Supporting Information

Efficient One-Step Synthesis of 3-Nitroflavones via Cascade Nitration-Cyclization

Yilin Yang [a], Chukai Shao [*a], Ruirui Hua [a], Rui Tian [a], Ziang Wang [a], Hongquan Yin [a,b], Houhua Zhu [c], Fu-Xue Chen [*a,b]

[a] *School of Chemistry & Chemical Engineering, Beijing Institute of Technology (Liangxiang Campus), No. 8 Liangxiang East Road, Fangshan District, Beijing City, Beijing 102488, China*

[b] *Key Laboratory of Medical Molecule Science and Pharmaceutics Engineering, Ministry of Industry and Information Technology, Beijing Institute of Technology (Liangxiang Campus), No. 8 Liangxiang East Road, Fangshan District, Beijing City, Beijing 102488, China*

[c] *Department of Biomedical Data Science, School of Science, China Pharmaceutical University No. 639 Longmian Avenue, Jiangning District, Nanjing City, Jiangsu 211198, China*

Contents

1. General experimental information.

Reactions were carried out using commercial available reagents in over-dried apparatus. CH_2Cl_2 was distilled over CaH_2 before use. Other chemicals were purchased without further purification. Column chromatography was performed using silica gel 60 (particle size 0.06−0.2 mm; 70−230 mesh ASTM). Thin-layer chromatography (TLC) was performed on silica gel F254 TLC glass plates and visualized with UV light. ^{19}F NMR were recorded with Brucker Avance (471 MHz) ^{19}F NMR chemical shifts are reported in ppm from trichlorofluoromethane. ^{1}H NMR spectra were recorded on Bruker Avance spectrometers at 400 MHz or 500 MHz. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) as the internal standard, ^{13}C NMR spectra were recorded with Brucker Avance spectrometer with complete proton decoupling at 101 MHz or 126 MHz. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, $\delta = 77.0$). s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, q = quartet, PE = petroleum ether, EA = ethyl acetate.

Infrared spectrometer: Bruker ALPHA FT-IR-Spektrometer. High resolution mass spectrum (HRMS): AGILENT Q-TOF 6520. Melting points were measured on a binocular microscope XT4A melting point apparatus (uncorrected).

2. Single Crystal Data of 2a.

Single Crystal Data of **2a** was analyzed by Bruker D8 VENTURE TXS PHOTON II diffractometer **(2a)**.

2a (20 mg) was dissolved in CH_2Cl_2, the solution slowly evaporated at room temperature and obtained the crystal. The single crystal structure was shown in Figure S1 and the crystallographic data was displayed in Table S1.

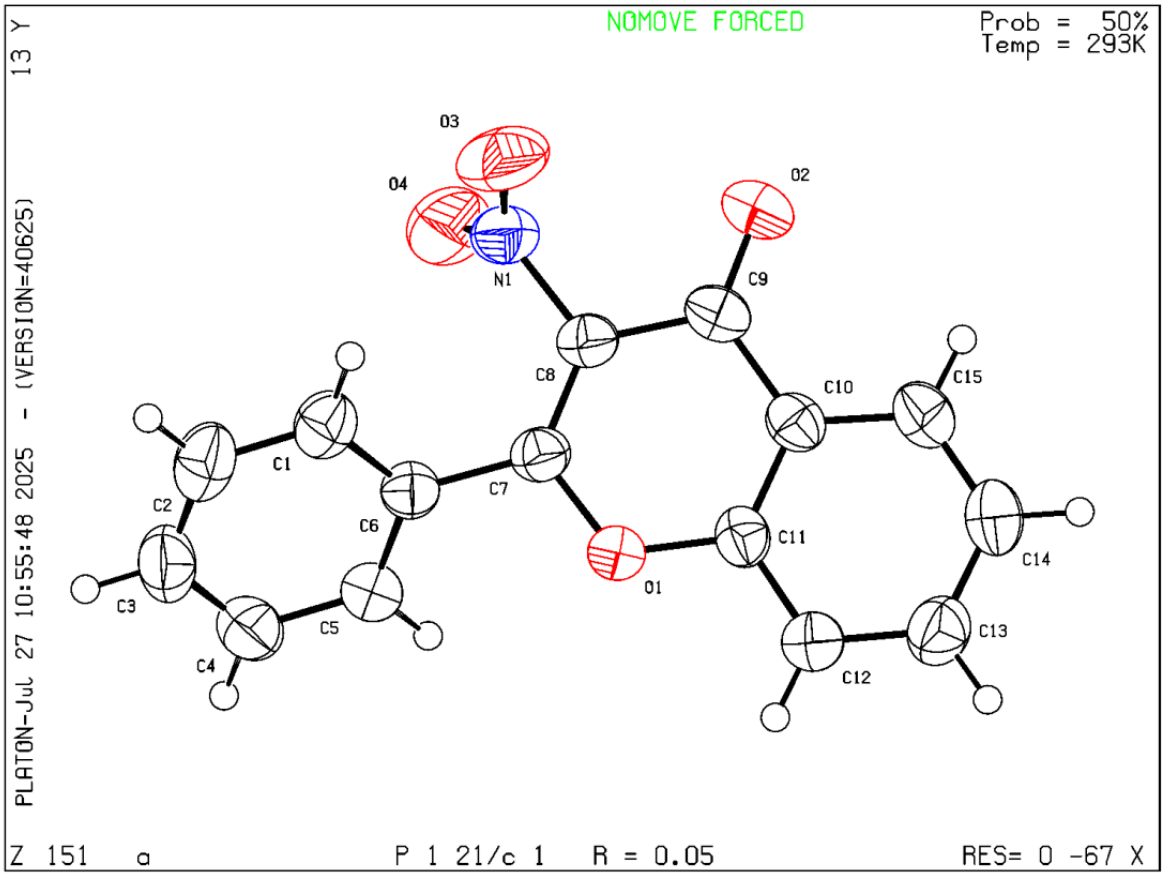


Figure S1 Single Crystal Structure of 2a

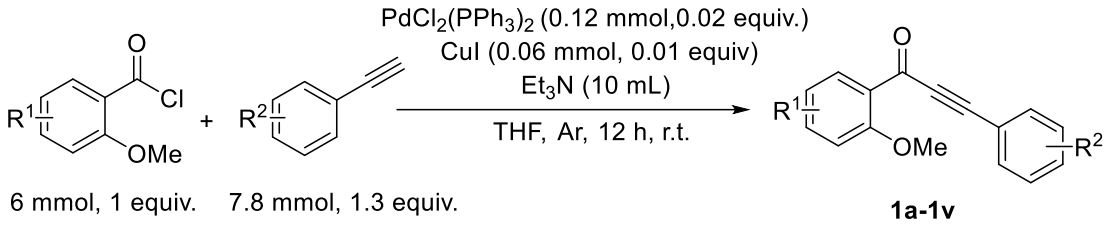
Table S1. Single Crystal Data of 2a

Compound	2a
CCDC	2521825
Empirical formula	$C_{15}H_9NO_4$
Formula weight	267.23
Temperature/K	293.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.963(3)
b/Å	9.033(3)
c/Å	13.398(4)
α/°	90
β/°	111.672(8)
γ/°	90
Volume/Å^3	1232.9(6)
Z	4
ρ_{calc}g/cm^3	1.440
μ/mm^{-1}	0.106
F(000)	552.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.572 to 55.096
Index ranges	$-13 \le h \le 14$, $-11 \le k \le 11$, $-17 \le l \le 13$
Reflections collected	11192
Independent reflections	2811 [R_{int} = 0.0640, R_{sigma} = 0.0548]
Data/restraints/parameters	2811/0/181
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1074
Final R indexes [all data]	R_1 = 0.0983, wR_2 = 0.1313
Largest diff. peak/hole / e Å^{-3}	0.16/-0.16

3. Typical procedure of substrates (1a-1v)

Alkynylbenzoates **1a–1v** are known compounds and were prepared according to the known literature procedure (Scheme S1). [1, 2]

Scheme S1



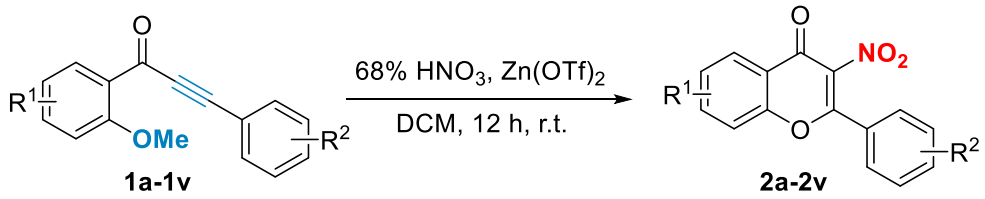
General procedure： To an oven dried flask was added $PdCl_2(PPh_3)_2$ (0.12 mmol, 0.02 equiv.), CuI (0.06 mmol, 0.01 equiv.), Et_3N (10 mL) in turn under Ar atmosphere at room temperature. Then, The acyl chloride substrate (6 mmol, 1 equiv.) was dissolved in anhydrous THF (15 mL), and the aryl alkyne (R^2-substituted phenylacetylene, 7.8 mmol, 1.3 equiv.) was added. Stir the reaction mixture at room temperature for 12 h. After the reaction is complete, remove the solvent from the solution by rotary evaporation.

The crude product was purified by silica gel column chromatography to obtain the target compound.

4. Synthesis, Scale-Up, and Synthetic Applications of Products

(1) Typical Procedure of 3-nitroflavone derivatives (2a-2v).

Scheme S2

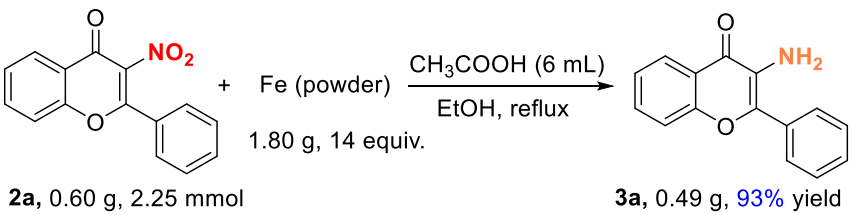


General procedure: In a dry glass tube, **1a**–**1v** (0.1 mmol) were dissolved in 1.0 mL dichloromethane at room temperature. Then, $Zn(OTf)_2$ (0.1 mmol) was added, followed by 68% HNO_3 (0.2 mmol). The mixture was stirred at room temperature for 12 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted with CH_2Cl_2 (3 × 5.0 mL) using a separatory funnel. The organic layer was collected, dried over Na_2SO_4, concentrated, and then charged onto a silica gel column. The desired product **2a**–**2v** was separated by column chromatography.

(2) Synthetic Transformations of 3-Nitroflavone

3a is known compounds and was prepared according to the known literature procedure (Scheme S3).[3]

Scheme S3



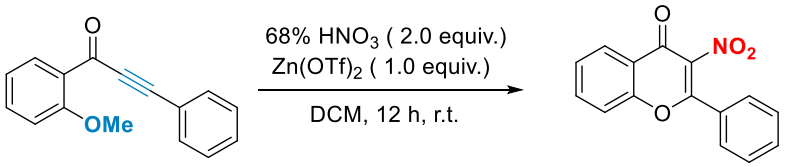
General procedure: To a stirred solution of 3-nitroflavone (0.60 g, 1.0 equiv.) in

absolute ethanol (15 mL) and glacial acetic acid (6 mL) was added iron powder (300 mesh, 1.8 g, 3.0 equiv.) at room temperature. The reaction mixture was then heated to reflux (70 °C) and stirred for 2 h. The reaction mixture was cooled to room temperature and diluted with saturated $NaHCO_3$ solution (20 mL), followed by filtration through Celite to remove iron residues. The filtrate was extracted with EtOAc (3×30 mL).

The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude 3-aminoflavone as a yellow solid. The product was purified by silica gel column chromatography (silica gel, EA/PE =1/10, v/v) to get **3a** (0.49 g, 93% yield); m.p. 128-130 °C.

(3) Gram-Scale Preparation of 3-Nitroflavone

Scheme S4



1a, 2.50 g, 10.59 mmol

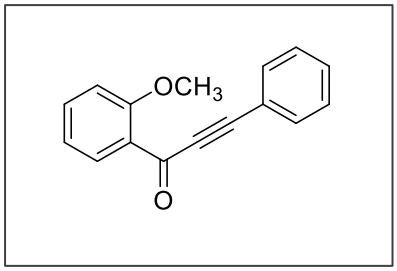
2a, 2.65 g, 94% yield

General procedure: To a stirred solution of alkynyl aryl ketone **1a** (2.50 g, 10.59 mmol) in CH_2Cl_2 (25 mL) was added $Zn(OTf)_2$ as the additive (1.0 equiv.) at room temperature. Subsequently, 68% HNO_3 (2.0 equiv.) was added dropwise, and the reaction mixture was stirred at room temperature for 12 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure.

The crude product was purified by silica gel column chromatography (silica gel, EA/PE =1/20, v/v) to afford **2a** (2.65 g, 94% yield) as a yellow solid; m.p. 131-133 ℃.

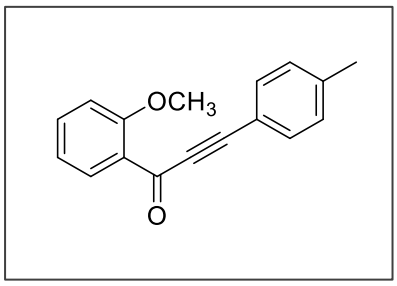
5. Characterization Data of 1a-1v, 2a-2v and 3a.

1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one (1a)[4]



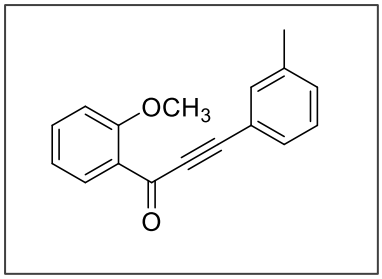
The reaction was accomplished according to the general experimental procedure described above, product **1a** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.6, yellow oil, 80% yield (1.8 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.53 (ddd, *J* = 8.8, 7.4, 1.8 Hz, 1H), 7.48 – 7.35 (m, 2H), 7.06 (td, *J* = 7.6, 1.0 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H).

1-(2-methoxyphenyl)-3-(p-tolyl)prop-2-yn-1-one (1b)[4]



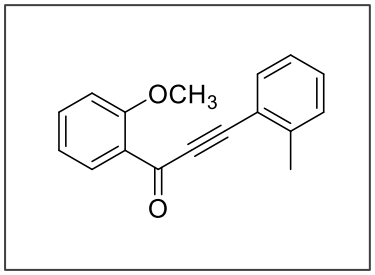
The reaction was accomplished according to the general experimental procedure described above, product **1b** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.6, yellow oil, 75% yield (1.1 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.05 (td, *J* = 7.6, 1.0 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H), 2.39 (s, 3H).

1-(2-methoxyphenyl)-3-(m-tolyl)prop-2-yn-1-one (1c)[4]



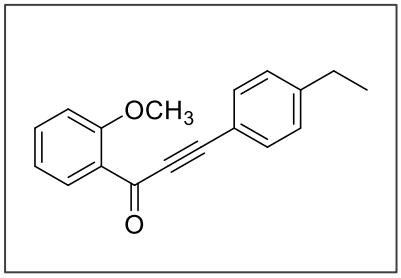
The reaction was accomplished according to the general experimental procedure described above, product **1c** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.6, yellow oil, 77% yield (1.1 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.59 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.7, 7.3, 1.8 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.05 (td, *J* = 7.5, 1.0 Hz, 1H), 7.02 (dd, *J* = 8.4, 1.0 Hz, 1H), 3.95 (s, 3H), 2.54 (s, 3H).

1-(2-methoxyphenyl)-3-(o-tolyl)prop-2-yn-1-one (1d)[4]



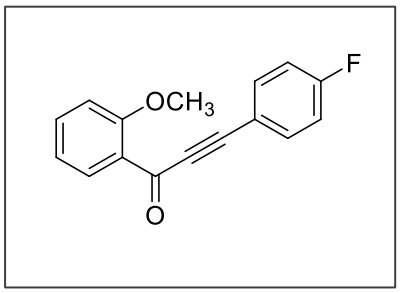
The reaction was accomplished according to the general experimental procedure described above, product **1d** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 72% yield (1.1 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.59 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.7, 7.3, 1.8 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.05 (td, *J* = 7.6, 1.0 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 2.54 (s, 3H).

3-(4-ethylphenyl)-1-(2-methoxyphenyl)prop-2-yn-1-one (1e)[5]



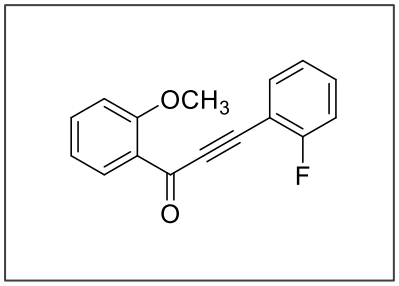
The reaction was accomplished according to the general experimental procedure described above, product **1e** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0. 5, yellow oil, 73% yield (1.2 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.58 – 7.49 (m, 3H), 7.25 – 7.20 (m, 2H), 7.05 (td, *J* = 7.5, 1.0 Hz, 1H), 7.01 (dd, *J* = 8.4, 1.0 Hz, 1H), 3.96 (s, 3H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H).

3-(4-fluorophenyl)-1-(2-methoxyphenyl)prop-2-yn-1-one (1f)[4]



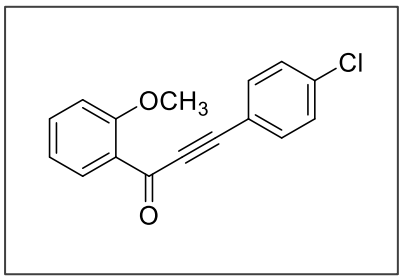
The reaction was accomplished according to the general experimental procedure described above, product **1f** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 67% yield (1.0 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.54 (ddd, *J* = 8.8, 7.4, 1.8 Hz, 1H), 7.14 – 6.99 (m, 4H), 3.96 (s, 3H). **^{19}F NMR** (471 MHz, CDCl3) δ -106.80.

3-(2-fluorophenyl)-1-(2-methoxyphenyl)prop-2-yn-1-one (1g)[6]



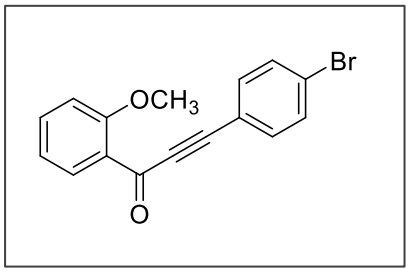
The reaction was accomplished according to the general experimental procedure described above, product **1g** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 58% yield (0.9 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.63 (td, *J* = 7.3, 1.8 Hz, 1H), 7.55 (ddd, *J* = 8.8, 7.3, 1.8 Hz, 1H), 7.44 (tdd, *J* = 7.4, 5.2, 1.8 Hz, 1H), 7.21 – 7.10 (m, 2H), 7.05 (td, *J* = 8.1, 1.0 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 3.97 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -107.26.

3-(4-chlorophenyl)-1-(2-methoxyphenyl)prop-2-yn-1-one (1h)[4]



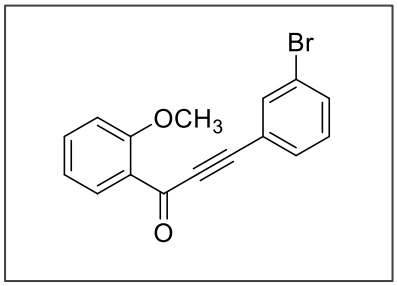
The reaction was accomplished according to the general experimental procedure described above, product **1h** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 60% yield (1.0 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.58 – 7.51 (m, 3H), 7.41 – 7.35 (m, 2H), 7.05 (td, *J* = 7.6, 1.0 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H).

3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-yn-1-one (1i)[5]



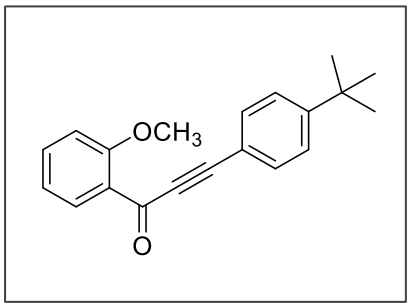
The reaction was accomplished according to the general experimental procedure described above, product **1i** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 60% yield (1.1 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.64 – 7.51 (m, 3H), 7.54 – 7.45 (m, 2H), 7.06 (td, *J* = 7.6, 1.0 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H).

3-(3-bromophenyl)-1-(2-methoxyphenyl)prop-2-yn-1-one (1j)[6]



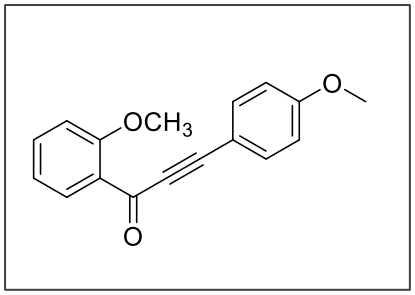
The reaction was accomplished according to the general experimental procedure described above, product **1j** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 63% yield (1.2 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.76 (t, *J* = 1.7 Hz, 1H), 7.62 – 7.51 (m, 3H), 7.28 – 7.23 (m, 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.0 Hz, 1H), 3.97 (s, 3H).

3-(4-(tert-butyl)phenyl)-1-(2-methoxyphenyl)prop-2-yn-1-one (1k)[7]



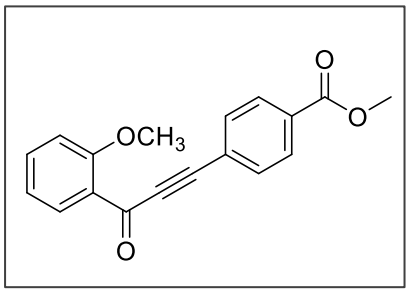
The reaction was accomplished according to the general experimental procedure described above, product **1k** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, yellow oil, 78% yield (1.4 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.44 – 7.39 (m, 2H), 7.05 (td, *J* = 7.6, 1.0 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 3H), 1.33 (s, 9H).

1-(2-methoxyphenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one (1l)[4]



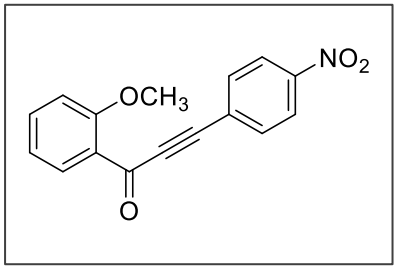
The reaction was accomplished according to the general experimental procedure described above, product **1l** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 75% yield (1.2 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.53 (ddd, *J* = 8.9, 7.3, 1.8 Hz, 1H), 7.09 – 6.98 (m, 2H), 6.95 – 6.87 (m, 2H), 3.97 (s, 3H), 3.85 (s, 3H).

methyl 4-(3-(2-methoxyphenyl)-3-oxoprop-1-yn-1-yl)benzoate (1m)



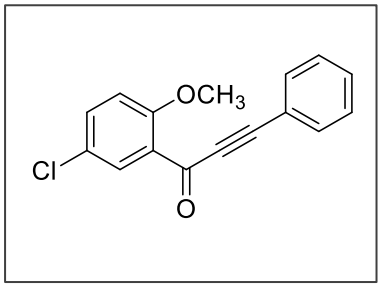
The reaction was accomplished according to the general experimental procedure described above, product **1m** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 75% yield (1.3 g). m.p. 74-76 ℃ **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 – 8.03 (m, 3H), 7.72 – 7.65 (m, 2H), 7.56 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.07 (td, *J* = 7.6, 1.1 Hz, 1H), 7.03 (dd, *J* = 8.4, 0.8 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.3, 166.1, 159.9, 135.3, 132.69, 132.64, 131.4, 129.6, 126.4, 125.2, 120.4, 112.2, 90.9, 89.7, 55.9, 52.4. **IR** (KBr): 3078, 2953, 2194, 1724, 1645, 1274, 752 cm^{-1} **HRMS** (ESI) m/z: calcd. for $C_{18}H_{15}O_4^+$ $[M + H]^+$295.0965, found 295.0976.

1-(2-methoxyphenyl)-3-(4-nitrophenyl)prop-2-yn-1-one (1n)[5]



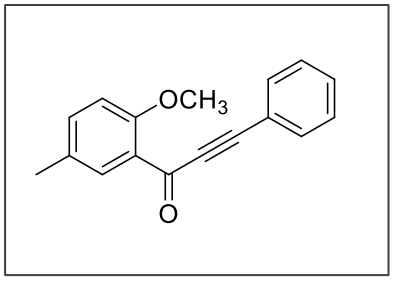
The reaction was accomplished according to the general experimental procedure described above, product **1n** was purified by flash column chromatography (silica gel, EA/PE =1/10, v/v). TLC R_f = 0.3, orange red solid, 60% yield (1.0 g). m.p. 134-136 ℃ **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 – 8.14 (m, 2H), 7.97 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.50 (ddd, *J* = 8.9, 7.4, 1.8 Hz, 1H), 7.03 – 6.93 (m, 2H), 3.89 (s, 3H).

1-(5-chloro-2-methoxyphenyl)-3-phenylprop-2-yn-1-one (1o)[4]



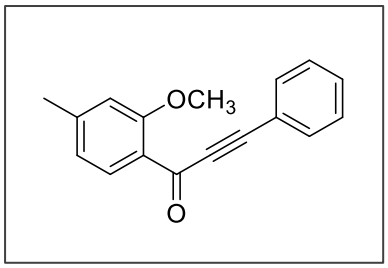
The reaction was accomplished according to the general experimental procedure described above, product **1o** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 70% yield (1.1 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.7 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.48 (td, *J* = 7.9, 2.1 Hz, 2H), 7.41 (dd, *J* = 8.2, 6.7 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 1H), 3.96 (s, 3H).

1-(2-methoxy-5-methylphenyl)-3-phenylprop-2-yn-1-one (1p)[7]



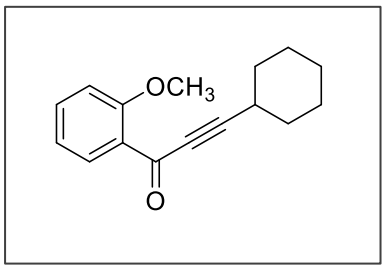
The reaction was accomplished according to the general experimental procedure described above, product **1p** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 77% yield (1.1 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.3 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.50 – 7.41 (m, 1H), 7.39 (dd, *J* = 8.0, 6.3 Hz, 2H), 7.34 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 3.94 (s, 3H), 2.35 (s, 3H).

1-(2-methoxy-4-methylphenyl)-3-phenylprop-2-yn-1-one (1q)[8]



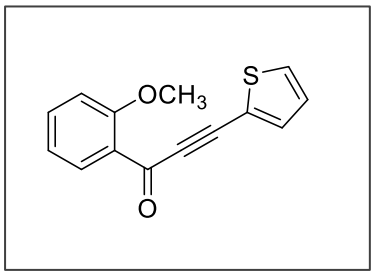
The reaction was accomplished according to the general experimental procedure described above, product **1q** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 74% yield (1.1 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.48 – 7.41 (m, 1H), 7.39 (dd, *J* = 8.2, 6.6 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.81 (s, 1H), 3.95 (s, 3H), 2.42 (s, 3H).

3-cyclohexyl-1-(2-methoxyphenyl)prop-2-yn-1-one (1r)[9]



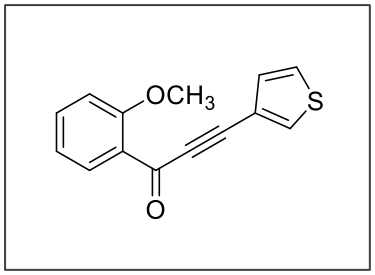
The reaction was accomplished according to the general experimental procedure described above, product **1r** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 77% yield (1.1 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.50 (ddd, *J* = 8.7, 7.3, 1.8 Hz, 1H), 7.01 (td, *J* = 7.5, 1.0 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 2.65 (tt, *J* = 8.8, 3.8 Hz, 1H), 1.88 (m, 2H), 1.80 – 1.70 (m, 2H), 1.57 (m, 3H), 1.37 (m, 3H).

1-(2-methoxyphenyl)-3-(thiophen-2-yl)prop-2-yn-1-one (1s)[6]



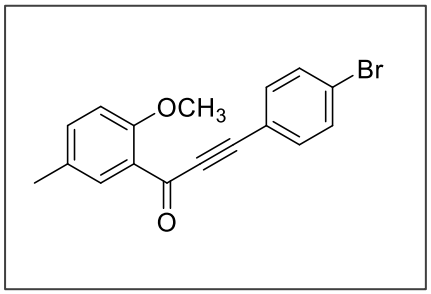
The reaction was accomplished according to the general experimental procedure described above, product **1s** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, brown oil, 75% yield (1.1 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.58 – 7.47 (m, 3H), 7.11 – 6.99 (m, 3H), 3.98 (s, 3H).

1-(2-methoxyphenyl)-3-(thiophen-3-yl)prop-2-yn-1-one (1t)[6]



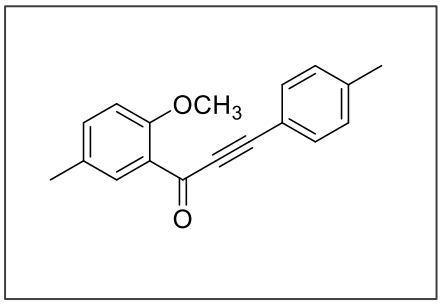
The reaction was accomplished according to the general experimental procedure described above, product **1t** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, brown oil, 75% yield (1.1 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.78 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.54 (ddd, *J* = 8.8, 7.4, 1.8 Hz, 1H), 7.35 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.28 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.06 (td, *J* = 7.6, 1.0 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 3H).

3-(4-bromophenyl)-1-(2-methoxy-5-methylphenyl)prop-2-yn-1-one (1u)



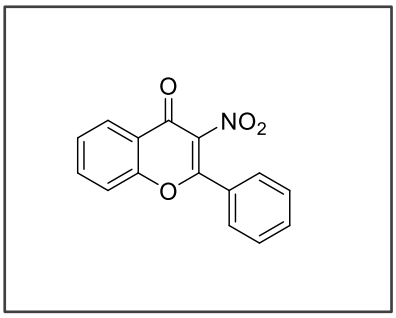
The reaction was accomplished according to the general experimental procedure described above, product **1u** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 73% yield (1.4 g). m.p. 80-82 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.6 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.50 – 7.44 (m, 2H), 7.33 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 3.93 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.5, 157.9, 135.8, 134.2, 132.4, 131.9, 129.7, 126.2, 125.1, 119.7, 112.3, 90.2, 90.0, 56.0, 20.3. **IR** (KBr): 3032, 2918, 2200, 1635, 1259, 750 cm^{-1} **HRMS** (ESI) m/z: calcd. for $C_{17}H_{14}BrO_2^+$ $[M + H]^+$ 329.0172, found 329.0183.

1-(2-methoxy-5-methylphenyl)-3-(p-tolyl)prop-2-yn-1-one (1v)



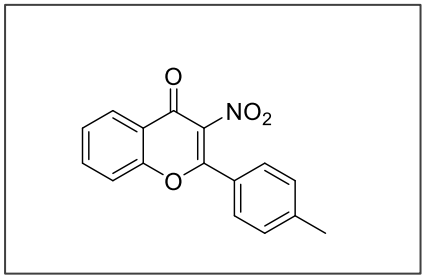
The reaction was accomplished according to the general experimental procedure described above, product **1v** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.5, yellow oil, 78% yield (1.2 g). m.p. 58-60 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.32 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 1H), 3.93 (s, 3H), 2.38 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.94, 157.88, 141.1, 135.5, 133.0, 132.5, 129.6, 129.4, 126.6, 117.7, 112.3, 92.2, 89.2, 56.0, 21.7, 20.3. **IR** (KBr): 3028, 2927, 2191, 1635, 1257, 815, 725 cm^{-1} **HRMS** (ESI) m/z: calcd. for $C_{18}H_{17}O_2^+$ $[M + H]^+$265.1224, found 265.1231.

3-nitro-2-phenyl-4H-chromen-4-one (2a)[10]



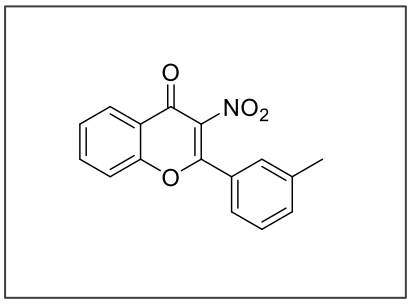
The reaction was accomplished according to the general experimental procedure described above, product **2a** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 94% yield (25.0 mg). m.p. 131-133 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.80 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.66 – 7.58 (m, 2H), 7.57 – 7.48 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.8, 159.7, 155.4, 138.1, 135.2, 132.9, 129.3, 128.4, 127.8, 126.5, 126.5, 123.4, 118.4. **IR** (KBr): 3057, 2922, 1656, 1624, 1527, 1373, 759 cm^{-1} **HRMS** (ESI) m/z: calcd. for $C_{15}H_{10}NO_4^+$ $[M + H]^+$268.0605, found 265.0616.

3-nitro-2-(p-tolyl)-4H-chromen-4-one (2b)



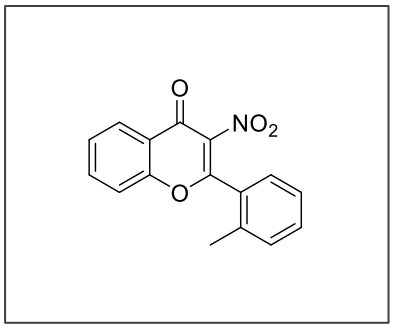
The reaction was accomplished according to the general experimental procedure described above, product **2b** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v).TLC R_f = 0.4, pale yellow solid, 97% yield (27.2 mg). m.p. 135-136 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.79 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.59 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.51 (td, *J* = 7.6, 1.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.8, 159.8, 155.4, 143.9, 137.9, 135.1, 130.1, 127.8, 126.5, 126.4, 125.6, 123.4, 118.4, 21.7. **IR**(KBr):3062, 1658, 1620, 1533, 1373, 1265, 759 cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{16}H_{12}NO_4^+$ [M + H]$^+$282.0761, found 282.0761.

3-nitro-2-(m-tolyl)-4H-chromen-4-one (2c)



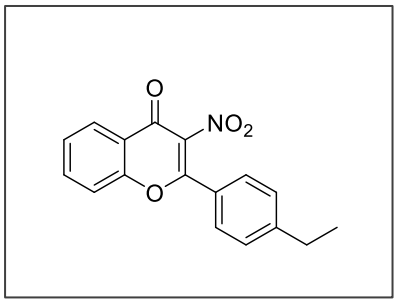
The reaction was accomplished according to the general experimental procedure described above, product **2c** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 96% yield (26.9 mg). m.p. 139-141 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.80 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.46 – 7.38 (m, 2H), 2.44 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.8, 160.0, 155.4, 139.4, 138.1, 135.1, 133.7, 129.2, 128.4, 128.2, 126.5, 126.5, 125.0, 123.4, 118.4, 21.4. **IR**(KBr):3057, 1656, 1618, 1525, 1369, 765 cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{16}H_{12}NO_4^+$ [M + H]$^+$ 282.0761, found 282.0769.

3-nitro-2-(o-tolyl)-4H-chromen-4-one (2d)



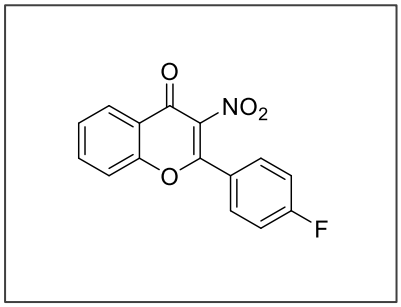
The reaction was accomplished according to the general experimental procedure described above, product **2d** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 94% yield (26.4 mg). m.p. 113-114 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.80 (ddd, *J* = 8.8, 7.2, 1.7 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.48 (td, *J* = 7.6, 1.4 Hz, 1H), 7.43 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.6, 162.3, 155.5, 139.5, 137.2, 135.2, 132.0, 131.0, 128.6, 128.1, 126.6, 126.6, 126.3, 123.8, 118.4, 19.5. **IR** (KBr): 3072, 1666, 1624, 1535, 1373, 1245, 759 cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{16}H_{12}NO_4^+$ $[M + H]^+$282.0761, found 282.0760.

2-(4-ethylphenyl)-3-nitro-4H-chromen-4-one (2e)



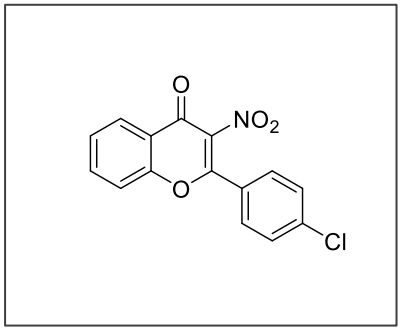
The reaction was accomplished according to the general experimental procedure described above, product **2e** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 97% yield (28.6 mg). m.p. 109-111 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.79 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.62 – 7.55 (m, 1H), 7.55 – 7.47 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 159.8, 155.4, 150.0, 137.9, 135.1, 128.9, 127.9, 126.5, 126.4, 125.7, 123.4, 118.4, 28.9, 15.0. **IR** (KBr): 3072, 1660, 1618, 1533, 1369, 763cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{17}H_{14}NO_4^+$ $[M + H]^+$296.0918, found 296.0926.

2-(4-fluorophenyl)-3-nitro-4H-chromen-4-one (2f)



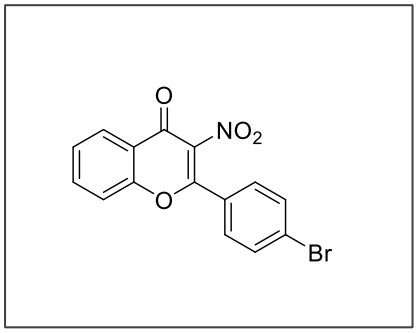
The reaction was accomplished according to the general experimental procedure described above, product **2f** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 83% yield (23.6 mg). m.p. 137-138 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.85 – 7.74 (m, 3H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 8.6 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.7, 166.3, 164.3, 158.6, 155.3, 135.3, 130.4, 126.6, 124.6, 123.4, 118.4, 116.9, 116.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -104.30. **IR** (KBr): 3078, 1656, 1618, 1531, 1369, 1242, 763cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{15}H_9FNO_4^+$ [M + H]$^+$286.0511, found 282.0511.

2-(4-chlorophenyl)-3-nitro-4H-chromen-4-one (2h)



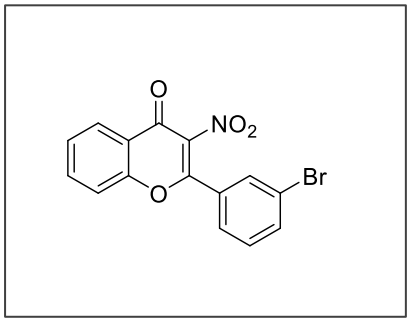
The reaction was accomplished according to the general experimental procedure described above, product **2h** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 64% yield (19.2 mg). m.p. 160-161 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.82 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.63 – 7.57 (m, 1H), 7.54 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.6, 158.5, 155.3, 139.5, 138.1, 135.3, 129.8, 129.2, 126.8, 126.68, 126.62, 123.4, 118.4. **IR** (KBr): 3093, 1660, 1618, 1531, 1373, 1259, 761 cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{15}H_9ClNO_4^+$ [M + H]$^+$302.0215, found 302.0215.

2-(4-bromophenyl)-3-nitro-4H-chromen-4-one (2i)



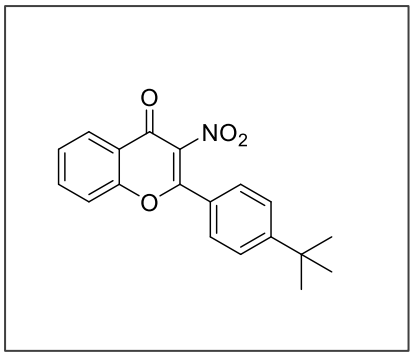
The reaction was accomplished according to the general experimental procedure described above, product **2i** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 55% yield (18.9 mg). m.p. 148-149 ℃ **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.82 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.64 – 7.58 (m, 3H), 7.58 – 7.50 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 158.6, 155.3, 138.1, 135.3, 132.8, 129.3, 128.0, 127.3, 126.7, 126.6, 123.4, 118.4. **IR** (KBr): 3072, 1664, 1618, 1533, 1369, 1260, 759cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{15}H_9BrNO_4^+$ $[M + H]^+$345.9710, found 345.9706.

2-(3-bromophenyl)-3-nitro-4H-chromen-4-one (2j)



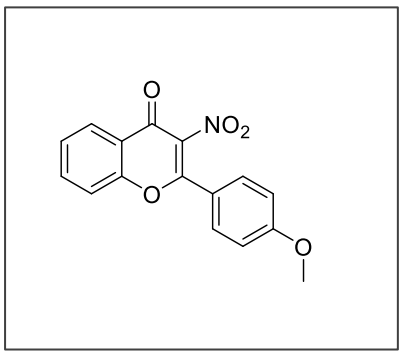
The reaction was accomplished according to the general experimental procedure described above, product **2j** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 37% yield (12.7 mg). m.p. 154-155 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.91 (d, *J* = 1.9 Hz, 1H), 7.83 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.76 (dt, *J* = 8.1, 1.5 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.6, 158.0, 155.3, 138.3, 135.9, 135.4, 130.8, 130.7, 130.3, 126.7, 126.6, 126.4, 123.48, 123.41, 118.5. **IR** (KBr): 3057, 1664, 1620, 1519, 1369, 1267, 763cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{15}H_9BrNO_4^+$ $[M + H]^+$345.9710, found 345.9706.

2-(4-(tert-butyl)phenyl)-3-nitro-4H-chromen-4-one (2k)



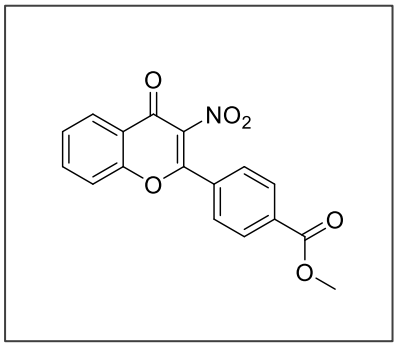
The reaction was accomplished according to the general experimental procedure described above, product **2k** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.3, yellow oil, 96% yield (31.0 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.79 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.61 – 7.49 (m, 4H), 1.36 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 159.7, 156.9, 155.4, 137.9, 135.1, 127.7, 127.5, 126.5, 126.4, 125.5, 123.4, 118.4, 35.2, 31.0. **IR** (KBr): 3068, 1664, 1620, 1525, 1373, 1262, 763cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{19}H_{18}NO_4^+$ $[M + H]^+$324.1231, found 324.1231.

2-(4-methoxyphenyl)-3-nitro-4H-chromen-4-one (2l)



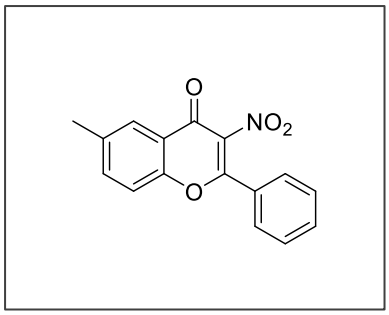
The reaction was accomplished according to the general experimental procedure described above, product **2l** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 97% yield (28.8 mg). m.p. 130-131 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.78 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.59 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.06 – 7.00 (m, 2H), 3.90 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 163.3, 159.4, 155.3, 137.4, 135.0, 129.8, 126.5, 126.3, 123.4, 120.4, 118.3, 114.9, 55.6. **IR** (KBr): 3072, 1656, 1602, 1527, 1377, 1261, 763 cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{16}H_{12}NO_5^+$ $[M + H]^+$298.0710, found 298.0711.

methyl 4-(3-nitro-4-oxo-4H-chromen-2-yl)benzoate (2m)



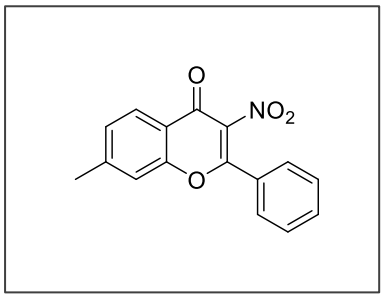
The reaction was accomplished according to the general experimental procedure described above, product **2m** was purified by flash column chromatography (silica gel, EA/PE =1/15, v/v). TLC R_f = 0.3, pale yellow solid, 32% yield (10.4 mg). m.p. 140-142 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.23 – 8.18 (m, 2H), 7.87 – 7.80 (m, 3H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.51 (m, 1H), 3.98 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.6, 165.7, 158.6, 155.4, 138.5, 135.4, 133.9, 132.3, 130.4, 127.9, 126.7, 126.6, 123.5, 118.4, 52.6. **IR** (KBr): 3078, 2922, 1726, 1660, 1602, 1533, 1367, 1286, 740 cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{17}H_{12}NO_4^+$ $[M + H]^+$326.0660, found 326.0670.

6-methyl-3-nitro-2-phenyl-4H-chromen-4-one (2p)



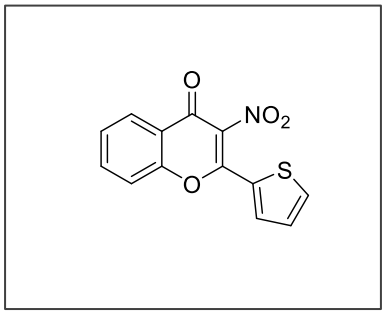
The reaction was accomplished according to the general experimental procedure described above, product 1u was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 96% yield (26.9 mg). m.p. 123-124 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (t, *J* = 1.6 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.65 – 7.57 (m, 2H), 7.54 (dd, *J* = 8.5, 7.1 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 1H), 2.50 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.8, 159.5, 153.7, 138.1, 136.8, 136.4, 132.8, 129.3, 128.6, 127.8, 125.8, 123.1, 118.2, 21.0. **IR** (KBr): 3068, 1658, 1620, 1533, 1365, 1266, 746cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{16}H_{12}NO_4^+$ $[M + H]^+$282.0761, found 282.0770.

7-methyl-3-nitro-2-phenyl-4H-chromen-4-one (2q)



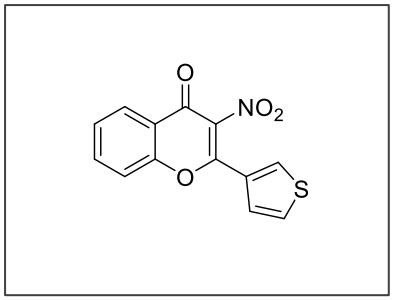
The reaction was accomplished according to the general experimental procedure described above, product **2q** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 96% yield (27.0 mg). m.p. 124-126 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.65 – 7.57 (m, 1H), 7.53 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.39 (s, 1H), 7.32 (dd, *J* = 8.1, 1.5 Hz, 1H), 2.53 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.7, 159.4, 155.5, 147.1, 138.1, 132.8, 129.3, 128.6, 128.0, 127.8, 126.2, 121.1, 118.2, 22.0. **IR** (KBr): 3062, 1664, 1625, 1533, 1373, 1230, 746cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{16}H_{12}NO_4^+$ $[M + H]^+$282.0761, found 282.0771.

3-nitro-2-(thiophen-2-yl)-4H-chromen-4-one (2s)



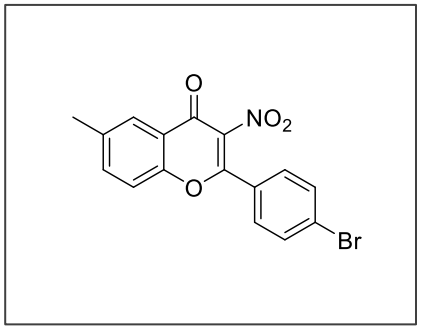
The reaction was accomplished according to the general experimental procedure described above, product **2s** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 90% yield (24.6 mg). m.p. 142-144 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.84 – 7.75 (m, 2H), 7.68 (dd, *J* = 4.0, 1.2 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.53 – 7.46 (m, 1H), 7.22 (dd, *J* = 5.0, 3.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.6, 155.0, 153.0, 135.2, 133.8, 132.2, 129.5, 129.3, 129.2, 126.4, 126.4, 123.2, 118.2. **IR** (KBr): 3013, 1658, 1616, 1527, 1381, 1232, 742cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{13}H_8NO_4S^+$ $[M + H]^+$274.0169, found 274.0179.

3-nitro-2-(thiophen-3-yl)-4H-chromen-4-one (2t)



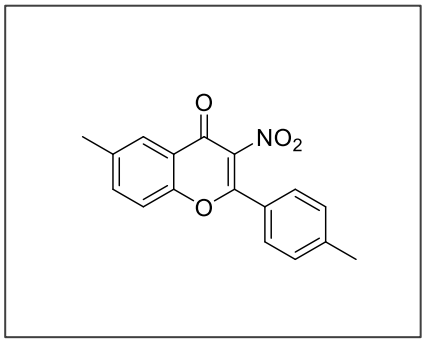
The reaction was accomplished according to the general experimental procedure described above, product **2t** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 97% yield (26.5 mg). m.p. 187-188 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.09 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.79 (ddd, *J* = 8.8, 7.2, 1.7 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.51 (m, *J* = 6.3, 3.6 Hz, 2H), 7.45 (dd, *J* = 5.3, 1.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 155.1, 153.9, 136.6, 135.2, 131.1, 128.8, 127.9, 126.4, 126.3, 125.9, 123.3, 118.3. **IR** (KBr): 3097, 1658, 1616, 1523, 1363, 1226, 746cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{13}H_8NO_4S^+$ [M + H]$^+$274.0169, found 274.0175.

2-(4-bromophenyl)-6-methyl-3-nitro-4H-chromen-4-one (2u)



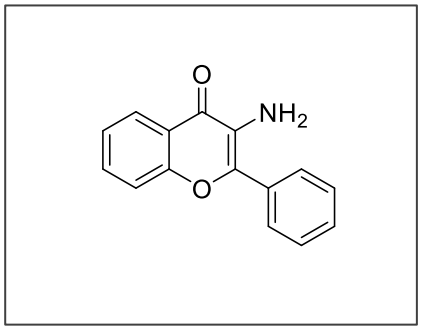
The reaction was accomplished according to the general experimental procedure described above, product **2u** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v).TLC R_f = 0.4, pale yellow solid, 76% yield (27.4 mg). m.p. 161-163 ℃ **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 – 8.06 (m, 1H), 7.73 – 7.65 (m, 2H), 7.65 – 7.57 (m, 3H), 7.49 (d, *J* = 8.6 Hz, 1H), 2.51 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 158.4, 153.7, 138.1, 137.0, 136.6, 132.7, 129.2, 127.9, 127.4, 125.8, 123.1, 118.1, 21.0. **IR** (KBr): 3078, 1658, 1620, 1533, 1365, 1226, 742cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{16}H_{11}BrNO_4^+$ [M + H]$^+$359.9877, found 359.9866.

6-methyl-3-nitro-2-(p-tolyl)-4H-chromen-4-one (2v)



The reaction was accomplished according to the general experimental procedure described above, product **2v** was purified by flash column chromatography (silica gel, EA/PE =1/20, v/v). TLC R_f = 0.4, pale yellow solid, 97% yield (28.6 mg). m.p. 161-163 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 1H), 7.65 – 7.60 (m, 2H), 7.58 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 2.48 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 159.6, 153.6, 143.8, 137.8, 136.7, 136.3, 130.0, 127.7, 125.7, 125.6, 123.0, 118.1, 21.7, 20.9. **IR** (KBr): 3057, 1656, 1617, 1531, 1367, 1238, 740cm^{-1}. **HRMS** (ESI) m/z: calcd. for $C_{17}H_{14}NO_4^+$ [M + H]$^+$296.0918, found 296.0926.

3-amino-2-phenyl-4H-chromen-4-one (3a)[11]



The reaction was accomplished according to the general experimental procedure described above, product **3a** was purified by flash column chromatography (silica gel, EA/PE =1/10, v/v). TLC R_f = 0.5, yellow solid, 93% yield (0.49 g). m.p. 128-130 ℃ **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.63 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.51 – 7.43 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 4.06 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.5, 155.5, 144.4, 132.9, 132.8, 129.7, 129.0, 128.1, 127.6, 125.7, 124.0, 121.0, 118.0.

5. References

[1] G. Albano, L. Aronica, Catalysts 10 (2019) 25.

[2] D. A. Alonso, C. Nájera, M. C. Pacheco, J. Org. Chem. 69 (2004) 1615–1619.

[3] C. Ramesh, Synlett 2011 (2011) 587–588.

[4] B. Godoi, A. Sperança, C. A. Bruning, D. F. Back, P. H. Menezes, C. W. Nogueira, G. Zeni, Adv. Synth. Catal. 353 (2011) 2042–2050.

[5] L.-F. Shi, X.-G. Zhang, X.-H. Zhang, Tetrahedron 72 (2016) 8617–8622.

[6] J. Xiao, Z. Ai, X. Li, S. Tao, B. Zhao, X. Wang, X. Wang, Y. Du, Green Synth. Catal. 3 (2022) 198–201.

[7] J.-R. Lai, F.-D. Yin, Q.-S. Guo, F. Yuan, B.-F. Nian, M. Zhang, Z.-B. Wu, H.-B. Zhang, E. Tang, Org. Biomol. Chem. 20 (2022) 5104–5114.

[8] X. Li, Y. Li, J. Yang, H. Shi, Z. Ai, C. Han, J. He, Y. Du, Org. Lett. 24 (2022) 7216–7221.

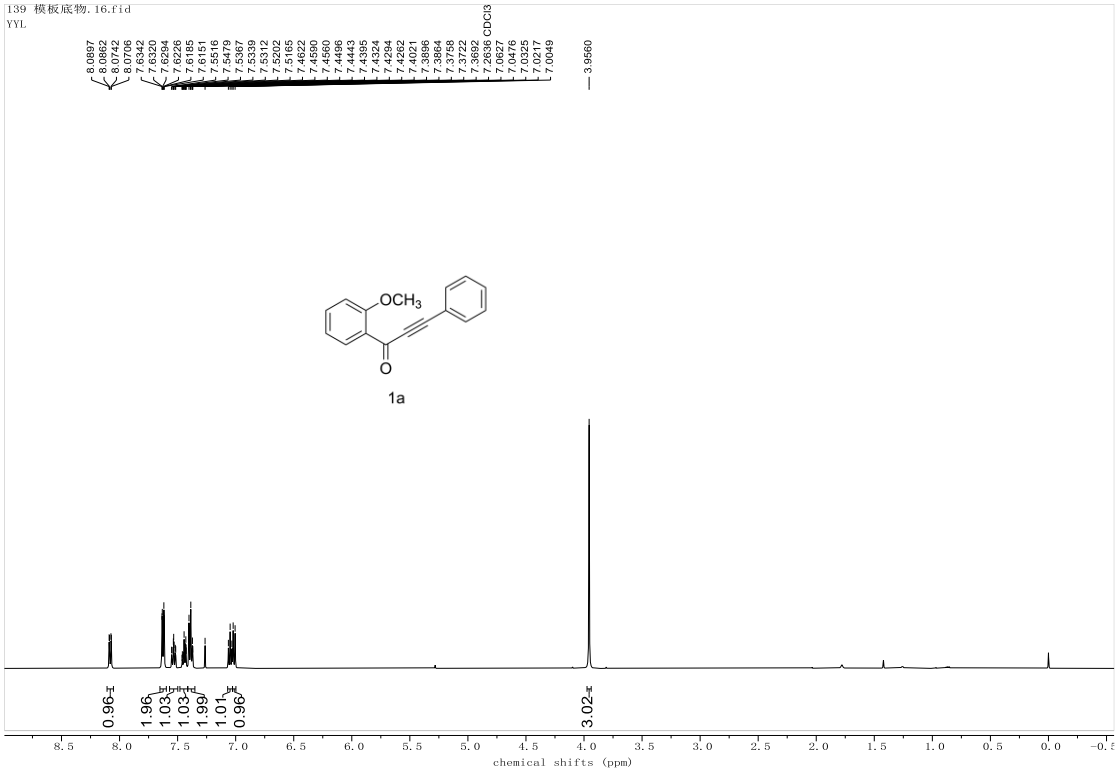
[9] G. R. Kumar, Y. K. Kumar, M. S. Reddy, Chem. Commun. 52 (2016) 6589–6592.

[10] D. Patoilo, A. Silva, J. Cavaleiro, Synlett 2010 (2010) 1381–1385.

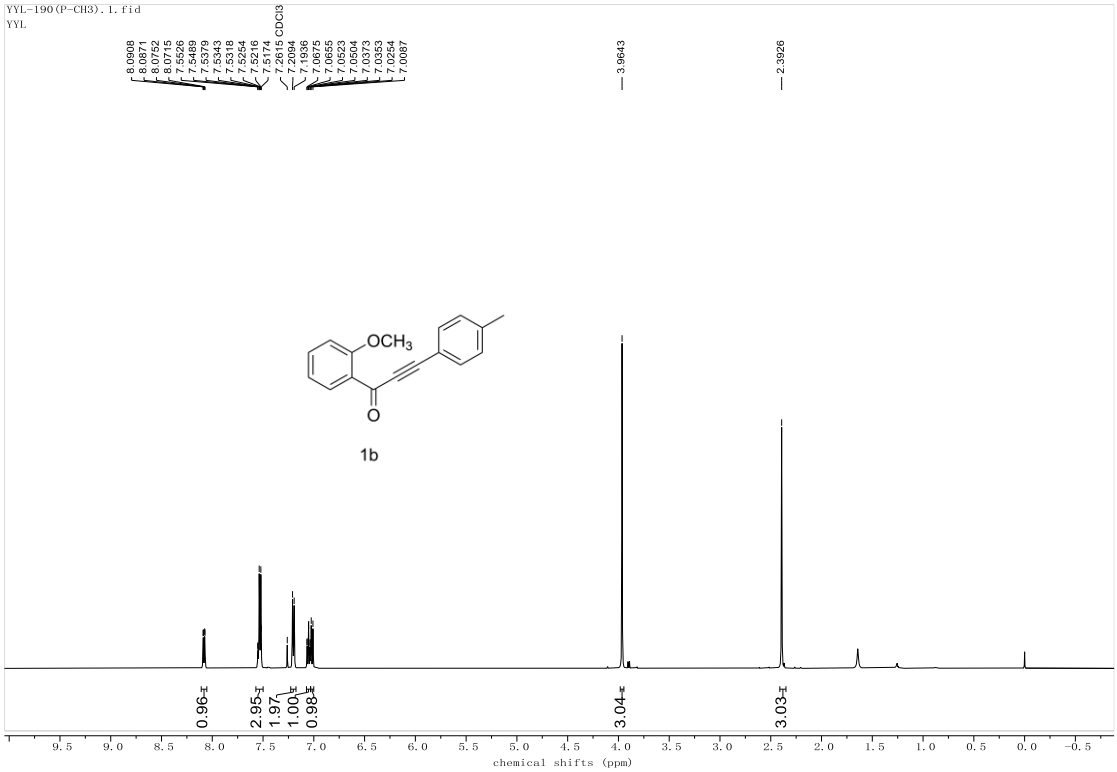
[11] B. Żurowska, A. Erxleben, Ł. Glinka, M. Łęczycka, E. Zyner, J. Ochocki, Inorg. Chim. Acta. 362 (2009) 739–744.

7. Copies of ^{1}H NMR and ^{13}C NMR Spectra

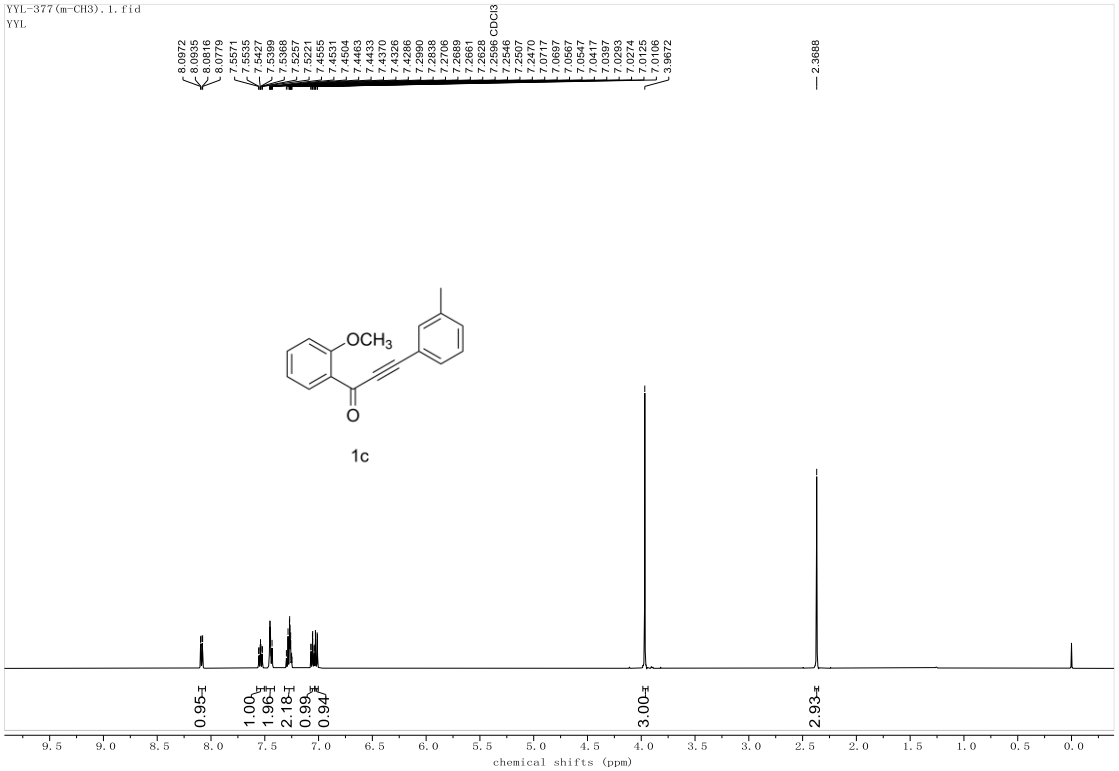
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1a**



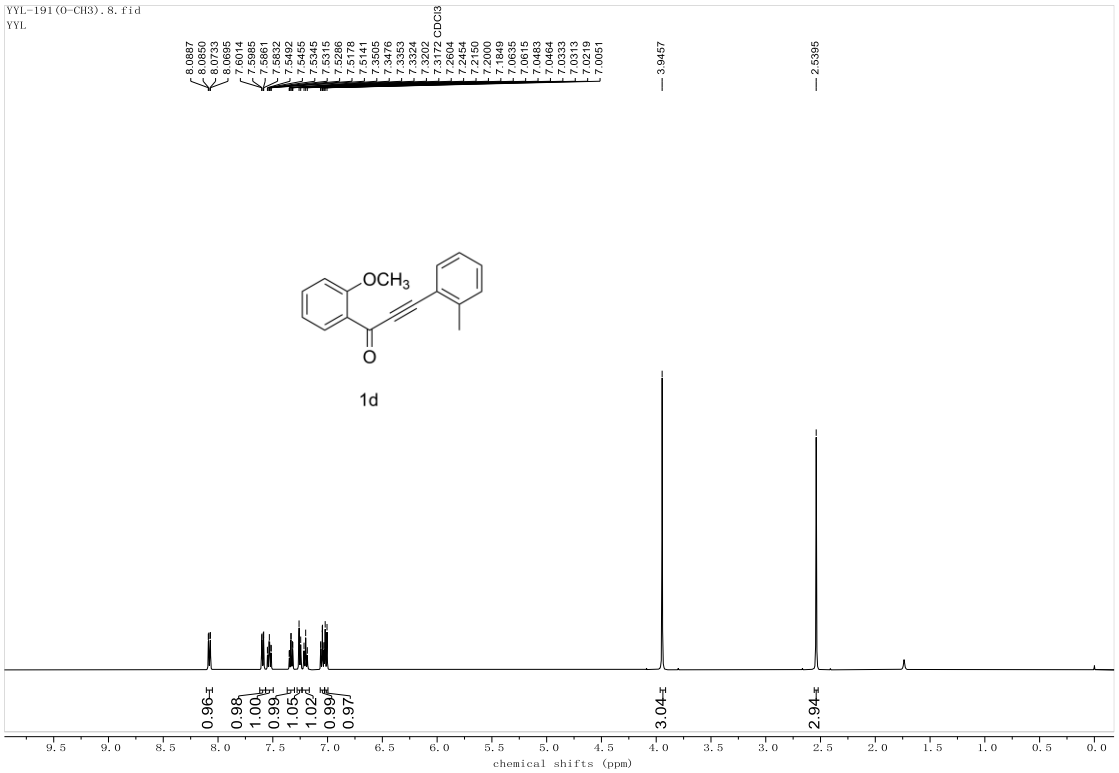
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1b**



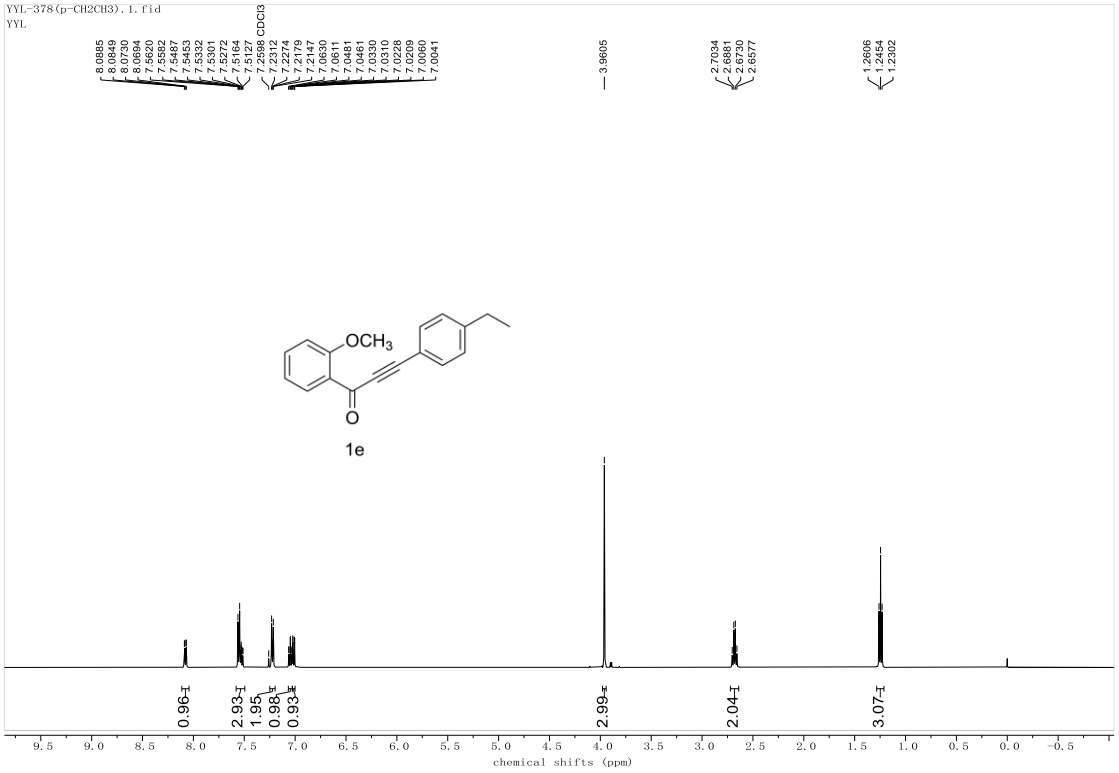
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1c**



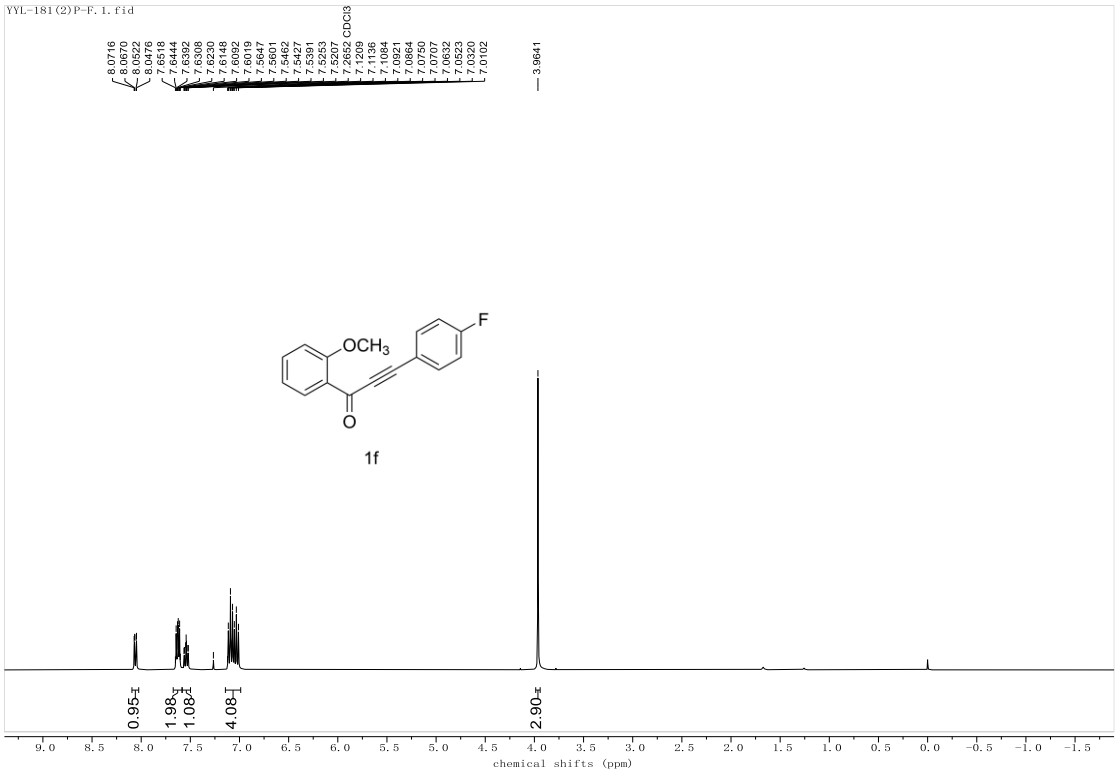
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1d**



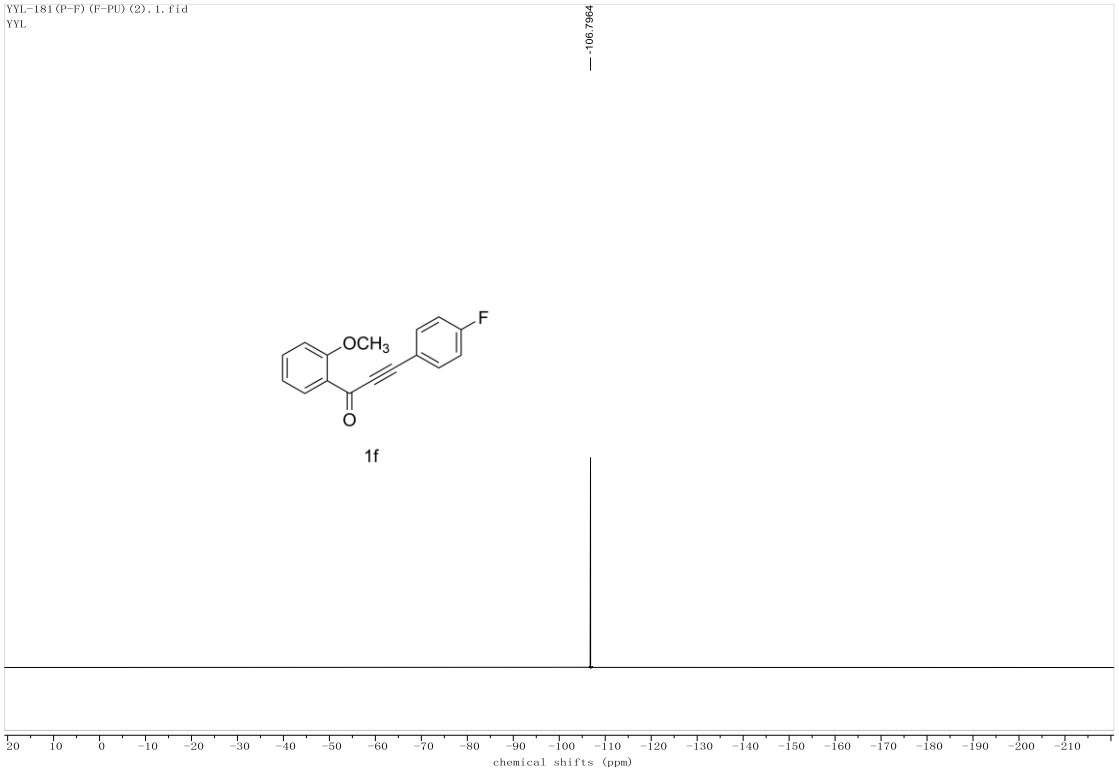
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1e**



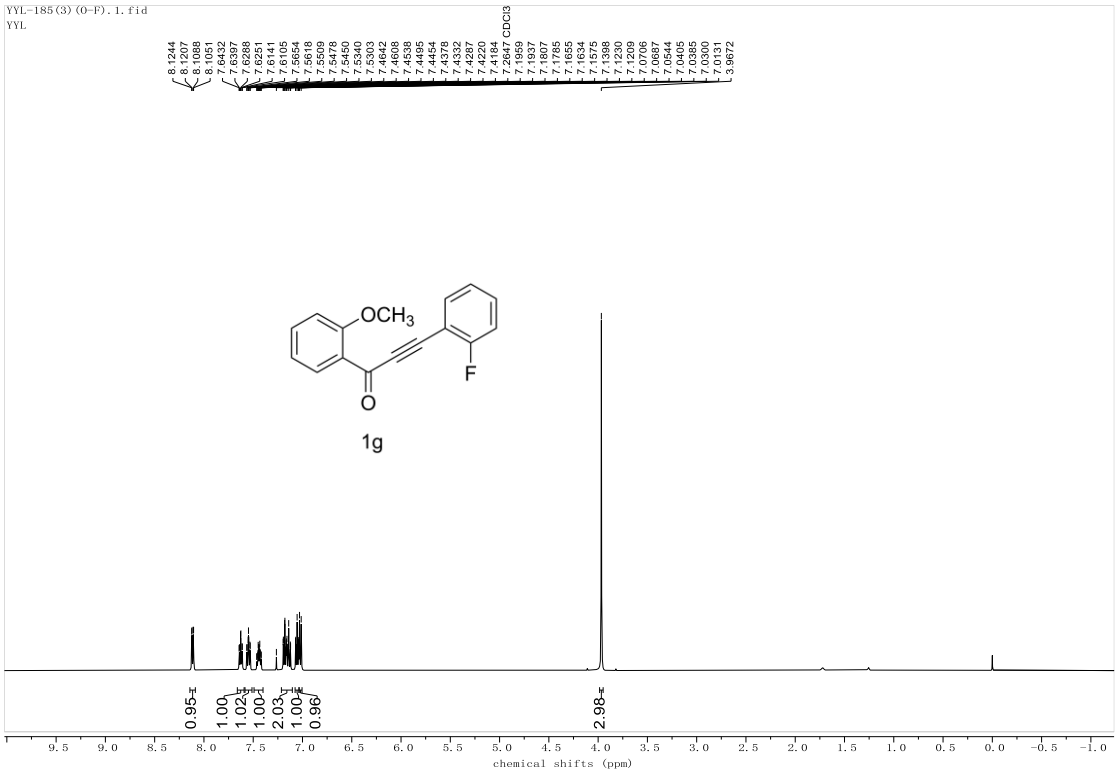
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1f**



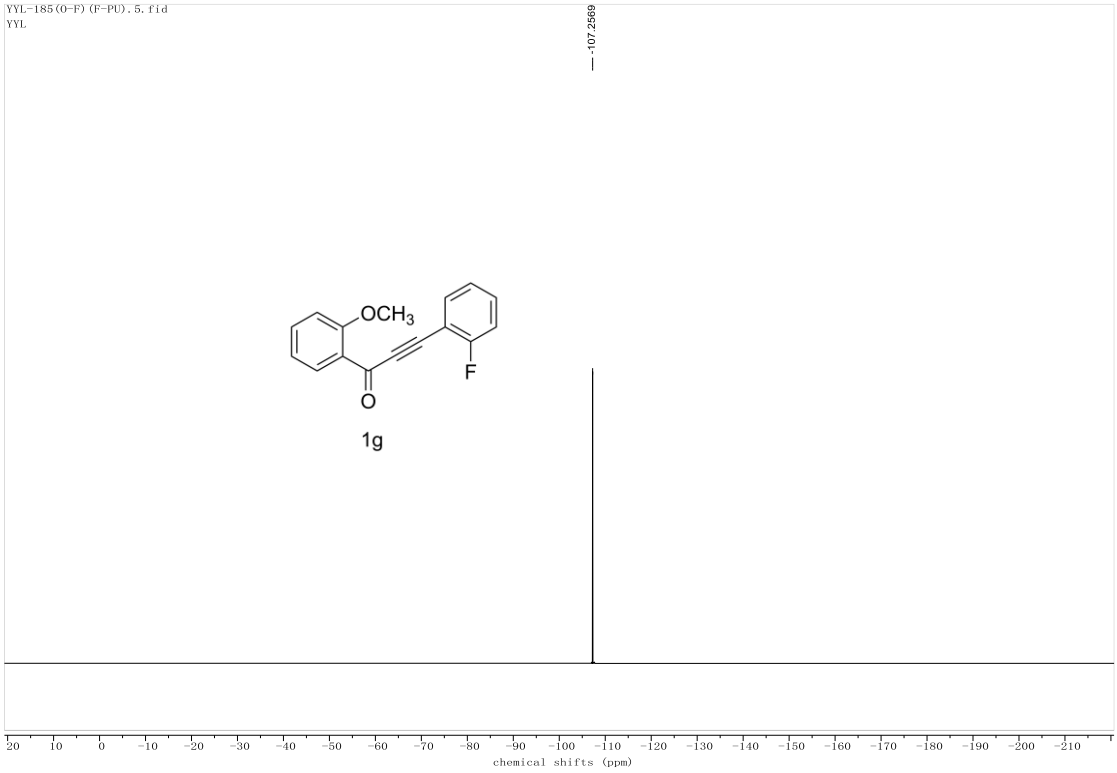
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **1f**



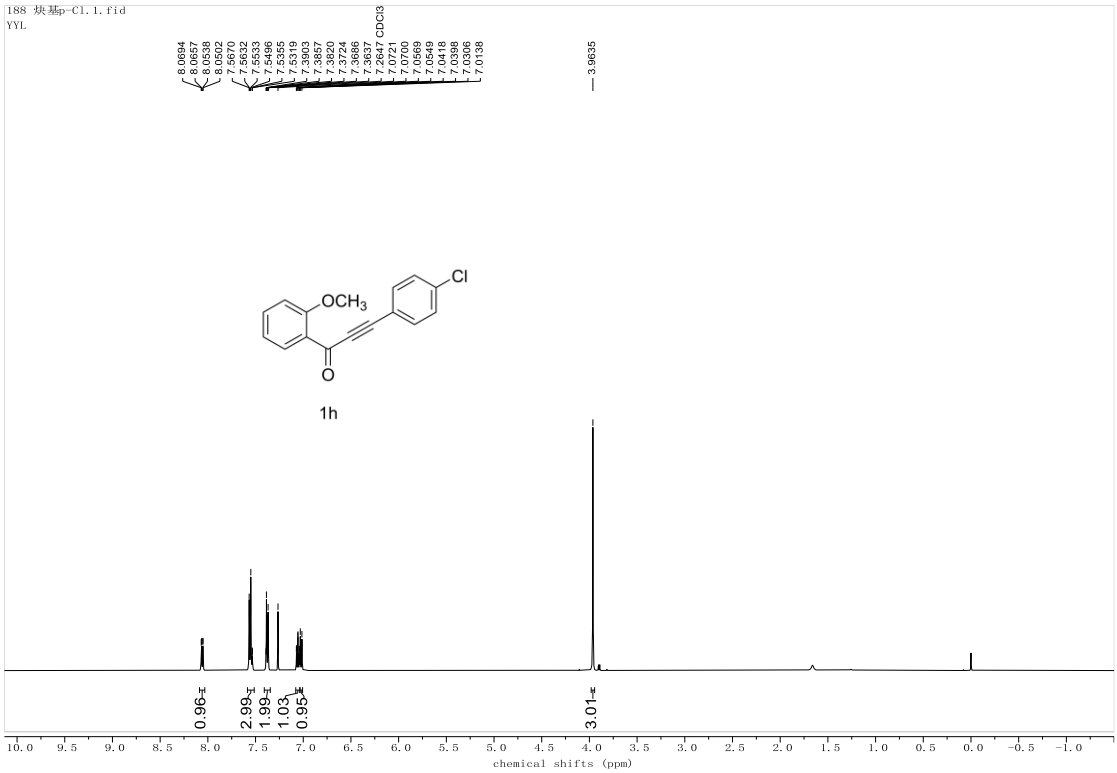
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1g**



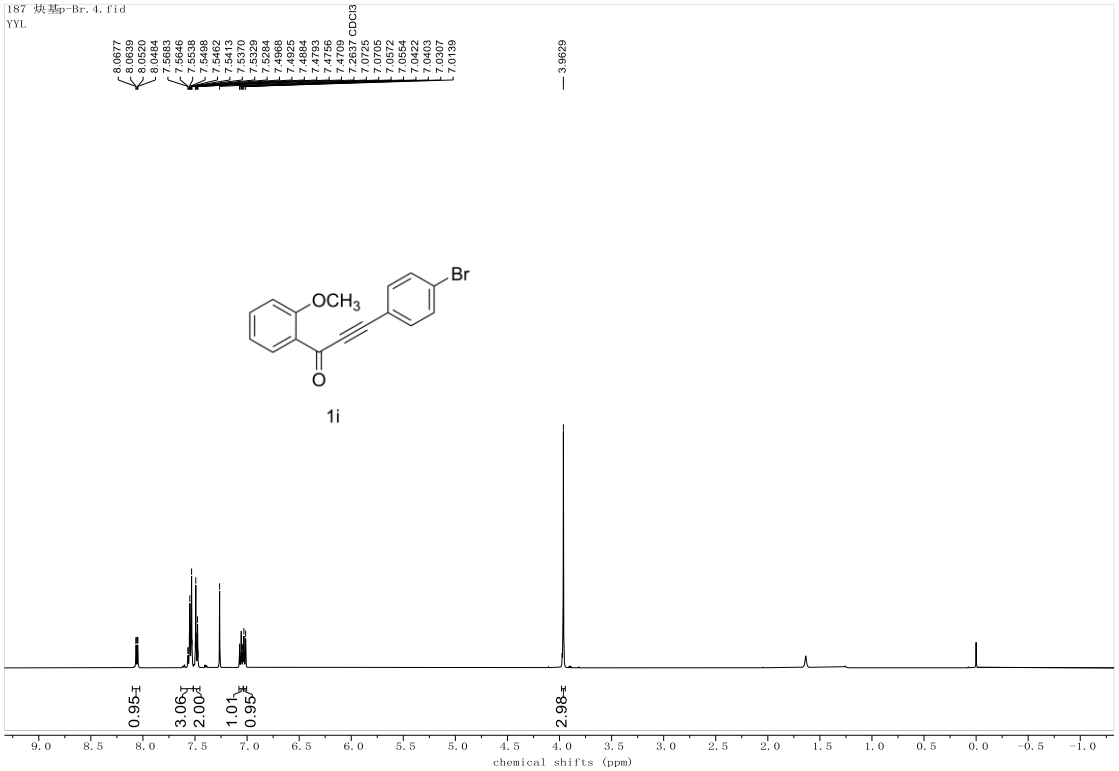
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **1g**



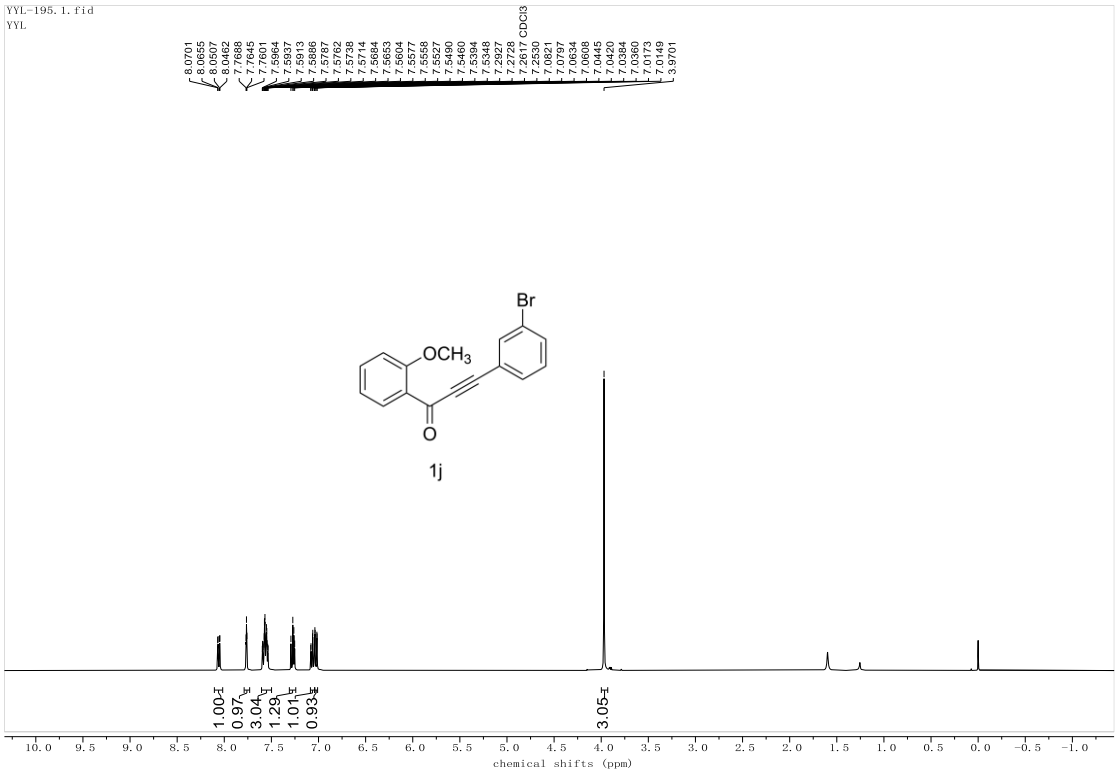
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1h**



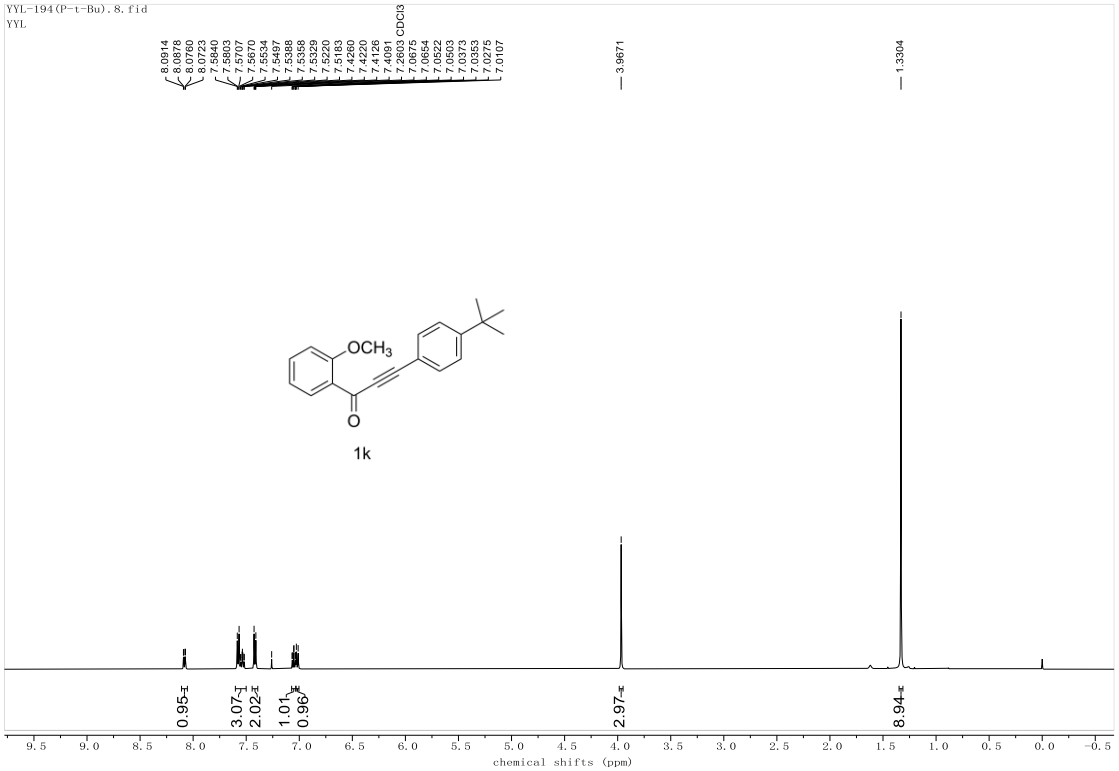
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1i**



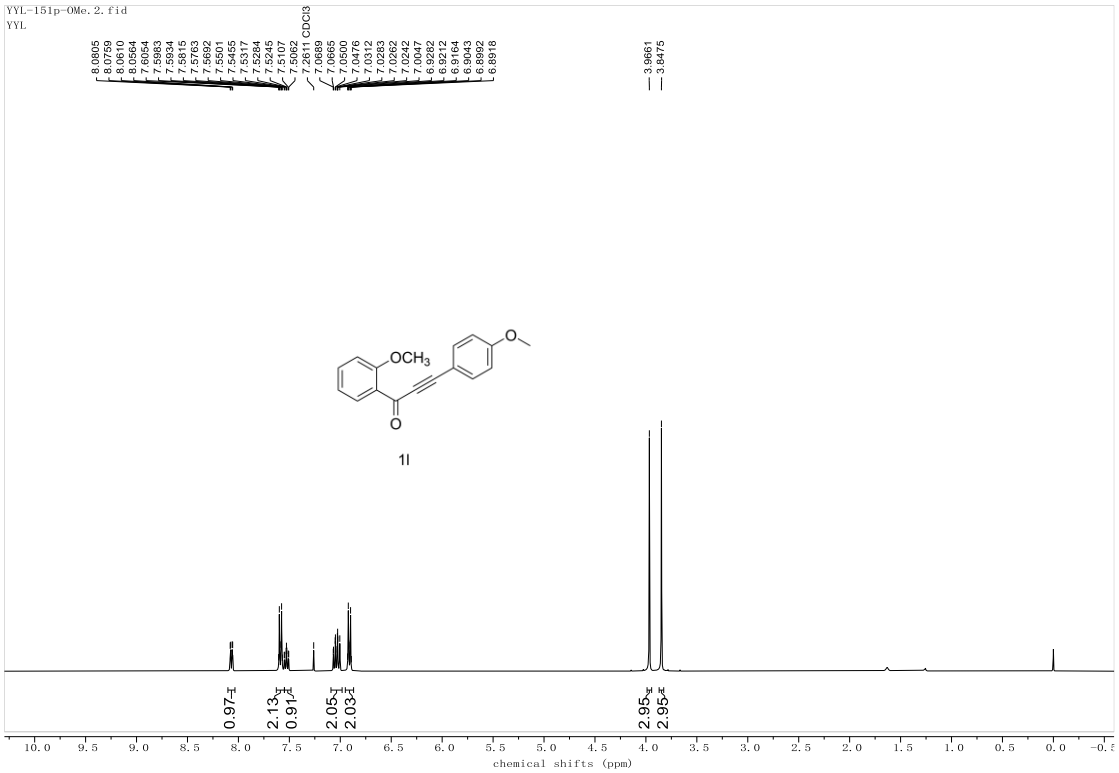
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1j**



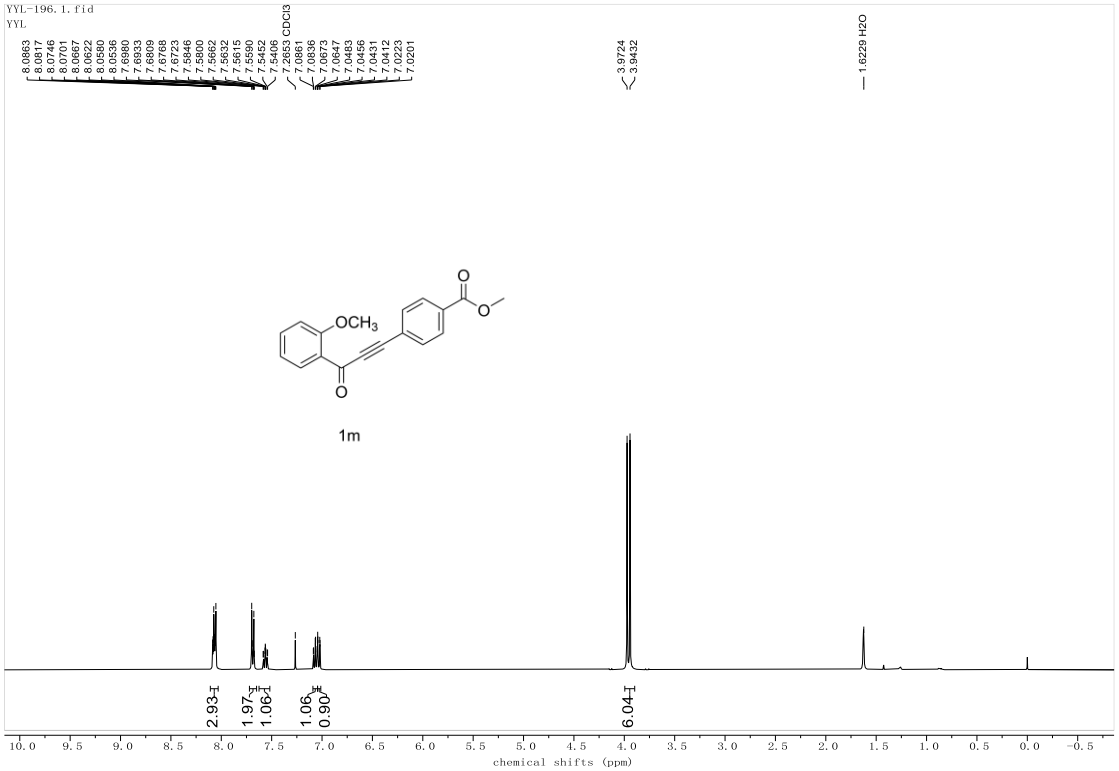
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1k**



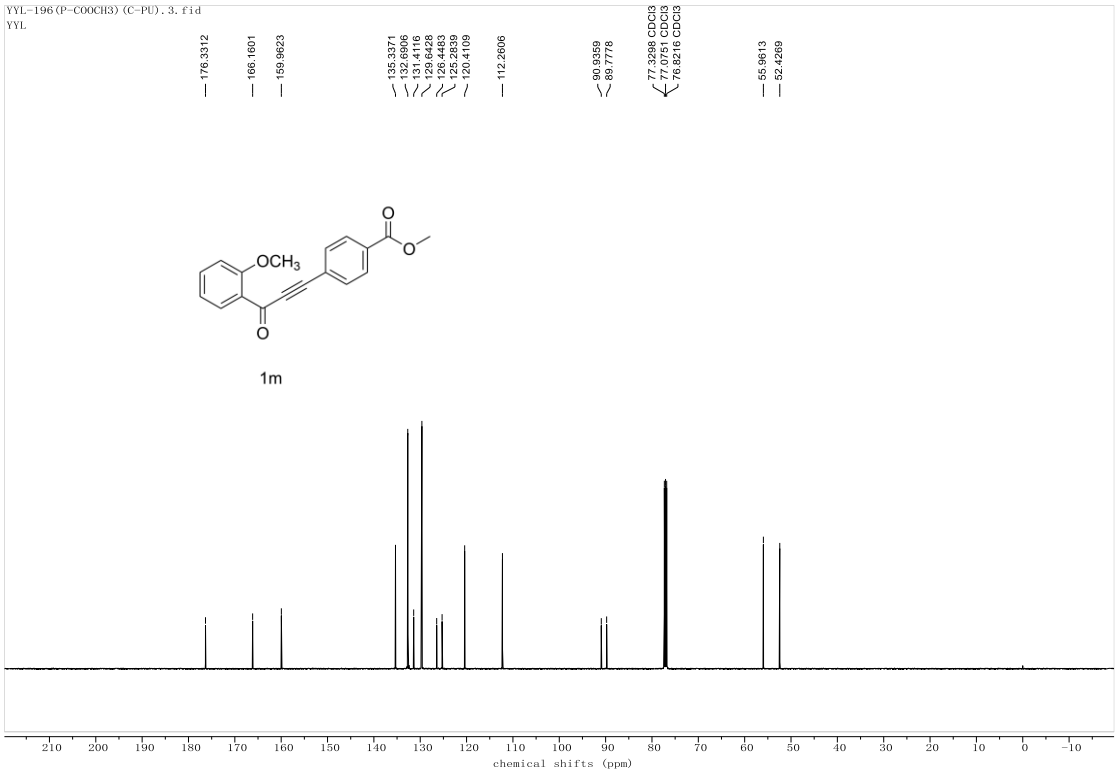
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1l**



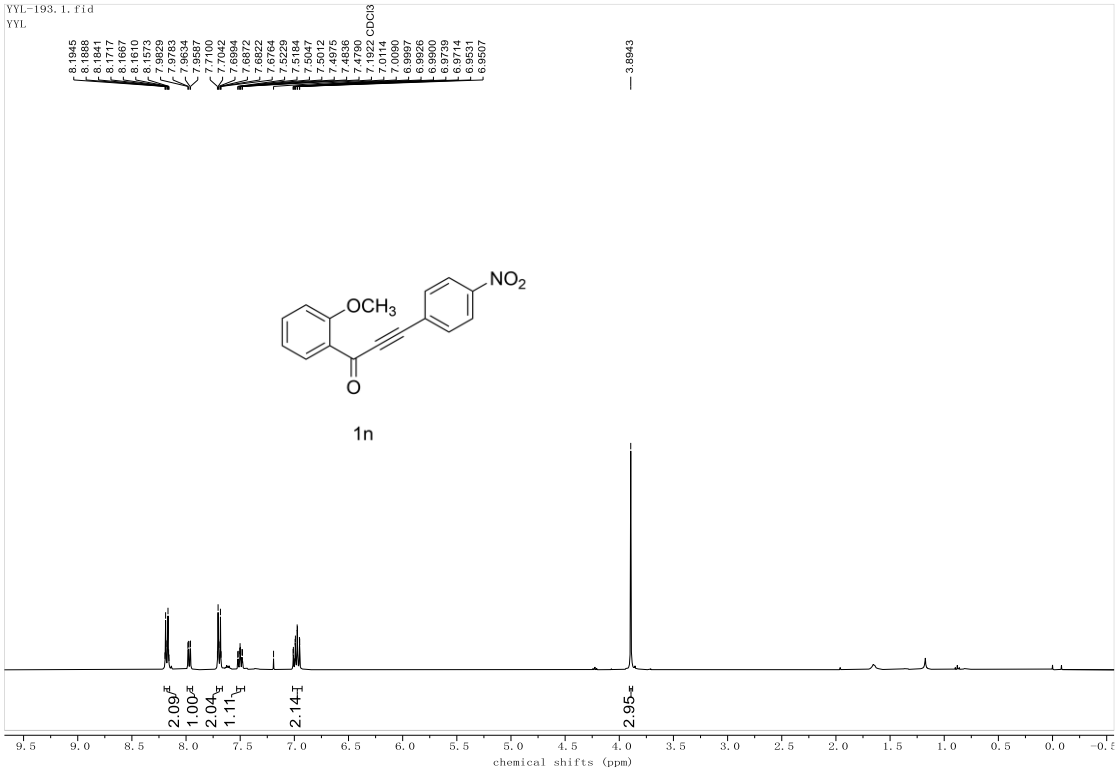
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1m**



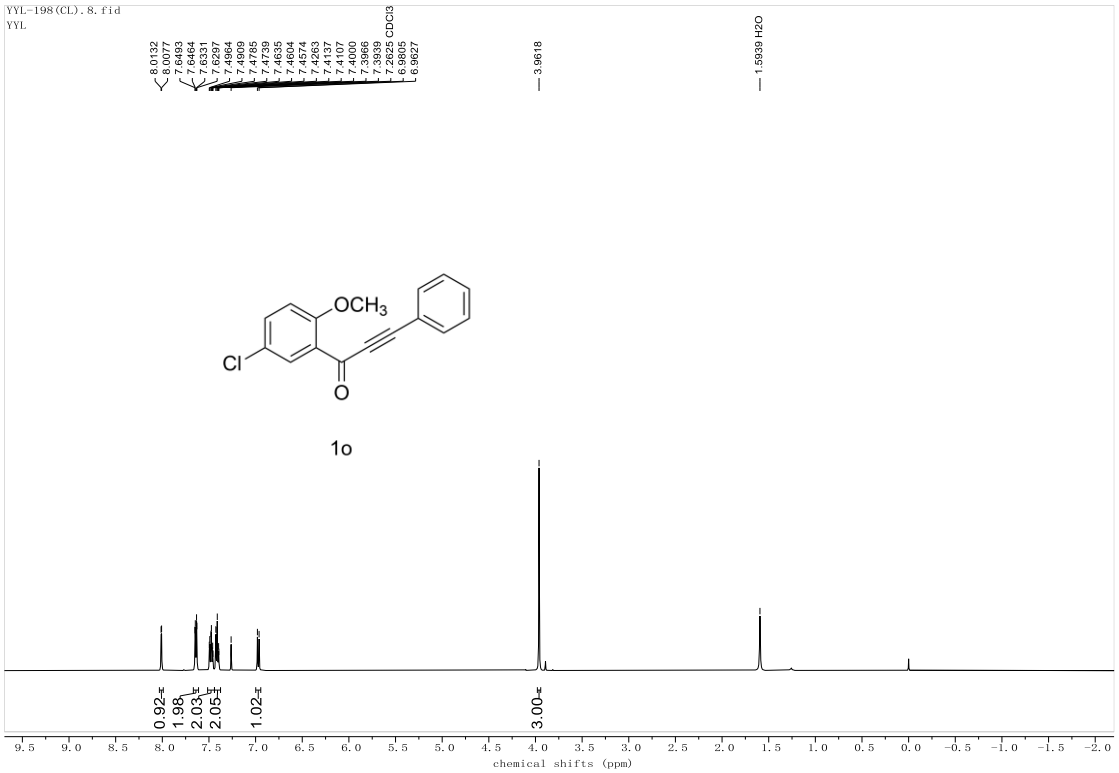
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1m**



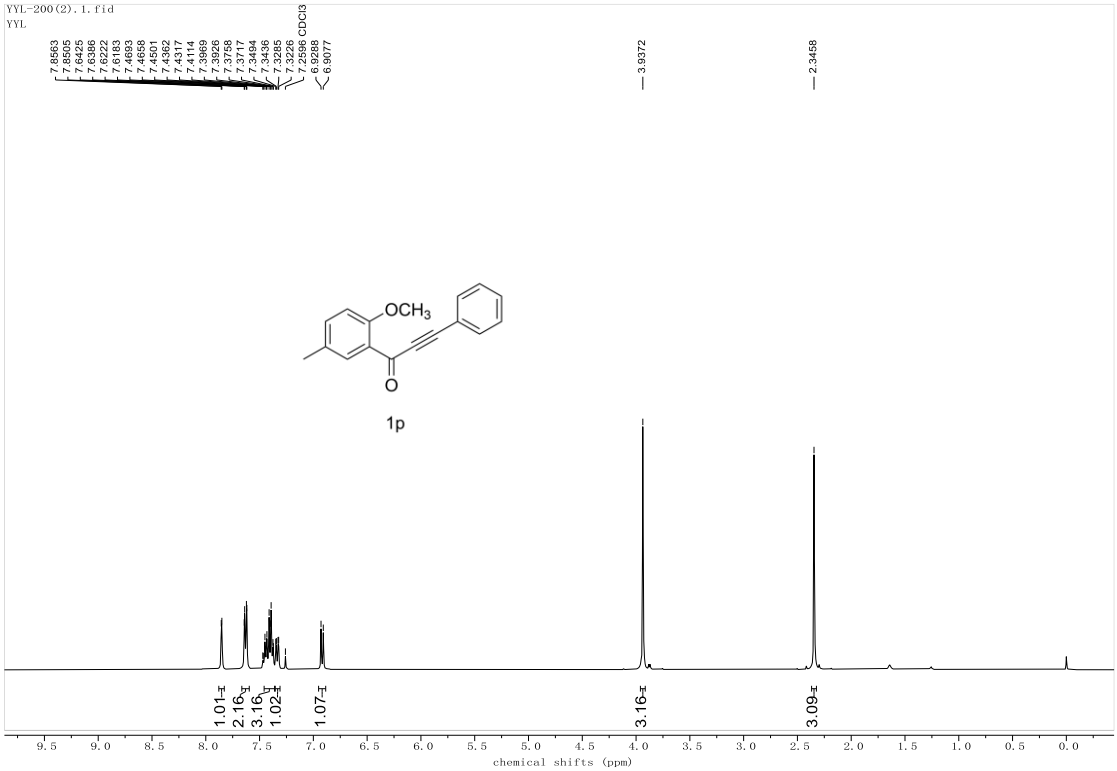
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1n**



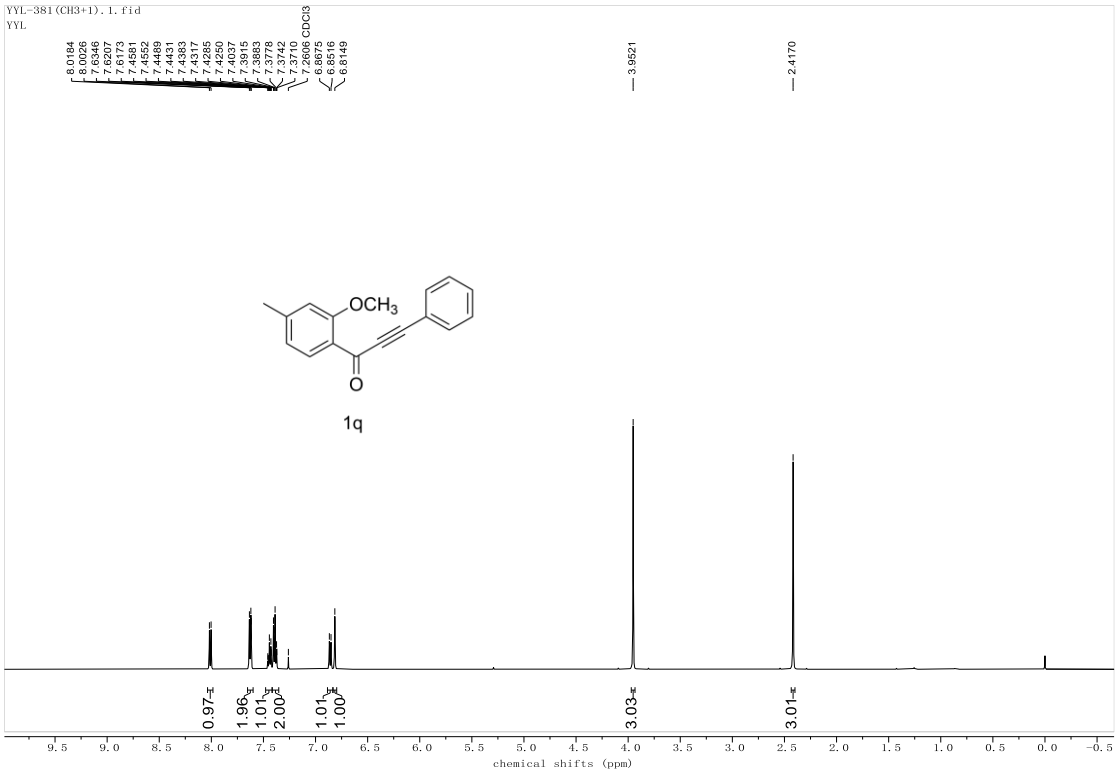
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1o**



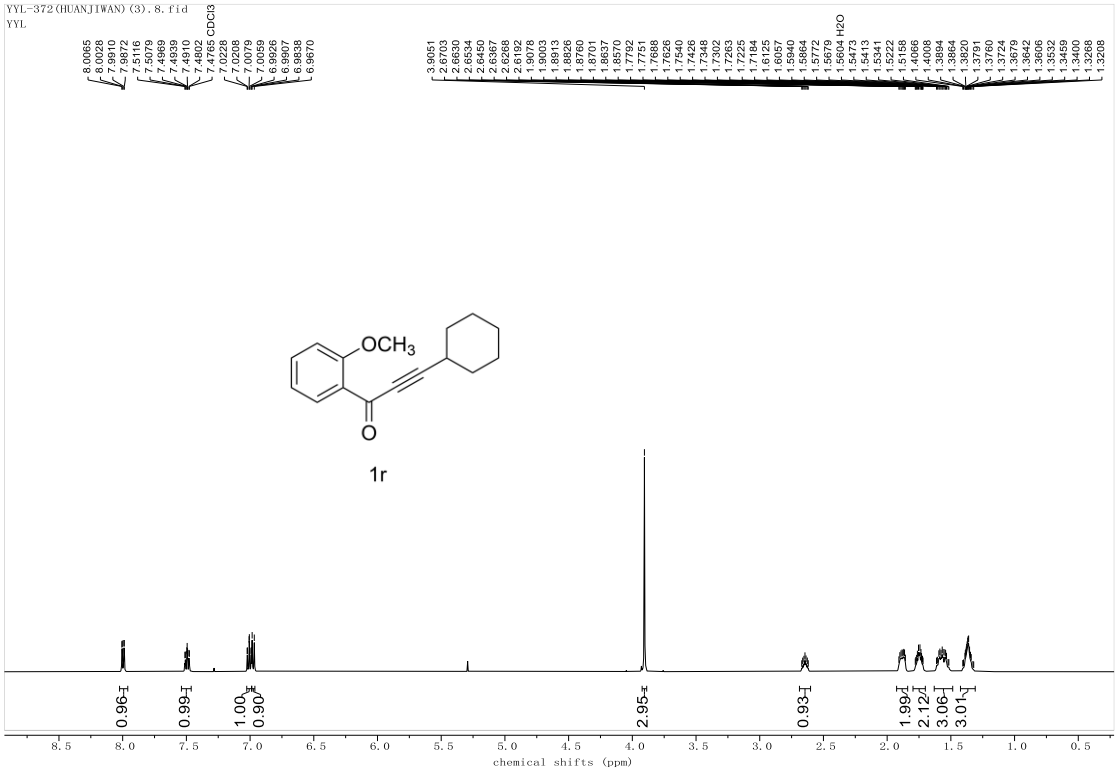
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1p**



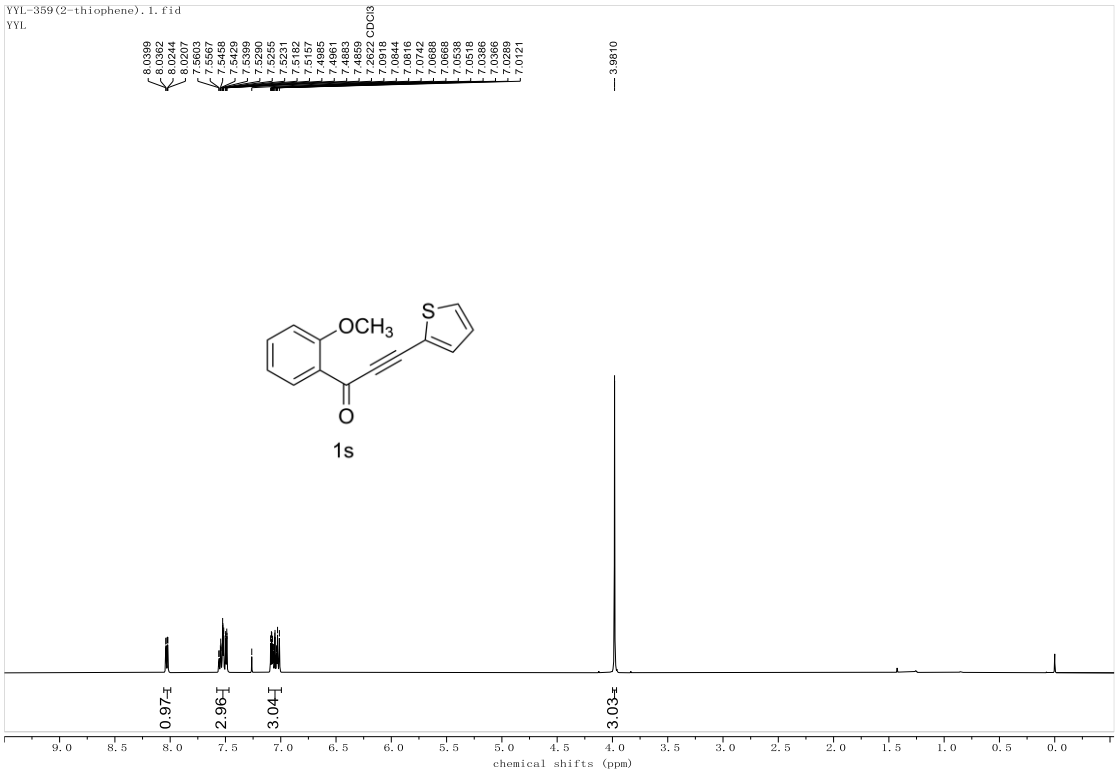
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1q**



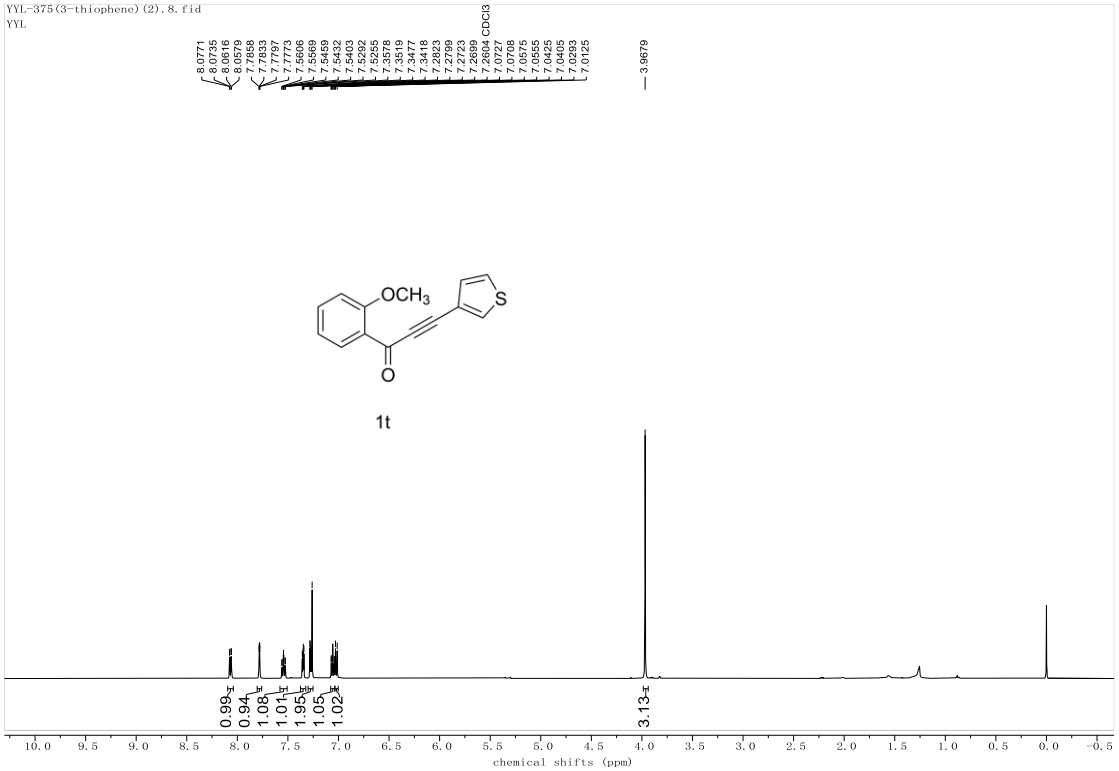
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1r**



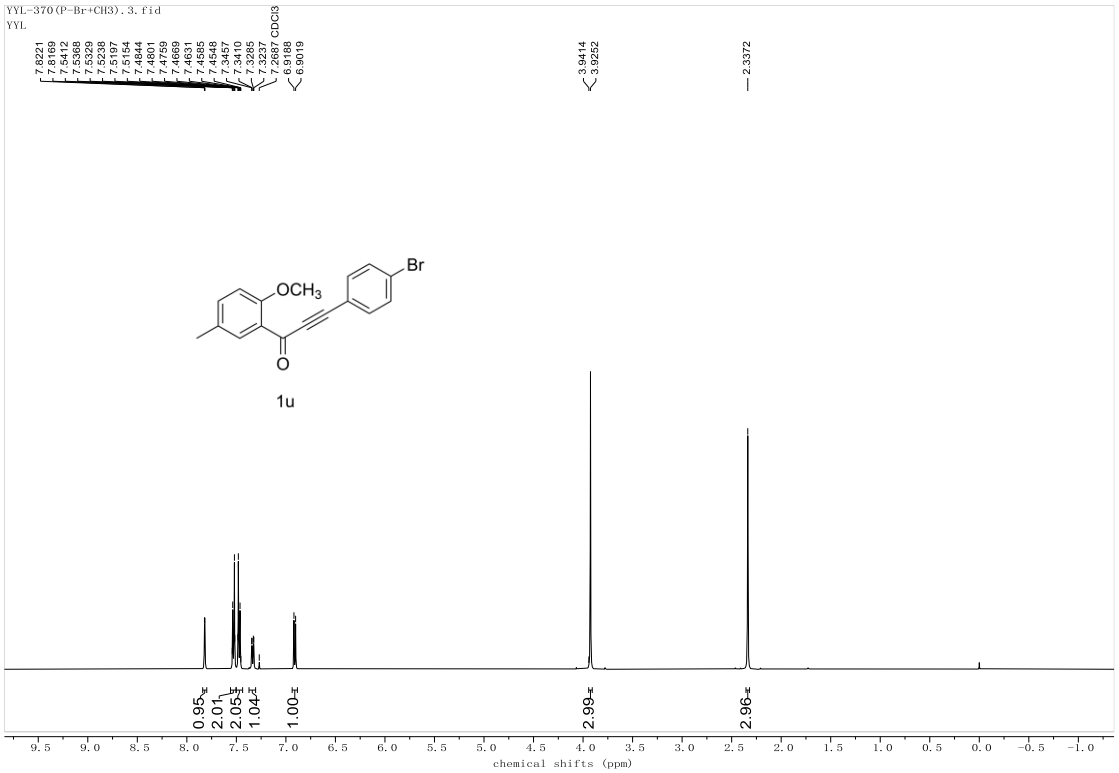
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1s**



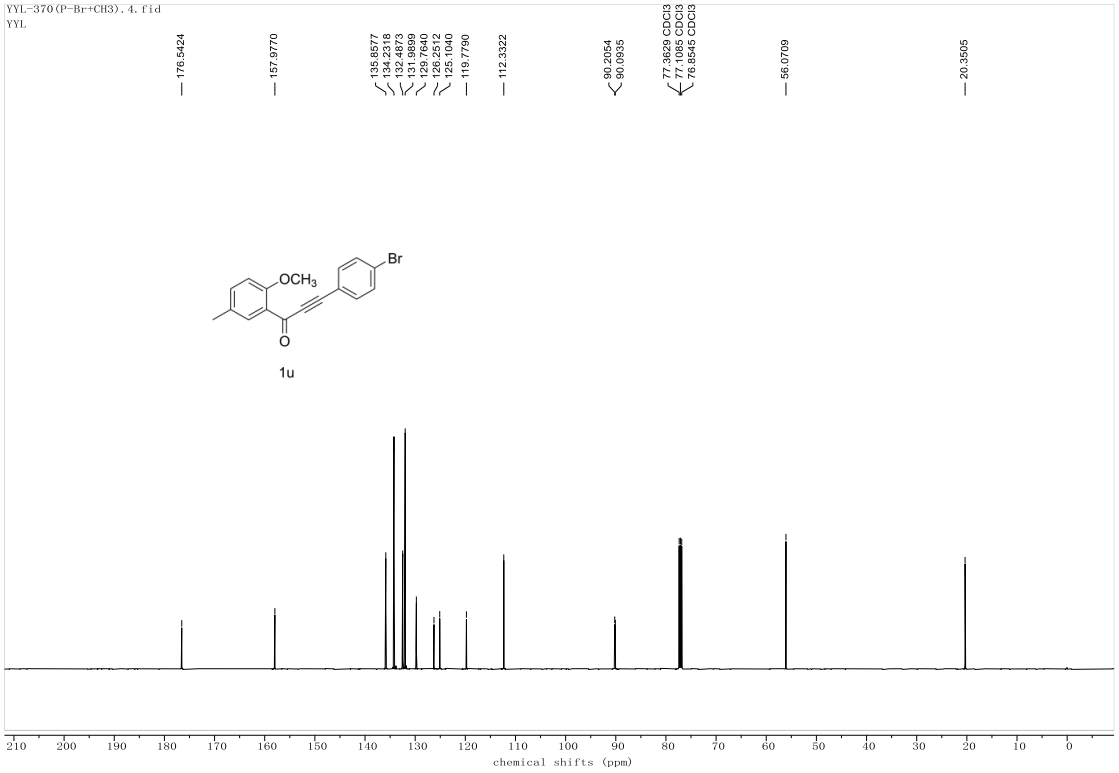
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1t**



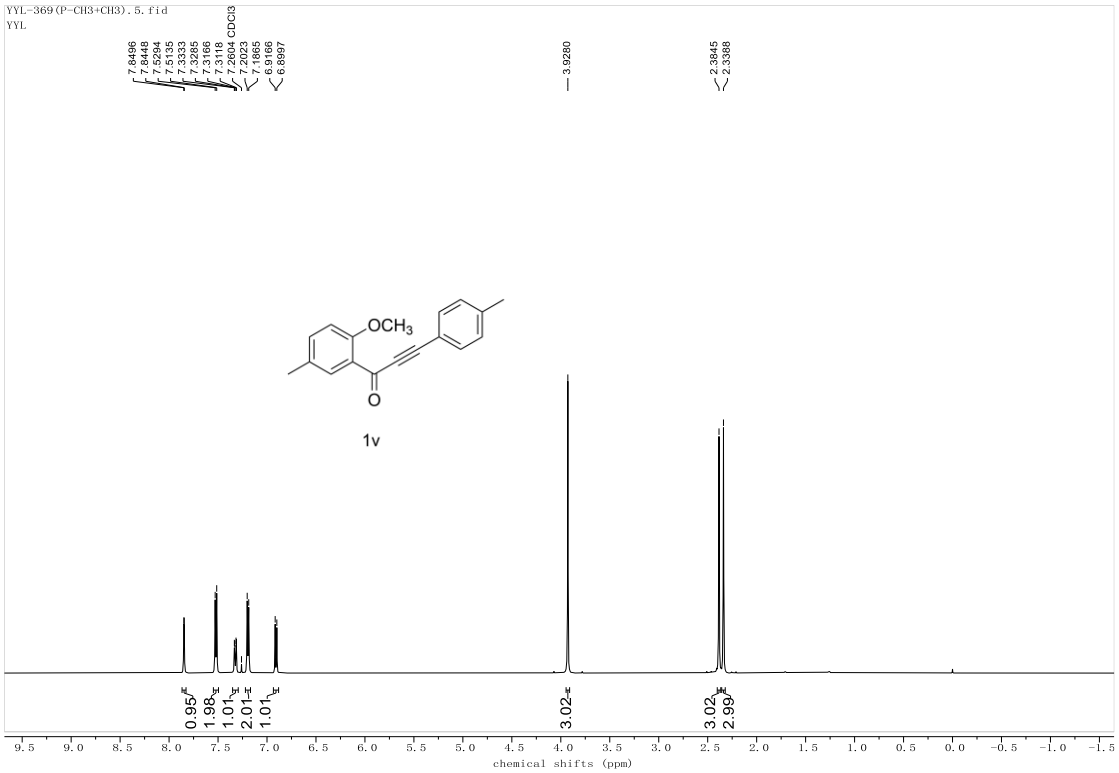
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1u**



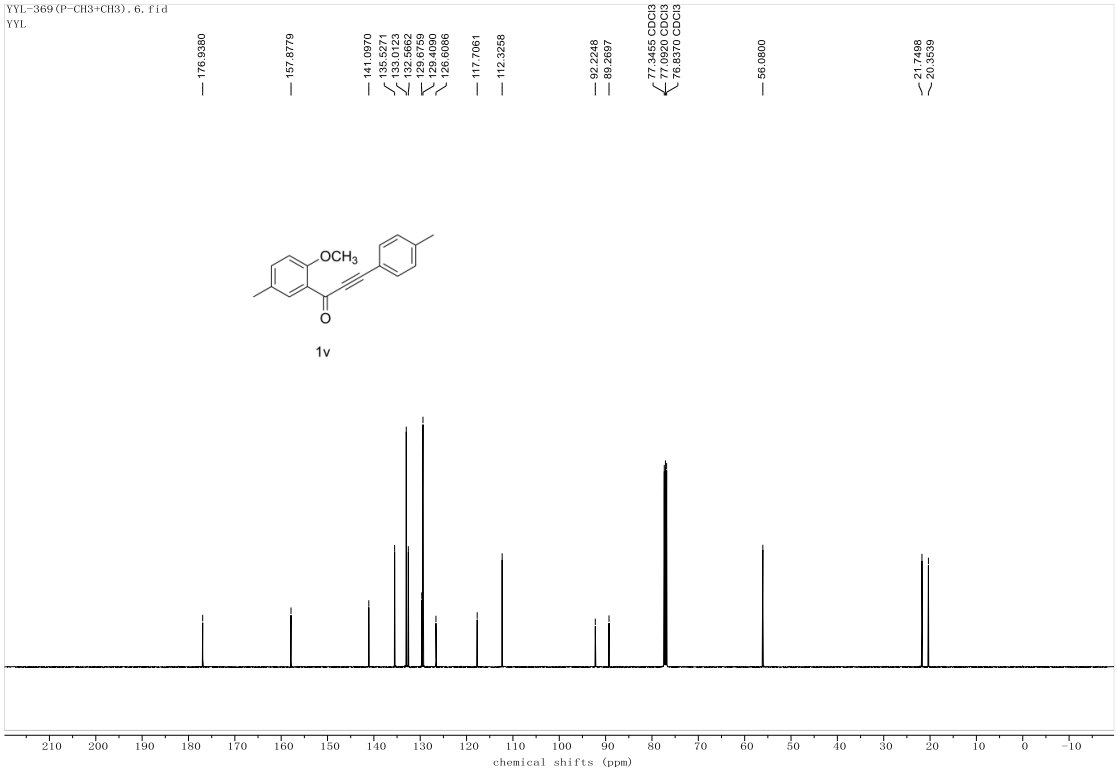
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1u**



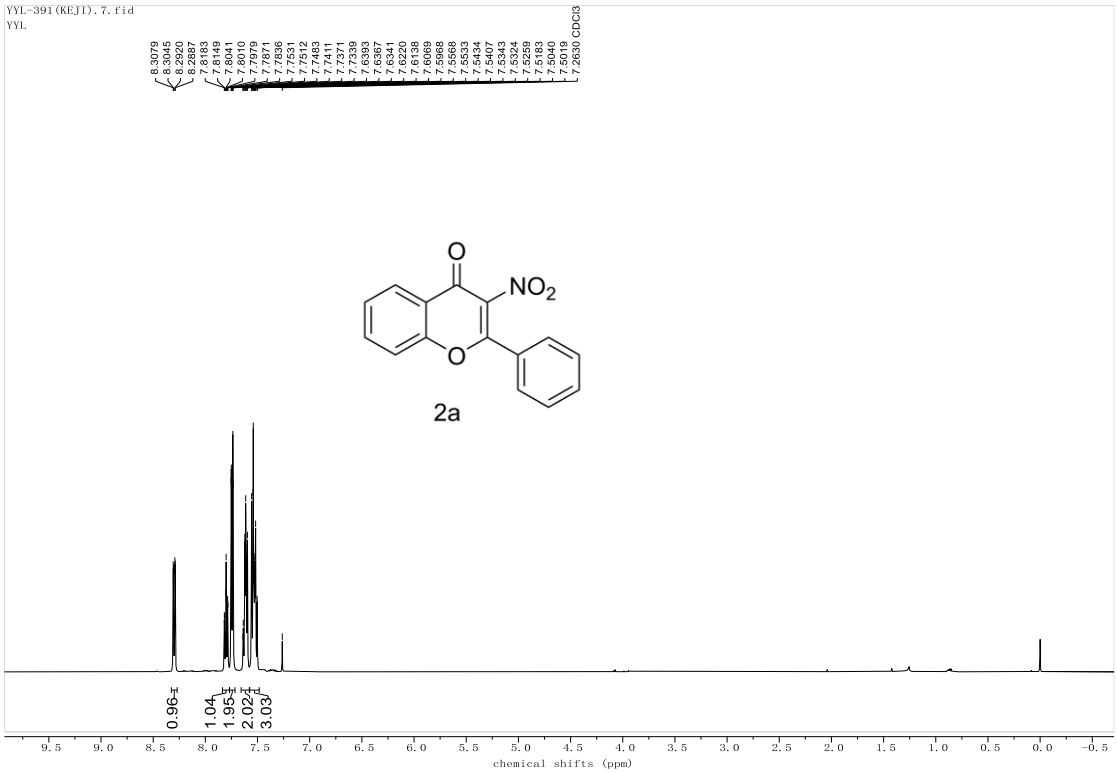
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1v**



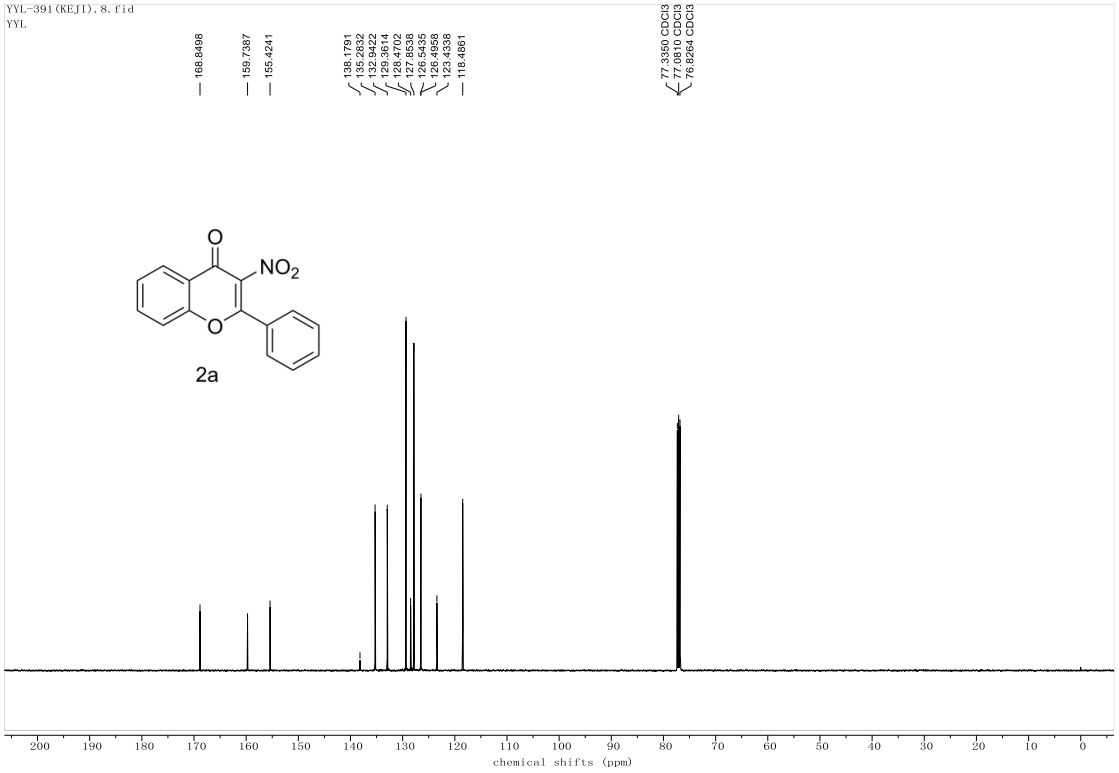
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1v**



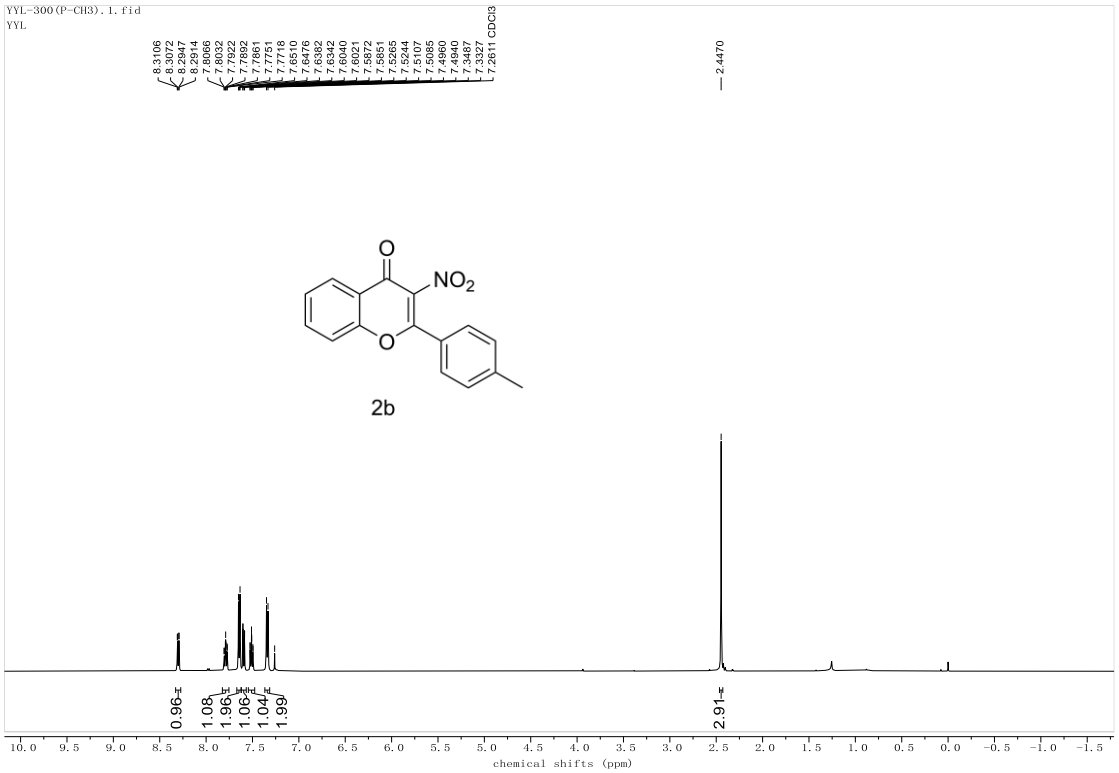
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2a**



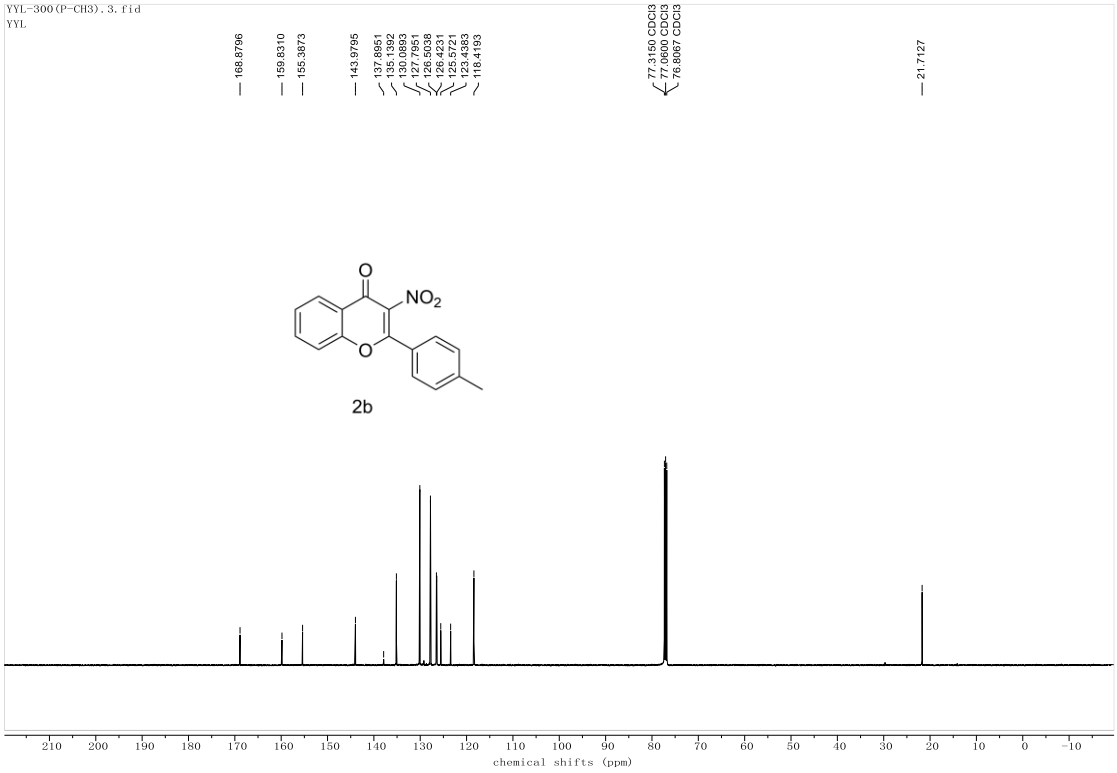
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2a**



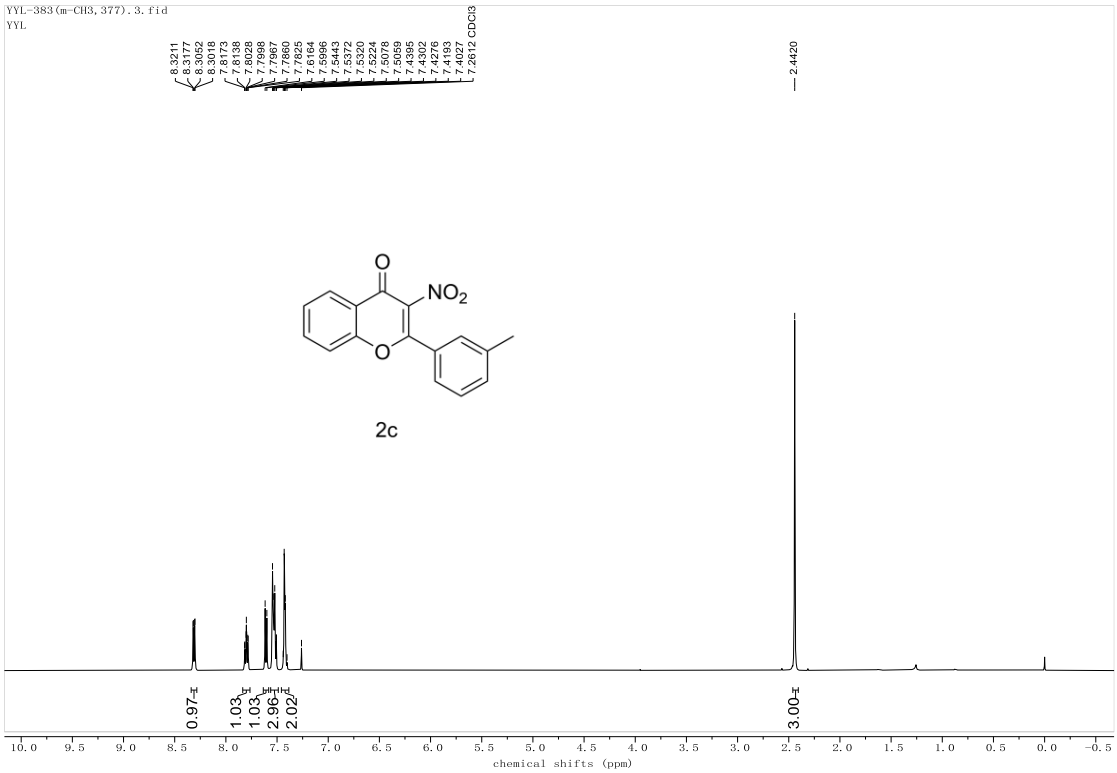
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2b**



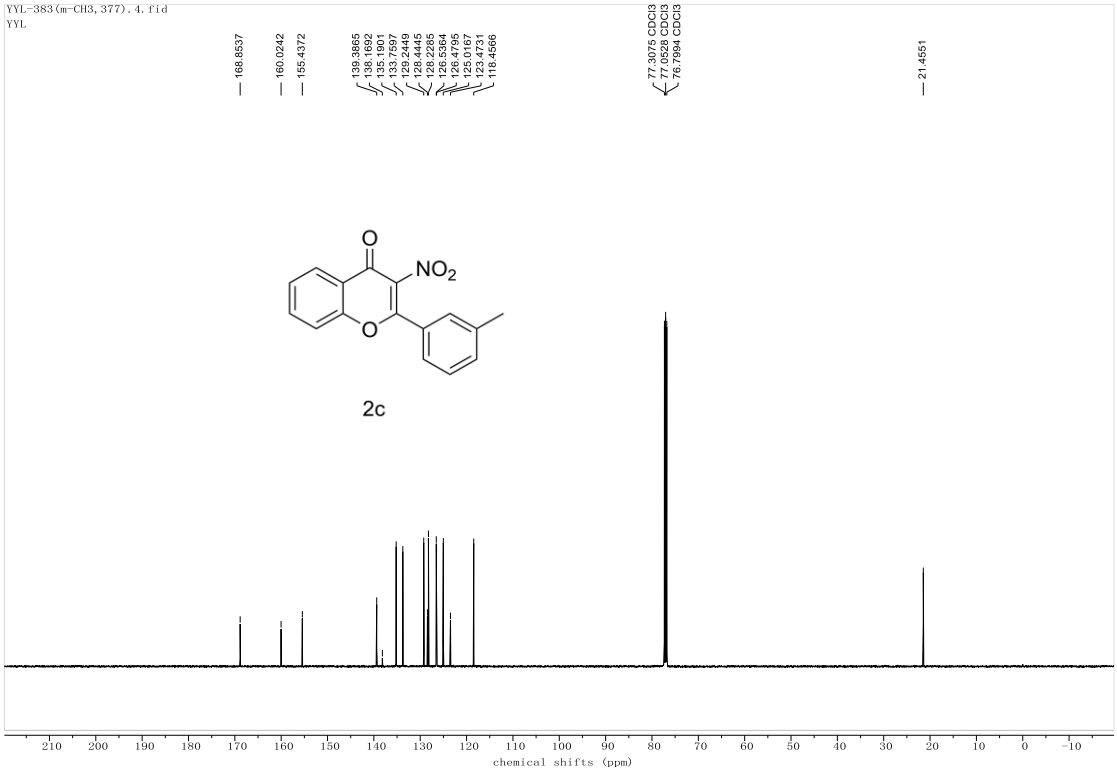
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2b**



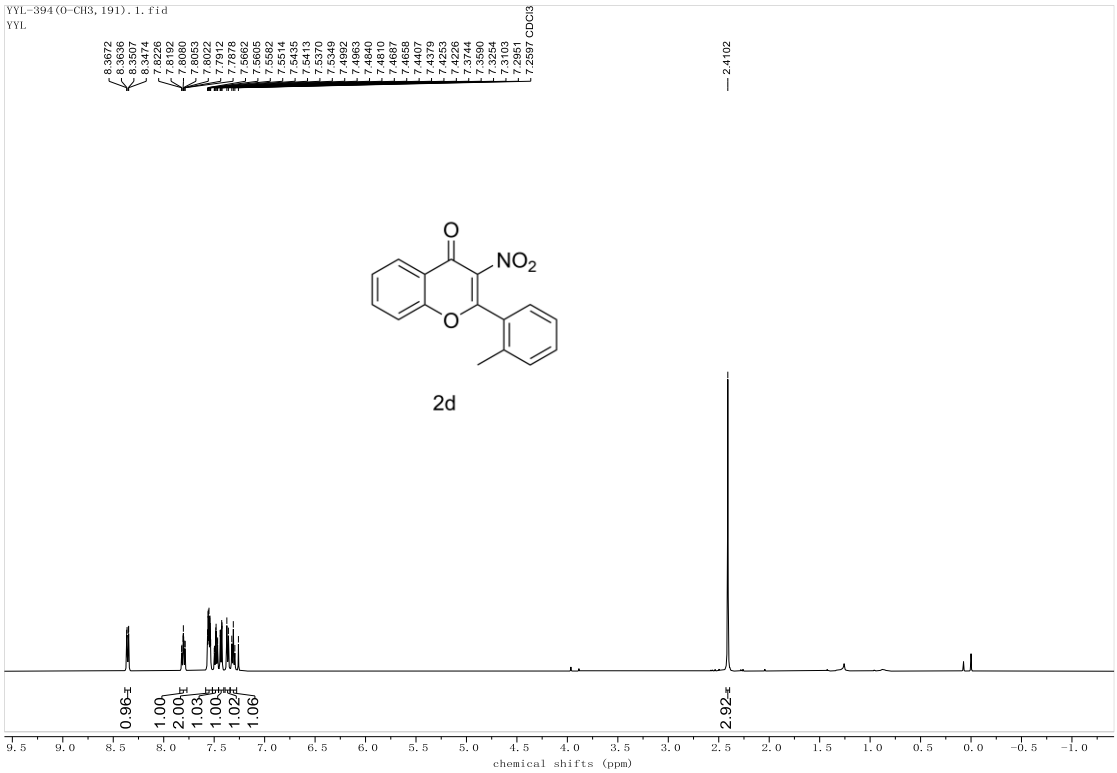
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2c**



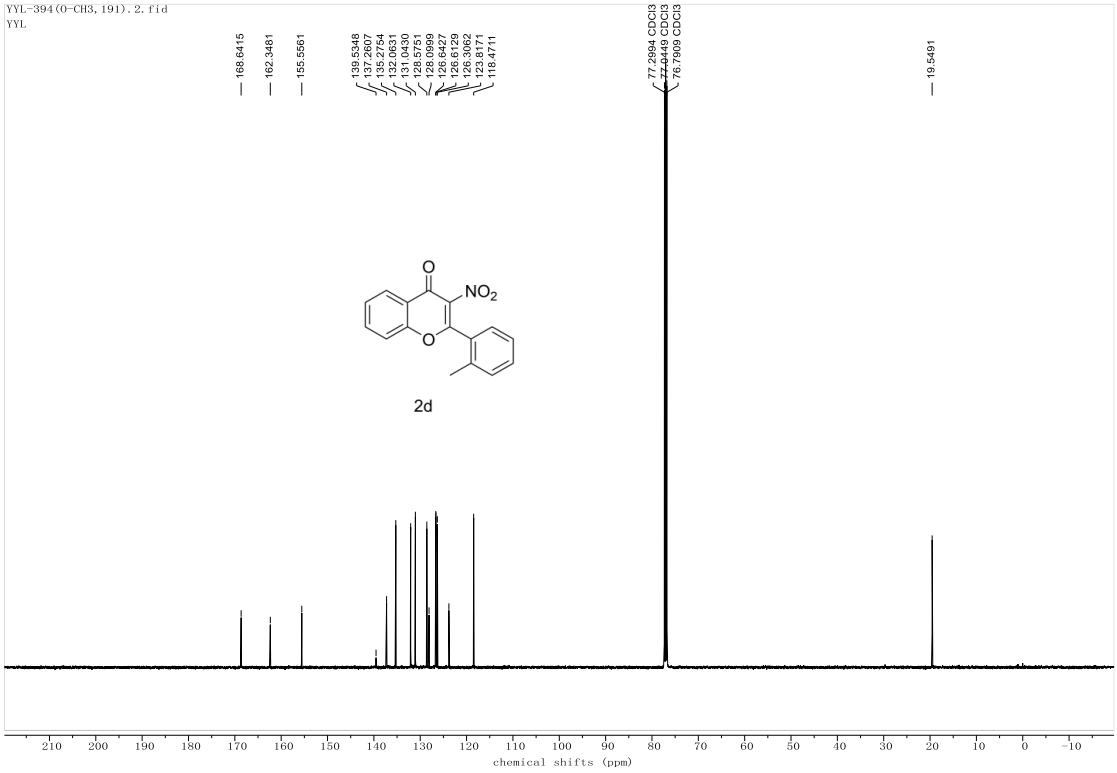
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2c**



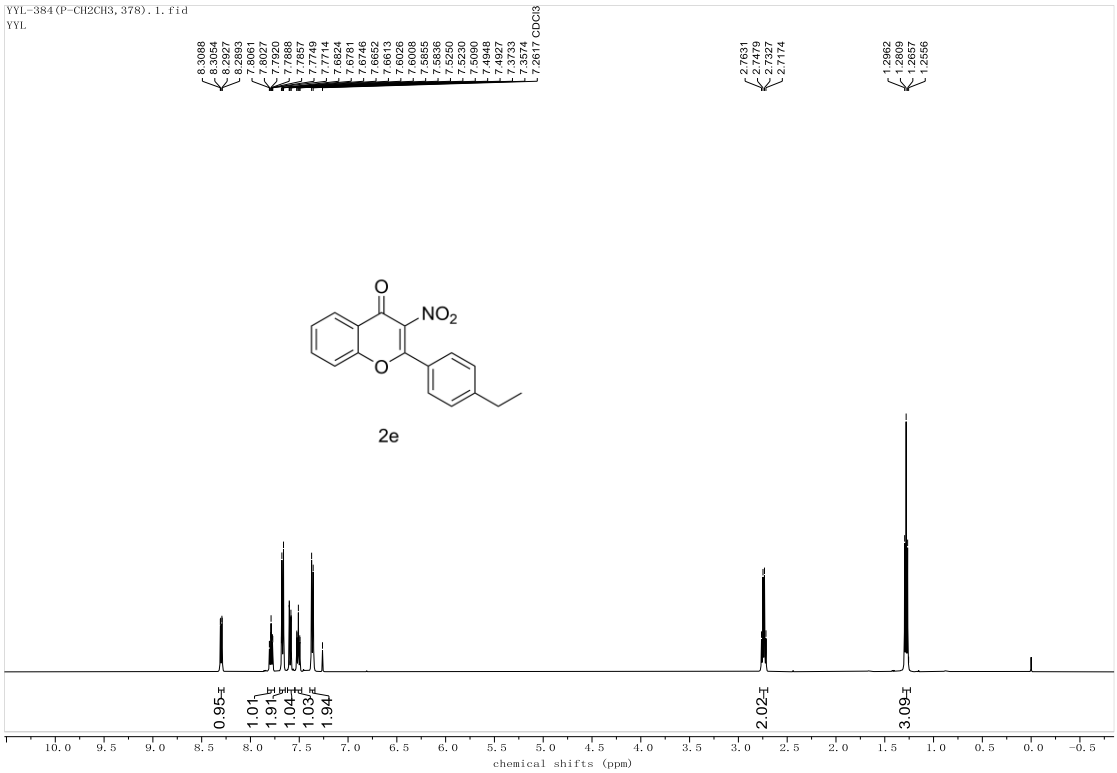
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2d**



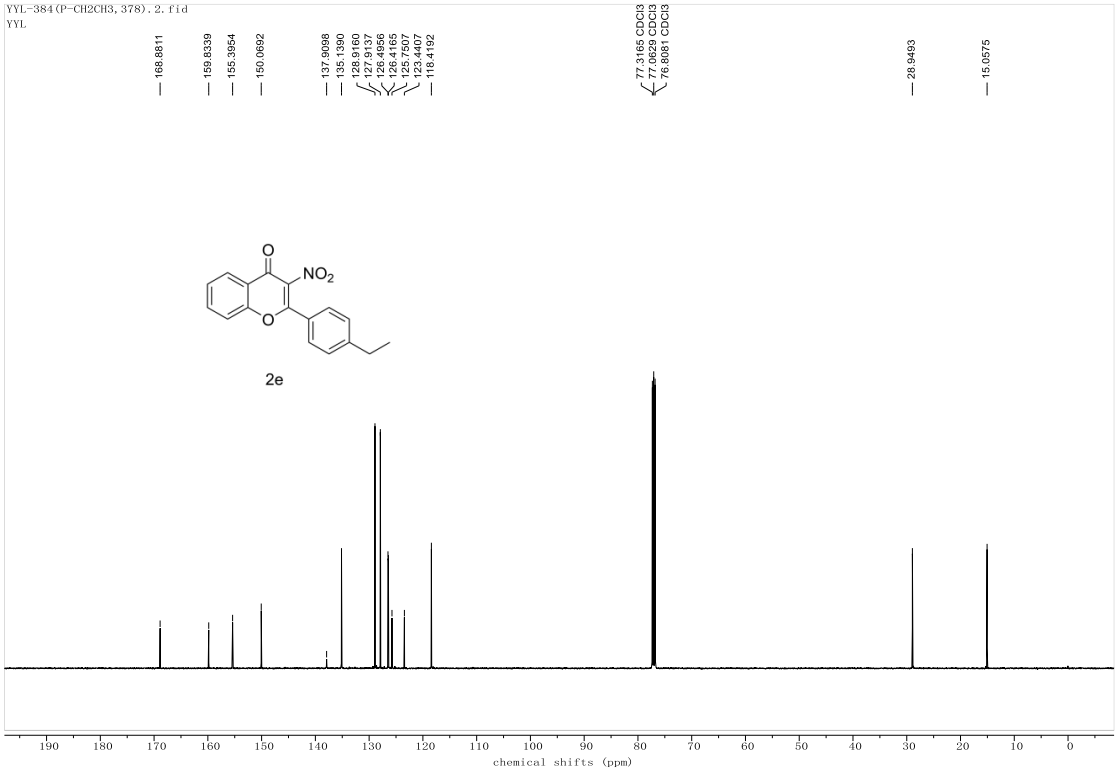
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2d**



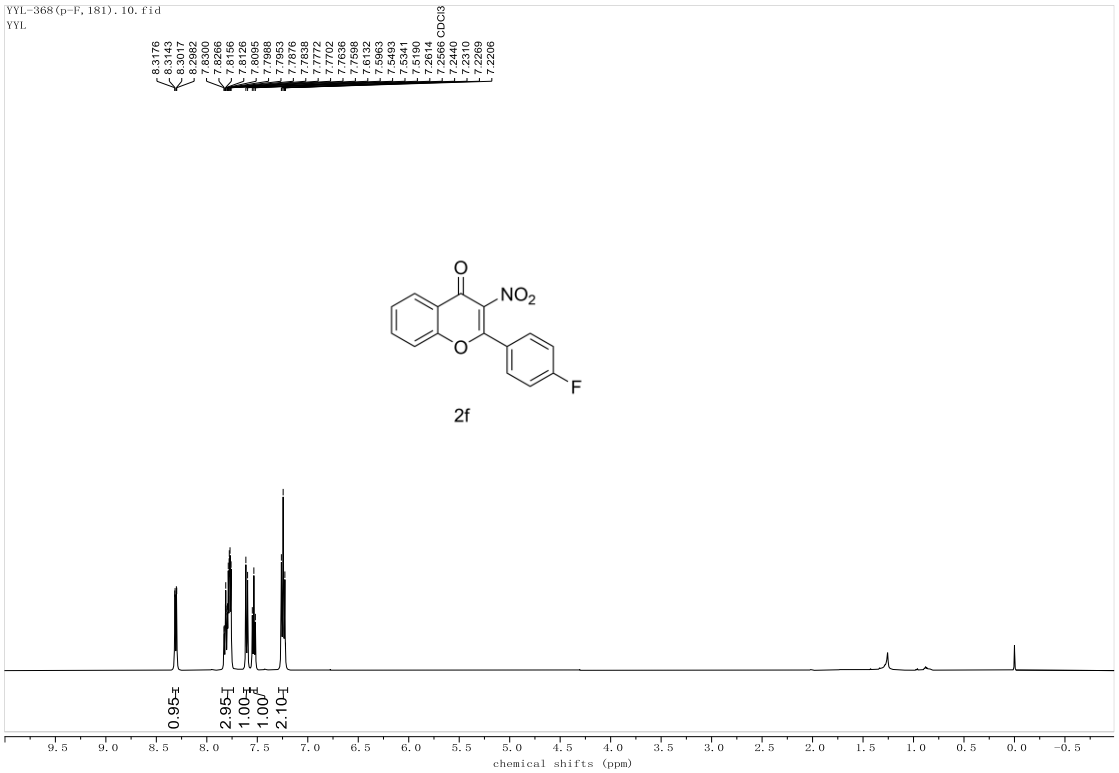
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2e**



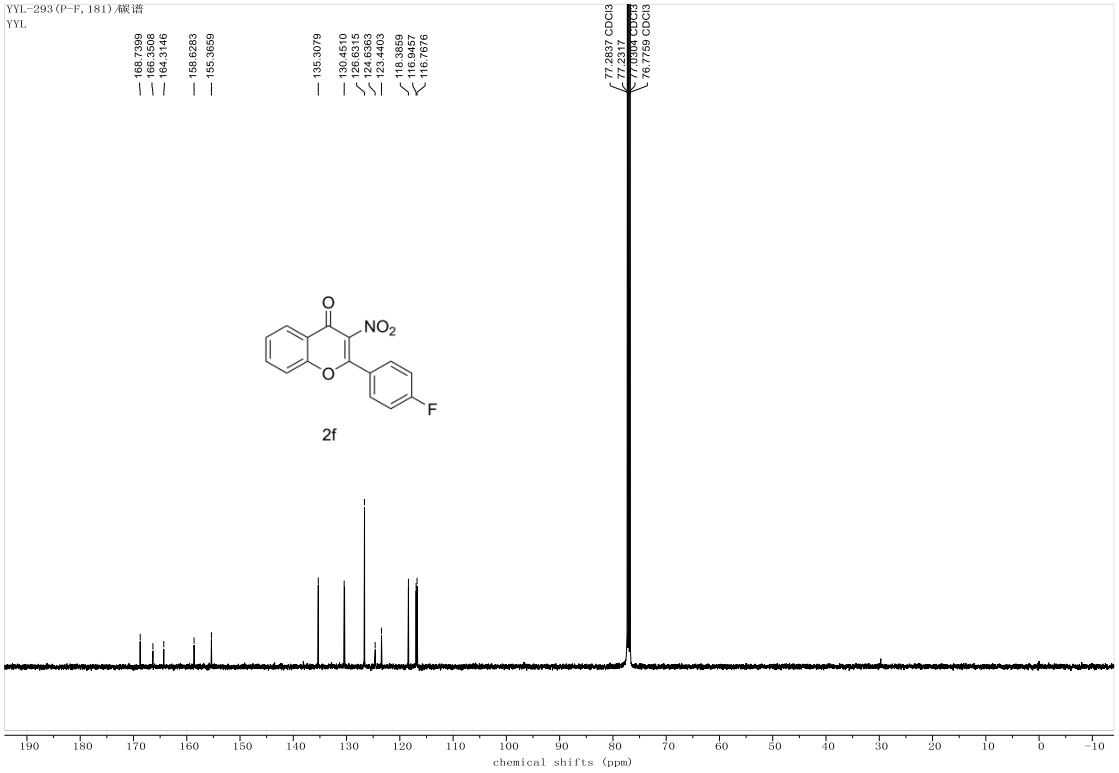
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2e**



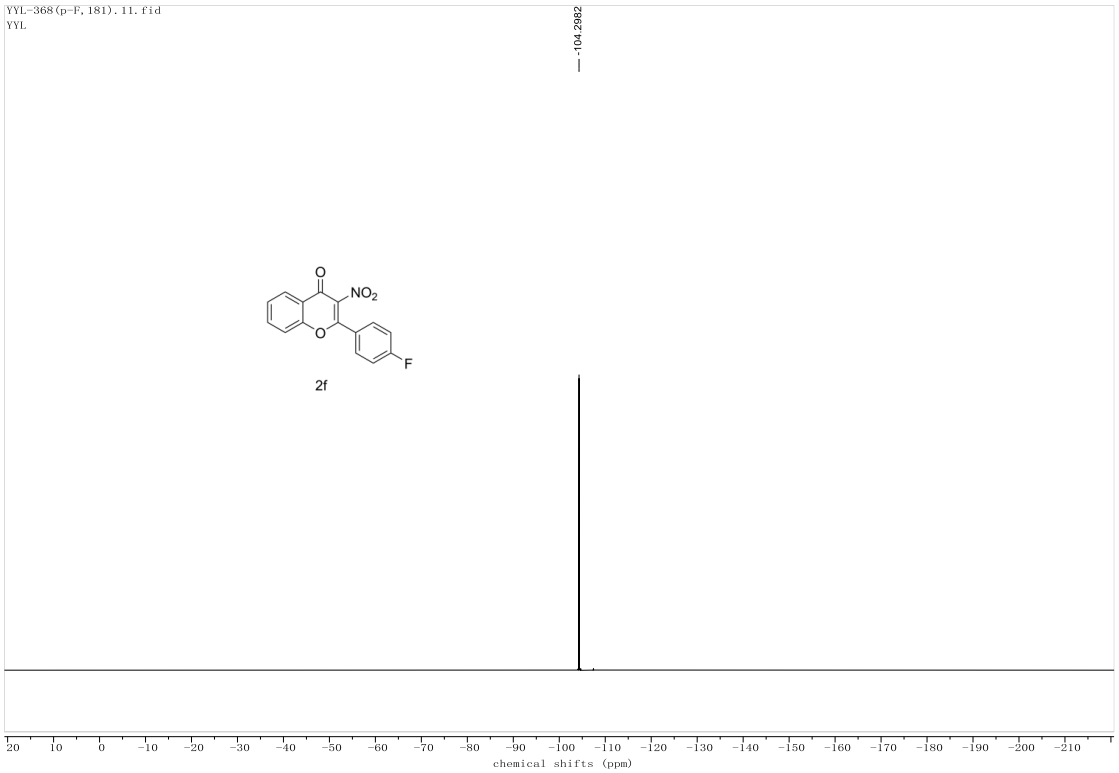
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2f**



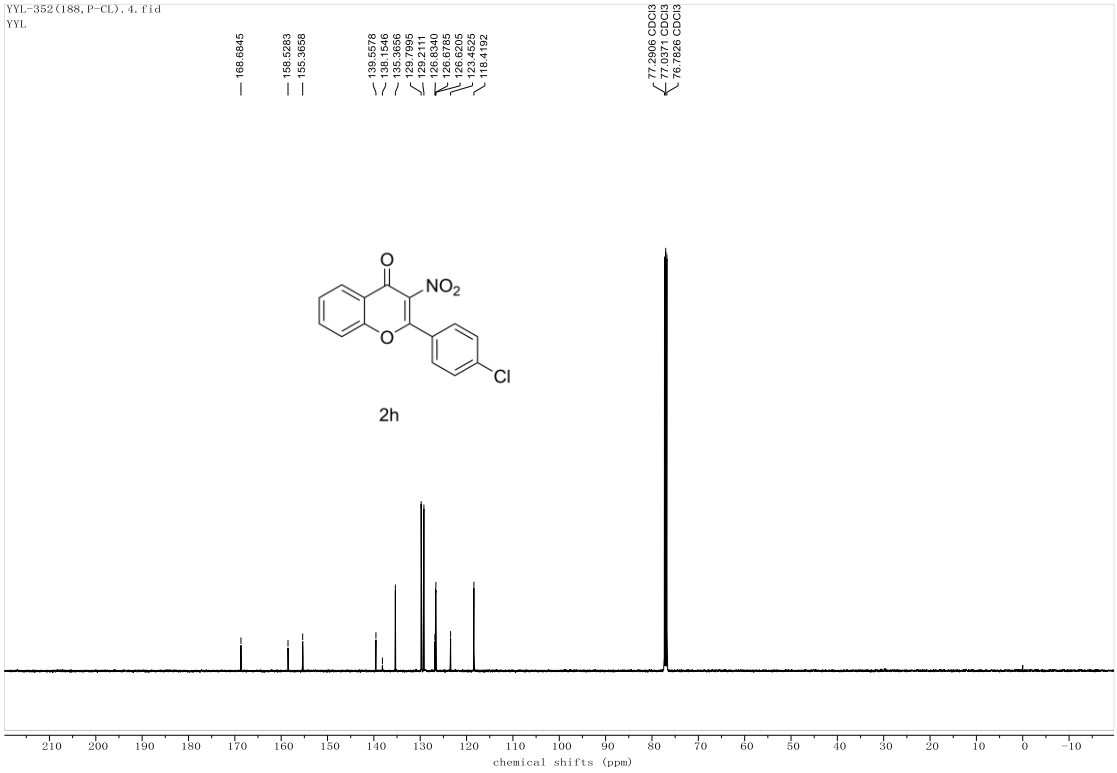
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2f**



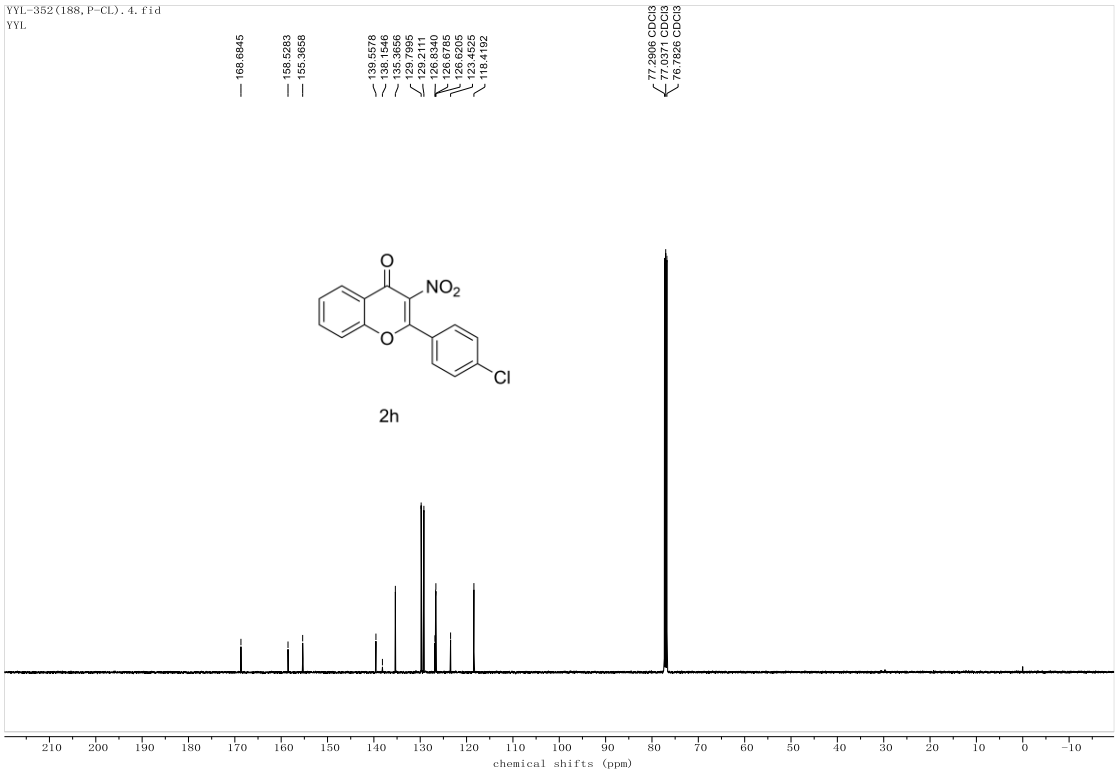
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **2f**



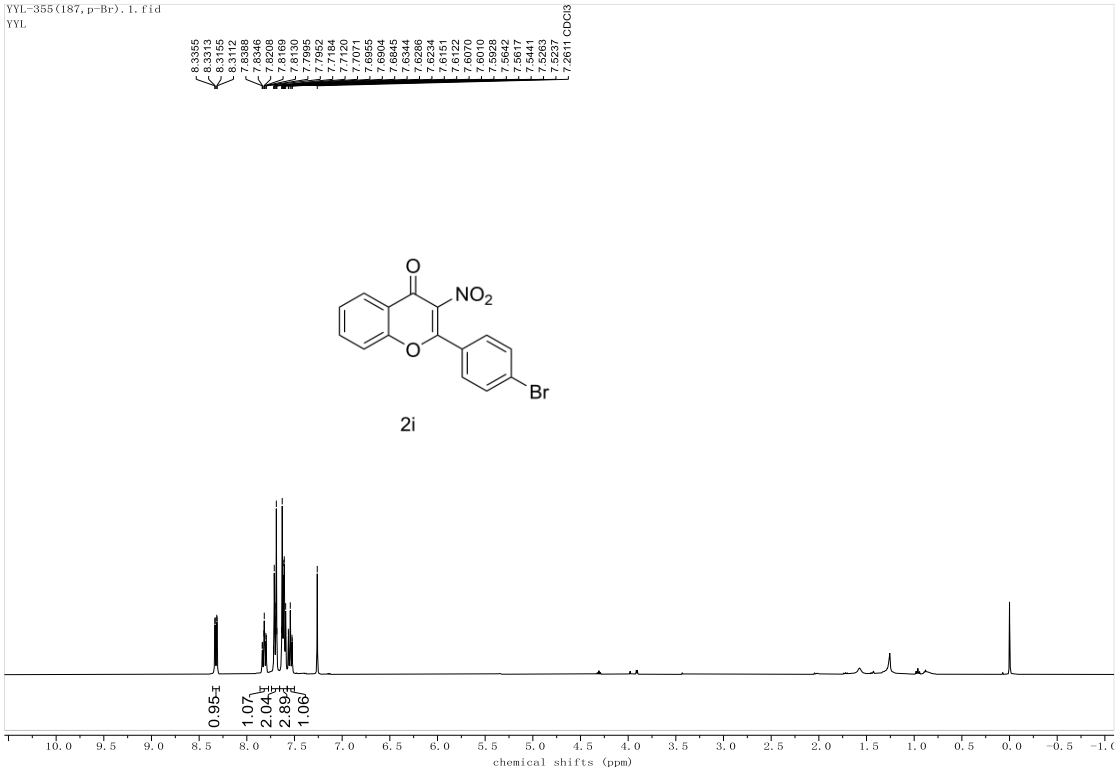
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2h**



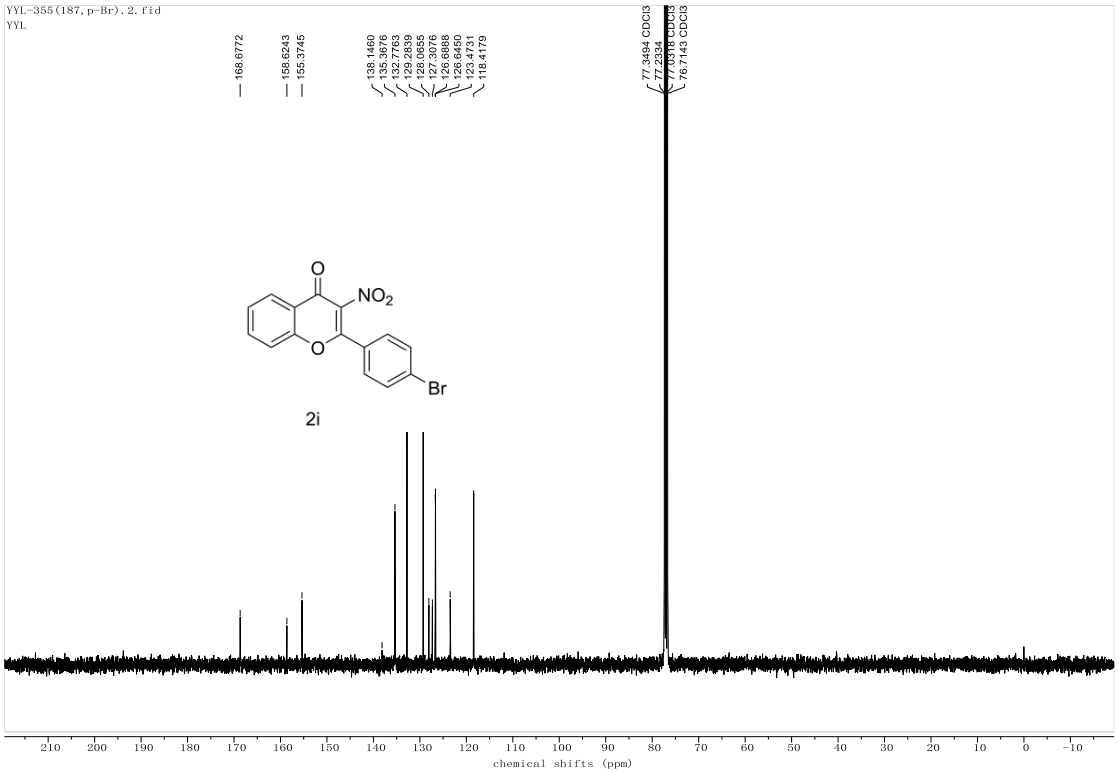
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2h**



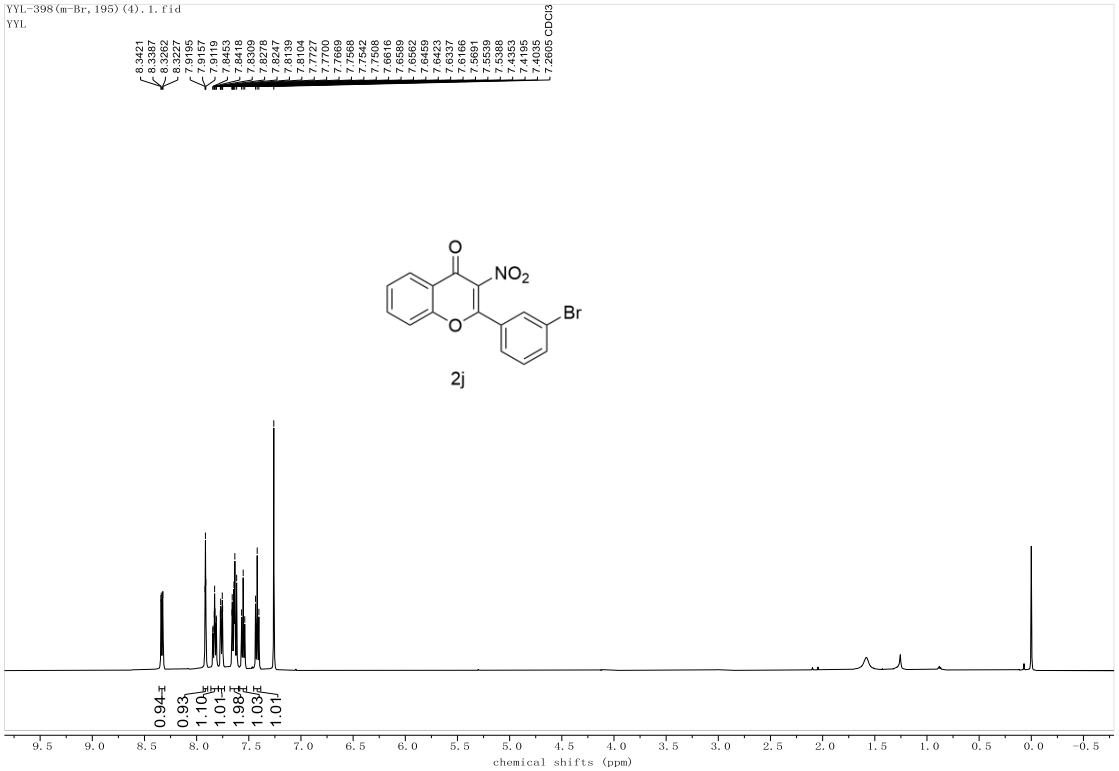
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2i**



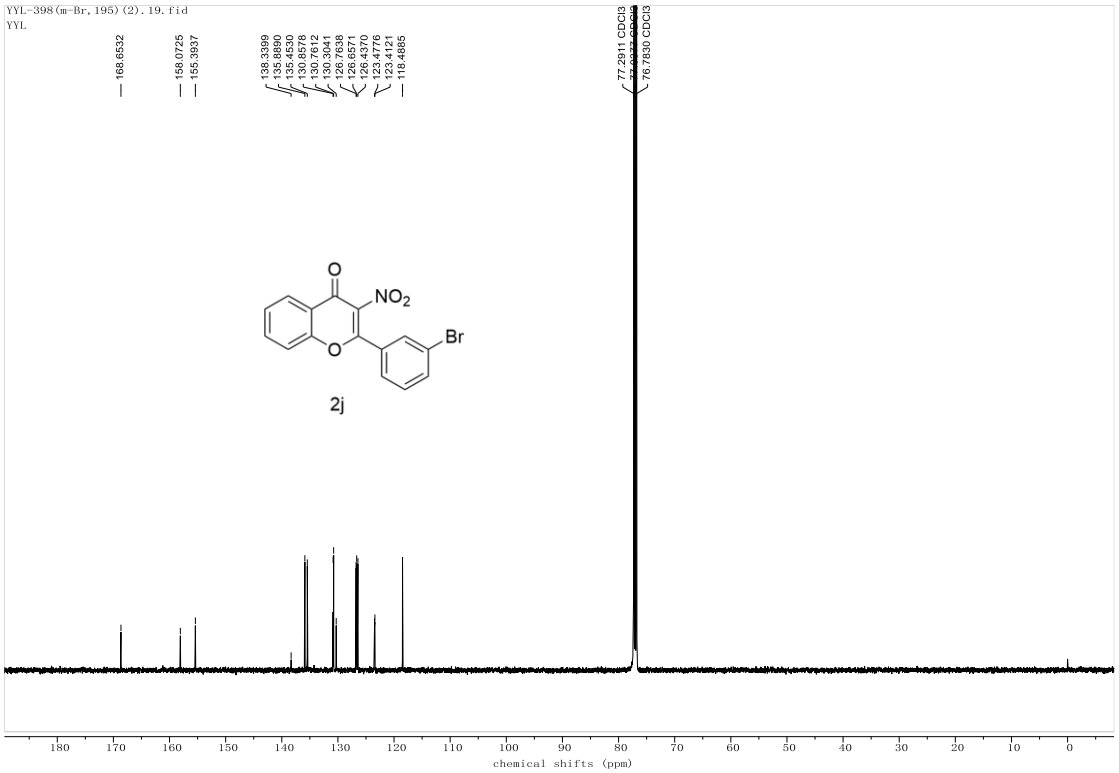
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2i**



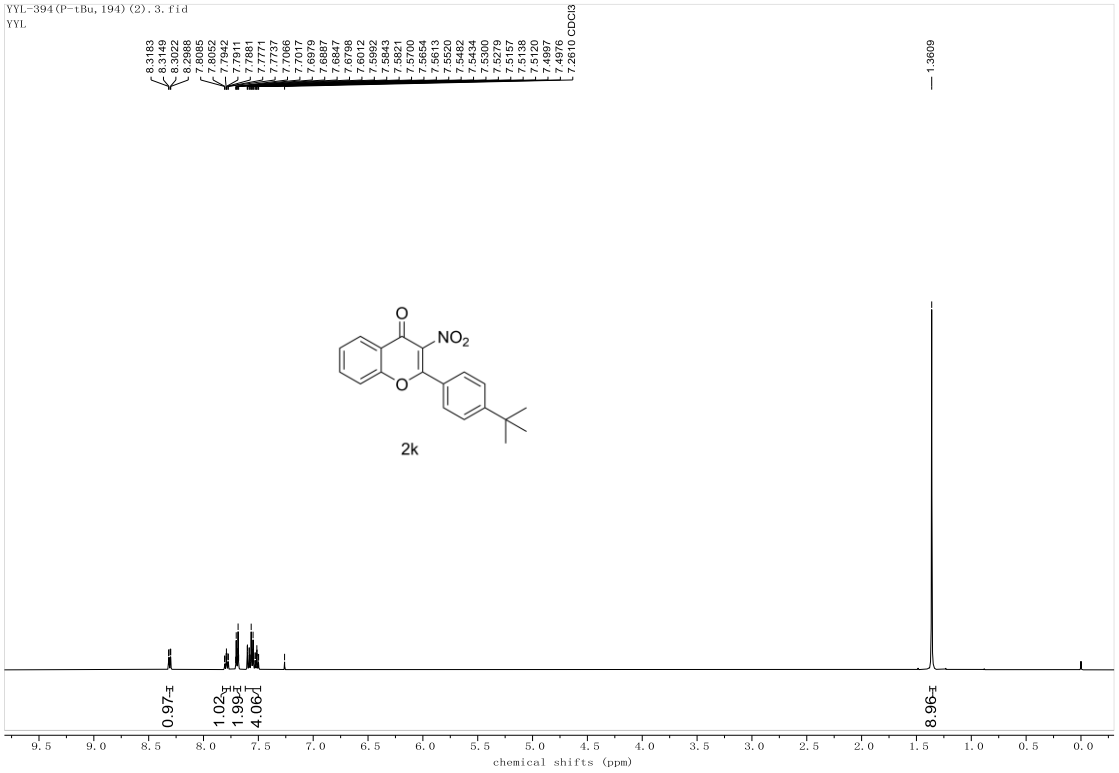
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2j**



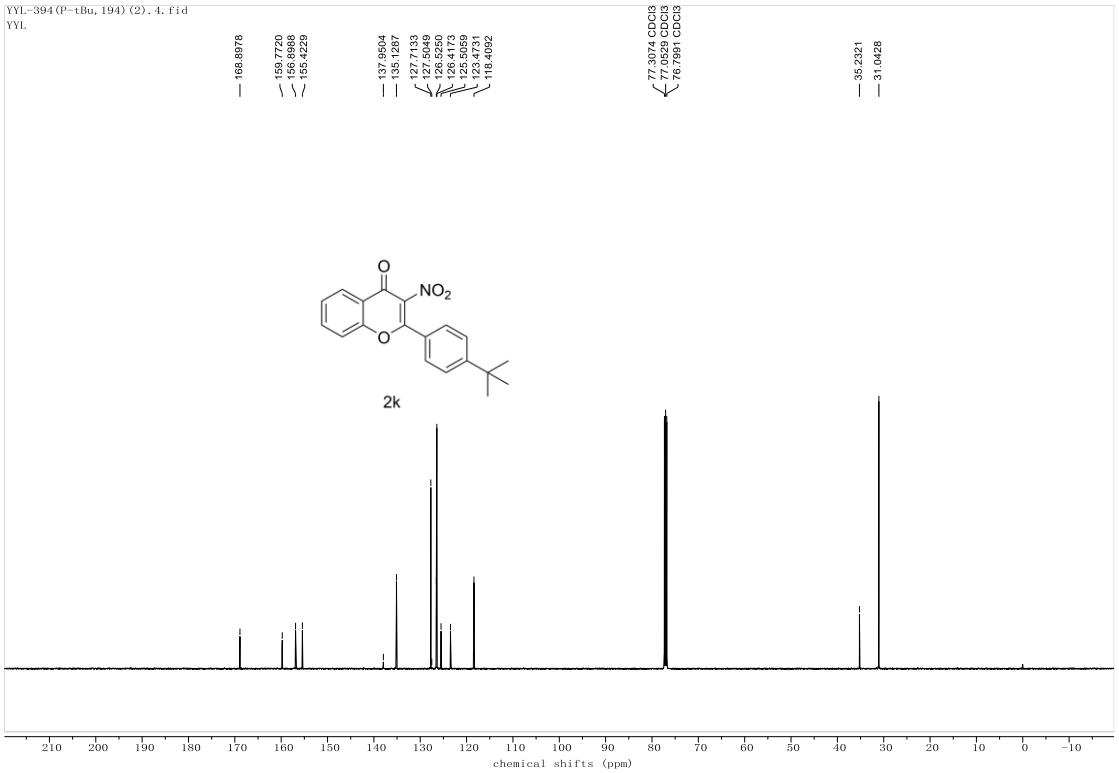
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2j**



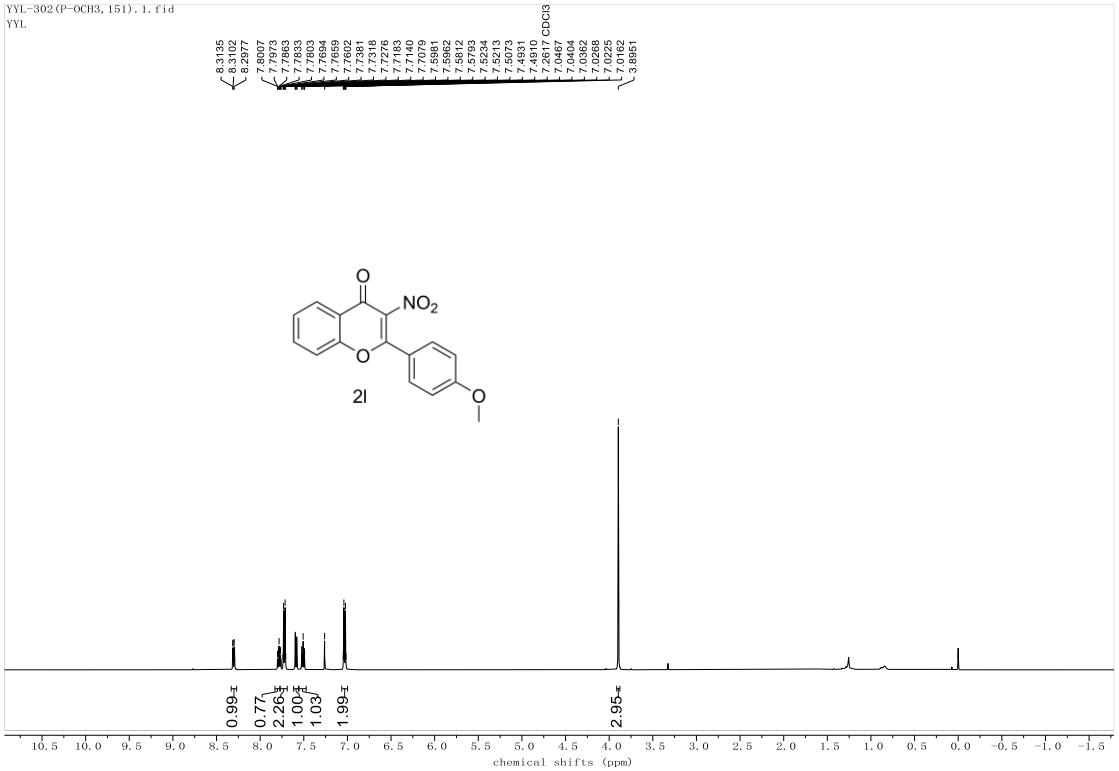
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2k**



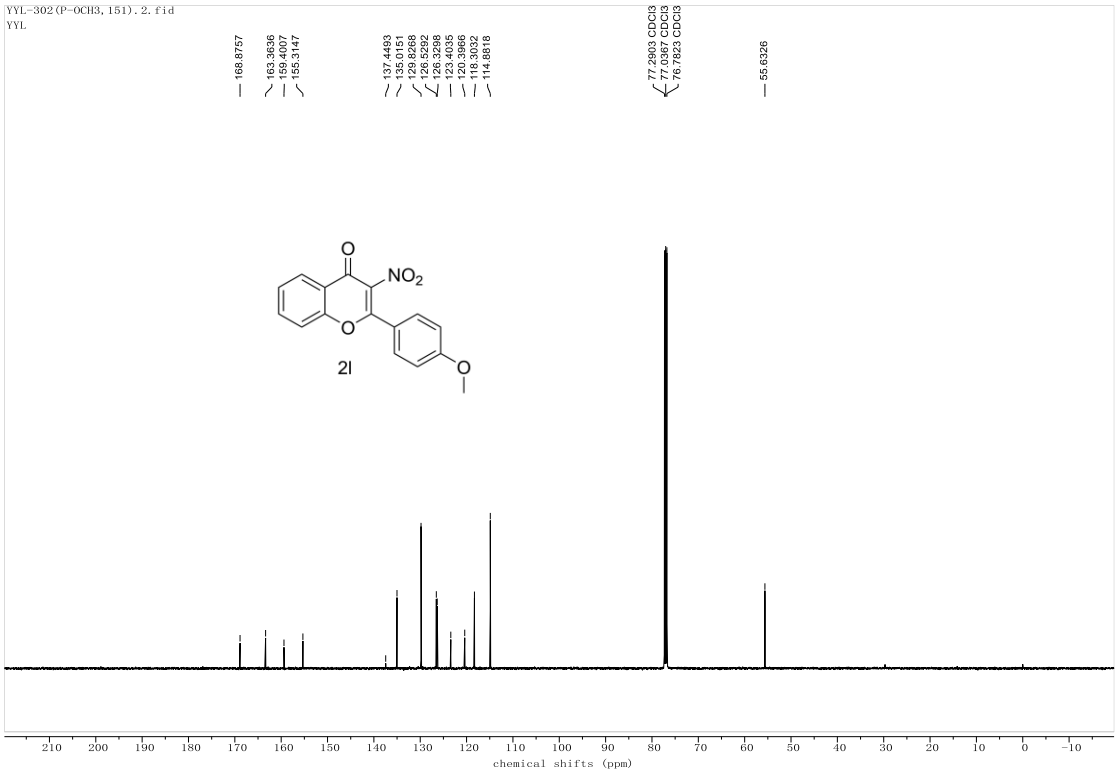
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2k**



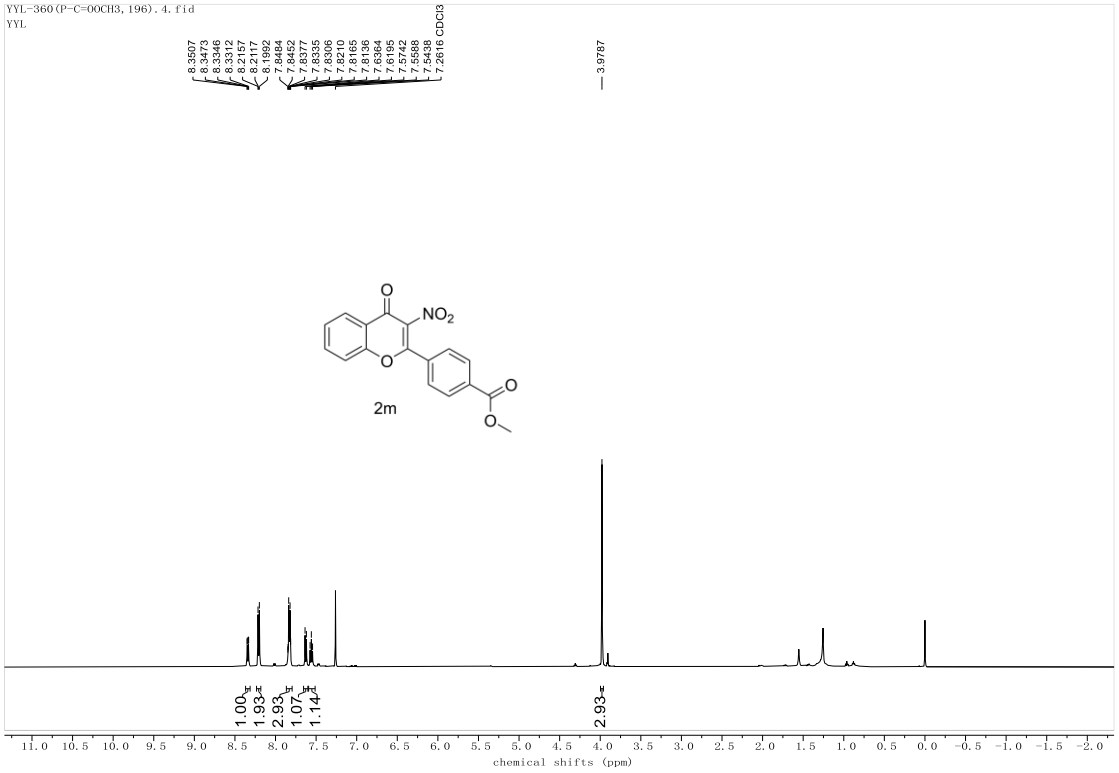
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2l**



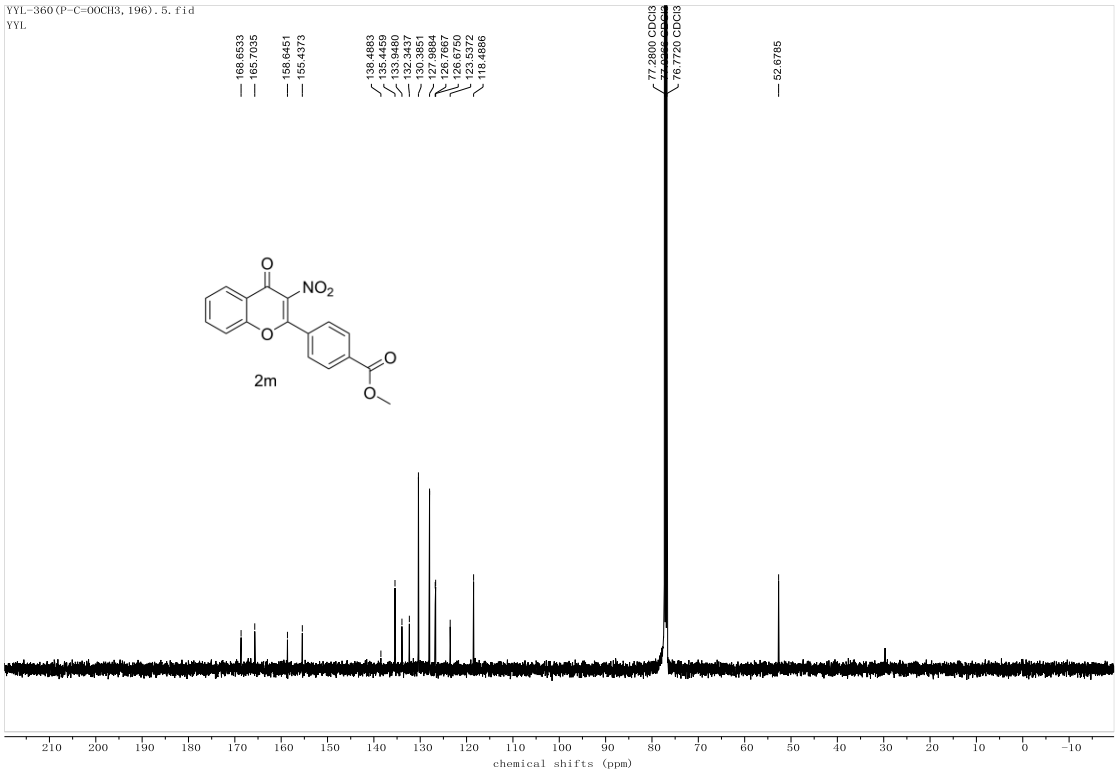
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2l**



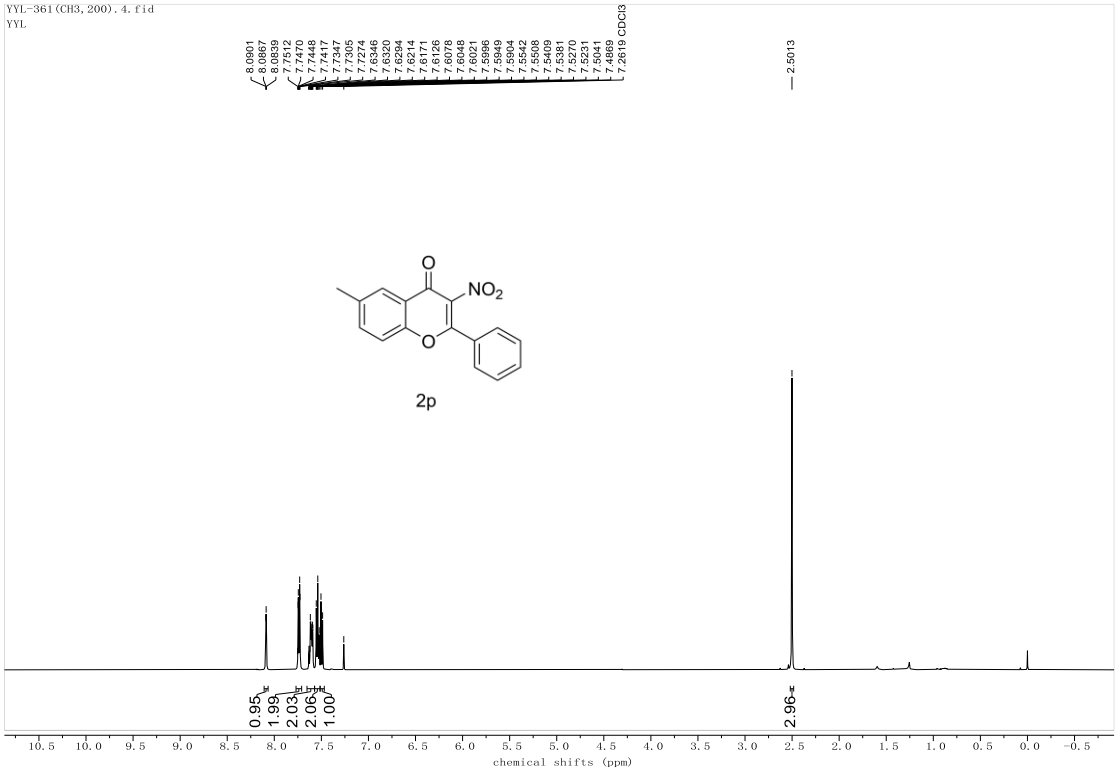
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2m**



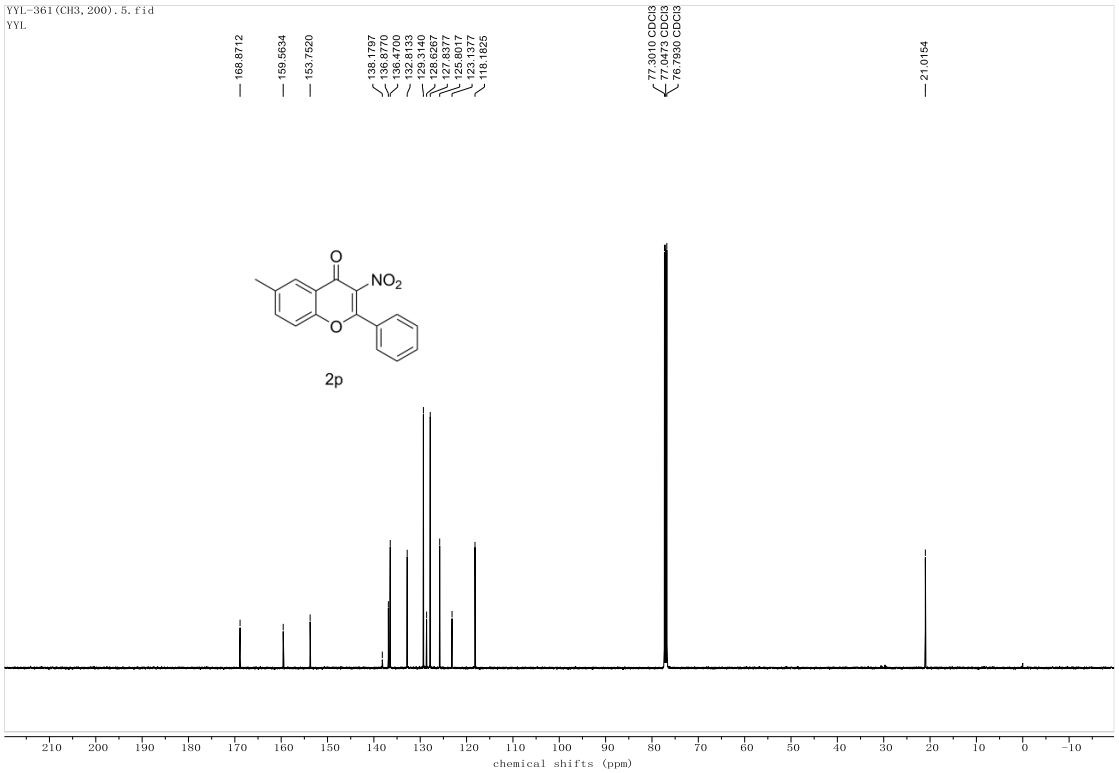
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2m**



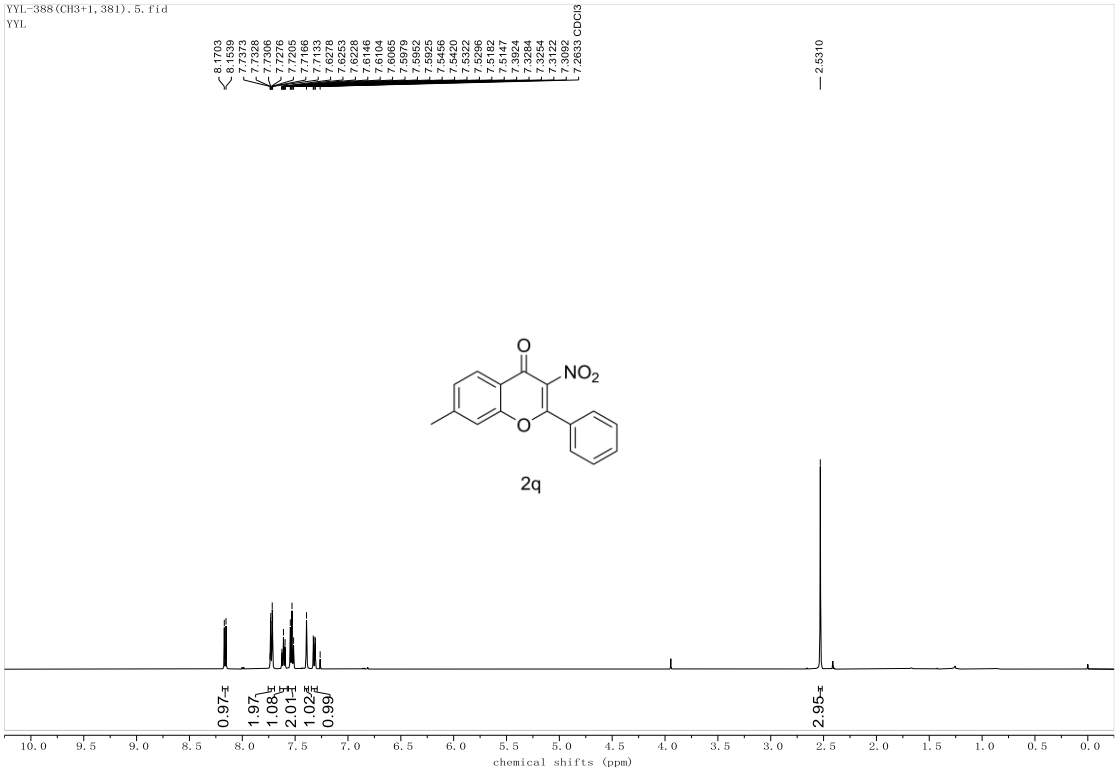
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2p**



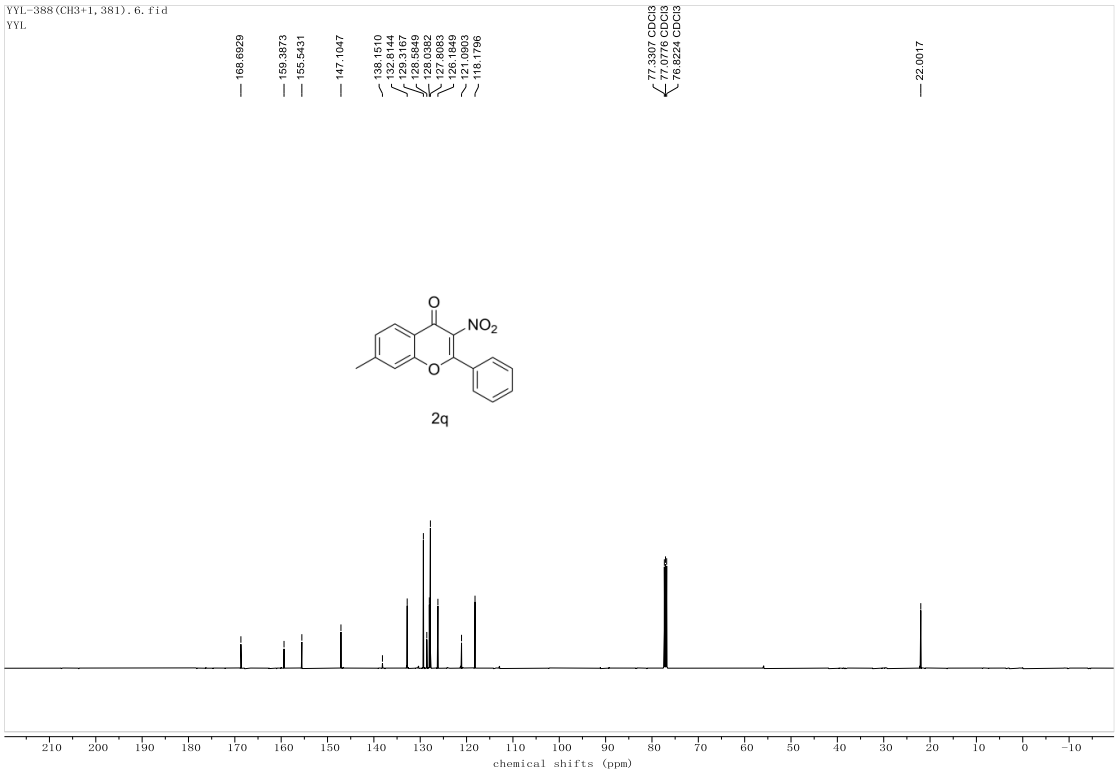
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2p**



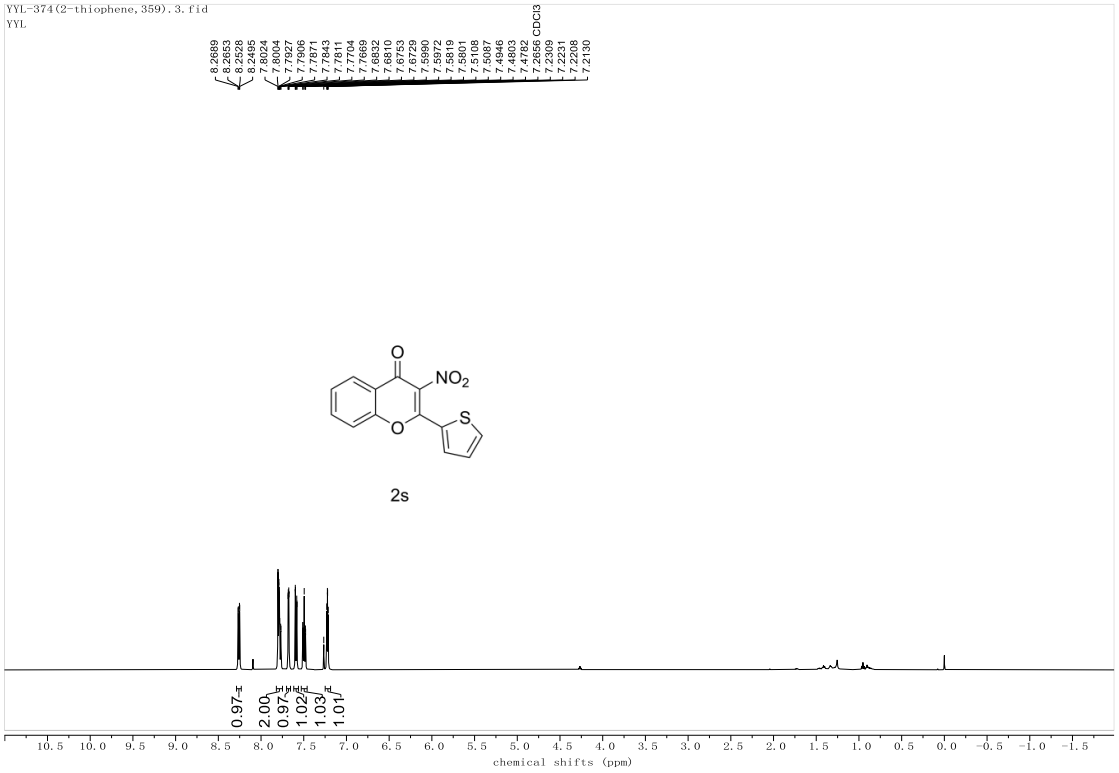
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2q**



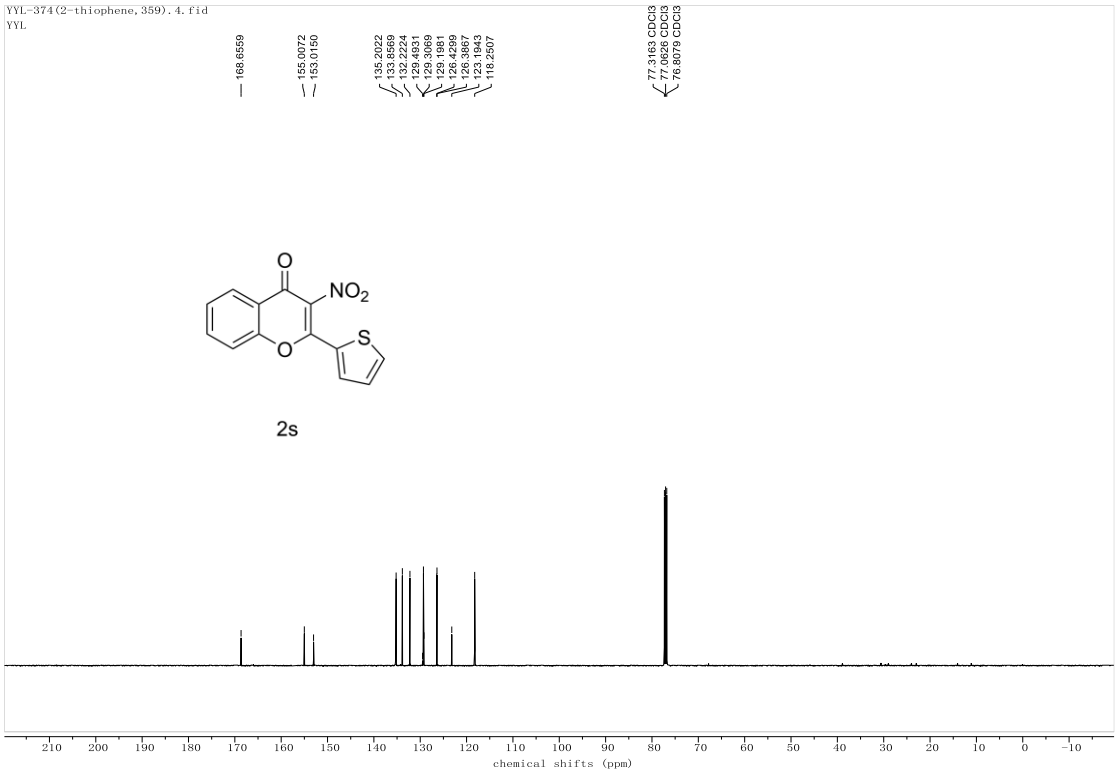
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2q**



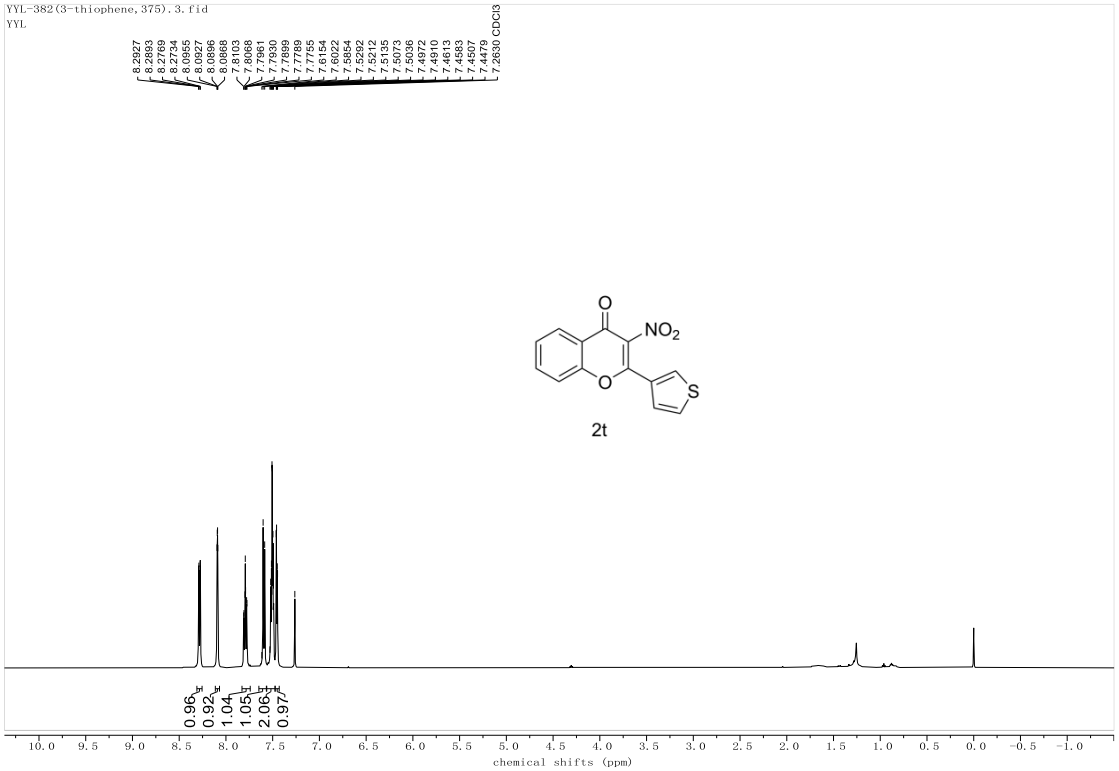
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2s**



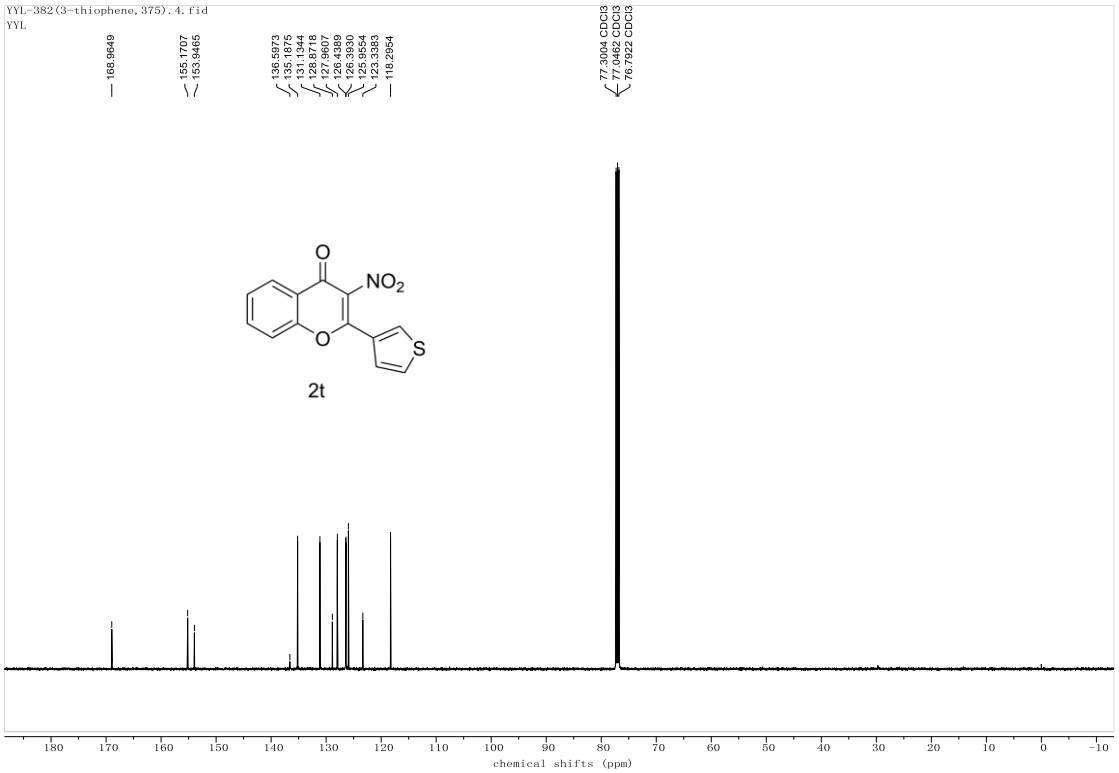
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2s**



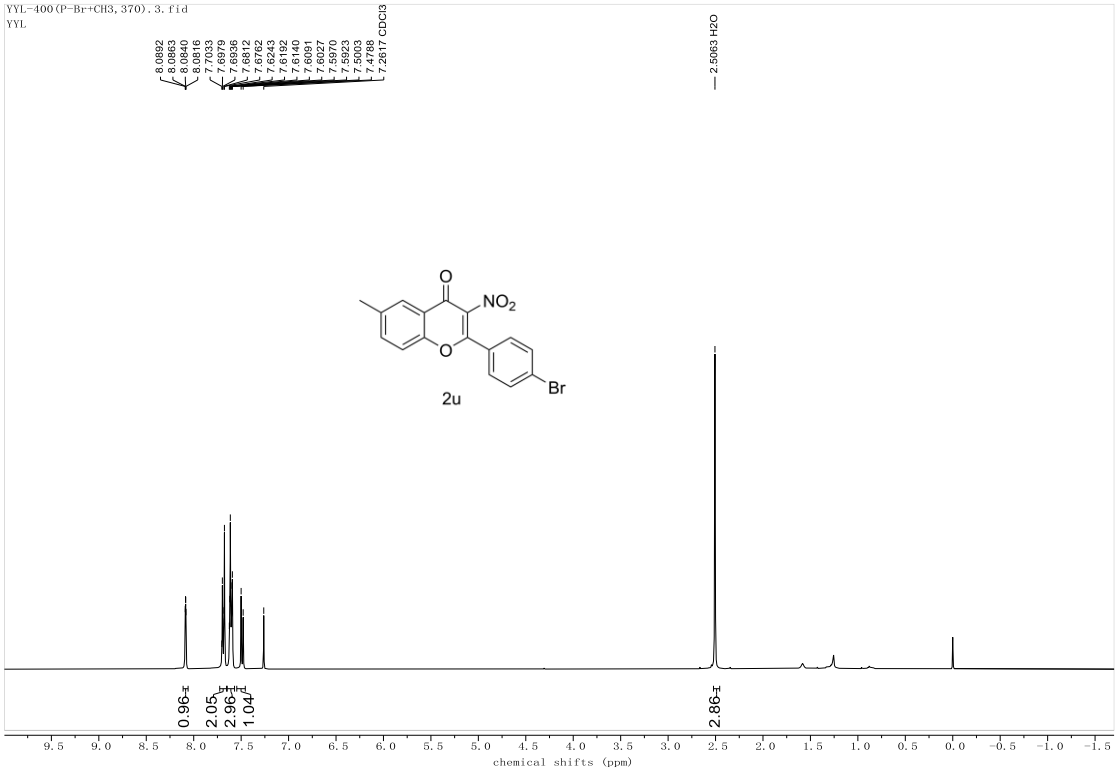
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2t**



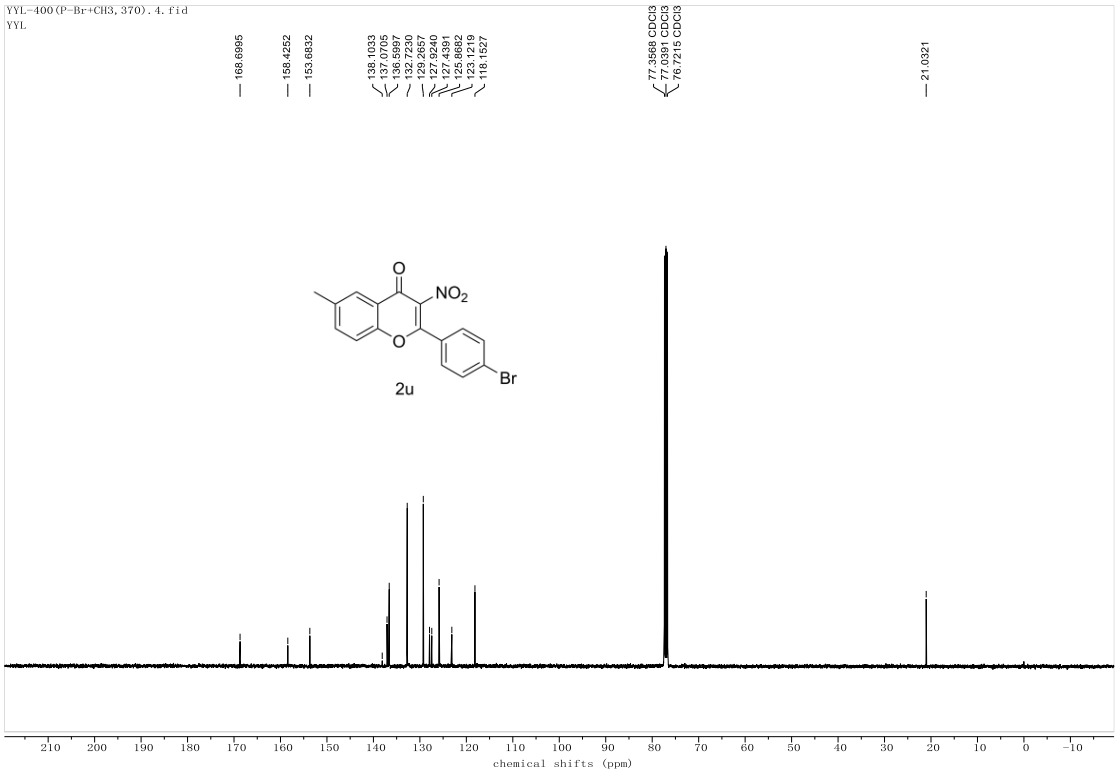
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2t**



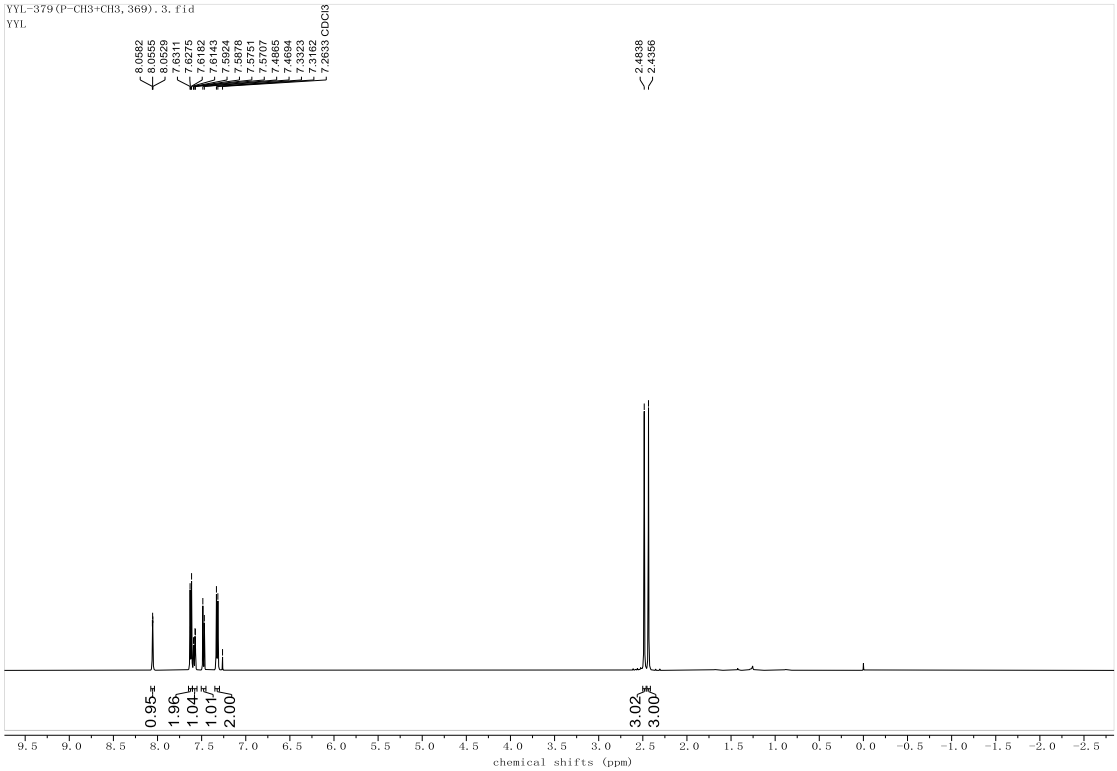
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2u**



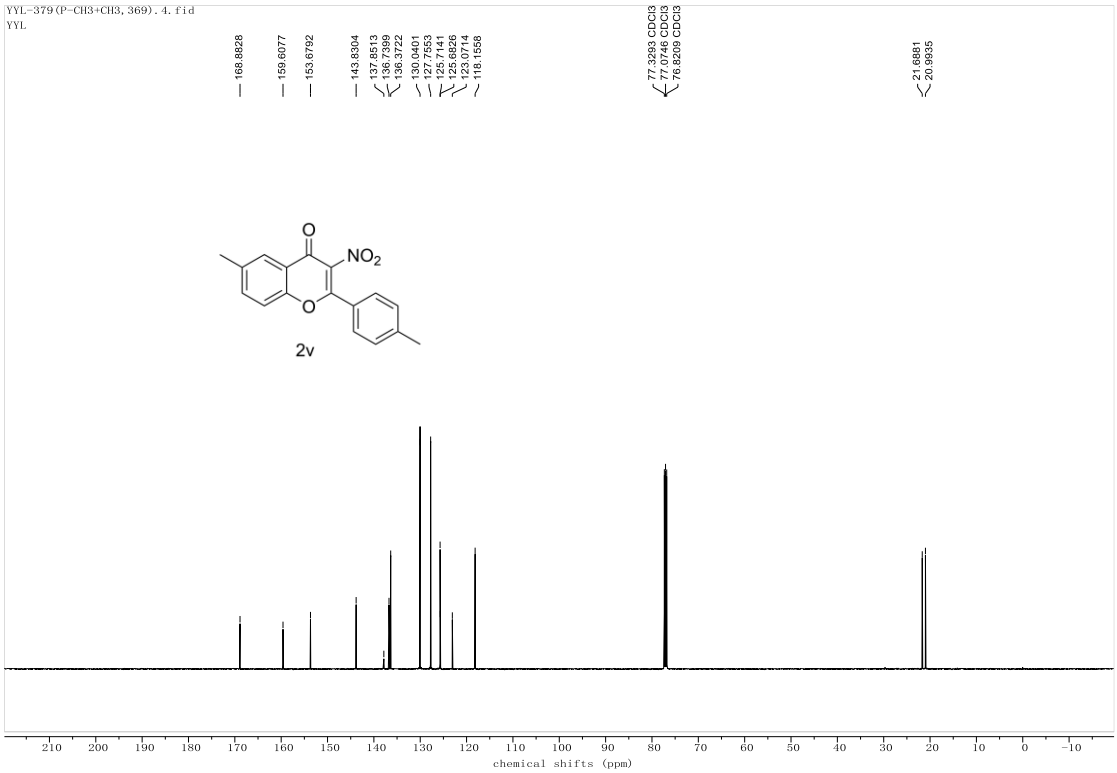
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2u**



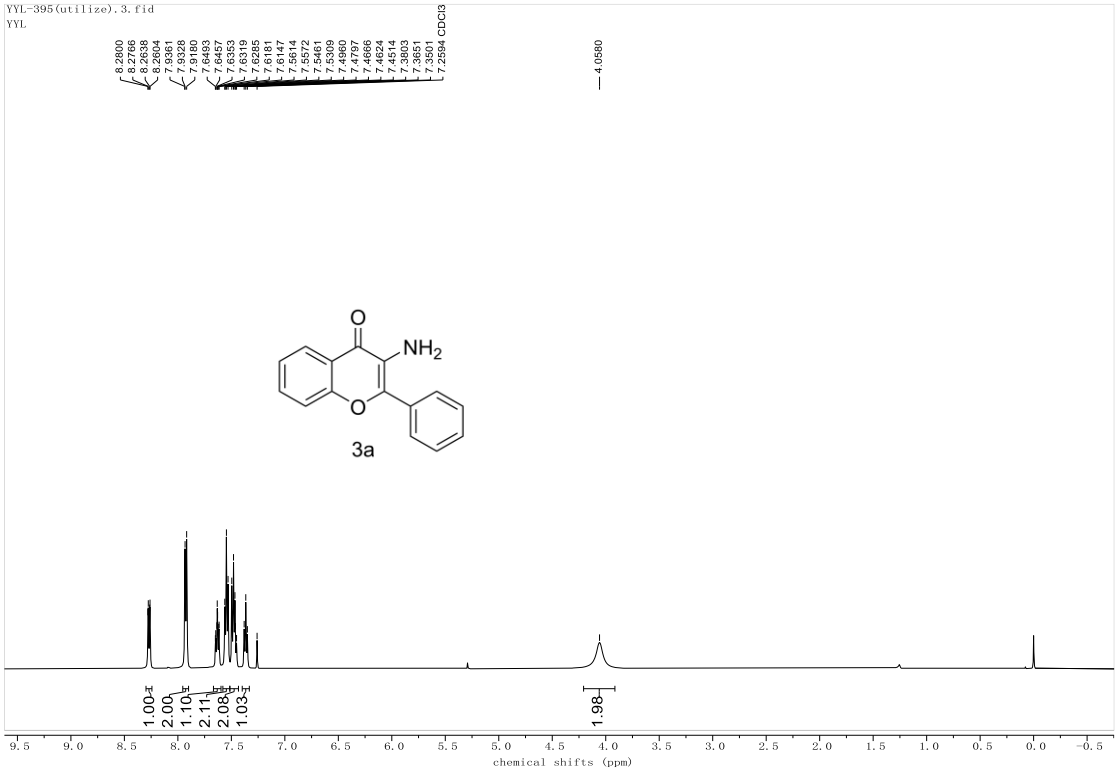
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2v**



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2v**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3a**



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3a**