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Supporting Information

Photoactivated H_2S donor based on coumarin structure with real-time monitoring capability

Nianwei Wang,[a] Yuxi Fang,[a] Xuan Wang,[a] Jiao Bai,*[a] Huiming Hua,[a] Dahong Li*[a]

[a]Key Laboratory of Structure-Based Drug Design & Discovery, Ministry of Education, and School of Traditional Chinese Materia Medica, Shenyang Pharmaceutical University, 103 Wenhua Road, Shenyang 110016, PR China.
Email: lidahong0203@163.com

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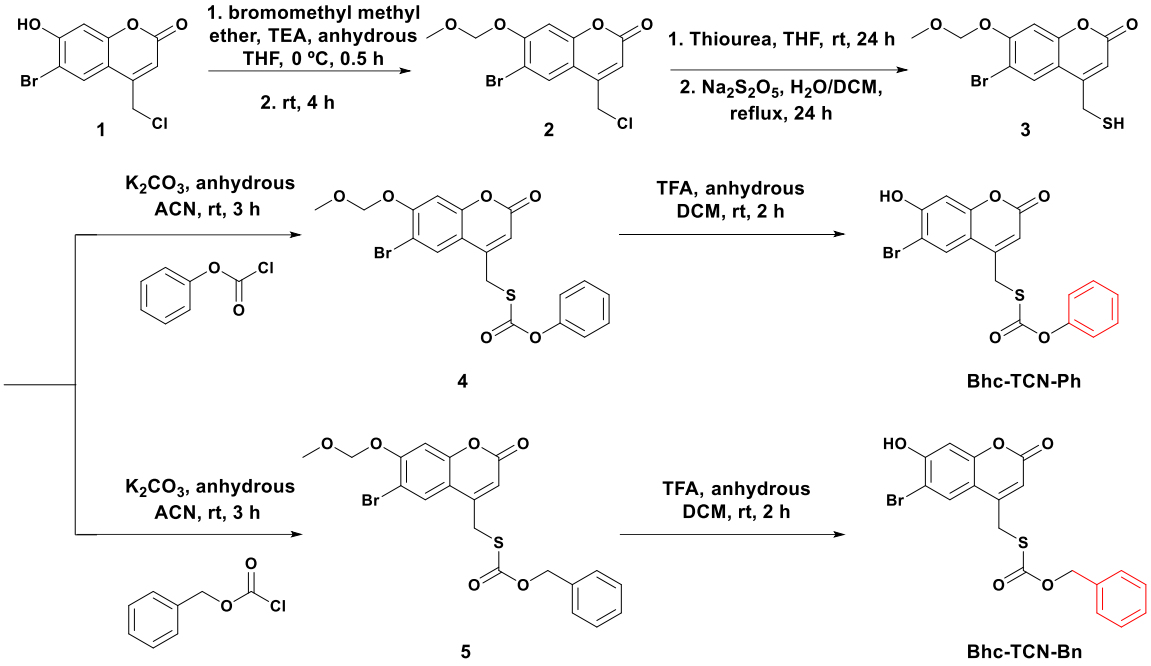
1. Materials and methods

The chemical reagents were purchased from Macklin and Aladdin companies with a purity of 98% or higher. Bovine red blood cells CA were purchased from Sigma company. MCF-7 cells were purchased from the American Typical Culture Collection (ATCC). Anhydrous THF, anhydrous DCM, and anhydrous ACN were prepared using a distillation apparatus. High-performance silica gel plates GF254 and column chromatography silica gel (100-200 mesh and 200-300 mesh) were purchased from Qingdao Marine Chemical Factory. Unless otherwise specified, all other reagents were obtained from qualified commercial suppliers and used without further purification.

Fluorescence emission spectra were recorded on a fluorescence spectrophotometer (Hitachi F-7100). Absorption spectra were measured on a UV-Visible spectrometer (UV-2201 spectrometer). Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker-ARX-400 spectrometer operating at 400 MHz and a Bruker-ARX-600 operating at 600 MHz. Chemical shifts (δ) were referenced to residual DMSO-d_6 (^{1}H NMR, δ 2.50) and $CDCl_3$ (^{1}H NMR, δ 7.26). High-resolution mass spectra (HRMS) were measured on a mass spectrometer (Agilent QTOF6520). The photodegradation rate and mechanism of the compounds were investigated using HPLC (Waters 1525 Breeze). Live cell imaging was performed using an inverted fluorescence microscope (Olympus IX73). Cytotoxicity assays were performed by recording the absorbance at 450 nm using an enzyme marker (Thermo Varioskan Flash). The UV light source (365 nm, 8 w) was used with a ZF-7A UV lamp from Shanghai Guang Hao.

2. Synthesis

The compounds **1**,[1] H_2S fluorescent probe **HSN2**,[2] NIR H_2S fluorescent probe **IS-NO$_2$**,[3] reference materials **PhotoTCM-1**,[4] and **Bhc-OH**[5] were synthesized following previously described methods, with the obtained analytical data in agreement with the published values. The ^{1}H NMR spectra for compounds **HSN2**, **IS-NO$_2$**,**PhotoTCM-1**, and **Bhc-OH** are included.



Scheme S1. Synthetic procedure of the **Bhc-TCN-Ph** and **Bhc-TCN-Bn**.

6-bromo-4-(chloromethyl)-7-(methoxymethoxy)-2*H*-chromen-2-one (2)

Briefly, **1** (680 mg, 2.65 mmol) was dissolved in anhydrous THF, and TEA (490 μL, 3.53 mmol) and MOMBr (325 μL, 3.98 mmol) were added sequentially under ice-cold conditions. The reaction mixture was stirred in an ice bath for 0.5 h and then allowed to warm up to room temperature. TLC monitoring showed complete reaction after 3 h. The reaction mixture was concentrated, diluted with water, extracted with DCM three times, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was further purified by silica gel column chromatography (PE:EA = 15:1) to afford white solid **2** (618 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (s, 1H, Ar-H), 7.14 (s, 1H, Ar-H), 6.51 (s, 1H, Ar-H), 5.31 (s, 2H, -OCH_2OCH_3), 4.85 (s, 2H, Ar-CH_2Cl), 3.52 (s, 3H, -OCH_2OCH_3).

6-bromo-4-(mercaptomethyl)-7-(methoxymethoxy)-2*H*-chromen-2-one (3)

Dissolve **2** (618 mg, 1.85 mmol) in THF and add thiourea (282 mg, 3.71 mmol) under stirring at room temperature. Monitor the reaction progress by TLC, and after 24 h, the reaction was complete. The resulting white solid was obtained by vacuum drying. Dissolve the crude product in 5 mL of water and add 3 mL of DCM. Then add $Na_2S_2O_5$ (1.4 g, 7.40 mmol) and reflux the mixture. After 24 h, there was no visible white precipitate in the aqueous layer, indicating complete reaction. Extract with DCM three times, combine the DCM layer, dry over anhydrous Na_2SO_4, filter, and concentrate. The crude product was further purified by silica gel column chromatography (PE:EA = 2:1) to yield white solid **3** (210 mg, 34%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (s, 1H, Ar-H), 7.16 (s, 1H, Ar-H), 6.37

(s, 1H, Ar-H), 5.32 (s, 2H, -OCH_2OCH_3), 3.77 (d, 2H, *J* = 8.0 Hz, Ar-CH_2SH), 3.52 (s, 3H, -OCH_2OCH_3), 1.88 (t, 1H, *J* = 8.0 Hz, -OCH_2OCH_3).

_S_-((6-bromo-7-(methoxymethoxy)-2-oxo-2_H_-chromen-4-yl)methyl) _O_-phenyl carbonothioate (4)

Compound **3** (100 mg, 0.30 mmol) was dissolved in anhydrous ACN, benzoyl chloride (38 μL, 0.30 mmol) was added dropwise followed by K_2CO_3 (126 mg, 0.91 mmol), the reaction was stirred at room temperature and monitored by TLC, and the reaction was complete after 3 h. The reaction was concentrated, water was added and extracted three times with DCM, the DCM layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was further purified by silica gel column chromatography (PE:EA = 8:1) to give a white solid **4** (85 mg, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.78 (s, 1H, Ar-H), 7.40 (t, 2H, *J* = 7.7 Hz, Ar-H), 7.27 (t, 1H, *J* = 7.4 Hz, Ar-H), 7.17 (s, 1H, Ar-H), 7.15 (d, 2H, *J* = 7.4 Hz, Ar-H), 6.49 (s, 1H, Ar-H), 5.32 (s, 2H, -OCH_2OCH_3), 4.19 (s, 2H, Ar-CH_2S-), 3.52 (s, 3H, -OCH_2OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.6, 160.1, 156.7, 154.6, 151.2, 149.0, 129.8 (×2), 128.2, 126.7, 121.2 (×2), 114.5, 113.6, 108.7, 104.4, 95.4, 56.8, 31.5; HR-ESIMS *m/z* calcd for $C_{19}H_{15}BrO_6S$ $[M + H]^+$ 450.9845, found 450.9854.

_O_-benzyl _S_-((6-bromo-7-(methoxymethoxy)-2-oxo-2_H_-chromen-4-yl)methyl) carbonothioate (5)

Referring to the synthesis of **4** to obtain **5**, a white solid in 60% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.78 (s, 1H, Ar-H), 7.40-7.34 (m, 5H, Ar-H), 7.15 (s, 1H, Ar-H), 6.45 (s, 1H, Ar-H), 5.31 (s, 2H, -OCH_2OCH_3), 5.28 (s, 2H, Ph-CH_2O-), 4.13 (s, 2H, Ar-CH_2S-), 3.52 (s, 3H, -OCH_2OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.3, 160.2, 156.6, 154.5, 149.4, 134.7, 129.0, 128.9, 128.7, 128.3, 127.8, 127.1, 114.3, 113.7, 108.7, 104.3, 95.3, 70.2, 56.8, 31.3; HR-ESIMS *m/z* calcd for $C_{20}H_{17}BrO_6S$ $[M + H]^+$ 465.0002, found 465.0006.

_S_-((6-bromo-7-hydroxy-2-oxo-2_H_-chromen-4-yl)methyl) _O_-phenyl carbono-thio ate (Bhc-TCN-Ph)

4 (85 mg, 0.19 mmol) was dissolved in anhydrous DCM, 200 μL of TFA was added, stirred at room temperature and the reaction was monitored by TLC for 2 h. The reaction was complete. The reaction was concentrated and spun dry, water and DCM were added, DCM was extracted three times, and the DCM layers were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was further purified by silica gel column chromatography (PE:EA = 4:1) to give a white solid **Bhc-TCN-Ph** (75 mg, 97%).^{1}H NMR (600 MHz, DMSO-d_6) δ: 11.52 (s, 1H, Ar-OH), 8.08 (s, 1H, Ar-H), 7.44 (t, 2H, *J* = 7.4 Hz, Ar-H), 7.31 (t, 1H, *J* = 7.4 Hz, Ar-H), 7.23 (d, 2H, *J* = 7.8 Hz, Ar-H), 6.92 (s, 1H, Ar-H), 6.38 (s, 1H, Ar-H), 4.42 (s, 2H, Ar-CH_2S-); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.6, 159.6, 157.5, 154.0, 150.6, 150.3, 129.8 (×2), 129.0, 126.7, 121.4 (×2), 112.3,

111.4, 106.3, 103.3, 30.8; HR-ESIMS *m/z* calcd for $C_{17}H_{11}BrO_5S$ $[M + H]^+$ 406.9583, found 406.9564.

***O*-benzyl *S*-((6-bromo-7-hydroxy-2-oxo-2*H*-chromen-4-yl)methyl) carbonot-hioate (Bhc-TCN-Bn)**

Reference to the synthesis of **Bhc-TCN-Ph** gives **Bhc-TCN-Bn**, a white solid in 95% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 11.51 (s, 1H, Ar-OH), 8.02 (s, 1H, Ar-H), 7.38-7.35 (m, 5H, Ar-H), 6.90 (s, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 5.28 (s, 2H, Ph-CH_2O-), 4.34 (s, 2H, Ar-CH_2S-); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.9, 159.6, 157.5, 154.0, 150.8, 135.0, 129.0, 128.6 (×3), 128.5 (×2), 112.0, 111.4, 106.2, 103.3, 69.4, 30.5; HR-ESIMS *m/z* calcd for $C_{18}H_{13}BrO_5S$ $[M + H]^+$ 420.9740, found 420.9727.

3. UV absorption spectroscopy and fluorescence emission spectroscopy experiments

The UV-visible absorption spectra of the two target compounds were measured using a UV spectrophotometer. Appropriate amounts of **Bhc-TCN-Ph** and **Bhc-TCN-Bn** were dissolved in 100 μL DMSO. Then, 20 μL of the DMSO solution was taken and dissolved in 20 mL PBS buffer to prepare a PBS buffer solution containing 200 μM of the sample (pH 7.4, 10 mM, 0.1% DMSO). For qualitative analysis of UV absorption, 2 mL of each sample solution was placed in a cuvette, and measurements were taken in the wavelength range of 250-480 nm. The remaining liquid was divided into four equal parts, and a UV lamp (365 nm) was placed 5 cm away from the liquid for irradiation times of 2, 6, 10, and 20 min, respectively. Subsequently, 2 mL of each solution with different irradiation times was placed in a cuvette, and their UV absorption in the wavelength range of 250-480 nm was similarly measured.

A fluorescence spectrophotometer was used to test the fluorescence spectrum of **Bhc-TCN-Ph**. 1.00 mg of **Bhc-TCN-Ph** was weighed and dissolved in 100 μL of DMSO to prepare the stock solution. Then, 20 μL of the **Bhc-TCN-Ph** stock solution was taken and dissolved in 20 mL of PBS buffer (pH 7.4, 10 mM), mixed well, and divided into 13 equal portions of 1 mL each. According to the absorption spectrum of **Bhc-TCN-Ph**, the maximum absorption occurs at 375 nm; thus, the excitation wavelength of the fluorescence spectrophotometer was set to 375 nm, and the emission wavelength range was set to 400-660 nm (λ_{ex} = 375 nm, λ_{scan} = 400-660 nm, slit width = 5 nm). Seven 1 mL portions were exposed to light for 0, 2, 4, 6, 8, 10, and 12 min, respectively. Afterward, the samples were transferred to cuvettes, and their emission spectra were measured.

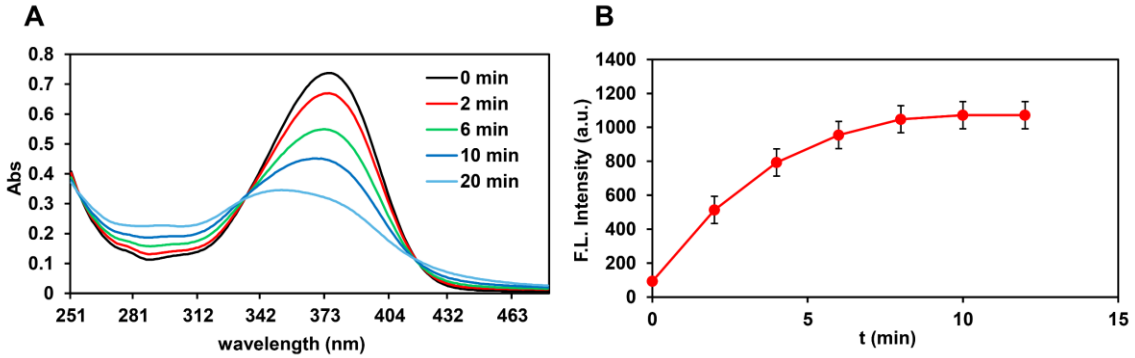


Figure S1. (a) UV absorption spectra of **Bhc-TCN-Bn**. (b) Plot of fluorescence intensity of **Bhc-TCN-Ph** at 483 nm versus light (365 nm) time. Solution: PBS buffer (pH 7.4, 10 mM, 0.1% DMSO). Light distance: 5 cm.

4. Donor photolysis rate test experiment

The photolysis rate of the samples was tested using HPLC. Sample solutions of **Bhc-TCN-Ph**, **Bhc-TCN-Bn**, and **PhotoTCM-1** were prepared at a concentration of 100 μM, and the mobile phase was prepared according to the corresponding requirements (HPLC grade ACN and water). The starting mobile phase was 90% (water:ACN) and a gradient elution was performed until the eluent was pure ACN, with a total elution time of 30 min, column washing for 20 min, and equilibrium for 15 min. First, the samples that were not subjected to photolysis were injected with a volume of 10 μL to determine the retention time and to measure the peak area as an indicator of the change in sample concentration in the solution. Afterwards, the peak areas of the samples subjected to 10, 20, and 30 min of photolysis were also measured, and the change in peak area was calculated. Three measurements were taken for each sample under the same solution and treatment conditions, and the corresponding scatter plot was generated based on the results.

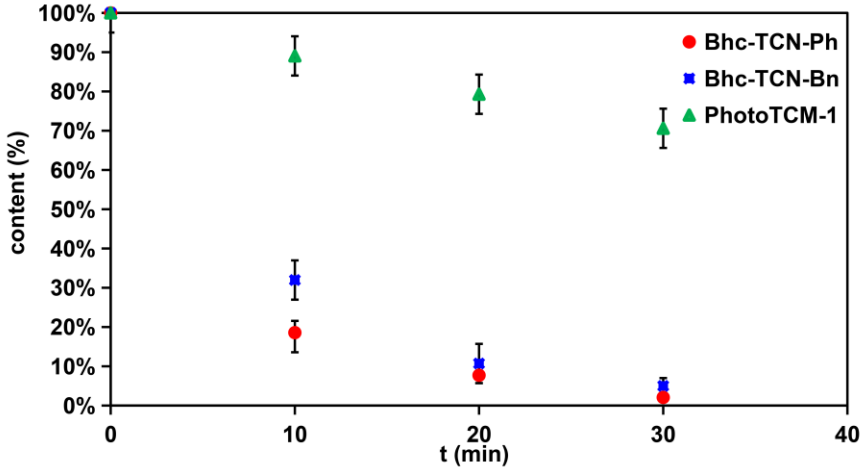


Figure S2. HPLC monitoring of **Bhc-TCN-Ph** (100 μM), **Bhc-TCN-Bn** (100 μM), and control (**PhotoTCM**, 100 μM) in ACN/H_2O (v:v = 1:1) solution after 365 nm light irradiation for 0, 10, 20 and 30 min. Light distance: 5 cm.

5. Quantum yield determination of donor photolysis

An UV lamp (365nm, 8W) was utilized as the light source, illuminating a solution containing 100μM (pH 7.4, 10 mM, 0.1% DMSO) Bhc-TCN-Ph and PhotoTCM-1. The quartz cuvette was consistently positioned 5 cm from the light source throughout the experiment. Every 10 min, a 10 μL sample was extracted for analysis by high-performance liquid chromatography (HPLC), with the peak area being recorded. The sample underwent

elution from an initial mobile phase comprising of acetonitrile and water (at a 1:9 ratio), transitioning gradually to pure acetonitrile, with a flow rate of 1mL/min. Following this, a scatter plot was produced, representing the correlation between HPLC peak area and illumination time, which was fitted to a first-order process using nonlinear regression analysis. The quantum yield of photolysis (Q_u) was computed using the equation $Q_u = (I_0 \sigma t_{90\%})^{-1}$.[6] In this equation, $t_{90\%}$ (s) denotes the duration of irradiation required for 90% of the initial sample to be consumed, I_0 signifies the irradiation intensity measured in einstein cm^{-2} s^{-1}, and σ_{365} (cm^2 mol^{-1}) is the decadic molar extinction coefficient of the sample at 365 nm (expressed as σ_{365} (cm^2 mol^{-1}) = $10^3 \varepsilon_{365}$ (M^{-1} cm^{-1})). The incident intensity (I_0) of the UV lamp was quantified using a potassium ferrioxalate actinometer.[7, 8]

6. Donor release in solution H_2S test experiment

6.1 Methylene blue (MB) method for the determination of H_2S

The experimental method was modified based on previous literature reports.[9] First, a calibration curve for H_2S was prepared using different concentrations of exogenous H_2S solution, which was prepared by Na_2S. The concentrations were 0, 5, 10, 20, 40, 60, and 80 μM. Next, 1 mL of the MB mixture solution and 2 mL of each concentration of Na_2S solution were mixed and reacted in the dark for 30 min. After the reaction, 2 mL of the reaction solution was taken and placed in a cuvette, and the absorbance at 663 nm was measured. This procedure was repeated three times, and a standard curve was plotted with the absorbance as the vertical coordinate and the corresponding Na_2S concentration as the horizontal coordinate.

Subsequently, the release of H_2S from the donor was investigated. Specifically, 2 mL of a PBS buffer (pH 7.4, 10 mM, 0.1% DMSO) containing 25 μg/mL of CA and 100 μM of **Bhc-TCN-Ph** was mixed with 1 mL of MB solution in a 5 mL transparent syringe, and the mixture was protected from light for 30 min. After 30 min, 2 mL of the reaction solution was taken and measured for absorbance at 663 nm.The PBS solution containing **Bhc-TCN-Ph** was measured three times under varying illumination times. The measured absorbance values were converted to H_2S concentrations using a standard curve, which were used as the y-axis, while illumination time was used as the x-axis to plot the curve showing the amount of H_2S released by **Bhc-TCN-Ph** at different illumination times. Similarly, an experimental procedure without illumination was conducted to determine the effect of illumination on H_2S release from **Bhc-TCN-Ph**, and the results were plotted as a scatter plot. The same procedure was performed for **Bhc-TCN-Bn** to study its H_2S release behavior.

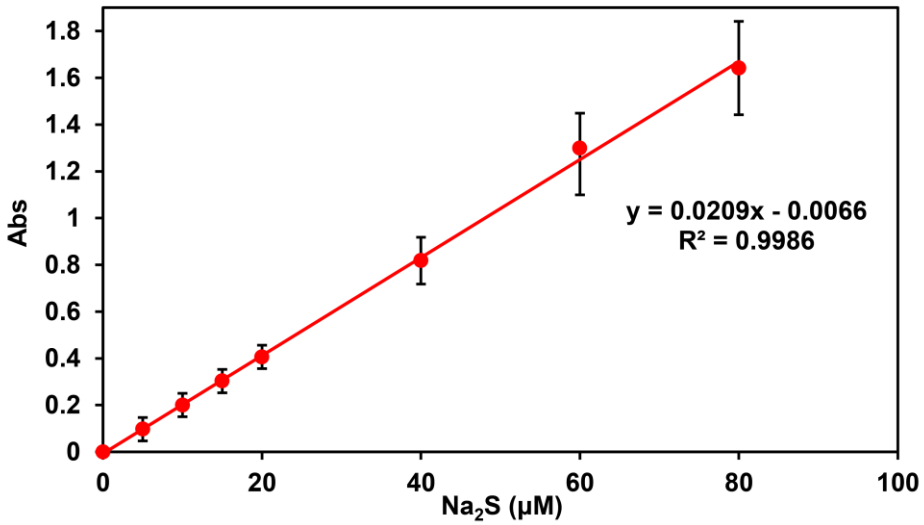


Figure S3. Standard calibration curves for different concentrations (0, 5, 10, 15, 20, 40, 60 and 80 μM) of Na_2S in PBS buffer (pH 7.4, 10 mM, 0.1% DMSO). Wavelength of measured absorption values: λ = 663 nm.

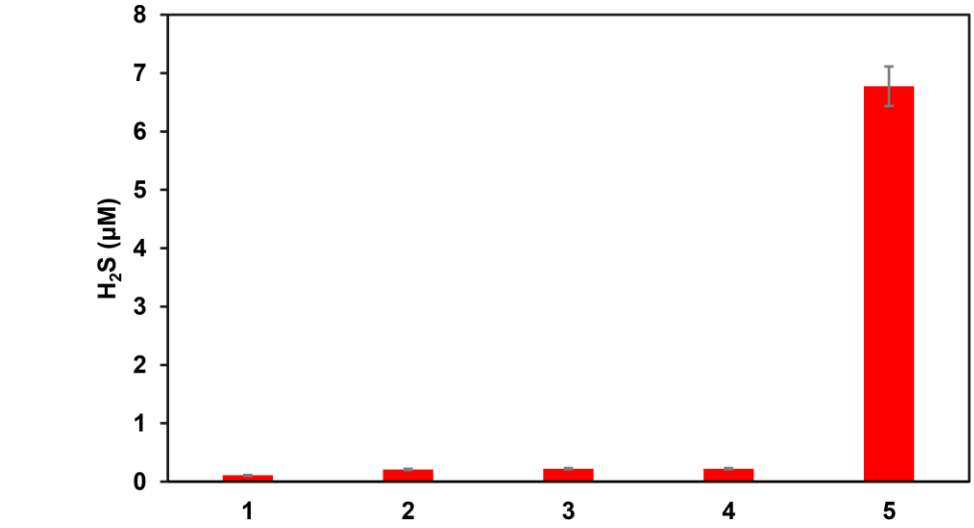


Figure S4. H_2S release from **Bhc-TCN-Ph** (100 μM) in PBS buffer (pH 7.4, 10 mM, 0.1% DMSO) under different conditions. Light duration was 12 min. Light distance: 5 cm.

6.2 Fluorometric determination of H_2S

Fluorescence method, in simple terms, is a method of measuring H_2S content by measuring the fluorescence intensity of a fluorescence probe after quantitative reaction with H_2S. We selected **HSN2** as the H_2S fluorescent probe and prepared a 50 mM stock

solution which was stored in the dark. We then designed four sets of experiments to investigate the release of H_2S from **Bhc-TCN-Ph**. In the first set, 4 μL of the stock solution was mixed with 20 mL of PBS buffer (pH 7.4, 10 mM, 0.1% DMSO), and incubated at 37 ºC in the dark for 1 h. In the second set, 4 μL of the stock solution was mixed with 20 mL of **Bhc-TCN-Ph** (100 μM) containing PBS buffer (pH 7.4, 10 mM, 0.1% DMSO) after 12 min of illumination, and incubated at 37 ºC in the dark for 1 h. In the third set, 4 μL of the stock solution was mixed with 20 mL of PBS buffer (pH 7.4, 10 mM, 0.1% DMSO) containing **Bhc-TCN-Ph** (100 μM) and CA (25 μg/mL) after 12 min of illumination, and incubated at 37 ºC in the dark for 1 h. In the fourth set, 0.60 mg of sodium hydrosulfide nonahydrate was dissolved in 50 mL of PBS buffer (pH 7.4, 10 mM, 0.1% DMSO). Then, 10 μL of the stock solution was mixed with the above solution, and incubated at 37 ºC in the dark for 1 h. Subsequently, 1 mL of each solution was placed in a cuvette and the maximum fluorescence intensity in the range of 450-700 nm with an excitation wavelength of 435 nm was measured (slit width = 5 nm). The above steps were repeated three times and corresponding column charts were generated.

7. Bhc-TCN-Ph H_2S release mechanism validation experiment

The H_2S-releasing mechanism of **Bhc-TCN-Ph** was verified using HPLC. Firstly, 1.00 mg of **Bhc-TCN-Ph** was dissolved in 20 μL of DMSO, and then 10 μL of this DMSO solution was added to 10 mL of PBS buffer to prepare a 200 μM **Bhc-TCN-Ph** solution, which was subsequently divided into four equal 2 mL aliquots. The appropriate mobile phase consisting of chromatography-grade ACN and pure water was prepared, with the starting mobile phase composed of 90% water and 10% ACN, followed by a gradient elution until the eluent was pure ACN. The elution time was set at 60 min, with 20 min of column washing and 15 min of equilibration. Next, 10 μL of the sample that was not subjected to light irradiation was injected, and the UV detector was set to a detection wavelength of 365 nm to determine the peak time of **Bhc-TCN-Ph**. Subsequently, the elution time of the solution was measured after light irradiation for 10, 20, and 30 min, and the appearance of new peaks and their elution times were observed. For comparison, **Bhc-OH** and phenol solutions were prepared at 200 μM using PBS buffer and subjected to HPLC testing under the same conditions, and their peak elution times were recorded.

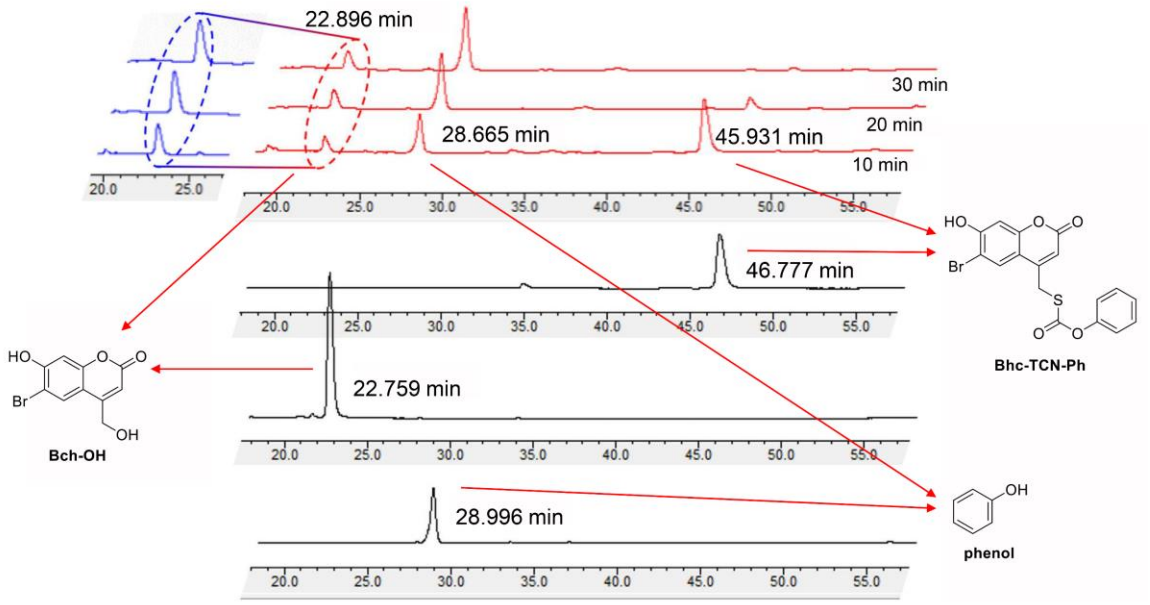


Figure S5. HPLC traces of **Bhc-TCN-Ph** (200 μM) in ACN/H_2O (v:v=1:1) solution before and after irradiation with 365 nm light for 10, 20 and 30 min. The UV lamp was 5 cm from the solution and the red and black lines in the figure are HPLC plots detected at 270 nm and the blue line is the HPLC plot obtained at 365 nm. Mobile phase: ACN/H_2O (v:v = 1:9-10:0, gradient elution for 1 h).

8. Test experiments on the effect of pH and various biological media on the photolysis of Bhc-TCN-Ph

First, 4 aliquots of 5 mL PBS buffer (pH 7.4, 10 mM) were taken and their pH values were adjusted to 5.5, 6.5, 7.4, 8.0, and 9.0, respectively, using a pH meter. Then, 5 μL of a 25 mM **Bhc-TCN-Ph** stock solution was added to each of the 4 buffer solutions, followed by 12 min of illumination, and the fluorescence intensity was measured at a wavelength of 483 nm. The above procedure was repeated three times, and corresponding scatter plots were generated.

To investigate the effect of various biological media on its fluorescence spectra, we selected 16 commonly used biological media for evaluation. The test concentration of hydrogen peroxide was 860 μM, and the test concentration of other biological media was 500 μM. 100 μL of **Bhc-TCN-Ph** stock solution was dissolved in a PBS solution containing 860 μM H_2O_2, and 15 aliquots of 5 μL of the **Bhc-TCN-Ph** solution were dissolved in PBS solutions containing other biological media at a concentration of 500 μM. After 1 h, the fluorescence intensity of each solution was measured at a wavelength of 483 nm. The above procedure was repeated three times, and corresponding bar graphs were generated.

9. Cell culture and cytotoxicity test

MCF-7 cells were cultured in DMEM medium containing 10% heat-inactivated fetal bovine serum (FBS) and 1% penicillin/streptomycin at 37 °C in a 5% CO_2 environment. The cells were then seeded in complete DMEM medium at a concentration of 5×10^3 cells/well in a 96-well plate overnight. The cells were then treated with different concentrations of **Bhc-TCN-Ph** (0, 2.5, 5, 10, 20 μM). One of the 96-well plates was exposed to ultraviolet light (18 W) at a wavelength of 365 nm for 30 min (the distance between the light source and the plate was 5 cm). The cells were then incubated at 37 °C in a 5% CO_2 environment for 24 h, both with and without irradiation. Subsequently, the complete medium was removed from the wells, and the cells were washed 1-2 times with PBS buffer. CCK-8 solution was diluted 10 times with DMEM, and 100 μL of the diluted solution was added to each well of the 96-well plate, which was then incubated at 37 °C in a 5% CO_2 environment for 2-4 h. The absorbance was measured at 450 nm using a microplate reader. Six replicates were set for each drug concentration, and each experiment was performed in triplicate.

10. Live cell imaging experiments

The MCF-7 cells were seeded at a concentration of 10^4 cells per well in a 96-well plate and incubated overnight at 37 °C and 5% CO_2. **Bhc-TCN-Ph** (20 μM) was added to the cells and incubated for 4 h in DMEM medium only. One of the plates was then exposed to ultraviolet light at 365 nm for 15 min, with the light source 5 cm away from the plate, followed by washing the cells three times with PBS buffer for both the irradiated and non-irradiated cells. Subsequently, live cell imaging was performed using an inverted fluorescence microscope to record bright field images of the cells, followed by fluorescent imaging of the cells using a UV excitation filter block (λ = 355-390 nm) to detect fluorescence.

To further confirm the release of H_2S, we employed the NIR H_2S fluorescent probe **IS-NO2** (λ_{ex} = 510 nm, λ_{em} = 650 nm) for live cell imaging of H_2S release in MCF-7 cells. Similar to previous methods, **Bhc-TCN-Ph** (200 μM) and **IS-NO2** (50 μM) were co-incubated with the cells for 4 h, and then separately irradiated with 365 nm UV light for 2 and 15 min, respectively. Finally, cell fluorescence imaging was recorded using the green excitation filter block (λ = 480-550 nm) of the inverted fluorescence microscope to detect fluorescence.

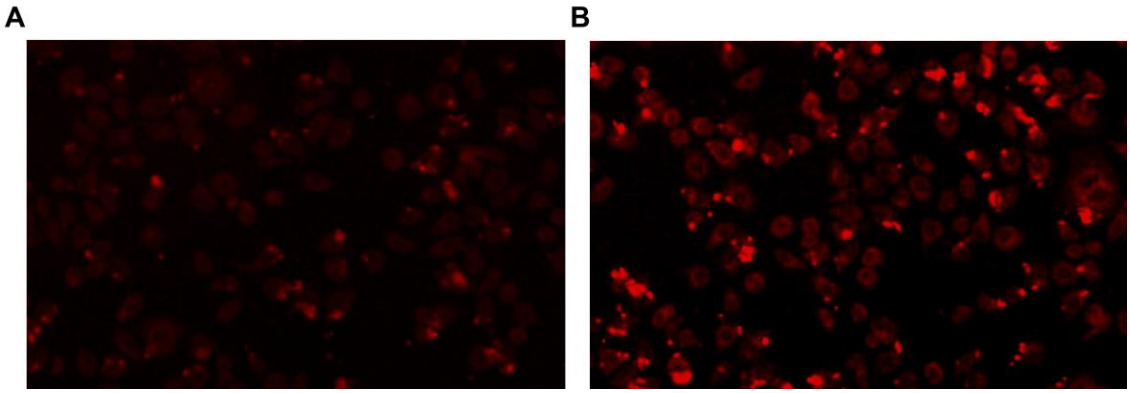


Figure S6. Inverted fluorescence images of H_2S release from **Bhc-TCN-Ph**. The gradual release of H_2S from **Bhc-TCN-Ph** was monitored using the H_2S fluorescent probe **IS-NO$_2$** at different time intervals during illumination with light (λ = 365 nm) for (a) 2 min (b) 15 min. Scale bar: 100 μm.

11. NMR spectra and HRMS

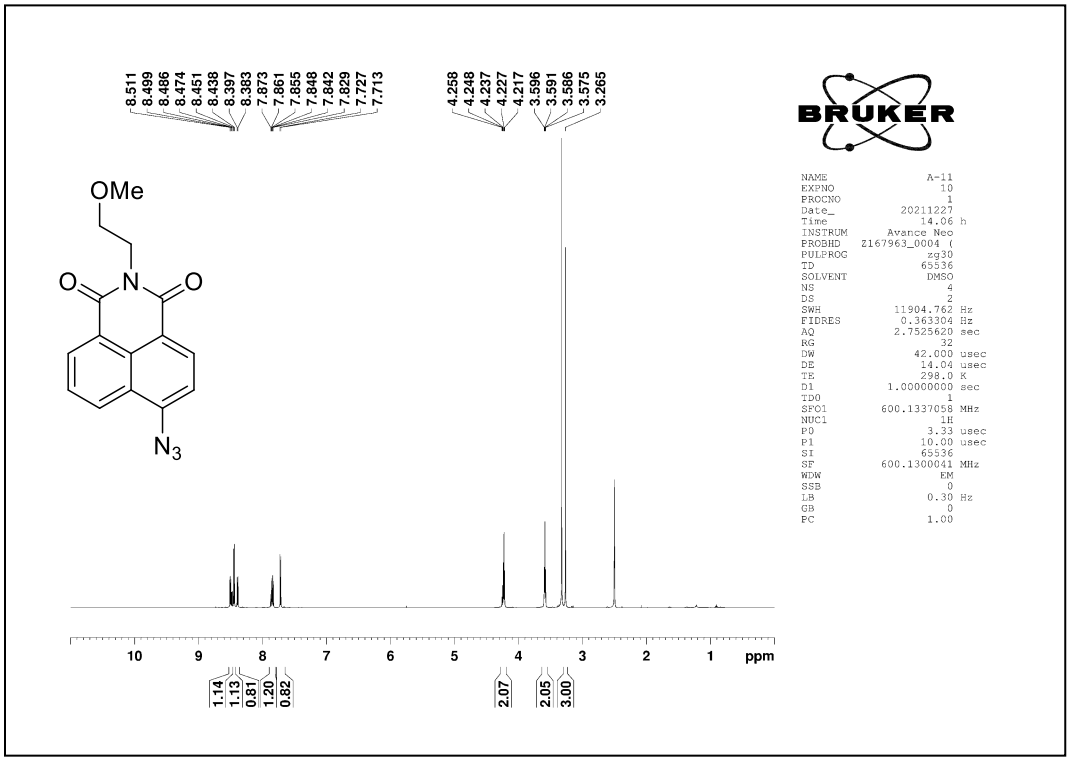


Figure S7. ^{1}H NMR spectrum of **HSN2** in DMSO-d_6 (600 MHz)

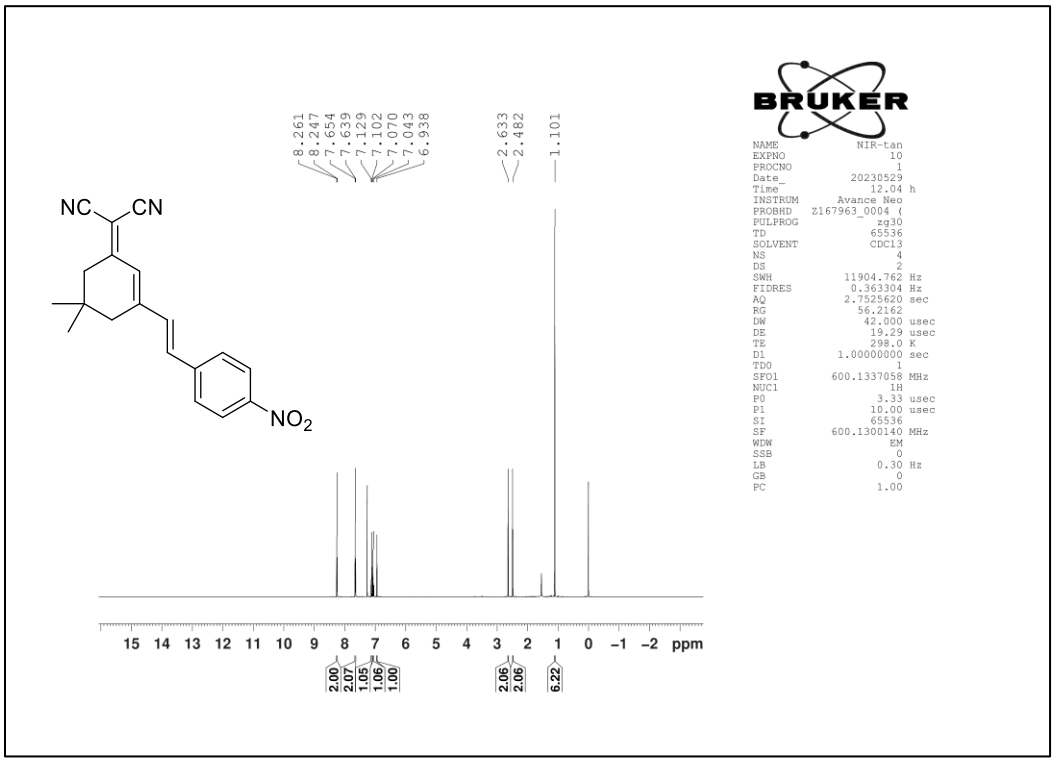


Figure S8. ^{1}H NMR spectrum of **IS-NO$_2$** in $CDCl_3$ (600 MHz)

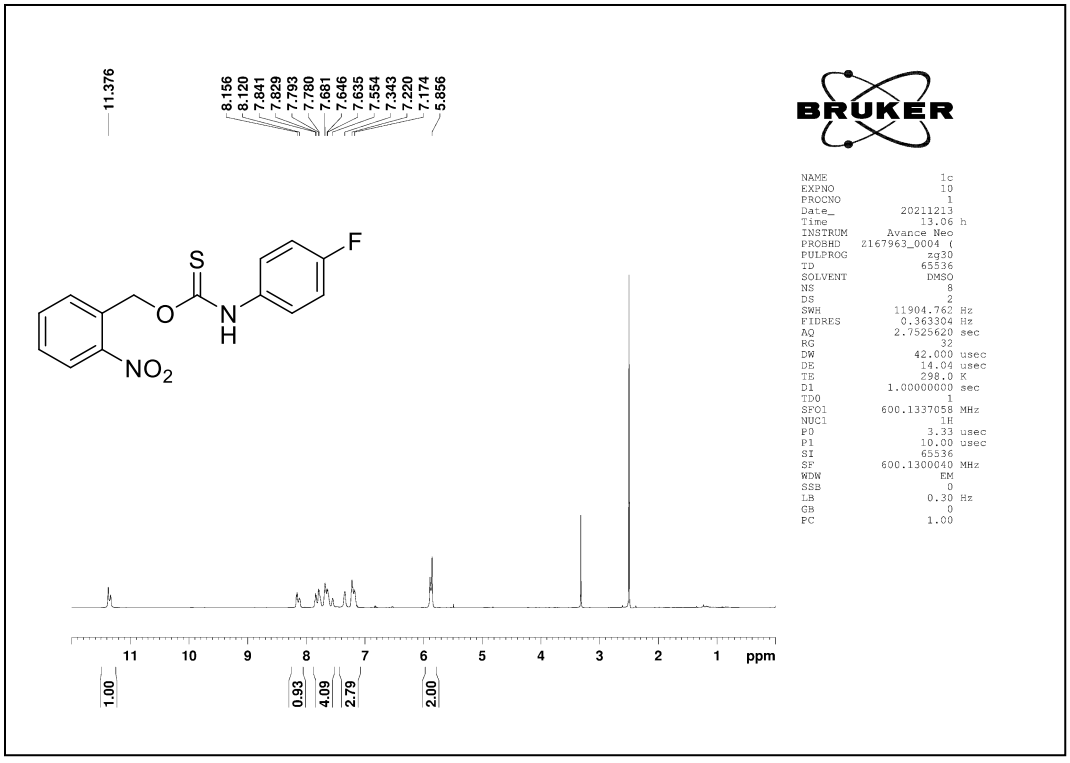


Figure S9. ^{1}H NMR spectrum of **PhotoTCM** in DMSO-d_6 (600 MHz)

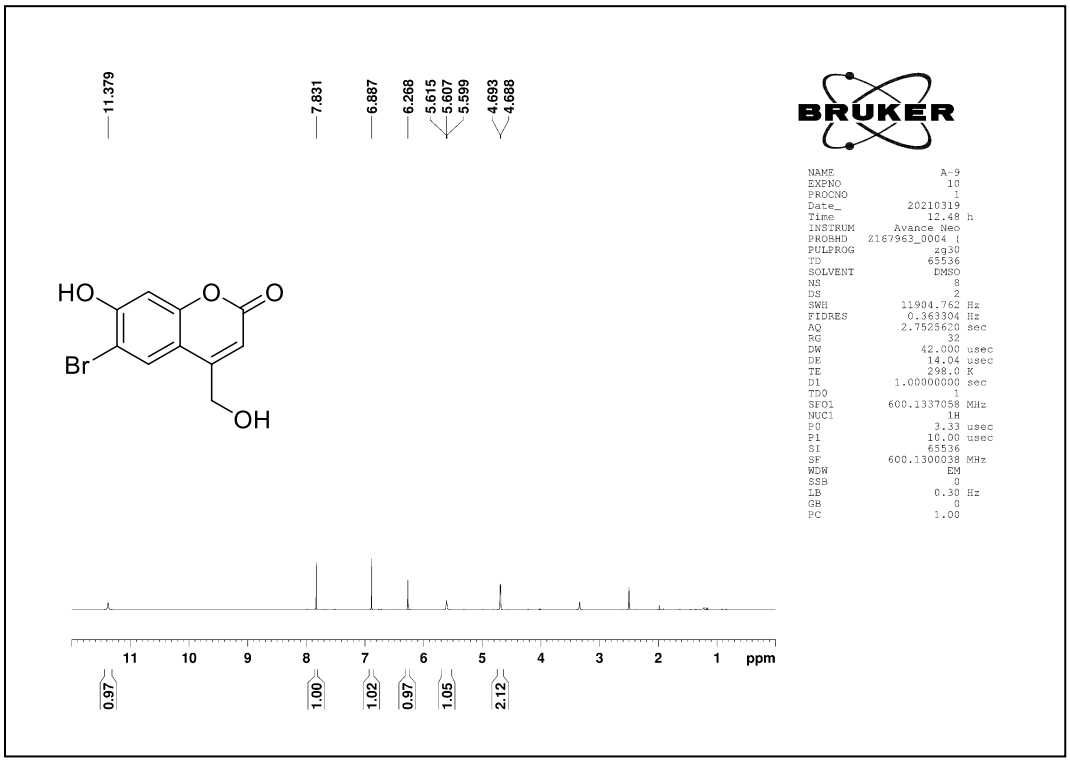


Figure S10. ^{1}H NMR spectrum of **Bhc-OH** in DMSO-d_6 (600 MHz)

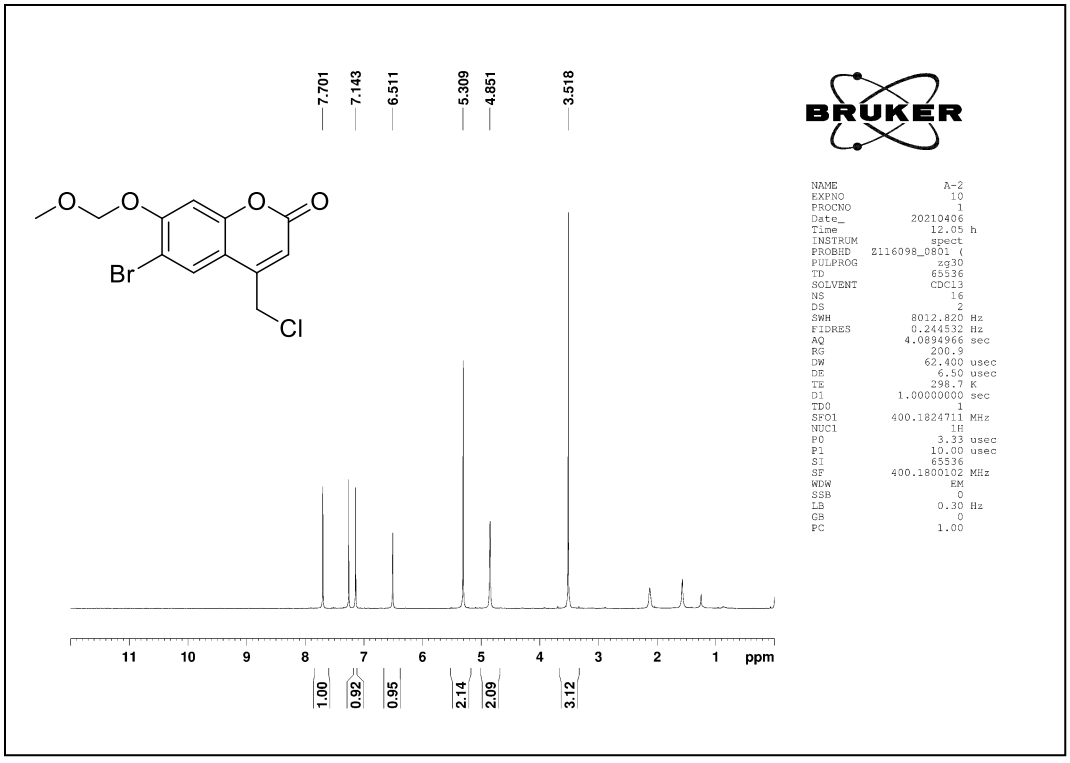


Figure S11. ^{1}H NMR spectrum of **2** in $CDCl_3$ (400 MHz)

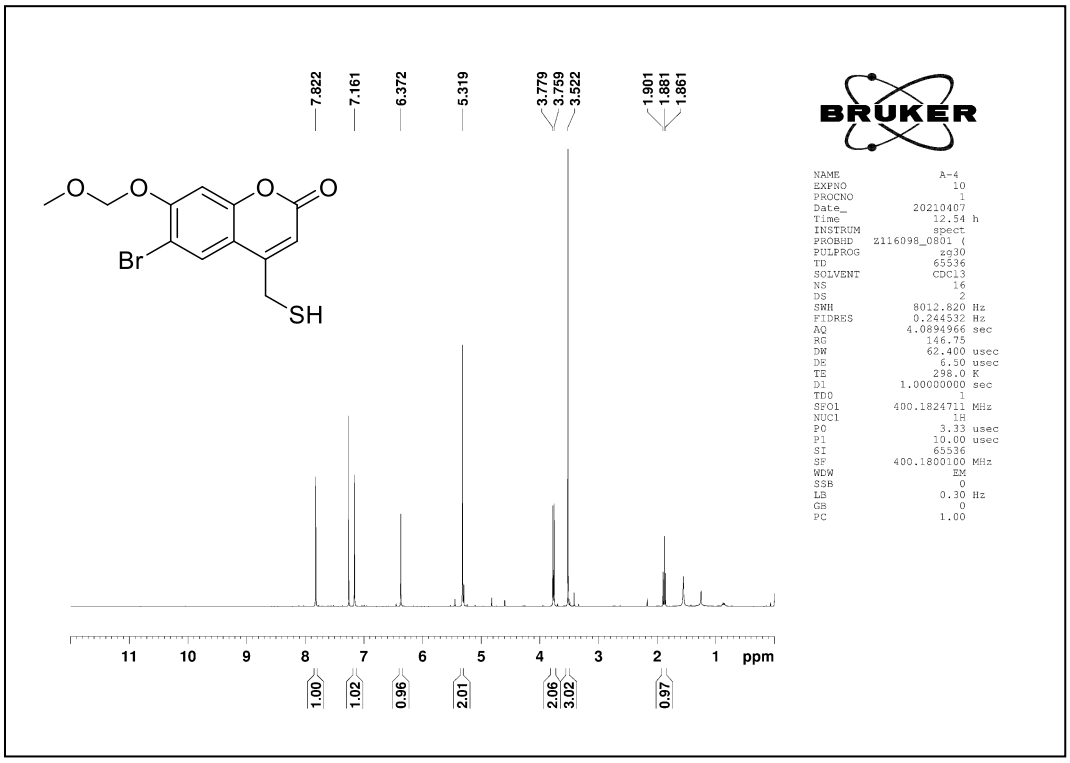


Figure S12. ^{1}H NMR spectrum of **3** in $CDCl_3$ (400 MHz)

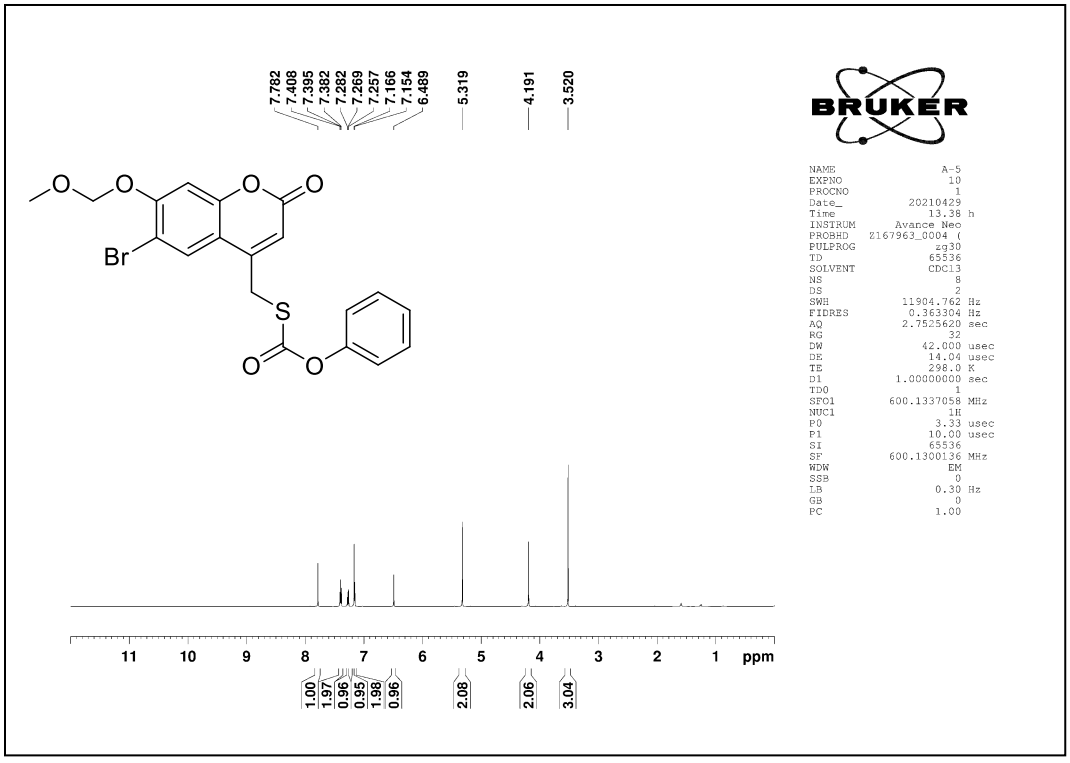


Figure S13. ^{1}H NMR spectrum of **4** in $CDCl_3$ (600 MHz)

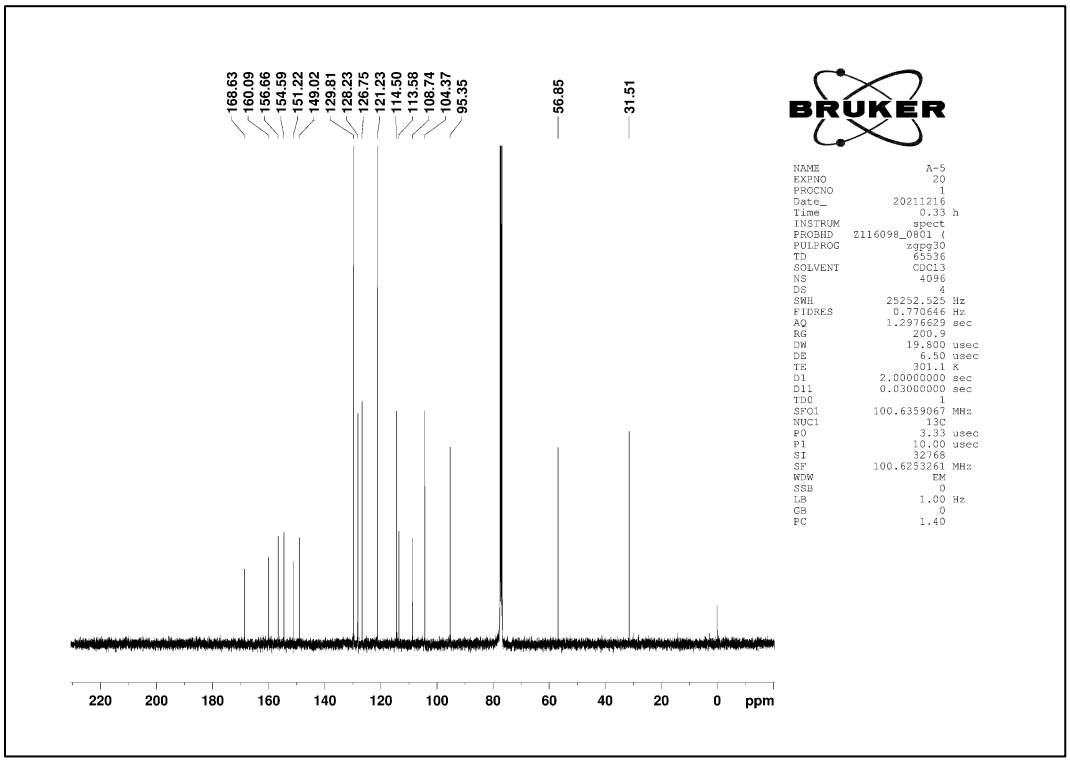


Figure S14. ^{13}C NMR spectrum of **4** in $CDCl_3$ (100 MHz)

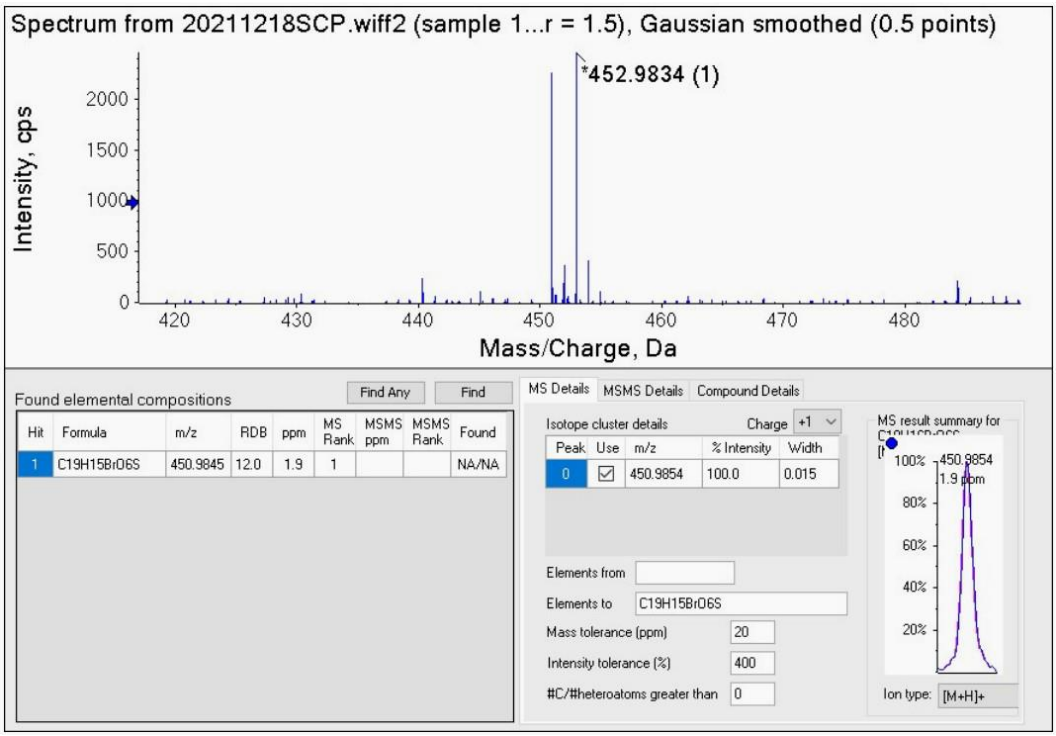


Figure S15. HRMS spectrum of **4**

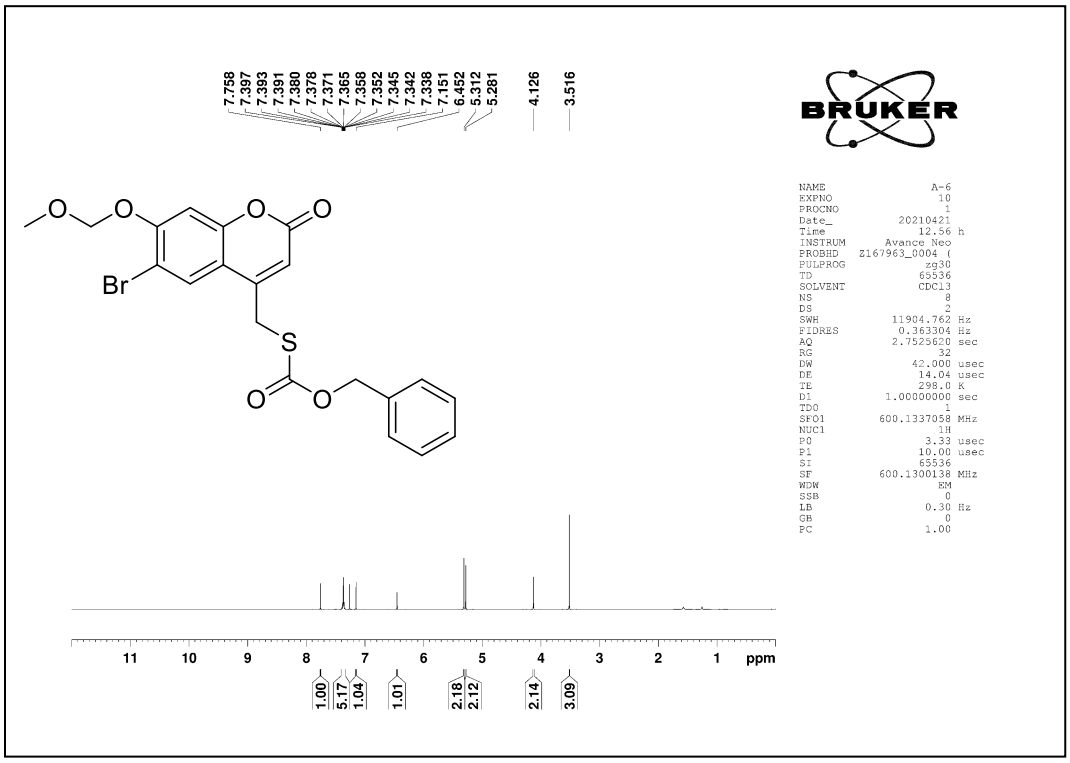


Figure S16. ^{1}H NMR spectrum of **5** in $CDCl_3$ (600 MHz)

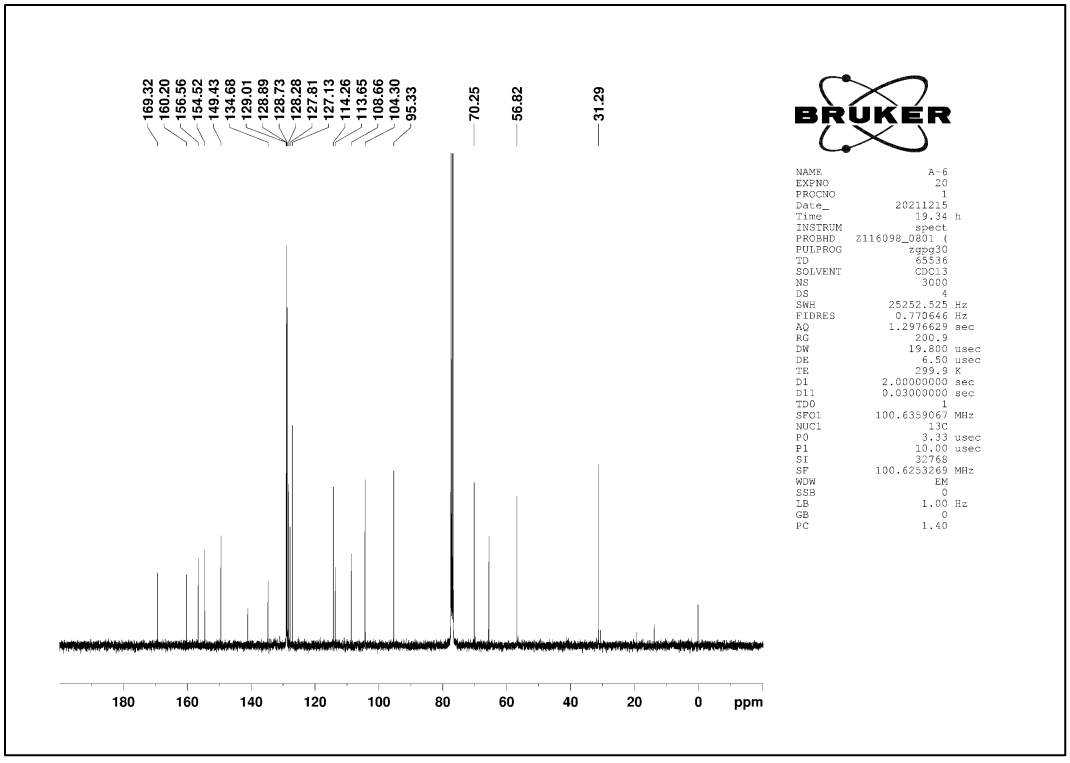


Figure S17. ^{13}C NMR spectrum of **5** in $CDCl_3$ (100 MHz)

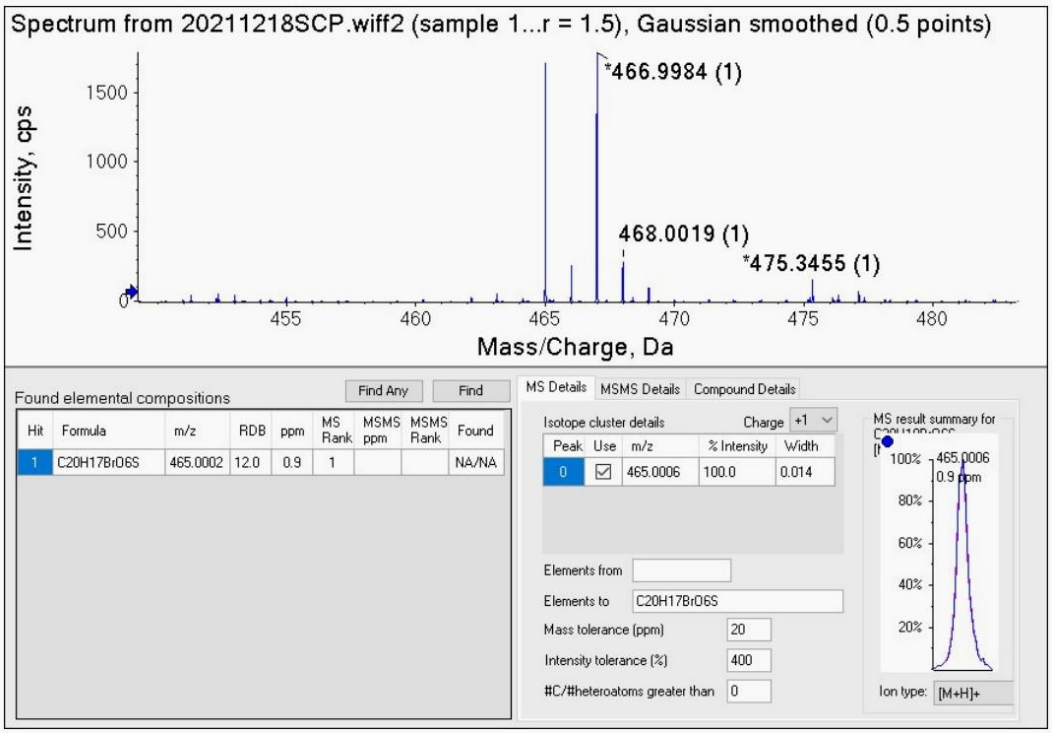


Figure S18. HRMS spectrum of **5**.

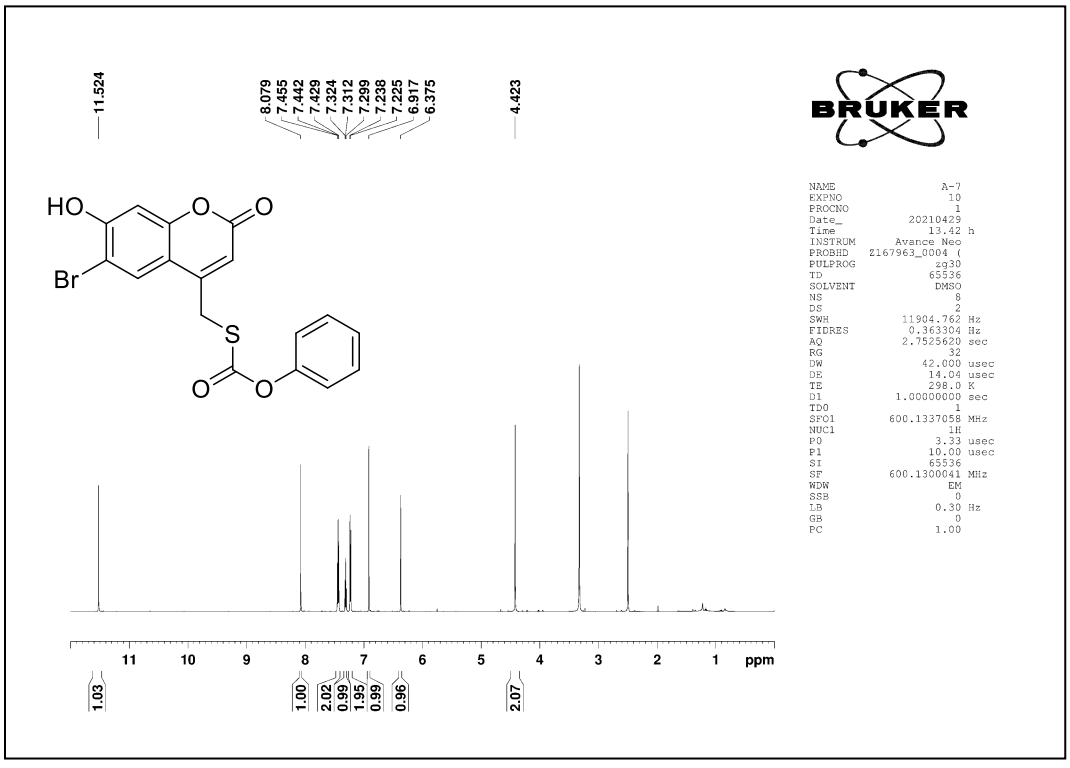


Figure S19. ^{1}H NMR spectrum of **Bhc-TCN-Ph** in DMSO-d_6 (600 MHz)

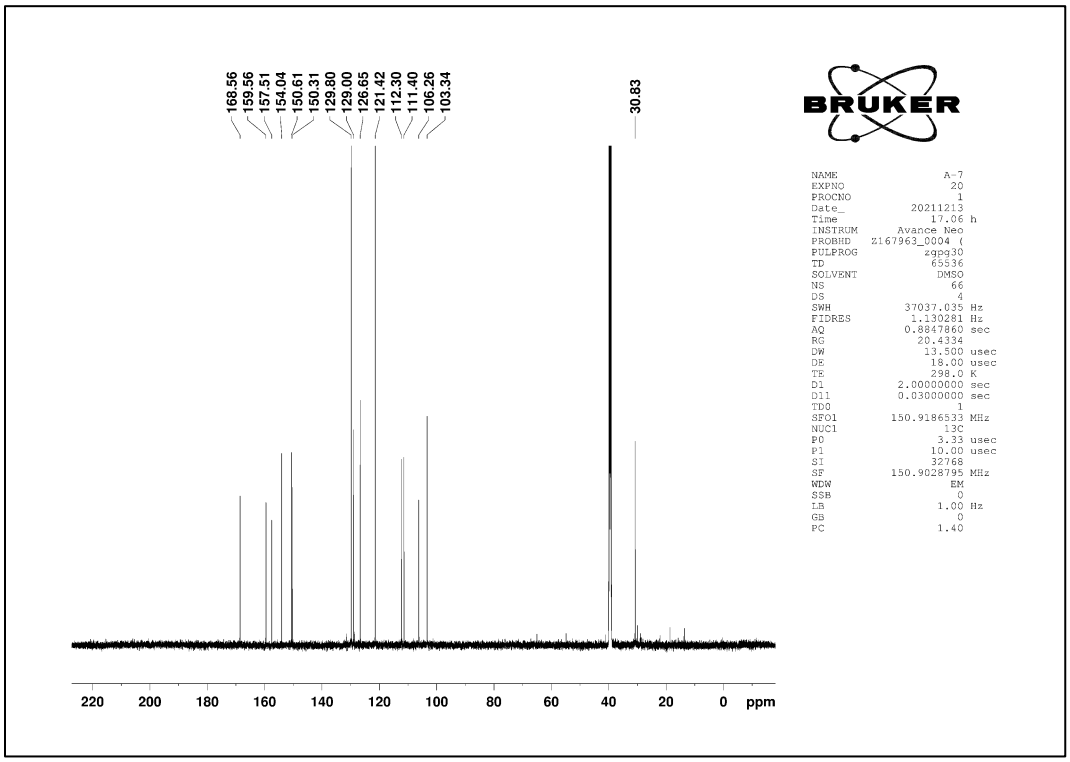


Figure S20. ^{13}C NMR spectrum of **Bhc-TCN-Ph** in DMSO-d_6 (100 MHz)

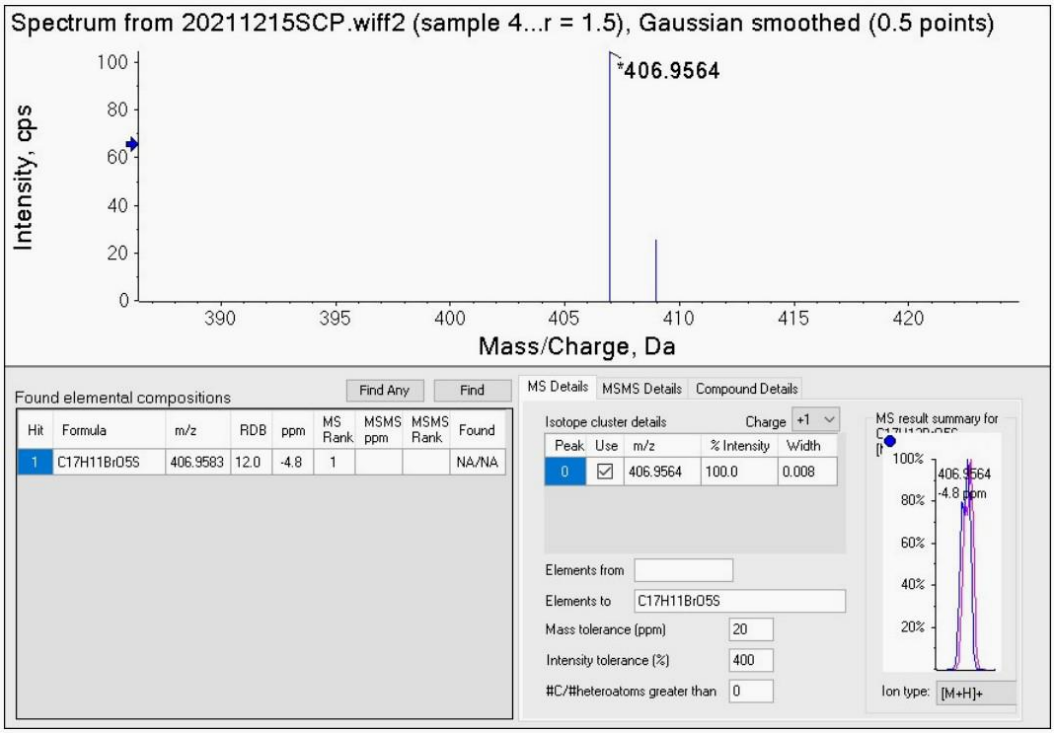


Figure S21. HRMS spectrum of **Bhc-TCN-Ph**

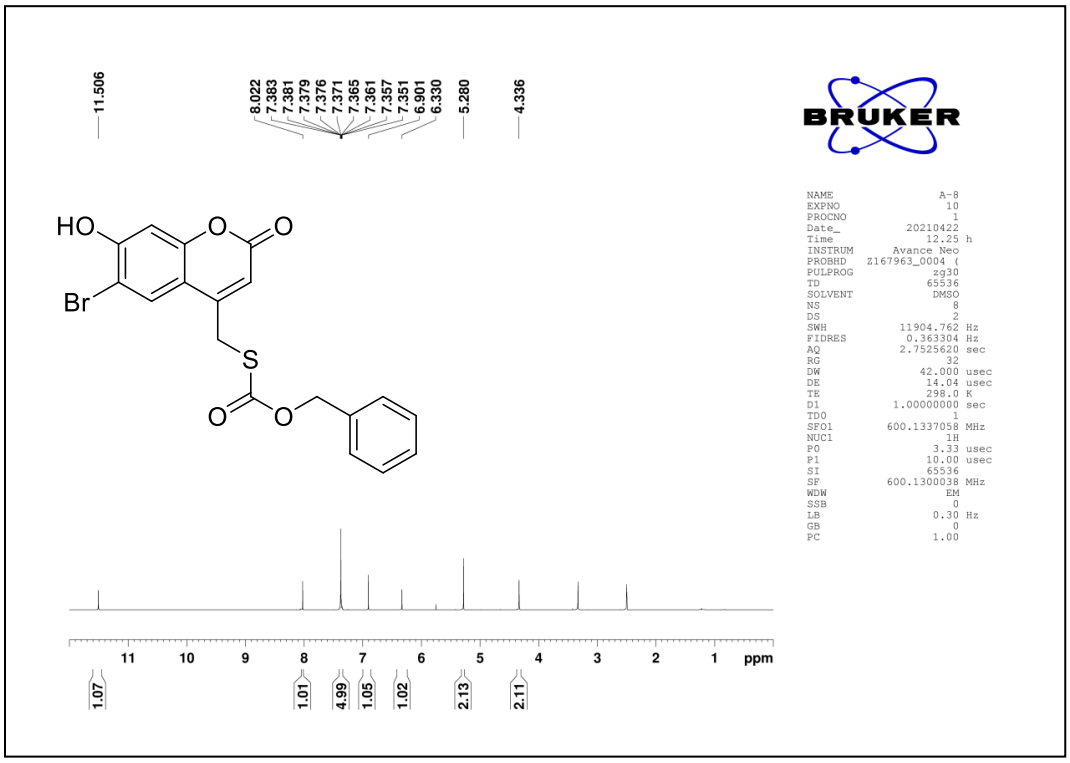


Figure S22. ^{1}H NMR spectrum of **Bhc-TCN-Bn** in DMSO-d_6 (600 MHz)

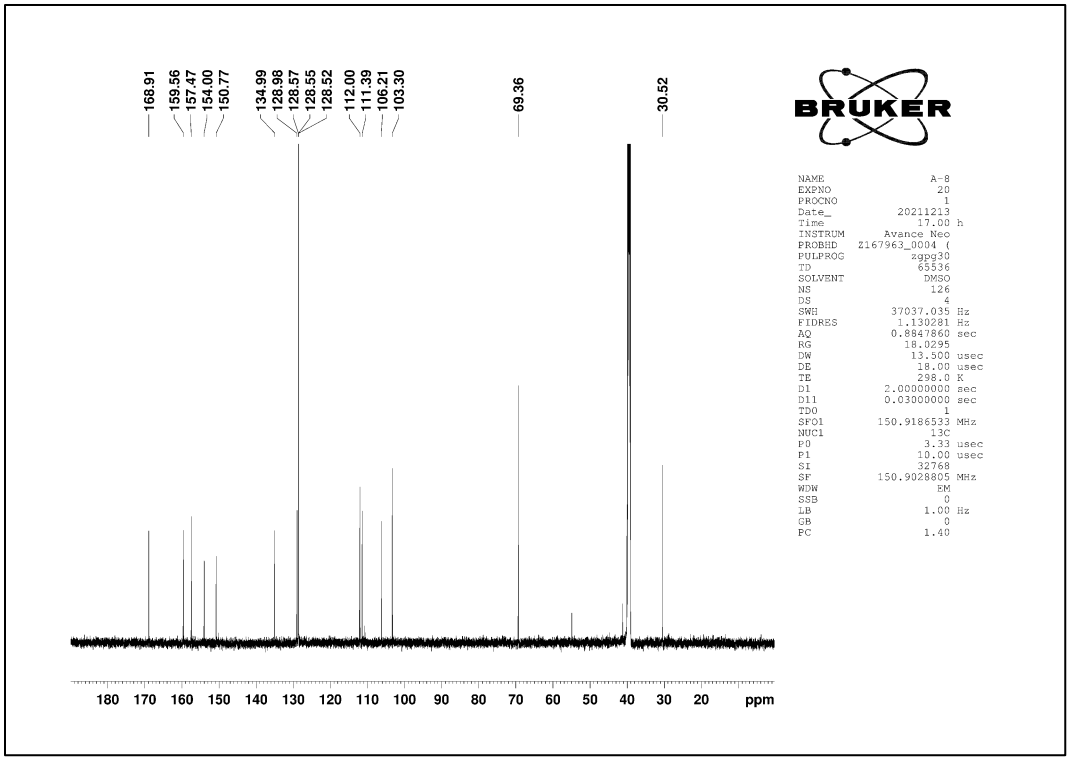


Figure S23. ^{13}C NMR spectrum of **Bhc-TCN-Bn** in DMSO-d_6 (100 MHz)

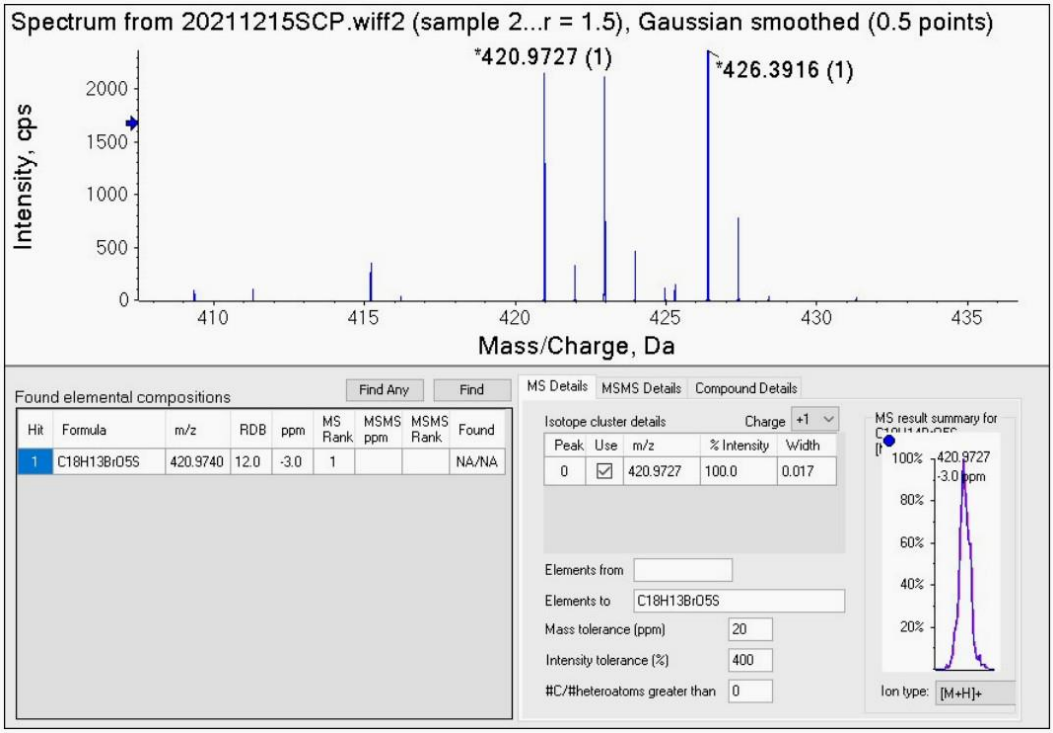


Figure S24. HRMS spectrum of **Bhc-TCN-Bn**

12. References

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