

Supplementary Information

Heterogeneous visible-light promoted dehydrogenative [4+2] annulation of benzothioamides and alkynes under aerobic conditions

Yanmin Guo, ^a Rong Chang, ^b Zhen Fu, ^c Cong-Ying Zhou, ^{*c} Zhen Guo, ^{*a}

^a College of Materials Science and Engineering, Key Laboratory of Interface Science and Engineering in Advanced Materials, Ministry of Education, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China. ^b College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, China. ^c College of Chemistry and Materials Science, Guangdong Provincial Key Laboratory of Functional Supramolecular Coordination Materials and Applications, Jinan University, Guangzhou, Guangdong 510632, China.

*E-Mail: guozhen@tyut.edu.cn; zhoucy2018@jnu.edu.cn.

Table of contents

1. Supplementary Methods	3
2. Experimental Details	4
3. Optimizing the Reaction Conditions	8
4. Mechanistic Experiments	9
5. Characterization of products	18
6. X-Ray Diffraction Data	30
7. NMR Spectra of Products	37
8. Cartesian Coordinates of DFT-Optimized Structures	80
9. References	85

1. Supplementary Methods

1.1 General information

All reagents purchased from commercial suppliers were used as received without further purification. Thiobenzamides and alkynes were prepared by using the reported procedure and purified through column chromatography respectively. All air or moisture sensitive reactions were carried out in a dry reaction vessel under argon or nitrogen atmosphere. Air or moisture sensitive liquids and solutions were transferred with syringe. Column chromatography was generally performed with silica gel (300–400 mesh) and reactions were monitored by thin-layer chromatography (TLC). All reactions that require heating were performed with oil bath and low temperatures are performed in a low temperature reaction bath (DFY 5/-80). Visible light mediated reactions were performed with a water-cooled LED module ($\lambda = 410$ nm). Photocatalyst was characterized on XRD (Bruker D8), FT-IR (Bruker TENSOR II), SEM (JSM-6700F) and UV-Vis DRS (LAMBDA1050+). The mobile phase consisted of water and methanol in 20:80 v/v ratio at a flow rate of 1.0 mL/ min at the scanning wavelength of 254 nm. High-resolution mass spectra (HRMS) were obtained by ESI on a quadrupole-orbitrap mass spectrometer (QExactive, ThermoFisher Scientific). Briefly, the mobile phase consisted of (A) Milli-Q water and (B) HPLC-grade methanol. The HPLC-MS was operated with electrospray ionization in positive/negative polarity mode. The luminescence spectrum was recorded by transient state Fluorescence Spectrometer, FLS980, Edinburgh Instruments, UK. PL spectra were recorded on F-4700(Hitachi) fluorescence spectrometer. Cyclic voltammograms were obtained on a CHI 660E potentiostat. EPR study was conducted on Bruker EMXplus-6/1. The HPLC were recorded on an Agilent 1260 Infinity Liquid Chromatograph using a reverse C18 chromatographic column. The mobile phase consisted of water and acetonitrile in 20:80 v/v ratio at a flow rate of 1.0 mL/ min at the scanning wavelength of 254 nm.

^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra obtained from measurements at ambient temperature on a Bruker AV-III 400 spectrometer (^1H : 400 MHz, ^{13}C : 100MHz). The Chemical shifts (δ) for ^1H and ^{13}C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^1H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale (TMS, 0 ppm for ^1H), CDCl_3 (7.26 and 77.02 ppm for ^1H and ^{13}C respectively) as internal standard. The following abbreviations were used to describe peak patterns when appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, td = triplet of doublet, m = multiple.

1.2 Preparation of graphitic carbon nitride (g- C_3N_4)

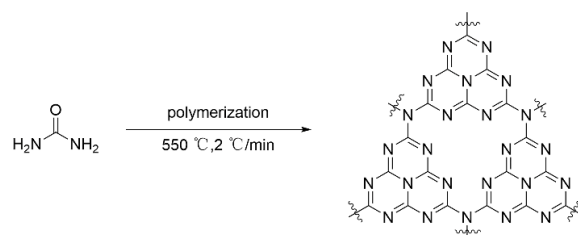


Figure S1. Synthesis of graphitic carbon nitride (g- C_3N_4)

g- C_3N_4 was synthesized with urea as precursor.¹⁻³ In a typical synthesis, urea was calcined at 550 °C for 3 hours with temperature ramping rate of 2 °C/min under air atmosphere (Figure S1.). The as prepared light-yellow sample was grounded into fine powder for photocatalytic reactions and characterizations (Figure S2.).

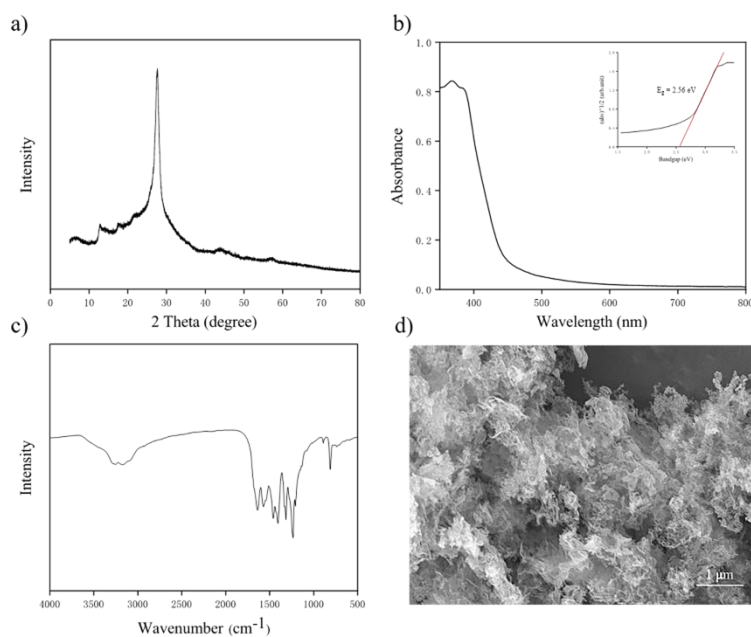
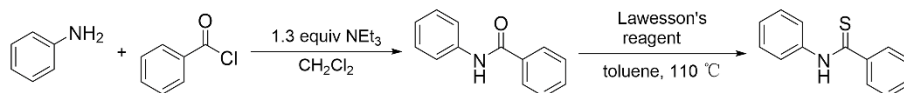


Figure S2. Characterization of the g-C₃N₄. (a) the X-ray diffraction (XRD); (b) UV-Vis diffuse reflectance spectrum; (c) the FT-IR spectrum; (d) Scanning electron microscopy (SEM) image

2. Experimental Details

2.1 Preparation of thiobenzamides

Substrates **1a-1x** were synthesized according to the following procedures:

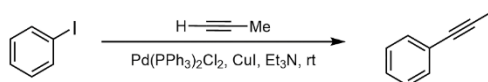


Preparation of **1a-1x**

A mixture of the aniline (5 mmol), NEt₃ (6.5 mmol) and CH₂Cl₂ (10 mL) was added into a 50 mL flask equipped with a stir-bar. Benzoyl chloride (5.5 mmol) was added slowly at room temperature for 3 h. After this period, the reaction mixture was washed with water and extracted with CH₂Cl₂ (20 mL × 2). The organic layers were combined, dried over Na₂SO₄, and concentrated under reduced pressure to obtain pure benzamide. A mixture of the benzamide (2.5 mmol) and Lawesson's reagent (1.5 mmol) in dry toluene (40 mL) was heated at reflux under an atmosphere of nitrogen for 2 h, after which it was concentrated, purified by column chromatography and recrystallized from *n*-hexane/EtOAc.²

2.2 Preparation of alkynes

Substrates **2a-2i**, **2q-2s** and **2t** are commercially available. Substrates **2j-2p** were synthesized according to the following procedures:

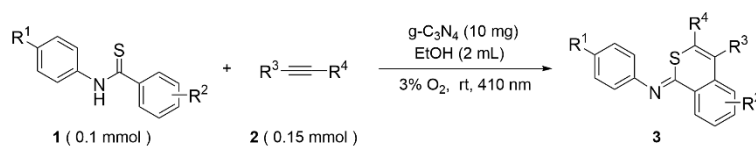


Preparation of **2j-2p**

1-Iodobenzene (5.09 g, 20 mmol) and alkyne (30 mmol) were dissolved in triethylamine (200 mL) and degassed once. A mixture of bis[triphenylphosphine]palladium dichloride (700 mg, 1 mmol) and copper iodide (200 mg, 1.0 mmol) were added. The reaction was stirred at room temperature for 3-6 h, after reaction was completed (monitored by TLC) TEA was evaporated and the residue was washed with sat NH₄Cl (50 mL), extracted with CH₂Cl₂ (150 mL × 2) and dry over Na₂SO₄. After

concentration the crude product was purified by column chromatography using petroleum ether/EtOAc 200/1 if needed.³

2.3 General procedures for visible light g-C₃N₄-catalyzed reaction



To a 10 mL test tube equipped with a magnetic stir bar were added **1** (0.1 mmol), **2** (0.15 mmol) and g-C₃N₄ (10 mg) in EtOH (2 mL) under a 3% O₂ atmosphere and irradiated with a 10 W blue LED at room temperature. The photocatalyst was filtered off and washed with EtOH after the reaction is completed. The product was purified by flash column chromatography on silica gel (petroleum ether/EtOAc).

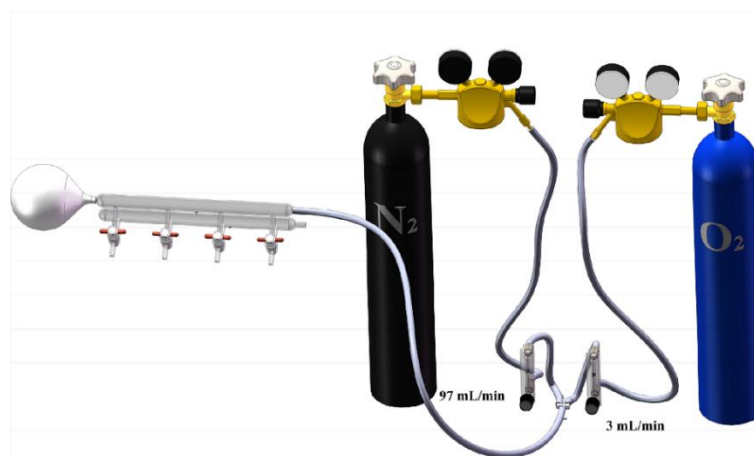
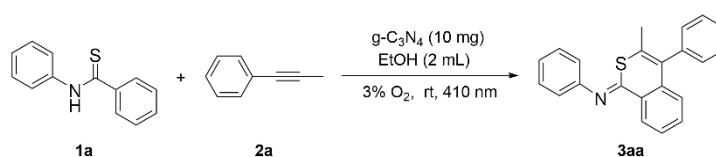


Figure S3. Gas control device

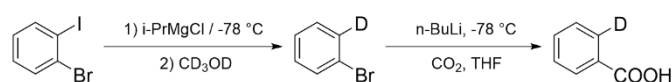
The reactor is connected to a balloon containing 3% O₂ via Schlenk Line as shown in Figure S3. During the course of the reaction, the balloon will be refilled with O₂ five times to guarantee O₂ enough for the oxidative dehydrogenation.

2.4 Gram scale reaction



1a (1.07 g, 5 mmol) and **2a** (968 μL, 7.5 mmol), recovered g-C₃N₄ (500 mg) and EtOH (100 mL) was added to a 250 mL beaker. The resulting mixture was stirred under a 3% O₂ atmosphere and irradiated with blue LED at room temperature for 72 h. After the reaction, the photocatalyst was filtered off and washed with ethanol. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc to give the desired product **3aa** (0.62 g, 2.93 mmol) in 62% yield.

2.5 Synthesis of 2-deuteriobenzoic acid

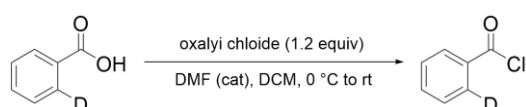


To a stirred solution of 1-Bromo-2-iodobenzene (8 g, 28.38 mmol) in a mixture of THF and Et₂O (190 mL, 1:1) at -78 °C was added dropwise isopropylmagnesium chloride (2 M in Et₂O, 14.4 mL, 28.8 mmol). The mixture was stirred at that temperature for 2 h and then, CD₃OD (3.2 g, 88.76 mmol)

was added. The solution was slowly warmed to room temperature, aq. HCl (10%, 160 mL) was added and the resulting mixture was stirred for 30 min at room temperature. The aqueous layer was extracted with Et₂O (3 × 50 mL). The combined organic phase was dried over MgSO₄, filtered and the solvents were removed under reduced pressure. The pure 2-Deuteriobromobenzene was obtained by distillation.⁴

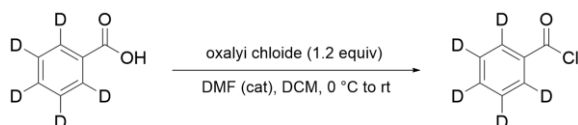
2-Deuteriobromobenzene (500 mg, 3.16 mmol) was added to in anhydrous THF (10 mL), a solution of *n*-BuLi in *n*-hexane (1.4 mL, 2.5 M, 3.48 mmol) was added dropwise at -78 °C for 10 min. The mixture was stirred at the same temperature for 30 min, and then CO₂ was bubbled through the mixture at -78 °C for 10 min. The mixture was allowed to warm to ambient temperature, quenched with H₂O (20 mL), acidified to pH = 1 with 1M HCl, and extracted with EtOAc (30 mL × 3). The combined organic phase was dried over MgSO₄, filtered and the solvents were removed in vacuum to give the product (335 mg, 67 %).

2.6 Synthesis of Benzoyl-2-*d* chloride



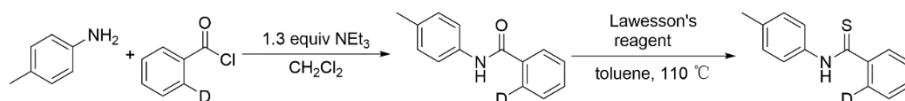
To a solution of the 2-Deuteriobenzoic acid (300 mg, 2.44 mmol) in dry CH₂Cl₂ (15 mL) at 0 °C under N₂ was added dropwise oxalyl chloride (372 mg, 2.93 mmol) followed by a catalytic amount of dry DMF (2 drops). The reaction was allowed to stir at room temperature for 4 h. The solvent was then removed under reduced pressure to afford the corresponding crude deuterated acid chloride.

2.7 Synthesis of benzoyl-2,3,4,5,6-*d*₅ chloride



To a solution of the benzoic-2,3,4,5,6-*d*₅ acid (300 mg, 2.44 mmol) in dry CH₂Cl₂ (15 mL) at 0 °C under N₂ was added dropwise oxalyl chloride (372 mg, 2.93 mmol) followed by a catalytic amount of dry DMF (2 drops). The reaction was allowed to stir at room temperature for 4 h. The solvent was then removed under reduced pressure to afford the corresponding crude benzoyl-2,3,4,5,6-*d*₅ chloride.

2.8 Preparation of 1b-*d*



To a 50 mL flask equipped with a stir-bar was added *p*-toluidine (5.0 mmol), NEt₃ (6.5 mmol) and 10 mL of CH₂Cl₂. Then benzene-2-*d*-chloride (5.5 mmol) was added slowly. The reaction mixture was stirred at room temperature for 3 h, then resulting mixture was washed with water and extracted with CH₂Cl₂ (20 mL × 2). The organic layers were combined, dried over Na₂SO₄, and concentrated under reduced pressure to obtain the crude *N*-phenylbenzamide-2-*d*. A Schlenk flask equipped with a stir-bar was charged with *N*-phenylbenzamide-2-*d* (4.0 mmol) and Lawesson's reagent (2.4 mmol) and purged with nitrogen. Anhydrous toluene (5 mL) was added to the reaction tube via a syringe. The resulting mixture was stirred at 110 °C for 3 h. After cooling to room temperature, the reaction mixture was directly purified by silica gel column chromatography using petroleum ether/EtOAc to obtain the **1b-*d***. Comparing the ¹H NMR spectra of **1b-*d*** (Figure S4.) and **1b**, 98% deuterium was contained.

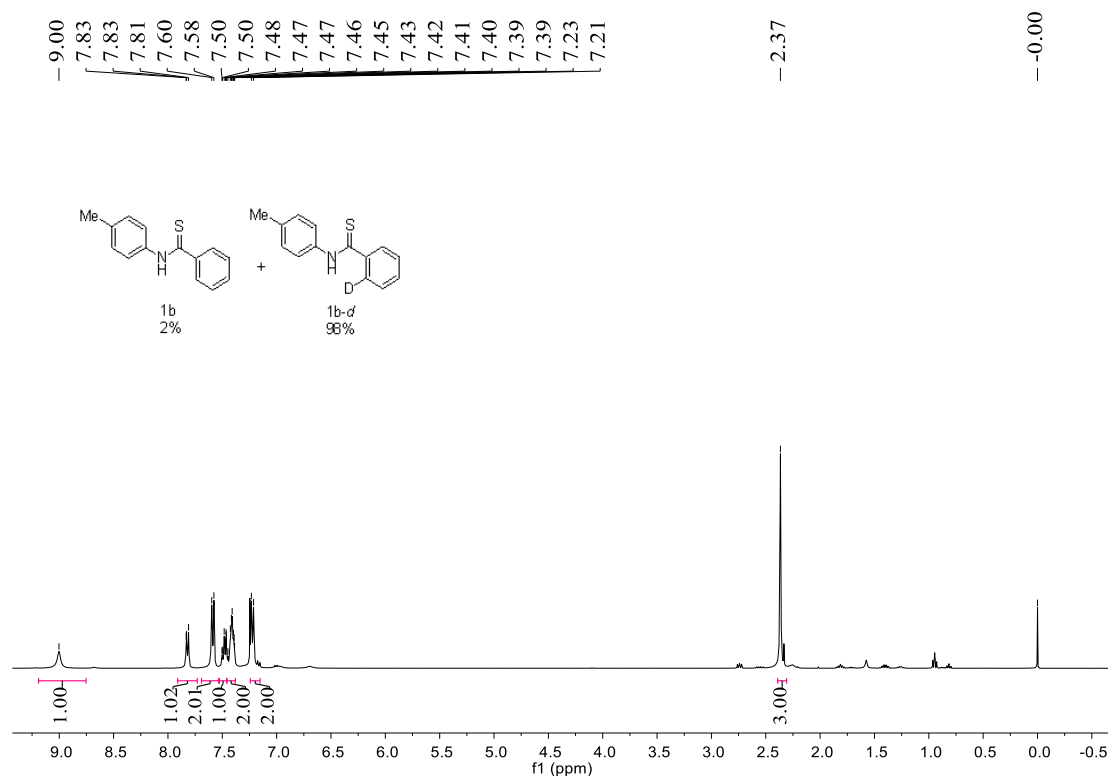
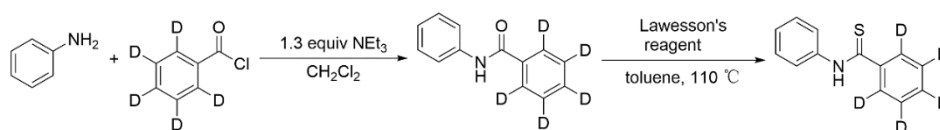


Figure S4. ^1H NMR spectrum of **1b-d**

2.9 Preparation of *N*-phenyl-(Benzo- d_5) thioamide (**1a-d₅**):

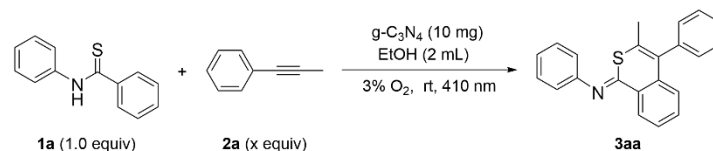


To a 50 mL flask equipped with a stir-bar was added aniline (5.0 mmol), NEt_3 (6.5 mmol) and 10 mL of CH_2Cl_2 . Then benzoyl-2,3,4,5,6- d_5 chloride (5.5 mmol) was added slowly. The reaction mixture was stirred at room temperature for 3 h, then resulting mixture was washed with water and extracted with CH_2Cl_2 (20 mL \times 2). The organic layers were combined, dried over Na_2SO_4 , and concentrated under reduced pressure to obtain the crude 2,3,4,5,6- d_5 -*N*-phenylbenzamide. A Schlenk flask equipped with a stir-bar was charged with 2,3,4,5,6- d_5 -*N*-phenylbenzamide (4.0 mmol) and Lawesson's reagent (2.4 mmol) and purged with nitrogen. Anhydrous toluene (5 mL) was added to the reaction tube via a syringe. The resulting mixture was stirred at 110 °C for 3 h. After cooling to room temperature, the reaction mixture was directly purified by silica gel column chromatography using petroleum ether/EtOAc to obtain the **1a-d₅**.

3. Optimizing the Reaction Conditions

The optimization reaction was performed according to **General procedures for the visible-light promoted [4+2] cycloaddition catalyzed by g-C₃N₄**. Yield was determined by HPLC analysis of the crude mixture using biphenyl as internal standard.

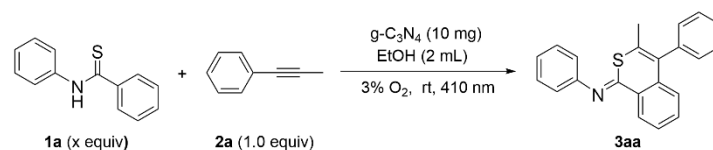
Table S1. The reaction with 1.0 equiv. of *N*-phenylbenzothioamide ^a



Entry	x	g-C ₃ N ₄	Solvent	Yield ^b %
1	1.0	10 mg	EtOH	80
2	1.2	10 mg	EtOH	84
3	1.5	10 mg	EtOH	88
4	1.7	10 mg	EtOH	86
5	2.0	10 mg	EtOH	88

^a Reaction conditions: **1a** (0.1 mmol), **2a** and g-C₃N₄ in EtOH (2 mL) irradiated by a 10 W blue LED for 15 h at rt. ^b Yields were determined by HPLC.

Table S2. The reaction with an excess amount of *N*-phenylbenzothioamide ^a



Entry	x	g-C ₃ N ₄	Solvent	Yield ^b %
1	1.2	10 mg	EtOH	86
2	1.5	10 mg	EtOH	84
3	2	10 mg	EtOH	86

^a Reaction conditions: **1a**, **2a** (0.15 mmol) and g-C₃N₄ in EtOH (2 mL) irradiated by a 10 W blue LED for 15 h at rt. ^b Yields were determined by HPLC.

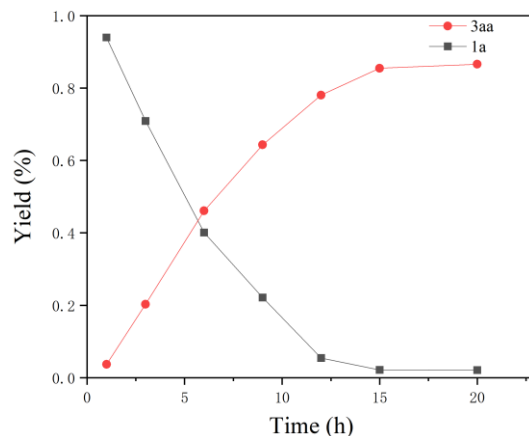


Figure S5. Kinetic profile of the reaction over time. Yields were determined by HPLC

4. Mechanistic Experiments

4.1 Radical trapping experiment with TEMPO

A mixture of *N*-phenylbenzothioamide **1a** (0.1 mmol, 1.0 equiv.), 1-Phenyl-1-propyne **2a** (0.15 mmol, 1.5 equiv.), g-C₃N₄ (10 mg) and TEMPO (0.2 mmol, 2.0 equiv.) in 2.0 mL EtOH was stirred under 3% O₂ atmosphere and irradiated with a 10 W blue LED (410 nm) at room temperature for about 15 h. HPLC analysis of this reaction mixture showed that the product **3aa** was not formed, a free radical-trapping adduct of TEMPO-**1a** acetate was observed by HRMS analysis of the reaction solution (Figure S6.). Analysis of the crude reaction mixture by HRMS.

HRMS (ESI): *m/z* calcd for C₂₂H₂₉N₂OS⁺: 369.1996 [M+H]⁺; found: 369.1992.

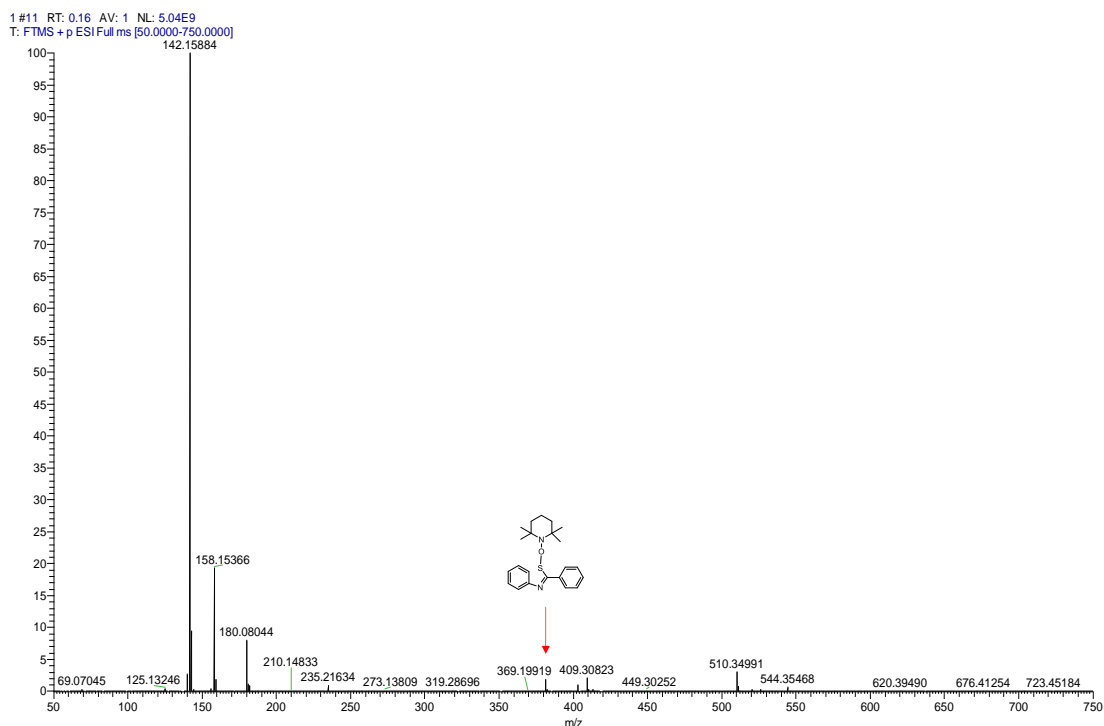


Figure S6. The positive-ion ESI mass spectrum of reaction mixture

4.2 General procedure for cyclic voltammetry (CV)

The cyclic voltammetry (CV) of **1a**, **1j**, **1l**, **1m**, **1p**, **1q** and **2a** were performed in a three-electrode cell at room temperature in N₂. The working electrode was a steady glassy carbon, the counter electrode was a platinum wire, and the reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. A solvent (5 mL MeCN) containing Et₄NPF₆ (0.1 M) were poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 100 mV/s, ranging from -0.5 V to 2.5 V of **1a**, **1j**, **1l**, **1m**, **1p**, **1q** (1 mM) and 0.0 V to 3.0 V of **1a**, **2a** (0.02 M). As is shown (Figure S1b.), the band gap value (E_g) was calculated by the UV-vis DRS, and the value of g-C₃N₄ is 2.56 eV. The CB minimum and VB maximum potentials of g-C₃N₄ were -1.05 V and 1.51 V (vs. NHE), or -0.85 V and 1.71 V (vs. Ag/AgCl), respectively. On the other hand, the VB of g-C₃N₄ is a sufficiently strong oxidant for **1a**, **1j**, **1l**, **1m**, **1p** and **1q** that these substrates possessed a wave oxidation potential of 1.342 V, 1.317 V, 1.308 V, 1.362 V, 1.384 V and 1.438 V (vs. Ag/AgCl) in MeCN (Figure S7.), respectively.⁵

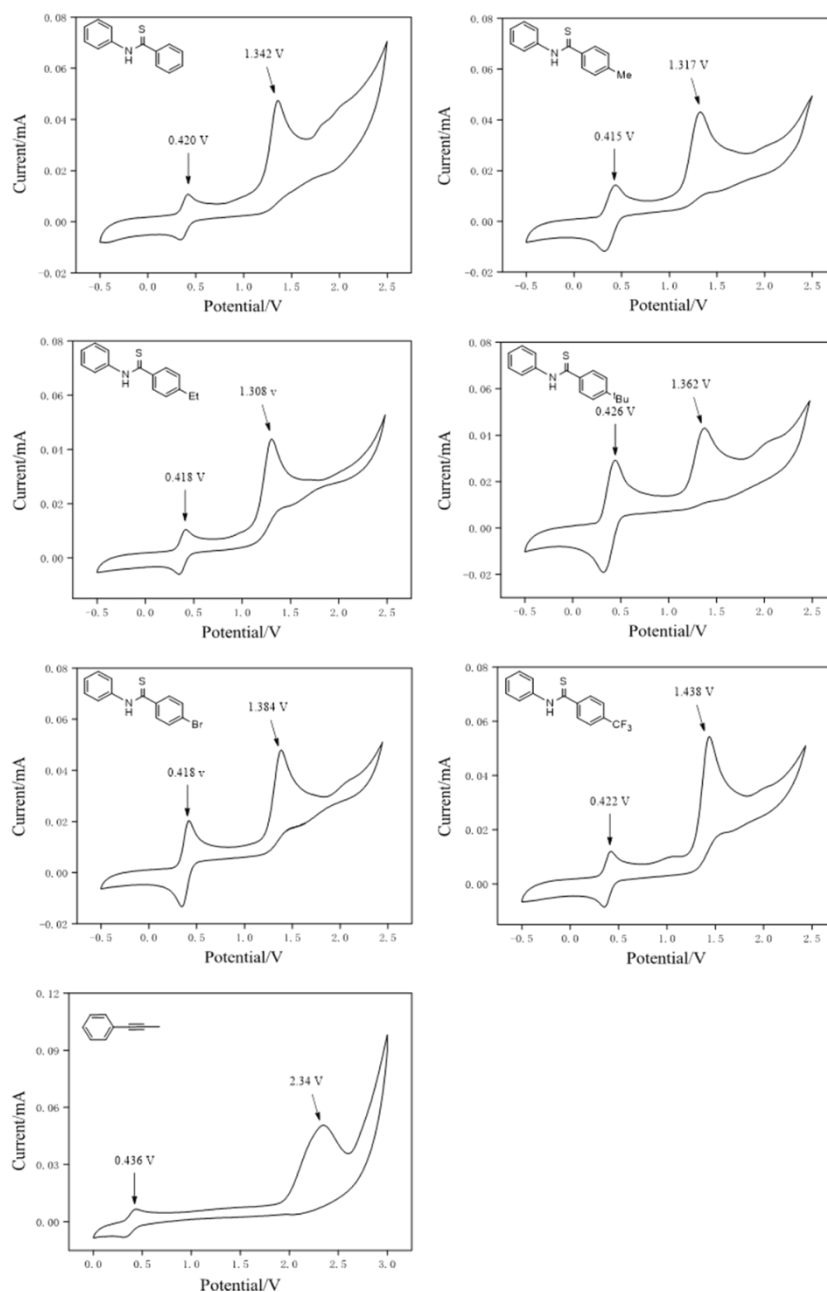


Figure S7. Cyclic voltammograms of **1a**, **1j**, **1l**, **1m** **1p**, **1q** (1 mM) and **2a** (0.02 M)

4.3 Steady-state emission spectra for g-C₃N₄ Suspension in EtOH

The g-C₃N₄ suspensions in EtOH were prepared by sonication and centrifugation. In a typical preparation, the mixture of g-C₃N₄ (10 g) and EtOH (50 ml) was treated by ultrasonic to form a milky solution and then the suspension was collected by centrifugation for the solution. Subsequently, the g-C₃N₄ suspensions with different concentrations of *N*-phenylbenzothioamide and 1-Phenyl-1-propyne (Figure S8.) were prepared. All experiments were carried out under air atmosphere. The g-C₃N₄ suspensions were irradiated at 400 nm and the luminescence was measured at 440 nm. The ratio of F_0/F was plotted as a function of the quencher concentration (F_0 = emission intensity of the photocatalyst in isolation at the specified wavelength; F = observed emission intensity of the photocatalyst with added quencher; K_{sv} = represent the Stern-Volmer quenching constant; k_q = bimolecular quenching rate constant, respectively; $[Q]$ is the concentration of the quencher, the average fluorescence lifetime of the macromolecule τ_0 is 5.62 ns for g-C₃N₄).⁶ The bathochromic shift of the emissive peak is attributed to

in situ generated complex between substrate and catalyst, where new electron donor level above the VB of g-C₃N₄ is formed.

$$F_0/F = 1 + k_q\tau_0[Q] = 1 + K_{sv}[Q]$$

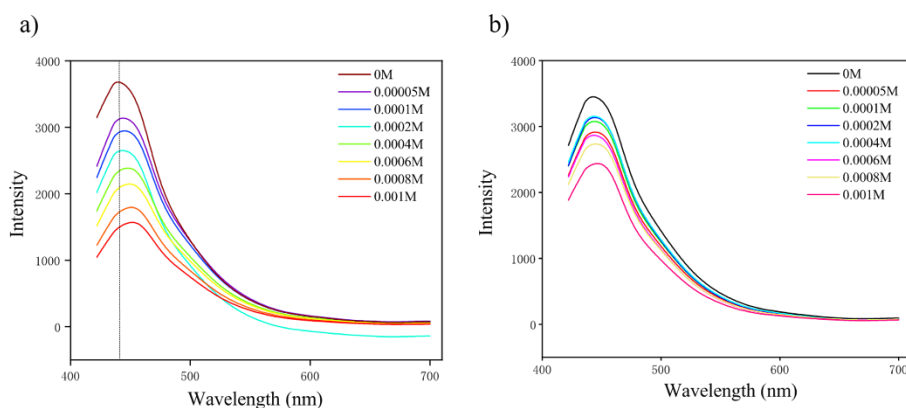


Figure S8. Effect of *N*-phenylbenzothioamide **1a** (a) and 1-Phenyl-1-propyne **2a** (b) on steady-state emission spectra of g-C₃N₄ in EtOH

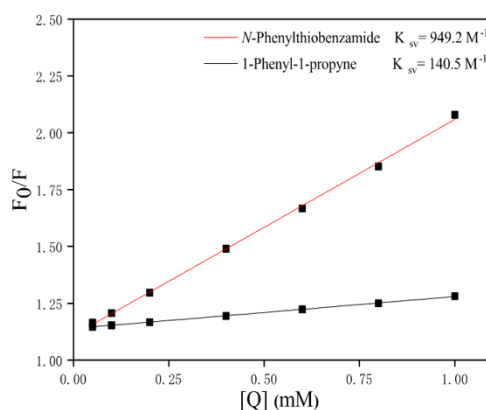


Figure S9. Stern-Volmer quenching experiments with photoexcited g-C₃N₄

4.4 Quenching mechanisms

Generally, fluorescence quenching mechanisms can be classified into dynamic quenching and static quenching. Static quenching is commonly caused by the formation of ground-state non-fluorescent molecules of fluorescence substance and quencher. By contrast, dynamic quenching is normally associated with collision between fluorescence substance and quencher. No new complex is formed and the absorption spectrum of the fluorescence substance does not change. At present, recording the change tendency of fluorescent lifetime is an effective method to analyze quenching mechanism.⁷ Whereas, for dynamic quenching effect the ratio τ_0/τ_1 of the lifetime is proportional to the ratio of F_0/F_1 with the increase of concentration of quencher: $F_0/F = \tau_0/\tau = 1 + K_{sv}[Q]$ (τ_0 and τ_1 are the fluorescence lifetimes in the absence and presence of quencher, respectively).

The g-C₃N₄ suspensions in EtOH were prepared by sonication and centrifugation. In a typical preparation, the mixture of g-C₃N₄ (10 g) and EtOH (50 ml) was treated by ultrasonic to form a milky solution and then the suspension was collected by centrifugation for the solution. Subsequently, the g-C₃N₄ suspensions with different concentrations of *N*-phenylbenzothioamide. All experiments were carried out under air atmosphere and all g-C₃N₄ suspensions were excited at 375 nm. The excited state lifetime remains constant no matter how to change the concentration of quencher (Figure S10.).

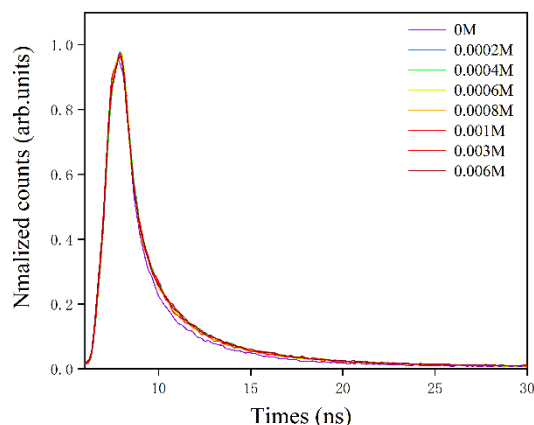


Figure S10. Dynamic fluorescence quenching of g-C₃N₄ with increasing concentration of **1a**

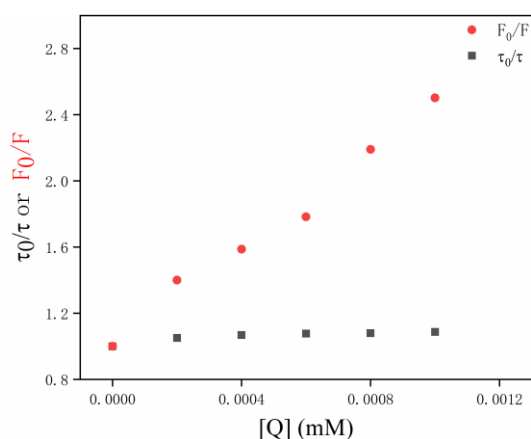
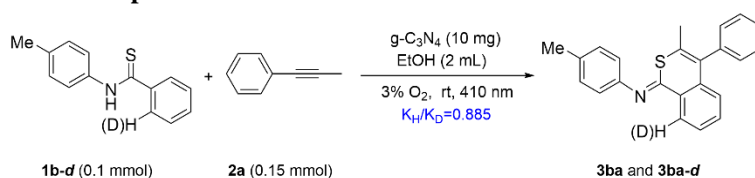


Figure S11. Dynamic fluorescence quenching and Stern-Volmer of g-C₃N₄ with increasing concentration of **1a**

4.5 Intermolecular KIE experiment



A mixture of **1b-d** (0.1 mmol, 99% of deuterium) and **2a** (0.15 mmol), recovered g-C₃N₄ (10 mg) and EtOH (2 mL) was added to a 10 mL test tube. The resulting mixture was stirred under a 3% O₂ atmosphere and irradiated with blue LED at room temperature. When the reaction was completed, the photocatalyst was filtered off and washed with ethanol. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc to give the desired **3ba-d** (Figure S12.). Based on ¹H NMR spectrum of **1b-d** and **3ba-d**, the KIE value was calculated to be 0.885.

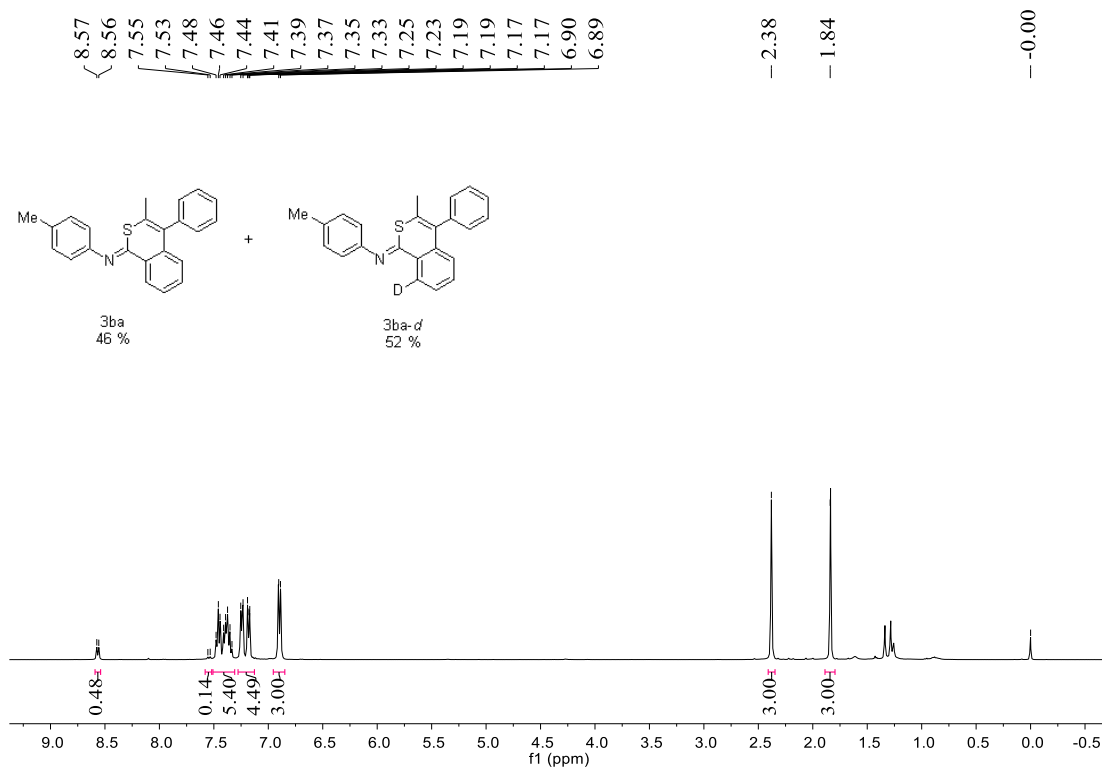
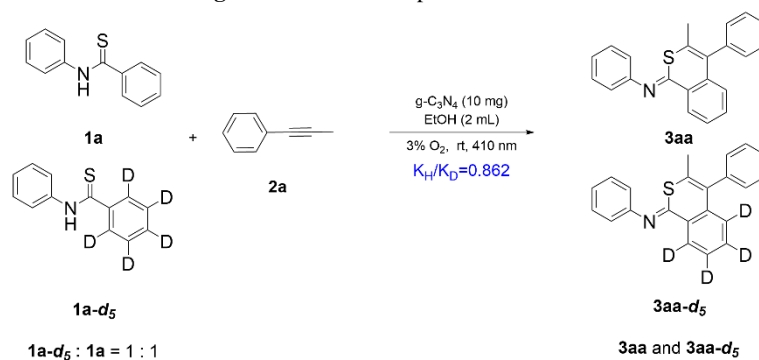


Figure S12. ^1H NMR spectrum of **3ba-d**



A mixture of **1a-d₅** (0.1 mmol), **1a** (0.1 mmol) and **2a** (0.15 mmol), recovered $\text{g-C}_3\text{N}_4$ (10 mg) and EtOH (2 mL) was added to a 10 mL test tube. The resulting mixture was stirred under a 3% O_2 atmosphere and irradiated with blue LED at room temperature. When the test tube stirred for half an hour, the photocatalyst was filtered off and washed with ethanol. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc to give the desired **3aa-d₅** and **3aa** in 15% combined yields (Figure S14.). Comparing the ^1H NMR spectrum of **3aa-d₅** and **3aa**, We found the ratio of **3aa-d₅** : **3aa** was 5 : (12.8–7) or 3 : (6.48–3) or 2 : (4.32–2) and the intermolecular KIE value was calculated to be 0.862.

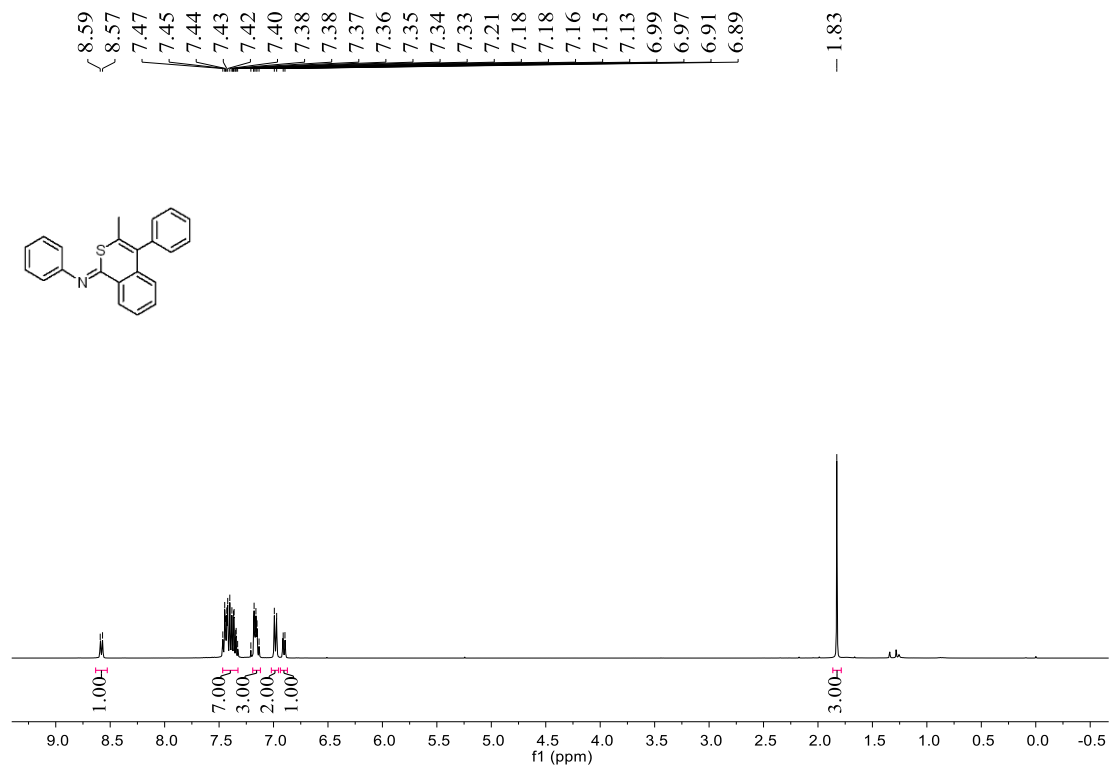


Figure S13. Comparison of the ^1H NMR of 3aa-d₅ and 3aa

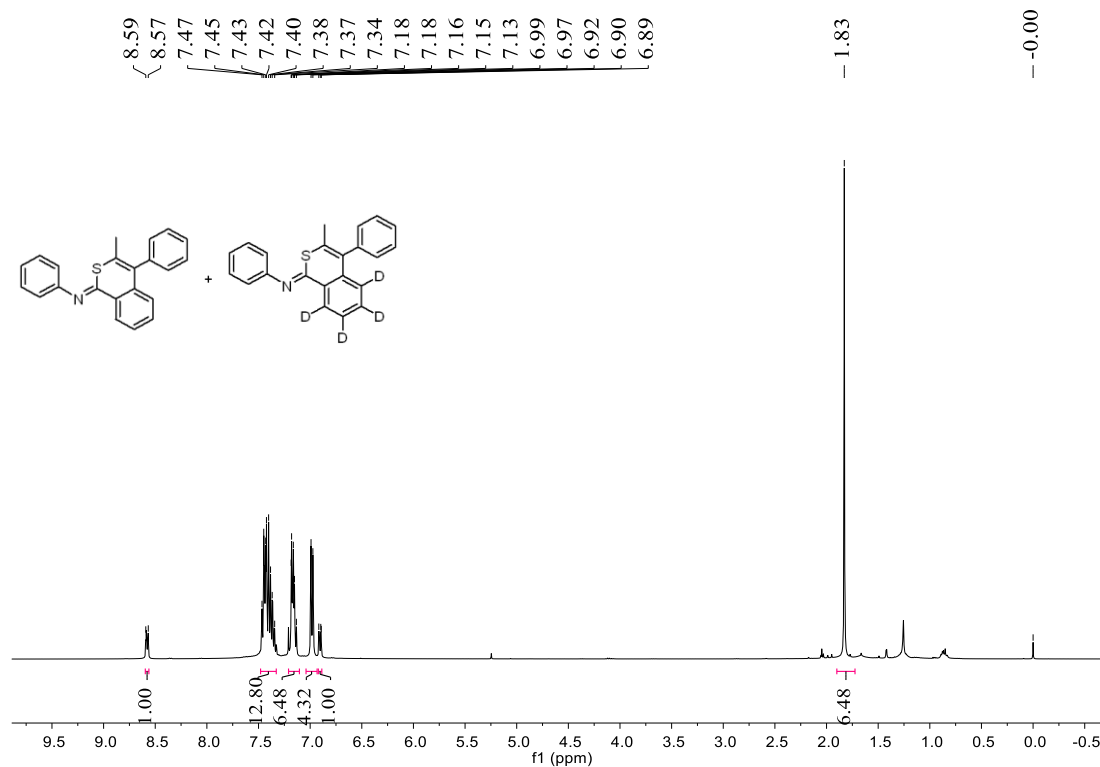


Figure S14. ¹H NMR of a mixture of **3aa-d₅** and **3aa**

4.6 EPR experiment

5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was used as spin-trapping agent and EPR signal were recorded on Bruker EMXPLUSA. In a typical procedure, **1a** (0.1 mmol), **2a** (0.15 mmol), DMPO (0.3 mmol) and g-C₃N₄ (10 mg) in EtOH (3 mL) was stirred until dispersion under an air atmosphere at room temperature. Subsequently, EPR signal were tested respectively under dark conditions and after 5 minutes of light (Figure S15).

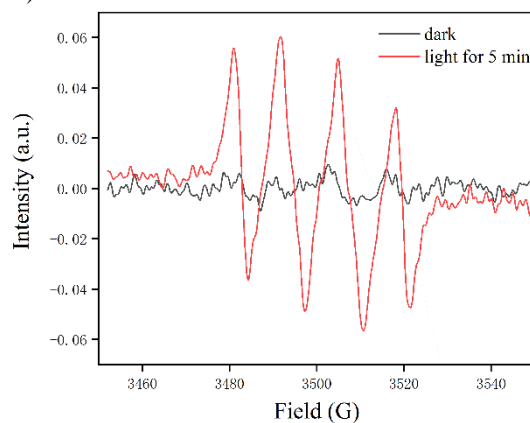


Figure S15. EPR measurements for O₂⁻

4.7 DFT calculations

All the DFT calculations were performed using the Gaussian 09 program package. Geometry optimizations and vibrational frequency calculations were carried out at the B3LYP-D3/6-311G(d,p).

Solvent effects were corrected by using the polarizable continuum model (PCM) in its integral equation formalism together with Ethanol (EtOH) as solvent (Figure S16.)

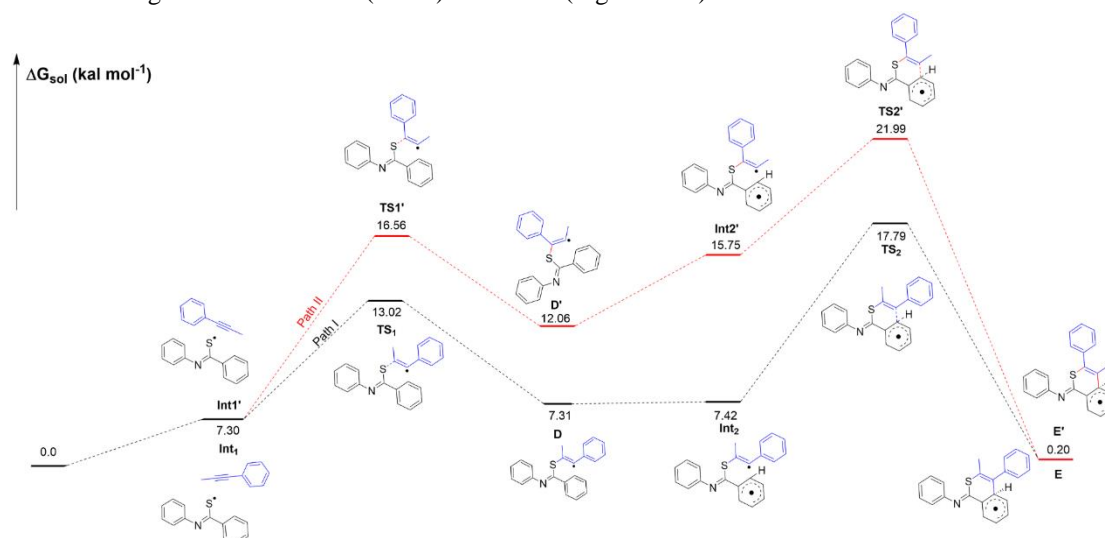


Figure S16. Mechanistic studies by DFT calculations

4.8 Reusability and stability of g-C₃N₄

The reusability and stability of g-C₃N₄ was tested through the reaction of *N*-phenylbenzothioamide **1a** and 1-Phenyl-1-propyne **2a**. In a typical procedure, the mixture of *N*-phenylbenzothioamide (0.1 mmol), 1-Phenyl-1-propyne (0.15 mmol) and g-C₃N₄ (10 mg) were stirred in EtOH (2 mL) irradiated with a 10 W blue LED for 15 h under an air atmosphere at room temperature. After the reactions, the photocatalyst was separated by centrifugation and washed twice with EtOH, and used for next run. The supernatants were combined and analyzed by HPLC. After 5 times cycles, the photocatalyst was characterized by XRD, FTIR and SEM (Figure S17., Figure S18.).

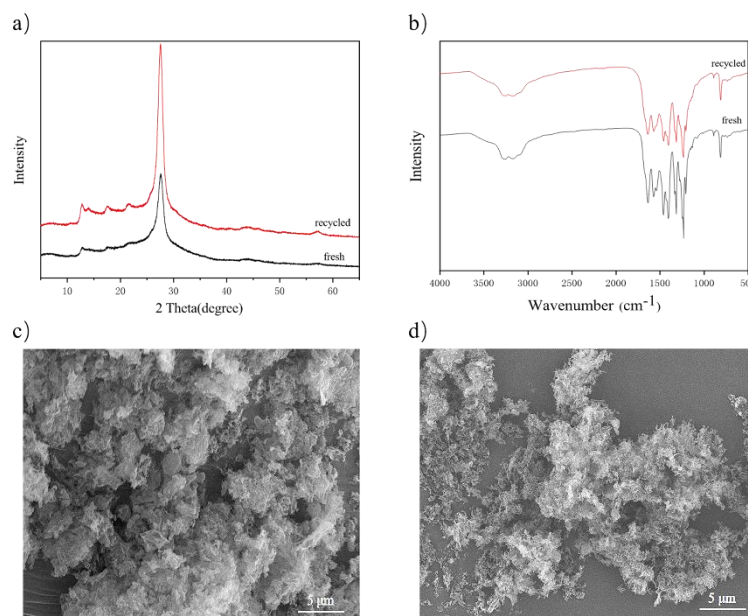


Figure S17. Reusability of the g-C₃N₄. (a) the X-ray diffractions (XRD) for the fresh and recycled g-C₃N₄. (b) the FT-IR spectra for the fresh and recycled g-C₃N₄. (c) Scanning electron microscopy (SEM) image for the fresh g-C₃N₄. (d) Scanning electron microscopy (SEM) image for the recycled g-C₃N₄

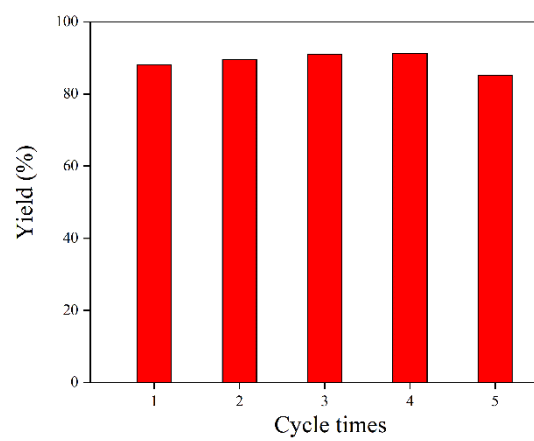
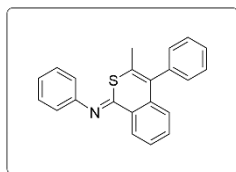


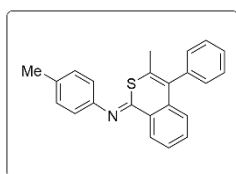
Figure S18. Recyclability of Catalyst g-C₃N₄

5. Characterization of products



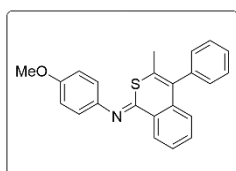
(Z)-3-Methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3aa).

Yellow solid (28.7 mg, 88%); **m.p.** 127 °C; $R_f = 0.66$ (*n*-hexane/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.58 (d, $J = 8.5$ Hz, 1H), 7.47 – 7.33 (m, 7H), 7.19 – 7.12 (m, 3H), 6.98 (d, $J = 8.6$ Hz, 2H), 6.90 (d, $J = 6.5$ Hz, 1H), 1.83 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.02, 151.18, 138.49, 136.91, 131.38, 130.25, 129.79, 129.67, 129.15, 128.97, 128.42, 127.71, 127.64, 127.60, 125.72, 124.19, 119.80, 21.48; MS: m/z (ESI) calcd for $\text{C}_{22}\text{H}_{17}\text{NS}$ $[\text{M}+\text{H}]^+$: 328.1115, found: 328.1147.



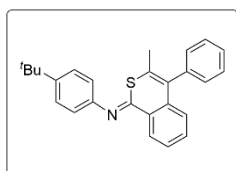
(Z)-3-Methyl-4-phenyl-N-(p-tolyl)-1H-isothiochromen-1-imine (3ba).

Yellow solid (28.72mg, 84%); **m.p.** 128.1 °C; $R_f = 0.72$ (*n*-hexane/ EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.48 (d, $J = 8.2$ Hz, 1H), 7.47 – 7.36 (m, 5H), 7.21 (dd, $J = 6.6$ Hz, 1H), 7.18 – 7.11 (m, 3H), 6.98 (d, $J = 7.1$ Hz, 2H), 6.69 (s, 1H), 2.23 (s, 3H), 1.80 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.04, 150.11, 136.13, 135.98, 134.28, 130.23, 128.99, 128.67, 128.55, 128.52, 127.93, 127.35, 126.63, 126.46, 124.57, 123.05, 118.71, 20.38, 20.25; HRMS: m/z (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{NS}$ $[\text{M}+\text{H}]^+$: 342.1275, found: 342.1303.



(Z)-N-(4-Methoxyphenyl)-3-methyl-4-phenyl-1H-isothiochromen-1-imine (3ca).

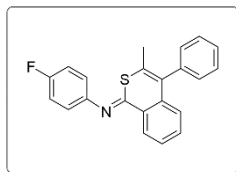
Yellow solid (27.9 mg, 78%); **m.p.** 135.2 °C; $R_f = 0.54$ (*n*-hexane /EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.56 (d, $J = 7.5$ Hz, 1H), 7.45 (dd, $J = 8.1, 6.5$ Hz, 2H), 7.41 – 7.32 (m, 3H), 7.18 (d, $J = 6.7$ Hz, 2H), 7.00 – 6.93 (m, 4H), 6.89 (d, $J = 5.7$ Hz, 1H), 3.83 (s, 3H), 1.84 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.78, 156.55, 144.25, 138.56, 136.84, 131.17, 130.23, 129.69, 129.05, 128.89, 128.29, 127.95, 127.51, 125.73, 121.03, 114.93, 55.46, 21.44; HRMS: m/z (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{NOS}$ $[\text{M}+\text{H}]^+$: 358.1221, found: 358.1248.



(Z)-N-(4-(Tert-butyl) phenyl)-3-methyl-4-phenyl-1H-isothiochromen-1-imine (3da).

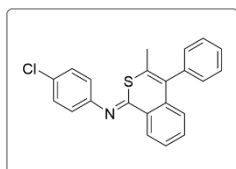
Yellow solid (32.2 mg, 84%); **m.p.** 128.2 °C; $R_f = 0.74$ (*n*-hexane/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.56 (d, $J = 7.6$ Hz, 1H), 7.45 (t, $J = 8.1$ Hz, 4H), 7.40 – 7.31 (m, 3H), 7.20 – 7.15 (m, 2H), 6.91 (dd, $J = 15.8, 8.1$ Hz, 3H), 1.84 (s, 3H), 1.35 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.39,

148.29, 146.99, 138.57, 136.86, 131.23, 130.26, 129.62, 129.18, 128.93, 128.33, 127.90, 127.58, 127.54, 126.52, 125.78, 119.32, 34.49, 31.58, 21.51; HRMS: m/z (ESI) calcd for $C_{26}H_{25}NS$ $[M+H]^+$: 384.1741, found: 384.1765.



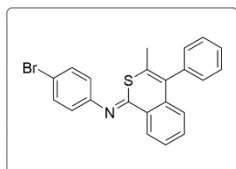
(Z)-N-(4-Fluorophenyl)-3-methyl-4-phenyl-1H-isothiochromen-1-imine (3ea).

Yellow solid (24.6 mg, 71%); **m.p.** 120.8 °C; R_f = 0.7 (*n*-hexane/EtOAc = 10:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 7.3 Hz, 1H), 7.45 (t, J = 7.3 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.17 (d, J = 6.7 Hz, 2H), 7.11 (t, J = 8.7 Hz, 2H), 6.97 – 6.89 (m, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.99, 158.61 (d, J = 6.5 Hz), 147.13 (d, J = 2.9 Hz), 138.41, 136.89, 131.42, 130.20, 129.82, 128.95, 128.92, 128.42, 127.68, 127.62 (d, J = 1.8 Hz), 125.66, 121.22, 116.56, 116.34, 21.42; HRMS: m/z (ESI) calcd for $C_{22}H_{16}FNS$ $[M+H]^+$: 346.1021, found: 346.1051.



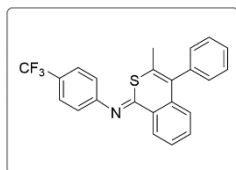
(Z)-N-(4-Chlorophenyl)-3-methyl-4-phenyl-1H-isothiochromen-1-imine (3fa).

Yellow solid (26.7 mg, 74%); **m.p.** 125.8 °C; R_f = 0.72 (*n*-hexane/EtOAc = 10:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 4.8 Hz, 1H), 7.43 – 7.25 (m, 7H), 7.08 (d, J = 7.2 Hz, 2H), 6.86 – 6.74 (m, 3H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.85, 149.60, 138.30, 136.91, 132.85, 131.59, 130.20, 129.91, 129.31, 129.00, 128.51, 127.71, 127.68, 127.49, 125.66, 121.78, 121.36, 21.45; HRMS: m/z (ESI) calcd for $C_{22}H_{16}ClNS$ $[M+H]^+$: 362.0702, found: 362.0735.



(Z)-N-(4-Bromophenyl)-3-methyl-4-phenyl-1H-isothiochromen-1-imine (3ga).

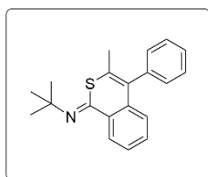
Yellow solid (31.2 mg, 77%); **m.p.** 127 °C; R_f = 0.72 (*n*-hexane/EtOAc = 10:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 7.3 Hz, 1H), 7.44 (d, J = 8.6 Hz, 2H), 7.39 – 7.27 (m, 5H), 7.09 (d, J = 6.7 Hz, 2H), 6.81 (dd, J = 20.5, 8.3 Hz, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.75, 150.10, 138.28, 136.90, 132.83, 131.57, 131.33, 130.18, 129.85, 128.98, 128.91, 128.49, 127.69, 127.47, 125.62, 121.75, 117.01, 21.42; HRMS: m/z (ESI) calcd for $C_{22}H_{16}BrNS$ $[M+H]^+$: 406.0231, found: 406.0247.



(Z)-3-Methyl-4-phenyl-N-(4-(trifluoromethyl)phenyl)-1H-isothiochromen-1-imine (3ha).

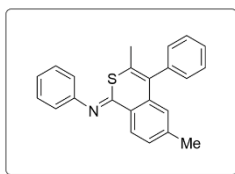
Yellow solid (28.4 mg, 72%); **m.p.** 153 °C; R_f = 0.74 (*n*-hexane/EtOAc = 10:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.54 (m, 1H), 7.67 (d, J = 8.3 Hz, 2H), 7.49 – 7.36 (m, 5H), 7.18 (d, J = 6.7 Hz, 2H),

7.05 (d, $J = 8.2$ Hz, 2H), 6.94 (d, $J = 7.0$ Hz, 1H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.96, 154.31, 138.20, 136.96, 131.73, 130.17, 129.97, 129.01, 128.85, 128.58, 127.73 (d, $J = 3.9$ Hz), 127.33, 127.08 (d, $J = 3.8$ Hz), 126.15, 125.85 (d, $J = 4.3$ Hz), 125.64, 123.17, 120.08, 21.37; HRMS: m/z (ESI) calcd for $\text{C}_{23}\text{H}_{16}\text{F}_3\text{NS}$ $[\text{M}+\text{H}]^+$: 396.0989, found: 396.1014.



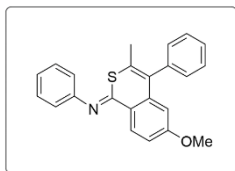
(Z)-N-(tert-butyl)-3-methyl-4-phenyl-1H-isothiochromen-1-imine (3ia)

Yellow solid (17.2 mg, 56%); **m.p.** 112 °C; $R_f = 0.83$ (n -hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 8.1$ Hz, 1H), 7.43 – 7.45 (m, 2H), 7.37 – 7.39 (m, 1H), 7.23 – 7.27 (m, 2H), 7.18 (d, $J = 7.0$ Hz, 2H), 6.79 (d, $J = 8.1$ Hz, 1H), 1.94 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.99, 139.01, 135.97, 130.41, 129.93, 129.62, 129.26, 129.09, 128.84, 128.05, 127.39, 127.32, 126.07, 56.25, 28.40, 21.73; HRMS: m/z (ESI) calcd for $\text{C}_{20}\text{H}_{21}\text{NS}$ $[\text{M}+\text{H}]^+$: 307.1342, found: 307.1355.



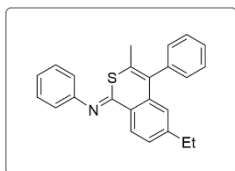
(Z)-3,6-Dimethyl-N,4-diphenyl-1H-isothiochromen-1-imine (3ja).

Yellow solid (28.6 mg, 84%); **m.p.** 142.3 °C; $R_f = 0.64$ (n -hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.48 (d, $J = 8.2$ Hz, 1H), 7.48 – 7.36 (m, 5H), 7.22 – 7.12 (m, 4H), 7.01 – 6.94 (m, 2H), 6.69 (s, 1H), 2.23 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.05, 151.27, 141.76, 138.57, 136.90, 130.25, 129.76, 129.67, 129.18, 128.93, 128.85, 128.58, 127.55, 125.79, 125.44, 124.08, 119.93, 21.72, 21.50; HRMS: m/z (ESI) calcd for $\text{C}_{22}\text{H}_{19}\text{NS}$ $[\text{M}+\text{H}]^+$: 342.1272, found: 342.1302.



(Z)-6-Methoxy-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3ka).

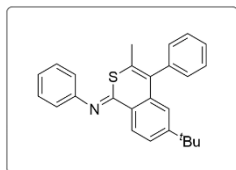
Yellow solid (28.64 mg, 80%); **m.p.** 153.2 °C; $R_f = 0.4$ (n -hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.54 (d, $J = 9.0$ Hz, 1H), 7.40 (m, 5H), 7.20 – 7.08 (m, 3H), 7.03 – 6.90 (m, 3H), 6.35 (d, $J = 4.8$ Hz, 1H), 3.62 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.01, 157.33, 151.33, 138.86, 138.47, 130.21, 130.17, 129.71, 129.55, 128.97, 127.98, 127.65, 123.97, 121.51, 120.08, 114.10, 112.61, 55.17, 21.56; HRMS: m/z (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{NOS}$ $[\text{M}+\text{H}]^+$: 358.1221, found: 358.1238.



(Z)-6-Ethyl-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3la).

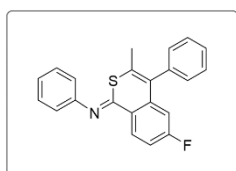
Yellow solid (28.4 mg, 80%); **m.p.** 161 °C; $R_f = 0.6$ (n -hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.50 (d, $J = 8.3$ Hz, 1H), 7.48 – 7.38 (m, 5H), 7.26 (dd, $J = 8.2, 1.8$ Hz, 1H), 7.16 (dd, $J = 14.2, 7.0$ Hz, 3H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.71 (d, $J = 1.6$ Hz, 1H), 2.53 (q, $J = 7.6$ Hz, 2H), 1.82 (s,

3H), 1.10 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.01, 151.29, 147.95, 138.56, 136.96, 130.23, 129.72, 129.08, 128.86, 127.56, 127.53, 127.50, 125.84, 125.63, 124.03, 119.89, 28.90, 21.45, 15.27; HRMS: m/z (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{NS}$ $[\text{M}+\text{H}]^+$: 356.1428, found: 356.1459.



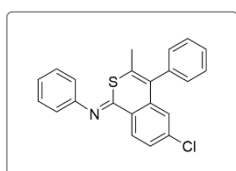
(Z)-6-(Tert-butyl)-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3ma).

Yellow solid (29.9 mg, 78%); **m.p.** 162.3 °C; $R_f = 0.66$ (n -hexane /EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.52 (d, $J = 8.5$ Hz, 1H), 7.47 – 7.36 (m, 6H), 7.20 – 7.12 (m, 3H), 7.00 – 6.95 (m, 2H), 6.92 (d, $J = 2.0$ Hz, 1H), 1.84 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.97, 154.62, 151.34, 138.61, 136.76, 130.24, 130.04, 129.77, 128.91, 128.86, 127.57, 125.52, 125.39, 125.24, 125.20, 124.09, 119.94, 34.96, 30.95, 21.50; HRMS: m/z (ESI) calcd for $\text{C}_{26}\text{H}_{25}\text{NS}$ $[\text{M}+\text{H}]^+$: 384.1741, found: 384.1767.



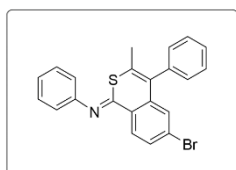
(Z)-6-Fluoro-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3na).

Yellow solid (25.2 mg, 73%); **m.p.** 162.3 °C; $R_f = 0.6$ (n -hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.59 (dd, $J = 9.0, 6.2$ Hz, 1H), 7.49 – 7.37 (m, 5H), 7.19 – 7.12 (m, 3H), 7.11 – 7.01 (m, 1H), 6.97 (d, $J = 7.1$ Hz, 2H), 6.56 (dd, $J = 11.0, 2.7$ Hz, 1H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.99, 163.50, 156.92, 150.91, 139.50 (d, $J = 8.8$ Hz), 137.82, 131.30, 130.11, 129.81, 129.17, 129.06 (d, $J = 2.5$ Hz), 128.76 (d, $J = 9.1$ Hz), 127.92, 124.26 (d, $J = 8.5$ Hz), 119.79, 115.41, 114.07, 21.60; HRMS: m/z (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{FNS}$ $[\text{M}+\text{H}]^+$: 346.1021, found: 346.1051.



(Z)-6-Chloro-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3oa).

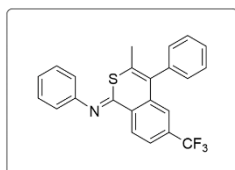
Yellow solid (27.4 mg, 76%); **m.p.** 178 °C; $R_f = 0.62$ (n -hexane/ EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.51 (d, $J = 8.7$ Hz, 1H), 7.50 – 7.40 (m, 5H), 7.34 (dd, $J = 8.7, 2.2$ Hz, 1H), 7.17 (tt, $J = 6.2, 1.2$ Hz, 3H), 7.00 – 6.95 (m, 2H), 6.86 (d, $J = 2.1$ Hz, 1H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.03, 150.81, 138.41, 137.89, 137.62, 131.22, 130.11, 129.79, 129.18, 128.80, 127.93, 127.81, 127.76, 127.55, 126.16, 124.36, 119.65, 21.61; HRMS: m/z (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{ClNS}$ $[\text{M}+\text{H}]^+$: 362.0735, found: 362.0755.



(Z)-6-Bromo-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3pa).

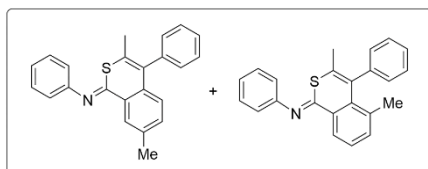
Yellow solid (31.6 mg, 78%); **m.p.** 148.7 °C; $R_f = 0.62$ (n -hexane/ EtOAc = 10:1); ^1H NMR (400 MHz,

CDCl₃) δ 8.35 (d, J = 8.7 Hz, 1H), 7.43 – 7.31 (m, 6H), 7.09 (t, J = 7.7 Hz, 3H), 6.95 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 8.1 Hz, 2H), 1.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.19, 150.75, 138.59, 137.57, 131.21, 130.77, 130.72, 130.11, 129.79, 129.19, 128.71, 127.95, 126.63, 126.55, 124.39, 119.65, 21.63; HRMS: m/z (ESI) calcd for C₂₂H₁₆BrNS [M+H]⁺: 406.0235, found: 406.0252.



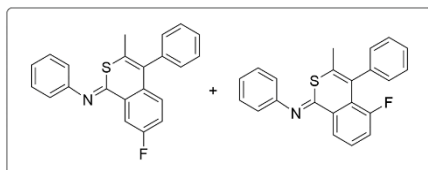
(Z)-3-Methyl-N,4-diphenyl-6-(trifluoromethyl)-1H-isothiochromen-1-imine (3qa).

Yellow solid (27.32 mg, 69%); **m.p.** 161.5 °C; R_f = 3.3 (*n*-hexane/EtOAc = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 8.68 (d, J = 8.4 Hz, 1H), 7.61 (dd, J = 8.4, 1.8 Hz, 1H), 7.52 – 7.41 (m, 5H), 7.22 – 7.15 (m, 4H), 7.01 – 6.96 (m, 2H), 1.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.84, 150.59, 137.30 (d, J = 5.5 Hz), 133.05, 132.72, 131.26, 130.06, 129.82, 129.24, 129.12, 128.08, 126.74, 125.10 (dt, J = 6.7, 3.3 Hz), 124.58, 123.76 (q, J = 3.5 Hz), 119.48, 21.59; HRMS: m/z (ESI) calcd for C₂₃H₁₆F₃NS [M+H]⁺: 396.0989, found: 396.1003.



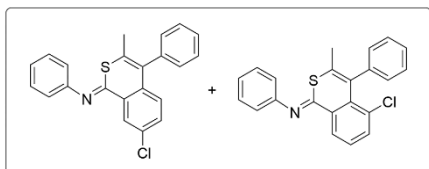
(Z)-3,7-Dimethyl-N,4-diphenyl-1H-isothiochromen-1-imine (3ra) and (Z)-3,5-dimethyl-N,4-diphenyl-1H-isothiochromen-1-imine (3r'a).

Yellow solid (28 mg, 82%); **m.p.** 112 °C; R_f = 2.9 and 2.7 (*n*-hexane/ EtOAc = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 8.32 (s, 1H), 8.23 (d, J = 8.0 Hz, 1H), 7.99 – 7.72 (m, 2H), 7.40 – 7.15 (m, 11H), 7.12 – 7.01 (m, 7H), 6.91 – 6.85 (m, 3H), 6.71 (d, J = 8.3 Hz, 1H), 2.32 (d, J = 11.7 Hz, 3H), 1.85 (s, 3H), 1.71 (s, 2H), 1.54 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.79, 158.48, 151.26, 150.84, 141.13, 138.62, 137.74, 137.05, 136.27, 135.88, 134.58, 132.50, 131.56, 130.53, 130.42, 130.23, 129.80, 129.60, 129.45, 128.90, 128.55, 128.25, 127.82, 127.72, 127.52, 127.46, 126.97, 125.57, 124.61, 124.33, 124.16, 120.04, 119.84, 24.54, 21.92, 21.29, 21.24; HRMS: m/z (ESI) calcd for C₂₃H₁₆NS [M+H]⁺: 342.1272, found: 342.1304.



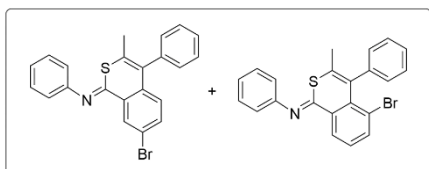
(Z)-7-Fluoro-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3sa) and (Z)-5-fluoro-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3s'a).

Yellow solid (26.3 mg, 76%); **m.p.** 110.1 °C; R_f = 0.6 and 0.52 (*n*-hexane/EtOAc = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, J = 8.1 Hz, 1H), 8.28 (dd, J = 10.2, 2.9 Hz, 1H), 7.49 – 7.30 (m, 12H), 7.22 – 7.15 (m, 6H), 7.12 – 6.87 (m, 7H), 1.82 (d, J = 6.7 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.22, 160.78 (d, J = 6.9 Hz), 158.29, 157.18 (d, J = 13.9 Hz), 151.24 – 150.27 (m), 140.46 (d, J = 4.8 Hz), 138.19, 133.42 (d, J = 2.6 Hz), 130.77 (d, J = 7.8 Hz), 130.65 (d, J = 4.0 Hz), 130.14, 129.76 (d, J = 9.8 Hz), 129.05, 128.95 – 128.81 (m), 128.72, 128.29, 128.12 (d, J = 2.5 Hz), 127.74, 126.94, 125.75, 125.26 (d, J = 7.6 Hz), 124.44 (d, J = 10.9 Hz), 122.06 (d, J = 3.6 Hz), 119.66 (d, J = 5.6 Hz), 119.34, 118.86 (d, J = 22.2 Hz), 111.74, 21.43, 21.28; HRMS: m/z (ESI) calcd for C₂₂H₁₆FNS [M+H]⁺: 346.1021, found: 346.1052.



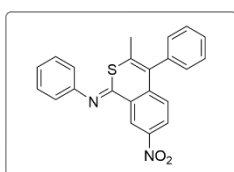
(Z)-7-Chloro-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3ta) and (Z)-5-chloro-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3t'a).

Yellow solid (29 mg, 80%); **m.p.** 107.2 °C; $R_f = 0.6$ and 0.54 (*n*-hexane/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.57 (d, $J = 2.4$ Hz, 1H), 8.38 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.49 – 7.39 (m, 8H), 7.38 – 7.26 (m, 6H), 7.20 – 7.14 (m, 6H), 6.99 – 6.95 (m, 4H), 6.84 (d, $J = 8.7$ Hz, 1H), 1.97 (s, 3H), 1.83 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.29, 156.78, 150.71, 150.33, 139.73, 137.94, 135.36, 135.17, 134.62, 133.83, 133.26, 133.13, 131.30, 130.89, 130.41, 130.13, 129.96, 129.81, 129.64, 129.49, 129.08, 129.06, 128.96, 128.85, 128.34, 128.04, 127.80, 126.97, 125.49, 125.34, 124.67, 124.43, 119.89, 119.60, 22.03, 21.43; HRMS: m/z (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{ClNS}$ $[\text{M}+\text{H}]^+$: 362.0731, found: 362.0756.



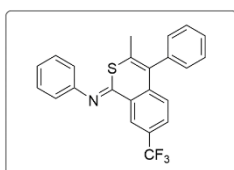
(Z)-7-Bromo-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3ua) and (Z)-5-bromo-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3u'a).

Yellow solid (34.1 mg, 84%); **m.p.** 112 °C; $R_f = 3.0$ and 2.8 (*n*-hexane/EtOAc = 10:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.72 (d, $J = 2.2$ Hz, 1H), 8.40 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.70 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.48 – 7.38 (m, 8H), 7.35 – 7.28 (m, 3H), 7.23 – 7.11 (m, 7H), 6.97 (td, $J = 7.6, 1.2$ Hz, 4H), 6.76 (d, $J = 8.7$ Hz, 1H), 2.02 (s, 3H), 1.82 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.11, 156.58, 150.69, 150.24, 139.11, 138.87, 137.87, 136.27, 135.73, 134.17, 133.81, 133.76, 131.24, 130.71, 130.12, 130.09, 129.87, 129.83, 129.80, 129.43, 129.12, 129.08, 128.52, 128.32, 127.97, 127.80, 127.10, 126.07, 124.69, 124.43, 122.58, 121.93, 119.92, 119.58, 22.24, 21.48; HRMS: m/z (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{BrNS}$ $[\text{M}+\text{H}]^+$: 406.0223, found: 406.0252.



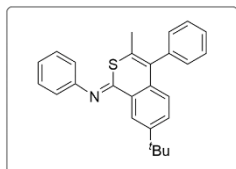
(Z)-3-Methyl-5-nitro-N,4-diphenyl-1H-isothiochromen-1-imine (3va).

Yellow solid (26.8 mg, 72%); **m.p.** 112.2 °C; $R_f = 2.1$ (*n*-hexane/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.38 (d, $J = 2.5$ Hz, 1H), 8.12 (dd, $J = 9.0, 2.6$ Hz, 1H), 7.55 – 7.40 (m, 6H), 7.26 – 7.14 (m, 4H), 7.04 (d, $J = 8.9$ Hz, 1H), 6.99 (dd, $J = 8.4, 1.2$ Hz, 2H), 1.89 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 155.41, 150.12, 146.59, 141.70, 137.19, 135.28, 129.97, 129.80, 129.45, 129.34, 129.02, 128.47, 128.17, 125.04, 124.76, 121.90, 119.38, 21.94; HRMS: m/z (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 373.0966, found: 373.0993.



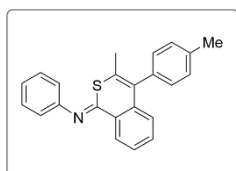
(Z)-3-Methyl-N,4-diphenyl-5-(trifluoromethyl)-1H-isothiochromen-1-imine (3wa).

Yellow solid (29.7 mg, 75%); **m.p.** 113.5 °C; $R_f = 3.1$ (*n*-hexane/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.83 (s, 1H), 7.50 (d, $J = 8.5$ Hz, 1H), 7.40 (dd, $J = 18.0, 7.5$ Hz, 5H), 7.15 – 7.10 (m, 3H), 6.96 (dd, $J = 14.6, 8.1$ Hz, 3H), 1.82 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.51, 150.62, 139.56, 137.74, 132.48, 130.11, 129.81, 129.64, 129.21, 129.10, 128.98, 128.03, 127.98, 127.37 (q, $J = 3.2$ Hz), 124.55, 123.39 (q, $J = 3.9$ Hz), 122.62, 119.55, 21.66; HRMS: m/z (ESI) calcd for $\text{C}_{23}\text{H}_{16}\text{F}_3\text{NS}$ $[\text{M}+\text{H}]^+$: 396.1089, found: 396.1099.



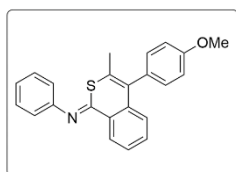
(Z)-5-(Tert-butyl)-3-methyl-N,4-diphenyl-1H-isothiochromen-1-imine (3xa).

Yellow solid (30.1 mg, 72%); **m.p.** 128.8 °C; $R_f = 2.3$ (*n*-hexane/ EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.64 (d, $J = 2.3$ Hz, 1H), 7.46 – 7.36 (m, 6H), 7.18 – 7.13 (m, 3H), 6.98 (s, 2H), 1.82 (s, 3H), 1.36 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.24, 151.48, 150.78, 138.68, 134.60, 130.25, 129.77, 129.43, 128.92, 128.88, 128.37, 128.16, 127.49, 127.31, 124.03, 121.97, 119.87, 34.97, 31.28, 21.27; HRMS: m/z (ESI) calcd for $\text{C}_{26}\text{H}_{25}\text{NS}$ $[\text{M}+\text{H}]^+$: 384.1841, found: 384.1868.



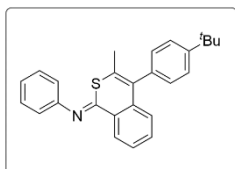
(Z)-3-Methyl-N-phenyl-4-(p-tolyl)-1H-isothiochromen-1-imine (3ab).

Yellow solid (25.1 mg, 73%); **m.p.** 138.4 °C; $R_f = 0.6$ (*n*-hexane/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.49 (d, $J = 9.5$ Hz, 1H), 7.36 – 7.25 (m, 4H), 7.19 – 7.13 (m, 2H), 7.07 (t, $J = 7.4$ Hz, 1H), 6.97 (d, $J = 7.8$ Hz, 2H), 6.88 (dd, $J = 14.6, 7.2$ Hz, 3H), 2.33 (s, 3H), 1.75 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.96, 150.13, 136.12, 135.97, 134.28, 130.21, 128.99, 128.66, 128.54, 128.51, 127.93, 127.34, 126.66, 126.44, 124.57, 123.03, 118.69, 20.37, 20.24; HRMS: m/z (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{NS}$ $[\text{M}+\text{H}]^+$: 342.1272, found: 342.1301.



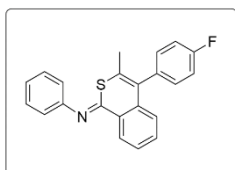
(Z)-4-(4-Methoxyphenyl)-3-methyl-N-phenyl-1H-isothiochromen-1-imine (3ac).

Yellow solid (25 mg, 70%); **m.p.** 155.0 °C; $R_f = 0.44$ (*n*-hexane/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.57 (dd, $J = 7.2, 2.3$ Hz, 1H), 7.45 – 7.35 (m, 4H), 7.16 (t, $J = 7.5$ Hz, 1H), 7.08 (d, $J = 8.6$ Hz, 2H), 7.00 – 6.95 (m, 5H), 3.86 (s, 3H), 1.85 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.95, 158.10, 151.16, 137.22, 131.34, 131.30, 130.44, 129.75, 129.30, 129.28, 128.41, 127.75, 127.54, 125.66, 124.15, 119.79, 114.34, 55.33, 21.48; HRMS: m/z (ESI) calcd for $\text{C}_{23}\text{H}_{13}\text{NOS}$ $[\text{M}+\text{H}]^+$: 358.1221, found: 358.1247.



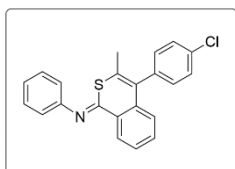
(Z)-4-(4-(*Tert*-butyl) phenyl)-3-methyl-*N*-phenyl-1*H*-isothiochromen-1-imine (3ad).

Yellow solid (28.3 mg, 74%); **m.p.** 213.4 °C; $R_f = 0.58$ (*n*-hexane/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.57 (dd, $J = 7.4, 2.2$ Hz, 1H), 7.48 – 7.34 (m, 6H), 7.18 – 7.08 (m, 3H), 6.97 (m, $J = 12.1, 7.3, 1.9$ Hz, 3H), 1.84 (s, 3H), 1.38 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.17, 151.22, 150.40, 137.08, 135.26, 131.32, 129.80, 129.74, 129.61, 129.03, 128.52, 127.68, 127.52, 125.75, 125.61, 124.12, 119.79, 34.68, 31.46, 21.53; HRMS: m/z (ESI) calcd for $\text{C}_{26}\text{H}_{25}\text{NS}$ $[\text{M}+\text{H}]^+$: 384.1741, found: 384.1768.



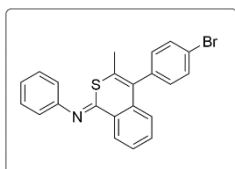
(Z)-4-(4-Fluorophenyl)-3-methyl-*N*-phenyl-1*H*-isothiochromen-1-imine (3ae).

Yellow solid (22.4 mg, 65%); **m.p.** 123.4 °C; $R_f = 0.66$ (*n*-hexane/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.58 (dd, $J = 7.4, 2.1$ Hz, 1H), 7.45 – 7.35 (m, 4H), 7.19 – 7.11 (m, 5H), 6.97 (dd, $J = 8.4, 1.3$ Hz, 2H), 6.88 (dd, $J = 7.6, 1.8$ Hz, 1H), 1.83 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.46, 161.01, 157.75, 151.07, 136.79, 134.24 (d, $J = 3.6$ Hz), 131.90 (d, $J = 8.0$ Hz), 131.44, 129.76 (d, $J = 4.2$ Hz), 128.61, 128.17, 127.75, 125.82, 124.24, 119.74, 116.12, 115.91, 21.47; HRMS: m/z (ESI) calcd for $\text{C}_{23}\text{H}_{16}\text{FNS}$ $[\text{M}+\text{H}]^+$: 346.1021, found: 346.1051.



(Z)-4-(4-Chlorophenyl)-3-methyl-*N*-phenyl-1*H*-isothiochromen-1-imine (3af).

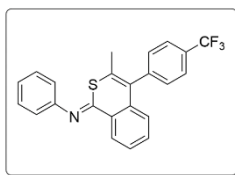
Yellow solid (24.5 mg, 68%); **m.p.** 168.7 °C; $R_f = 0.6$ (*n*-hexane/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.63 – 8.53 (m, 1H), 7.48 – 7.35 (m, 6H), 7.20 – 7.10 (m, 3H), 7.01 – 6.94 (m, 2H), 6.91 – 6.82 (m, 1H), 1.84 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.75, 150.98, 136.86, 136.53, 133.65, 131.66, 131.48, 129.80, 129.70, 129.27, 128.45, 128.13, 127.83, 127.65, 125.84, 124.28, 119.72, 21.47; HRMS: m/z (ESI) calcd for $\text{C}_{23}\text{H}_{16}\text{ClNS}$ $[\text{M}+\text{H}]^+$: 362.0722, found: 362.0751.



(Z)-4-(4-Bromophenyl)-3-methyl-*N*-phenyl-1*H*-isothiochromen-1-imine (3ag).

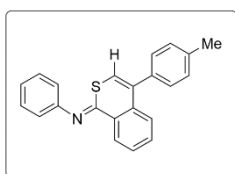
Yellow solid (28.4 mg, 70%); **m.p.** 177.8 °C; $R_f = 0.6$ (*n*-hexane/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.57 (d, $J = 7.6$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.45 – 7.35 (m, 4H), 7.16 (t, $J = 7.4$ Hz, 1H), 7.06 (d, $J = 8.4$ Hz, 2H), 7.00 – 6.95 (m, 2H), 6.87 (d, $J = 7.9$ Hz, 1H), 1.83 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.60, 151.03, 137.40, 136.46, 132.24, 132.02, 131.47, 129.79, 129.68, 128.46, 128.12, 127.84, 127.71, 125.87, 124.27, 121.83, 119.72, 21.49; HRMS: m/z (ESI) calcd for

$C_{23}H_{16}BrNS$ $[M+H]^+$: 406.0223, found: 406.0250.



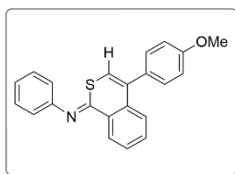
(Z)-3-Methyl-N-phenyl-4-(4-(trifluoromethyl)phenyl)-1H-isothiochromen-1-imine (3ah).

Yellow solid (23.7 mg, 60%); **m.p.** 167.4 °C; R_f = 0.58 (*n*-hexane/EtOAc = 10:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.3 Hz, 2H), 7.49 – 7.36 (m, 5H), 7.18 (d, J = 6.7 Hz, 2H), 7.05 (d, J = 8.2 Hz, 2H), 6.94 (d, J = 7.0 Hz, 1H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.46, 150.98, 142.47 (q, J = 1.4 Hz), 136.23, 131.53, 130.78, 130.10, 129.94, 129.81, 128.36, 128.01, 127.97, 127.67, 125.99 (dd, J = 7.2, 3.5 Hz), 125.51, 124.32, 122.80, 119.68, 21.45; HRMS: m/z (ESI) calcd for $C_{23}H_{16}F_3NS$ $[M+H]^+$: 396.0989, found: 396.1010.



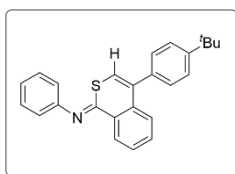
(Z)-N-Phenyl-4-(p-tolyl)-1H-isothiochromen-1-imine (3ai).

Yellow solid (24.9 mg, 76%); **m.p.** 123.4 °C; R_f = 0.66 (*n*-hexane/EtOAc = 10:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 9.6 Hz, 1H), 7.50 – 7.40 (m, 4H), 7.32 – 7.29 (m, 1H), 7.24 – 7.12 (m, 5H), 6.96 (d, J = 7.1 Hz, 2H), 6.49 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.00, 151.13, 137.60, 136.93, 135.15, 133.19, 131.30, 129.81, 129.32, 129.26, 129.23, 128.78, 128.28, 126.24, 124.29, 119.70, 119.61, 21.29; HRMS: m/z (ESI) calcd for $C_{22}H_{17}NOS$ $[M+H]^+$: 328.1115, found: 328.1148.



(Z)-4-(4-Methoxyphenyl)-N-phenyl-1H-isothiochromen-1-imine (3aj).

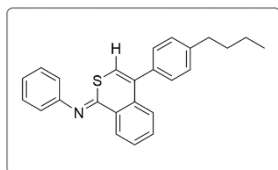
Yellow solid (24.8 mg, 72%); **m.p.** 130.8 °C; R_f = 0.64 (*n*-hexane/ EtOAc = 10:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.49 (m, 1H), 7.42 – 7.33 (m, 4H), 7.23 (dd, J = 6.5, 1.5 Hz, 1H), 7.17 – 7.14 (m, 2H), 7.08 (tt, J = 7.4, 1.2 Hz, 1H), 6.89 – 6.84 (m, 4H), 6.41 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.14, 155.92, 150.03, 134.19, 131.75, 131.04, 130.23, 129.47, 128.71, 128.15, 127.68, 127.16, 125.14, 123.20, 118.60, 118.44, 112.86, 54.29; HRMS: m/z (ESI) calcd for $C_{22}H_{17}NOS$ $[M+H]^+$: 345.1098, found: 345.1123.



(Z)-4-(4-(Tert-butyl)phenyl)-N-phenyl-1H-isothiochromen-1-imine (3ak).

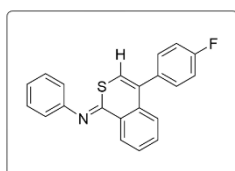
Yellow solid (17.1 mg, 68%); **m.p.** 148.8 °C; R_f = 0.7 (*n*-hexane/ EtOAc = 10:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 9.4 Hz, 1H), 7.50 – 7.32 (m, 7H), 7.25 (d, J = 7.9 Hz, 2H), 7.15 (t, J = 6.9 Hz, 1H), 6.96 (d, J = 7.8 Hz, 2H), 6.51 (s, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.08, 151.11, 150.80, 136.85, 135.14, 133.20, 131.31, 129.80, 129.20, 129.09, 128.77, 128.36, 126.23, 125.47,

124.30, 119.72, 119.63, 34.69, 31.43; HRMS: m/z (ESI) calcd for $C_{25}H_{23}NS$ $[M+H]^+$: 370.1715, found: 370.1744.



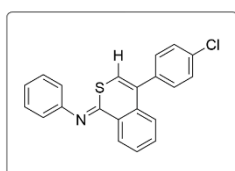
(Z)-4-(4-Butylphenyl)-N-phenyl-1H-isothiochromen-1-imine (3al).

Yellow solid (23.6 mg, 64%); **m.p.** 113.0 °C; R_f = 0.7 (*n*-hexane/EtOAc = 10:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.57 (m, 1H), 7.52 – 7.37 (m, 4H), 7.36 – 7.28 (m, 1H), 7.24 (s, 3H), 7.15 (t, J = 7.5 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.49 (s, 1H), 2.70 – 2.61 (m, 2H), 1.70 – 1.58 (m, 2H), 1.39 (dt, J = 14.7, 7.4 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.02, 151.14, 142.62, 137.10, 135.18, 133.26, 131.30, 129.81, 129.31, 129.25, 128.77, 128.60, 128.33, 126.25, 124.29, 119.72, 119.62, 77.42, 77.10, 76.78, 35.46, 33.67, 22.49, 14.06; HRMS: m/z (ESI) calcd for $C_{25}H_{23}NS$ $[M+H]^+$: 370.1585, found: 370.1610.



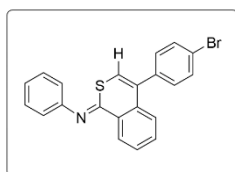
(Z)-4-(4-Fluorophenyl)-N-phenyl-1H-isothiochromen-1-imine (3am).

Yellow solid (23.2 mg, 70%); **m.p.** 130.1 °C; R_f = 0.62 (*n*-hexane/EtOAc = 10:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, J = 7.6, 1.9 Hz, 1H), 7.55 – 7.38 (m, 4H), 7.31 – 7.21 (m, 3H), 7.19 – 7.07 (m, 3H), 6.97 (d, J = 7.1 Hz, 2H), 6.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.64, 161.18, 150.88, 135.72 (d, J = 3.4 Hz), 134.92, 132.24, 131.43, 131.10 (d, J = 8.0 Hz), 129.81, 129.16, 128.97, 128.01, 126.37, 124.40, 120.21, 119.66, 115.56 (d, J = 21.5 Hz); HRMS: m/z (ESI) calcd for $C_{21}H_{14}FNS$ $[M+H]^+$: 332.0865, found: 332.0884.



(Z)-4-(4-Chlorophenyl)-N-phenyl-1H-isothiochromen-1-imine (3an).

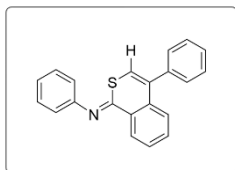
Yellow solid (26.0 mg, 75%); **m.p.** 137.5 °C; R_f = 0.66 (*n*-hexane/EtOAc = 10:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.56 (m, 1H), 7.52 – 7.38 (m, 6H), 7.24 (dd, J = 9.5, 7.3 Hz, 3H), 7.19 – 7.14 (m, 1H), 6.99 – 6.91 (m, 2H), 6.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.60, 150.89, 138.23, 134.65, 133.85, 132.11, 131.47, 130.79, 129.84, 129.18, 129.06, 128.84, 127.96, 126.42, 124.44, 120.40, 119.64; HRMS: m/z (ESI) calcd for $C_{21}H_{14}ClNS$ $[M+H]^+$: 348.0594, found: 348.0602.



(Z)-4-(4-Bromophenyl)-N-phenyl-1H-isothiochromen-1-imine (3ao).

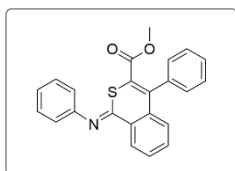
Yellow solid (29.1 mg, 74%); **m.p.** 143.8 °C; R_f = 0.66 (*n*-hexane/EtOAc = 10:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.57 (m, 1H), 7.58 – 7.40 (m, 6H), 7.26 – 7.13 (m, 4H), 6.95 (dd, J = 8.4, 1.2 Hz, 2H),

6.51 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.46, 150.93, 138.74, 134.57, 132.11, 131.79, 131.43, 131.10, 129.81, 129.22, 129.04, 127.93, 126.41, 124.40, 121.98, 120.38, 119.60; HRMS: m/z (ESI) calcd for $\text{C}_{21}\text{H}_{14}\text{BrNS}$ $[\text{M}+\text{H}]^+$: 393.0045, found: 393.0070.



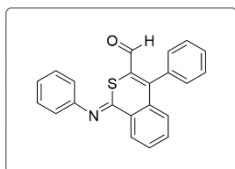
(Z)-N,4-Diphenyl-1H-isothiochromen-1-imine (3ap).

Yellow solid (25.0 mg, 80%); **m.p.** 118.2 °C; R_f = 0.6 (*n*-hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.61 (dd, J = 7.8, 1.8 Hz, 1H), 7.48 – 7.35 (m, 7H), 7.32 – 7.24 (m, 3H), 7.14 (td, J = 7.3, 1.2 Hz, 1H), 6.99 – 6.91 (m, 2H), 6.49 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.87, 151.13, 139.90, 135.03, 133.28, 131.38, 129.86, 129.49, 129.26, 128.89, 128.64, 128.28, 127.87, 126.33, 124.36, 120.00, 119.73; HRMS: m/z (ESI) calcd for $\text{C}_{21}\text{H}_{15}\text{NS}$ $[\text{M}+\text{H}]^+$: 314.1063, found: 314.1093.



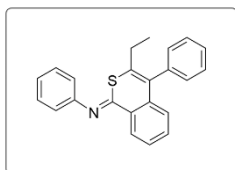
Methyl (Z)-4-phenyl-1-(phenylimino)-1H-isothiochromene-3-carboxylate (3aq).

Yellow solid (30.4 mg, 82%); **m.p.** 143.5 °C; R_f = 0.36 (*n*-hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.60 (dd, J = 8.0, 1.5 Hz, 1H), 7.53 (m, J = 8.2, 7.2, 1.3 Hz, 1H), 7.43 (m, J = 8.9, 4.5, 2.3, 1.4 Hz, 6H), 7.24 – 7.15 (m, 3H), 7.08 (dd, J = 8.2, 1.3 Hz, 1H), 7.01 – 6.94 (m, 2H), 3.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.33, 155.77, 150.38, 138.05, 137.20, 135.42, 131.45, 130.34, 130.23, 129.80, 129.77, 129.29, 128.33, 127.93, 126.03, 124.48, 123.99, 119.49, 77.35, 77.03, 76.71, 52.52; HRMS: m/z (ESI) calcd for $\text{C}_{23}\text{H}_{17}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 372.1038, found: 372.1040.



(Z)-4-Phenyl-1-(phenylimino)-1H-isothiochromene-3-carbaldehyde (3ar).

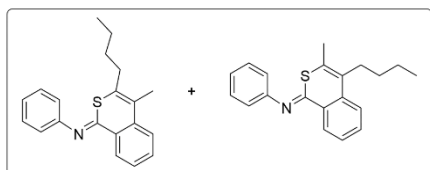
Yellow solid (26.6 mg, 78%); **m.p.** 138.5 °C; R_f = 0.32 (*n*-hexane/ EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 9.33 (s, 1H), 8.67 (dd, J = 8.1, 1.1 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.51 (td, J = 8.5, 2.5 Hz, 4H), 7.47 – 7.40 (m, 2H), 7.37 – 7.32 (m, 2H), 7.19 – 7.14 (m, 2H), 6.98 – 6.95 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.24, 155.62, 150.34, 145.54, 134.88, 134.62, 131.88, 131.78, 131.54, 131.18, 130.49, 130.37, 129.84, 129.03, 128.76, 126.50, 124.60, 119.33; HRMS: m/z (ESI) calcd for $\text{C}_{22}\text{H}_{15}\text{NOS}$ $[\text{M}+\text{H}]^+$: 342.0908, found: 342.0941.



(Z)-3-Ethyl-N,4-diphenyl-1H-isothiochromen-1-imine (3as).

Yellow solid (22.2 mg, 65%); **m.p.** 119.2 °C; R_f = 0.7 (*n*-hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.59 (d, J = 7.8 Hz, 1H), 7.47 – 7.31 (m, 7H), 7.22 – 7.12 (m, 3H), 6.99 (d, J = 8.6 Hz, 2H),

6.86 (d, $J = 7.6$ Hz, 1H), 2.16 (td, $J = 7.5, 1.9$ Hz, 2H), 0.94 (td, $J = 7.5, 1.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.06, 151.21, 138.38, 137.04, 136.07, 131.34, 130.32, 129.77, 129.01, 128.90, 128.68, 127.73, 127.63, 125.69, 124.12, 119.85, 28.50, 14.55; HRMS: m/z (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{NS}$ $[\text{M}+\text{H}]^+$: 342.1272, found: 342.1302.



(Z)-3-Butyl-4-methyl-N-phenyl-1H-isothiochromen-1-imine (3at) and (Z)-4-Butyl-3-methyl-N-phenyl-1H-isothiochromen-1-imine (3at').

Yellow solid (26.5 mg, 86%); **m.p.** 123.5 °C; $R_f = 0.7$ and 0.66 (n -hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.58 (dd, $J = 3.9, 1.5$ Hz, 1H), 8.56 (dd, $J = 3.9, 1.5$ Hz, 1H), 7.65 (td, $J = 8.3, 1.3$ Hz, 2H), 7.58 (m, $J = 8.3, 7.1, 1.6$ Hz, 2H), 7.42 (m, $J = 9.4, 7.4, 6.3, 1.1$ Hz, 6H), 7.14 (td, $J = 7.4, 1.2$ Hz, 2H), 6.99 – 6.90 (m, 4H), 2.75 – 2.66 (m, 2H), 2.47 – 2.38 (m, 2H), 2.26 (s, 3H), 2.12 (s, 3H), 1.53 – 1.28 (m, 8H), 0.97 (t, $J = 7.1$ Hz, 3H), 0.89 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.53, 158.44, 151.14, 151.13, 136.86, 135.72, 132.14, 131.56, 131.49, 129.62, 129.59, 128.58, 128.26, 127.39, 127.28, 126.62, 126.34, 126.19, 125.88, 125.34, 125.15, 123.97, 123.89, 120.87, 119.83, 119.80, 34.94, 31.76, 31.19, 28.77, 22.92, 22.49, 20.63, 15.54, 13.97, 13.82; HRMS: m/z (ESI) calcd for $\text{C}_{20}\text{H}_{21}\text{NS}$ $[\text{M}+\text{H}]^+$: 308.1435, found: 308.1460.

6. X-Ray Diffraction Data

Single crystals of **3ta**, **3t'a**, **3ua**, **3u'a** and **3xa** were prepared by slow evaporation of CH₂Cl₂ and *n*-hexane solution. Single crystal X-ray diffraction data were collected at 100 K on XtaLAB Synergy (Dualflex, HyPix) & XtaLAB Synergy R (DW system, HyPix). X-Ray single diffractometer using Cu K α ($\lambda = 1.54184$ Å) micro-focus X-ray sources (PhotonJet (Cu) X-Ray Source). The raw data were collected and reduced by CrysAlisPro software. The structure was solved by the ShelXT⁹ with Intrinsic Phasing and refined on F² by full-matrix least-squares methods with the ShelXL⁹ and Olex2¹⁰ were used as GUI.

X-Ray Diffraction Data of **3ta** (CCDC: 2223004)

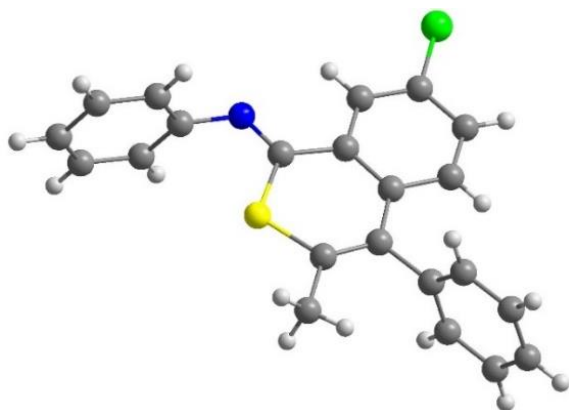


Table S3. Crystal data and structure refinement for **3ta** (cr-0724-2).

Identification code	cr-0724-2
Empirical formula	C ₂₂ H ₁₇ ClNS
Formula weight	362.88
Temperature/K	100.00(10)
Space group	P2 ₁ /m
Crystal system	monoclinic
<i>a</i> /Å	10.1263(3)
<i>b</i> /Å	6.9258(2)
<i>c</i> /Å	12.6138(4)
α /°	90
β /°	92.516(3)
γ /°	90
Volume/Å ³	883.79(5)
<i>Z</i>	2
ρ_{calc} /cm ³	1.364

μ/mm^{-1}	3.026
F(000)	378.0
Crystal size/ mm^3	$0.158 \times 0.135 \times 0.103$
Radiation	Cu K α ($\lambda = 1.54184$)
2Θ range for data collection/ $^\circ$	7.014 to 131.302
Index ranges	$-9 \leq h \leq 11, -8 \leq k \leq 8, -14 \leq l \leq 13$
Reflections collected	8365
Independent reflections	1643 [$R_{\text{int}} = 0.0727, R_{\text{sigma}} = 0.0503$]
Data/restraints/parameters	1643/0/140
Goodness-of-fit on F^2	0.916
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0342, wR_2 = 0.1099$
Final R indexes [all data]	$R_1 = 0.0375, wR_2 = 0.1159$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.30/-0.30

X-Ray Diffraction Data of 3t'a (CCDC: 2223003)

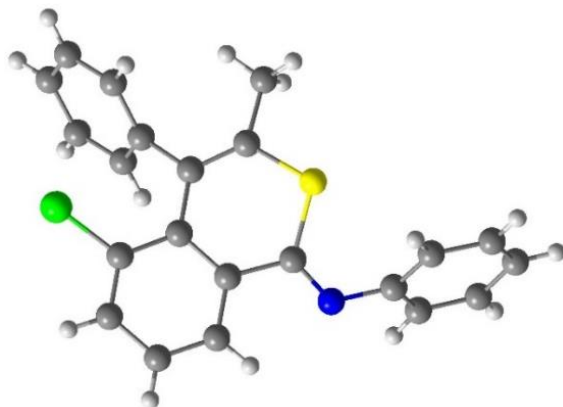


Table S4. Crystal data and structure refinement for **3t'a** (cr-0724-1_auto)

Identification code	cr-0724-1_auto
Empirical formula	$\text{C}_{22}\text{H}_{16}\text{ClNS}$
Formula weight	361.87
Temperature/K	100.00(10)
Crystal system	C2/c
Space group	monoclinic
$a/\text{\AA}$	24.9095(5)

b/Å	5.86690(10)
c/Å	25.8562(6)
α /°	90
β /°	111.533(2)
γ /°	90
Volume/Å ³	3514.94(13)
Z	8
ρ_{calc} /cm ³	1.368
μ /mm ⁻¹	3.043
F(000)	1504.0
Crystal size/mm ³	0.29 × 0.246 × 0.146
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	7.35 to 131.646
Index ranges	-25 ≤ h ≤ 28, -4 ≤ k ≤ 6, -30 ≤ l ≤ 30
Reflections collected	9079
Independent reflections	2959 [R _{int} = 0.0348, R _{sigma} = 0.0341]
Data/restraints/parameters	2959/0/227
Goodness-of-fit on F ²	1.089
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0348, wR ₂ = 0.0865
Final R indexes [all data]	R ₁ = 0.0382, wR ₂ = 0.0899
Largest diff. peak/hole / e Å ⁻³	0.23/-0.38

X-Ray Diffraction Data of 3ua (CCDC: 2223000)

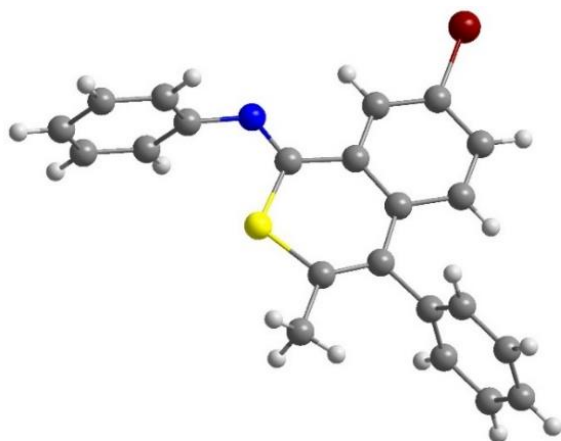


Table S5. Crystal data and structure refinement for **3ua** (cr-br-up-0807_auto)

Identification code	cr-br-up-0807_auto
Empirical formula	C ₂₂ H ₁₆ BrNS
Formula weight	406.33
Temperature/K	100.00(10)
Crystal system	P2 ₁ /m
Space group	monoclinic
a/Å	10.2654(2)
b/Å	7.04540(10)
c/Å	12.4963(3)
α /°	90
β /°	92.802(2)
γ /°	90
Volume/Å ³	902.70(3)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.495
μ/mm^{-1}	4.194
F(000)	412.0
Crystal size/mm ³	0.24 × 0.159 × 0.082
Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/°	7.082 to 131.616
Index ranges	-9 ≤ h ≤ 12, -8 ≤ k ≤ 6, -14 ≤ l ≤ 13
Reflections collected	4894
Independent reflections	1648 [R_{int} = 0.0306, R_{sigma} = 0.0311]
Data/restraints/parameters	1648/0/140
Goodness-of-fit on F ²	1.007
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0280, wR_2 = 0.0782
Final R indexes [all data]	R_1 = 0.0303, wR_2 = 0.0805
Largest diff. peak/hole / e Å ⁻³	0.67/-0.42

X-Ray Diffraction Data of 3u'a (CCDC: 2222984)

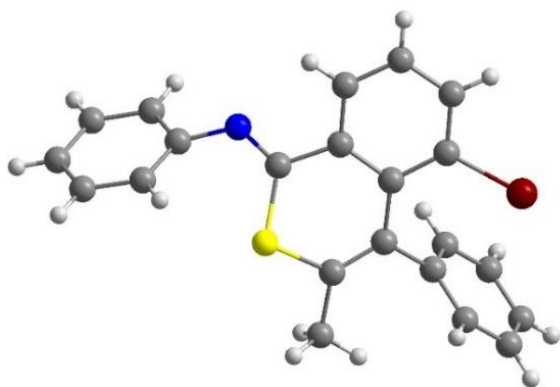


Table S6. Crystal data and structure refinement for **3u'a** (cr-jianxiu-g-xia-20221005)

Identification code	cr-jianxiu-g-xia-20221005
Empirical formula	C ₂₂ H ₁₆ BrNS
Formula weight	406.33
Temperature/K	100.00(10)
Crystal system	P2 ₁ 2 ₁ 2
Space group	orthorhombic
a/Å	22.70389(13)
b/Å	13.29859(7)
c/Å	5.82409(3)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	1758.467(17)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.535
μ/mm^{-1}	4.306
F(000)	824.0
Crystal size/mm ³	0.291 × 0.147 × 0.131
Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/°	7.704 to 134.15
Index ranges	-25 ≤ h ≤ 26, -15 ≤ k ≤ 15, -6 ≤ l ≤ 6
Reflections collected	17577
Independent reflections	3067 [R_{int} = 0.0227, R_{sigma} = 0.0137]

Data/restraints/parameters	3067/0/227
Goodness-of-fit on F^2	1.068
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0167$, $wR_2 = 0.0430$
Final R indexes [all data]	$R_1 = 0.0168$, $wR_2 = 0.0430$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.15/-0.37

X-Ray Diffraction Data of 3xa (CCDC: 2223005)

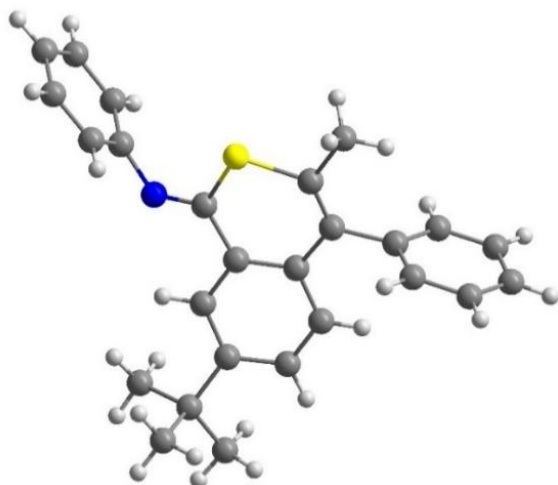


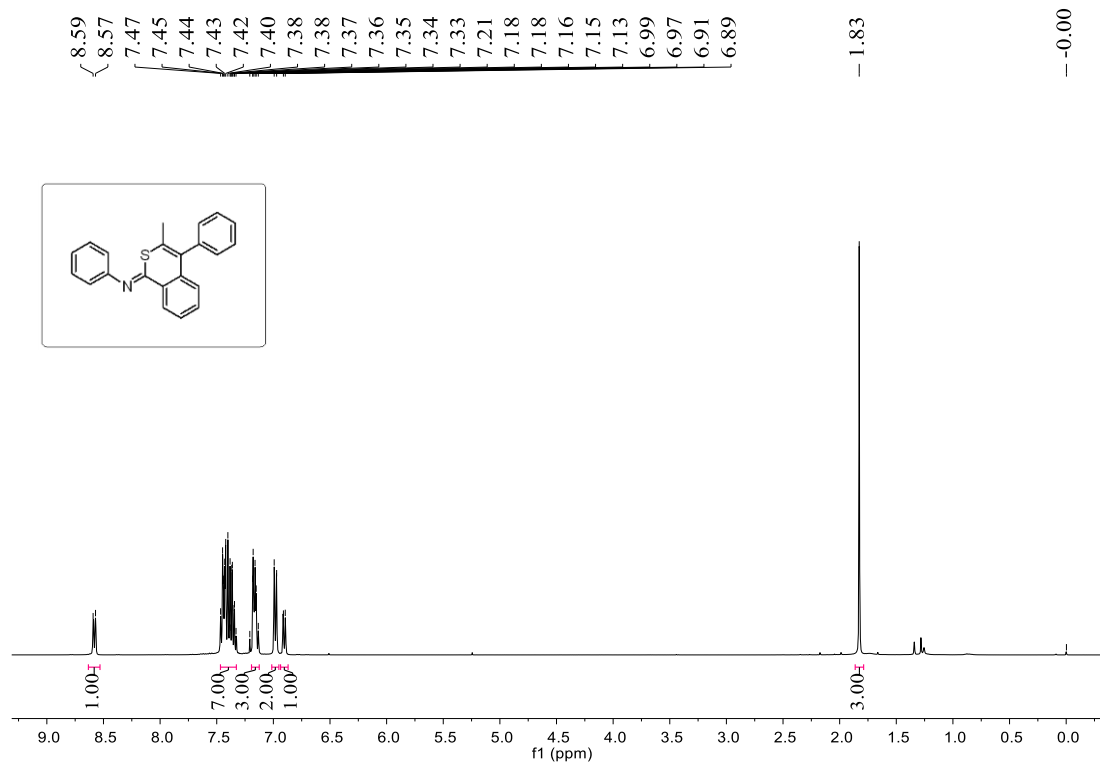
Table S7. Crystal data and structure refinement for **3xa** (cr-ea-hex_auto)

Identification code	cr-ea-hex_auto
Empirical formula	$C_{26}H_{25}NS$
Formula weight	383.53
Temperature/K	99.99(10)
Crystal system	P-1
Space group	triclinic
$a/\text{\AA}$	11.3822(2)
$b/\text{\AA}$	12.2394(3)
$c/\text{\AA}$	16.8294(4)
$\alpha/^\circ$	74.050(2)
$\beta/^\circ$	80.114(2)
$\gamma/^\circ$	67.955(2)
Volume/ \AA^3	2083.27(9)
Z	4

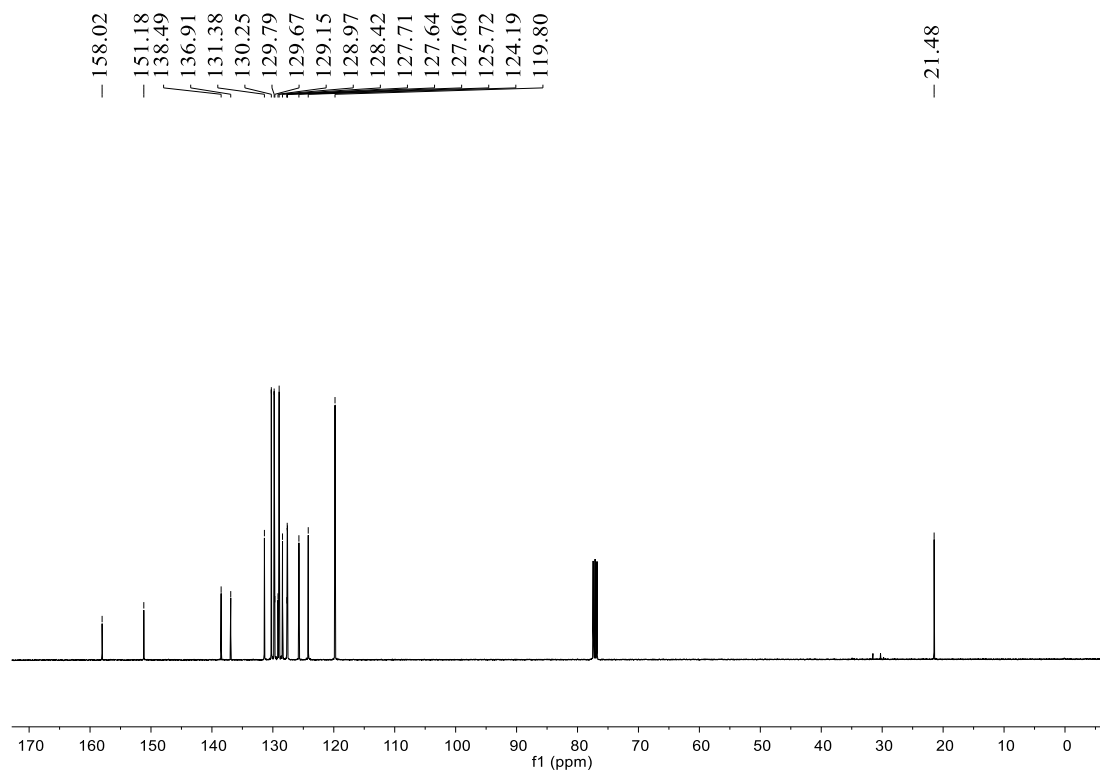
$\rho_{\text{calc}}/\text{cm}^3$	1.223
μ/mm^{-1}	1.439
F(000)	816.0
Crystal size/ mm^3	$0.22 \times 0.176 \times 0.066$
Radiation	Cu K α ($\lambda = 1.54184$)
2Θ range for data collection/ $^\circ$	5.478 to 134.14
Index ranges	$-13 \leq h \leq 9, -14 \leq k \leq 12, -19 \leq l \leq 19$
Reflections collected	21719
Independent reflections	7193 [$R_{\text{int}} = 0.0281, R_{\text{sigma}} = 0.0313$]
Data/restraints/parameters	7193/12/507
Goodness-of-fit on F^2	1.046
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0658, wR_2 = 0.1765$
Final R indexes [all data]	$R_1 = 0.0704, wR_2 = 0.1816$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.19/-0.36

7. NMR Spectra of Products

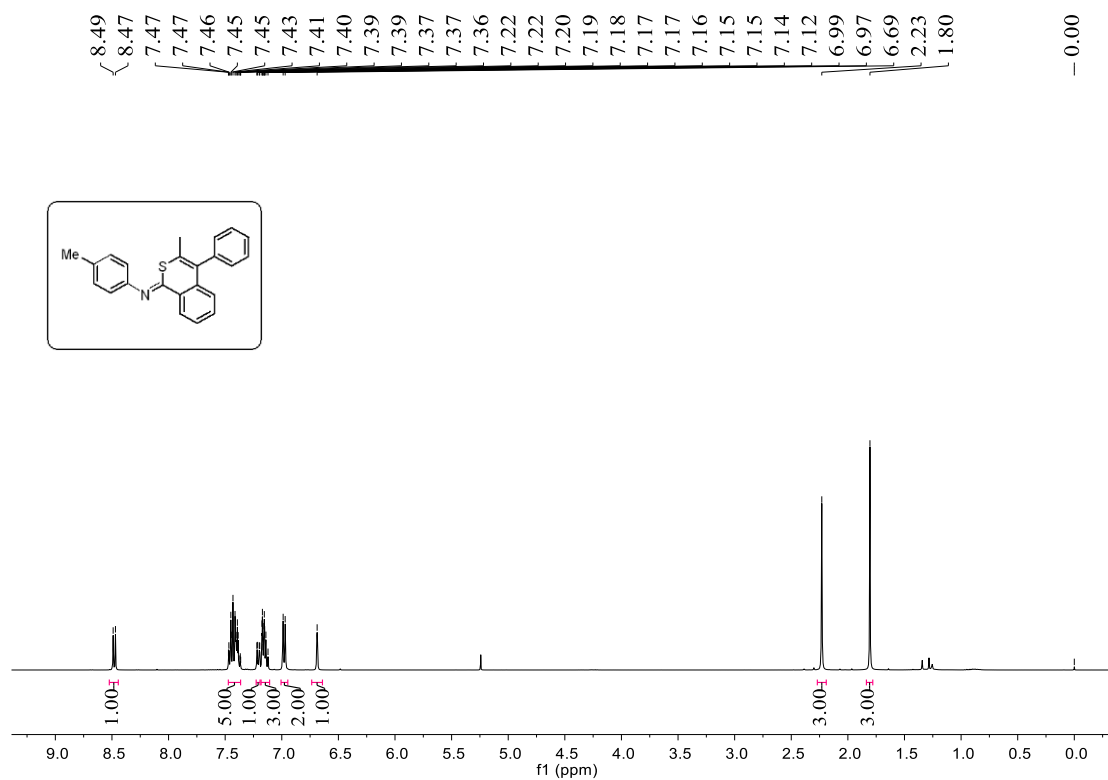
^1H NMR (400 MHz, CDCl_3) of compound **3aa**.



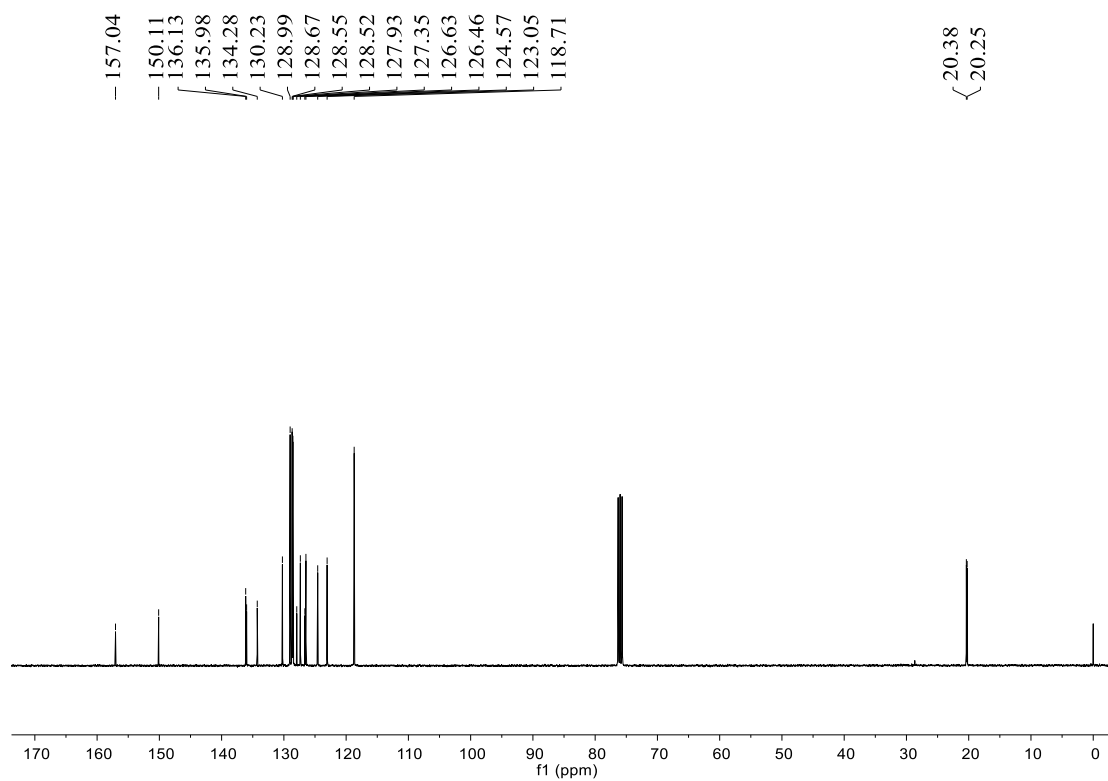
^{13}C NMR (100 MHz, CDCl_3) of compound **3aa**.



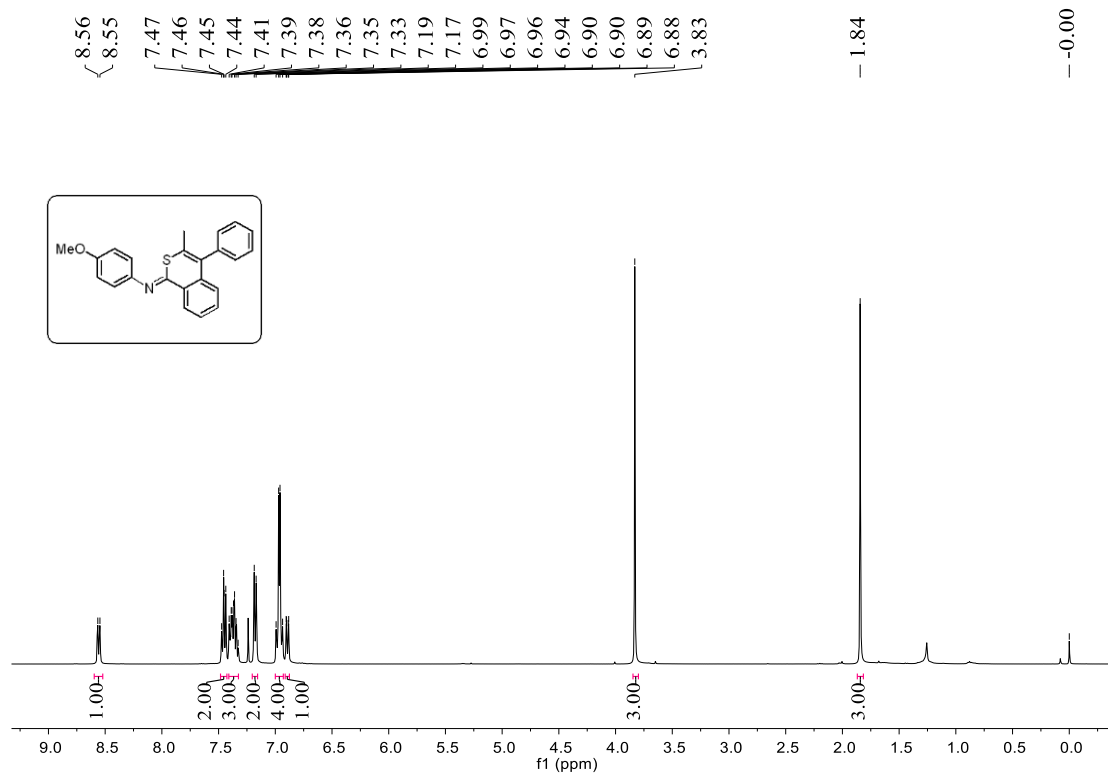
^1H NMR (400 MHz, CDCl_3) of compound **3ba**.



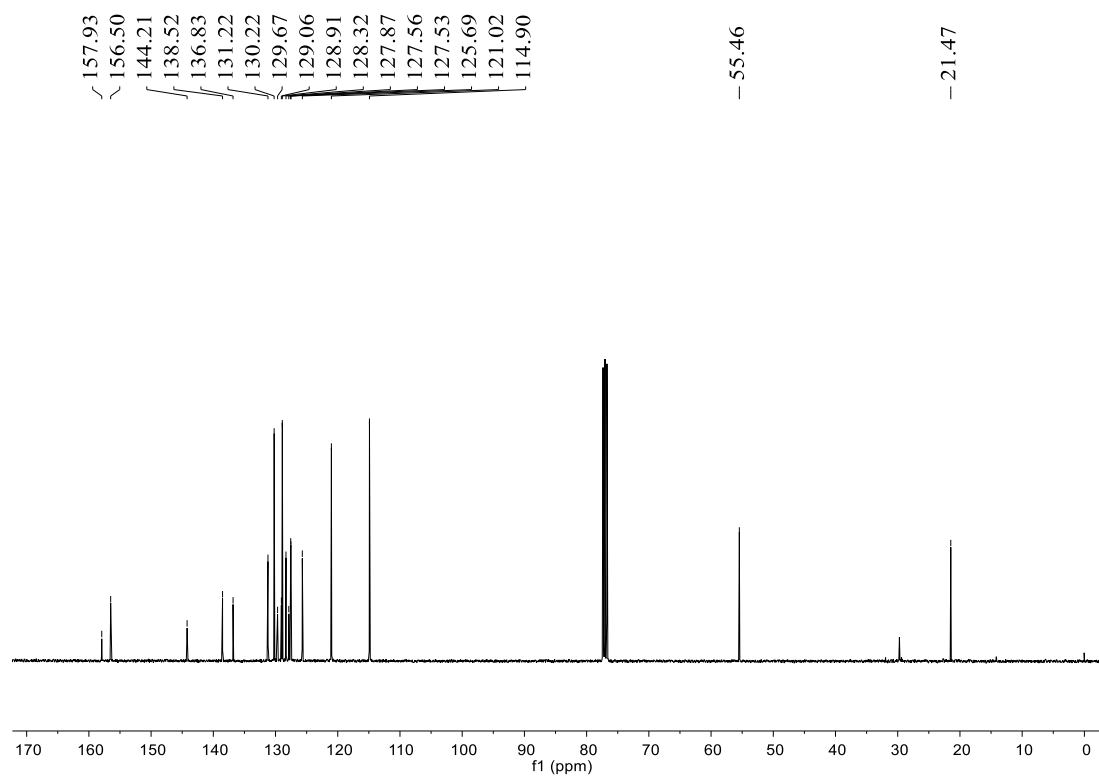
^{13}C NMR (100 MHz, CDCl_3) of compound **3ba**.



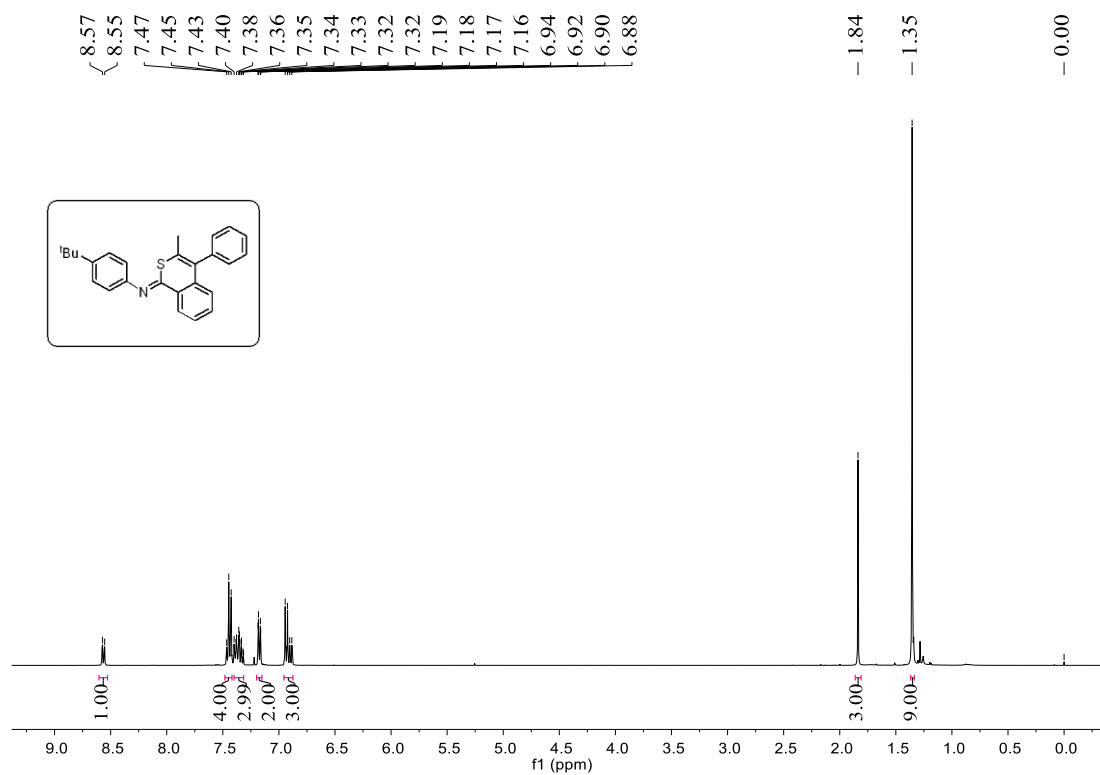
¹H NMR (400 MHz, CDCl₃) of compound **3ca**.



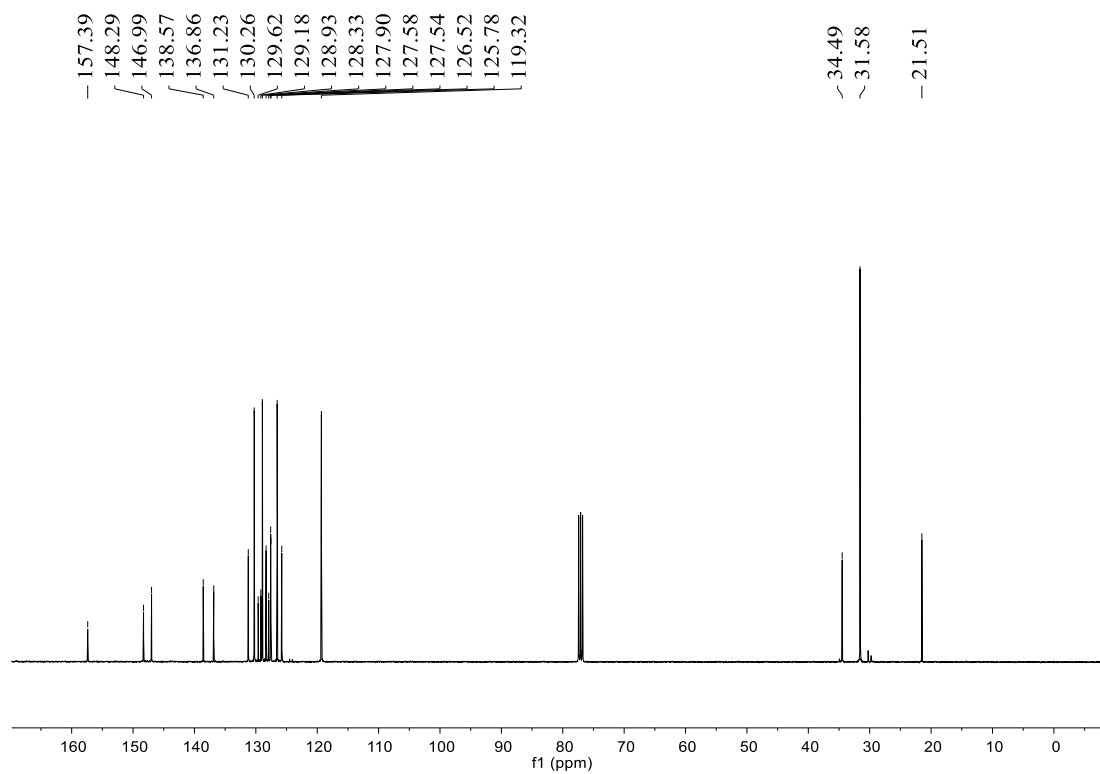
¹³C NMR (100 MHz, CDCl₃) of compound **3ca**.



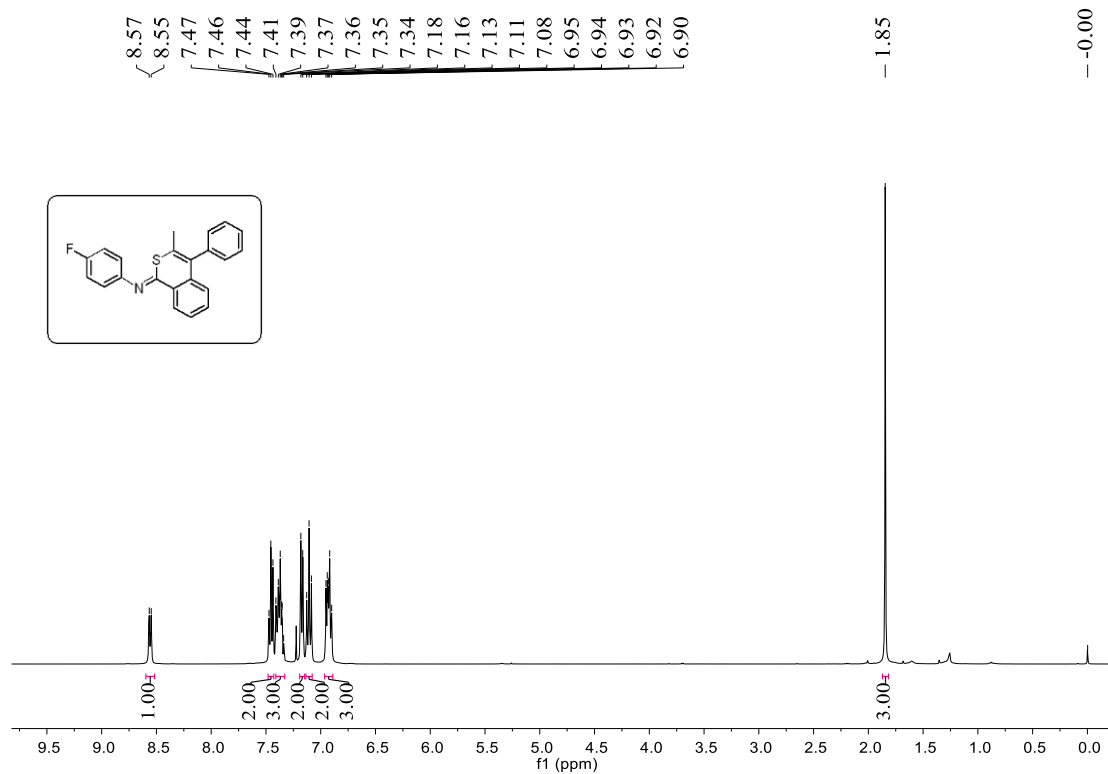
^1H NMR (400 MHz, CDCl_3) of compound **3da**.



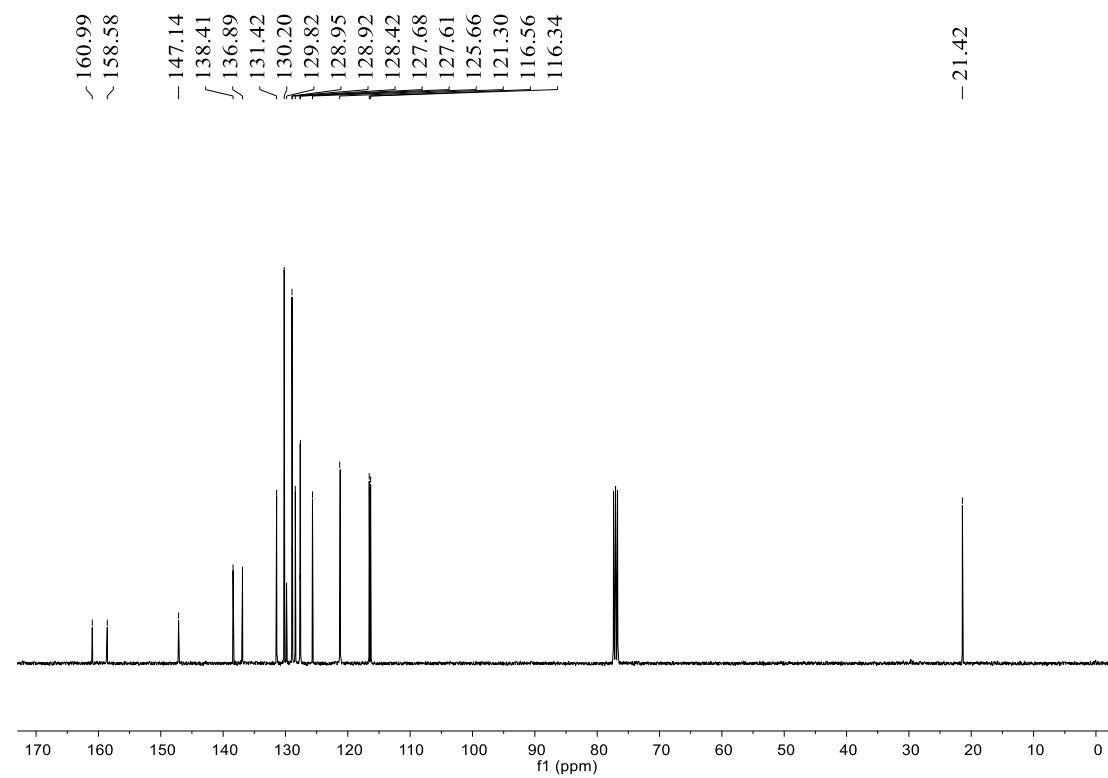
^{13}C NMR (100 MHz, CDCl_3) of compound **3da**.



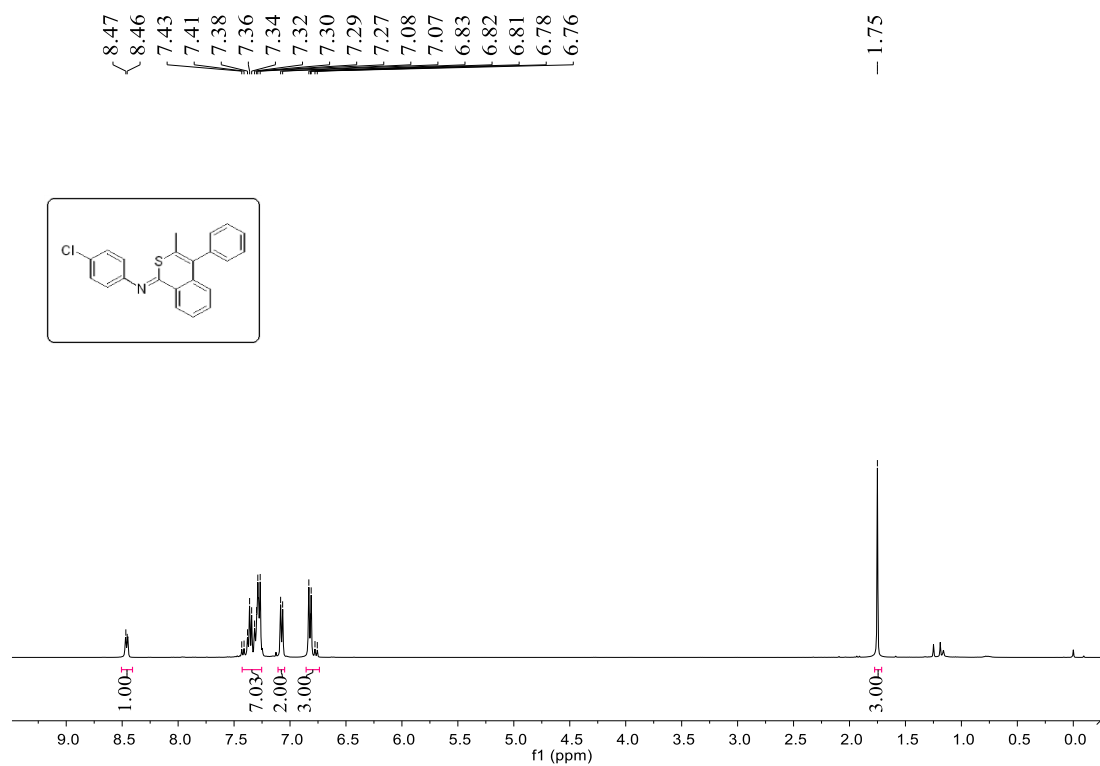
¹H NMR (400 MHz, CDCl₃) of compound **3ea**.



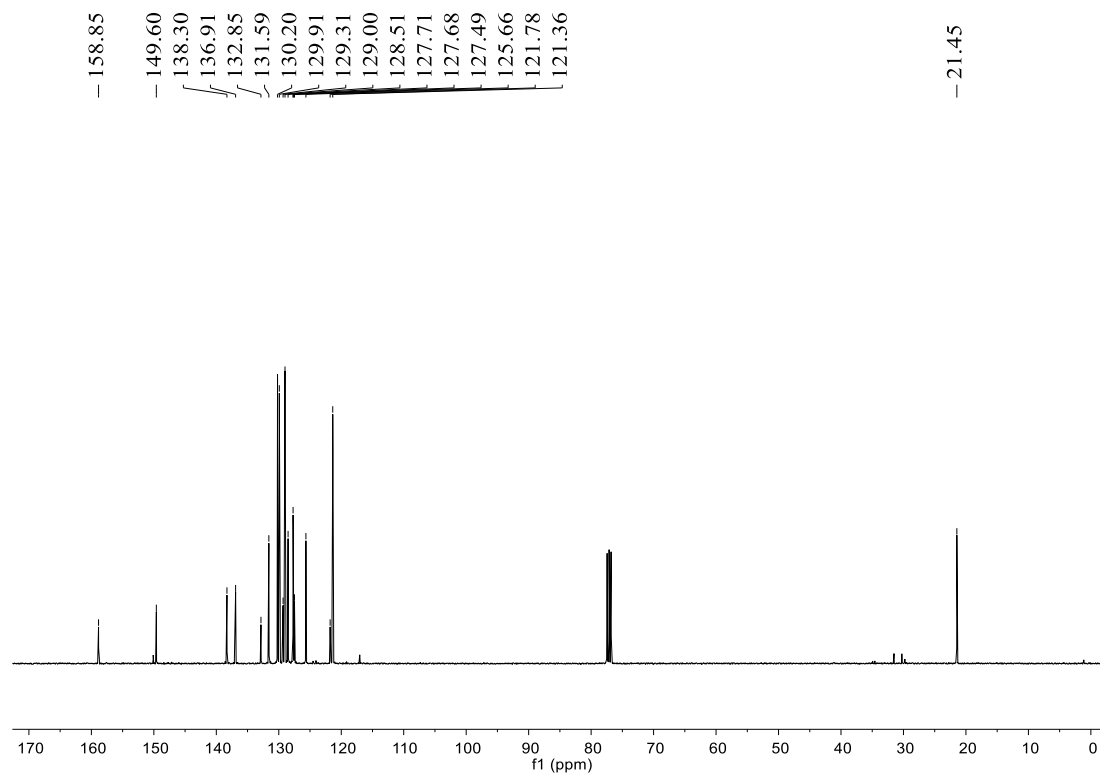
¹³C NMR (100 MHz, CDCl₃) of compound **3ea**.



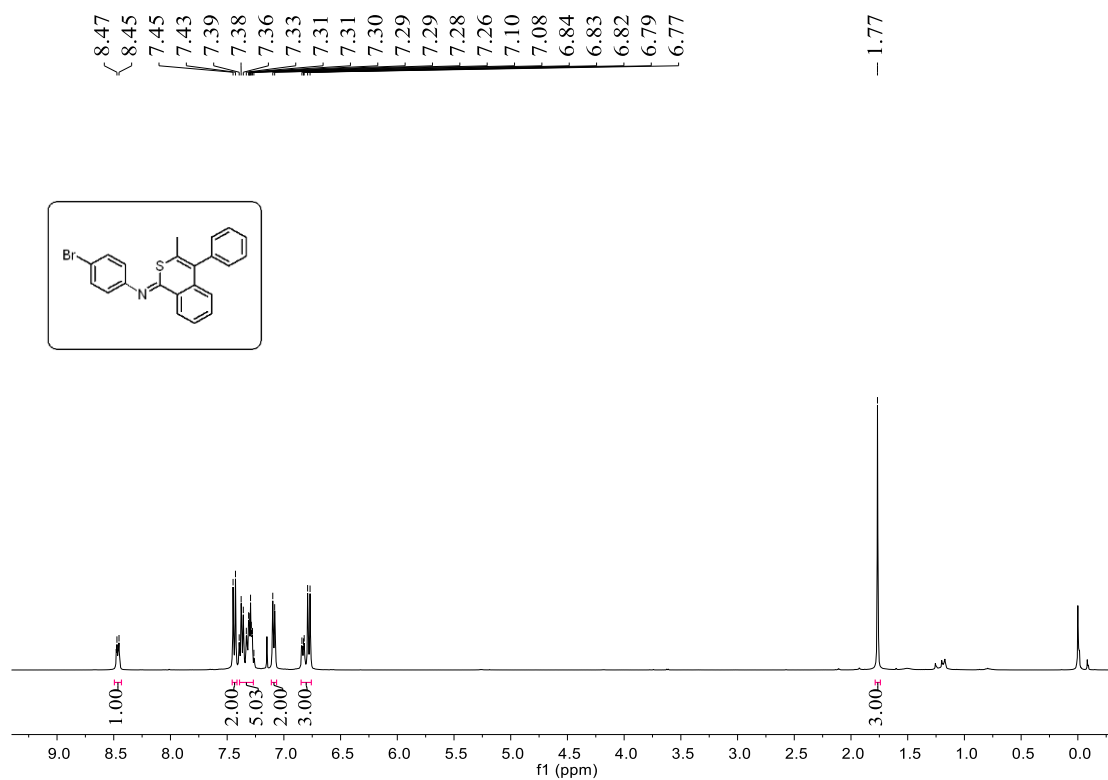
^1H NMR (400 MHz, CDCl_3) of compound **3fa**.



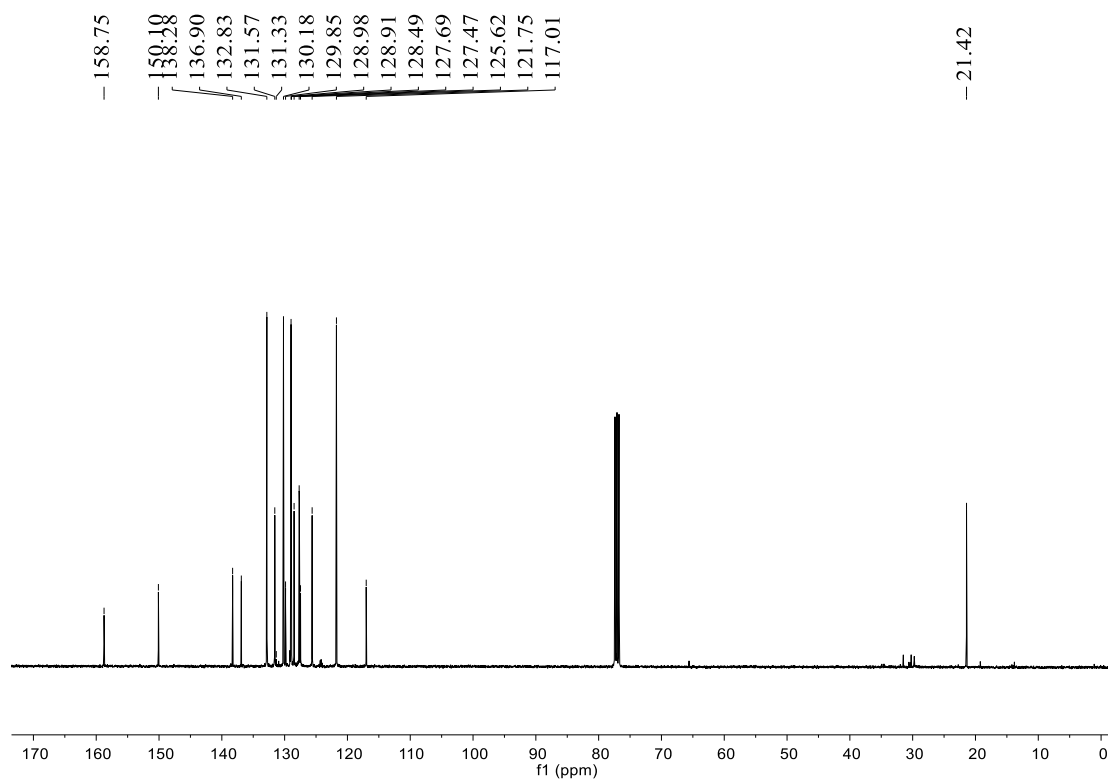
^{13}C NMR (100 MHz, CDCl_3) of compound **3fa**.



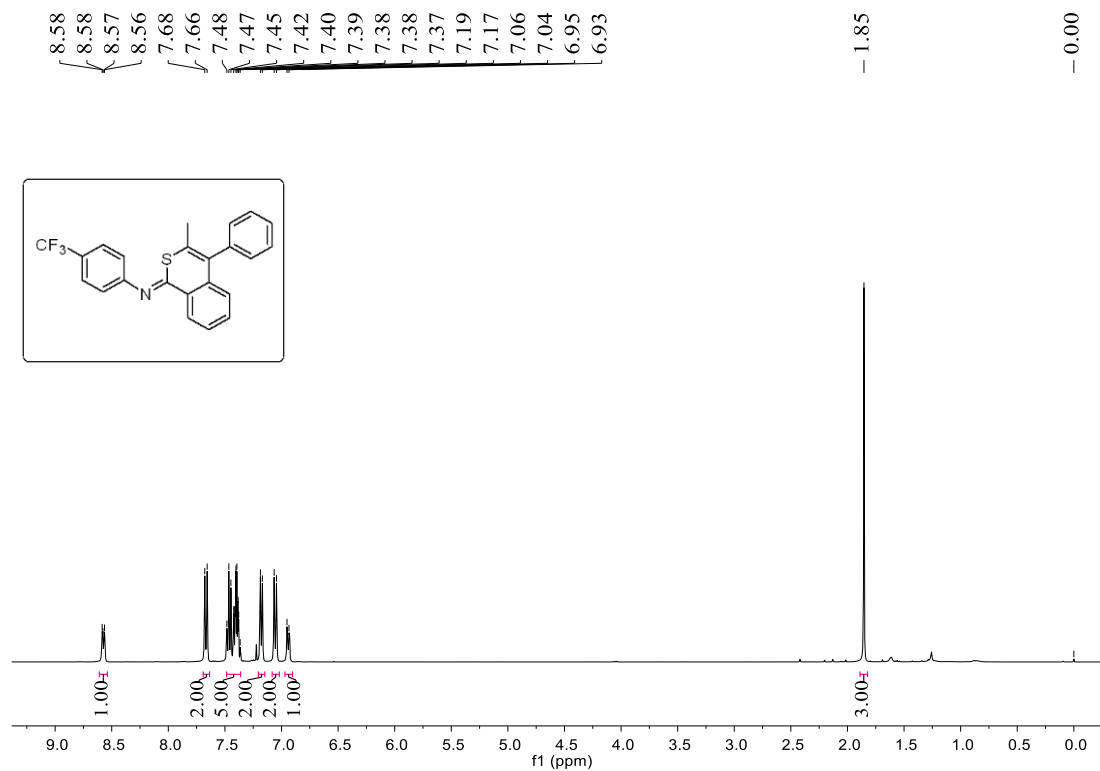
^1H NMR (400 MHz, CDCl_3) of compound **3ga**.



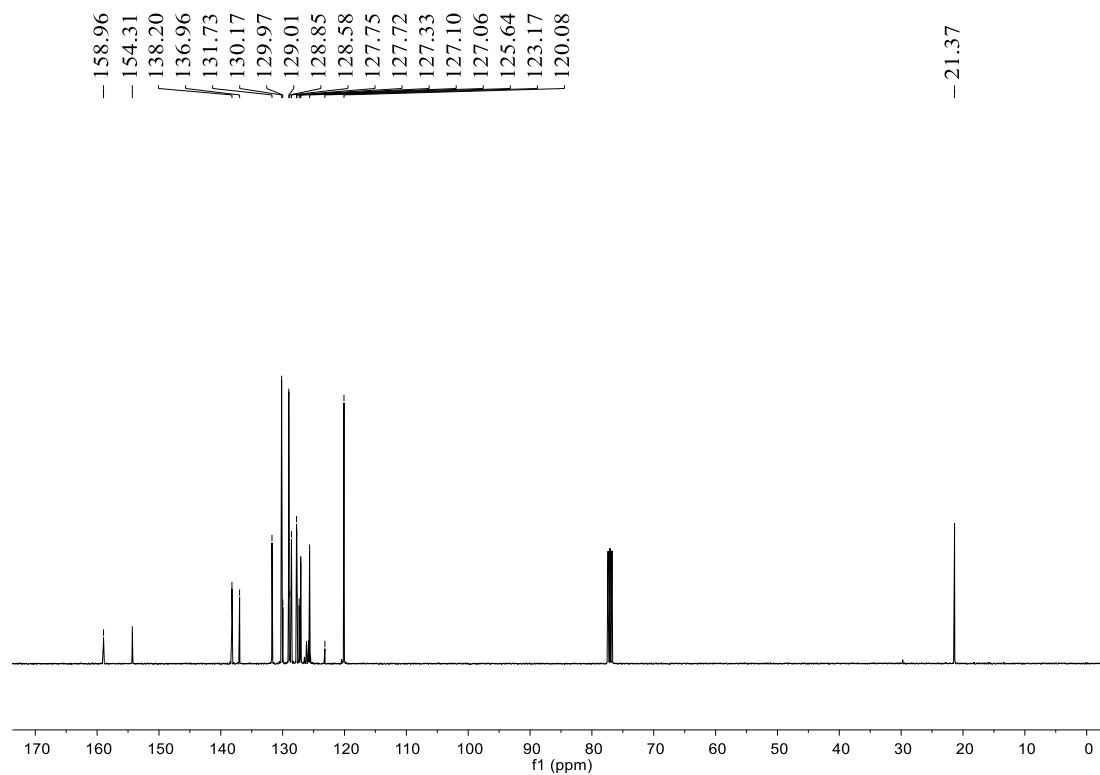
^{13}C NMR (100 MHz, CDCl_3) of compound **3ga**.



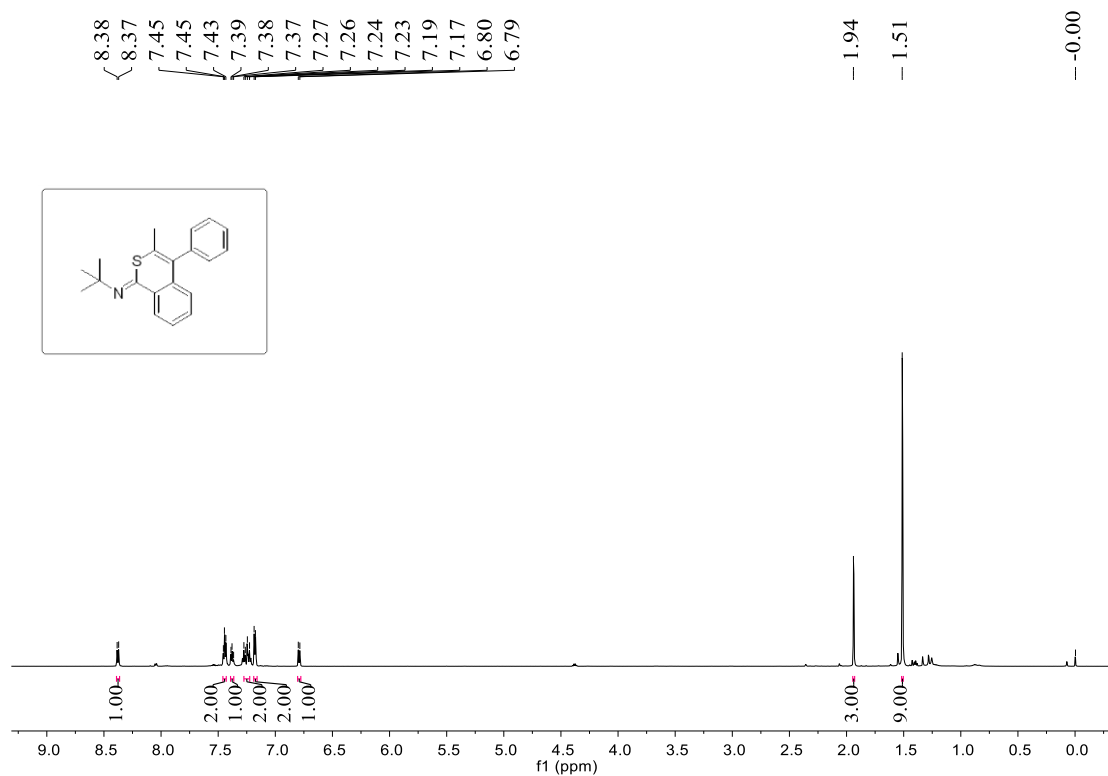
¹H NMR (400 MHz, CDCl₃) of compound **3ha**.



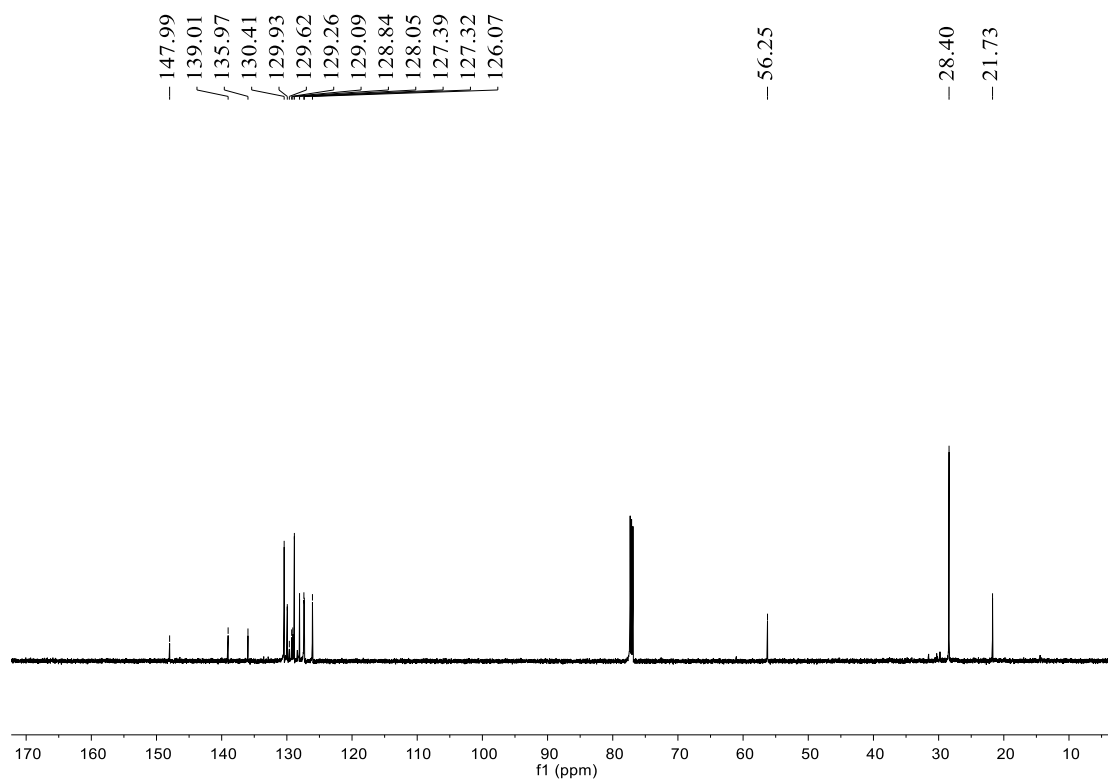
¹³C NMR (100 MHz, CDCl₃) of compound **3ha**.



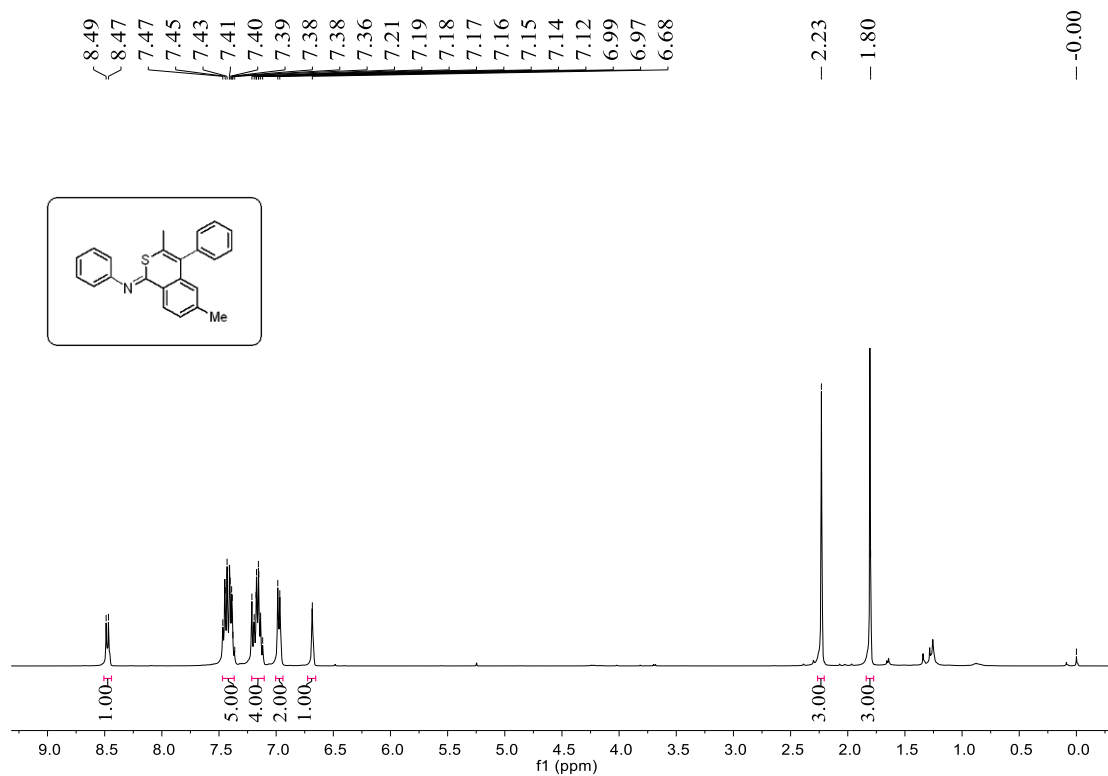
^1H NMR (400 MHz, CDCl_3) of compound **3ia**.



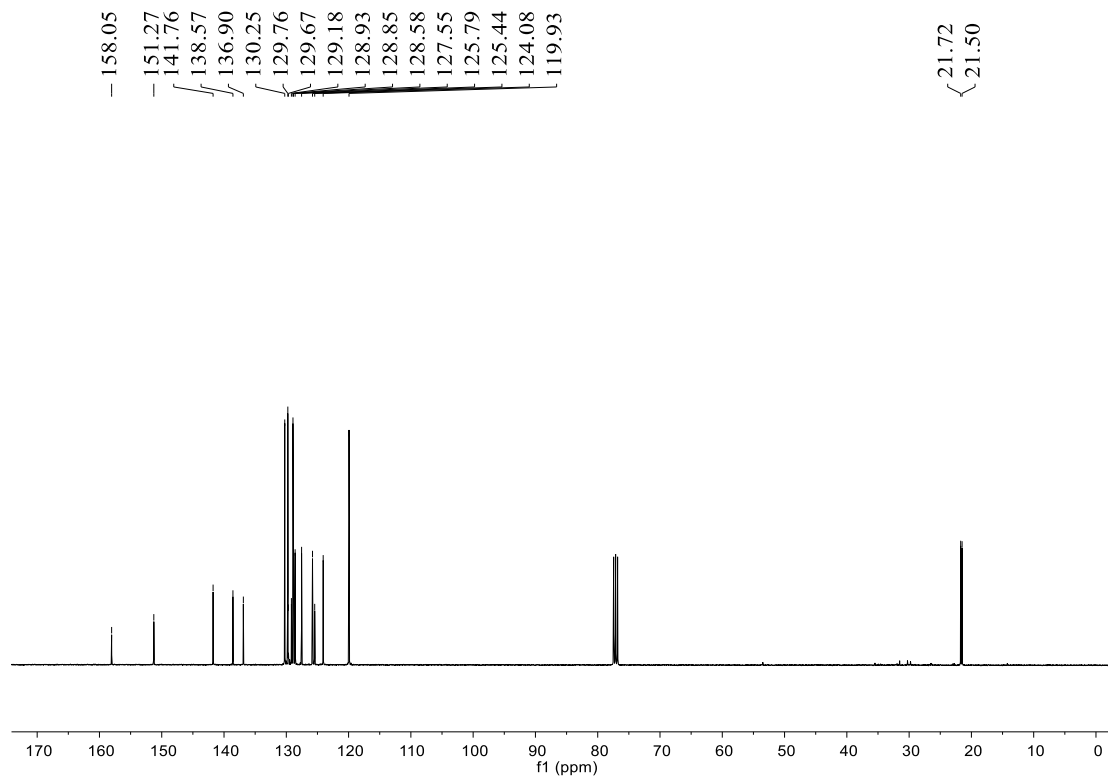
^{13}C NMR (100 MHz, CDCl_3) of compound **3ia**.



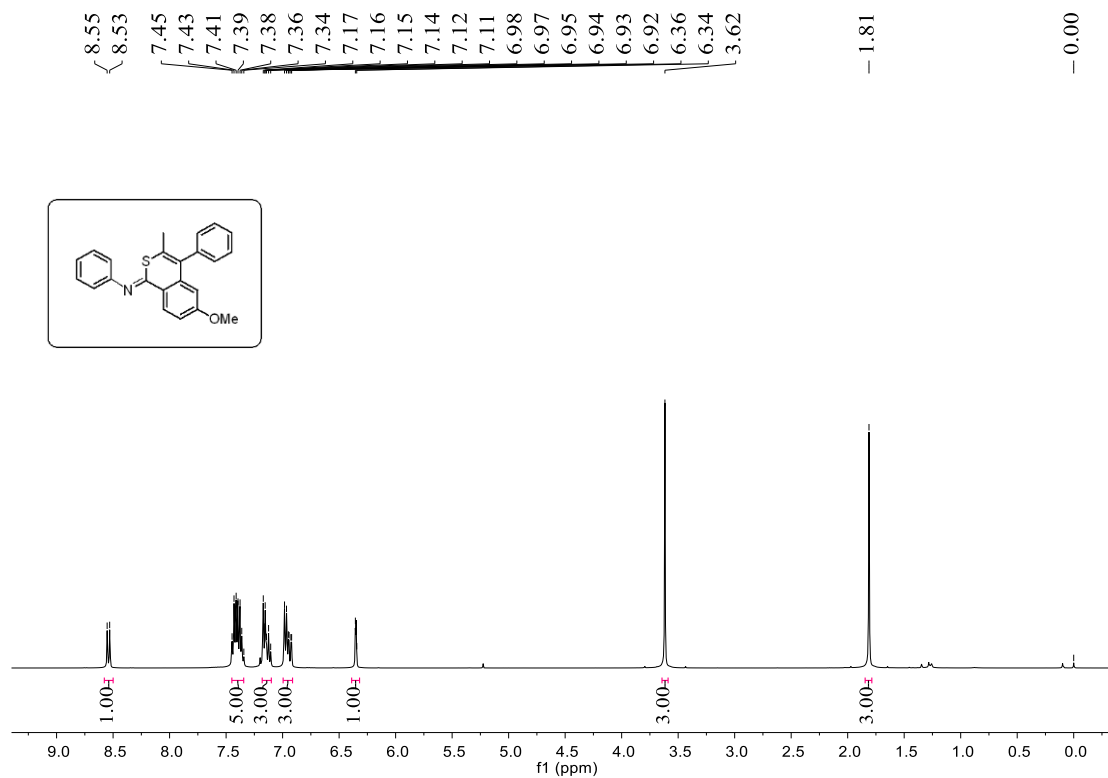
^1H NMR (400 MHz, CDCl_3) of compound **3ja**.



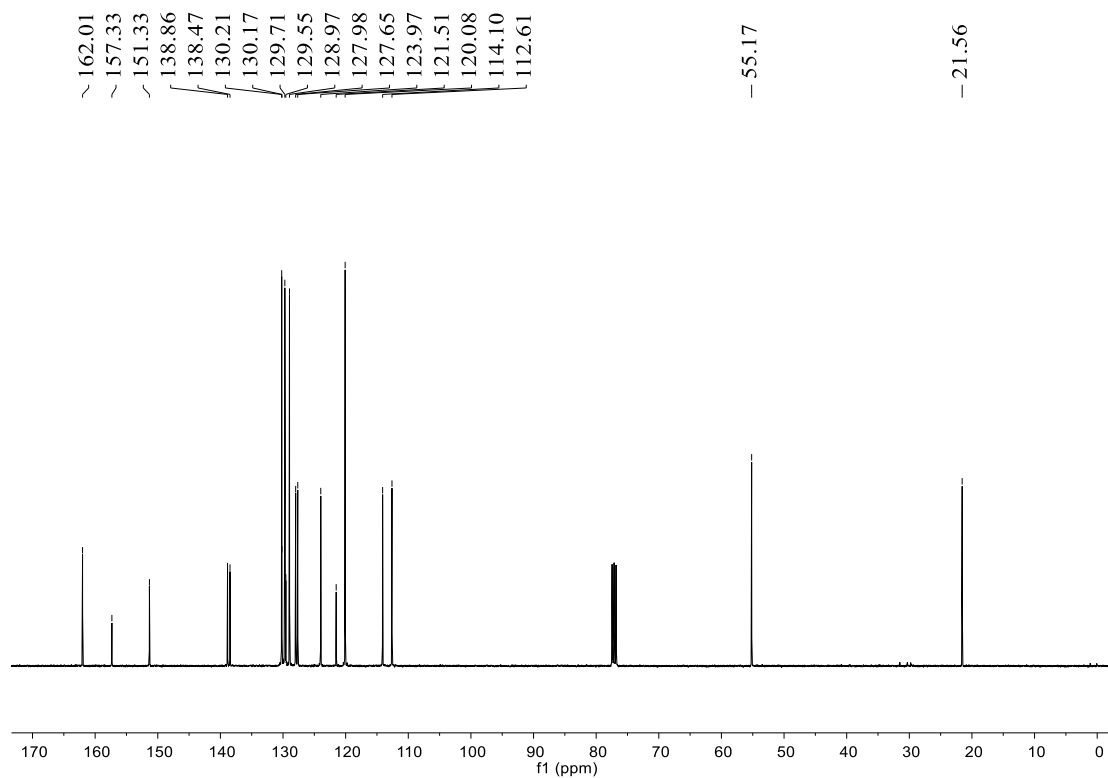
^{13}C NMR (100 MHz, CDCl_3) of compound **3ja**.



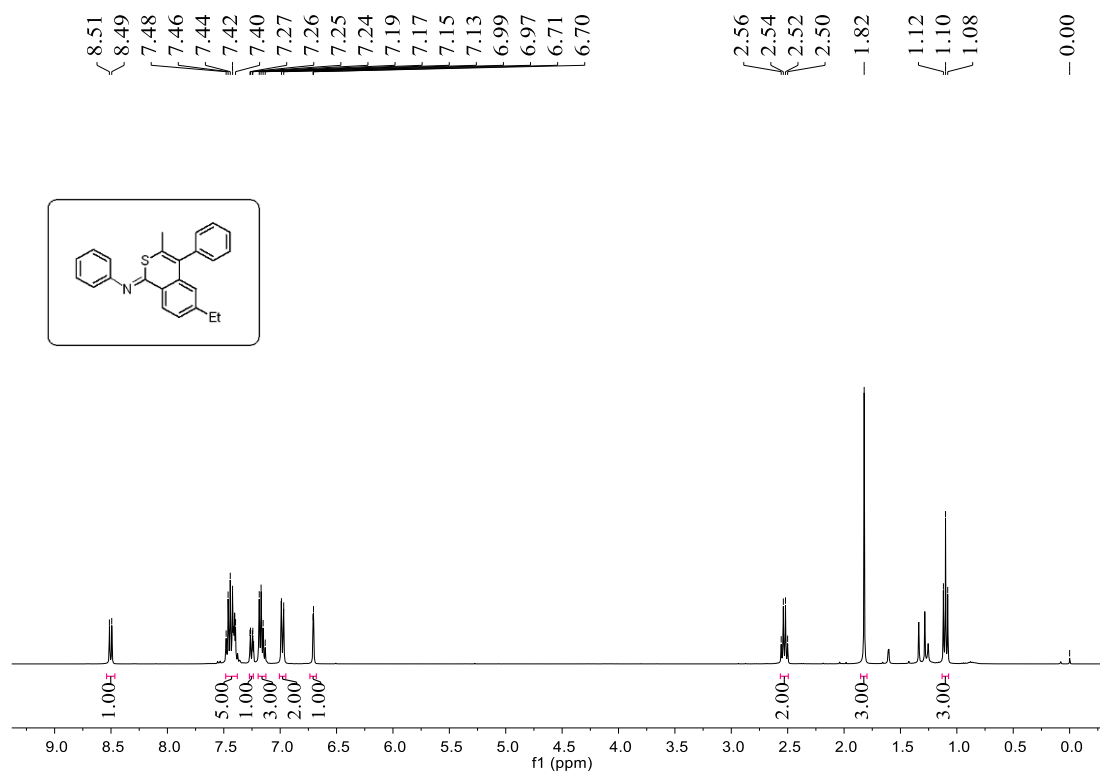
^1H NMR (400 MHz, CDCl_3) of compound **3ka**.



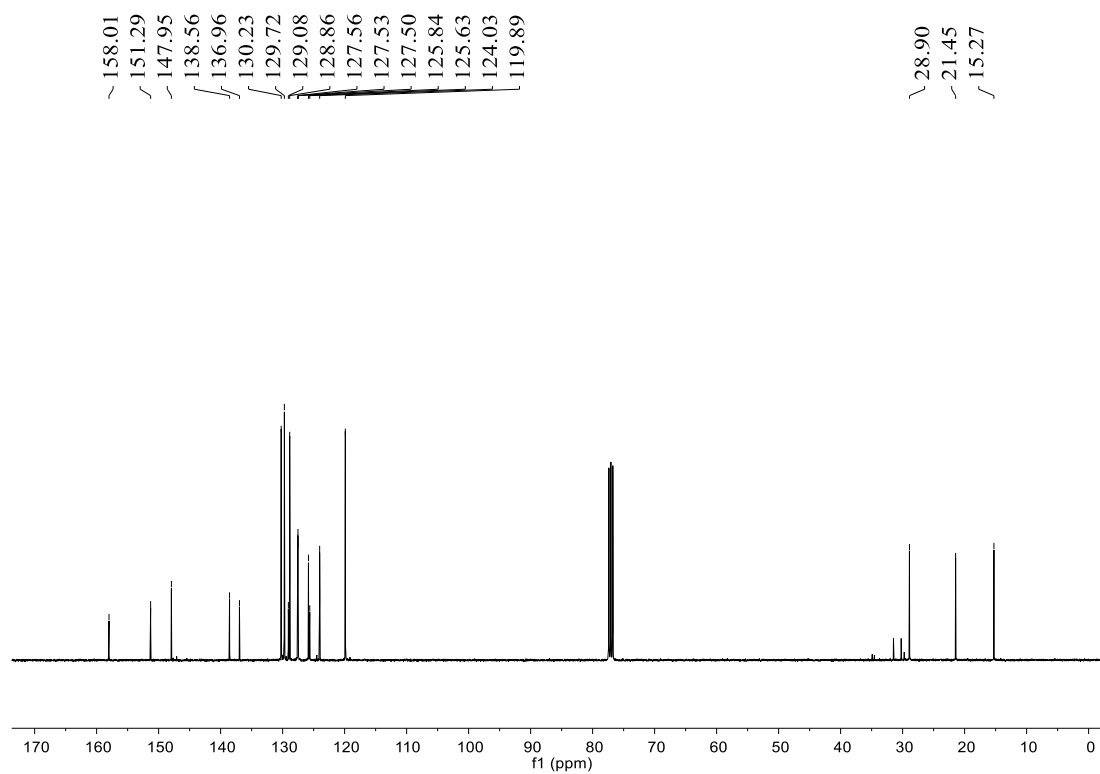
^{13}C NMR (100 MHz, CDCl_3) of compound **3ka**.



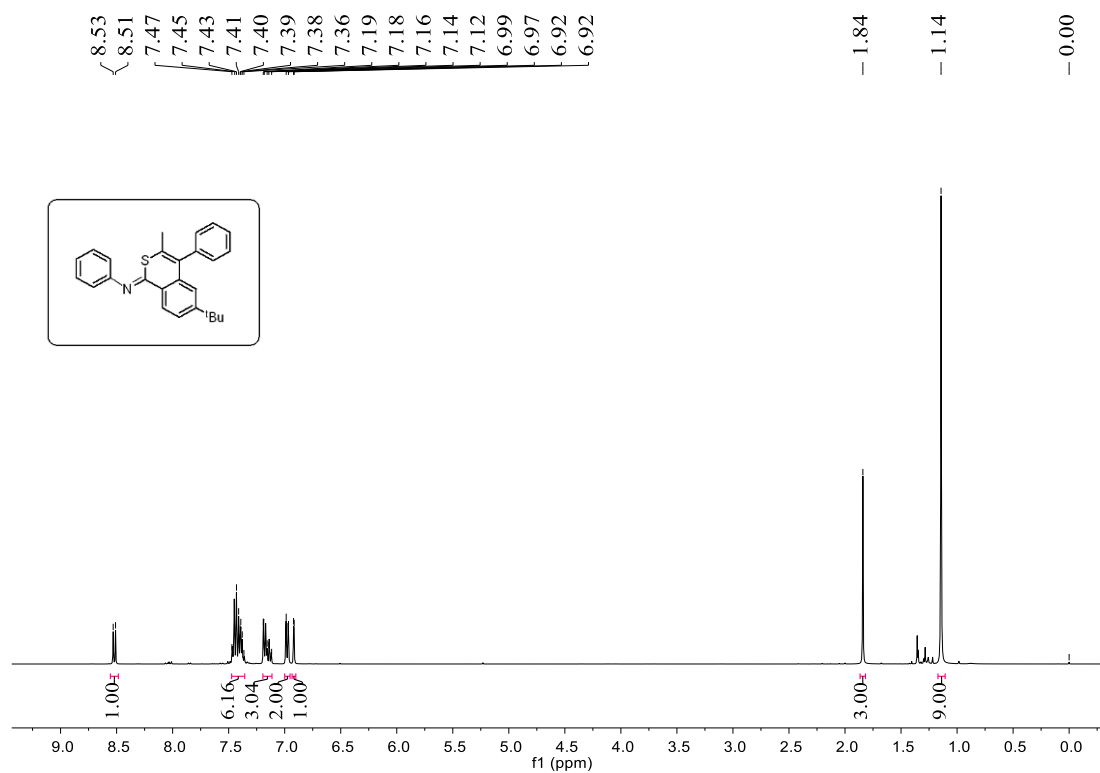
^1H NMR (400 MHz, CDCl_3) of compound **3la**.



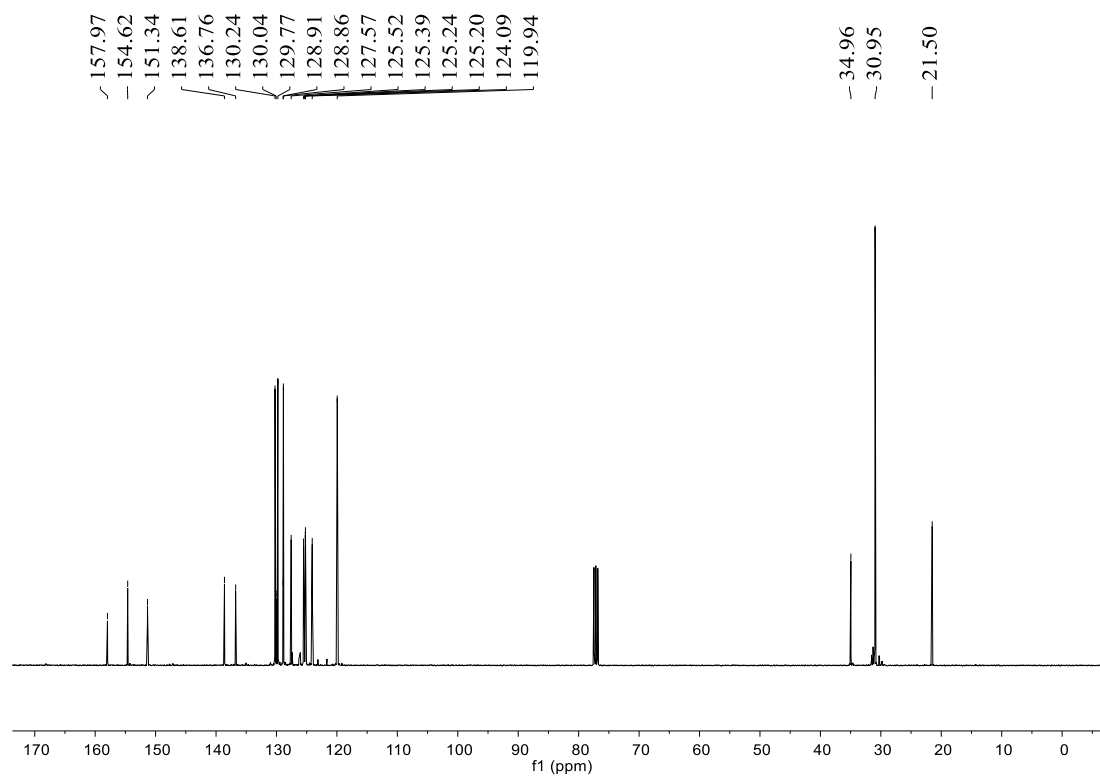
^{13}C NMR (100 MHz, CDCl_3) of compound **3la**.



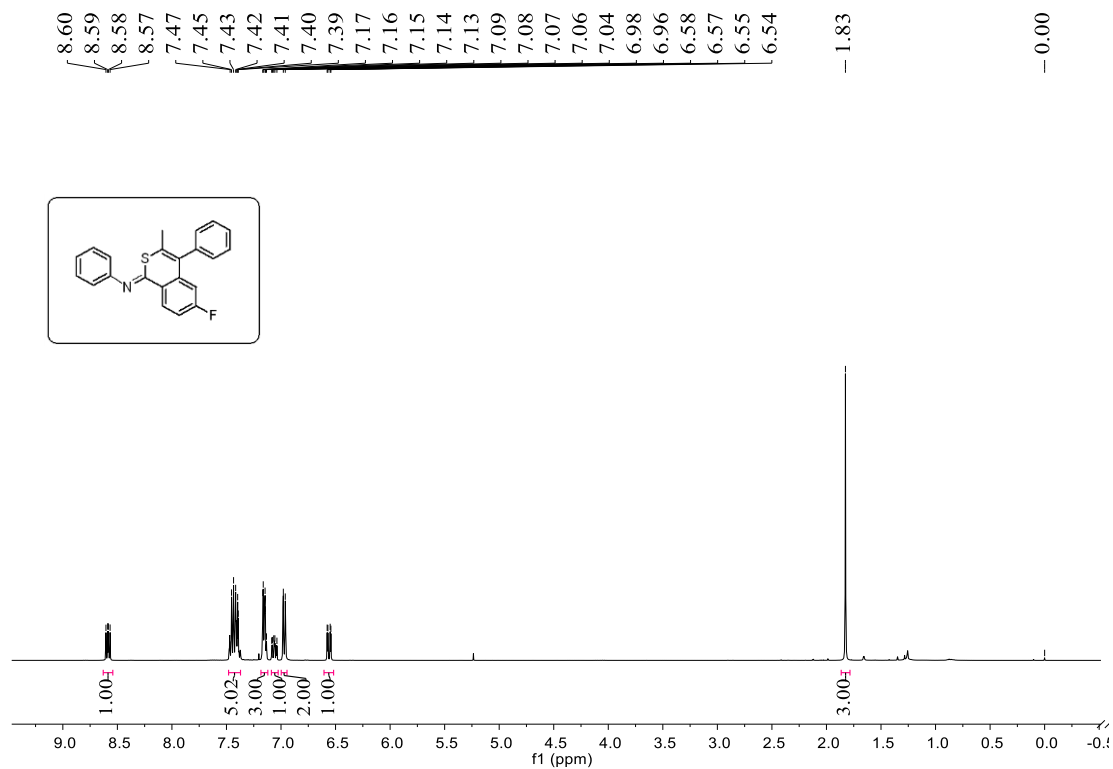
^1H NMR (400 MHz, CDCl_3) of compound **3ma**.



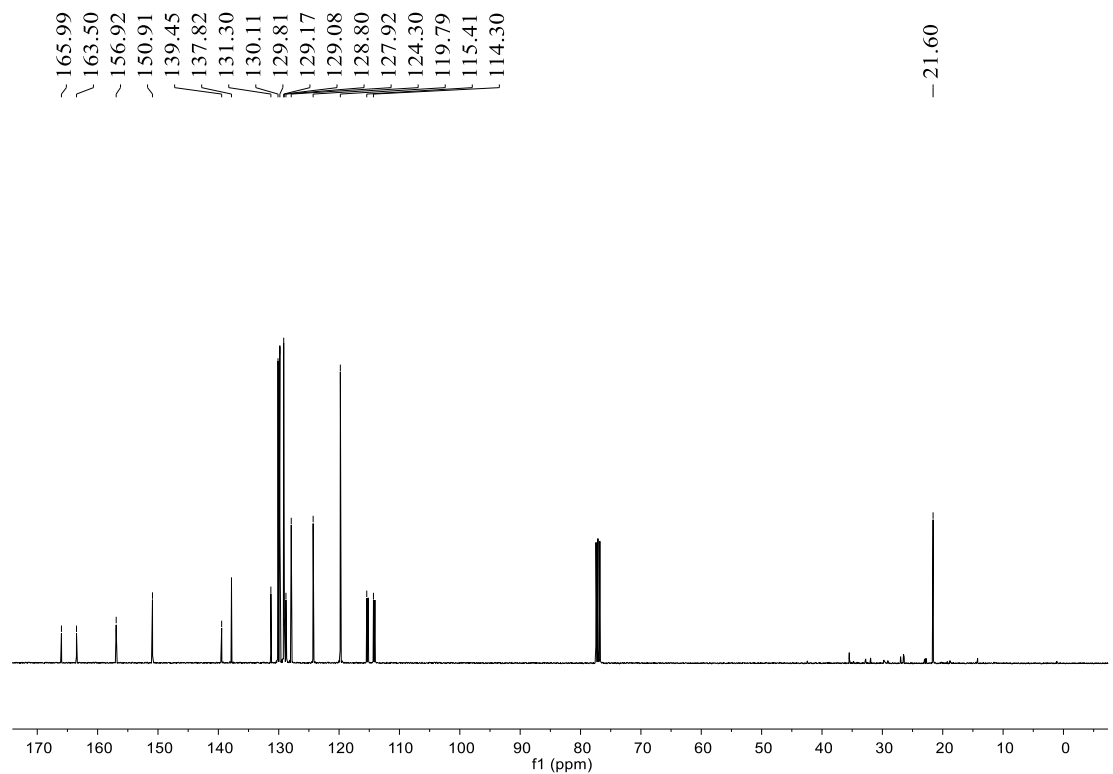
^{13}C NMR (100 MHz, CDCl_3) of compound **3ma**.



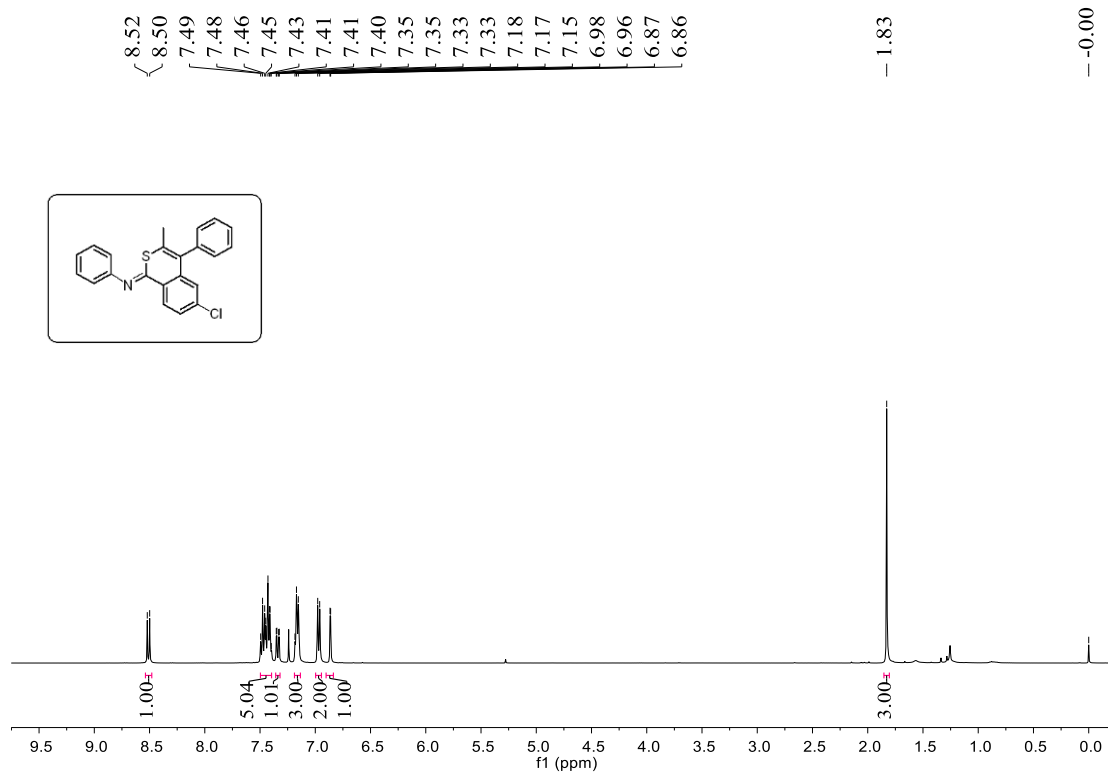
^1H NMR (400 MHz, CDCl_3) of compound **3na**.



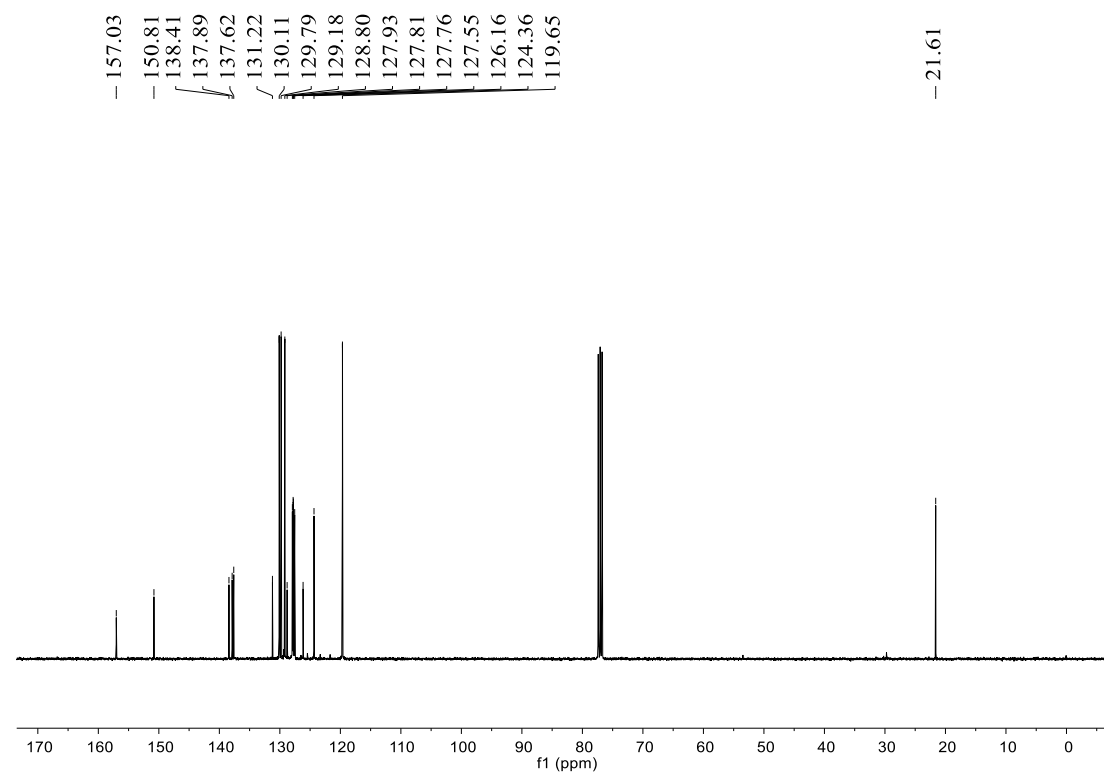
^{13}C NMR (100 MHz, CDCl_3) of compound **3na**.



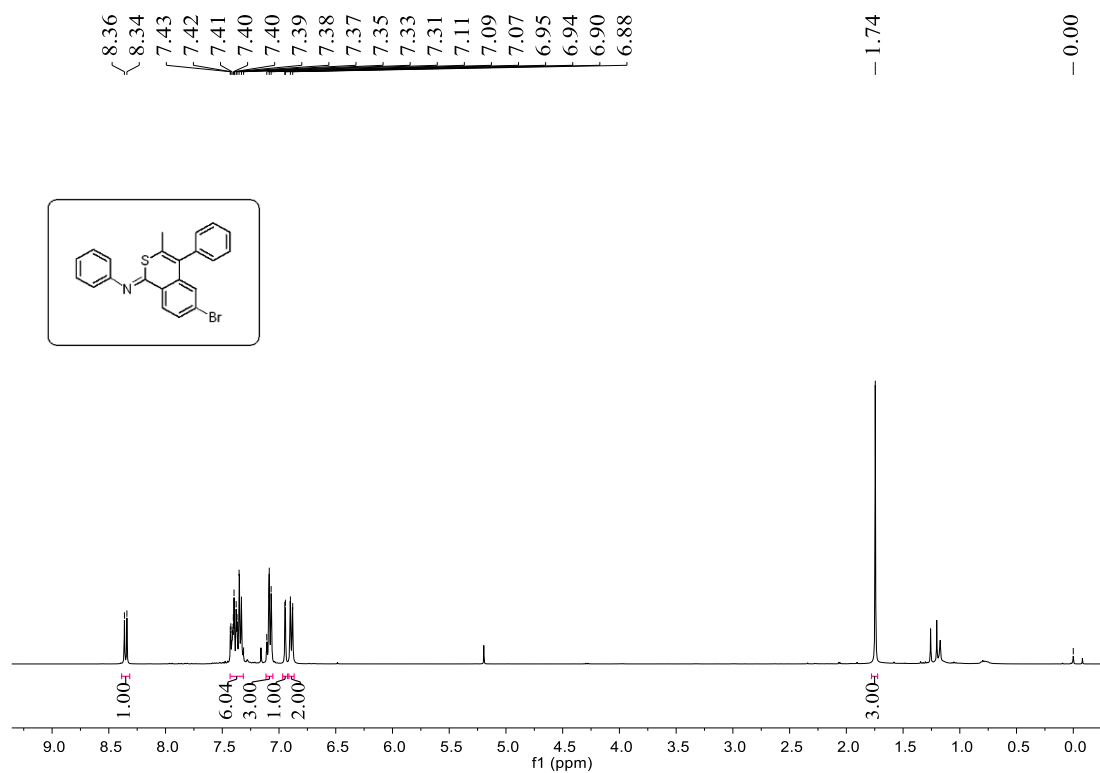
^1H NMR (400 MHz, CDCl_3) of compound **30a**.



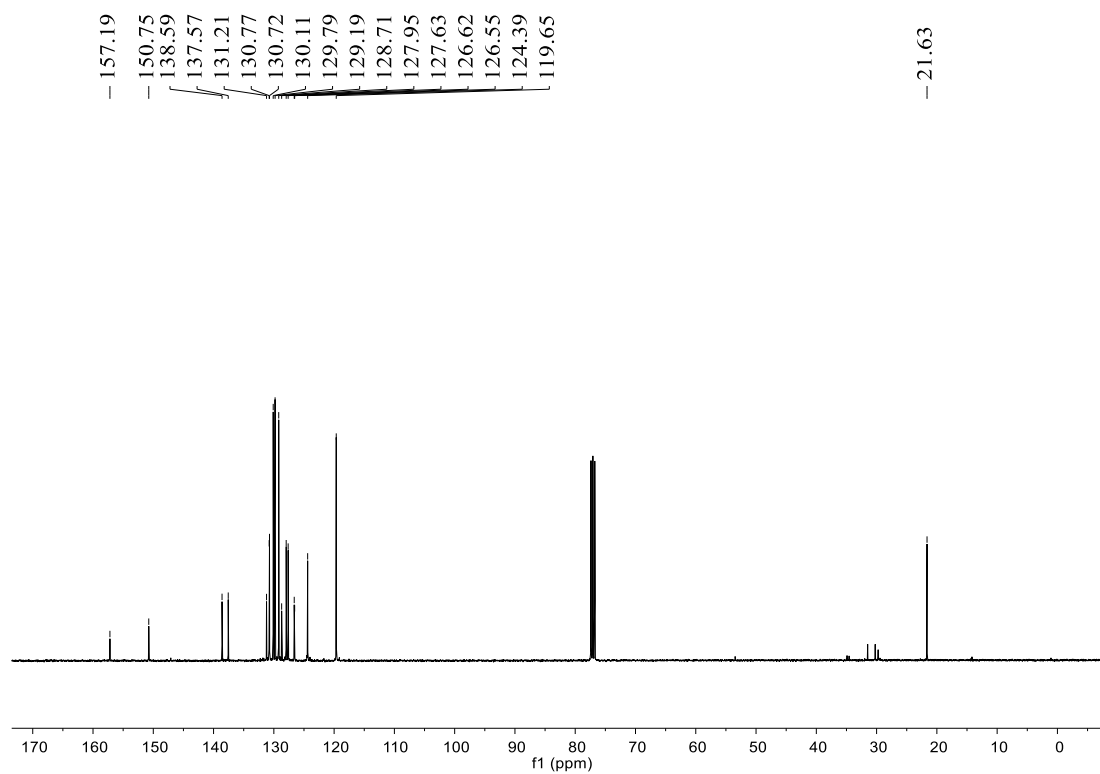
^{13}C NMR (100 MHz, CDCl_3) of compound **30a**.



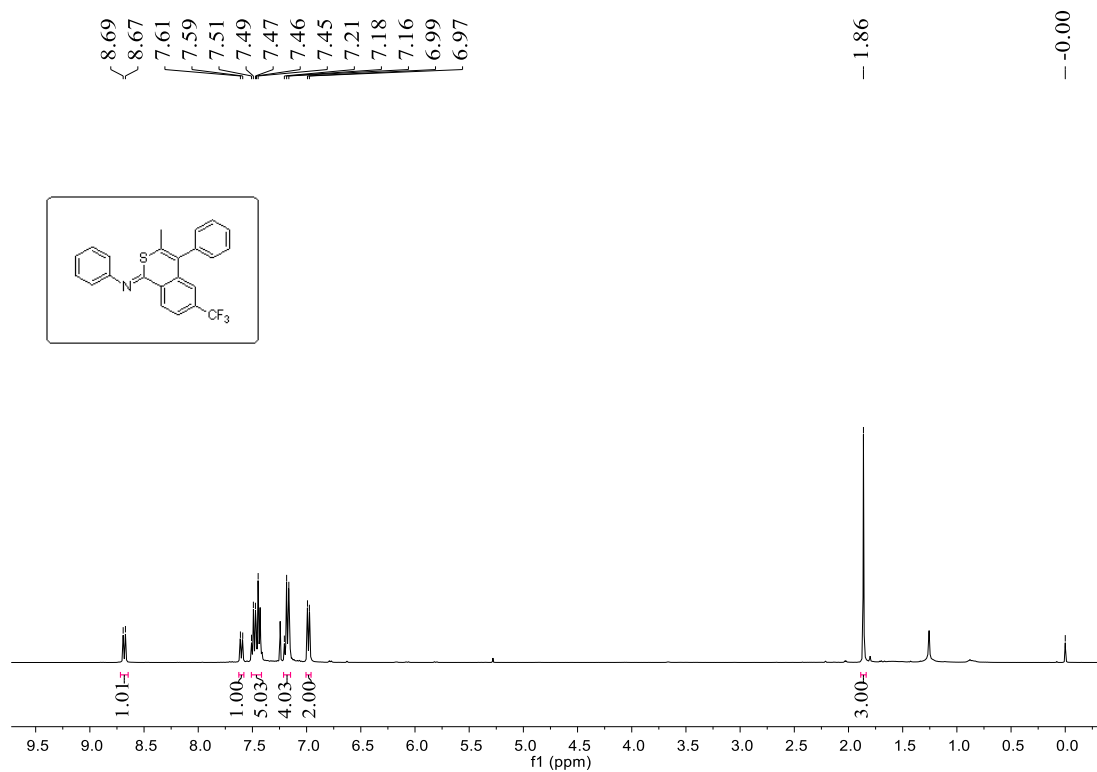
^1H NMR (400 MHz, CDCl_3) of compound **3pa**.



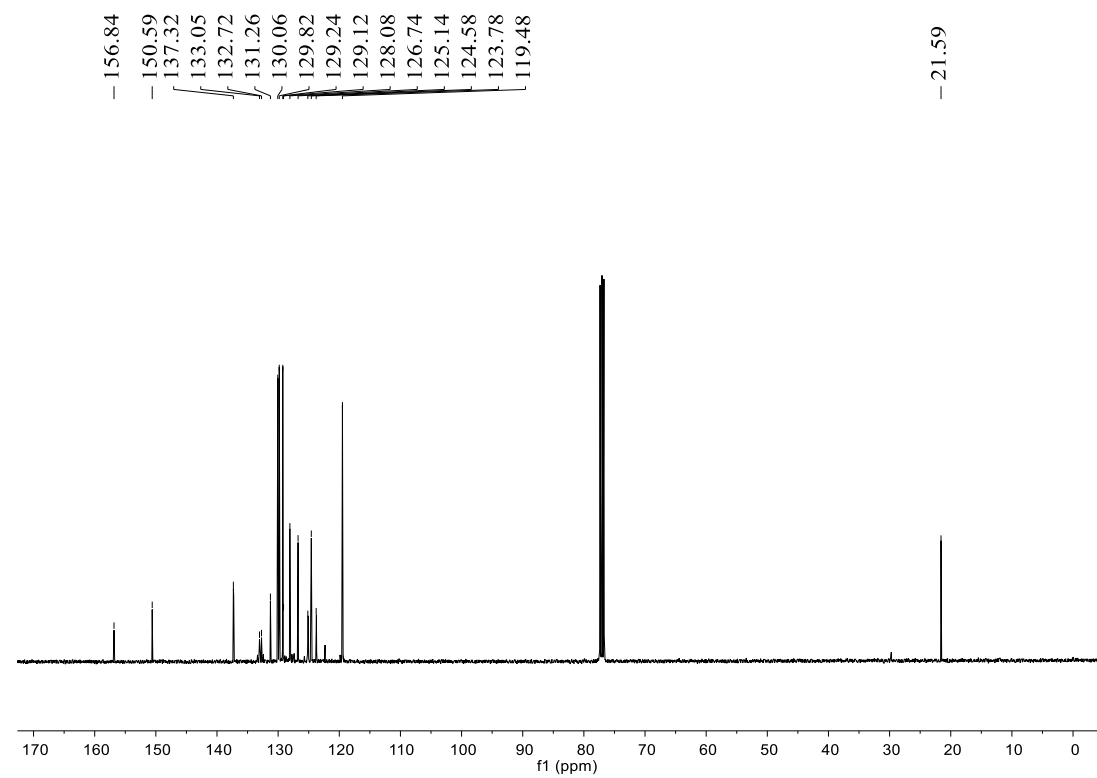
^{13}C NMR (100 MHz, CDCl_3) of compound **3pa**.



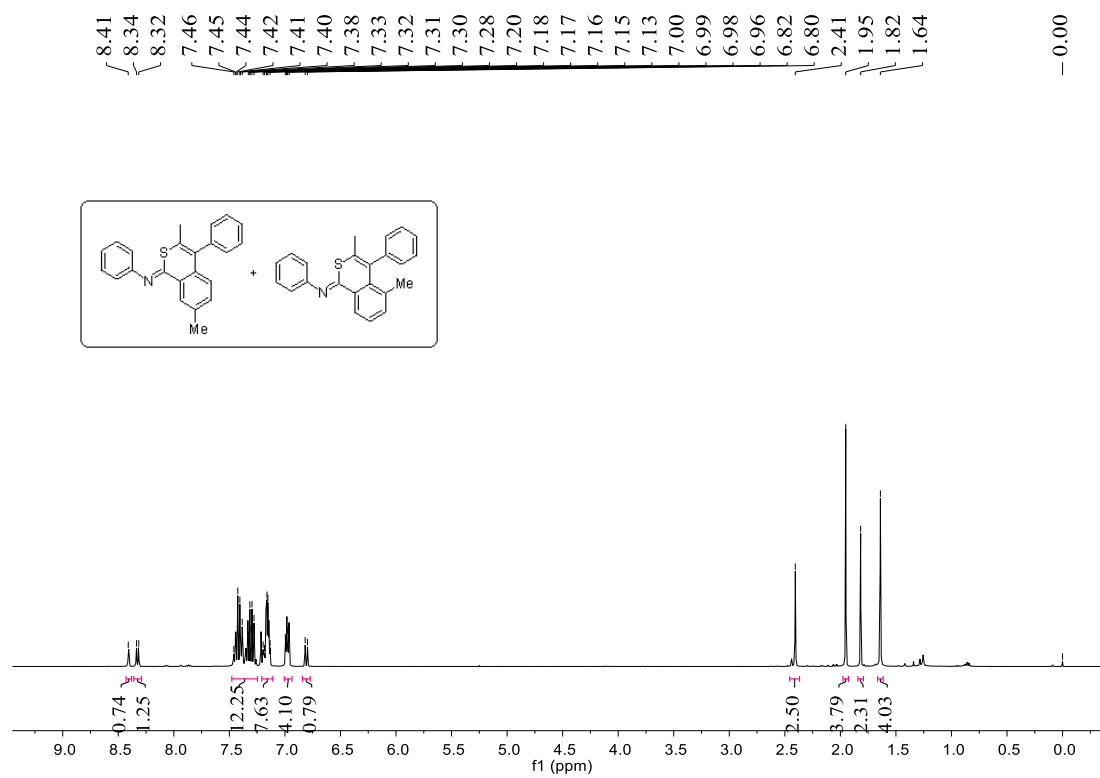
^1H NMR (400 MHz, CDCl_3) of compound **3qa**.



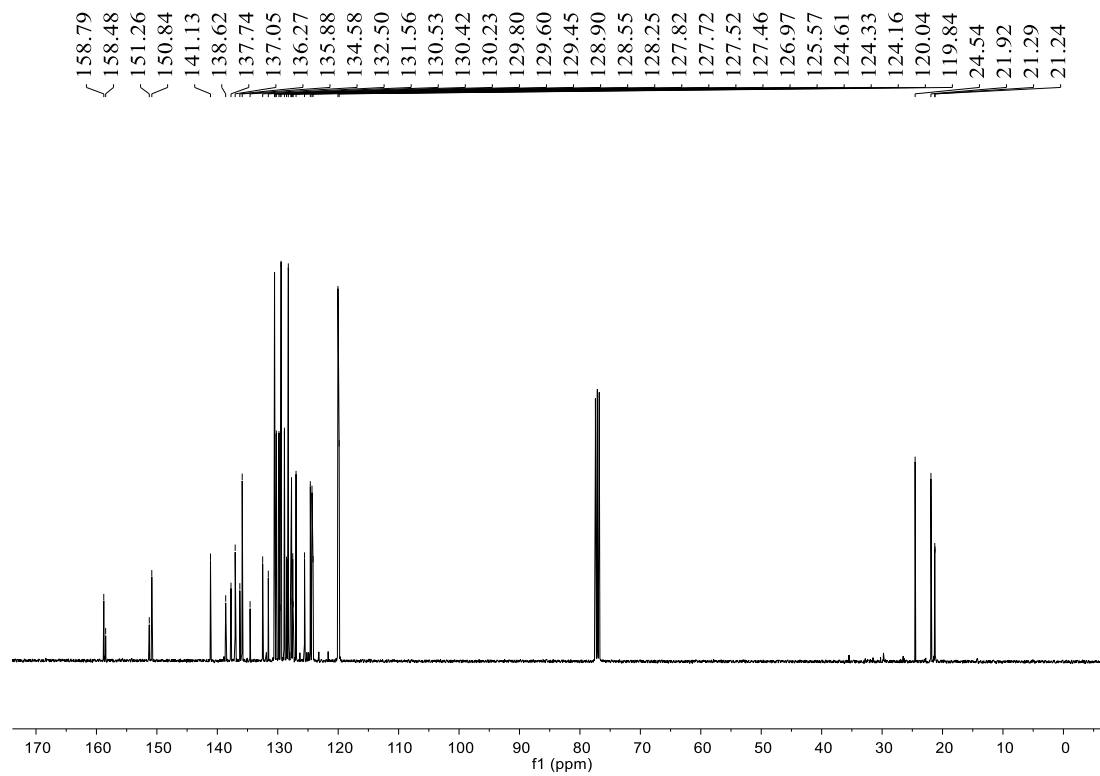
^{13}C NMR (100 MHz, CDCl_3) of compound **3qa**.



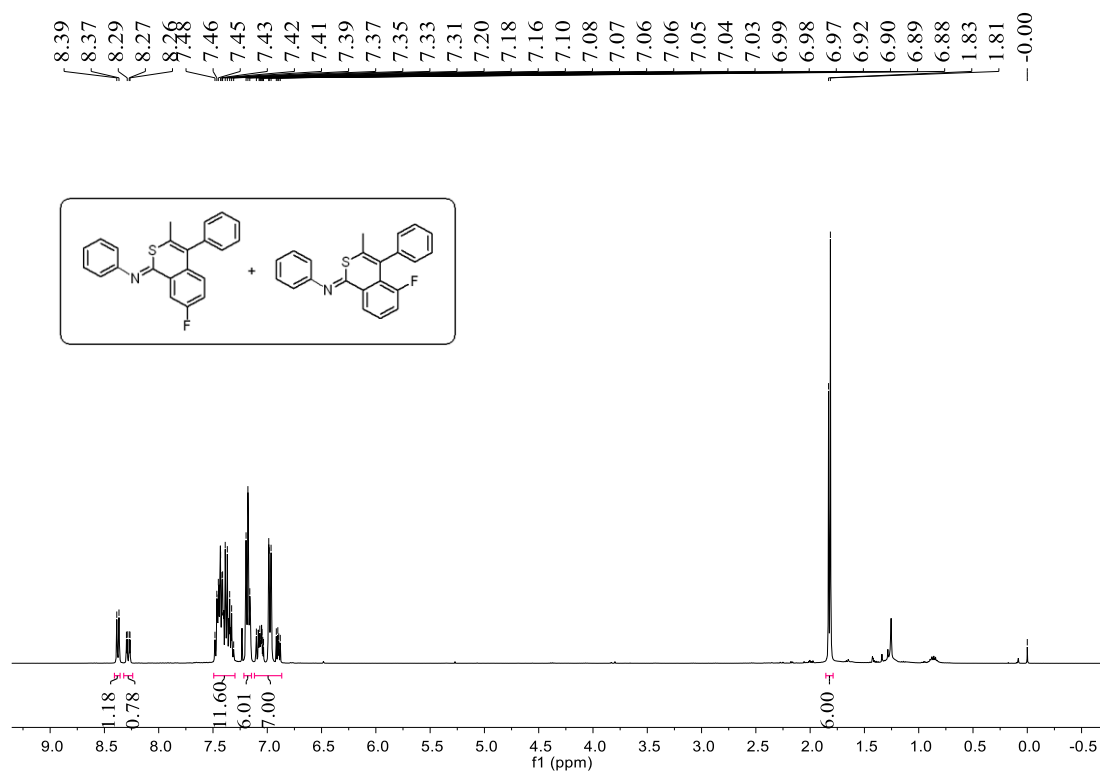
^1H NMR (400 MHz, CDCl_3) of compound **3ra** and **3r'a**.



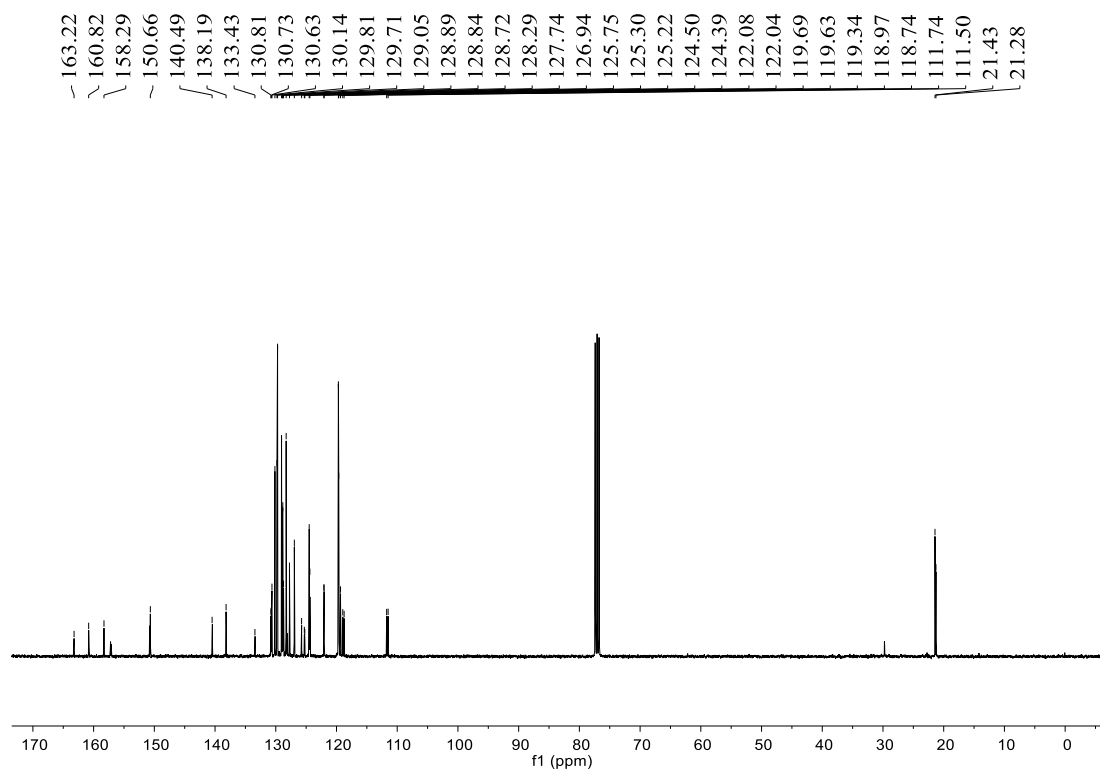
^{13}C NMR (100 MHz, CDCl_3) of compound **3ra** and **3r'a**.



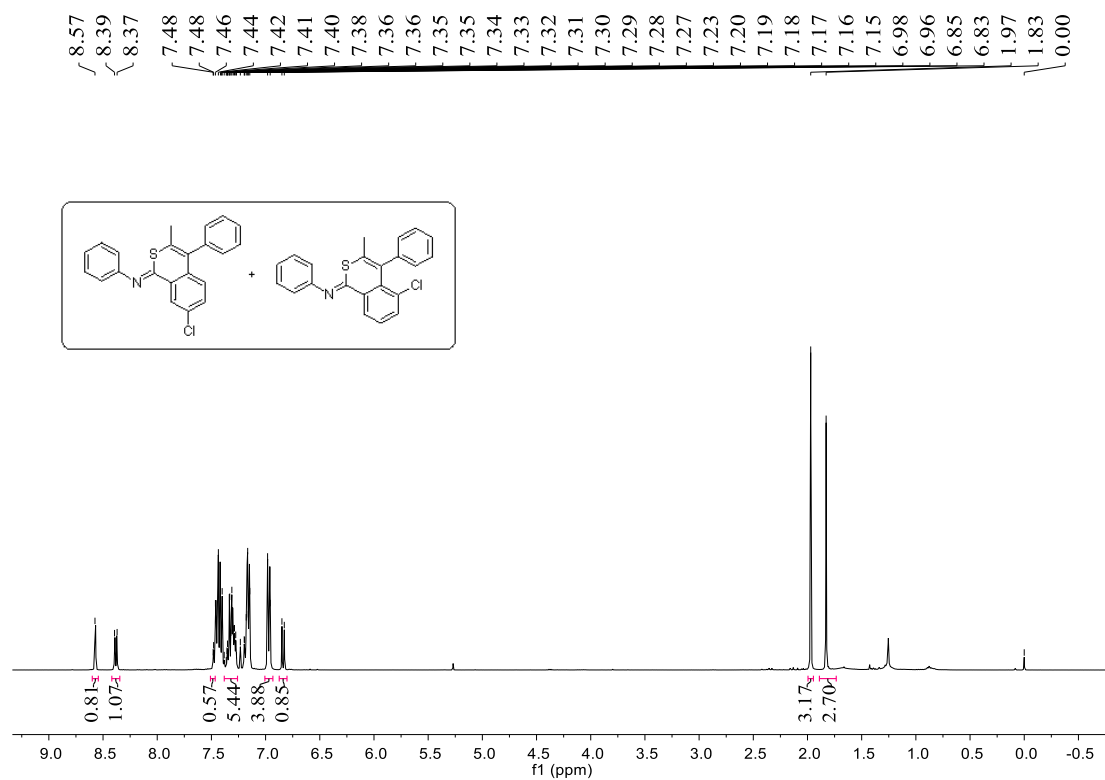
^1H NMR (400 MHz, CDCl_3) of compound **3sa** and **3s'a**.



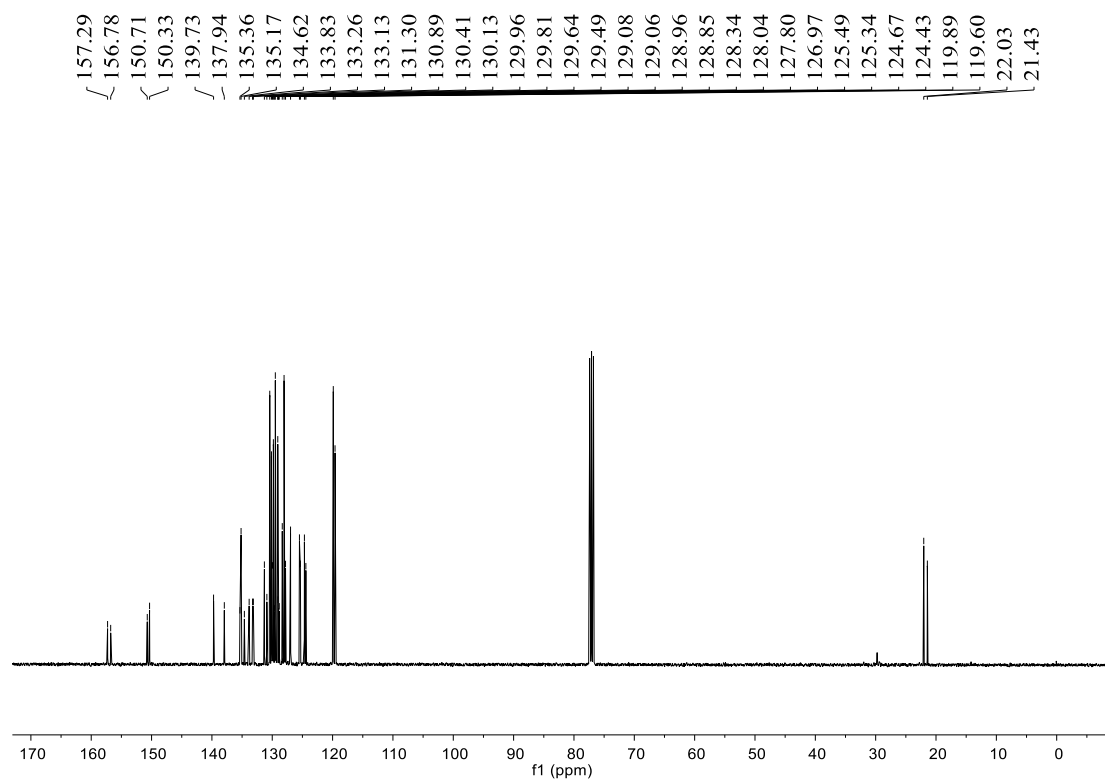
^{13}C NMR (100 MHz, CDCl_3) of compound **3sa** and **3s'a**.



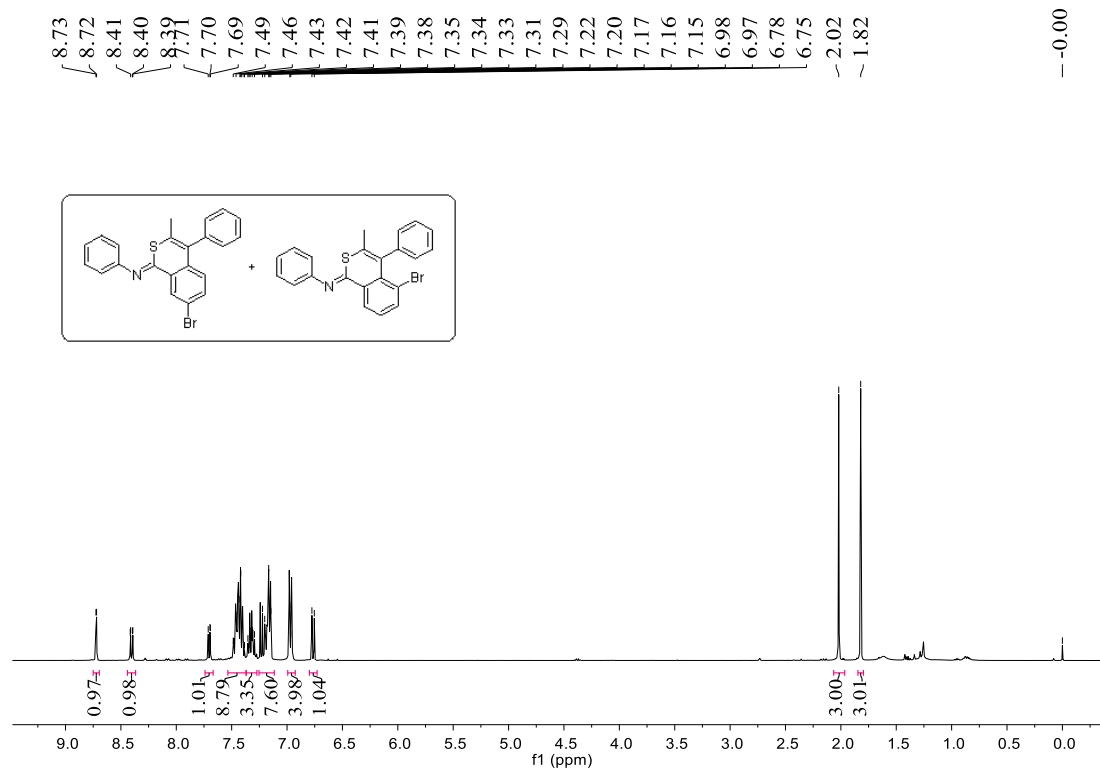
^1H NMR (400 MHz, CDCl_3) of compound **3ta** and **3t'a**.



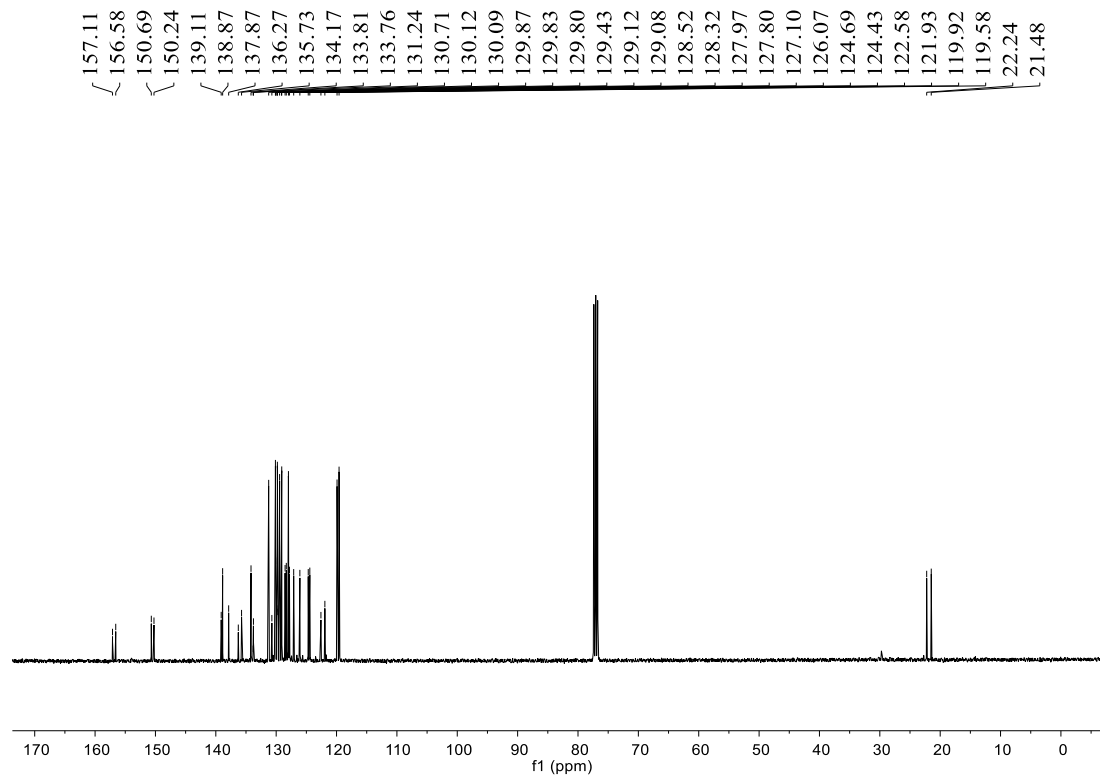
^{13}C NMR (100 MHz, CDCl_3) of compound **3ta** and **3t'a**.



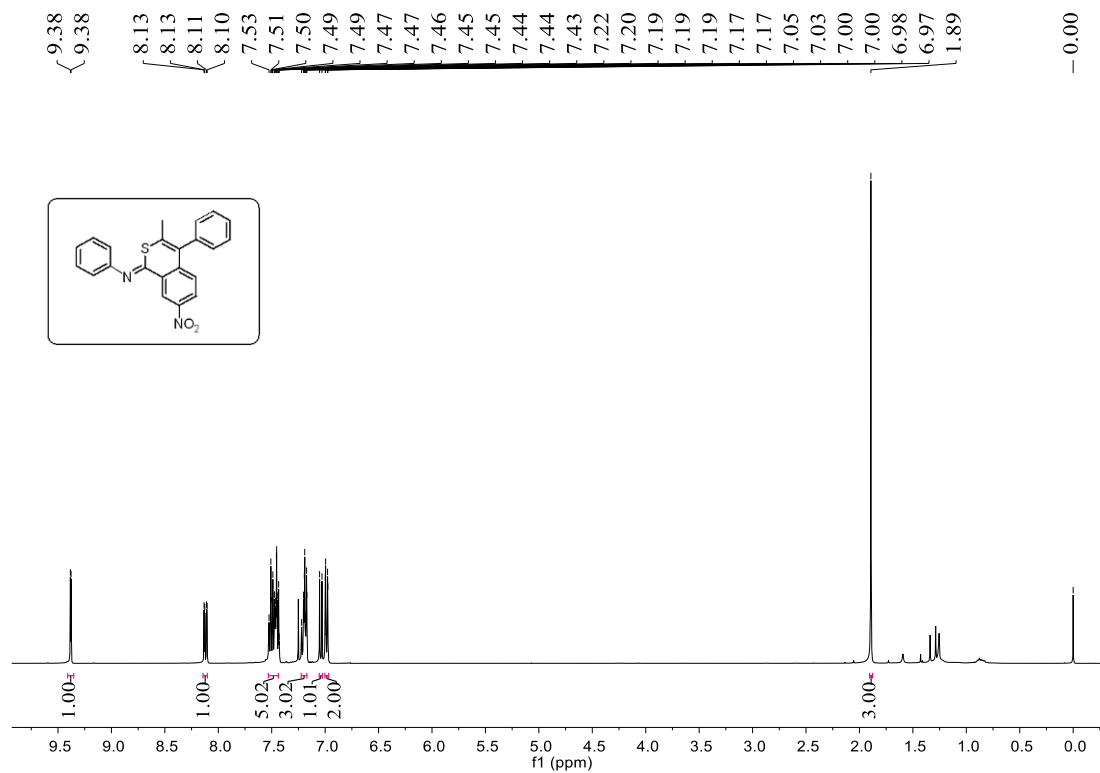
^1H NMR (400 MHz, CDCl_3) of compound **3ua** and **3u'a**.



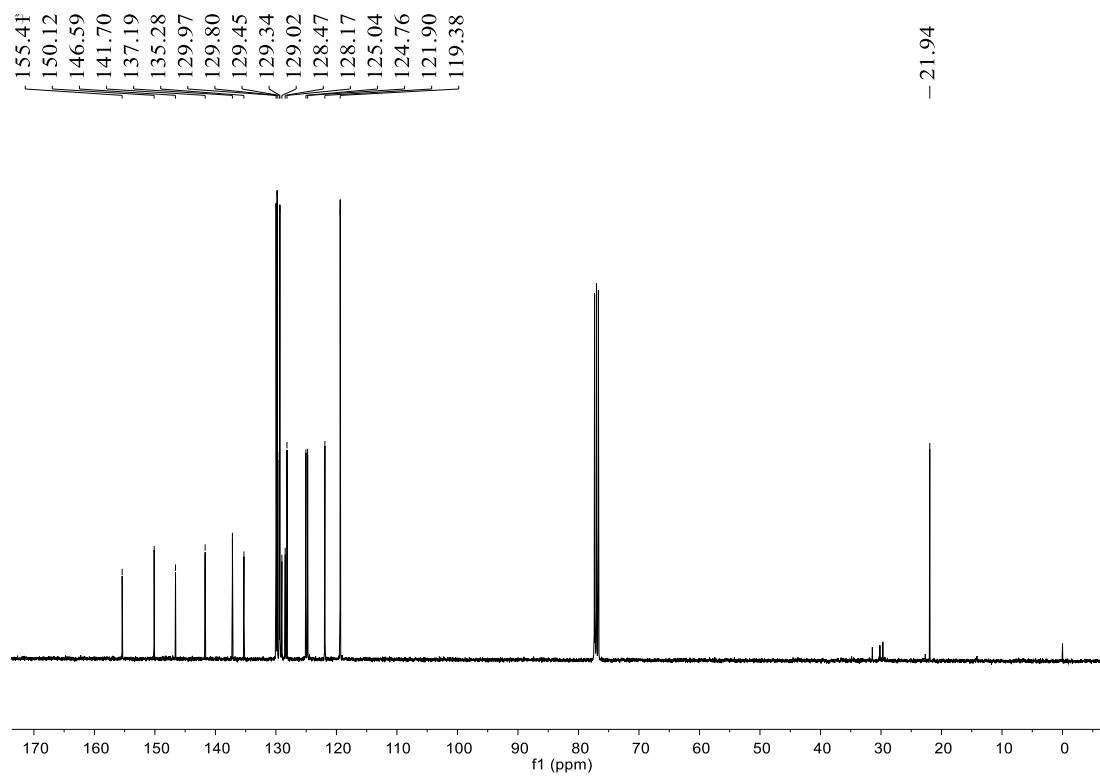
^{13}C NMR (100 MHz, CDCl_3) of compound **3ua** and **3u'a**.



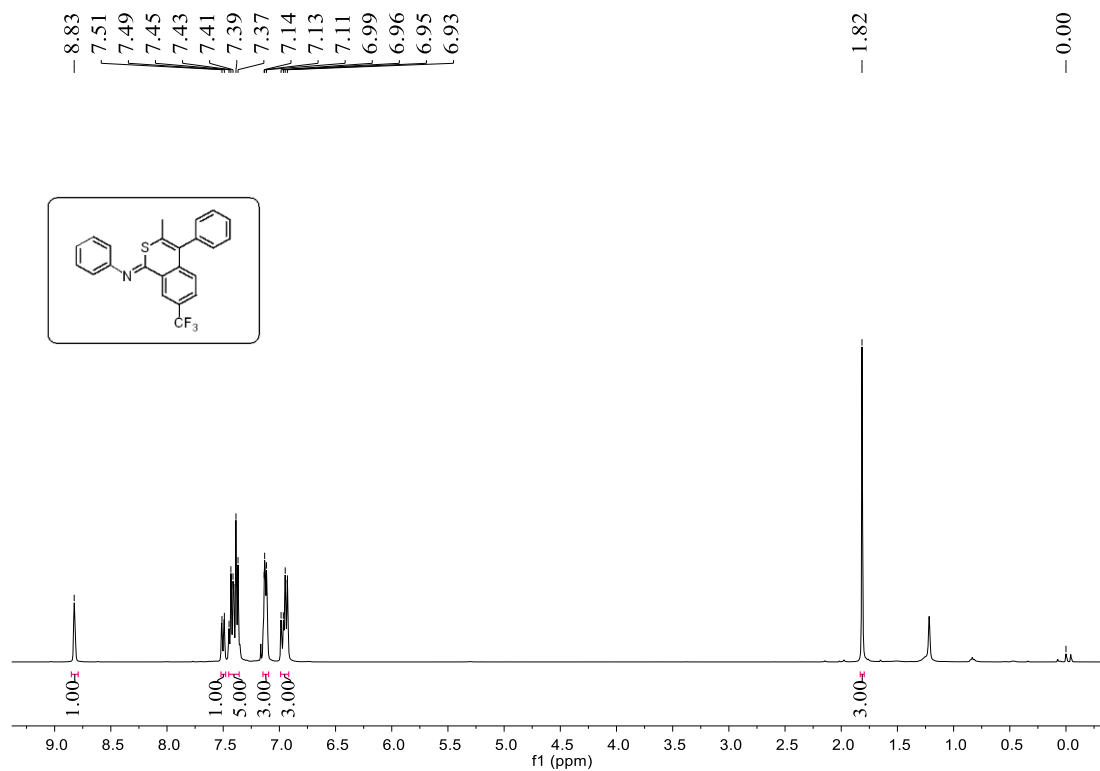
¹H NMR (400 MHz, CDCl₃) of compound **3va**.



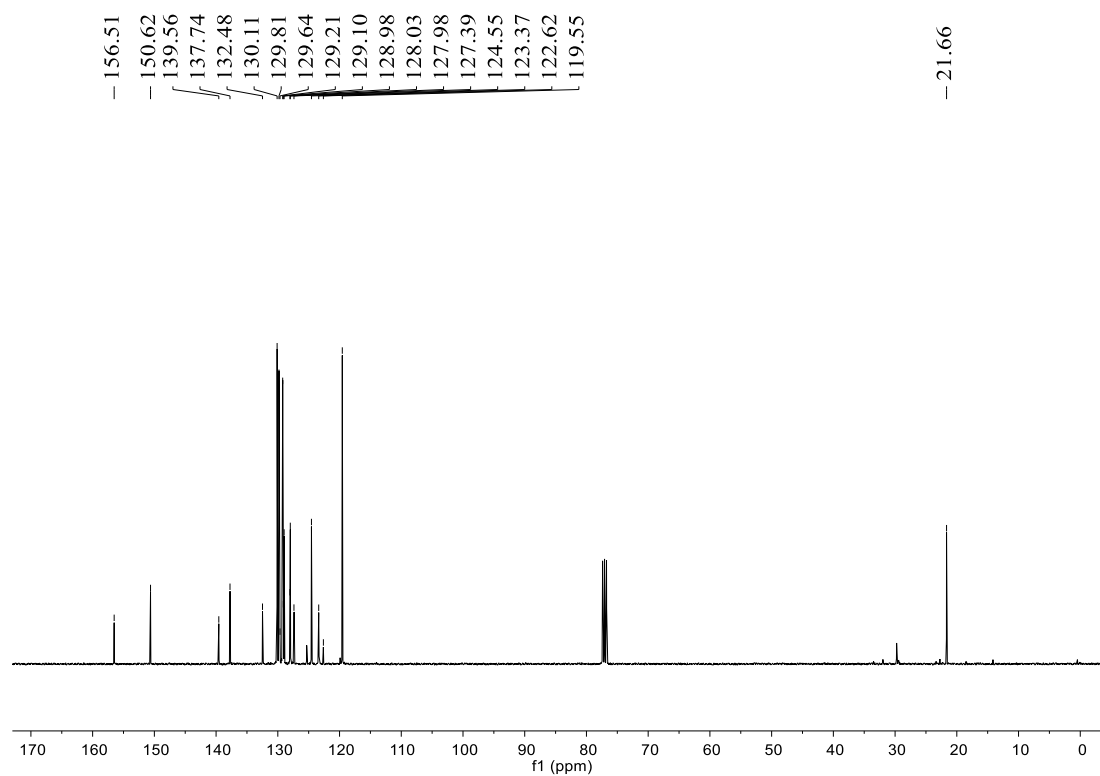
¹³C NMR (100 MHz, CDCl₃) of compound **3va**.



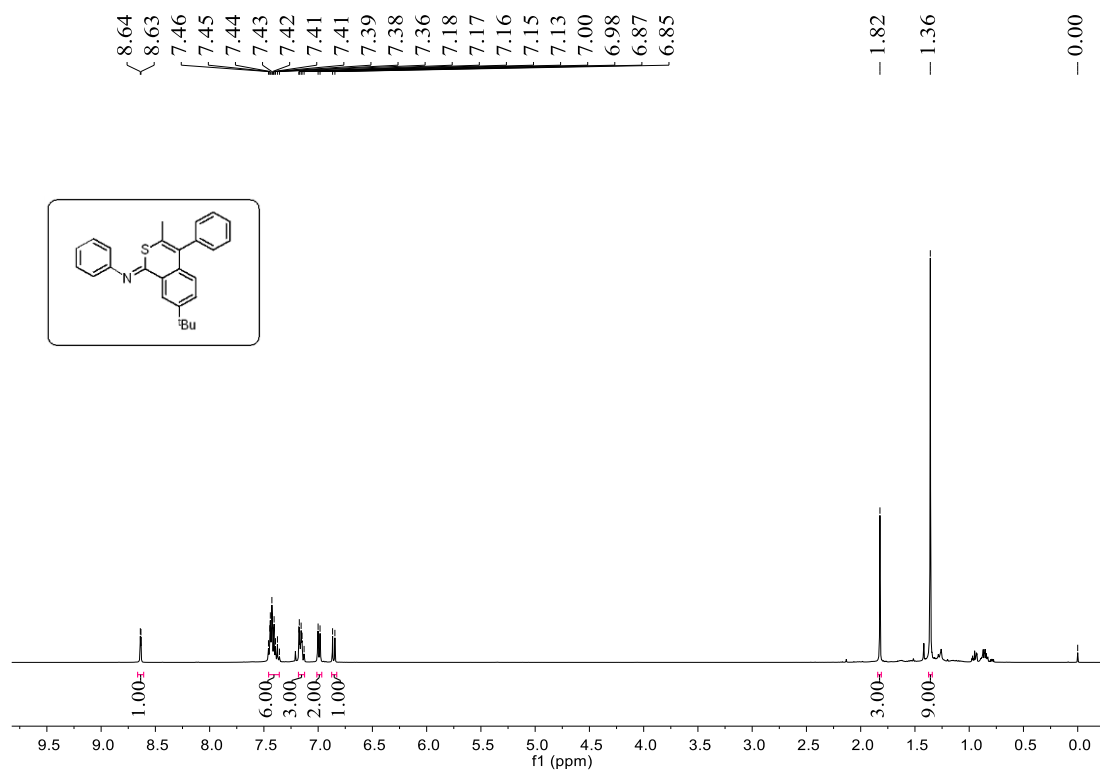
^1H NMR (400 MHz, CDCl_3) of compound **3wa**.



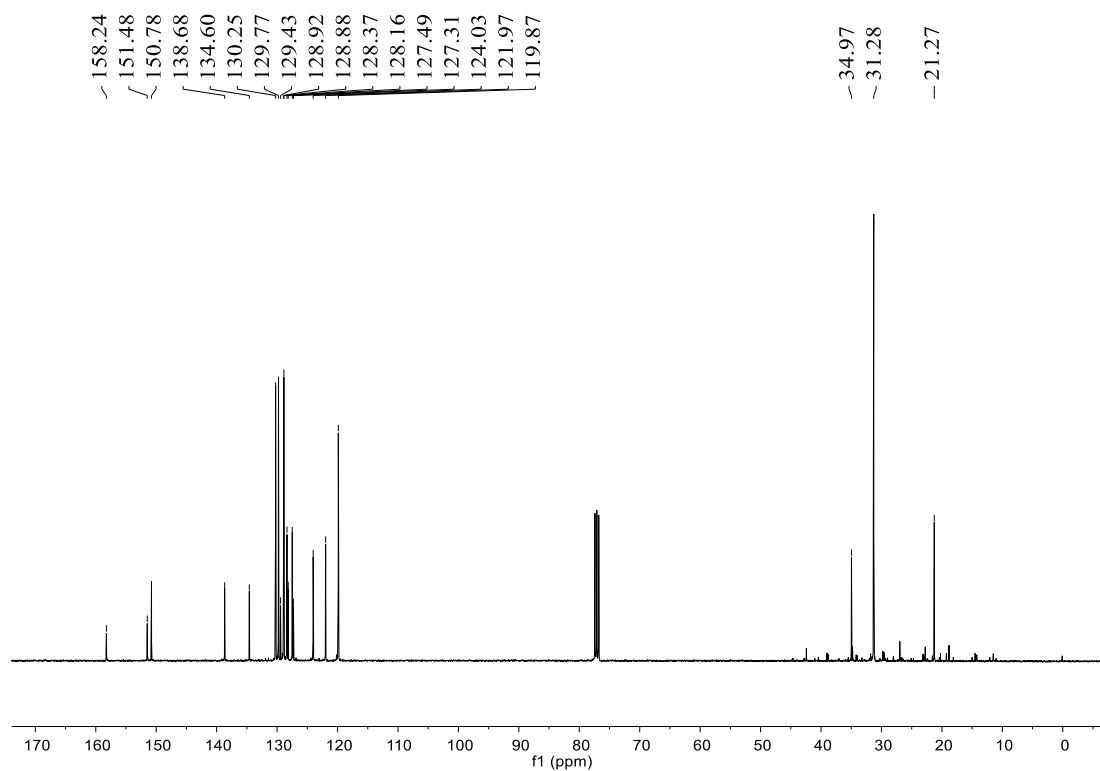
^{13}C NMR (100 MHz, CDCl_3) of compound **3wa**.



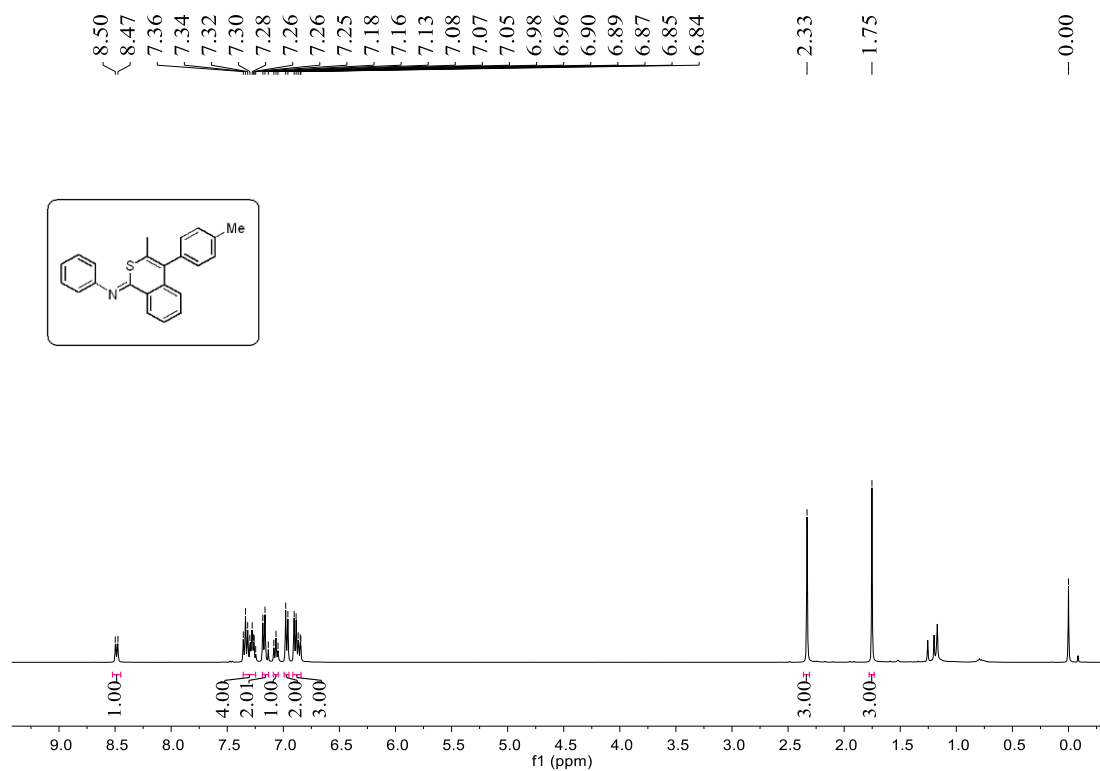
^1H NMR (400 MHz, CDCl_3) of compound **3xa**.



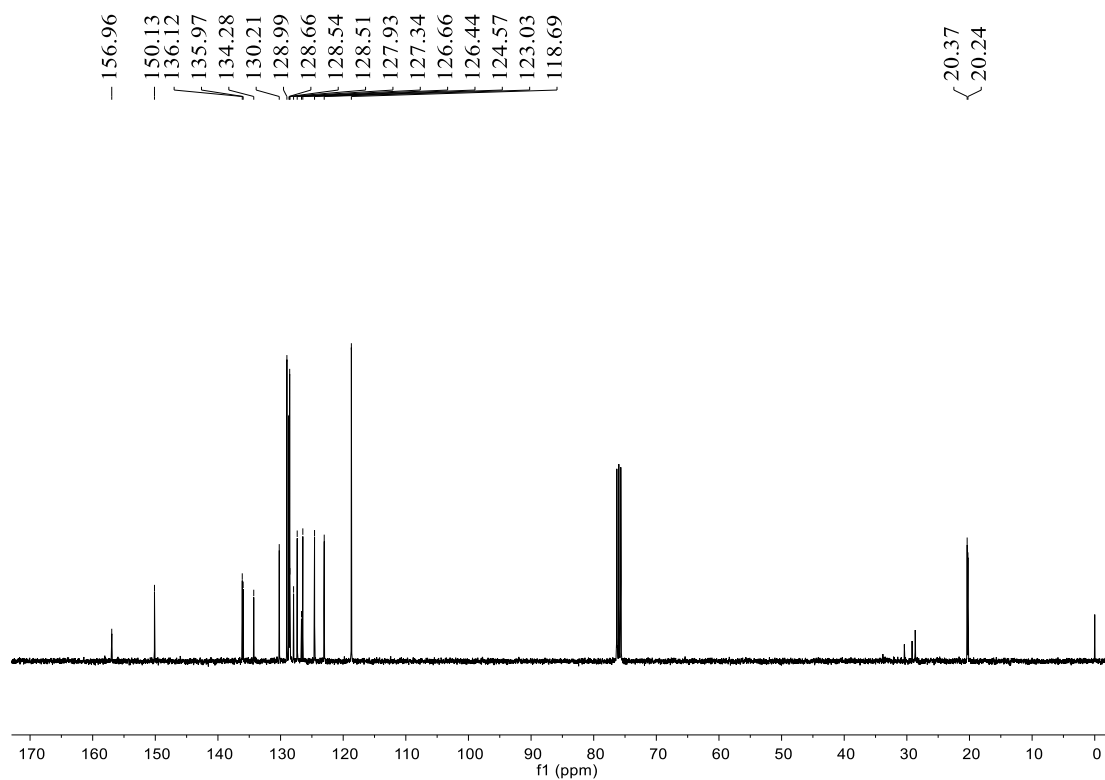
^{13}C NMR (100 MHz, CDCl_3) of compound **3xa**.



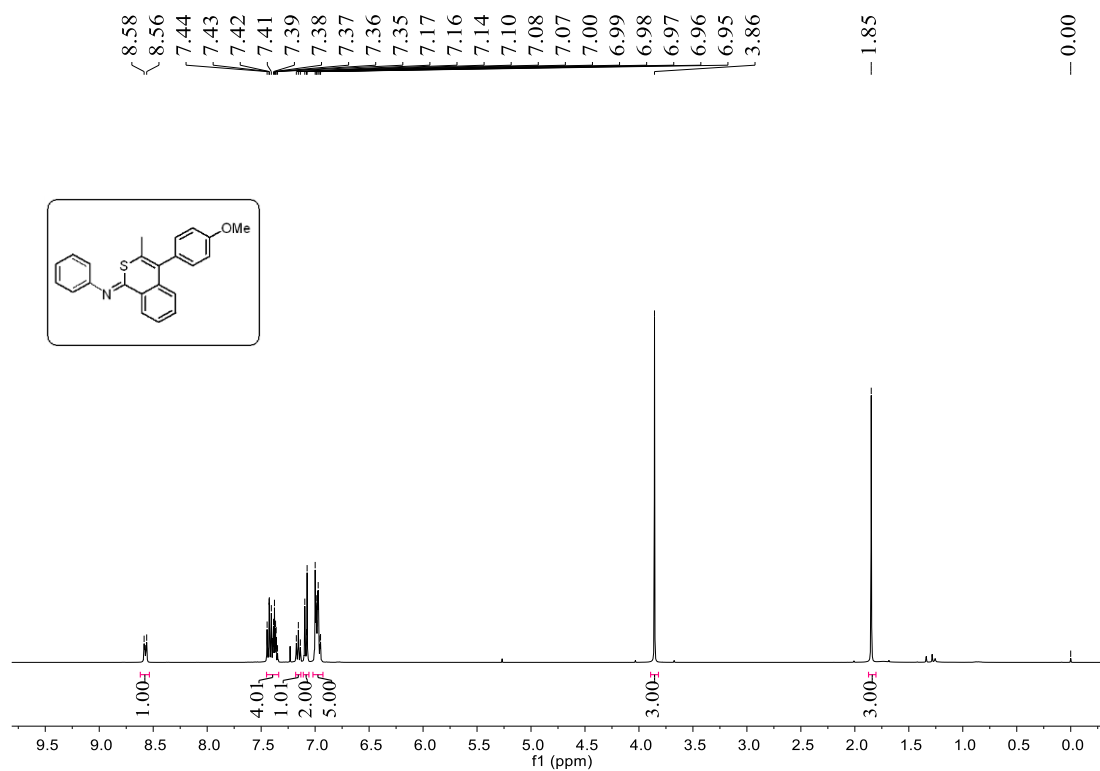
^1H NMR (400 MHz, CDCl_3) of compound **3ab**.



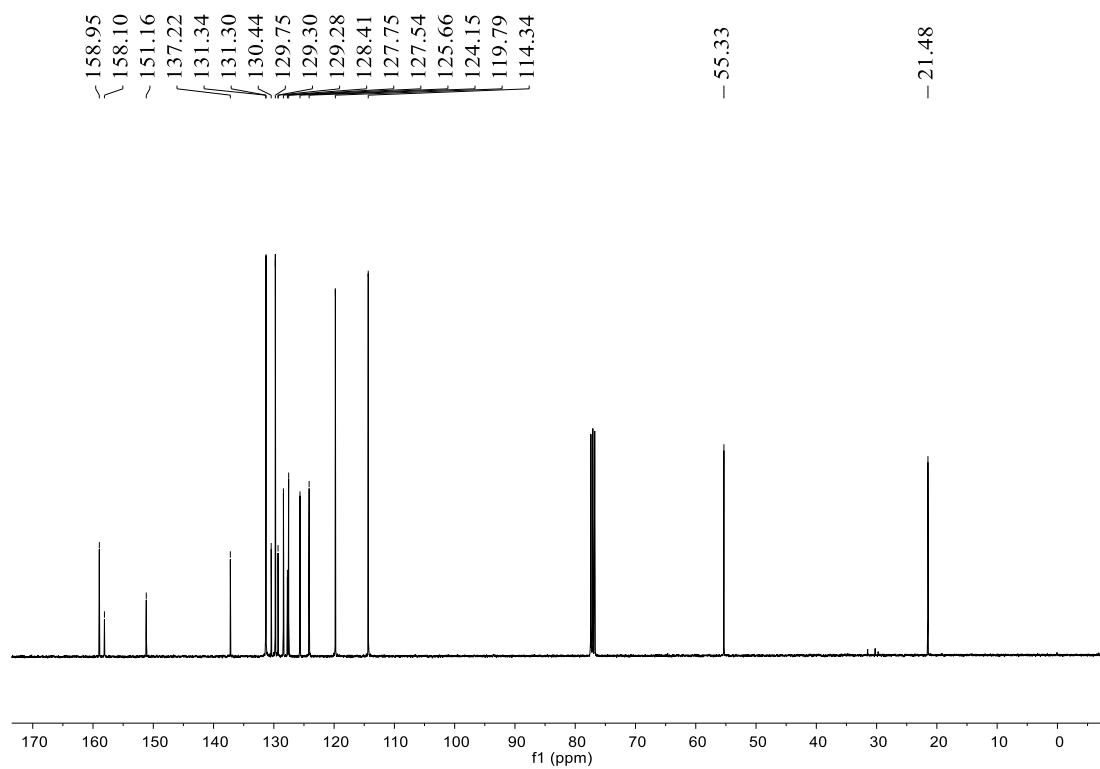
^{13}C NMR (100 MHz, CDCl_3) of compound **3ab**.



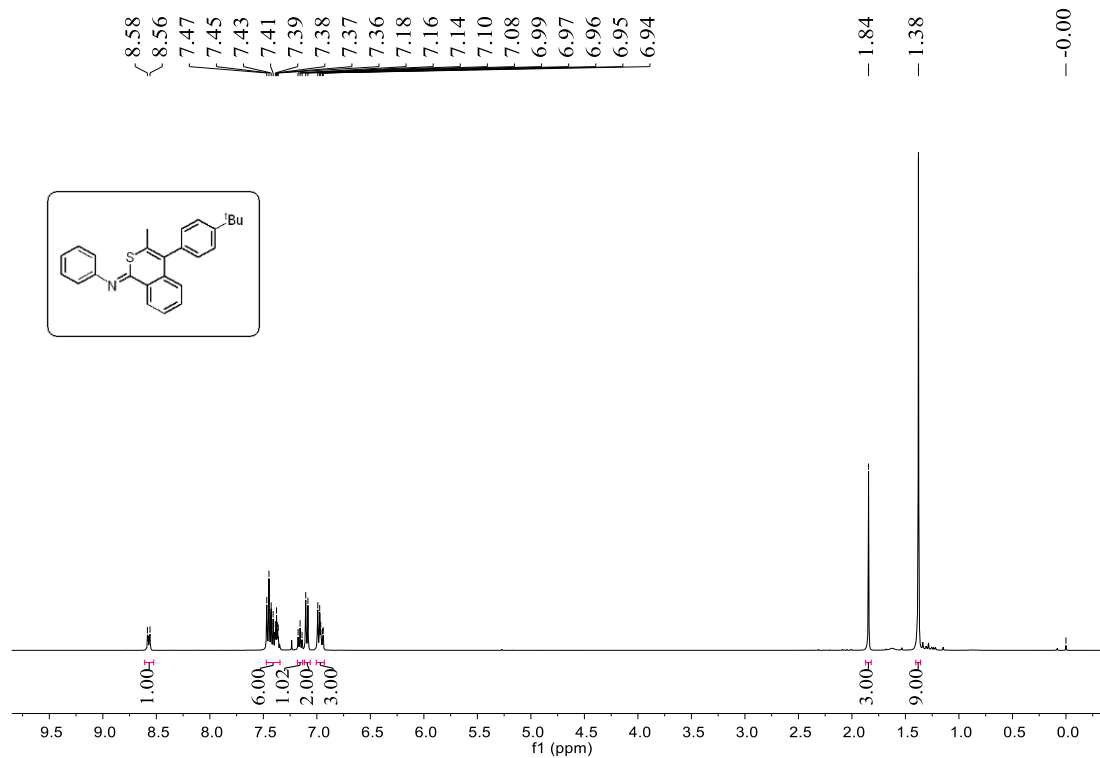
¹H NMR (400 MHz, CDCl₃) of compound **3ac**.



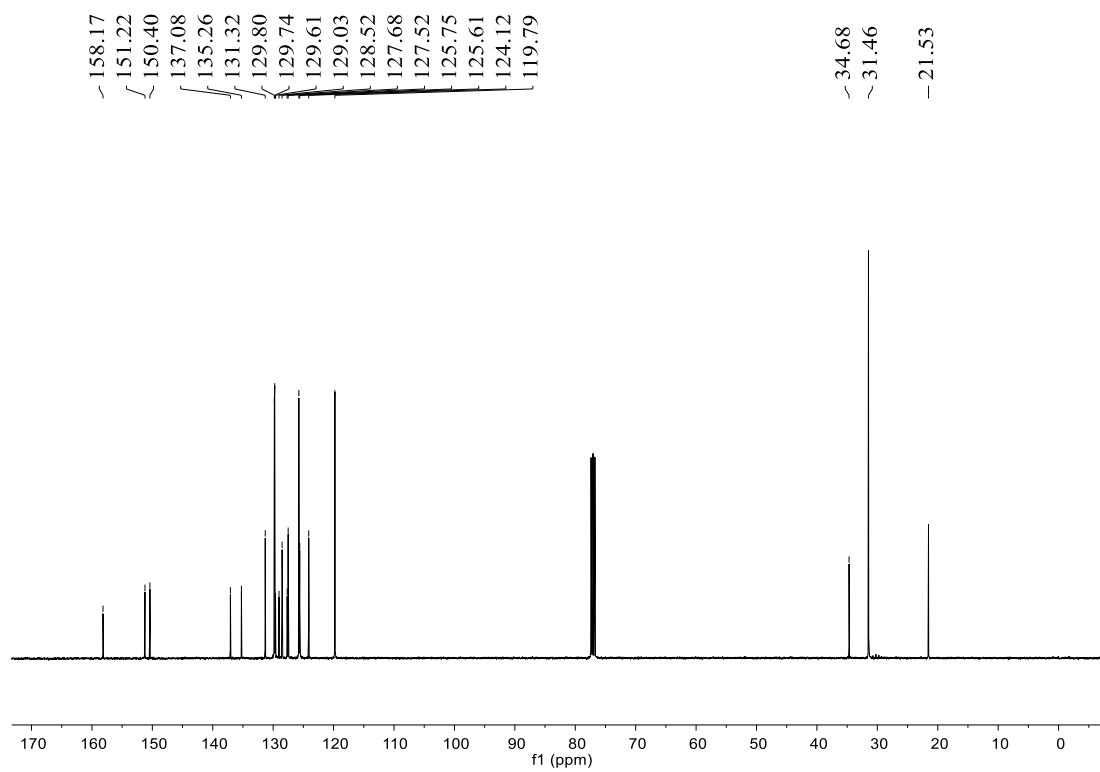
¹³C NMR (100 MHz, CDCl₃) of compound **3ac**.



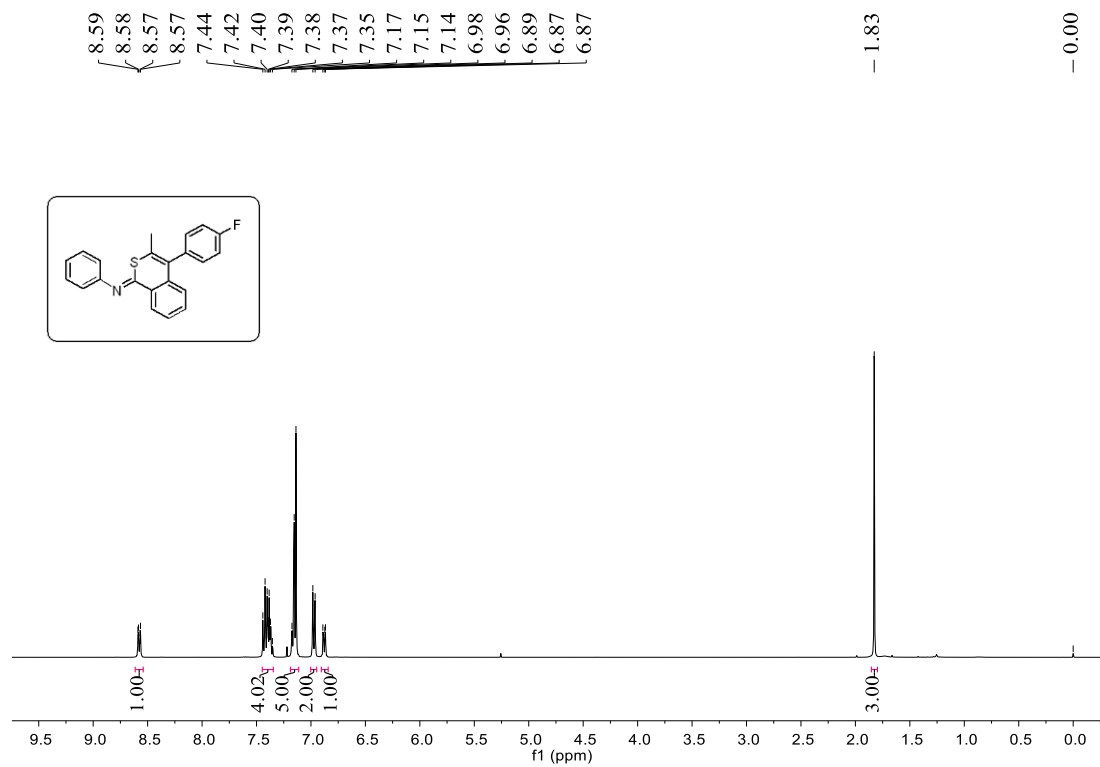
^1H NMR (400 MHz, CDCl_3) of compound **3ad**.



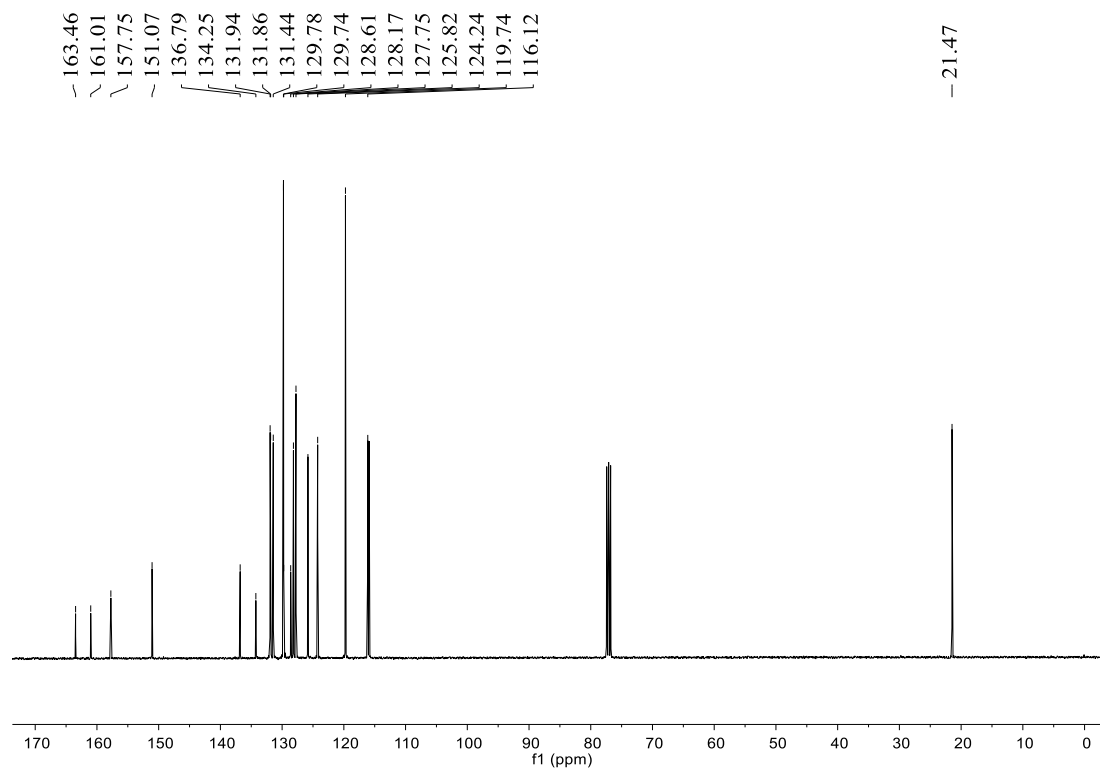
^{13}C NMR (100 MHz, CDCl_3) of compound **3ad**.



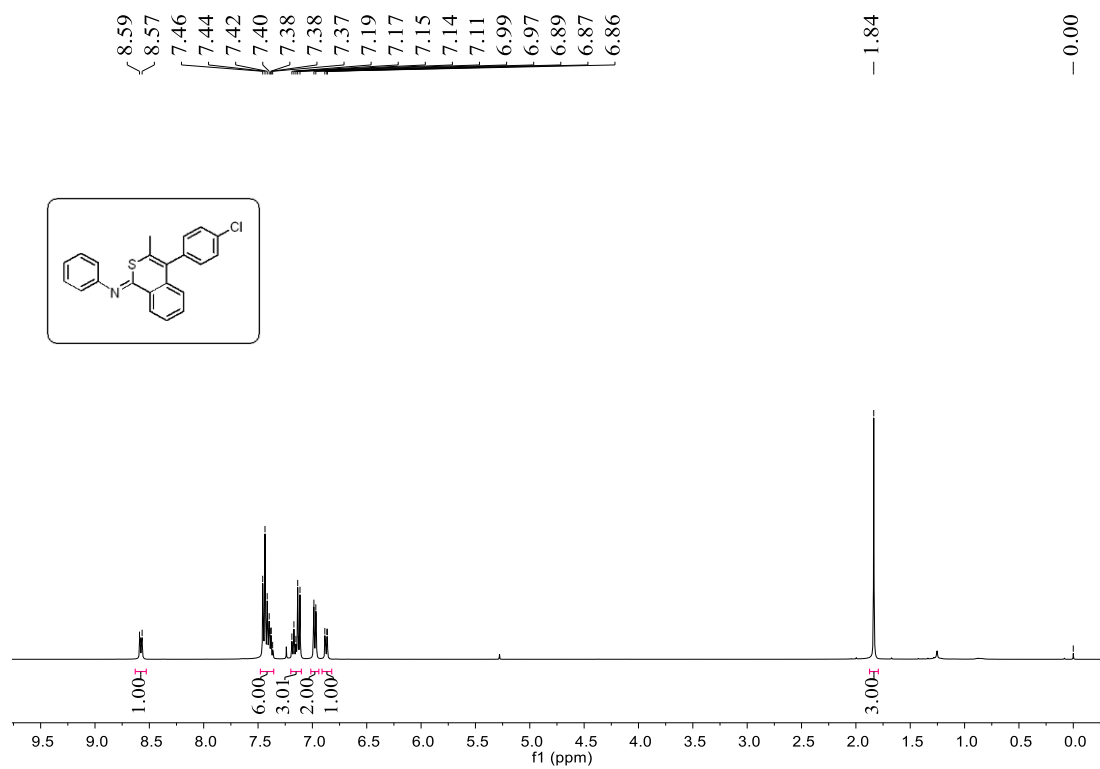
^1H NMR (400 MHz, CDCl_3) of compound **3ae**.



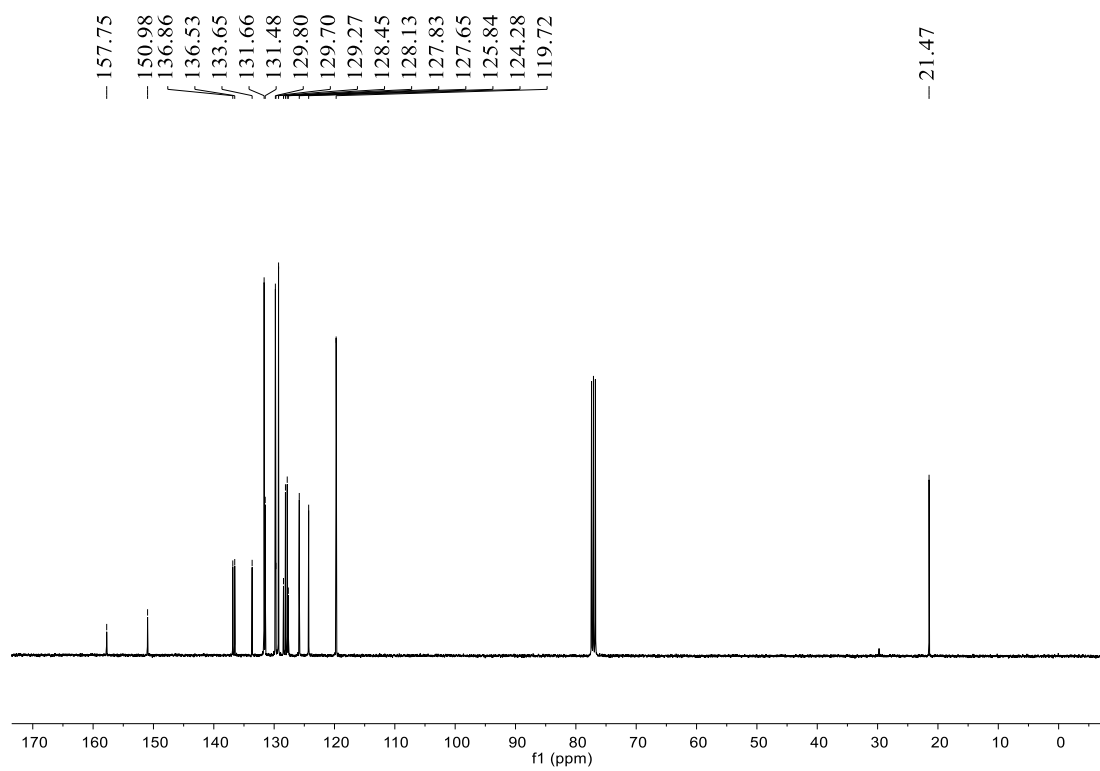
^{13}C NMR (100 MHz, CDCl_3) of compound **3ae**.



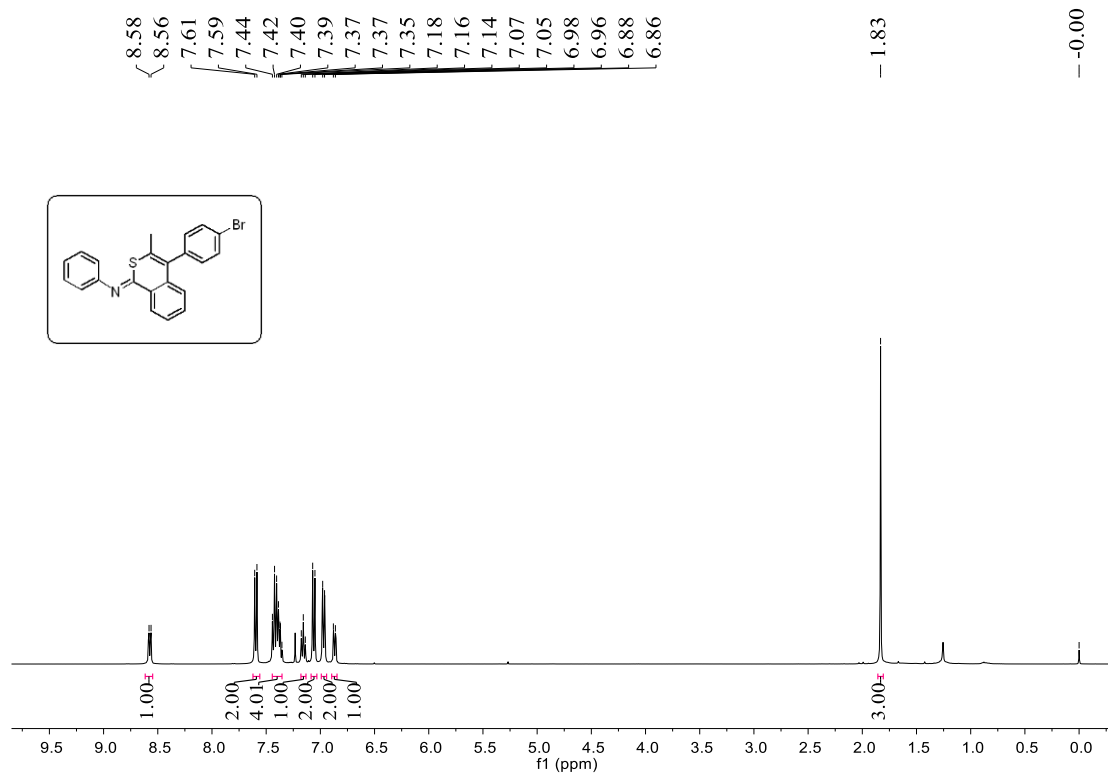
¹H NMR (400 MHz, CDCl₃) of compound **3af**.



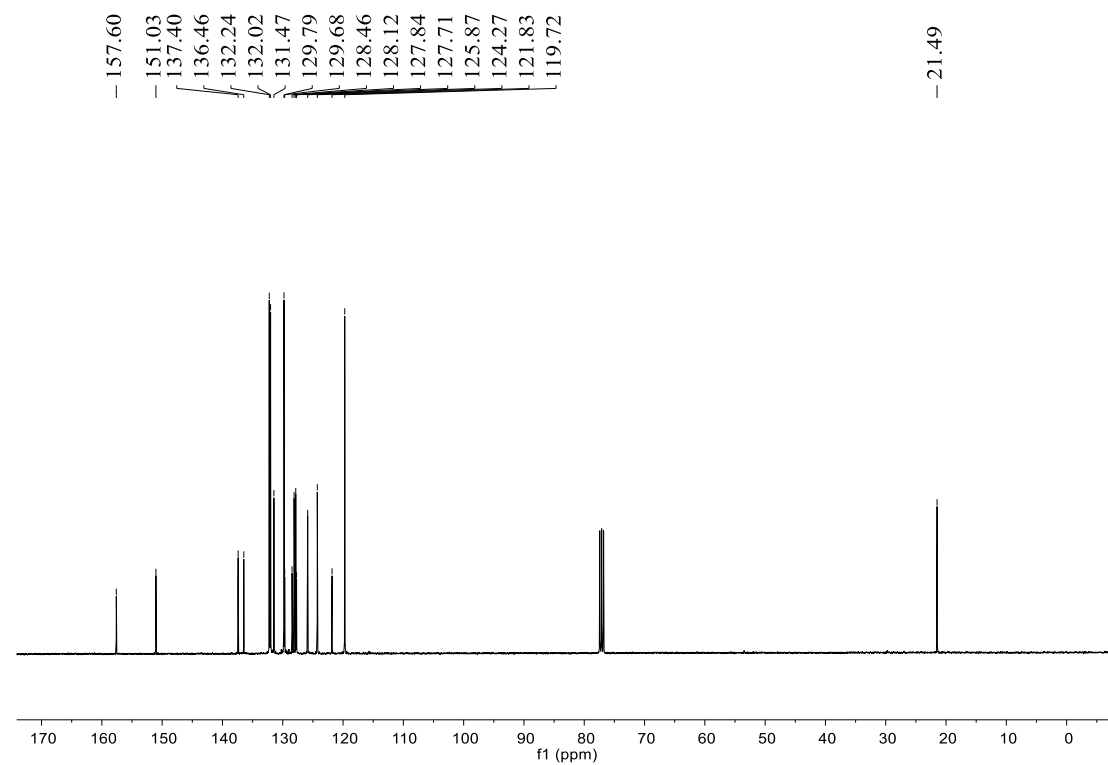
¹³C NMR (100 MHz, CDCl₃) of compound **3af**.



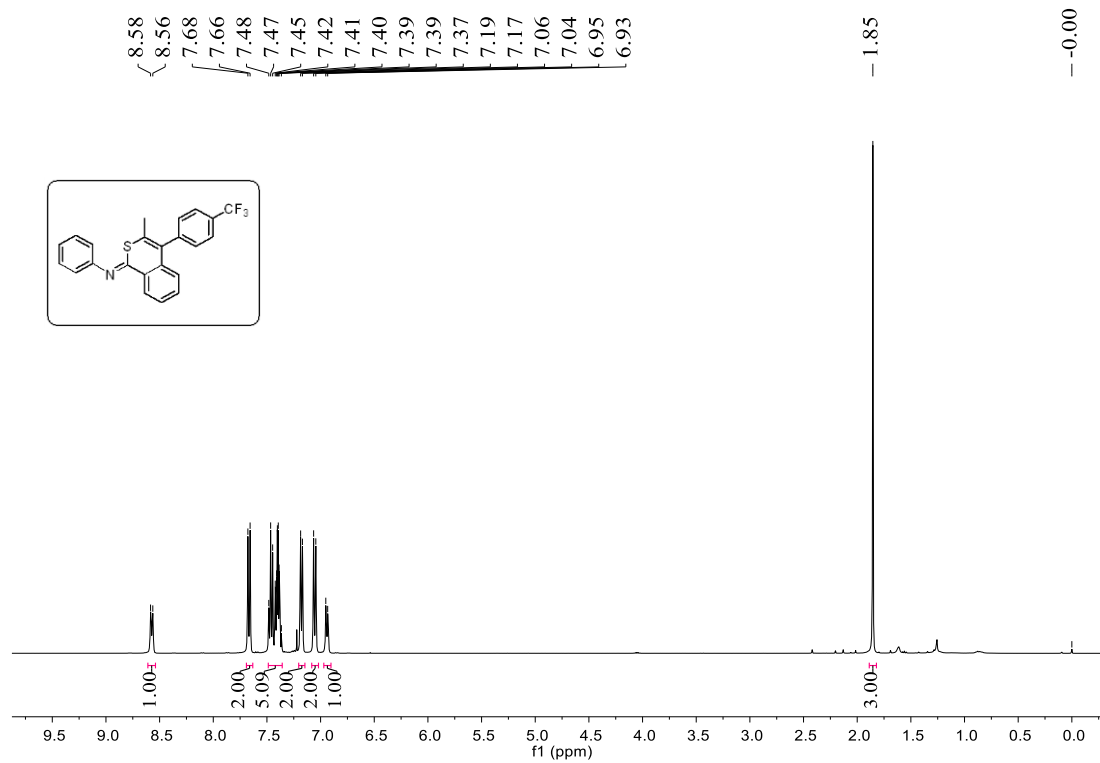
^1H NMR (400 MHz, CDCl_3) of compound **3ag**.



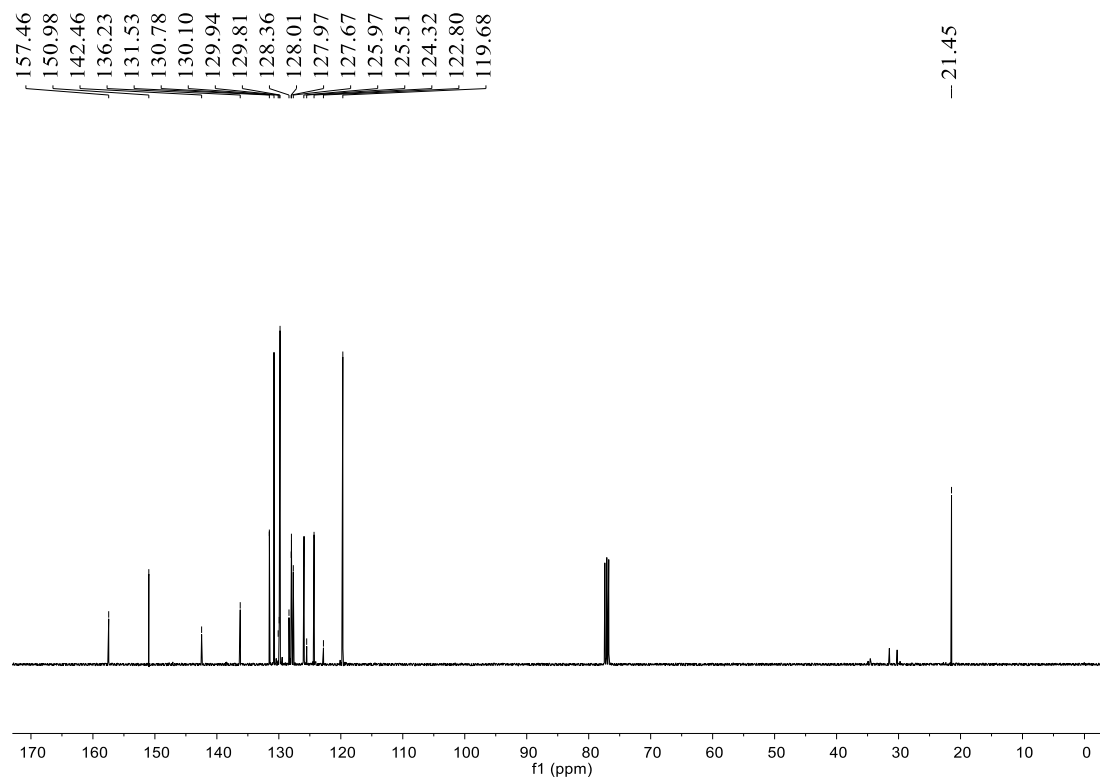
^{13}C NMR (100 MHz, CDCl_3) of compound **3ag**.



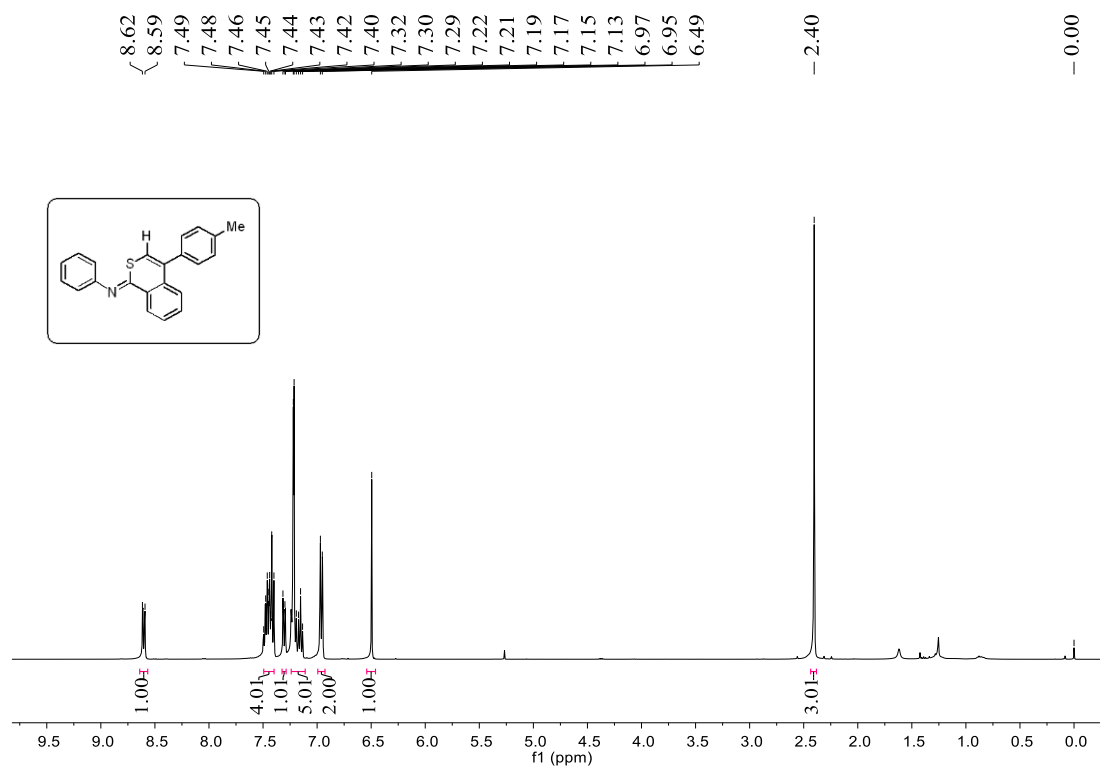
^1H NMR (400 MHz, CDCl_3) of compound **3ah**.



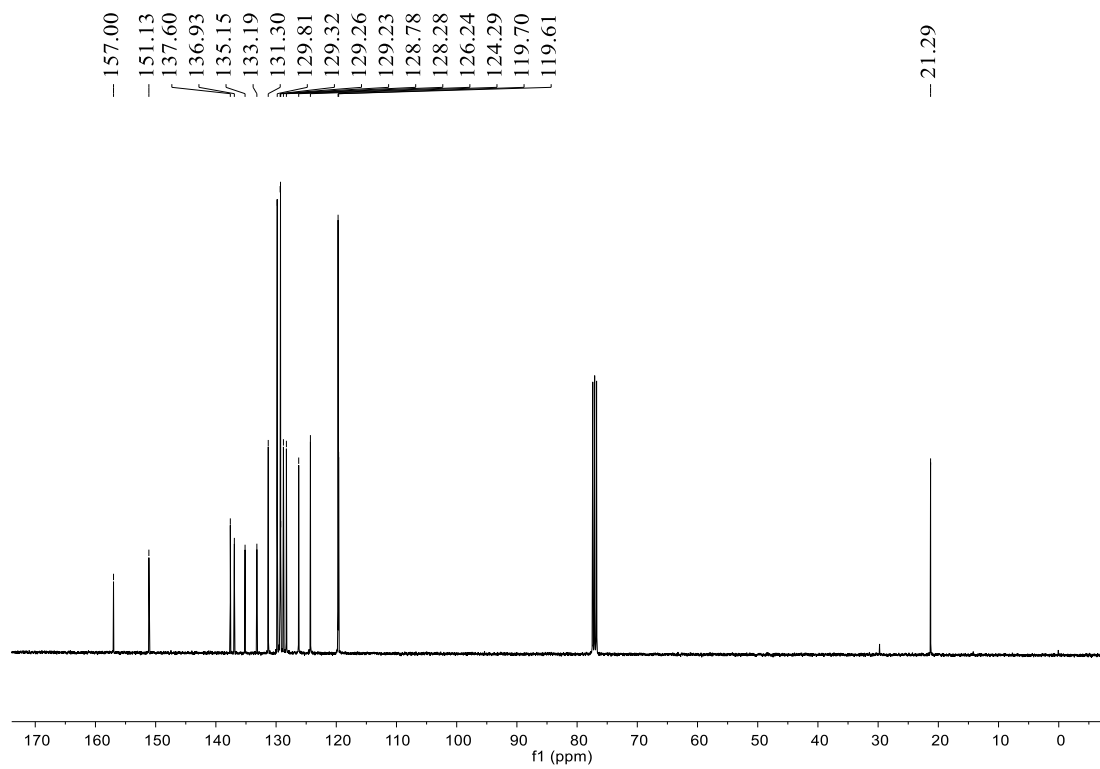
^{13}C NMR (100 MHz, CDCl_3) of compound **3ah**.



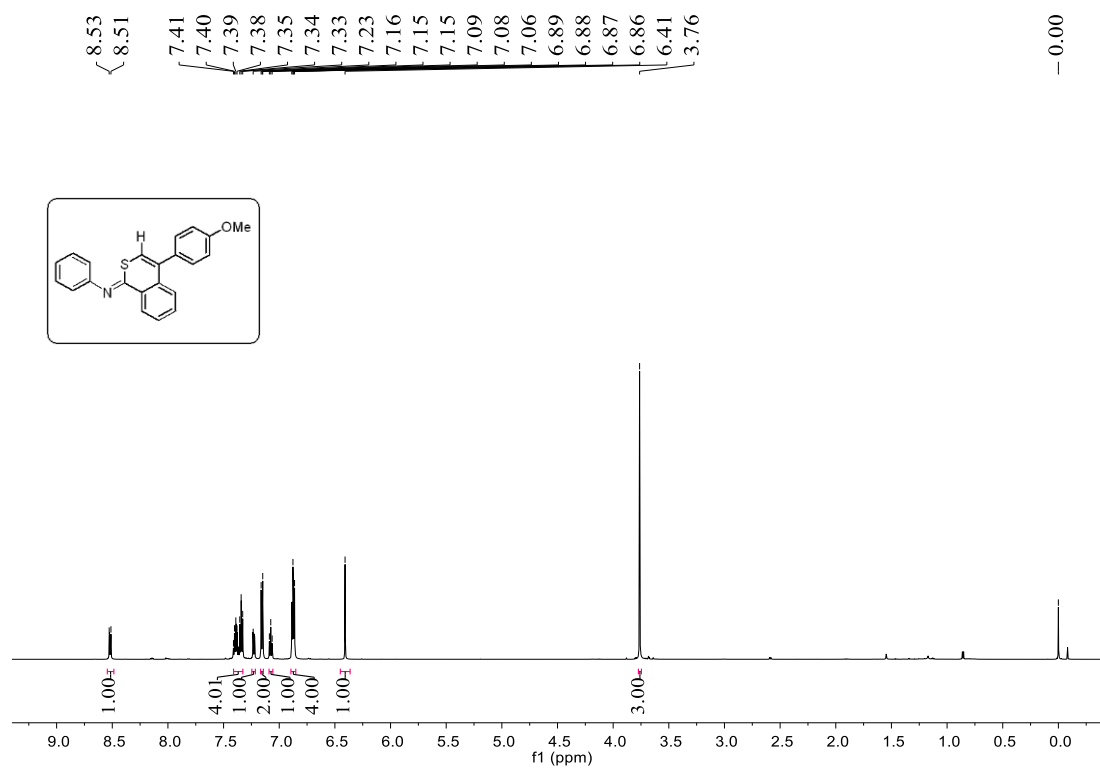
¹H NMR (400 MHz, CDCl₃) of compound **3ai**.



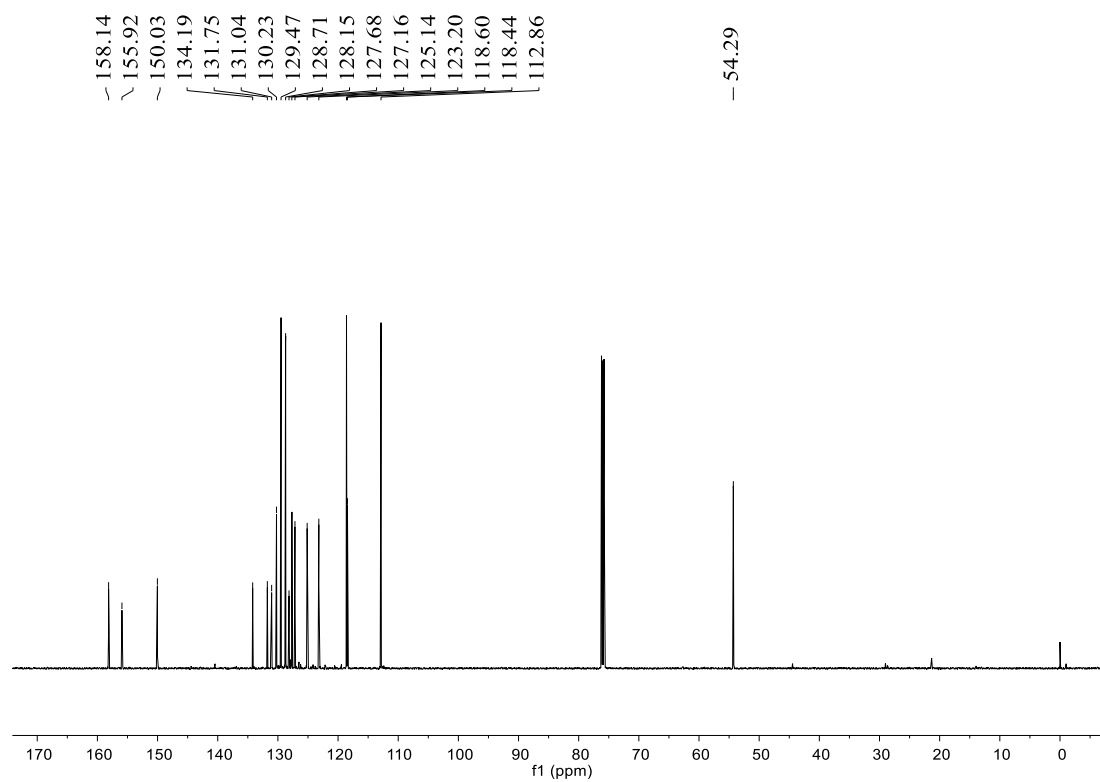
¹³C NMR (100 MHz, CDCl₃) of compound **3ai**.



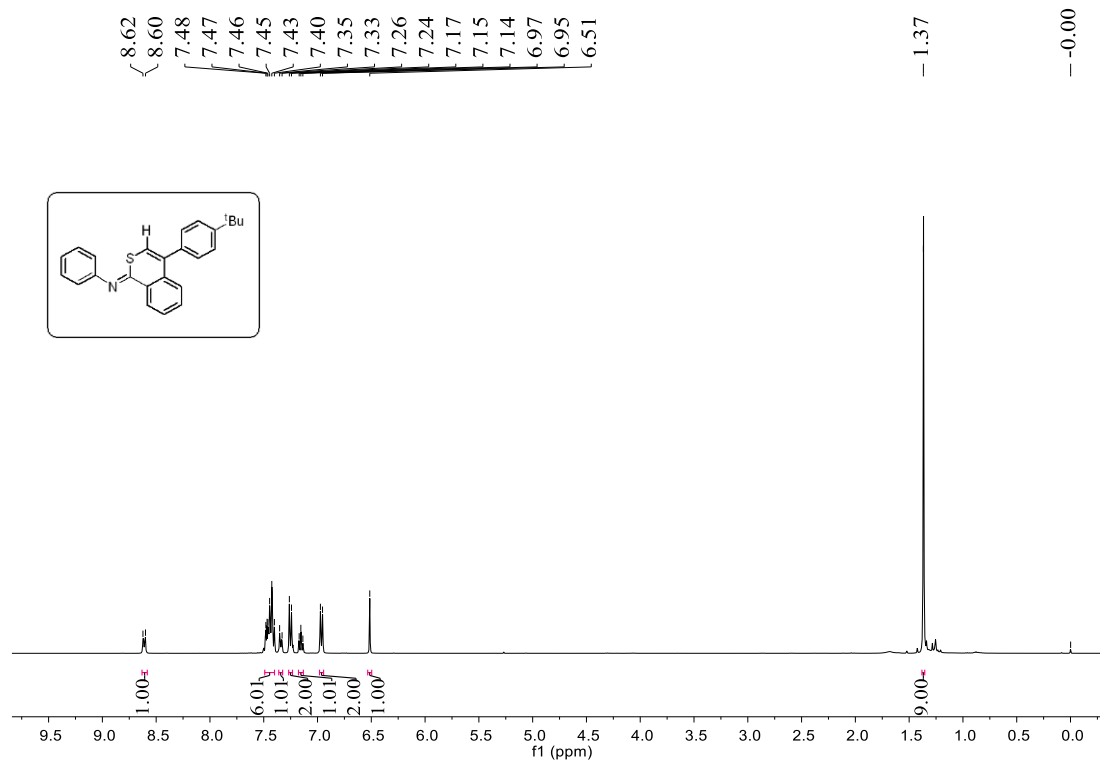
^1H NMR (400 MHz, CDCl_3) of compound **3aj**.



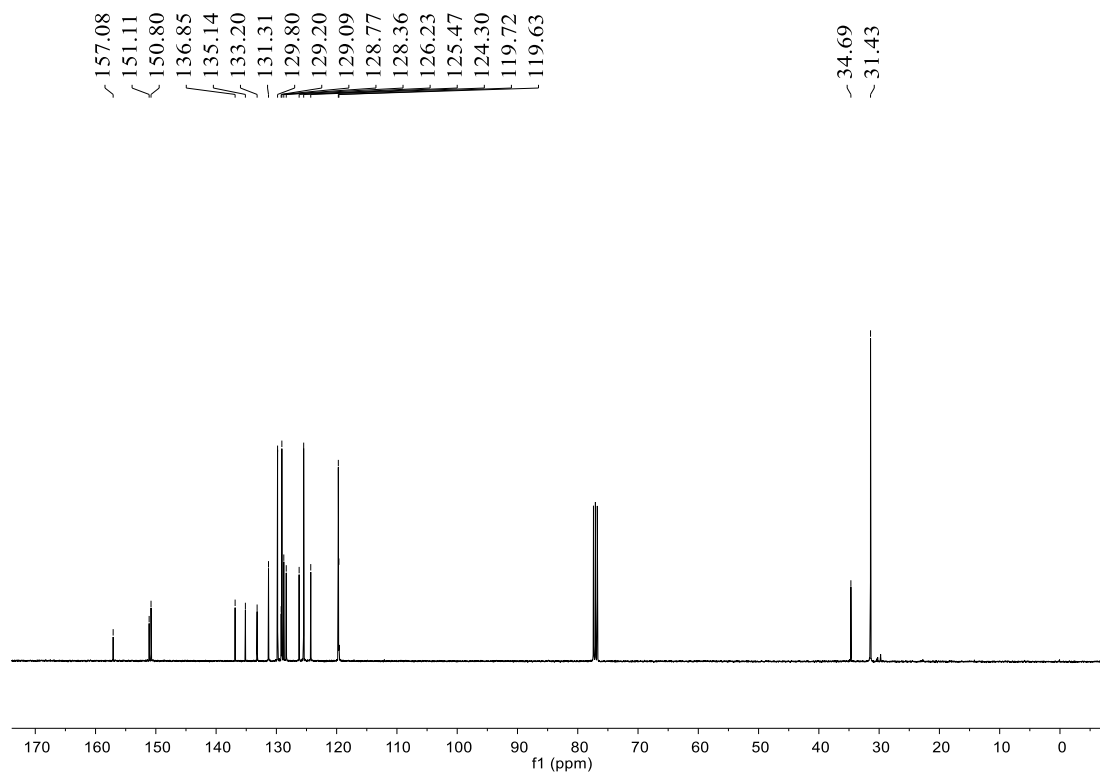
^{13}C NMR (100 MHz, CDCl_3) of compound **3aj**.



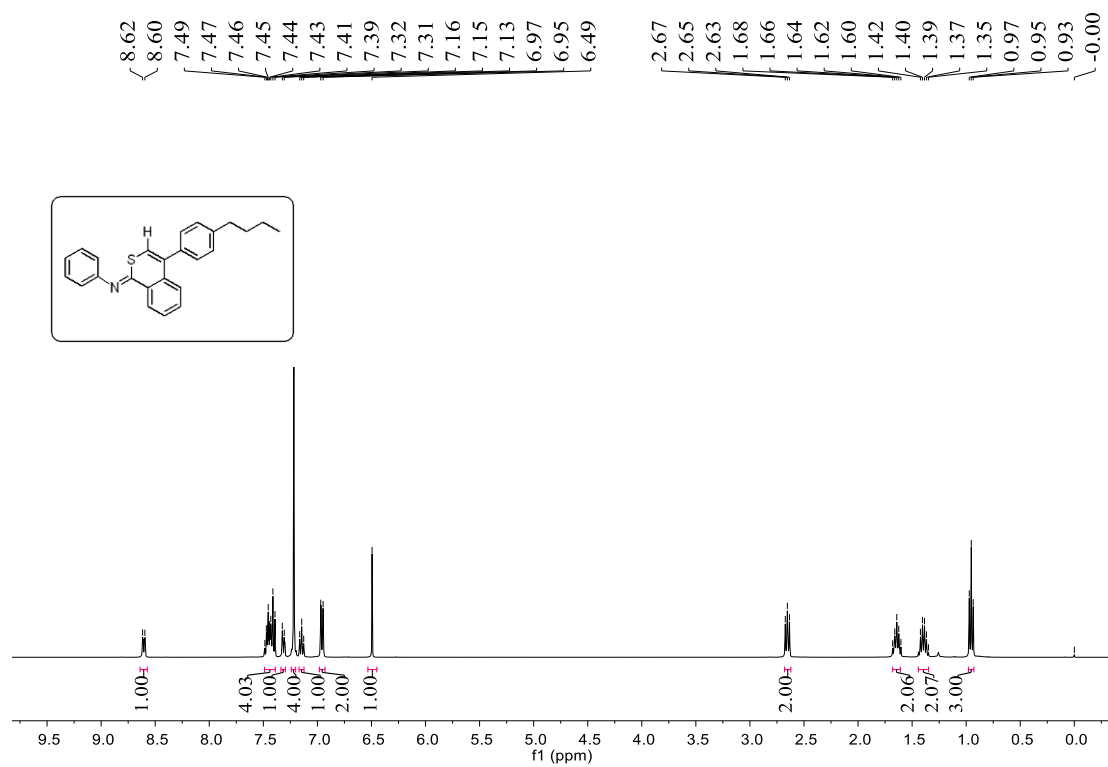
^1H NMR (400 MHz, CDCl_3) of compound **3ak**.



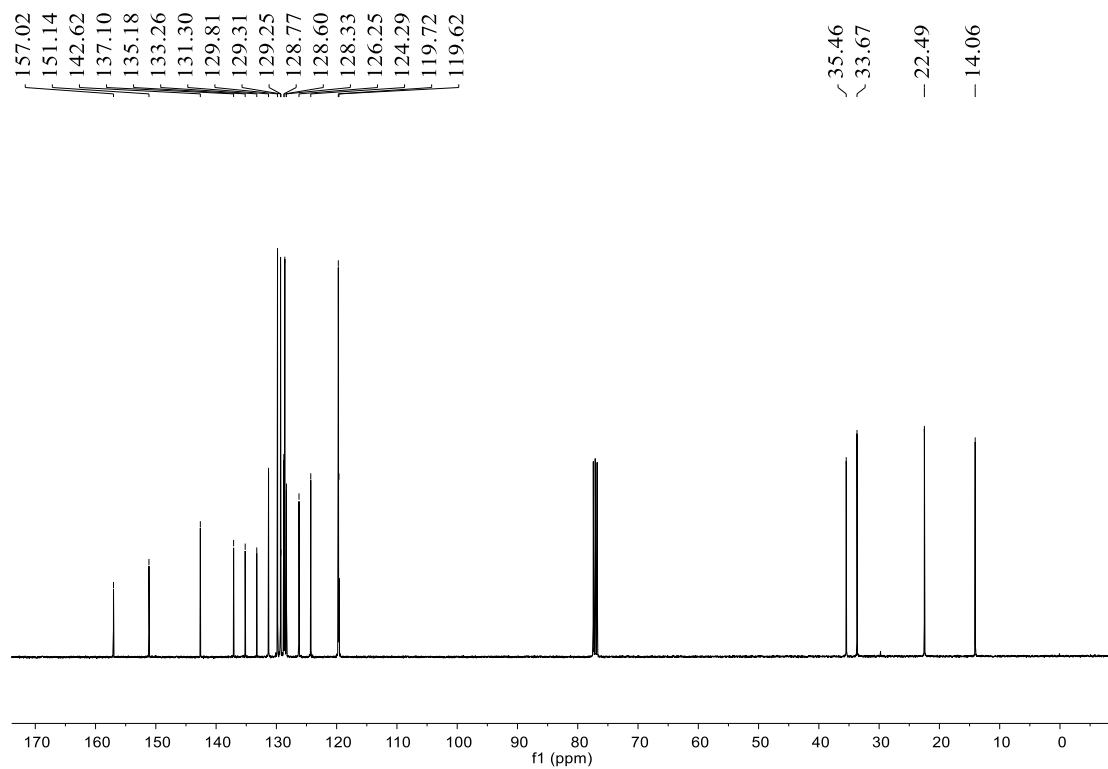
^{13}C NMR (100 MHz, CDCl_3) of compound **3ak**.



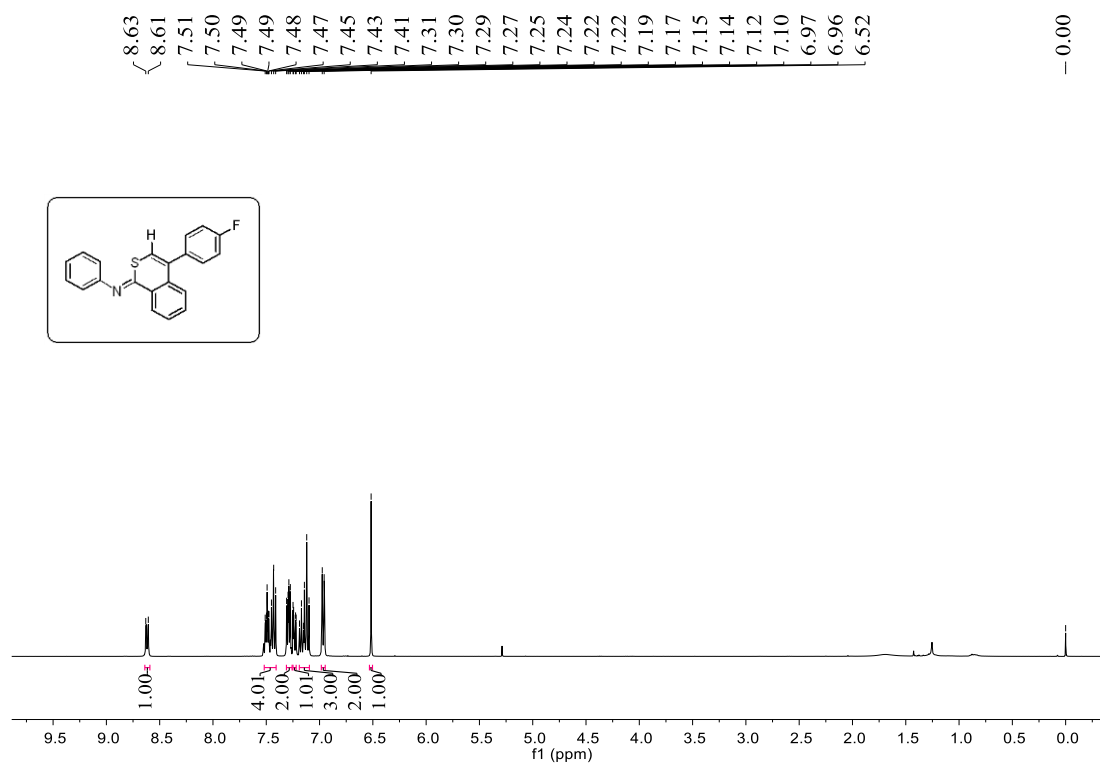
^1H NMR (400 MHz, CDCl_3) of compound **3al**.



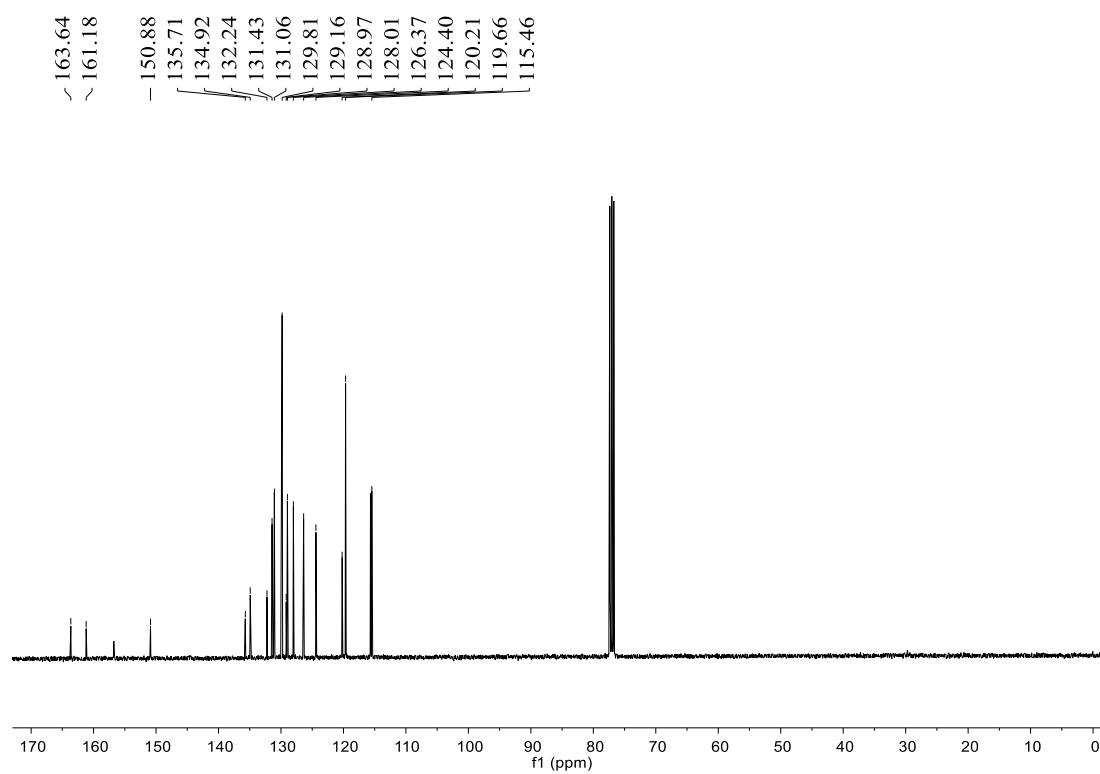
^{13}C NMR (100 MHz, CDCl_3) of compound **3al**.



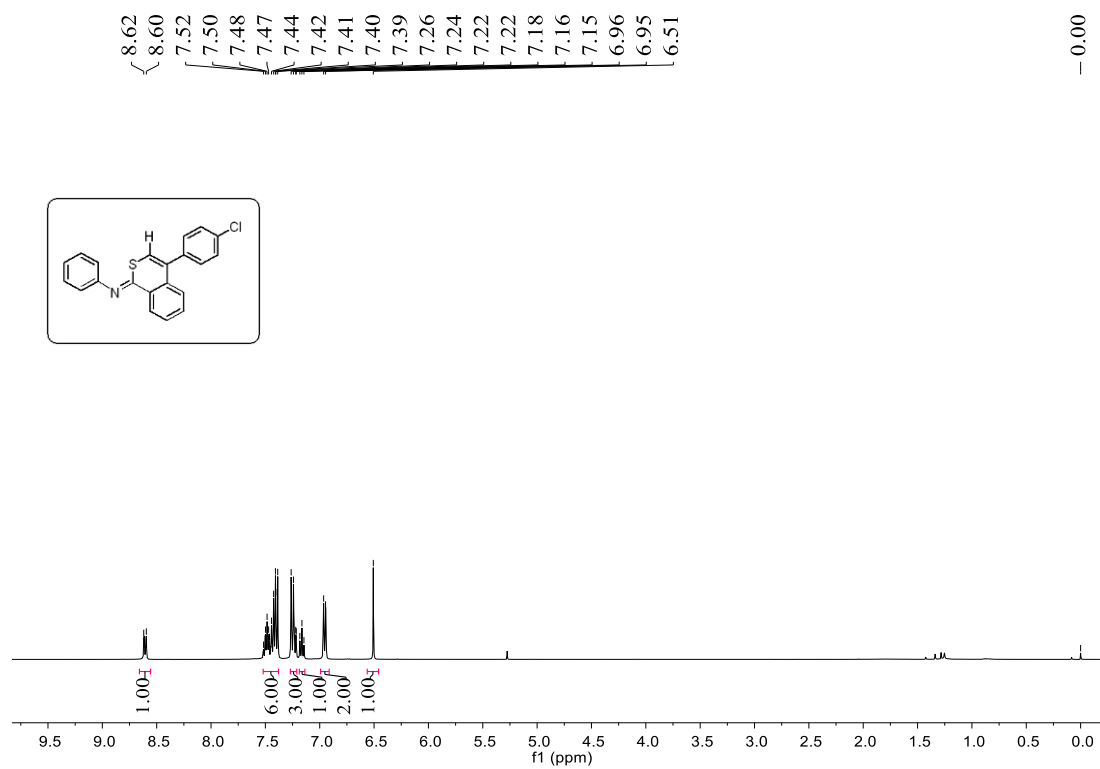
^1H NMR (400 MHz, CDCl_3) of compound **3am**.



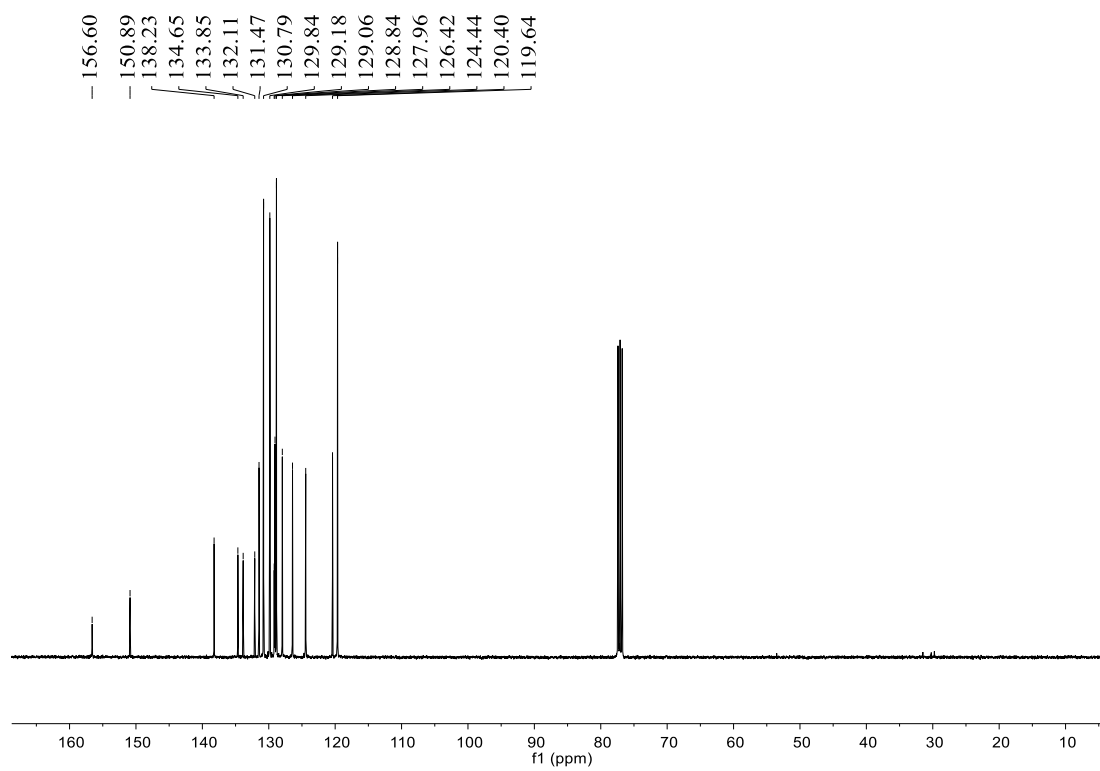
^{13}C NMR (100 MHz, CDCl_3) of compound **3am**.



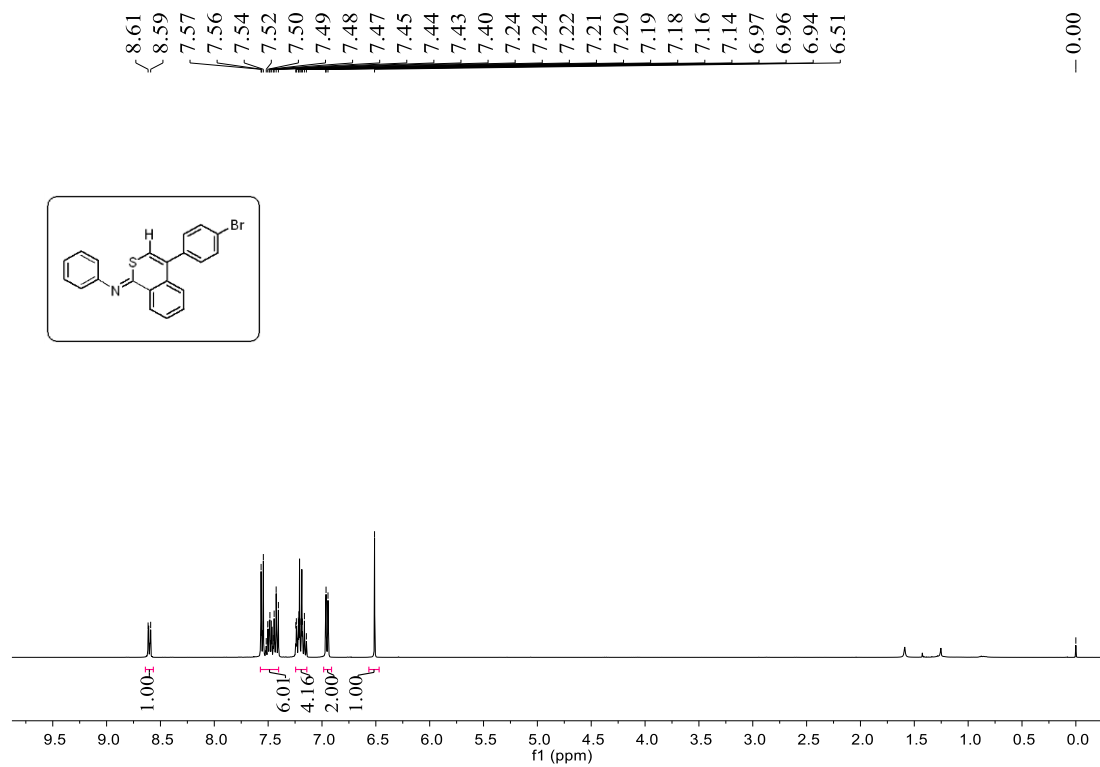
^1H NMR (400 MHz, CDCl_3) of compound **3an**.



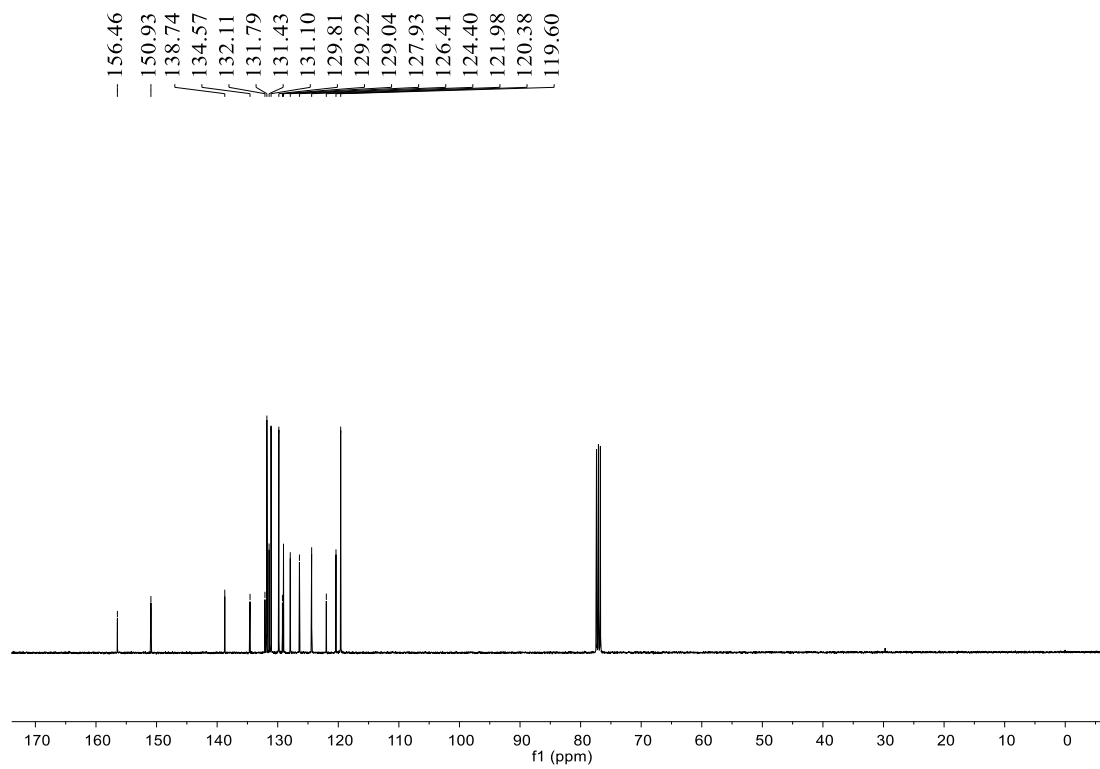
^{13}C NMR (100 MHz, CDCl_3) of compound **3an**.



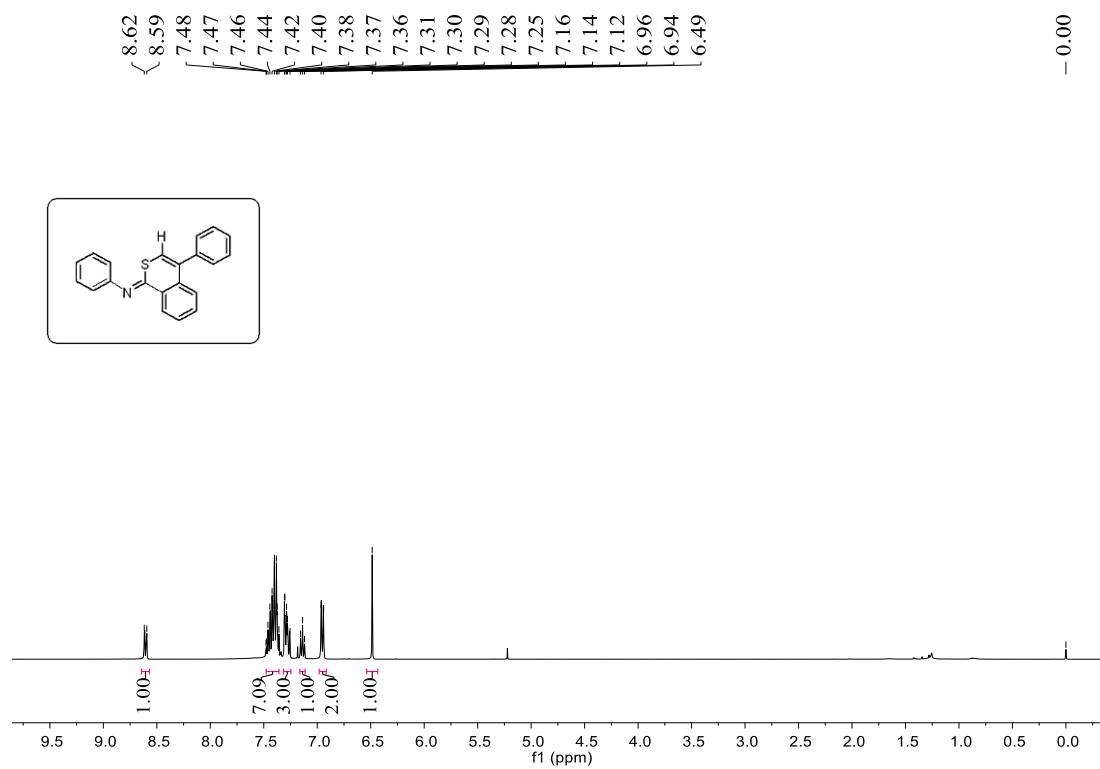
^1H NMR (400 MHz, CDCl_3) of compound **3ao**.



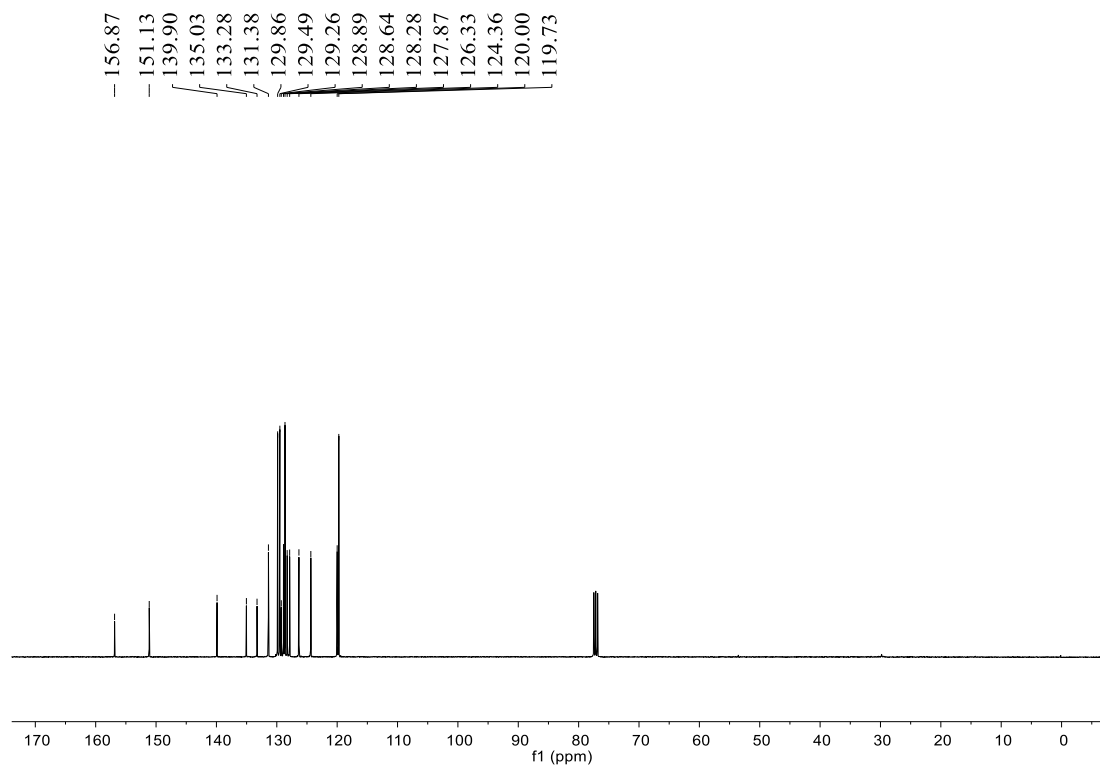
^{13}C NMR (100 MHz, CDCl_3) of compound **3ao**.



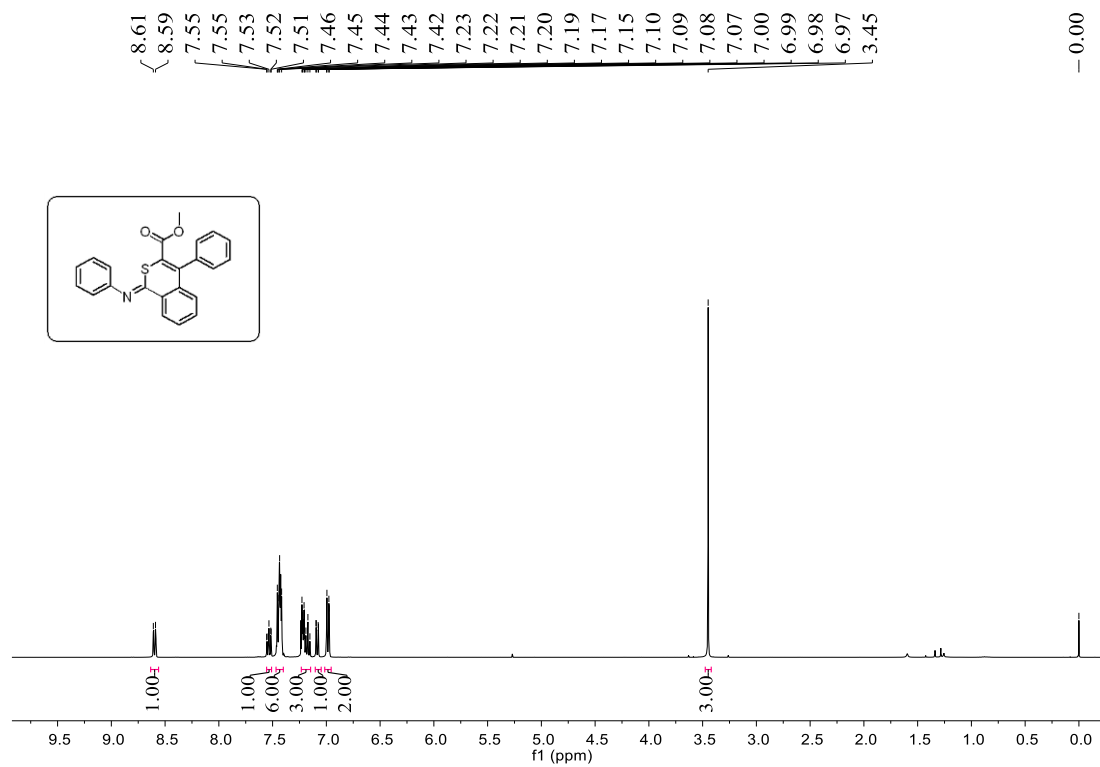
^1H NMR (400 MHz, CDCl_3) of compound **3ap**.



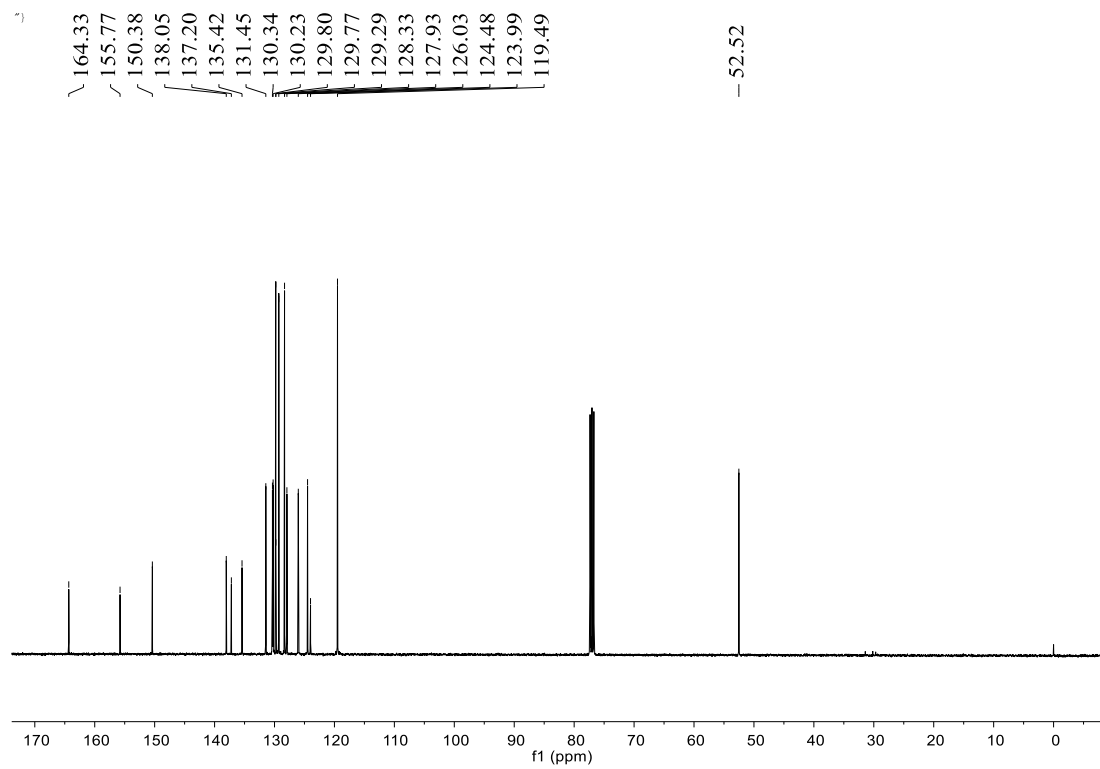
^{13}C NMR (100 MHz, CDCl_3) of compound **3ap**.



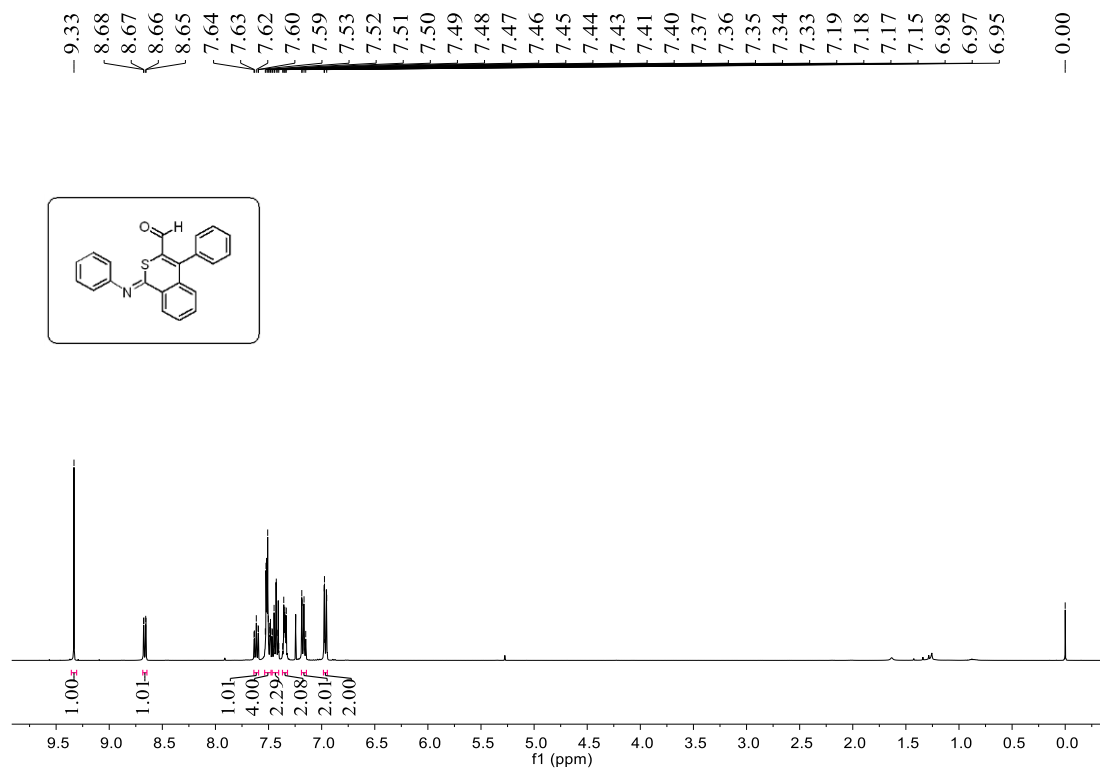
^1H NMR (400 MHz, CDCl_3) of compound **3aq**.



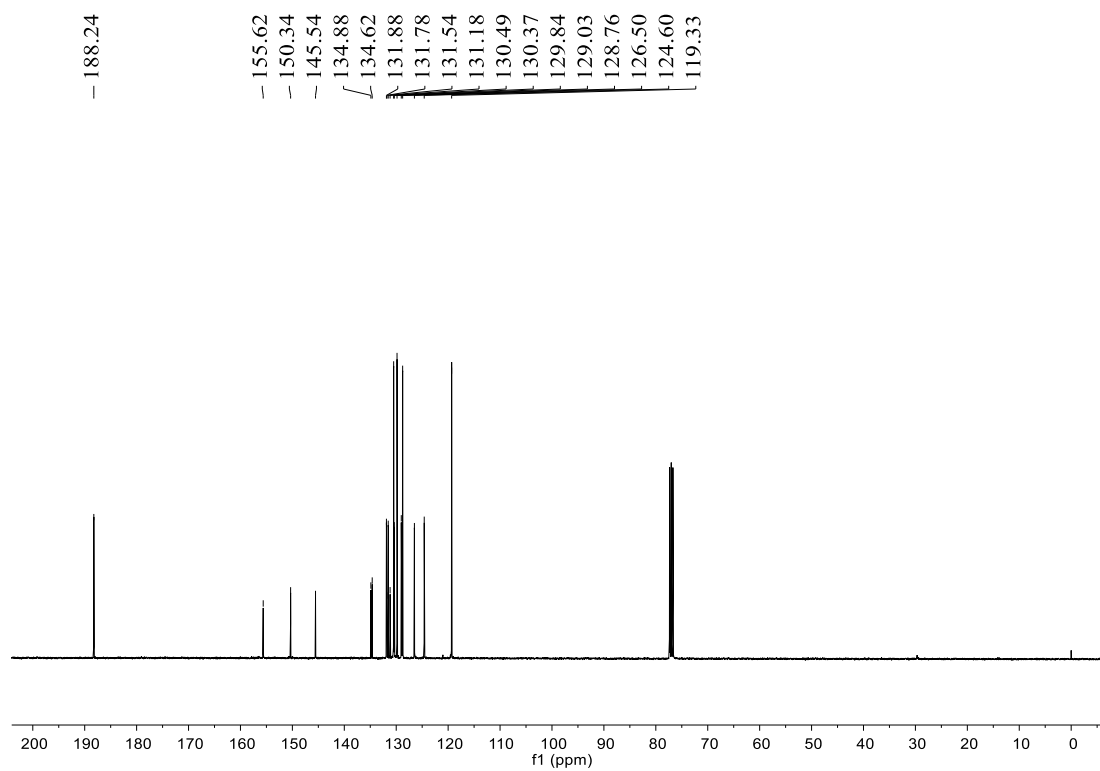
^{13}C NMR (100 MHz, CDCl_3) of compound **3aq**.



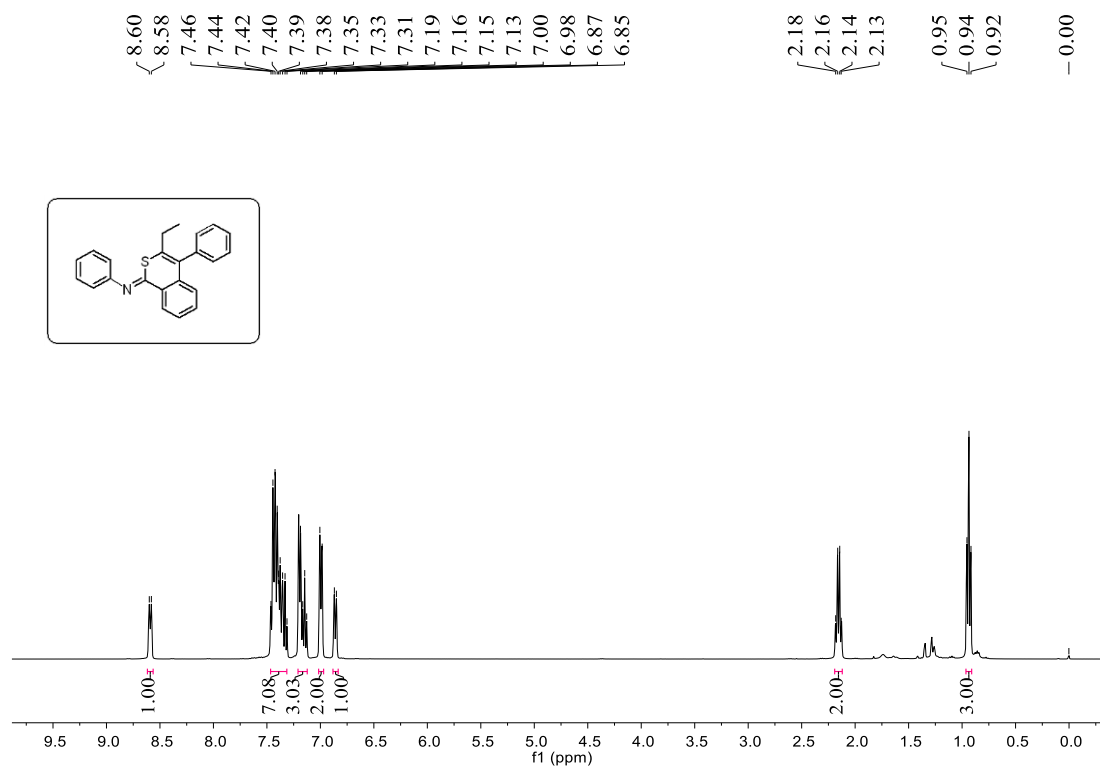
^1H NMR (400 MHz, CDCl_3) of compound **3ar**.



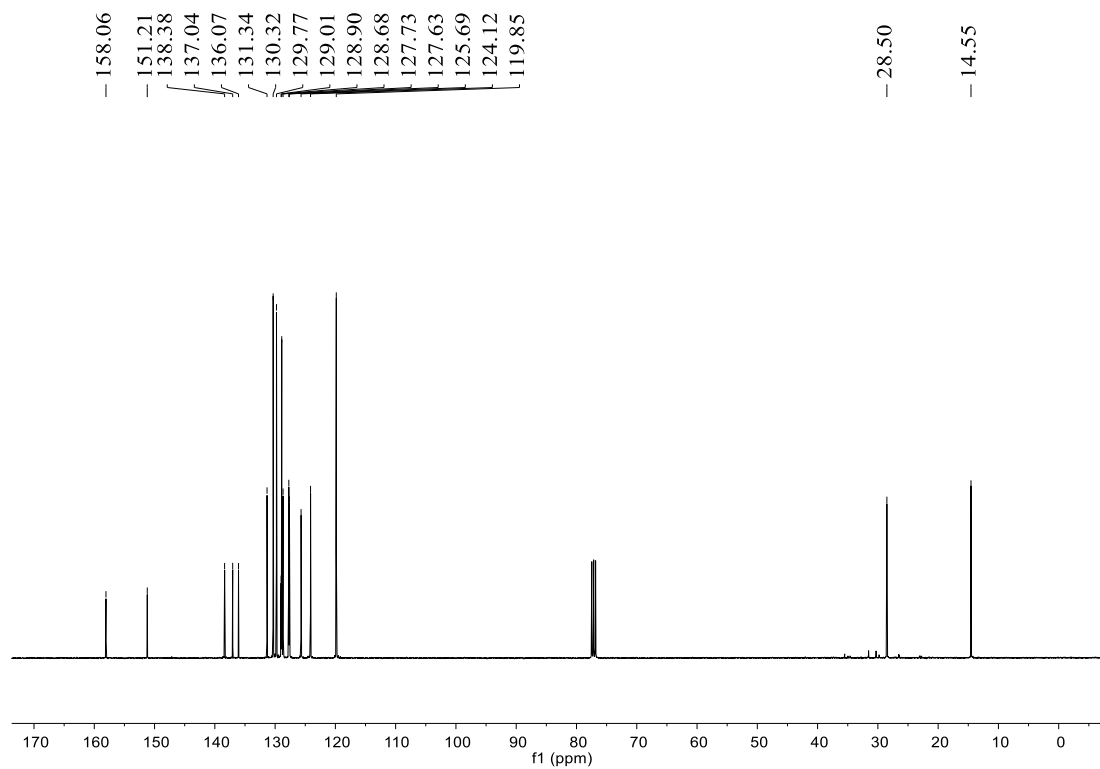
^{13}C NMR (100 MHz, CDCl_3) of compound **3ar**.



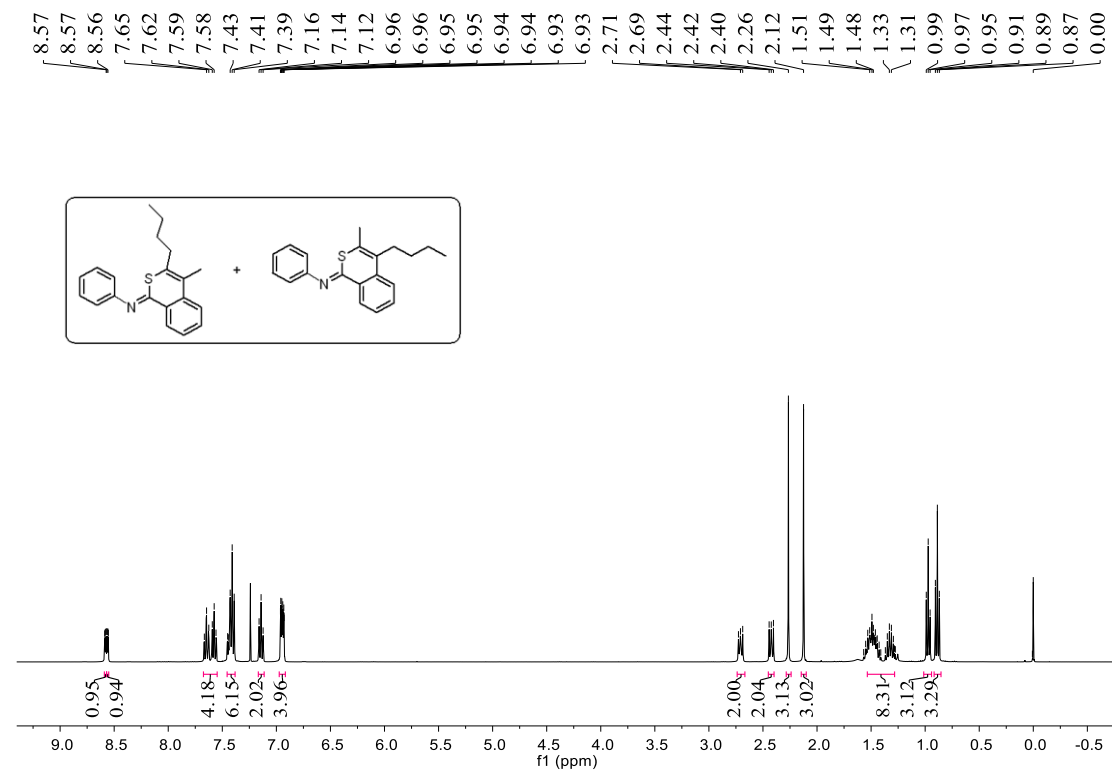
^1H NMR (400 MHz, CDCl_3) of compound **3as**.



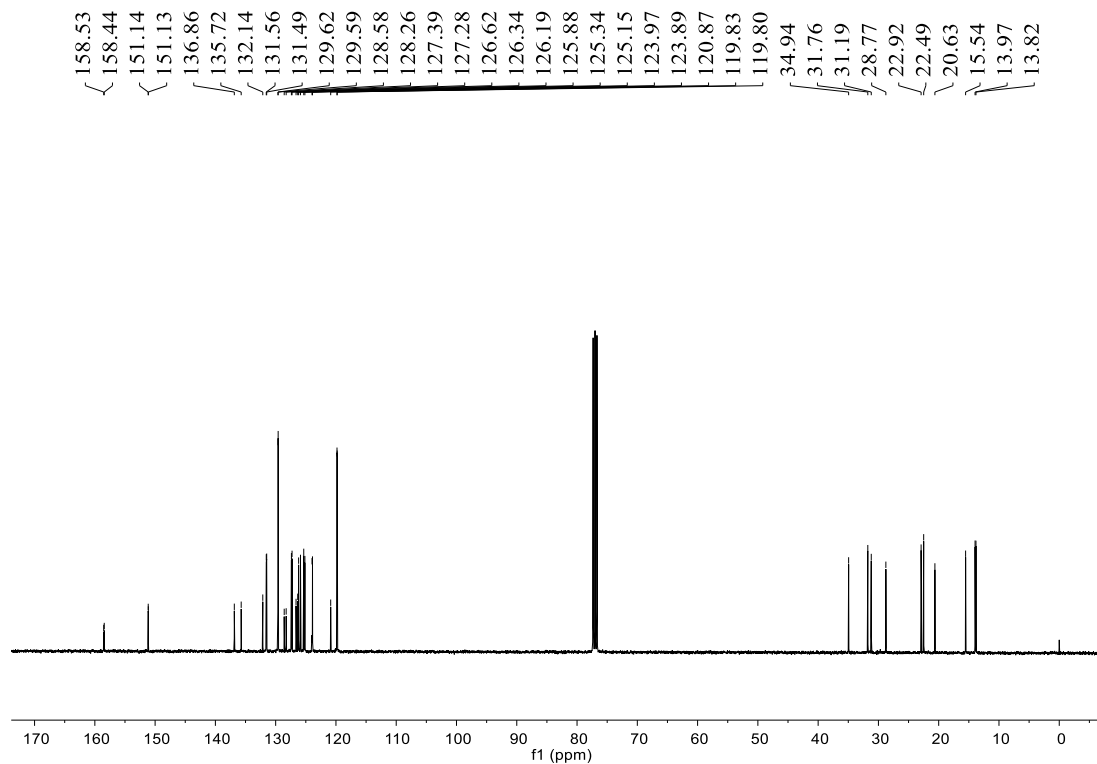
^{13}C NMR (100 MHz, CDCl_3) of compound **3as**.



^1H NMR (400 MHz, CDCl_3) of compound **3at** and **3at'**.



^{13}C NMR (100 MHz, CDCl_3) of compound **3at** and **3at'**.



8. Cartesian Coordinates of DFT–Optimized Structures

All of the calculations were carried out with the Gaussian 09 program package.¹¹ The geometric optimization and frequency analyses of all substrates were carried out at the B3LYP–D3/6–311G¹² (d,p) level of theory with SMD solvation model in ethanol solution.

Table S8. Cartesian Coordinates of DFT–Optimized Structures

N-Phenylbenzothioamide (**1a**)

C	-5.79119	-0.67700	0.00000
C	-4.39603	-0.67700	0.00000
C	-3.69849	0.53075	0.00000
C	-4.39615	1.73926	-0.00120
C	-5.79097	1.73918	-0.00168
C	-6.48857	0.53098	-0.00068
C	-6.34095	-1.62932	0.00045
C	-3.84652	-1.62951	0.00132
C	-3.84595	2.69140	-0.00126
C	-6.34109	2.69146	-0.00263
C	-7.58818	0.53116	-0.00068
C	-2.22849	0.53086	0.00085
C	-1.73914	-0.16155	1.20168
C	-2.73641	-0.85970	2.14488
C	-4.10172	-0.83429	1.85898
C	-2.27475	-1.51752	3.28493
C	-5.00517	-1.46601	2.71334
C	-4.46543	-0.31494	0.96052
C	-3.17826	-2.15033	4.13912
C	-1.19869	-1.53780	3.51032
C	-4.54330	-2.12456	3.85360
C	-6.08140	-1.44549	2.48838
C	-2.81393	-2.66926	5.03771
C	-5.25582	-2.62263	4.52705
C	-0.20680	-0.19170	1.52517

1-Phenyl-1-propyne (**2a**)

C	-7.21044	0.41599	0.41599
C	-5.81528	0.41599	0.41599
C	-5.11774	1.62374	1.62374
C	-5.81540	2.83225	2.83225
C	-7.21022	2.83217	2.83217
C	-7.90782	1.62396	1.62396
H	-7.76020	-0.53633	-0.53633
H	-5.26577	-0.53653	-0.53653
H	-5.26520	3.78439	3.78439
H	-7.76034	3.78445	3.78445
H	-9.00743	1.62415	1.62415
C	-3.57774	1.62385	1.62385
C	-1.67314	1.62399	1.62399
H	-1.31592	1.78870	1.78870
H	-1.31661	0.67974	0.67974

H	-1.31690	2.40360	2.40360
C	-2.74314	1.62391	1.62391
D			
C	3.57343	-0.28016	-1.90416
C	2.44717	0.31314	-1.34658
C	2.24106	0.26126	0.03891
C	3.20048	-0.34998	0.85533
C	4.33844	-0.91757	0.28919
C	4.52678	-0.89456	-1.09105
H	3.70958	-0.25664	-2.97980
H	1.70387	0.79475	-1.96906
H	3.05405	-0.35923	1.92888
H	5.07690	-1.38484	0.93116
H	5.41070	-1.34398	-1.52872
N	1.11478	0.90015	0.56760
C	0.19434	0.36006	1.25401
C	-0.94543	1.20085	1.71464
C	-1.2545	2.36465	0.99709
C	-1.71740	0.86867	2.83324
C	-2.32765	3.16058	1.37531
H	-0.64266	2.62132	0.14221
C	-2.78516	1.67501	3.21774
H	-1.47166	-0.01605	3.40547
C	-3.10024	2.81671	2.48549
H	-2.56477	4.05086	0.80357
H	-3.37078	1.40978	4.09071
H	-3.93893	3.43800	2.77874
S	0.11039	-1.42581	1.65782
C	-0.96809	0.96715	-3.22246
C	-1.45170	0.41718	-2.04673
C	-1.13669	-0.92347	-1.69103
C	-0.33373	-1.68049	-2.58658
C	0.14297	-1.11275	-3.75731
C	-0.16842	0.21018	-4.08572
H	-1.20952	1.99472	-3.47055
H	-2.06150	1.00537	-1.37273
H	-0.07661	-2.69914	-2.32433
H	0.77237	-1.69952	-4.41668
H	0.20943	0.64765	-5.00247
C	-1.60248	-1.47203	-0.49295
C	-2.59334	-2.46279	1.61519
H	-2.93489	-1.77197	2.39080
H	-2.18724	-3.34796	2.11298
H	-3.44851	-2.76177	1.00702
C	-1.54140	-1.80022	0.76074
D'			
C	3.91872	-0.58415	-1.95987
C	2.81046	0.14656	-1.54858
C	2.51145	0.26161	-0.18383
C	3.36749	-0.32224	0.75817
C	4.48917	-1.03141	0.33755
C	4.76495	-1.17524	-1.02030
H	4.12895	-0.68476	-3.01902

H	2.14894	0.61273	-2.26792
H	3.15725	-0.19866	1.81387
H	5.14663	-1.47641	1.07608
H	5.63606	-1.73283	-1.34429
N	1.40065	1.02636	0.18929
C	0.43030	0.62585	0.90100
C	-0.70336	1.54880	1.17388
C	-1.05838	2.48102	0.19204
C	-1.43858	1.49486	2.36339
C	-2.13434	3.33698	0.39373
H	-0.48847	2.50848	-0.72738
C	-2.50387	2.36517	2.57040
H	-1.17023	0.77182	3.12294
C	-2.86011	3.28280	1.58335
H	-2.41014	4.04527	-0.37940
H	-3.05810	2.32526	3.50147
H	-3.69888	3.95179	1.73989
S	0.21924	-1.09102	1.51860
C	0.02344	-1.59501	-2.96935
C	-0.1817	-1.81282	-1.61143
C	-1.25931	-1.22041	-0.94133
C	-2.13769	-0.40742	-1.67647
C	-1.92591	-0.18453	-3.03753
C	-0.84151	-0.77161	-3.68813
H	0.87449	-2.05436	-3.45892
H	0.52079	-2.41732	-1.05188
H	-2.96054	0.07731	-1.16465
H	-2.60189	0.46329	-3.58473
H	-0.66941	-0.58496	-4.74228
C	-1.40447	-1.37770	0.53687
C	-3.13821	-1.75644	2.51256
H	-3.75396	-2.65997	2.55953
H	-3.78651	-0.89703	2.71395
H	-2.38902	-1.81523	3.31490
C	-2.49578	-1.61517	1.20633
E			
C	-1.18629	1.84733	0.00000
C	0.24782	2.15249	-0.34591
C	0.59881	3.22675	-1.10012
C	-0.37248	4.18983	-1.50836
C	-1.66530	4.11677	-0.99767
C	-2.06378	3.05762	-0.19010
H	1.00010	1.43827	-0.03175
H	1.63540	3.36714	-1.38762
H	-0.08949	5.00492	-2.16341
H	-2.39038	4.89305	-1.21070
C	-1.87599	0.63072	-0.80326
H	-1.24131	1.52540	1.05109
C	-1.07309	-0.06497	-1.86265
C	-0.46797	-1.31206	-1.63866
C	-0.78497	0.59784	-3.06555
C	0.42664	-1.85336	-2.56547
H	-0.67466	-1.84236	-0.71541

C	0.10496	0.05750	-3.99107
H	-1.23995	1.56338	-3.25484
C	0.72608	-1.16498	-3.73918
H	0.89676	-2.80904	-2.36099
H	0.32193	0.59977	-4.90477
H	1.43286	-1.57697	-4.45069
C	-3.16069	0.35402	-0.50874
S	-4.02773	1.32928	0.74039
C	-3.40574	3.00503	0.35637
N	-4.10380	4.06758	0.50264
C	-5.40156	4.11146	1.01071
C	-5.74120	3.59797	2.27178
C	-6.38294	4.77019	0.25461
C	-7.04197	3.72266	2.74964
H	-4.97600	3.12952	2.87948
C	-7.68398	4.86906	0.73001
H	-6.10448	5.18600	-0.70630
C	-8.02077	4.34840	1.98028
H	-7.29053	3.32806	3.72861
H	-8.43756	5.36437	0.12771
H	-9.03368	4.43983	2.35479
C	-4.07750	-0.69554	-1.10615
H	-4.90867	-0.21347	-1.62902
H	-3.54344	-1.34164	-1.80442
H	-4.51128	-1.32043	-0.31875
E'			
C	-0.24055	-1.21720	3.05809
C	0.15909	-2.35763	3.74846
C	1.45710	-2.90091	3.50702
C	2.24422	-2.41902	2.50615
C	1.74627	-1.39545	1.51150
C	0.54747	-0.66479	2.05287
H	-0.48234	-2.79168	4.50578
H	1.82801	-3.68927	4.15416
H	3.24591	-2.81094	2.36790
C	0.86336	-1.00355	-0.87154
S	0.80277	0.72613	-0.34218
C	0.12617	0.52984	1.34678
N	-0.70323	1.34872	1.87526
C	-1.18103	2.50558	1.26113
C	-2.57066	2.67653	1.17250
C	-0.33534	3.52614	0.80173
C	-3.09875	3.82305	0.59326
H	-3.21502	1.89358	1.55416
C	-0.87435	4.68136	0.24461
H	0.73745	3.41641	0.90826
C	-2.25469	4.83255	0.12855
H	-4.17439	3.93566	0.51371
H	-0.21098	5.46607	-0.10172
H	-2.67007	5.73242	-0.30993
H	2.54811	-0.67735	1.29337
H	-1.17539	-0.72446	3.29676
C	0.38754	-1.17875	-2.29902

C	-0.80594	-0.58049	-2.75873
C	1.13311	-1.91881	-3.23221
C	-1.24790	-0.75756	-4.06967
H	-1.39221	0.02131	-2.07500
C	0.69155	-2.09293	-4.54567
H	2.07516	-2.35696	-2.92311
C	-0.50473	-1.52014	-4.97041
H	-2.17676	-0.29538	-4.3851
H	1.29254	-2.67327	-5.23703
H	-0.84782	-1.6567	-5.98978
C	1.29057	-1.93008	0.02402
C	1.23007	-3.42076	-0.21585
H	0.70356	-3.90960	0.60967
H	0.71771	-3s.65948	-1.14835
H	2.23412	-3.85861	-0.25085

9. References

- 1 (a) M. Ren, X. Zhang and Y. Liu, *ACS Catal.* 2022, **12**, 5077 – 5093; (b) Y. Liu, C. Shen and N. Jiang, *ACS Catal.* 2017, **7**, 8228 – 8234; (c) Y. Zhang, L. Shi, Z. Geng, T. Ren and Z. Yang, *Sci. Rep.* 2019, **9**, 19090.
- 2 (a) G. Zhang, C. Liu and H. Yi, *J. Am. Chem. Soc.* 2015, **137**, 9273 – 9280; (b) J. Bai, S. Yan, Z. Zhang, Z. Guo and C. Zhou, *Org. Lett.* 2021, **23**, 4843 – 4848.
- 3 (a) Z. Fang, S. Zheng, Z. Guo, J. Guo, B. Tan and X. Liu, *Angew. Chem. Int. Ed.* 2015, **54**, 9528 – 9532; (b) S. Gao, H. Liu, Z. Wu, H. Yao and A. Lin, *Green Chem.* 2017, **19**, 1861 – 1865.
- 4 J. Karthikeyan, R. Haridharan and C. Chen, *Angew. Chem. Int. Ed.* 2012, **51**, 12343 – 12347.
- 5 W. B. Du, N. N. Wang, C. Pan, *Green Chem.* 2021, **23**, 2420 – 2426.
- 6 Z. J. Liu, X. F. Guo, Z. Feng, L. H. Jia, *J. Solution Chem.* 2015, **44**, 293 – 306.
- 7 (a) S. Song, Y. Li and Q. Liu, *J. Hazard Mater.* 2021, **412**, 125158; (b) X. Xiang, Q. Sun and N. Gan, *Food Hydrocolloids.* 2022, **123**, 107168; (c) Y. Yang, W. Lei, Y. Xu, T. Zhou, M. Xia and Q. Hao, *Microchim. Acta.* 2018, **185**, 39.
- 8 G. M. Sheldrick, *Acta Crystallogr. Sect. A.* 2015, **8**.
- 9 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339 – 341(2009).
- 10 W. Trucks and H. B. Schlegel, *Gaussian.* 2009.
- 11 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.* 1980, **72**, 650 – 654.
- 12 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.* 2005, **105**, 2999 – 3094.