Electronic Supplementary Material (ESI) for ChemComm.

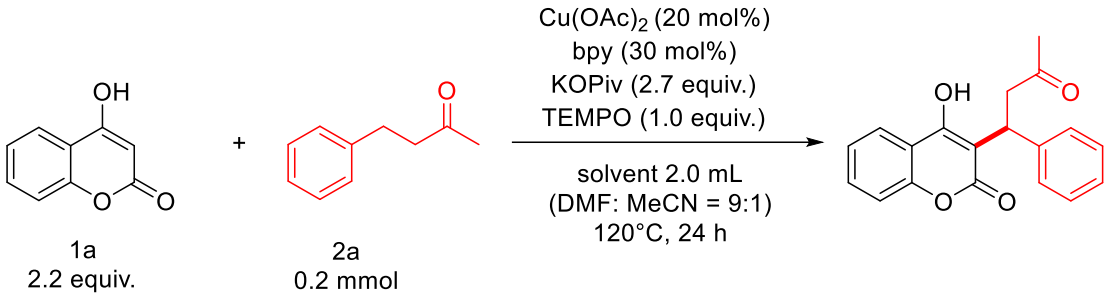

# content

# I. General Information

All reactions were conducted under a nitrogen atmosphere. Unless otherwise noted, materials were purchased from commercial suppliers (Sigma-Aldrich, J&K Chemicals, Acros Organics, Alfa Aesar, Adamas-beta®, Innochem, Aladdin, TCI,Accela,Sinocompound, Laajoo, Bidepharm, Energy Chemicals and 3A Chemicals) and were used as received. Dioxane and toluene were distilled from Na and stored under nitrogen. Flash chromatography was performed with Sepaflash columns produced by Santai Technologies. $^{1}$H NMR (400 MHz), $^{13}$C NMR (101 MHz), $^{19}$F NMR (376 MHz) spectra were recorded in $CDCl_3$ or DMSO-$d_6$ solutions using a Bruker AVANCE 400 spectrometer. Calibration was done using tetramethylsilane (0 ppm) or residual undeuterated solvent $CDCl_3$ (7.26 ppm for $^{1}$H NMR and 77.0 ppm for $^{13}$C NMR). HRMS were performed by the Shanghai Mass Spectrometry Center in Shanghai Institute of Organic Chemistry, Chinese Academic of Sciences (Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS, Operation Mode: ESI Positive Ion Mode, Analyzer Type: TOF).

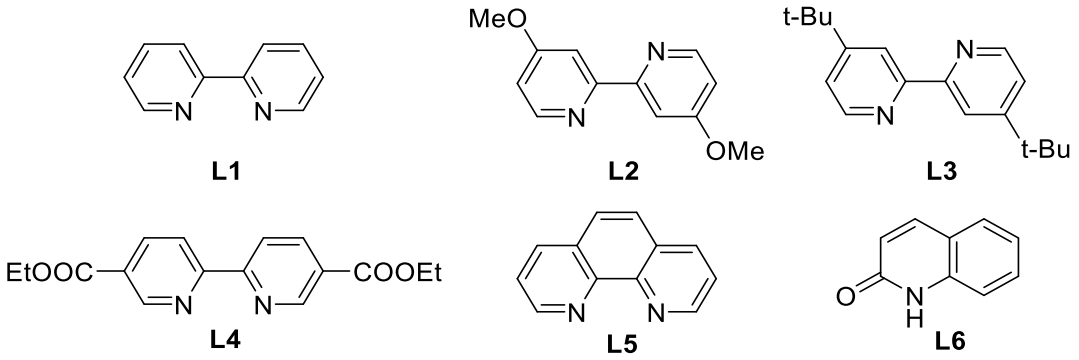
# II. Optimization of Reaction Conditions

## Table S1. Optimization of reaction conditions




| entry | variation from the standard conditions | Yield[b](%) |
|---|---|---|
| 1 | none | 84(81) |
| 2 | W/O $Cu(OAc)_2$ | 26 |
| 3 | W/O KOPiv | 0 |
| 4 | W/O bpy | 64 |
| 5 | W/O TEMPO | 0 |
| 6 | L2 instead of bpy | 80 |
| 7 | L3 instead of bpy | 74 |
| 8 | L4 instead of bpy | 79 |
| 9 | L5 instead of bpy | 81 |
| 10 | L6 instead of bpy | 67 |
| 11 | 2.0 mL DMF as solvent | 71 |
| 12 | 2.0 mL MeCN as solvent | 13 |
| 13 | 2.0 mL o-dichlorobenzene as solvent | 0 |
| 14 | $CuCl_2$ instead of $Cu(OAc)_2$ | 58 |
| 15 | $Cu(OTf)_2$ instead of $Cu(OAc)_2$ | 59 |
| 16 | CuOAc instead of $Cu(OAc)_2$ | 75 |
| 17 | 100℃ instead of 120℃ | 38 |
| 18 | KF instead of KOPiv | 0 |
| 19 | NaOAc instead of KOPiv | 61 |
| 20 | KOAc instead of KOPiv | 69 |
| 21 | CsOAc instead of KOPiv | 65 |
| 22 | $K_2CO_3$ instead of KOPiv | 7 |
| 23 | $Cs_2CO_3$ instead of KOPiv | 0 |
| 24 | Air atomsphere | 38 |
| 25 | 20 mol% bpy instead of 30 mol% bpy | 75 |
| 26 | 1equiv. 1a, 1equiv. KOPiv instead of 2.2equiv. 1a, 2.7equiv. KOPiv | 29 |
| 27 | 2equiv. 1a, 2equiv. KOPiv instead of 2.2equiv. 1a, 2.7equiv. KOPiv | 63 |
| 28 | 2.2equiv. KOPiv instead of 2.7equiv. KOPiv | 73 |

| | | |
|---|---|---|
| 29 | 2.5equiv. KOPiv instead of 2.7equiv. KOPiv | 82 |
| 30 | 3equiv. KOPiv instead of 2.7equiv. KOPiv | 81 |

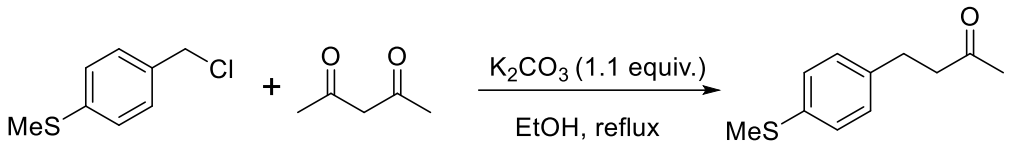



[a] Reaction conditions: The reaction was carried out on the 0.2 mmol scale.

[b] Yields were determined by LC analysis using Pyrazinecarbonitrile as internal standard, and isolated yield is listed in parentheses.

# III. Synthesis and Characterization of Part of Ketones

**Synthesis of 4-(4-(methylthio)phenyl)butan-2-one (SI-1)**[1]




The compound was synthesized according to a modified literature procedure.[1]

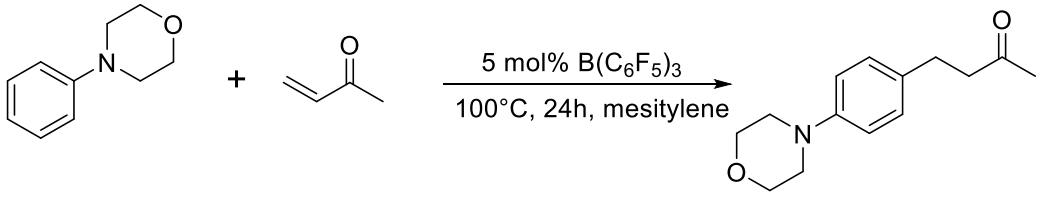
A mixture of 0.5 g (5 mmol) of pentane-2,4-dione, 0.906 g (5 mmol) of 4-methylthio-benzyl chloride, 0.75 g (1.1equiv.) of potassium carbonate and 7 mL of ethanol is heated under reflux for 15 hours. After cooling, the mixture is diluted to about three times the original volume using approximately identical amounts by volume of water and DCM, the organic phase is separated off after vigorous shaking, dried with $Na_2SO_4$ and filtered. The filtrate is concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (eluent = petroleum ether/ ethyl acetate (19: 1)) to provide the corresponding product.

White solid (0.481 g, 50% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 2.13 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 207.90, 138.11, 135.82, 128.93, 127.19, 45.15, 30.19, 29.22, 16.28.

**Synthesis of 4-(4-morpholinophenyl)butan-2-one (SI-2)**[2]




The compound was synthesized according to a modified literature procedure.[2]

A 35 $cm^3$ pressure tube equipped with screw cap and stiring was charged with $B(C_6F_5)_3$ (55 mg, 0.108 mmol) and dissolved in mesitylene (2 mL). Subsequently 2.10mmol 4-

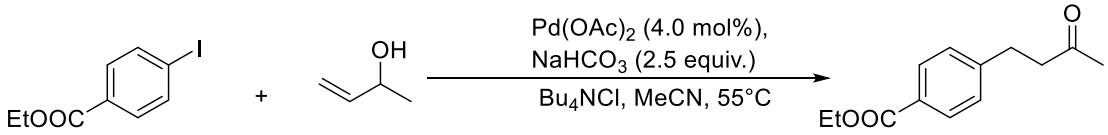
phenylmorpholine (342 mg, 2.10 mmol) and but-3-en-2-one (285 mg, 4.07 mmol) were added. The reaction mixture was stirred for 24 h at 80 °C. The rection mixture was cooled to room temperature and directly purifite by column chromatography (cyclohexane: ethyl acetate = 20:1). to afforded. After removal of all volatiles in vaccuo the desired products were obtained.

Yellow liquid (0.318 g, 65% yield)

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.85 (t, *J* = 5.2, 4.7 Hz, 4H), 3.11 (t, *J* = 4.7, 4.3 Hz, 4H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.1 Hz, 2H), 2.13 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 208.37, 149.73, 132.62, 129.11, 116.07, 67.04, 49.73, 45.48, 30.23, 28.97.

**Synthesis of ethyl 4-(3-oxobutyl)benzoate (SI-3)**[3]




The compound was synthesized according to a modified literature procedure.[3]

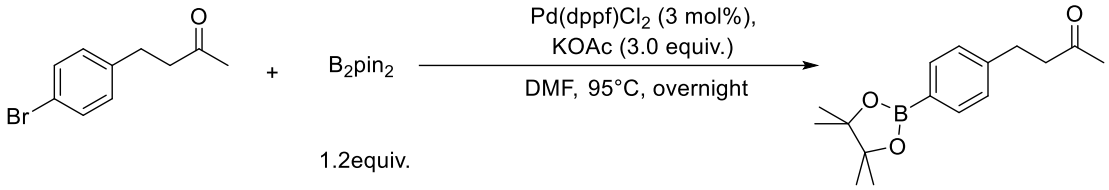
An oven-dried 50 mL round bottom flask equipped with a magnetic stirbar and rubber septum was attached to a double manifold and cooled under vacuum. The flask was backfilled with $N_2$, the rubber septum was removed, $NaHCO_3$ (1.05 g, 12.5 mmol, 2.5 equiv.), $Pd(OAc)_2$ (45.0 mg, 0.2 mmol, 4mol%), tetrabutylammonium chloride (1.38g, 5mmol, 1equiv), and ethyl 4-iodobenzoate (0.85 mL, 5mmol) were added. The septum was replaced, the falsk was purged with $N_2$ for 15 minutes, and acetonitrile (25 mL) was added. 3-buten-2-ol (1.09 mL, 12.5 mmol, 2.5equiv.) was added via syringe and then the reaction mixture was stirred in an oil bath at 55 ℃ for 48h. TLC indicated complete consumption of the starting aryl iodide. Silica gel was added, and volatiles removed in vacuo. Crude residue was purified via silica gel flash chromatography (hexanes:ethyl acetate = 4:1) to afford desired ketone .

White solid (1.045 g, 95% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 1H), 2.95 (t, *J* = 7.5 Hz, 1H), 2.78 (t, *J* = 7.5 Hz, 1H), 2.15 (s, 1H), 1.38 (t, *J* = 7.1 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 207.52, 166.68, 146.51, 129.92, 128.60, 128.45, 60.99, 44.75, 30.23, 29.75, 14.47.

**Synthesis of 4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butan-2-one(SI-4)**[4]




The compound was synthesized according to a modified literature procedure.[4]

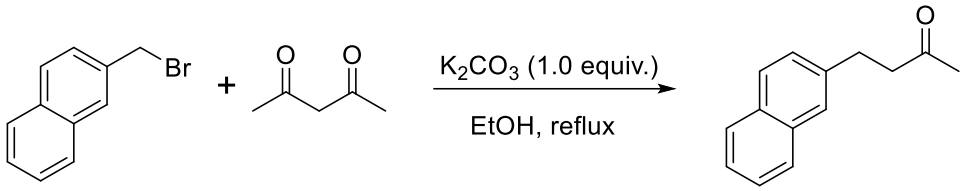
A 20 mL crimp cap vial was charged with $Pd(dppf)Cl_2$ (22.0 mg, 30 μmol, 3 mol%), KOAc (294.4 mg, 3 mmol, 3 equiv.), $B_2pin_2$ (304.7 mg, 1.2 mmol, 1.2 equiv.) and 4-(4-Bromophenyl)butan-2-one (168.6 μL, 1 mmol, 1 equiv.). The vial was set under a $N_2$-atmosphere, DMF (6.0 mL) was added and the reaction mixture was stirred at 95 °C overnight. After cooling to room temperature, $H_2O$ (15 mL) and EtOAc (10 mL) were added. The phases were separated and the water phase was extracted with EtOAc (2x10 mL). The combined organic phases were washed with $H_2O$ (3x10 mL) followed by brine (3x10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (PE/EtOAc 5: 1) to yield the titled compound.

Colorless liquid (0.189 g, 69% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.12 (s, 1H), 1.32 (s, 12H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 207.80, 144.43, 135.09, 127.80, 83.73, 44.99, 30.14, 29.96, 24.91.

**Synthesis of 4-(naphthalen-2-yl)butan-2-one (SI-5)** [5]




The compound was synthesized according to a modified literature procedure.[5]

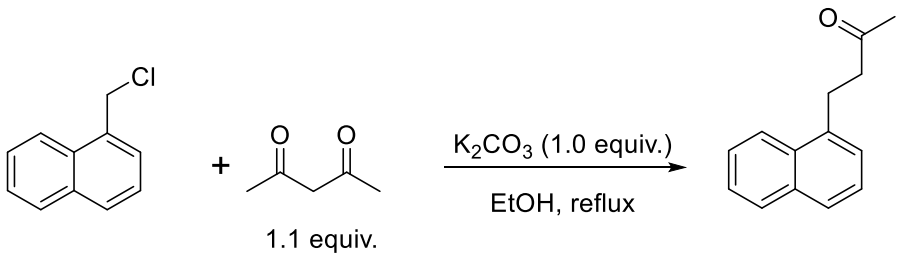
A 35 $cm^3$ pressure tube equipped with screw cap and stiring was charged with 2-(bromo-methyl)naphthalene (0.553 g, 2.5 mmol),acetylacetone (0.26 mL, 2.5 mmol), and $K_2CO_3$ (0.352 g, 2.5 mmol) in dry EtOH (13 mL) was refluxed for 16h. After cooling, the mixture is diluted to about three times the original volume using approximately identical amounts by volume of water and DCM, the organic phase is separated off after vigorous shaking, dried with $Na_2SO_4$ and filtered. The filtrate is concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (eluent = petroleum ether/ ethyl acetate (50:1)) to provide the corresponding product.

White solid (0.272 g, 55% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.73 (m, 3H), 7.63 (s, 1H), 7.49 – 7.40 (m, 2H), 7.33 (dd, *J* = 8.4, 1.7 Hz, H), 3.07 (t, *J* = 7.6 Hz, 2H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.16 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 208.02, 138.62, 133.70, 132.18, 128.23, 127.74, 127.57, 127.17, 126.52, 126.16, 125.46, 45.22, 30.29, 30.01.

**Synthesis of 4-(naphthalen-1-yl)butan-2-one (SI-6)**[6]




The compound was synthesized according to a modified literature procedure.[6]

A 35 $cm^3$ pressure tube equipped with screw cap and stiring was charged with 1-(chloromethyl)naphthalene (0.44 g, 2.5 mmol),acetylacetone (0.29 mL, 2.75 mmol),

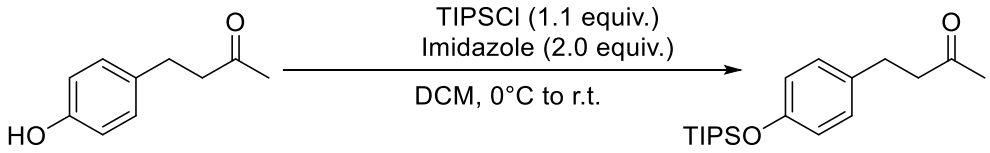
and $K_2CO_3$ (0.352 g, 2.5 mmol) in dry EtOH (6 mL) was refluxed for 16h. After cooling, the mixture is diluted to about three times the original volume using approximately identical amounts by volume of water and DCM, the organic phase is separated off after vigorous shaking, dried with $Na_2SO_4$ and filtered. The filtrate is concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (eluent = petroleum ether/ ethyl acetate (50: 1)) to provide the corresponding product.

Colorless liquid (0.310 g, 63% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.82 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.35 (t, *J* = 8.0, 7.1 Hz, 1H), 7.28 (dd, *J* = 7.1, 1.2 Hz, 1H), 3.32 (t, *J* = 8.0, 7.3 Hz, 2H), 2.82 (t, *J* = 8.2, 7.6 Hz, 2H), 2.10 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 207.92, 137.03, 133.90, 131.60, 128.92, 126.97, 126.05, 125.99, 125.62, 125.61, 123.44, 44.38, 30.07, 26.73.

**Synthesis of 4-(4-((triisopropylsilyl)oxy)phenyl)butan-2-one (SI-7)**[7]




The compound was synthesized according to a modified literature procedure.[7]

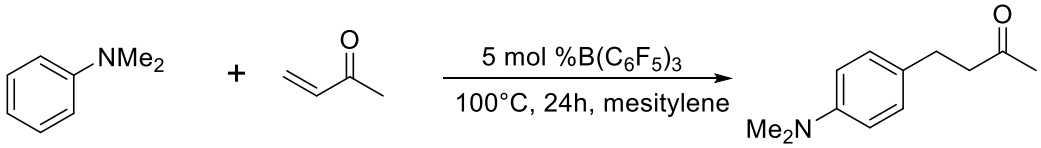
To a flame-dried round-bottom flask equipped with a magnetic stir bar was added 4-(4-hydroxyphenyl)butan-2-one (3.28 g, 20 mmol) and imidazole (2.72 g, 40 mmol). The flask was fitted with a rubber septum, evacuated and backfilled $N_2$. Anhydrous DCM (40 mL) was added to the flask and cooled to 0 ºC in an ice bath. triisopropylsilyl chloride (4.7 mL, 20 mmol) was added dropwise over 3 minutes. The reactions warmed to room temperature and stirred to 16 hours. The reaction was quenched with 1M HCl (100 mL), extracted with DCM (3x50 mL), washed with water (100 mL), brine (100 mL), dried with $MgSO_4$ and the solvent was removed under reduced pressure. Ketone (SI-7) was isolated as a colorless liquid and was used without further purification.

Colorless liquid (6.27 g ,98% yield).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.11 (s, 3H), 1.23 (m, 3H), 1.09 (d, *J* = 7.4 Hz, 18H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 208.48, 154.40, 133.35, 129.19, 119.93, 45.59, 30.29, 29.16, 18.03, 12.75.

**Synthesis of 4-(4-(dimethylamino)phenyl)butan-2-one (SI-8)**[2]




The compound was synthesized according to a modified literature procedure.[2]

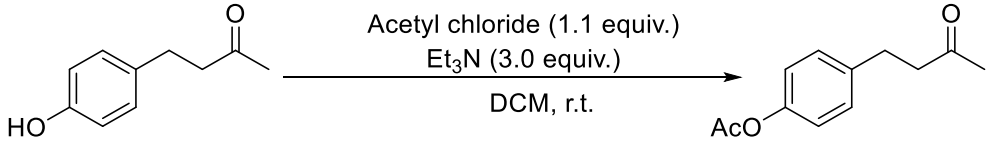
A 35 $cm^3$ pressure tube equipped with screw cap and stiring was charged with $B(C_6F_5)_3$ (51 mg, 0.10 mmol 5 mol%) and dissolved in mesitylene (2 mL). Subsequently N,N-dimethylaniline (247 mg, 2.04 mmol) and but-3-en-2-one (294 mg, 4.20 mmol) were added. The reaction mixture was stirred for 24 h at 100 °C. The rection mixture was cooled to room temperature and directly purifite by column chromatography (cyclohexane: ethyl acetate = 20:1). to afforded. After removal of all volatiles in vaccuo the desired products were obtained.

White solid (0.310 g, 79% yield).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 2.91 (s, 3H), 2.81 (t, *J* = 8.0 Hz, 1H), 2.72 (t, *J* = 8.5, 7.7 Hz, 1H), 2.13 (s, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 208.70, 149.33, 129.01, 113.15, 45.81, 40.99, 30.25, 28.99.

**Synthesis of 4-(3-oxobutyl)phenyl acetate (SI-9)**[4]




The compound was synthesized according to a modified literature procedure.[4]

Acetyl chloride (0.393 mL, 5.50 mmol, 1.1 eq.) was added dropwise to a mixture of 4-(4-hydroxyphenyl)butan-2-one (821 mg, 5.00 mmol, 1.0 eq.) and triethylamine (2.09

mL, 15.0 mmol, 3.0 eq.) in dry DCM and the mixture was stirred at room temperature overnight. The mixture was poured into 100 mL ice-water and the organic phase was washed with $NaHCO_3$ (aq., 5 wt%, 50 mL) followed by $H_2O$ (50 mL), dried over $Na_2SO_4$ and filtered. The solvent was evaporated and the residue purified by column chromatography (PE/EtOAc 15-30%) to afford the titled compound.

Colorless liquid (0.756 g, 73% yield).

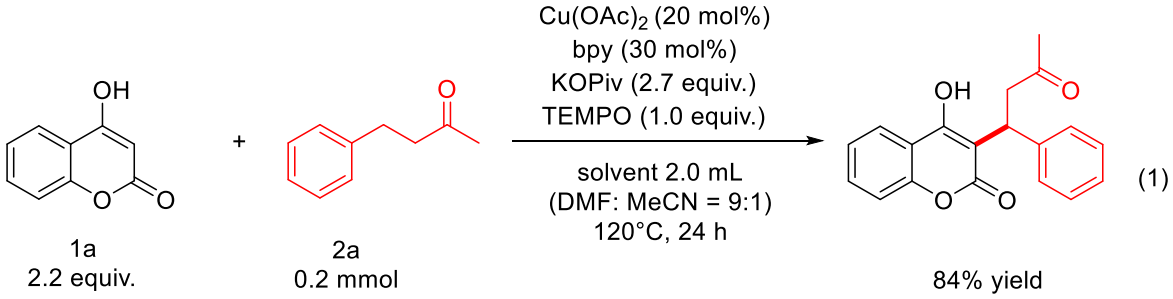
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 2.84 (t, *J* = 7.5 Hz, 1H), 2.71 (t, *J* = 7.5 Hz, 1H), 2.24 (s, 1H), 2.09 (s, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 207.76, 169.65, 148.94, 138.63, 129.31, 121.53, 45.02, 30.08, 29.00, 21.12.

# IV. Mechanic Study

## Control experiment:

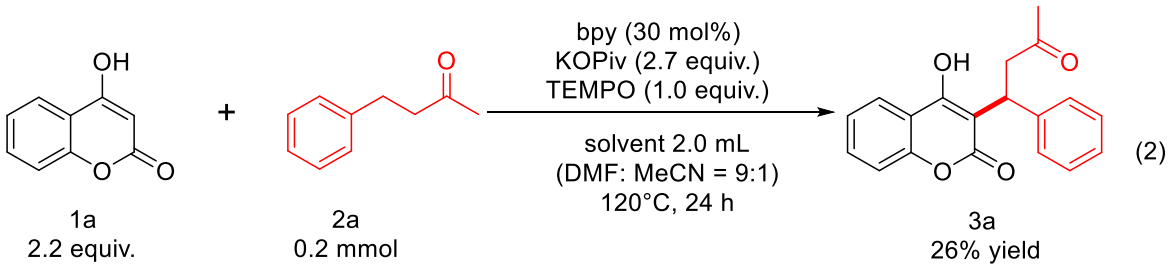
### 1). Standard condition:




(1)

In a nitrogen-filled glovebox, a 35 mL Schlenk tube equipped with a stir bar was charged with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol). The tube was fitted with a rubber septum and moved out of the glove box. Then DMF (1.8 mL), MeCN(0.2 mL) and 4-phenylbutan-2-one (0.030 mL, 0.20 mmol) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 120 ℃ for 24 h. Then the yield was determined by LC analysis (84%, Pyrazinecarbonitrile as internal standard).

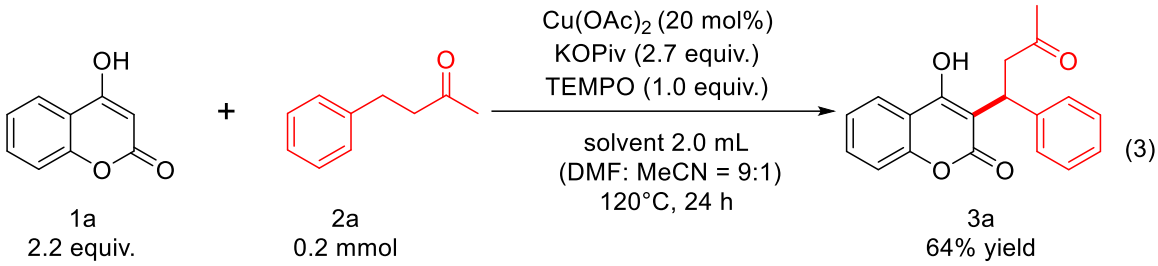
### 2). Without Copper Source:




(2)

The above experiment (1) procedure was followed except no $Cu(OAc)_2$ was added to the reaction mixture.

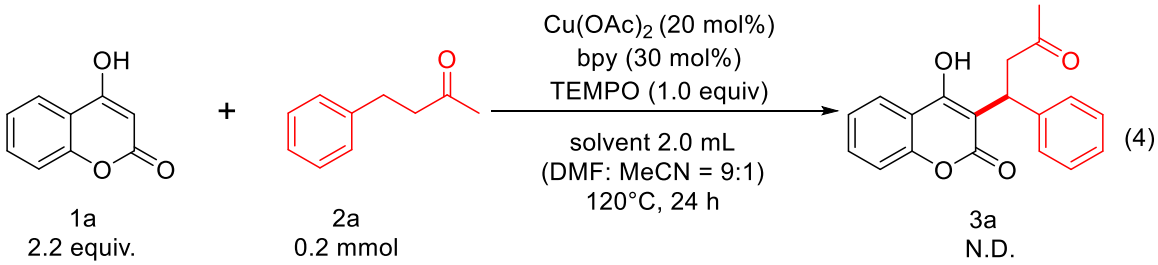
## 3). Without bpy:




(3)

The above experiment (1) procedure was followed except no bpy was added to the reaction mixture.

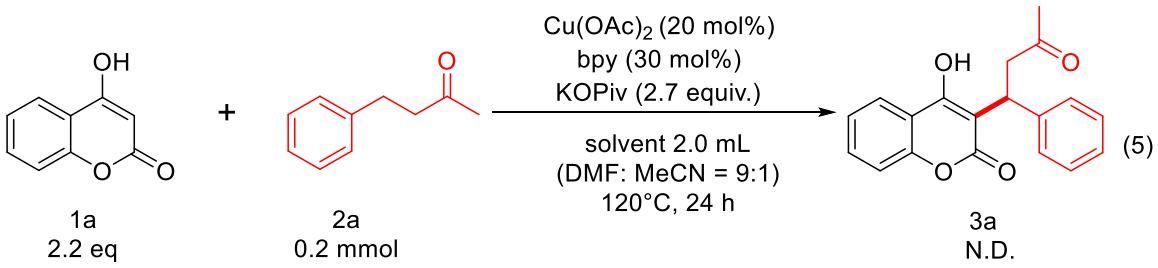
## 4). Without base:




(4)

The above experiment (1) procedure was followed except no KOPiv was added to the reaction mixture.

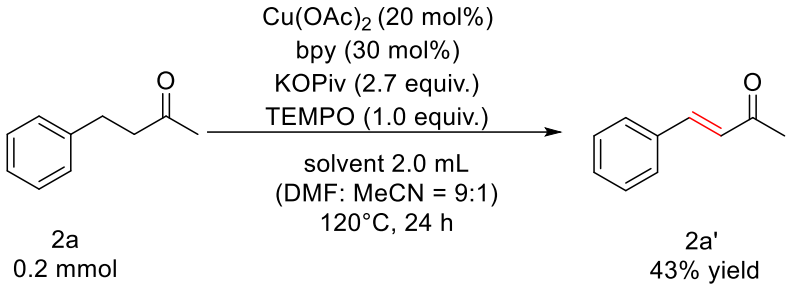
## 5). Without TEMPO:




(5)

The above experiment (1) procedure was followed except no TEMPO was added to the reaction mixture.

## Identification of enone as reaction intermediate:

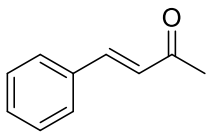



(6)

In a nitrogen-filled glovebox, a 35 mL Schlenk tube equipped with a stir bar was charged with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol). The tube was fitted with a rubber septum and moved out of the glove box. Then DMF (1.8 mL), MeCN(0.2 mL) and 4-phenylbutan-2-one (0.030 mL, 0.20 mmol) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 120 ℃ for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate, followed by filtration through a pad of silica gel. Then, $H_2O$ (15 mL) was added. The phases were separated and the water phase was extracted with ethyl acetate (2×10 mL). The combined organic phases were washed with brine(3×10 mL) and dried over $Na_2SO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to provide the corresponding product.

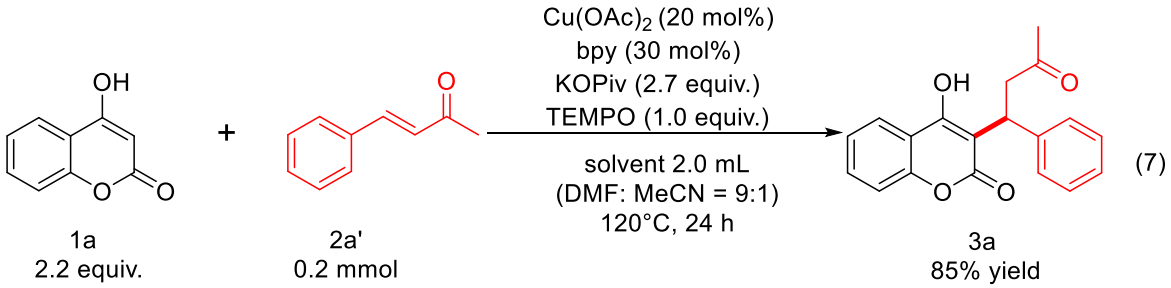
Yellow solid (12.6 mg, 43% yield, eluent = petroleum ether/ ethyl acetate (19: 1)).

**(E)-4-phenylbut-3-en-2-one (2a')** [8]




**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 3H), 7.42 – 7.37 (m, 3H), 6.72 (d, *J* = 16.2 Hz, 1H), 2.38 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 198.67, 143.63, 134.44, 130.63, 129.05, 128.35, 127.19, 77.48, 77.16, 76.84, 27.58.(All characterization data are in accordance with the literature [8]).




1a
2.2 equiv.

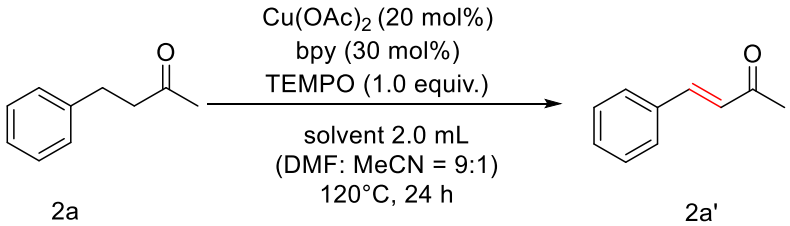
2a'
0.2 mmol

3a
85% yield

(7)

In a nitrogen-filled glovebox, a 35 mL Schlenk tube equipped with a stir bar was charged with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), KOPiv (0.0768 g, 0.54 mmol), TEMPO (0.0313 g, 0.2 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), (E)-4-phenylbut-3-en-2-one (0.0293g, 0.2 mmol). The tube was fitted with a rubber septum and moved out of the glove box. Then DMF (1.8 mL), MeCN (0.2 mL) and were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 120 ℃ for 24 h. Then the yield was determined by LC analysis (85% yield, Pyrazinecarbonitrile as internal standard).

## Identification of the role of base:




2a
0.2 mmol

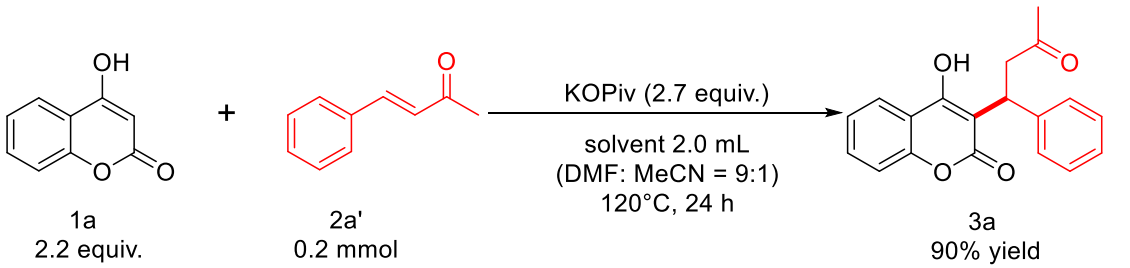
2a'
91% yield

(8)

In a nitrogen-filled glovebox, a 35 mL Schlenk tube equipped with a stir bar was charged with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol). The tube was fitted with a rubber septum and moved out of the glove box. Then DMF (1.8 mL), MeCN(0.2 mL) and 4-phenylbutan-2-one

(0.030 mL, 0.20 mmol) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 120 ℃ for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate, followed by filtration through a pad of silica gel. Then, $H_2O$ (15 mL) was added. The phases were separated and the water phase was extracted with ethyl acetate (2×10 mL). The combined organic phases were washed with brine(3×10 mL) and dried over $Na_2SO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to provide the corresponding product.

Yellow solid (26.6 mg, 91% yield, eluent = petroleum ether/ ethyl acetate (19: 1)).




1a
2.2 equiv.

2a'
0.2 mmol

3a
90% yield

(9)

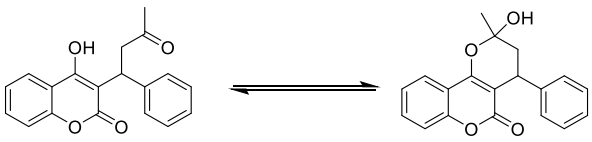
In a nitrogen-filled glovebox, a 35 mL Schlenk tube equipped with a stir bar was charged with KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), (E)-4-phenylbut-3-en-2-one (0.0293g, 0.2 mmol). The tube was fitted with a rubber septum and moved out of the glove box. Then DMF (1.8 mL), MeCN (0.2 mL) and were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 120 ℃ for 24 h. Then the yield was determined by LC analysis (90% yield, Pyrazinecarbonitrile as internal standard).

# V. Synthesis and Characterization of Products

## General Procedure for Copper Catalyzed Dehydrogenation-Conjugate Addition Reaction:

In a nitrogen-filled glovebox, a 35 mL Schlenk tube equipped with a stir bar was charged with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol). The tube was fitted with a rubber septum and moved out of the glove box. Then DMF (1.8 mL), MeCN(0.2 mL) and ketone (0.2 mmol) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 120 ℃ for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate, followed by filtration through a pad of silica gel. Then, $H_2O$ (15 mL) was added. The phases were separated and the water phase was extracted with ethyl acetate (2×10 mL). The combined organic phases were washed with brine(3×10 mL) and dried over $Na_2SO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to provide the corresponding product. (All characterization data are in accordance with the literature [9]).

**Warfarin(3a) [9]**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2

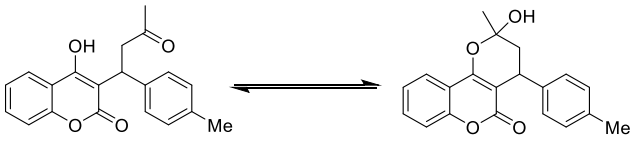
mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 4-phenylbutan-2-one (0.030 mL, 0.20 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^{o}$C for 24 h.

Pale yellow solid (49.9 mg, 81% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.52 (s, 0.23H), 7.94 (dd, *J* = 7.9, 1.6 Hz, 0.22H), 7.90 (dd, *J* = 7.9, 1.5 Hz, 0.88H), 7.84 – 7.78 (m, 1.04H), 7.60 – 7.53 (m, 0.93H), 7.49 (td, *J* = 7.8, 1.6 Hz, 1.36H), 7.36 – 7.19 (m, 15.99H), 4.70 (dd, *J* = 10.1, 2.5 Hz, 0.25H), 4.28 (dd, *J* = 7.0, 3.3 Hz, 0.91H), 4.16 (dd, *J* = 11.4, 6.8 Hz, 1.07H), 3.86 (dd, *J* = 19.5, 10.1 Hz, 0.28H), 3.42 (s, 1.00H), 3.26 (s, 0.90H), 2.54 (dd, *J* = 14.2, 3.3 Hz, 0.93H), 2.51 – 2.37 (m, 2.04H), 2.29 (s, 0.76H), 2.00 (dd, *J* = 14.0, 11.5 Hz, 1.09H), 1.69 (d, *J* = 15.1 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 212.82, 162.27, 161.38, 159.79, 158.87, 153.11, 153.03, 143.30, 141.53, 132.14, 131.90, 131.69, 129.36, 128.75, 128.30, 128.09, 127.35, 127.16, 127.08, 126.81, 126.63, 124.06, 123.97, 123.75, 123.18, 122.83, 116.79, 116.71, 116.65, 116.32, 115.99, 115.67, 108.02, 104.32, 101.25, 100.62, 99.09, 45.29, 42.64, 40.10, 35.47, 34.97, 34.28, 30.21, 28.36, 27.87.

**4-hydroxy-3-(3-oxo-1-(p-tolyl)butyl)-2H-chromen-2-one(3b)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(p-tolyl)butan-2-one (0.0324g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^{o}$C for 24 h.

White solid (48.9 mg, 76% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

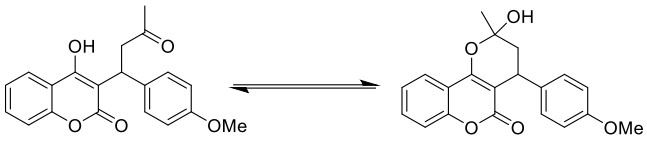
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.9, 1.6 Hz, 0.88H), 7.78 (dd, *J* = 8.3, 1.7 Hz, 1.01H), 7.55 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 0.92H), 7.48 – 7.43 (m, 1.34H), 7.34 – 7.07 (m, 13.42H), 4.23 (dd, *J* = 6.9, 3.4 Hz, 0.92H), 4.12 (dd, *J* = 11.4, 6.8 Hz, 0.88H), 3.92

(s, 0.98H), 3.49 (s, 0.98H), 2.50 (dd, *J* = 14.2, 3.4 Hz, 0.96H), 2.43 (dd, *J* = 14.0, 6.8 Hz, 1.18H), 2.36 (dd, *J* = 14.2, 6.9 Hz, 1.12H), 2.30 (d, *J* = 2.9 Hz, 6.11H), 1.96 (dd, *J* = 14.0, 11.4 Hz, 1.20H), 1.66 (d, *J* = 8.7 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.34, 161.52, 159.75, 158.91, 153.03, 152.93, 140.28, 138.36, 136.93, 135.99, 132.05, 131.56, 130.06, 129.42, 127.00, 126.90, 124.01, 123.67, 123.15, 122.81, 116.71, 116.53, 116.02, 115.68, 104.37, 101.39, 100.68, 99.18, 42.77, 40.08, 35.01, 33.88, 28.16, 27.76, 21.19, 21.14.

**HRMS-ESI** (positive) M = $C_{20}H_{18}O_4$: Calcd. for $C_{20}H_{19}O_4$($[M + H]^+$) m/z : 323.1278, found($[M + H]^+$) m/z : 323.1278.

**4-hydroxy-3-(1-(4-methoxyphenyl)-3-oxobutyl)-2H-chromen-2-one(3c)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(4-methoxyphenyl)butan-2-one (0.036 mL, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^oC$ for 24 h.

Pale yellow solid (43.1 mg, 64% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

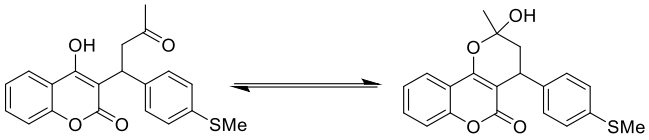
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.54 (s, 0.13H), 7.87 (dd, *J* = 7.9, 1.6 Hz, 1.00H), 7.77 (dd, *J* = 8.2, 1.6 Hz, 1.07H), 7.53 (td, *J* = 8.0, 1.6 Hz, 0.80H), 7.43 (td, *J* = 7.7, 1.7 Hz, 1.27H), 7.33 – 7.25 (m, 1.95H), 7.22 – 7.13 (m, 4.16H), 7.13 – 7.08 (m, 2.13H), 6.86 – 6.76 (m, 4.20H), 4.66 (dd, *J* = 9.8, 3.2 Hz, 0.26H), 4.18 (dd, *J* = 6.8, 3.6 Hz, 0.82H), 4.11 (dd, *J* = 11.2, 6.8 Hz, 1.08H), 3.75 (d, *J* = 3.6 Hz, 6.17H), 2.48 (d, *J* = 3.7 Hz, 0.30H), 2.46 – 2.43 (m, 0.75H), 2.43 – 2.38 (m, 0.80H), 2.37 – 2.29 (m, 0.91H), 2.24 (s, 0.68H), 1.95 (dd, *J* = 14.0, 11.3 Hz, 1.07H), 1.65 (d, *J* = 6.4 Hz, 5.87H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 212.48, 162.41, 161.66, 159.79, 159.03, 158.58, 158.10, 152.95, 152.85, 135.37, 133.39, 132.03, 131.52, 129.13, 128.15, 128.10, 124.02, 123.91, 123.68, 123.14, 122.84, 116.63, 116.43, 116.03, 115.67, 114.60, 114.08,

113.62, 104.31, 101.54, 100.73, 99.35, 99.32, 55.32, 55.29, 45.56, 42.80, 40.13, 34.57, 34.31, 33.63, 30.14, 28.00, 27.60.

**HRMS-ESI** (positive) M = $C_{20}H_{18}O_5$: Calcd. for $C_{20}H_{19}O_5$([M + H]$^+$)m/z : 339.1227, found([M + H]$^+$) m/z : 339.1225.

**4-hydroxy-3-(1-(4-(methylthio)phenyl)-3-oxobutyl)-2H-chromen-2-one(3d)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(4-(methylthio)phenyl)butan-2-one (0.0388 g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^oC$ for 24 h.

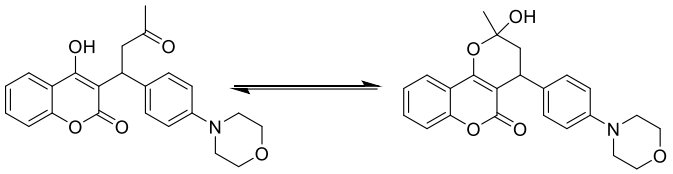
Pale yellow solid (41.6 mg, 59% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.9, 1.6 Hz, 0.67H), 7.77 (dd, *J* = 7.9, 1.6 Hz, 1.14H), 7.52 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 0.78H), 7.43 (ddd, *J* = 8.7, 7.4, 1.7 Hz, 1.31H), 7.30 – 7.24 (m, 2.15H), 7.20 – 7.09 (m, 10.05H), 4.17 – 4.07 (m, 2.04H), 2.65 (d, *J* = 9.1 Hz, 0.49H), 2.47 – 2.29 (m, 9.06H), 2.25 (s, 0.59H), 1.92 (dd, *J* = 14.0, 11.4 Hz, 1.03H), 1.65 (d, *J* = 7.8 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.36, 161.65, 159.91, 159.23, 152.92, 152.82, 140.49, 138.82, 136.87, 135.98, 132.07, 131.63, 128.57, 127.71, 127.67, 127.27, 124.03, 123.74, 123.11, 122.84, 116.63, 116.44, 115.95, 115.63, 103.93, 101.34, 100.62, 99.25, 42.60, 40.14, 34.92, 34.25, 28.01, 27.50, 16.19, 15.97.

**HRMS-ESI** (positive) M = $C_{20}H_{18}O_4S$: Calcd. for $C_{20}H_{19}O_4S$([M + H]$^+$)m/z : 355.0999, found([M + H]$^+$) m/z : 355.0994.

**4-hydroxy-3-(1-(4-morpholinophenyl)-3-oxobutyl)-2H-chromen-2-one(3e)**



(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(4-morpholinophenyl)butan-2-one (0.0466 g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^oC$ for 24 h.

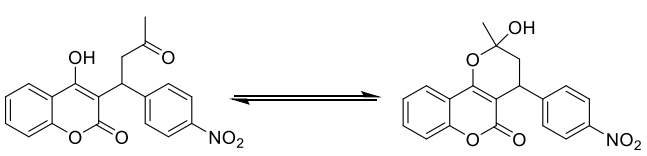
Pale yellow solid (33.4 mg, 43% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.6 Hz, 1.02H), 7.83 – 7.78 (m, 0.88H), 7.56 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 0.88H), 7.51 – 7.45 (m, 1.25H), 7.36 – 7.30 (m, 1.74H), 7.23 (t, *J* = 7.6 Hz, 2.80H), 7.20 – 7.10 (m, 3.84H), 6.90 – 6.83 (m, 3.96H), 4.22 (dd, *J* = 6.7, 3.3 Hz, 1.11H), 4.11 (dd, *J* = 11.4, 6.8 Hz, 1.14H), 3.85 (dd, *J* = 4.2, 2.2 Hz, 8.32H), 3.12 (dd, *J* = 6.1, 3.5 Hz, 8.05H), 2.43 (dd, *J* = 14.0, 6.9 Hz, 1.03H), 2.36 (dd, *J* = 14.2, 6.8 Hz, 1.02H), 2.28 (s, 0.75H), 2.08 – 1.89 (m, 1.11H), 1.68 (d, *J* = 8.0 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.35, 161.49, 159.70, 158.86, 153.02, 152.92, 132.04, 131.56, 127.92, 127.87, 124.01, 123.69, 123.16, 122.81, 116.69, 116.58, 116.52, 116.26, 116.05, 115.69, 104.38, 101.43, 100.72, 99.27, 66.94, 66.87, 49.72, 49.37, 42.68, 39.95, 34.58, 33.36, 28.14, 27.73.

**HRMS-ESI** (positive) M = $C_{23}H_{23}O_5N$: Calcd. for $C_{23}H_{24}O_5N([M + H]^+)$m/z : 394.1649, found($[M + H]^+$) m/z : 394.1643.

**Acenocounarol(3f)**



(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$

(0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(4-nitrophenyl)butan-2-one (0.0386g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 °C for 24 h.

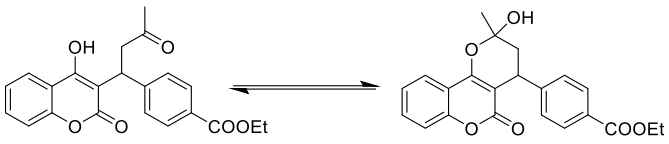
Yellow solid (32.5 mg, 46% yield, eluent = petroleum ether/ ethyl acetate (7: 3)).

**$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 8.10 (t, *J* = 9.3 Hz, 4.34H), 7.85 (d, *J* = 7.8 Hz, 1.94H), 7.63 (t, *J* = 8.1 Hz, 2.22H), 7.57 – 7.45 (m, 5.52H), 7.43 – 7.34 (m, 4.22H), 4.17 (dd, *J* = 11.6, 5.8 Hz, 1.98H), 2.35 (dd, *J* = 14.1, 6.9 Hz, 1.90H), 2.24 (dd, *J* = 14.0, 4.9 Hz, 0.72H), 2.06 (s, 1.28H), 1.89 (t, *J* = 12.7 Hz, 1.38H), 1.64 (d, *J* = 27.4 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 161.02, 160.38, 159.72, 159.35, 152.51, 152.38, 145.91, 145.62, 132.29, 132.21, 128.89, 128.55, 124.20, 124.14, 123.46, 122.98, 122.82, 122.73, 116.39, 116.29, 115.54, 115.40, 102.45, 100.98, 100.86, 99.62, 41.89, 35.31, 35.23, 31.38, 27.16, 26.47.

**HRMS-ESI** (positive) M = $C_{19}H_{15}O_6N$: Calcd. for $C_{19}H_{16}O_6N$ ($[M + H]^+$) m/z : 354.0972, found ($[M + H]^+$) m/z : 354.0975.

**ethyl 4-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl)-3-oxobutyl)benzoate(3g)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), ethyl 4-(3-oxobutyl)benzoate (0.0440 g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 °C for 24 h.

White solid (64.3 mg, 85% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

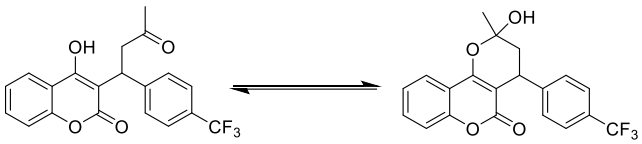
**$^1$H NMR** ($CDCl_3$) δ 7.97 – 7.90 (m, 4.35H), 7.86 (dd, *J* = 7.8, 1.5 Hz, 0.66H), 7.78 (dd, *J* = 8.0, 1.5 Hz, 1.25H), 7.53 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 0.74H), 7.45 (ddd, *J* = 8.6, 7.5, 1.6 Hz, 1.32H), 7.31 – 7.23 (m, 6.07H), 7.20 (t, *J* = 8.4 Hz, 2.42H), 4.48 (s,

0.96H), 4.37 – 4.28 (m, 4.26H), 4.24 – 4.17 (m, 1.94H), 3.93 (s, 0.57H), 3.52 (t, *J* = 4.7 Hz, 0.26H), 3.47 (t, *J* = 6.7 Hz, 0.26H)2.46 – 2.36 (m, 2.39H), 2.28 (s, 0.47H), 1.91 (dd, *J* = 13.9, 11.7 Hz, 1.72H), 1.68 (d, *J* = 15.8 Hz, 6.00H), 1.38 – 1.32 (m, 6.36H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 212.25, 166.77, 166.75, 162.28, 161.58, 160.06, 159.43, 152.97, 152.88, 149.04, 148.03, 132.15, 131.79, 130.08, 129.96, 129.46, 128.73, 128.69, 128.04, 127.45, 127.17, 124.08, 123.84, 123.10, 122.88, 116.69, 116.53, 115.88, 115.64, 103.55, 101.27, 100.45, 99.13, 61.01, 60.96, 42.34, 40.15, 35.56, 35.30, 28.06, 27.48, 14.43, 14.

**HRMS-ESI** (positive) M = $C_{22}H_{20}O_6$: Calcd. for $C_{22}H_{21}O_6$([M + H]$^+$) m/z: 381.1333, found ([M + H]$^+$) m/z: 381.1334.

**4-hydroxy-3-(3-oxo-1-(4-(trifluoromethyl)phenyl)butyl)-2H-chromen-2-one(3h)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(4-(trifluoromethyl)phenyl)butan-2-one (0.0432 g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^o$C for 24 h.

White solid (66.2 mg, 88% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.9, 1.6 Hz, 0.67H), 7.80 (dd, *J* = 7.9, 1.6 Hz, 1.16H), 7.59 – 7.45 (m, 6.60H), 7.40 – 7.28 (m, 5.12H), 7.28 – 7.20 (m, 3.26H), 5.21 (s, 0.12H), 4.22 (dd, *J* = 11.7, 6.5 Hz, 1.82H), 3.84 (s, 0.94H), 3.39 (s, 0.45H), 2.48 – 2.35 (m, 2.51H), 2.00 (s, 1.37H), 1.92 (dd, *J* = 13.9, 11.8 Hz, 1.31H), 1.70 (d, *J* = 13.9 Hz, 6.00H).

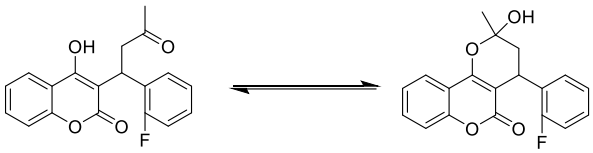
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.26, 161.52, 160.01, 159.42, 153.05, 153.03, 153.00, 152.98, 147.69, 146.69, 133.32, 132.28, 131.96, 127.89, 127.53, 125.73 (q, *J* = 3.4 Hz), 125.61 (q, *J* = 3.4 Hz), 124.14, 123.93, 123.08, 122.89, 117.39, 116.81, 116.66, 115.84,

115.59, 103.53, 101.20, 100.27, 99.04, 42.37, 39.89, 35.46, 34.98, 28.24, 27.86.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -62.29, -62.32.

**HRMS-ESI** (positive) M = $C_{20}H_{15}O_4F_3$: Calcd. for $C_{20}H_{16}O_4F_3$ ($[M + H]^+$) m/z: 377.0995, found ($[M + H]^+$) m/z: 377.0994.

**3-(1-(2-fluorophenyl)-3-oxobutyl)-4-hydroxy-2H-chromen-2-one(3i)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(2-fluorophenyl)butan-2-one (0.0332g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^oC$ for 24 h.

White solid (47.3 mg, 73% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

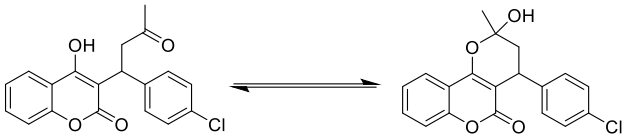
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.6 Hz, 0.82H), 7.78 (dd, *J* = 7.8, 1.5 Hz, 1.13H), 7.58 – 7.52 (m, 1.11H), 7.46 (td, *J* = 7.8, 1.6 Hz, 1.37H), 7.33 – 7.27 (m, 1.95H), 7.24 – 7.07 (m, 7.26H), 7.06 – 6.97 (m, 3.18H), 4.49 – 4.41 (m, 1.92H), 4.00 (s, 0.74H), 3.45 (s, 0.72H), 2.53 (dd, *J* = 14.4, 3.4 Hz, 0.81H), 2.46 (dd, *J* = 13.8, 6.8 Hz, 1.15H), 2.34 (dd, *J* = 14.4, 7.2 Hz, 0.88H), 2.27 (s, 0.61H), 2.03 (dd, *J* = 13.8, 11.4 Hz, 1.35H), 1.69 (d, *J* = 9.6 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 212.14, 162.28, 162.11, 162.07, 161.50, 160.17, 159.84, 159.63, 159.03, 153.00, 152.85, 132.15, 131.65, 129.83, 129.69, 128.87, 128.74, 128.72, 128.63, 128.25, 128.21, 128.15, 128.07, 124.32, 124.29, 124.22, 124.18, 124.06, 123.76, 123.07, 122.83, 116.74, 116.53, 116.20, 116.05, 116.00, 115.84, 115.79, 115.65, 115.57, 103.37, 100.63, 100.47, 99.16, 45.21, 40.09, 37.90, 28.16, 27.93.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -116.69, -117.98.

**HRMS-ESI** (positive) M = $C_{19}H_{15}O_4F$: Calcd. for $C_{19}H_{16}O_4F$ ($[M + H]^+$) m/z: 327.1027, found ($[M + H]^+$) m/z: 327.1027.

**Coumachlor(3j)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(4-chlorophenyl)butan-2-one (0.0364g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^oC$ for 24 h.

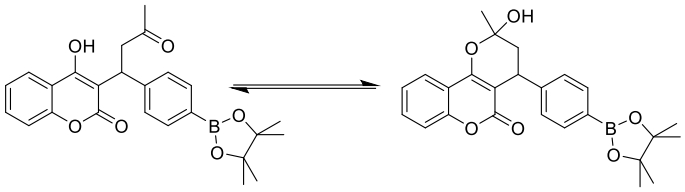
White solid (54.3 mg, 79% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.8, 1.0 Hz, 0.68H), 7.77 (dd, *J* = 8.0, 1.5 Hz, 1.26H), 7.53 (td, *J* = 7.8, 1.5 Hz, 0.73H), 7.44 (td, *J* = 8.2, 1.5 Hz, 1.42H), 7.30 – 7.08 (m, 13.48H), 4.33 (s, 0.97H), 4.15 – 4.08 (m, 2.00H), 3.76 (s, 0.69H), 3.71 (t, *J* = 4.6 Hz, 0.42H), 3.51 (t, *J* = 4.7 Hz, 0.35H) 3.46 (t, *J* = 6.7 Hz, 0.36H) , 2.40 (dd, *J* = 14.1, 7.1 Hz, 1.65H), 2.37 – 2.30 (m, 0.82H), 2.25 (s, 0.52H), 1.98 (s, 0.34H), 1.89 (dd, *J* = 13.9, 11.6 Hz, 1.43H), 1.65 (d, *J* = 10.3 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.32, 161.63, 159.96, 159.35, 152.84, 152.75, 141.94, 140.81, 132.33, 132.09, 131.98, 131.71, 128.74, 128.72, 128.47, 124.02, 123.77, 123.02, 122.80, 116.60, 116.42, 115.81, 115.53, 103.61, 101.25, 100.40, 99.12, 42.47, 40.04, 34.85, 34.43, 27.95, 27.51.

**HRMS-ESI** (positive) M = $C_{19}H_{15}O_4Cl$: Calcd. for $C_{19}H_{16}O_4Cl$ ($[M + H]^+$) m/z: 343.0732, found ($[M + H]^+$) m/z: 343.0731.

**4-hydroxy-3-(3-oxo-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butyl)-2H-chromen-2-one(3k)**



(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-Hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butan-2-one (0.0548g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^oC$ for 24 h.

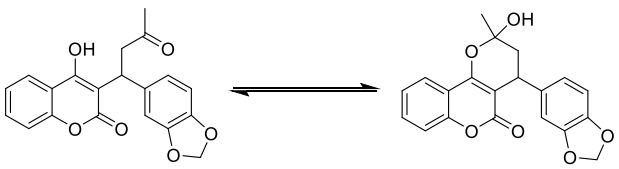
White solid (53.5 mg, 62% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.9, 1.6 Hz, 0.74H), 7.79 (dd, *J* = 8.0, 1.6 Hz, 1.23H), 7.77 – 7.73 (m, 3.81H), 7.56 – 7.51 (m, 0.85H), 7.44 (td, *J* = 7.8, 1.6 Hz, 1.27H), 7.33 – 7.18 (m, 9.08H), 4.24 – 4.13 (m, 2.37H), 2.48 – 2.36 (m, 2.49H), 2.27 (s, 0.67H), 1.94 (dd, *J* = 13.9, 11.5 Hz, 1.69H), 1.66 (d, *J* = 10.9 Hz, 6.00H), 1.32 (s, 21.23H), 1.22 (s, 3.13H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.19, 161.50, 159.88, 159.10, 153.05, 152.95, 146.84, 145.29, 135.65, 135.34, 134.81, 132.06, 131.62, 127.36, 126.58, 126.52, 124.01, 123.72, 123.15, 122.85, 116.73, 116.56, 115.98, 115.69, 104.02, 101.31, 100.62, 99.13, 83.85, 83.74, 42.52, 40.33, 35.63, 35.01, 28.18, 27.51, 24.96, 24.91.

**HRMS-ESI** (positive) M = $C_{25}H_{27}O_6B$: Calcd. for $C_{25}H_{28}O_6{}^{10}B$ ($[C_{25}H_{27}O_6{}^{10}B + H]^+$)m/z : 434.2010, found($[C_{25}H_{27}O_6{}^{10}B + H]^+$) m/z : 434.2006.

**3-(1-(benzo[d][1,3]dioxol-5-yl)-3-oxobutyl)-4-hydroxy-2H-chromen-2-one(3l)**



(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$

(0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-Hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(benzo[d][1,3]dioxol-5-yl)butan-2-one (0.0384 g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^{o}$C for 24 h.

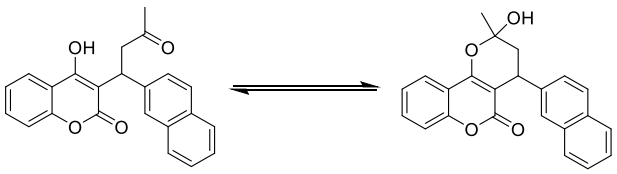
Pale yellow solid (46.6 mg, 66% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.6 Hz, 0.82H), 7.75 (dd, *J* = 7.0, 1.9 Hz, 1.13H), 7.52 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 0.84H), 7.46 – 7.39 (m, 1.19H), 7.32 – 7.23 (m, 1.65H), 7.21 – 7.13 (m, 2.48H), 6.76 – 6.62 (m, 6.33H), 5.88 (d, *J* = 4.7 Hz, 4.34H), 4.30 (s, 0.08H), 4.12 (dd, *J* = 6.9, 3.8 Hz, 0.83H), 4.07 (dd, *J* = 11.3, 6.8 Hz, 1.21H), 2.46 – 2.36 (m, 1.97H), 2.30 (dd, *J* = 14.2, 6.9 Hz, 0.91H), 2.07 (s, 0.11H), 2.03 (s, 0.16H), 1.98 (s, 0.13H), 1.91 (dd, *J* = 13.9, 11.4 Hz, 1.21H), 1.65 (d, *J* = 9.1 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.42, 161.74, 159.90, 159.19, 152.88, 152.77, 148.30, 147.73, 146.62, 146.03, 137.30, 135.64, 132.07, 131.57, 124.02, 123.70, 123.10, 122.83, 120.24, 119.75, 116.59, 116.38, 115.93, 115.57, 108.62, 108.40, 107.91, 107.48, 104.09, 101.40, 101.17, 100.92, 100.69, 99.31, 42.78, 40.16, 35.09, 34.27, 27.92, 27.50.

**HRMS-ESI** (positive) M = $C_{20}H_{16}O_6$: Calcd. for $C_{20}H_{17}O_6$ ($[M + H]^+$) m/z: 353.1020, found ($[M + H]^+$) m/z: 353.1016.

**4-hydroxy-3-(1-(naphthalen-2-yl)-3-oxobutyl)-2H-chromen-2-one(3m)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-Hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(naphthalen-2-yl)butan-2-one (0.0396g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^{o}$C for 24 h.

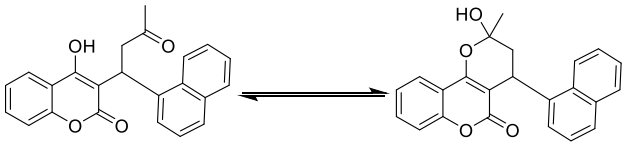
Pale yellow solid (49.8 mg, 70% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.5 Hz, 0.82H), 7.79 – 7.61 (m, 8.98H), 7.55 – 7.50 (m, 0.73H), 7.44 – 7.33 (m, 6.17H), 7.33 – 7.22 (m, 2.76H), 7.17 (t, *J* = 7.7 Hz, 2.48H), 4.47 (s, 0.75H), 4.36 – 4.24 (m, 1.86H), 3.84 (s, 0.67H), 3.70 – 3.67 (t, *J* = 4.5 Hz, 0.37H), 3.50 – 3.47 (t, *J* = 4.6 Hz, 0.39H), 3.44 (t, *J* = 6.7 Hz, 0.39H), 2.51 (dd, *J* = 14.2, 3.9 Hz, 0.67H), 2.41 – 2.29 (m, 1.85H), 1.96 (dd, *J* = 14.0, 11.3 Hz, 0.97H), 1.56 (d, *J* = 14.7 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.48, 161.80, 160.11, 159.38, 152.99, 152.85, 140.85, 139.34, 133.69, 133.57, 132.57, 132.44, 132.12, 131.61, 129.04, 128.36, 127.83, 127.67, 126.27, 125.95, 125.85, 125.76, 125.72, 125.47, 125.35, 125.22, 124.06, 123.73, 123.20, 122.88, 116.67, 116.45, 116.00, 115.68, 103.93, 101.26, 100.80, 99.28, 77.48, 77.16, 76.84, 71.66, 71.16, 61.85, 42.55, 39.89, 35.50, 34.82, 31.73, 27.85, 27.42, 19.32, 14.00.

**HRMS-ESI** (positive) M = $C_{23}H_{18}O_4$: Calcd. for $C_{23}H_{19}O_4$ ($[M + H]^+$) m/z: 359.1278, found ($[M + H]^+$) m/z: 359.1280.

**4-hydroxy-3-(1-(naphthalen-1-yl)-3-oxobutyl)-2H-chromen-2-one(3n)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-Hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(naphthalen-1-yl)butan-2-one (0.0396g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^{o}$C for 24 h.

Pale yellow solid (45.7 mg, 64% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

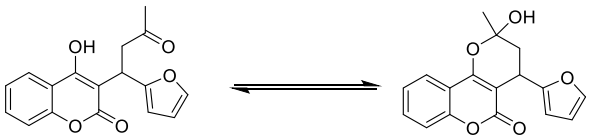
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.75 (s, 0.19H), 8.10 (d, *J* = 8.4 Hz, 1.03H), 7.95 – 7.82 (m, 3.36H), 7.80 – 7.72 (m, 2.62H), 7.68 (d, *J* = 8.3 Hz, 1.04H), 7.61 – 7.13 (m, 14.16H), 5.30 (dd, *J* = 10.4, 2.7 Hz, 0.21H), 4.97 (dd, *J* = 5.8, 2.0 Hz, 1.75H), 4.40 (s, 0.71H),

4.04 (dd, *J* = 19.1, 10.3 Hz, 0.20H), 3.64 (s, 0.85H), 3.36 (dd, *J* = 19.2, 2.7 Hz, 0.23H), 2.68 (dd, *J* = 14.2, 2.3 Hz, 0.92H), 2.46 (dd, *J* = 14.2, 7.3 Hz, 1.04H), 2.26 (s, 0.67H), 1.93 (s, 0.73H), 1.72 (t, *J* = 8.7, 7.4 Hz, 0.74H), 1.56 (d, *J* = 24.7 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 212.81, 162.28, 161.85, 161.56, 160.81, 160.25, 153.02, 152.87, 137.19, 135.03, 134.82, 134.19, 133.76, 132.17, 131.84, 131.79, 131.57, 131.27, 130.85, 129.57, 129.17, 128.51, 128.01, 127.01, 126.60, 126.12, 125.67, 125.47, 125.09, 124.11, 123.99, 123.86, 123.73, 123.20, 123.13, 122.95, 122.84, 122.79, 116.73, 116.50, 116.14, 116.11, 115.66, 107.77, 101.24, 100.48, 99.46, 46.76, 37.76, 31.72, 30.04, 28.25, 27.90.

**HRMS-ESI** (positive) M = $C_{23}H_{18}O_4$: Calcd. for $C_{23}H_{19}O_4$ ($[M + H]^+$) m/z: 359.1278, found ($[M + H]^+$) m/z: 359.1276.

**Coumafuryl(3o)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-Hydroxycoumarin (0.0712 g, 0.44 mmol), 4-(furan-2-yl)butan-2-one (0.0276g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^oC$ for 24 h.

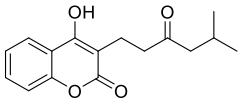
Pale yellow solid (30.1 mg, 51% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.9, 1.5 Hz, 1.19H), 7.79 (d, *J* = 7.9 Hz, 0.48H), 7.59 – 7.44 (m, 2.39H), 7.39 – 7.22 (m, 7.06H), 6.31 (dd, *J* = 3.2, 1.9 Hz, 2.13H), 6.18 (d, *J* = 3.2 Hz, 1.14H), 6.14 (dd, *J* = 10.5, 3.2 Hz, 0.95H), 5.34 (d, *J* = 4.8 Hz, 0.12H), 5.10 (s, 0.20H), 4.75 (d, *J* = 8.2 Hz, 0.41H), 4.36 – 4.28 (m, 2.51H), 3.91 (s, 0.04H), 3.65 (dd, *J* = 19.6, 8.4 Hz, 0.39H), 3.32 (dd, *J* = 19.7, 3.0 Hz, 0.43H), 2.88 (dd, *J* = 9.6, 6.5 Hz, 0.36H), 2.70 (dd, *J* = 14.4, 1.8 Hz, 1.18H), 2.38 – 2.33 (m, 0.98H), 2.30 – 2.24 (m, 2.53H), 1.69 (d, *J* = 28.3 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.04, 159.32, 153.99, 152.92, 142.32, 141.34, 140.96, 132.24, 132.05, 131.74, 124.80, 124.00, 123.67, 123.21, 122.81, 116.64, 115.49, 110.90, 110.51, 106.82, 106.42, 106.20, 99.66, 99.08, 45.08, 38.17, 35.89, 34.31, 31.64, 30.30, 28.08, 28.06.

**HRMS-ESI** (positive) M = $C_{17}H_{14}O_5$: Calcd. for $C_{17}H_{15}O_5$([M + H]$^+$) m/z: 299.0914, found ([M + H]$^+$) m/z: 299.0915.

**4-hydroxy-3-(5-methyl-3-oxohexyl)-2H-chromen-2-one(3p)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0626 g, 0.4 mmol), KOPiv (0.0341 g, 0.24 mmol), 4-hydroxycoumarin (0.0324 g, 0.2 mmol), 5-methylhexan-3-one ((0.085mL, 0.6 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^o$C for 24 h.

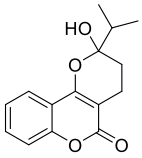
Yellow solid (23.7 mg, 43% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.32 – 7.25 (m, 2H), 2.94 (t, 2H), 2.80 – 2.75 (m, 2H), 2.37 (d, *J* = 7.0 Hz, 2H), 2.25 – 2.08 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 217.26, 164.22, 161.86, 152.70, 131.80, 123.98, 123.87, 116.62, 116.39, 104.52, 51.43, 42.86, 25.08, 22.59, 17.57.

**HRMS-ESI** (positive) M = $C_{16}H_{18}O_4$: Calcd. for $C_{16}H_{19}O_4$([M + H]$^+$) m/z: 275.1278, found ([M + H]$^+$) m/z: 275.1278.

**2-hydroxy-2-isopropyl-3,4-dihydro-2H,5H-pyrano[3,2-c]chromen-5-one(3q)**



(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0148 g, 0.08 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0626 g, 0.4 mmol), KOPiv (0.0341 g, 0.24 mmol), 4-hydroxycoumarin (0.0324 g, 0.2 mmol), 2-methylpentan-3-one (0.075mL, 0.6 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 °C for 24 h.

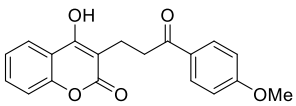
Yellow solid (15.7 mg, 31% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.50 (td, *J* = 7.7, 1.7 Hz, 2H), 7.31 – 7.25 (m, 1H), 3.00 (t, *J* = 4.3 Hz, 2H), 2.77 (t, *J* = 5.4 Hz, 2H), 2.69 (p, *J* = 7.0 Hz, 1H), 1.12 (d, *J* = 7.0 Hz, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.26, 161.96, 152.64, 131.74, 123.93, 123.83, 116.62, 116.35, 104.46, 40.78, 39.96, 18.48, 17.66.

**HRMS-ESI** (positive) M = $C_{15}H_{16}O_4$: Calcd. for $C_{15}H_{17}O_4$($[M + H]^+$) m/z: 261.1121, found ($[M + H]^+$) m/z: 261.1121.

**4-hydroxy-3-(3-(4-methoxyphenyl)-3-oxopropyl)-2H-chromen-2-one(3r)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO(0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 1-(4-methoxyphenyl) -propan-1-one (0.035mL, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 °C for 24 h.

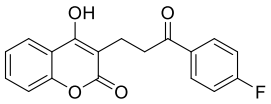
White solid (30.5 mg, 47% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.94 (s, 1H), 8.01 – 7.95 (m, 2H), 7.92 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.52 – 7.43 (m, 1H), 7.31 – 7.20 (m, 2H), 6.96 – 6.88 (m, 1H), 3.86 (s, 3H), 3.45 (t, *J* = 5.3 Hz, 2H), 2.96 (t, *J* = 5.5 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.58, 164.64, 164.32, 162.03, 152.63, 131.64, 131.13, 128.45, 123.86, 123.76, 116.67, 116.27, 114.02, 104.65, 55.64, 37.58, 17.84.

**HRMS-ESI** (positive) M = $C_{19}H_{16}O_5$: Calcd. for $C_{19}H_{17}O_5$([M + H]$^+$) m/z: 325.1071, found ([M + H]$^+$) m/z: 325.1072.

**3-(3-(4-fluorophenyl)-3-oxopropyl)-4-hydroxy-2H-chromen-2-one(3s)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 1-(4-fluorophenyl) -propan-1-one (0.031mL, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^oC$ for 24 h.

Pale yellow solid (28.1 mg, 45% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

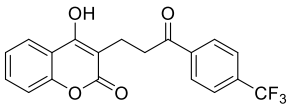
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 8.12 – 8.02 (m, 2H), 7.93 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.50 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.28 (ddd, *J* = 8.6, 4.9, 1.4 Hz, 2H), 7.15 (t, *J* = 8.6 Hz, 2H), 3.50 (t, *J* = 5.5 Hz, 2H), 2.97 (t, *J* = 5.6 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.76, 166.64 (d, $J^1_{C\text{-}F}$ = 257.2 Hz), 164.29, 161.97, 152.69, 131.99 (d, $J^4_{C\text{-}F}$ = 2.5 Hz), 131.83, 131.54 (d, $J^2_{C\text{-}F}$ = 9.6 Hz), 124.00, 123.82, 116.58, 116.34 (d, $J^3_{C\text{-}F}$ = 9.2 Hz), 116.07, 104.48, 38.00, 17.85.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -102.29.

**HRMS-ESI** (positive) M = $C_{18}H_{13}O_4F$: Calcd. for $C_{18}H_{14}O_4F$([M + H]$^+$) m/z: 313.0871, found ([M + H]$^+$) m/z: 313.0873.

**4-hydroxy-3-(3-oxo-3-(4-(trifluoromethyl)phenyl)propyl)-2H-chromen-2-one (3t)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 1-(4-(trifluoromethyl) -phenyl)propan-1-one (0.0404 g, 0.2 mmol), and solvent(1.8 mL

DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 °C for 24 h.

Pale yellow solid (32.7 mg, 45% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

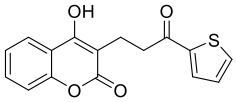
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.13 (d, *J* = 8.1 Hz, 2H), 7.95 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.51 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.33 – 7.24 (m, 2H), 3.56 (t, *J* = 5.3 Hz, 2H), 3.01 (t, *J* = 5.3 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 203.45, 164.10, 161.76, 152.58, 138.02, 136.51, 135.60 (q, $J^{2}_{C\text{-}F}$ = 33.1 Hz), 131.82, 128.95, 125.92 (q, $J^{3}_{C\text{-}F}$ = 3.6 Hz), 123.95, 123.71, 123.33 (q, $J^{1}_{C\text{-}F}$ = 272.9 Hz), 116.31, 104.19, 38.35, 17.68.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -63.30.

**HRMS-ESI** (positive) M = $C_{19}H_{13}O_4F_3$: Calcd. for $C_{19}H_{14}O_4F_3$($[M + H]^+$) m/z: 363.0839, found ($[M + H]^+$) m/z: 363.0840.

**4-hydroxy-3-(3-oxo-3-(thiophen-2-yl)propyl)-2H-chromen-2-one(3u)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-Hydroxycoumarin (0.0712 g, 0.44 mmol), 1-(thiophen-2-yl)propan-1-one (0.025mL, 0.2 mmol), and solvent(1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 °C for 24 h.

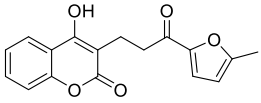
Pale yellow solid (32.2 mg, 54% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.94 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.84 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.73 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.50 (td, *J* = 7.7, 1.7 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.18 – 7.15 (m, 1H), 3.49 (t, *J* = 5.3 Hz, 2H), 2.97 (t, *J* = 5.2 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.87, 164.32, 162.03, 152.71, 142.24, 135.76, 134.29, 131.83, 128.77, 124.01, 123.90, 116.65, 116.38, 104.45, 38.45, 17.76.

**HRMS-ESI** (positive) M = $C_{16}H_{12}O_4S$: Calcd. for $C_{16}H_{13}O_4S$($[M + H]^+$) m/z: 301.0529, found ($[M + H]^+$) m/z: 301.0529.

**4-hydroxy-3-(3-(5-methylfuran-2-yl)-3-oxopropyl)-2H-chromen-2-one(3v)**



(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-Hydroxycoumarin (0.0712 g, 0.44 mmol), 1-(5-methylfuran-2-yl)propan-1-one (0.028mL, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^oC$ for 24 h.

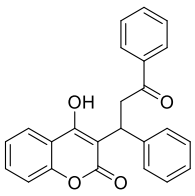
Pale yellow solid (30.3 mg, 51% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.56 – 7.41 (m, 1H), 7.32 – 7.22 (m, 3H), 6.21 (d, *J* = 3.6 Hz, 1H), 3.34 (td, *J* = 5.3, 1.6 Hz, 2H), 2.94 (td, *J* = 5.3, 1.6 Hz, 2H), 2.40 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 192.30, 164.34, 162.03, 159.79, 158.38, 152.71, 150.52, 131.74, 123.95, 123.91, 117.19, 116.73, 116.34, 109.87, 104.59, 37.09, 17.26, 14.27.

**HRMS-ESI** (positive) M = $C_{17}H_{14}O_5$: Calcd. for $C_{17}H_{15}O_5$($[M + H]^+$) m/z: 299.0914, found ($[M + H]^+$) m/z: 299.0916.

**4-hydroxy-3-(3-oxo-1,3-diphenylpropyl)-2H-chromen-2-one(3w)**



(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin (0.0712 g, 0.44 mmol), 1,3-diphenylpropan-1-one (0.0420 g , 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^oC$ for 24 h.

Pale yellow solid (40.3 mg, 54% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

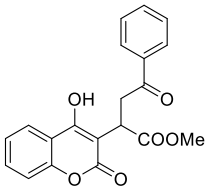
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.95 (brs, 1H), 8.08 – 8.01 (m, 2H), 7.97 (dd, *J* = 7.9,

1.6 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.39 (m, 5H), 7.30 – 7.19 (m, 5H), 4.97 (dd, *J* = 9.9, 2.7 Hz, 1H), 4.45 (dd, *J* = 19.1, 9.9 Hz, 1H), 3.78 (dd, *J* = 19.1, 2.7 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.71, 162.39, 161.55, 152.93, 140.20, 135.87, 134.51, 131.80, 128.92, 128.76, 128.30, 128.16, 126.73, 124.09, 123.88, 116.88, 116.32, 108.01, 40.21, 35.21.

**HRMS-ESI** (positive) M = $C_{24}H_{18}O_4$: Calcd. for $C_{24}H_{19}O_4$([M + H]$^+$) m/z: 371.1278, found ([M + H]$^+$) m/z: 371.1276.

**methyl 2-(4-hydroxy-2-oxo-2H-chromen-3-yl)-4-oxo-4-phenylbutanoate(3x)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0616 g, 0.4 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxycoumarin(0.0712 g, 0.44 mmol), methyl 4-oxo-4-phenylbutanoate (0.038mL , 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^o$C for 24 h.

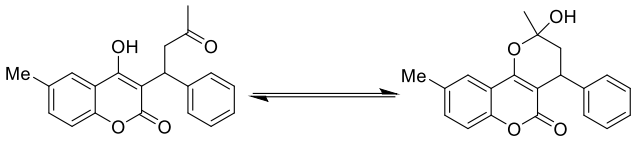
Yellow solid (23.8 mg, 34% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 8.05 (dd, 2H), 7.99 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.54 (td, *J* = 7.8, 1.6 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 4.37 (dd, *J* = 9.5, 2.7 Hz, 1H), 4.18 (dd, *J* = 19.8, 2.8 Hz, 1H), 3.85 – 3.78 (m, 1H), 3.76 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.46, 172.81, 162.93, 162.40, 152.85, 135.26, 134.82, 132.37, 129.01, 128.89, 124.23, 124.17, 116.61, 116.54, 104.19, 53.10, 40.29, 36.38.

**HRMS-ESI** (positive) M = $C_{20}H_{16}O_6$: Calcd. for $C_{20}H_{17}O_6$([M + H]$^+$) m/z: 353.1020, found ([M + H]$^+$) m/z: 353.1023.

**4-hydroxy-6-methyl-3-(3-oxo-1-phenylbutyl)-2H-chromen-2-one(3y)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxy-6-methyl-2H-chromen-2-one (0.0774 g, 0.44 mmol), 4-phenylbutan-2-one (0.030mL, 0.20 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 °C for 24 h.

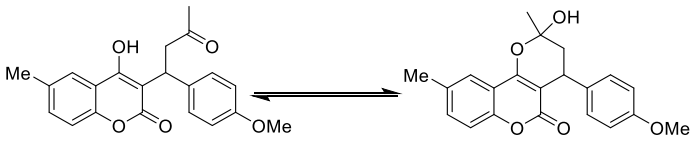
Pale yellow solid (46.1 mg, 72% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.1 Hz, 0.74H), 7.55 (d, *J* = 2.1 Hz, 1.16H), 7.33 – 7.13 (m, 14.01H), 7.04 (d, *J* = 8.5 Hz, 1.45H), 4.64 (bs, 1.06H), 4.20 – 4.08 (m, 2.00H), 3.84 (bs, 0.74H), 2.48 – 2.24 (m, 9.62H), 2.23 (s, 0.52H), 1.97 – 1.86 (m, 1.58H), 1.61 (d, *J* = 6.7 Hz, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.65, 162.00, 160.01, 159.34, 151.03, 150.92, 143.53, 141.88, 133.75, 133.36, 133.02, 132.50, 129.01, 128.56, 128.18, 127.96, 127.07, 126.99, 126.37, 122.75, 122.46, 116.33, 116.12, 115.62, 115.23, 103.80, 101.19, 100.68, 99.22, 42.76, 40.34, 35.37, 34.71, 27.84, 27.28, 20.95, 20.92.

**HRMS-ESI** (positive) M = $C_{20}H_{18}O_4$: Calcd. for $C_{20}H_{19}O_4$($[M + H]^+$) m/z: 323.1278, found ($[M + H]^+$) m/z: 323.1281.

**4-hydroxy-3-(1-(4-methoxyphenyl)-3-oxobutyl)-6-methyl-2H-chromen-2-one(3z)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxy-6-methyl-2H-chromen-2-one (0.0774 g, 0.44 mmol), 4-(4-methoxyphenyl)butan-2-one (0.036mL, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 °C for

24 h.

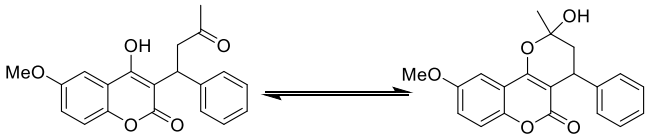
Pale yellow solid (40.7 mg, 58% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.66 (s, 0.84H), 7.57 (s, 1.04H), 7.33 (dd, *J* = 8.5, 2.1 Hz, 0.94H), 7.28 – 7.03 (m, 8.46H), 6.81 (t, *J* = 7.9 Hz, 4.63H), 4.18 (dd, *J* = 6.8, 3.5 Hz, 0.95H), 4.10 (dd, *J* = 11.1, 6.8 Hz, 1.09H), 3.75 (d, *J* = 3.2 Hz, 6.62H), 2.53 – 2.24 (m, 8.98H), 1.99 – 1.86 (m, 1.36H), 1.65 (s, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 212.54, 162.61, 161.85, 159.77, 159.00, 158.58, 158.06, 151.10, 151.01, 135.43, 133.76, 133.38, 133.04, 132.52, 129.10, 128.12, 128.07, 122.78, 122.47, 116.40, 116.22, 115.64, 115.27, 114.62, 114.06, 113.59, 104.15, 101.36, 100.65, 99.23, 55.31, 55.28, 42.79, 40.09, 34.57, 33.55, 28.03, 27.64, 21.00, 20.96.

**HRMS-ESI** (positive) M = $C_{21}H_{20}O_5$: Calcd. for $C_{21}H_{21}O_5$($[M + H]^+$) m/z: 353.1384, found ($[M + H]^+$) m/z: 353.1385.

**4-hydroxy-6-methoxy-3-(3-oxo-1-phenylbutyl)-2H-chromen-2-one(3aa)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$(0.0074 g, 0.04 mmol), 2,2'-bipyridine(0.0094 g, 0.06 mmol), TEMPO(0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxy-6-methoxy-2H-chromen-2-one (0.0845 g, 0.44 mmol), 4-phenylbutan-2-one (0.030mL, 0.20 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^{o}$C for 24 h.

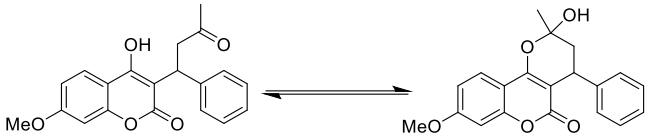
Pale yellow solid (33.4 mg, 49% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^{1}$H NMR** (400 MHz, DMSO-$d_6$) δ 7.44 (s, 1.30H), 7.37 – 7.29 (m, 2.35H), 7.28 – 7.20 (m, 8.83H), 7.16 (d, *J* = 7.1 Hz, 6.07H), 3.98 (dd, *J* = 11.0, 6.7 Hz, 2.02H), 3.82 (s, 6.38H), 2.35 – 2.22 (m, 1.77H), 2.12 (dd, *J* = 13.9, 6.8 Hz, 1.00H), 1.96 – 1.83 (m, 1.45H), 1.60 (d, *J* = 26.6 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 160.92, 160.50, 159.26, 158.65, 155.47, 146.76, 144.09, 128.35, 127.99, 127.37, 127.15, 126.02, 125.75, 119.71, 119.56, 117.60, 116.15, 115.99, 104.81, 104.65, 103.78, 102.31, 101.59, 99.83, 55.82, 42.93, 41.69, 36.22, 35.32, 27.31, 25.79.

**HRMS-ESI** (positive) M = $C_{20}H_{18}O_5$: Calcd. for $C_{20}H_{19}O_5$([M + H]$^+$) m/z: 339.1227, found ([M + H]$^+$) m/z: 339.1228.

**4-hydroxy-7-methoxy-3-(3-oxo-1-phenylbutyl)-2H-chromen-2-one(3ab)**




(0.2 mmol scale) was synthesized following the General Procedure with Cu(OAc)$_2$(0.0074 g, 0.04 mmol), 2,2'-bipyridine(0.0094 g, 0.06 mmol), TEMPO(0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxy-7-methoxy-2H-chromen-2-one (0.0845 g, 0.44 mmol), 4-phenylbutan-2-one (0.030mL, 0.20 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^o$C for 24 h.

Pale yellow solid (44.2 mg, 65% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 7.72 (d, $J$ = 9.4 Hz, 2.01H), 7.40 (s, 1.52H), 7.30 – 7.19 (m, 5.51H), 7.19 – 7.10 (m, 6.29H), 6.96 (d, $J$ = 7.0 Hz, 4.04H), 4.02 – 3.92 (m, 2.08H), 3.84 (d, $J$ = 3.5 Hz, 6.18H), 2.36 – 2.23 (m, 1.94H), 2.17 – 2.06 (m, 1.05H), 1.92 – 1.79 (m, 1.52H), 1.59 (d, $J$ = 25.4 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 162.49, 162.41, 161.21, 160.76, 159.96, 159.38, 154.20, 144.29, 144.17, 128.32, 127.95, 127.38, 127.13, 125.97, 125.69, 123.94, 112.08, 108.84, 108.70, 101.28, 100.72, 100.39, 99.58, 99.25, 55.96, 43.01, 41.67, 35.98, 35.12, 27.35, 25.92.

**HRMS-ESI** (positive) M = $C_{20}H_{18}O_5$: Calcd. for $C_{20}H_{19}O_5$([M + H]$^+$) m/z: 339.1227, found ([M + H]$^+$) m/z: 339.1230.

**6-fluoro-4-hydroxy-3-(1-(4-methoxyphenyl)-3-oxobutyl)-2H-chromen-2-one(3ac)**


(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 6-fluoro-4-hydroxy-2H-chromen-2-one (0.0792 g, 0.44 mmol), 4-(4-methoxyphenyl)butan-2-one (0.036mL, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 °C for 24 h. Yellow solid (26.2 mg, 37% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.5, 2.6 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 3H), 7.30 – 7.21 (m, 3H), 7.17 – 7.07 (m, 15H), 6.82 (dd, *J* = 8.4, 5.8 Hz, 10H), 4.19 – 4.16 (m, 1H), 4.11 (dd, *J* = 11.4, 6.8 Hz, 3H), 3.75 (d, *J* = 3.3 Hz, 13H), 2.51 – 2.39 (m, 2H), 2.34 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.02 – 1.86 (m, 5H), 1.65 (s, 15H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.14, 161.40, 159.95, 159.76, 159.04, 158.56, 158.28, 158.14, 157.53, 157.34, 149.00, 148.88, 135.07, 133.24, 129.14, 128.16, 128.11, 119.59, 119.34, 119.01, 118.77, 118.27, 118.19, 118.02, 117.94, 117.01, 116.92, 116.65, 116.57, 114.52, 114.09, 113.62, 108.99, 108.74, 108.66, 108.40, 105.22, 102.46, 101.04, 99.65, 55.29, 55.28, 42.71, 40.06, 34.60, 33.76, 27.86, 27.50.

**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -117.22, -117.75.

**HRMS-ESI** (positive) M = $C_{20}H_{17}O_5F$: Calcd. for $C_{20}H_{18}O_5F([M + H]^+)$ m/z: 357.1133, found ($[M + H]^+$) m/z: 357.1132.

**6-fluoro-4-hydroxy-3-(1-(4-nitrophenyl)-3-oxobutyl)-2H-chromen-2-one(3ad)**


(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 6-fluoro-4-hydroxy-2H-chromen-2-one (0.0792

g, 0.44 mmol), 4-(4-nitrophenyl)butan-2-one (0.0390g, 0.2 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 °C for 24 h.

Brown solid (23.6 mg, 32% yield, eluent = petroleum ether/ ethyl acetate (7: 3)).

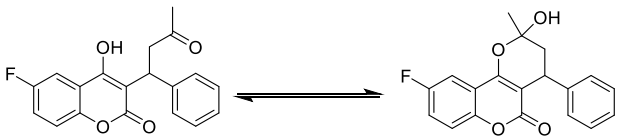
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.22 – 8.07 (m, 5.25H), 7.62 (dd, *J* = 8.1, 3.2 Hz, 0.63H), 7.53 – 7.49 (m, 0.94H), 7.46 (dd, *J* = 8.3, 2.5 Hz, 1.97H), 7.38 (dd, *J* = 11.9, 8.3 Hz, 4.73H), 7.28 (d, *J* = 6.9 Hz, 1.73H), 7.22 – 7.18 (m, 3.19H), 4.33 – 4.16 (m, 2.53H), 2.51 – 2.39 (m, 2.54H), 1.95 – 1.84 (m, 2.36H), 1.73 (d, *J* = 18.3 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.19, 161.32, 160.07, 159.95, 159.40, 158.99, 157.66, 157.53, 151.19, 150.52, 149.14, 149.07, 148.99, 146.74, 146.53, 128.79, 128.64, 128.09, 124.12, 123.62, 123.20, 120.01, 119.72, 119.48, 118.51, 118.43, 118.33, 118.25, 116.71, 116.62, 108.97, 108.83, 108.72, 108.58, 103.87, 101.80, 100.39, 99.39, 41.97, 39.34, 35.55, 35.12, 28.04, 27.99.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -116.80, -117.02.

**HRMS-ESI** (positive) M = $C_{19}H_{14}O_6NF$: Calcd. for $C_{19}H_{15}O_6NF$ ($[M + H]^+$) m/z: 372.0878, found ($[M + H]^+$) m/z: 372.0877.

**6-fluoro-4-hydroxy-3-(3-oxo-1-phenylbutyl)-2H-chromen-2-one(3ae)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 6-fluoro-4-hydroxy-2H-chromen-2-one (0.0792 g, 0.44 mmol), 4-phenylbutan-2-one (0.030mL, 0.20 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 °C for 24 h.

Pale yellow solid (33.3 mg, 51% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ (bs, 0.15H), 7.52 (dd, *J* = 8.4, 2.6 Hz, 0.81H), 7.41 (d, *J* = 8.4 Hz, 1.44H), 7.32 – 7.22 (m, 8.20H), 7.22 – 7.16 (m, 4.60H), 7.13 (dd, *J* = 6.5, 1.8 Hz, 2.71H), 4.69 (dd, *J* = 10.0, 2.8 Hz, 0.21H), 4.21 (dd, *J* = 7.0, 3.9 Hz, 0.71H),

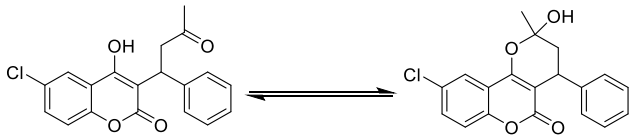
4.14 (dd, *J* = 11.5, 6.8 Hz, 1.41H), 3.80 (dd, *J* = 19.4, 10.0 Hz, 0.36H), 3.31 (dd, *J* = 19.4, 2.8 Hz, 0.26H), 2.50 – 2.33 (m, 2.67H), 2.27 (s, 0.55H), 1.95 – 1.88 (m, 1.49H), 1.63 (d, *J* = 3.4 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 212.72, 162.15, 161.46, 159.99, 159.80, 159.20, 158.47, 157.56, 157.38, 149.03, 148.90, 148.88, 143.12, 141.52, 139.56, 129.11, 128.69, 128.28, 128.05, 127.18, 127.13, 127.11, 126.84, 126.60, 119.66, 119.42, 119.09, 118.84, 118.31, 118.23, 118.05, 117.97, 117.00, 116.91, 116.65, 116.56, 109.02, 108.77, 108.70, 108.45, 105.02, 102.23, 101.02, 99.59, 42.65, 40.15, 35.44, 34.66, 27.88, 27.46.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -117.25, -117.78.

**HRMS-ESI** (positive) M = $C_{19}H_{15}O_4F$: Calcd. for $C_{19}H_{16}O_4F([M + H]^+)$ m/z: 327.1027, found ($[M + H]^+$) m/z: 327.1028.

**6-chloro-4-hydroxy-3-(3-oxo-1-phenylbutyl)-2H-chromen-2-one(3af)**




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 6-chloro-4-hydroxy-2H-chromen-2-one (0.0862 g, 0.44 mmol), 4-phenylbutan-2-one (0.030mL, 0.20 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^oC$ for 24 h.

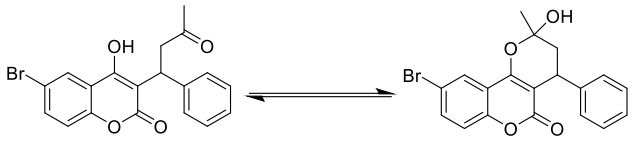
White solid (45.4 mg, 67% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 40.9 Hz, 2.18H), 7.50 – 7.33 (m, 2.66H), 7.33 – 7.16 (m, 11.24H), 7.09 (d, *J* = 8.8 Hz, 1.52H), 4.18 (d, *J* = 32.6 Hz, 2.27H), 2.56 – 2.33 (m, 2.61H), 2.05 – 1.87 (m, 1.47H), 1.63 (d, *J* = 7.3 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.86, 161.18, 158.93, 151.20, 143.04, 141.43, 132.04, 131.53, 129.21, 128.70, 127.19, 126.68, 122.74, 122.44, 117.92, 105.17, 102.54, 101.06, 99.63, 42.63, 40.12, 35.46, 34.63, 27.99, 27.60.

**HRMS-ESI** (positive) M = $C_{19}H_{15}O_4Cl$: Calcd. for $C_{19}H_{16}O_4Cl([M + H]^+)$ m/z: 343.0732, found ($[M + H]^+$) m/z: 343.0728.

**6-bromo-4-hydroxy-3-(3-oxo-1-phenylbutyl)-2H-chromen-2-one(3ag)** [9]



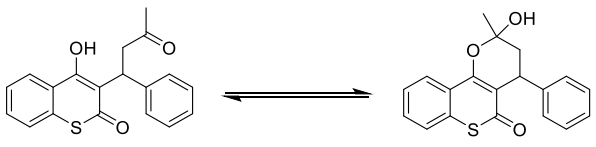

(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 6-Bromo-4-hydroxy-2H-chromen-2-one (0.1056 g, 0.44 mmol), 4-phenylbutan-2-one (0.030mL, 0.20 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^oC$ for 24 h.

White solid (44.8 mg, 58% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 45.7, 2.4 Hz, 2.24H), 7.59 (dd, *J* = 8.8, 2.4 Hz, 0.68H), 7.47 (dd, *J* = 8.8, 2.4 Hz, 1.53H), 7.33 – 7.12 (m, 12.57H), 7.01 (d, *J* = 8.8 Hz, 1.72H), 4.66 (s, 1.11H), 4.19 (dd, *J* = 6.9, 4.1 Hz, 0.63H), 4.13 (dd, *J* = 11.6, 6.8 Hz, 1.11H), 2.50 – 2.29 (m, 2.13H), 1.99 – 1.88 (m, 1.37H), 1.61 (d, *J* = 13.9 Hz, 6.00H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.94, 161.00, 158.85, 158.14, 152.03, 143.61, 141.87, 134.81, 133.86, 129.07, 128.26, 127.14, 126.20, 125.74, 125.36, 119.07, 118.14, 117.60, 117.24, 116.88, 116.54, 107.17, 102.53, 101.12, 99.69, 42.62, 40.20, 36.99, 34.79, 29.82, 27.39.

**4-hydroxy-3-(3-oxo-1-phenylbutyl)-2H-thiochromen-2-one(3ah)** [9]




(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0768 g, 0.54 mmol), 4-hydroxy-2H-thiochromen-2-one (0.0783 g,0.44 mmol), 4-phenylbutan-2-one (0.030mL, 0.20 mmol), and solvent (1.8 mL

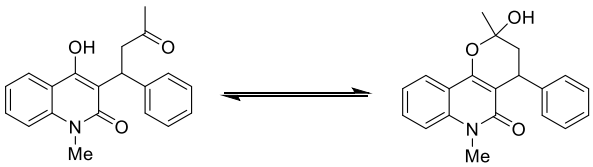
DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^{o}$C for 24 h.

Pale yellow solid (20.6 mg, 32% yield, eluent = petroleum ether/ ethyl acetate (4: 1)).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.18 (dd, *J* = 8.1, 1.5 Hz, 0.97H), 7.55 – 7.49 (m, 1.21H), 7.47 – 7.41 (m, 3.14H), 7.40 – 7.31 (m, 3.01H), 7.30 – 7.23 (m, 7.26H), 7.21 – 7.15 (m, 3.18H), 4.47 (dd, *J* = 7.0, 3.3 Hz, 1.11H), 4.28 (dd, *J* = 11.4, 7.3 Hz, 1.24H), 3.53 (s, 1.05H), 3.24 (s, 1.06H), 2.54 (dd, *J* = 14.1, 3.3 Hz, 1.06H), 2.46 (dd, *J* = 13.9, 7.3 Hz, 1.13H), 2.36 (dd, *J* = 14.1, 6.9 Hz, 1.21H), 2.01 (dd, *J* = 13.9, 11.3 Hz, 1.32H), 1.68 (d, *J* = 11.7 Hz, 6.96H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 183.66, 183.22, 160.35, 159.44, 144.38, 142.05, 135.93, 135.80, 130.21, 129.77, 129.31, 128.63, 127.19, 126.99, 126.98, 126.44, 126.32, 126.12, 126.03, 125.47, 125.29, 124.10, 123.73, 115.78, 112.71, 100.04, 98.47, 42.62, 39.77, 36.35, 34.51, 28.30, 27.88.

**4-hydroxy-1-methyl-3-(3-oxo-1-phenylbutyl)quinolin-2(1H)-one(3ai)** [9]



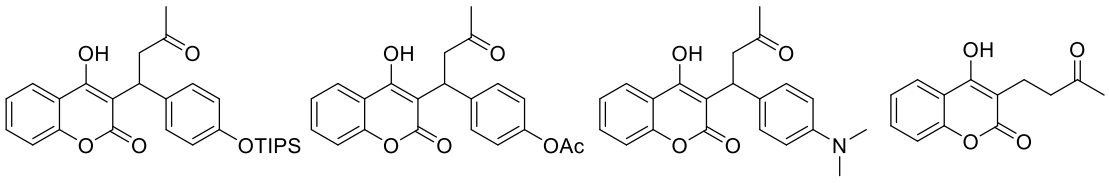

(0.2 mmol scale) was synthesized following the General Procedure with $Cu(OAc)_2$ (0.0074 g, 0.04 mmol), 2,2'-bipyridine (0.0094 g, 0.06 mmol), TEMPO (0.0313 g, 0.2 mmol), KOPiv (0.0483 g, 0.34 mmol), $Cs_2CO_3$(0.0652 g, 0.2 mmol), 4-hydroxy-1-methylquinolin-2(1H)-one (0.0770 g, 0.44 mmol), 4-phenylbutan-2-one (0.030mL, 0.20 mmol), and solvent (1.8 mL DMF+0.2 mL MeCN), The reaction mixture was stirred at 120 $^{o}$C for 24 h.

Pale yellow solid (31.2 mg, 49% yield, eluent = petroleum ether/ ethyl acetate (1: 1)).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.97 – 7.93 (m, 1.2H), 7.57 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1.15H), 7.48 – 7.42 (m, 1.36H), 7.33 (d, *J* = 8.4 Hz, 1.49H), 7.26 – 7.19 (m, 8.12H), 7.19 – 7.11 (m, 8.31H), 4.64 (s, 0.96H), 4.31 (dd, *J* = 7.0, 3.8 Hz, 0.99H), 4.24 (dd, *J* = 11.0, 7.1 Hz, 1.25H), 3.63 (s, 3.28H), 3.52 (s, 0.48H), 3.41 (s, 3.75H), 2.46 – 2.37 (m, 2.25H), 2.31 – 2.24 (m, 0.92H), 1.99 – 1.90 (m, 1.67H), 1.59 (d, *J* = 5.3 Hz, 6.82H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.50, 162.17, 156.19, 155.58, 145.06, 143.02, 139.18, 138.97, 130.84, 130.37, 129.00, 128.43, 128.03, 127.86, 127.04, 127.00, 126.74, 126.01, 123.44, 123.08, 121.78, 121.44, 116.37, 116.06, 114.00, 113.78, 109.49, 106.76, 99.49, 98.20, 43.28, 40.48, 36.06, 34.94, 29.54, 29.29, 28.08, 27.52.

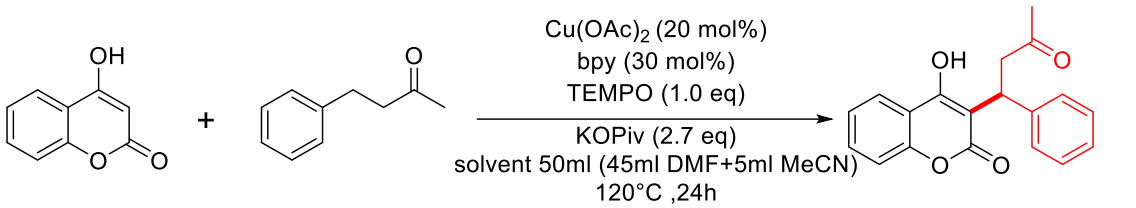
## Substrates with low conversion



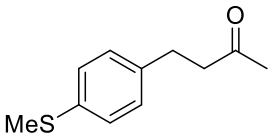
# VI. Synthetic Applications

## Gram-Scale Experiment

In a nitrogen-filled glovebox, a 150 mL Schlenk tube equipped with a stir bar was charged with $Cu(OAc)_2$ (0.185 g, 1.00 mmol), 2,2'-bipyridine (0.235 g, 1.5 mmol), TEMPO (0.783 g, 5 mmol), KOPiv (1.920 g, 13.5 mmol), 4-hydroxycoumarin (1.780 g, 11.0 mmol), DMF (45 mL), MeCN(5 mL) and 4-phenylbutan-2-one (0.750mL, 0.5 mmol) were added in turn to the Schlenk tube. Then the tube was fitted with a Teflon screwcap and moved out of the glovebox. The reaction mixture was stirred at 120 ℃ for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 40 mL of ethyl acetate, followed by filtration through a pad of silica gel. Then, $H_2O$ (40mL) was added. The phases were separated and the water phase was extracted with ethyl acetate (2×40mL). The combined organic phases were washed with brine(3×40mL) and dried over $Na_2SO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to afford **3a** (0.957 g, 62%).

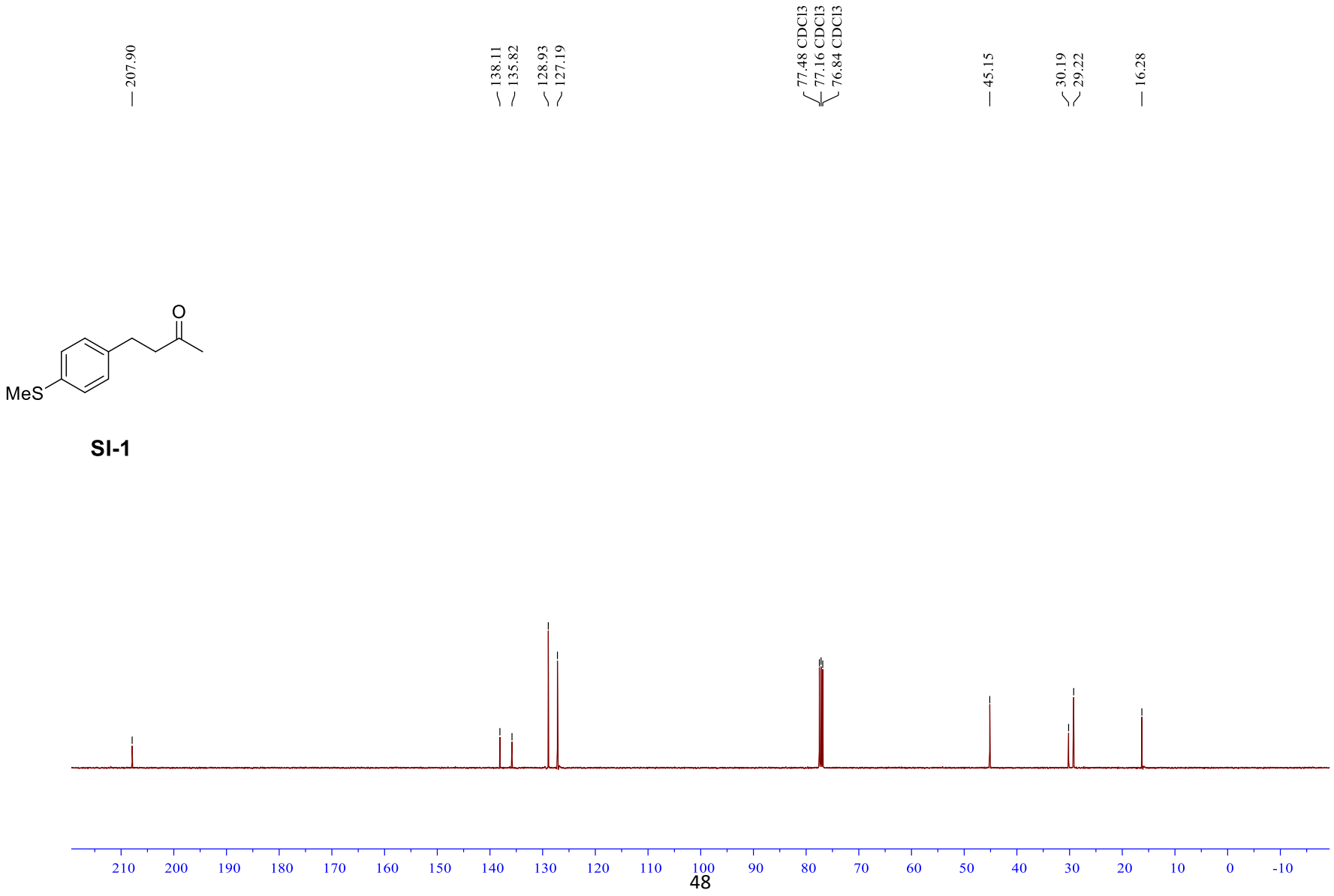


# VII. Spectra Data

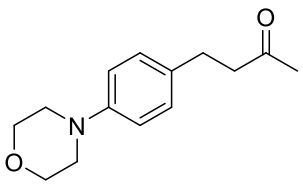

O
MeS

**SI-1**


7.26 CDCl3
7.19
7.17
7.11
7.09
2.87
2.87
2.85
2.83
2.75
2.73
2.71
2.71
2.45
2.13
2.11
2.08
2.05
1.99
3.20
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

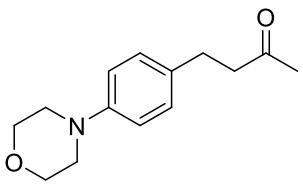

207.90
138.11
135.82
128.93
127.19
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
45.15
30.19
29.22
16.28
O
MeS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

**SI-1**


O
N
O

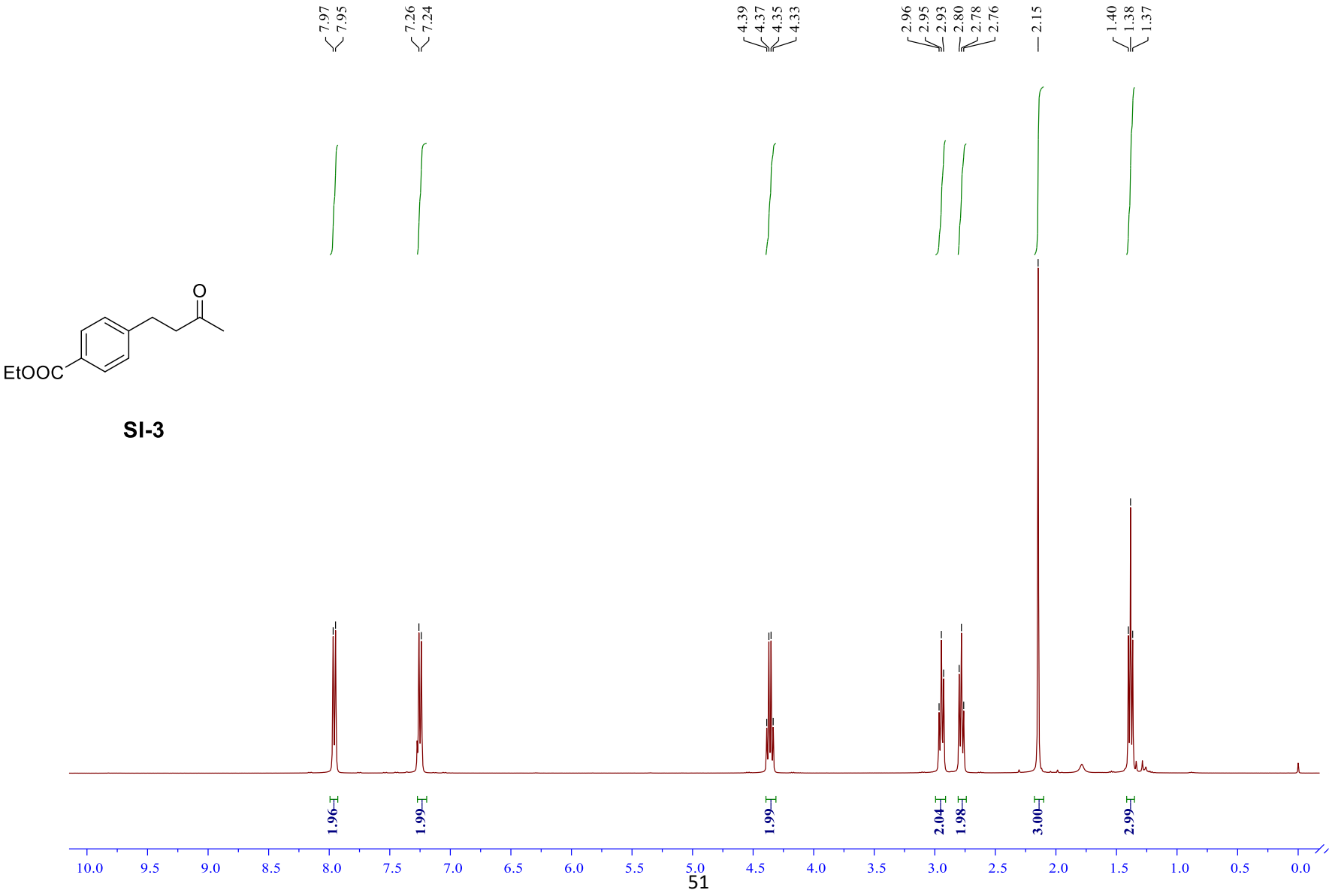
**SI-2**


7.26 CDCl3
7.11
7.08
6.85
6.83
3.86
3.85
3.84
3.13
3.12
3.10
2.84
2.82
2.80
2.74
2.72
2.70
2.13
1.97
2.01
3.95
3.95
1.98
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

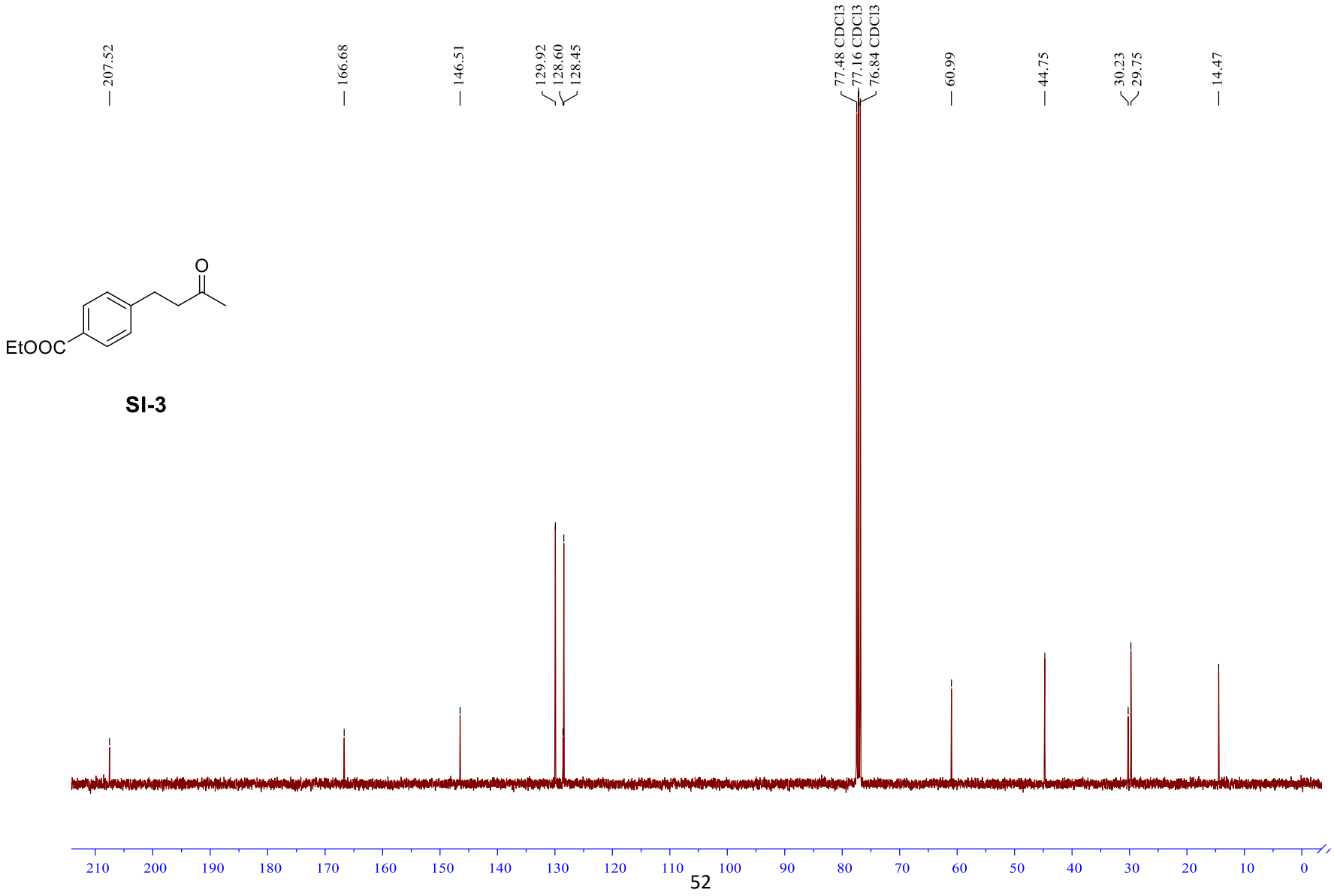

O
N
O

**SI-2**

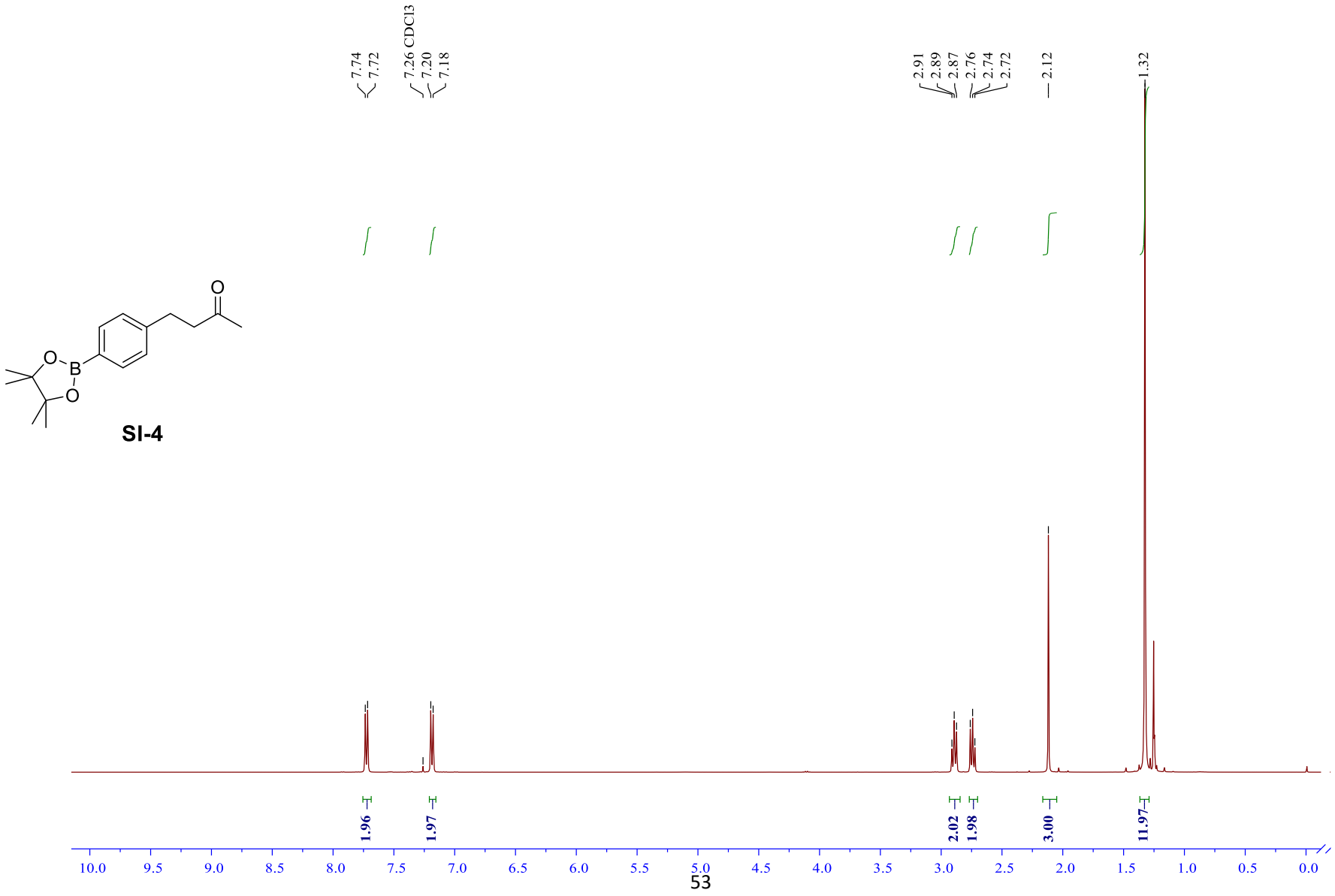

208.37
149.73
132.62
129.11
116.07
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.04
49.73
45.48
30.29
30.23
28.97
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.97
7.95
7.26
7.24
4.39
4.37
4.35
4.33
2.96
2.95
2.93
2.80
2.78
2.76
2.15
1.40
1.38
1.37
O
EtOOC
1.96
1.99
1.99
2.04
1.98
3.00
2.99
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

**SI-3**


207.52
166.68
146.51
129.92
128.60
128.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
60.99
44.75
30.23
29.75
14.47
O
EtOOC
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

**SI-3**


7.74
7.72
7.26 CDCl3
7.20
7.18
2.91
2.89
2.87
2.76
2.74
2.72
2.12
1.32
O
O
B
O
SI-4
1.96
1.97
2.02
1.98
3.00
11.97
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
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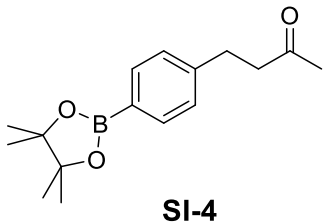
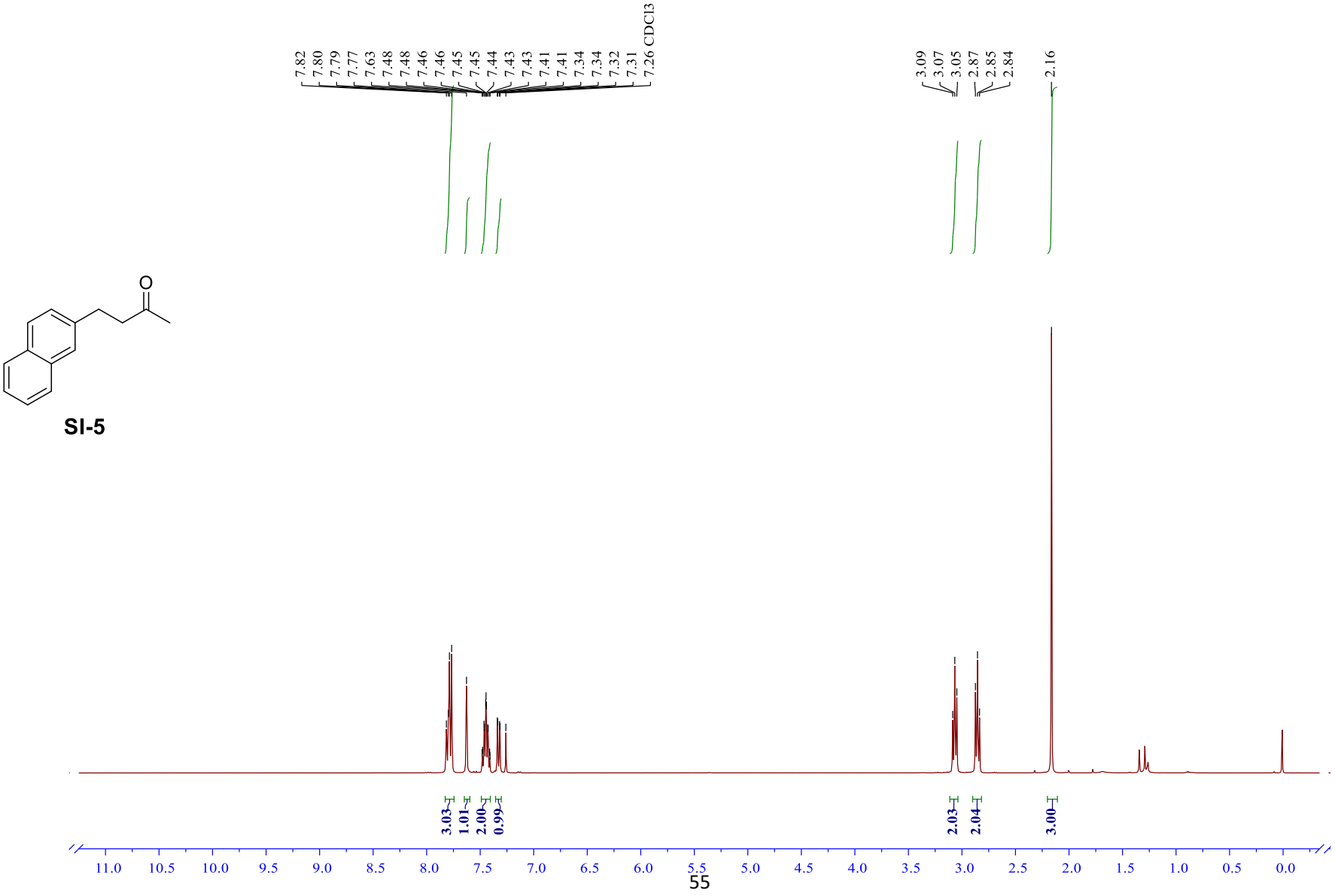
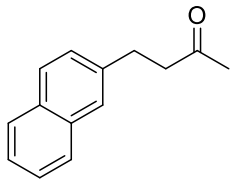

O
O
B
O

**SI-4**

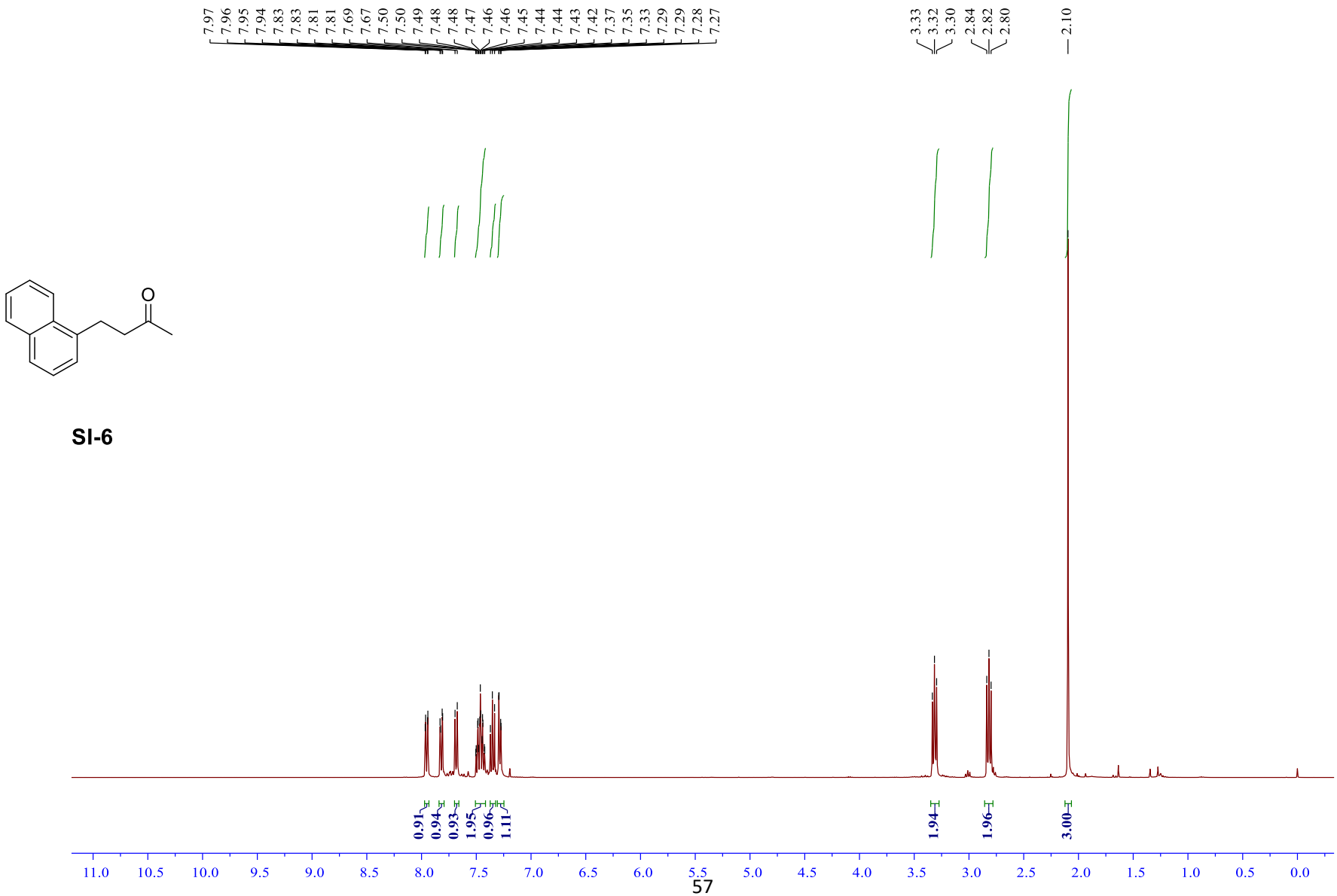

207.80
144.43
135.09
127.80
83.73
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
44.99
30.14
29.96
24.91
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.82
7.80
7.79
7.77
7.63
7.48
7.48
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.41
7.41
7.34
7.34
7.32
7.31
7.26 CDCl3
3.09
3.07
3.05
2.87
2.85
2.84
2.16
O
SI-5
3.03
1.01
2.00
0.99
2.03
2.04
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

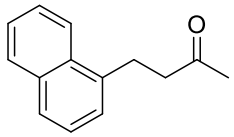


**SI-5**

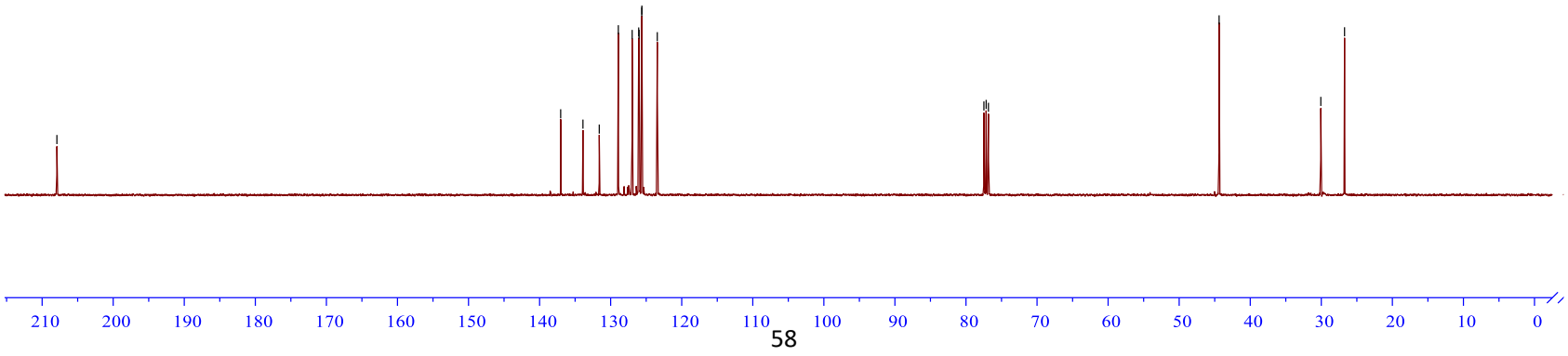

208.02
138.62
133.70
132.18
128.23
127.74
127.57
127.17
126.52
126.16
125.46
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
45.22
30.29
30.01
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

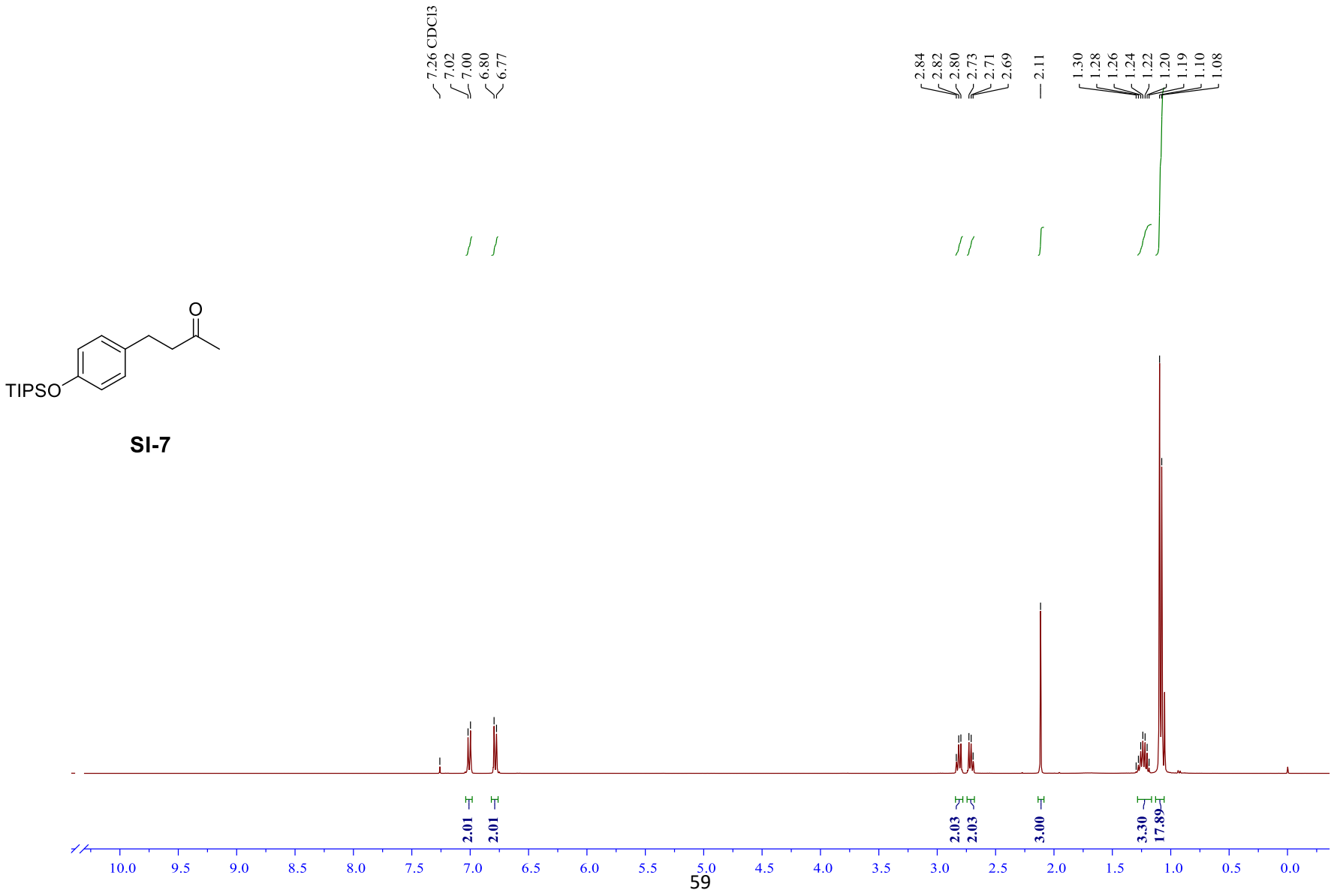

7.97
7.96
7.95
7.94
7.83
7.83
7.81
7.81
7.69
7.67
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.37
7.35
7.33
7.29
7.29
7.28
7.27
3.33
3.32
3.30
2.84
2.82
2.80
2.10
O
0.91
0.94
0.93
1.95
0.96
1.11
1.94
1.96
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

**SI-6**

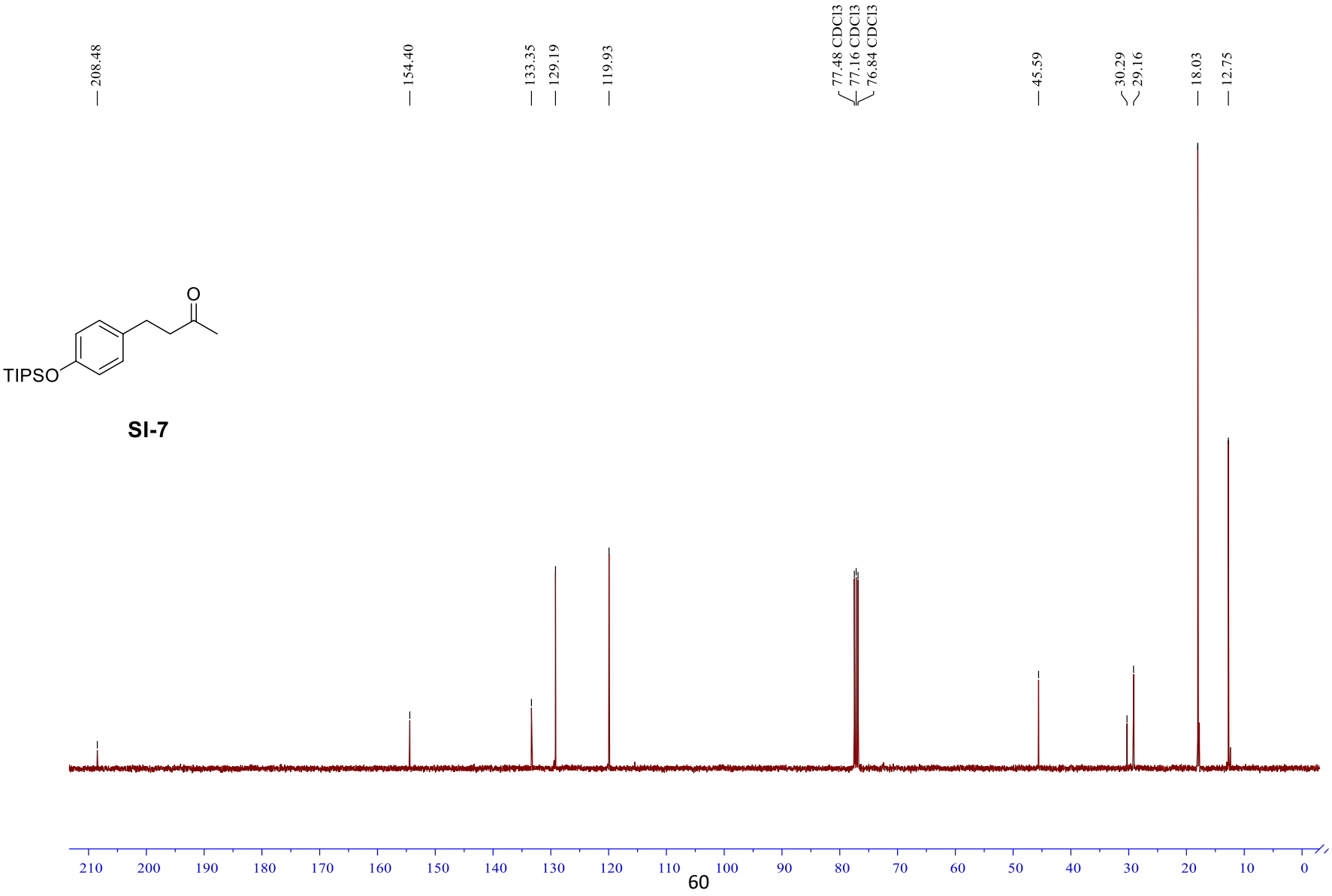

O

**SI-6**

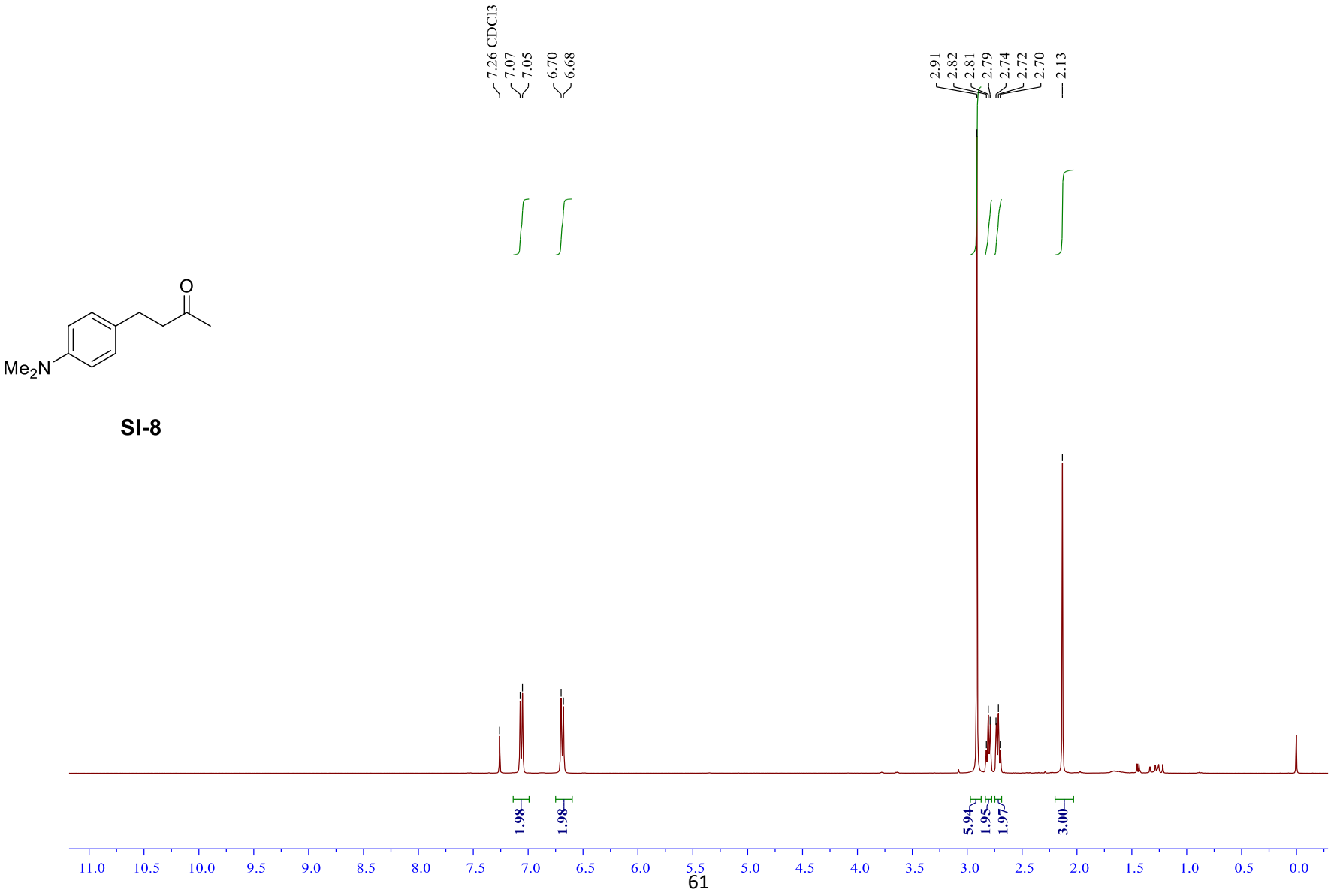

207.92
137.03
133.90
131.60
128.92
126.97
126.05
125.99
125.62
125.61
123.44
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
44.38
30.07
26.73
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.26 CDCl3
7.02
7.00
6.80
6.77
2.84
2.82
2.80
2.73
2.71
2.69
2.11
1.30
1.28
1.26
1.24
1.22
1.20
1.19
1.10
1.08
O
TIPSO
2.01
2.01
2.03
2.03
3.00
3.30
17.89
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

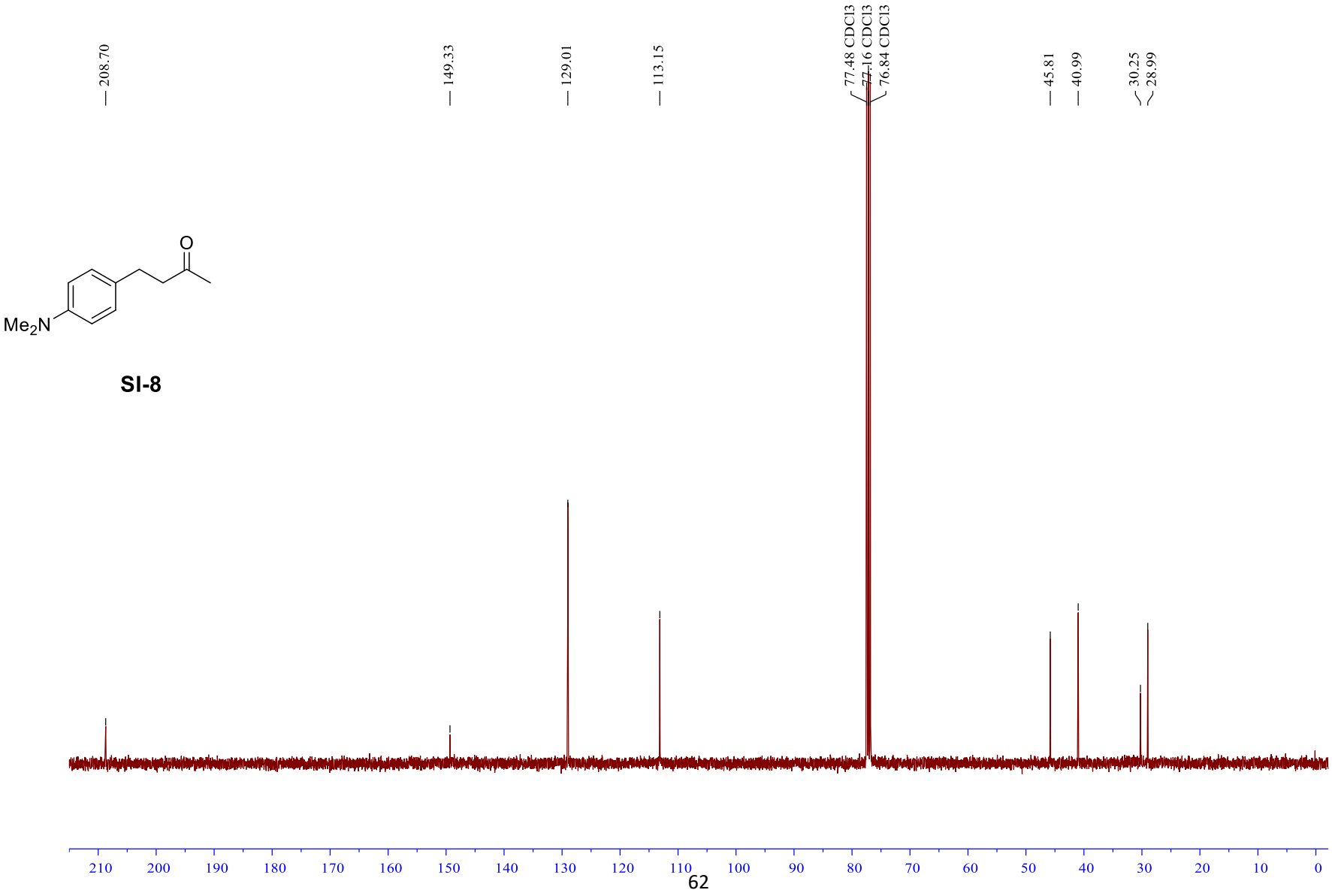
**SI-7**


208.48
154.40
133.35
129.19
119.93
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
45.59
30.29
29.16
18.03
12.75
O
TIPSO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

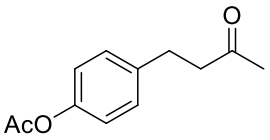
**SI-7**


7.26 CDCl3
7.07
7.05
6.70
6.68
2.91
2.82
2.81
2.79
2.74
2.72
2.70
2.13
O
Me2N
1.98
1.98
5.94
1.95
1.97
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

**SI-8**

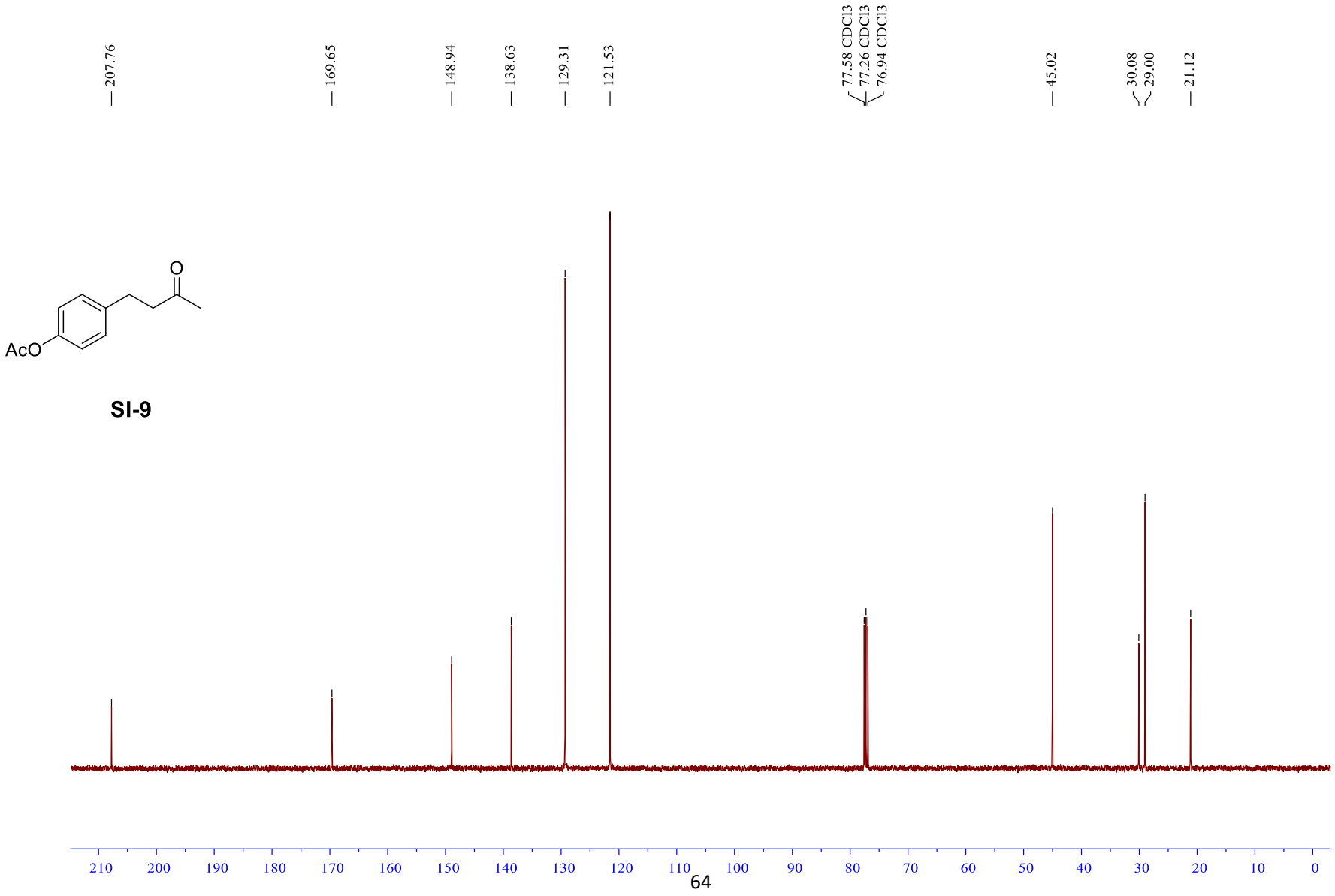

208.70
149.33
129.01
113.15
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
45.81
40.99
30.25
28.99
O
Me2N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

**SI-8**

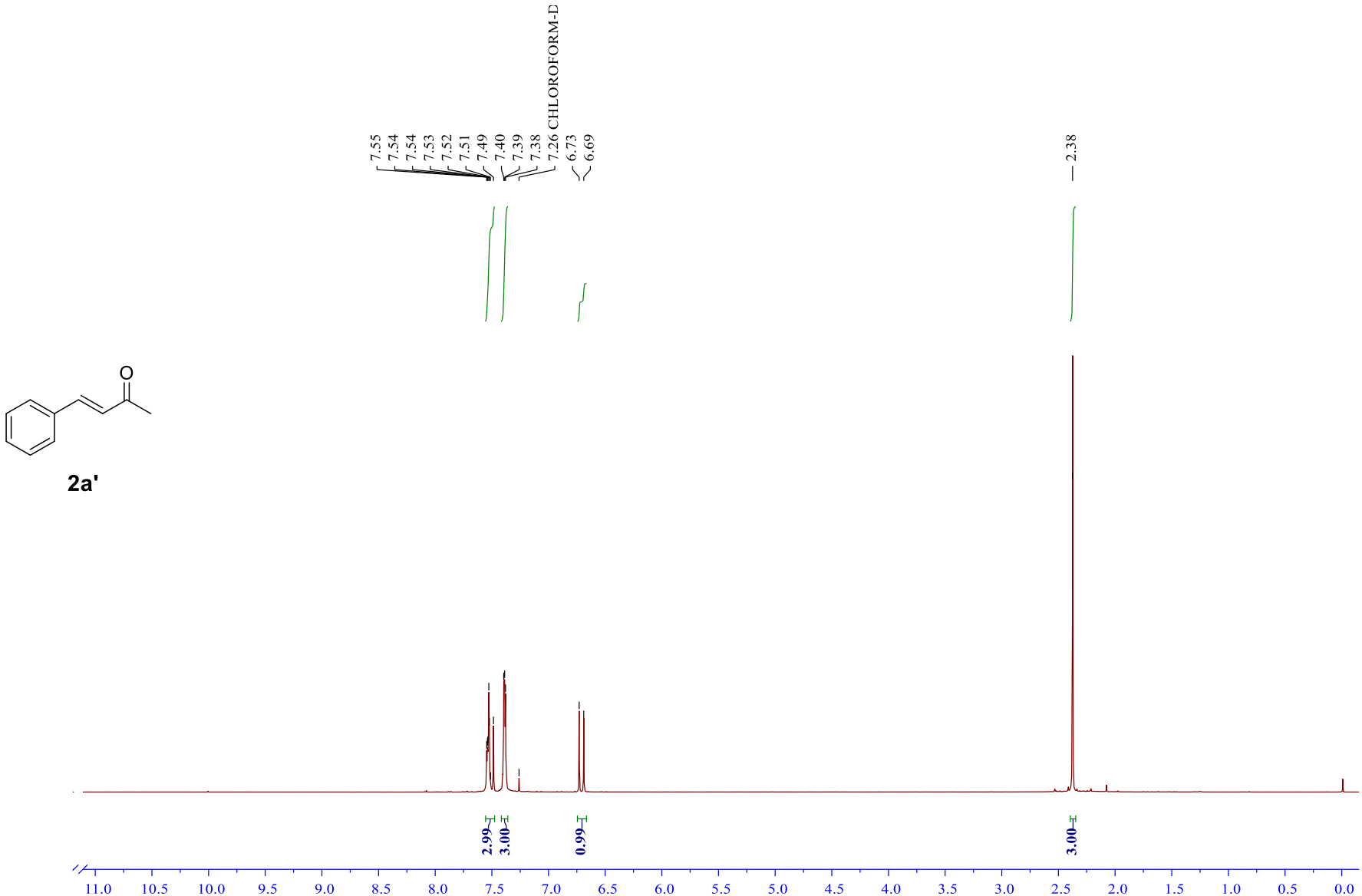

O
AcO

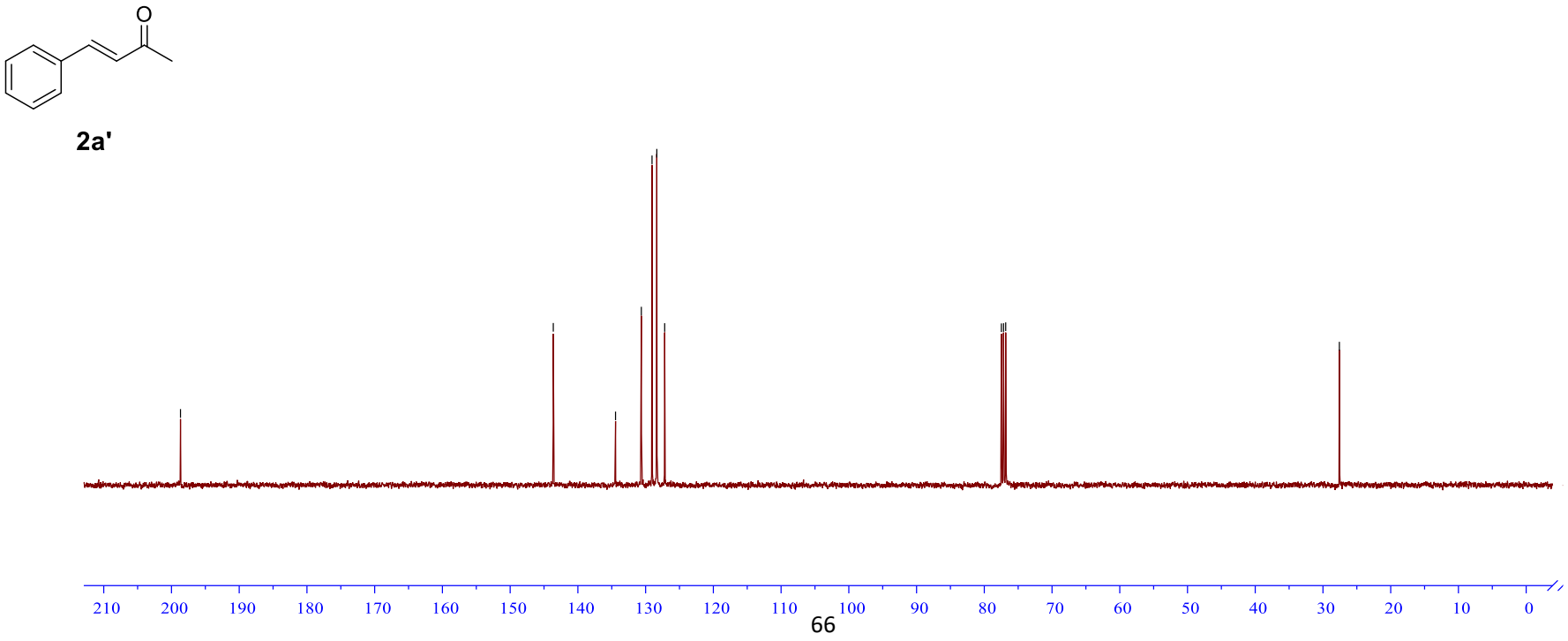
**SI-9**

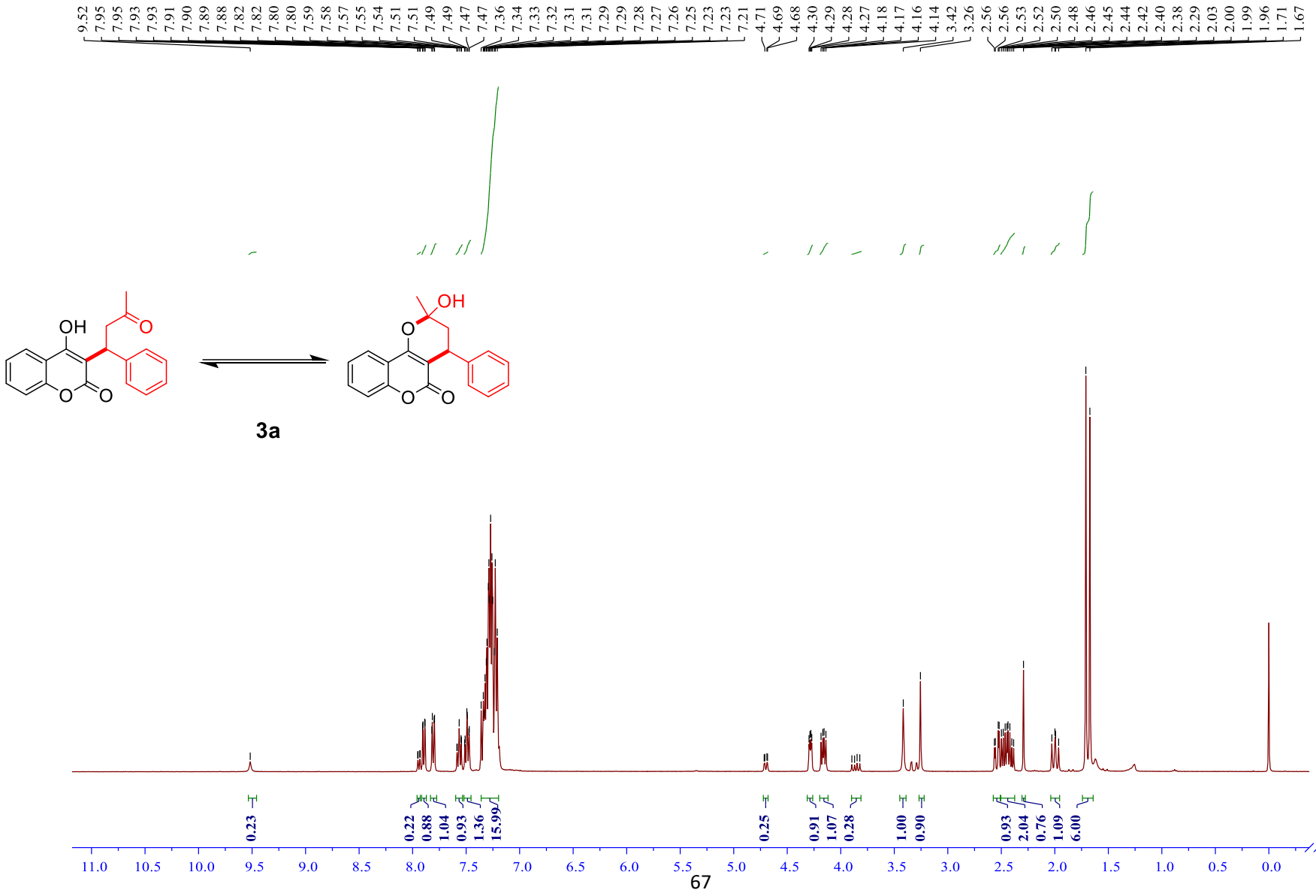

7.16
7.14
6.97
6.94
2.86
2.84
2.82
2.73
2.71
2.69
2.24
2.09
1.99
1.98
2.04
2.00
3.02
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

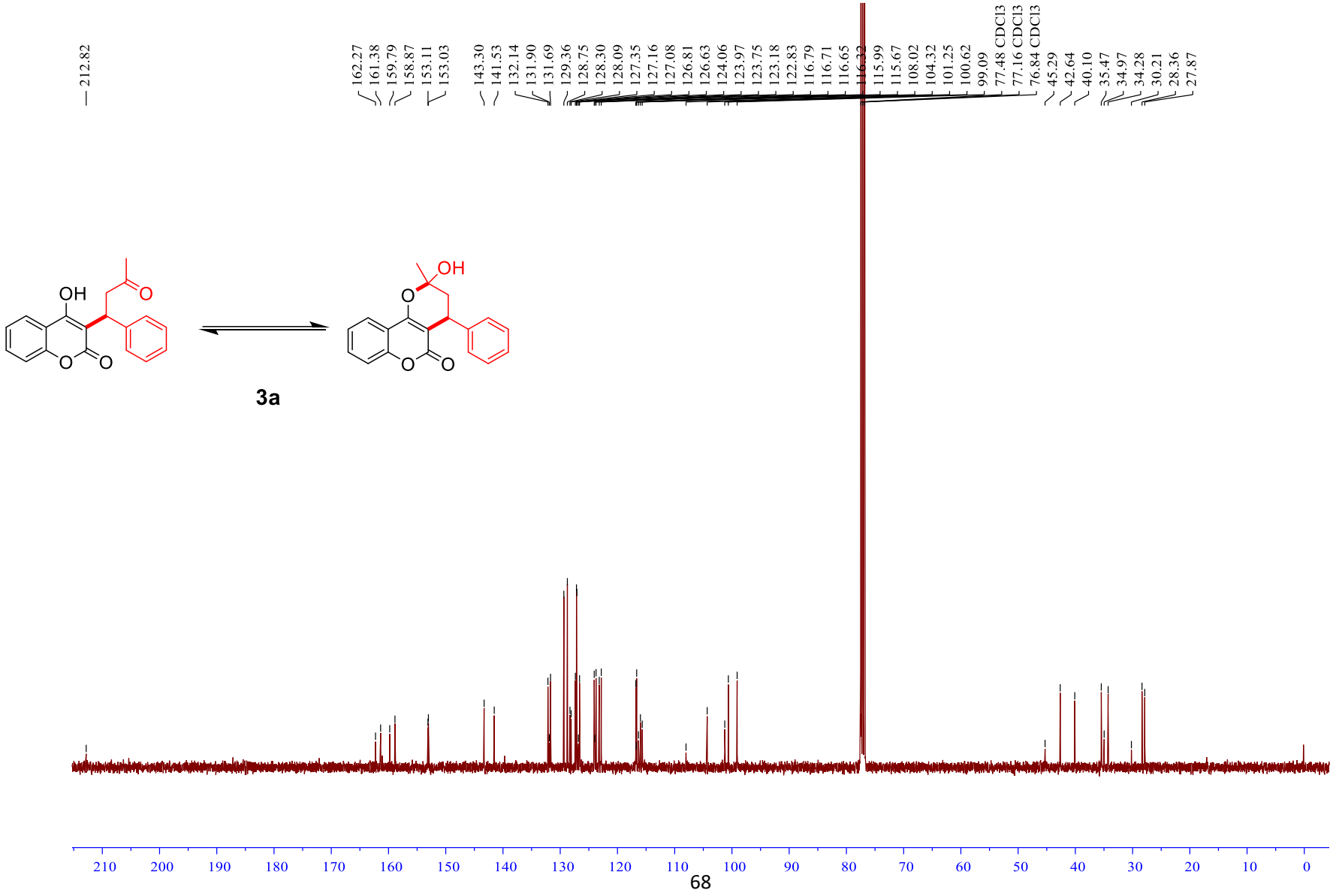

207.76
169.65
148.94
138.63
129.31
121.53
77.58 CDCl3
77.26 CDCl3
76.94 CDCl3
45.02
30.08
29.00
21.12
O
AcO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

**SI-9**


7.55
7.54
7.54
7.53
7.52
7.51
7.49
7.40
7.39
7.38
7.26 CHLOROFORM-D
6.73
6.69
2.38
O
2a'
2.99
3.00
0.99
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


198.67
143.63
134.44
130.63
129.05
128.35
127.19
77.48 CHLOROFORM-D
77.16 CHLOROFORM-D
76.84 CHLOROFORM-D
27.58
O
2a'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


9.52
7.95
7.95
7.93
7.93
7.91
7.90
7.89
7.88
7.82
7.82
7.80
7.80
7.59
7.58
7.57
7.55
7.54
7.51
7.51
7.49
7.49
7.47
7.47
7.36
7.34
7.33
7.32
7.31
7.31
7.29
7.29
7.28
7.27
7.26
7.25
7.23
7.23
7.21
4.71
4.69
4.68
4.30
4.29
4.28
4.27
4.18
4.17
4.16
4.14
3.42
3.26
2.56
2.56
2.53
2.52
2.50
2.48
2.46
2.45
2.44
2.42
2.40
2.38
2.29
2.03
2.00
1.99
1.96
1.71
1.67
OH
O
O
O
OH
O
O
O
3a
0.23
0.22
0.88
1.04
0.93
1.36
15.99
0.25
0.91
1.07
0.28
1.00
0.90
0.93
2.04
0.76
1.09
6.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


212.82
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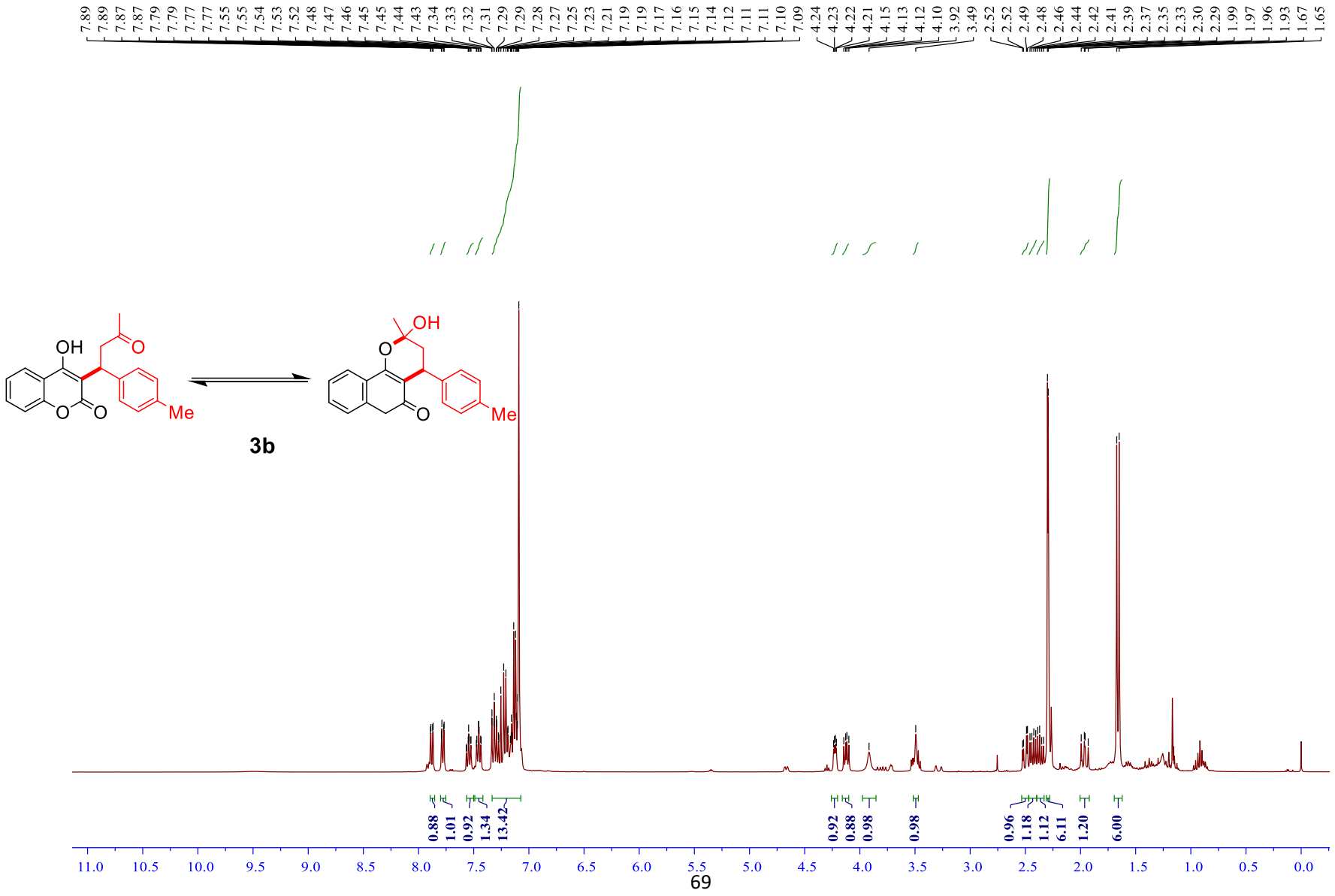
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4.24 4.23 4.22 4.21 4.15 4.13 4.12 4.10 3.92 3.49
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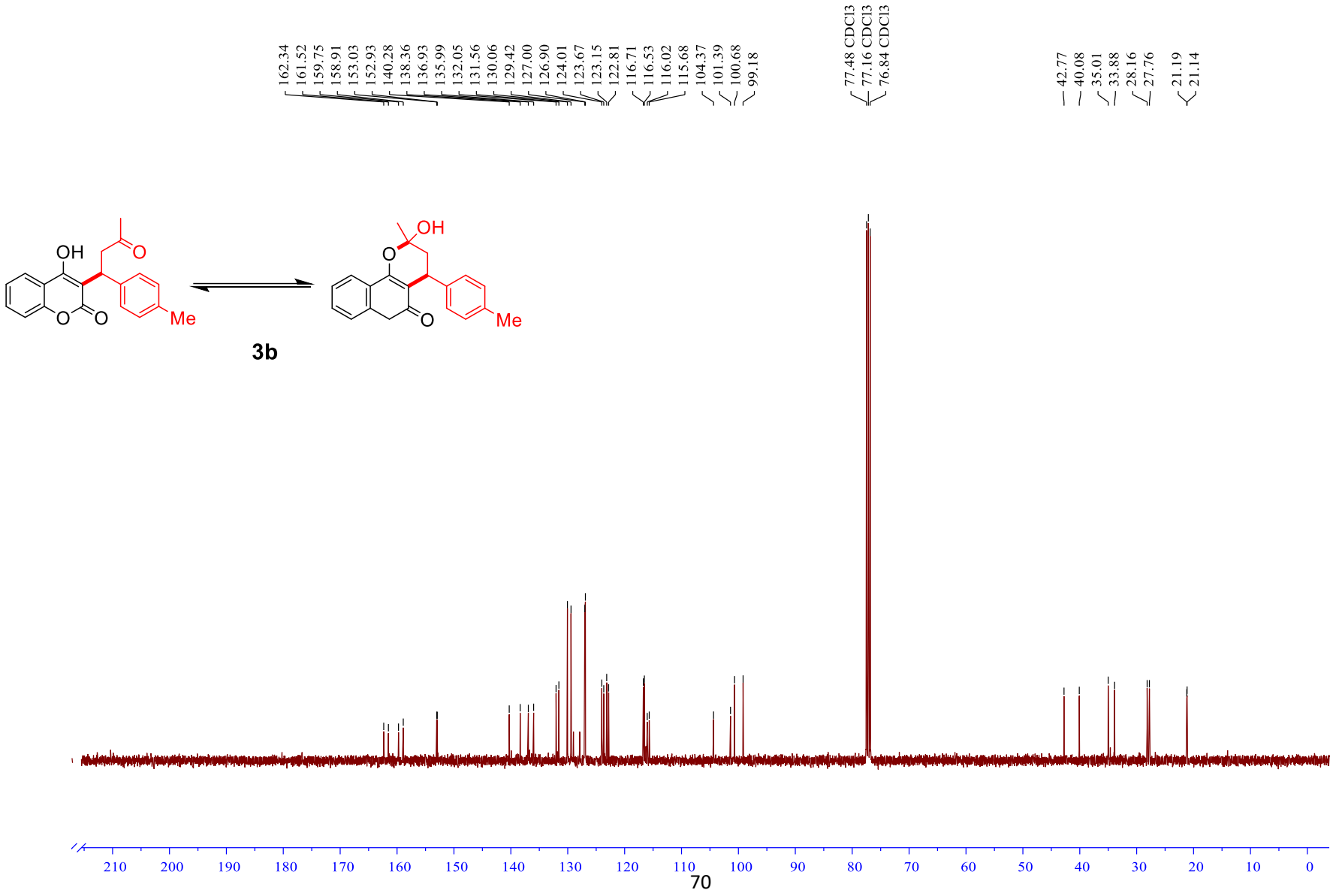
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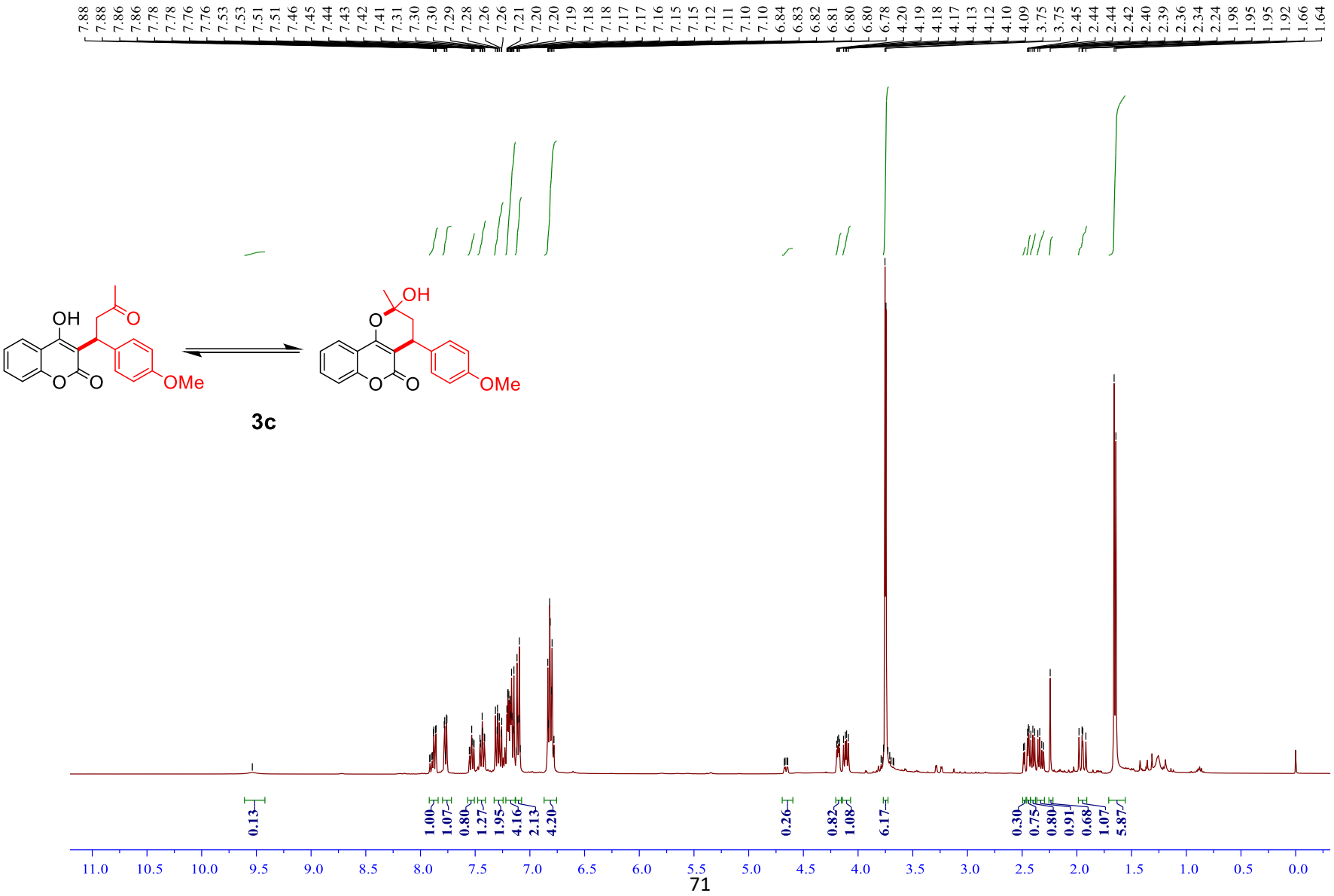
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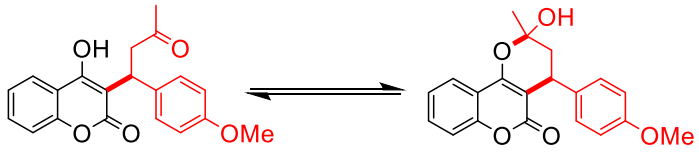


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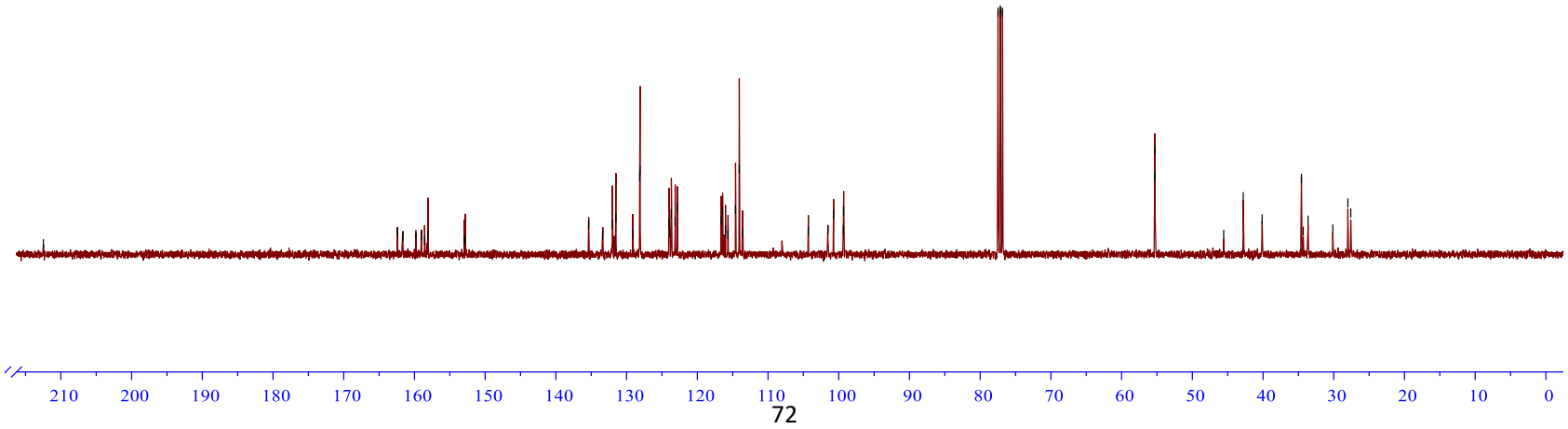

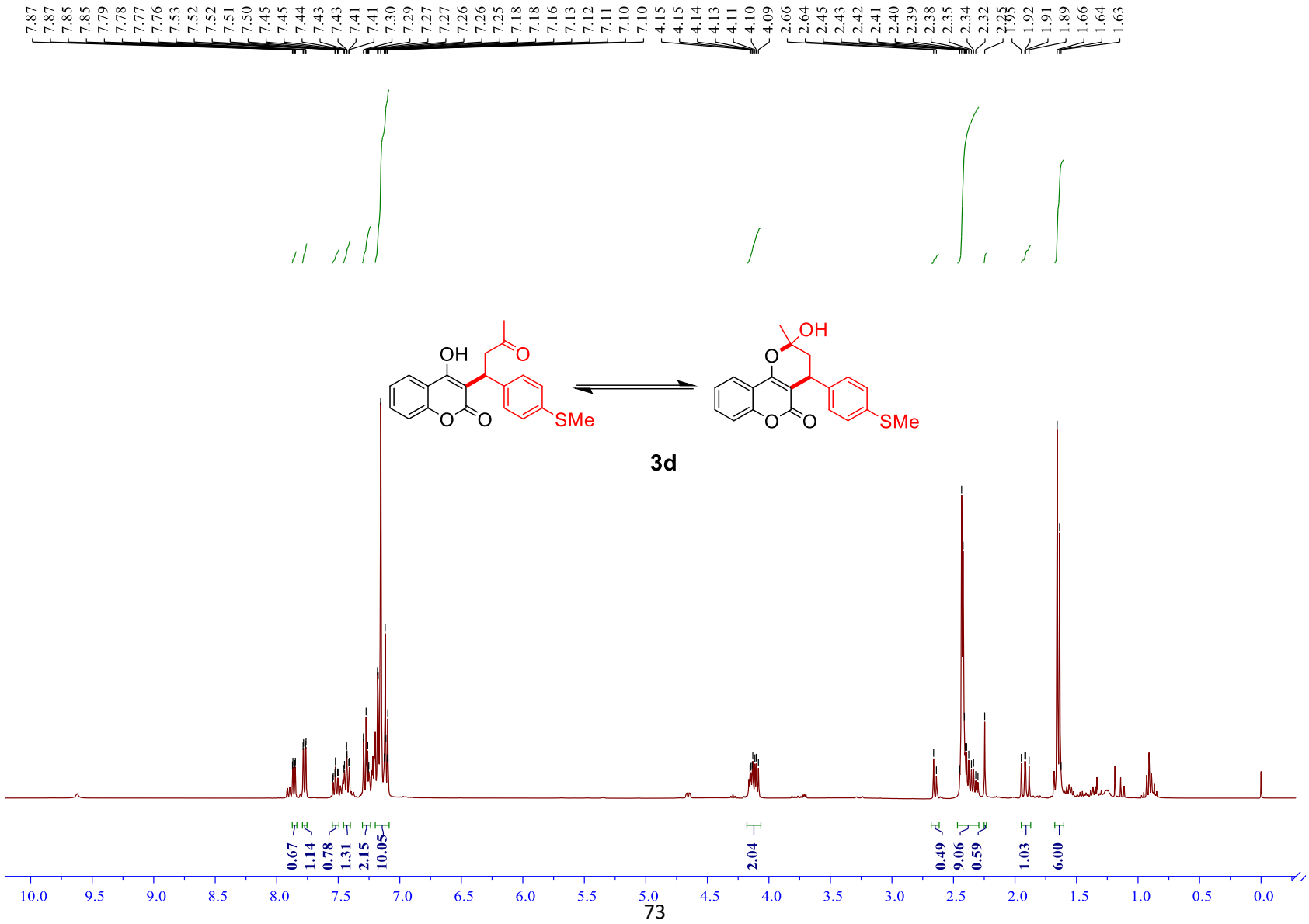
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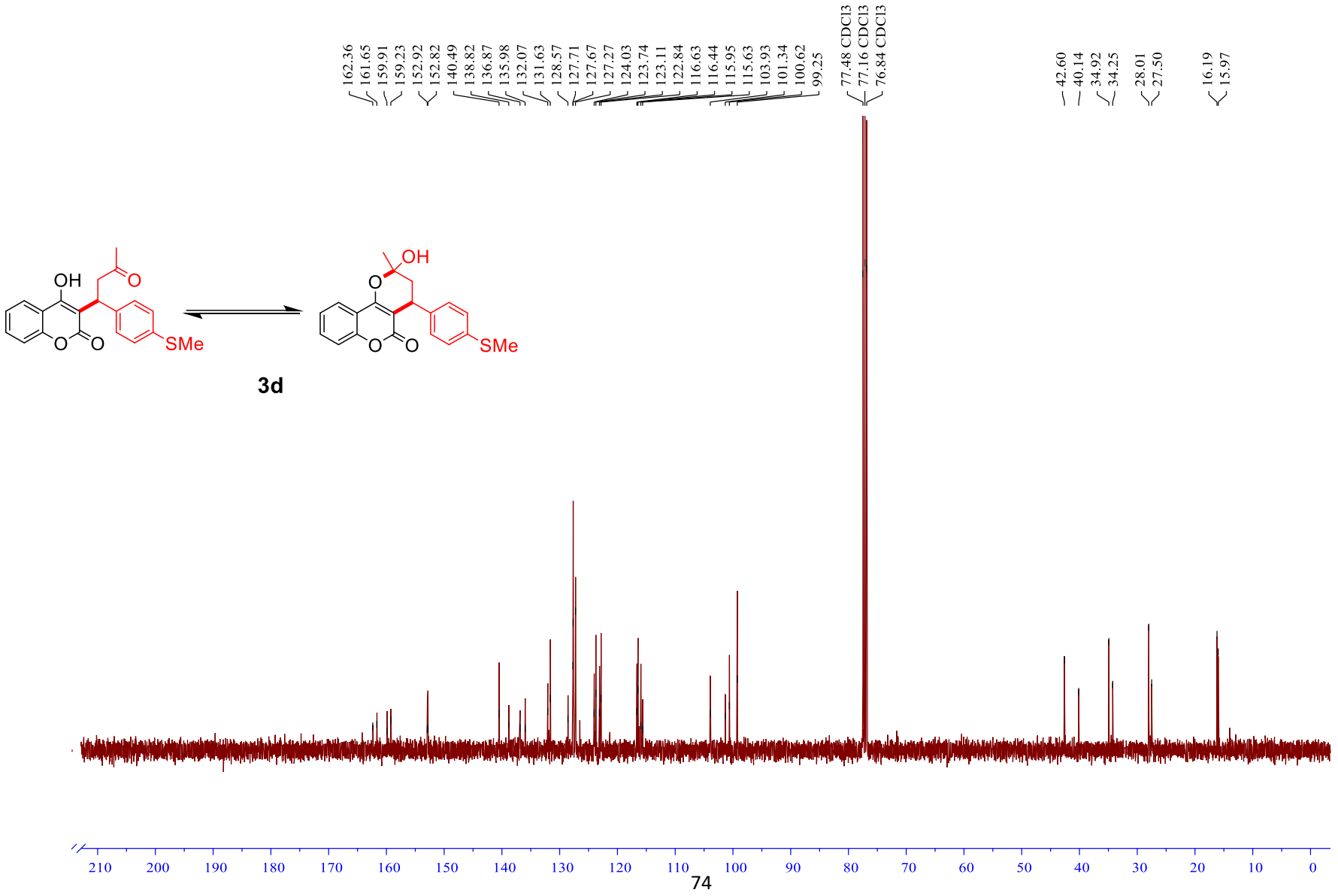
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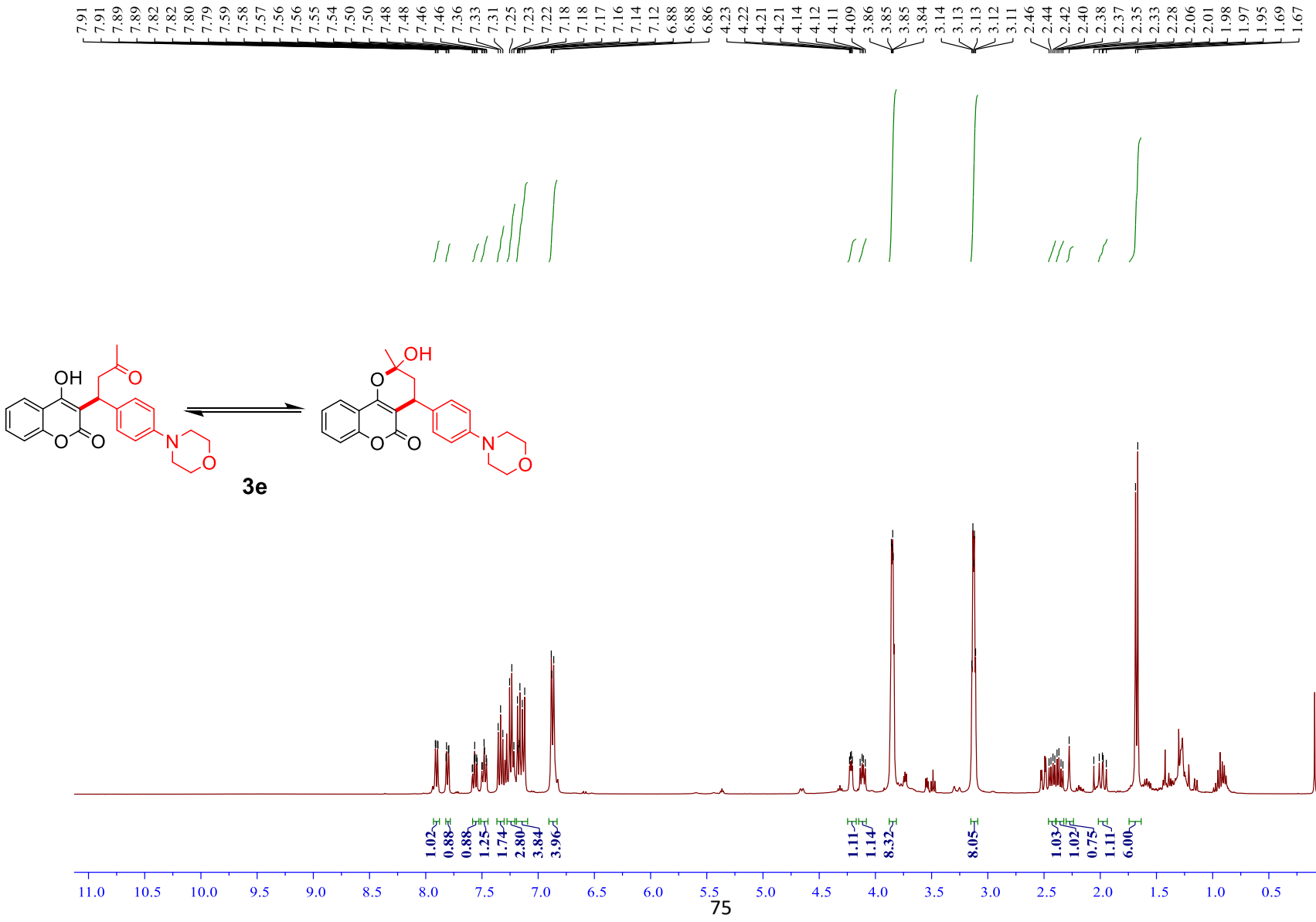
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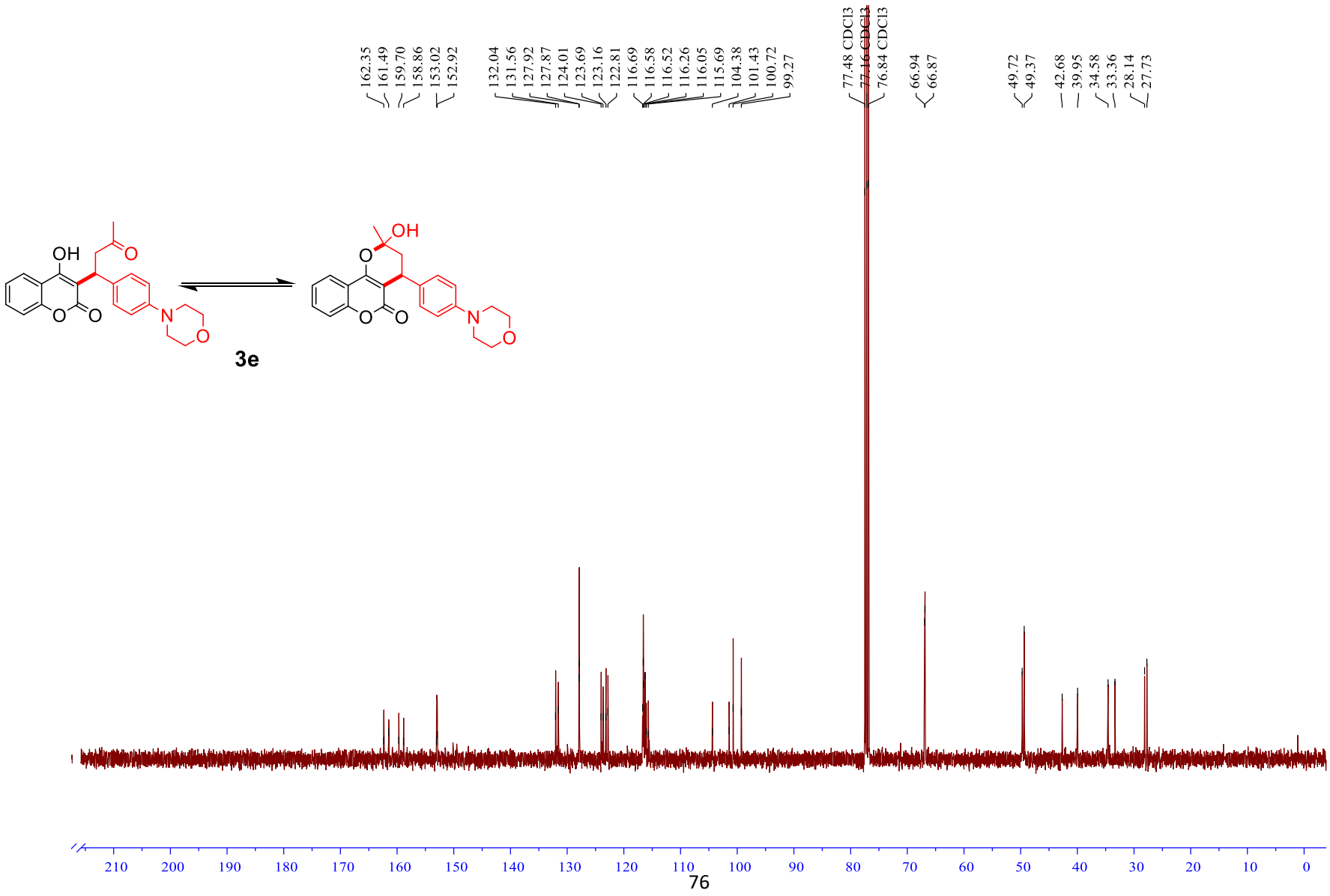
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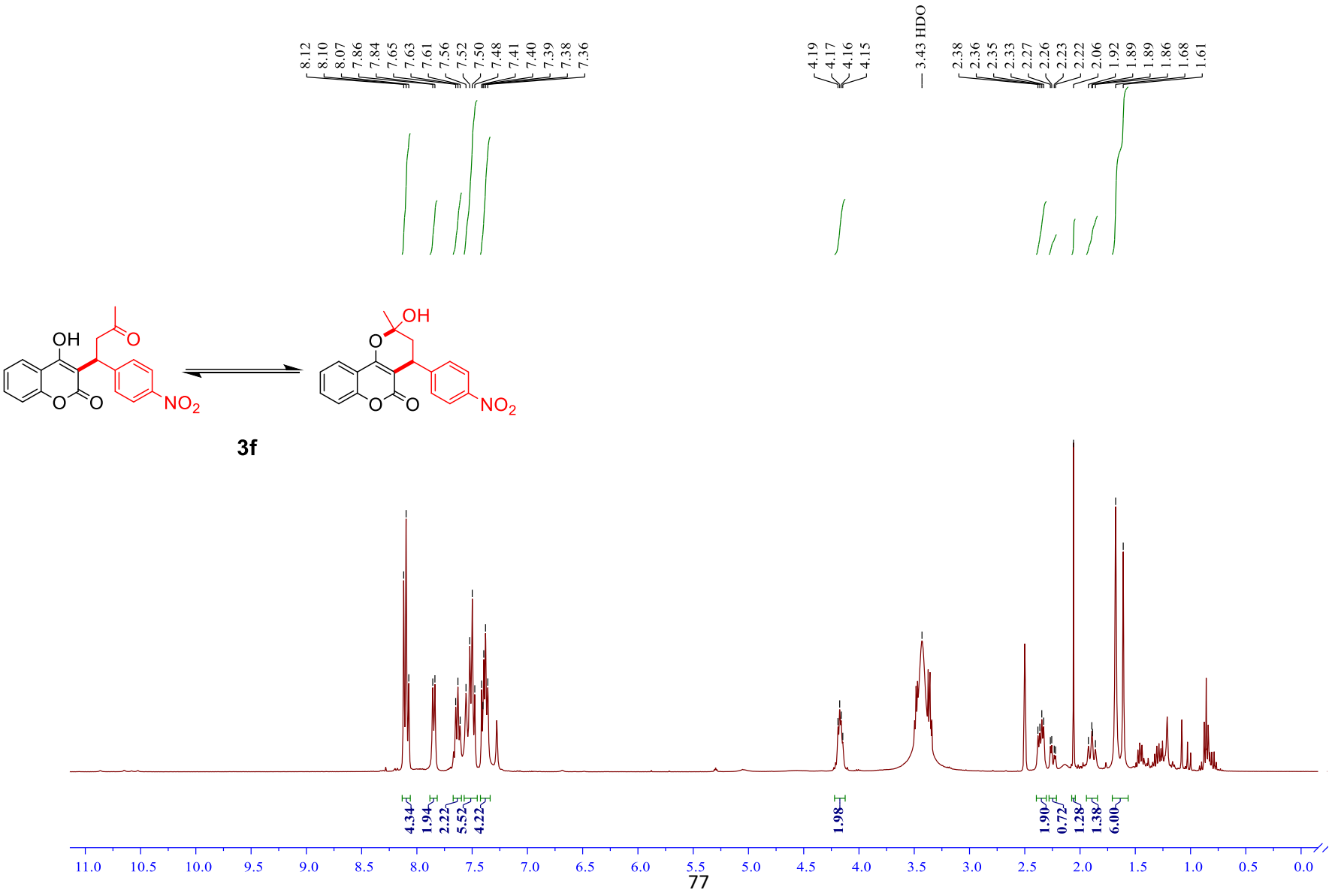
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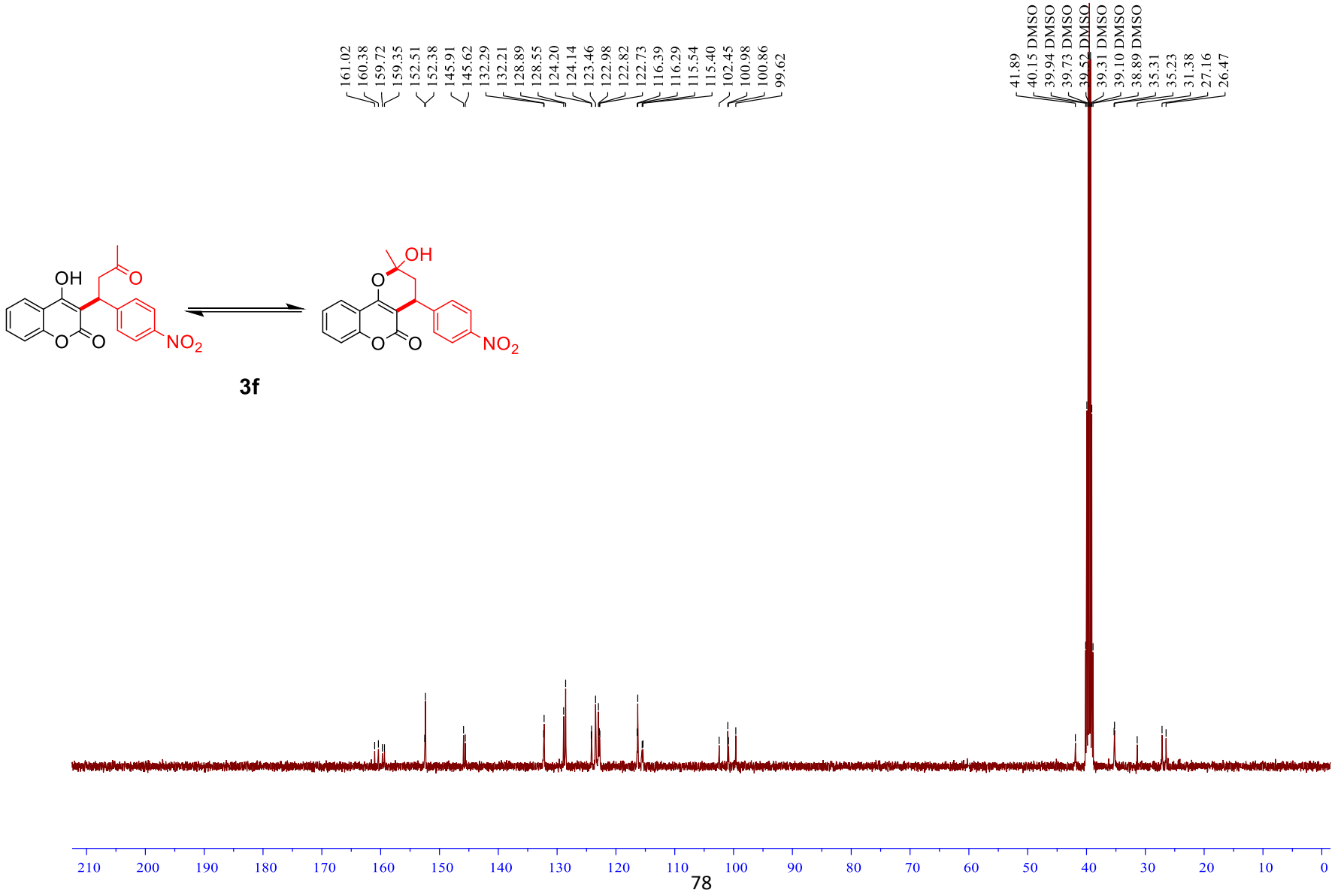
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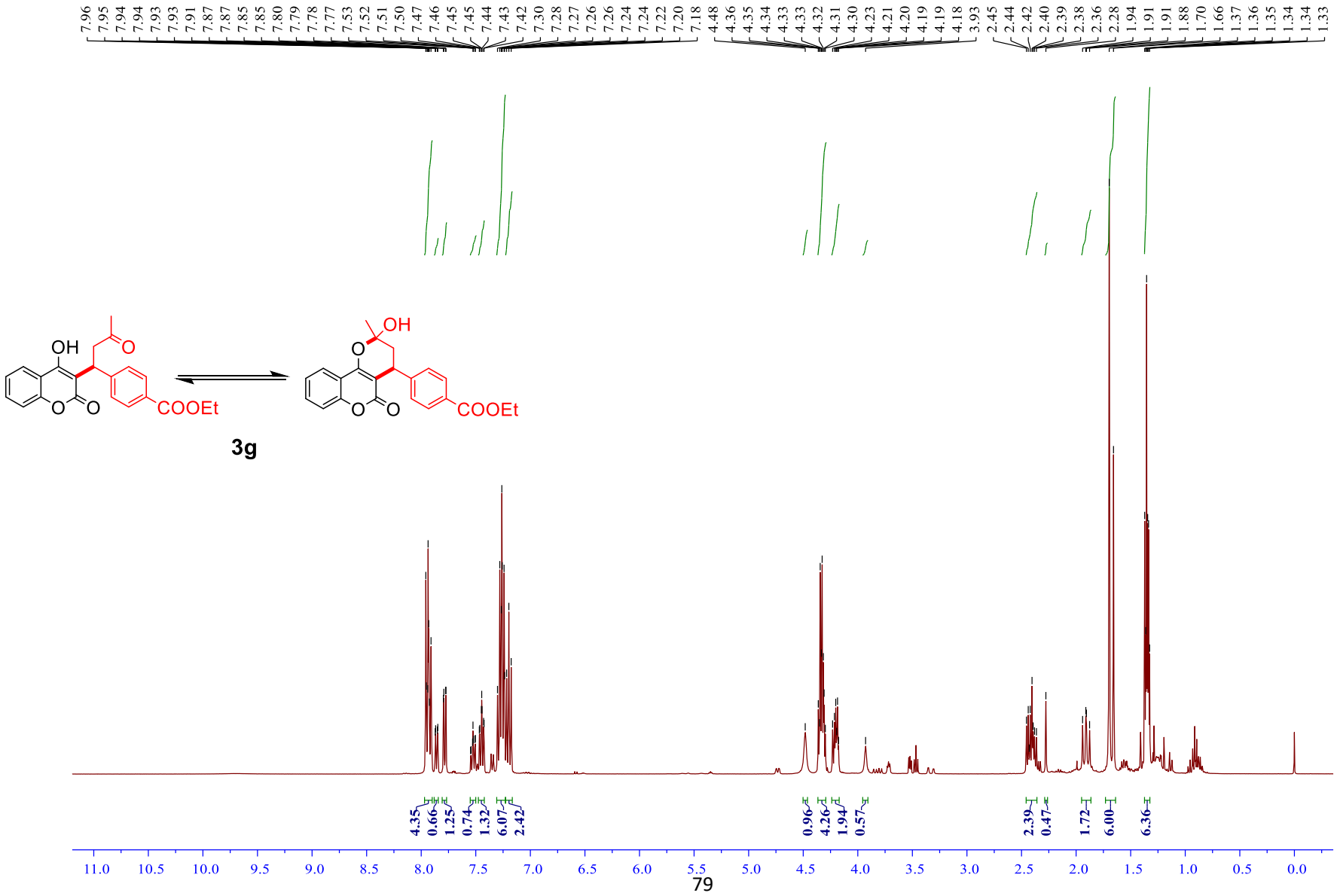
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0.96 4.26 1.94 0.57
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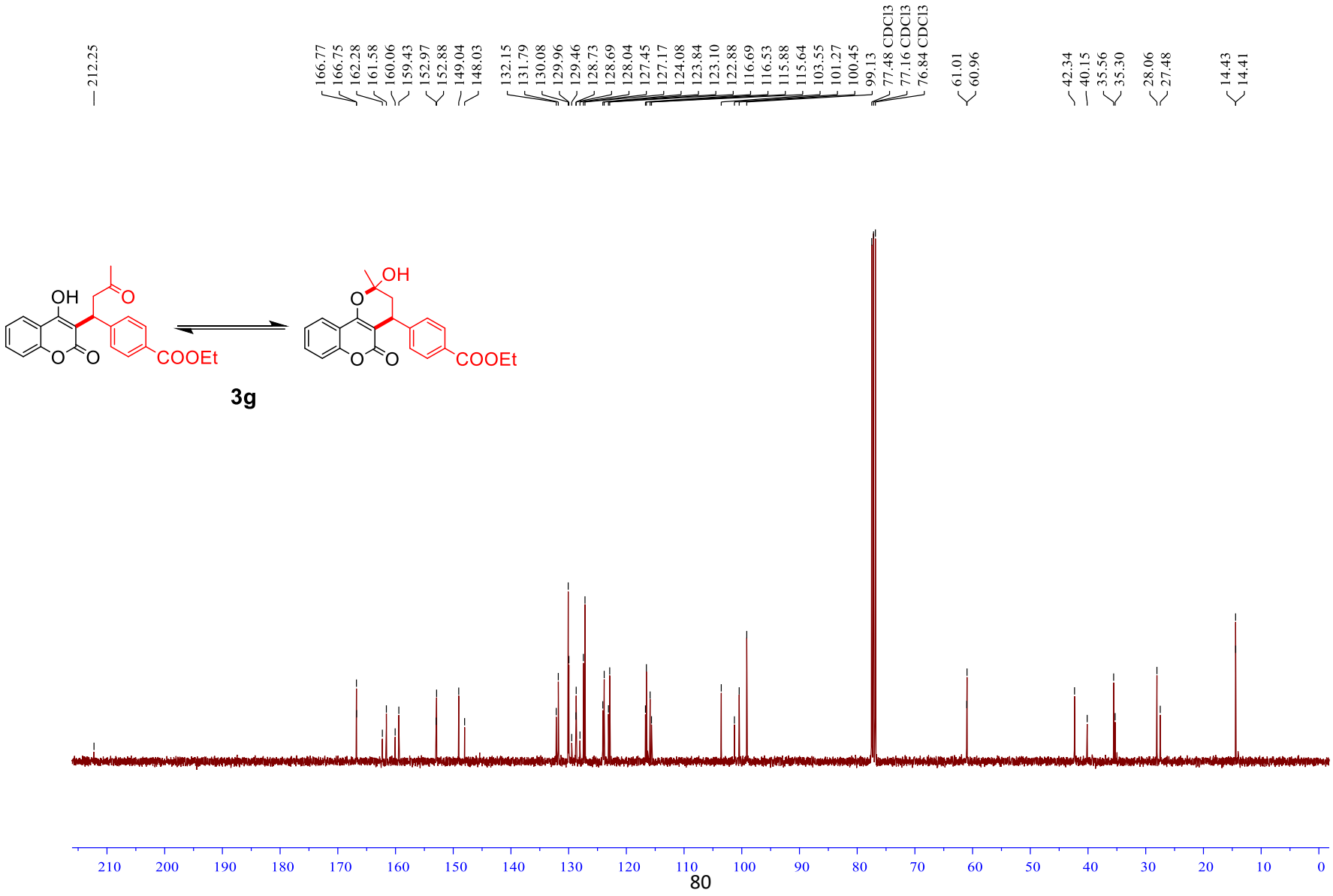
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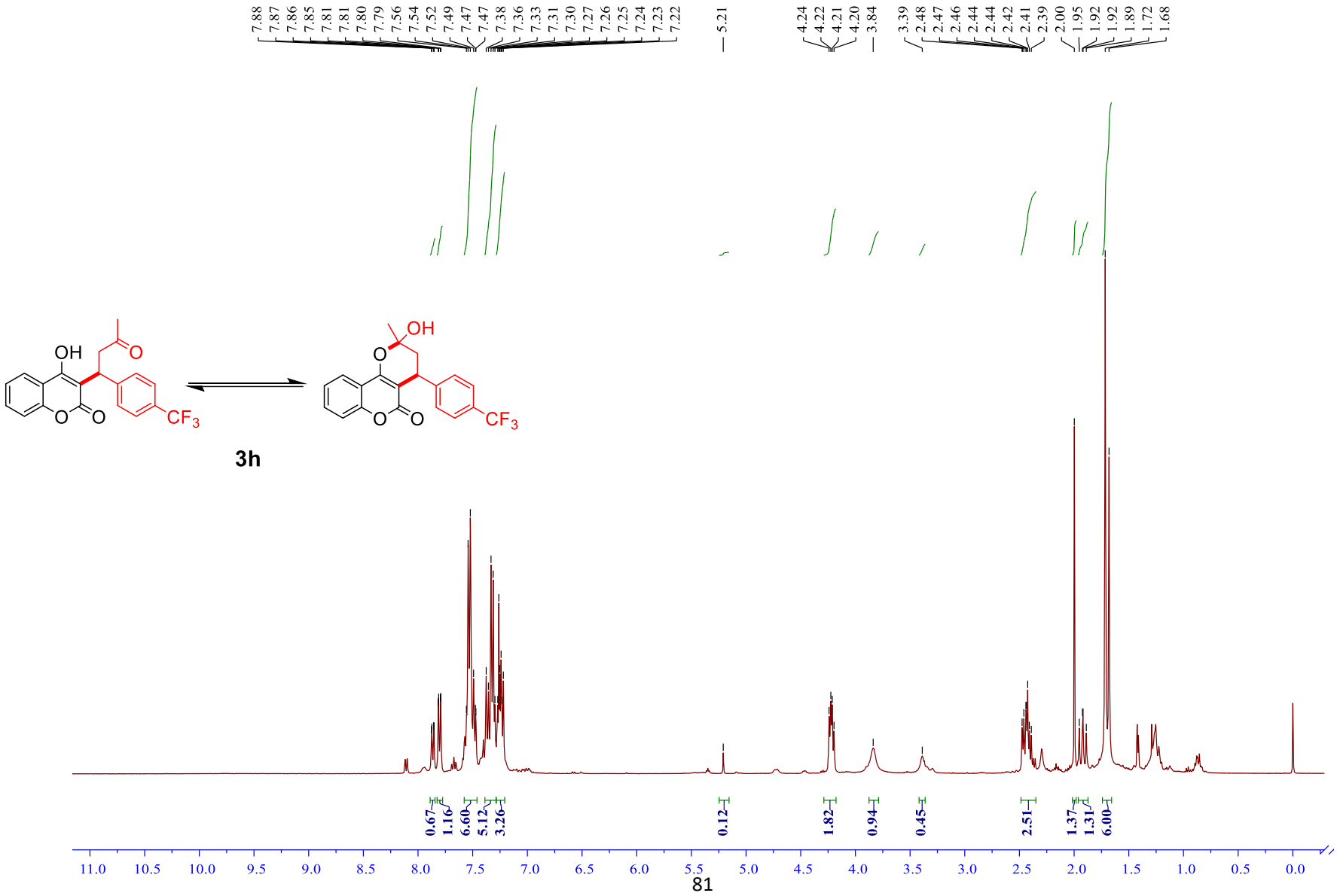
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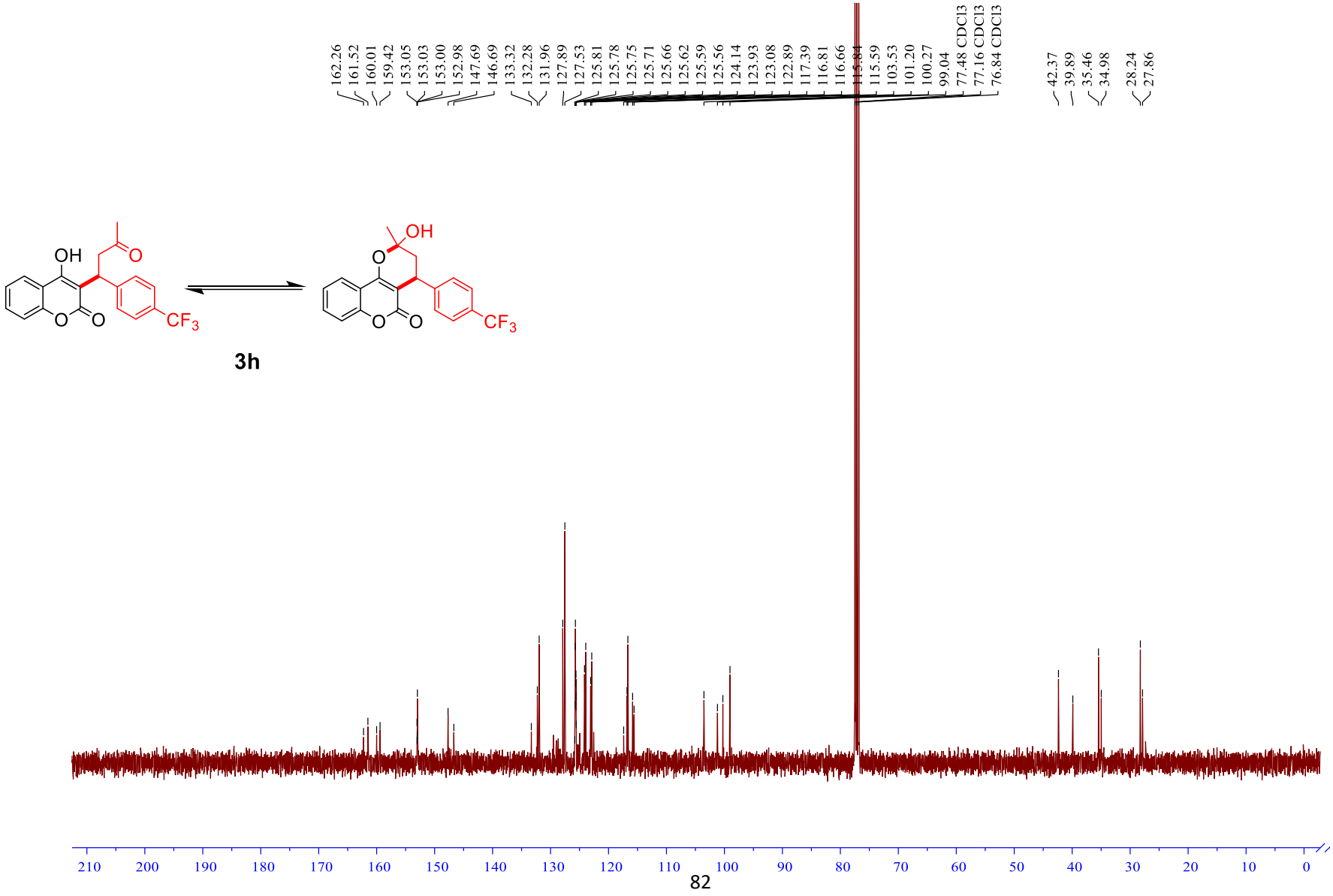
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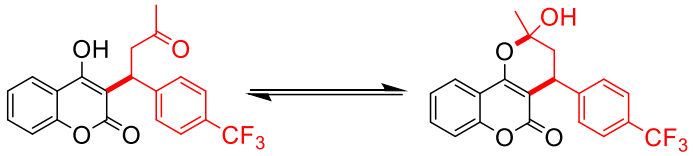
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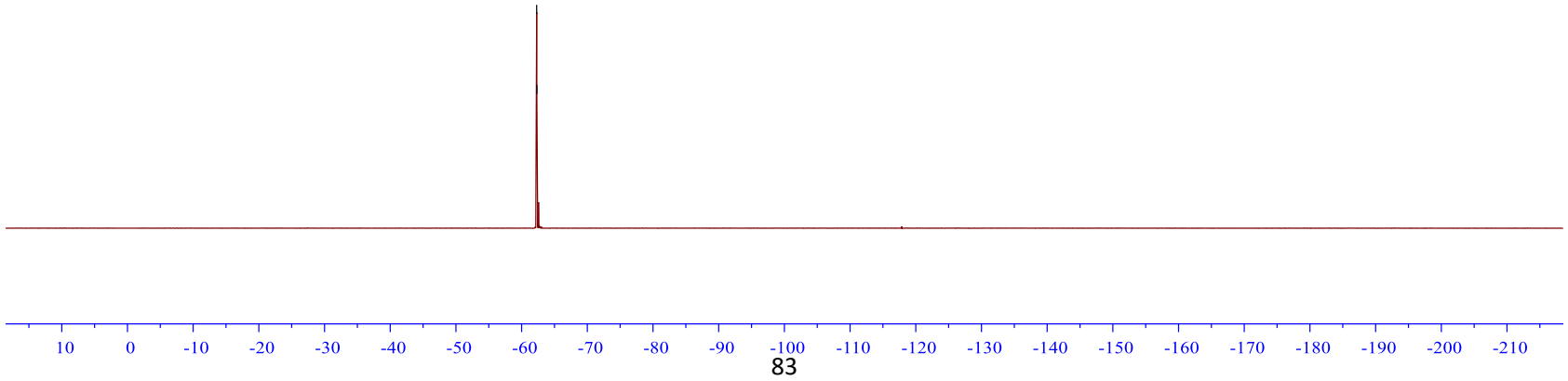
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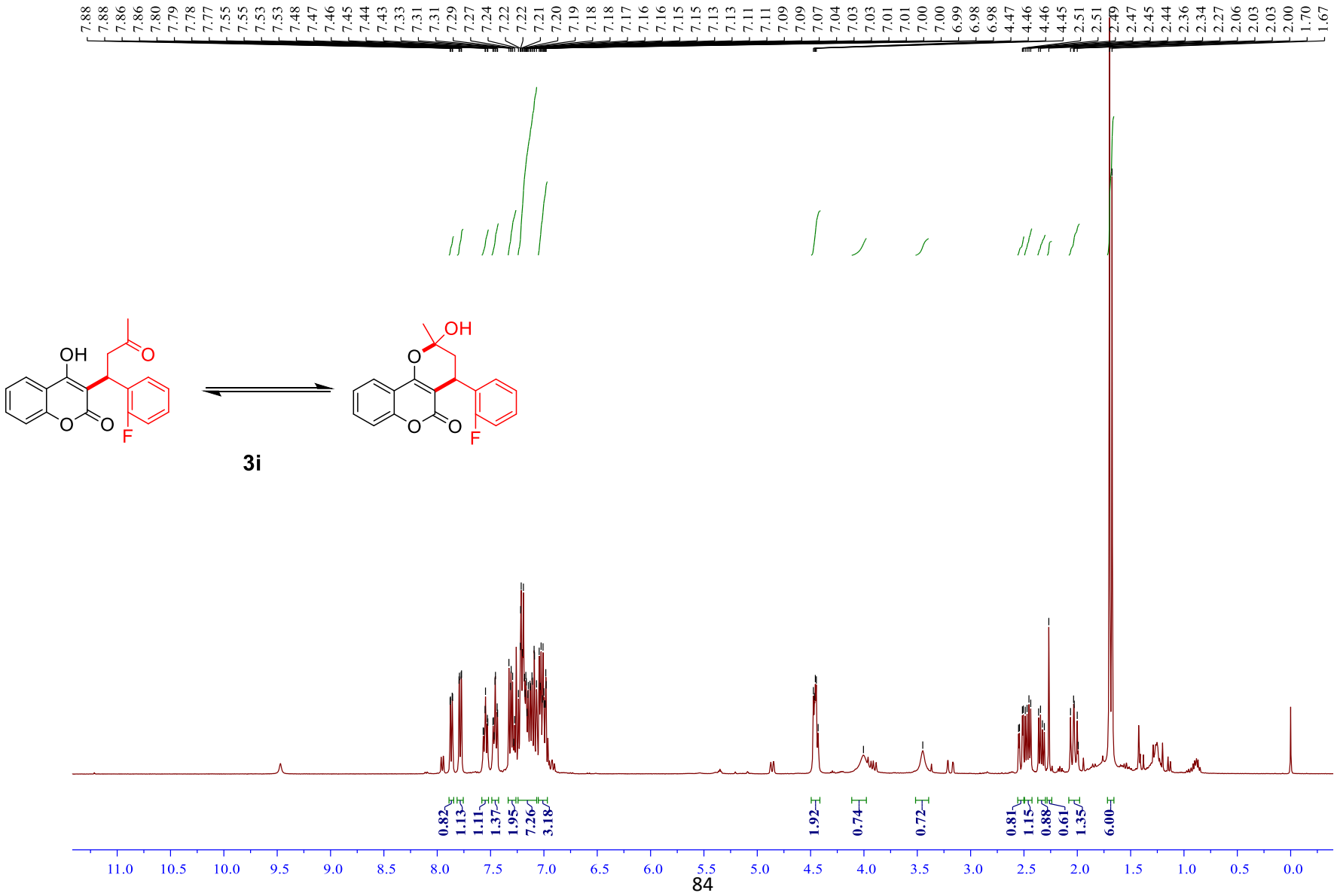
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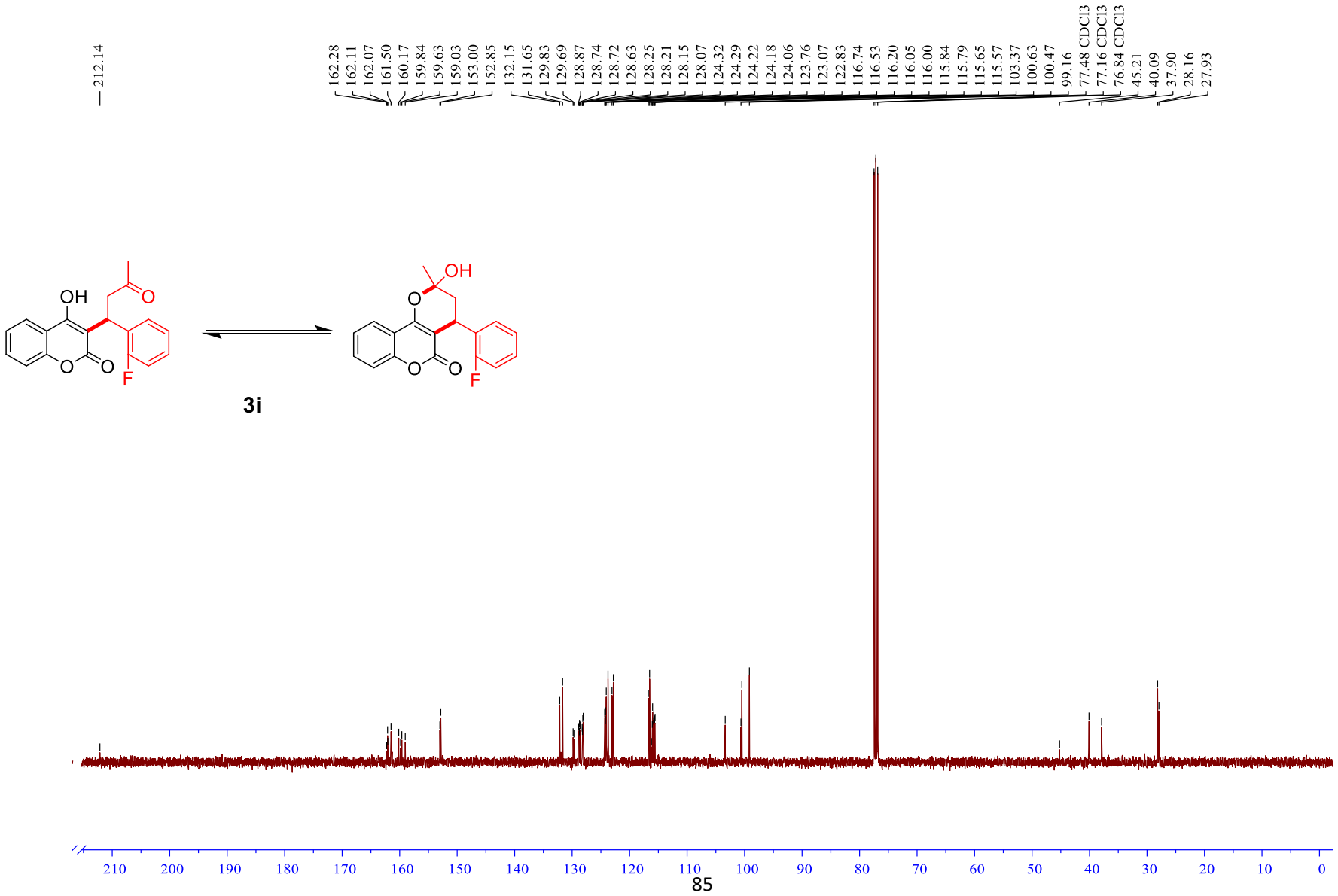
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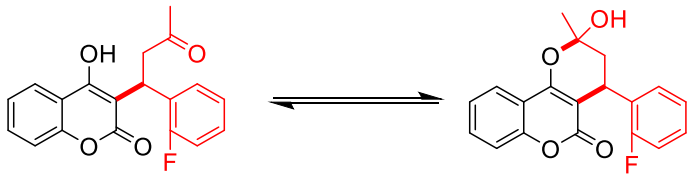
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F
OH
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O
F

**3i**


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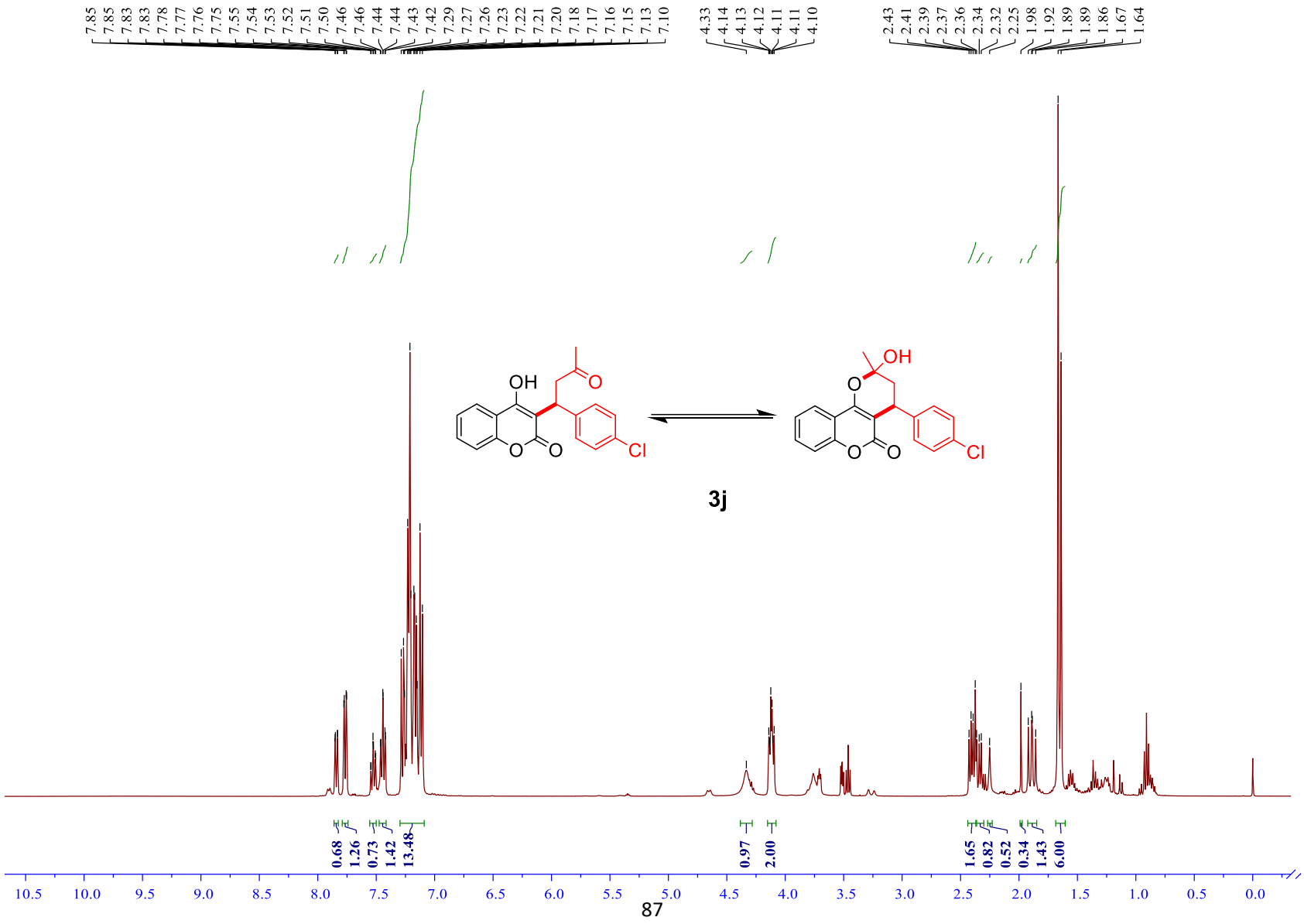
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4.33 4.14 4.13 4.12 4.11 4.11 4.10
2.43 2.41 2.39 2.37 2.36 2.34 2.32 2.25 1.98 1.92 1.89 1.89 1.86 1.67 1.64
OH
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Cl
OH
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O
O
Cl
3j
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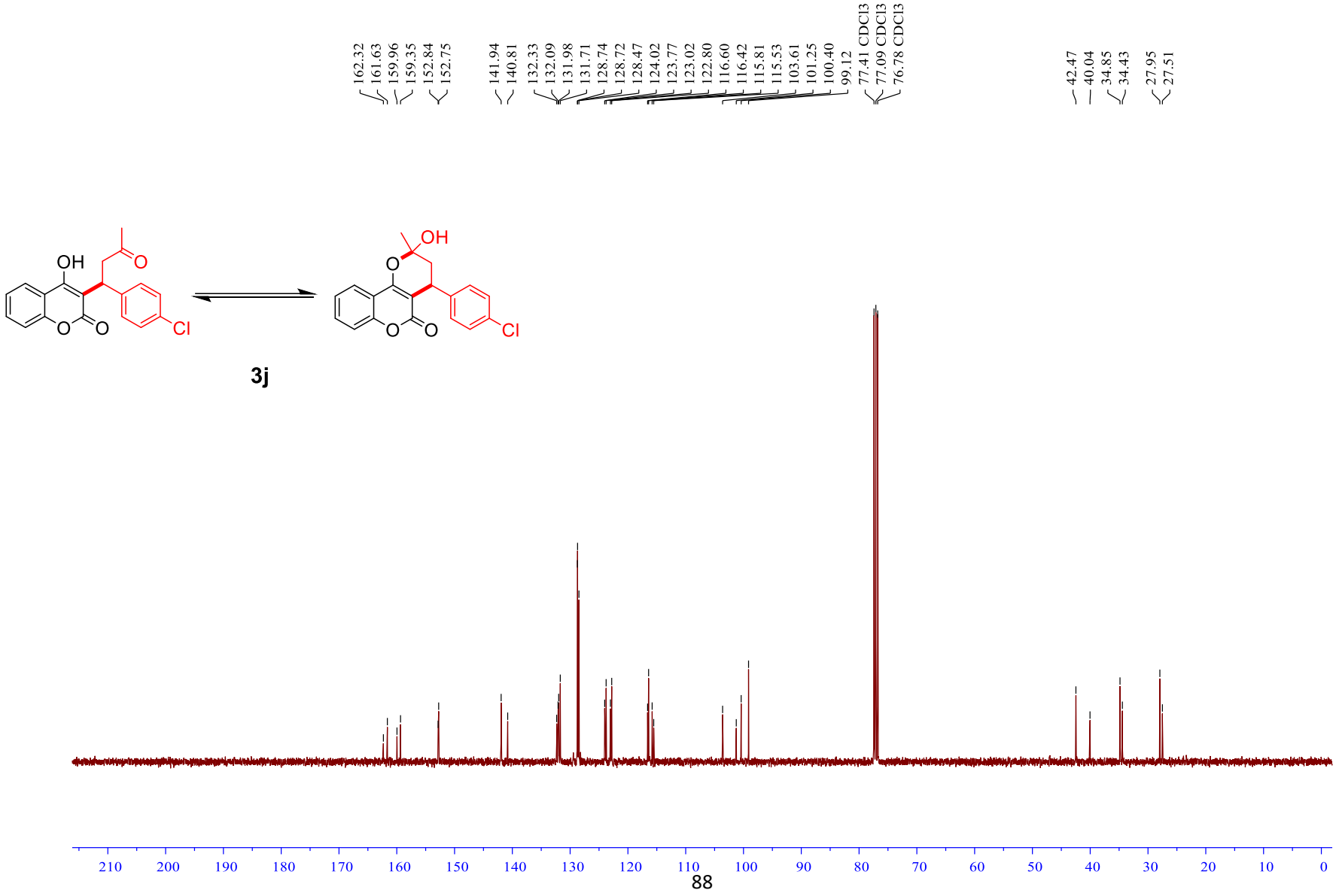
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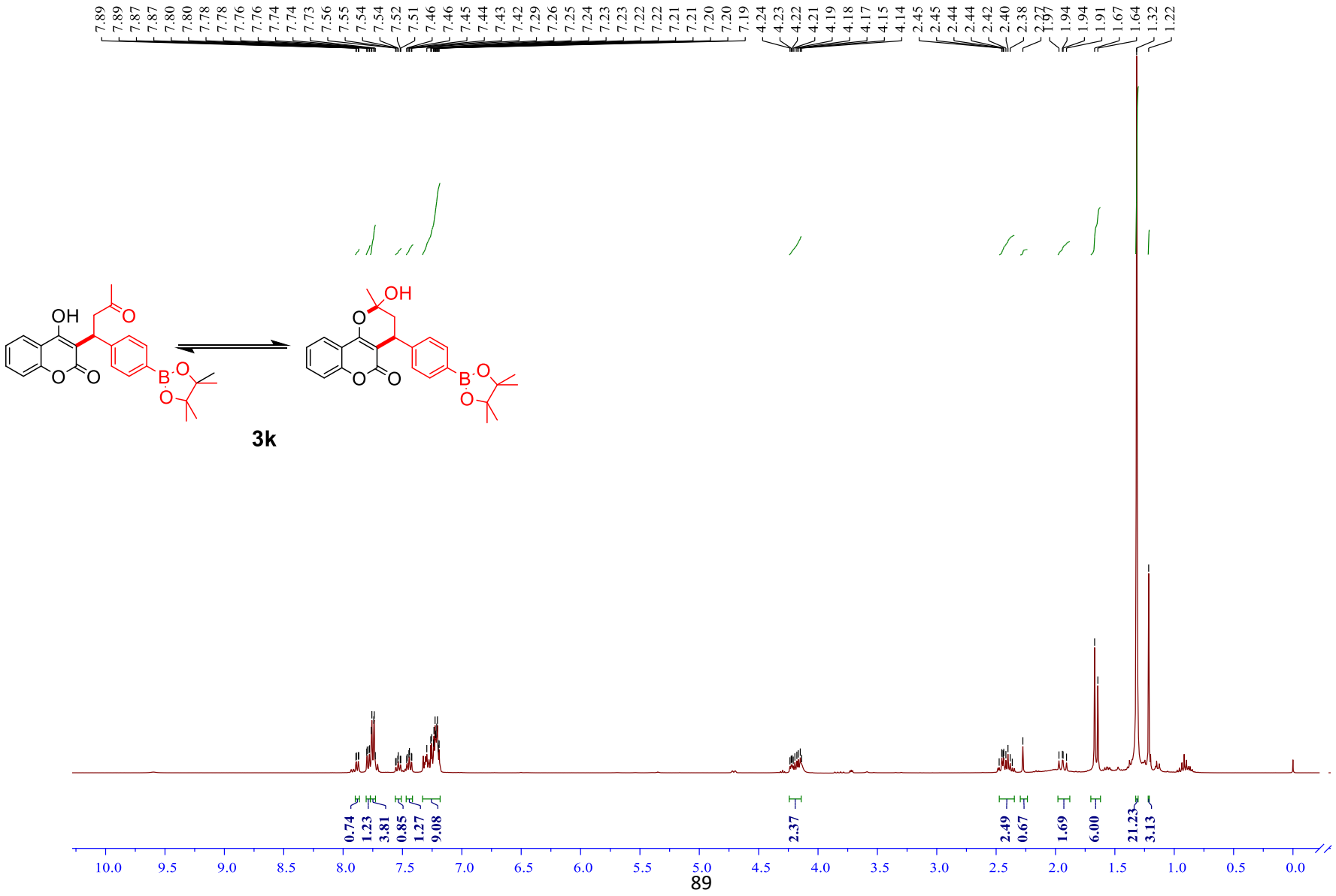
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OH
O
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B
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O
3k
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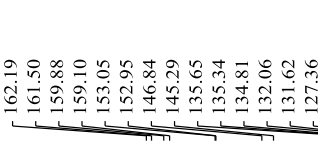
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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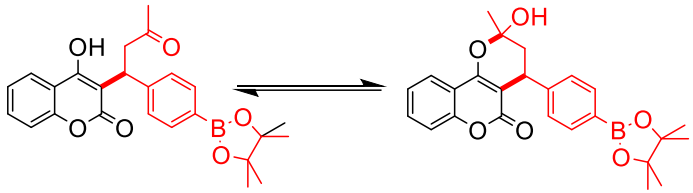
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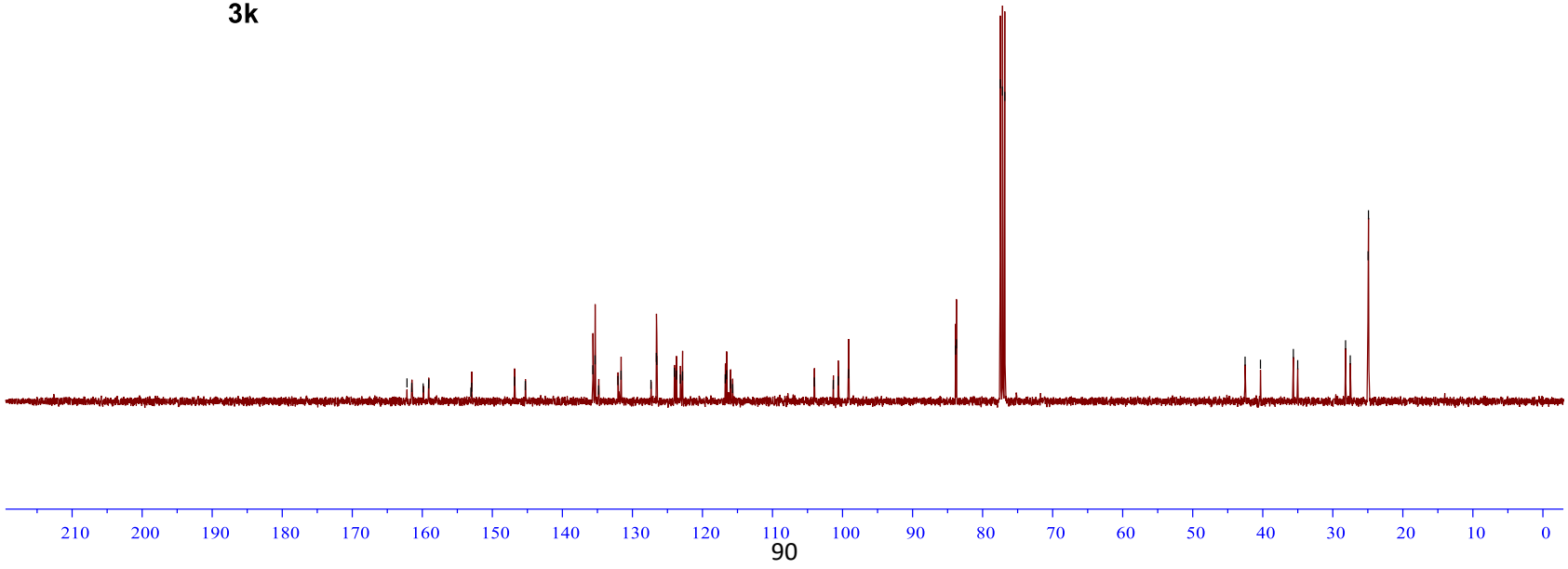
**3k**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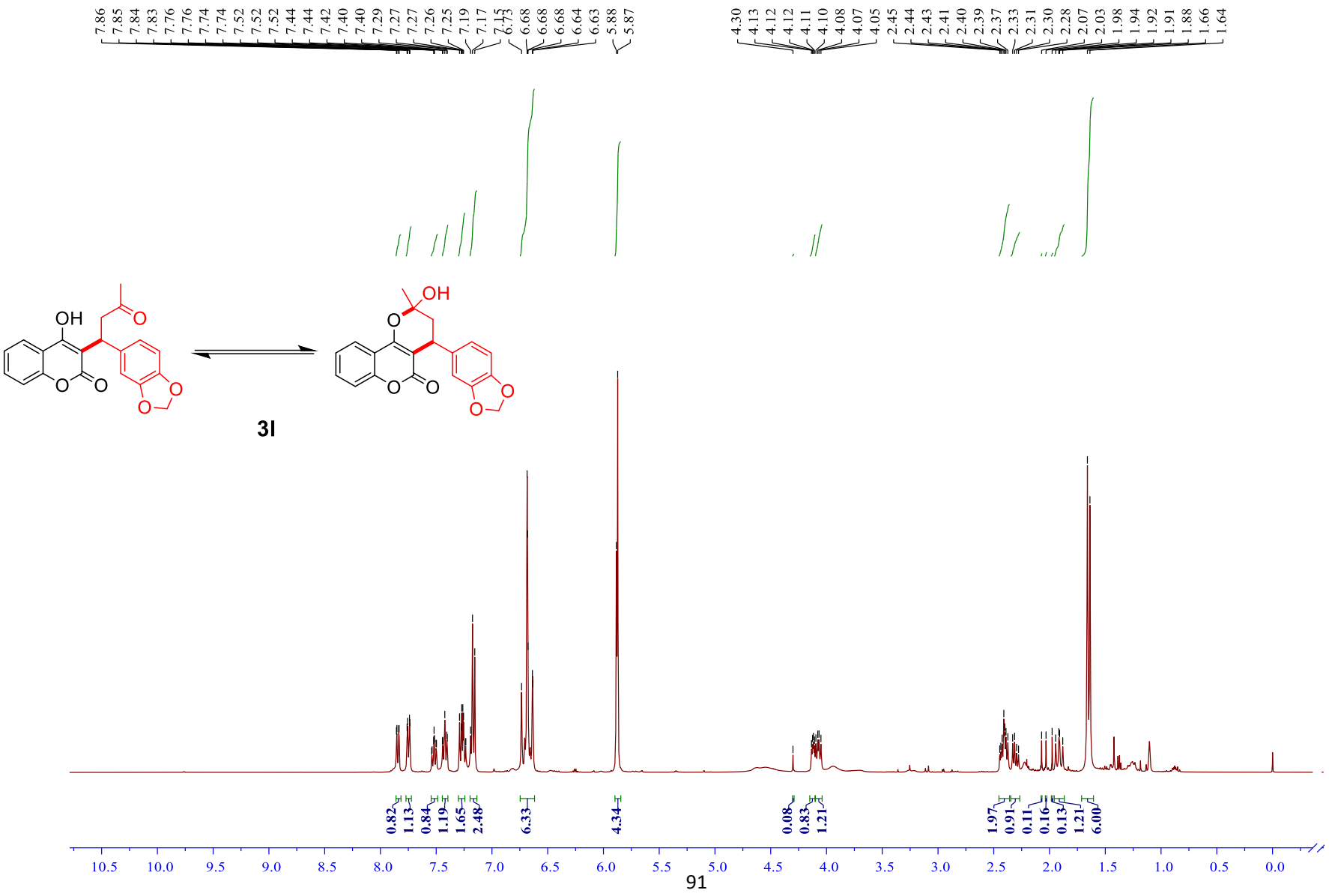
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4.08
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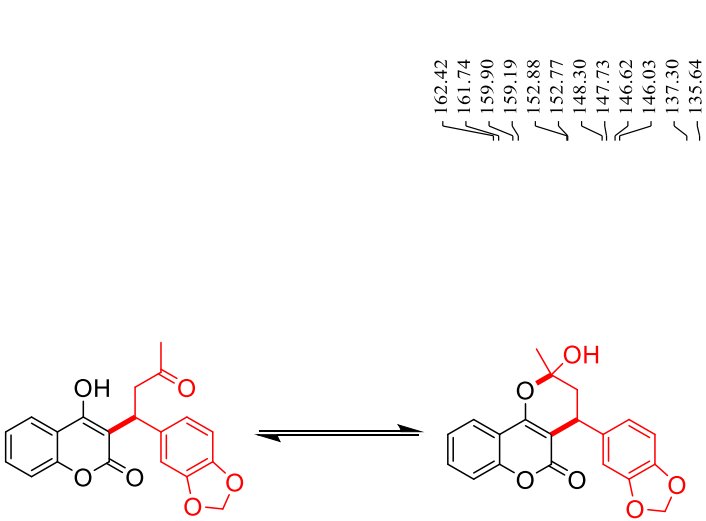
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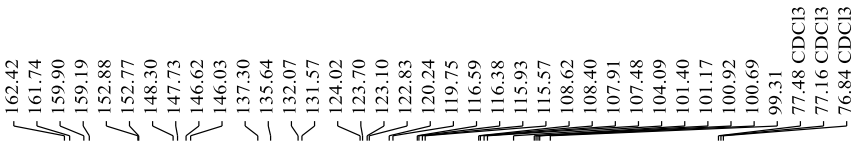
**3l**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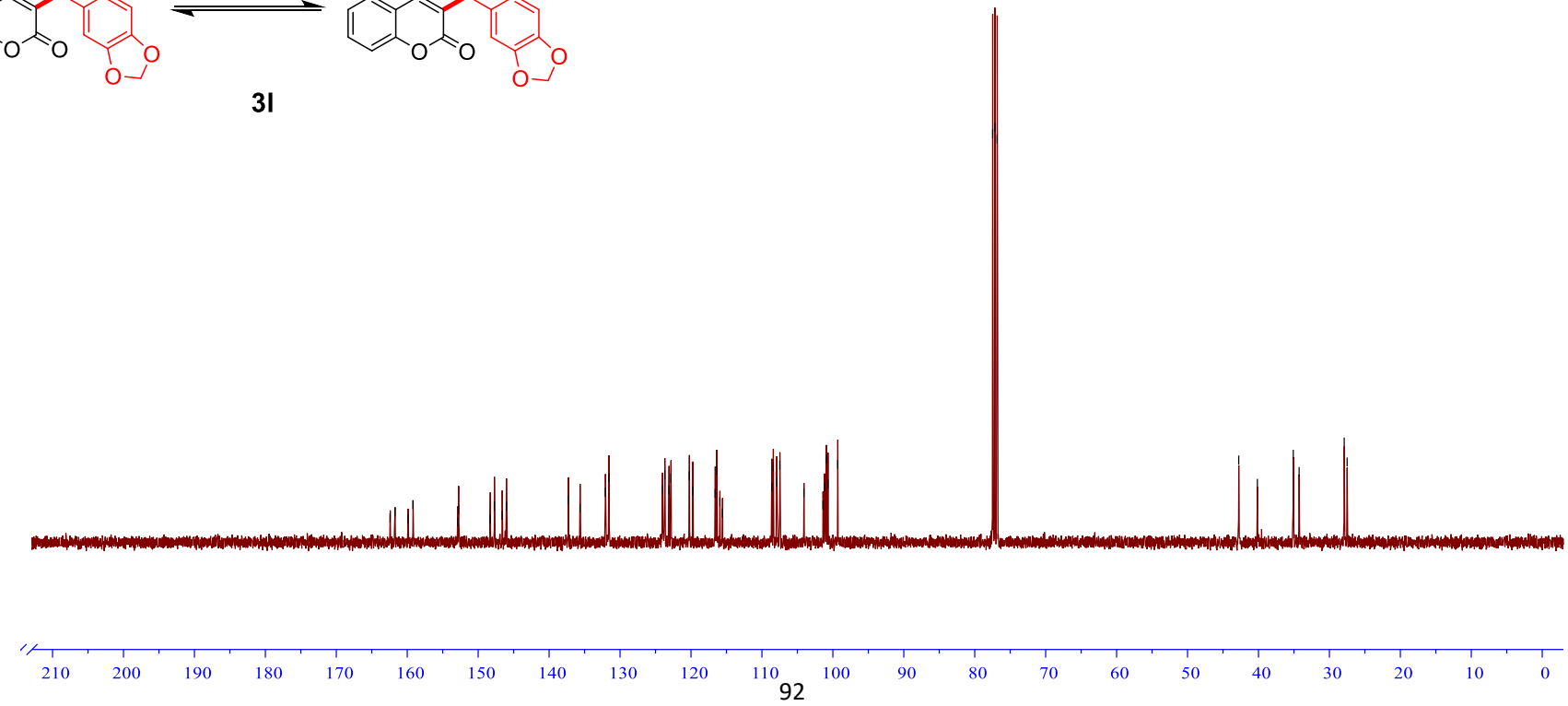
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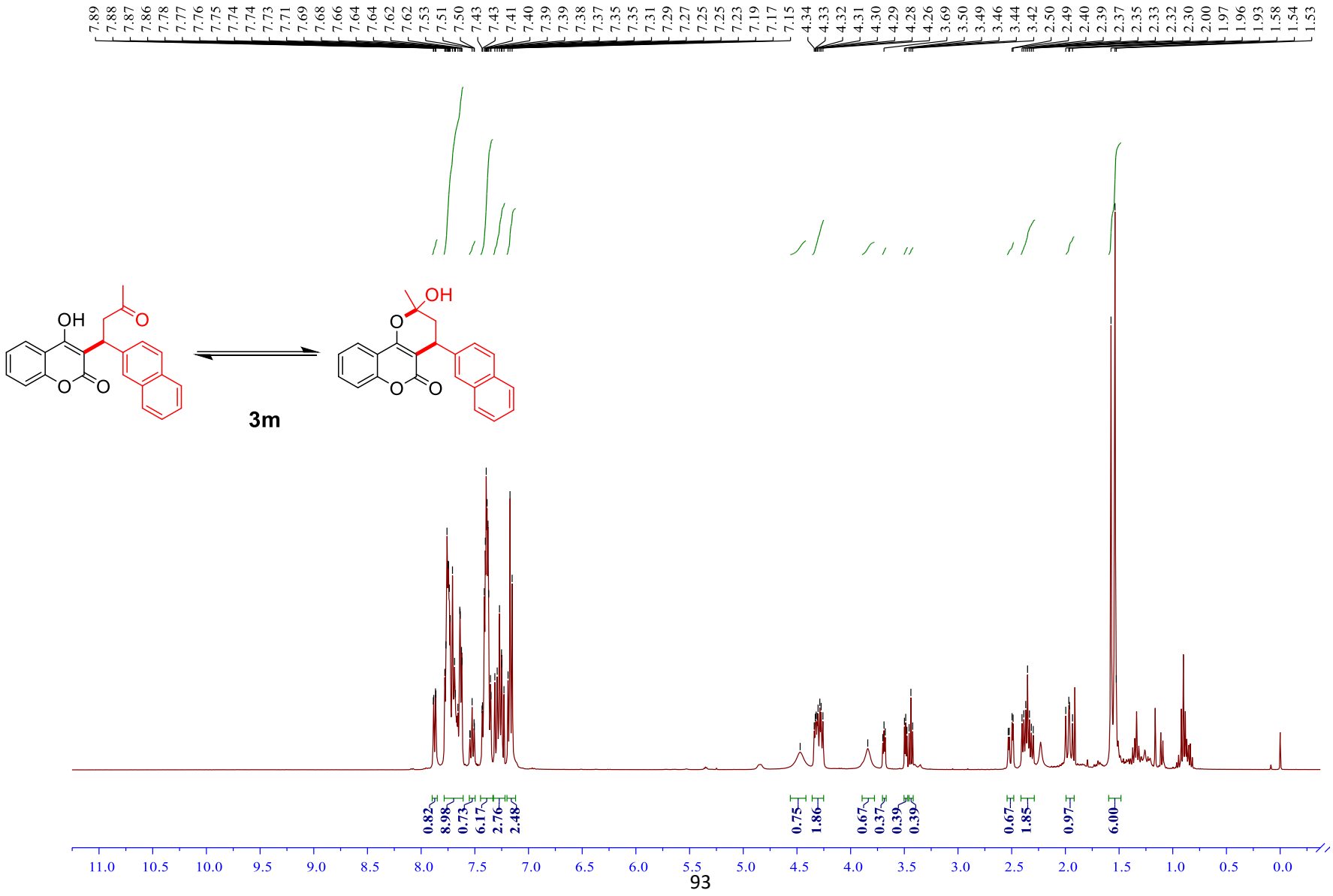
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4.34 4.33 4.32 4.31 4.30 4.29 4.28 4.26 3.69 3.50 3.49 3.46 3.44 3.42 2.50 2.49 2.40 2.39 2.37 2.35 2.33 2.32 2.30 2.00 1.97 1.96 1.93 1.58 1.54 1.53
OH
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O
OH
O
O
3m
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0.75 1.86 0.67 0.37 0.39 0.39 0.67 1.85 0.97 6.00
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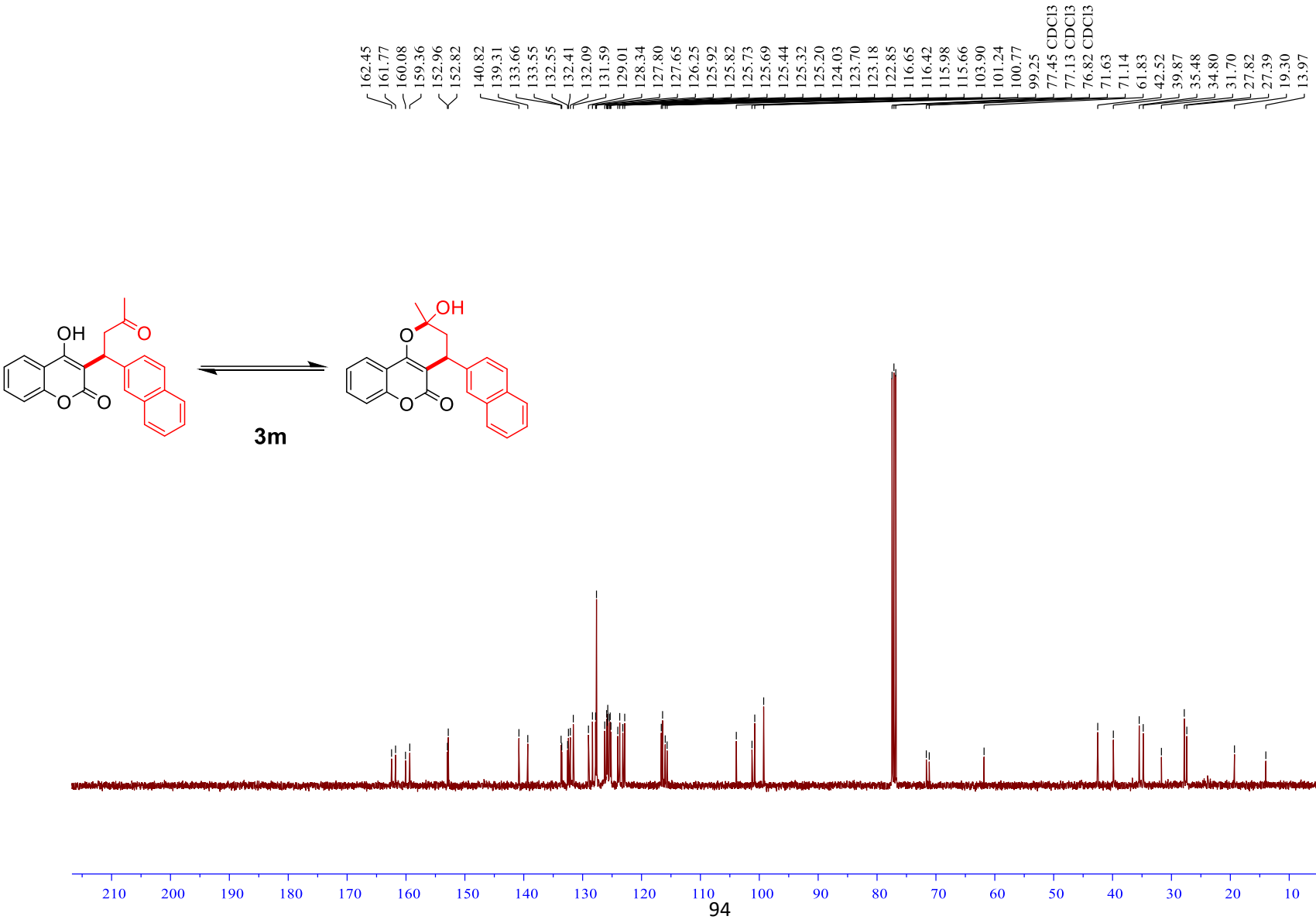
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O
OH
O
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3m
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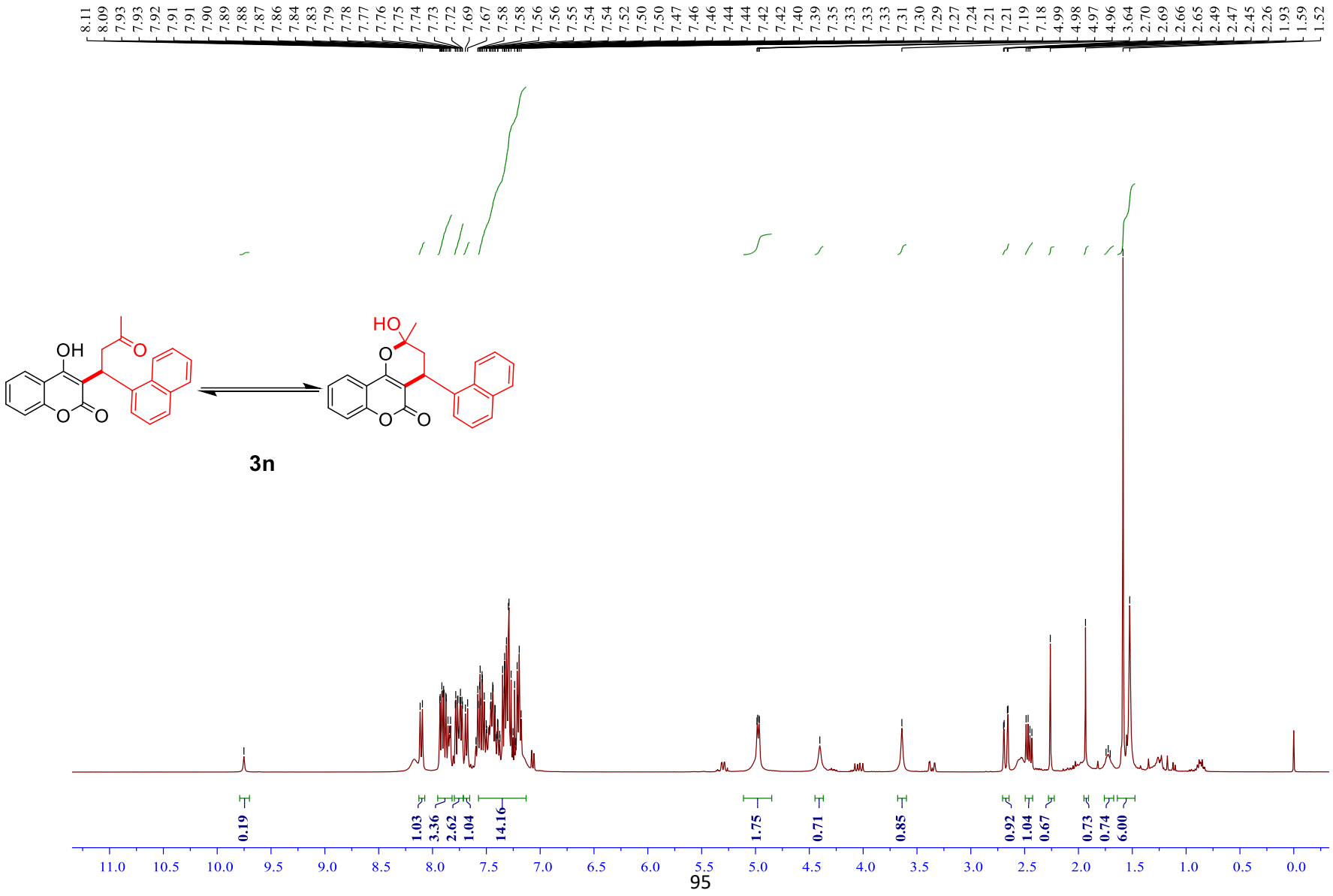
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OH
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O
HO
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2.62
1.04
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1.75
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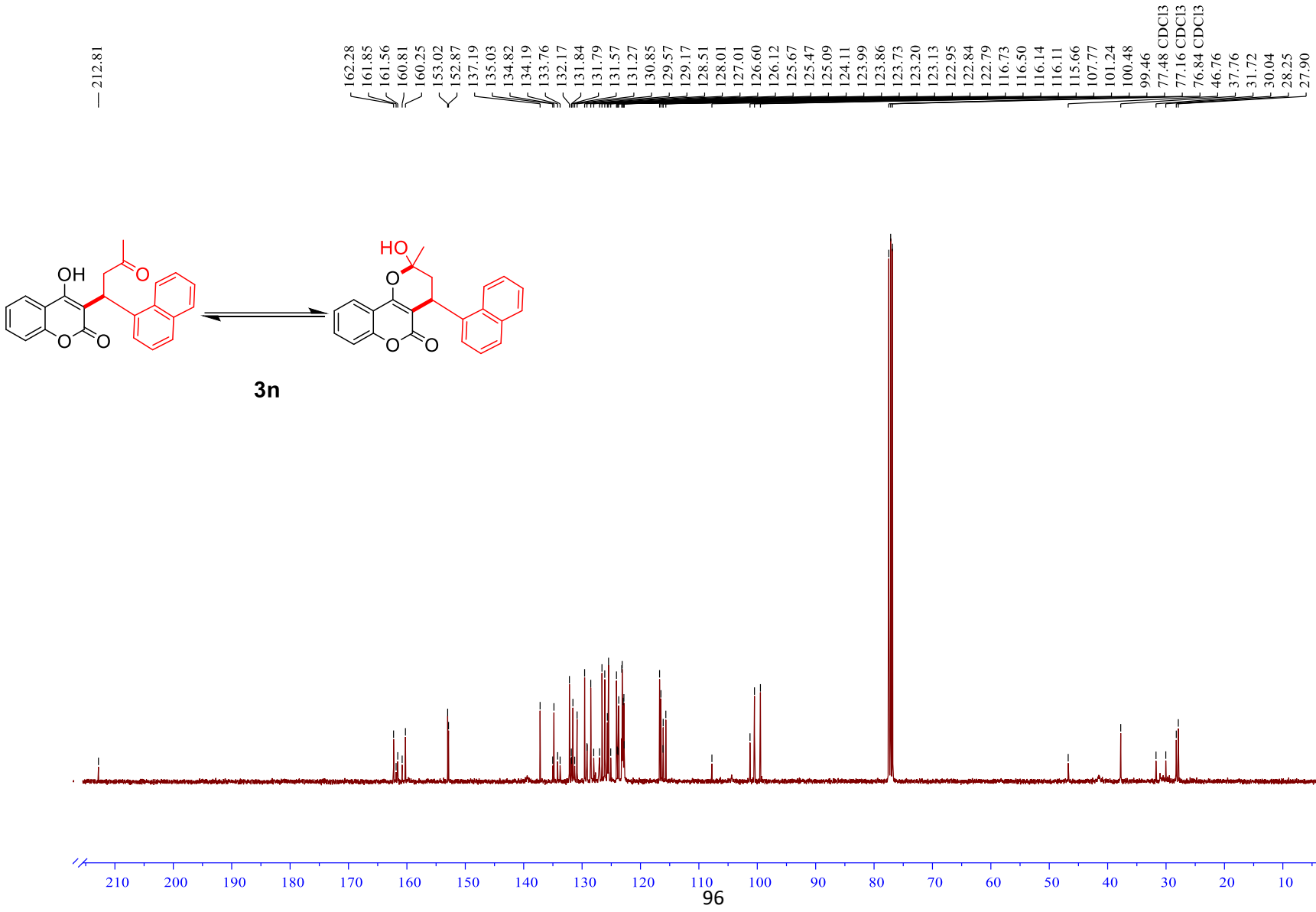
0.85
0.92
1.04
0.67
0.73
0.74
6.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

**3n**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HO
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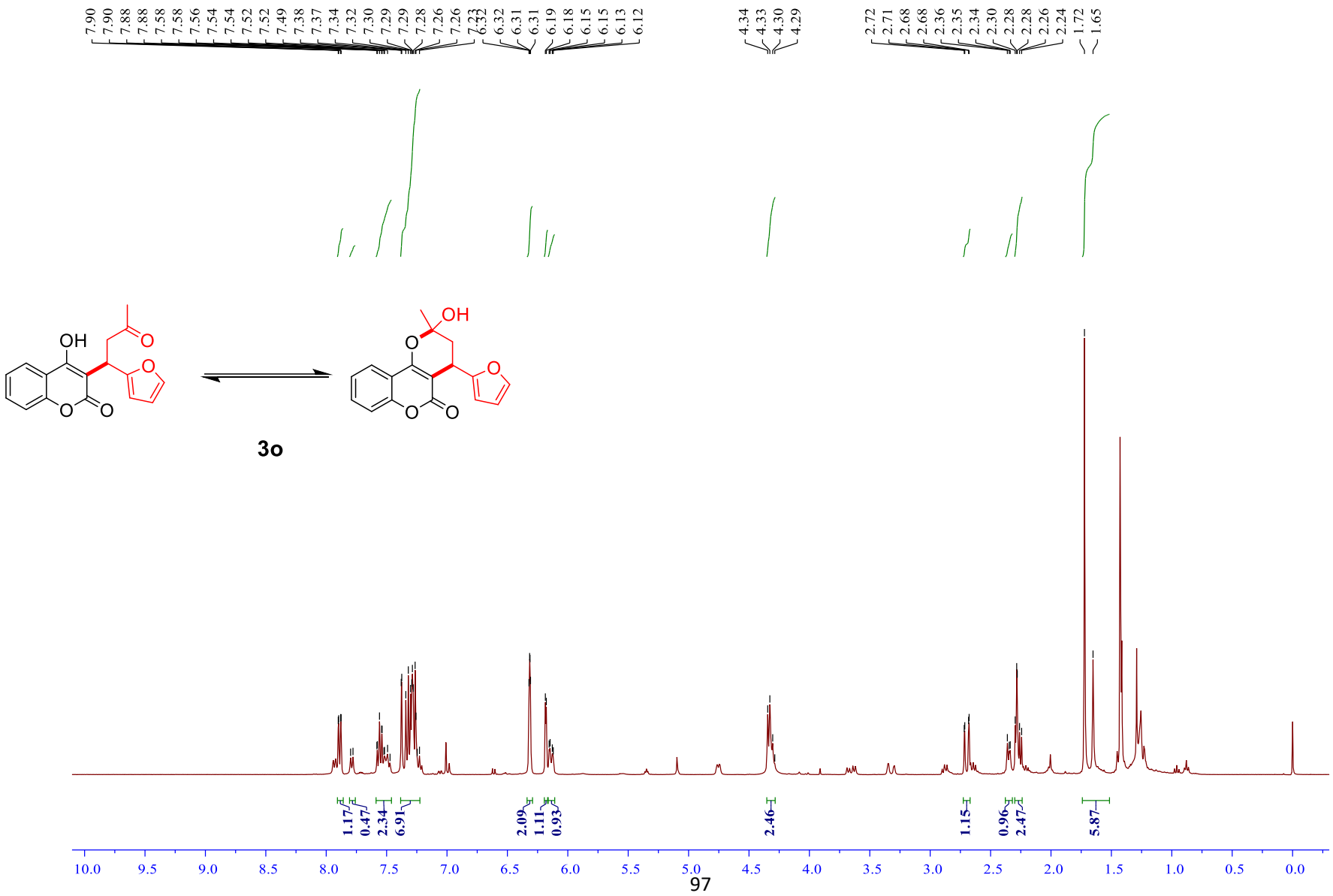
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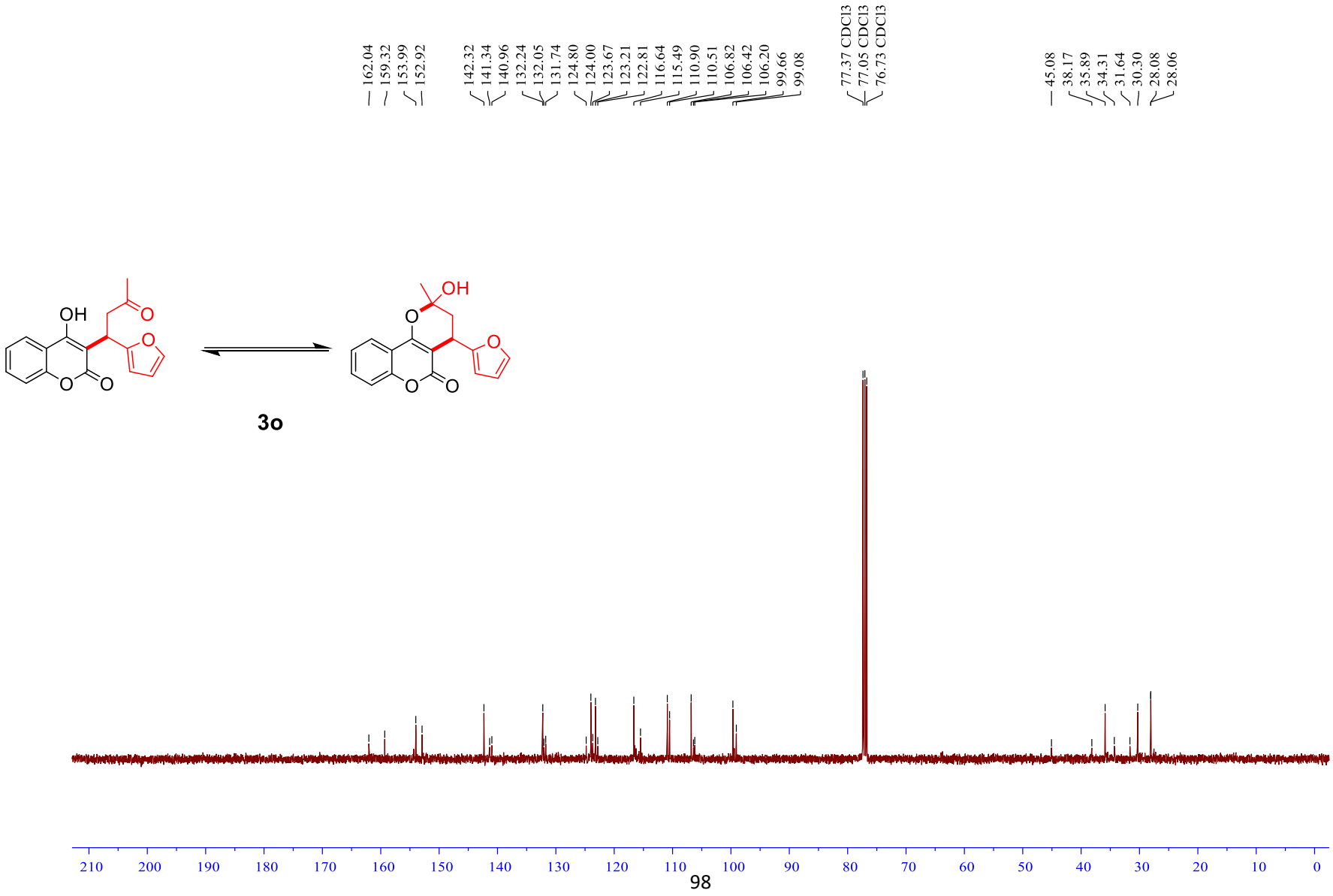
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99.08
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77.05 CDCl3
76.73 CDCl3
45.08
38.17
35.89
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31.64
30.30
28.08
28.06
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O
O
O
OH
O
O
O
O
3o
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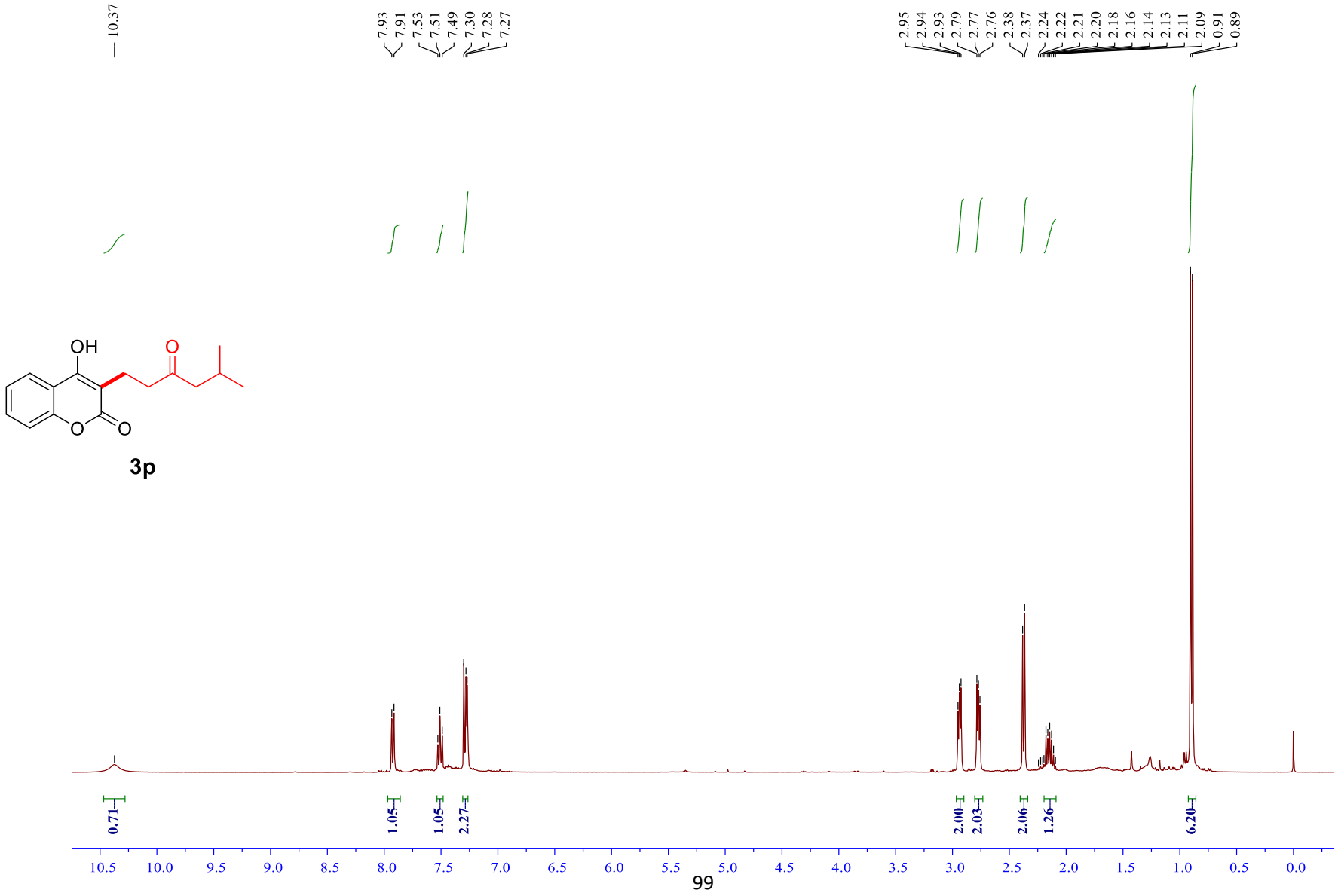
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2.11
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9.0
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6.5
6.0
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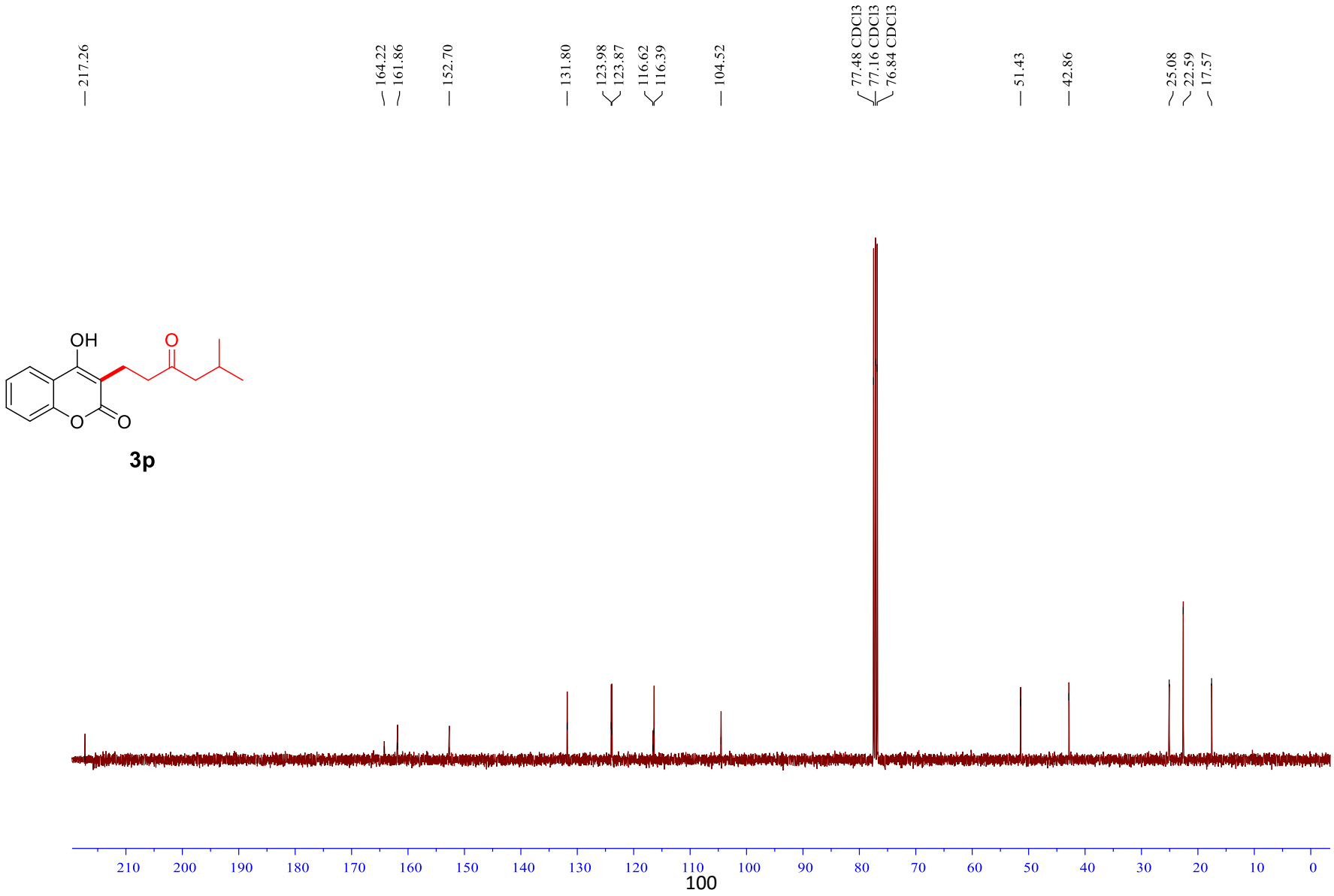
**3p**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77.16 CDCl3
76.84 CDCl3
51.43
42.86
25.08
22.59
17.57
OH
O
O
O
3p
210
200
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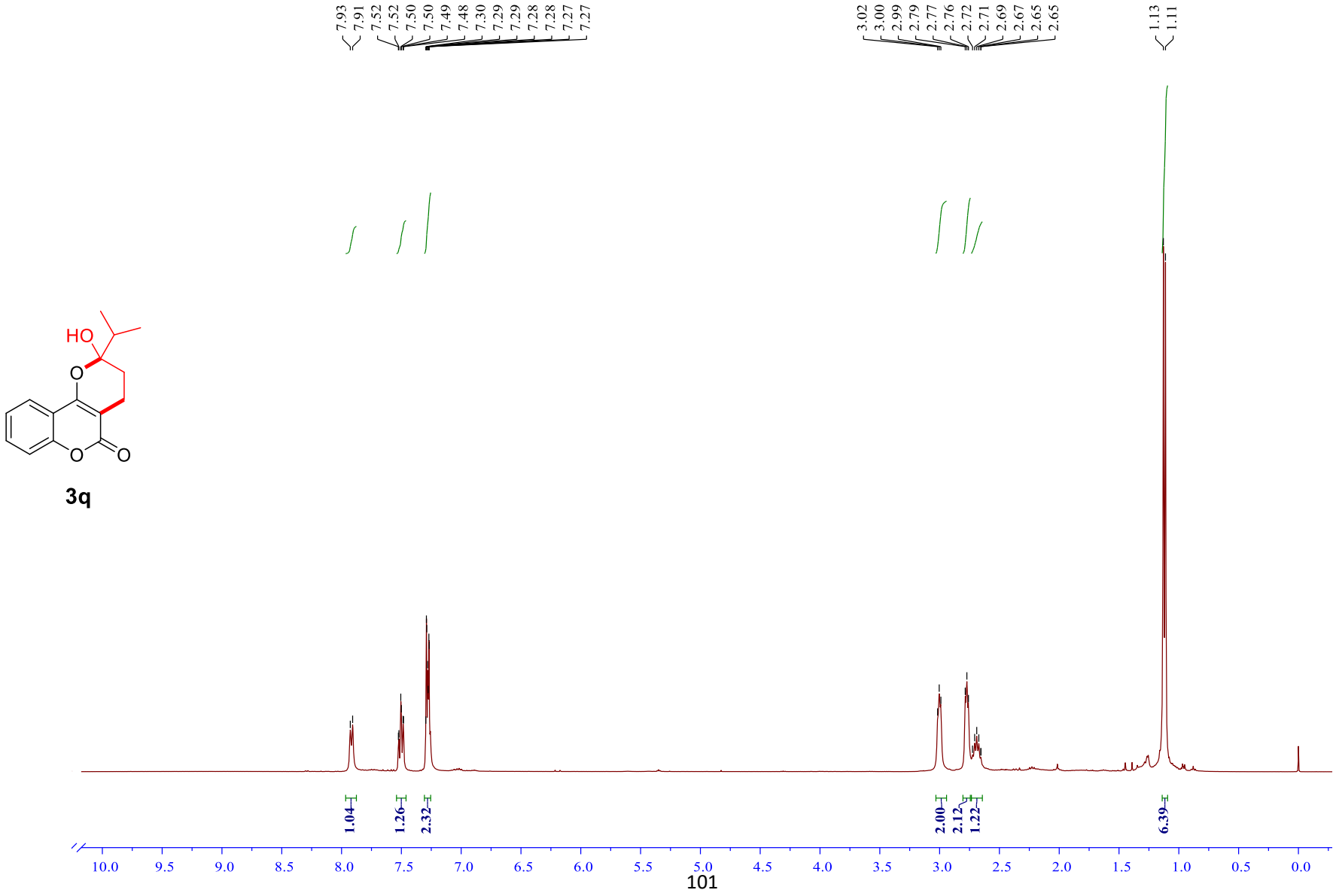
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O
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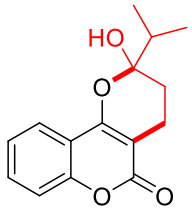
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**3q**


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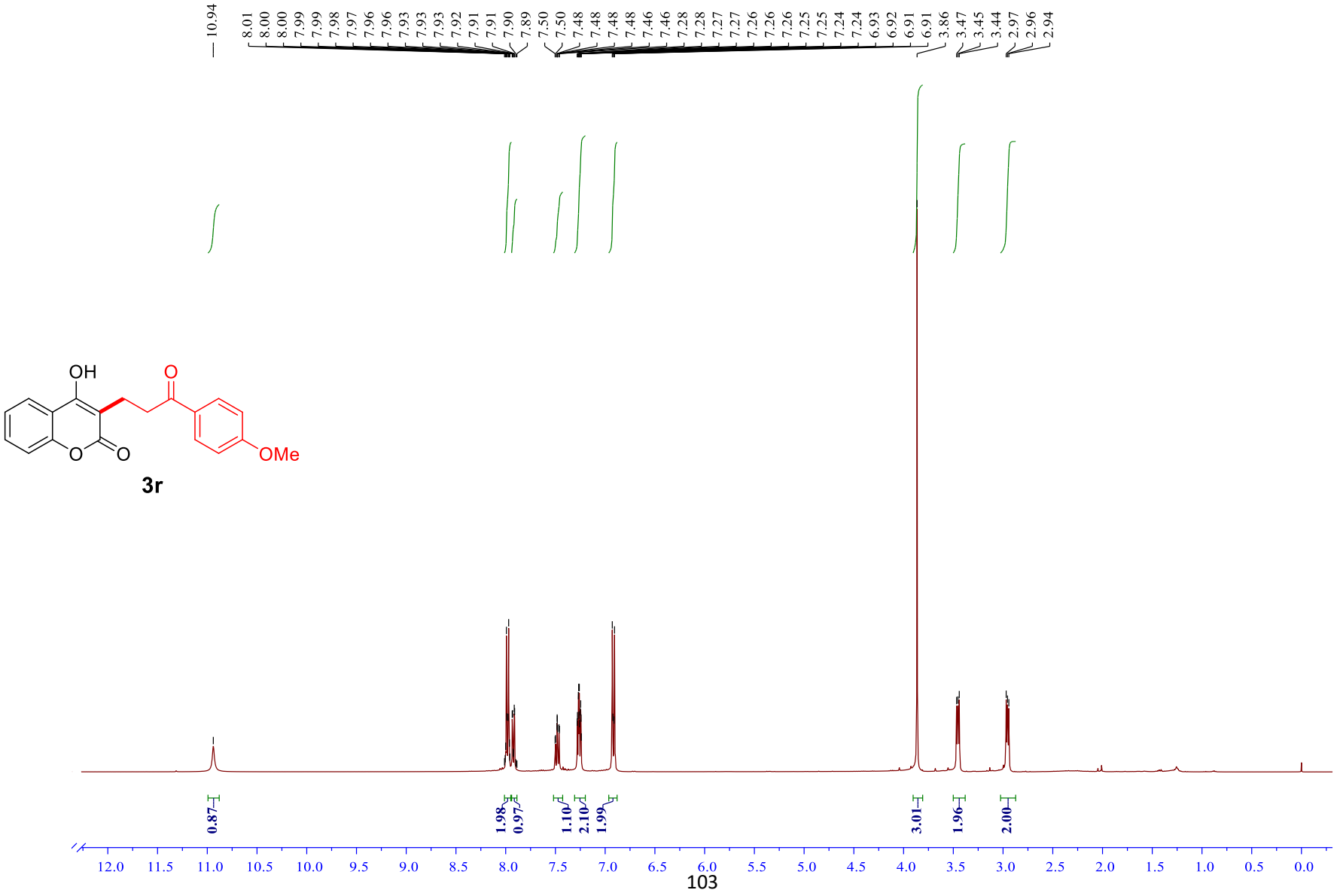
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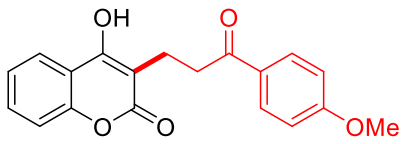
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OMe

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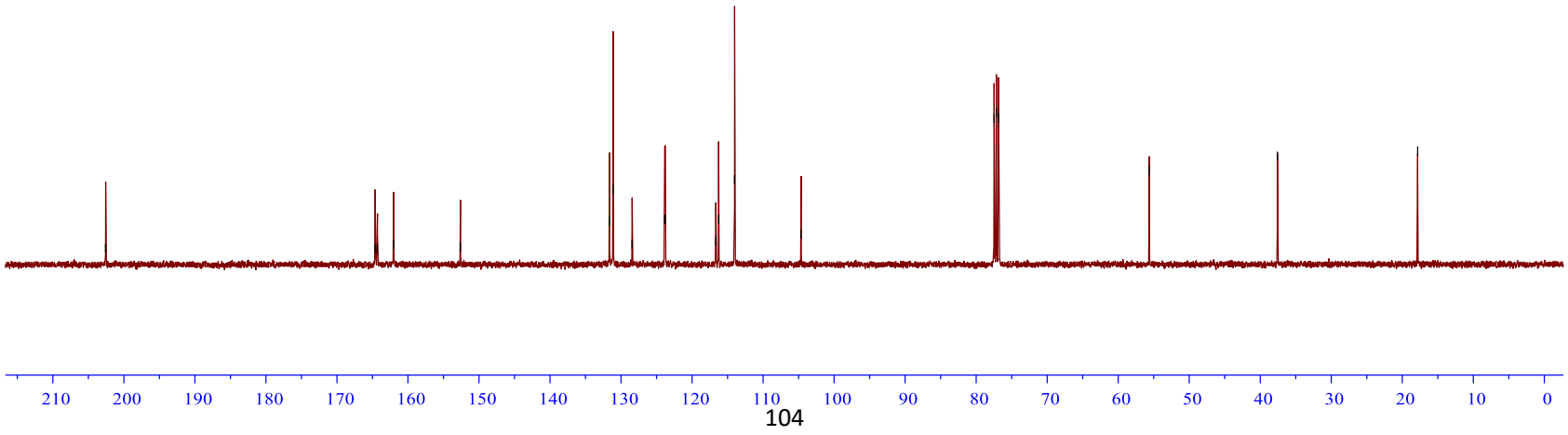
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77.16 CDCl3
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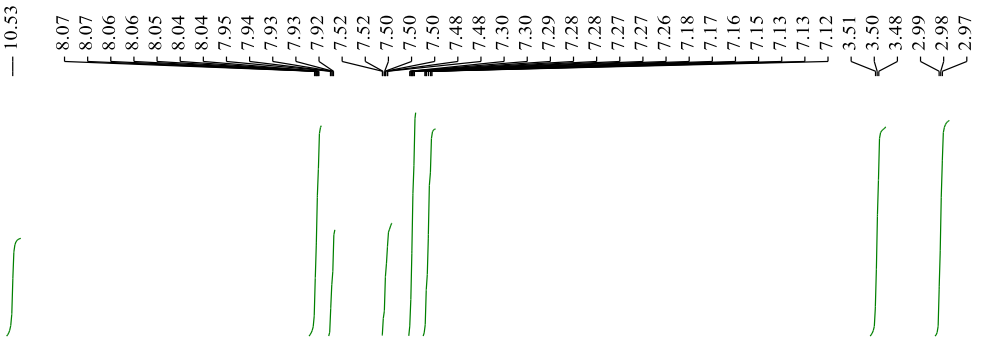
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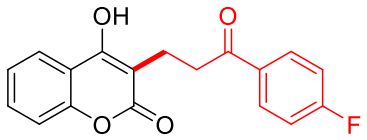
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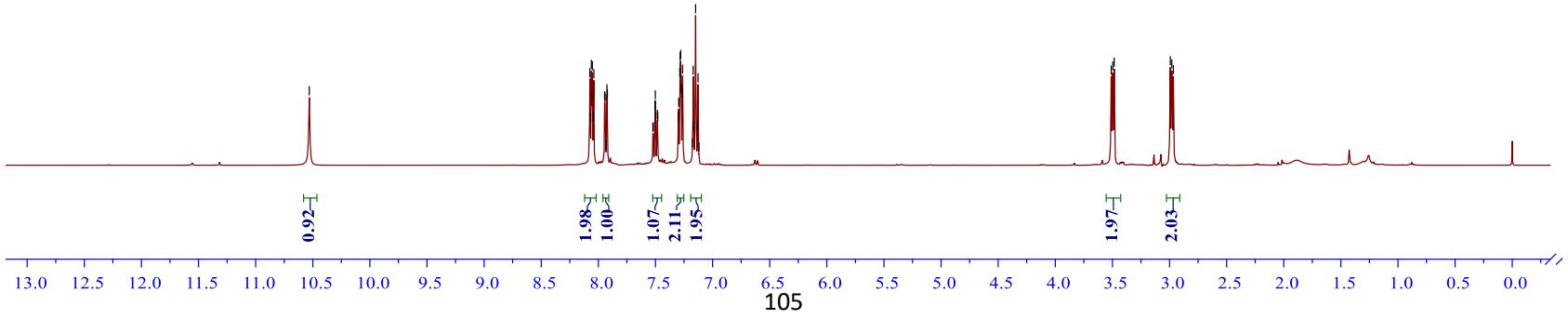
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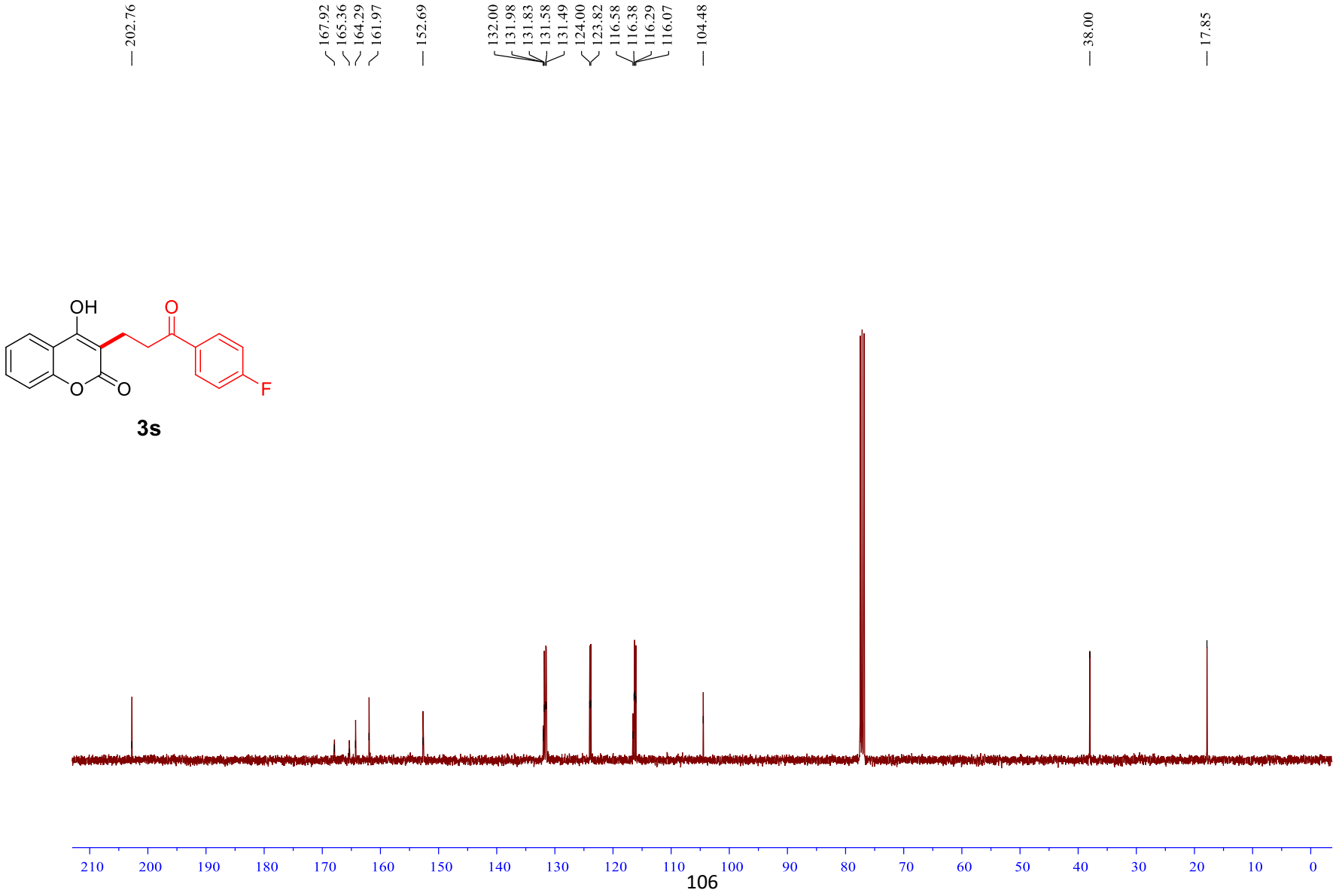
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O
O
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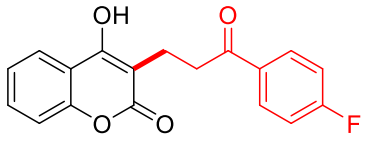
**3s**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**3s**


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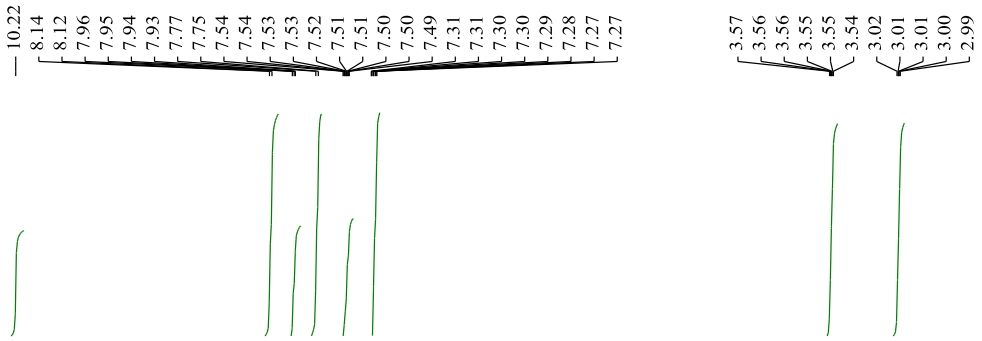
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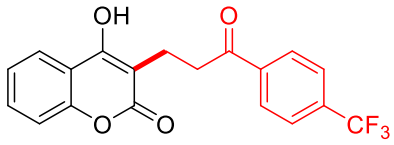
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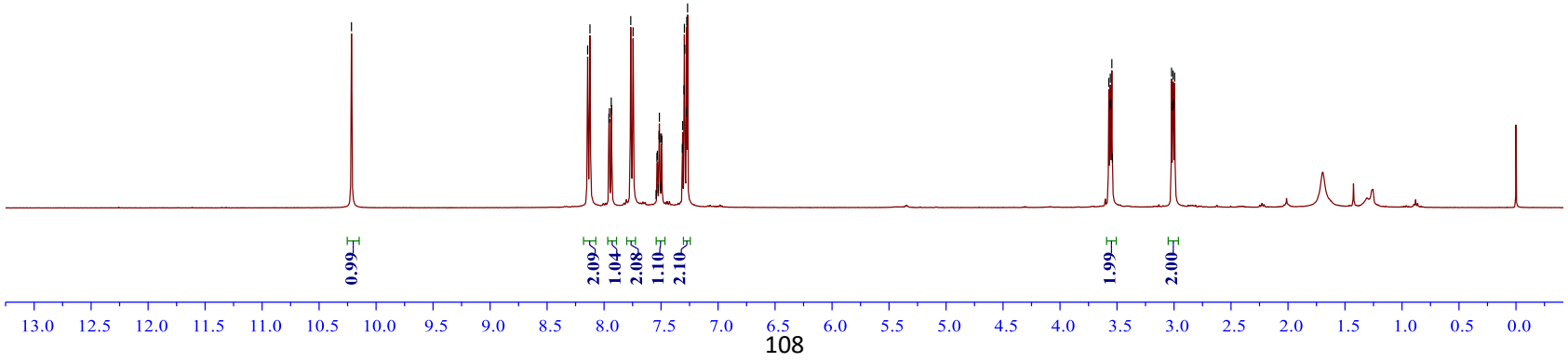
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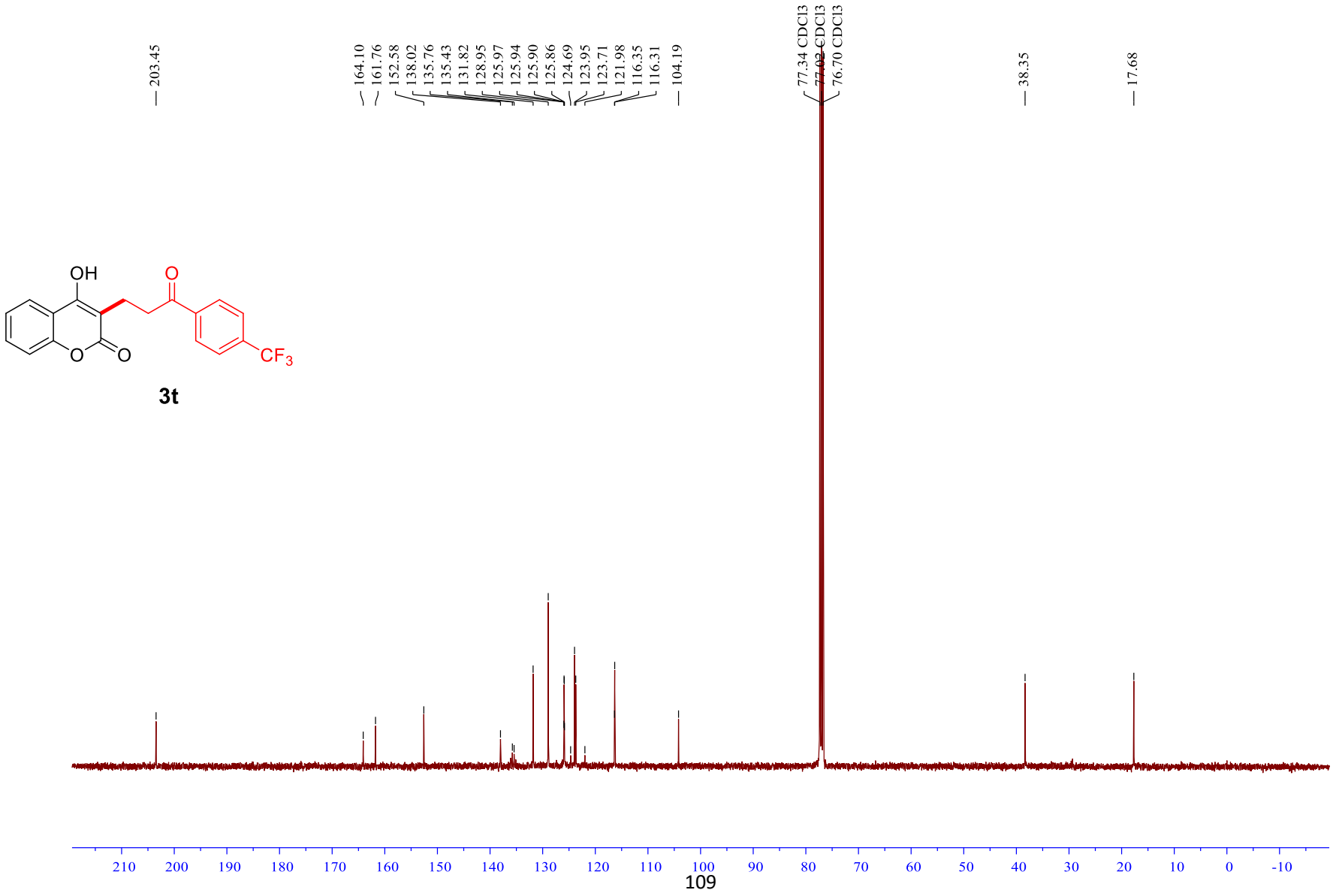
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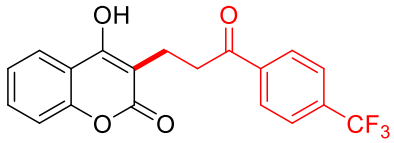
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**3t**


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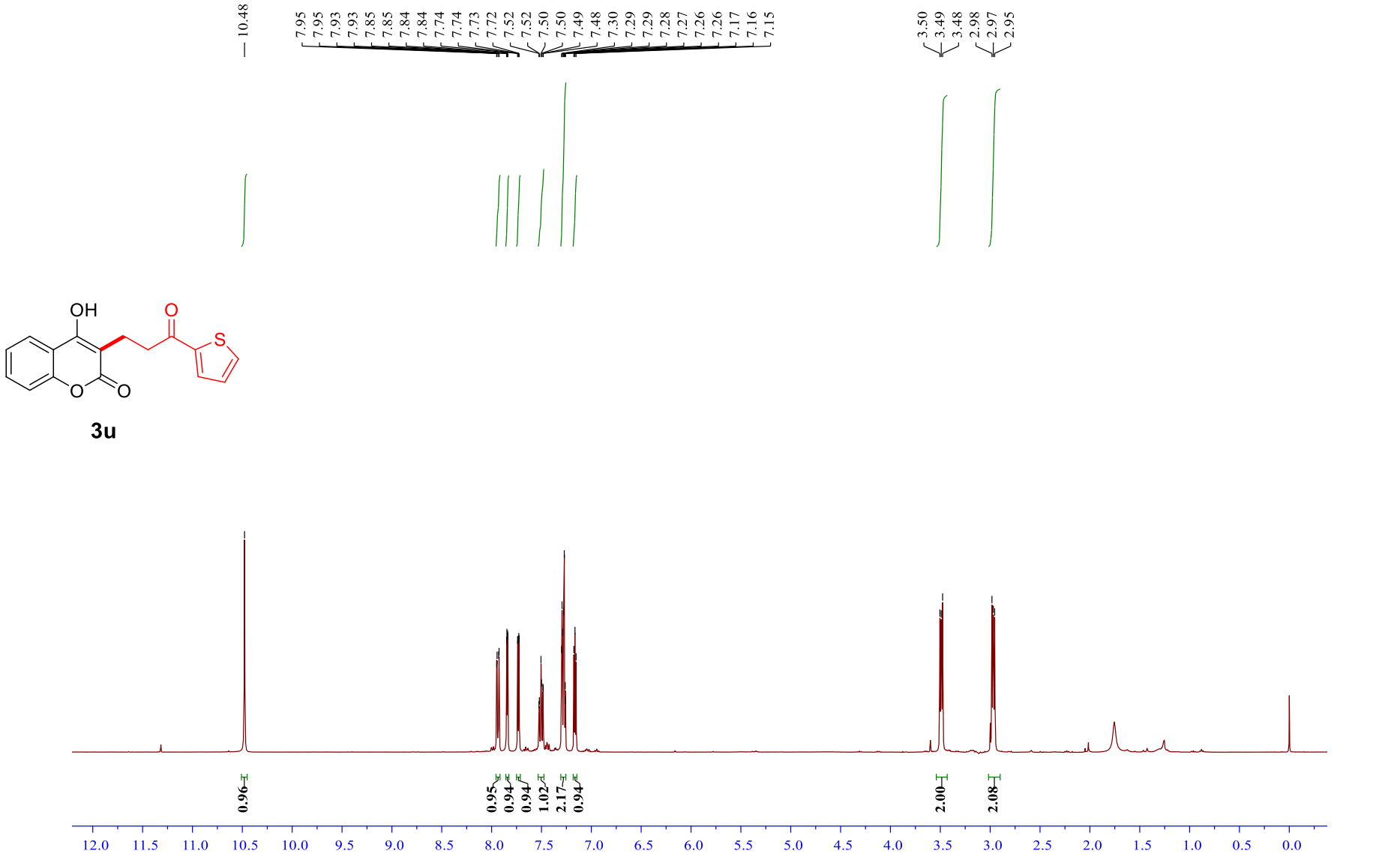
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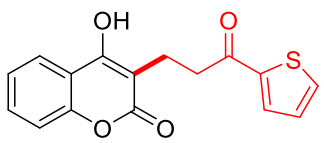
**3u**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**3u**


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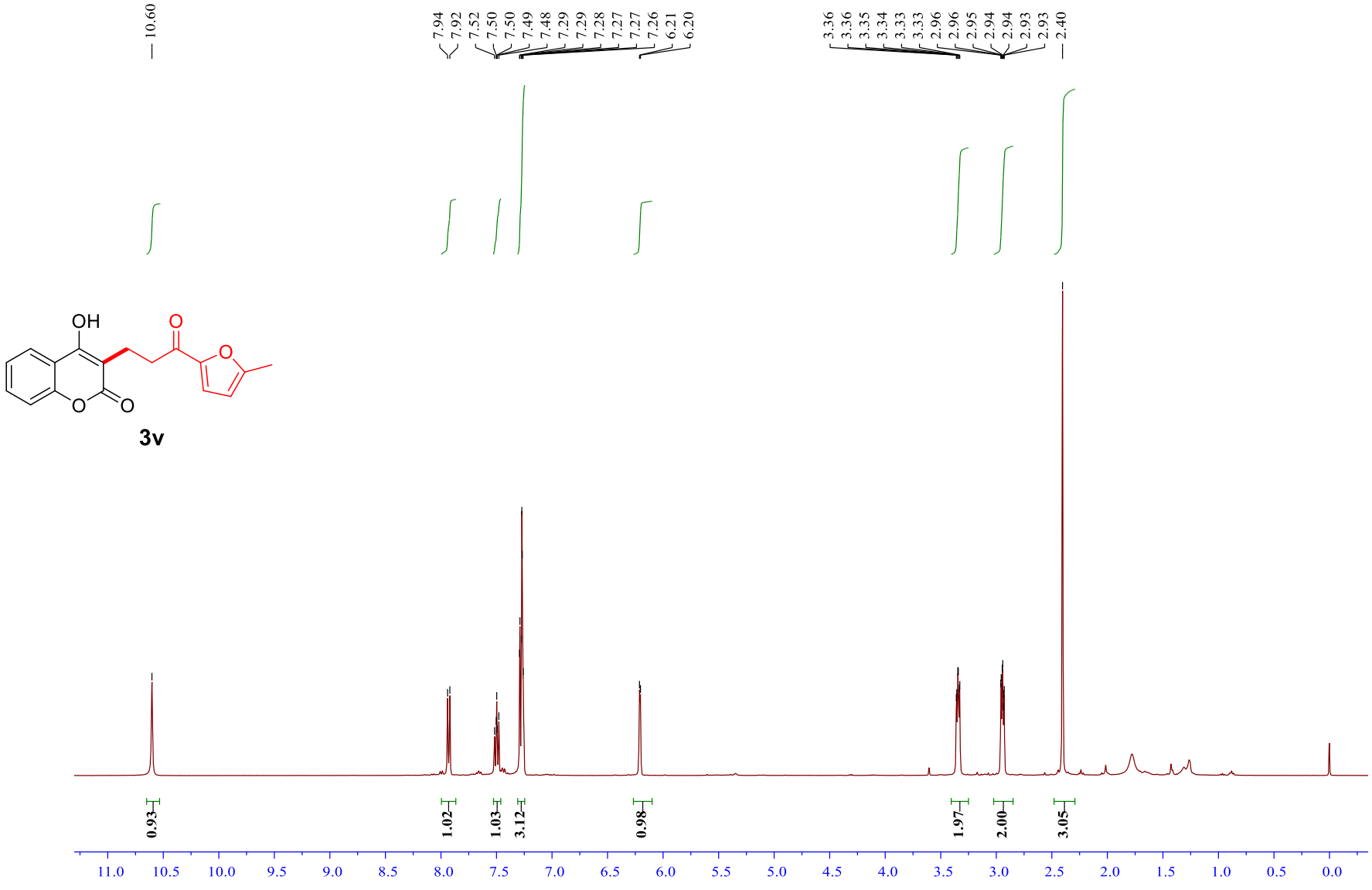
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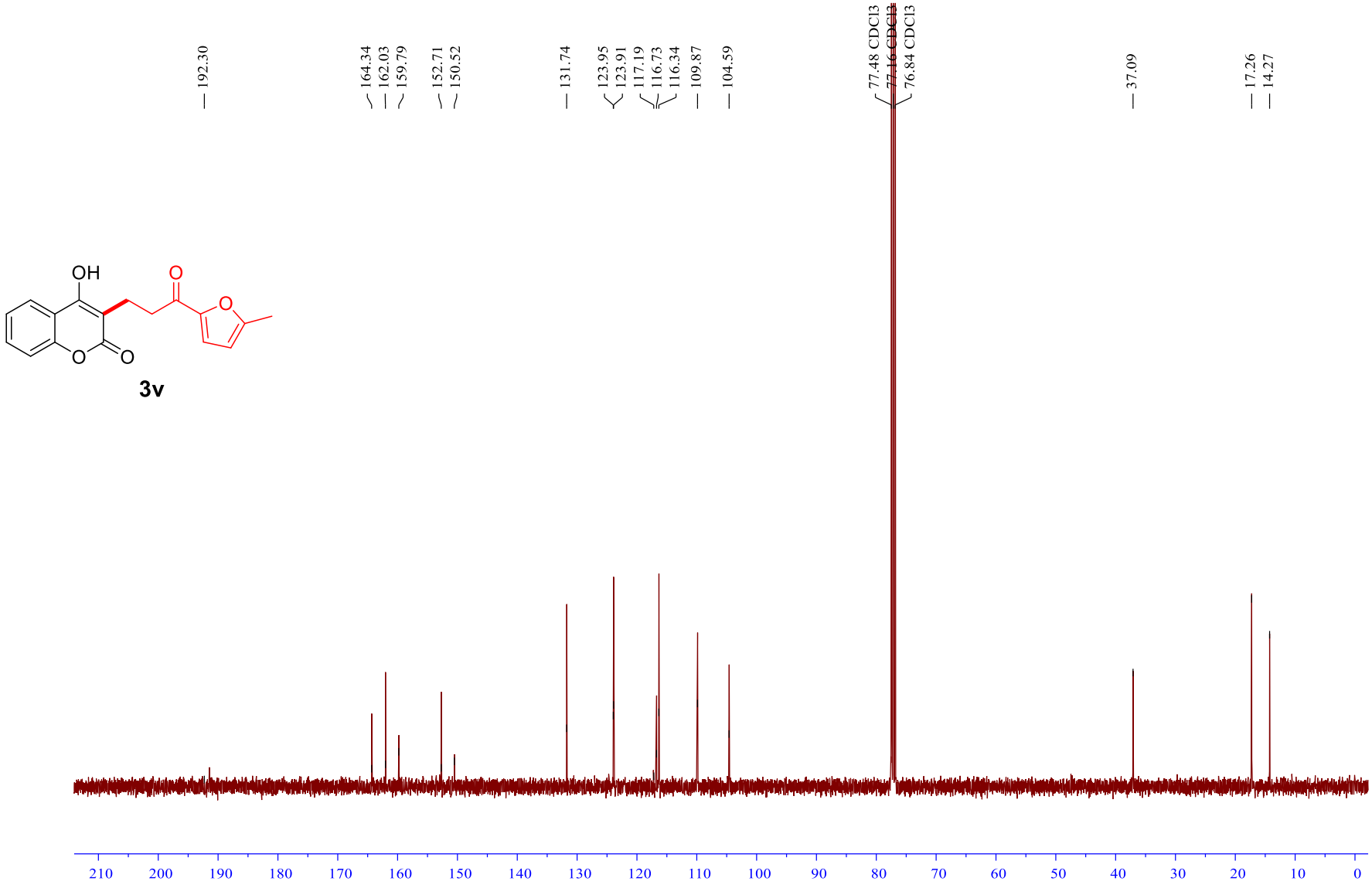
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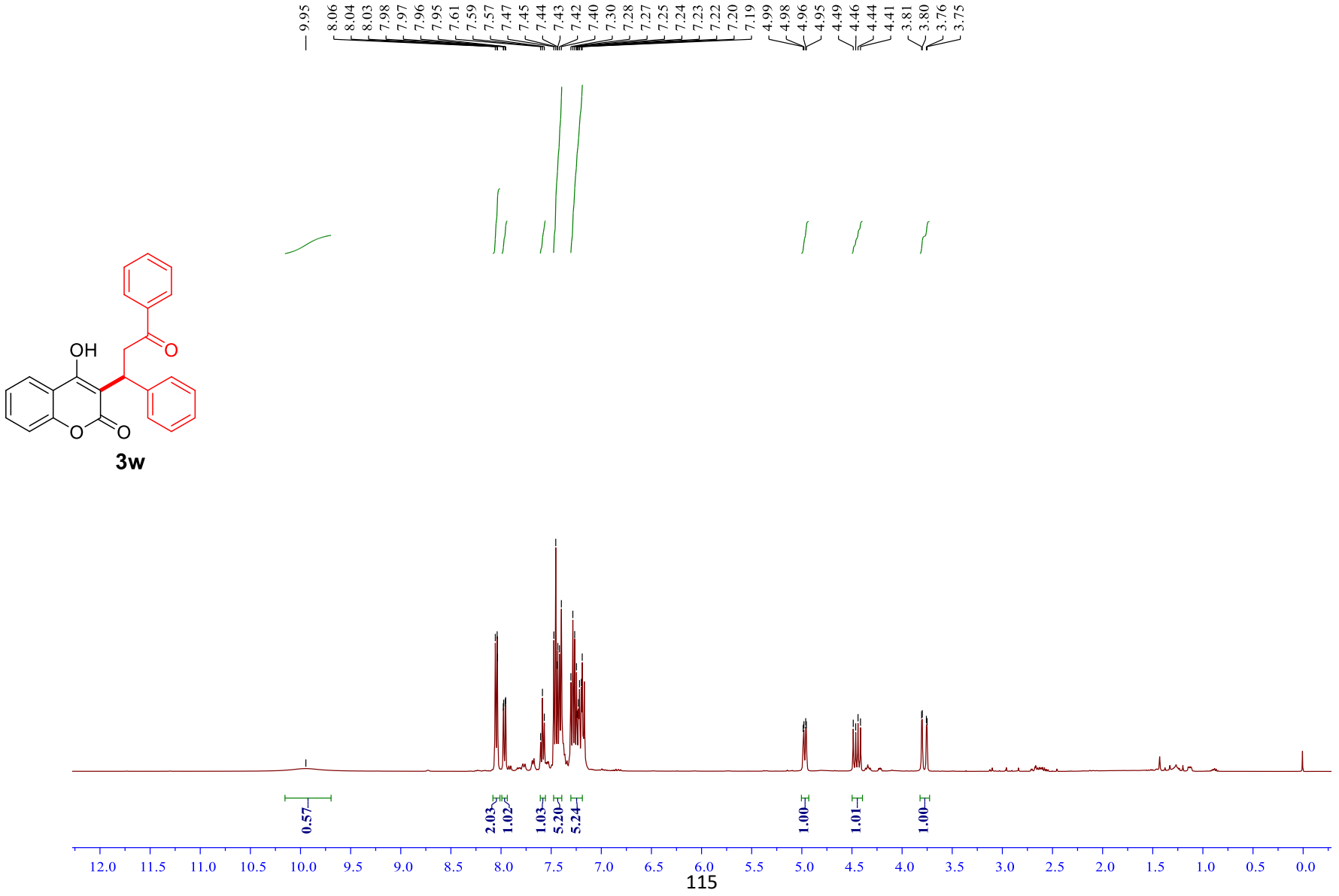
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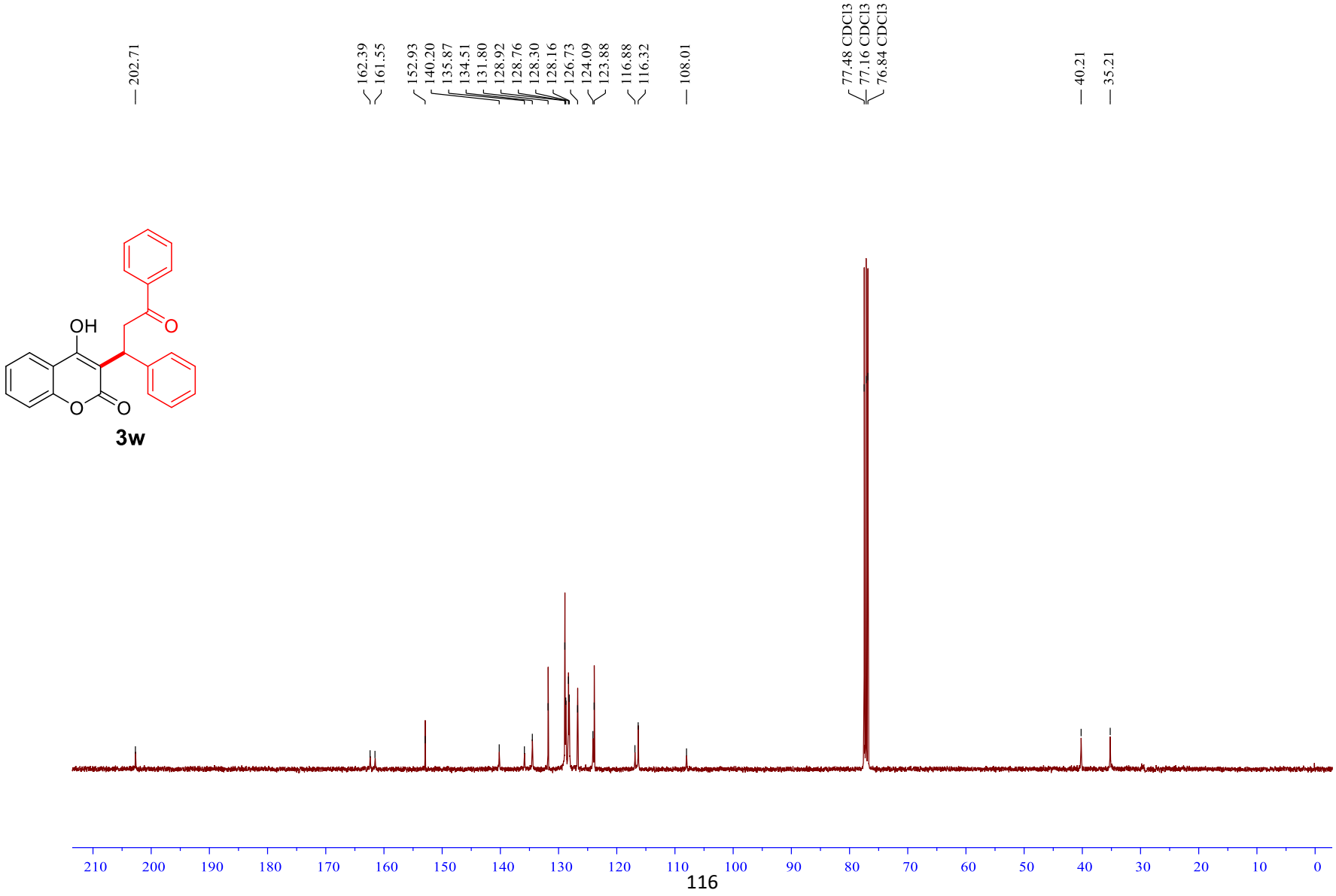
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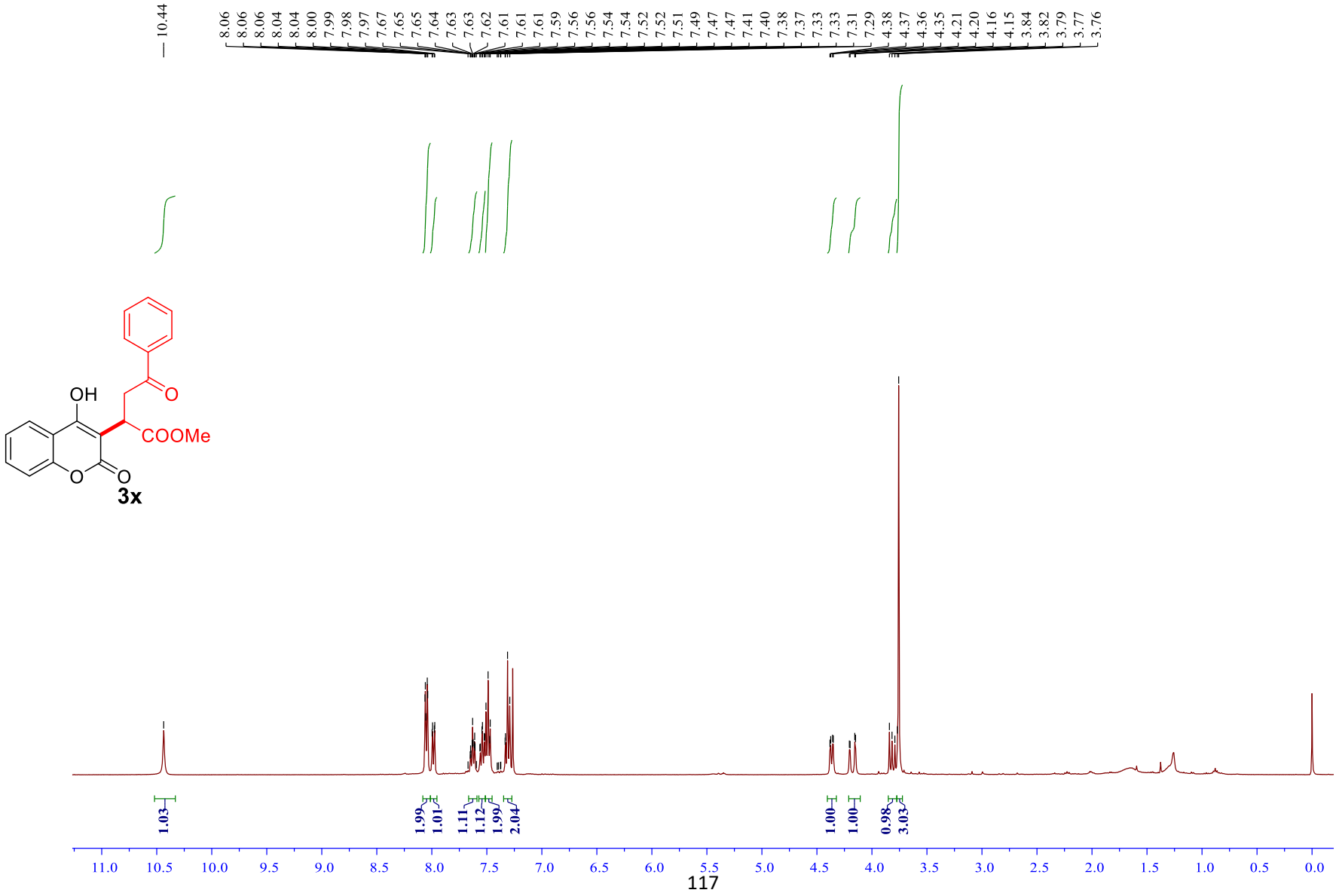
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COOMe
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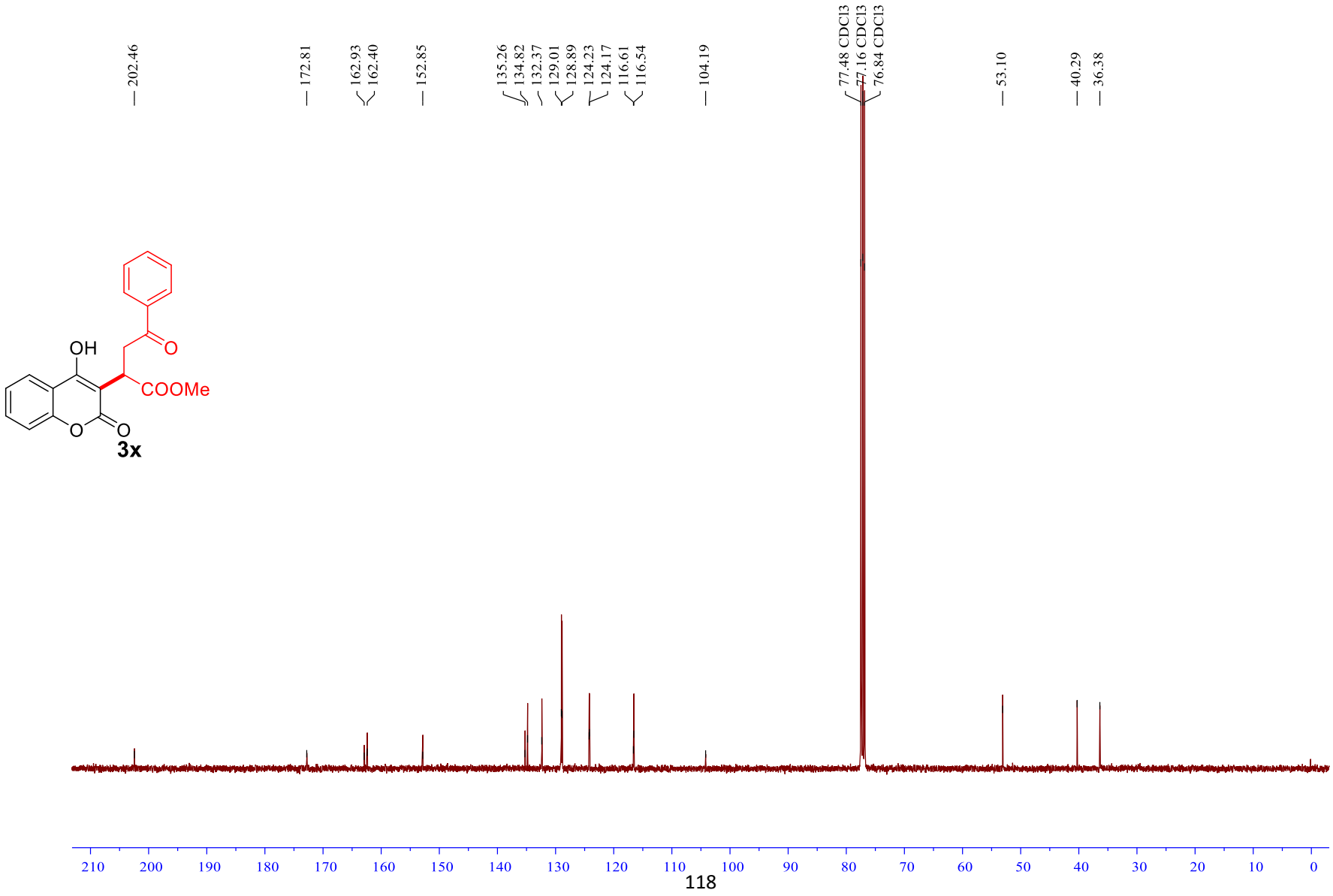
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COOMe
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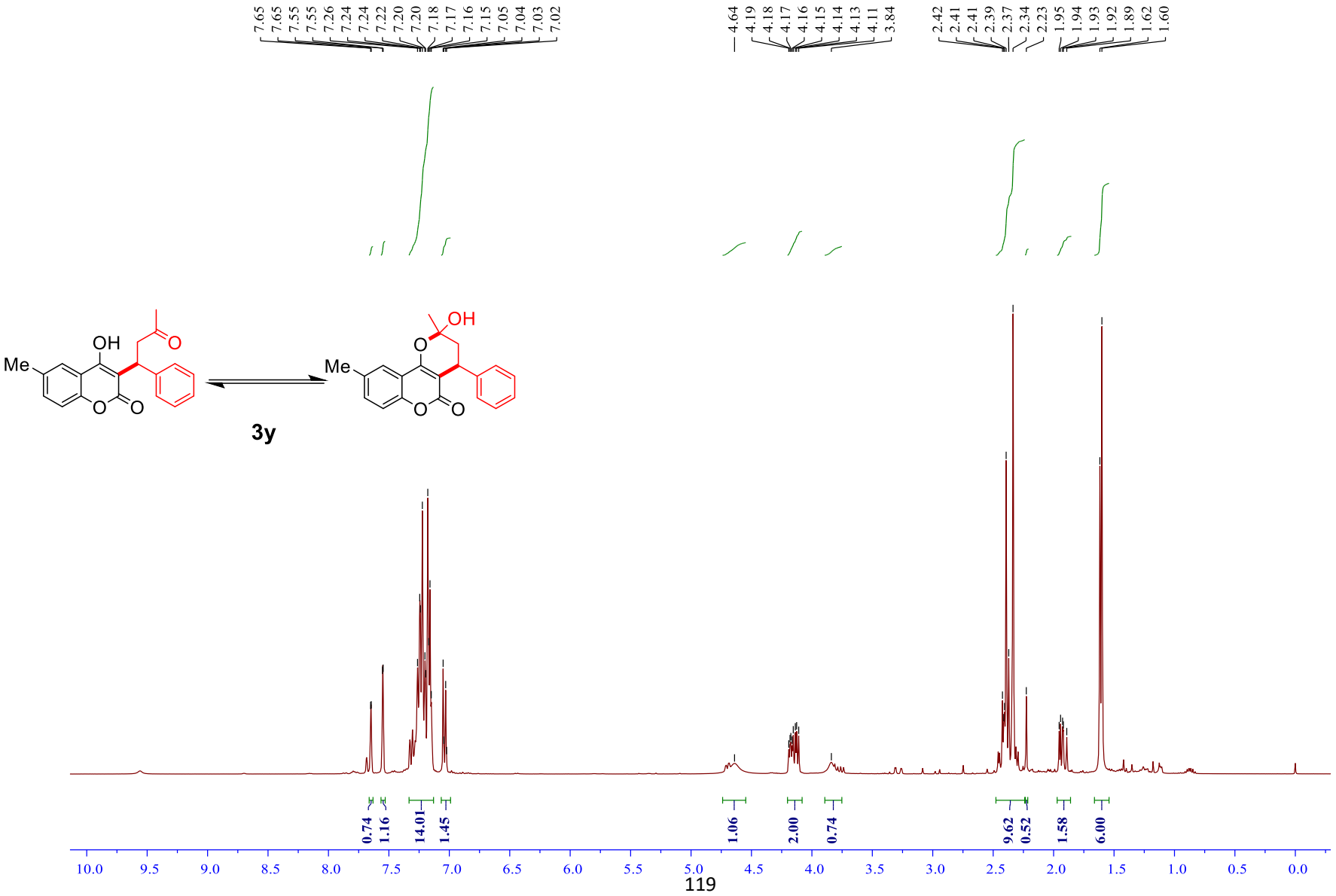
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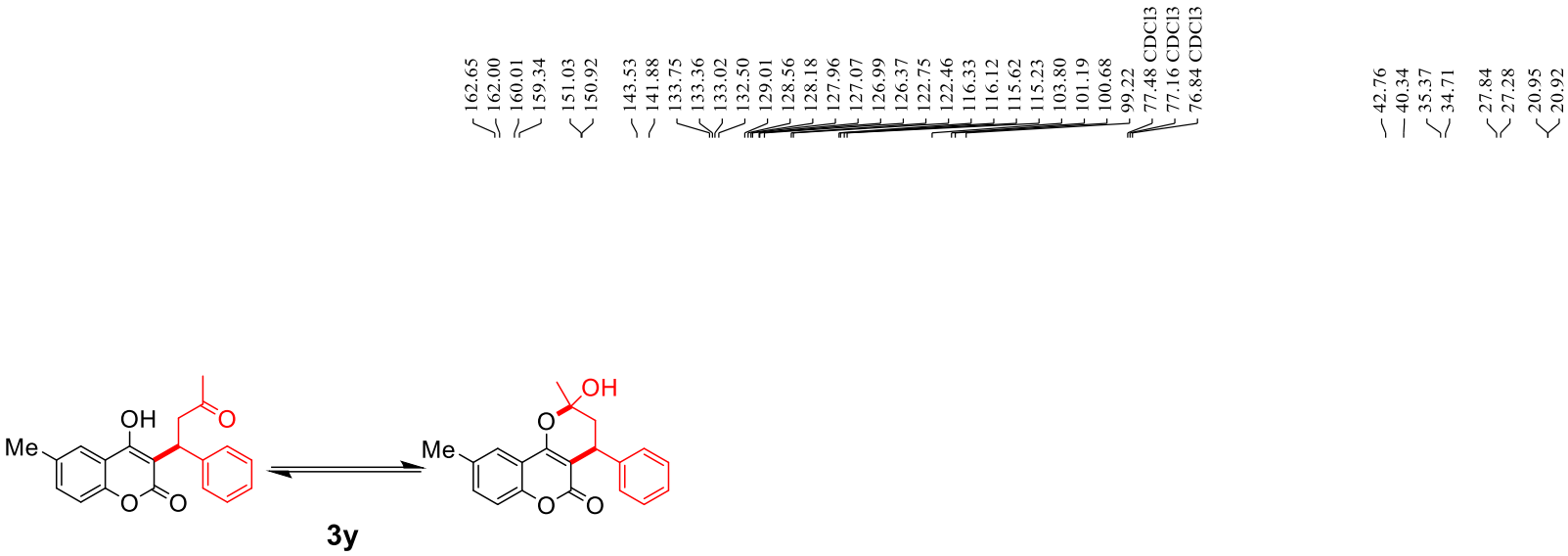
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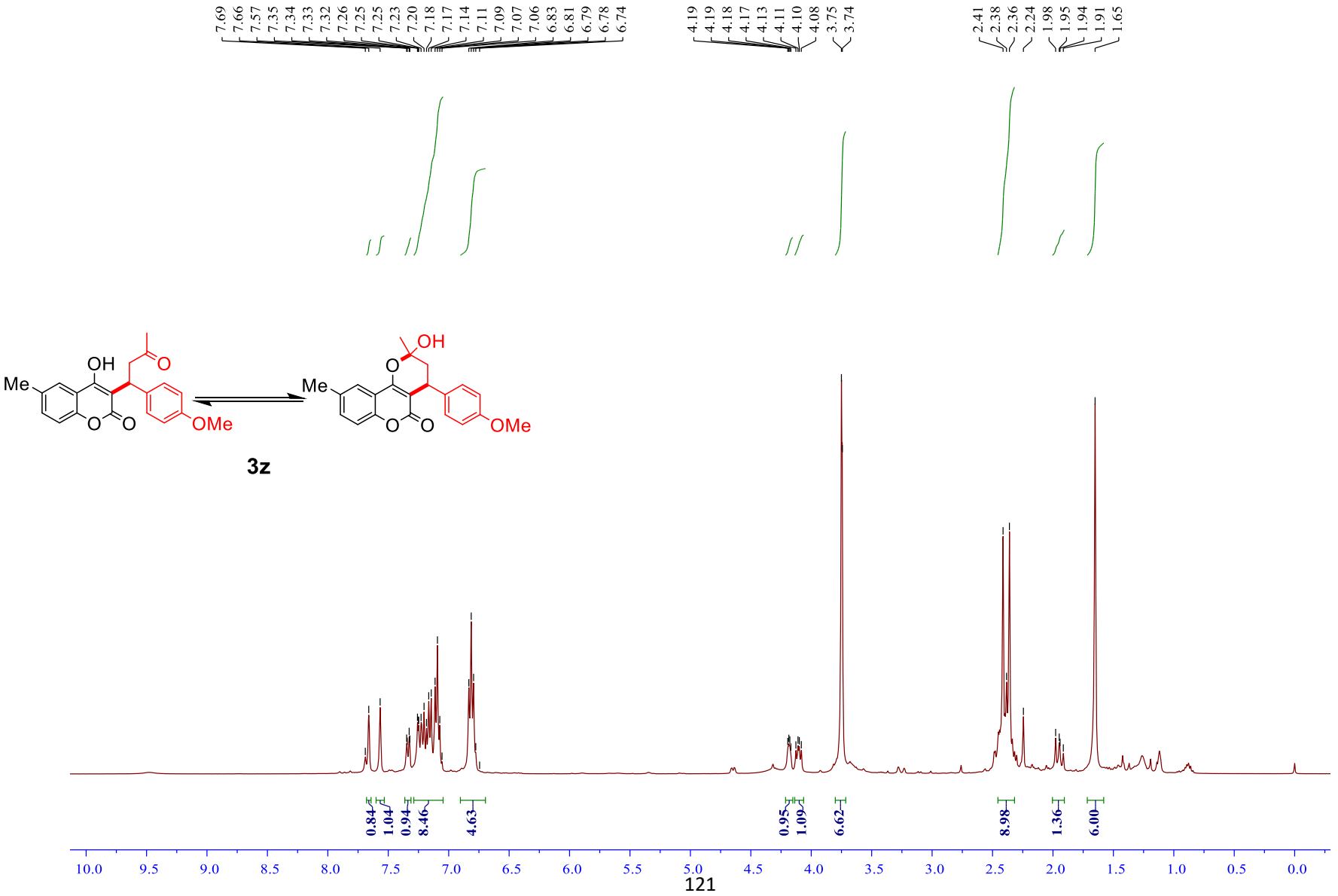
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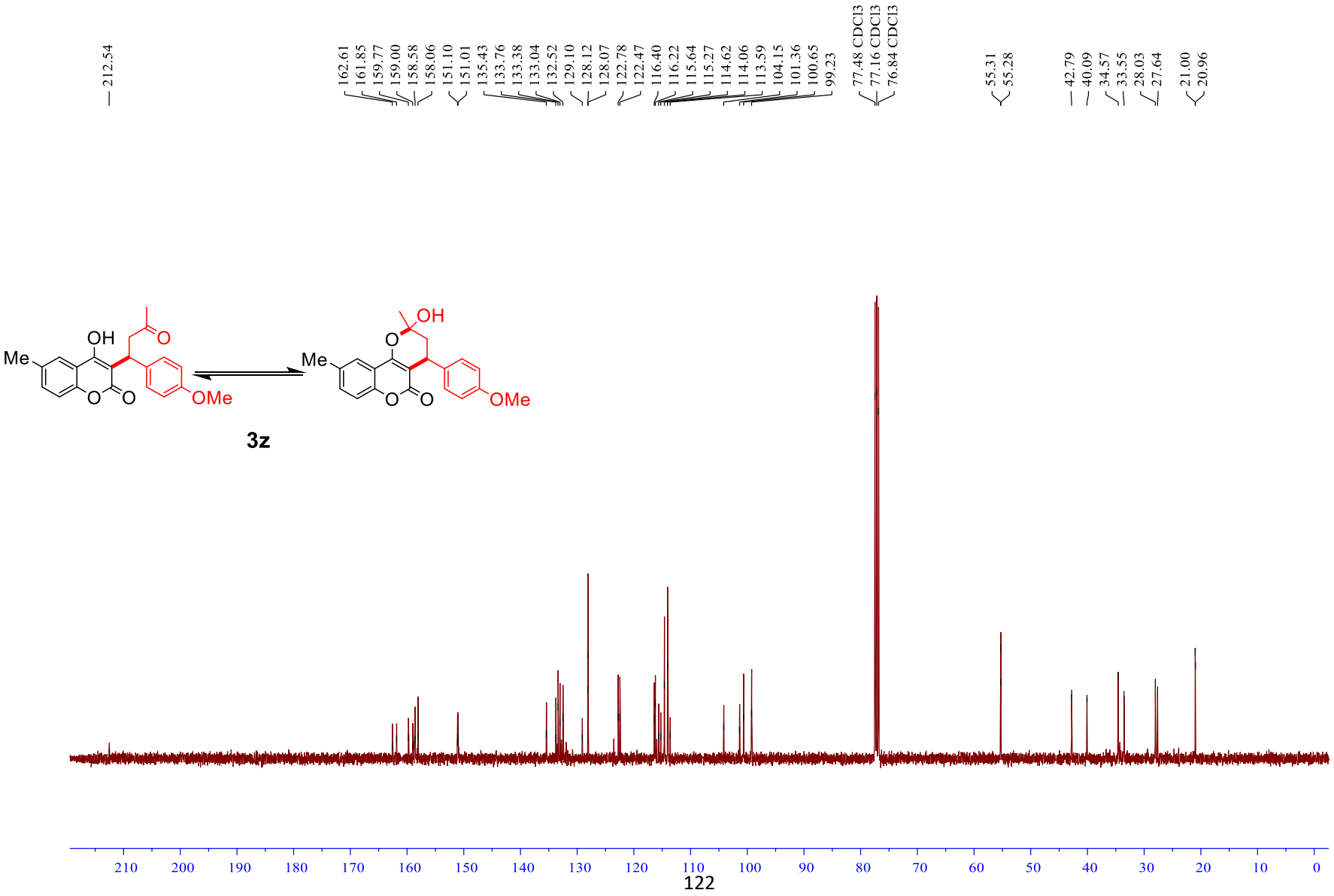
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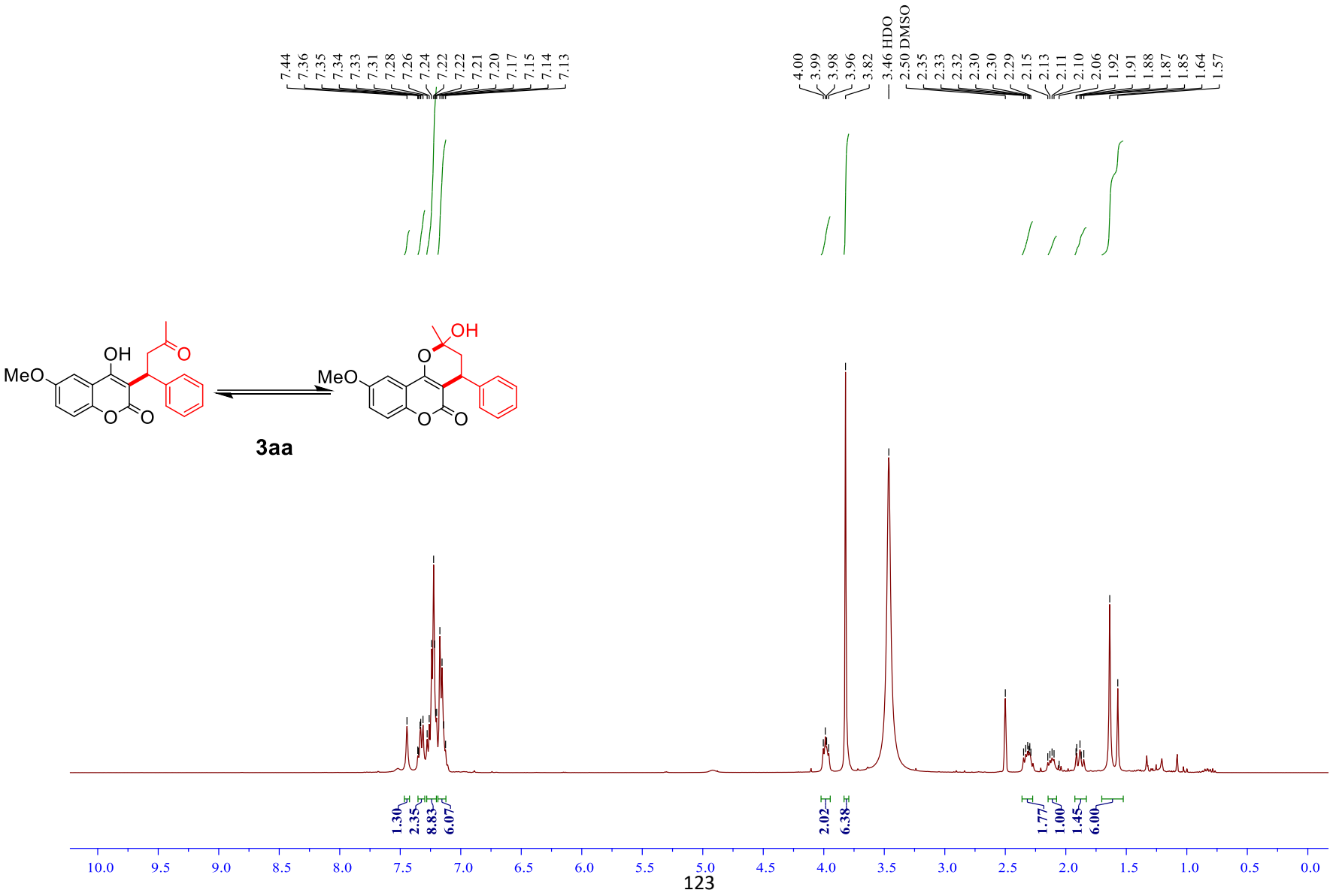
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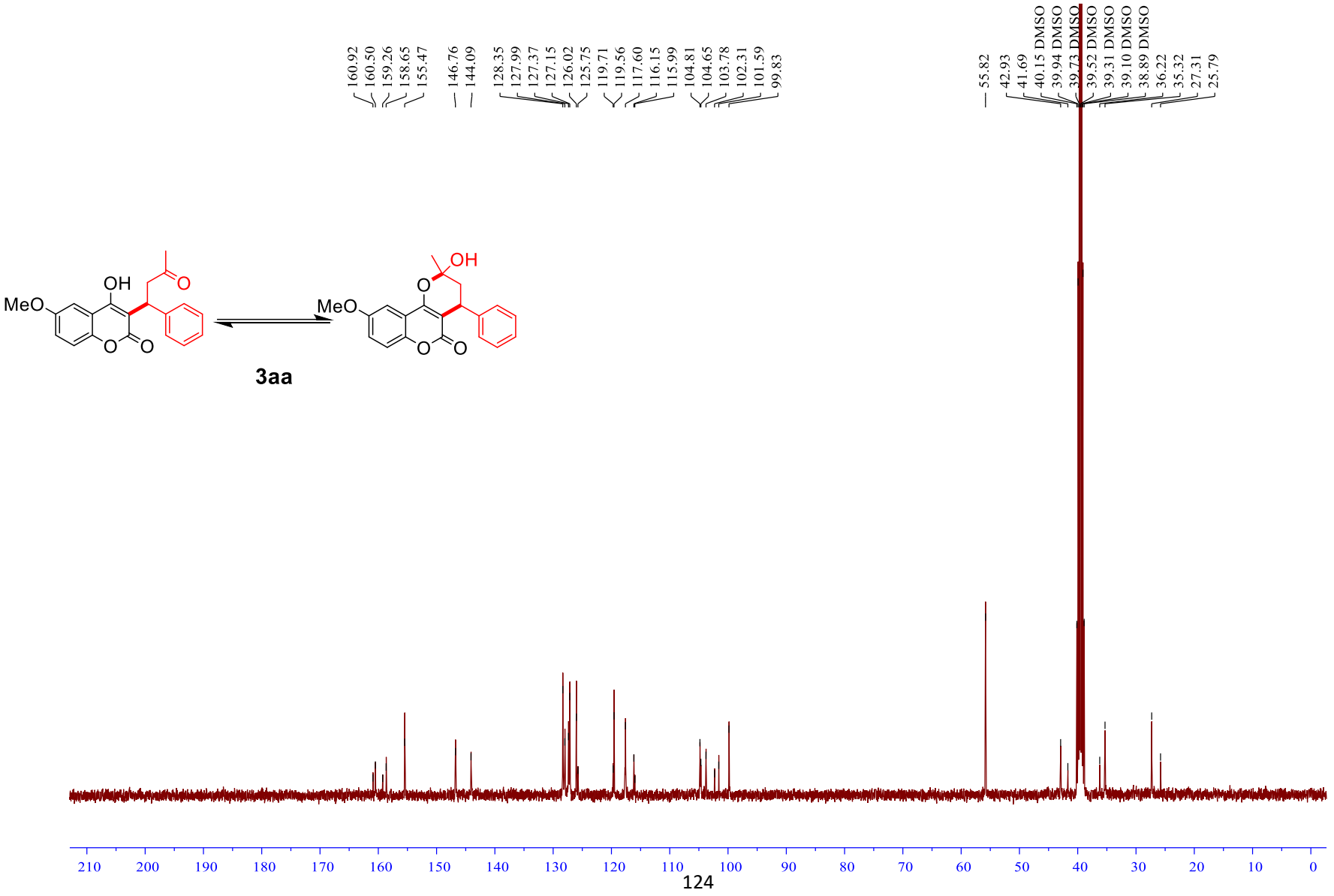
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39.94 DMSO
39.73 DMSO
39.52 DMSO
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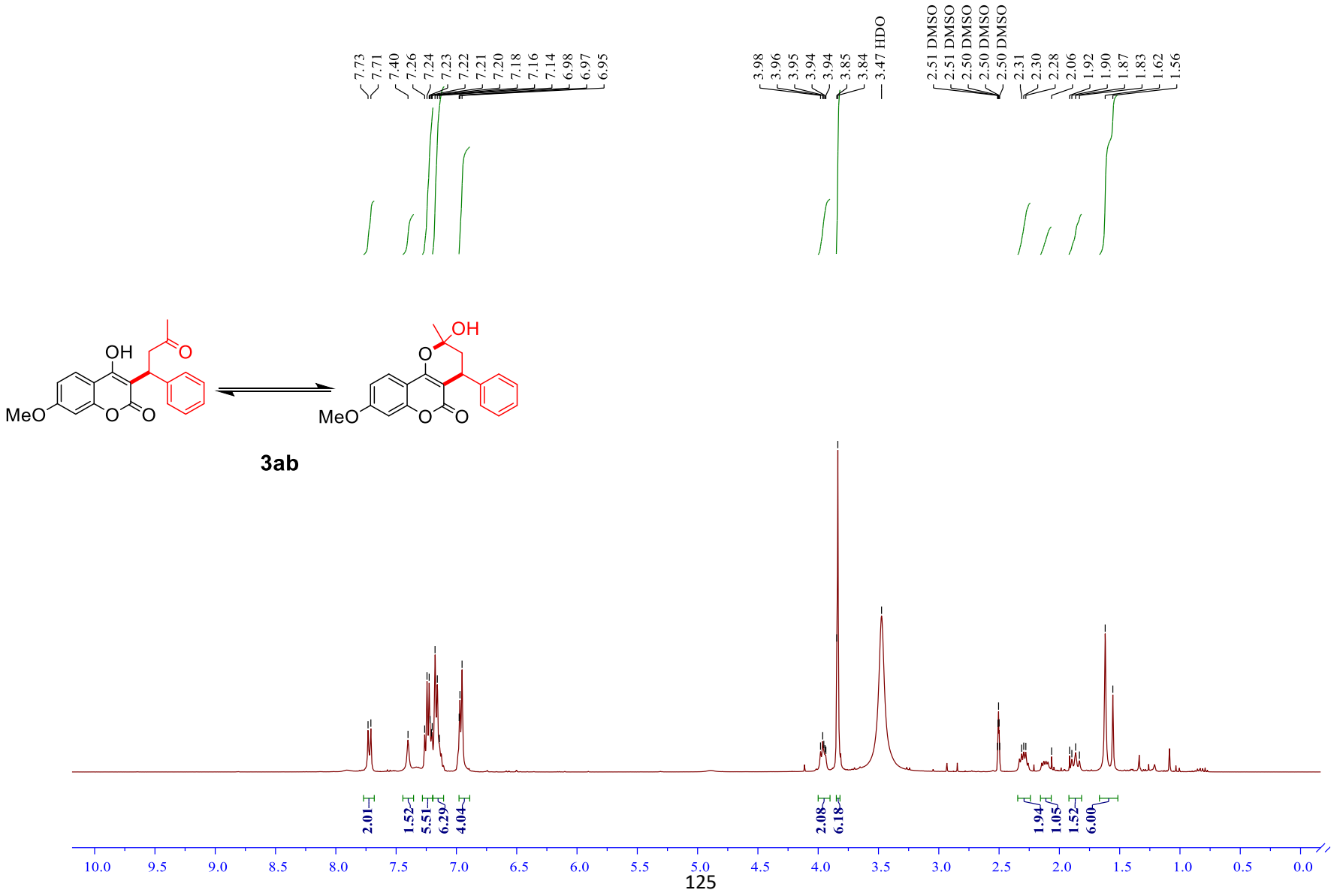
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3.94
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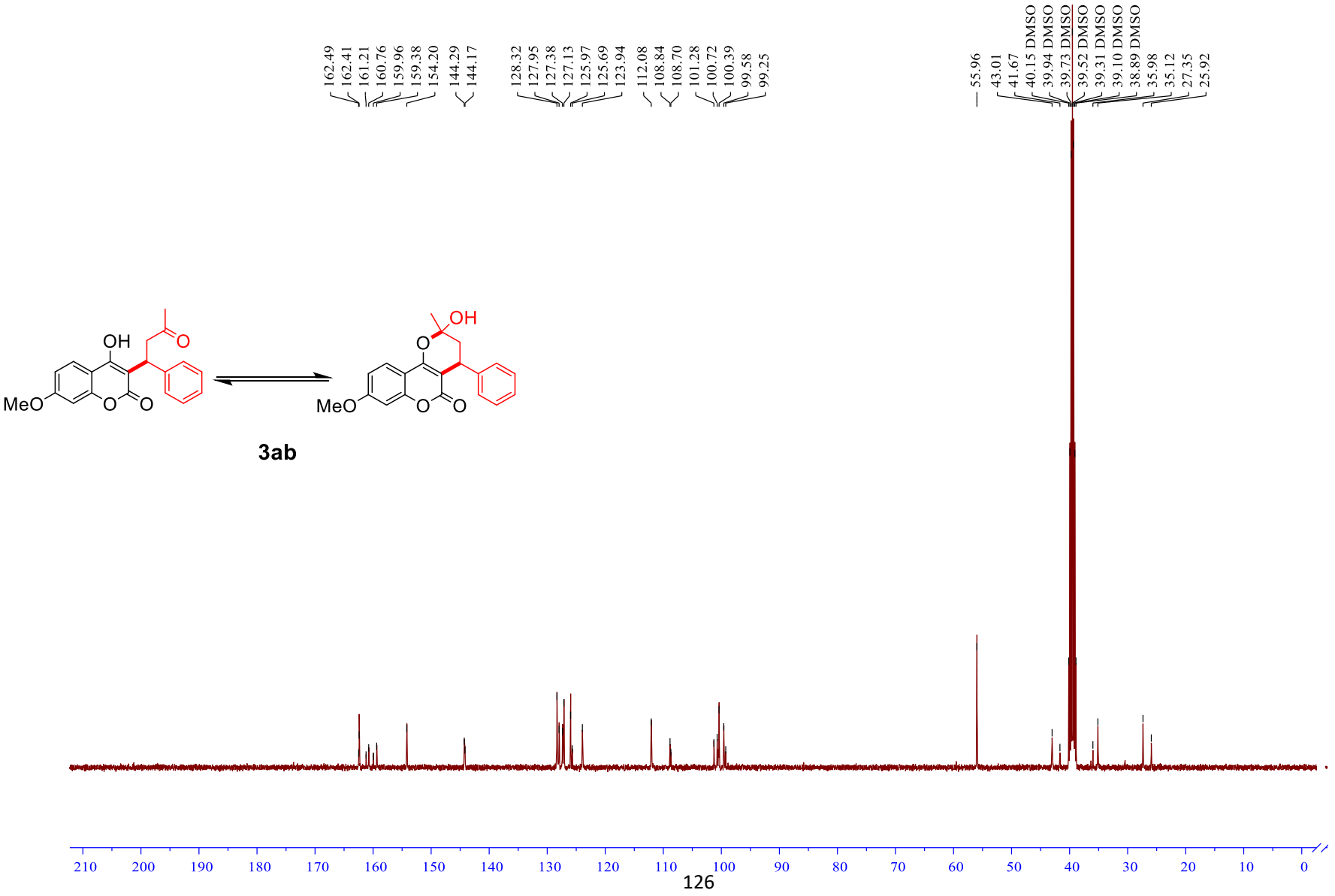
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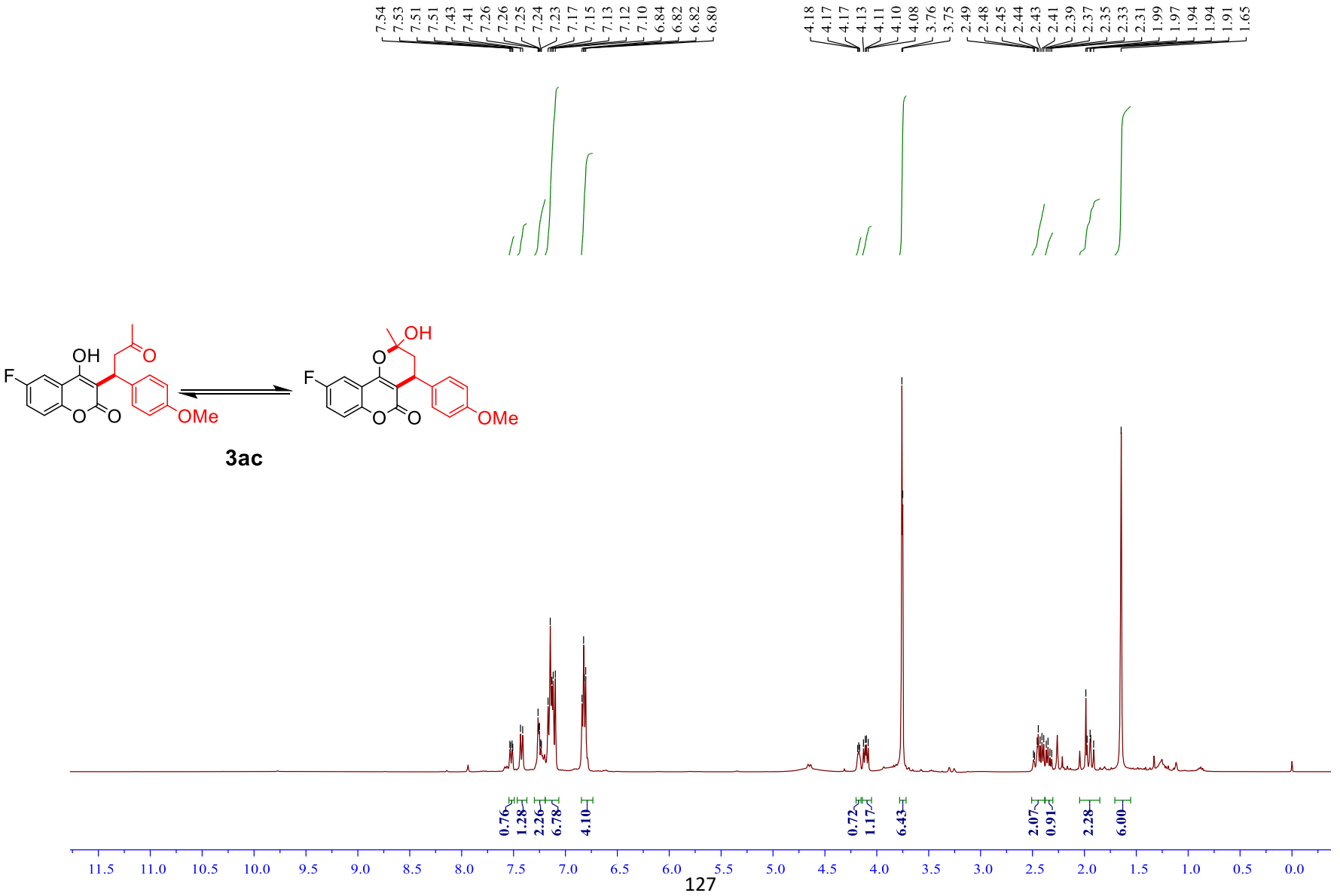
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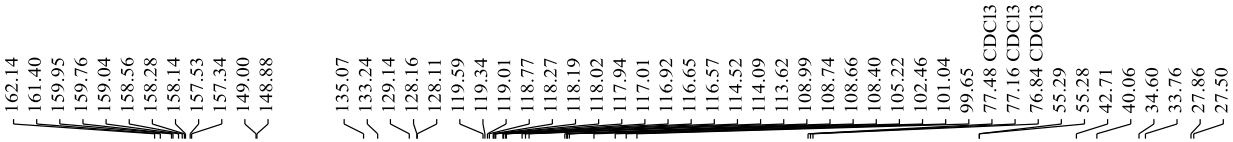
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101.04
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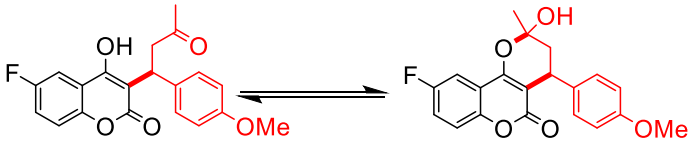
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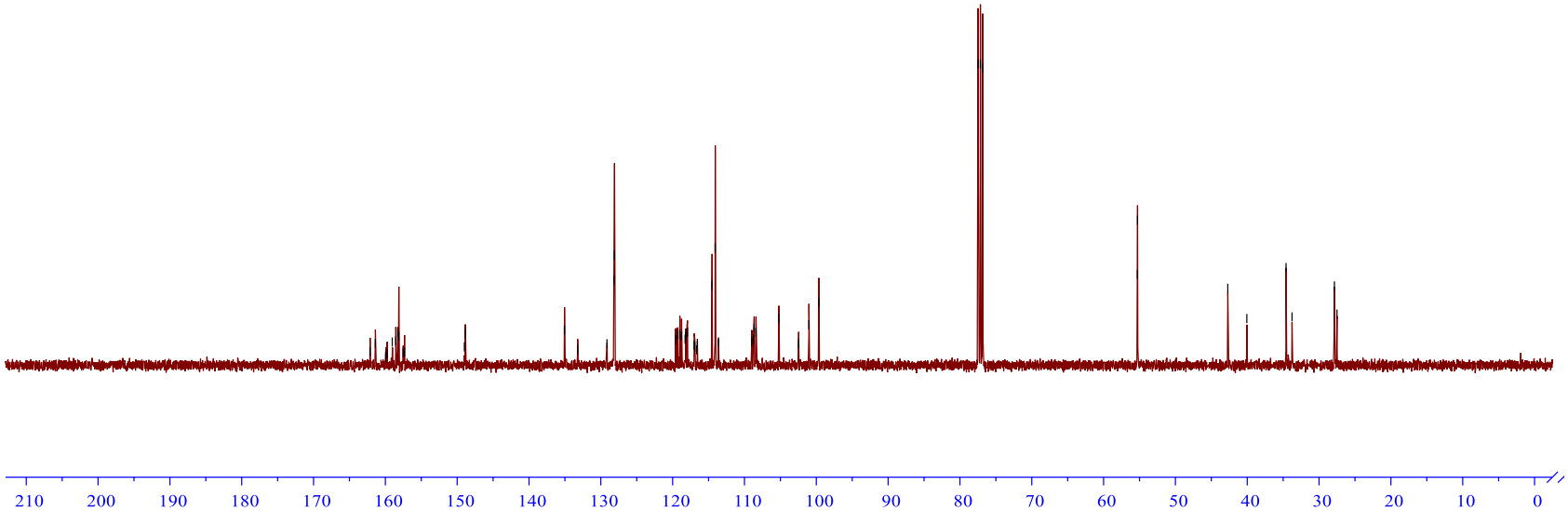
**3ac**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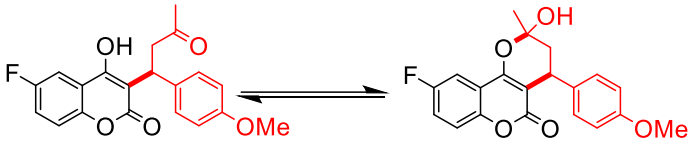
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**3ac**


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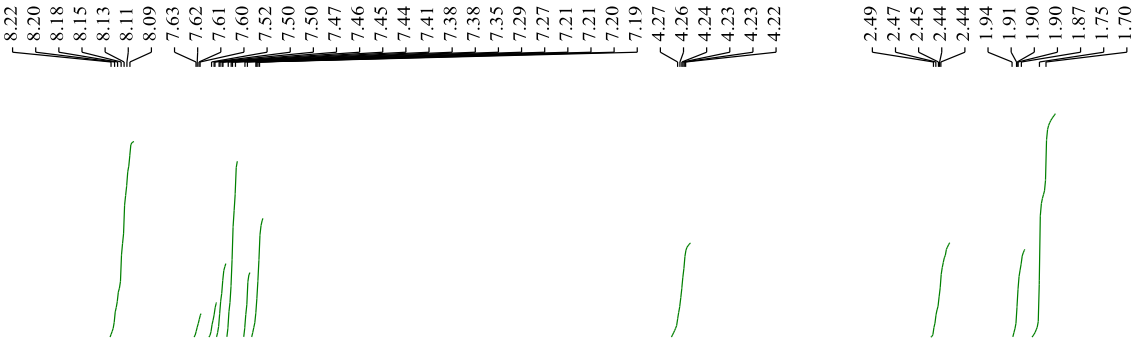
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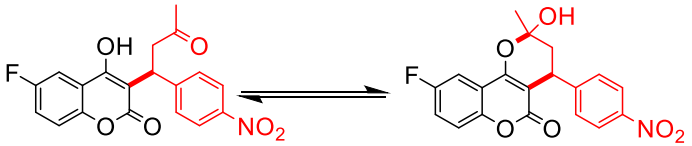
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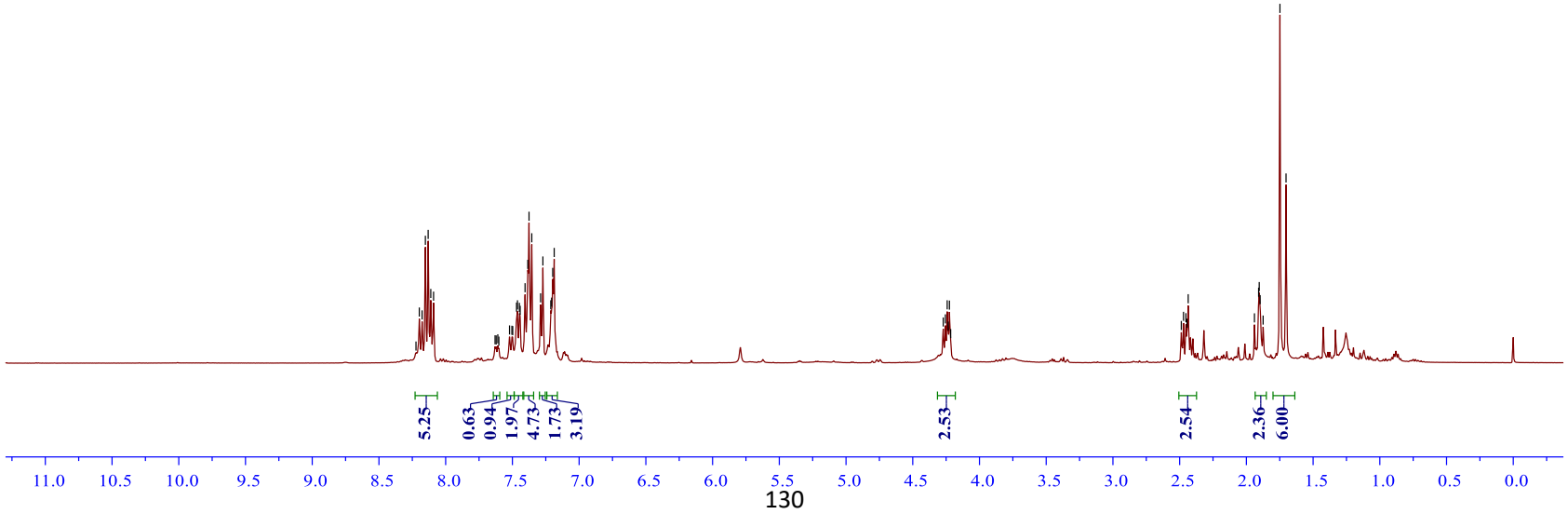
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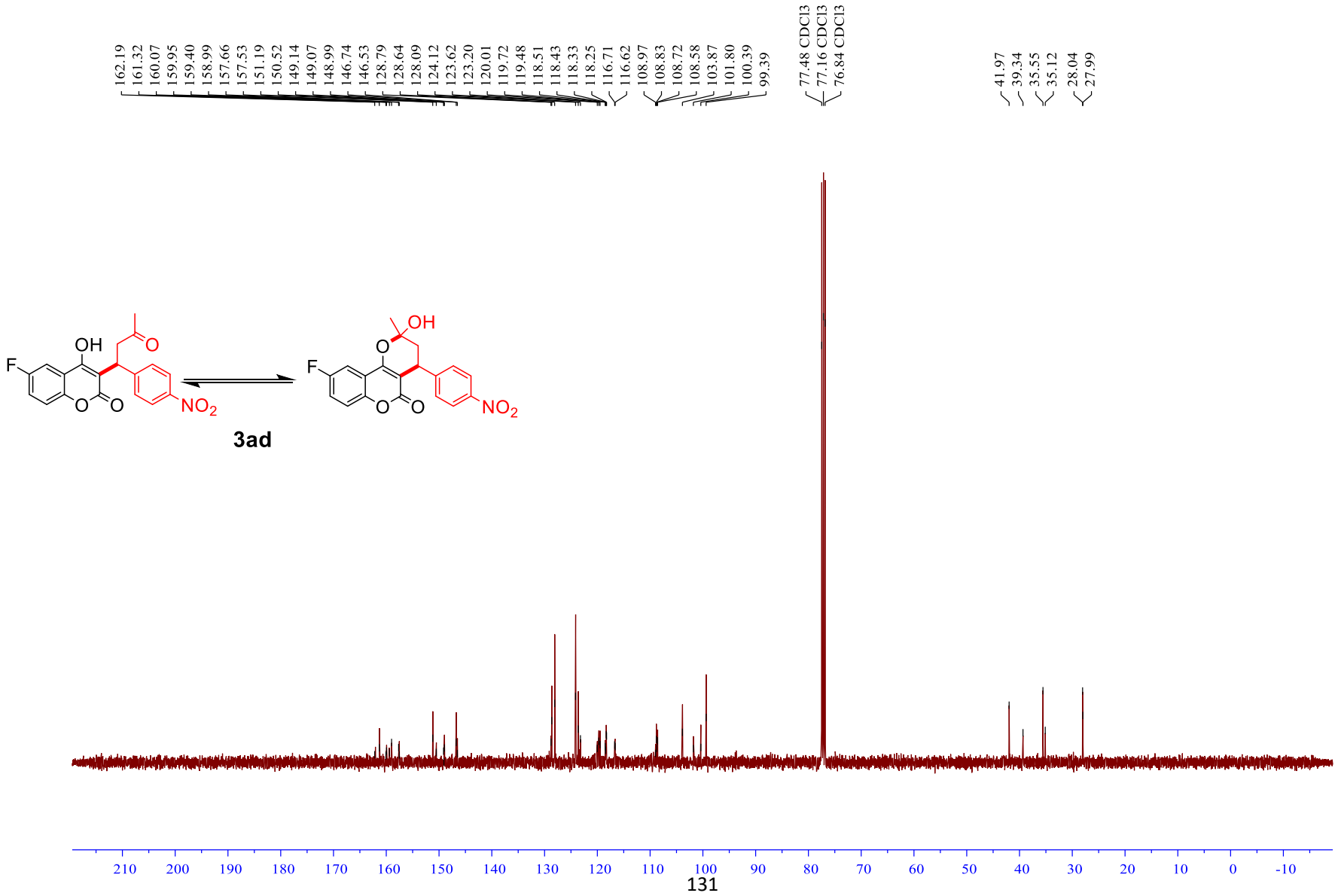
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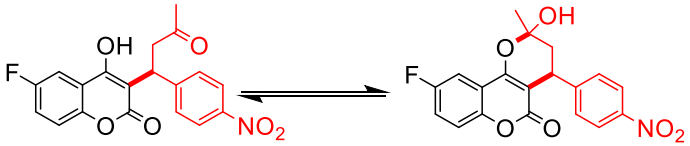


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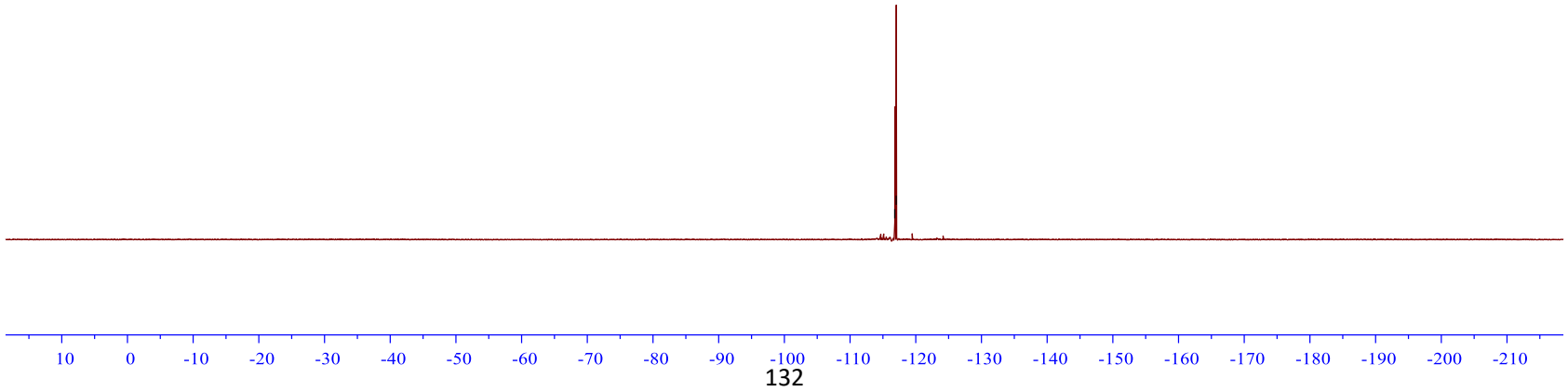

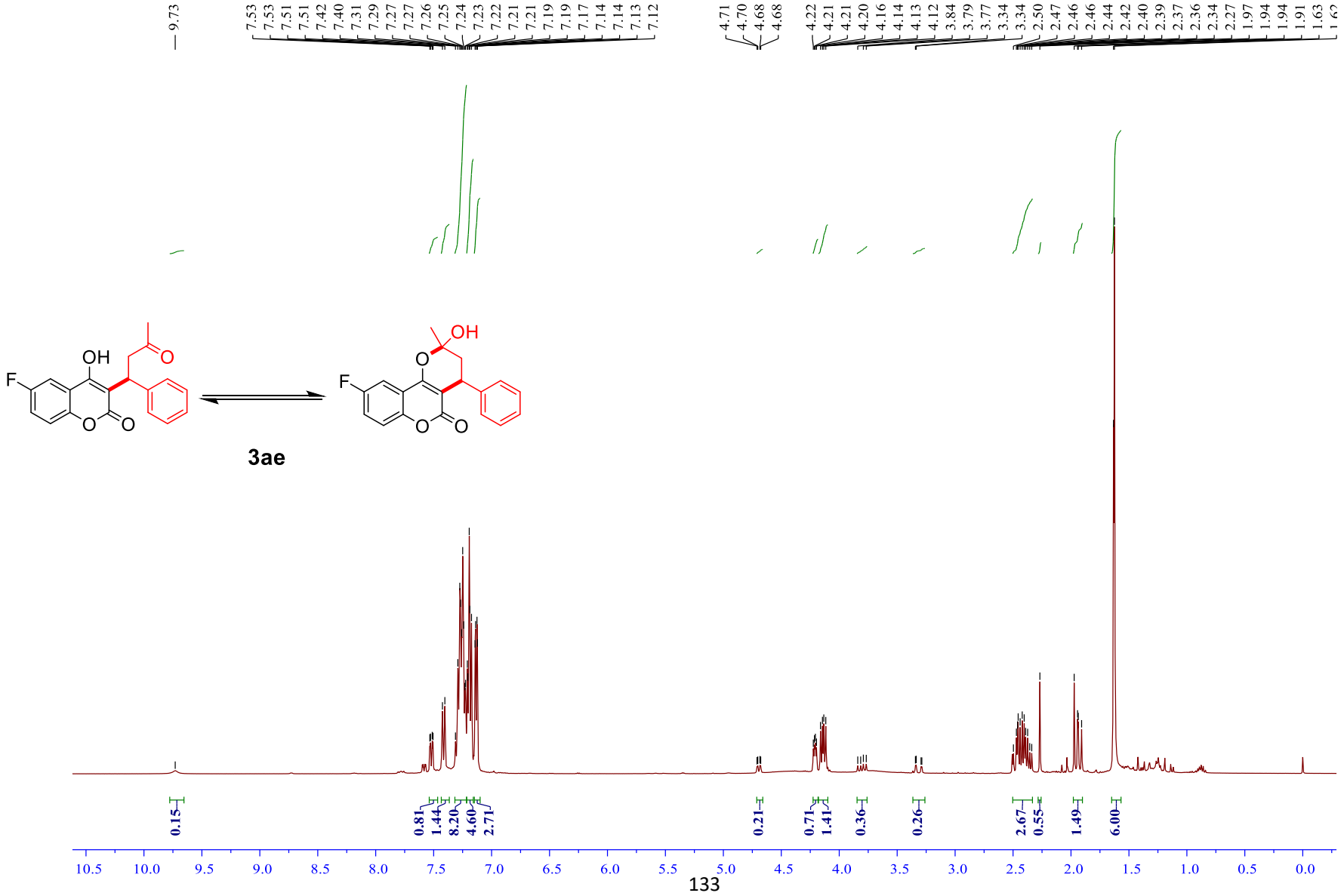
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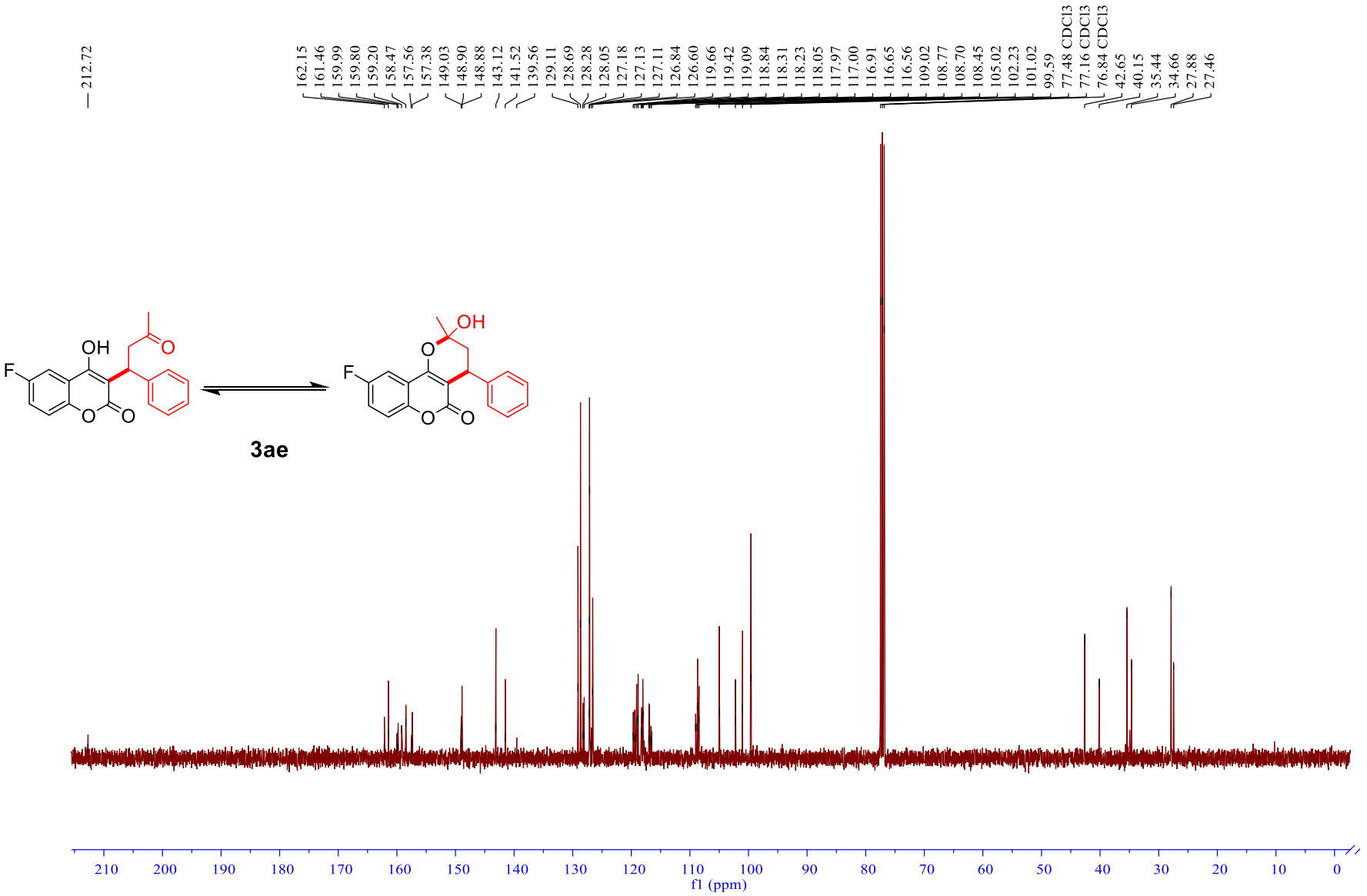
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OH
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F
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3ae
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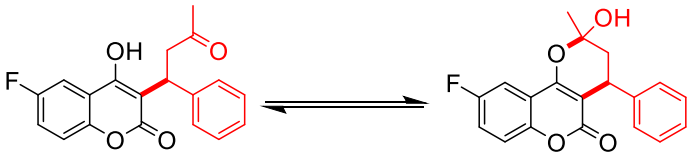


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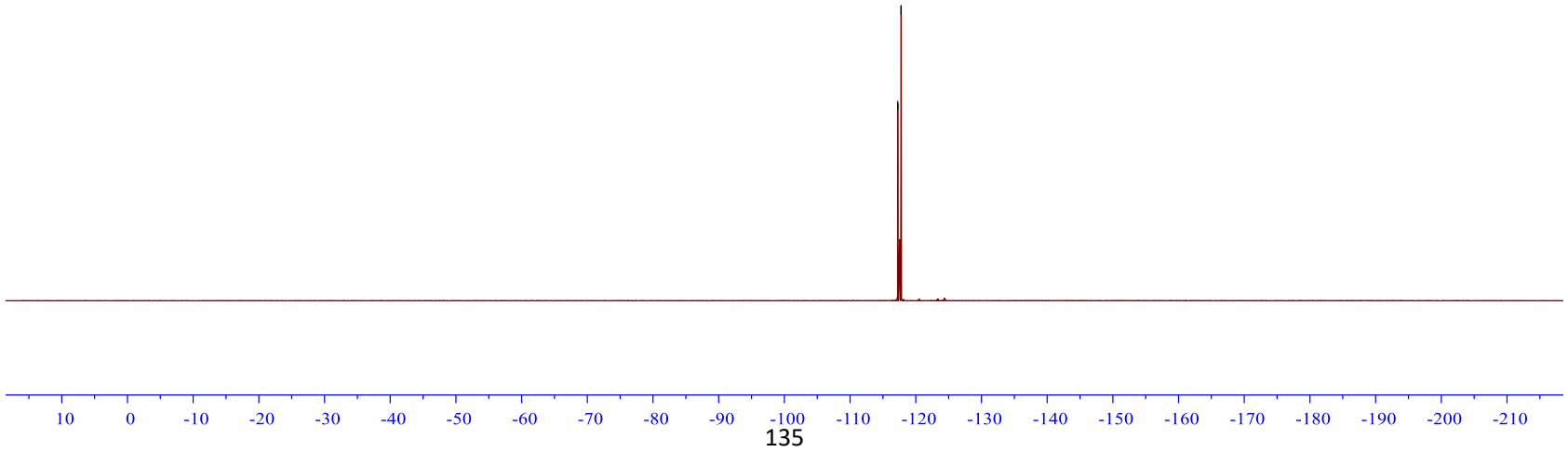

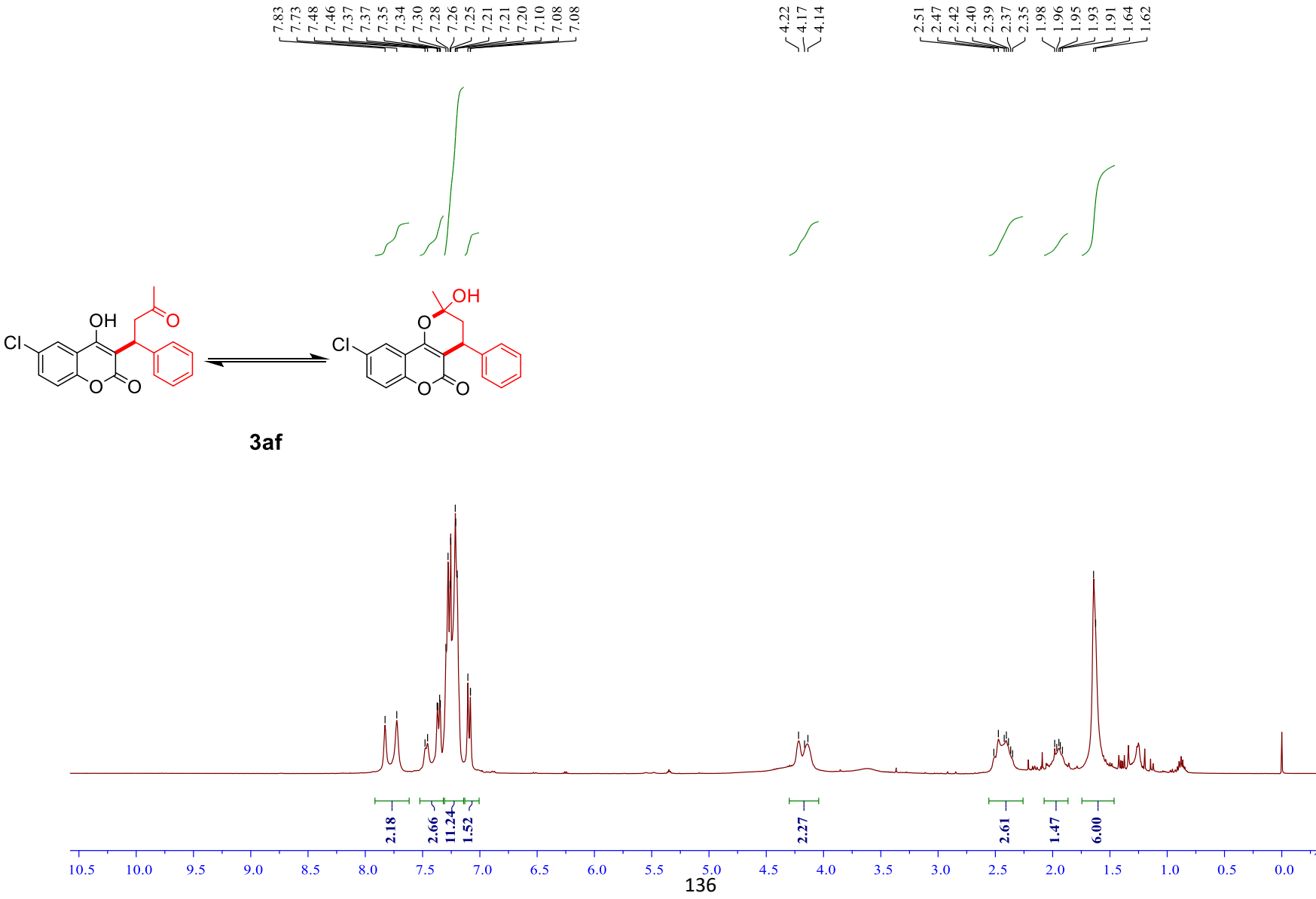
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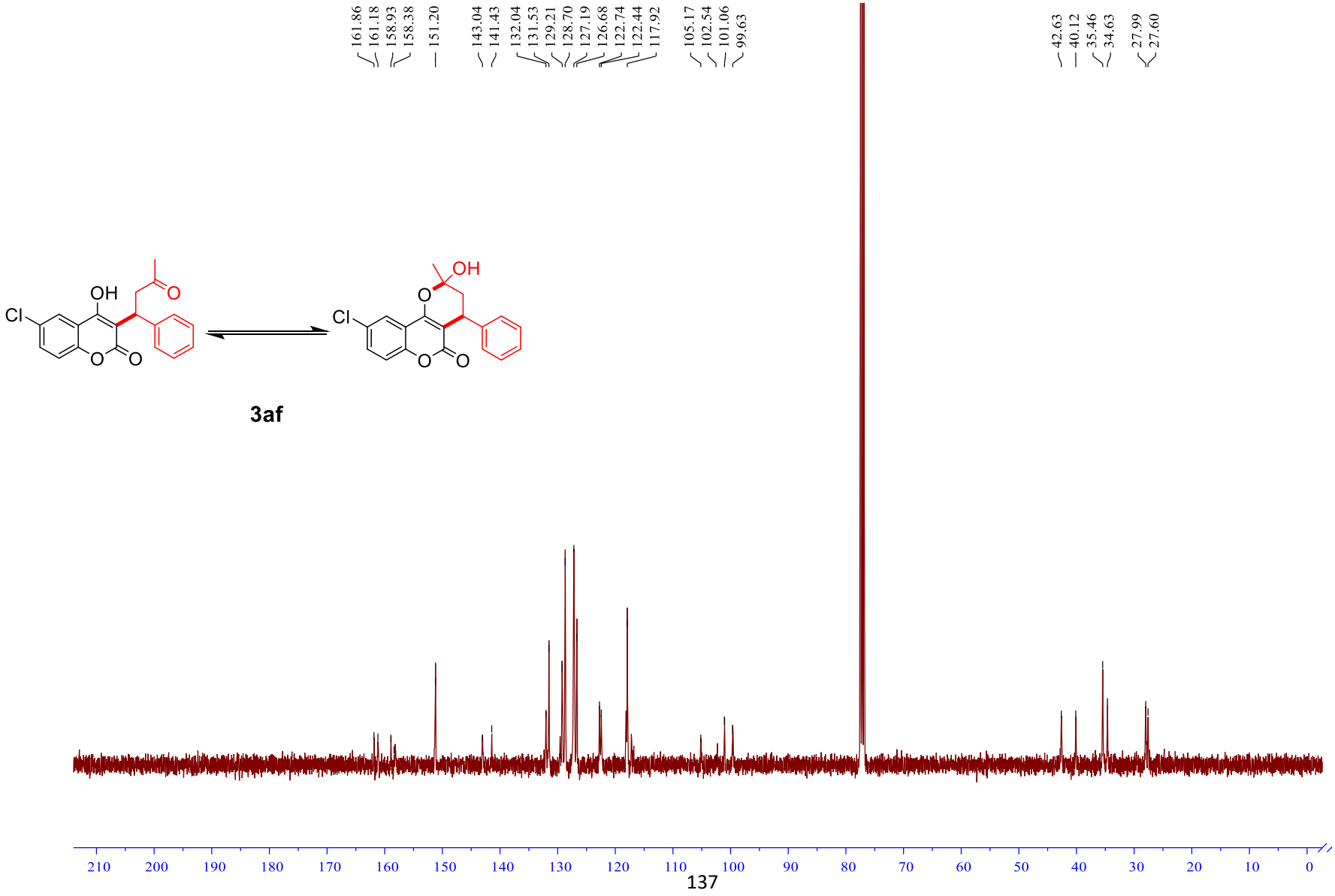
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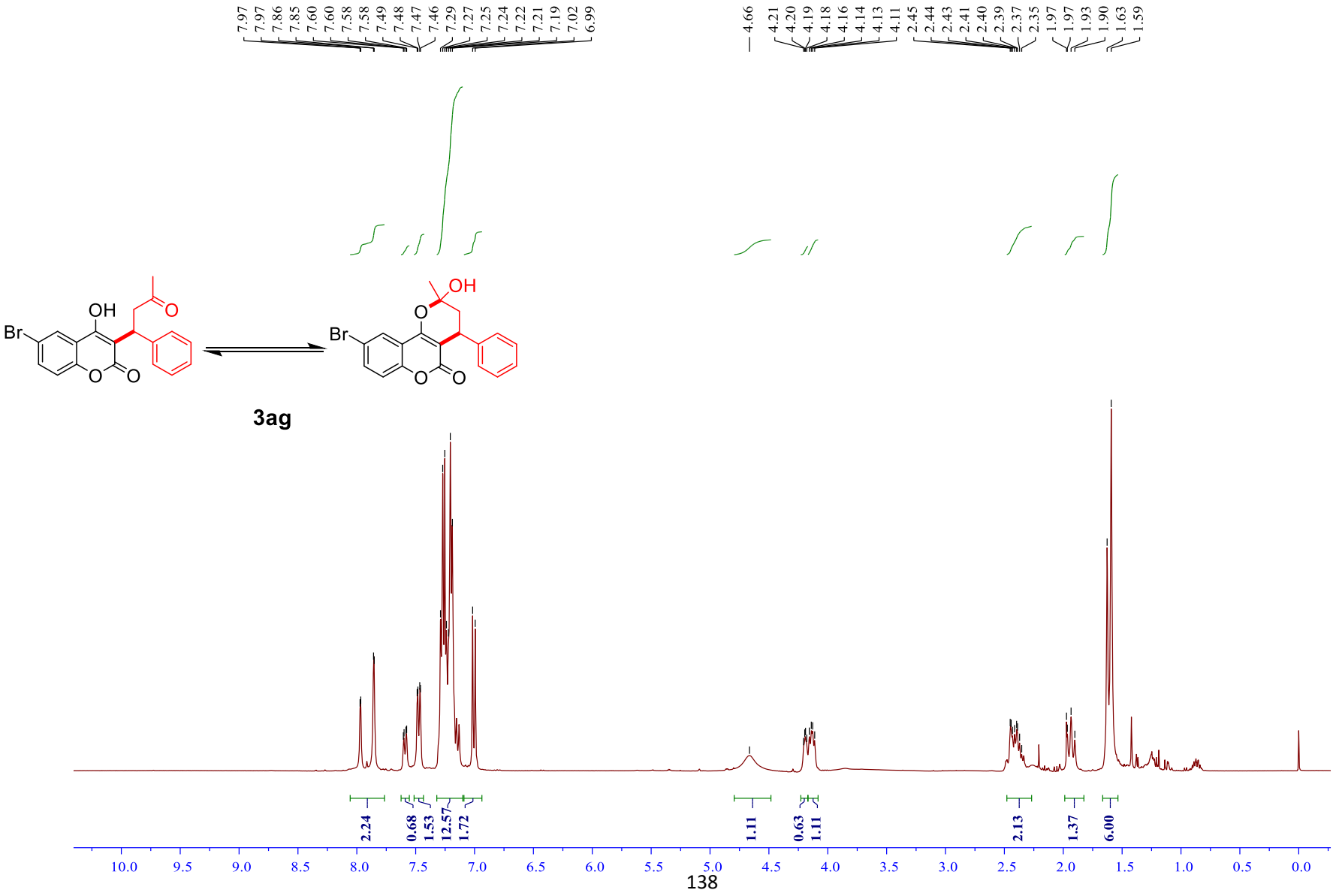
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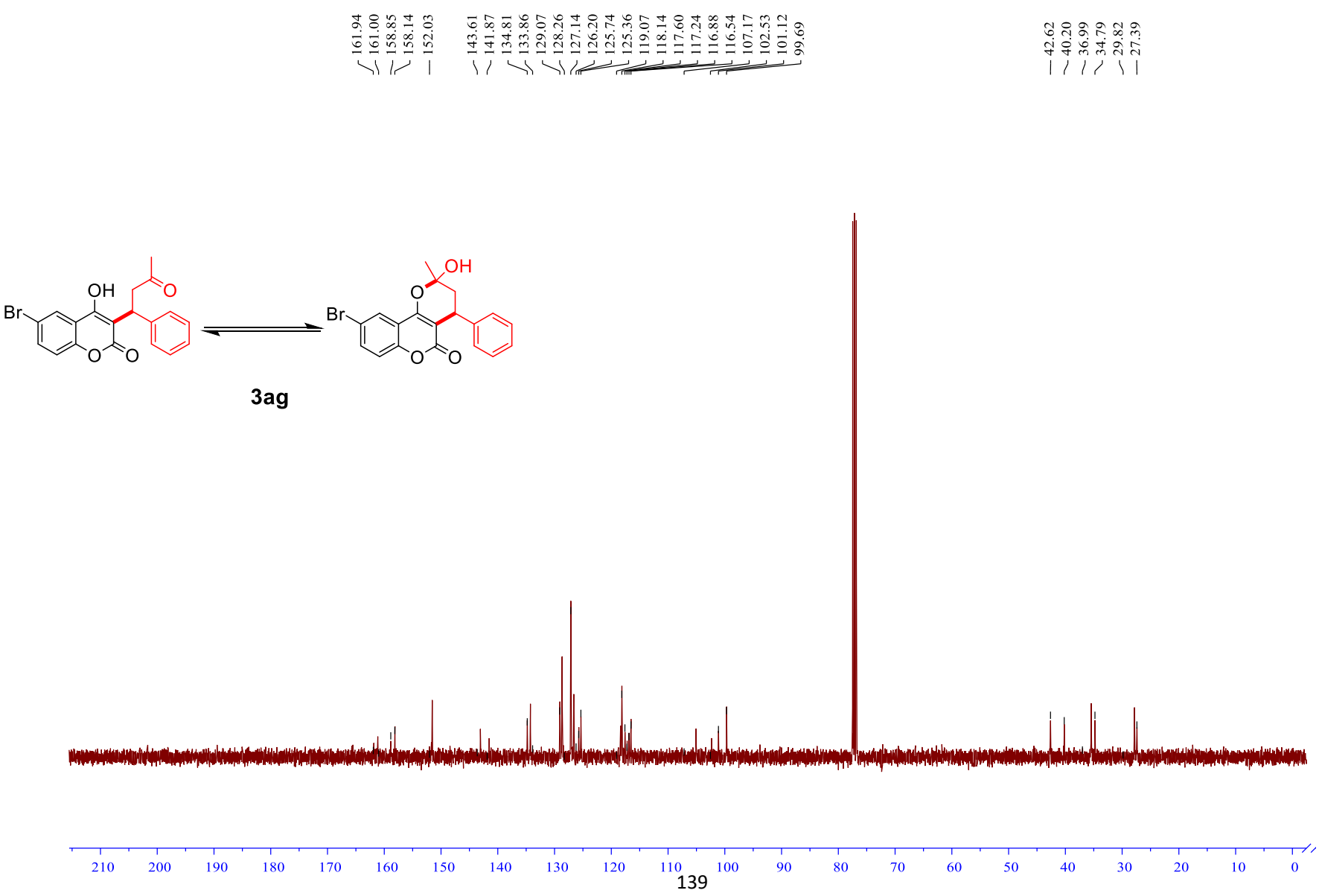
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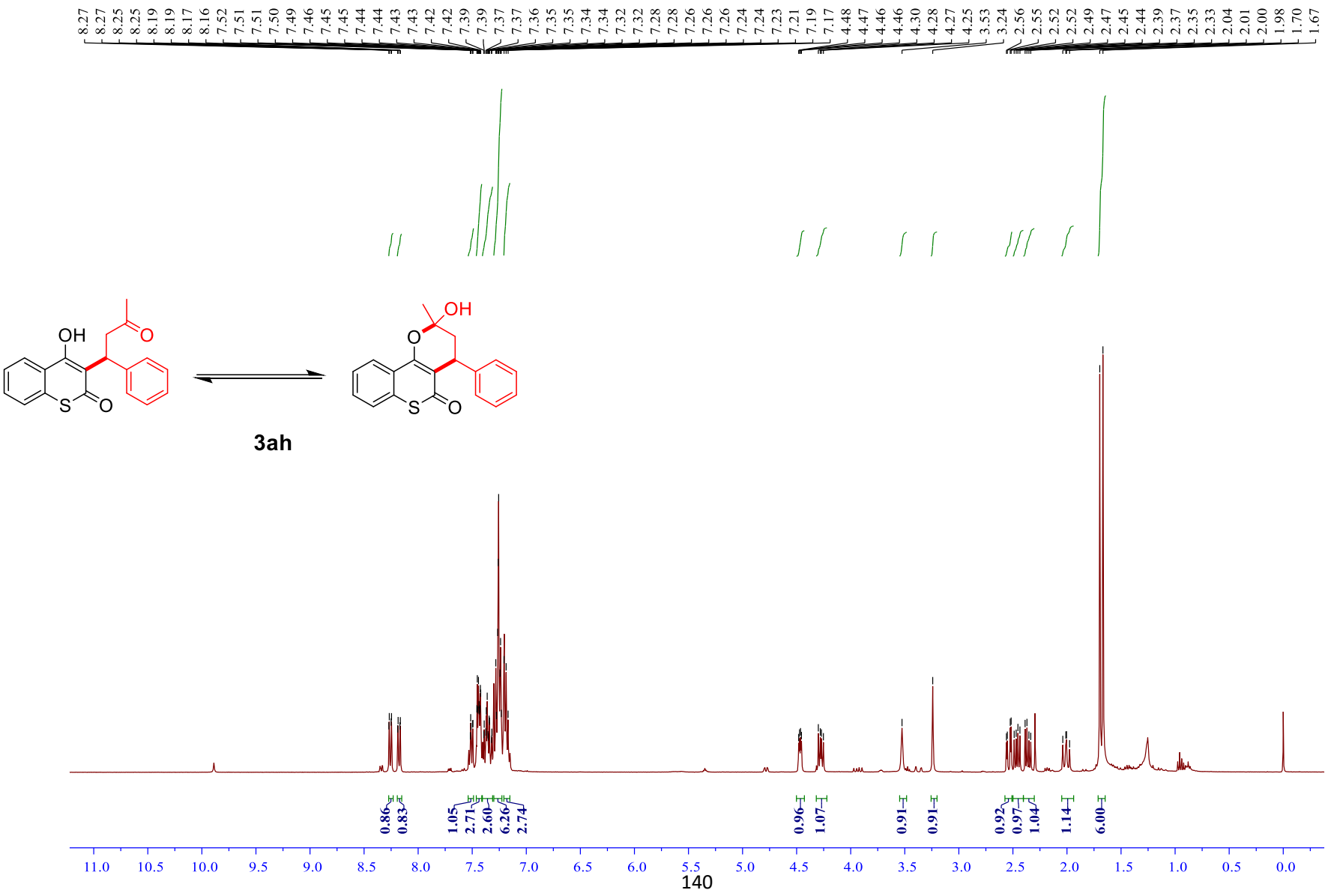
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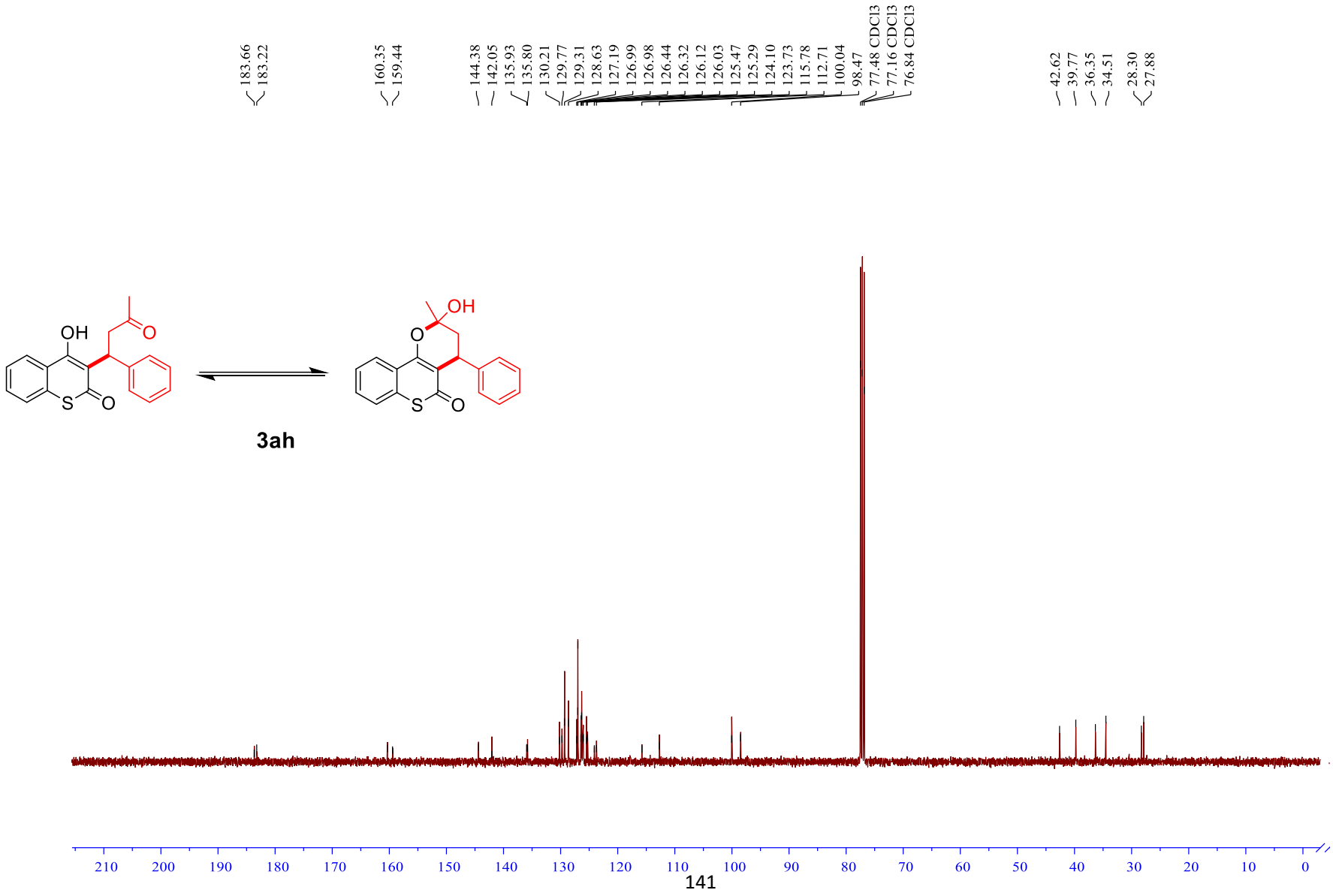
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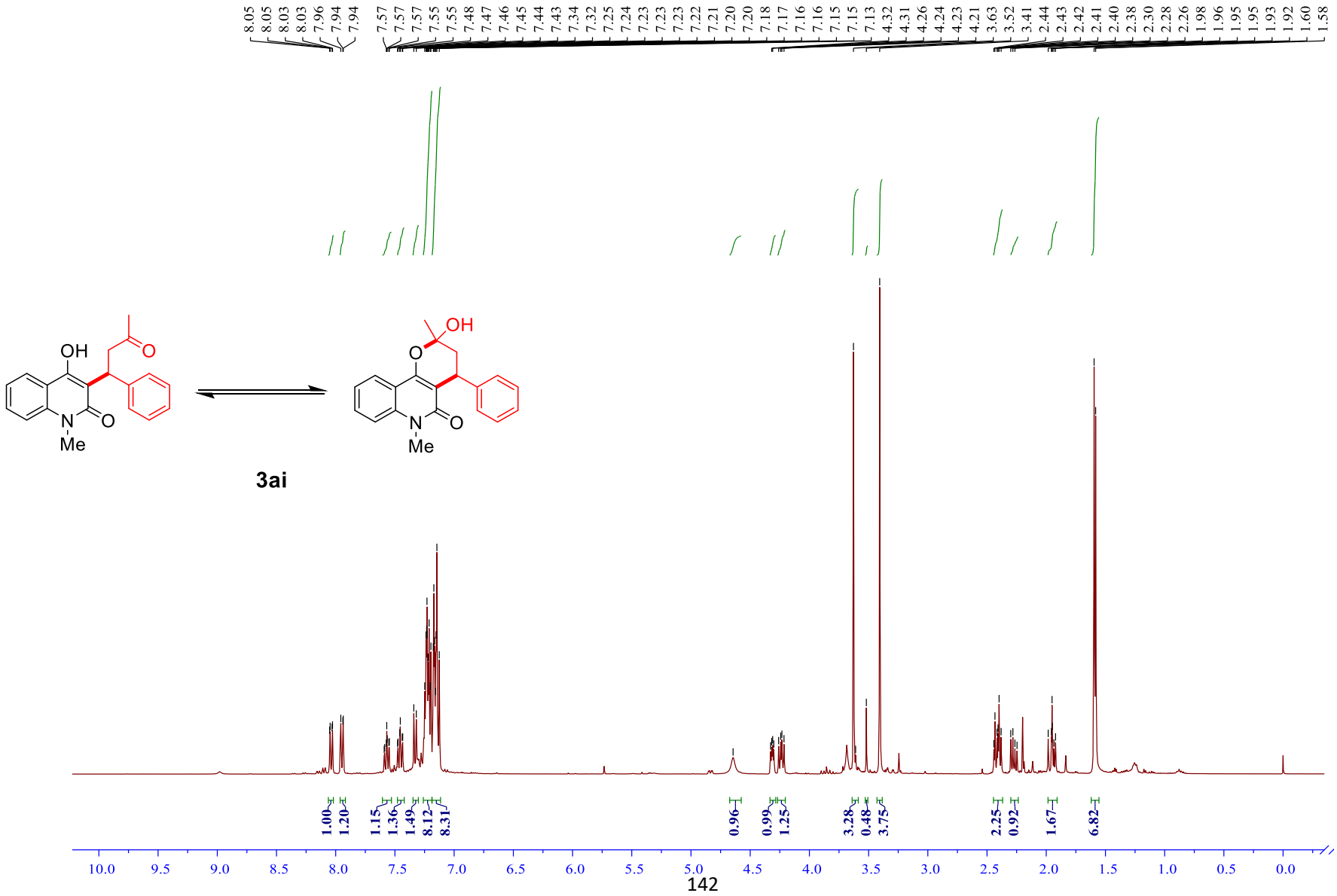
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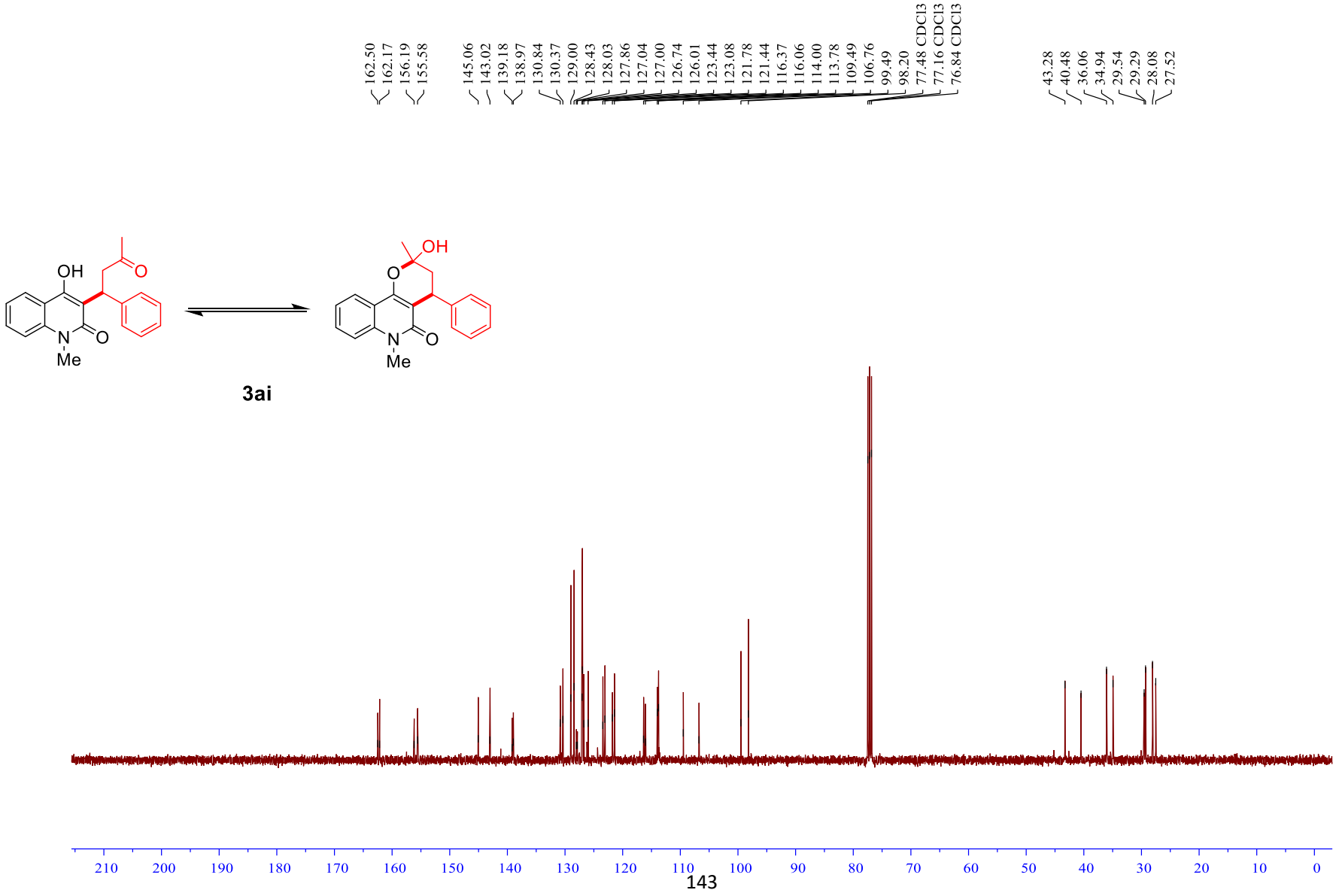
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