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 CaH₂ 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 KMnO₄ stain. Yields reported were for isolated, spectroscopically pure compounds.

¹H and ¹³C 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 (¹³C) 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 Cs₂CO₃ (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 Na₂SO₄ 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.

![Experimental setup for photochemical Heck arylation of vinylphenols.](image)

**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$_2$CO$_3$ (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$_2$CO$_3$ 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 Cs₂CO₃, and mixtures of 1, 2 and Cs₂CO₃ 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 Cs₂CO₃ (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 Cs₂CO₃ 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$_2$CO$_3$) 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]

$$E(2/2^*) = E(2/2^-) - E_{0,0}(2^-*/2^-)$$

The peak potential of electrochemical oxidation of the phenolate anion of 2 ($E_p = 0.36$ V) was used for $E(2/2^-)$. $E_{0,0}(2^-*/2^-)$, 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 $E_{0-0}(2^*/2)$ of 2.79 eV for the phenolate anion of 2.

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

**Supplementary Figure 6.** Normalized absorption and emission spectra of the phenolate anion of 2 in dry -DMSO ($5 \times 10^{-5}$ 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\textsubscript{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 saturated calomel electrode (SCE) at 0.1 V/s scan rate. A completely irreversible reduction wave was observed with $E_p = -1.83 \text{ V vs. SCE}$ 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 Cs₂CO₃ (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 Na₂SO₄ 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): ¹H NMR (600 MHz, CDCl₃):  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); ¹³C NMR (150 MHz, CDCl₃): 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 C₁₇H₂₅O₂NNa [M + Na]⁺, 298.1778, found 298.1776.

**Methyl 2-(4-acetylphenyl)-3-(4-hydroxyphenyl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate** (57): ¹H NMR (600 MHz, CD₃CN):  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); ¹³C NMR (150 MHz, CD₃CN): 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$_3$N [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*. 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 $\text{Fe(phen)}_3^{2+}$ 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 $\mu$L of sulfuric acid (96%) were added to a 100 mL volumetric flask, and filled to the mark with water (HPLC grade).

2. Phenanthroline 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 1,4'-bromoacetophenone 1 (99.5 mg, 0.50 mmol), 2 (178.0 mg, 1.00 mmol), Cs$_2$CO$_3$ (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:

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

where $V_1$ is the irradiated volume (1 mL), $V_2$ is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), $V_3$ is the final volume after complexation with phenanthroline (10 mL), $\ell$ is the optical path-length of the irradiation cell (1 cm), $\Delta A \ (510 \ nm)$ the optical difference in absorbance between the irradiated solution and the one stored in the dark, $\varepsilon \ (510 \ nm)$ 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 ($q_{n,p}$) by the use of the following Equation: $^{[4]}

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

Where $dx/dt$ is the rate of change of a measurable quantity (spectral or any other property), the quantum yield ($\Phi$) for Fe$^{2+}$ at 450 nm is 0.9,$^{[5]}$ and the absorbance $A(\lambda)$ of the actinometer at $\lambda = 450$ nm was measured by UV/Vis spectroscopy to be 0.327. $q_{n,p}^0$, which is the photon flux, was determined to be $1.32 \times 10^{-8}$ 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: $\Phi \cdot (1 - 10^{-A(450 \text{ nm})}) \cdot q^0_{n,p}$, where $\Phi$ is the quantum yield to be determined and the absorption $A(450 \text{ nm})$ of the reaction was determined by UV/Vis spectroscopy to be more than 4, thus $(1 - 10^{-A(450 \text{ nm})}) > 1 - 10^{-4} = 0.9999$ (approximated to 1). The calculation yields the quantum yield ($\Phi$) of the photoreaction = 0.58. The procedure was repeated a second time to provide a similar value: quantum yield ($\Phi$) at 450 nm of 0.52.
Identification of Compounds

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$_2$CO$_3$ (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$_4$Na [M + Na]$^+$, 319.0941, found 319.0942.

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$_2$CO$_3$ (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$_3$): $\delta$ 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$_3$): $\delta$ 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.

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$_2$CO$_3$ (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-$d_6$): $\delta$ 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.

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), Cs₂CO₃ (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). ¹H NMR (400 MHz, CD₃CN): 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); ¹³C NMR (100 MHz, CD₃CN): 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 C₁₇H₁₁NO₃ [M - H] -, 278.0823, found 278.0824.

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), Cs₂CO₃ (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). ¹H NMR (600 MHz, CD₃CN): 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); ¹³C NMR (150 MHz, CD₃CN): 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 C₁₇H₁₁NO₃ [M - H] -, 278.0823, found 278.0823.
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), Cs₂CO₃ (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). ¹H NMR (600 MHz, Acetone-d₆): 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); ¹³C NMR (151 MHz, Acetone-d₆): 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 C₁₇H₁₂NO₃ [M - H]⁻, 278.0823, found 278.0825.

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), Cs₂CO₃ (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). ¹H NMR (400 MHz, Acetone-d₆): 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); ¹³C NMR (100 MHz, Acetone-d₆): 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 C₁₆H₁₃O₃ [M -
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), Cs₂CO₃ (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). ¹H NMR (400 MHz, Acetone-d₆): 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); ¹³C NMR (100 MHz, Acetone-d₆): 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 C₁₇H₁₅O₃ [M - H]⁻, 267.1027, found 267.1027.

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), Cs₂CO₃ (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). ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): δ 167.0, 159.1, 156.4, 140.1, 132.6,
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), Cs₂CO₃ (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-­d₆): 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); ^13C NMR (150 MHz, Acetone-­d₆): 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 C₁₈H₁₈NO₄ [M + H]^+ 312.1230, found 312.1227.

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), Cs₂CO₃ (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, CD₃CN): δ 7.67 (s, 1H), 7.22 (s, 1H), 7.11 (t, 1H, J = 8.5 Hz), 7.00 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 8.5 Hz, 2H), 3.71 (s, 3H), 2.13 (s, 3H); HR-ESI-MS (m/z): calcd. for C₁₉H₁₈N₂O₄ [M + H]^+ 326.1386, found 326.1384.
$J = 8.0, 1H), 6.95 (d, J = 8.7, 2H), 6.70 – 6.57 (m, 3H), 6.48 – 6.39 (m, 2H), 4.13 (s, 2H), 3.69 (s, 3H); ^{13}C$ NMR (150 MHz, CD$_3$CN): $\delta$ 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.

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$_2$CO$_3$ (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-$d_6$): $\delta$ 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-$d_6$): $\delta$ 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$_4$Na [M + Na]$^+$, 293.0784, found 293.0785.

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$_2$CO$_3$ (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$_3$): $\delta$ 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$_3$): $\delta$ 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.

(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$_2$CO$_3$ (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-$d_6$): $\delta$ 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-$d_6$): $\delta$ 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.

(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), Cs₂CO₃ (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). ¹H NMR (600 MHz, Acetone-ᵈₛ): 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); ¹³C NMR (150 MHz, Acetone-ᵈₛ): 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 C₁₇H₁₄O₅Na [M + Na]⁺ 321.0733, found 321.0733.

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\text{HO} \quad \text{O} \quad \text{O} \\
\text{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), Cs₂CO₃ (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). ¹H NMR (600 MHz, Acetone-ᵈₛ): 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); ¹³C NMR (150 MHz, Acetone-ᵈₛ): 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 C₁₆H₁₂NO₅ [M - H]⁻ 298.0721, found 298.0722.

\[
\text{HO} \quad \text{O} \\
\text{19}
\]

**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$_2$CO$_3$ (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). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 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$_3$CN): $\delta$ 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.

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$_2$CO$_3$ (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). $^1$H NMR (600 MHz, CD$_3$OD): $\delta$ 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$_3$OD): $\delta$ 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.
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$_2$CO$_3$ (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-$d_6$): $\delta$ 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-$d_6$): $\delta$ 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.

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$_2$CO$_3$ (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-$d_6$): $\delta$ 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, $J = 8.7, 1.6, 1$H), 7.07 (d, $J = 8.7, 2$H), 6.62 (d, $J = 8.7, 2$H), 3.76 (s, 3H); $^{13}$C NMR (150 MHz, Acetone-$d_6$): $\delta$ 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$_3$Na [M + Na]$^+$, 377.1148, found 377.1150.

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$_2$CO$_3$ (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$_3$): $\delta$ 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$_3$): $\delta$ 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.

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$_2$CO$_3$ (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-$d_6$): $\delta$ 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-$d_6$): $\delta$ 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.

![Structure of 25](image)

**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$_2$CO$_3$ (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$_3$): $\delta$ 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$_3$): $\delta$ 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.

![Structure of 26](image)

**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), Cs₂CO₃ (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). ¹H NMR (600 MHz, DMSO-𝑑₆): 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); ¹³C NMR (151 MHz, DMSO-𝑑₆): 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 C₁₉H₁₆NO₃ [M + H]⁺, 306.1125, found 306.1125.

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), Cs₂CO₃ (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). ¹H NMR (600 MHz, DMSO-𝑑₆): 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); ¹³C NMR (150 MHz, DMSO-𝑑₆): 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 C₁₉H₁₆NO₃ [M + H]⁺, 306.1125, found 306.1126.
**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$_2$CO$_3$ (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.

**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$_2$CO$_3$ (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,
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), Cs₂CO₃ (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, CD₃CN) 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); ¹³C NMR (150 MHz, CD₃CN): 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 C₁₉H₁₆NO₃ [M + H]⁺, 306.1125, found 306.1125.

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), Cs₂CO₃ (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, CD₃CN): 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$_3$CN): $\delta$ 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$_3$S $[M + H]^+$, 261.0580, found 261.0580.

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$_2$CO$_3$ (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$_3$): $\delta$ 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$_3$): $\delta$ 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$_3$Na $[M + Na]^+$, 442.1414, found 442.1411.

$S$-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),
Cs₂CO₃ (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). ¹H NMR
(600 MHz, CDCl₃): 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); ¹³C NMR (150 MHz, CDCl₃): 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 C₁₉H₁₈O₃SNa [M + Na]⁺, 349.0869, found 349.0872.

(33)

(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),
Cs₂CO₃ (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). ¹H NMR
(600 MHz, DMSO-d₆): 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); ¹³C NMR (150 MHz, DMSO-d₆): 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 C₁₉H₁₈NO₃ [M - H]⁻, 308.1292, found 308.1294.
(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), Cs₂CO₃ (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). ¹H NMR (600 MHz, CD₃CN): 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); ¹³C NMR (151 MHz, CD₃CN): 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 C₁₈H₁₅O₃ [M - H]⁺, 279.1027, found 279.1025.

MeO

(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), Cs₂CO₃ (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). ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): δ 198.2, 197.7, 147.4, 146.0, 142.9, 140.5, 137.7,
(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\textsubscript{2}CO\textsubscript{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 \textbf{37} as a colorless oil (25.8 mg, 71% yield, E/Z = 8:1). \textsuperscript{1}H NMR (600 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) 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); \textsuperscript{13}C NMR (150 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) 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\textsubscript{23}H\textsubscript{17}O\textsubscript{3} [M - H], 341.1183, found 341.1183.

(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\textsubscript{2}CO\textsubscript{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 \textbf{38} as a
colorless oil (15.0 mg, 63% yield, E/Z = 15:1). $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 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-$d_6$): $\delta$ 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$_2$Na [M + Na]$^+$, 261.0886, found 261.0887.

![Image](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$_2$CO$_3$ (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$_3$): $\delta$ 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$_3$): $\delta$ 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.

![Image](40)

$(E)$-1-(4-(1-(3,5-dimethoxyphenyl)-2-(4-hydroxyphenyl)vinyl)phenyl)ethan-1-one
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$_2$CO$_3$ (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$_3$): $\delta$ 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$_3$): $\delta$ 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.

\[
\text{Methyl (E)-2-(4-acetylphenyl)-3-(4-hydroxyphenyl)but-2-enoate (41)}
\]

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$_2$CO$_3$ (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$_3$): $\delta$ 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$_3$): $\delta$ 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.
**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$_2$CO$_3$ (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$_3$): $\delta$ 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$_3$): $\delta$ 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.

**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$_2$CO$_3$ (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$_3$): $\delta$ 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$_3$): $\delta$ 197.6, 167.7, 146.6, 141.9, 141.6, 136.3, 130.5, 129.1, 128.7, 125.2, 107.9,
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), Cs₂CO₃ (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).

¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): 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 C₂₆H₃₁O₄ [M - H]⁻, 407.2228, found 407.2222.

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), Cs₂CO₃ (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). ¹H NMR
(400 MHz, Acetone-\textit{d}_6): \(\delta = 8.03\) (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-\textit{d}_6): \(\delta 196.9, 167.2, 147.1, 144.7, 141.8, 140.9, 136.3, 130.2, 128.5, 126.2, 124.3, 117.2, 115.1, 51.5, 25.9\); HR-ESI-MS (\textit{m/z}): calcd. for C\textsubscript{18}H\textsubscript{15}O\textsubscript{5} [M - H], 311.0925, found 311.0926.

![Methyl (E)-2-(4-acetylphenyl)-3-(3-hydroxyphenyl)acrylate (46)](image)

\textbf{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\textsubscript{2}CO\textsubscript{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\textsubscript{3}): \(\delta 7.95\) (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\textsubscript{3}): \(\delta 198.0, 167.6, 155.5, 141.0, 136.4, 135.6, 131.7, 130.2, 129.6, 128.6, 123.3, 116.9, 116.7, 52.5, 26.6\); HR-ESI-MS (\textit{m/z}): calcd. for C\textsubscript{18}H\textsubscript{15}O\textsubscript{4} [M - H], 295.0976, found 295.0976.

![image]

\textbf{(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$_2$CO$_3$ (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-$d_6$): $\delta$ 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-$d_6$): $\delta$ 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 ($m/\zeta$): calcd. for C$_{23}$H$_{17}$O$_3$ [M - H], 341.1183, found 341.1181.

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$_2$CO$_3$ (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-$d_6$): $\delta$ 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-$d_6$): $\delta$ 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 ($m/\zeta$): calcd. for C$_{17}$H$_{11}$O$_4$ [M - H], 279.0663, found 279.0661.
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), Cs₂CO₃ (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-d₆): 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); ¹³C NMR (100 MHz, DMSO-d₆): 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 C₂₃H₁₆O₅Na [M + Na]⁺, 395.0890, found 395.0889.

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), Cs₂CO₃ (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-$d_6$): $\delta$ 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-$d_6$): $\delta$ 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.

![Image of compound 51](image1.png)

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$_2$CO$_3$ (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-$d_6$): $\delta$ 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-$d_6$): $\delta$ 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.

![Image of compound 52](image2.png)
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$_2$CO$_3$ (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). $^1$H NMR (400 MHz, Acetone-$d_6$): $\delta$ 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-$d_6$): $\delta$ 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.

(1S,3R,4R,5R)-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$_2$CO$_3$ (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$_3$OH/H$_2$O 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). $^1$H NMR (600 MHz, CD$_3$OD): $\delta$ 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$_3$OD): $\delta$ 199.0, 175.4, 167.1, 147.3, 144.6, 142.1, 141.7, 136.0, 130.3, 128.5, 128.0, 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.

![Structure 54](image)

3-(4-acetylphenyl)-7-hydroxy-6-(((2S,3R,4S,5S,6R)-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$_2$CO$_3$ (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$_3$OH/H$_2$O 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$_3$OH). $^1$H NMR (600 MHz, CD$_3$OD): $\delta$ 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$_3$OD): $\delta$ 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$_{23}$O$_{10}$Na [M + Na]$^+$, 481.1105, found 481.1108.
(2S,3S,4S,5R,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$_2$CO$_3$ (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$_3$OH/H$_2$O 1:4) to afford the product 55 as a yellow powder (23.2 mg, 40% yield). $[\alpha]_D^{21} = \text{-}250$ (c = 0.20, CH$_3$OH). $^1$H NMR (600 MHz, CD$_3$OD): $\delta$ 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$_3$OD): $\delta$ 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
[4] a) Braslavsky, S. E. Glossary of terms used in photochemistry, (IUPAC Recommendations

Crystal data and structure refinement for compound 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, $\alpha = 90^\circ$
  b = 11.8883(10) Å, $\beta = 90^\circ$
  c = 24.935(2) Å, $\gamma = 90^\circ$
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
HO
O
Me

25

HO
O
O
Me

25

71
The image contains a chemical structure labeled as 33, along with a 2D NMR spectrum. The spectrum shows various peaks at different chemical shifts, indicated by the ppm values on the x-axis and the intensity on the y-axis.
51