# Supporting Information

# Bifunctional Ligand-Assisted Cu-Catalytic Cyclohexenone γ-C(sp3)-H Amination: Controlled Synthesis of p-Aminophenols

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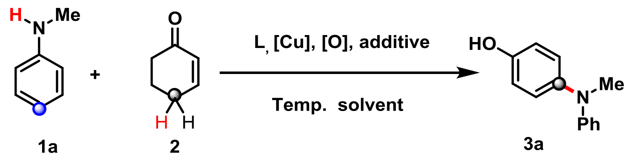
# 1. General Information

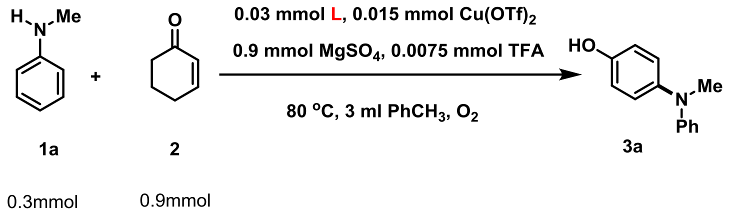
Unless otherwise noted, all reactions were carried out in a flamedried, sealed Schlenk reaction tube under an atmosphere of $O_2$. Materials ,unless otherwise noted, were purchased from Energy Chemical. Solvents were purchased from Tansoole. Solvents were purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (W. L. F. Armarego, D. D. Perrin, Butterworth-Heinemann: 1997). Analytical thin layer chromatography (TLC) was performed on silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV (254 and 365 nm) light. Flash column chromatography was carried out using silica gel (200-300 mesh) at increased pressure. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker Advance spectrometer at 500MHz and 125 MHz. Chemical shift values are reported in δ (ppm) relative to $CHCl_3$ ($^{1}H$ NMR, δ = 7.26; $^{13}C$ NMR, δ = 77.16) or Methanol ($^{1}H$ NMR, δ = 3.31; $^{13}C$ NMR, δ =49.00). Signal shapes are shown as s (singlet), d (doublet), t (triplet), dd (doublet of doublets),td (triplet double), m (multiplet). High resolution mass spectrometry (HRMS) was performedwith a Thermo Scientific LTQ Orbitrap XL.

# 2. Screening conditions




All conditions screening reactions were carried out under 1a (0.3 mmol), 2 (0.9 mmol), [Cu] 0.05 mmol%, L 0.1 mmol%, additives , temperature and oxidants were selected as described.

## Table S1 Optimization of the ligands

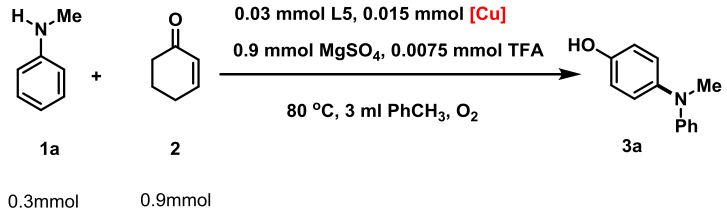



| entry | catalyst | ligand | additive(equiv) | temp. | oxidant | solvent | t(h) | yield(%)[a] |
|---|---|---|---|---|---|---|---|---|
| 1 | $Cu(OTf)_2$ | - | $MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | NR |
| 2 | $Cu(OTf)_2$ | - | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | 10% |
| 3 | $Cu(OTf)_2$ | L1 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | messy |
| 4 | $Cu(OTf)_2$ | L2 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | 29 |
| 5 | $Cu(OTf)_2$ | L3 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | 32 |
| 6 | $Cu(OTf)_2$ | L4 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | 27 |
| ***7*** | ***$Cu(OTf)_2$*** | ***L5*** | ***TFA(2.5%)+$MgSO_4$(3)*** | ***80°C*** | ***$O_2$*** | ***$PhCH_3$*** | ***8*** | ***73*** |
| 8 | $Cu(OTf)_2$ | L6 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | 44 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 9 | $Cu(OTf)_2$ | L7 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | 43 |
| 10 | $Cu(OTf)_2$ | L8 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | 68 |
| 11 | $Cu(OTf)_2$ | L9 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | 47 |

[a] Isolated yield.

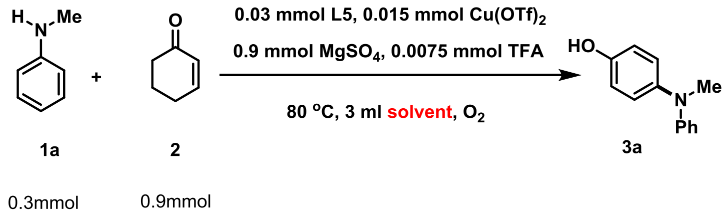
## Table S2 Optimization of the catalysts




| entry | catalyst | ligand | additive (equiv) | temp. | oxidant | solvent | t(h) | yield(%)[a] |
|---|---|---|---|---|---|---|---|---|
| 1 | $Cu(acac)_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | messy |
| 2 | $CuCl_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | messy |
| 3 | $Cu(OAc)_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | <5 |
| 4 | CuOTf | L5 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | 35 |
| 5 | CuI | L5 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | 33 |
| 6 | CuTc | L5 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $PhCH_3$ | 8 | 26 |

[a] Isolated yield.

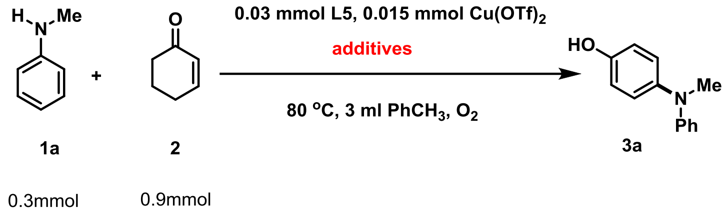
## Table S3 Optimization of the solvents




| entry | catalyst | ligand | additive (equiv) | temp. | oxidant | solvent | t(h) | yield(%)[a] |
|---|---|---|---|---|---|---|---|---|
| 1 | $Cu(OTf)_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | DCE | 8 | 42 |
| 2 | $Cu(OTf)_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | DMSO | 8 | NR |
| 3 | $Cu(OTf)_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $CH_3NO_2$ | 8 | trace |
| 4 | $Cu(OTf)_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | PhCl | 8 | 66 |
| 5 | $Cu(OTf)_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | EtOH | 8 | messy |
| 6 | $Cu(OTf)_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | 80°C | $O_2$ | $CH_3OH$ | 8 | <5 |

[a] Isolated yield.

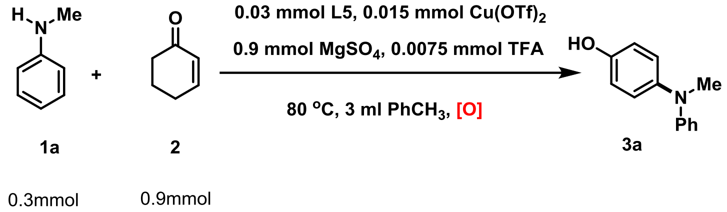
## Table S4 Optimization of the additives




| entry | catalyst | ligand | additive (equiv) | temp. | oxidant | solvent | t(h) | yield(%)[a] |
|---|---|---|---|---|---|---|---|---|
| 1 | Cu(OTf)$_2$ | L5 | TsOH(2.5%)+MgSO$_4$(3) | 80°C | $O_2$ | PhCH$_3$ | 8 | 30 |
| 2 | Cu(OTf)$_2$ | L5 | TCA(2.5%)+MgSO$_4$(3) | 80°C | $O_2$ | PhCH$_3$ | 8 | 22 |
| 3 | Cu(OTf)$_2$ | L5 | AcOH(2.5%)+MgSO$_4$(3) | 80°C | $O_2$ | PhCH$_3$ | 8 | <5 |
| 4 | Cu(OTf)$_2$ | L5 | HCOOH(2.5%)+MgSO$_4$(3) | 80°C | $O_2$ | PhCH$_3$ | 8 | <5 |
| 5 | Cu(OTf)$_2$ | L5 | TFA(5%)+MgSO$_4$(3) | 80°C | $O_2$ | PhCH$_3$ | 8 | 64 |
| 6 | Cu(OTf)$_2$ | L5 | TFA(1%)+MgSO$_4$(3) | 80°C | $O_2$ | PhCH$_3$ | 8 | 37 |
| 7 | Cu(OTf)$_2$ | L5 | $Na_2CO_3$(0.2)+MgSO$_4$(3) | 80°C | $O_2$ | PhCH$_3$ | 8 | messy |
| 8 | Cu(OTf)$_2$ | L5 | TFA(2.5%)+$H_2O$(1) | 80°C | $O_2$ | PhCH$_3$ | 8 | messy |

[a] Isolated yield.

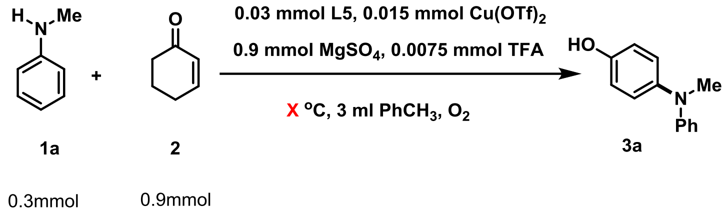
## Table S5 Optimization of the oxidants




| enty | catalyst | ligand | additive(equiv) | temp. | oxidant(equiv) | solvent | t(h) | yield(%)[b] |
|---|---|---|---|---|---|---|---|---|
| 1 | Cu(OTf)$_2$ | L5 | TFA(2.5%)+MgSO$_4$(3) | 80°C | Air | PhCH$_3$ | 12 | 24 |
| 2[b] | Cu(OTf)$_2$ | L5 | TFA(2.5%)+MgSO$_4$(3) | 80°C | FeCl$_3$(1.1) | PhCH$_3$ | 8 | <5 |
| 3[b] | Cu(OTf)$_2$ | L5 | TFA(2.5%)+MgSO$_4$(3) | 80°C | DDQ(1.1) | PhCH$_3$ | 8 | <5 |
| 4[b] | Cu(OTf)$_2$ | L5 | TFA(2.5%)+MgSO$_4$(3) | 80°C | IBX(1.1) | PhCH$_3$ | 8 | messy |
| 5[b] | Cu(OTf)$_2$ | L5 | TFA(2.5%)+MgSO$_4$(3) | 80°C | TBHP(1.1) | PhCH$_3$ | 8 | messy |
| 6[b] | Cu(OTf)$_2$ | L5 | TFA(2.5%)+MgSO$_4$(3) | 80°C | m-CPBA(1.1) | PhCH$_3$ | 8 | messy |
| 7 | Cu(OTf)2 | L5 | TFA(2.5%)+MgSO4(3) | 80°C | N2 | PhCH3 | 8 | NR |

[a] Isolated yield. [b] Under Nitrogen atmosphere.

## Table S6 Optimization of the temperatures




| entry | catalyst | ligand | additive (equiv) | temp. | oxidant | solvent | t(h) | yield(%)[b] |
|---|---|---|---|---|---|---|---|---|
| 1 | $Cu(OTf)_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | rt. | $O_2$ | $PhCH_3$ | 8 | 25 |
| 2 | $Cu(OTf)_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | 50°C | $O_2$ | $PhCH_3$ | 8 | 38 |
| 3 | $Cu(OTf)_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | 60°C | $O_2$ | $PhCH_3$ | 8 | 50 |
| 4 | $Cu(OTf)_2$ | L5 | TFA(2.5%)+$MgSO_4$(3) | 100°C | $O_2$ | $PhCH_3$ | 4 | 39 |

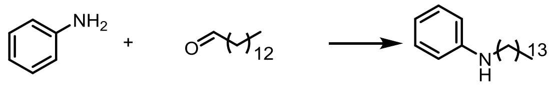
[a] Isolated yield.

# 3. General Procedure for Preparation of compound

## 3.1 Synthesis of substrates

Substrates **1a-1e** and **1h-1t** were commercially available. And the materials of **1d, 1v, 1x, 1ab, 1ac** were commercially available. **1f**[1], **1g**[2], **1aa**[3], **1z**[4], **1ad**[5] and **2a**[6] were reported compounds.

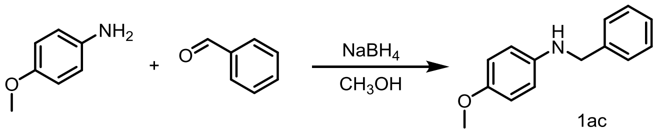
**Synthesis of *N*-tetradecylaniline (1d).**




1d

To a 100 mL round flask that was equipped with a stirring bar, aniline (930 mg, 10.0 mmol, 1 eq), aldehyde (2.33 g, 11.0 mmol, 1.1 eq), $NaSO_4$ (2.84 g, 20.0 mmol, 2.0 eq) and methanol (20.00 mL) was added successively. The resulting mixture was stirred at 80 °C in atmosphere and monitored by TLC. When aniline was converted completely, the mixture was cooled to room temperature, and $NaBH_4$ (418 mg, 11.0 mmol, 1.1 eq) was added to the reaction mixture in portions. The continuous stirring was kept for additional 4 hours at 80 °C. TLC monitored the completion of the reaction. The solvent was evaporated, then water added to quench the reaction. The solution was extracted by ethyl acetate (×3). The resulting residue was purified by column chromatography on silica gel (petroleum ether, 50:1 to 20:1) afford secondary amine (2.23 g, 77 %), light yellow solid.

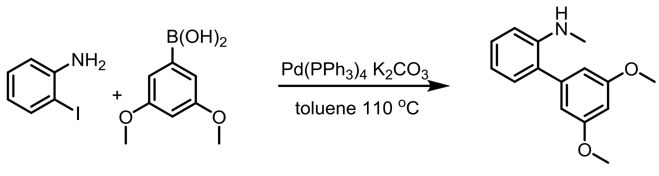
**1ac** was synthesized in the same way, 83 % yield, white crystalline solid.




1ac

83 %

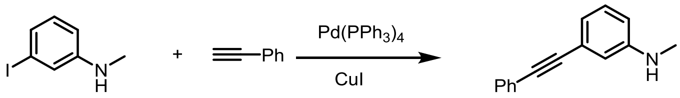
**Synthesis of 4-((3',5'-dimethoxy-[1,1'-biphenyl]-2-yl)-(methyl)amino)phenol (1v).**



**1v**

To a 100 mL round flask that was equipped with a stirring bar, 2-iodoaniline (2.19 g, 10.0 mmol, 1.0 eq), boric acid (2.00 g, 11.0 mmol, 1.1 eq), $K_2CO_3$ (2.76 g, 20.0 mmol, 2.0 eq), $Pd(PhP_3)_4$ (557 mg, 5 mol%) and toluene (20.0 mL) was added successively under $N_2$. The resulting mixture was reluxed at 110 °C and monitored by TLC. Then the solvent was evaporated and the resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) afford secondary amine (2.19 g, 90 %), white solid.

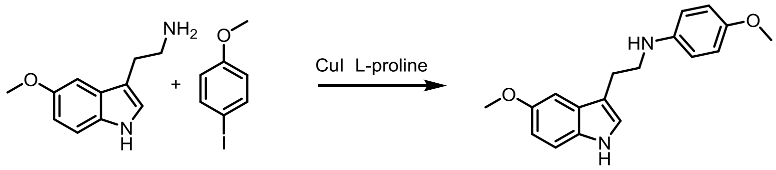
**Synthesis of *N*-methyl-3-(phenylethynyl)aniline (1x)**



1x

To a solution of 3-iodo-*N*-methylaniline (1.167 g, 5 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (175 mg, 5 mol%) and copper iodide (94.5 mg, 10 mol%) in THF (10 mL) in a Schlenk tube under $N_2$ were successively added phenylacetylene (612 mg, 6.0 mmol, 1.2 equiv) and triethylamine (10.0 mmol, 5 equiv). The resulting mixture was stirred at rt over 24 hours. Water was added then the crude product was extracted with EtOAc, washed with water and brine, dried with $MgSO_4$, concentrated under reduced pressure and purified by silica gel chromatography (petroleum ether/EtOAc = 10:1 to 5:1) to afford 932 mg of **1x** (90 %) as a red solid.

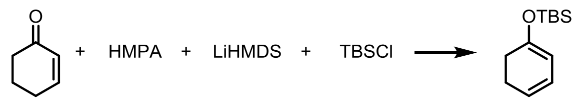
**Synthesis of 4-methoxy-*N*-(2-(5-methoxy-1H-indol-3-yl)ethyl)aniline (1ab).**



**1ab**

An oven-dried flask was charged with copper iodide (378 mg, 2 mmol, 0.2 eq) and *l*-proline (460 mg, 4 mmol, 0.4 eq), the *p*-Iodoanisole (2.34 g, 10.0 mmol, 1.0 eq) was also introduced at this stage. The flask was evacuated under high vacuum and backfilled with $N_2$ three times, then fitted with a rubber septum. DMSO (10.0 mL) was next added. The resulting blue solution was stirred for 5 min before adding the 2-(5-methoxy-1H-indol-3-yl)ethan-1-amine (5.7 g, 30.0 mmol, 3.0 eq). The resulting mixture was stirred under argon at room temperature for 41 h. Upon completion, the reaction mixture was diluted with 70 mL of water and extracted twice with 15 mL of diethyl ether. The crude was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1 to 1:1) to afford the desired pure product **1ab** 1.69 g (57 %) as a brownish solid.

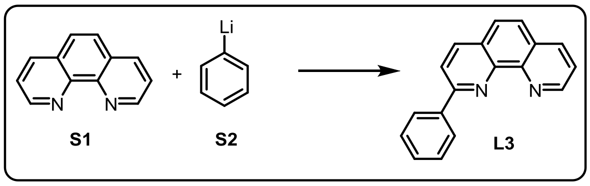
**Synthesis of tert-butyl(cyclohexa-1,3-dien-1-yloxy)dimethylsilane (2a).**

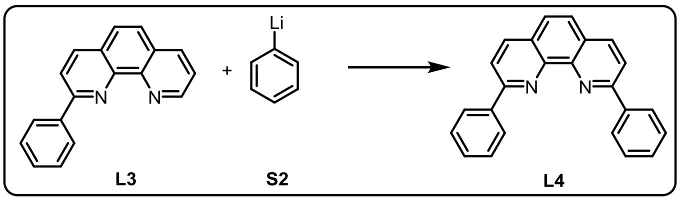



An oven-dried 100 mL round bottom flask equipped with a magnetic stirring bar, was sealed with a rubber septum and then evacuated and backfilled with nitrogen (three cycles). The flask was charged with a solution of enone (5 mmol, 1.0 equiv) in anhydrous THF (20 mL) and HMPA (2.17 mL, 12.5 mmol, 2.5 equiv) and then cooled to ﹣78 °C. After stirring the mixture for 5 min, a solution of LiHMDS (1.0 M soln in THF, 5.5 mL, 5.5 mmol, 1.1 equiv) was added dropwise over 3 min. Stirring was continued for 1 h at –78 °C, and then the mixture was warmed to 0 °C and stirred for 1 h. The reaction mixture was cooled to –78 °C and a solution of TBSCl (1.13 g, 7.5 mmol, 1.5 equiv) in THF (10 mL) was added dropwise over 5 min. Stirring was continued for 30 min, at which time TLC indicated complete consumption of the enone. The reaction was quenched by addition of saturated NaHCO3 solution (20 mL) and then hexanes (30 mL) was added. The phases were separated and the aqueous phase was extracted with hexanes (2 x 20 mL). The combined organic phases were washed with brine (1 x 20 mL), dried over anhydrous $Na_2SO_4$, filtered through cotton, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the desired product **2a,** 91% yeild.

## 3.2 Synthesis of ligands

**General procedure for the synthesis of 2-phenyl-1,10-phenanthroline(L3) and 2,9-diphenyl-1,10-phenanthroline (L4)**

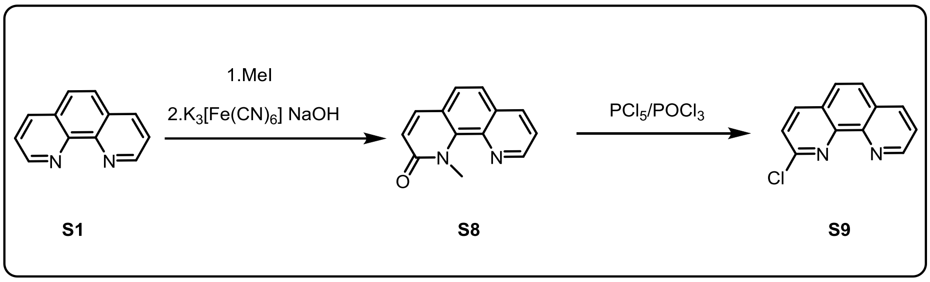



The synthesis of **L3** and **L4** refers to the reported literature.[7]

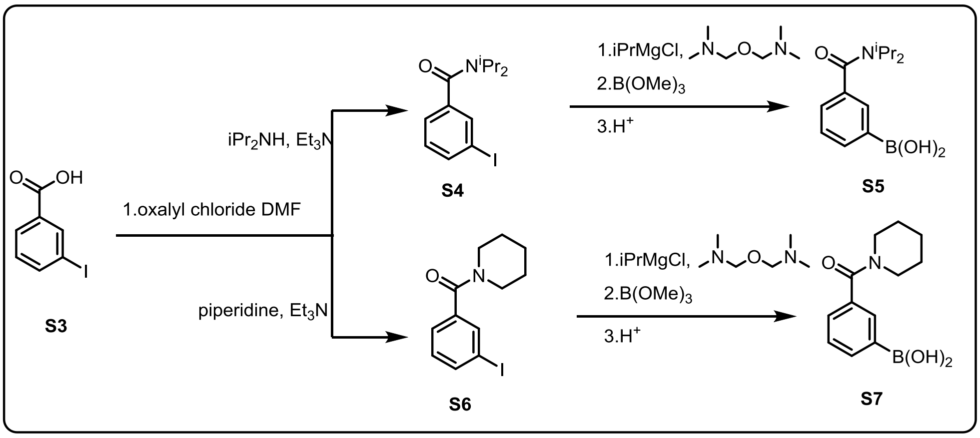
**General procedure for the synthesis of :**

***N,N*-diisopropyl-3-(1,10-phenanthrolin-2-yl)benzamide (L5) , (3-(1,10-phenanthrolin-2-yl)phenyl)(piperidin-1-yl)methanone (L6), N,N-diisopropyl-2-(1,10-phenanthrolin-2-yl)benzamide (L7), N,N-diisopropyl-4-(1,10-phenanthrolin-2-yl)benzamide (L8).**



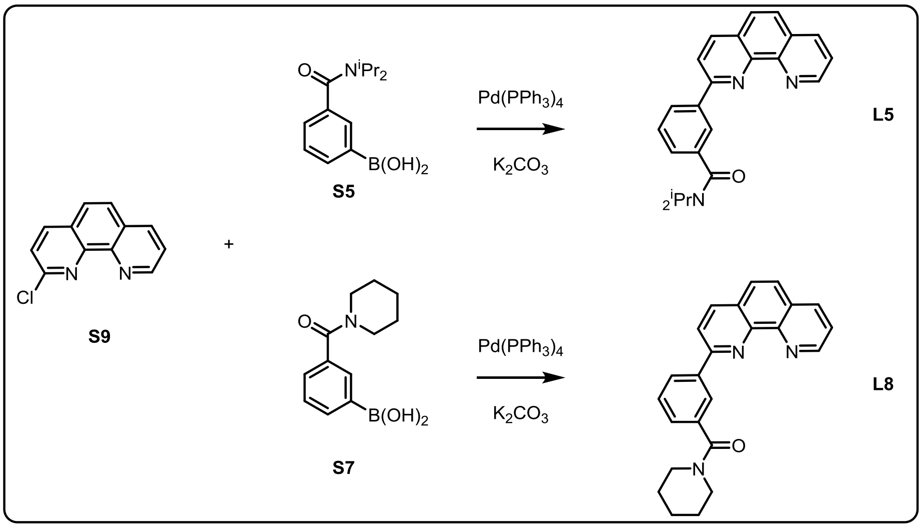

1,10-Phenanthroline (**S1**) (1.0 g, 5.5 mmol) was dissolved in acetonitrile (5 ml). Methyl iodide (1.0 mL, 16.1 mmol) was added and the mixture heated to reflux for 1.5 h. The solution was allowed to cool and the yellow precipitate that formed was collected by filtration (1.64 g, 5.09 mmol, 91 % yield). Potassium ferricyanide (4.27 g, 12.97 mmol) was dissolved in water (30 mL) and NaOH (5.90 g, 147 mmol in 30 mL of water) was gradually added under stirring. The flask was then placed in an ice/water bath and a solution of 1-methyl-1,10-phenanthrolin-1-ium iodide (1.64 g, 5.09 mmol) in water (60 mL, dissolution is complete only by heating at 50 °C) was added dropwise over a period of 30 min. The mixture was stirred for an additional hour while keeping the flask cooled, filtered and washed abundantly with water. The obtained yellow solid was dissolved in the minimum amount of $CH_2Cl_2$ and dried over $Na_2SO_4$. Evaporation of the solvent afforded the product as a straw yellow solid (0.97 g, 4.63 mmol, 90 %). The product (**S8**) was employed in the subsequent synthetic step without further purification.

In an oven-dried Schlenk flask, 1-methyl-1,10-phenanthrolin-2(1H)-one (**S8**) (0.97 g, 4.63 mmol) and $PCl_5$ (1.23 g, 5.91 mmol) were suspended in $POCl_3$ (8 ml) under a $N_2$ atmosphere. The flask was fitted with an oven-dried reflux condenser and the mixture was refluxed for 8 h. The $POCl_3$ excess was removed under reduced pressure while heating at 50 °C. Cold water (20 mL) was then added to the residual solid and the mixture was brought to pH 10 with NaOH pellets. The obtained suspension was extracted with $CH_2Cl_2$ (4 × 30 mL). The combined organic layers were dried over $Na_2SO_4$ and the solvent was evaporated in vacuo affording a tan solid (0.91 g, 4.26 mmol, 92 %). The product (**S9**) was employed in the subsequent synthetic step without further purification.

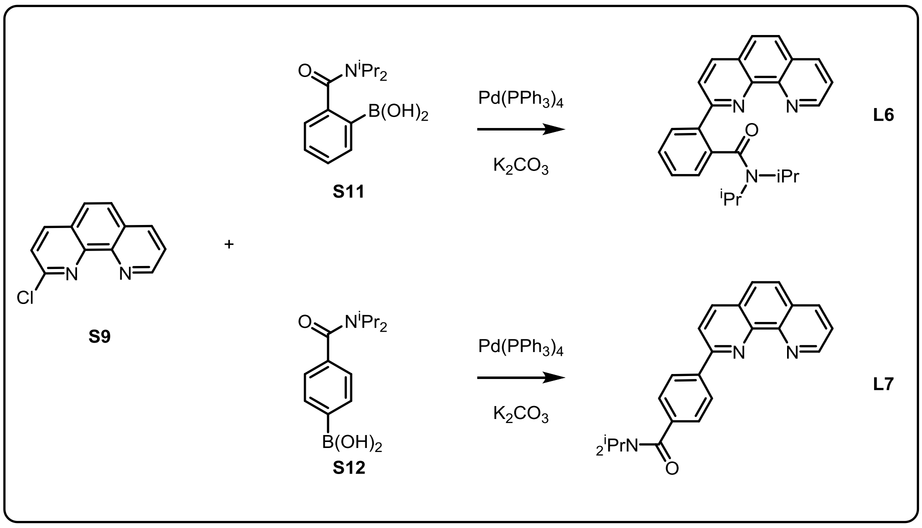



To a dispersion of 10 mmol 3-iodobenzoic acid (**S3**) (2.48 g, 1 eq) in 50 ml dry $CH_2Cl_2$ was added 25 mmol oxalyl chloride (3.18 g, 2.5 eq) and three drops of *N, N*-dimethylformamide (DMF), and the mixture was stirred for 2-4 h at room temperature. The reaction mixture was evaporated under reduced pressure and dried under vacuum to yield 3-iodobenzoyl chloride, which was dissolved in 50 ml dry $CH_2Cl_2$ again and cooled in an ice bath. A 10 ml $CH_2Cl_2$ solution containing 15 mmol amine (1.5 eq) and 20 mmol $Et_3N$ (2.02 g, 2.0 eq) was then added and the reaction mixture was stirred at room temperature under nitrogen atmosphere. After 1 h, the solution was treated with 50 ml water and 100 ml dichloromethane, and the organic phase was separated, dried, evaporated and then purified by column chromatography to form **S4** or **S6** with more than 90% yield.

To a solution of bis[2-(*N,N*-dimethyl- aminoethyl)] ether (2.2 mL, 12 mmol) in anhydrous THF (50 mL) was added isopropylmagnesium chloride (6.0 mL, 12 mmol, 2 M solution in THF) at 15 °C. The mixture was stirred at this temperature for 20 min. **S4** (3.74 g, 10 mmol) or **S6** (3.15 g, 10 mmol) was added. After the resulting mixture was stirred at 22-25 °C for 10 min, trimethylborate (2.3 mL, 20.0 mmol) was added at 0 °C. The mixture was then quenched with 0.1 N HCl and extracted with EtOAc. The extract was dried over $MgSO_4$ and concentrated. The residue was purified by cr5ystallization in hexane to give **S5** (2.34 g, 85%) and **S7** (1.60 g, 69%).

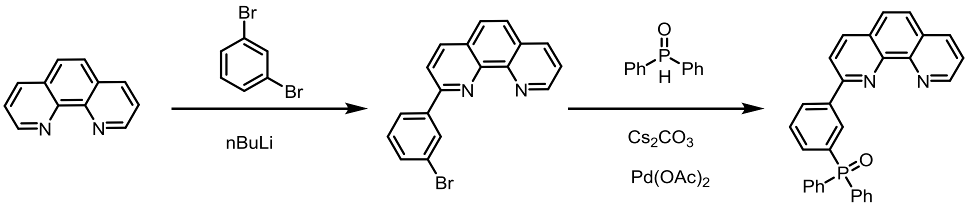



An oven-dried flask (250 mL) was charged with **S9** (2.14 g, 10 mmol) and **S5** (2.67 g, 9.2 mmol) or **S7** (2.14 g, 9.2 mmol). The mixture was dissolved in toluene (80 mL) and purged with $N_2$ for 10 min. Aq. $K_2CO_3$ (1M, 40 mL) was added under $N_2$ purging, followed by $Pd(PPh_3)_4$ (530 mg, 5 mol %). After purging with $N_2$ for an additional 10 min, the pressure tube was closed and heated at 100 °C for 48 h. Upon cooling to room temperature, the reaction mixture was filtered to remove insoluble impurities. The filtrate was then extracted with $CH_2Cl_2$ (3×50 mL). The organic layers were collected, dried over $Na_2SO_4$ and evaporated to yield a brown viscous liquid that was purified by chromatography on neutral $Al_2O_3$ (petroleum ether/EtOAc = 1/1) to give **L5** and **L8** a yellow solid (2.95 g, 77 %, 2.39 g, 65 %), or recrystallization via (petroleum ether/EtOAc = 3:1) obtain the **L5** (2.49 g, 65%), **L8** (2.05 g, 56 %), light yellow solid.




**S11** (44 %) and **S12** (65 %) were obtained by the same method, and offered **L6** and **L7** 53 % and 71 % yield respectively.

**General procedure for the synthesis of (3-(1,10-phenanthrolin-2-yl)phenyl)diphenylphosphine oxide (L9).**



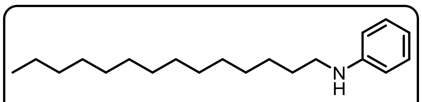

**S10** **L9**

A solution of 1-lithio-3-bromobenzene （prepared from 1,3-dibromobenzene (944 mg, 4 mmol) by interconversion with *n*BuLi (2.5 mL, 4.0 mmol) at 2-4 $^oC$ in diethyl ether (12 mL) was added to a degassed solution (15 mL) of anhydrous 1,10-phenanthroline (684 mg, 3.8 mmol) in THF also maintained at 2-4 $^oC$. After stirring for 2 h at 3-4 $^oC$, the mixture was hydrolyzed by injection of water (5 mL) at a low temperature (0-5 $^oC$). The solvents were evaporated and the dark-yellow crude taken up in $CH_2Cl_2/H_2O$. After decanting the mixture, the aqueous layer was extracted with $CH_2Cl_2$ (3×10 mL). The combined organic phases were subsequently rearomatized with $MnO_2$ (3 g) and dried with $MgSO_4$. Filtration of the $MnO_2/MgSO_4$ slurry through sintered glass and evaporation of the solvent afforded crude **S10**. Pure **S10** was obtained by column chromatography over silica gel ($CH_2Cl_2$/ MeOH = 95/5) as a pale-yellow glass in 32 % yield (409 mg).

An oven-dried Schlenk flask was evacuated and back-filled with $N_2$ three times. **S8** (1.0 eq, 335 mg), $Cs_2CO_3$ (1.5 eq, 488 mg) and a solution of diphenylphosphine oxide (1.2 eq, 242 mg) in anhydrous DMF (5 mL/mmol) were added to the flask. The solution was bubbled with $N_2$ for 10 min and $Pd(OAc)_2$ (1 mol%, 2.24 mg) and ferrocene-based bidentate phosphine ligand (2 mol%, 11.09 mg) were added to the flask simultaneously. The resulting mixture was heated at 120 $^oC$ for 7 h. Final purification of crude products was achieved by column chromatography on silica gel using $CH_2Cl_2$-MeOH as eluent, give **L9** as yellow solid (80 %, 365 mg).

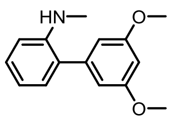
## 3.3 Characterization of Substrates and ligands

## Substrates:



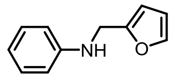
1d

***N*-tetradecylaniline(1d).** **$^{1}$H NMR** (500 MHz, Chloroform-*d*) δ = 7.22 (t, *J* = 7.6 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 2H), 3.62 (s, 1H), 3.15 (t, *J* = 7.2 Hz, 2H), 1.66 (p, *J* = 7.3 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.33 (s, 20H), 0.95 (t, *J* = 6.8 Hz, 3H). **$^{13}$C NMR** (125 MHz, Chloroform-d) δ = 148.61, 129.27, 117.12, 112.74, 44.08, 32.05, 29.82, 29.80, 29.79, 29.73, 29.69, 29.58, 29.49, 27.30, 22.81, 14.23. **HRMS** (ESI) m/z calcd for $C_{20}H_{36}N^{+}$ $(M^{+}H)^{+}$ 290.28423, found 290.28418.



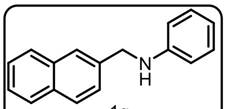
1v

**3',5'-dimethoxy-*N*-methyl-[1,1'-biphenyl]-2-amine(1v).** **$^{1}$H NMR** (500 MHz, Chloroform-*d*) δ = 7.30 – 7.25 (m, 1H), 7.11 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.76 (td, *J* = 7.4, 1.1 Hz, 1H), 6.69 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.56 (d, *J* = 2.3 Hz, 2H), 6.46 (t, *J* = 2.3 Hz, 1H), 3.82 (s, 6H), 2.81 (s, 3H). **$^{13}$C NMR** (125 MHz, Chloroform-d) δ = 160.81, 145.77, 141.20, 129.31, 128.52, 127.06, 116.23, 109.38, 106.88, 98.92, 54.77, 30.20. **HRMS** (ESI) m/z calcd for $C_{15}H_{18}NO_2^{+}$ $(M+H)^{+}$ 244.13321, found 244.13315.



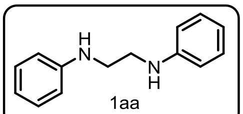
1f

***N*-(furan-2-ylmethyl)aniline(1f).** **$^{1}$H NMR** (500 MHz, Chloroform-*d*) δ = 7.39 (d, *J* = 1.8 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.73 – 6.67 (m, 2H), 6.35 – 6.34 (m, 1H), 6.26 (d, *J* = 3.1 Hz, 1H), 4.34 (s, 2H), 4.03 (s, 1H).



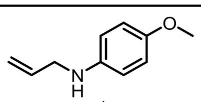
1g

***N*-(naphthalen-2-ylmethyl)aniline(1g).** **$^{1}$H NMR** (500 MHz, Chloroform-*d*) δ = 8.11 – 8.06 (m, 1H), 7.94 – 7.89 (m, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.25 – 7.20 (m, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.3 Hz, 2H), 4.75 (s, 2H), 4.01 (s, 1H).



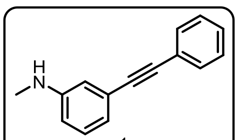
1aa

***$N^{1}$,$N^{2}$*-diphenylethane-1,2-diamine(1aa)**. **$^{1}$H NMR** (500 MHz, Chloroform-*d*) δ = 7.22 (t, *J* = 7.8 Hz, 4H), 6.76 (t, *J* = 7.3 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 4H), 3.83 (s, 2H), 3.41 (s, 4H).



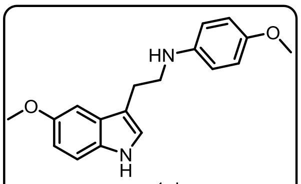
1z

***N*-allyl-4-methoxyaniline(1z)**. **$^{1}$H NMR** (500 MHz, Chloroform-*d*) δ = 6.79 (d, *J* = 8.9 Hz, 1H), 6.61 (d, *J* = 8.9 Hz, 1H), 6.02 – 5.91 (m, 1H), 5.30 (d, *J* = 1.7 Hz, 1H), 5.27 (d, *J* = 1.6 Hz, 1H), 5.17 (d, *J* = 1.5 Hz, 1H), 5.15 (d, *J* = 1.6 Hz, 1H), 3.75 (s, 3H), 3.74 (dt, *J* = 5.4, 1.7 Hz, 2H).



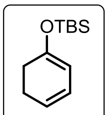
1x

***N*-methyl-3-(phenylethynyl)aniline(1x).** **$^{1}$H NMR** (500 MHz, Chloroform-*d*) δ = 7.54 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.91 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.81 – 6.76 (m, 1H), 6.62 – 6.57 (m, 1H), 3.73 (s, 1H), 2.85 (s,3H). **$^{13}$C NMR** (125 MHz, Chloroform-d) δ = 149.03, 131.46, 129.00, 128.21, 128.00, 123.60, 123.30, 120.50, 114.62, 112.93, 90.06, 88.41, 30.40. **HRMS** (ESI) m/z calcd for $C_{15}H_{14}N^{+}$ $(M+H)^{+}$ 208.11208, found 208.11218.



1ab

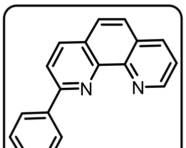
**4-methoxy-*N*-(2-(5-methoxy-1H-indol-3-yl)ethyl)aniline(1ab).** $^{1}$**H NMR** (500 MHz, Methanol-d4) δ = 7.22 (d, *J* = 8.8 Hz, 1H), 7.03 – 6.97 (m, 2H), 6.77 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.73 – 6.67 (m, 2H), 6.61 – 6.54 (m, 2H), 3.74 (t, *J* = 1.9 Hz, 3H), 3.63 (t, *J* = 2.6 Hz, 3H), 3.27 (t, *J* = 7.2 Hz, 2H), 2.92 (t, *J* = 7.2 Hz, 2H). $^{13}$**C NMR** (125 MHz, Methanol-d4) δ = 154.83, 153.77, 143.71, 133.28, 129.08, 124.22, 116.32, 115.73, 113.40, 112.94, 112.57, 101.28, 56.20, 56.06, 46.95, 25.87. **HRMS** (ESI) m/z calcd for $C_{18}H_{21}N_2O_2^+$ $(M+H)^+$ 297.15975, found 297.15967.



**2a**

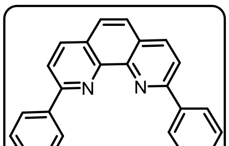
**tert-butyl(cyclohexa-1,3-dien-1-yloxy)dimethylsilane(2a).** $^{1}$**H NMR** (400 MHz, Chloroform-*d*) δ = 5.84 – 5.77 (m, 1H), 5.44 – 5.37 (m, 1H), 5.11 (d, *J* = 5.9 Hz,1H), 2.31 – 2.16 (m, 4H), 0.93 (s, 9H), 0.17 (s, 6H).

# Ligands:



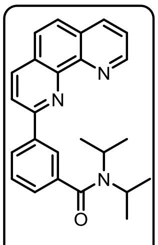
L3

**2-phenyl-1,10-phenanthroline(L3)**. $^{1}$**H NMR** (500 MHz, Chloroform-*d*) δ = 9.22 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.35 – 8.29 (m, 2H), 8.28 – 8.16 (m, 2H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.73 (q, *J* = 8.7 Hz, 2H), 7.60 (dd, *J* = 8.0, 4.3 Hz, 1H), 7.53 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.49 – 7.42 (m, 1H).



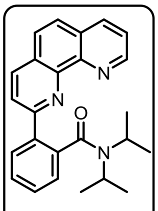
L4

**2,9-diphenyl-1,10-phenanthroline(L4).** $^{1}$**H NMR** (500 MHz, Chloroform-*d*) δ = 8.48 (d, *J* = 6.9 Hz, 4H), 8.28 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 2H), 7.76 (s, 2H), 7.60 (t, *J* = 7.7 Hz, 4H), 7.51 (t, *J* = 7.3 Hz, 2H).



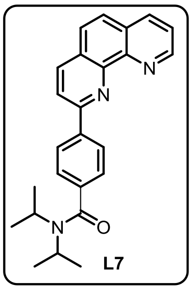
L5

***N,N*-diisopropyl-3-(1,10-phenanthrolin-2-yl)benzamide(L5).** $^{1}$**H NMR** (500 MHz, Chloroform-*d*) δ = 9.14 (s, 1H), 8.37 (d, *J* = 7.7 Hz, 1H), 8.17 (dd, *J* = 27.7, 8.1 Hz, 2H), 8.05 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.67 (q, *J* = 8.7 Hz, 2H), 7.52 (dt, *J* = 15.8, 6.4 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 3.71 (d, *J* = 213.5 Hz, 2H), 1.32 (d, *J* = 206.5 Hz, 12H). $^{13}$**C NMR** (125 MHz, Chloroform-d) δ = 170.62, 156.90, 150.08, 146.05, 145.82, 140.16, 138.95, 136.75, 135.88, 128.81, 128.81, 128.61, 127.38, 126.23, 126.09, 126.06, 124.97, 122.73, 120.62, 50.75, 45.60, 20.57. **HRMS** (ESI) m/z calcd for $C_{25}H_{26}N_3O^+$ $(M+H)^+$ 384.20704, found 384.20728.

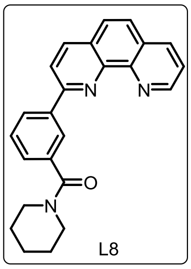


L6

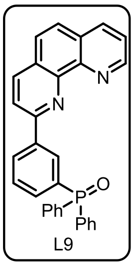
**N,N-diisopropyl-2-(1,10-phenanthrolin-2-yl)benzamide (L6).** $^{1}$**H NMR** (500 MHz, Chloroform-*d*) δ = 9.17 (s, 1H), 8.37 – 7.99 (m, 4H), 7.76 (q, *J* = 8.7 Hz, 2H), 7.58 (dd, *J* = 8.1, 4.4 Hz, 1H), 7.47 (dt, *J* = 33.2, 7.6 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 1H), 3.76 (p, *J* = 6.7 Hz, 1H), 3.20 (p, *J* = 7.0 Hz, 1H), 1.50 (d, *J* = 6.9 Hz, 3H), 1.27 (d, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H), 0.23 (d, *J* = 6.7 Hz, 3H). $^{13}$**C NMR** (125 MHz, Chloroform-*d*) δ = 170.51, 157.77, 150.25, 146.41, 146.22, 138.03, 137.20, 136.06, 135.95, 131.00, 129.03, 128.95, 128.93, 127.54, 126.53, 126.34, 126.21, 124.53, 122.89, 50.75, 45.69, 20.71, 20.51, 19.56, 19.44. **HRMS** (ESI) m/z calcd for $C_{25}H_{26}N_3O^+$ $(M+H)^+$ 384.20704, found 384.20726.




**N,N-diisopropyl-4-(1,10-phenanthrolin-2-yl)benzamide (L7).** $^{1}$**H NMR** (500 MHz, Chloroform-*d*) δ = 9.16 (d, *J* = 4.5 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 2H), 8.17 (dd, *J* = 21.8, 8.2 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.68 (q, *J* = 8.6 Hz, 2H), 7.54 (dd, *J* = 8.1, 4.4 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 3.67 (d, *J* = 146.9 Hz, 2H), 1.31 (d, *J* = 181.0 Hz, 12H). $^{13}$**C NMR** (125 MHz, Chloroform-*d*) δ = 170.81, 156.85, 150.39, 146.37, 146.12, 140.04, 139.60, 136.88, 136.03, 129.05, 128.17, 127.61, 126.41, 126.27, 126.04, 122.89, 120.55, 50.34, 46.20, 20.74. **HRMS** (ESI) m/z calcd for $C_{25}H_{26}N_3O^+$ $(M+H)^+$ 384.20704, found 384.20725.




**(3-(1,10-phenanthrolin-2-yl)phenyl)(piperidin-1-yl)methanone(L8).** $^{1}$**H NMR** (500 MHz, Chloroform-*d*) δ = 9.17 – 9.11 (m, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.25 – 8.19 (m, 2H), 8.14 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.57 – 7.49 (m, 2H), 7.42 (d, *J* = 7.7 Hz, 1H), 3.70 (s, 2H), 3.37 (s, 2H), 1.62 (s, 4H), 1.49 (s, 2H). $^{13}$**C NMR** (125 MHz, Chloroform-d)δ = 170.27, 157.02, 150.44, 146.41, 146.19, 140.34, 137.09, 137.02, 136.25, 129.43, 129.20, 129.04, 127.79, 127.58, 126.60, 126.48, 126.45, 123.10, 120.85, 49.04, 43.34, 26.68, 25.78, 24.74. **HRMS** (ESI) m/z calcd for $C_{24}H_{22}N_3O^+$ $(M+H)^+$ 368.17574, found 368.17529.

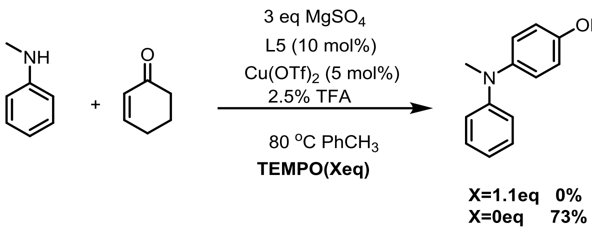



**(3-(1,10-phenanthrolin-2-yl)phenyl)diphenylphosphine oxide(L9)**. $^{1}$**H NMR** (500 MHz, Chloroform-*d*) δ = 9.19 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.74 (dd, *J* = 7.1, 1.8 Hz, 1H), 8.54 (d, *J* = 12.4 Hz, 1H), 8.31 – 8.17 (m, 2H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.79 – 7.67 (m, 6H), 7.66 – 7.59 (m, 3H), 7.56 – 7.51 (m, 2H), 7.50 – 7.41 (m, 4H). $^{13}$**C NMR** (125 MHz, Chloroform-d) δ = 156.40, 150.38, 146.30, 146.10, 140.46, 140.36, 137.06, 136.14, 133.21, 132.91, 132.70, 132.61, 132.38, 132.27, 132.25, 132.23, 132.15, 132.08, 132.06, 132.04, 131.64, 131.08, 131.00, 129.22, 129.12, 129.10, 128.65, 128.60, 128.55, 127.79, 126.65, 126.32, 123.05, 120.77. **HRMS** (ESI) m/z calcd for $C_{30}H_{22}N_2OP^+$ $(M+H)^+$ 457.14643, found 457.14658.

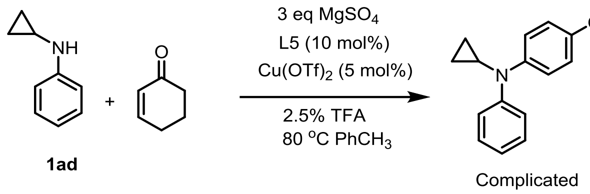
# 4. General Reaction Procedure

To a reaction tube equipped with stir bar, $MgSO_4$ (3.0 eq), $Cu(OTf)_2$ (5 mol%) and L5 (10 mol%) were added. The tube was capped with a rubber stopper, evacuated and refilled with $O_2$ (×3). To a solution of cyclohexenone (3.0 eq.), *N*-methylaniline (1.0 eq.), and TFA (2.5 mol%. toluene solution of TFA, and which was ready to use) was added via syringe. The resulting mixture was stirred 8-60 h at the corresponding temperature. After the reaction completed, the insoluble solid was filtrated off, then washed with Ethyl acetate for 3 times, and the filtrate was concentrated under vacuum. The subsequent residue was purified by column chromatography to get the desired compounds.

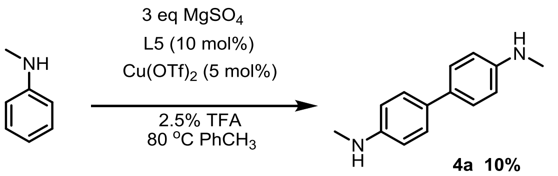
# 5. Mechanistic study



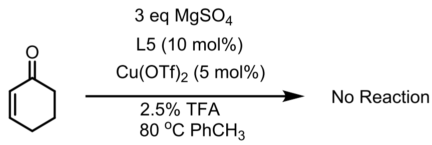

eq 1



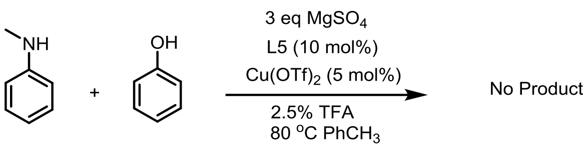

eq 2



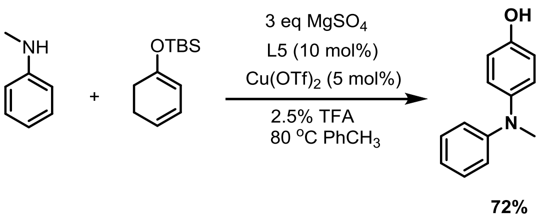

eq 3




eq 4




eq 5




eq 6

All of the reactions were conducted in 0.3 mmol scales. We invested the radical scavenger test (eq 1) and radical clock experiments (eq 2), which could give us 2 hints: a) the reaction may proceed via a radical process, because the radical scavenger did work; b) radical clock experiment shows that there may be a ring-opening process during the reaction, resulting in a complex hydrogen abstraction products. Eq 3 and eq 4 suggest that the N-centered radical was produced in this reaction, at the same time, the cyclohexanone could not aromatized to phenol under this condition. Eq 5 and eq 6 suggest that aromatization and amination may be a concerted process.

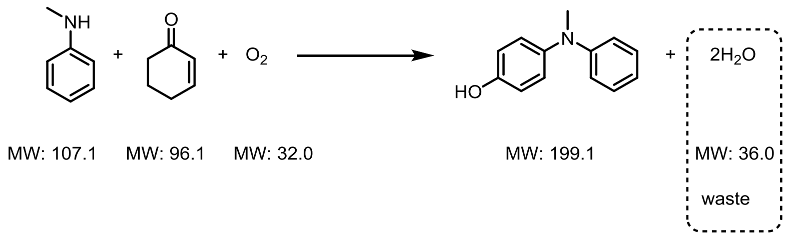
# 6. Green Chemistry Parameters

The most important and widely used parameters to calculate the “green” character of a reaction are: Ideally, atom efficiency and carbon efficiency should approach to 100% while the E factor should be as low as possible. Typical E-factors for the production of fine chemicals and pharmaceuticals in industry are in the range of 5-50 and 25-100, respectively. [8]

$$\textbf{atom economy=} \frac{\text{mass of atoms in desired product}}{\text{mass of atoms in reactants}}$$

$$\textbf{carbon economy=} \frac{\text{number of carbon atoms in the product}}{\text{number of carbon atoms in reagents}}$$

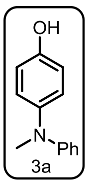
$$\textbf{E-factor=} \frac{\text{mass of produced waste}}{\text{mass of desired product}}$$



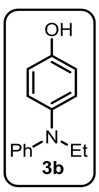

| Green Chemistry Parameter | Result |
|---|---|
| **atom efficiency** | **84.65%** |
| **carbon efficiency** | **100.00%** |
| **E-factor** | **0.18** |

# 7. Characterization of Products

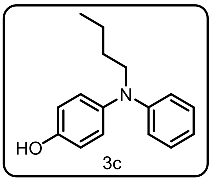
**3a**[9] and **4a**[10] were reported compounds.



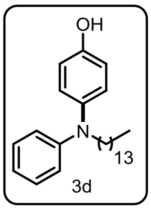
**4-(methyl(phenyl)amino)phenol (3a) :** dark blue oil, 44 mg, 73% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 7.15 – 7.08 (m, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.74 – 6.66 (m, 3H), 3.17 (d, *J* = 10.4 Hz, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 155.41, 151.47, 142.72, 129.70, 127.81, 118.92, 117.12, 116.31, 40.92.



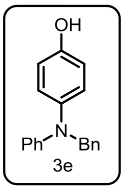
**4-(ethyl(phenyl)amino)phenol (3b):** black oily, 51 mg, 79% yield. **$^1$H NMR** (500MHz, Methanol-d4): δ = 7.08-7.05(m, 2H), 6.94(d, *J* = 10Hz, 2H), 6.79(d, *J* = 5Hz, 2H), 6.65 – 6.61(m, 3H), 3.64(q, *J* = 6.7 Hz, 2H), 1.14(t, *J*=7.5Hz, 3H) . **$^{13}$C NMR** (125 MHz, Methanol-d4): δ = 155.7, 150.4, 140.6, 129.8, 129.2, 118.3, 117.2, 116.0, 47.3, 13.0.
**HRMS** (ESI) m/z calcd for $C_{14}H_{16}NO^+$ $(M+H)^+$: 214.12264, found 214.12256.



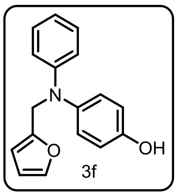
**4-(butyl(phenyl)amino)phenol (3c):** black oil, 50 mg, 69% yield. $^{1}$**H NMR** (500 MHz, Methanol-d4) δ = 6.99 (t, *J* = 10.0 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.59 – 6.52 (m, 3H), 3.49 (t, *J* = 10.0 Hz, 2H), 1.56 – 1.46 (m, 2H), 1.31–1.26 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). $^{13}$**C NMR** (125 MHz, Methanol-d4) δ = 155.55, 150.77, 141.12, 129.73, 129.02, 118.36, 117.19, 116.17, 53.12, 30.80, 21.25, 14.30. **HRMS** (ESI) m/z calcd for $C_{16}H_{20}NO^+$ $(M+H)^+$: 242.15394, found 242.15398.



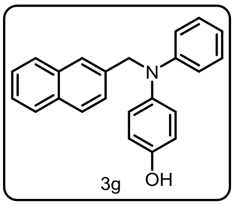
**4-(phenyl(tetradecyl)amino)phenol (3d):** yellowish brown solid, 61 mg, 53% yield. $^{1}$**H NMR**(500MHz, Methanol-d4): δ = 7.09 (t, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.66 (d, *J* = 8.1 Hz, 3H), 3.58 (t, *J* = 7.6 Hz, 2H), 1.63 (t, *J* = 7.4 Hz, 2H), 1.32 – 1.27 (m, 22H), 0.92 (t, *J* = 6.7 Hz, 3H). $^{13}$C NMR (125 MHz, Methanol-d4): δ = 155.56, 150.72, 141.07, 129.74, 129.02, 118.35, 117.20, 116.16, 53.39, 33.07, 30.80, 30.77, 30.75, 30.72, 30.69, 30.56, 30.48, 28.56, 28.12, 23.78, 23.74, 14.50. **HRMS** (ESI) m/z calcd for $C_{26}H_{40}NO^+(M+H)^+$: 382.31044, found 382.31000.



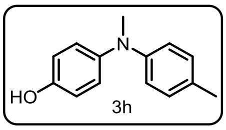
**4-(benzyl(phenyl)amino)phenol (3e):** white solid, 62 mg, 75% yield. $^{1}$**H NMR** (500 MHz, Methanol-d4) δ = 7.31 (d, *J* = 7.17 Hz, 2H), 7.25 (t, *J* = 7.65 Hz, 2H), 7.17 (t, *J* = 7.14 Hz, 1H), 7.07 – 7.01 (m, 4H), 6.77 (d, *J* = 8.83 Hz, 2H), 6.71 – 6.68 (m, 2H), 6.65 (t, *J* = 7.29 Hz, 1H), 4.84 (s, 2H). $^{13}$**C NMR** (125 MHz, Methanol-d4) δ = 155.45, 150.52, 141.46, 140.88, 129.72, 129.37, 128.32, 127.83, 127.65, 118.91, 117.17, 116.56, 57.60. **HRMS** (ESI) m/z calcd for $C_{19}H_{18}NO^+(M+H)^+$: 276.13829, found 276.13812.



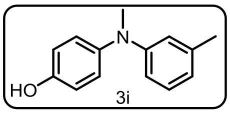
**4-((furan-2-ylmethyl)(phenyl)amino)phenol (3f):** faint yellow solid, 64 mg, 81% yield. $^{1}$**H NMR** (500 MHz, Methanol-d4) δ = 7.41 (d, *J* = 1.9 Hz, 1H), 7.13 – 7.09 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.79 (t, *J* = 8.6 Hz, 4H), 6.70(tt, *J* = 5 Hz, 1H), 6.31 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.17 (dd, *J* = 3.2, 1.9 Hz, 1H), 4.79 (s, 2H). $^{13}$**C NMR** (125 MHz, Methanol-d4) δ = 155.76, 153.96, 150.24, 142.78, 140.85, 129.68, 128.83, 119.01, 117.12, 116.52, 111.15, 108.61, 50.41. HRMS (ESI) m/z calcd for $C_{17}H_{16}NO_2^+(M+H)^+$: 266.11756, found 266.11700.



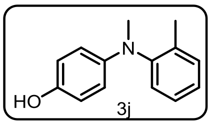
**4-((naphthalen-2-ylmethyl)(phenyl)amino)phenol (3g):** faint yellow solid, 64 mg, 66% yield. $^{1}$**H NMR**(500MHz, Methanol-d4): δ = 8.07 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* =7.5 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.12 – 7.03 (m, 4H), 6.78 – 6.66 (m, 5H), 5.30 (s, 2H). $^{13}$**C NMR** (125 MHz, Methanol-d4) δ = 155.61, 150.75, 141.19, 135.28, 134.92, 132.50, 129.80, 129.78, 128.51, 128.35, 127.01, 126.60, 126.31, 125.78, 123.92, 119.02, 117.12, 116.44, 55.45. **HRMS** (ESI) m/z calcd for $C_{23}H_{20}NO^+$ $(M+H)^+$: 326.15394, found 326.15323.



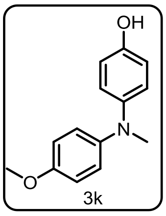
**4-(methyl(p-tolyl)amino)phenol (3h):** yellowish brown solid, 58 mg, 91% yield. $^{1}$**H NMR** (500 MHz, Methanol-d4) δ = 6.97 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 3.16 (s, 3H), 2.23 (s, 3H). $^{13}$**C NMR** (125 MHz, Methanol-d4) δ = 152.76, 147.34, 141.36, 128.29, 126.87, 124.62, 115.62, 114.97, 39.15, 18.50. **HRMS** (ESI) m/z calcd for $C_{14}H_{16}NO^+$:$(M+H)^+$:214.12264, found 214.12251.



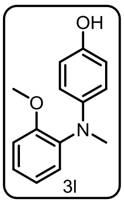
**4-(methyl(m-tolyl)amino)phenol (3i):** black oily, 52 mg, 81% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 7.02 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.58 – 6.50 (m, 3H), 3.18 (s, 3H), 2.22 (s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 153.96, 150.20, 141.55, 137.99, 128.23, 126.36, 118.56, 115.78, 115.72, 112.40, 39.62, 20.42. **HRMS** (ESI) m/z calcd for $C_{14}H_{16}NO^+$:$(M+H)^+$:214.12264, found 214.12255.



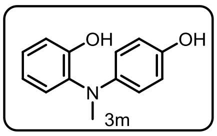
**4-(methyl(o-tolyl)amino)phenol (3j):** black oily, 45 mg, 70% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 7.23 – 7.16 (m, 2H), 7.11 – 7.05 (m, 2H), 6.63 (d, *J* = 8.9 Hz, 2H), 6.45 (d, *J* = 8.9 Hz, 2H), 3.13 (s, 3H), 2.08 (s, 3H).
**$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 148.35, 147.56, 142.82, 134.93, 130.23, 126.28, 125.58, 124.36, 115.01, 114.63, 38.58, 16.30. **HRMS** (ESI) m/z calcd for $C_{14}H_{16}NO^+$:$(M+H)^+$:214.12264, found 214.12253.



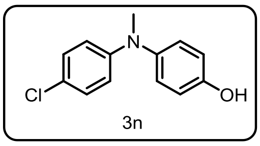
**4-((4-methoxyphenyl)(methyl)amino)phenol (3k):** yellowish brown solid, 64 mg, 93% yield. **$^1$H NMR**(500MHz, Methanol-d4):δ = 6.82-6.76(m, 6H), 6.73-6.69(m, 2H), 3.71(s, 3H), 3.12(s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4): δ = 155.3, 153.6, 145.6, 144.2, 124.2, 121.3, 116.8, 115.4, 56.0, 41.6. **HRMS** (ESI) m/z calcd for $C_{14}H_{16}NO_2^+$$(M+H)^+$: 230.11756, found 230.11744.



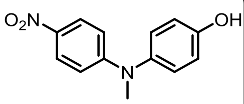
**4-((2-methoxyphenyl)(methyl)amino)phenol (3l):** black oily, 49 mg, 71% yield. **$^1$H NMR**(500MHz, Methanol-d4):δ = 7.15 (t, *J* = 8.07 1H), 7.04 (dd, *J* = 10.40 2H), 6.92 (t, *J* = 7.81 1H), 6.62 (d, *J* = 8.95 Hz, 2H), 6.54 (d, *J* = 8.95 Hz, 2H), 3.73 (s, 3H), 3.11 (s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4): δ = 156.81, 150.72, 144.81, 139.85, 128.45, 127.07, 122.31, 117.47, 116.37, 113.85, 56.01, 40.26. **HRMS** (ESI) m/z calcd for $C_{14}H_{16}NO_2^+$$(M+H)^+$: 230.11756, found 230.11749.



**2-((4-hydroxyphenyl)(methyl)amino)phenol (3m):** orange solid, 76% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 7.06 (td, *J* = 7.7, 1.7 Hz, 1H), 6.99 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.91 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.82 (td, *J* = 7.6, 1.5 Hz, 1H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 3.10 (s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 154.55, 150.85, 144.75, 138.51, 128.23, 127.66, 121.48, 117.51, 117.13, 116.44, 40.31. **HRMS** (ESI) m/z calcd for $C_{13}H_{14}NO_2^+$$(M+H)^+$: 216.10191, found 216.10190.

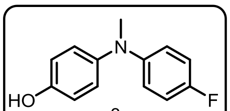


**4-((4-chlorophenyl)(methyl)amino)phenol (3n):** faint yellow solid, 48 mg, 68% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 7.08 – 7.03 (m, 2H), 6.99 – 6.94 (m, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.64 – 6.60 (m, 2H), 3.16 (d, *J* = 4.7 Hz, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 155.96, 150.16, 141.99, 129.47, 128.36, 123.21, 117.31, 116.78, 40.96. **HRMS** (ESI) m/z calcd for $C_{13}H_{13}ClNO^+$$(M+H)^+$: 234.06802, found 234.06802.



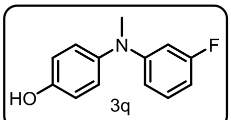

3o

**4-(methyl(4-nitrophenyl)amino)phenol (3o):** yellow solid, 30 mg, 41% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 8.01 (d, *J* = 9.4 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 9.5 Hz, 2H), 3.34 (s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 157.71, 156.13, 139.47, 138.56, 129.37, 126.63, 117.78, 112.86, 41.05. **HRMS** (ESI) m/z calcd for $C_{13}H_{13}N_2O_3^+$(M+H)$^+$: 245.09207, found 245.09212.



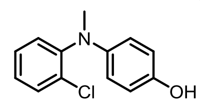

3p

**4-((4-fluorophenyl)(methyl)amino)phenol (3p):** grey solid, 50 mg, 77% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 6.92 (d, *J* = 8.68 Hz, 2H), 6.87 (t, *J* = 8.80 Hz, 2H), 6.77 (d, *J* = 8.78 Hz, 2H), 6.73 – 6.69 (m, 2H), 3.16 (s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 158.72 ($J_{CF}$ = 235.68 Hz), 155.14, 148.23($J_{CF}$ = 2.22 Hz), 143.12, 126.85, 118.45($J_{CF}$ = 7.63 Hz), 117.13, 116.13($J_{CF}$ = 22.53 Hz), 41.40. **HRMS** (ESI) m/z calcd for $C_{13}H_{13}FNO^+$(M+H)$^+$:218.09757, found 218.09753.



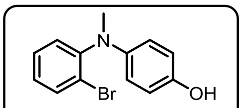

3q

**4-((3-fluorophenyl)(methyl)amino)phenol (3q):** grey solid, 40 mg, 62% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 7.05 (q, *J* = 5.0Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.41 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.36 – 6.28 (m, 2H), 3.18 (d, *J* = 0.9 Hz, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 166.11($J_{CF}$ = 240.5 Hz), 156.44, 153.40($J_{CF}$ = 10.5 Hz), 141.57, 130.89($J_{CF}$ = 10.4 Hz), 128.94, 117.37, 110.77($J_{CF}$ = 2.2 Hz), 104.32, ($J_{CF}$ = 21.9 Hz), 101.67($J_{CF}$ = 26.2 Hz), 40.82. **HRMS** (ESI) m/z calcd for $C_{13}H_{13}FNO^+$(M+H)$^+$:218.09757, found 218.09756.



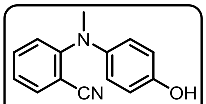

3r

**4-((2-chlorophenyl)(methyl)amino)phenol (3r):** dark blue oil, 44 mg, 63% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 7.45 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.56 (d, *J* = 8.9 Hz, 2H), 3.19 (s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 151.31, 148.26, 144.02, 133.30, 131.82, 129.41, 129.18, 127.18, 118.13, 116.58, 40.49. **HRMS (ESI)** m/z calcd for $C_{13}H_{13}ClNO^+$(M+H)$^+$: 234.06802, found 234.06801.



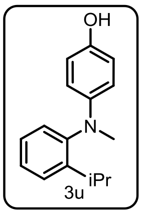

3s

**4-((2-bromophenyl)(methyl)amino)phenol (3s):** black solid, 52 mg, 63% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 7.66 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 3.18 (s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 151.08, 149.80, 144.02, 135.07, 130.05, 129.94, 127.81, 124.16, 117.74, 116.58, 40.48. **HRMS** (ESI) m/z calcd for $C_{13}H_{13}BrNO^+$(M+H)$^+$: 278.01750, found 278.01703.

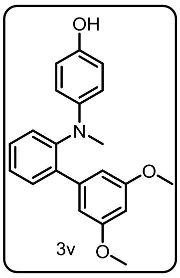



3t

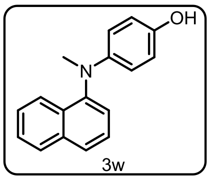
**2-((4-hydroxyphenyl)(methyl)amino)benzonitrile (3t):** faint yellow solid, 25 mg, 37% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 7.58 – 7.49 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.34 (s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 155.25, 154.56, 143.20, 135.94, 135.12, 125.63, 121.89, 121.60, 119.00, 117.13, 105.03, 42.68. **HRMS** (ESI) m/z calcd for $C_{14}H_{13}N_2O^+$(M+H)$^+$:225.10224, found 225.10229.



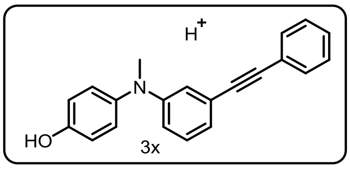
**4-((2-isopropylphenyl)(methyl)amino)phenol (3u):** black oily, 46 mg, 63% yield. **$^1$H NMR**(500MHz, Methanol-d4):δ = 7.35(d, *J* = 7.63, 1H), 7.23-7.16(m, 2H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.62-6.59 (m, 2H), 6.41-6.37 (m, 2H), 3.20-3.14 (m, 1H), 3.11 (s, 3H), 1.13 (d, *J* = 6.9 Hz, 6H). **$^{13}$C NMR** (125 MHz, Methanol-d4): δ = 149.88, 148.53, 148.50, 145.55, 128.94, 128.28, 127.83, 127.62, 116.54, 115.96, 41.15, 28.64, 24.16. **HRMS** (ESI) m/z calcd for $C_{16}H_{20}NO^+(M+H)^+$: 242.15394, found 242.15347.



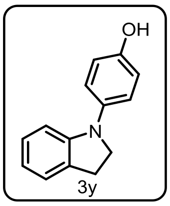
**4-((3',5'-dimethoxy-[1,1'-biphenyl]-2-yl)(methyl)amino)phenol (3v):** brown oily, 84 mg, 74% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 7.44 (d, *J* = 7.60 Hz, 1H), 7.37 (t, *J* = 7.61 Hz, 1H), 7.29 (t, *J* = 7.5 1Hz, 1H), 7.24 (d, *J* = 7.90 Hz, 1H), 6.68 (d, *J* = 9.02 Hz, 2H), 6.58 – 6.53 (m, 4H), 6.41 (t, *J* = 2.30 Hz, 1H), 3.66 (s, 6H), 2.87 (s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 162.00, 150.11, 148.23, 144.84, 143.52, 140.95, 132.32, 129.75, 129.46, 126.57, 116.68, 116.42, 107.59, 100.46, 55.61, 40.07. **HRMS** (ESI) m/z calcd for $C_{21}H_{22}NO_3^+(M+H)^+$: 336.15942, found 336.15909.



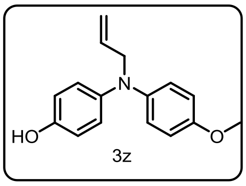
**4-(methyl(naphthalen-1-yl)amino)phenol (3w):** purple solid, 40 mg, 53% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 7.92 – 7.83 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 9.0 Hz, 2H), 3.31 (s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 149.58, 146.81, 144.46, 135.20, 130.74, 127.98, 125.91, 125.56, 125.32, 124.98, 123.79, 122.46, 116.84, 115.23, 40.48. **HRMS** (ESI) m/z calcd for $C_{17}H_{16}NO^+$ $(M+H)^+$: 250.12264, found 250.12273.



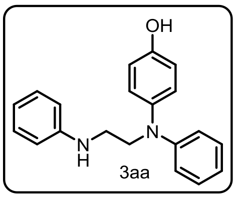
**4-(methyl(3-(phenylethynyl)phenyl)amino)phenol (3x):** faint yellow solid, 65 mg, 72% yield. **$^1$H NMR** (500 MHz, Methanol-d4) δ = 7.47 – 7.42 (m, 2H), 7.35 – 7.27 (m, 3H), 7.10 (td, *J* = 8.1, 4.3 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.86 – 6.79 (m, 4H), 6.67 (dt, *J* = 6.7, 3.2 Hz, 1H), 3.19 (d, *J* = 5.9 Hz, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ =156.07, 151.41, 141.96, 132.45, 129.85, 129.43, 129.16, 128.56, 124.74, 124.69, 121.76, 118.07, 117.37, 115.96, 91.01, 89.11, 40.85. **HRMS** (ESI) m/z calcd for $C_{21}H_{17}NO^+$ $(M+H)^+$: 300.13829, found 300.13870.



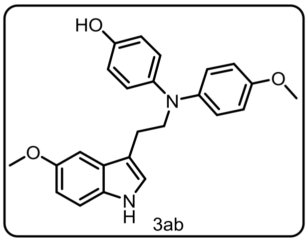
**4-(indolin-1-yl)phenol (3y):** dark red solid, 37 mg, 59% yield. **H NMR** (500 MHz, Methanol-*d*$_4$) δ = 6.97 – 6.91 (m, 3H), 6.87 – 6.80 (m, 1H), 6.77 – 6.70 (m, 2H), 6.65 (d, *J* = 7.9 Hz, 1H), 6.53 (t, *J* = 7.3 Hz, 1H), 3.56 (t, *J* = 8.4 Hz, 2H), 2.83 (t, *J* = 8.4 Hz, 2H). **$^{13}$C NMR** (125MHz, Methanol-*d*$_4$) δ = 151.44, 148.08, 136.39, 129.67, 125.84, 123.60, 120.26, 116.97, 114.71, 106.23, 52.31, 27.01. **HRMS (ESI) m/z** calcd for $C_{14}H_{14}NO^+$ $(M+H)^+$ : 212.10699, found 212.10684.



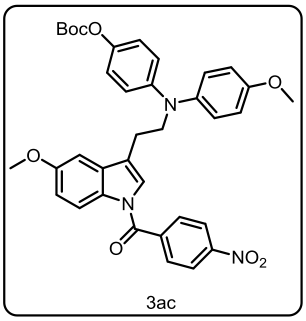

**4-(allyl(4-methoxyphenyl)amino)phenol (3z):** black solid, 54 mg, 71% yield. **$^{1}$H NMR** (500 MHz, Methanol-d4) δ = 6.88 – 6.78 (m, 6H), 6.72 (d, *J* = 8.8 Hz, 2H), 5.99 – 5.90 (m, 1H), 5.23 (dd, *J* = 17.2, 1.9 Hz, 1H), 5.12 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.23 (dt, *J* = 5.2, 1.7 Hz, 2H), 3.75 (s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 155.11, 153.54, 144.24, 142.65, 136.47, 124.72, 121.51, 116.81, 116.42, 115.45, 56.55, 56.03. **HRMS** (ESI) m/z calcd for $C_{16}H_{18}NO_2^+$ $(M+H)^+$: 256.13321, found 256.13318.



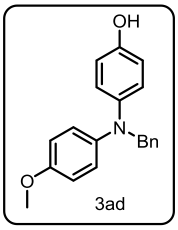

**2-(phenyl(2-(phenylamino)ethyl)amino)phenol (3aa):** black solid, 43mg, 47% yield. **$^{1}$H NMR** (500 MHz, Methanol-d4) δ = 7.15 – 7.05 (m, 4H), 7.04 – 6.95 (m, 2H), 6.91 – 6.78 (m, 2H), 6.75 – 6.65 (m, 3H), 6.65 – 6.56 (m, 3H), 3.81 (t, *J* = 6.9 Hz, 2H), 3.35 – 3.32 (m, 2H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 155.82, 150.73, 149.83, 140.75, 130.07, 129.88, 129.09, 118.87, 118.14, 117.31, 116.36, 114.06, 52.37, 42.38. **HRMS** (ESI) m/z calcd for $C_{20}H_{21}N_2O^+$ $(M+H)^+$: 305.16484, found 305.16495.



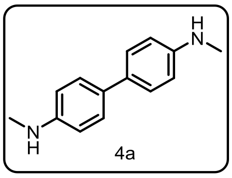

**4-((2-(5-methoxy-1H-indol-3-yl)ethyl)(4-methoxyphenyl)amino)phenol (3ab):** brown oil, 1.03 g (5 mmol), 53% yield. **$^{1}$H NMR** (500 MHz, Methanol-d4) δ = 7.24 (d, *J* = 8.7 Hz, 1H), 7.02 (s, 1H), 6.92 – 6.61 (m, 10H), 3.84 (d, *J* = 7.6 Hz, 2H), 3.76 (d, *J* = 10.9 Hz, 6H), 3.01 (d, *J* = 7.9 Hz, 2H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 155.01, 154.81, 153.43, 144.32, 142.67, 133.31, 129.17, 124.90, 124.10, 121.69, 121.66, 116.92, 116.81, 115.58, 113.71, 112.88, 112.54, 101.17, 56.26, 56.06, 54.90, 24.41. **HRMS** (ESI) m/z calcd for $C_{24}H_{25}N_2O_3^+$ $(M+H)^+$: 389.18597, found 389.18555.




**tert-butyl(4-((2-(5-methoxy-1-(4-nitrobenzoyl)-1H-indol-3-yl)ethyl)(4-methoxyphenyl)amino)phenyl) carbonate (3ac):** orange solid, 287 mg (0.5 mmol), 90% yield (from **3ab**). **$^{1}$H NMR** (500 MHz, Chloroform-*d*) δ = 8.36 – 8.28 (m, 3H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.01 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.96 (t, *J* = 8.9, 8.4 Hz, 4H), 6.91 (d, *J* = 2.5 Hz, 1H), 6.86 – 6.83 (m, 3H), 6.69 (d, *J* = 9.1 Hz, 2H), 3.91 (t, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.79 (s, 3H), 2.96 (t, *J* = 7.8 Hz, 2H), 1.55 (s, 9H). **$^{13}$C NMR** (125 MHz, Chloroform-d) δ = 165.73, 157.22, 156.56, 152.55, 149.42, 146.40, 143.41, 140.38, 140.30, 132.14, 130.69, 129.78, 126.73, 124.28, 123.87, 121.84, 120.95, 117.63, 116.62, 115.01, 113.88, 102.01, 83.31, 55.73, 55.53, 51.90, 27.74, 23.08. **HRMS** (ESI) m/z calcd for $C_{36}H_{36}N_3O_8^+$$(M+H)^+$: 638.24969, found 638.24963.




**4-(benzyl(4-methoxyphenyl)amino)phenol (3ad):** dark oil, 68 mg, 74% yield. **$^{1}$H NMR** (500 MHz, Methanol-d4) δ = 7.34 (d, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 9.2 Hz, 2H), 6.75 (d, *J* = 9.1 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 4.82 (s, 2H), 3.72 (s, 3H). **$^{13}$C NMR** (125 MHz, Methanol-d4) δ = 153.75, 152.14, 143.01, 141.56, 139.83, 127.95, 126.61, 126.24, 123.20, 120.16, 115.47, 114.09, 56.67, 54.62. **HRMS** (ESI) m/z calcd for $C_{20}H_{20}NO_2^+$ $(M+H)^+$ 306.14886, found 306.14859.




**N4,N4'-dimethyl-[1,1'-biphenyl]-4,4'-diamine (4a):** Same as described in literature,[12] 6.36 mg, 10% yeild. **$^1$H NMR** (500 MHz, Chloroform-*d*) δ = 7.00 (d, *J* = 8.5 Hz, 4H), 6.55 (d, *J* = 8.4 Hz, 4H), 3.58 (s, 2H), 2.81 (s, 6H).

# 8. References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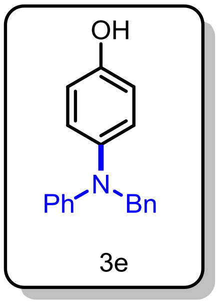
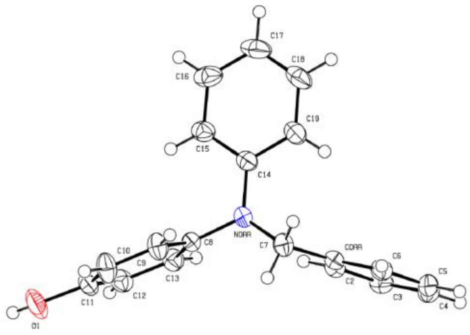
10. Seth, K., Raha Roy, S. & Chakraborti, A. K. Synchronous double C–N bond formation via C–H activation for a novel synthetic route to phenazine. *Chem. Commun.* **52**, 922-925 (2016).


# 9. NMR Spectra and X-ray structure of 3t and 3ab

### 9.1 X-ray data of 3e has been deposited at the Cambridge Crystallographic CCDC numbers 2019297.



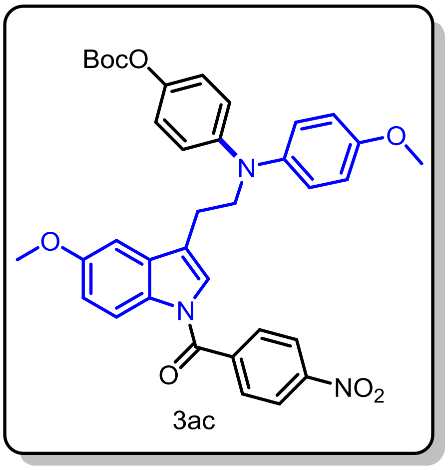
X-Ray structure of 3e

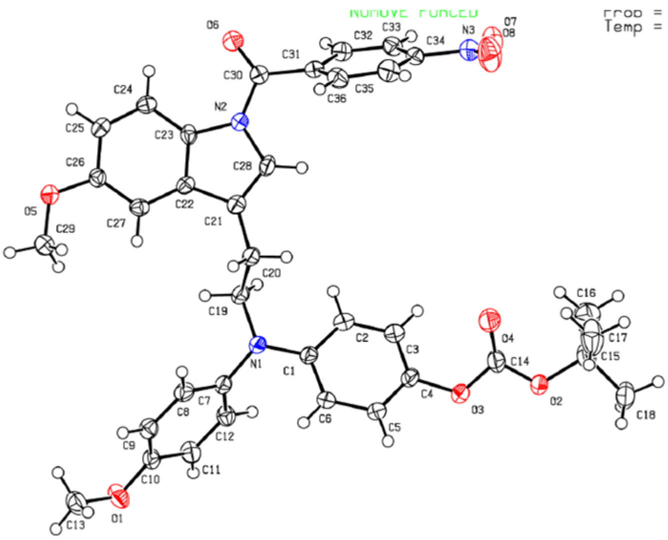
**Table 1 Crystal data and structure refinement for 3e.**

| | |
|---|---|
| Identification code | 3e |
| Empirical formula | $C_{19}H_{17}NO$ |
| Formula weight | 275.33 |
| Temperature/K | 100.01(10) |
| Crystal system | orthorhombic |
| Space group | Pbcn |
| a/Å | 26.2423(10) |
| b/Å | 15.2953(4) |
| c/Å | 7.4169(2) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2977.02(16) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.229 |
| μ/mm$^{-1}$ | 0.590 |
| F(000) | 1168.0 |
| Crystal size/mm$^3$ | 0.13 × 0.12 × 0.1 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.688 to 147.126 |
| Index ranges | -17 ≤ h ≤ 32, -18 ≤ k ≤ 17, -5 ≤ l ≤ 9 |
| Reflections collected | 7296 |
| Independent reflections | 2930 [$R_{int}$ = 0.0297, $R_{sigma}$ = 0.0334] |
| Data/restraints/parameters | 2930/1/194 |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.096 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0534, $wR_2$ = 0.1327 |
| Final R indexes [all data] | $R_1$ = 0.0630, $wR_2$ = 0.1403 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.17/-0.26 |

**9.2 X-ray data of 3ac has been deposited at the Cambridge Crystallographic CCDC numbers 2019298.**



X-Ray structure of 3ac

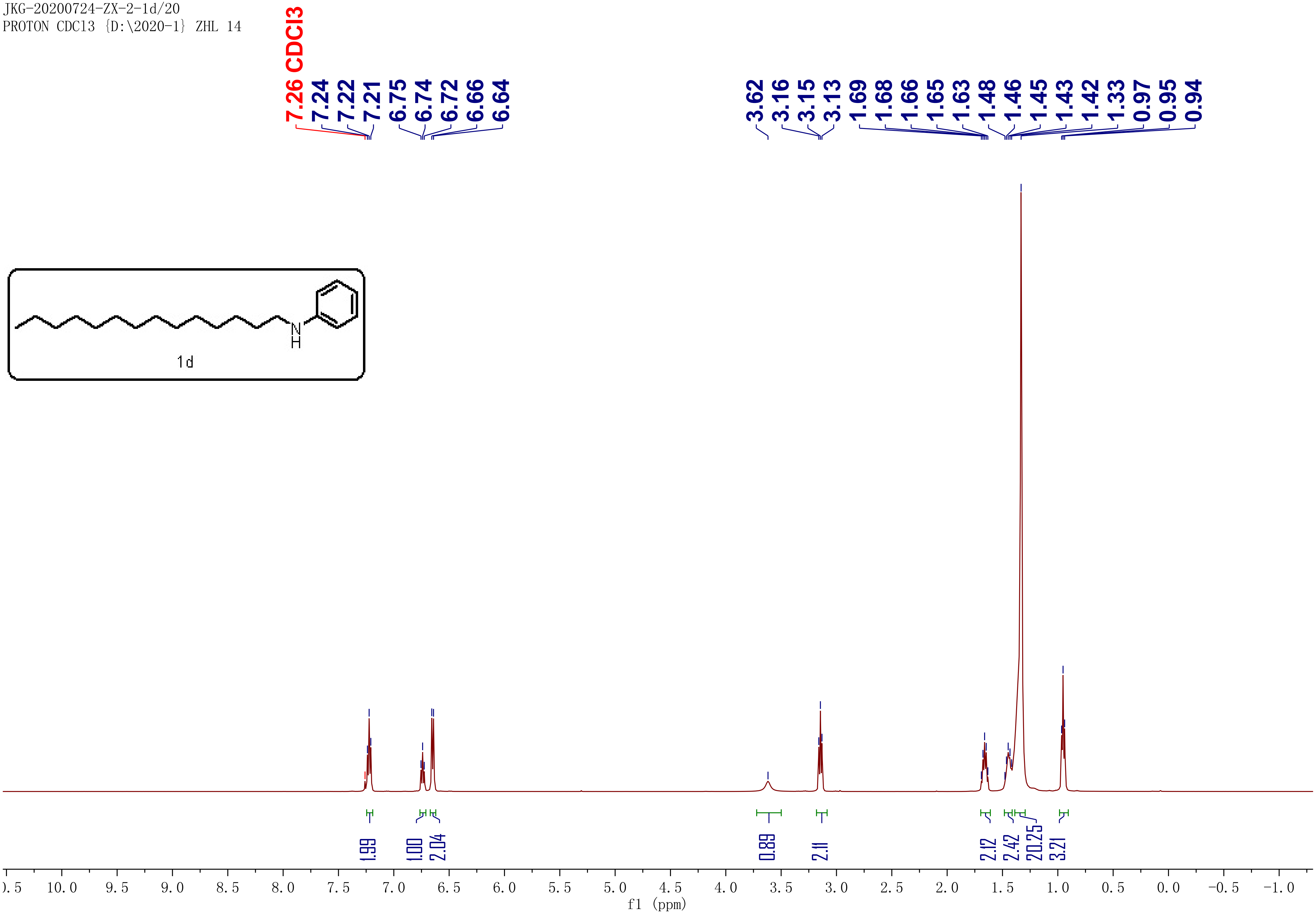
**Table 1 Crystal data and structure refinement for 3ac.**

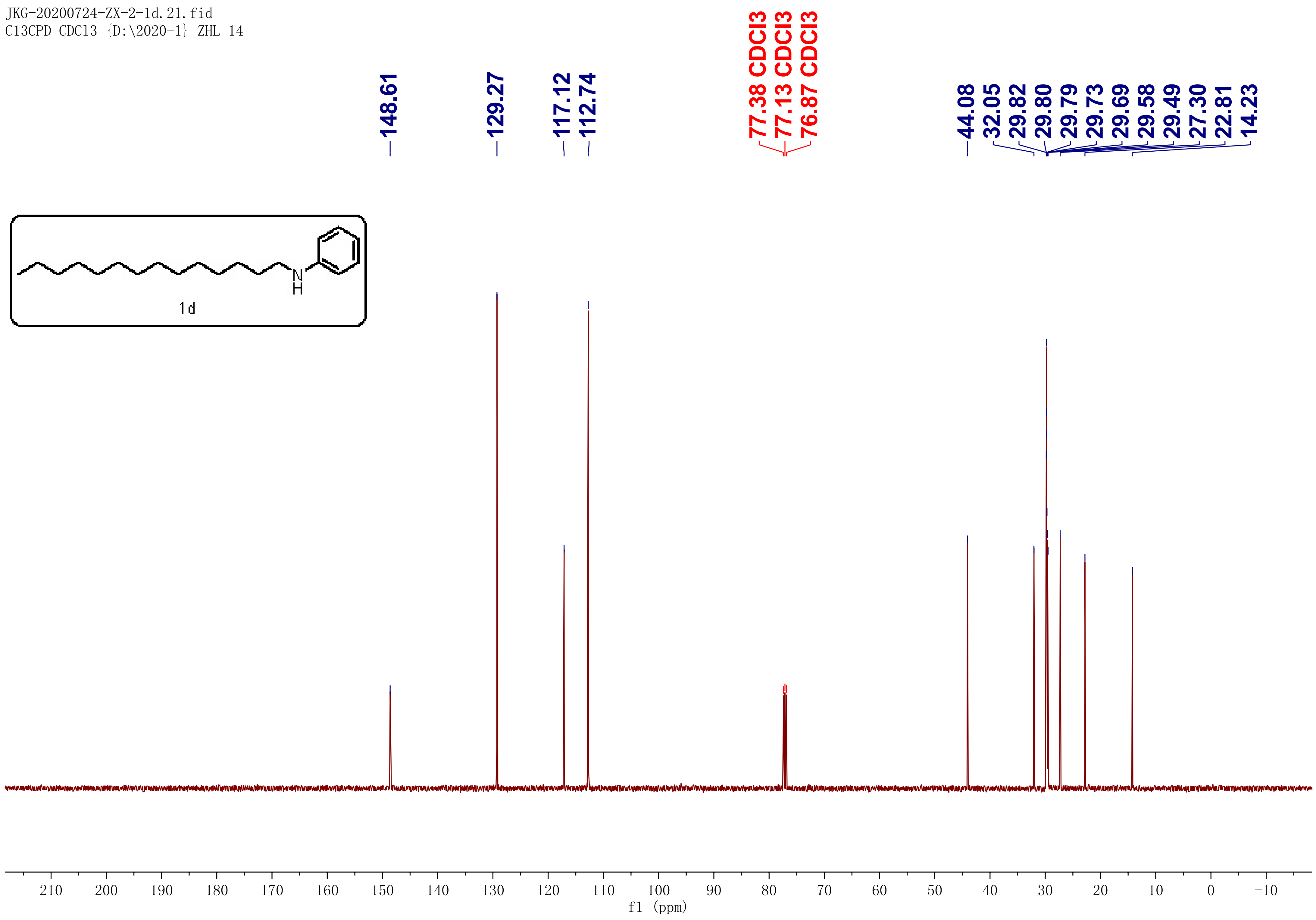
| | |
|---|---|
| Identification code | 3ac |
| Empirical formula | $C_{36}H_{35}N_3O_8$ |
| Formula weight | 637.67 |
| Temperature/K | 100.0(2) |
| Crystal system | triclinic |
| Space group | P-1 |

| | |
|---|---|
| a/Å | 6.8134(5) |
| b/Å | 14.9283(8) |
| c/Å | 16.4870(9) |
| α/° | 87.748(4) |
| β/° | 78.963(5) |
| γ/° | 79.267(5) |
| Volume/$Å^3$ | 1617.12(17) |
| Z | 2 |
| $\rho_{calc}g/cm^3$ | 1.310 |
| μ/$mm^{-1}$ | 0.093 |
| F(000) | 672.0 |
| Crystal size/$mm^3$ | 0.14 × 0.12 × 0.11 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.034 to 49.998 |
| Index ranges | -8 ≤ h ≤ 8, -17 ≤ k ≤ 14, -19 ≤ l ≤ 19 |
| Reflections collected | 13346 |
| Independent reflections | 5679 [$R_{int}$ = 0.0799, $R_{sigma}$ = 0.1004] |
| Data/restraints/parameters | 5679/0/429 |
| Goodness-of-fit on $F^2$ | 1.042 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0703, $wR_2$ = 0.1649 |
| Final R indexes [all data] | $R_1$ = 0.0994, $wR_2$ = 0.1945 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.27/-0.29 |

## 9.3 NMR Spectra

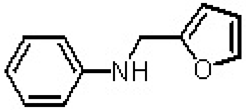
JKG-20200724-ZX-2-1d/20
PROTON CDCl3 {D:\2020-1} ZHL 14



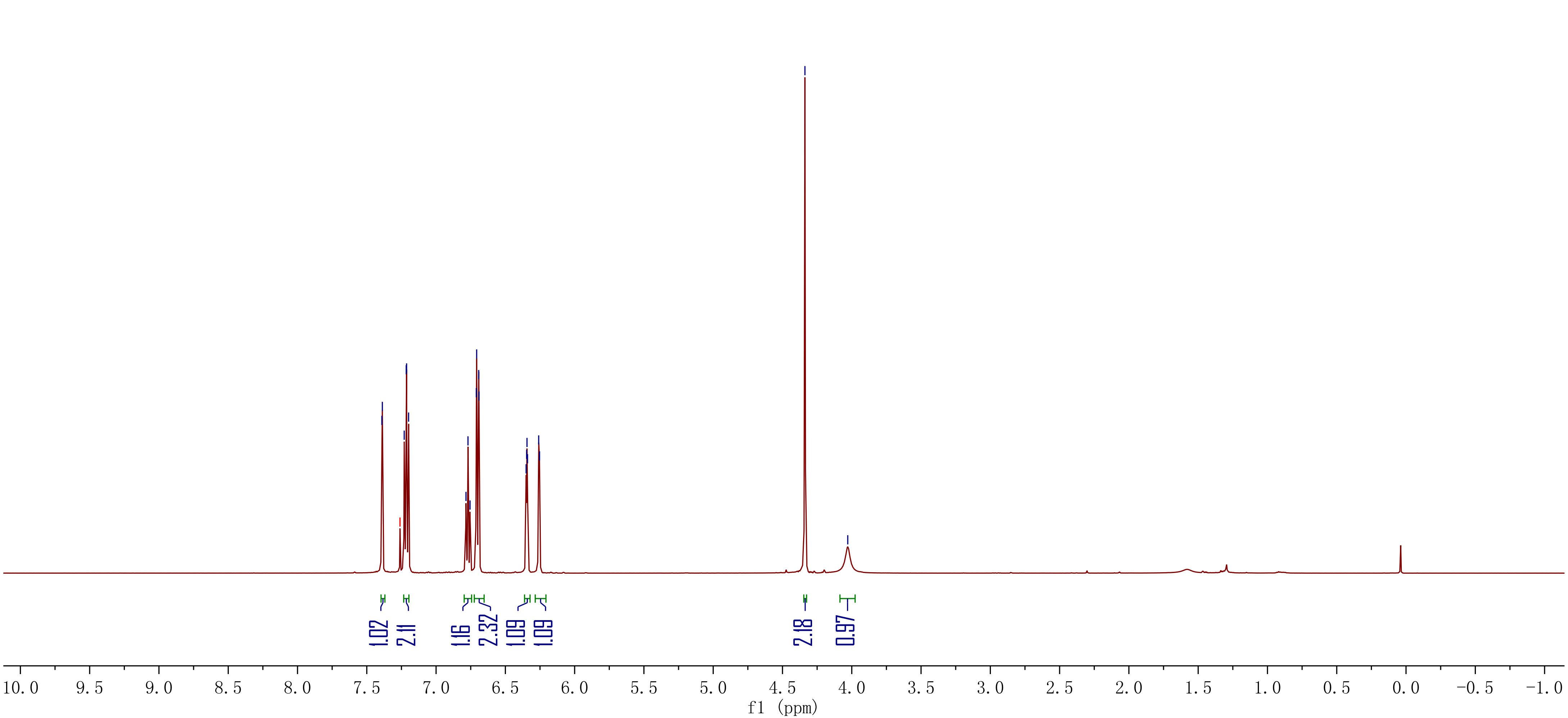


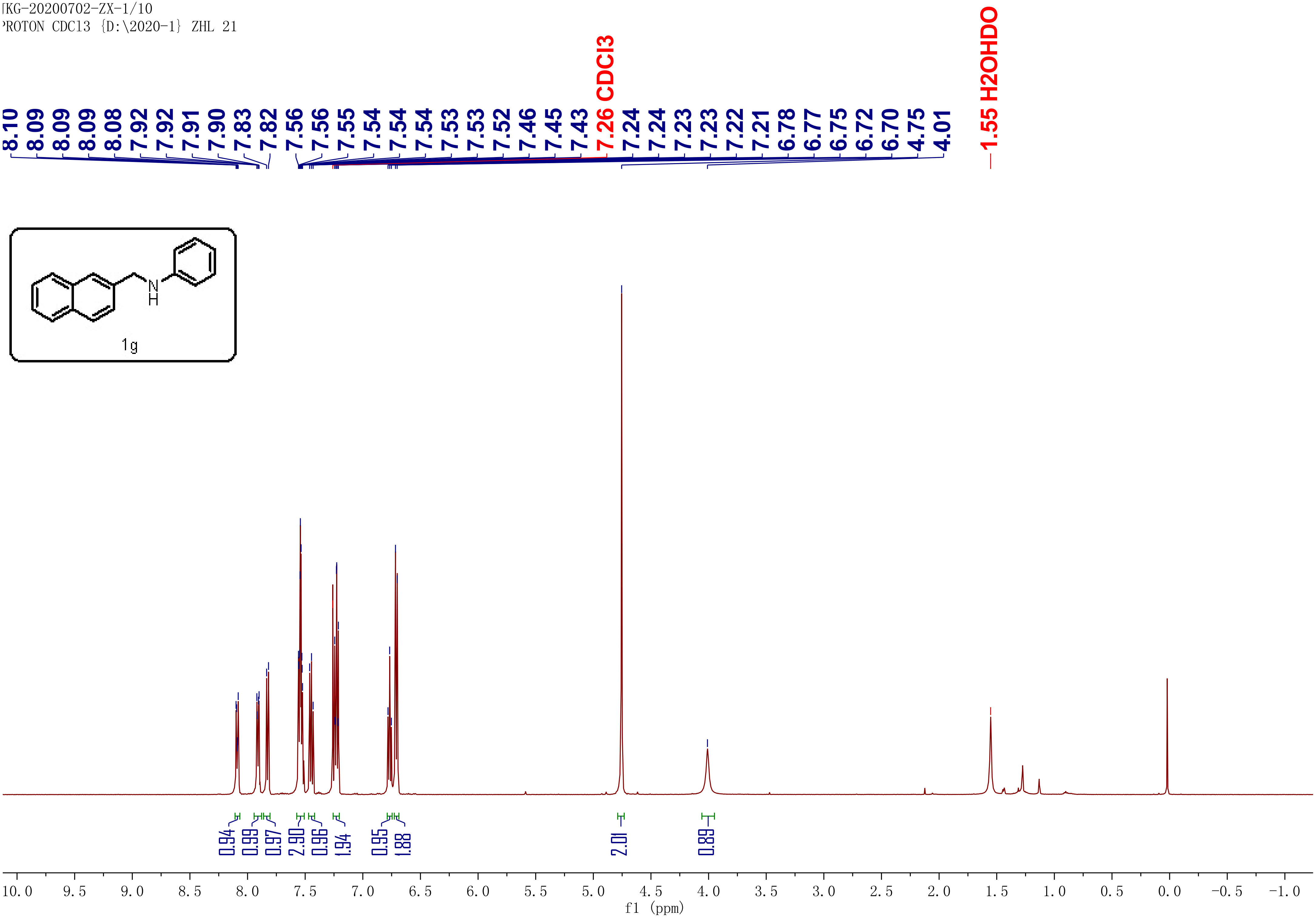
JKG-20200724-ZX-2-1d.21.fid
C13CPD CDCl3 {D:\2020-1} ZHL 14
148.61
129.27
117.12
112.74
77.38 CDCl3
77.13 CDCl3
76.87 CDCl3
44.08
32.05
29.82
29.80
29.79
29.73
29.69
29.58
29.49
27.30
22.81
14.23
N
H
1d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

JKG-20200702-ZX-2/10
PROTON CDCl3 {D:\2020-1} ZHL 22



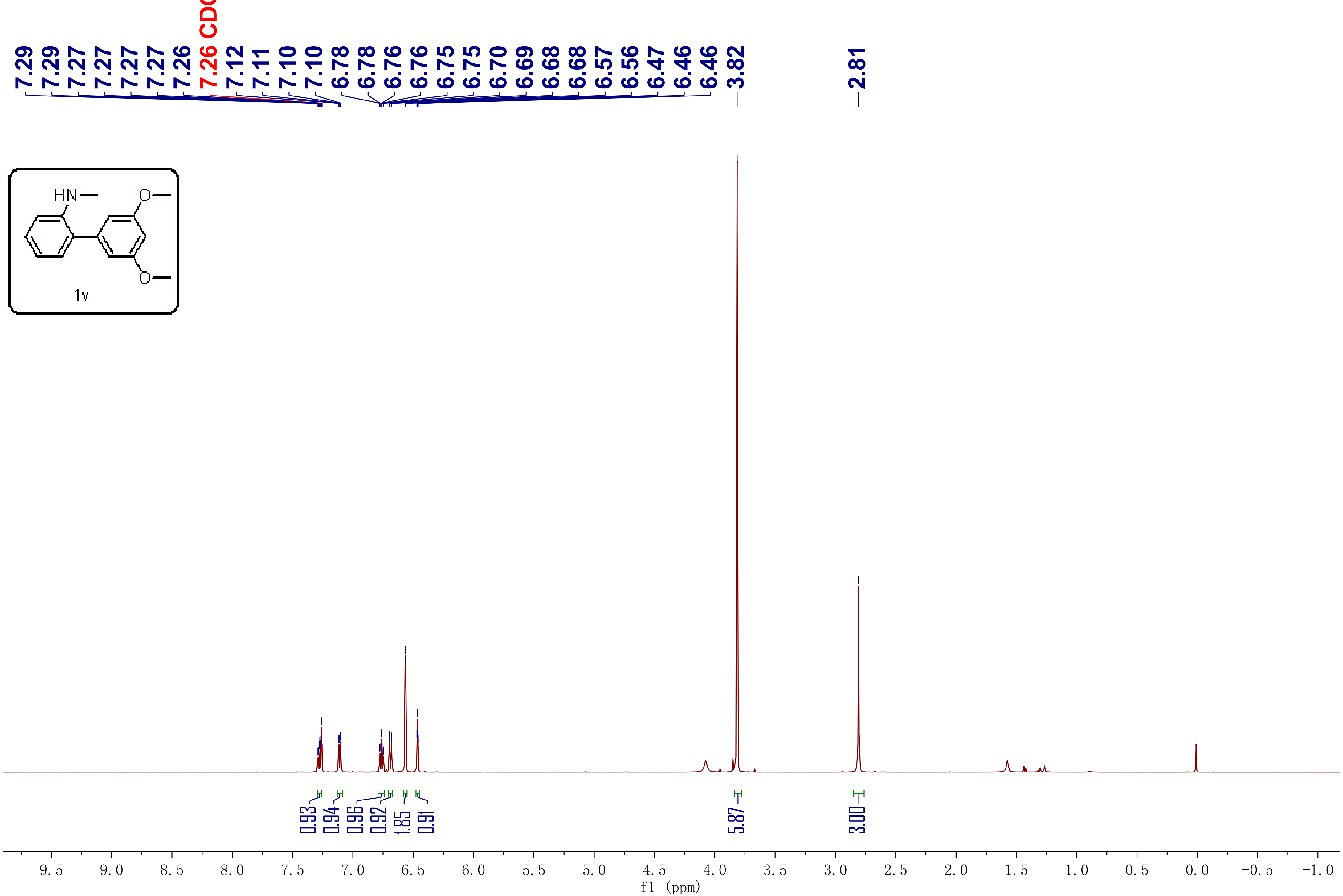
1f



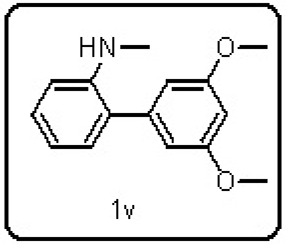


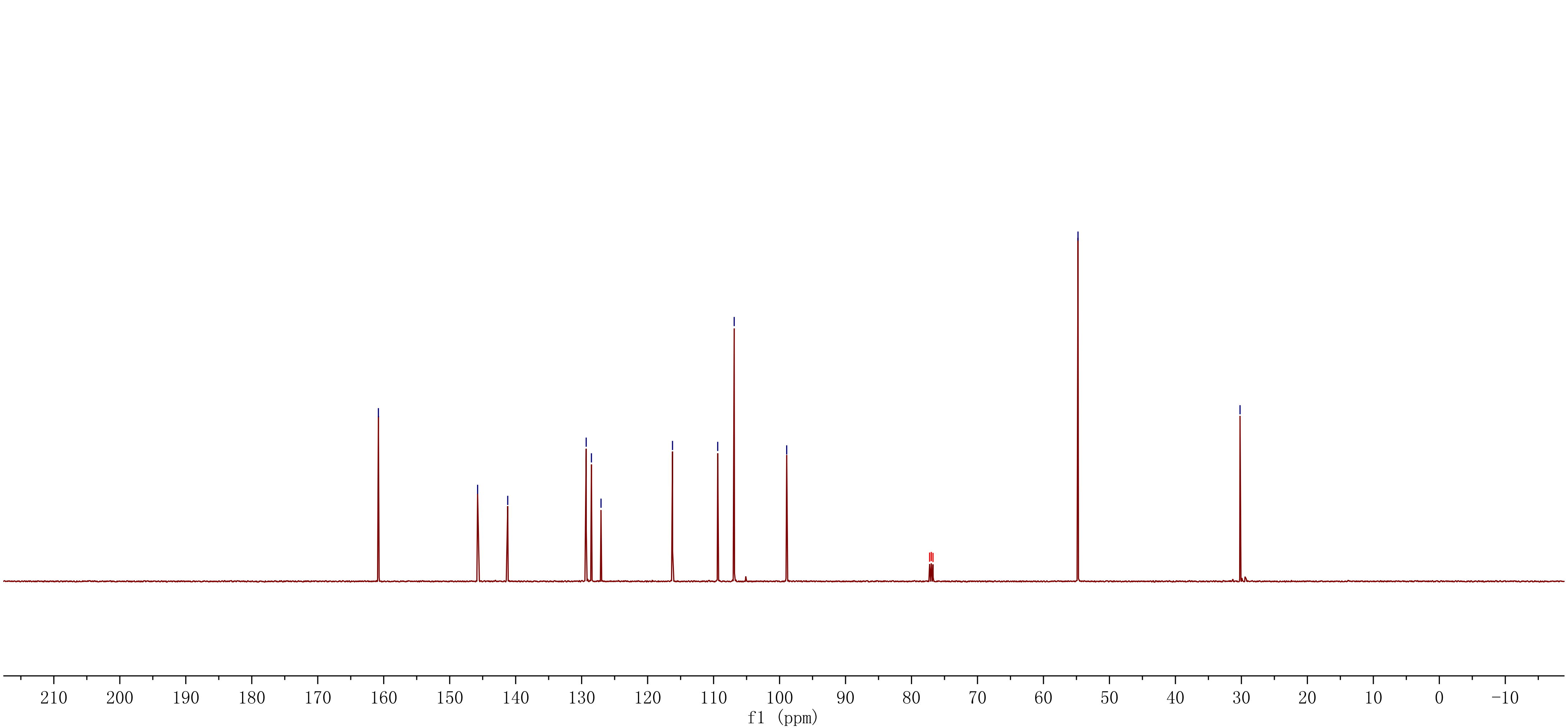
KG-20200702-ZX-1/10
PROTON CDCl3 {D:\2020-1} ZHL 21
8.10 8.09 8.09 8.09 8.08 7.92 7.92 7.91 7.90 7.83 7.82 7.56 7.56 7.55 7.54 7.54 7.54 7.53 7.53 7.52 7.46 7.45 7.43 7.26 CDCl3 7.24 7.24 7.23 7.23 7.22 7.21 6.78 6.77 6.75 6.72 6.70 4.75 4.01
1.55 H2OHDO
N
H
1g
0.94 0.99 0.97 2.90 0.96 1.94 0.95 1.88 2.01 0.89
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)

JKG-20200701-ZX-2/10
PROTON CDCl3 {D:\2020-1} ZHL 16

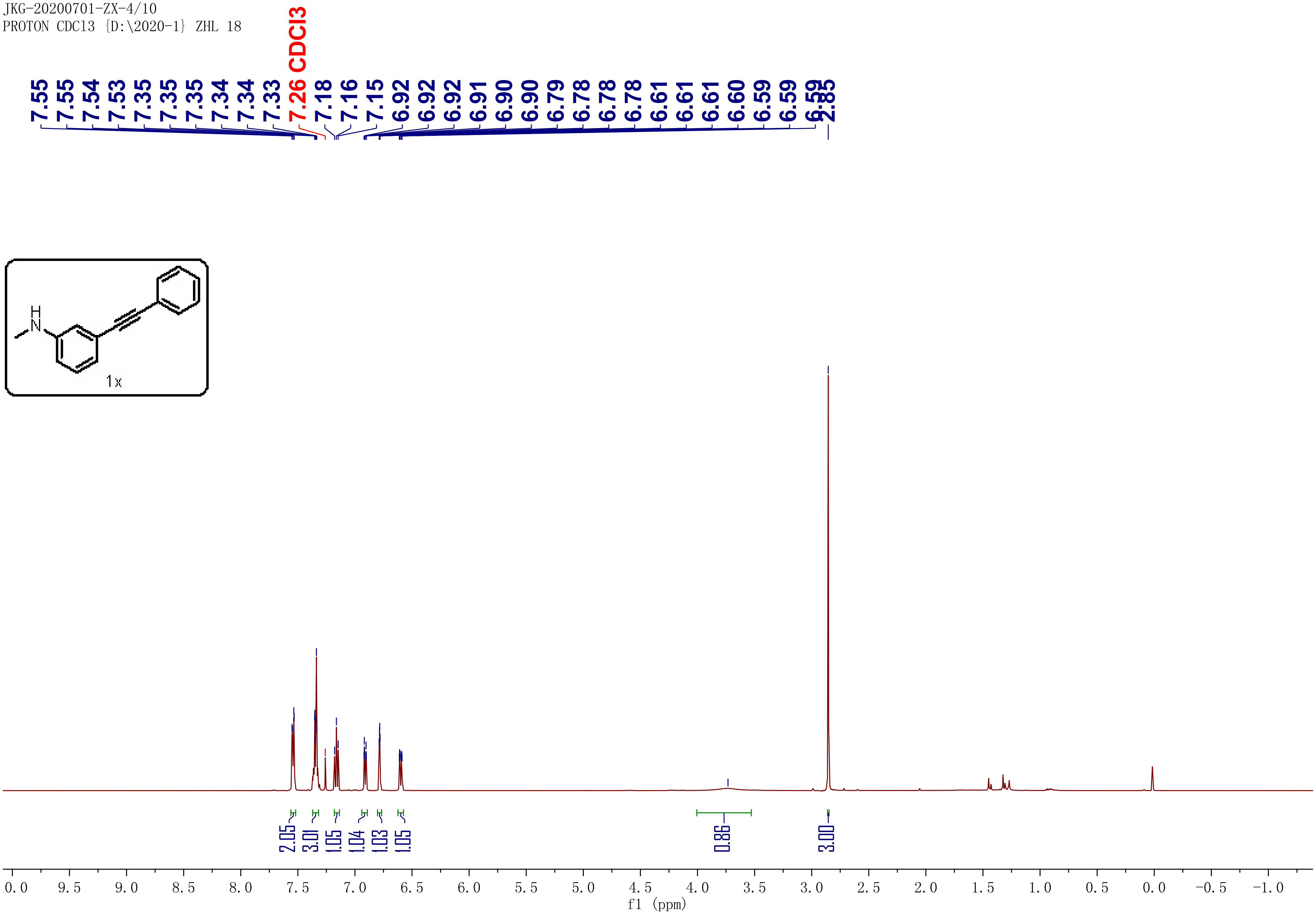


JKG-20200724-ZX-2-1g/20
C13CPD CDCl3 {D:\2020-1} ZHL 15

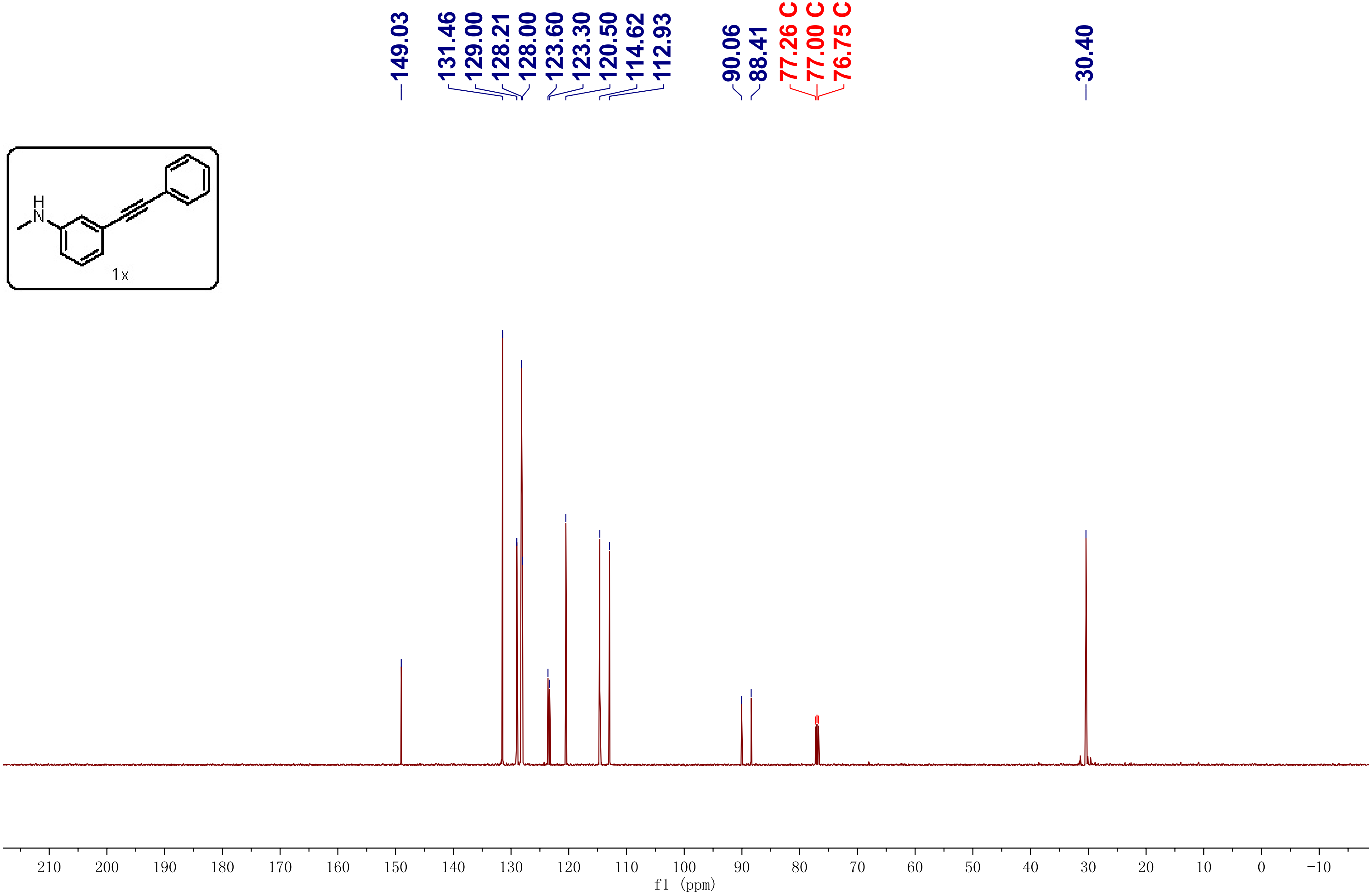

1v



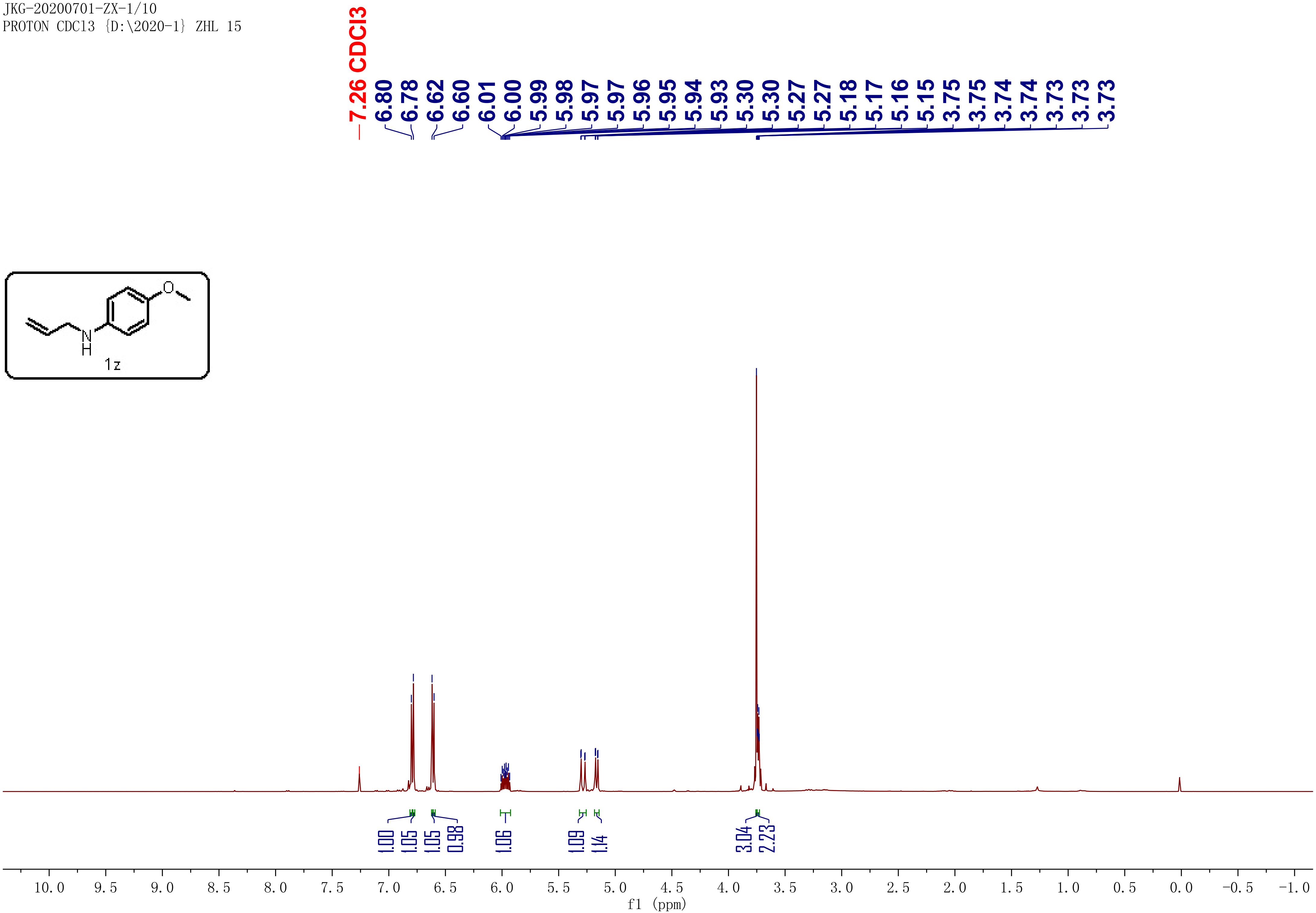
JKG-20200701-ZX-4/10
PROTON CDCl3 {D:\2020-1} ZHL 18



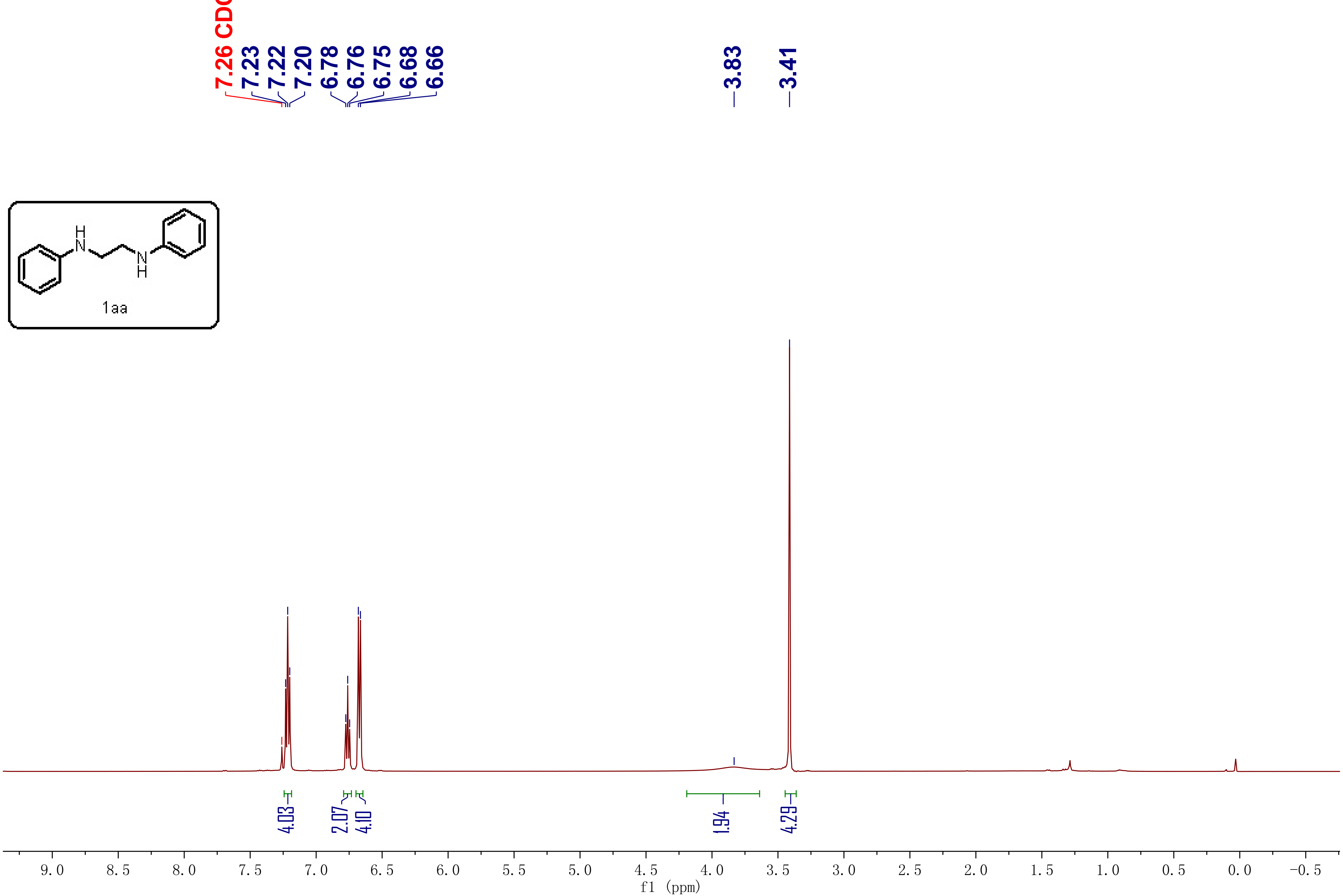
JKG-20200724-ZX-2-1aa/10
C13CPD CDCl3 {D:\2020-1} ZHL 25



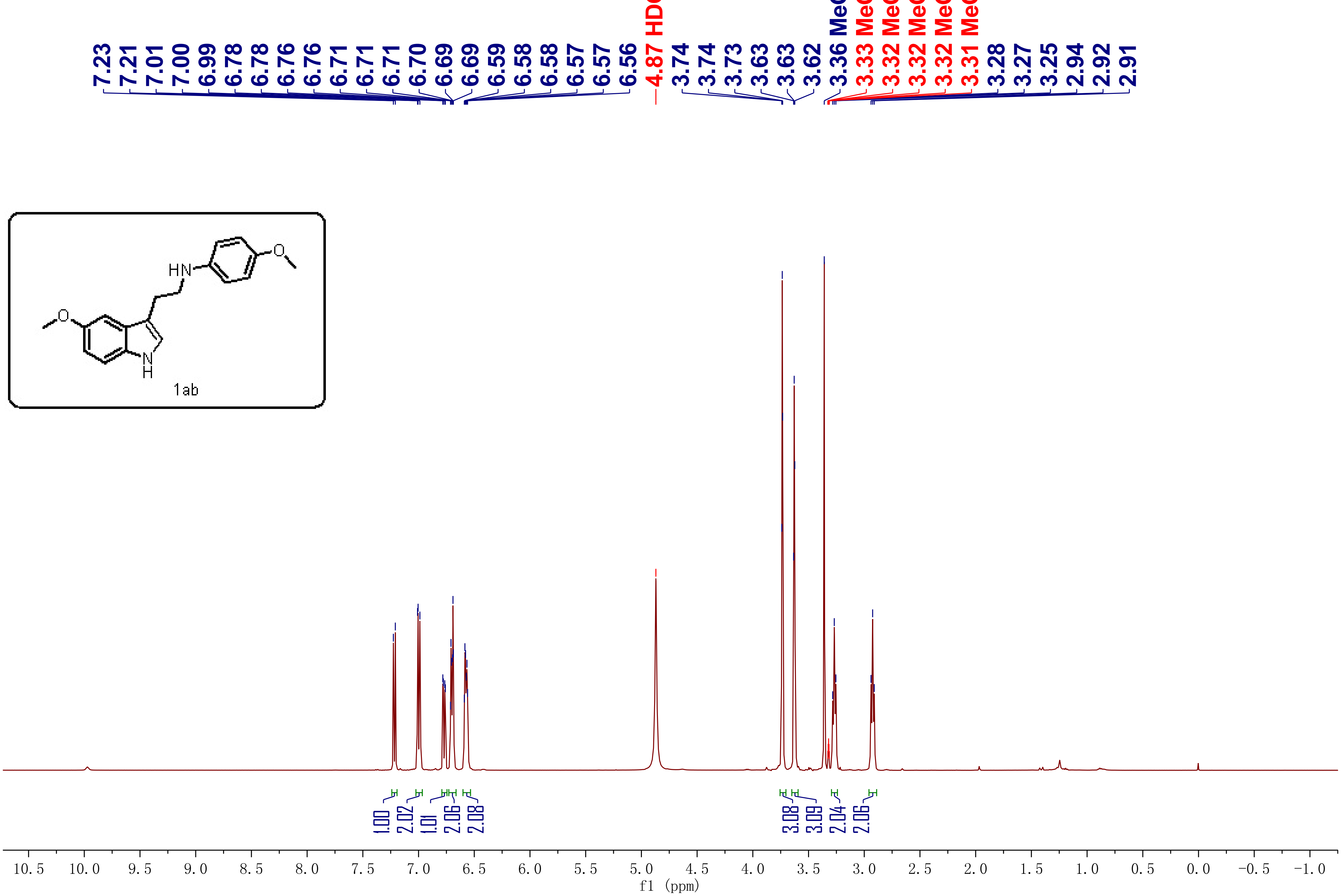
JKG-20200701-ZX-1/10
PROTON CDCl3 {D:\2020-1} ZHL 15


1z

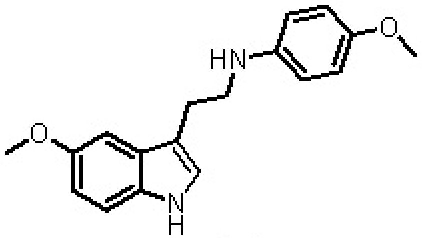
JKG-20200702-ZX-3/10
PROTON CDCl3 {D:\2020-1} ZHL 23

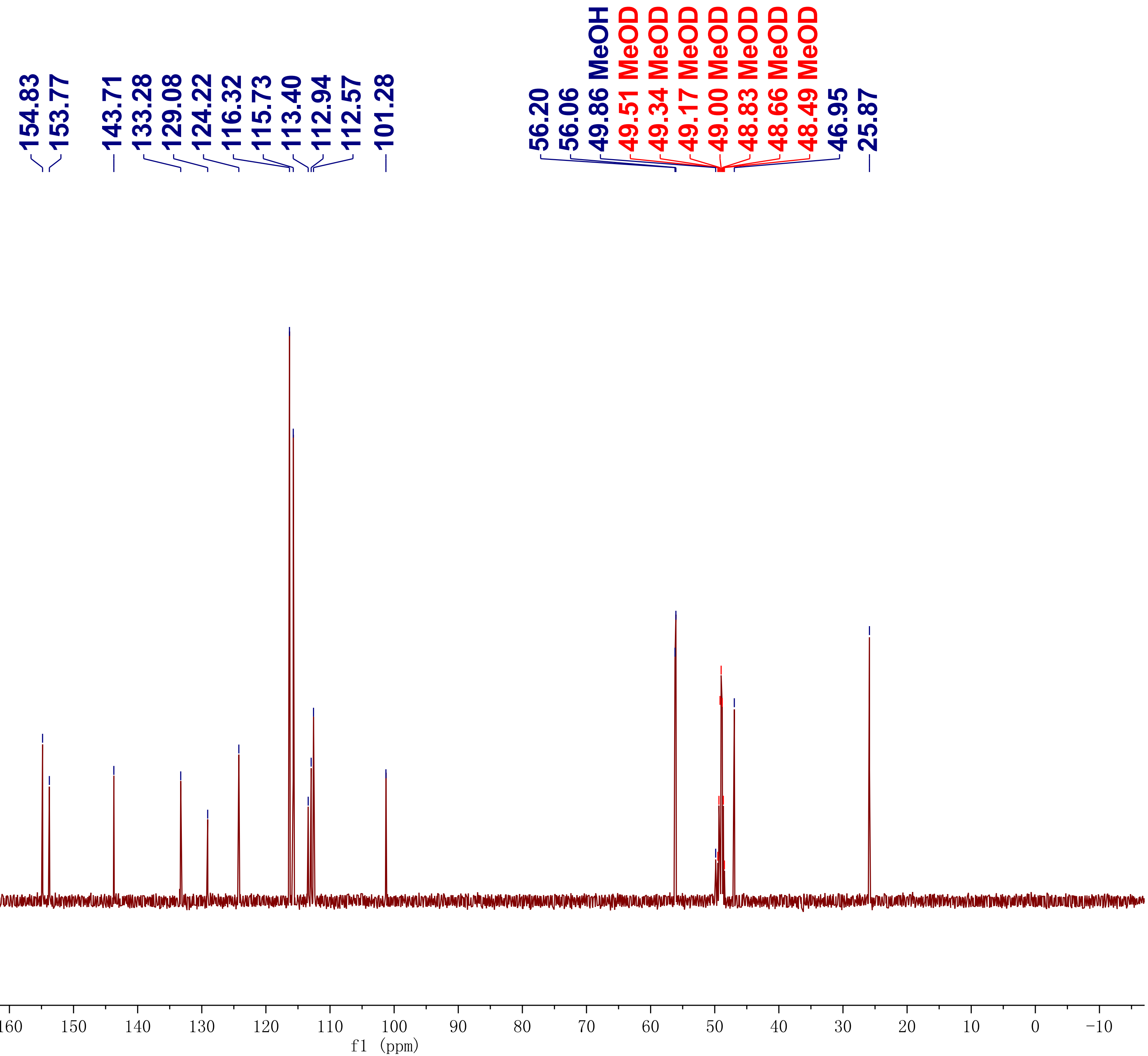


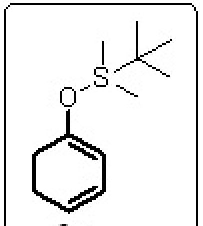
JKG-20190507-ZX-150-01/10
H



JKG-20190507-ZX-150-01/11
C

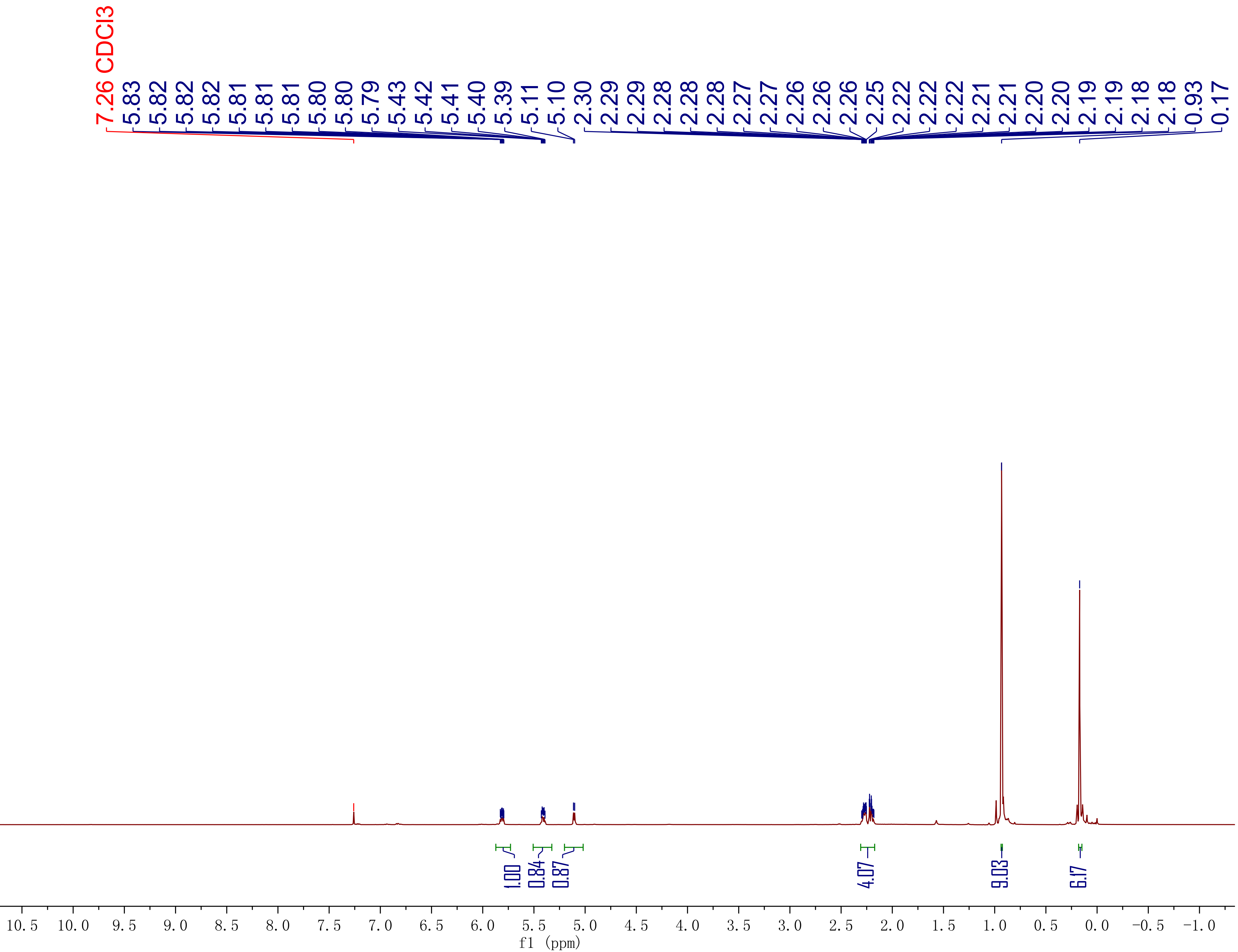

1ab





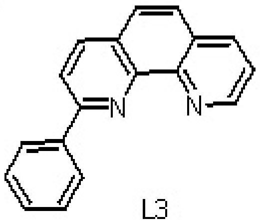
O
Si

2a

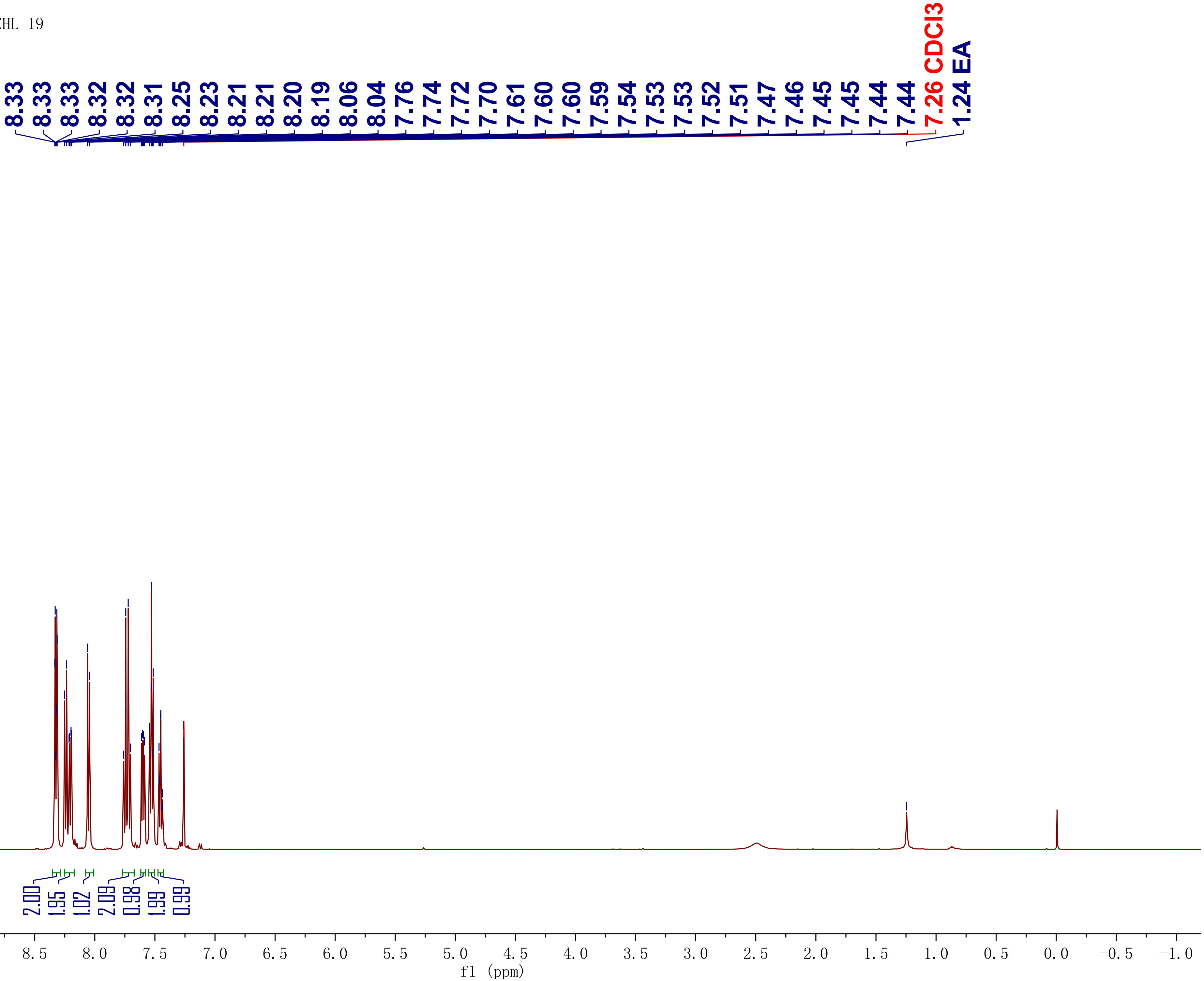


pdata/1
H
7.26 CDCl3
5.83
5.82
5.82
5.82
5.81
5.81
5.81
5.80
5.80
5.79
5.43
5.42
5.41
5.40
5.39
5.11
5.10
2.30
2.29
2.29
2.28
2.28
2.28
2.27
2.27
2.26
2.26
2.26
2.25
2.22
2.22
2.22
2.21
2.21
2.20
2.20
2.19
2.19
2.18
2.18
0.93
0.17
1.00
0.84
0.87
4.07
9.03
6.17
f1 (ppm)

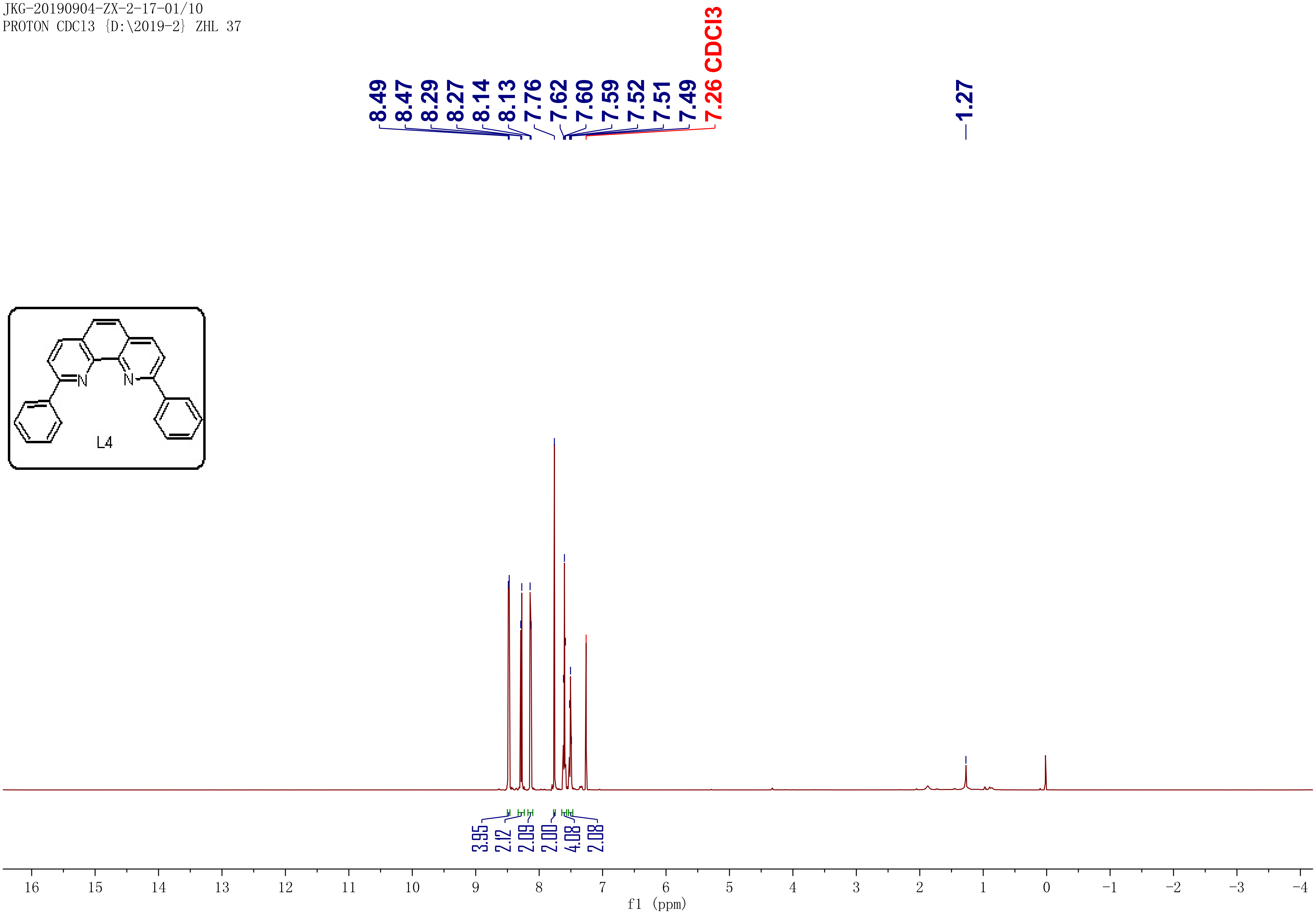
JKG-20200701-ZX-2-PH/10
PROTON CDCl3 {D:\2020-1} ZHL 19



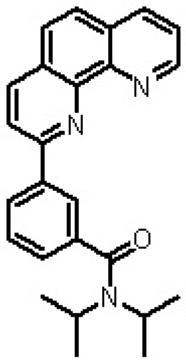
L3



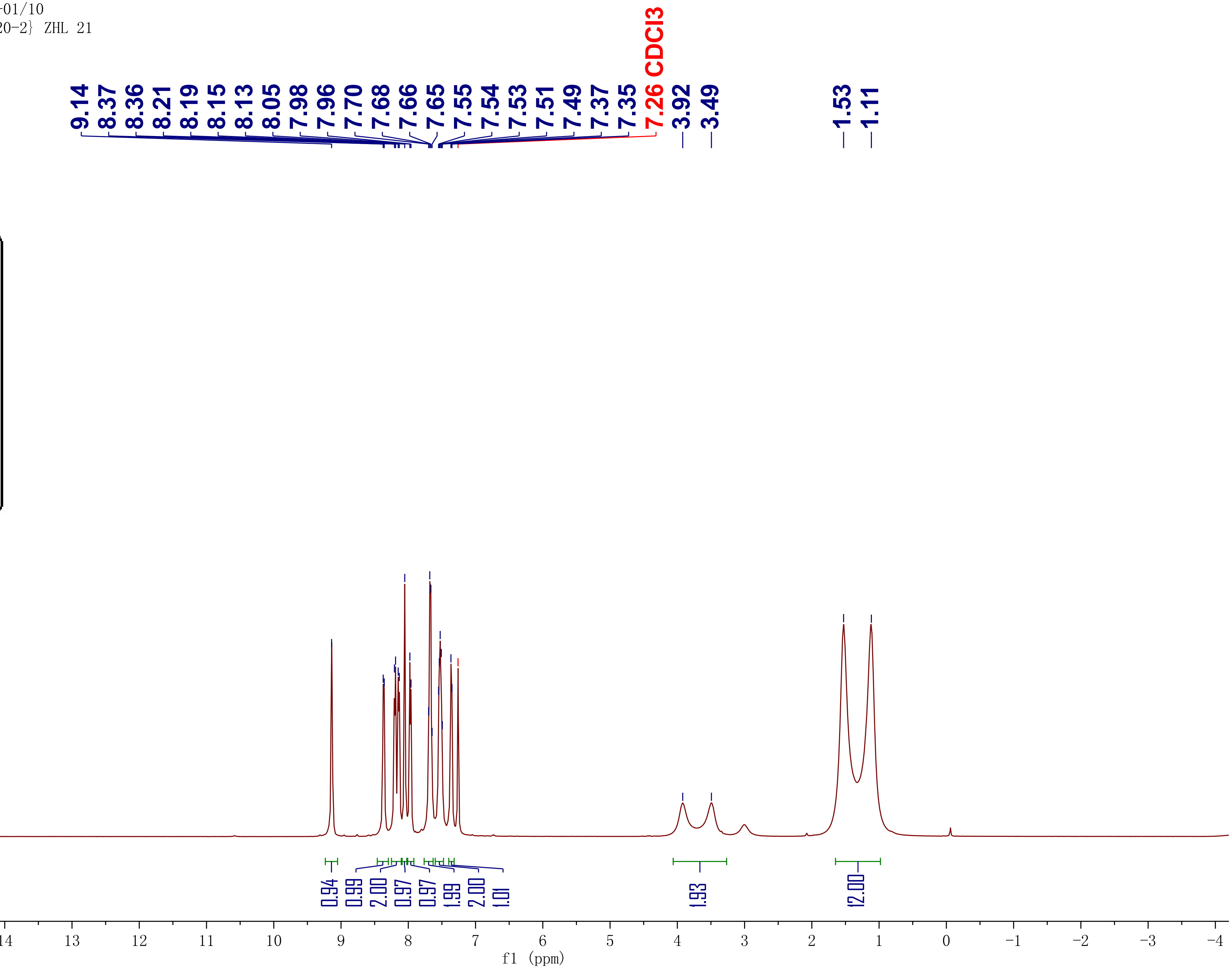
JKG-20190904-ZX-2-17-01/10
PROTON CDC13 {D:\2019-2} ZHL 37

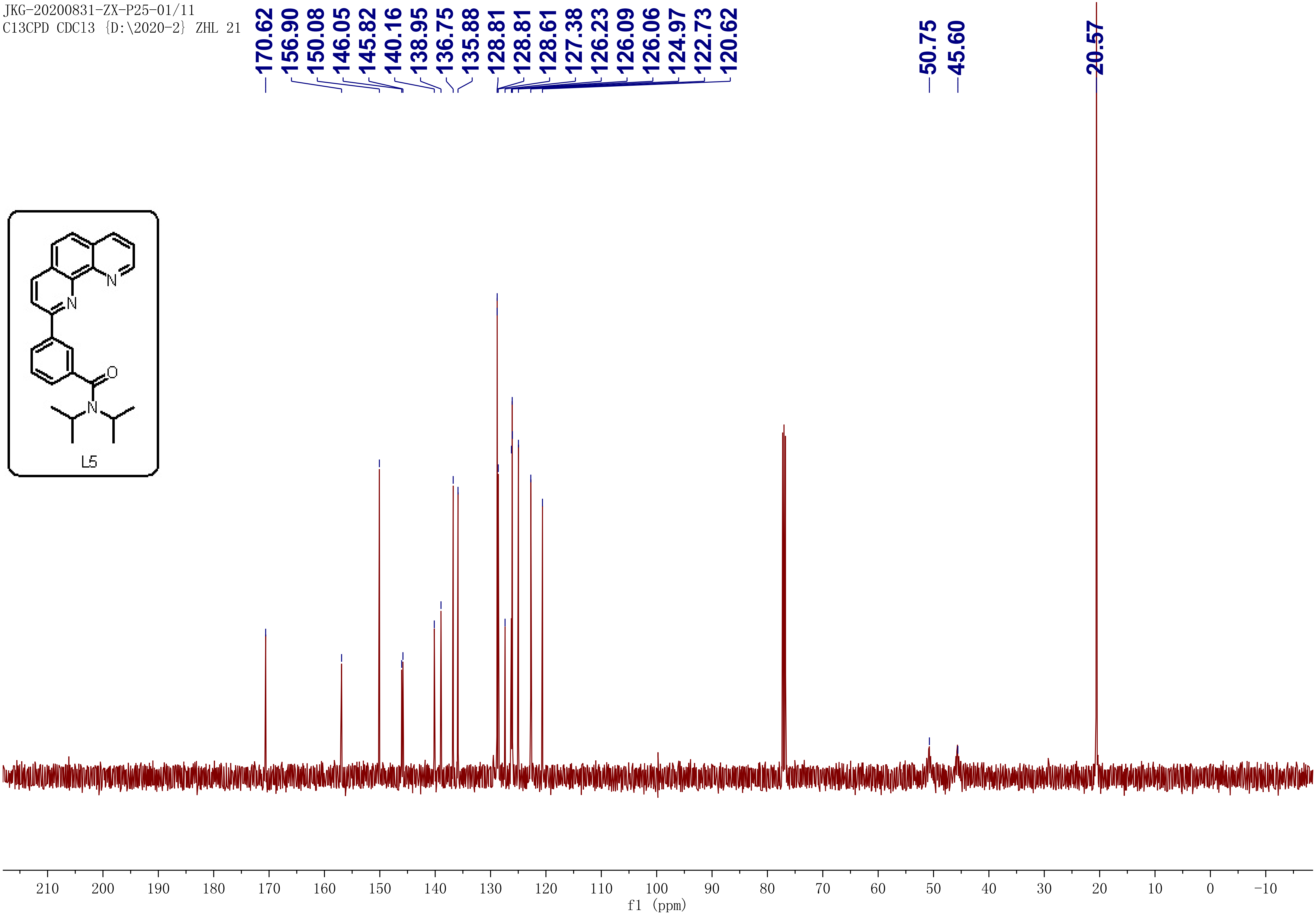


JKG-20200831-ZX-P25-01/10
PROTON CDCl3 {D:\2020-2} ZHL 21

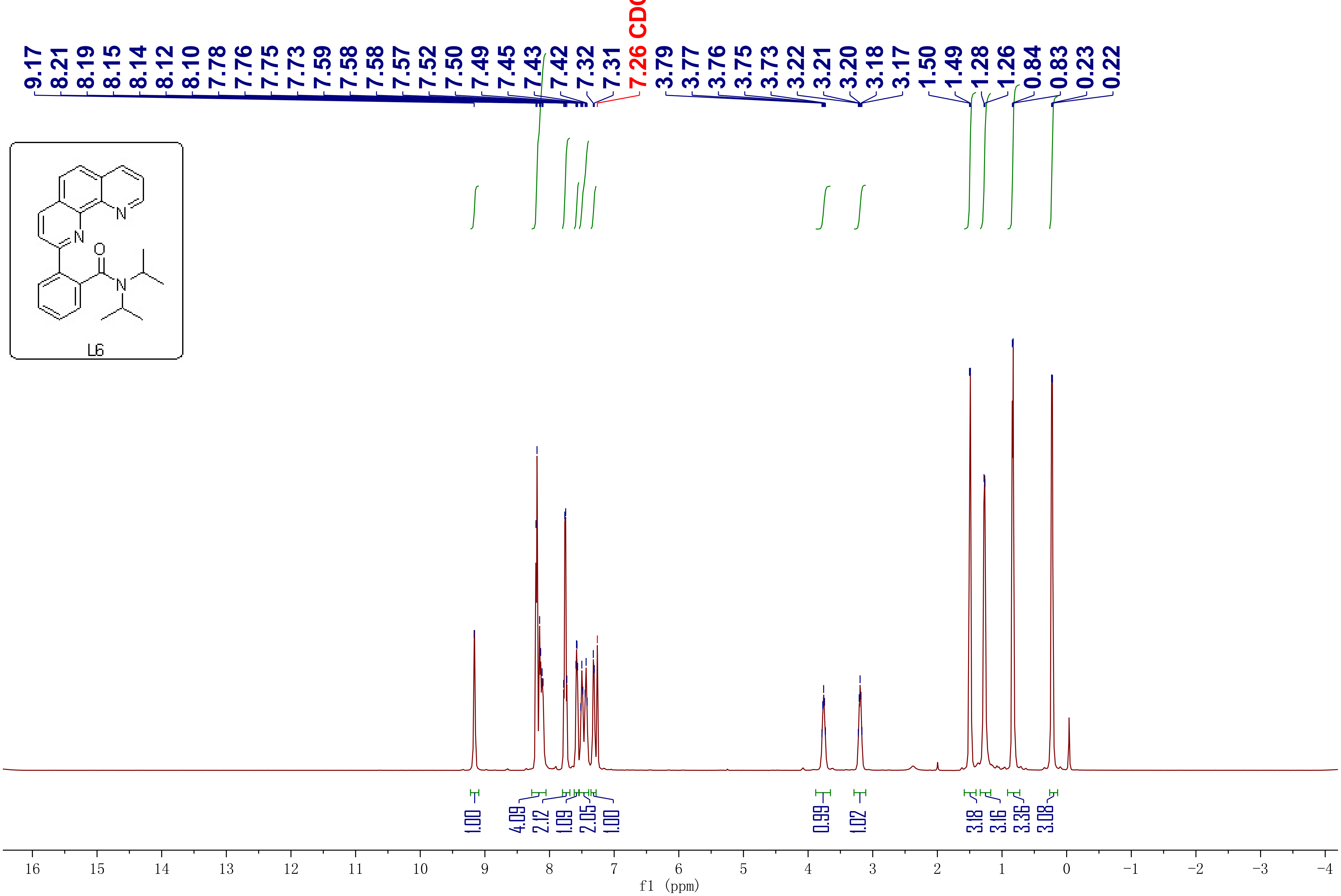


L5

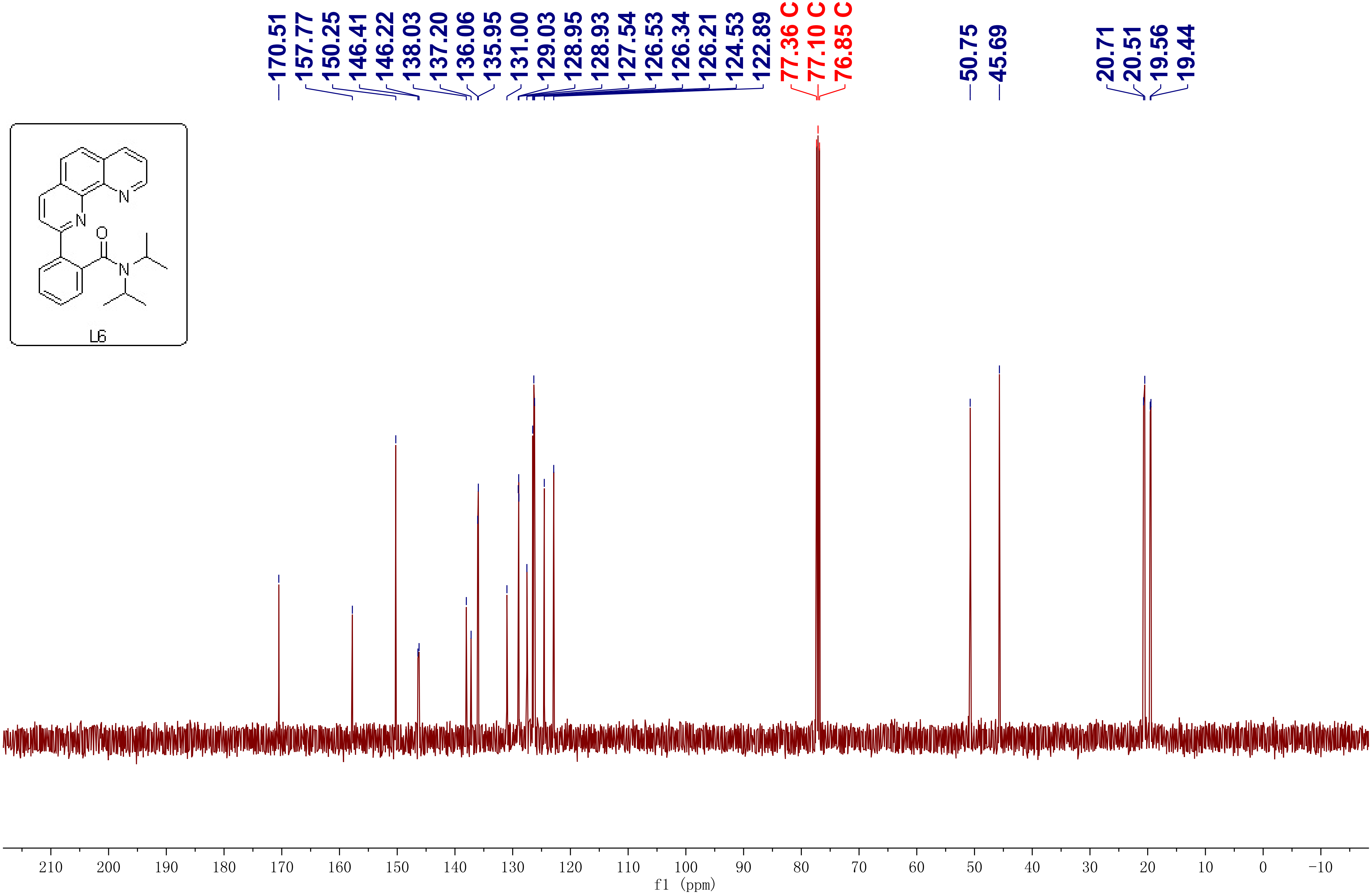



JKG-20200831-ZX-P25-01/11
C13CPD CDCl3 {D:\2020-2} ZHL 21
170.62
156.90
150.08
146.05
145.82
140.16
138.95
136.75
135.88
128.81
128.81
128.61
127.38
126.23
126.09
126.06
124.97
122.73
120.62
50.75
45.60
20.57
L5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

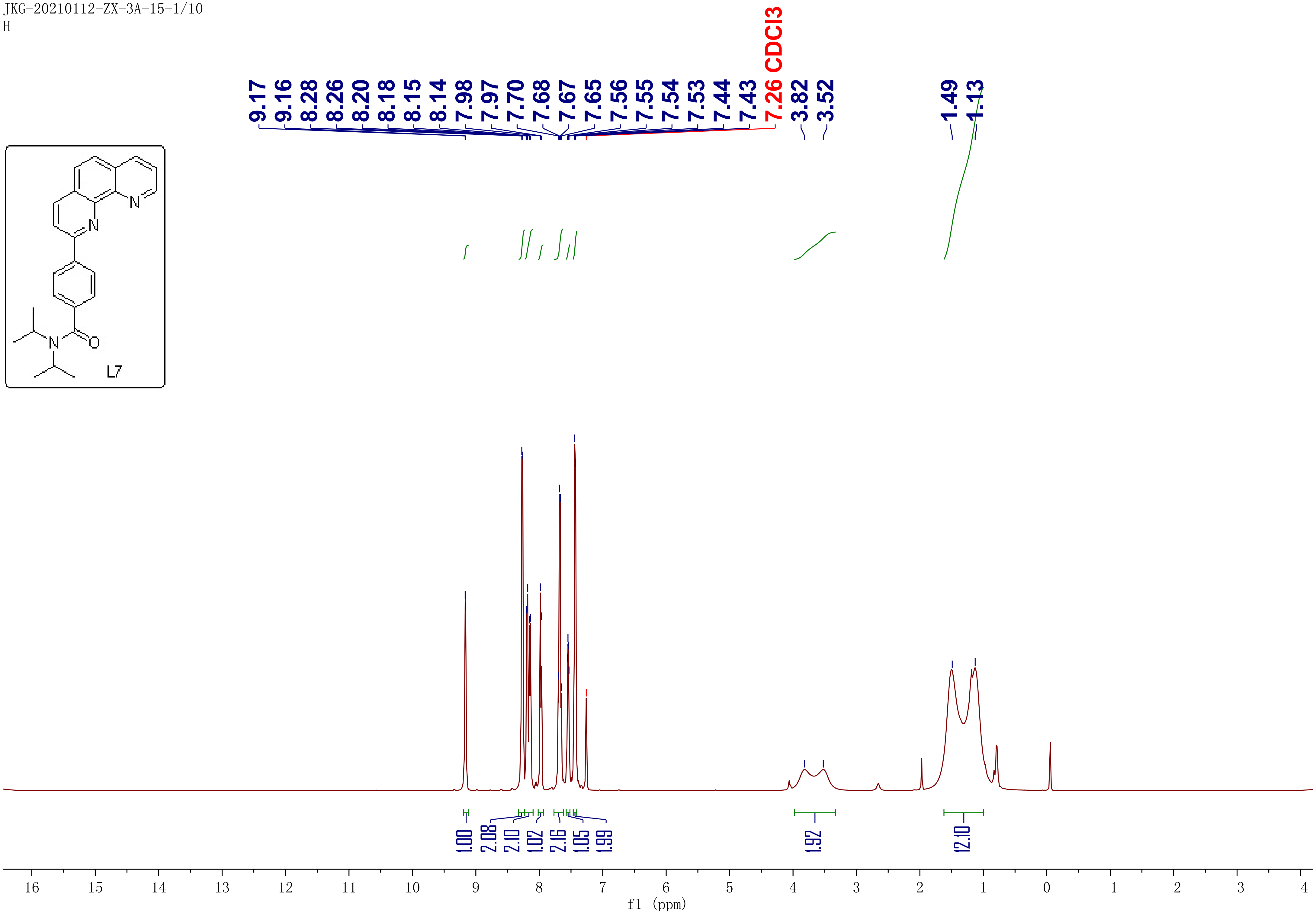
JKG-20210112-ZX-3A-15-2/10
H

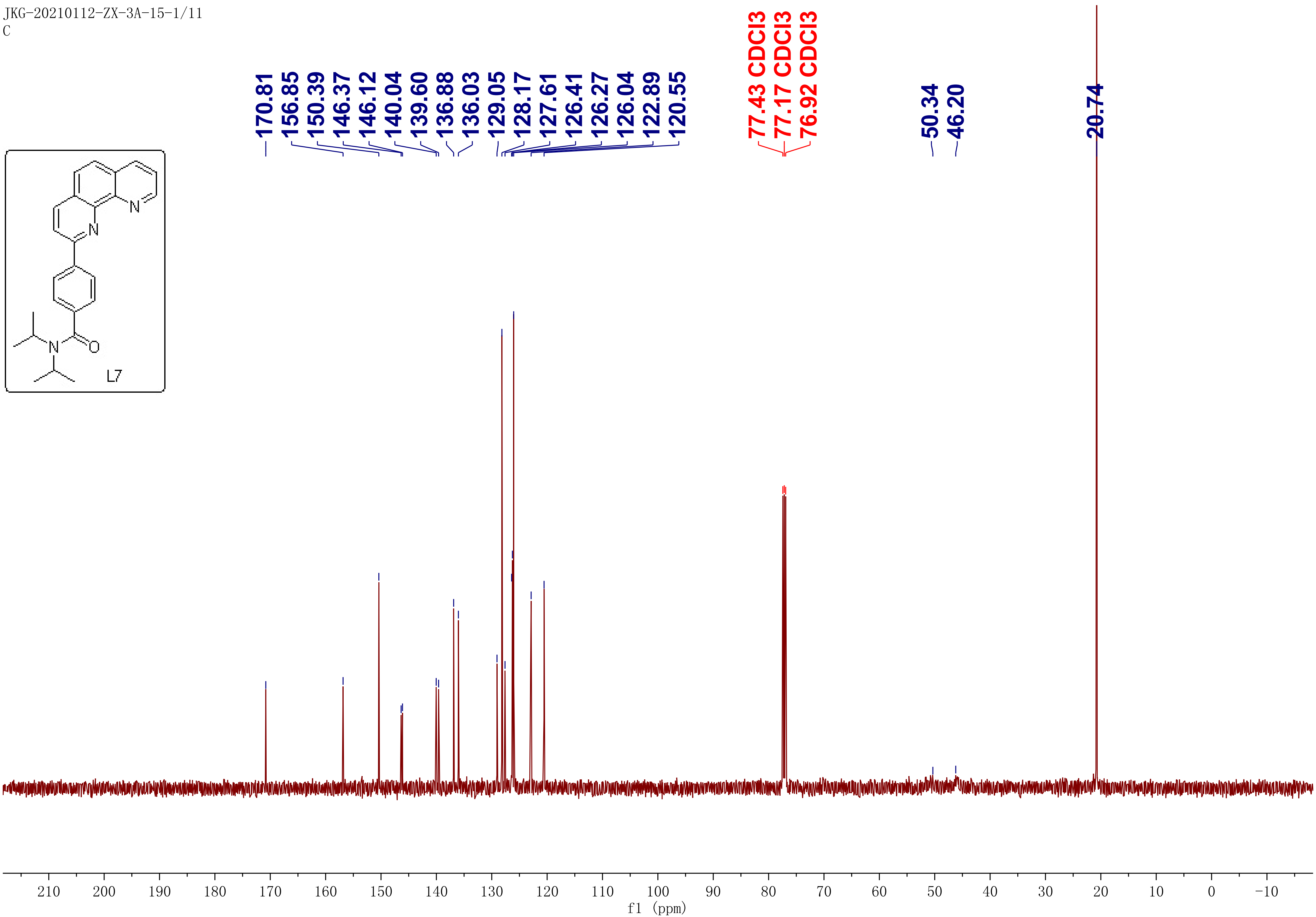


JKG-20210112-ZX-3A-15-2/11
C



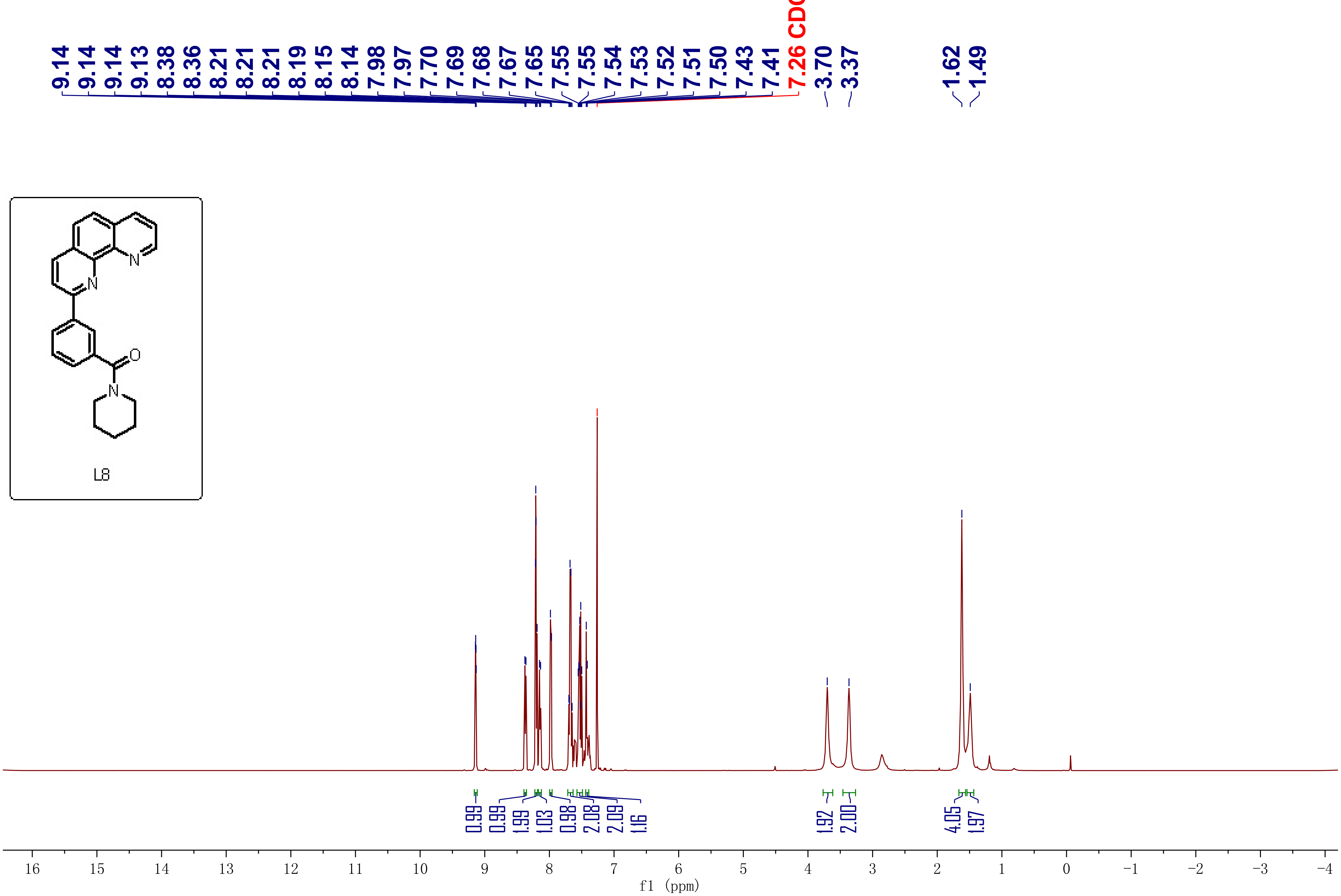
JKG-20210112-ZX-3A-15-1/10
H





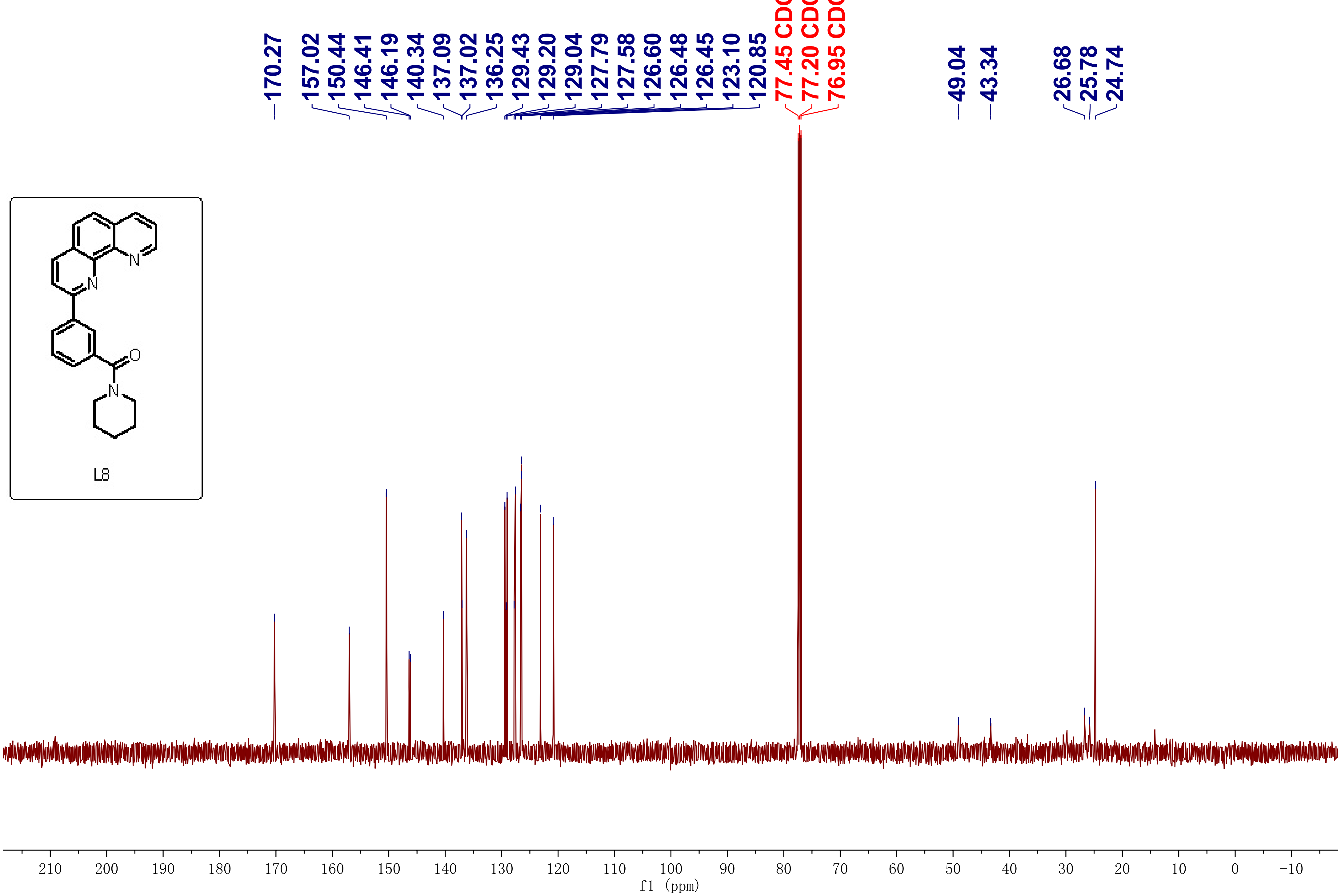
JKG-20210112-ZX-3A-15-1/11
C
170.81
156.85
150.39
146.37
146.12
140.04
139.60
136.88
136.03
129.05
128.17
127.61
126.41
126.27
126.04
122.89
120.55
77.43 CDCl3
77.17 CDCl3
76.92 CDCl3
50.34
46.20
20.74
N
N
N
O
L7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

JKG-20200701-ZX-2-PD/10
PROTON CDCl3 {D:\2020-1} ZHL 20

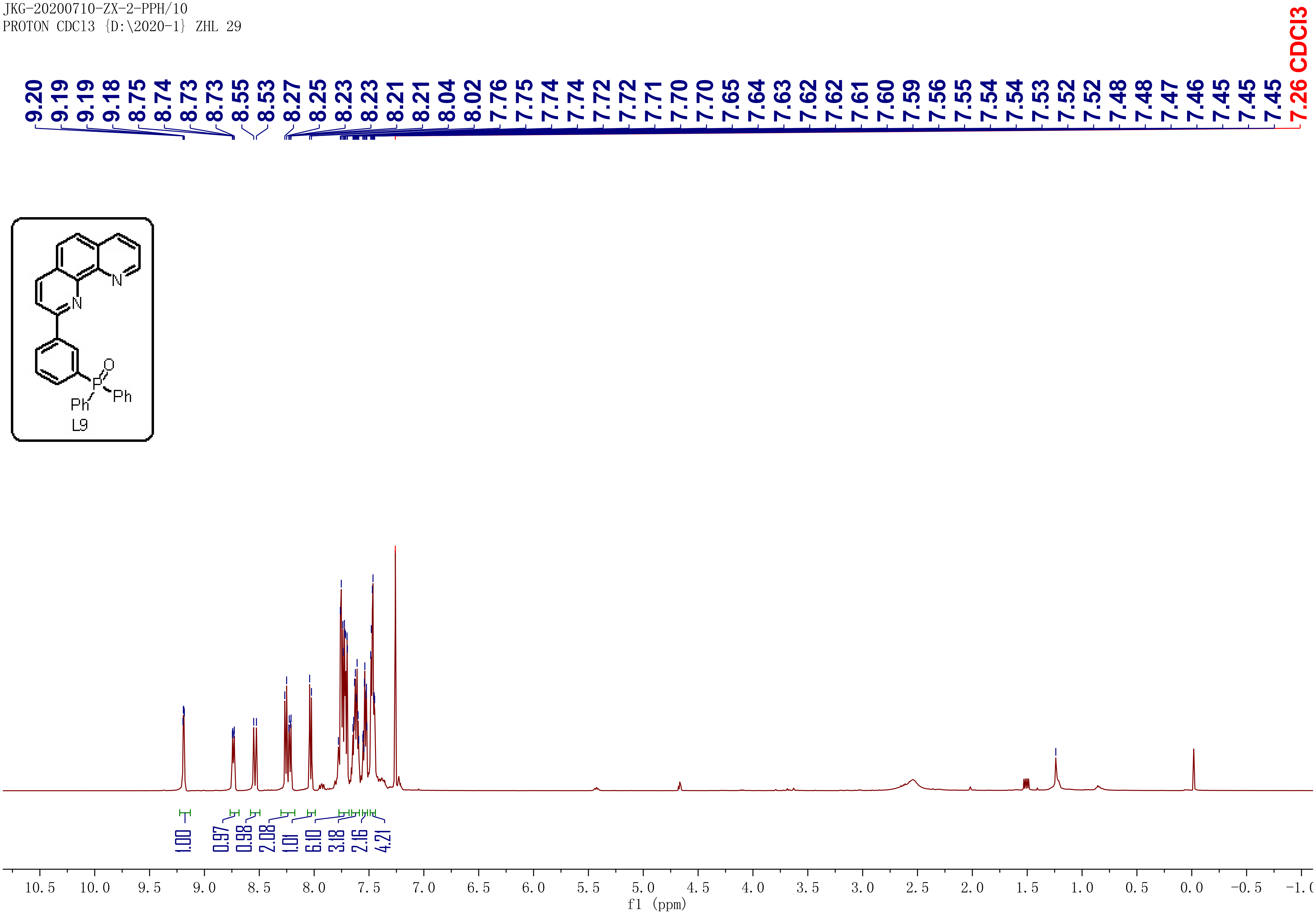



L8

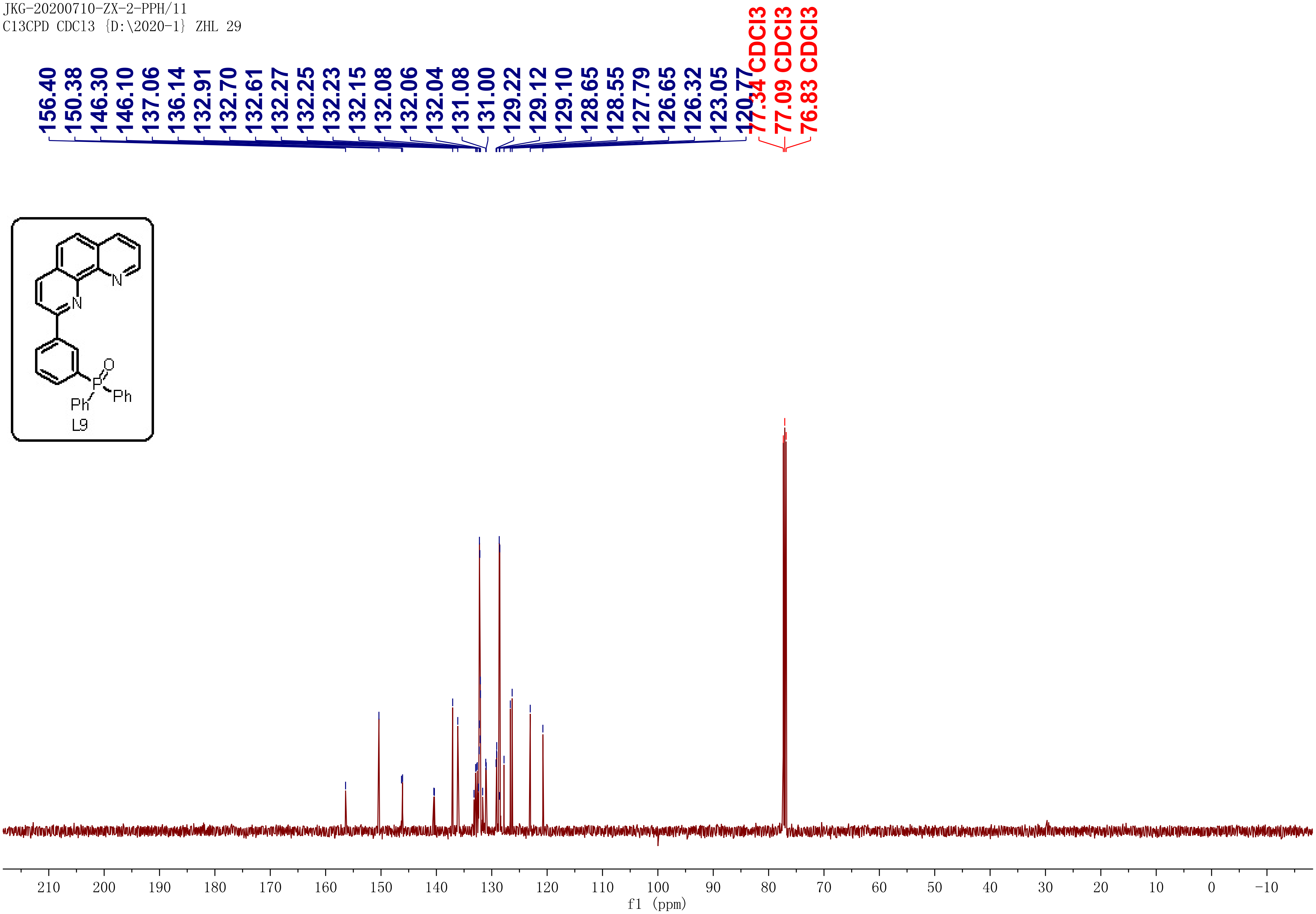
JKG-20180929-ZX-25-02/11
C13CPD CDCl3 {D:\2018-3} ZHL 47



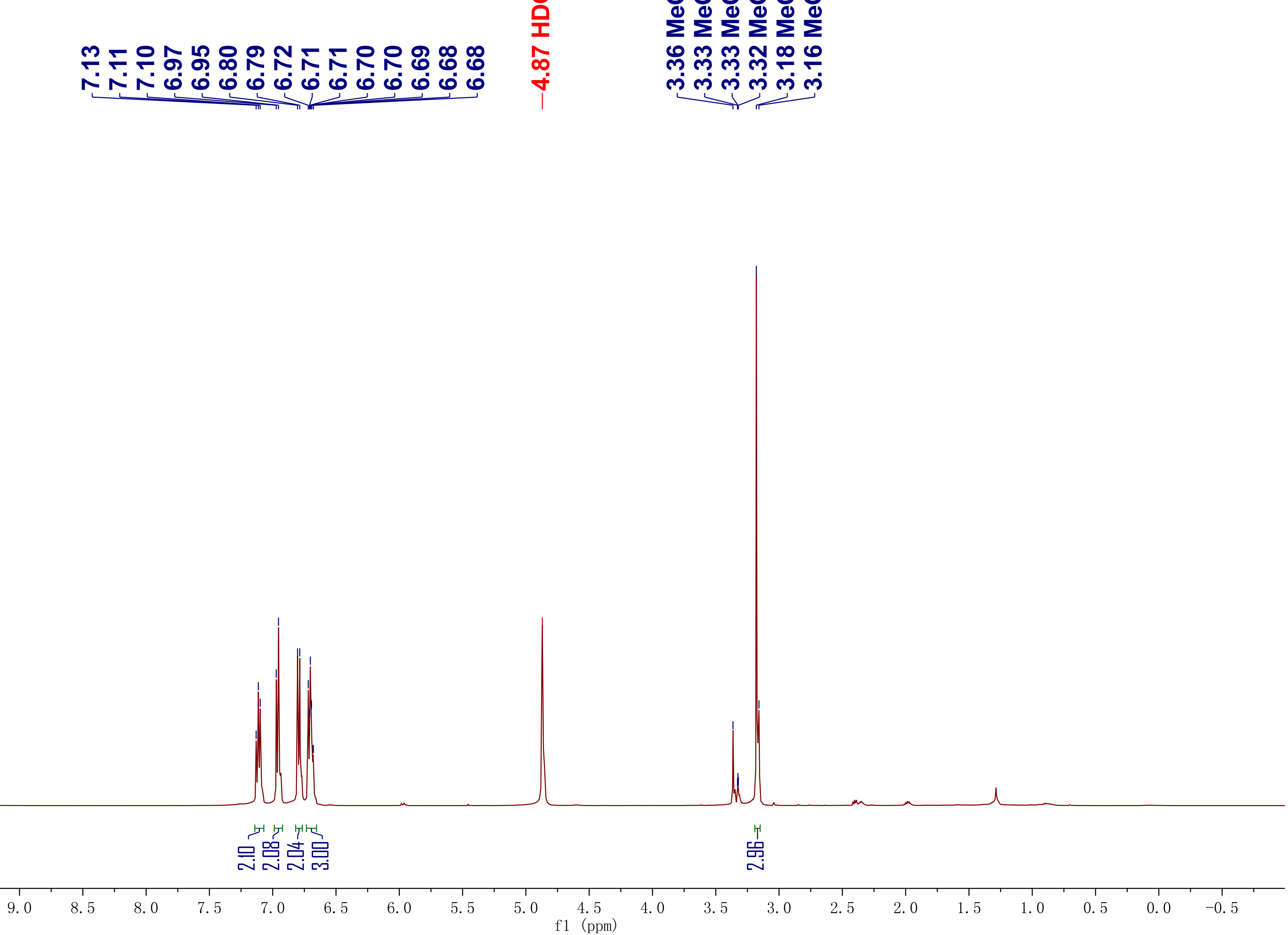
JKG-20200710-ZX-2-PPH/10
PROTON CDCl3 {D:\2020-1} ZHL 29

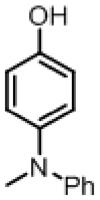


JKG-20200710-ZX-2-PPH/11
C13CPD CDCl3 {D:\2020-1} ZHL 29



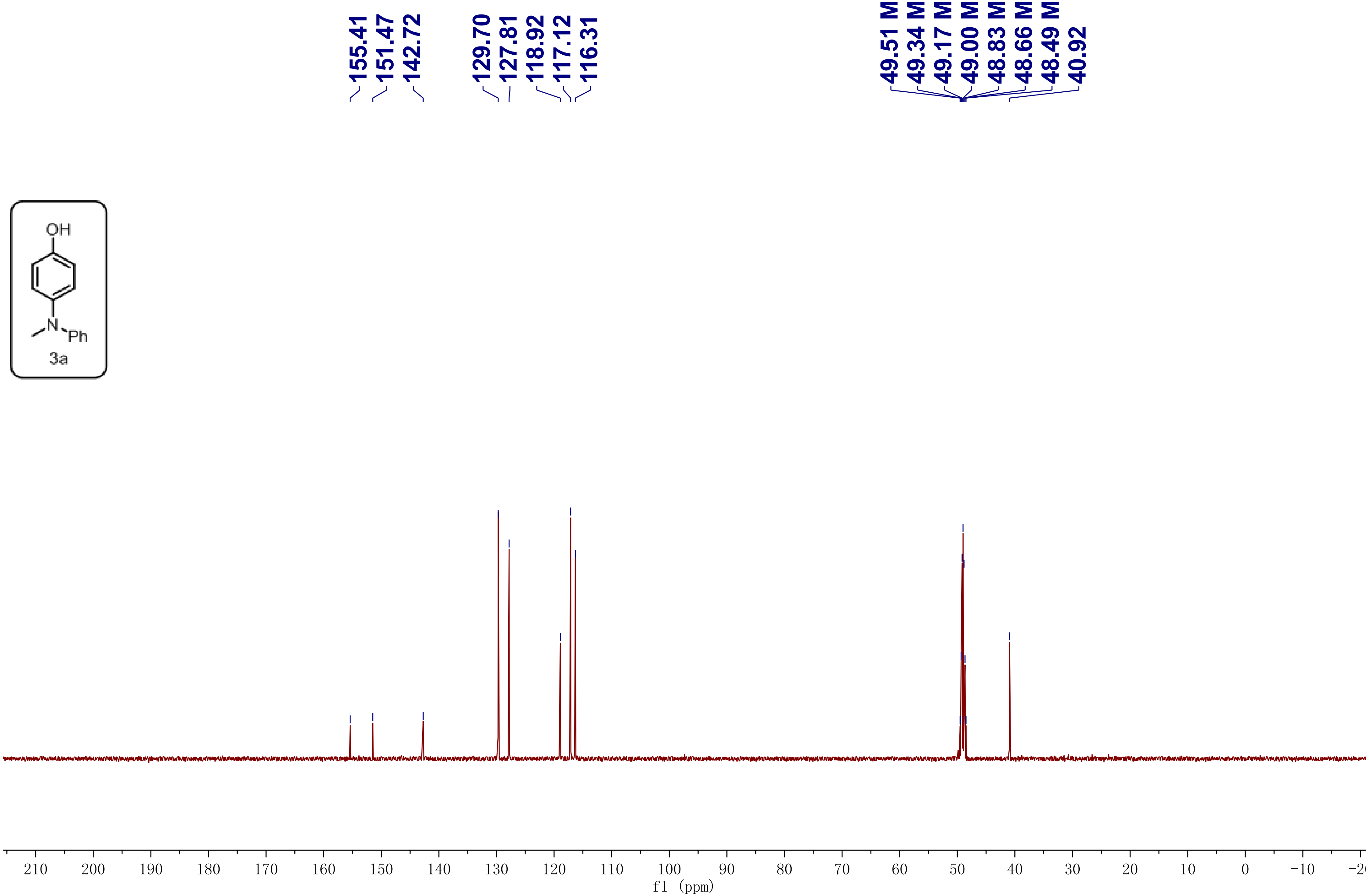
JKG-20191007-ZX-63-02/10
PROTON CDCl3 {D:\2019-3} ZHL 39

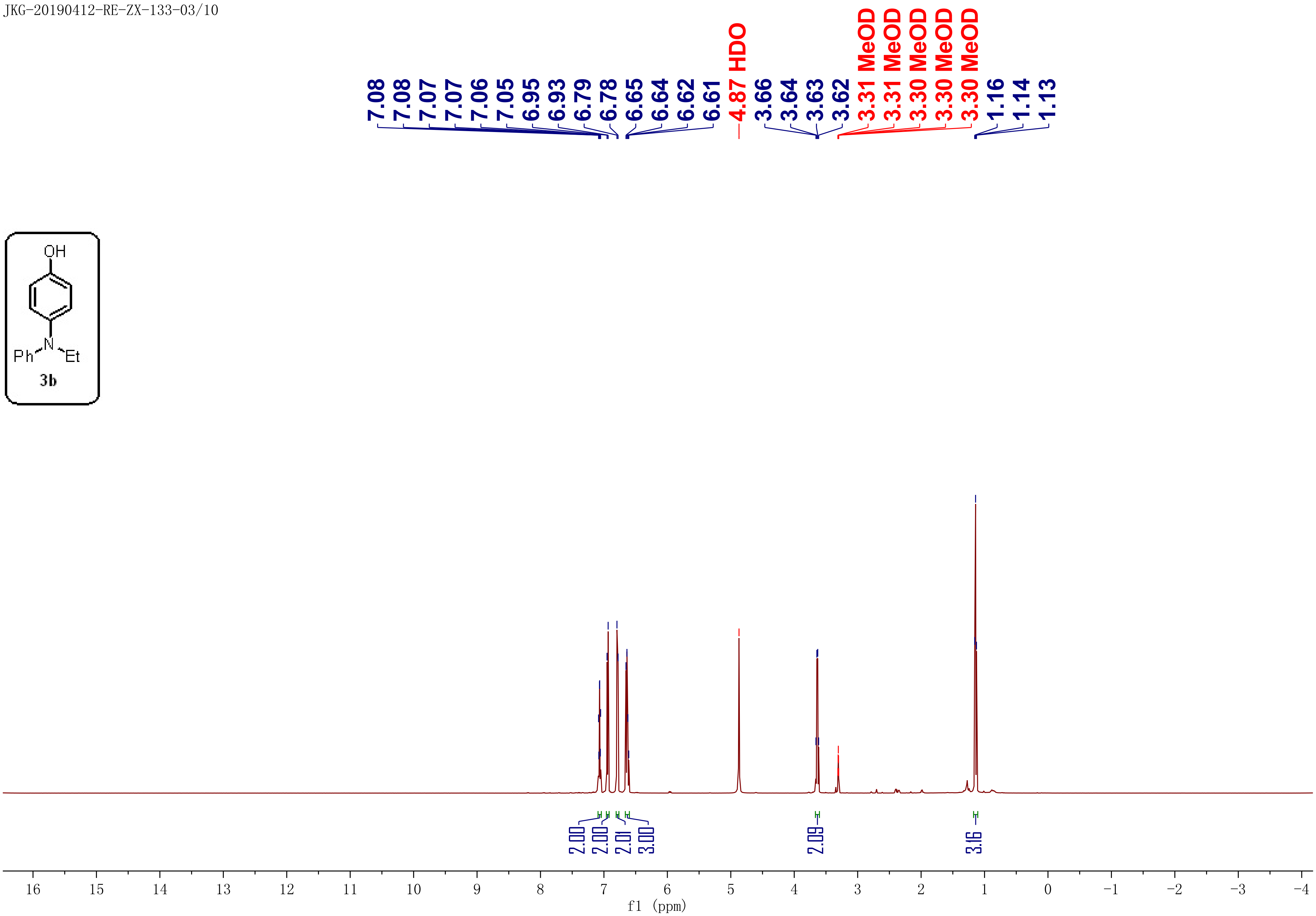


3a

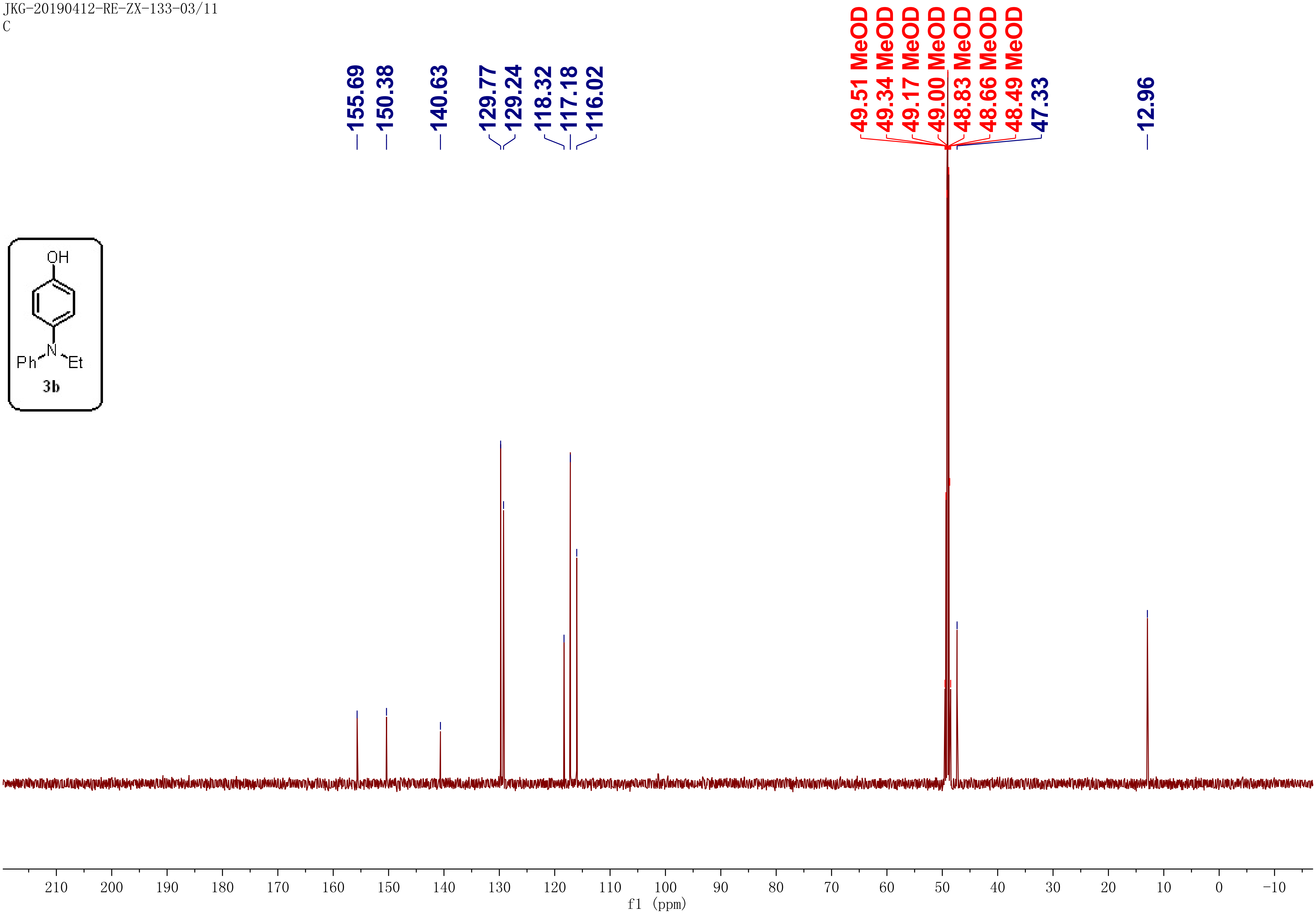
C13CPD CDCl3 {D:\2019-3} ZHL 39

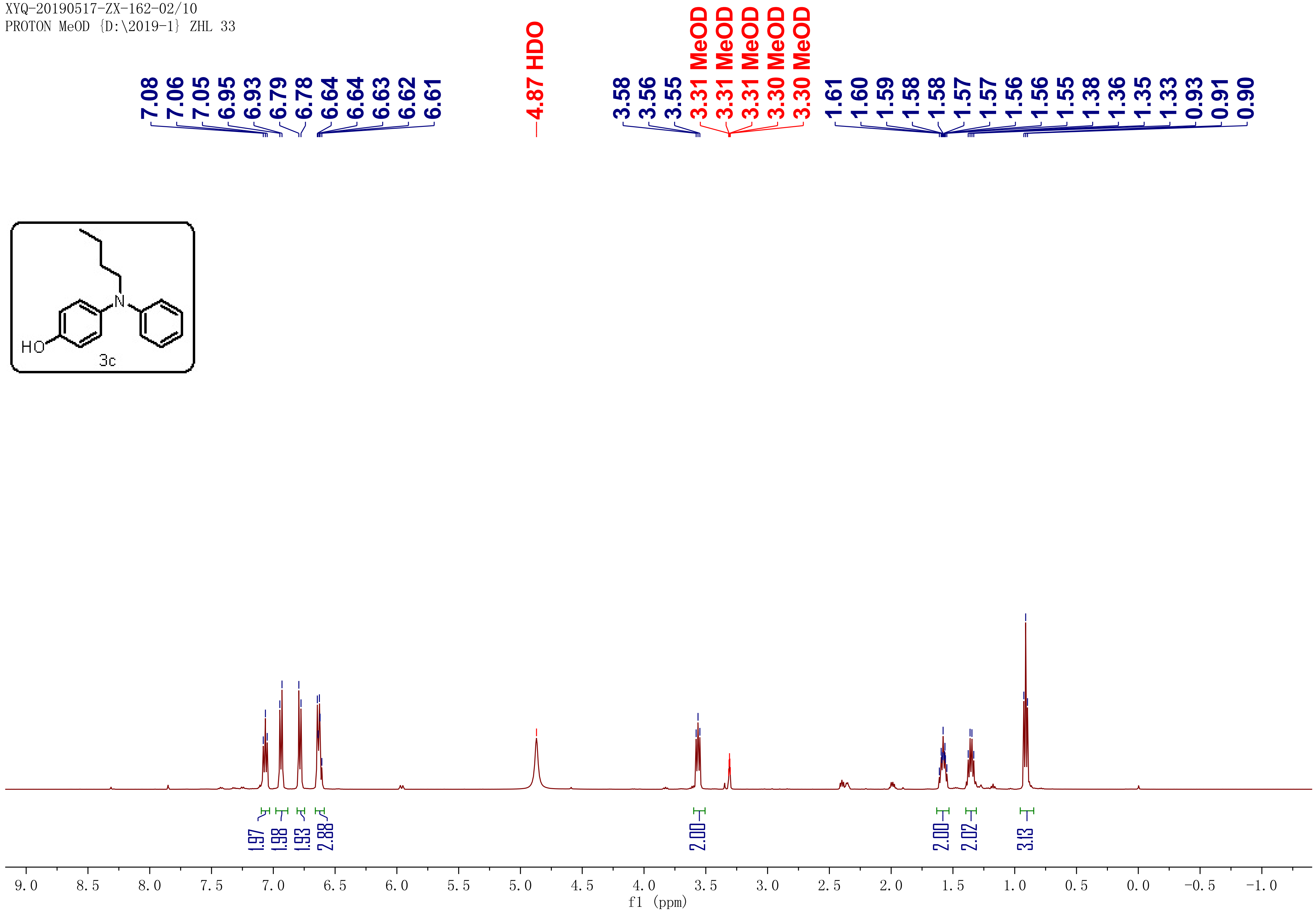




JKG-20190412-RE-ZX-133-03/10
7.08
7.08
7.07
7.07
7.06
7.05
6.95
6.93
6.79
6.78
6.65
6.64
6.62
6.61
4.87 HDO
3.66
3.64
3.63
3.62
3.31 MeOD
3.31 MeOD
3.30 MeOD
3.30 MeOD
3.30 MeOD
1.16
1.14
1.13
OH
N
Ph
Et
3b
2.00
2.00
2.01
3.00
2.09
3.16
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

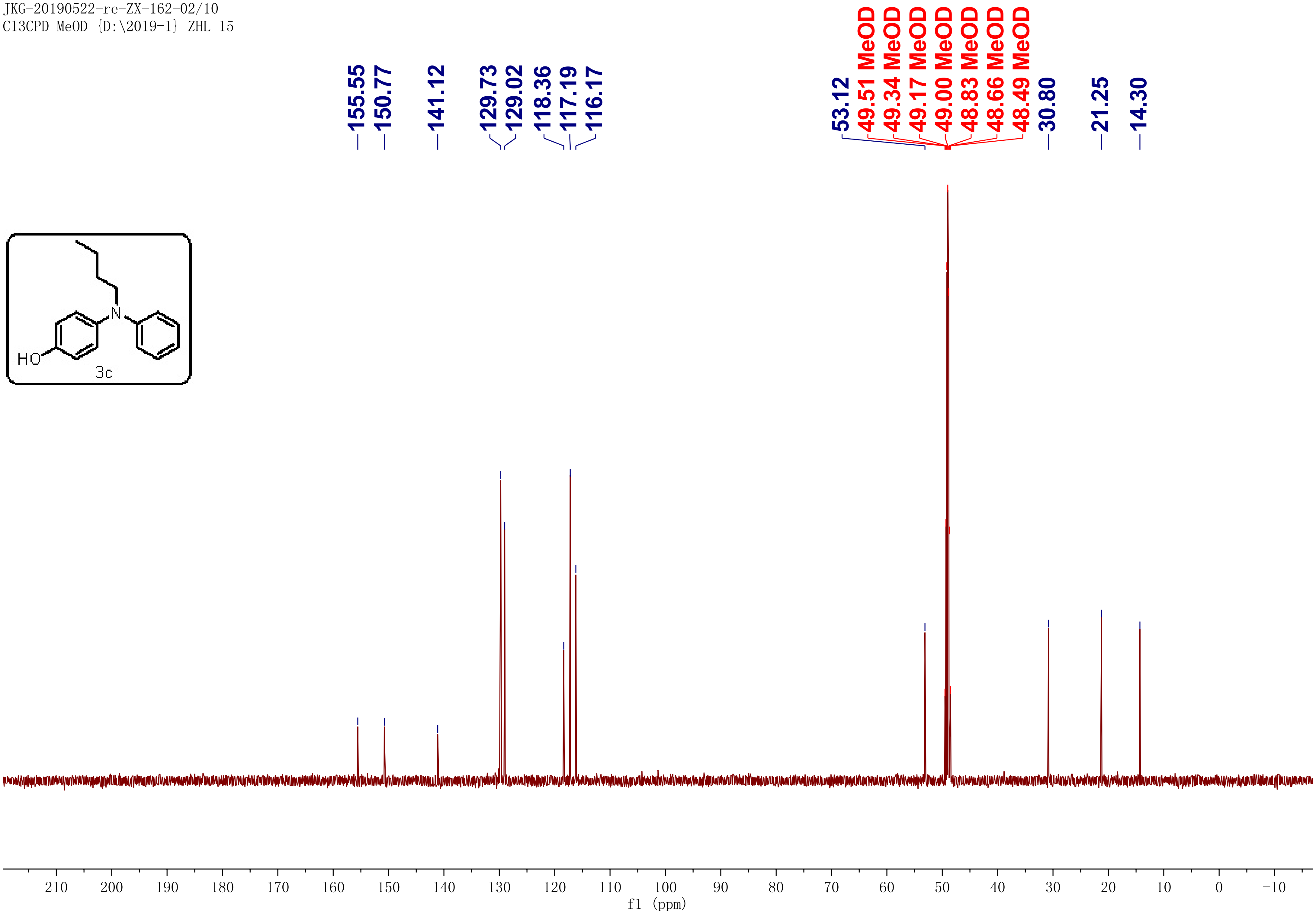
JKG-20190412-RE-ZX-133-03/11
C



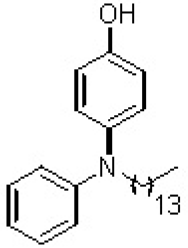


XYQ-20190517-ZX-162-02/10
PROTON MeOD {D:\2019-1} ZHL 33
7.08 7.06 7.05 6.95 6.93 6.79 6.78 6.64 6.64 6.63 6.62 6.61
4.87 HDO
3.58 3.56 3.55
3.31 MeOD 3.31 MeOD 3.31 MeOD 3.30 MeOD 3.30 MeOD
1.61 1.60 1.59 1.58 1.58 1.57 1.57 1.56 1.56 1.55 1.38 1.36 1.35 1.33 0.93 0.91 0.90
HO
N
3c
1.97 1.98 1.93 2.88 2.00 2.00 2.02 3.13
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)

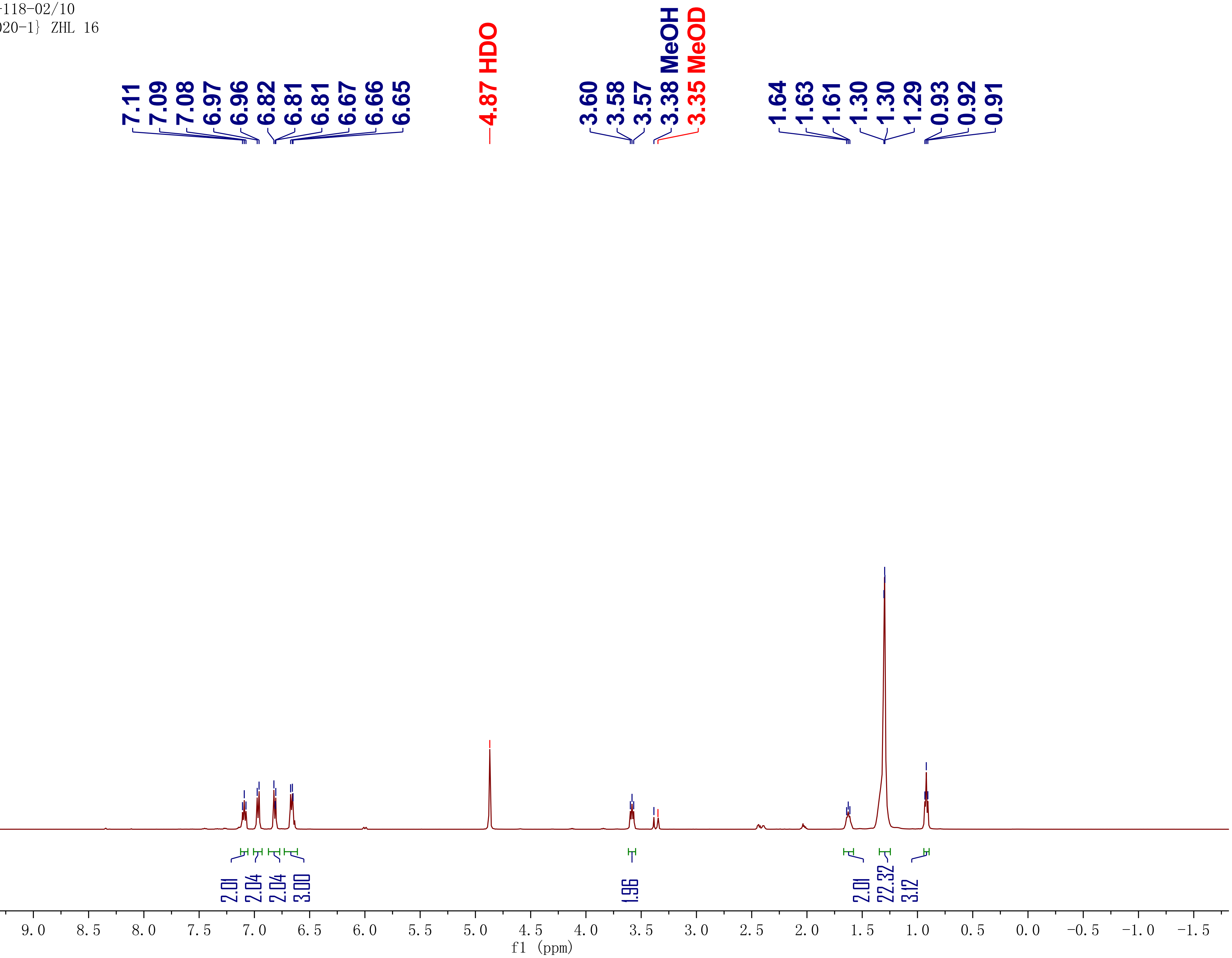
JKG-20190522-re-ZX-162-02/10
C13CPD MeOD {D:\2019-1} ZHL 15



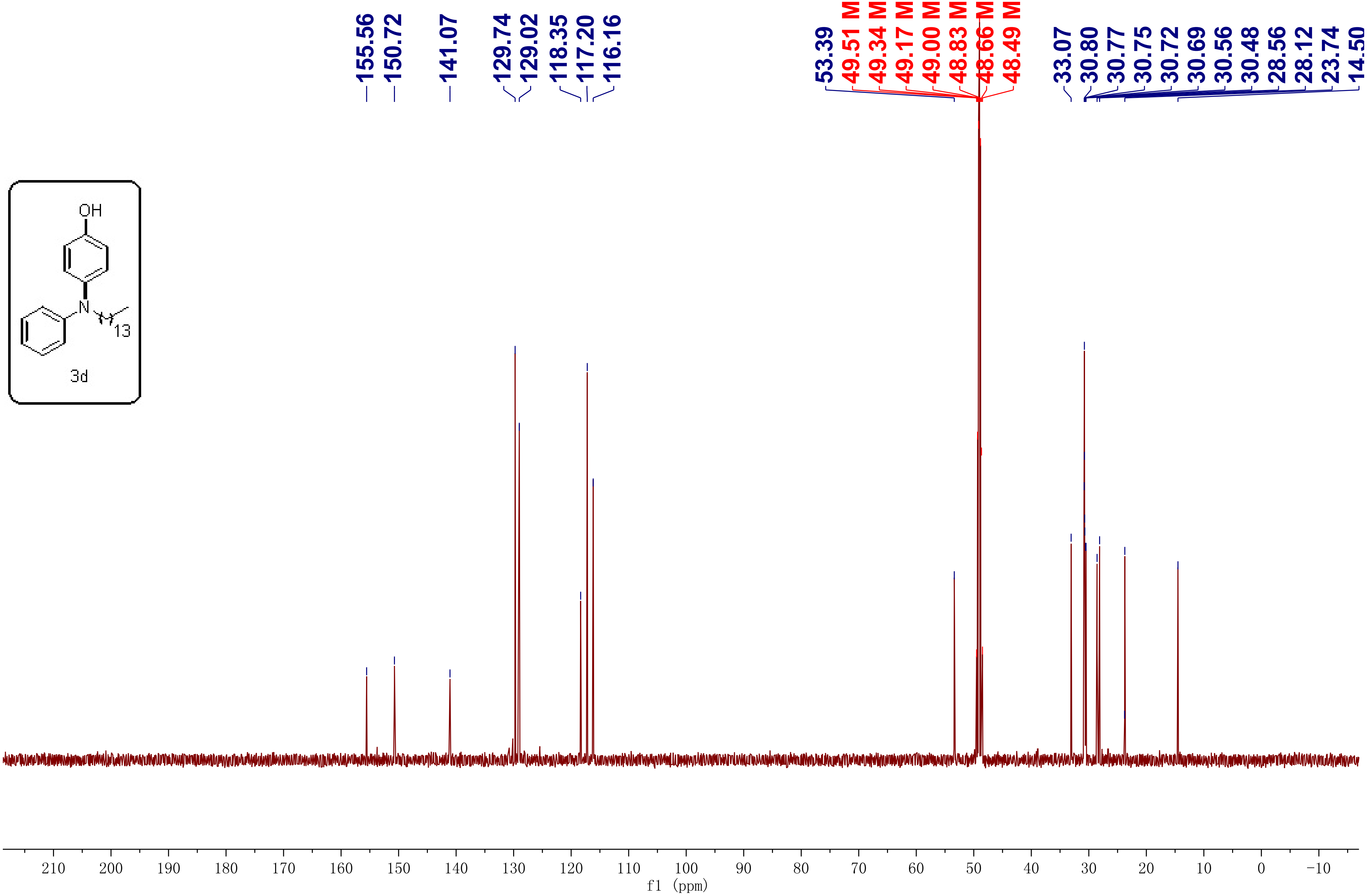
JKG-20200506-ZX-2-118-02/10
PROTON MeOD {D:\2020-1} ZHL 16

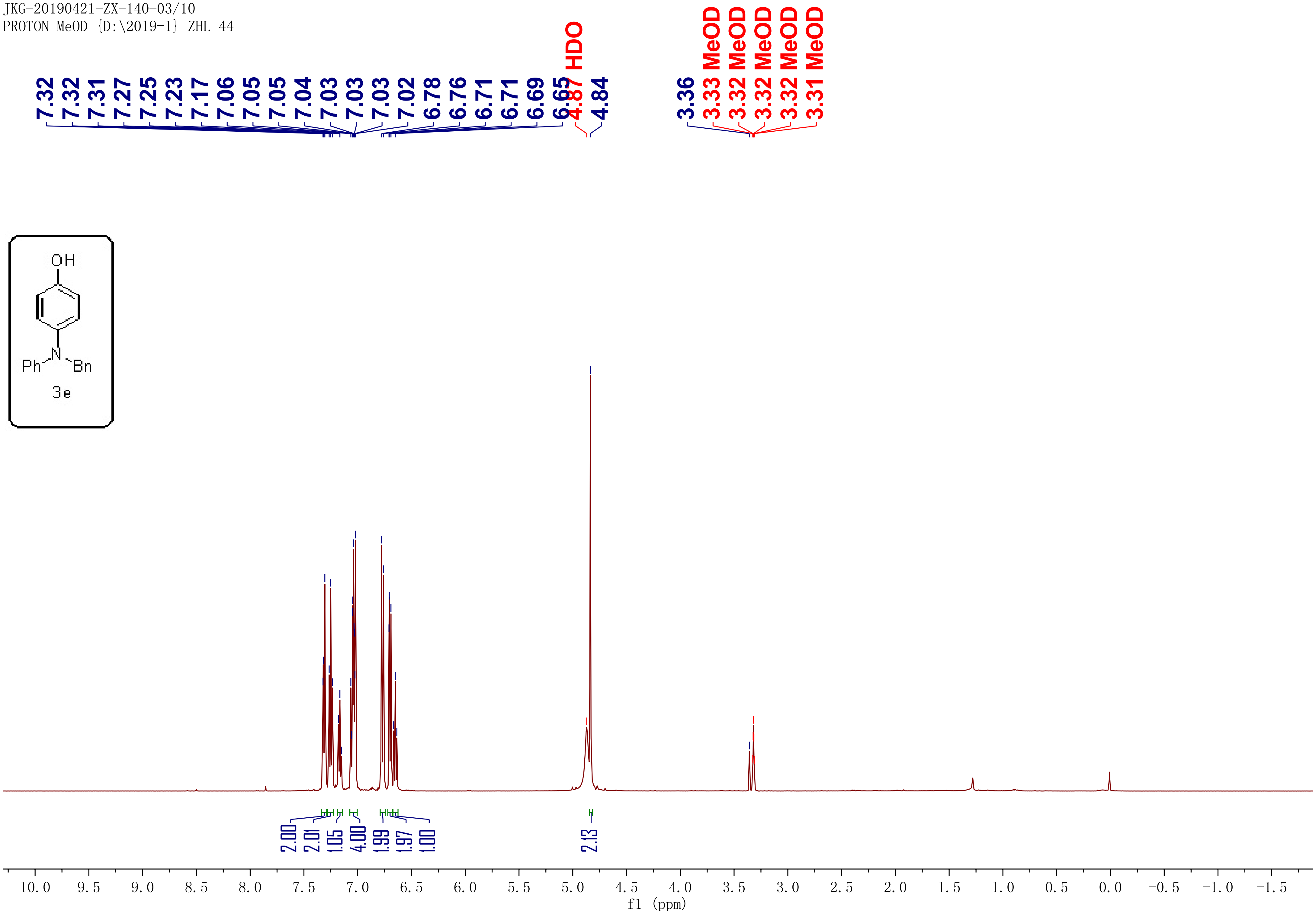



3d



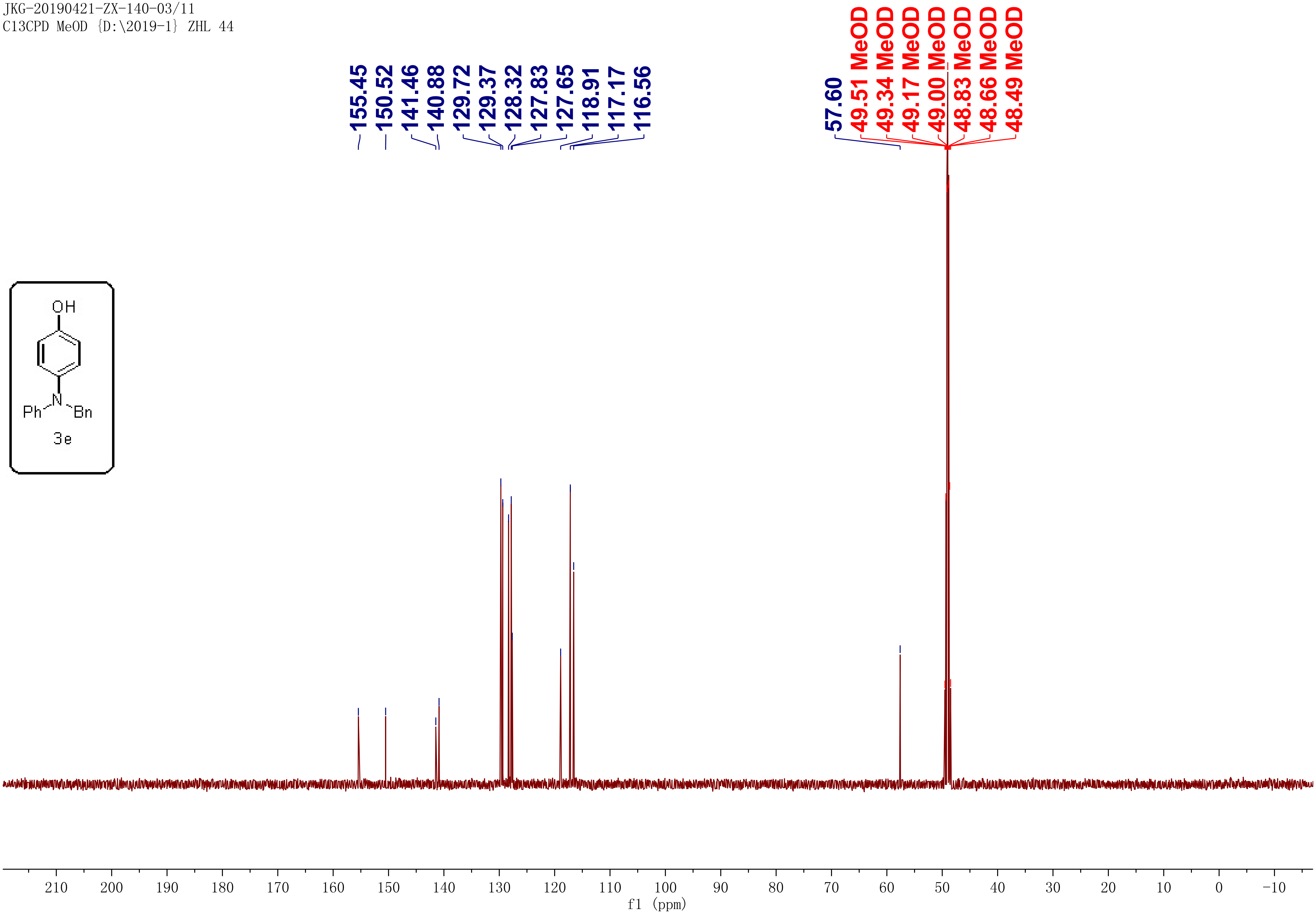
JKG-20200506-ZX-2-118-02/11
C13CPD MeOD {D:\2020-1} ZHL 16

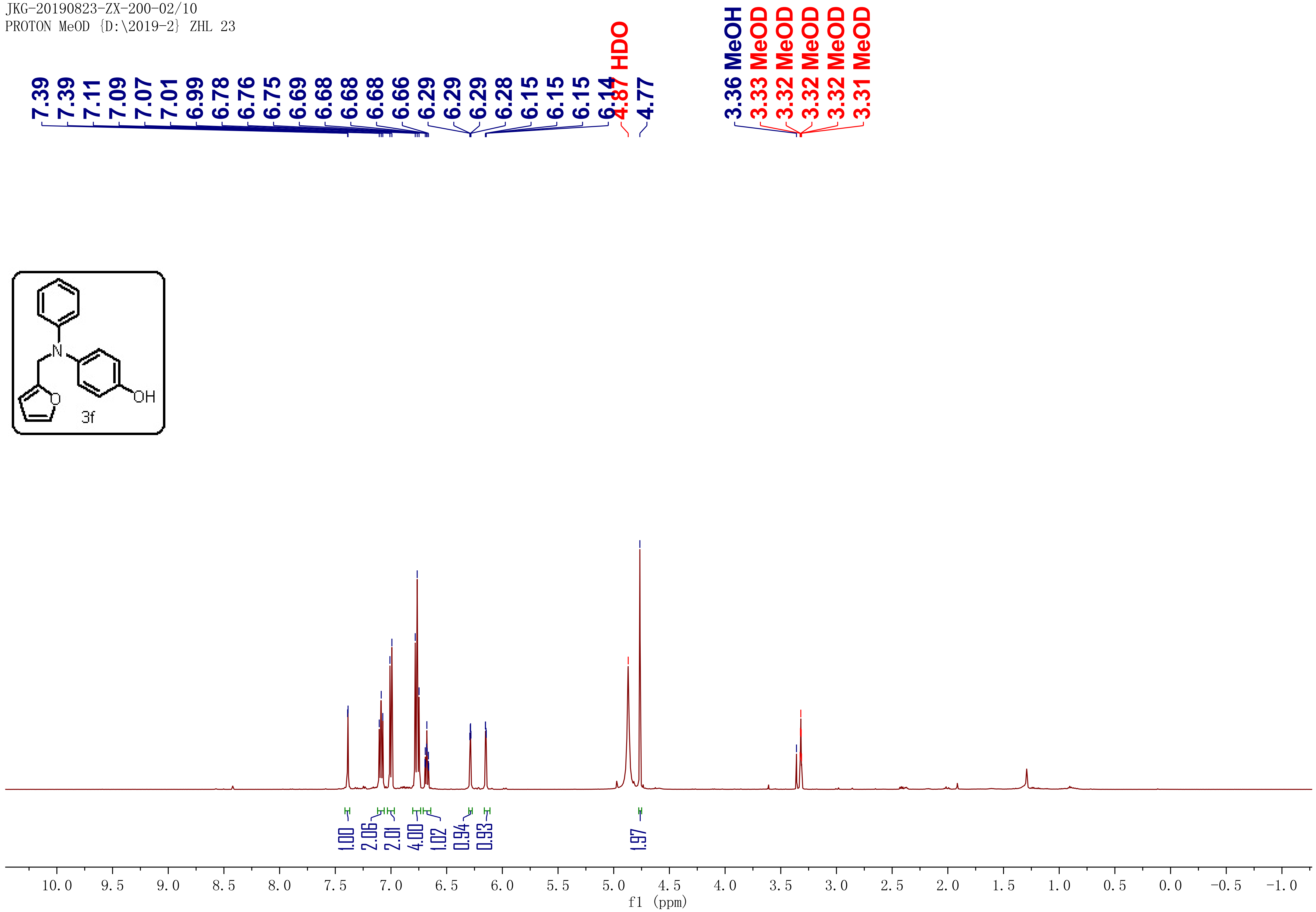




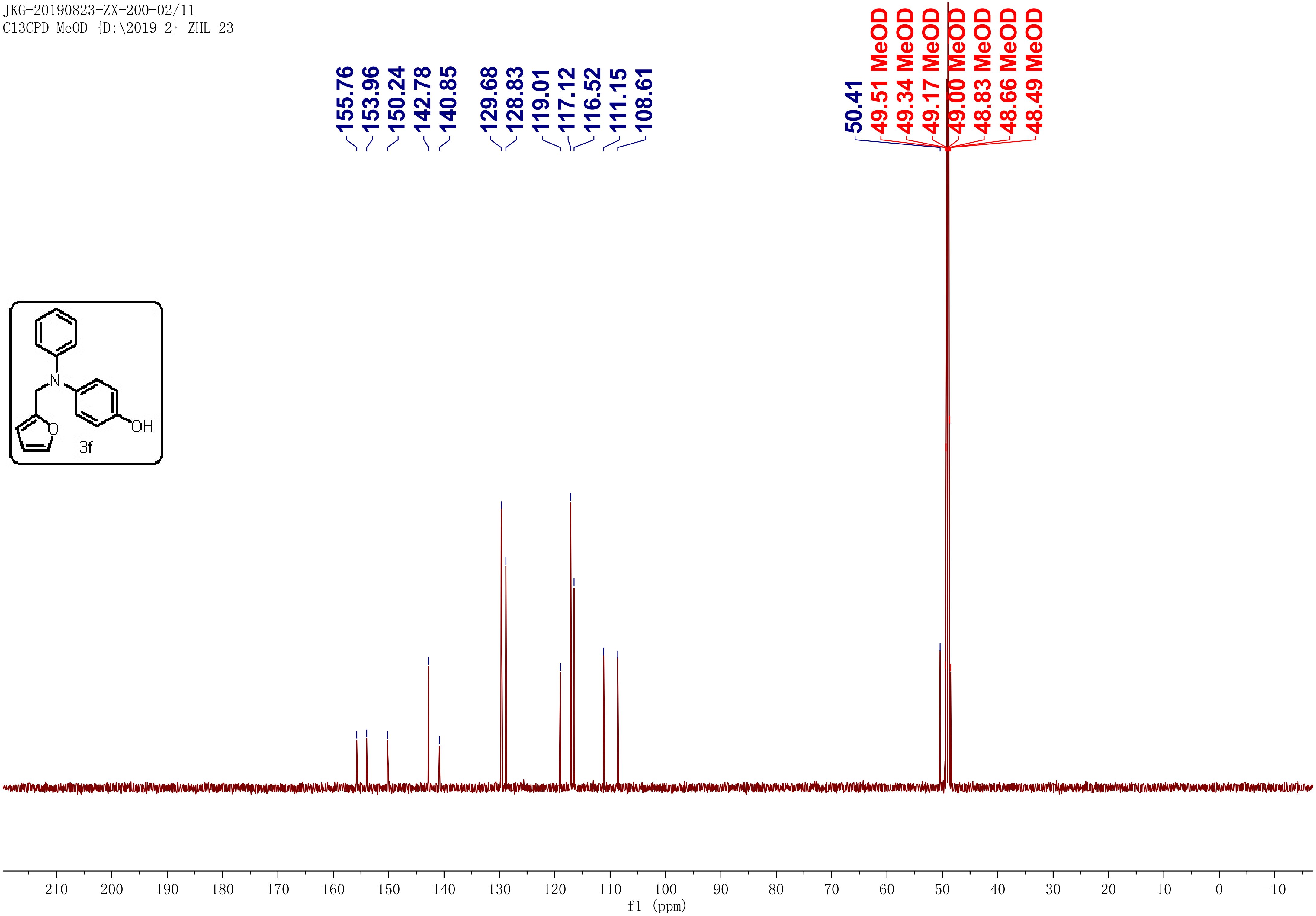
JKG-20190421-ZX-140-03/10
PROTON MeOD {D:\2019-1} ZHL 44
7.32
7.32
7.31
7.27
7.25
7.23
7.17
7.06
7.05
7.05
7.04
7.03
7.03
7.03
7.02
6.78
6.76
6.71
6.71
6.69
6.65
4.87 HDO
4.84
3.36
3.33 MeOD
3.32 MeOD
3.32 MeOD
3.32 MeOD
3.31 MeOD
OH
N
Ph
Bn
3e
2.00
2.01
1.05
4.00
1.99
1.97
1.00
2.13
10.0
9.5
9.0
8.5
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
-1.5
f1 (ppm)

JKG-20190421-ZX-140-03/11
C13CPD MeOD {D:\2019-1} ZHL 44

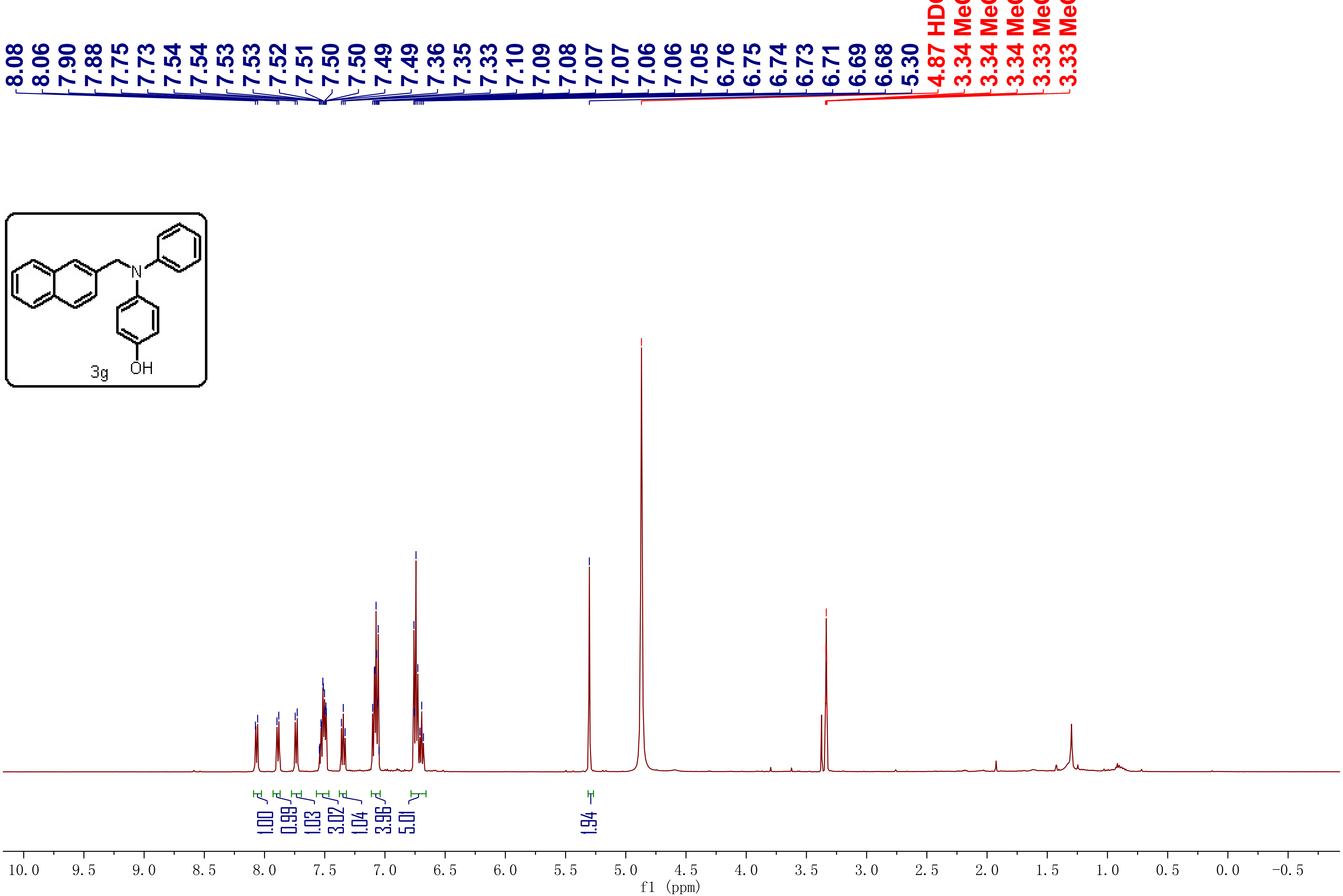



JKG-20190823-ZX-200-02/10
PROTON MeOD {D:\2019-2} ZHL 23
7.39 7.39 7.11 7.09 7.07 7.01 6.99 6.78 6.76 6.75 6.69 6.68 6.68 6.68 6.66 6.29 6.29 6.29 6.28 6.15 6.15 6.15 6.14
4.87 HDO
4.77
3.36 MeOH
3.33 MeOD
3.32 MeOD
3.32 MeOD
3.32 MeOD
3.31 MeOD
N
O
OH
3f
1.00 2.06 2.01 4.00 1.02 0.94 0.93
1.97
10.0 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)

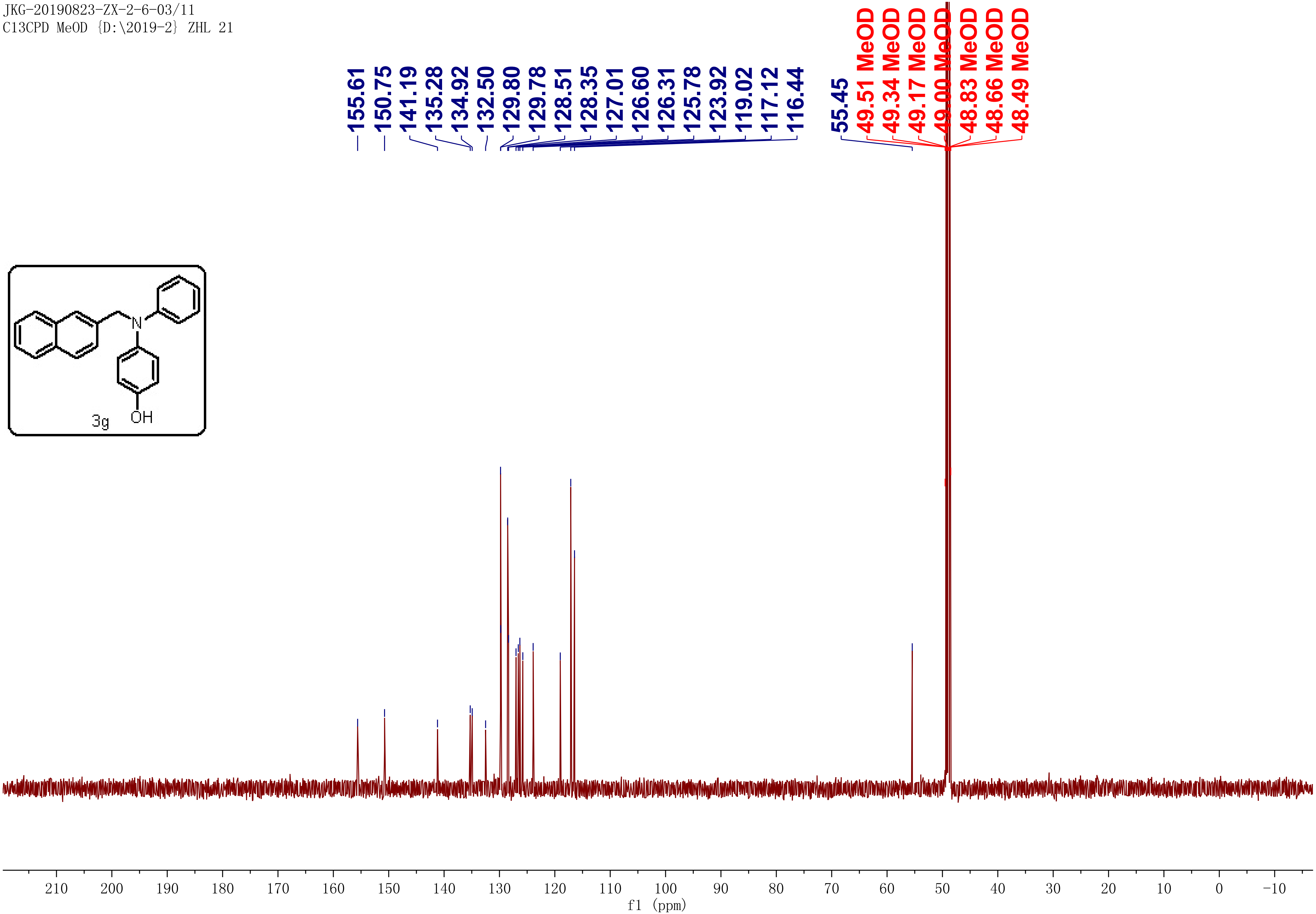
JKG-20190823-ZX-200-02/11
C13CPD MeOD {D:\2019-2} ZHL 23

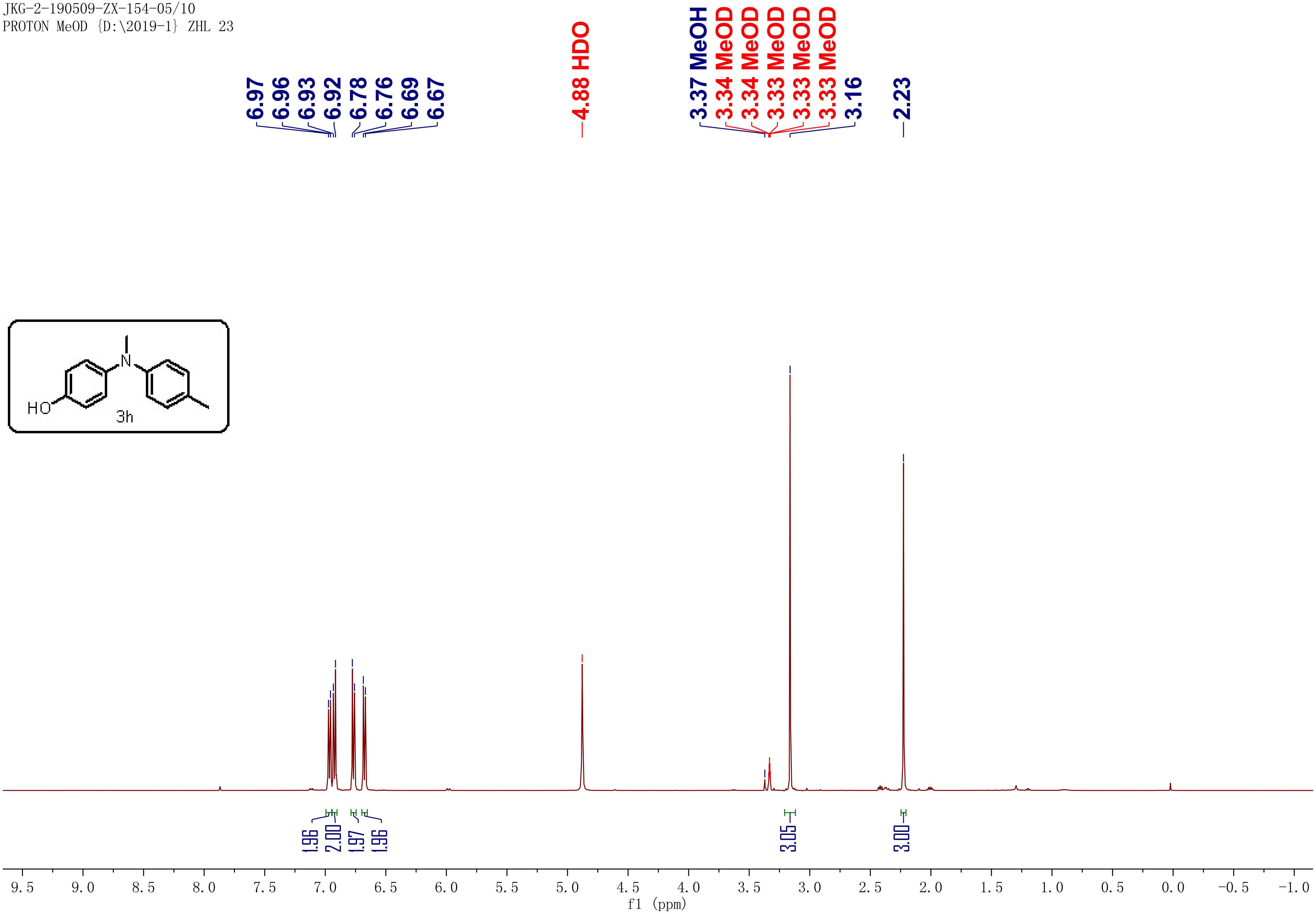


JKG-20190823-ZX-2-6-03/10
PROTON MeOD {D:\2019-2} ZHL 21

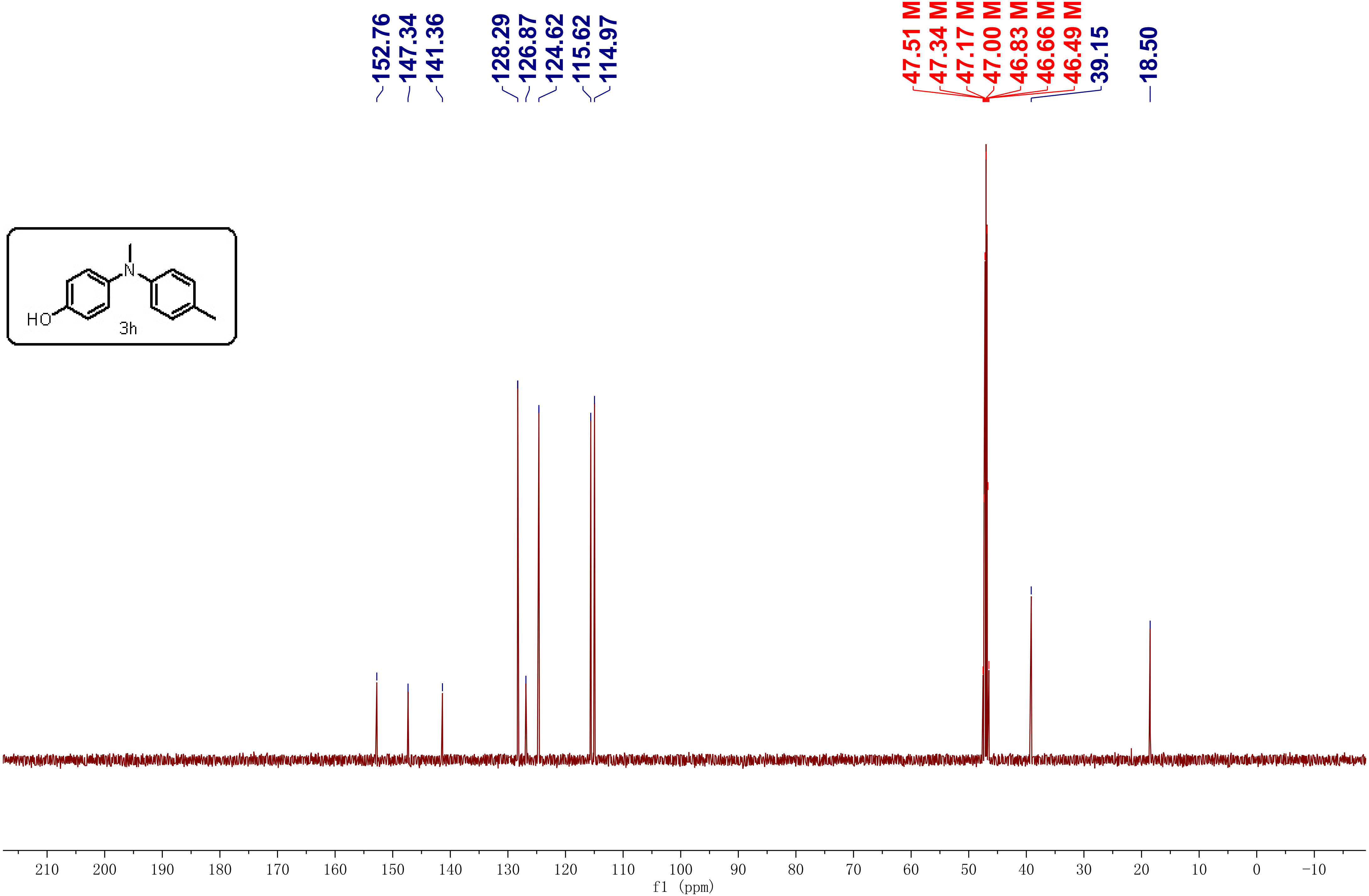


JKG-20190823-ZX-2-6-03/11
C13CPD MeOD {D:\2019-2} ZHL 21

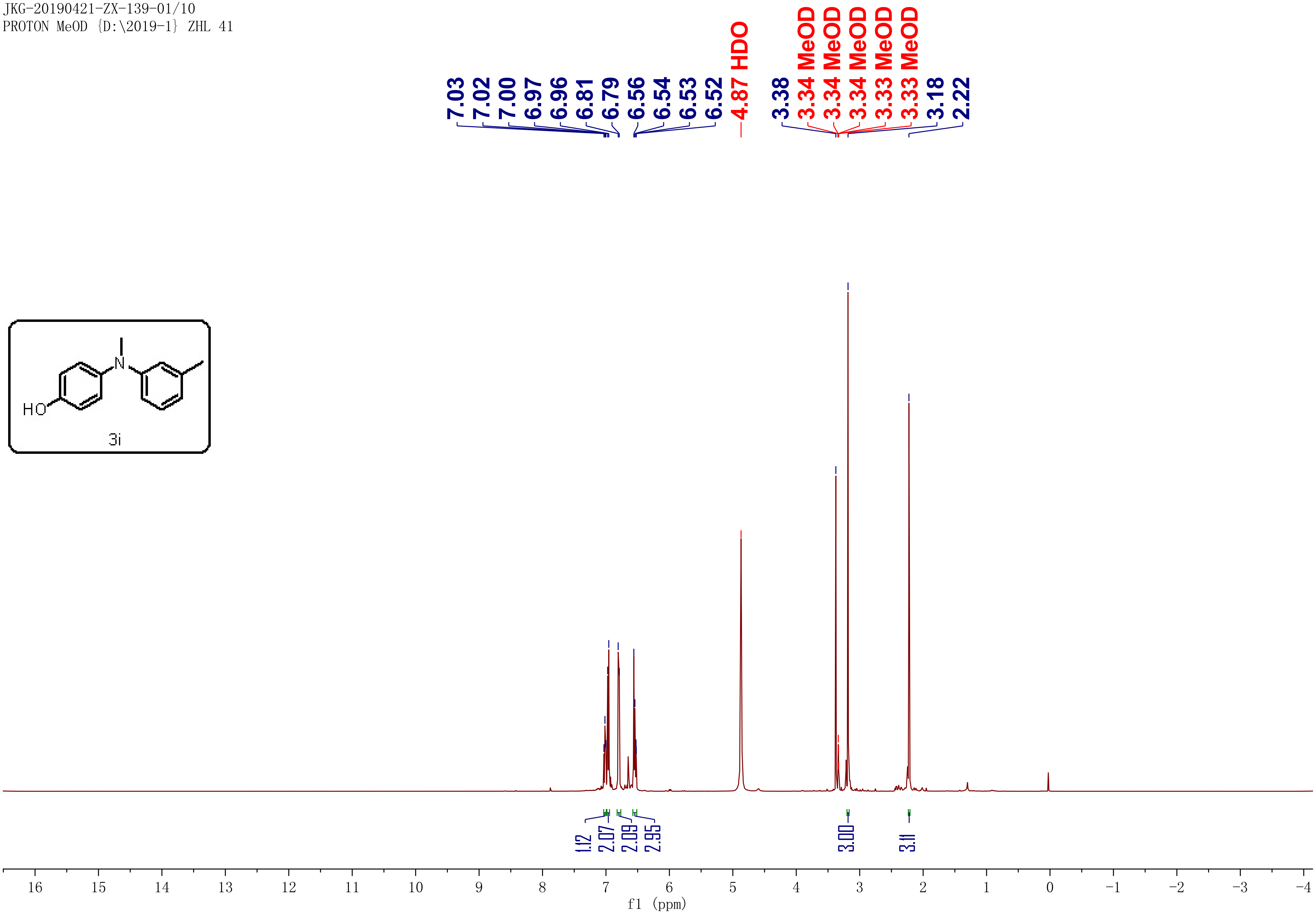


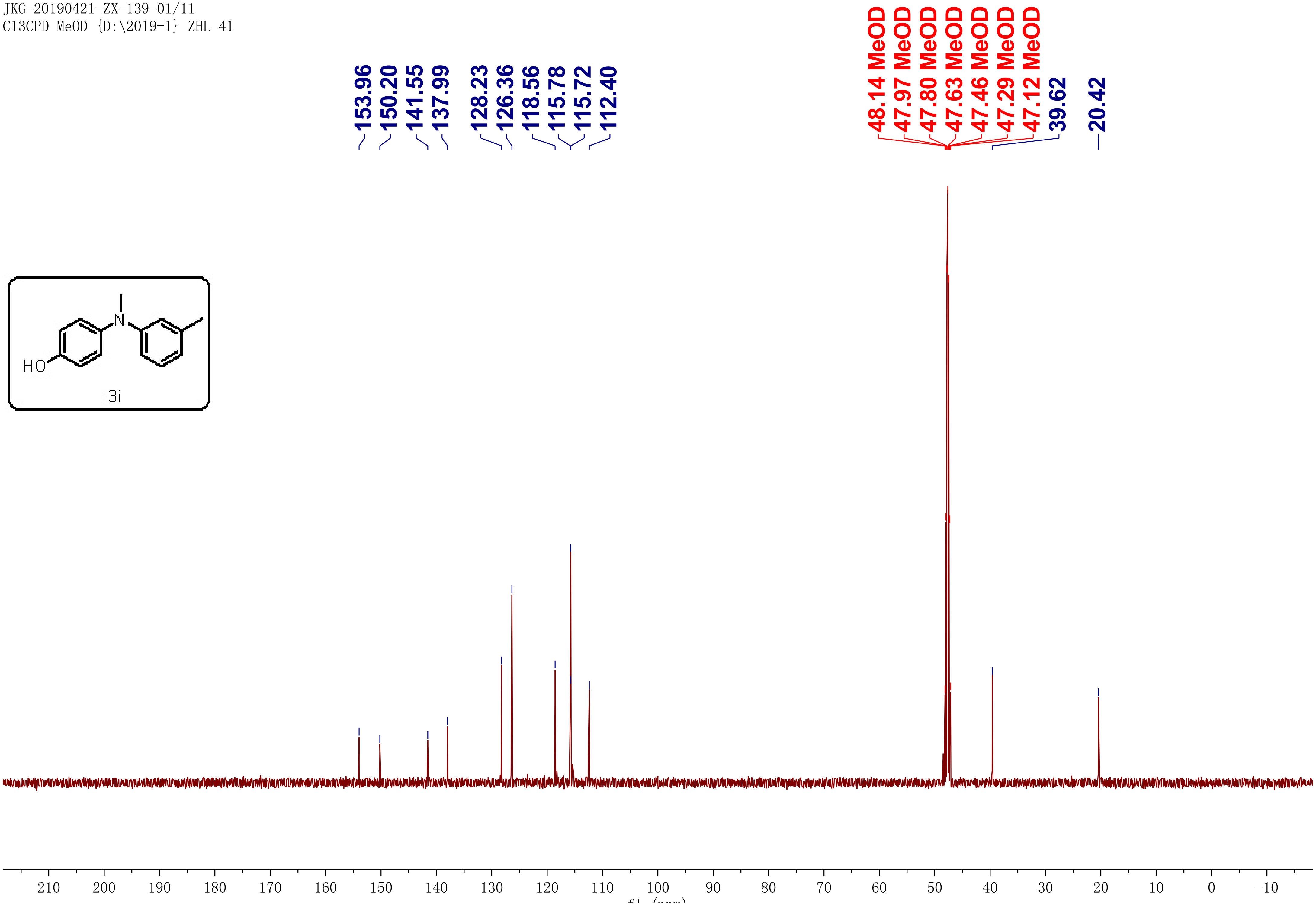

JKG-2-190509-ZX-154-05/10
PROTON MeOD {D:\2019-1} ZHL 23
6.97
6.96
6.93
6.92
6.78
6.76
6.69
6.67
4.88 HDO
3.37 MeOH
3.34 MeOD
3.34 MeOD
3.33 MeOD
3.33 MeOD
3.33 MeOD
3.16
2.23
N
HO
3h
1.96
2.00
1.97
1.96
3.05
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

JKG-2-190509-ZX-154-05/11
C13CPD MeOD {D:\2019-1} ZHL 23

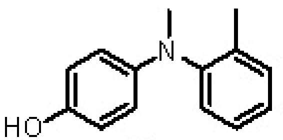


JKG-20190421-ZX-139-01/10
PROTON MeOD {D:\2019-1} ZHL 41

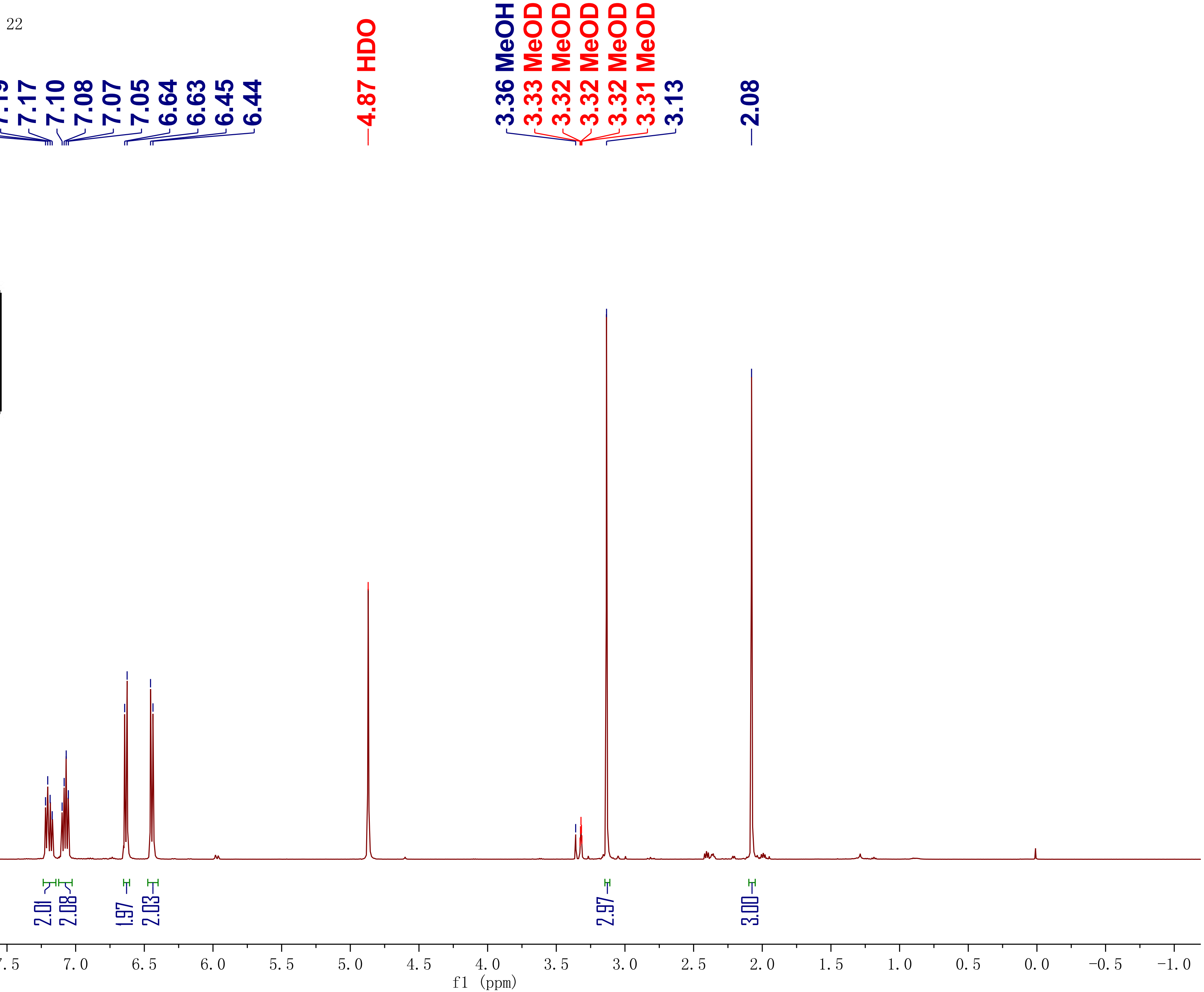



JKG-20190421-ZX-139-01/11
C13CPD MeOD {D:\2019-1} ZHL 41
153.96
150.20
141.55
137.99
128.23
126.36
118.56
115.78
115.72
112.40
48.14 MeOD
47.97 MeOD
47.80 MeOD
47.63 MeOD
47.46 MeOD
47.29 MeOD
47.12 MeOD
39.62
20.42
HO
N
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

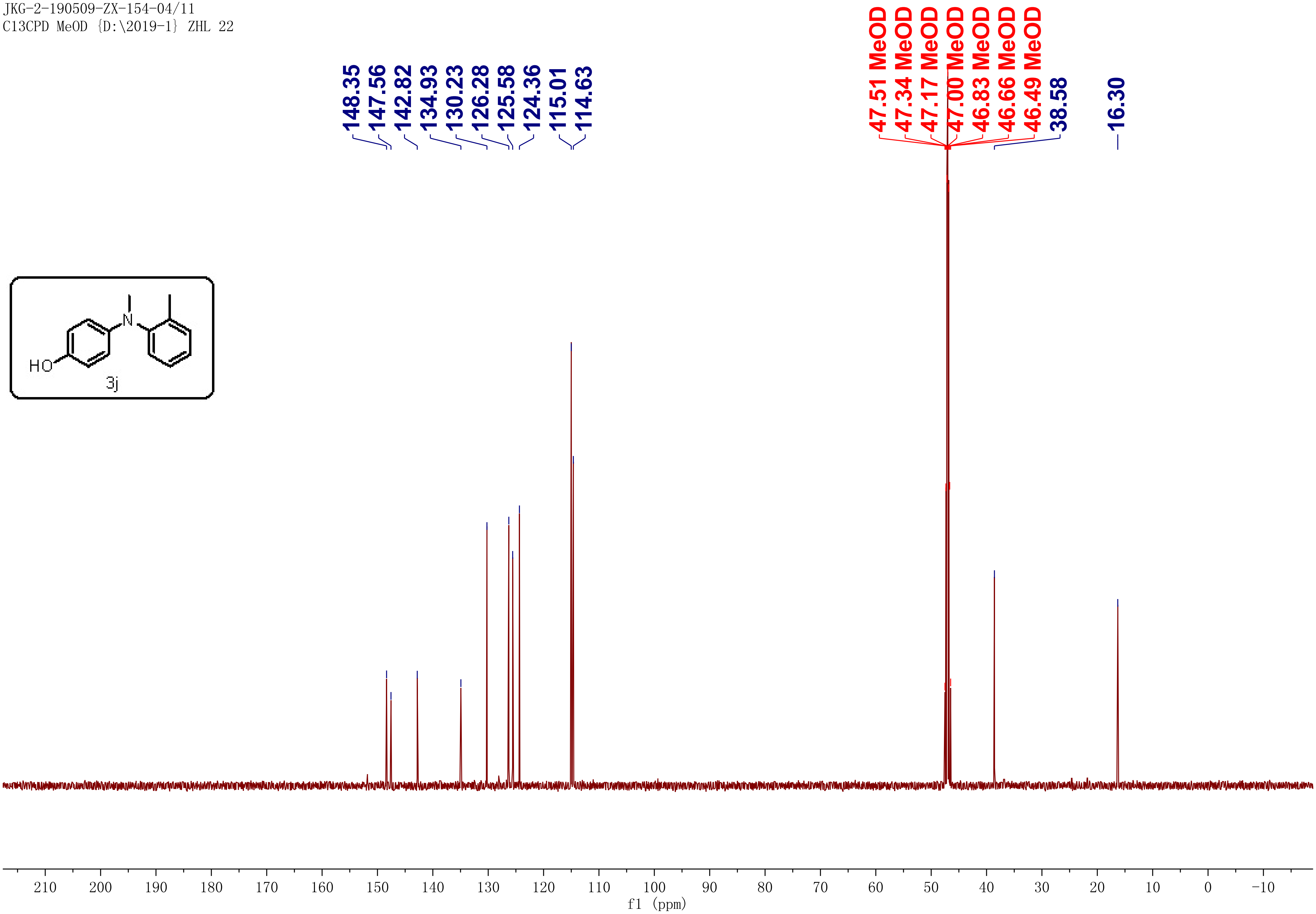
JKG-2-190509-ZX-154-04/10
PROTON MeOD {D:\2019-1} ZHL 22

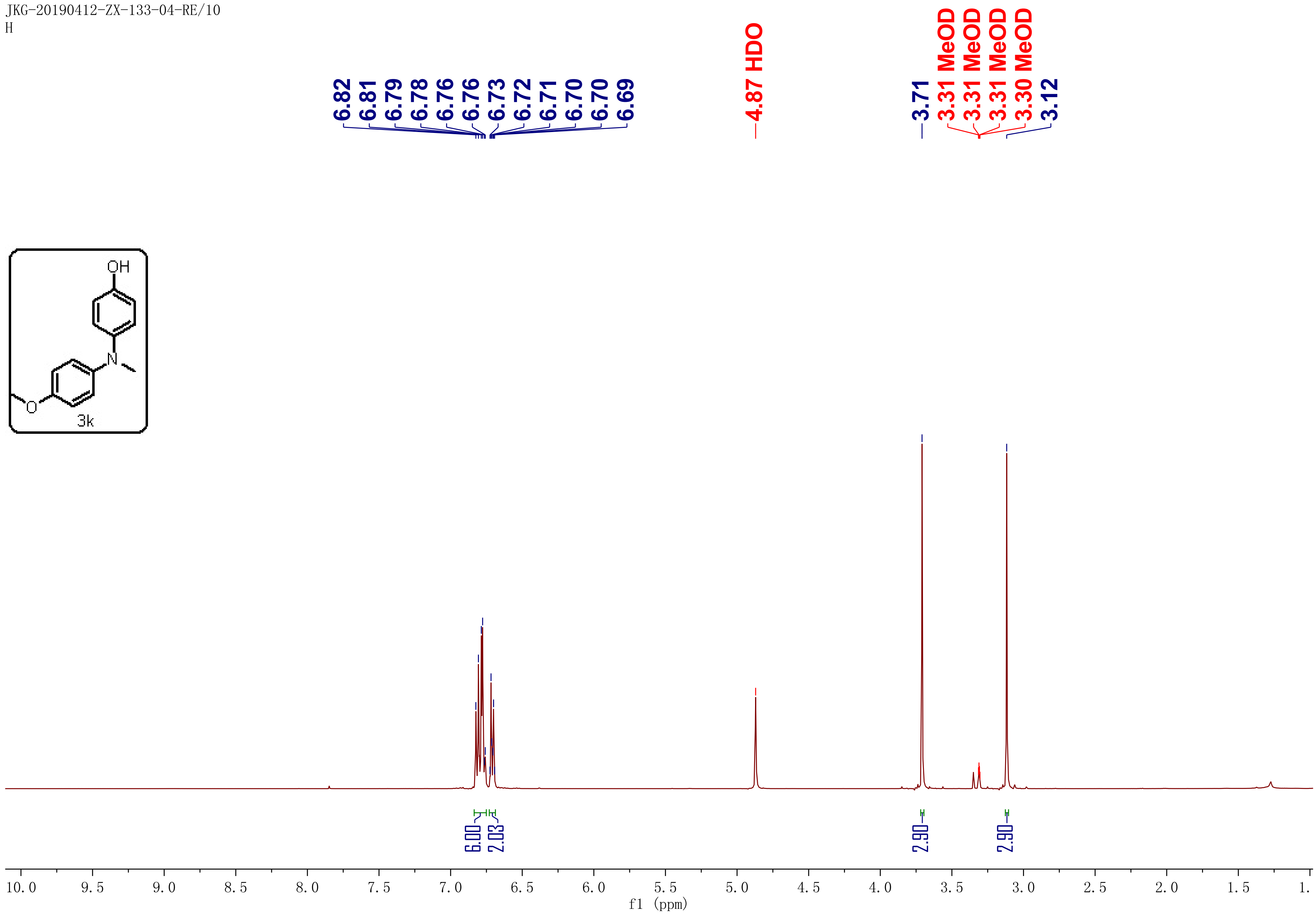


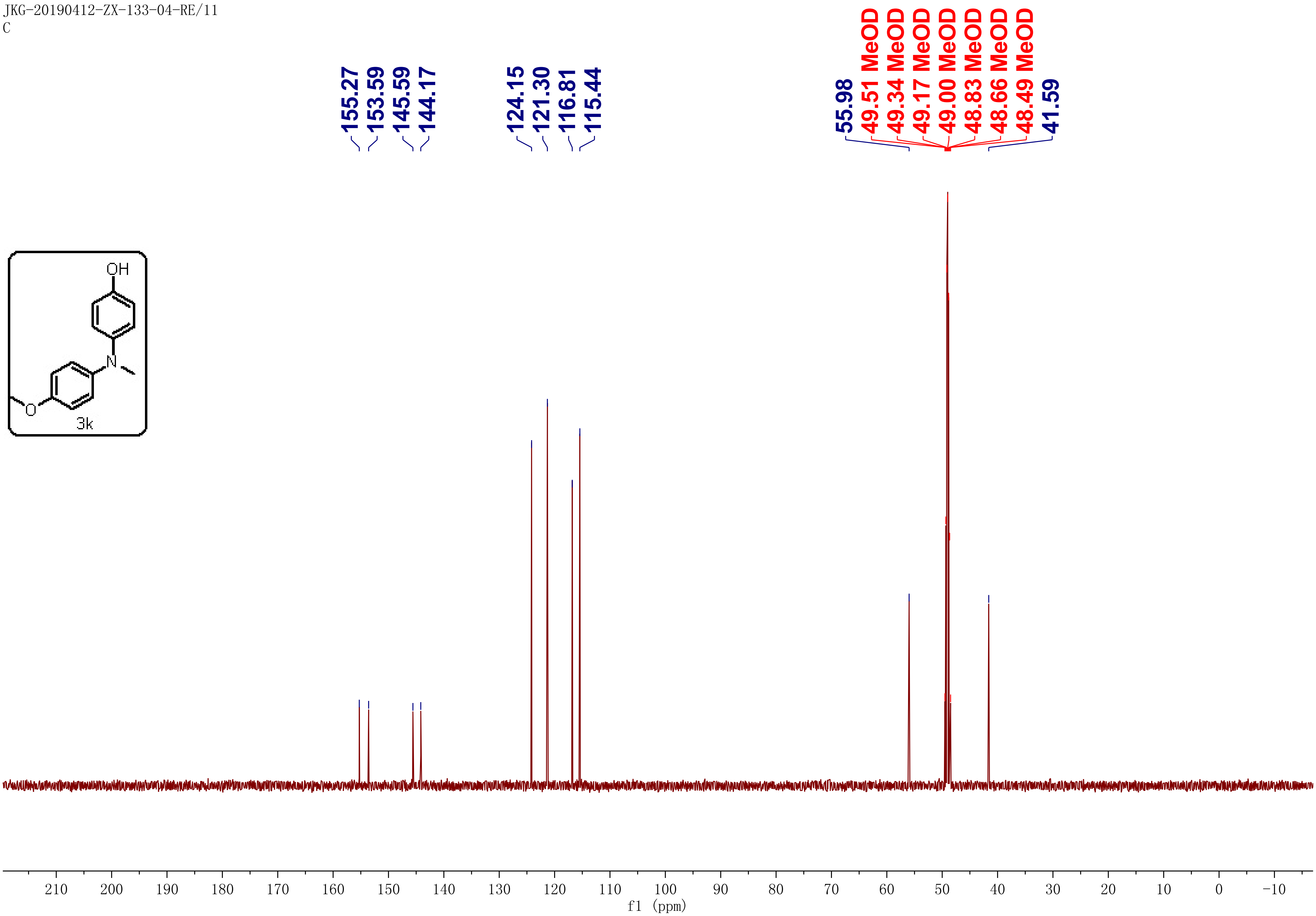
3j



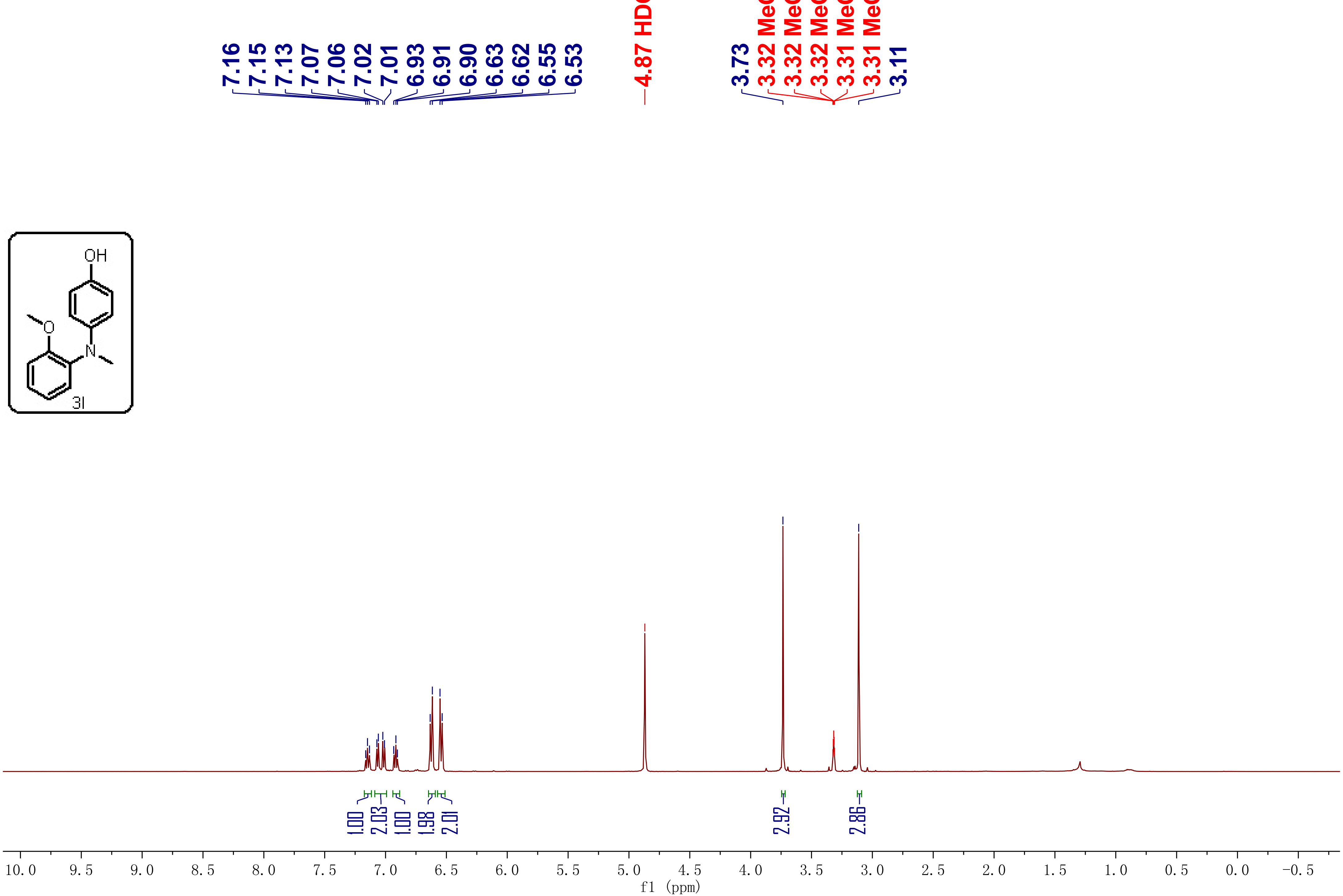
JKG-2-190509-ZX-154-04/11
C13CPD MeOD {D:\2019-1} ZHL 22

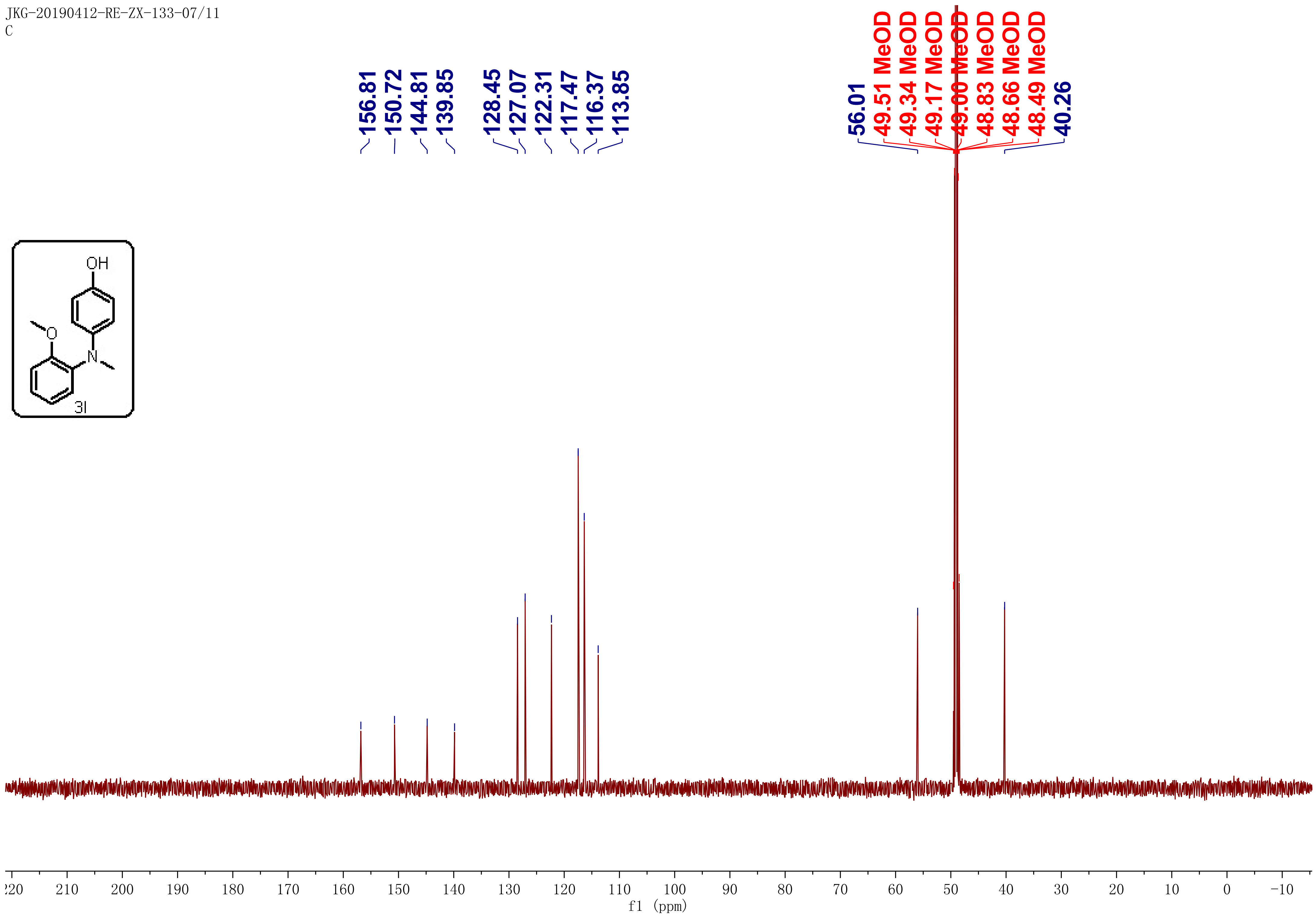



JKG-20190412-ZX-133-04-RE/10
H
6.82 6.81 6.79 6.78 6.76 6.76 6.73 6.72 6.71 6.70 6.70 6.69
4.87 HDO
3.71
3.31 MeOD 3.31 MeOD 3.31 MeOD 3.30 MeOD
3.12
OH
N
O
3k
6.00 2.03
2.90
2.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.
f1 (ppm)


JKG-20190412-ZX-133-04-RE/11
C
155.27
153.59
145.59
144.17
124.15
121.30
116.81
115.44
55.98
49.51 MeOD
49.34 MeOD
49.17 MeOD
49.00 MeOD
48.83 MeOD
48.66 MeOD
48.49 MeOD
41.59
OH
N
O
3k
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)

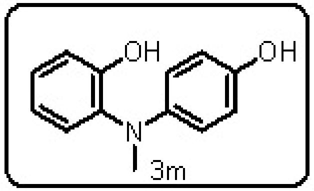
JKG-20190412-RE-ZX-133-07/10
H

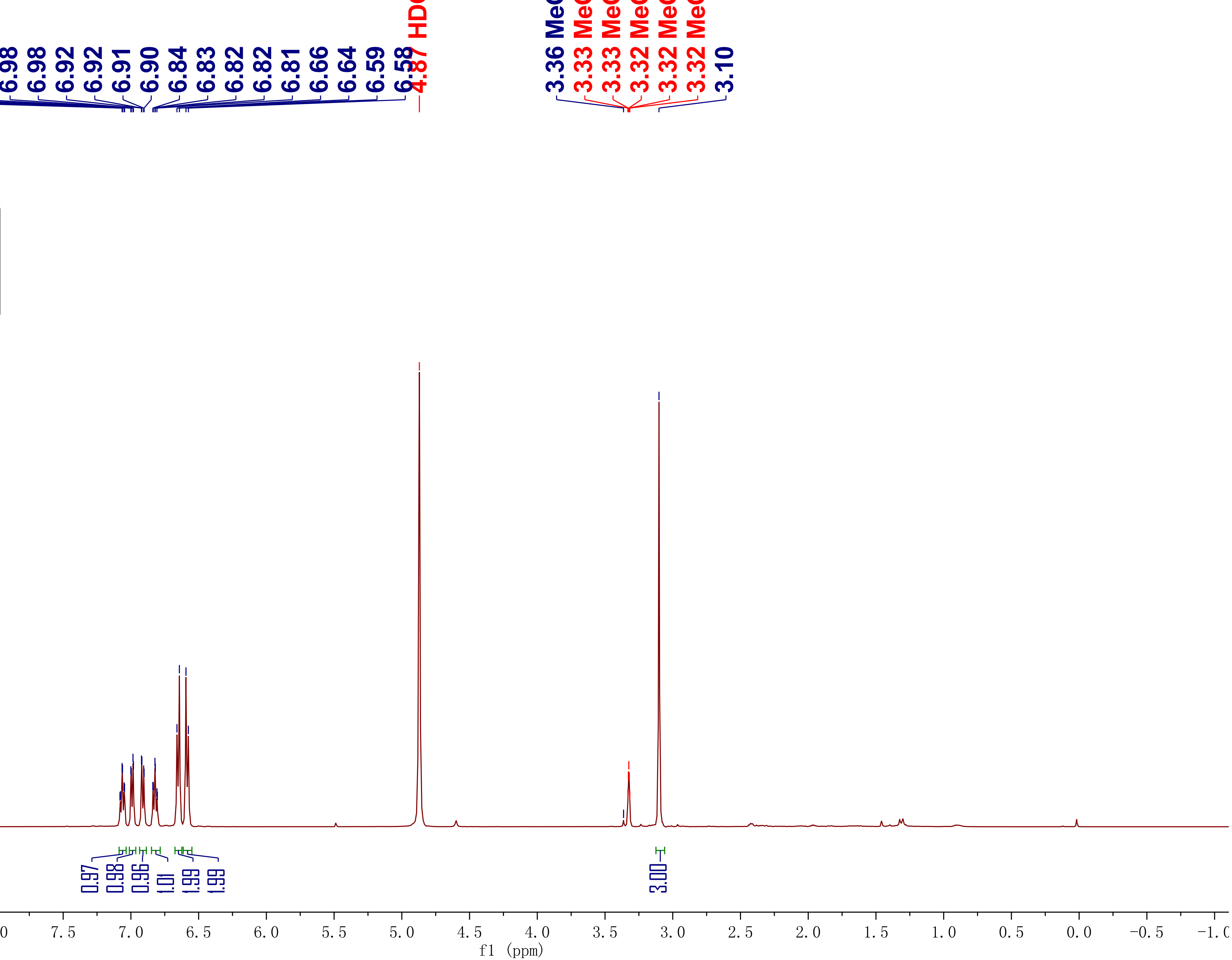


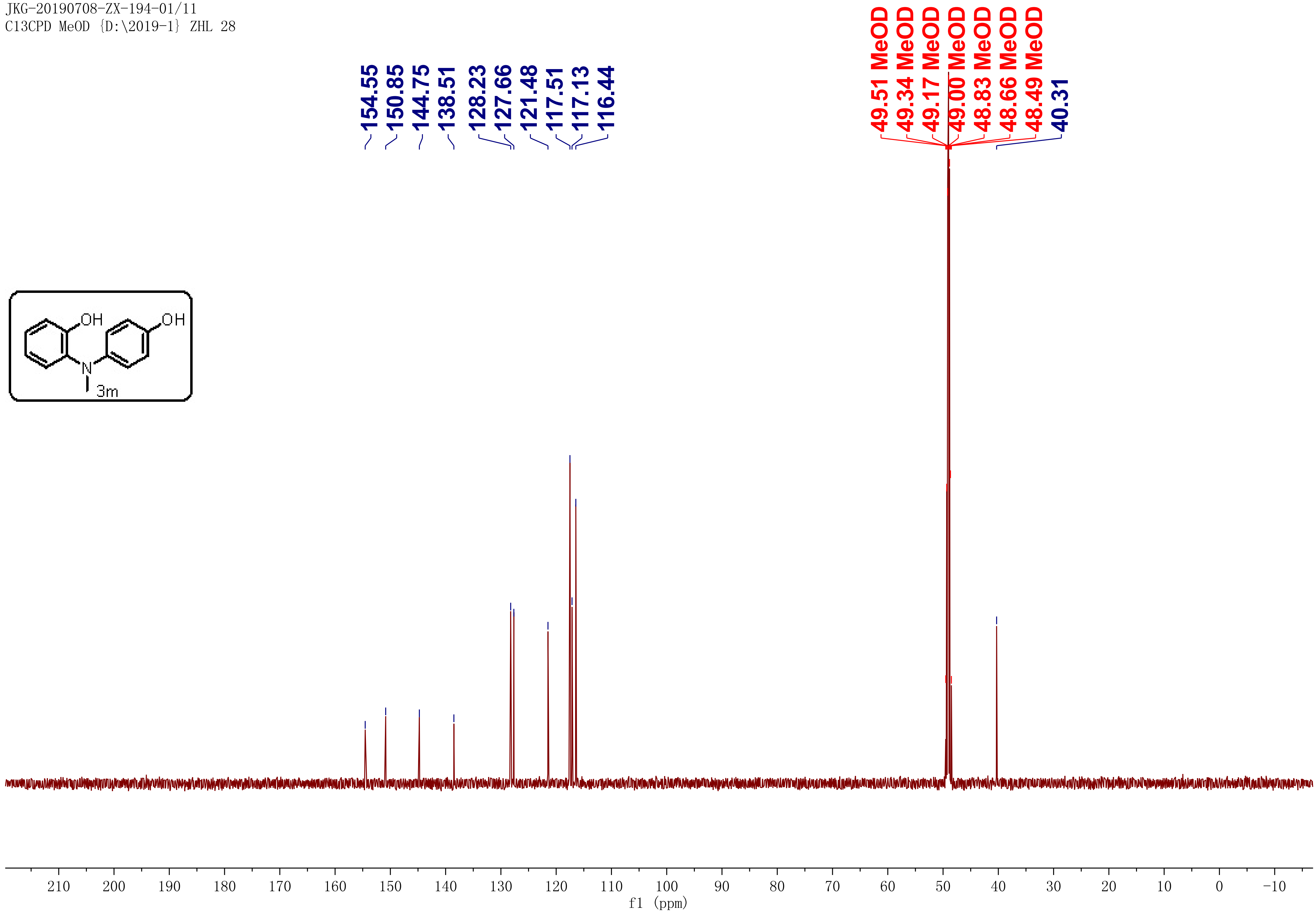


JKG-20190412-RE-ZX-133-07/11
C
156.81
150.72
144.81
139.85
128.45
127.07
122.31
117.47
116.37
113.85
56.01
49.51 MeOD
49.34 MeOD
49.17 MeOD
49.00 MeOD
48.83 MeOD
48.66 MeOD
48.49 MeOD
40.26
OH
O
N
3l
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

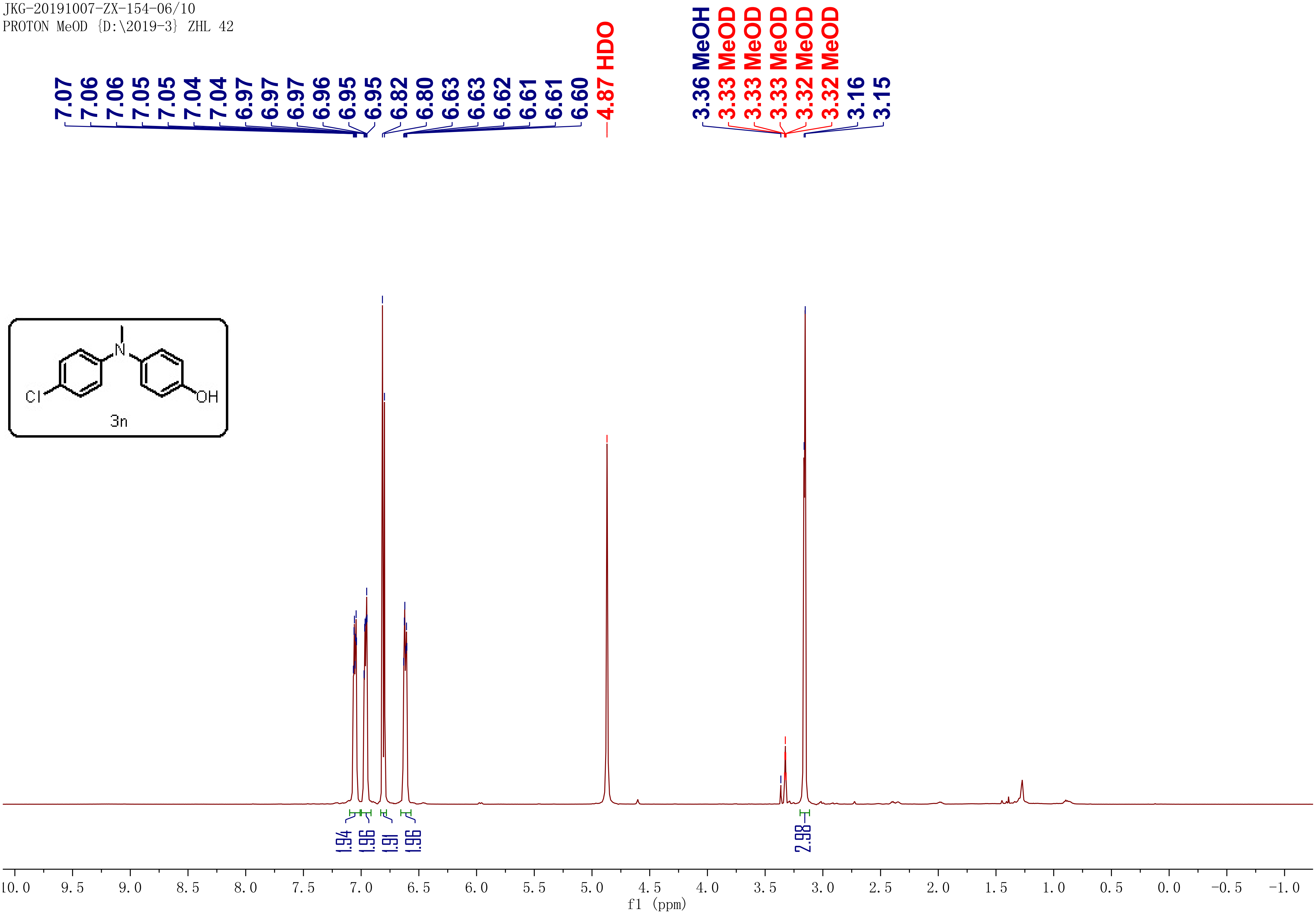
JKG-20190708-ZX-194-01/10
PROTON MeOD {D:\2019-1} ZHL 28



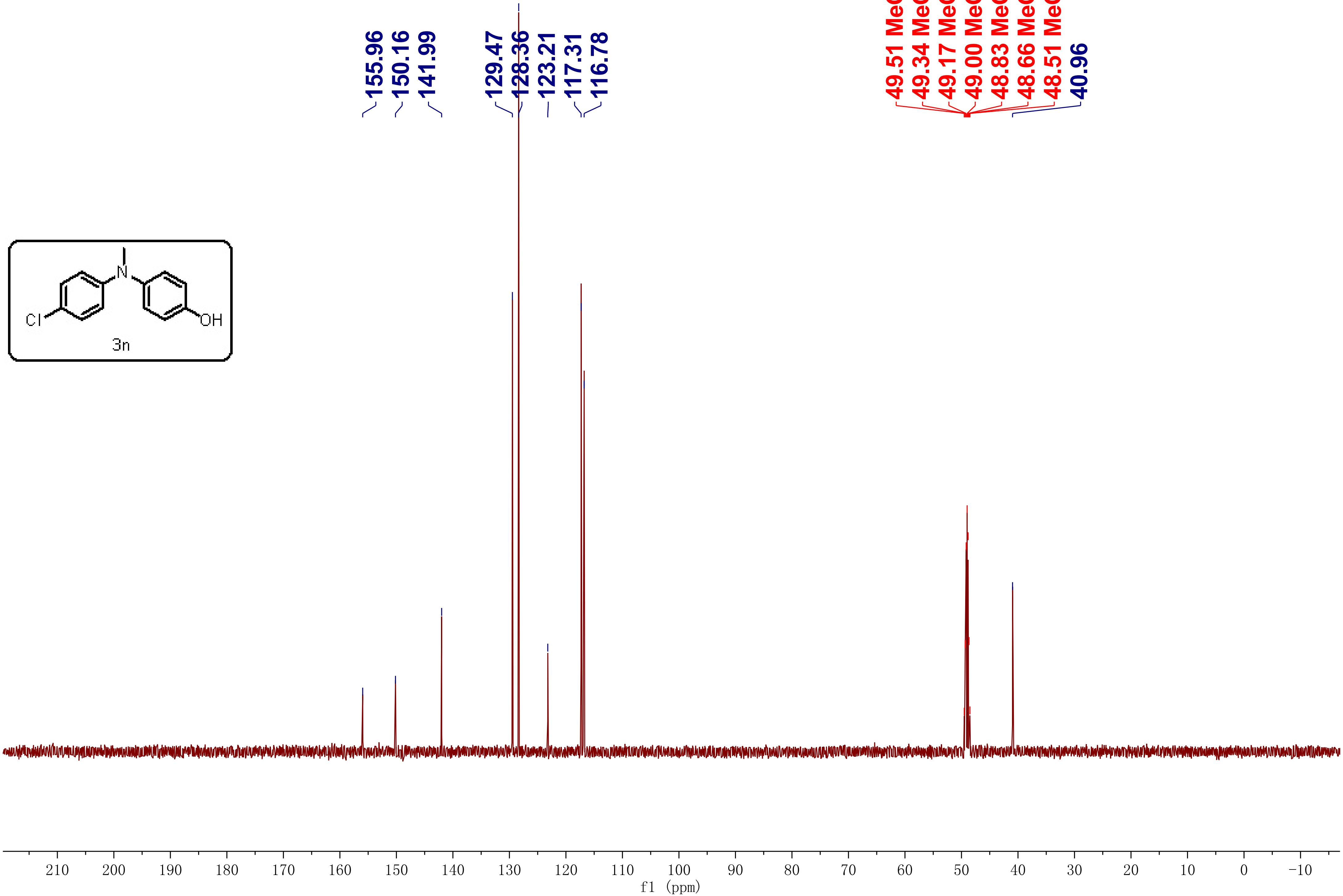




JKG-20190708-ZX-194-01/11
C13CPD MeOD {D:\2019-1} ZHL 28
154.55
150.85
144.75
138.51
128.23
127.66
121.48
117.51
117.13
116.44
49.51 MeOD
49.34 MeOD
49.17 MeOD
49.00 MeOD
48.83 MeOD
48.66 MeOD
48.49 MeOD
40.31
OH
OH
N
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

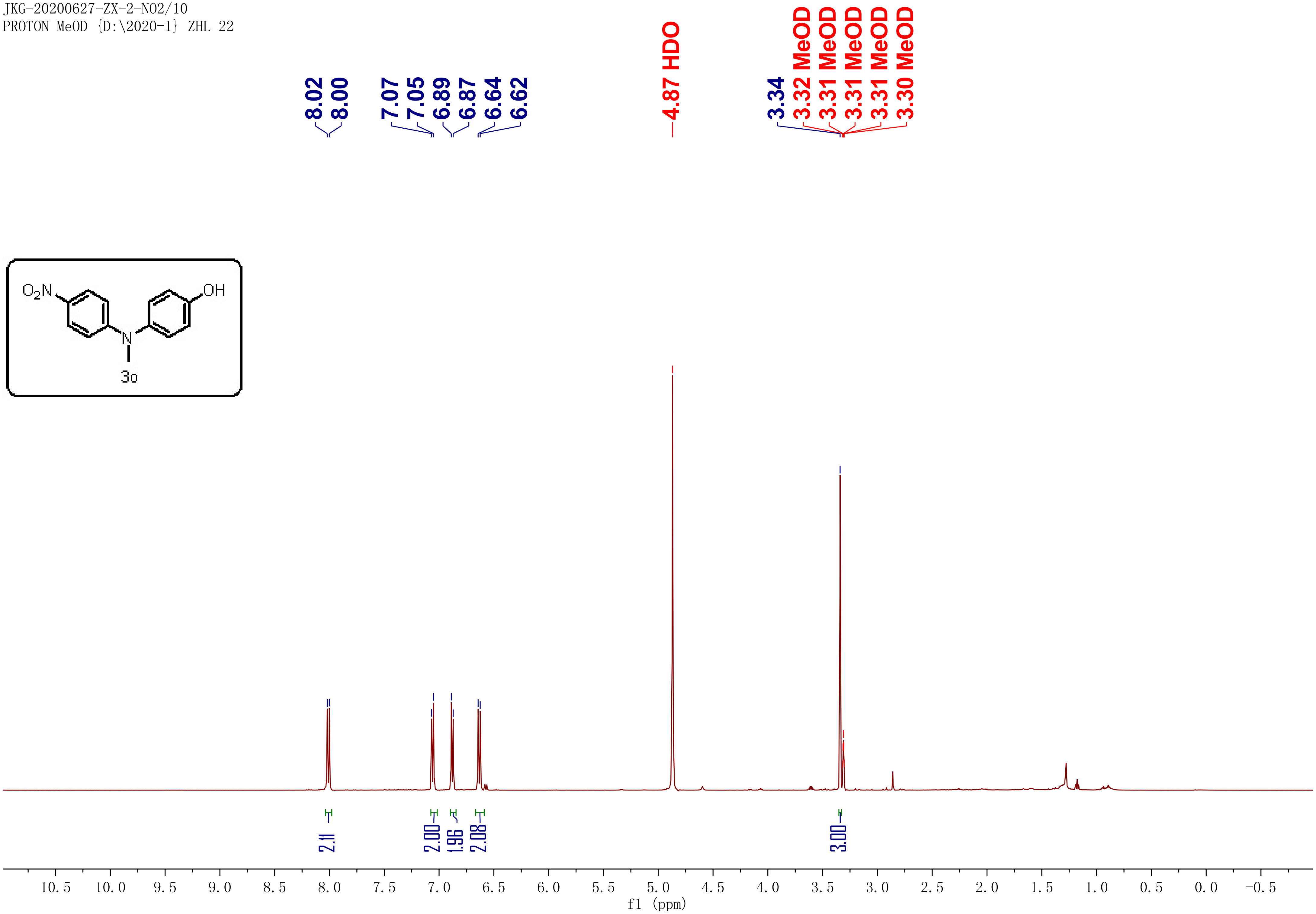
JKG-20191007-ZX-154-06/10
PROTON MeOD {D:\2019-3} ZHL 42

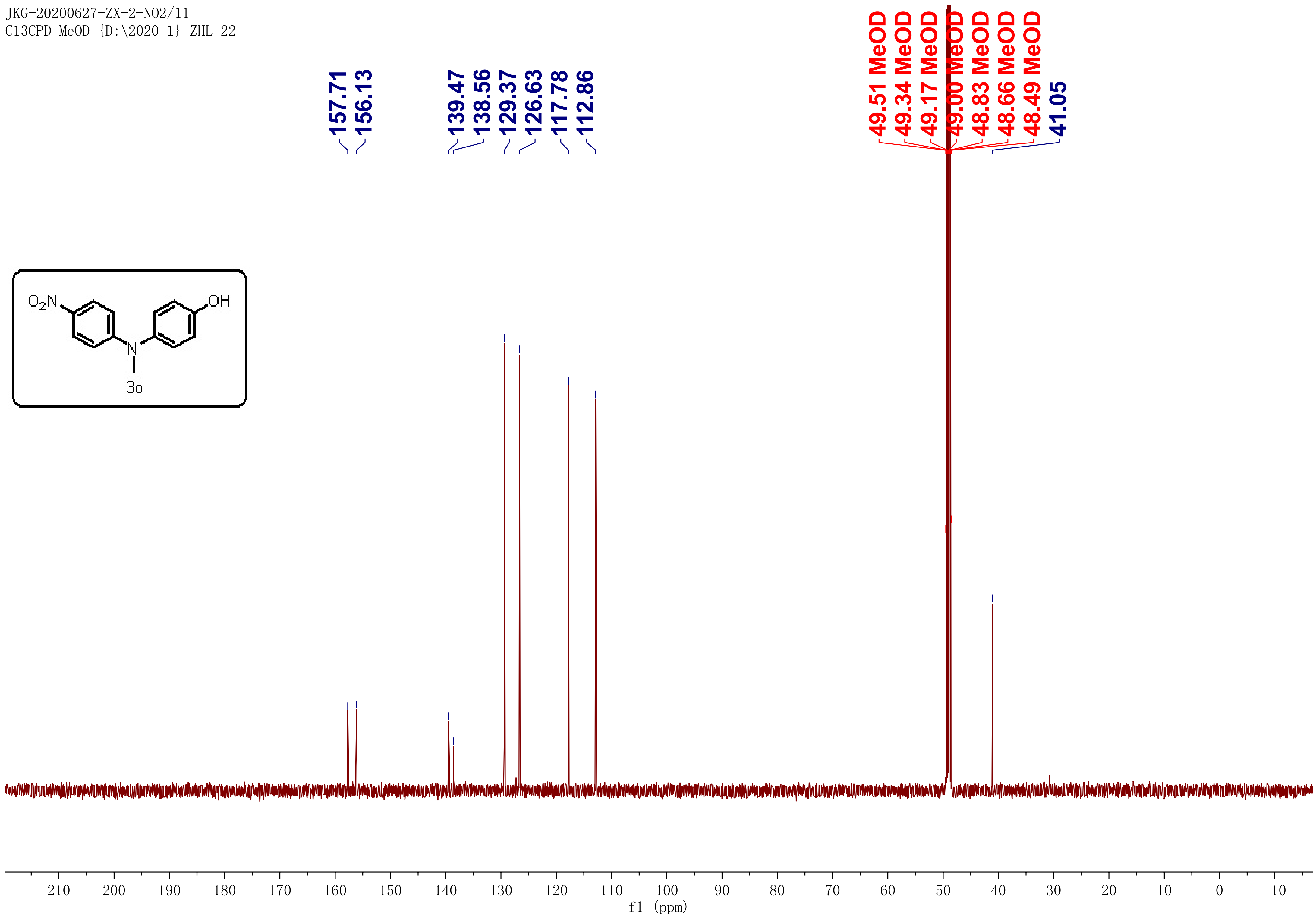


JKG-20191007-ZX-154-06/11
C13CPD MeOD {D:\2019-3} ZHL 42

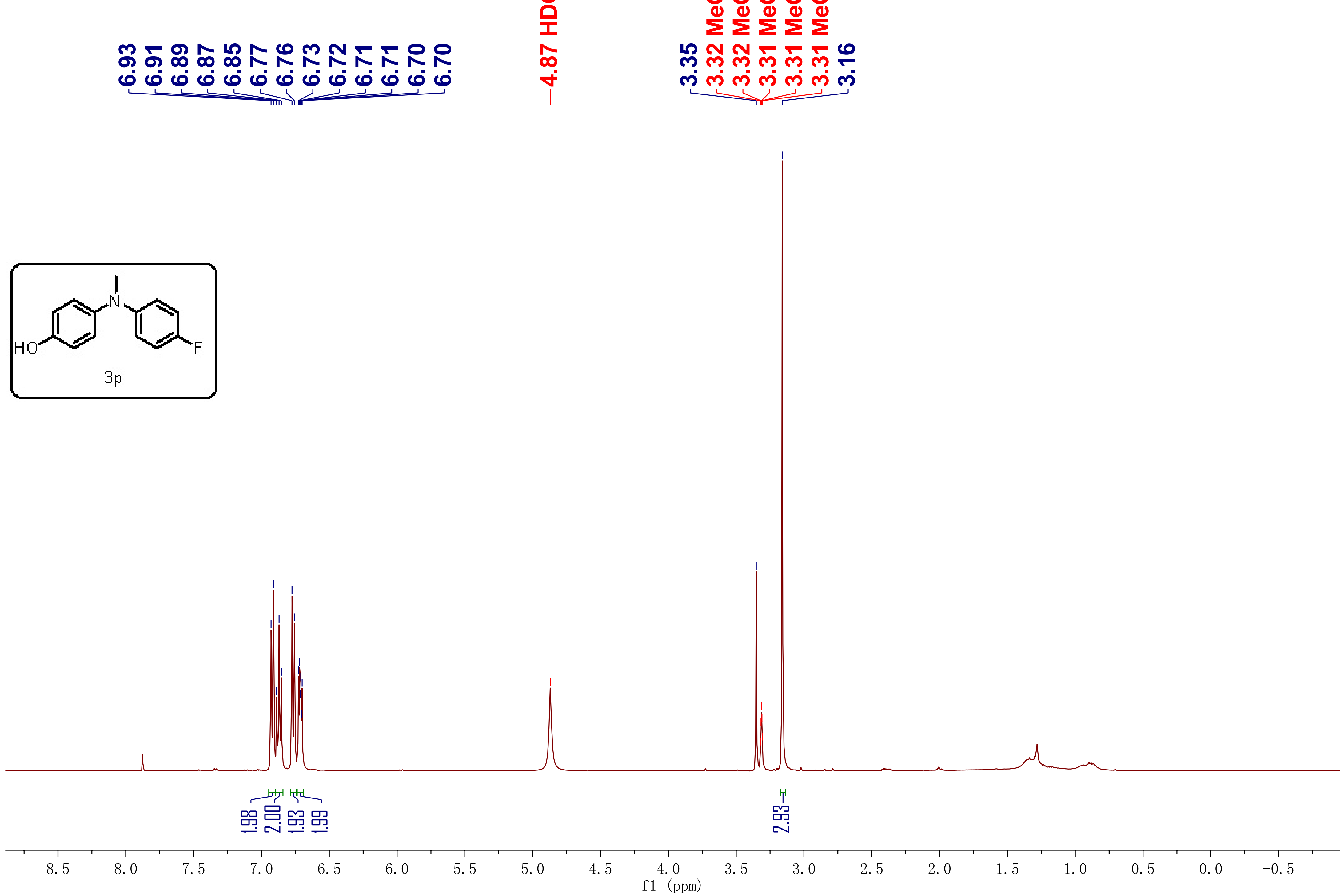


JKG-20200627-ZX-2-NO2/10
PROTON MeOD {D:\2020-1} ZHL 22

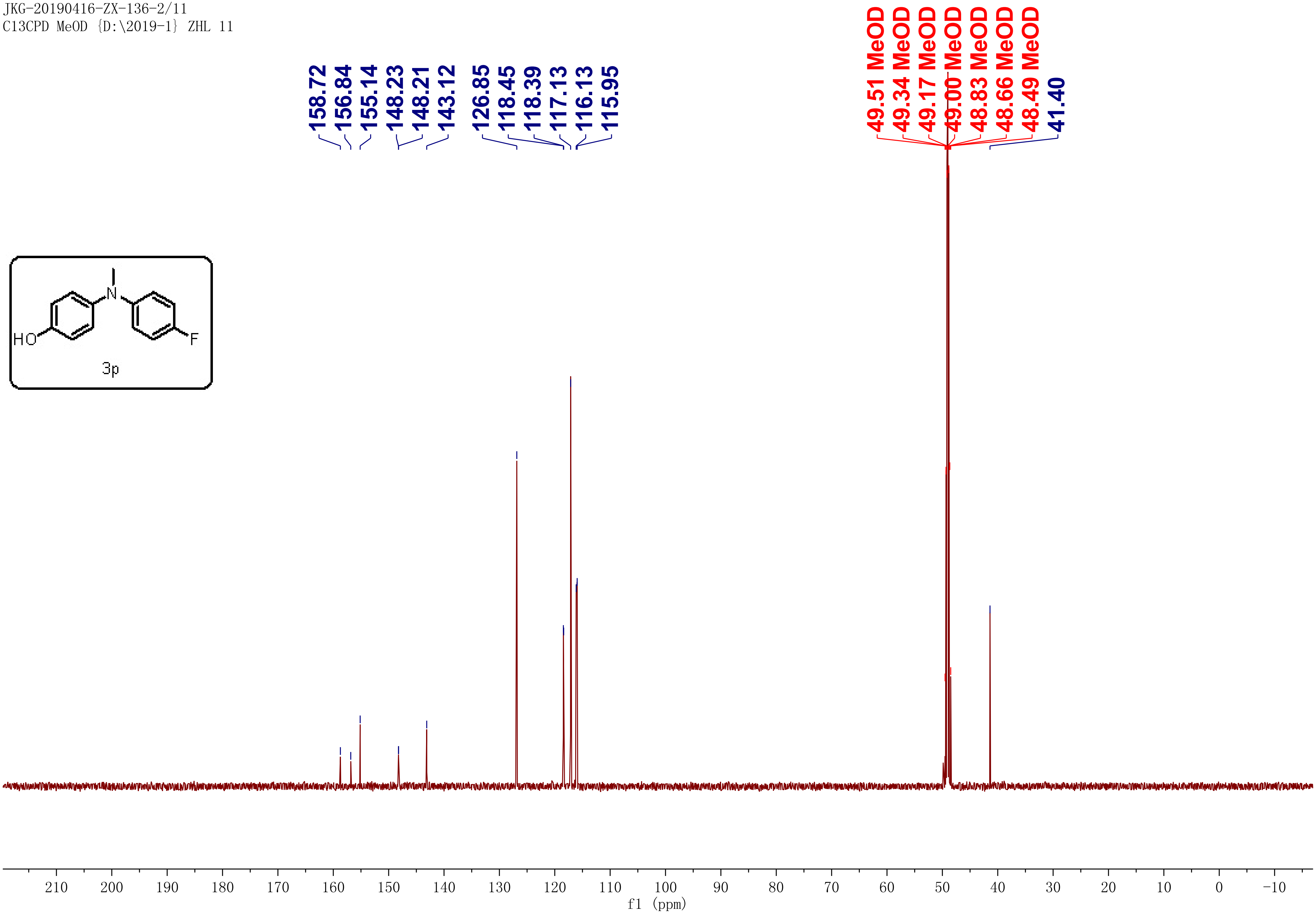



JKG-20200627-ZX-2-NO2/11
C13CPD MeOD {D:\2020-1} ZHL 22
157.71
156.13
139.47
138.56
129.37
126.63
117.78
112.86
49.51 MeOD
49.34 MeOD
49.17 MeOD
49.00 MeOD
48.83 MeOD
48.66 MeOD
48.49 MeOD
41.05
O2N
OH
N
3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

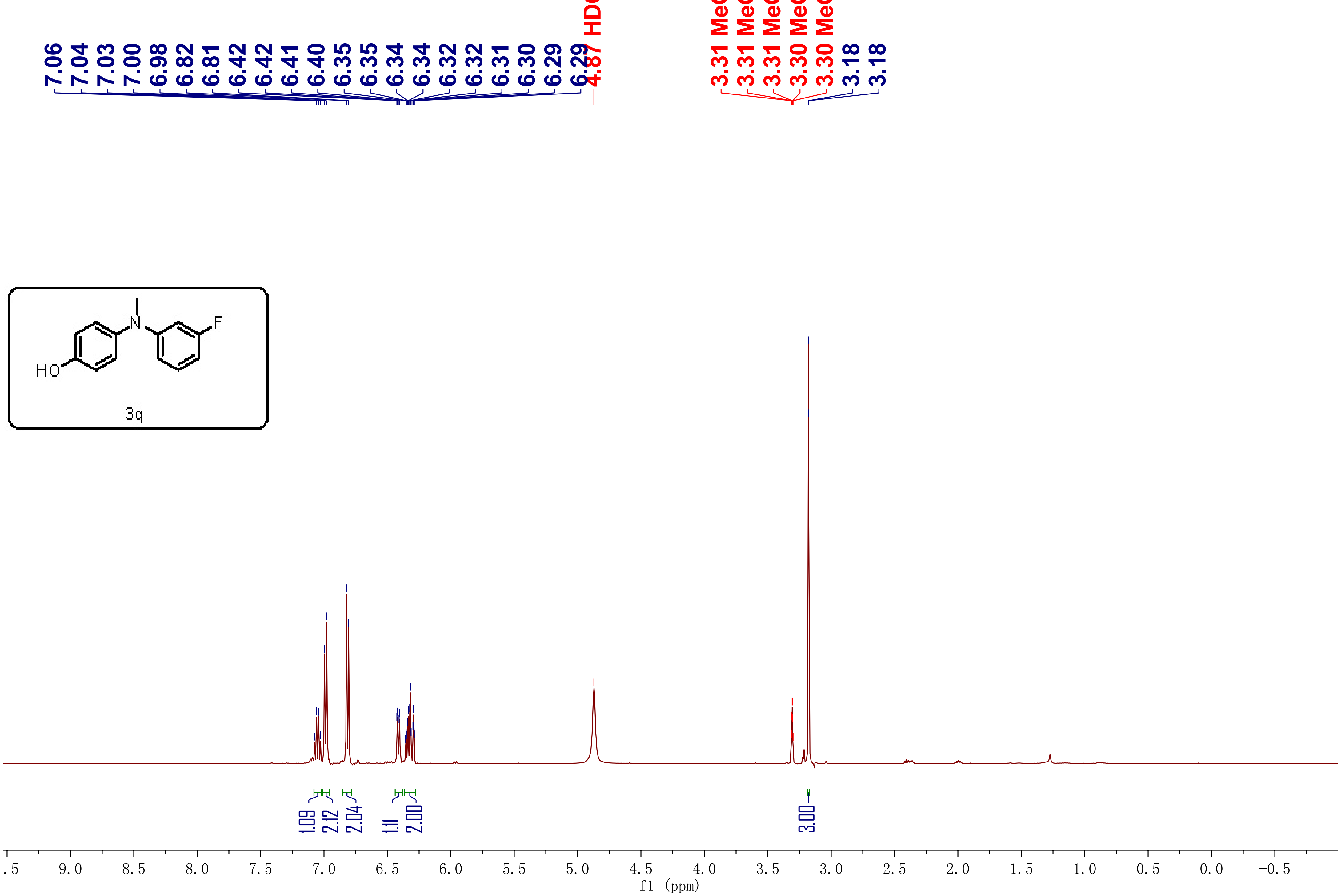
JKG-20190416-ZX-136-2/10
PROTON MeOD {D:\2019-1} ZHL 11



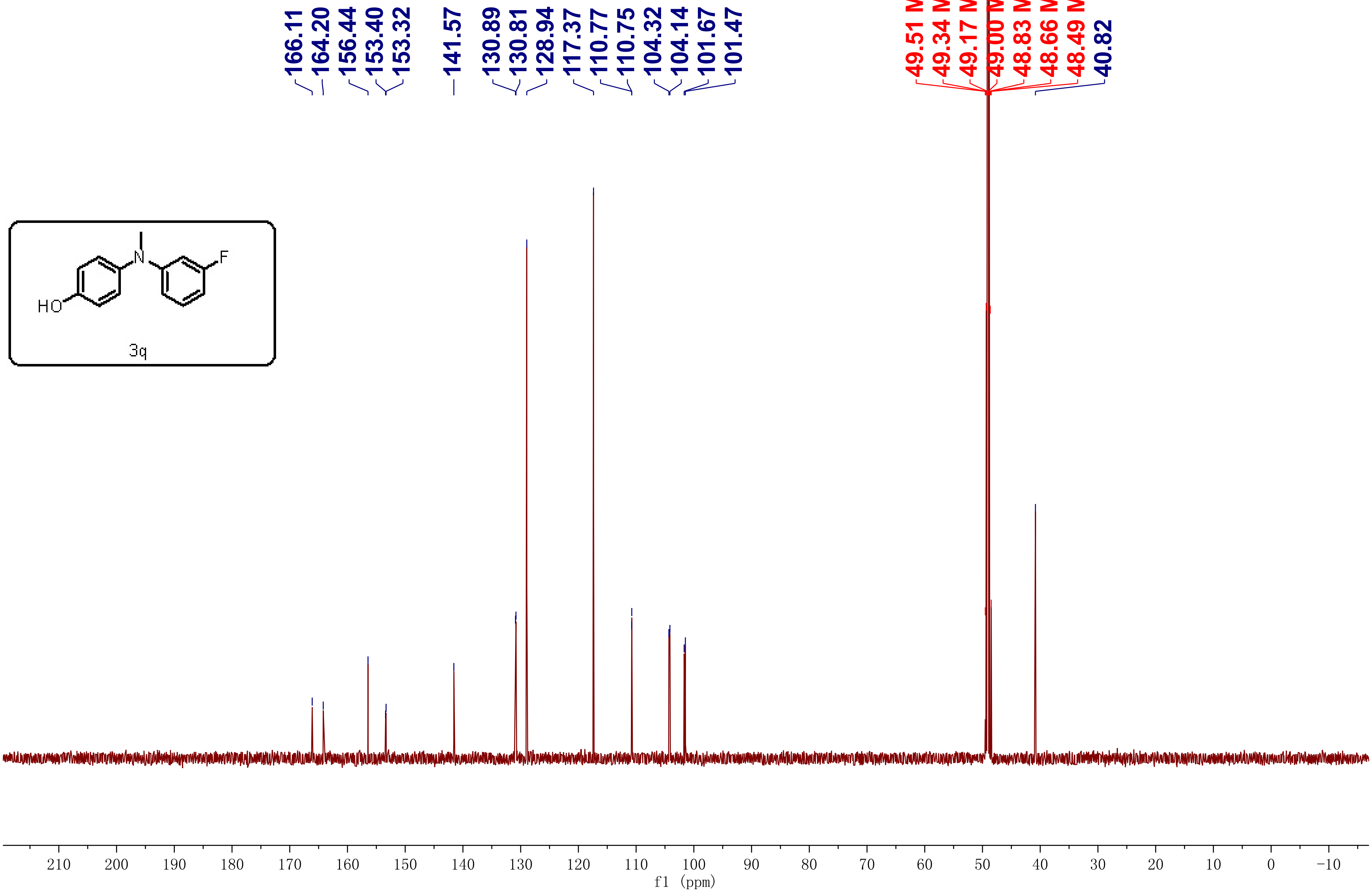
JKG-20190416-ZX-136-2/11
C13CPD MeOD {D:\2019-1} ZHL 11



JKG-20191007-ZX-177-03/10
PROTON MeOD {D:\2019-3} ZHL 46

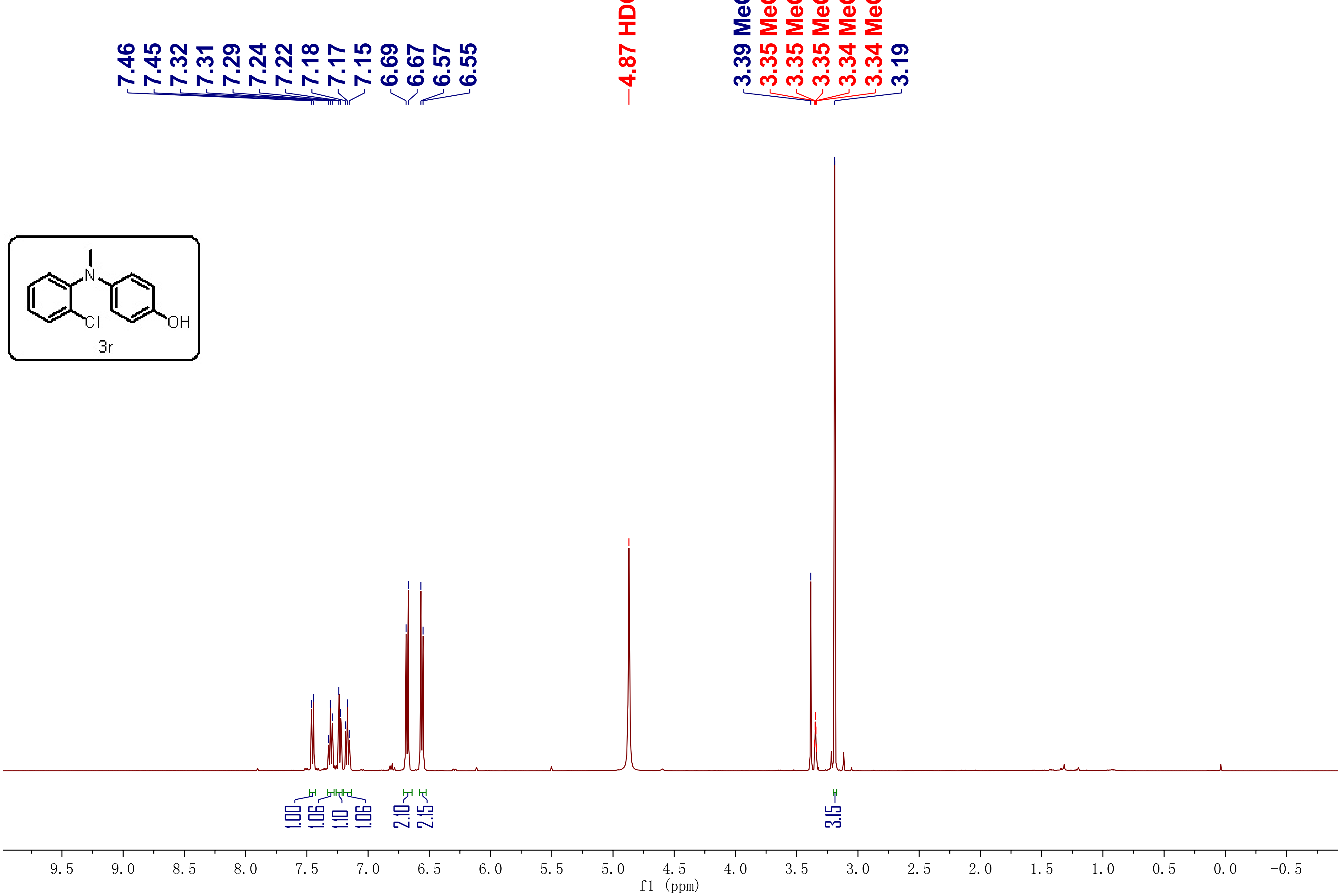


JKG-20191007-ZX-177-03/11
C13CPD MeOD {D:\2019-3} ZHL 46

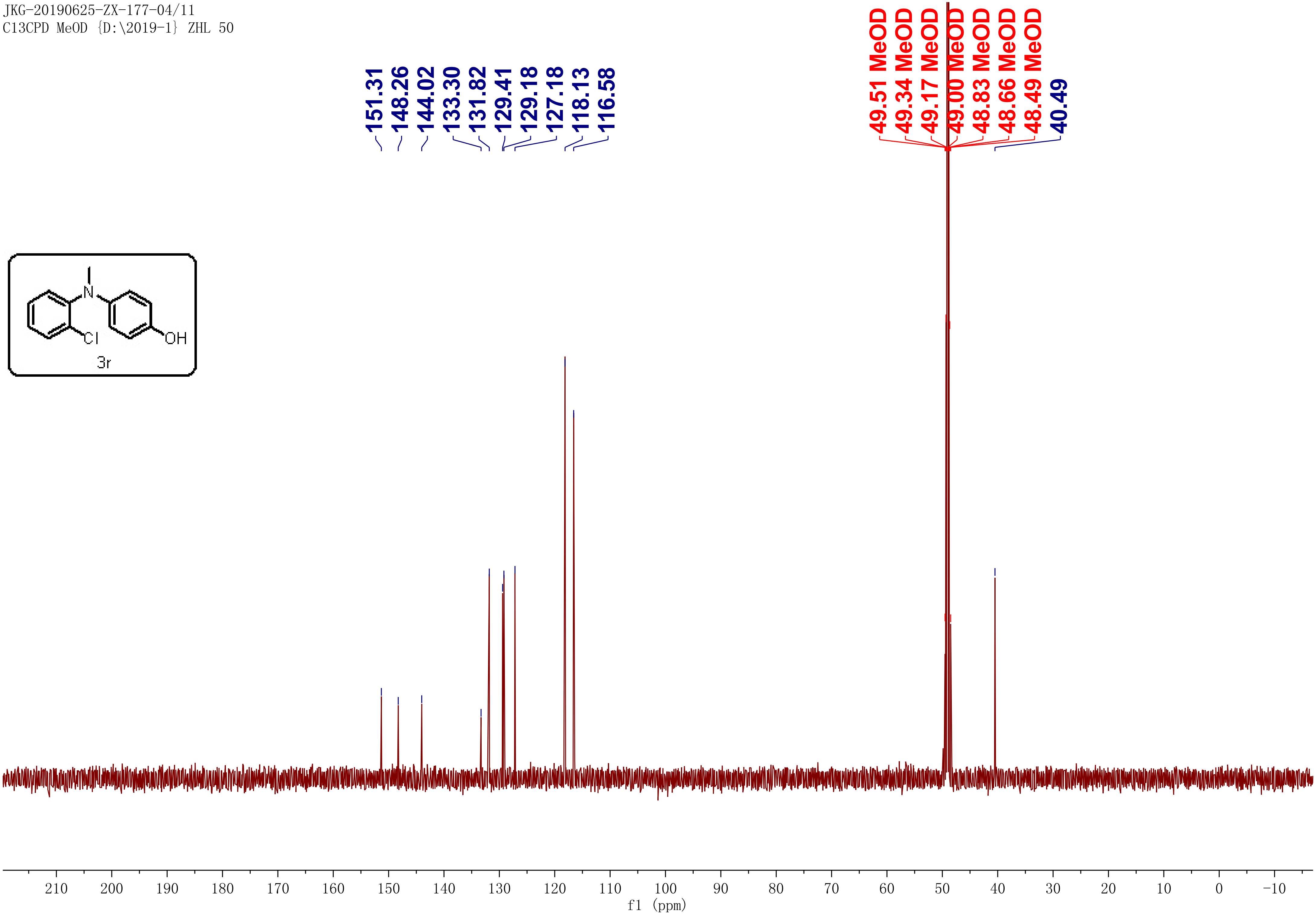



3q

JKG-20190625-ZX-177-04/10
PROTON MeOD {D:\2019-1} ZHL 50

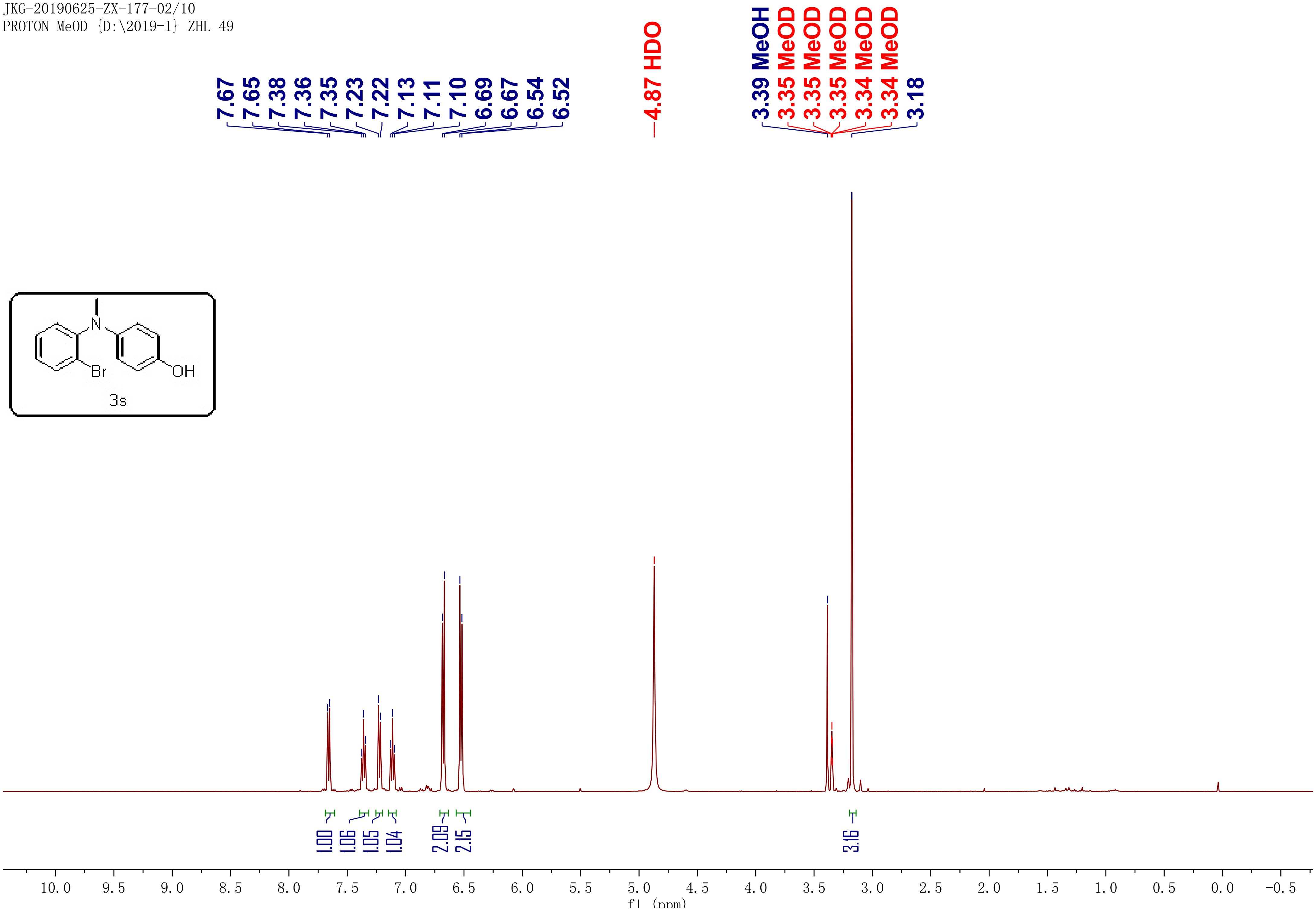


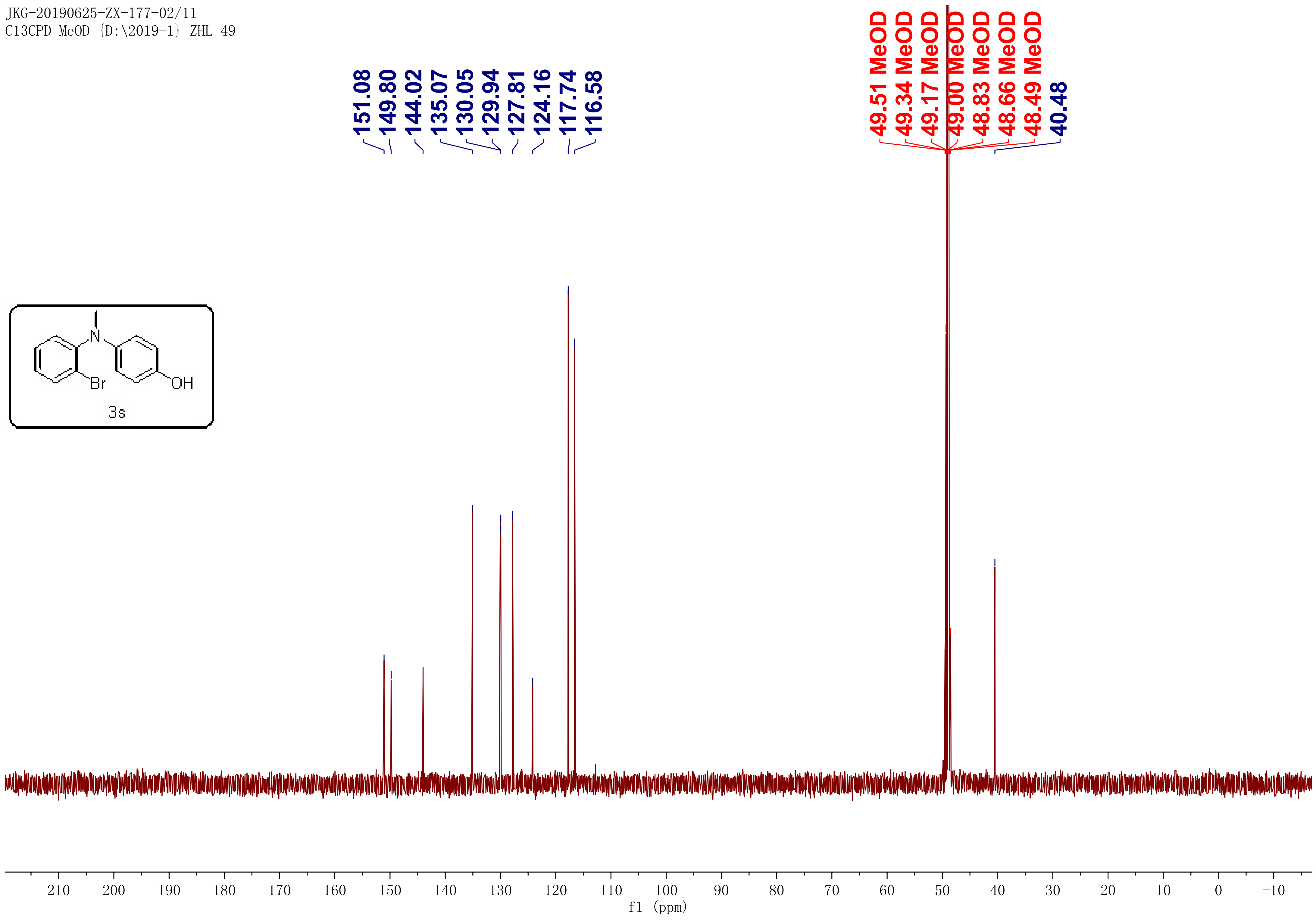
JKG-20190625-ZX-177-04/11
C13CPD MeOD {D:\2019-1} ZHL 50



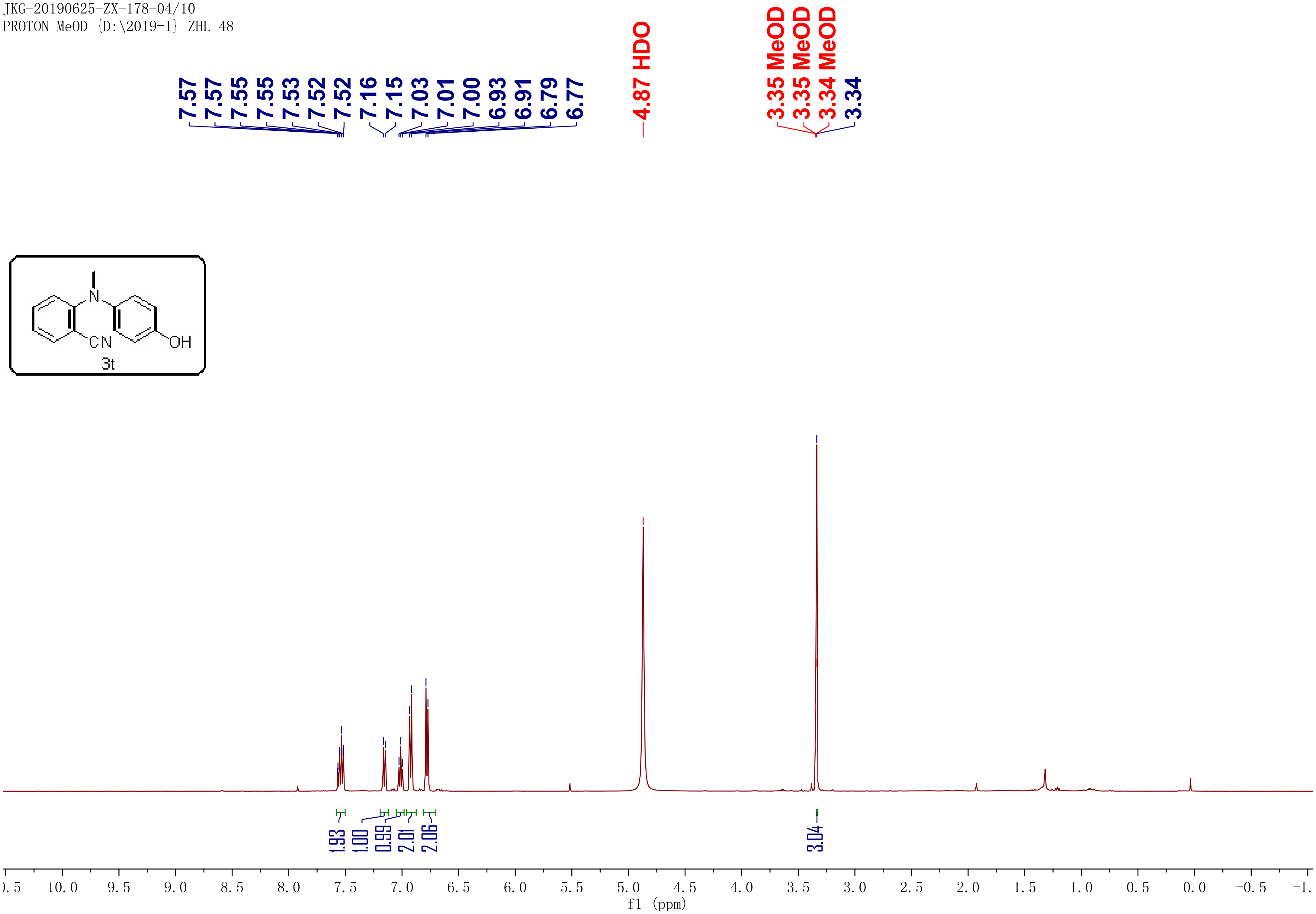
3r

JKG-20190625-ZX-177-02/10
PROTON MeOD {D:\2019-1} ZHL 49

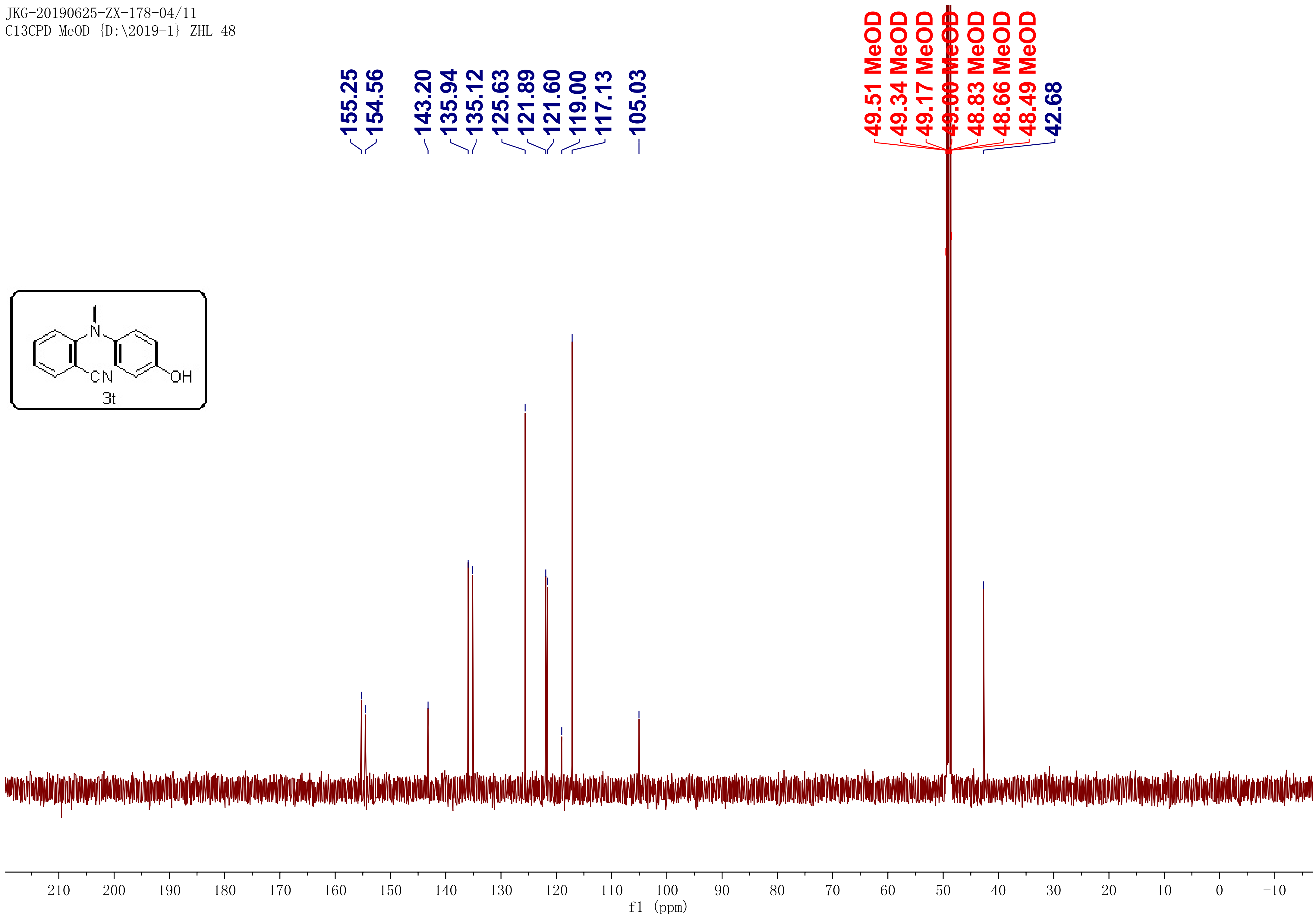



JKG-20190625-ZX-177-02/11
C13CPD MeOD {D:\2019-1} ZHL 49
151.08
149.80
144.02
135.07
130.05
129.94
127.81
124.16
117.74
116.58
49.51 MeOD
49.34 MeOD
49.17 MeOD
49.00 MeOD
48.83 MeOD
48.66 MeOD
48.49 MeOD
40.48
N
Br
OH
3s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

JKG-20190625-ZX-178-04/10
PROTON MeOD {D:\2019-1} ZHL 48

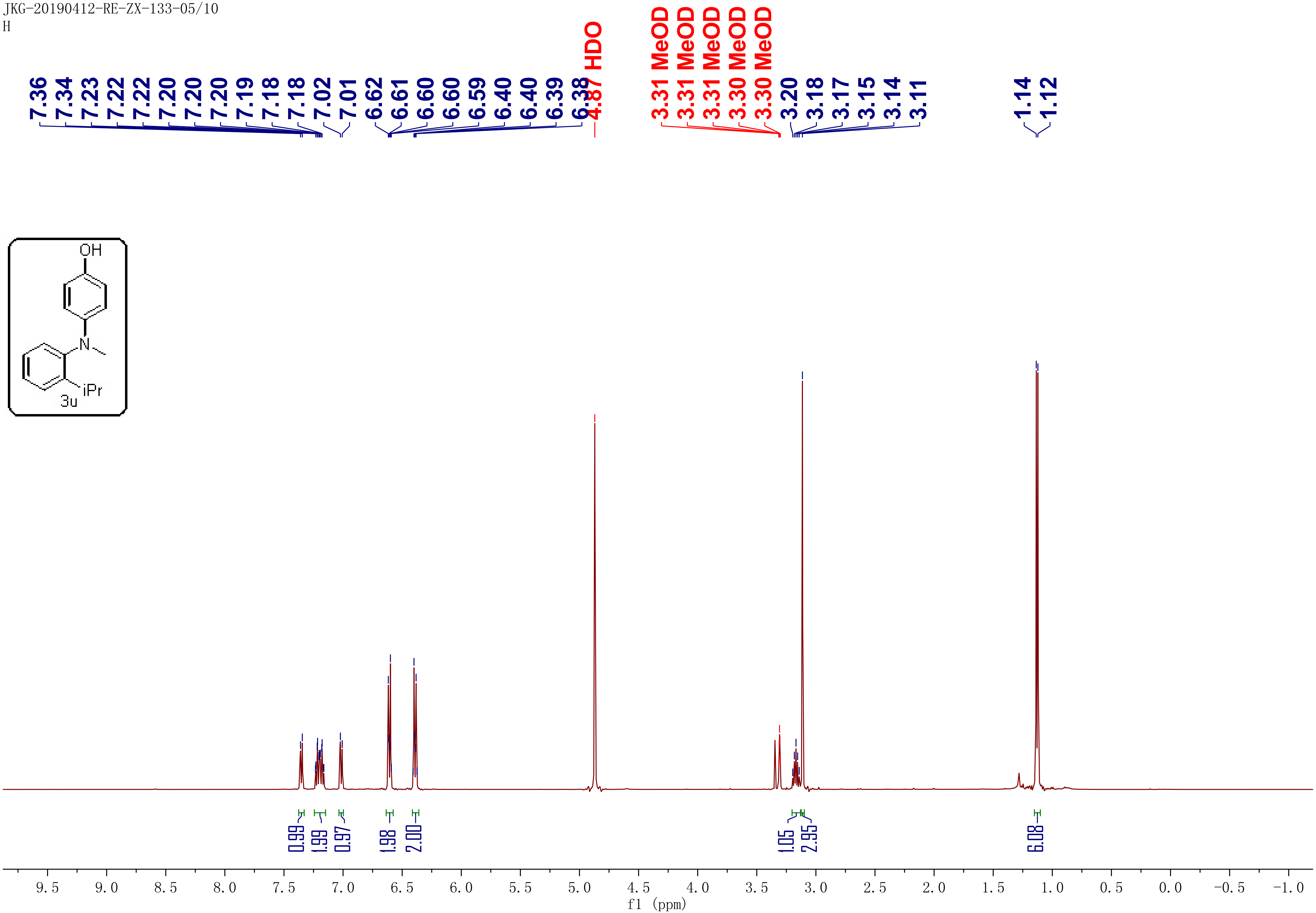



3t

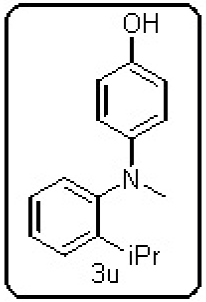


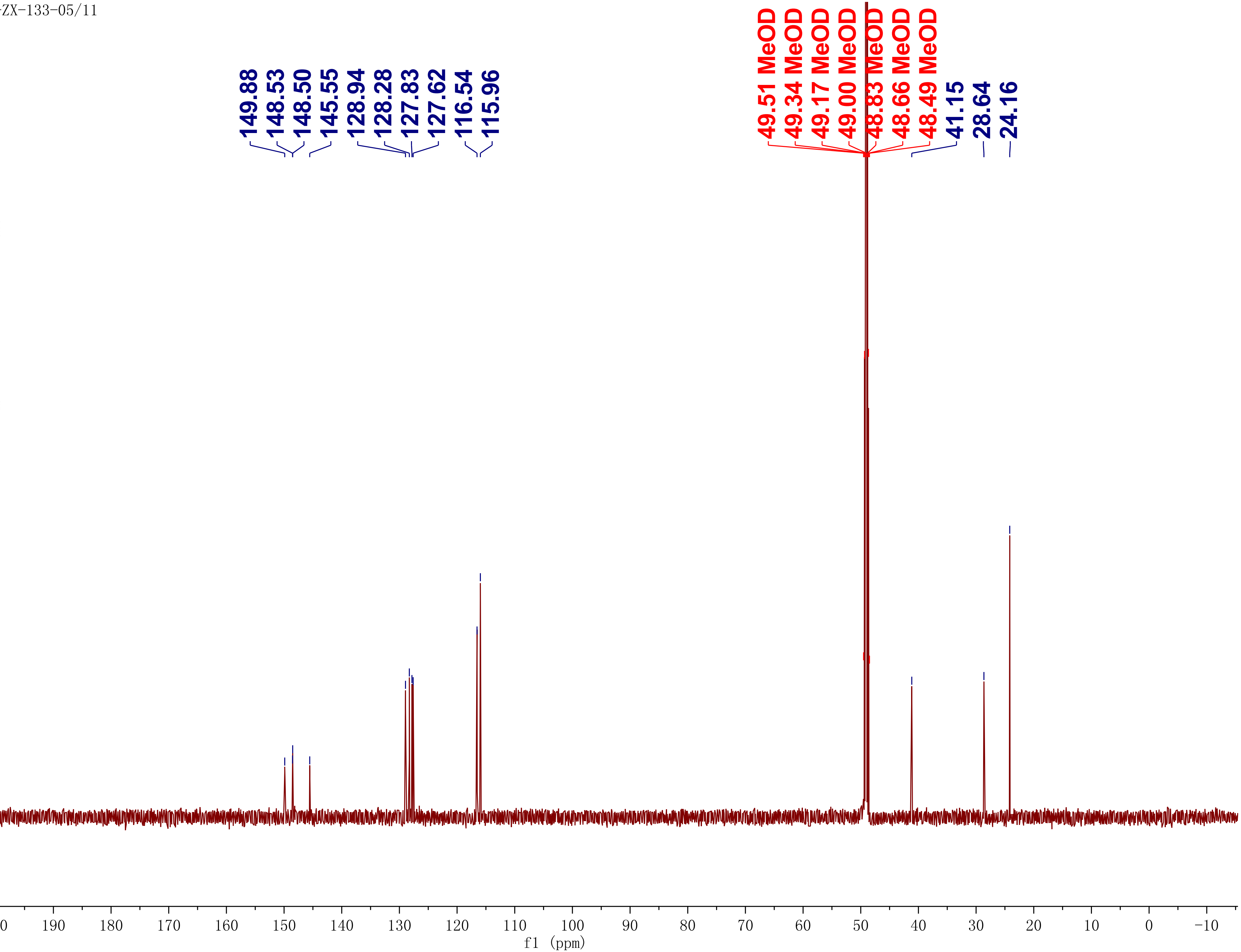
JKG-20190625-ZX-178-04/11
C13CPD MeOD {D:\2019-1} ZHL 48
155.25
154.56
143.20
135.94
135.12
125.63
121.89
121.60
119.00
117.13
105.03
49.51 MeOD
49.34 MeOD
49.17 MeOD
49.00 MeOD
48.83 MeOD
48.66 MeOD
48.49 MeOD
42.68
N
CN
OH
3t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

JKG-20190412-RE-ZX-133-05/10
H

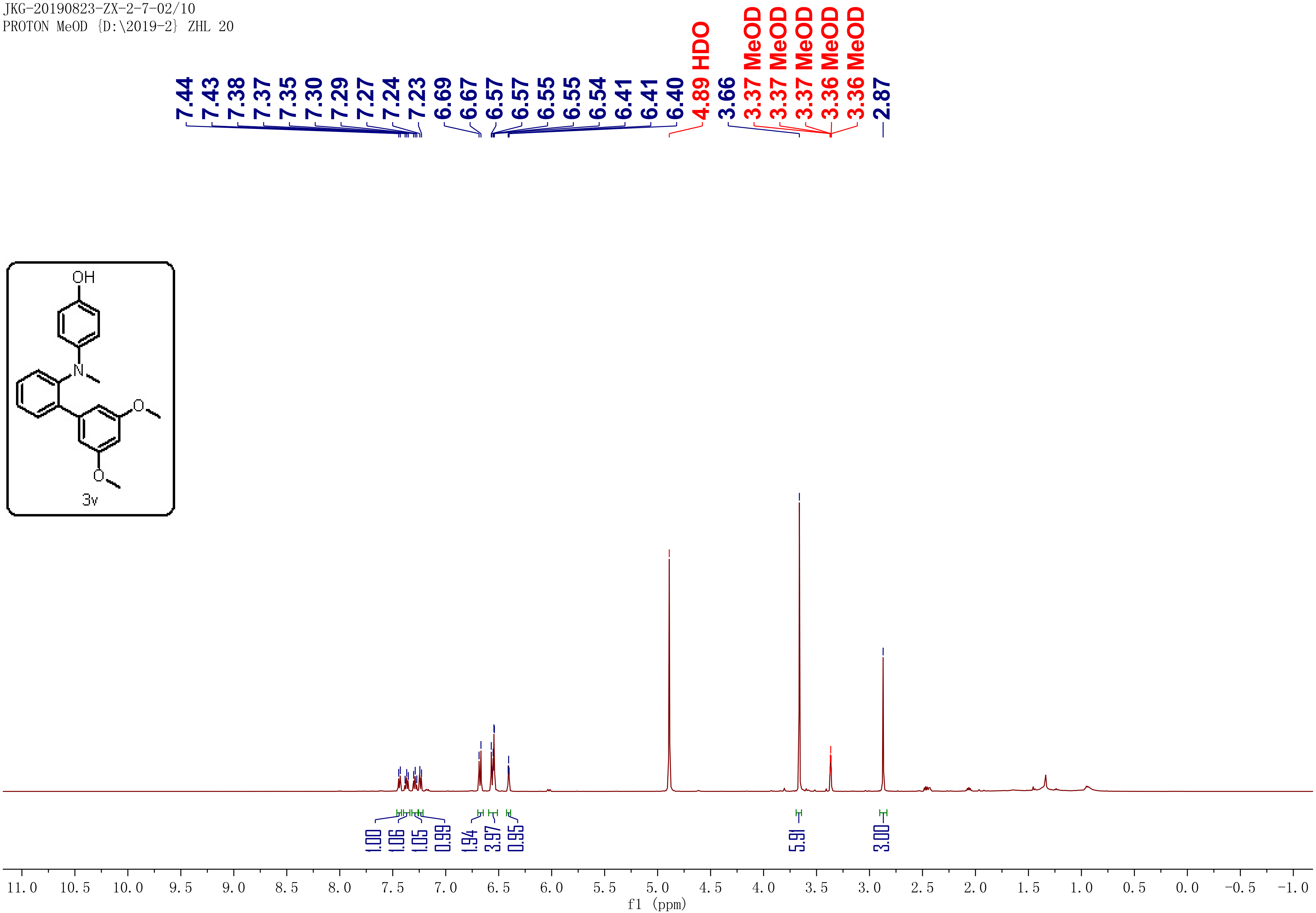


JKG-20190412-RE-ZX-133-05/11
C

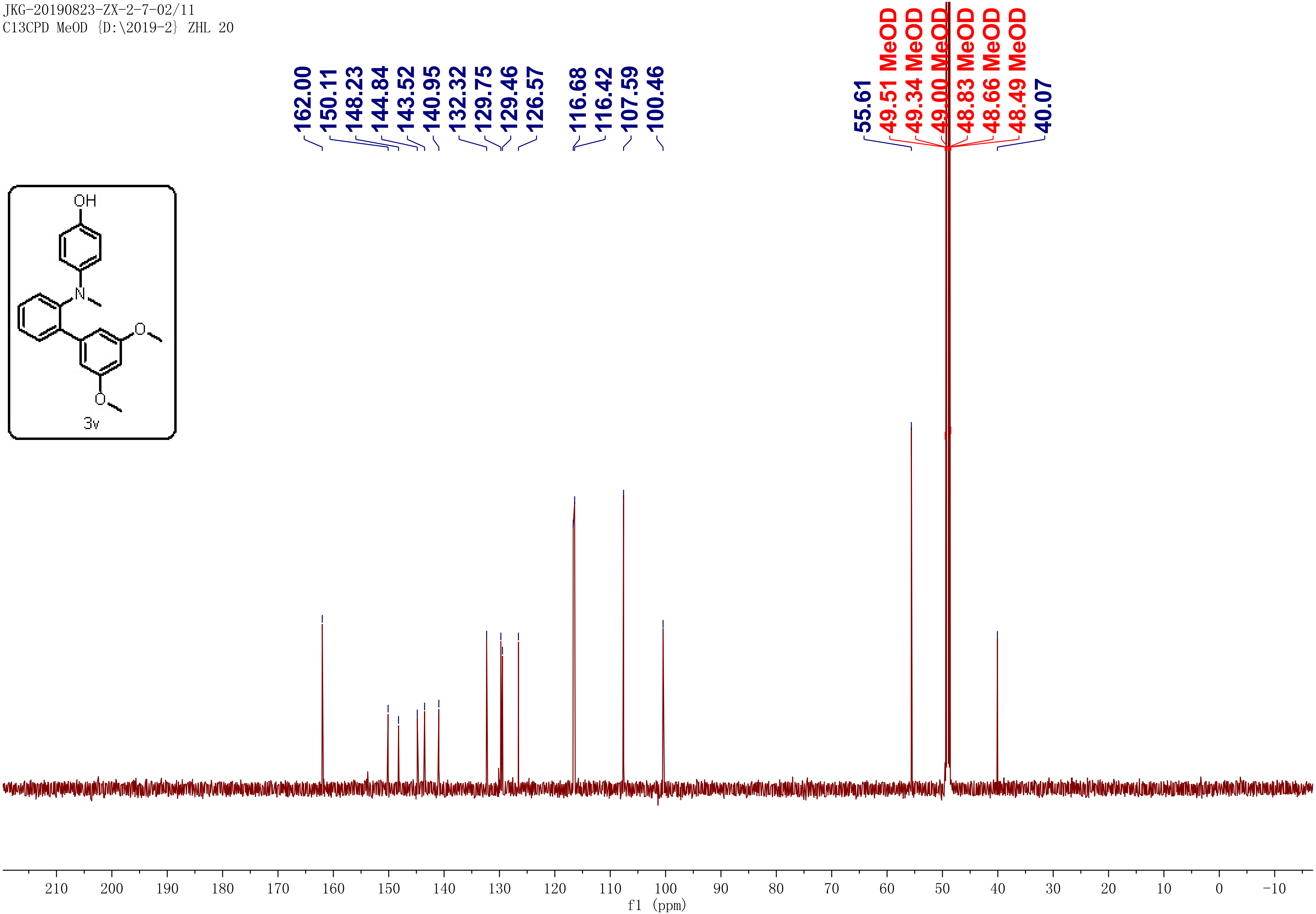




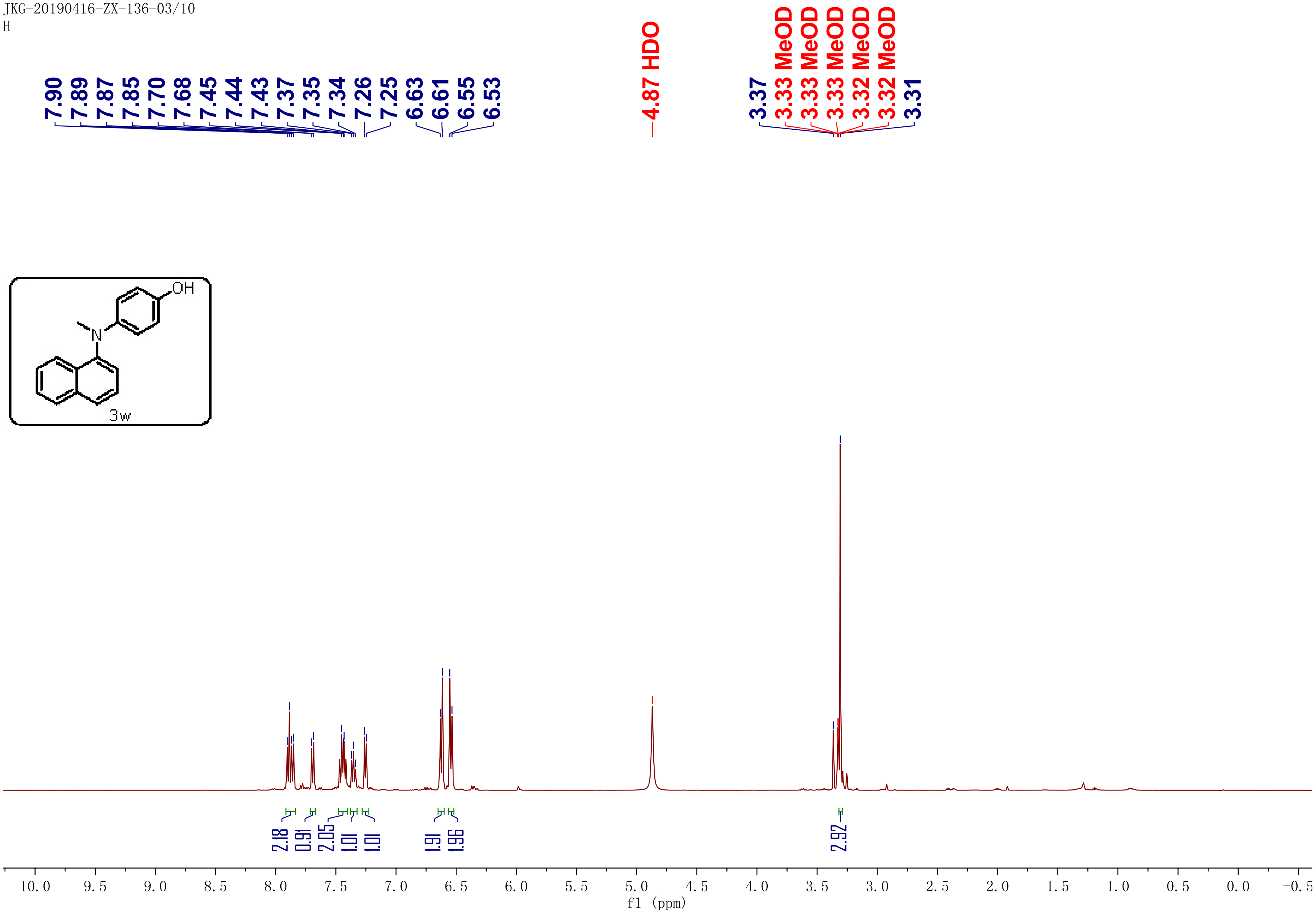
JKG-20190823-ZX-2-7-02/10
PROTON MeOD {D:\2019-2} ZHL 20



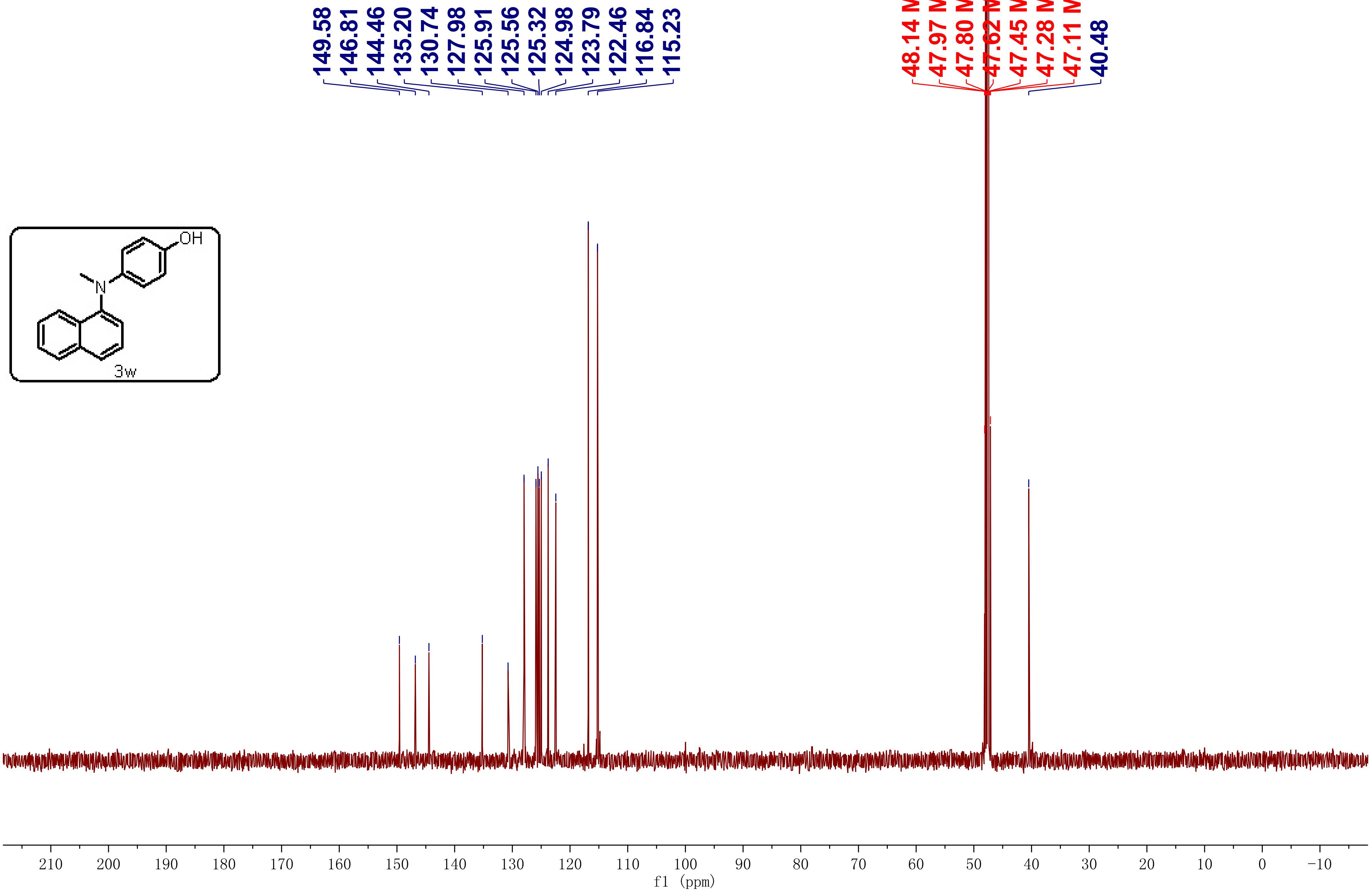
JKG-20190823-ZX-2-7-02/11
C13CPD MeOD {D:\2019-2} ZHL 20



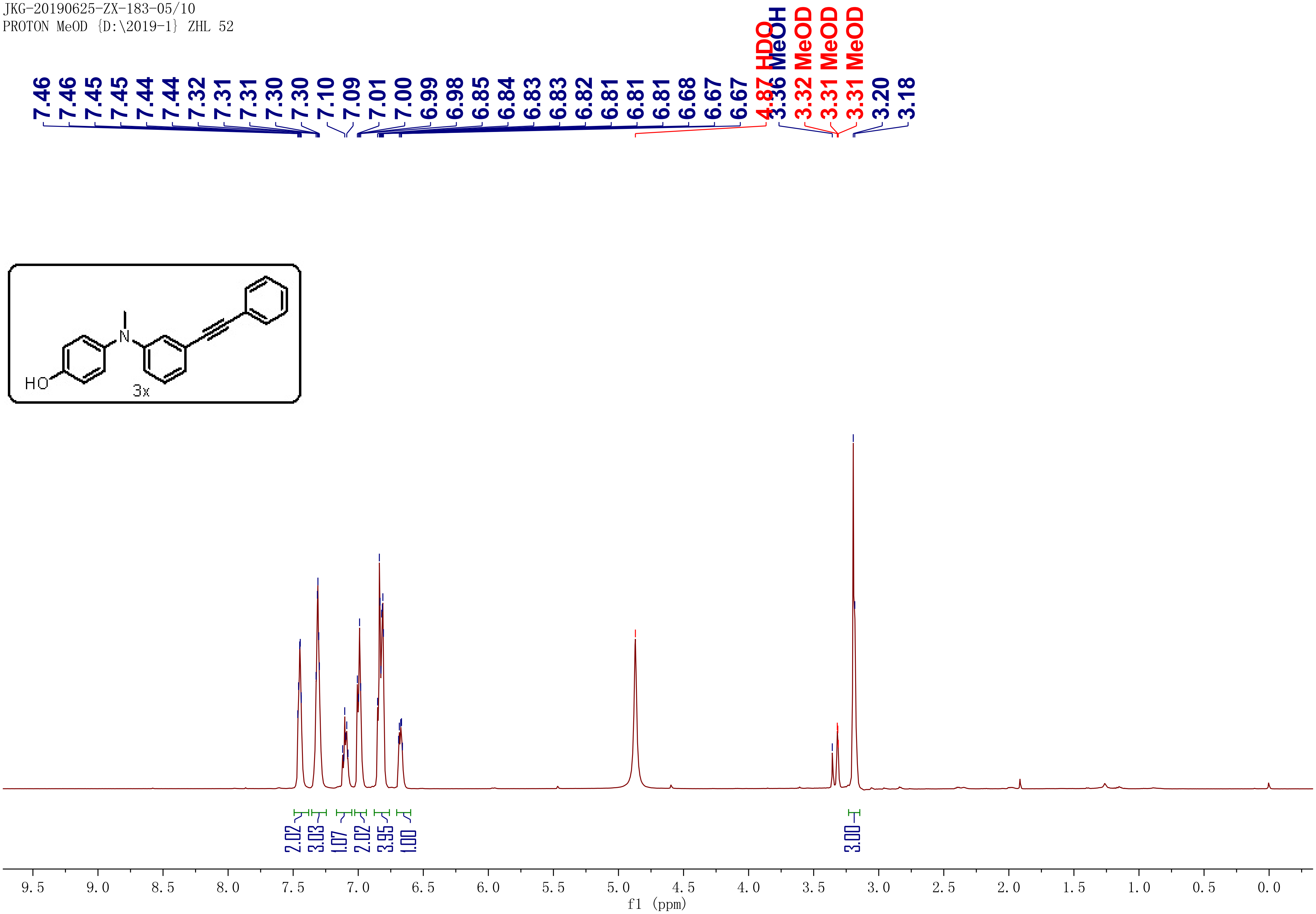
JKG-20190416-ZX-136-03/10
H

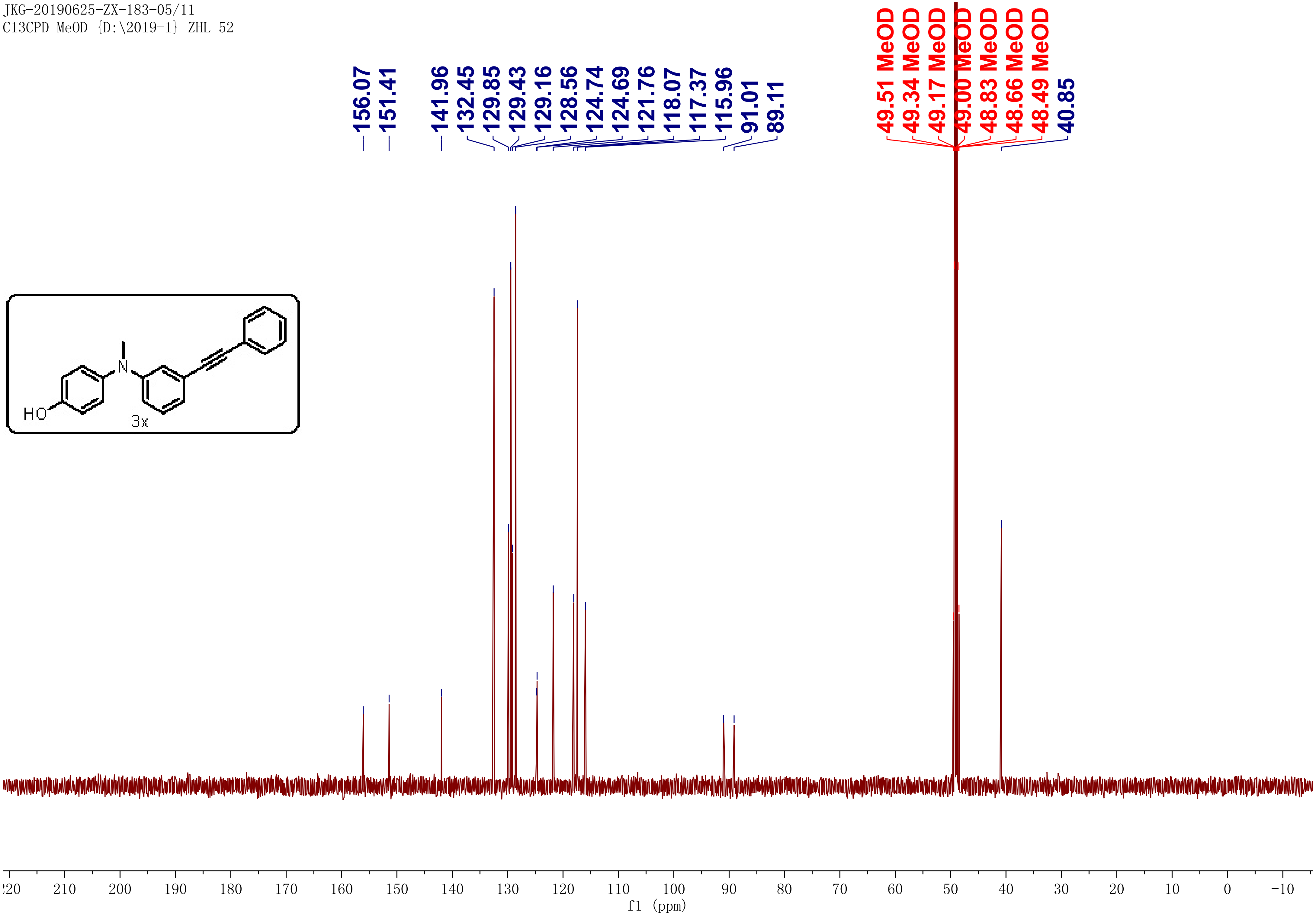


JKG-20190416-ZX-136-03/11
C

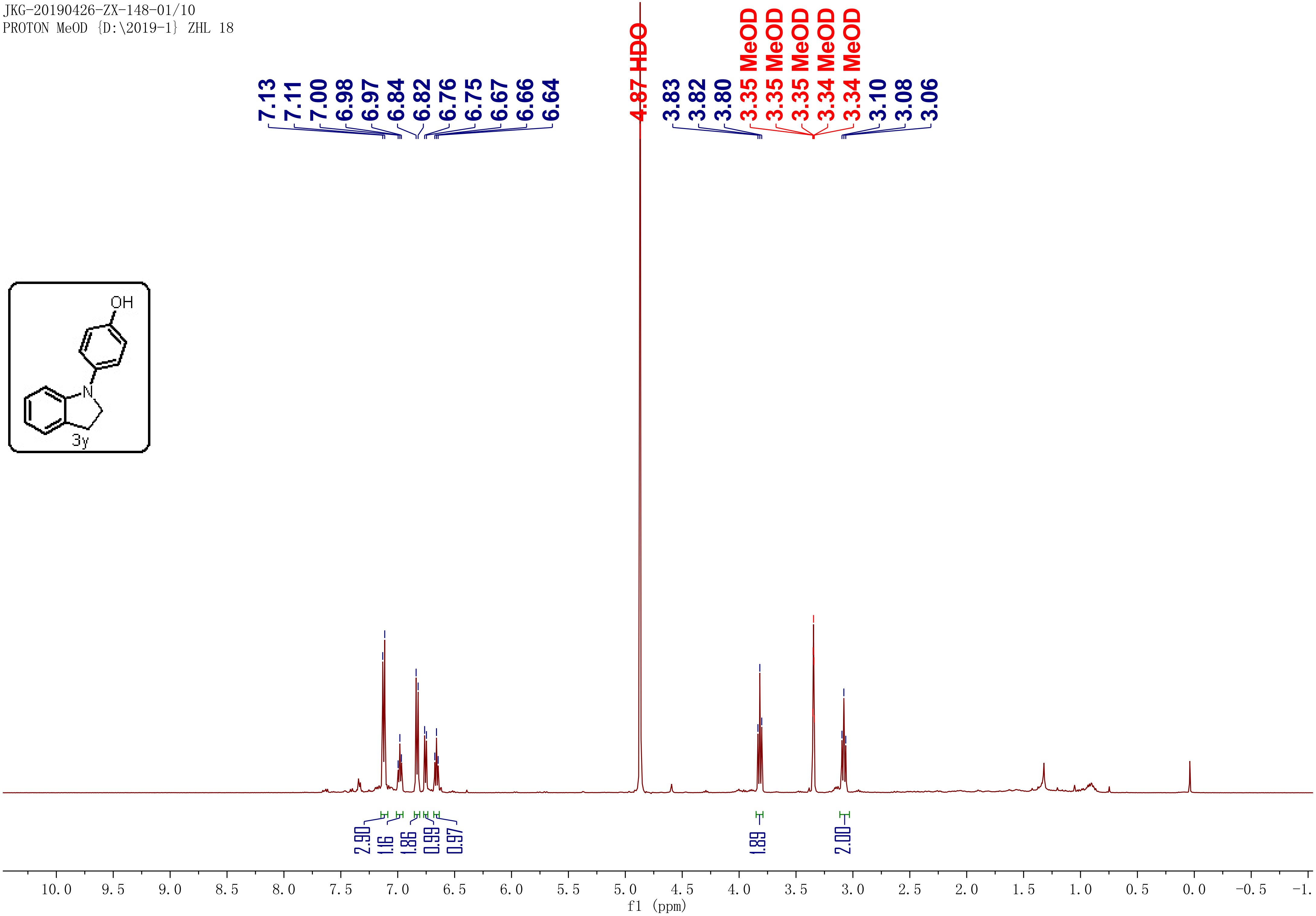


JKG-20190625-ZX-183-05/10
PROTON MeOD {D:\2019-1} ZHL 52

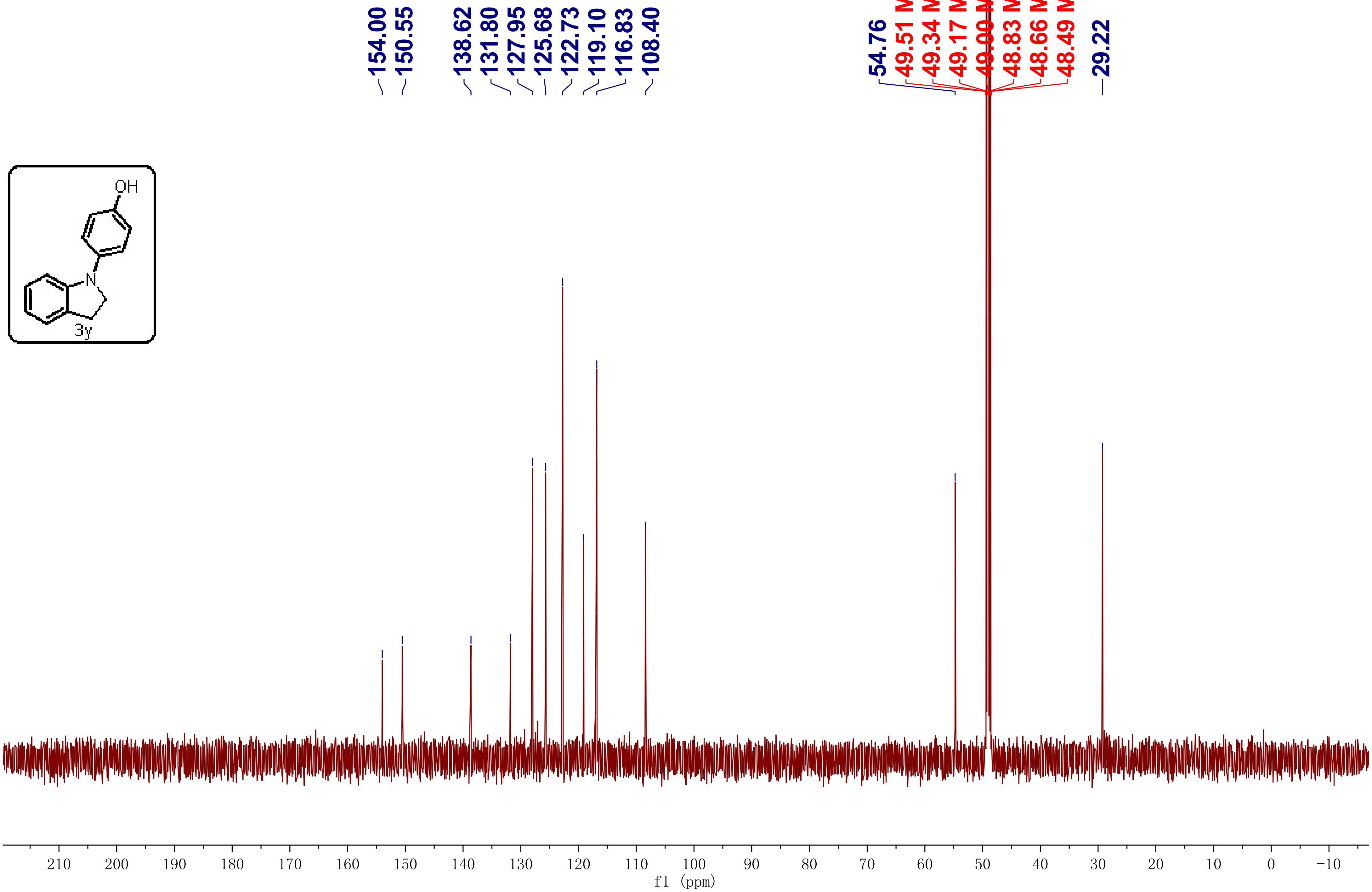



JKG-20190625-ZX-183-05/11
C13CPD MeOD {D:\2019-1} ZHL 52
156.07
151.41
141.96
132.45
129.85
129.43
129.16
128.56
124.74
124.69
121.76
118.07
117.37
115.96
91.01
89.11
49.51 MeOD
49.34 MeOD
49.17 MeOD
49.00 MeOD
48.83 MeOD
48.66 MeOD
48.49 MeOD
40.85
N
HO
3x
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

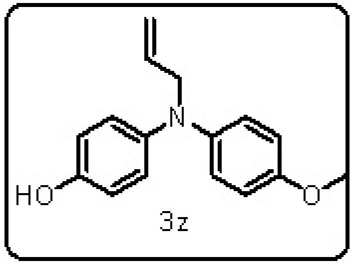
JKG-20190426-ZX-148-01/10
PROTON MeOD {D:\2019-1} ZHL 18

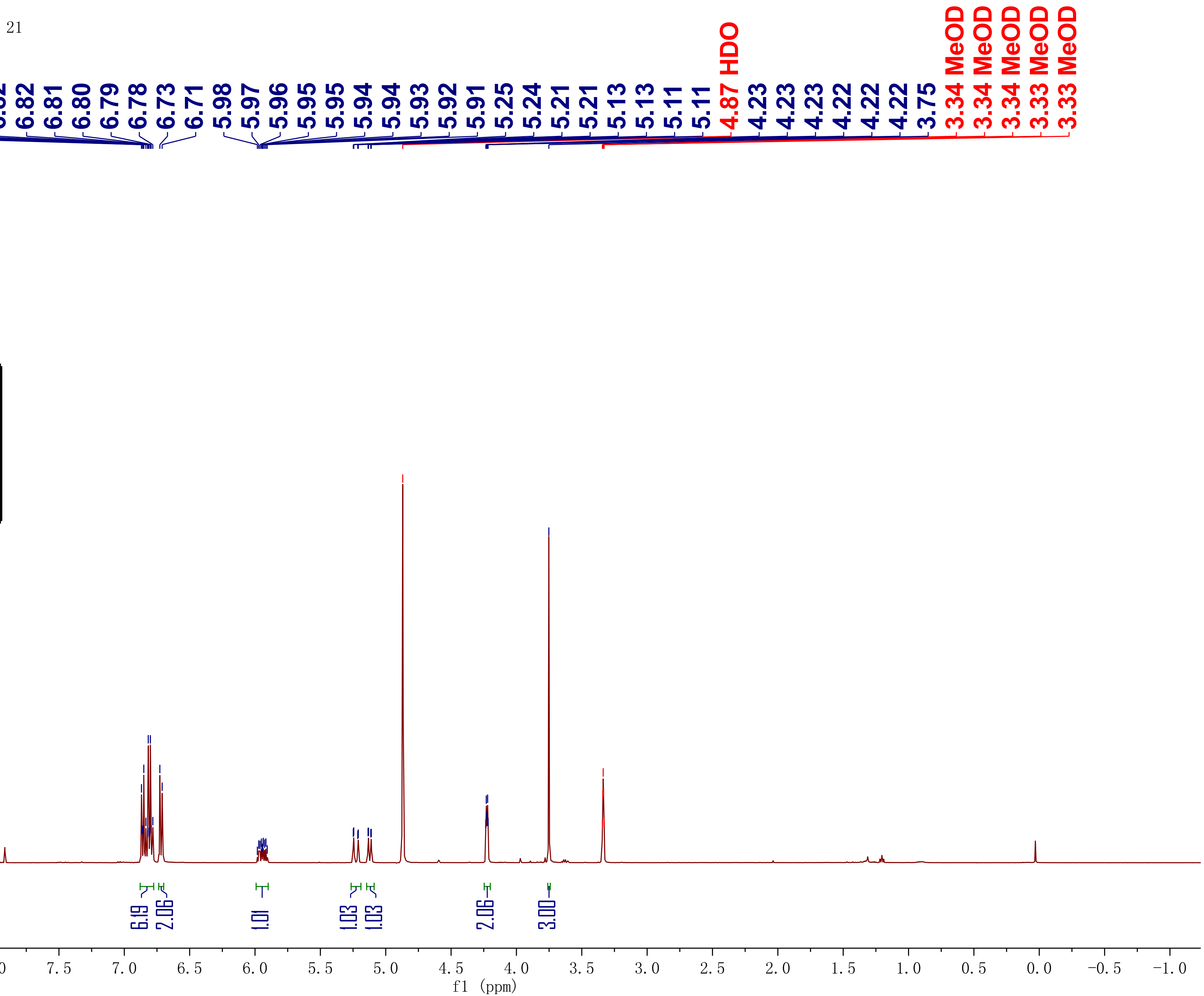


JKG-20190426-ZX-148-01/11
C13CPD MeOD {D:\2019-1} ZHL 18

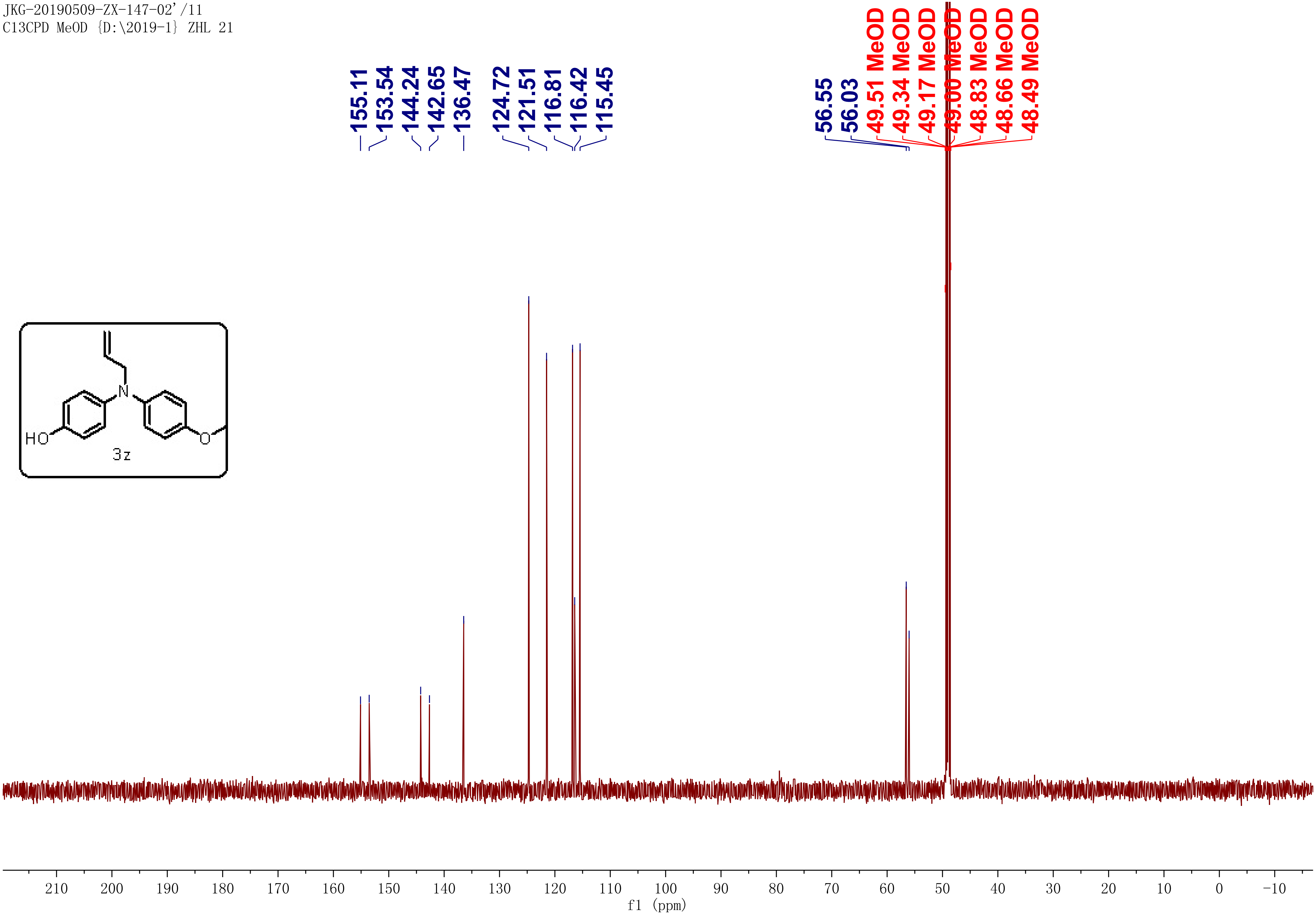


JKG-20190509-ZX-147-02'/10
PROTON MeOD {D:\2019-1} ZHL 21


3z

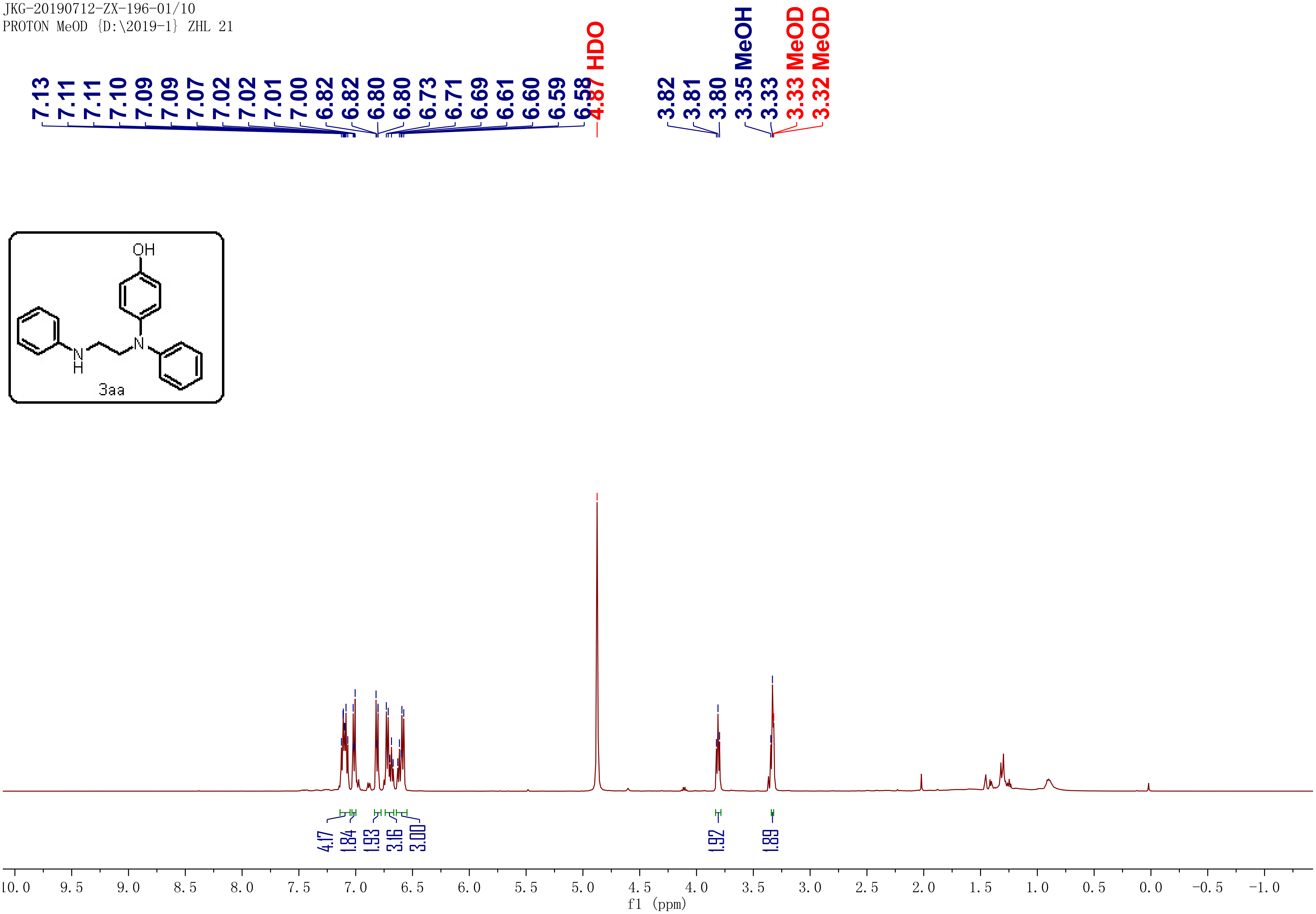


JKG-20190509-ZX-147-02'/11
C13CPD MeOD {D:\2019-1} ZHL 21

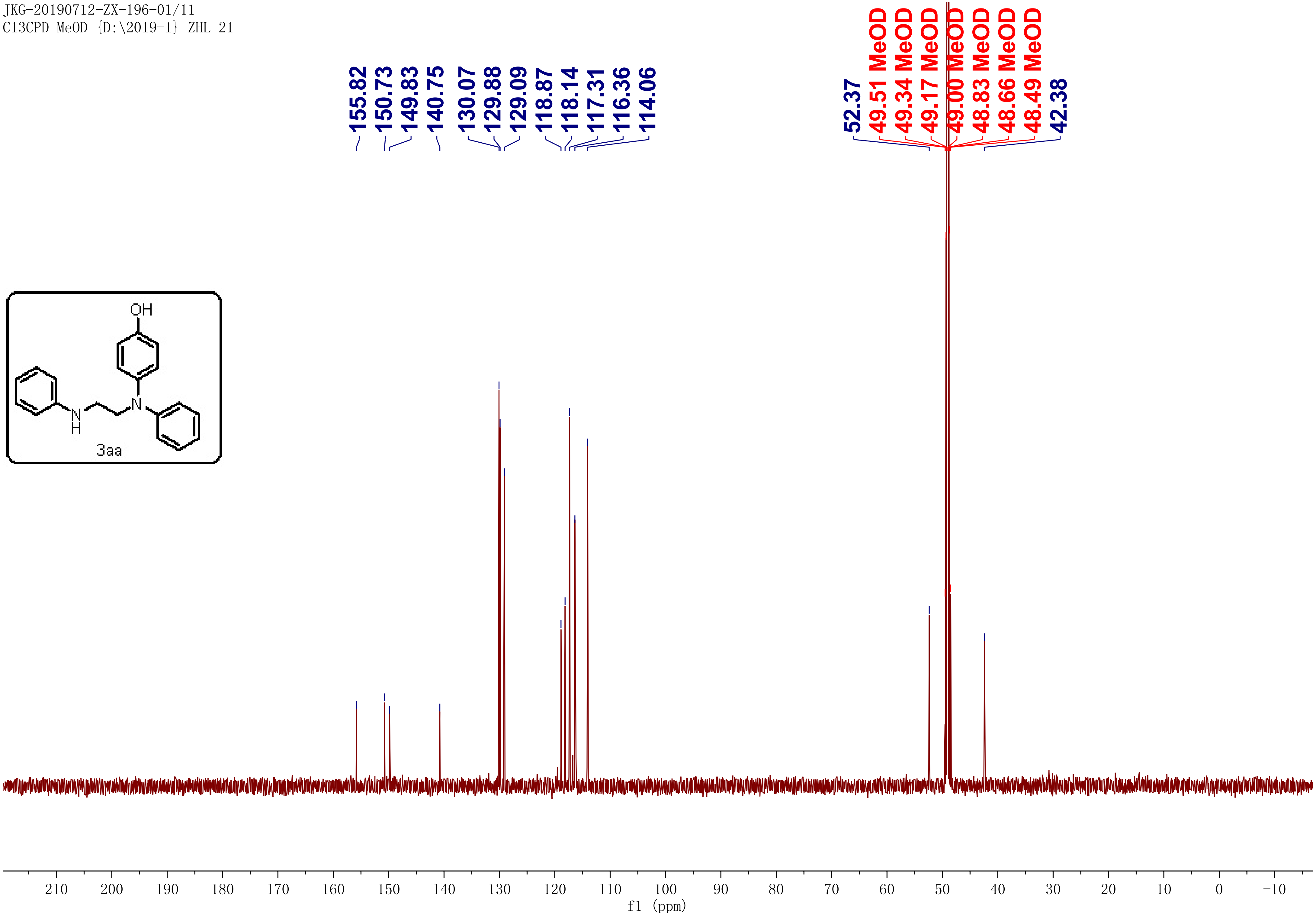



3z

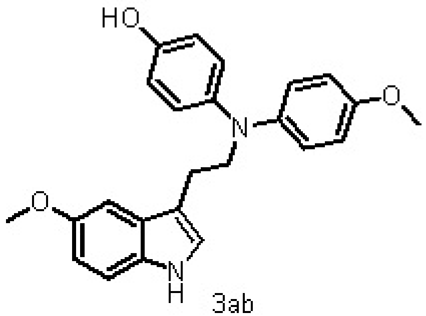
JKG-20190712-ZX-196-01/10
PROTON MeOD {D:\2019-1} ZHL 21



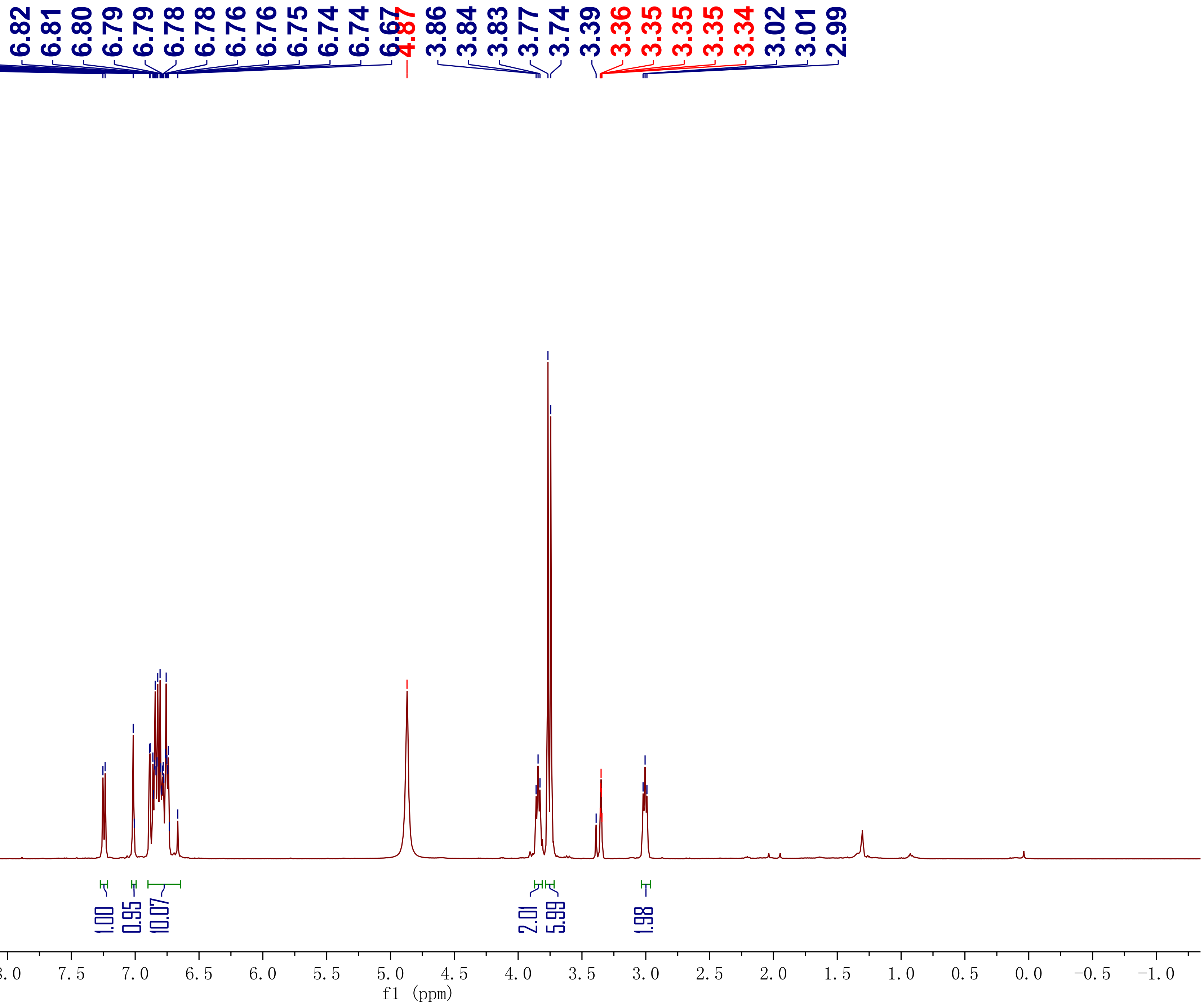
JKG-20190712-ZX-196-01/11
C13CPD MeOD {D:\2019-1} ZHL 21



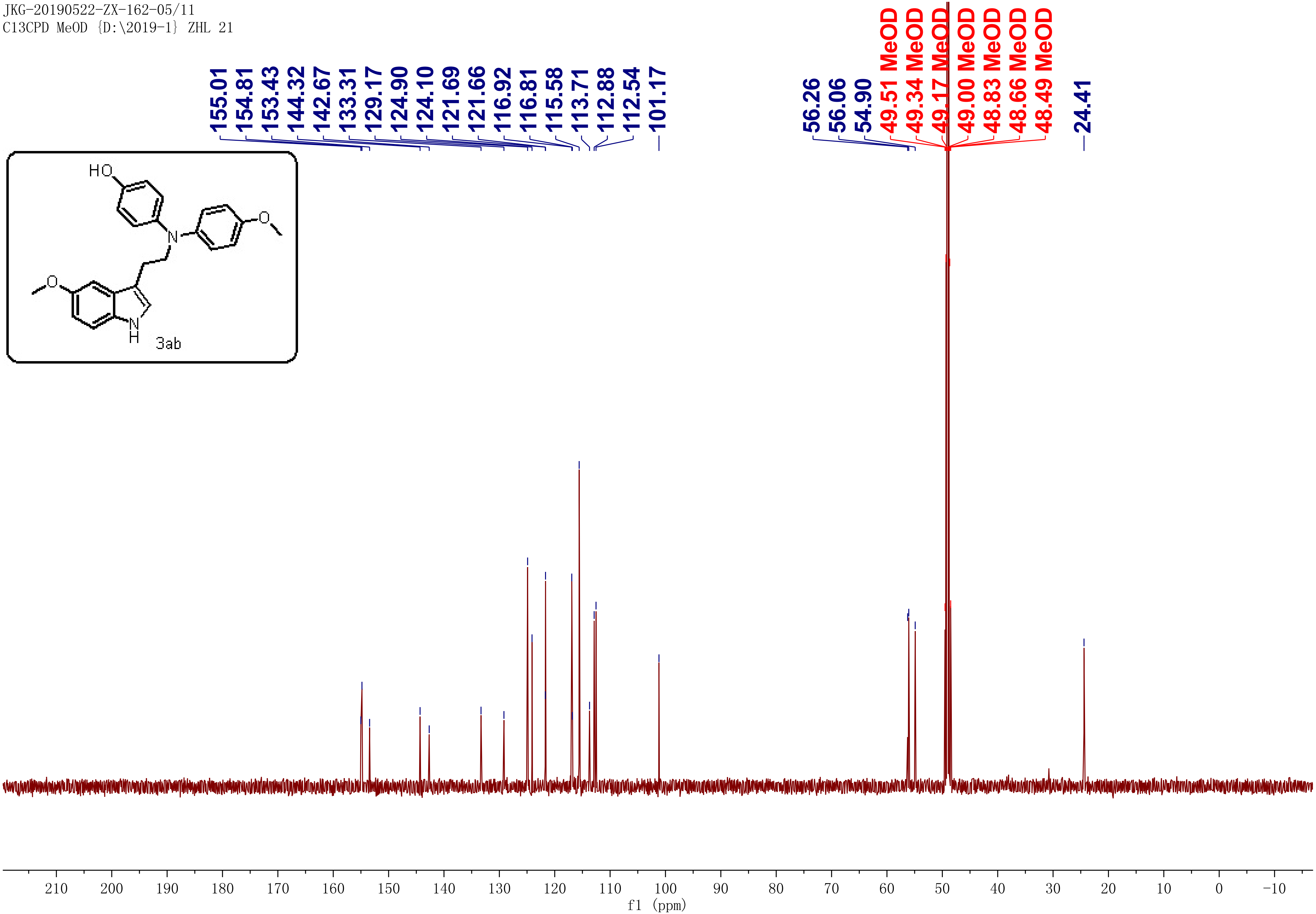
JKG-20190522-ZX-162-05/10
PROTON MeOD {D:\2019-1} ZHL 21



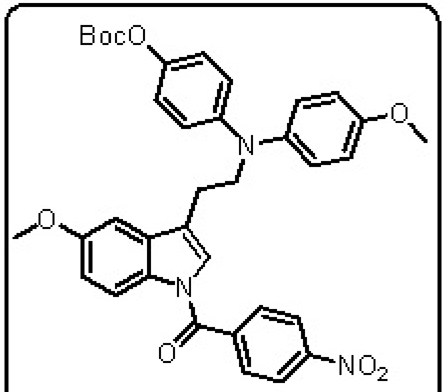
3ab



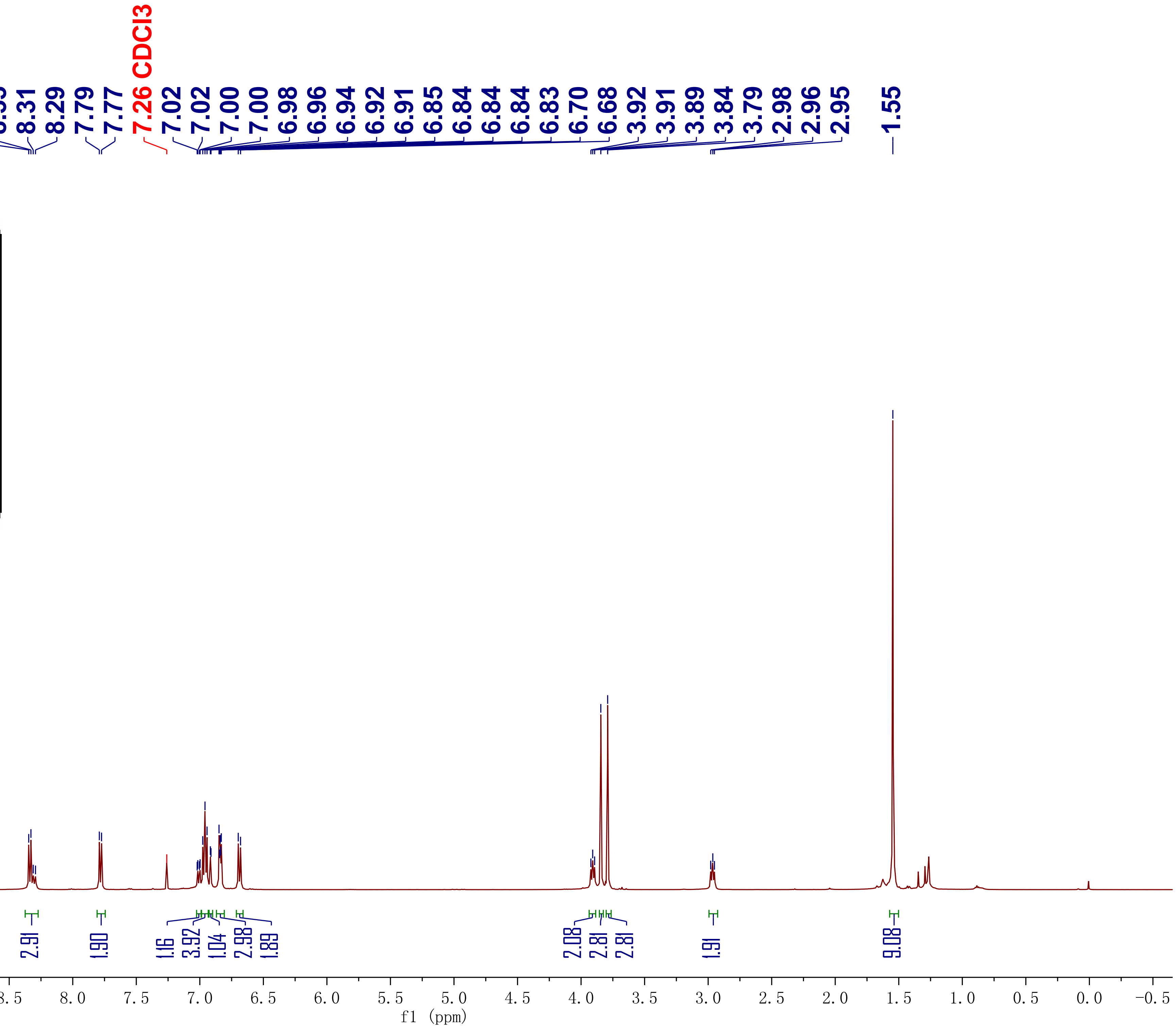
JKG-20190522-ZX-162-05/11
C13CPD MeOD {D:\2019-1} ZHL 21



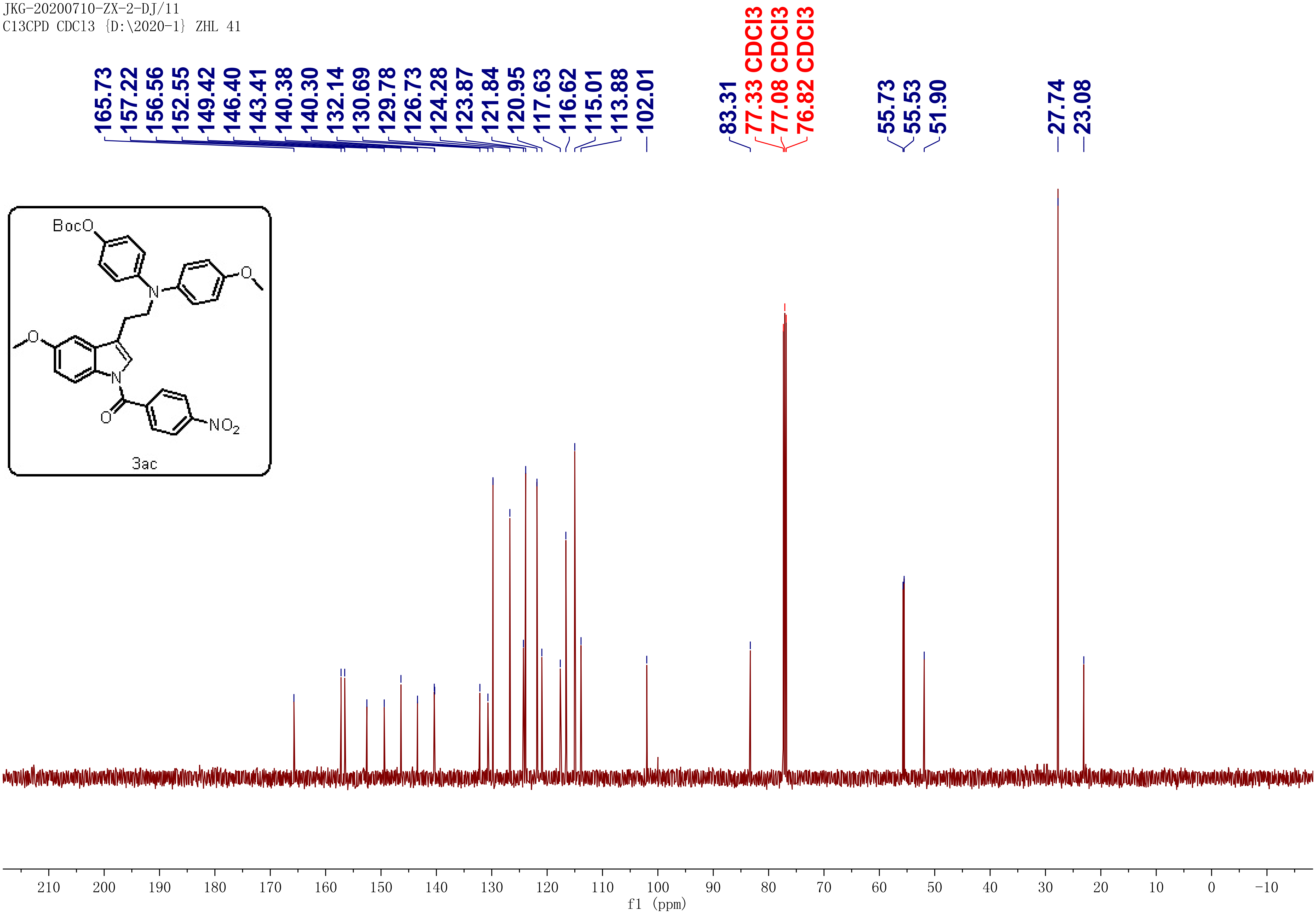
JKG-20200710-ZX-2-DJ/10
PROTON CDCl3 {D:\2020-1} ZHL 41



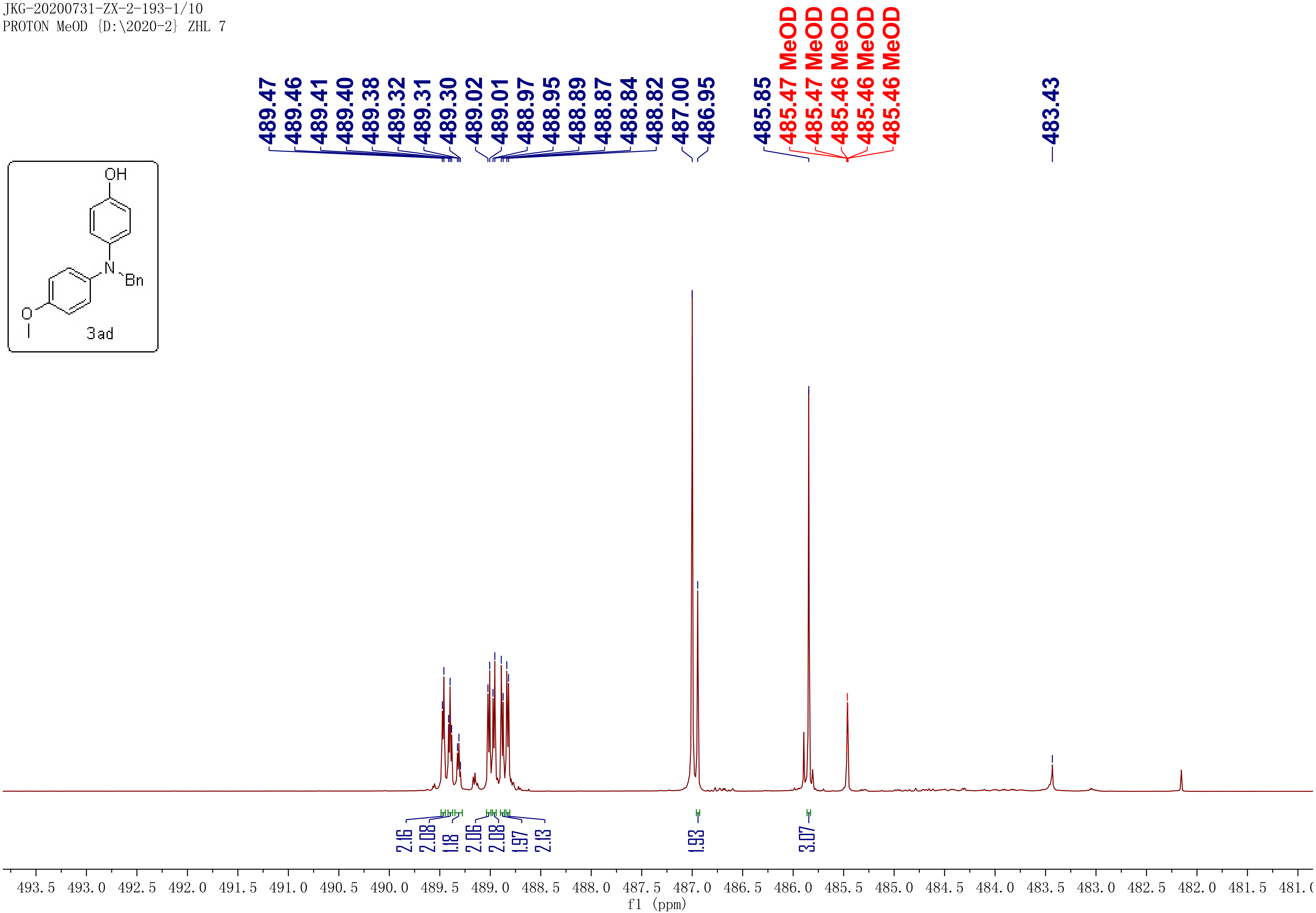
3ac

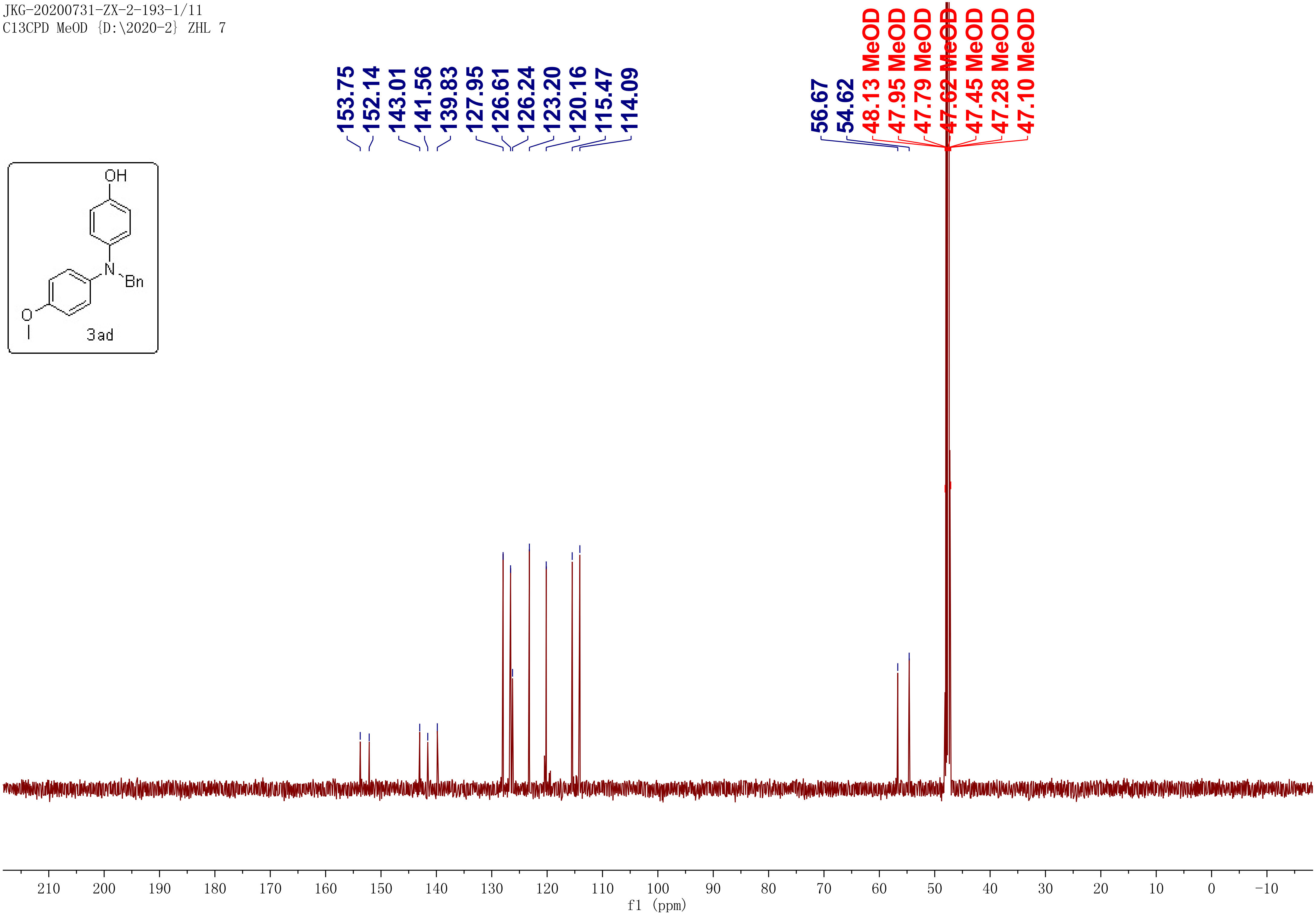


JKG-20200710-ZX-2-DJ/11
C13CPD CDCl3 {D:\2020-1} ZHL 41

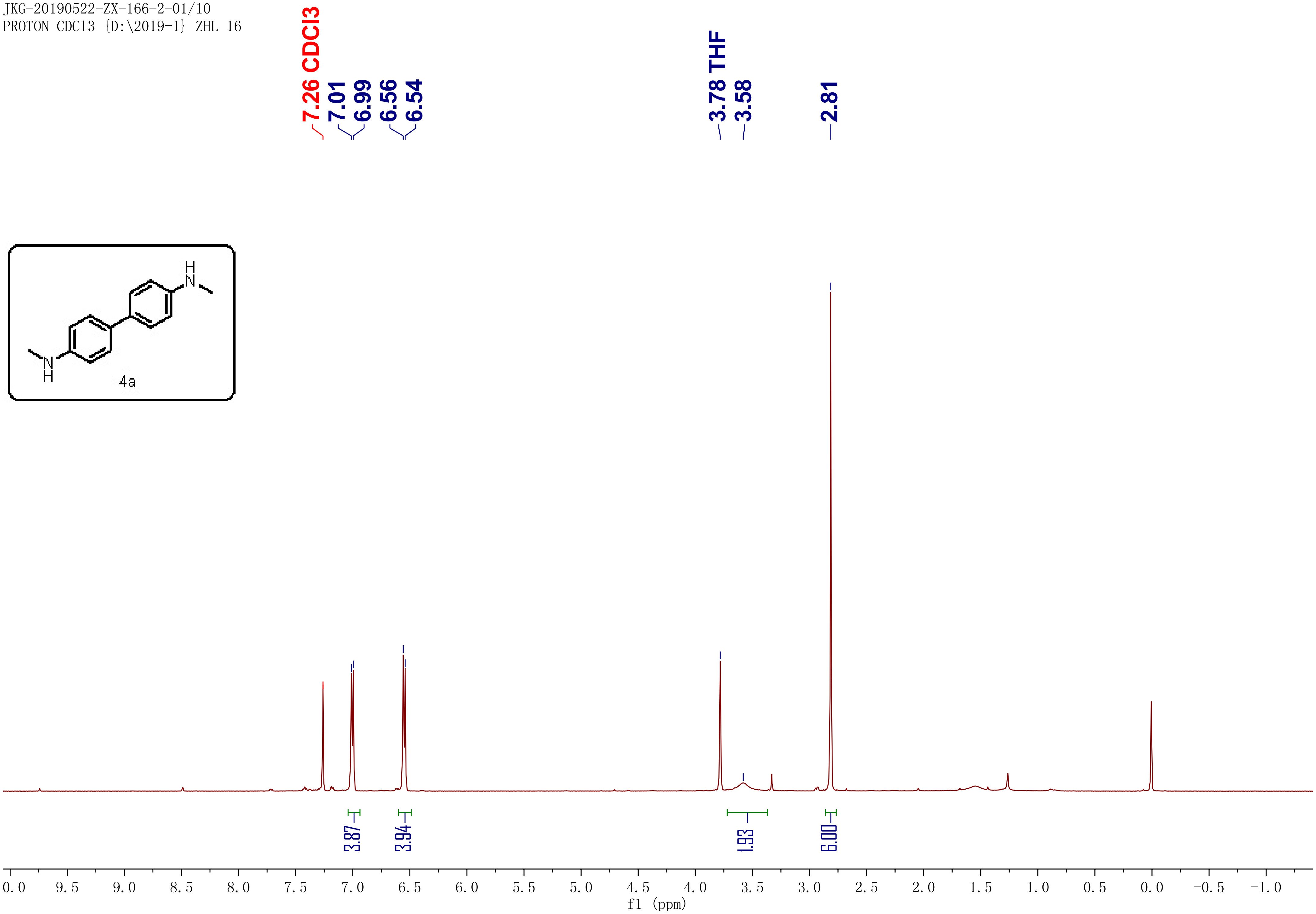


JKG-20200731-ZX-2-193-1/10
PROTON MeOD {D:\2020-2} ZHL 7





JKG-20200731-ZX-2-193-1/11
C13CPD MeOD {D:\2020-2} ZHL 7
153.75
152.14
143.01
141.56
139.83
127.95
126.61
126.24
123.20
120.16
115.47
114.09
56.67
54.62
48.13 MeOD
47.95 MeOD
47.79 MeOD
47.62 MeOD
47.45 MeOD
47.28 MeOD
47.10 MeOD
OH
N
Bn
O
3ad
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)


JKG-20190522-ZX-166-2-01/10
PROTON CDCl3 {D:\2019-1} ZHL 16
7.26 CDCl3
7.01
6.99
6.56
6.54
3.78 THF
3.58
2.81
4a
3.87
3.94
1.93
6.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)