Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Visible-light-induced tandem radical addition/cyclization of 2-alkenylphenols and CBr_4 for synthesis of 4-arylcoumarins

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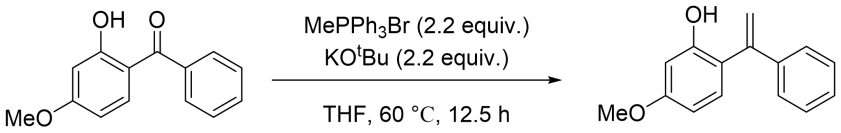
1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 MHz spectrometers. Chemical shifts were reported on the delta (δ) scale in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded at 100 MHz with complete proton decoupling. Chemical shifts are reported in ppm relative to the central line of the triplet at 77.0 ppm for $CDCl_3$. ^{19}F NMR spectra were recorded on 376 MHz with complete proton decoupling spectrophotometers. The high resolution mass spectra (HRMS) were measured on Bruker micrOTOF-II mass spectrometer by ESI. IR spectra were recorded on an IR spectrophotometer.

2. Preparation of substrates

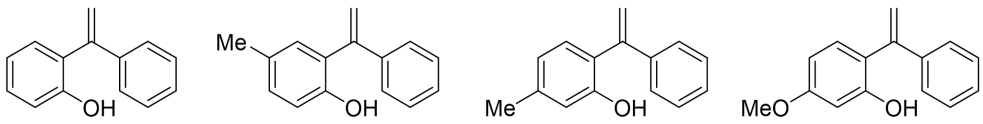
Materials: The hydroxystyrenes[1][2] were prepared according to the reported methods. Tetrabromomethane are commercially available. Anhydrous solvent (THF, DCM, MeCN, DMF and Toluene) were taken from JC-Meyer solvent purification system.

General Procedure A:



S1 **1g**

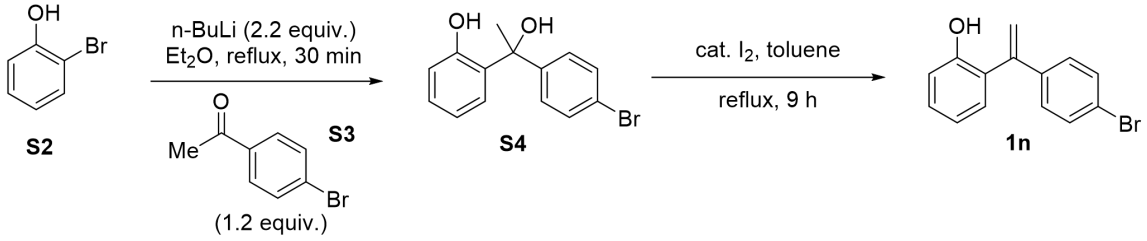
To an oven-dried three-necked round bottom flask charged with a magnetic stir-bar was added methyltriphenylphosphonium bromide (7.86 g, 22 mmol), KO^{t}Bu (2.50 g, 22 mmol) and THF (50 mL) at room temperature.The resulting yellow mixture was stirred for 1 h at room temperature. A solution of 2-hydroxy-4-methoxybenzophenone (2.28 g, 10 mmol) in THF (10 mL) was added at 0 ºC and the reaction mixture was heated at 60 ºC for 12.5 h. Sat. NH_4Cl aq. was added and the reaction mixture was extracted with ethyl acetate three times. The combined organic layer was washed with water and sat. NaCl aq. and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a crude product, which was purified by silica-gel column chromatography (hexanes : AcOEt =20:1) to afford **1g** as a yellow oil.



1a **1b** **1f** **1g**

Substrates 1a, **1b** and **1f** were prepared according to the general procedure A.

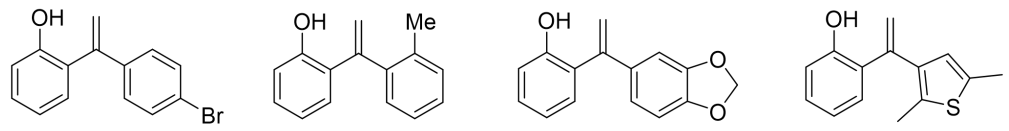
General Procedure B:



S2 **S3** **S4** **1n**

To a stirred solution of n-butyllithium (2.4 M sol. in hexane, 9.2 ml, 22 mmol) in Et_2O (50 mL) was added 2-bromophenol (1.05 ml, 15.0 mmol) at 0 ℃. The resulting solution was heated at reflux for 30 min. A solution of 4'-bromoacetophenone (2.38 g, 12 mmol) in Et_2O (10 ml) was added slowly at 0 ºC, and the mixture was stirred at room temperature for overnight. Sat. NH_4Cl aq. was added and the reaction

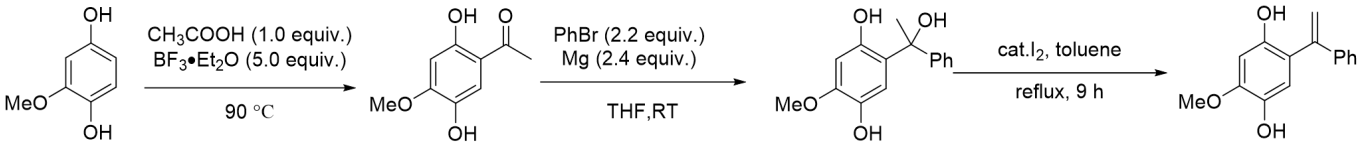
mixture was extracted with ethyl acetate three times. The combined organic layer was washed with water and sat. NaCl aq. and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a crude product, which was purified by silica-gel column chromatography (hexanes : AcOEt =20:1) to afford **S4** as a white solid. Then an oven-dried two-necked round bottom flask charged with a magnetic stir-bar was added **S4**, Iodine (7.9 mg, 0.031 mmol) and Toluene (10 mL) at room temperature, The resulting solution was heated at reflux for 9 h. The reaction mixture was cooled and washed with sat. $Na_2S_2O_3$ aq. twice and sat. NaCl aq. and dried over $MgSO_4$. After removal of solvent under reduced pressure, the residue was purified by silica-gel column chromatography (hexanes : AcOEt =10:1) to afford **1n** as a yellow oil.



1n **1p** **1s** **1t**

Substrates 1p, 1s and **1t** were prepared according to the general procedure B.

General Procedure C:

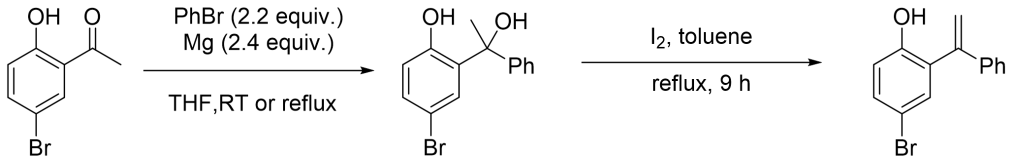


S5 **S6** **S7** **1y**

A mixture of the 2-methoxybenzene-1,4-diol (1.4 g, 10 mmol), acetic acid (0.6 mL, 10 mmol) and $BF_3.Et_2O$ (50 mmol) was stirred at 90 ℃ for 90 min. The crude compounds were purified by column chromatography on silica gel using hexanes : AcOEt (10:1) to yield **S6** as a yellow solid. Then to magnesium turning (584 mg, 24 mmol) in THF (20 ml) was added dropwise bromobenzene (2.3 mL, 22 mmol), 2-Hydroxyacetophenone (1.2 mL, 10 mmol) was added to the resulting solution at 0 ℃. The reaction mixture was warmed to room temperature and stirred overnight.Sat. NH_4Cl aq. was added and the reaction mixture was extracted with ethyl acetate three times. The combined organic layer was washed with water and sat. NaCl aq. and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a crude product, which was purified by silica-gel column chromatography (hexanes : AcOEt =20:1) to afford **S7** as a white solid. Then an oven-dried two-necked round bottom flask charged with a magnetic stir-bar was added **S7**, Iodine (7.9 mg, 0.031 mmol) and Toluene (10 mL) at room

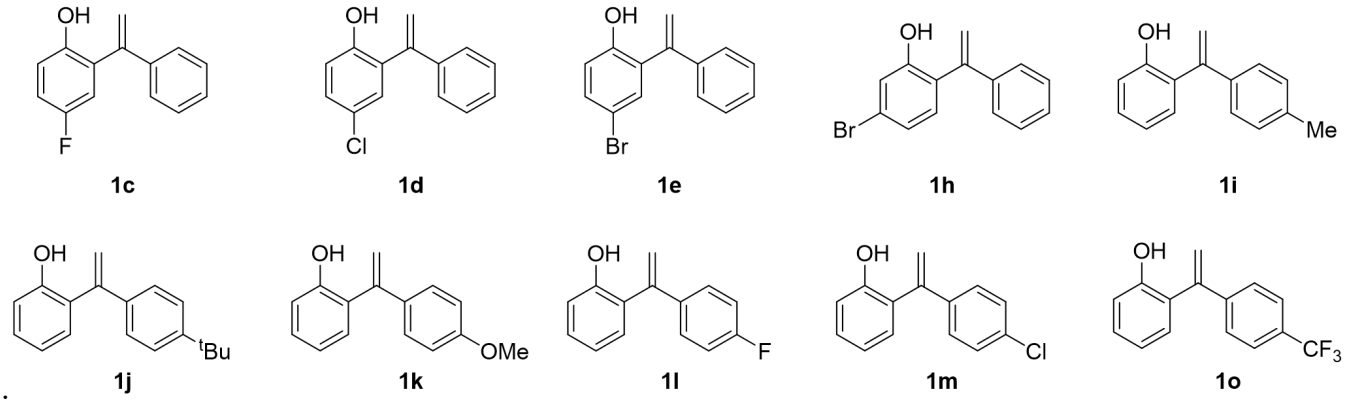
temperature, The resulting solution was heated at reflux for 9 h. The reaction mixture was cooled and washed with sat. $Na_2S_2O_3$ aq. twice and sat. NaCl aq. and dried over $MgSO_4$. After removal of solvent under reduced pressure, the residue was purified by silica-gel column chromatography (hexanes : AcOEt =10:1) to afford **1y** as a white solid.[3]

General Procedure D:



S8 **S9** **1e**

To magnesium turning (584 mg, 24 mmol) in THF (20 ml) was added dropwise bromobenzene (2.3 mL, 22 mmol), 1-(5-bromo-2-hydroxyphenyl)ethan-1-one (2.2 g, 10 mmol) was added to the resulting solution at 0℃. The reaction mixture was warmed to room temperature and stirred overnight.Sat. NH_4Cl aq. was added and the reaction mixture was extracted with ethyl acetate three times. The combined organic layer was washed with water and sat. NaCl aq. and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a crude product, which was purified by silica-gel column chromatography (hexanes : AcOEt =20:1) to afford **S9** as a white solid. Then an oven-dried two-necked round bottom flask charged with a magnetic stir-bar was added **S9**, iodine (7.9 mg, 0.031 mmol) and Toluene (10 mL) at room temperature, The resulting solution was heated at reflux for 9 h. The reaction mixture was cooled and washed with sat. $Na_2S_2O_3$ aq. twice and sat. NaCl aq. and dried over $MgSO_4$. After removal of solvent under reduced pressure, the residue was purified by silica-gel column chromatography (hexanes : AcOEt =10:1) to afford **1e** as a yellow oil.



1c **1d** **1e** **1h** **1i**

1j **1k** **1l** **1m** **1o**

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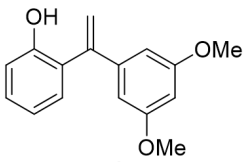
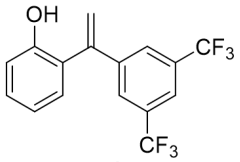
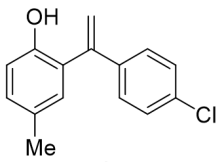


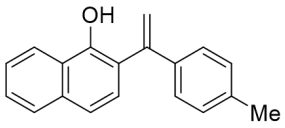
1q



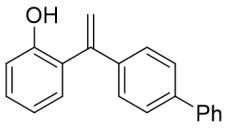
1r



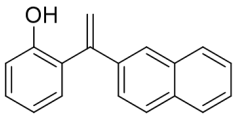
1u



1v



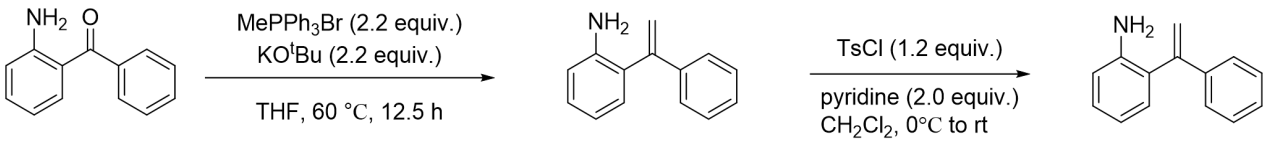
1w



1x

Substrates 1c, 1d, 1h, 1i, 1j, 1k, 1l, 1m, 1o, 1q, 1r, 1u, 1v, 1w, and 1x were prepared according to the general procedure D

General Procedure E[4]:



S10 **s11** **1z**

To an oven-dried three-necked round bottom flask charged with a magnetic stir-bar was added methyltriphenylphosphonium bromide (7.86 g, 22 mmol), KO^{t}Bu (2.50 g, 22 mmol) and THF (50 mL) at room temperature.The resulting yellow mixture was stirred for 1 h at room temperature. A solution of (2-aminophenyl)(phenyl)methanone (1.97 g, 10 mmol) in THF (10 mL) was added at 0 ºC and the reaction mixture was heated at 60 ºC for 8 h. Sat. NH_4Cl aq. was added and the reaction mixture was extracted with ethyl acetate three times. The combined organic layer was washed with water and sat. NaCl aq. and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a crude product, which was purified by silica-gel column chromatography (hexanes : AcOEt =20:1) to afford **S11** as a white solid.To a solution of 2-(1-phenylvinyl)aniline (1.36 g, 7 mmol) in CH_2Cl_2 (50 mL) were added pyridine (1.10 g, 14 mmol) and TsCl (1.43 g, 8.4 mmol) at 0 ℃. After being stirred at 25 ℃ overnight, the reaction mixture was poured into water and the product was extracted with CH_2Cl_2 (3 times), dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude mixture was purified by column chromatography on silica gel (PE/EA = 10/1) to afford the corresponding product **1z** as a white solid.

References:

[1] K. Sasano, J. Takaya., K.Iwasawa. *J. Am. Chem. Soc.*, **2013**, *135*, 10954.

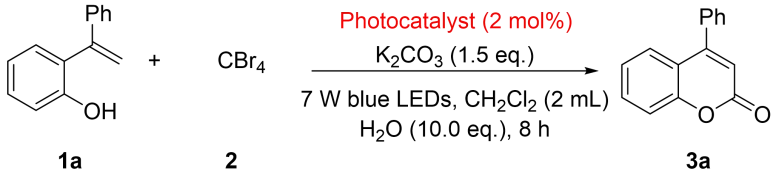
[2] D. S. Tian, A. Millán, R. H. Xu, J. B. Zhu, J. X. Huang, W. Dong, J.Claverie , W. J. Tang. *Angew. Chem. Int. Ed.,* **2021**, *60*, 6305

[3] S. Kumar, C. S. Reddy L, Y. Kumar, A. Kumar, B. K. Singh, V. Kumar, S. Malhotra, M. K. Pandey, R. Jain, R. Thimmulappa, S. K. Sharma, A. K. Prasad, S. Biswal, E. V. Eycken, A. L.DePass, S. V. Malhotra, B.Ghosh, V. S. Parmar. *Arch. Pharm. Chem. Life Sci.* **2012***, 345,* 368

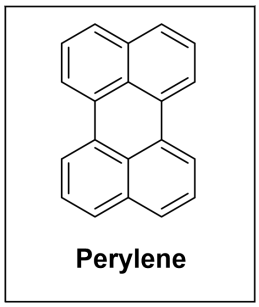
[4]X. S. Ning, X. Liang, K. F. Hu, C. Z. Yao, J. P. Qu, Y. B. Kang. *Adv. Synth. Catal.,* **2017** , 360, 1590

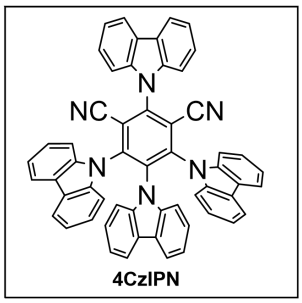
3. Optimization studies

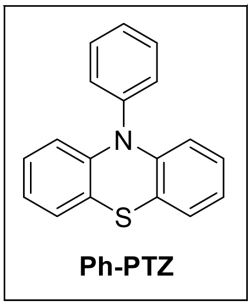
3.1 Screening of photocatalysts[a]



1a 2 3a







Entry	Photocatalyst	Yield (%)[b]
1	***fac*-Ir(ppy)$_3$**	**87**
2	[Ir(ppy)$_2$(dtbbpy)]PF$_6$	60
3	Ru(bpy)$_3$Cl$_2$·6H$_2$O	67
4	Perylene (5 mol%)	NR
5	4CzIPN	18
6	Ph-PTZ[c]	68

[a] Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol, 1.5 equiv.), photocatalyst (0.02 mmol, 2.0 mol %), H_2O (1.0 mmol, 10.0 equiv.), K_2CO_3 (0.15 mmol, 1.5 equiv.), CH_2Cl_2 (2.0 mL), rt, 8 h, irradiation with 7 W blue LEDs. [b] Yields determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal standard. [c] Under the irradiation of 2 x 3 W purple LEDs.

3.2 Screening of base[a]

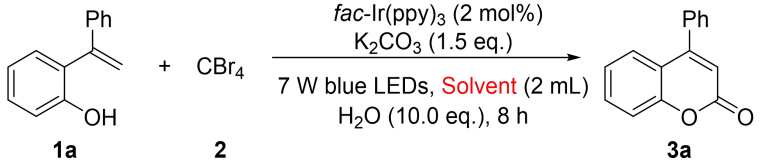
1a 2 3a

Entry	Base	Yield (%)[b]	Entry	Base	Yield (%)[b]
1	Na_2CO_3	55	8	*i*Pr$_2$NH	38
2	**K_2CO_3**	**87**	9	DBU	30
3	Cs_2CO_3	74	10	TMG	50

4	NaOH	16	11	DMAP	60
5	Na_2HPO_4	55	12	DABCO	66
6	NaOAc	76	13	NEt_3	50
7	K_3PO_4	71	14	4-Methylmorpholine	52

[a] Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.02 mmol, 2.0 mol %), H_2O (1.0 mmol, 10 equiv.) base (0.15 mmol, 1.5 equiv.), CH_2Cl_2 (2.0 mL), rt, 8 h, irradiation with 7 W blue LEDs. [b] Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard.

3.3 Screening of the solvent[a]

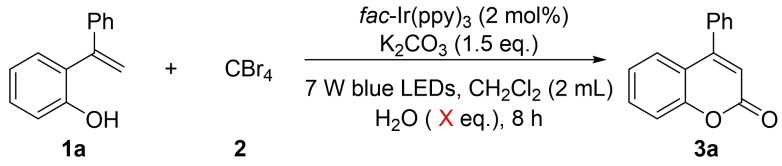


1a **2** **3a**

Entry	Solvent	Yield (%)[b]
1	**CH_2Cl_2**	**87**
2	CH_3CN	32
3	THF	82
4	Toluene	36
5	DMF	81

[a] Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.02 mmol, 2.0 mol %), H_2O (1.0 mmol, 10 equiv.) K_2CO_3 (0.15 mmol, 1.5 equiv.), solvent (2.0 mL), rt, 8 h, irradiation with 7 W blue LEDs. [b] Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard.

3.4 Screening of the ratio of H_2O[a]

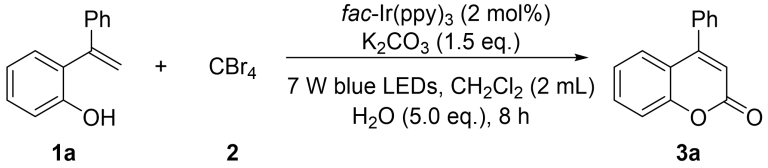


1a **2** **3a**

Entry	H_2O (X eq.)	Yield (%)[b]
1	1	50
2	2.5	75
3	**5**	**87**
4	10	86

[a] Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.02 mmol, 2.0 mol %), K_2CO_3 (0.15 mmol, 1.5 equiv.), CH_2Cl_2 (2.0 mL), rt, 8 h, irradiation with 7 W blue LEDs. [b] Yields determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal standard.

3.5 Control experiments[a]

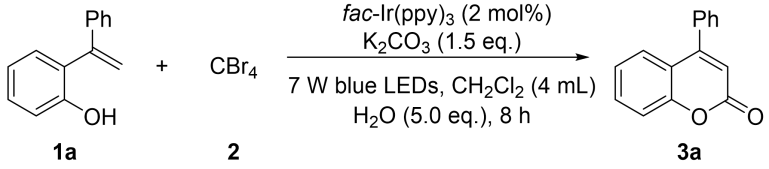


1a **2** **3a**

Entry[a]	Condition	Yield (%)[b]
1	-	**87 (80)** [c]
2	No PC	0
3	No light	0
4	No H_2O	20
5	No Base	28

[a] Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.02 mmol, 2.0 mol %), H_2O (0.5mmol, 5 equiv.) K_2CO_3 (0.15 mmol, 1.5 equiv.), CH_2Cl_2 (2.0 mL), rt, 8 h, irradiation with 7 W blue LEDs. [b] Yields determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal standard. [c] Isolated yield.

4. Representative procedure for preparation of the products 3

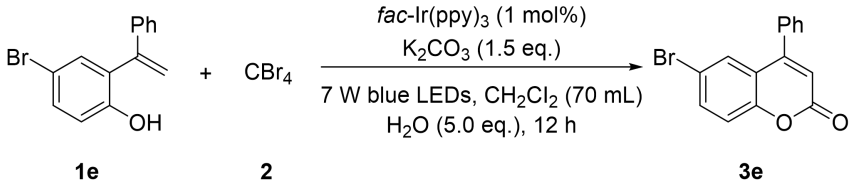


1a **2** **3a**

1a (39.3 mg, 0.2 mmol), **2** (99.5 mg, 1.5 eq.), H_2O (18 μL, 5.0 equiv.), *fac*-Ir(ppy)$_3$ (2.6 mg, 2.0 mol%), K_2CO_3 (41.5 mg, 1.5 eq.) and anhydrous CH_2Cl_2 (4.0 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stir bar. The resulting mixture was degassed by a "freeze-pump-thaw" procedure (3 times) under argon atmosphere. Then the solution was stirred at a distance of ca. 5 cm from a 7 W blue LEDs. Upon the completion of reaction as monitored by TLC, the solvent was removed by vacuum and the crude reaction mixture was purified by flash chromatography on silica gel (silica: 200–300; eluent: petroleum ether/ethyl acetate (20 : 1 – 10 : 1) to provide the pure product **3a** as a white solid.

5. Synthetic application

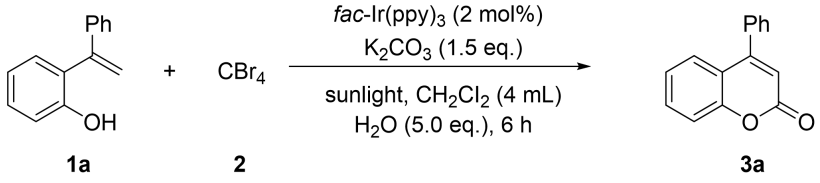
5.1 Gram-scale reaction



1e **2** **3e**

1e (2.0 g, 7.2 mmol), **2** (3.6 g, 1.5 eq.), H_2O (6.5 mL, 5.0 eq.), *fac*-Ir(ppy)$_3$ (46.8 mg, 1.0 mol%), K_2CO_3 (1.6 mg, 1.5 eq.) and anhydrous CH_2Cl_2 (70.0 mL) were added to a 100 mL Schlenk flask equipped with a magnetic stir bar. The resulting mixture was degassed by a "freeze-pump-thaw" procedure (3 times) under argon atmosphere. Then the solution was stirred at a distance of ca. 5 cm from a 7 W blue LEDs. Upon the completion of reaction as monitored by TLC, the solvent was removed by vacuum and the crude reaction mixture was purified by flash chromatography on silica gel (silica: 200–300; eluent: petroleum ether/ethyl acetate (20 : 1 – 10 : 1) to provide the pure product **3e** (5.8 mmol, 1.74 g) as a white solid in 80 % yield.

5.2 Sun-light-driven reaction

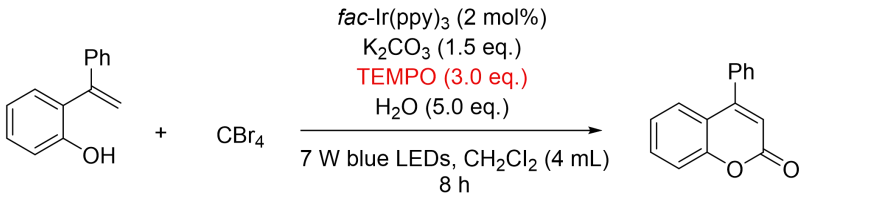


1a **2** **3a**

1a (39.3 mg, 0.2 mmol), **2** (99.5 mg, 1.5 eq.), H_2O (18 μL, 5.0 equiv.), *fac*-Ir(ppy)$_3$ (2.6 mg, 2.0 mol%), K_2CO_3 (41.5 mg, 1.5 eq.) and anhydrous CH_2Cl_2 (4.0 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stir bar. The resulting mixture was degassed by a "freeze-pump-thaw" procedure (3 times) under argon atmosphere. Then the solution was stirring under sun light for 6 h. Upon the completion of reaction as monitored by TLC, the solvent was removed by vacuum and the crude reaction mixture was purified by flash chromatography on silica gel (silica: 200–300; eluent: petroleum ether/ethyl acetate (20 : 1–10 : 1) to provide the pure product **3a** as a white solid in 72% yield.

6. Mechanistic Studies

6.1 TEMPO-quenching experiment



1a 0.20 mmol + **2** 0.30 mmol → **3a**, N.D. no TEMPO, 86% yield

Scheme S1. TEMPO-quenching experiment.

In the presence of stoichiometric radical quenchers, such as TEMPO, significant inhibition of the reactivity was observed, which supports that the process involves radical steps. (Scheme S1)

6.2 Luminescence quenching experiment

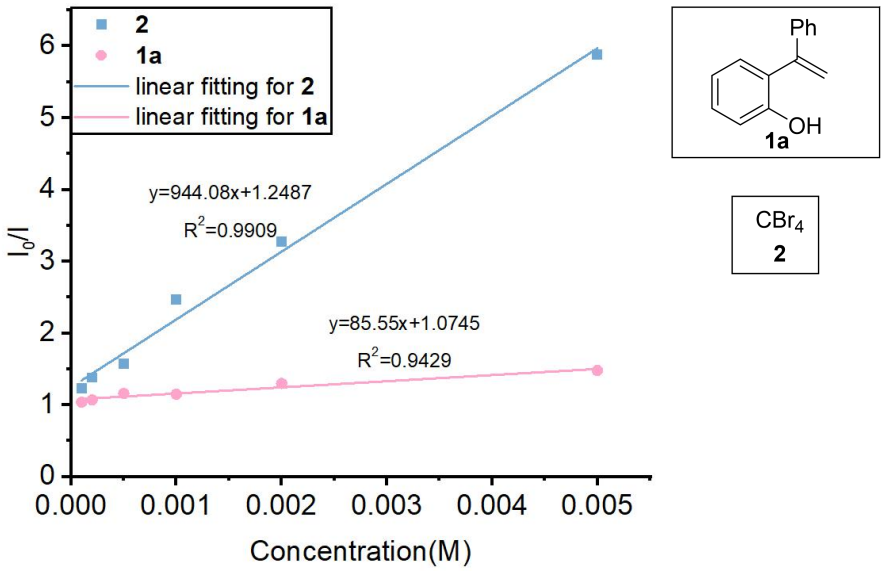
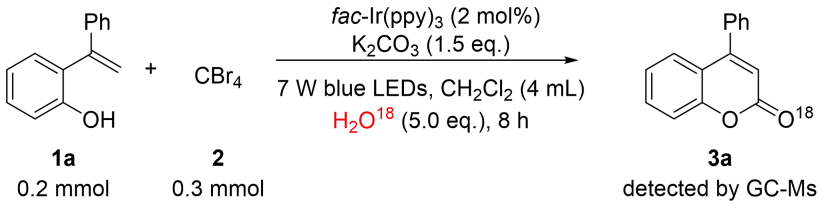


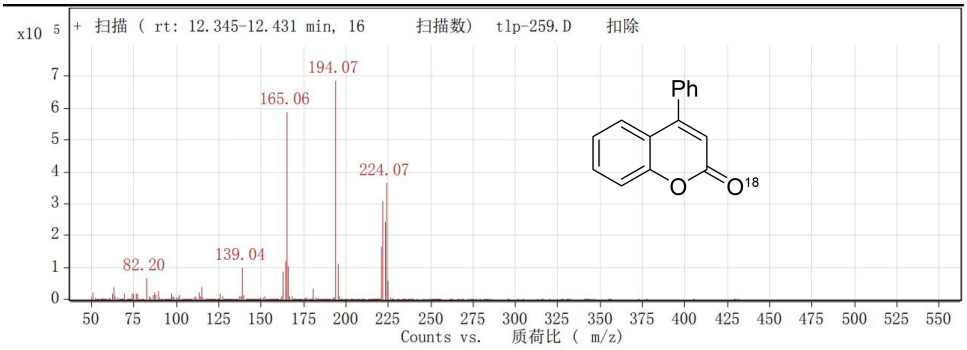
Figure S1. *fac*-Ir(ppy)$_3$ emission quenching by **1a** and **2**.

Fluorescence spectra was collected on Agilent Fluorescence Spectrophotometer G9800AS24 for all experiments. All *fac*-Ir(ppy)$_3$ solutions were excited at 350 nm and the emission intensity was collected at 510 nm. In a typical experiment, the emission spectrum of a 1×10^{-5} M solution of *fac*-Ir(ppy)$_3$ in CH_2Cl_2 was collected. The significant decrease of *fac*-Ir(ppy)$_3$ luminescence could be observed in the presence of substrate **2**. And a slightly decrease of *fac*-Ir(ppy)$_3$ luminescence was observed in the presence of substrate **1a**. (Figure S1).

6.3 ^{18}O-Labeling experiments reaction

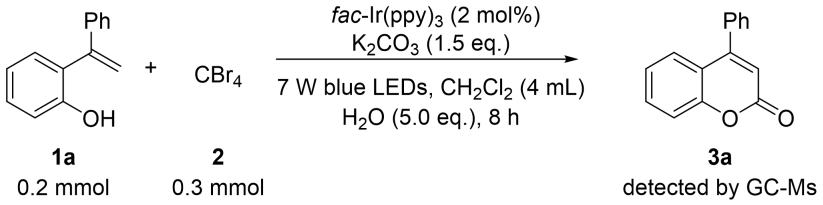


1a 0.2 mmol **2** 0.3 mmol **3a** detected by GC-Ms

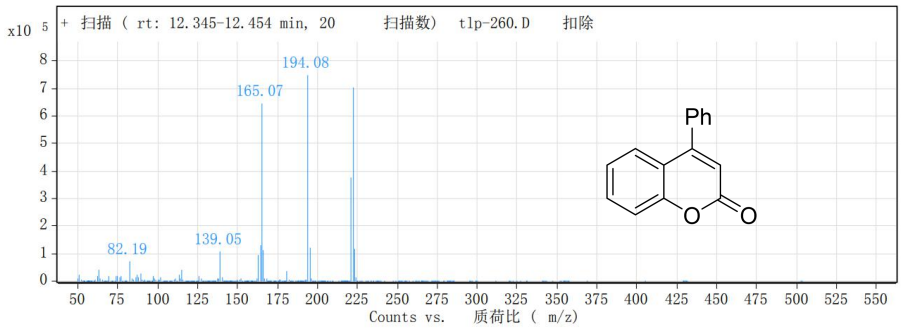


峰列表

m/z	z	丰度
139.04	1	98499.8
164.08		118181.88
165.06	1	587308.25
166.06	1	103266.48
194.07	1	685977.81
195.07	1	109465.2
221.06		164052.44
222.07		309439
223.07		241252.8
224.07	1	365106.06



1a 0.2 mmol **2** 0.3 mmol **3a** detected by GC-Ms

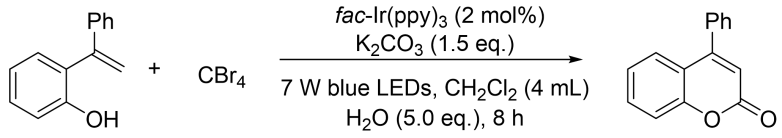


峰列表

m/z	z	丰度
139.05	1	108466.94
163.06		95953.75
164.09		129453.91
165.07	1	646069.44
166.07	1	113873.91
194.08	1	749137.5
195.08	1	119422.38
221.07		375744.13
222.08	1	702735.13
223.08	1	116902.39

When 5.0 equiv of $H_2{}^{18}O$ was added to the standard reaction system, a large portion of ^{18}O from water was successfully introduced into the product.

6.4 Determination of quantum yield



1a 0.2 mmol | **2** 0.3 mmol | **3a** 2.3% yield

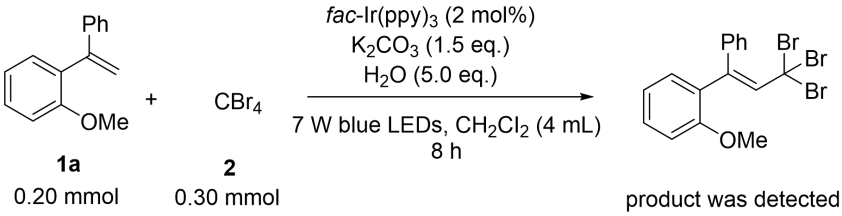
A cuvette was charged with **1a** (0.2 mmol, 1.0 eq.), **2** (0.3 mmol, 1.5 eq.), *fac*-Ir(ppy)$_3$ (2.6 mg, 2.0 mol%), K_2CO_3 (41.5 mg, 1.5 eq.) and anhydrous CH_2Cl_2 (4.0 mL). The sample was irradiated (λ =455 nm, slit width = 3.0 mm, slit height 5.0 mm with intensity of 3.572 mW•cm^{-2}) for 11700 s (3 h 15 min). After irradiation, the yield of product formed was determined by ^{1}H NMR based on a 1,3,5-trimethoxybenzene standard. The quantum yield was determined as follows.

ϕ = Mole number for product/Mole number for absorption of photons = 0.193

$$\Phi = \frac{nN_A/t}{f\,P\,\lambda/hc}$$

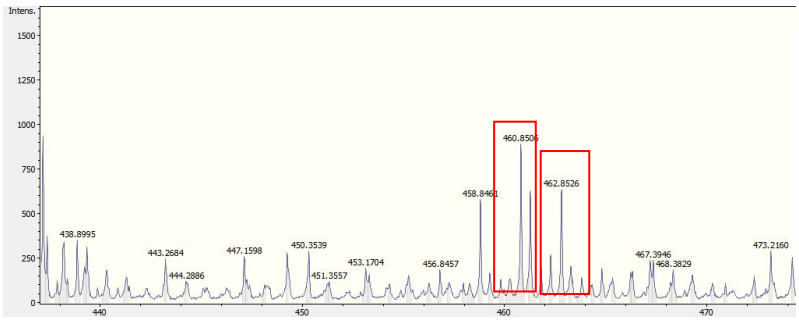
n: the mole number of the product **3a**; t: reaction time (11700 s); NA: 6.02×10^{23} /mol; f: $1\text{-}10^{-A}$ (455 nm, A= 0.23); P: P=E*S (E: illumination intensity, E= 3.572 mW/cm^2 ; S: the area that irradiated S= 0.15 cm^2); λ : wavelength ($\lambda = 4.55\times10^{-7}$ m); h: planck constant (h = 6.626×10^{-34} J*s); c: velocity of light (c = 3×10^8 m/s).

6.5 Monitoring of intermediates



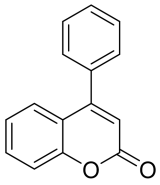
1a 0.20 mmol | **2** 0.30 mmol | product was detected by HRMS

HRMS calcd. for $[M+H]^+$: 462.8549, found: 462.8526



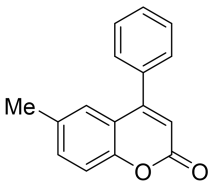
7. Spectral data of products

4-Phenyl-2*H*-chromen-2-one[4] (3a)



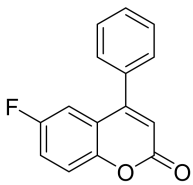
35.6 mg, white solid, yield: 80%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.58 – 7.49 (m, 5H), 7.47 – 7.45 (m, 2H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.24 (t, *J* = 8.0 Hz, 1H), 6.39 (s, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.8, 155.7, 154.2, 135.2, 131.9, 129.7, 128.9, 128.4, 127.0, 124.2, 119.0, 117.3, 115.2 . **HRMS** (ESI) for: $C_{15}H_{10}O_2$ $[M + H]^+$: calcd: 223.0754, found: 223.0751.

6-Methyl-4-phenyl-2*H*-chromen-2-one[4] (3b)



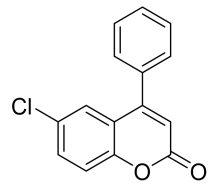
30.8 mg, white solid, yield: 64%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.55 – 7.52 (m, 3H), 7.46 – 7.43 (m, 2H), 7.36 (dd, *J* = 8.4 ,1.9 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.25 (s, 1H), 6.35 (s, 1H), 2.34 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.9, 155.6, 152.2, 135.3, 133.8, 132.9, 129.5, 128.8, 128.4 , 126.6, 118.6, 117.0, 115.1, 20.9. **HRMS** (ESI) for: $C_{16}H_{12}O_2$ $[M + H]^+$: calcd: 237.0910, found: 237.0904.

6-fluoro-4-phenyl-2H-chromen-2-one[2] (3c)



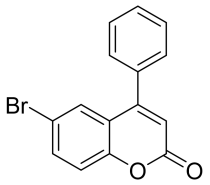
43.2 mg, white solid, yield: 90%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.56 – 7.53 (m, 3H), 7.47 – 7.43 (m, 2H), 7.41 – 7.38 (m, 1H), 7.30 – 7.25 (m, 1H),7.18 (dd, *J* = 9.1, 3.0 Hz, 1H), 6.43 (s, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.3, 158.6 (d, J = 242.2 Hz), 154.7 (d, J = 2.5 Hz), 150.2 (d, J = 1.8 Hz), 134.6, 129.9, 129.0, 128.2, 119.9 (d, J = 8.6 Hz), 119.3 (d, J = 24.2 Hz), 118.8 (d, J = 8.4 Hz), 116.0, 112.5 (d, J = 25.1 Hz). ^{19}**F NMR** (376 MHz, $CDCl_3$) δ (ppm) -116.9. **HRMS** (ESI) for: $C_{15}H_9FO_2$ $[M + H]^+$: calcd: 241.0659, found: 241.0653.

6-Chloro-4-phenyl-2*H*-chromen-2-one[2] (3d)



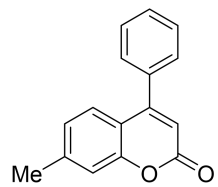
42.5 mg, white solid, yield: 83%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.58 – 7.55 (m, 3H), 7.51 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.46 – 7.43 (m, 3H), 7.36 (d, *J* = 8.8 Hz, 1H), 6.42 (s, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.0 , 154.6, 152.5, 134.4, 131.8, 130.0, 129.6, 129.1, 128.3, 126.3, 120.1, 118.7, 116.1 . **HRMS** (ESI) for: $C_{15}H_9ClO_2$ $[M + H]^+$: calcd: 257.0363, found: 257.0361.

6-bromo-4-phenyl-2H-chromen-2-one[2] (3e)



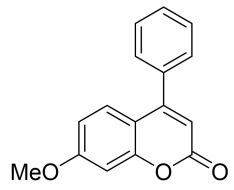
52.4 mg, white solid, yield: 87%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.65 – 7.62(m, 1H), 7.60 – 7.55 (m, 4H), 7.45 – 7.42(m, 2H), 7.31 – 7.27, (m, 1H), 6.40 (s, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 159.9, 154.4, 153.0, 134.7, 134.5, 130.00, 129.3, 129.1, 128.3, 120.6, 119.0, 117.00, 116.1. **HRMS** (ESI) for: $C_{15}H_9BrO_2$ $[M + H]^+$: calcd: 300.9858, found: 300.9859.

7-Methyl-4-phenyl-2*H*-chromen-2-one[2] (3f)



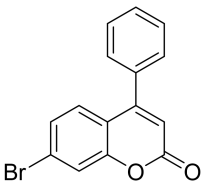
31.8 mg, white solid, yield: 66%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.53 – 7.51 (m, 3H), 7.46 – 7.43 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.21 (s, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.31 (s, 1H), 2.46 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 161.0 , 155.6 , 154.2 , 143.1 , 135.3, 129.6, 128.8, 128.4, 126.6, 125.3 , 117.4 , 116.5 , 113.9 , 21,6 . **HRMS** (ESI) for: $C_{16}H_{12}O_2$ $[M + H]^+$: calcd: 237.0910, found: 237.0902.

7-Methoxy-4-phenyl-2*H*-chromen-2-one[4] (3g)



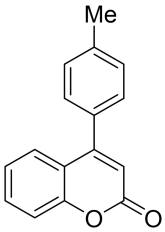
29.1 mg, white solid, yield: 58%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.53 – 7.50 (m, 3H), 7.46 – 7.43 (m, 2H), 7.39 (d, *J* = 8.9 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.80 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.22 (s, 1H), 3.89 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 162.7, 161.3, 155.9, 155.8, 135.5, 129.6, 128.8, 128.4, 128.0, 112.3, 111.8, 101.0, 55.8 . **HRMS** (ESI) for: $C_{16}H_{12}O_3$ $[M + H]^+$: calcd: 253.0859, found: 253.0855.

7-bromo-4-phenyl-2H-chromen-2-one[2] (3h)



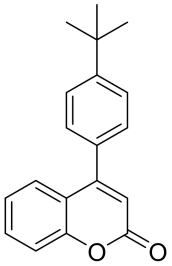
45.1 mg, white solid, yield: 75%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.58 (s, 1H), 7.55 – 7.52(m, 3H), 7.45 – 7.42 (m, 2H), 7.36 (S, 2H), 6.38 (s, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 159.9, 155.1, 154.4, 134.7, 129.9, 129.0, 128.3, 128.0, 127.5, 125.9, 120.5, 118.0, 115.2. **HRMS** (ESI) for: $C_{15}H_9BrO_2$ $[M + H]^+$: calcd: 300.9858, found: 300.9858.

4-(*p*-Tolyl)-2*H*-chromen-2-one[5] (3i)



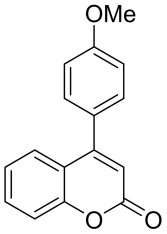
42.9 mg, white solid, yield: 91%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.57 – 7.52 (m, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.32 (m, 4H), 7.23 (td, *J* = 7.6, 2.5 Hz, 1H), 6.37 (s, 1H), 2.46 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.9, 155.7, 154.2, 139.9, 132.3, 131.8, 129.5, 128.4, 127.0, 124.1, 119.0, 117.3, 114.9, 21.3 . **HRMS** (ESI) for: $C_{16}H_{12}O_2$ $[M + H]^+$: calcd: 237.0910, found: 237.0904.

4-(4-(tert-butyl)phenyl)-2H-chromen-2-one[2] (3j)



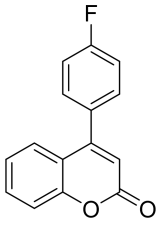
46.7 mg, white solid, yield: 84%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.59 – 7.53 (m, 4H), 7.40 – 7.42 (m, 3H), 7.26 – 7.22(m, 1H), 6.38 (s, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.9 , 155.7 , 154.2 , 153.0 , 132.2 , 131.8 , 128.2 , 127.1 , 125.8 , 124.1 , 119.0 , 117.3, 114.9, 34.8, 31.2 . **HRMS** (ESI) for: $C_{19}H_{18}O_2$ $[M + H]^+$: calcd: 279.1379, found: 279.1375.

4-(4-Methoxyphenyl)-2*H*-chromen-2-one[4] (3k)



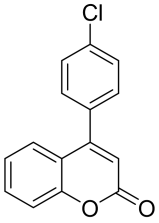
40.9 mg, white solid, yield: 81%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.57 – 7.53 (m, 2H), 7.43 – 7.40 (m, 3H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 8.5 Hz ,2H), 6.36 (s, 1H), 3.90 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.9, 160.8, 155.3, 154.2, 131.8, 129.9, 127.4, 127.0, 124.1, 119.1, 117.3, 114.6, 114.3, 55.4 . **HRMS** (ESI) for: $C_{16}H_{12}O_3$ $[M + H]^+$: calcd: 253.0859, found: 253.0856.

4-(4-fluorophenyl)-2H-chromen-2-one[2] (3l)



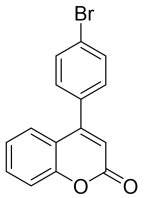
45.6 mg, white solid, yield: 95%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.60 – 7.55 (m, 3H), 7.48 – 7.44 (m, 4H), 7.28 – 7.22 (m, 3H), 6.37 (s, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 163.5 (d, *J* = 248.6 Hz) , 160.6, 154.6 , 154.1, 132.1, 131.1 (d, *J* = 3.2 Hz), 130.4 (d, *J* = 8.4 Hz), 126.7 , 124.3 , 118.8 , 117.4 , 116.1(d, *J* = 21.7 Hz) , 115.3 . ^{19}**F NMR** (376 MHz, $CDCl_3$) δ (ppm) -110.8 .**HRMS** (ESI) for: $C_{15}H_9F_1O_2$ $[M + H]^+$: calcd: 241.0659, found: 241.0651.

4-(4-chlorophenyl)-2H-chromen-2-one[2] (3m)



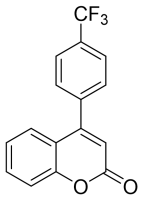
42.1 mg, white solid, yield: 82%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.60 – 7.56 (m, 1H), 7.53 – 7.51 (m, 2H), 7.46 – 7.40(m, 4H), 7.24 – 7.29(m, 1H), 6.37 (s, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.5 , 154.4 , 154.1 , 135.9 , 133.5 , 132.1 , 129.8 , 129.1 , 126.6 , 124.3 , 118.6 , 117.4, 115.3 . **HRMS** (ESI) for: $C_{15}H_9ClO_2$ $[M + H]^+$: calcd: 257.0363, found: 257.0362.

4-(4-Bromophenyl)-2*H*-chromen-2-one[8] (3n)



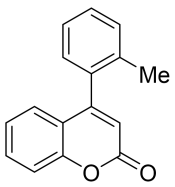
57.3 mg, pale yellow solid, yield: 95%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.68 (dd, *J* = 8.5, 2.3 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.35 – 7.33 (m, 2H), 7.27 – 7.23 (m, 1H), 6.36 (s, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.4 , 154.4 , 154.1 , 134.0 , 132.2 , 132.1 , 130.0 , 126.6 , 124.3 , 124.1 , 118.5 , 117.4 , 115.3 . **HRMS** (ESI) for: $C_{15}H_9BrO_2$ $[M + H]^+$: calcd: 300.9859, found: 300.9859.

4-(4-Trifluoromethylphenyl)-2*H*-chromen-2-one[1] (3o)



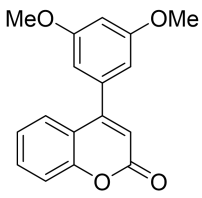
45.9 mg, white solid, yield: 79%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.82 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 3H), 7.42 (dd, *J* = 16.8, 8.1 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 6.40 (s, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.2 , 154.1 , 138.7 , 132.3 , 131.8 (q, *J* = 34 Hz), 128.9 , 126.5 , 125.9 (q, *J* = 3.9 Hz), 124.4 , 123.7 (q, *J* = 273 Hz), 118.4 , 117.5 , 115.8 . ^{19}**F NMR** (376 MHz, $CDCl_3$) δ (ppm) -62.80 . **HRMS** (ESI) for: $C_{16}H_9F_3O_2$ $[M + H]^+$: calcd: 291.0627, found: 291.0625.

4-(o-tolyl)-2H-chromen-2-one[6] (3p)



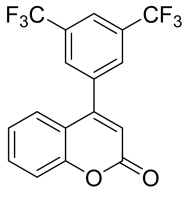
37.8 mg, pale red oil, yield: 80%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.56-7.52 (m, 1H), 7.43-7.39 (m, 2H), 7.35-7.30 (m, 2H), 7.18 (t, J = 7.2 Hz, 2H), 7.26-7.06 (m, 1H), 6.33 (s, 1H), 2.16 (s, 3H) . ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.8, 156.1, 153.8, 135.3, 134.7, 131.9, 130.5, 129.2, 128.4, 126.9, 126.1, 124.3, 119.4, 117.1, 115.7, 19.7. **HRMS** (ESI) for: $C_{16}H_{12}O_2$ $[M + H]^+$: calcd: 237.0910, found: 237.0903.

4-(3,5-dimethoxyphenyl)-2H-chromen-2-one (3q)



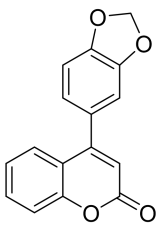
39.6 mg, white solid, yield: 70%, mp 106-109 °C. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.58-7.53 (m, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.26-7.22 (m, 1H), 6.60-6.57 (m, 3H), 6.40 (s, 1H), 3.84 (s, 6H) . ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 161.0, 160.8, 155.6, 154.1, 137.0, 131.9, 127.0, 124.2, 118.9, 117.3, 115.0, 106.6, 101.3, 55.5. **IR** (in KBr): 1730, 1591, 1453, 1379, 1205, 1157, 1062 cm^{-1}. **HRMS** (ESI) for: $C_{17}H_{14}O_4$ $[M + H]^+$: calcd: 283.0964, found:283.0958.

4-(3,5-bis(trifluoromethyl)phenyl)-2H-chromen-2-one (3r)



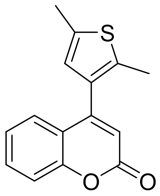
58.1 mg, white solid, yield: 81%, mp 96-99 °C. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.07 (s, 1H), 7.93 (s, 2H), 7.65-7.61 (m, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.32-7.28 (m, 2H), 6.44 (s, 1H) . ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 159.7, 154.2, 152.4, 137.2, 132.8, 132.6 (q, J = 33.9 Hz), 128.6, 128.6, 126.0, 124.8, 123.6 (hept, J = 4.0 Hz), 122.8 (q, J = 271.4 Hz), 118.0, 117.8, 116.6. ^{19}**F NMR** (376 MHz, $CDCl_3$) δ (ppm) -62.8 . **IR** (in KBr): 3632, 3526, 3320, 1730, 1563, 1350, 1239 cm^{-1}. **HRMS** (ESI) for: $C_{17}H_8F_6O_2$ $[M + H]^+$: calcd: 369.0501, found: 369.0496.

4-(benzo[d][1,3]dioxol-5-yl)-2H-chromen-2-one[7] (3s)



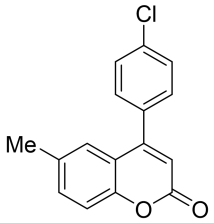
30.5 g, white solid, yield: 56%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.59-7.53 (m, 2H), 7.41 (d, J = 8.2 Hz, 1H),7.24 (d, J = 7.4 Hz, 1H), 6.96 (s, 2H), 6.94 (d, J = 1.1 Hz, 1H), 6.35 (s, 1H), 6.08 (s, 2H) . ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.8, 155.2, 154.1, 148.9, 148.0, 131.9, 128.8, 126.9, 124.1, 122.6, 118.9 , 117.3 , 114.8, 108.8, 108.8, 101.6. **HRMS** (ESI) for: $C_{16}H_{10}O_4$ $[M + H]^+$: calcd: 267.0651, found: 267.0647.

4-(2,5-dimethylthiophen-3-yl)-2H-chromen-2-one[1] (3t)



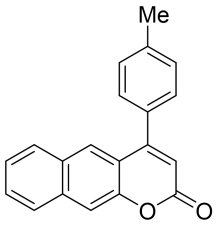
29.3 mg, yellow oil, yield: 57%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm)7.54 (t, J = 7.7 Hz, 1H), 7.41 (dd, J = 142.8 Hz, 2H), 7.25-7.22 (m, 1H), 6.62 (s, 1H), 6.29 (s, 1H), 2.48 (s, 3H), 2.33 (s, 1H) . ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.9, 154.0, 151.1, 137.3, 136.0, 131.8, 131.4, 127.1, 126.2, 124.1, 119.4 , 117.1 , 115.7, 15.1, 13.9. **HRMS** (ESI) for: $C_{15}H_{12}O_2S$ $[M + H]^+$: calcd: 257.0630, found: 257.0629.

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



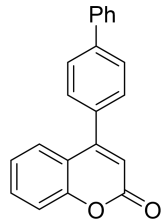
49.3 mg, white solid, yield: 91%, mp 174-177 °C. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.54-7.51 (m, 2H), 7.41-7.36(m, 3H),7.31 (d, J = 8.4 Hz, 1H), 7.18 (s, 1H), 6.33 (s, 1H), 2.35 (s, 3H) . ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.8, 154.4, 152.3, 135.9, 134.1, 133.7, 133.2, 129.8, 129.2, 126.4, 118.4, 117.2, 115.4, 21.0,. **IR** (in KBr): 3321, 3195, 1728, 1571, 1399, 1181, 821 cm^{-1}. **HRMS** (ESI) for: $C_{16}H_{11}ClO_2$ $[M + H]^+$: calcd: 271.0520, found: 271.0520.

4-(p-tolyl)-2H-benzo[g]chromen-2-one (3v)



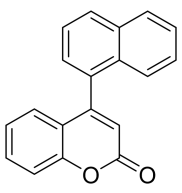
30.3 mg, yellow oil, yield: 53%, mp 136-139 °C. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.64-8.62 (m, 1H), 7.87-7.85 (m, 1H), 7.67-7.64 (m, 2H),7.62 (d, J = 8.9 Hz, 1H), 7.52 (d, J = 8.7 Hz, 1H), 7.38 (q, J = 7.8 Hz, 4H), 6.46 (s, 1H), 2.47 (s, 3H) . ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.9, 156.7, 151.4, 139.8, 134.7, 132.6, 129.5, 128.8, 128.4, 127.6, 127.1, 123.8, 123.3, 122.7, 122.4, 114.3, 114.2. 21.4. **IR** (in KBr): 1730, 1467, 1369, 1092, 930, 820, 754 cm^{-1}. **HRMS** (ESI) for: $C_{20}H_{14}O_2$ $[M + H]^+$: calcd: 287.1066, found: 287.1061.

4-([1,1'-biphenyl]-4-yl)-2H-chromen-2-one[2] (3w)



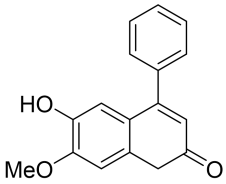
31.1 mg, white solid, yield: 52%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.77-7.75 (m, 2H), 7.68-7.65 (m, 2H), 7.60-7.48 (m, 6H), 7.44-7.40 (m, 2H), 7.26 (t, J = 6.4 Hz, 1H), 6.44 (s, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.8, 155.3, 154.2, 142.7, 140.0, 134.0, 131.9, 129.0, 127.9, 127.5, 127.1, 127.0, 124.2, 118.9, 117.4, 115.1. **HRMS** (ESI) for: $C_{21}H_{14}O_2$ $[M + H]^+$: calcd: 299.1066, found: 299.1061.

4-(naphthalen-1-yl)-2H-chromen-2-one[2] (3x)



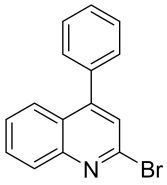
28.3 mg, white solid, yield: 52%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm)8.00 (d, J = 8.3 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.62-7.51 (m, 4H), 7.46-7.41 (m, 3H), 7.08 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 7.9 Hz, 1H), 6.51 (s, 1H) . ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 160.7, 155.2, 153.7, 133.4, 132.7, 132.0, 130.8, 129.7, 128.5, 127.4, 126.9 , 126.5 , 126.5, 125.3, 125.3, 124.2, 120.0, 117.1, 116.8. **HRMS** (ESI) for: $C_{19}H_{12}O_2$ $[M + H]^+$: calcd: 273.0910, found: 273.0905.

6-hydroxy-7-methyl-4-phenyl-2H-chromen-2-one[3] (3y)



37.3 mg, white solid, yield: 74%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.52-7.50 (m, 3H), 7.44-7.42(m, 2H), 7.00 (s, 1H), 6.91 (s, 1H), 6.25 (s, 1H), 5.61 (s, 1H), 4.00 (s, 3H) . ^{13}**C NMR** (101 MHz, $CDCl_3$) δ (ppm) 161.5, 155.8, 150.0, 149.3, 142.4, 135.6, 129.5, 128.8, 128.3, 112.5, 112.3, 110.5, 99.6, 56.4,. **HRMS** (ESI) for: $C_{16}H_{12}O_4$ $[M + H]^+$: calcd: 269.0808, found: 269.0804.

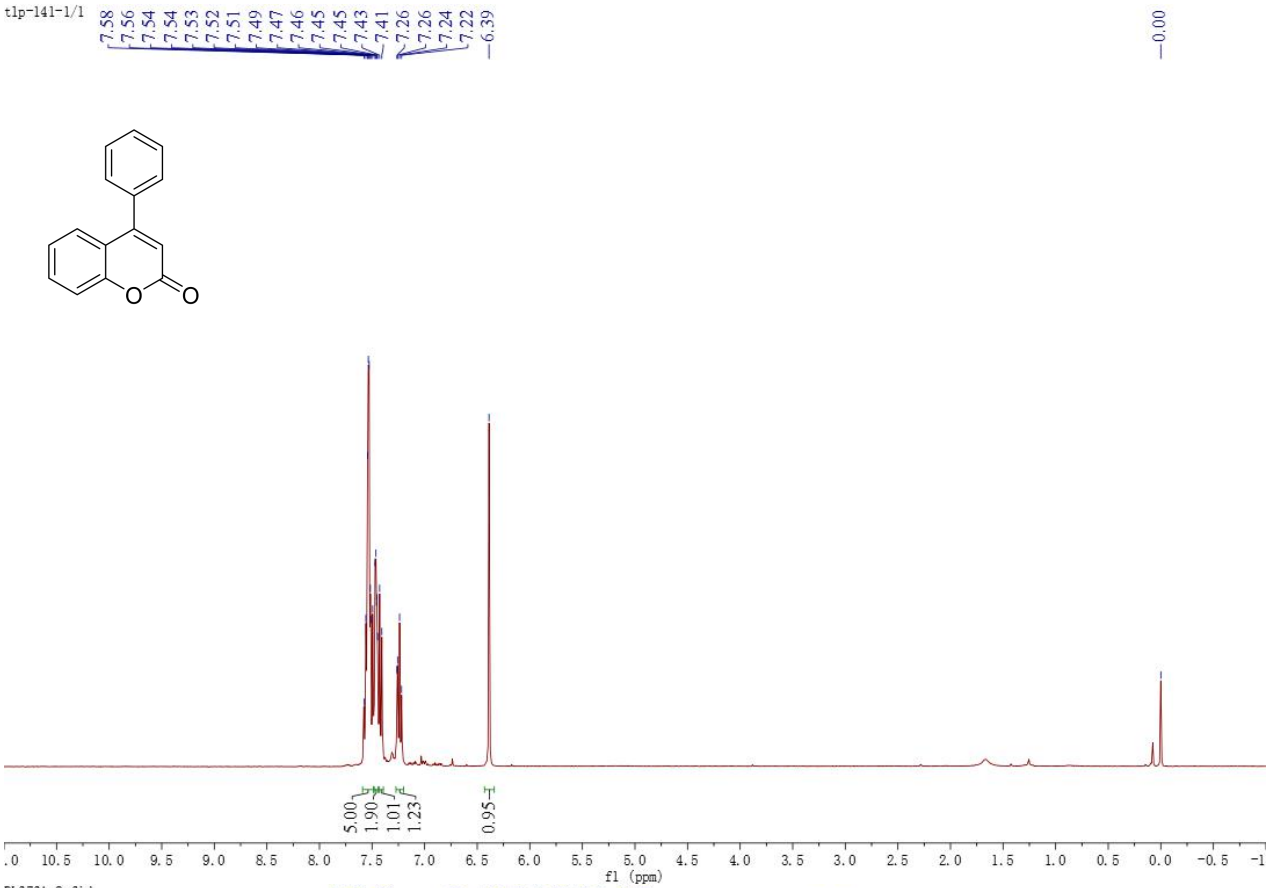
2-bromo-4-phenylquinoline[9] (3z)

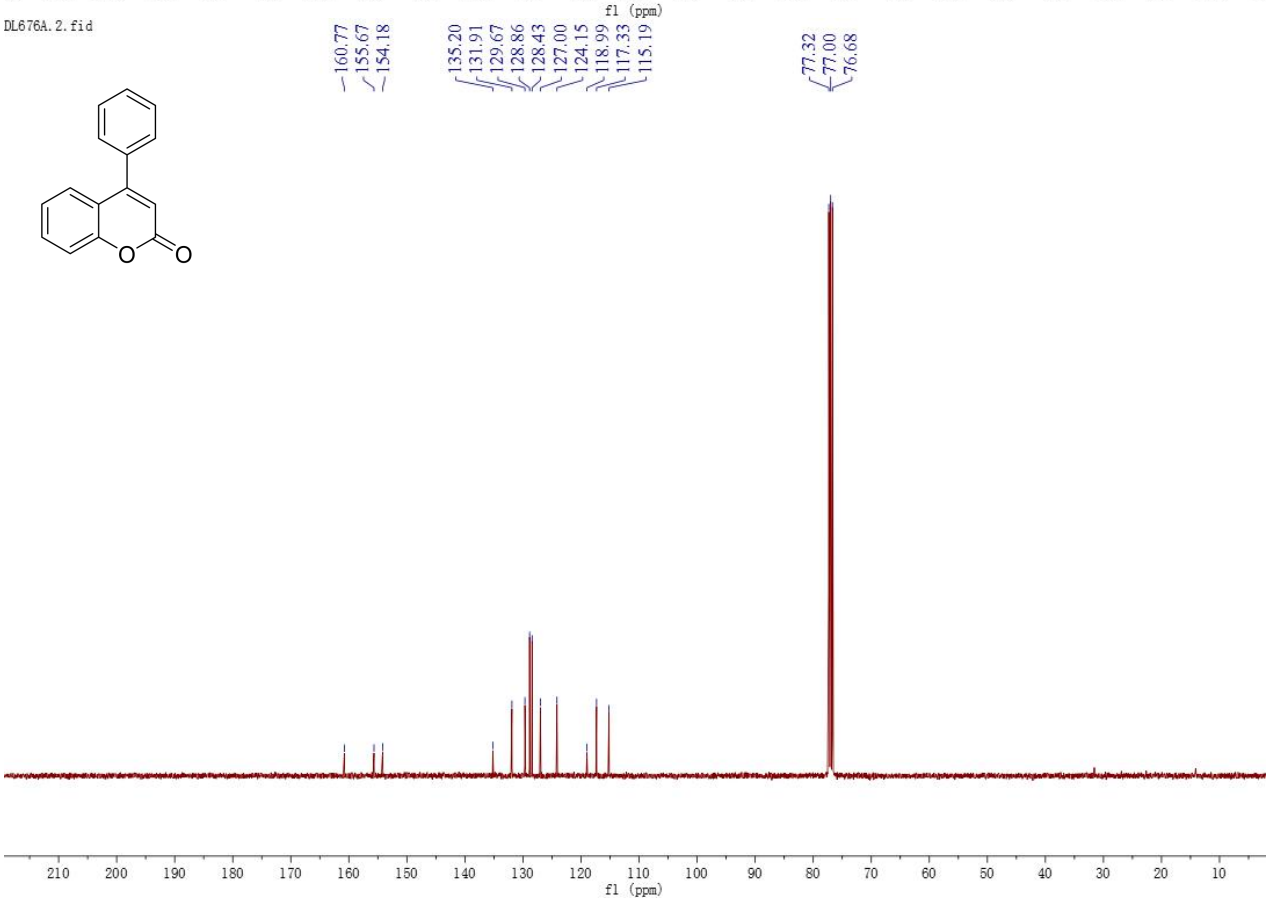


23.6 mg, white solid, yield: 42%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.11 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.76-7.72 (m, 1H), 7.54-7.48 (m,7H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 151.1, 149.0, 141.6, 136.6, 130.4, 129.4, 129.1, 128.9, 128.7, 127.1, 126.1, 125.5. **HRMS** (ESI) for: $C_{15}H_{10}BrN$ $[M + H]^+$: calcd: 284.0069, found: 284.0074.

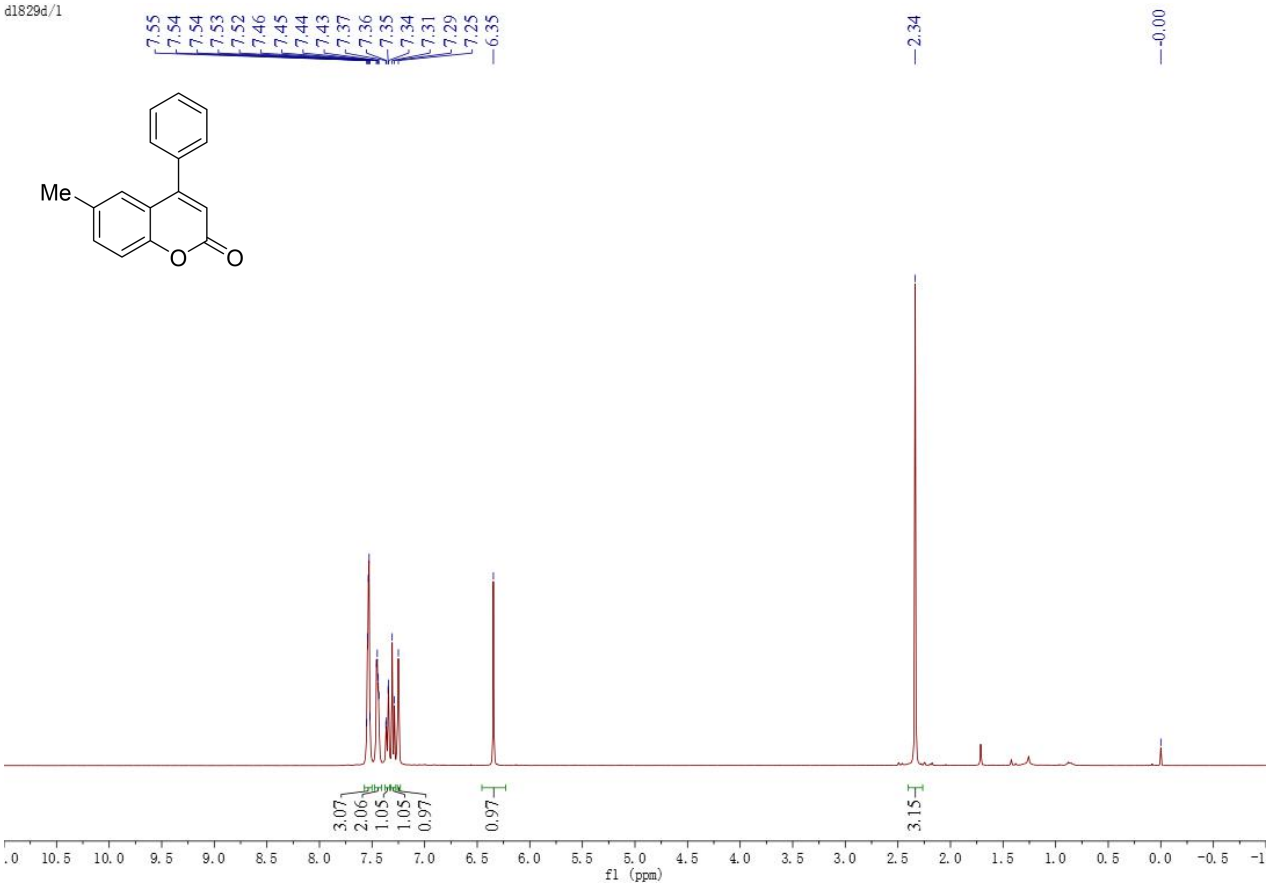
8. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra

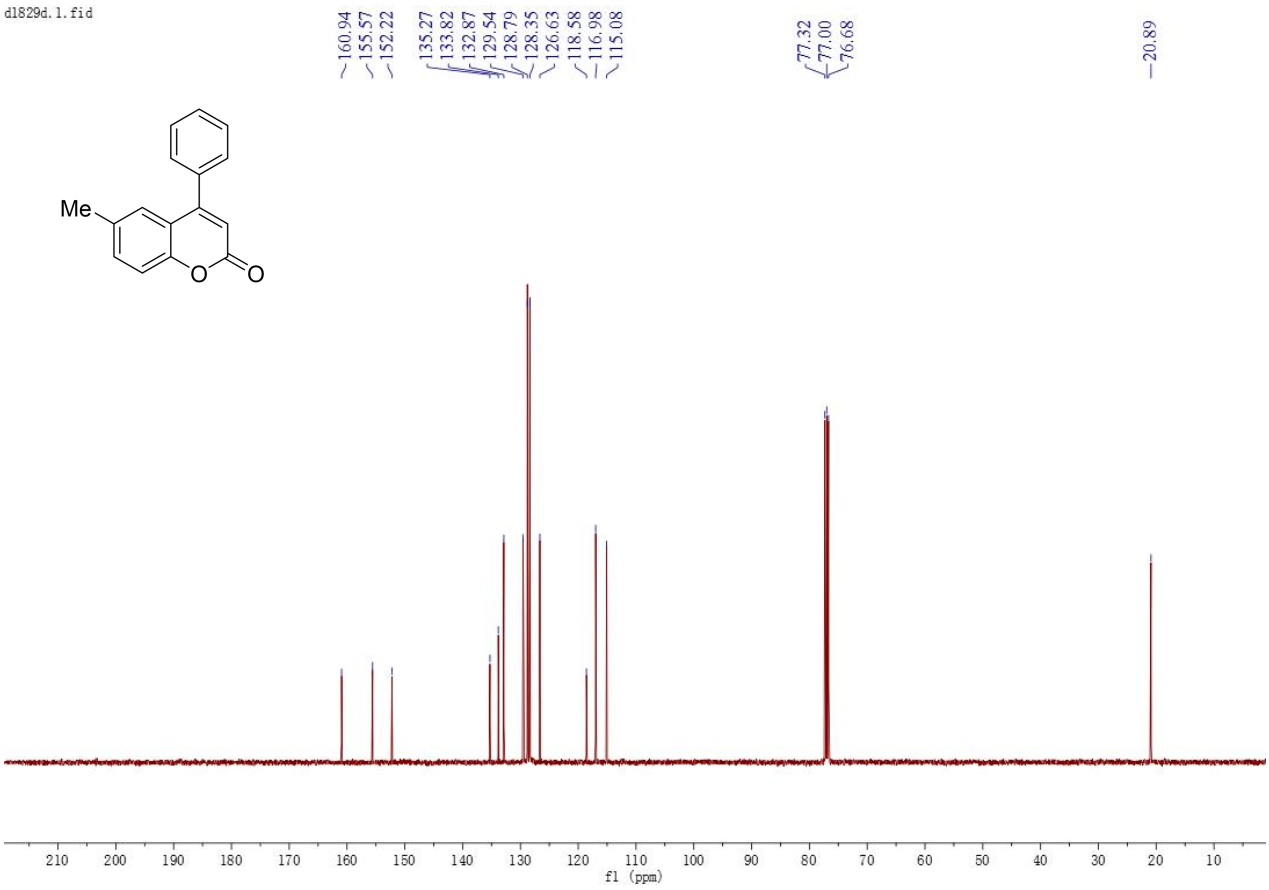
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3a



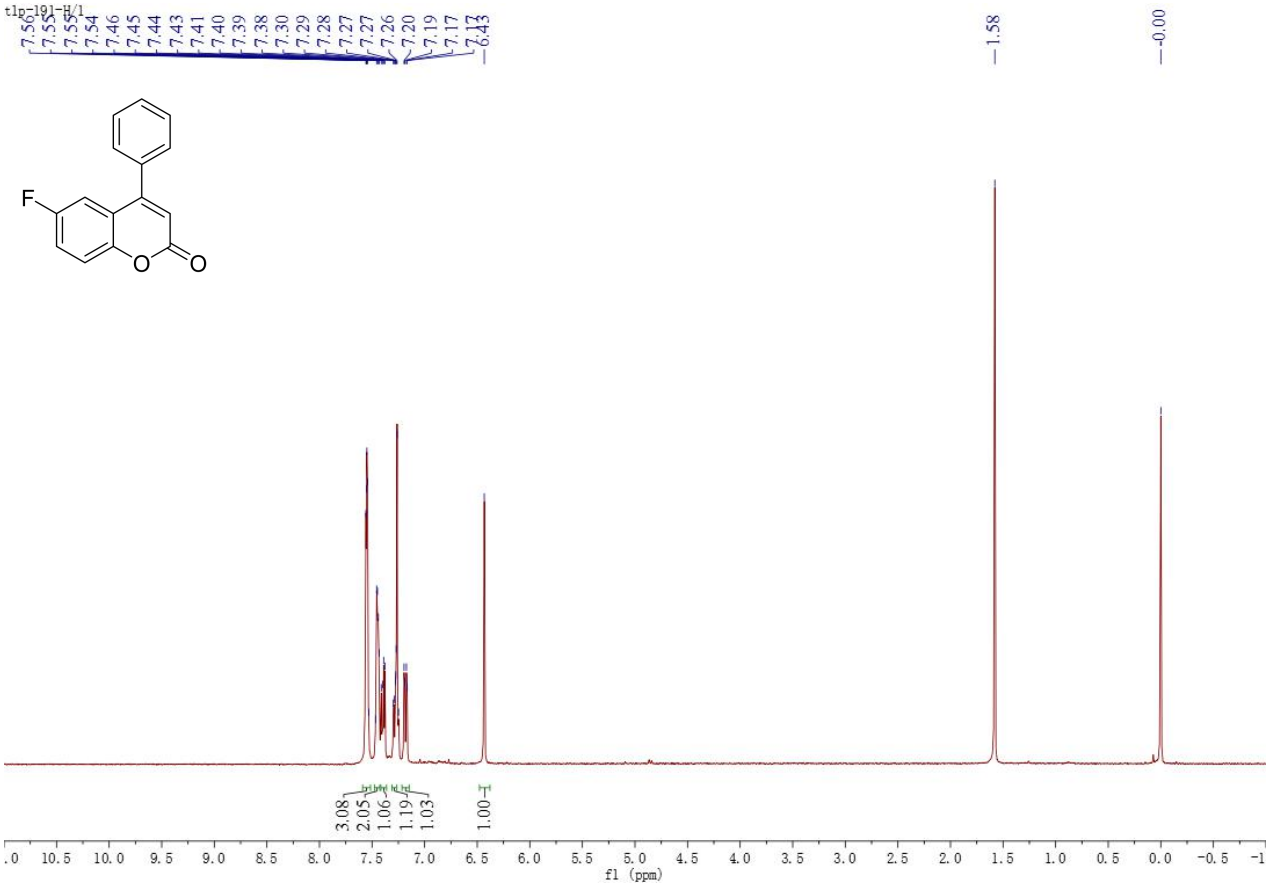


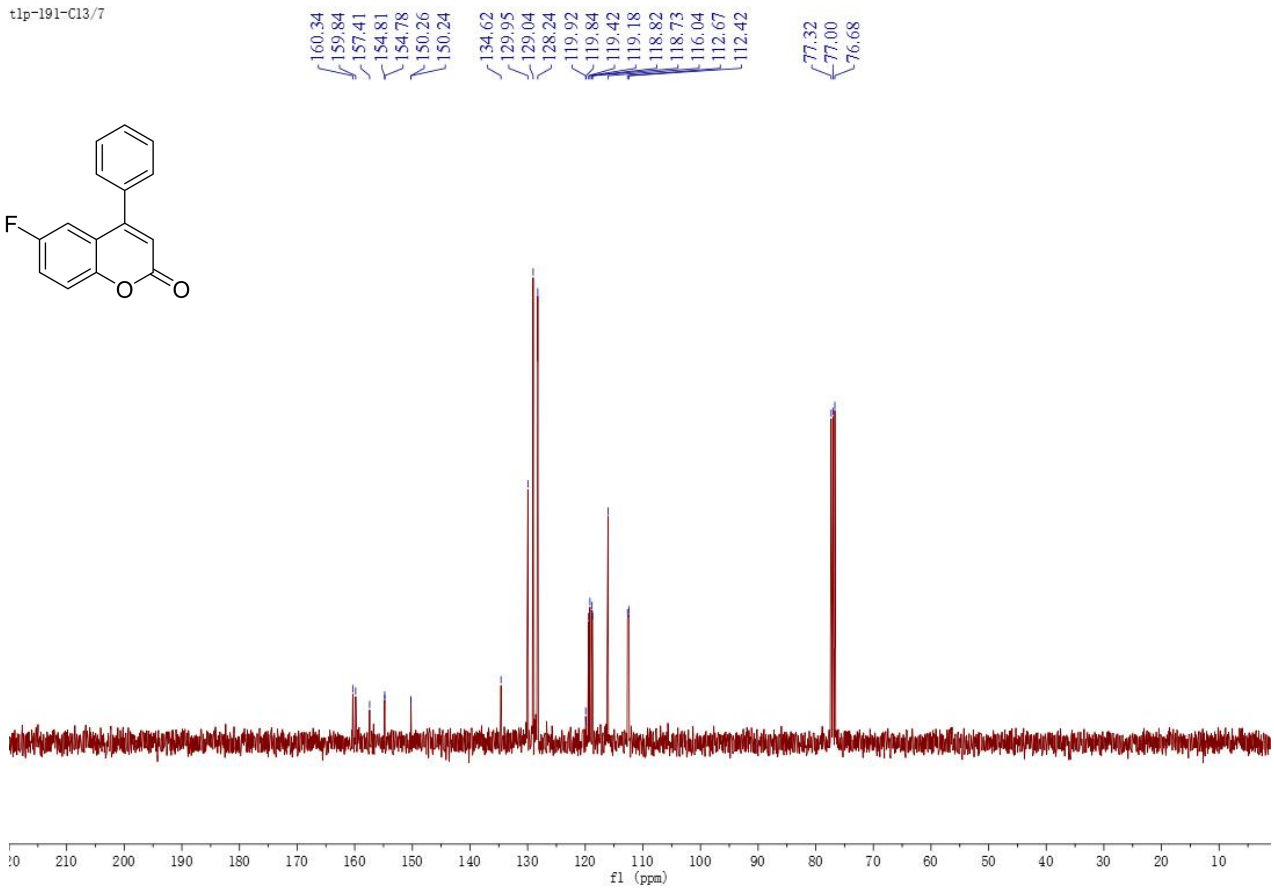
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3b

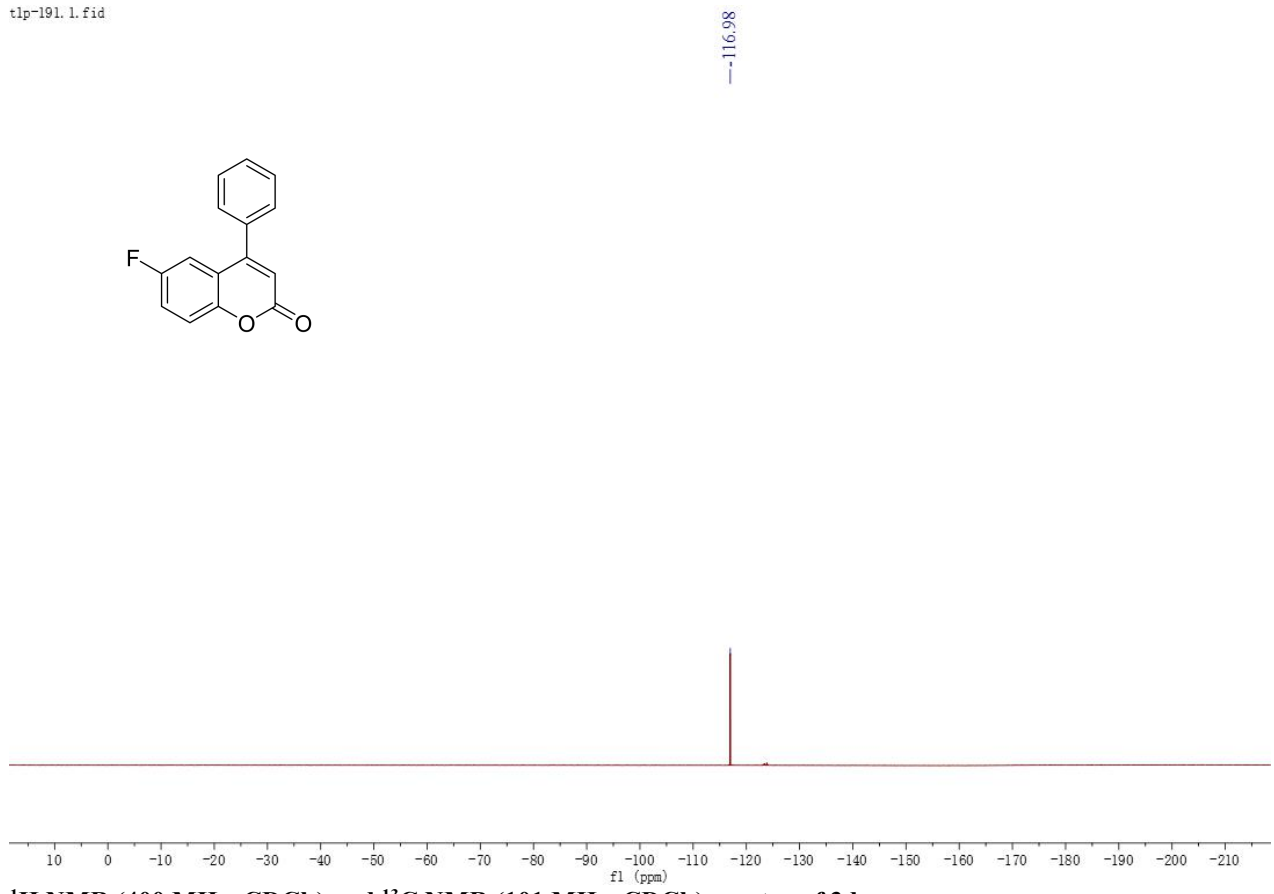




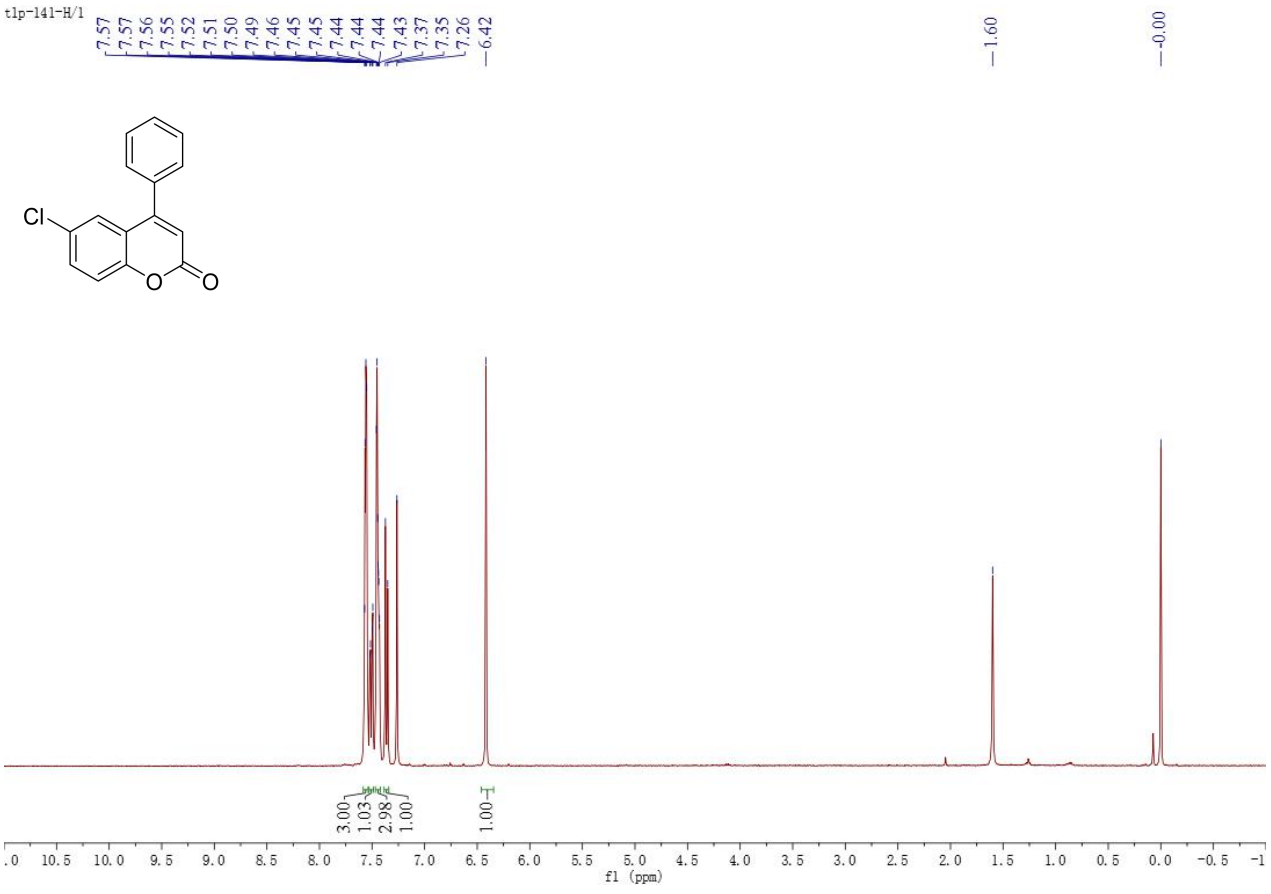
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of 3c

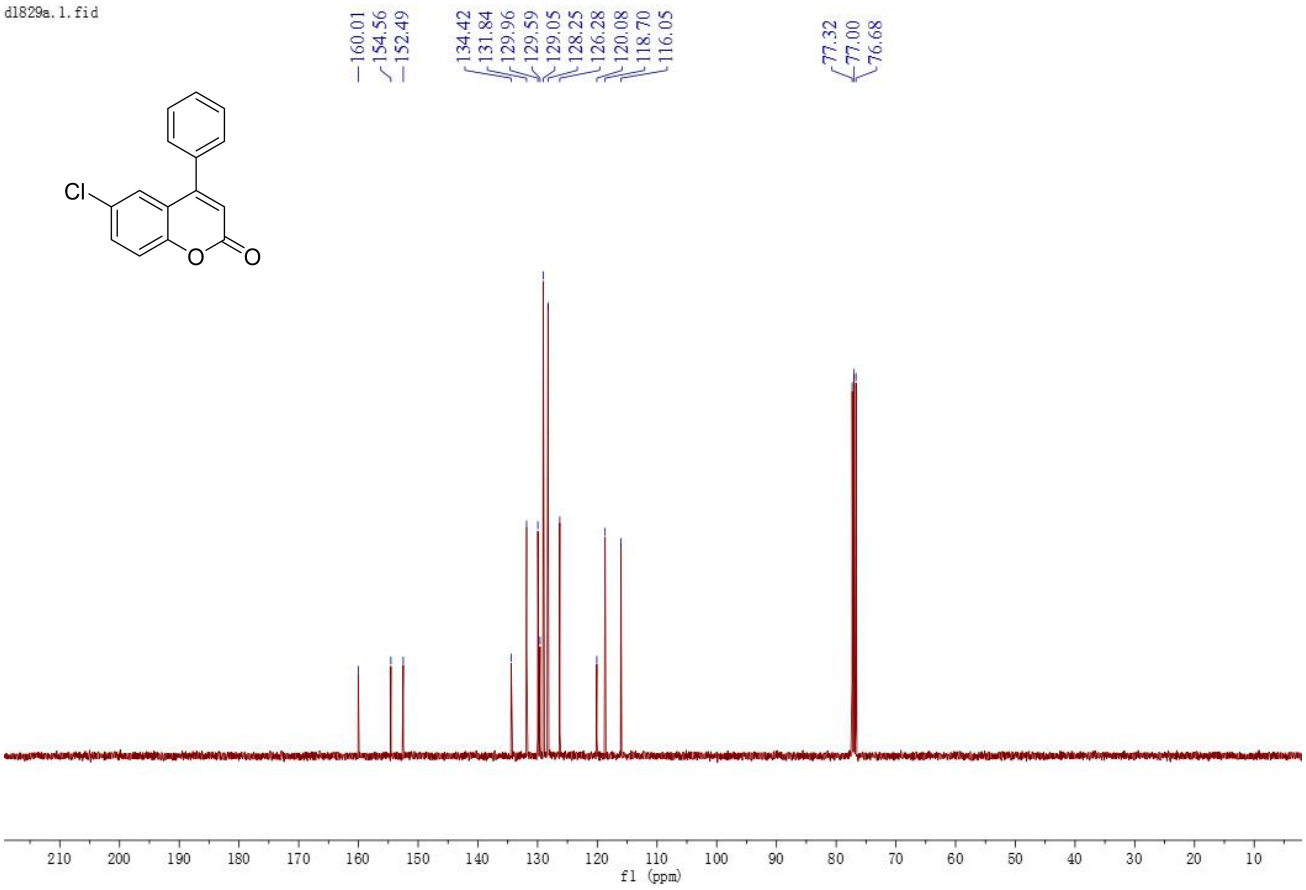




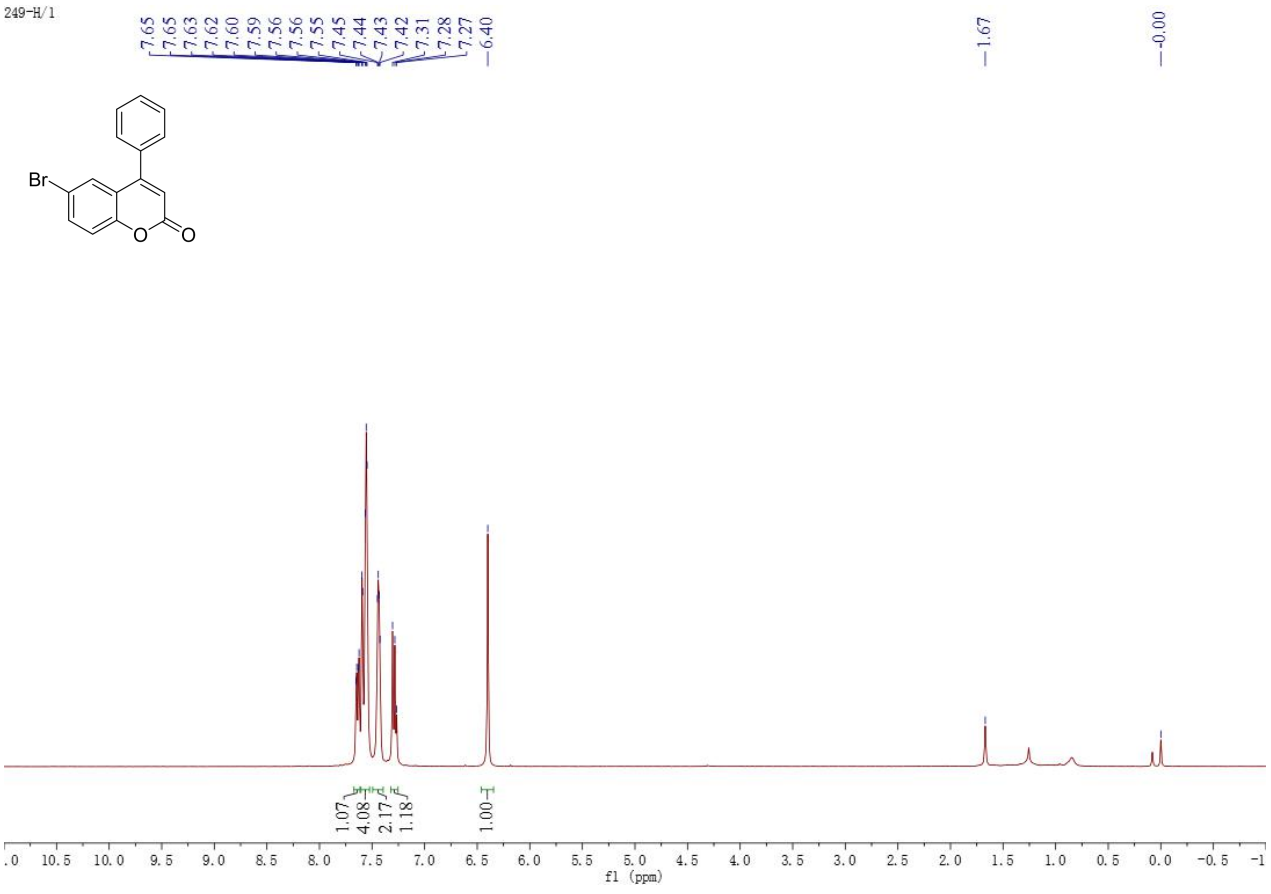


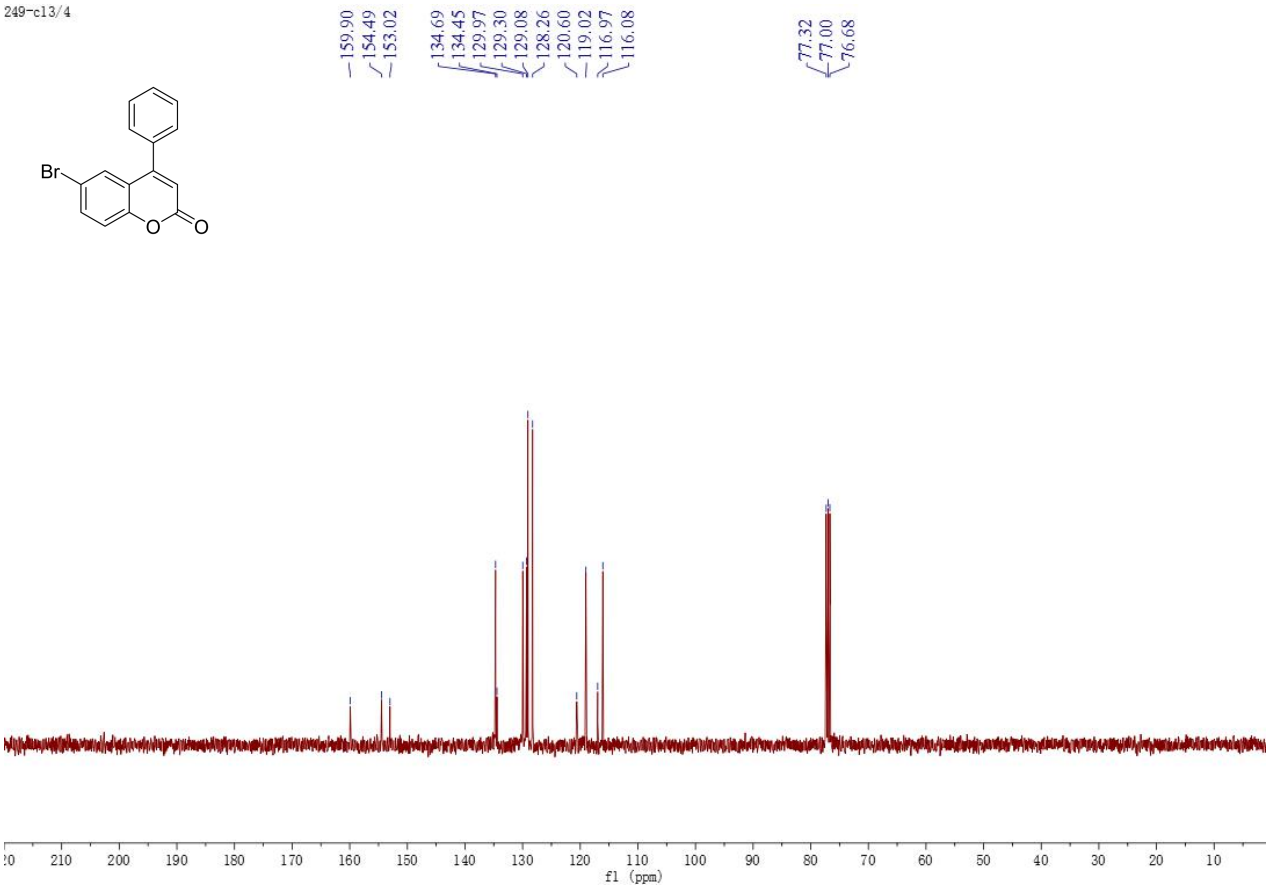
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3d



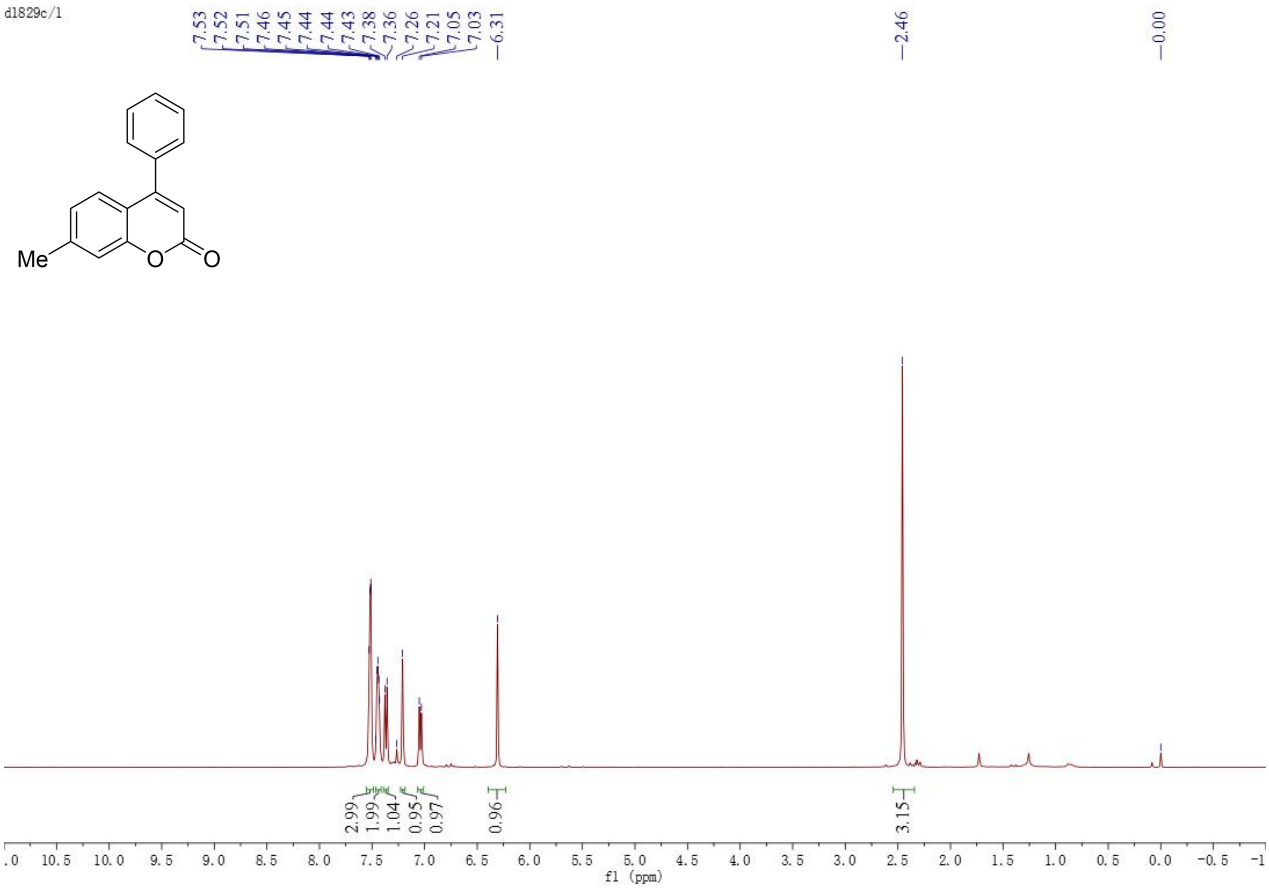


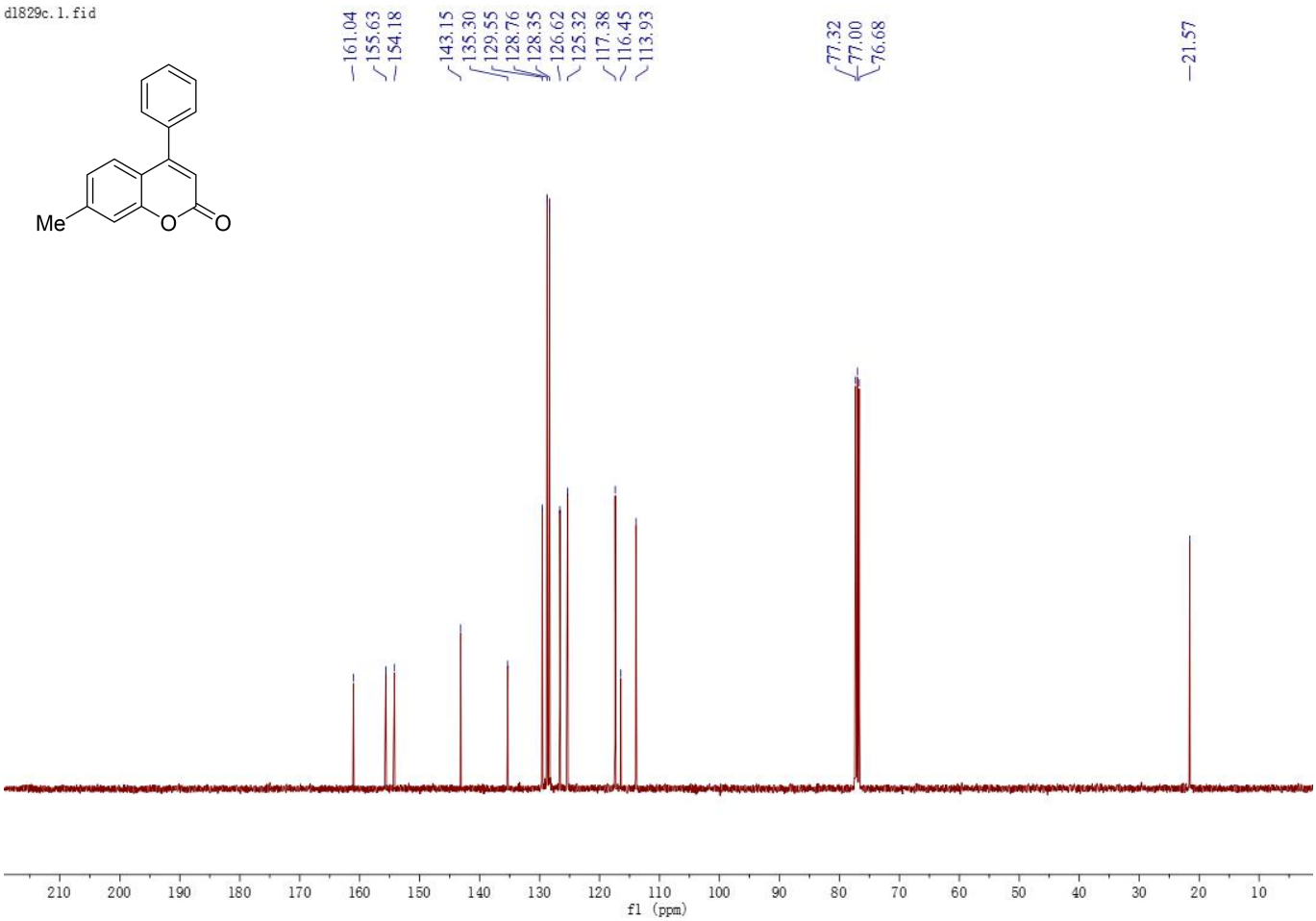
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3e



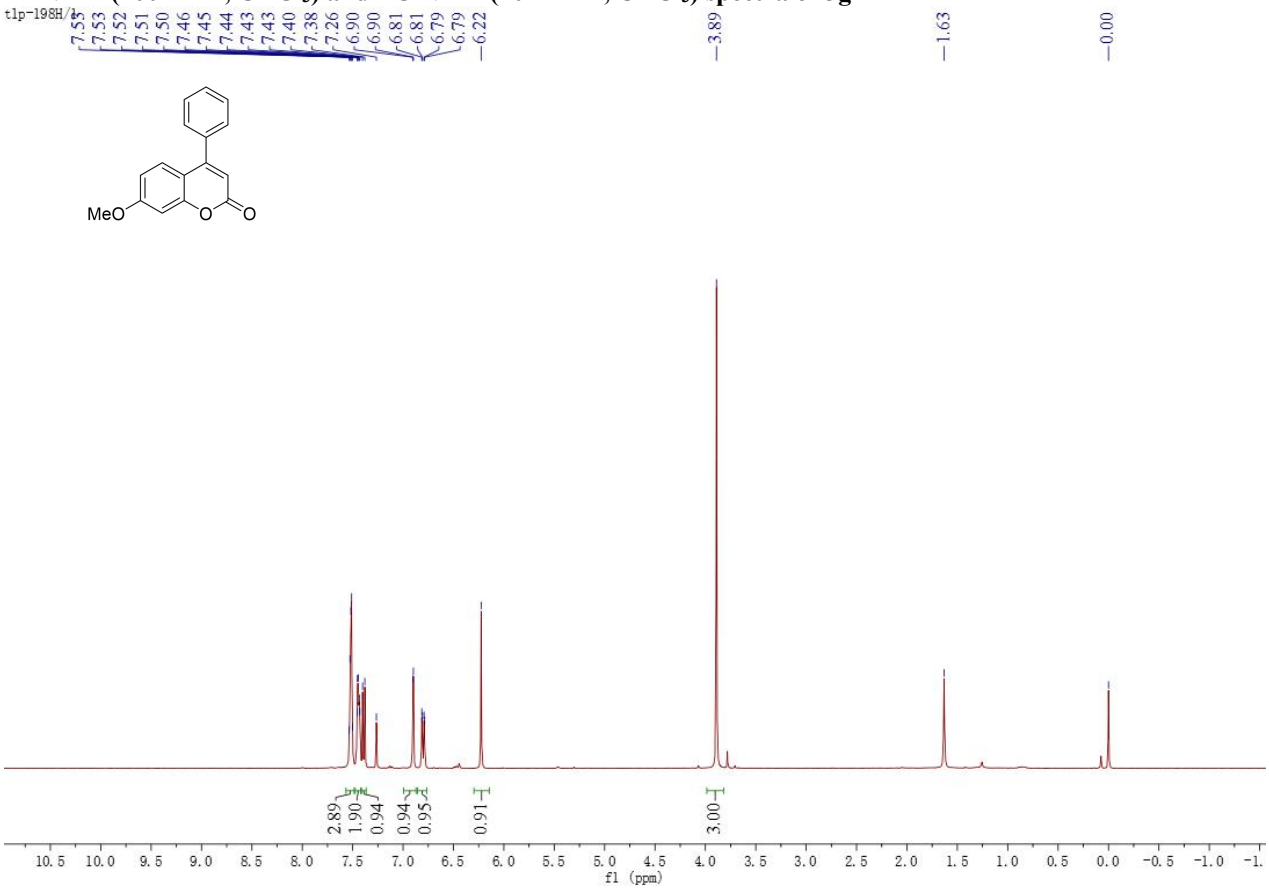


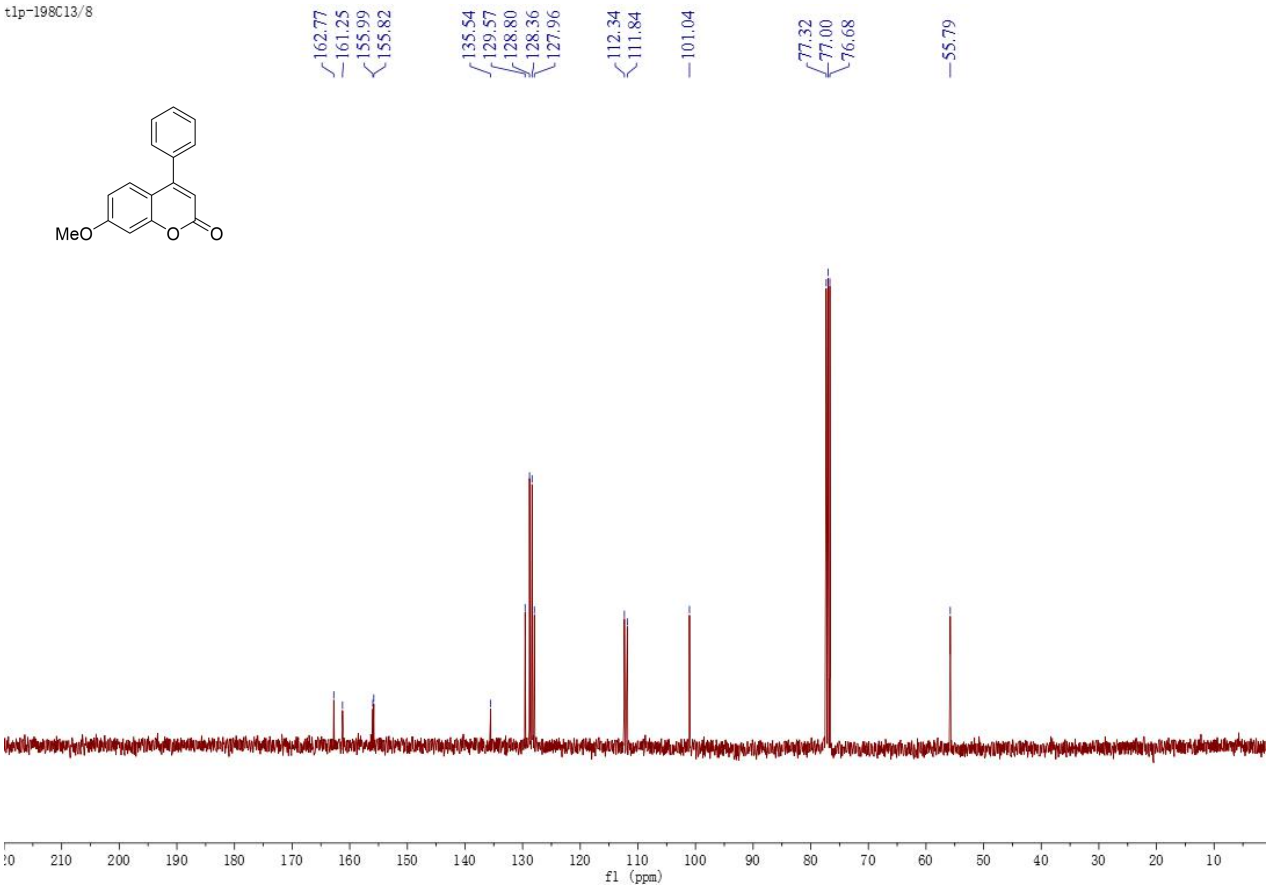
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3f



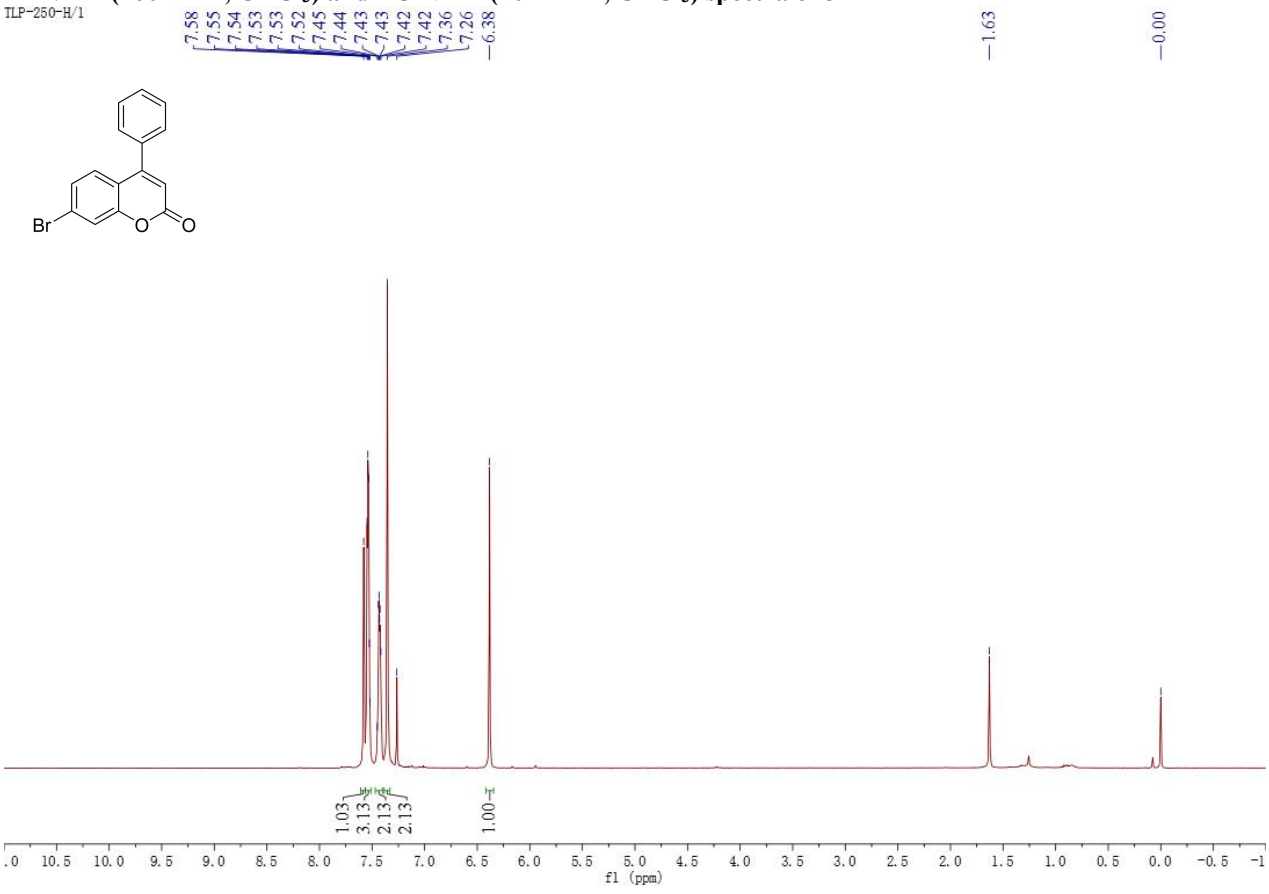


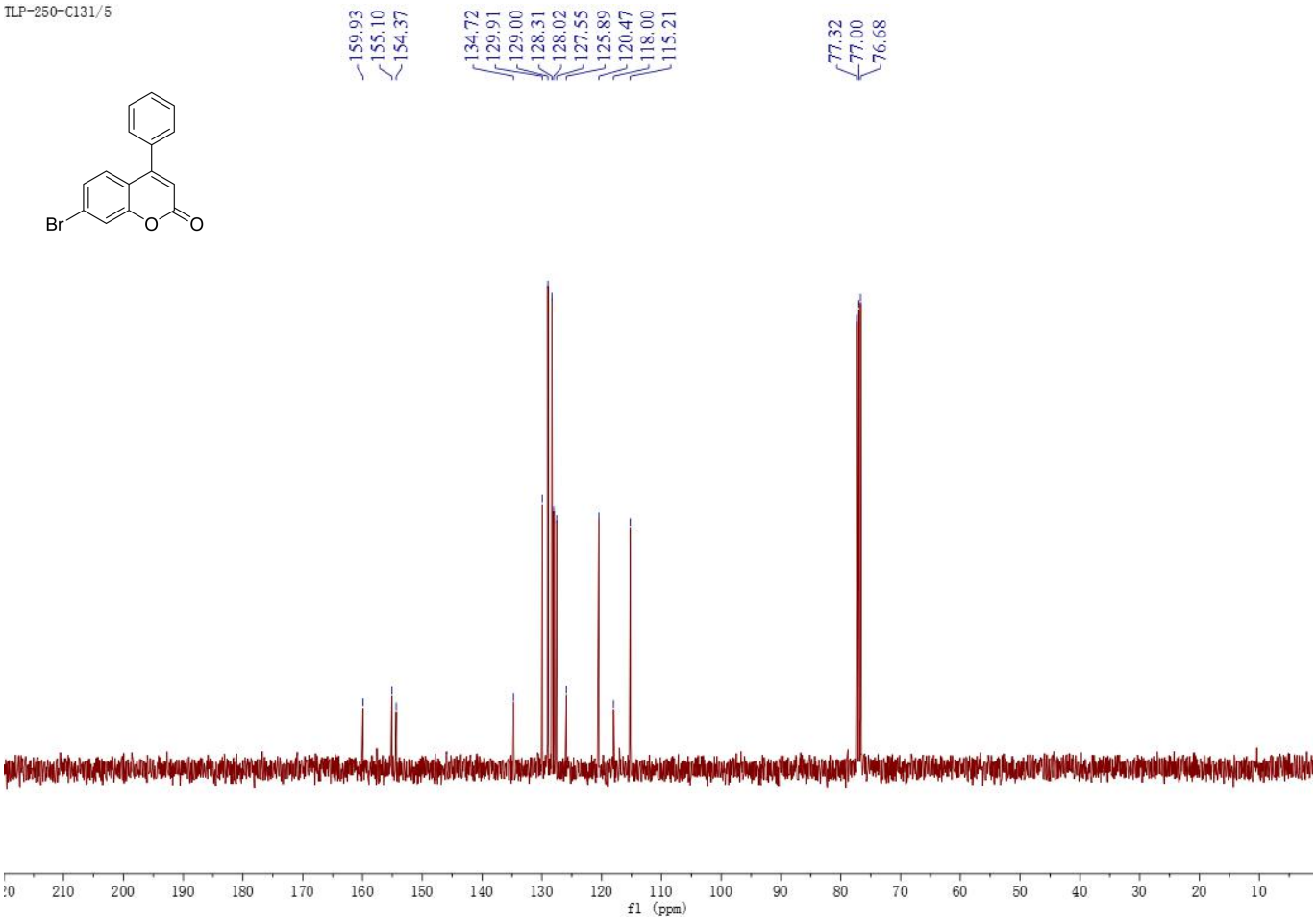
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3g



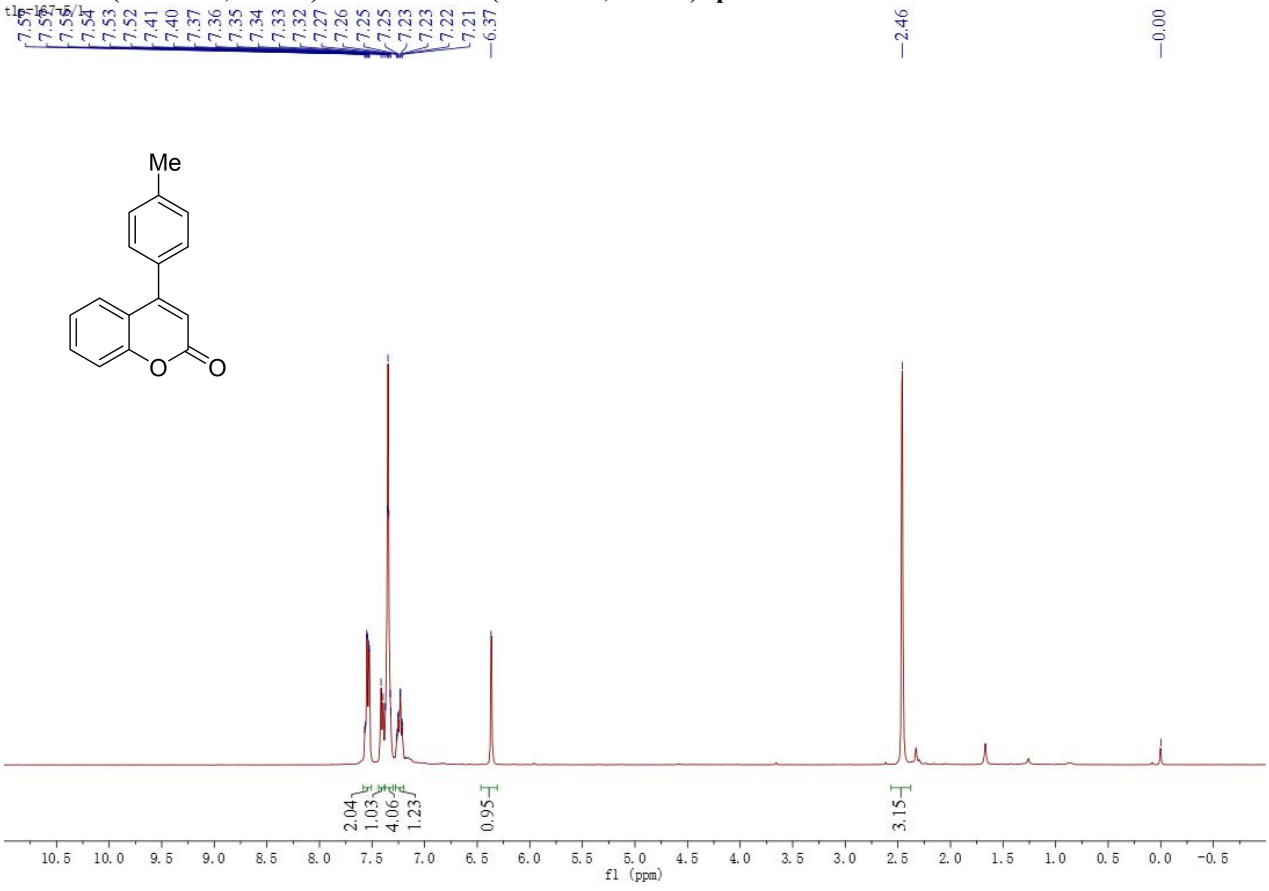


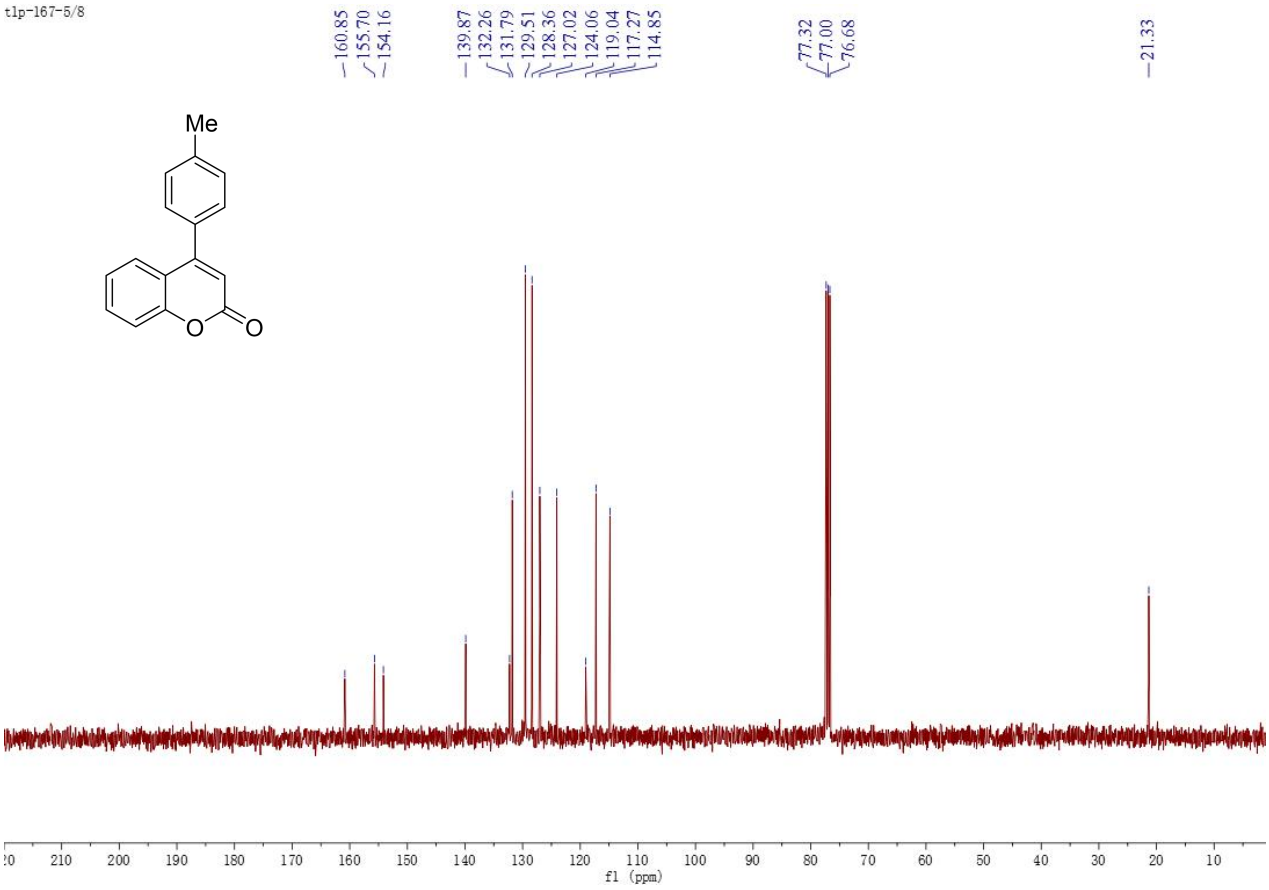
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3h



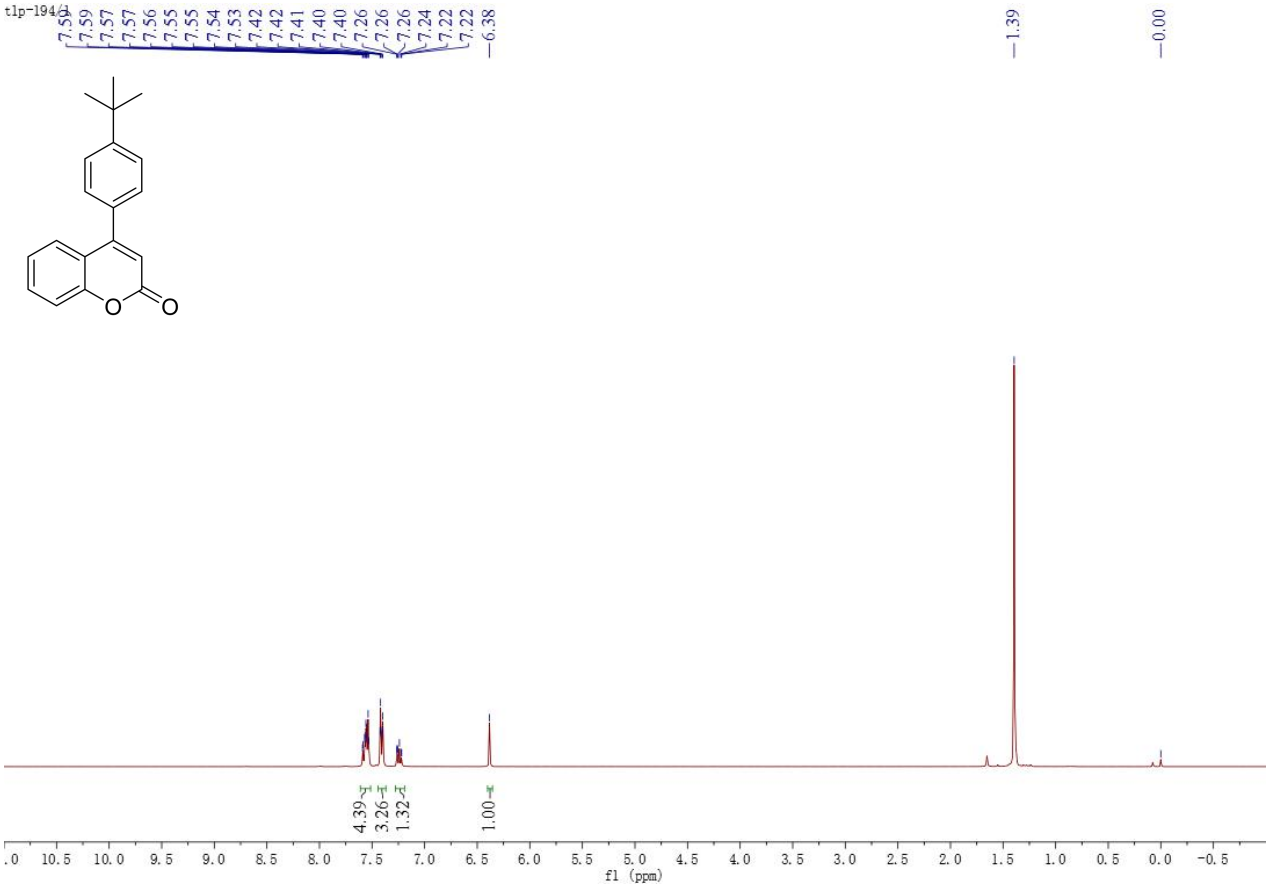


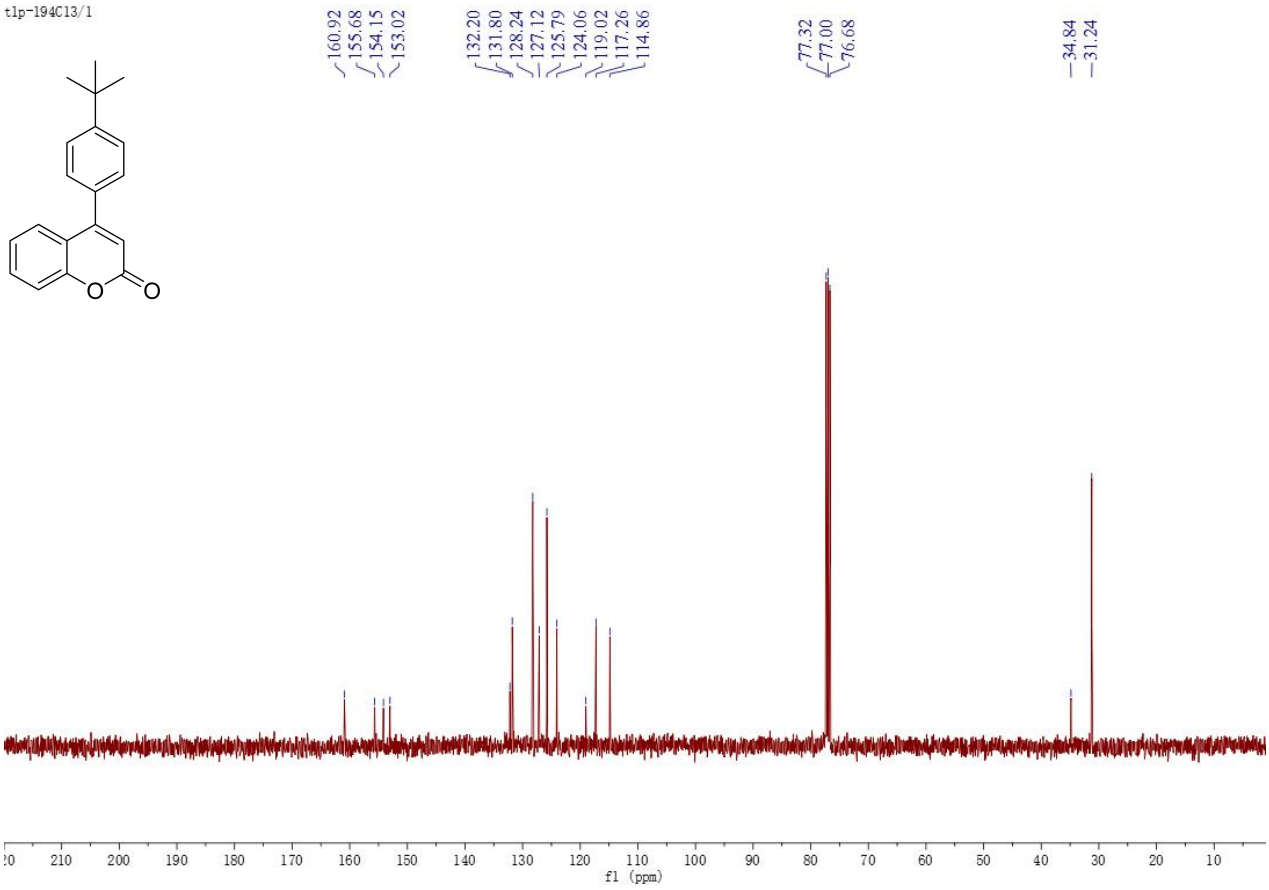
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3i



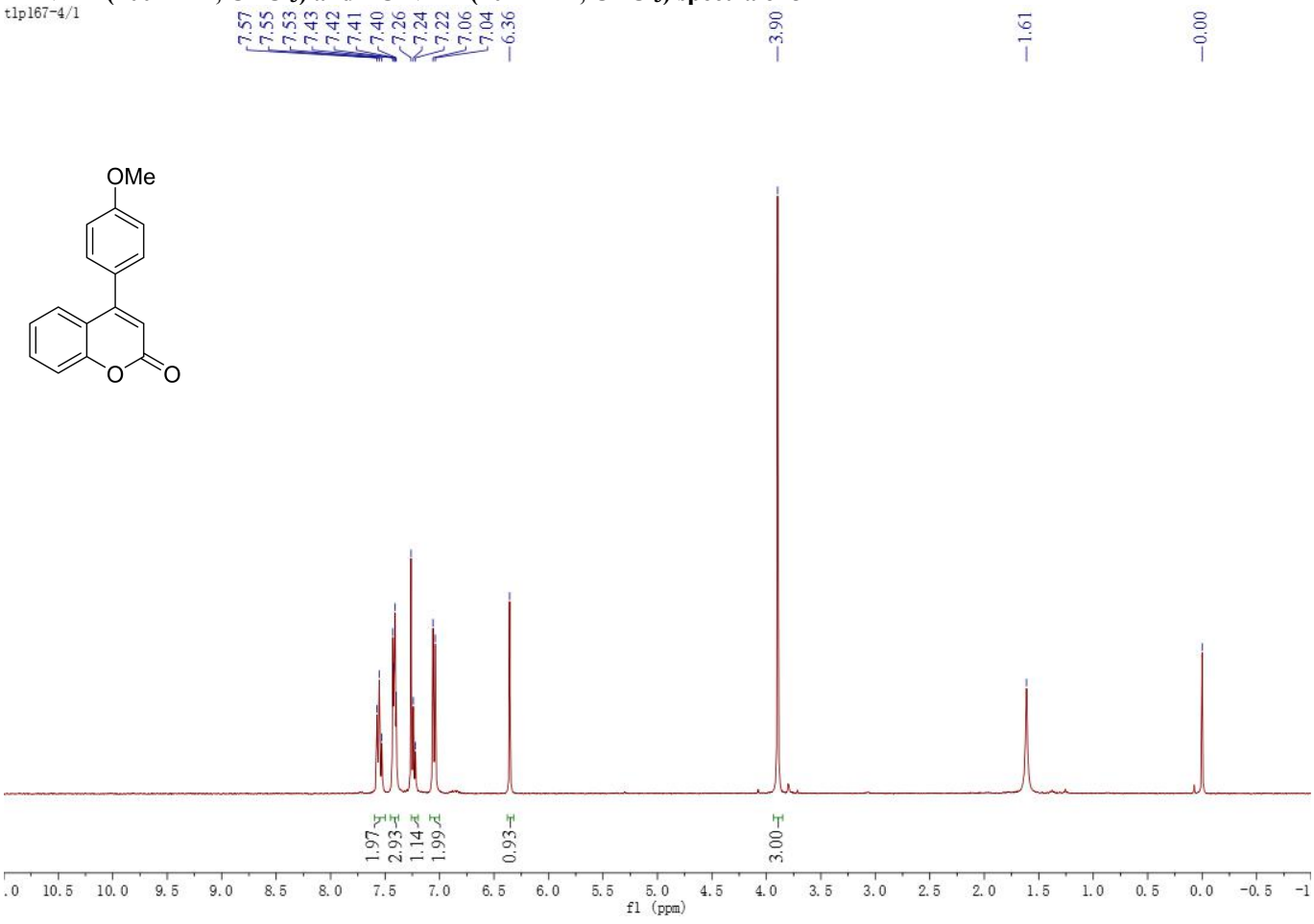


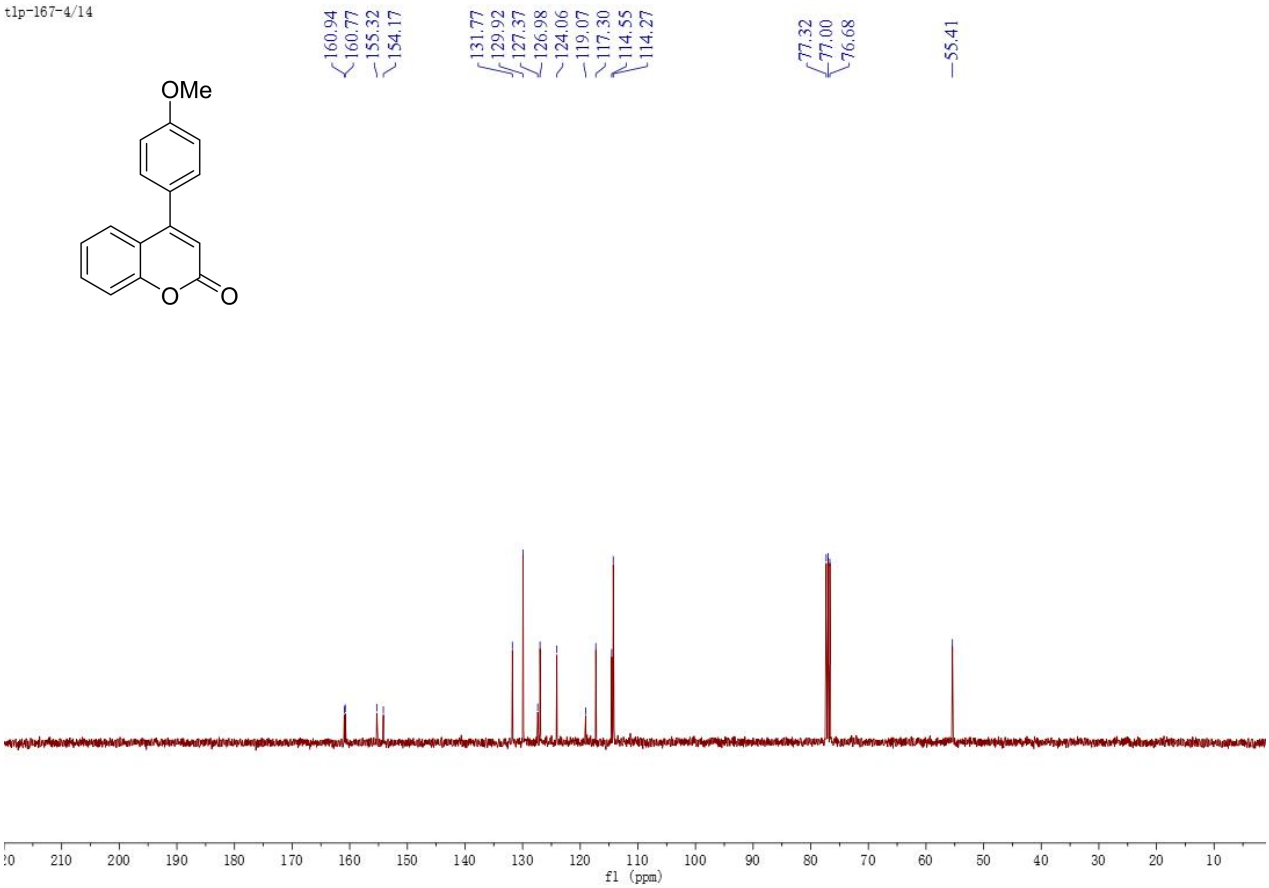
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3j



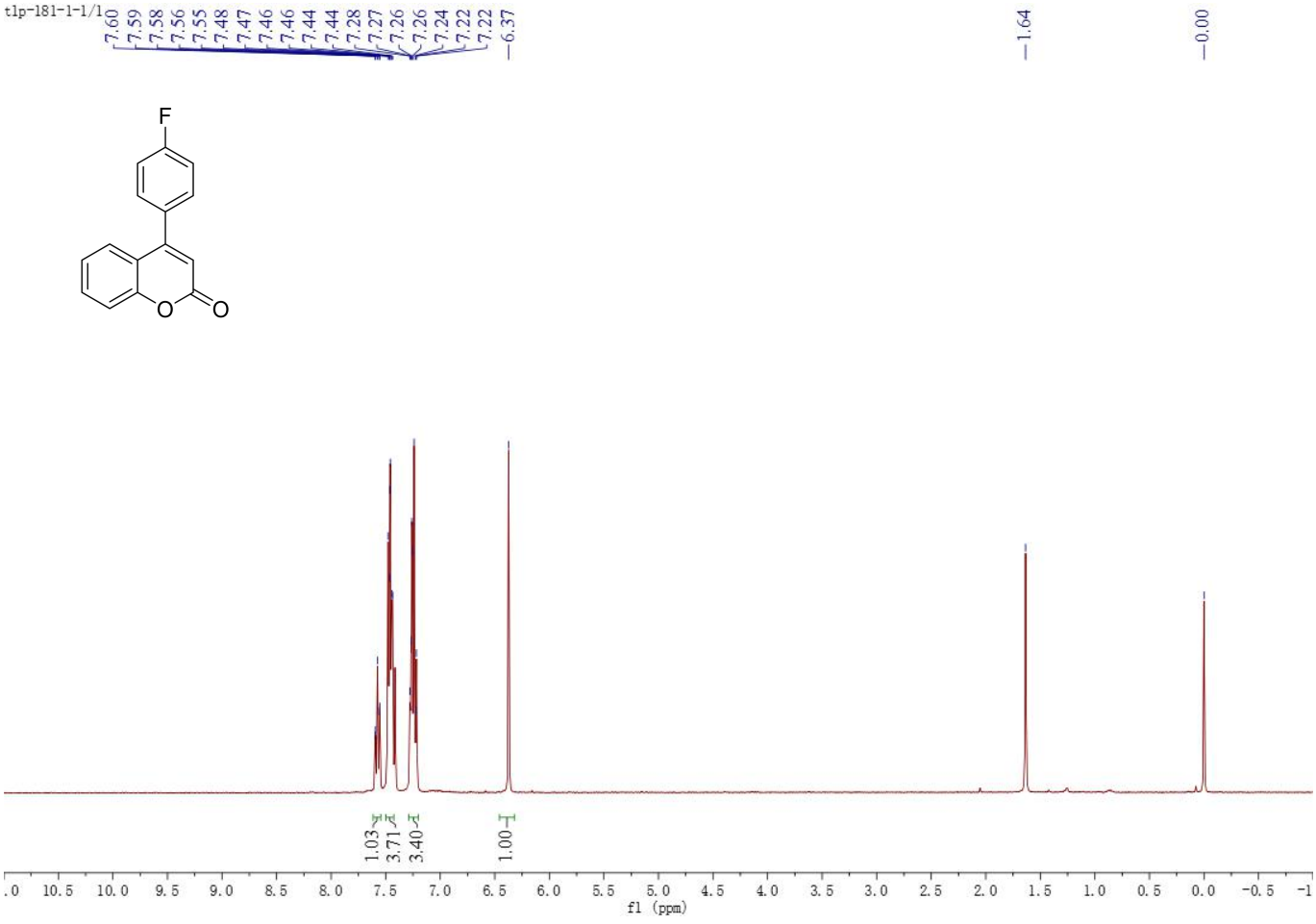


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3k

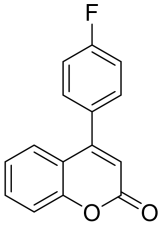




^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of 3l



tlp-181-1-1C13/10



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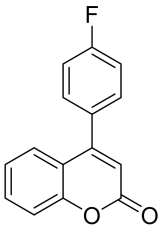
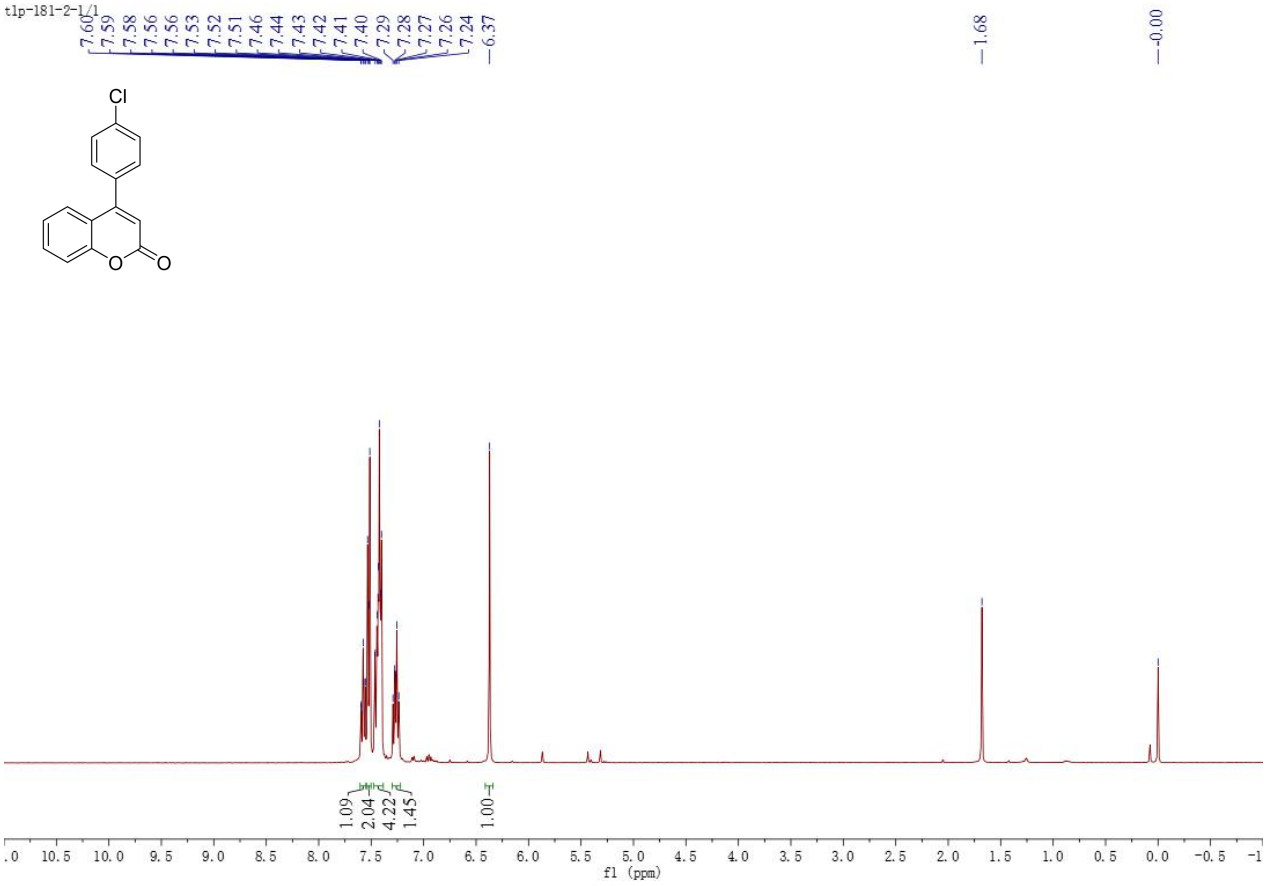
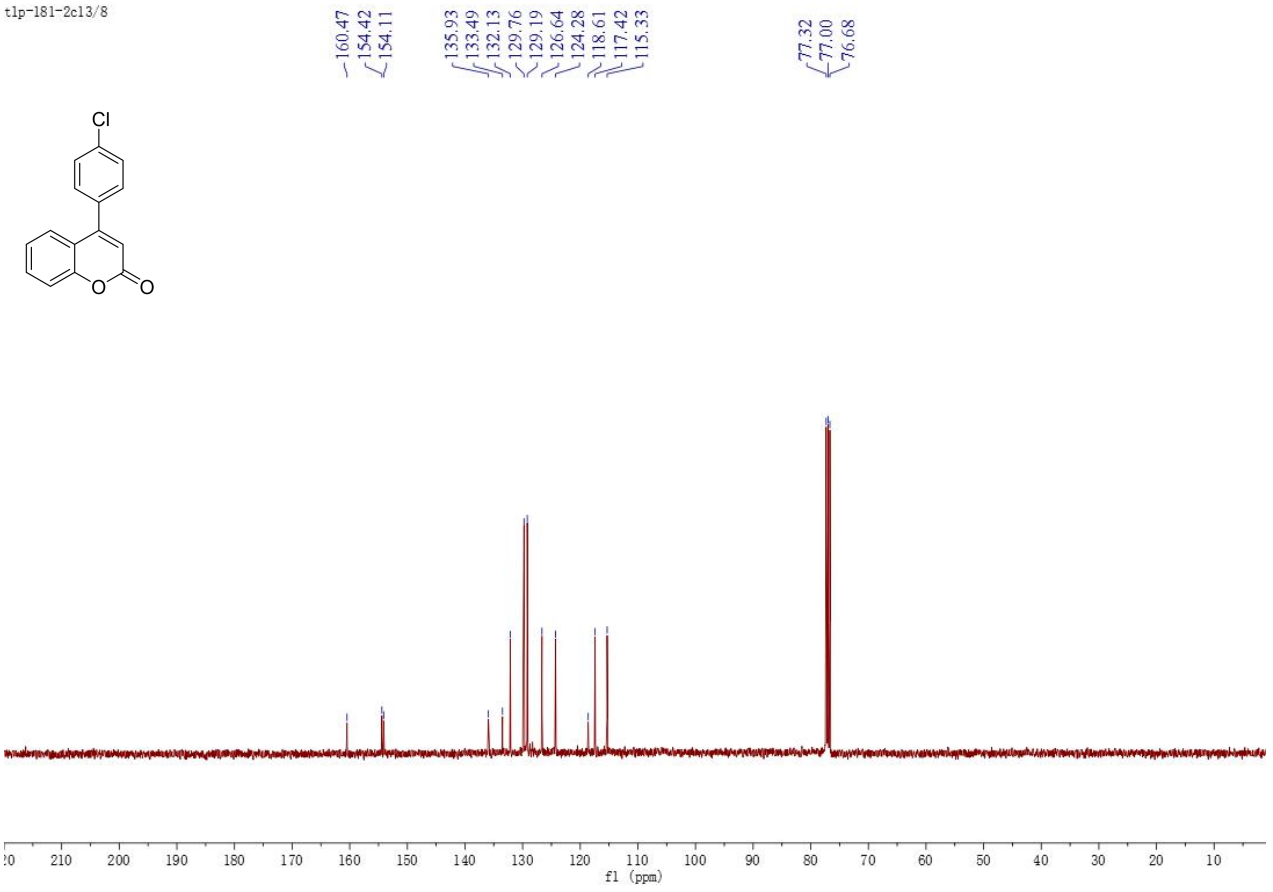
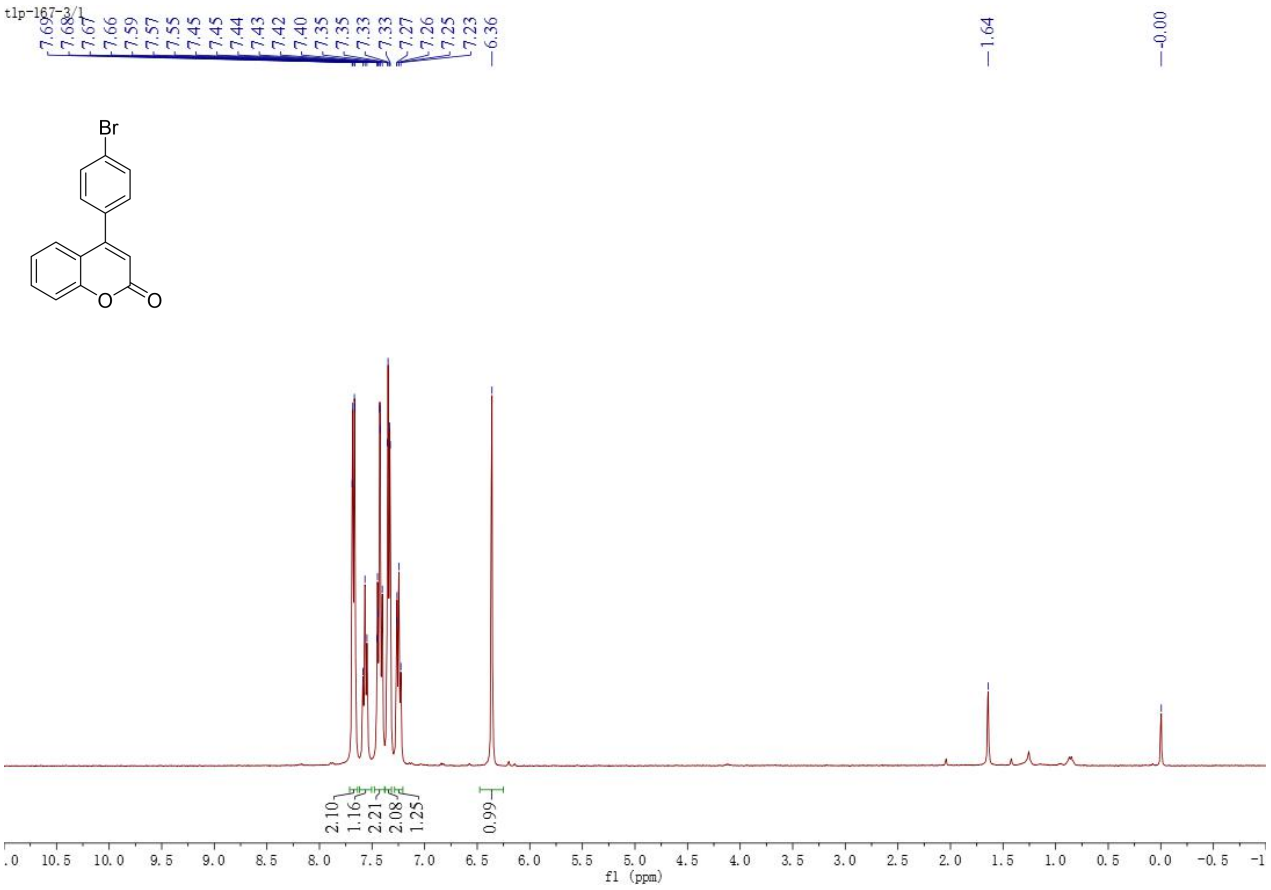


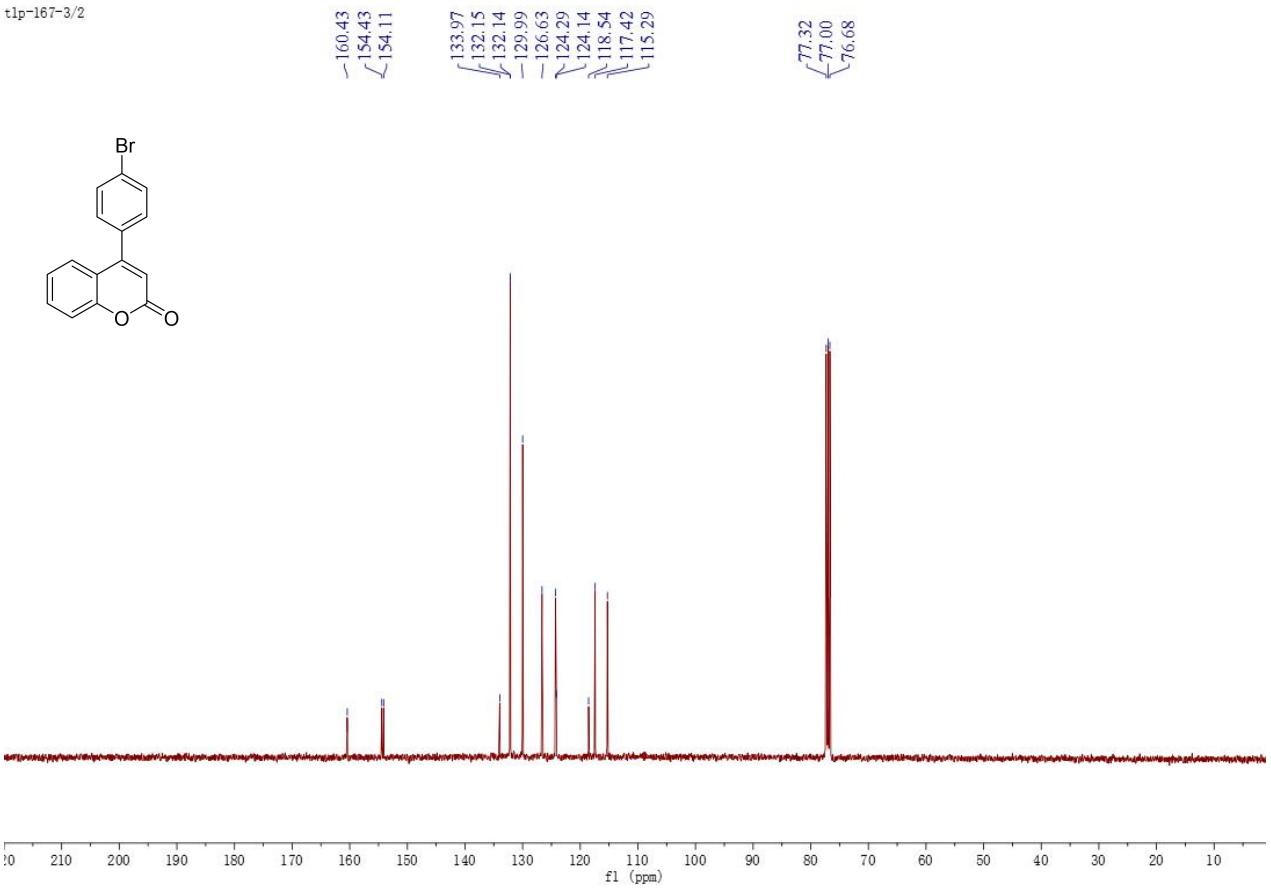
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3m



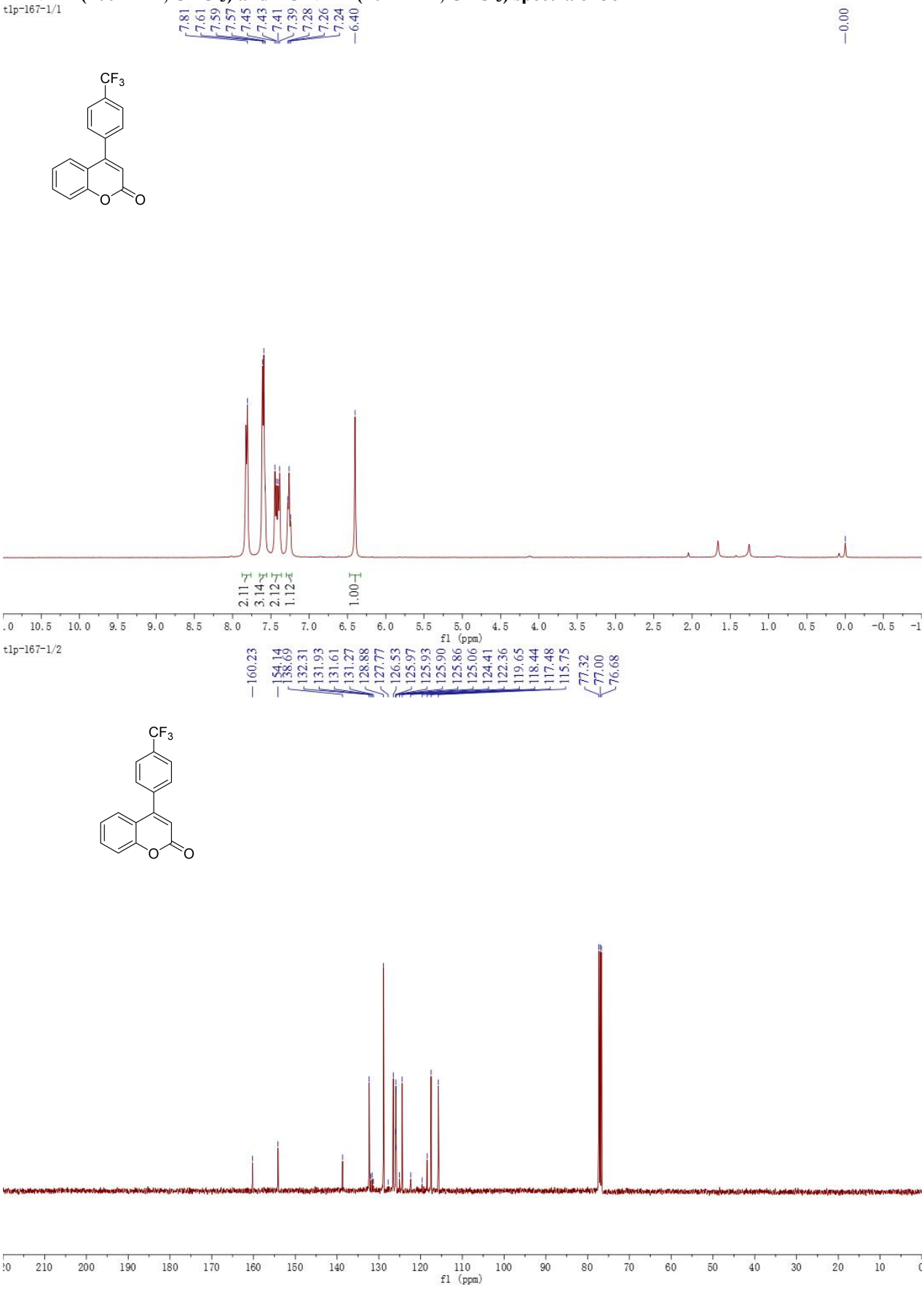


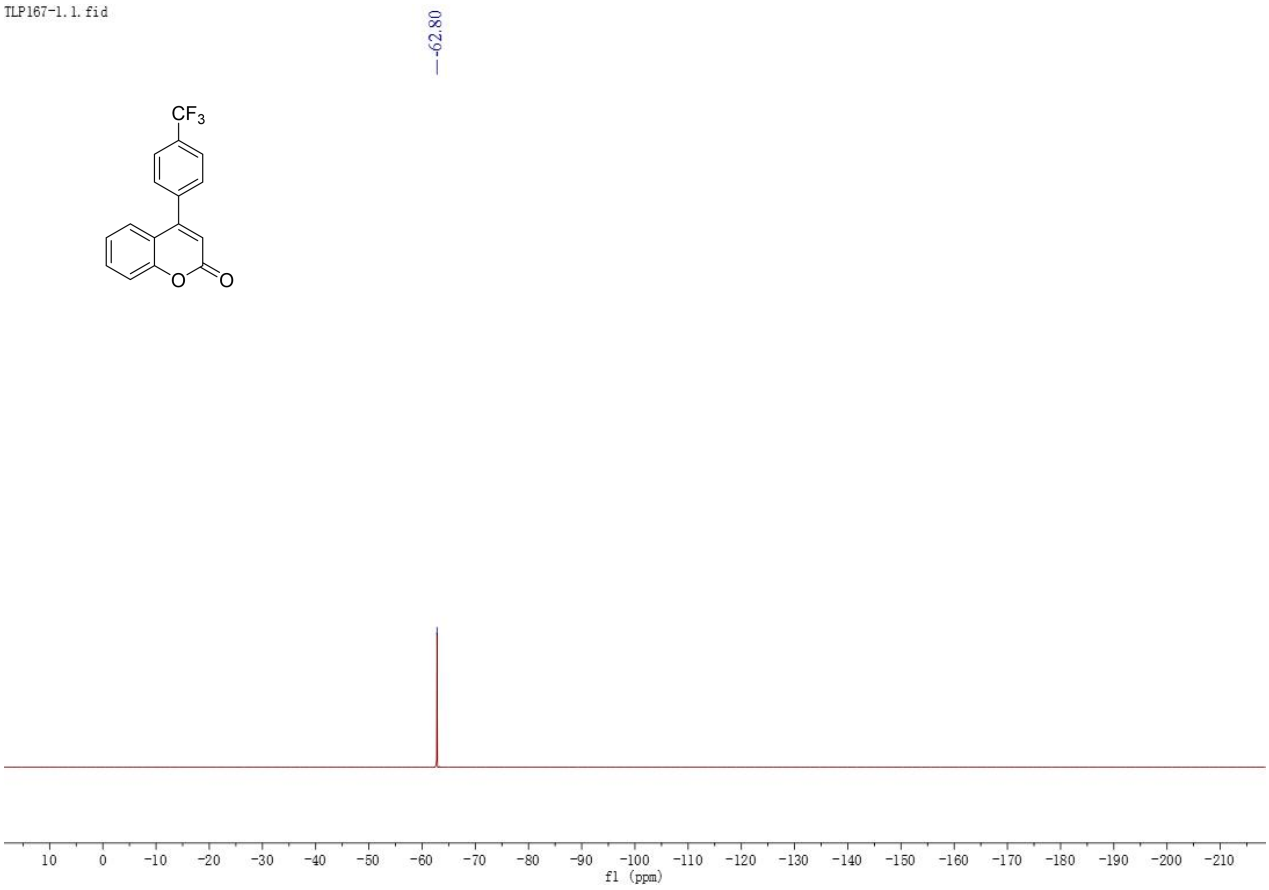
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3n



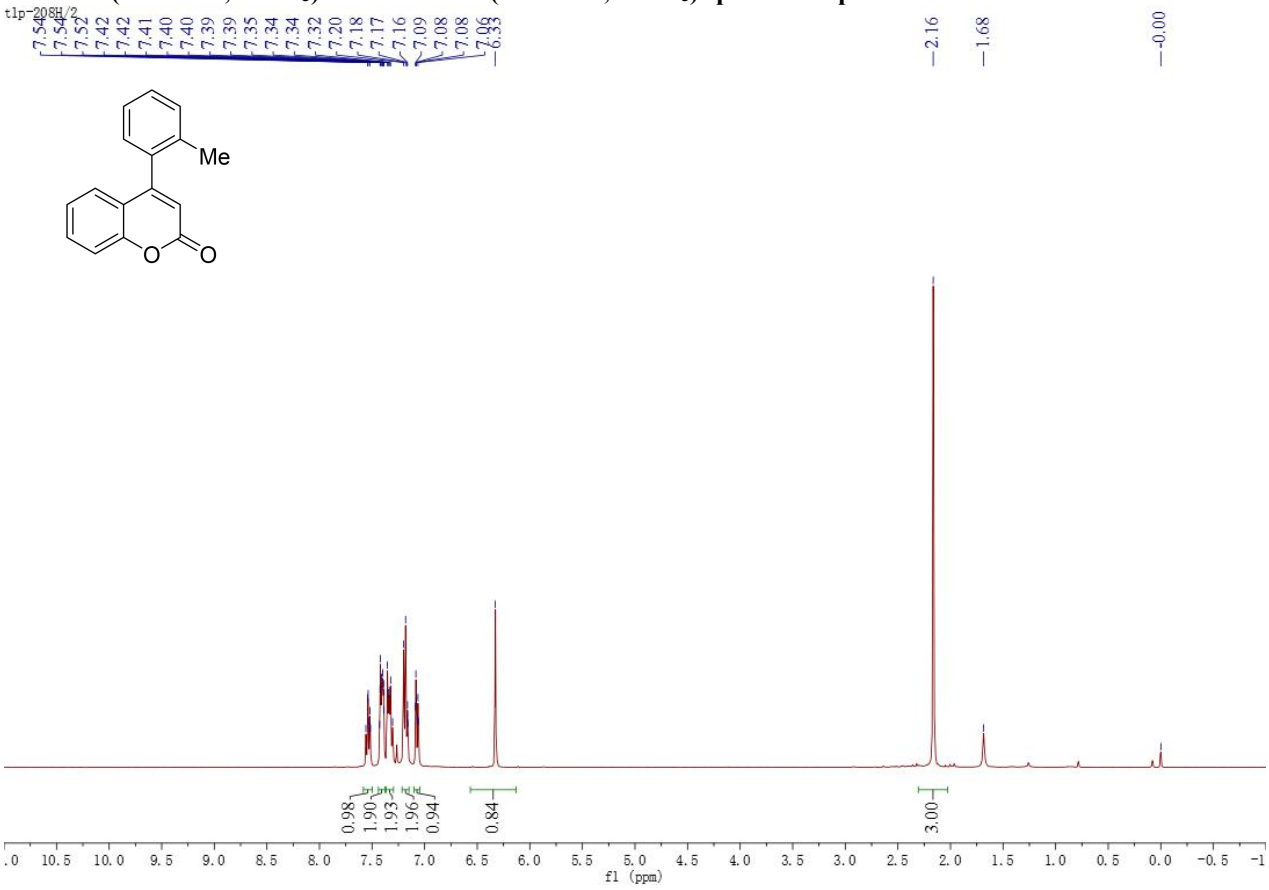


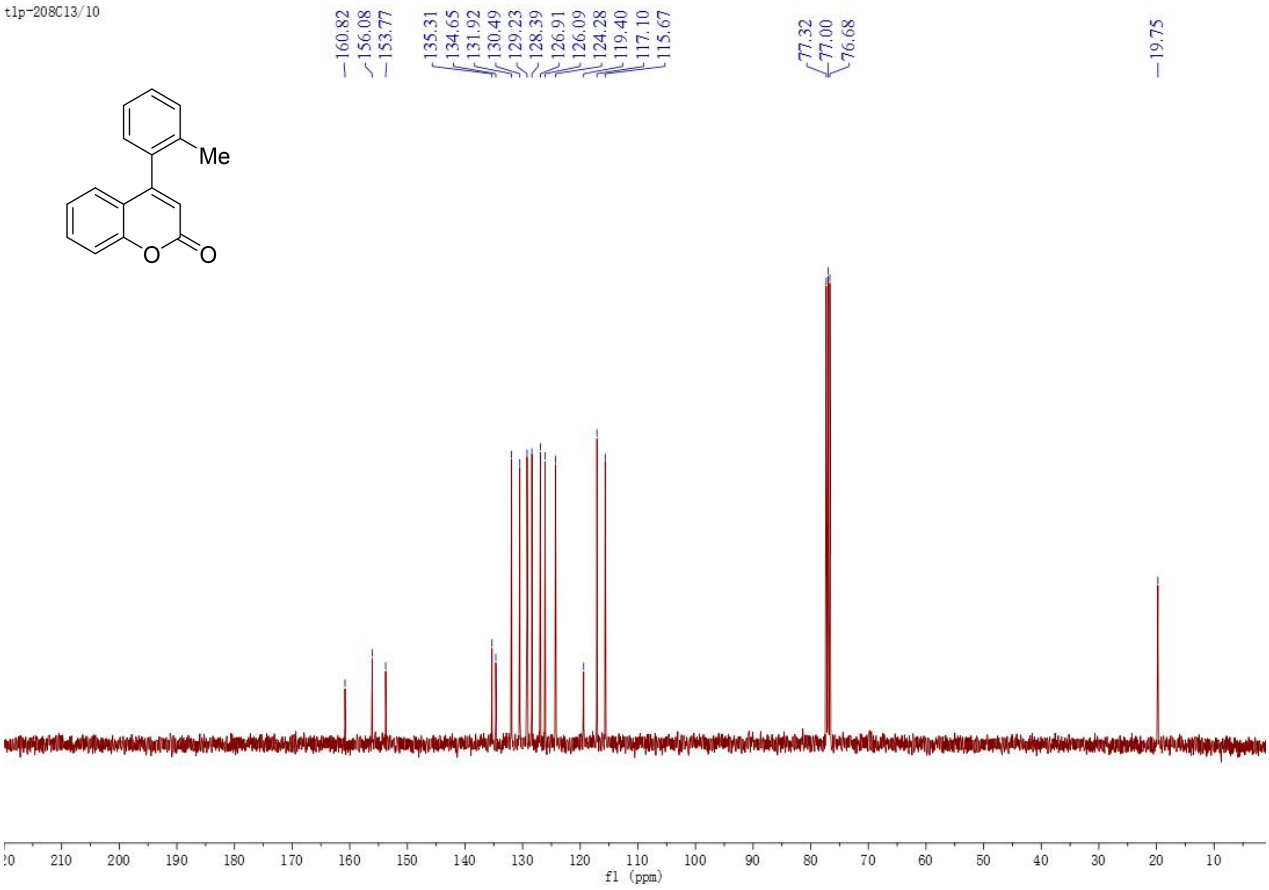
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3o



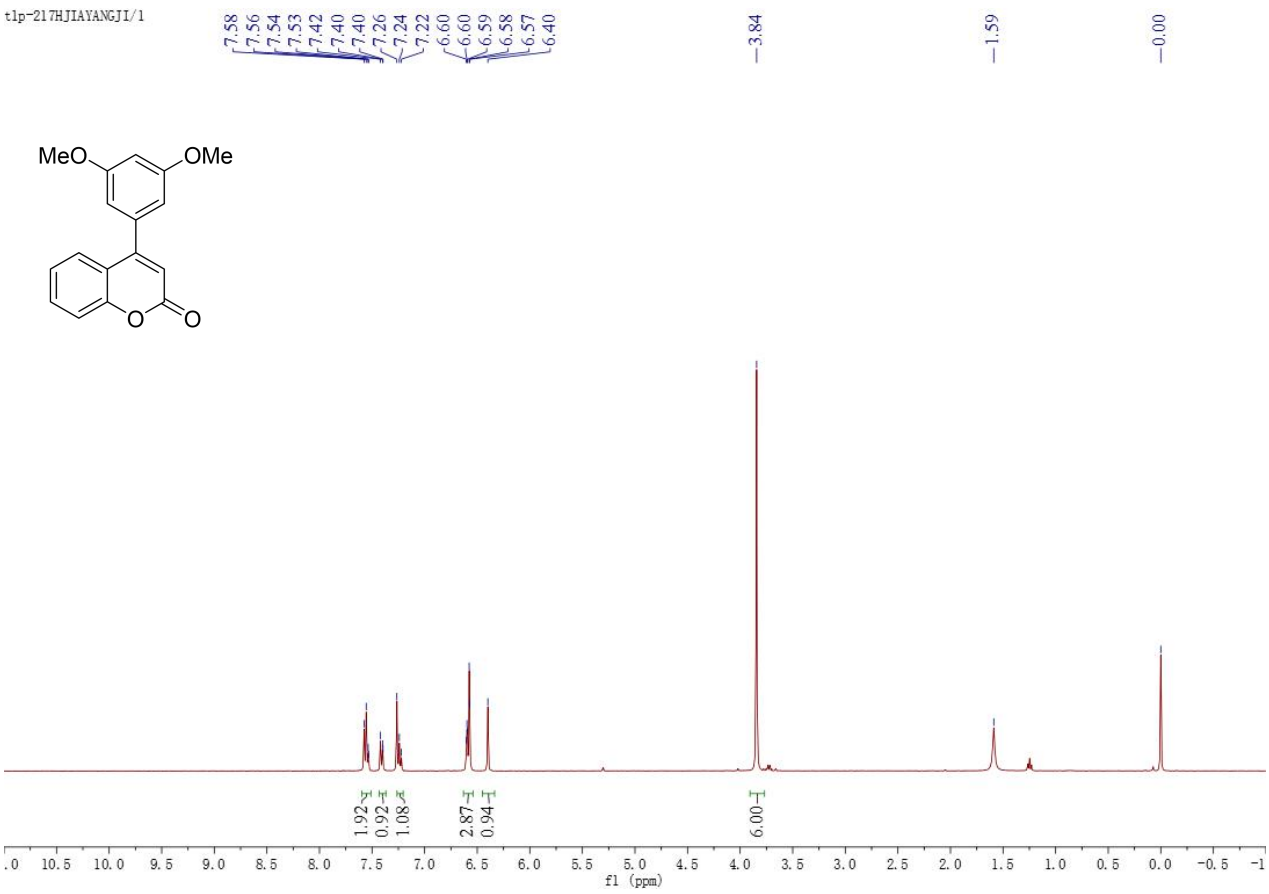


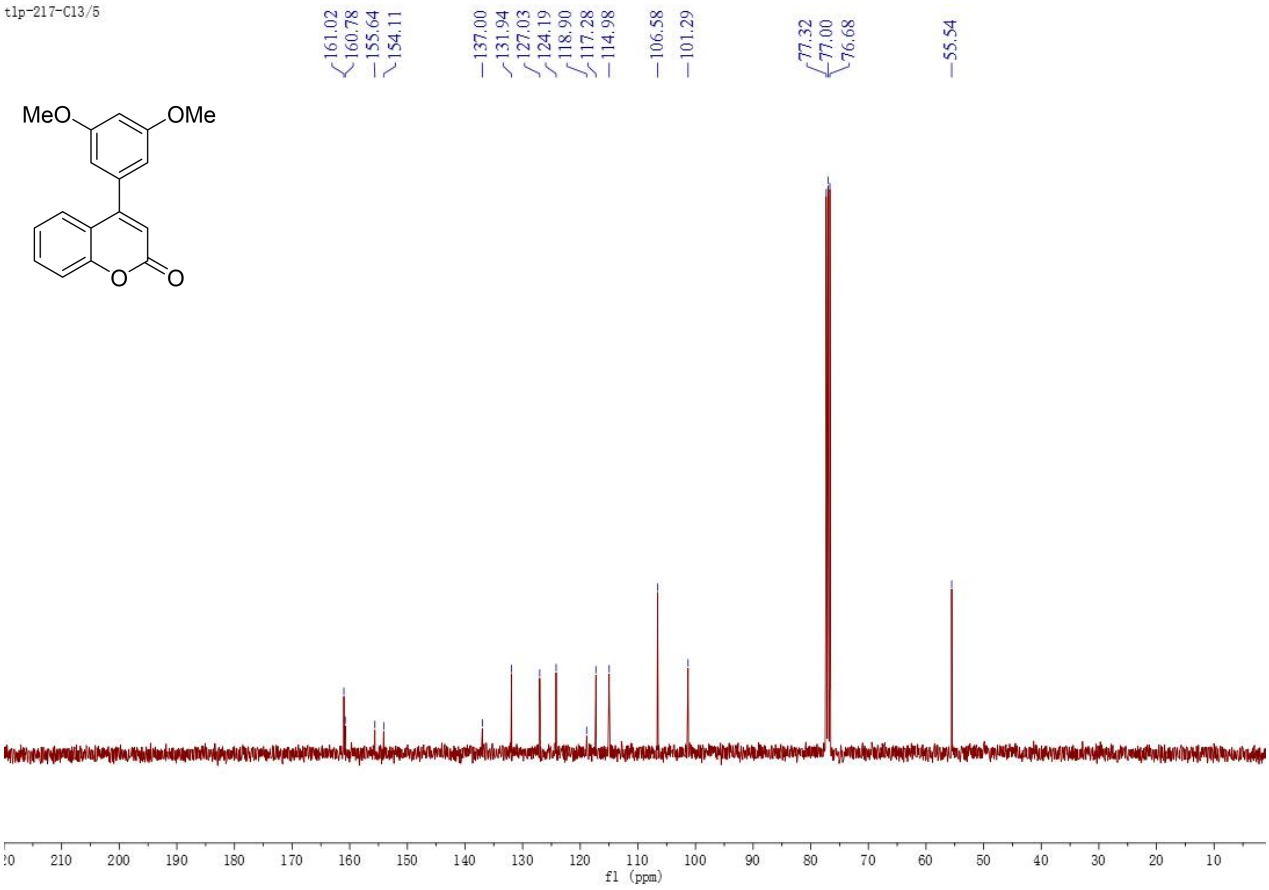
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3p



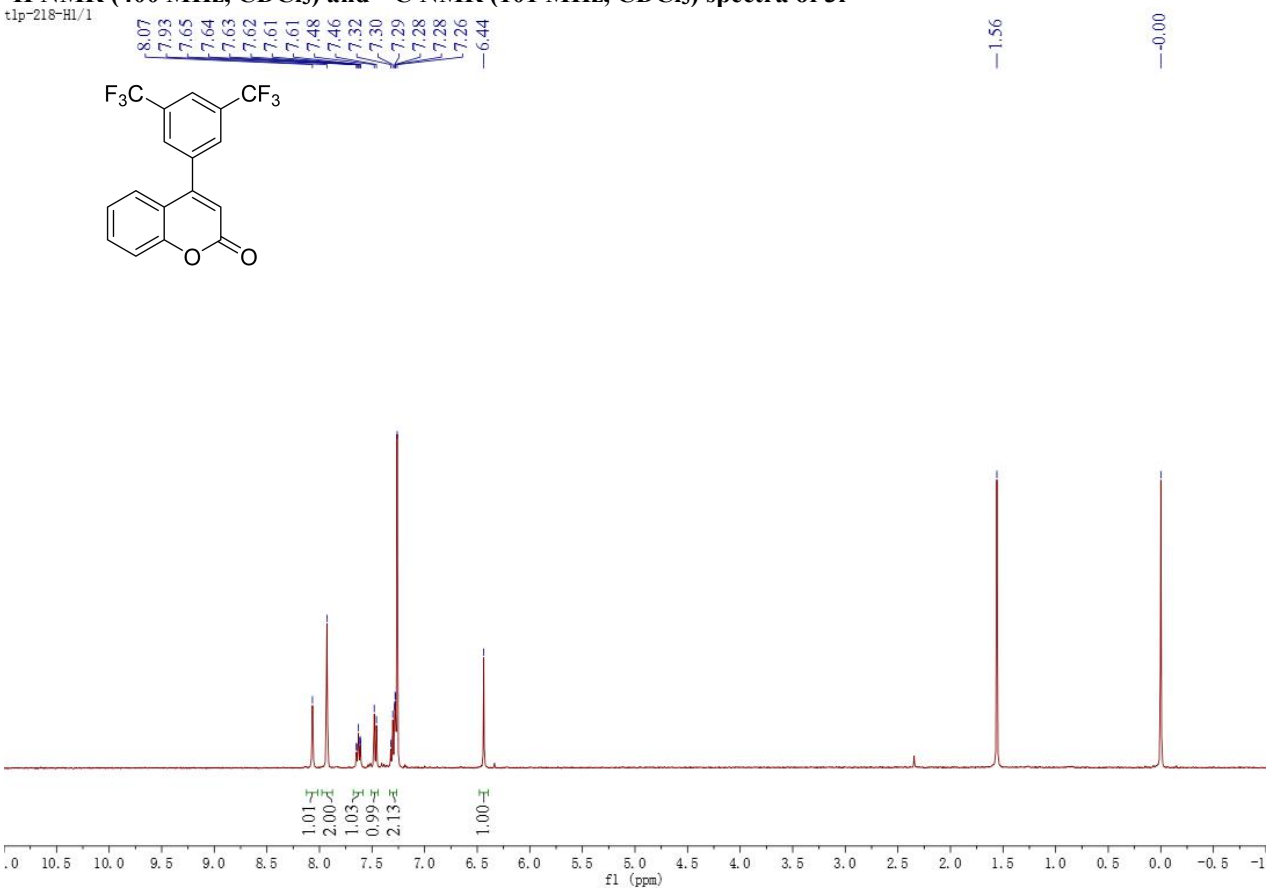


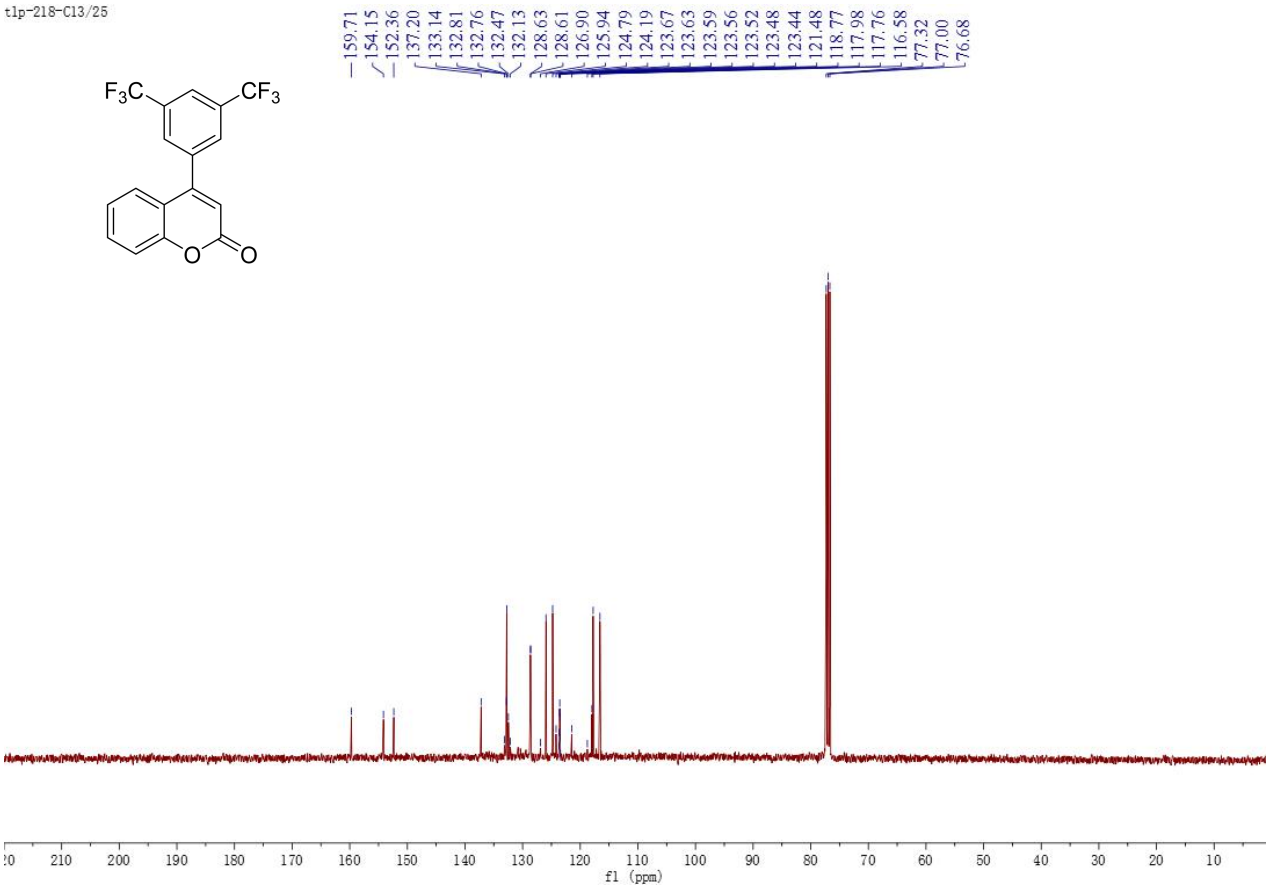
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3q

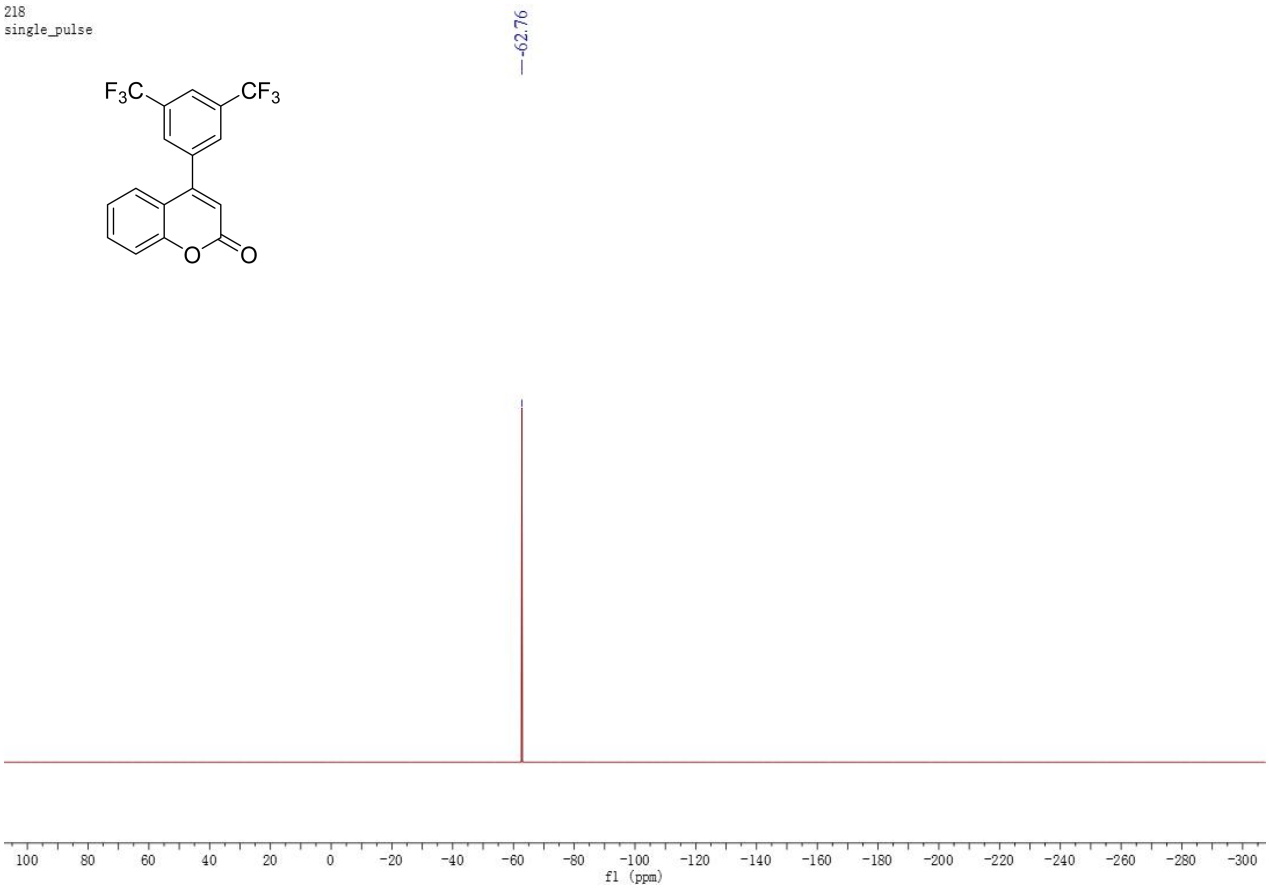




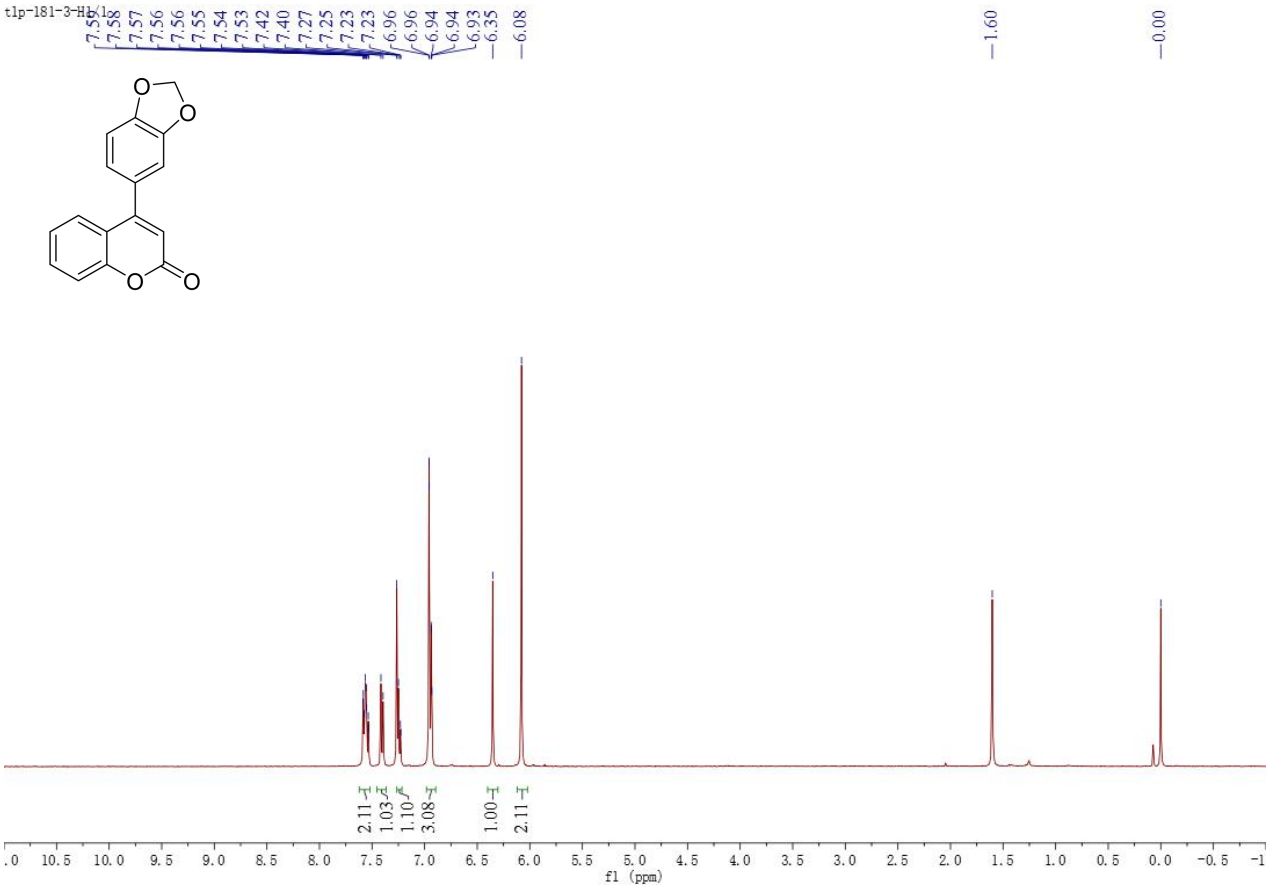
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3r







^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3s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7.58
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7.56
7.56
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7.54
7.53
7.42
7.40
7.27
7.25
7.23
7.23
6.96
6.96
6.94
6.94
6.93
6.35
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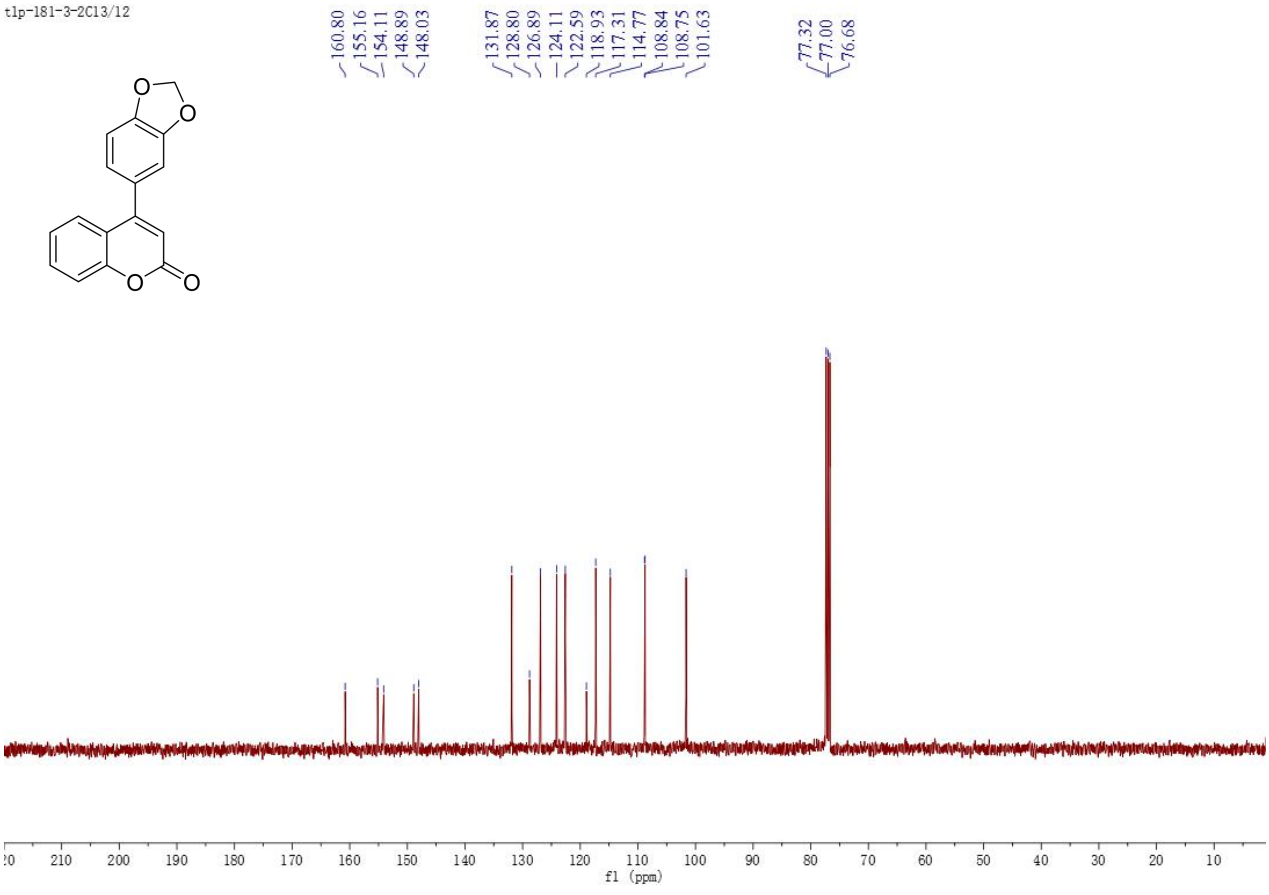
1.60
0.00
2.11
1.03
1.10
3.08
1.00
2.11
f1 (ppm)


tlp-181-3-2C13/12
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124.11
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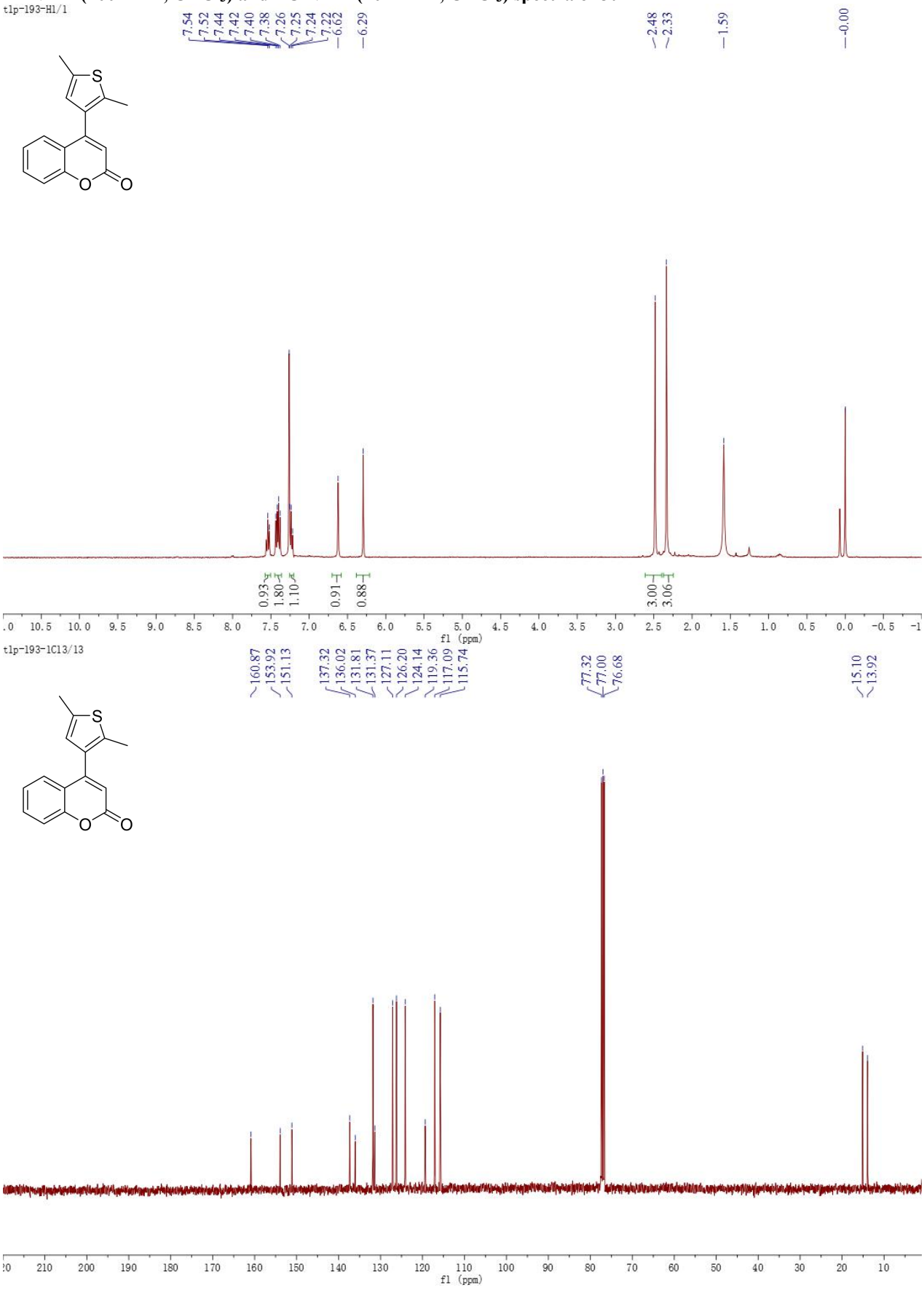
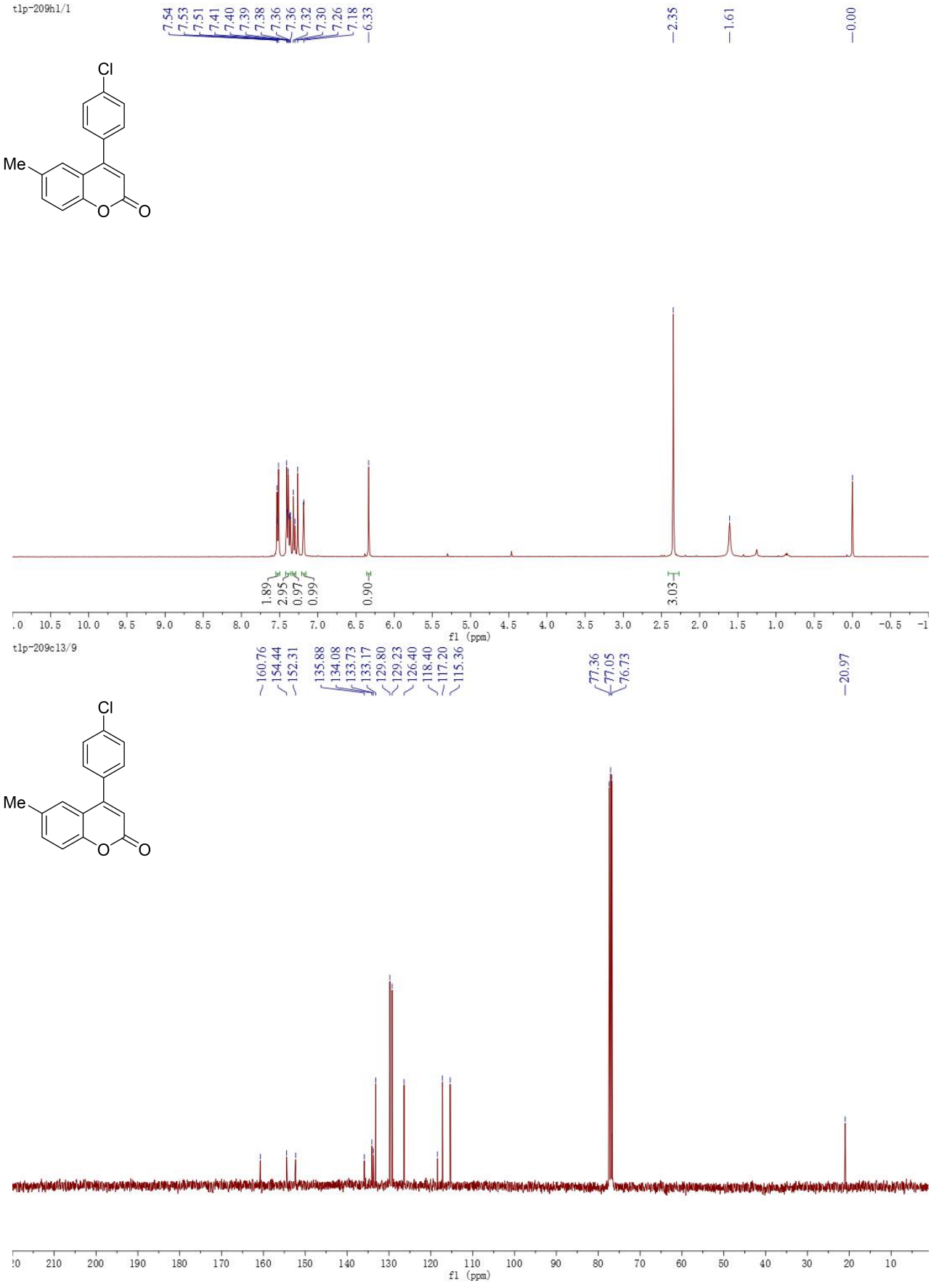
108.84
108.75
101.63
77.32
77.00
76.68
f1 (ppm)

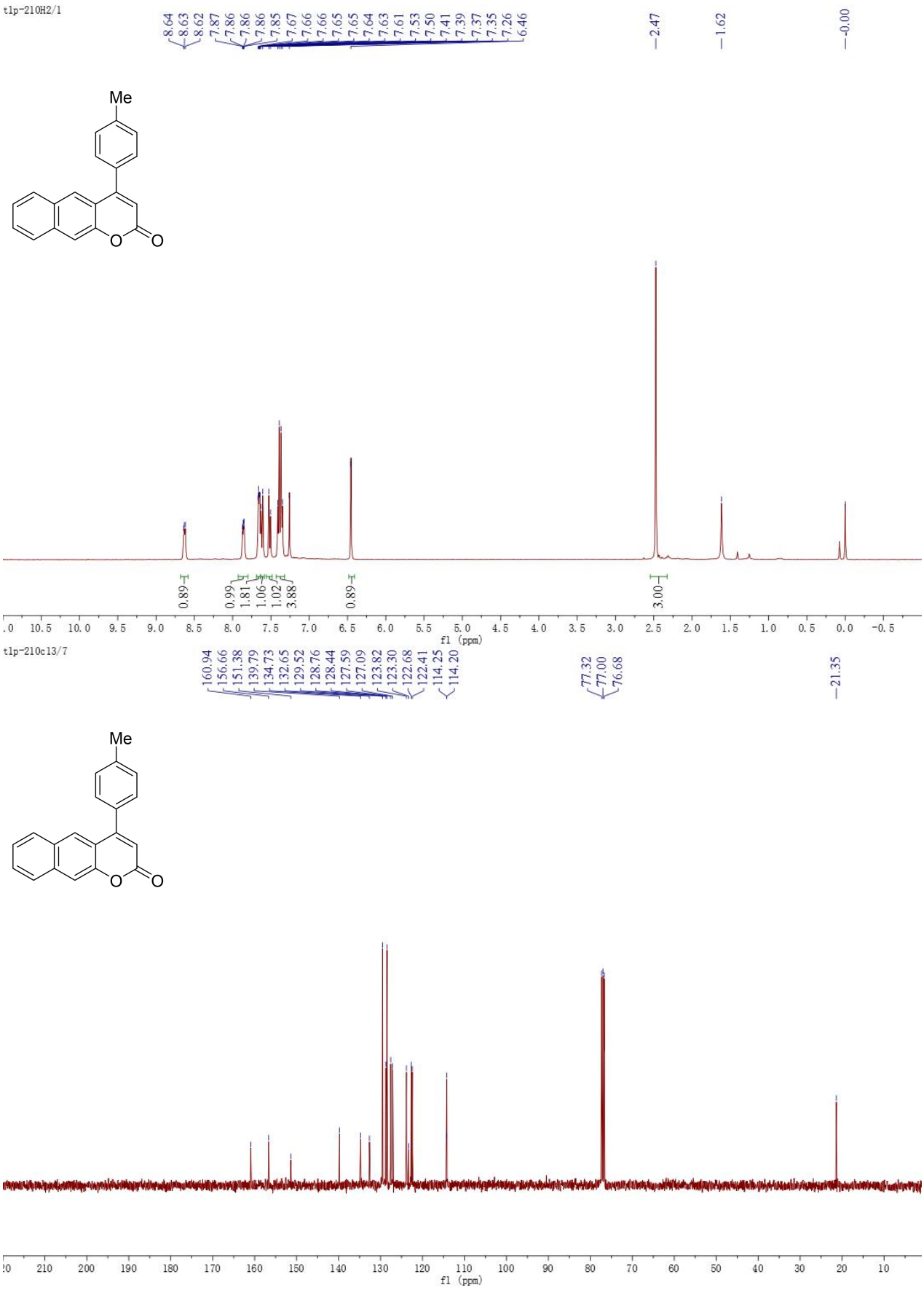
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3t



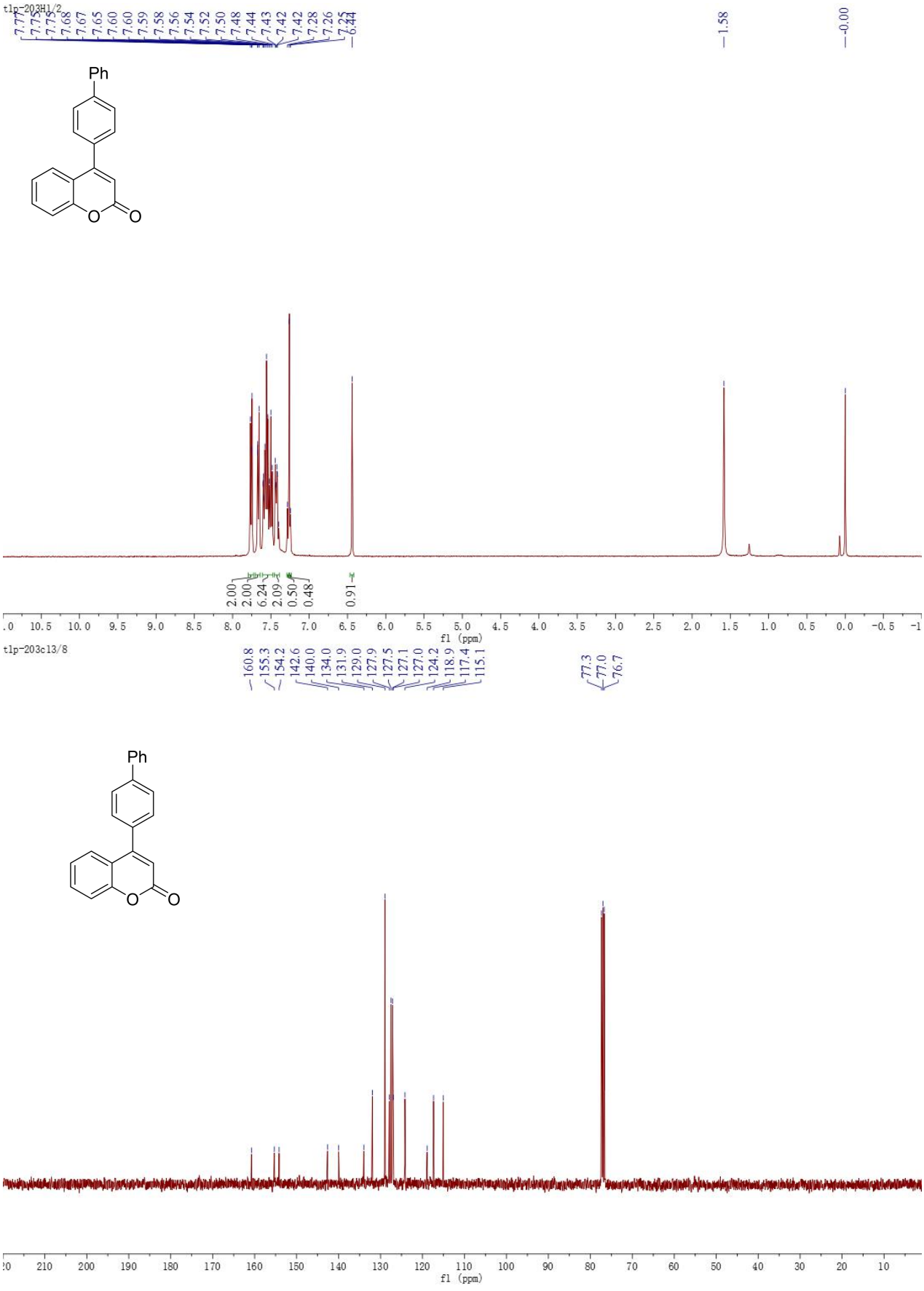
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3u



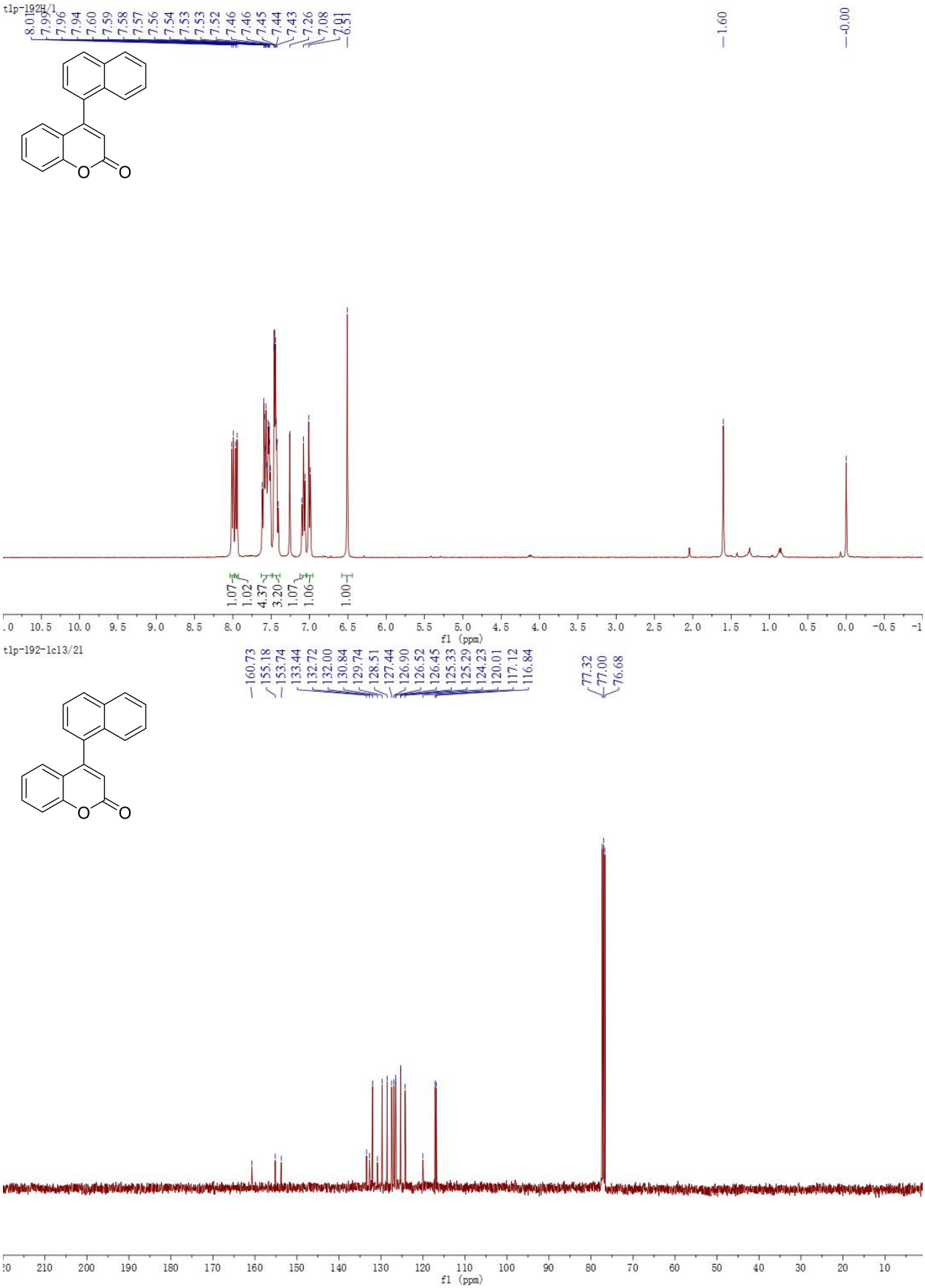
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3v



^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of 3w

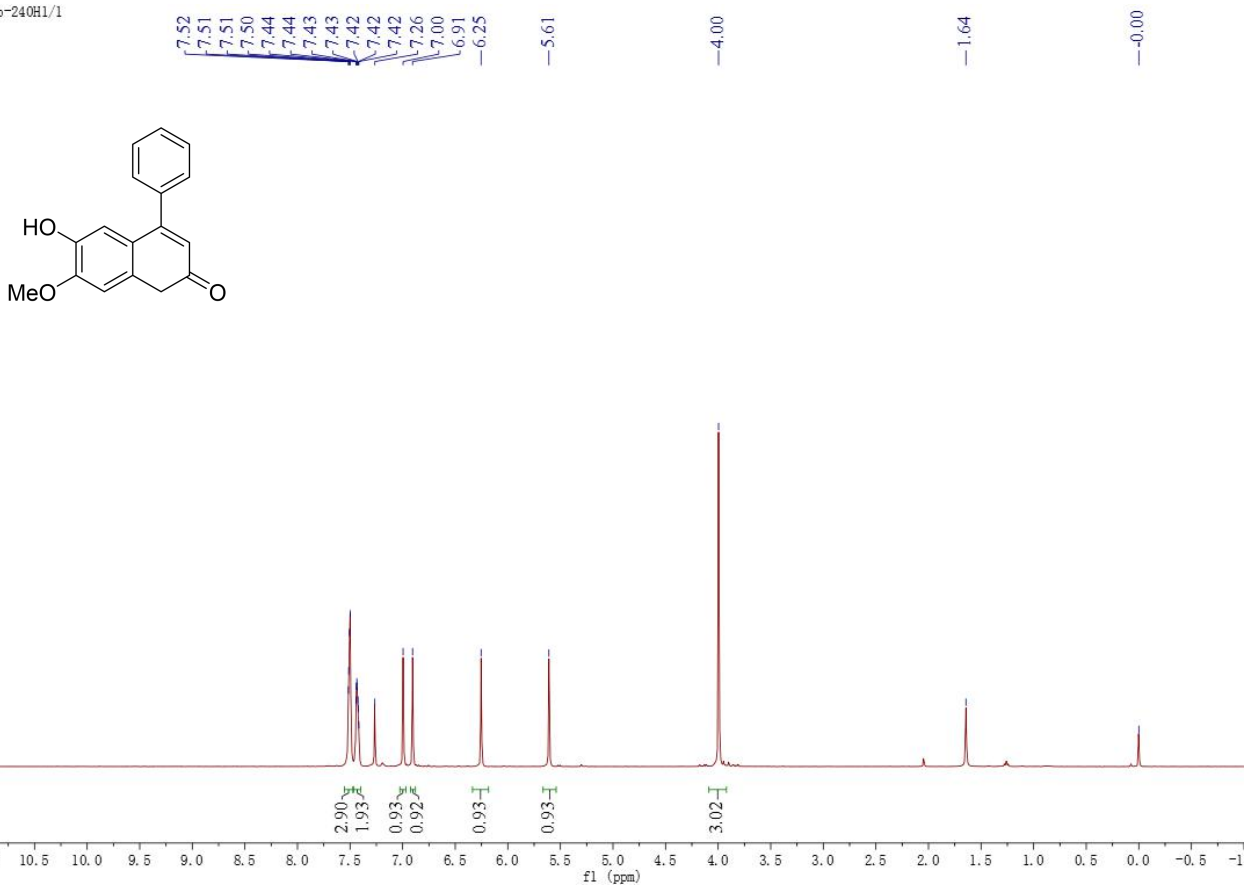


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3x

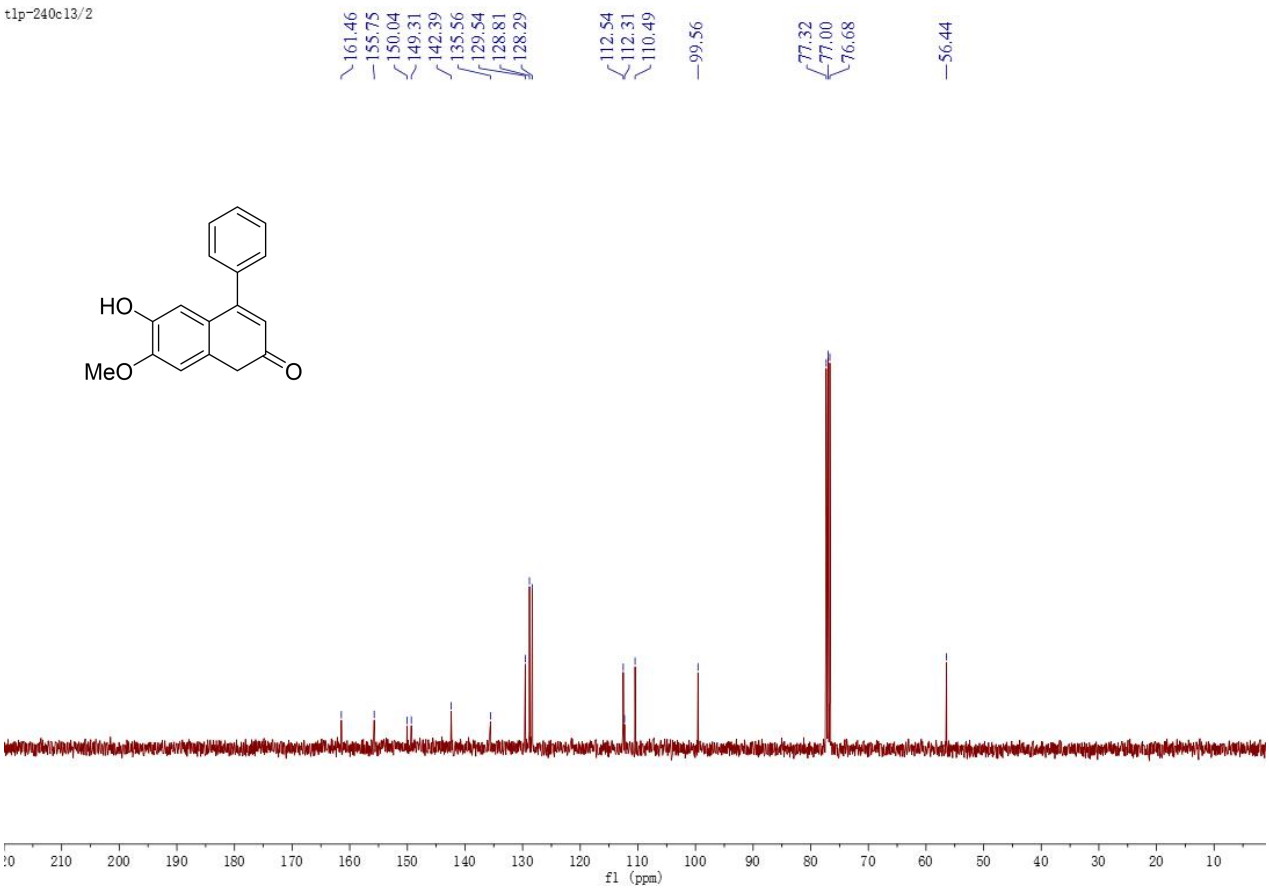


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3y

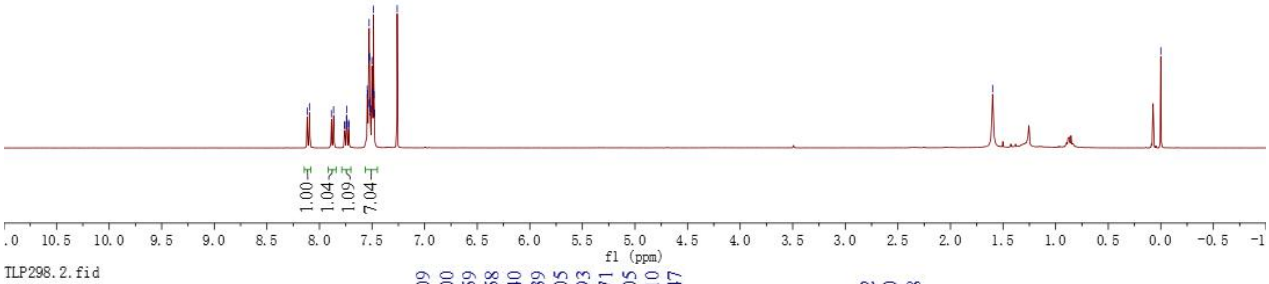
tlp-240H1/1

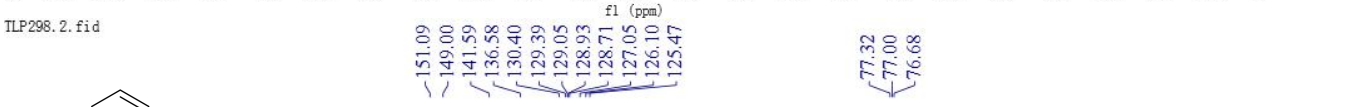


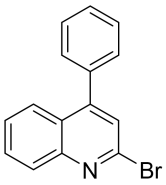
tlp-240c13/2

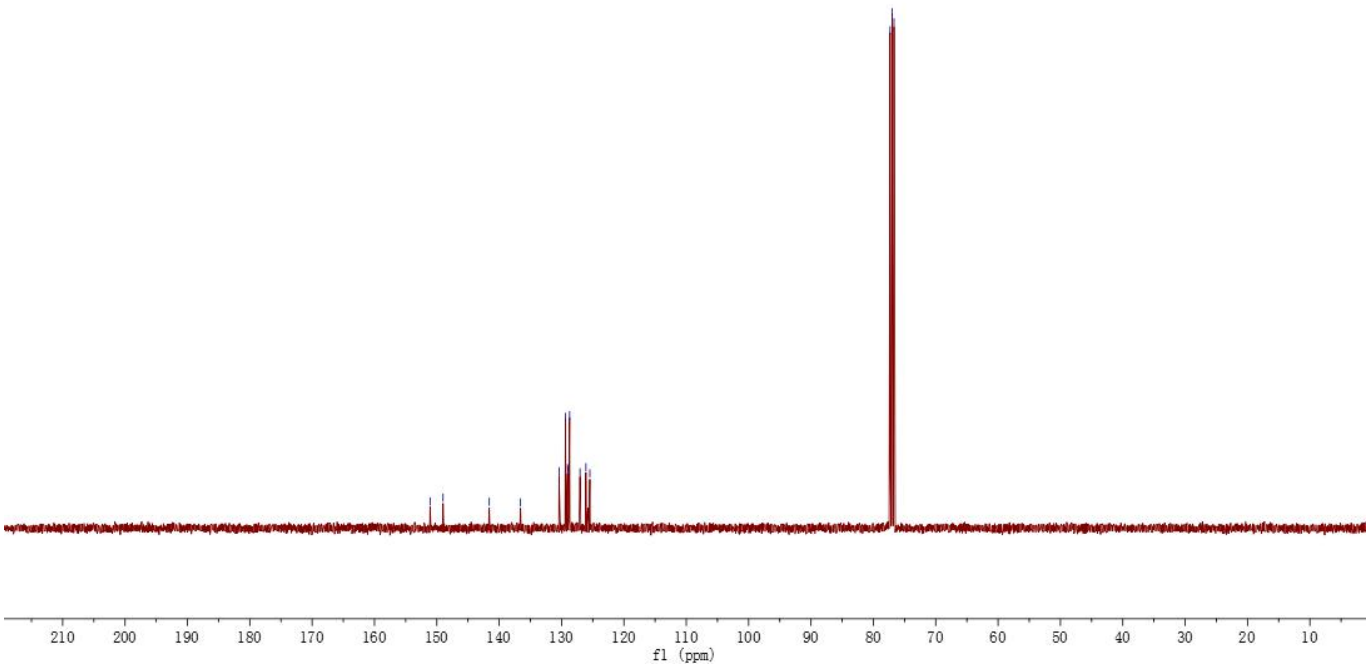


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 3z









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