Supplementary Information for

Redox-Neutral Photochemical Heck-Type Arylation of Vinylphenols Activated by Visible Light

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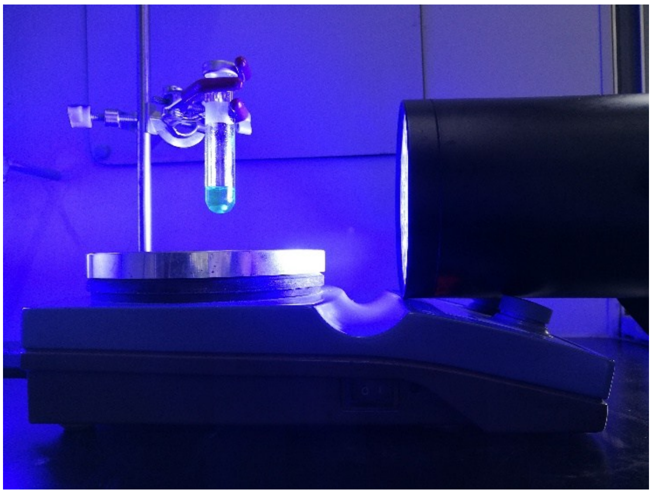
General Information

All reactions were performed under argon atmosphere using flame-dried glassware unless otherwise noted. DMSO was distilled over CaH_2 and rigorously degassed by freeze/pump/thaw. All reagents were commercially available and used without further purification unless indicated otherwise. Thin layer chromatographies were carried out on GF254 plates (0.25 mm layer thickness). Flash chromatography was performed with 200-300 mesh silica gels. Visualization of the developed chromatogram was performed by fluorescence quenching or by ceric ammonium molybdate, or $KMnO_4$ stain. Yields reported were for isolated, spectroscopically pure compounds.

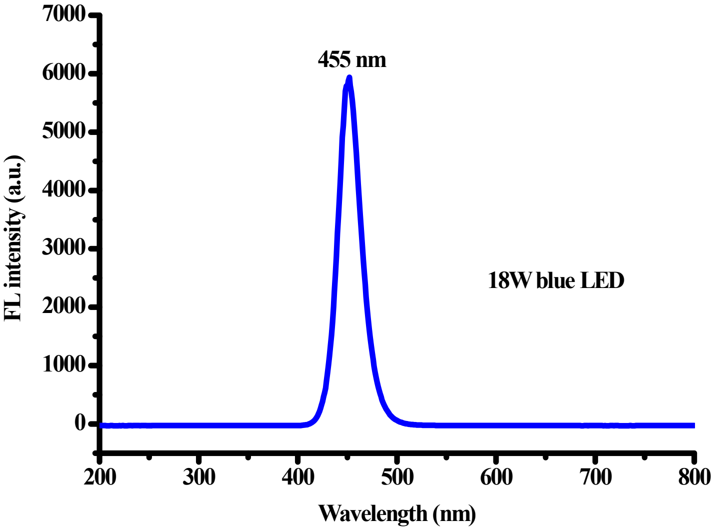
^1H and ^{13}C NMR spectra were recorded on Bruker Avance 400 and 600 MHz spectrophotometers. Chemical shifts (δ) are expressed in ppm., and J-values are given in Hz. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ESIMS and HRESIMS were taken on AB QSTAR Pulsar mass spectrometer or Aglient LC/MSD TOF mass spectrometer. UV-Vis measurements were carried out on a Hitachi UV-1900 UV-Visible spectrophotometer. Cyclic voltammetry studies was carried out on a CHI 760E electrochemical workstation (Shanghai CH Instruments Co., China). The emission spectra were recorded in a Hitachi F-7000 fluorescence spectrometer. Optical rotations were recorded on a JASCO P-2000 polarimeter.

General Procedure for Photochemical Heck Arylation of Vinylphenols

To an oven dried 10 mL glass tube with a magnetic stirring bar was added vinylphenols (0.20 mmol) and Cs_2CO_3 (0.30 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMSO (1.0 mL) and (hetero)aryl halides (0.10 mmol) were carefully added under Argon. The reaction mixture was stirred under an 18 W blue light emitting diode (LED) lamp (the distance was about 10 cm) irradiation for the indicated time at room temperature. Irradiation was stopped and the reaction was quenched with aqueous HCl (1M). The aqueous phase was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was subjected to column chromatography (acetone/petroleum ether) on silica gel to afford the product.



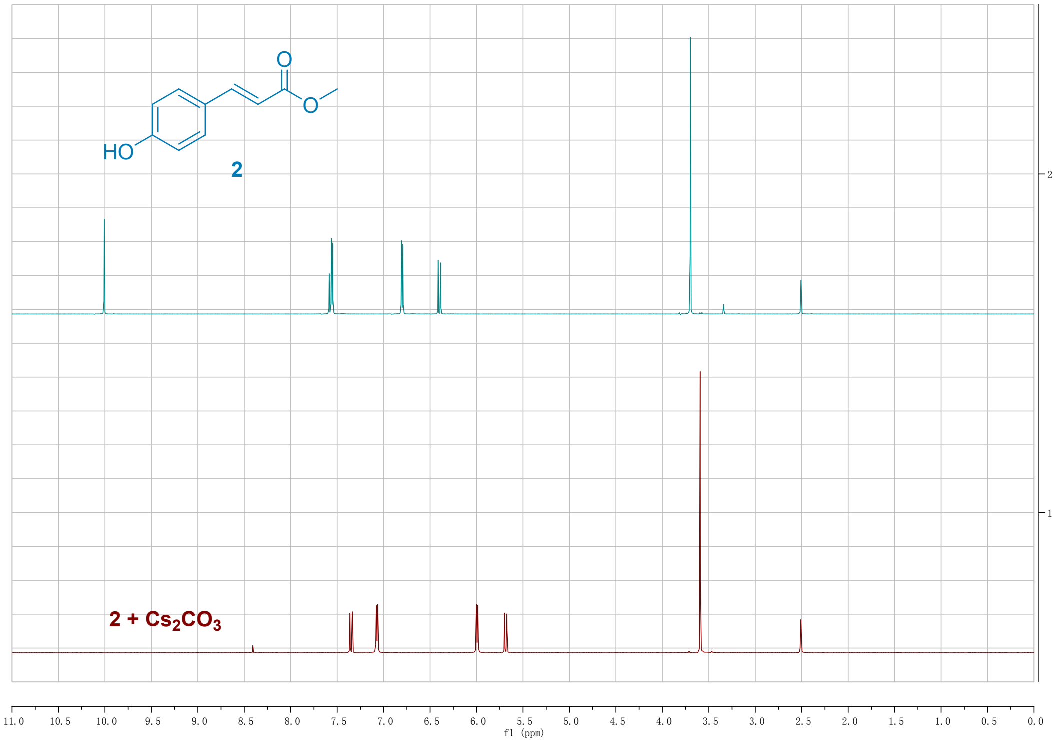
Supplementary Figure 1. Experimental setup for photochemical Heck arylation of vinylphenols.



Supplementary Figure 2. Emission spectra of the 18W blue LED lamp.

Supplementary Note 1. ^{1}H NMR Spectroscopic Studies

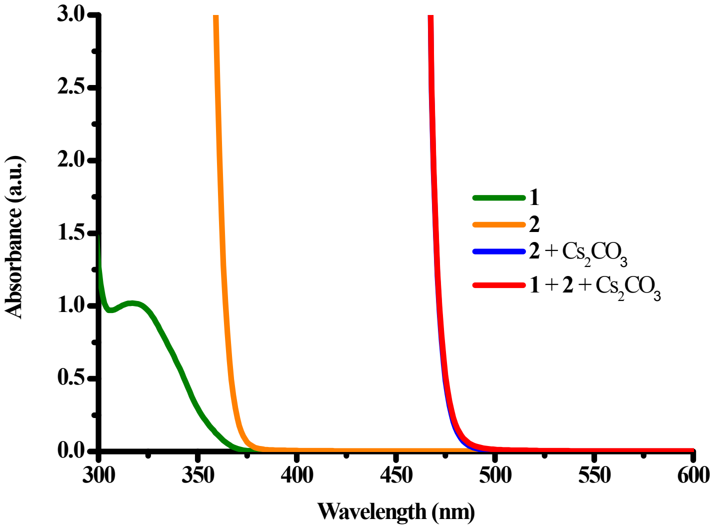
The ^{1}H NMR analysis was made on a solution containing **2** (8.9 mg, 0.05 mmol) and Cs_2CO_3 (17.9 mg, 0.055 mmol) in 0.5 mL of DMSO-d_6 (rigorously degassed by freeze/pump/thaw). Under these conditions, **2** was completely deprotonated by Cs_2CO_3 and significant upfield peak shifting of hydrogens were observed.



Supplementary Figure 3. Comparison of ^{1}H NMR spectra of **2** and the phenolate anion of **2** in DMSO-d_6.

Supplementary Note 2. UV-Vis Spectroscopic Measurements

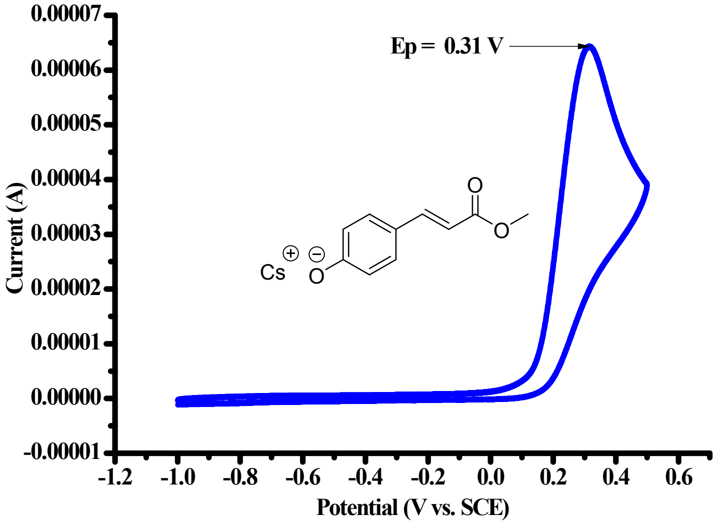
The UV-Vis absorption spectra of DMSO solutions (0.1 M) of **1**, **2**, mixtures of **2a** and Cs_2CO_3, and mixtures of **1**, **2** and Cs_2CO_3 were recorded on Hitachi UV-1900 UV-Visible spectrophotometer (1 mm short light path cuvettes have been employed in order to avoid fast signal saturation). The colorless solution of vinylphenol **2** (orange line) was immediately turned to a bright yellow color upon addition of Cs_2CO_3 (blue line) and no new color change after the aryl halide **1** was added to the solution of the phenolate anion of **2** (red line) indicating that no EDA ground state association occurred and the photon-absorbing ability of the phenolate anion of **2** in the visible spectral region was responsible for triggering the aryl radical from its halide **1**.



Supplementary Figure 4. UV-Vis absorption spectra of mixtures of **1**, **2**, and Cs_2CO_3 in DMSO at concentrations of 0.1M.

Supplementary Note 3. Electrochemical Measurements

Tetrabutylammonium hexafluorophosphate (387 mg, 1.0 mmol) was added to a 0.01 M solution of the phenolate anion of **2** (generated *in situ* by the deprotonation of **2** with 1.1 equiv Cs_2CO_3) in 10 mL of dry DMSO and the solution was vigorously bubbled with N_2 for 5 minutes prior to the measurement. The oxidation potential was measured using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) at 0.1 V/s scan rate. A completely irreversible reduction wave was observed with $E_p = 0.31$ V vs. SCE in DMSO.



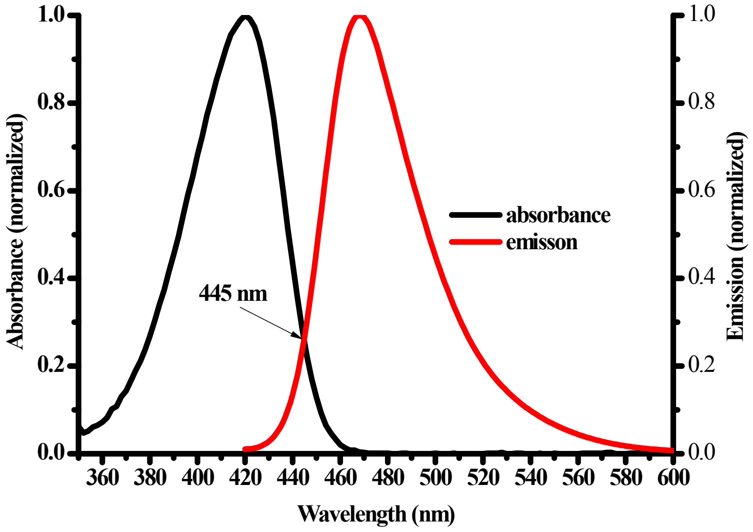
Supplementary Figure 5. The cyclic voltammogram of the phenolate anion of **2** vs SCE in DMSO at 0.1V/s.

With this data in hand we calculated the redox potential of the excited phenolate anion of **2** employing the following equation: [1]

$$E(\mathbf{2}^{\bullet}/\mathbf{2}^{-*}) = E(\mathbf{2}^{\bullet}/\mathbf{2}^{-}) - E_{0\text{-}0}(\mathbf{2}^{-*}/\mathbf{2}^{-})$$

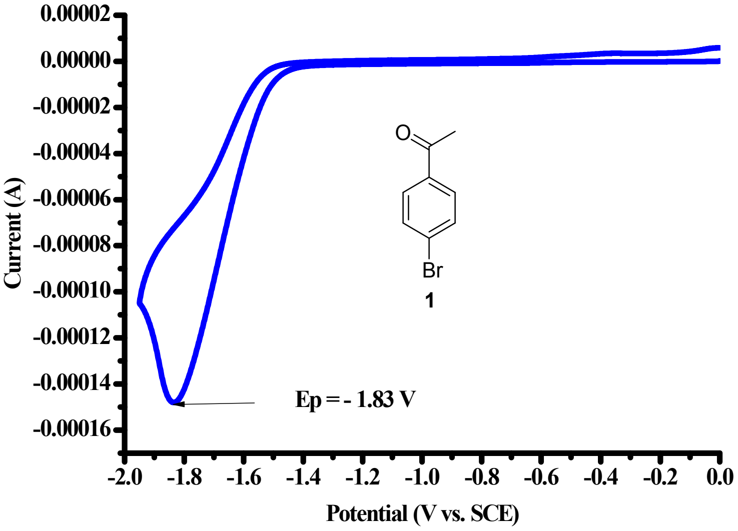
The peak potential of electrochemical oxidation of the phenolate anion of **2** (E_p = 0.36 V) was used for $E(\mathbf{2}^{\bullet}/\mathbf{2}^{-})$. $E_{0\text{-}0}(\mathbf{2}^{-*}/\mathbf{2}^{-})$, the excited state energy of the phenolate anion of **2**, was estimated from the intersection of the normalized absorbance and emission spectra.[2] This corresponds to 445 nm, which translates into an $E_{0\text{-}0}(\mathbf{2}^{-}{*}/\mathbf{2}^{-})$ of 2.79 eV for the phenolate anion of **2**.

$$E(\mathbf{2}^{\bullet}/\mathbf{2}^{-}{*}) = E(\mathbf{2}^{\bullet}/\mathbf{2}^{-}) - E_{0\text{-}0}(\mathbf{2}^{-}{*}/\mathbf{2}^{-}) = 0.31 - 2.79 = -\ 2.48 \text{ V vs. SCE}$$



Supplementary Figure 6. Normalized absorption and emission spectra of the phenolate anion of **2** in dry -DMSO (5 × 10^{-5} M), the intersect wavelength was considered to be 445 nm.

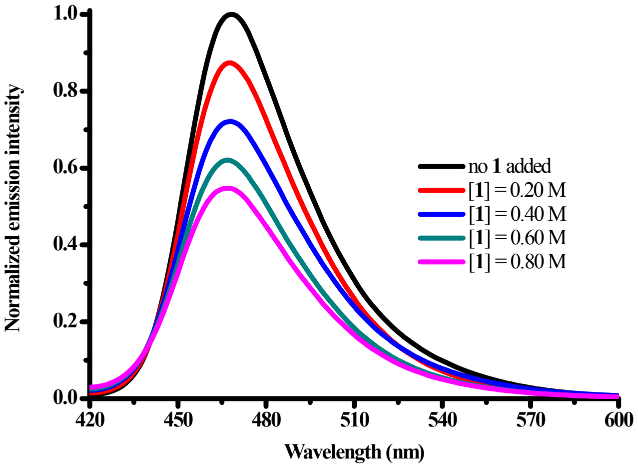
The cyclic voltammetry of 4'-bromoacetophenone **1** was also carried out. Tetrabutylammonium hexafluorophosphate (378.0 mg, 1.0 mmol) and **1** (19.9 mg, 0.10 mmol) were dissolved in dry DMSO (10 mL) and the solution was vigorously bubbled with N_2 for 5 minutes prior to the measurement. The reduction potential was measured using a glassy carbon working electrode, a platinum wire counter electrode, and a a saturated calomel electrode (SCE) at 0.1 V/s scan rate. A completely irreversible reduction wave was observed with E_p = -1.83 V vs. SCE in DMSO.



Supplementary Figure 7. The cyclic voltammogram of **1** vs SCE in DMSO at 0.1V/s.

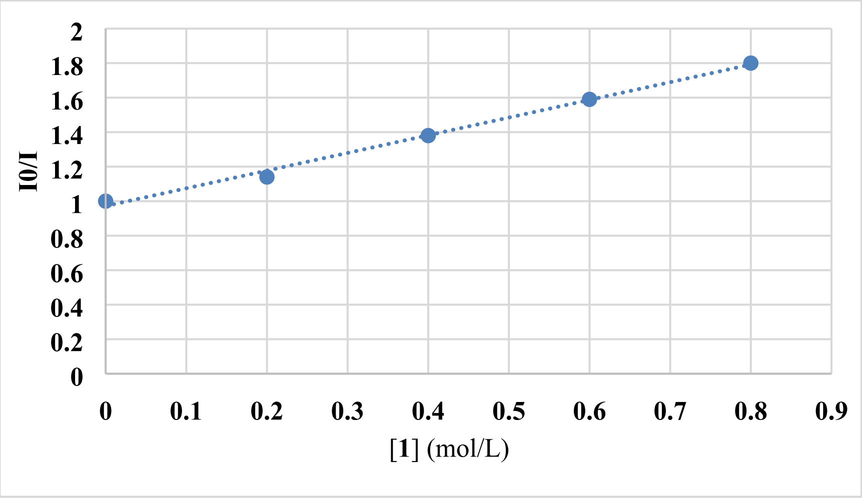
Supplementary Note 4. Stern-Volmer Experiments

The samples were prepared mixing the phenolate anion of **2** (5×10^{-5} M, freshly prepared *in situ* by the deprotonation of **2** with 1.1 equiv Cs_2CO_3) with the required amount of **1** in a total volume of 1 mL of dry DMSO (rigorously degassed by freeze/pump/thaw) in a 10 × 10 mm light path quartz fluorescence cuvette under an argon atmosphere. The samples were vigorously bubbled with dry argon for 5 minutes prior to the measurement. The excitation wavelength was fixed at 400 nm, the emission light was acquired from 420 nm to 600 nm.



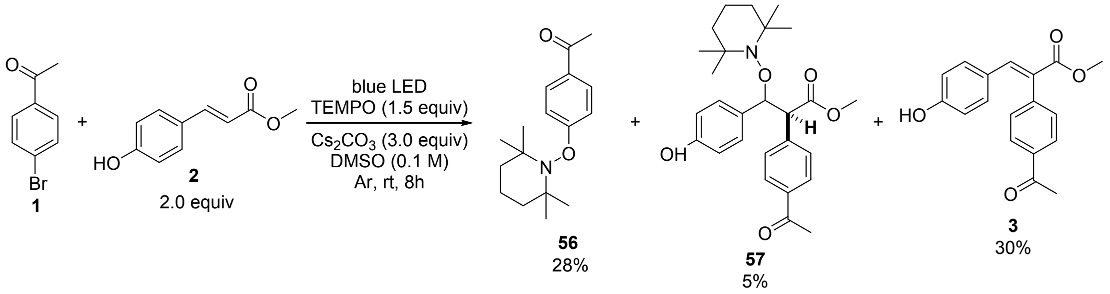
Supplementary Figure 8. Quenching of the phenolate anion of **2** emission (5×10^{-5} M in DMSO) in the presence of increasing amounts of **1**.

The Stern-Volmer plot shows a linear correlation between the amounts of **1** and the ratio I_0/I.



Supplementary Figure 9. Stern-Volmer quenching plot.

Supplementary Note 5. Radical Trapping Experiments



To an oven dried 10 mL glass tube with a magnetic stirring bar was added **2** (106.8 mg, 0.60 mmol) and Cs_2CO_3 (293.4 mg, 0.90 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMSO (3.0 mL), compound **1** (59.9 mg, 0.30 mmol) and TEMPO (70.2 mg, 0.45 mmol) were carefully added under Argon. The reaction mixture was stirred under an 18 W blue light emitting diode (LED) lamp (the distance was about 10 cm) irradiation for 8 h at room temperature. Irradiation was stopped and the reaction was then adjusted to Ph ~ 6 with 1% aqueous HCl. The aqueous phase was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was subjected to column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford **56** (23.1 mg, 28% yield), **57** (6.8 mg, 5% yield) ,and the **3** (27.0 mg, 30% yield).

1-(4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)phenyl)ethan-1-one (**56**): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.9, 2H), 7.25 (br, 2H), 2.54 (s, 3H), 1.73 – 1.54 (m, 5H), 1.52 – 1.39 (m, 1H), 1.24 (s, 6H), 0.99 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.7, 167.6, 130.1, 113.8, 60.6, 39.7, 32.4, 26.2, 20.5, 17.0; HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{25}O_2NNa$ $[M + Na]^+$, 298.1778, found 298.1776.

Methyl 2-(4-acetylphenyl)-3-(4-hydroxyphenyl)-3-((2,2,6,6-tetramethyl piperidin-1-yl)oxy)propanoate (**57**): ^{1}H NMR (600 MHz, CD_3CN): δ 7.74 (d, *J* = 8.4, 2H), 7.41 (d, *J* = 8.4, 2H), 7.16 (d, *J* = 8.5, 2H), 6.56 (d, *J* = 8.6, 2H), 5.55 (d, *J* = 11.0, 1H), 4.40 (d, *J* = 11.0, 1H), 3.70 (s, 3H), 2.45 (s, 3H), 1.54 (s, 3H), 1.48 – 1.44 (s, 2H), 1.36 – 1.18 (m, 4H), 1.16 (s, 3H), 0.99 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (150 MHz, CD_3CN): δ 198.0, 173.4, 157.4, 141.9, 136.8, 133.0, 130.1, 129.4, 128.7, 114.5, 85.2, 55.7, 52.4, 41.6, 40.6, 34.4, 33.5, 26.5, 20.5, 20.3, 17.5; HR-ESI-MS (*m/z*): calcd. for

$C_{27}H_{36}O_5N$ $[M + H]^+$, 454.2588, found 454.2591.

Supplementary Note 6. Quantum Yield Measurements

The quantum yield for the model reaction was measured by using Melchiorre's procedure.[1b]

A standard ferrioxalate actinometer solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in *Handbook of Photochemistry*.[3] The ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex $Fe(phen)_3^{2+}$ formed are related to moles of photons absorbed.

The solutions were prepared and stored in dark:

1. Potassium ferrioxalate solution: 589.5 mg of potassium ferrioxalate (commercially available from Alfa Aesar) and 278 μL of sulfuric acid (96%) were added to a 100 mL volumetric flask, and filled to the mark with water (HPLC grade).

2. Phenantroline solution: 0.2% by weight of 1,10-phenanthroline in water (200 mg in 100 mL volumetric flask).

3. Buffer solution: to a 100 mL volumetric flask, 4.94 g of NaOAc and 1 mL of sulfuric acid (96%) were added and filled to the mark with water (HPLC grade).

4. Model reaction solution: a stock solution containing 4'-bromoacetophenone **1** (99.5 mg, 0.50 mmol), **2** (178.0 mg, 1.00 mmol), Cs_2CO_3 (489.0 mg, 1.50 mmol), and DMSO (5.0 mL, rigorously degassed by freeze/pump/thaw). The mixture was stirred in the dark under Argon for 40 minutes in order to prepare the phenolate anion solution. Concomitantly, 1 mL of this mixture was degassed and used to run the experiment.

Procedure: 1 mL of the actinometer solution and 1 mL of the degassed model reaction were added to two identical quartz cuvettes (l = 10 mm). The cuvettes were placed 10 cm away from the light source and irradiated at $\lambda = 450$ nm (emission slit width at 10.0 nm) without stirring. This procedure was repeated 3 times, quenching the reactions after different time intervals: 1.0, 2.0, 3.0, and 4.0 minutes.

The actinometer measurements were done as follows:

1. After irradiation, the actinometer solution was removed and placed in a 10 mL

volumetric flask containing 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution. This flask was filled to the mark with water (HPLC grade).

2. The UV-Vis spectra of the complexed actinometer samples were recorded for each time interval. The absorbance of the complexed actinometer solution was monitored at 510 nm.

The moles of Fe^{2+} formed for each sample are determined according to the Beer's Law:

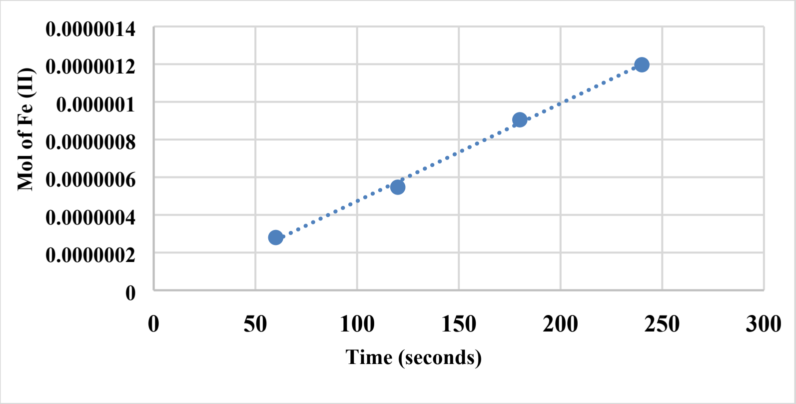
$$mol\, Fe^{2+} = \frac{V_1 \cdot V_3 \cdot \Delta A\ (510\ nm)}{10^3 \cdot V_2 \cdot l \cdot \varepsilon\ (510\ nm)}$$

where $\mathbf{V_1}$ is the irradiated volume (1 mL), $\mathbf{V_2}$ is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), $\mathbf{V_3}$ is the final volume after complexation with phenanthroline (10 mL), **l** is the optical path-length of the irradiation cell (1 cm), **ΔA (510 nm)** the optical difference in absorbance between the irradiated solution and the one stored in the dark, **ε (510 nm)** is that of the complex $Fe(phen)_3^{2+}$ (11100 L mol^{-1} cm^{1}).

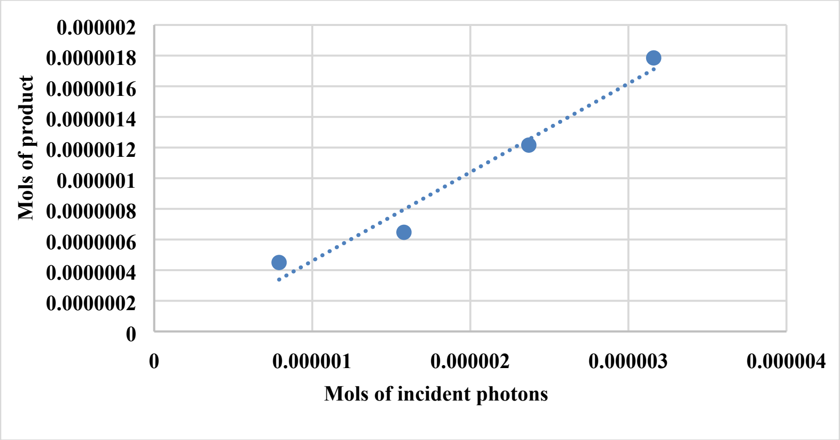
The moles of Fe^{2+} formed (x) are plotted as a function of time (t). The slope of this line was correlated to the moles of incident photons by unit of time ($q^0_{n,p}$) by the use of the following Equation: [4]

$$\Phi(\lambda) = \frac{dx/dt}{q^0_{n,p}[1 - 10^{-A(\lambda)}]}$$

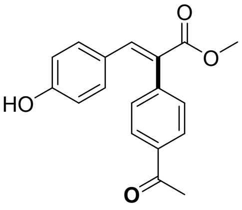
Where **dx/dt** is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (**Φ**) for Fe^{2+} at 450 nm is 0.9,[5] and the absorbance **A(λ)** of the actinometer at $\lambda = 450$ nm was measured by UV/Vis spectroscopy to be 0.327. $\mathbf{q^0_{n,p}}$, which is the photon flux, was determined to be 1.32×10^{-8} einstein s^{-1}.



The measurements for the reaction under study were done as follows: the moles of product **3** formed were determined by ^{1}H NMR spectroscopy. The moles of product per unit of time are related to the number of photons absorbed. The photons absorbed are correlated to the number of incident photons by the use of the equation displayed in the previous point. According to equation the slope (dx/dt) is equal to: $\mathbf{\Phi\cdot(1\text{-}10^{-A(450\ nm)})\cdot q^{0}_{n,p}}$, where $\mathbf{\Phi}$ is the quantum yield to be determined and the absorption **A(450 nm)** of the reaction was determined by UV/Vis spectroscopy to be more than 4, thus $\mathbf{(1\text{-}10^{-A(450\ nm)})} > 1 - 10^{-4} = 0.9999$ (approximated to 1). The calculation yields the quantum yield (**Φ**) of the photoreaction = **0.58**. The procedure was repeated a second time to provide a similar value: quantum yield (**Φ**) at 450 nm of **0.52**



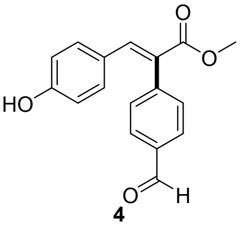
Identification of Compounds



3

Methyl (*E*)-2-(4-acetylphenyl)-3-(4-hydroxyphenyl)acrylate (3)

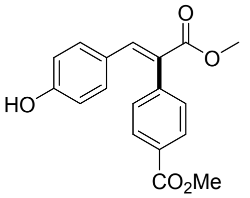
Prepared according to the general procedure using 4'-bromoacetophenone **1** (19.9 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = I, 12 hours; X = Br, 16 hours; X = Cl, 36 hours). The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **3** as a white powder (X = I, 23.4 mg, 79% yield, E/Z > 19:1; X = Br, 25.8 mg, 87% yield, E/Z > 19:1; X = Cl, 19.8 mg, 67% yield, E/Z > 19:1). Stereochemistry determined by X-ray analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.2, 2H), 7.85 (s, 1H), 7.34 (d, *J* = 8.2, 2H), 6.91 (d, *J* = 8.6, 2H), 6.63 (d, *J* = 8.6, 2H), 6.06 (s, 1H), 3.78 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 168.0, 157.2, 141.9, 141.3, 136.2, 132.7, 130.4, 128.8, 128.7, 126.6, 115.5, 52.5, 26.7; HR-ESI-MS (*m/z*): calcd. for $C_{18}H_{16}O_4Na$ $[M + Na]^+$, 319.0941, found 319.0942.



4

Methyl (*E*)-2-(4-formylphenyl)-3-(4-hydroxyphenyl)acrylate (4)

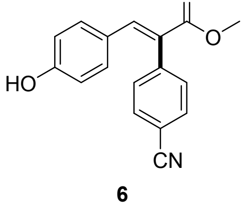
Prepared according to the general procedure using 4-iodobenzaldehyde (23.2 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = I, 12 hours; X = Br, 16 hours; X = Cl, 24 hours). The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **4** as a colorless oil (X = I, 25.1 mg, 89% yield, E/Z > 19:1; X = Br, 23.7 mg, 84% yield, E/Z > 19:1; X = Cl, 15.5 mg, 55% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, CDCl$_3$): δ 10.02 (s, 1H), 7.89 (d, *J* = 8.2, 2H), 7.86 (s, 1H), 7.41 (d, *J* = 8.2, 2H), 6.89 (d, *J* = 8.7, 2H), 6.63 (d, *J* = 8.7, 2H), 6.43 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 192.5, 168.0, 157.5, 143.3, 141.7, 135.5, 132.7, 130.9, 130.2 128.4, 126.3, 115.5, 52.5; HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{15}O_4$ [M + H]$^+$, 283.0965, found 283.0965.



5

Methyl (*E*)-4-(1-(4-hydroxyphenyl)-3-methoxy-3-oxoprop-1-en-2-yl)benzoate (5)

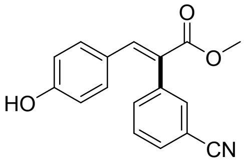
Prepared according to the general procedure using methyl 4-iodobenzenecarboxylate (26.2 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = I, 16 hours; X = Br, 20 hours; X = Cl, 36 hours). The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **5** as a colorless oil (X = I, 26.2 mg, 84% yield, E/Z > 19:1; X = Br, 25.9 mg, 83% yield, E/Z > 19:1; X = Cl, 24.3 mg, 78% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, Acetone-*d*$_6$): 8.88 (s, 1H), 8.06 (d, *J* = 8.3, 2H), 7.83 (s, 1H), 7.39 (d, *J* = 8.3, 2H), 6.98 (d, *J* = 8.8, 2H), 6.69 (d, *J* = 8.8, 2H), 3.93 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (150 MHz, Acetone-*d*$_6$): δ 167.1, 166.2, 158.9, 142.0, 140.6, 132.6, 130.3, 129.7, 129.4, 128.6, 125.9, 125.7, 115.3, 51.5; HR-ESI-MS (*m/z*): calcd. for $C_{18}H_{17}O_5$ [M + H]$^+$, 313.1071, found 313.1071.



6

Methyl (*E*)-2-(4-cyanophenyl)-3-(4-hydroxyphenyl)acrylate (6)

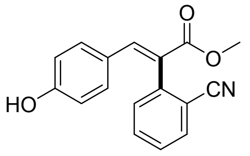
Prepared according to the general procedure using 4-iodobenzonitrile (22.9 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = I, 12 hours; X = Br, 16 hours; X = Cl, 24 hours). The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **6** as a colorless oil (X = I, 23.4 mg, 84% yield, E/Z > 19:1; X = Br, 20.6 mg, 74% yield, E/Z > 19:1; X = Cl, 20.6 mg, 74% yield, E/Z > 19:1). ^{1}H NMR (400 MHz, CD_3CN): δ 7.85 (s, 1H), 7.78 (d, *J* = 8.3, 2H), 7.41 (d, *J* = 8.3, 2H), 6.93 (d, *J* = 8.7, 2H), 6.65 (d, *J* = 8.7, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 167.7, 159.0, 142.6, 141.6, 133.2, 133.1, 131.6, 128.7, 126.2, 119.3, 111.7, 52.4; HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{12}NO_3$ $[M - H]^-$, 278.0823, found 278.0824.



7

Methyl (*E*)-2-(3-cyanophenyl)-3-(4-hydroxyphenyl)acrylate (7)

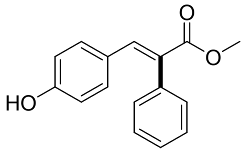
Prepared according to the general procedure using 3-iodobenzonitrile (22.9 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = I, 10 hours; X = Br, 12 hours; X = Cl, 16 hours). The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **7** as a colorless oil (X = I, 20.9 mg, 75% yield, E/Z > 19:1; X = Br, 23.2 mg, 83% yield, E/Z > 19:1; X = Cl, 17.9 mg, 64% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, CD_3CN): δ 7.83 (s, 1H), 7.73 (dt, *J* = 7.7, 1.4, 1H), 7.59 (t, *J* = 1.4, 1H), 7.55 (t, *J* = 7.7, 1H), 7.50 (dt, *J* = 7.7, 1.4, 1H), 7.34 (s, 1H), 6.91 (d, *J* = 8.7, 2H), 6.64 (d, *J* = 8.7, 2H), 3.72 (s, 3H); ^{13}C NMR (150 MHz, CD_3CN): δ 167.9, 159.0, 141.8, 138.8, 135.5, 134.3, 133.2, 132.0, 130.4, 128.4, 126.4, 119.1, 116.0, 113.2, 52.4; HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{12}NO_3$ $[M - H]^-$, 278.0823, found 278.0823.



8

Methyl (*E*)-2-(2-cyanophenyl)-3-(4-hydroxyphenyl)acrylate (8)

Prepared according to the general procedure using 2-iodobenzonitrile (22.9 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = I, 10 hours; X = Br, 12 hours; X = Cl, 16 hours). The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **8** as a colorless oil (X = I, 21.8 mg, 78% yield, E/Z > 19:1; X = Br, 20.9 mg, 75% yield, E/Z > 19:1; X = Cl, 21.2 mg, 76% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, Acetone-*d*$_6$): δ 9.03 (s, 1H), 7.97 (s, 1H), 7.90 (d, *J* = 7.8, 1H), 7.77 (td, *J* = 7.7, 1.0, 1H), 7.64 (td, *J* =7.7, 1.0, 1H), 7.47 (d, *J* = 7.8, 1H), 6.94 (d, *J* = 8.7, 2H), 6.72 (d, *J* = 8.7, 2H), 3.76 (s, 3H); ^{13}C NMR (151 MHz, Acetone-*d*$_6$): δ 166.5, 159.3, 142.6, 140.9, 133.3, 133.1, 132.6, 131.2, 128.6, 125.8, 125.3, 117.3, 115.6, 113.6, 51.6; HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{12}NO_3$ $[M - H]^-$, 278.0823, found 278.0825.

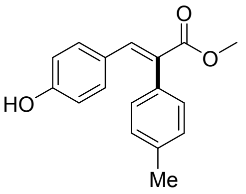


9

Methyl (*E*)-3-(4-hydroxyphenyl)-2-phenylacrylate (9)

Prepared according to the general procedure using iodobenzene (20.4 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **9** as a colorless oil (21.6 mg, 85% yield, E/Z > 19:1). ^{1}H NMR (400 MHz, Acetone-*d*$_6$): δ 8.67 (s, 1H), 7.62 (s, 1H), 7.28 – 720 (m, 3H), 7.11 – 7.02 (m, 2H), 6.81 (d, *J* = 8.8, 2H), 6.51 (d, *J* = 8.8, 2H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, Acetone-*d*$_6$): δ 167.7, 158.6, 139.9, 136.9, 132.6, 129.8, 129.5, 128.6, 127.5, 126.1, 115.2, 51.4; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{13}O_3$ [M -

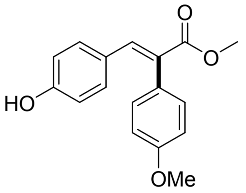
H]$^-$, 253.0870, found 253.0871.



10

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(p-tolyl)acrylate (10)

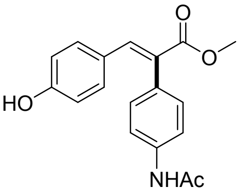
Prepared according to the general procedure using 4-iodotoluene (21.8 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **10** as a colorless oil (22.0 mg, 82% yield, E/Z > 19:1). ^{1}H NMR (400 MHz, Acetone-*d*$_6$): δ 8.71 (s, 1H), 7.60 (s, 1H), 7.07 (d, *J* = 8.0, 2H), 6.95 (d, *J* = 8.0, 2H), 6.84 (d, *J* = 8.7, 2H), 6.51 (d, *J* = 8.7, 2H), 3.55 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, Acetone-*d*$_6$): δ 167.9, 158.6, 139.7, 137.1, 133.8, 132.5, 129.7, 129.5, 129.3, 126.2, 115.2, 51.3, 20.5; HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{15}O_3$ [M - H]$^-$, 267.1027, found 267.1027.



11

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(4-methoxyphenyl)acrylate (11)

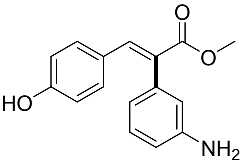
Prepared according to the general procedure using 4-iodoanisole (23.4 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **11**as a colorless oil (23.9 mg, 84% yield, E/Z > 19:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.14 (d, *J* = 8.7, 2H), 6.97 (d, *J* = 8.7, 2H), 6.92 (d, *J* = 8.7, 2H), 6.62 (d, *J* = 8.7, 2H), 5.17 (s, 1H), 3.84 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 159.1, 156.4, 140.1, 132.6, 131.0, 129.6, 128.3, 127.6, 115.2, 114.2, 55.2, 52.4; HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{15}O_4$ $[M - H]^-$, 283.0976, found 283.0977.



12

Methyl (*E*)-2-(4-acetamidophenyl)-3-(4-hydroxyphenyl)acrylate (12)

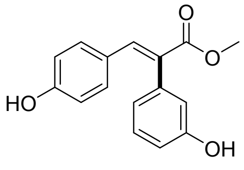
Prepared according to the general procedure using *N*-(4-iodophenyl)acetamide (26.1 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product **12** as a colorless oil (16.2 mg, 52% yield, E/Z = 12:1). ^1H NMR (600 MHz, Acetone-d_6): δ 9.30 (s, 1H), 8.85 (s, 1H), 7.75 (s, 1H), 7.70 (d, J = 8.5, 2H), 7.15 (d, J = 8.5, 2H), 7.03 (d, J = 8.7, 2H), 6.69 (d, J = 8.7, 2H), 3.71 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (150 MHz, Acetone-d_6): δ 168.2, 167.7, 158.6, 139.8, 139.0, 132.5, 131.4, 130.2, 129.8, 126.2, 119.1, 115.4, 51.3, 23.4; HR-ESI-MS (*m/z*): calcd. for $C_{18}H_{18}NO_4$ $[M + H]^+$, 312.1230, found 312.1227.



13

Methyl (*E*)-2-(3-aminophenyl)-3-(4-hydroxyphenyl)acrylate (13)

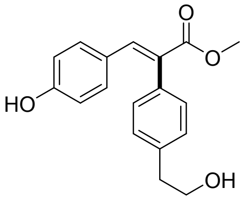
Prepared according to the general procedure using 3-iodoaniline (21.9 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:2) to afford the product **13** as a colorless oil (14.3 mg, 52% yield, E/Z > 19:1). ^1H NMR (600 MHz, CD_3CN): δ 7.67 (s, 1H), 7.22 (s, 1H), 7.11 (t, *J* = 8.0, 1H), 6.95 (d, *J* = 8.7, 2H), 6.70 – 6.57 (m, 3H), 6.48 – 6.39 (m, 2H), 4.13 (s, 2H), 3.69 (s, 3H); ^{13}C NMR (150 MHz, CD_3CN): δ 168.8, 158.7, 149.1, 139.8, 138.2, 133.1, 131.0, 130.1, 127.3, 119.0, 116.0, 115.7, 114.4, 52.2; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{14}NO_3$ $[M - H]^-$, 268.0979, found 268.0978.



14

Methyl (*E*)-2-(3-hydroxyphenyl)-3-(4-hydroxyphenyl)acrylate (14)

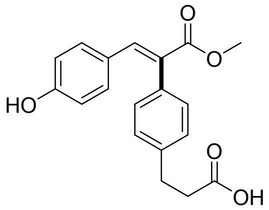
Prepared according to the general procedure using 3-iodophenol (22.0 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:2) to afford the product **14** as a colorless oil (11.1 mg, 41% yield, E/Z = 10:1). ^{1}H NMR (600 MHz, Acetone-*d*$_6$): δ 8.79 (s, 1H), 8.38 (s, 1H), 7.73 (s, 1H), 7.24 (t, *J* = 7.8, 1H), 7.03 (d, *J* = 9.1, 2H), 6.90 – 6.84 (m, 1H), 6.72 – 6.68 (m, 4H), 3.71 (s, 3H); ^{13}C NMR (150 MHz, Acetone-*d*$_6$): δ 167.7, 158.6, 157.7, 139.7, 138.1, 132.6, 129.7, 129.5, 126.1, 120.8, 116.5, 115.2, 114.6, 51.3; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{14}O_4Na$ $[M + Na]^+$, 293.0784, found 293.0785.



15

Methyl (*E*)-2-(4-(2-hydroxyethyl)phenyl)-3-(4-hydroxyphenyl)acrylate (15)

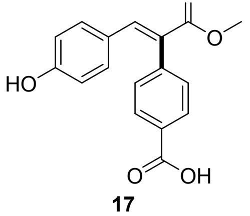
Prepared according to the general procedure using 2-(4-iodophenyl)ethan-1-ol (24.8 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:2) to afford the product **15** as a colorless oil (21.5 mg, 72% yield, E/Z = 12:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.24 (d, *J* = 8.1, 2H), 7.16 (d, *J* = 8.1, 2H), 6.93 (d, *J* = 8.6, 2H), 6.60 (d, *J* = 8.6, 2H), 5.42 (s, 1H), 3.90 (t, *J* = 6.6, 2H), 3.78 (s, 3H), 2.92 (t, *J* = 6.6, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.7, 156.6, 140.3, 137.9, 134.4, 132.5, 130.1, 129.8, 129.4, 127.3, 115.2, 63.6, 52.3, 39.0; HR-ESI-MS (*m/z*): calcd. for $C_{18}H_{17}O_4$ [M - H]$^-$, 297.1132, found 297.1130.



16

(*E*)-3-(4-(1-(4-hydroxyphenyl)-3-methoxy-3-oxoprop-1-en-2-yl)phenyl)propanoic acid (16)

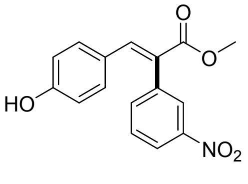
Prepared according to the general procedure using 3-(4-iodophenyl)propanoic acid (27.6 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:1) to afford the product **16** as a colorless oil (21.2 mg, 65% yield, E/Z = 16:1). ^{1}H NMR (600 MHz, Acetone-d_6): δ 8.79 (s, 1H), 7.75 (s, 1H), 7.32 (d, *J* = 7.9, 2H), 7.15 (d, *J* = 7.9, 2H), 6.96 (d, *J* = 8.8, 2H), 6.66 (d, *J* = 8.8, 2H), 3.72 (s, 3H), 2.99 (t, *J* = 7.7, 2H), 2.69 (t, *J* = 7.7, 2H); ^{13}C NMR (150 MHz, Acetone-d_6): δ 173.1, 167.8, 158.6, 140.5, 139.9, 134.5, 132.5, 129.8, 129.5, 128.6, 126.2, 115.2, 51.3, 35.0, 30.5; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{19}O_5$ [M + H]$^+$, 327.1227, found 327.1228.



17

(*E*)-4-(1-(4-hydroxyphenyl)-3-methoxy-3-oxoprop-1-en-2-yl)benzoic acid (17)

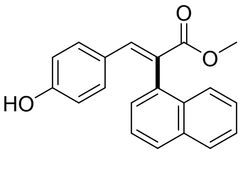
Prepared according to the general procedure using 4-iodobenzoic acid (24.8 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:1) to afford the product **17** as a colorless oil (18.2 mg, 61% yield, E/Z = 16:1). ^{1}H NMR (600 MHz, Acetone-*d*$_6$): δ 8.89 (s, 1H), 8.09 (d, *J* = 8.3, 2H), 7.83 (s, 1H), 7.39 (d, *J* = 8.3, 2H), 6.99 (d, *J* = 8.7, 2H), 6.70 (d, *J* = 8.7, 2H), 3.74 (s, 3H); ^{13}C NMR (150 MHz, Acetone-*d*$_6$): δ 167.2, 166.6, 158.9, 141.9, 140.6, 132.6, 129.9, 129.7, 128.7, 125.8, 125.7, 115.3, 51.4; HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{14}O_5Na$ $[M + Na]^+$,321.0733, found 321.0733.



18

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(3-nitrophenyl)acrylate (18)

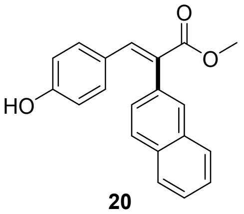
Prepared according to the general procedure using 1-iodo-3-nitrobenzene (25.0 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 18 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **18** as a colorless oil (18.2 mg, 61% yield, E/Z = 11:1). ^{1}H NMR (600 MHz, Acetone-*d*$_6$): δ 8.94 (s, 1H), 8.30 – 8.25 (m, 1H), 8.16 (s, 1H), 7.92 (s, 1H), 7.78 – 7.65 (m, 2H), 7.01 (d, *J* = 8.7, 2H), 6.71 (d, *J* = 8.7, 2H), 3.76 (s, 3H); ^{13}C NMR (150 MHz, Acetone-*d*$_6$): δ 166.9, 159.1, 148.6, 141.5, 138.6, 136.7, 132.7, 130.0, 127.2, 125.3, 125.0, 122.5, 115.4, 51.6; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{12}NO_5$ $[M - H]^-$, 298.0721, found 298.0722.



19

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(naphthalen-1-yl)acrylate (19)

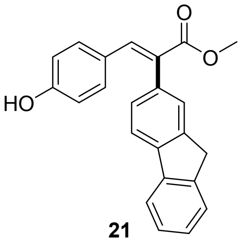
Prepared according to the general procedure using 1-iodonaphthalene (25.4 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **19** as a colorless oil (22.2 mg, 73% yield, E/Z > 19:1). ^1H NMR (400 MHz, CD_3CN): δ 8.07 (s, 1H), 7.99 (d, *J* = 8.3, 2H), 7.77 (d, *J* = 8.4, 1H), 7.66 – 7.51 (m, 2H), 7.51 – 7.42 (m, 1H), 7.37 (d, *J* = 7.0, 1H), 7.27 (s, 1H), 6.82 (d, *J* = 8.7, 2H), 6.51 (d, *J* = 8.7, 2H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 168.7, 158.8, 142.0, 135.1, 134.4, 132.9, 132.3, 129.1, 128.7, 128.0, 127.9, 127.0, 126.8, 126.6, 125.4, 115.7, 52.3; HR-ESI-MS (*m/z*): calcd. for $C_{20}H_{17}O_3$ $[M + H]^+$, 305.1172, found 305.1172.



20

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(naphthalen-2-yl)acrylate (20)

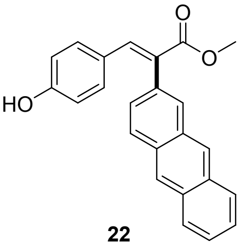
Prepared according to the general procedure using 2-iodonaphthalene (25.4 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **20** as a colorless oil (21.3 mg, 70% yield, E/Z = 13:1). ^1H NMR (600 MHz, CD_3OD): δ 7.90 – 7.84 (m, 3H), 7.77 (d, *J* = 7.8, 1H), 7.67 (s, 1H), 7.52 – 7.42 (m, 2H), 7.27 (dd, *J* = 8.4, 1.4, 1H), 6.89 (d, *J* = 8.7, 2H), 6.50 (d, *J* = 8.7, 2H), 3.74 (s, 3H); ^{13}C NMR (150 MHz, CD_3OD): δ 168.9, 158.8, 140.8, 134.0, 133.7, 132.8, 132.4, 128.8, 128.5, 127.9, 127.7 127.6, 127.3, 125.9, 125.8, 125.7, 114.8, 51.3; HR-ESI-MS (*m/z*): calcd. for $C_{20}H_{15}O_3$ $[M - H]^-$, 303.1027, found 303.1029.



21

Methyl (*E*)-2-(9H-fluoren-2-yl)-3-(4-hydroxyphenyl)acrylate (21)

Prepared according to the general procedure using 2-iodo-9H-fluorene (29.2 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **21** as a colorless oil (17.8 mg, 52% yield, E/Z > 19:1). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 9.93 (s, 1H), 7.93 (d, *J* = 7.7, 2H), 7.75 (s, 1H), 7.60 (d, *J* = 7.4, 1H), 7.49 – 7.39 (m, 2H), 7.34 (t, *J* = 7.3, 1H), 7.19 (d, *J* = 7.6, 1H), 6.97 (d, *J* = 8.7, 2H), 6.57 (d, *J* = 8.7, 2H), 3.93 (s, 2H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 168.2, 159.3, 143.9, 143.7, 141.3, 141.0, 140.4, 135.3, 133.0, 129.2, 128.7, 127.4, 127.3, 126.7, 125.7, 125.5, 120.8, 120.6, 115.8, 52.5, 36.9; HR-ESI-MS (*m/z*): calcd. for $C_{23}H_{17}O_3$ $[M - H]^-$, 341.1183, found 341.1184.

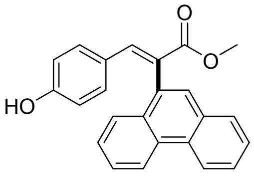


22

Methyl (*E*)-2-(anthracen-2-yl)-3-(4-hydroxyphenyl)acrylate (22)

Prepared according to the general procedure using 2-iodoanthracene (30.4 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **22** as a colorless oil (27.6 mg, 78% yield, E/Z = 10:1). ^{1}H NMR (600 MHz, Acetone-*d*$_6$): δ 8.82 (s, 1H), 8.60 (s, 1H), 8.52 (s, 1H), 8.19 – 8.04 (m, 3H), 7.96 (d, *J* = 0.6, 1H), 7.90 (s, 1H), 7.57

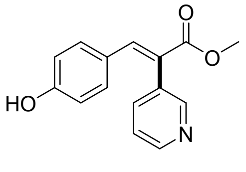
– 7.51 (m, 2H), 7.36 (dd, *J* = 8.7, 1.6, 1H), 7.07 (d, *J* = 8.7, 2H), 6.62 (d, *J* = 8.7, 2H), 3.76 (s, 3H); ^{13}C NMR (150 MHz, Acetone-*d*$_6$): δ 167.7, 140.3, 133.9, 132.6, 132.1, 131.8, 131.0, 128.8, 128.4, 128.1, 127.9, 126.3, 126.1, 125.6, 115.3, 51.4; HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{18}O_3Na$ [M + Na]$^+$, 377.1148, found 377.1150.



23

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(phenanthren-9-yl)acrylate (23)

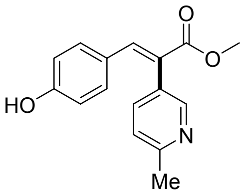
Prepared according to the general procedure using 9-iodophenanthrene (30.4 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **23** as a colorless oil (21.6 mg, 61% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.77 – 8.72 (m, 2H), 8.12 (s, 1H), 7.86 – 7.82 (m, 2H), 7.69 – 7.65 (m, 2H), 7.63 – 7.56 (m, 2H), 7.52 (t, *J* = 7.5, 1H), 6.94 (d, *J* = 8.8, 2H), 6.45 (d, *J* = 8.8, 2H), 5.07 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.9, 156.7, 142.0, 132.9, 132.7, 131.8, 130.8, 130.7, 130.4, 128.8, 127.9, 127.1, 127.0, 126.9, 126.8, 126.7, 125.7, 123.1, 122.6, 115.4, 52.4; HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{17}O_3$ [M - H]$^-$, 353.1183, found 353.1184.



24

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(pyridin-3-yl)acrylate (24)

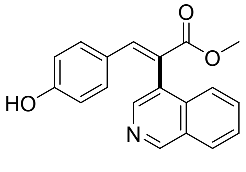
Prepared according to the general procedure using 3-iodopyridine (20.5 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **24** as a colorless oil (19.9 mg, 78% yield, E/Z = 14:1). ^{1}H NMR (600 MHz, DMSO-d_6): δ 10.01 (s, 1H), 8.58 (dd, *J* = 4.8, 1.6, 1H), 8.36 (d, *J* = 1.6, 1H), 7.83 (s, 1H), 7.70 – 7.64 (m, 1H), 7.47 – 7.43 (m, 1H), 6.90 (d, *J* = 8.7, 2H), 6.62 (d, *J* = 8.7, 2H), 3.74 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 167.6, 159.6, 150.5, 149.1, 142.1, 138.1, 133.0, 132.8, 125.7, 125.0, 124.2, 115.9, 52.6; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{14}NO_3$ $[M + H]^+$, 256.0968, found 256.0965.



25

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(6-methylpyridin-3-yl)acrylate (25)

Prepared according to the general procedure using 5-bromo-2-methylpyridine (17.1 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **25** as a colorless oil (16.1 mg, 60% yield, E/Z = 15:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.30 (d, *J* = 1.8, 1H), 7.86 (s, 1H), 7.66 (dd, *J* = 8.0, 1.8, 1H), 7.32 (d, *J* = 8.0, 1H), 6.91 (d, *J* = 8.8, 2H), 6.52 (d, *J* = 8.8, 2H), 3.78 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.9, 160.1, 156.4, 148.6, 142.5, 139.8, 132.7, 130.6, 124.8, 124.3, 123.9, 115.5, 52.3, 23.0; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{16}NO_3$ $[M + H]^+$, 270.1125, found 270.1124.

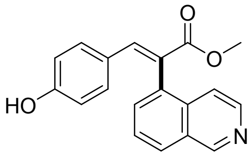


26

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(isoquinolin-4-yl)acrylate (26)

Prepared according to the general procedure using 4-bromoisoquinoline (20.7 mg, 0.10

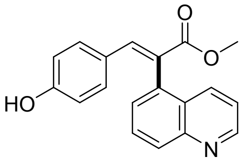
mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 10 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product **26** as a colorless oil (28.1 mg, 92% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, DMSO-*d*$_6$): δ 9.97 (s, 1H), 9.38 (s, 1H), 8.32 (d, *J* = 7.5, 1H), 8.23 (dd, *J* = 7.0, 2.0, 1H), 8.09 (s, 1H), 7.75 – 7.70 (m, 2H), 7.71 – 7.63 (m, 1H), 6.79 (d, *J* = 8.8, 2H), 6.50 (d, *J* = 8.8, 2H), 3.65 (s, 3H); ^{13}C NMR (151 MHz, DMSO-*d*$_6$): δ 167.9, 159.7, 152.9, 143.5, 134.4, 132.7, 131.6, 128.8, 128.5, 128.2, 125.1, 124.1, 123.3, 116.0, 52.6; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{16}NO_3$ $[M + H]^+$, 306.1125, found 306.1125.



27

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(isoquinolin-5-yl)acrylate (27)

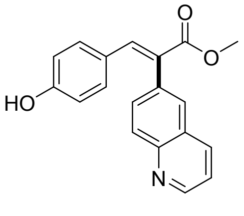
Prepared according to the general procedure using 5-bromoisoquinoline (20.7 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 20 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product **27** as a colorless oil (24.4 mg, 80% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, DMSO-*d*$_6$): δ 9.96 (s, 1H), 9.40 (s, 1H), 8.43 (d, *J* = 5.9, 1H), 8.20 (d, *J* = 8.2, 1H), 8.05 (s, 1H), 7.81 – 7.71 (m, 1H), 7.63 (dd, *J* = 7.0, 0.8, 1H), 7.48 (d, *J* = 5.9, 1H), 6.74 (d, *J* = 8.8, 2H), 6.48 (d, *J* = 8.8, 2H), 3.64 (s, 3H); ^{13}C NMR (150 MHz, DMSO-*d*$_6$): δ 167.9, 159.6, 153.4, 143.9, 142.7, 134.2, 133.8, 132.8, 132.2, 129.0, 128.3, 128.1, 125.0, 117.9, 115.9, 52.6; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{16}NO_3$ $[M + H]^+$, 306.1125, found 306.1126.



28

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(quinolin-5-yl)acrylate (28)

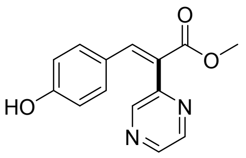
Prepared according to the general procedure using 5-bromoquinoline (20.7 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product **28** as a colorless oil (20.4 mg, 67% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, DMSO-d_6): δ 9.94 (s, 1H), 8.92 (dd, *J* = 4.1, 1.6, 1H), 8.13 – 7.96 (m, 3H), 7.82 (dd, *J* = 8.5, 7.1, 1H), 7.53 – 7.41 (m, 2H), 6.74 (d, *J* = 8.8, 2H), 6.47 (d, *J* = 8.8, 2H), 3.64 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 167.9, 159.6, 151.2, 148.5, 142.6, 135.2, 133.5, 132.8, 130.1, 129.6, 128.2, 126.9, 125.3, 125.1, 122.3, 115.9, 52.6; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{16}NO_3$ $[M + H]^+$, 306.1125, found 306.1125.



29

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(quinolin-6-yl)acrylate (29)

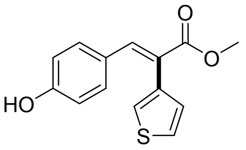
Prepared according to the general procedure using 6-bromoquinoline (20.7 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product **29** as a colorless oil (20.7 mg, 68% yield, E/Z = 10:1). ^{1}H NMR (600 MHz, Acetone-d_6): δ 8.95 (dd, *J* = 4.2, 1.7, 1H), 8.87 (s, 1H), 8.30 (d, *J* = 7.8, 1H), 8.10 (d, *J* = 8.6, 1H), 7.90 (s, 1H), 7.83 (d, *J* = 1.8, 1H), 7.62 (dd, *J* = 8.6, 1.8, 1H), 7.53 (dd, *J* = 7.8, 4.2, 1H), 7.00 (d, *J* = 8.7, 2H), 6.64 (d, *J* = 8.7, 2H), 3.74 (s, 3H); ^{13}C NMR (150 MHz, Acetone-d_6): δ 167.5, 158.8, 150.7, 147.8, 140.6, 135.8, 135.1, 132.6, 131.6, 129.6, 128.9, 128.5, 125.9, 121.5, 115.3, 115.2, 51.4; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{16}NO_3$ $[M + H]^+$, 306.1125, found 306.1125.



30

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(pyrazin-2-yl)acrylate (30)

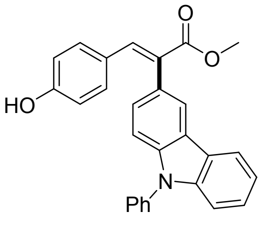
Prepared according to the general procedure using 2-iodopyrazine (20.6 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 12 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product **30** as a colorless oil (18.7 mg, 73% yield, E/Z = 11:1). ^1H NMR (600 MHz, CD_3CN) δ = 8.71 – 8.67 (m, 1H), 8.59 (d, *J* = 2.5, 1H), 8.49 (d, *J* = 1.2, 1H), 7.97 (s, 1H), 7.52 (s, 1H), 6.85 (d, *J* = 8.7, 2H), 6.68 (d, *J* = 8.7, 2H), 3.75 (s, 3H); ^{13}C NMR (150 MHz, CD_3CN): δ 167.7, 159.3, 152.6, 146.7, 145.2, 144.1, 143.7, 133.1, 131.4, 126.9, 126.1, 116.3, 116.0, 52.5; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{13}N_2O_3$ $[M + H]^+$, 257.0921, found 257.0921.



31

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(thiophen-3-yl)acrylate (31)

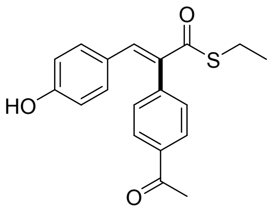
Prepared according to the general procedure using 3-iodothiophene (21.0 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **31** as a colorless oil (14.6 mg, 56% yield, E/Z = 13:1). ^1H NMR (600 MHz, CD_3CN): δ 7.78 (s, 1H), 7.48 (dd, J = 4.9, 3.0, 1H), 7.36 (s, 1H), 7.23 (dd, J = 3.0, 1.1, 1H), 7.01 (d, J = 8.7, 2H), 6.96 (dd, J = 4.9, 1.1, 1H), 6.68 (d, J = 8.7, 2H), 3.75 (s, 3H); ^{13}C NMR (150 MHz, CD_3CN): δ 168.8, 159.1, 141.6, 137.0, 133.1, 130.1, 127.5, 126.8, 125.7, 125.5, 116.1, 52.6; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{13}O_3S$ $[M + H]^+$, 261.0580, found 261.0580.



32

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(9-phenyl-9H-carbazol-3-yl)acrylate (32)

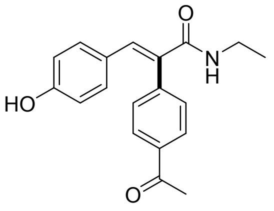
Prepared according to the general procedure using 3-iodo-9-phenyl-9H-carbazole (36.9 mg, 0.10 mmol), **2** (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **32** as a colorless oil (23.0 mg, 55% yield, E/Z = 18:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, J = 7.7, 1H), 8.01 (d, J = 1.1, 1H), 7.87 (s, 1H), 7.66 – 7.57 (m, 4H), 7.49 – 7.37 (m, 4H), 7.31 – 7.27 (m, 1H), 7.24 – 7.20 (m, 1H), 6.96 (d, J = 8.8, 2H), 6.55 (d, J = 8.8, 2H), 3.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.3, 156.5, 141.2, 140.4, 140.2, 137.6, 132.7, 130.5, 129.9, 127.8, 127.7, 127.5, 127.1, 126.1, 123.8, 123.4, 121.6, 120.5, 120.0, 115.2, 110.2, 109.9, 52.3; HR-ESI-MS (*m/z*): calcd. for $C_{28}H_{21}NO_3Na$ $[M + Na]^+$, 442.1414, found 442.1411.



33

***S*-ethyl (*E*)-2-(4-acetylphenyl)-3-(4-hydroxyphenyl)prop-2-enethioate (33)**

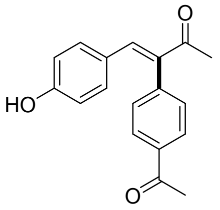
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), *S*-ethyl (*E*)-3-(4-hydroxyphenyl)prop-2-enethioate (41.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 16 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **33** as a colorless oil (26.1 mg, 80% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.3, 2H), 7.70 (s, 1H), 7.41 (d, *J* = 8.3, 2H), 6.91 (d, *J* = 8.7, 2H), 6.64 (d, *J* = 8.7, 2H), 5.94 (s, 1H), 2.93 (q, *J* = 7.4, 2H), 2.66 (s, 3H), 1.26 (t, *J* = 7.4, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.3, 192.6, 157.3, 141.4, 136.9, 136.8, 135.9, 133.1, 131.2, 128.9, 126.4, 115.6, 26.7, 24.3, 14.4; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{18}O_3SNa$ $[M + Na]^+$, 349.0869, found 349.0872.



34

(*E*)-2-(4-acetylphenyl)-*N*-ethyl-3-(4-hydroxyphenyl)acrylamide (34)

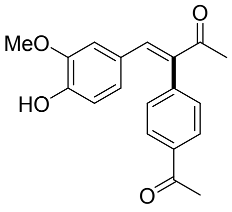
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), (*E*)-*N*-ethyl-3-(4-hydroxyphenyl)acrylamide (38.2 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:2) to afford the product **34** as a colorless oil (18.2 mg, 59% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, DMSO-d_6): δ 9.71 (s, 1H), 7.99 (d, *J* = 8.3, 2H), 7.38 (t, *J* = 5.6, 1H), 7.35 (s, 1H), 7.30 (d, *J* = 8.3, 2H), 6.81 (d, *J* = 8.7, 2H), 6.55 (d, *J* = 8.7, 2H), 3.18 – 3.11 (m, 2H), 2.61 (s, 3H), 1.02 (t, *J* = 7.1, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 198.1, 167.3, 158.3, 142.5, 136.4, 134.8, 133.4, 131.9, 130.6, 129.2, 126.0, 115.7, 34.6, 27.2, 15.3; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{18}NO_3$ $[M - H]^-$, 308.1292, found 308.1294.



35

(*E*)-3-(4-acetylphenyl)-4-(4-hydroxyphenyl)but-3-en-2-one (35)

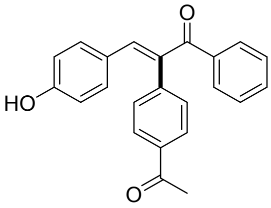
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), (*E*)-4-(4-hydroxyphenyl)but-3-en-2-one (32.4 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **35** as a colorless oil (25.8 mg, 92% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, CD_3CN): δ 7.98 (d, *J* = 8.4, 2H), 7.70 (s, 1H), 7.30 (s, 1H), 7.25 (d, *J* = 8.4, 2H), 6.93 (d, *J* = 8.7, 2H), 6.61 (d, *J* = 8.7, 2H), 2.59 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (151 MHz, CD_3CN): δ 198.8, 198.3, 159.0, 143.4, 141.0, 138.7, 137.0, 133.3, 130.8, 129.2, 126.9, 115.9, 26.9, 26.6; HR-ESI-MS (*m/z*): calcd. for $C_{18}H_{15}O_3$ [M - H]$^-$, 279.1027, found 279.1025.



36

(*E*)-3-(4-acetylphenyl)-4-(4-hydroxy-3-methoxyphenyl)but-3-en-2-one (36)

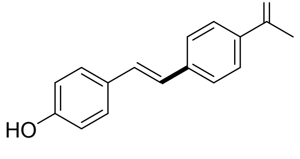
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), (*E*)-4-(4-hydroxy-3-methoxyphenyl)but-3-en-2-one (38.4 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **36** as a colorless oil (25.4 mg, 82% yield, E/Z > 19:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.3, 2H), 7.64 (s, 1H), 7.33 (d, *J* = 8.3, 2H), 6.82 – 6.69 (m, 2H), 6.36 (d, *J* = 1.3, 1H), 5.84 (s, 1H), 3.42 (s, 3H), 2.64 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 197.7, 147.4, 146.0, 142.9, 140.5, 137.7, 136.4, 130.4, 129.0, 126.4, 114.4, 112.2, 55.26, 27.4, 26.7; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{17}O_4$ $[M - H]^-$, 309.1132, found 309.1133.



37

(*E*)-2-(4-acetylphenyl)-3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one (37)

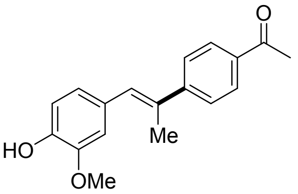
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), (*E*)-3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one (44.8 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **37** as a colorless oil (25.8 mg, 71% yield, E/Z = 8:1). ^{1}H NMR (600 MHz, DMSO-d_6): δ 9.96 (s, 1H), 8.00 (d, *J* = 8.1, 2H), 7.78 (d, *J* = 7.4, 2H), 7.62 (t, *J* = 7.1, 1H), 7.53 (t, *J* = 7.6, 2H), 7.41 (d, *J* = 8.1, 2H), 7.26 (s, 1H), 6.93 (d, *J* = 8.7, 2H), 6.61 (d, *J* = 8.7, 2H), 2.62 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 198.0, 197.0, 159.5, 142.7, 138.8, 136.8, 136.4, 132.9, 132.4, 130.6, 129.7, 129.1, 128.9, 126.3, 125.2, 115.9, 27.2; HR-ESI-MS (*m/z*): calcd. for $C_{23}H_{17}O_3$ $[M - H]^-$, 341.1183, found 341.1183.



38

(*E*)-1-(4-(4-hydroxystyryl)phenyl)ethan-1-one (38)

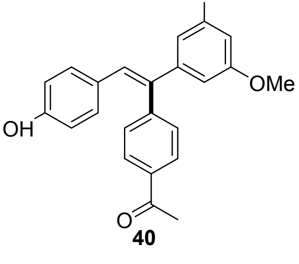
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), 4-vinylphenol (24.0 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **38** as a colorless oil (15.0 mg, 63% yield, E/Z = 15:1). ^{1}H NMR (600 MHz, DMSO-d_6): δ 9.68 (s, 1H), 7.94 (d, *J* = 8.4, 2H), 7.68 (d, *J* = 8.4, 2H), 7.49 (d, *J* = 8.6, 2H), 7.33 (d, *J* = 16.4, 1H), 7.11 (d, *J* = 16.4, 1H), 6.80 (d, *J* = 8.6, 2H), 2.57 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 197.6, 158.4, 142.8, 135.5, 131.8, 129.2, 128.8, 128.2, 126.5, 124.5, 116.1, 27.1; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{14}O_2Na$ [M + Na]$^+$, 261.0886, found 261.0887.



39

(*E*)-1-(4-(1-(4-hydroxy-3-methoxyphenyl)prop-1-en-2-yl)phenyl)ethan-1-one (39)

Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), (*E*)-2-methoxy-4-(prop-1-en-1-yl)phenol (32.8 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **39** as a colorless oil (15.5 mg, 55% yield, E/Z = 17:1). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.9 (d, *J* = 8.5, 2H), 7.59 (d, *J* = 8.5, 2H), 6.97 – 6.91 (m, 2H), 6.89 (s, 1H), 6.87 (s, 1H), 5.66 (s, 1H), 3.92 (s, 3H), 2.62 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 197.6, 148.8, 146.3, 144.8, 135.6, 134.9, 130.2, 129.6, 128.5, 126.0, 122.6, 114.3, 111.8, 56.0, 26.5, 17.3; HR-ESI-MS (*m/z*): calcd. for $C_{18}H_{17}O_3$ [M - H]$^-$, 281.1183, found 281.1187.

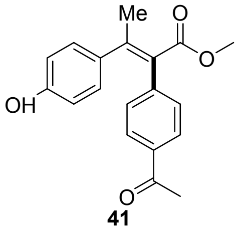


40

(*E*)-1-(4-(1-(3,5-dimethoxyphenyl)-2-(4-hydroxyphenyl)vinyl)phenyl)ethan-1-one

(40)

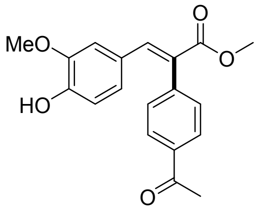
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), (*E*)-4-(3,5-dimethoxystyryl)phenol (51.2 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **40** as a colorless oil (20.9 mg, 56% yield, E/Z = 6:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.3, 2H), 7.31 (d, *J* = 8.3, 2H), 6.96 (s, 1H), 6.88 (d, *J* = 8.6, 2H), 6.62 (d, *J* = 8.6, 2H), 6.40 (s, 3H), 3.75 (s, 6H), 2.62 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.5, 160.7, 155.2, 145.1, 139.4, 135.9, 131.1, 130.8, 129.1, 128.8, 127.2, 115.2, 108.1, 106.1, 99.5, 55.4, 26.6; HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{21}O_4$ $[M - H]^-$, 373.1445, found 373.1444.



41

Methyl (*E*)-2-(4-acetylphenyl)-3-(4-hydroxyphenyl)but-2-enoate (41)

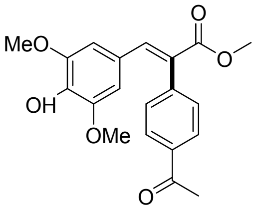
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), methyl (*E*)-3-(4-hydroxyphenyl)but-2-enoate (38.4 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **41** as a colorless oil (16.1 mg, 52% yield, E/Z = 10:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.5, 2H), 7.09 (d, *J* = 8.5, 2H), 6.87 (d, *J* = 8.7, 2H), 6.60 (d, *J* = 8.7, 2H), 5.21 (s, 1H), 3.77 (s, 3H), 2.52 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 197.9, 169.3, 155.1, 146.9, 143.0, 135.2, 133.8, 130.3, 130.2, 130.0, 128.0, 115.1, 52.0, 26.5, 23.4. HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{17}O_4$ $[M - H]^-$, 309.1132, found 309.1134.



42

Methyl (*E*)-2-(4-acetylphenyl)-3-(4-hydroxy-3-methoxyphenyl)acrylate (42)

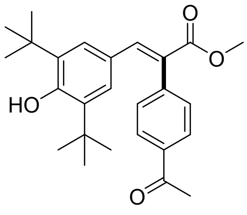
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), methyl (*E*)-3-(4-hydroxy-3-methoxyphenyl)acrylate (41.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **42** as a colorless oil (31.0 mg, 92% yield, E/Z > 19:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.3, 2H), 7.83 (s, 1H), 7.38 (d, *J* = 8.3, 2H), 6.79 – 6.68 (m, 2H), 6.38 (d, *J* = 1.4, 1H), 5.80 (s, 1H), 3.78 (s, 3H), 3.43 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 167.8, 147.2, 146.0, 141.9, 141.5, 136.3, 130.5, 128.7, 128.6, 126.4, 126.0, 114.4, 112.2, 55.3, 52.4, 26.7; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{17}O_5$ $[M - H]^-$, 325.1081, found 325.1078.



43

Methyl (*E*)-2-(4-acetylphenyl)-3-(4-hydroxy-3,5-dimethoxyphenyl)acrylate (43)

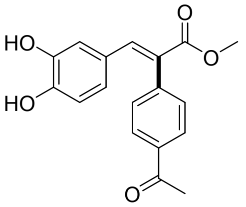
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0. 10 mmol), methyl (*E*)-3-(4-hydroxy-3,5-dimethoxyphenyl)acrylate (47.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **43** as a colorless oil (31.0 mg, 87% yield, E/Z = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.3, 2H), 7.82 (s, 1H), 7.39 (d, *J* = 8.3, 2H), 6.29 (s, 2H), 5.69 (s, 1H), 3.79 (s, 3H), 3.56 (s, 6H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 167.7, 146.6, 141.9, 141.6, 136.3, 130.5, 129.1, 128.7, 125.2, 107.9, 55.8, 52.5, 26.7; HR-ESI-MS (*m/z*): calcd. for $C_{20}H_{19}O_6$ $[M - H]^-$, 355.1187, found 355.1186.



44

Methyl (*E*)-2-(4-acetylphenyl)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)acrylate (44)

Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), methyl (*E*)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)acrylate (58.0 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **44** as a colorless oil (35.9 mg, 88% yield, E/Z > 19:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.2, 2H), 7.85 (s, 1H), 7.38 (d, *J* = 8.2, 2H), 6.92 (s, 2H), 5.43 (s, 1H), 3.77 (s, 3H), 2.63 (s, 3H), 1.22 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 168.1, 155.5, 142.5, 142.4, 136.2, 135.7, 130.4, 128.8, 128.7, 127.7, 125.2, 52.3, 34.1, 29.9, 26.7; HR-ESI-MS (*m/z*): calcd. for $C_{26}H_{31}O_4$ $[M - H]^-$, 407.2228, found 407.2222.

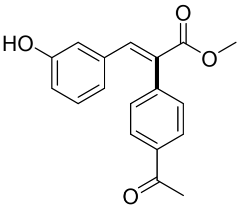


45

Methyl (*E*)-2-(4-acetylphenyl)-3-(3,4-dihydroxyphenyl)acrylate (45)

Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), methyl (*E*)-3-(3,4-dihydroxyphenyl)acrylate (38.8 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product **45** as a colorless oil (25.0 mg, 80% yield, E/Z = 14:1). ^{1}H NMR

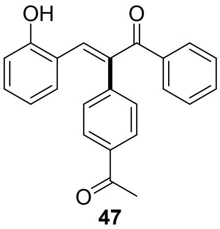
(400 MHz, Acetone-d_6): δ = 8.03 (d, J = 8.3, 3H), 7.77 (s, 1H), 7.38 (d, J = 8.3, 2H), 6.70 (d, J = 8.2, 1H), 6.63 – 6.53 (m, 2H), 3.72 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d_6): δ 196.9, 167.2, 147.1, 144.7, 141.8, 140.9, 136.3, 130.2, 128.5, 126.2, 124.3, 117.2, 115.1, 51.5, 25.9; HR-ESI-MS (*m/z*): calcd. for $C_{18}H_{15}O_5$ [M - H]$^-$, 311.0925, found 311.0926.



46

Methyl (*E*)-2-(4-acetylphenyl)-3-(3-hydroxyphenyl)acrylate (46)

Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), methyl (*E*)-3-(3-hydroxyphenyl)acrylate (35.6 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **46** as a colorless oil (11.8 mg, 40% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.95 (d, J = 8.4, 2H), 7.84 (s, 1H), 7.34 (d, J = 8.4, 2H), 7.07 – 7.01 (m, 1H), 6.72 (dd, J = 8.0, 2.2, 1H), 6.63 (d, J = 7.7, 1H), 6.48 (s, 1H), 3.80 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 198.0, 167.6, 155.5, 141.0, 136.4, 135.6, 131.7, 130.2, 129.6, 128.6, 123.3, 116.9, 116.7, 52.5, 26.6; HR-ESI-MS (*m/z*): calcd. for $C_{18}H_{15}O_4$ [M - H]$^-$, 295.0976, found 295.0976.

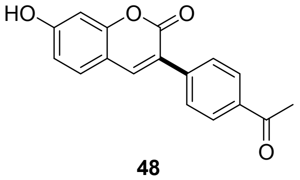


47

(*E*)-2-(4-acetylphenyl)-3-(2-hydroxyphenyl)-1-phenylprop-2-en-1-one (47)

Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), (*E*)-3-(2-hydroxyphenyl)-1-phenylprop-2-en-1-one (44.8 mg, 0.20 mmol),

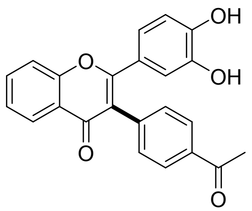
Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 36 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **47** as a colorless oil (15.4 mg, 45% yield, E/Z > 19:1). ^{1}H NMR (600 MHz, DMSO-*d*$_6$): δ 10.03 (s, 1H), 7.96 (d, *J* = 8.3, 2H), 7.87 – 7.76 (m, 2H), 7.64 (t, *J* = 7.4, 1H), 7.58 – 7.50 (m, 3H), 7.39 (d, *J* = 8.3, 2H), 7.18 – 7.05 (m, 1H), 6.87 (d, *J* = 7.7, 1H), 6.74 – 6.59 (m, 1H), 6.51 (t, *J* = 7.5, 1H), 2.59 (s, 3H); ^{13}C NMR (150 MHz, DMSO-*d*$_6$): δ 198.0, 197.2, 157.1, 142.5, 138.7, 138.6, 137.7, 136.3, 132.7, 131.4, 130.6, 130.2, 129.8, 128.9, 121.5, 119.1, 116.3, 27.1; HR-ESI-MS (*m/z*): calcd. for $C_{23}H_{17}O_3$ [M - H]$^-$, 341.1183, found 341.1181.



48

3-(4-acetylphenyl)-7-hydroxy-2H-chromen-2-one (48)

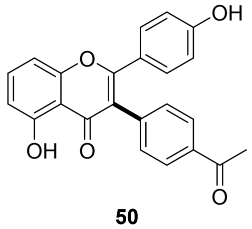
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), 7-hydroxy-2H-chromen-2-one (32.4 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = Br, 24 hours; X = Cl, 36 hours). The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product **48** as a colorless oil (X = Br, 21.8 mg, 78% yield; X = Cl, 11.8 mg, 42% yield). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 10.75 (s, 1H), 8.31 (s, 1H), 8.02 (d, *J* = 8.5, 2H), 7.87 (d, *J* = 8.5, 2H), 7.65 (d, *J* = 8.6, 1H), 6.85 (dd, *J* = 8.6, 2.2, 1H), 6.78 (d, *J* = 2.2, 1H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 198.0, 162.2, 160.3, 155.7, 142.7, 140.2, 136.4, 130.8, 128.8, 128.5, 121.4, 114.1, 112.3, 102.2, 27.3; HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{11}O_4$ [M - H]$^-$, 279.0663, found 279.0661.



49

3-(4-acetylphenyl)-2-(3,4-dihydroxyphenyl)-4H-chromen-4-one (49)

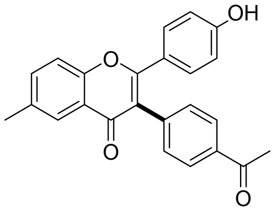
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), 2-(3,4-dihydroxyphenyl)-4H-chromen-4-one (50.8 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = Br, 24 hours; X = Cl, 36 hours). The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:2) to afford the product **49** as a yellow powder (X = Br, 31.6 mg, 85% yield; X = Cl, 17.1 mg, 46% yield). ^1H NMR (400 MHz, DMSO-d_6): δ 9.75 (s, 1H), 9.26 (s, 1H), 8.09 (dd, *J* = 7.9, 1.3, 1H), 7.92 (d, *J* = 8.2, 2H), 7.89 – 7.82 (m, 1H), 7.72 (d, *J* = 8.3, 1H), 7.52 (t, *J* = 7.5, 1H), 7.35 (d, *J* = 8.2, 2H), 6.91 (d, *J* = 1.7, 1H), 6.71 – 6.61 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.1, 176.2, 162.6, 155.9, 148.4, 145.4, 139.4, 135.8, 134.8, 131.9, 128.3, 125.9, 125.8, 123.7, 123.1, 122.3, 120.8, 118.8, 117.2, 115.6, 27.2; HR-ESI-MS (*m/z*): calcd. for $C_{23}H_{16}O_5Na$ $[M + Na]^+$, 395.0890, found 395.0889.



50

3-(4-acetylphenyl)-5-hydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one (50)

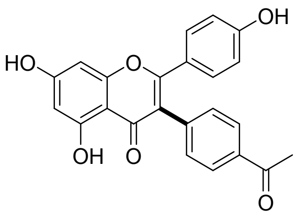
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), 5-hydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one (50.8 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = Br, 24 hours; X = Cl, 36 hours). The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:2) to afford the product **50** as a yellow powder (X = Br, 26.0 mg, 70% yield; X = Cl, 16.7 mg, 45% yield). ^1H NMR (400 MHz, DMSO-d_6): δ 12.72 (s, 1H), 10.20 (s, 1H), 7.93 (d, *J* = 8.2, 2H), 7.71 (t, *J* = 8.3, 1H), 7.38 (d, *J* = 8.2, 2H), 7.26 (d, *J* = 8.7, 2H), 7.16 (d, *J* = 8.3, 1H), 6.85 (d, *J* = 8.2, 1H), 6.70 (d, *J* = 8.7, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.1, 182.1, 163.7, 160.5, 160.4, 156.1, 138.0, 136.6, 136.2, 132.0, 128.5, 122.7, 119.5, 115.7, 111.3, 109.9, 107.8, 27.2; HR-ESI-MS (*m/z*): calcd. for $C_{23}H_{15}O_5$ [M - H]$^-$, 371.0925, found 371.0930.



51

3-(4-acetylphenyl)-2-(4-hydroxyphenyl)-6-methyl-4H-chromen-4-one (51)

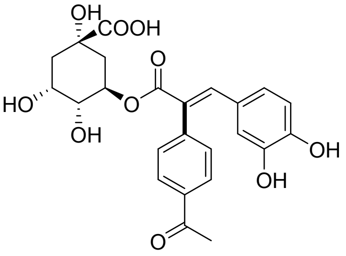
Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), 4'-hydroxy-6-methylflavone (50.4 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = Br, 24 hours; X = Cl, 36 hours). The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product **51** as a yellow powder (X = Br, 25.9 mg, 70% yield; X = Cl, 18.5 mg, 50% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.13 (s, 1H), 7.95 – 7.85 (m, 3H), 7.70 – 7.55 (m, 2H), 7.33 (d, *J* = 8.3, 2H), 7.23 (d, *J* = 8.7, 2H), 6.70 (d, *J* = 8.7, 2H), 2.59 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.1, 176.1, 162.3, 159.9, 154.2, 140.1, 139.4, 135.9, 135.4, 132.0, 131.8, 128.3, 125.0, 123.4, 122.8, 120.7, 118.7, 115.6, 27.2, 21.0; HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{17}O_4$ [M - H]$^-$, 369.1132, found 369.1136.



52

3-(4-acetylphenyl)-5,7-dihydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one (52)

Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), 5,7-dihydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one (54.0 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = Br, 24 hours; X = Cl, 36 hours). The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:2) to afford the product **52** as a yellow powder (X = Br, 30.3 mg, 78% yield; X = Cl, 15.5 mg, 40% yield). ^1H NMR (400 MHz, Acetone-*d*$_6$): δ 12.83 (s, 1H), 7.81 (d, *J* = 8.4, 2H), 7.27 (d, *J* = 8.4, 2H), 7.18 (d, *J* = 8.7, 2H), 6.65 (d, *J* = 8.7, 2H), 6.37 (d, *J* = 1.6, 1H), 6.17 (d, *J* = 1.6, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, Acetone-*d*$_6$): δ 196.8, 180.8, 164.3, 162.7, 159.7, 157.8, 138.0, 136.1, 131.7, 131.6, 127.8, 123.6, 119.0, 115.1, 104.0, 98.9, 93.7, 25.8; HR-ESI-MS (*m/z*): calcd. for $C_{23}H_{15}O_6$ $[M - H]^-$, 387.0874, found 387.0876.

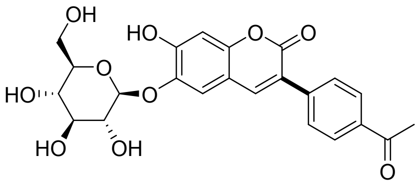


53

(1*S*,3*R*,4*R*,5*R*)-3-(((*E*)-2-(4-acetylphenyl)-3-(3,4-dihydroxyphenyl)acryloyl)oxy)-1,4,5-trihydroxycyclohexane-1-carboxylic acid (53)

Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), chlorogenic acid (70.8 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = Br, 24 hours; X = Cl, 36 hours). The crude mixture was purified by C_{18}-reversed phase silica gel chromatography (CH_3OH/H_2O 1:6) to afford the product **53** as a white powder (X = Br, 27.4 mg, 58% yield, E/Z = 9:1; X = Cl, 18.4 mg, 39% yield, E/Z = 9:1). $[\alpha]_D^{21}$ = -57 (c = 0.14, CH_3OH). ^1H NMR (600 MHz, CD_3OD): δ 8.04 (d, *J* = 8.3, 2H), 7.79 (s, 1H), 7.39 (d, *J* = 8.3, 2H), 6.60 (d, *J* = 8.3, 1H), 6.60 – 6.50 (m, 1H), 6.51 (d, *J* = 2.0, 1H), 5.35 (td, *J* = 8.5, 4.5, 1H), 4.09 (dt, *J* = 6.2, 3.2, 1H), 3.66 (dd, *J* = 8.1, 3.2, 1H), 2.66 (s, 3H), 2.25 – 2.07

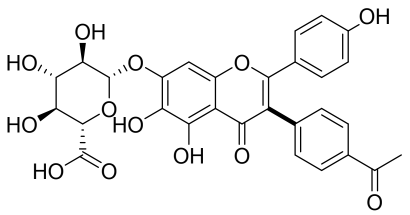
(m, 3H), 2.10 – 2.00 (m, 1H); ^{13}C NMR (150 MHz, CD_3OD): δ 199.0, 175.4, 167.1, 147.3, 144.6, 142.1, 141.7, 136.0, 130.3, 128.5, 128.4, 128.0, 126.0, 124.1, 117.2, 114.6, 74.6, 71.5, 36.7, 25.4; HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{24}O_{10}Na$ $[M + Na]^+$, 495.1262, found 495.1261.



54

3-(4-acetylphenyl)-7-hydroxy-6-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)-2H-chromen-2-one (54)

Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), esculin (68.0 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: (X = Br, 24 hours; X = Cl, 36 hours). The crude mixture was purified by C_{18}-reversed phase silica gel chromatography (CH_3OH/H_2O 1:9) to afford the product **54** as a white powder (X = Br, 36.6 mg, 80% yield; X = Cl, 21.1 mg, 46% yield). $[\alpha]_D^{21}$ = -60 (c = 0.23, CH_3OH). ^{1}H NMR (600 MHz, CD_3OD): δ 8.02 (s, 1H), 7.93 (d, *J* = 8.5, 2H), 7.75 (d, *J* = 8.5, 2H), 7.41 (s, 1H), 6.74 (s, 1H), 4.76 – 4.74 (m, 1H), 3.87 (dd, *J* = 12.0, 2.0, 1H), 3.63 (dd, *J* = 12.0, 6.1, 1H), 3.51 – 3.37 (m, 3H), 3.35 – 3.33 (m, 1H), 2.53 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD): δ 198.7, 161.1, 152.2, 151.0, 143.3, 142.2, 140.1, 136.3, 128.3, 128.0, 122.4, 115.5, 112.0, 102.8, 77.1, 76.2, 73.4, 70.0, 61.2, 25.3; HR-ESI-MS (*m/z*): calcd. for $C_{23}H_{22}O_{10}Na$ $[M + Na]^+$, 481.1105, found 481.1108.



55

(2*S*,3S,4*S*,5*R*,6S)-6-((3-(4-acetylphenyl)-5,6-dihydroxy-2-(4-hydroxyphenyl)-4-oxo-4H-chromen-7-yl)oxy)-3,4,5-trihydroxytetrahydro-2H-pyran-2-carboxylic acid (55)

Prepared according to the general procedure using 4'-bromoacetophenone (19.9 mg, 0.10 mmol), scutellarin (92.4 mg, 0.20 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol), and DMSO (1.0 mL). Time of irradiation: 24 hours. The crude mixture was purified by C_{18}-reversed phase silica gel chromatography (CH_3OH/H_2O 1:4) to afford the product **55** as a yellow powder (23.2 mg, 40% yield). $[\alpha]_D^{21}$ = -250 (c = 0.20, CH_3OH). ^1H NMR (600 MHz, CD_3OD): δ 7.92 (d, *J* = 8.1, 2H), 7.32 (d, *J* = 8.1, 2H), 7.18 (d, *J* = 8.6, 2H), 6.88 (s, 1H), 6.62 (d, *J* = 8.6, 2H), 5.17 (d, *J* = 7.5, 1H), 4.14 (d, *J* = 9.8, 1H), 3.68 – 3.56 (m, 3H), 2.59 (s, 3H); ^{13}C NMR (150 MHz, CD_3OD): δ 198.9, 181.3, 170.6, 163.7, 159.9, 151.2, 149.7, 146.9, 138.3, 135.9, 131.6, 130.5, 127.9, 123.0, 118.3, 115.6, 114.7, 105.9, 100.9, 94.1, 75.4, 75.2, 73.0, 71.5, 25.3; HR-ESI-MS (*m/z*): calcd. for $C_{29}H_{24}O_{13}Na$ $[M + Na]^+$, 603.1109, found 603.1105.

References

[1] a) Silvi, M., Arceo, E., Jurberg, I.D., Cassani, C., Melchiorre, P. *J. Am. Chem. Soc.* **2015**, *137*, 6120-6123. b) Bahamonde, A., Melchiorre, P. *J. Am. Chem. Soc.* **2016**, *138*, 8019-8030.

[2] Liang, M., Wang, Z.-Y., Zhang, L., Han, H.-Y., Sun Z., Xue, S. *Renewable Energy* **2011**, *36*, 2711-2716.

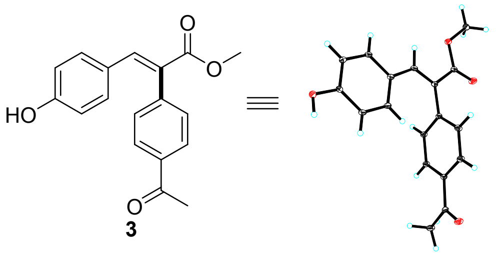
[3] S. Murov, L., *Handbook of Photochemistry*, Marcel Dekker, New York, **1973**

[4] a) Braslavsky, S. E. Glossary of terms used in photochemistry, (IUPAC Recommendations

2006). *Pure and Applied Chemistry* **2007**, *79*, 293-465. b) Sun, L. Bolton, J. R. *J. Phys. Chem.* **1996**, *100*, 4127-4134.

[5] Hamai, S.; Hirayama, F. *J. Phys. Chem.* **1983**, *87*, 83-89.

Crystal data and structure refinement for compound 3

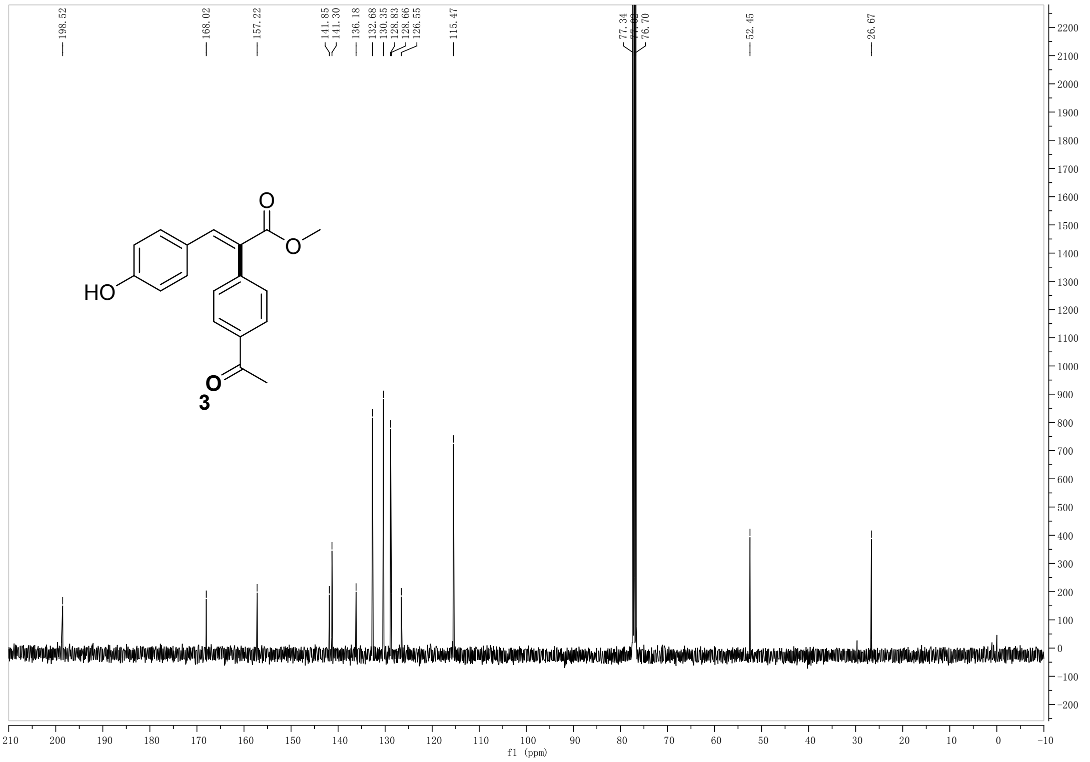


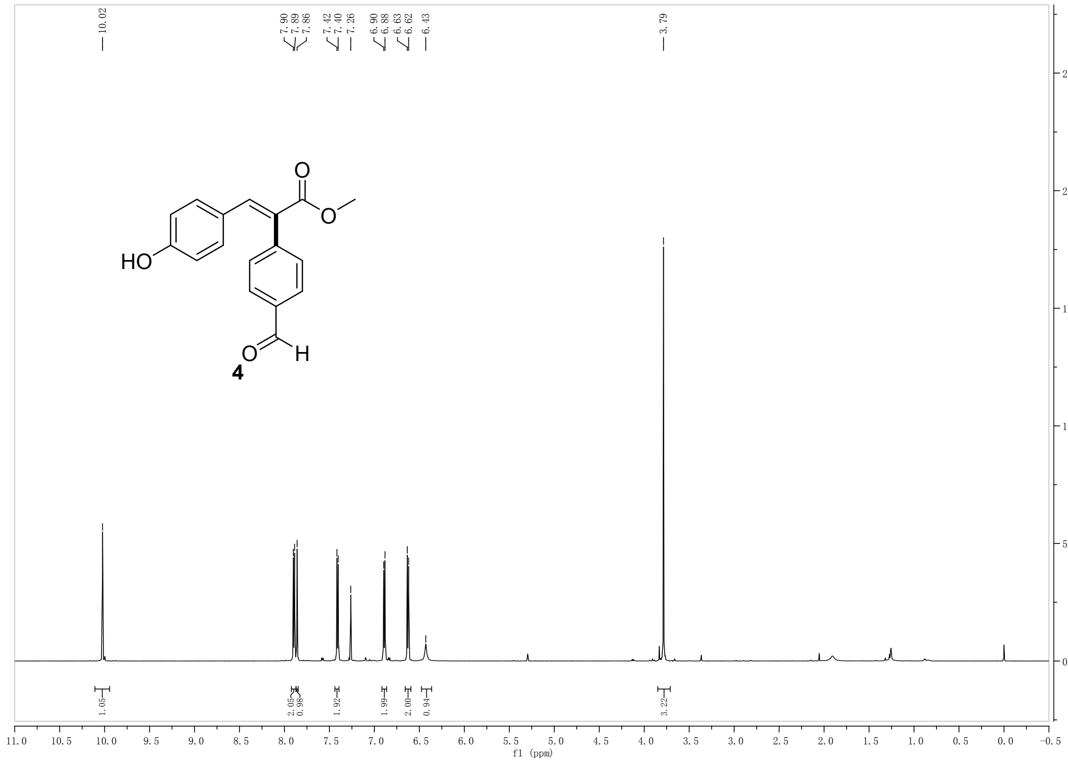
3

Table S1. Crystal data and structure refinement for 3. *CCDC1917425*

Identification code	mo_xlb301_0m	
Empirical formula	C18 H16 O4	
Formula weight	296.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 9.7263(8) Å	α= 90°.
	b = 11.8883(10) Å	β= 90°.
	c = 24.935(2) Å	γ = 90°.
Volume	2883.2(4) Å^3	
Z	8	
Density (calculated)	1.365 Mg/m^3	
Absorption coefficient	0.096 mm^{-1}	
F(000)	1248	
Crystal size	0.660 x 0.440 x 0.360 mm^3	
Theta range for data collection	1.633 to 31.234°.	
Index ranges	-13<=h<=13, -16<=k<=16, -35<=l<=36	
Reflections collected	30553	
Independent reflections	4416 [R(int) = 0.0324]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4416 / 0 / 204	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0417, wR2 = 0.1080	
R indices (all data)	R1 = 0.0511, wR2 = 0.1148	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.550 and -0.248 e.Å^{-3}	

NMR Spectral Data

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O
H
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2.05
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1.99
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3.22
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20000
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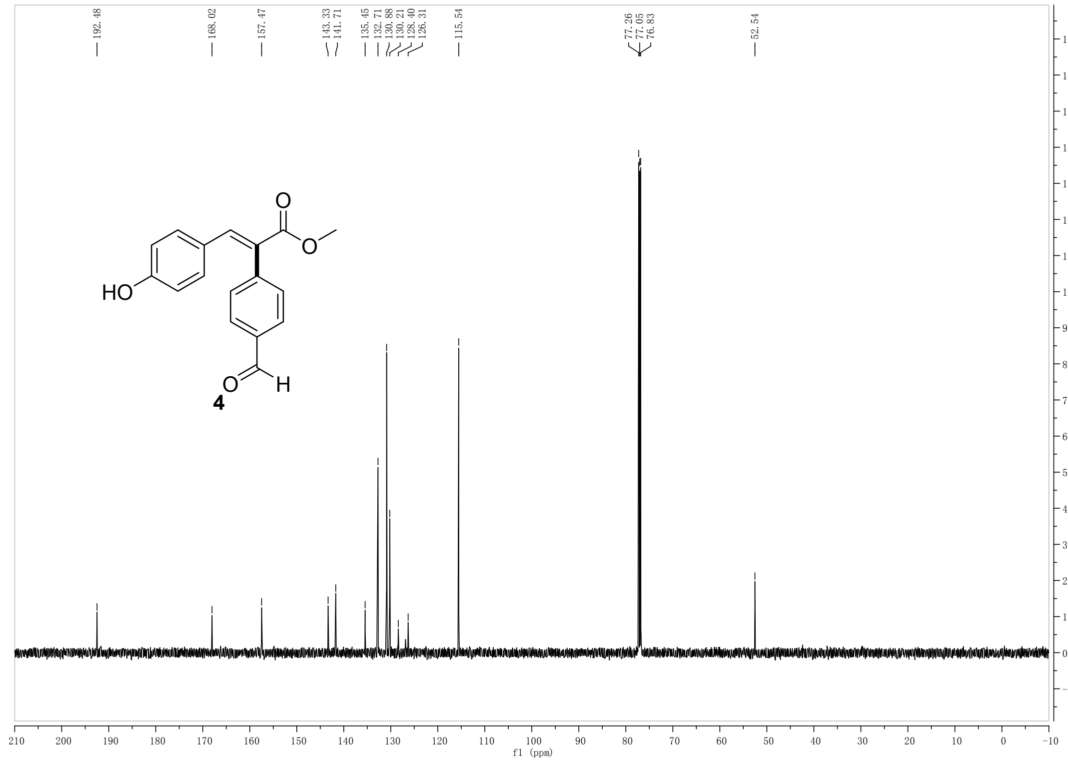
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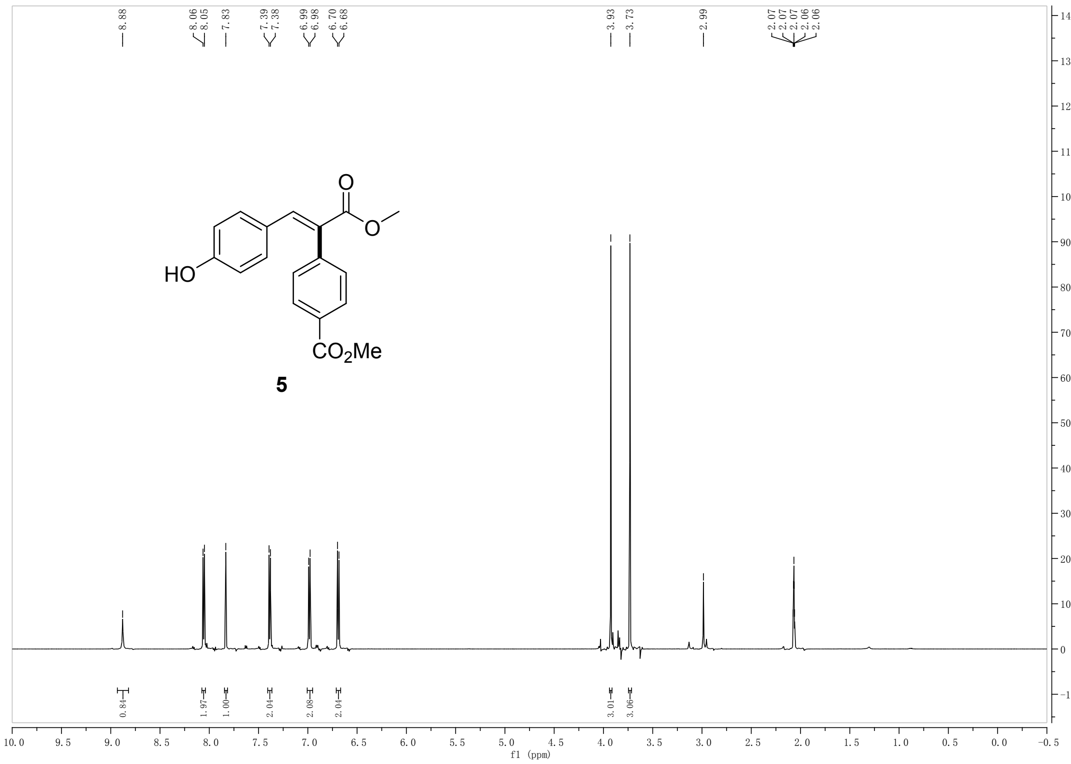
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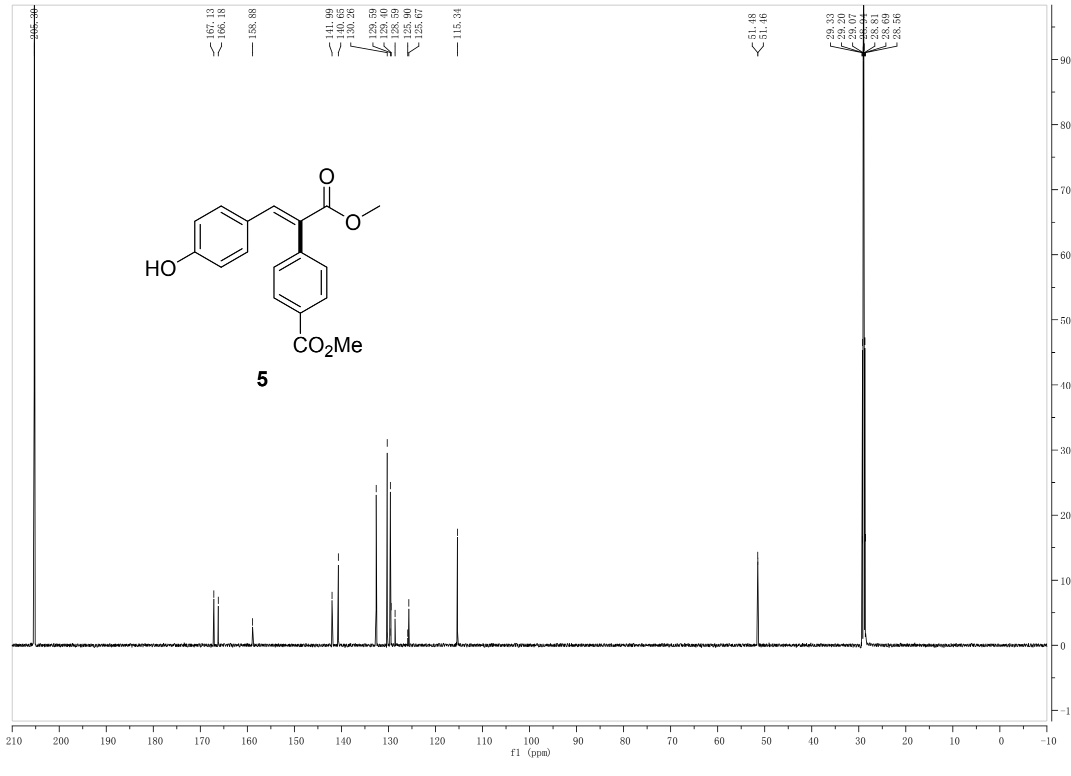
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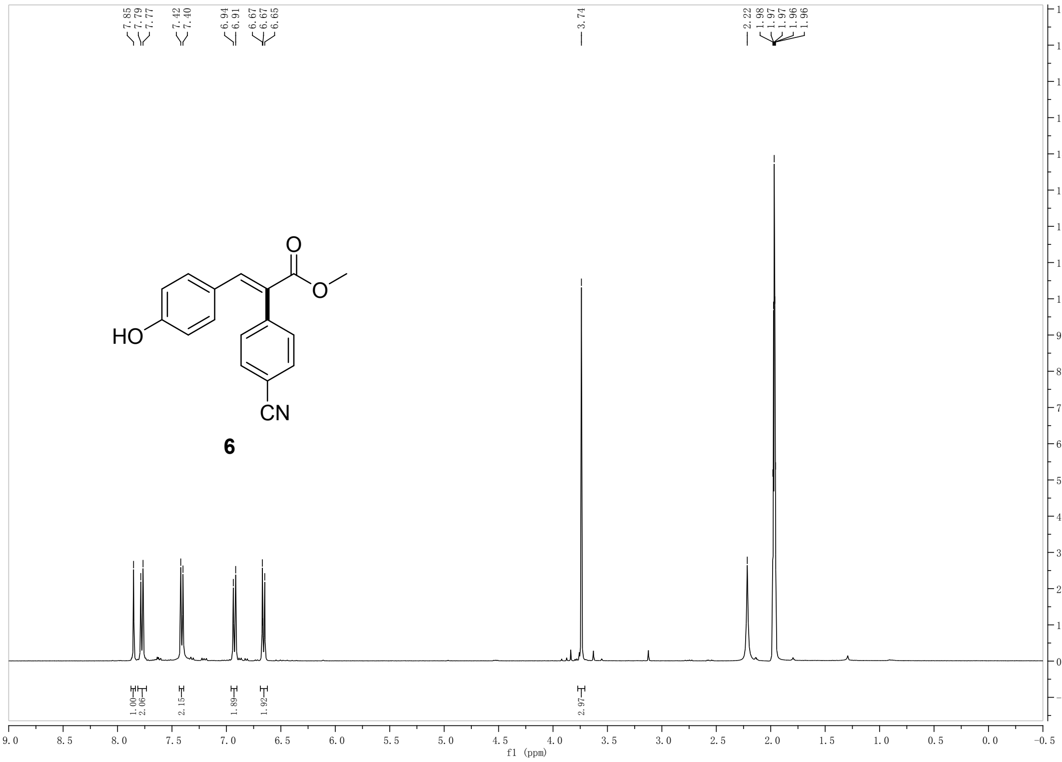
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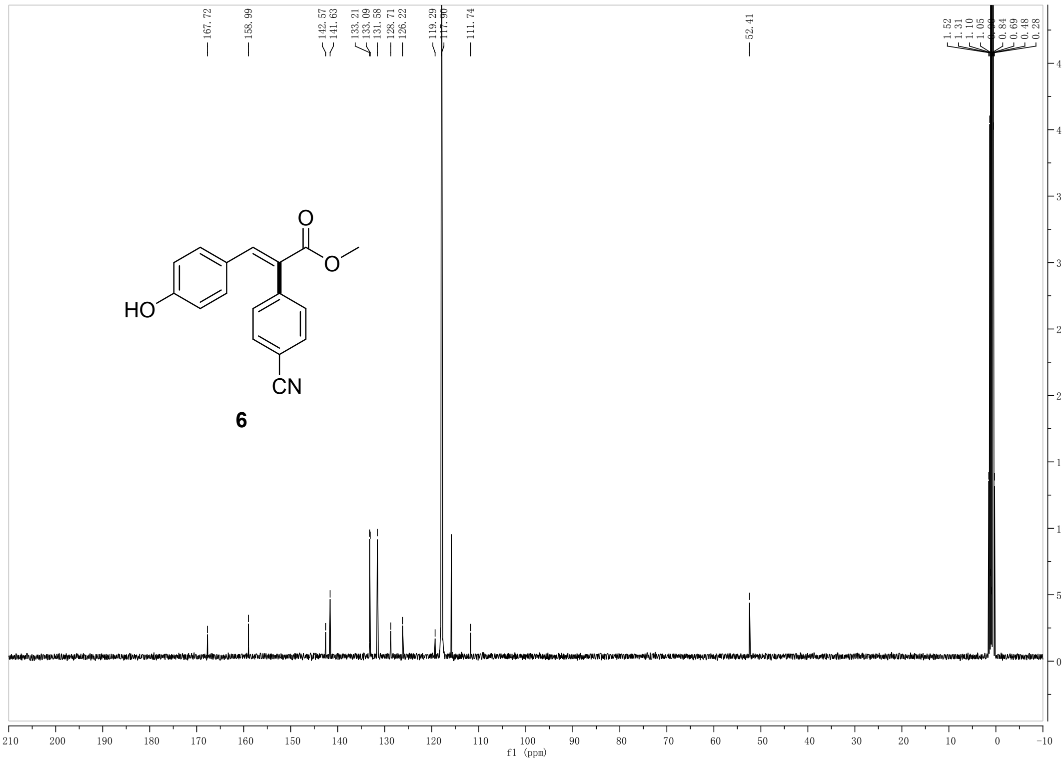
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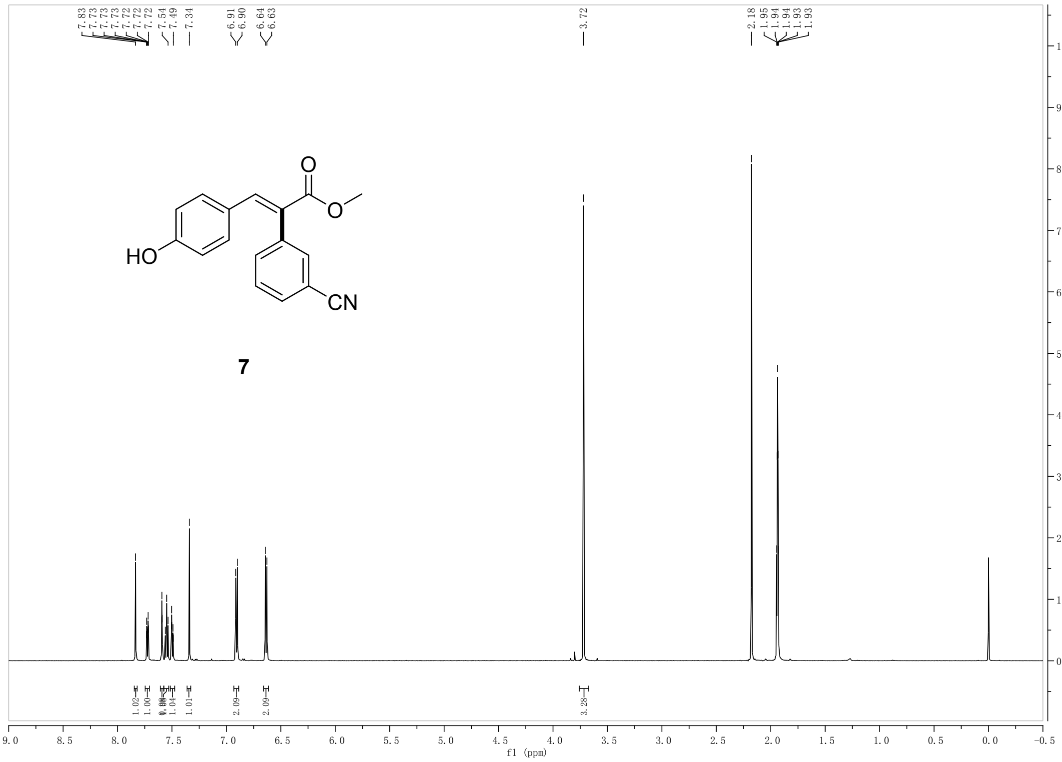

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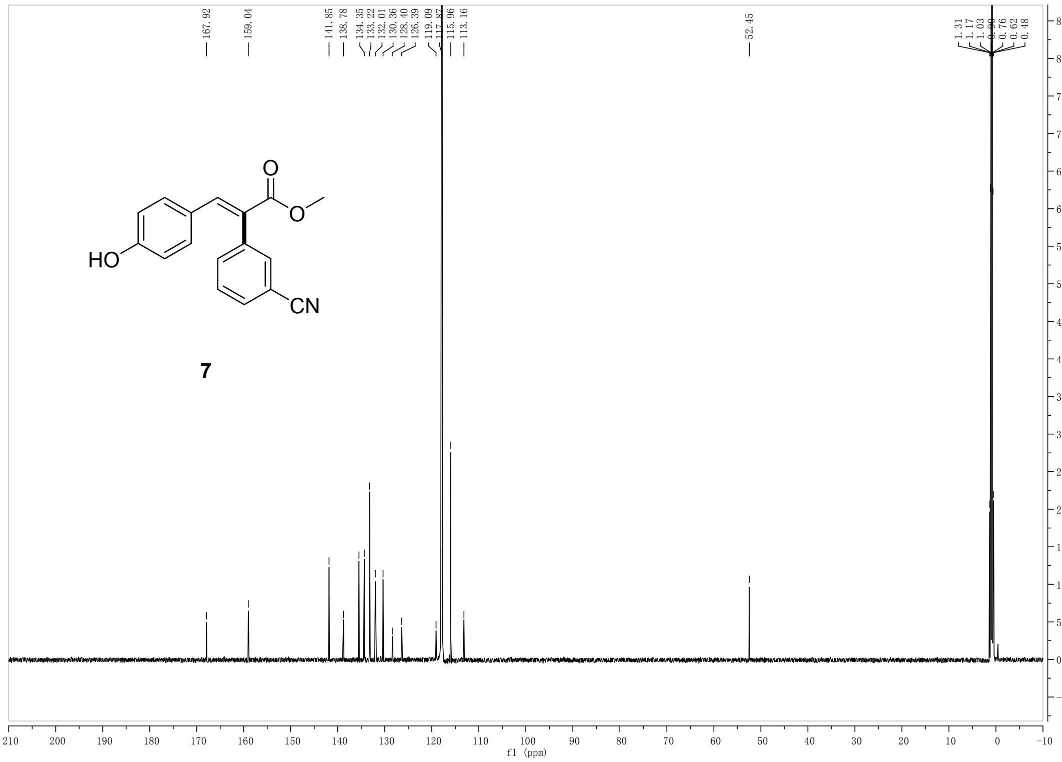

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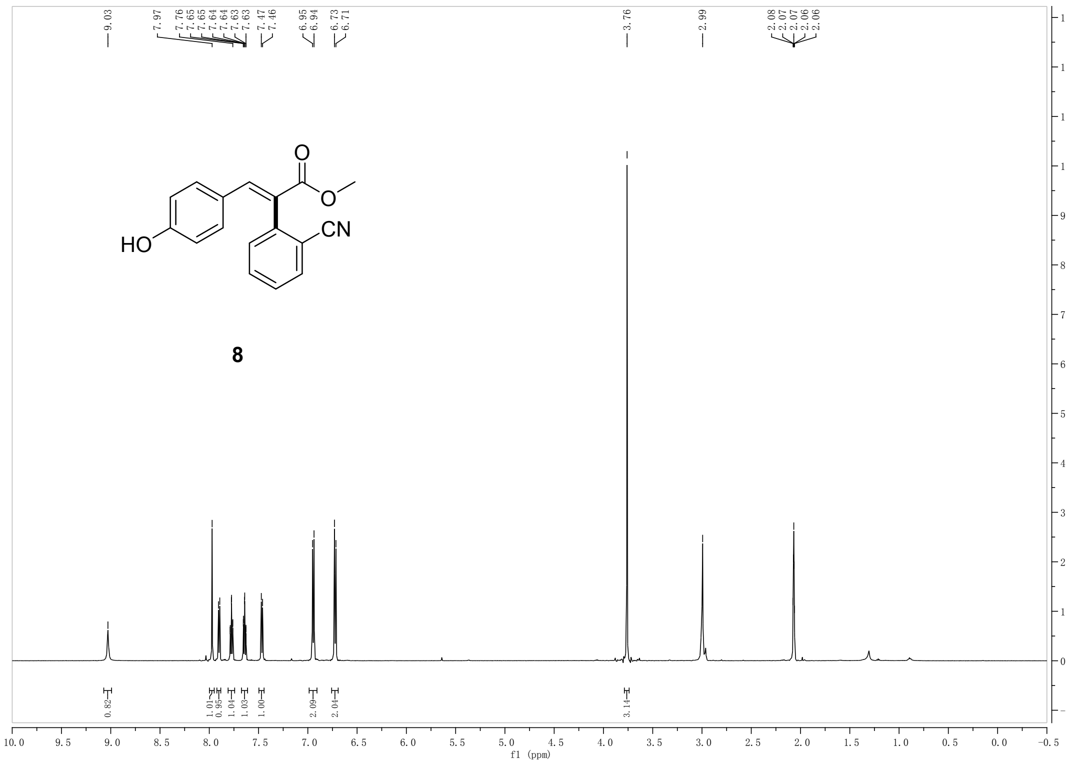
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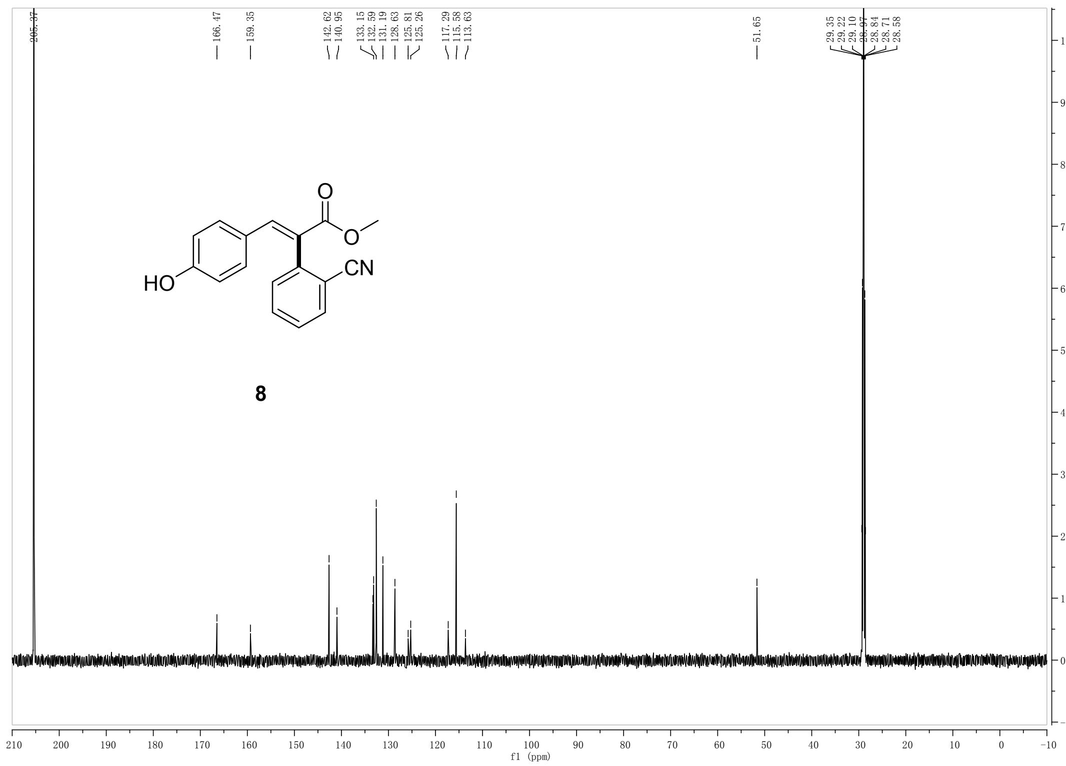
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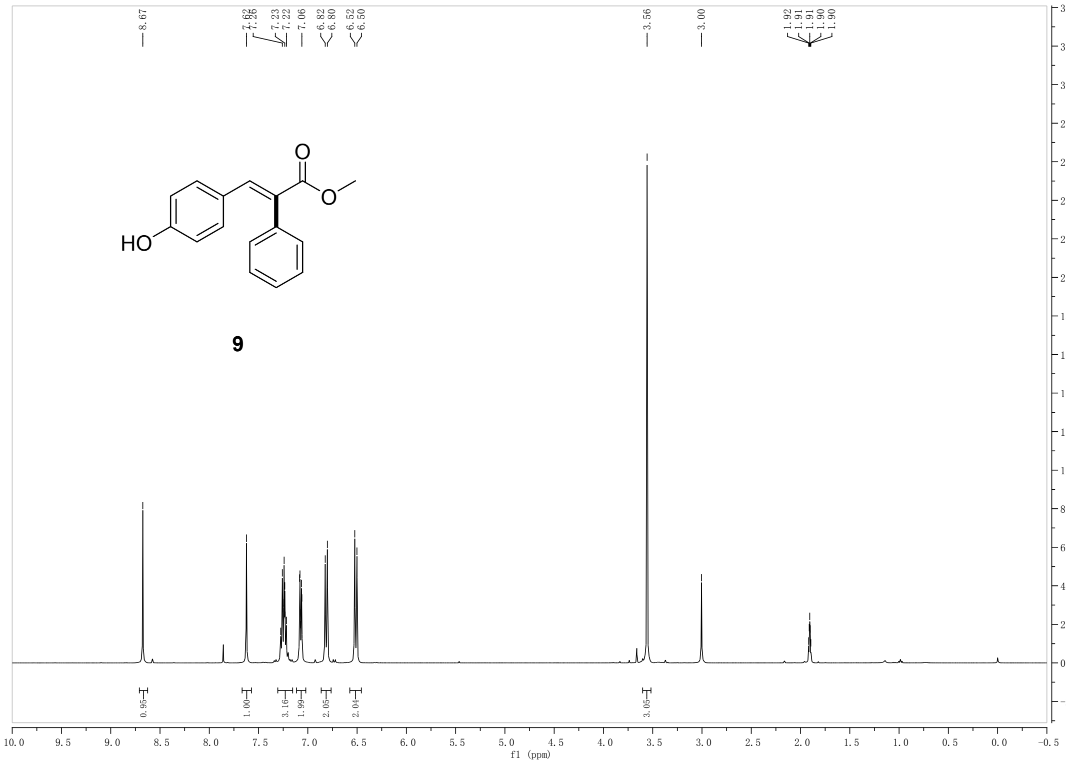
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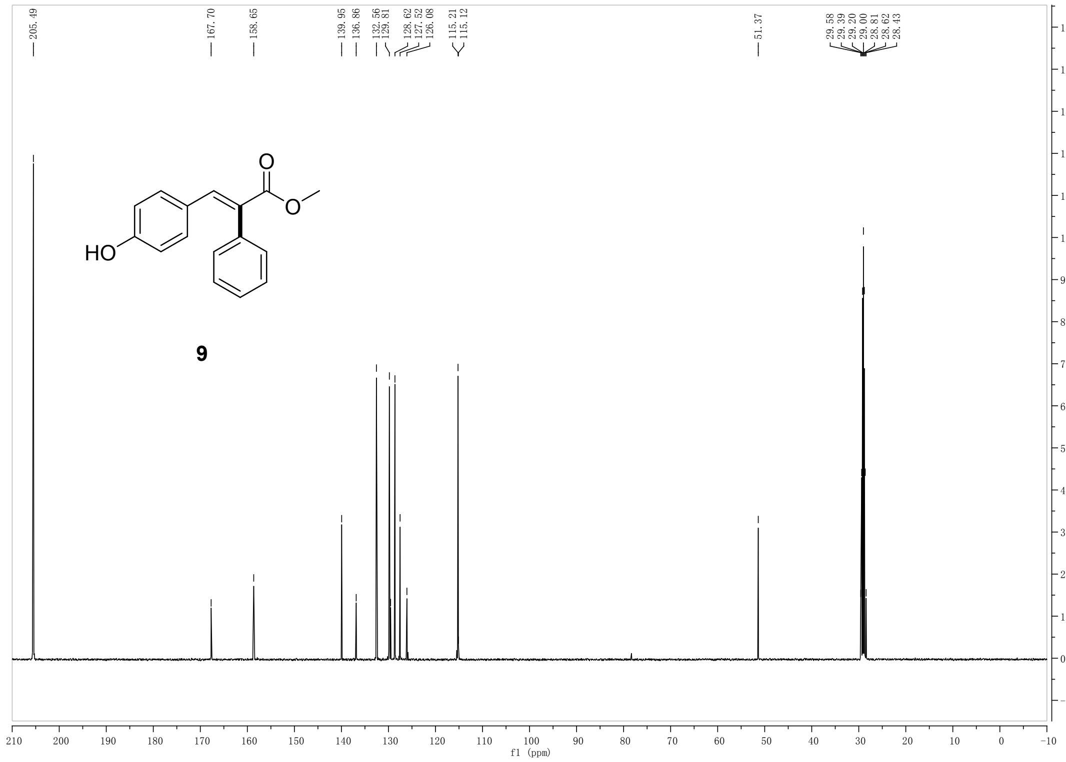
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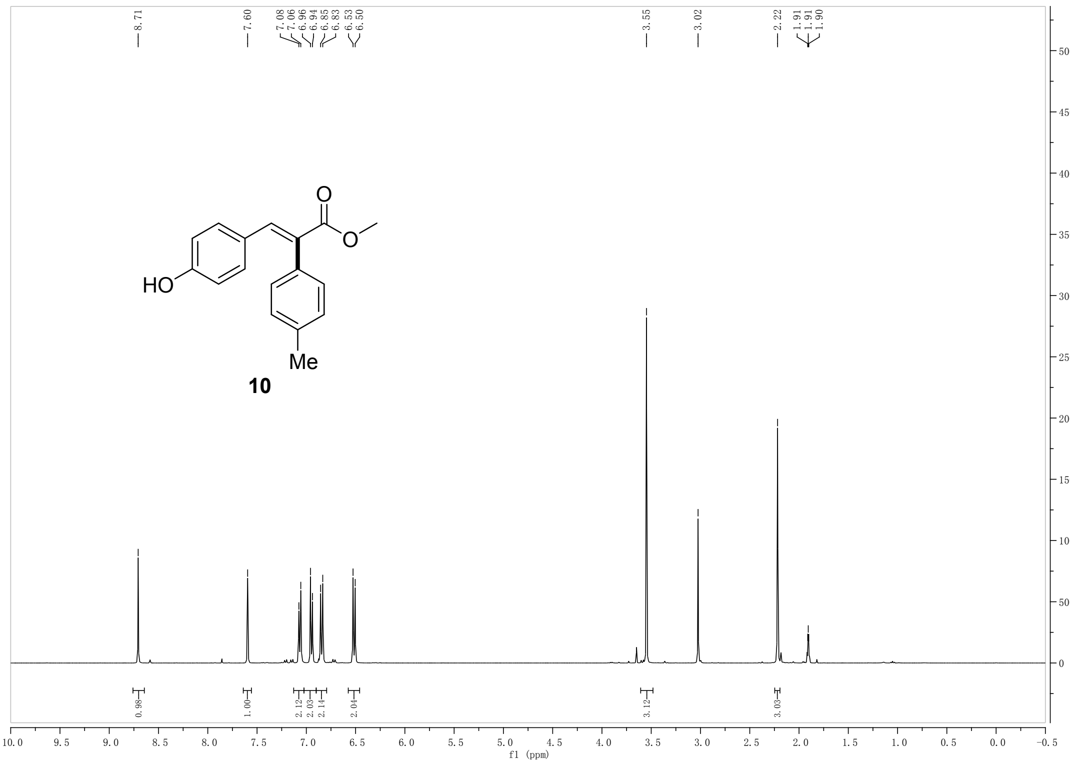
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f1 (ppm)
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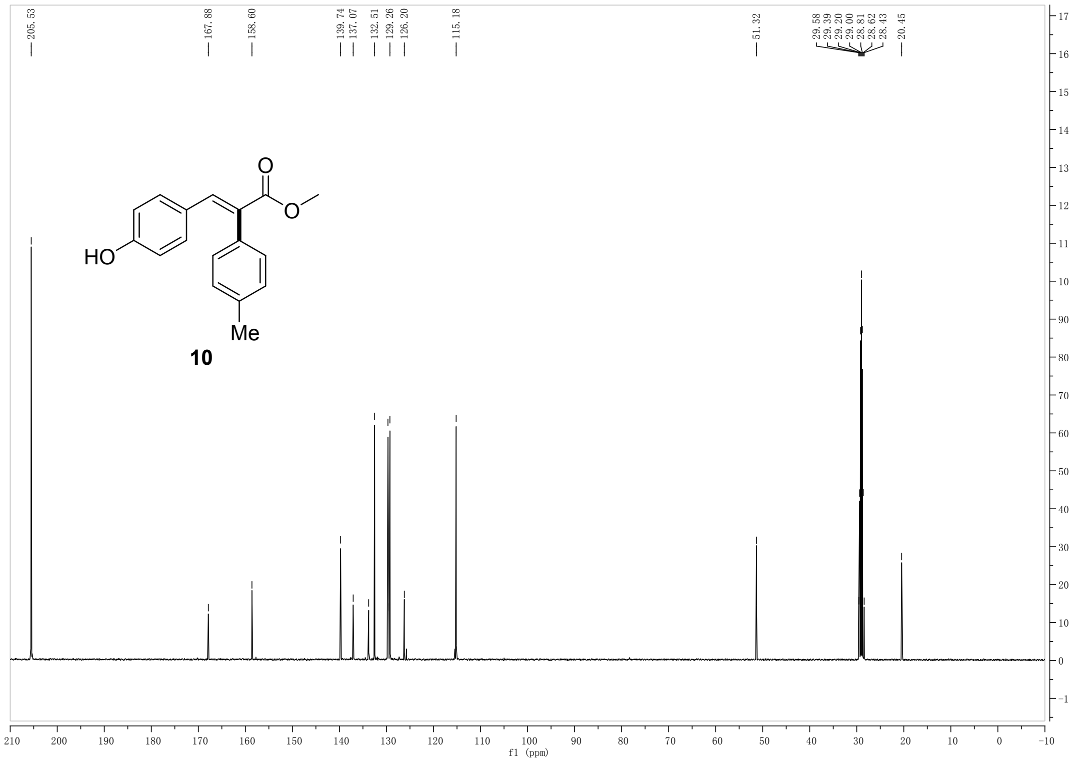
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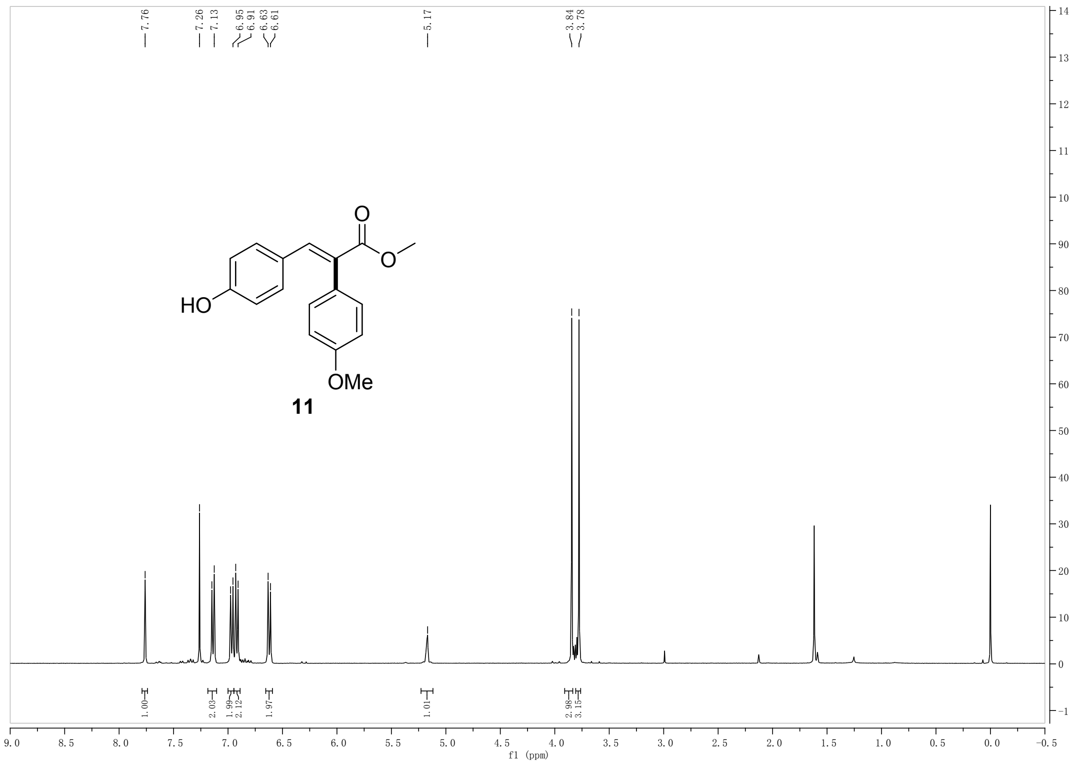
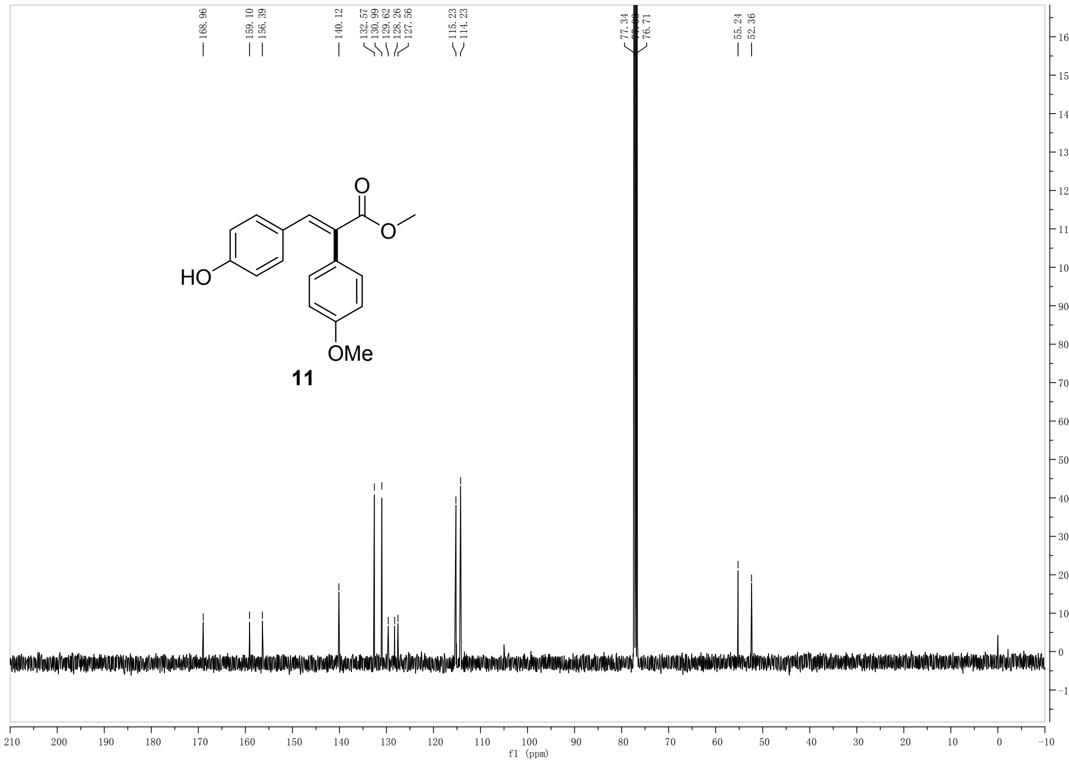
167.88
158.60
139.74
137.07
132.51
129.26
126.20
115.18
51.32
29.58
29.39
29.20
29.00
28.81
28.62
28.43
20.45
HO
O
O
Me
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000


7.76
7.26
7.13
6.95
6.91
6.63
6.61
5.17
3.84
3.78
O
O
HO
OMe
11
1.00
2.03
1.99
2.12
1.97
1.01
2.88
3.15
f1 (ppm)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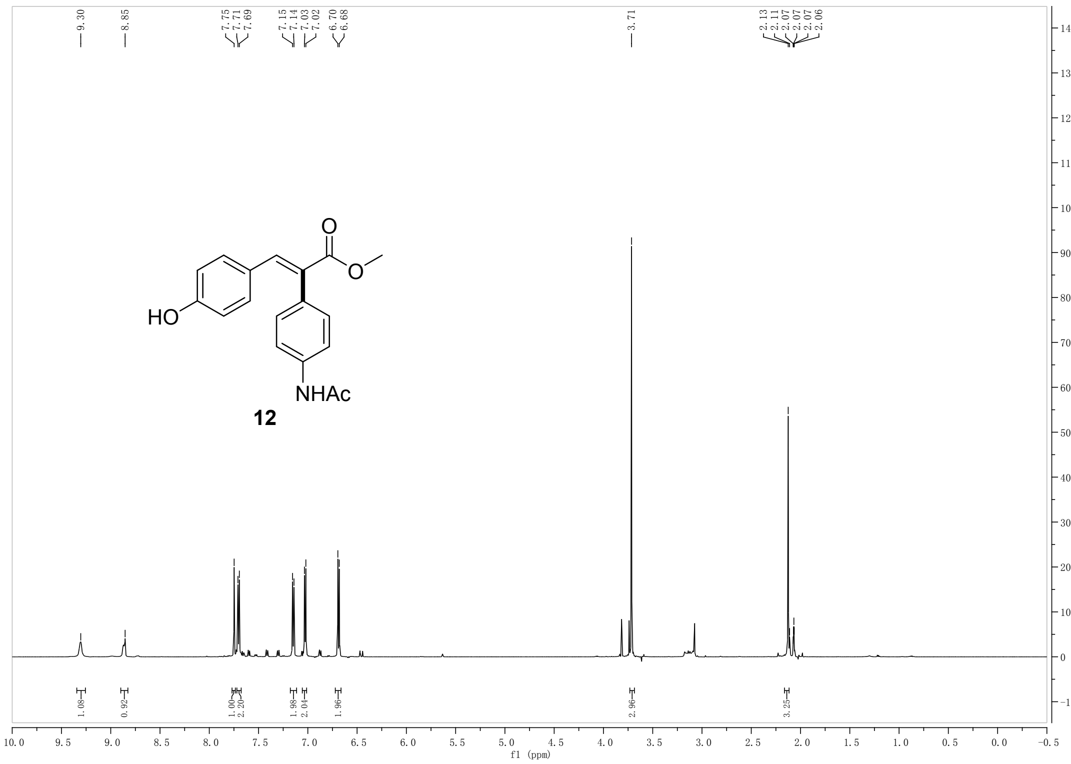
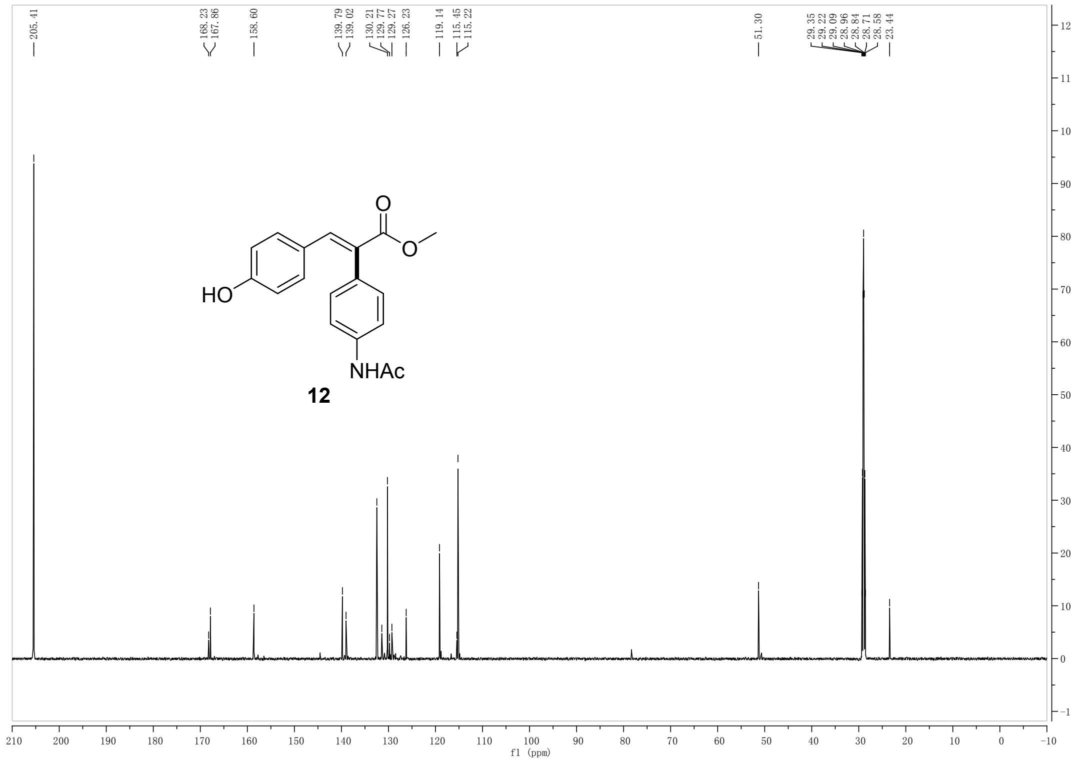
159.10
156.39
140.12
132.57
130.99
129.62
128.26
127.56
115.23
114.23
77.34
76.71
55.24
52.36
O
O
HO
OMe
11
f1 (ppm)


9.30
8.85
7.75
7.71
7.69
7.15
7.14
7.03
7.02
6.70
6.68
3.71
2.13
2.11
2.07
2.07
2.07
2.06
HO
O
O
NHAc
12
1.08
0.92
1.00
2.20
1.98
2.04
1.96
2.96
3.25
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)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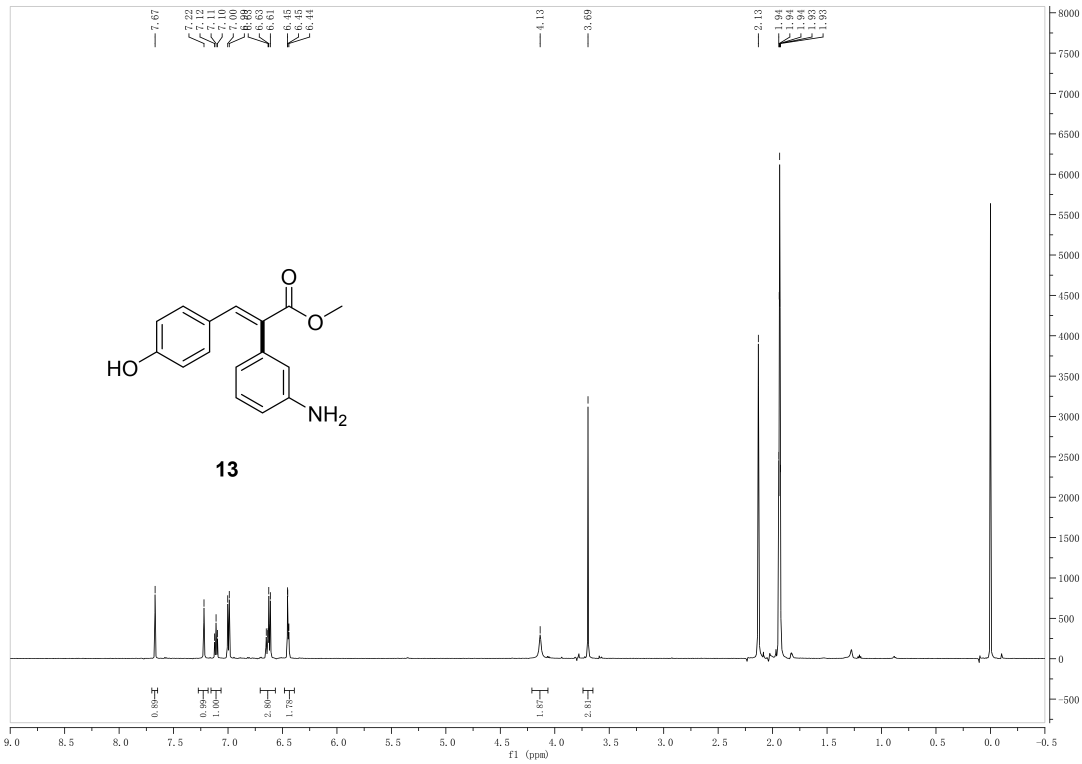
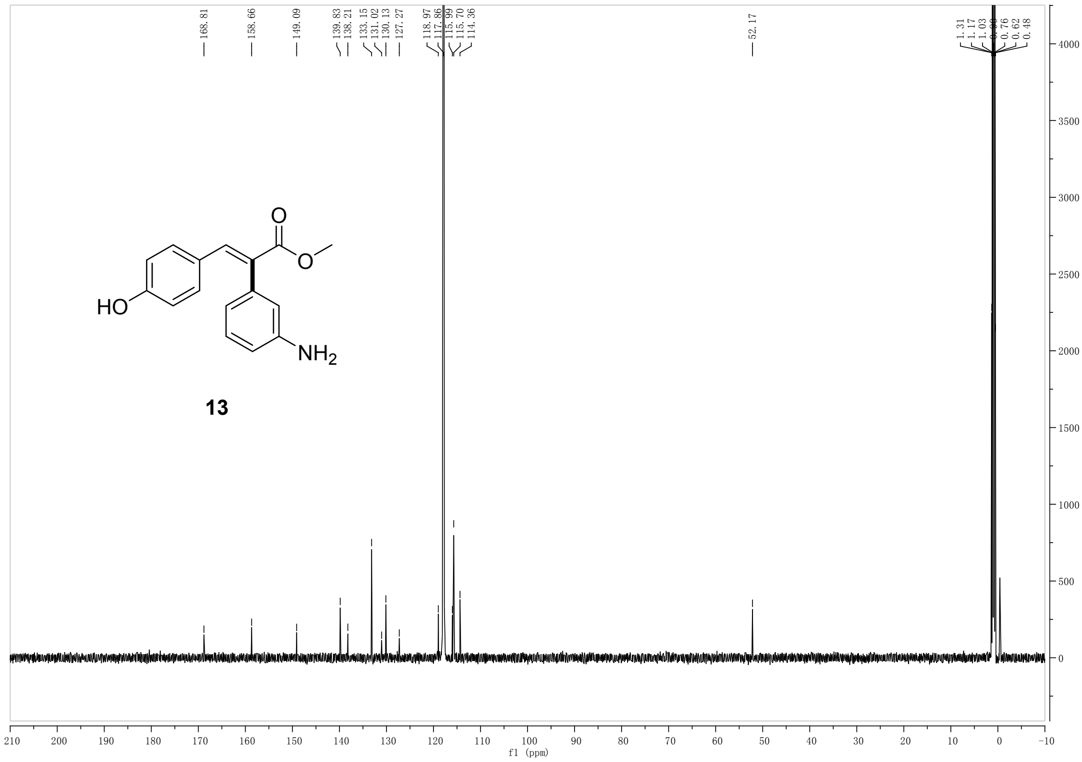
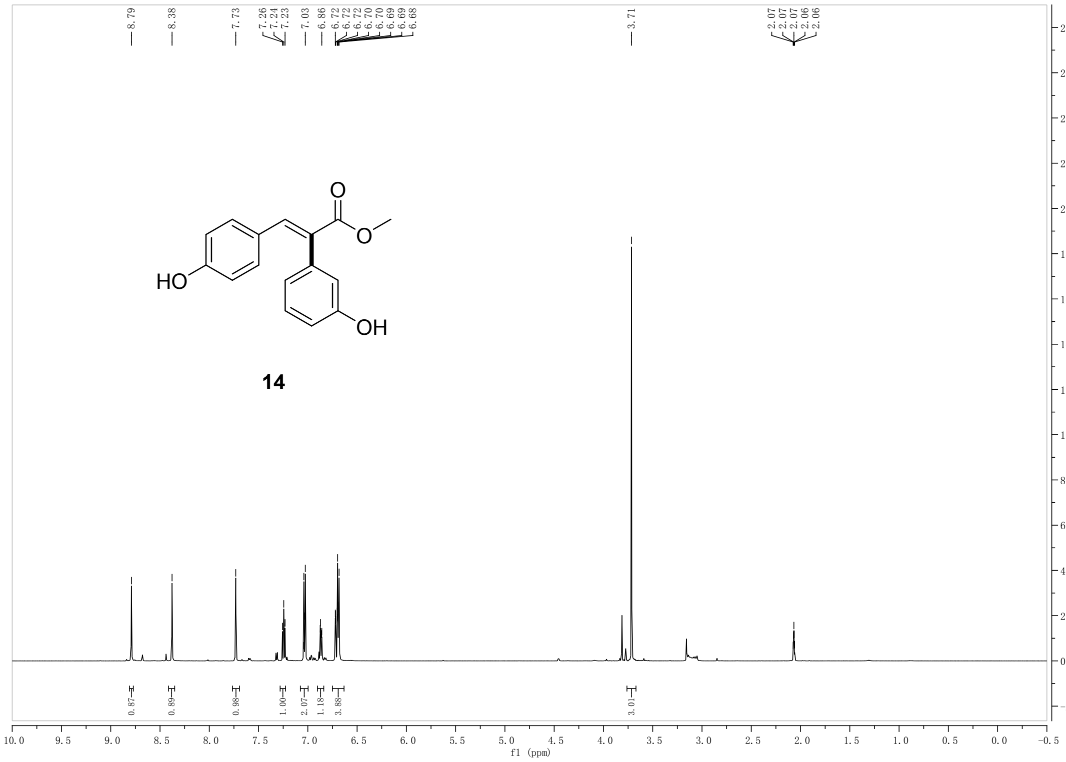
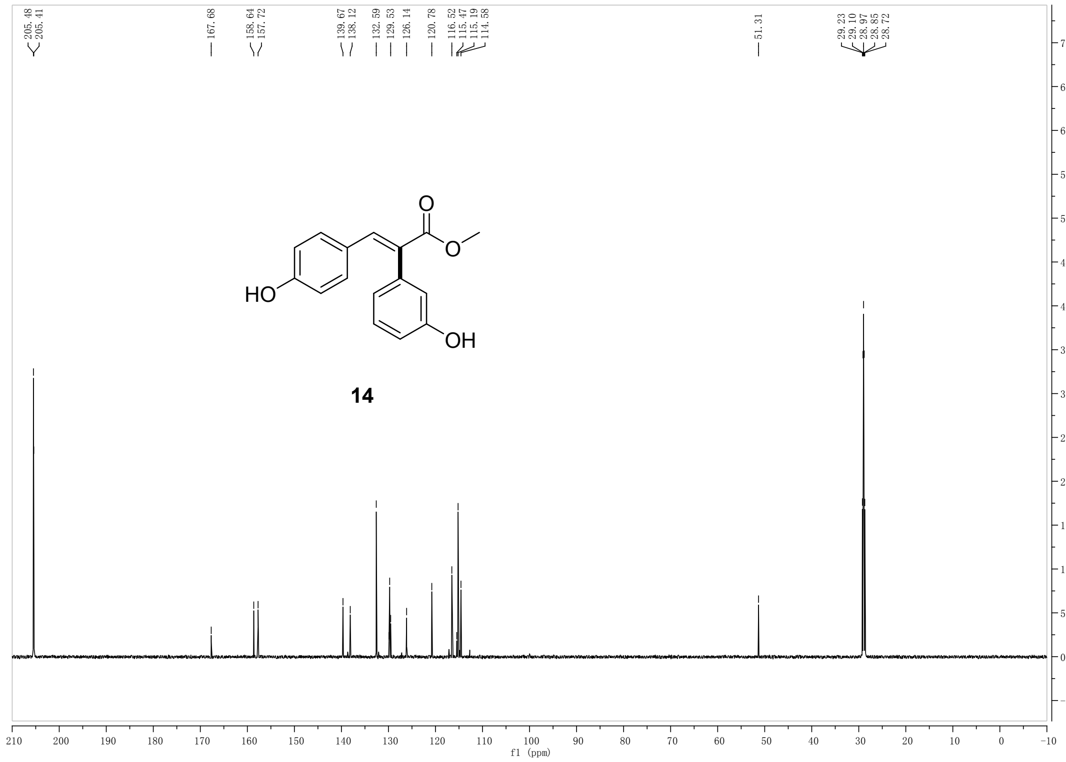
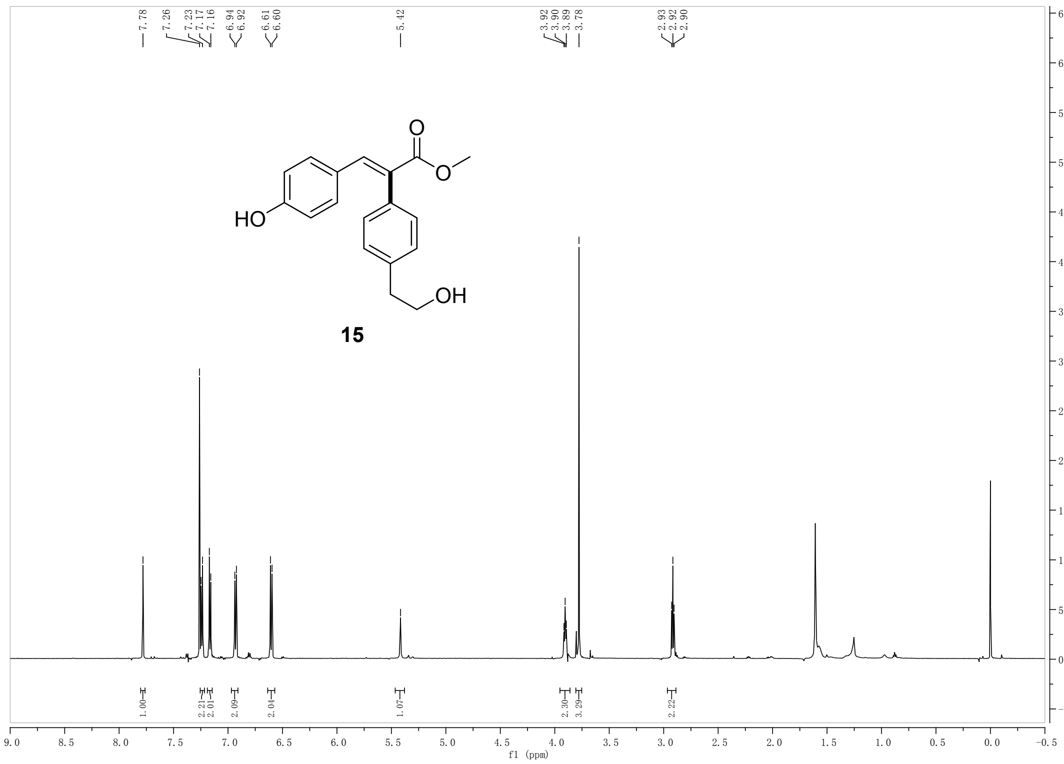
168.23
167.86
158.60
139.79
139.02
130.21
129.77
129.27
126.23
119.14
115.45
115.22
51.30
29.35
29.22
29.09
28.96
28.84
28.71
28.58
23.44
HO
O
O
NHAc
12
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

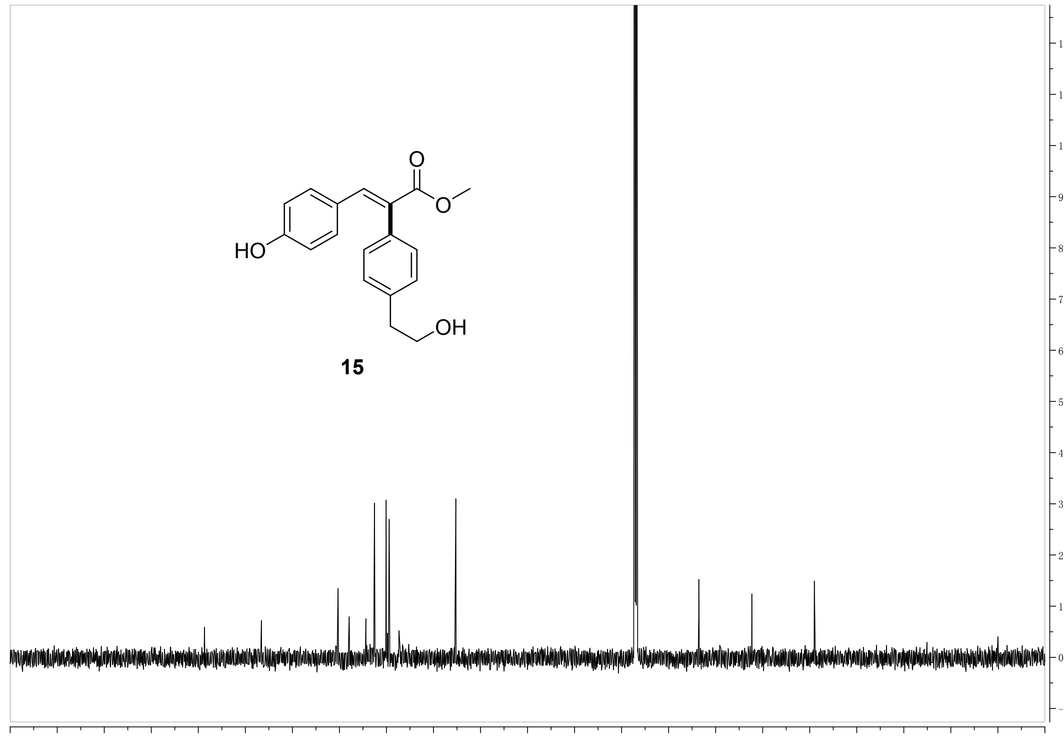

7.67
7.22
7.12
7.11
7.10
7.00
6.63
6.61
6.45
6.45
6.44
4.13
3.69
2.13
1.94
1.94
1.94
1.93
1.93
0.89
0.99
1.00
2.80
1.78
1.87
2.81
HO
O
O
NH2
13
f1 (ppm)

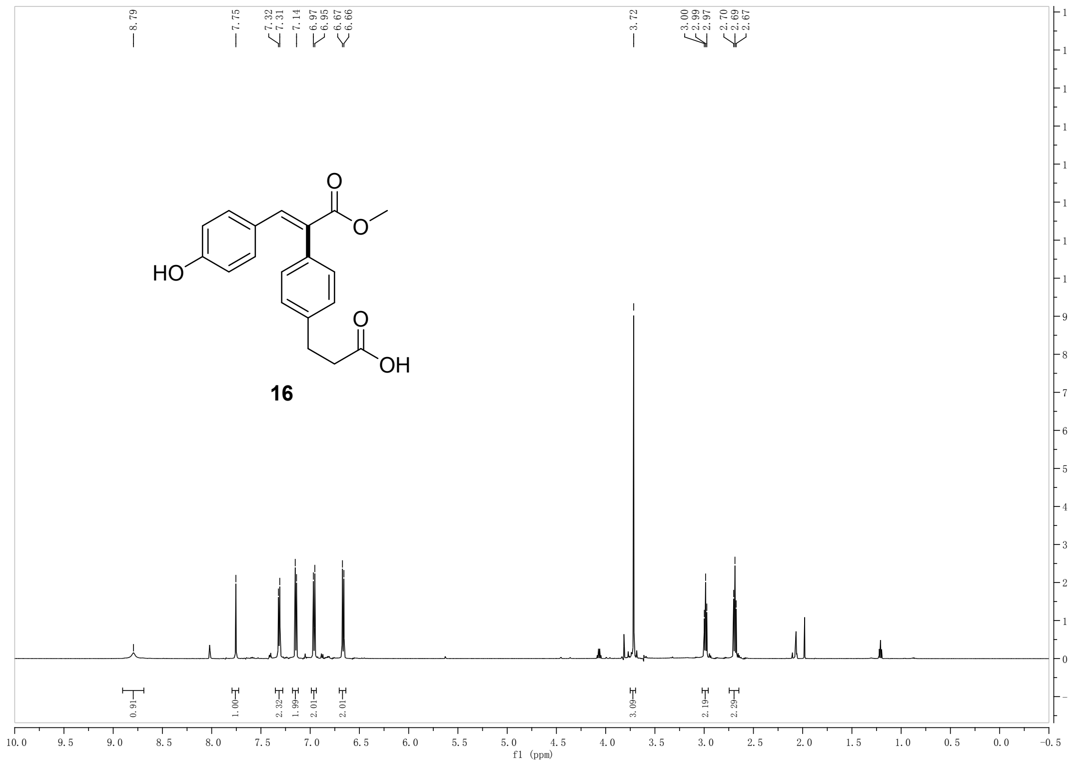

168.81
158.66
149.09
139.83
138.21
133.15
131.02
130.13
127.27
118.97
117.86
115.99
115.70
114.36
52.17
1.31
1.17
1.03
0.76
0.62
0.48
HO
O
O
NH2
13
f1 (ppm)

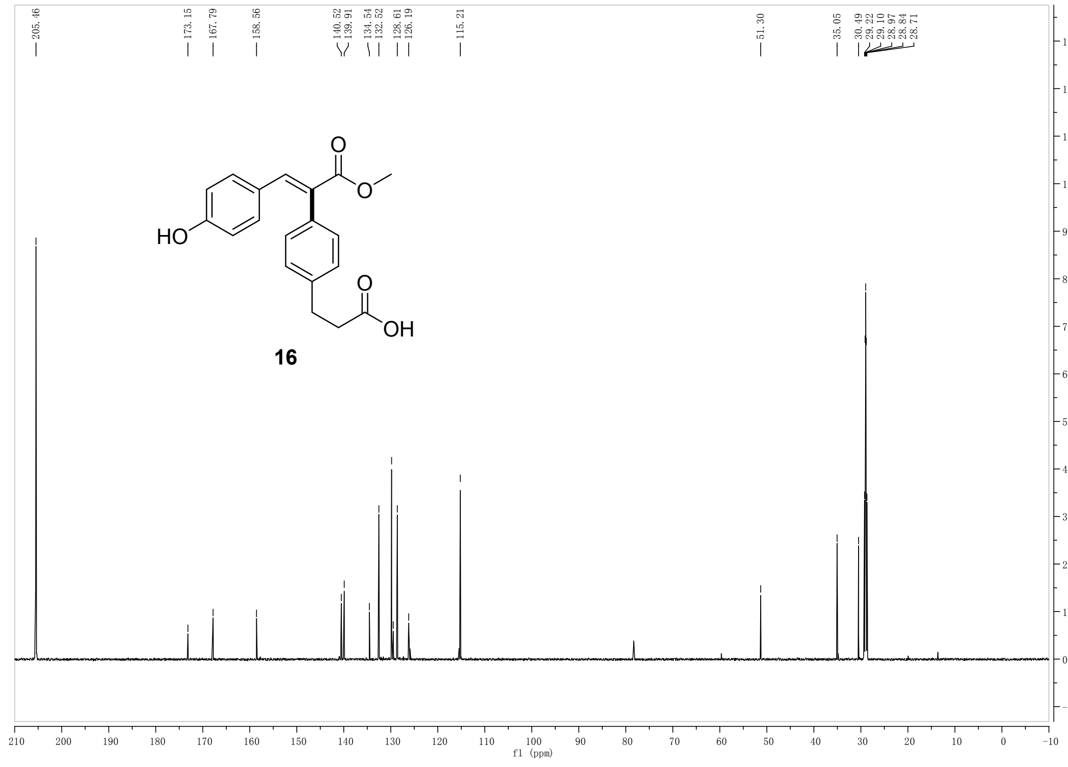

8.79
8.38
7.73
7.26
7.24
7.23
7.03
6.86
6.72
6.72
6.72
6.70
6.70
6.69
6.69
6.68
3.71
2.07
2.07
2.07
2.06
2.06
HO
O
O
OH
14
0.87
0.89
0.98
1.00
2.07
1.18
3.88
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000


205.48
205.41
167.68
158.64
157.72
139.67
138.12
132.59
129.53
126.14
120.78
116.52
115.47
115.19
114.58
51.31
29.23
29.10
28.97
28.85
28.72
HO
O
O
OH
14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500


7.78
7.26
7.23
7.17
7.16
6.94
6.92
6.61
6.60
5.42
3.92
3.90
3.89
3.78
2.93
2.92
2.90
HO
O
O
OH
15
1.00
2.21
2.01
2.09
2.04
1.07
2.30
3.29
2.22
f1 (ppm)


O
O
HO
OH
15
f1 (ppm)


8.79
7.75
7.32
7.31
7.14
6.97
6.95
6.67
6.66
3.72
3.00
2.99
2.97
2.70
2.69
2.67
HO
O
O
O
OH
16
0.91
1.00
2.32
1.99
2.01
2.01
3.09
2.19
2.29
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000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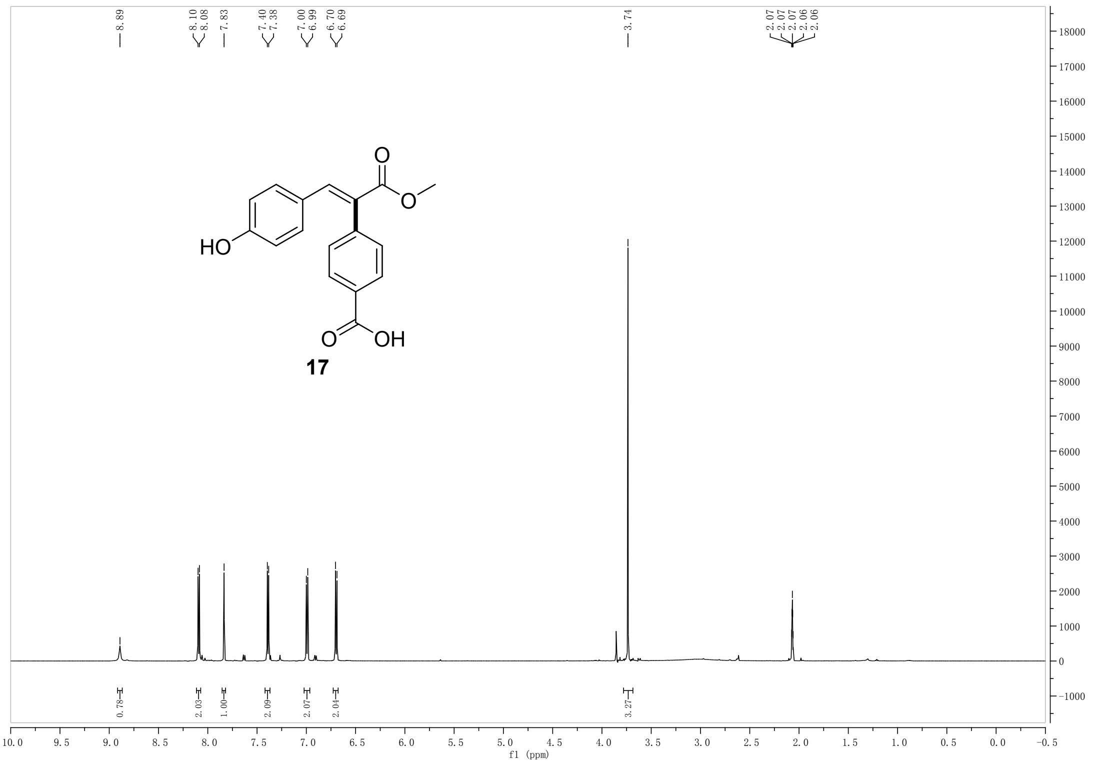
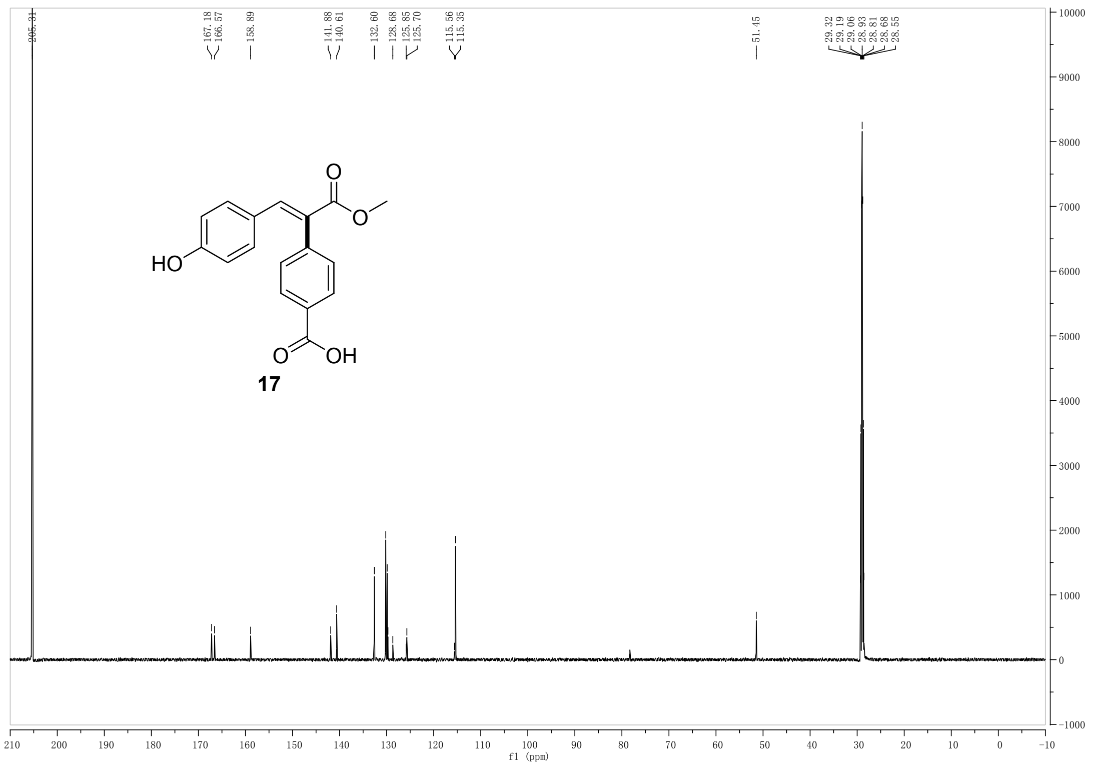
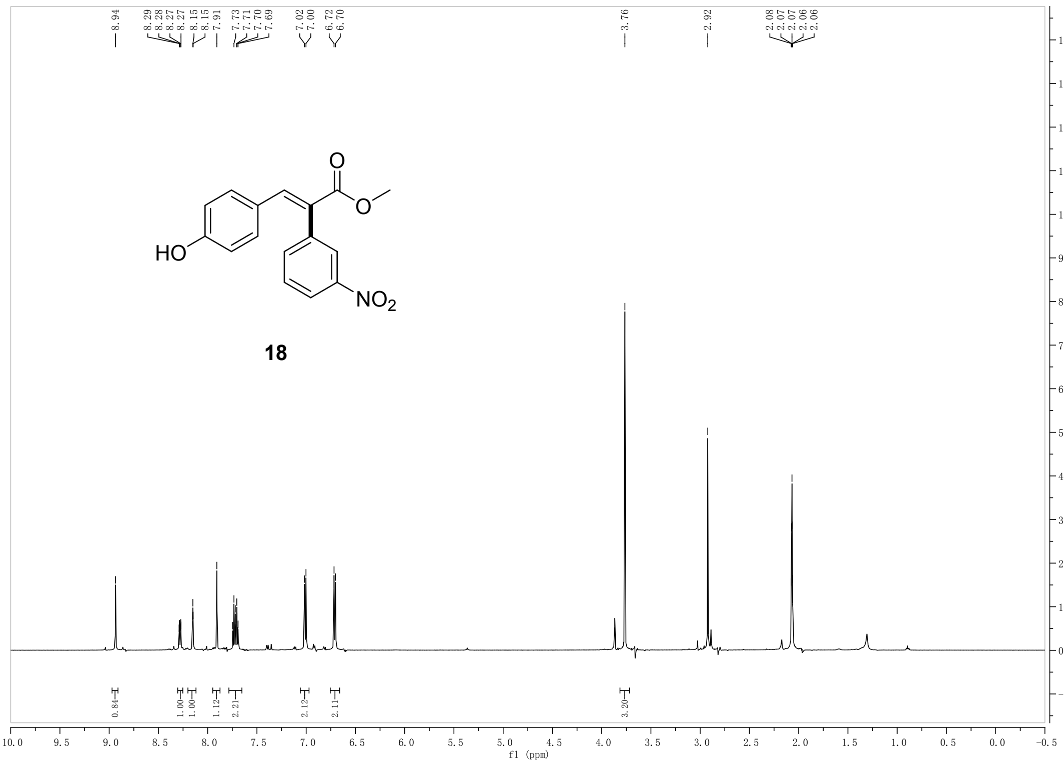
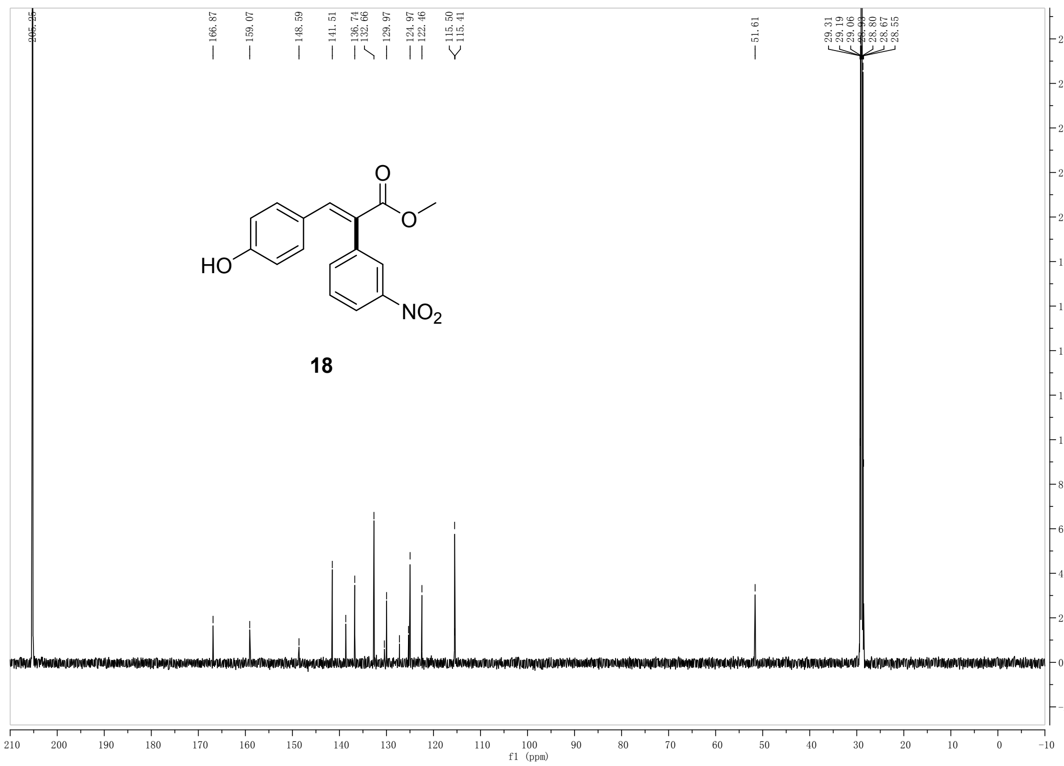
173.15
167.79
158.56
140.52
139.91
134.54
132.52
128.61
126.19
115.21
51.30
35.05
30.49
29.22
29.10
28.97
28.84
28.71
HO
O
O
O
OH
16
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


8.89
8.10
8.08
7.83
7.40
7.38
7.00
6.99
6.70
6.69
3.74
2.07
2.07
2.07
2.06
2.06
HO
O
O
O
OH
17
0.78
2.03
1.00
2.09
2.07
2.04
3.27
f1 (ppm)

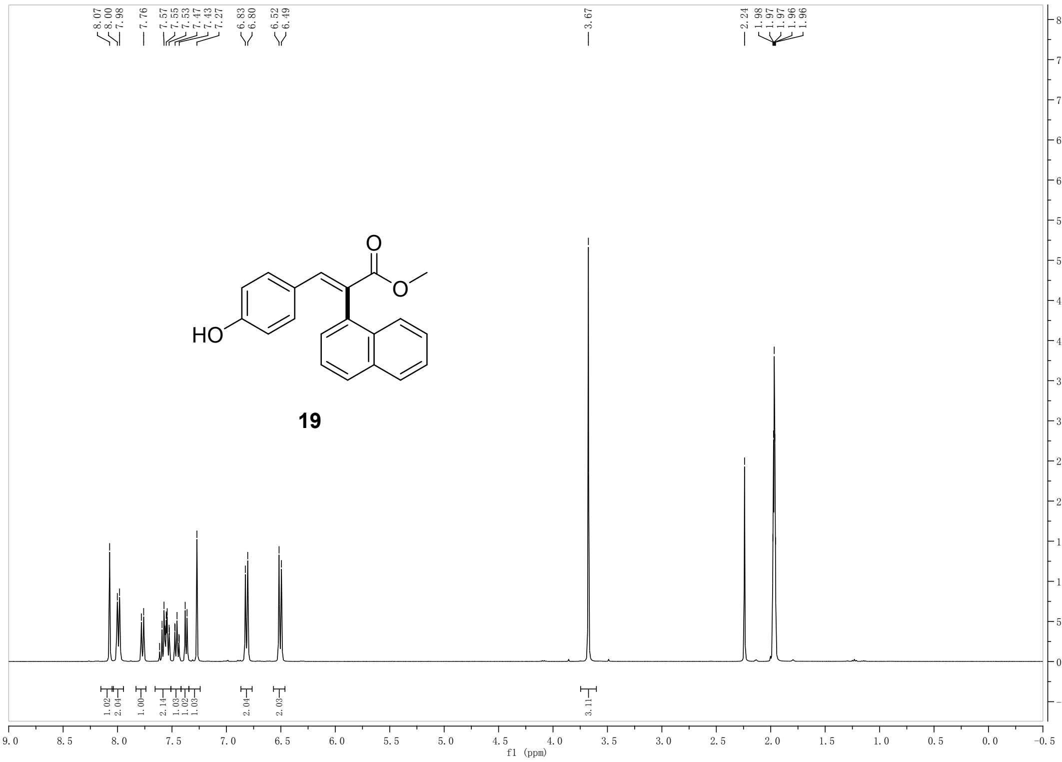

205.31
167.18
166.57
158.89
141.88
140.61
132.60
128.68
125.85
125.70
115.56
115.35
51.45
29.32
29.19
29.06
28.93
28.81
28.68
28.55
HO
O
O
O
OH
17
f1 (ppm)

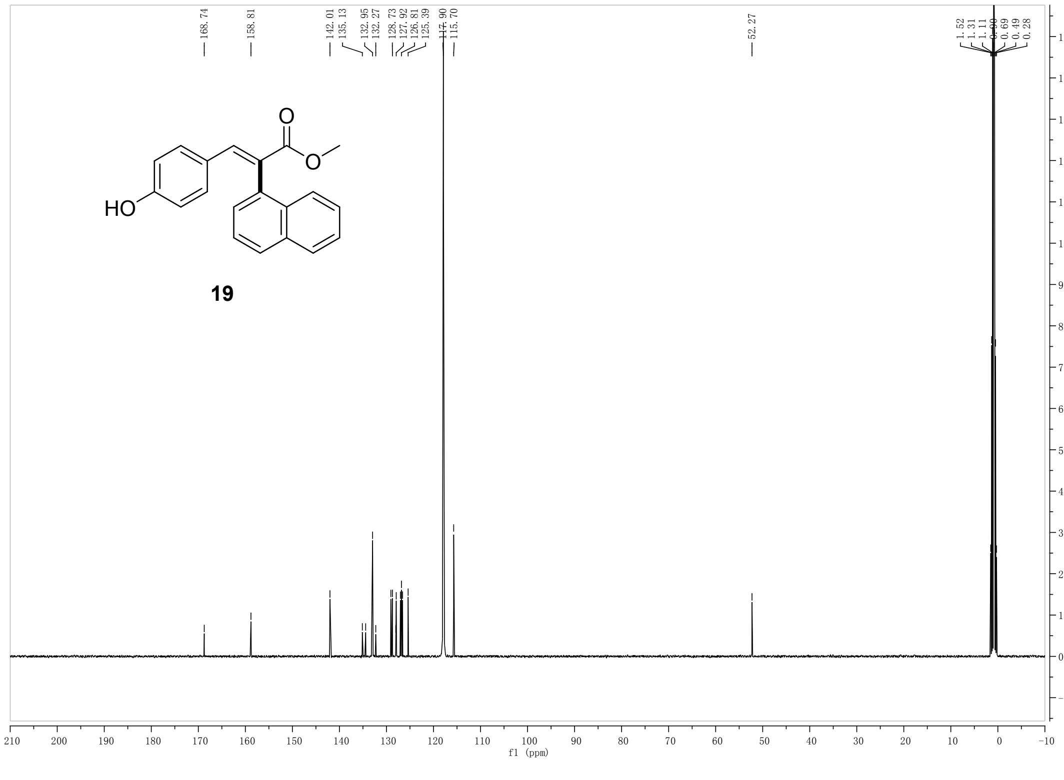

8.94
8.29
8.28
8.27
8.27
8.15
8.15
7.91
7.73
7.71
7.70
7.69
7.02
7.00
6.72
6.70
3.76
2.92
2.08
2.07
2.07
2.06
2.06
HO
O
O
NO_2
0.84
1.00
1.00
1.12
2.21
2.12
2.11
3.20
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

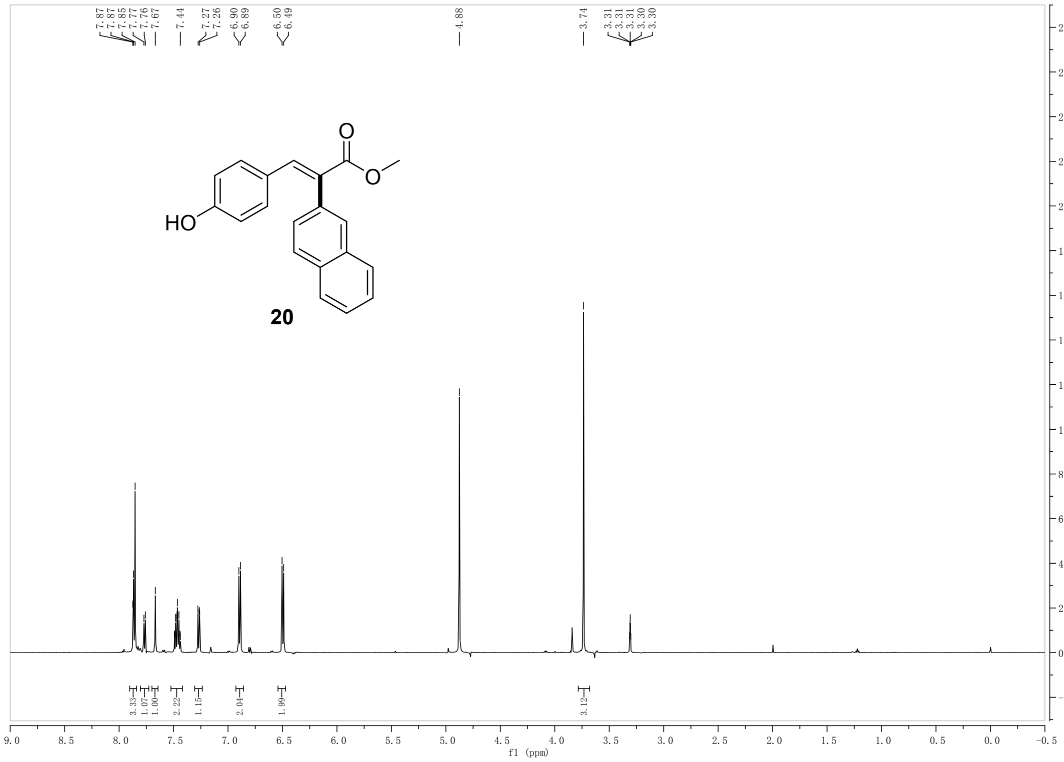
18


205.25
166.87
159.07
148.59
141.51
136.74
132.66
129.97
124.97
122.46
115.50
115.41
51.61
29.31
29.19
29.06
28.93
28.80
28.67
28.55
HO
O
O
NO_2
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

18


8.07
8.00
7.98
7.76
7.57
7.55
7.53
7.47
7.43
7.27
6.83
6.80
6.52
6.49
3.67
2.24
1.98
1.97
1.97
1.96
1.96
HO
O
O
19
1.02
2.04
1.00
2.14
1.03
1.02
1.03
2.04
2.03
3.11
f1 (ppm)


168.74
158.81
142.01
135.13
132.95
132.27
128.73
127.92
126.81
125.39
117.90
115.70
52.27
1.52
1.31
1.11
0.90
0.69
0.49
0.28
HO
O
O
19
f1 (ppm)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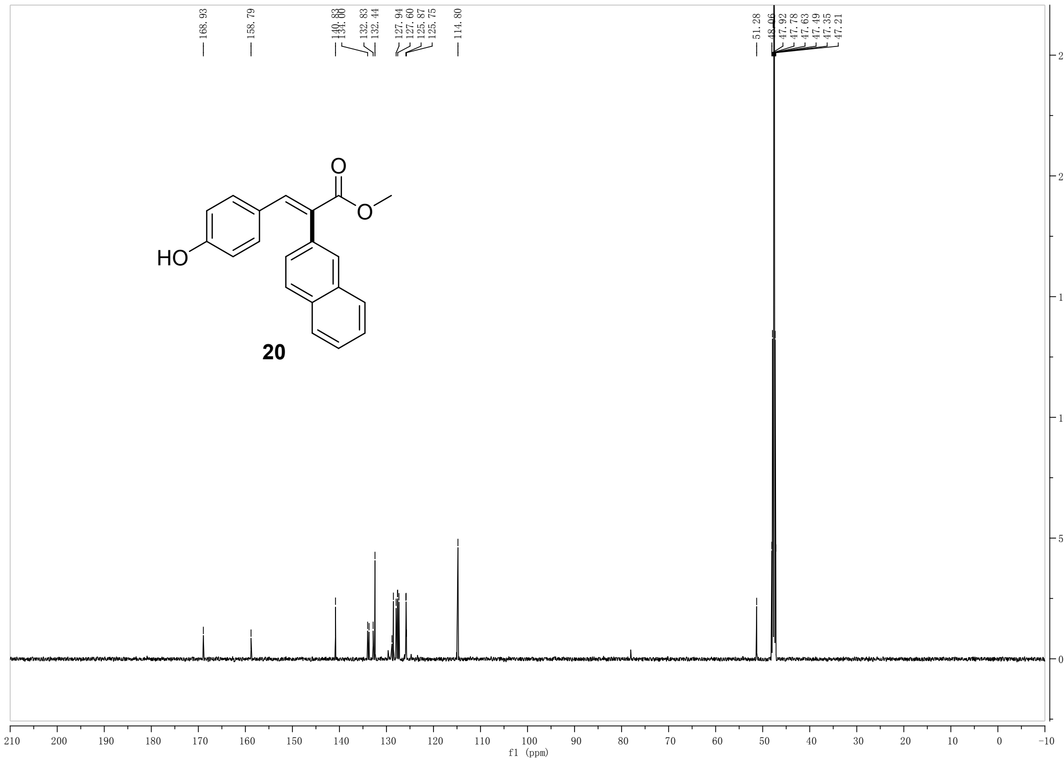
7.87
7.85
7.77
7.76
7.67
7.44
7.27
7.26
6.90
6.89
6.50
6.49
4.88
3.74
3.31
3.31
3.31
3.30
3.30
HO
O
O
20
3.33
1.07
1.00
2.22
1.15
2.04
1.99
3.12
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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158.79
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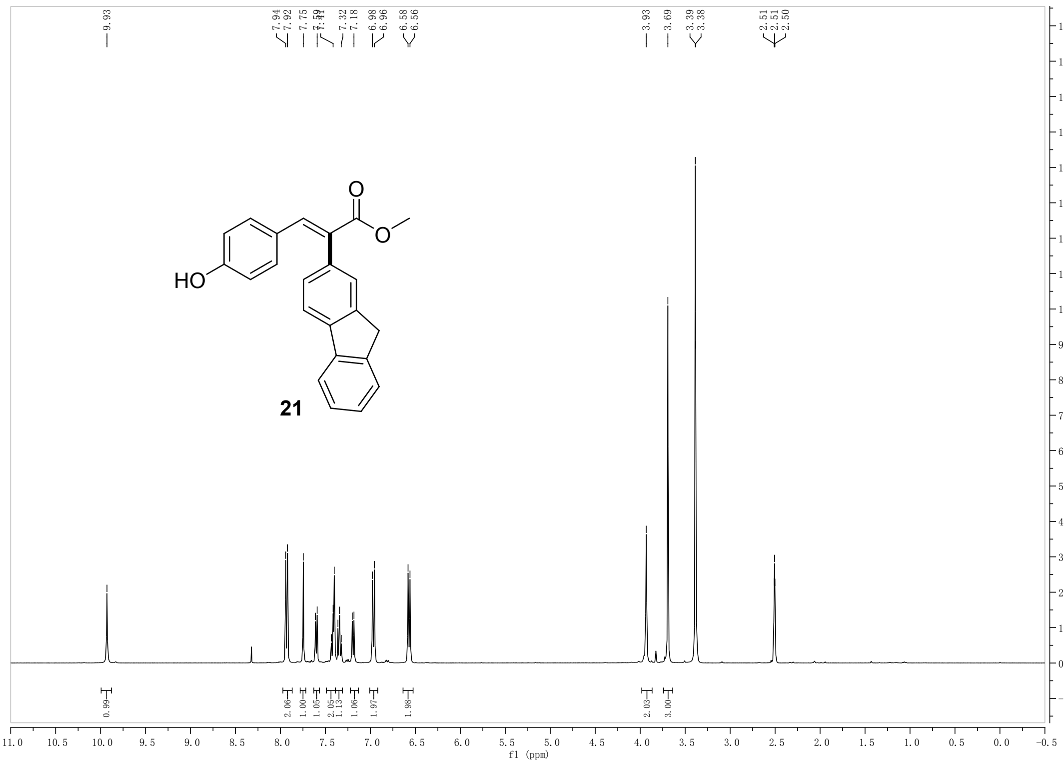
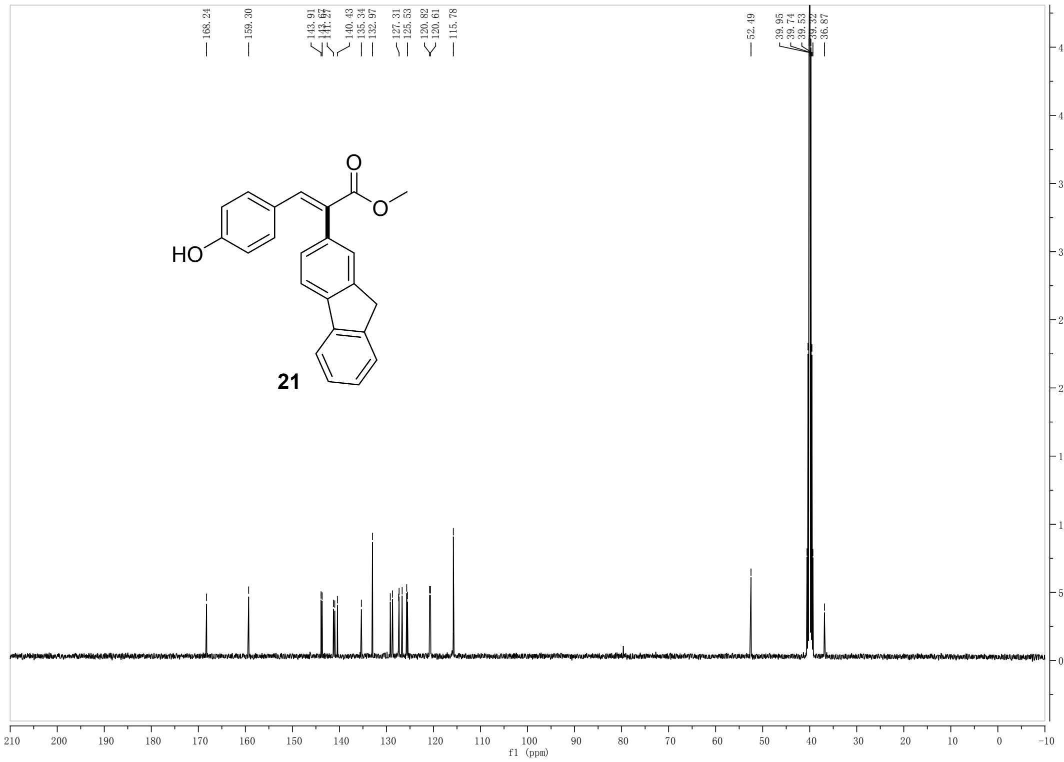
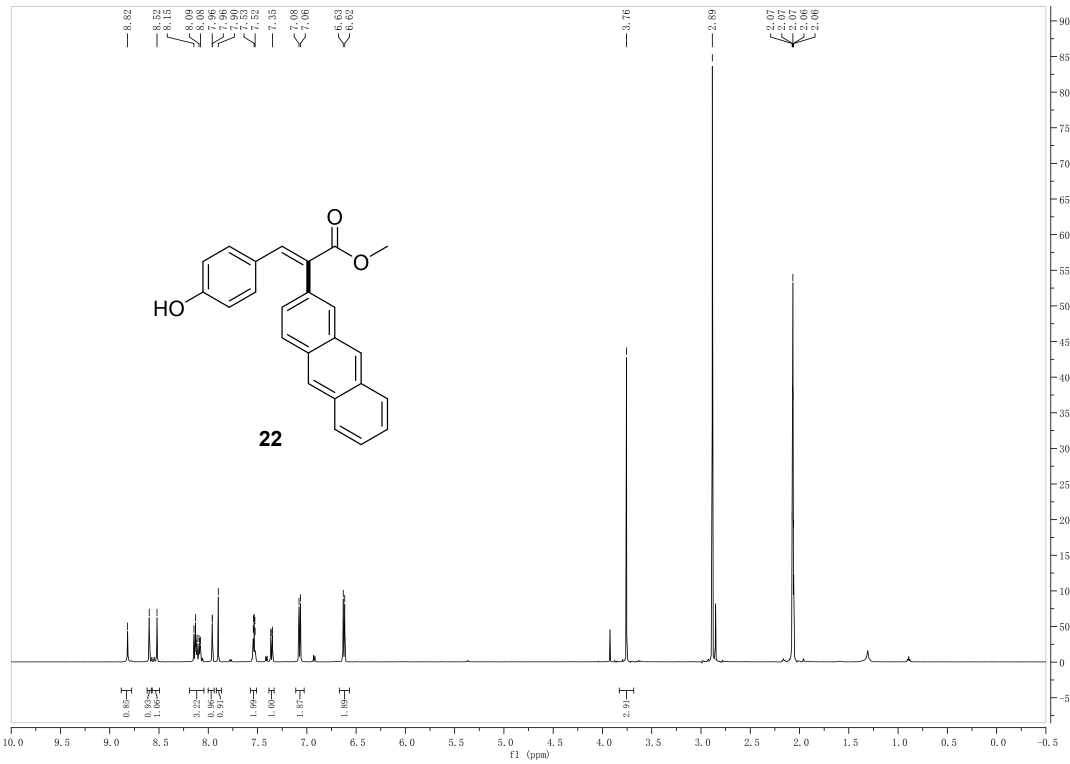
134.00
132.83
132.44
127.94
127.60
125.87
125.75
114.80
51.28
48.06
47.92
47.78
47.63
47.49
47.35
47.21
HO
O
O
20
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

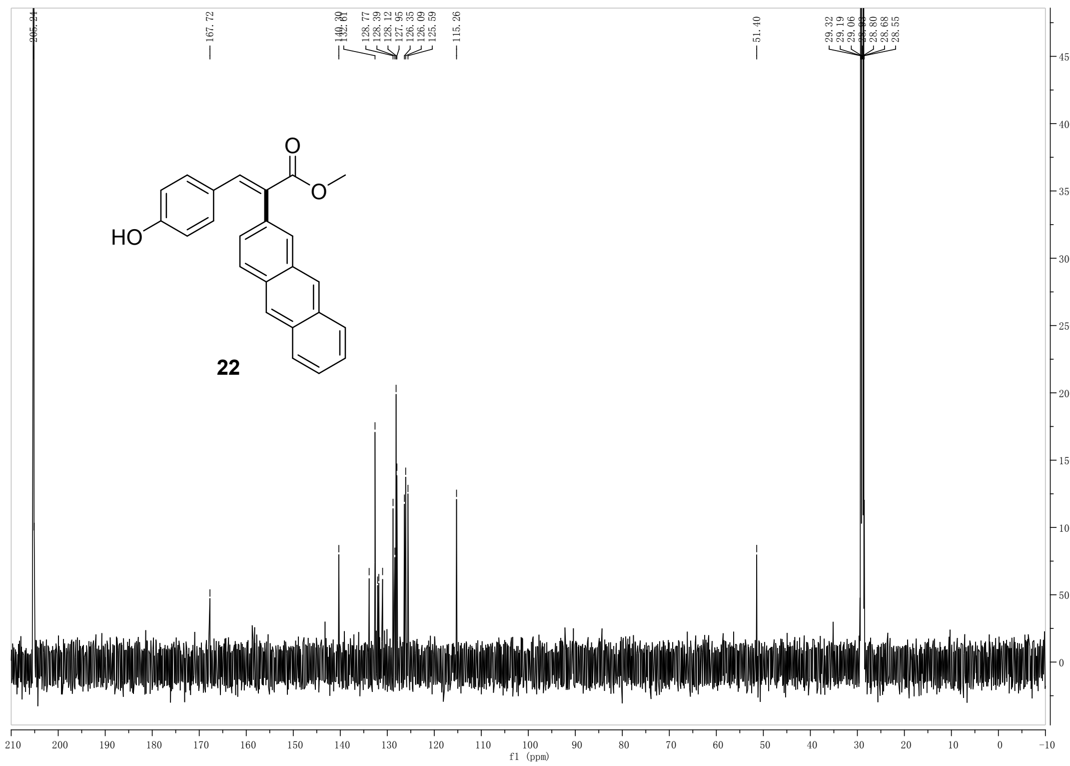

9.93
7.94
7.92
7.75
7.59
7.41
7.32
7.18
6.98
6.96
6.58
6.56
3.93
3.69
3.39
3.38
2.51
2.51
2.50
HO
O
O
0.99
2.06
1.00
1.05
2.05
1.13
1.06
1.97
1.98
2.03
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

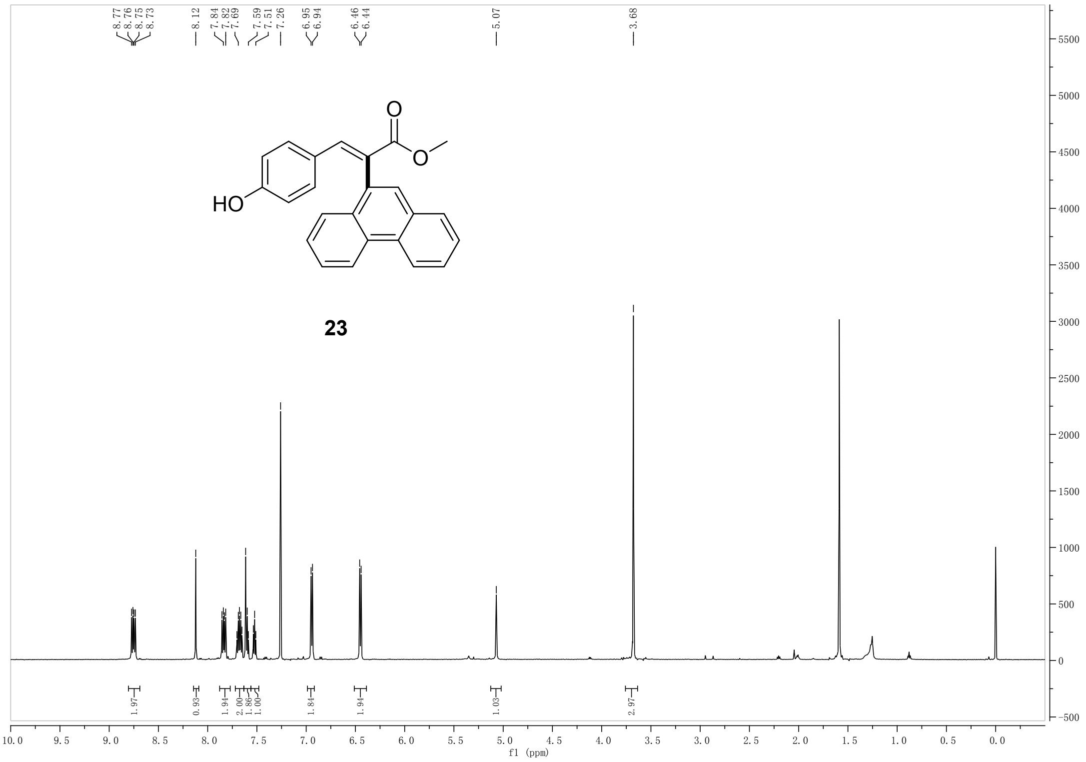
21

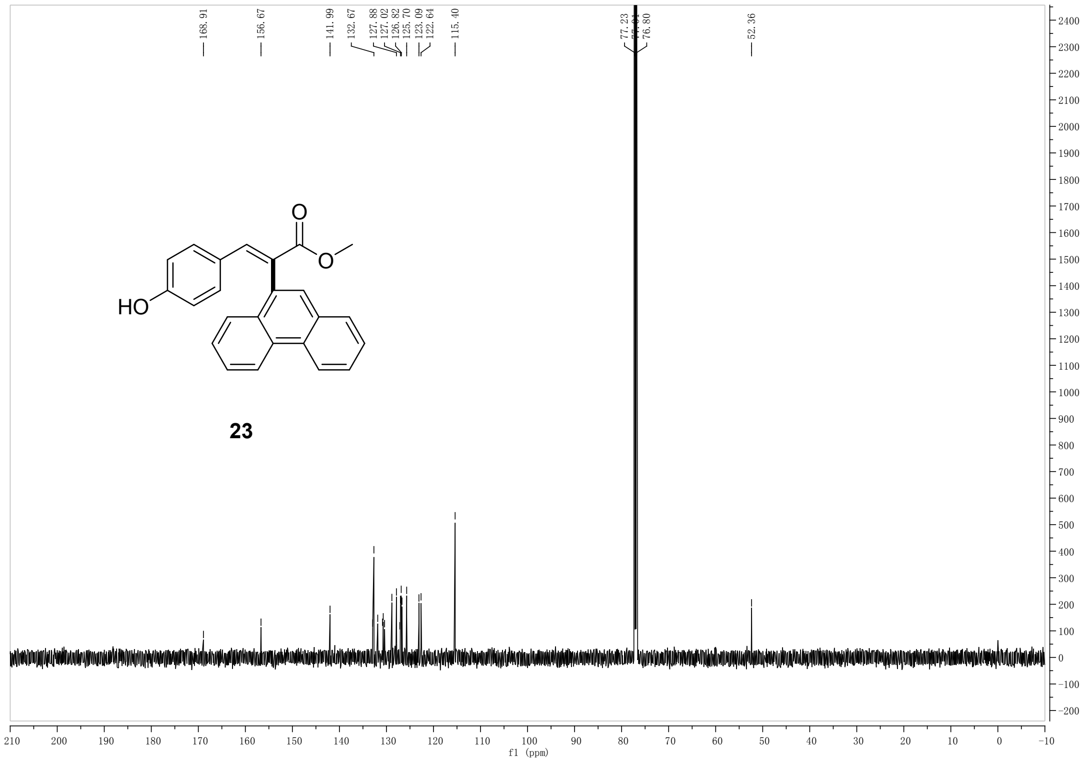

168.24
159.30
143.91
143.67
141.27
140.43
135.34
132.97
127.31
125.53
120.82
120.61
115.78
52.49
39.95
39.74
39.53
39.32
36.87
HO
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0

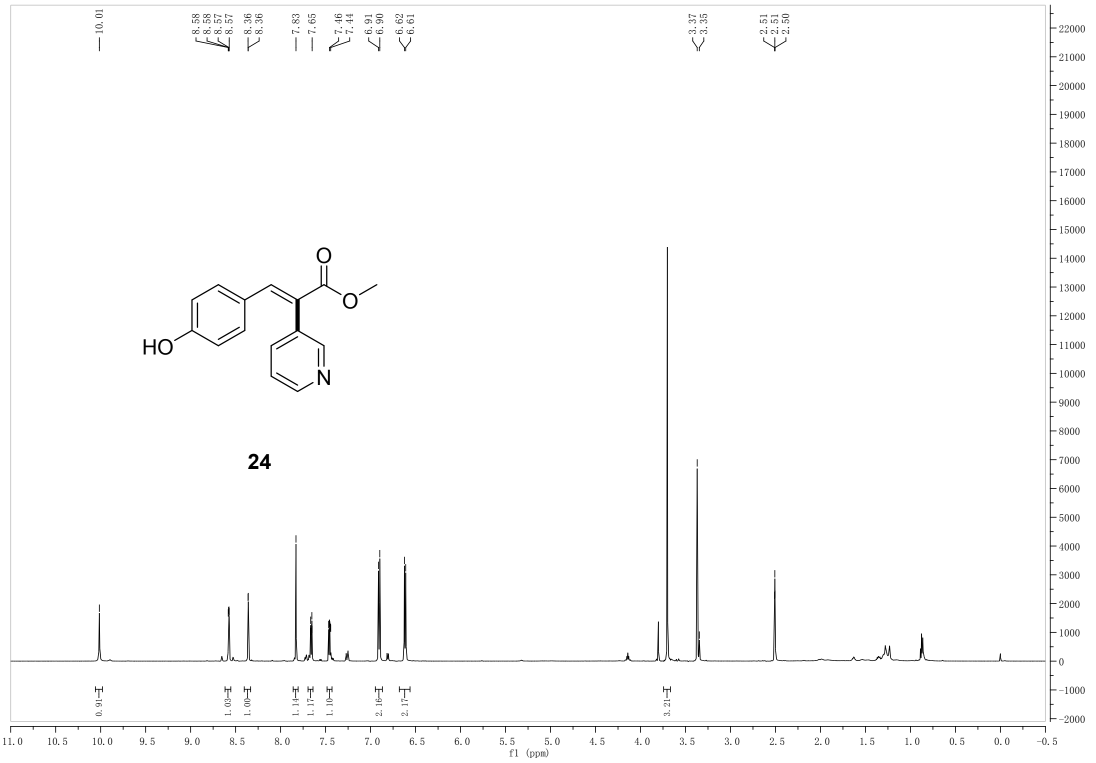
21


8.82
8.52
8.15
8.09
8.08
7.96
7.96
7.90
7.53
7.52
7.35
7.08
7.06
6.63
6.62
3.76
2.89
2.07
2.07
2.07
2.06
2.06
HO
O
O
22
0.85
0.93
1.06
3.22
0.96
0.91
1.99
1.00
1.87
1.89
2.91
f1 (ppm)


205.24
167.72
140.30
132.61
128.77
128.39
128.12
127.95
126.35
126.09
125.59
115.26
51.40
29.32
29.19
29.06
28.80
28.68
28.55
HO
O
O
22
f1 (ppm)


8.77
8.76
8.75
8.73
8.12
7.84
7.82
7.69
7.59
7.51
7.26
6.95
6.94
6.46
6.44
5.07
3.68
O
O
HO
23
1.97
0.93
1.94
2.00
1.86
1.00
1.84
1.94
1.03
2.97
f1 (ppm)


168.91
156.67
141.99
132.67
127.88
127.02
126.82
125.70
123.09
122.64
115.40
77.23
76.80
52.36
O
O
HO
23
f1 (ppm)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8.57
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8.36
7.83
7.65
7.46
7.44
6.91
6.90
6.62
6.61
3.37
3.35
2.51
2.51
2.50
HO
O
O
N
24
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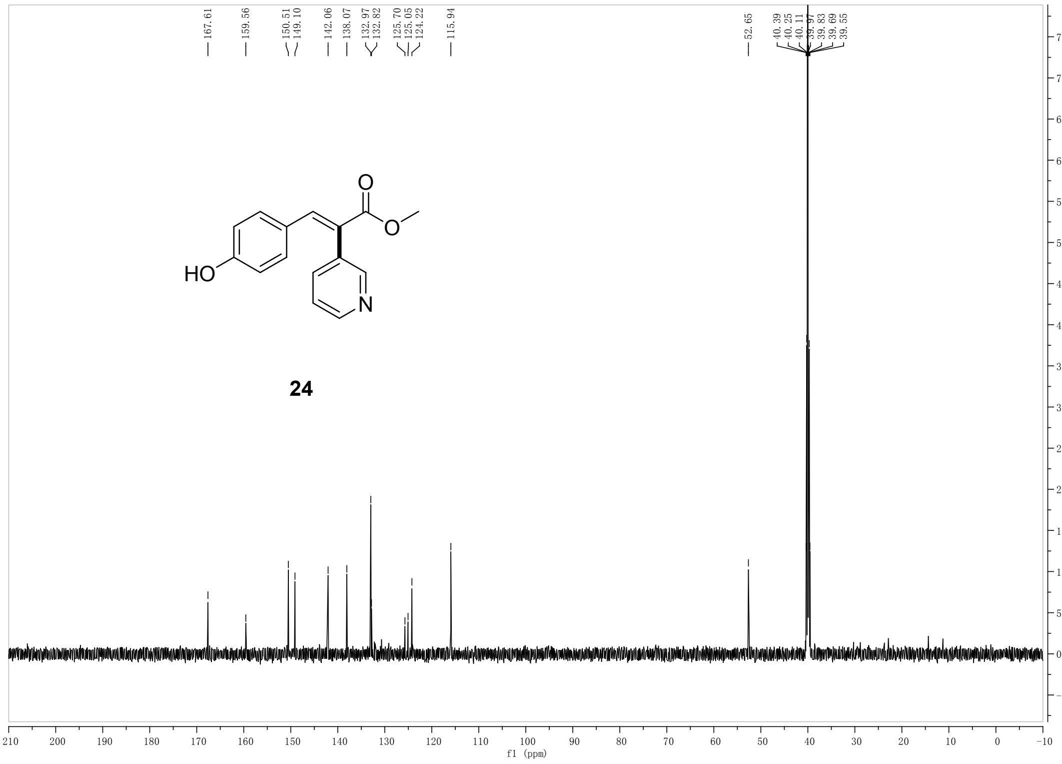
1.03
1.00
1.14
1.17
1.10
2.16
2.17
3.21
f1 (ppm)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142.06
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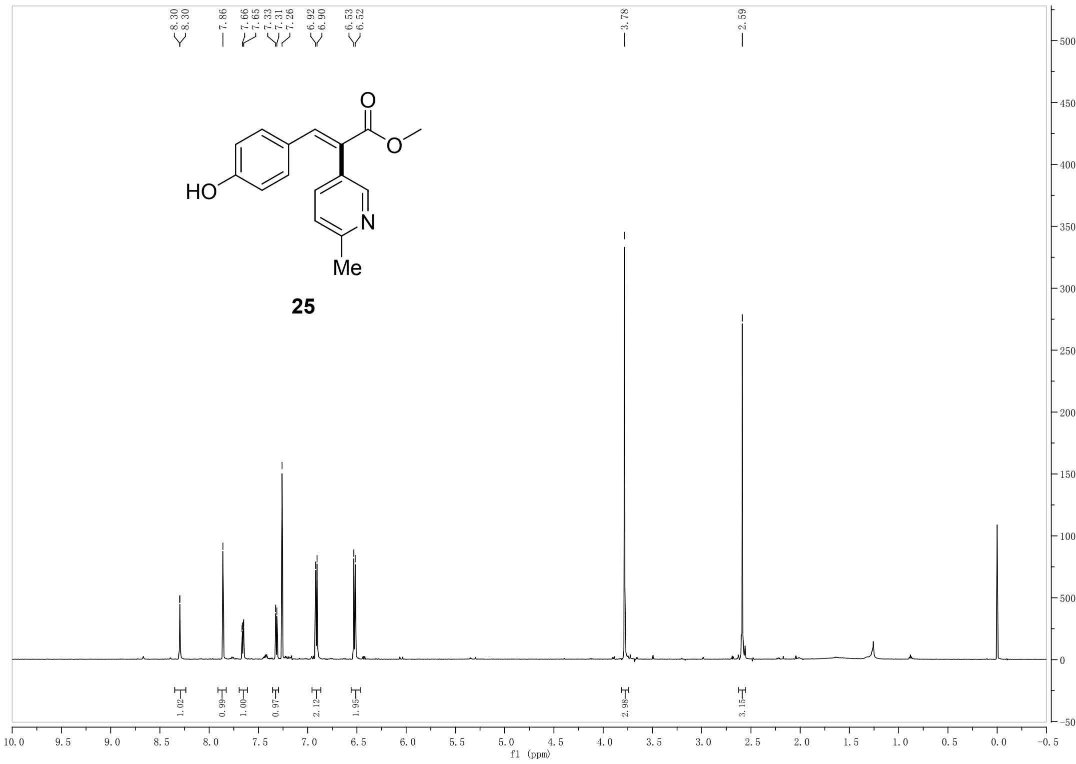
132.97
132.82
125.70
125.05
124.22
115.94
52.65
40.39
40.25
40.11
39.97
39.83
39.69
39.55
HO
O
O
N
24
f1 (ppm)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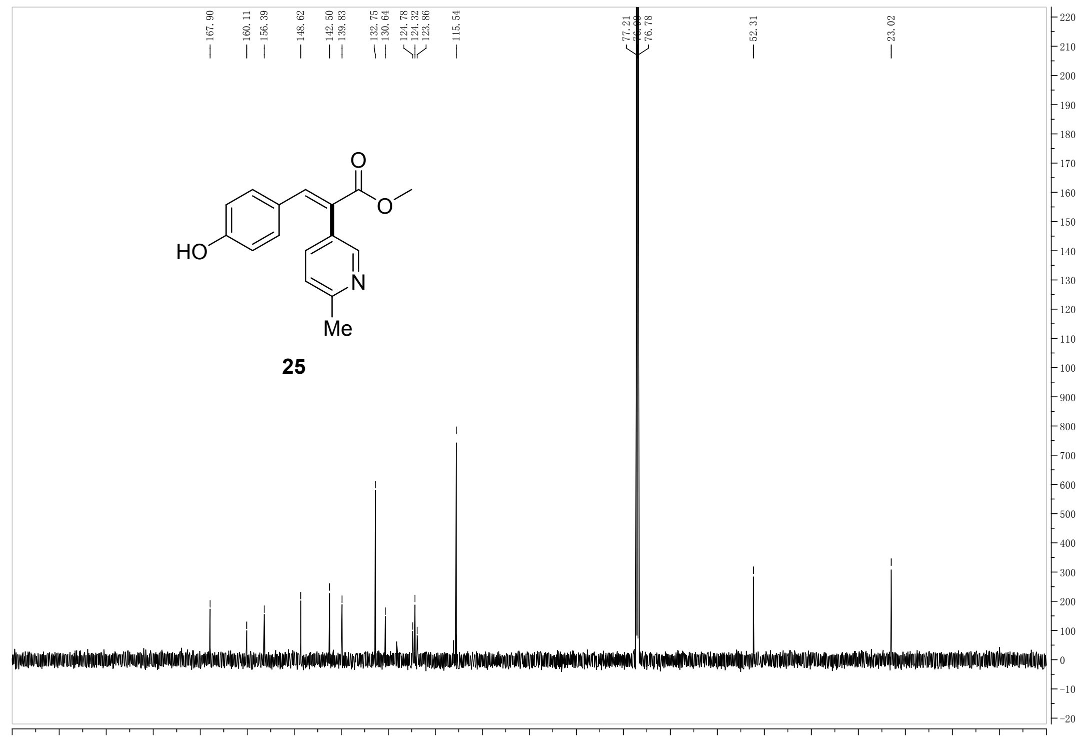
7.86
7.66
7.65
7.33
7.31
7.26
6.92
6.90
6.53
6.52
3.78
2.59
HO
O
O
N
Me
25
1.02
0.99
1.00
0.97
2.12
1.95
2.98
3.15
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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132.75
130.64
124.78
124.32
123.86
115.54
77.21
76.78
52.31
23.02
HO
O
O
N
Me
25
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
210
200
190
180
170
160
150
140
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120
110
100
90
80
70
60
50
40
30
20
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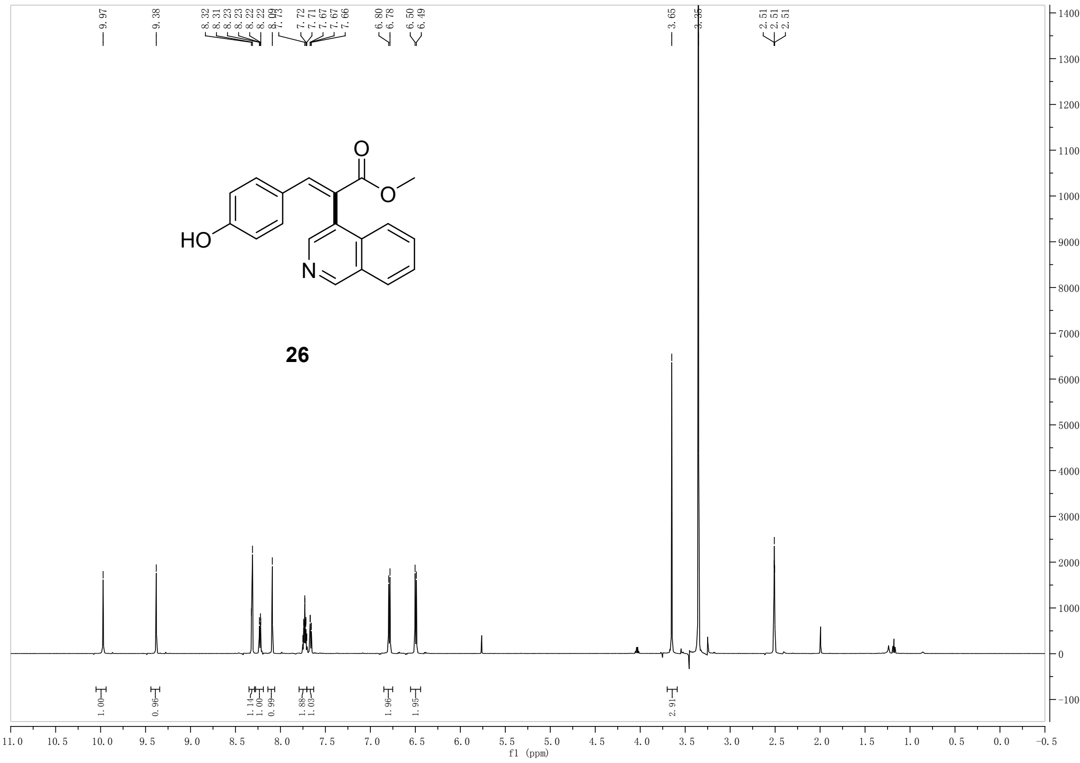
0
-10
f1 (ppm)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8.23
8.22
8.22
8.09
7.73
7.72
7.71
7.67
7.67
7.66
6.80
6.78
6.50
6.49
3.65
3.35
2.51
2.51
2.51
HO
N
O
O
26
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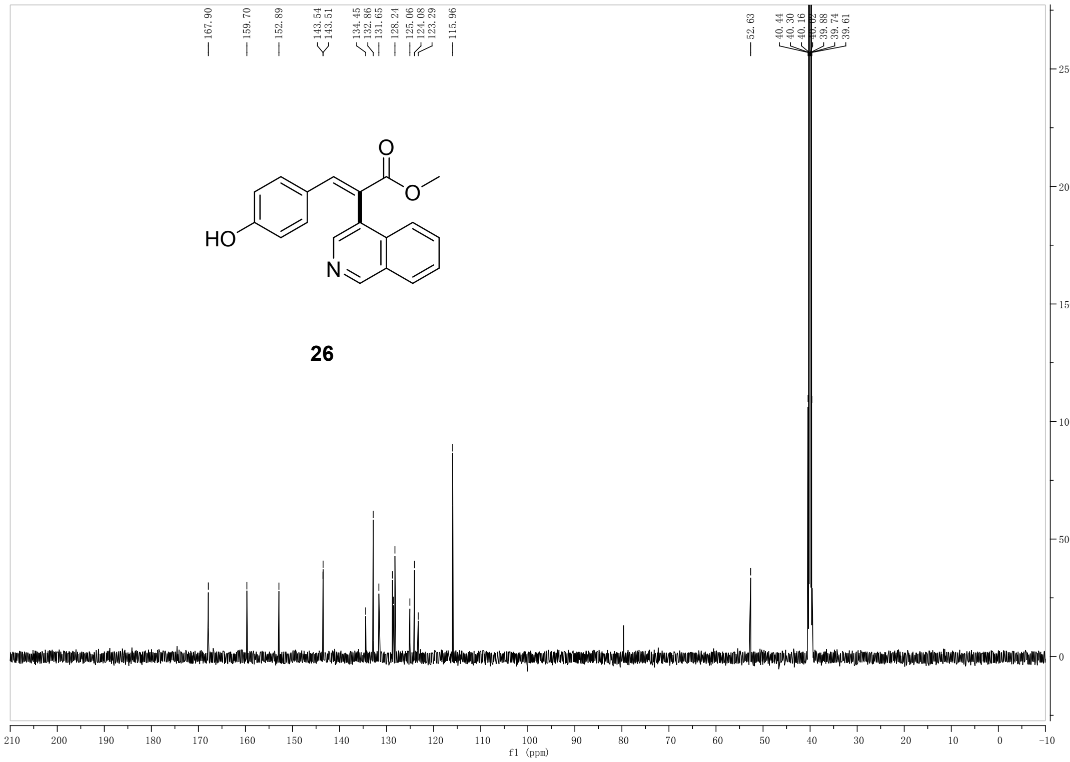
1.14
1.00
0.99
1.88
1.03
1.96
1.95
2.91
f1 (ppm)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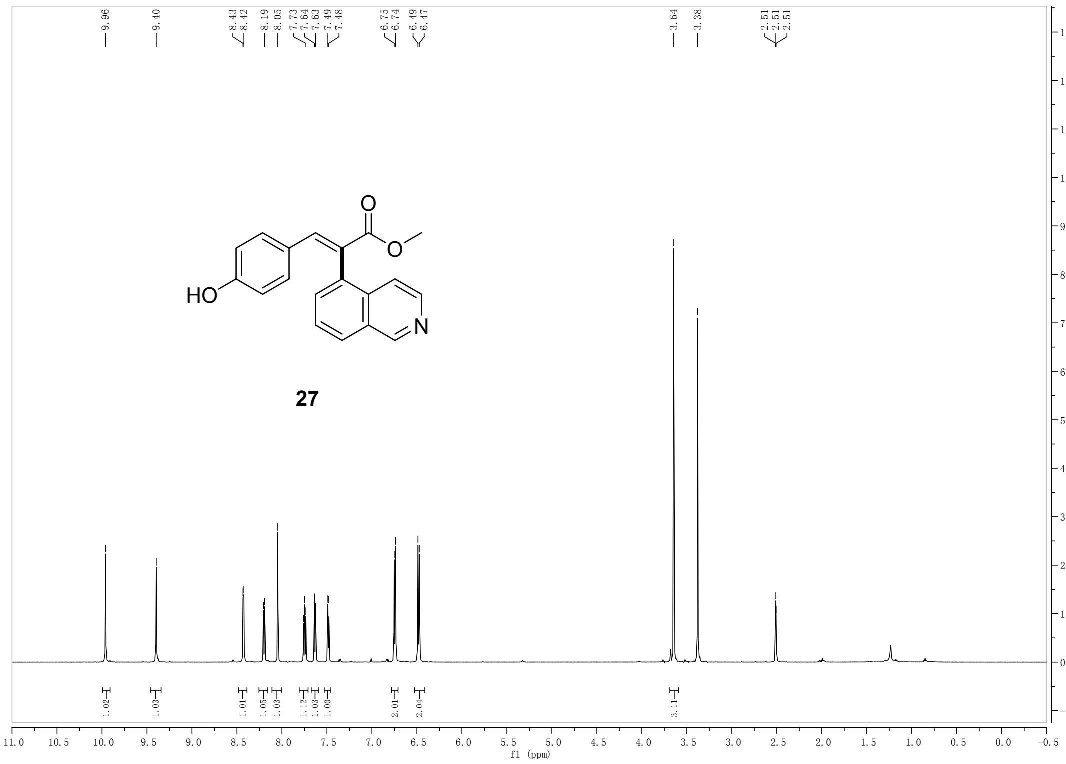
152.89
143.54
143.51
134.45
132.86
131.65
128.24
125.06
124.08
123.29
115.96
52.63
40.44
40.30
40.16
40.02
39.88
39.74
39.61
HO
N
O
O
26
f1 (ppm)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8.43
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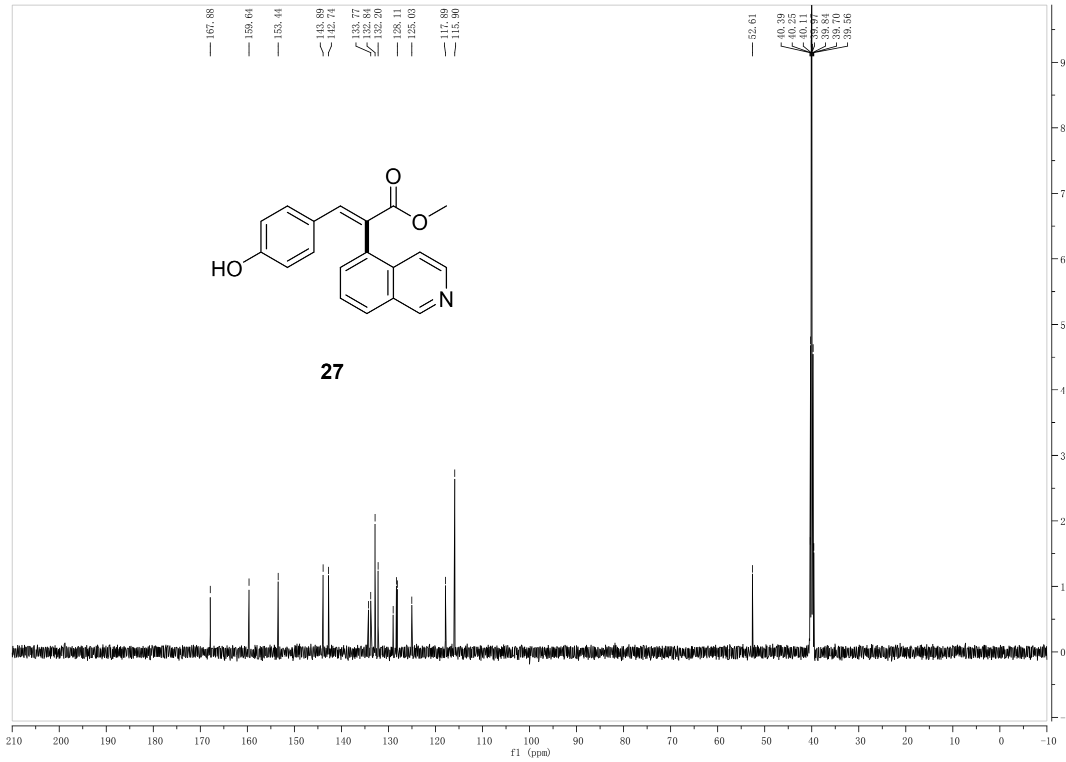
8.19
8.05
7.73
7.64
7.63
7.49
7.48
6.75
6.74
6.49
6.47
3.64
3.38
2.51
2.51
2.51
HO
O
O
N
27
1.02
1.03
1.01
1.05
1.03
1.12
1.03
1.00
2.01
2.04
3.11
f1 (ppm)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153.44
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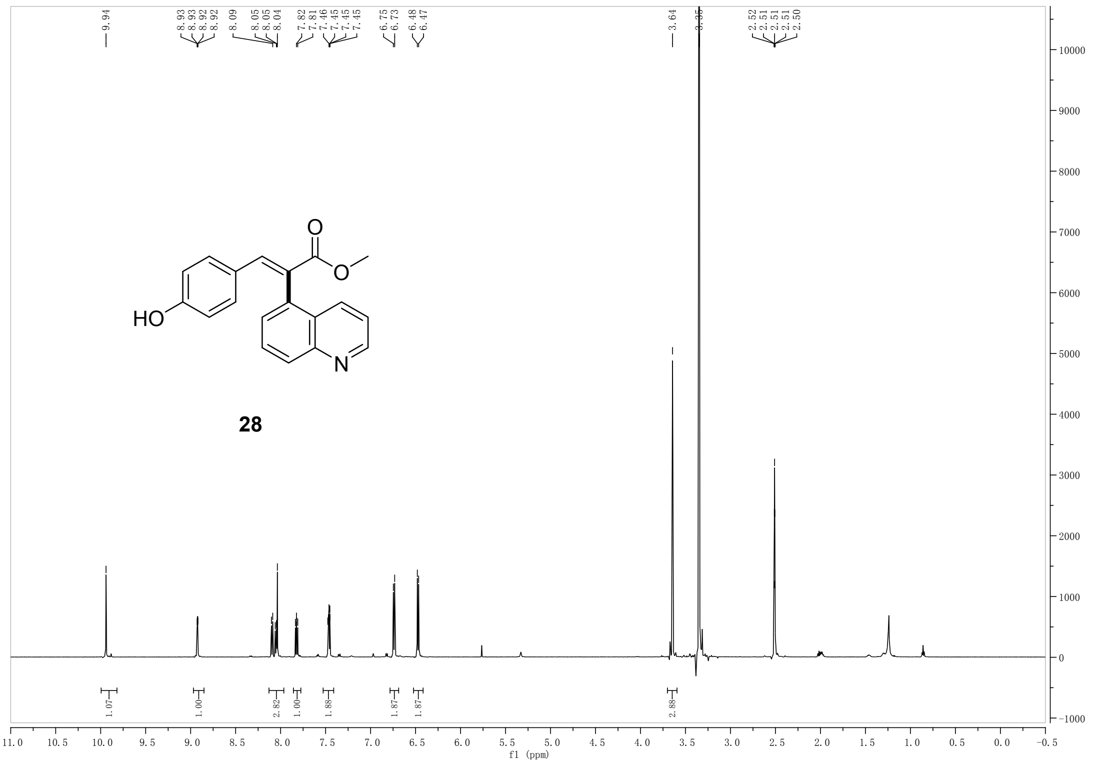
142.74
133.77
132.84
132.20
128.11
125.03
117.89
115.90
52.61
40.39
40.25
40.11
39.97
39.84
39.70
39.56
HO
O
O
N
27
f1 (ppm)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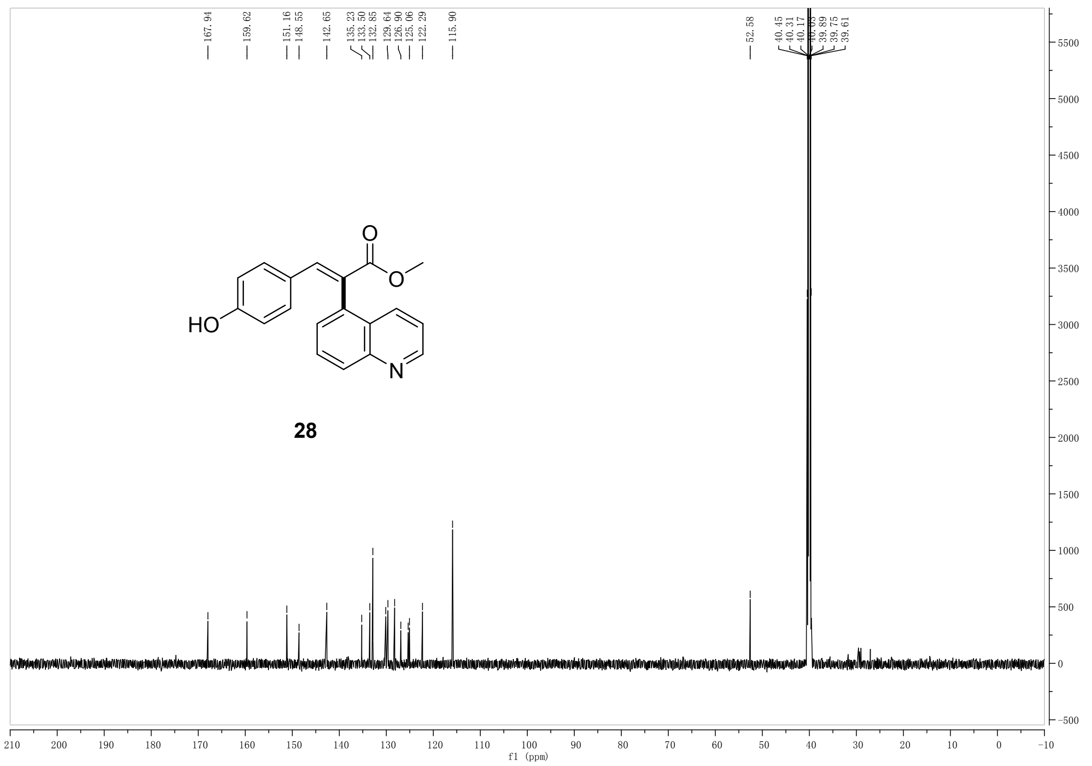
8.92
8.92
8.09
8.05
8.05
8.04
7.82
7.81
7.46
7.45
7.45
7.45
6.75
6.73
6.48
6.47
3.64
3.35
2.52
2.51
2.51
2.51
2.50
HO
O
O
N
28
1.07
1.00
2.82
1.00
1.88
1.87
1.87
2.88
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)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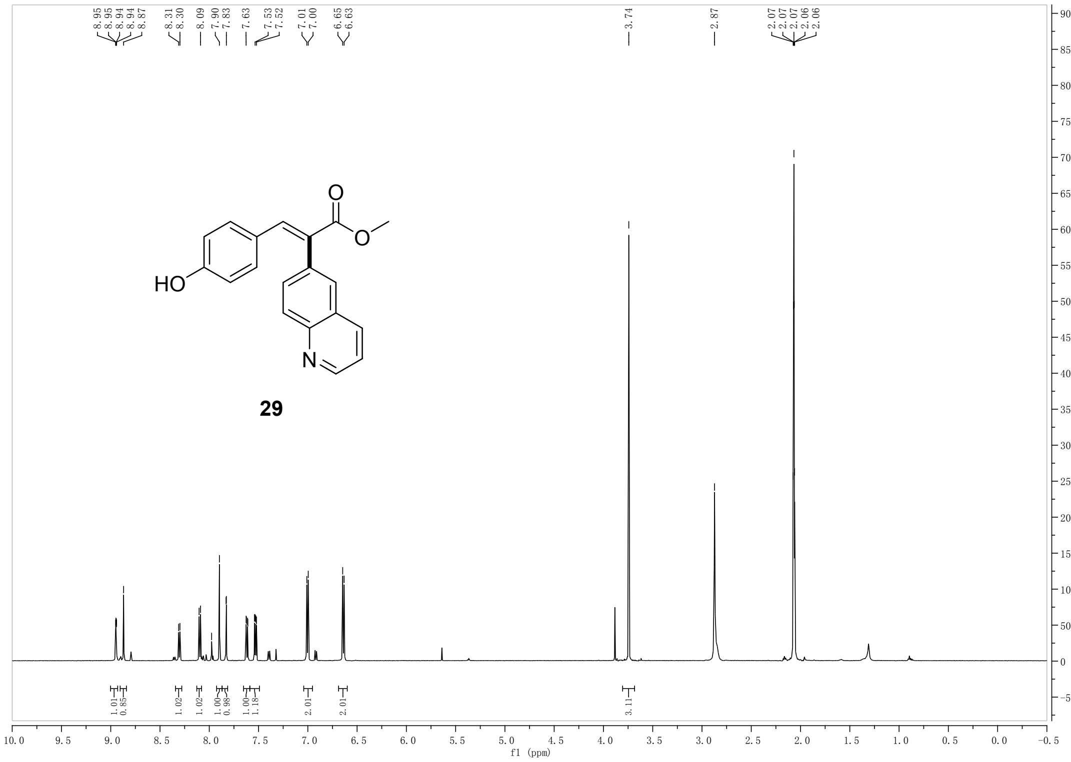
148.55
142.65
135.23
133.50
132.85
129.64
126.90
125.06
122.29
115.90
52.58
40.45
40.31
40.17
40.03
39.89
39.75
39.61
HO
O
O
N
28
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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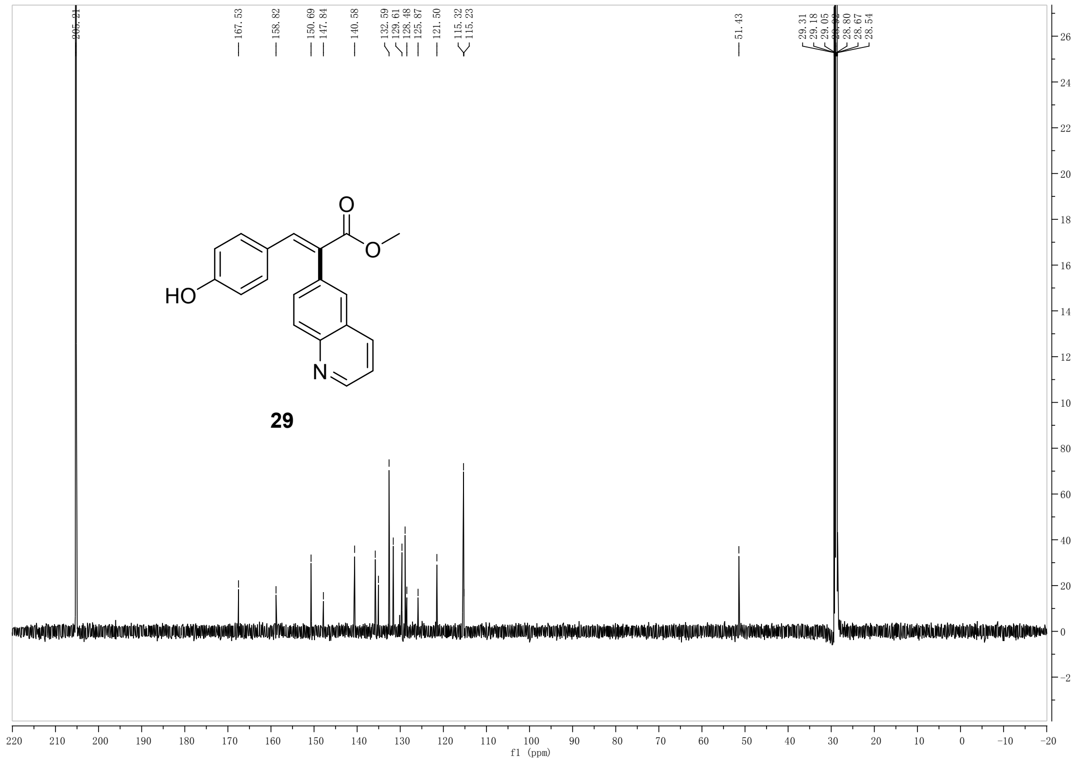
8.95
8.94
8.94
8.87
8.31
8.30
8.09
7.90
7.83
7.63
7.53
7.52
7.01
7.00
6.65
6.63
3.74
2.87
2.07
2.07
2.07
2.06
2.06
HO
O
O
N
29
1.01
0.85
1.02
1.02
1.00
0.88
1.00
1.18
2.01
2.01
3.11
f1 (ppm)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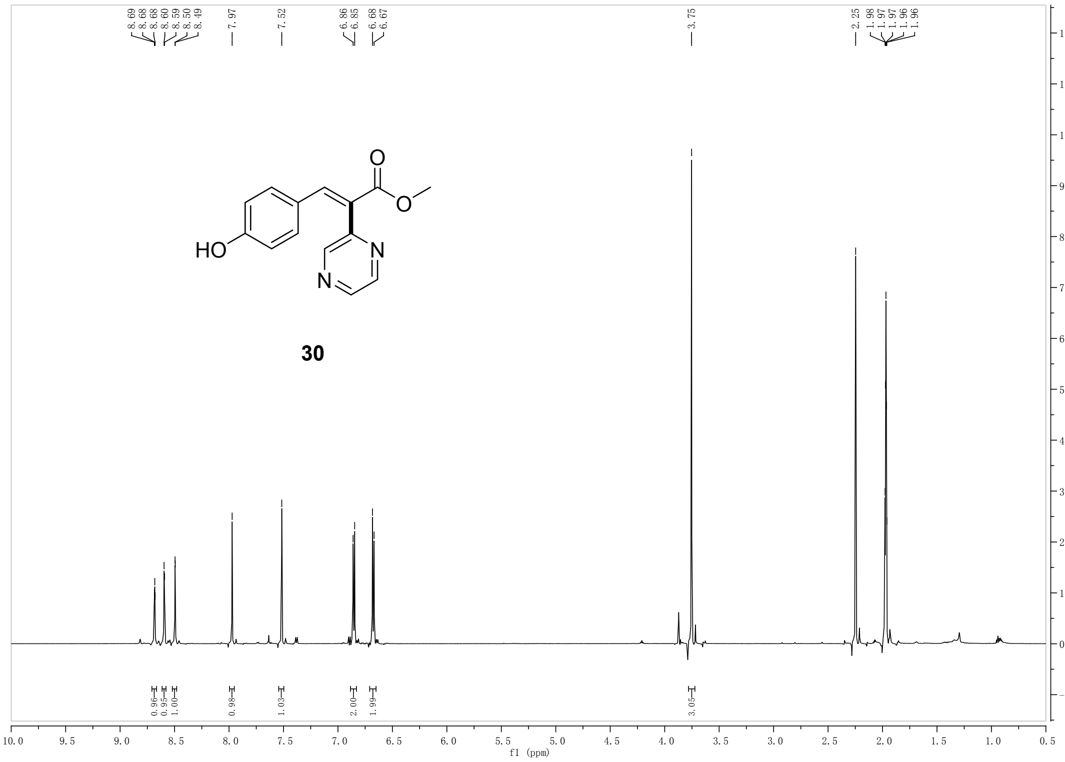
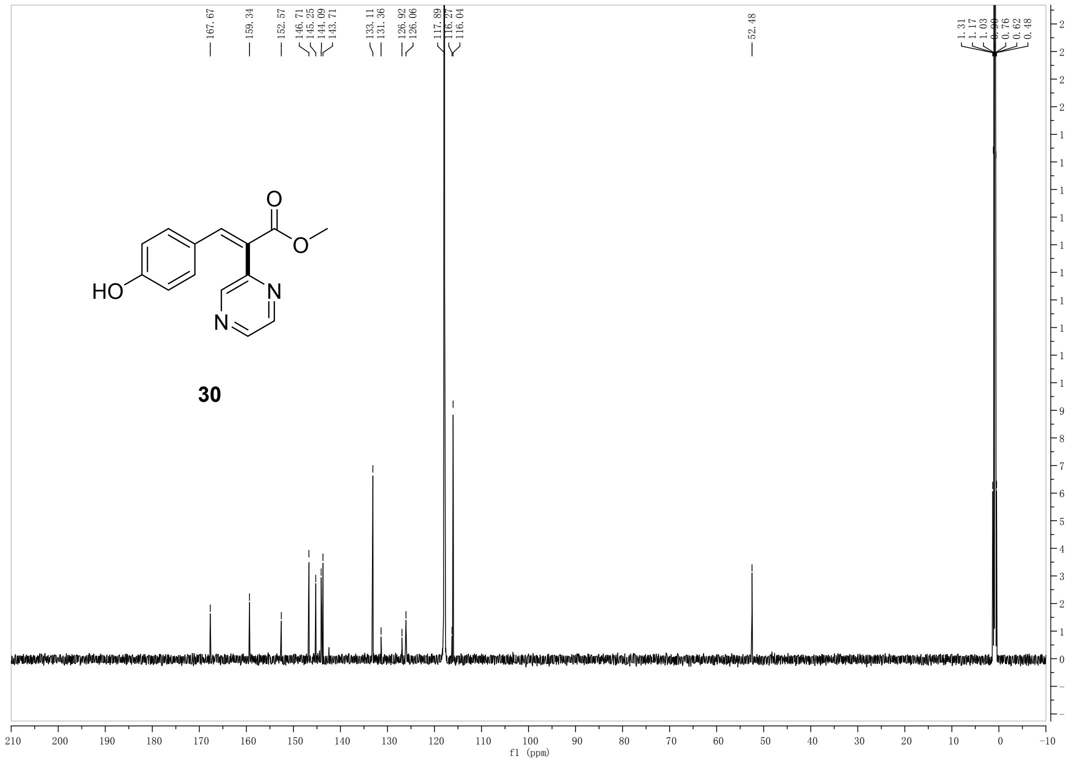
167.53
158.82
150.69
147.84
140.58
132.59
129.61
128.48
125.87
121.50
115.32
115.23
51.43
29.31
29.18
29.05
28.92
28.80
28.67
28.54
HO
O
O
N
29
f1 (ppm)



30

8.69
8.68
8.68
8.60
8.59
8.50
8.49
7.97
7.52
6.86
6.85
6.68
6.67
3.75
2.25
1.98
1.97
1.96
1.96
0.96
0.95
1.00
0.98
1.03
2.00
1.99
3.05
O
O
HO
N
N
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
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
f1 (ppm)



30

167.67
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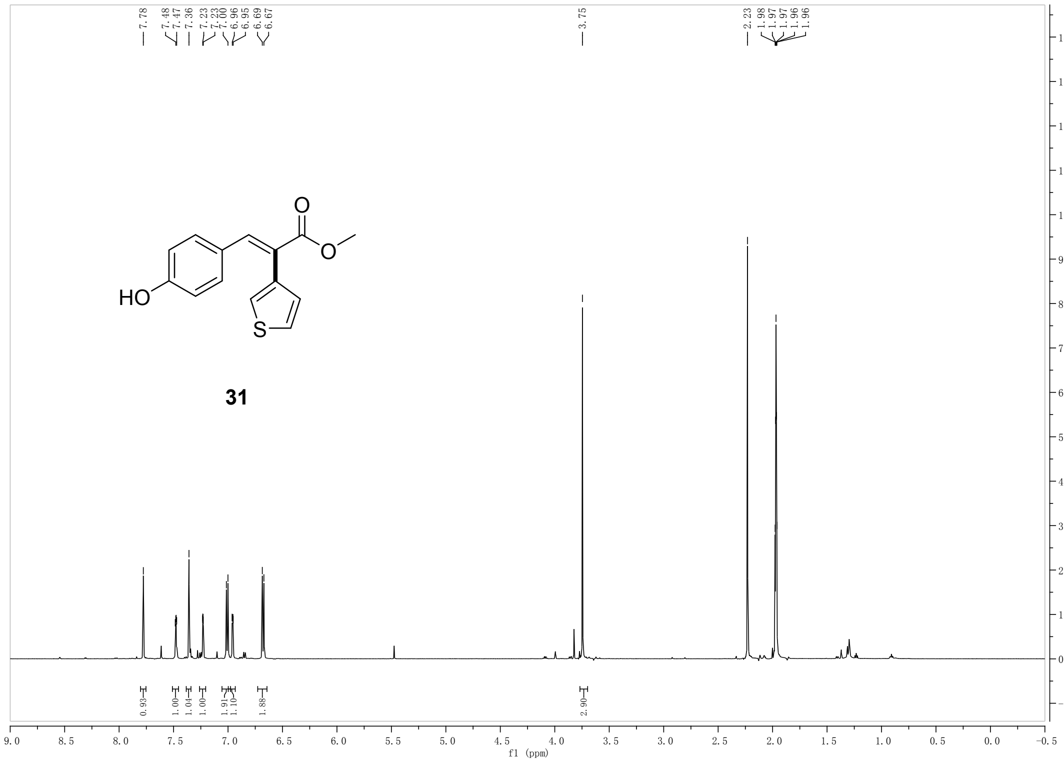
152.57
146.71
145.25
144.09
143.71
133.11
131.36
126.92
126.06
117.89
116.27
116.04
52.48
1.31
1.17
1.03
0.90
0.76
0.62
0.48
O
O
HO
N
N
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.78
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7.36
7.23
7.23
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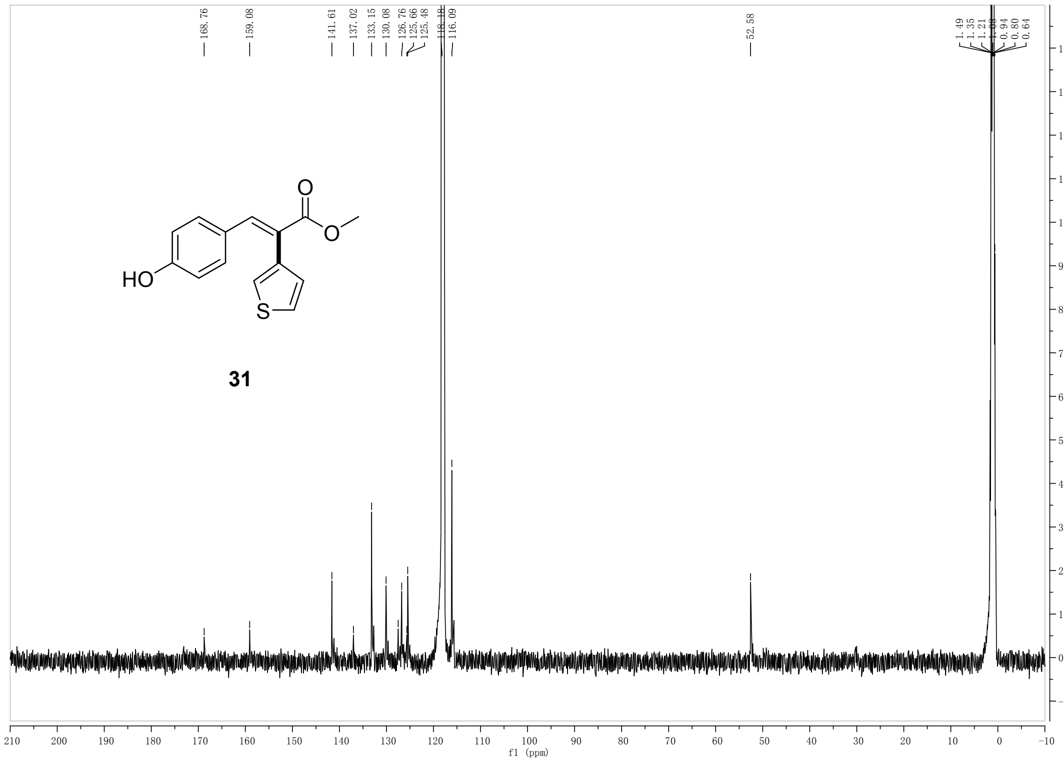
6.96
6.95
6.69
6.67
3.75
2.23
1.98
1.97
1.96
1.96
HO
O
O
S
31
0.93
1.00
1.04
1.00
1.91
1.10
1.88
2.90
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)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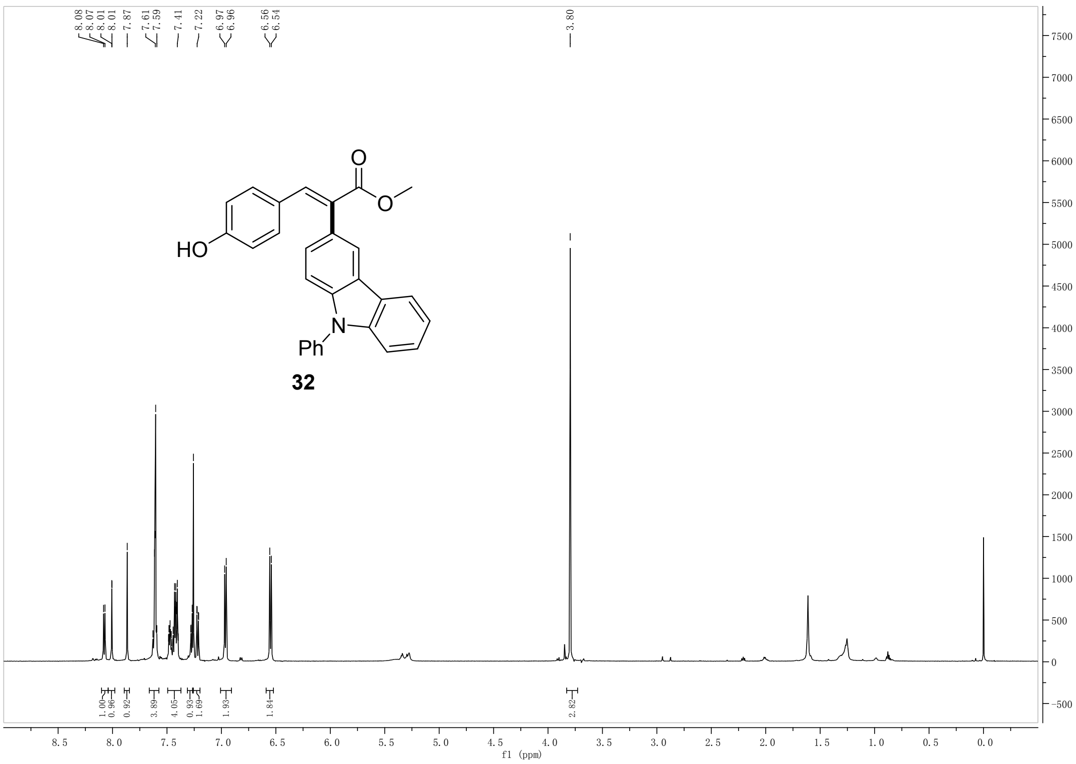
137.02
133.15
130.08
126.76
125.66
125.48
118.18
116.09
52.58
1.49
1.35
1.21
1.08
0.94
0.80
0.64
HO
O
O
S
31
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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8.01
7.87
7.61
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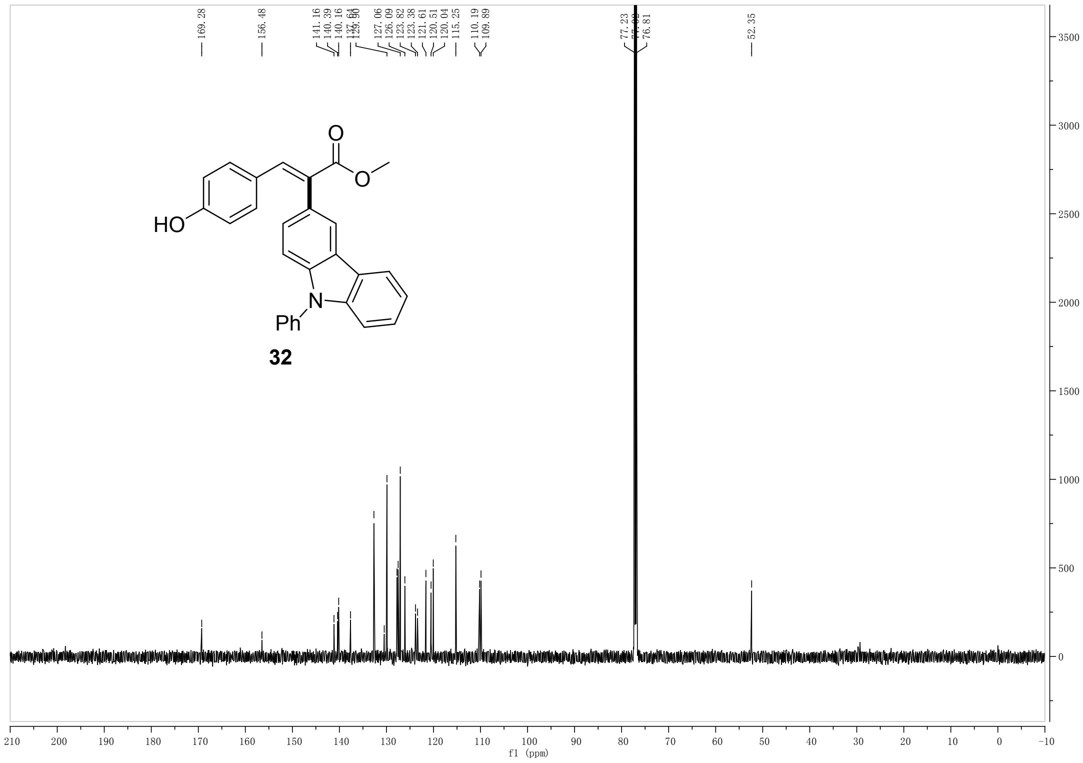
7.41
7.22
6.97
6.96
6.56
6.54
3.80
HO
O
O
N
Ph
32
1.00
0.96
0.92
3.89
4.05
0.93
1.69
1.93
1.84
2.82
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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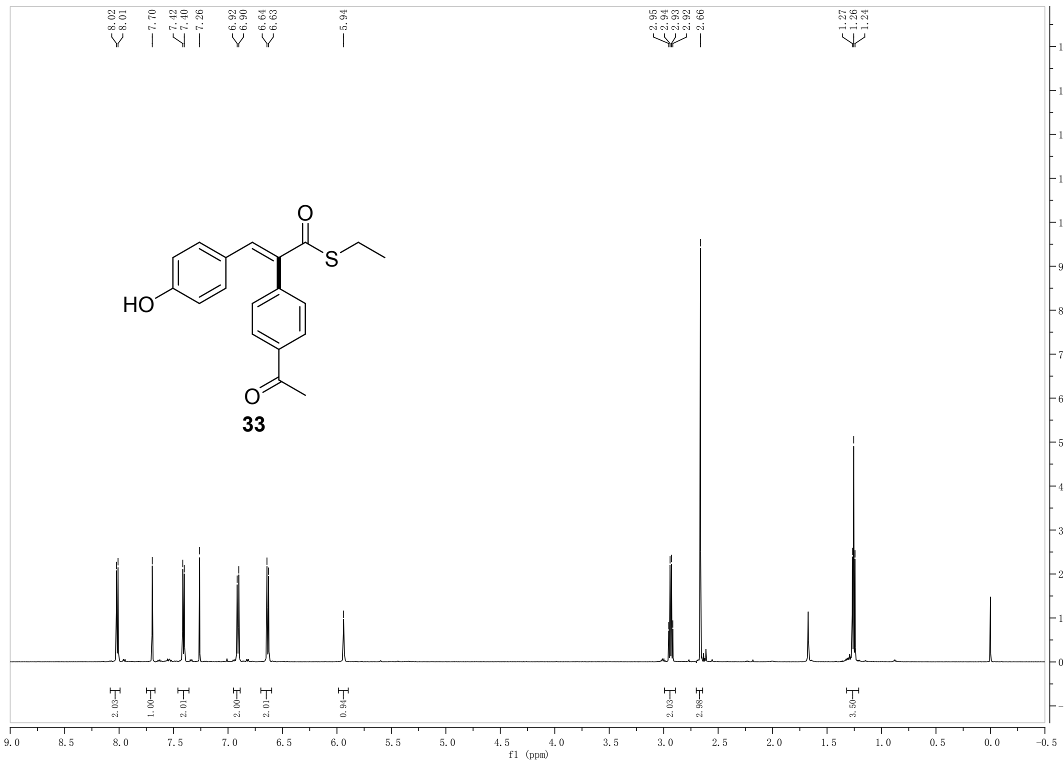
127.06
126.09
123.82
123.38
121.61
120.51
120.04
115.25
110.19
109.89
77.23
76.81
52.35
HO
O
O
N
Ph
32
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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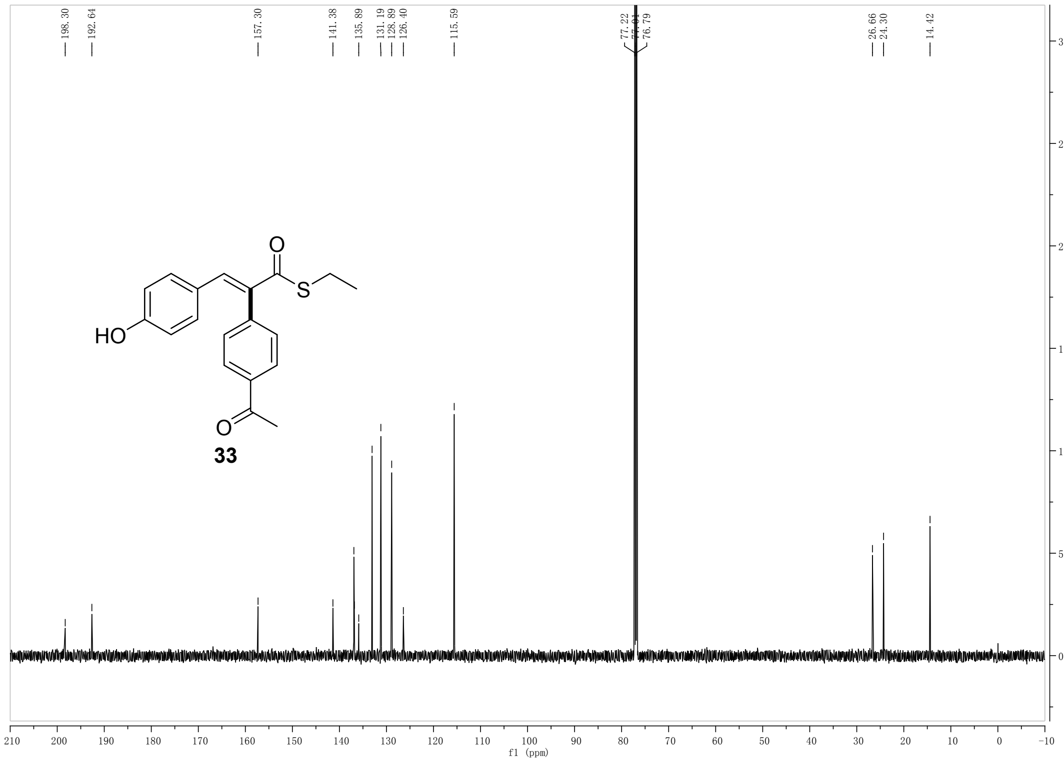
7.40
7.26
6.92
6.90
6.64
6.63
5.94
2.95
2.94
2.93
2.92
2.66
1.27
1.26
1.24
2.03
1.00
2.01
2.00
2.01
0.94
2.03
2.98
3.50
HO
O
S
O
33
f1 (ppm)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135.89
131.19
128.89
126.40
115.59
77.22
77.01
76.79
26.66
24.30
14.42
HO
O
S
O
33
f1 (ppm)


9.71
7.99
7.98
7.38
7.37
7.35
7.31
7.30
6.82
6.81
6.56
6.55
3.17
3.15
3.14
3.14
3.13
3.12
2.61
1.03
1.02
1.01
O
N
H
HO
O
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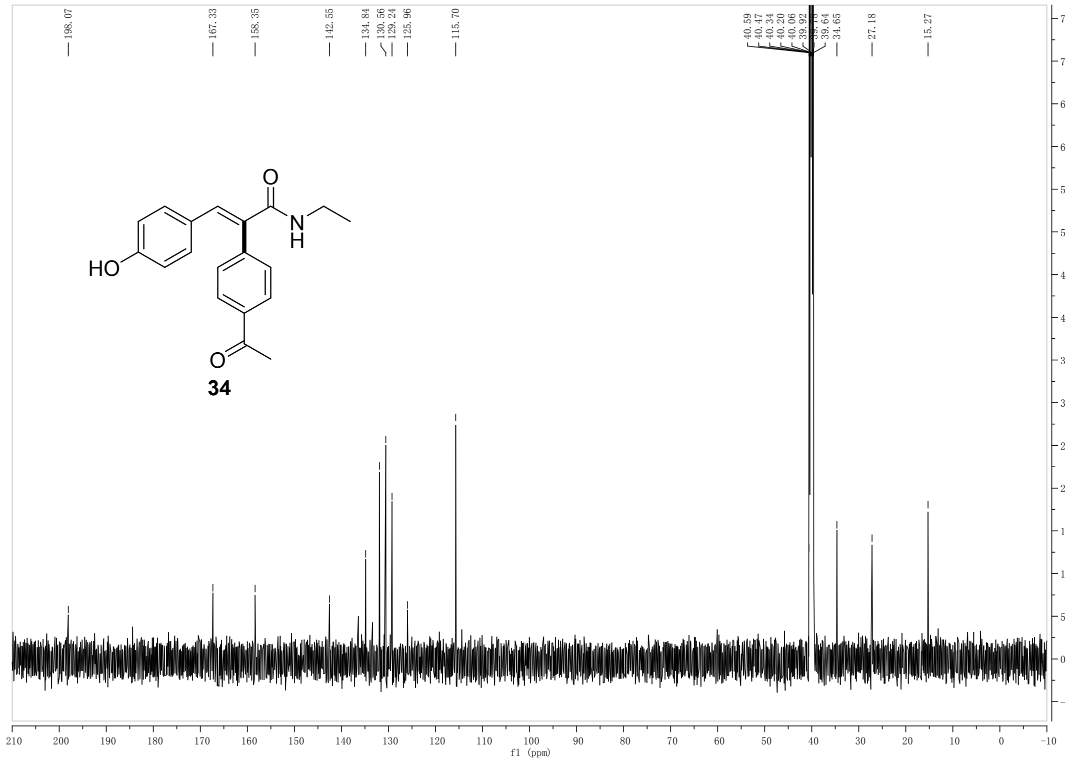
0.98
2.00
1.04
1.00
1.95
1.99
1.99
1.97
3.21
3.09
f1 (ppm)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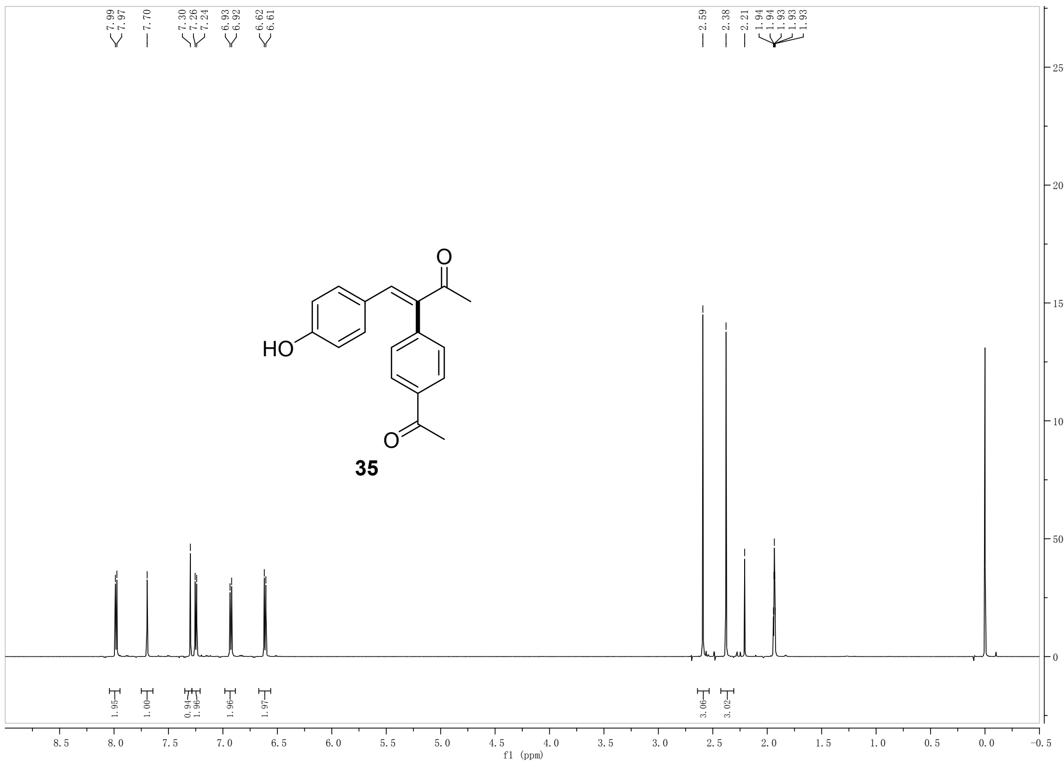
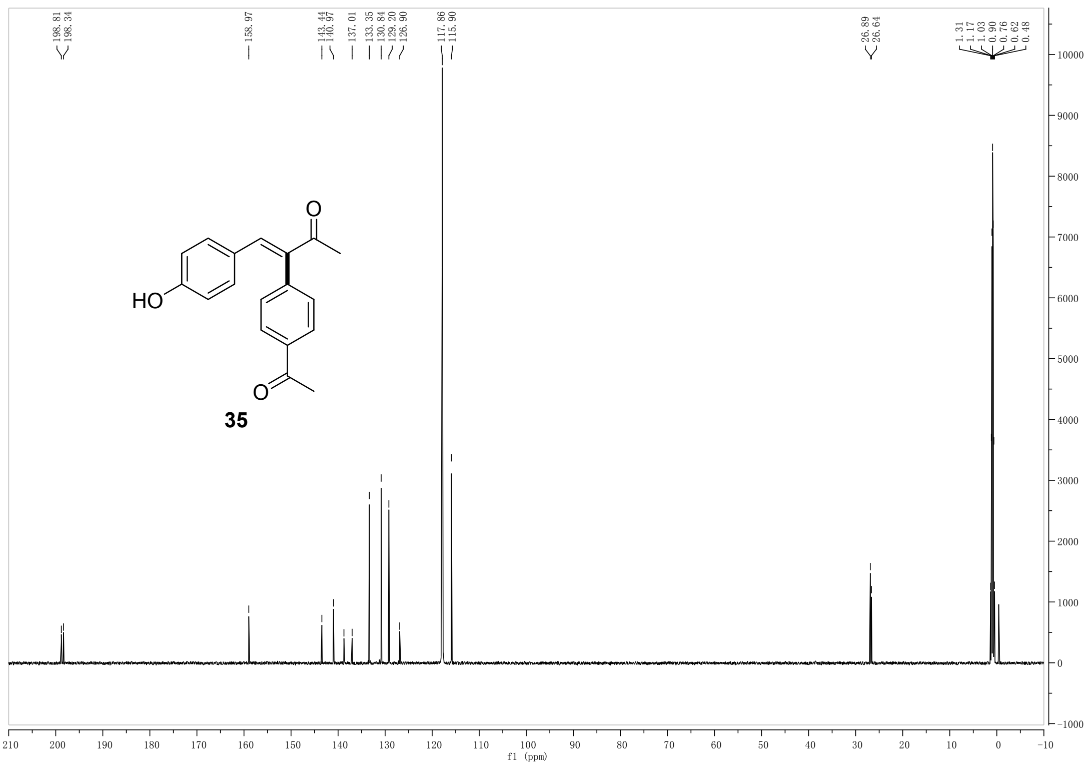
129.24
125.96
115.70
40.59
40.47
40.34
40.20
40.06
39.92
39.78
39.64
34.65
27.18
15.27
O
N
H
HO
O
34
f1 (ppm)


7.99
7.97
7.70
7.30
7.26
7.24
6.93
6.92
6.62
6.61
2.59
2.38
2.21
1.94
1.94
1.93
1.93
1.93
HO
O
O
35
1.95
1.00
0.94
1.96
1.96
1.97
3.06
3.02
25000
20000
15000
10000
5000
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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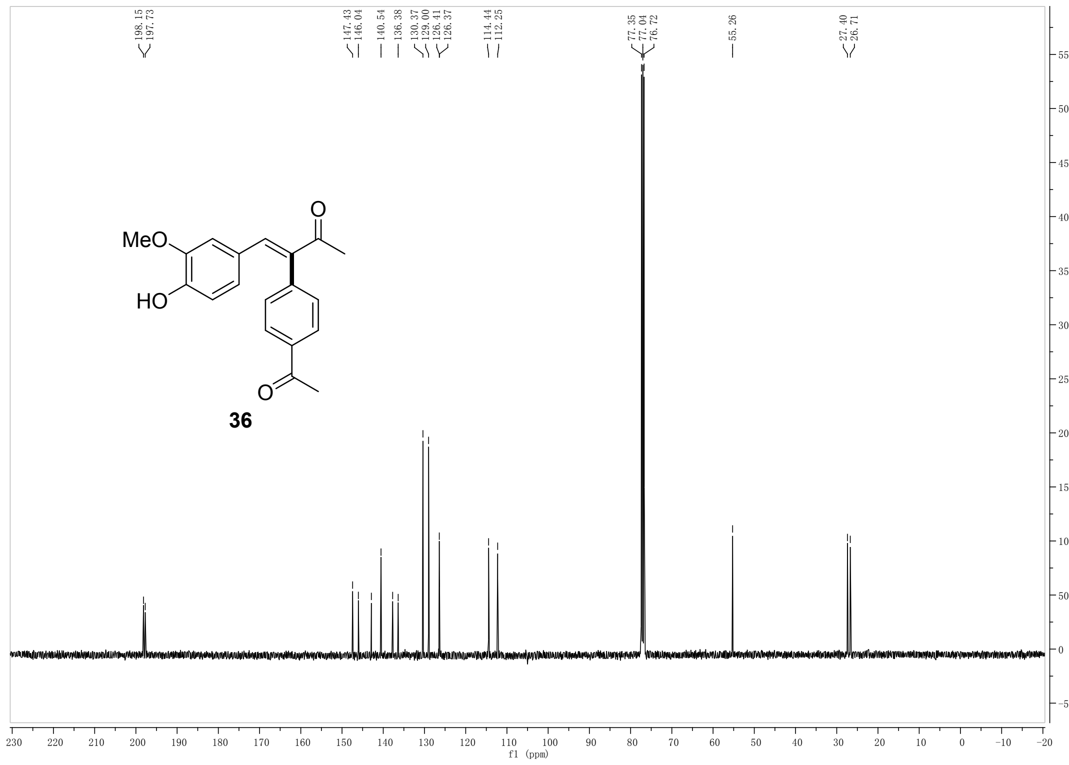
137.01
133.35
130.84
129.20
126.90
117.86
115.90
26.89
26.64
1.31
1.17
1.03
0.90
0.76
0.62
0.48
HO
O
O
35
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.04
8.02
7.64
7.34
7.32
7.27
6.77
6.76
6.76
6.74
6.74
6.36
6.36
5.84
3.42
2.64
2.38
MeO
HO
O
O
36
1.97
1.00
1.93
1.96
0.99
1.05
3.06
3.03
3.07
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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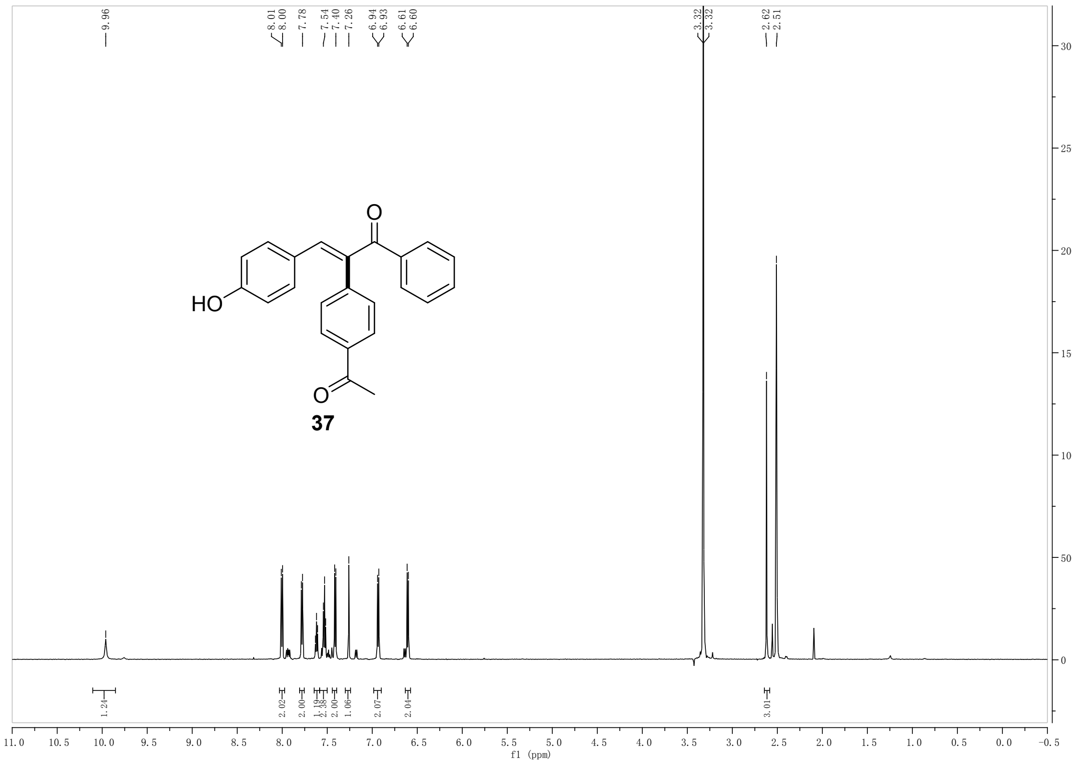
146.04
140.54
136.38
130.37
129.00
126.41
126.37
114.44
112.25
77.35
77.04
76.72
55.26
27.40
26.71
MeO
HO
O
O
36
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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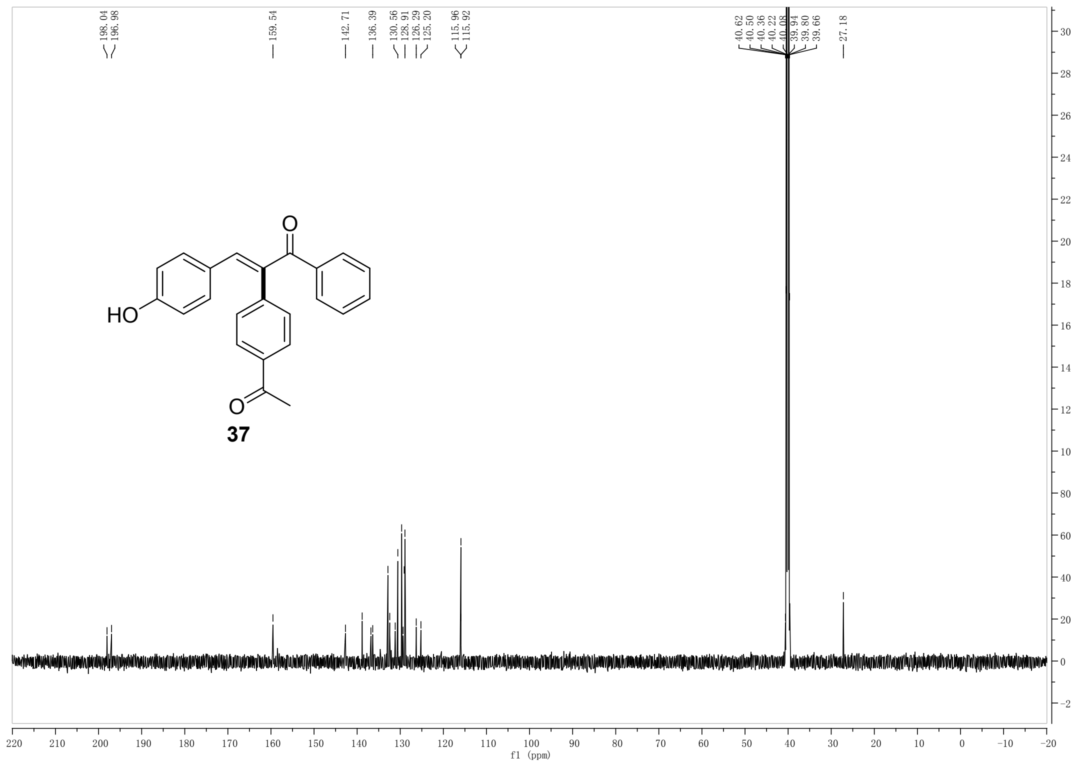
8.00
7.78
7.54
7.40
7.26
6.94
6.93
6.61
6.60
3.32
3.32
2.62
2.51
O
HO
O
37
1.24
2.02
2.00
1.19
2.38
2.00
1.06
2.07
2.04
3.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
3000
2500
2000
1500
1000
500
0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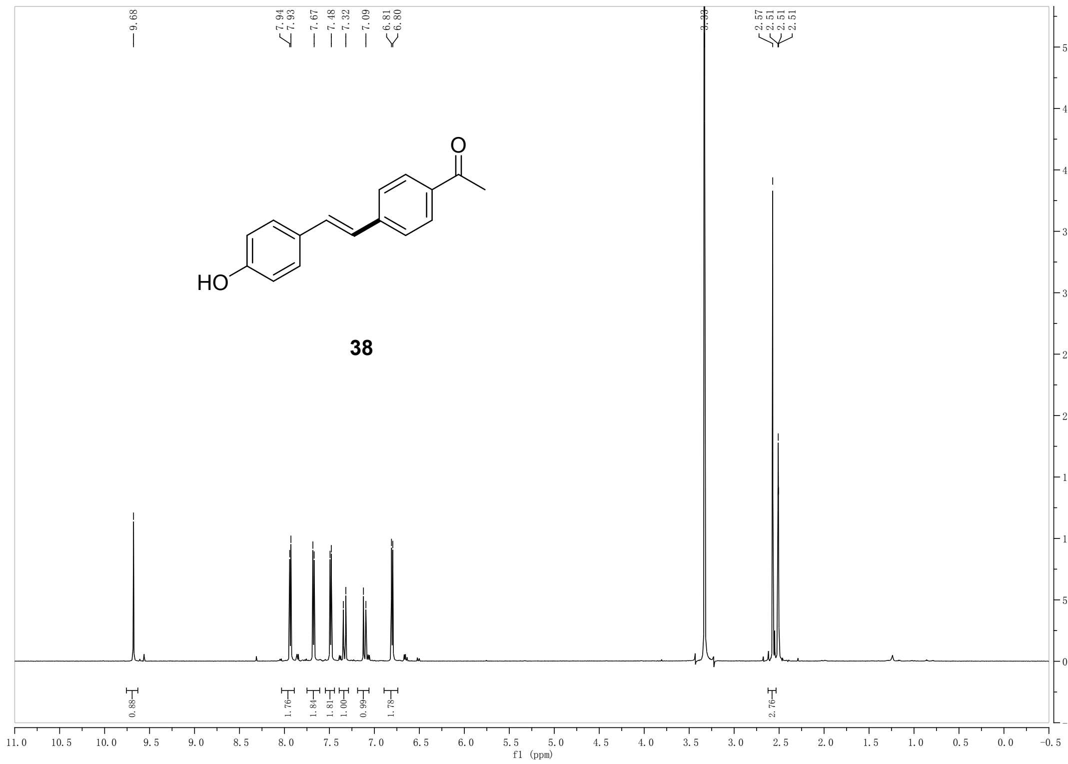
142.71
136.39
130.56
128.91
126.29
125.20
115.96
115.92
40.62
40.50
40.36
40.22
40.08
39.94
39.80
39.66
27.18
O
HO
O
37
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200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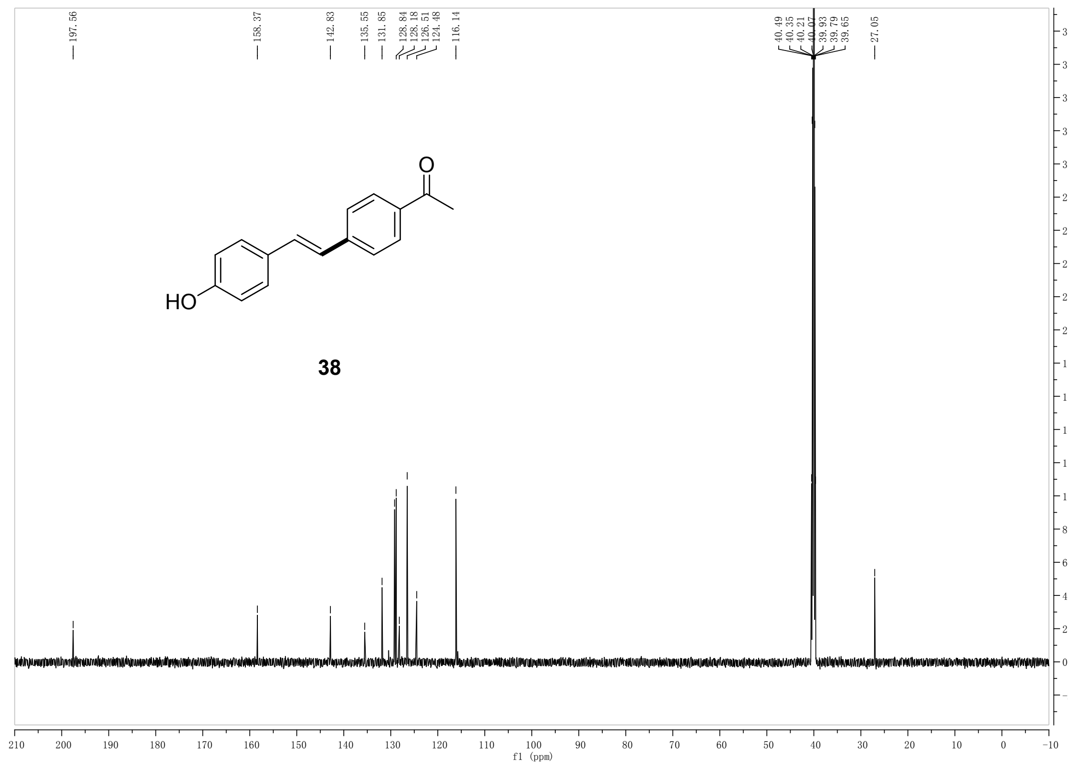
7.94
7.93
7.67
7.48
7.32
7.09
6.81
6.80
3.33
2.57
2.51
2.51
2.51
HO
O
38
0.88
1.76
1.84
1.81
1.00
0.99
1.78
2.76
f1 (ppm)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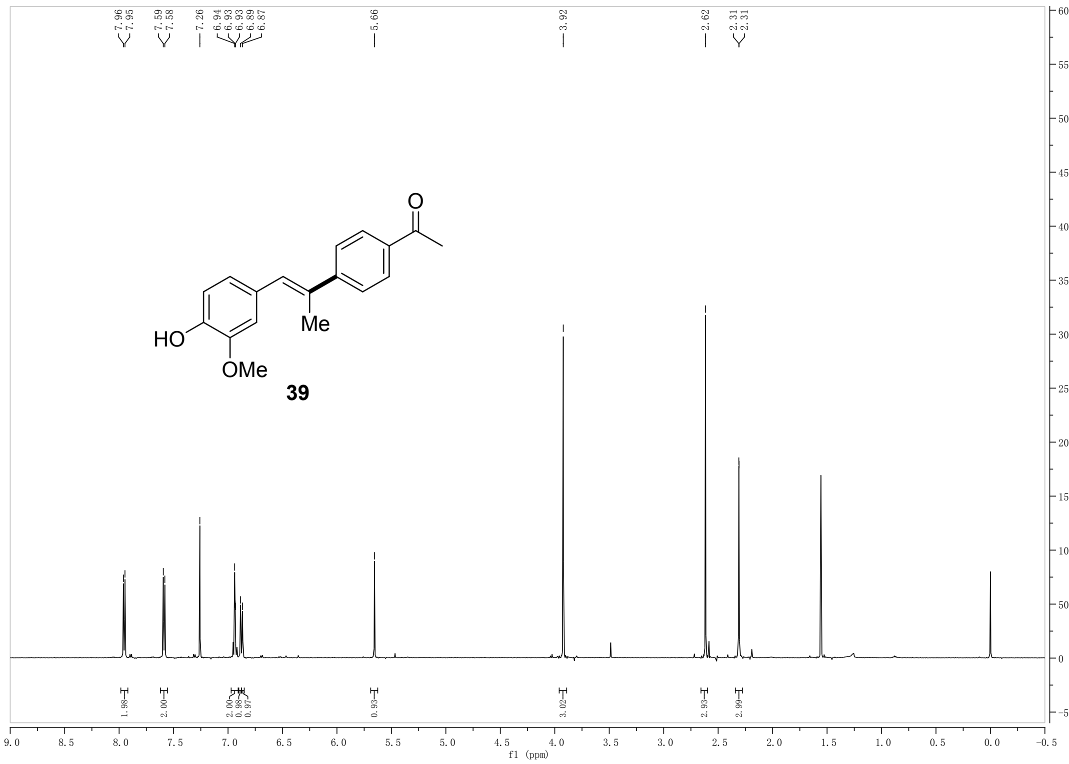
158.37
142.83
135.55
131.85
128.84
128.18
126.51
124.48
116.14
40.49
40.35
40.21
40.07
39.93
39.79
39.65
27.05
HO
O
38
f1 (ppm)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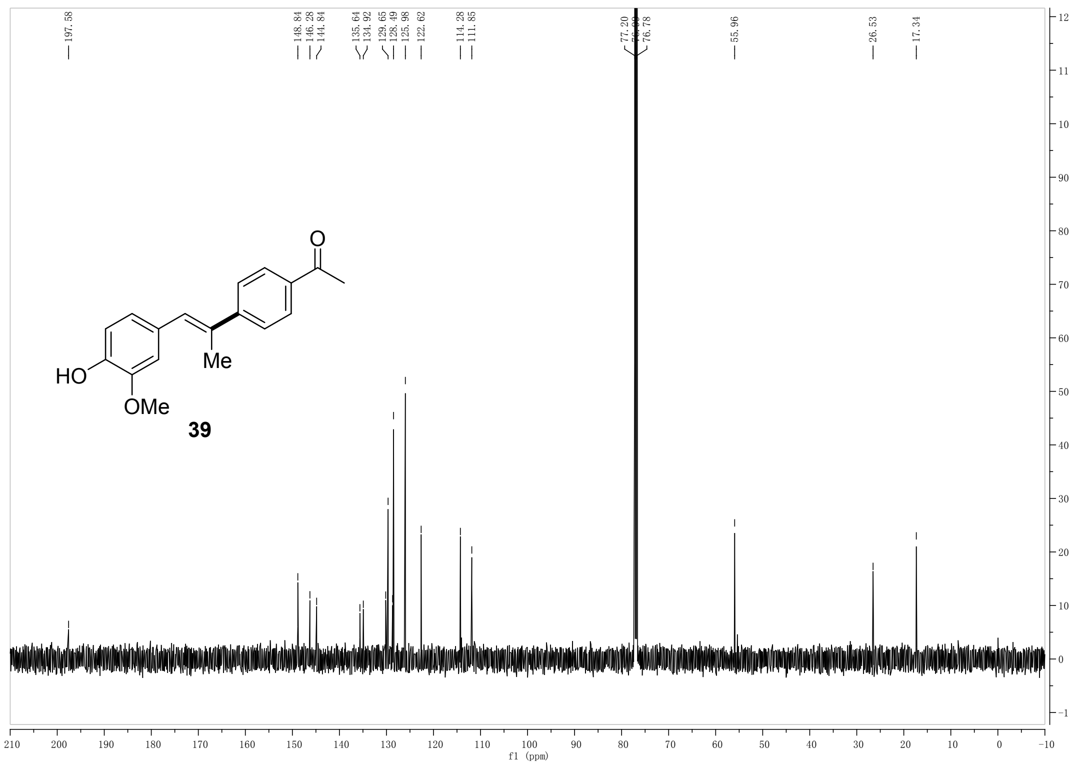
7.95
7.59
7.58
7.26
6.94
6.93
6.93
6.89
6.87
5.66
3.92
2.62
2.31
2.31
O
Me
HO
OMe
39
1.98
2.00
2.00
0.89
0.97
0.93
3.02
2.93
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500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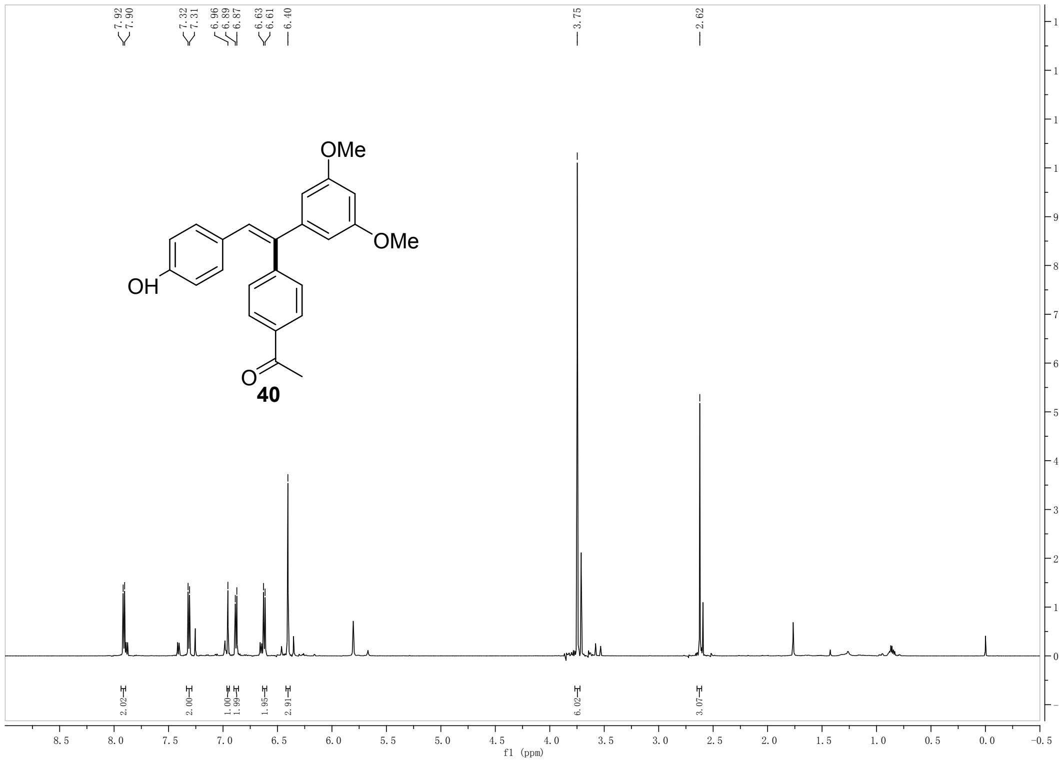
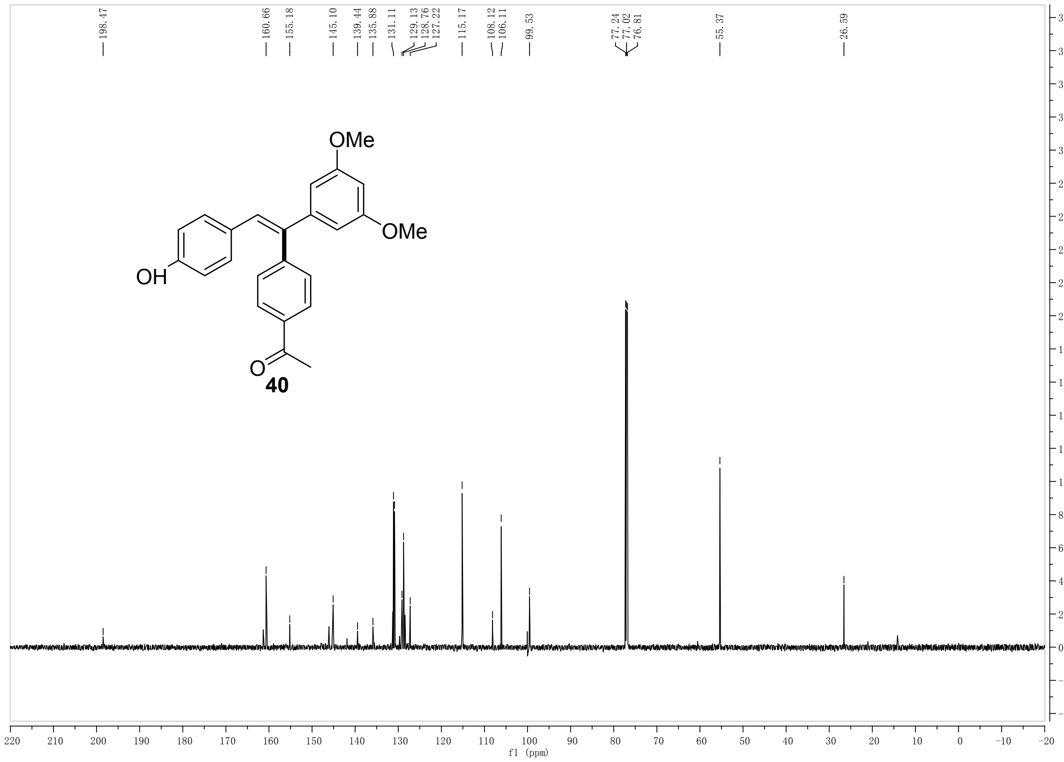
148.84
146.28
144.84
135.64
134.92
129.65
128.49
125.98
122.62
114.28
111.85
77.20
76.78
55.96
26.53
17.34
O
Me
HO
OMe
39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


7.92
7.90
7.32
7.31
6.96
6.89
6.87
6.63
6.61
6.40
3.75
2.62
OMe
OMe
OH
O
40
2.02
2.00
1.00
1.99
1.95
2.91
6.02
3.07
f1 (ppm)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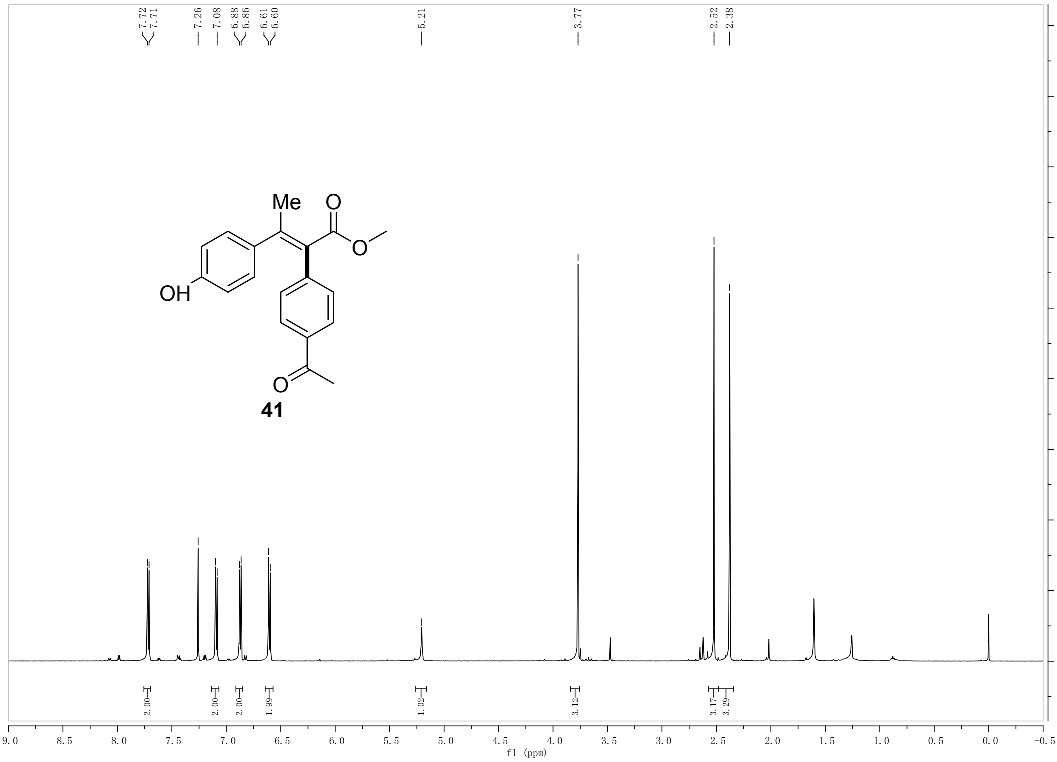
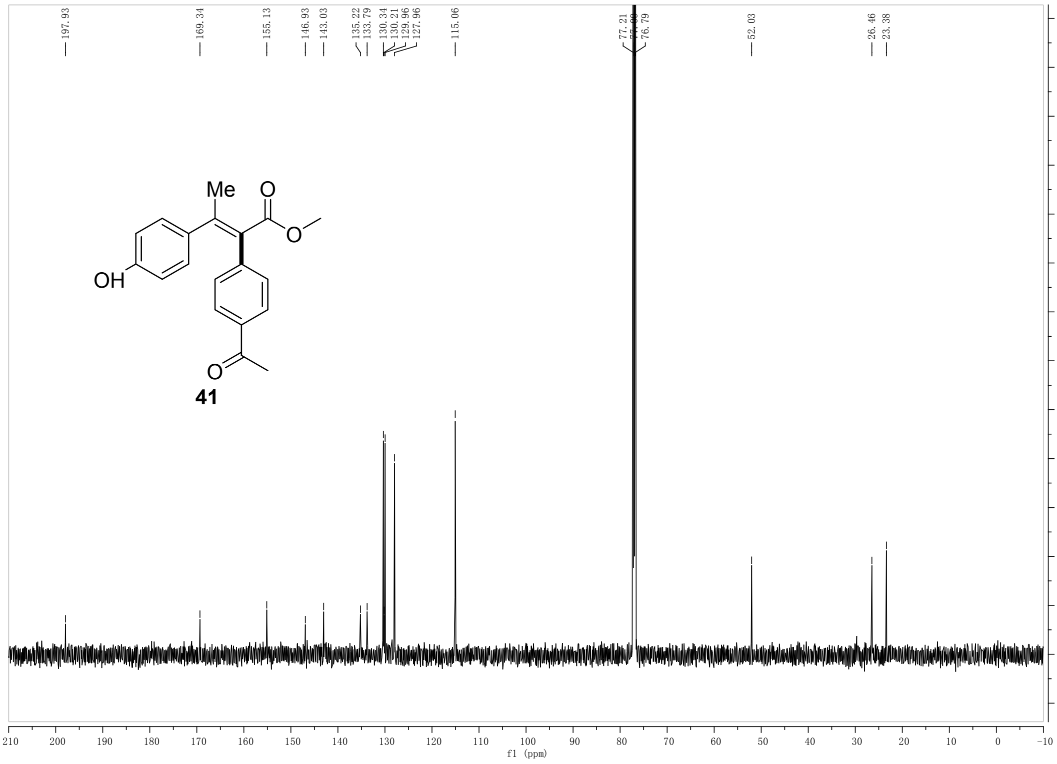
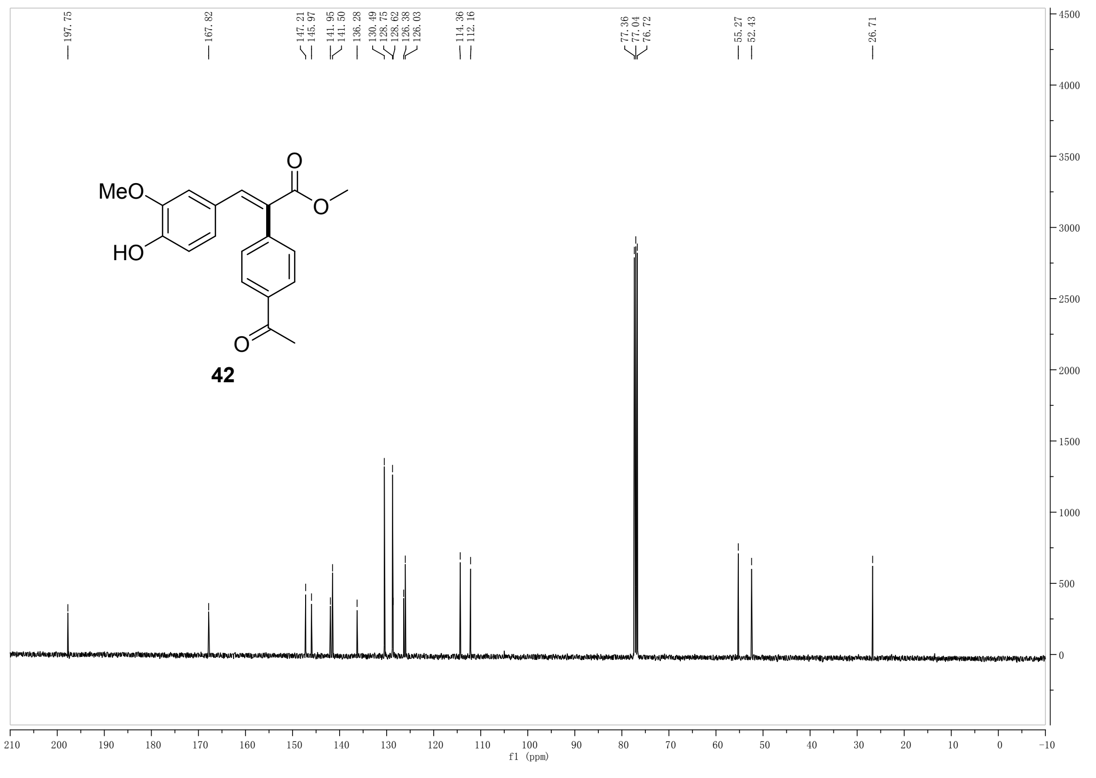
160.66
155.18
145.10
139.44
135.88
131.11
129.13
128.76
127.22
115.17
108.12
106.11
99.53
77.24
77.02
76.81
55.37
26.59
OMe
OMe
OH
O
40
f1 (ppm)


7.72
7.71
7.26
7.08
6.88
6.86
6.61
6.60
5.21
3.77
2.52
2.38
Me
O
O
OH
O
41
2.00
2.00
2.00
1.99
1.02
3.12
3.17
3.29
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


197.93
169.34
155.13
146.93
143.03
135.22
133.79
130.34
130.21
129.96
127.96
115.06
77.21
77.00
76.79
52.03
26.46
23.38
Me
O
O
OH
O
41
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.02
8.00
7.83
7.39
7.37
7.27
6.77
6.75
6.74
6.74
6.72
6.39
6.38
5.80
3.78
3.43
2.63
MeO
HO
O
O
O
42
2.10
1.00
2.01
1.99
1.01
0.99
2.87
2.99
3.18
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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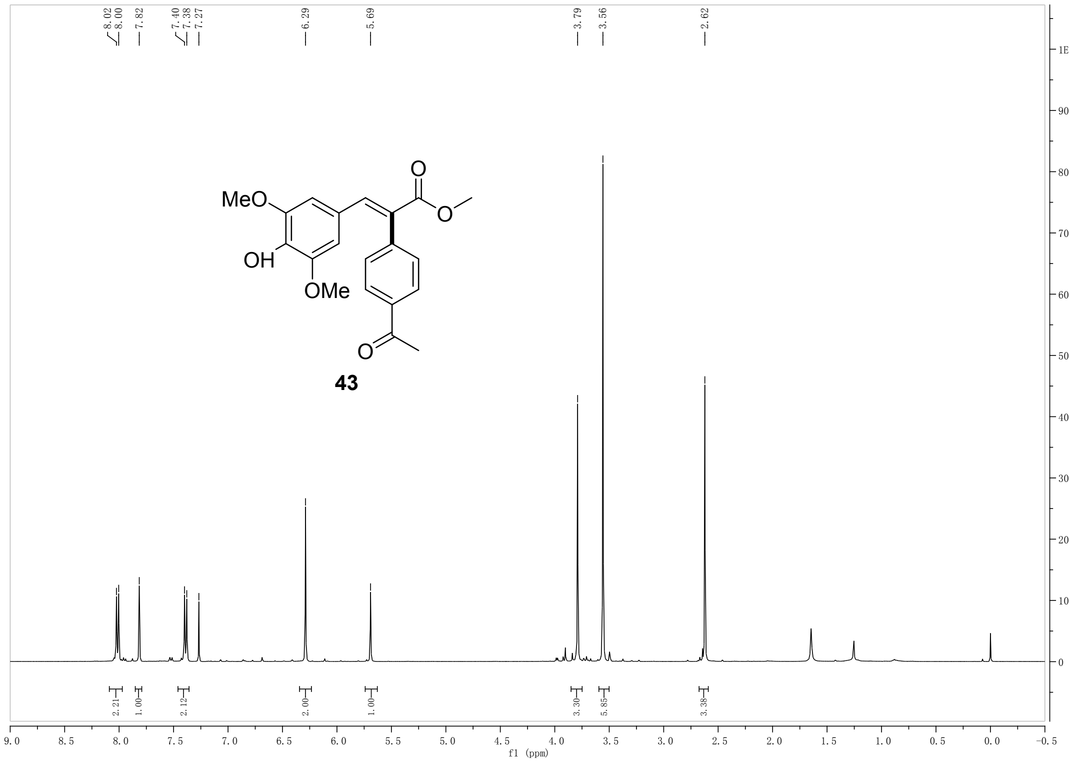
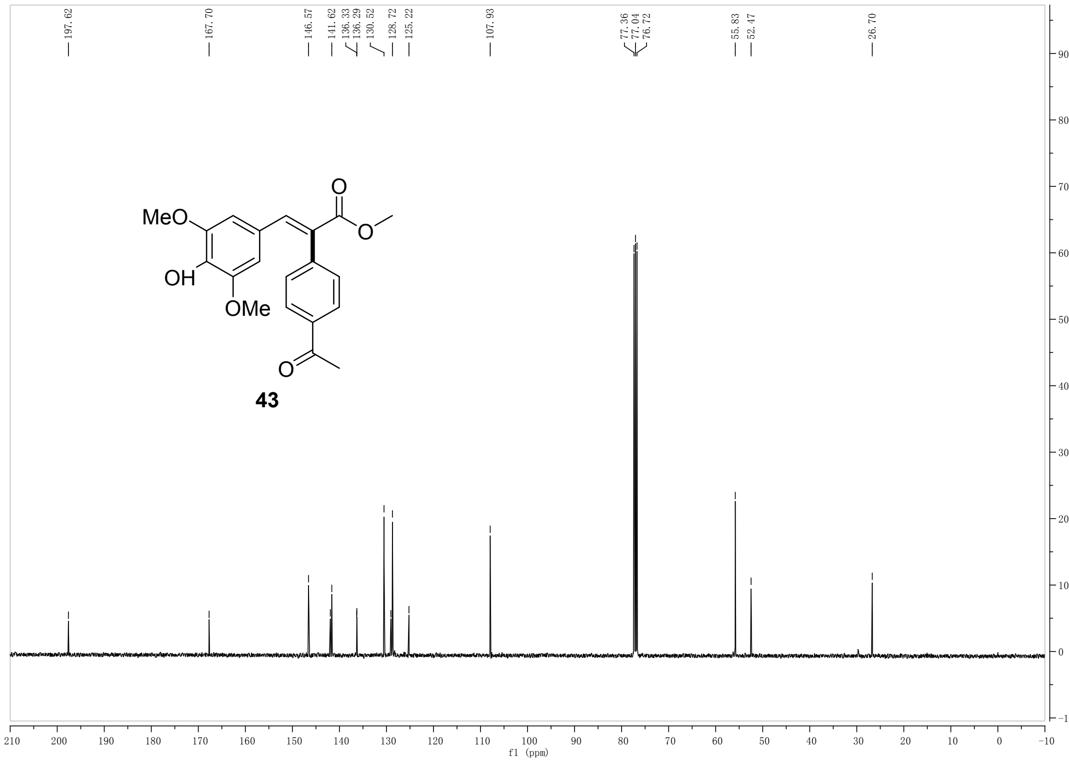
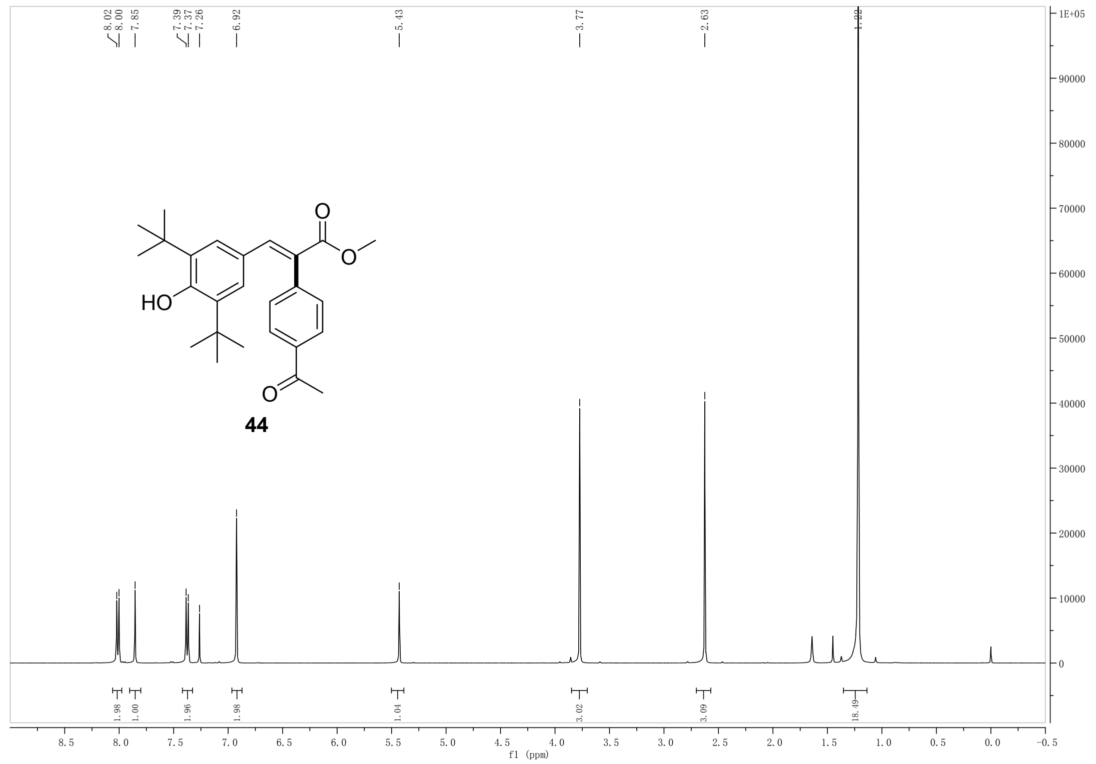
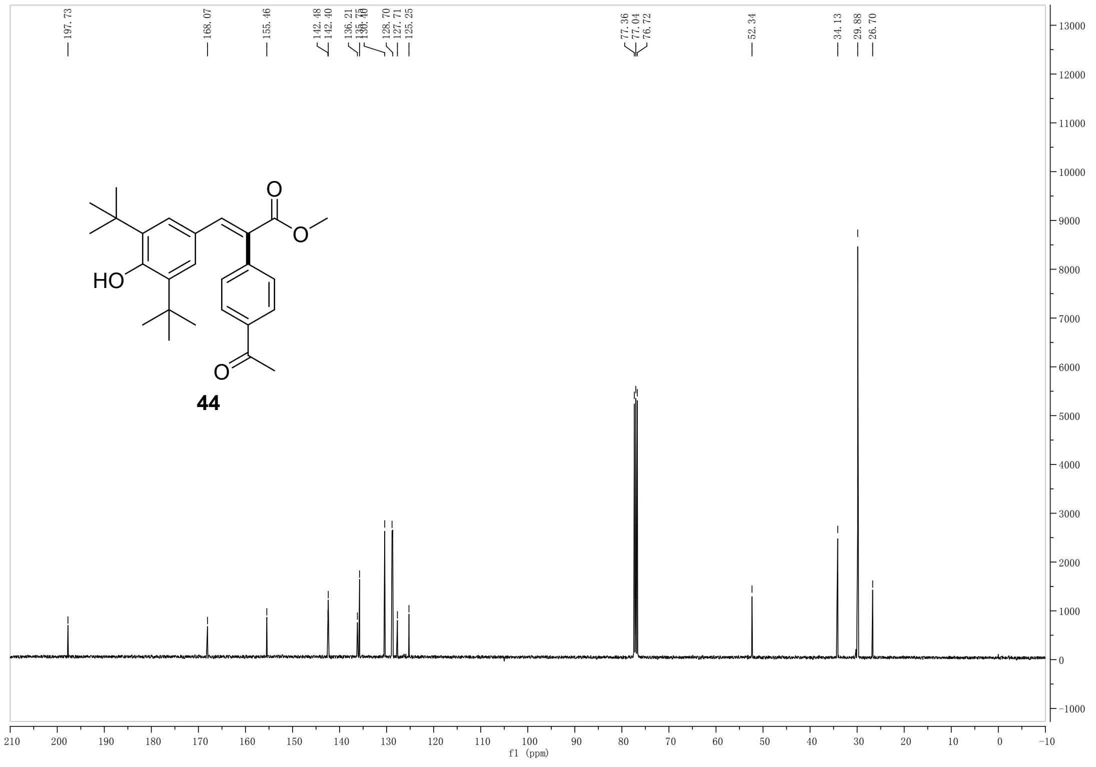
167.82
147.21
145.97
141.95
141.50
136.28
130.49
128.75
128.62
126.38
126.03
114.36
112.16
77.36
77.04
76.72
55.27
52.43
26.71
MeO
HO
O
O
O
42
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.02
8.00
7.82
7.40
7.38
7.27
6.29
5.69
3.79
3.56
2.62
MeO
OH
OMe
O
O
O
43
2.21
1.00
2.12
2.00
1.00
3.30
5.85
3.38
f1 (ppm)
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


197.62
167.70
146.57
141.62
136.33
136.29
130.52
128.72
125.22
107.93
77.36
77.04
76.72
55.83
52.47
26.70
MeO
OH
OMe
O
O
O
43
f1 (ppm)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


8.02
8.00
7.85
7.39
7.37
7.26
6.92
5.43
3.77
2.63
1.22
HO
O
O
O
44
1.98
1.00
1.96
1.98
1.04
3.02
3.09
18.49
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0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168.07
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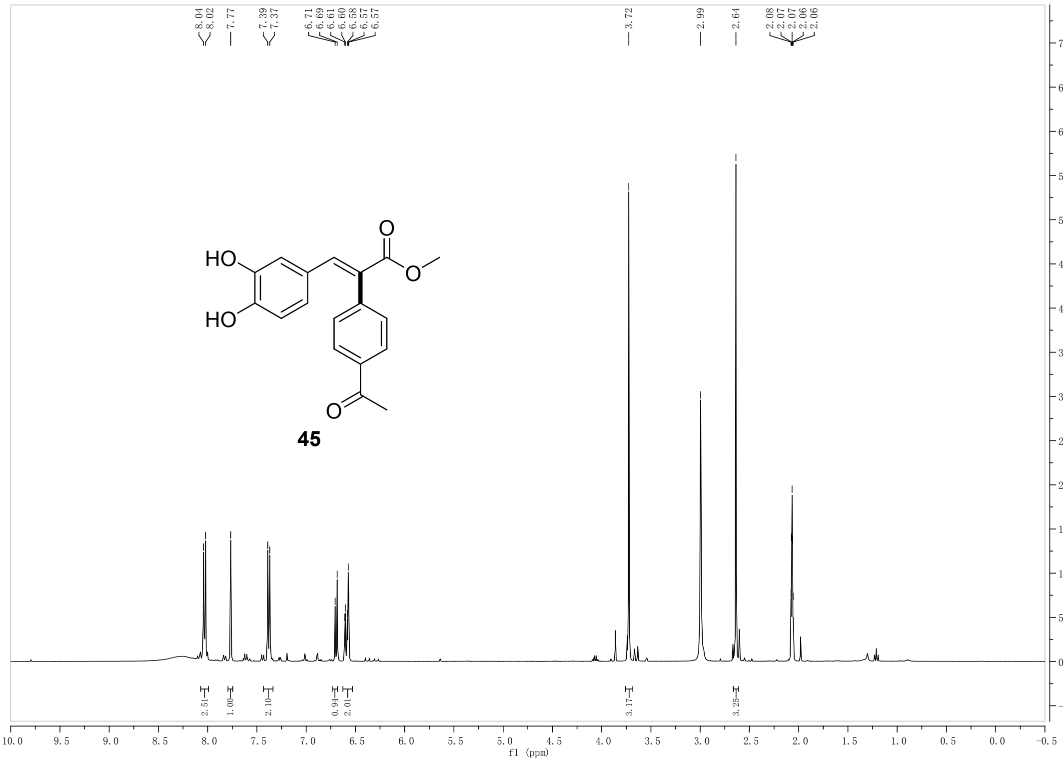
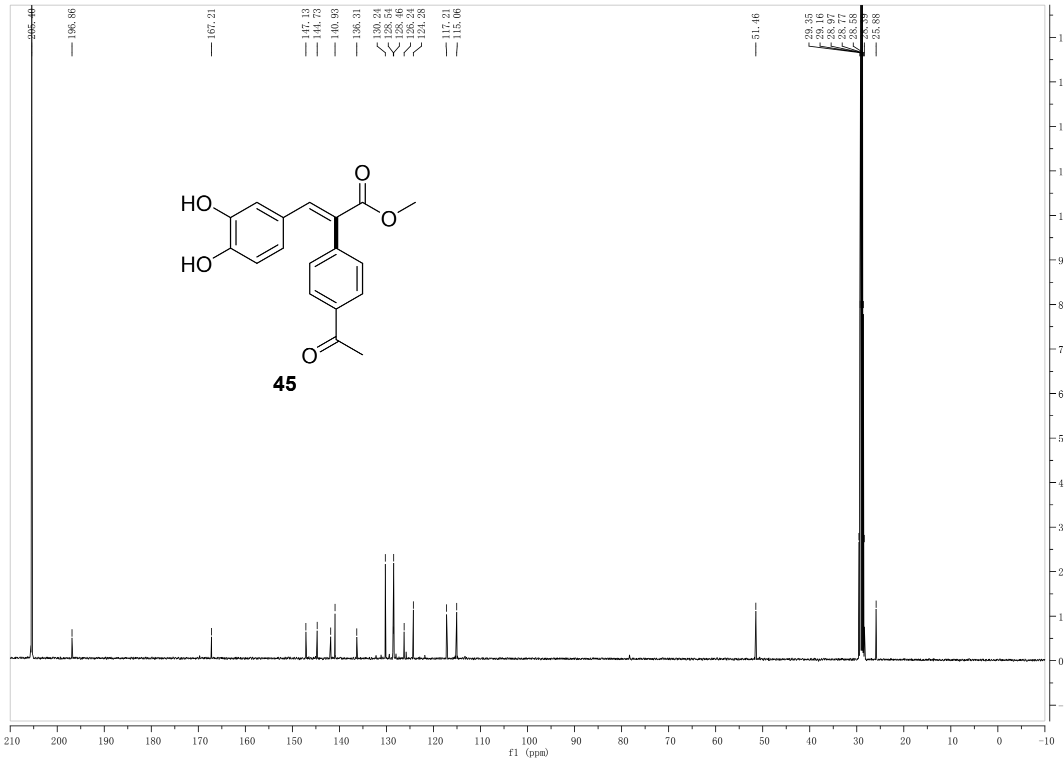
142.48
142.40
136.21
135.75
130.40
128.70
127.71
125.25
77.36
77.04
76.72
52.34
34.13
29.88
26.70
HO
O
O
O
44
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


8.04
8.02
7.77
7.39
7.37
6.71
6.69
6.61
6.60
6.58
6.57
6.57
3.72
2.99
2.64
2.08
2.07
2.07
2.06
2.06
HO
HO
O
O
O
45
2.51
1.00
2.10
0.94
2.01
3.17
3.25
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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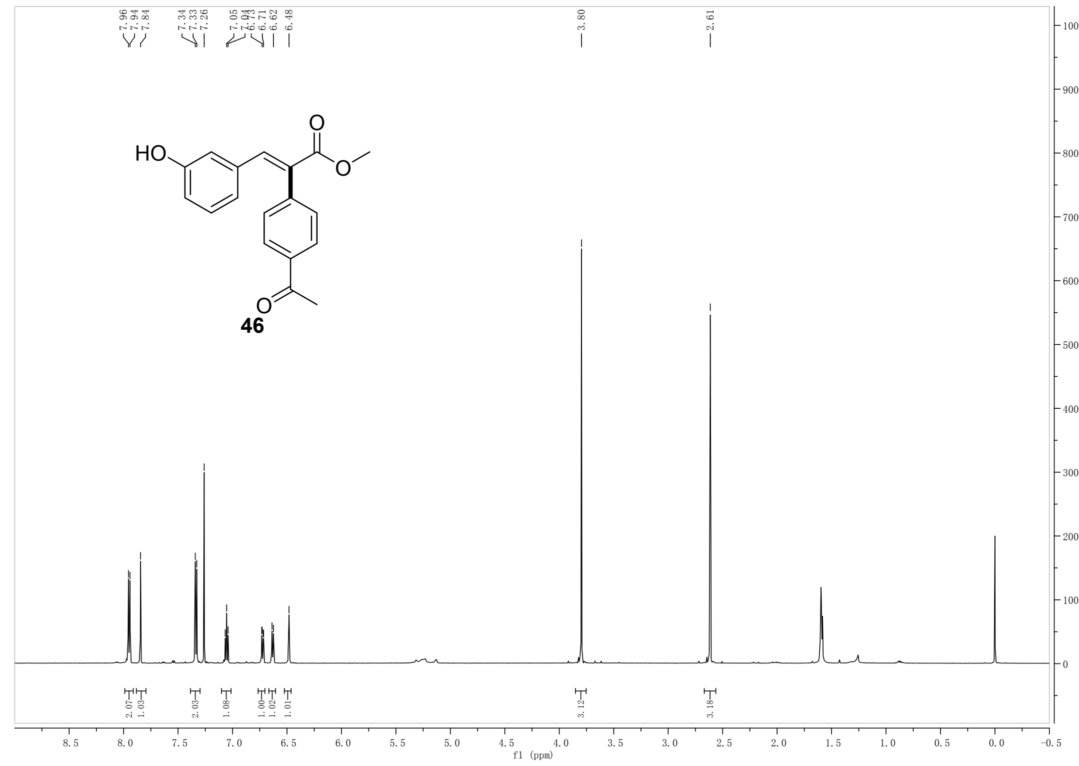
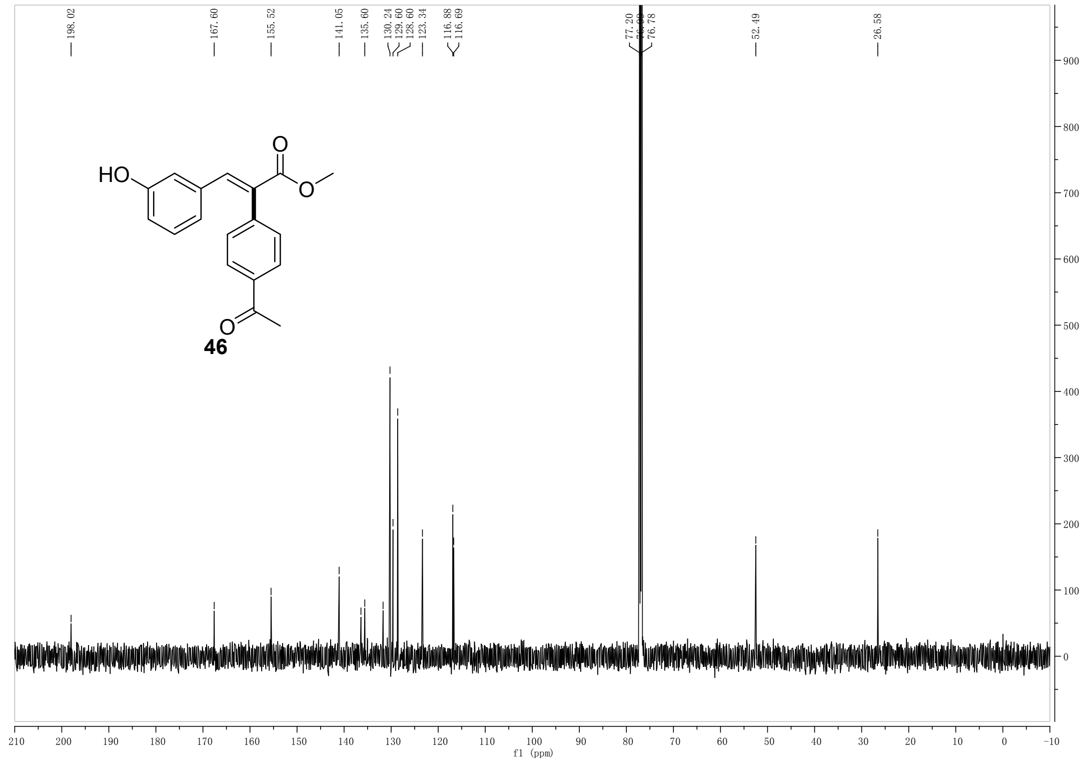
167.21
147.13
144.73
140.93
136.31
130.24
128.54
128.46
126.24
124.28
117.21
115.06
51.46
29.35
29.16
28.97
28.77
28.58
28.39
25.88
HO
HO
O
O
O
45
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.96
7.94
7.84
7.34
7.33
7.26
7.05
7.04
6.73
6.71
6.62
6.48
3.80
2.61
HO
O
O
O
46
2.07
1.03
2.03
1.08
1.00
1.02
1.01
3.12
3.18
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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167.60
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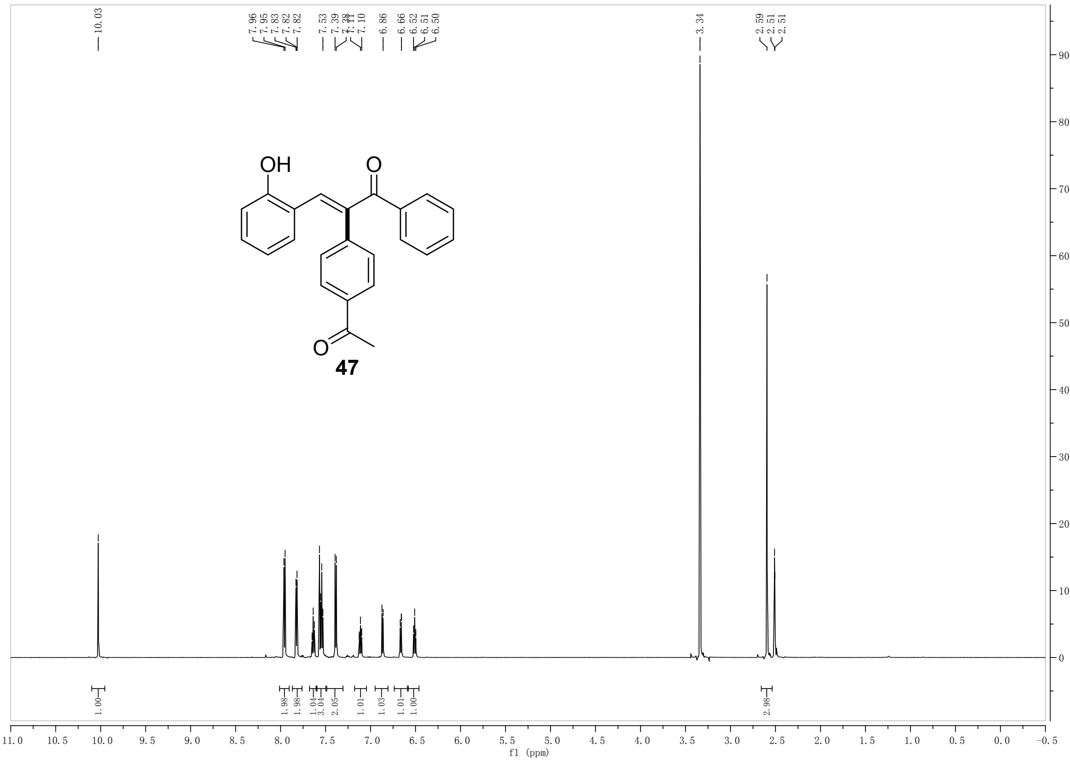
141.05
135.60
130.24
129.60
128.60
123.34
116.88
116.69
77.20
76.78
52.49
26.58
HO
O
O
O
46
900
800
700
600
500
400
300
200
100
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


10.03
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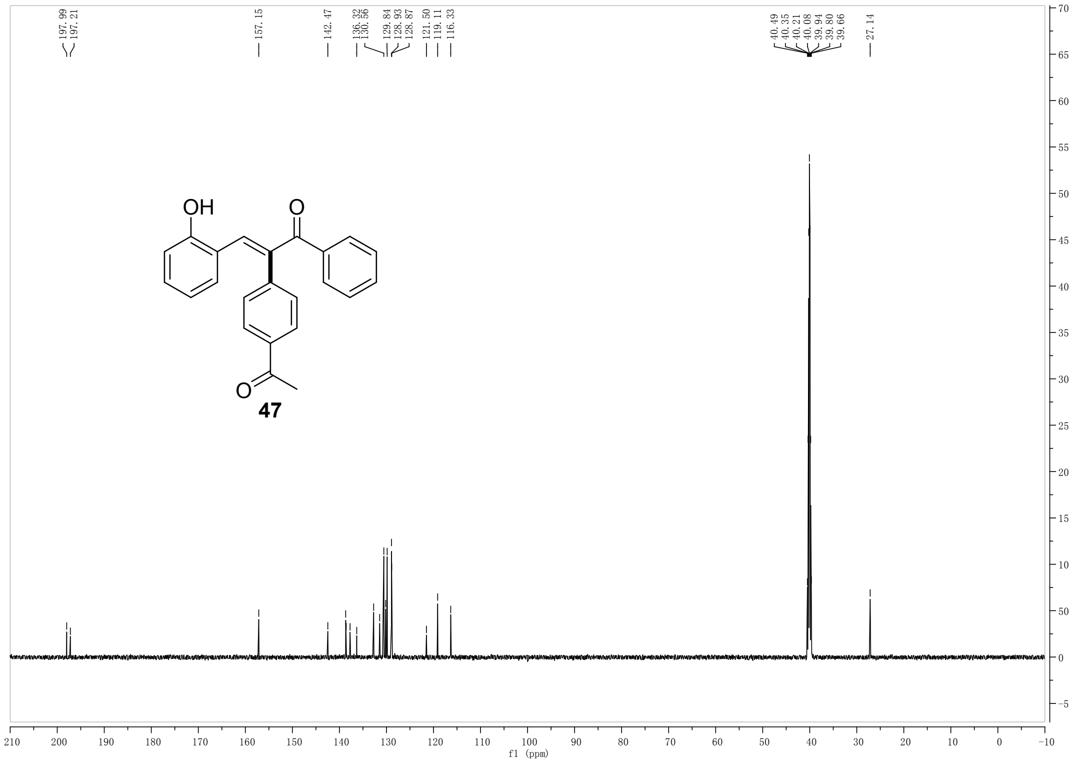
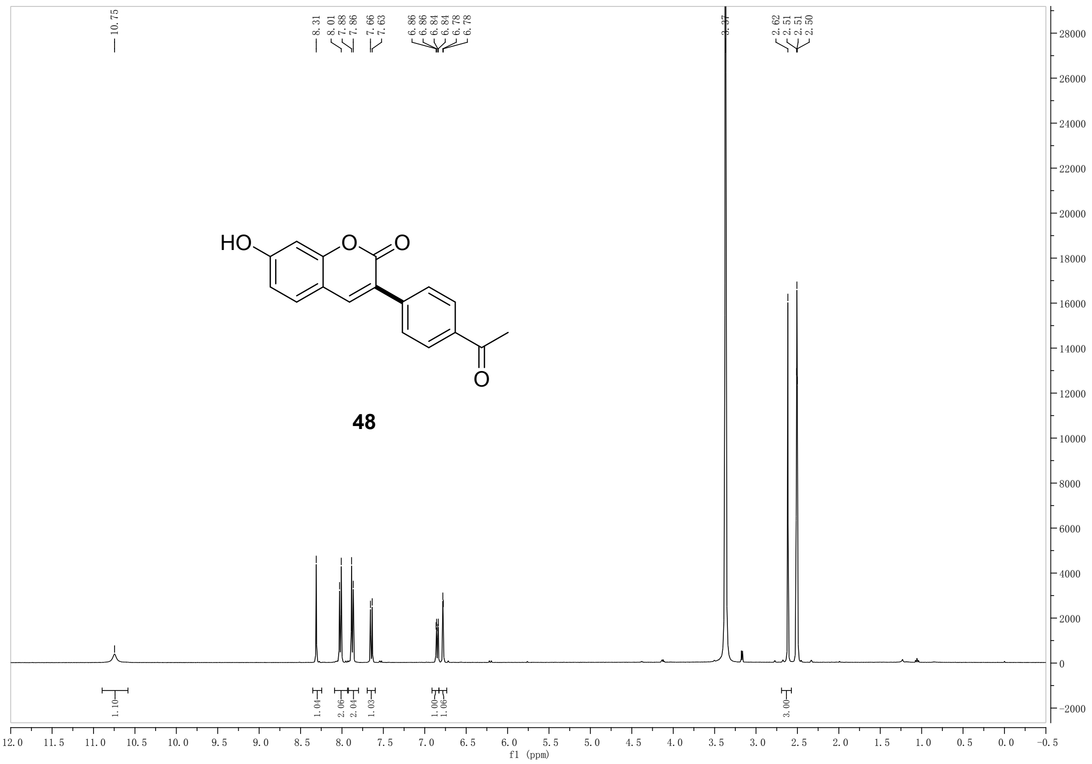
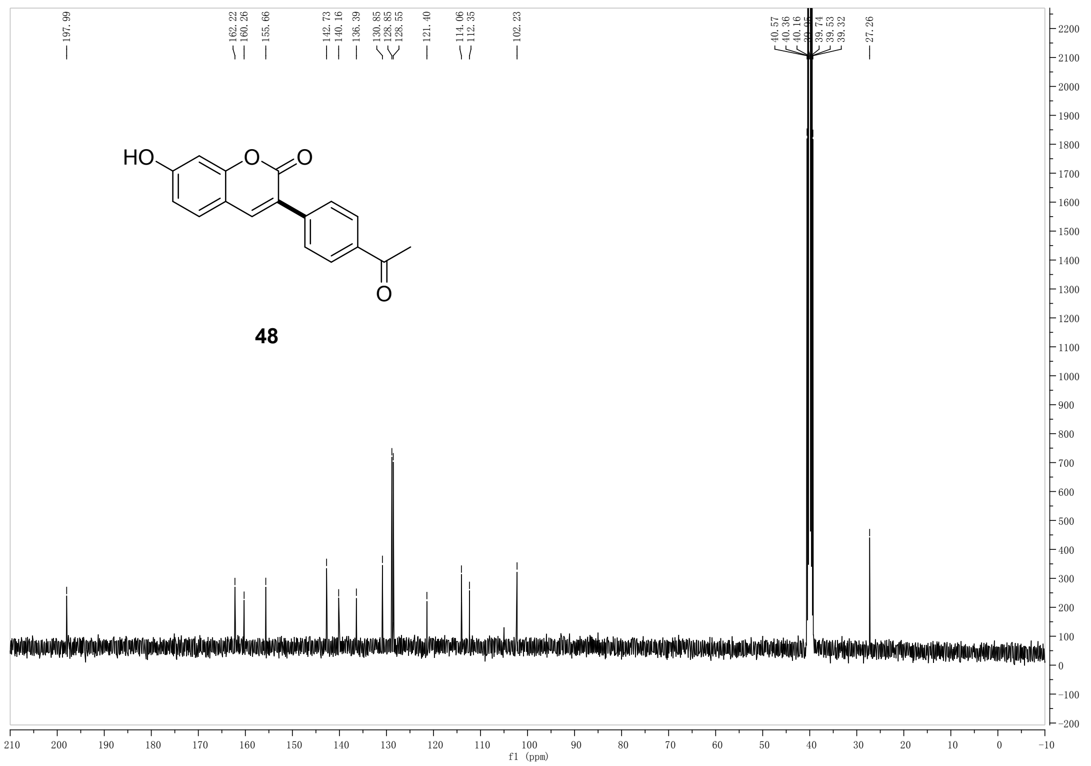
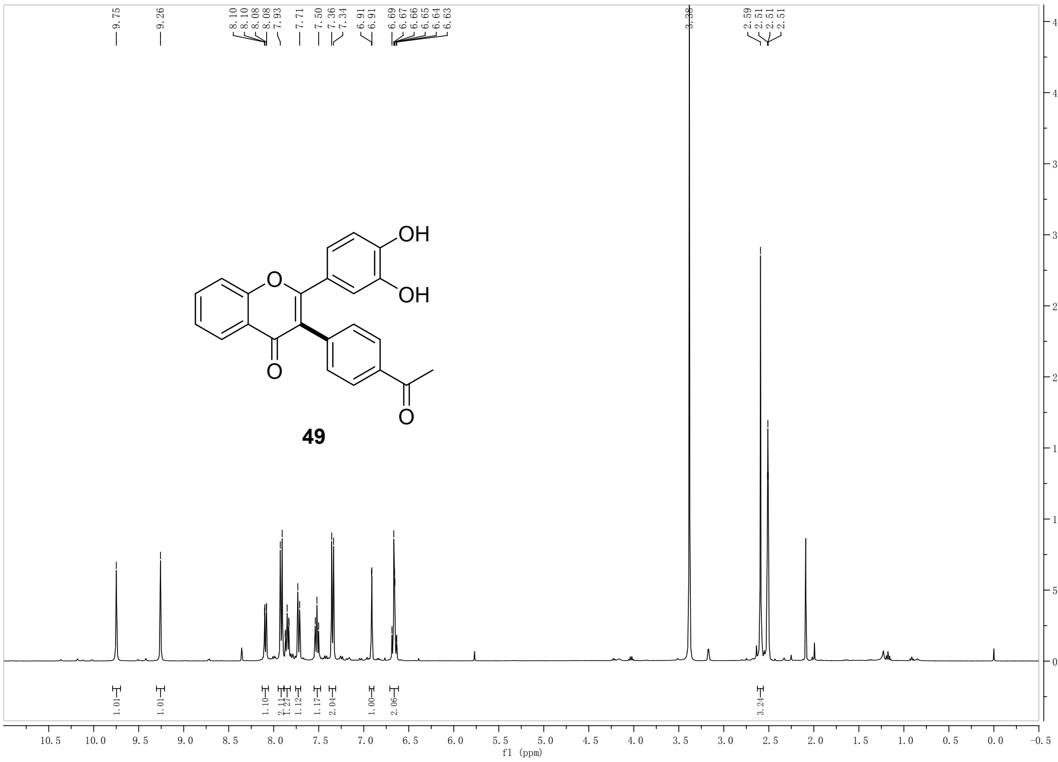
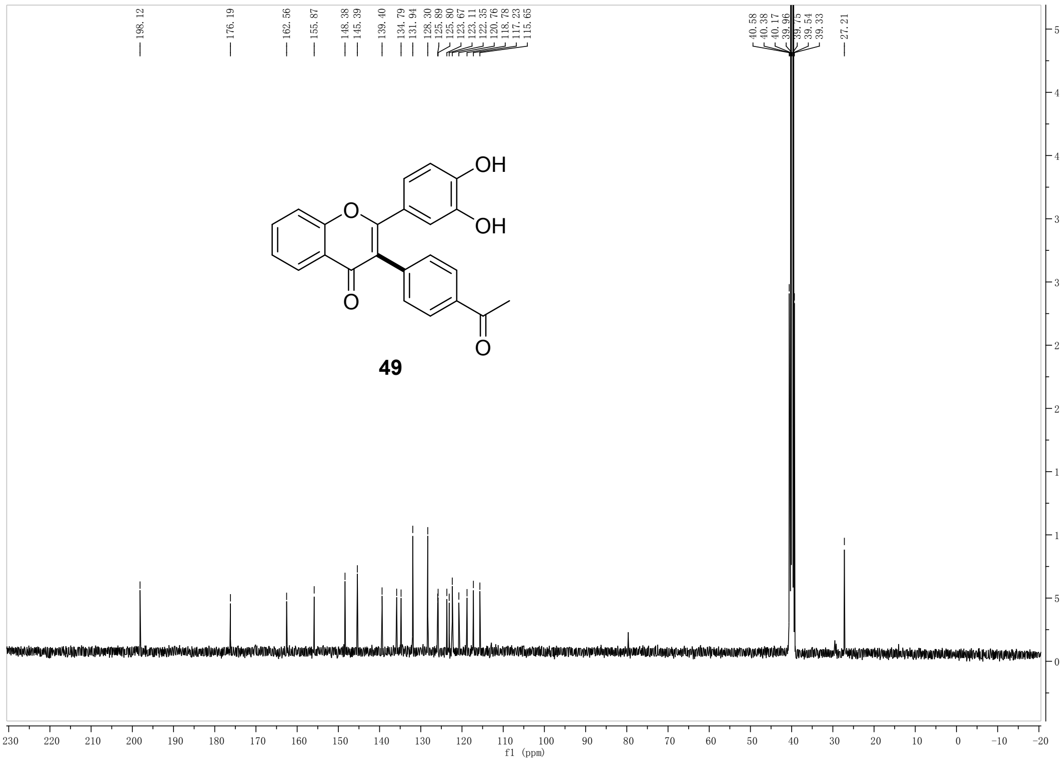
7.95
7.83
7.82
7.82
7.53
7.39
7.38
7.11
7.10
6.86
6.66
6.52
6.51
6.50
3.34
2.59
2.51
2.51
OH
O
O
47
1.00
1.98
1.98
1.04
3.04
2.05
1.01
1.03
1.01
1.00
2.98
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

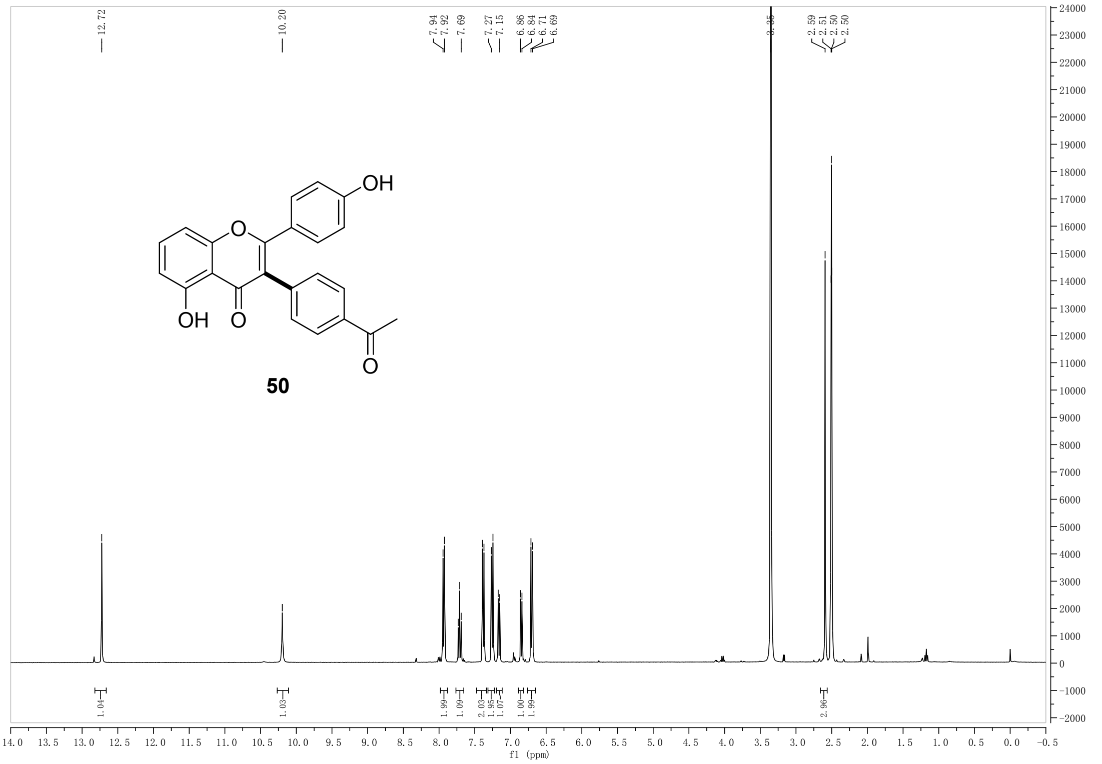

197.99
197.21
157.15
142.47
136.32
130.56
129.84
128.93
128.87
121.50
119.11
116.33
40.49
40.35
40.21
40.08
39.94
39.80
39.66
27.14
OH
O
O
47
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

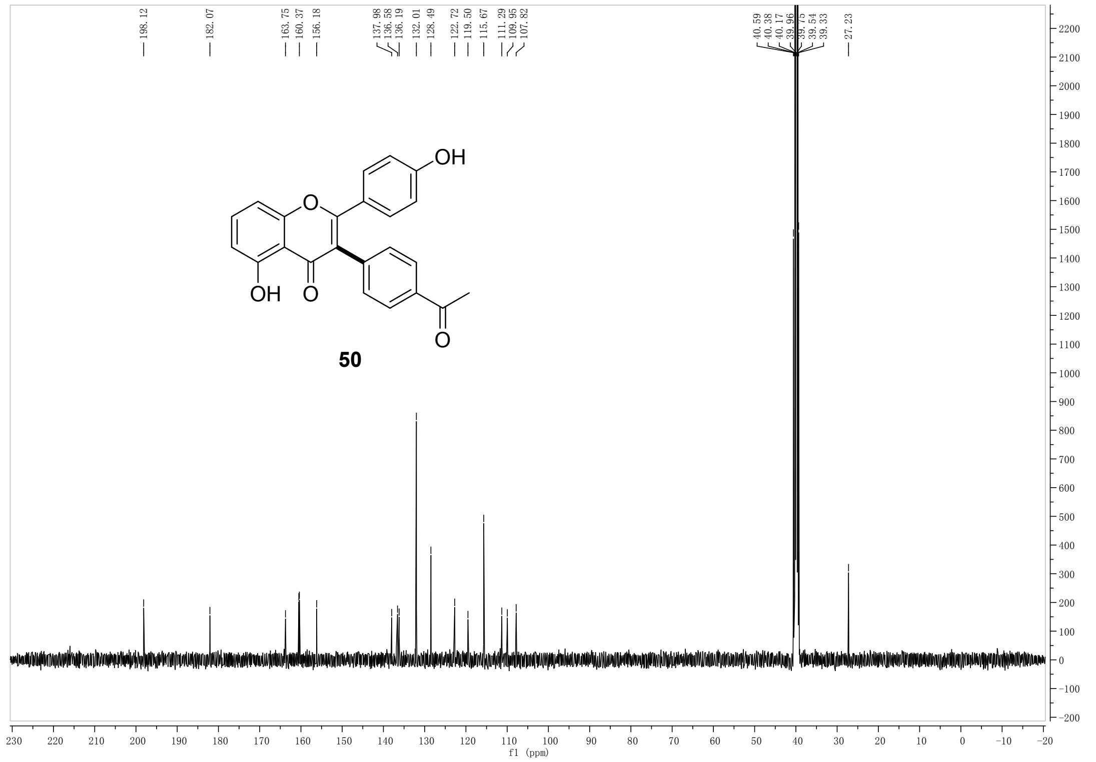

10.75
8.31
8.01
7.88
7.86
7.66
7.63
6.86
6.86
6.84
6.84
6.78
6.78
3.37
2.62
2.51
2.51
2.50
HO
O
O
O
48
1.10
1.04
2.06
2.04
1.03
1.00
1.06
3.00
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

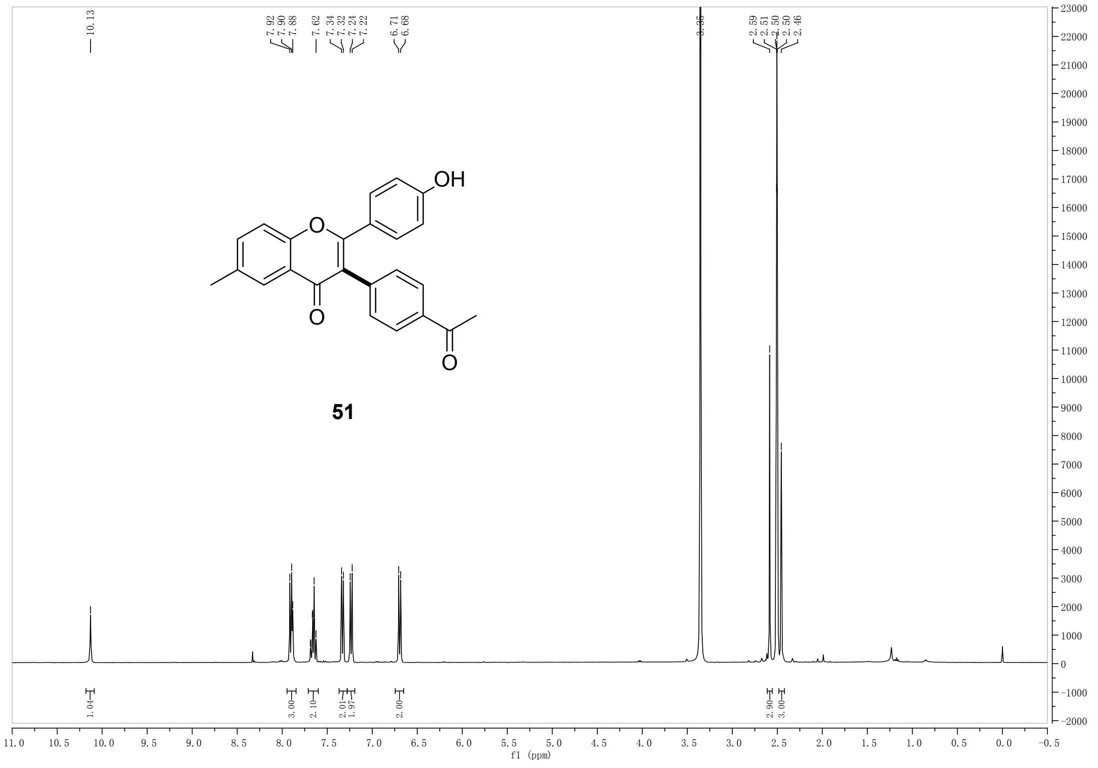

197.99
162.22
160.26
155.66
142.73
140.16
136.39
130.85
128.85
128.55
121.40
114.06
112.35
102.23
40.57
40.36
40.16
39.95
39.74
39.53
39.32
27.26
HO
O
O
O
48
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

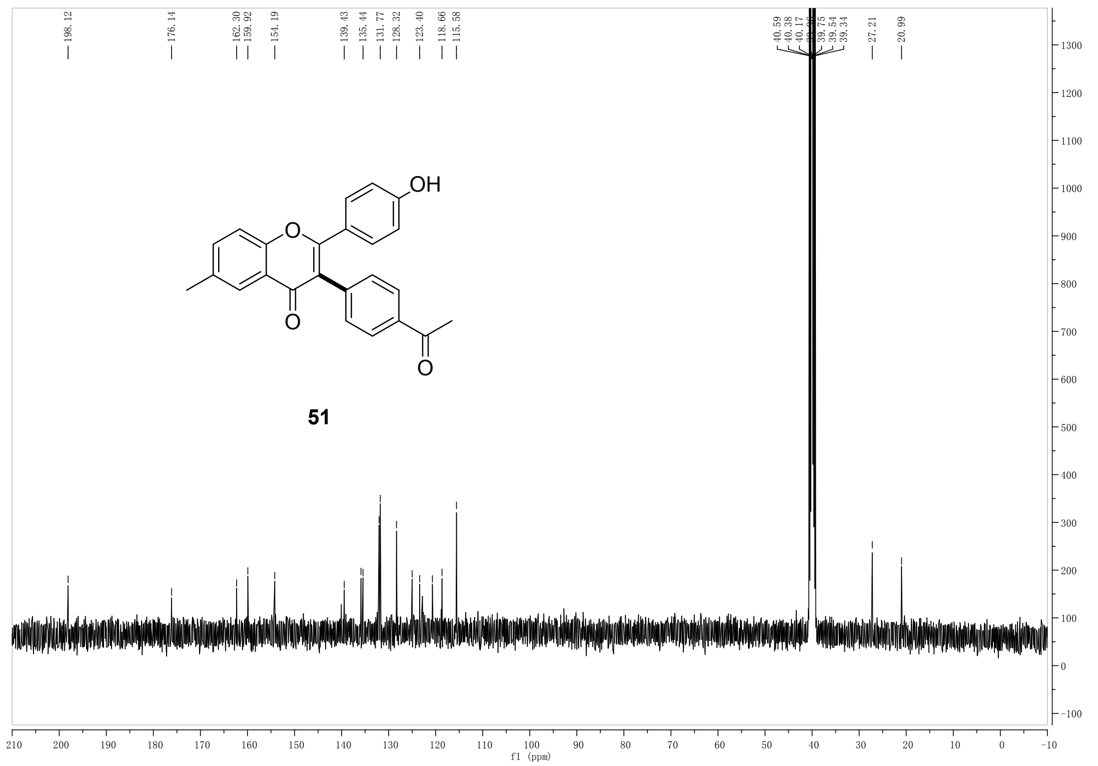

9.75
9.26
8.10
8.10
8.08
8.08
7.93
7.71
7.50
7.36
7.34
6.91
6.91
6.69
6.67
6.66
6.65
6.64
6.63
3.38
2.59
2.51
2.51
2.51
OH
OH
O
O
O
49
1.01
1.01
1.10
2.11
1.27
1.12
1.17
2.04
1.00
2.06
3.24
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

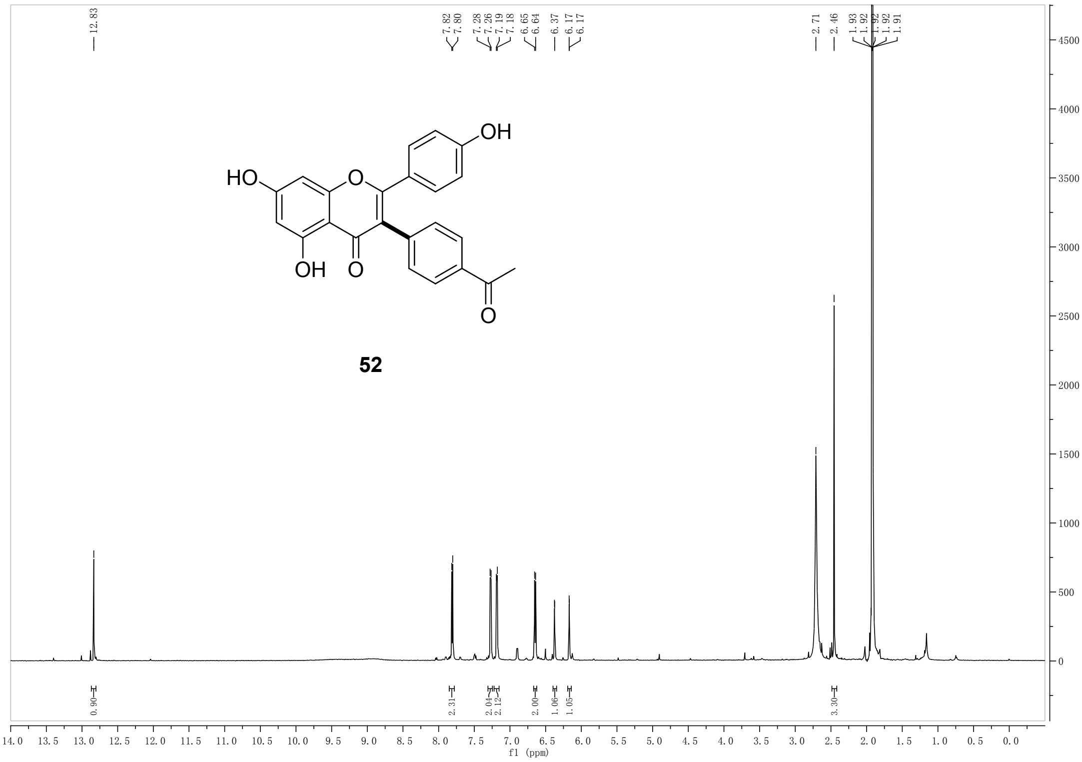

198.12
176.19
162.56
155.87
148.38
145.39
139.40
134.79
131.94
128.30
125.89
125.80
123.67
123.11
122.35
120.76
118.78
117.23
115.65
40.58
40.38
40.17
39.96
39.75
39.54
39.33
27.21
OH
OH
O
O
O
49
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


12.72
10.20
7.94
7.92
7.69
7.27
7.15
6.86
6.84
6.71
6.69
3.35
2.59
2.51
2.50
2.50
OH
O
OH
O
O
50
1.04
1.03
1.99
1.09
2.03
1.95
1.07
1.00
1.99
2.96
f1 (ppm)

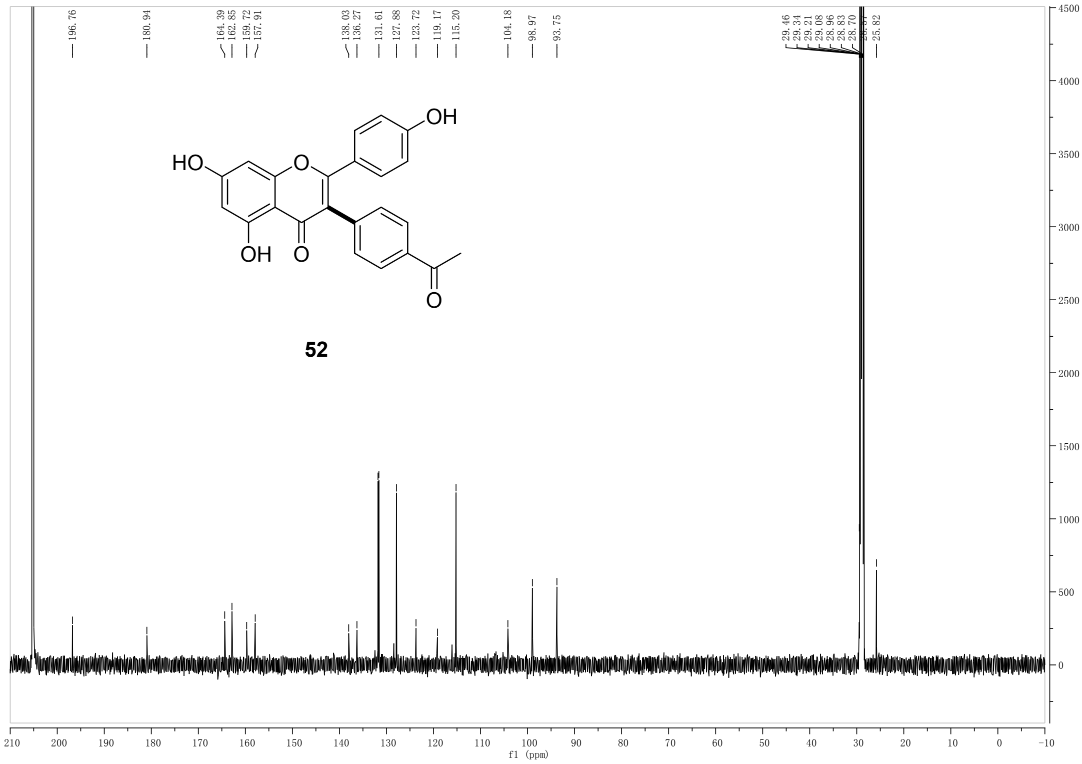

198.12
182.07
163.75
160.37
156.18
137.98
136.58
136.19
132.01
128.49
122.72
119.50
115.67
111.29
109.95
107.82
40.59
40.38
40.17
39.96
39.75
39.54
39.33
27.23
OH
O
OH
O
O
50
f1 (ppm)


10.13
7.92
7.90
7.88
7.62
7.34
7.32
7.24
7.22
6.71
6.68
3.35
2.59
2.51
2.50
2.50
2.46
OH
O
O
O
51
1.04
3.00
2.10
2.01
1.97
2.00
2.90
3.00
f1 (ppm)

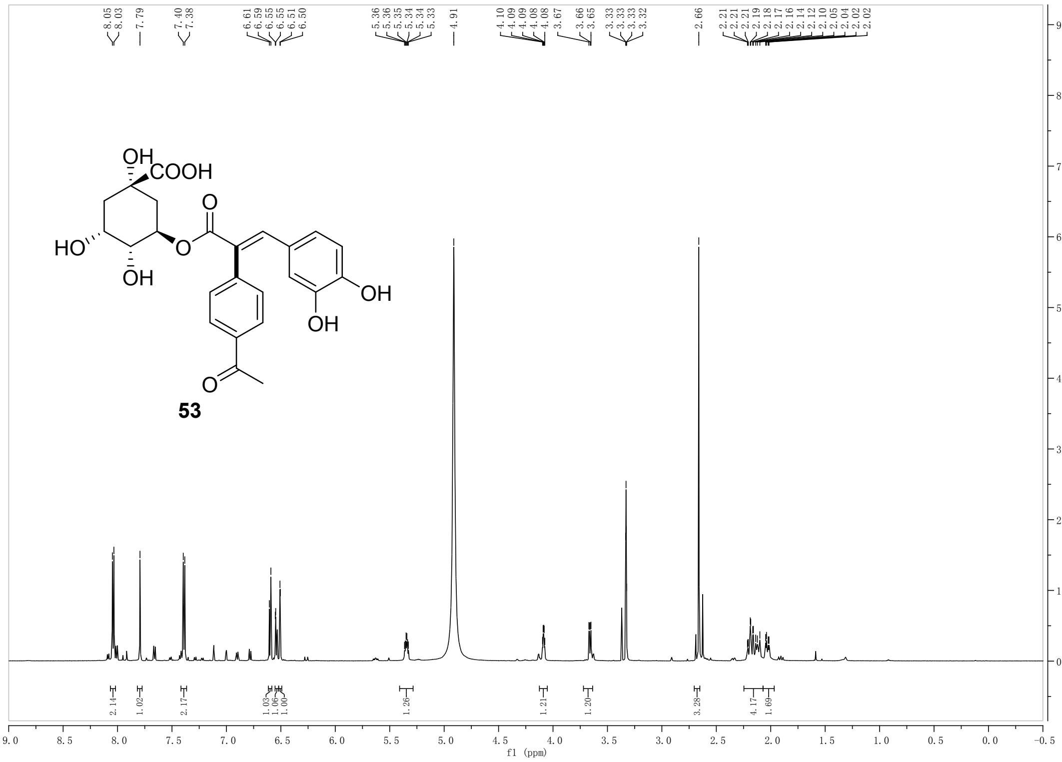

198.12
176.14
162.30
159.92
154.19
139.43
135.44
131.77
128.32
123.40
118.66
115.58
40.59
40.38
40.17
39.96
39.75
39.54
39.34
27.21
20.99
OH
O
O
O
51
f1 (ppm)

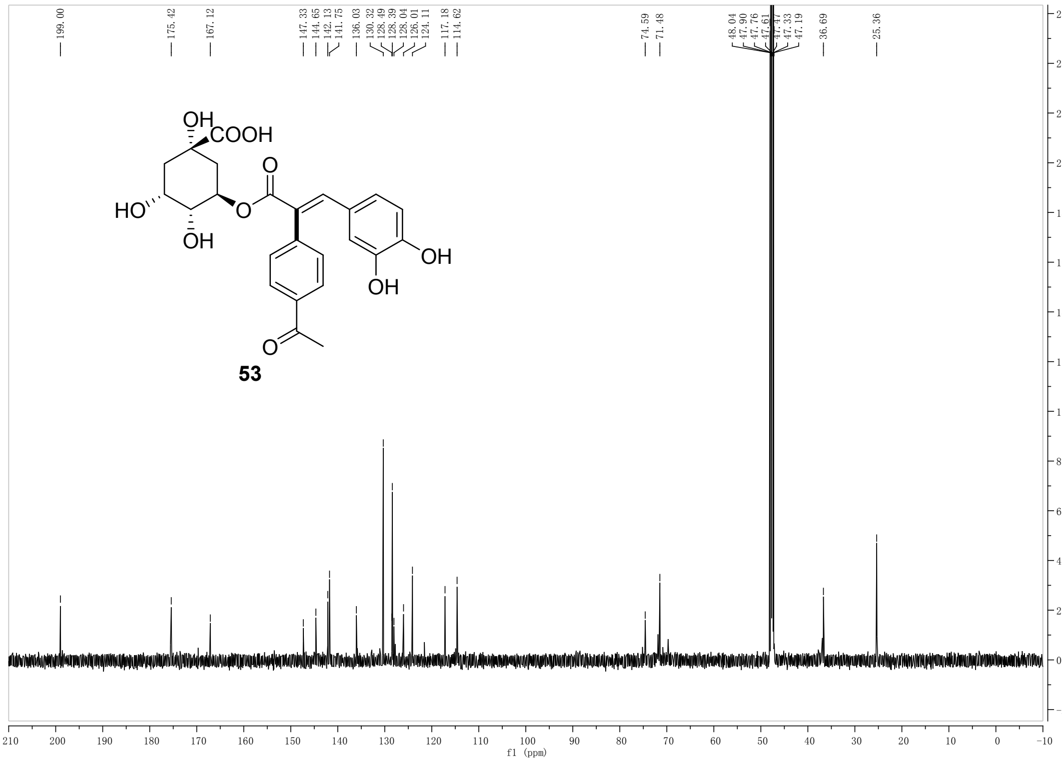

12.83
7.82
7.80
7.28
7.26
7.19
7.18
6.65
6.64
6.37
6.17
6.17
2.71
2.46
1.93
1.92
1.92
1.92
1.91
HO
OH
O
OH
O
O
0.90
2.31
2.04
2.12
2.00
1.06
1.05
3.30
4500
4000
3500
3000
2500
2000
1500
1000
500
0
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

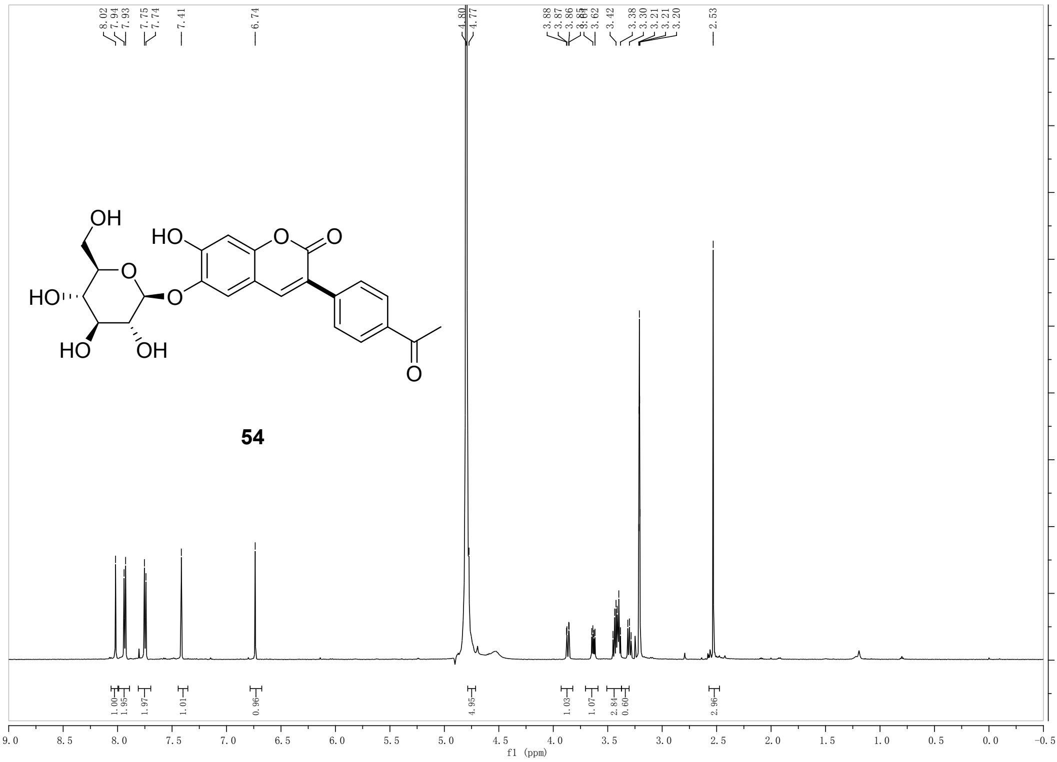
52

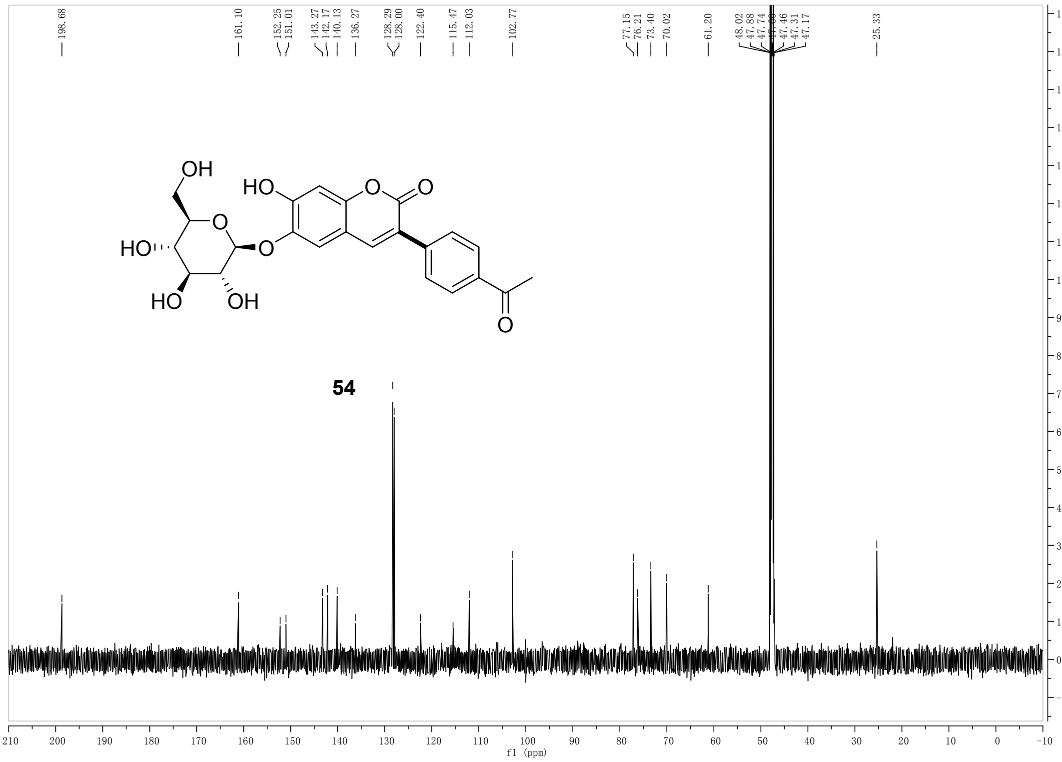

196.76
180.94
164.39
162.85
159.72
157.91
138.03
136.27
131.61
127.88
123.72
119.17
115.20
104.18
98.97
93.75
29.46
29.34
29.21
29.08
28.96
28.83
28.70
28.57
25.82
HO
OH
O
OH
O
O
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

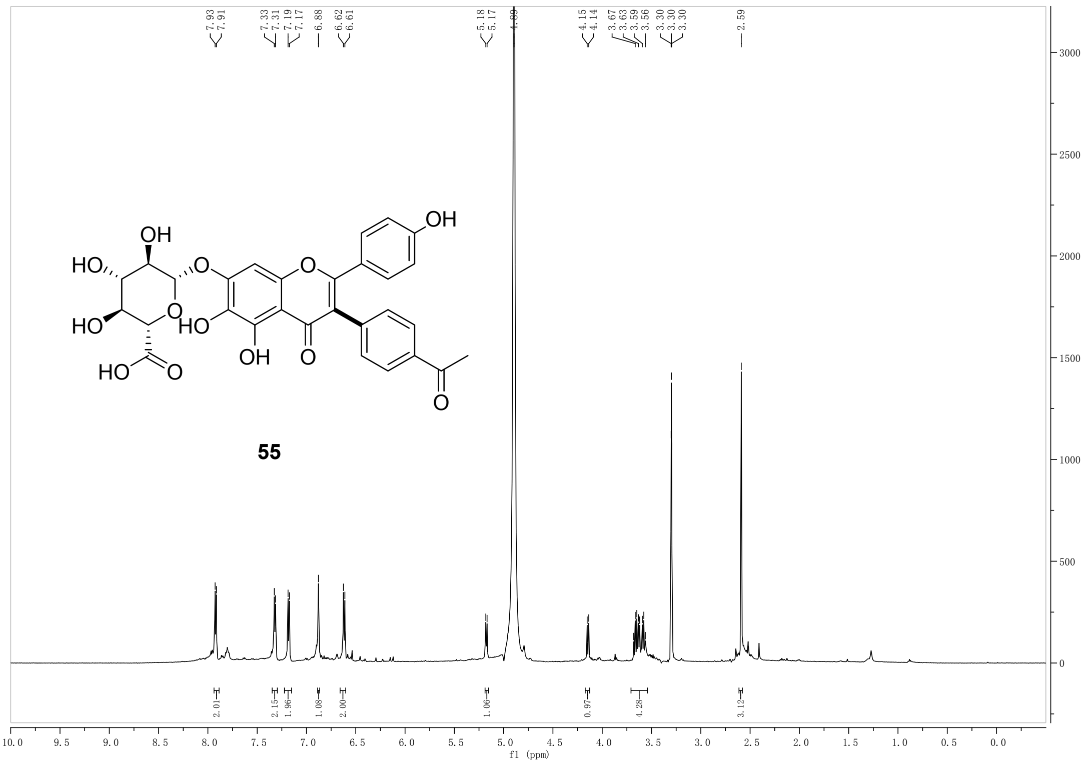
52

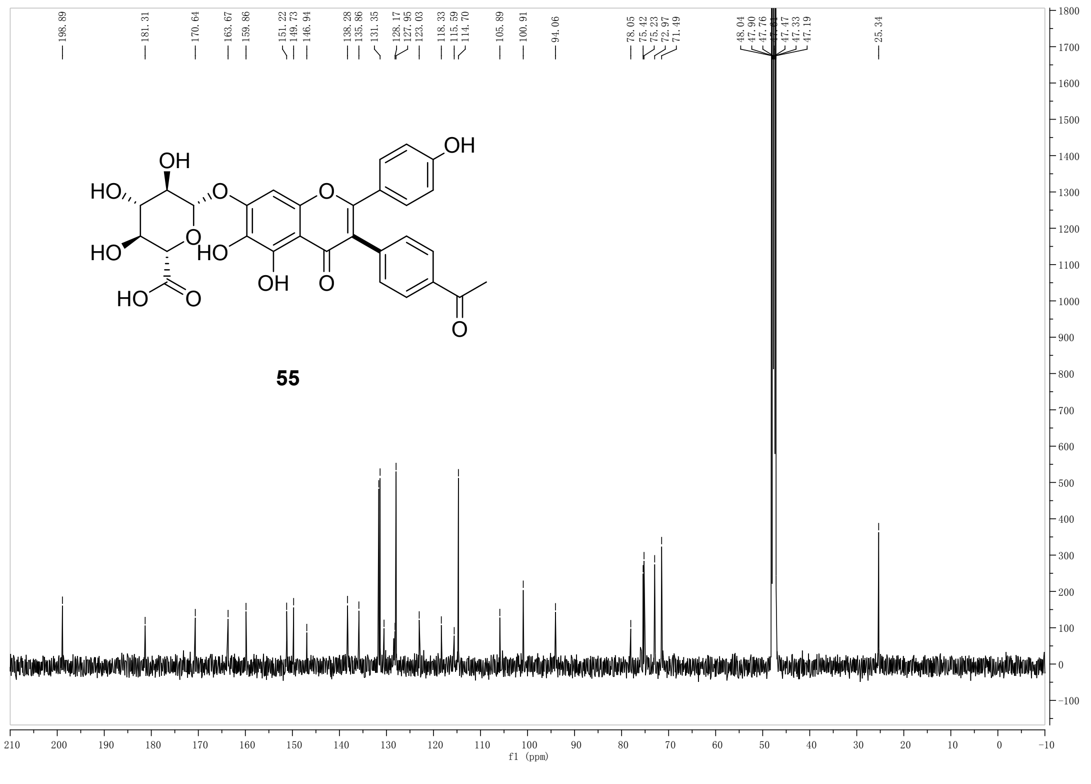

8.05
8.03
7.79
7.40
7.38
6.61
6.59
6.55
6.55
6.51
6.50
5.36
5.36
5.35
5.34
5.34
5.33
4.91
4.10
4.09
4.09
4.08
4.08
3.67
3.66
3.65
3.33
3.33
3.33
3.32
2.66
2.21
2.21
2.21
2.19
2.18
2.17
2.16
2.14
2.12
2.10
2.05
2.04
2.02
2.02
OH
COOH
HO
O
OH
OH
OH
O
O
53
2.14
1.02
2.17
1.03
1.06
1.00
1.26
1.21
1.20
3.28
4.17
1.69
f1 (ppm)

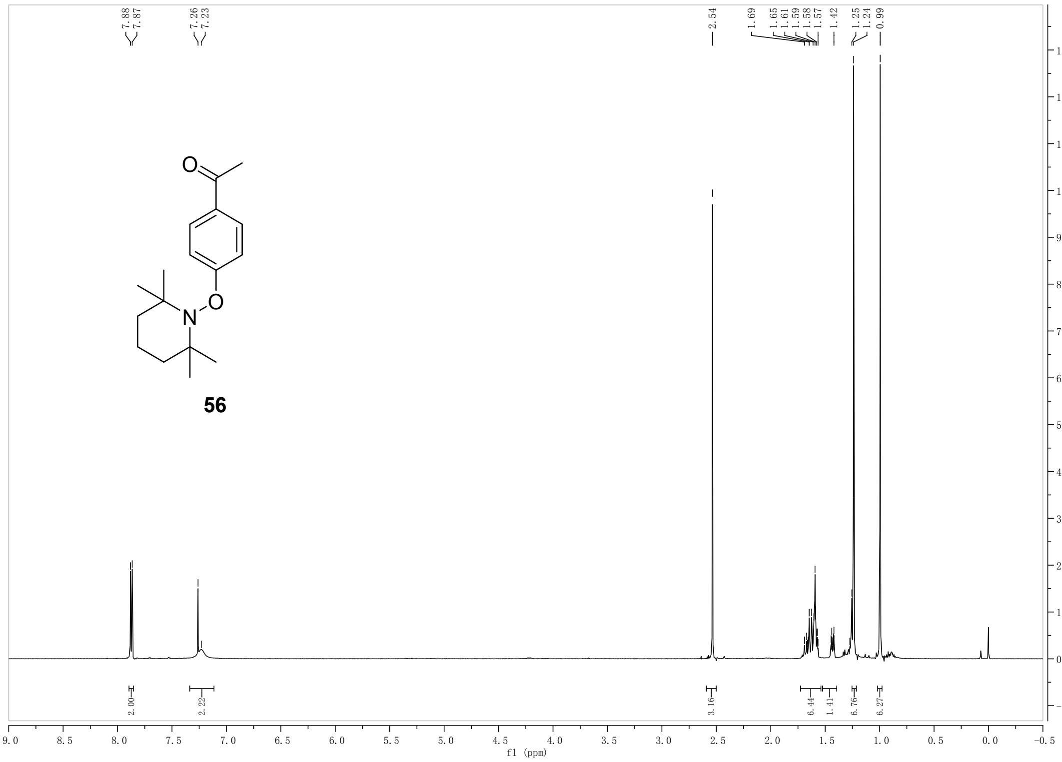

199.00
175.42
167.12
147.33
144.65
142.13
141.75
136.03
130.32
128.49
128.39
128.04
126.01
124.11
117.18
114.62
74.59
71.48
48.04
47.90
47.76
47.61
47.47
47.33
47.19
36.69
25.36
OH
COOH
HO
O
OH
OH
OH
O
O
53
f1 (ppm)


8.02
7.94
7.93
7.75
7.74
7.41
6.74
4.80
4.77
3.88
3.87
3.86
3.85
3.64
3.62
3.42
3.38
3.30
3.21
3.21
3.20
2.53
1.00
1.95
1.97
1.01
0.96
4.95
1.03
1.07
2.84
0.60
2.96
OH
HO
O
O
HO
O
HO
OH
O
54
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0

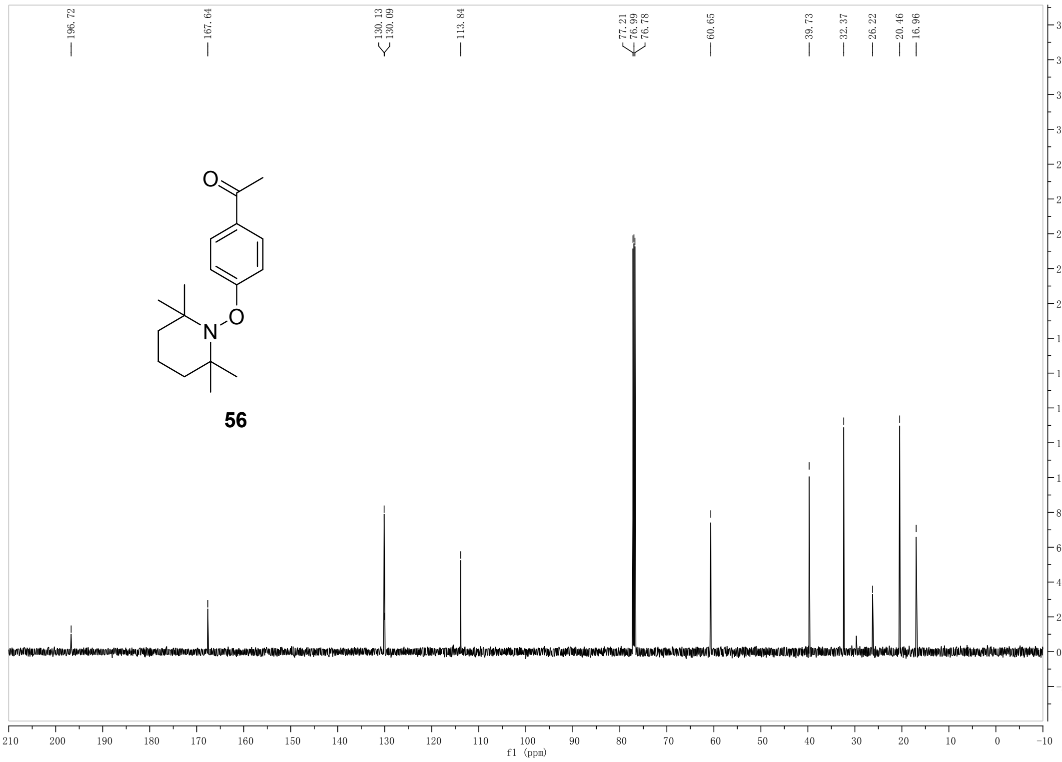

198.68
161.10
152.25
151.01
143.27
142.17
140.13
136.27
128.29
128.00
122.40
115.47
112.03
102.77
77.15
76.21
73.40
70.02
61.20
48.02
47.88
47.74
47.60
47.46
47.31
47.17
25.33
OH
HO
O
O
HO
O
HO
OH
O
54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


7.93
7.91
7.33
7.31
7.19
7.17
6.88
6.62
6.61
5.18
5.17
4.89
4.15
4.14
3.67
3.63
3.59
3.56
3.30
3.30
3.30
2.59
2.01
2.15
1.96
1.08
2.00
1.06
0.97
4.28
3.12
OH
HO
O
HO
O
HO
O
HO
OH
O
OH
O
O
55
3000
2500
2000
1500
1000
500
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

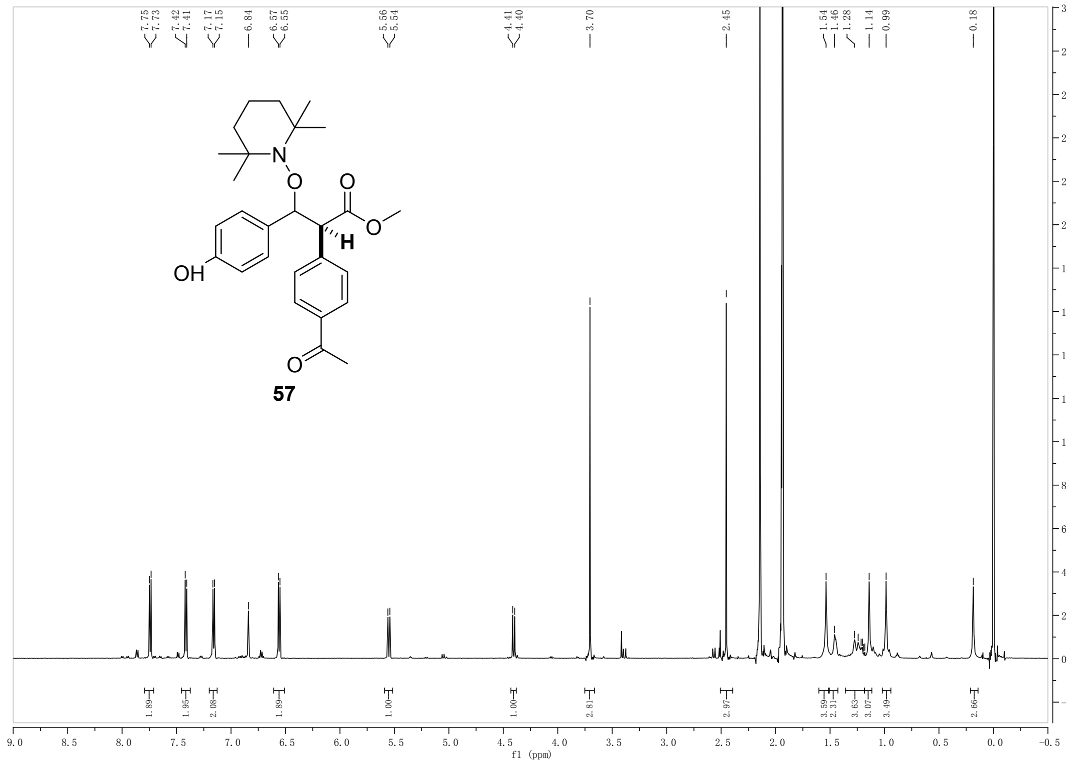

198.89
181.31
170.64
163.67
159.86
151.22
149.73
146.94
138.28
135.86
131.35
128.17
127.95
123.03
118.33
115.59
114.70
105.89
100.91
94.06
78.05
75.42
75.23
72.97
71.49
48.04
47.90
47.76
47.47
47.33
47.19
25.34
OH
HO
O
HO
O
HO
O
HO
OH
O
OH
O
O
55
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



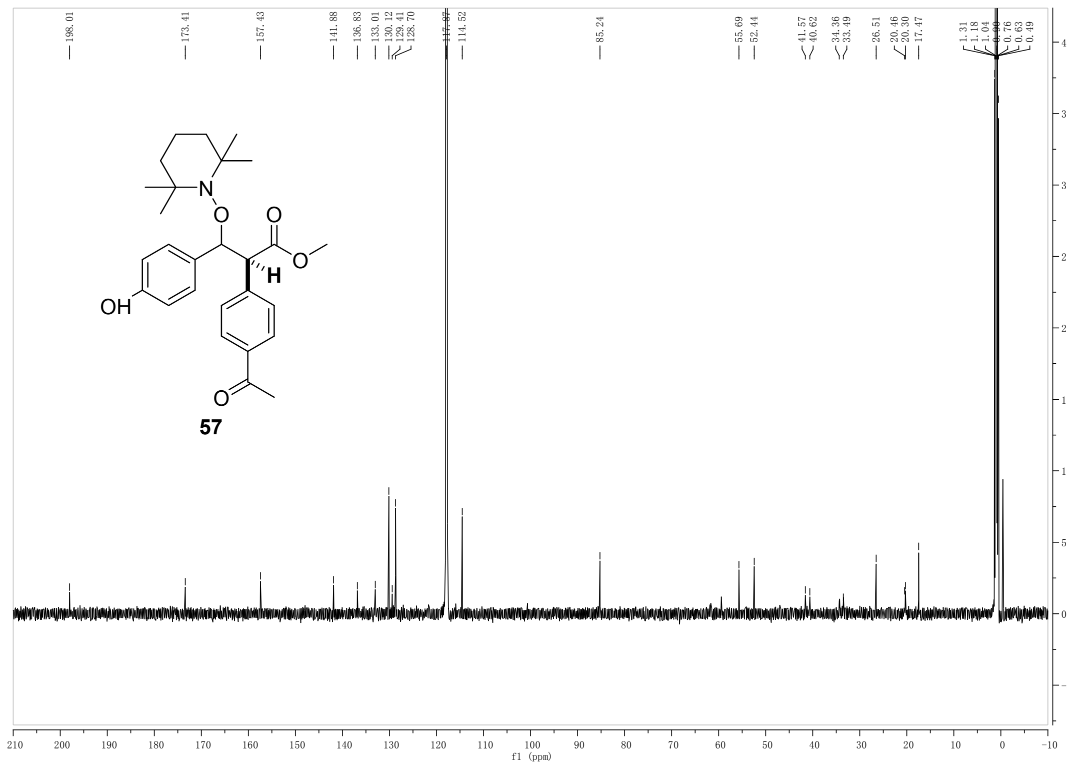
7.88
7.87
7.26
7.23
2.54
1.69
1.65
1.61
1.59
1.58
1.57
1.42
1.25
1.24
0.99
2.00
2.22
3.16
6.44
1.41
6.76
6.27
56
f1 (ppm)



196.72
167.64
130.13
130.09
113.84
77.21
76.99
76.78
60.65
39.73
32.37
26.22
20.46
16.96
56
f1 (ppm)



7.75
7.73
7.42
7.41
7.17
7.15
6.84
6.57
6.55
5.56
5.54
4.41
4.40
3.70
2.45
1.54
1.46
1.28
1.14
0.99
0.18
1.89
1.95
2.08
1.89
1.00
1.00
2.81
2.97
3.59
2.31
3.63
3.07
3.49
2.66
N
O
O
O
H
OH
O
57
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200



198.01
173.41
157.43
141.88
136.83
133.01
130.12
129.41
128.70
117.87
114.52
85.24
55.69
52.44
41.57
40.62
34.36
33.49
26.51
20.46
20.30
17.47
1.31
1.18
1.04
0.76
0.63
0.49
N
O
O
O
H
OH
O
57
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
-500