# Supporting information

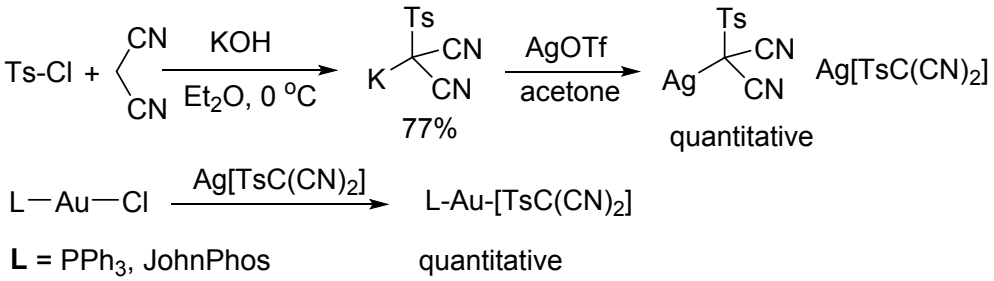
## Table of Contents

# 1. General

All reactions were carried out under ambient atmosphere without protection. Commercial reagents and solvents were obtained from the commercial providers and used without further purification. The products were purified using a commercial flash chromatography system or a regular glass column. TLC was developed on silica gel 60 F254 glass plates.

$^{1}$H NMR (400 MHz) and $^{13}$C NMR (101 MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in δ (ppm) values ($^{1}$H and $^{13}$C NMR relative to $CHCl_3$, δ 7.26 ppm for $^{1}$H NMR and δ 77.0 ppm for $^{13}$C NMR). Or alternatively, $^{1}$H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants (*J*), are reported in Hertz (Hz). GC analyses were performed using a Shimadzu GC-2010 ultra gas chromatography–mass spectrometry instrument equipped with a Shimadzu AOC-20s autosampler.

# 2. Synthesis of L-Au-[TsC(CN)$_2$]




## 2.1 Synthesis of K[TsC(CN)$_2$]

Tosyl chloride (1.9 g, 0.01mol) and malononitrile (0.66 g, 0.01 mol) in 20 mL of $Et_2O$ were added dropwise to a solution of potassium hydroxide (1.12 g, 0.02 mol) in 20 mL of EtOH at 0 °C for 0.5 h, and the resulting solution was stirred for 5 h. After removal of solvent, a light yellow solid was obtained, which was re-dissolved in by acetone, then the acetone solution were filtered to remove potassium chloride. Then excess amount of diethyl ether was added to the filtrate to precipitate the K[TsC(CN)$_2$]. After filtration, the solid was washed with diethyl ether three times (10 mL for each) and dried in vacuum affording the desirable product in a yield of 2.03 g (77%). $^{1}$H NMR (400 MHz, *d*$^{6}$-DMSO) δ 7.34-7.36 (m, 2H), 7.60 – 7.62 (m, 2H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, *d*$^{6}$-DMSO) δ 144.30, 141.95, 129.87, 125.36, 119.85, 43.11, 21.37. High-Resolution ESI(-): calc. for $C_{10}H_7N_2O_2S$ $[M-K]^-$ m/z: 219.0234, found 219.0234.

### 2.2 Synthesis of Ag[TsC(CN)$_2$]

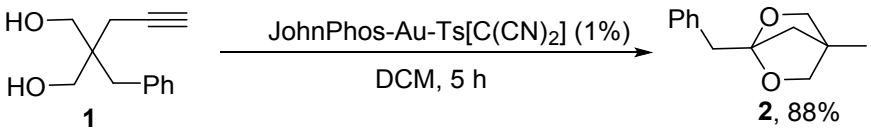
Under stirring, K[TsC(CN)$_2$] (0.258 g, 1 mmol) and AgOTf (0.27g,1.05mmol) was added to dry acetone (5 mL). The suspension was stirred at room temperature for 3 h. Then the reaction mixture was filtered and washed with small amount of acetone. The yellow solid obtained was dried under vacuum to give the product in quantitative yield. $^1$H NMR (400 MHz, $d^6$-DMSO) δ 7.61 (d, $J$ = 8.0 Hz, 2H), 7.35 (d, $J$ = 8.0 Hz, 2H), 2.37 (s, 3H). $^{13}$C NMR (100 MHz, $d^6$-DMSO) δ 143.46, 141.79, 129.54, 124.99, 119.87, 43.11, 20.95. High Resolution ESI(-): calc. for $C_{10}H_7N_2O_2S$ [M-Ag]$^-$ m/z: 219.0234, found 219.0233.

### 2.3 Synthesis of JohnPhos-Au[TsC(CN)$_2$]

Under stirring, JohnPhos-Au-Cl (265 mg, 0.5 mmol) and Ag[TsC(CN)$_2$] (179 mg, 0.55mmol) was added to dry DCM (5 mL). After stirred at room templeture for 2 h, the reaction was filtrate over celite to remove the silver chloride and the excess of Ag[TsC(CN)$_2$]. JohnPhos-Au[TsC(CN)$_2$] was obtained quantitatively by removal of solvent and drying in vacuum. This compound appeared to be a mixture of two rotamers. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, $J$ = 11.4 Hz, 3H), 7.64 – 7.53 (m, 4H), 7.48 (t, $J$ = 7.8 Hz, 1H), 7.36 (dd, $J$ = 25.5, 8.0 Hz, 3H), 7.24 (d, $J$ = 7.1 Hz, 1H), 7.13 (d, $J$ = 7.3 Hz, 1H), 2.47 (d, $J$ = 11.2 Hz, 3H), 1.53 (s, 3H), 1.49 (s, 3H), 1.46 (s, 6H), 1.42 (s, 6H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ 60.64, 57.33. $^{13}$C NMR (100 MHz, $CDCl_3$) δ 149.90, 149.76, 149.64, 149.51, 145.15, 142.65, 142.58, 142.02, 141.95, 141.70, 141.63, 135.01, 133.87, 133.36, 133.29, 133.05, 132.97, 131.24, 130.98, 129.86, 129.66, 129.46, 129.15, 129.09, 129.02, 128.96, 128.69, 128.49, 127.31, 127.24, 127.12, 127.05, 126.08, 125.41, 124.98, 124.64, 124.14, 113.58, 113.53, 46.10, 38.03, 37.92, 37.75, 30.97, 30.91, 30.85, 21.72, 21.55. High Resolution ESI(+): calc. for $C_{30}H_{34}AuN_2O_2PS$ [M]$^+$ m/z: 715.1817, found 715.1820.

## 3. Procedures for Model Reactions

### Gold-Catalyzed Cycloisomerization of Bis-homopropargylic Diols

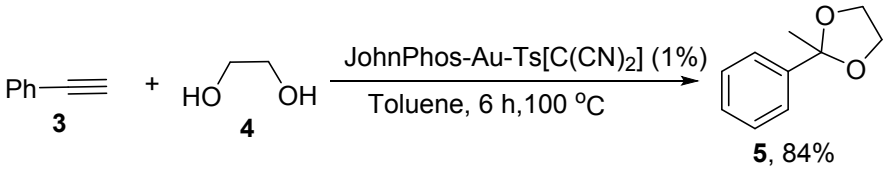



**1** **2**, 88%

A mixture of 2-benzyl-2-(prop-2-yn-1-yl)propane-1,3-diol **1** (0.2 mol, 40.8 mg), JohnPhos-Au[TsC(CN)$_2$] (0.002 mol, 1.42 mg) in dry DCM (0.5 mL) was stirred under argon atmosphere at room temperature. The progress of reaction was monitored by TLC. After the reaction was completed, the reaction was quenched with a drop of $Et_3N$, then the reaction mixture was filtered through a pad of silica pre-impregnated with dichloromethane. The solvent in filtrate was removed in vacuum and the crude residue was purified by silica gel column chromatography to give desired product **2** in 88%yeild.

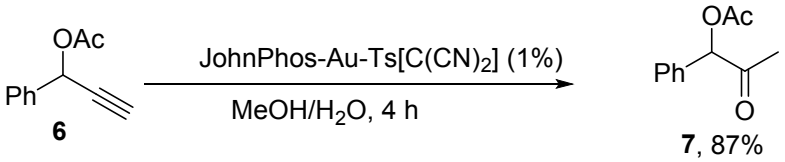
1-Methyl-4-phenyl-2,6-dioxabicyclo[2.2.1]heptane **2**.[1] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 3H), 7.11 (d, *J* = 7.1 Hz, 2H), 3.77 (s, 4H), 2.90 (s, 2H), 1.73 (s, 2H), 1.54 (s, 3H).

## Gold Catalyzed Acetalization of Alkynes.



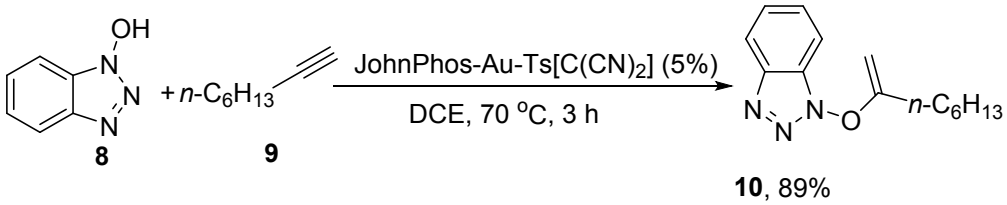

To a mixture of phenylacetylene **3** (1.1 mmol, 112 mg) and the ethane-1,2-diol **4** (1 mmol, 62 mg) in 1 mL of dry toluene was added catalytic amount of JohnPhos-Au[$TsC(CN)_2$] (0.02 mmol, 14.3 mg) under $N_2$ atmosphere. The reaction mixture was stirred at 100 °C and the progress of reaction was monitored by TLC. After the reaction was completed, the reaction was quenched by one drop of $Et_3N$. Then the mixture mixture was filtered through a pad of silica pre-impregnated with dichloromethane. The solvent was removed from filtrate and the crude residue was purified by silica gel column chromatography give desired product. 2-Methyl-2-phenyl-1,3-dioxolane **5**.[2] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.41 – 7.22 (m, 3H), 4.03 (s, 2H), 3.77 (s, 2H), 1.66 (s, 3H).

## Gold-Catalyzed Hydration of Propargyl Acetates



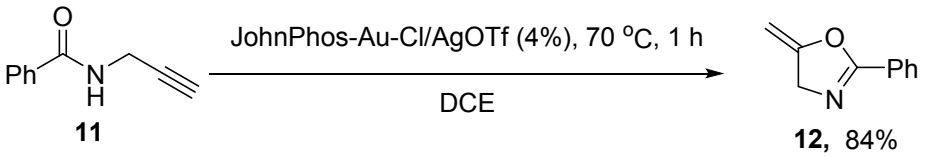

To a stirred solution of 1-phenylprop-2-yn-1-yl acetate **6** (0.5 mmol, 87 mg) and in a mixed solvent (MeOH / water = 4:1) was added JohnPhos-Au[$TsC(CN)_2$] (0.005, 3.57 mg). The reaction mixture was stirred at room temperature and the progress of reaction was monitored by TLC. After the reaction was completed, the mixture was filtered through a pad of silica pre-impregnated with dichloromethane. The solvent was removed from filtrate and the crude residue was purified by silica gel column chromatography give desired. 2-Oxo-1-phenylpropyl acetate **7**.[3] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 5H), 6.00 (s, 1H), 2.22 (s, 3H), 2.14 (s, 3H).

## Gold Catalyzed Addition of N-Hydroxy Heterocycles to Alkynes



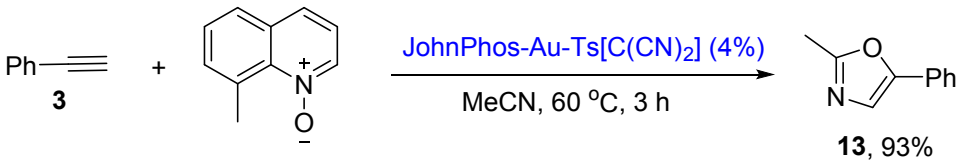

N-hydroxybenzotriazole **8** (45 mg, 0.336 mmol, 1.1 equiv) was added into a solution of the 1-octyne **9** (33.6 mg, 0.306 mmol) and JohnPhos-Au[TsC(CN)$_2$] (7.6 mg, 0.0153 mmol, 5 mol%) in dichloroethane (2mL). The reaction was stirred at the 70 °C, and the progress of reaction was monitored by TLC. After completion, the reaction mixture was filtered through a pad of silica pre-impregnated with dichloromethane. The solvent was removed from the filtrate and the crude residue was purified by silica gel column chromatography to give desired product **10**. 1-(oct-1-en-2-yloxy)-1H-benzo[d][1,2,3]triazole **10**.[4] $^1$H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, $J$ = 8.4 Hz, 1H), 7.63 – 7.53 (m, 1H), 7.50 (d, $J$ = 8.1 Hz, 1H), 7.44 (t, $J$ = 7.6 Hz, 1H), 4.26 (d, $J$ = 3.7 Hz, 1H), 3.63 (d, $J$ = 3.7 Hz, 1H), 2.47 (t, $J$ = 7.6 Hz, 2H), 1.86 – 1.71 (m, 2H), 1.56 – 1.45 (m, 2H), 1.39 (d, $J$ = 3.7 Hz, 4H), 0.95 (t, $J$ = 6.4 Hz, 3H).

## Gold-Catalyzed cycloisomerization of propargyl amide




A glass vial was charged with propargyl amide **1** (0.2 mmol, 31.8 mg) in dry DCE (0.8 mL), followed by the addition of JohnPhos-Au[TsC(CN)$_2$] (0.008 mmol, 5.71 mg). The reaction was allowed to stir at 70 °C and was monitored by TLC. After the reaction was completed, the reaction mixture was filtered through a pad of silica pre-impregnated with dichloromethane. The solvent was removed from the filtrate and the crude residue was purified by silica gel column chromatography give desired product. 5-Methylen-2-phenyl-4,5-dihydrooxazole **12**.[5] $^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, $J$ = 7.8 Hz, 1H), 7.53 (d, $J$ = 7.3 Hz, 1H), 7.46 (t, $J$ = 7.5 Hz, 1H), 4.84 (d, $J$ = 2.8 Hz, 1H), 4.68 (s, 1H), 4.39 (d, $J$ = 2.0 Hz, 1H).

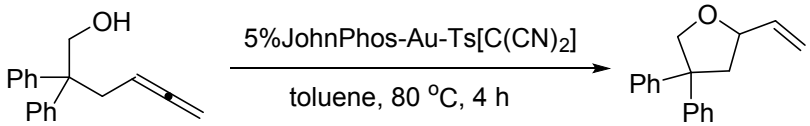
## Gold Catalyzed Oxygen Transfer Reaction.



Phenylacetylene (0.3 mmol, 30.6 mg), 8-Methylquinoline N-oxide (0.39 mmol, 62.1mg), JohnPhos-Au[TsC(CN)$_2$] (0.0012 mmol, 8.5 mg) were added into a small vial with 0.5 mL acetonitrile as solvent. The reaction was conducted at 60 $^o$C and the progress of reaction was monitored by TLC. After the reaction was completed, the reaction mixture was quenched with a drop of $Et_3N$, then was filtered through a pad of silica pre-impregnated with dichloromethane. The solvent was removed from the filtrate and the crude residue was purified by silica gel column chromatography give desired product. 2-Methyl-5-phenyloxazole **13**.[6] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.23 (s, 1H), 2.55 (s, 3H).

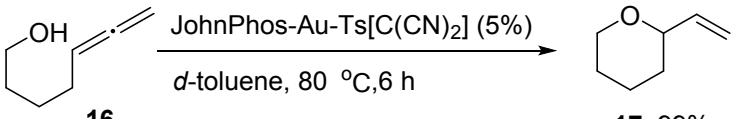
## Gold Catalyzed Intramolecular Addition of Oxygen Nucleophiles to Allenes.

**General procedure.** A mixture of JohnPhos-Au[TsC(CN)$_2$] (0.01mmol,7.14 mg) in dry toluene or toluene-*d*8 (0.4 mL) was stirred at room temperature for 10 min and then a solution of substrate **14** or **16** (0.2 mmol, 1 equiv) in dry toluene or toluene-*d*8 (0.6 mL) was added. The resulting suspension was stirred at 80 $^o$C until completion (monitored by $^1$H NMR or TLC). The reaction mixture was filtered through a pad of silica pre-impregnated with DCM, and the solvent was removed from the filtrate and the crude residue was purified by silica gel column chromatography give desired product.




**14** **15**, 92%

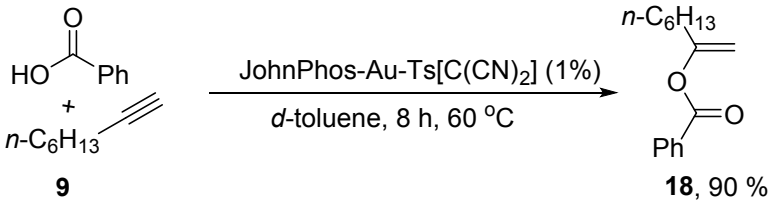
Benzyl 4,4-diphenyl-2-vinylpyrrolidine-1-carboxylate (**15**).[7] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 10H), 5.92 (ddd, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.27 (d, *J* = 17.1 Hz, 1H), 5.13 (d, *J* = 10.3 Hz, 1H), 4.71 (d, *J* = 8.7 Hz, 1H), 4.52 – 4.40 (m, 1H), 4.18 (d, *J* = 8.7 Hz, 1H), 2.74 – 2.62 (m, 1H), 2.48 (dd, *J* = 12.1, 9.8 Hz, 1H).




**16** **17**, 99%

2-Vinyltetrahydropyran (**17**).[7] $^1$H NMR (400 MHz, Tol) δ 5.86 (ddd, *J* = 17.4, 10.7, 4.8 Hz, 1H), 5.31 (dt, *J* = 17.4, 1.8 Hz, 1H), 5.09 – 4.96 (m, 1H), 3.96 – 3.86 (m, 1H), 3.63 (ddd, *J* = 8.7, 4.6, 2.3 Hz, 1H), 3.25 (td, *J* = 11.7, 2.3 Hz, 1H), 1.49 – 1.36 (m, 2H), 1.32 – 1.22 (m, 2H), 1.22 – 1.15 (m, 2H).

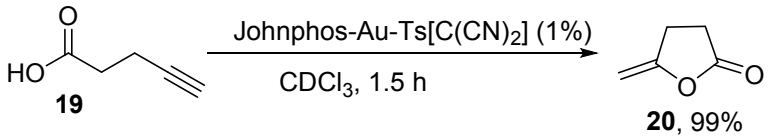
## Gold Catalyzed Addition of Carbonic Acid to Alkyne.




**9** **18**, 90 %

1-Octyne **9** (1 mmol, 110 mg), benzoic acid (1.2 mmol, 146 mg), and JohnPhos-Au[TsC(CN)$_2$] (0.01 mmol, 7.14 mg) were added into a small vial with 0.5 mL d$^8$-toluene as solvent. The reactions were conducted at 60 $^o$C monitored by $^1$H NMR. Oct-1-en-2-yl benzoate **18**.[8]

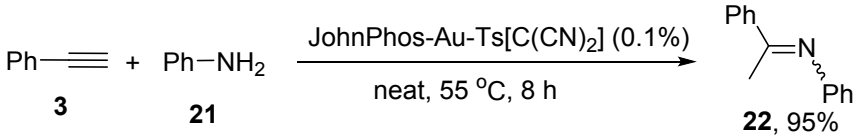
## Gold Catalyzed Intramolecular Addition of Carbonic Acid to Alkyne




**19** **20**, 99%

4-Pentynoic acid **19** (0.45 mmol, 44.1 mg) and JohnPhos-Au[TsC(CN)$_2$] (0.0045 mmol, 3.2 mg) were added into a NMR tube with 0.5 mL $CDCl_3$ as solvent. The reactions were conducted at room temperature and monitored by $^1$H NMR. 5-Methylene-dihydrofuran-2-one (**20**).[9] $^1$H NMR (400 MHz, $CDCl_3$) δ 4.76 (dd, $J$ = 4.3, 2.1 Hz, 1H), 4.33 (d, $J$ = 2.0 Hz, 1H), 2.90 (dd, $J$ = 9.6, 7.5 Hz, 2H), 2.70 (dd, $J$ = 9.8, 7.2 Hz, 2H).

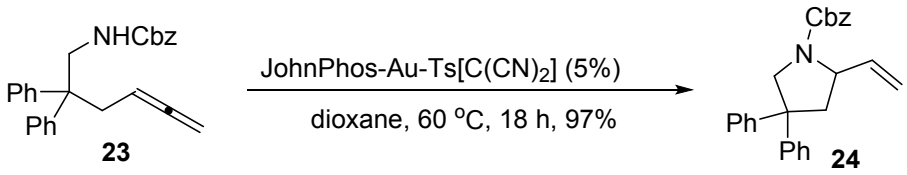
## Gold Catalyzed Hydroamination of Aniline with Phenylacetylene.




**3** **21** **22**, 95%

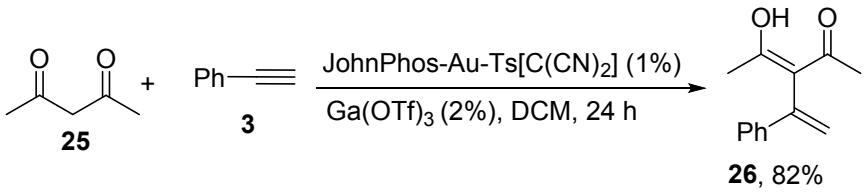
A mixture of aniline **21** (4.5 mmol, 0.419 g), phenylacetylene **3** (5.4 mmol, 0.551 g) and JohnPhos-Au[TsC(CN)$_2$] (0.0045 mmol, 3.2 mg) was added to a 10 mL glass vial, and resultant mixture was stirred at 55 $^o$C. An aliquot (ca. 3 μL) from reaction mixture was dissolved in $CDCl_3$ (0.5 mL) and was analyzed by $^1$HNMR to monitor the progress of the reaction. Phenyl(1-phenylethyl)amine (**22**).[10] $^1$H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.93 (m, 2H), 7.57 – 7.44 (m, 3H), 7.36 (dt, $J$ = 8.6, 5.2 Hz, 2H), 7.21 – 7.10 (m, 1H), 6.83 (t, $J$ = 6.3 Hz, 2H), 2.27 (s, 3H).

## Intramolecular Addition of Amine to Allene.



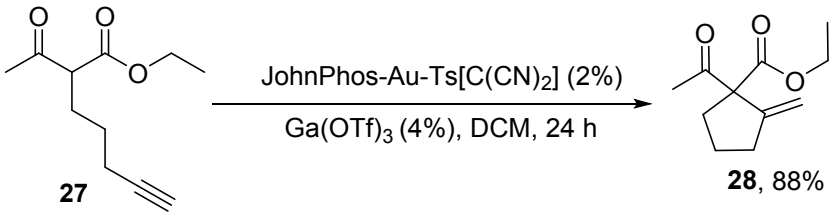

A mixture of JohnPhos-Au[TsC(CN)$_2$] (7.14 mg, 0.01 mmol, 5 mol%) in dry toluene or toluene-*d*8 (0.4 mL) was stirred at room temperature for 10 min and then a solution of substrate **23** (0.2 mmol, 1 equiv) in dry toluene or toluene-*d*8 (0.6 mL) was added. The resulting suspension was stirred at 80 °C until completion (monitored by $^1$H NMR or TLC). The reaction mixture was filtered through a pad of silica pre-impregnated with DCM, and the solvent was removed from filtrate and the crude residue was purified by silica gel column chromatography give desired product. 4,4-Diphenyl-2-vinyltetrahydrofuran (**24**).[7] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.17-7.43 (m, 15 H), 5.81 (td, *J* = 17.3, 10.2 Hz, 1H), 5.29 (dd, *J* = 36.2, 14.7 Hz, 1H), 5.21 – 5.10 (m, 2H), 5.07 (dd, *J* = 11.9, 7.2 Hz, 1H), [4.79 (d, *J* = 10.8 Hz, ), 4.64 (d, *J* = 11.3 Hz, ), 1:1, 1 H], 4.24 – 4.10 (m, 1H), [3.75 (d, *J* = 8.9 Hz), 3.72 (d, *J* = 9.1 Hz, ), 1:1, 1 H ], 2.93 – 2.81 (m, 1H), [2.53 – 2.46 (m), 2.43 (dd, *J* = 18.1, 8.3 Hz, ), 1:1, 1 H].

## Gold-Catalyzed Nakamura Reaction.



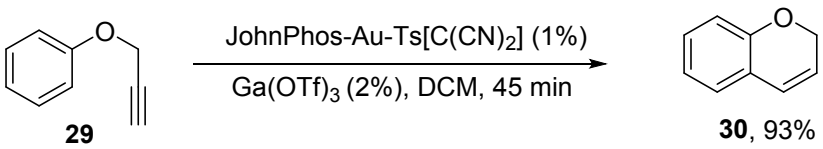

A glass vial was charged with 2,4-pentadione **25** (40 mg, 0.4 mmol) and phenylacetylene **3** (81.6 mg, 0.8 mmol) in dry DCM (0.8 mL), then JohnPhos-Au[TsC(CN)$_2$] (0.004 mol, 3 mg) and Ga(OTf)$_3$ (0.008 mol, 4.1 mg) was added. The vial was allowed to stir at room temperature and the progress of reaction was monitored by TLC. After the reaction was completed, the reaction mixture was filtered through a pad of silica pre-impregnated with dichloromethane, the solvent was removed from filtrate and the crude residue was purified by silica gel column chromatography to give desired product. 3-Acetyl-2-phenyl-1-penten-4-one (**26**).[11] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.35 (m, *J* = 10.9, 10.0, 5.4 Hz, 3H), 5.94 (s, 1H), 5.27 (s, 1H), 2.02 (s, 6H).

## Gold(I) Catalyzed Conia-ene Reaction



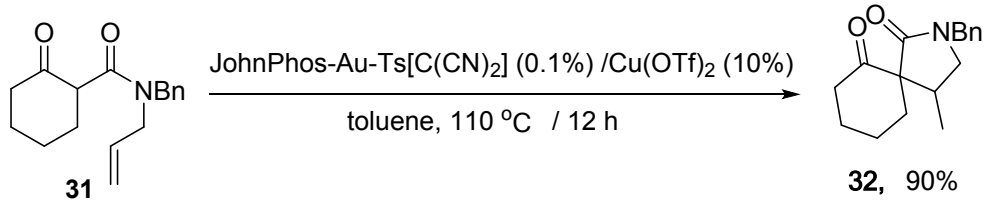

To a solution of ethyl 2-acetylhept-6-ynoate **27** (0.4 mmol, 78.4 mg) in dry DCM (1 mL), $Ga(OTf)_3$ (0.016 mmol, 8.3 mg) and JohnPhos-Au[$TsC(CN)_2$] (0.008 mol, 5.7 mg) was added. The reaction mixture was stirred at rt and the progress of reaction was monitored by TLC. After the reaction was completed, the reaction mixture was filtered through a pad of silica pre-impregnated with DCM. The solvent was removed from filtrate and the crude residue was purified by silica gel column chromatography give desired product. Ethyl 1-(1-Oxoethyl)-2-methylenecyclopentanecarboxylate (**28**).[12] $^1$H NMR (400 MHz, $CDCl_3$) δ 5.31 (t, *J* = 2.1 Hz, 1H), 5.25 (t, *J* = 2.3 Hz, 1H), 4.23 (qd, *J* = 7.1, 1.0 Hz, 2H), 2.44 (m, *J* = 13.7, 9.5, 5.7, 3.2 Hz, 3H), 2.24 (s, 3H), 2.22 – 2.14 (m, 1H), 1.73 (m, *J* = 10.5, 7.0, 3.4 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H).

## Hydroarylation of Alkynes




Under stirring, to a stirred solution of 3,4-methylenedioxyphenyl propargyl ether **29** (0.25 mmol, 63 mg) in dry DCM (0.5 mL), $Ga(OTf)_3$ (0.005 mmol, 2.6 mg) and JohnPhos-Au[$TsC(CN)_2$] (0.0025 mmol, 1.8 mg) were added. The reaction mixture was stirred at rt, and the progress of reaction was monitored by TLC. After the reaction was completed, the reaction mixture was filtered through a pad of silica pre-impregnated with dichloromethane. The solvent was removed from filtrate and the crude residue was purified by silica gel column chromatography give desired product. 6,7-methylendioxy-2H-1-benzopyrane (**30**).[13] $^1$H NMR (400 MHz, $CDCl_3$) δ 6.50 (s, 1H), 6.42 (s, 1H), 6.34 (d, *J* = 9.7 Hz, 1H), 5.91 (s, 2H), 5.69 (dt, *J* = 9.7, 3.7 Hz, 1H), 4.73 (dd, *J* = 3.7, 1.7 Hz, 2H).

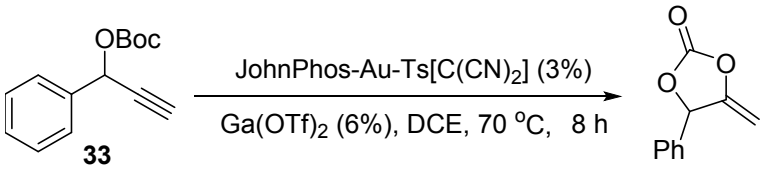
## Gold Catalyzed Hydroalkylation of Olefin




**31** **32,** 90%

In a 5.0 mL round bottom flask containing steering bar, ene-β-ketoamide (0.4 mmol, 108.4 mg) in 1mL dry toluene was added to $Cu(OTf)_2$ (0.04mmol, 14.4mg) and JohnPhos-Au[$TsC(CN)_2$] (0.0004mmol,0.3mg) under argon atmosphere, The reaction was conducted at 110℃and monitored by TLC. After the reaction was completed then filtered through a pad of silica pre-impregnated with dichloromethane,The solvent was removed and the crude residue was purified by silica gel column chromatography to give the product. 2-Benzyl-4-methyl-2-azaspiro[4,5]decane-1,6-dione (**32**).[14]
Major diastereomer $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.28 (dd, *J* = 14.2, 7.0 Hz, 3H), 4.49 (q, *J* = 15.0 Hz, 2H), 3.16 (t, *J* = 8.5 Hz, 1H), 3.03 (t, *J* = 9.1 Hz, 1H), 2.68 – 2.56 (m, 1H), 2.39 – 2.14 (m, 4H), 2.02 – 1.81 (m, 3H), 1.82 – 1.69 (m, 1H), 1.12 (d, *J* = 7.0 Hz, 3H). Minor diastereomer: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 5H), 4.50 (d, *J* = 14.7 Hz, 1H), 4.41 (d, *J* = 14.7 Hz, 1H), 3.27 (t, *J* = 8.4 Hz, 1H), 3.11 (td, *J* = 12.7, 5.8 Hz, 1H), 3.01 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.73 (t, *J* = 8.4 Hz, 1H), 2.50 (d, *J* = 13.8 Hz, 1H), 2.27 (t, *J* = 12.6 Hz, 1H), 2.17 – 1.97 (m, 1H), 1.81 – 1.64 (m, 3H), 0.95 (d, *J* = 6.9 Hz, 3H).

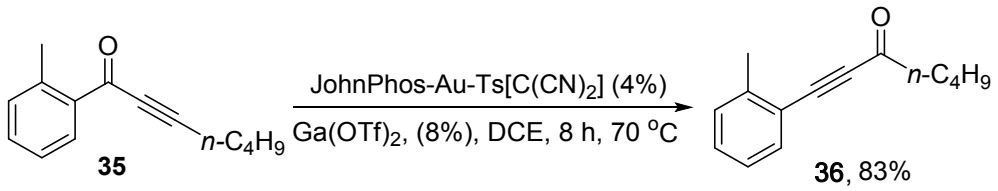
## Cyclization of Propargylic *tert*-Butylcarbonates




**33** **34**, 91%

To a solution of JohnPhos-Au[$TsC(CN)_2$] (0.012mmol,8.5mg) and $Ga(OTf)_3$ (0.024mmol12.3mg) in dry 1,2-dichloroethane (1.5mL) at room temperature under $N_2$ atmosphere was added propargylic tert-butylcarbonate(0.4mmol,92.8mg). The reaction mixture stirred at 70 °C until judged completed by TLC. Then filtered through a pad of silica pre-impregnated with dichloromethane. The solvent was removed and the crude residue was purified by silica gel column chromatography give desired product. 4-methylene-1,3-dioxolan-2-one (**34**).[15] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.52 (s, 3H), 1.84 – 1.73 (m, 2H), 1.43 (dd, *J* = 14.7, 7.4 Hz,2H), 0.98 (t, *J* = 7.2 Hz, 3H).

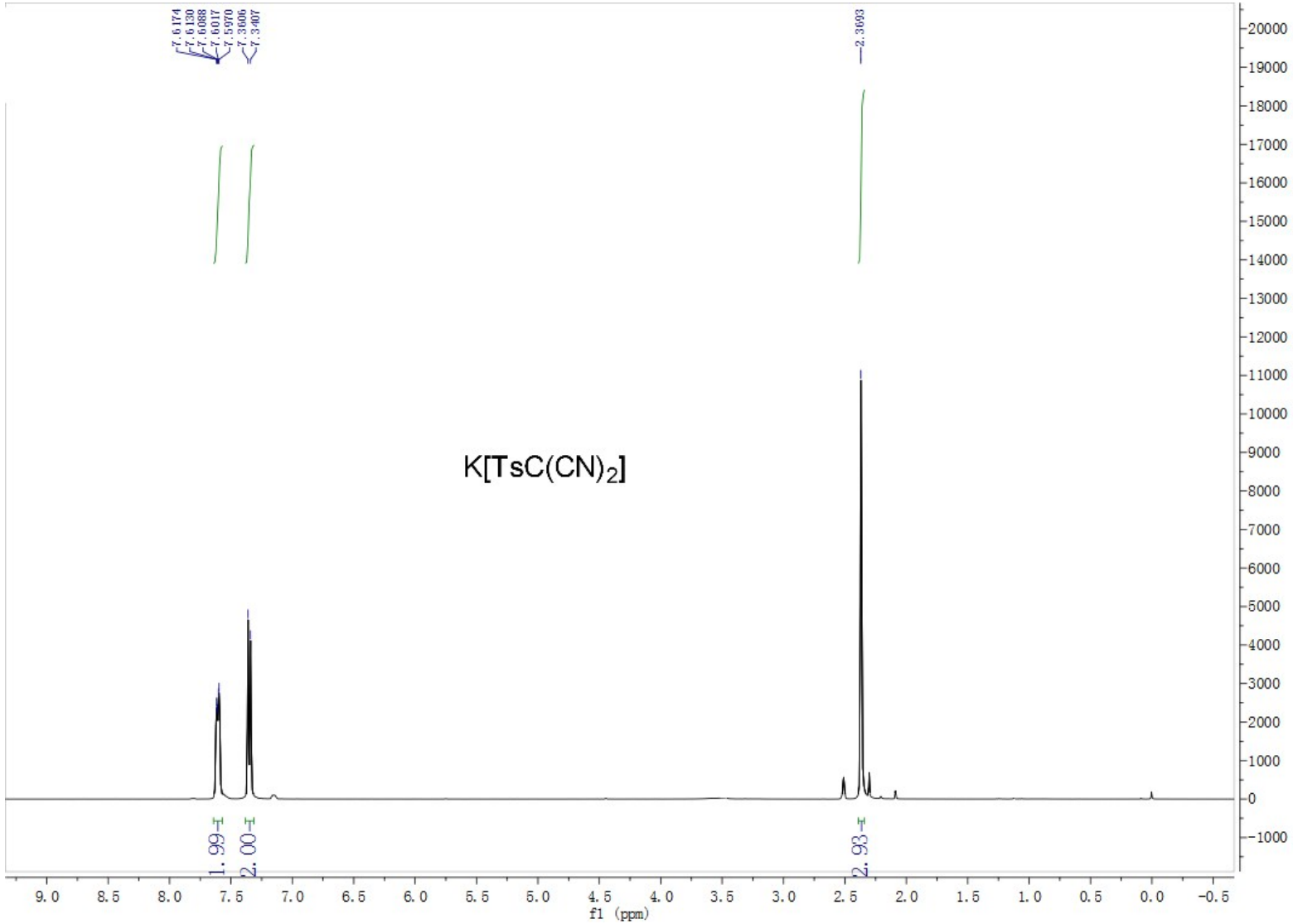
## Gold-Catalyzed 1,3-Transposition of Ynones

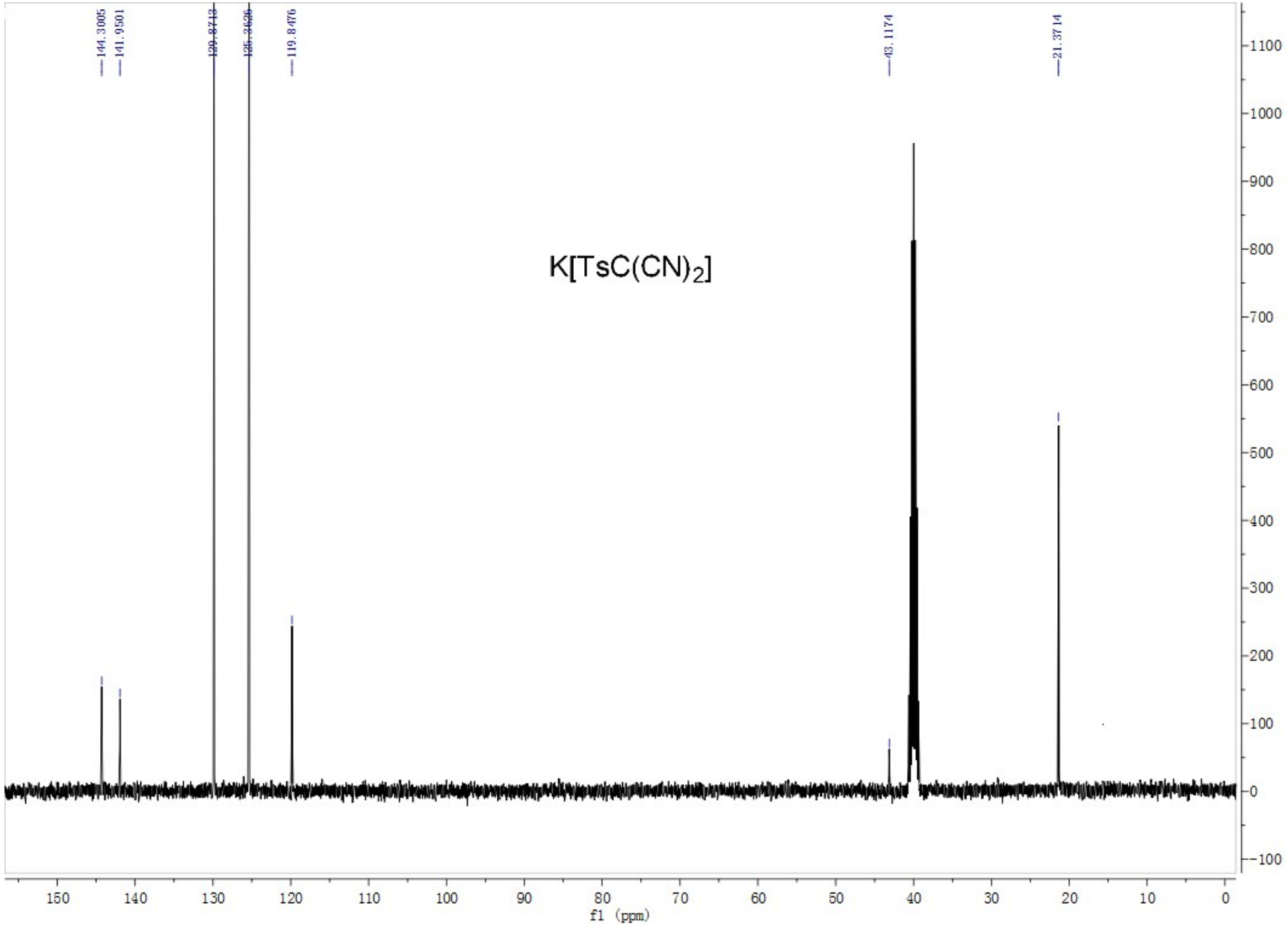



**35** **36**, 83%

An oven dried10 mL V-shape vial equipped with magnetic stir bar was loaded with JohnPhos-Au[TsC(CN)$_2$] (0.016 mmol, 11.42 mg), Ga(OTf)$_3$ (0.032mmol,16.5mg) and dry 1,2-dichloroethane (1.5 mL) was added and reaction mixture was stirred for 5 min at room temperature $N_2$ atmosphere.1-o-tolylhept-2-yn-1-one (0.4 mmol, 80 mg) as a solution in dry 1,2-dichloroethane(1 mL) was then added through injection syringe and the reaction mixture stirred at70°Cuntil judged completed by TLC. Then filtered through a pad of silica pre-impregnated with dichloromethane. The solvent was removed and the crude residue was purified by silica gel column chromatography give desired product. 1-o-tolylhept-1-yn-3-one (**36**).[16] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.52 (s, 3H), 1.84 – 1.73 (m, 2H), 1.43 (dd, *J* = 14.7, 7.4 Hz,2H), 0.98 (t, *J* = 7.2 Hz, 3H).

## 4. Copies of NMR Spectra.

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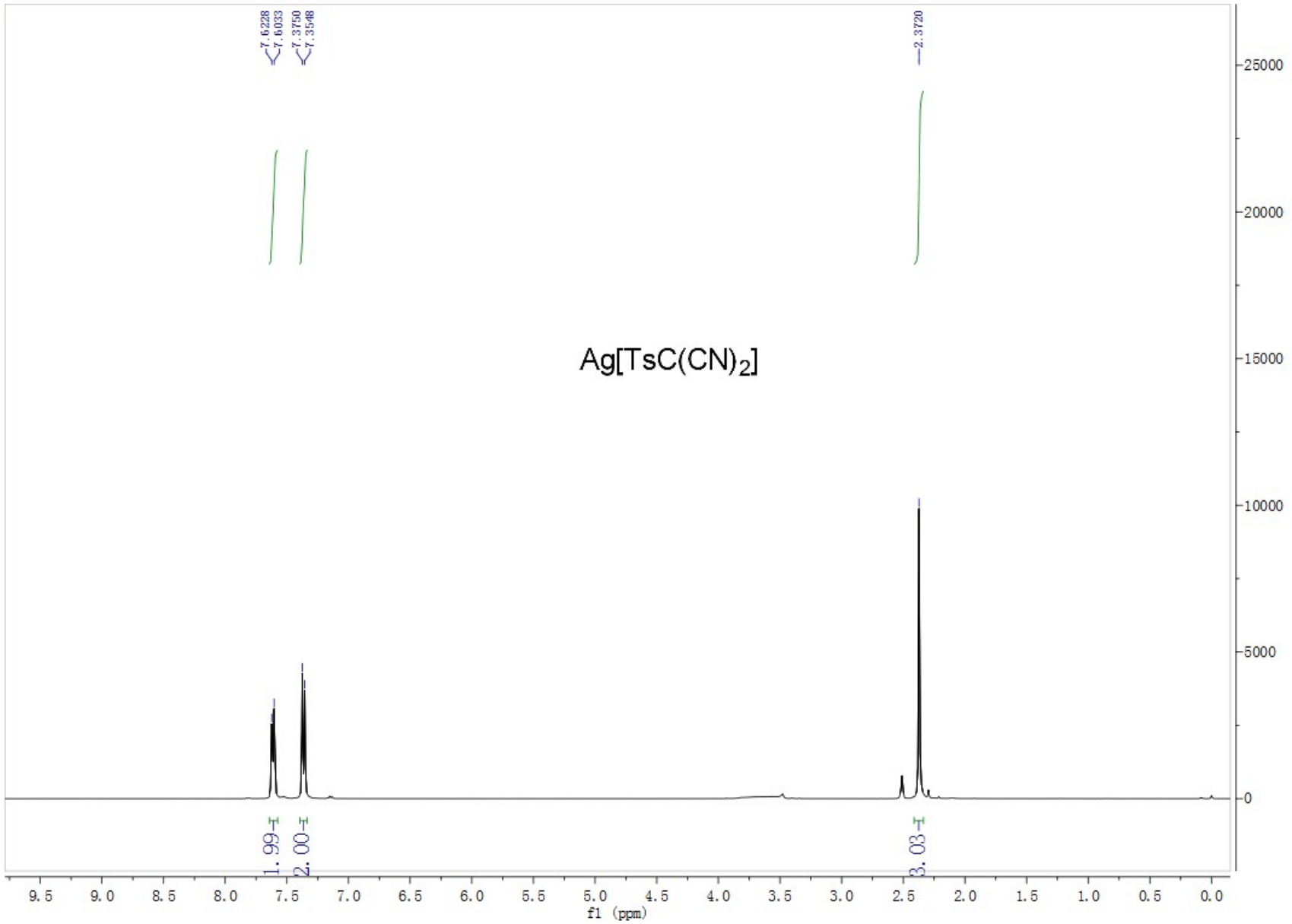
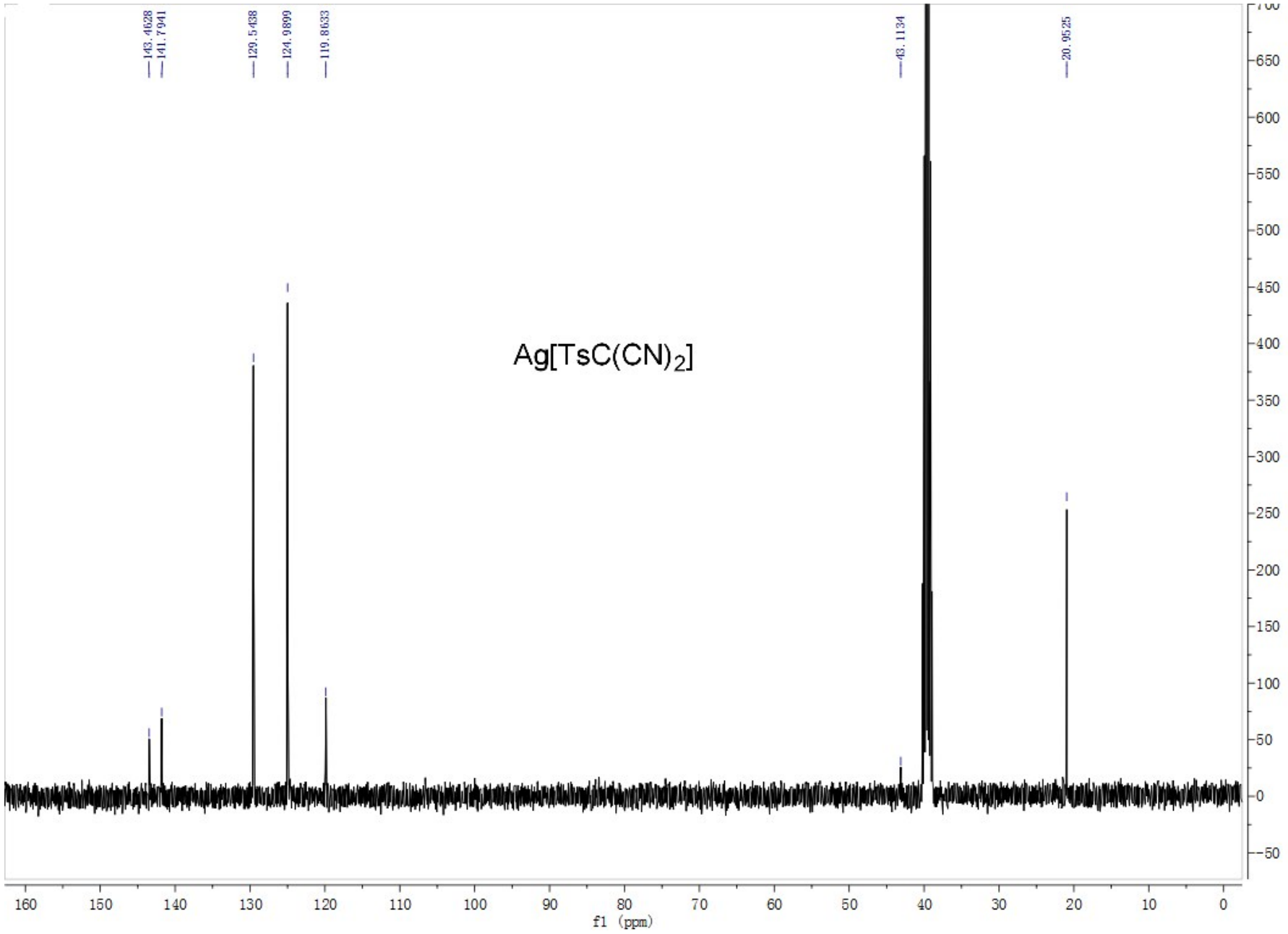
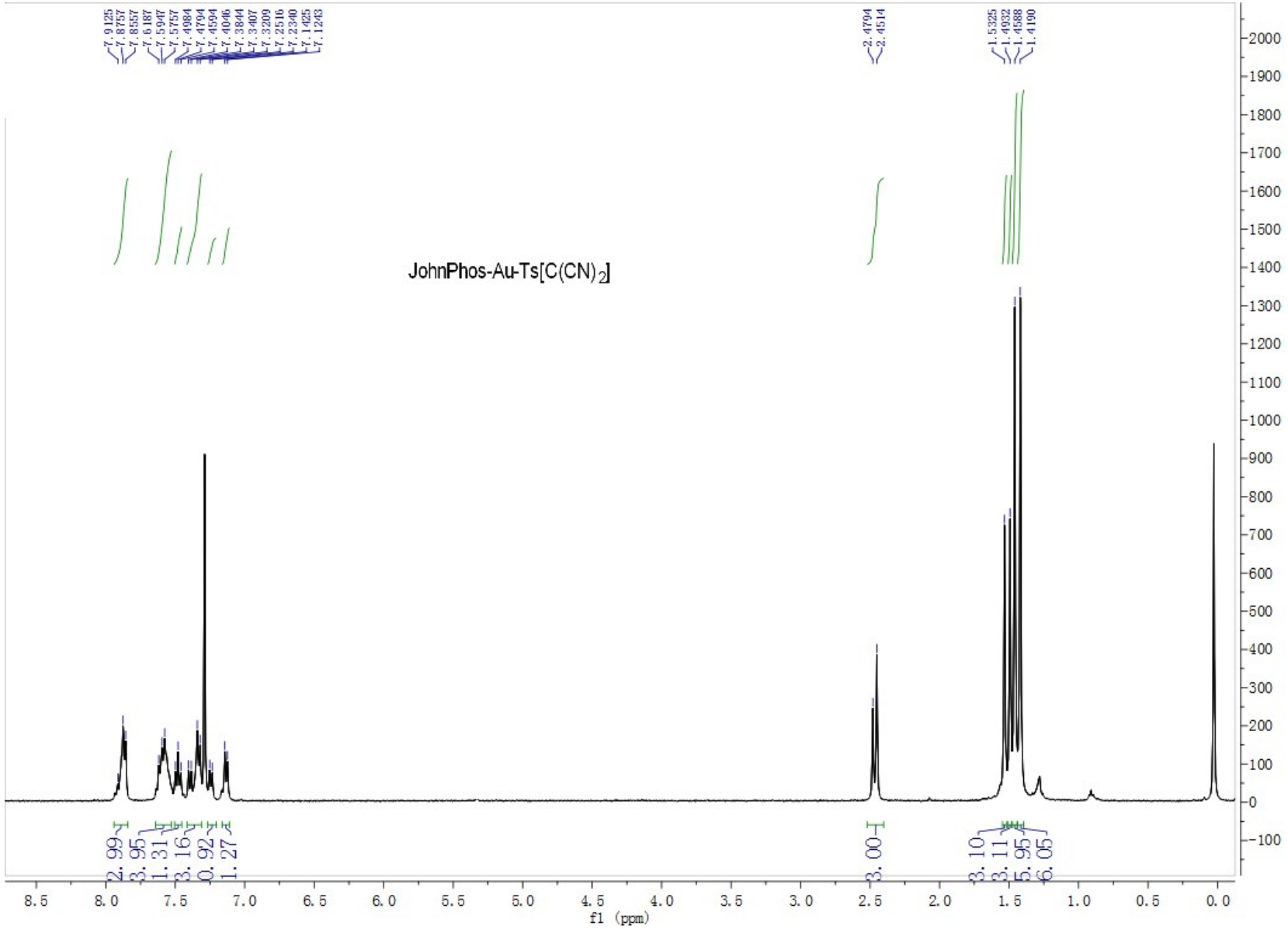
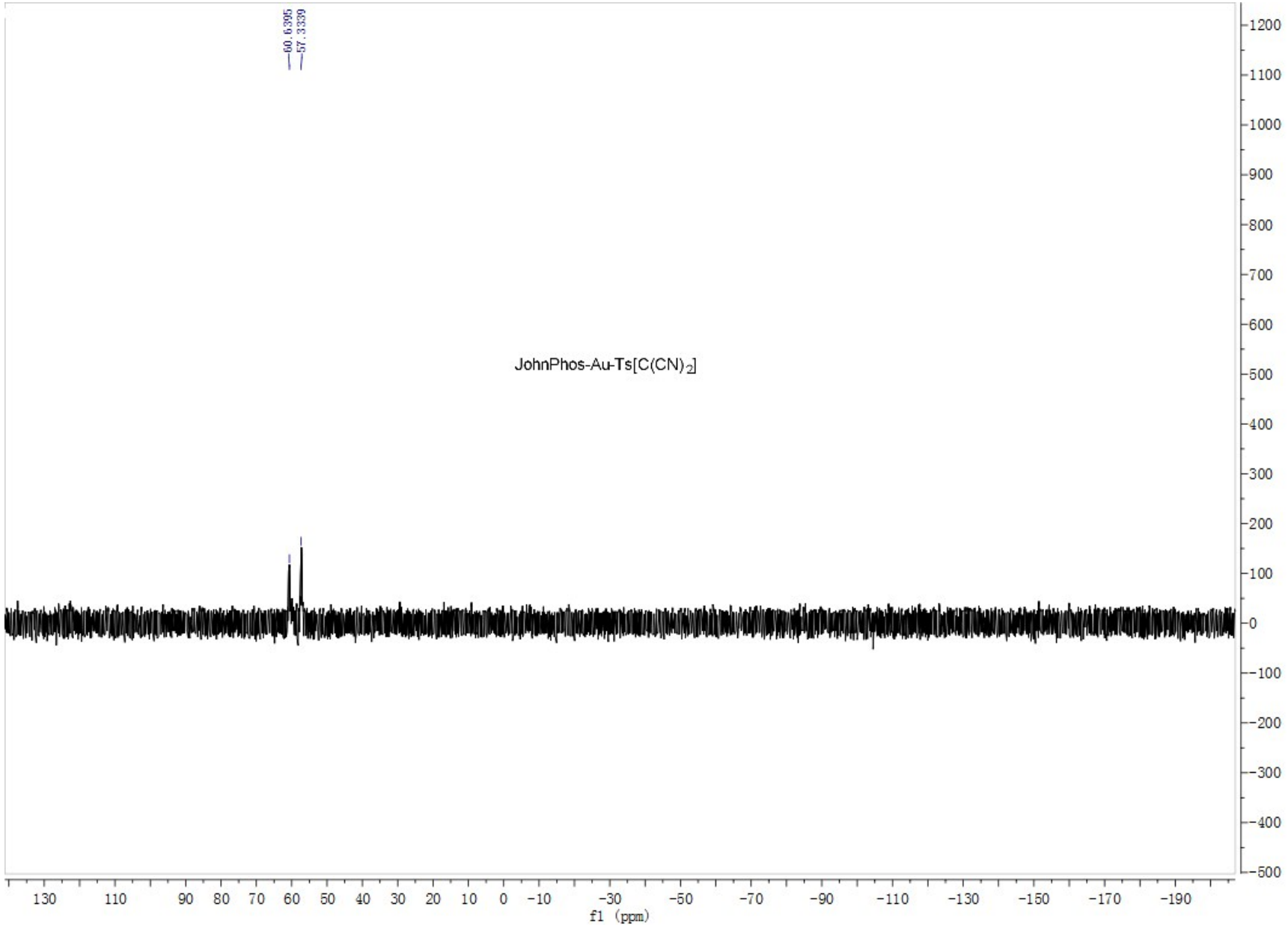
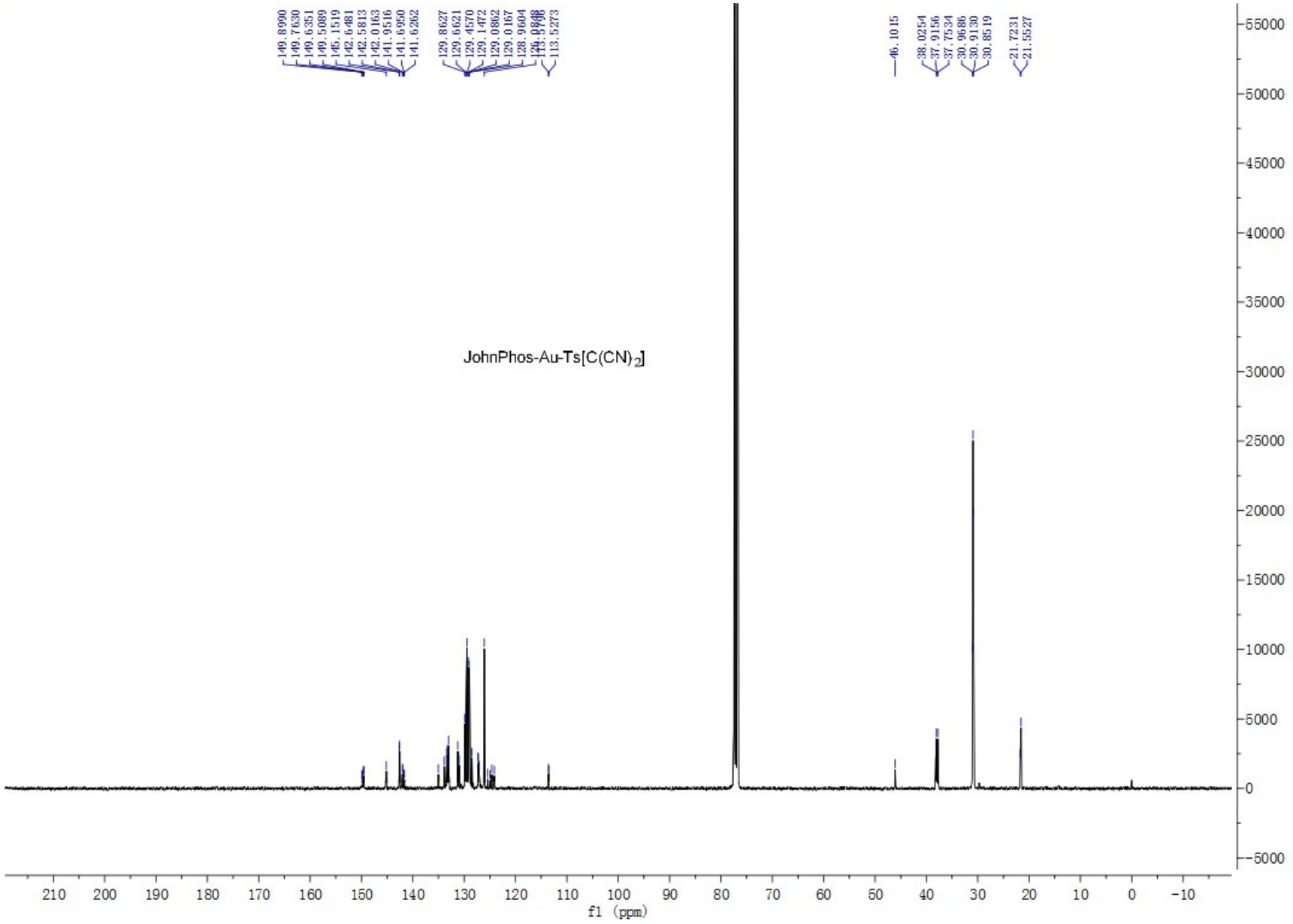
141.9501
129.8713
125.3626
119.8476
43.1174
21.3714
K[TsC(CN)2]
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.6228
7.6033
7.3750
7.3548
2.3720
Ag[TsC(CN)2]
25000
20000
15000
10000
5000
0
1.99
2.00
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


143.4628
141.7941
129.5438
124.9899
119.8633
43.1134
20.9525
Ag[TsC(CN)2]
f1 (ppm)


JohnPhos-Au-Ts[C(CN)2]
f1 (ppm)


60.6395
57.3339
JohnPhos-Au-Ts[C(CN)2]
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)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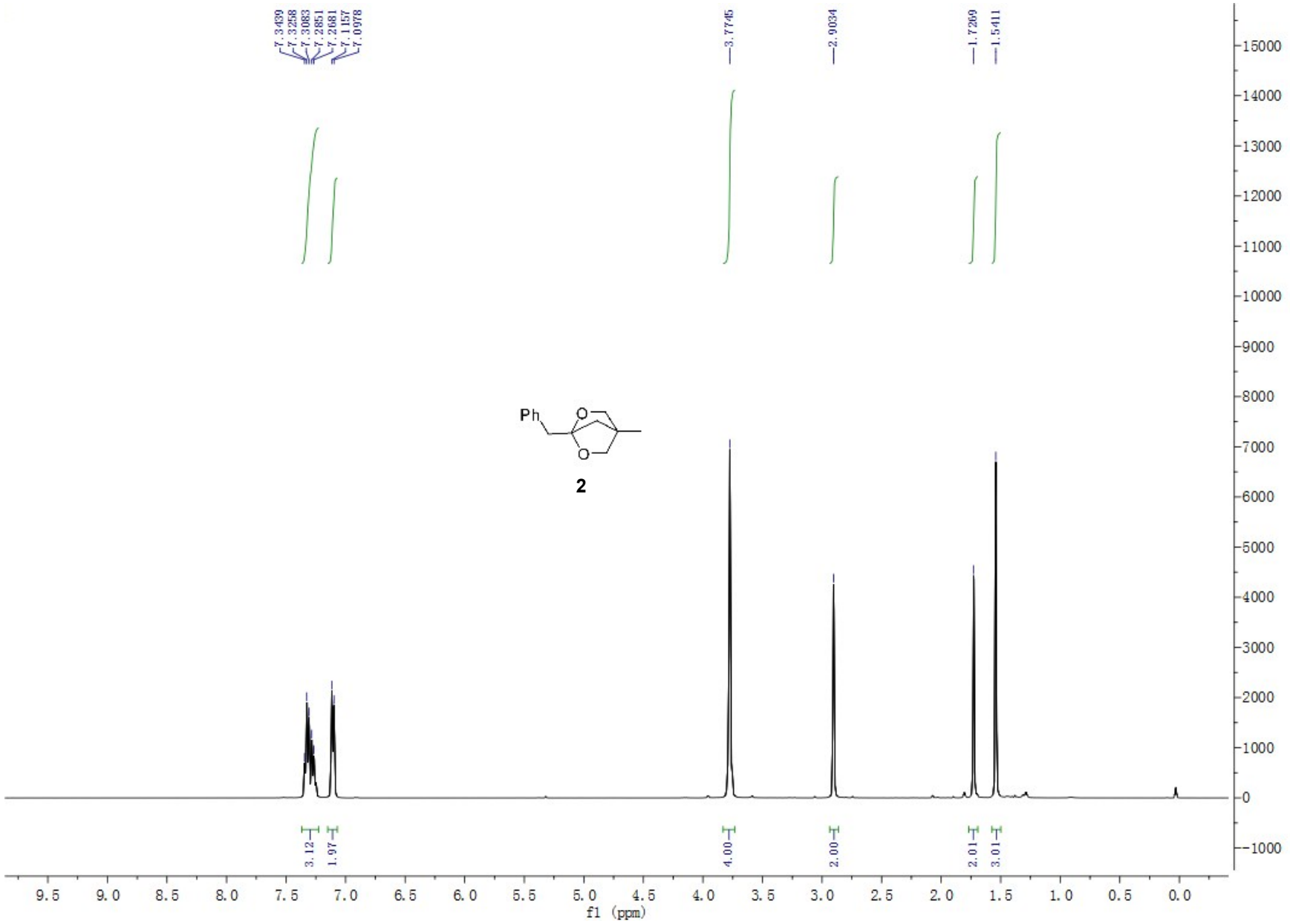
149.7630
149.6351
149.5089
145.1519
142.6481
142.5813
142.0163
141.9516
141.6950
141.6262
129.8627
129.6621
129.4570
129.1472
129.0862
129.0167
128.9604
113.5273
46.1015
38.0254
37.9156
37.7534
30.9686
30.9130
30.8519
21.7231
21.5527
JohnPhos-Au-Ts[C(CN)2]
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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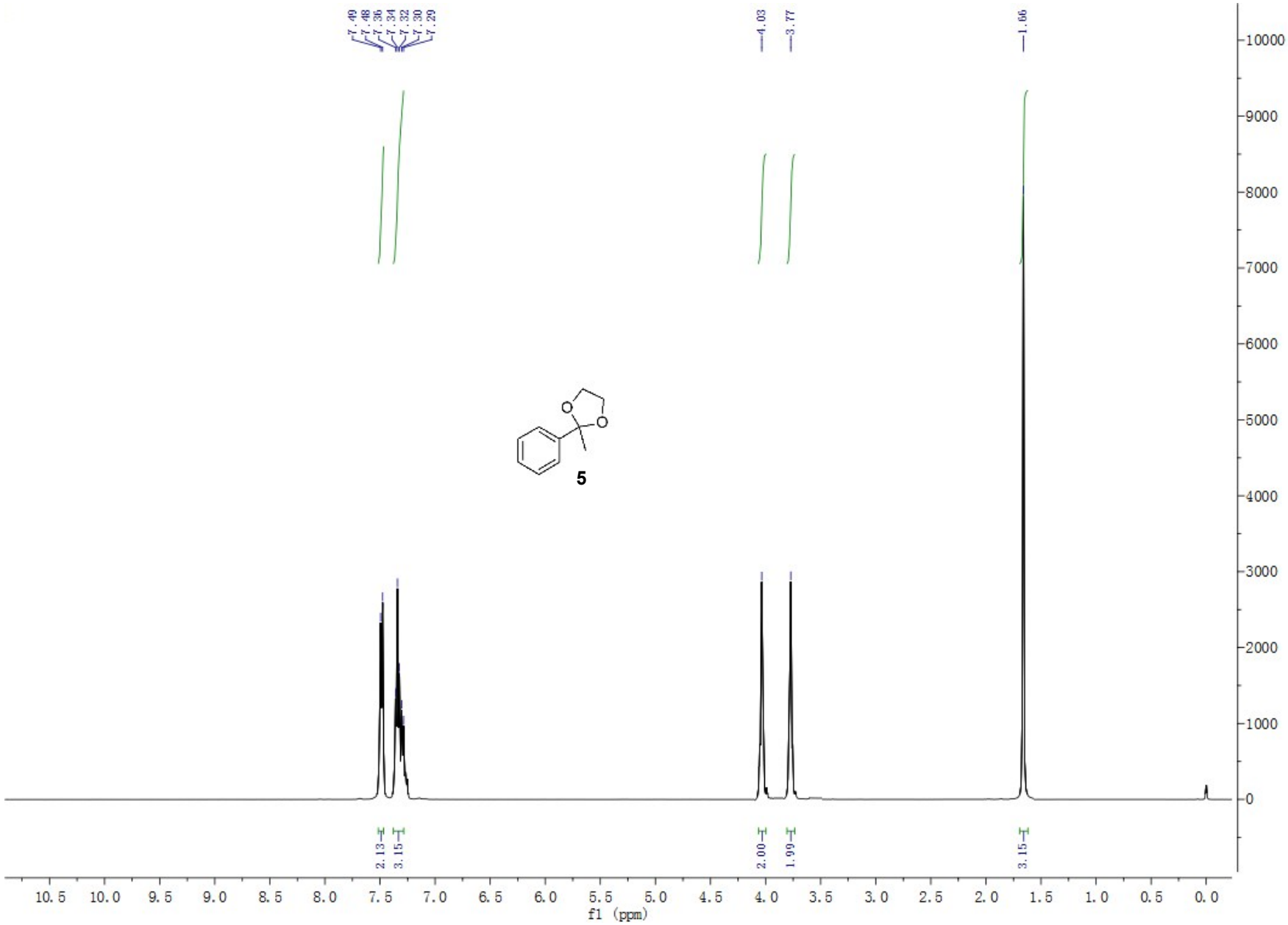
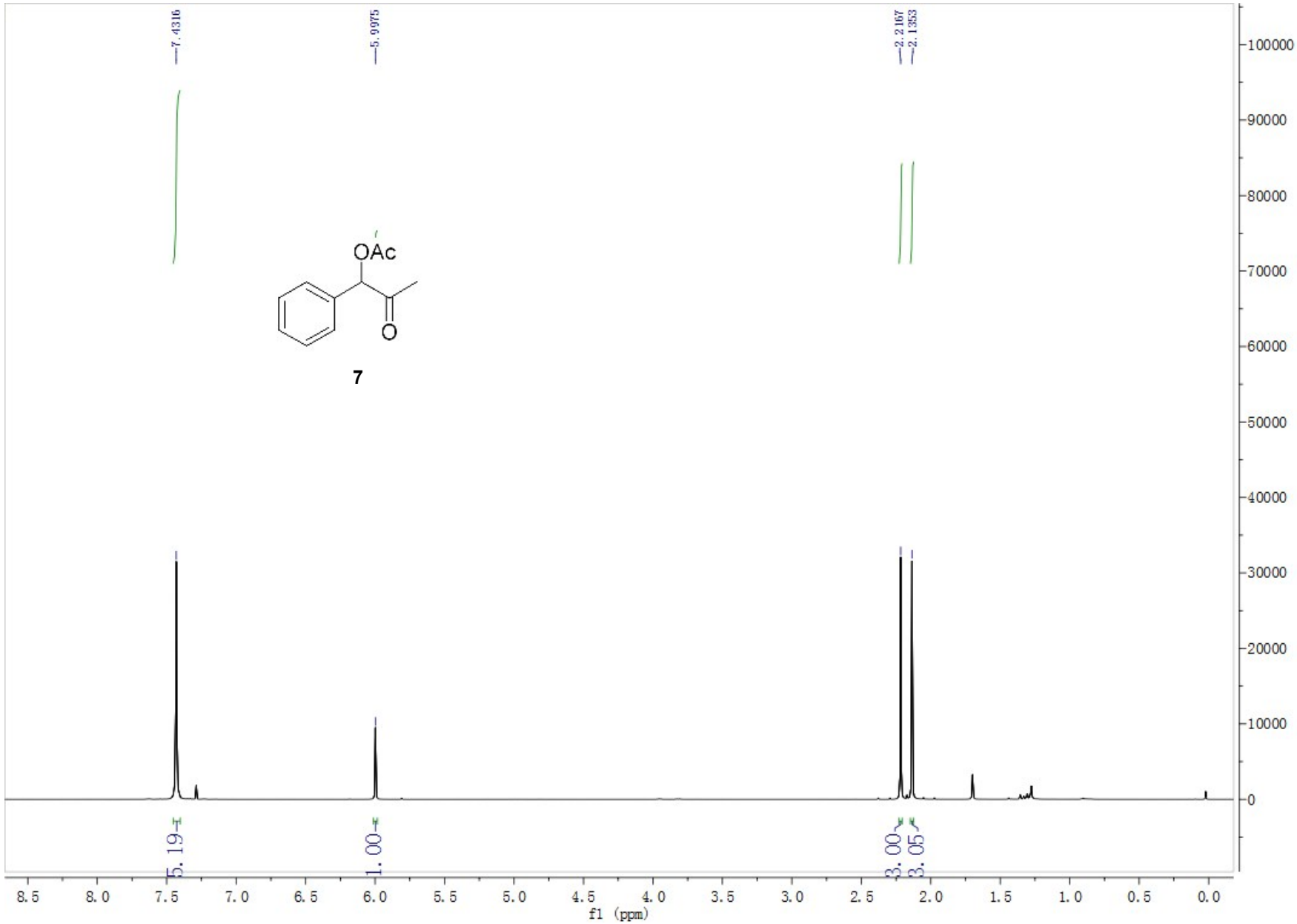
7.3083
7.2851
7.2681
7.1157
7.0978
3.7745
2.9034
1.7269
1.5411
Ph
O
O
2
3.12
1.97
4.00
2.00
2.01
3.01
f1 (ppm)

**2**


7.49
7.48
7.36
7.34
7.32
7.30
7.29
4.03
3.77
1.66
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
2.13
3.15
2.00
1.99
3.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

**5**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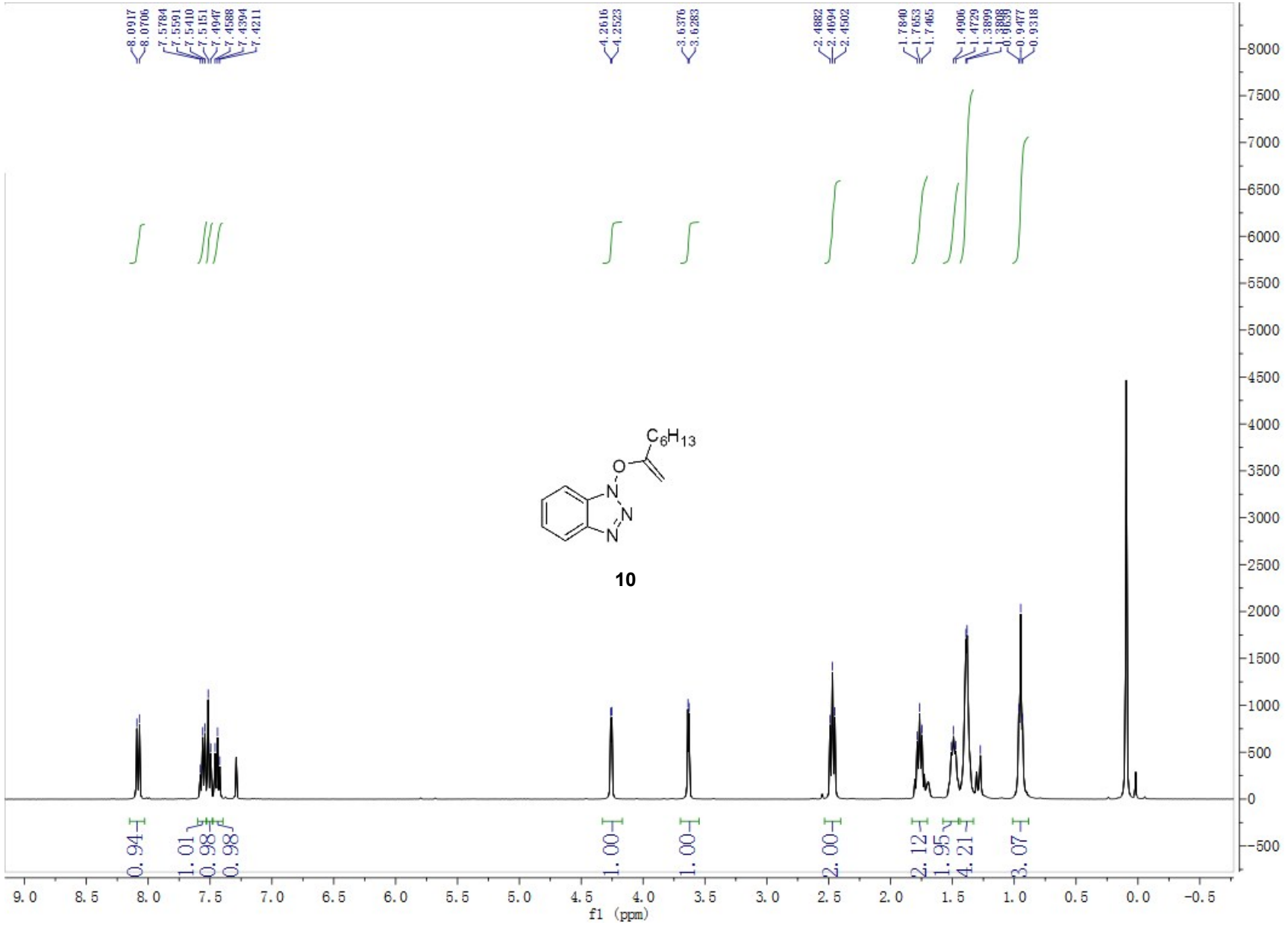
5.9975
2.2167
2.1353
OAc
O
7
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
5.19
1.00
3.00
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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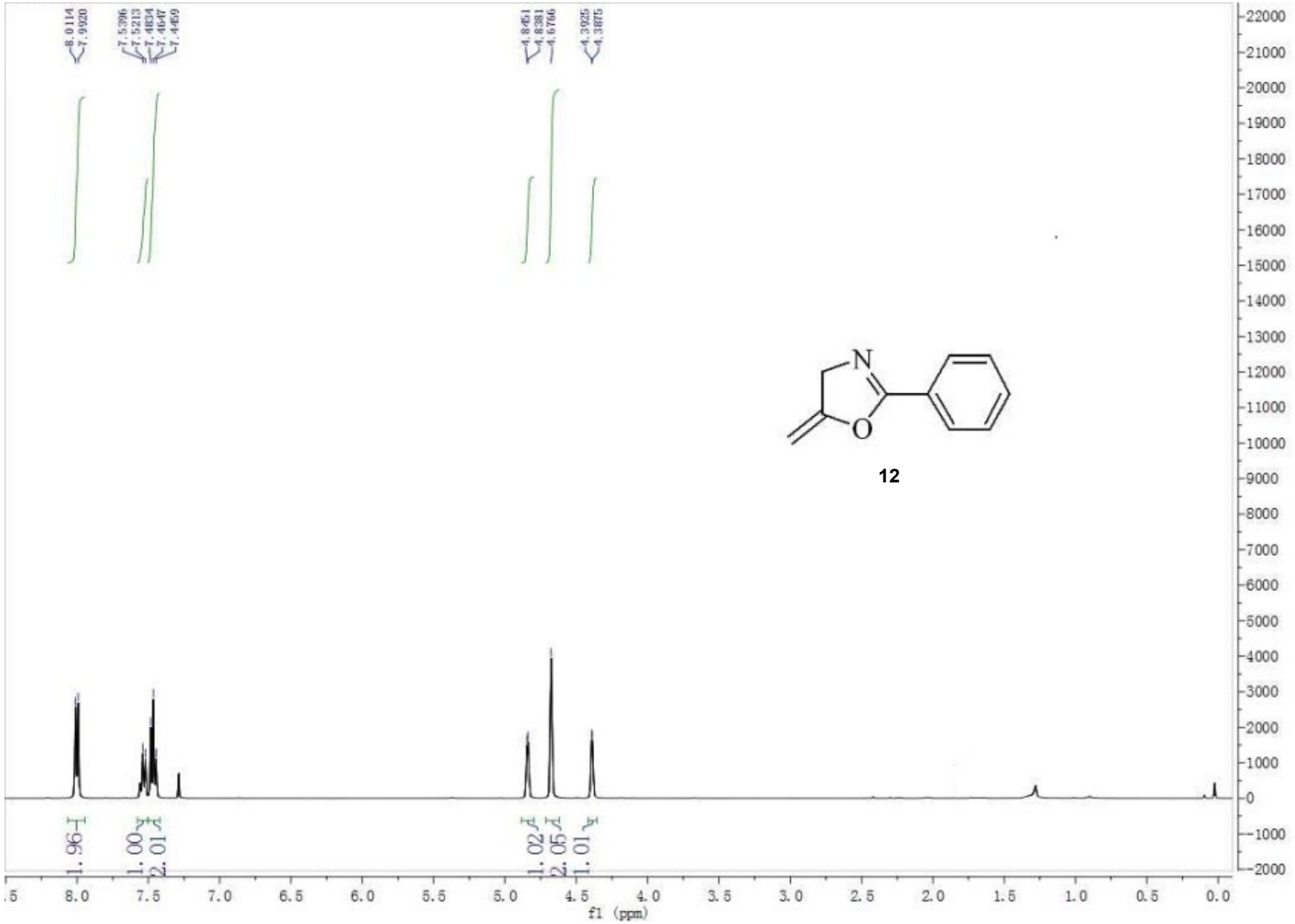
8.0706
7.5784
7.5591
7.5410
7.5151
7.4947
7.4588
7.4394
7.4211
4.2616
4.2523
3.6376
3.6283
2.4882
2.4694
2.4502
1.7840
1.7653
1.7465
1.4906
1.4729
1.3899
0.9477
0.9318
C6H13
O
N
N
N
10
0.94
1.01
0.98
0.98
1.00
1.00
2.00
2.12
1.95
4.21
3.07
f1 (ppm)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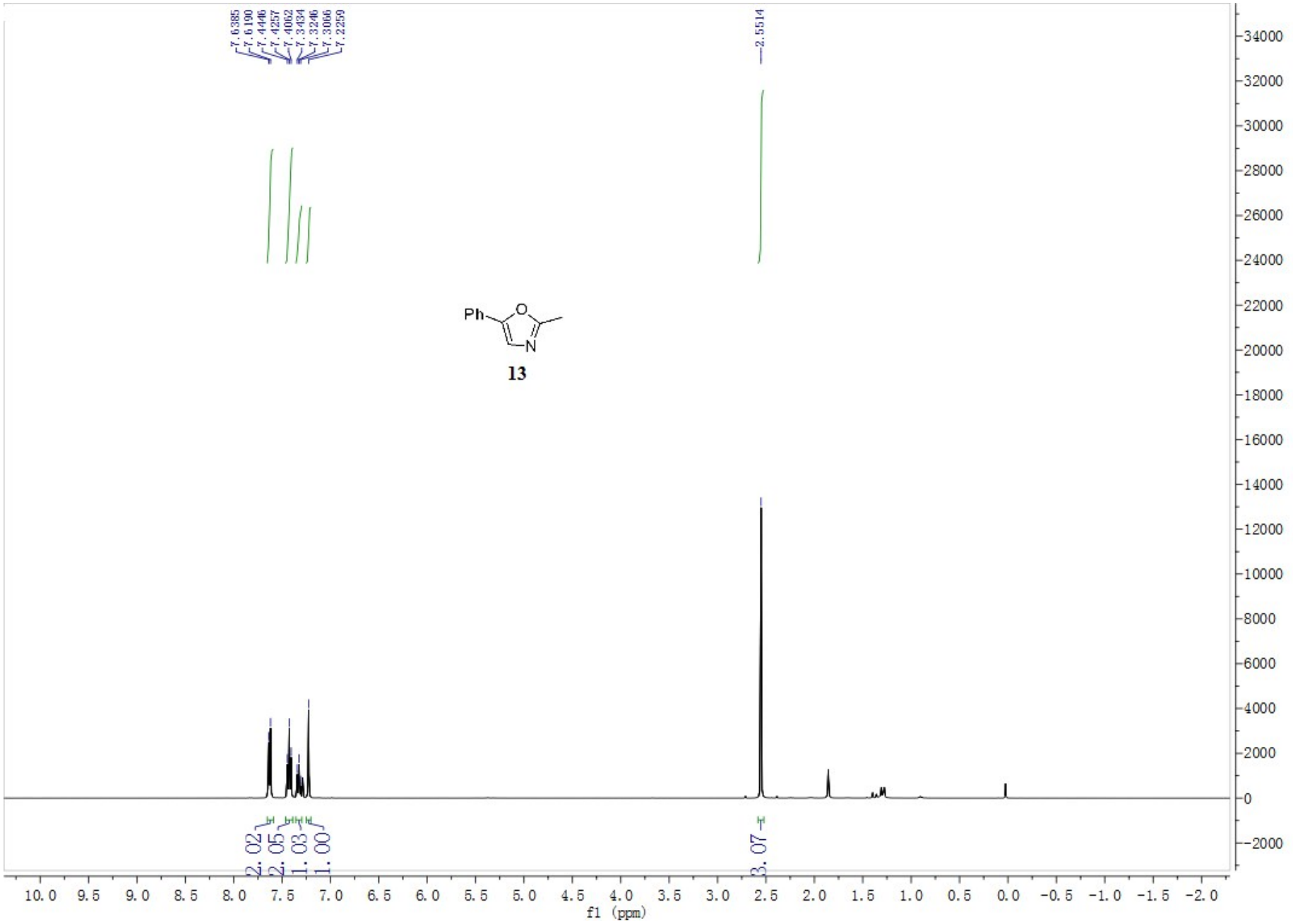
7.9920
7.5396
7.5213
7.4834
7.4647
7.4469
4.8451
4.8381
4.6766
4.3925
4.3875
N
O
12
1.96
1.00
2.01
1.02
2.05
1.01
f1 (ppm)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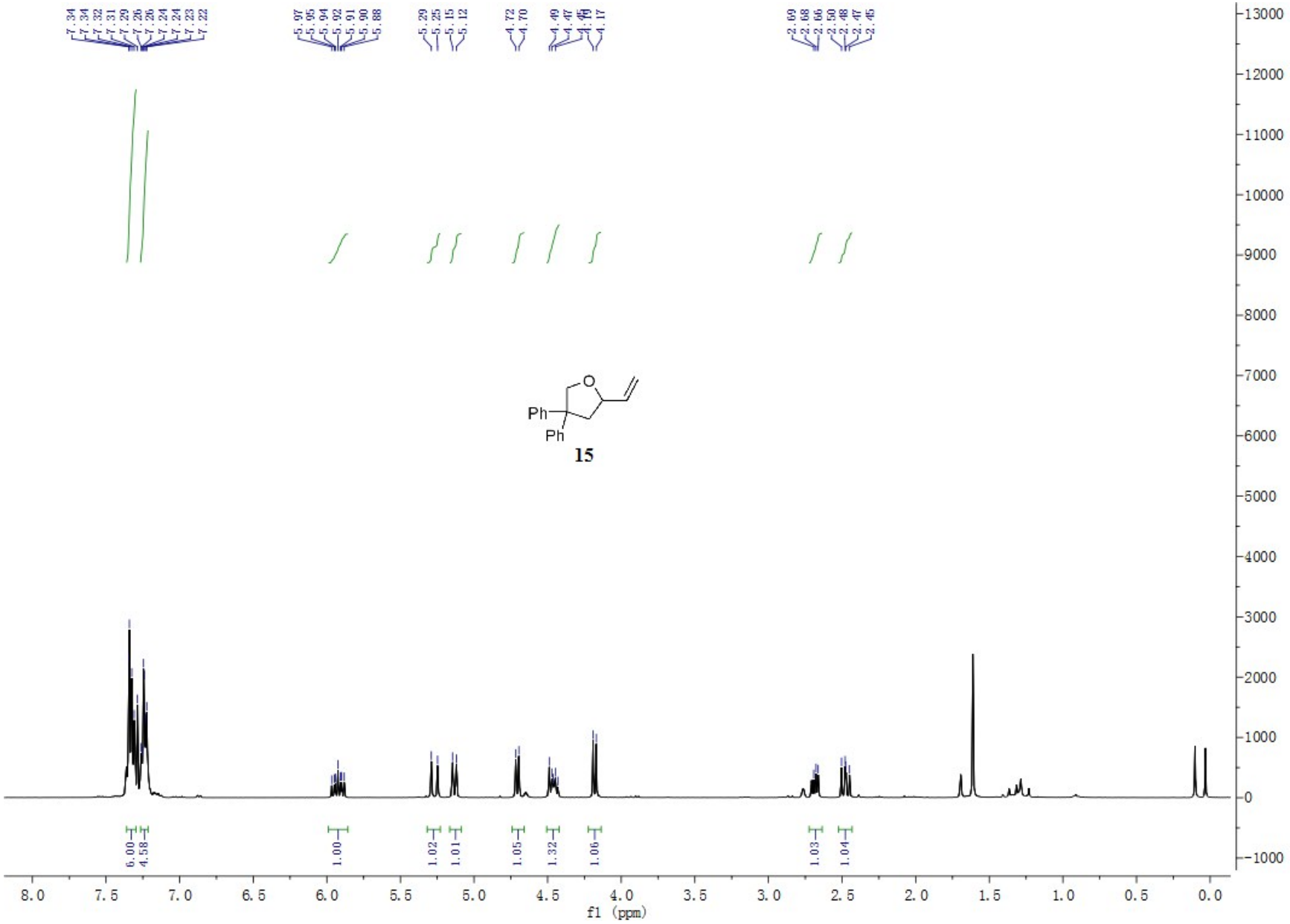
7.6190
7.4446
7.4257
7.4062
7.3434
7.3246
7.3066
7.2259
2.5514
Ph
O
N
13
2.02
2.05
1.03
1.00
3.07
f1 (ppm)


7.34
7.34
7.32
7.31
7.29
7.26
7.26
7.24
7.24
7.23
7.22
5.97
5.95
5.94
5.92
5.91
5.90
5.88
5.29
5.25
5.15
5.12
4.72
4.70
4.49
4.47
4.19
4.17
2.69
2.68
2.66
2.50
2.48
2.47
2.45
Ph
Ph
O
15
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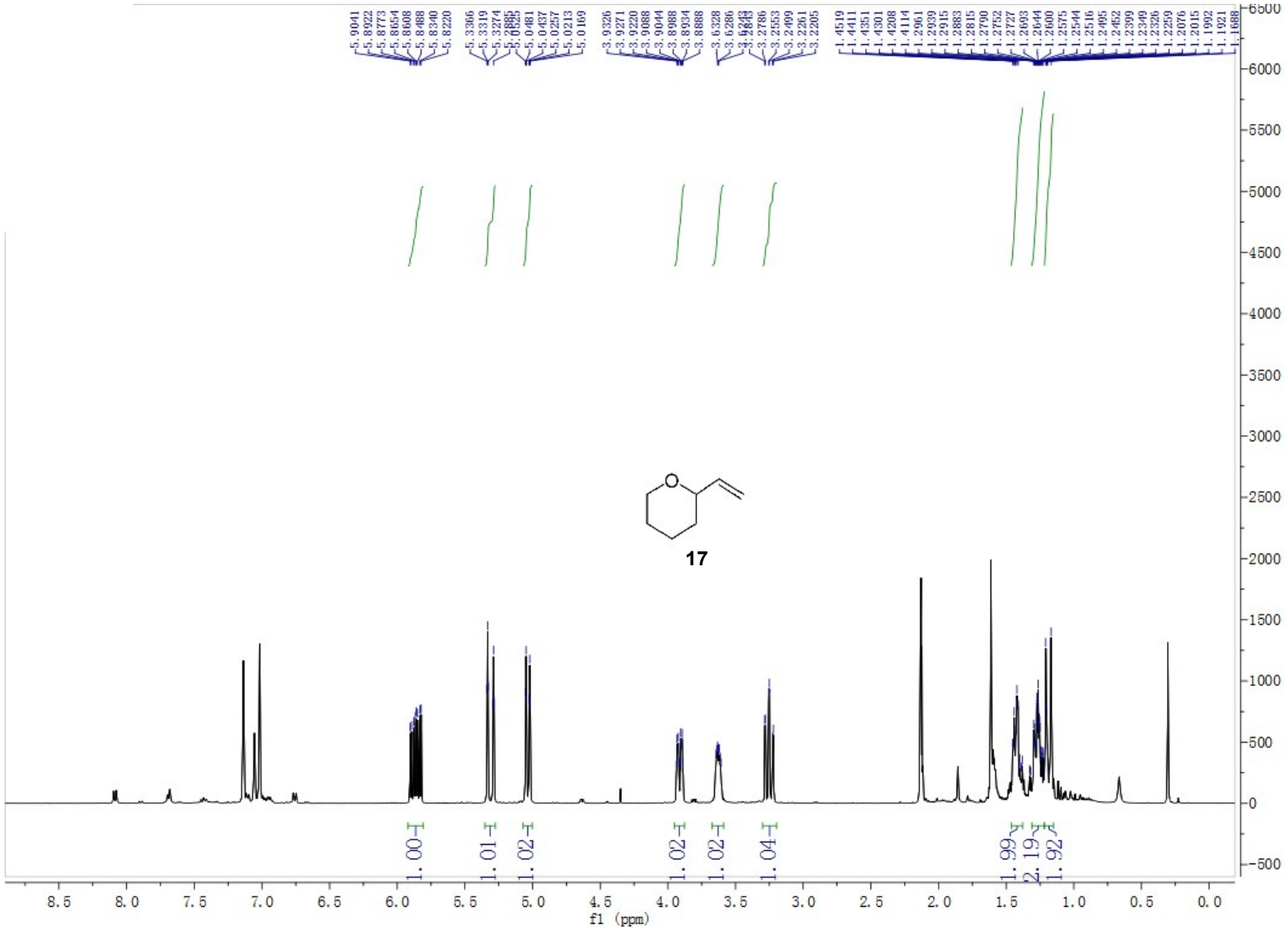
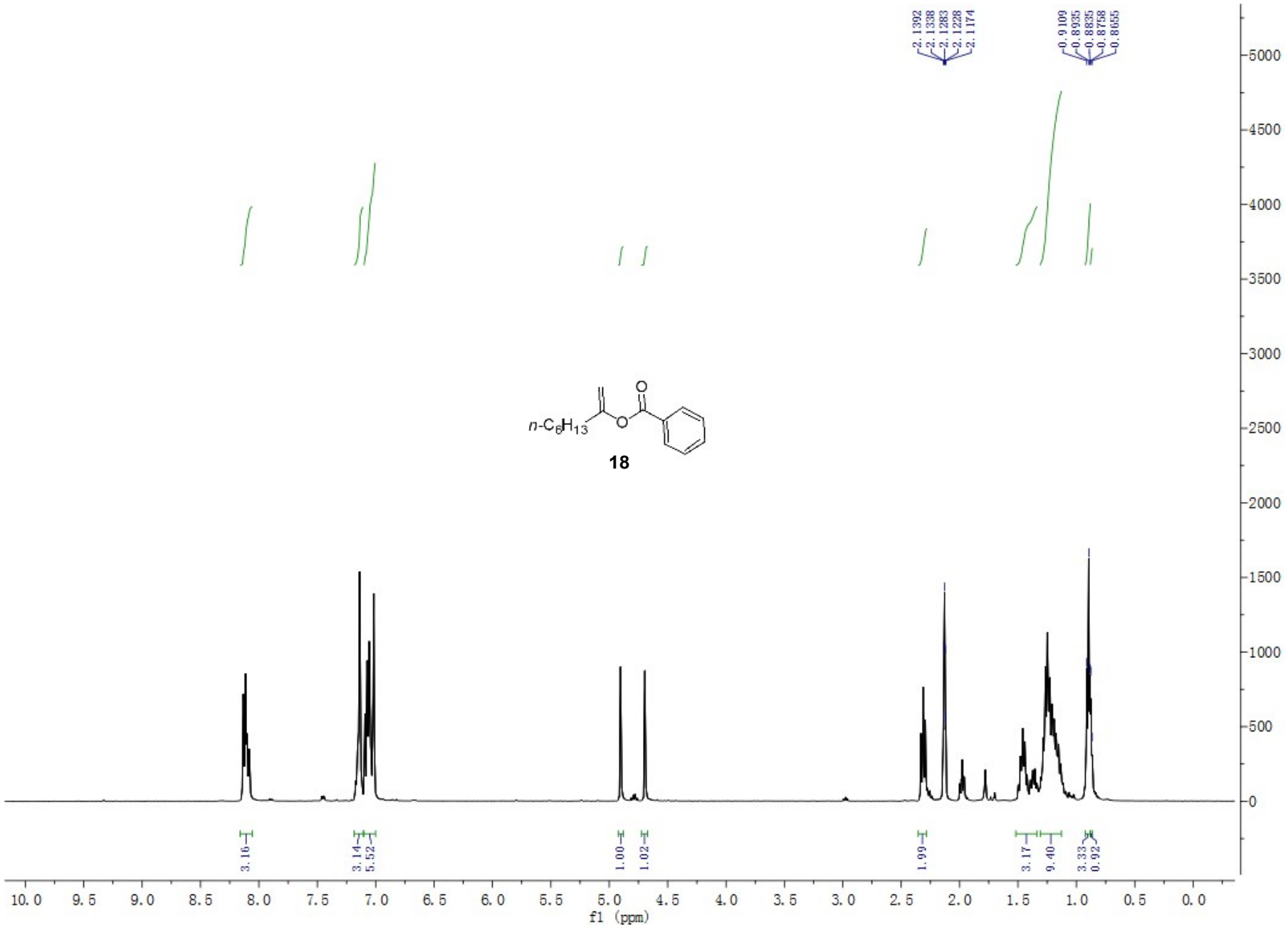
4.58
1.00
1.02
1.01
1.05
1.32
1.06
1.03
1.04
f1 (ppm)


17
f1 (ppm)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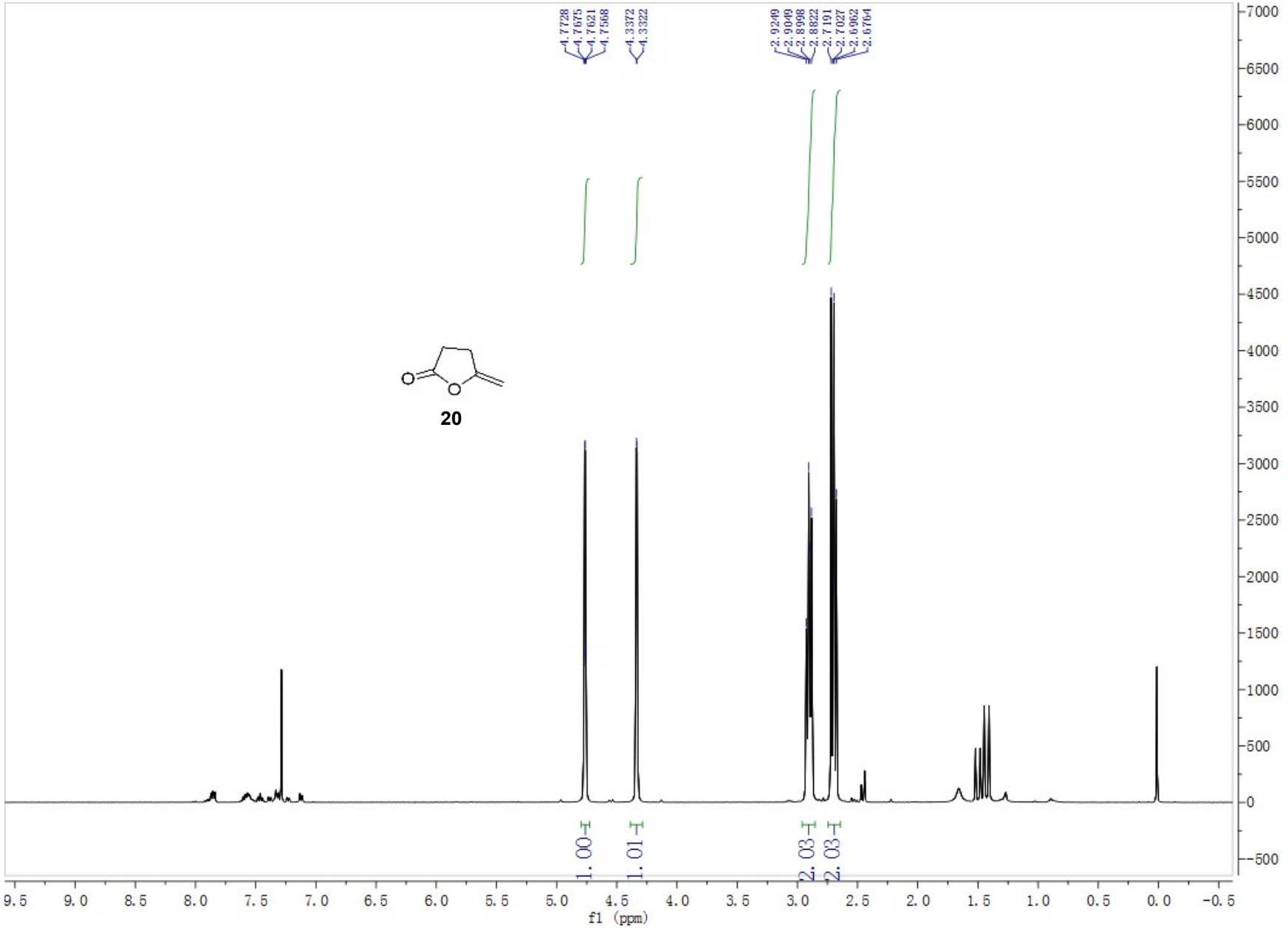
2.1338
2.1283
2.1228
2.1174
0.9109
0.8935
0.8835
0.8758
0.8655
n-C6H13
O
O
18
3.16
3.14
5.52
1.00
1.02
1.99
3.17
9.40
3.33
0.92
f1 (ppm)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4.7675
4.7621
4.7568
4.3372
4.3322
2.9249
2.9049
2.8998
2.8822
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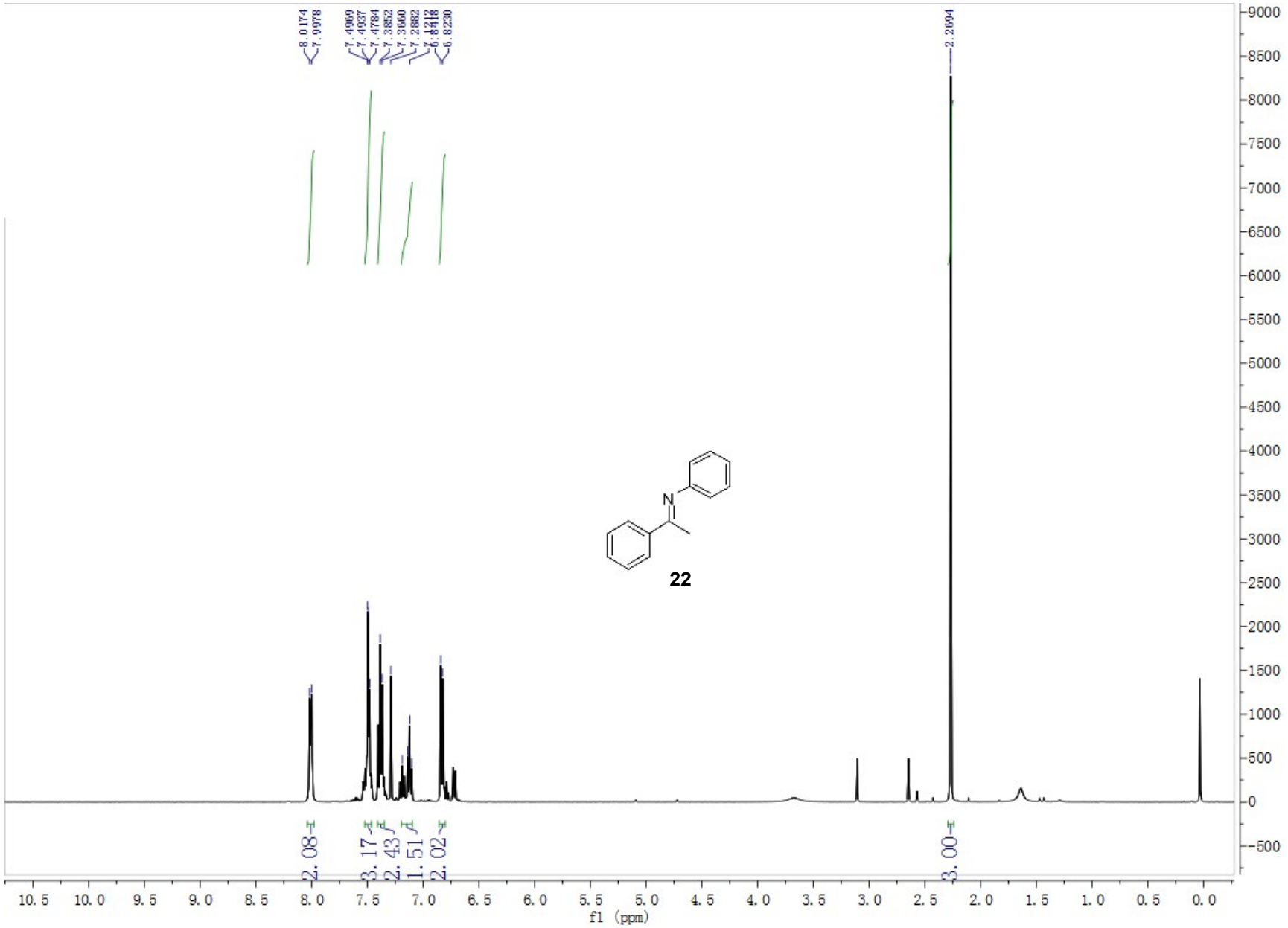
20
1.00
1.01
2.03
2.03
f1 (ppm)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7.9978
7.4969
7.4937
7.4784
7.3852
7.3660
7.2882
7.1418
6.8230
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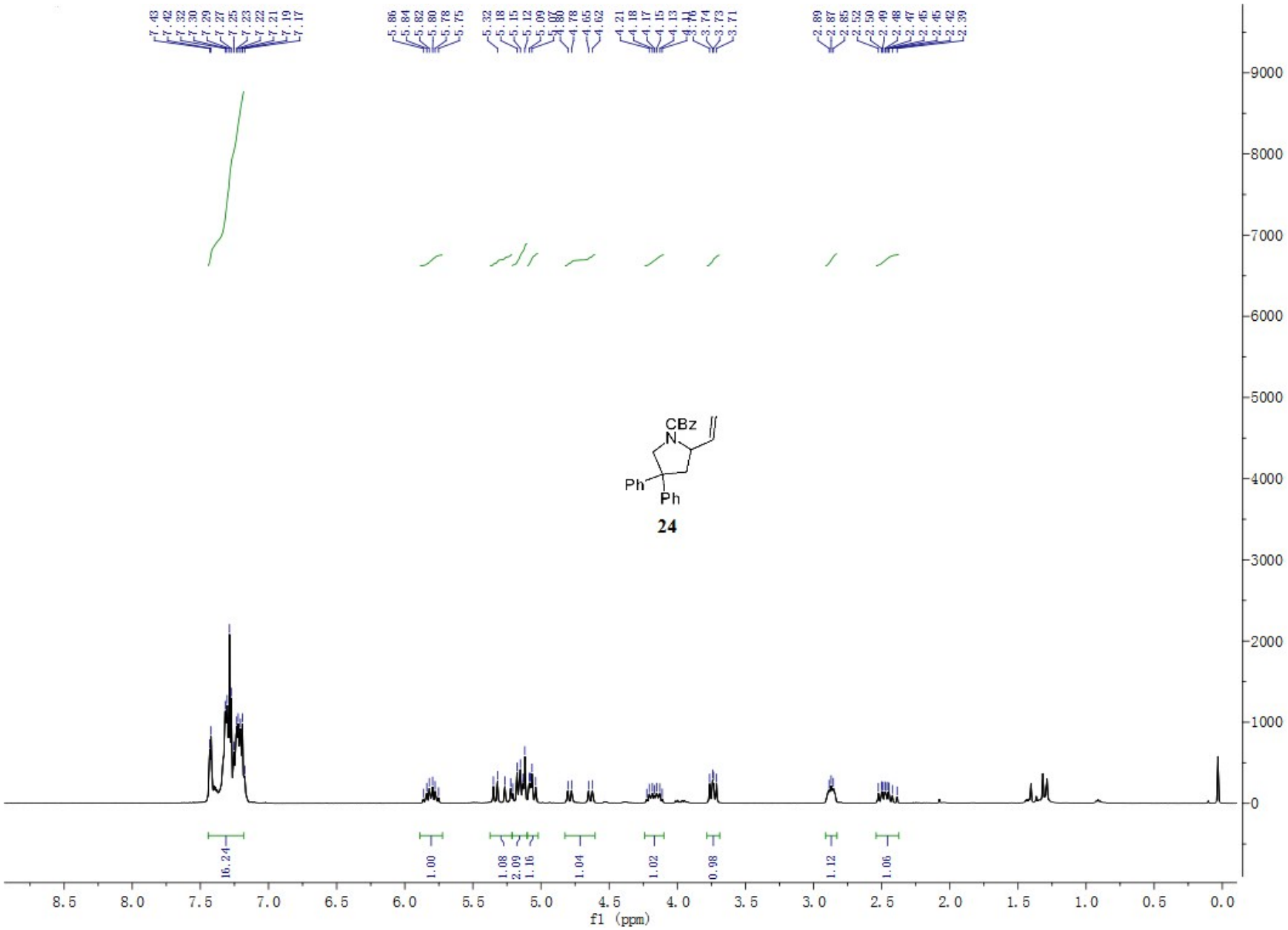
2.43
1.51
2.02
3.00
f1 (ppm)


7.43
7.42
7.32
7.30
7.29
7.27
7.25
7.23
7.22
7.21
7.19
7.17
5.86
5.84
5.82
5.80
5.78
5.75
5.32
5.18
5.15
5.12
5.09
4.78
4.65
4.62
4.21
4.18
4.17
4.15
4.13
3.74
3.73
3.71
2.89
2.87
2.85
2.52
2.50
2.49
2.48
2.47
2.45
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2.42
2.39
CBz
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Ph
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8000
7000
6000
5000
4000
3000
2000
1000
0
16.24
1.00
1.08
2.09
1.16
1.04
1.02
0.98
1.12
1.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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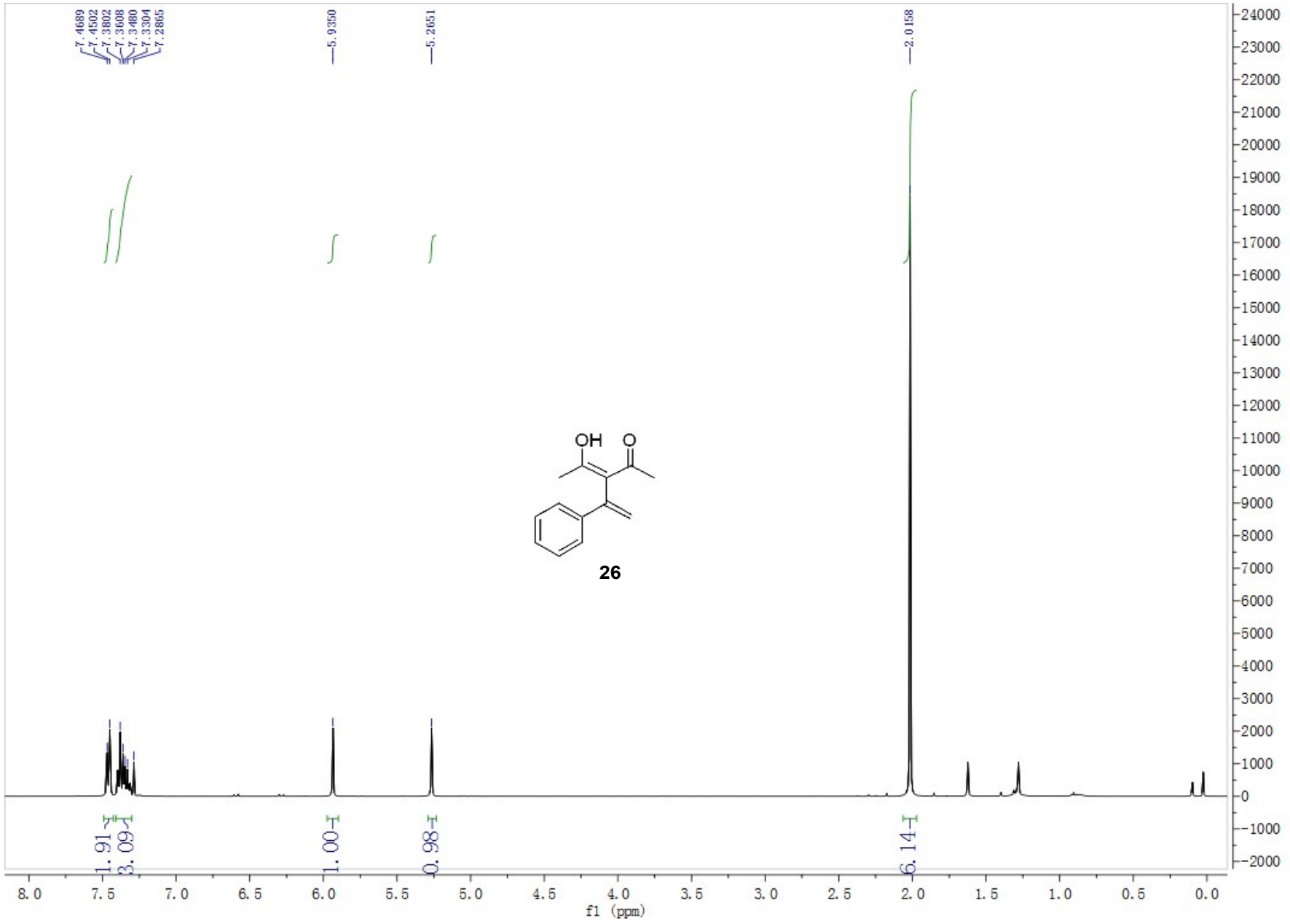
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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7.3304
7.2865
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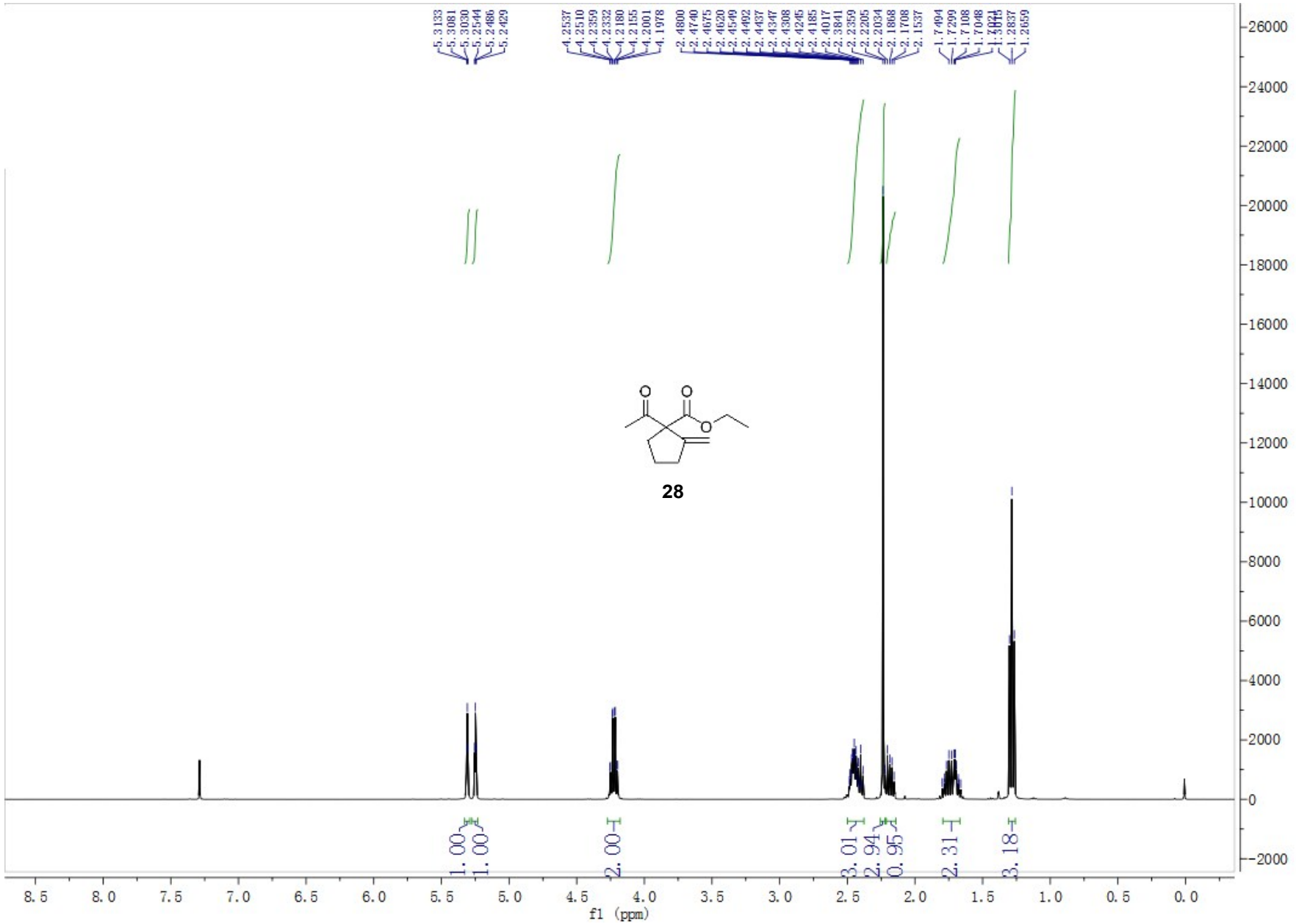
OH
O
26
1.91
3.09
1.00
0.98
6.14
f1 (ppm)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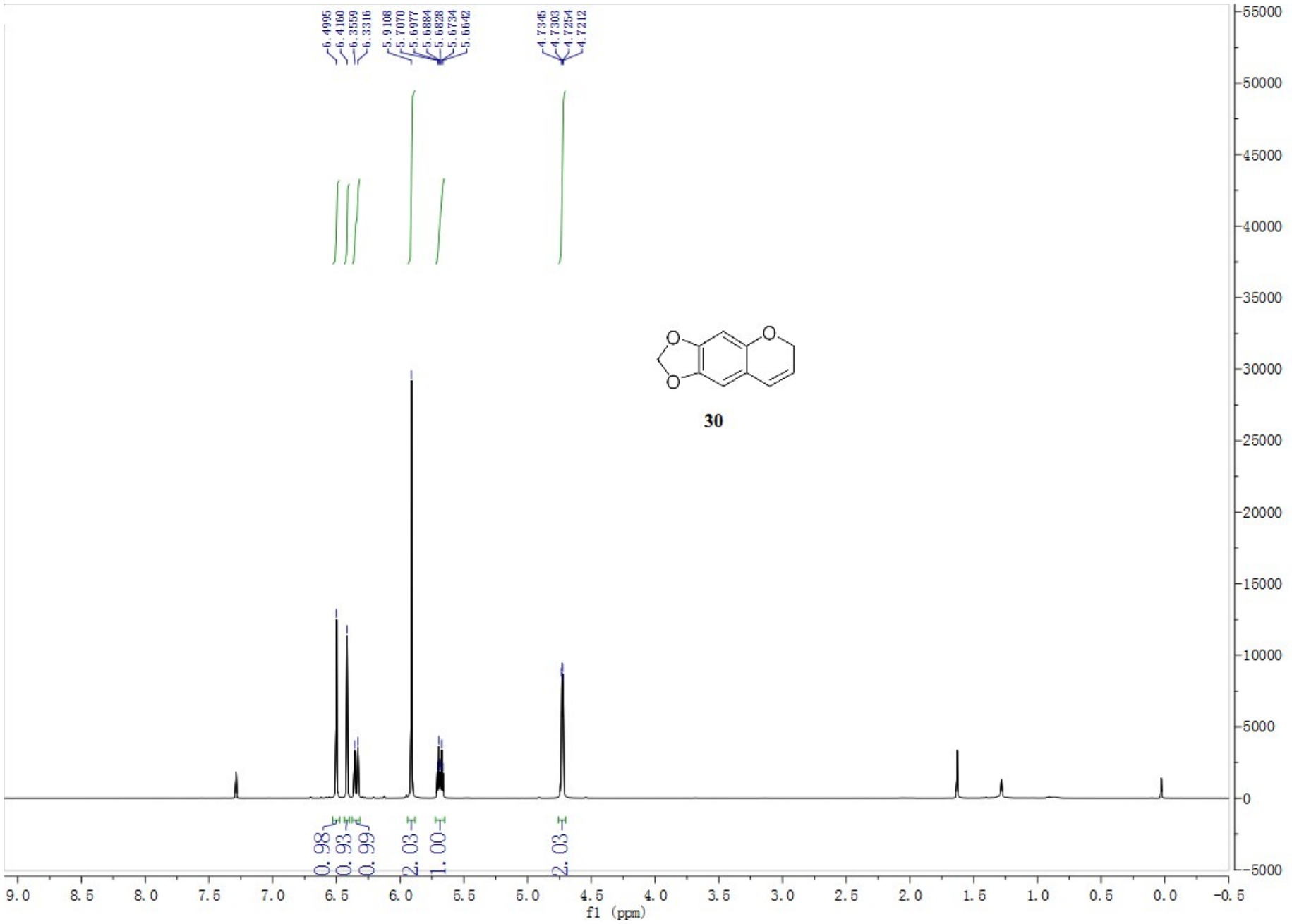
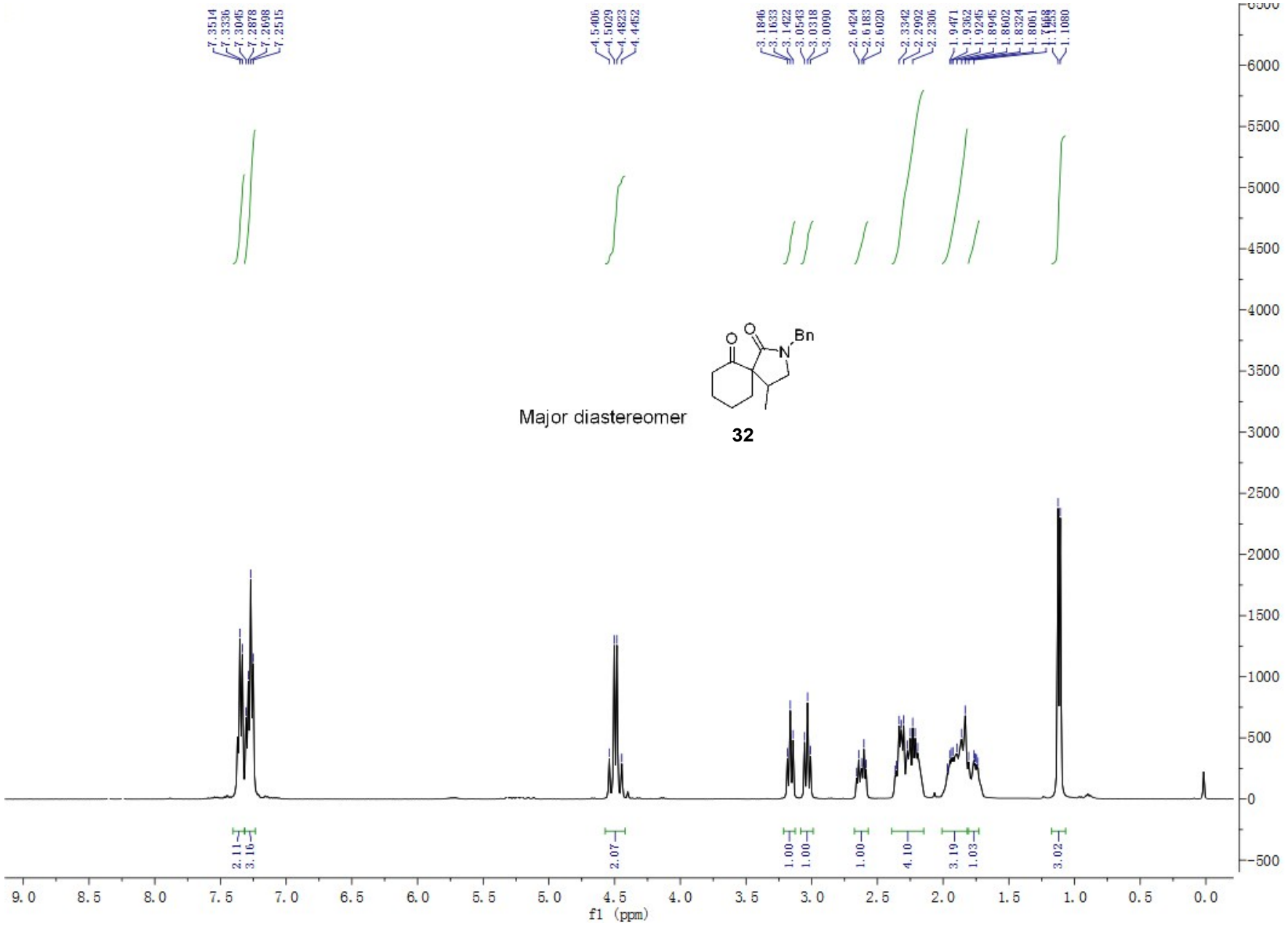
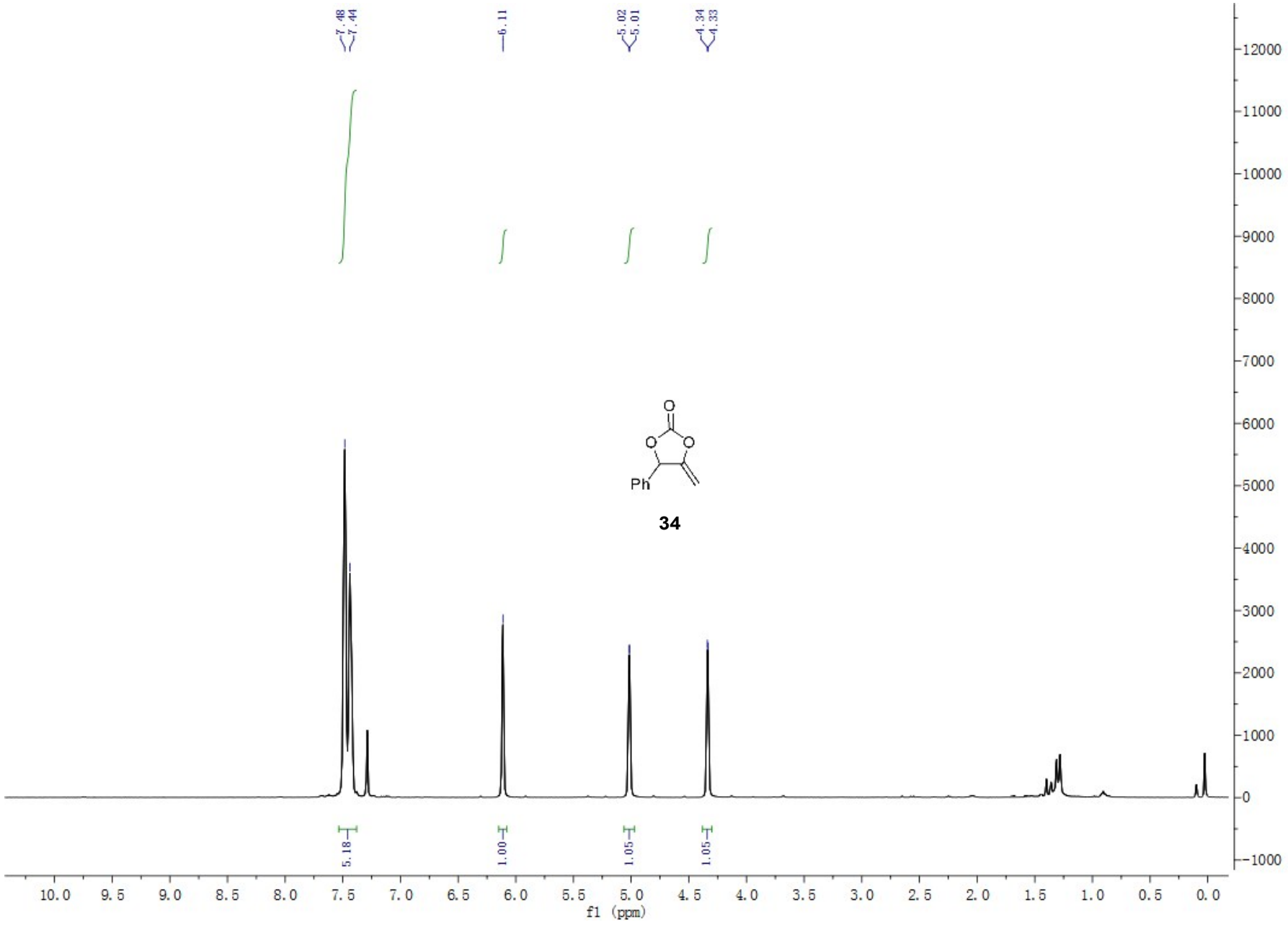
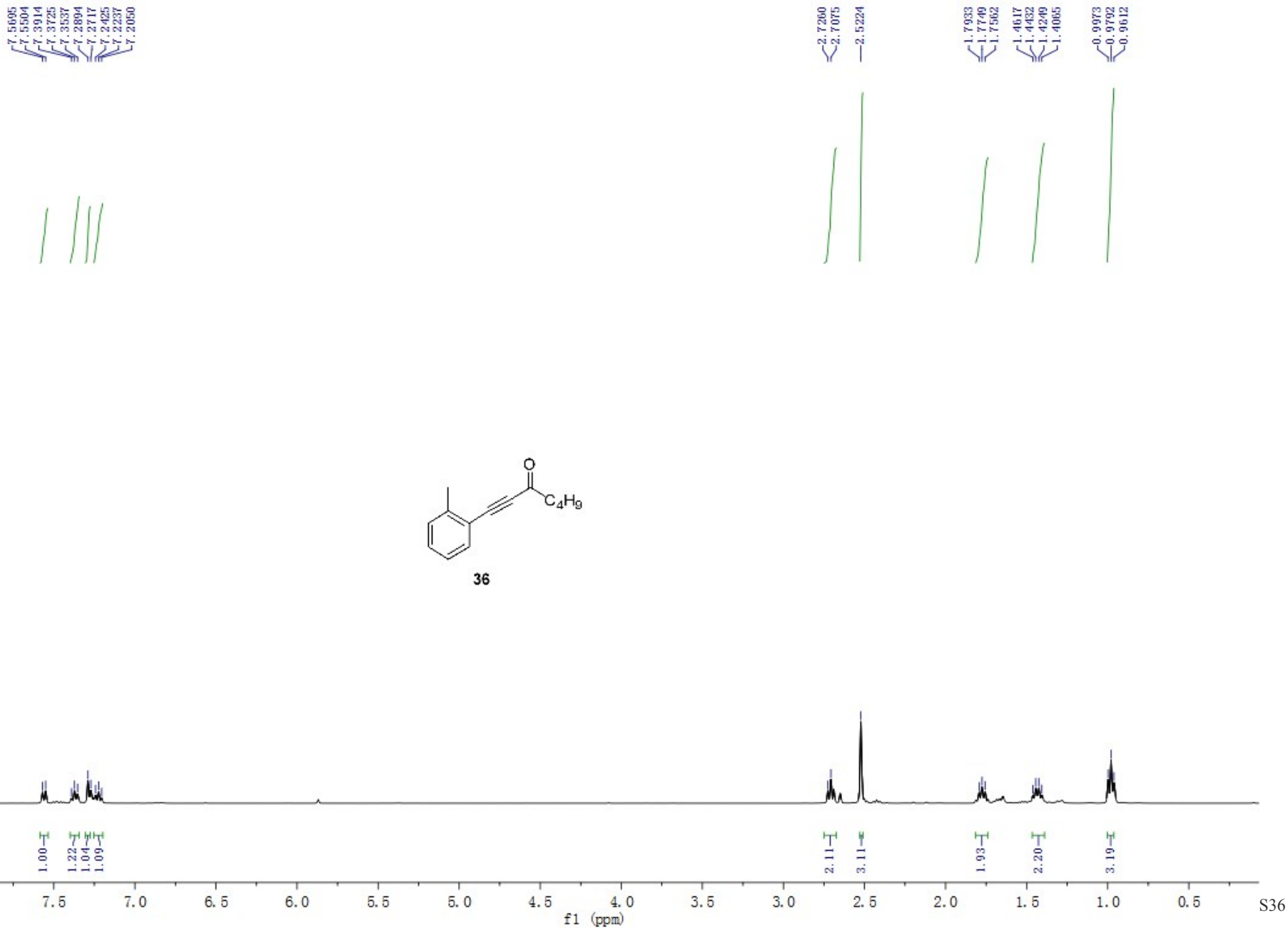
4.2359
4.2332
4.2180
4.2155
4.2001
4.1978
2.4800
2.4740
2.4675
2.4620
2.4549
2.4492
2.4437
2.4347
2.4308
2.4245
2.4185
2.4017
2.3841
2.2359
2.2205
2.2034
2.1868
2.1708
2.1537
1.7494
1.7299
1.7108
1.7048
1.2837
1.2659
O
O
O
28
1.00
1.00
2.00
3.01
2.94
0.95
2.31
3.18
f1 (ppm)


6.4995
6.4160
6.3559
6.3316
5.9108
5.7070
5.6977
5.6884
5.6828
5.6734
5.6642
4.7345
4.7303
4.7254
4.7212
0.98
0.93
0.99
2.03
1.00
2.03
f1 (ppm)

**30**


7.3514
7.3336
7.3045
7.2878
7.2698
7.2515
4.5406
4.5029
4.4823
4.4452
3.1846
3.1633
3.1422
3.0543
3.0318
3.0090
2.6424
2.6183
2.6020
2.3342
2.2992
2.2306
1.9471
1.9362
1.9245
1.8945
1.8602
1.8324
1.8061
1.1080
Bn
Major diastereomer
32
2.11
3.16
2.07
1.00
1.00
1.00
4.10
3.19
1.03
3.02
f1 (ppm)


7.48
7.44
6.11
5.02
5.01
4.34
4.33
O
O
O
Ph
34
5.18
1.00
1.05
1.05
f1 (ppm)


7.5695
7.5504
7.3914
7.3725
7.3537
7.2894
7.2717
7.2425
7.2237
7.2050
2.7260
2.7075
2.5224
1.7933
1.7740
1.7562
1.4617
1.4432
1.4249
1.4065
0.9973
0.9792
0.9612
O
C4H9
1.00
1.22
1.04
1.09
2.11
3.11
1.93
2.20
3.19
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
f1 (ppm)

**36**

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