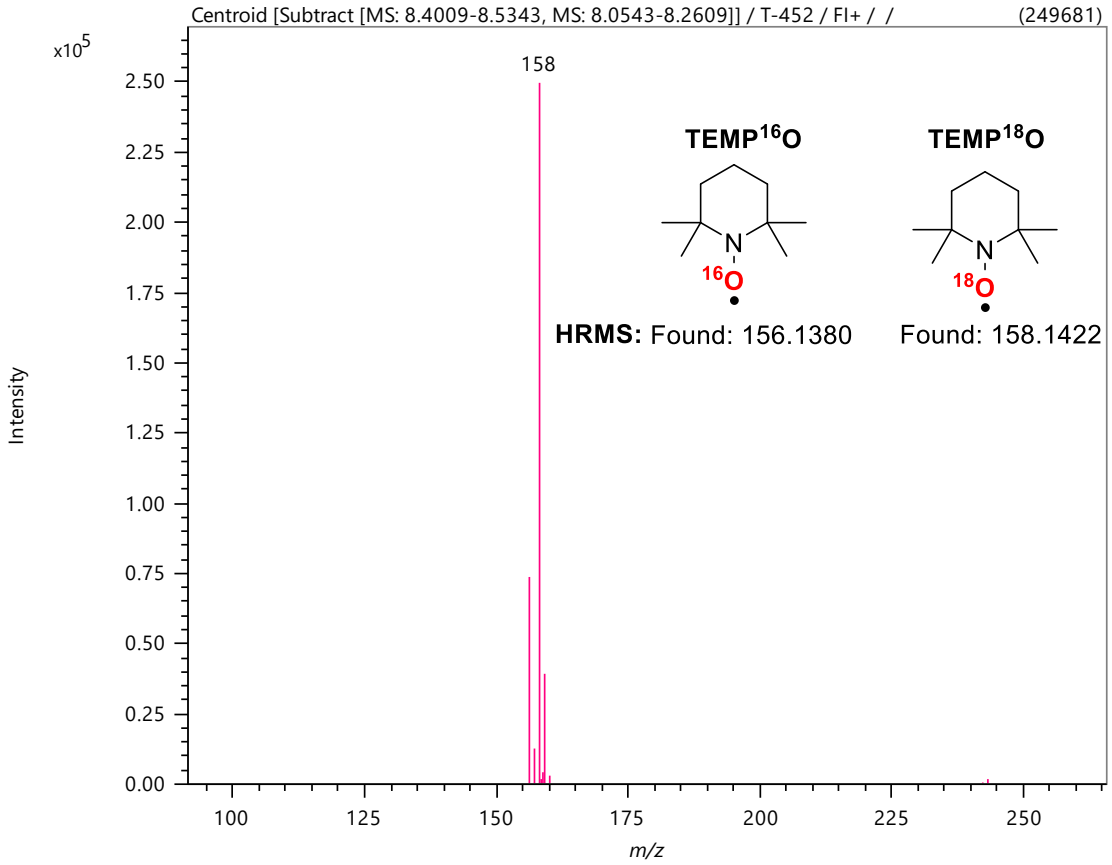
charged with 4-phenylcyclohexanone (37.6 mg, 0.20 mmol)，*p*-toluenesulfonic acid (34.4 mg, 0.20 mmol), tetrabutylammonium *p*-toluenesulfonate (41.3 mg, 0.10 mmol) and oxidant, then dioxane (0.4 mL) was added to the pressure tube via syringe. Later, the vial was capped with a screw cap fitted with a PTFE-faced silicone septum, removed from the glove box, and stirred at 120 °C for 36 hours with a speed of 300 rpm. After the reaction was finished, the mixture was filtered through a short plug of silica gel and washed with 10 mL of ethyl acetate. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel to provide **1** in isolated yield.

5.5 ^{18}O-labeling experiment



To confirm the oxygen source of catechol, the TEMP^{18}O was prepared and used under standard condition. In a nitrogen-filled glovebox, a 35 mL pressure tube equipped with a stir bar was charged with 4-phenylcyclohexanone (37.6 mg, 0.20 mmol)，*p*-toluenesulfonic acid (34.4 mg, 0.20 mmol), tetrabutylammonium *p*-toluenesulfonate (41.3 mg, 0.10 mmol) and TEMP^{18}O (120.0 mg, 0.38 mmol), then dioxane (0.4 mL) was added to the pressure tube via syringe. Later, the vial was capped with a screw cap fitted with a PTFE-faced silicone septum, removed from the glove box, and stirred at 120 °C for 36 hours with a speed of 300 rpm. After the reaction was finished, the mixture was filtered through a short plug of silica gel and washed with 10 mL of ethyl acetate. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel to provide the corresponding product. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel (eluent = PE/EA = 9: 1) to provide the product (**1-^{18}O**) in 62 % yield (23.0 mg, white solid). Characterization data matched that obtained on 0.2 mmol scale (vide infra). Isotopic distribution analysis by HRMS was demonstrated below.

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
158.1422	158.1421	0.49	-11.0	$H_{22}O_5{}^{18}OF_2$
	158.1424	-1.00	-9.5	$CH_{19}{}^{18}ONF_5$
	158.1421	1.04	-8.5	$C_2H_{24}O_4NS$
	158.1425	-1.82	-3.0	$C_5H_{19}O_2N_2F$
	158.1425	-2.00	1.5	$C_9H_{18}{}^{18}ON$

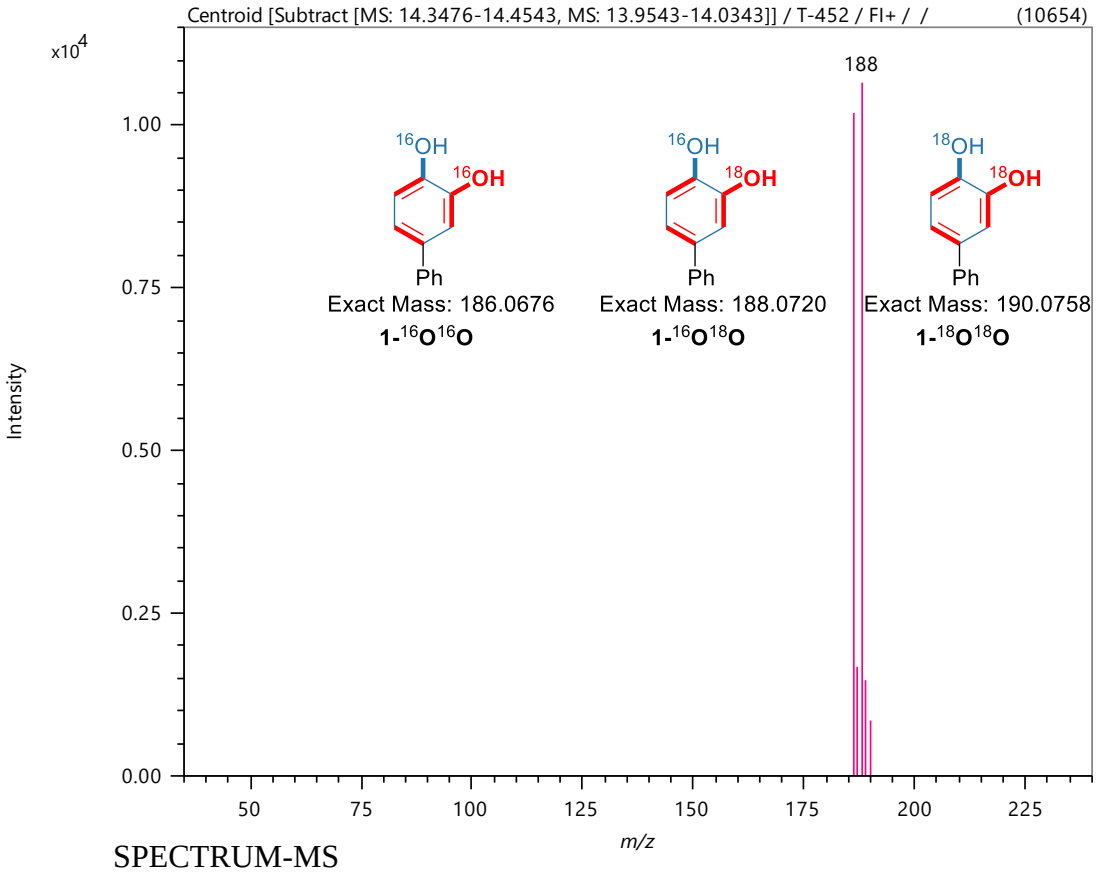


SPECTRUM-MS

m/z	**Intensity**	Intensity [%]
156.13795	**100268.02**	**29.43**
157.14278	15932.36	4.68
158.14222	**340704.59**	**100.00**
159.14677	49042.19	14.39

Figure S1. The HRMS spectra of TEMP^{18}O.

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
188.0720	188.0718	1.19	8.0	$C_{12}H_{10}O\,{}^{18}O$
	188.0717	1.34	3.5	$C_8H_{11}O_3NF$
	188.0723	-1.42	-5.0	$CH_{15}O_4\,{}^{18}O\,N_2FS$
	188.0716	2.03	-3.0	$C_4H_{11}O\,{}^{18}O\,F_5$
	188.0716	2.19	-7.5	$H_{12}O_3NF_6$



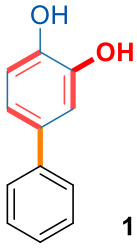
SPECTRUM-MS

m/z	**Intensity**	Intensity [%]
186.06760	**12774.70**	**94.63**
187.07025	2189.63	16.22
188.07200	**13499.11**	**100.00**
189.07587	2045.85	15.16
190.07575	**1234.69**	**9.60**

Figure S2. The HRMS spectra of **1-^{18}O**

6 Product Characterizations

[1,1'-Biphenyl]-3,4-diol (1)



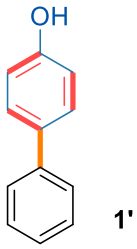
1

1 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **1** was obtained in 82% yield (30.5 mg, white solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 7.06 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 5.26 (dd, *J* = 16.6, 3.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.63, 142.99, 140.59, 134.81, 128.70, 126.86, 126.74, 119.93, 115.71, 114.29, 77.32.

[1,1'-Biphenyl]-4-ol (1')



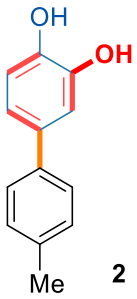
1'

1' (0.2 mmol scale) was synthesized following ***General Procedure*** but using 4-phenyl-2-cyclohexenone as starting material. After concentration and purification by flash chromatography on silica gel eluent = petroleum ether/ethyl acetate = 10: 1), the product **1'** was obtained in 86% yield (29.3 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.82 (s, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 154.99, 140.71, 134.04, 128.72, 128.39, 126.71, 115.62.

4'-Methyl-[1,1'-biphenyl]-3,4-diol (2)



2

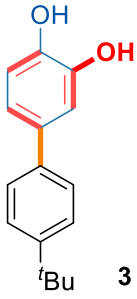
2 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **2** was obtained in 75% yield (30.0 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.03 (s, 2H), 7.40 (d, J = 7.7 Hz, 2H), 7.19 (d, J = 7.7 Hz, 2H), 7.01 (s, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 146.09, 145.44, 138.14, 135.95, 132.07, 129.90, 126.32, 117.90, 116.54, 114.27, 21.13.

HRMS (FI+): Calcd. for $C_{13}H_{12}O_2$ ([M+H]$^+$): 200.0832, found: 200.0835.

4'-(*tert*-Butyl)-[1,1'-biphenyl]-3,4-diol (3)



3

3 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **3** was obtained in 67% yield (32.4

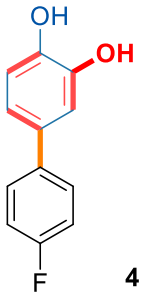
mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.03 (d, J = 3.5 Hz, 2H), 7.42 (q, J = 8.4 Hz, 4H), 7.02 (d, J = 2.2 Hz, 1H), 6.90 (dd, J = 8.2, 2.2 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 149.16, 146.07, 145.47, 138.14, 132.00, 126.13, 126.03, 117.96, 116.52, 114.30, 34.64, 31.67.

HRMS (FI+): Calcd. for $C_{16}H_{18}O_2$ ([M+H]$^+$): 242.1301, found: 242.1302.

4'-Fluoro-[1,1'-biphenyl]-3,4-diol (4)



4

4 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **4** was obtained in 83% yield (33.9 mg, white solid).

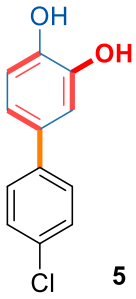
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (d, J = 16.4 Hz, 2H), 7.54 (dd, J = 8.6, 5.5 Hz, 2H), 7.22 (t, J = 8.8 Hz, 2H), 7.01 (d, J = 2.3 Hz, 1H), 6.91 (dd, J = 8.1, 2.2 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 161.73 (d, $^{1}J_{C\text{-}F}$ = 242.8 Hz), 145.92 (d, $^{2}J_{C\text{-}F}$ = 46.7 Hz), 137.52, 137.49, 131.10, 128.30 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 118.16, 116.58, 116.12, 115.91, 114.47.

^{19}F NMR (376 MHz, DMSO-d_6) δ -116.98.

HRMS (FI +): Calcd. for $C_{12}H_9O_2F$ ([M+H]$^+$): 204.0581, found: 204.0578.

4'-Chloro-[1,1'-biphenyl]-3,4-diol (5)



5

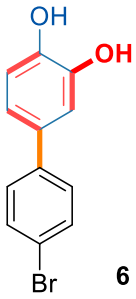
5 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **5** was obtained in 83% yield (36.5mg, white solid).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.18 (s, 1H), 9.10 (s, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 2.3 Hz, 1H), 6.94 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H).

^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 146.22, 146.07, 139.79, 131.56, 130.66, 129.22, 128.15, 118.21, 116.62, 114.38.

HRMS (FI +): Calcd. for $C_{12}H_9O_2Cl$ ($[M+H]^+$): 220.0286, found: 220.0282.

4'-Bromo-[1,1'-biphenyl]-3,4-dio (6)



6

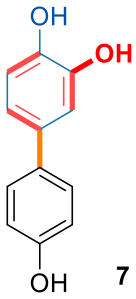
6 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **6** was obtained in 74% yield (39.1 mg, white solid).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.15 (s, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.03 (s, 1H), 6.93 (d, *J* = 9.6 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 146.22, 146.09, 140.14, 132.11, 130.65, 128.50, 120.04, 118.15, 116.63, 114.32.

HRMS (ESI－): Calcd. for $C_{12}H_8O_2Br$ ($[M]^-$): 262.97132, found: 262.97112.

[1,1'-Biphenyl]-3,4,4'-triol (7)



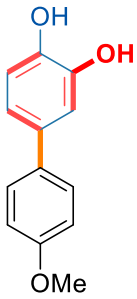
7

7 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 4: 1), the product **7** was obtained in 71% yield (28.7 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.14 (d, J = 138.3 Hz, 3H), 7.32 (d, J = 8.0 Hz, 2H), 6.94 (s, 1H), 6.79 (q, J = 10.5, 10.0 Hz, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 156.73, 145.98, 144.78, 132.35, 131.92, 127.50, 117.43, 116.49, 116.06, 113.96.

4'-Methoxy-[1,1'-biphenyl]-3,4-diol (8)



8

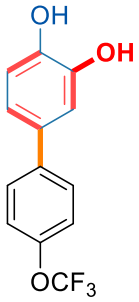
8 (0.2 mmol scale) was synthesized following ***General Procedure A***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **8** was obtained in 70% yield (30.3 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.97 (s, 2H), 7.44 (d, J = 8.2 Hz, 2H), 6.99 – 6.92 (m, 3H), 6.86 (dd, J = 8.2, 2.1 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 158.58, 146.05, 145.08, 133.50, 131.89, 127.50, 117.65, 116.52, 114.70, 114.09, 55.59.

HRMS (FI+): Calcd. for $C_{13}H_{12}O_3$ ($[M+H]^+$): 216.0781, found: 216.0785.

4'-(Trifluoromethoxy)-[1,1'-biphenyl]-3,4-diol (9)



9

9 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **9** was obtained in 86% yield (46.4 mg, white solid).

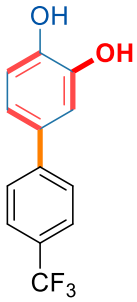
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.20 (s, 1H), 9.13 (s, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 2.3 Hz, 1H), 6.96 (dd, J = 8.1, 2.1 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 147.53, 146.24, 146.15, 140.36, 130.57, 128.17, , 121.88, 120.69 (d, $^{1}J_{C\text{-}F}$ = 257.6 Hz), 118.41, 116.63, 114.57.

^{19}F NMR (376 MHz, DMSO-d_6) δ -56.84.

HRMS (FI+): Calcd. for $C_{13}H_9O_3F_3$ ($[M+H]^+$): 270.0498, found: 270.0501.

4'-(Trifluoromethyl)-[1,1'-biphenyl]-3,4-diol (10)



10

10 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **10** was obtained in 93% yield (47.3 mg, white solid).

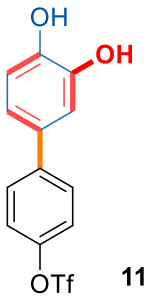
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.30 (s, 1H), 9.18 (s, 1H), 7.73 (s, 4H), 7.12 (s, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 146.74, 146.35, 144.92, 130.28, 129.09, 127.34, 127.03, 126.71, 126.39, 126.16 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 125.04 (d, $^{1}J_{C\text{-}F}$ = 270.6 Hz), 123.68, 118.71, 116.70, 114.68.

^{19}F NMR (376 MHz, DMSO-d_6) δ -60.76.

HRMS (EI+): Calcd. for $C_{13}H_9O_2F_3$ ($[M+H]^+$): 254.0549, found: 254.0547.

3',4'-Dihydroxy-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (11)



11

11 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 4: 1), the product **11** was obtained in 74% yield (49.4 mg, white solid).

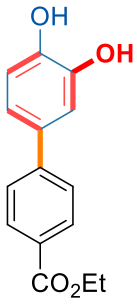
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.25 (s, 1H), 9.15 (s, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 7.06 (s, 1H), 6.97 (d, J = 7.9 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 148.37, 146.42, 146.28, 141.70, 130.08, 128.45, 122.24, 118.80 (q, $^{1}J_{C\text{-}F}$ = 320.4 Hz) 118.58, 116.65, 114.64.

^{19}F NMR (376 MHz, DMSO-d_6) δ -72.82.

HRMS (FI+): Calcd. for $C_{13}H_9F_3O_5S$ ([M+H]$^+$): 334.0117, found: 334.0120.

Ehyl 3',4'-dihydroxy-[1,1'-biphenyl]-4-carboxylate (12)



12

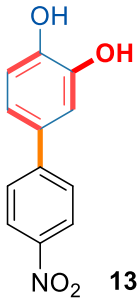
12 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ ethyl acetate = 4: 1), the product **12** was obtained in 72% yield (37.2 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.28 (s, 1H), 9.15 (s, 1H), 7.97 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 2.3 Hz, 1H), 7.04 (dd, J = 8.3, 2.2 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.13, 146.68, 146.27, 145.39, 130.48, 130.21, 128.00, 126.43, 118.66, 116.64, 114.58, 61.08, 14.70.

HRMS (EI+): Calcd. for $C_{15}H_{14}O_4$ ([M+H]$^+$): 258.0887, found: 258.0889.

4'-Nitro-[1,1'-biphenyl]-3,4-diol (13)



13

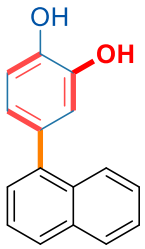
13 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 2: 1), the product **13** was obtained in 83% yield (38.4 mg, yellow brown solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.45 (s, 1H), 9.26 (s, 1H), 8.24 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.17 (s, 1H), 7.10 (dd, J = 8.1, 2.1 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 147.47, 146.45, 146.17, 129.37, 127.17, 124.62, 119.22, 116.77, 114.82

HRMS (EI+): Calcd. for $C_{12}H_9O_4N$ ([M+H]$^+$): 231.0526, found: 231.0532.

4-(Naphthalen-1-yl)benzene-1,2-diol (14)



14

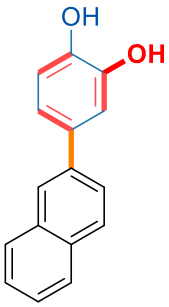
14 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **14** was obtained in 89% yield (42.0 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.12 (d, J = 8.8 Hz, 2H), 7.98 – 7.85 (m, 3H), 7.55 – 7.45 (m, 3H), 7.36 (dd, J = 7.1, 1.3 Hz, 1H), 6.94 – 6.82 (m, 2H), 6.73 (dd, J = 8.0, 2.1 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.60, 145.41, 140.38, 133.99, 131.58, 128.76, 127.41, 127.02, 126.52, 126.27, 126.10, 126.07, 121.26, 117.71, 116.15.

HRMS (FI+): Calcd. for $C_{16}H_{12}O_2$ ($[M+H]^+$): 236.0832, found: 236.0833.

4-(Naphthalen-2-yl)benzene-1,2-diol (15)



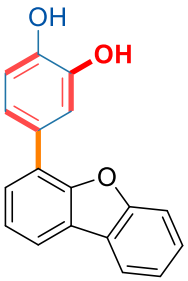
15

15 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **15** was obtained in 84% yield (40.0 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (s, 1H), 9.11 (s, 1H), 8.05 (s, 1H), 7.94 (t, J = 7.4 Hz, 2H), 7.89 (d, J = 7.1 Hz, 1H), 7.73 (dd, J = 8.5, 1.9 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.21 (d, J = 2.3 Hz, 1H), 7.10 (dd, J = 8.3, 2.2 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 146.26, 145.92, 138.34, 133.96, 132.26, 131.81, 128.75, 128.48, 127.94, 126.76, 126.07, 125.45, 124.41, 118.56, 116.67, 114.75

4-(Dibenzo[*b*,*d*]furan-4-yl)benzene-1,2-diol (16)



16

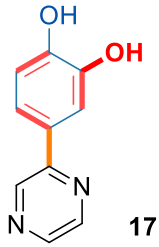
16 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **16** was obtained in 69% yield (38.1 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (d, *J* = 20.9 Hz, 2H), 8.17 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.46 – 7.37 (m, 3H), 7.21 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 155.87, 152.90, 146.08, 145.88, 128.13, 127.26, 126.78, 125.99, 124.75, 124.15, 124.13, 123.62, 121.68, 120.24, 119.69, 116.45, 116.41, 112.19.

HRMS (ESI－): Calcd. for $C_{18}H_{11}O_3$ ([M]$^-$): 275.07137, found: 275.07125.

4-(Pyrazin-2-yl)benzene-1,2-diol (17)



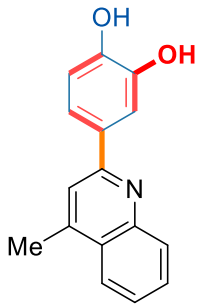
17

17 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 4: 1), the product **17** was obtained in 84% yield (31.6 mg, yellow solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.46 (s, 1H), 9.25 (s, 1H), 9.07 (d, *J* = 1.6 Hz, 1H), 8.61 (dd, *J* = 2.6, 1.5 Hz, 1H), 8.47 (d, *J* = 2.5 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.46 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 152.21, 148.12, 146.30, 144.45, 142.45, 141.60, 127.59, 118.79, 116.44, 114.37

4-(4-Methylquinolin-2-yl)benzene-1,2-diol (18)



18

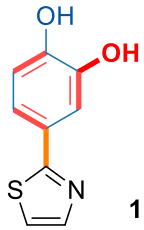
18 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 4: 1), the product **18** was obtained in 50% yield (25.1 mg, light yellow solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (s, 1H), 9.19 (s, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.87 (s, 1H), 7.78 (t, J = 1.9 Hz, 1H), 7.72 (dd, J = 8.4, 6.8 Hz, 1H), 7.58 – 7.51 (m, 2H), 6.87 (d, J = 8.3 Hz, 1H), 2.71 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 156.30, 147.97, 147.83, 146.09, 145.05, 130.61, 129.90, 129.79, 127.04, 126.06, 124.55, 119.31, 119.11, 116.19, 114.86, 18.95.

HRMS (FI+): Calcd. for $C_{16}H_{13}O_2N$ ($[M+H]^+$): 251.0941, found: 251.0938.

4-(Thiazol-2-yl)benzene-1,2-diol (19)



19

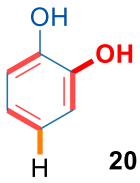
19 (0.2 mmol scale) was synthesized following ***General Procedure.*** After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 3: 1), the product **19** was obtained in 86% yield (33.2 mg, yellow solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.49 (s, 1H), 9.37 (s, 1H), 7.79 (d, J = 3.3 Hz, 1H), 7.60 (d, J = 3.3 Hz, 1H), 7.38 (d, J = 2.2 Hz, 1H), 7.24 (dd, J = 8.2, 2.2 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 168.24, 148.25, 146.19, 143.86, 125.36, 119.20, 118.61, 116.56, 113.78

HRMS (DART+): Calcd. for $C_9H_7O_2NS$ ($[M+H]^+$): 193.0192, found: 193.0194.

Pyrocatechol (20)



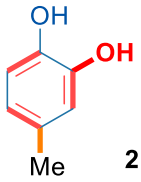
20

20 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **20** was obtained in 73% yield (16.1 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.84 (s, 2H), 6.73 (dd, J = 5.9, 3.6 Hz, 2H), 6.60 (dd, J = 5.9, 3.6 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.82, 119.83, 116.24

4-Methylbenzene-1,2-diol (21)



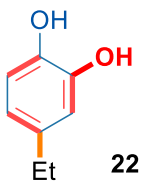
21

21 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **21** was obtained in 47% yield (11.7 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.63 (s, 2H), 6.60 (d, J = 7.9 Hz, 1H), 6.54 (s, 1H), 6.39 (d, J = 7.4 Hz, 1H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.51, 143.38, 128.41, 120.00, 116.92, 115.97, 20.89.

4-Ethylbenzene-1,2-diol (22)



22

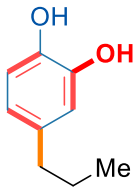
22 (0.2 mmol scale) was synthesized following ***General Procedure***. After

concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **22** was obtained in 54% yield (15.0 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.66 (s, 2H), 6.62 (d, J = 7.9 Hz, 1H), 6.58 (s, 1H), 6.43 (d, J = 7.9 Hz, 1H), 2.41 (q, J = 7.6 Hz, 2H), 1.10 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.53, 143.57, 135.13, 118.73, 115.96, 115.68, 28.05, 16.48.

4-Propylbenzene-1,2-diol (23)



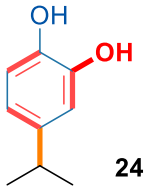
23

23 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **23** was obtained in 42% yield (12.8 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.65 (s, 2H), 6.62 (d, J = 8.0 Hz, 1H), 6.56 (d, J = 2.2 Hz, 1H), 6.41 (dd, J = 7.9, 2.1 Hz, 1H), 2.36 (t, J = 7.6 Hz, 2H), 1.50 (q, J = 7.4 Hz, 2H), 0.85 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.47, 143.62, 133.48, 119.42, 116.25, 115.91, 37.25, 24.89, 14.19.

4-Isopropylbenzene-1,2-diol (24)



24

24 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ ethyl acetate = 5: 1), the product **24** was obtained in 55% yield (16.7

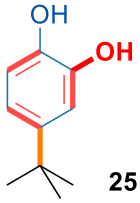
mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.65 (s, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 2.2 Hz, 1H), 6.46 (dd, *J* = 8.1, 2.2 Hz, 1H), 2.69 (p, *J* = 6.9 Hz, 1H), 1.12 (d, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.49, 143.64, 139.95, 117.24, 115.90, 114.18, 33.24, 24.78.

HRMS (FI+): Calcd. for $C_9H_{12}O_2$ ($[M+H]^+$): 152.0832, found: 152.0835.

4-(*tert*-Butyl)benzene-1,2-diol (25)



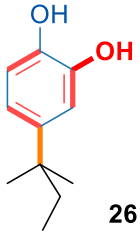
25

25 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **25** was obtained in 67% yield (22.3 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.64 (s, 2H), 6.75 (d, *J* = 2.2 Hz, 1H), 6.64 (d, *J* = 8.3 Hz, 1H), 6.60 (dd, *J* = 8.3, 2.2 Hz, 1H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.08, 143.31, 142.25, 116.13, 115.57, 113.46, 34.13, 31.99.

4-(*tert*-pentyl)benzene-1,2-diol (26)



26

26 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ ethyl acetate = 5: 1), the product **26** was obtained in 71% yield (25.6

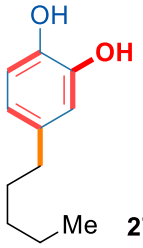
mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.63 (s, 2H), 6.69 (s, 1H), 6.64 (d, J = 8.2 Hz, 1H), 6.54 (dd, J = 8.2, 2.2 Hz, 1H), 1.51 (q, J = 7.4 Hz, 2H), 1.15 (s, 6H), 0.61 (t, J = 7.4 Hz, 3H)

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.08, 143.20, 140.32, 116.88, 115.58, 114.01, 37.25, 36.92, 29.08, 9.63.

HRMS (FI+): Calcd. for $C_{11}H_{16}O_2$ ([M+H]$^+$): 180.1145, found: 180.1149.

4-Pentylbenzene-1,2-diol (27)



27

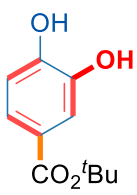
27 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **27** was obtained in 61% yield (22.0 mg, colorless oil).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.64 (s, 1H), 8.54 (s, 1H), 6.57 (d, J = 8.0 Hz, 1H), 6.51 (d, J = 2.0 Hz, 1H), 6.37 (dd, J = 8.0, 2.1 Hz, 1H), 2.34 (t, J = 7.6 Hz, 2H), 1.44 (p, J = 7.4 Hz, 2H), 1.26 – 1.18 (m, 4H), 0.81 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.45, 143.55, 133.65, 119.31, 116.15, 115.89, 35.02, 31.46, 31.39, 22.53, 14.47.

HRMS (FI+): Calcd. for $C_{11}H_{16}O_2$ ([M+H]$^+$): 180.1145, found: 180.1146.

***tert*-Butyl 3,4-dihydroxybenzoate (28)**



28

28 (0.2 mmol scale) was synthesized following ***General Procedure***. After

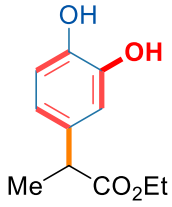
concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ ethyl acetate = 4: 1), the product **28** was obtained in 81% yield (34.0 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.51 (s, 2H), 7.31 (s, 1H), 7.25 (d, J = 8.3 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.49, 150.50, 145.39, 122.78, 122.08, 116.72, 115.61, 80.07, 28.40.

HRMS (FI+): Calcd. for $C_{11}H_{14}O_4$ ($[M+H]^+$): 210.0887, found: 210.0891.

Ethyl (S)-2-(3,4-dihydroxyphenyl)propanoate (29)



29

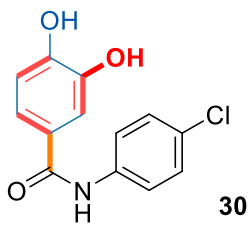
29 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 4: 1), the product **29** was obtained in 43% yield (18.1 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.88 (s, 2H), 6.69 – 6.64 (m, 2H), 6.51 (dd, J = 8.1, 2.2 Hz, 1H), 4.02 (ddt, J = 14.1, 7.1, 3.5 Hz, 2H), 3.54 (q, J = 7.1 Hz, 1H), 1.30 (d, J = 7.2 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.84, 145.78, 144.88, 132.16, 118.67, 116.13, 115.08, 60.65, 44.46, 19.30, 14.62.

HRMS (FI+): Calcd. for $C_{11}H_{14}O_4$ ($[M+H]^+$): 210.0887, found: 210.0883.

***N*-(4-chlorophenyl)-3,4-dihydroxybenzamide (30)**



30

30 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 2: 1), the product **30** was obtained in 74% yield (39.0 mg, yellow solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.08 (s, 1H), 9.68 (s, 1H), 9.29 (s, 1H), 7.80 (d, J = 8.9 Hz, 2H), 7.39 – 7.33 (m, 4H), 6.84 (d, J = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.88, 149.55, 145.52, 139.06, 128.94, 127.25, 126.12, 122.17, 120.24, 115.94, 115.45

HRMS (EI+): Calcd. for $C_{13}H_{10}O_3NCl$ ([M+H]$^+$): 263.0344, found: 263.0350

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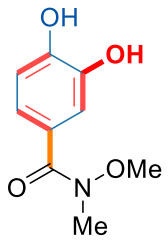
3,4-Dihydroxy-N-methoxy-*N*-methylbenzamide (31)



31

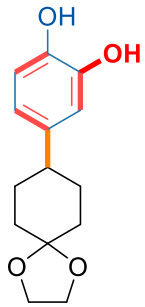
31 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 2: 1), the product **31** was obtained in 72% yield (28.4 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.32 (s, 2H), 7.10 (s, 1H), 7.01 (d, J = 8.1 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 3.54 (s, 3H), 3.20 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 169.43, 148.59, 145.05, 125.07, 120.88, 116.49, 115.36, 60.95, 34.27.

HRMS (FI+): Calcd. for $C_9H_{11}O_4N$ ([M+H]$^+$): 197.0683, found: 197.0685.

4-(1,4-Dioxaspiro[4.5]decan-8-yl)benzene-1,2-diol (32)



32

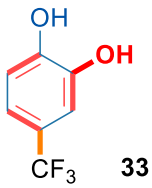
32 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **32** was obtained in 41% yield (20.5 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.72 (s, 1H), 8.61 (s, 1H), 6.61 (d, J = 7.9 Hz, 1H), 6.57 (s, 1H), 6.44 (d, J = 8.0 Hz, 1H), 3.87 (s, 4H), 2.36 (dd, J = 13.3, 5.8 Hz, 1H), 1.75 – 1.66 (m, 4H), 1.56 (d, J = 8.3 Hz, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.40, 143.71, 137.91, 117.53, 115.85, 114.37, 108.16, 64.11, 64.04, 42.03, 35.12, 31.98.

HRMS (FI+): Calcd. for $C_{14}H_{18}O_4$ ($[M+H]^+$): 250.1200, found: 250.1203.

4-(Trifluoromethyl)benzene-1,2-diol (33)



33

33 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **33** was obtained in 33% yield (11.7 mg, white solid).

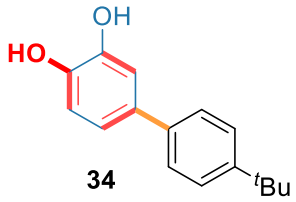
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.71 (s, 2H), 7.02 – 6.94 (m, 2H), 6.88 (d, J = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ149.50, 146.15, 125.14 (q, J = 270.8 Hz), 120.15 (q, J = 31.7 Hz), 117.11 (q, J = 4.2 Hz), 116.15, 112.55 (q, J = 3.7 Hz).

^{19}F NMR (376 MHz, DMSO-d_6) δ -59.61.

HRMS (FI+): Calcd. for $C_7H_5O_2F_3$ ($[M+H]^+$): 178.0236, found: 178.0238.

4'-(*tert*-Butyl)-[1,1'-biphenyl]-3,4-diol (34)

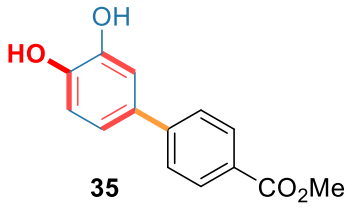


34 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **34** was obtained in 58% yield (28.1 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.02 (s, 2H), 7.42 (q, J = 8.5 Hz, 4H), 7.01 (d, J = 2.2 Hz, 1H), 6.90 (dd, J = 8.2, 2.2 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 149.13, 146.04, 145.44, 138.11, 131.97, 126.10, 126.00, 117.93, 116.50, 114.28, 34.62, 31.65.

Methyl 3',4'-dihydroxy-[1,1'-biphenyl]-4-carboxylate (35)



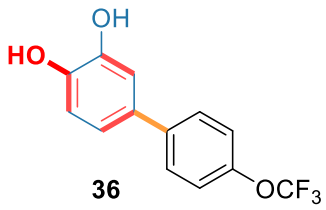
35 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **35** was obtained in 53% yield (25.9 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.25 (s, 2H), 7.98 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H), 7.14 (s, 1H), 7.05 (d, J = 7.9 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.67, 146.73, 146.30, 145.48, 130.46, 130.28, 127.74, 126.47, 118.68, 116.68, 114.62, 52.56

HRMS (EI+): Calcd. for $C_{14}H_{12}O_4$ ([M+H]$^+$): 244.0730, found: 244.0732.

4'-(Trifluoromethoxy)-[1,1'-biphenyl]-3,4-diol (36)



36

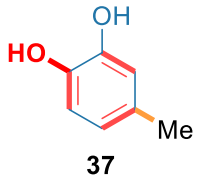
36 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **36** was obtained in 71% yield (38.3 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.19 (s, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 2.3 Hz, 1H), 6.96 (dd, J = 8.2, 2.3 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 147.52, 146.24, 146.15, 140.35, 130.56, 128.15, 124.50, 121.96, 121.84, 119.42, 118.39, 116.87, 116.63, 114.57

^{19}F NMR (376 MHz, DMSO-d_6) δ -56.86..

4-Methylbenzene-1,2-diol (37)



37

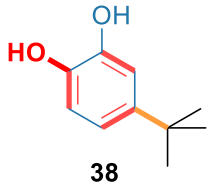
37 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **37** was obtained in 44% yield (11.0 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.71 (s, 1H), 8.58 (s, 1H), 6.59 (d, J = 7.9 Hz, 1H), 6.53 (d, J = 2.1 Hz, 1H), 6.39 (dd, J = 8.0, 2.1 Hz, 1H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.51, 143.38, 128.42, 120.01, 116.93, 115.98,

20.90.

4-(*tert*-Butyl)benzene-1,2-diol (38)



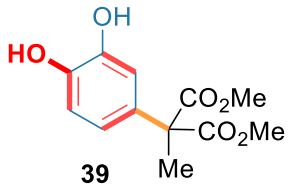
38

38 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **38** was obtained in 49% yield (16.3 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.66 (s, 2H), 6.80 – 6.71 (m, 1H), 6.68 – 6.56 (m, 2H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.07, 143.30, 142.23, 116.11, 115.58, 113.46, 34.11, 31.98.

Dimethyl 2-(3,4-dihydroxyphenyl)-2-methylmalonate (39)



39

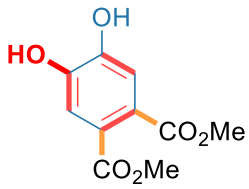
39 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 4: 1), the product **39** was obtained in 62% yield (31.5 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.98 (s, 2H), 6.72 – 6.66 (m, 2H), 6.55 (dd, J = 8.3, 2.4 Hz, 1H), 3.66 (s, 6H), 1.69 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 172.28, 145.31, 145.19, 129.29, 118.38, 115.70, 115.54, 58.10, 53.15, 22.72.

HRMS (FI+): Calcd. for $C_{12}H_{14}O_6$ ([M+H]$^+$): 254.0785, found: 254.0780.

Dimethyl 4,5-dihydroxyphthalate(40)



40

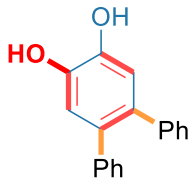
40 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 4: 1), the product **40** was obtained in 45% yield (20.3 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.03 (s, 2H), 7.05 (s, 2H), 3.74 (s, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.85, 148.30, 123.77, 116.38, 52.72

HRMS (FI+): Calcd. for $C_{10}H_{10}O_6$ ($[M+H]^+$): 226.0472, found: 226.0474.

[1,1':2',1''-Terphenyl]-4',5'-diol (41)



41

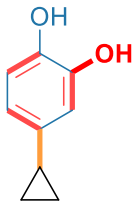
41 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **41** was obtained in 44% yield (23.1 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.20 (s, 2H), 7.20 – 7.11 (m, 6H), 7.02 (d, J = 6.3 Hz, 4H), 6.79 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.30, 141.90, 131.57, 129.99, 128.34, 126.37, 118.24.

HRMS (FI+): Calcd. for $C_{18}H_{10}O_2$ ($[M+H]^+$): 262.0988, found: 262.0986.

4-Cyclopropylbenzene-1,2-diol (42)



42

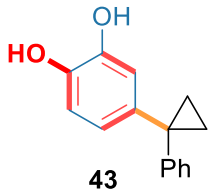
42 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **42** was obtained in 41% yield (12.3 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.64 (s, 2H), 6.59 (d, J = 8.0 Hz, 1H), 6.42 (d, J = 2.2 Hz, 1H), 6.33 (dd, J = 8.1, 2.2 Hz, 1H), 1.72 (tt, J = 8.4, 5.1 Hz, 1H), 0.82 – 0.77 (m, 2H), 0.50 – 0.45 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.62, 143.47, 134.72, 116.76, 115.93, 113.37, 14.97, 9.01.

HRMS (FI+): Calcd. for $C_9H_{10}O_2$ ($[M+H]^+$): 150.0675, found: 150.0673.

4-(1-Phenylcyclopropyl)benzene-1,2-diol (43)



43

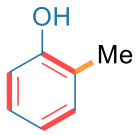
43 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **43** was obtained in 58% yield (26.2 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.78 (s, 2H), 7.24 (dd, J = 8.2, 6.7 Hz, 2H), 7.19 – 7.10 (m, 3H), 6.67 – 6.58 (m, 2H), 6.51 (dd, J = 8.0, 2.2 Hz, 1H), 1.13 (d, J = 1.9 Hz, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 146.82, 145.36, 144.10, 136.67, 128.61, 128.20, 126.08, 119.61, 116.80, 115.81, 29.77, 16.27.

HRMS (FI+): Calcd. for $C_{15}H_{14}O_2$ ($[M+H]^+$): 226.0988, found: 229.0984.

_o_-Cresol (44a)



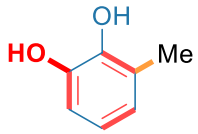
44a

44a (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 10: 1), the product **44a** was obtained in 27% yield (5.8 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.24 (s, 1H), 7.04 (d, J = 7.4 Hz, 1H), 6.98 (t, J = 7.7 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.68 (t, J = 7.3 Hz, 1H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 155.93, 131.10, 127.17, 124.30, 119.31, 115.10, 16.53.

3-Methylbenzene-1,2-diol (44b)



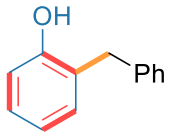
44b

44b (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **44b** was obtained in 24% yield (6.0 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11 (s, 1H), 8.53 – 7.77 (m, 1H), 6.65 – 6.57 (m, 1H), 6.52 (q, J = 3.3, 2.6 Hz, 2H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.38, 143.86, 125.06, 121.62, 119.13, 113.56, 16.58.

2-Benzylphenol (45a)



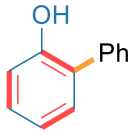
45a

45a (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 10: 1), the product **45a** was obtained in 14% yield (5.2 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.35 (s, 1H), 7.28 – 7.18 (m, 5H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 8.2 Hz, 2H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 3.86 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 155.47, 141.81, 130.82, 129.16, 128.68, 127.87, 127.68, 126.14, 119.44, 115.53, 35.74.

[1,1'-Biphenyl]-2-ol (46a)



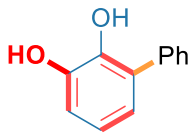
46a

46a (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 10: 1), the product **46a** was obtained in 90% yield (30.6 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.56 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.22 (m, 2H), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.89 (td, *J* = 7.5, 1.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 154.85, 139.17, 130.91, 129.64, 129.03, 128.47, 128.28, 127.03, 120.00, 116.58

[1,1'-Biphenyl]-2,3-diol (46b)



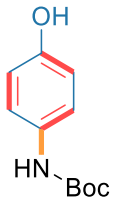
46b

46b (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **46b** was obtained in 6% yield (2.2 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.87 (s, 2H), 7.52 (dd, J = 8.3, 1.3 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.30 – 7.25 (m, 1H), 6.79 (dd, J = 6.6, 2.9 Hz, 1H), 6.73 – 6.67 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 146.08, 143.08, 139.28, 129.58, 128.89, 128.37, 126.94, 121.13, 119.66, 114.83

***tert*-Butyl (4-hydroxyphenyl)carbamate (47a)**



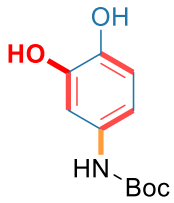
47a

47a (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **47a** was obtained in 33% yield (13.8 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (s, 1H), 8.99 (s, 1H), 7.21 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.8 Hz, 2H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 153.52, 153.02, 131.52, 120.46, 115.52, 78.93, 28.70.

***tert*-Butyl (3,4-dihydroxyphenyl)carbamate (47b)**



47b

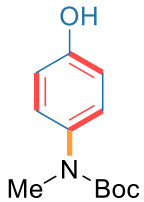
47b (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 3: 1), the product **47b** was obtained in 24% yield (10.8 mg, yellow solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.71 (d, J = 163.0 Hz, 3H), 6.96 (s, 1H), 6.64 (d, J = 7.8 Hz, 1H), 6.57 (d, J = 8.4 Hz, 1H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 153.38, 145.49, 140.89, 131.97, 115.79, 109.91, 107.60, 78.85, 28.72.

HRMS (EI+): Calcd. for $C_{11}H_{15}O_4N$ ($[M+H]^+$): 225.0996, found: 225.0992.

***tert*-Butyl (4-hydroxyphenyl)(methyl)carbamate (48a)**



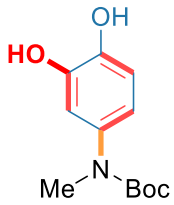
48a

48a (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **48a** was obtained in 29% yield (12.9 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.40 (s, 1H), 7.02 (d, J = 8.2 Hz, 2H), 6.70 (d, J = 8.2 Hz, 2H), 3.09 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 155.52, 154.63, 135.50, 127.36, 115.52, 79.42, 37.95, 28.60, 28.47.

***tert*-Butyl (3,4-dihydroxyphenyl)(methyl)carbamate (48b)**



48b

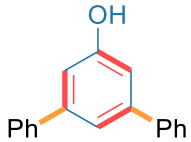
48b (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 3: 1), the product **48b** was obtained in 31% yield (14.8 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.92 (s, 2H), 6.66 (d, J = 8.4 Hz, 1H), 6.62 (s, 1H), 6.47 (d, J = 9.1 Hz, 1H), 3.07 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 154.65, 145.39, 143.69, 135.79, 116.88, 115.54, 114.24, 79.40, 38.05, 28.53.

HRMS (EI+): Calcd. for $C_{12}H_{17}O_4N$ ($[M+H]^+$): 239.1152, found: 239.1157.

[1,1':3',1''-Terphenyl]-5'-ol (49a)



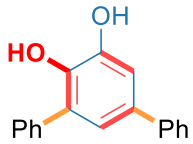
49a

49a (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 10: 1), the product **49a** was obtained in 35% yield (17.2 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.75 (s, 1H), 7.71 – 7.67 (m, 4H), 7.47 (t, J = 7.5 Hz, 4H), 7.40 – 7.36 (m, 2H), 7.32 (t, J = 1.6 Hz, 1H), 7.04 (d, J = 1.6 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 158.81, 142.76, 140.85, 129.41, 128.08, 127.34, 116.79, 113.26

[1,1':3',1''-Terphenyl]-4',5'-diol (49b)



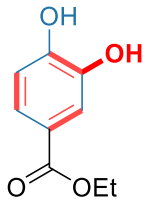
49b

49b (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 5: 1), the product **49b** was obtained in 41% yield (21.5 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.76 (s, 1H), 8.54 (s, 1H), 7.64 – 7.54 (m, 4H), 7.41 (t, *J* = 7.5 Hz, 4H), 7.33 – 7.27 (m, 2H), 7.08 (d, *J* = 2.3 Hz, 1H), 7.00 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 146.49, 142.96, 140.94, 139.17, 131.86, 129.70, 129.34, 129.20, 128.42, 127.13, 127.04, 126.64, 119.57, 113.07

Ethyl 3,4-dihydroxybenzoate (50)



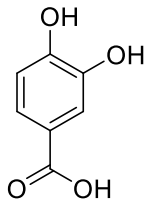
50

50 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 4: 1), the product **50** was obtained in 81% yield (29.5 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.56 (s, 2H), 7.36 (s, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.34, 151.01, 145.69, 122.40, 121.44, 116.89, 115.94, 60.65, 14.85.

3,4-Dihydroxybenzoic acid (51)

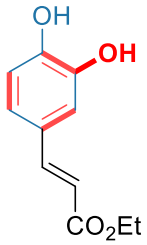


51

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.31 (brs, 1H), 9.71 (brs, 1H), 9.32 (brs, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.31 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.90, 150.58, 145.45, 122.48, 122.20, 117.10, 115.73.

Ethyl (*E*)-3-(3,4-dihydroxyphenyl)acrylate (52)



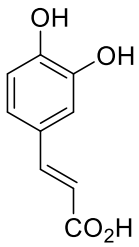
52

52 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 4: 1), the product **52** was obtained in 72% yield (29.8 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.87 – 9.49 (s, 1H), 9.18 (s, 1H), 7.49 (d, *J* = 15.9 Hz, 1H), 7.07 (s, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.28 (d, *J* = 15.9 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.11, 148.92, 146.11, 145.56, 126.06, 121.90, 116.27, 115.35, 114.58, 60.25, 14.81.

(*E*)-3-(3,4-dihydroxyphenyl)acrylic acid (53)

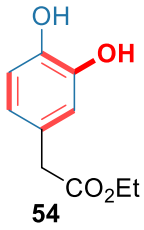


53

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.07 (brs, 1H), 9.36 (brs, 2H), 7.45 (d, *J* = 15.8 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 6.99 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.20 (d, *J* = 15.9 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 168.57, 148.73, 146.15, 145.24, 126.30, 121.80, 116.35, 115.71, 115.24.

Ethyl 2-(3,4-dihydroxyphenyl)acetate (54)



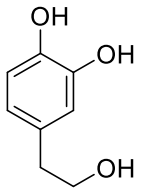
54

54 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 4: 1), the product **54** was obtained in 30% yield (11.8 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.80 (s, 2H), 6.65 (d, *J* = 7.7 Hz, 2H), 6.48 (d, *J* = 8.0 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 172.10, 145.62, 144.73, 125.57, 120.50, 117.10, 115.97, 60.61 , 40.41, 14.64.

4-(2-Hydroxyethyl)benzene-1,2-diol (55)

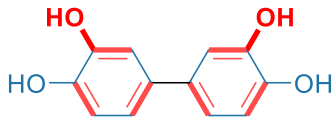


55

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.60 (s, 1H), 6.62 – 6.57 (m, 2H), 6.43 (d, *J* = 8.0 Hz, 1H), 4.55 (s, 1H), 3.52 – 3.47 (m, 2H), 2.55 – 2.51 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.39, 143.82, 130.63, 119.93, 116.76, 115.84, 63.16, 39.06.

[1,1'-Biphenyl]-3,3',4,4'-tetraol (56)



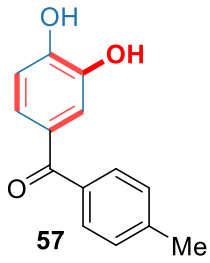
56

56 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel (eluent = dichlormethan/methanol = 9: 1), the product **56** was obtained in 33% yield (14.4 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.91 (s, 4H), 6.88 (d, *J* = 2.0 Hz, 2H), 6.78 – 6.72 (m, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 145.89, 144.73, 132.54, 117.36, 116.44, 113.91

(3,4-Dihydroxyphenyl)(p-tolyl)methaone (57)



57

57 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel eluent = petroleum ether/ ethyl acetate = 4: 1), the product **57** was obtained in 78% yield (33.6

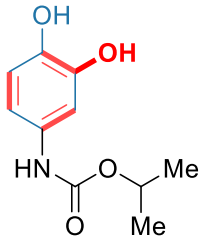
mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.90 (s, 1H), 9.44 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 2.1 Hz, 1H), 7.10 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 194.64, 150.95, 145.64, 142.40, 136.03, 129.87, 129.35, 128.98, 123.78, 117.37, 115.55, 21.62.

HRMS (EI+): Calcd. for $C_{14}H_{12}O_3$ ($[M+H]^+$): 228.0781, found: 228.0784.

Isopropyl (3,4-dihydroxyphenyl)carbamate (58)



58

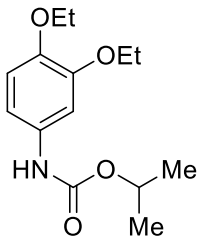
58 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel eluent = petroleum ether/ ethyl acetate = 2: 1), the product **58** was obtained in 31% yield (13.1 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.12 (s, 1H), 8.89 (s, 1H), 8.50 (s, 1H), 6.96 (s, 1H), 6.71 – 6.63 (m, 1H), 6.59 (d, *J* = 8.6 Hz, 1H), 4.83 (p, *J* = 6.3 Hz, 1H), 1.22 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 153.71, 145.57, 141.10, 131.77, 115.85, 109.94, 107.62, 67.41, 22.59.

HRMS (EI+): Calcd. for $C_{10}H_{13}O_4N$ ($[M+H]^+$): 211.0839, found: 211.0842.

Isopropyl (3,4-diethoxyphenyl)carbamate (59)

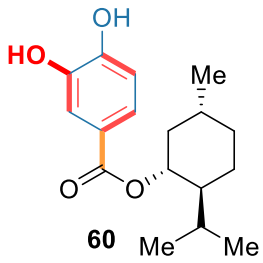


59

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 6.80 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.50 (s, 1H), 5.00 (hept, *J* = 6.3 Hz, 1H), 4.11 – 4.02 (m, 4H), 1.46 – 1.40 (m, 6H), 1.29 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.42, 149.09, 144.59, 131.84, 114.22, 110.50, 105.28, 68.50, 65.02, 64.35, 29.65, 22.08, 14.86, 14.70.

(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 3,4-dihydroxybenzoate (60)



60

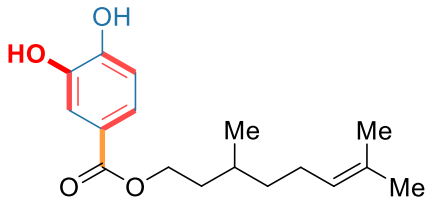
60 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel eluent = petroleum ether/ ethyl acetate = 4: 1), the product **60** was obtained in 81% yield (47.4 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.55 (s, 2H), 7.39 (s, 1H), 7.33 (d, *J* = 5.1 Hz, 1H), 6.83 (s, 1H), 4.74 (t, *J* = 8.8 Hz, 1H), 1.95 (d, *J* = 10.7 Hz, 1H), 1.86 (s, 1H), 1.61 (d, *J* = 10.6 Hz, 2H), 1.44 (s, 2H), 1.01 (q, *J* = 12.4, 11.7 Hz, 3H), 0.85 (d, *J* = 4.2 Hz, 6H), 0.72 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.71, 150.90, 145.61, 122.29, 121.57, 116.85, 115.78, 73.76, 47.26, 41.28, 34.35, 31.47, 26.71, 23.82, 22.43, 21.00, 17.00.

HRMS (EI+): Calcd. for $C_{17}H_{24}O_4$ ($[M+H]^+$): 292.1669, found: 292.1672.

3,7-Dimethyloct-6-en-1-yl 3,4-dihydroxybenzoate (61)



61

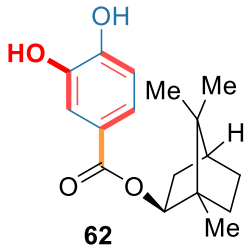
61 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel eluent = petroleum ether/ ethyl acetate = 4: 1), the product **61** was obtained in 64% yield (37.4 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.58 (d, J = 133.9 Hz, 2H), 7.37 (s, 1H), 7.31 (d, J = 7.8 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H), 5.04 (d, J = 7.3 Hz, 1H), 4.21 (q, J = 6.2 Hz, 2H), 1.94 (p, J = 8.0 Hz, 2H), 1.72 – 1.66 (m, 1H), 1.60 (s, 3H), 1.54 (s, 3H), 1.46 (dq, J = 13.1, 6.5 Hz, 2H), 1.33 (q, J = 6.3, 5.5 Hz, 1H), 1.20 – 1.14 (m, 1H), 0.90 (d, J = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.23, 150.91, 145.62, 131.14, 125.02, 122.23, 121.34, 116.84, 115.78, 62.79, 37.01, 35.60, 29.46, 26.00, 25.43, 19.83, 18.01.

HRMS (EI+): Calcd. for $C_{17}H_{24}O_4$ ([M+H]$^+$): 292.1669, found: 292.1675.

(1*R*,2*R*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 3,4-dihydroxybenzoate (62)



62

62 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel eluent = petroleum ether/ ethyl acetate = 4: 1), the product **62** was obtained in 86% yield (49.9 mg, white solid).

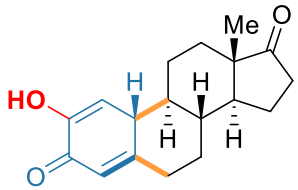
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.77 – 9.38 (m, 2H), 7.37 (d, J = 2.1 Hz, 1H), 7.30 (dd, J = 8.3, 2.1 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 4.79 – 4.72 (m, 1H), 1.84 – 1.73 (m, 3H), 1.68 (t, J = 11.5 Hz, 1H), 1.59 – 1.52 (m, 1H), 1.24 – 1.12 (m, 2H), 1.08 (s,

3H), 0.85 (d, *J* = 3.1 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.60, 150.86, 145.58, 122.09, 121.61, 116.73, 115.82, 80.56, 49.03, 47.12, 44.97, 39.01, 33.73, 27.16, 20.48, 20.44, 11.98.

HRMS (EI+): Calcd. for $C_{17}H_{22}O_4$ ($[M+H]^+$): 290.1513, found: 290.1515.

(8*R*,9*S*,10*R*,13*S*,14*S*)-13-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-1*H*-Cyclopenta[*a*]phenanthrene-2,3,17(6*H*)-trione (63)



63

63 (0.2 mmol scale) was synthesized following ***General Procedure***. After concentration and purification by flash chromatography on silica gel eluent = petroleum ether/ ethyl acetate = 5: 1), the product **63** was obtained in 27% yield (15.5 mg, white solid).

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.35 (t, *J* = 8.3 Hz, 2H), 5.75 (s, 1H), 2.44 (d, *J* = 17.2 Hz, 2H), 2.34 (d, *J* = 5.7 Hz, 3H), 2.20 (d, *J* = 8.8 Hz, 1H), 2.06 (dd, *J* = 16.6, 6.9 Hz, 2H), 1.79 (d, *J* = 13.3 Hz, 1H), 1.63 (d, *J* = 26.7 Hz, 2H), 1.45 (t, *J* = 8.7 Hz, 2H), 1.31 (d, *J* = 12.8 Hz, 1H), 1.23 (s, 1H), 1.07 (d, *J* = 11.0 Hz, 1H), 0.88 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 219.56, 199.25, 159.18, 141.36, 129.19, 124.29, 48.29, 48.04, 46.08, 40.42, 37.86, 35.69, 31.44, 26.92, 24.55, 21.35, 13.76.

HRMS (FI+): Calcd. for $C_{18}H_{22}O_3$ ($[M+H]^+$): 286.1563, found: 286.1559.

7 Supplementary References

[1] B. Xu and W. Su, A tandem dehydrogenation-driven cross-coupling between cyclohexanones and primary amines for construction of benzoxazoles, *Angew. Chem. Int. Ed.*, 2022, **61**, e202203365.

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[3] H. Yin, C. Zhao, H. You, K. Lin and H. Gong, Mild ketone formation via Ni-catalyzed reductive coupling of unactivated alkyl halides with acid anhydrides, *Chem. Commun.*, 2012, **48**, 7034.

[4] G. Deng, Y. Jiang, Q. Liu, C. Liang, Z.-K. Wang, W. S. Cheung, Z.-L. Cheng, Y. Xu, Dihydropyrimidine derivatives and uses thereof in the treatment of HBV infection or of HBV-induced diseases, WO 2020001448A1, 2020.

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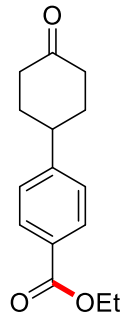
[6] C. Zheng, G. Z. Wang and R. Shang, Catalyst-free Decarboxylation and Decarboxylative Giese Additions of Alkyl Carboxylates through Photoactivation of Electron Donor-Acceptor Complex, *Adv. Syn. Catal.*, 2019, **361**, 4500.

[7] F. Wu, W. Lu, Q. Qian, Q. Ren and H. Gong, Ketone Formation via Mild Nickel-Catalyzed Reductive Coupling of Alkyl Halides with Aryl Acid Chlorides, *Org. Lett.*, 2012, **14**, 3044.

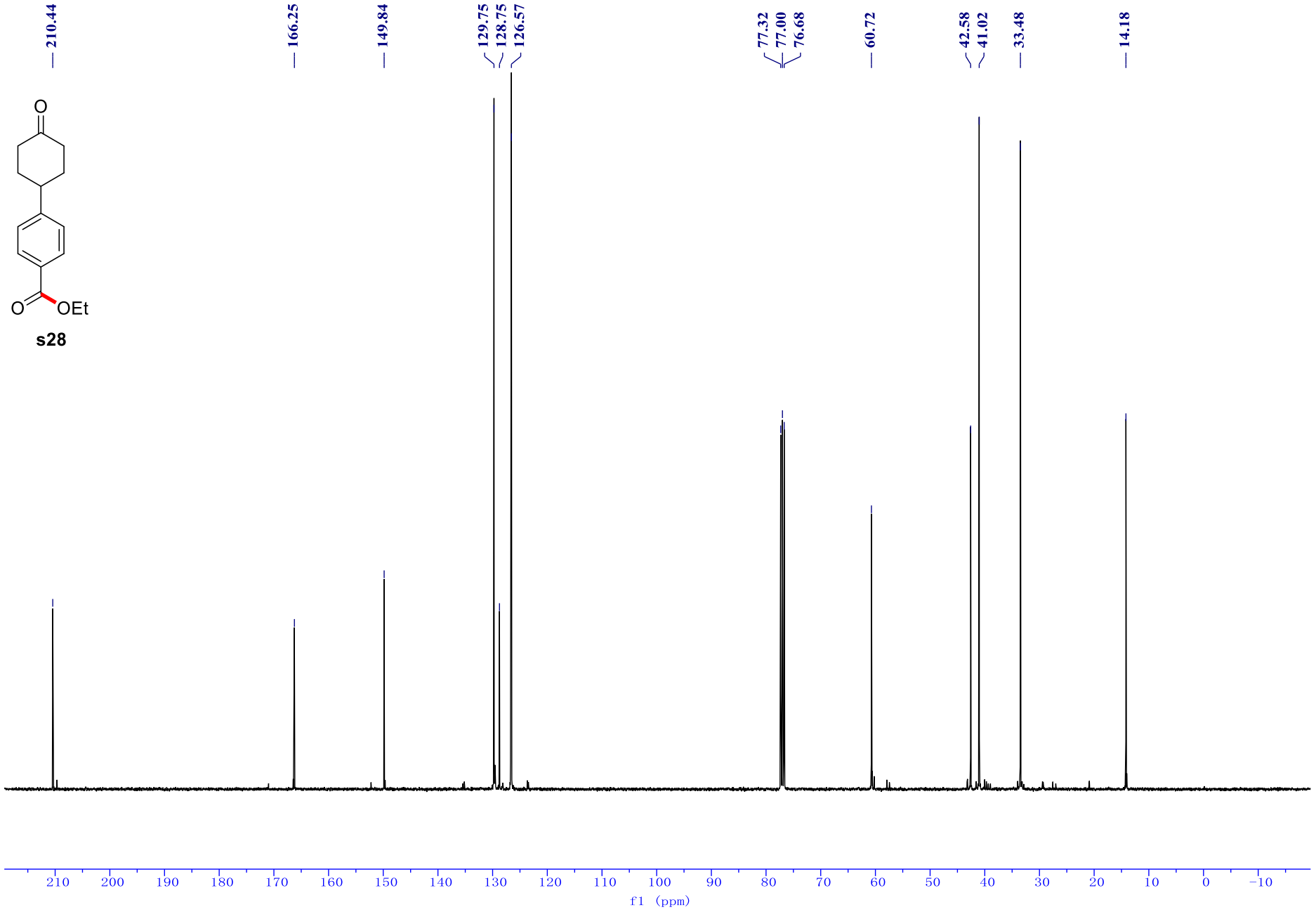
[8] W. Lu, Z. Liang, Y. Zhang, F. Wu, Q. Qian and H. Gong, Gram-Scale Ketone Synthesis by Direct Reductive Coupling of Alkyl Iodides with Acid Chlorides, *Synthesis*, 2013, **45**, 2234.

[9] Z. Zhang, B. Xiao, Q. Chen and X. Y. Lian, *J. Nat. Prod.*, 2010, **73**, 252.

8. NMR Spectra of Products



s28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126.57
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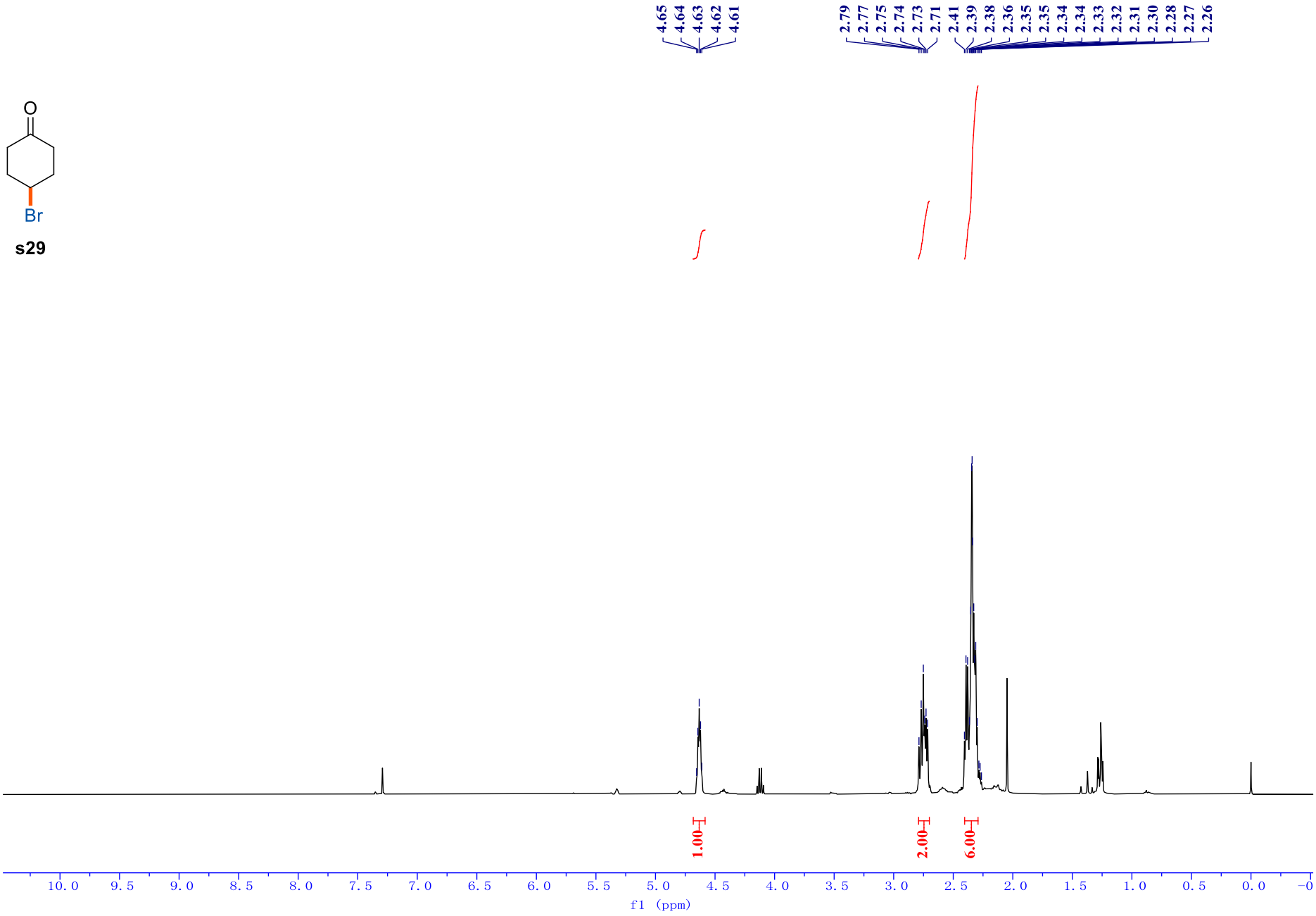
77.00
76.68
60.72
42.58
41.02
33.48
14.18
O
O
OEt
s28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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2.31
2.30
2.28
2.27
2.26
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Br
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2.00
6.00
10.0
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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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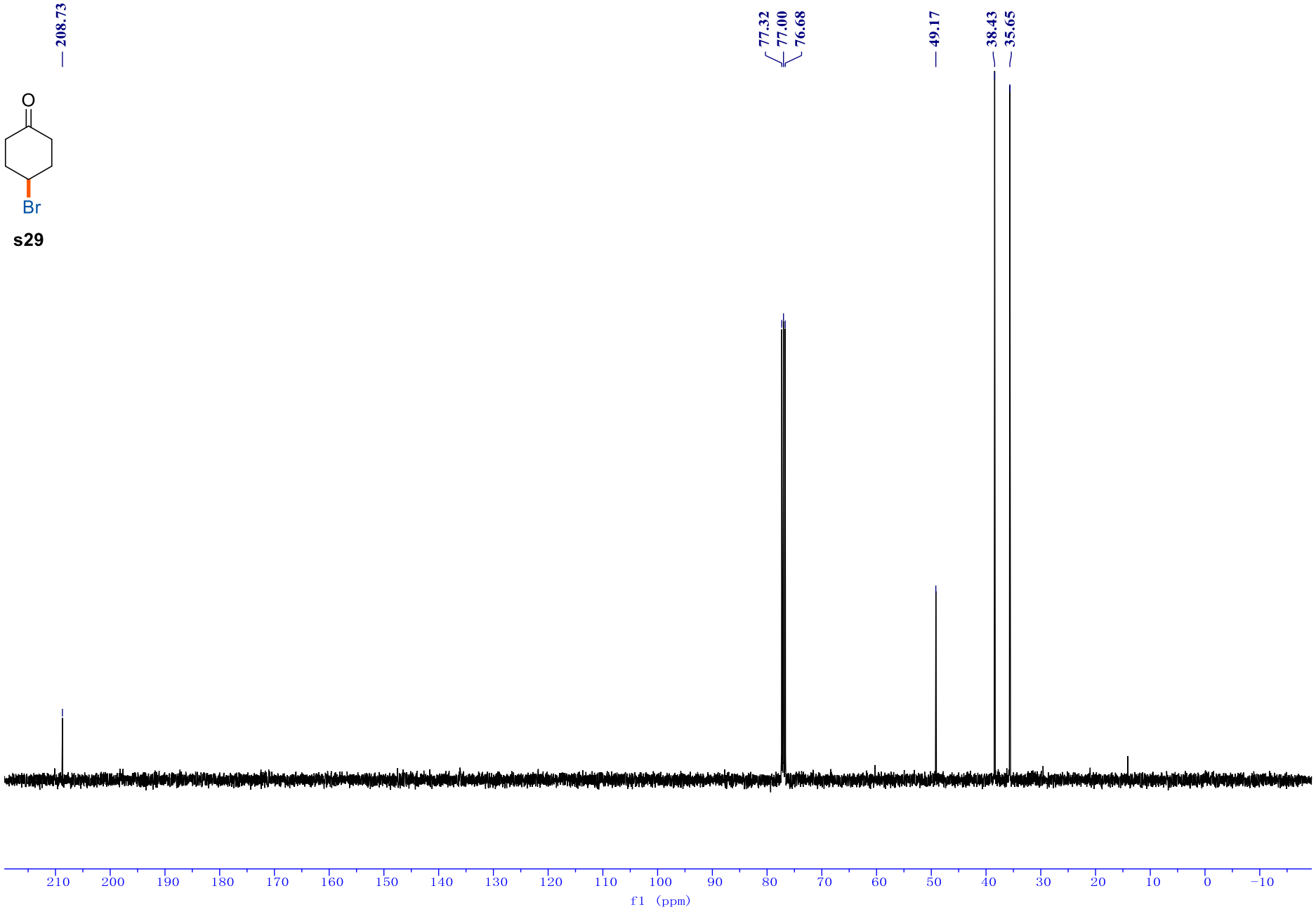
s29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120
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100
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80
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40
30
20
10
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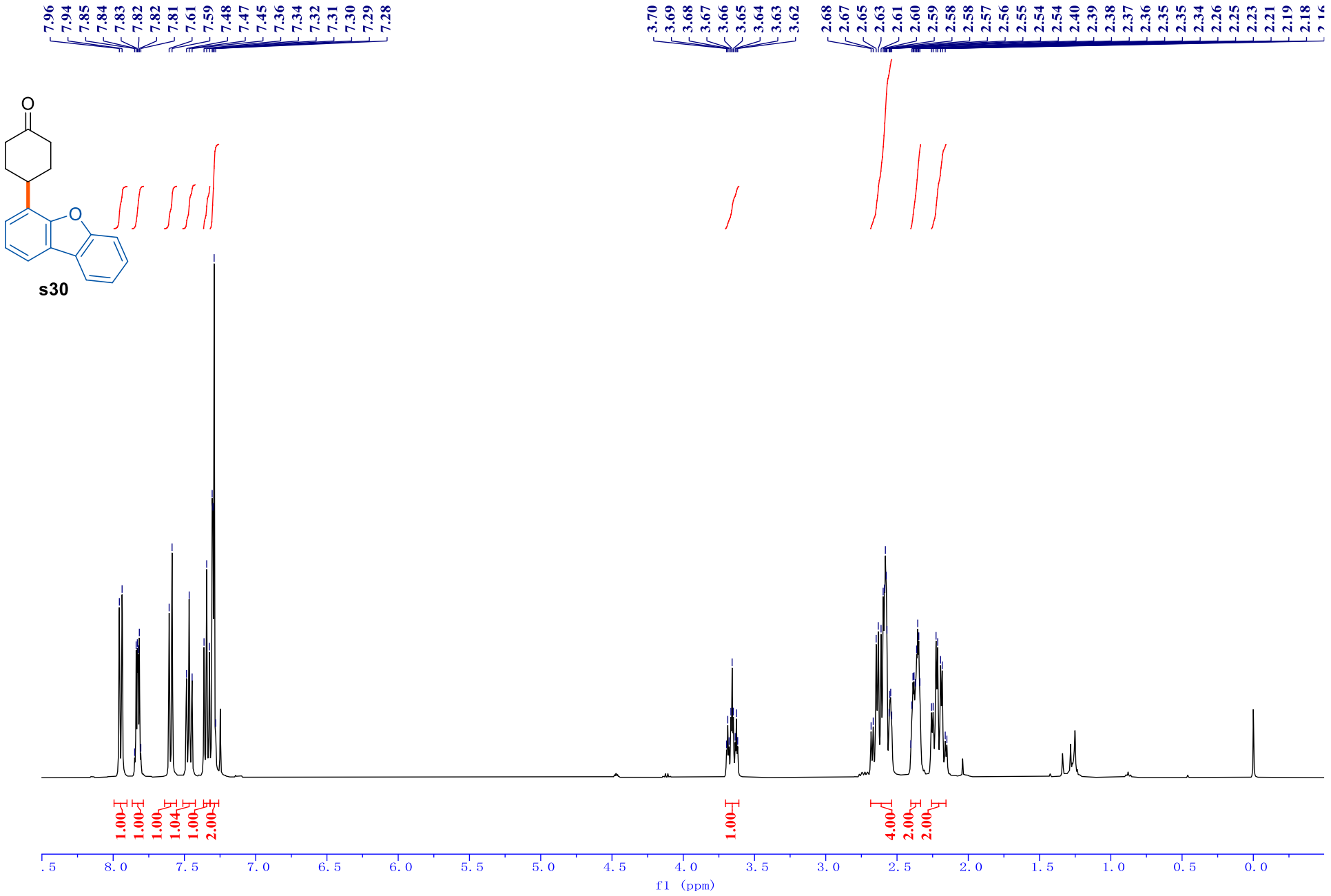
−10
f1 (ppm)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2.25
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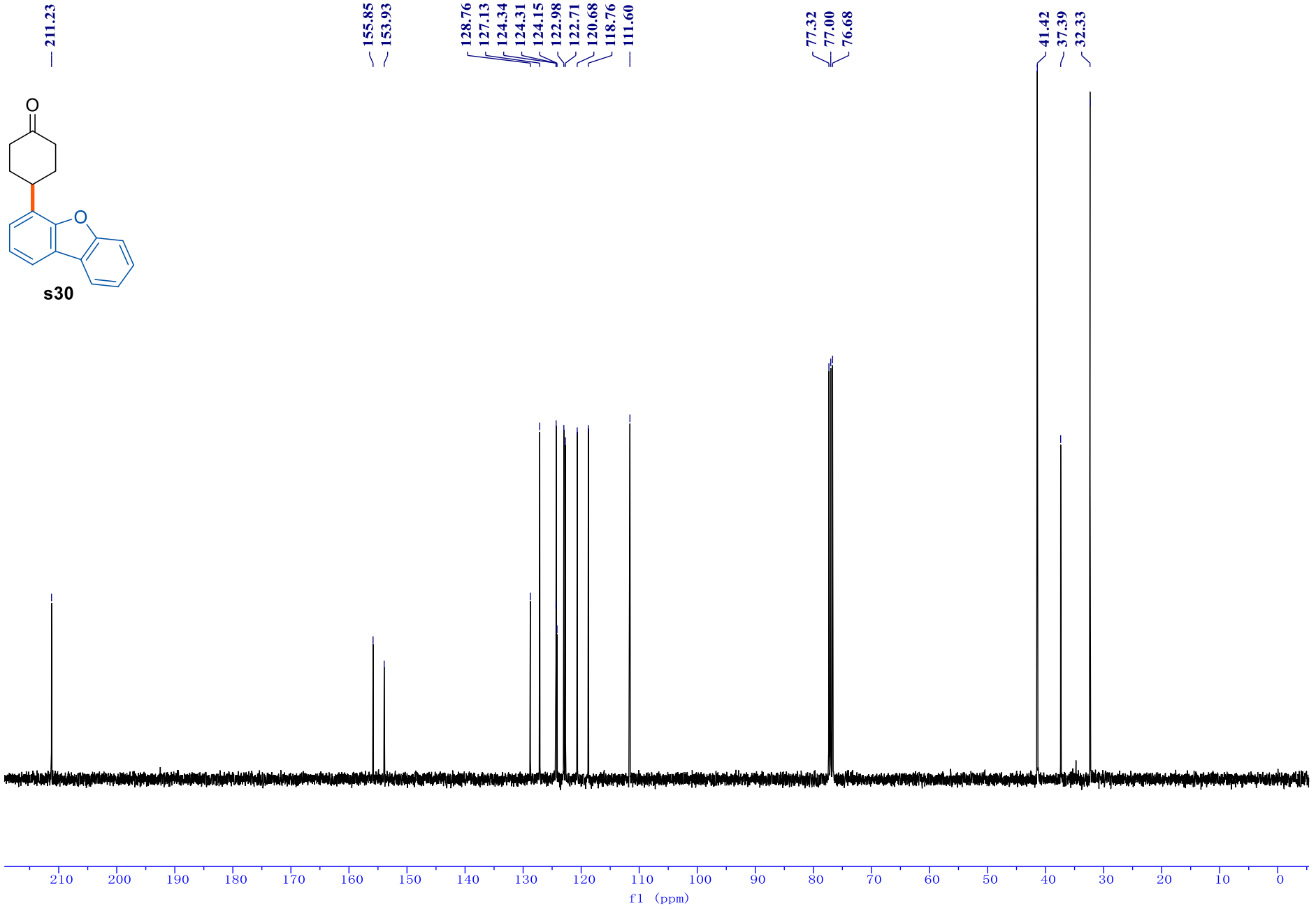
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s30
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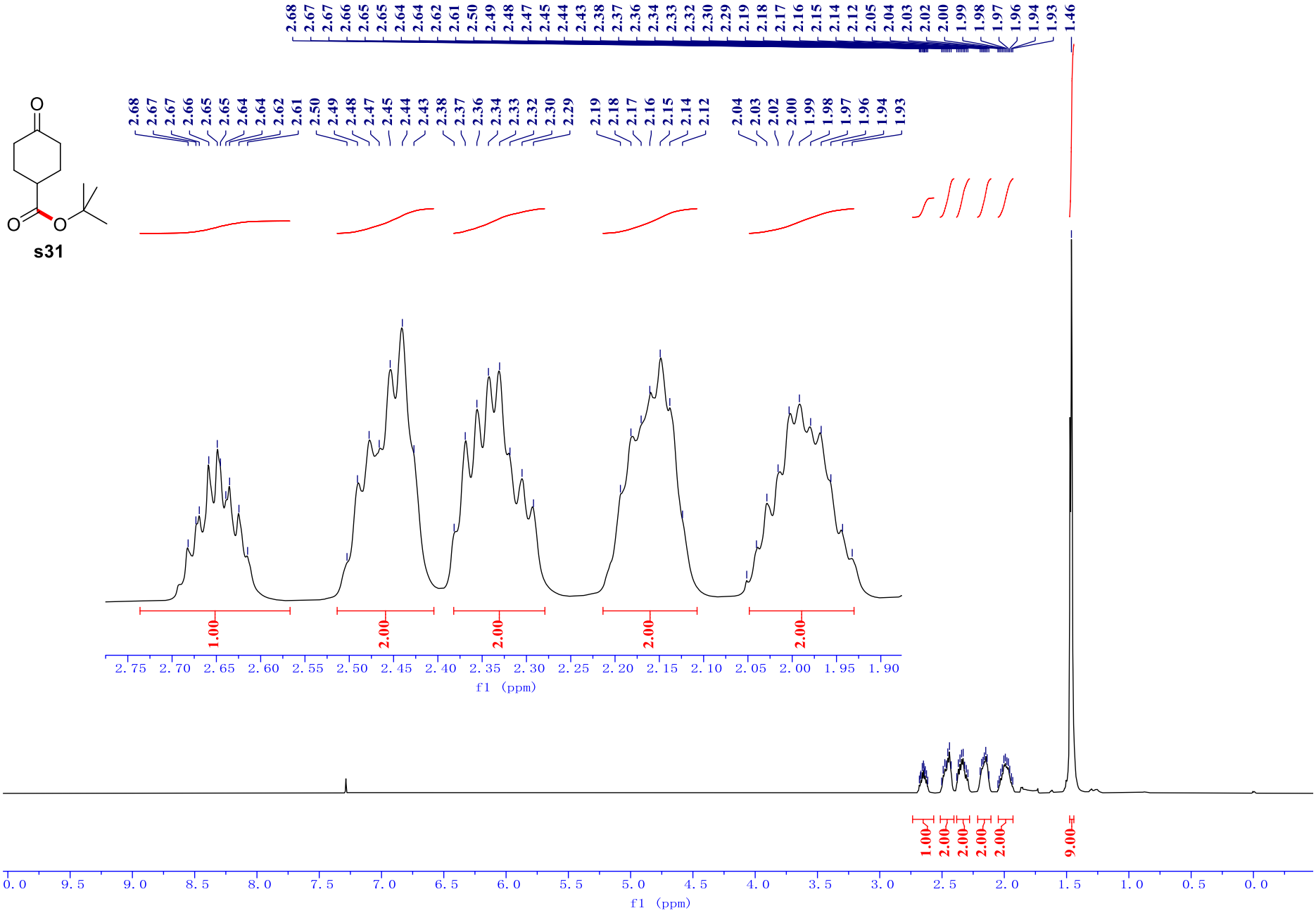
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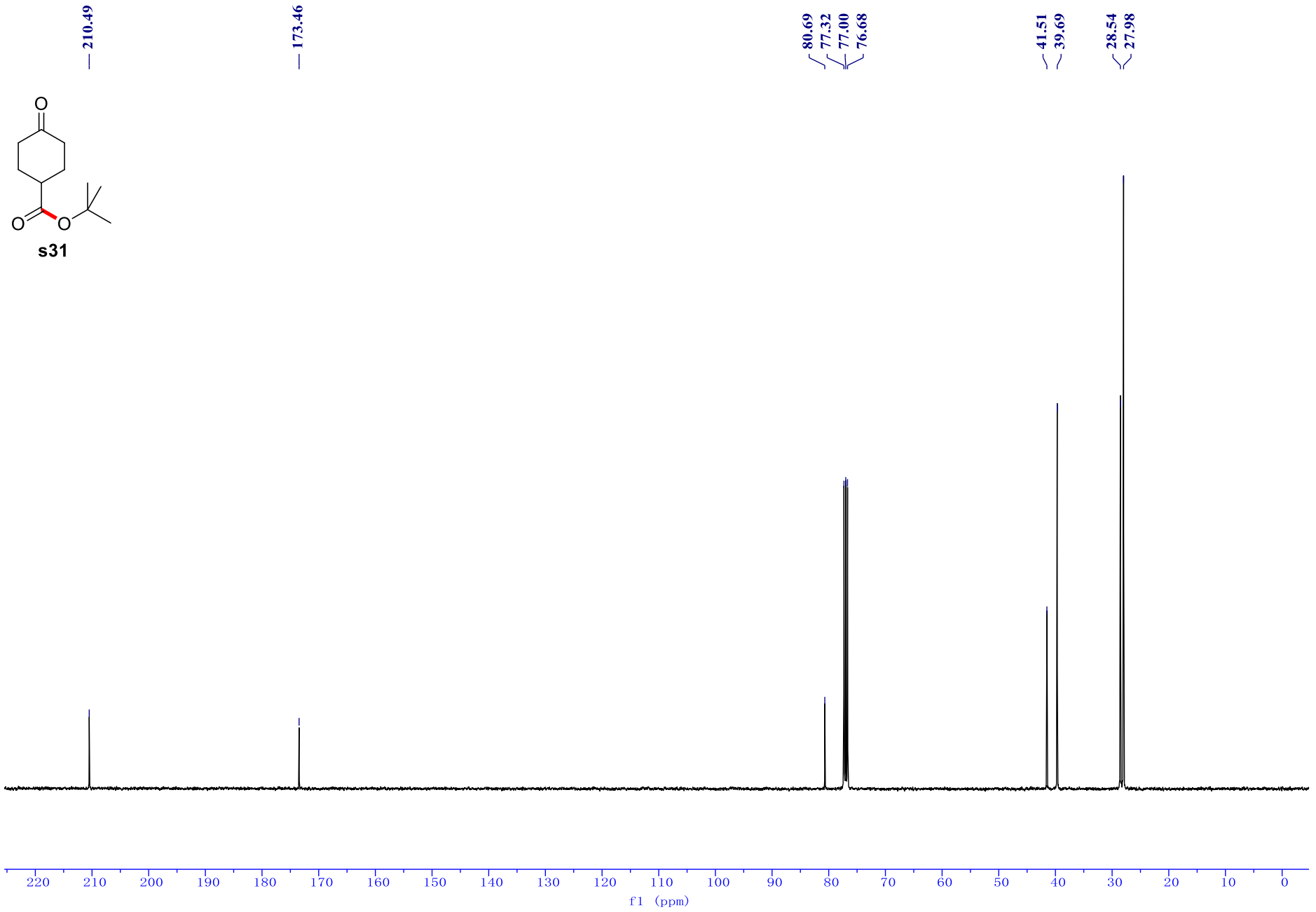
f1 (ppm)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40
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20
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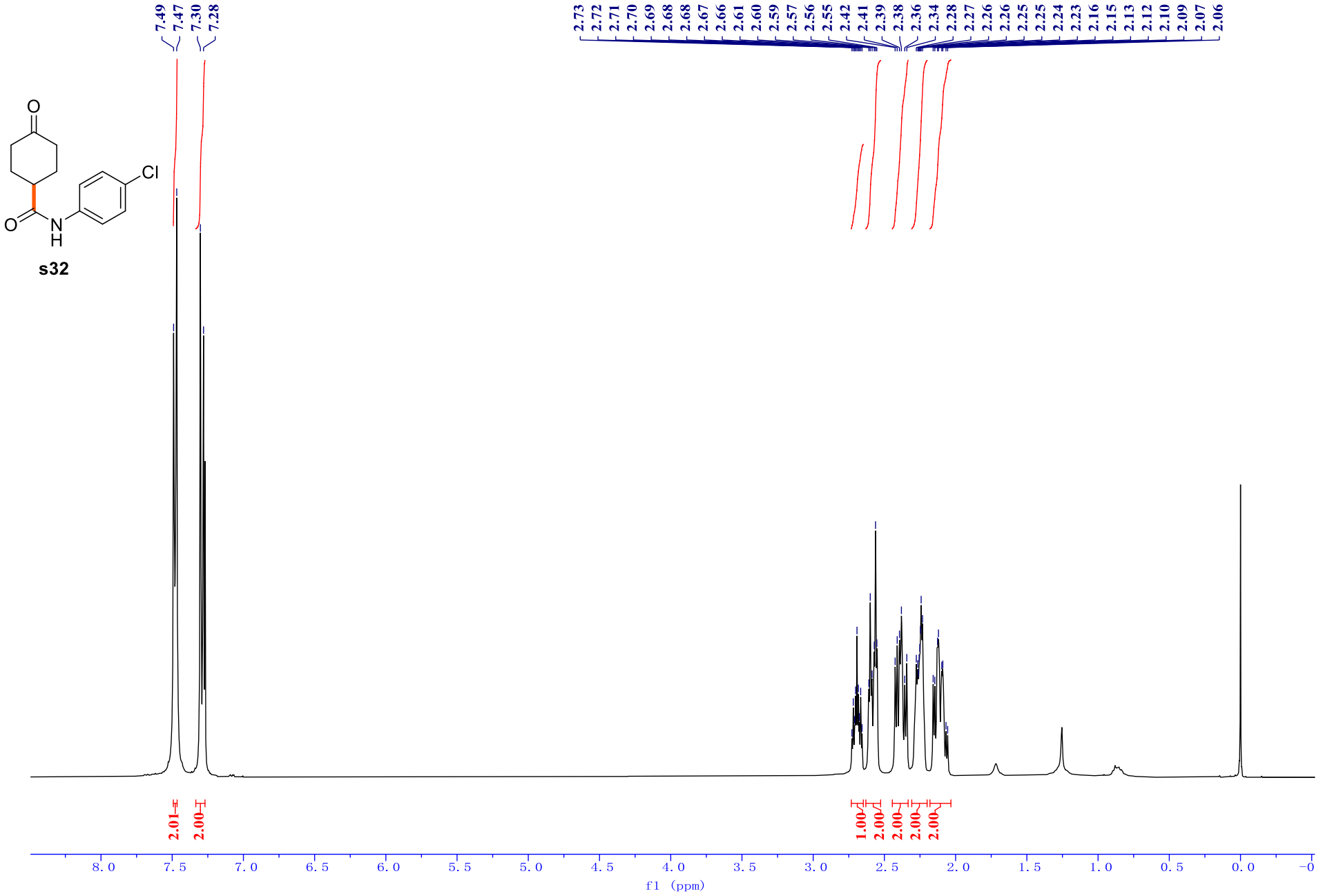
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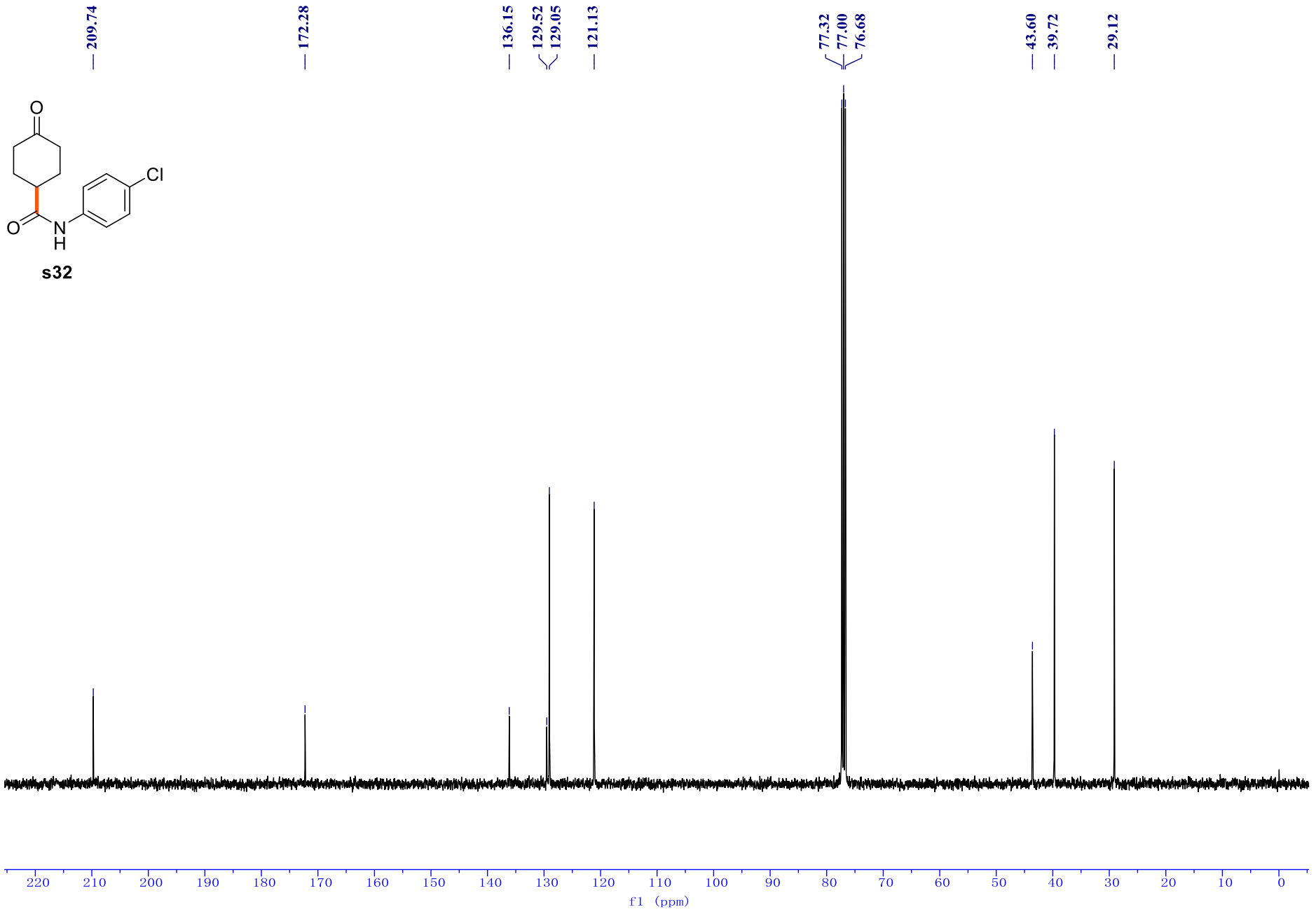
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O
N
H
Cl
s32
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200
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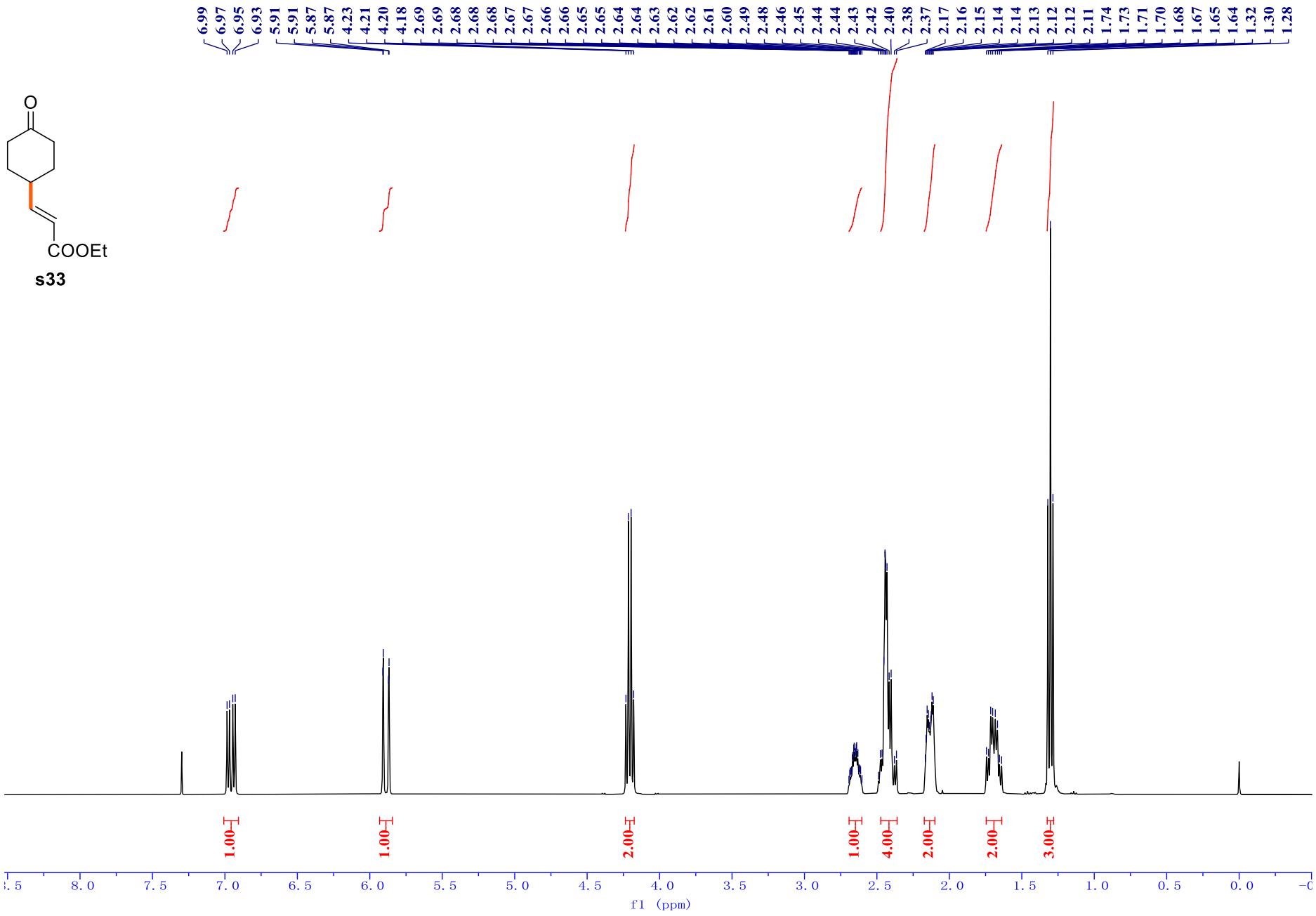
20
10
0
f1 (ppm)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s33
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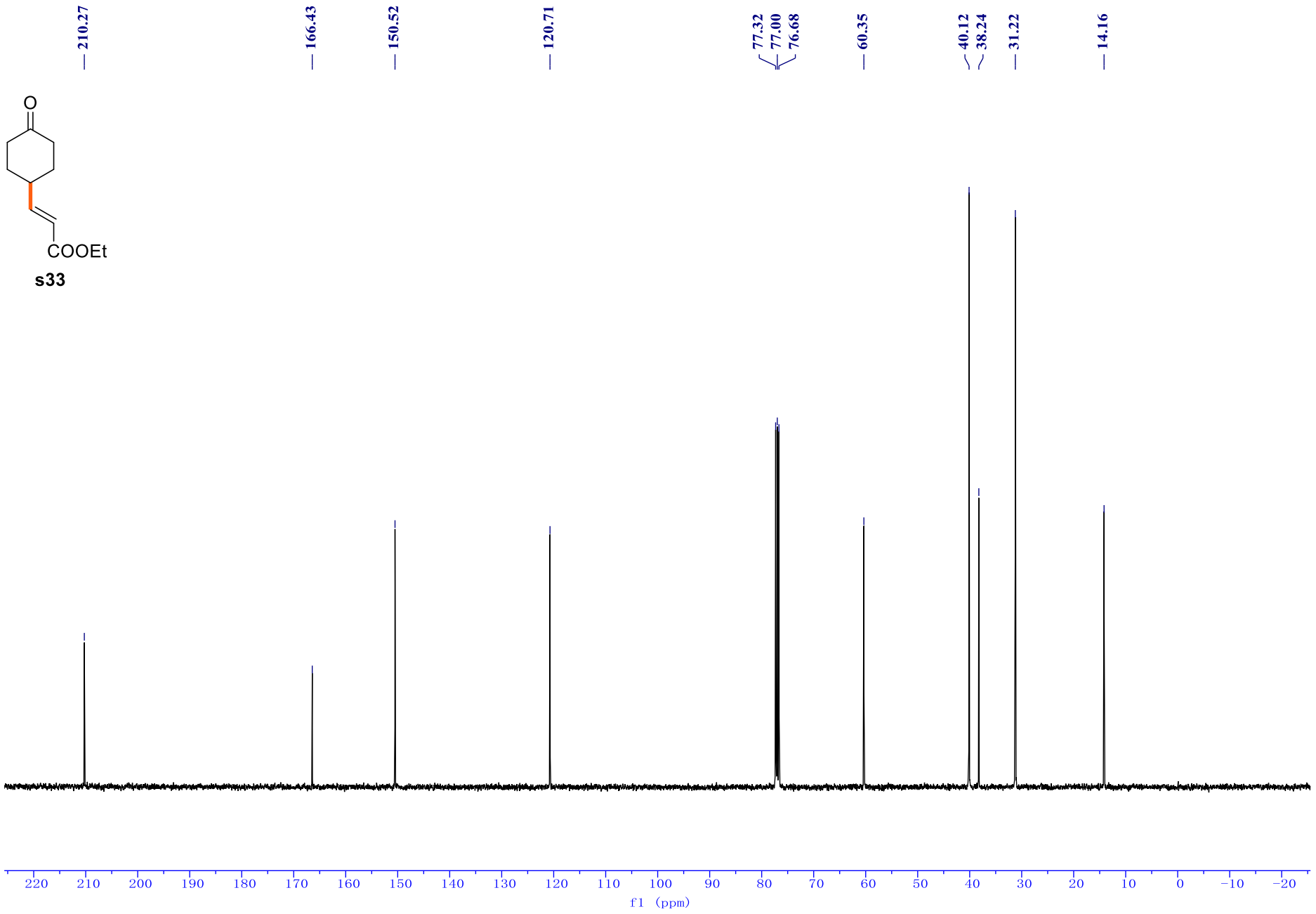
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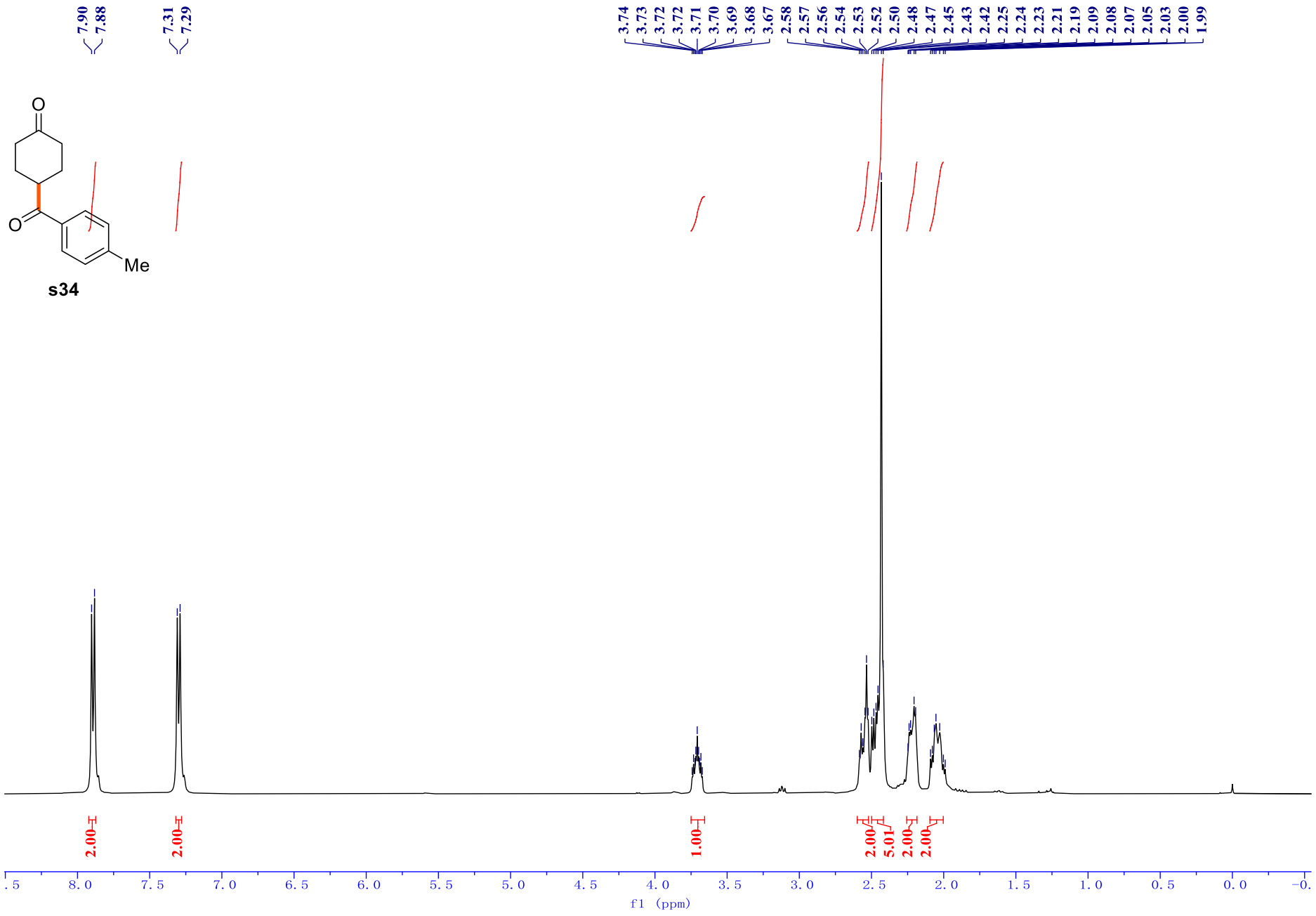
f1 (ppm)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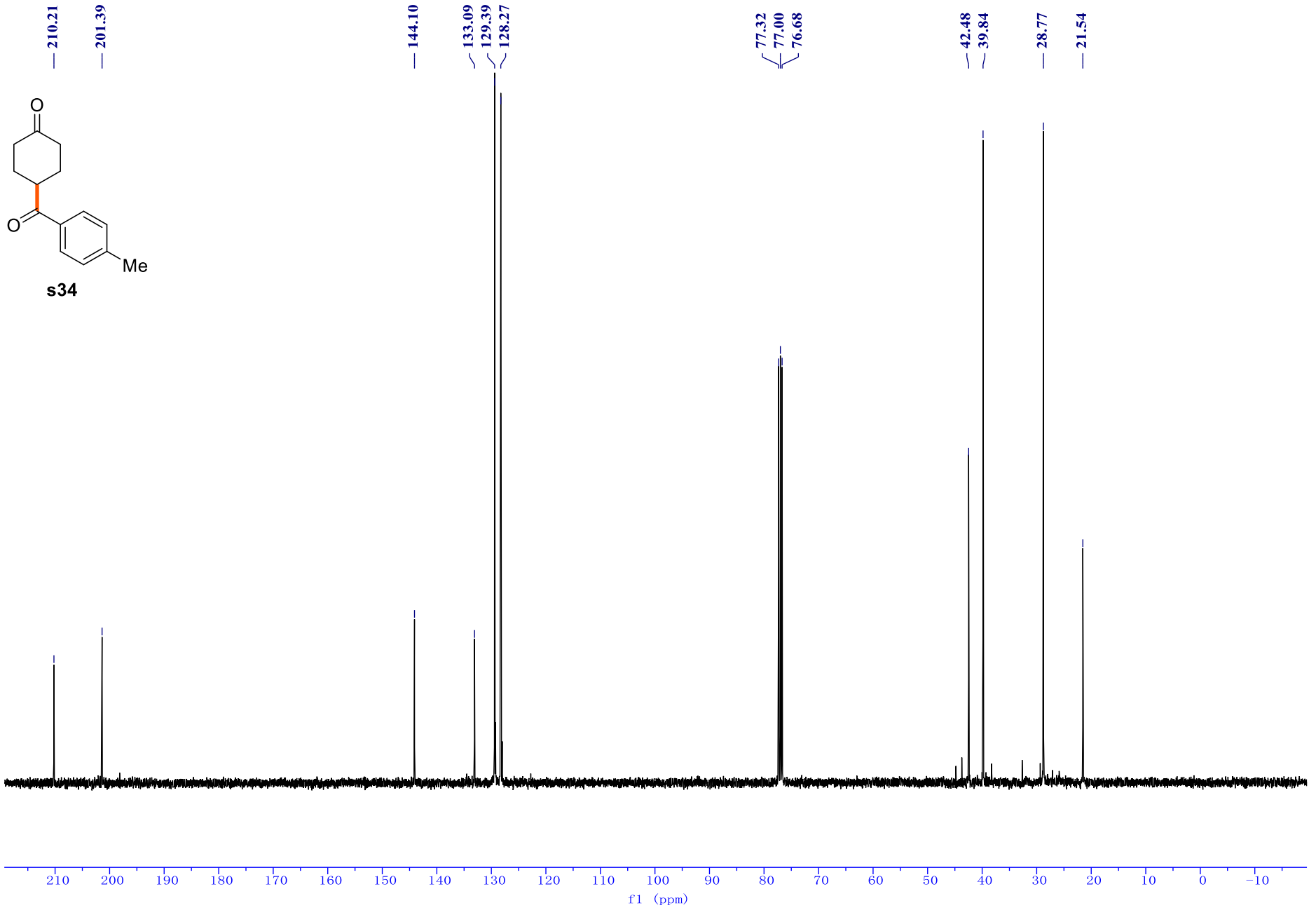
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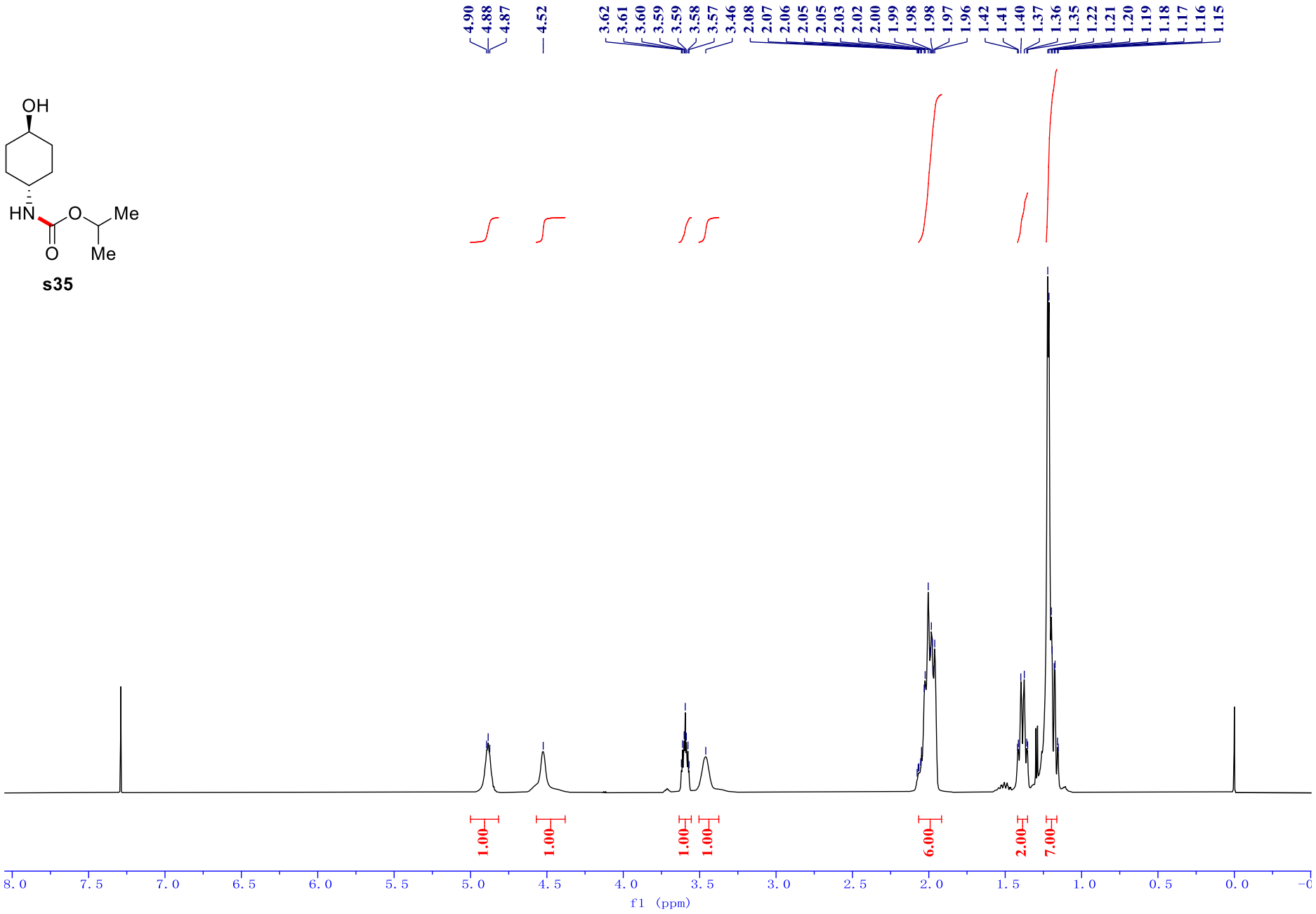
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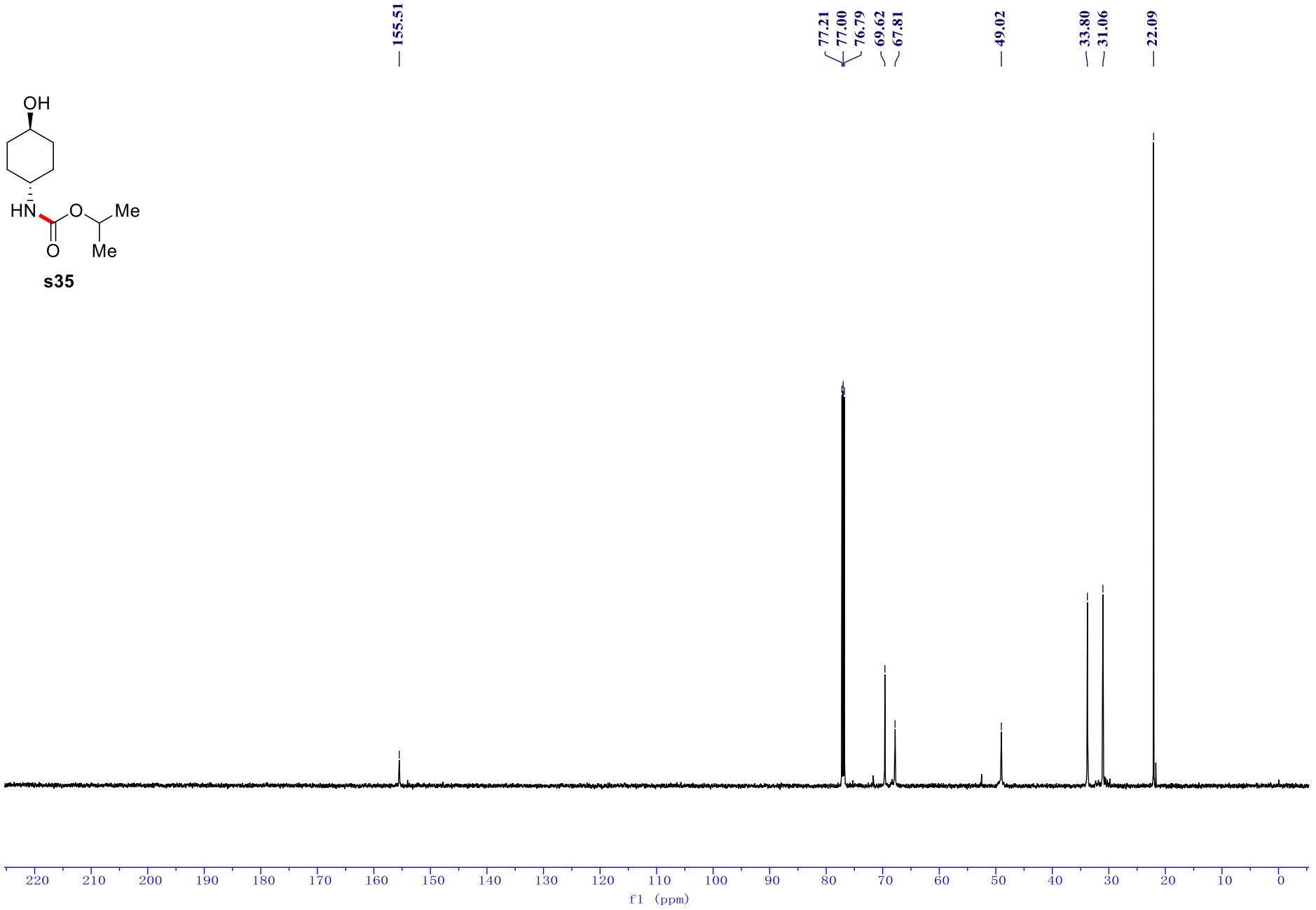
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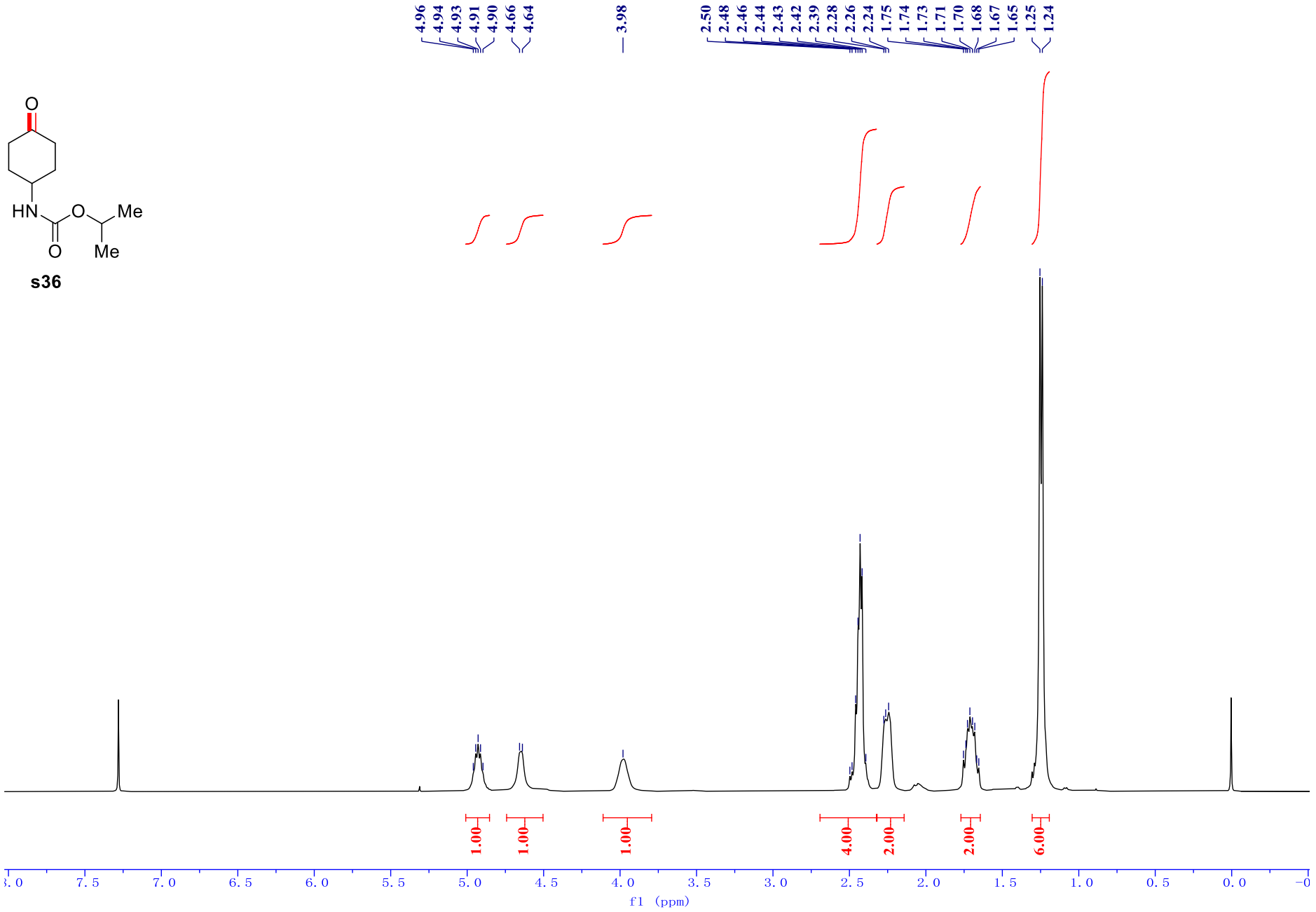
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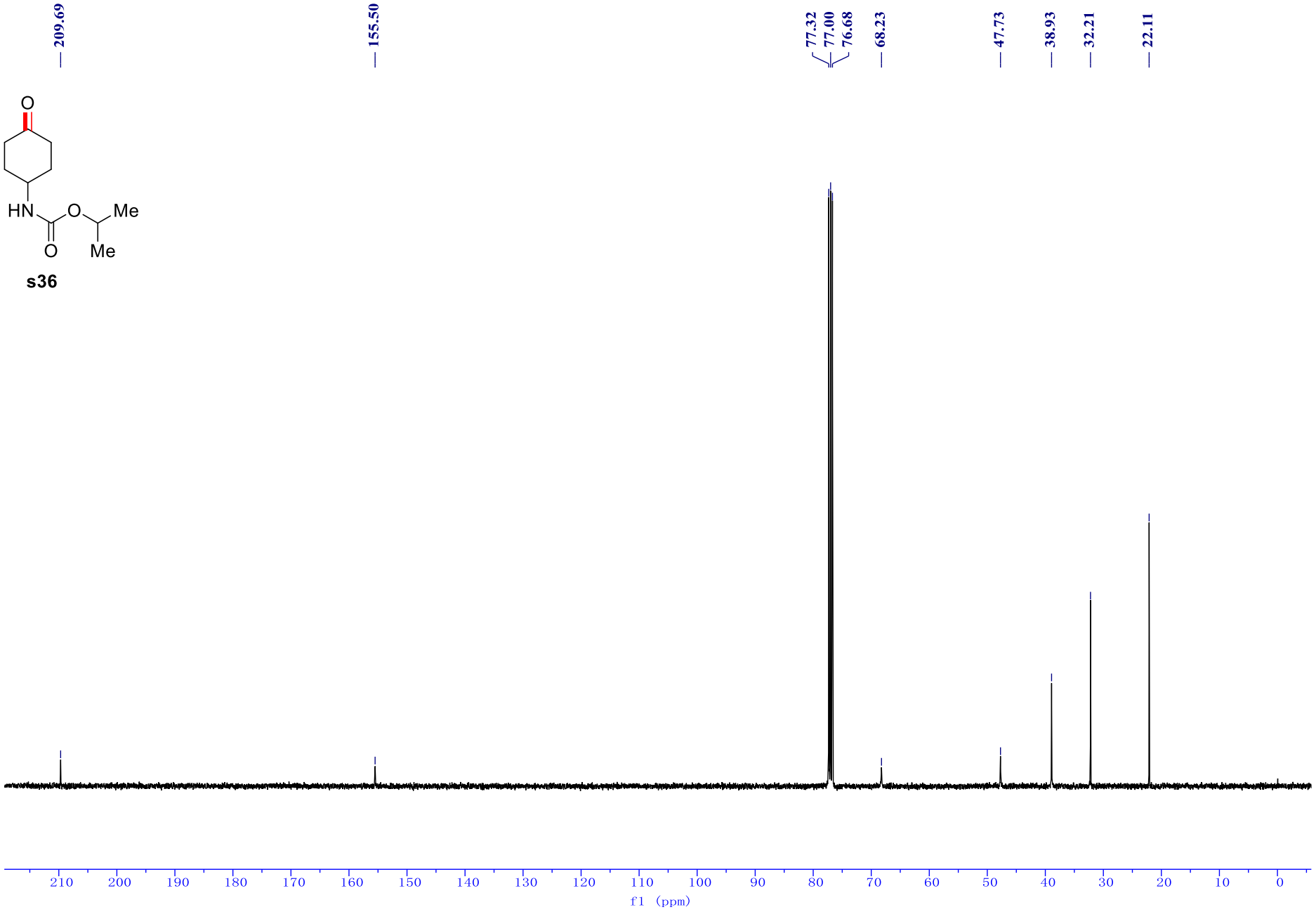
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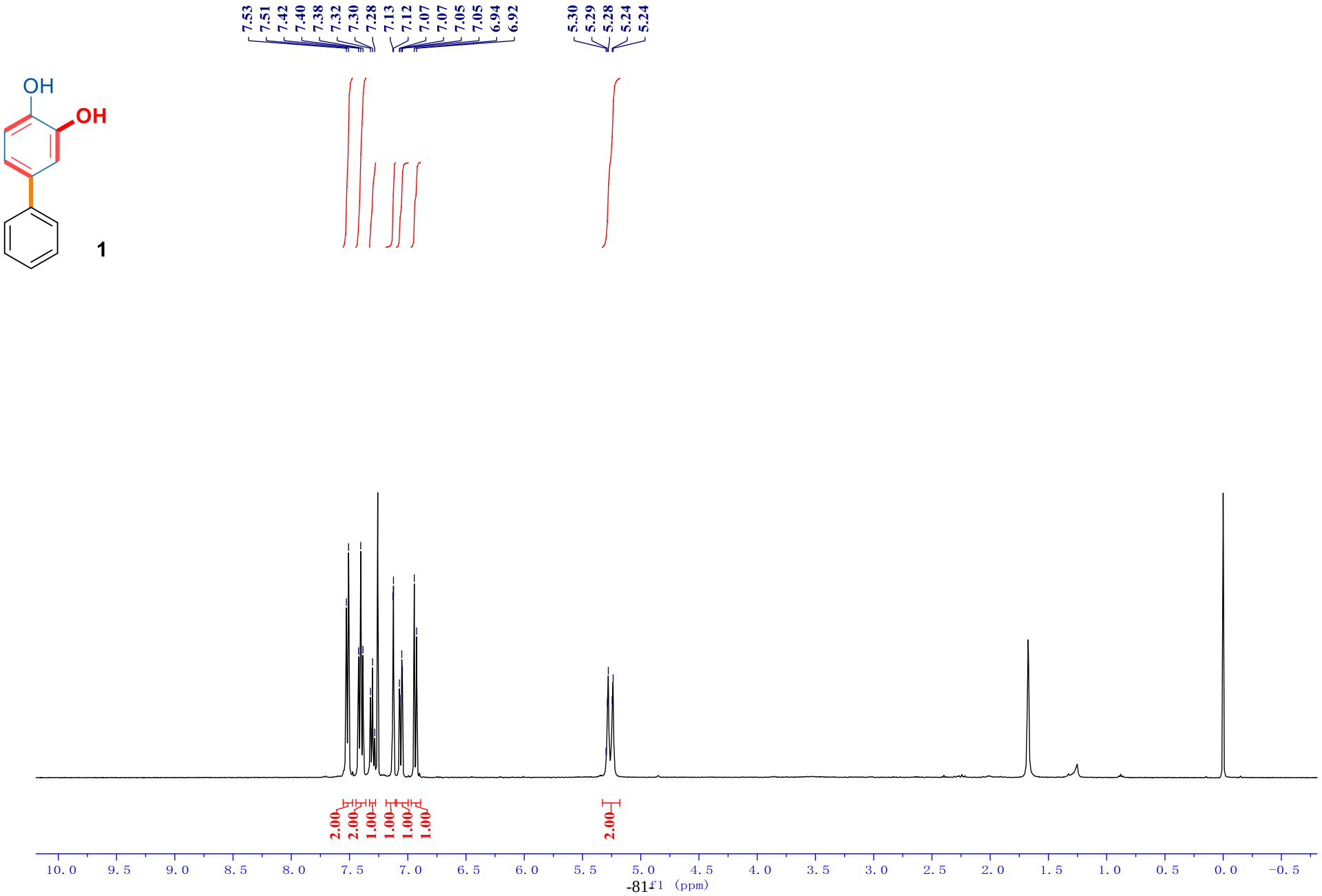
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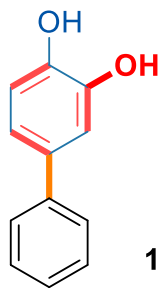
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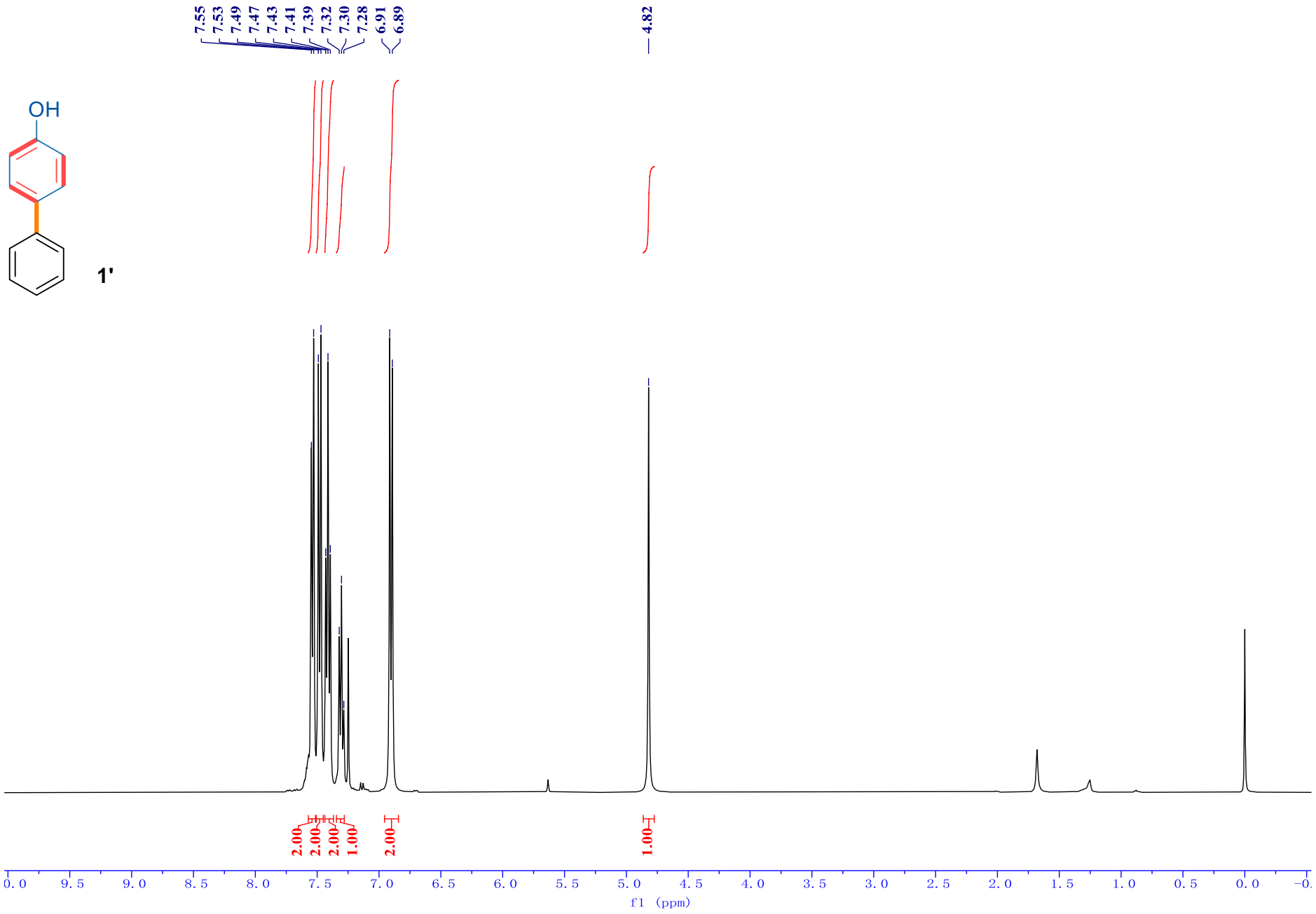
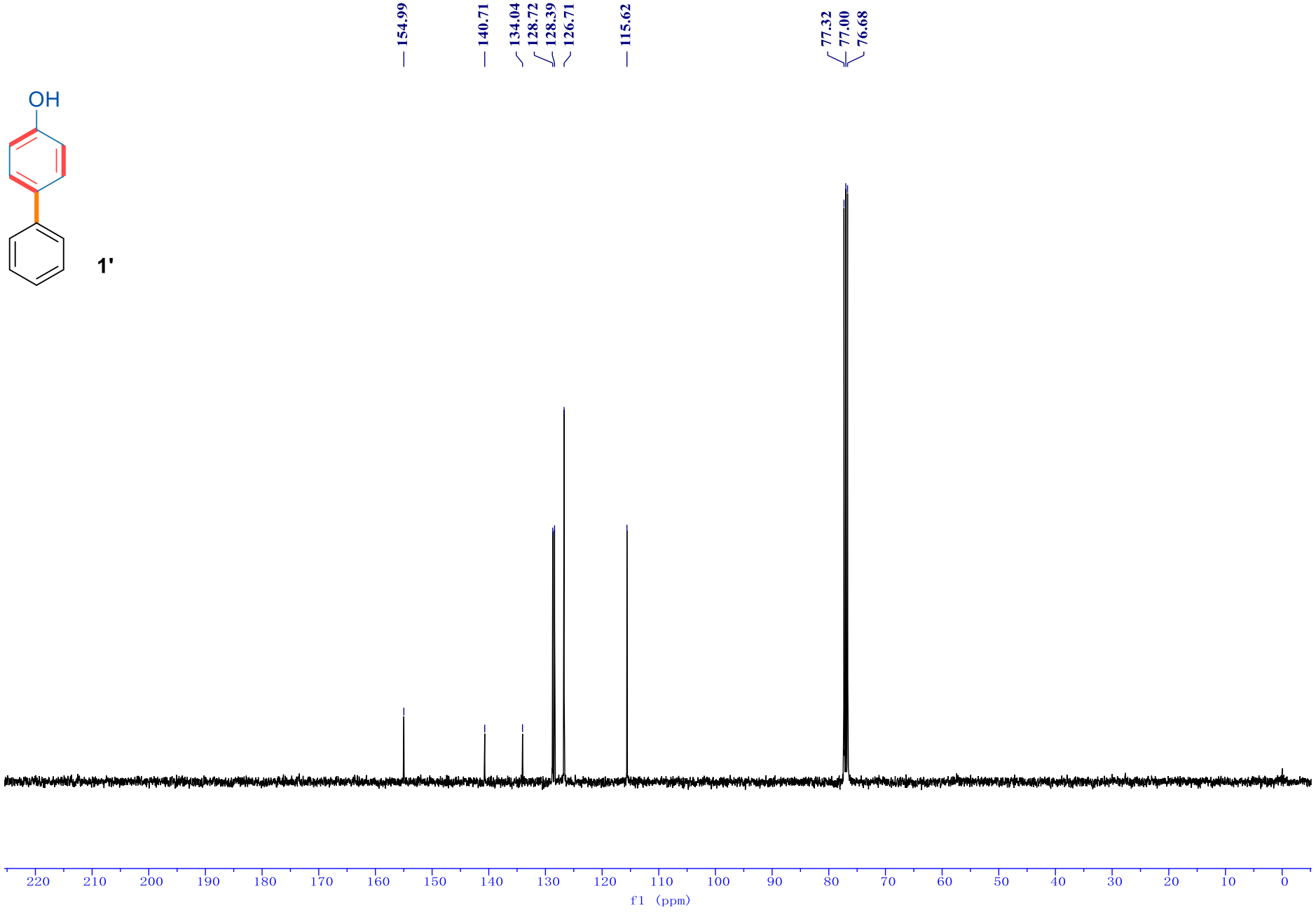
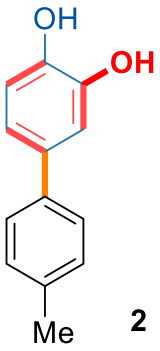
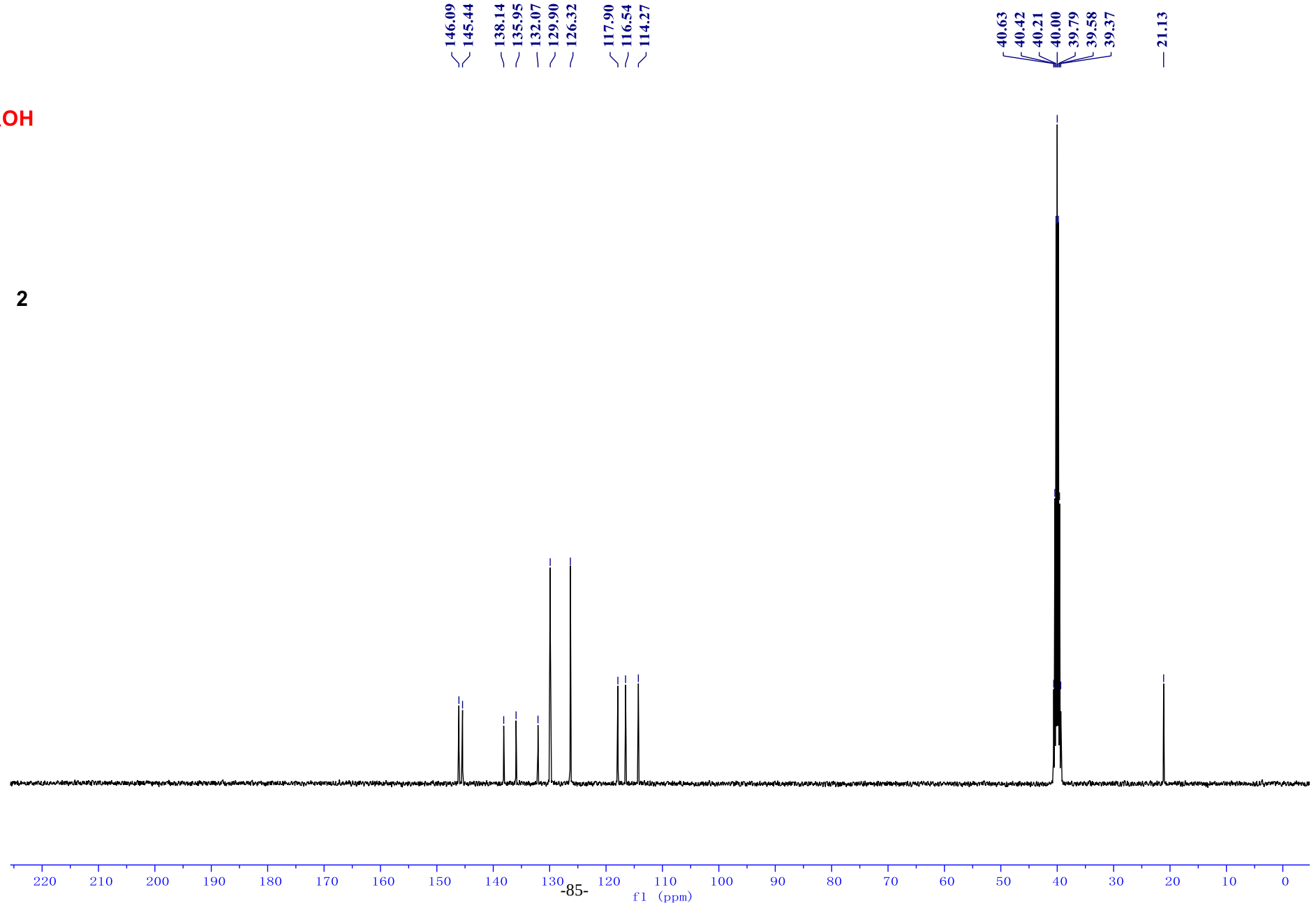
50
40
30
20
10
0
f1 (ppm)

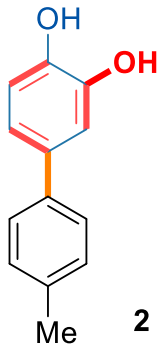

7.55
7.53
7.49
7.47
7.43
7.41
7.39
7.32
7.30
7.28
6.91
6.89
4.82
OH
1'
2.00
2.00
2.00
1.00
2.00
1.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


154.99
140.71
134.04
128.72
128.39
126.71
115.62
77.32
77.00
76.68
OH
1'
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)

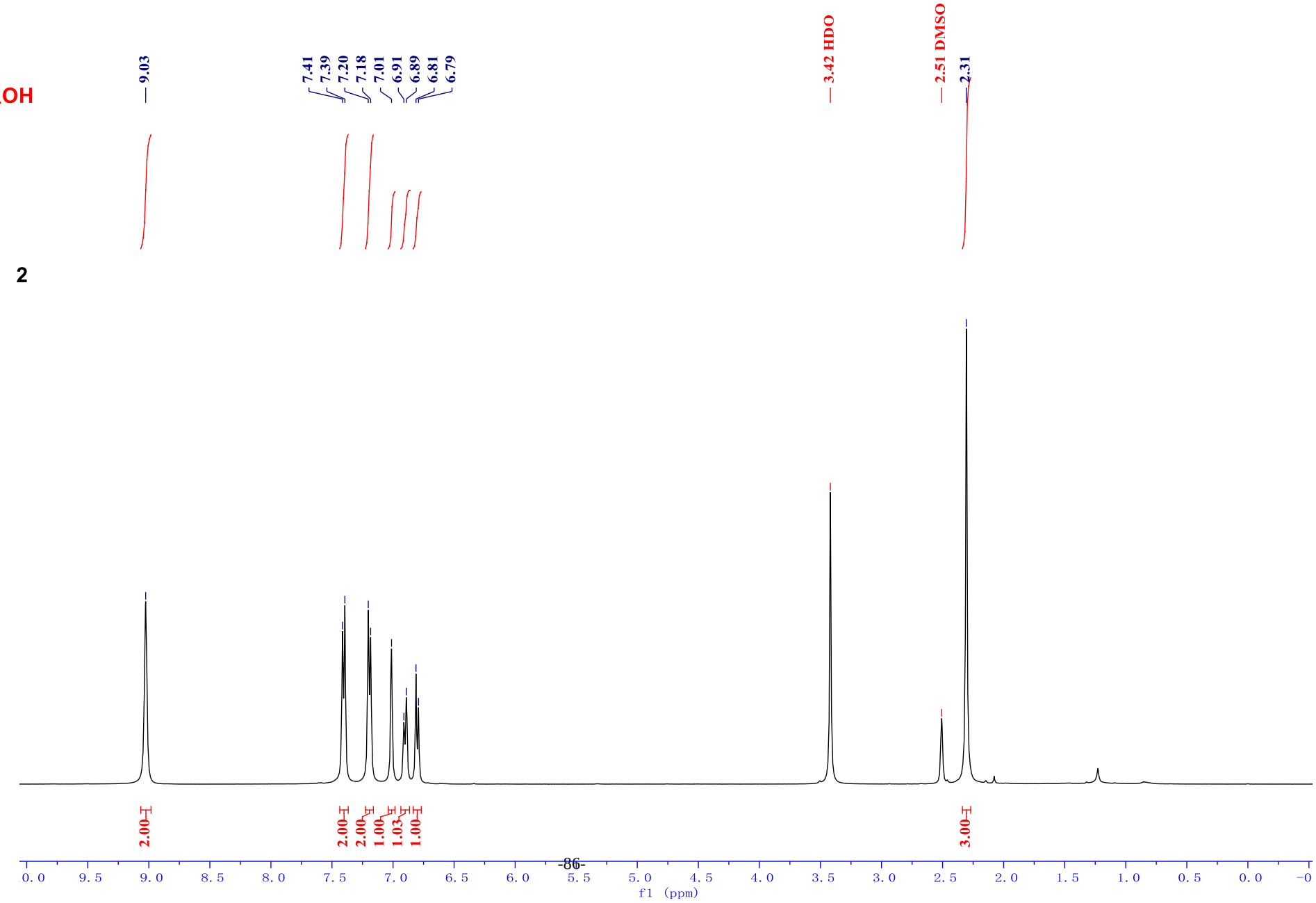

OH
OH
Me

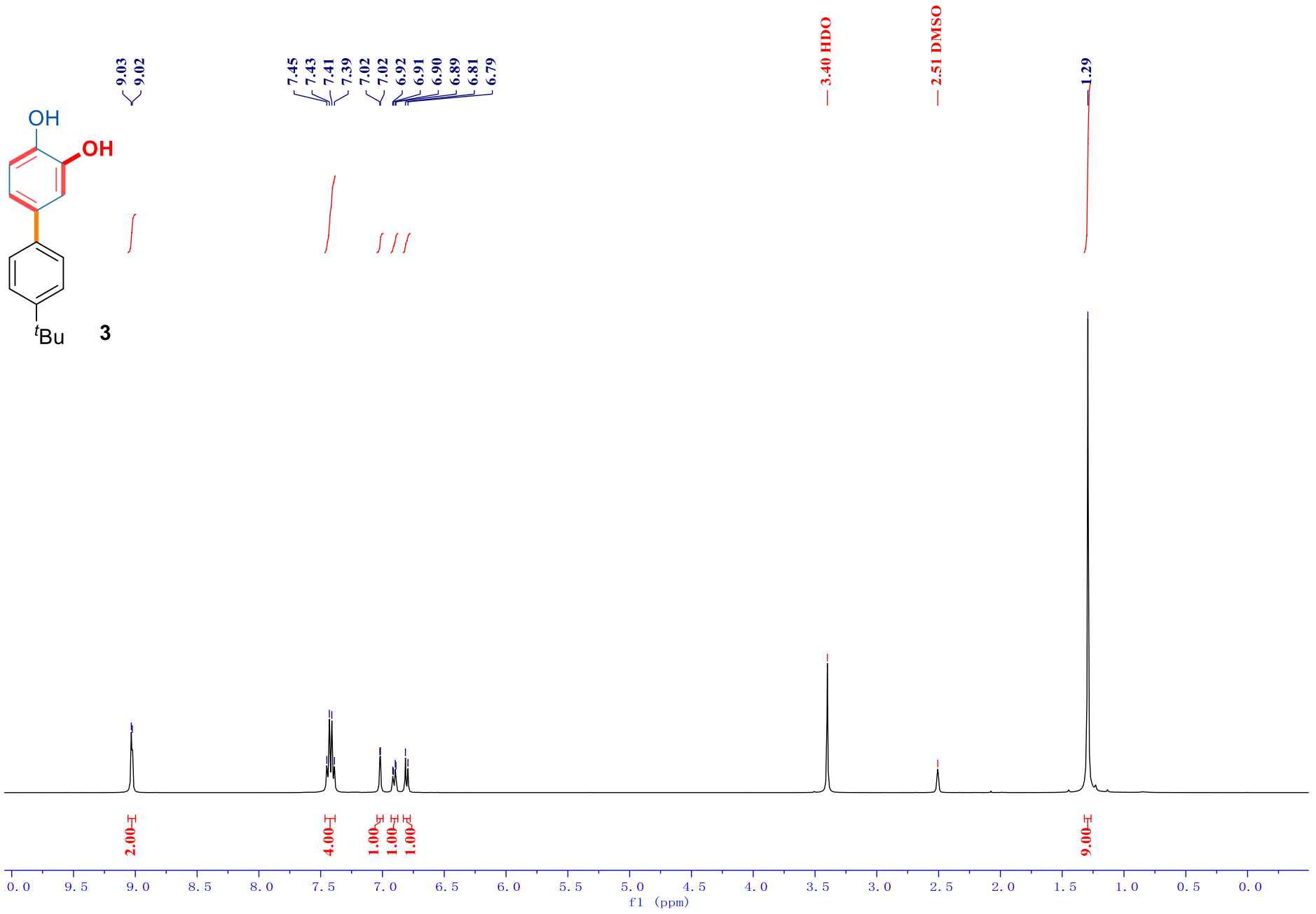
2

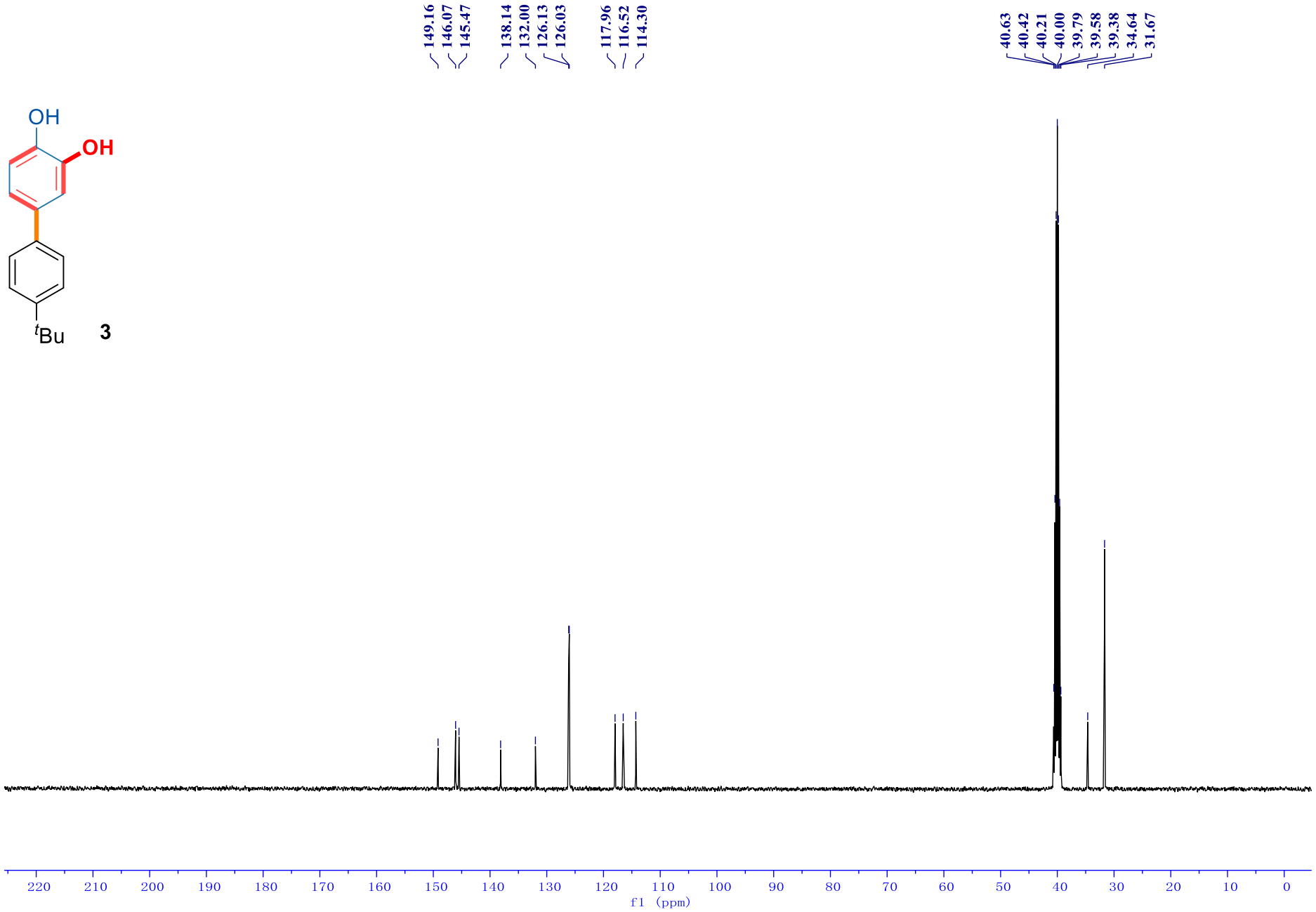

146.09
145.44
138.14
135.95
132.07
129.90
126.32
117.90
116.54
114.27
40.63
40.42
40.21
40.00
39.79
39.58
39.37
21.13
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

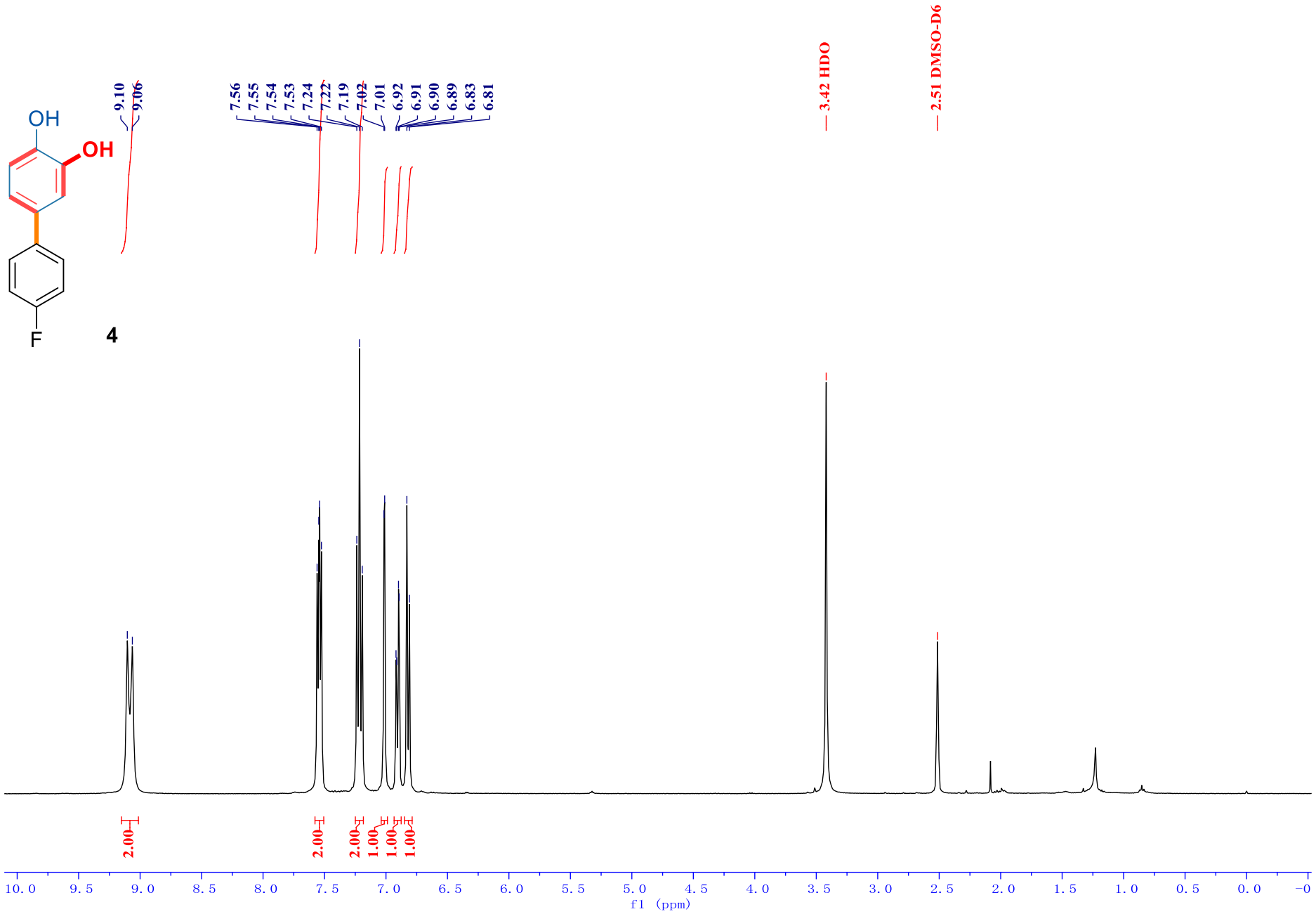

OH
OH
Me

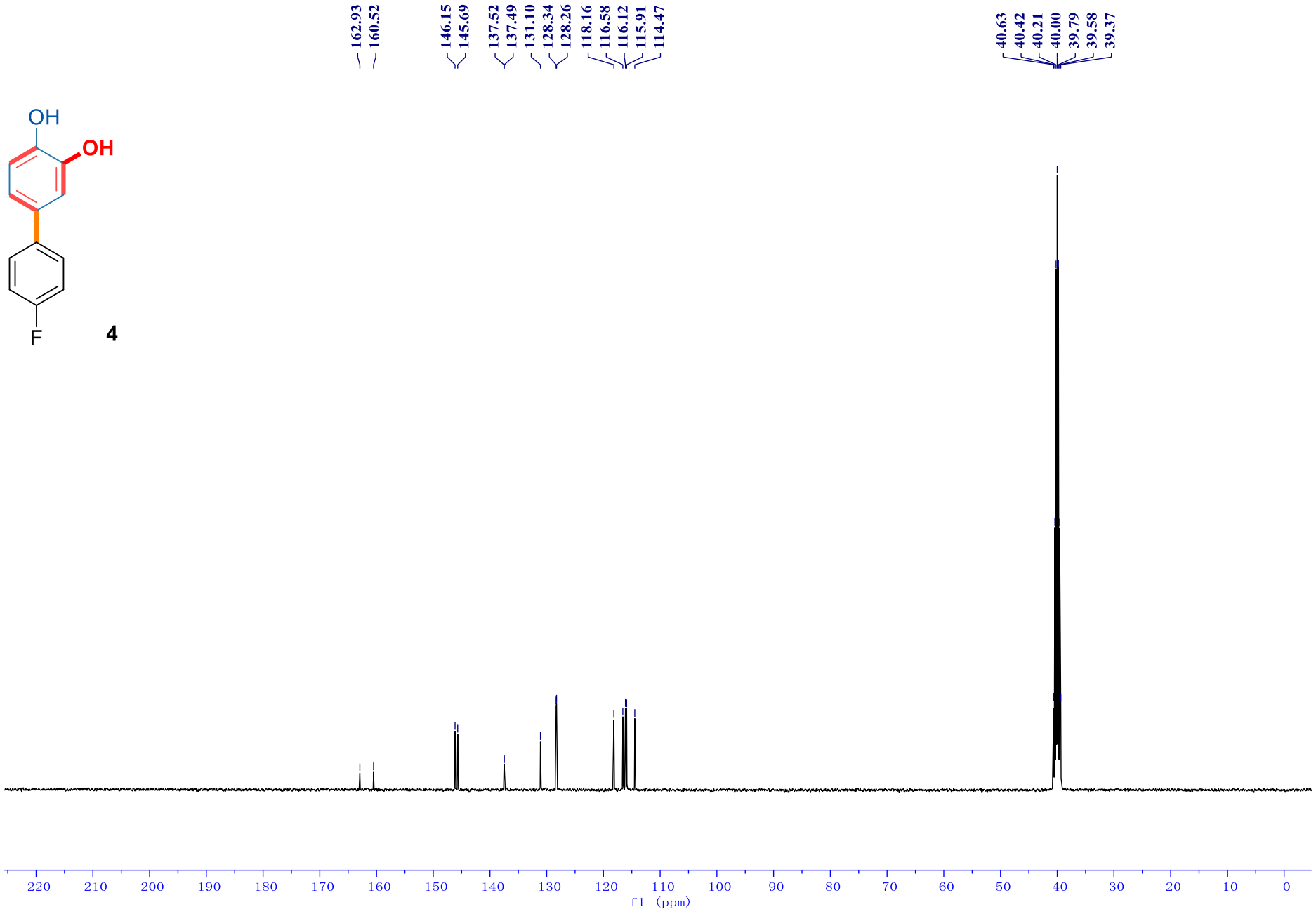
2

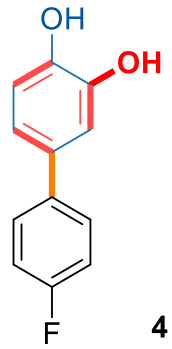

9.03
7.41
7.39
7.20
7.18
7.01
6.91
6.89
6.81
6.79
3.42 HDO
2.51 DMSO
2.31
2.00
2.00
2.00
1.00
1.03
1.00
3.00
f1 (ppm)


9.03
9.02
7.45
7.43
7.41
7.39
7.02
7.02
6.92
6.91
6.90
6.89
6.81
6.79
3.40 HDO
2.51 DMSO
1.29
OH
OH
tBu
3
2.00
4.00
1.00
1.00
1.00
9.00
f1 (ppm)


149.16
146.07
145.47
138.14
132.00
126.13
126.03
117.96
116.52
114.30
40.63
40.42
40.21
40.00
39.79
39.58
39.38
34.64
31.67
OH
OH
tBu
3
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)

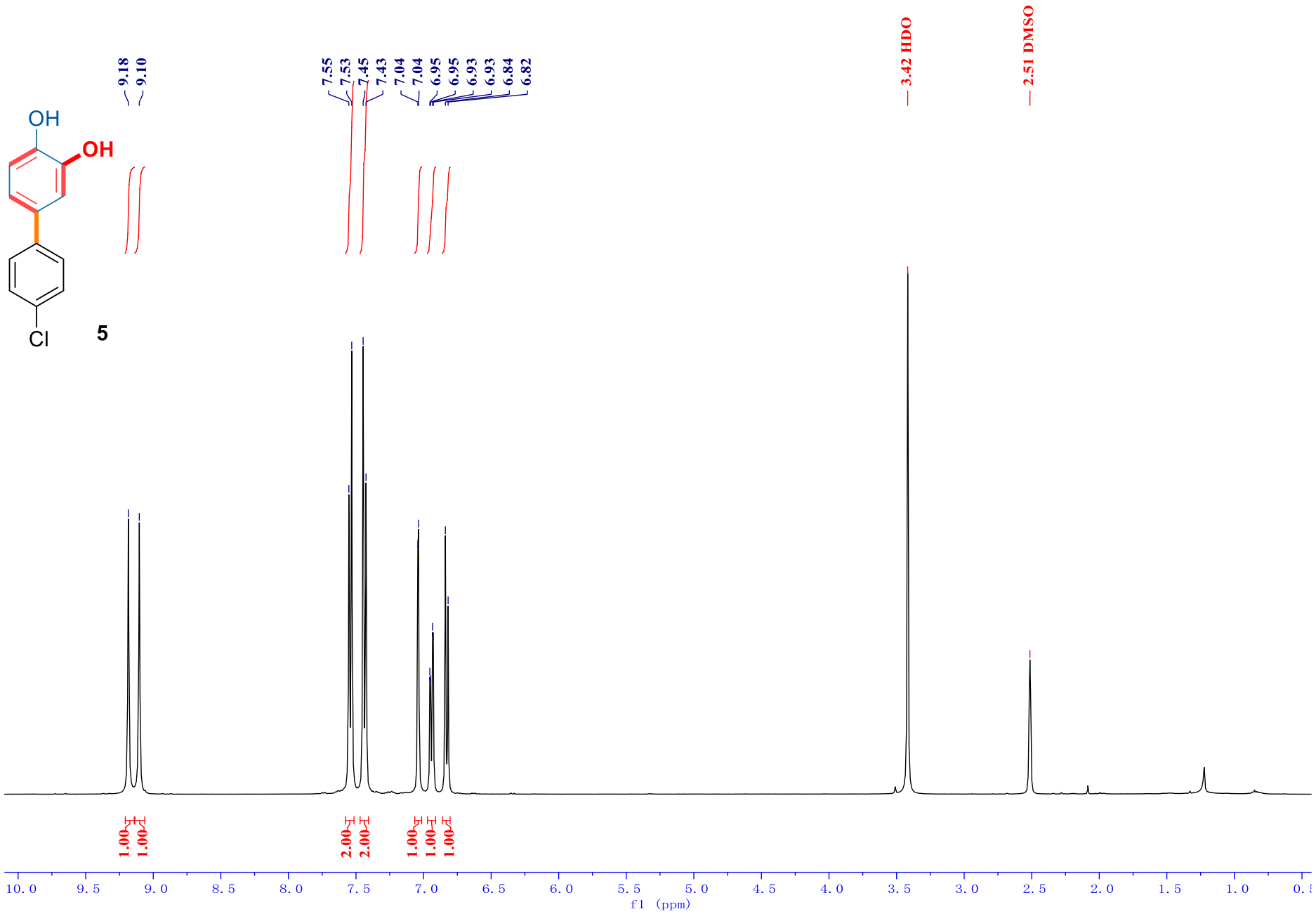

OH
OH
F
4
9.10
9.06
7.56
7.55
7.54
7.53
7.24
7.22
7.19
7.02
7.01
6.92
6.91
6.90
6.89
6.83
6.81
3.42 HDO
2.51 DMSO-D6
2.00
2.00
2.00
1.00
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

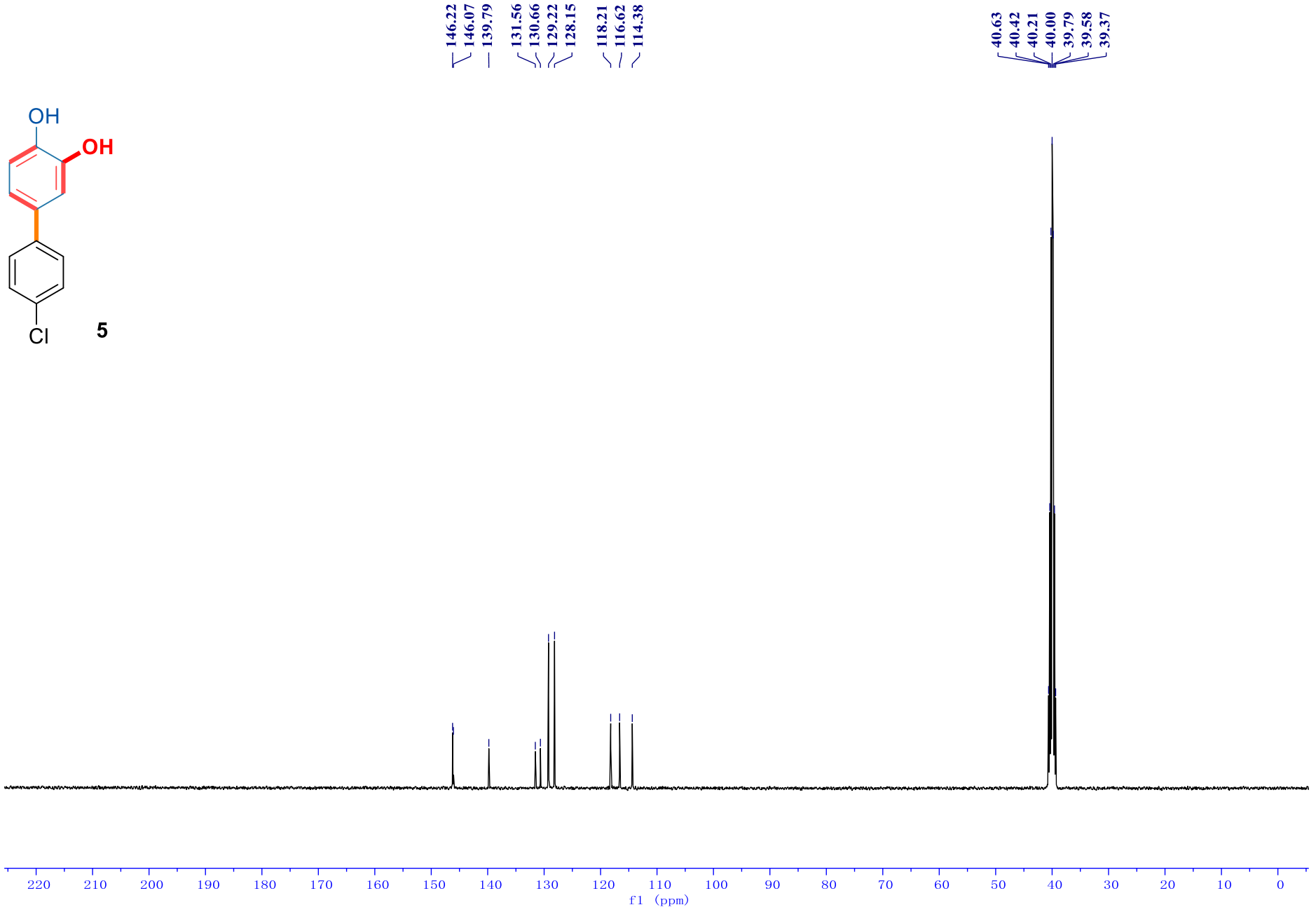

162.93
160.52
146.15
145.69
137.52
137.49
131.10
128.34
128.26
118.16
116.58
116.12
115.91
114.47
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
F
4
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

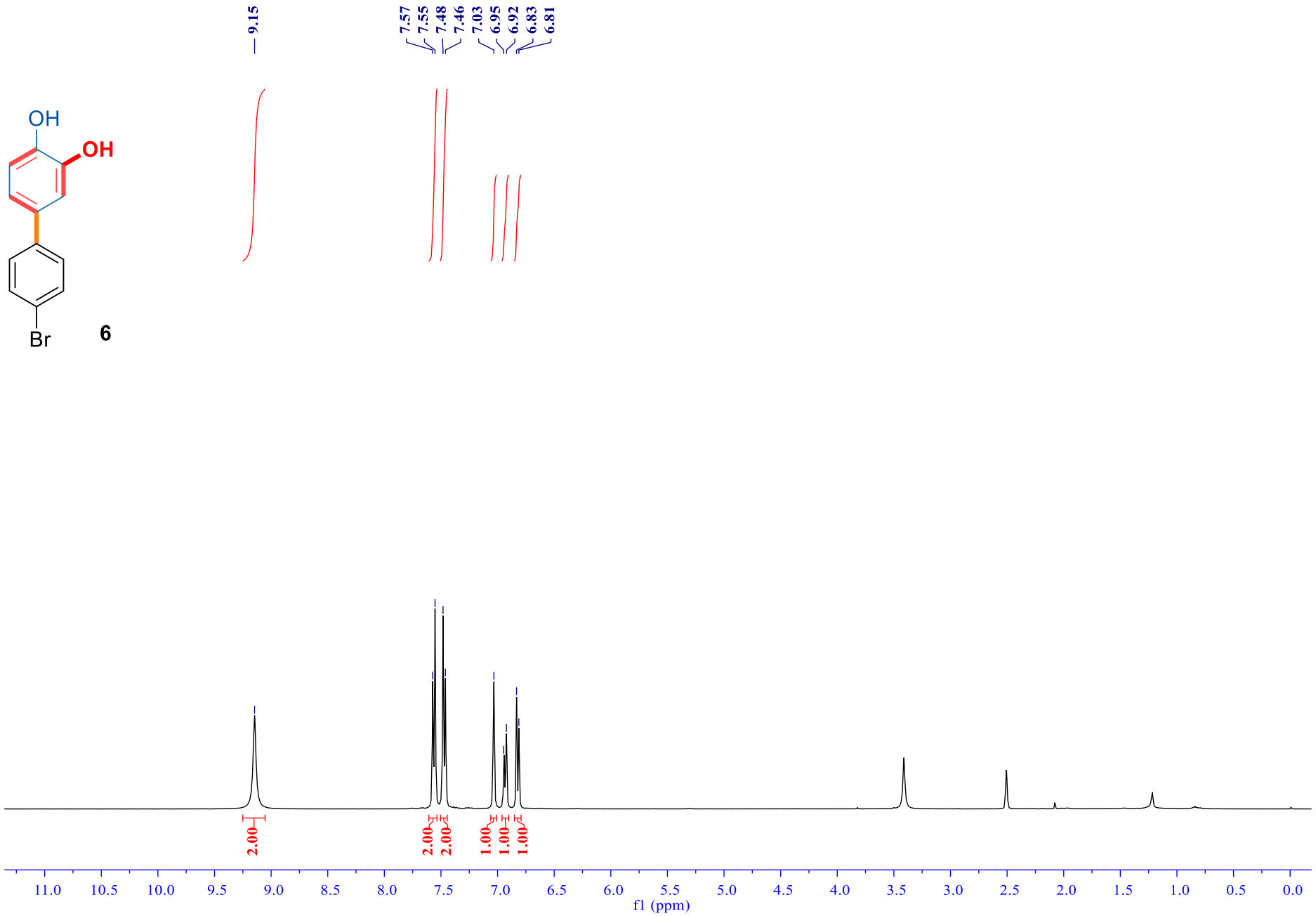

OH
OH
F

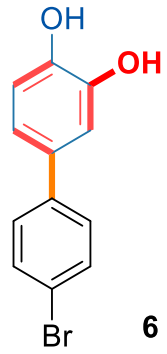
4

-116.98
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)


9.18
9.10
7.55
7.53
7.45
7.43
7.04
7.04
6.95
6.95
6.93
6.93
6.84
6.82
3.42 HDO
2.51 DMSO
OH
OH
Cl
5
1.00
1.00
2.00
2.00
1.00
1.00
1.00
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
f1 (ppm)

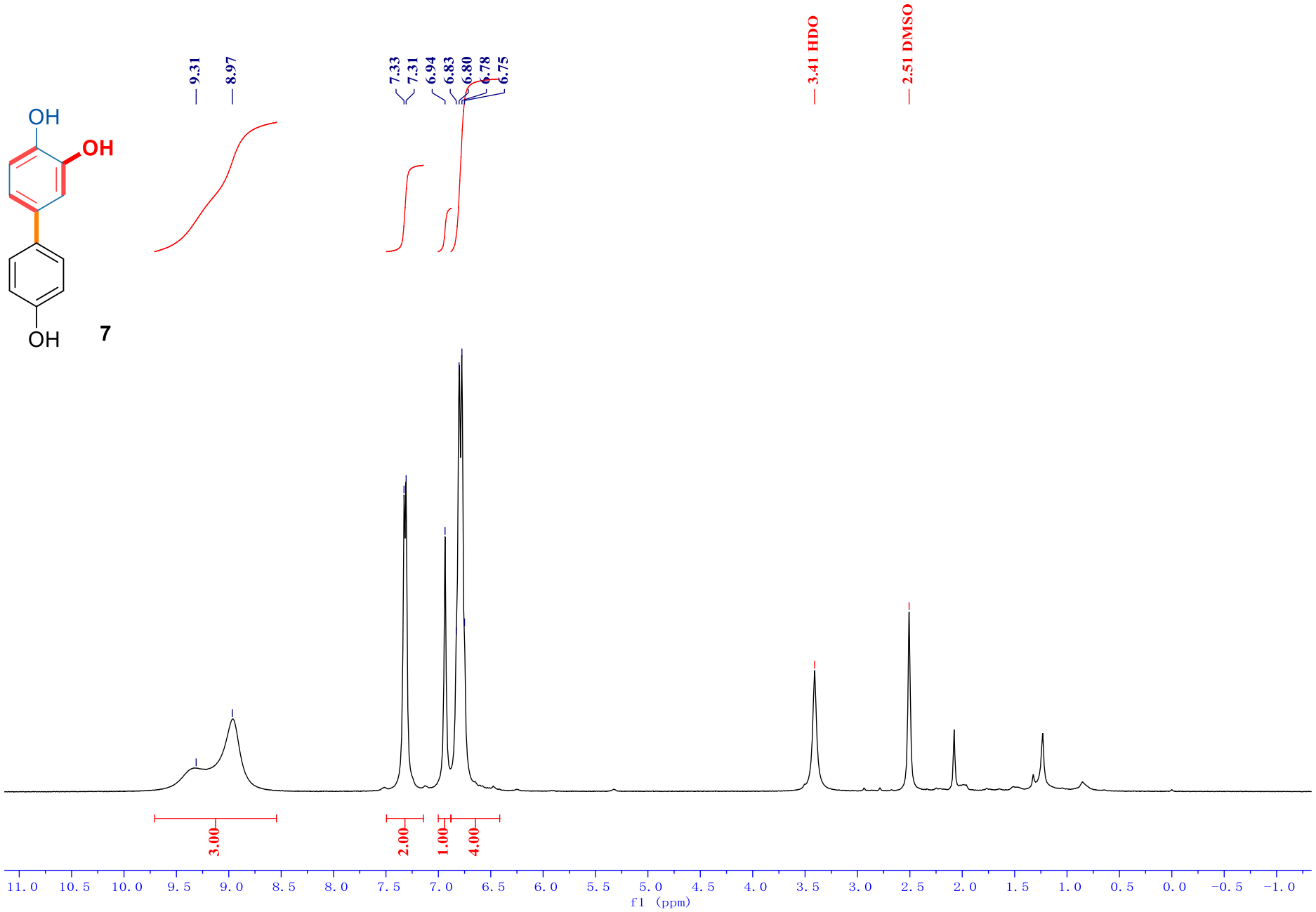

146.22
146.07
139.79
131.56
130.66
129.22
128.15
118.21
116.62
114.38
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
Cl
5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

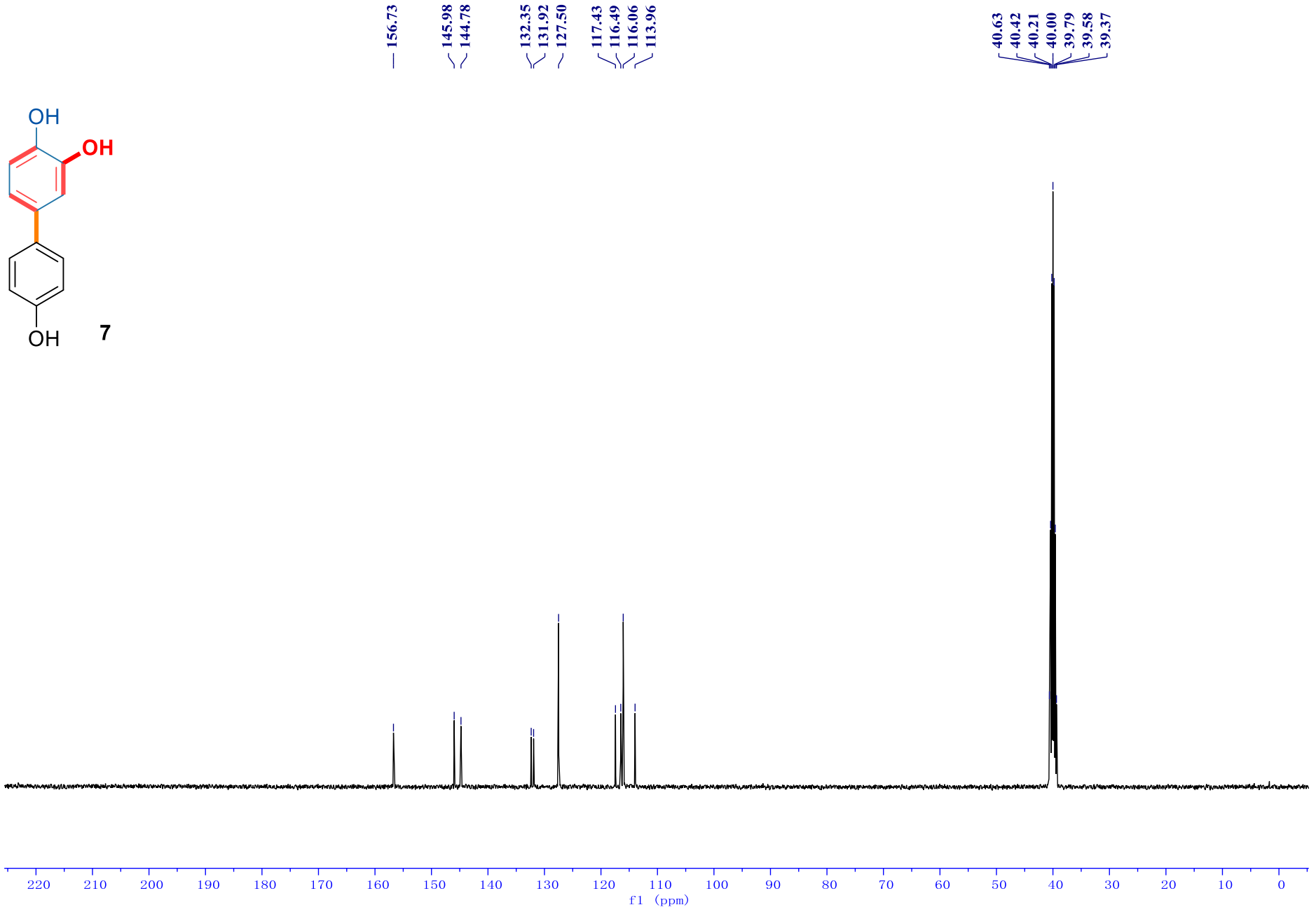

9.15
7.57
7.55
7.48
7.46
7.03
6.95
6.92
6.83
6.81
OH
OH
Br
6
2.00
2.00
2.00
1.00
1.00
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

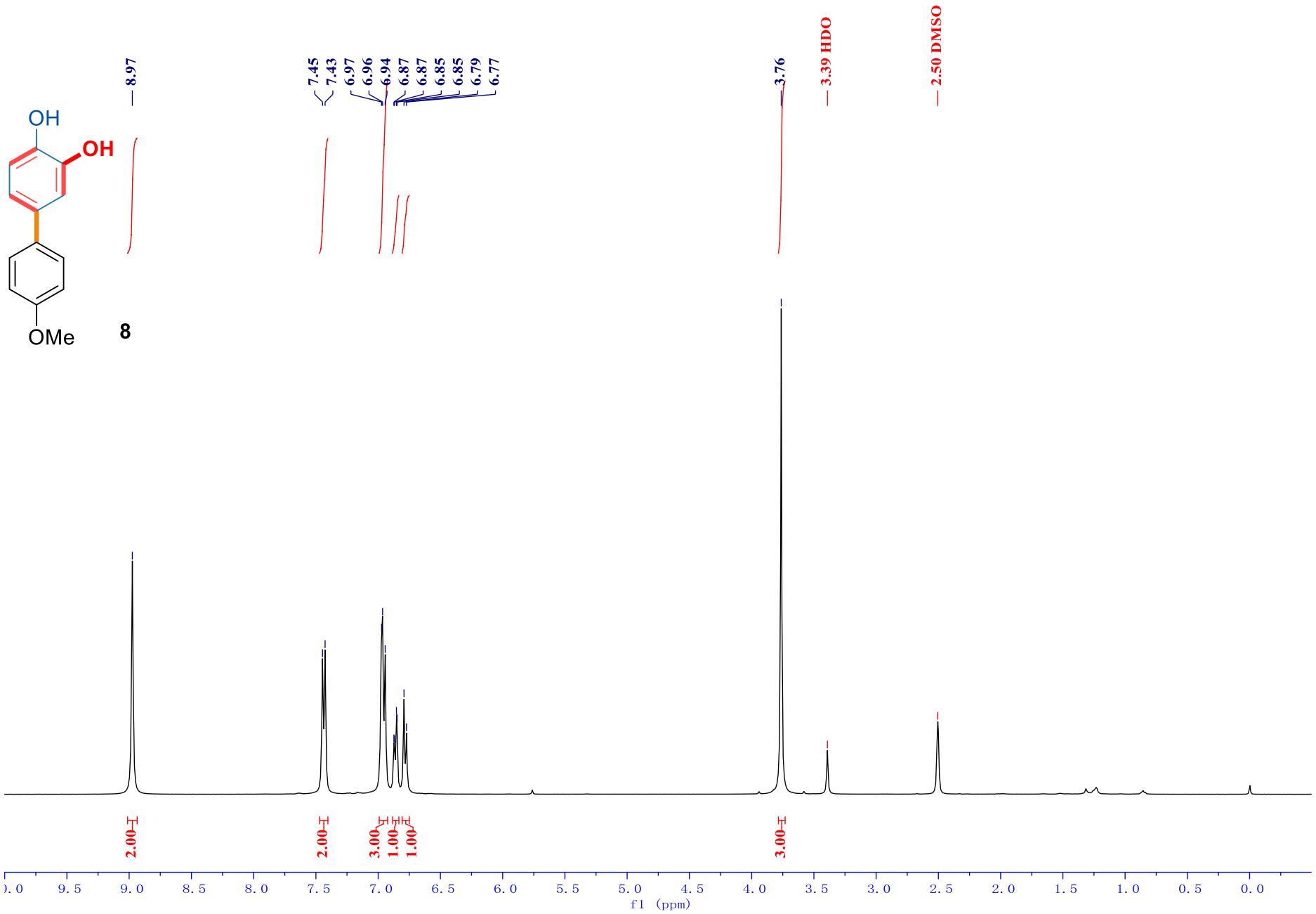

OH
OH
Br

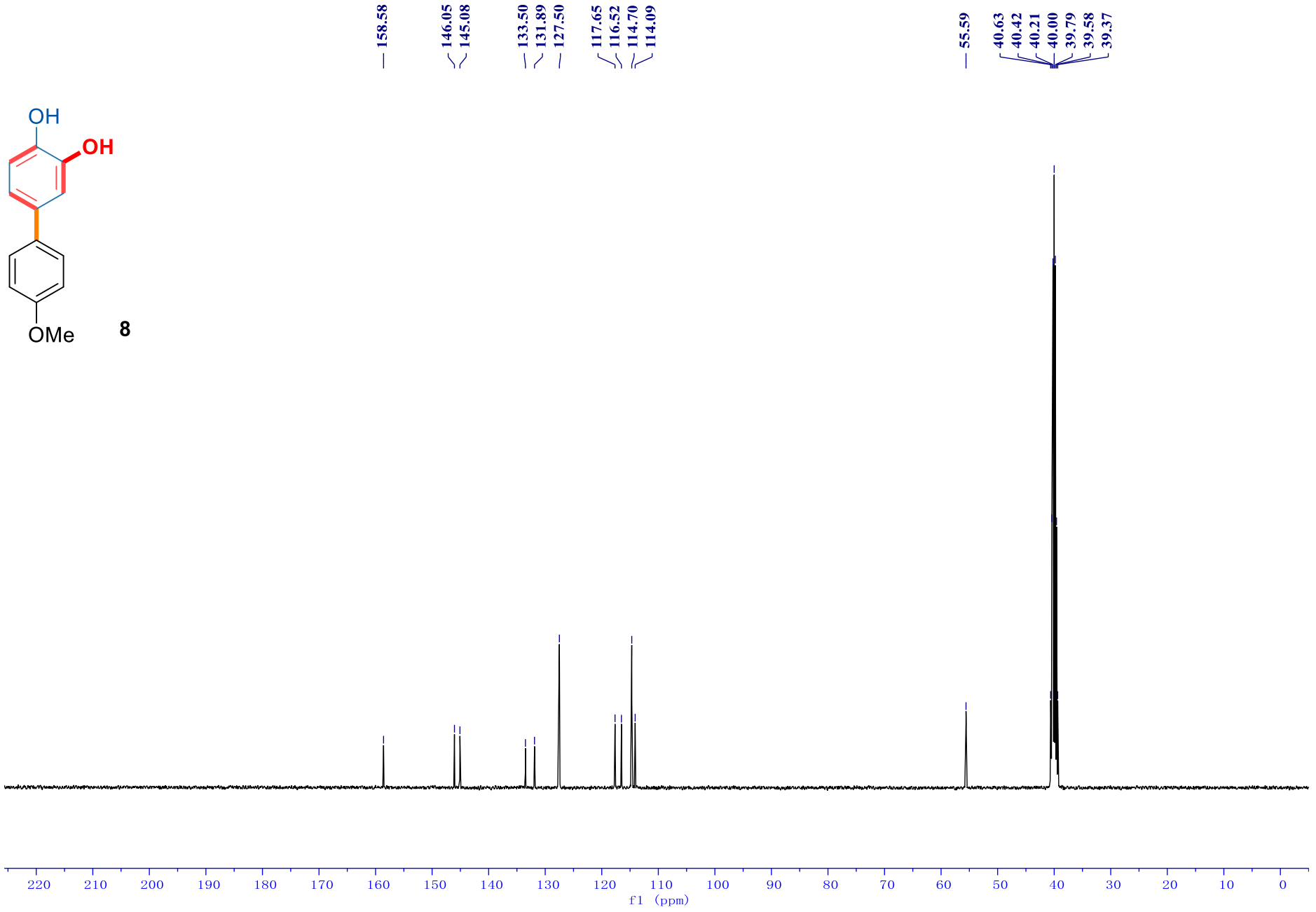
6

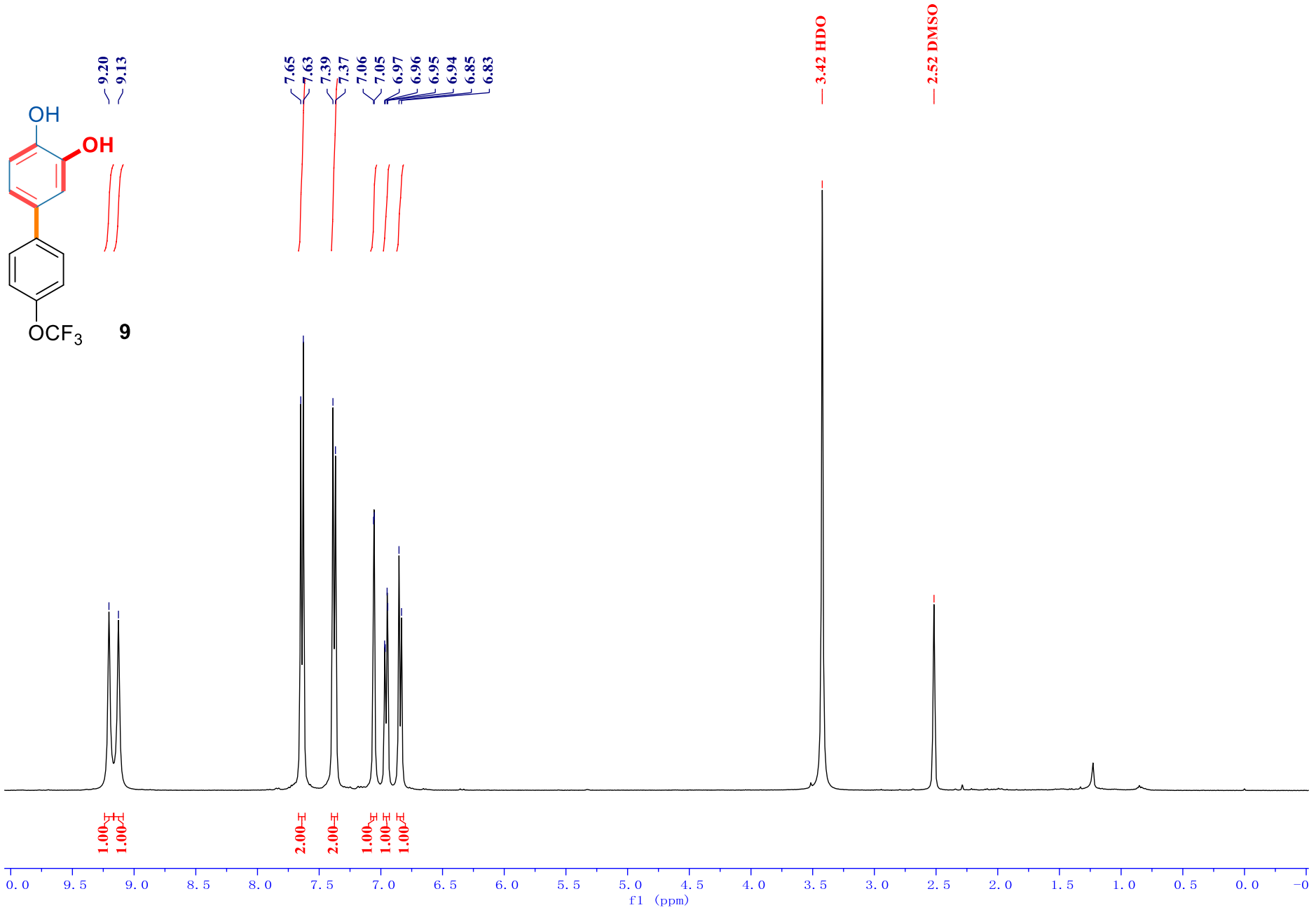
146.22
146.09
140.14
132.11
130.65
128.50
120.04
118.15
116.63
114.32
40.63
40.42
40.21
40.00
39.79
39.58
39.37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

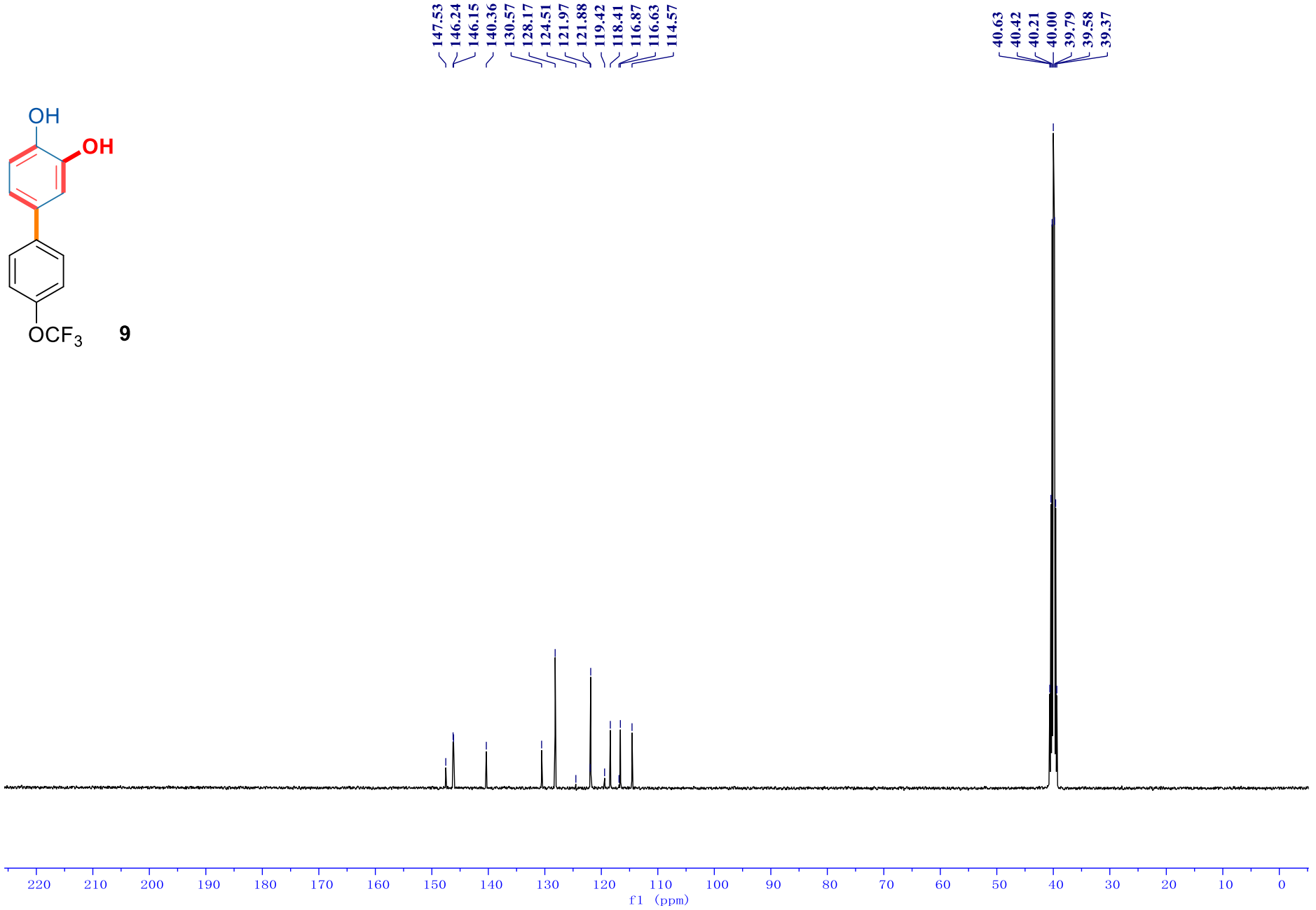

9.31
8.97
7.33
7.31
6.94
6.83
6.80
6.78
6.75
3.41 HDO
2.51 DMSO
OH
OH
OH
7
3.00
2.00
1.00
4.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

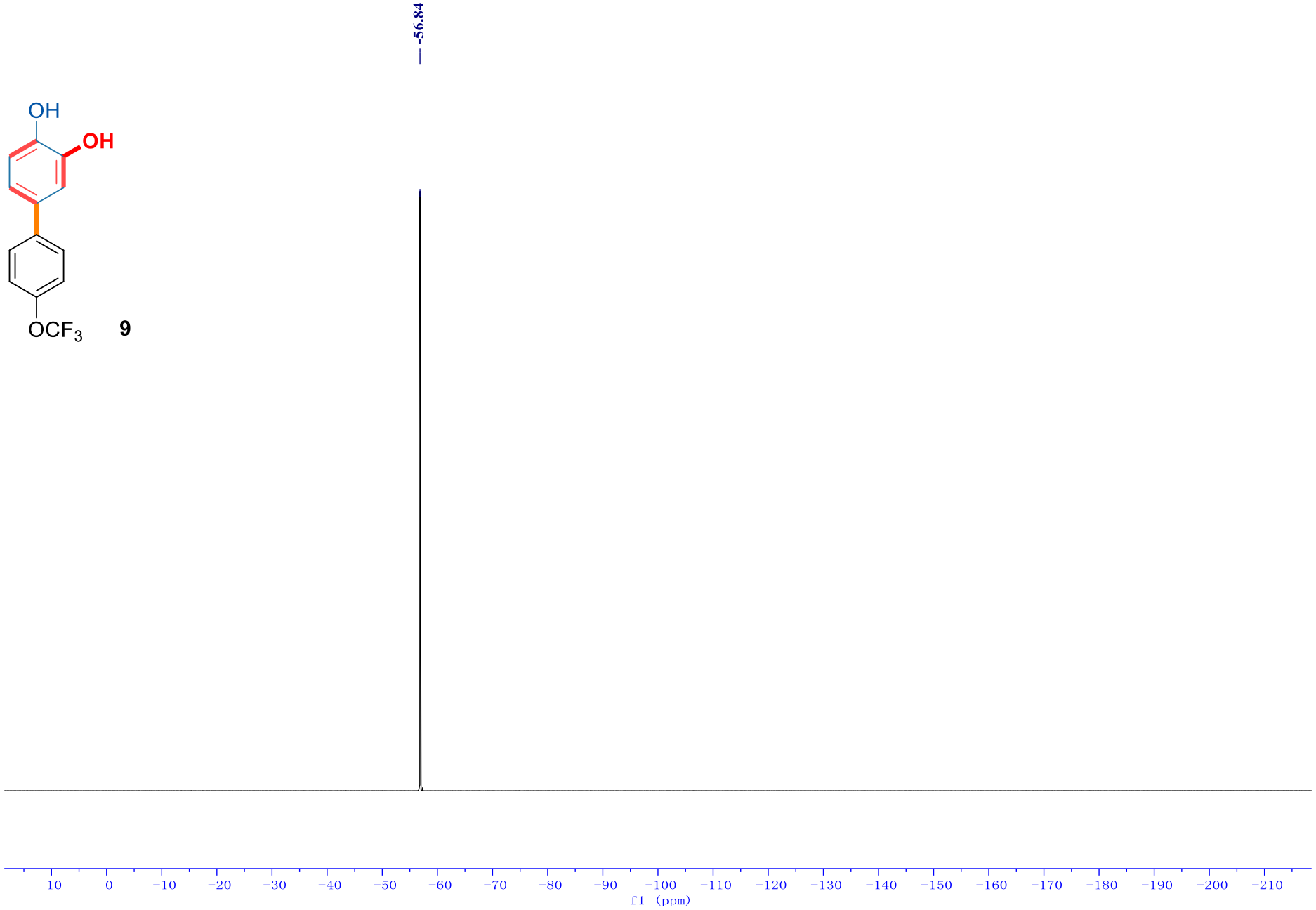

156.73
145.98
144.78
132.35
131.92
127.50
117.43
116.49
116.06
113.96
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
OH
7
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

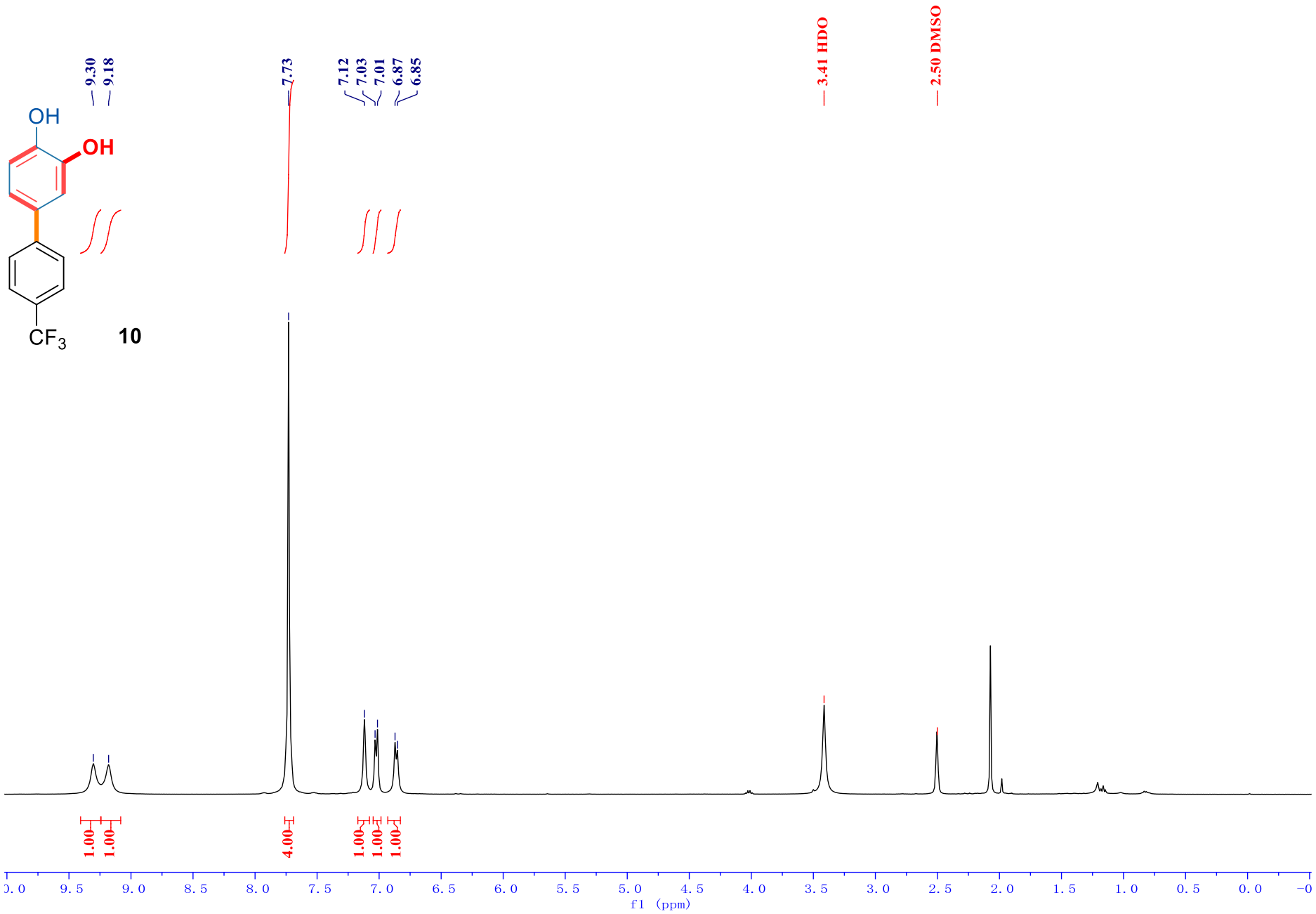

8.97
7.45
7.43
6.97
6.96
6.94
6.87
6.87
6.85
6.85
6.79
6.77
3.76
3.39 HDO
2.50 DMSO
OH
OH
OMe
8
2.00
2.00
3.00
1.00
1.00
3.00
f1 (ppm)

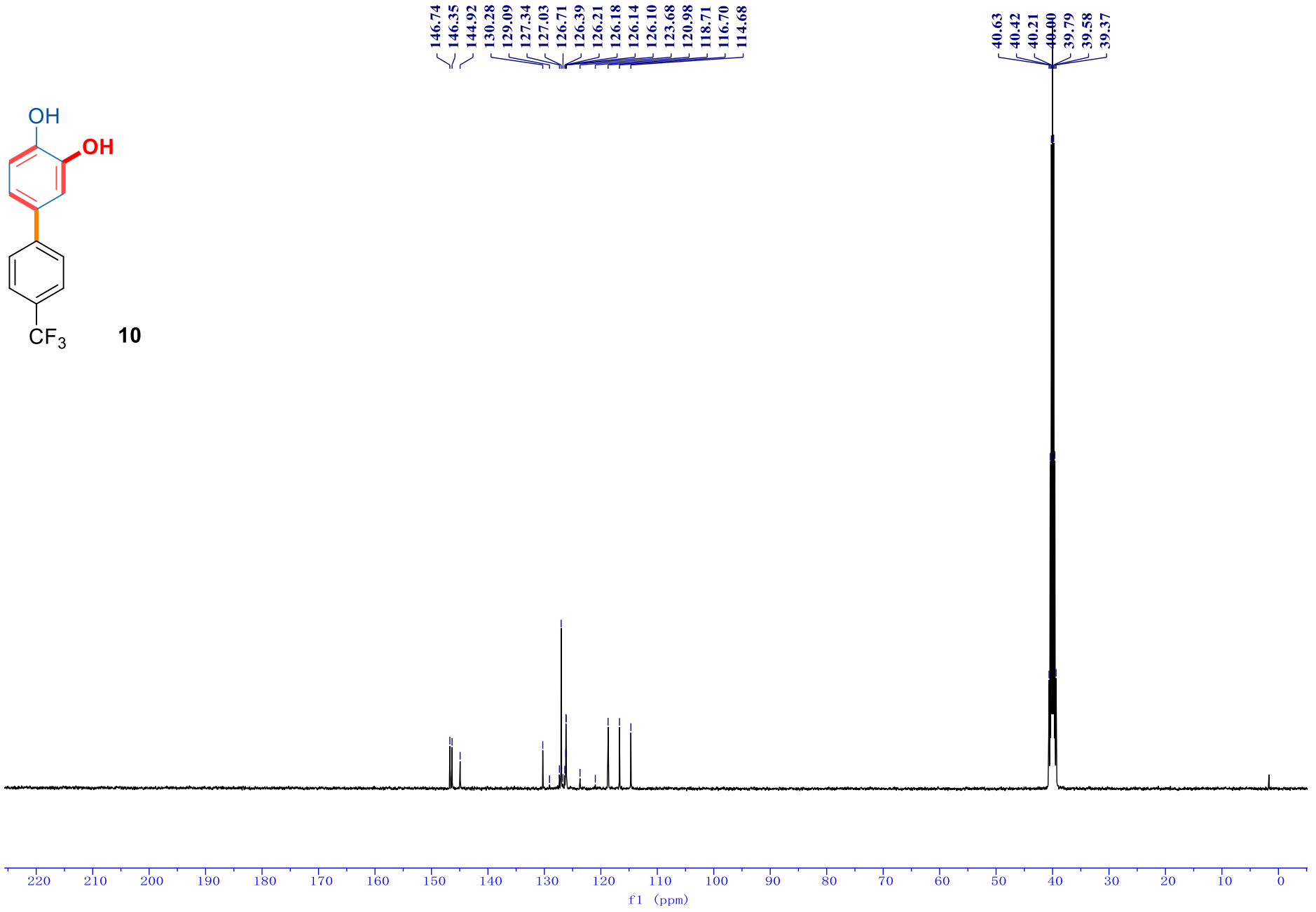

158.58
146.05
145.08
133.50
131.89
127.50
117.65
116.52
114.70
114.09
55.59
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
OMe
8
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

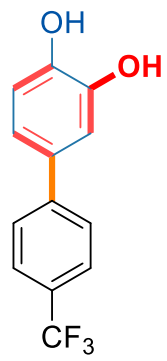

9.20
9.13
7.65
7.63
7.39
7.37
7.06
7.05
6.97
6.96
6.95
6.94
6.85
6.83
3.42 HDO
2.52 DMSO
OH
OH
OCF3
9
1.00
1.00
2.00
2.00
1.00
1.00
1.00
f1 (ppm)


147.53
146.24
146.15
140.36
130.57
128.17
124.51
121.97
121.88
119.42
118.41
116.87
116.63
114.57
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
OCF3
9
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)


-56.84
OH
OH
OCF3
9
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)

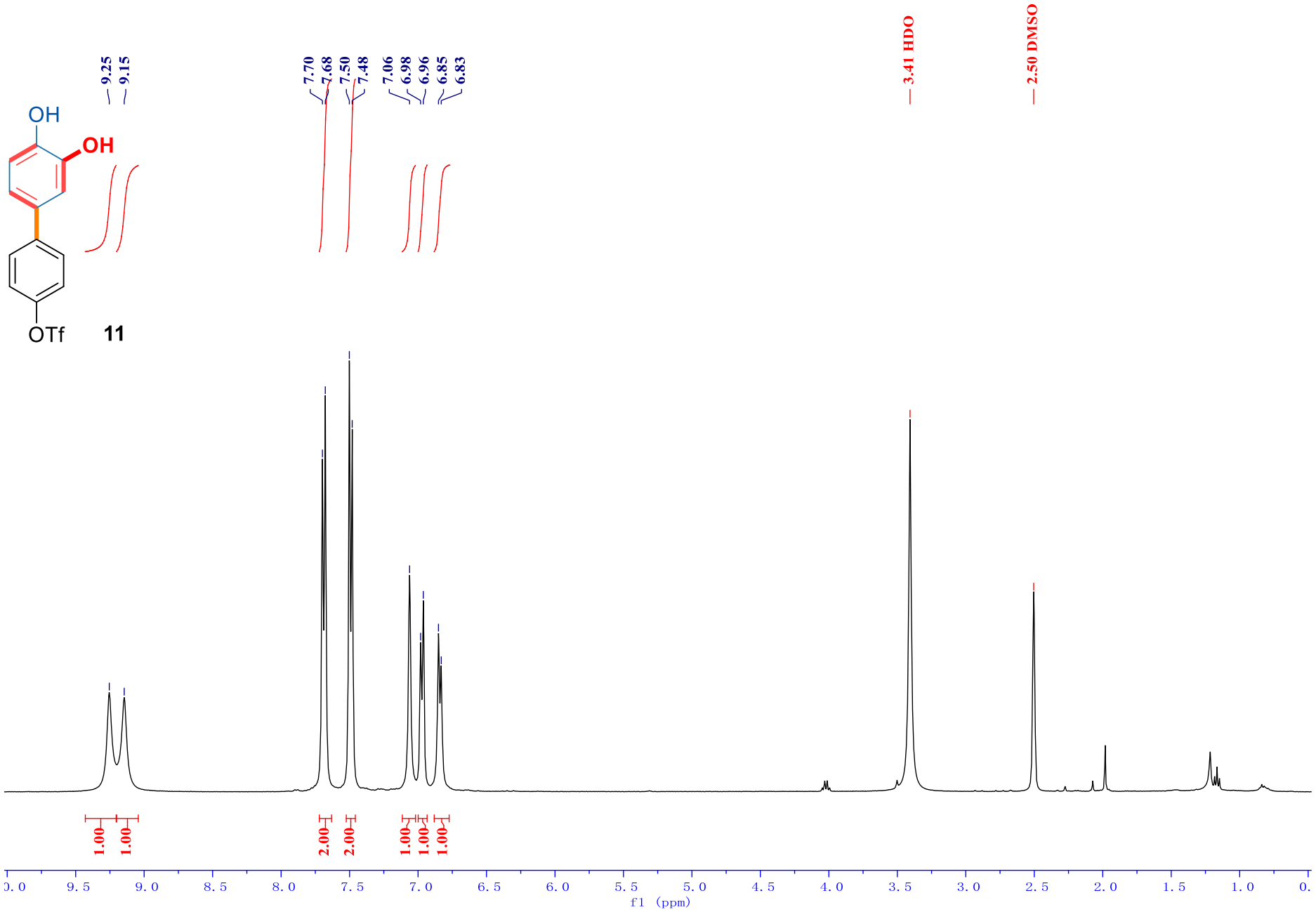

9.30
9.18
7.73
7.12
7.03
7.01
6.87
6.85
3.41 HDO
2.50 DMSO
OH
OH
CF3
10
1.00
1.00
4.00
1.00
1.00
1.00
f1 (ppm)

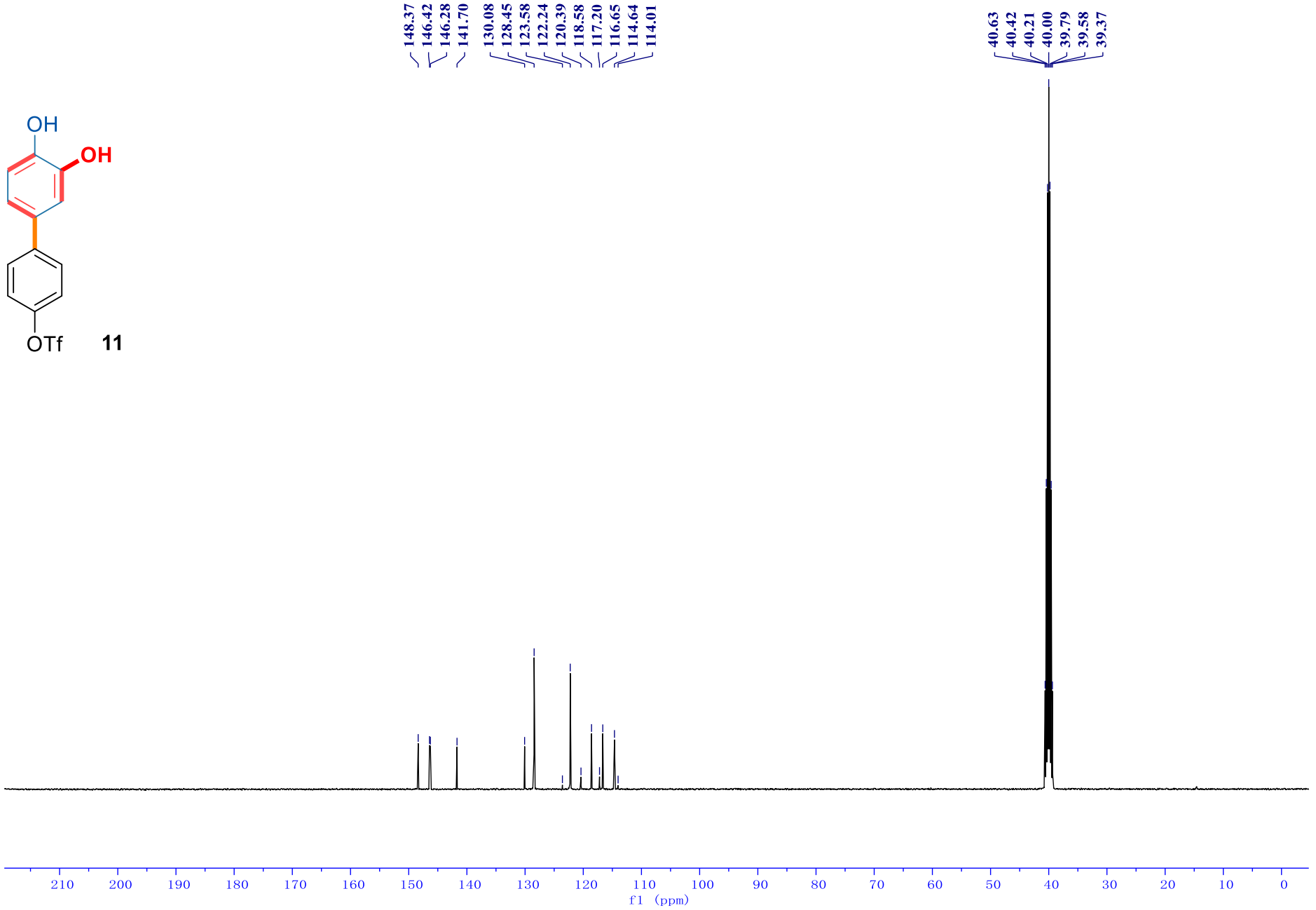

146.74
146.35
144.92
130.28
129.09
127.34
127.03
126.71
126.39
126.21
126.18
126.14
126.10
123.68
120.98
118.71
116.70
114.68
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
CF3
10
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

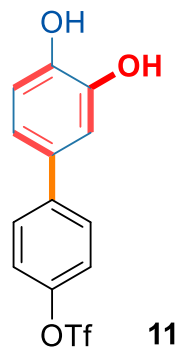

OH
OH
CF3

10

-60.76
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)

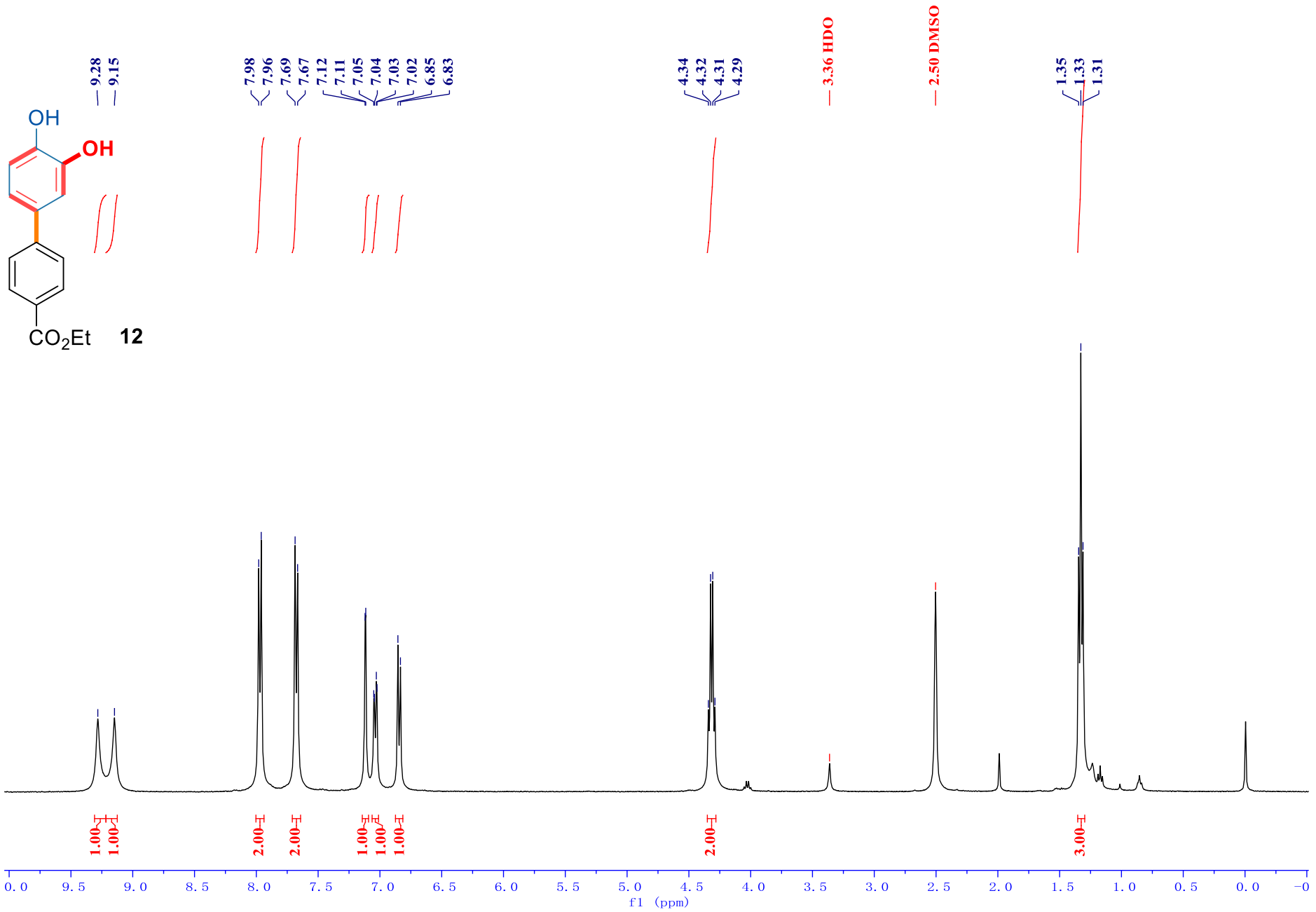

9.25
9.15
7.70
7.68
7.50
7.48
7.06
6.98
6.96
6.85
6.83
3.41 HDO
2.50 DMSO
OH
OH
OTf
11
1.00
1.00
2.00
2.00
1.00
1.00
1.00
f1 (ppm)


148.37
146.42
146.28
141.70
130.08
128.45
123.58
122.24
120.39
118.58
117.20
116.65
114.64
114.01
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
OTf
11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
OH
OTf

11

-72.82
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)


9.28
9.15
7.98
7.96
7.69
7.67
7.12
7.11
7.05
7.04
7.03
7.02
6.85
6.83
4.34
4.32
4.31
4.29
3.36 HDO
2.50 DMSO
1.35
1.33
1.31
OH
OH
CO2Et
12
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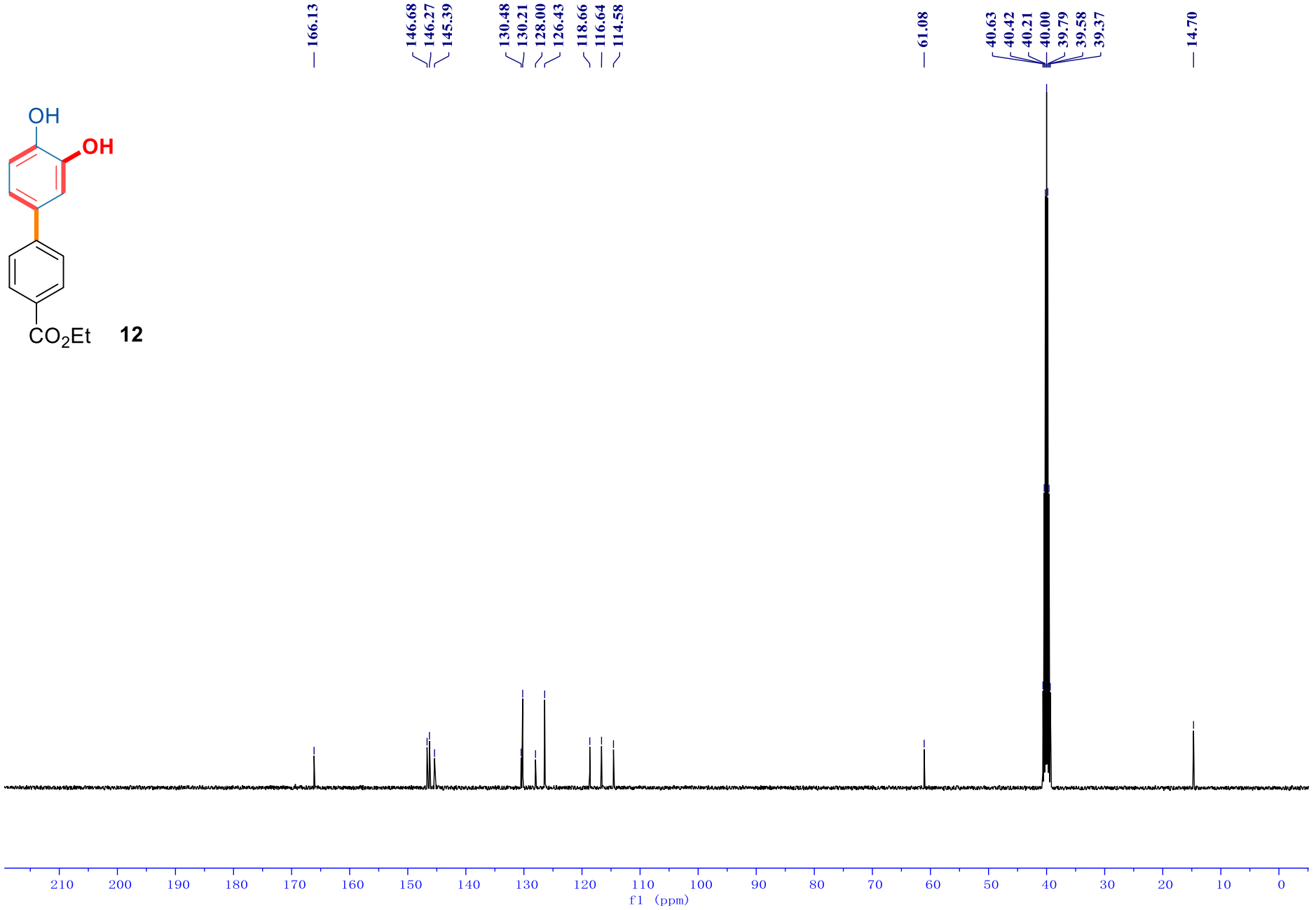
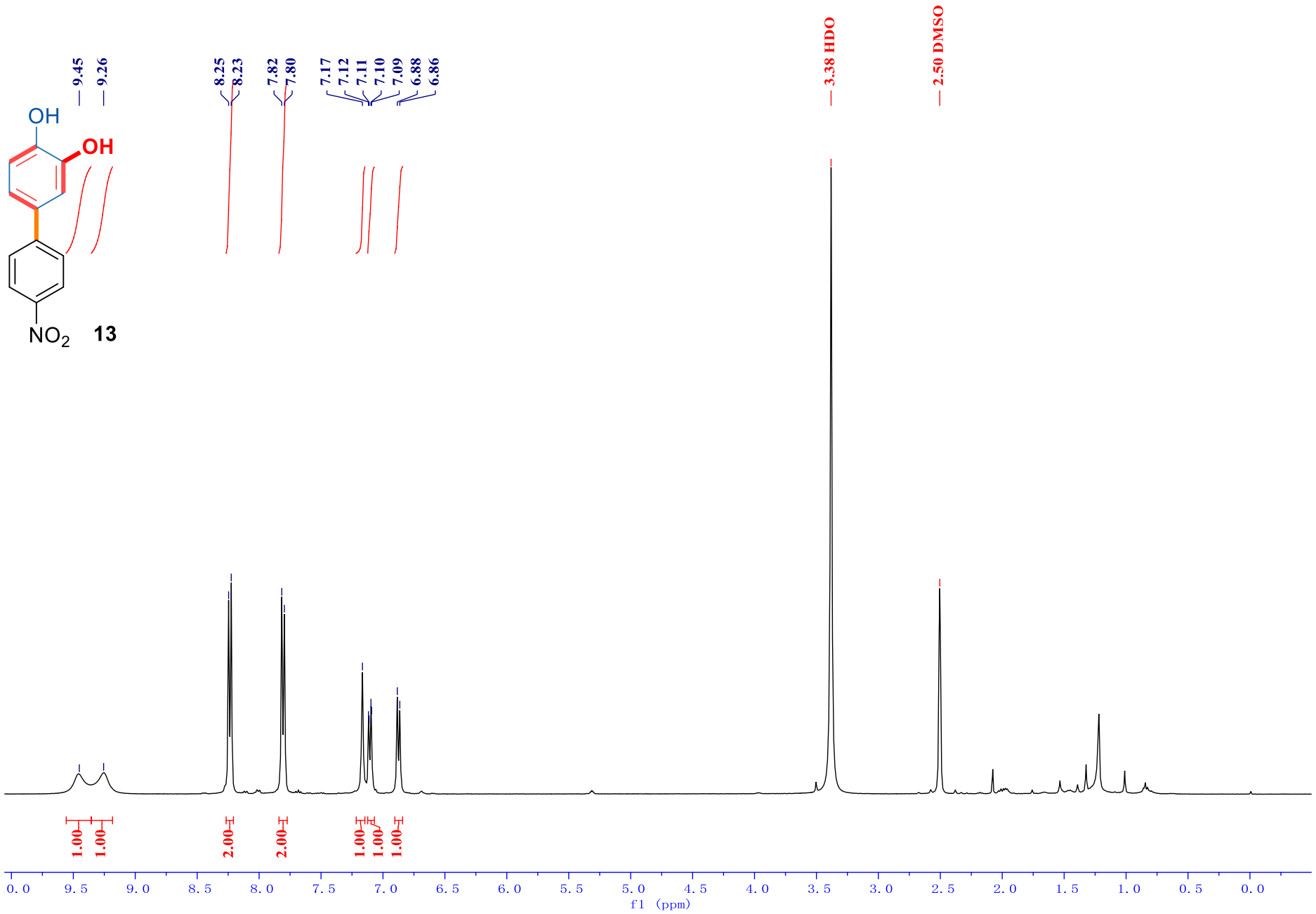
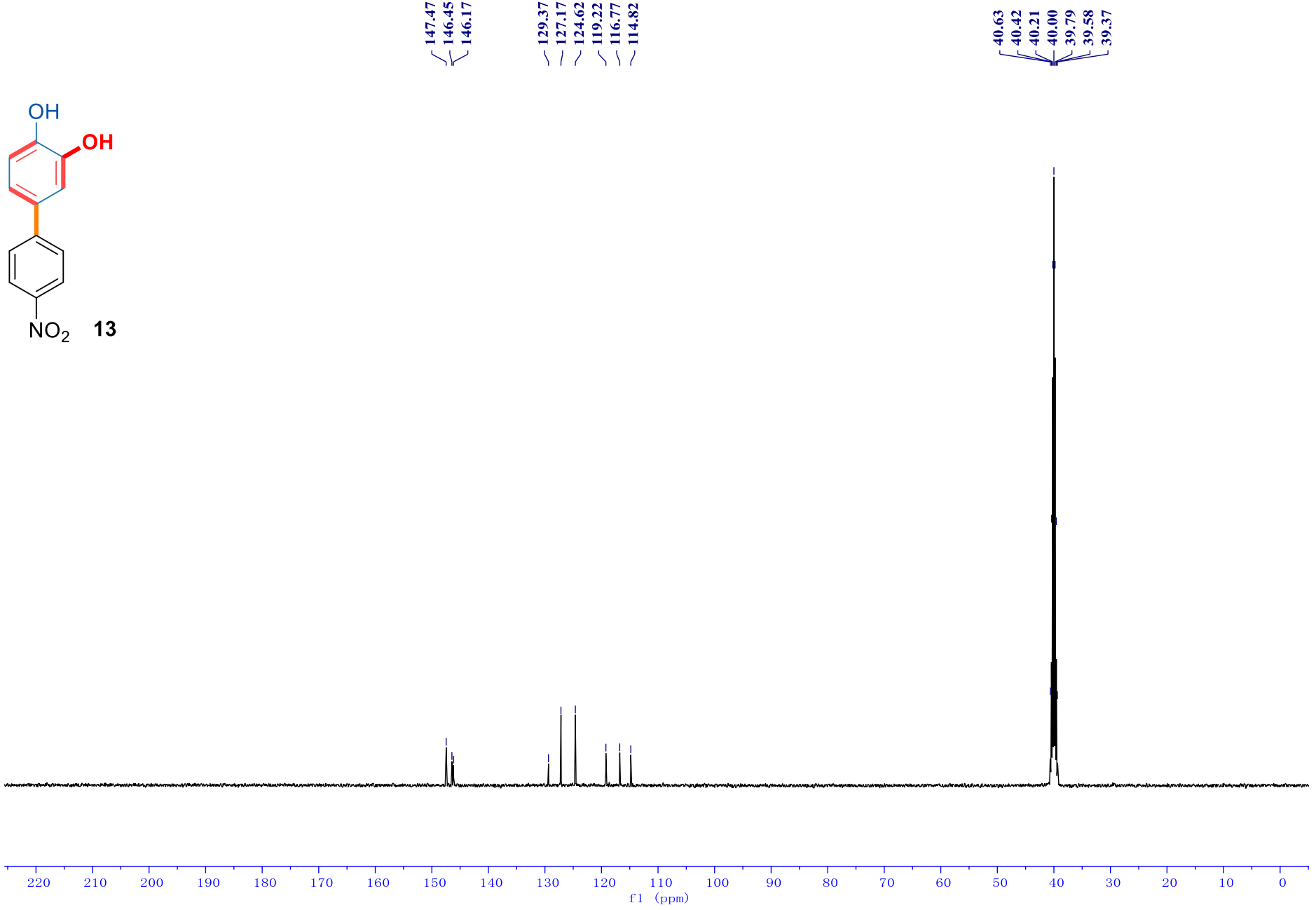
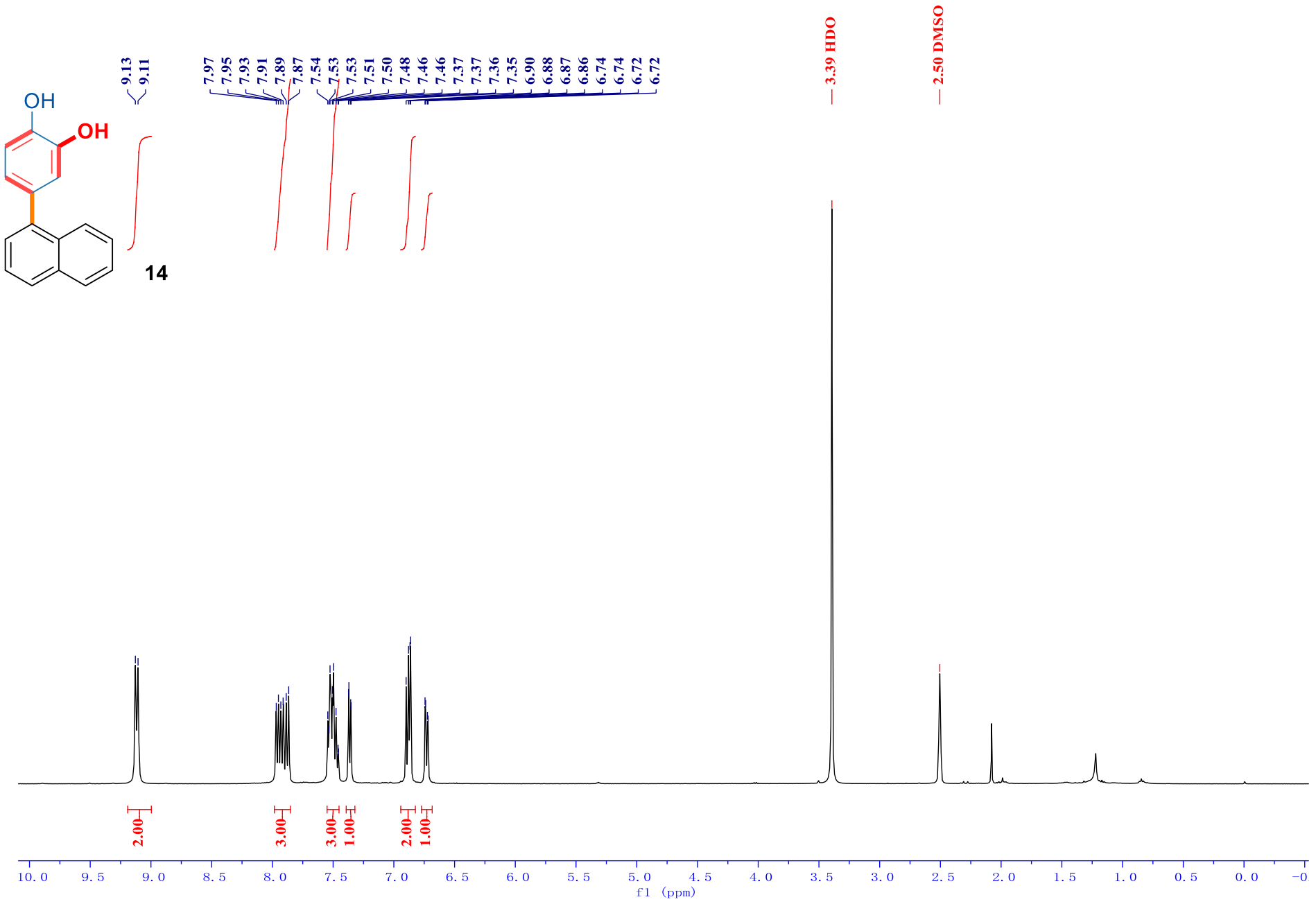
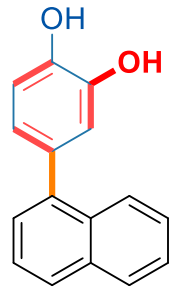
1.00
2.00
2.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)


166.13
146.68
146.27
145.39
130.48
130.21
128.00
126.43
118.66
116.64
114.58
61.08
40.63
40.42
40.21
40.00
39.79
39.58
39.37
14.70
OH
OH
CO2Et
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.45
9.26
8.25
8.23
7.82
7.80
7.17
7.12
7.11
7.10
7.09
6.88
6.86
3.38 HDO
2.50 DMSO
OH
OH
NO2
13
1.00
1.00
2.00
2.00
1.00
1.00
1.00
f1 (ppm)

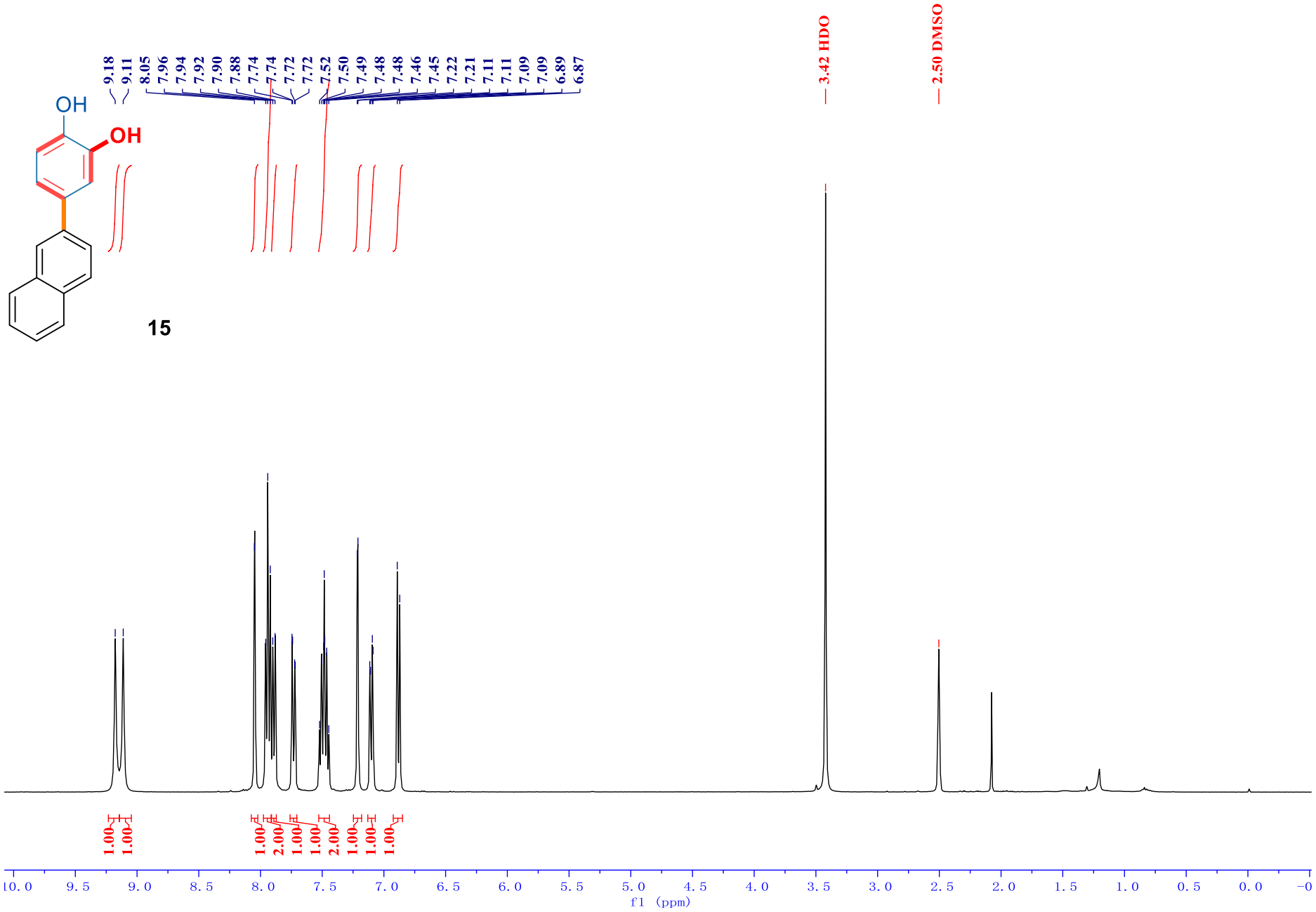

147.47
146.45
146.17
129.37
127.17
124.62
119.22
116.77
114.82
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
NO2
13
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

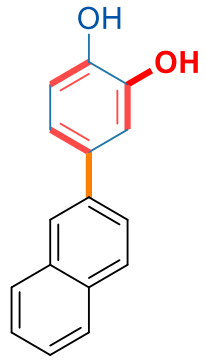

OH
OH
14
9.13
9.11
7.97
7.95
7.93
7.91
7.89
7.87
7.54
7.53
7.53
7.51
7.50
7.48
7.46
7.46
7.37
7.37
7.36
7.35
6.90
6.88
6.87
6.86
6.74
6.74
6.72
6.72
3.39 HDO
2.50 DMSO
2.00
3.00
3.00
1.00
2.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)


OH
OH

14

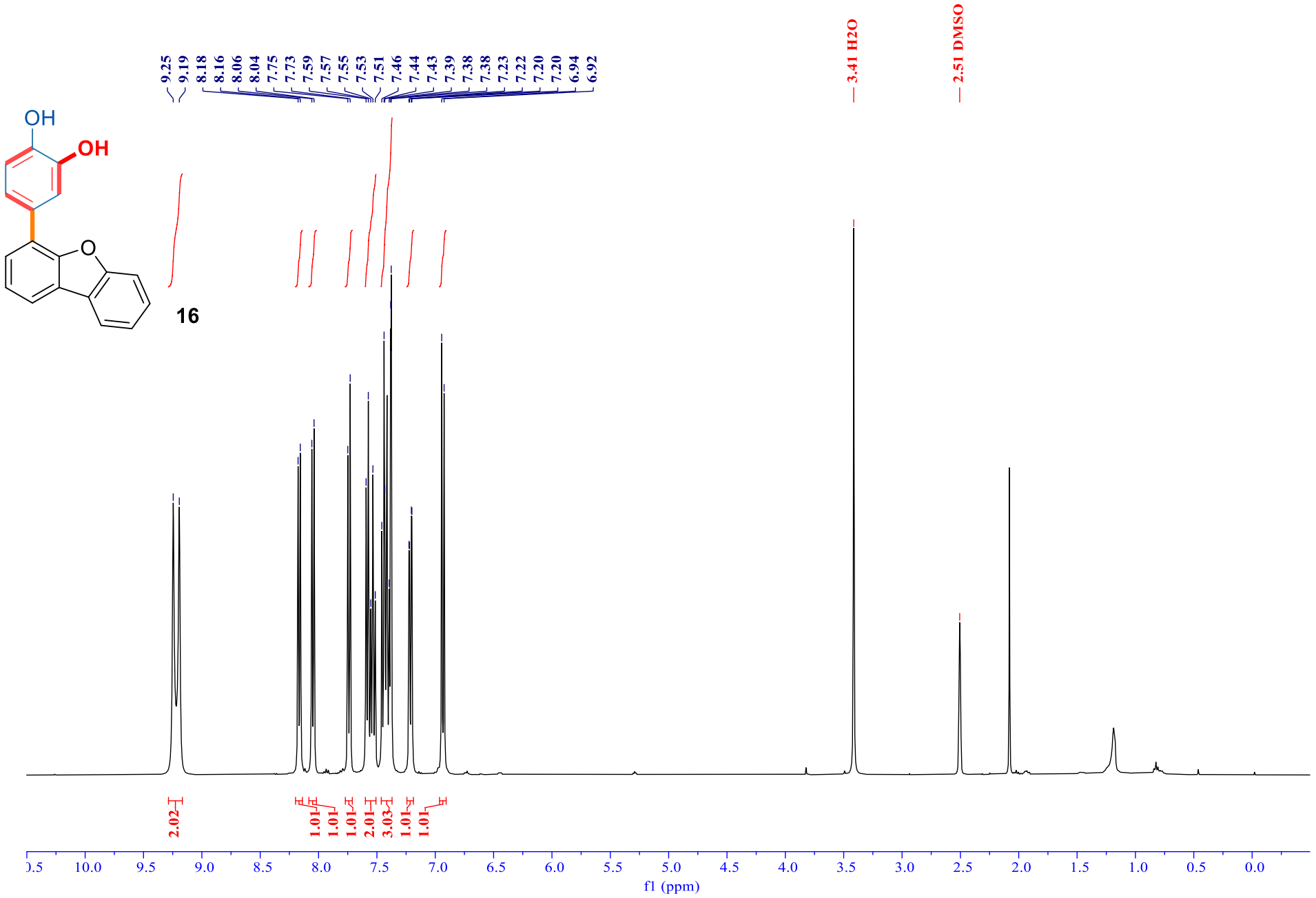
145.60
145.41
140.38
133.99
131.58
128.76
127.41
127.02
126.52
126.27
126.10
126.07
121.26
117.71
116.15
40.63
40.42
40.21
40.00
39.79
39.58
39.37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

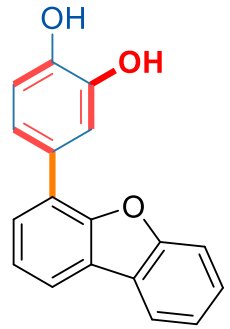

9.18
9.11
8.05
7.96
7.94
7.92
7.90
7.88
7.74
7.74
7.72
7.72
7.52
7.50
7.49
7.48
7.48
7.46
7.45
7.22
7.21
7.11
7.11
7.09
7.09
6.89
6.87
3.42 HDO
2.50 DMSO
OH
OH
15
1.00
1.00
1.00
2.00
1.00
1.00
2.00
1.00
1.00
1.00
f1 (ppm)


OH
OH

15

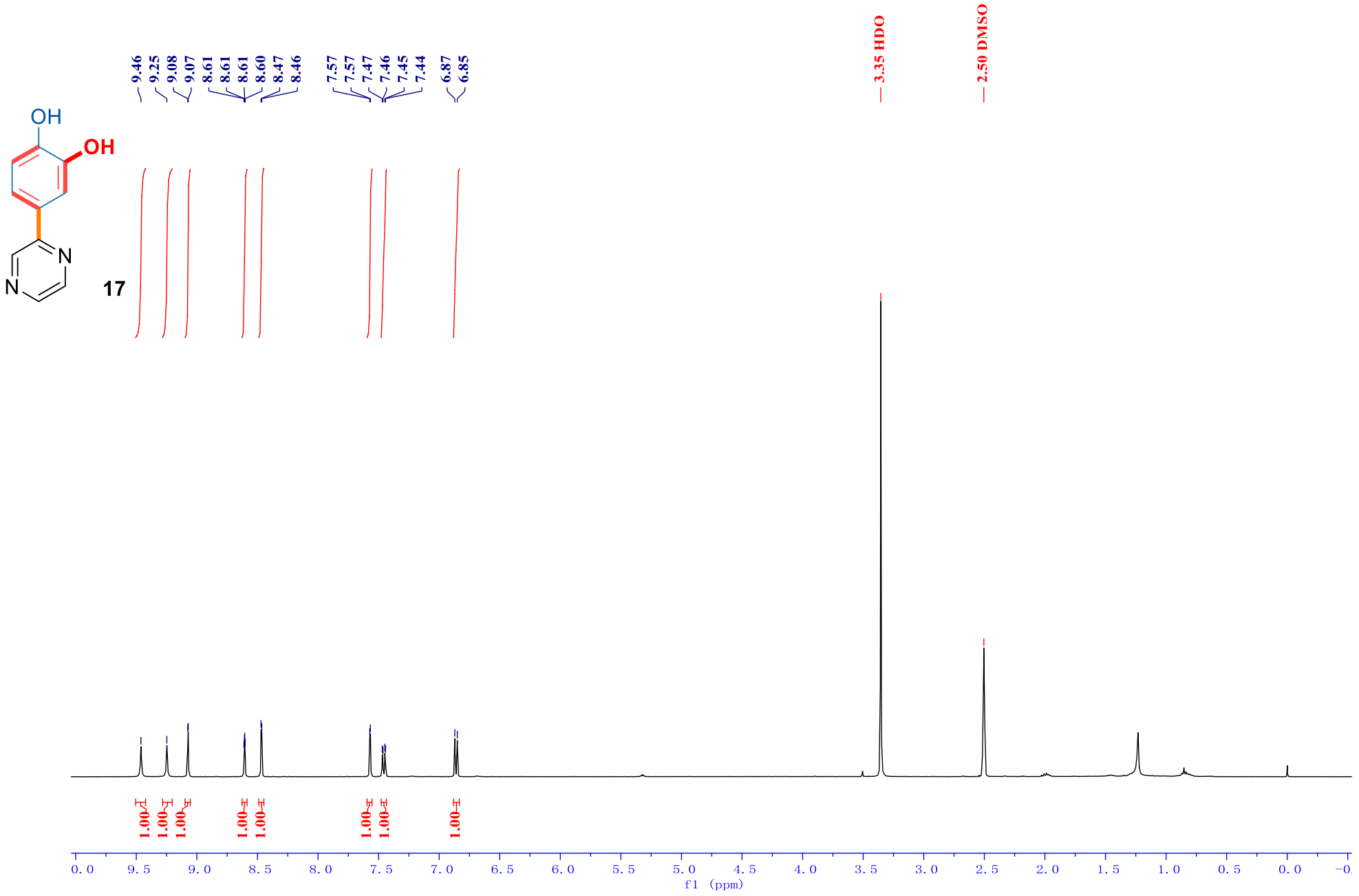
146.26
145.92
138.34
133.96
132.26
131.81
128.75
128.48
127.94
126.76
126.07
125.45
124.41
118.56
116.67
114.75
40.63
40.42
40.21
40.00
39.79
39.58
39.37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

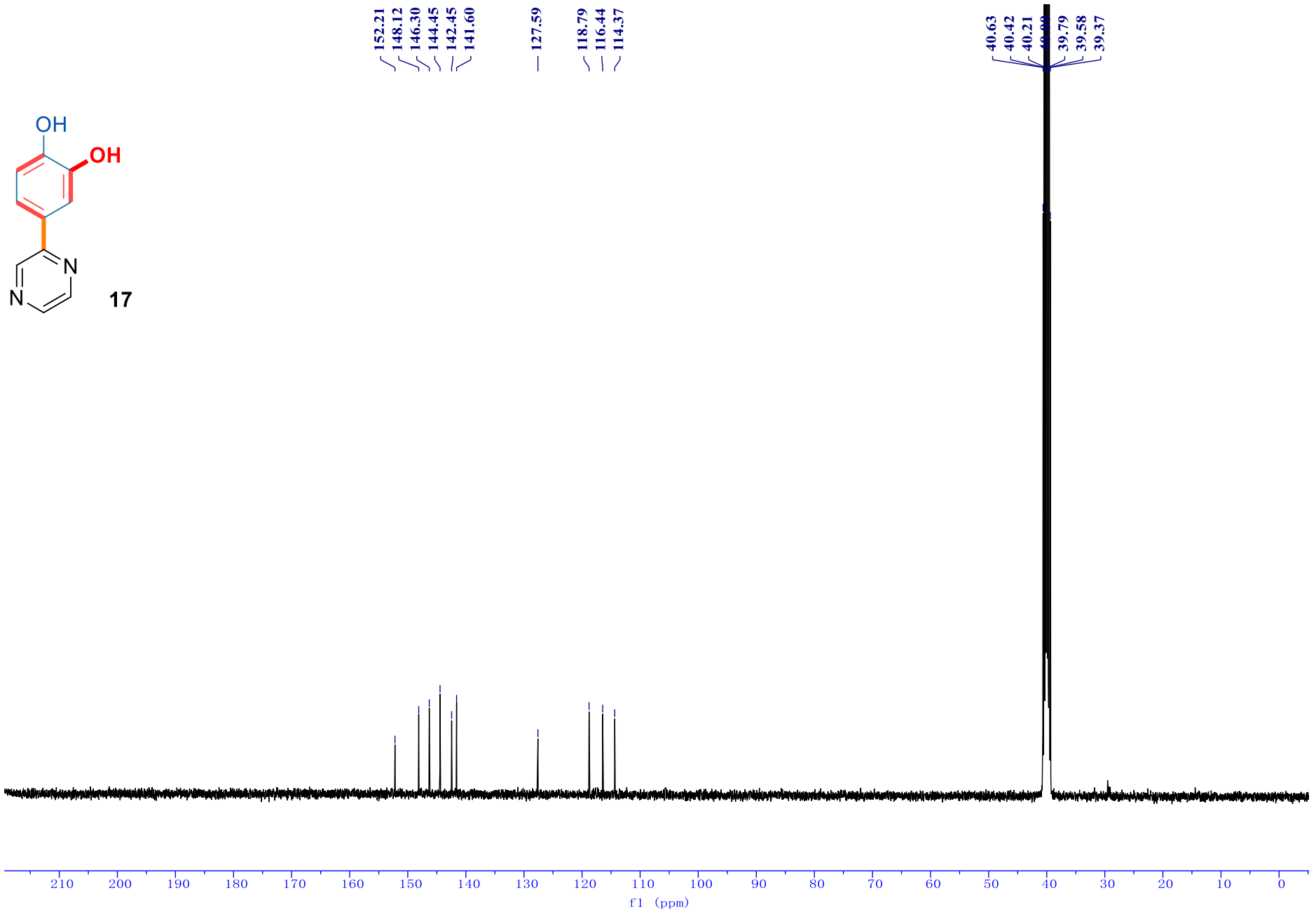

9.25
9.19
8.18
8.16
8.06
8.04
7.75
7.73
7.59
7.57
7.55
7.53
7.51
7.46
7.44
7.43
7.39
7.38
7.38
7.23
7.22
7.20
7.20
6.94
6.92
3.41 H2O
2.51 DMSO
OH
OH
O
16
2.02
1.01
1.01
1.01
2.01
3.03
1.01
1.01
f1 (ppm)

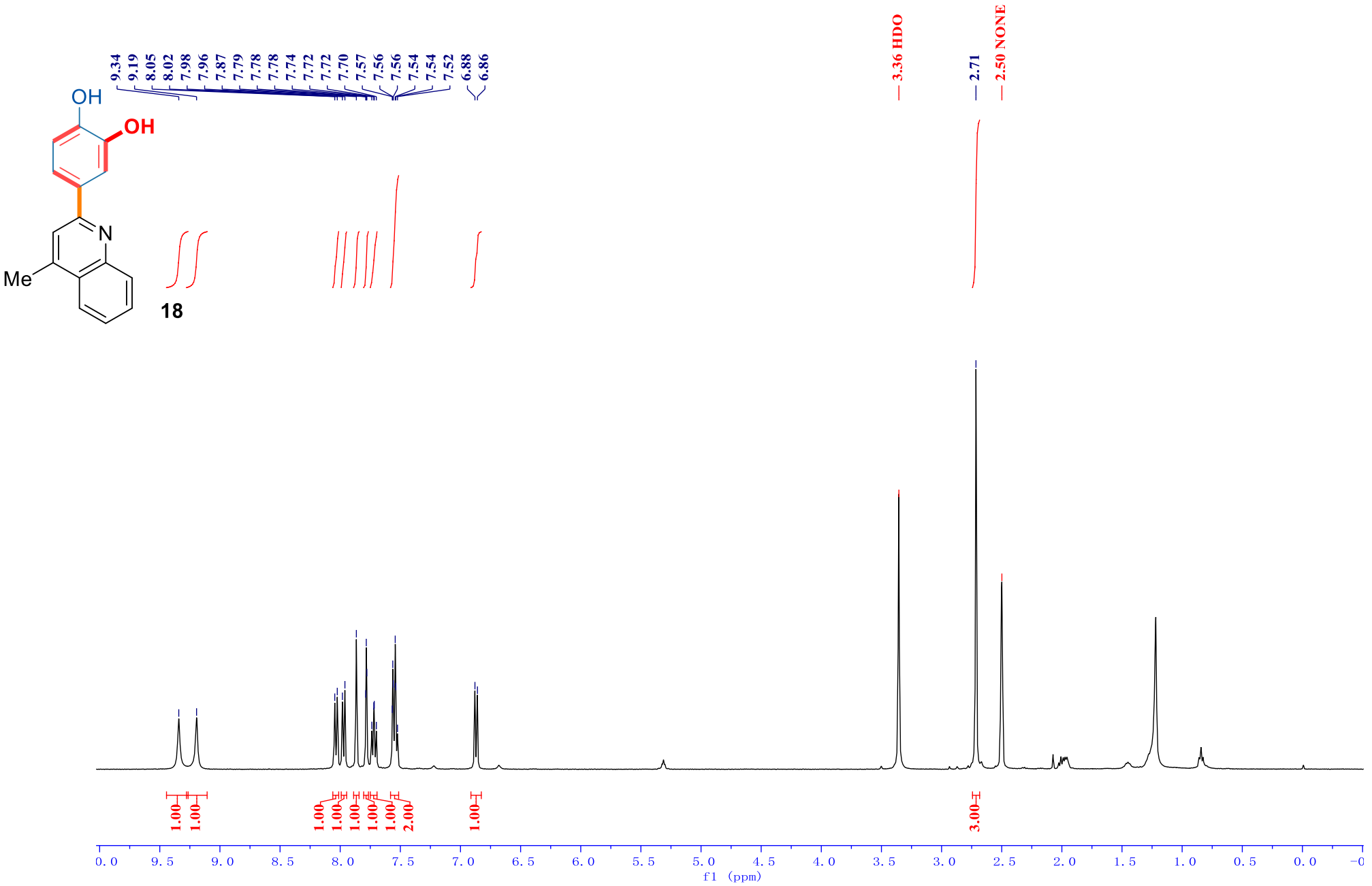

OH
OH
O

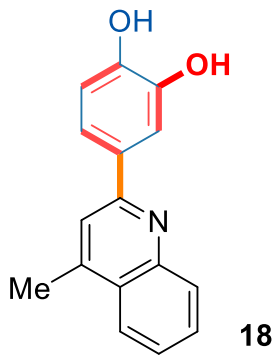
16

155.87
152.90
146.08
145.88
128.13
127.26
126.78
125.99
124.75
124.15
124.13
123.62
121.68
120.24
119.69
116.45
116.41
112.19
40.63
40.42
40.21
40.00
39.79
39.58
39.37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.46
9.25
9.08
9.07
8.61
8.61
8.61
8.60
8.47
8.46
7.57
7.57
7.47
7.46
7.45
7.44
6.87
6.85
3.35 HDO
2.50 DMSO
OH
OH
N
N
17
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
f1 (ppm)

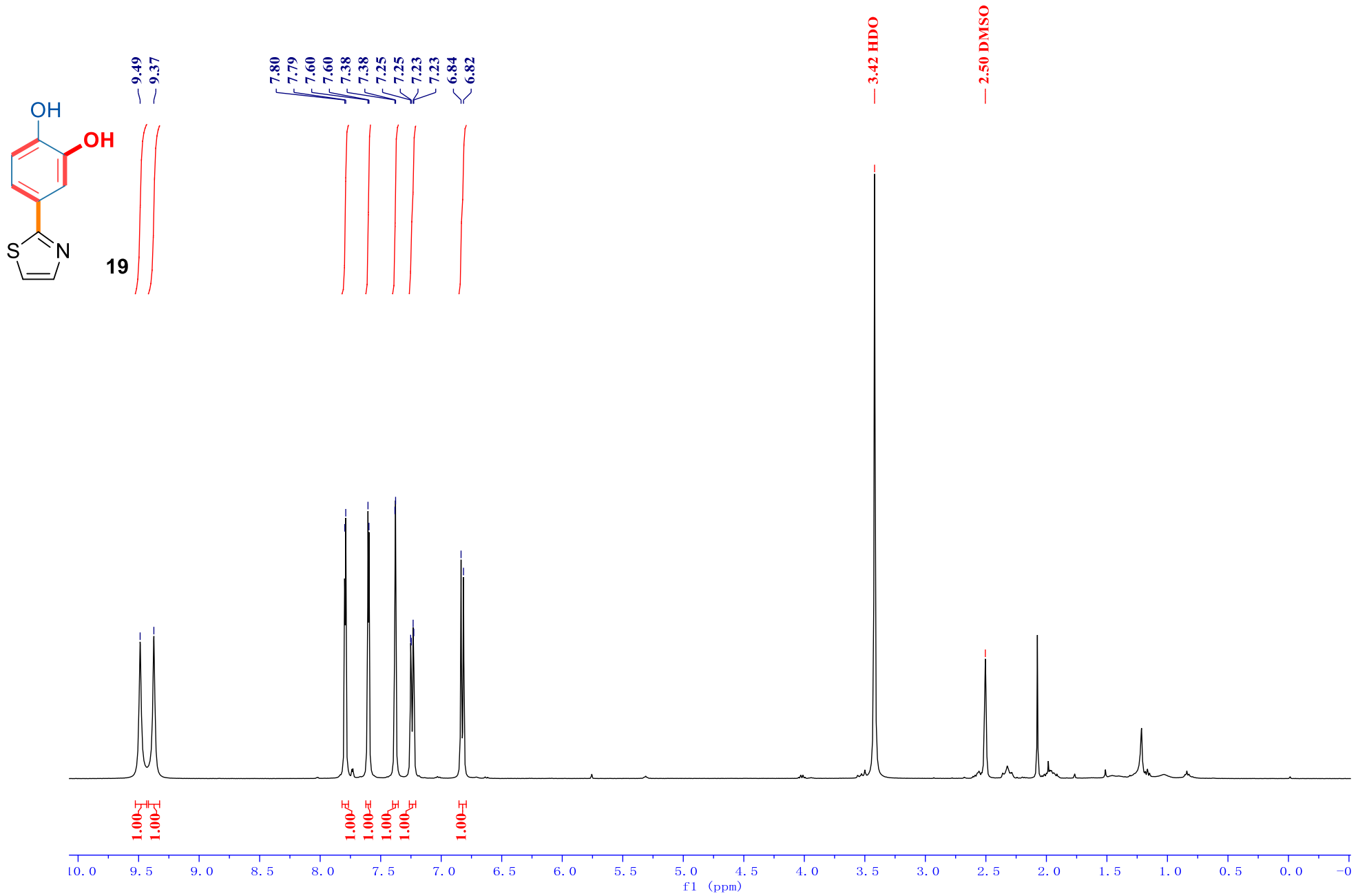

152.21
148.12
146.30
144.45
142.45
141.60
127.59
118.79
116.44
114.37
40.63
40.42
40.21
39.79
39.58
39.37
OH
OH
N
N
17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

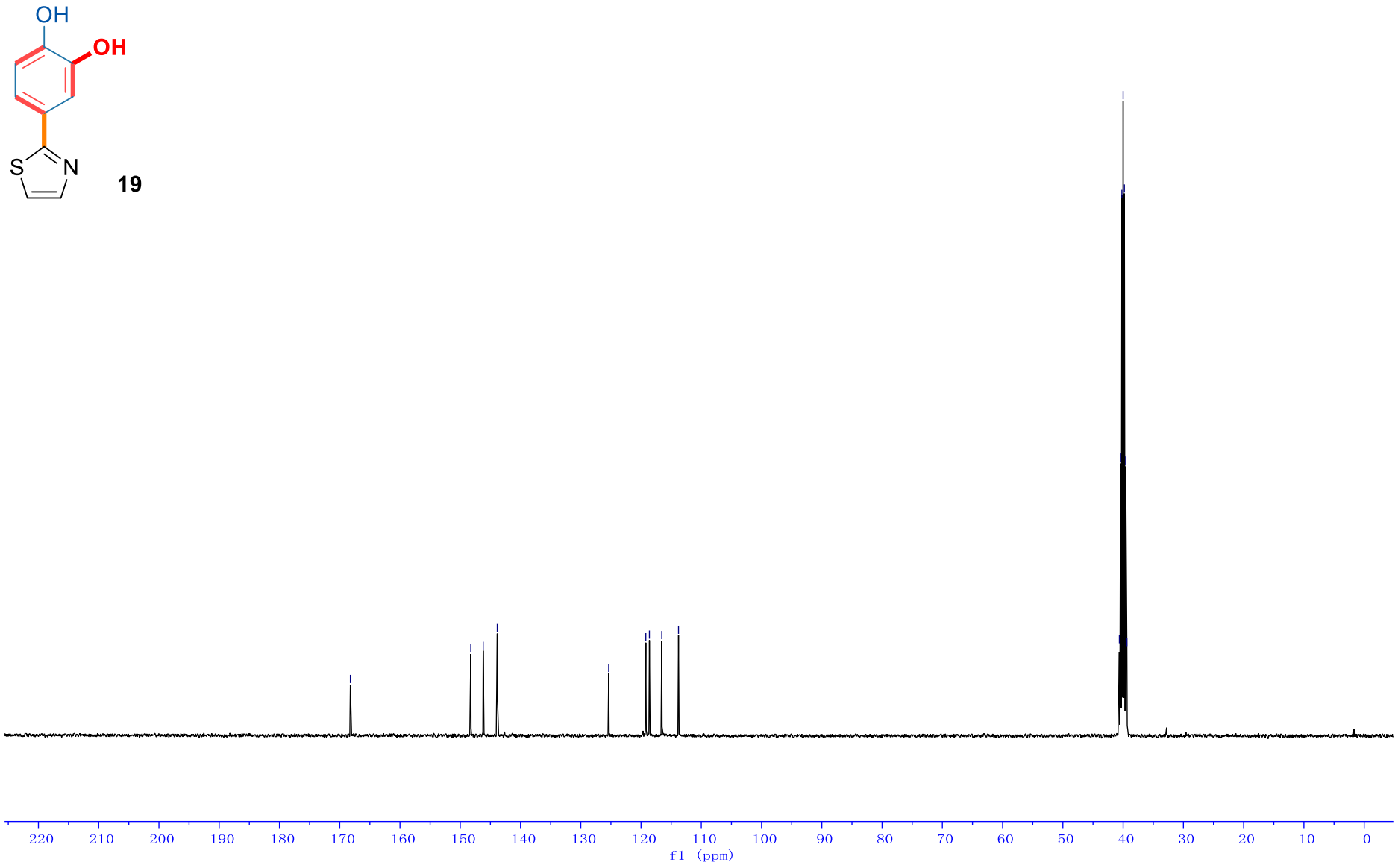

9.34
9.19
8.05
8.02
7.98
7.96
7.87
7.79
7.78
7.78
7.74
7.72
7.72
7.70
7.57
7.56
7.56
7.54
7.54
7.52
6.88
6.86
3.36 HDO
2.71
2.50 NONE
OH
OH
N
Me
18
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
3.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

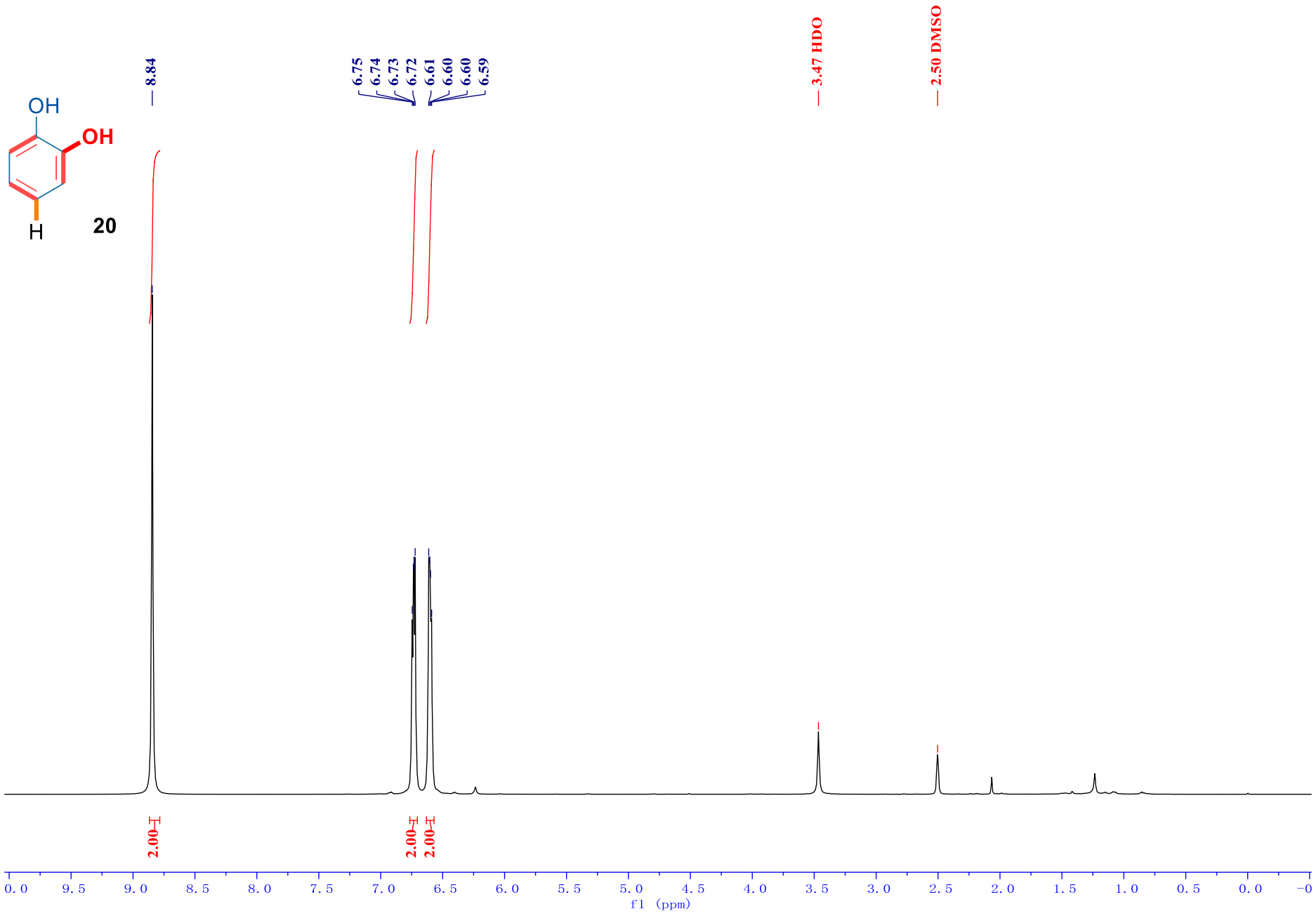

OH
OH
N
Me

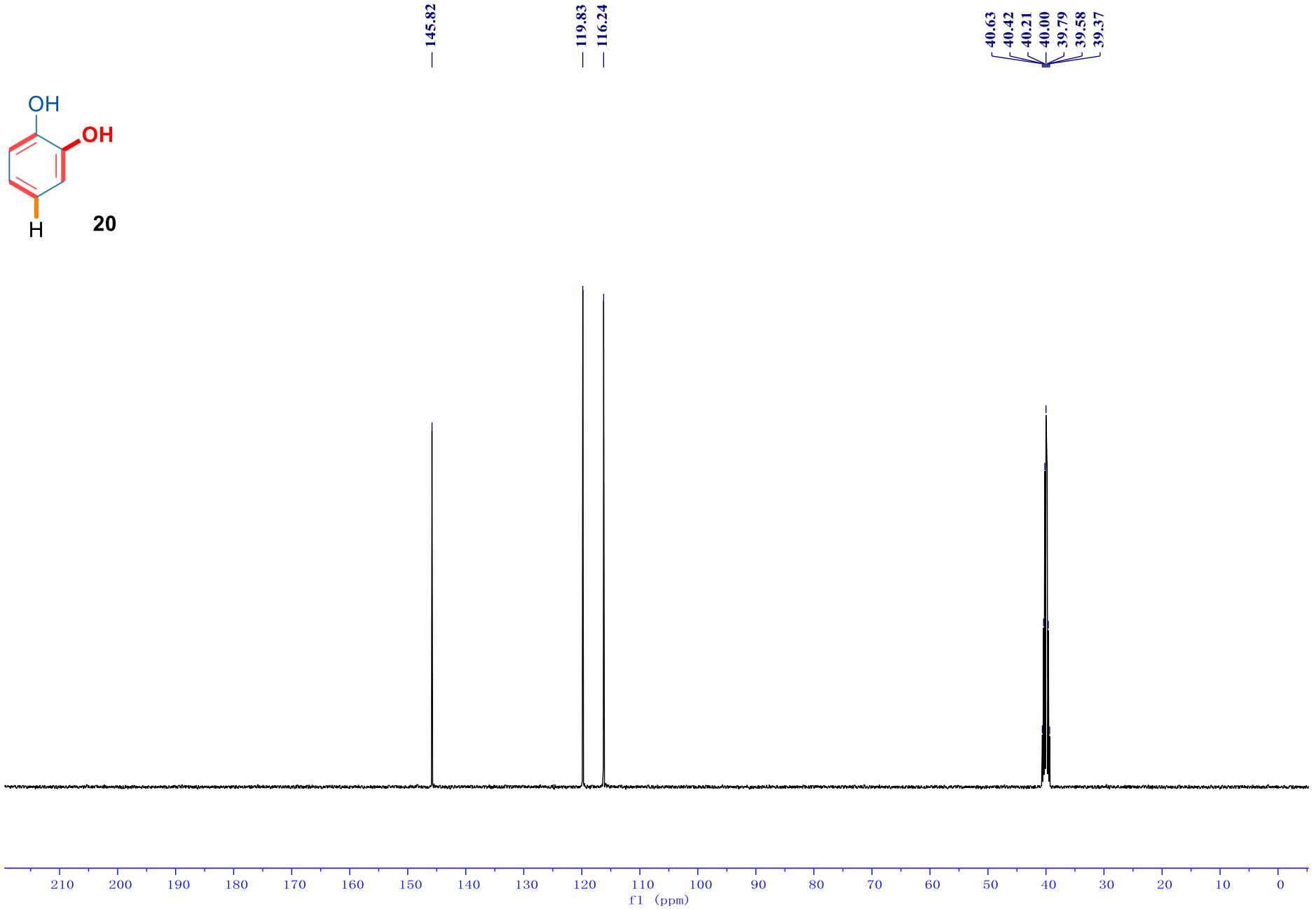
18

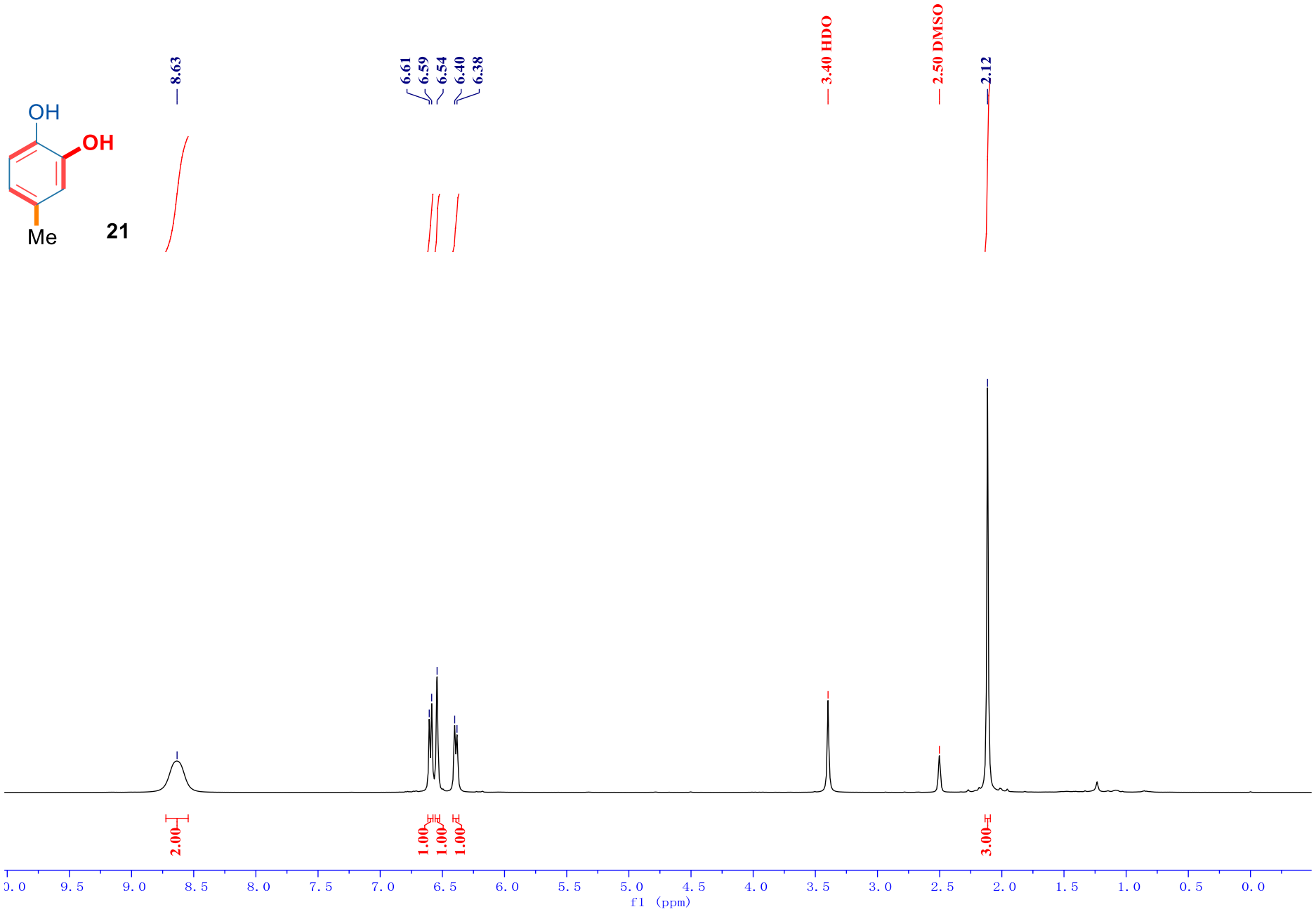
156.30
147.97
147.83
146.09
145.05
130.61
129.90
129.79
127.04
126.06
124.55
119.31
119.11
116.19
114.86
40.63
40.42
40.21
40.00
39.79
39.58
39.37
18.95
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

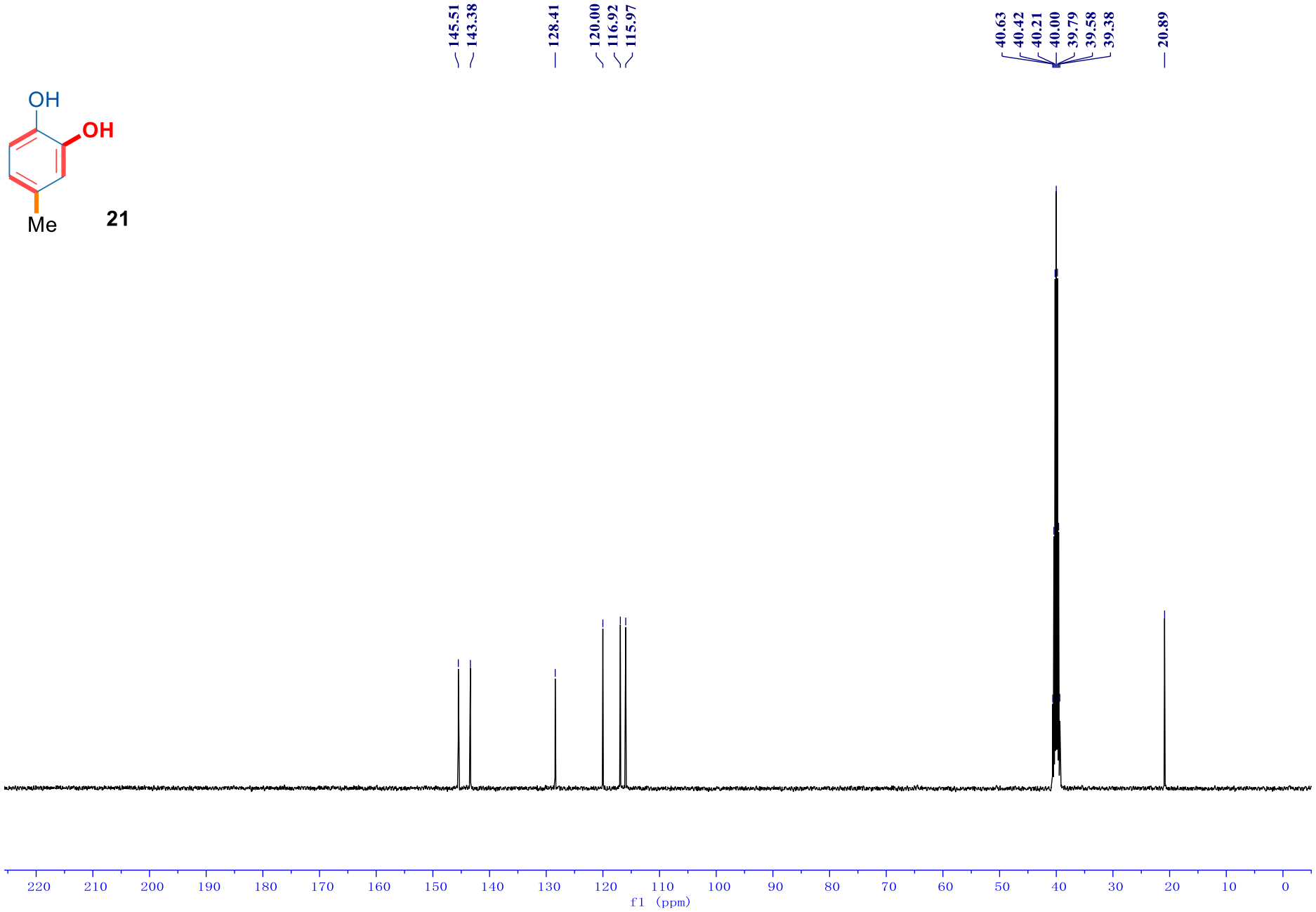

OH
OH
S
N
19
9.49
9.37
7.80
7.79
7.60
7.60
7.38
7.38
7.25
7.25
7.23
7.23
6.84
6.82
3.42 HDO
2.50 DMSO
1.00
1.00
1.00
1.00
1.00
1.00
f1 (ppm)

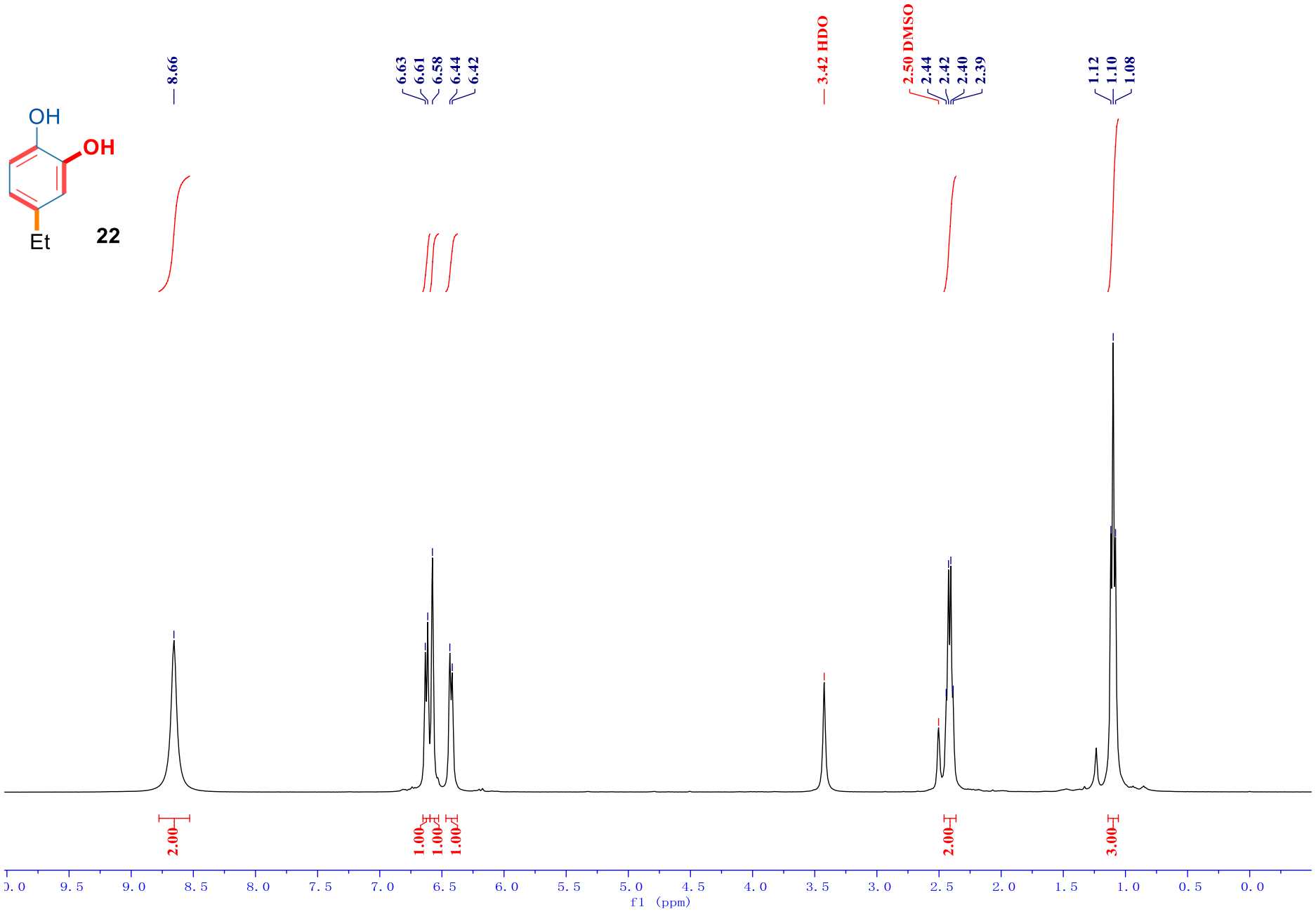

168.24
148.25
146.19
143.86
125.36
119.20
118.61
116.56
113.78
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
S
N
19
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

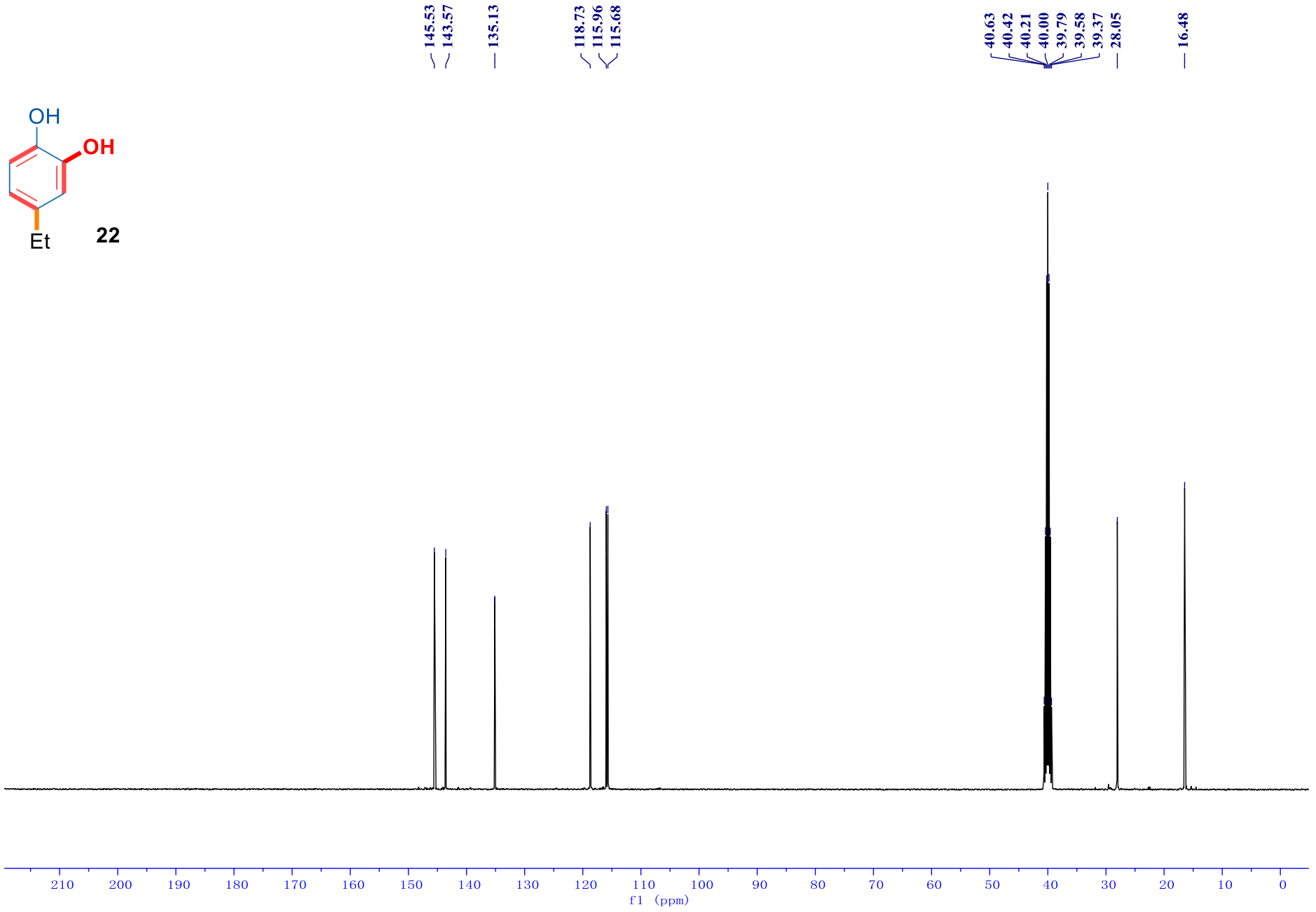

OH
OH
H
20
8.84
6.75
6.74
6.73
6.72
6.61
6.60
6.60
6.59
3.47 HDO
2.50 DMSO
2.00
2.00
2.00
f1 (ppm)

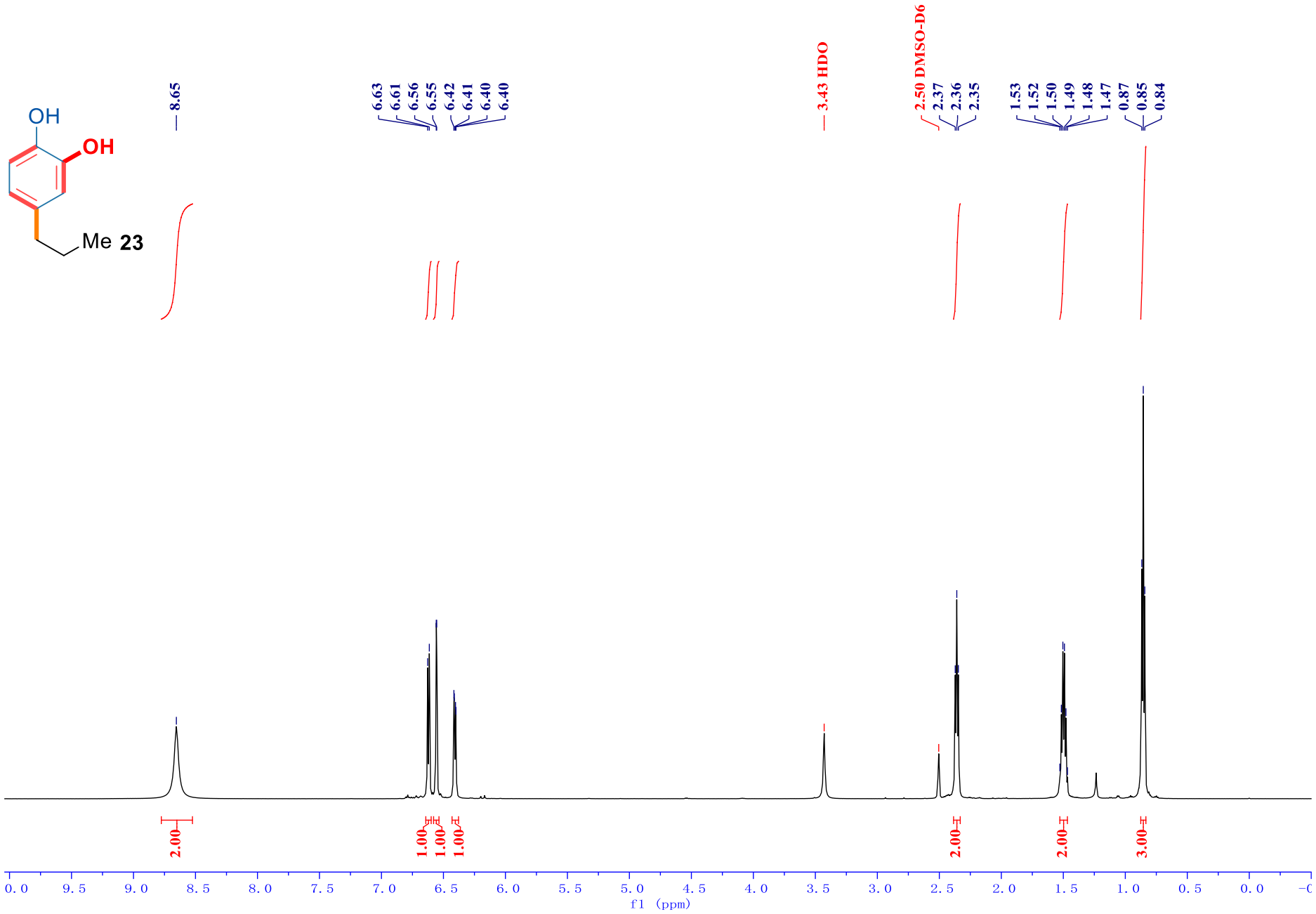

145.82
119.83
116.24
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
H
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

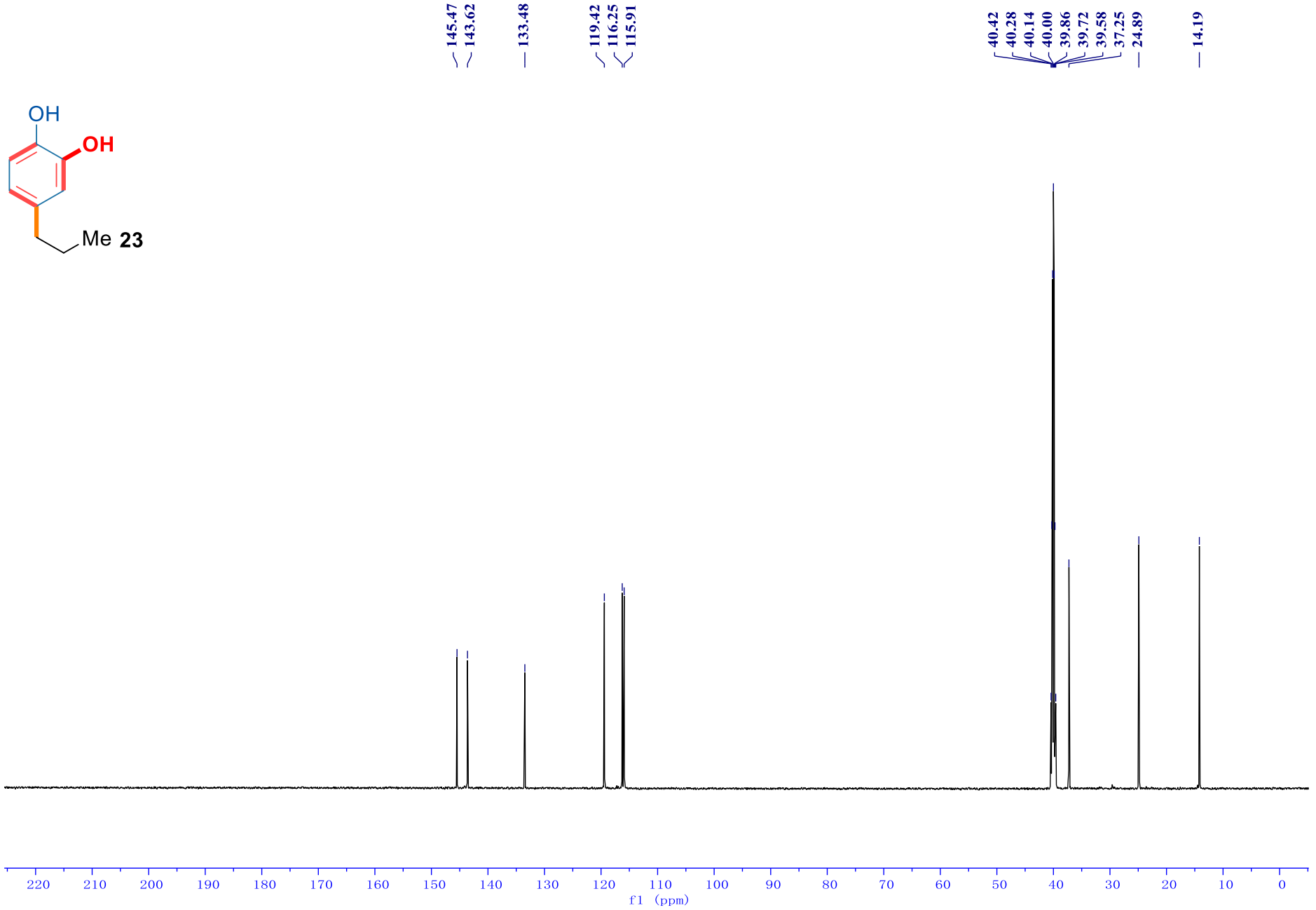

OH
OH
Me
21
8.63
6.61
6.59
6.54
6.40
6.38
3.40 HDO
2.50 DMSO
2.12
2.00
1.00
1.00
1.00
3.00
f1 (ppm)

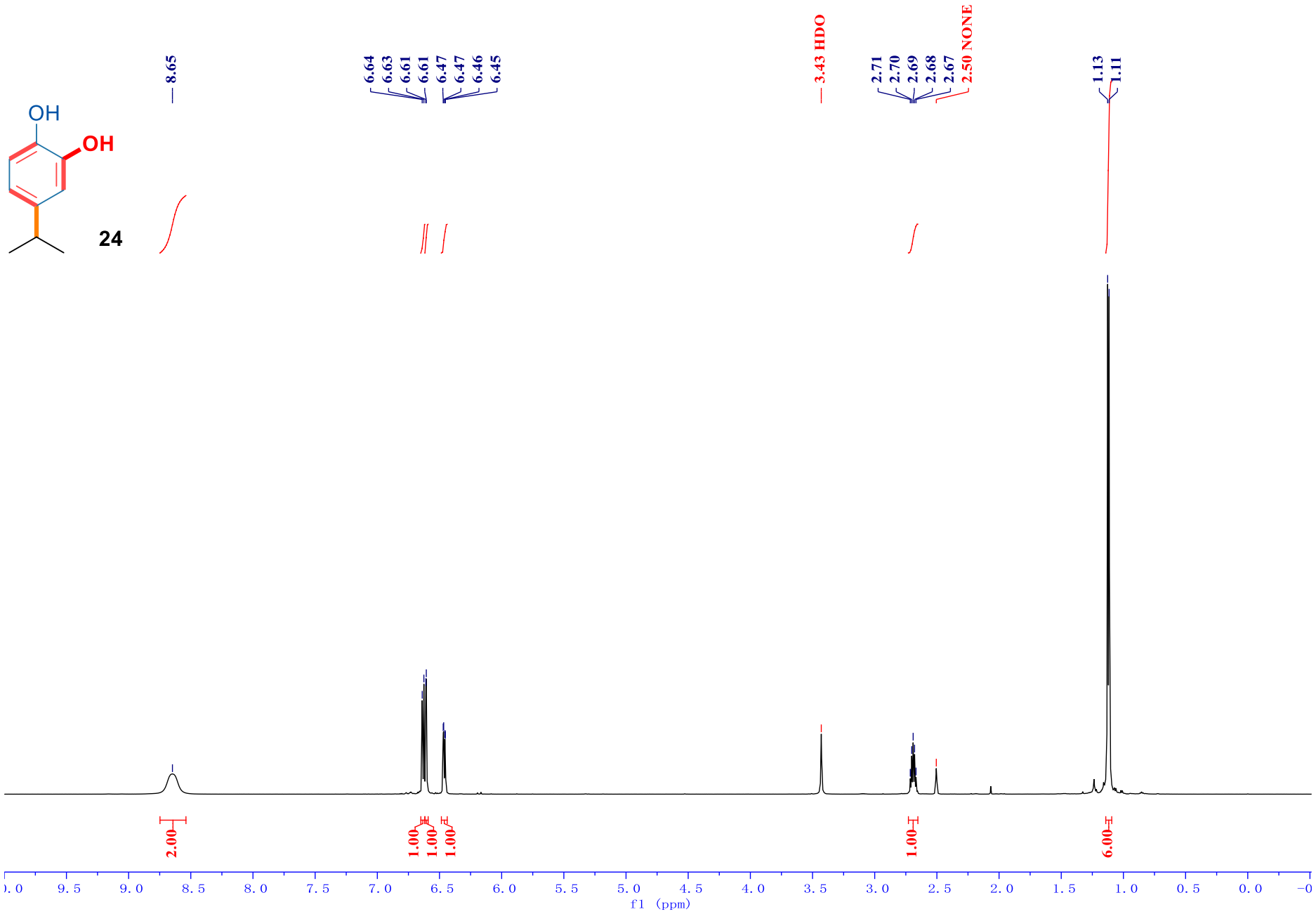

145.51
143.38
128.41
120.00
116.92
115.97
40.63
40.42
40.21
40.00
39.79
39.58
39.38
20.89
OH
OH
Me
21
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

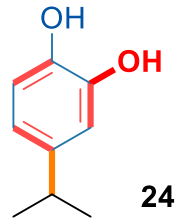

OH
OH
Et
22
8.66
6.63
6.61
6.58
6.44
6.42
3.42 HDO
2.50 DMSO
2.44
2.42
2.40
2.39
1.12
1.10
1.08
2.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)


145.53
143.57
135.13
118.73
115.96
115.68
40.63
40.42
40.21
40.00
39.79
39.58
39.37
28.05
16.48
OH
OH
Et
22
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
OH
Me
23
8.65
6.63
6.61
6.56
6.55
6.42
6.41
6.40
6.40
3.43 HDO
2.50 DMSO-D6
2.37
2.36
2.35
1.53
1.52
1.50
1.49
1.48
1.47
0.87
0.85
0.84
2.00
1.00
1.00
1.00
2.00
2.00
3.00
f1 (ppm)

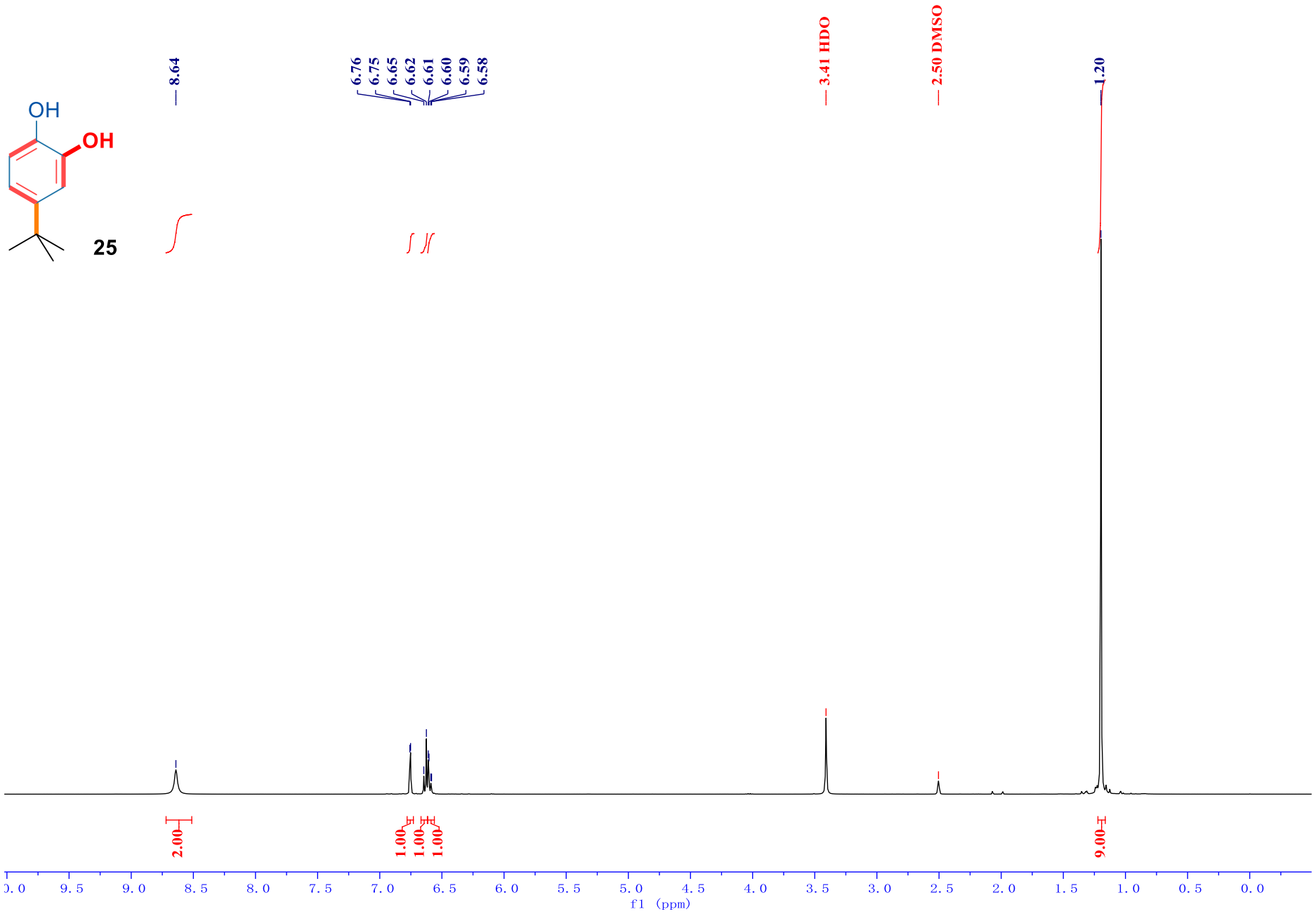

145.47
143.62
133.48
119.42
116.25
115.91
40.42
40.28
40.14
40.00
39.86
39.72
39.58
37.25
24.89
14.19
OH
OH
Me
23
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

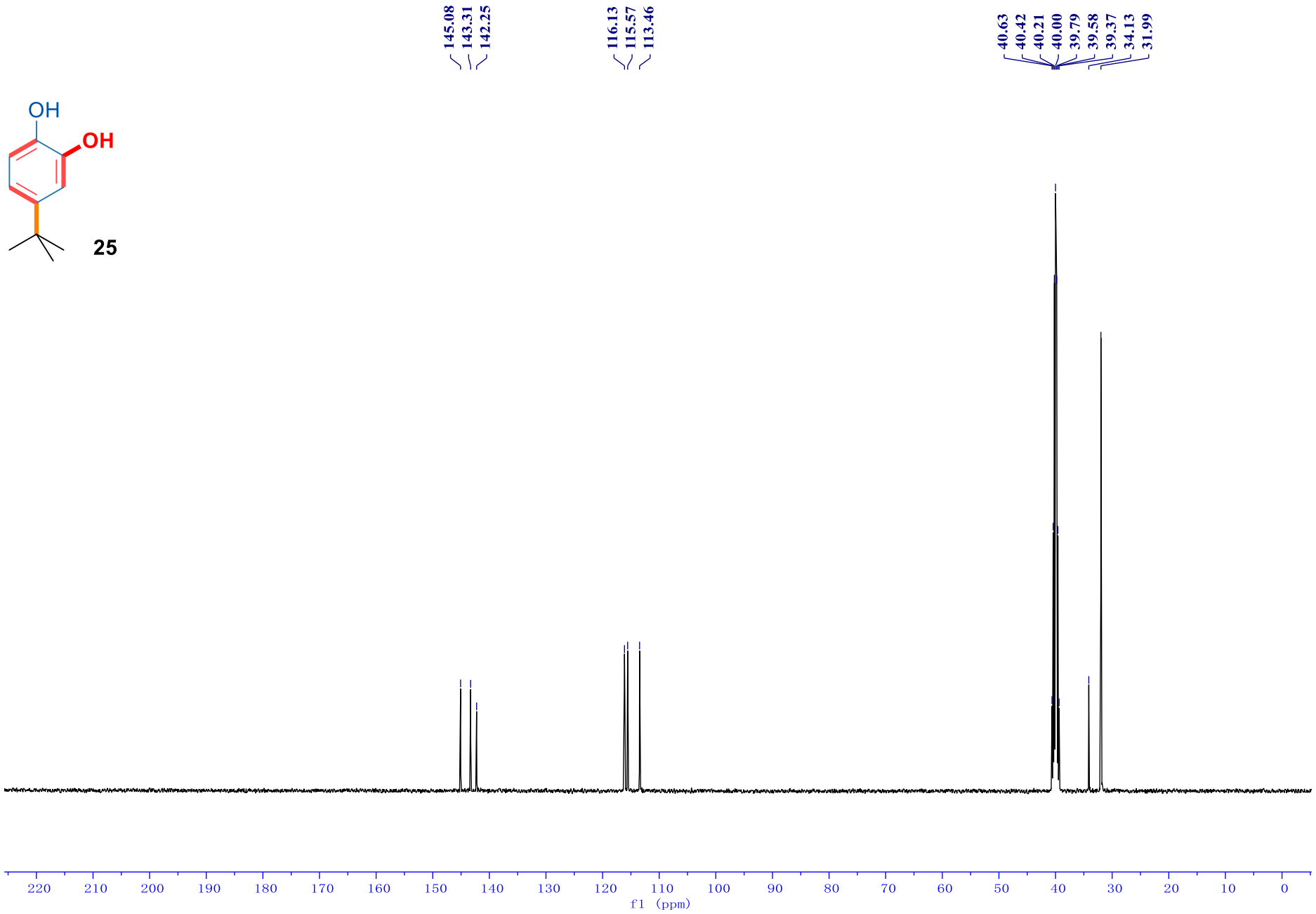

OH
OH
24
8.65
6.64
6.63
6.61
6.61
6.47
6.47
6.46
6.45
3.43 HDO
2.71
2.70
2.69
2.68
2.67
2.50 NONE
1.13
1.11
2.00
1.00
1.00
1.00
1.00
6.00
f1 (ppm)

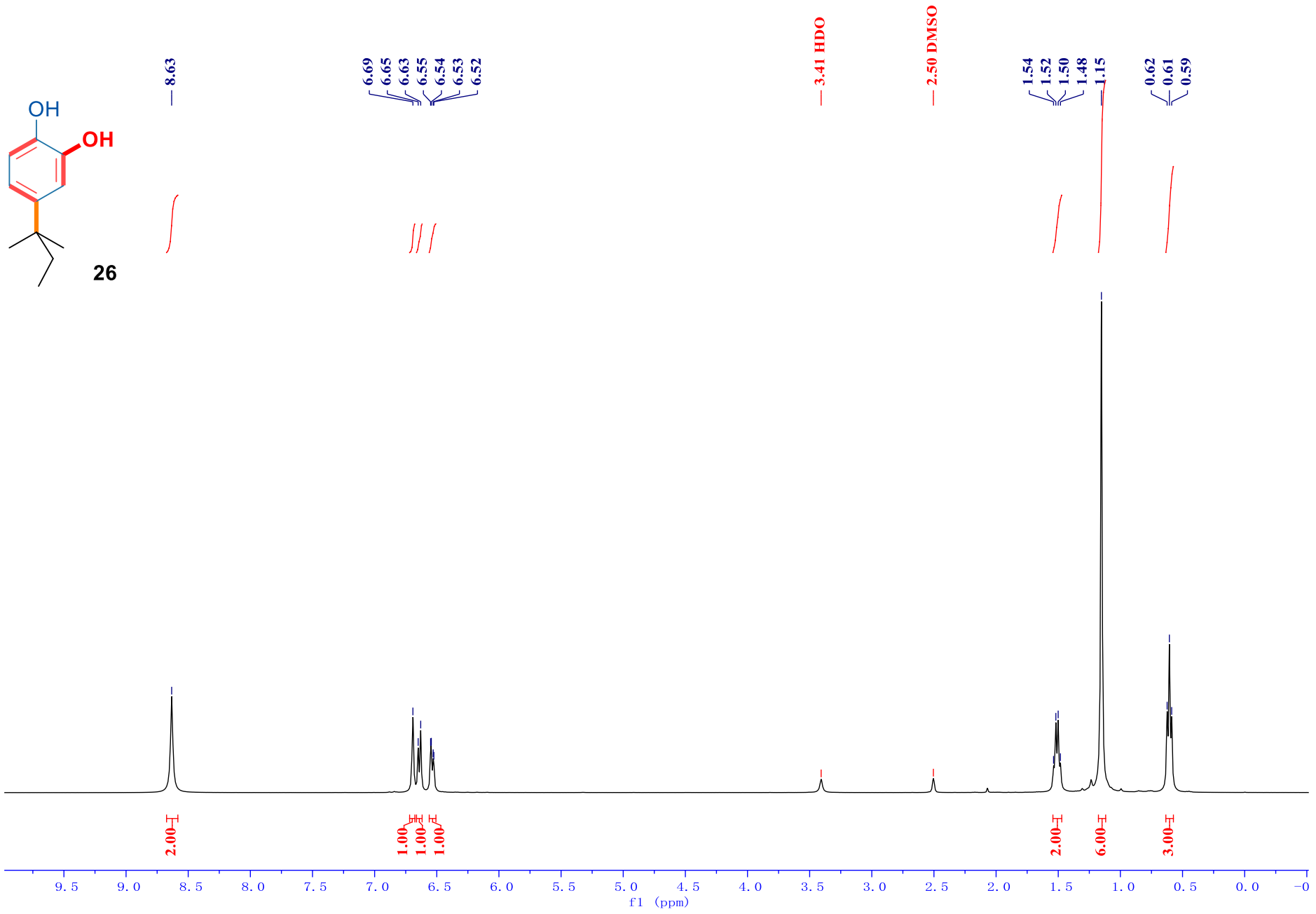

OH
OH

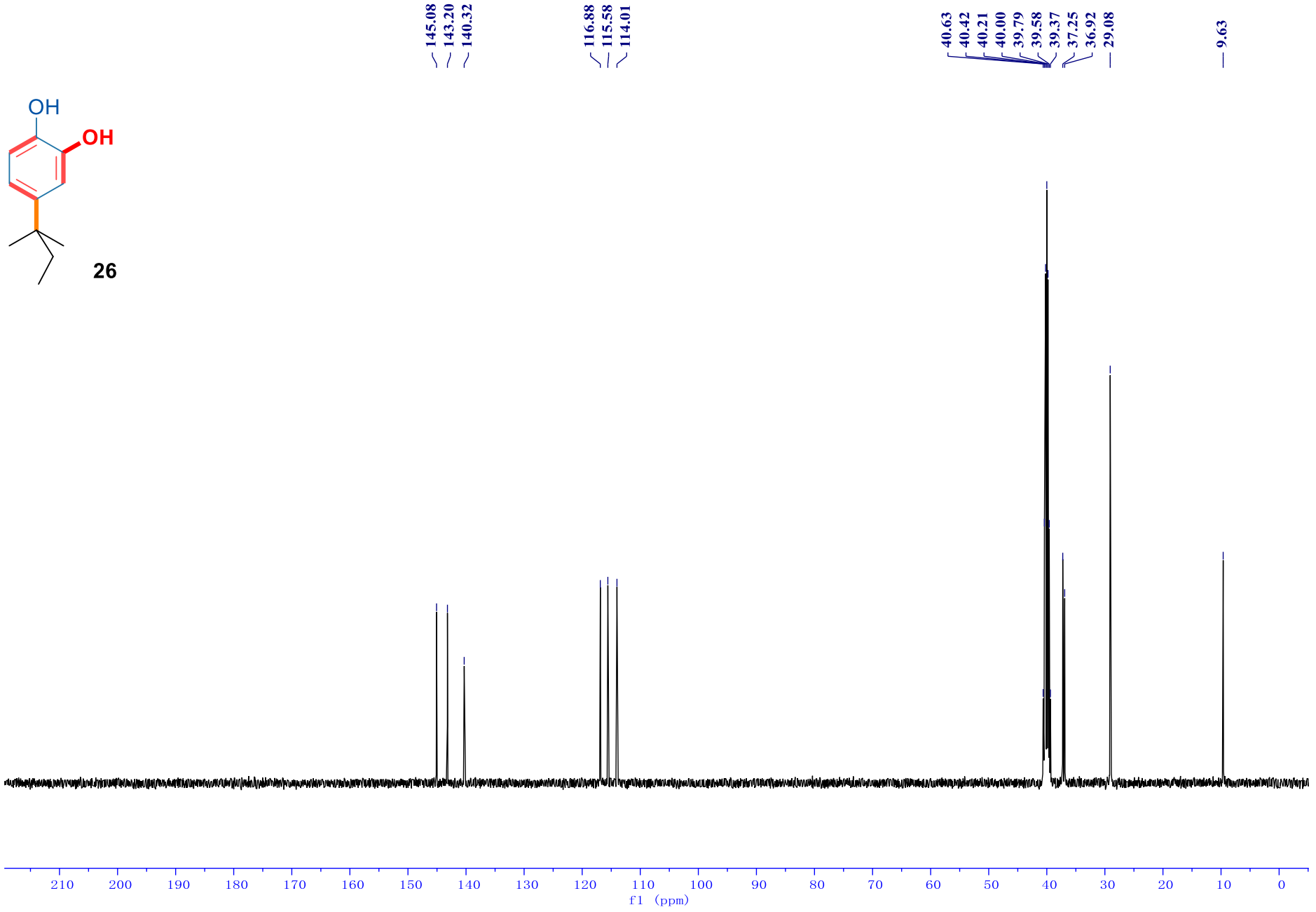
24

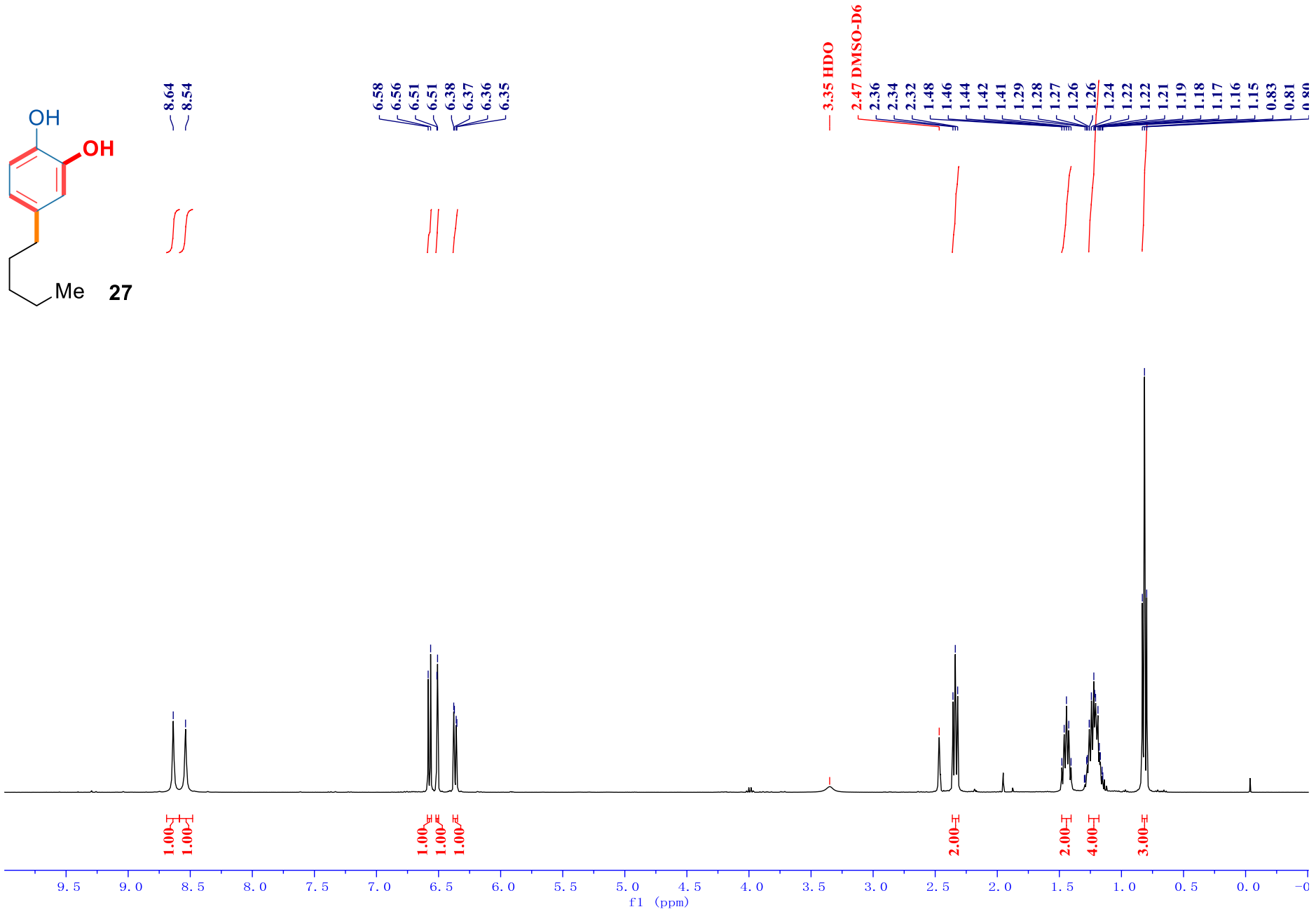
145.49
143.64
139.95
117.24
115.90
114.18
40.42
40.28
40.14
40.00
39.86
39.72
39.58
33.24
24.78
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

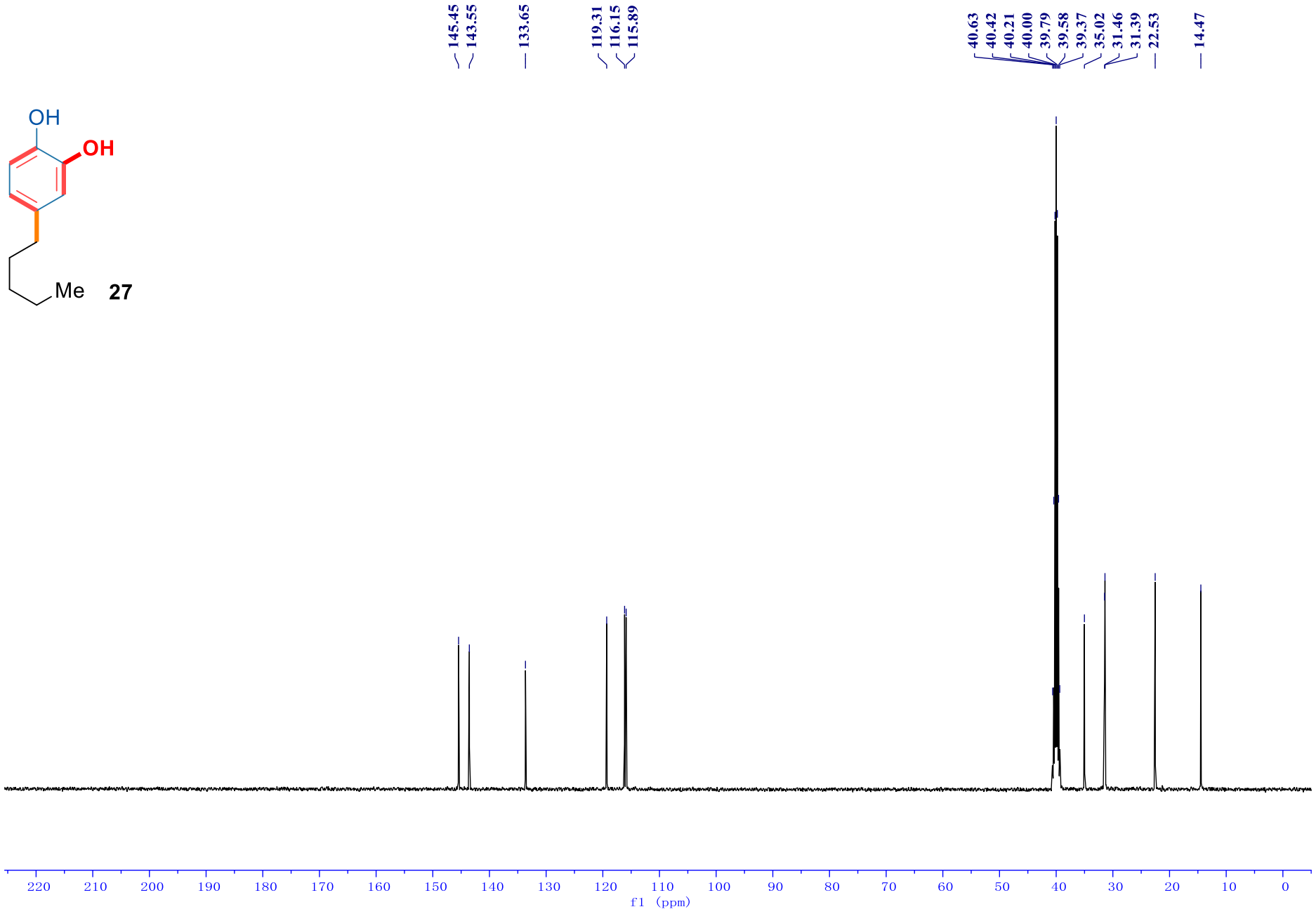

OH
OH
25
8.64
6.76
6.75
6.65
6.62
6.61
6.60
6.59
6.58
3.41 HDO
2.50 DMSO
1.20
2.00
1.00
1.00
1.00
9.00
f1 (ppm)

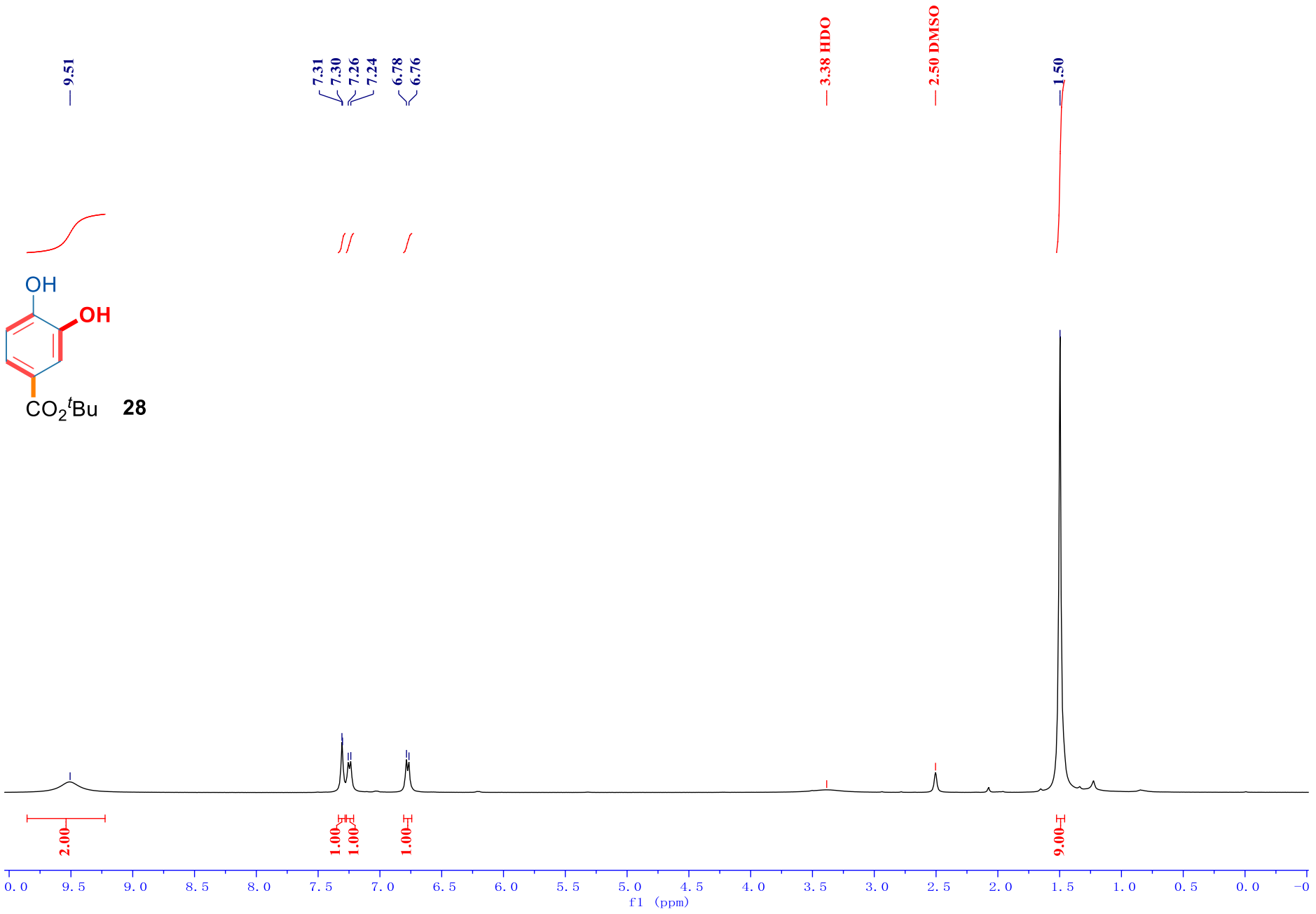

145.08
143.31
142.25
116.13
115.57
113.46
40.63
40.42
40.21
40.00
39.79
39.58
39.37
34.13
31.99
OH
OH
25
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

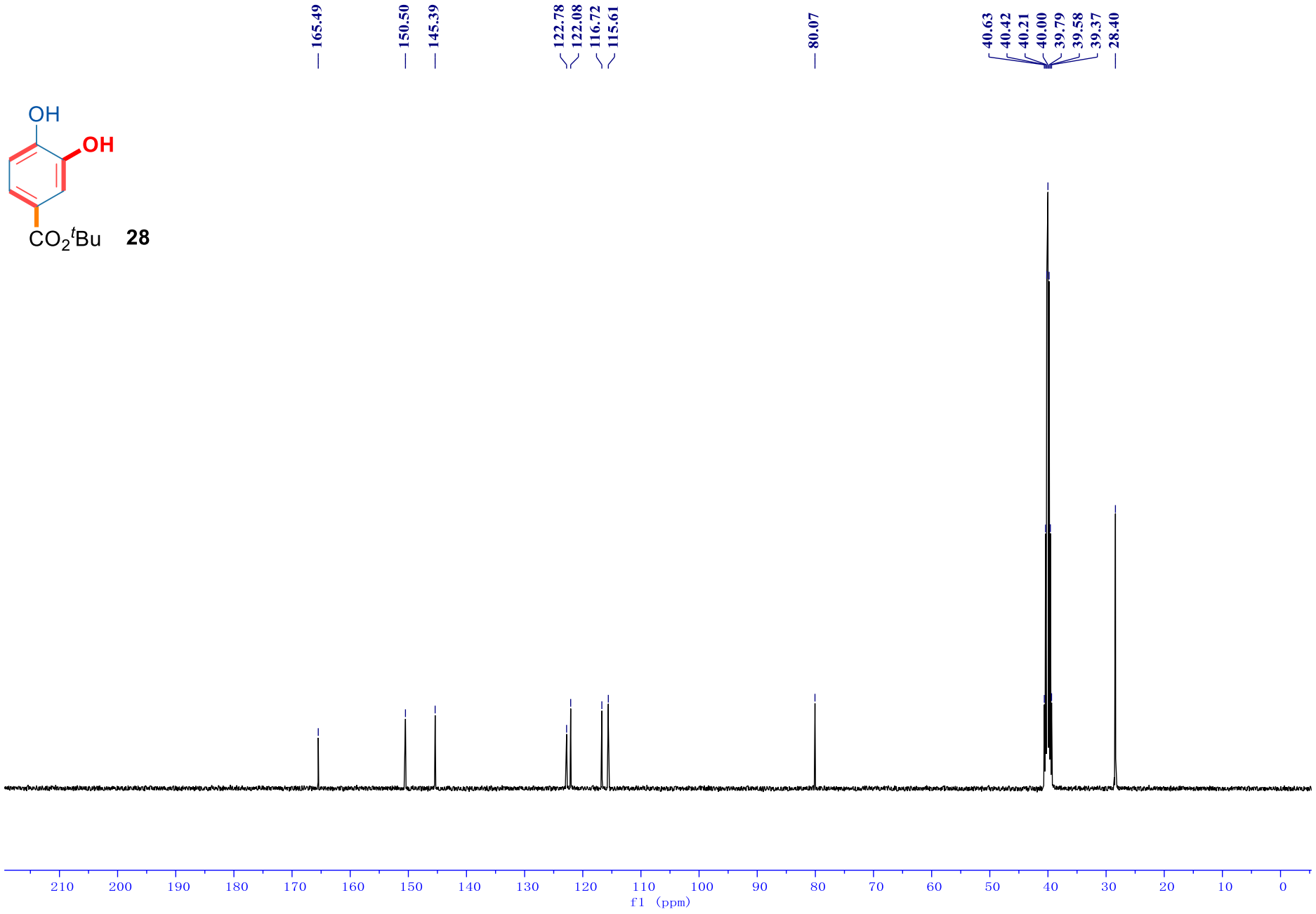

OH
OH
26
8.63
6.69
6.65
6.63
6.55
6.54
6.53
6.52
3.41 HDO
2.50 DMSO
1.54
1.52
1.50
1.48
1.15
0.62
0.61
0.59
2.00
1.00
1.00
1.00
2.00
6.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

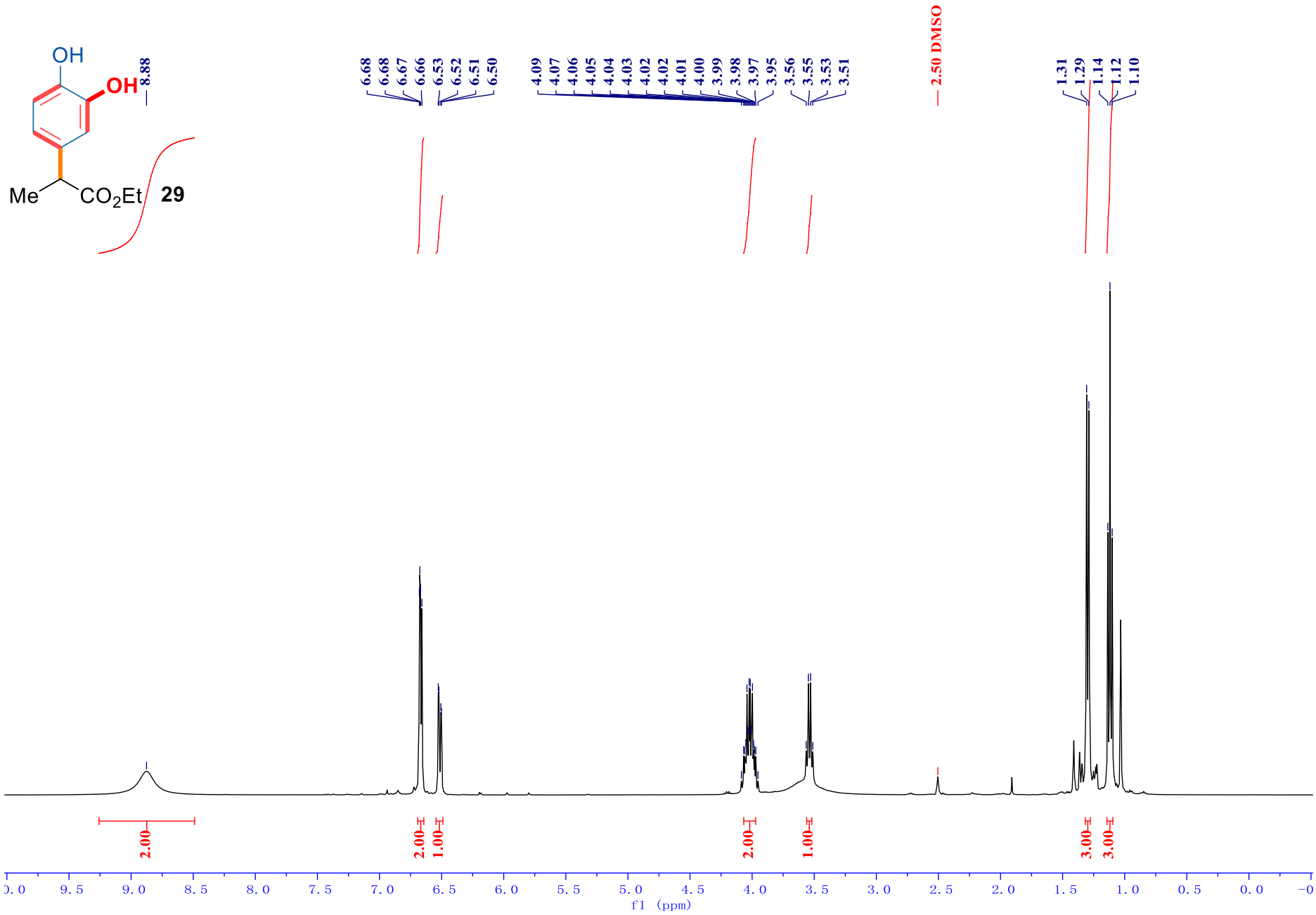

145.08
143.20
140.32
116.88
115.58
114.01
40.63
40.42
40.21
40.00
39.79
39.58
39.37
37.25
36.92
29.08
9.63
OH
OH
26
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

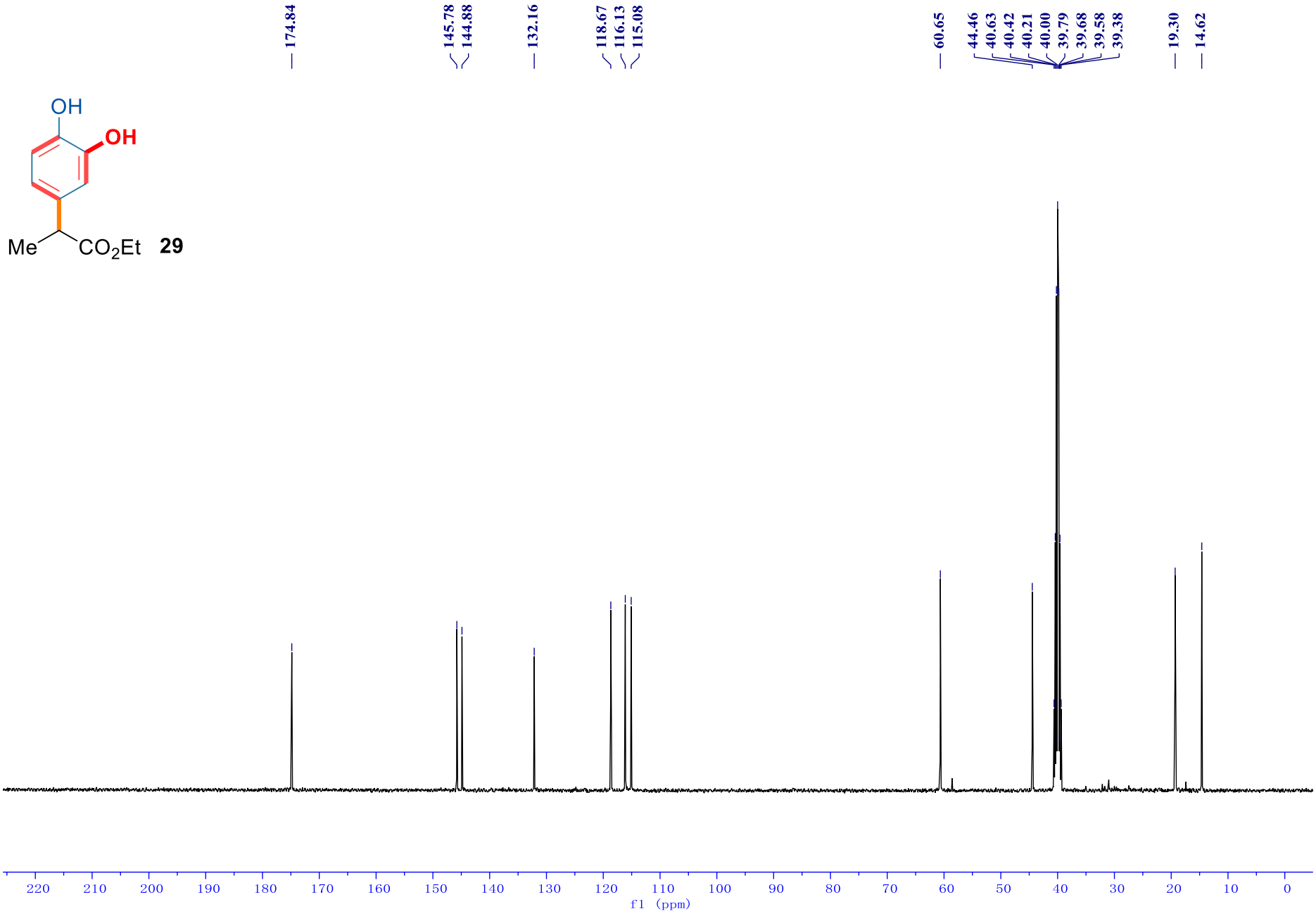

OH
OH
Me
27
8.64
8.54
6.58
6.56
6.51
6.51
6.38
6.37
6.36
6.35
3.35 HDO
2.47 DMSO-D6
2.36
2.34
2.32
1.48
1.46
1.44
1.42
1.41
1.29
1.28
1.27
1.26
1.26
1.24
1.22
1.22
1.21
1.19
1.18
1.17
1.16
1.15
0.83
0.81
1.00
1.00
1.00
1.00
1.00
2.00
2.00
4.00
3.00
f1 (ppm)

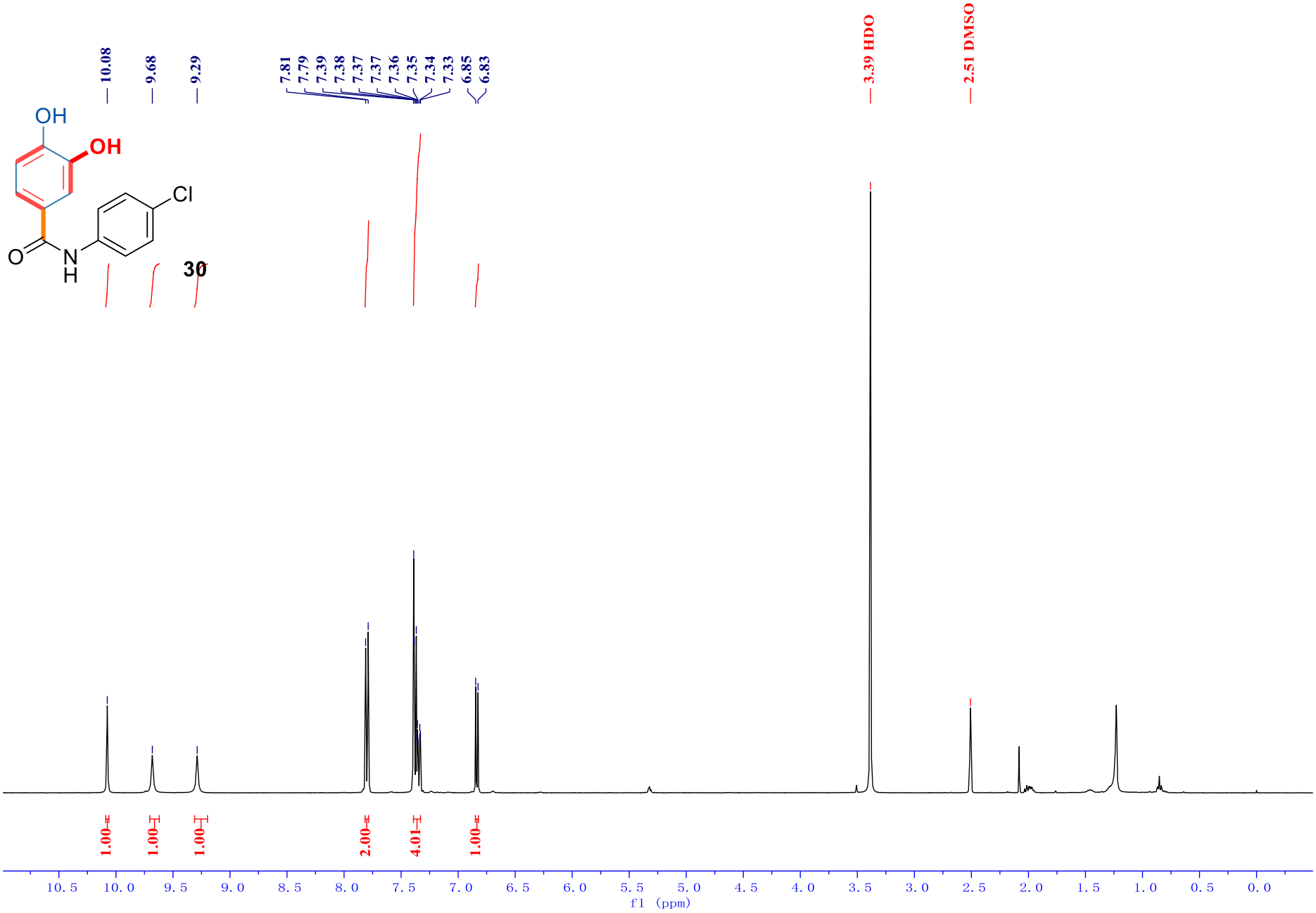

145.45
143.55
133.65
119.31
116.15
115.89
40.63
40.42
40.21
40.00
39.79
39.58
39.37
35.02
31.46
31.39
22.53
14.47
OH
OH
Me
27
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

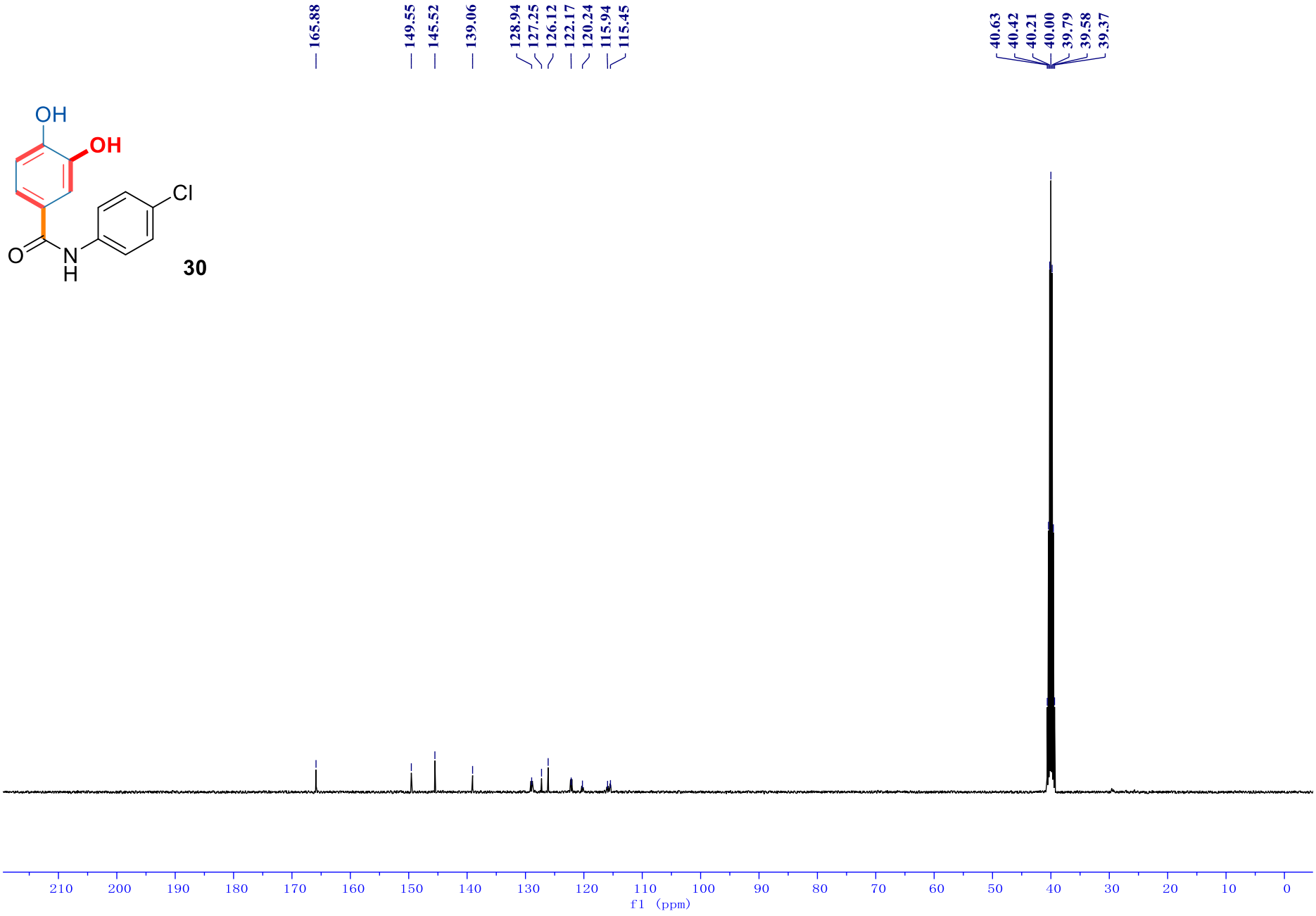

9.51
7.31
7.30
7.26
7.24
6.78
6.76
3.38 HDO
2.50 DMSO
1.50
OH
OH
CO2tBu
28
2.00
1.00
1.00
1.00
9.00
f1 (ppm)

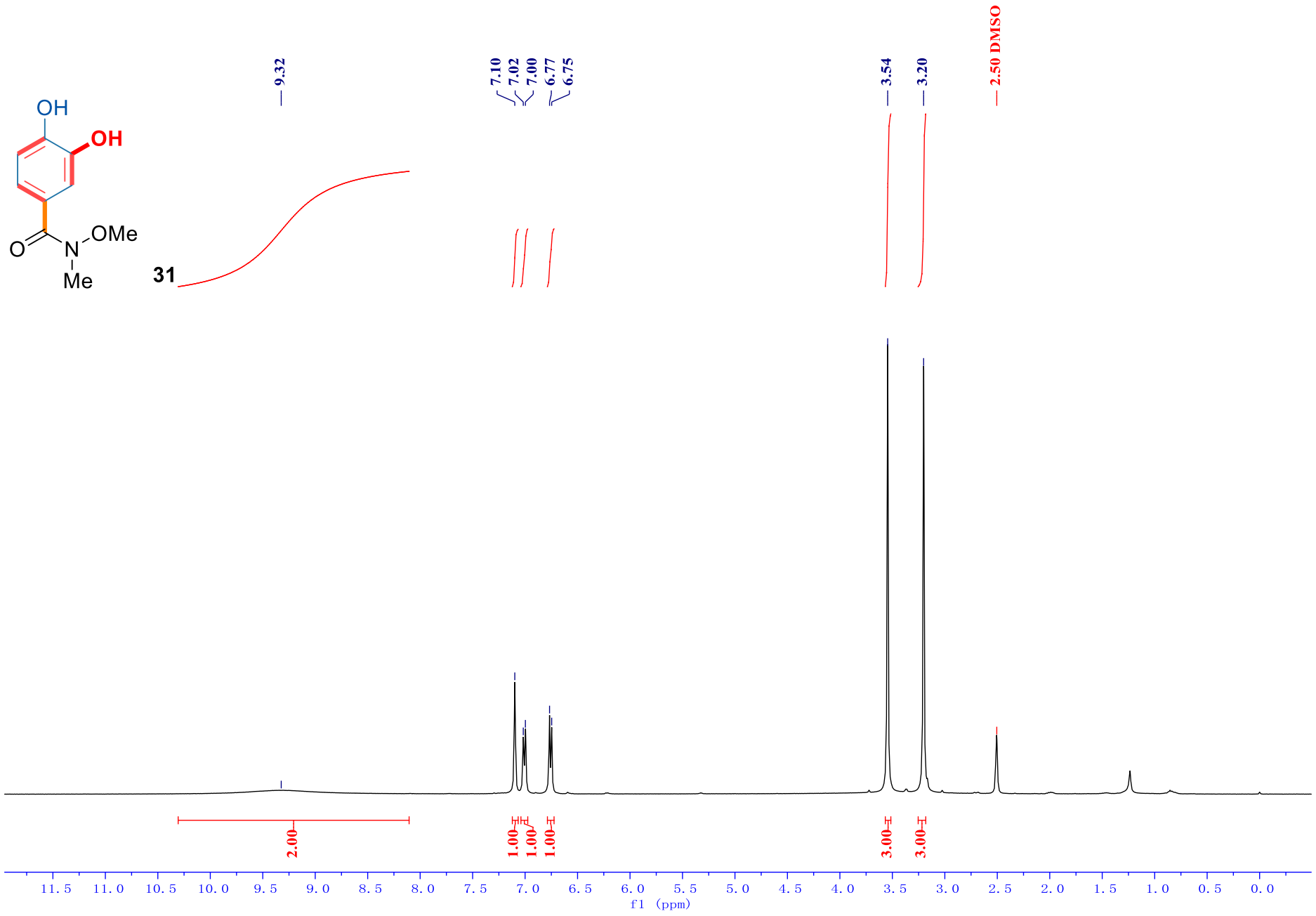

165.49
150.50
145.39
122.78
122.08
116.72
115.61
80.07
40.63
40.42
40.21
40.00
39.79
39.58
39.37
28.40
OH
OH
CO2tBu
28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

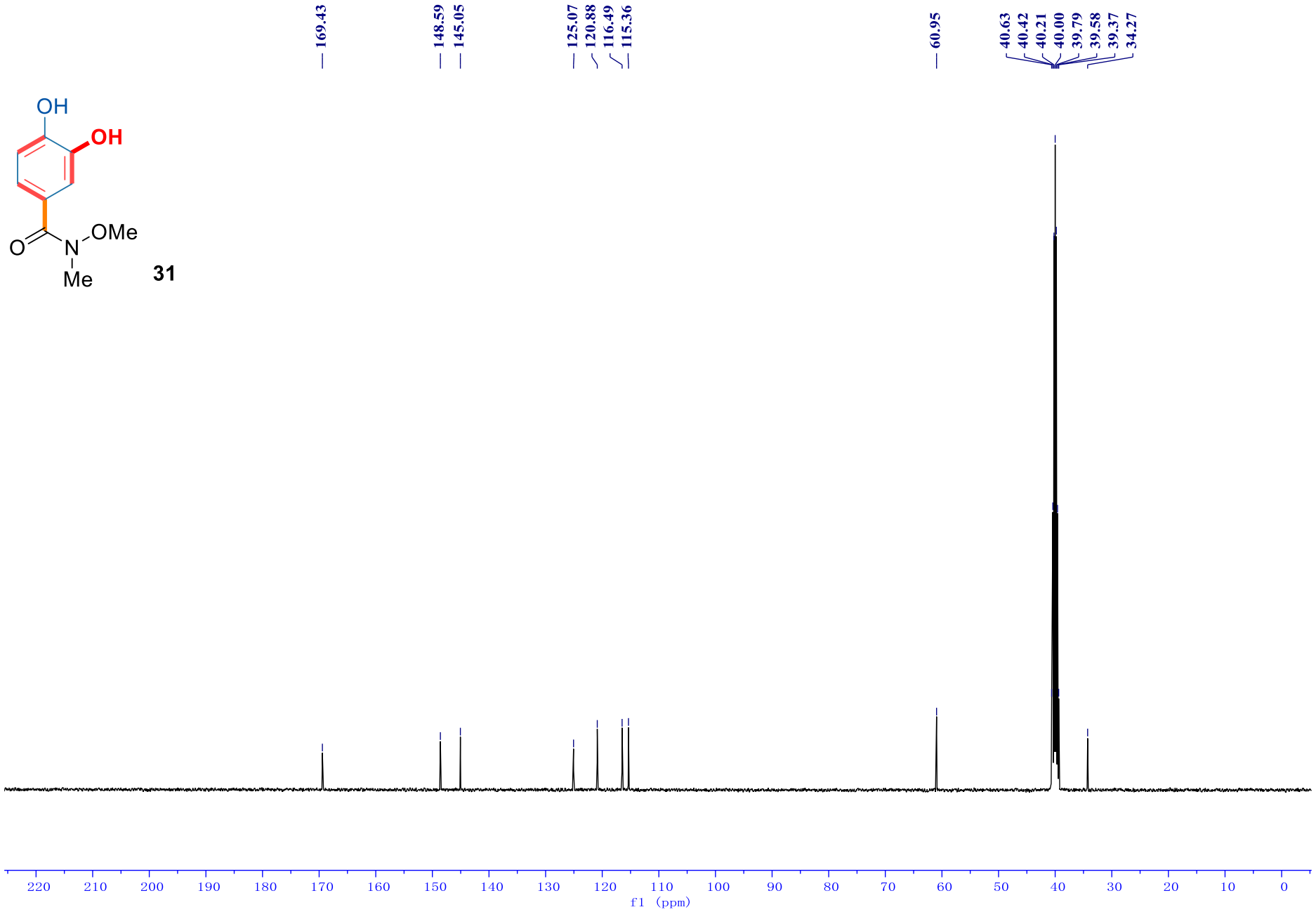

OH
OH
8.88
Me
CO2Et
29
6.68
6.68
6.67
6.66
6.53
6.52
6.51
6.50
4.09
4.07
4.06
4.05
4.04
4.03
4.02
4.02
4.01
4.00
3.99
3.98
3.97
3.95
3.56
3.55
3.53
3.51
2.50 DMSO
1.31
1.29
1.14
1.12
1.10
2.00
2.00
1.00
2.00
1.00
3.00
3.00
f1 (ppm)

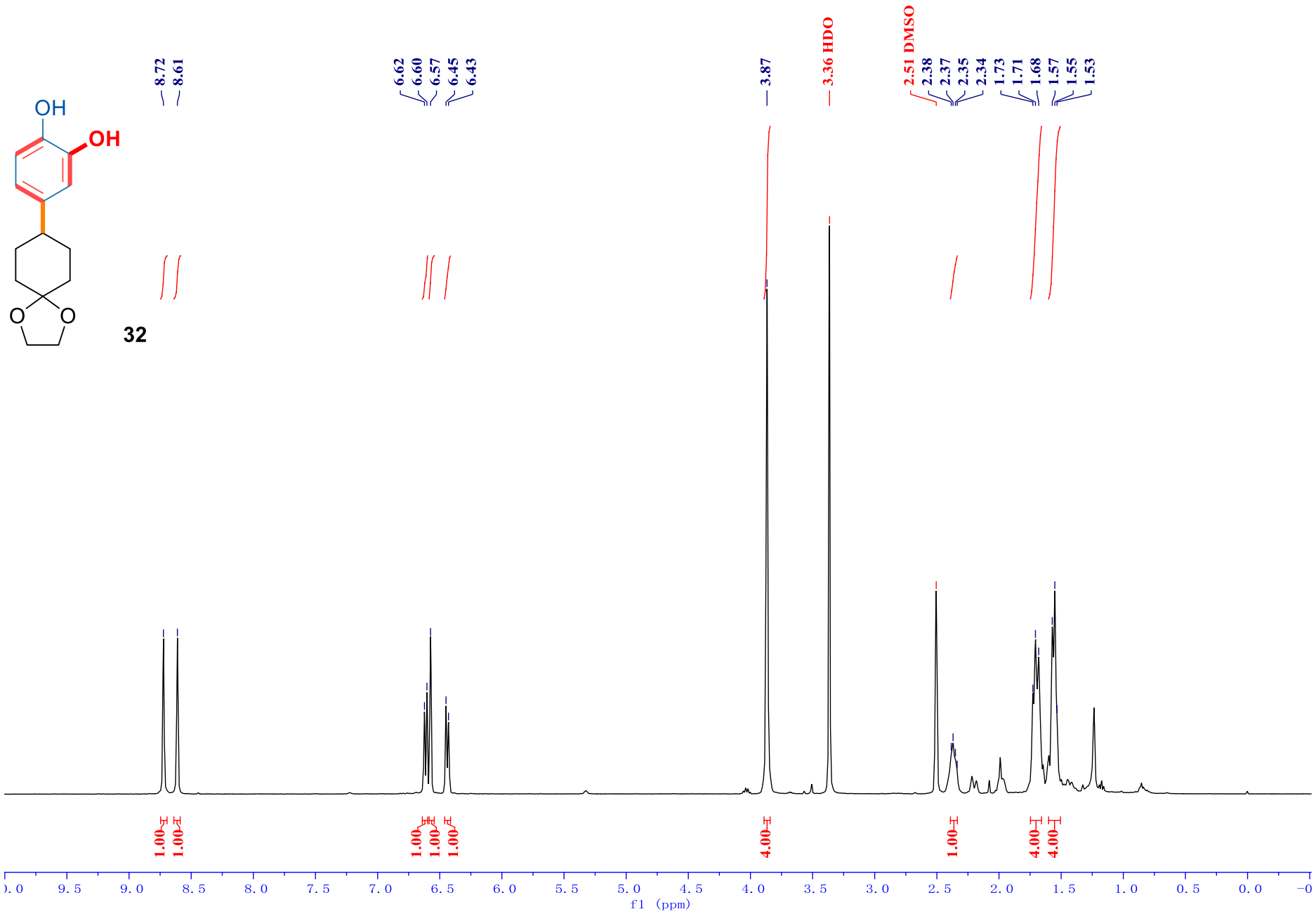

174.84
145.78
144.88
132.16
118.67
116.13
115.08
60.65
44.46
40.63
40.42
40.21
40.00
39.79
39.68
39.58
39.38
19.30
14.62
OH
OH
Me
CO2Et
29
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

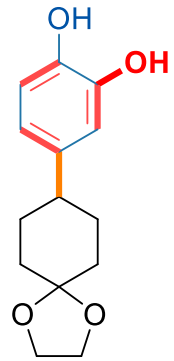

10.08
9.68
9.29
7.81
7.79
7.39
7.38
7.37
7.37
7.36
7.35
7.34
7.33
6.85
6.83
3.39 HDO
2.51 DMSO
OH
OH
Cl
O
N
H
30
1.00
1.00
1.00
2.00
4.01
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


165.88
149.55
145.52
139.06
128.94
127.25
126.12
122.17
120.24
115.94
115.45
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
Cl
O
N
H
30
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
OH
O
N
OMe
Me
31
9.32
7.10
7.02
7.00
6.77
6.75
3.54
3.20
2.50 DMSO
2.00
1.00
1.00
1.00
3.00
3.00
11.5 11.0 10.5 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)

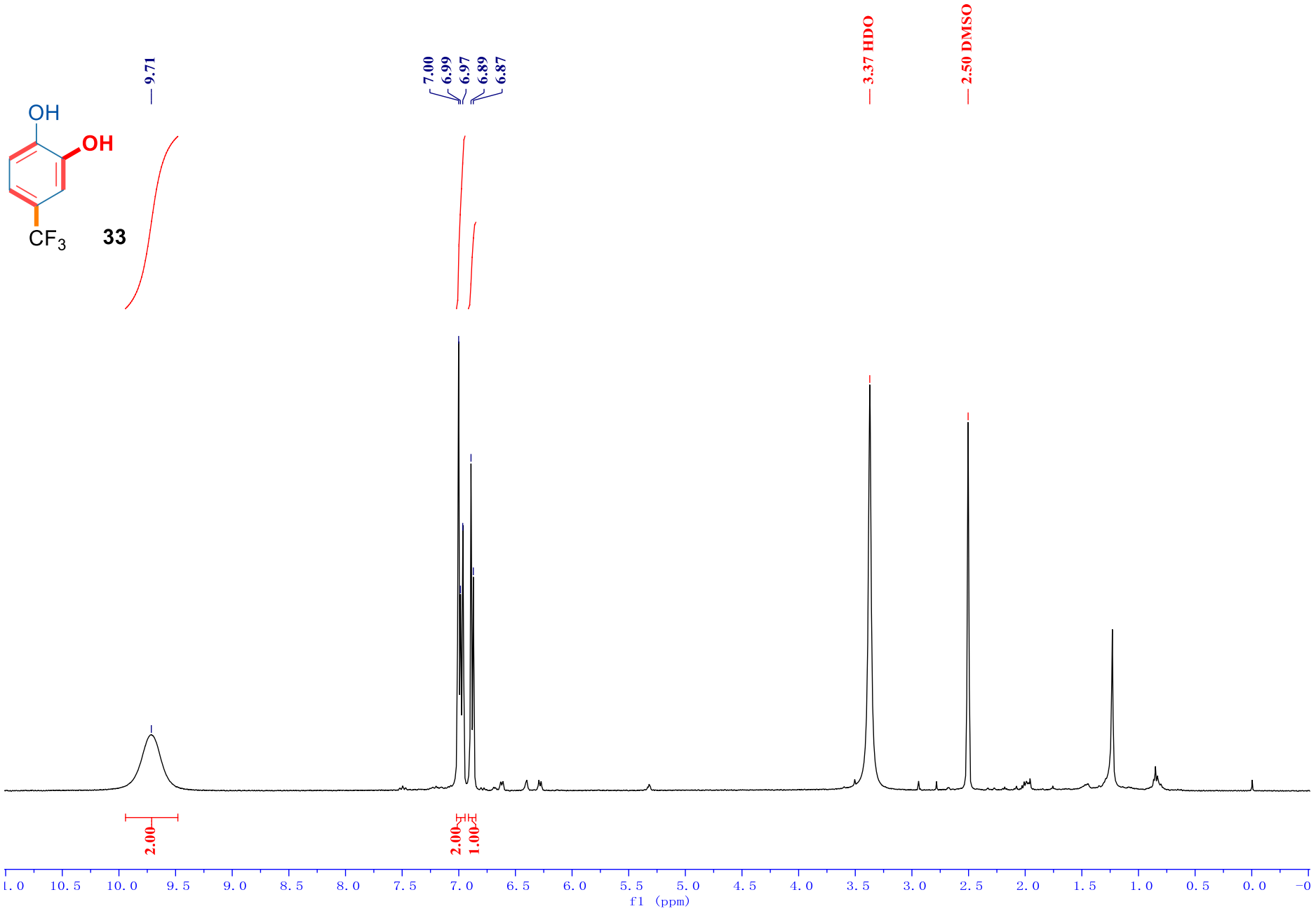

169.43
148.59
145.05
125.07
120.88
116.49
115.36
60.95
40.63
40.42
40.21
40.00
39.79
39.58
39.37
34.27
OH
OH
O
N
OMe
Me
31
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

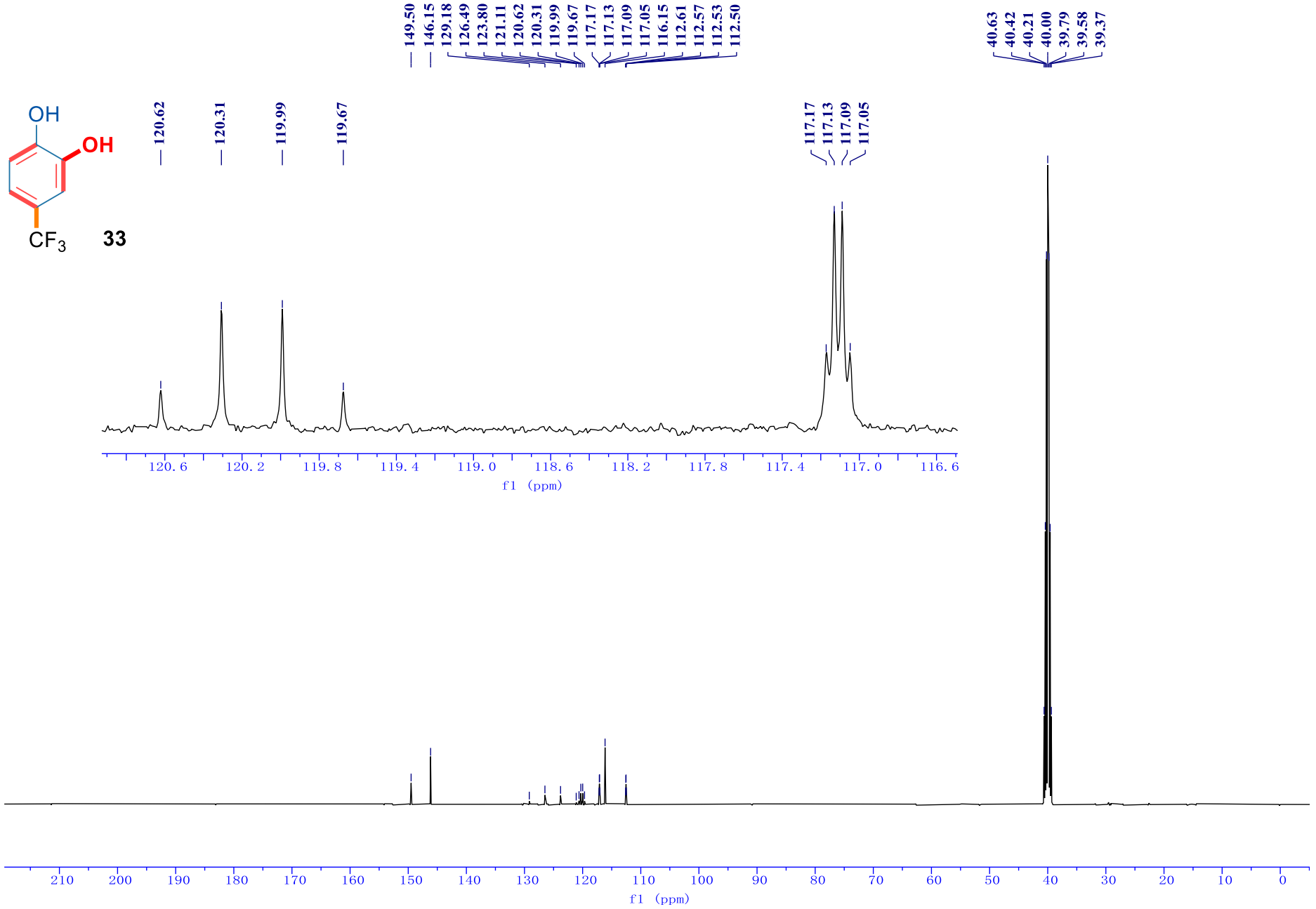

OH
OH
O
O
32
8.72
8.61
6.62
6.60
6.57
6.45
6.43
3.87
3.36 HDO
2.51 DMSO
2.38
2.37
2.35
2.34
1.73
1.71
1.68
1.57
1.55
1.53
1.00
1.00
1.00
1.00
1.00
4.00
1.00
4.00
4.00
f1 (ppm)

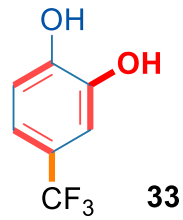

OH
OH
O
O

32

145.40
143.71
137.91
117.53
115.85
114.37
108.16
64.11
64.04
42.03
40.58
40.37
40.16
39.95
39.74
39.53
39.33
35.12
31.98
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

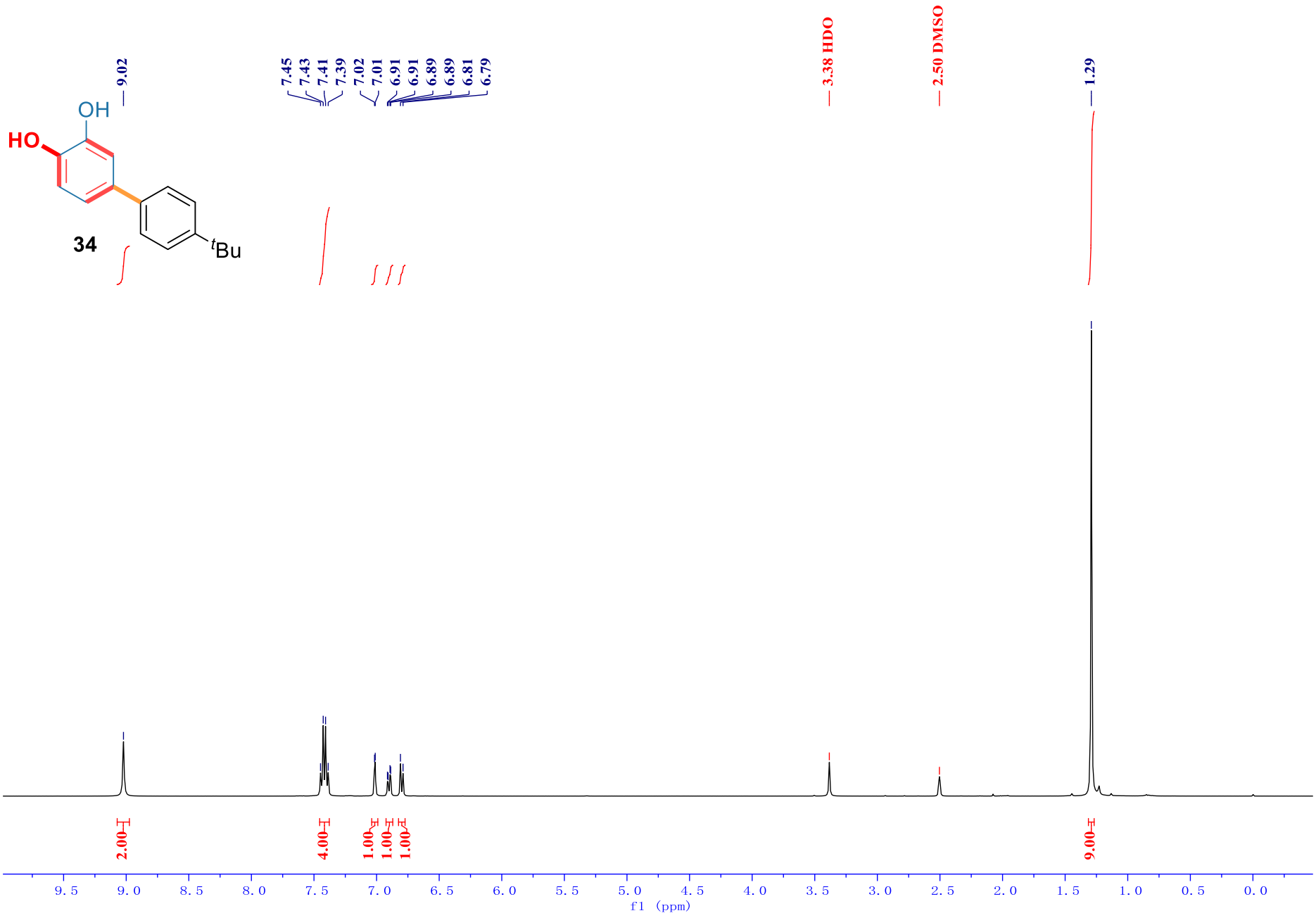

OH
OH
CF3
33
9.71
7.00
6.99
6.97
6.89
6.87
3.37 HDO
2.50 DMSO
2.00
2.00
1.00
f1 (ppm)

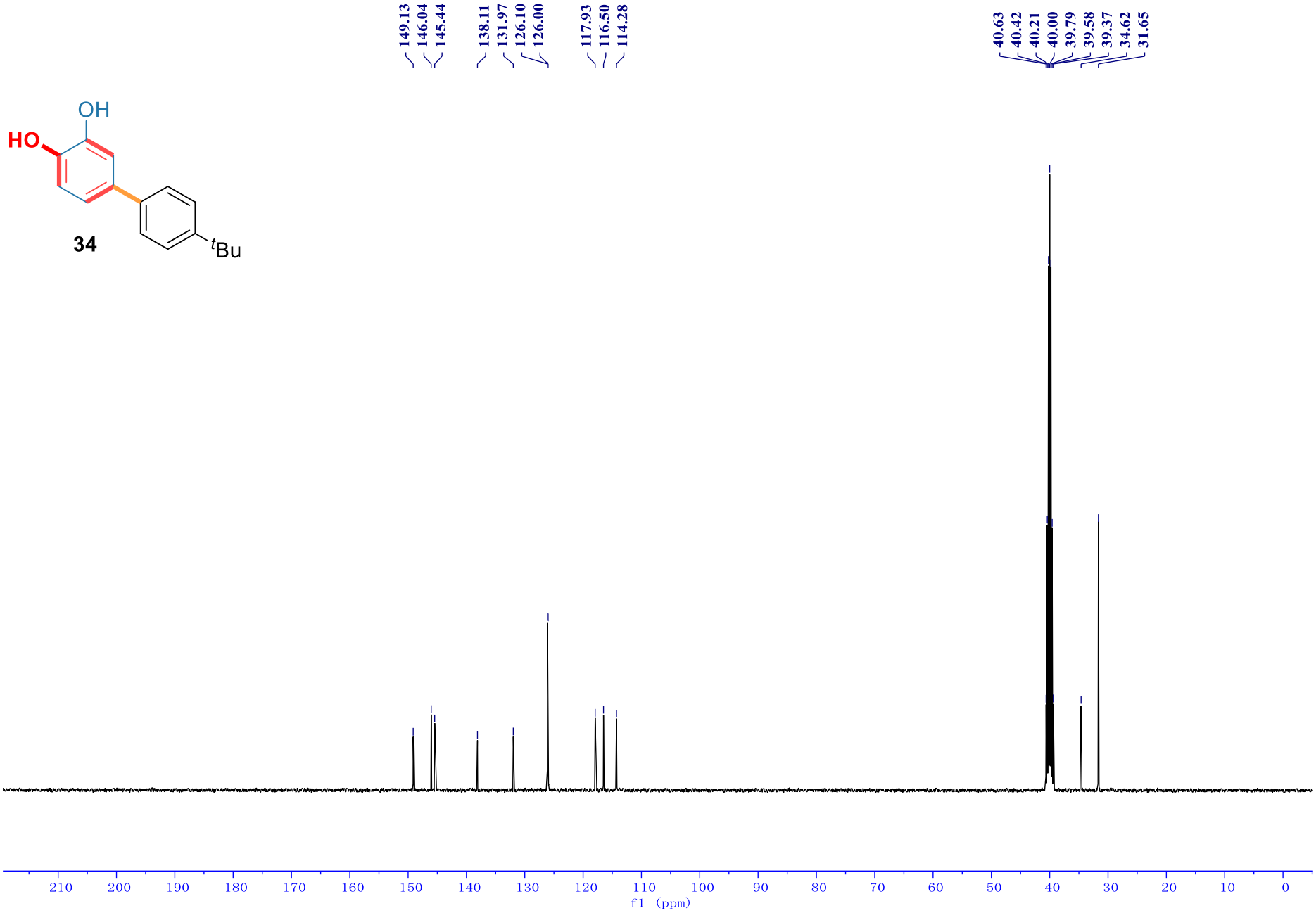

149.50
146.15
129.18
126.49
123.80
121.11
120.62
120.31
119.99
119.67
117.17
117.13
117.09
117.05
116.15
112.61
112.57
112.53
112.50
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
CF3
33
120.62
120.31
119.99
119.67
117.17
117.13
117.09
117.05
120.6
120.2
119.8
119.4
119.0
118.6
118.2
117.8
117.4
117.0
116.6
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

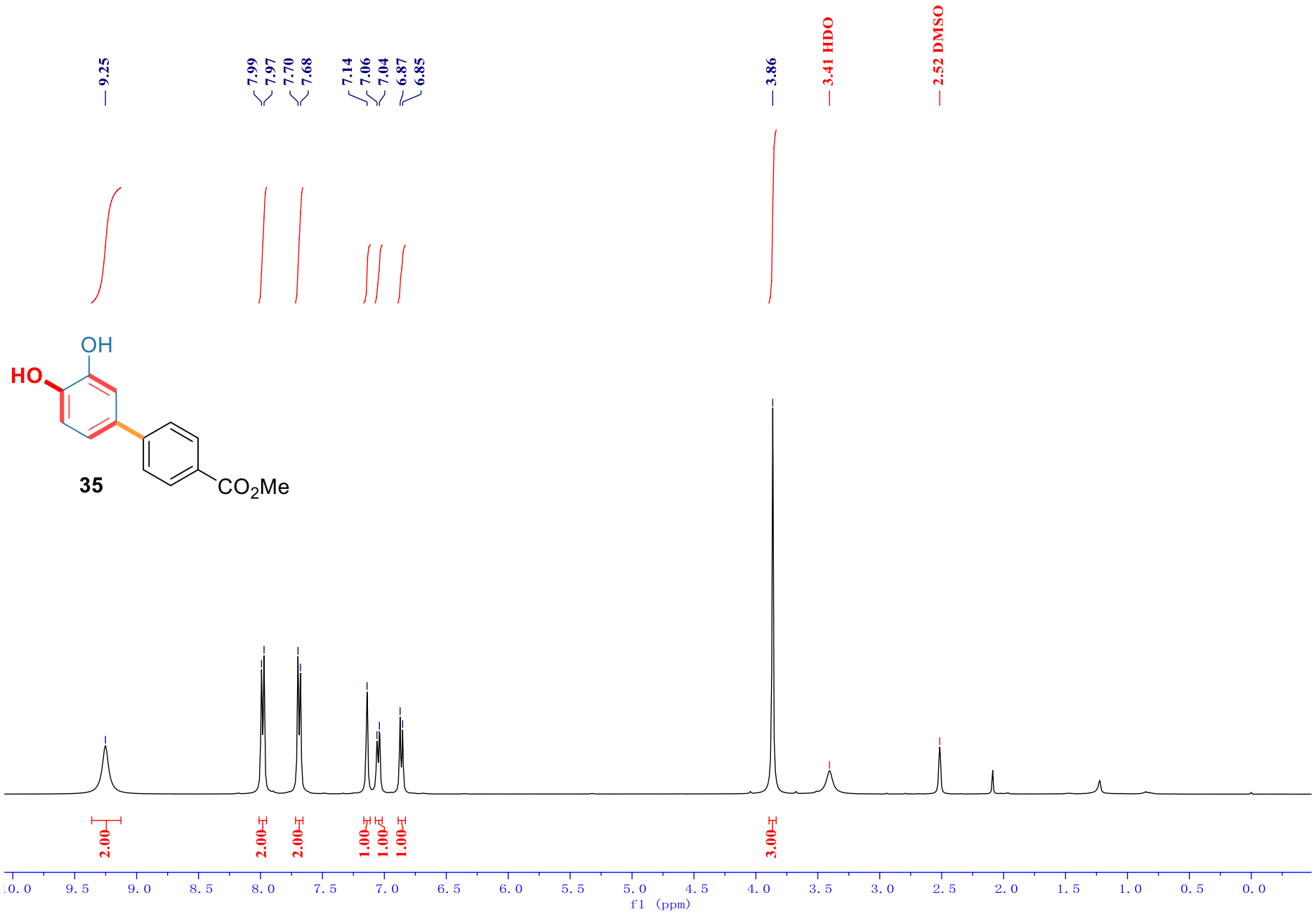

OH
OH
CF3

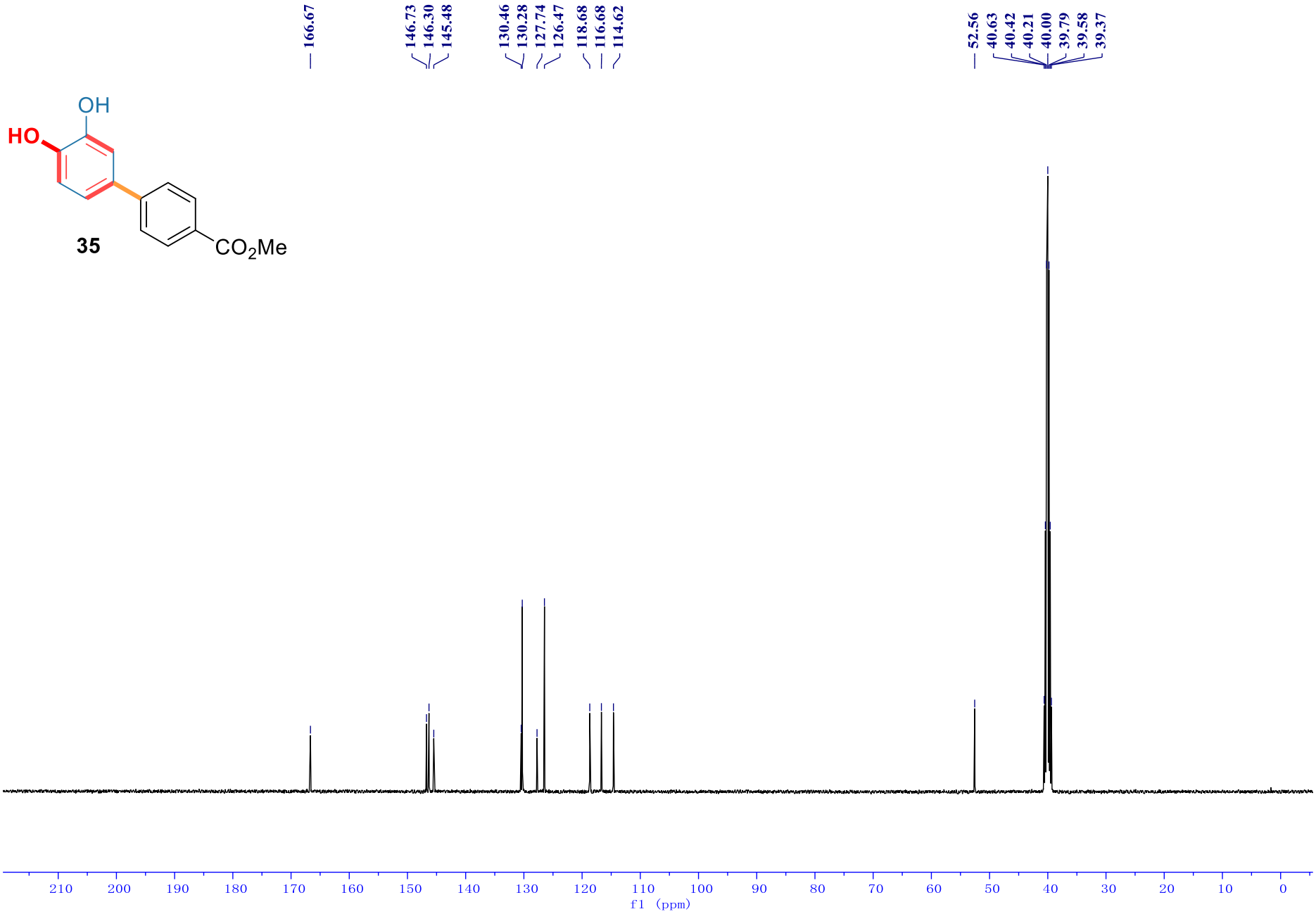
33

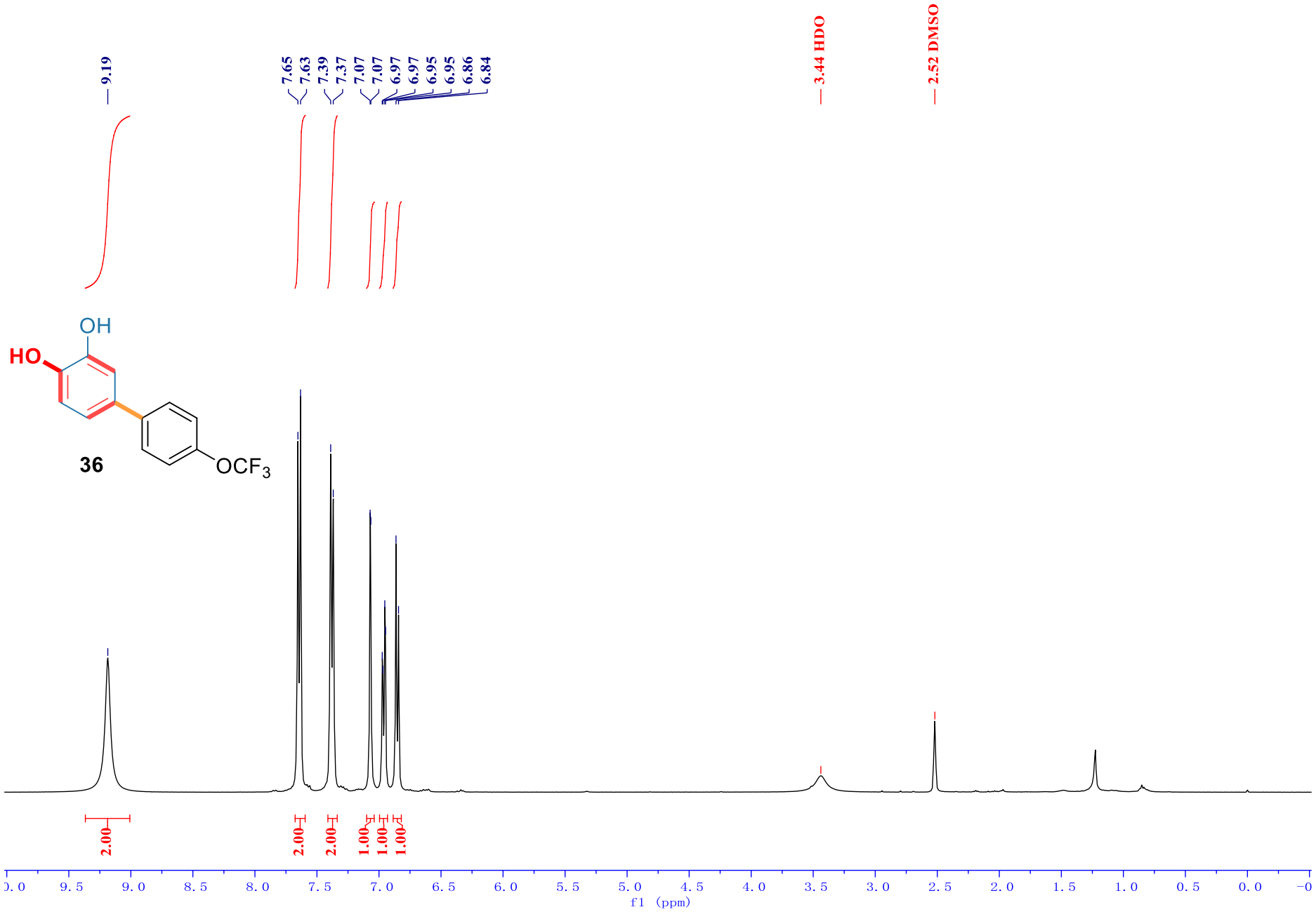
-59.61
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

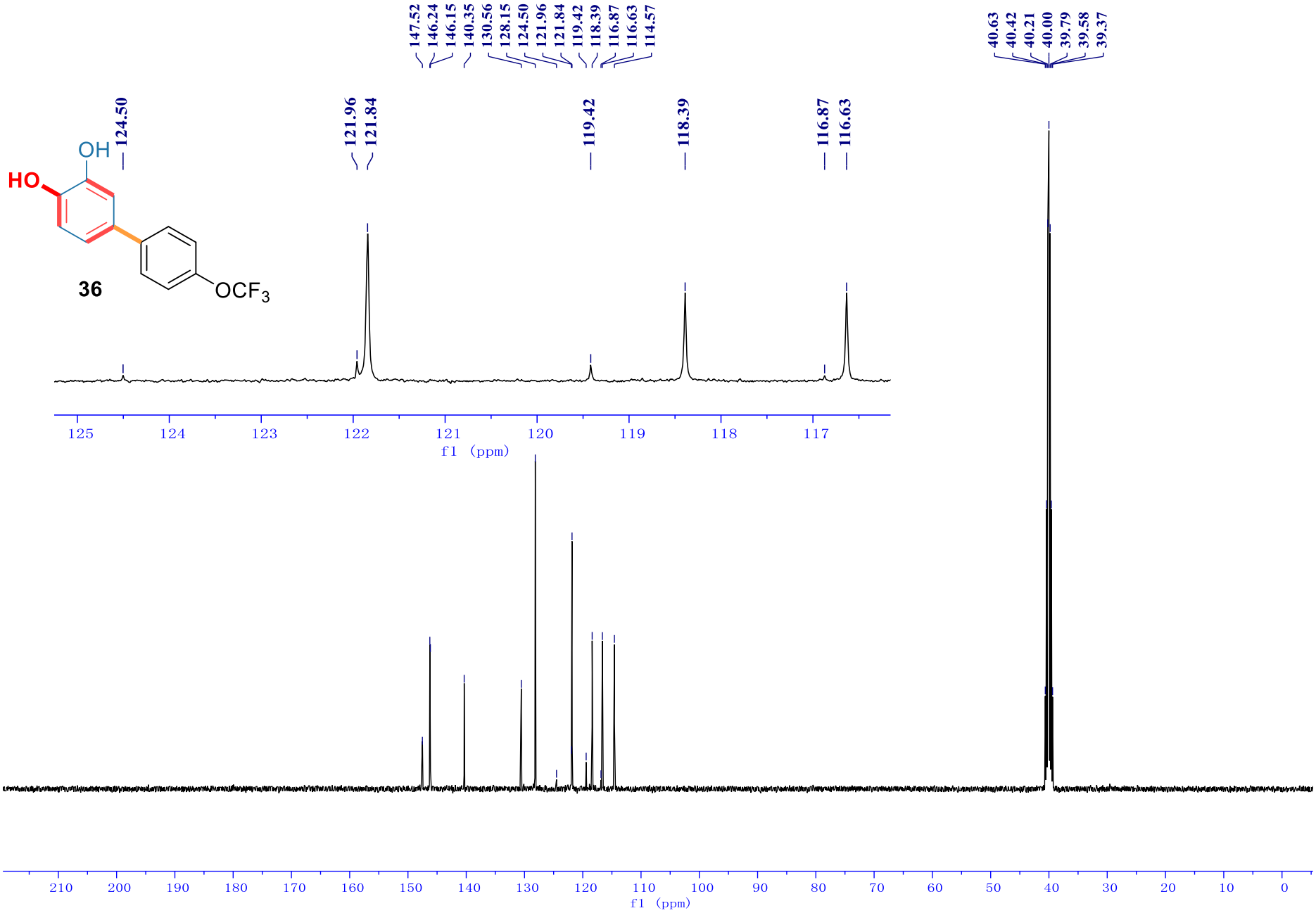

9.02
7.45
7.43
7.41
7.39
7.02
7.01
6.91
6.91
6.89
6.89
6.81
6.79
3.38 HDO
2.50 DMSO
1.29
OH
HO
34
tBu
2.00
4.00
1.00
1.00
1.00
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

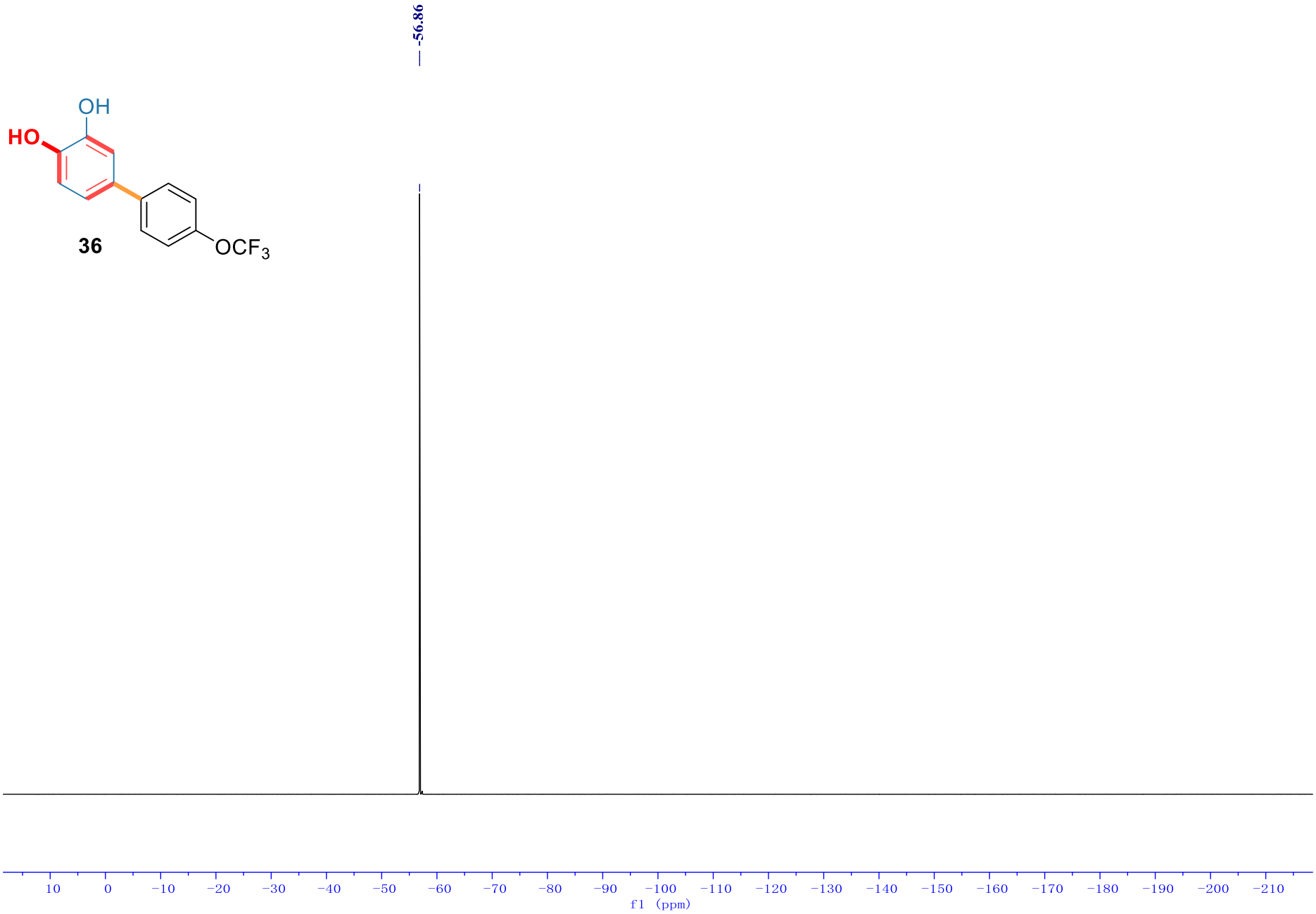

149.13
146.04
145.44
138.11
131.97
126.10
126.00
117.93
116.50
114.28
40.63
40.42
40.21
40.00
39.79
39.58
39.37
34.62
31.65
OH
HO
34
tBu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

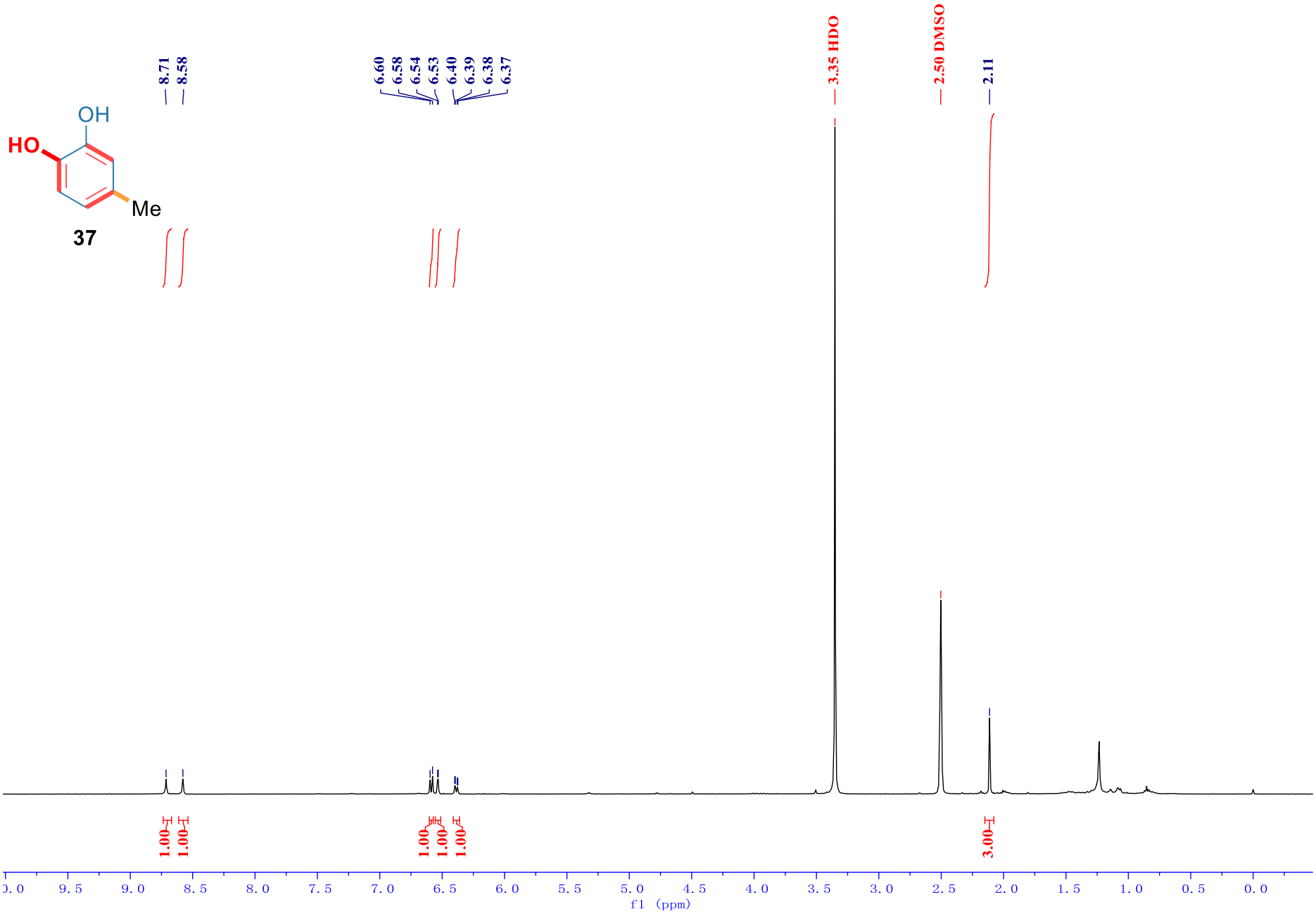

9.25
7.99
7.97
7.70
7.68
7.14
7.06
7.04
6.87
6.85
3.86
3.41 HDO
2.52 DMSO
OH
HO
35
CO2Me
2.00
2.00
2.00
1.00
1.00
1.00
3.00
f1 (ppm)

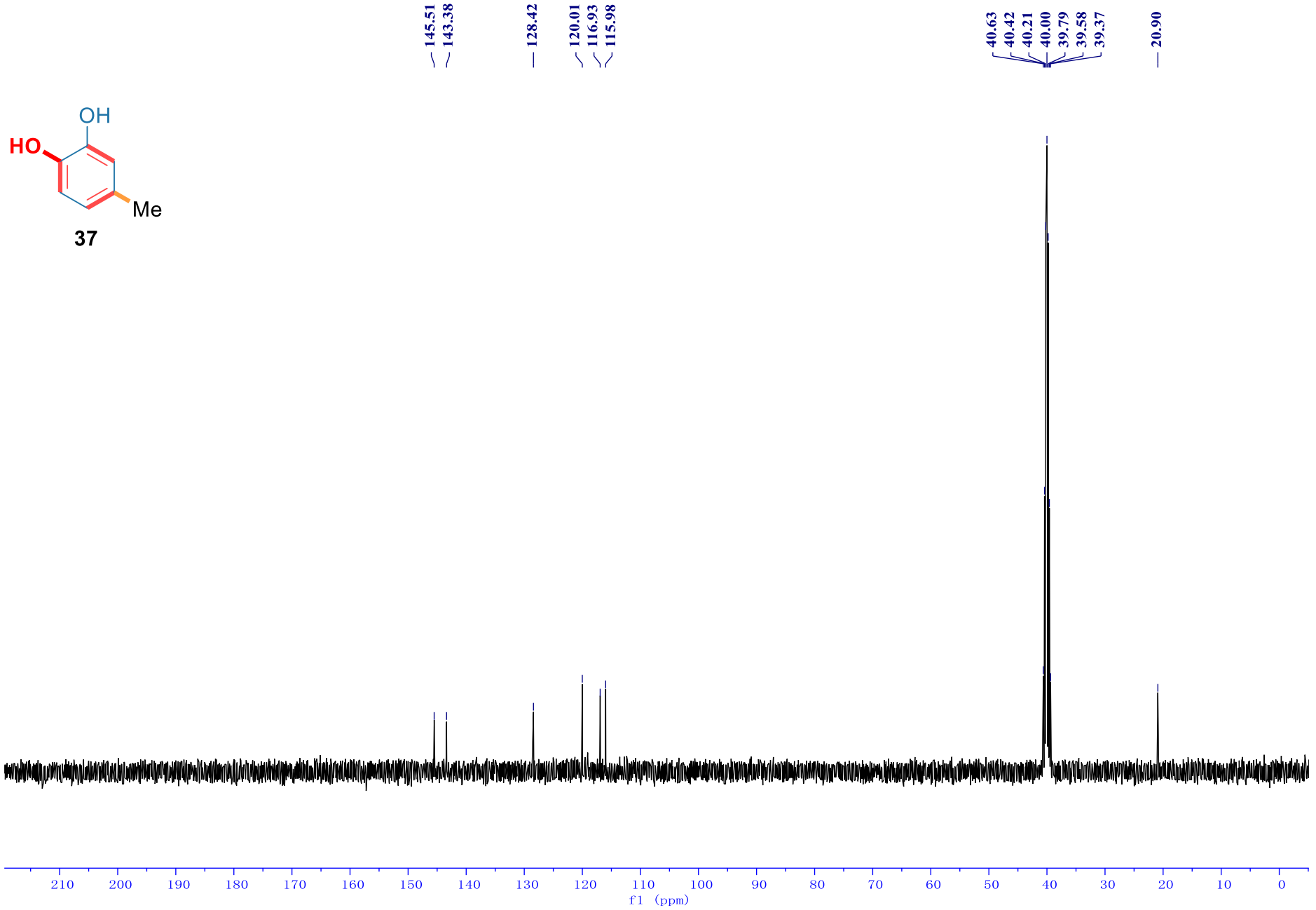

166.67
146.73
146.30
145.48
130.46
130.28
127.74
126.47
118.68
116.68
114.62
52.56
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
HO
35
CO2Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

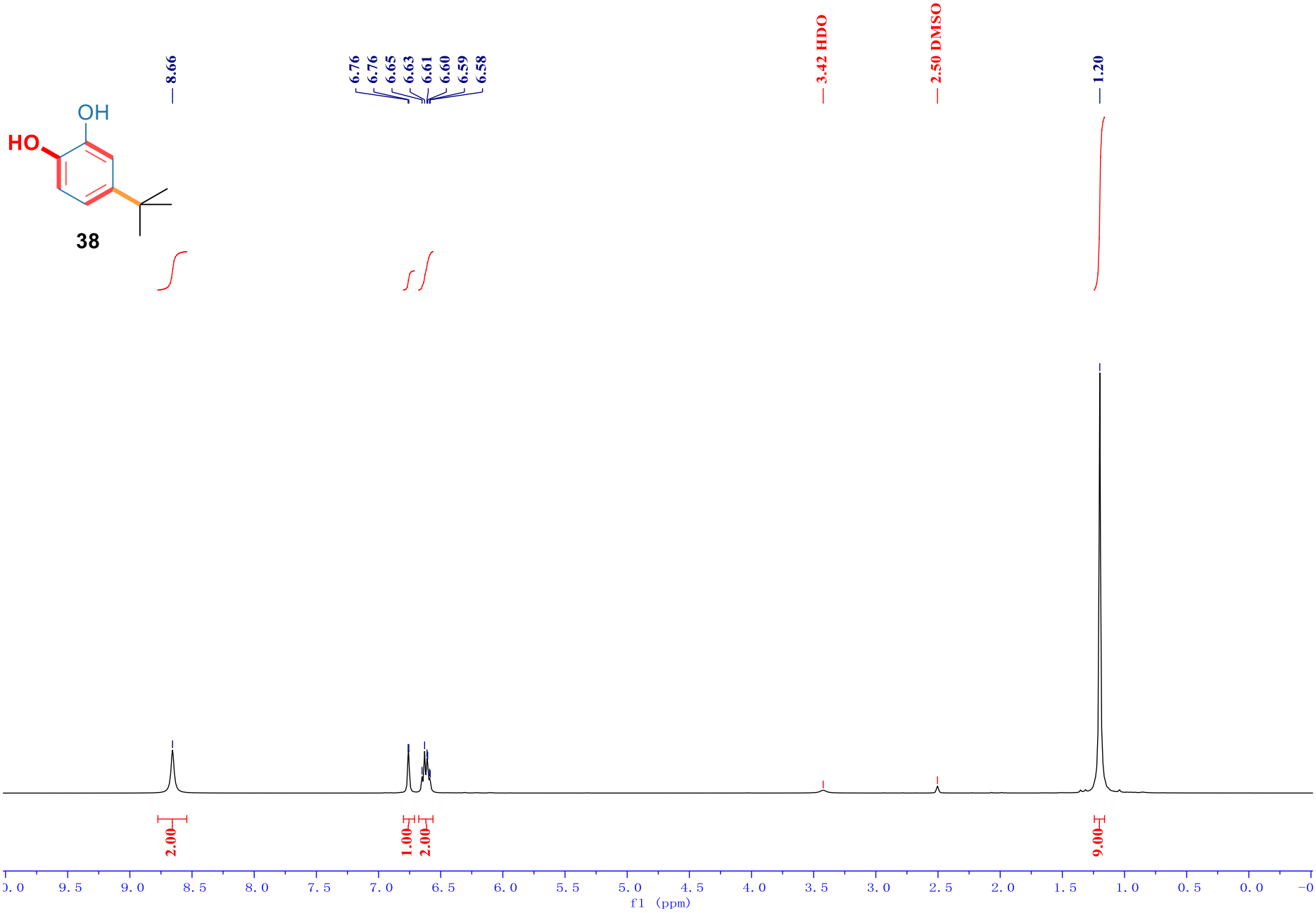

9.19
7.65
7.63
7.39
7.37
7.07
7.07
6.97
6.97
6.95
6.95
6.86
6.84
3.44 HDO
2.52 DMSO
OH
HO
OCF3
36
2.00
2.00
2.00
1.00
1.00
1.00
f1 (ppm)

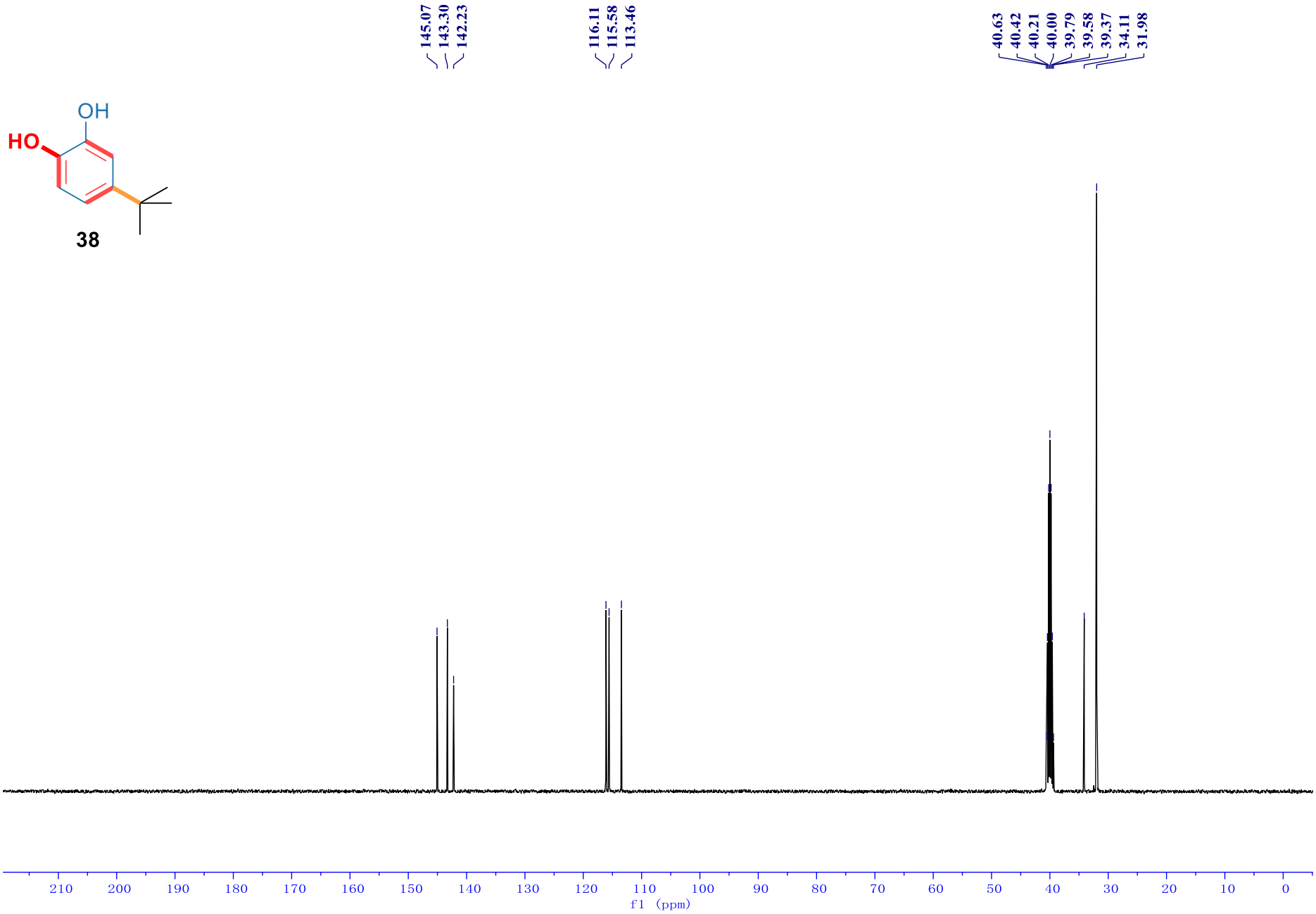

147.52
146.24
146.15
140.35
130.56
128.15
124.50
121.96
121.84
119.42
118.39
116.87
116.63
114.57
40.63
40.42
40.21
40.00
39.79
39.58
39.37
124.50
121.96
121.84
119.42
118.39
116.87
116.63
OH
HO
OCF3
36
125
124
123
122
121
120
119
118
117
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

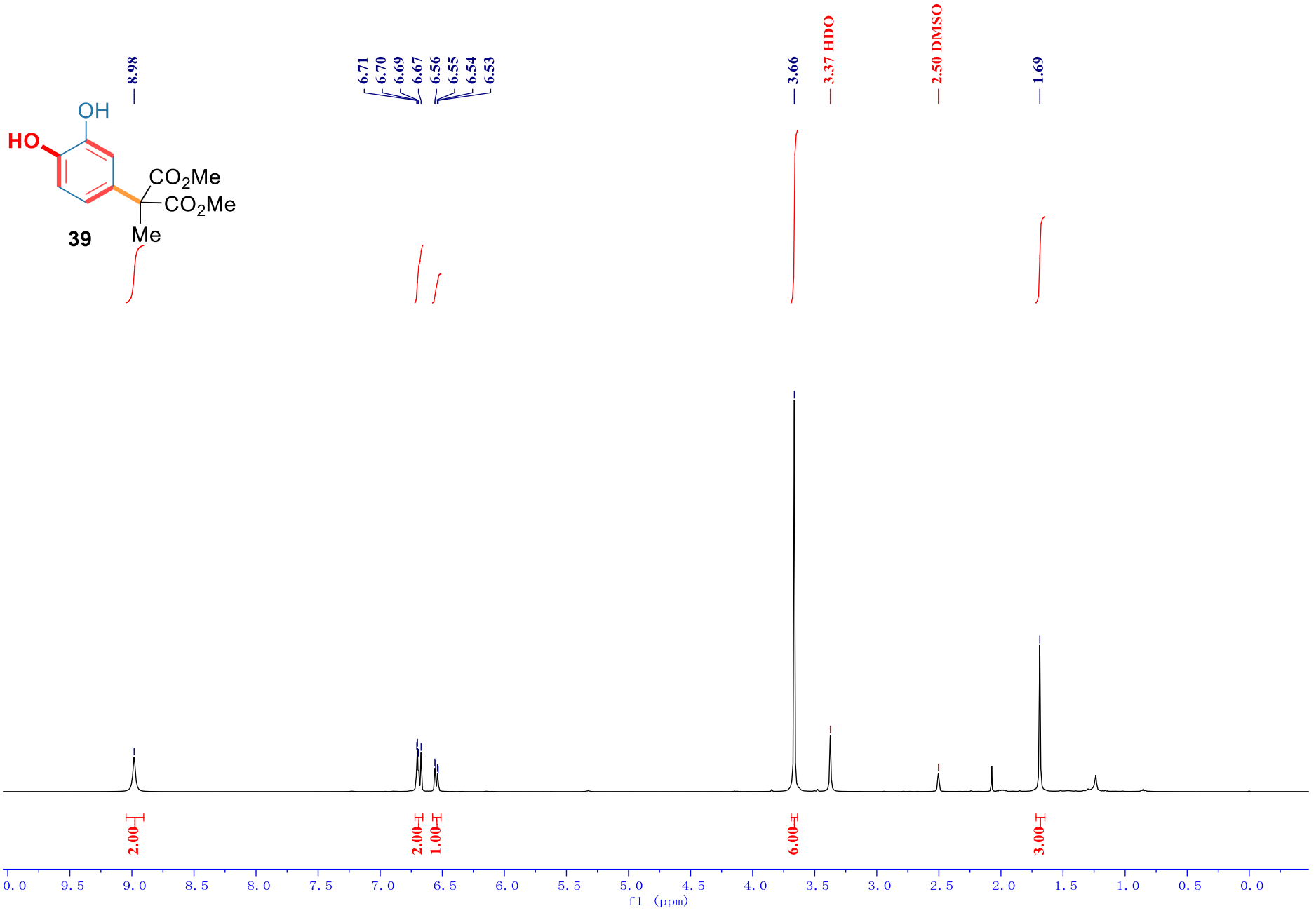

-56.86
OH
HO
OCF3
36
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

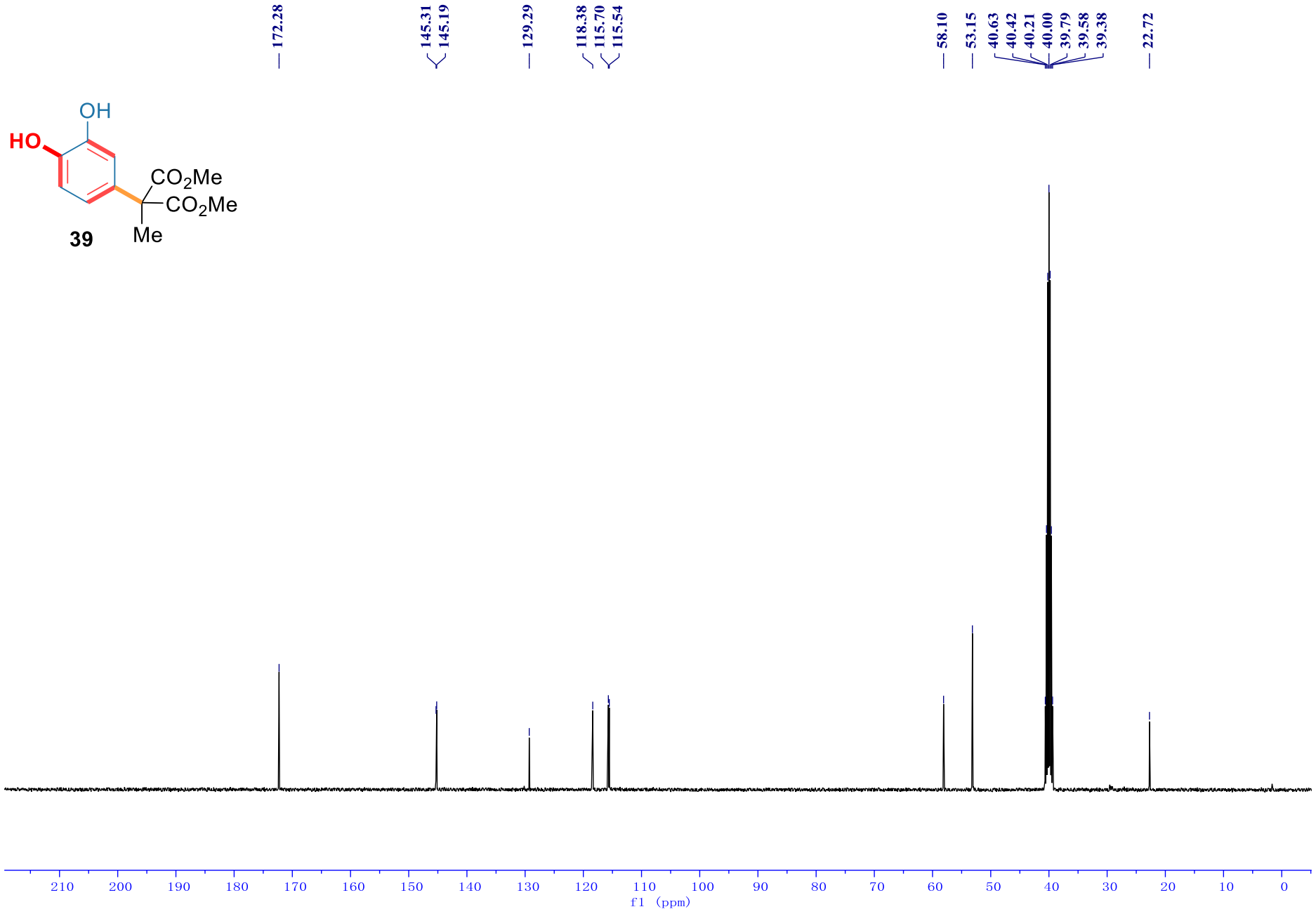

8.71
8.58
6.60
6.58
6.54
6.53
6.40
6.39
6.38
6.37
3.35 HDO
2.50 DMSO
2.11
OH
HO
Me
37
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

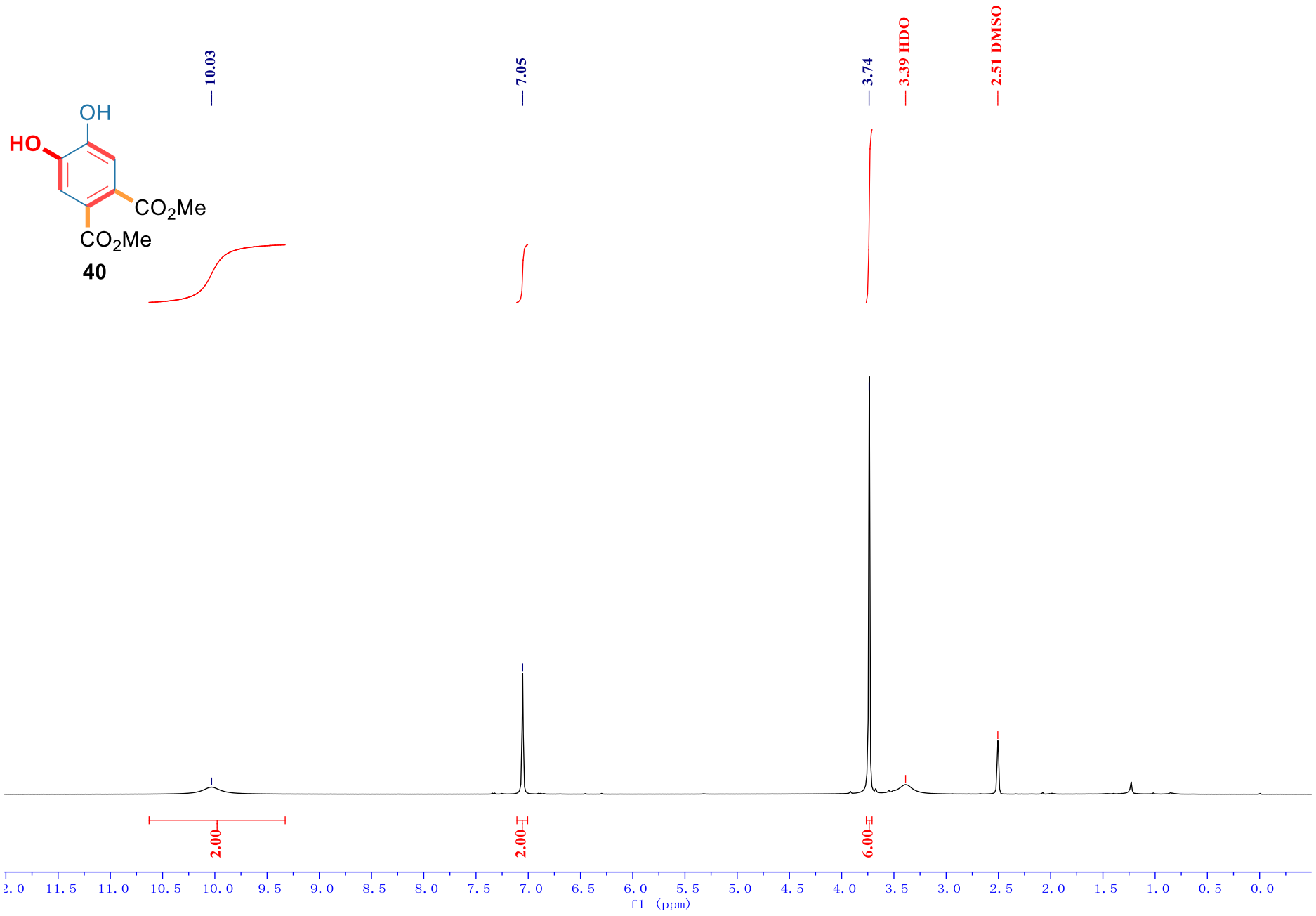

145.51
143.38
128.42
120.01
116.93
115.98
40.63
40.42
40.21
40.00
39.79
39.58
39.37
20.90
OH
HO
Me
37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

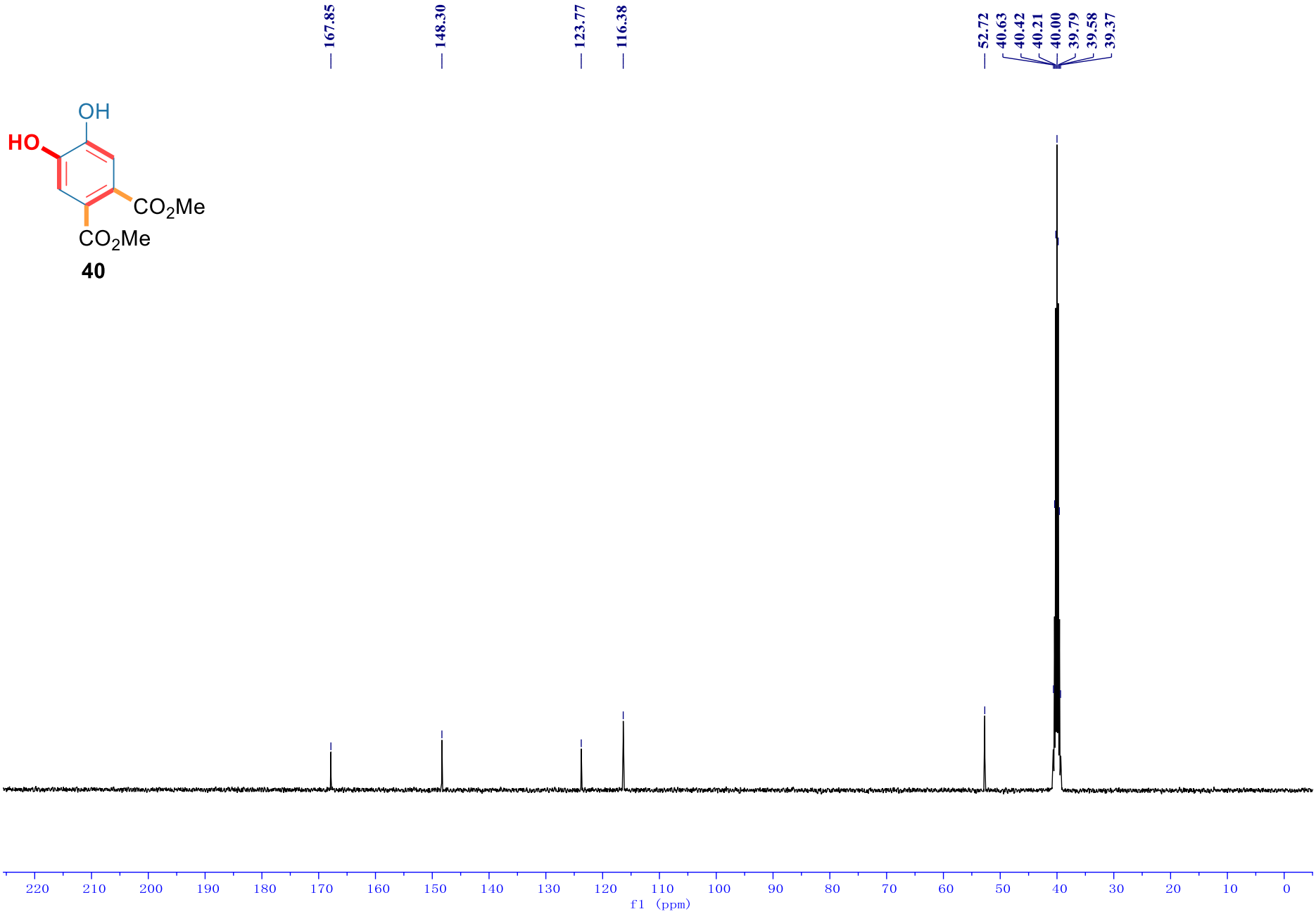

OH
HO
38
8.66
6.76
6.76
6.65
6.63
6.61
6.60
6.59
6.58
3.42 HDO
2.50 DMSO
1.20
2.00
1.00
2.00
9.00
f1 (ppm)

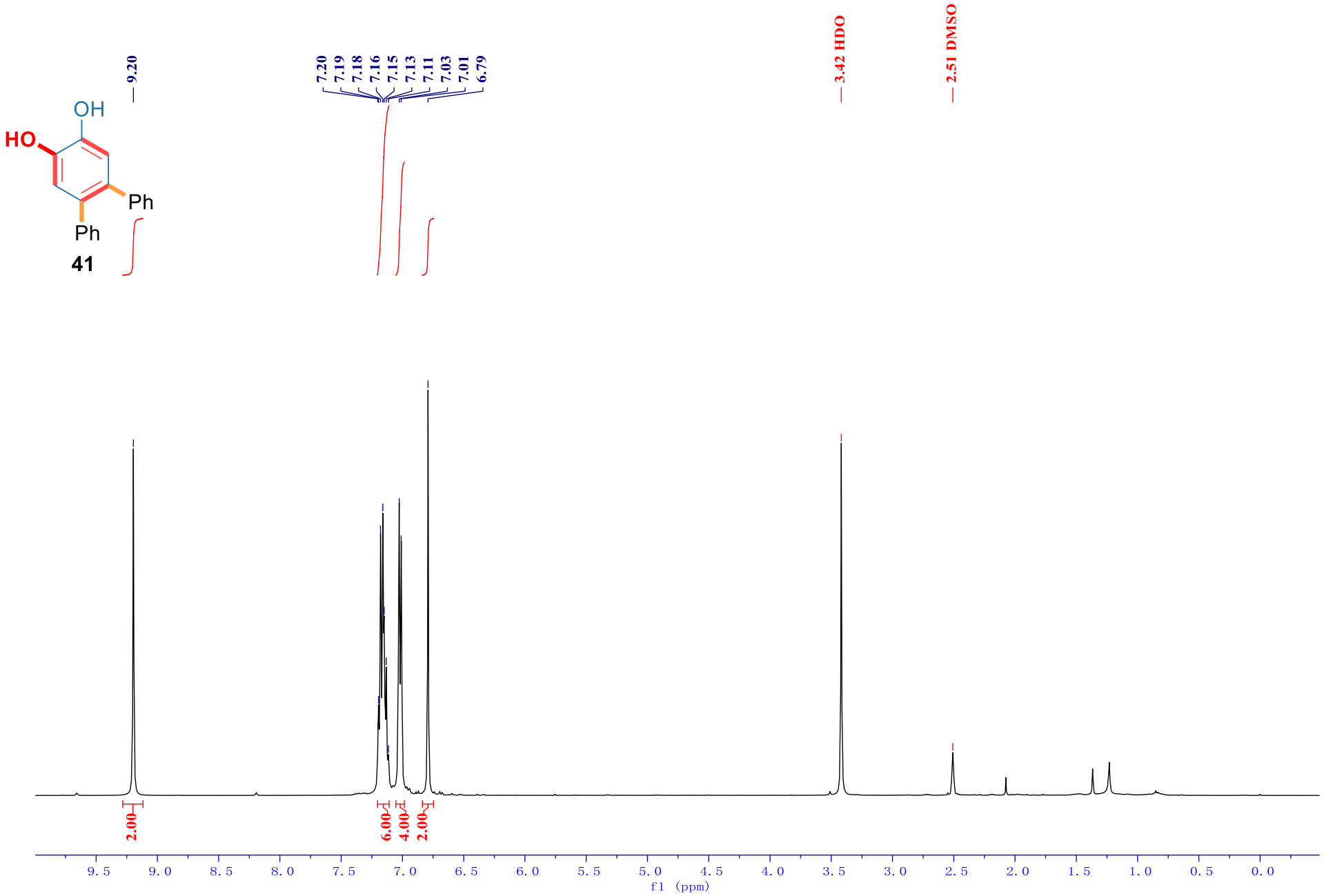

145.07
143.30
142.23
116.11
115.58
113.46
40.63
40.42
40.21
40.00
39.79
39.58
39.37
34.11
31.98
OH
HO
38
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

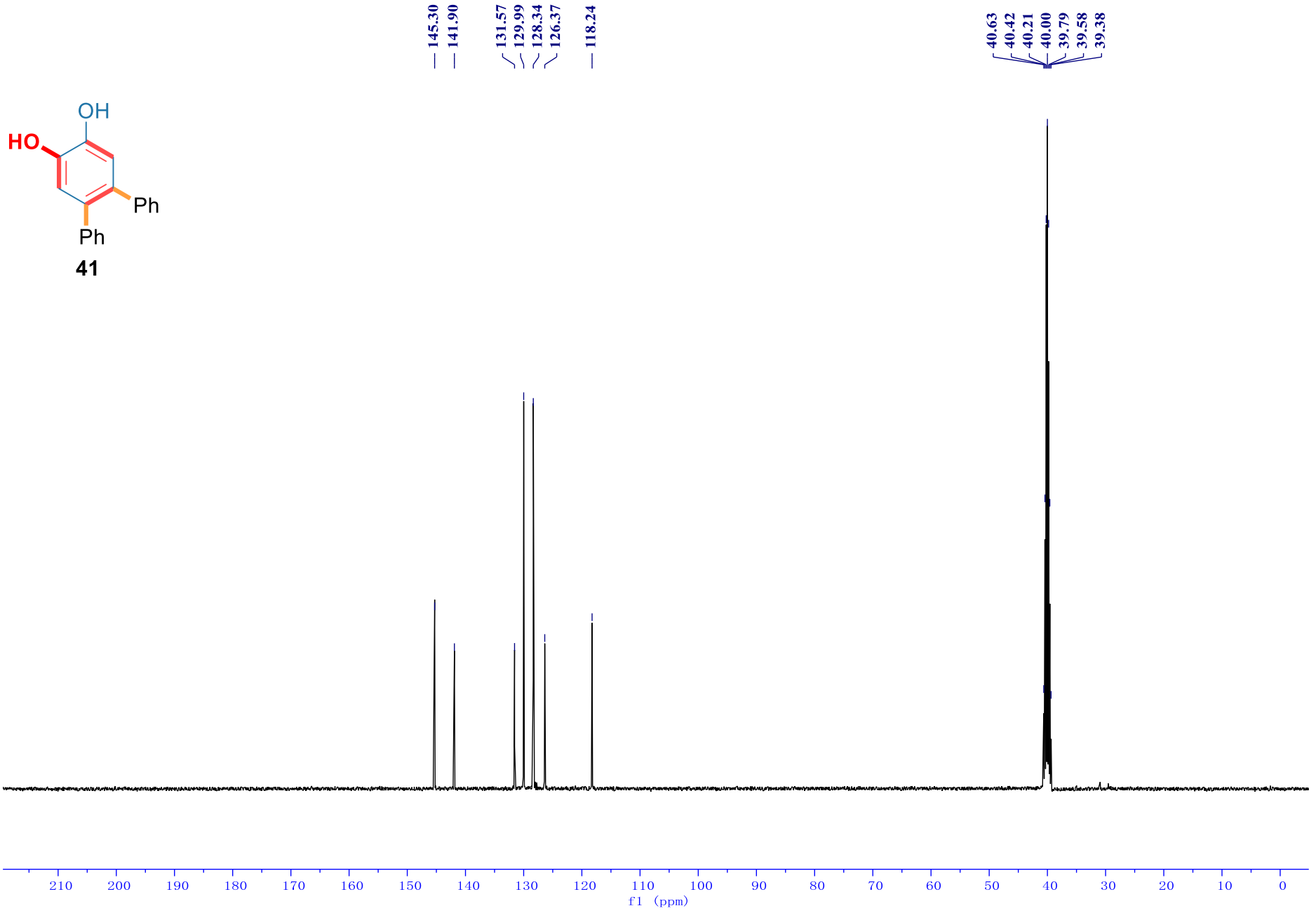

8.98
6.71
6.70
6.69
6.67
6.56
6.55
6.54
6.53
3.66
3.37 HDO
2.50 DMSO
1.69
OH
HO
CO2Me
CO2Me
Me
39
2.00
2.00
1.00
6.00
3.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

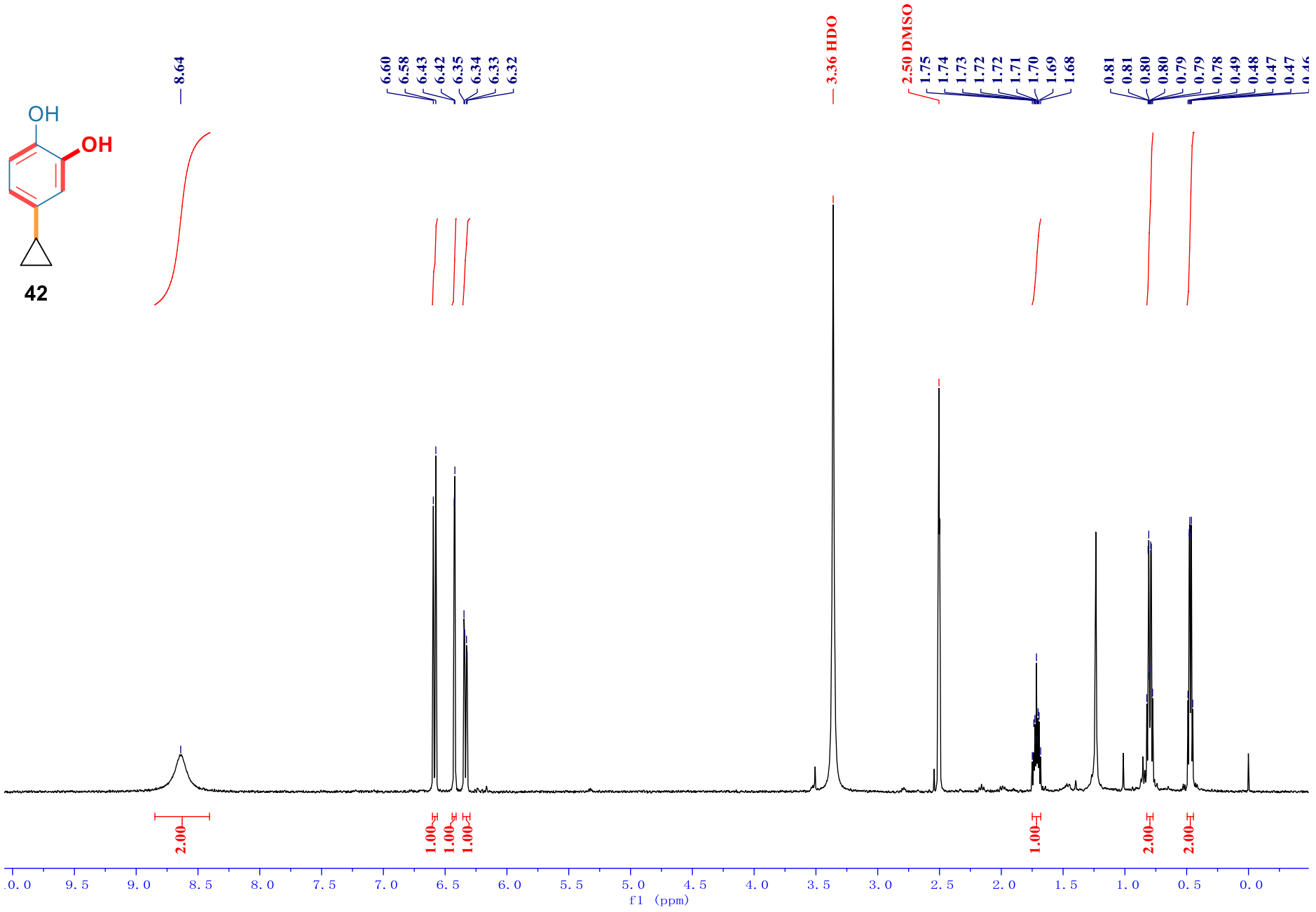

172.28
145.31
145.19
129.29
118.38
115.70
115.54
58.10
53.15
40.63
40.42
40.21
40.00
39.79
39.58
39.38
22.72
OH
HO
CO2Me
CO2Me
Me
39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

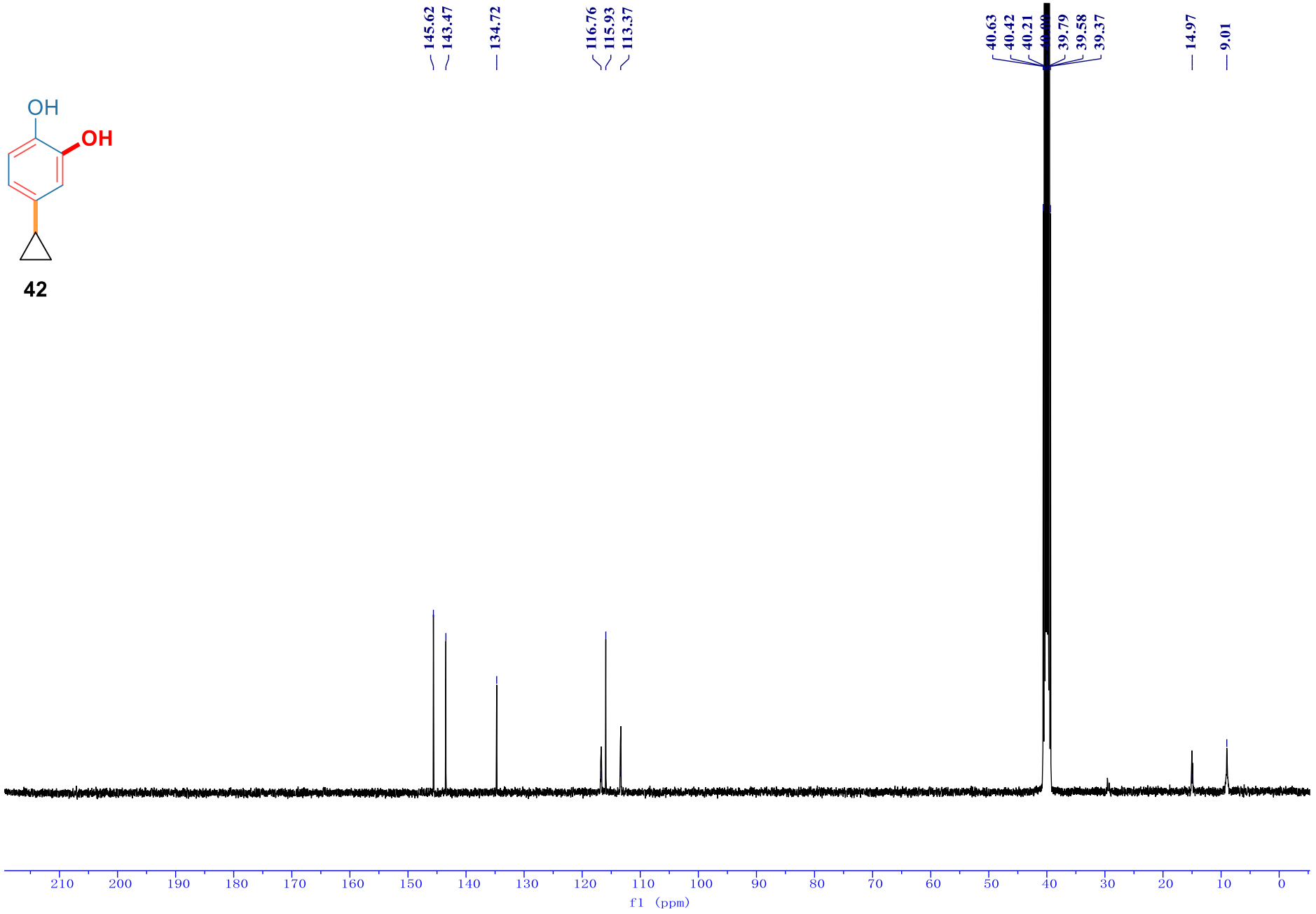

10.03
7.05
3.74
3.39 HDO
2.51 DMSO
OH
HO
CO2Me
CO2Me
40
2.00
2.00
6.00
f1 (ppm)

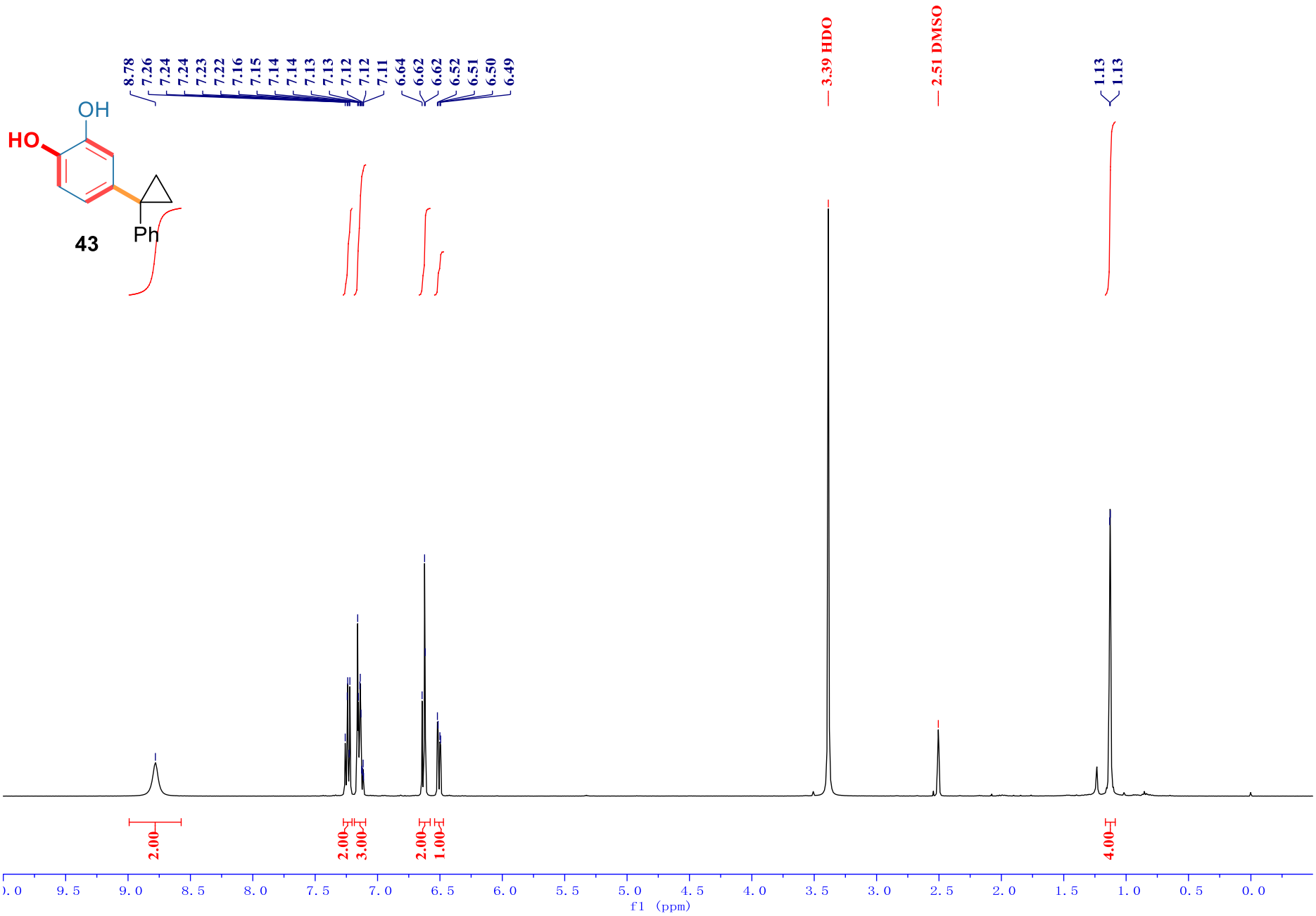

167.85
148.30
123.77
116.38
52.72
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
HO
CO2Me
CO2Me
40
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

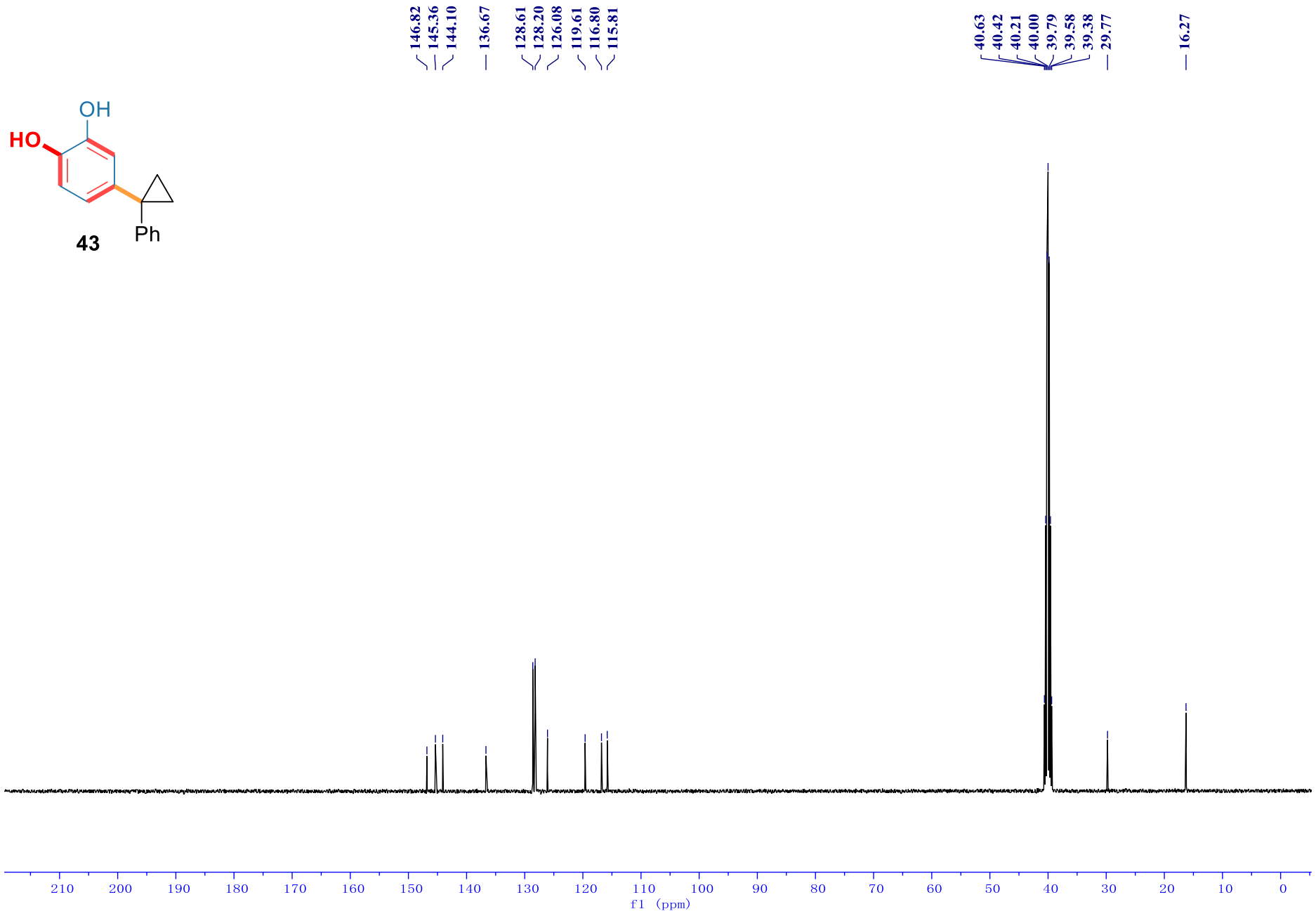

9.20
7.20
7.19
7.18
7.16
7.15
7.13
7.11
7.03
7.01
6.79
3.42 HDO
2.51 DMSO
OH
HO
Ph
Ph
41
2.00
6.00
4.00
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

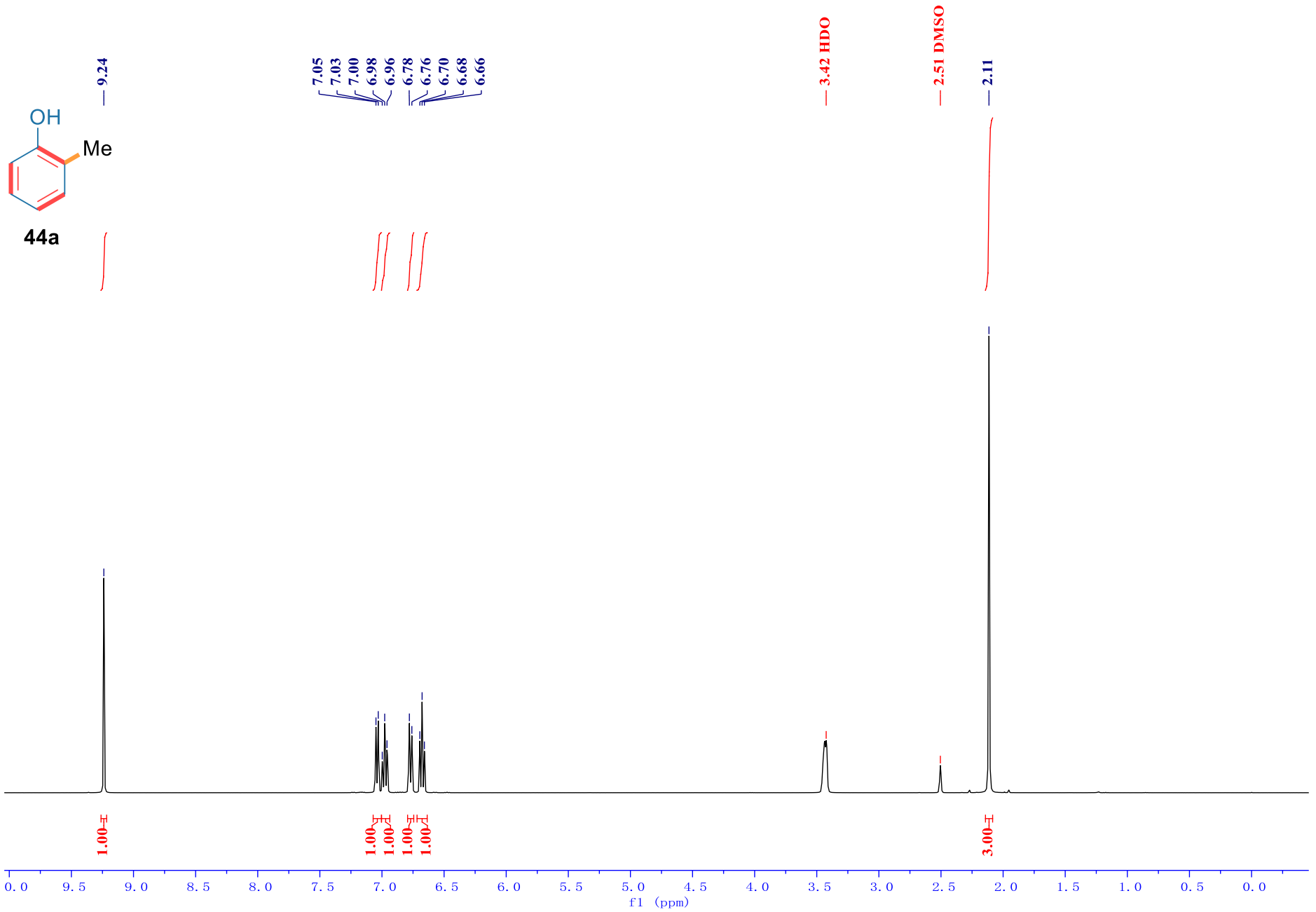

145.30
141.90
131.57
129.99
128.34
126.37
118.24
40.63
40.42
40.21
40.00
39.79
39.58
39.38
OH
HO
Ph
Ph
41
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

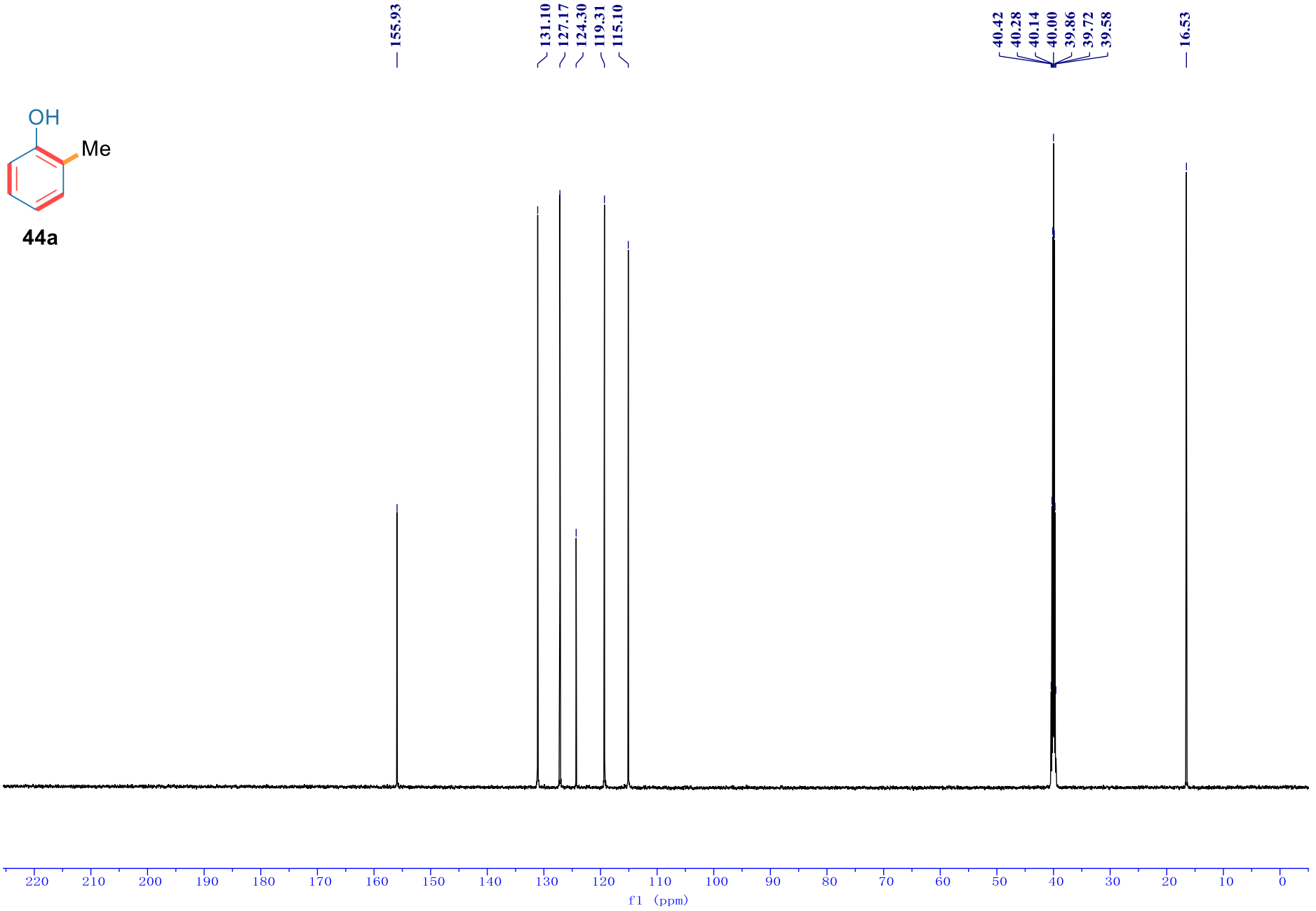

OH
OH
42
8.64
6.60
6.58
6.43
6.42
6.35
6.34
6.33
6.32
3.36 HDO
2.50 DMSO
1.75
1.74
1.73
1.72
1.72
1.71
1.70
1.69
1.68
0.81
0.81
0.80
0.80
0.79
0.79
0.78
0.49
0.48
0.47
0.47
2.00
1.00
1.00
1.00
1.00
2.00
2.00
f1 (ppm)

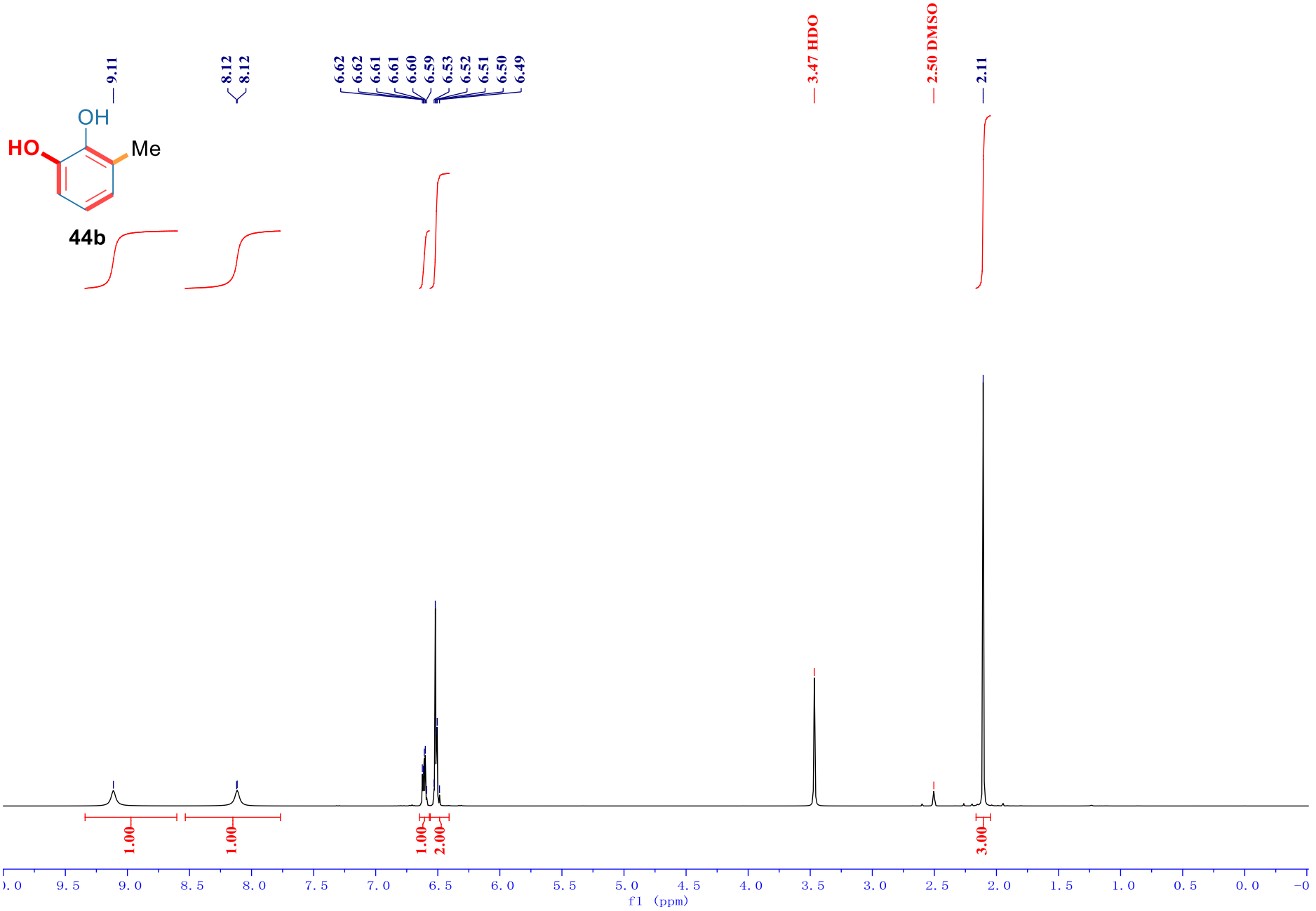

145.62
143.47
134.72
116.76
115.93
113.37
40.63
40.42
40.21
40.00
39.79
39.58
39.37
14.97
9.01
OH
OH
42
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

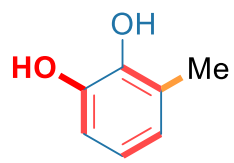

8.78
7.26
7.24
7.24
7.23
7.22
7.16
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
6.64
6.62
6.62
6.52
6.51
6.50
6.49
3.39 HDO
2.51 DMSO
1.13
1.13
OH
HO
Ph
43
2.00
2.00
3.00
2.00
1.00
4.00
f1 (ppm)


146.82
145.36
144.10
136.67
128.61
128.20
126.08
119.61
116.80
115.81
40.63
40.42
40.21
40.00
39.79
39.58
39.38
29.77
16.27
OH
HO
Ph
43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.24
7.05
7.03
7.00
6.98
6.96
6.78
6.76
6.70
6.68
6.66
3.42 HDO
2.51 DMSO
2.11
OH
Me
44a
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

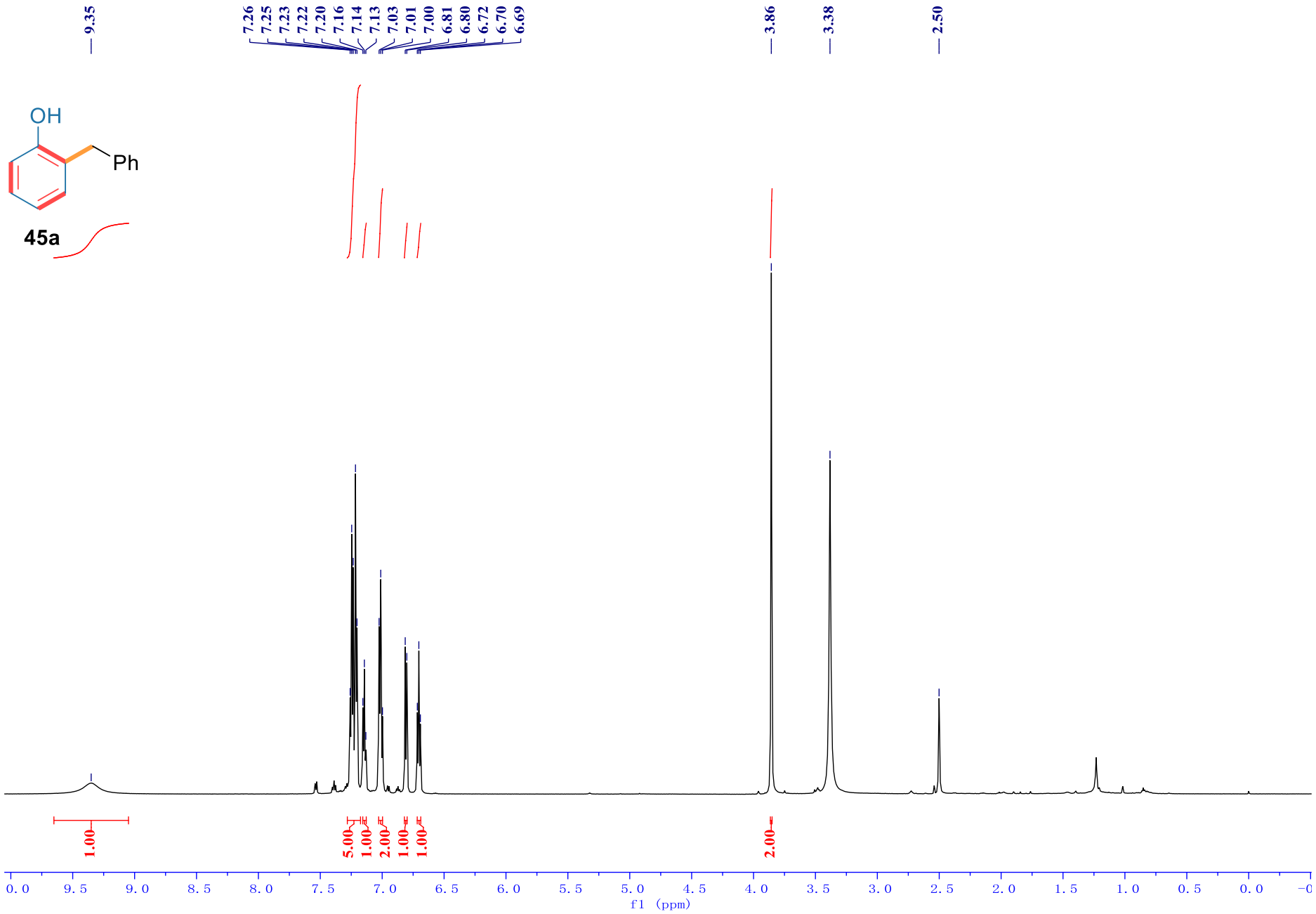

155.93
131.10
127.17
124.30
119.31
115.10
40.42
40.28
40.14
40.00
39.86
39.72
39.58
16.53
OH
Me
44a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

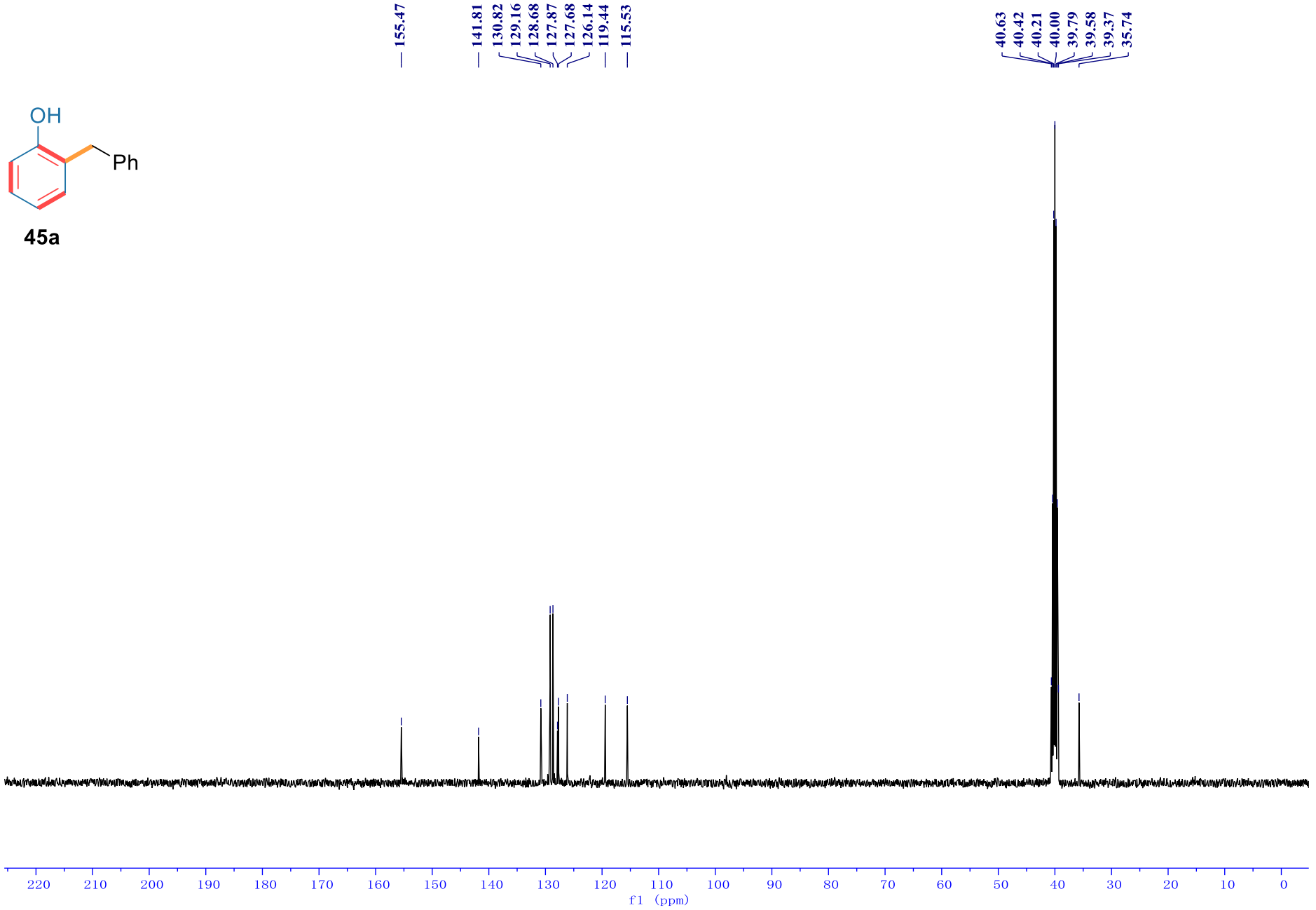

9.11
8.12
8.12
6.62
6.62
6.61
6.61
6.60
6.59
6.53
6.52
6.51
6.50
6.49
3.47 HDO
2.50 DMSO
2.11
OH
HO
Me
44b
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

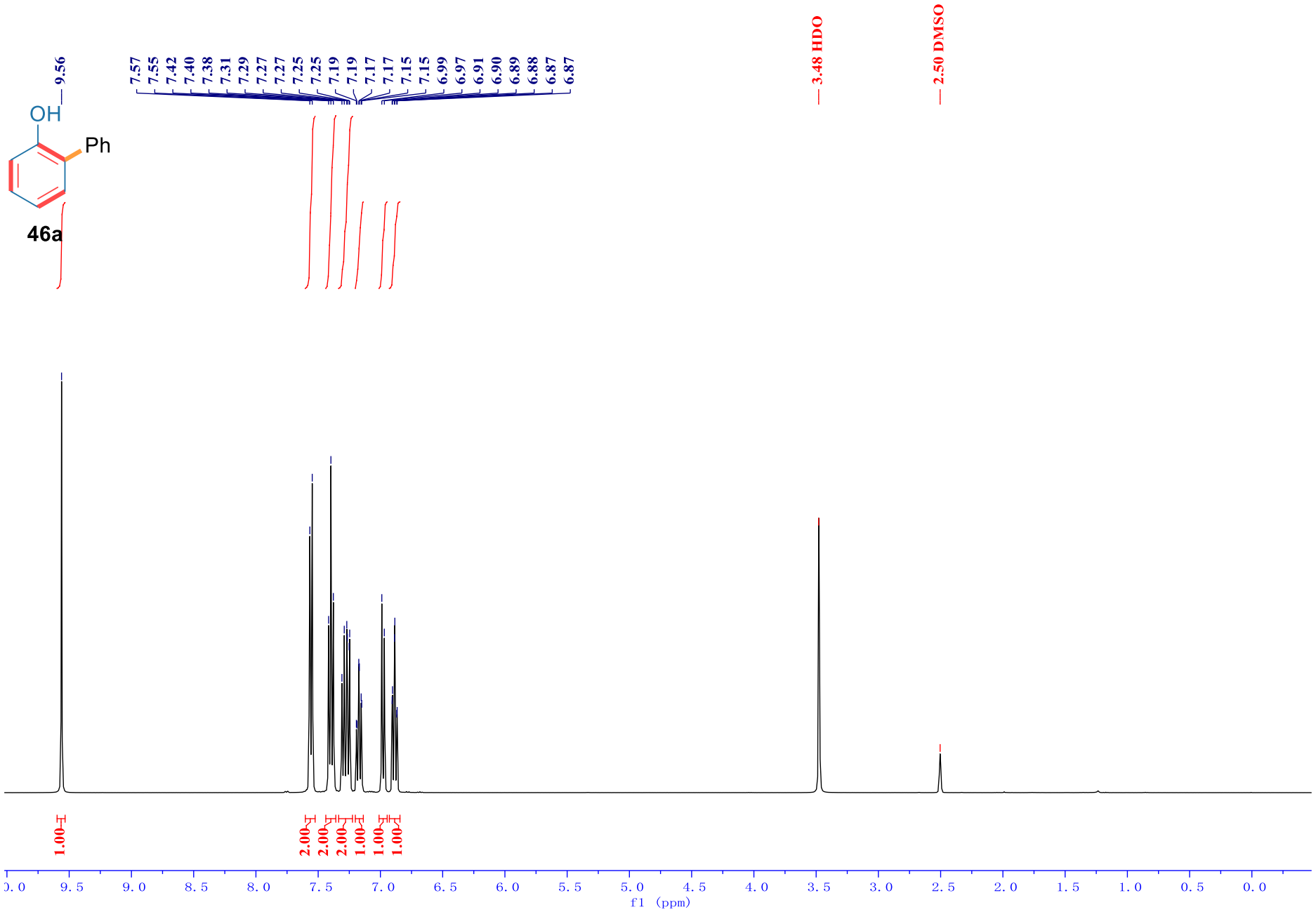

OH
HO
Me

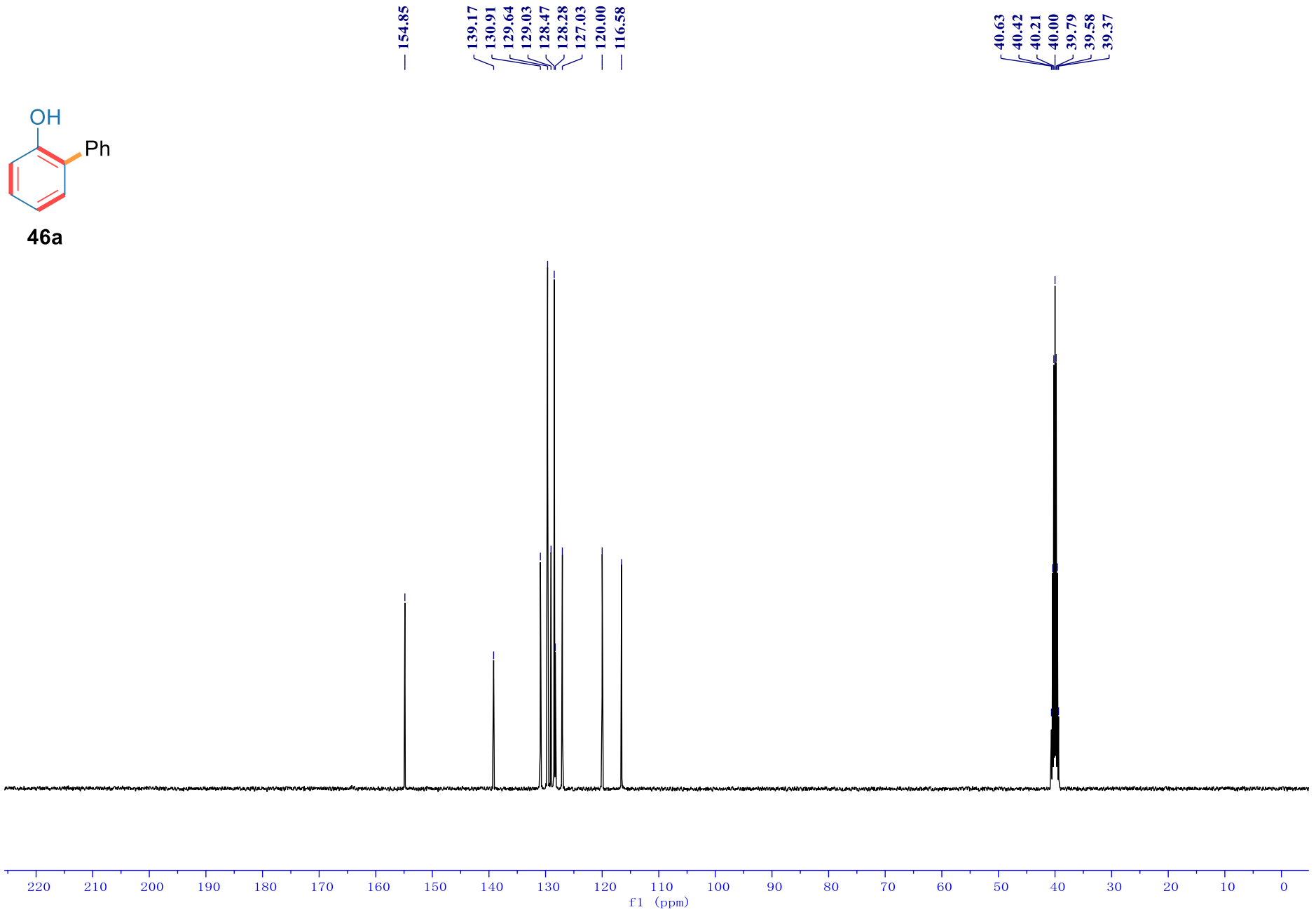
44b

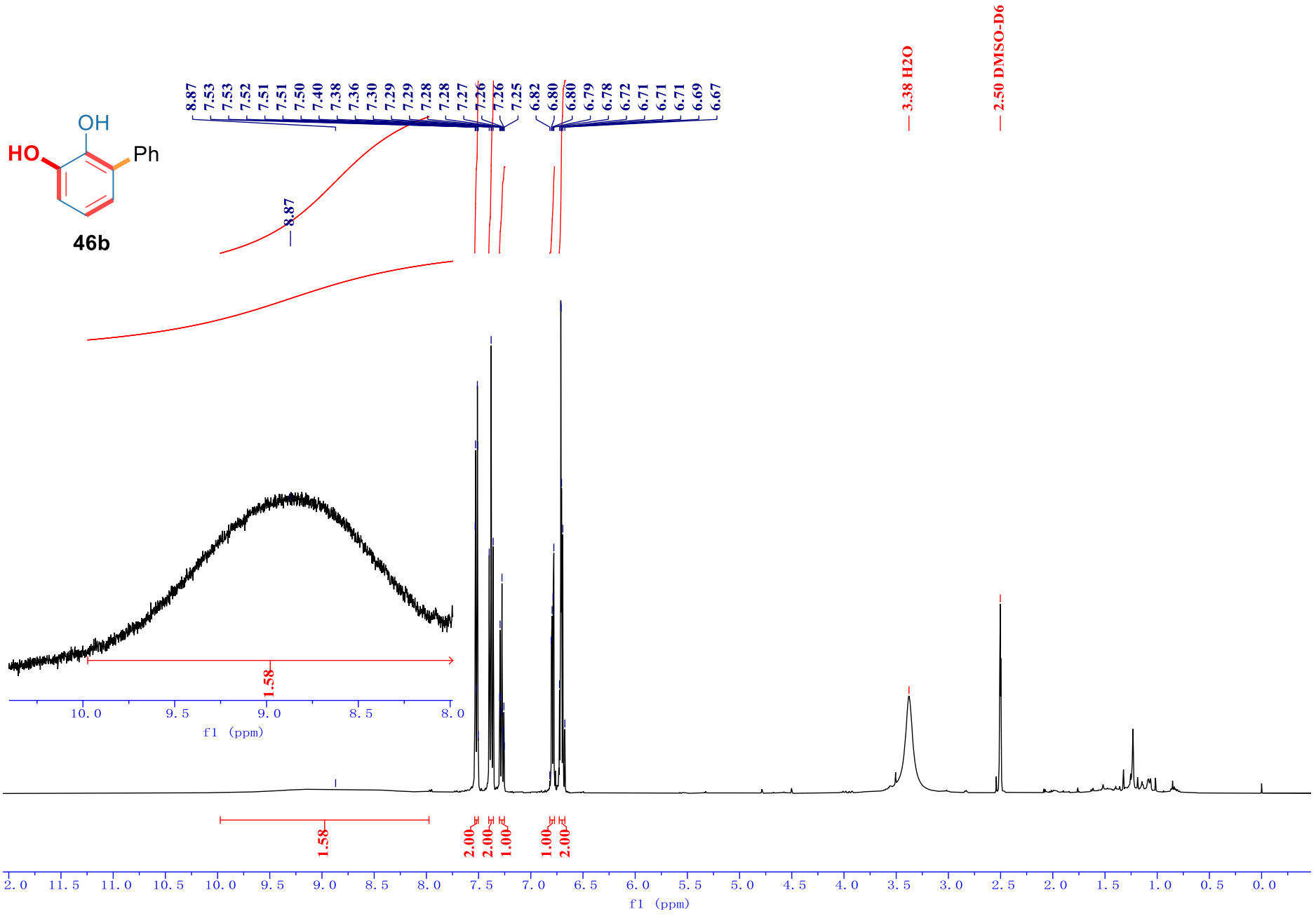
145.38
143.86
125.06
121.62
119.13
113.56
40.63
40.42
40.21
40.00
39.79
39.58
39.37
16.58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

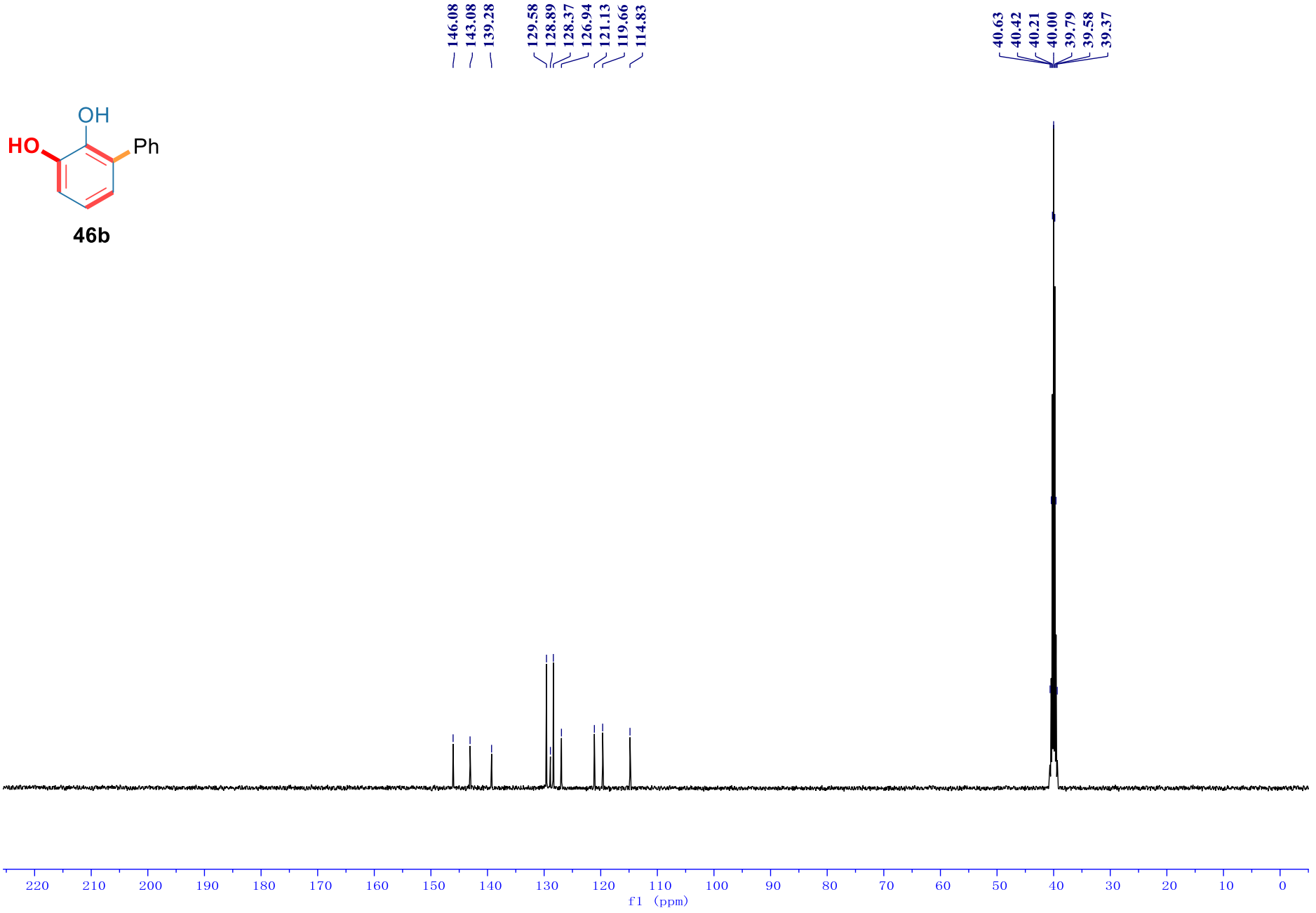

9.35
7.26
7.25
7.23
7.22
7.20
7.16
7.14
7.13
7.03
7.01
7.00
6.81
6.80
6.72
6.70
6.69
3.86
3.38
2.50
OH
Ph
45a
1.00
5.00
1.00
2.00
1.00
1.00
2.00
f1 (ppm)

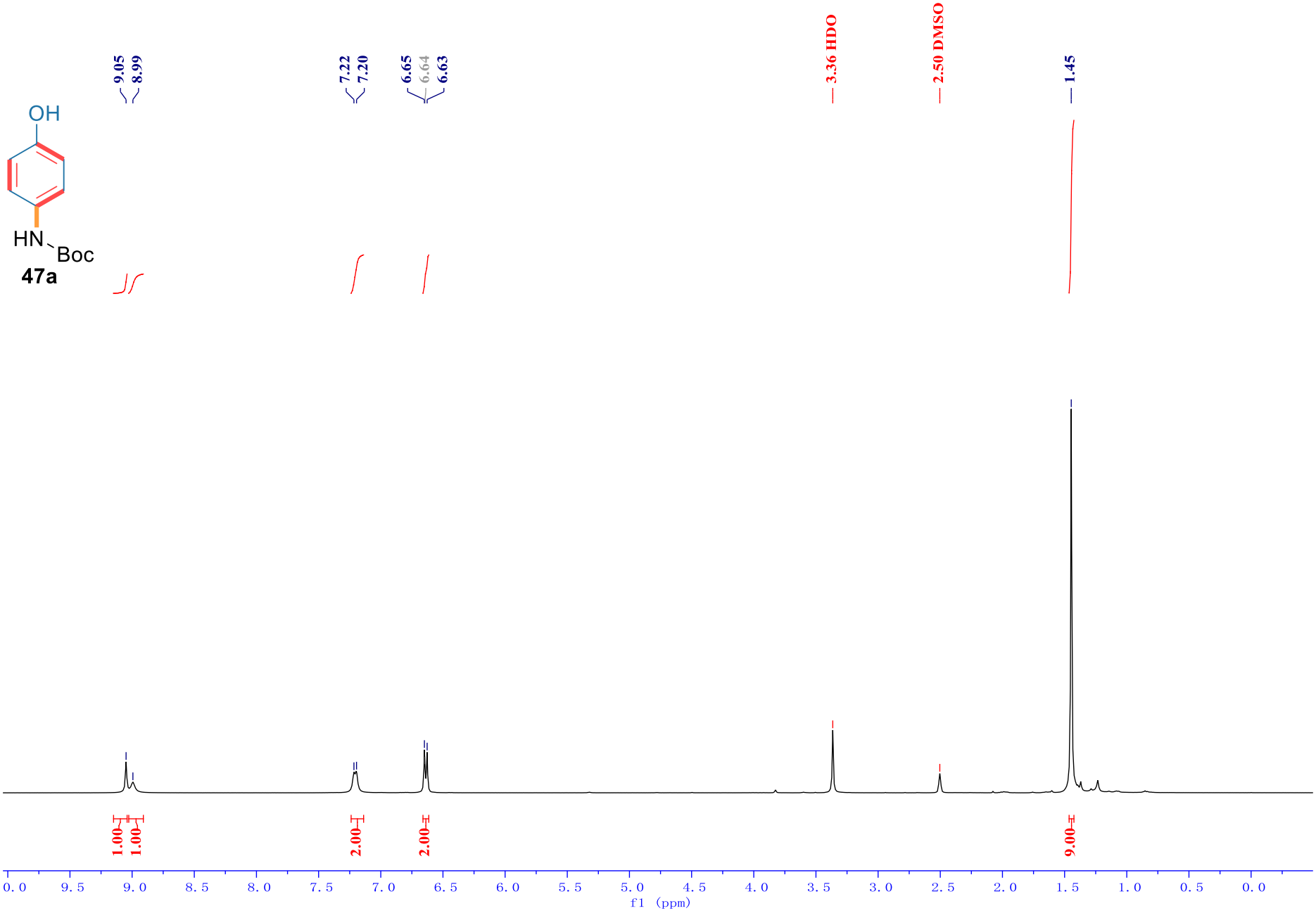

155.47
141.81
130.82
129.16
128.68
127.87
127.68
126.14
119.44
115.53
40.63
40.42
40.21
40.00
39.79
39.58
39.37
35.74
OH
Ph
45a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

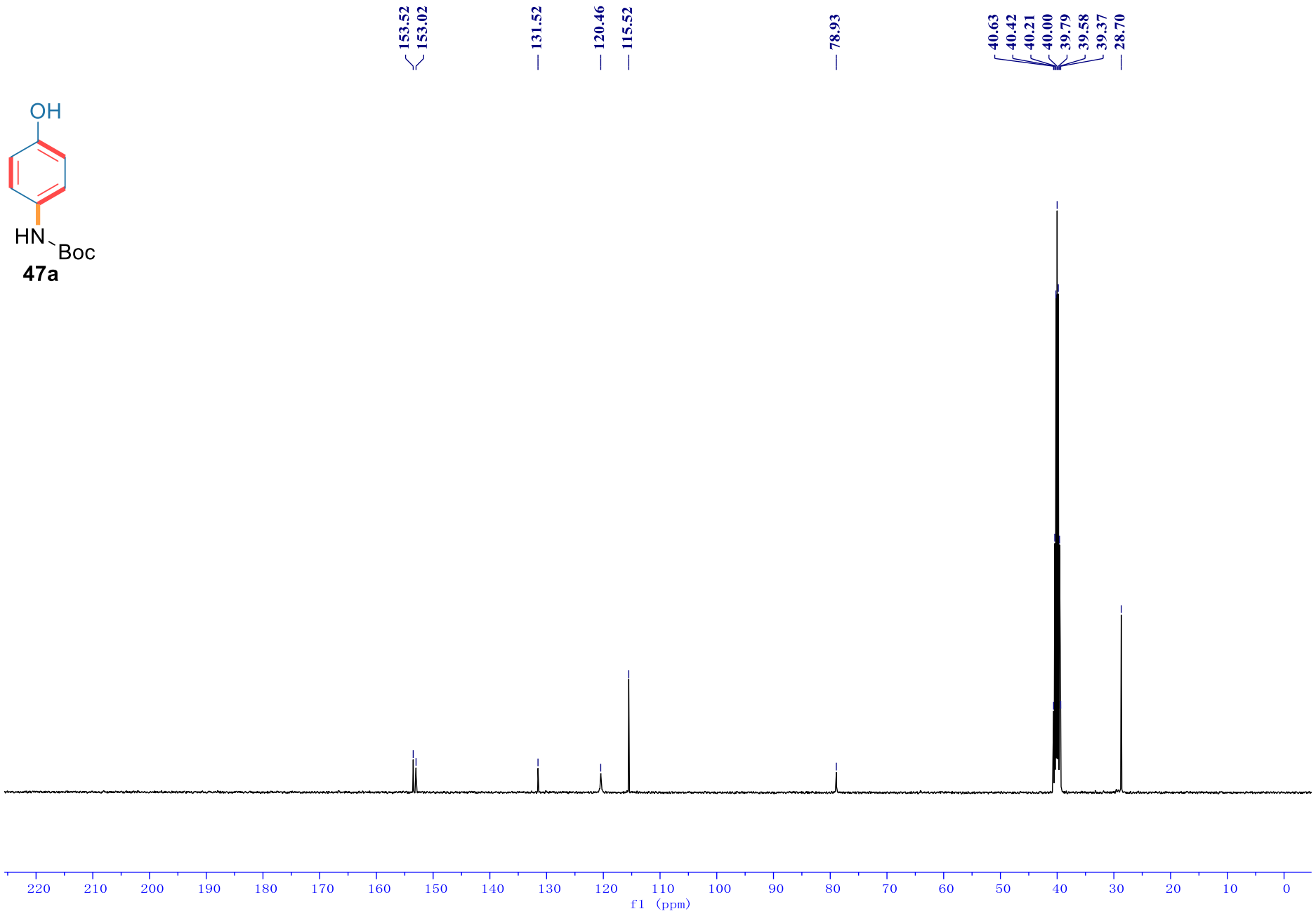

9.56
7.57
7.55
7.42
7.40
7.38
7.31
7.29
7.27
7.27
7.25
7.25
7.19
7.19
7.17
7.17
7.15
7.15
6.99
6.97
6.91
6.90
6.89
6.88
6.87
6.87
3.48 HDO
2.50 DMSO
OH
Ph
46a
1.00
2.00
2.00
2.00
1.00
1.00
1.00
f1 (ppm)

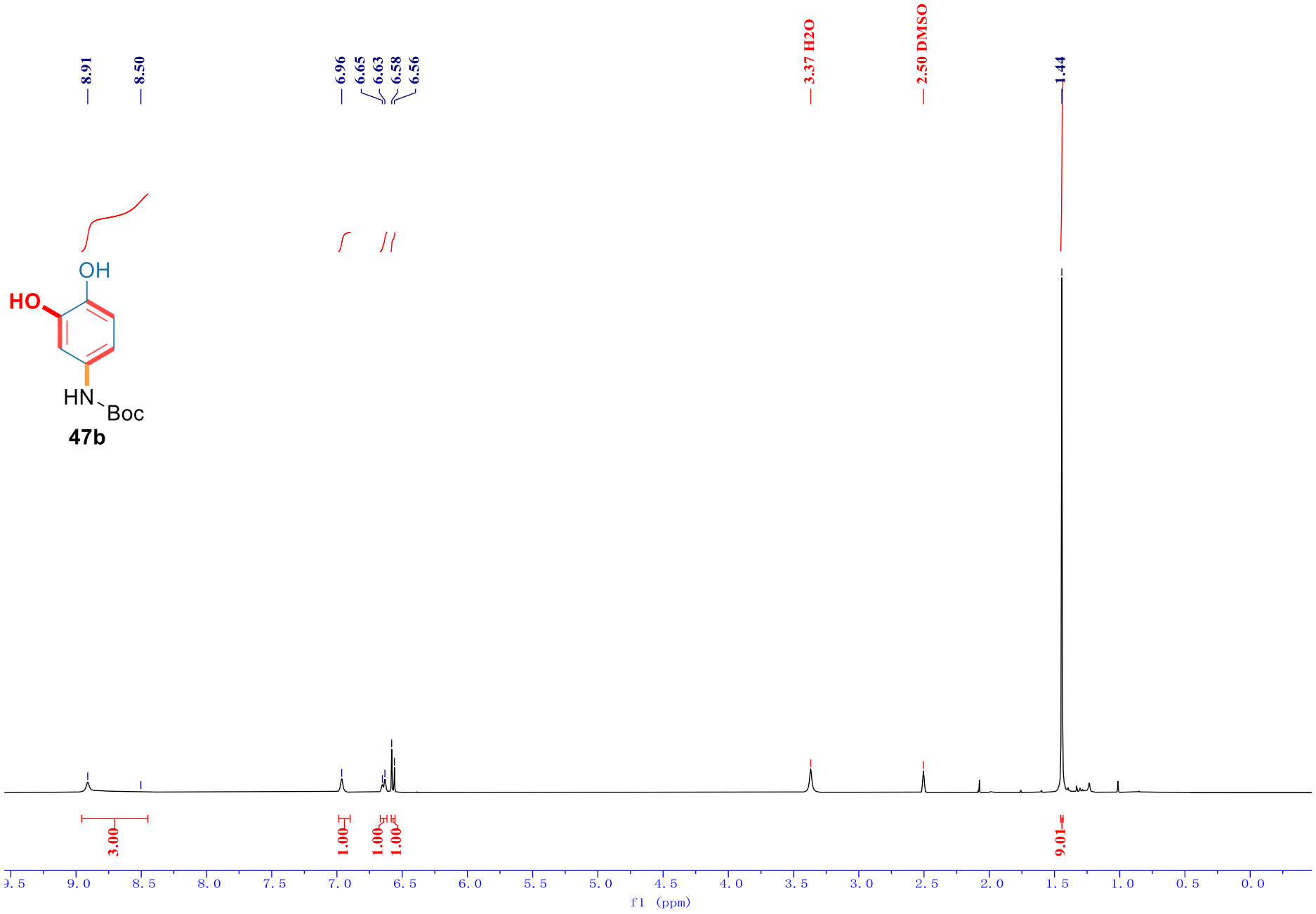

154.85
139.17
130.91
129.64
129.03
128.47
128.28
127.03
120.00
116.58
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
Ph
46a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

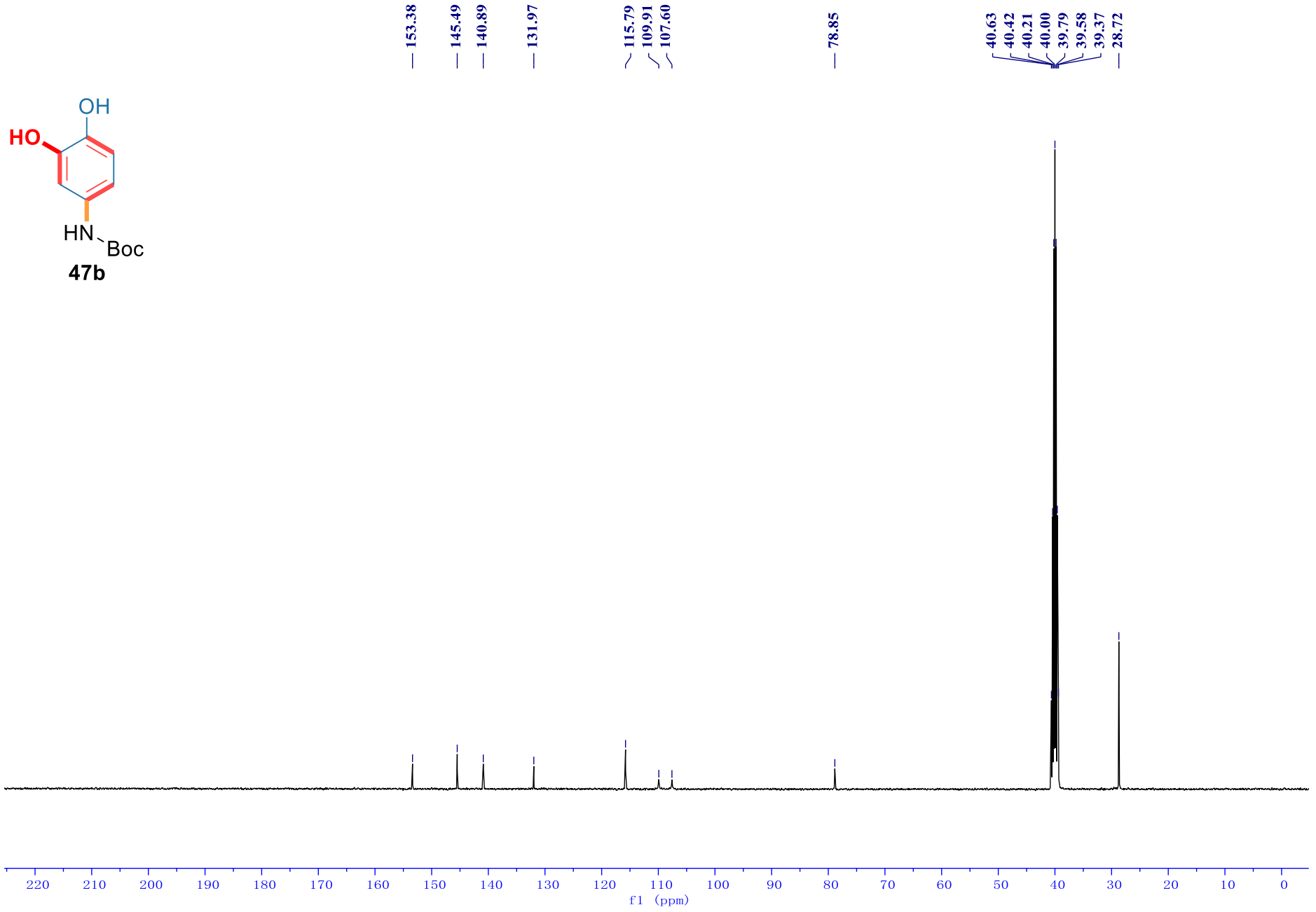

OH
HO
Ph
46b
8.87
7.53
7.53
7.52
7.51
7.51
7.50
7.40
7.38
7.36
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
6.82
6.80
6.80
6.79
6.78
6.72
6.71
6.71
6.71
6.69
6.67
3.38 H2O
2.50 DMSO-D6
1.58
10.0
9.5
9.0
8.5
8.0
f1 (ppm)
1.58
2.00
2.00
1.00
1.00
2.00
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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)

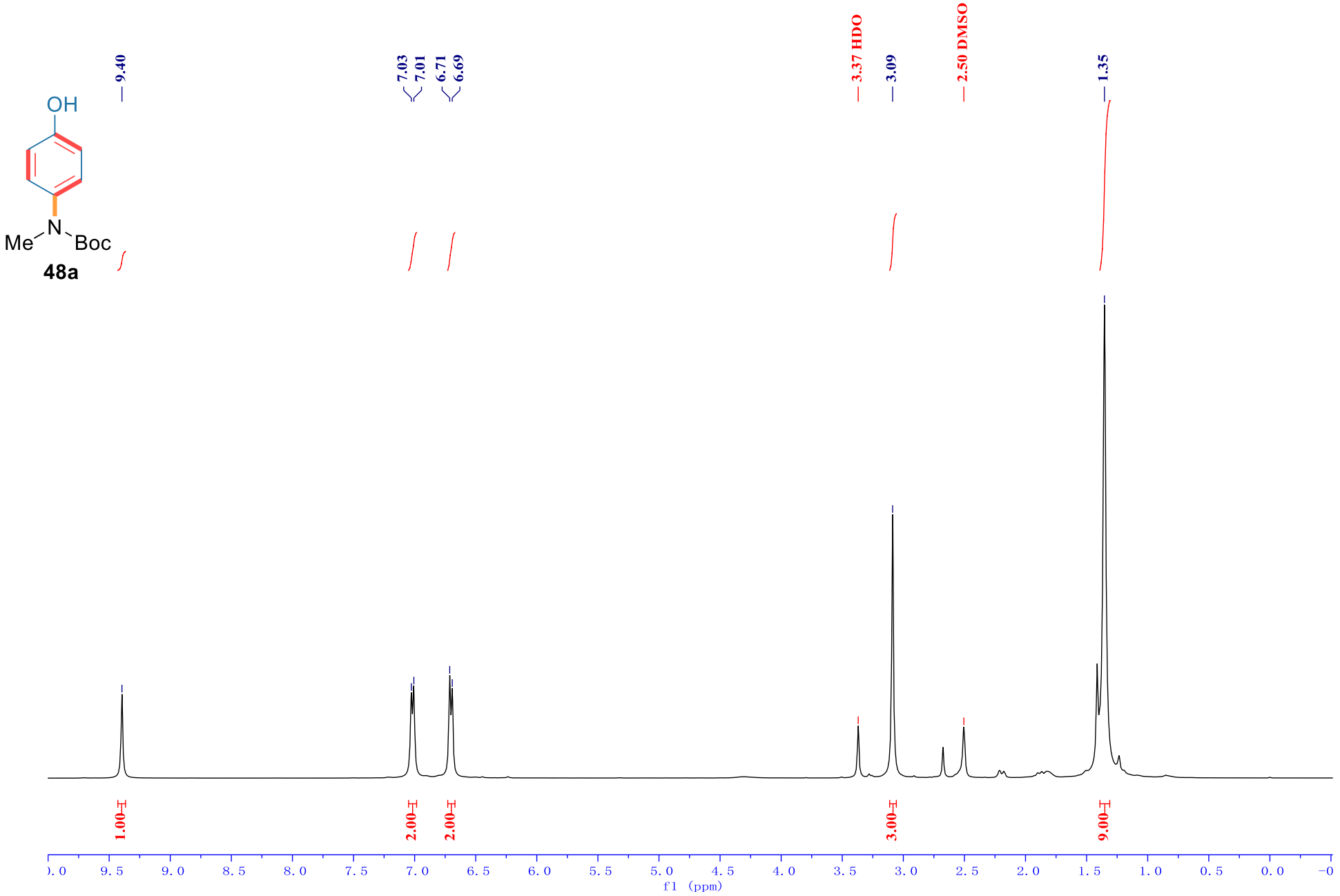

146.08
143.08
139.28
129.58
128.89
128.37
126.94
121.13
119.66
114.83
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
HO
Ph
46b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

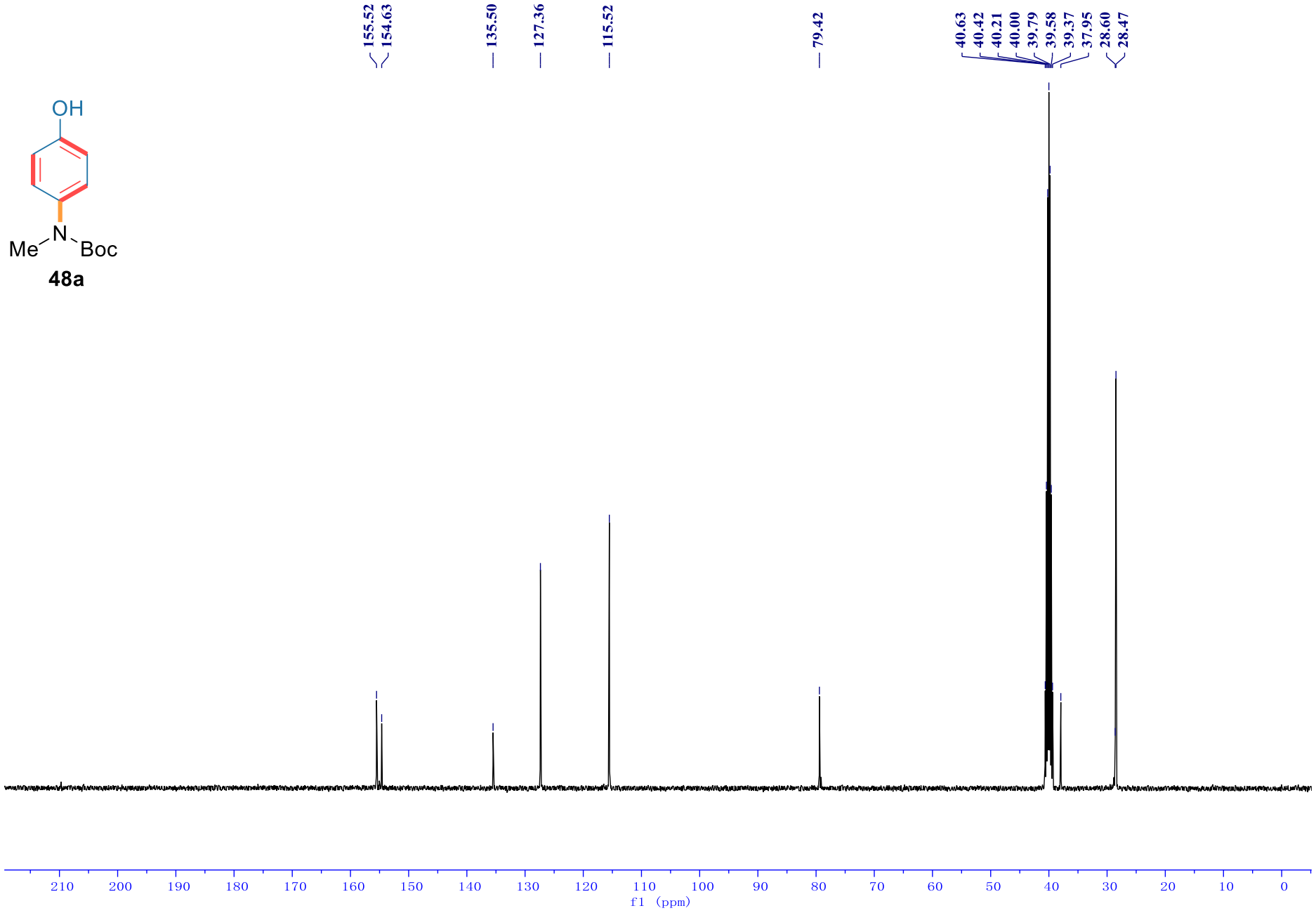

OH
HN
Boc
47a
9.05
8.99
7.22
7.20
6.65
6.64
6.63
3.36 HDO
2.50 DMSO
1.45
1.00
1.00
2.00
2.00
9.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


153.52
153.02
131.52
120.46
115.52
78.93
40.63
40.42
40.21
40.00
39.79
39.58
39.37
28.70
OH
HN
Boc
47a
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)


8.91
8.50
6.96
6.65
6.63
6.58
6.56
3.37 H2O
2.50 DMSO
1.44
OH
HO
HN
Boc
47b
3.00
1.00
1.00
1.00
9.01
f1 (ppm)


153.38
145.49
140.89
131.97
115.79
109.91
107.60
78.85
40.63
40.42
40.21
40.00
39.79
39.58
39.37
28.72
OH
HO
HN
Boc
47b
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)


OH
N
Me
Boc
48a
9.40
7.03
7.01
6.71
6.69
3.37 HDO
3.09
2.50 DMSO
1.35
1.00
2.00
2.00
3.00
9.00
f1 (ppm)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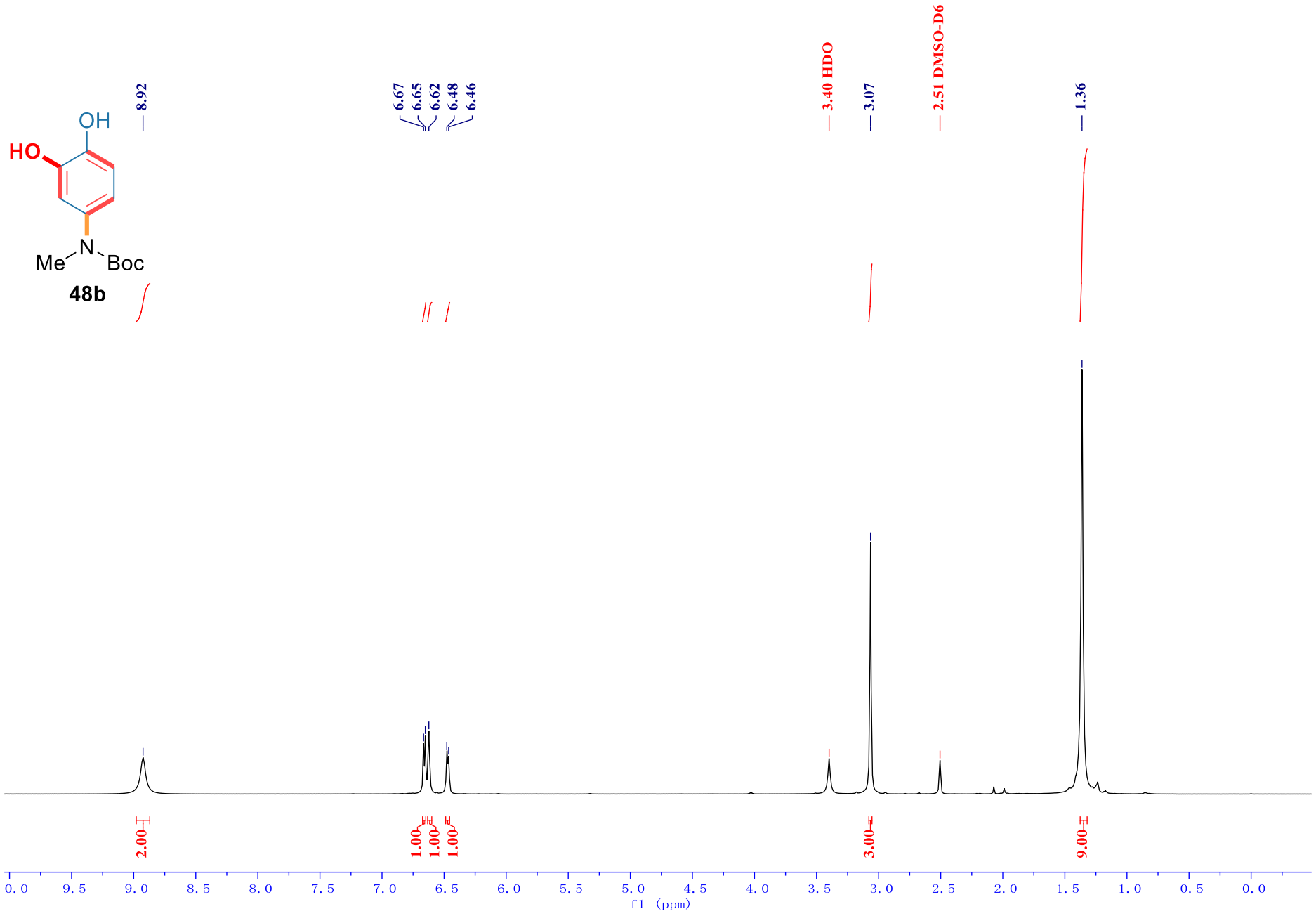
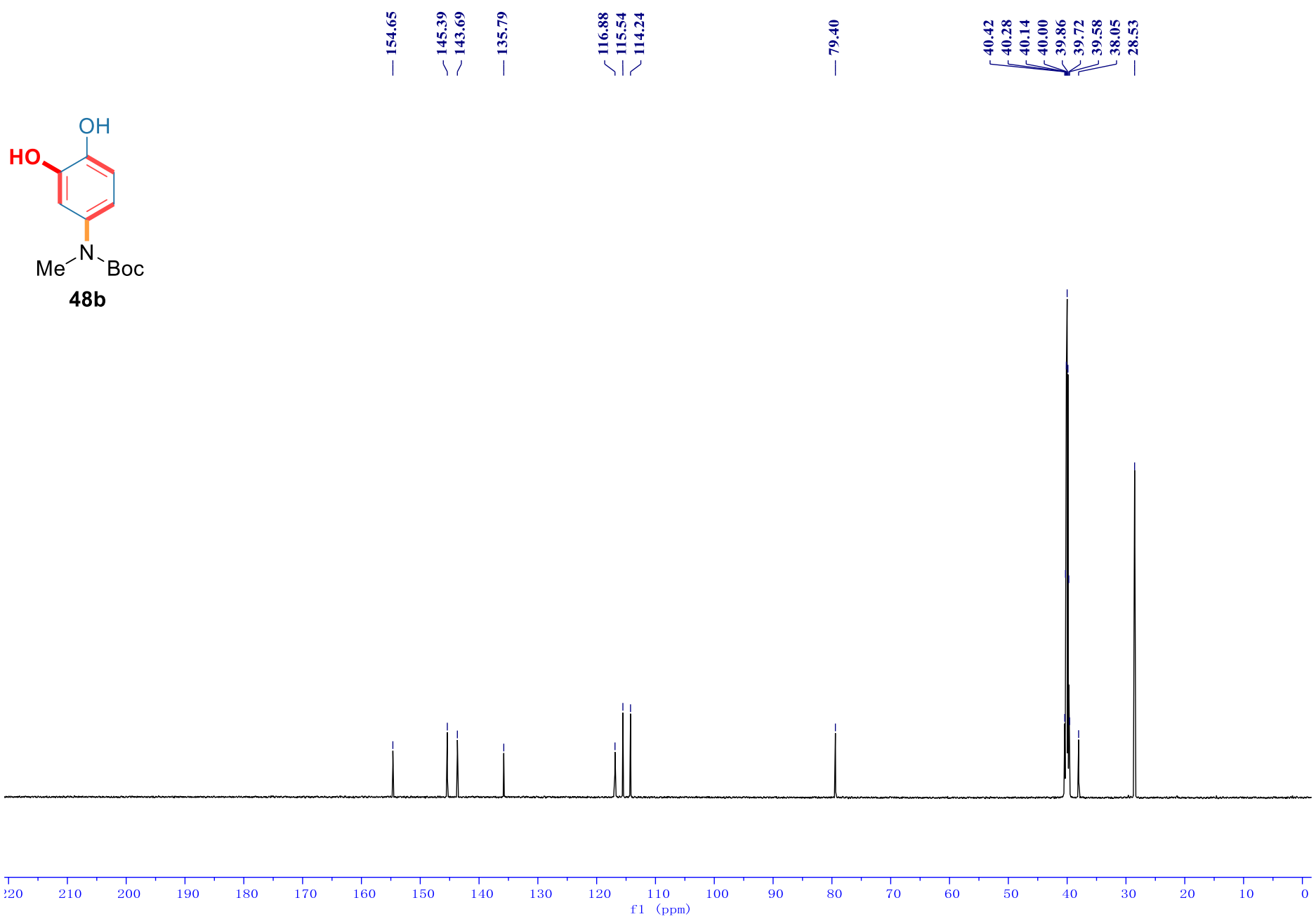
154.63
135.50
127.36
115.52
79.42
40.63
40.42
40.21
40.00
39.79
39.58
39.37
37.95
28.60
28.47
OH
N
Me
Boc
48a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
HO
N
Me
Boc
48b
8.92
6.67
6.65
6.62
6.48
6.46
3.40 HDO
3.07
2.51 DMSO-D6
1.36
2.00
1.00
1.00
1.00
3.00
9.00
f1 (ppm)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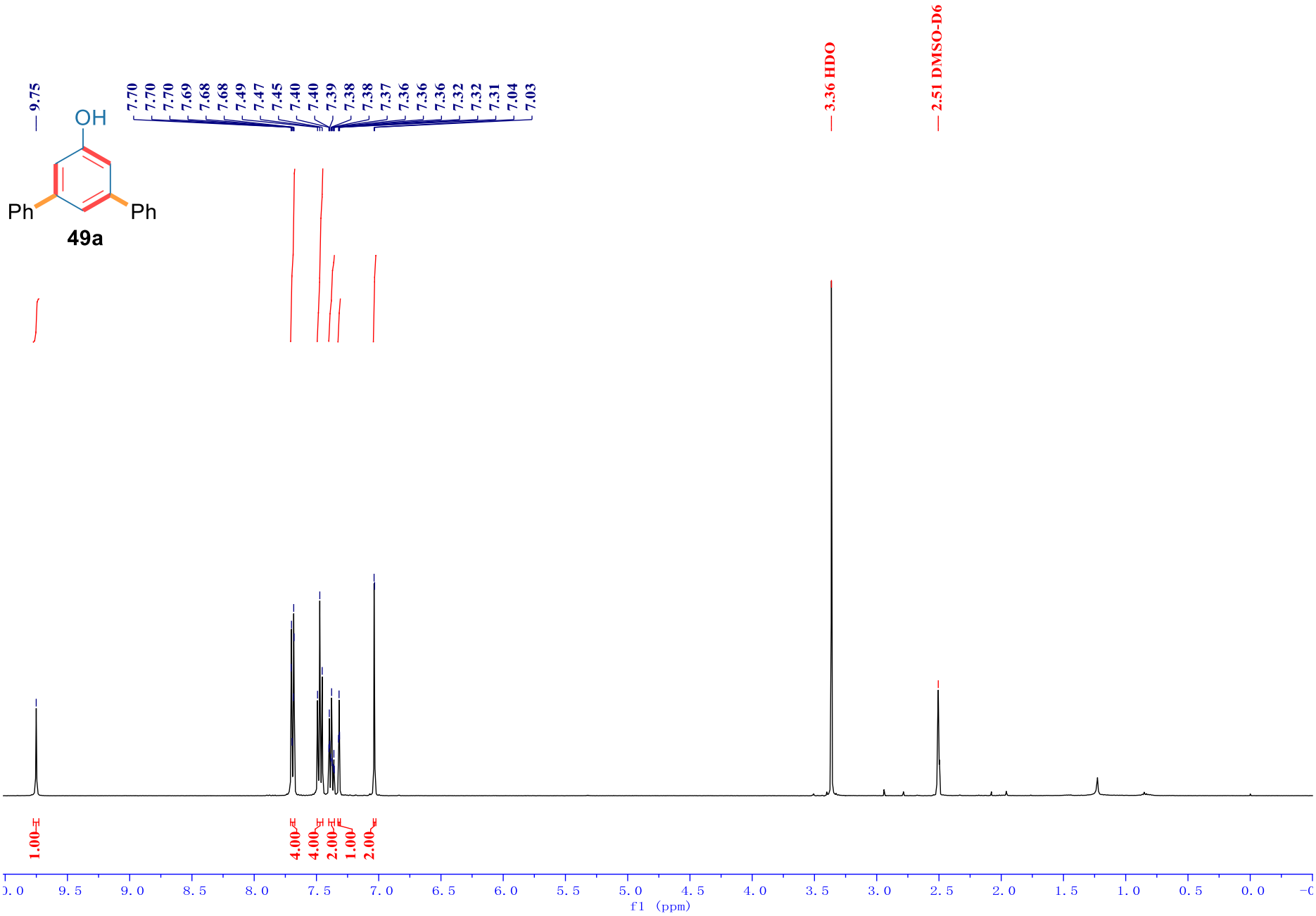
135.79
116.88
115.54
114.24
79.40
40.42
40.28
40.14
40.00
39.86
39.72
39.58
38.05
28.53
OH
HO
N
Me
Boc
48b
f1 (ppm)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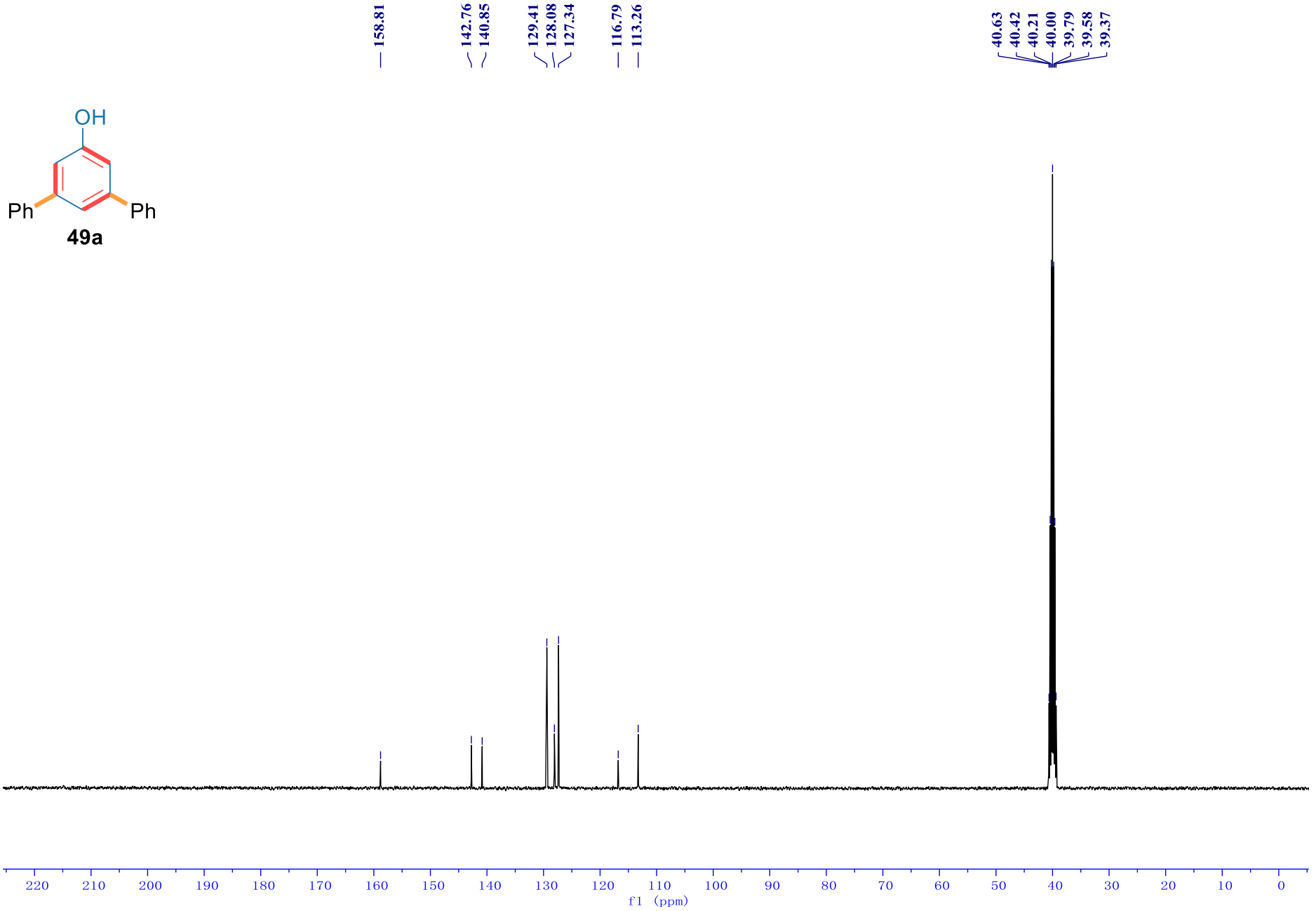
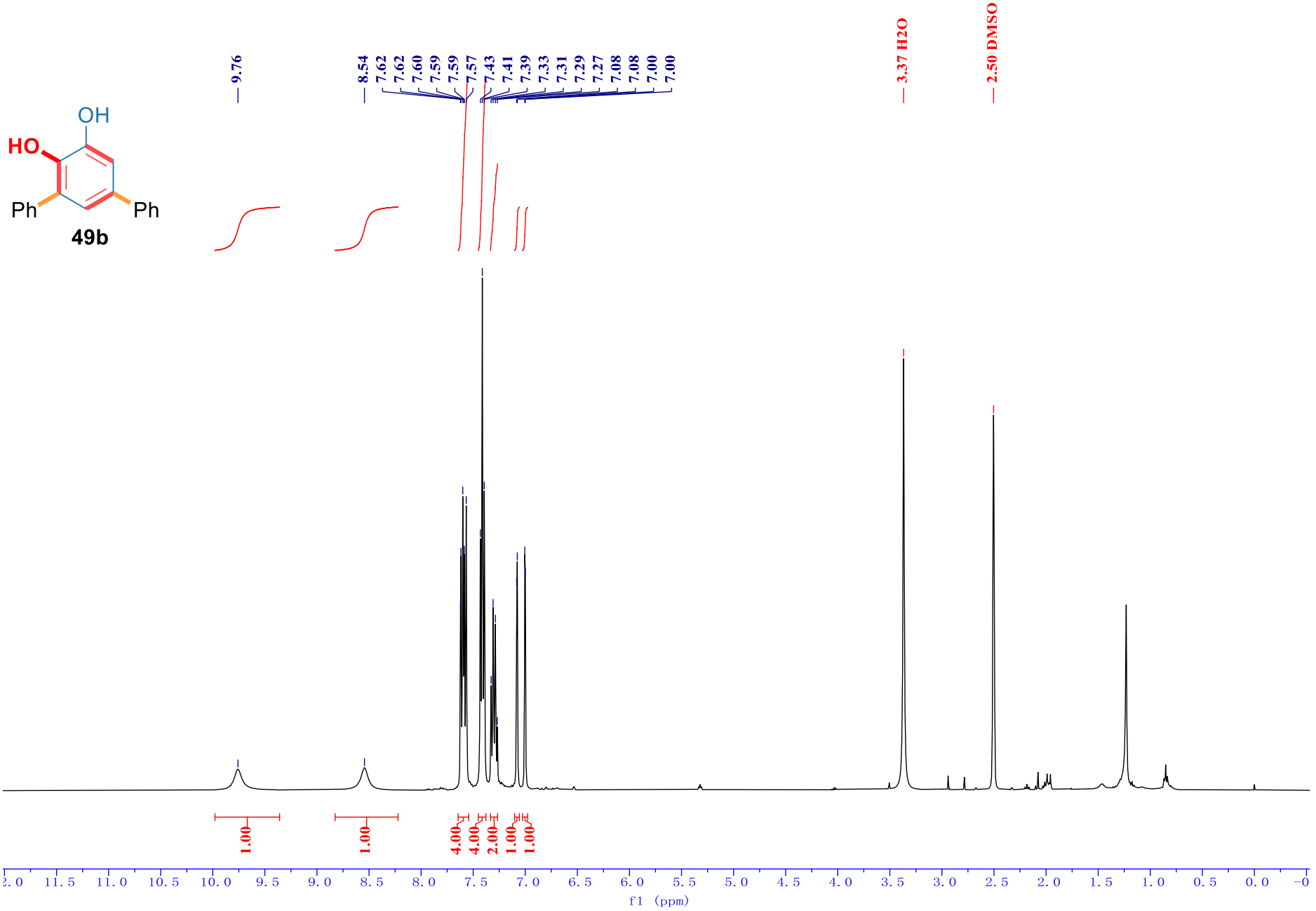
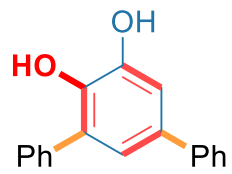
7.70
7.70
7.70
7.69
7.68
7.68
7.49
7.47
7.45
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.32
7.32
7.31
7.04
7.03
3.36 HDO
2.51 DMSO-D6
OH
Ph
Ph
49a
1.00
4.00
4.00
2.00
1.00
2.00
f1 (ppm)

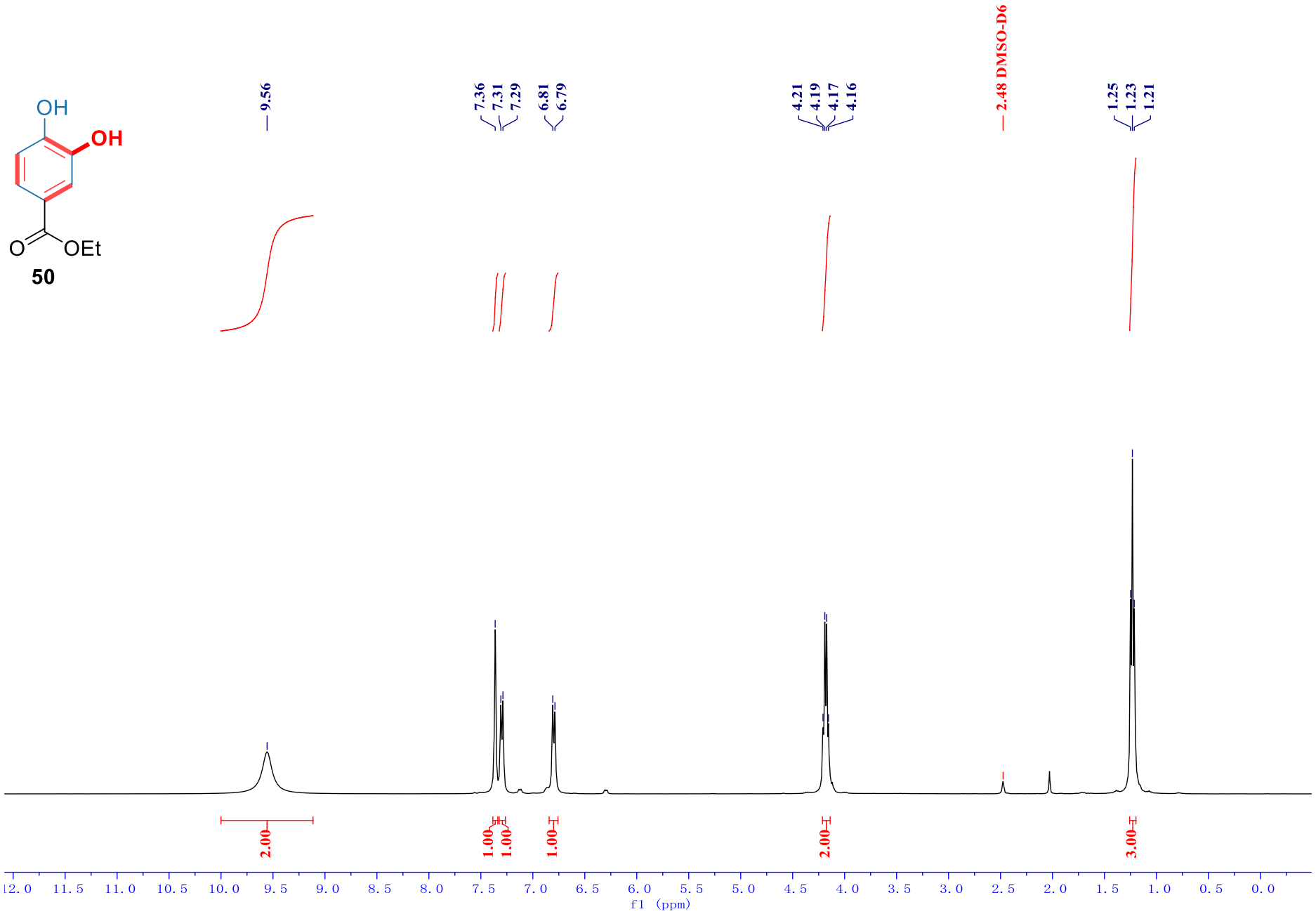

158.81
142.76
140.85
129.41
128.08
127.34
116.79
113.26
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
Ph
Ph
49a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

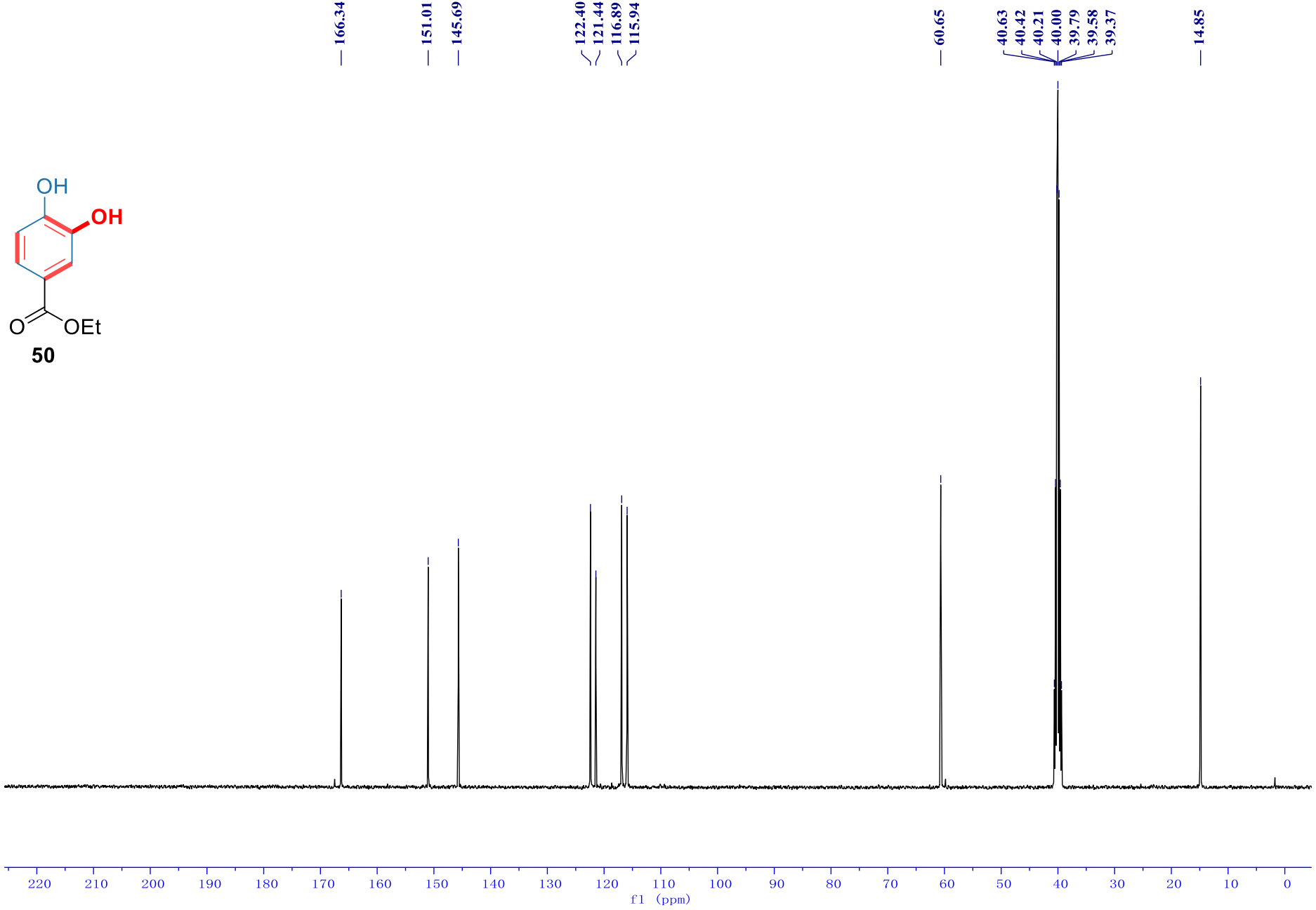

OH
HO
Ph
Ph
49b
9.76
8.54
7.62
7.62
7.60
7.59
7.59
7.57
7.43
7.41
7.39
7.33
7.31
7.29
7.27
7.08
7.08
7.00
7.00
3.37 H2O
2.50 DMSO
1.00
1.00
4.00
4.00
2.00
1.00
1.00
f1 (ppm)

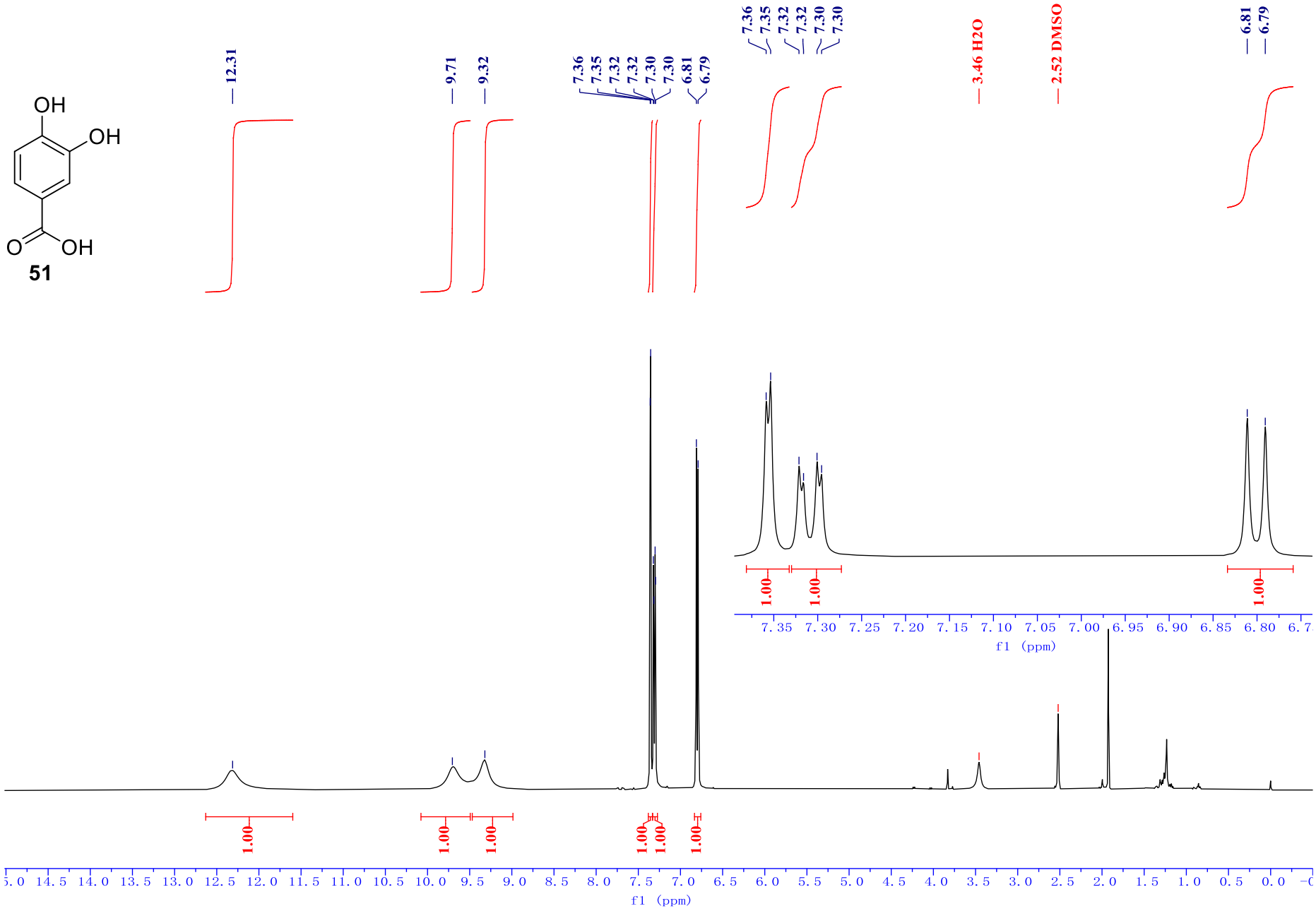

OH
HO
Ph
Ph

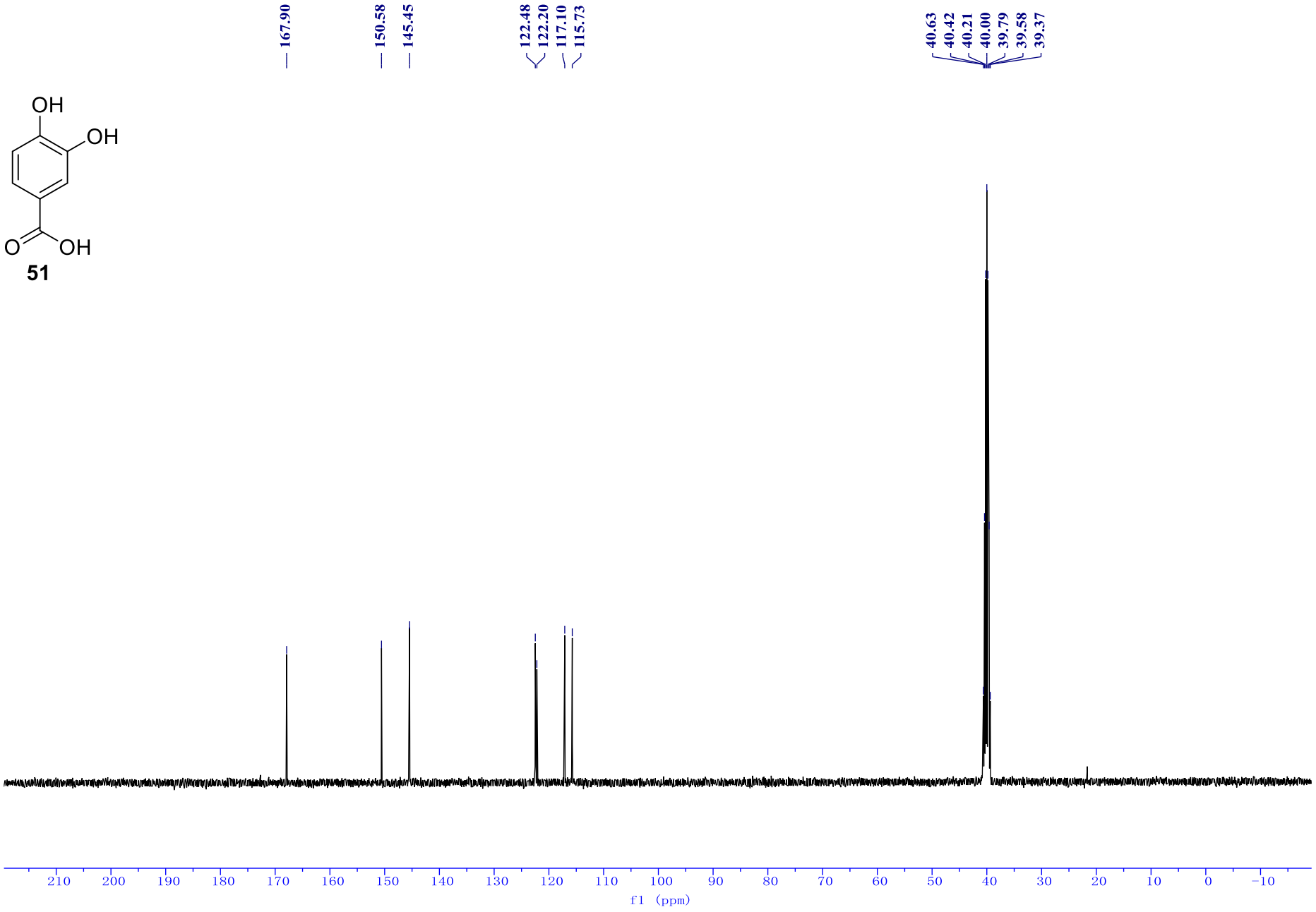
49b

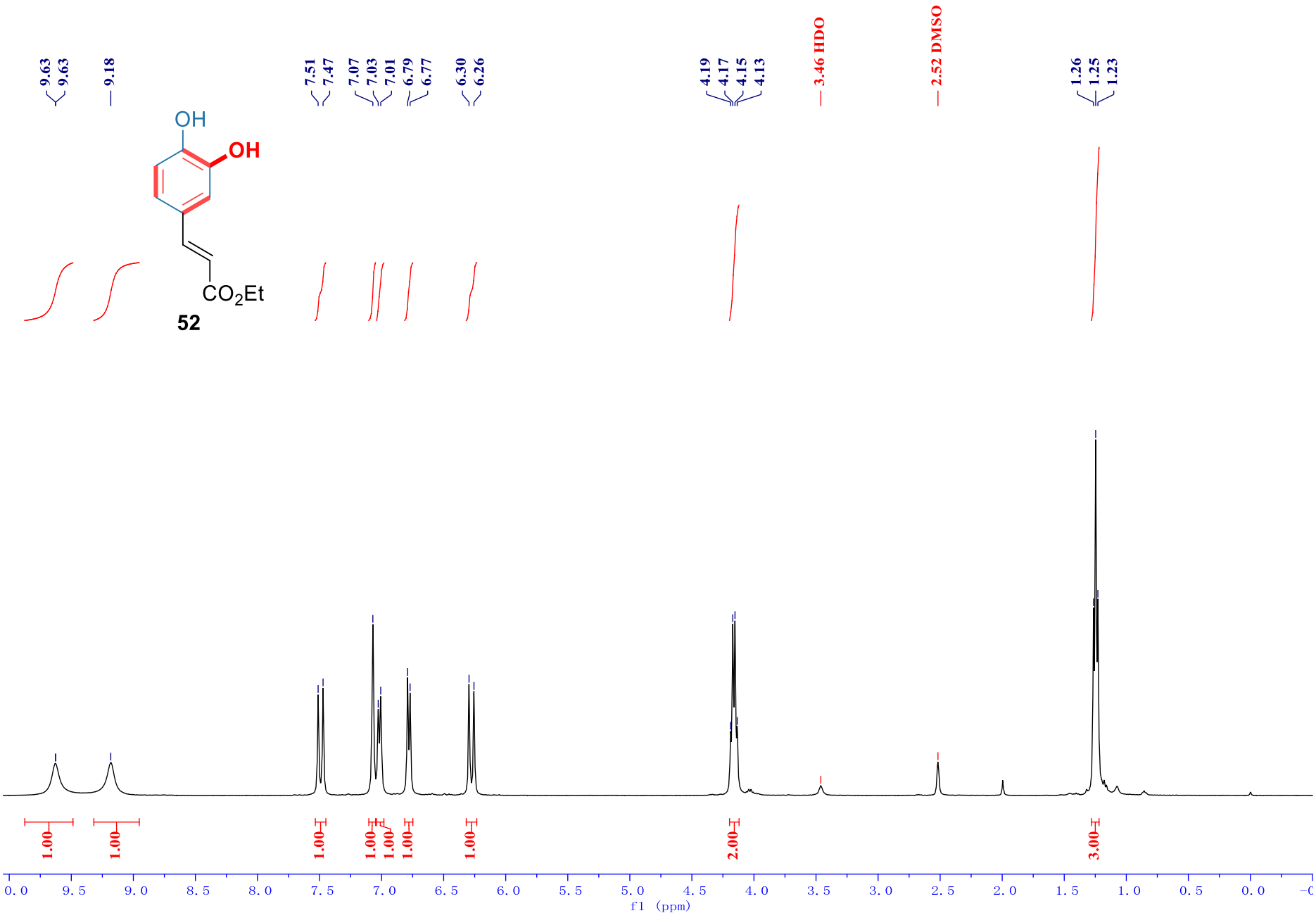
146.49
142.96
140.94
139.17
131.86
129.70
129.34
129.20
128.42
127.13
127.04
126.64
119.57
113.07
40.63
40.42
40.21
40.00
39.79
39.58
39.38
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

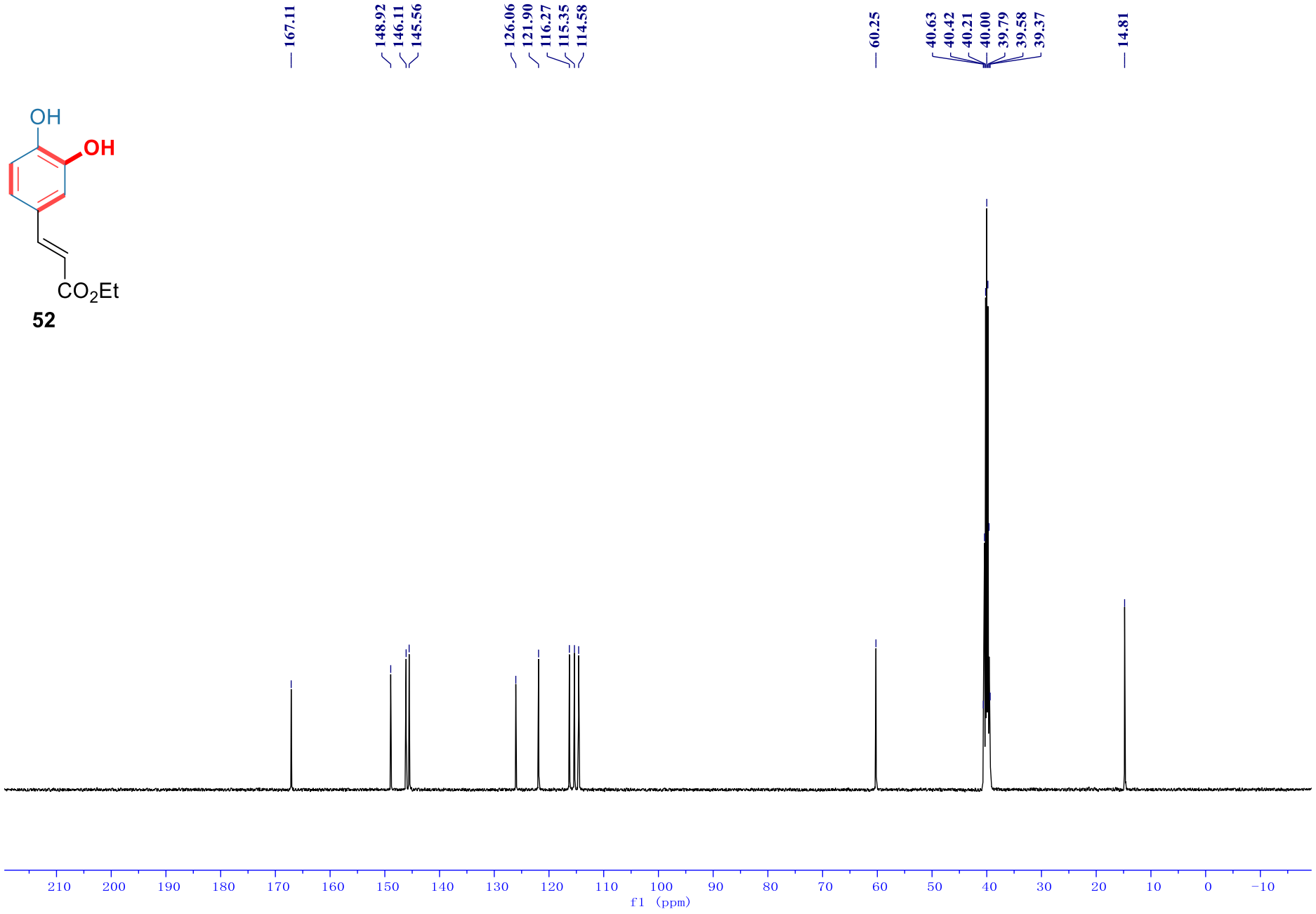

OH
OH
O
OEt
50
9.56
7.36
7.31
7.29
6.81
6.79
4.21
4.19
4.17
4.16
2.48 DMSO-D6
1.25
1.23
1.21
2.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

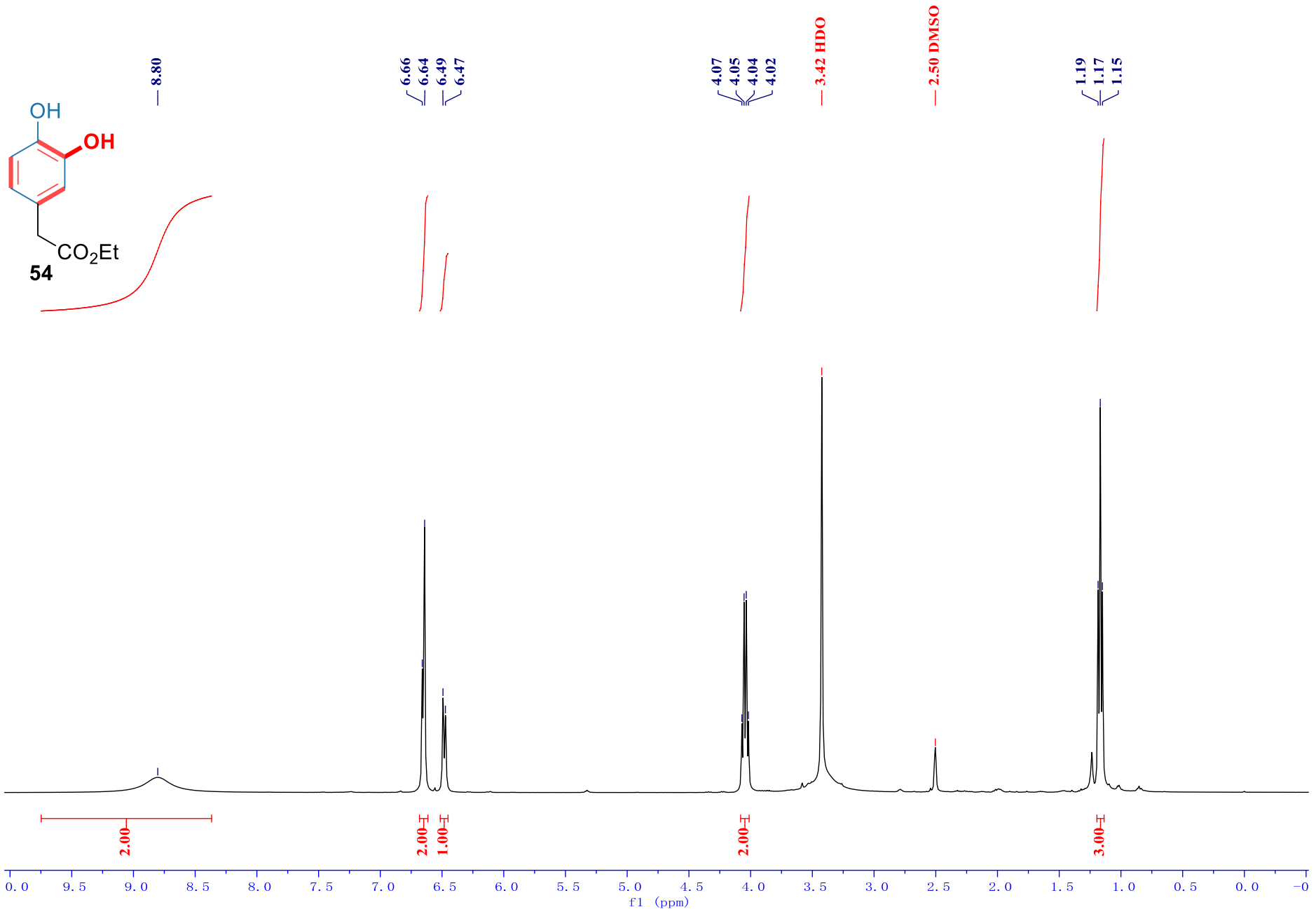

166.34
151.01
145.69
122.40
121.44
116.89
115.94
60.65
40.63
40.42
40.21
40.00
39.79
39.58
39.37
14.85
OH
OH
O
OEt
50
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

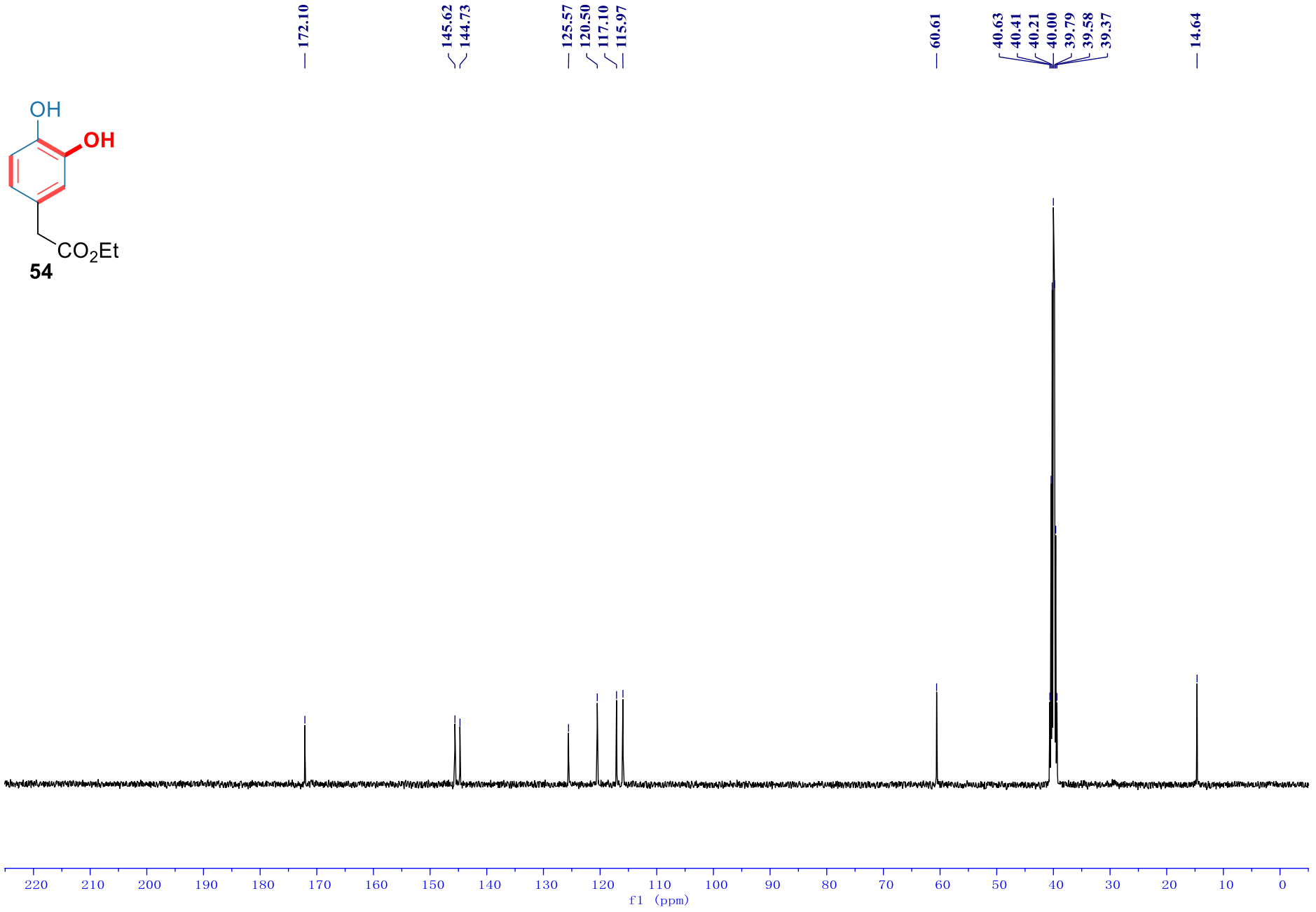

OH
OH
O
OH
51
12.31
9.71
9.32
7.36
7.35
7.32
7.32
7.30
7.30
6.81
6.79
3.46 H2O
2.52 DMSO
1.00
f1 (ppm)

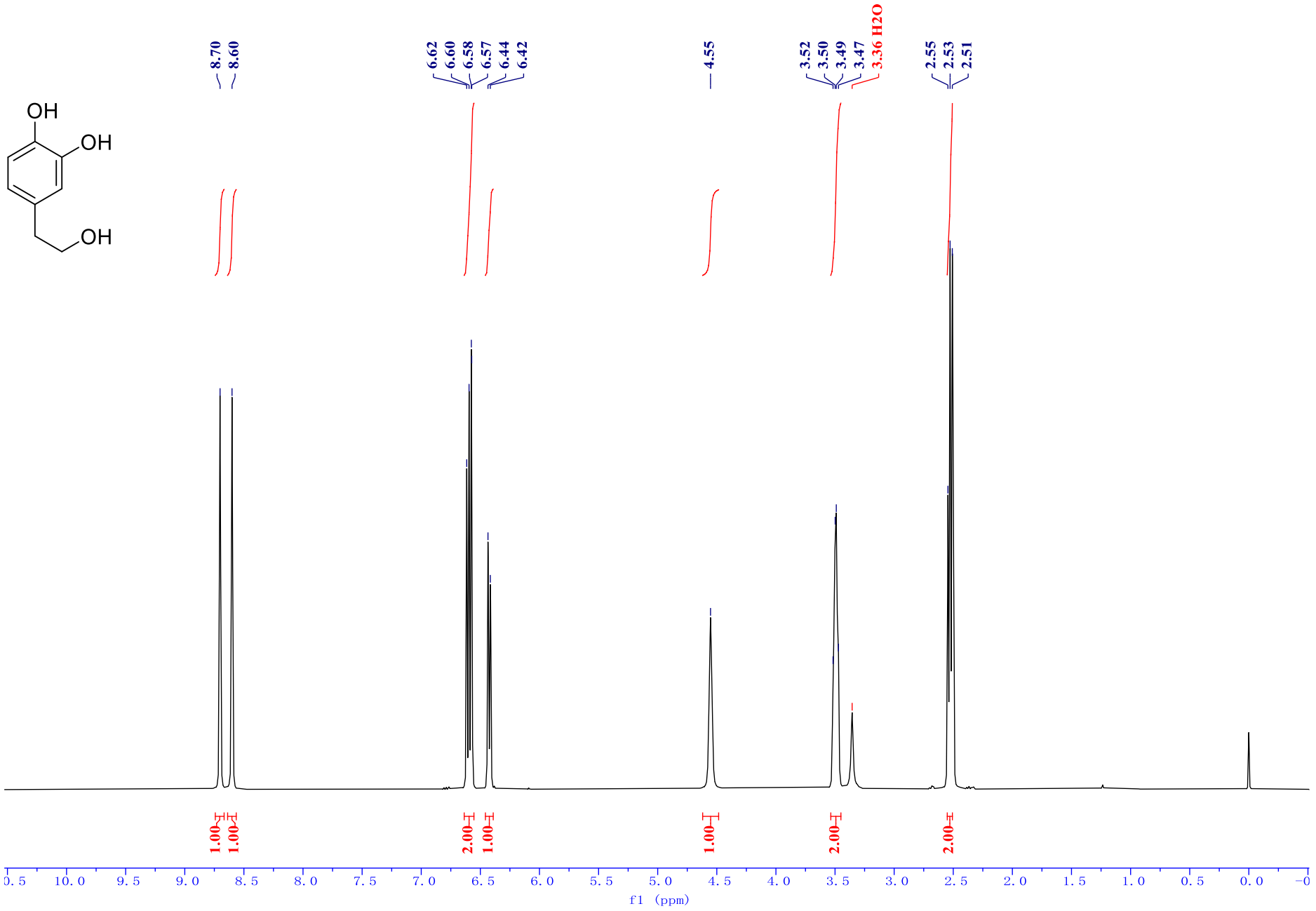

167.90
150.58
145.45
122.48
122.20
117.10
115.73
40.63
40.42
40.21
40.00
39.79
39.58
39.37
OH
OH
O
OH
51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

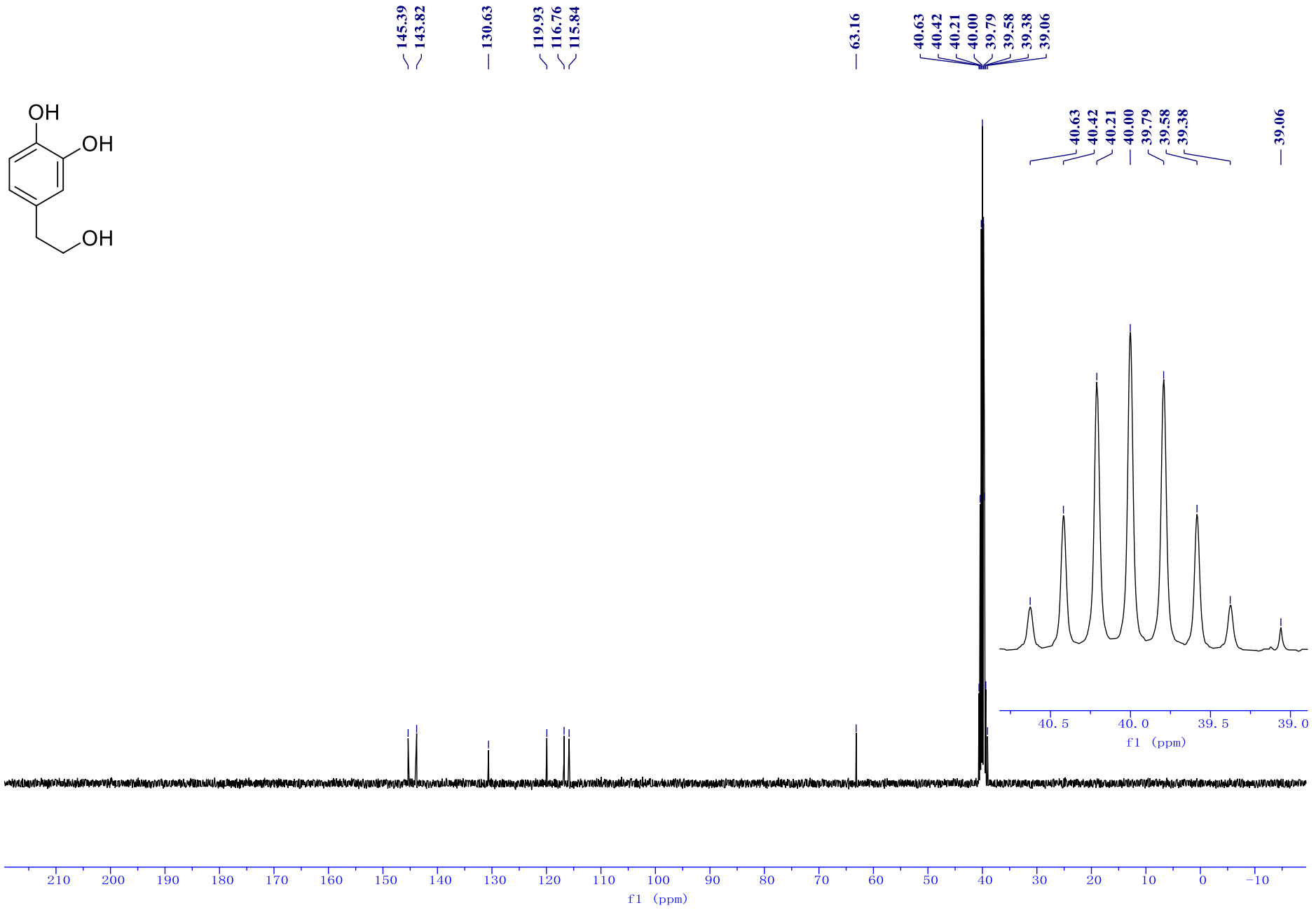

9.63
9.63
9.18
7.51
7.47
7.07
7.03
7.01
6.79
6.77
6.30
6.26
4.19
4.17
4.15
4.13
3.46 HDO
2.52 DMSO
1.26
1.25
1.23
OH
OH
CO2Et
52
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

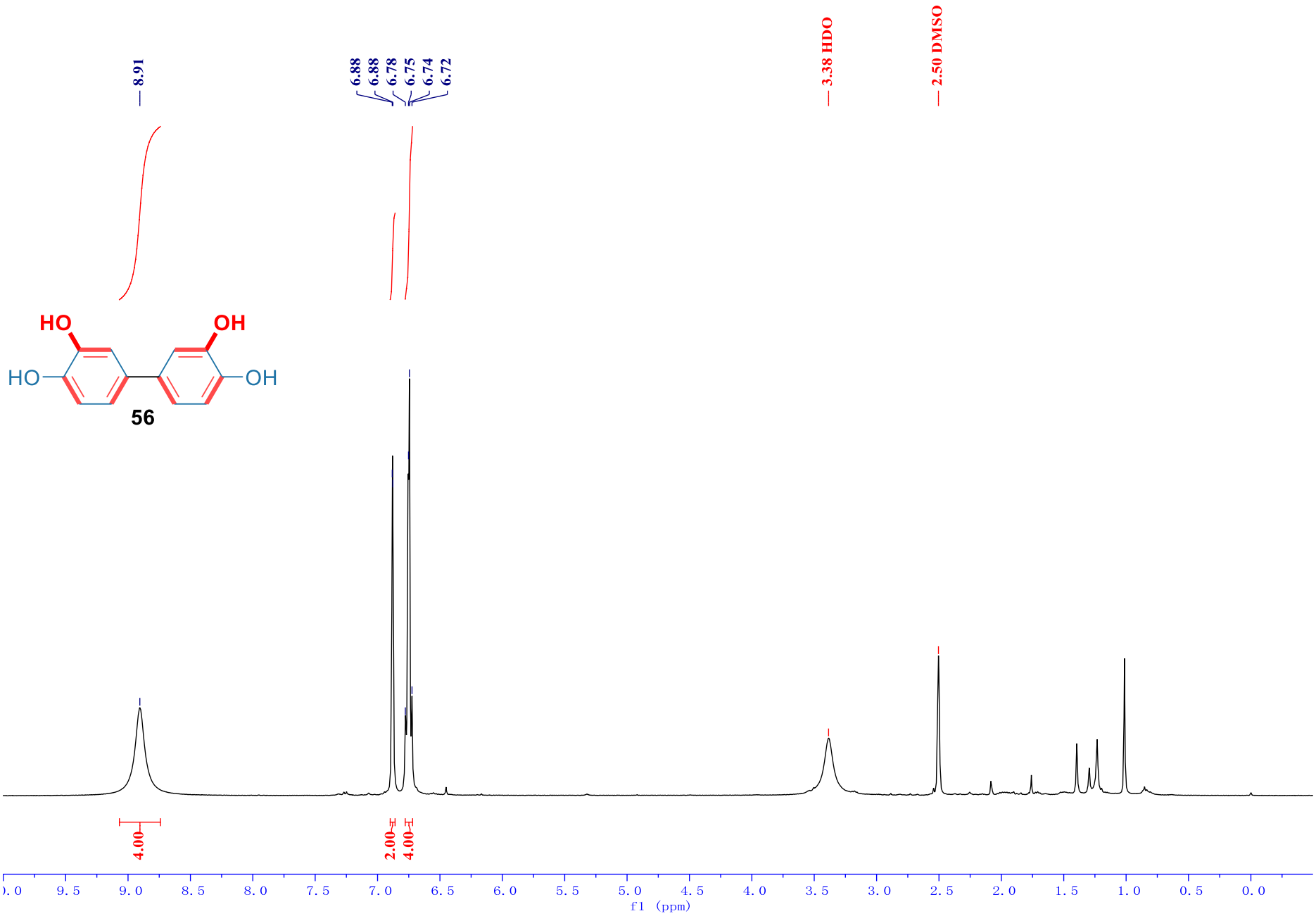

167.11
148.92
146.11
145.56
126.06
121.90
116.27
115.35
114.58
60.25
40.63
40.42
40.21
40.00
39.79
39.58
39.37
14.81
OH
OH
CO2Et
52
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

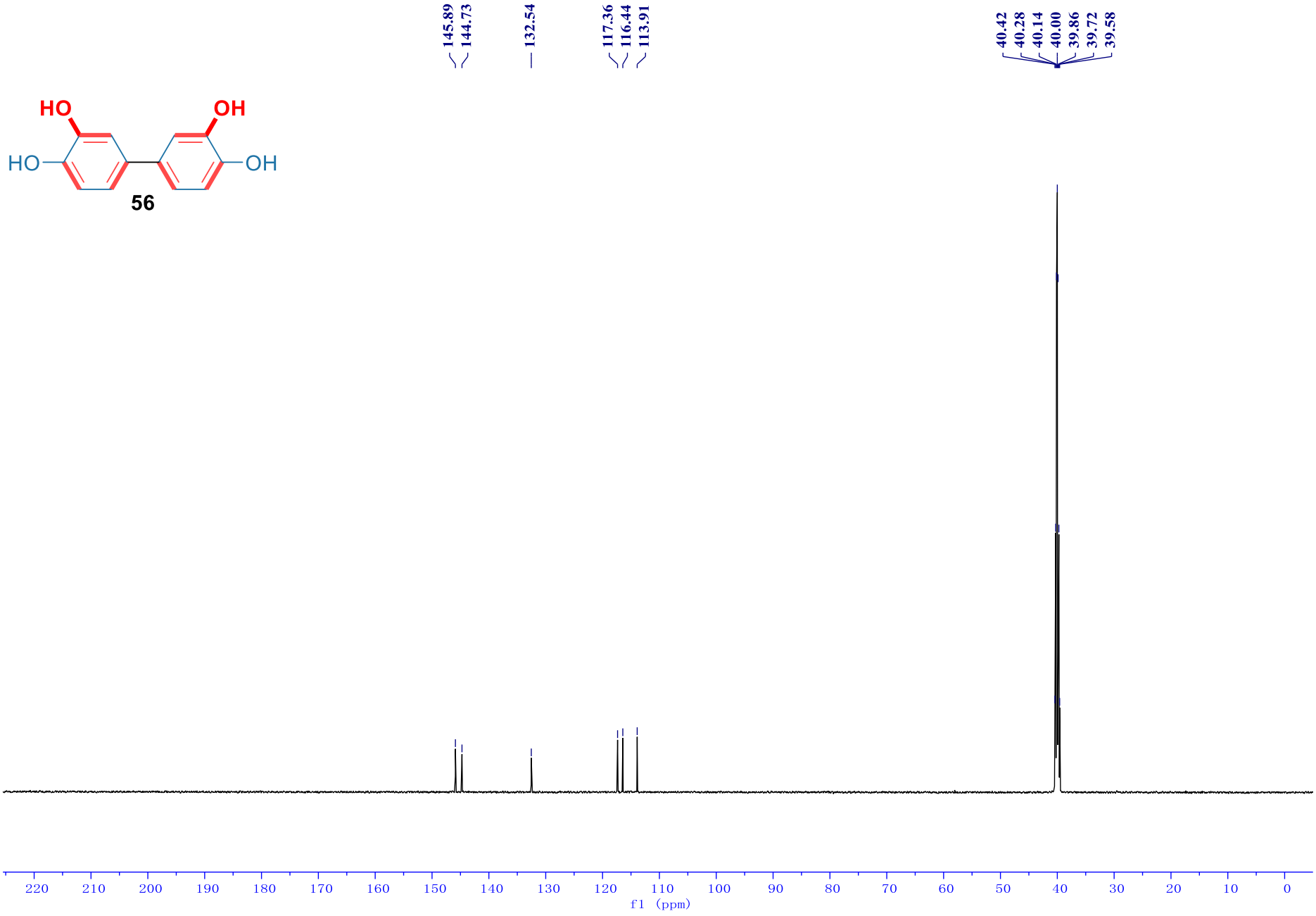

8.80
6.66
6.64
6.49
6.47
4.07
4.05
4.04
4.02
3.42 HDO
2.50 DMSO
1.19
1.17
1.15
OH
OH
CO2Et
54
2.00
2.00
1.00
2.00
3.00
f1 (ppm)

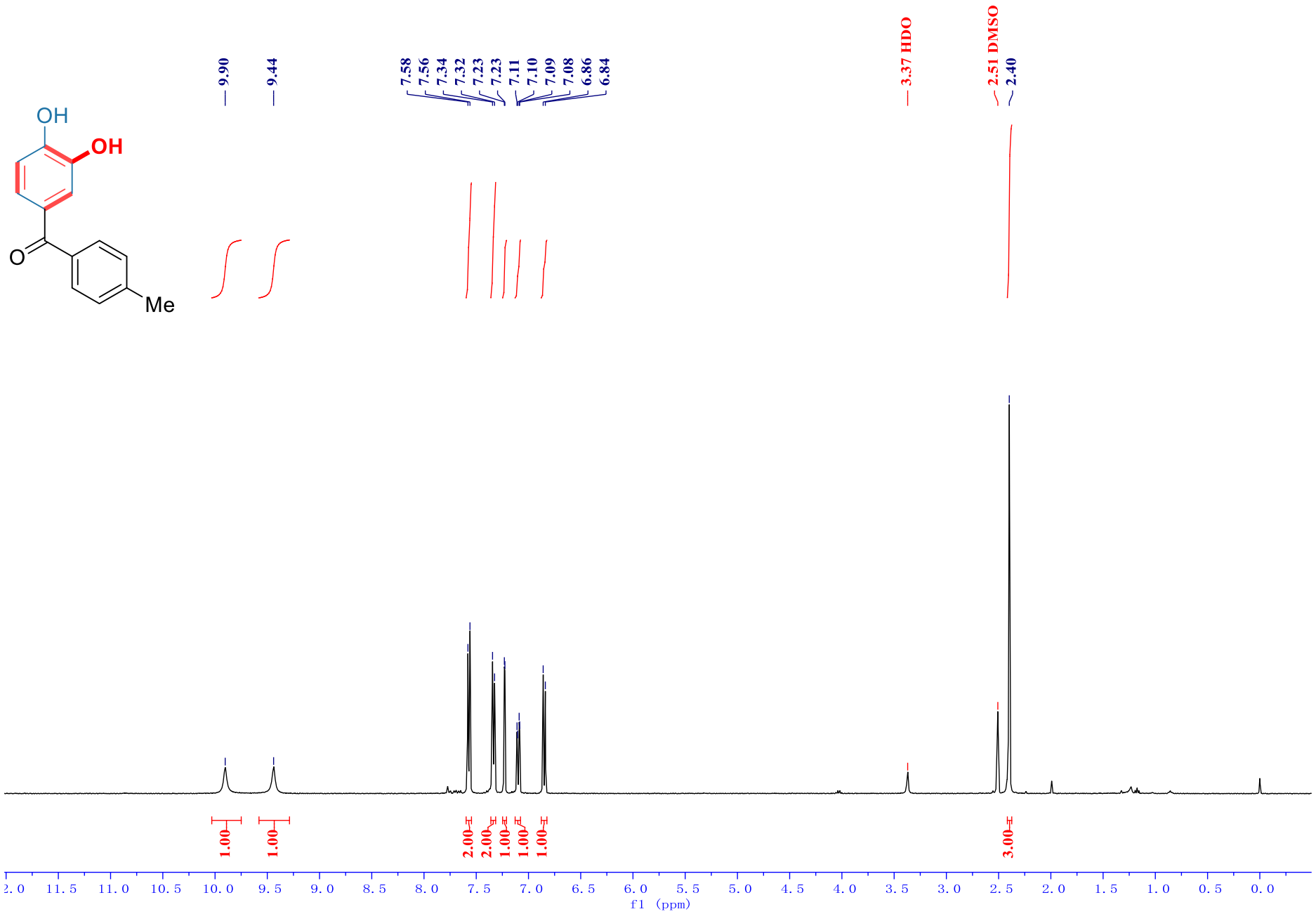

172.10
145.62
144.73
125.57
120.50
117.10
115.97
60.61
40.63
40.41
40.21
40.00
39.79
39.58
39.37
14.64
OH
OH
CO2Et
54
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

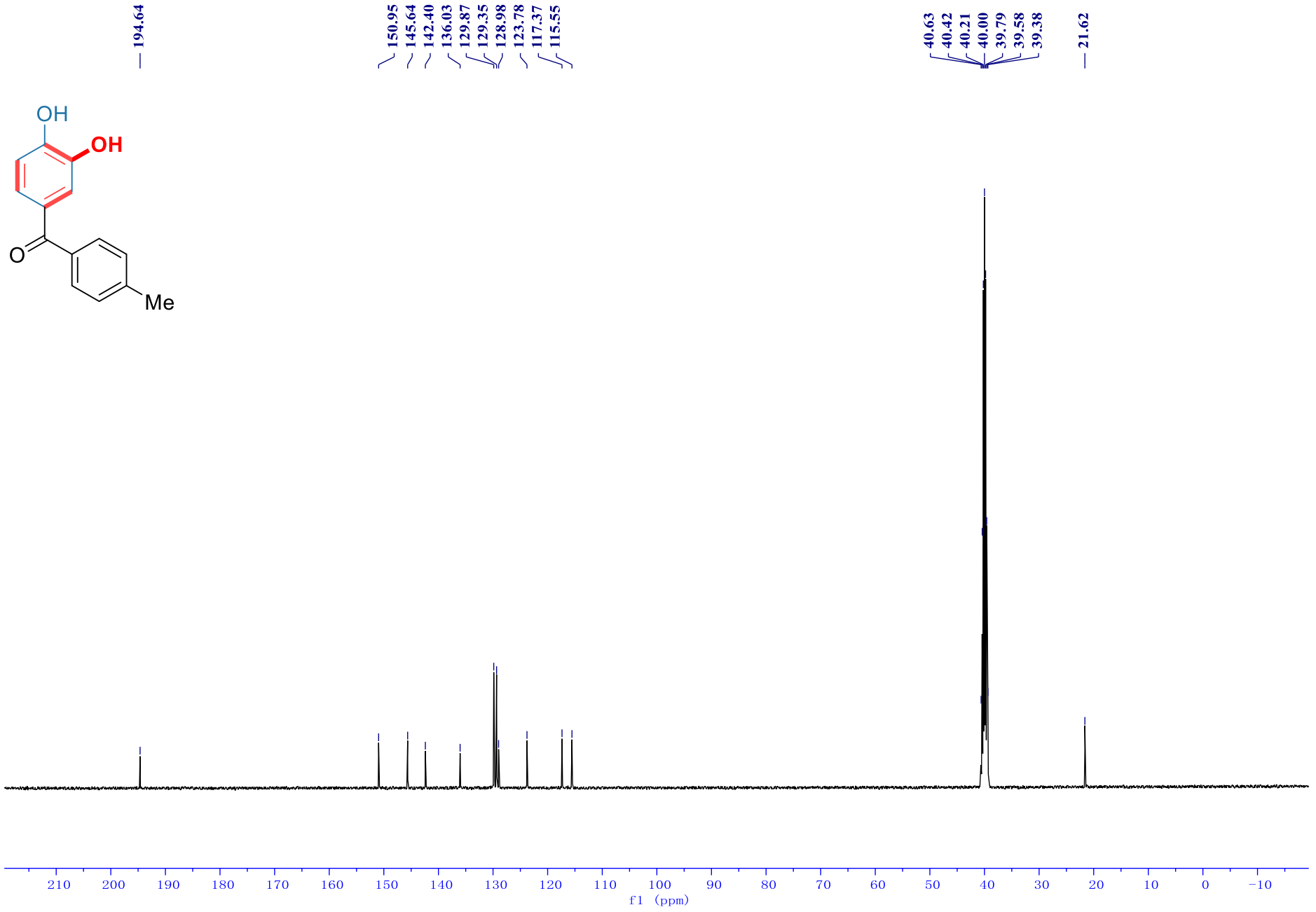

OH
OH
OH
8.70
8.60
6.62
6.60
6.58
6.57
6.44
6.42
4.55
3.52
3.50
3.49
3.47
3.36 H2O
2.55
2.53
2.51
1.00
1.00
2.00
1.00
1.00
2.00
2.00
f1 (ppm)


145.39
143.82
130.63
119.93
116.76
115.84
63.16
40.63
40.42
40.21
40.00
39.79
39.58
39.38
39.06
OH
OH
OH
f1 (ppm)


8.91
6.88
6.88
6.78
6.75
6.74
6.72
3.38 HDO
2.50 DMSO
HO
OH
HO
OH
56
4.00
2.00
4.00
f1 (ppm)


145.89
144.73
132.54
117.36
116.44
113.91
40.42
40.28
40.14
40.00
39.86
39.72
39.58
HO
OH
HO
OH
56
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)


OH
OH
O
Me
9.90
9.44
7.58
7.56
7.34
7.32
7.23
7.23
7.11
7.10
7.09
7.08
6.86
6.84
3.37 HDO
2.51 DMSO
2.40
1.00
1.00
2.00
2.00
1.00
1.00
1.00
3.00
f1 (ppm)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150.95
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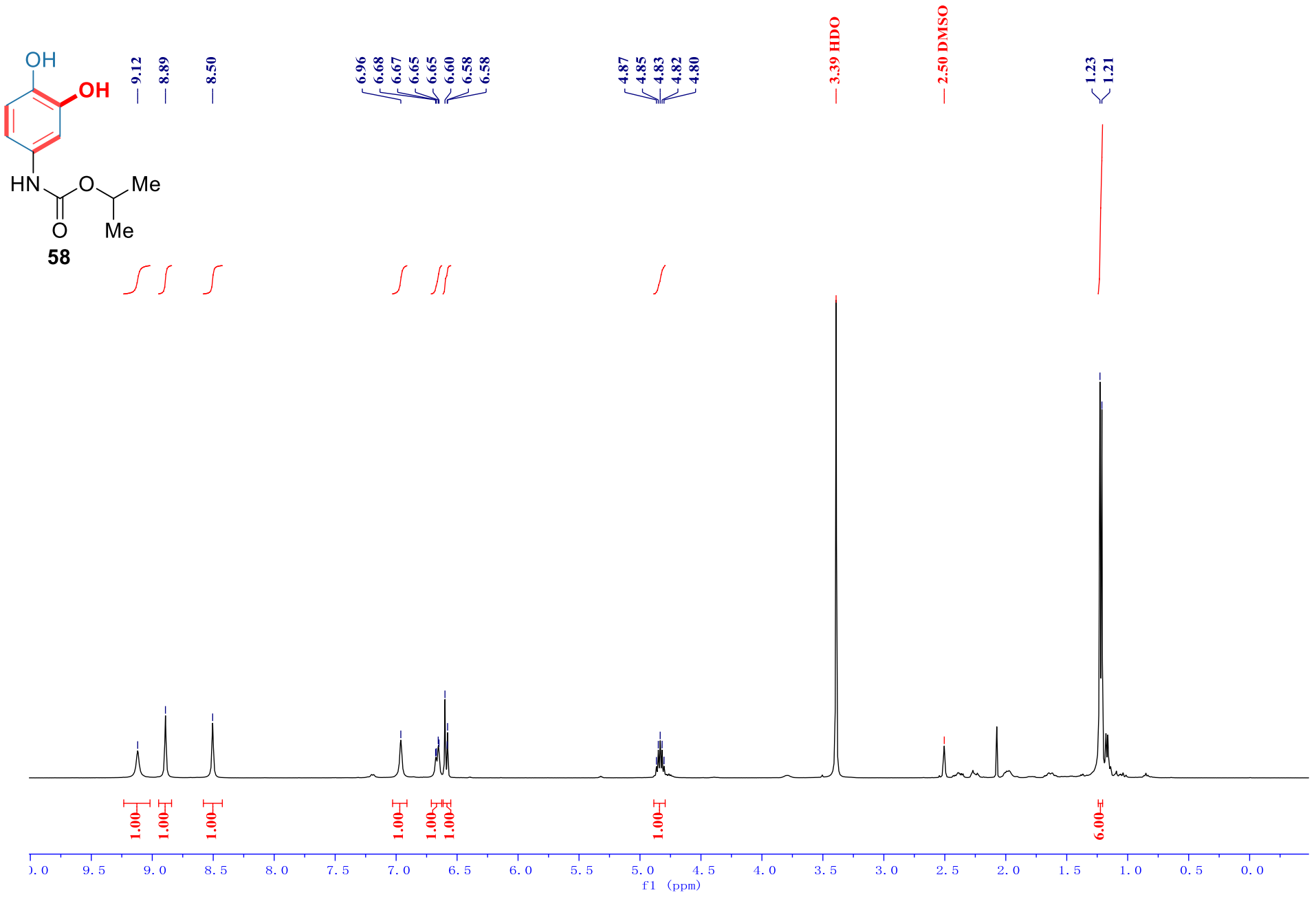
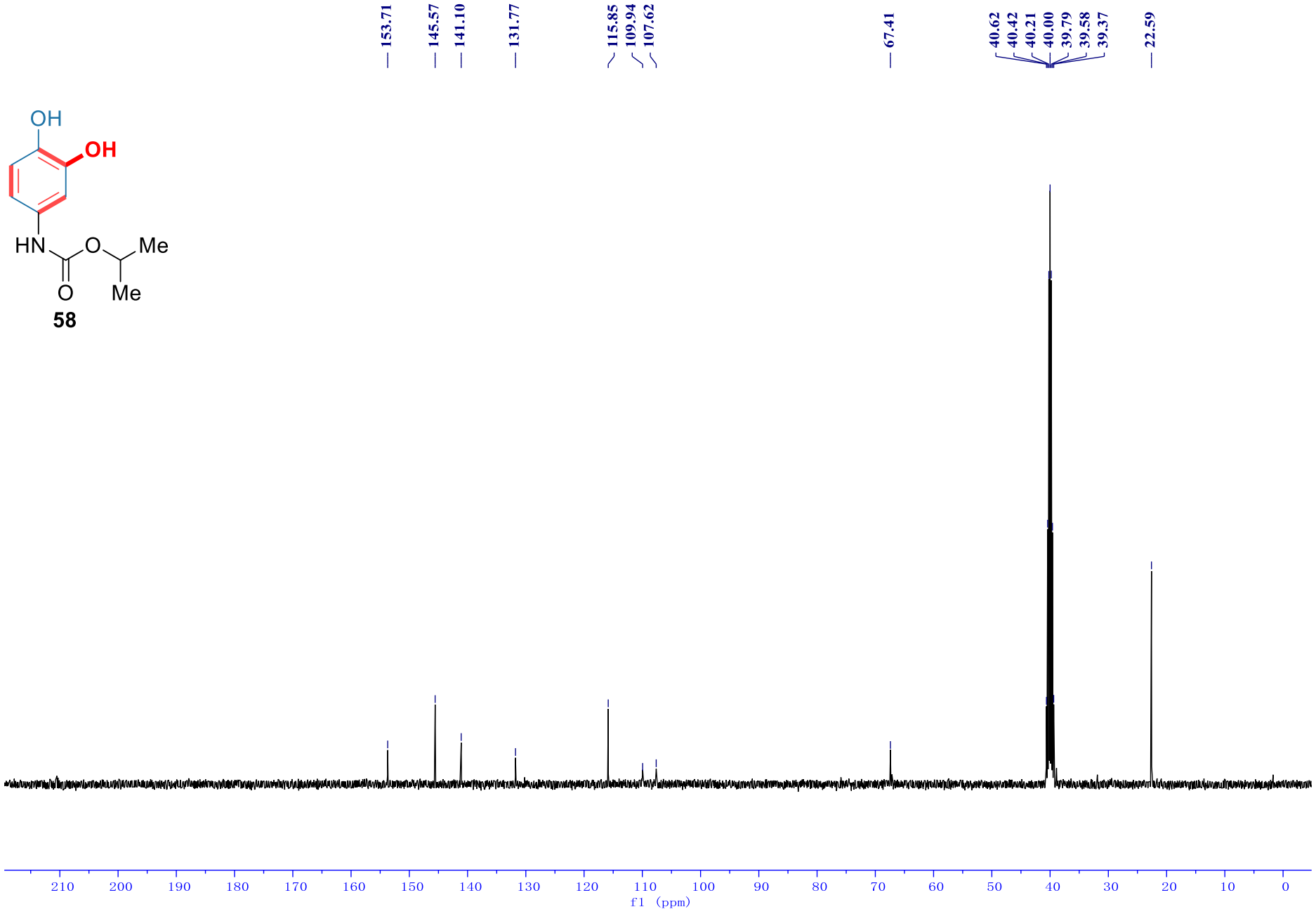
142.40
136.03
129.87
129.35
128.98
123.78
117.37
115.55
40.63
40.42
40.21
40.00
39.79
39.58
39.38
21.62
OH
OH
O
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


OH
OH
HN
O
Me
O
Me
58
9.12
8.89
8.50
6.96
6.68
6.67
6.65
6.65
6.60
6.58
6.58
4.87
4.85
4.83
4.82
4.80
3.39 HDO
2.50 DMSO
1.23
1.21
1.00
1.00
1.00
1.00
1.00
1.00
6.00
f1 (ppm)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145.57
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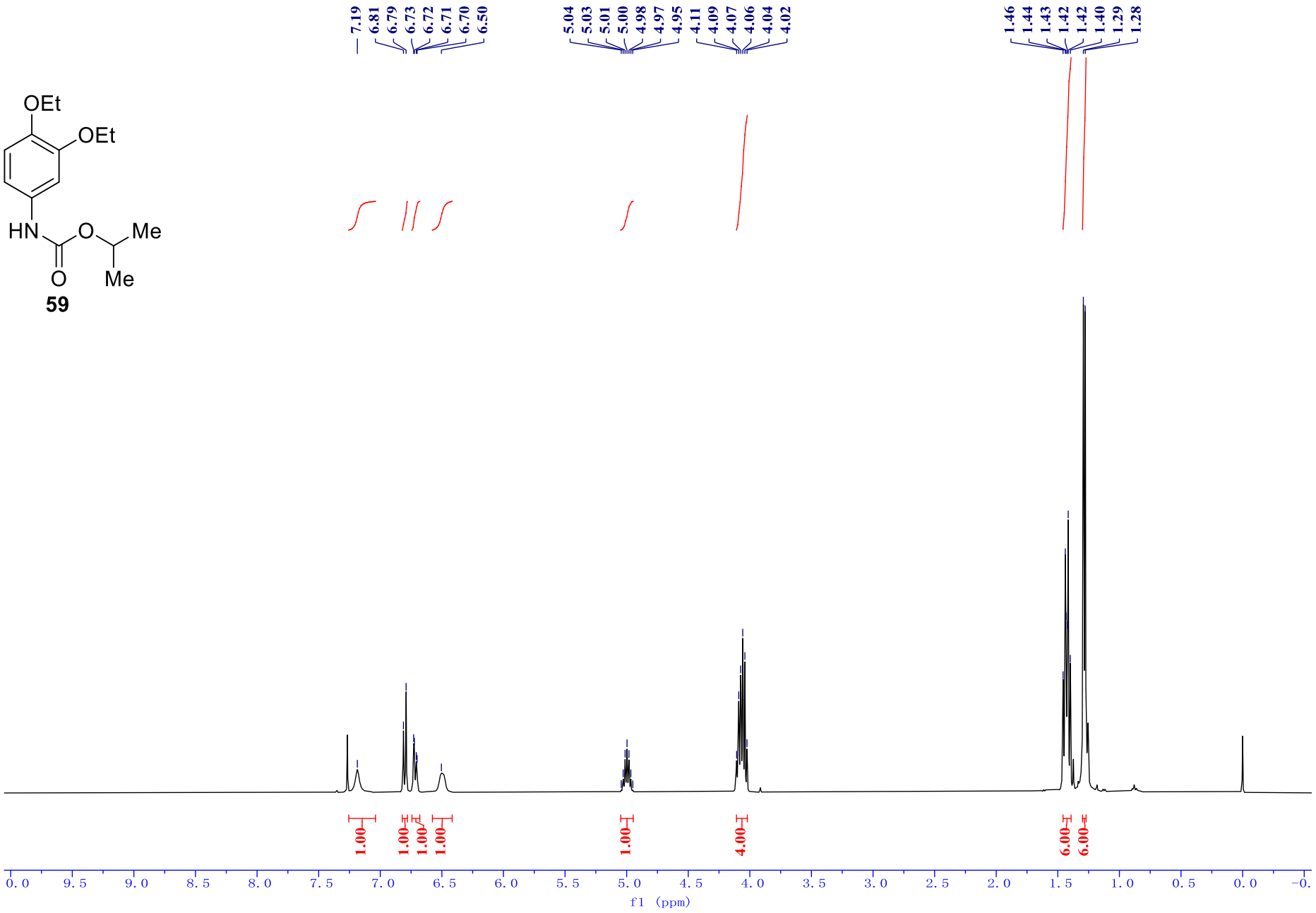
131.77
115.85
109.94
107.62
67.41
40.62
40.42
40.21
40.00
39.79
39.58
39.37
22.59
OH
OH
HN
O
Me
O
Me
58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.19
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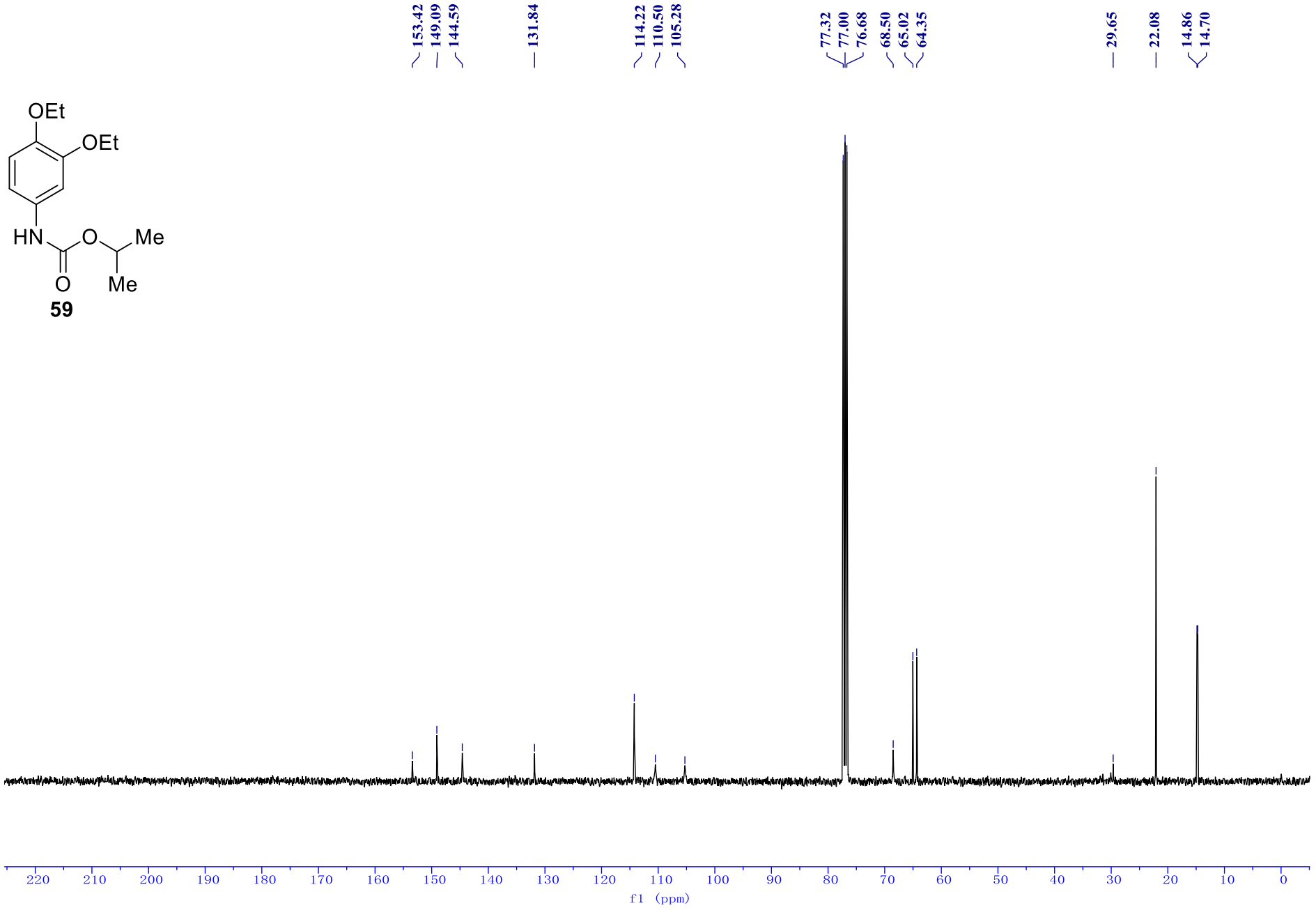
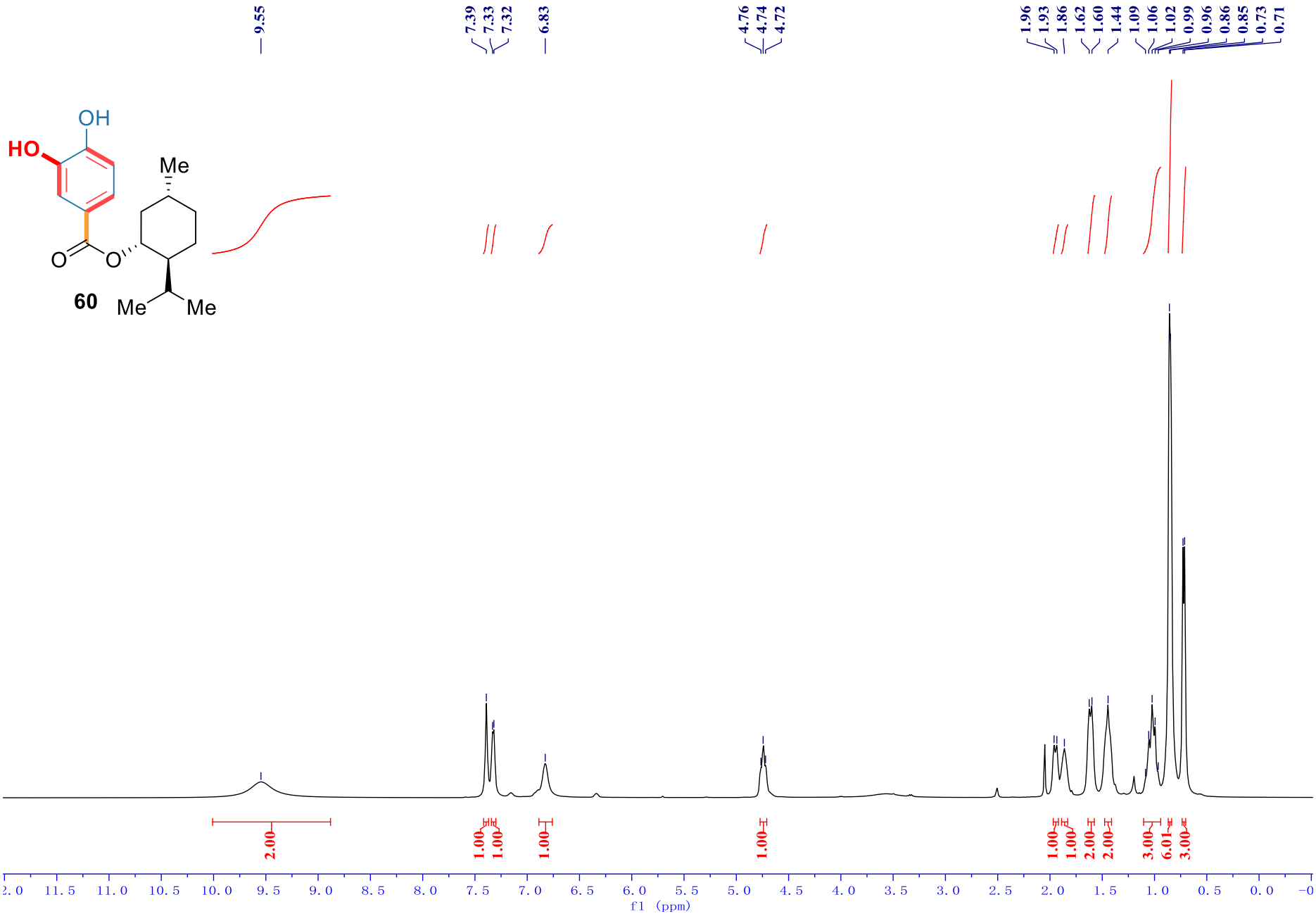
6.79
6.73
6.72
6.71
6.70
6.50
5.04
5.03
5.01
5.00
4.98
4.97
4.95
4.11
4.09
4.07
4.06
4.04
4.02
1.46
1.44
1.43
1.42
1.42
1.40
1.29
1.28
OEt
OEt
HN
O
Me
O
Me
59
1.00
1.00
1.00
1.00
4.00
6.00
6.00
f1 (ppm)


153.42
149.09
144.59
131.84
114.22
110.50
105.28
77.32
77.00
76.68
68.50
65.02
64.35
29.65
22.08
14.86
14.70
OEt
OEt
HN
O
Me
O
Me
59
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)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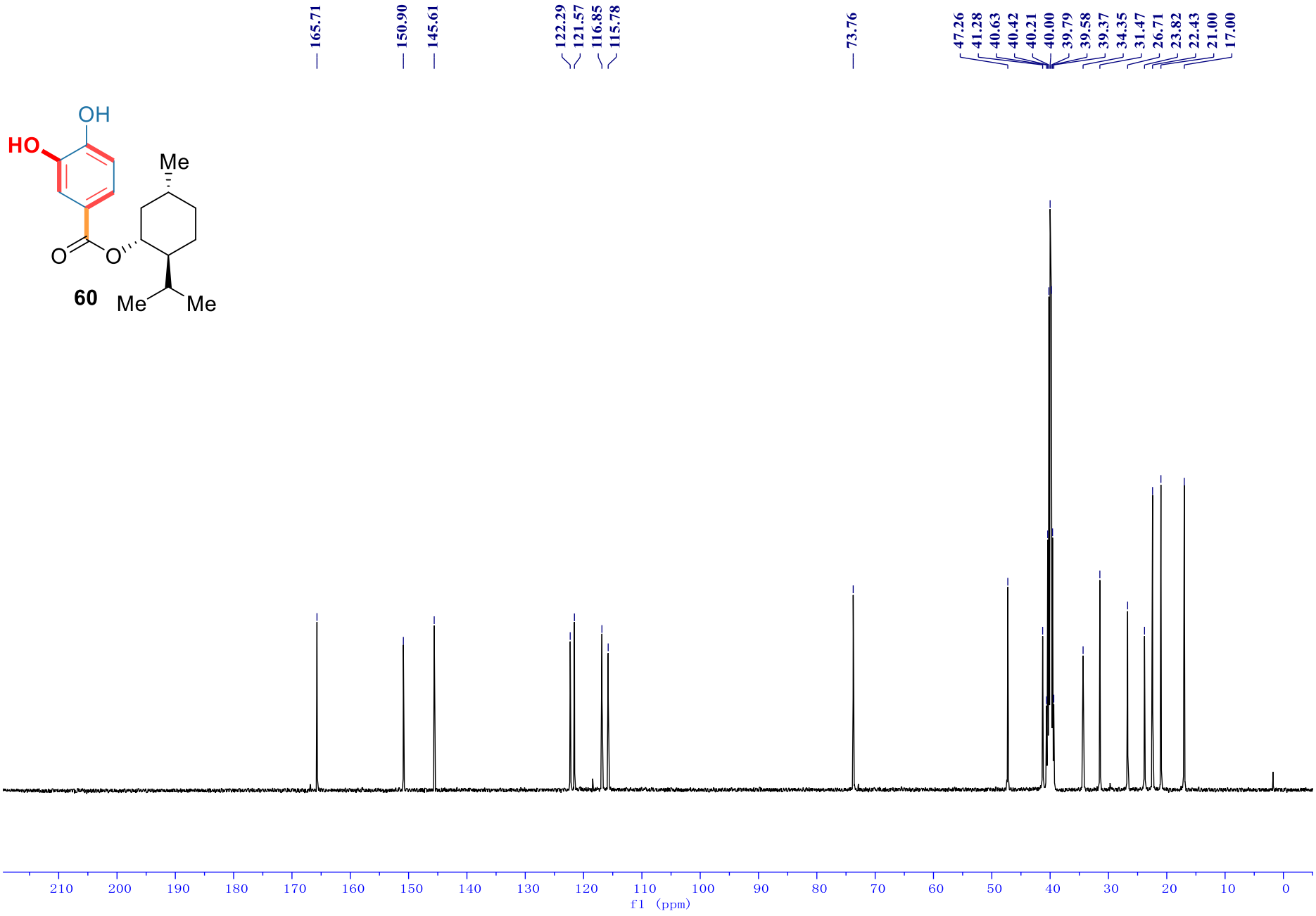
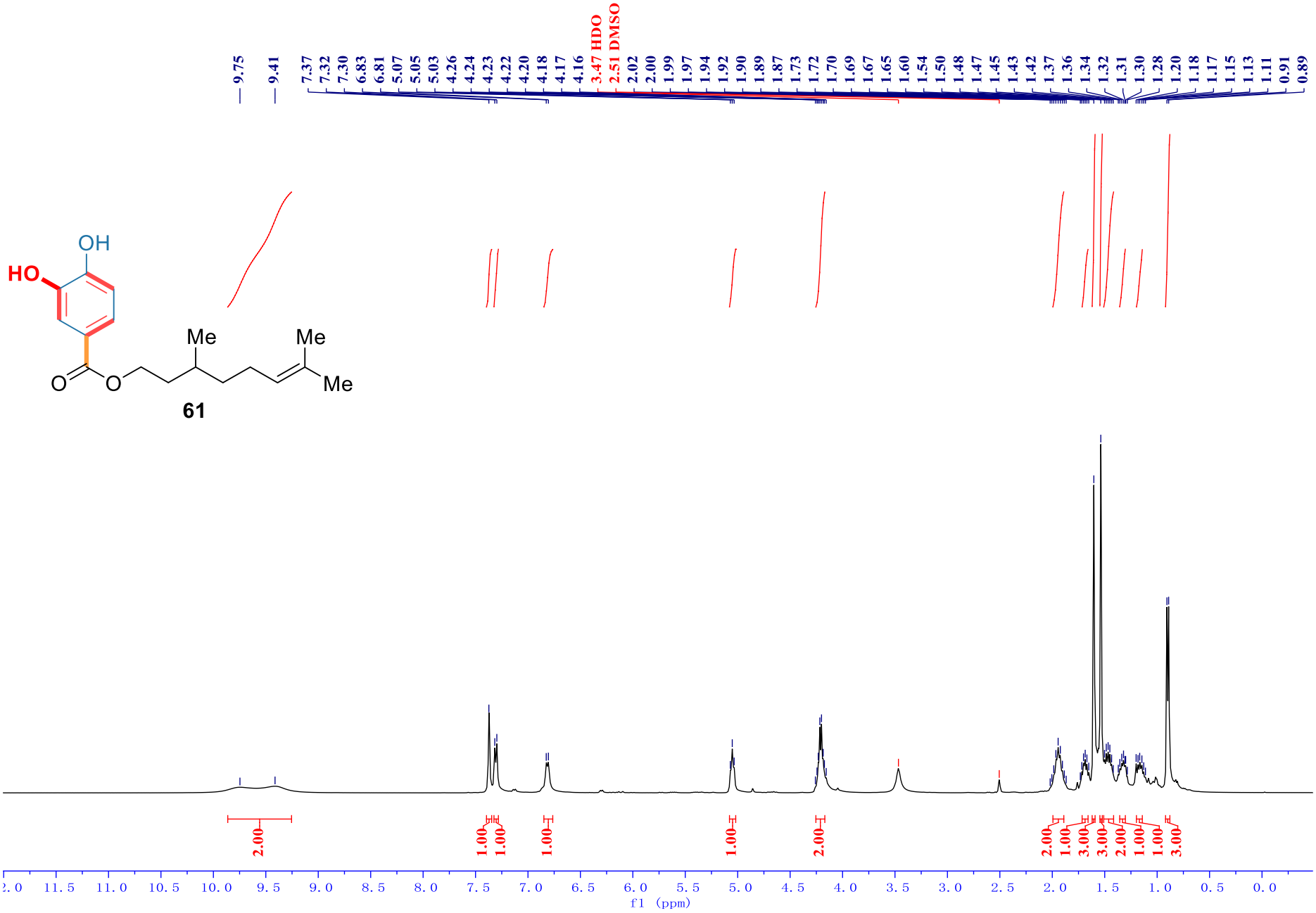
7.39
7.33
7.32
6.83
4.76
4.74
4.72
1.96
1.93
1.86
1.62
1.60
1.44
1.09
1.06
1.02
0.99
0.96
0.86
0.85
0.73
0.71
OH
HO
Me
O
O
60
Me
Me
2.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
2.00
3.00
6.01
3.00
f1 (ppm)


165.71
150.90
145.61
122.29
121.57
116.85
115.78
73.76
47.26
41.28
40.63
40.42
40.21
40.00
39.79
39.58
39.37
34.35
31.47
26.71
23.82
22.43
21.00
17.00
OH
HO
Me
O
O
60
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.75
9.41
7.37
7.32
7.30
6.83
6.81
5.07
5.05
5.03
4.26
4.24
4.23
4.22
4.20
4.18
4.17
4.16
3.47 HDO
2.51 DMSO
2.02
2.00
1.99
1.97
1.94
1.92
1.90
1.89
1.87
1.73
1.72
1.70
1.69
1.67
1.65
1.60
1.54
1.50
1.48
1.47
1.45
1.43
1.42
1.37
1.36
1.34
1.32
1.31
1.30
1.28
1.20
1.18
1.17
1.15
1.13
1.11
0.91
0.89
OH
HO
Me
Me
Me
O
O
61
2.00
1.00
1.00
1.00
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3.00
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1.00
3.00
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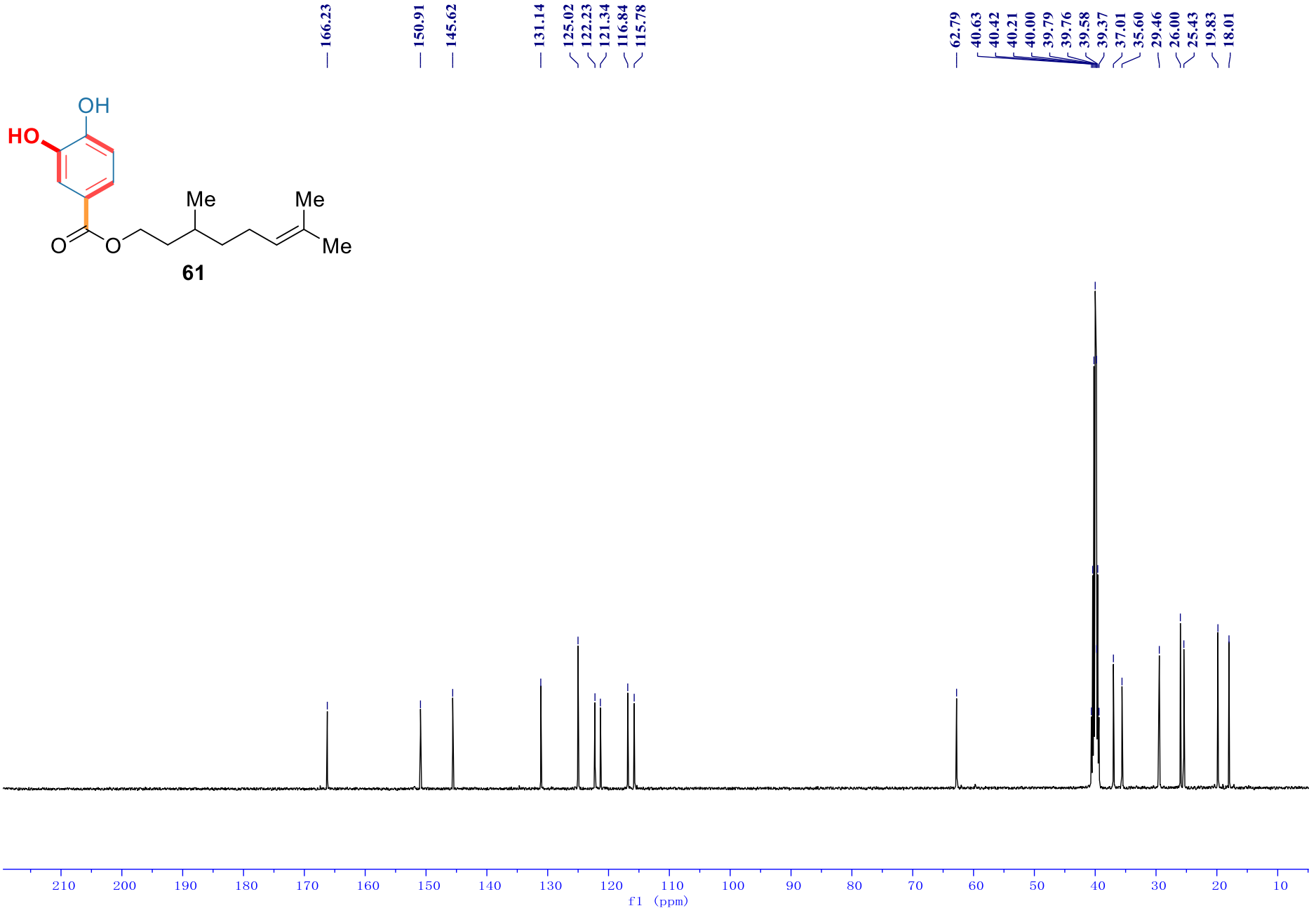
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131.14
125.02
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121.34
116.84
115.78
62.79
40.63
40.42
40.21
40.00
39.79
39.76
39.58
39.37
37.01
35.60
29.46
26.00
25.43
19.83
18.01
OH
HO
Me
Me
Me
O
O
61
210
200
190
180
170
160
150
140
130
120
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100
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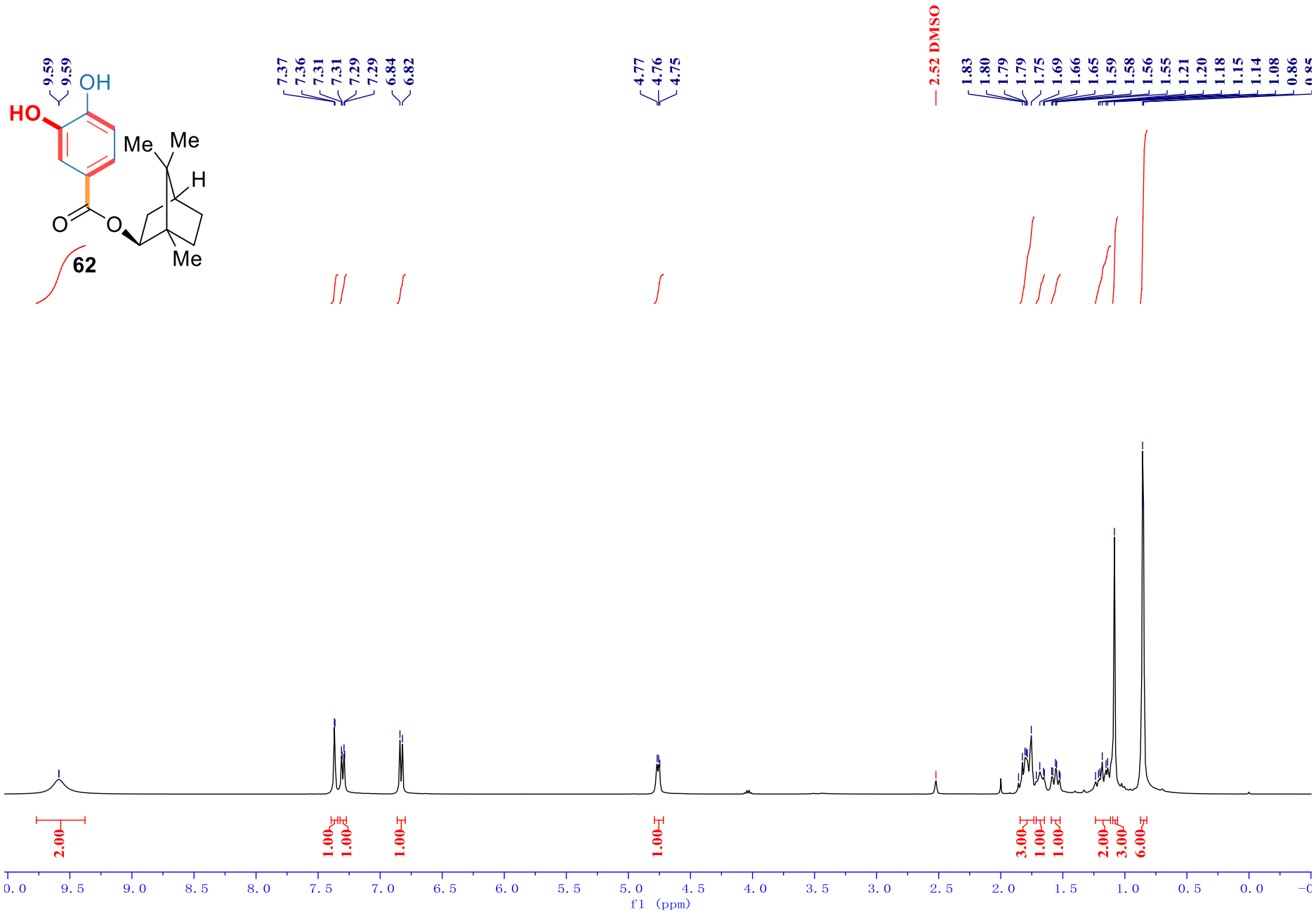
60
50
40
30
20
10
f1 (ppm)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9.59
7.37
7.36
7.31
7.31
7.29
7.29
6.84
6.82
4.77
4.76
4.75
2.52 DMSO
1.83
1.80
1.79
1.79
1.75
1.69
1.66
1.65
1.59
1.58
1.56
1.55
1.21
1.20
1.18
1.15
1.14
1.08
0.86
OH
HO
Me
Me
H
O
O
Me
62
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3.00
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2.00
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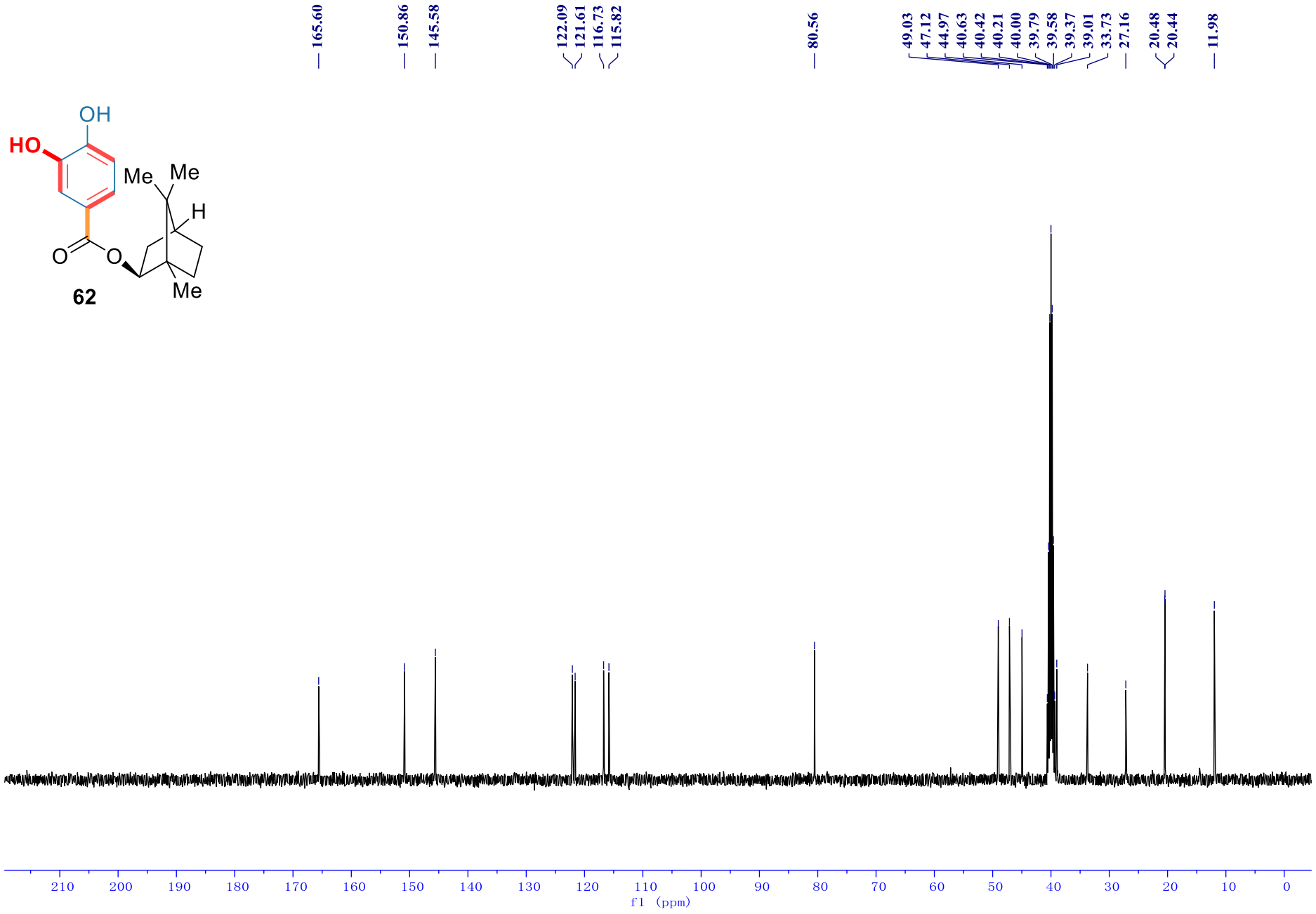
6.00
f1 (ppm)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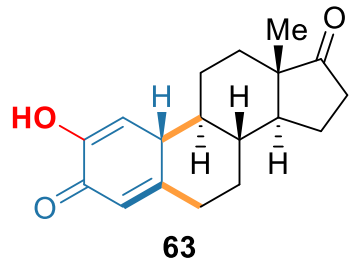
150.86
145.58
122.09
121.61
116.73
115.82
80.56
49.03
47.12
44.97
40.63
40.42
40.21
40.00
39.79
39.58
39.37
39.01
33.73
27.16
20.48
20.44
11.98
OH
HO
Me
Me
H
O
O
Me
62
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
H
H
H
H
Me
O
O

63

6.37
6.35
6.33
6.31
5.75
3.35 HDO
2.50 DMSO
2.46
2.42
2.34
2.33
2.29
2.21
2.19
2.13
2.11
2.09
2.08
2.05
2.03
2.01
1.80
1.77
1.69
1.66
1.62
1.59
1.47
1.45
1.43
1.42
1.40
1.36
1.33
1.30
1.25
1.23
1.20
1.11
1.09
1.06
1.04
0.88
2.00
1.00
2.00
3.00
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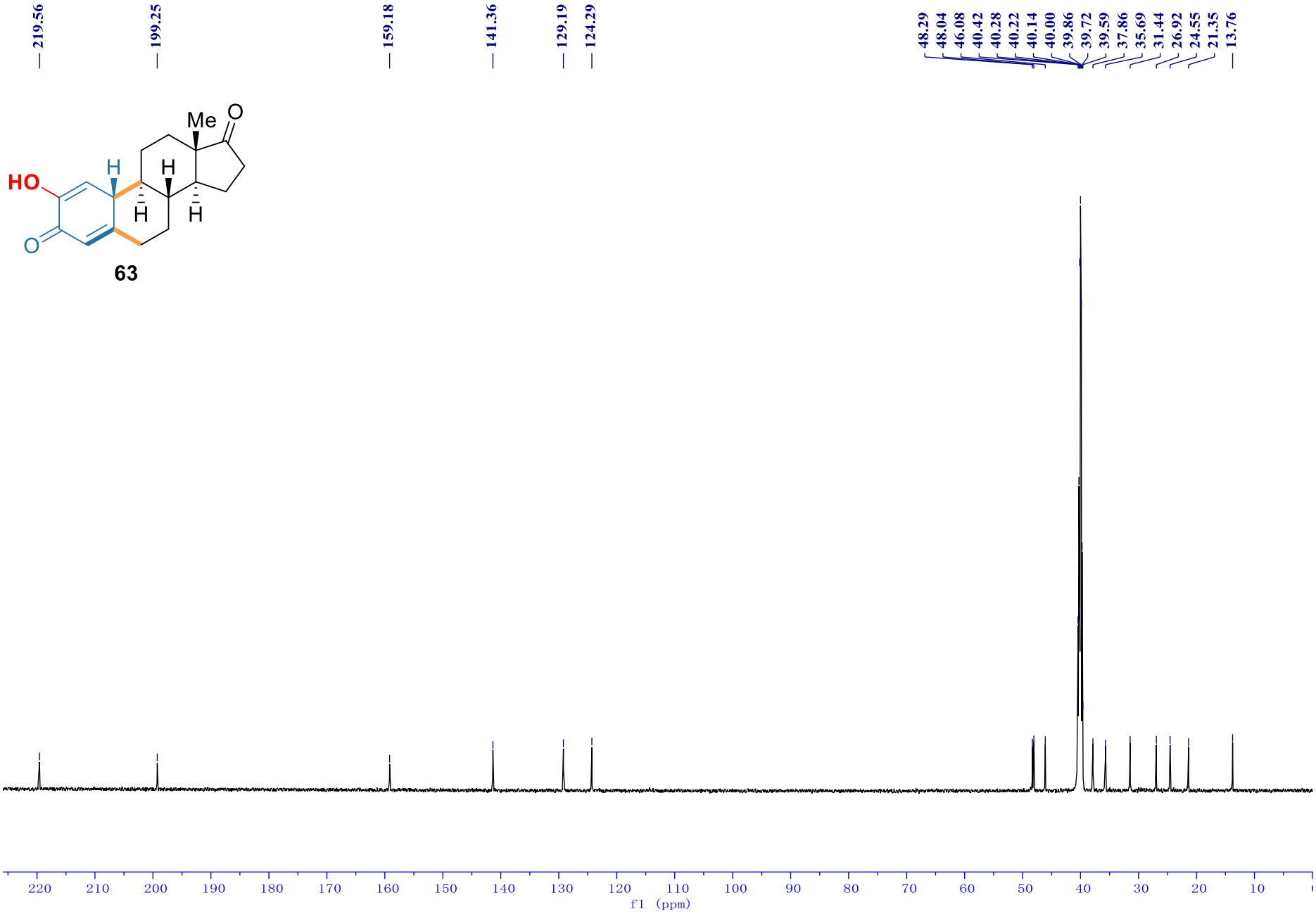
2.00
1.00
2.00
2.00
1.00
1.00
1.00
3.00
f1 (ppm)


219.56
199.25
159.18
141.36
129.19
124.29
48.29
48.04
46.08
40.42
40.28
40.22
40.14
40.00
39.86
39.72
39.59
37.86
35.69
31.44
26.92
24.55
21.35
13.76
Me
O
HO
H
H
H
H
O
63
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)