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Supporting Information

Regioselective Synthesis of Fused Oxa-Heterocycles via Iodine-Mediated Annulation of Cyclic 1,3-Dicarbonyl Compounds with Propargylic Alcohols

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content

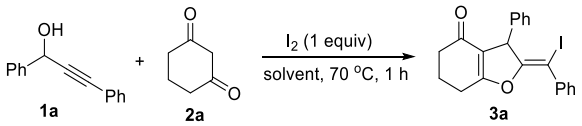
1 General Methods

Unless otherwise noted, commercially available reagents were used as received. Propargylic alcohols **1** and 4-Hydroxycoumarins **2g**–**2j** were prepared according to literature procedures.[1, 2] Compounds **2a**–**2f** were commercially available. All solvents for chromatographic separations were distilled before use. Solvents for the water-free reactions were dried with standard procedures and stored with Schlenk flasks over molecular sieves. Column chromatography was carried out with 200–300 mesh silica gel. Thin-layer chromatography (TLC) was performed on glassbacked silica plates. UV light, I_2, and solutions of 2,4-dinitrophenylhydrazine were used to visualize products. Concentrating a solution under reduced pressure refers to distillation using a rotary evaporator attached to a vacuum pump (3–10 mmHg). Products obtained as solids or high boiling oils were dried under vacuum (1–3 mmHg). 1 H and 13C NMR spectra were recorded on a 600 MHz NMR spectrometer at 293 K, and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (CDCl3 at 7.26 ppm for 1 H, and at 77.00 ppm for 13C). Data are reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. The yields in the text refer to isolated yields of compounds.

2 Reaction optimizations

2.1 Optimization for the reaction with cyclic 1,3-diones as 1,3-bis-nucleophiles.

Table S1. Optimization for the iodine-mediated propargylation/iodocyclization with cyclic 1,3-diones as 1,3-bis-nucleophiles.[a]

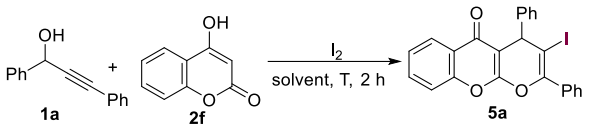


Entry	Solvent	Yield (%)
1	DMF	trace
2	DMSO	trace
3	THF	40
4	DCE	59
5	Toluene	61
6	CH_3CN	64
7	$MeNO_2$	70
8	$EtNO_2$	65
9[b]	$MeNO_2$	42
10[c]	$MeNO_2$	55
11[d]	$MeNO_2$	51
12[e]	$MeNO_2$	77
13[f]	**$MeNO_2$**	**86**
14[g]	$MeNO_2$	71

[a] *Conditions*: **1a** (0.3 mmol), **2a** (0.3 mmol), solvent (2 mL), at 70 °C, 1 h, unless otherwise noted. Isolated yields are given. DMF: *N*,*N*-dimethylformamide. DMSO: dimethyl sulfoxide. DCE: 1,2-dichloroethane. THF: tetrahydrofuran. [b] at roomtemperature. [c] at 50 °C. [d] at 90 °C. [e] 0.45 mmol of **1a** was used. [f] 0.6 mmol of **1a** was used. [g] 0.6 mmol of **2a** was used.

2.2 Optimization for the reaction with 4-hydroxycoumarins as 1,3-bis-nucleophiles.

Table S2. Optimization for the iodine-mediated propargylation/iodocyclization with 4-hydroxycoumarins as 1,3-bis-nucleophiles. [a]

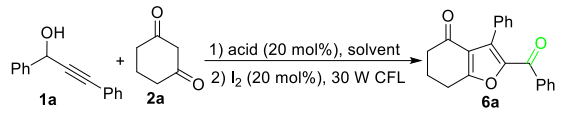


Entry	Solvent	T(°C)	Yield (%)
1	1,4-dioxane	70	trace
2	Toluene	70	trace
3	DMSO	70	trace
4	DCE	70	42
5	CH_3CN	70	57
6	**$MeNO_2$**	**70**	**67**
7	$EtNO_2$	70	61
8	$MeNO_2$	25	trace
9	$MeNO_2$	40	37
10	$MeNO_2$	60	51
11	$MeNO_2$	80	62
12	$MeNO_2$	100	53
13[b]	$MeNO_2$	70	8
14[c]	$MeNO_2$	70	52
15[d]	$MeNO_2$	70	43
16[e]	$MeNO_2$	70	76
17[f]	$MeNO_2$	70	82
18[g]	**$MeNO_2$**	**70**	**86**
19[h]	$MeNO_2$	70	69

[a] *Conditions*: **1a** (0.3 mmol), **2f** (0.3 mmol), I_2 (0.3 mmol), solvent (3 mL), 2 h, unless otherwise noted. Isolated yields are given. DMSO: dimethyl sulfoxide. DCE: 1,2-dichloroethane. [b] I_2 (0.03 mmol) was used. [c] I_2 (0.45 mmol) was used. [d] I_2 (0.6 mmol) was used. [e] **1a** (0.45 mmol) was used. [f] **1a** (0.45 mmol) and I_2 (0.36 mmol) were used. [g] **1a** (0.45 mmol) was used. One portion of I_2 (0.03 mmol) was added at the beginning. After the mixture was stirred at RT for 1 h, another portion of I_2 (0.33 mmol) was added, and the mixture was stirred at 70 °C for 1 h. [h] 0.6 mmol of **2f** was used.

2.3 Optimization for the catalytic synthesis of 2-acyl-dihydrobenzofuranones

Table S3. Optimization of the one-pot catalytic synthesis of 2-acyl-6,7-dihydrobenzofuran-4(5*H*)-ones [a]

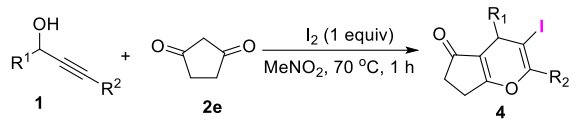


Entry	Solvent	Acid	Yield (%)
1	DCE	$TsOH{\cdot}H_2O$	40
2	DCE	TFA	16
3	DCE	$FeCl_3$	ND
4	DCE	$BF_3{\cdot}Et_2O$	51
5	DCE	$BF_3{\cdot}Et_2O$	47
6	**DCE**	**$BF_3{\cdot}Et_2O$**	**57**
7	$MeNO_2$	$BF_3{\cdot}Et_2O$	trace
8	$PhOCH_3$	$BF_3{\cdot}Et_2O$	trace
9	PhCl	$BF_3{\cdot}Et_2O$	53
10	CCl_4	$BF_3{\cdot}Et_2O$	56
11	EtOAc	$BF_3{\cdot}Et_2O$	ND
12	**toluene**	**$BF_3{\cdot}Et_2O$**	**73**

[a] *Conditions*: **1a** (0.3 mmol for entries 1–5, 0.36 mmol for entries 6–12), **2** (0.3 mmol), acid (0.06 mmol), solvent (10 mL), 70 °C for 1 h (entries 1–4) or 0.5 h (entries 5–12). Then I_2 (0.06 mmol) at RT, 30 W CFL, RT for 12 h (entries 1–8) or 5 h (entries 9–12). Isolated yields are given. The reaction vessel was general heavy-wall glass flask. CFL: household compact fluorescent lamp, a white household light bulb. DCE: 1,2-dichloroethane. TsOH: 4-toluenesulfonic acid. TFA: trifluoroacetic acid. ND: no detection.

3 Scope for the cascade annulation of cyclo-pentane-1,3-dione

Table S4. Scope for the propargylation/iodocyclization of cyclopentane-1,3-dione with propargyl alcohols [a]

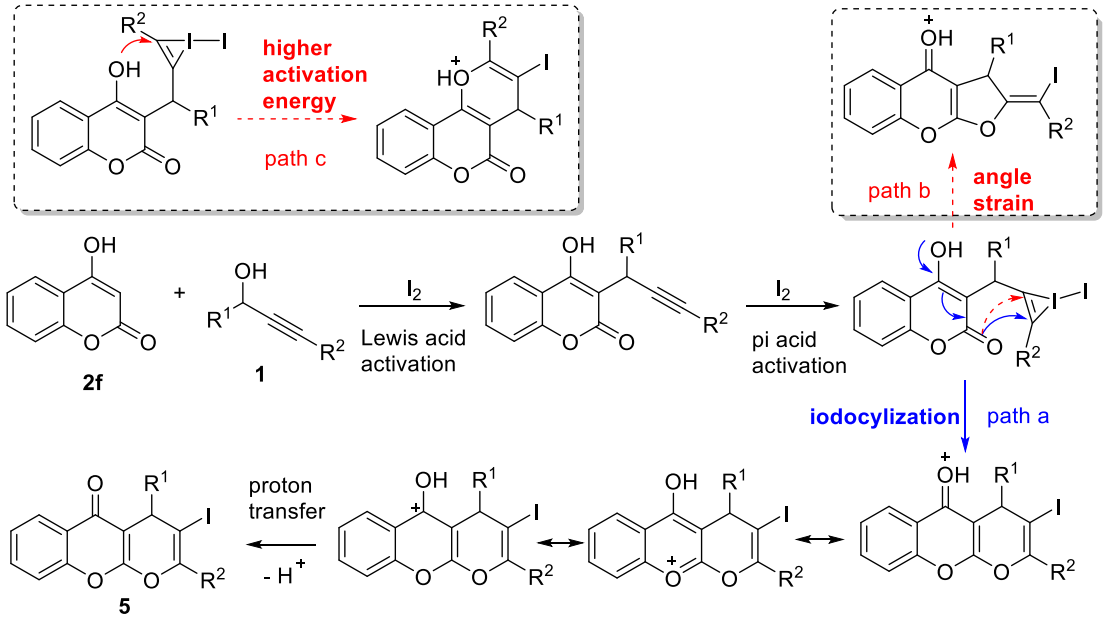


Entry	R^1	R^2	**4**	Yield
1	Ph	Ph	**4a**	88%
2	*p*-MeC_6H_4	Ph	**4b**	84%
3	*p*-EtC_6H_4	Ph	**4c**	79%
4	*p*-$^{i}PrC_6H_4$	Ph	**4d**	81%
5	*p*-$^{t}BuC_6H_4$	Ph	**4e**	73%
6	*p*-$MeOC_6H_4$	Ph	**4f**	81%
7	*p*-FC_6H_4	Ph	**4g**	89%
8	*p*-ClC_6H_4	Ph	**4h**	80%
9	*p*-BrC_6H_4	Ph	**4i**	68%
10	*m*-$MeOC_6H_4$	Ph	**4j**	73%
11	*m*-MeC_6H_4	Ph	**4k**	82%
12	*o*-MeC_6H_4	Ph	**4l**	70%
13	*o*-$MeOC_6H_4$	Ph	**4m**	53%
14	*o*-ClC_6H_4	Ph	**4n**	67%
15	2,4-$Cl_2C_6H_3$	Ph	**4o**	67%
16	3,5-$F_2C_6H_3$	Ph	**4p**	57%
17	BDO	Ph	**4q**	80%
18	3-Tp	Ph	**4r**	78%
19	Ph	*p*-MeC_6H_4	**4s**	63%
20	Ph	*p*-BrC_6H_4	**4t**	74%
21	Ph	2-Tp	**4u**	45%
22	Ph	*t*-Bu	**4v**	80%

[a] *Conditions*: **1** (0.6 mmol), **2e** (0.3 mmol), nitromethane (2 mL), at 70 °C, 1 h, unless otherwise noted. Isolated yields are given. TFA: trifluoroacetic acid. BDO: benzo[*d*][1,3]dioxol-5-yl. PMP: *p*-methoxyphenyl. 3-Tp: thiophen-3-yl. 2-Tp: thiophen-2-yl.

4 Investigations on the mechanism of cascade electrophilic cyclization

4.1 Regioselectivity of the cascade annulations of 4-hydroxycoumarin series



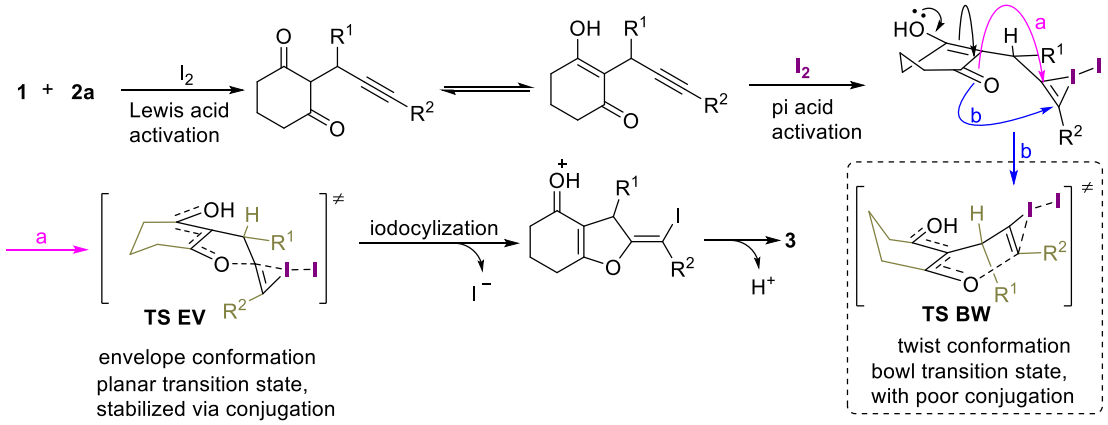
Scheme S1. Regioselectivity of the cascade annulations of 4-hydroxycoumarins.

Comments:

(1) Paths a vs b: The cyclization that gave the fused furan derivative (path b) would lead to angle strain due to the fact that the bond angles of the carbon bearing geminal dioxy in the fused furan derivative deviate somewhat from the ideal bond angle of an sp^2 carbon, whereas the corresponding pyran derivative does not require the deviation of the bond angle (path a).

(2) Paths a vs c: The activation energy of iodocyclization in path a is lower than that in path c because the positive charge of the iodocyclization intermediate in path a is stablized through electron delocalization.

4.2 Regioselectivity of the cascade annulations of cyclohexane-1,3-dione series

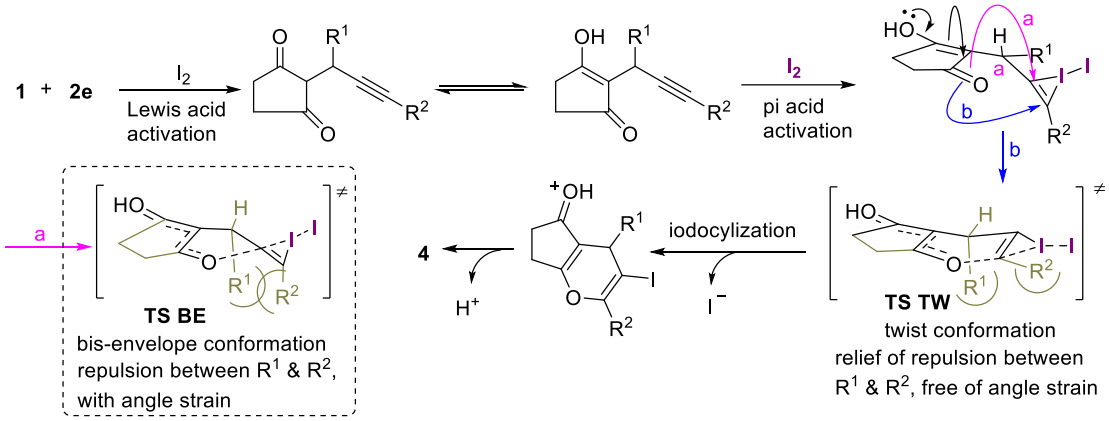


Scheme S2. Regioselectivity of the cascade annulations of cyclohexane-1,3-diones

Comments: The flexible cyclohexane-1,3-dione intermediate enables the iodocyclization

undergoes planar transition state **TS EV** (path a) that has low energy than bowl transition state **TS BW** (path b) due to the conjugation stablization.

4.3 Regioselectivity of the cascade annulations of cyclopentane-1,3-dione series

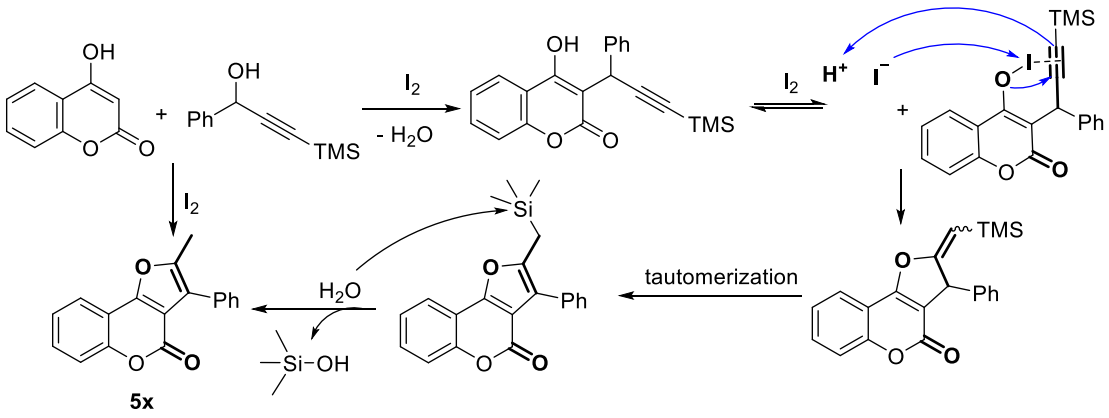


Scheme S3. Regioselectivity of the iodocyclization of propargylated cyclopentane-1,3-diones

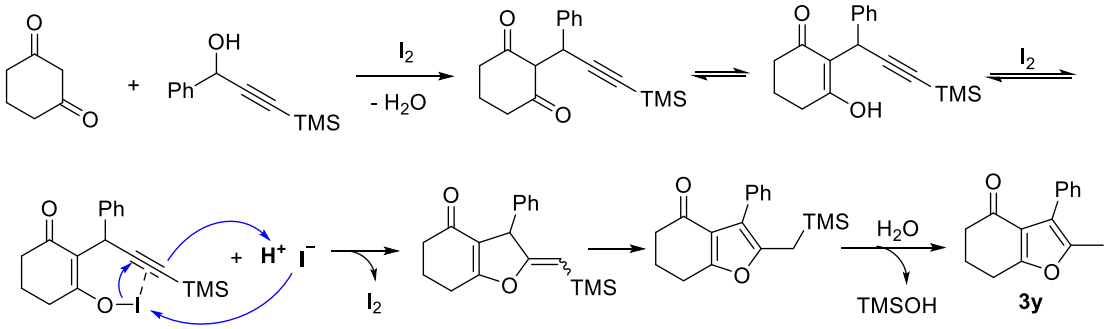
Comments: To relief the repulsion between R^1 and R^2, and angle strain, the rigid enolized cyclopentane-1,3-dione intermediate requires the iodocyclization undergoes transition state **TS TW** (path b) that has low energy than transition state **TS BE** (path a).

4.4 Proposed mechanism for the formations of 5x, 3y and 3z

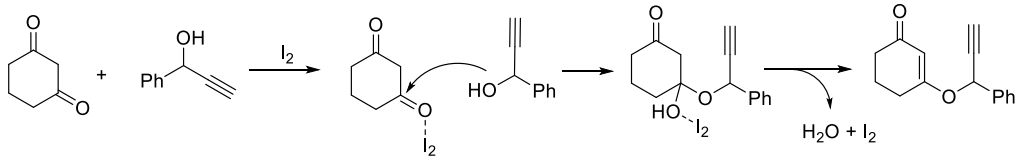
Comments: The steric hindrance of the distal silyl of alkyne moiety is unfavorable to the collision of iodine with the carbon-carbon triple bond, which prevents the intermolecular coordination of iodine with the carbon-carbon triple bond of diones. Thus, we propose that the nucleophilic annulation of hydroxyl undergoes a mechanism of intramolecular iodine-activation.



Scheme S4. Proposed mechanism for the formation of **5x**.



Scheme S5. Proposed mechanism for the formation of **3y**.



Scheme S6. Proposed mechanism for the formation of **3z**.

Comments: Absence of substituent at the distal position of alkynyl decreases the steric hindrance of the hydroxyl oxygen atom and the stability of propargyl cation, so that the hydroxyl oxygen of propargylic alcohol acts as a donor.

5 Crystallographic data of 3a, 4a and 5a

5.1 Crystallographic data of 3a

Table S5 Crystal data and structure refinement for **3a**.

Formula weight	$C_{42}H_{34}I_2O_4$
Temperature/K	856.49
Crystal system	294(1)
Space group	triclinic
a/Å	$P\bar{1}$
b/Å	8.33351(14)
c/Å	12.8458(2)
α/°	16.7190(3)
β/°	80.1645(13)
γ/°	83.2021(14)
Volume/Å^3	87.9997(14)
Z	1750.88(5)
ρ_{calcd} (g·cm^{-3})	2
μ/mm^{-1}	1.625
F(000)	14.440
Crystal size/mm^3	848.0
Radiation	0.48 × 0.43 × 0.39
2ϑrange for data collection/°	CuKα (λ = 1.54184)
Index ranges	6.984 to 143.806
Reflections collected	-10 ≤ h ≤ 8, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20
Independent reflections	31932
Data/restraints/parameters	6774 [R_{int} = 0.0526, R_{sigma} = 0.0321]
Goodness-of-fit on F^2	6774/0/433
Final R indexes [I>2σ (I)]	1.057
Final R indexes [all data]	R_1 = 0.0468, wR_2 = 0.1178
Largest diff. peak/hole / e Å^{-3}	R_1 = 0.0480, wR_2 = 0.1195
Empirical formula	0.82/-2.35

Table S6. Selected bond lengths [Å] and angles [°] for **3a**.

I1-C15	2.111(3)	C26-C27	1.335(5)
I2-C36	2.111(3)	C26-C25	1.476(5)
C15-C16	1.484(4)	C7-C14	1.526(4)
C15-C14	1.329(5)	C7-C6	1.501(4)
O2-C5	1.374(4)	C27-C22	1.453(5)

O2-C14	1.409(4)	C9-C10	1.387(6)
O4-C35	1.406(4)	C6-C1	1.450(5)
O4-C26	1.375(4)	C22-C23	1.517(6)
O3-C22	1.226(5)	C33-C32	1.368(7)
O1-C1	1.222(5)	C42-C41	1.395(5)
C36-C35	1.337(5)	C17-C18	1.398(5)
C36-C37	1.477(4)	C21-C20	1.385(5)
C34-C29	1.381(5)	C10-C11	1.371(7)
C34-C33	1.395(6)	C25-C24	1.517(6)
C35-C28	1.525(4)	C11-C12	1.394(6)
C28-C29	1.528(5)	C38-C39	1.378(6)
C28-C27	1.508(5)	C30-C31	1.387(6)
C29-C30	1.388(5)	C18-C19	1.378(6)
C16-C17	1.389(5)	C1-C2	1.509(6)
C16-C12	1.392(5)	C32-C31	1.388(7)
C8-C7	1.523(5)	C13-C12	1.375(6)
C8-C9	1.391(4)	C3-C4	1.479(7)
C8-C13	1.393(5)	C3-C2	1.445(8)
C37-C42	1.396(5)	C41-C40	1.382(6)
C37-C38	1.399(5)	C40-C39	1.373(7)
C5-C6	1.338(5)	C20-C19	1.380(6)
C5-C4	1.481(5)	C24-C23	1.515(7)
C16-C15-I1	117.1(2)	O2-C14-C7	109.3(3)
C14-C15-I1	116.3(2)	C26-C27-C28	110.0(3)
C14-C15-C16	126.6(3)	C26-C27-C22	120.8(3)
C5-O2-C14	106.2(2)	C22-C27-C28	129.1(3)
C26-O2-C35	106.6(2)	C10-C9-C8	120.2(4)
C35-C36-I2	115.3(2)	C5-C6-C7	109.4(3)
C35--C36-C37	127.2(3)	C5-C6-C1	122.2(3)
C37-C36-I2	117.5(2)	C1-C6-C7	128.4(3)
C29-C34-C33	120.2(4)	O3-C22-C27	122.9(4)
O4-C35-C28	109.5(3)	O3-C22-C23	122.5(4)
C36-C35-O4	119.2(3)	C27-C22-C23	114.6(3)
C36-C35-C28	131.2(3)	C32-C33-C34	120.4(4)
C35-C28-C29	115.1(3)	C41-C42-C37	120.8(4)
C27-C28-C35	99.0(2)	C16-C17-C18	120.1(4)
C27-C28-C29	111.7(3)	C20-C21-C16	121.0(4)
C34-C29-C28	119.9(3)	C11-C10-C9	120.8(3)
C34-C29-C30	119.1(3)	C26-C25-C24	107.5(3)
C30-C29-C28	120.9(3)	C10-C11-C12	119.4(4)
C17-C16-C15	121.4(3)	C39-C38-C37	121.2(4)
C17-C16-C21	118.5(3)	C31-C30-C29	120.7(4)
C21-C16-C15	120.2(3)	C19-C18-C17	120.7(4)
C9-C8-C7	121.5(3)	O1-C1-C6	122.1(4)

C9-C8-C13	118.5(3)	O1-C1-C2	123.8(4)
C13-C8-C7	120.0(3)	C6-C1-C2	114.1(3)
C42-C37-C36	121.0(3)	C33-C32-C31	120.0(4)
C42-C37-C38	117.6(3)	C12-C13-C8	121.0(3)
C38-C37-C36	121.4(3)	C2-C3-C4	120.9(5)
O2-C5-C4	119.1(3)	C3-C4-C5	109.7(4)
C6-C5-O2	113.6(3)	C40-C41-C42	120.1(4)
C6-C5-C4	127.2(3)	C30-C31-C32	119.6(4)
O4-C26-C25	118.5(3)	C39-C40-C41	119.7(4)
C27-C26-O4	113.0(3)	C19-C20-C21	120.4(4)
C27-C26-C25	128.4(3)	C23-C24-C25	112.7(4)
C8-C7-C14	111.7(3)	C13-C12-C11	120.0(4)
C6-C7-C8	111.8(3)	C18-C19-C20	119.3(3)
C6-C7-C14	99.4(2)	C24-C23-C22	114.1(4)
C15-C14-O2	119.4(3)	C3-C2-C1	117.5(4)
C15-C14-C7	131.3(3)	C40-C39-C38	120.6(4)

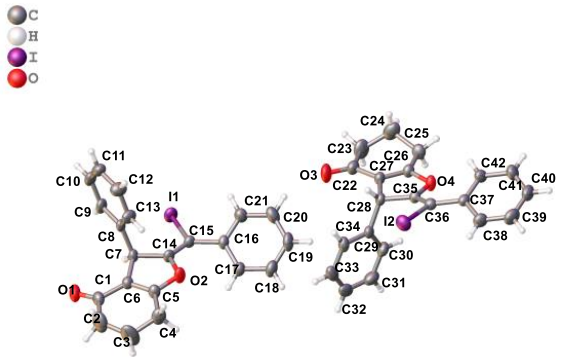


Figure S1. ORTEP drawing of **3a** with thermal ellipsoids at 50 % probability.

5.2 Crystallographic data of 4a

Table S7 Crystal data and structure refinement for **4a**

Empirical formula	$C_{20}H_{15}IO_2$
Formula weight	414.22
Temperature/K	294.6(3)
Crystal system	monoclinic
Space group	$P\bar{1}$
a/Å	10.95418(6)
b/Å	20.51469(11)
c/Å	7.29169(5)
α/°	90
β/°	98.0140(6)
γ/°	90

Volume/Å^3	1622.598(17)
Z	4
ρ_{calcd} (g·cm^{-3})	1.696
μ/mm^{-1}	15.559
F(000)	816.0
Crystal size/mm^3	0.48 × 0.23 × 0.21
Radiation	CuKα (λ = 1.54184)
2ϑrange for data collection/°	8.15 to 146.098
Index ranges	-13 ≤ h ≤ 13, -25 ≤ k ≤ 25, -9 ≤ l ≤ 6
Reflections collected	29764
Independent reflections	3220 [R_{int} = 0.0616, R_{sigma} = 0.0250]
Data/restraints/parameters	3220/0/208
Goodness-of-fit on F^2	1.024
Final R indexes [I>2σ (I)]	R_1 = 0.0445, wR_2 = 0.1251
Final R indexes [all data]	R_1 = 0.0451, wR_2 = 0.1262
Largest diff. peak/hole / e Å^{-3}	1.37/-2.17

Table S8. Selected bond lengths [Å] and angles [°] for **4a**.

I1-C13	2.099(3)	C5-C1	1.460(4)
C13-C14	1.342(4)	C15-C16	1.400(4)
C13-C6	1.517(4)	C15-C20	1.387(4)
O2-C14	1.410(3)	C11-C10	1.358(6)
O2-C4	1.353(3)	C4-C3	1.484(6)
O1-C1	1.212(4)	C9-C10	1.363(8)
C14-C15	1.481(4)	C9-C8	1.395(6)
C7-C6	1.532(4)	C1-C2	1.527(5)
C7-C12	1.382(5)	C2-C3	1.538(5)
C7-C8	1.380(4)	C18-C19	1.369(5)
C6-C5	1.503(4)	C18-C17	1.387(5)
C12-C11	1.394(5)	C16-C17	1.383(4)
C5-C4	1.334(4)	C20-C19	1.392(5)
C14-C13-I1	123.2(2)	C20-C15-C16	118.9(3)
C14-C13-C6	123.9(3)	C10-C11-C12	120.3(4)
C6-C13-I1	112.90(19)	O2-C4-C3	119.6(3)
C4-O2-C14	116.8(2)	C5-C4-O2	124.3(3)
C13-C14-O2	120.2(3)	C5-C4-C3	116.0(3)
C13-C14-C15	131.5(3)	C10-C9-C8	121.5(4)
O2-C14-C15	108.3(2)	O1-C1-C5	127.2(3)
C12-C7-C6	122.9(3)	O1-C1-C2	125.4(3)
C8-C7-C6	119.7(3)	C5-C1-C2	107.5(3)
C8-C7-C12	117.3(3)	C1-C2-C3	105.9(3)

C13-C6-C7	113.0(2)	C19-C18-C17	120.1(3)
C5-C6-C13	106.5(2)	C17-C16-C15	120.5(3)
C5-C6-C7	110.5(2)	C15-C20-C19	120.1(3)
C7-C12-C11	121.6(3)	C18-C19-C20	120.6(3)
C4-C5-C6	122.2(3)	C4-C3-C2	102.1(3)
C4-C5-C1	108.4(3)	C11-C10-C9	118.8(4)
C1-C5-C6	129.3(3)	C16-C17-C18	119.8(3)
C16-C15-C14	119.3(3)	C7-C8-C9	120.4(4)
C20-C15-C14	121.6(3)		

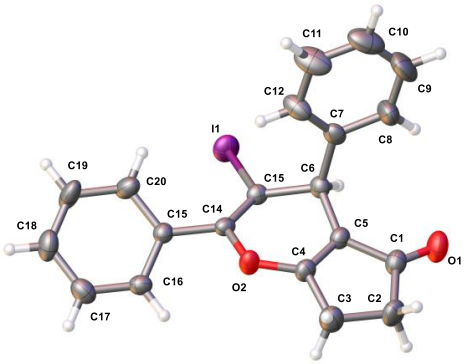


Figure S2. ORTEP drawing of **4a** with thermal ellipsoids at 50 % probability.

5.3 Crystallographic data of 5a

Table S9 Crystal data and structure refinement for **5a**

Empirical formula	$C_{24}H_{15}IO_3$
Formula weight	478.26
Temperature/K	295.20(10)
Crystal system	monoclinic
Space group	$P\bar{1}$
a/Å	11.08772(6)
b/Å	9.53388(7)
c/Å	18.28445(12)
α/°	90
β/°	99.8957(6)
γ/°	90
Volume/Å^3	1904.07(2)
Z	4
ρ_{calcd} (g·cm^{-3})	1.668
μ/mm^{-1}	13.399
F(000)	944.0
Crystal size/mm^3	0.39 × 0.38 × 0.37

Radiation	Cu *K*α (λ = 1.54184)
2ϑrange for data collection/°	8.716 to 143.64
Index ranges	-13 ≤ h ≤ 13, -10 ≤ k ≤ 11, -22 ≤ l ≤ 22
Reflections collected	34182
Independent reflections	3722 [R_{int} = 0.0779, R_{sigma} = 0.0293]
Data/restraints/parameters	3722/0/253
Goodness-of-fit on F^2	1.060
Final R indexes [I>2σ (I)]	R_1 = 0.0415, wR_2 = 0.1085
Final R indexes [all data]	R_1 = 0.0422, wR_2 = 0.1098
Largest diff. peak/hole / e Å^{-3}	1.10/-2.15

Table S10. Selected bond lengths [Å] and angles [°] for **5a**.

I1-C11	2.098(3)	C12-C12	1.333(4)
O1-C9	1.232(4)	C12-C13	1.480(4)
O2-C6	1.376(3)	C11-C10	1.512(3)
O2-C7	1.347(3)	C10-C19	1.530(4)
O3-C7	1.339(3)	C19-C20	1.392(5)
O3-C12	1.410(4)	C19-C24	1.380(6)
C1-C2	1.374(5)	C20-C21	1.378(6)
C1-C6	1.384(4)	C21-C22	1.356(9)
C2-C3	1.397(6)	C22-C23	1.398(8)
C3-C4	1.371(5)	C23-C24	1.397(5)
C4-C5	1.394(4)	C14-C15	1.396(5)
C5-C6	1.387(4)	C14-C13	1.396(4)
C5-C9	1.479(4)	C15-C16	1.377(6)
C7-C8	1.347(4)	C16-C17	1.376(6)
C8-C9	1.449(4)	C17-C18	1.388(4)
C8-C10	1.509(4)	C18-C13	1.389(5)
C7-O2-C6	117.2(2)	C11-C12-C13	132.3(3)
C7-O3-C12	117.8(2)	C12-C11-I1	122.3(2)
C2-C1-C6	118.9(3)	C12-C11-C10	124.2(2)
C1-C2-C3	120.1(3)	C10-C11-I1	113.51(18)
C4-C3-C2	120.2(3)	C8-C10-C11	109.0(2)
C3-C4-C5	120.7(3)	C8-C10-C19	111.5(2)
C4-C5-C9	121.7(3)	C11-C10-C19	112.8(2)
C6-C5-C4	118.0(3)	C20-C19-C10	118.5(3)
C6-C5-C9	120.3(3)	C24-C19-C10	122.1(3)
O2-C6-C1	116.2(3)	C24-C19-C20	119.4(3)
O2-C6-C5	121.8(3)	C21-C20-C19	120.0(5)

C1-C6-C5	122.1(3)	C22-C21-C20	121.0(5)
O3-C7-O2	107.4(2)	C21-C22-C23	120.2(4)
O3-C7-C8	125.8(2)	C24-C23-C22	119.1(5)
C8-C7-O2	126.8(2)	C19-C24-C23	120.3(4)
C7-C8-C9	118.7(3)	C15-C14-C13	120.1(3)
C7-C8-C10	119.3(2)	C16-C15-14	120.2(3)
C9-C8-C10	121.9(2)	C17-16-C15	120.0(3)
O1-C9-C5	121.8(3)	C16-C17-C18	120.4(3)
O1-C9-C8	123.6(3)	C17-C18-C13	120.5(3)
C8-C9-C5	114.6(2)	C14-C13-C12	118.9(3)
O3-C12-C13	108.2(2)	C18-C13-C12	122.1(3)
C11-C12-O3	119.5(2)	C18-C13-C14	118.9(3)

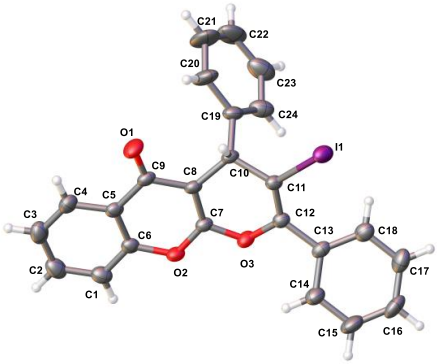


Figure S3. ORTEP drawing of **5a** with thermal ellipsoids at 50 % probability.

6 Syntheses of compounds 3–6

6.1 General procedure for the synthesis of 3 and 4

To the solution of **1** (0.6 mmol) and **2** (0.3 mmol) in CH_3NO_2 (2mL) was added iodine (76 mg, 0.3 mmol) under stirring. The reaction mixture was continually stirred at 70 °C in an oil bath until **1** was consumed as indicated by TLC (ca. 1 h). The mixture was cooled to RT, diluted with a saturated aqueous solution of sodium thiosulfate (5 mL), and extracted with ethyl acetate (3 × 5 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate as the eluent) to give the desired product.

(*E*)-2-(iodo(phenyl)methylene)-3-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3a**). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3a** (110mg, 86%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.3 Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.33 (q, *J* = 8.0 Hz, 4H), 7.25 (q, *J* = 7.0 Hz, 2H), 5.06 (s, 1H), 2.61 – 2.47 (m, 2H), 2.30 (t, *J* = 6.5 Hz, 2H), 2.04 (dd, *J* = 12.8, 6.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0, 173.1, 157.3, 139.0, 138.8, 129.7, 128.5, 128.4, 128.2, 128.1, 127.0, 119.3, 77.8, 53.2, 36.8, 23.4, 21.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}IO_2$ 429.0346; found 429.0346.

(*E*)-2-(iodo(phenyl)methylene)-3-(p-tolyl)-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3b**). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3b** (109 mg, 82%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.25 (t, *J* = 3.7 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.03 (s, 1H), 2.61 – 2.47 (m, 2H), 2.32 (s, 3H), 2.31 – 2.27 (m, 2H), 2.04 (dd, *J* = 12.7, 6.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.1, 173.0, 157.4, 138.8, 136.6 135.9, 129.7, 129.2, 128.2, 128.1, 119.4, 77.6, 52.9, 36.9, 23.4, 21.4, 21.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}IO_2$ 443.0502; found 443.0507

(*E*)-2-(iodo(phenyl)methylene)-3-(4-isopropylphenyl)-3,5,6,7tetrahydrobenzofuran-4(2*H*)-one (**3c**). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3c** (117 mg, 83%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.36 – 7.29 (m, 4H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 5.04 (s, 1H), 2.88 (m, 1H), 2.59 – 2.47 (m, 2H), 2.30 (t, *J* = 6.5 Hz, 2H), 2.07 – 2.00 (m, 2H), 1.24 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.2, 173.1, 157.5, 147.4, 138.8, 136.2, 129.7, 128.2, 128.0, 126.5, 119.5, 77.7, 52.8, 36.9, 33.7, 23.9, 23.4, 21.4.HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{23}IO_2$ 471.0815; found 471.0813

(*E*)-2-(iodo(phenyl)methylene)-3-(4-methoxyphenyl)-3,5,6,7tetrahydrobenzofuran-4(2*H*)-one (**3d**). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3d** (100 mg, 73%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.3 Hz, 2H), 7.33 (dd, *J* = 16.8, 8.2 Hz, 4H), 7.25 (d, *J* = 5.4 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.02 (s, 1H), 3.79 (s, 3H), 2.61 – 2.47 (m, 2H), 2.30 (t, *J* = 6.5 Hz, 2H), 2.04 (dd, *J* = 12.2, 6.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.2, 172.9, 158.5, 157.4, 138.8, 131.1, 129.7, 129.4, 128.1, 119.4, 113.9, 77.7, 55.2, 52.5, 36.9, 23.4, 21.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}IO_3$ 459.0452; found 459.0451.

(*E*)-3-(4-fluorophenyl)-2-(iodo(phenyl)methylene)-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3e**).Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3e** (118 mg, 88%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.31 (m, 4H), 7.27 – 7.24 (m, 1H), 7.00 (t, *J* = 8.6 Hz, 2H), 5.04 (s, 1H), 2.60 – 2.47 (m, 2H), 2.29 (t, *J* = 6.5 Hz, 2H), 2.04 (dd, *J* = 13.6, 6.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.1, 173.2, 162.6, 161.0, 157.0, 138.6, 134.81 (d, *J* = 3.2 Hz), 129.94 (d, *J* = 8.1 Hz), 129.6, 128.22 (d, *J* = 18.2 Hz), 119.1, 115.4, 115.3, 78.2, 52.5, 36.8, 23.4, 21.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{16}FIO_2$ 447.0252; found 447.0246

(*E*)-3-(4-chlorophenyl)-2-(iodo(phenyl)methylene)-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3f**). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3f** (121 mg, 87%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.33 (m, 4H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.25 (s, 1H), 5.04 (s, 1H), 2.60 – 2.49 (m, 2H), 2.30 (t, *J* = 6.6 Hz, 2H), 2.09 – 1.99 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0, 173.3, 156.7, 138.5, 137.5, 132.8, 129.7,129.6, 128.7, 128.3 128.1, 118.9, 78.3, 52.6, 36.8, 23.4, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{16}ClIO_2$ 462.9956; found 462.9956

(*E*)-3-(4-bromophenyl)-2-(iodo(phenyl)methylene)-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3g**). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3g** (126 mg, 83%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 13.1, 5.9 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.26 (m, 3H), 5.03 (s, 1H), 2.63 – 2.48 (m, 2H), 2.30 (t, *J* = 6.6 Hz, 2H), 2.05 (dd, *J* = 11.2, 5.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0, 173.3, 156.7, 138.5, 138.0, 131.6, 130.0, 129.6, 128.3, 128.1, 121.0, 118.8, 78.3, 52.7, 36.8, 23.4, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{16}BrIO_2$ 506.9451; found 506.9453

(*E*)-2-(iodo(phenyl)methylene)-3-(4-iodophenyl)-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3h**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3h** (106 mg, 64%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.26 (s, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 5.01 (s, 1H), 2.59 – 2.51 (m, 2H), 2.30 (d, *J* = 6.0 Hz, 2H), 2.08 – 2.02 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.1, 173.4, 156.6, 138.7, 138.5, 137.6, 130.3, 129.6, 128.3, 128.1, 118.8, 92.6, 78.3, 52.8, 36.8, 23.4, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{16}I_2O_2$ 554.9312; found 554.9313.

Methyl (*E*)-4-(2-(iodo(phenyl)methylene)-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-3-yl)benzoate (**3i**). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3i** (70 mg, 48%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 5.12 (s, 1H), 3.90 (s, 3H), 2.61 – 2.52 (m, 2H), 2.30 (t, *J* = 5.8 Hz, 2H), 2.09 – 2.03 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0, 173.5, 166.9, 156.6, 144.1 138.5, 129.9, 129.6, 128.9, 128.4, 128.3, 128.1, 118.7, 78.4, 53.2, 52.0, 36.8, 23.4, 21.3.HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{19}IO_4$ 487.0401; found 487.0401.

(*E*)-2-(iodo(phenyl)methylene)-3-(3-methoxyphenyl)-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3j**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3j** (90mg, 65%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.2, 0.9 Hz, 2H), 7.33 (dd, *J* = 10.6, 4.8 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.15 (dd, *J* = 6.3, 3.6 Hz, 3H), 7.07 (s, 1H), 5.15 (s, 1H), 2.68 (s, 3H), 2.55 (m, *J* = 13.2, 9.9, 4.2 Hz, 2H), 2.30 – 2.25 (m, 2H), 2.04 (dd, *J* = 12.1, 6.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0, 173.2, 159.7, 157.1, 140.4, 138.7, 129.7, 129.3, 128.1, 120.8, 119.2, 114.5, 112.2, 78.0, 55.2, 53.1, 36.8, 23.4, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}IO_3$ 459.0452; found 459.0451.

(*E*)-2-(iodo(phenyl)methylene)-3-(m-tolyl)-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3k**). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3j** (87 mg, 65%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.03 – 6.96 (m, 2H), 6.80 (dd, *J* = 8.0, 2.2 Hz, 1H), 5.04 (s, 1H), 3.82 (s, 3H), 2.60 – 2.47 (m, 2H), 2.31 (t, *J* = 6.5 Hz, 2H), 2.08 – 2.02 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 192.92 (s), 173.09 (s), 138.83 (s), 137.33 (s), 130.11 (s), 129.70 (s), 128.10 (d, *J* = 2.3 Hz), 127.12 (s), 126.49 (s), 36.92 (s), 23.47 (s), 21.48 (s), 20.19 (s). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}IO_2$ 443.0502; found 443.0507

(*E*)-3-(3-chlorophenyl)-2-(iodo(phenyl)methylene)-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3l**). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3l** (113 mg, 85%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.34 (dt, *J* = 5.8, 4.5 Hz, 4H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.26 – 7.22 (m, 2H), 5.04 (s, 1H), 2.62 – 2.50

(m, 2H), 2.33 – 2.30 (m, 2H), 2.09 – 2.04 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0, 173.5, 156.6, 140.9, 138.5, 134.3, 129.6, 128.3, 128.1, 127.3, 127.0, 118.8, 78.5, 52.8, 36.8, 23.4, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{16}ClO_2$ 462.9956; found 462.9954

(*E*)-2-(iodo(phenyl)methylene)-3-(o-tolyl)-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3m**). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3m** (105 mg, 76%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.20 (d, *J* = 6.6 Hz, 3H), 7.07 – 7.04 (m, 1H), 5.02 (d, *J* = 0.9 Hz, 1H), 2.62 – 2.48 (m, 2H), 2.35 (s, 3H), 2.33 – 2.28 (m, 2H), 2.07 – 2.01 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 193.1, 173.1, 157.4, 138.8, 137.9, 129.7, 129.1, 128.3, 128.1, 127.8, 125.4, 119.4, 77.7, 53.1, 36.9, 23.4, 21.5, 21.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}IO_2$ 443.0502; found 443.0501

(*E*)-3-(2-chlorophenyl)-2-(iodo(phenyl)methylene)-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3n**). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3n** (75 mg, 54%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.42 – 7.31 (m, 6H), 7.28 – 7.24 (m, 2H), 5.05 (d, *J* = 16.7 Hz, 1H), 2.61 – 2.49 (m, 2H), 2.31 (t, *J* = 6.5 Hz, 2H), 2.06 (dd, *J* = 11.8, 5.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.1, 172.9, 157.9, 157.3, 138.7, 131.3, 130.1, 129.7, 128.4, 128.1, 127.1, 122.1, 119.4, 77.8, 53.2, 36.8, 23.4, 21.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{16}IO_2$ 462.9956; found 462.9959

(*E*)-3-(2,4-dichlorophenyl)-2-(iodo(phenyl)methylene)-3,5,6,7-tetrahydrobenzofura-4(2*H*)-one (**3o**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3o** (92 mg, 62%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 17.3, 9.8 Hz, 3H), 7.28 – 7.22 (m, 3H), 5.33 (s, 1H), 2.61 – 2.49 (m, 2H), 2.32 (dd, *J* = 13.8, 7.5 Hz, 2H), 2.06 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 138.7, 133.6, 131.8, 129.7, 129.5, 128.2, 127.4, 77.9, 53.2, 36.8, 23.4, 21.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{15}ClIO_2$ 496.9567; found 496.9567

(*E*)-3-(benzo[d][1,3]dioxol-5-yl)-2-(iodo(phenyl)methylene)-3,5,6,7-tetrahydro benzofuran-4(2*H*)-one (**3p**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl

acetate (8/1, v/v) gave **3p** (101 mg, 71%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.25 (m, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 1.6 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.94 (d, *J* = 1.8 Hz, 2H), 4.97 (s, 1H), 2.60 – 2.48 (m, 2H), 2.31 (t, *J* = 6.5 Hz, 2H), 2.07 – 2.03 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.2, 173.1, 157.2, 147.7, 146.6, 138.7, 132.8, 129.7, 128.2, 128.1, 122.0, 119.3, 108.6, 108.2, 101.0, 78.0, 52.8, 36.9, 23.4, 21.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}IO_4$ 473.0244; found 473.0242

(*E*)-2-(iodo(phenyl)methylene)-3-(thiophen-3-yl)-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3q**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3q** (105 mg, 76%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.14 (dd, *J* = 5.0, 1.1 Hz, 1H), 5.20 (s, 1H), 2.57 – 2.48 (m, 2H), 2.34 – 2.31 (m, 2H), 2.07 – 2.02 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.2, 173.4, 156.7, 138.7, 138.4, 129.7. 129.6, 128.2, 127.5, 125.4, 122.8, 118.5, 77.7, 48.4, 36.8, 23.4, 21.3.HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{15}IO_2S$ 434.9910; found 434.9912

(*E*)-2-(iodo(p-tolyl)methylene)-3-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3r**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3r** (100 mg, 75%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 12.3, 7.9 Hz, 3H), 7.36 (d, *J* = 4.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 6.0 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.05 (s, 1H), 2.62 – 2.47 (m, 2H), 2.36 (s, 3H), 2.29 (t, *J* = 6.5 Hz, 2H), 2.04 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.2, 173.3, 156.9, 139.1, 138.2, 135.9, 133.6, 130.1, 129.5, 128.8, 128.67 – 128.3, 127.6, 127.0, 119.3, 78.2, 65.3, 53.1, 36.8, 23.4, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}IO_2$ 443.0502; found 443.0504

(*E*)-2-((4-bromophenyl)iodomethylene)-3-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3s**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3s** (105 mg, 87%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.39 (dd, *J* = 13.3, 7.9 Hz, 4H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 1H), 5.04 (s, 1H), 2.62 – 2.48 (m, 2H), 2.30 (t, *J* = 6.5 Hz, 2H), 2.05 (dd, *J* = 12.7, 6.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0, 157.9, 138.7, 137.7, 131.3, 129.7, 128.5 , 128.4, 128.3, 128.1, 127.1, 122.1, 119.4, 53.3, 36.8, 23.4, 21.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{16}BrO_2$ 506.9451; found 506.9450.

(*E*)-2-(1-iodopentylidene)-3-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3t**)**.** Purification by

flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3t** (92 mg,75%) as a yellow oil. ^{1}HNMR(600 MHz, $CDCl_3$) δ 7.30 (m, 3H), 7.26 (d, *J* = 3.1 Hz, 1H), 7.21 (m,1H), 4.84 (s, 1H), 2.71 – 2.60 (m, 2H), 2.59 – 2.53 (m, 2H), 2.29 (t, *J* = 6.6 Hz, 2H), 2.09 – 2.05 (m, 2H), 1.47 (dd, *J* = 15.0, 7.4 Hz, 2H), 1.34 (dd, *J* = 15.0, 7.4 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.2, 173.0, 156.4, 139.5, 128.3, 126.8, 119.0, 84.4, 51.8, 36.8, 36.1, 31.3, 23.4, 21.4, 13.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{21}IO_2$ 409.0659; found 409.0663.

(*E*)-2-(iodo(phenyl)methylene)-6-methyl-3-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3u**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3u** (114 mg,86%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.37 – 7.35 (m, 2H), 7.34 (s, 1H), 7.32 (d, *J* = 4.3 Hz, 2H), 7.25 (s, 1H), 5.05 (s, 1H), 2.64 – 2.56 (m, 1H), 2.35 (dd, *J* = 17.8, 14.8 Hz, 2H), 2.28 – 2.18 (m, 1H), 2.08 – 2.02 (m, 1H), 1.08 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.8, 173.0, 157.5, 140.96, 139.09 , 138.9, 138.7, 129.7, 128.6, 128.2 , 128.1, 127.6, 127.0, 119.0, 118.7, 78.0, 77.7, 65.3, 53.3, 53.1, 45.5, 45.2, 31.4, 31.3, 29.9, 29.4, 20.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}IO_2$ 443.0502; found 443.0502.

(*E*)-2-(iodo(phenyl)methylene)-6,6-dimethyl-3-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (**3v**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3v** (111 mg, 81%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H), 7.40 – 7.38 (m, 2H), 7.35 – 7.31 (m, 4H), 7.26 (dd, *J* = 6.1, 3.8 Hz, 2H), 5.06 (s, 1H), 2.43 (dd, *J* = 19.5, 9.9 Hz, 2H), 2.17 (q, *J* = 16.2 Hz, 2H), 1.10 (s, 3H), 1.04 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 192.5, 172.1, 157.6, 139.0, 138.7, 129.7, 128.5, 128.3, 128.1, 127.0 117.9, 77.8, 53.2, 51.2, 37.2, 34.2, 28.8, 28.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}IO_2$ 457.0659; found 457.0662.

(*E*)-2-(iodo(phenyl)methylene)-3,6-diphenyl-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3w**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3w** (70 mg, 46%) as a yellow soild. mp 105−107^{o} C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.31 (m, 6H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.20 (d, *J* = 7.3 Hz, 2H), 5.12 (d, *J* = 2.3 Hz, 1H), 3.45 – 3.38 (m, 1H), 2.87 – 2.82 (m, 1H), 2.77 – 2.72 (m, 1H), 2.57 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.6, 172.5, 157.4, 142.0, 139.0, 138.6, 129.7, 128.9, 128.6, 128.3, 128.2, 128.1, 127.2, 127.1, 126.6, 119.3, 78.3, 53.1, 44.1, 39.8, 31.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{21}IO_2$ 505.0659; found 505.0658.

(*E*)-2-(iodo(phenyl)methylene)-3-(4-methoxyphenyl)-6-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**3x**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3x** (83 mg, 52%) as a white solid. mp 85−87° C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.0, 5.9 Hz, 2H), 7.33 (m, 8H), 7.19 (dd, *J* = 17.4, 7.4 Hz, 2H), 6.88 (dd, *J* = 20.7, 8.6 Hz, 2H), 5.07 (s, 1H), 3.80 (d, *J* = 4.5 Hz, 3H), 3.44 (dd, *J* = 22.1, 19.0 Hz, 1H), 2.86 – 2.73 (m, 2H), 2.62 – 2.55 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.9, 172.4, 171.9, 158.6, 157.5, 142.2, 142.0, 138.7, 131.1, 130.7, 129.7, 129.4, 128.8, 128.1, 127.2, 126.7, 119.4, 119.2, 113.9, 78.1, 77.9, 55.2, 52.5, 52.3, 44.2, 40.3, 39.8, 31.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{23}IO_3$535.0765 ; found 535.0772.

2-methyl-3-phenyl-6,7-dihydrobenzofuran-4(5H)-one (**3y**)**.**[3] Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3y** (44 mg, 65%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 4H), 7.31 – 7.28 (m, 1H), 2.88 (t, *J* = 6.3 Hz, 2H), 2.50 – 2.47 (m, 2H), 2.31 (s, 3H), 2.20 – 2.14 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.9, 165.6, 148.7, 131.7, 129.8, 127.8, 127.0, 119.7, 119.2, 38.6, 23.7, 22.5, 11.9.

3-((1-phenylprop-2-yn-1-yl)oxy)cyclohex-2-en-1-one (**3z**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (8/1, v/v) gave **3z** (39 mg, 57%) as a white solid. mp 160−162 ° C . ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.39 (d, *J* = 6.6 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 5.53 (s, 1H), 5.30 (s, 1H), 2.60 – 2.48 (m, 2H), 2.35 (m, 2H), 2.01 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.3, 175.1, 135.7, 129.1, 128.8, 126.9, 121.3, 105.4, 94.2, 86.1, 36.6, 29.0, 21.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{14}O_2$ 227.1067 ; found 227.1064.

3-iodo-2,4-diphenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (**4a**)**.** Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4a** (109 mg, 88%) as a yellow solid. mp. 128−130 ° C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.44 (dd, *J* = 4.9, 1.6 Hz, 3H), 7.37 (s, 2H), 7.36 (s, 1H), 7.29 (dd, *J* = 10.3, 4.1 Hz, 1H), 4.65 (s, 1H), 2.72 – 2.68 (m, 2H), 2.48 – 2.43 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 176.9, 149.2, 141.9, 135.5, 129.8, 129.6, 128.5, 128.2, 127.5, 116.8, 81.1, 48.1, 33.8 , 25.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{15}IO_2$ 415.0189 ; found 415.0190.

3-iodo-2-phenyl-4-(p-tolyl)-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4b). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4b** (108 mg, 84%) as a yellow solid. mp. 130 − 132 ° C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 6.3, 2.9 Hz, 2H),

7.44 – 7.42 (m, 3H), 7.26 (s, 1H), 7.25 (s, 1H), 7.16 (d, *J* = 7.7 Hz, 2H), 4.60 (s, 1H), 2.68 (td, *J* = 6.6, 2.3 Hz, 2H), 2.44 (m, *J* = 10.0, 6.3, 3.2 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.4, 176.9, 149.0, 139.1, 137.2, 135.6, 129.8, 129.6, 129.3, 128.3, 128.2, 116.9, 81.6, 47.7, 33.8, 25.3, 21.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}IO_2$ 429.0346 ; found 429.0346 .

4-(4-ethylphenyl)-3-iodo-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4c). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4c** (109 mg, 79 %) as a yellow solid. mp 105 − 107 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 6.4, 2.9 Hz, 2H), 7.36 (dd, *J* = 4.8, 1.5 Hz, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.54 (s, 1H), 2.64 – 2.58 (m, 2H), 2.58 – 2.55 (m, 2H), 2.41 – 2.34 (m, 2H), 1.16 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.5, 176.9, 149.0, 143.4, 139.2, 135.6, 129.8, 129.6, 128.3, 128.2, 128.0, 116.9, 81.5, 47.7, 33.8, 28.5, 25.3, 15.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}IO_2$ 443.0502 ; found 429.0500 .

3-iodo-4-(4-isopropylphenyl)-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4d). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4d** (110 mg, 81%) as a yellow solid. mp 98 −100 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 6.3, 2.9 Hz, 2H), 7.43 (dd, *J* = 4.8, 1.6 Hz, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.61 (s, 1H), 2.92 – 2.87 (m, 1H), 2.69 (dd, *J* = 10.6, 4.1 Hz, 2H), 2.48 – 2.43 (m, 2H), 1.24 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.5, 176.9, 149.0, 147.9, 139.2, 135.6, 129.8, 129.7, 128.3, 128.2, 126.6, 117.0, 81.4, 47.7, 33.8, 33.7, 25.2, 23.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{21}IO_2$ 457.0659 ; found 457.0648.

4-(4-(tert-butyl)phenyl)-3-iodo-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4e). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4e** (103 mg, 73%) as a yellow solid. mp 152−154 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.36 (dd, *J* = 4.8, 1.5 Hz, 3H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 4.55 (s, 1H), 2.66 – 2.58 (m, 2H), 2.41 – 2.34 (m, 2H), 1.24 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.5, 176.9, 150.2, 149.0, 138.8, 135.6,129.8, 129.6, 128.2, 128.0, 125.5, 117.0, 81.3, 47.6, 34.5, 33.9, 31.3, 25.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{23}IO_2$ 471.0815; found 471.0807.

3-iodo-4-(4-methoxyphenyl)-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4f). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4f** (109 mg, 88%) as a yellow solid. mp. 70−72 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.55 (m,

2H), 7.48 – 7.43 (m, 3H), 7.26 (s, 1H), 6.91 (d, *J* = 5.9 Hz, 2H), 6.74 (m, 1H), 4.64 (s, 1H), 2.78 – 2.70 (m, 2H), 2.49 (m, 2H), 1.57 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.5, 176.7, 158.9, 148.9, 135.6, 134.3, 129.7,129.6, 129.5,128.2, 116.9, 113.9, 81.9, 55.2, 47.3, 33.8, 25.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}IO_3$ 445.0295 ; found 445.0286.

4-(4-fluorophenyl)-3-iodo-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4g). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4g** (116 mg, 89%) as a yellow solid. mp 122−124 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.47 – 7.42 (m, 3H), 7.34 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 4.63 (s, 1H), 2.74 – 2.67 (m, 2H), 2.51 – 2.42 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.4, 177.0, 163.0, 161.3, 149.3, 137.8, 135.4, 130.1 (d, *J* = 8.2 Hz), 129.9, 129.6, 116.5, 115.5, 115.4, 81.0, 47.4, 33.8, 25.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}FIO_2$ 433.0095 ; found 433.0090.

4-(4-chlorophenyl)-3-iodo-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4h). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4h** (107 mg, 80 %) as a yellow solid. mp 118−120 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.46 – 7.43 (m, 3H), 7.34 – 7.32 (m, 2H), 7.32 – 7.30 (m, 2H), 4.63 (s, 1H), 2.73 – 2.67 (m, 2H), 2.46 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 177.1, 149.5, 140.4, 135.3, 133.4, 129.9, 129.9, 129.6, 128.8, 128.3, 116.4, 80.4, 47.6, 33.8, 25.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}ClIO_2$ 448.9800 ; found 448.9794

4-(4-bromophenyl)-3-iodo-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4i). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4i** (100 mg, 68%) as a yellow solid. mp 124−126 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 3.0 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.43 (m, 3H), 7.26 (s, 1H), 7.25 (s, 1H), 4.62 (s, 1H), 2.75 – 2.68 (m, 2H), 2.51 – 2.42 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 177.1, 149.5, 140.9, 135.3, 131.7, 130.2, 129.9, 129.6, 128.3, 121.6, 116.3, 80.3, 47.6, 33.8, 25.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}BrIO_2$ 492.9295 ; found 492.9294.

3-iodo-4-(3-methoxyphenyl)-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4j). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4j** (72 mg, 53%) as a yellow solid. mp 75−77 °C . ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.45 – 7.43 (m, 3H), 7.29 (d, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.93 (s, 1H), 6.83 (dd, *J* = 8.1, 1.8 Hz, 1H), 4.62 (s, 1H), 3.83 (s, 3H), 2.74 – 2.67 (m, 2H), 2.48 (m, *J* = 14.9, 8.7,

5.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.4, 177.0, 159.7, 149.2, 143.5, 135.5, 131.7, 129.8, 129.6, 129.4, 128.2, 121.0, 114.7, 112.6, 80.8, 55.2, 48.0, 33.8, 25.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}IO_3$ 445.0295 ; found 445.0297.

3-iodo-2-phenyl-4-(m-tolyl)-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4k). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4k** (105 mg, 82%) as a yellow solid. mp 133−135 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 6.3, 2.8 Hz, 2H), 7.43 (dd, *J* = 4.9, 1.7 Hz, 3H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.15 (d, *J* = 6.7 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 4.60 (s, 1H), 2.74 – 2.66 (m, 2H), 2.44 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.4, 176.9, 149.0, 141.9, 138.1, 135.5, 129.8, 129.6, 129.3, 128.4(d, *J* = 4.9 Hz), 128.2, 125.5, 116.8, 99.9, 81.4, 48.0, 33.8, 25.3, 21.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}IO_2$ 429.0346 ; found 429.0342.

3-iodo-2-phenyl-4-(o-tolyl)-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4l). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave 4a (90 mg, 70%) as a yellow solid. mp 138−140 °C . ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.37 – 7.33 (m, 3H), 7.14 (s, 1H), 7.09 (dd, *J* = 10.5, 2.2 Hz, 2H), 4.82 (s, 1H), 2.50 (s, 2H), 2.38 – 2.29 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 176.8, 148.6, 140.9, 136.7, 135.4, 130.4, 129.8, 129.6, 128.2, 127.3, 126.6, 117.6, 81.8, 43.7, 33.7, 25.4, 19.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}IO_2$ 429.0346 ; found 429.0341 .

3-iodo-4-(2-methoxyphenyl)-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4m). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4m** (70 mg, 53%) as a yellow solid. mp 139−141 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.45 – 7.42 (m, 3H), 7.29 (d, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.93 (s, 1H), 6.83 (dd, *J* = 8.1, 1.8 Hz, 1H), 4.62 (s, 1H), 3.83 (s, 3H), 2.74 – 2.67 (m, 2H), 2.47 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.4, 177.0, 159.7, 149.2, 143.5, 135.5, 129.8, 129.6, 129.4, 128.2, 121.0, 116.7, 114.7, 112.6, 80.8, 55.2, 48.0, 33.8, 25.3.HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}IO_3$ 445.0295 ; found 445.0286.

4-(2-chlorophenyl)-3-iodo-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4n). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4n** (90 mg, 67%) as a yellow solid. mp 147−149 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.3, 2.7 Hz, 2H), 7.45 – 7.42 (m, 3H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.26 (s, 1H), 7.23 (d, *J*

= 7.4 Hz, 1H), 5.10 (s, 1H), 2.71 (dd, *J* = 11.4, 4.8 Hz, 2H), 2.48 – 2.43 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.0, 177.7,149.1, 135.5, 134.2, 130.2, 129.8, 129.5, 128.9, 128.2, 127.1, 114.5, 79.8, 45.6, 33.7, 25.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}ClIO_2$ 448.9800 ; found 448.9801.

4-(2,4-dichlorophenyl)-3-iodo-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4o). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4o** (90 mg, 67%) as a yellow solid. mp 138−140 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 6.2, 2.9 Hz, 2H), 7.45 – 7.42 (m, 3H), 7.39 (s, 1H), 7.26 (d, *J* = 4.7 Hz, 2H), 5.07 (s, 1H), 2.74 – 2.69 (m, 2H), 2.46 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.9, 177.9, 149.4, 135.3, 134.8, 134.0,130.0, 129.9, 129.4, 128.2, 127.5,114.9, 79.09 , 44.9,33.6, 25.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{13}Cl_2IO_2$ 482.9410 ; found 482.9394.

4-(3,5-difluorophenyl)-3-iodo-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4p). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4p** (77 mg, 57%) as a yellow solid. mp 152−154 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.47 – 7.44 (m, 3H), 6.91 (d, *J* = 5.9 Hz, 2H), 6.74 (m, *J* = 8.8, 5.5, 2.1 Hz, 1H), 4.64 (s, 1H), 2.78 – 2.70 (m, 2H), 2.49 (td, *J* = 6.7, 3.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.1, 177.4, 163.9, 162.3, 149.8, 145.7, 135.1, 130.0, 129.5, 128.3, 115.8, 111.6 (dd, *J* = 20.2, 5.1 Hz), 103.11 (d, *J* = 25.4 Hz), 79.1, 47.8, 33.8, 25.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{13}F_2IO_2$ 451.0001 ; found 450.9999.

4-(benzo[*d*][1,3]dioxol-5-yl)-3-iodo-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4q). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4q** (108 mg, 80%) as a yellow solid. mp 140−142 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 3.6 Hz, 2H), 7.38 – 7.35 (m, 3H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.75 (s, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.88 (d, *J* = 1.9 Hz, 2H), 4.47 (s, 1H), 2.68 – 2.59 (m, 2H), 2.39 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.5, 176.9, 149.0 147.9, 147.0, 136.1, 135.5, 129.8, 129.6, 128.2, 122.1, 116.7, 108.7, 108.2, 101.1, 81.7, 47.7, 33.8, 25.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{15}IO_4$ 459.0088 ; found 459.0083.

3-iodo-2-phenyl-4-(thiophen-3-yl)-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4r). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4r** (92 mg, 73%) as a yellow solid. mp 140−142 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 3.7 Hz, 2H), 7.46 – 7.43 (m, 3H), 7.28 (s, 1H), 7.26 (d, *J* = 5.2 Hz, 2H), 7.09 (d, *J* = 4.6 Hz, 1H), 4.78 (s, 1H), 2.72 – 2.66 (m, 2H), 2.50 – 2.46 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.4, 177.1, 149.1, 142.5, 135.5,

129.8, 129.6, 128.2, 127.3, 125.7, 123.1, 116.5, 80.3, 43.2, 33.9, 25.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}IO_2S$ 420.9754 ; found 420.9753 .

3-iodo-4-phenyl-2-(*p*-tolyl)-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4s). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4s** (80 mg, 63%) as a white solid. mp 134−136 °C .^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 5.5 Hz, 5H), 7.18 (s, 2H), 4.57 (s, 1H), 2.66 – 2.59 (m, 2H), 2.41 – 2.35 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.4, 176.0, 148.2, 141.0, 139.0, 131.6, 128.5, 127.9, 127.5, 126.5, 115.7, 79.8, 47.1, 32.8, 24.3, 20.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}BrIO_2$ 492.9295 ; found 492.9297.

2-(4-bromophenyl)-3-iodo-4-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4t). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4t** (98 mg, 74%) as a white solid. mp 157−159 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.46 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.36 (d, *J* = 5.2 Hz, 4H), 7.30 (dd, *J* = 5.9, 2.3 Hz, 1H), 4.63 (s, 1H), 2.71 (dd, *J* = 19.0, 4.7 Hz, 2H), 2.46 (dd, *J* = 10.1, 4.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.2, 176.7, 148.1, 141.7, 134.3, 131.5, 131.3, 128.6, 128.5, 127.6, 124.1, 116.8, 81.7, 48.1, 33.8, 25.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}IO_2$ 429.0346 ; found 429.0349.

3-iodo-4-phenyl-2-(thiophen-2-yl)-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4u). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **4u** (58 mg, 45%) as a yellow solid. mp 165−167 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 1H), 7.45 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.35 (d, *J* = 3.6 Hz, 1H), 7.34 – 7.33 (m, 3H), 7.27 (s, 1H), 7.10 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.66 (s, 1H), 2.78 – 2.70 (m, 2H), 2.49 – 2.42 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.2, 176.4, 143.7, 141.9, 135.9, 130.5, 128.6, 128.5, 127.8, 127.6, 126.7, 116.7, 80.66, 49.0, 33.9, 25.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}IO_2S$ 420.9754 ; found 420.9753 .

2-(*tert*-butyl)-3-iodo-4-phenyl-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4v). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (5/1, v/v) gave **4v** (94 mg, 80%) as a white solid. mp 149−151 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.4 Hz, 2H), 7.26 (s, 1H), 7.25 (s, 2H), 4.57 (s, 1H), 2.63 – 2.57 (m, 2H), 2.38 (m, 2H), 1.49 (s, 9H). ^{13}C NMR (151 MHz,

$CDCl_3$) δ 201.3 , 176.2, 154.6, 142.7, 128.4, 128.3, 127.2, 117.0, 75.9, 50.8, 37.8, 33.8, 29.3, 25.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}IO_2$ 395.0502 ; found 395.0501.

6.2 General procedure for the synthesis of 5

To the solution of **1** (0.45 mmol) and **2f-2j** (0.3 mmol) in CH_3NO_2 (2 mL) was added iodine (8 mg, 0.03 mmol) under stirring. The reaction mixture was continually stirred at RT until **1** was consumed as indicated by TLC (ca. 1 h). Another portion of iodine (83 mg, 0.33 mmol) was added. The solution was stirred at 70 °C in the oil bath until the intermediate was consumed as indicated by TLC (ca. 1 h). The mixture was cooled to RT, diluted with a saturated aqueous solution of sodium thiosulfate (5 mL), and extracted with ethyl acetate (3 × 5 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate as the eluent) to give the desired product **5**.

3-iodo-2,4-diphenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5a). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5a** (123 mg, 86%) as a white solid. mp 170-172 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 3.5 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 3.1 Hz, 3H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 3H), 7.27 (t, *J* = 7.3 Hz, 1H), 5.13 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 159.9, 152.99 , 147.3, 142.2, 134.1, 133.5, 130.1, 129.7, 128.7, 128.6, 128.3 , 127.6, 126.0, 125.3, 123.3, 117.3, 98.1, 80.1, 48.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{15}IO_3$ 479.0139 ; found 479.0138.

3-iodo-2-phenyl-4-(*p*-tolyl)-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one(5*b*). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5b** (121 mg, 82%) as a white solid. mp 162-164 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.08 (m, 1H), 7.68 – 7.65 (m, 2H), 7.62 – 7.59 (m, 1H), 7.47 – 7.44 (m, 3H), 7.39 (dd, *J* = 8.2, 2.6 Hz, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 5.09 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 159.8, 152.9, 147.1, 139.3, 137.2, 134.2, 133.4, 130.0, 129.7, 129.3, 128.5, 128.2, 126.0, 125.2, 123.3, 117.3, 98.2, 80.5, 48.5, 21.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{17}IO_3$ 493.0295; found493.0290.

4-(4-(*tert*-butyl)phenyl)-3-iodo-2-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5c). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5c** (120 mg, 75%) as a white solid. mp 174-176 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.68 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.60 (d, *J* = 7.0 Hz, 1H), 7.47 – 7.45 (m, 3H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 3H), 5.12 (s, 1H), 1.29 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 159.8, 152.9, 150.3, 147.2, 139.0, 134.1, 133.4, 130.0, 129.7, 128.28, 128.1, 126.0, 125.5, 125.3, 123.4, 117.3, 98.4, 80.2, 48.3, 34.5, 31.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{23}IO_3$ 535.0765 ; found 535.0781.

3-iodo-4-(4-methoxyphenyl)-2-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5d). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5d** (115 mg, 76%) as a white solid. mp 194-196 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.67 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.63 – 7.60 (m, 1H), 7.47 – 7.45 (m, 3H), 7.43 (s, 1H), 7.42 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.07 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 159.8, 159.0, 152.9, 147.0, 134.5, 134.1, 133.4, 130.0, 129.7, 128.2, 126.0, 125.3, 124.6, 123.3, 117.3 113.9, 98.2, 80.7, 55.2, 48.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{17}IO_4$ 509.0244 ; found 509.0252 .

4-(4-fluorophenyl)-3-iodo-2-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5e). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5e** (132 mg, 89%) as a white solid. mp 174-176 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.64 – 7.61 (m, 1H), 7.50 – 7.45 (m, 5H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.36 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.05 – 7.02 (m, 2H), 5.11 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.24 (s), 163.02 (s), 161.39 (s), 159.86 (s), 152.99 (s), 147.42 (s), 138.09 (d, *J* = 3.1 Hz), 134.01 (s), 133.63 (s), 130.34 – 130.10 (m), 129.71 (s), 128.34 (s), 125.98 (s), 125.44 (s), 123.28 (s), 117.43 (s), 115.53 (s), 115.39 (s), 97.96 (s), 80.01 (s), 48.26 (s). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{14}FIO_3$ 497.0044 ; found 497.0037.

4-(4-chlorophenyl)-3-iodo-2-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5f). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5f** (130 mg, 85%) as a white solid. mp 196-198 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.67 – 7.65 (m, 2H), 7.64 – 7.62 (m, 1H), 7.46 (dd, *J* = 6.6, 3.1 Hz, 4H), 7.44 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.36 (m, 1H), 7.33 (s, 1H), 7.32 (s, 1H), 5.11 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ

176.2, 159.9, 152.9, 147.5, 140.8, 133.9, 133.6, 133.4, 130.2, 130.0, 129.6, 128.7, 128.3, 125.9, 125.4, 123.2, 117.4, 97.7, 79.4, 48.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{14}ClIO_3$ 512.9749 ; found 512.9755.

4-(4-bromophenyl)-3-iodo-2-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5g). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5g** (138 mg, 83%) as a white solid. mp 200-202 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.65 (d, *J* = 3.5 Hz, 2H), 7.63 (dd, *J* = 4.8, 3.5 Hz, 1H), 7.48 (s, 1H), 7.48 – 7.46 (m, 4H), 7.40 (d, *J* = 9.4 Hz, 2H), 7.37 (d, *J* = 8.9 Hz, 2H), 5.10 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 159.9, 152.9, 147.6, 141.3, 133.6, 131.7, 130.3, 130.2, 129.6, 128.3, 125.9, 125.4, 124.7, 123.2, 121.6, 117.4, 97.7, 79.3, 48.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{14}BrIO_3$ 556.9244 ; found 556.9248 .

3-iodo-2-phenyl-4-(*m*-tolyl)-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5h). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5h** (115 mg, 78%) as a white solid. mp 160-162 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.9 Hz, 1H), 7.67 (dd, *J* = 6.3, 2.7 Hz, 2H), 7.60 (dd, *J* = 8.3, 7.3 Hz, 1H), 7.46–7.44 (m, 3H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.30 (s, 2H), 7.24 (dd, *J* = 4.1, 3.6 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 5.08 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 159.9, 153.0 147.1 142.1, 138.0, 134.1, 133.4, 130.0, 129.7, 129.4, 128.5, 128.3, 128.2, 126.0, 125.7, 125.3, 123.3, 117.3, 98.2, 80.4, 48.8, 21.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{17}IO_3$ 493.0295; found 493.0294.

3-iodo-4-(3-methoxyphenyl)-2-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5i). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5i** (125 mg, 82%) as a white solid. mp 164-166 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.63 – 7.60 (m, 1H), 7.47 – 7.44 (m, 3H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.36 (dd, *J* = 11.2, 3.9 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 1.9 Hz, 1H), 6.83 – 6.80 (m, 1H), 5.11 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 159.9, 159.7, 152.9, 147.3, 143.7, 134.1, 133.5, 130.1, 129.7, 129.4, 128.3, 126.0, 125.3, 123.3, 121.1, 117.3, 114.7, 112.7, 98.0, 79.9, 55.2, 48.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{17}IO_4$ 509.0244 ; found 509.0251 .

3-iodo-2-phenyl-4-(*o*-tolyl)-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5j). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5j** (106 mg, 72%) as a white solid. mp 206-208 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 1H), 7.65 – 7.63 (m, 2H), 7.62 – 7.59 (m, 1H), 7.46 – 7.43 (m, 3H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.34

(d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.19 – 7.15 (m, 3H), 5.34 (s, 1H), 2.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 160.1, 152.9, 146.4, 141.5, 137.0, 134.1, 133.4, 130.4, 130.0, 129.7, 128.2, 127.4, 126.5, 125.9, 125.3, 123.2, 117.3, 99.0, 81.0, 44.2, 20.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{17}IO_3$ 493.0295; found 493.0294.

3-iodo-4-(2-methoxyphenyl)-2-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5k). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5k** (105 mg, 69%) as a white solid. mp 176-178 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.63 – 7.59 (m, 3H), 7.45 – 7.42 (m, 4H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 6.5 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 5.30 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 160.7, 158.2, 152.9, 147.0, 134.6, 133.2, 131.4, 129.8, 129.6, 129.0, 128.2, 125.9, 125.1, 123.4, 120.6, 117.3, 111.6, 97.1, 79.3, 55.8, 45.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{17}IO_4$ 509.0244 ; found 509.0241 .

4-(2-chlorophenyl)-3-iodo-2-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5l). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5l** (110 mg, 72%) as a white solid. mp 175-177 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 5.7 Hz, 3H), 7.49 (d, *J* = 7.1 Hz, 1H), 7.46 (d, *J* = 2.8 Hz, 3H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.37 (dd, *J* = 13.1, 7.6 Hz, 2H), 7.29 (d, *J* = 6.7 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 5.53 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 160.4, 152.9, 147.3, 139.2, 134.4, 134.2, 131.9, 130.3, 130.2, 129.6, 128.9, 128.3, 127.0, 125.9, 125.4, 123.2, 117.4, 96.8,78.4, 46.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{14}ClIO_3$ 512.9749 ; found 512.9753.

4-(benzo[*d*][1,3]dioxol-5-yl)-3-iodo-2-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5m). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5m** (117 mg, 75%) as a white solid. mp 198-200 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.64 – 7.61 (m, 1H), 7.47 – 7.44 (m, 3H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.00 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.96 (d, *J* = 1.6 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.92 (dd, *J* = 7.8, 1.2 Hz, 2H), 5.03 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 159.8, 152.9, 147.8, 147.1, 147.0, 136.2, 134.1, 133.5, 130.1, 129.7, 128.3, 126.0, 125.3, 123.3, 122.3, 117.4, 108.9, 108.2, 101.0, 98.1, 80.5, 48.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for$C_{25}H_{15}IO_5$ 523.0037 ; found 523.0033.

4-(2,4-dichlorophenyl)-3-iodo-2-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5n). Purification by

flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5n** (126 mg, 77%) as a white solid. mp 184-186 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.65 – 7.63 (m, 1H), 7.63 – 7.62 (m, 2H), 7.46 (d, *J* = 2.4 Hz, 2H), 7.45 (d, *J* = 0.7 Hz, 1H), 7.42 (s, 1H), 7.42 – 7.39 (m, 2H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 2.0 Hz, 1H), 5.48 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 160.4, 152.9, 147.5, 134.9, 134.0, 133.6, 132.5,130.2, 130.1, 129.5, 128.3, 127.4, 125.9, 125.5, 123.1, 117.4, 96.6, 78.2, 46.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{13}Cl_2IO_3$ 546.9359 ; found 546.9364.

3-iodo-2-phenyl-4-(thiophen-3-yl)-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5o). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5o** (106 mg, 73%) as a white solid. mp 176-178 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.63 (dd, *J* = 11.3, 4.3 Hz, 1H), 7.47 – 7.45 (m, 3H), 7.39 (t, *J* = 8.8 Hz, 3H), 7.27 – 7.25 (m, 1H), 7.19 (dd, *J* = 5.0, 1.1 Hz, 1H), 5.30 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 159.8, 152.9, 147.4, 142.4, 134.0, 133.5, 130.1, 129.7, 128.3, 127.3, 126.0, 125.7, 125.3, 124.7, 123.3, 117.4, 97.9, 78.9, 43.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{13}IO_3S$ 484.9703 ; found 484.9703.

3-iodo-4-phenyl-2-(*p*-tolyl)-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5p). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5p** (107 mg, 73%) as a white solid. mp 182-184 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.35 (dd, *J* = 10.2, 4.8 Hz, 3H), 7.26 (d, *J* = 7.7 Hz, 3H), 5.12 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 159.9, 153.0, 147.4, 142.3, 140.3, 133.4, 131.2, 129.6, 128.9, 128.6, 128.5, 127.5, 126.0, 125.3, 123.3, 117.3, 98.2, 79.7, 48.9, 21.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{17}IO_3$ 493.0295; found 493.0304.

3-iodo-2-(4-methoxyphenyl)-4-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5q). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5q** (103 mg, 68%) as a white solid. mp 168-170 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 3H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 3H), 7.27 (d, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 5.12 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 160.8, 159.9, 153.0 , 147.2, 142.3, 133.4, 131.2, 128.6, 128.5, 127.5, 126.3, 126.01, 125.2, 123.3, 117.3, 113.6, 98.2, 79.3, 55.3, 49.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{17}IO_4$ 509.0244 ; found 509.0254 .

2-(4-bromophenyl)-3-iodo-4-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5r). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5r** (133 mg, 80%) as a white solid. mp 168-170 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.59 (s, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 5.12 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1 159.7, 152.9, 146.2, 142.0, 133.5, 132.9, 131.6 131.3, 128.6, 127.7, 126.0, 125.4, 124.4, 123.3, 117.3, 98.0, 80.6, 48.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{14}BrIO_3$ 556.9244 ; found 556.9250 .

3-iodo-4-phenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5s). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5s** (86 mg, 72%) as a white solid. mp 126-128 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.48 – 7.45 (m, 3H), 7.41 (dd, *J* = 11.1, 4.0 Hz, 1H), 7.34 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.26 (s, 1H), 6.34 (d, *J* = 2.4 Hz, 1H), 5.25 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 157.5, 153.2, 136.3, 132.7, 130.0, 129.1, 128.6, 128.2, 124.2, 122.8, 116.9, 114.8, 101.7, 85.5. 47.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{11}IO_3$ 402.9826; found 402.9820.

3-iodo-7-methyl-2,4-diphenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5t). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5t** (125 mg, 85%) as a white solid. mp 182-184 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 1.0 Hz, 1H), 7.68 – 7.66 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.45 (m, 3H), 7.41 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.26 (d, *J* = 7.3 Hz, 1H), 5.14 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 159.8, 151.1, 147.3, 142.2, 135.3, 134.6, 134.1, 130.0, 129.7, 128.6, 128.5, 128.2, 127.5, 125.5, 122.9, 117.1, 98.0, 80.0, 48.9, 20.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{17}IO_3$ 493.0295; found 493.0293.

7-chloro-3-iodo-2,4-diphenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5u). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5u** (124 mg, 81%) as a white solid. mp 196-198 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.4 Hz, 1H), 7.66 (dd, *J* = 6.3, 2.9 Hz, 2H), 7.56 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.48 – 7.45 (m, 3H), 7.37 (d, *J* = 6.8 Hz, 2H), 7.35 (s, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 5.12 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 159.9, 153.0, 147.4, 142.3, 140.3, 133.4, 131.2, 129.6, 128.9, 128.6, 128.5, 127.5, 126.0, 125.3, 117.3, 98.2, 79.7, 48.9, 21.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{14}ClIO_3$ 512.9749 ; found 512.9737.

7-bromo-3-iodo-2,4-diphenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5v). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5v** (137 mg, 82%) as a white solid. mp 192-194 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.1 Hz, 1H), 7.70 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.48 – 7.45 (m, 3H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.27 (m, 2H), 5.12 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.8, 160.0, 151.7, 147.3, 141.9, 136.4, 133.9, 130.1, 129.7, 128.7, 128.6, 128.3, 127.7, 124.7, 119.2, 118.8, 98.4, 79.9, 48.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{14}BrIO_3$ 556.9244 ; found 556.9233 .

3-iodo-7-nitro-2,4-diphenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (5w). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5w** (81 mg, 52%) as a white solid. mp 184-186 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (d, *J* = 2.7 Hz, 1H), 8.46 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.67 (dd, *J* = 5.5, 1.9 Hz, 2H), 7.55 (d, *J* = 9.1 Hz, 1H), 7.51 (d, *J* = 1.1 Hz, 1H), 7.50 (s, 1H), 7.48 (dd, *J* = 5.0, 1.6 Hz, 3H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 5.14 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 160.2, 155.7, 147.3 145.0, 141.5, 133.6, 130.3, 129.7, 128.7, 128.6, 128.4, 127.9, 123.7, 122.6, 119.0, 98.8, 79.9, 48.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{14}NIO_5$ 523.9989 ; found 523.9988 .

2-methyl-3-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (5x).[4] Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (15/1, v/v) gave **5x** (43 mg, 52%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.53 – 7.49 (m, 3H), 7.49 – 7.47 (m, 1H), 7.46 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.35 – 7.33 (m, 1H), 2.53 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.6, 156.3, 152.4, 151.6, 130.2, 130.0, 129.9, 128.2, 127.7, 124.2, 120.6, 120.5, 117.1, 112.8, 109.7, 12.5.

6.3 General procedure for the synthesis of 6

To the solution of **1** (0.36 mmol) and **2** (0.3 mmol) in toluene (10 mL) was added BF_3Et_2O (7 μL, 0.06 mmol) under stirring. The reaction mixture was continually stirred at 70 °C until **1** was consumed as indicated by TLC. The mixture was cooled to RT. Iodine (15 mg, 0.06 mmol) was added. The mixture was stirred at RT under the irradiation of 30w CFL lamp until the intermediate was consumed as indicated by TLC. It was then quenched with a saturated aqueous solution of sodium thiosulfate (5 mL), and extracted with ethyl acetate (3 × 5 mL). The combined

organic layer was washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate as the eluent) to give the desired product **6.**

2-benzoyl-3-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (6a).[5] Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6a** (68 mg, 72%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.26 (dd, *J* = 6.3, 4.8 Hz, 2H), 7.19 (dt, *J* = 20.0, 7.2 Hz, 5H), 3.05 (t, *J* = 6.3 Hz, 2H), 2.58 – 2.54 (m, 2H), 2.26 (dd, *J* = 12.8, 6.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.3, 184.5, 169.2, 147.0, 136.8, 132.4, 130.4, 129.6, 129.4, 128.3, 127.9, 127.4, 120.6, 38.8, 24.1, 22.0.

2-benzoyl-3-(*p*-tolyl)-6,7-dihydrobenzofuran-4(5*H*)-one (6b).[5] Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6b** (63 mg, 64%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 3.04 (t, *J* = 6.3 Hz, 2H), 2.58 – 2.55 (m, 2H), 2.28 (s, 3H), 2.25 (dd, *J* = 12.8, 6.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.3, 184.4, 169.2, 146.9, 138.3, 136.9, 132.7, 132.2, 130.2, 129.4, 128.2, 127.9, 126.5, 120.7, 38.8, 24.1, 22.0, 21.3.

2-benzoyl-3-(4-isopropylphenyl)-6,7-dihydrobenzofuran-4(5*H*)-one (6c). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6c** (69 mg, 64%) as a white solid. mp 105-107 °C. ^{1}HNMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 6.8 Hz, 1H), 7.22 – 7.13 (m, 4H), 7.00 (d, *J* = 7.1 Hz, 2H), 3.06 (t, *J* = 5.5 Hz, 2H), 2.81 (m, 1H), 2.60 – 2.55 (m, 2H), 2.30 – 2.21 (m, 2H), 1.18 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.5, 184.7, 169.4, 149.1, 147.0, 136.9, 132.8, 132.1, 130.4, 129.3, 127.8, 126.8, 125.5, 120.6, 38.8, 33.9, 24.1, 23.7, 22.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{23}O_3$ 359.1642 ; found 359.1638.

2-benzoyl-3-(4-methoxyphenyl)-6,7-dihydrobenzofuran-4(5*H*)-one (6d). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6d** (65 mg, 63%) as a white solid. mp 90-92 °C. ^{1}HNMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 5.4 Hz, 2H), 7.17 – 7.16 (m, 2H), 6.65 (d, *J* = 8.6 Hz, 2H), 3.69 (d, *J* = 13.8 Hz, 3H), 2.97 (t, *J* = 6.2 Hz, 2H), 2.52 – 2.47 (m, 2H), 2.18 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.5, 184.5, 169.3, 159.8, 146.8, 137.0, 132.4, 132.3, 131.9, 129.4, 128.0, 121.7, 120.6, 113.0, 55.2, 38.8, 24.1, 22.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{18}O_4$ 347.1278 ; found 347.1272.

2-benzoyl-3-(4-fluorophenyl)-6,7-dihydrobenzofuran-4(5*H*)-one (6e). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6e** (61 mg, 60%) as a white solid. mp 105-107 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.26 (m, 4H), 6.89 (t, *J* = 8.6 Hz, 2H), 3.06 (t, *J* = 6.2 Hz, 2H), 2.59 – 2.55 (m, 2H), 2.29 – 2.25 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193., 184.3, 169.3, 163.6, 161.9, 147.0, 136.8, 132., 132.32 (d, *J* = 8.4 Hz), 129.4, 128.0, 125.5, 120.5, 114.55 (d, *J* = 21.7 Hz), 38.7, 24.1, 22.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{15}FO_3$ 335.1078 ; found 335.1072.

2-benzoyl-3-(4-chlorophenyl)-6,7-dihydrobenzofuran-4(5*H*)-one (6f). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6f** (73 mg, 69%) as a white solid. mp 115-117 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.24 (m, 4H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.06 (t, *J* = 6.3 Hz, 2H), 2.60 – 2.54 (m, 2H), 2.26 (dd, *J* = 12.7, 6.4 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 193.4, 184.1, 169.2, 147.0, 136.7, 134.5, 132.6, 131.7, 131.3, 129.4, 128.1, 127.7, 120.5, 38.7, 24.1, 22.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{15}ClO_3$ 351.0782 ; found 351.0783.

2-benzoyl-3-(4-bromophenyl)-6,7-dihydrobenzofuran-4(5*H*)-one (6g). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6g** (73 mg, 69%) as a white solid. mp 115-117 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 3.05 (t, *J* = 6.3 Hz, 2H), 2.60 – 2.55 (m, 2H), 2.29 – 2.23 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.4, 184.1, 169.3, 147.0, 136.7, 132.6, 131.9, 131.3, 130.6, 129.4, 128.6, 128.1, 122.8, 120.4, 38.7, 24.1, 22.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{15}BrO_3$ 395.0277; found 395.0281

2-benzoyl-3-(3-chlorophenyl)-6,7-dihydrobenzofuran-4(5*H*)-one (6h). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6h** (71 mg, 67%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 3H), 7.22 – 7.18 (m, 2H), 7.16 – 7.13 (m, 1H), 3.06 (t, *J* = 6.3 Hz, 2H), 2.60 – 2.55 (m, 2H), 2.31 – 2.24 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.3, 184.2, 169.2, 147.2, 136.7, 133.4, 132.6, 131.5, 130.9, 130.4, 129.3, 128.7, 128.5, 128.4, 128.0, 120.5, 38.7, 24.1, 22.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{15}ClO_3$ 351.0782 ; found 351.0788.

2-benzoyl-6,7-dihydrobenzofuran-4(5*H*)-one (6i).[6] Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (5/1, v/v) gave **6i** (44 mg, 62%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.51 (dd, *J* = 10.5, 4.7 Hz, 2H), 7.38 (d, *J* = 2.2 Hz, 1H), 3.05 (dd, *J* = 8.0, 4.2 Hz, 2H), 2.58 (dd, *J* = 8.5, 4.3 Hz, 2H), 2.26 (dd, *J* = 8.4, 4.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.7, 182.5, 170.7, 151.3, 136.8, 133.0, 129.1, 128.6, 122.6, 116.7, 37.7, 23.7, 22.1.

2-(4-methylbenzoyl)-3-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (6j).[5] Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6j** (54 mg, 55%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 6.5 Hz, 2H), 7.23 – 7.18 (m, 3H), 7.03 (d, *J* = 7.9 Hz, 2H), 3.05 (t, *J* = 6.3 Hz, 2H), 2.59 – 2.55 (m, 2H), 2.31 (s, 3H), 2.26 (dd, *J* = 12.8, 6.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.4, 184.1, 169.0, 147.2, 143.3, 134.1, 132.0, 130.3, 129.7,129.6, 128.6, 128.2, 127.4, 120.6, 38.8, 24.1, 22.0, 21.5.

2-(4-bromobenzoyl)-3-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (6k). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6k** (70 mg, 59%) as a white solid. mp 130-132 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 5.1 Hz, 3H), 7.24 – 7.19 (m, 2H), 3.06 (t, *J* = 6.3 Hz, 2H), 2.59 – 2.55 (m, 2H), 2.30 – 2.24 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.2, 183.2, 169.4, 146.7, 135.6, 132.9, 131.2, 130.8, 130.3, 129.4, 128.6, 127.6, 127.4, 120.7, 38.8, 24.1, 22.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{15}BrO_3$ 395.0277; found 395.0273.

2-pentanoyl-3-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (6l). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6l** (70 mg, 65%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.7 Hz, 5H), 3.01 (t, *J* = 6.2 Hz, 2H), 2.53 (d, *J* = 7.2 Hz, 2H), 2.52 – 2.49 (m, 2H), 2.26 – 2.21 (m, 2H), 1.56 – 1.51 (m, 2H), 1.21 (dd, *J* = 14.9, 7.4 Hz, 2H), 0.81 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.2, 190.4, 168.5, 147.4, 130.8, 130.2, 129.7, 128.6, 127.8, 121.3, 39.5, 38.6, 26.0, 24.0, 22.2, 22.0, 13.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{20}O_3$ 297.1485; found 297.1485.

3-phenyl-2-(3-phenylpropanoyl)-6,7-dihydrobenzofuran-4(5*H*)-one (6m). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (5/1, v/v) gave **6m** (72 mg, 65%) as a white solid. mp 117-119 °C. ^{1}HNMR (600 MHz, $CDCl_3$) δ 7.40 (s, 3H), 7.39 (s, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.16 (t, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 2H), 2.97 (t, *J* = 6.1 Hz, 2H), 2.89 (s, 4H),

2.49 (d, *J* = 6.2 Hz, 2H), 2.22 – 2.18 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0, 184.5, 169.0, 147.2, 136.8, 132.4, 130.4, 129.6, 129.4, 128.4, 127.9, 127.4, 120.2, 47.2, 32.0, 30.2, 21.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{20}O_3$ 345.1485; found 345.1484.

3-(4-methoxyphenyl)-4-oxo-4,5,6,7-tetrahydrobenzofuran-2-carbaldehyde (6n). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (5/1, v/v) gave **6n** (47 mg, 57%) as a white solid. mp 130-132 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 3.04 (t, *J* = 6.3 Hz, 2H), 2.58 (t, *J* = 6.5 Hz, 2H), 2.28 – 2.23 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 193.3, 177.9, 171.2, 160.8, 147.6, 137.3, 131.9, 120.3, 120.0, 113.7, 55.3, 38.7, 24.1, 21.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}O_4$ 271.0965; found 271.0962.

4-oxo-4,5,6,7-tetrahydrobenzofuran-2-carbaldehyde (6o). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6o** (32 mg, 57%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (d, *J* = 2.1 Hz, 1H), 7.46 (s, 1H), 3.01 (d, *J* = 5.7 Hz, 2H), 2.59 – 2.56 (m, 2H), 2.27 – 2.24 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.3, 177.5, 171.3, 152.2, 122.8, 117.7, 37.6, 23.6, 22.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_8O_3$ 165.0546; found 165.0543.

3-(4-methoxyphenyl)-6,6-dimethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran-2-carbaldehyde (6p). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (5/1, v/v) gave **6p** (54 mg, 60%) as a white solid. mp 108-110 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.51 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 2.89 (s, 2H), 2.46 (s, 2H), 1.19 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.8, 177.8, 170.5, 160.8, 148.0, 137.1, 132.0, 120.0, 119.2, 113.8, 55.3, 53.1, 37.9, 34.6, 28.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{18}O_4$ 299.1278 ; found 299.1275.

6,6-dimethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran-2-carbaldehyde (6q). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (20/1, v/v) gave **6q** (31 mg, 53%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.46 (s, 1H), 2.87 (s, 2H), 2.45 (s, 2H), 1.17 (s, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 192.8, 177.4, 170.5, 152.6, 121.7, 117.6, 52.0, 37.5, 35.1, 28.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{12}O_3$ 193.0859 ; found 193.0856.

2-benzoyl-6,6-dimethyl-3-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (6r).[5] Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) gave **6r** (73 mg,

71%) as a white solid. ^{1}HNMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 6.9 Hz, 2H), 7.19 (dt, *J* = 14.0, 7.3 Hz, 5H), 2.93 (s, 2H), 2.46 (s, 2H), 1.21 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.9, 184.5, 168.5, 147.4, 136.8, 132.4, 130.4, 129.5, 129.4, 128.4, 127.9, 127.4, 119.5, 53.1, 38.0, 34.8, 28.5.

2-benzoyl-6-methyl-3-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (6s). Purification by flash column chromatography eluting with petroleum ether/ethyl acetate (20/3, v/v) gave **6s** (68 mg, 69%) as a white solid. mp 107-109 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.28 (s, 1H), 7.27 (s, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 4.9 Hz, 2H), 7.17 (s, 1H), 3.14 (dd, *J* = 17.5, 4.7 Hz, 1H), 2.70 (dd, *J* = 17.5, 10.0 Hz, 1H), 2.60 (dd, *J* = 16.2, 3.2 Hz, 1H), 2.56 – 2.51 (m, 1H), 2.34 (d, *J* = 11.5 Hz, 1H), 1.22 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.2, 176.4, 143.7, 141.9, 135.9, 130.5, 128.6, 128.5, 127.8, 127.6, 127.0, 126.7, 116.7, 80.6, 65.3, 49.0, 33.9, 25.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for$C_{22}H_{18}O_3$ 331.1329 ; found 331.1328.

7 Scale-up synthesis and synthetic transformations of 3a

7.1 Scale-up synthesis of 3a

To a solution of **1a** (1.25 g, 6 mmol) in CH_3NO_2 (40 mL) was added **2a** (337 mg, 3 mmol) and iodine (0.95 g, 3 mmol). The reaction mixture was heated at 70 °C for 70 min in an oil bath. It was then quenched with a saturated aqueous solution of sodium thiosulfate (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (hexanes/ethyl acetate = 20:1) to give the desired product **3a** (0.95 g, 74 %).

7.2 Base-catalyzed hydrolysis of 3a

To a solution of **3a** (86 mg, 0.2 mmol) in CH_3NO_2 (5mL) was added DBU (60 μL, 0.4 mmol). The reaction mixture was heated at 70 °C in an oil bath until **3a** was consumed as indicated by TLC (10 h). It was then diluted with a saturated aqueous solution of NH_4Cl (5 mL). The organic layer was concentrated in vacuo. The crude was purified by column chromatography on silica gel (hexanes/ethyl acetate = 5:1) to give **2-(hydroxy(phenyl)methyl)-3-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one** (**7**) as a colorless oil (47 mg, 75 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44

– 7.40 (m, 4H), 7.40 – 7.35 (m, 4H), 7.34 – 7.25 (m, 2H), 5.79 (s, 1H), 2.89 (m, 2H), 2.48 (m, 2H), 2.17 (dd, *J* = 12.8, 6.3 Hz, 2H), 1.26 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.8, 167.1, 150.7, 140.7, 130.6, 129.9, 128.5, 128.0, 127.9, 127.8, 126.4, 122.2, 119.7, 67.6, 38.5, 23.8, 22.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}O_3$ 319.1329 ; found 319.1331.

7.3 Pd-catalyzed cross couplings of 3a

2-(Diphenylmethylene)-3-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**8**). A mixture of **3a** (86 mg, 0.2 mmol), K_2CO_3 (83 mg, 0.6 mmol), $Pd(PPh_3)_4$ (2.3 mg, 0.002 mmol) and phenylboronic acid (30.0 mg, 0.24 mmol) in H_2O/1,4-Dioxane (1:1, 4 mL) were degassed with Ar for 20 min. It was heated at 70 °C in an oil bath until **3a** was consumed as indicated by TLC (10 h). The micture was deluted with EtOAc (5 mL). The organic layer was concentrated in vacuo. The crude was purified by column chromatography on silica gel (hexanes/ethyl acetate = 8:1) to give **8** (69 mg, 91%) as a white solid. mp 170-172 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.18 (m, 2H), 7.13 (dd, *J* = 7.9, 6.7 Hz, 2H), 7.06 – 7.03 (m, 3H), 6.87 (d, *J* = 7.6 Hz, 2H), 6.81 (dd, *J* = 6.2, 2.9 Hz, 2H), 4.95 (s, 1H), 2.78 – 2.61 (m, 2H), 2.32 (t, *J* = 6.5 Hz, 2H), 2.15 – 2.09 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.2, 173.5, 156.4, 140.5, 138.3, 138.0, 130.0, 129.1, 128.3, 127.9, 127.3, 127.1, 126.9, 126.4, 119.9, 119.3, 48.4, 36.9, 23.4, 21.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{22}O_2$ 376.1693 ; found 376.1699.

(*E*)-2-(1,3-Diphenylprop-2-yn-1-ylidene)-3-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (**9**)**.** To a solution of **3a** (86 mg, 0.2 mmol) in triethylamine (3 mL) was added $Pd(PPh3)_2Cl_2$ (4.2 mg, 0.006 mmol) and copper(I)iodide (1.9 mg, 0.006 mmol) in a flame-dried flask. The mixture was degassed with Ar for 20 min. Phenylacetylene (25 mg, 0.24 mmol) was added. The mixture was stirred at 70 °C in an oil bath until **3a** was consumed as indicated by TLC (12 h). It was then concentrated in a vacuum. The residue was diluted and extracted with EtOAc (5 mL × 2). The combined organic layer was dried with anhydrous Na_2SO_4, and concentrated in vacuo. The crude was purified by column chromatography on silica gel (hexanes/ethyl acetate = 10:1) to give **9** (66 mg, 82%) as a yellow solid. mp 96-98 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.39 (t, *J* = 6.7 Hz, 4H), 7.32 – 7.24 (m, 7H), 7.22 – 7.18 (m, 2H), 5.32 (s, 1H), 2.77 – 2.65 (m, 2H), 2.38 – 2.33 (m, 2H), 2.16 – 2.09 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.1, 172.7, 163.5, 139.0, 134.4, 131.2, 128.3, 128.2, 128.1, 127.4, 126.9, 123.2, 119.8, 102.9, 95.5, 86.2, 50.8, 37.0, 23.3, 21.5.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{22}O_2$ 403.1693 ; found 403.1694.

7.4 Synthesis of 11 from 3a

2-Benzoyl-3-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (**6a**). The solution of **3a** (86 mg, 0.2 mmol,) in EtOAc (2 mL) was stirred at RT under the irradiation of 30 W CFL lamp until **3a** was consumed as indicated by TLC (2 h). It was then quenched with a saturated aqueous solution of sodium thiosulfate (5 mL), and extracted with ethyl acetate (3 × 5 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. the crude was purified by column chromatography on silica gel (hexanes/ethyl acetate = 5:1) to give **6a** (58 mg, 92%) as a white solid.

2-Benzoyl-5-bromo-3-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one(10). To a solution of **6a** (64 mg, 0.2 mmol) in methanol (3 mL) was added $CuBr_2$ (90mg, 0.4mmol, 2.0 equiv). It was refluxed in an oil bath until **6a** was consumed as indicated by TLC (2 h). The mixture was dissolved in EtOAc (5 mL), and concentrated in vacuo. The crude was purified by column chromatography on silica gel (hexanes/ethyl acetate = 80:1) to give **10** (72 mg, 91%) as a white solid. mp 155-157 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.21 (m, 5H), 4.56 (t, *J* = 3.2 Hz, 1H), 3.31 (m,1H), 3.06 (m, 1H), 2.65 – 2.54 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.1, 184.3, 167.5, 147.4, 136.5, 132.8, 132.6, 130.3, 129.4, 129.0, 128.6, 128.0, 127.5, 118.0, 49.4, 30.6, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{15}BrO_3$ 395.0277 ; found 395.0266.

(4-Hydroxy-3-phenylbenzofuran-2-yl)(phenyl)methanone (**11**).[7] To a solution of **10** (109 mg, 0.2758 mmol) in triethylamine (3 mL) was added a mixture of PPh_3 (4.3 mg, 0.016 mmol), $Pd(OAc)_2$ (1.8 mg, 0.008 mmol) in a flame-dried flask. The mixture was degassed with Ar for 20 min, and heated at 80 °C in an oil bath until **10** was consumed as indicated by TLC (8 h). It was then diluted with EtOAc (5 mL), and quenched with a saturated aqueous solution of NH_4Cl (5 mL) The organic layer was concentrated in vacuo. The crude was purified by column chromatography on silica gel (hexanes/ethyl acetate = 10:1) to give **11** (76 mg, 88%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.52 (s, 1H), 7.50 (d, *J* = 12.2 Hz, 2H), 7.43 (s, 1H), 7.41 (s, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 5.31 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 184.9, 155.5, 152.1, 146.5, 137.1, 132.6, 131.4, 129.7, 129.5, 129.0, 128.1, 127.8, 116.1, 109.4, 104.7.

8 Reference

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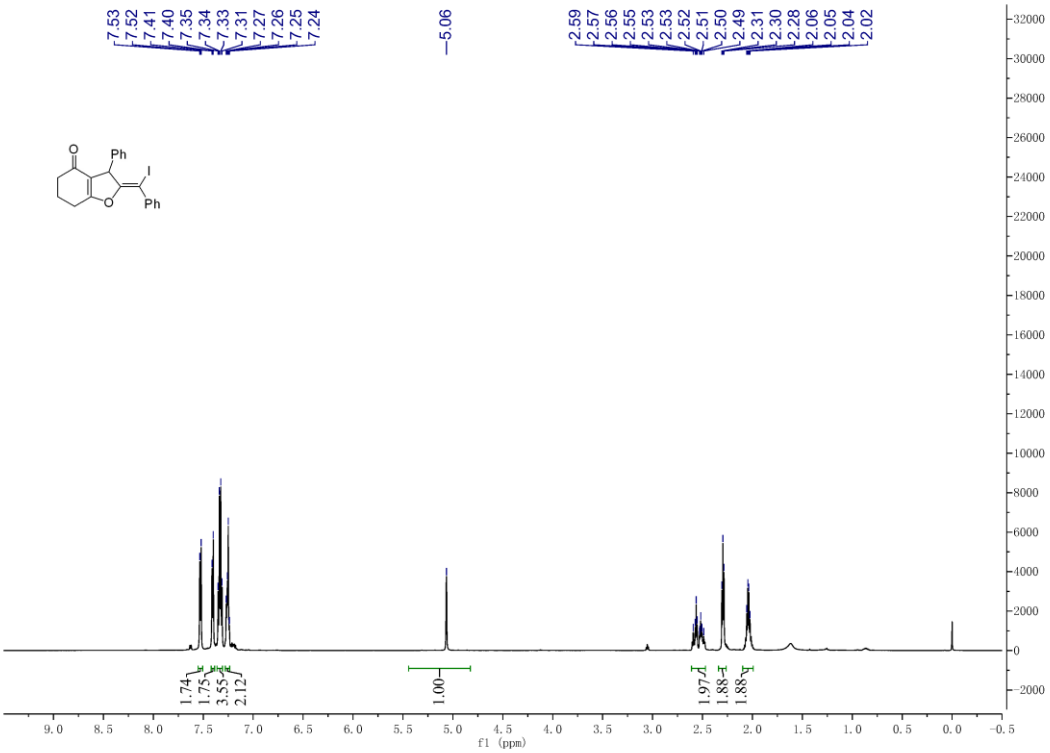
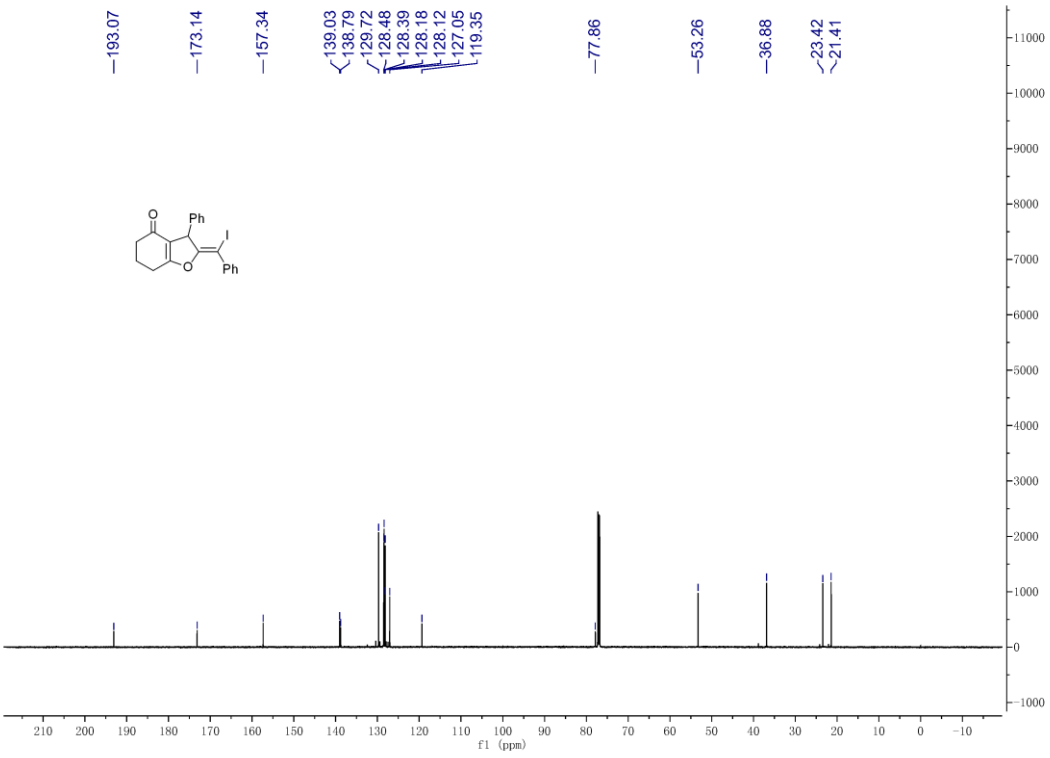
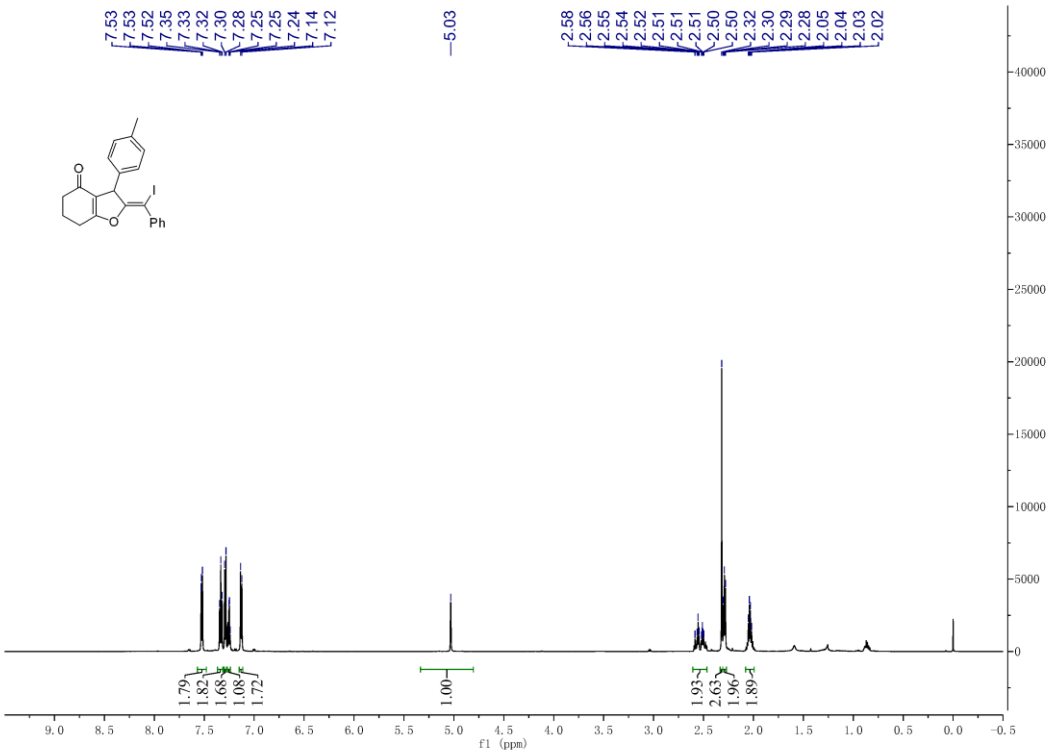
9 NMR spectra of compounds 3–11



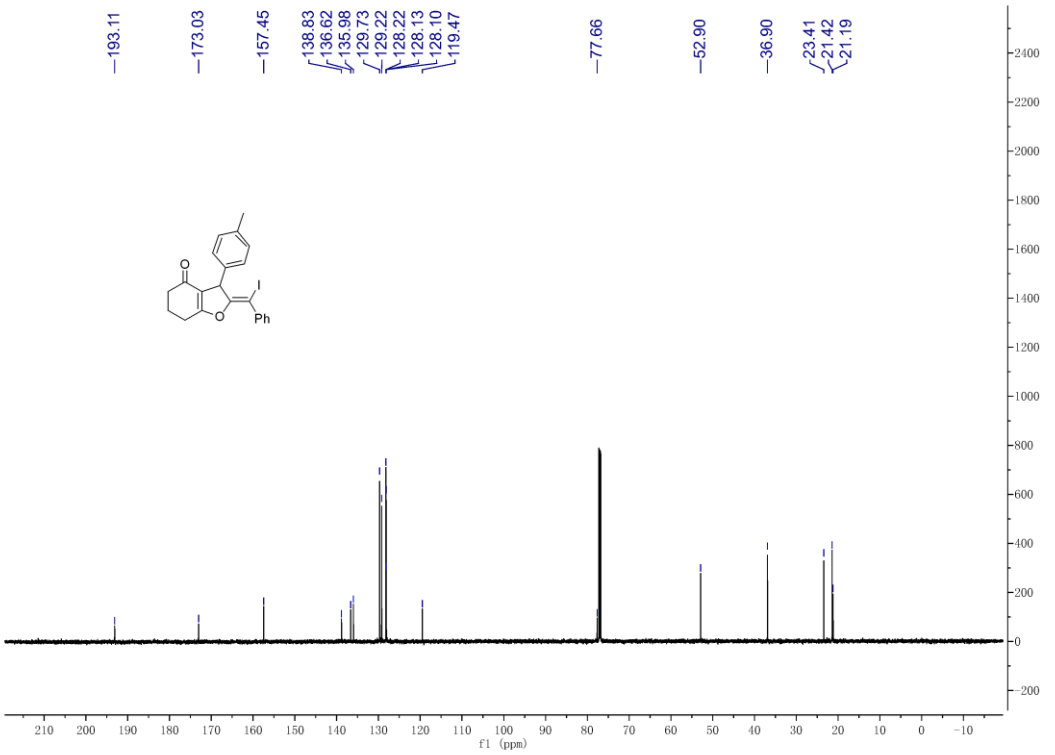
^{1}H NMR spectrum of **3a** (600 MHz, $CDCl_3$)



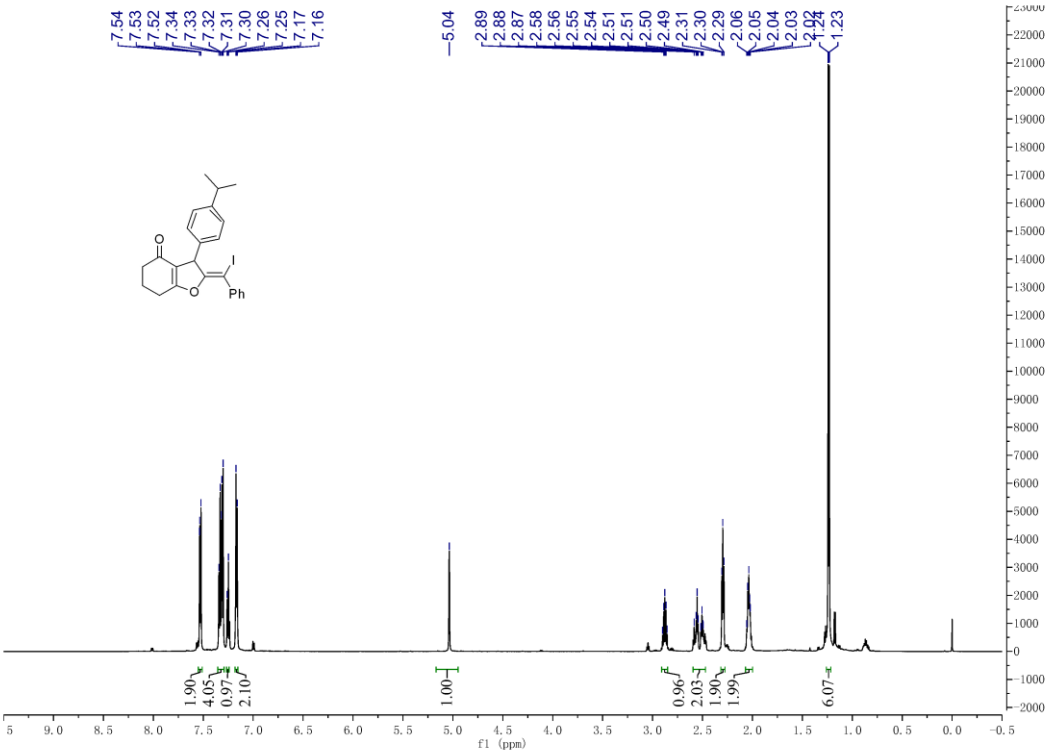
^{13}C NMR spectrum of **3a** (151 MHz, $CDCl_3$)



^{1}H NMR spectrum of **3b** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3b**(151 MHz, $CDCl_3$)



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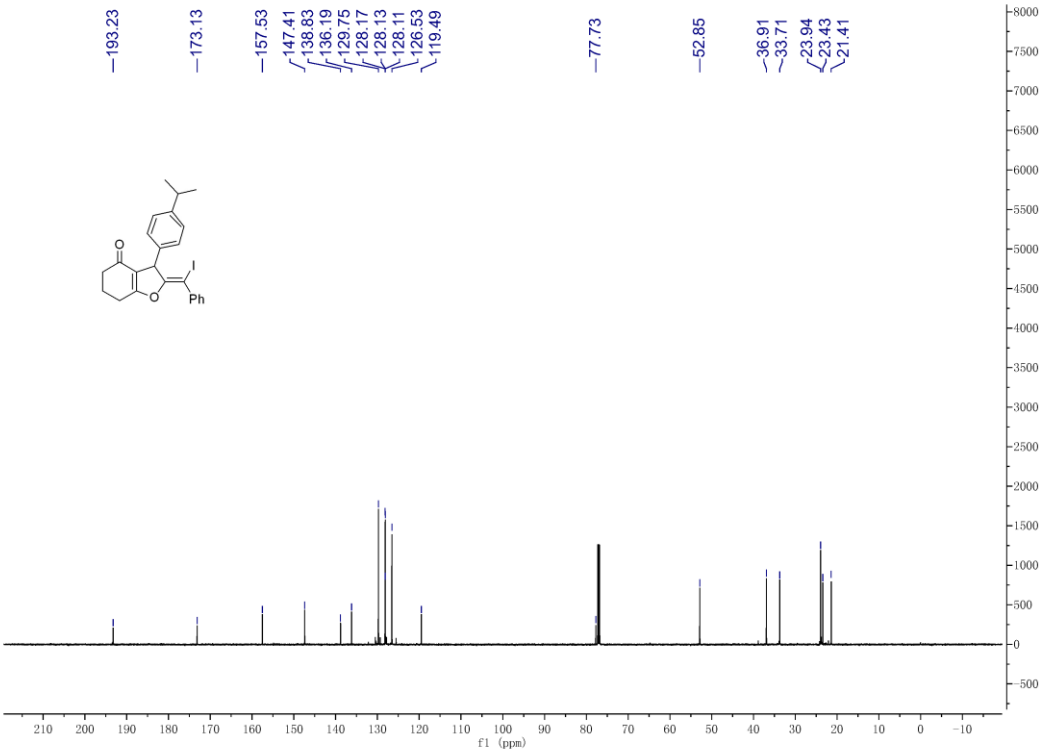

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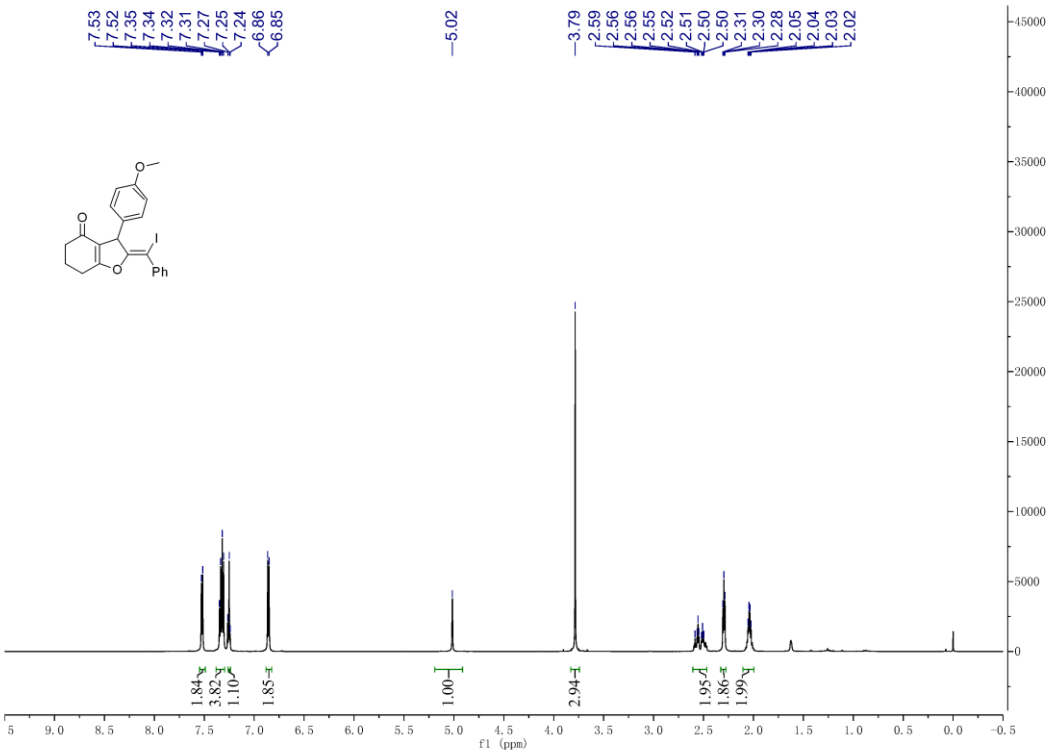
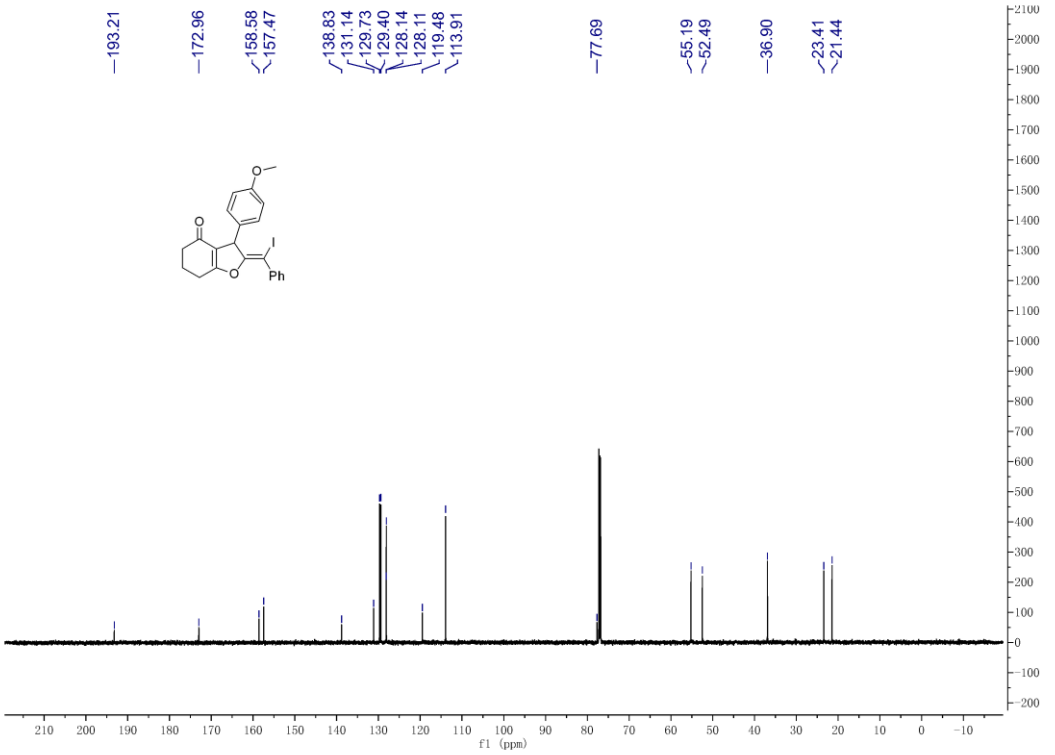
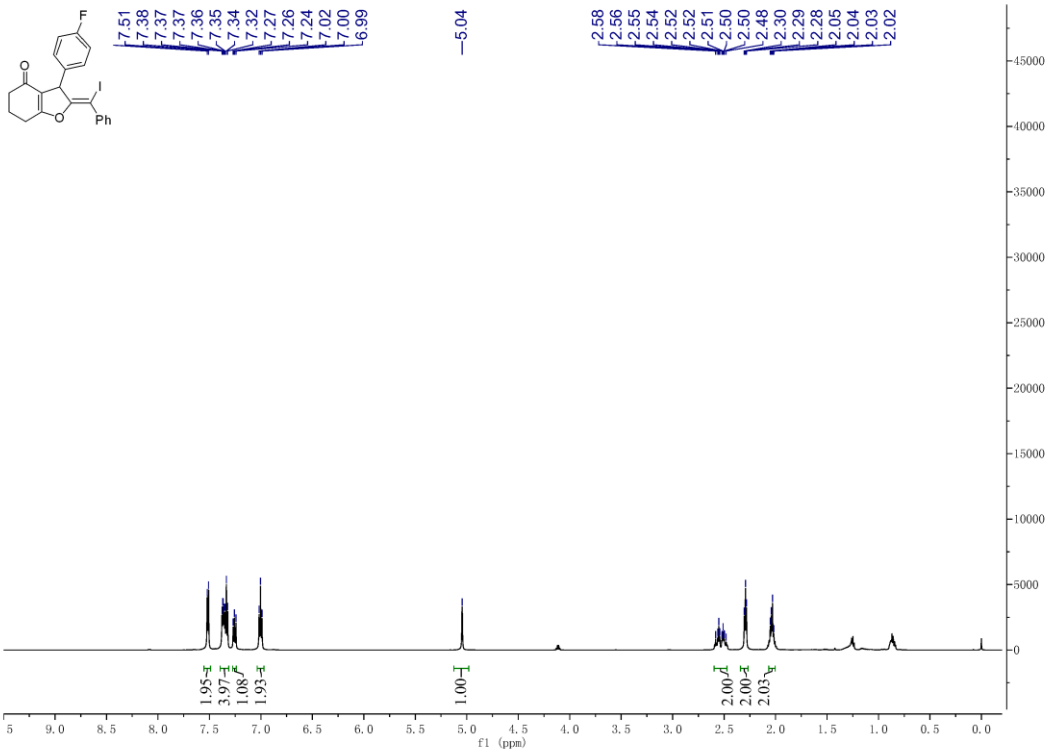


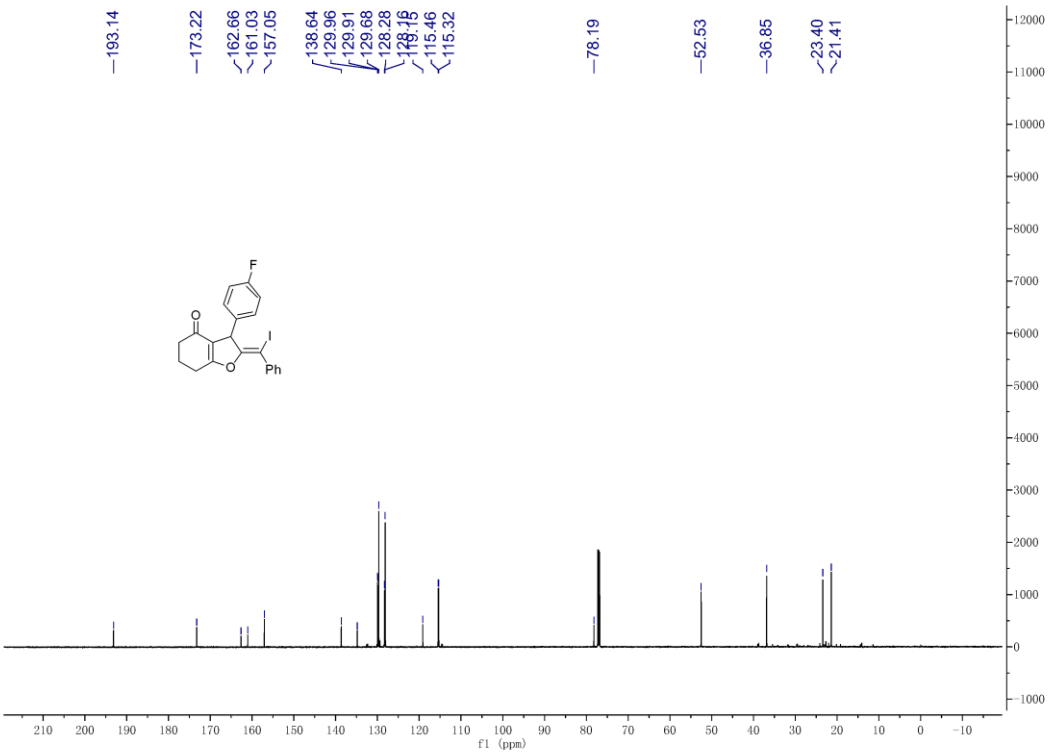
^{1}H NMR spectrum of **3d**(600 MHz, $CDCl_3$)



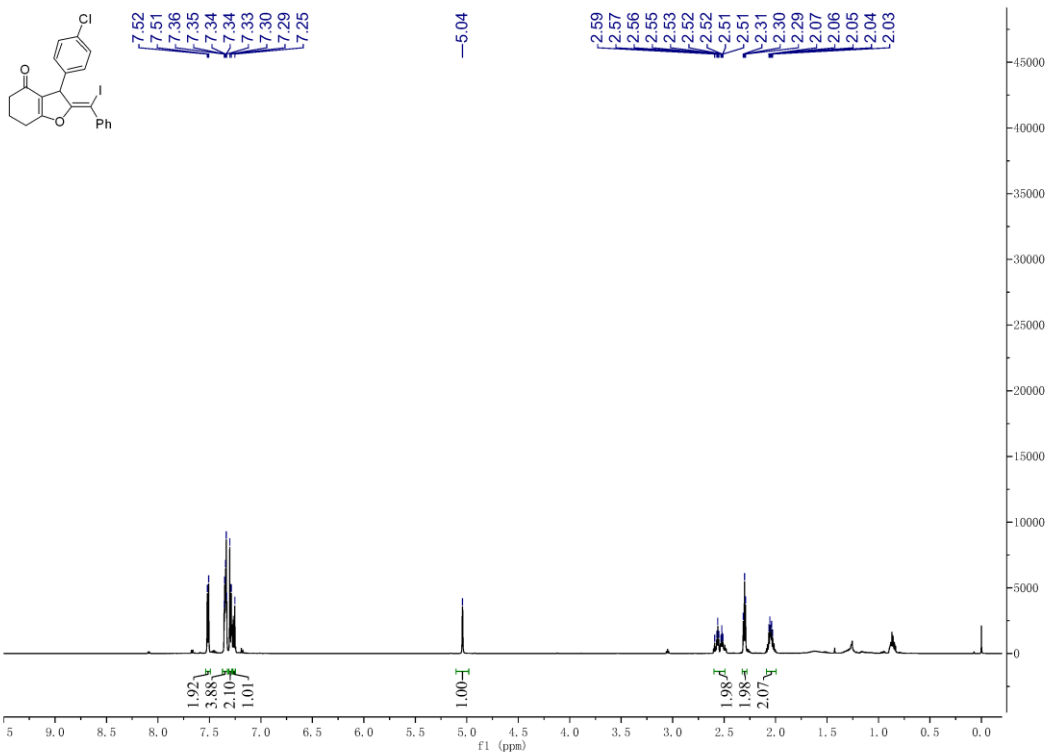
^{13}C NMR spectrum of **3c** (151 MHz, $CDCl_3$)



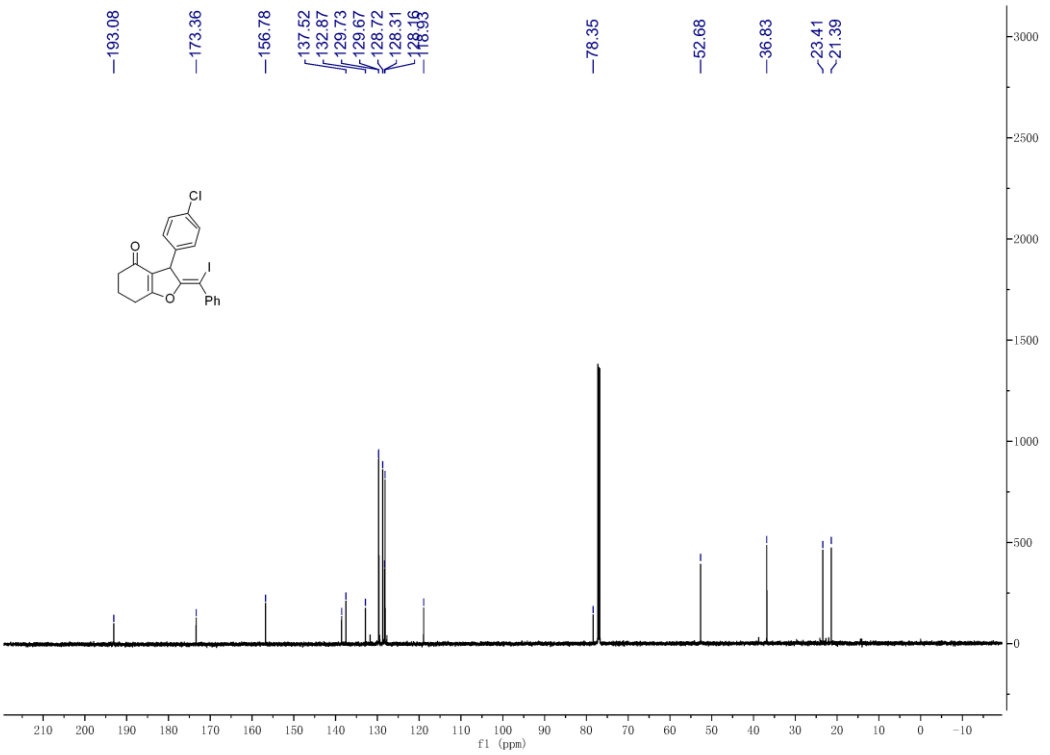
^{1}H NMR spectrum of **3e** (600 MHz, $CDCl_3$)



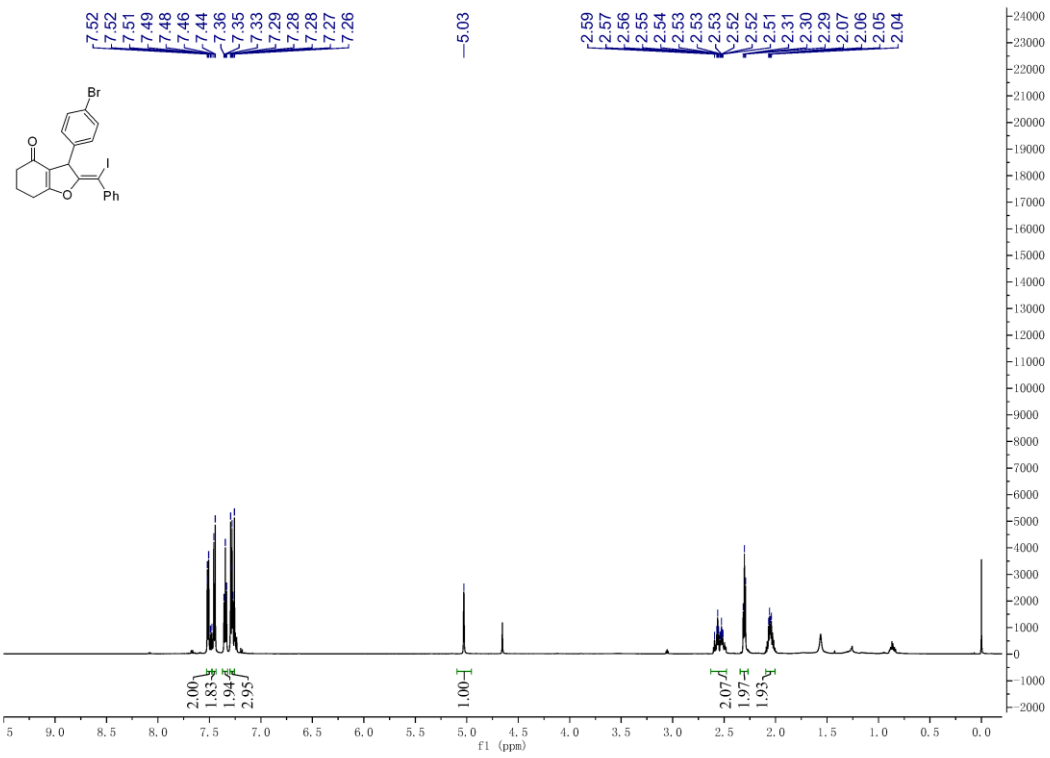
^{13}C NMR spectrum of **3e**(151 MHz, $CDCl_3$)



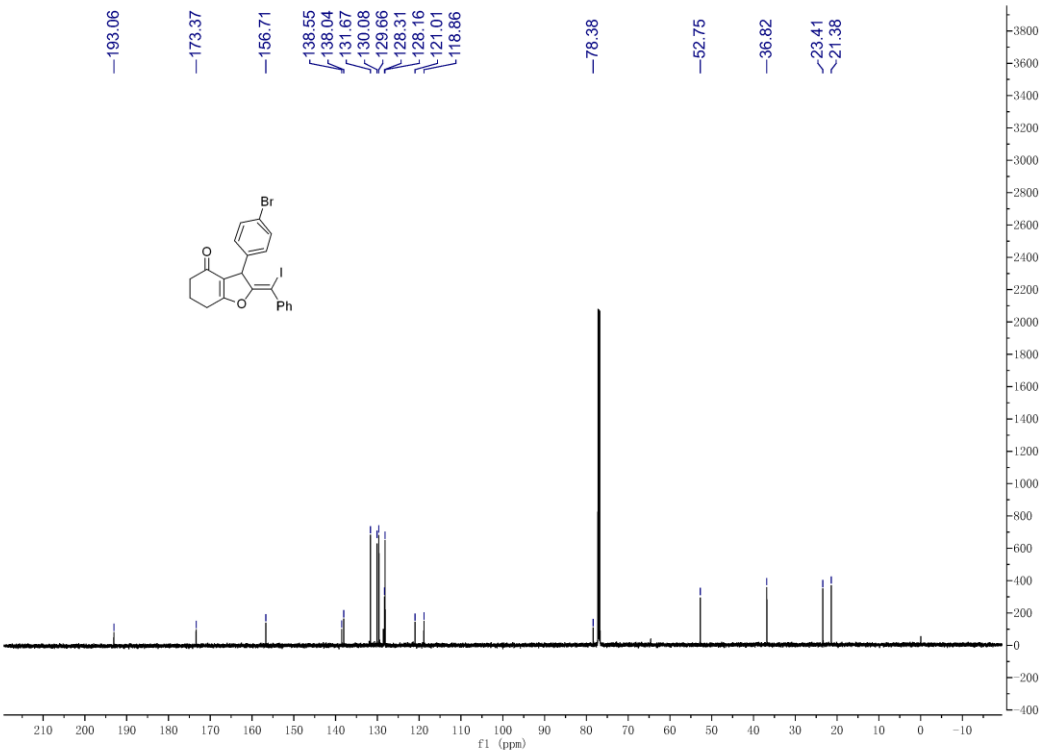
^{1}H NMR spectrum of **3f** (600 MHz, $CDCl_3$)



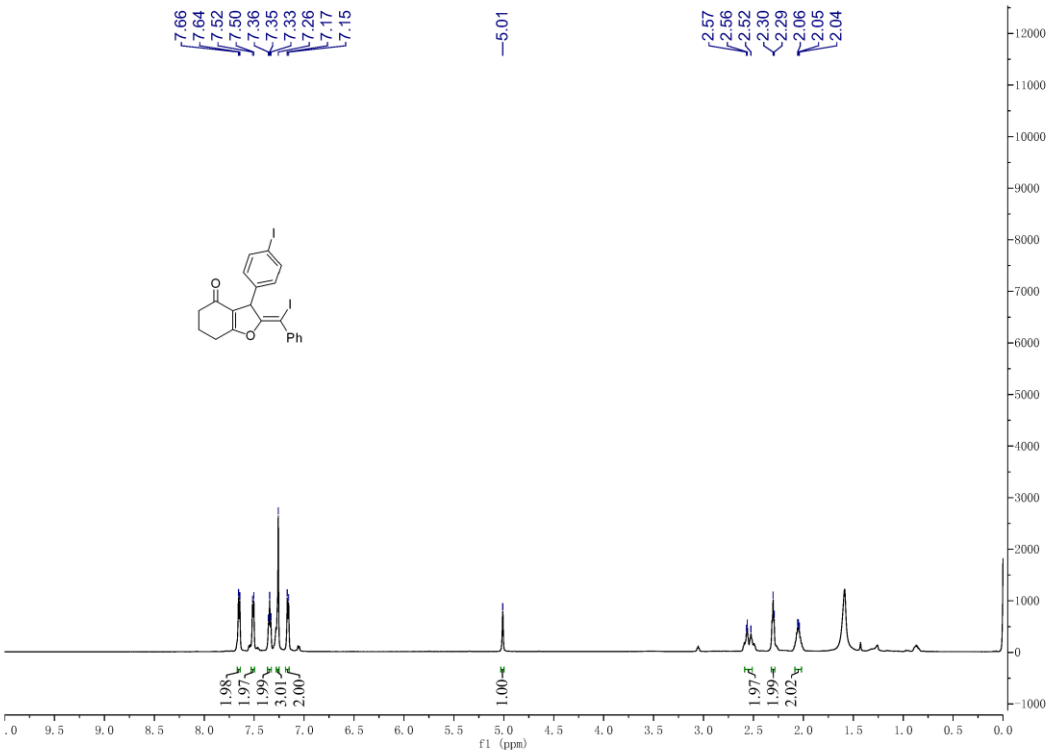
^{13}C NMR spectrum of **3f** (151 MHz, $CDCl_3$)



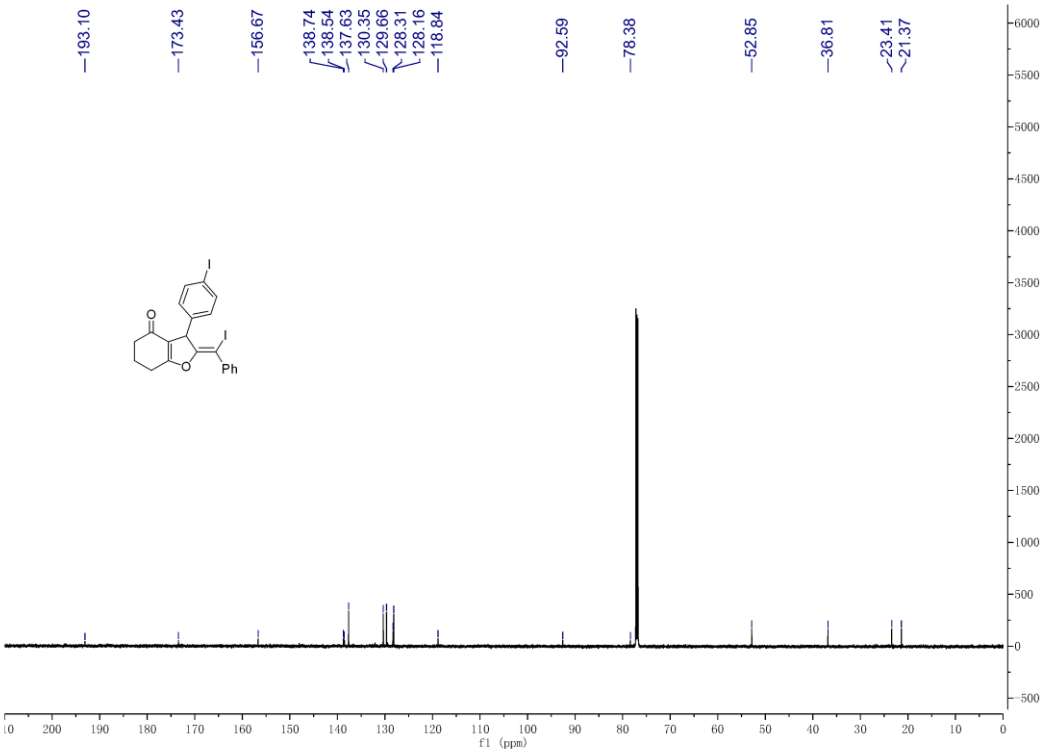
^{1}H NMR spectrum of **3g** (600 MHz, $CDCl_3$)



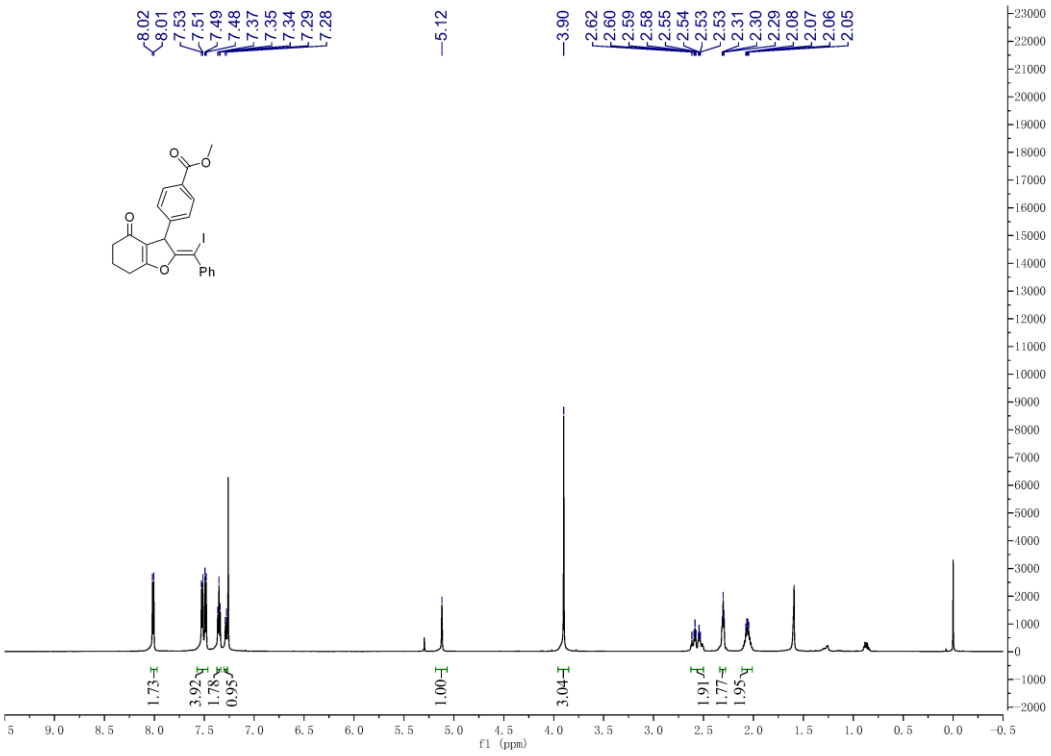
^{13}C NMR spectrum of **3g** (151 MHz, $CDCl_3$)



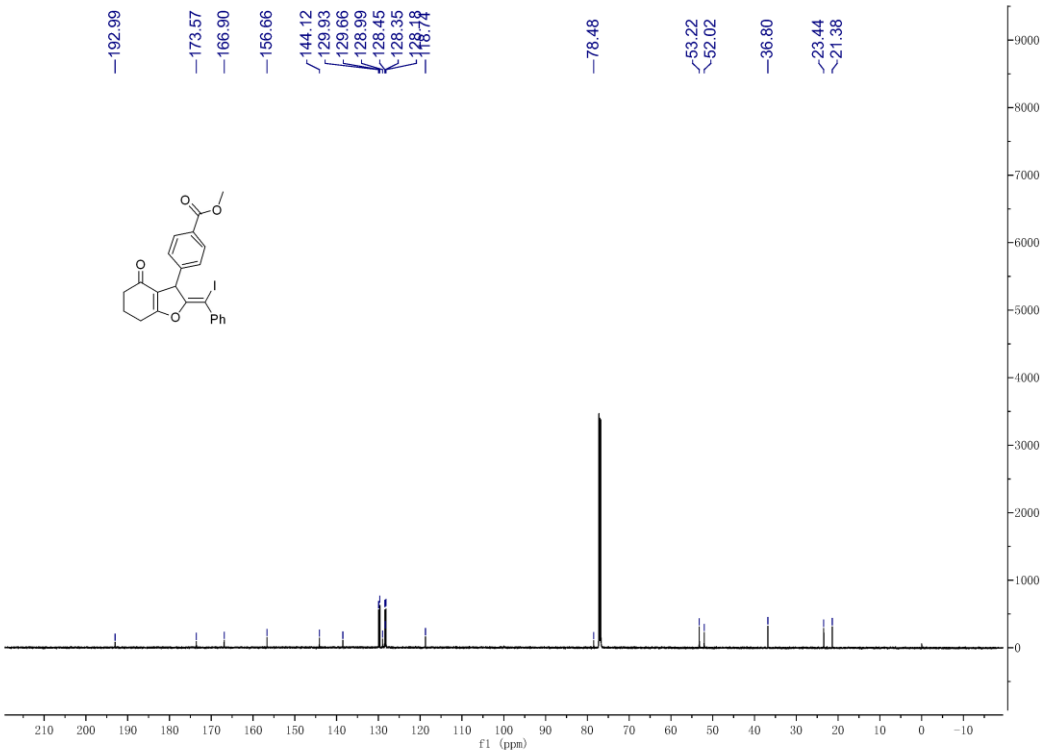
^{1}H NMR spectrum of **3h** (600 MHz, $CDCl_3$)



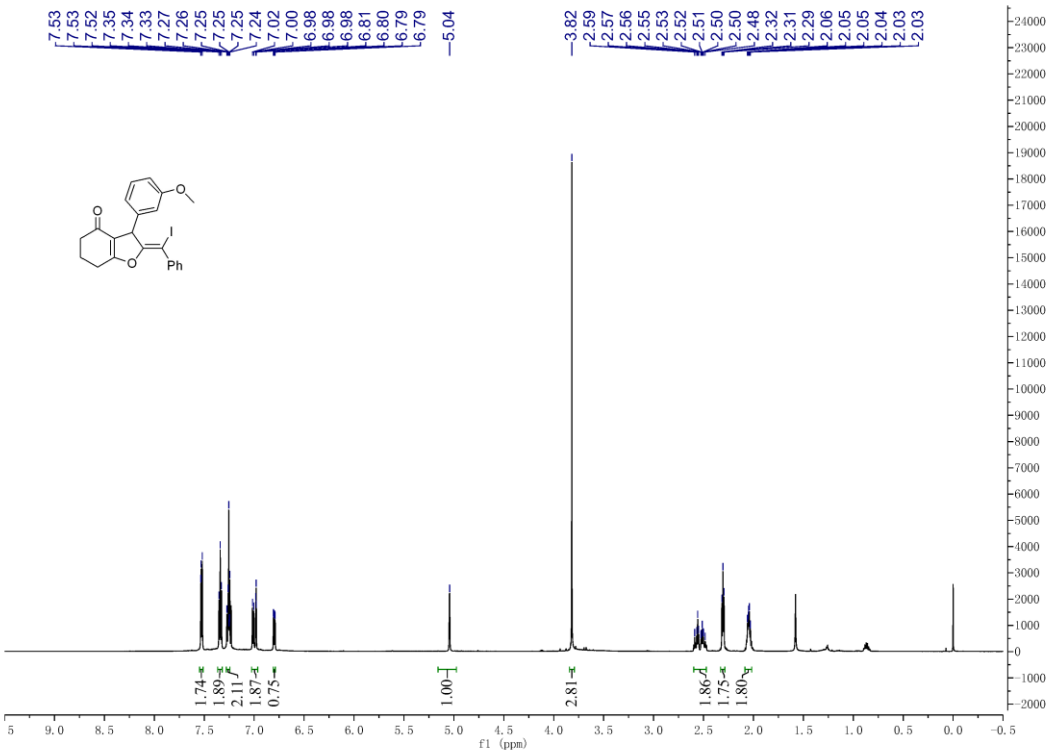
^{13}C NMR spectrum of **3h** (151 MHz, $CDCl_3$)



^{1}H NMR spectrum of **3i** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3i** (151 MHz, $CDCl_3$)



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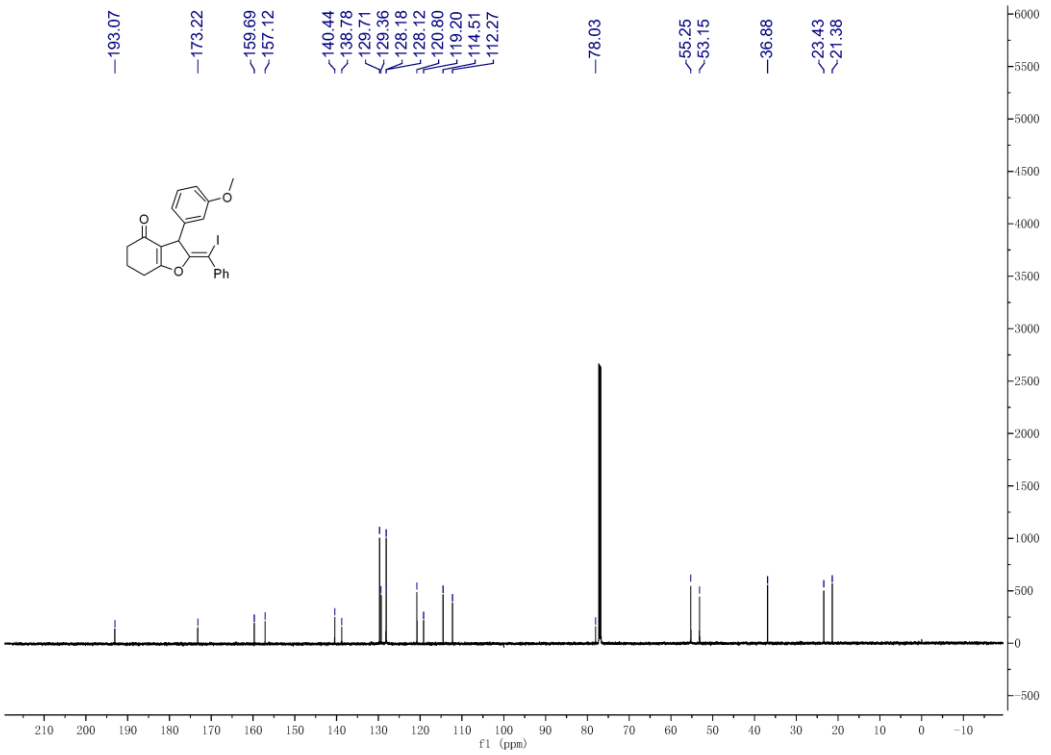

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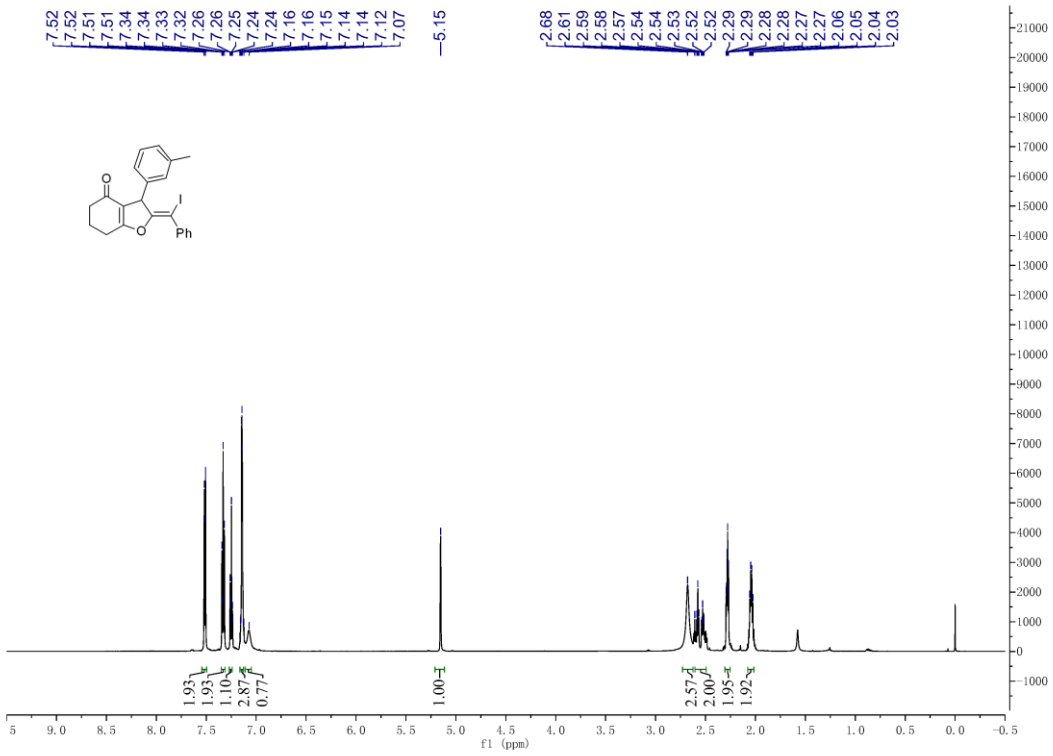
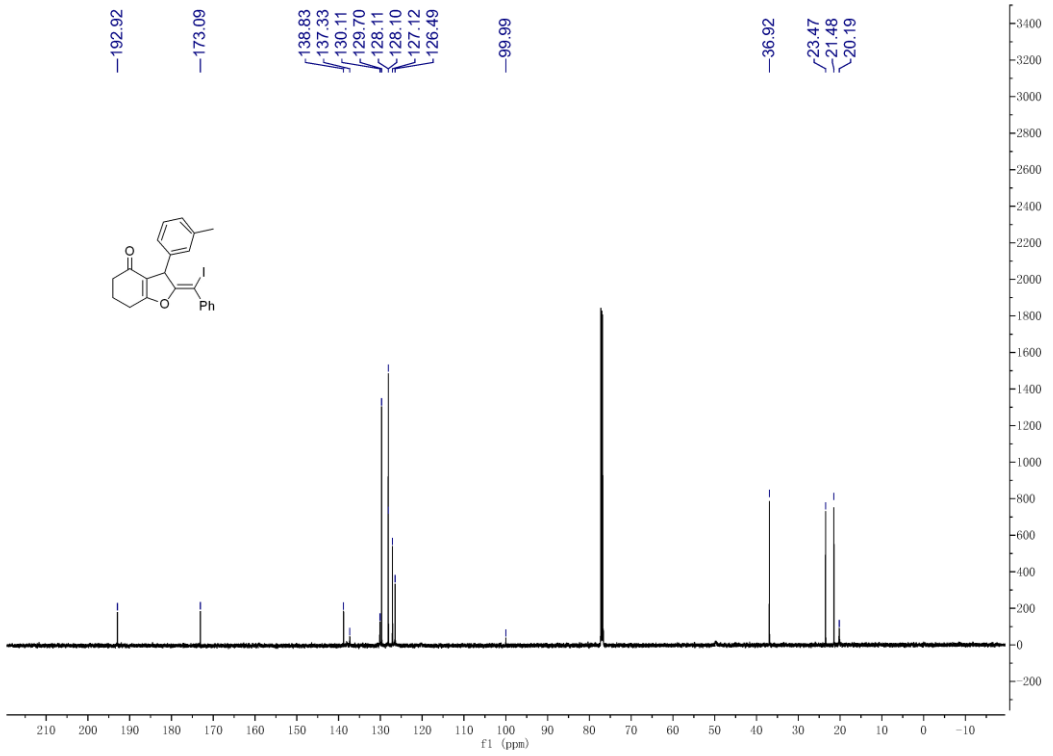
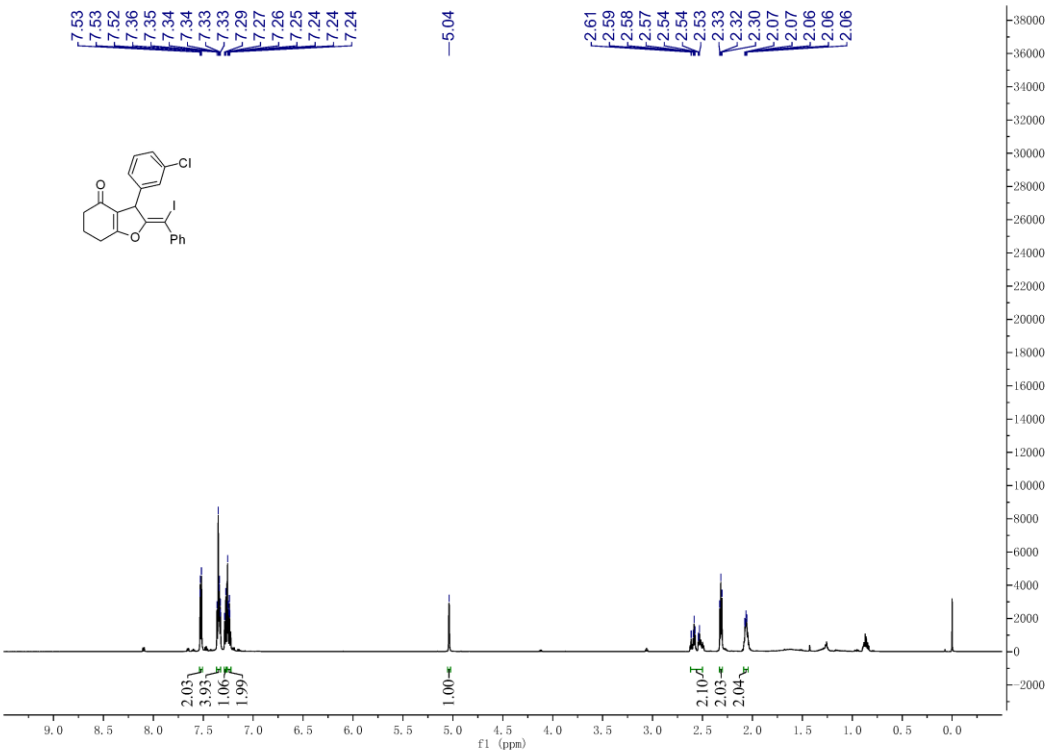


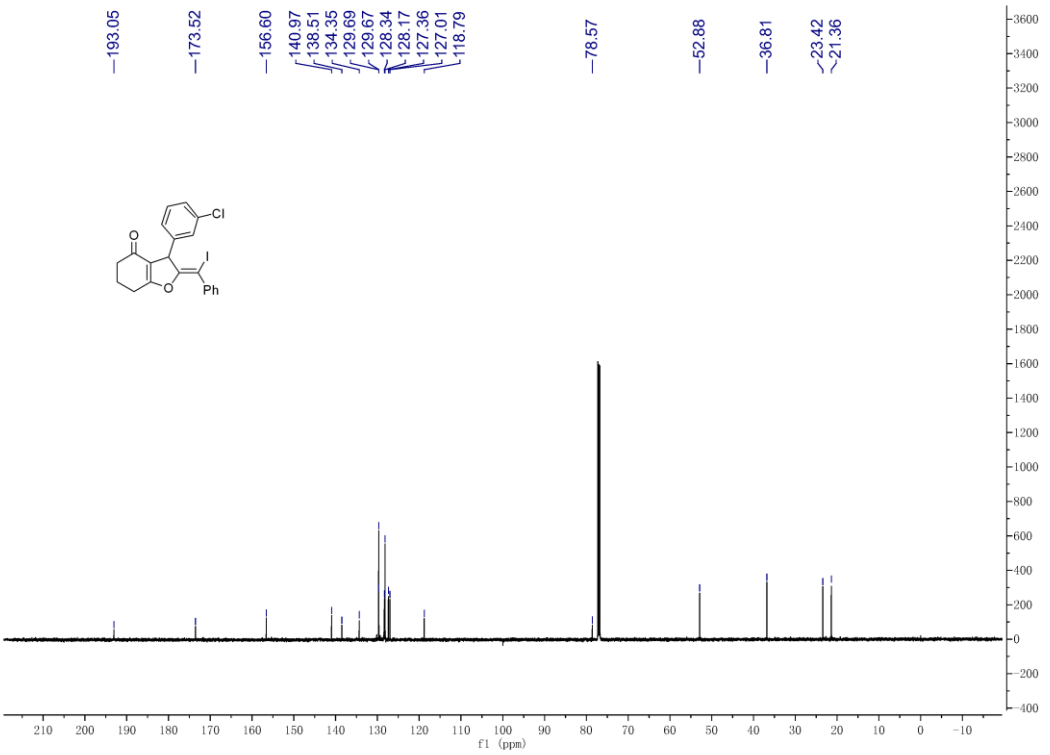
^{1}H NMR spectrum of **3k** (600 MHz, $CDCl_3$)



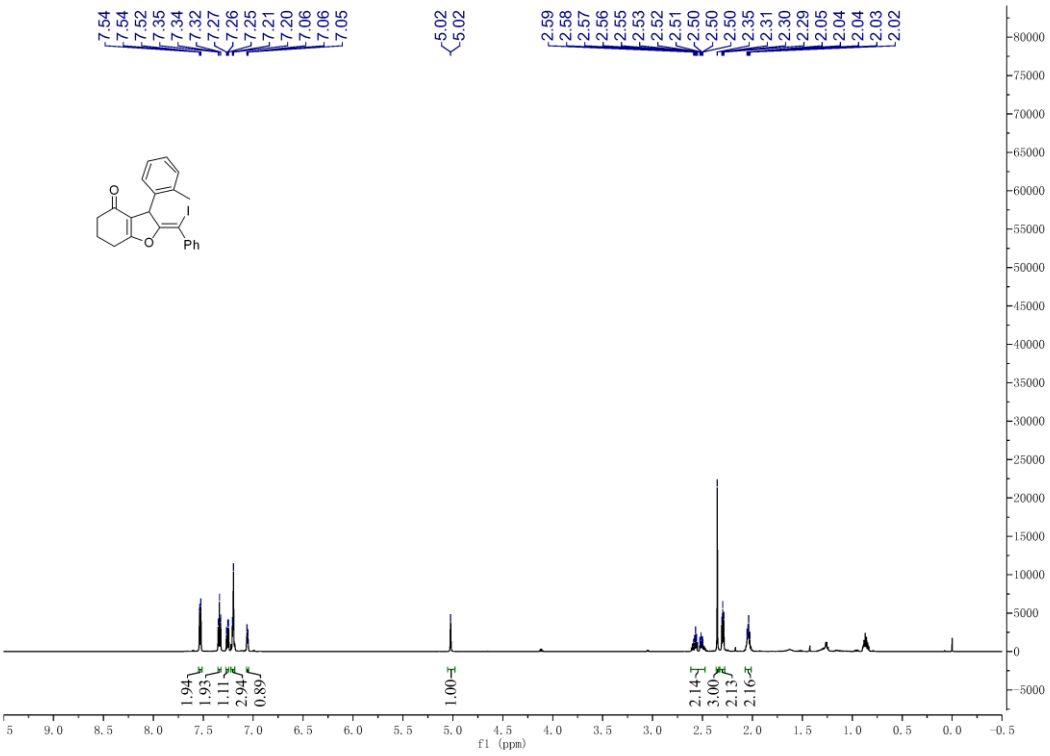
^{13}C NMR spectrum of **3k** (151 MHz, $CDCl_3$)



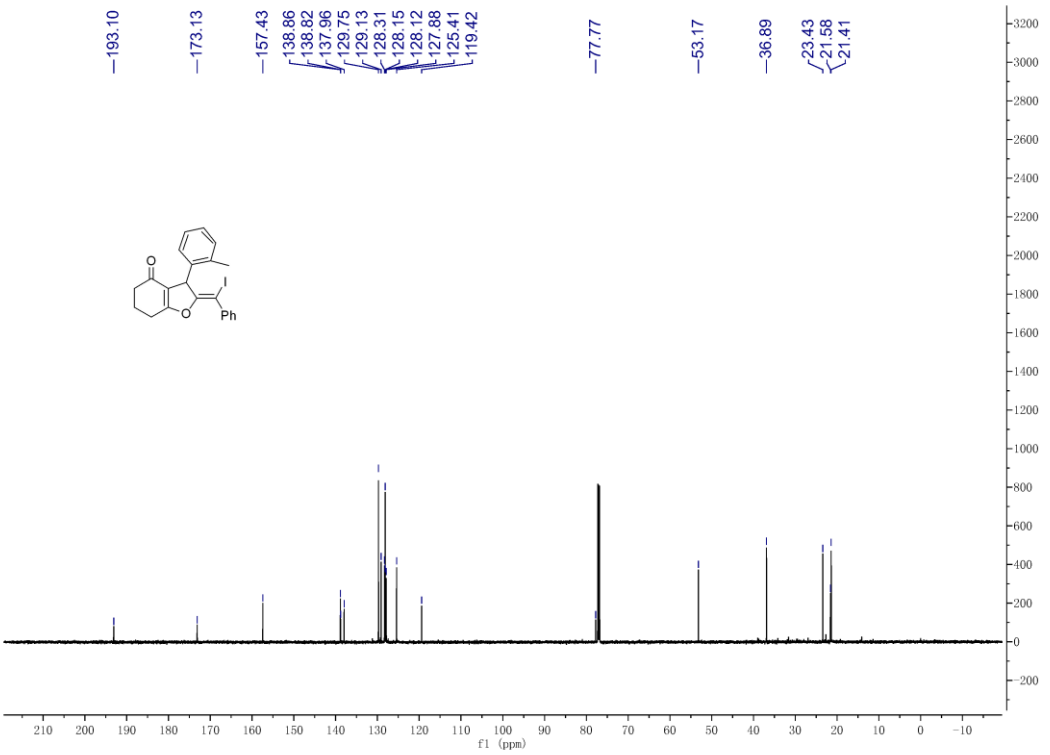
^{1}H NMR spectrum of **3l** (600 MHz, $CDCl_3$)



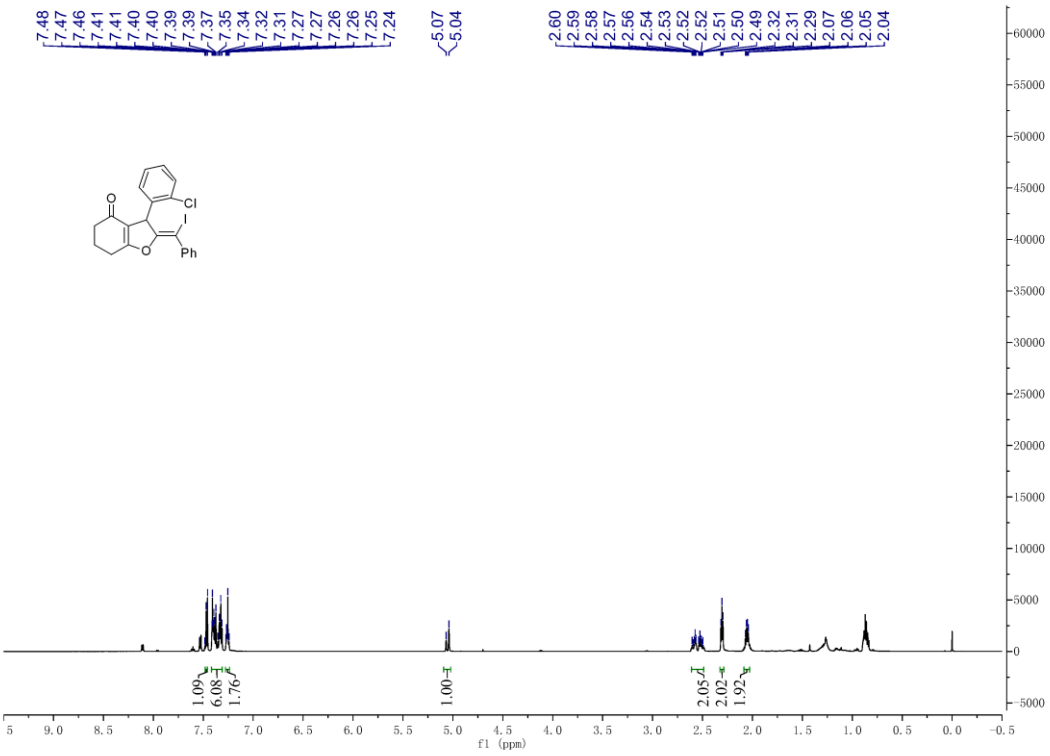
^{13}C NMR spectrum of **3l** (151 MHz, $CDCl_3$)



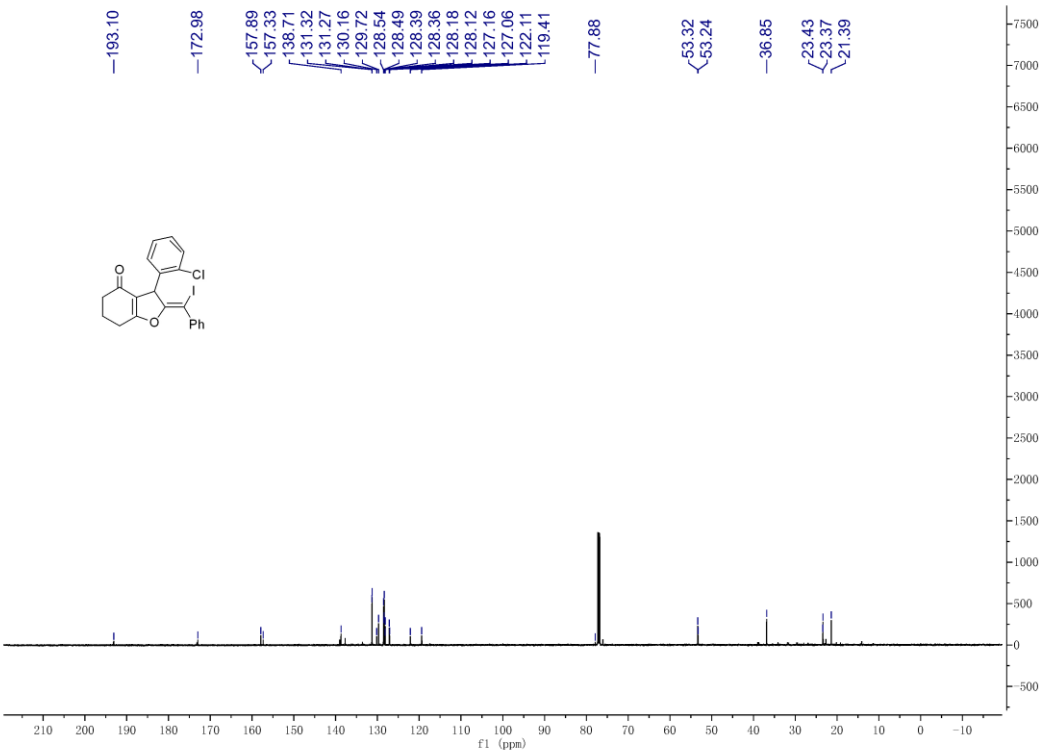
^{1}H NMR spectrum of **3m** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3m** (151 MHz, $CDCl_3$)



^{1}H NMR spectrum of **3n** (600 MHz, $CDCl_3$)



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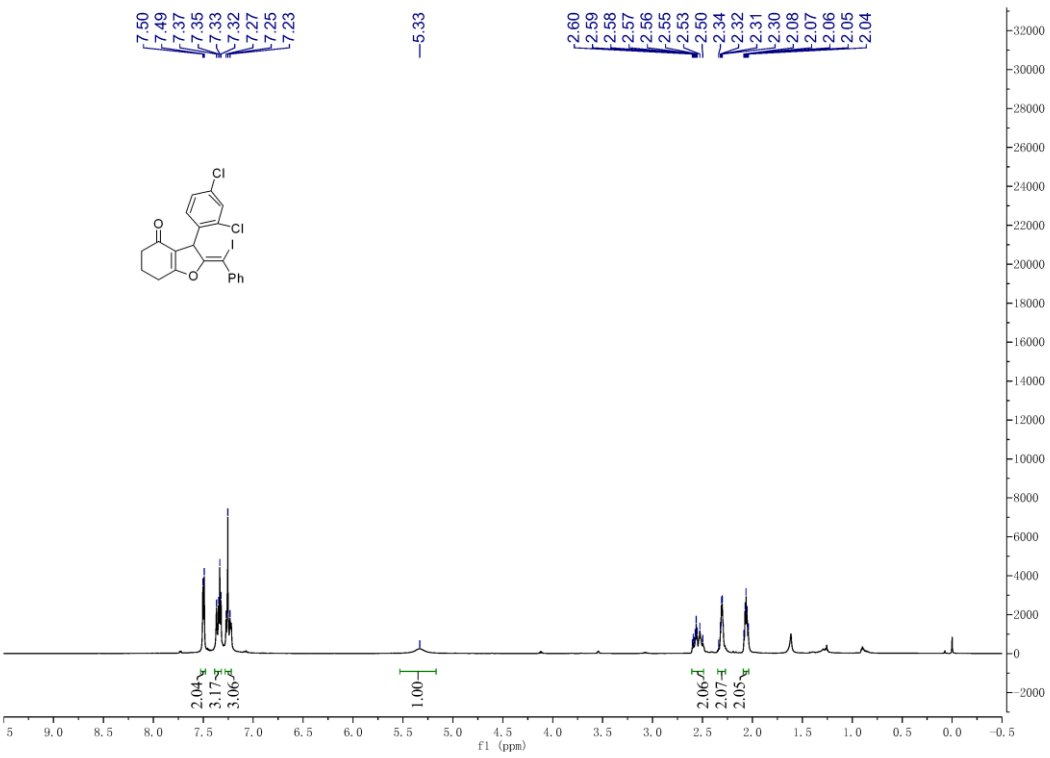
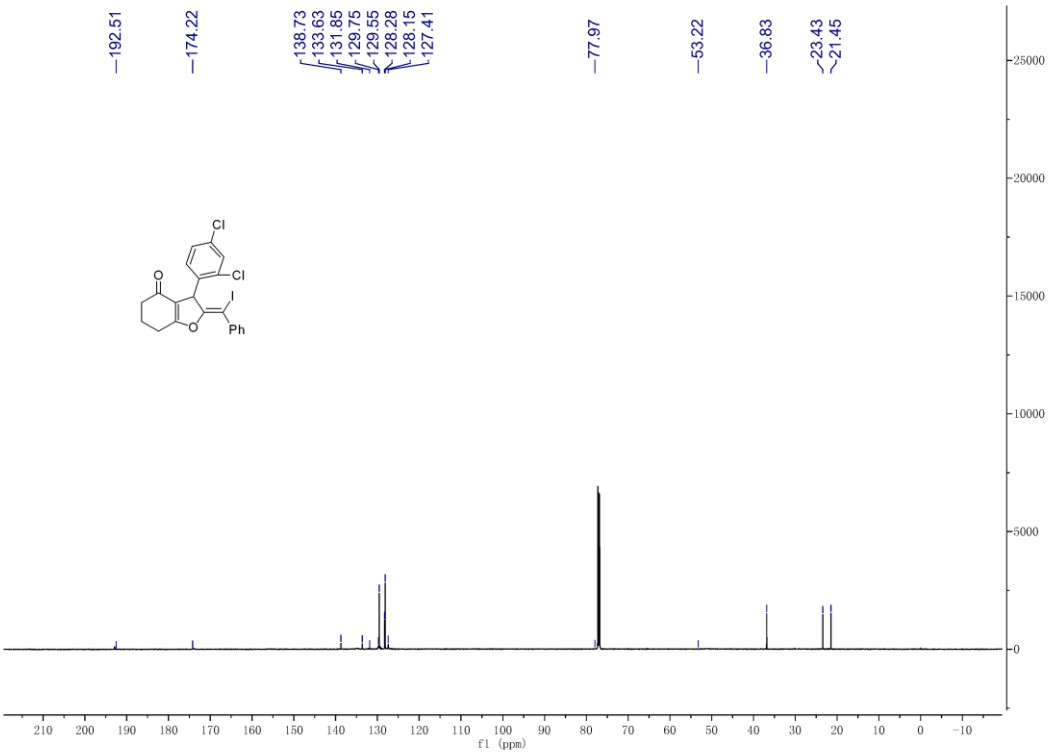
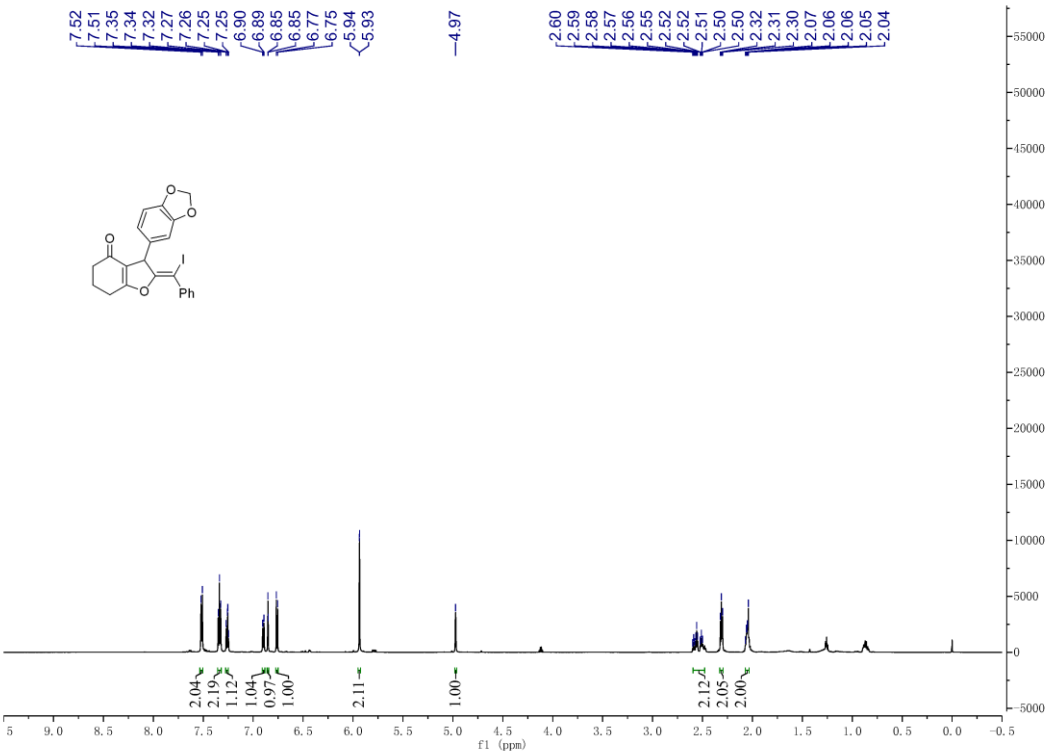


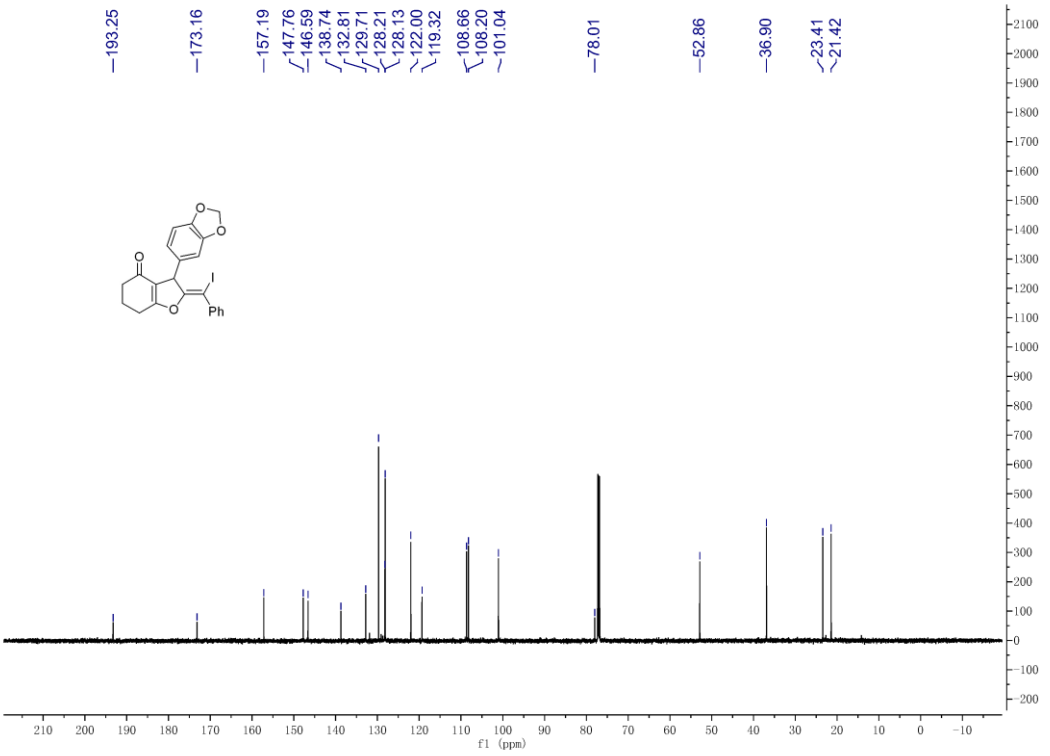
^{1}H NMR spectrum of **3o** (600 MHz, $CDCl_3$)



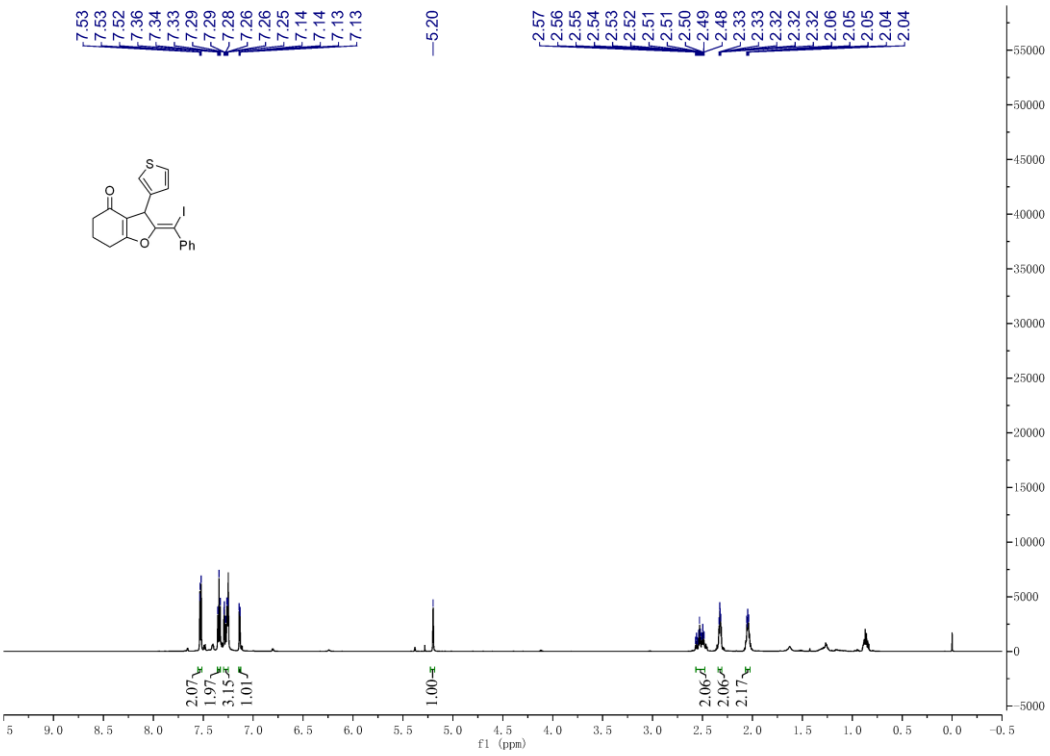
^{13}C NMR spectrum of **3o** (151 MHz, $CDCl_3$)



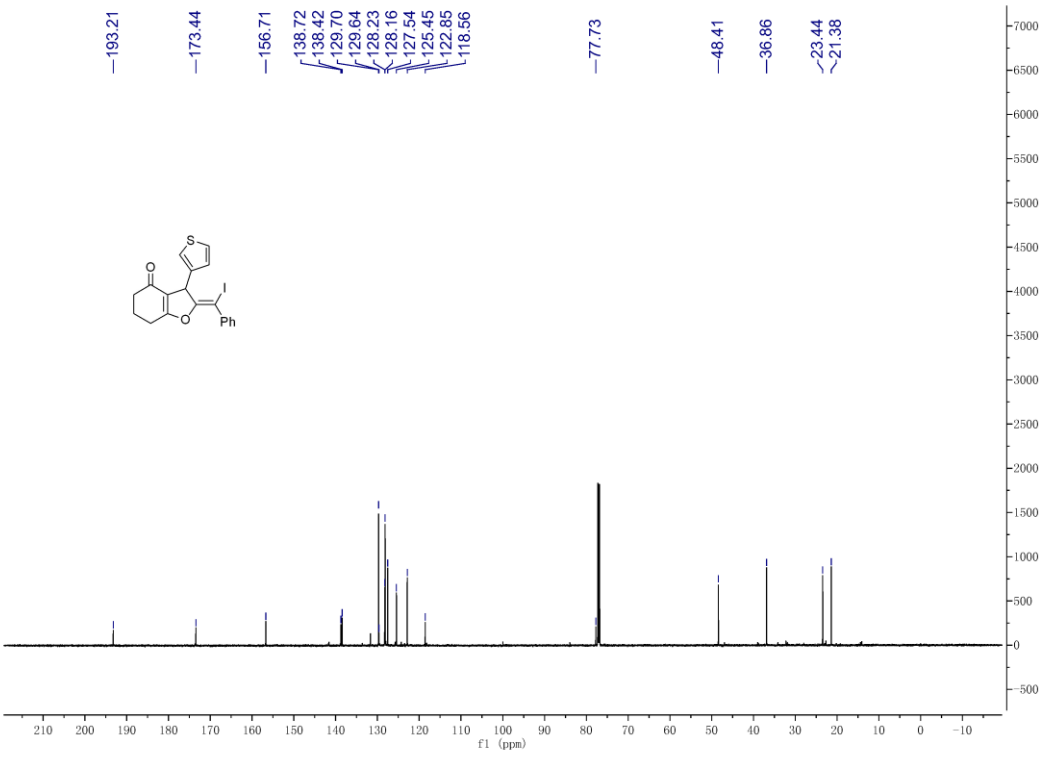
^{1}H NMR spectrum of **3p** (600 MHz, $CDCl_3$)



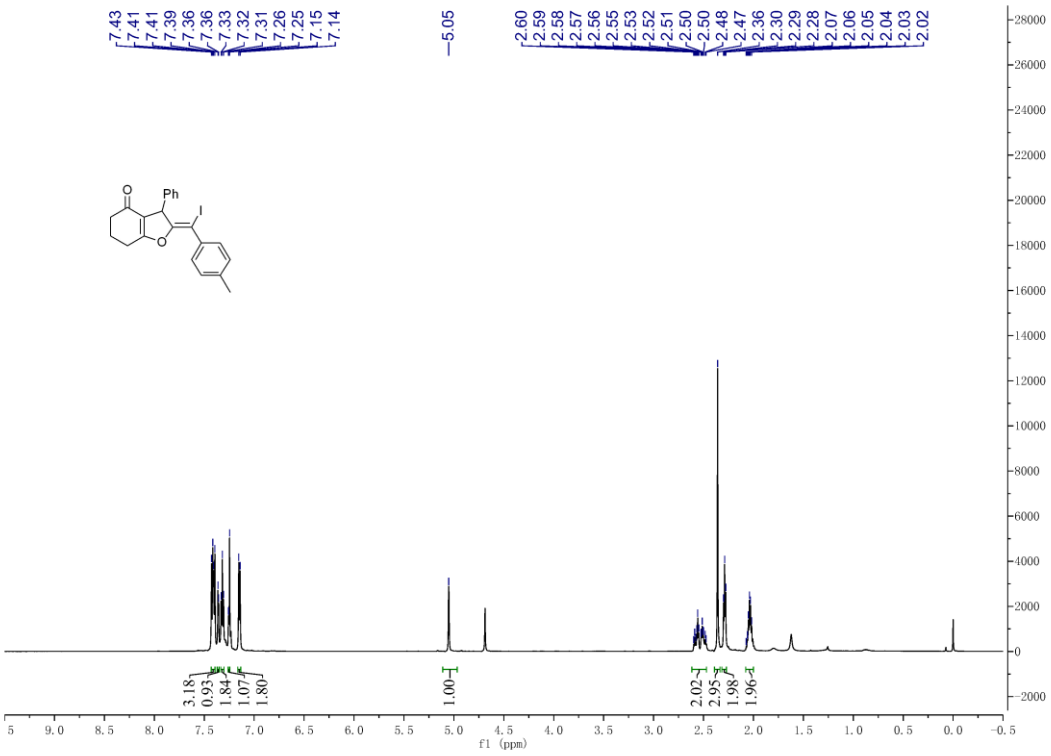
^{13}C NMR spectrum of **3p** (151 MHz, $CDCl_3$)



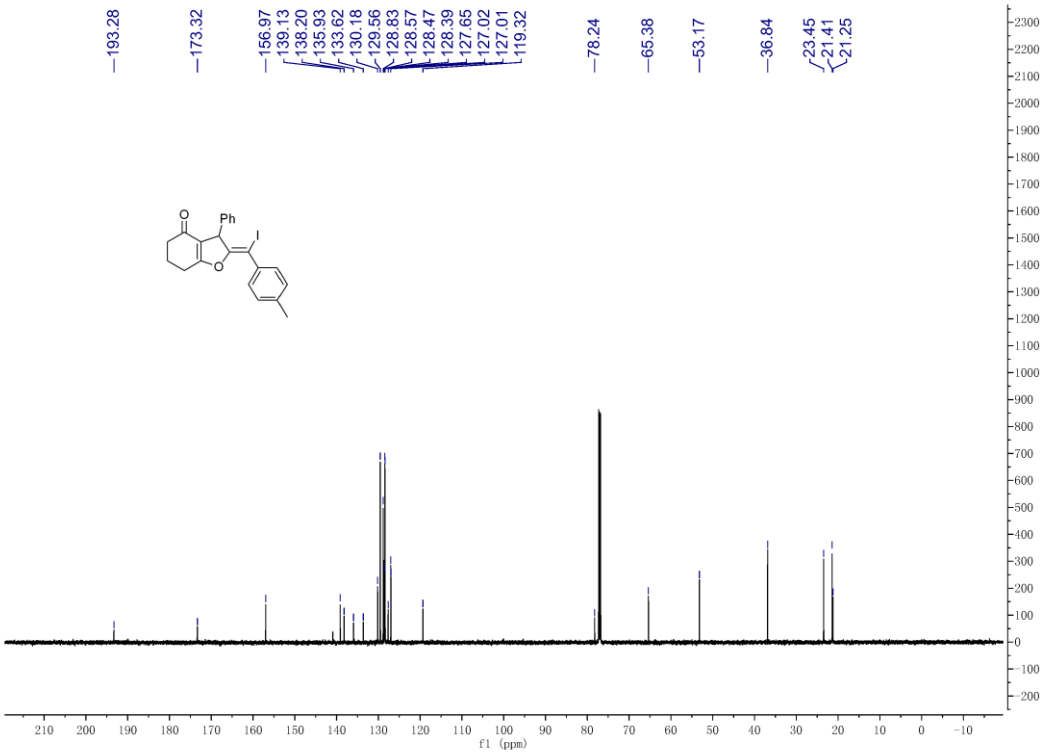
^{1}H NMR spectrum of **3q** (600MHz, $CDCl_3$)



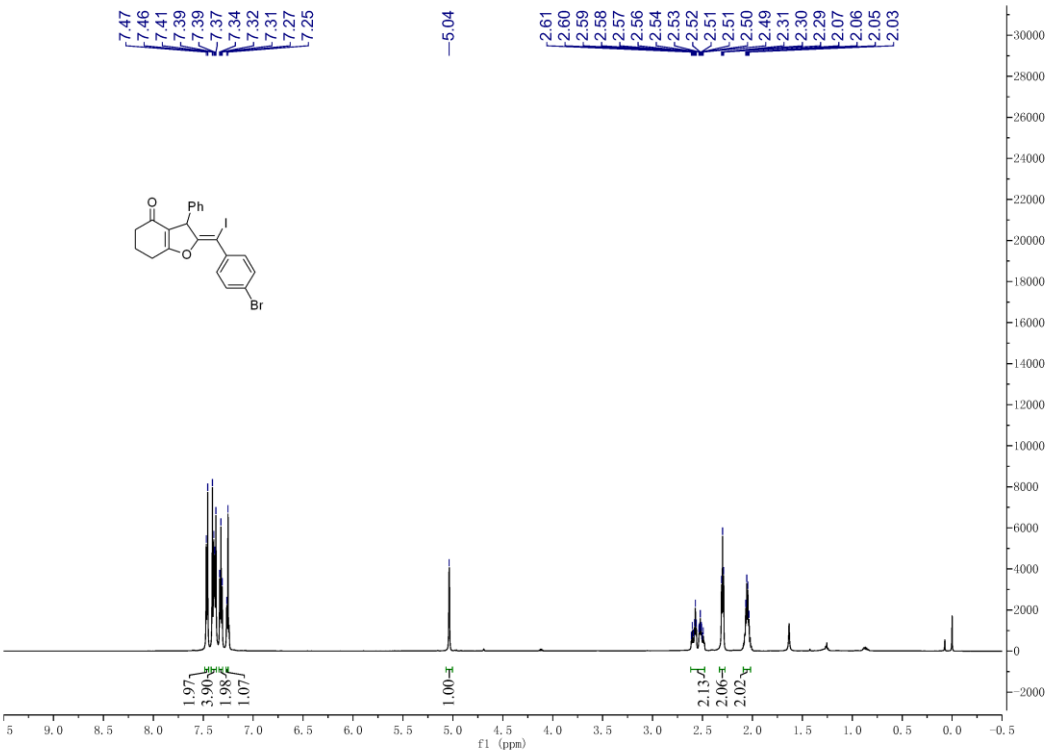
^{13}C NMR spectrum of **3q** (151 MHz, $CDCl_3$)



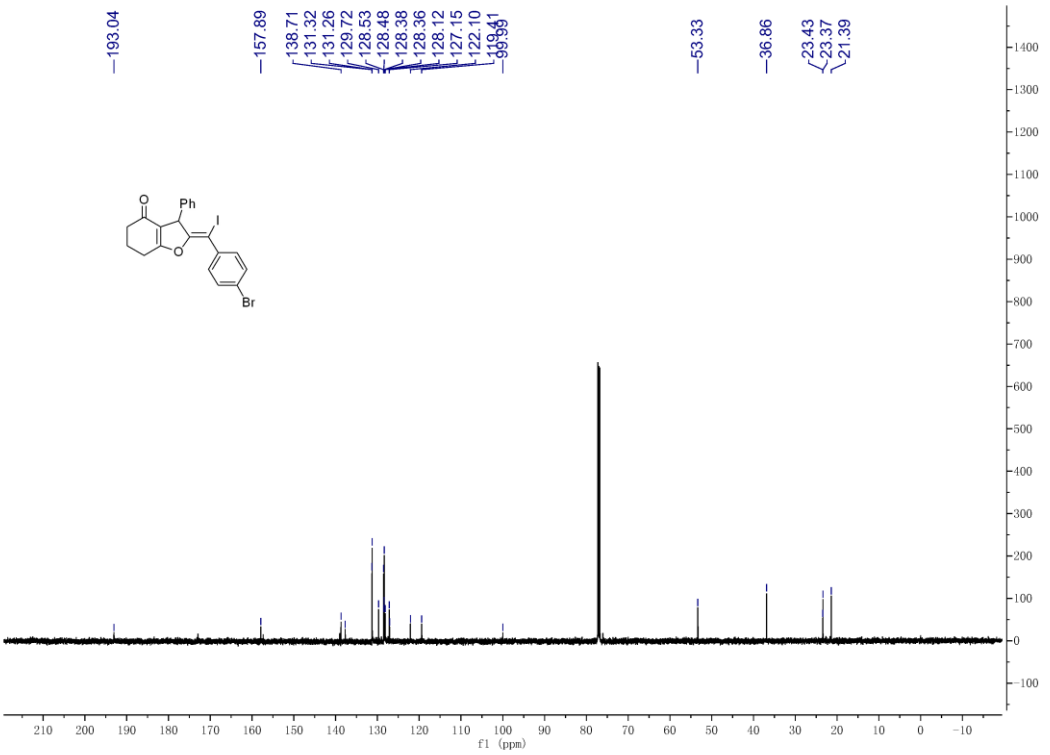
^{1}H NMR spectrum of **3r** (600MHz, $CDCl_3$)



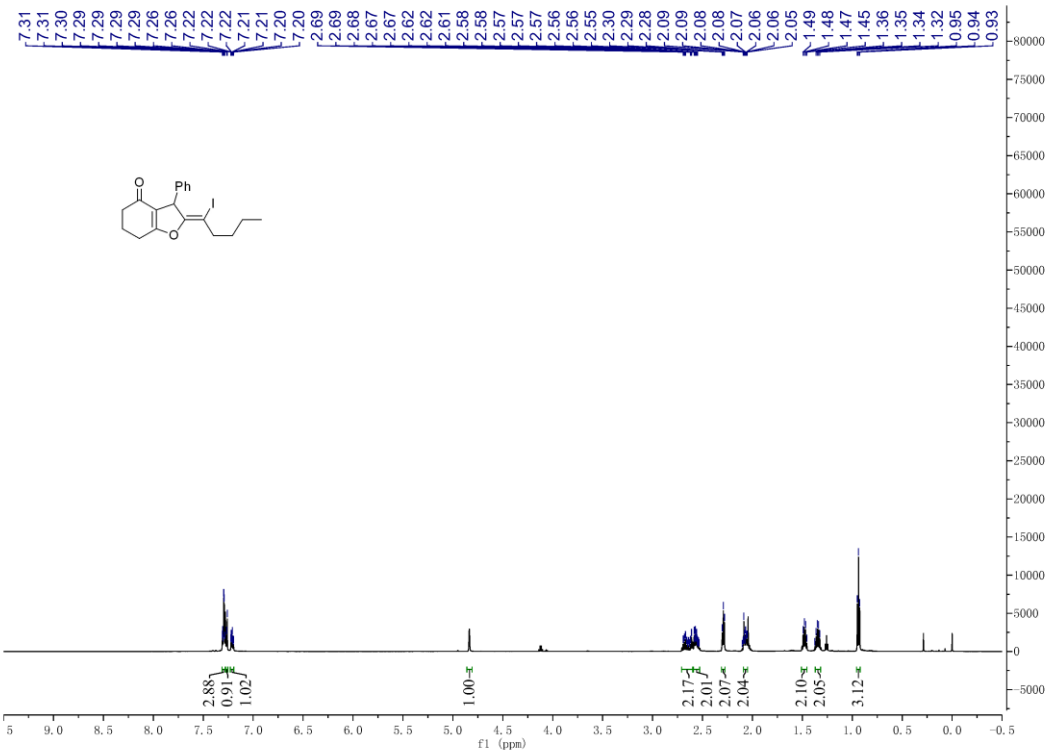
^{13}C NMR spectrum of **3r** (151 MHz, $CDCl_3$)



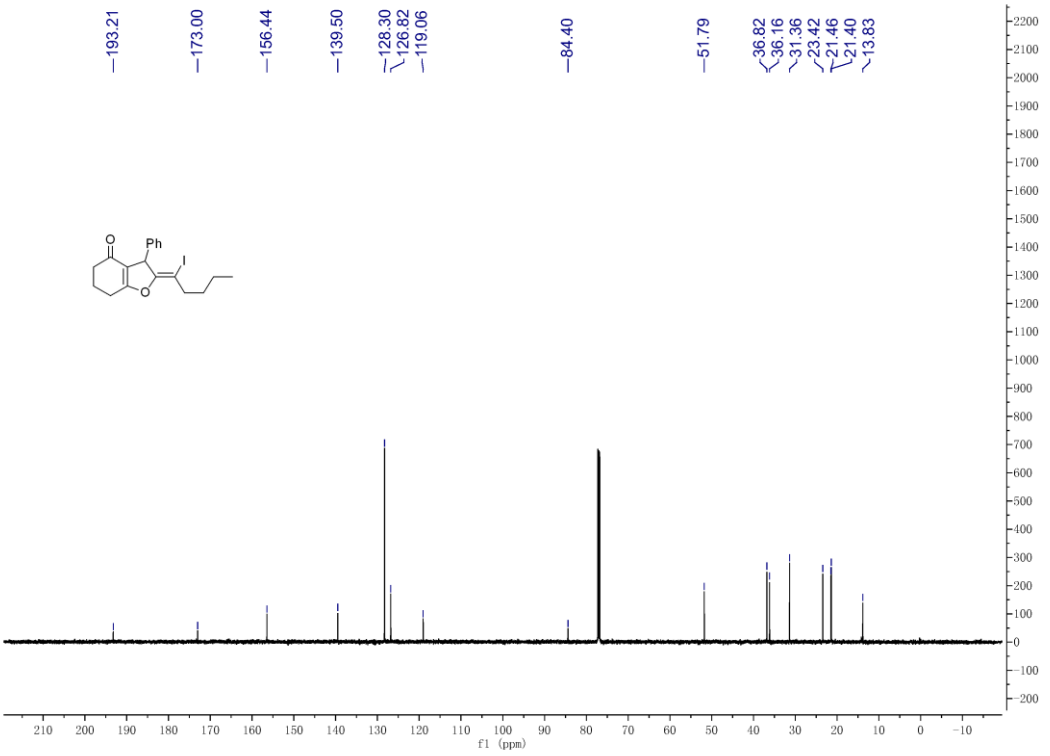
^{1}H NMR spectrum of **3s** (600MHz, $CDCl_3$)



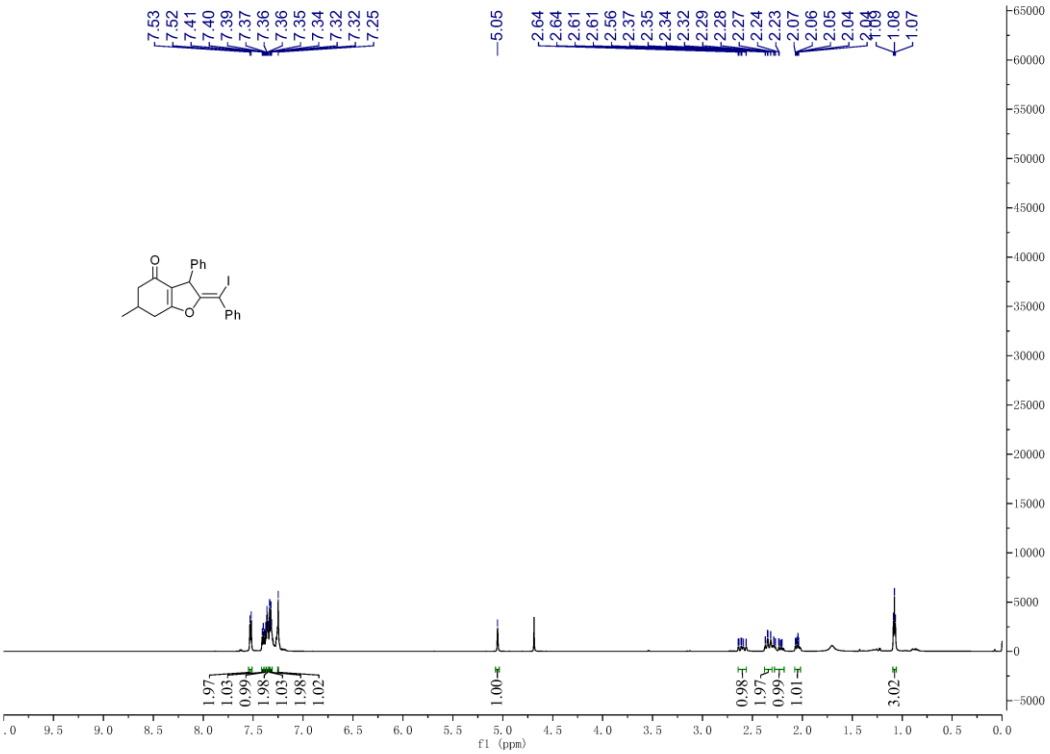
^{13}C NMR spectrum of **3s** (151 MHz, $CDCl_3$)



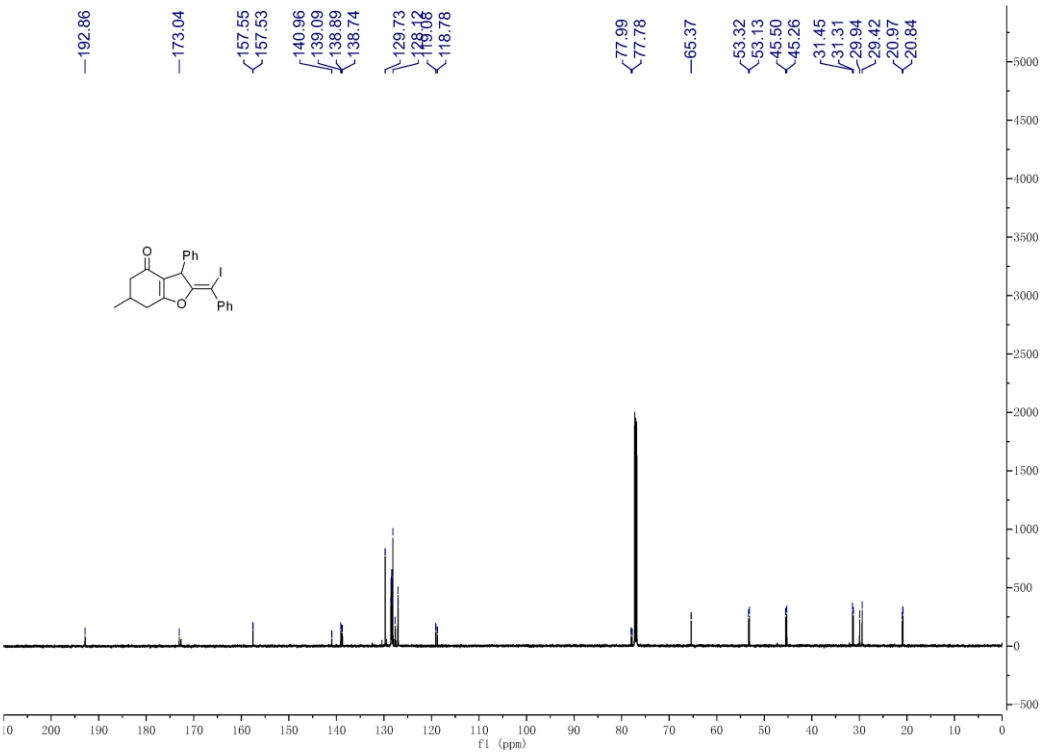
^{1}H NMR spectrum of **3t** (600MHz, $CDCl_3$)



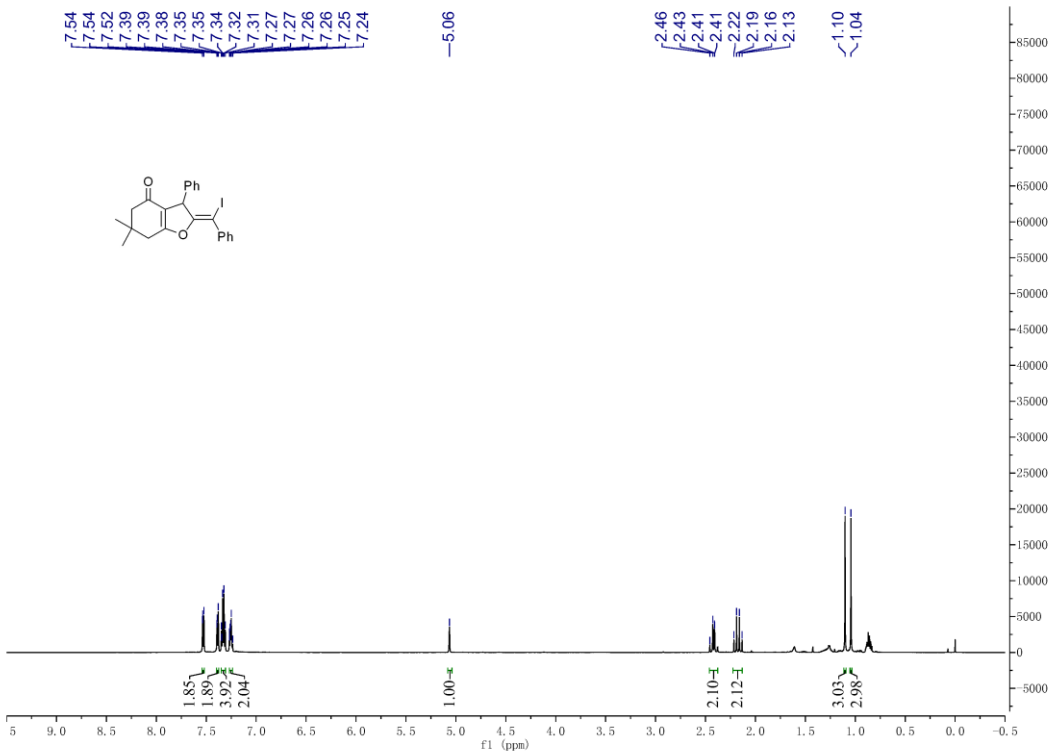
^{13}C NMR spectrum of **3t** (151 MHz, $CDCl_3$)



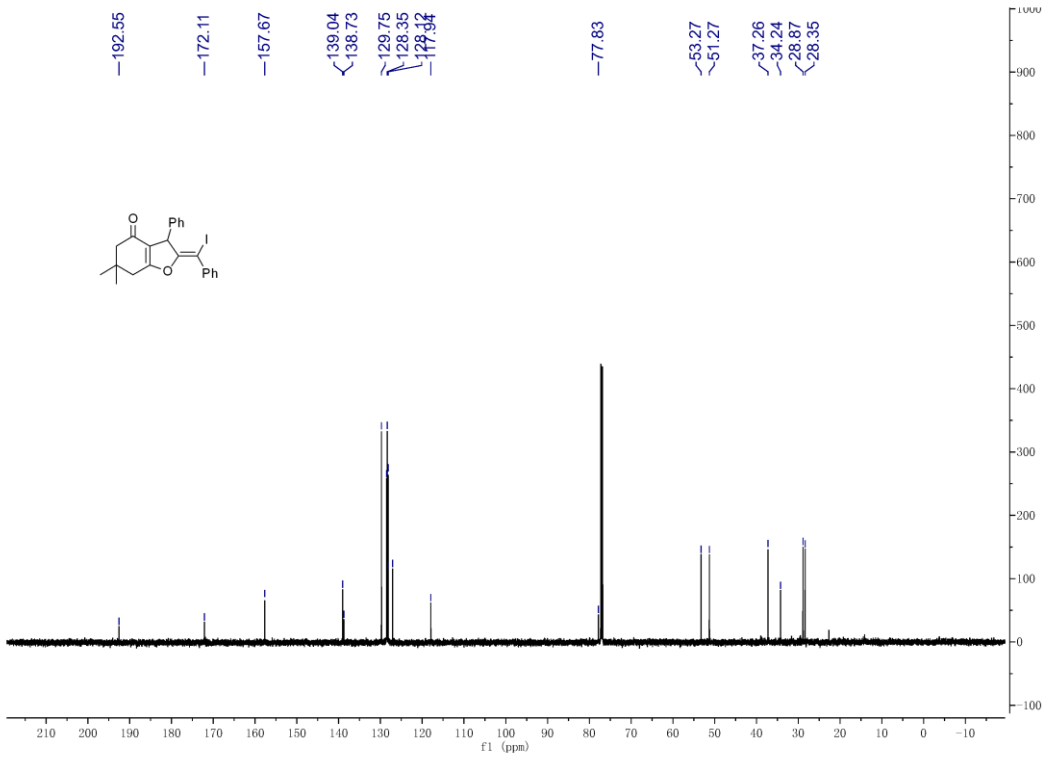
^{1}H NMR spectrum of **3u** (600MHz, $CDCl_3$)



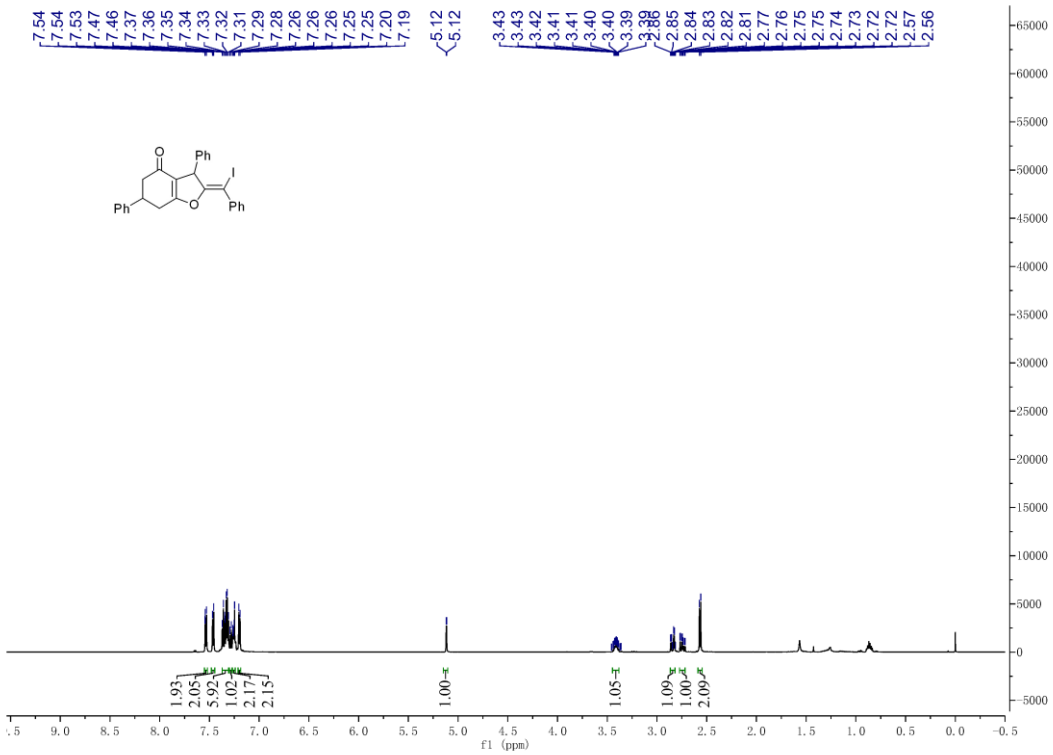
^{13}C NMR spectrum of **3u** (151 MHz, $CDCl_3$)



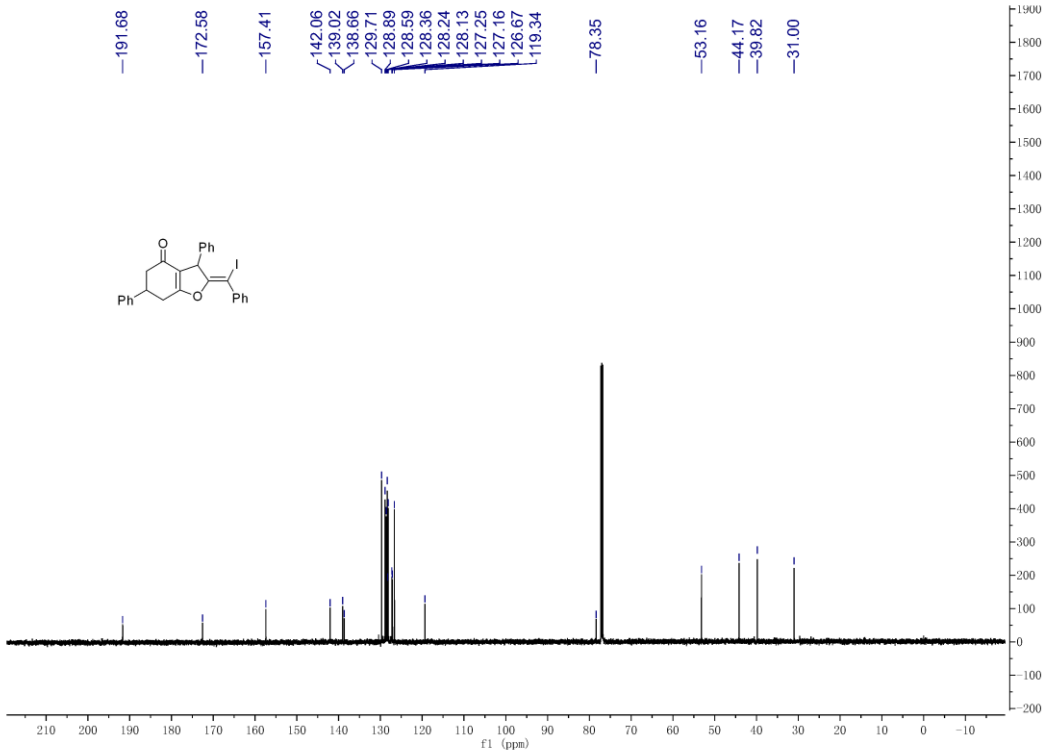
^{1}H NMR spectrum of **3v** (600MHz, $CDCl_3$)



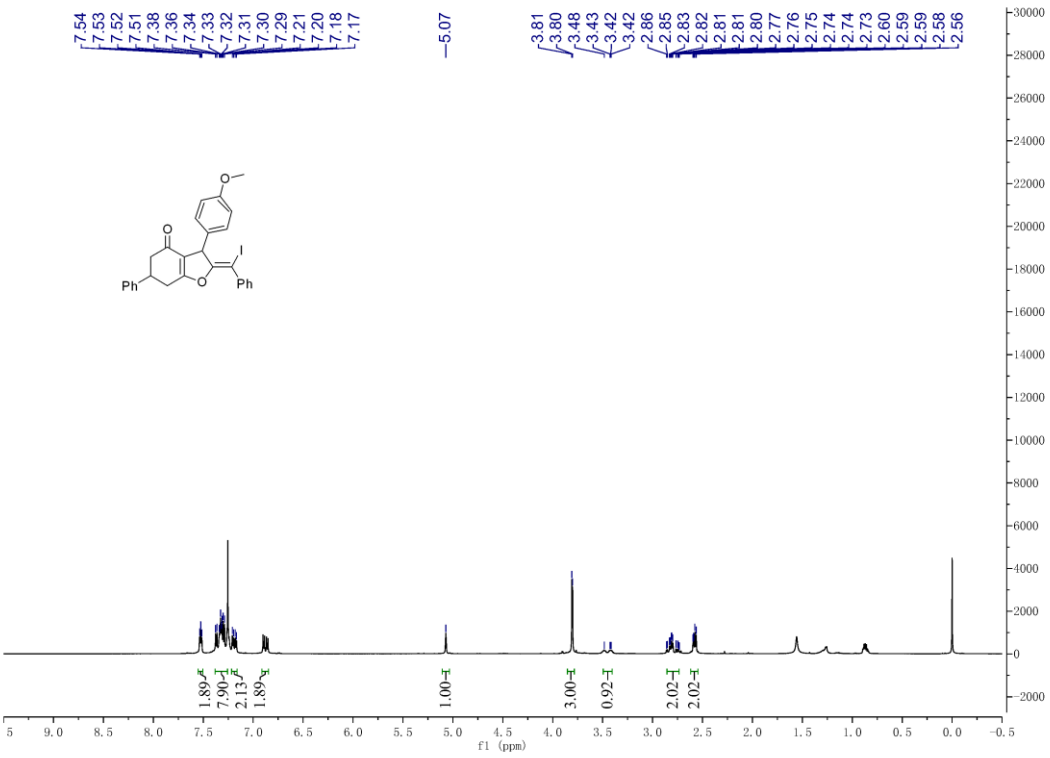
^{13}C NMR spectrum of **3v** (151 MHz, $CDCl_3$)



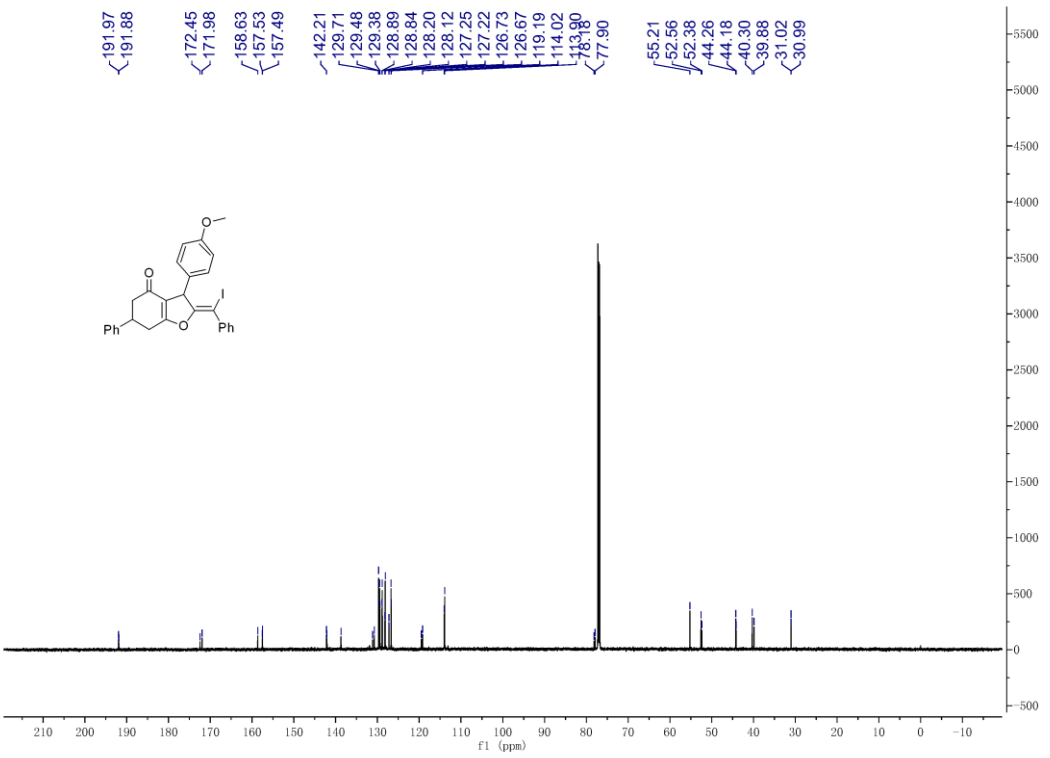
^{1}H NMR spectrum of **3w** (600MHz, $CDCl_3$)



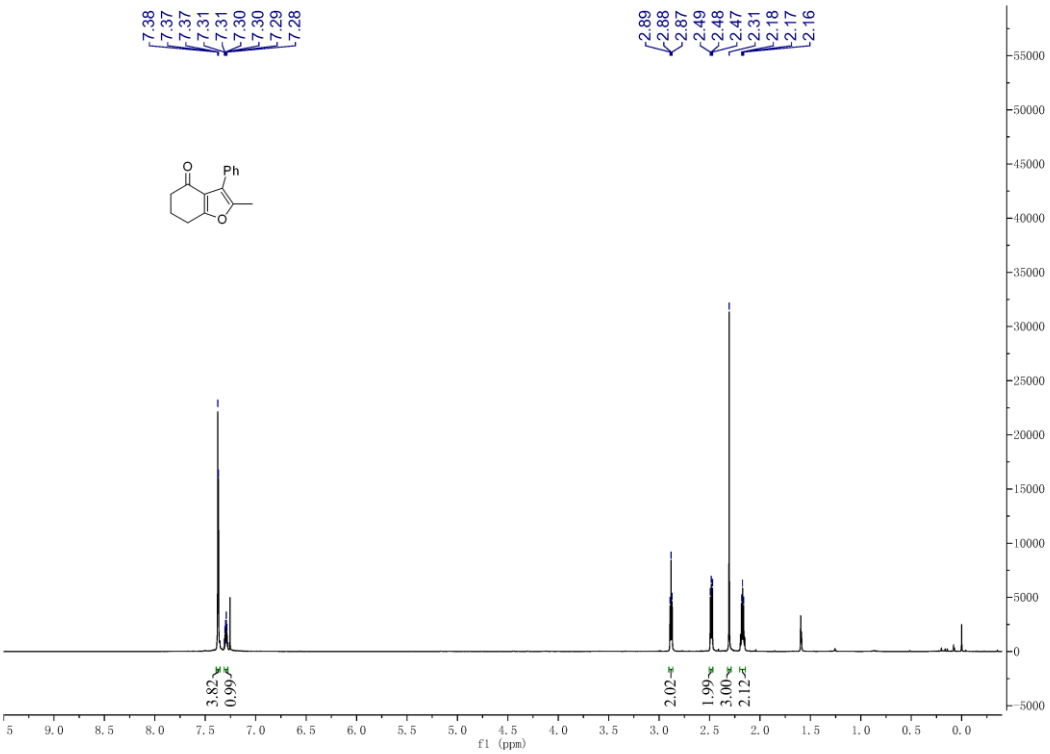
^{13}C NMR spectrum of **3w** (151 MHz, $CDCl_3$)



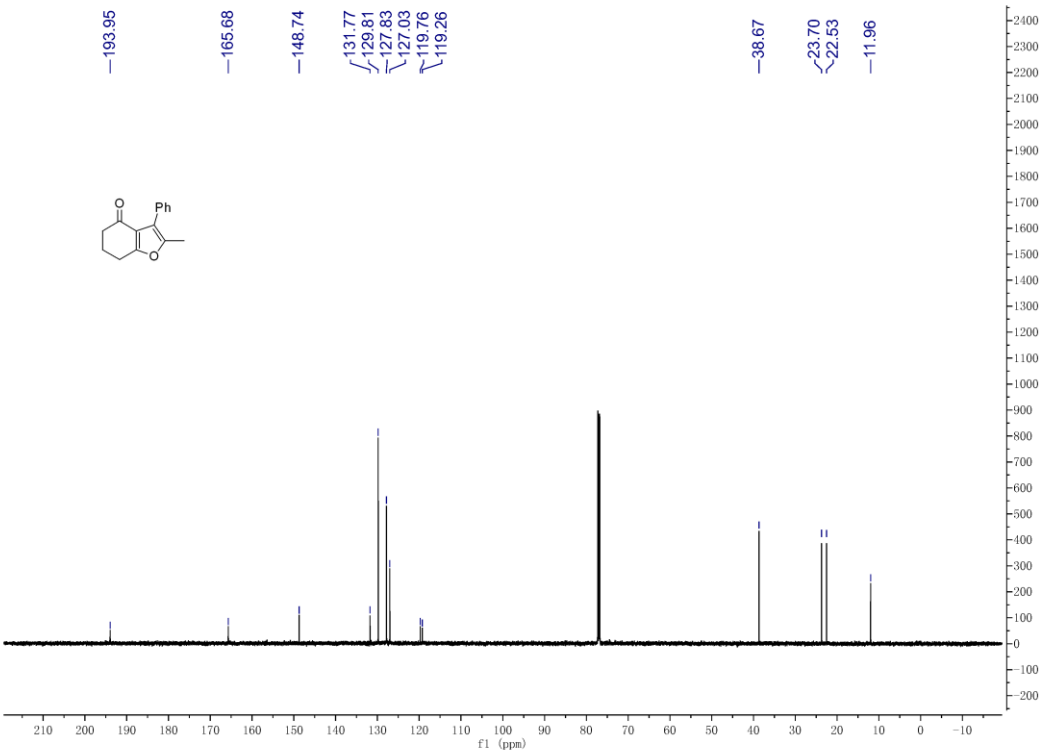
^{1}H NMR spectrum of **3x** (600MHz, $CDCl_3$)



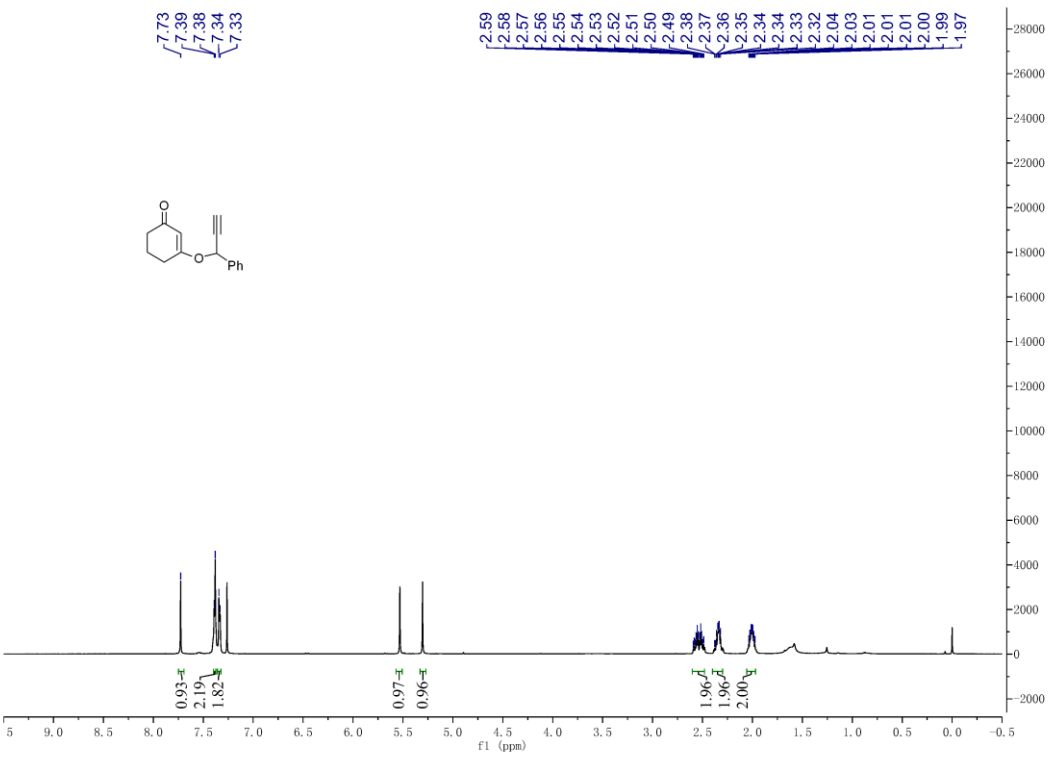
^{13}C NMR spectrum of **3x** (151 MHz, $CDCl_3$)



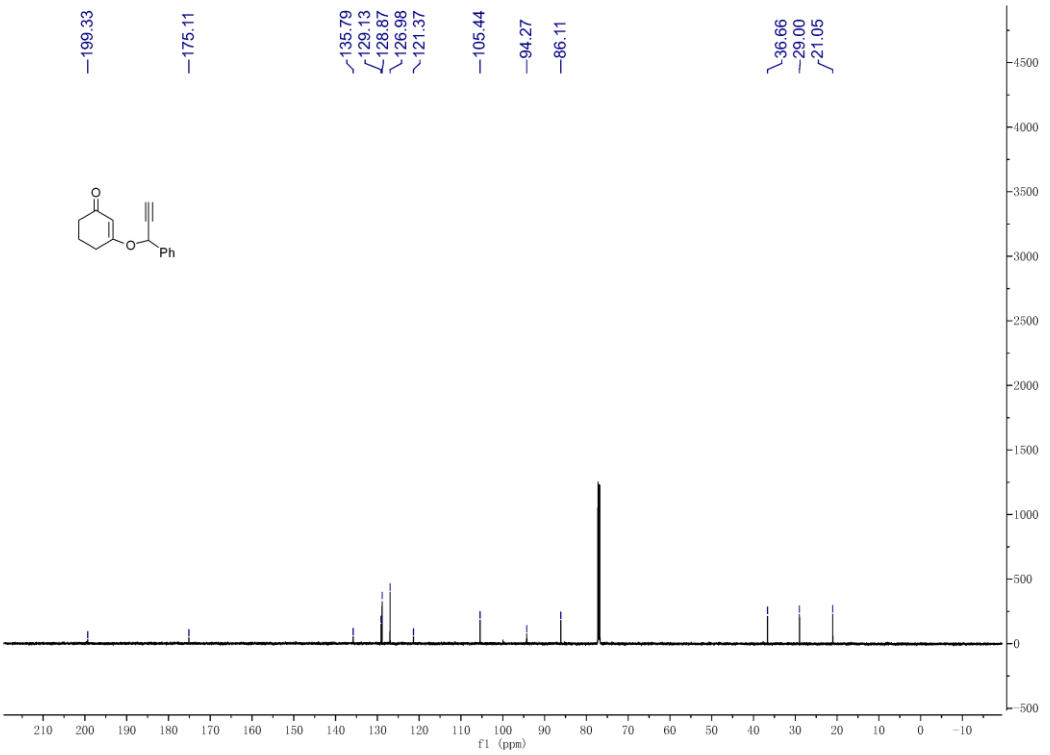
^{1}H NMR spectrum of **3y**(600MHz, $CDCl_3$)



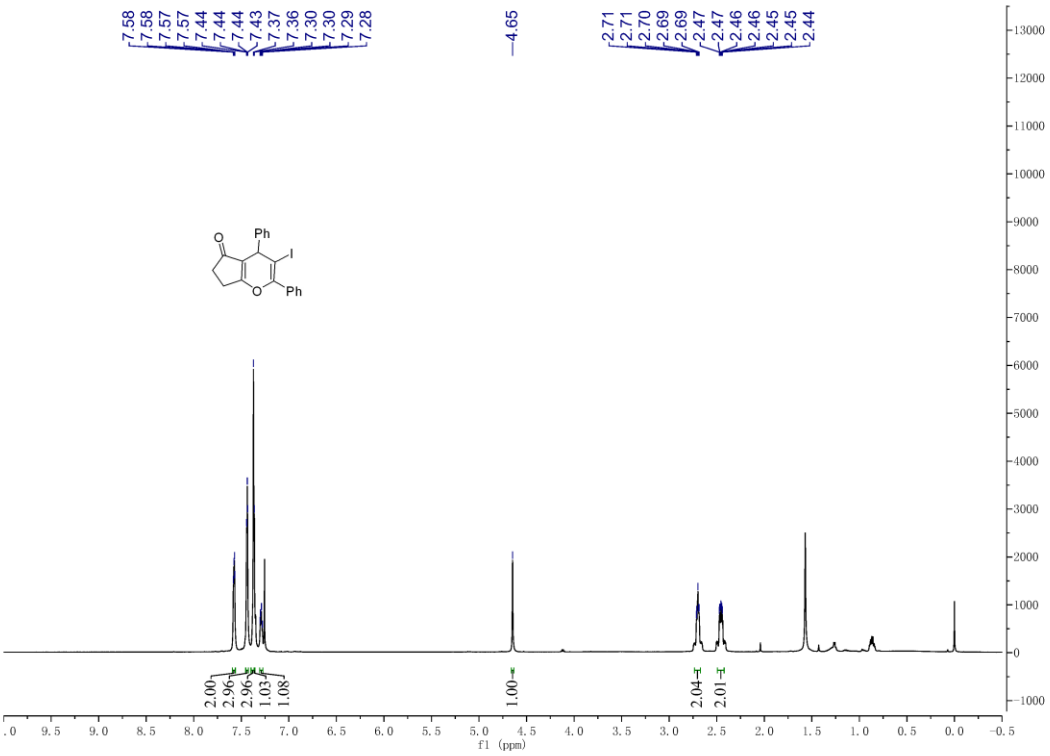
^{13}C NMR spectrum of **3y** (151 MHz, $CDCl_3$)



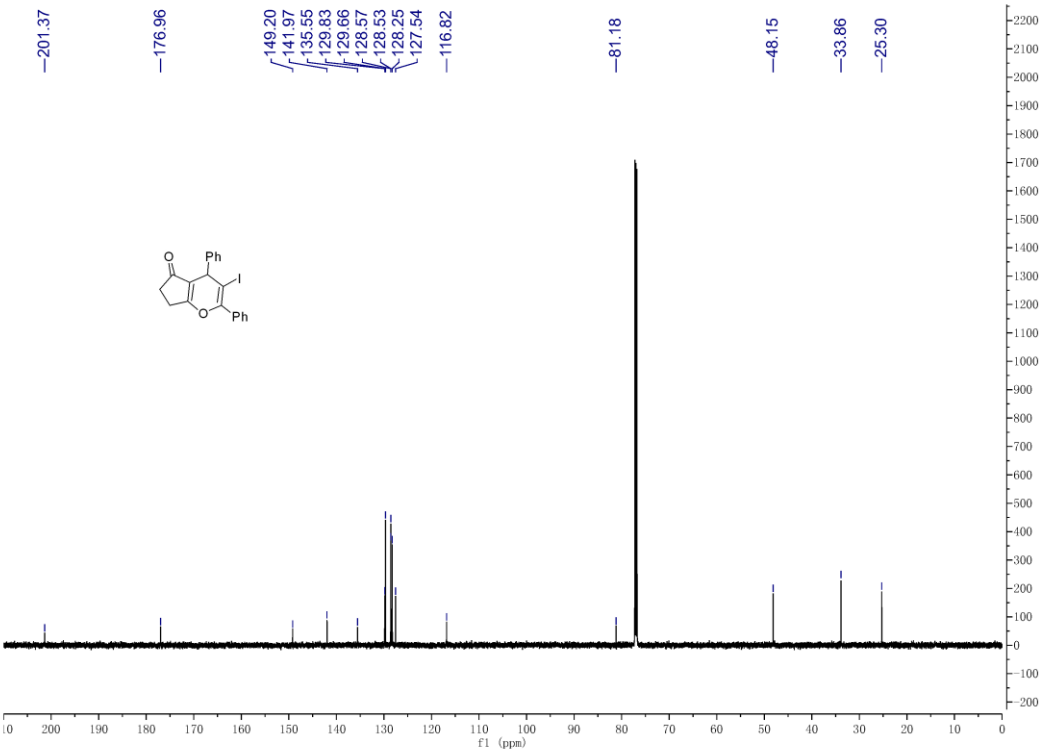
^{1}H NMR spectrum of **3z** (600MHz, $CDCl_3$)



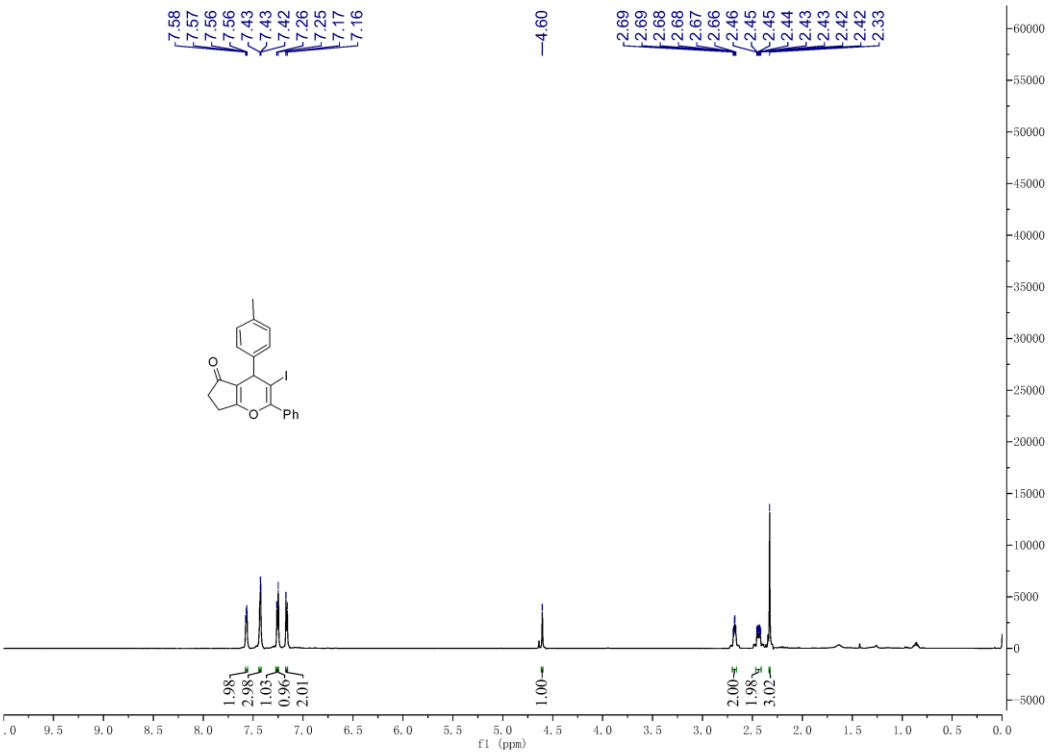
^{13}C NMR spectrum of **3z**(151 MHz, $CDCl_3$)



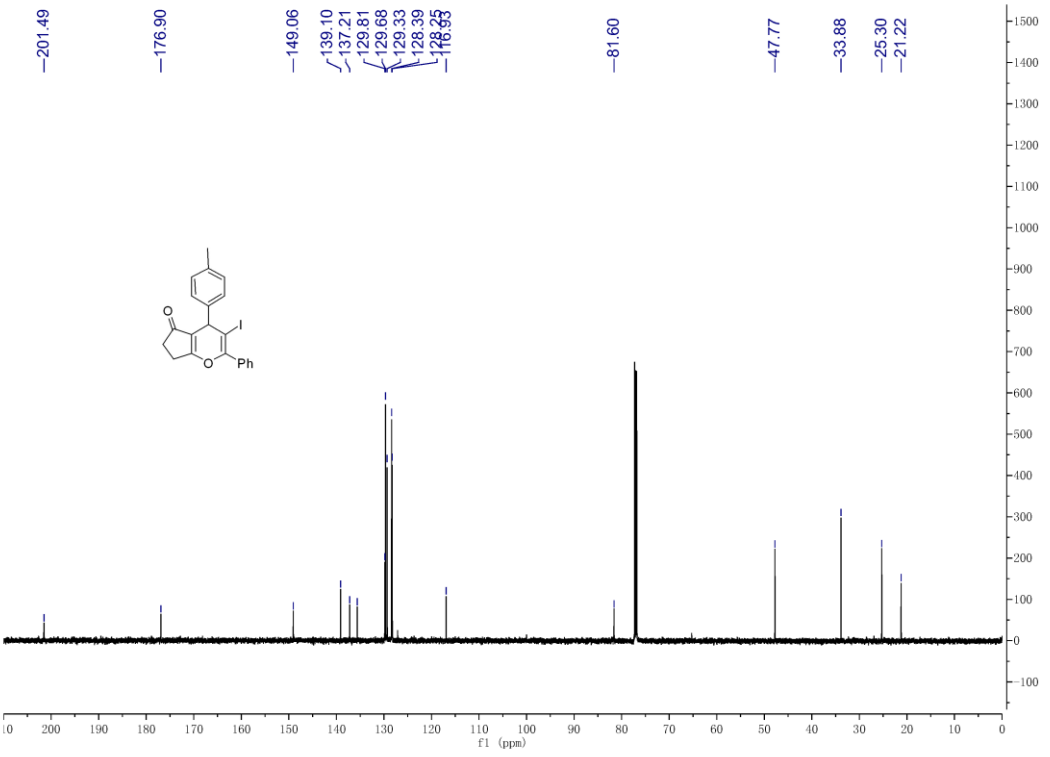
^{1}H NMR spectrum of **4a** (600MHz, $CDCl_3$)



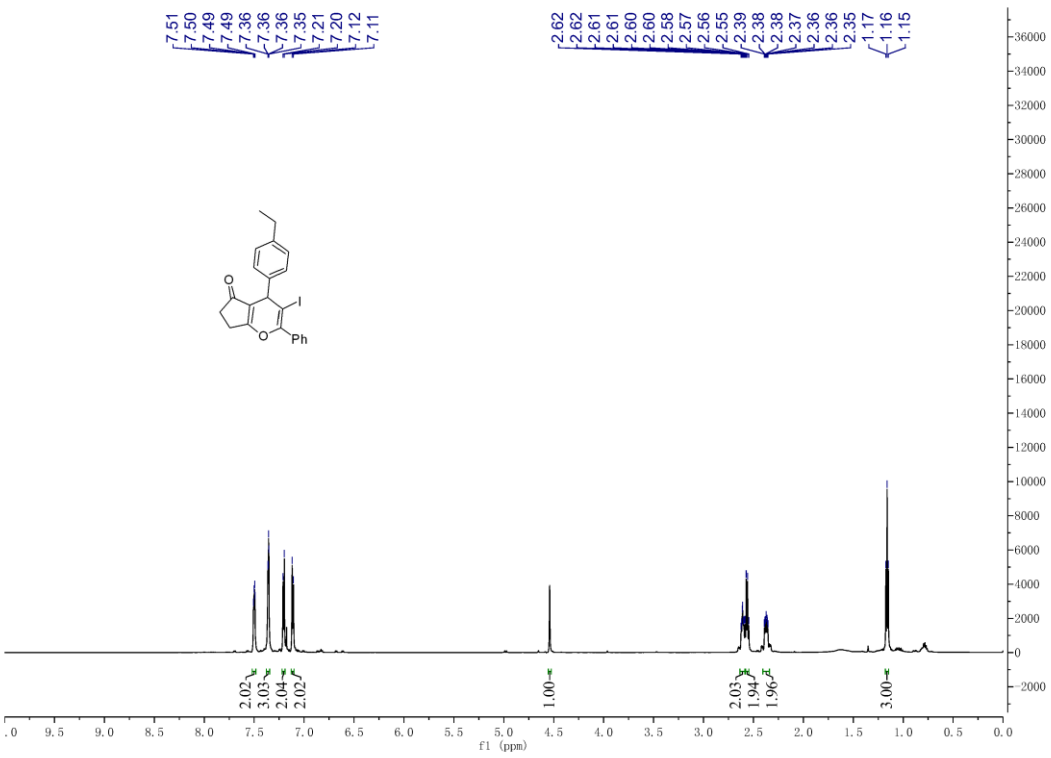
^{13}C NMR spectrum of **4a** (151 MHz, $CDCl_3$)



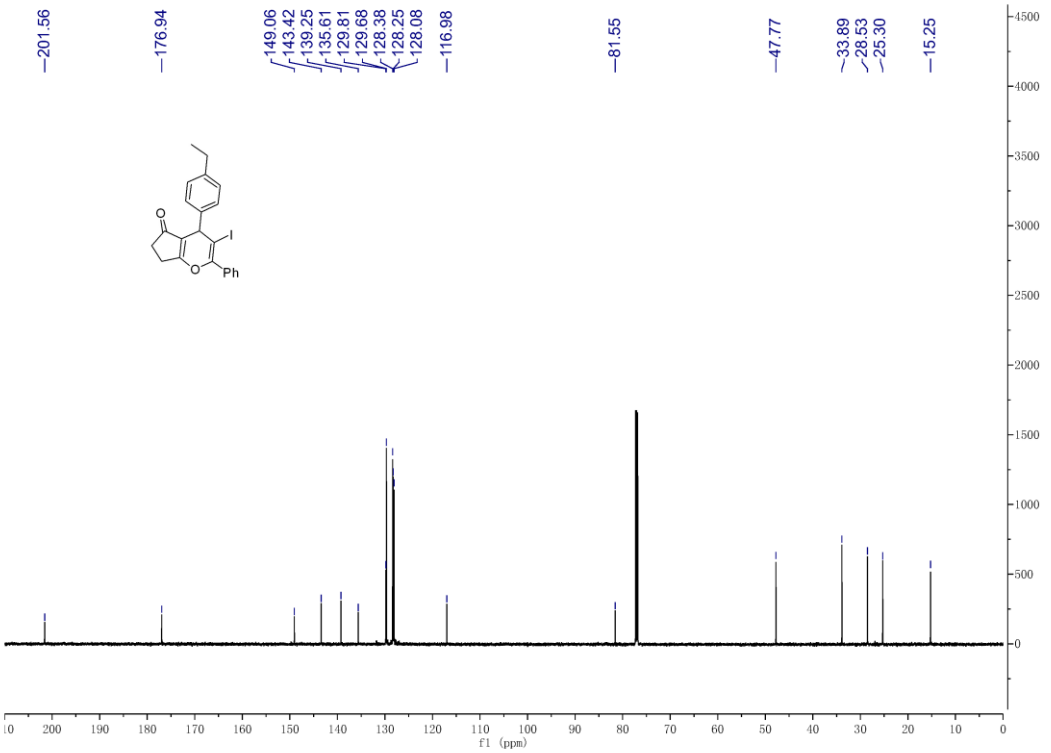
^{1}H NMR spectrum of **4b** (600MHz, $CDCl_3$)



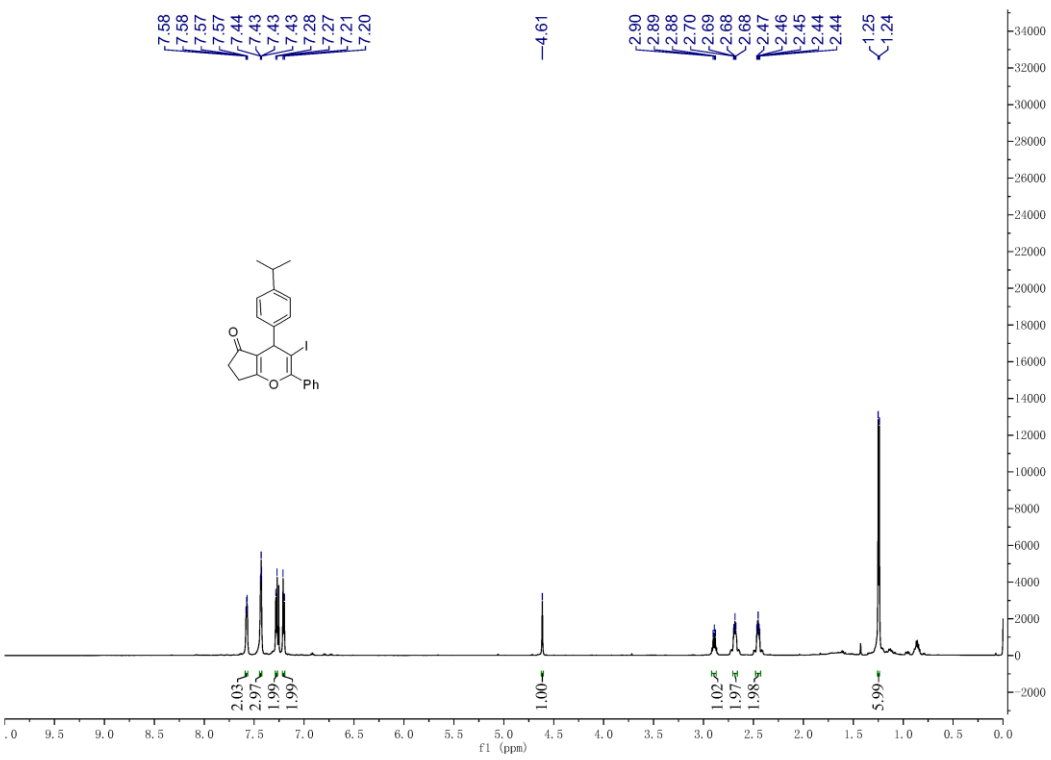
^{13}C NMR spectrum of **4b** (151 MHz, $CDCl_3$)



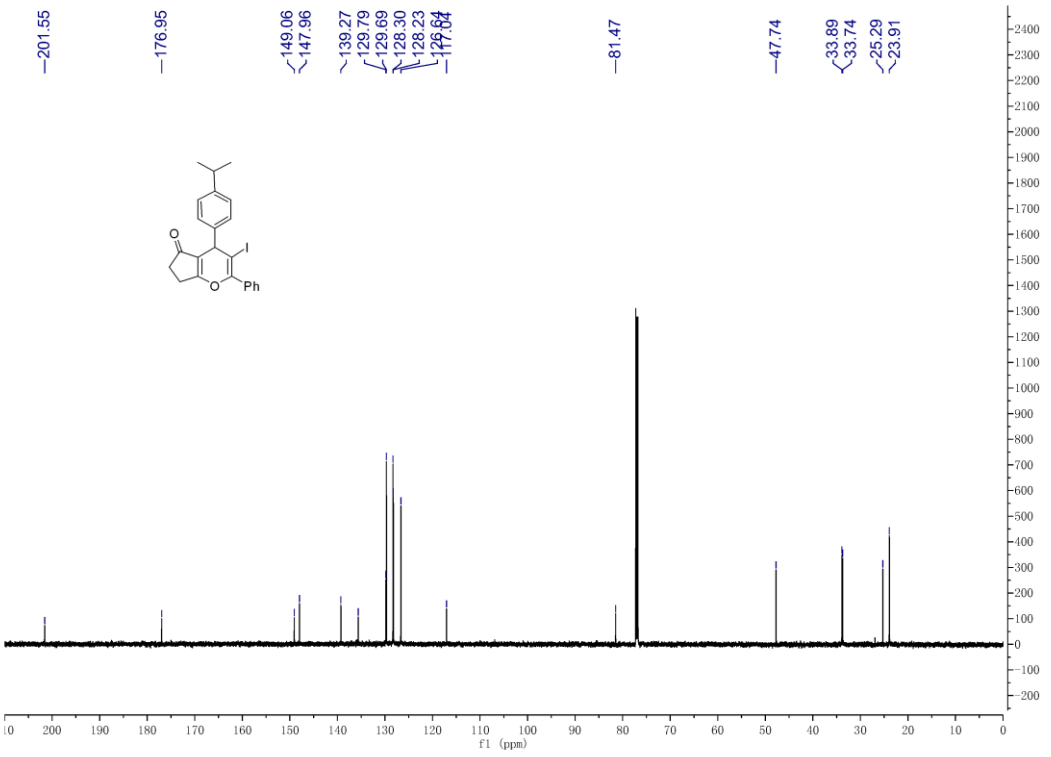
^{1}H NMR spectrum of **4c** (600MHz, $CDCl_3$)



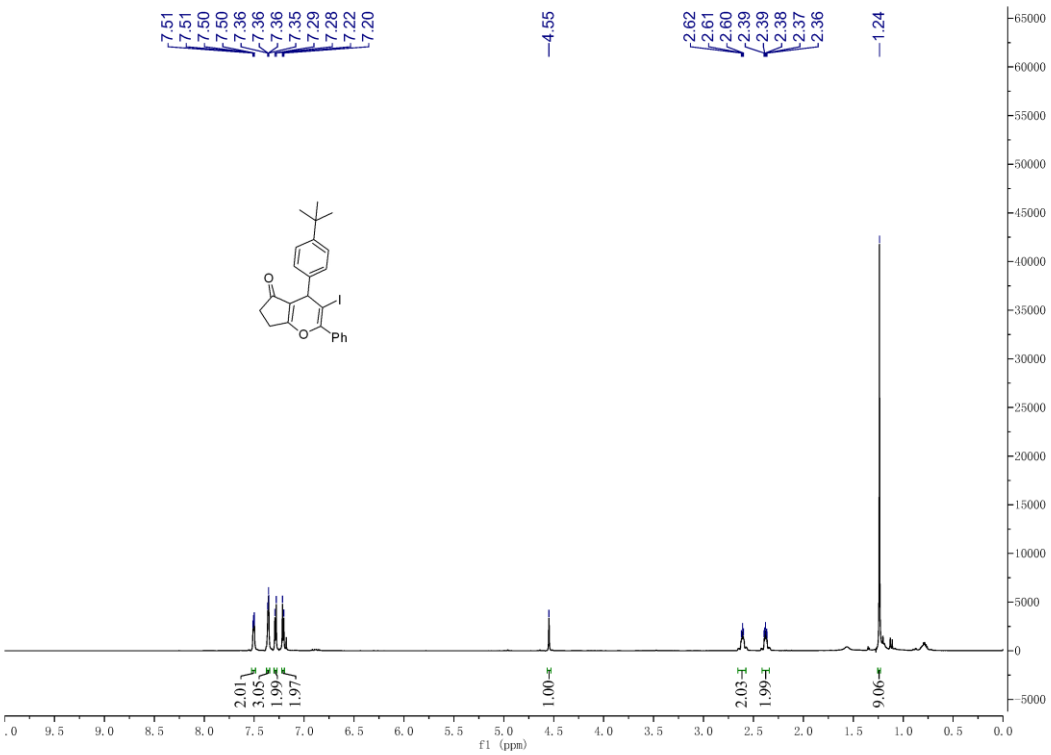
^{13}C NMR spectrum of **4c** (151 MHz, $CDCl_3$)



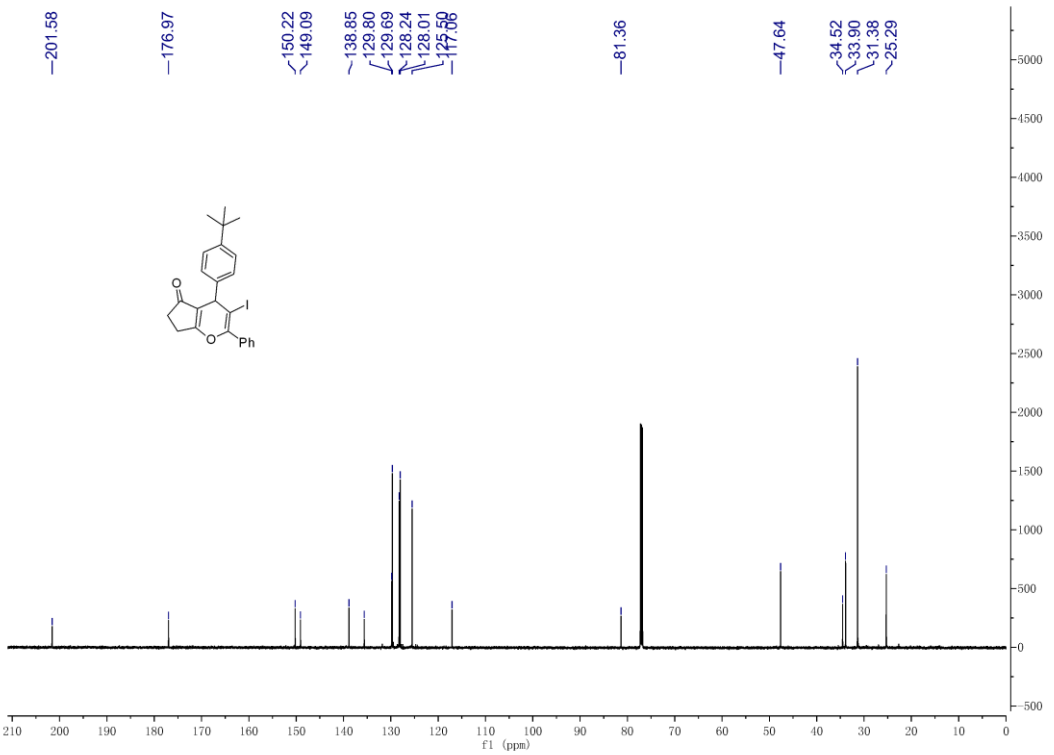
^{1}H NMR spectrum of **4d** (600MHz, $CDCl_3$)



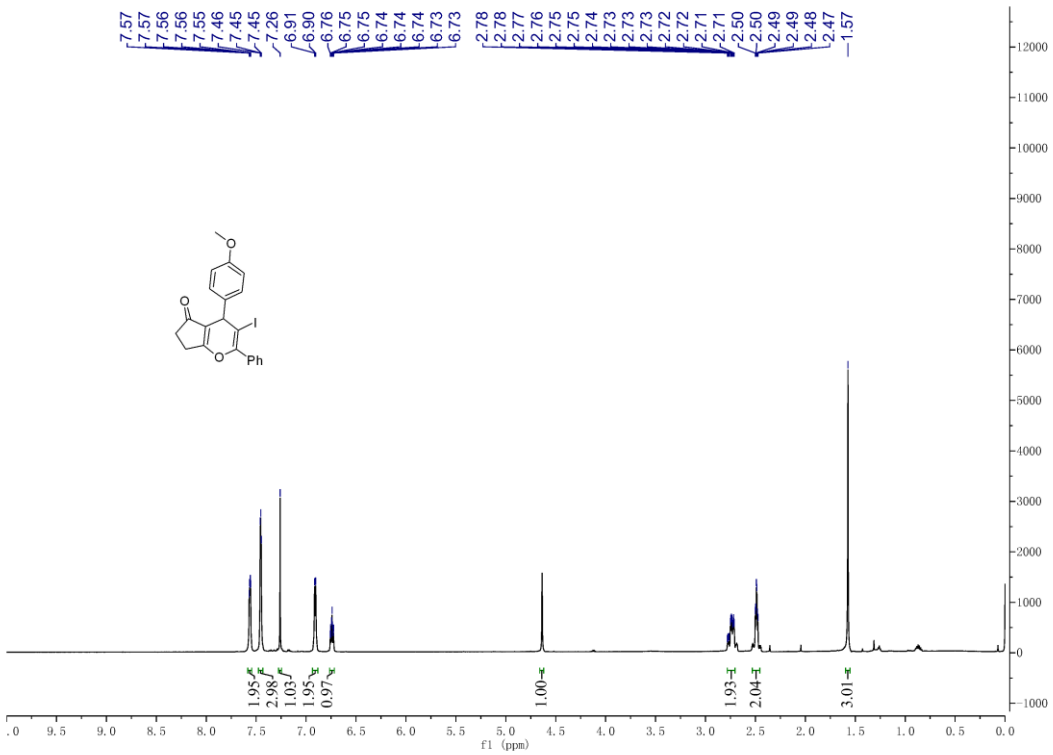
^{13}C NMR spectrum of **4d** (151 MHz, $CDCl_3$)



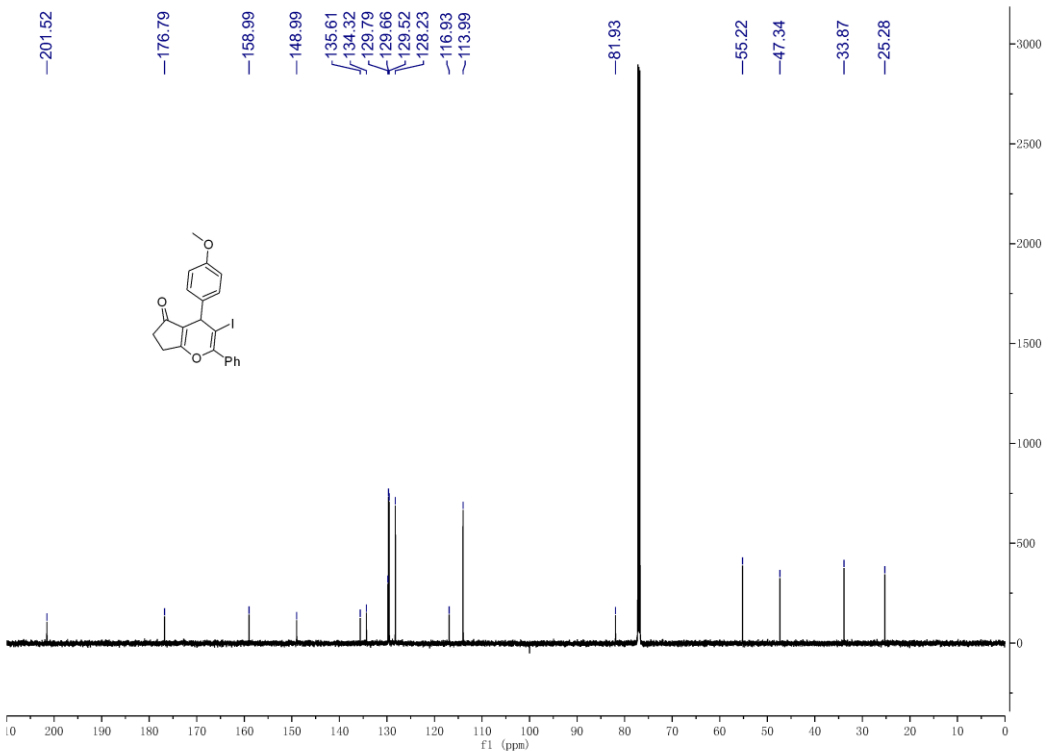
^{1}H NMR spectrum of **4e** (600MHz, $CDCl_3$)



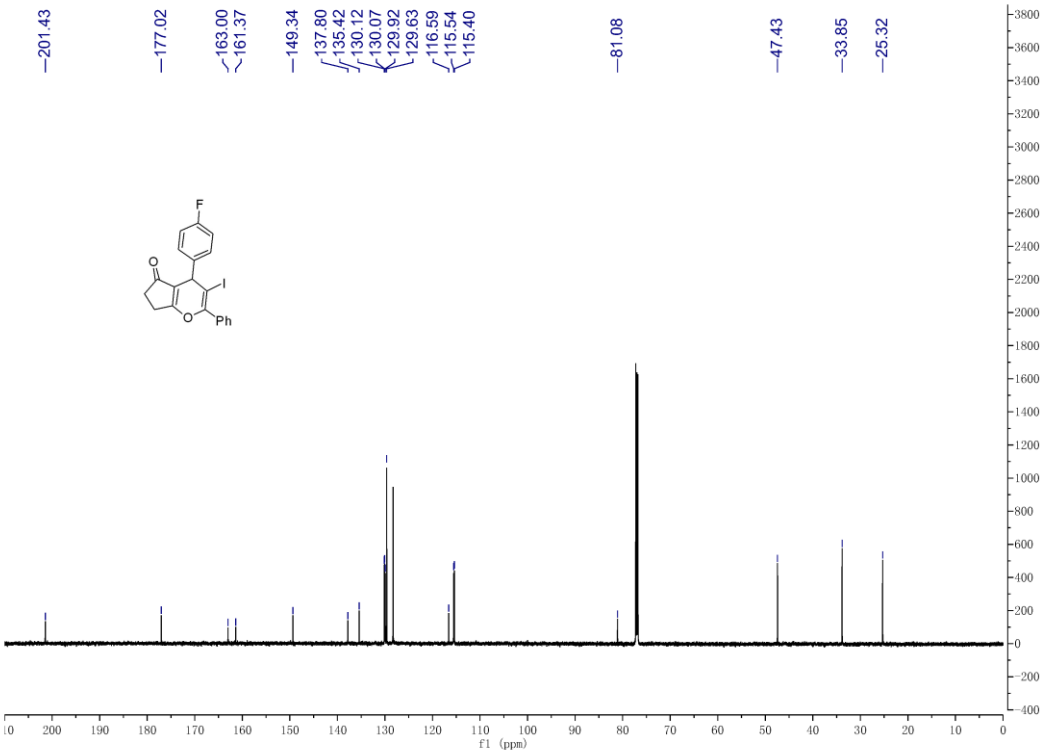
^{13}C NMR spectrum of **4e** (151 MHz, $CDCl_3$)



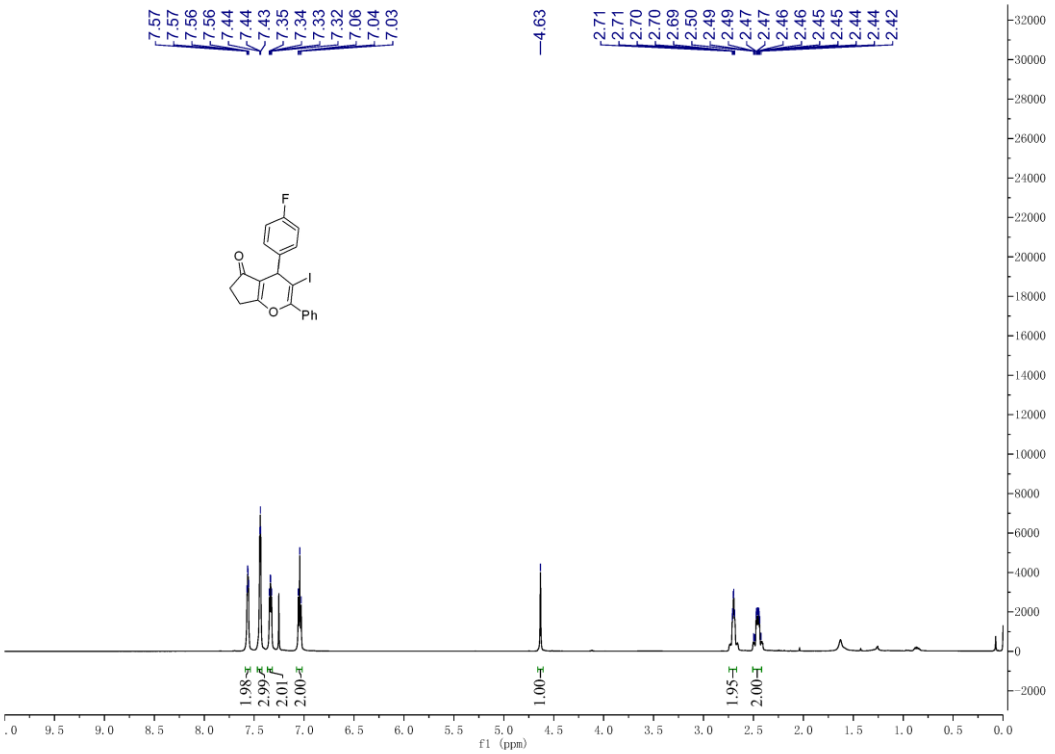
^{1}H NMR spectrum of **4f** (600MHz, $CDCl_3$)



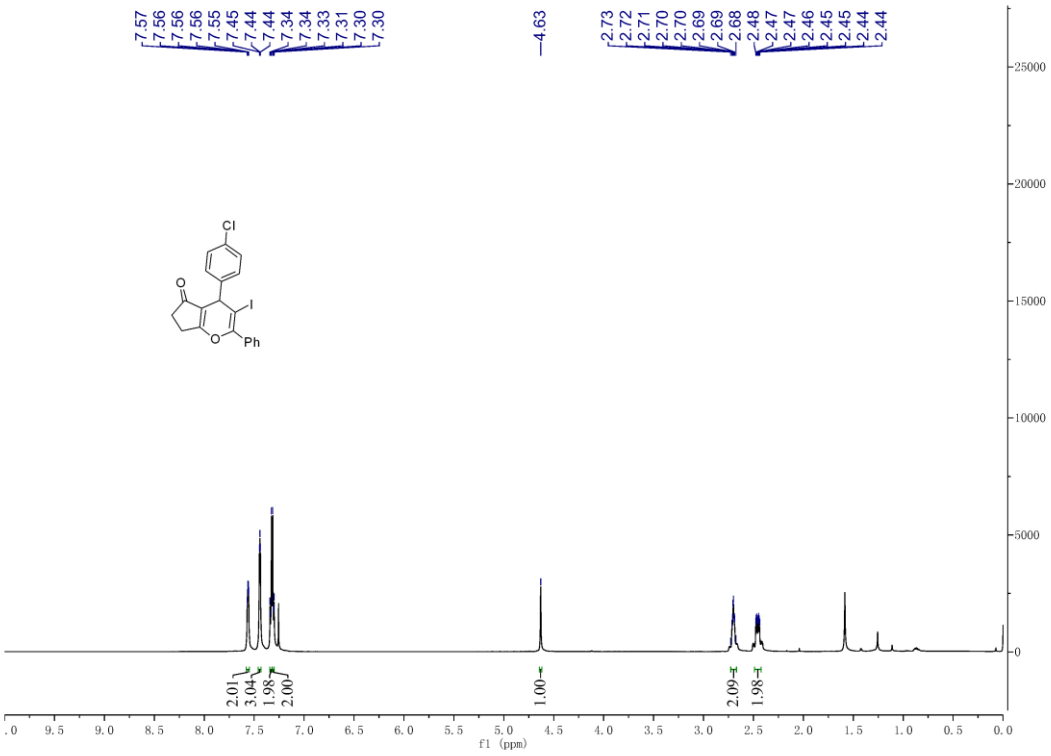
^{13}C NMR spectrum of **4f** (151 MHz, $CDCl_3$)



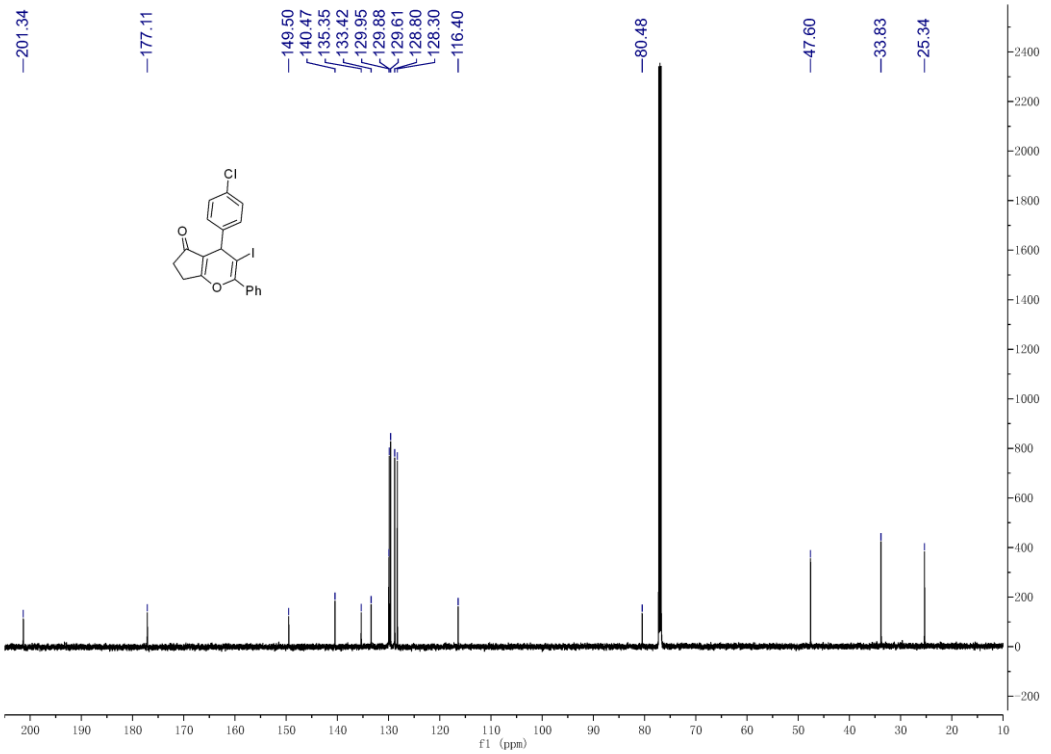
^{1}H NMR spectrum of **4g** (600MHz, $CDCl_3$)



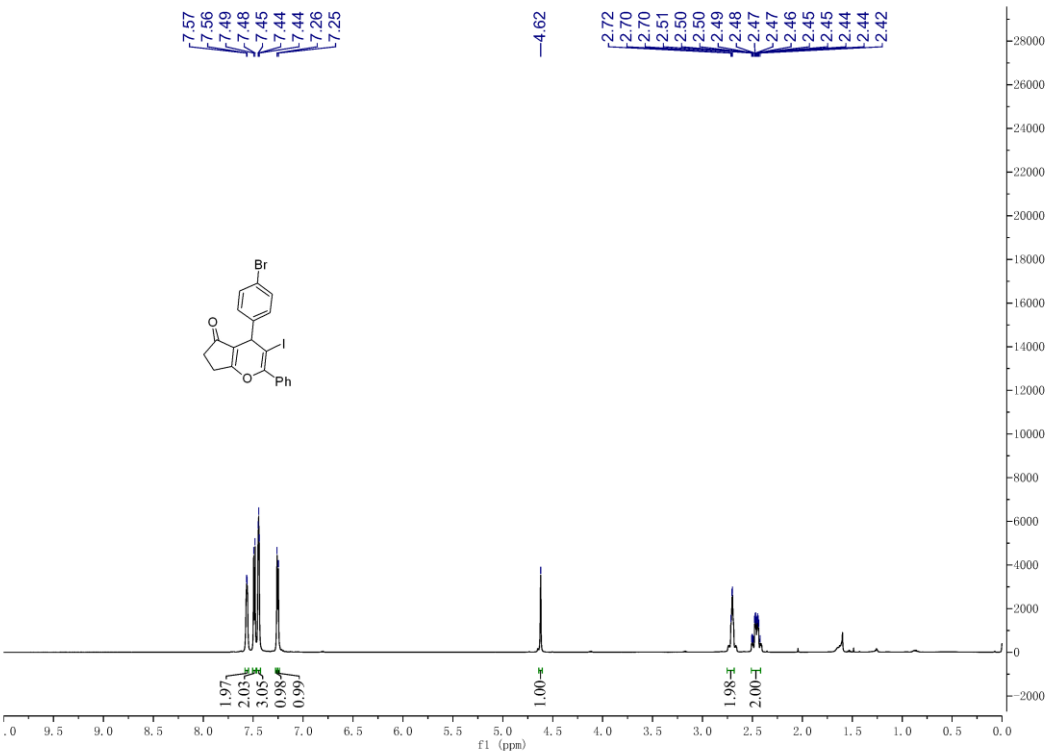
^{13}C NMR spectrum of **4g** (151 MHz, $CDCl_3$)



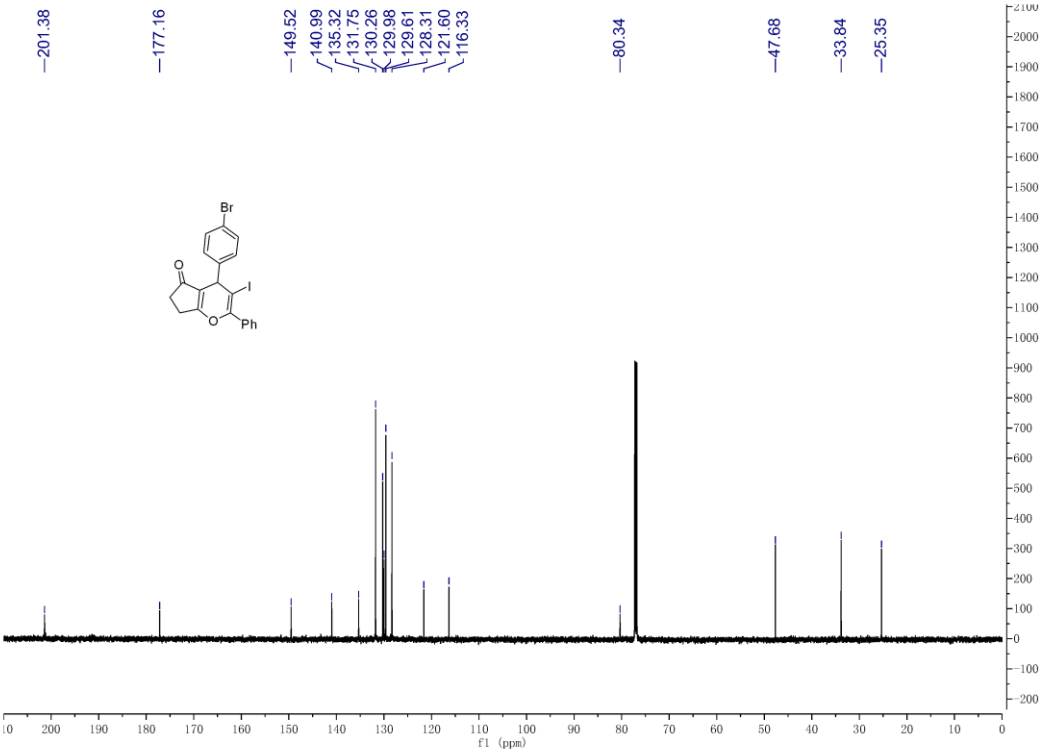
^{1}H NMR spectrum of **4h** (600MHz, $CDCl_3$)



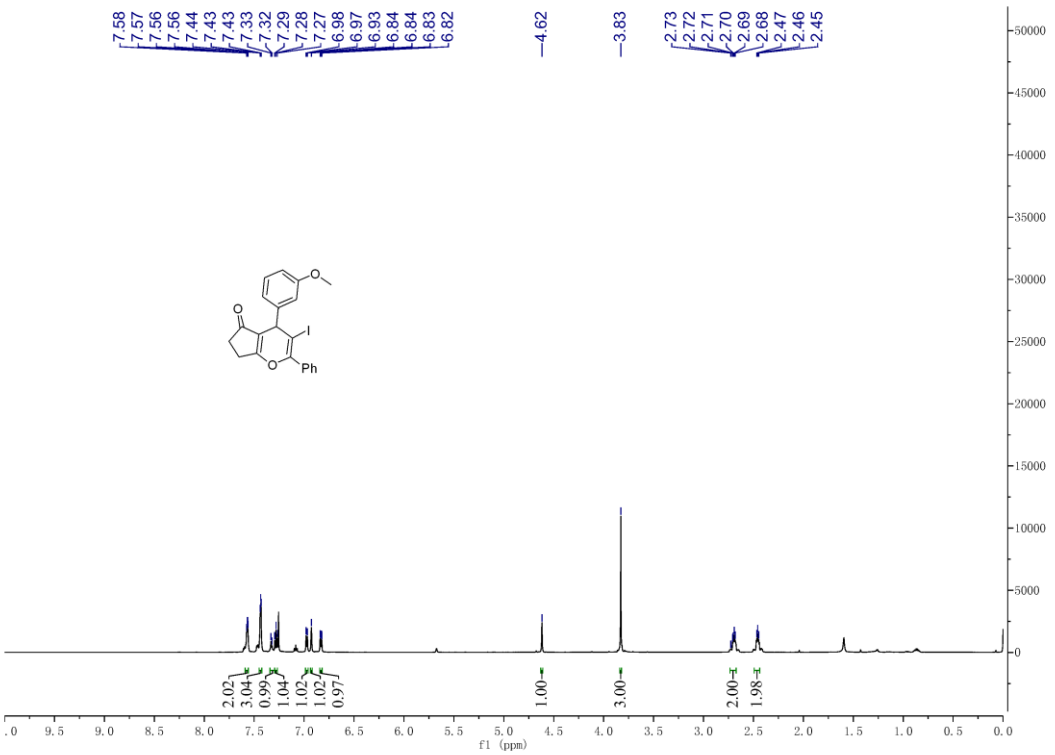
^{13}C NMR spectrum of **4h** (151 MHz, $CDCl_3$)



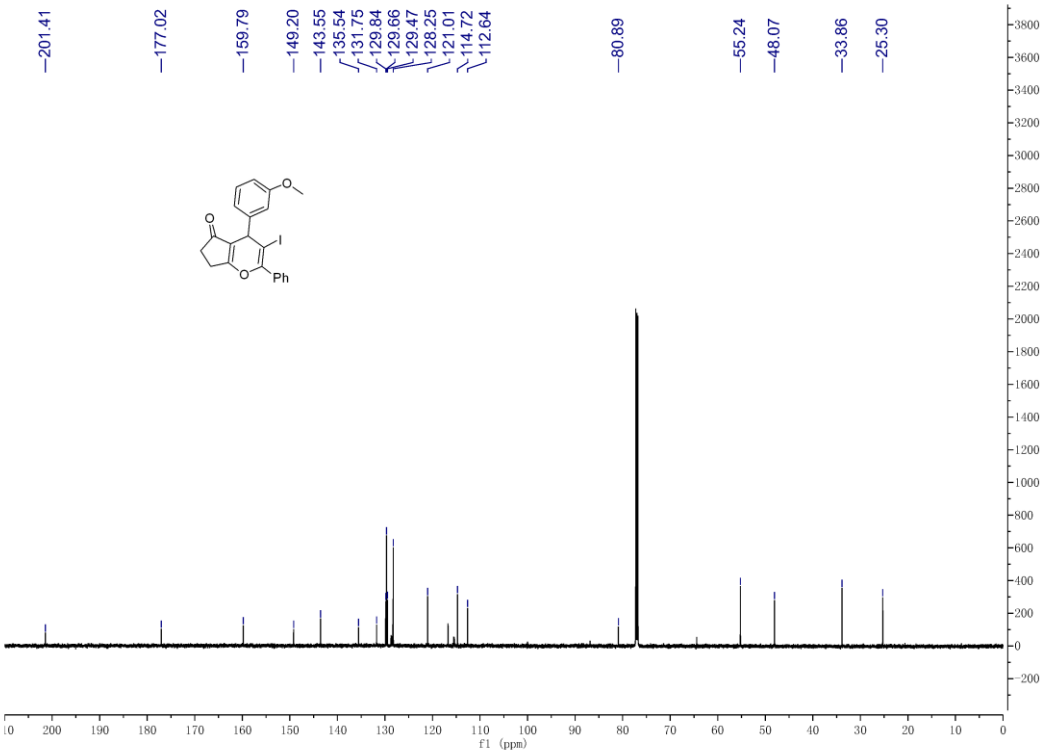
^{1}H NMR spectrum of **4i** (600MHz, $CDCl_3$)



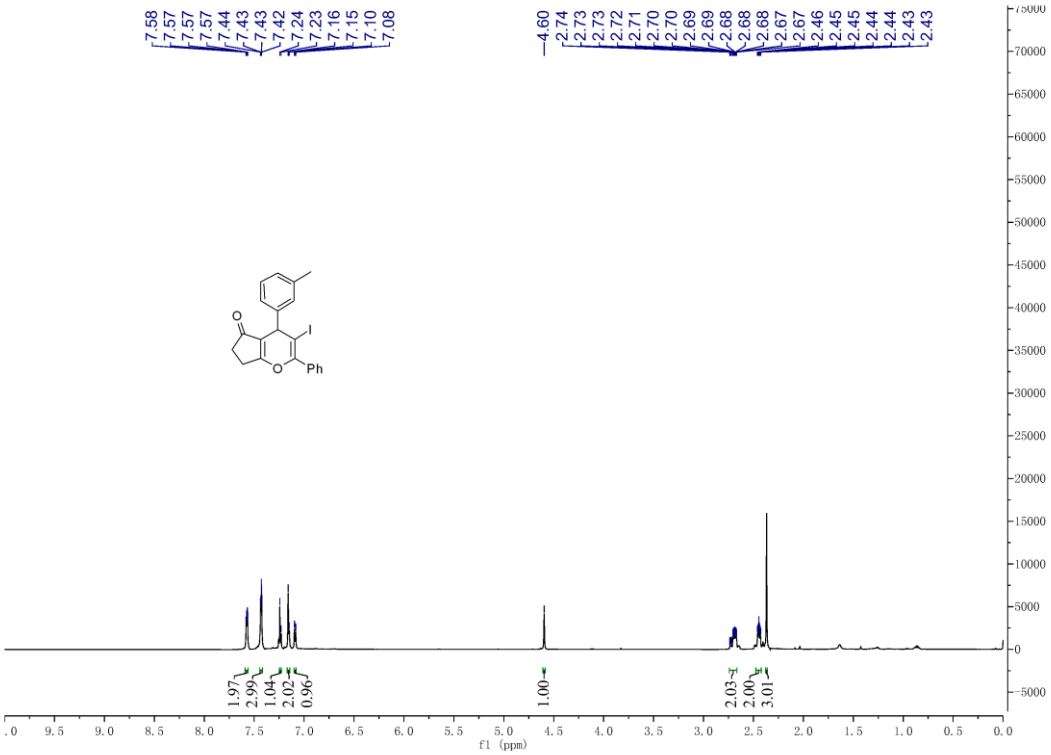
^{13}C NMR spectrum of **4i** (151 MHz, $CDCl_3$)



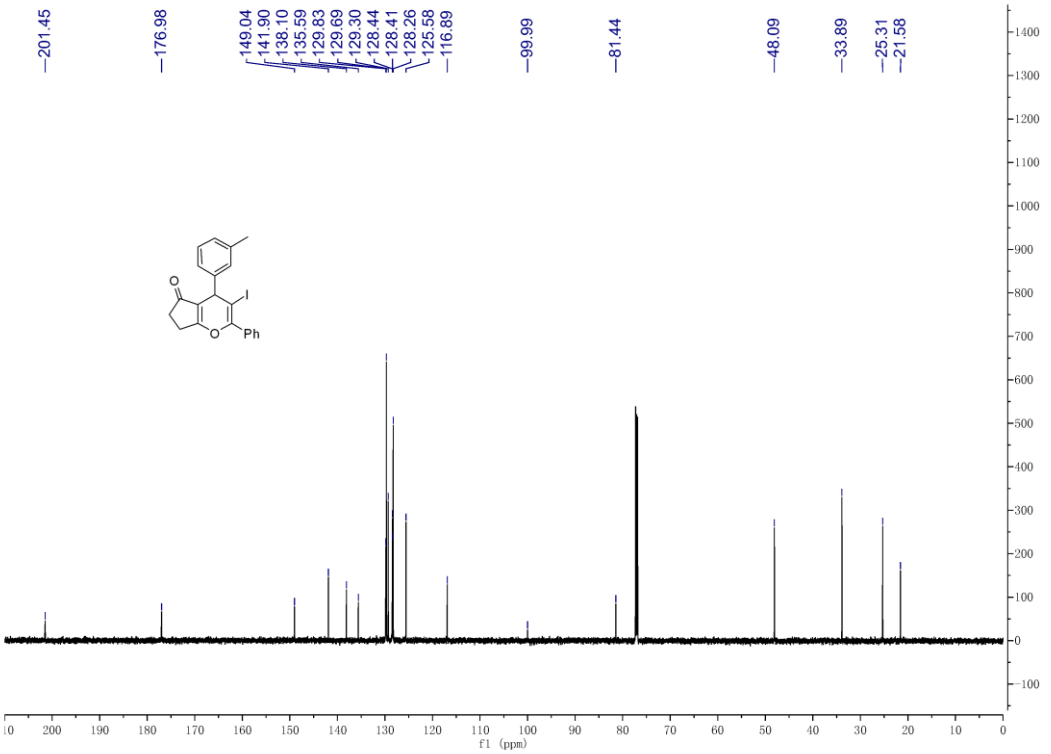
^{1}H NMR spectrum of **4j**(600MHz, $CDCl_3$)



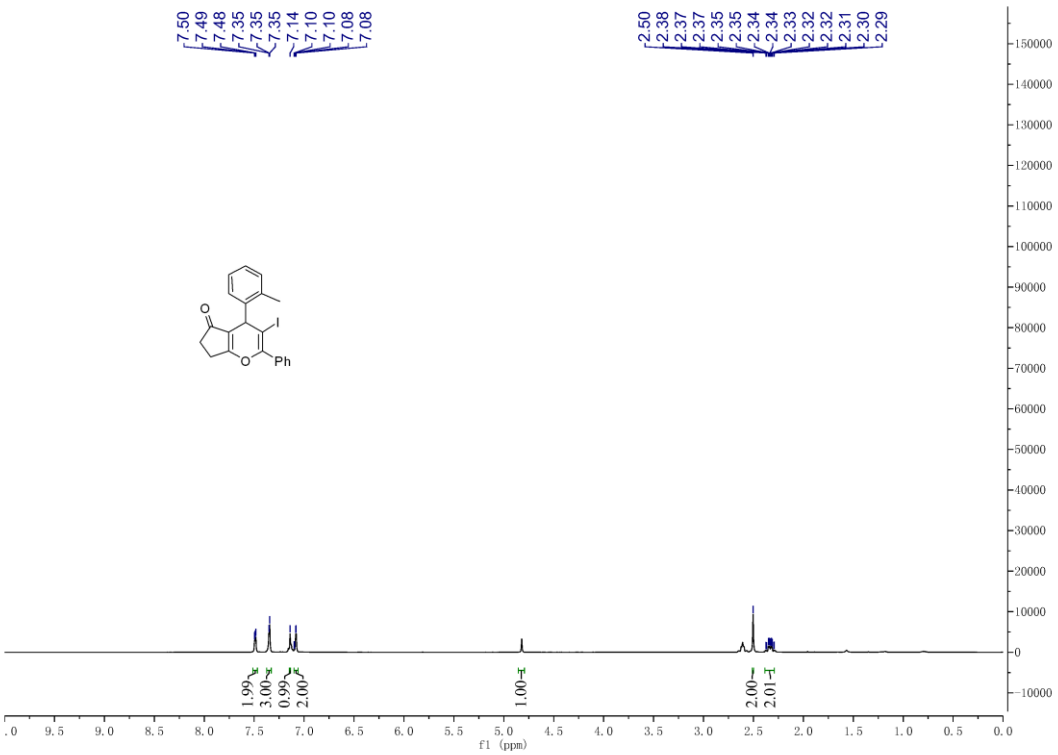
^{13}C NMR spectrum of **4j** (151 MHz, $CDCl_3$)



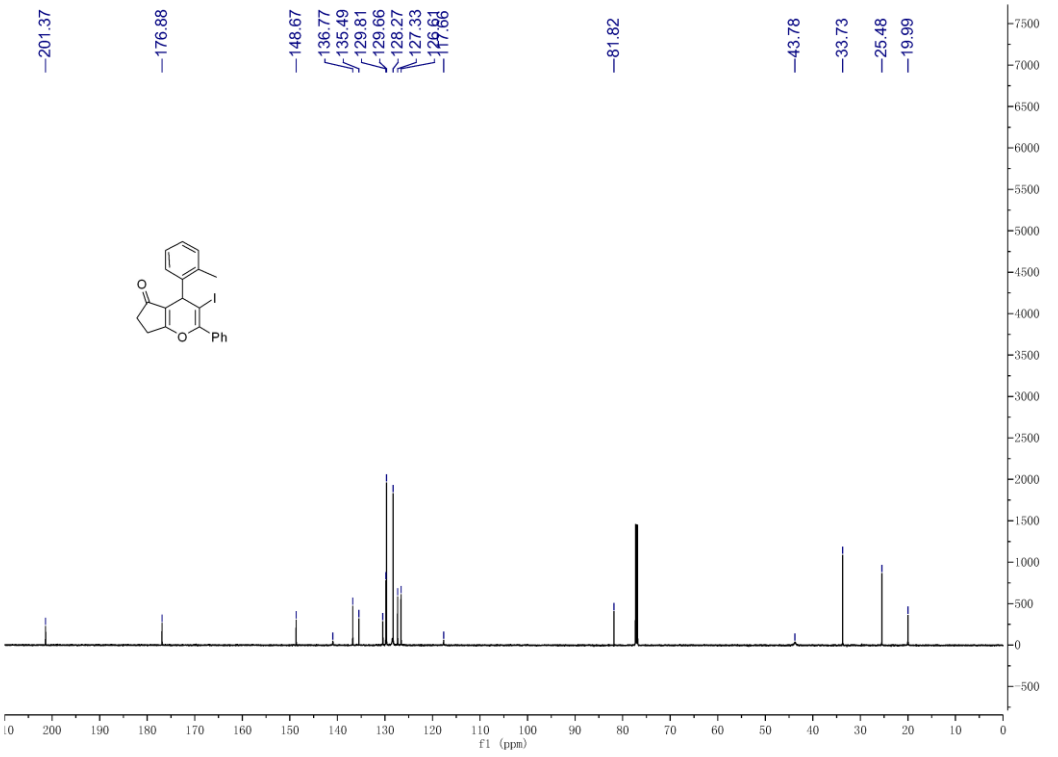
^{1}H NMR spectrum of **4k** (600MHz, $CDCl_3$)



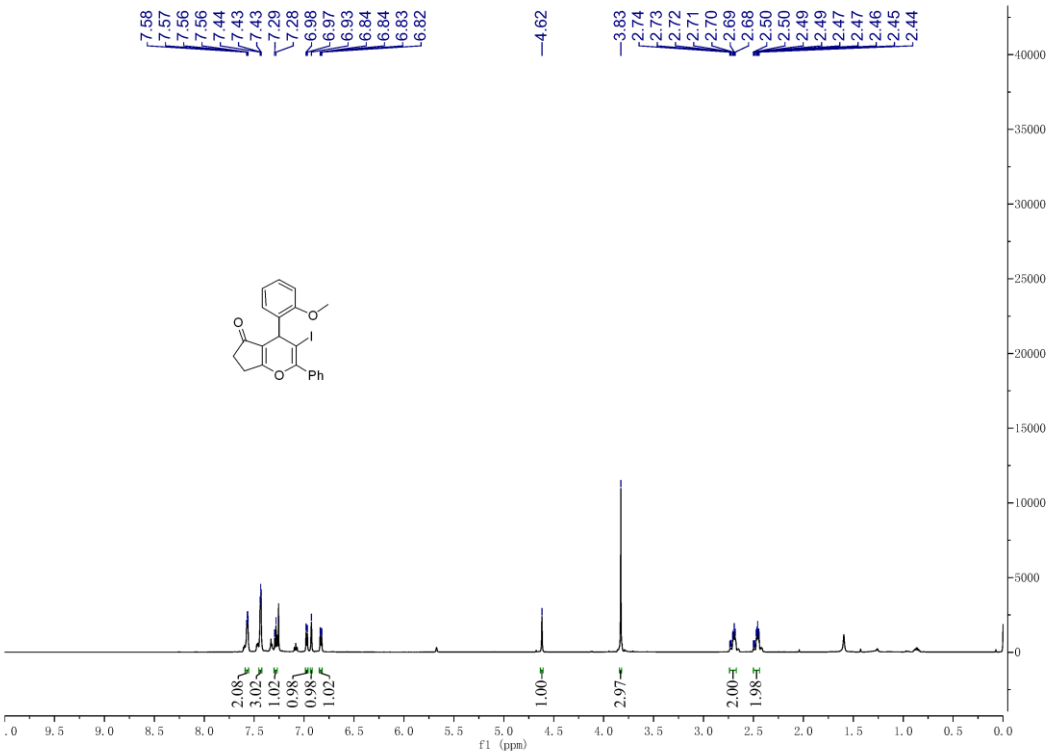
^{13}C NMR spectrum of **4k** (151 MHz, $CDCl_3$)



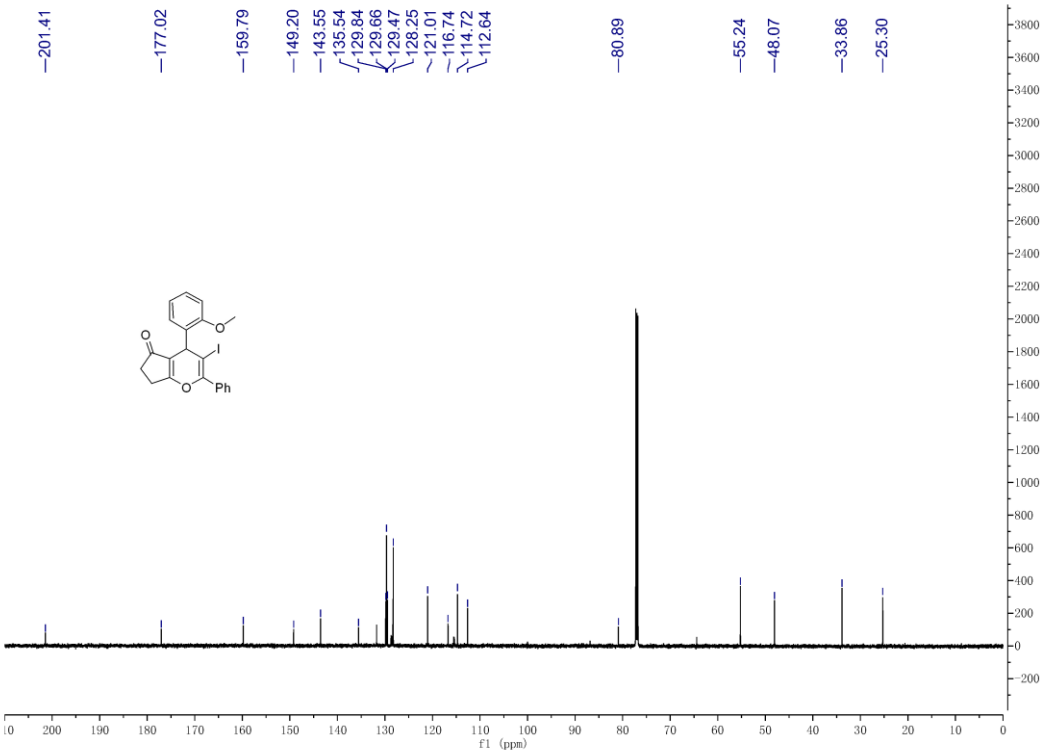
^{1}H NMR spectrum of **4l** (600MHz, $CDCl_3$)



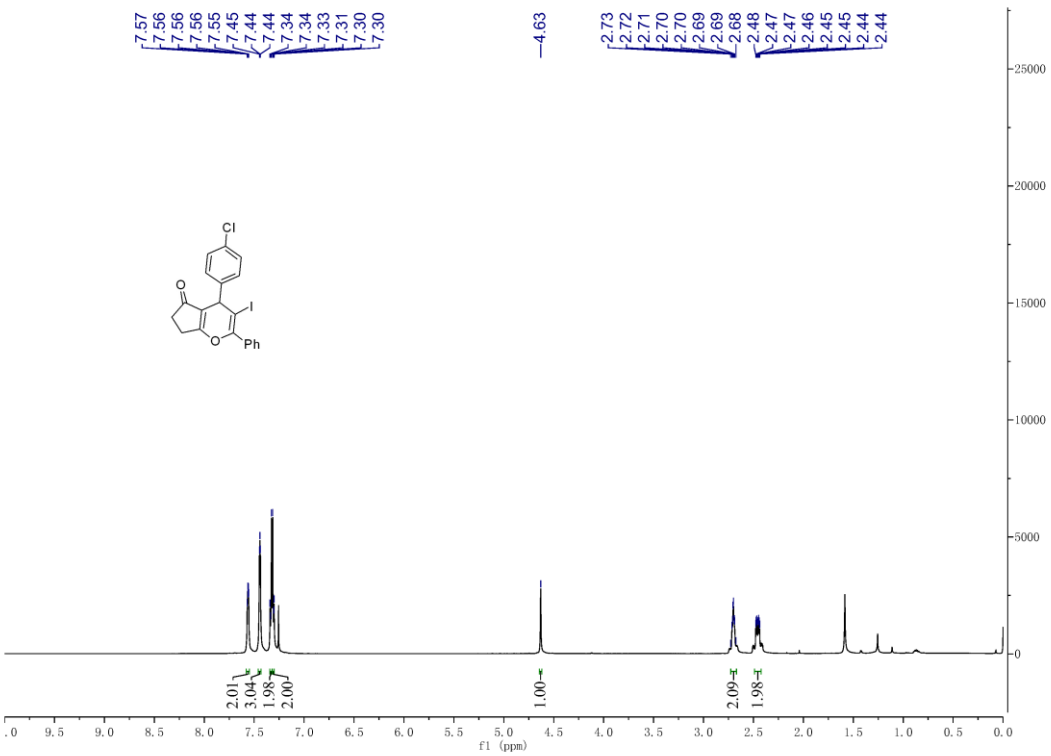
^{13}C NMR spectrum of **4l** (151 MHz, $CDCl_3$)



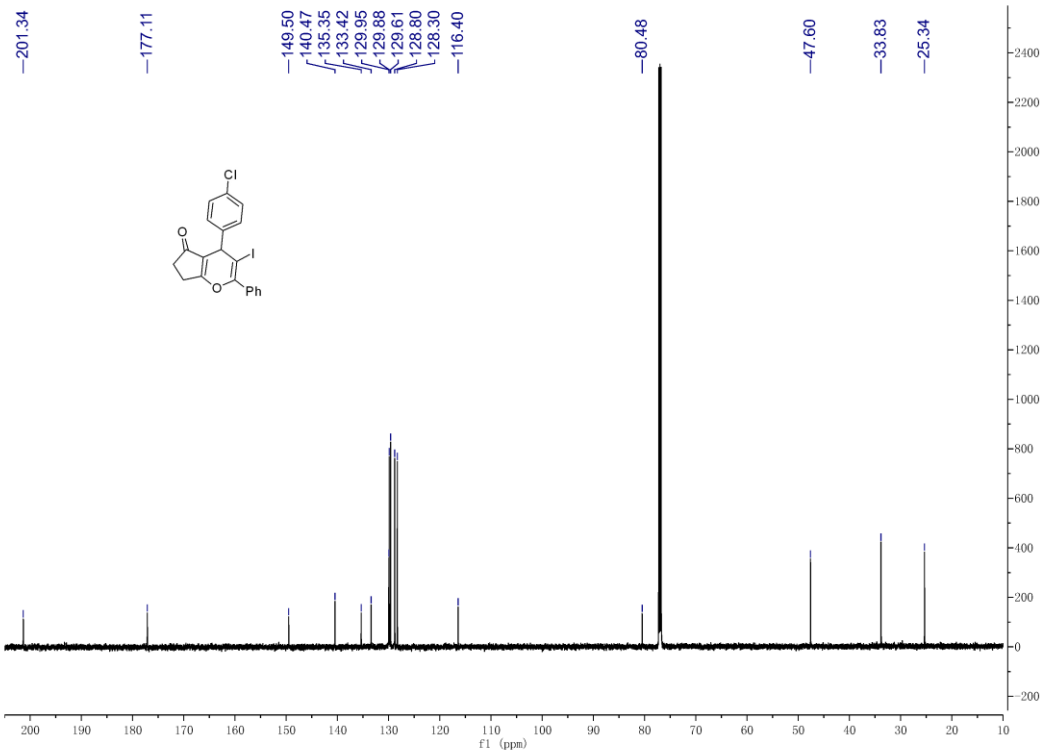
^{1}H NMR spectrum of **4m** (600MHz, $CDCl_3$)



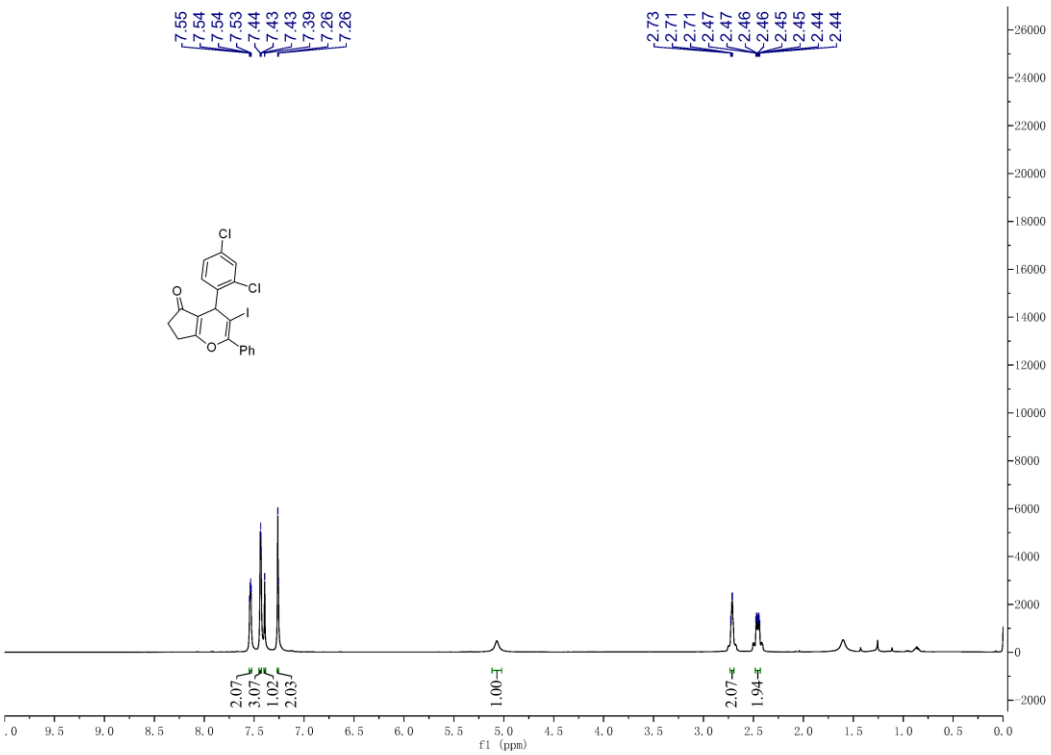
^{13}C NMR spectrum of **4m** (151 MHz, $CDCl_3$)



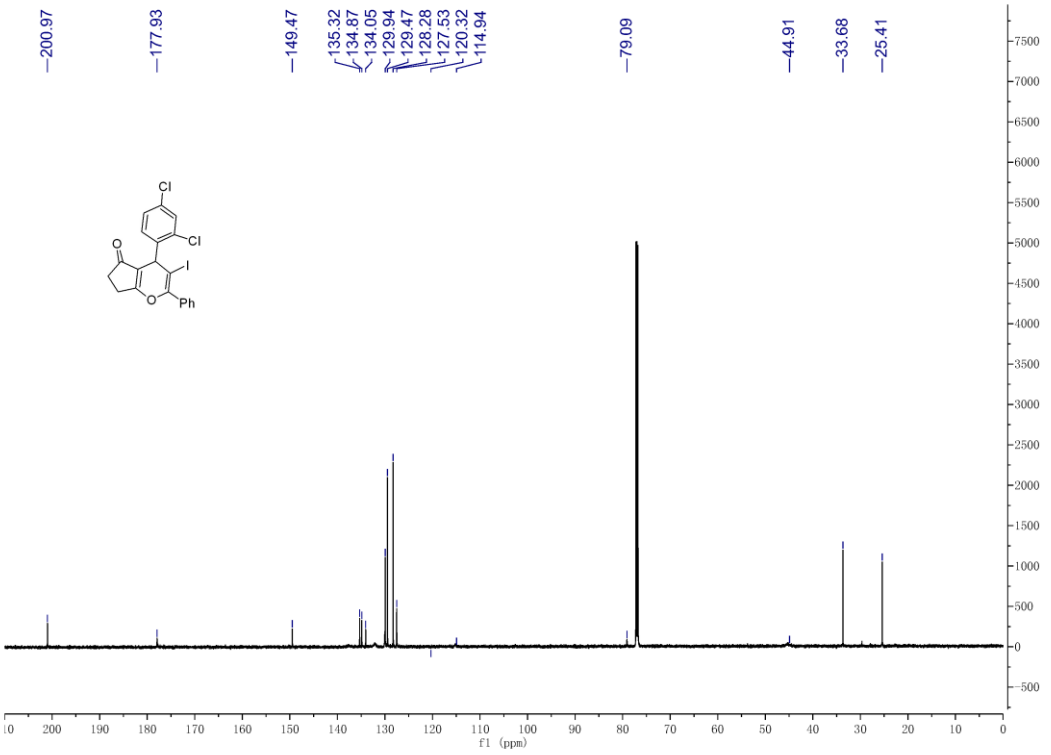
^{1}H NMR spectrum of **4n** (600MHz, $CDCl_3$)



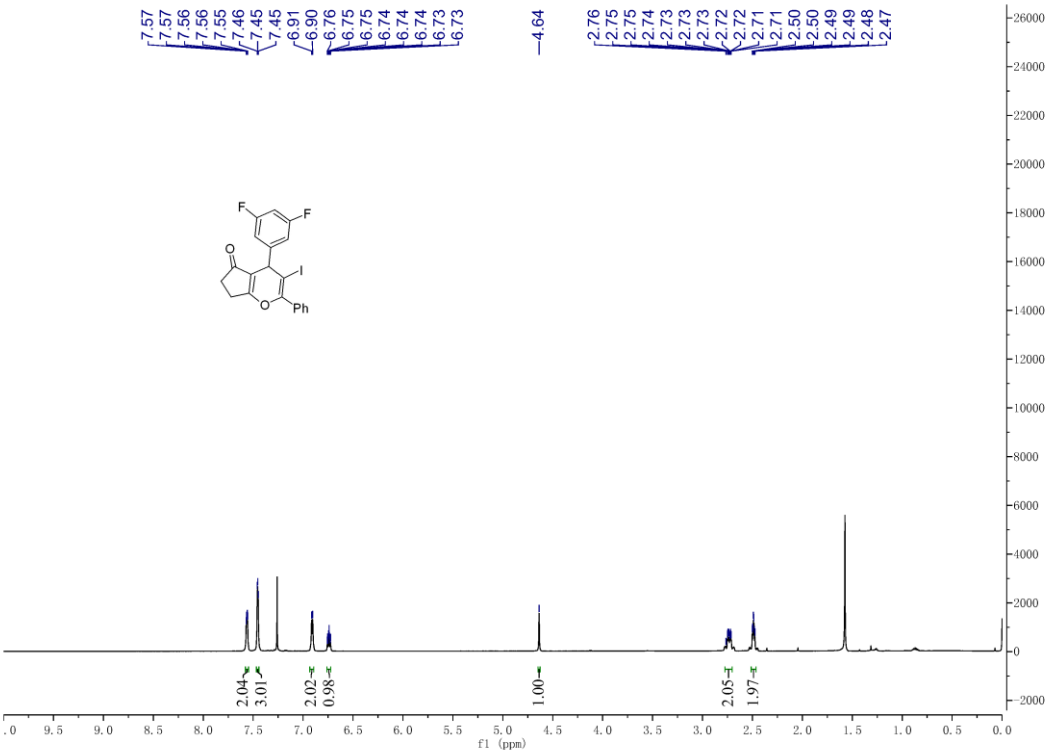
^{13}C NMR spectrum of **4n** (151 MHz, $CDCl_3$)



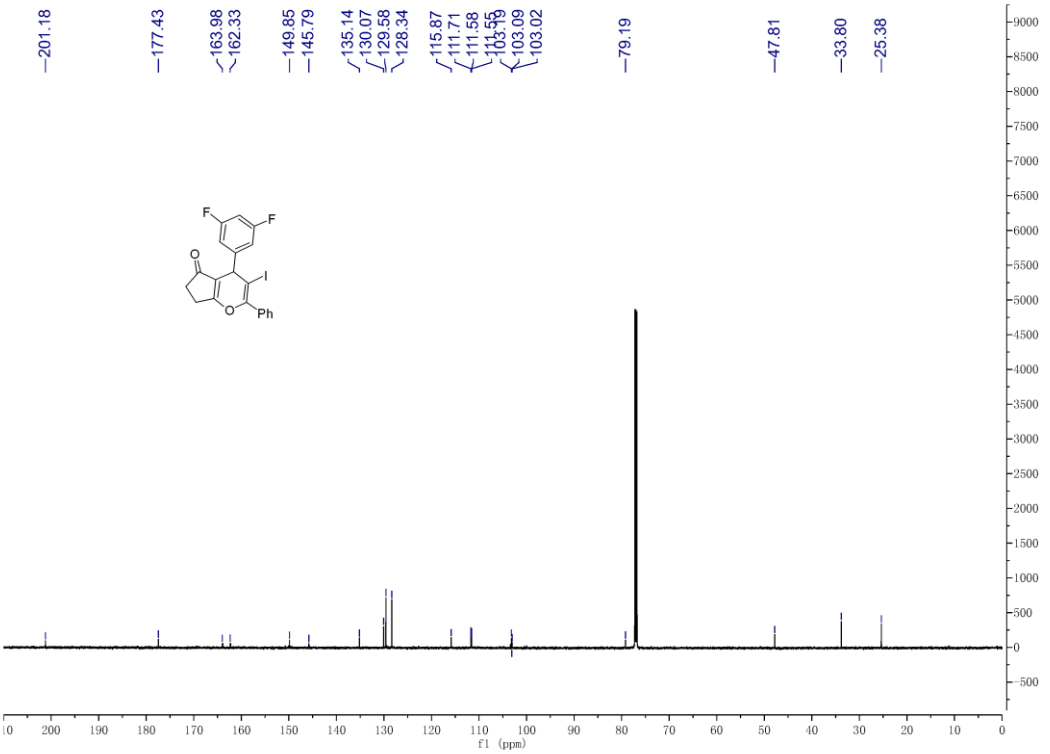
^{1}H NMR spectrum of **4o** (600MHz, $CDCl_3$)



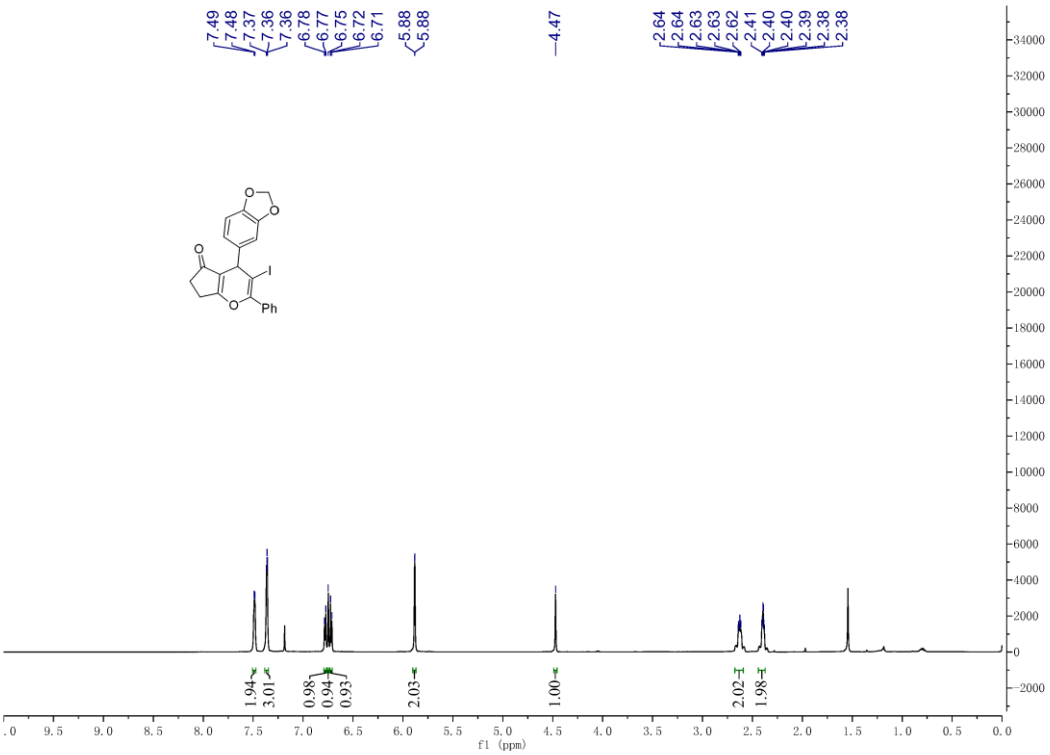
^{13}C NMR spectrum of **4o** (151 MHz, $CDCl_3$)



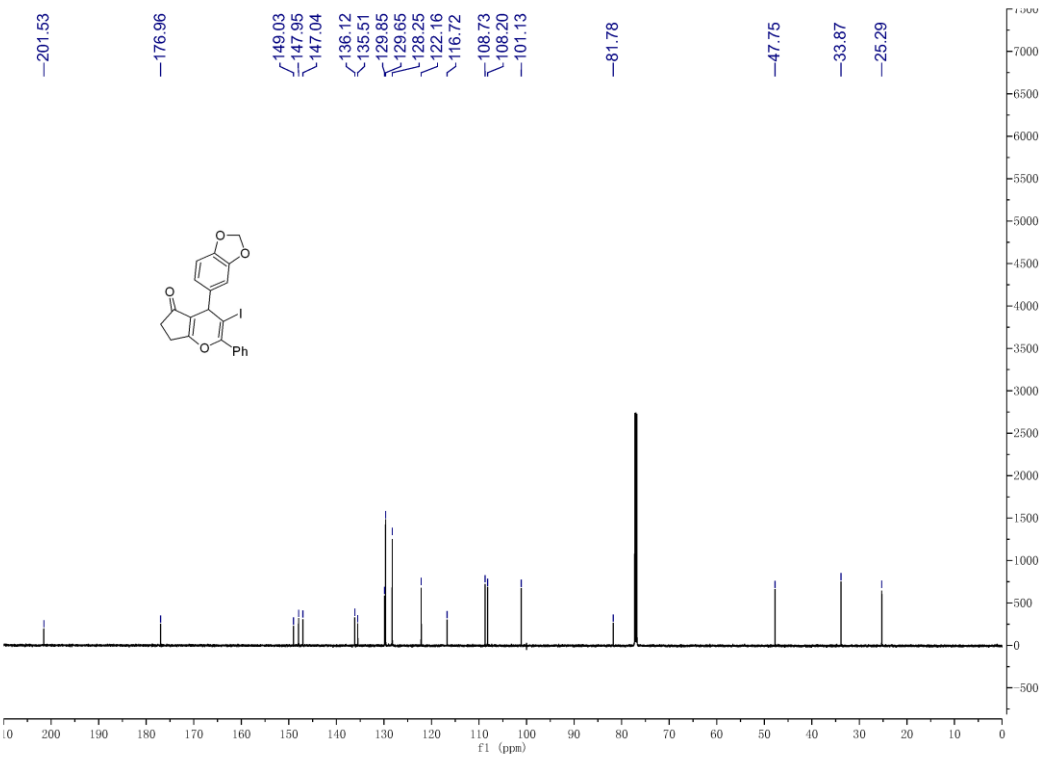
^{1}H NMR spectrum of **4p** (600MHz, $CDCl_3$)



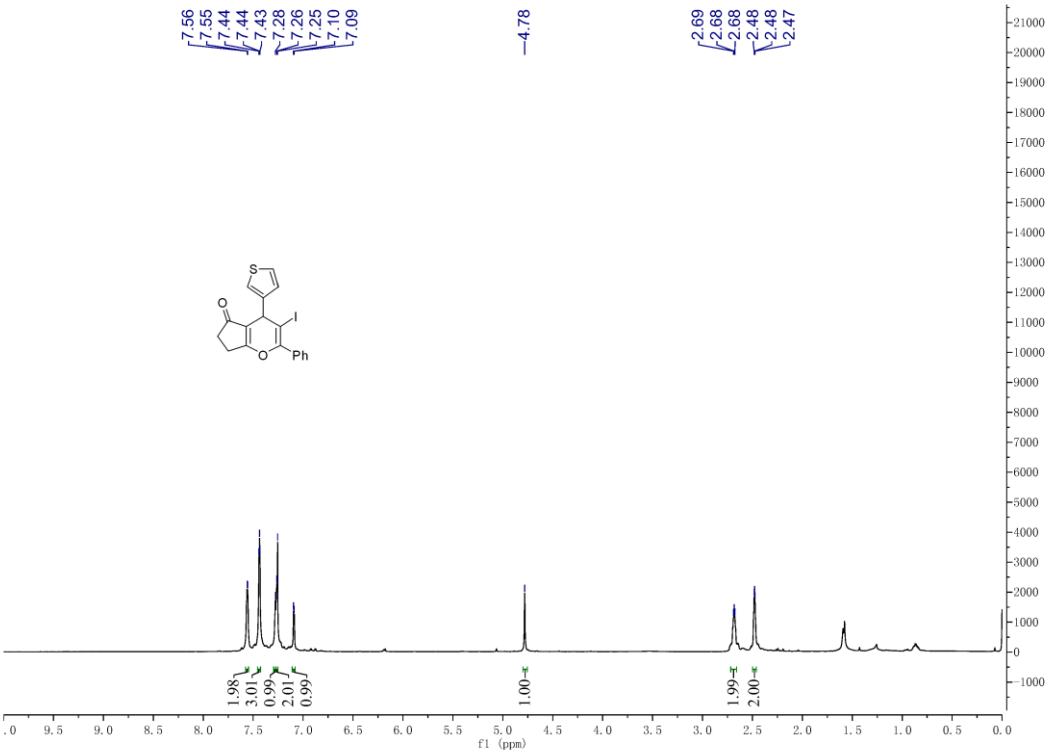
^{13}C NMR spectrum of **4p** (151 MHz, $CDCl_3$)



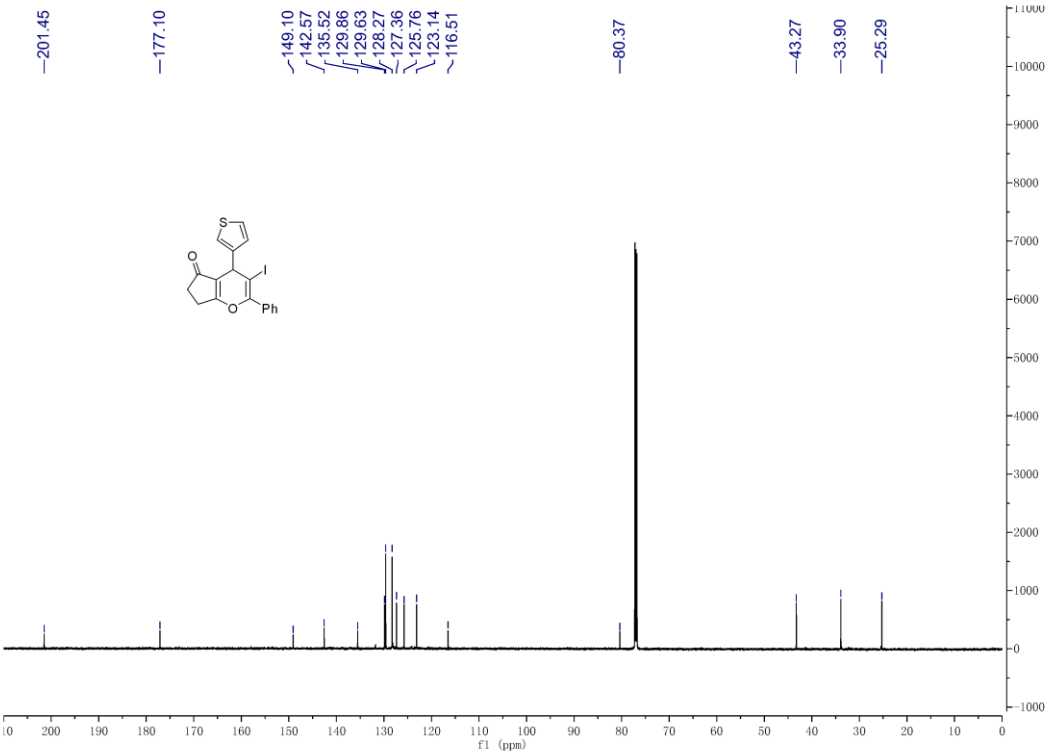
^{1}H NMR spectrum of **4q** (600MHz, $CDCl_3$)



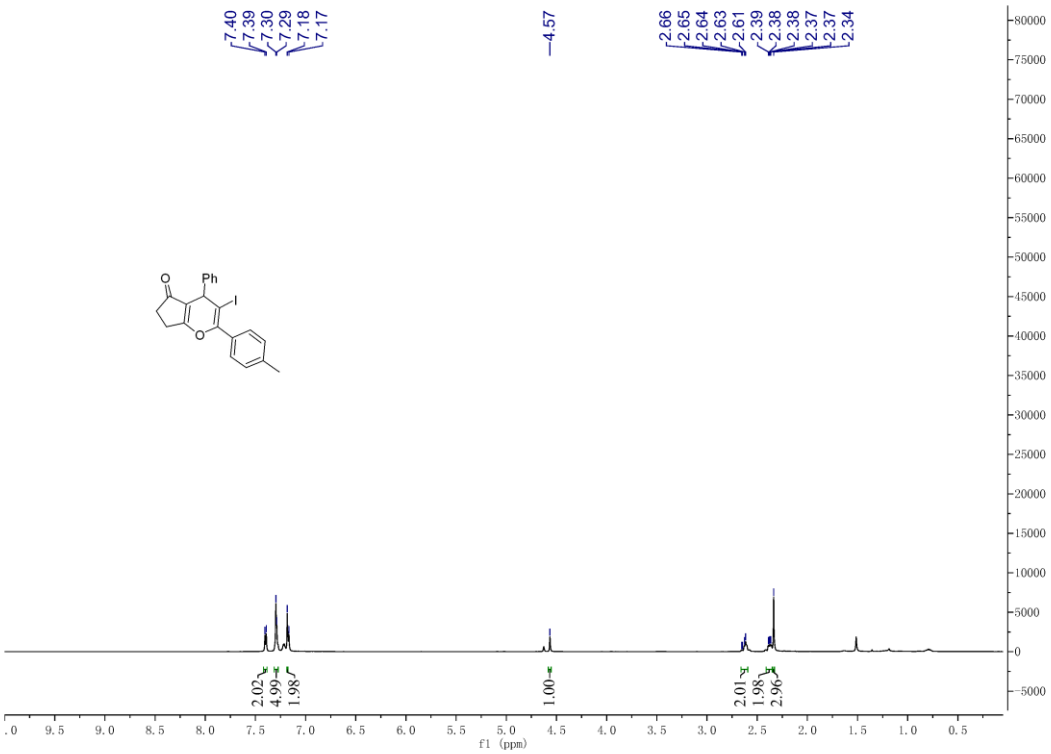
^{13}C NMR spectrum of **4q** (151 MHz, $CDCl_3$)



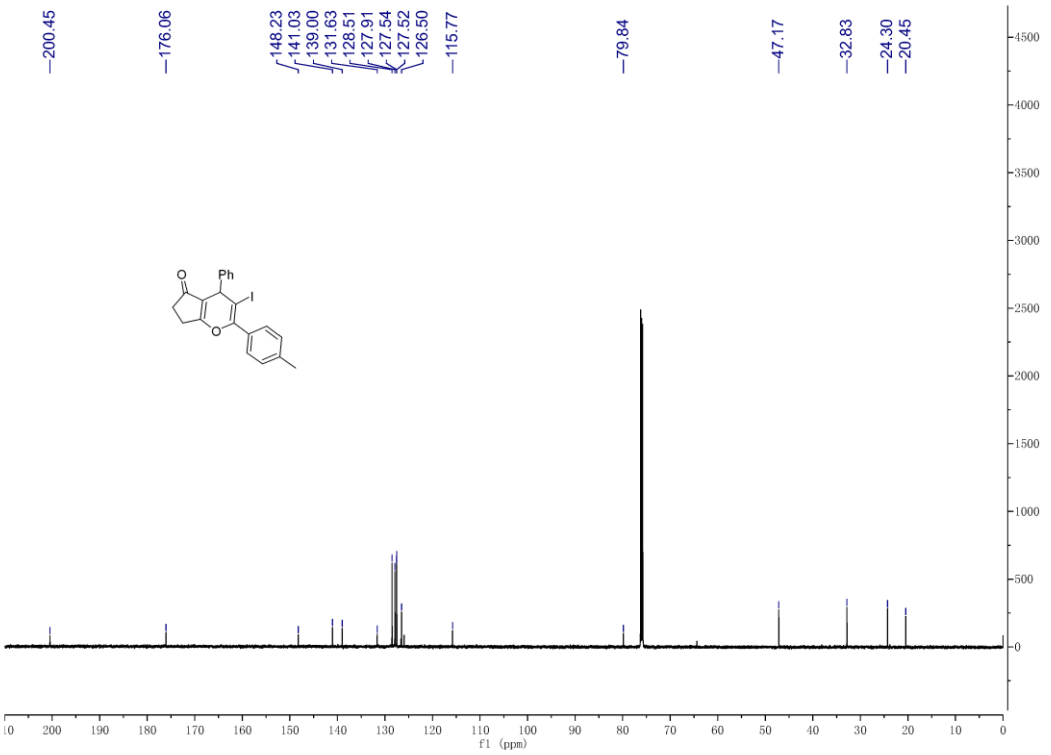
^{1}H NMR spectrum of **4r** (600MHz, $CDCl_3$)



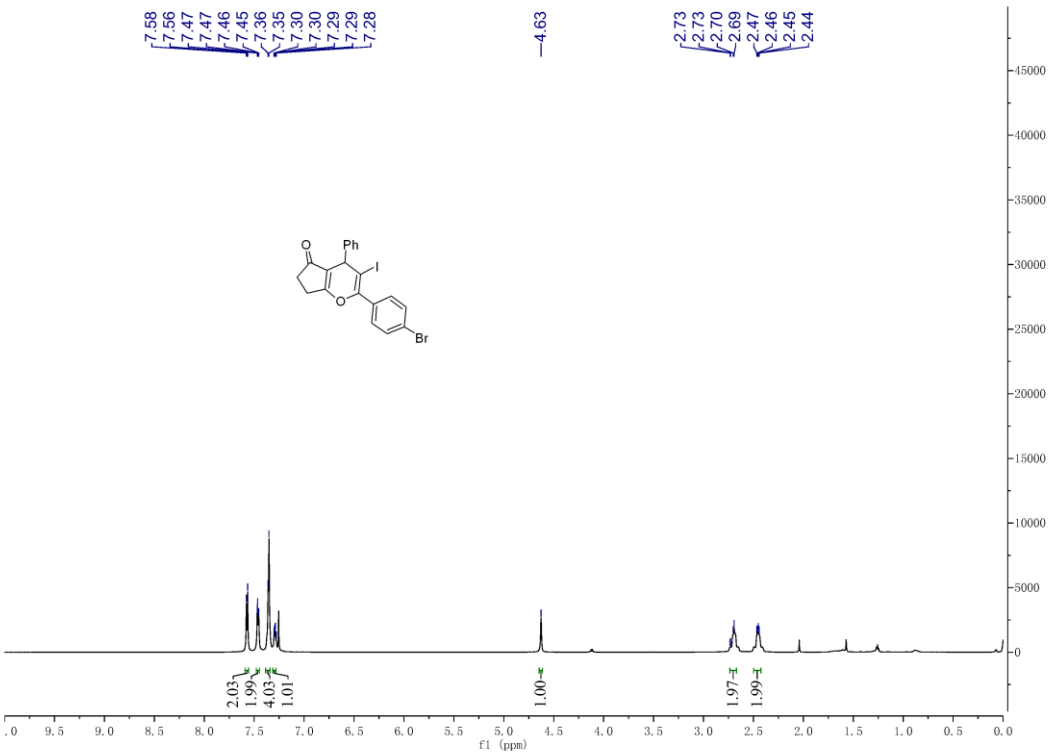
^{13}C NMR spectrum of **4r** (151 MHz, $CDCl_3$)



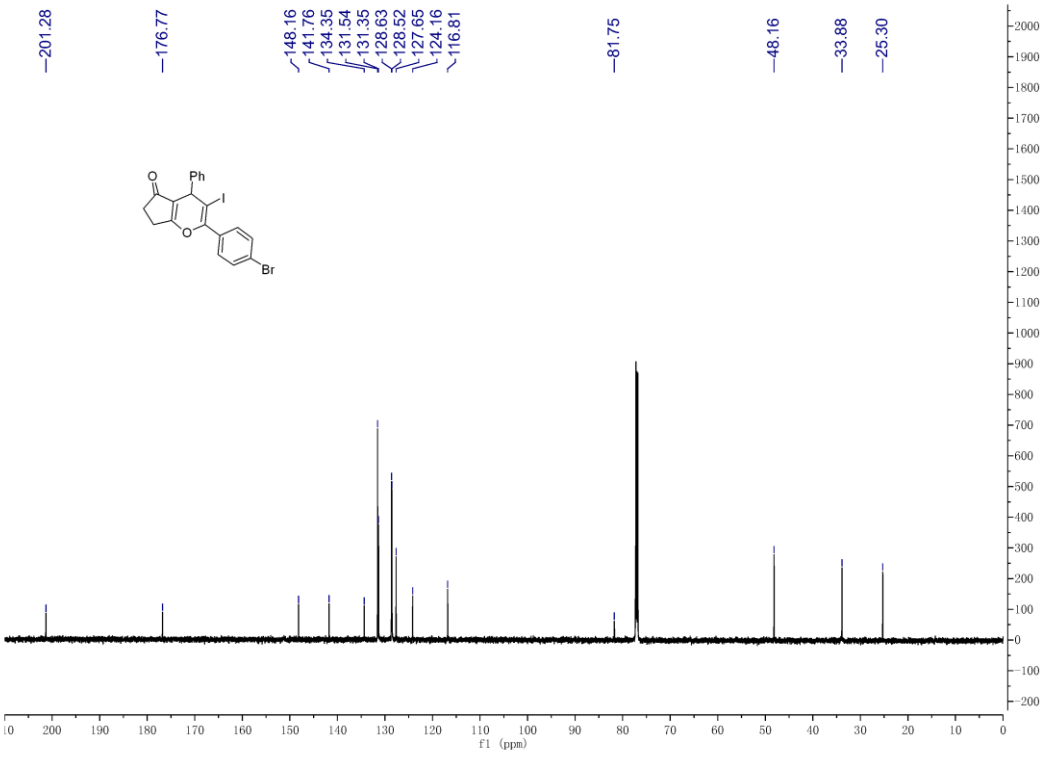
^{1}H NMR spectrum of **4s** (600MHz, $CDCl_3$)



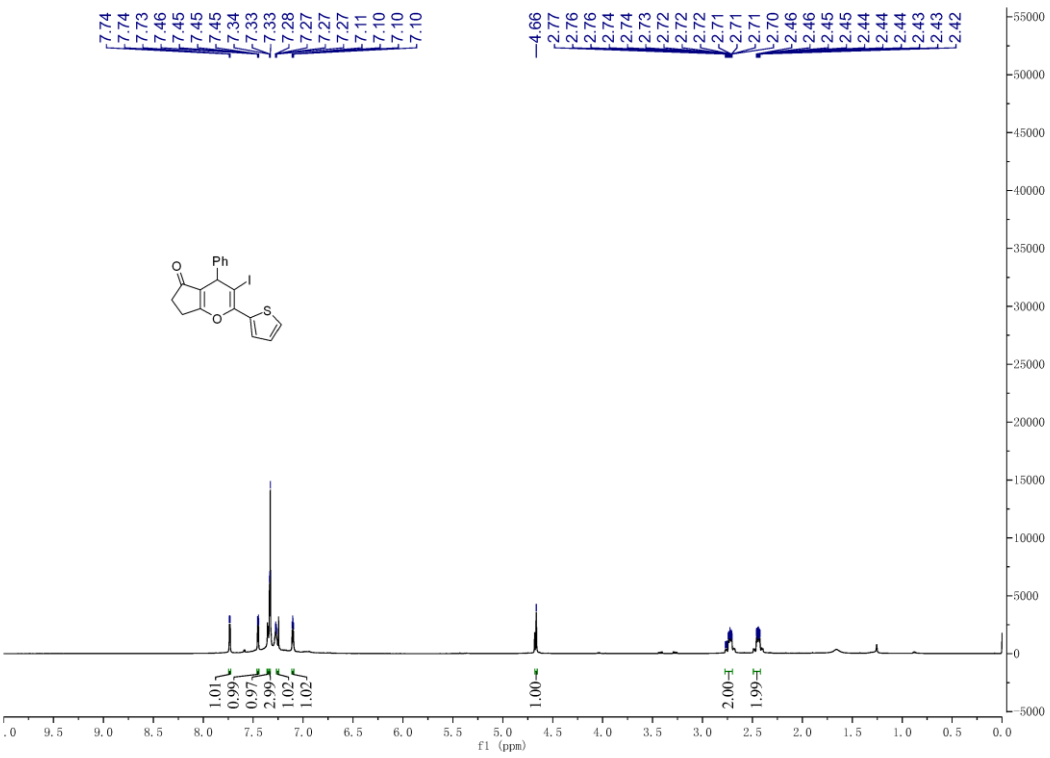
^{13}C NMR spectrum of **4s** (151 MHz, $CDCl_3$)



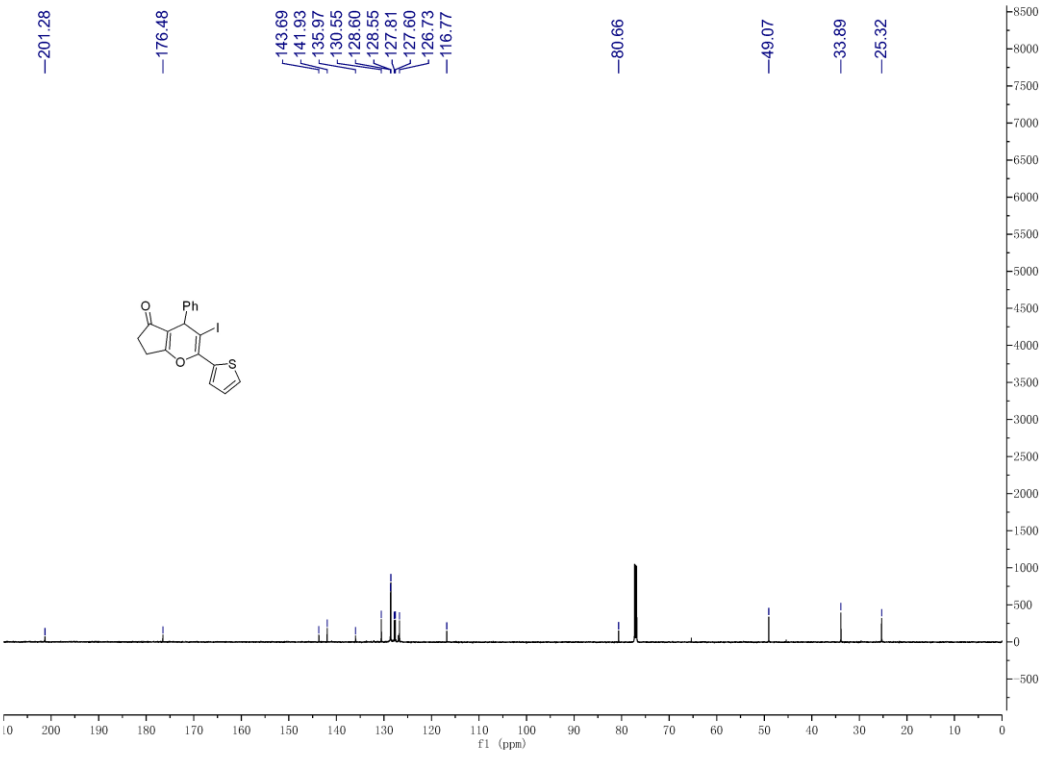
^{1}H NMR spectrum of **4t** (600MHz, $CDCl_3$)



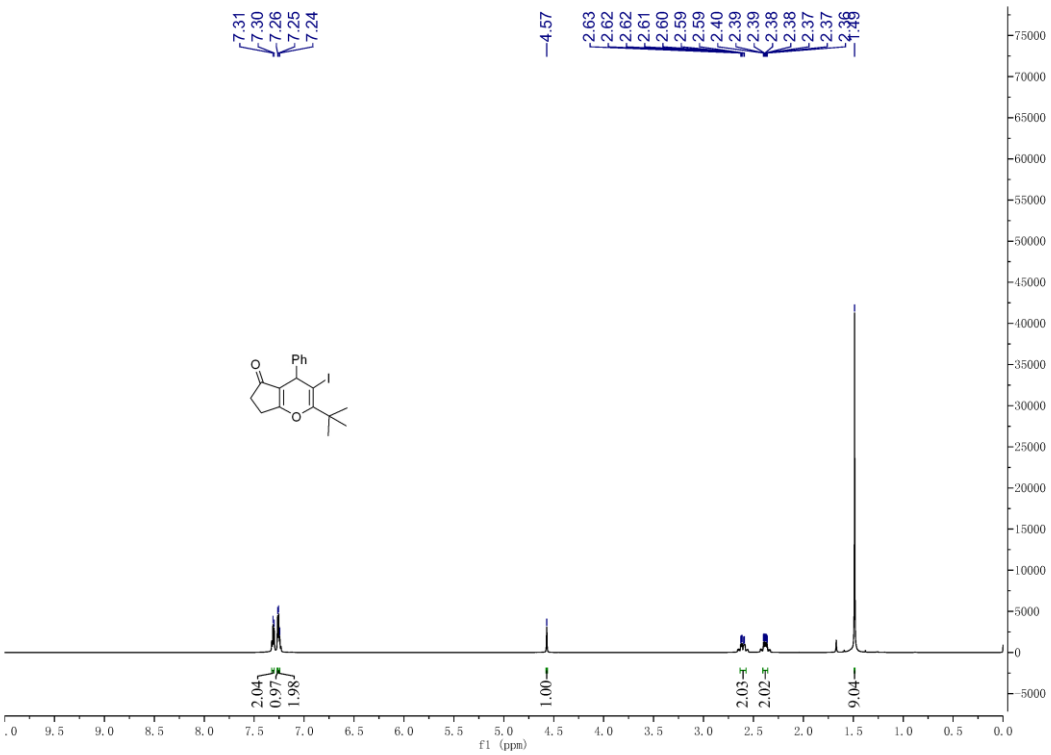
^{13}C NMR spectrum of **4t** (151 MHz, $CDCl_3$)



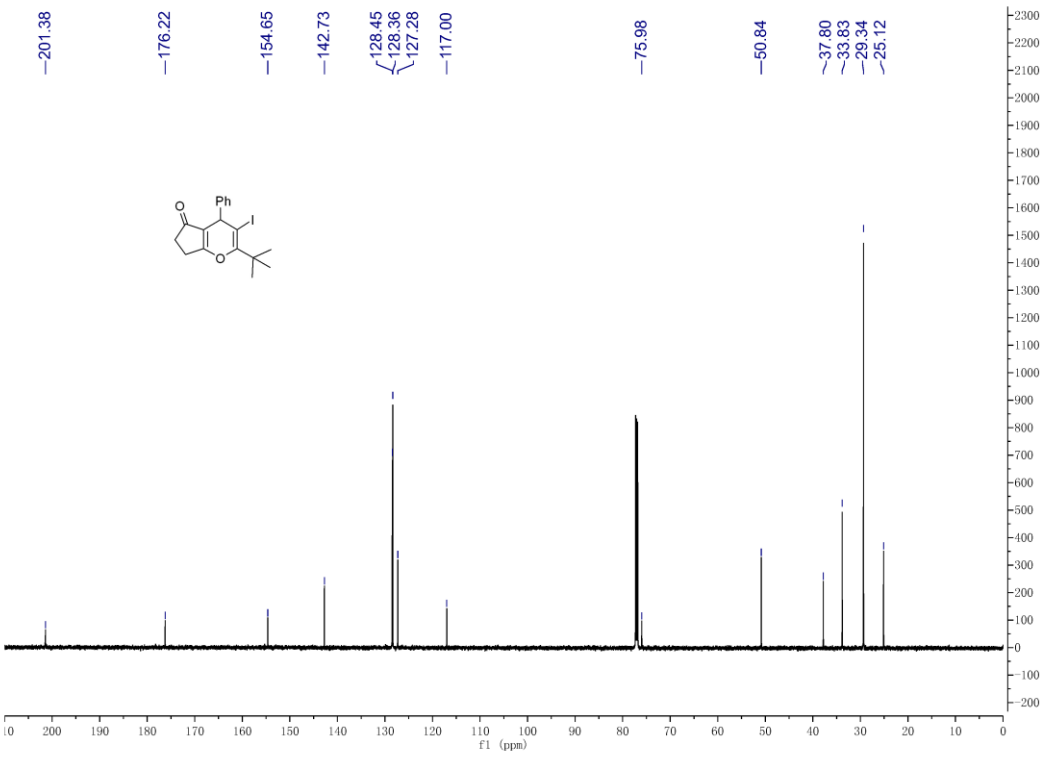
^{1}H NMR spectrum of **4u** (600MHz, $CDCl_3$)



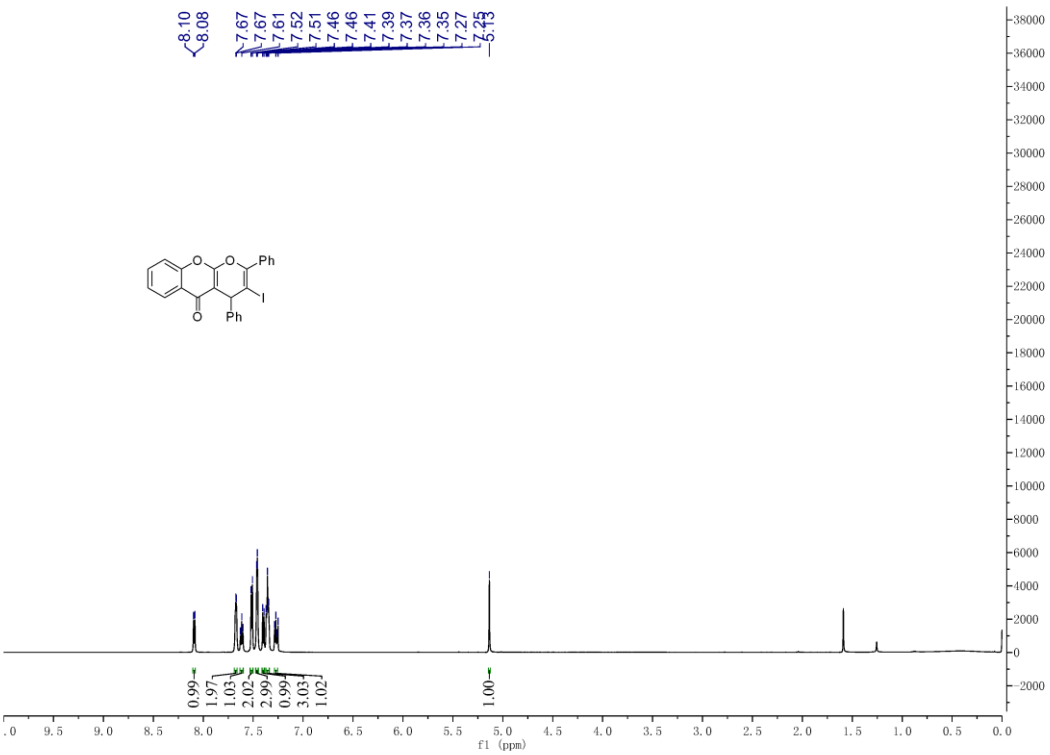
^{13}C NMR spectrum of **4u** (151 MHz, $CDCl_3$)



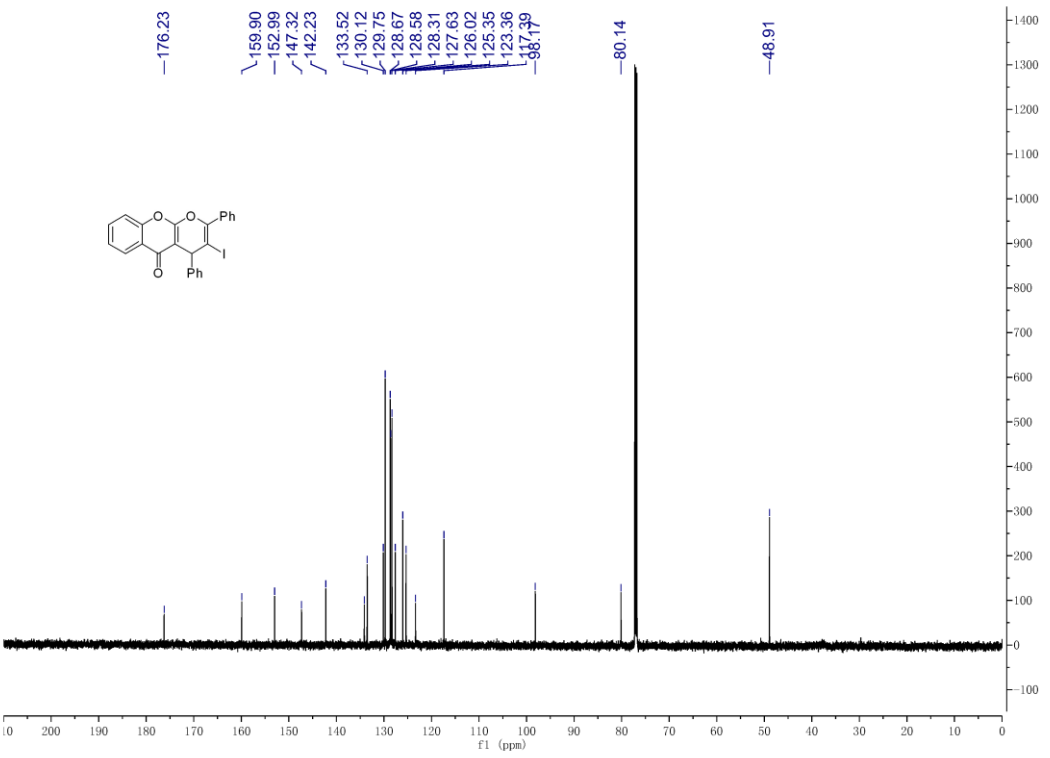
^{1}H NMR spectrum of **4v** (600MHz, $CDCl_3$)



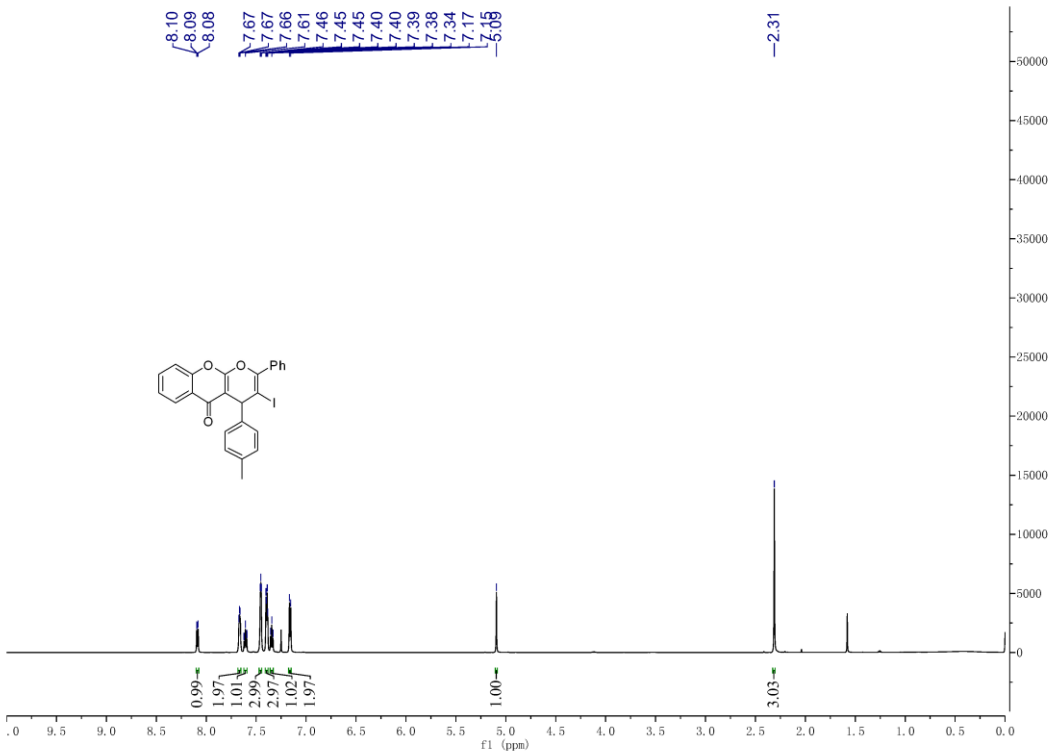
^{13}C NMR spectrum of **4v** (151 MHz, $CDCl_3$)



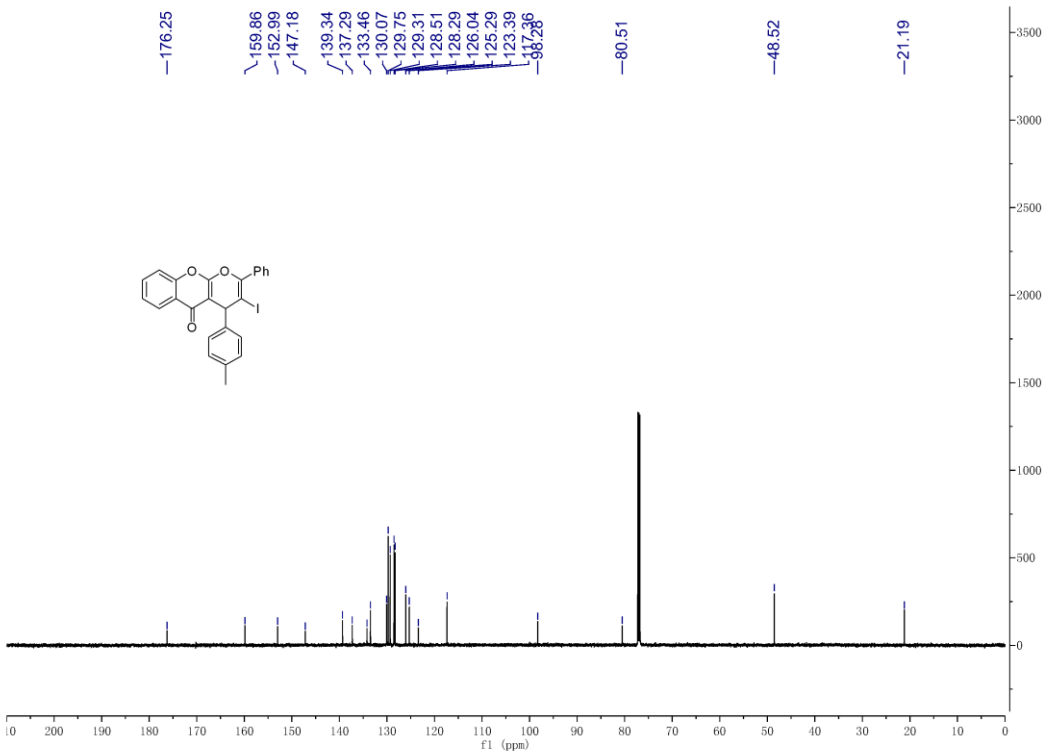
^{1}H NMR spectrum of **5a** (600MHz, $CDCl_3$)



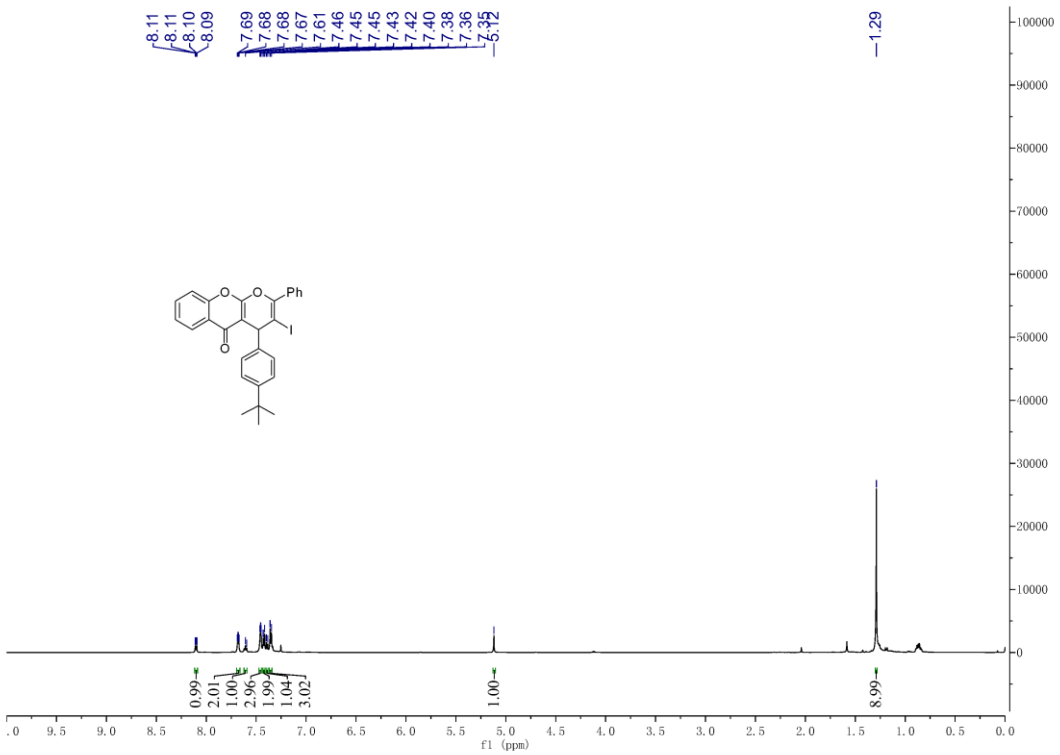
^{13}C NMR spectrum of **5a** (151 MHz, $CDCl_3$)



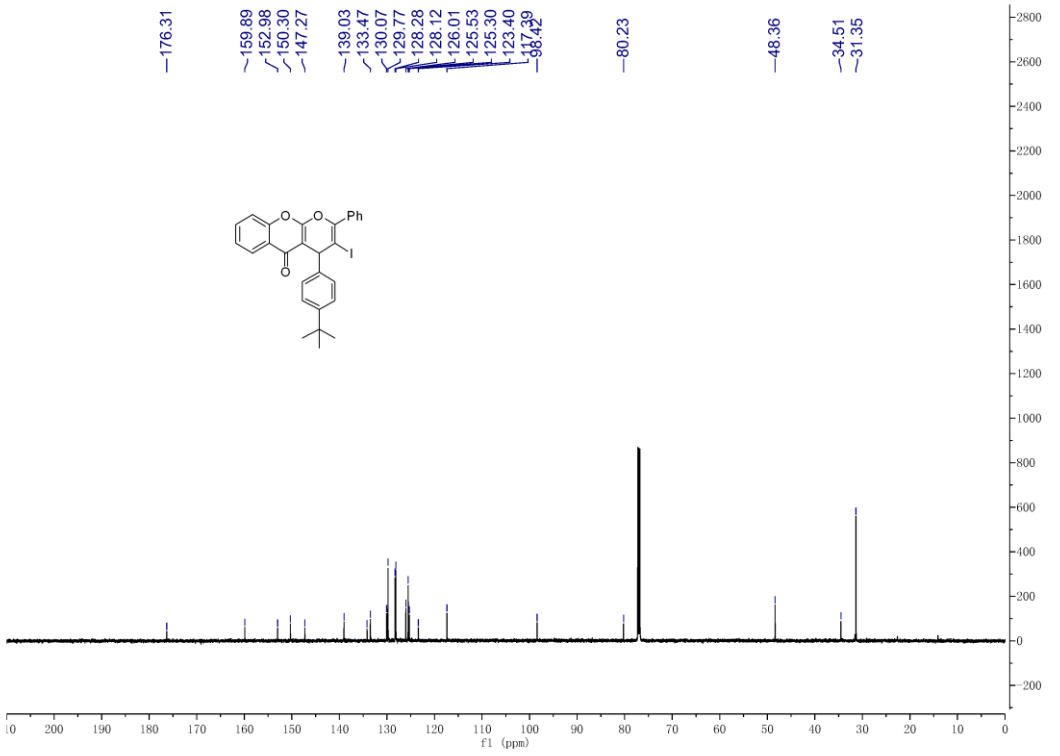
^{1}H NMR spectrum of **5b** (600MHz, $CDCl_3$)



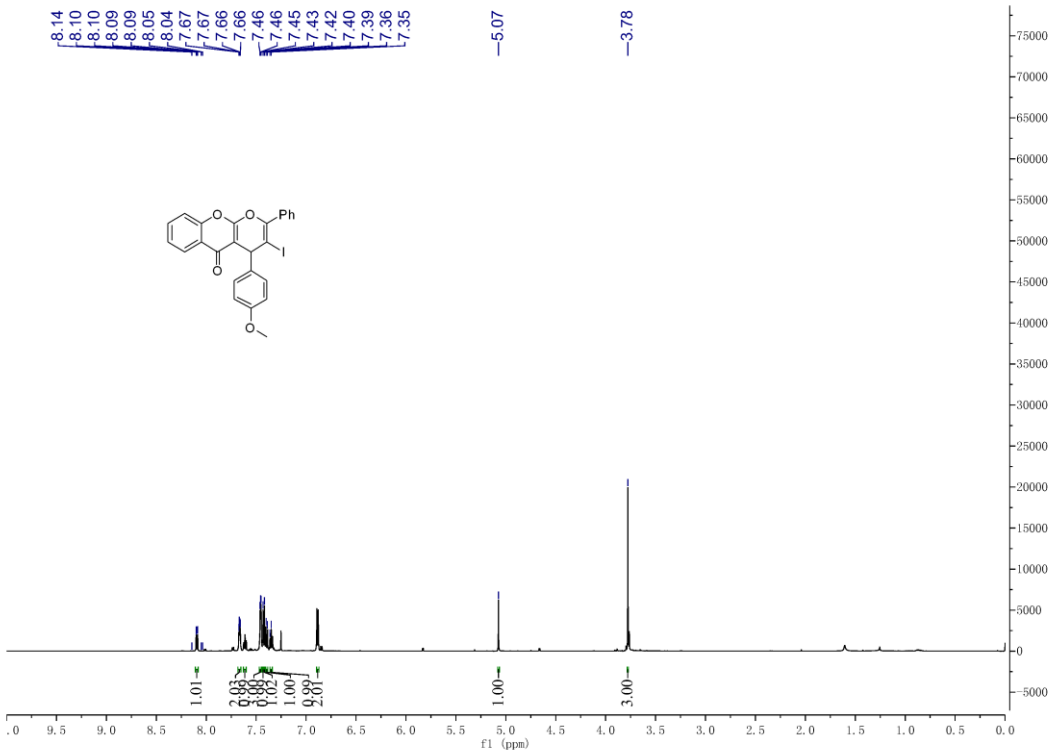
^{13}C NMR spectrum of **5b** (151 MHz, $CDCl_3$)



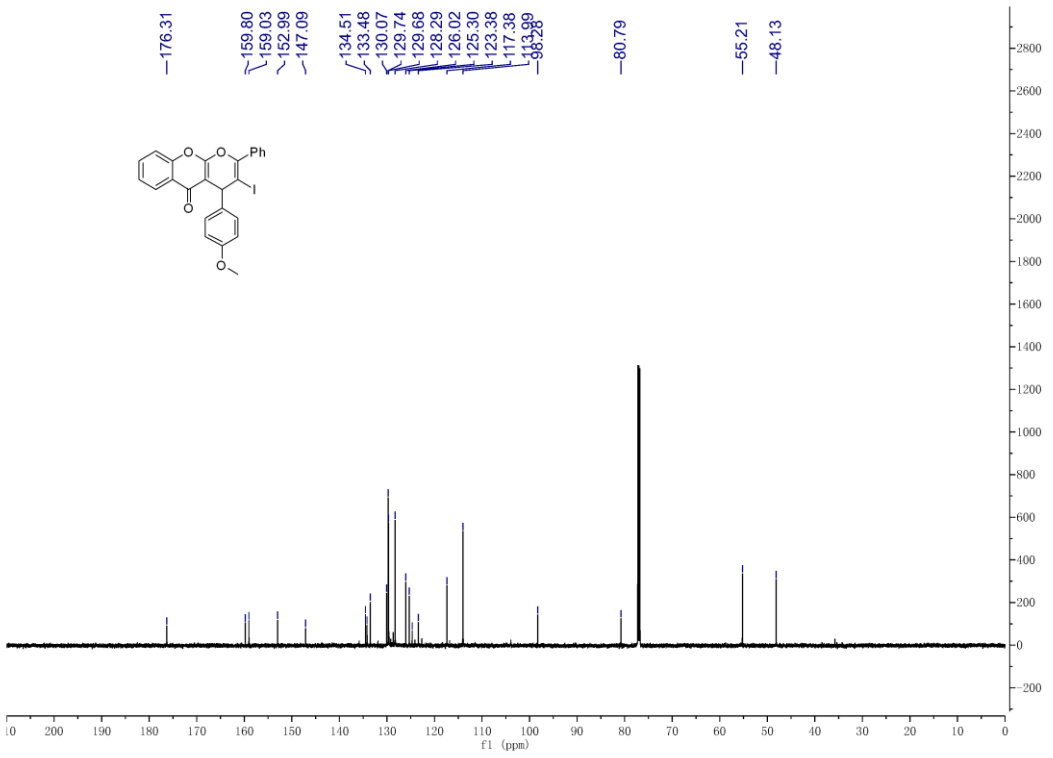
^{1}H NMR spectrum of **5c** (600MHz, $CDCl_3$)



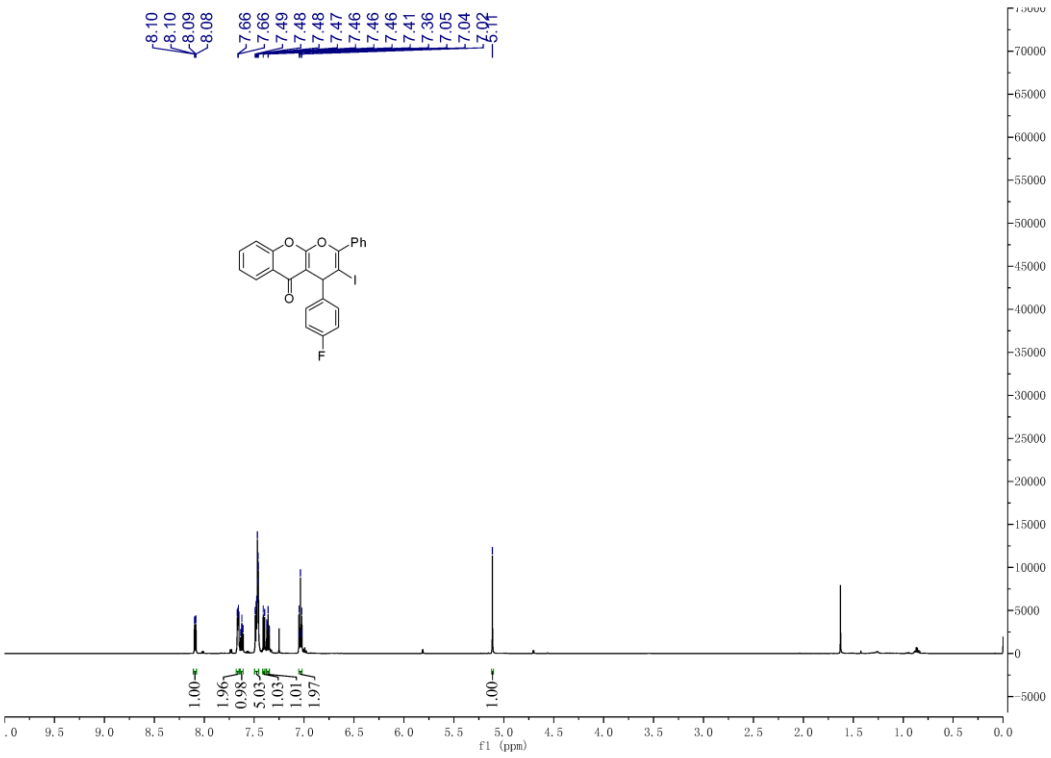
^{13}C NMR spectrum of **5c** (151 MHz, $CDCl_3$)



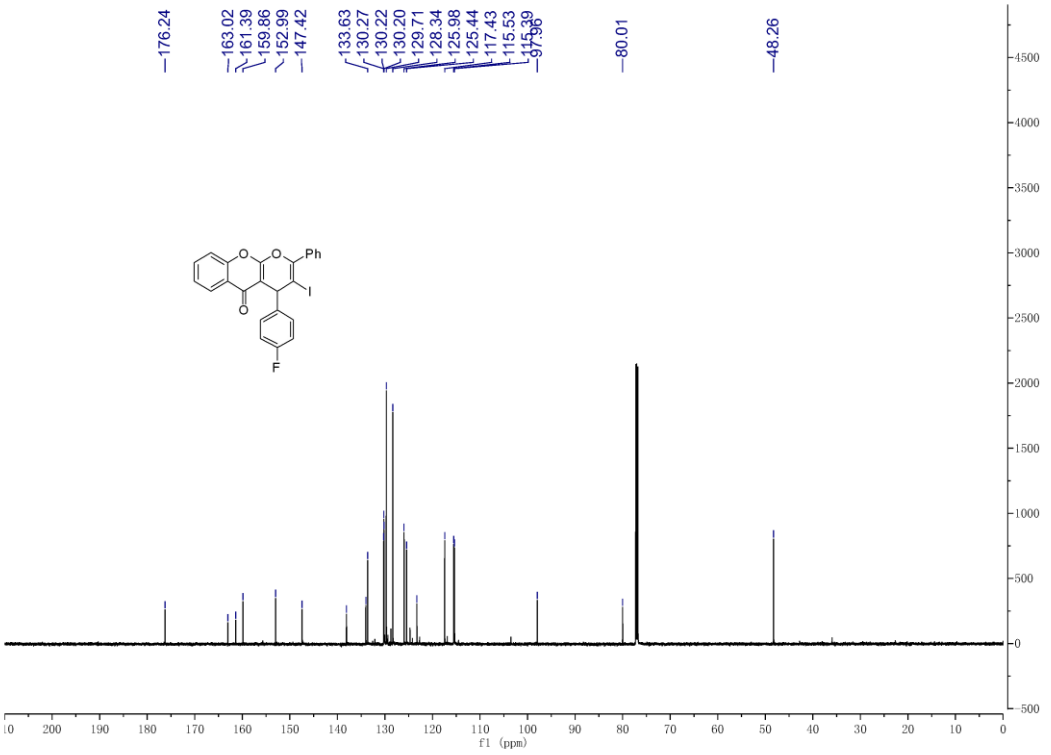
^{1}H NMR spectrum of **5d** (600MHz, $CDCl_3$)



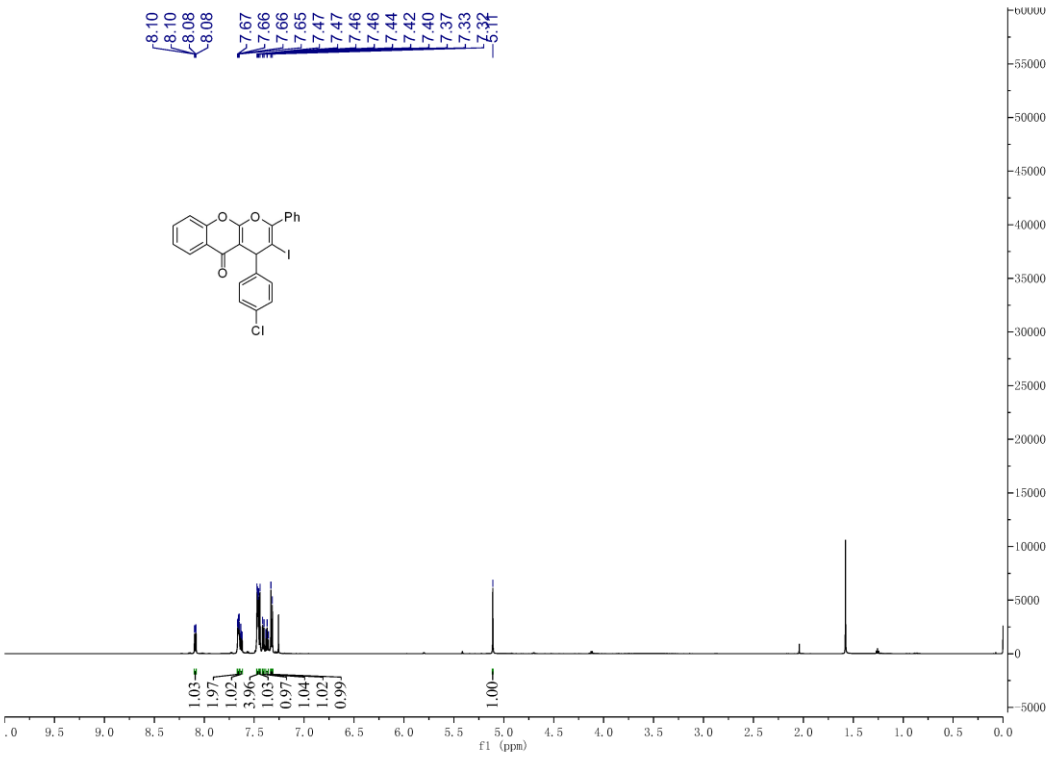
^{13}C NMR spectrum of **5d** (151 MHz, $CDCl_3$)



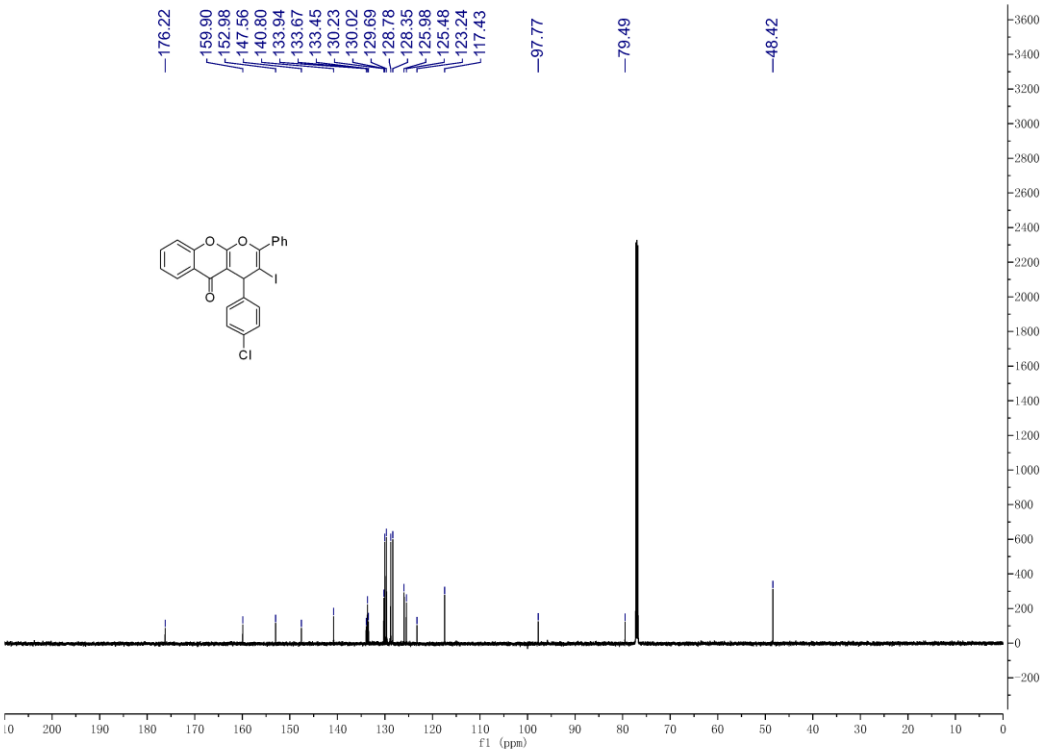
^{1}H NMR spectrum of **5e** (600MHz, $CDCl_3$)



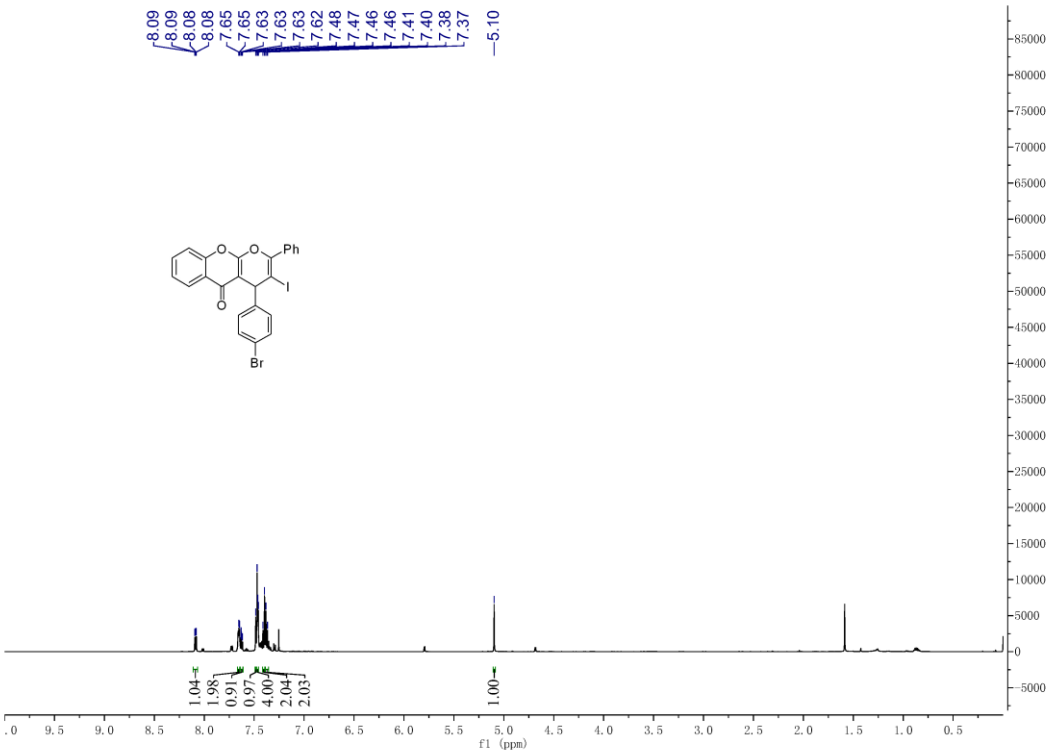
^{13}C NMR spectrum of **5e** (151 MHz, $CDCl_3$)



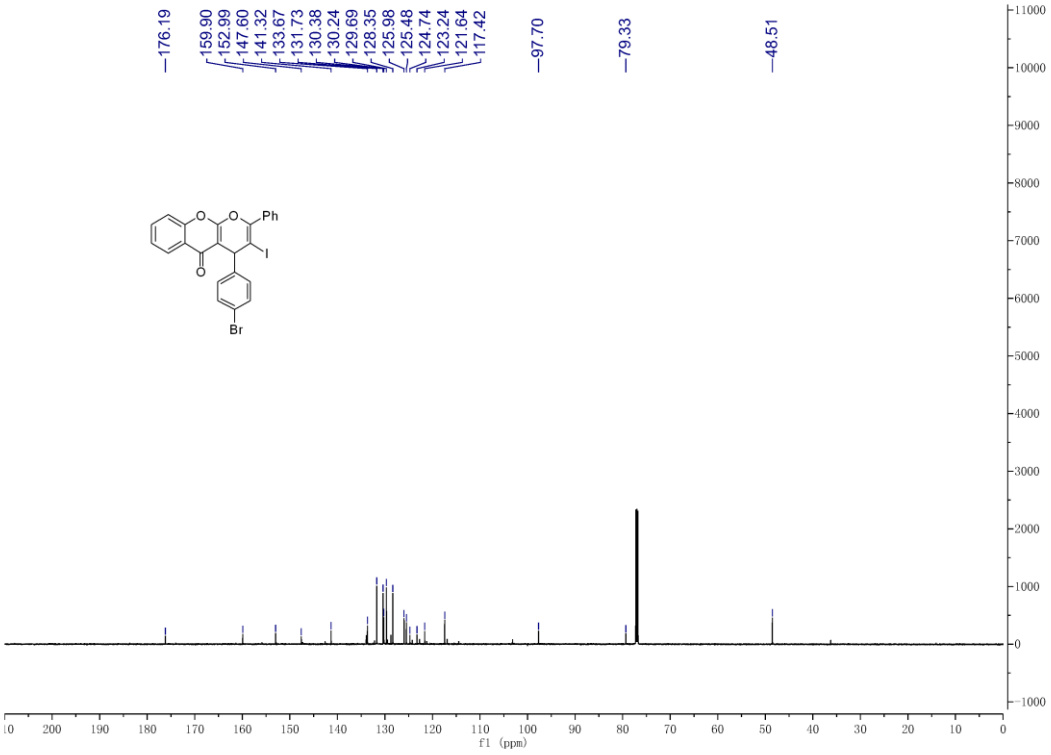
^{1}H NMR spectrum of **5f** (600MHz, $CDCl_3$)



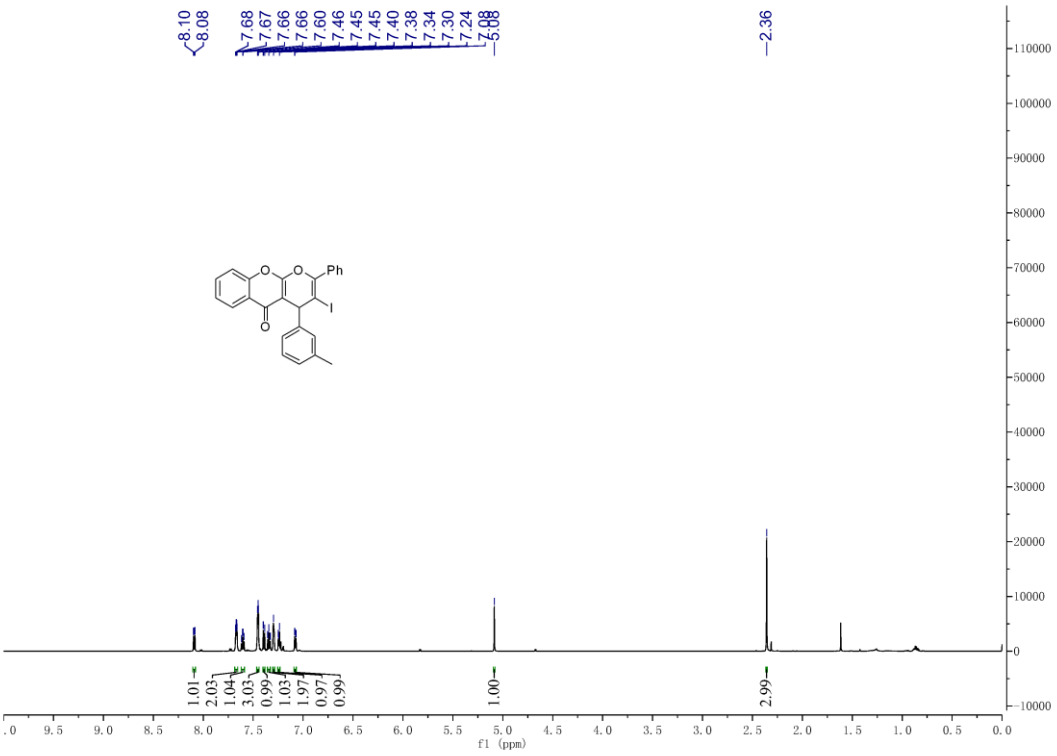
^{13}C NMR spectrum of **5f** (151 MHz, $CDCl_3$)



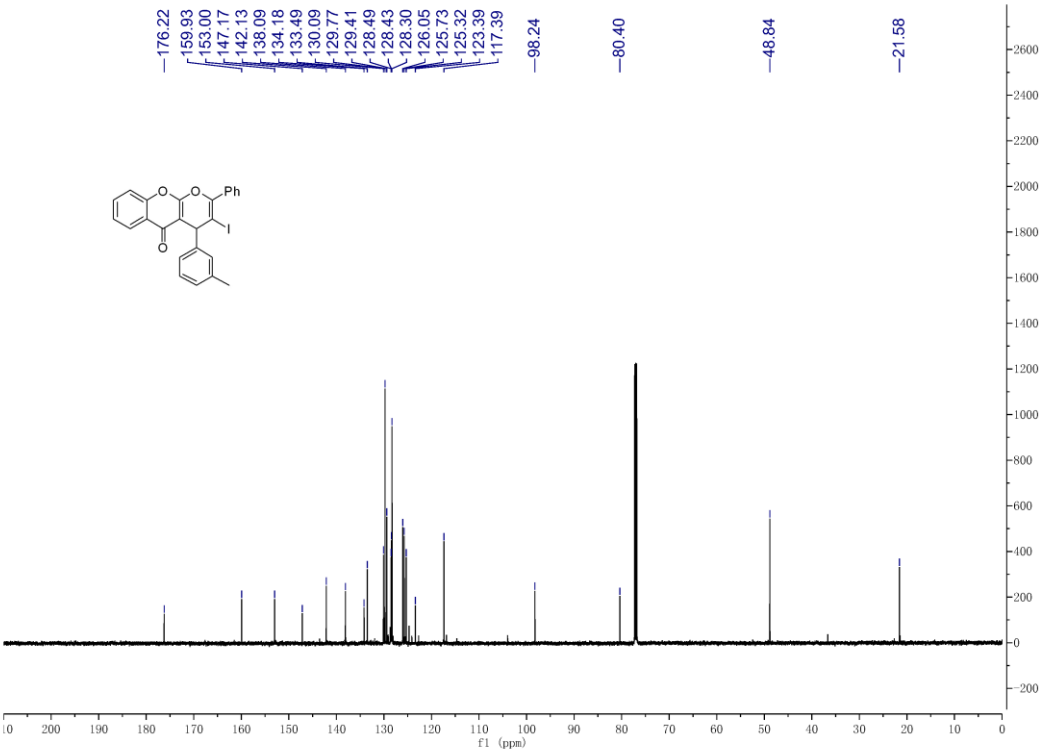
^{1}H NMR spectrum of **5g**(600MHz, $CDCl_3$)



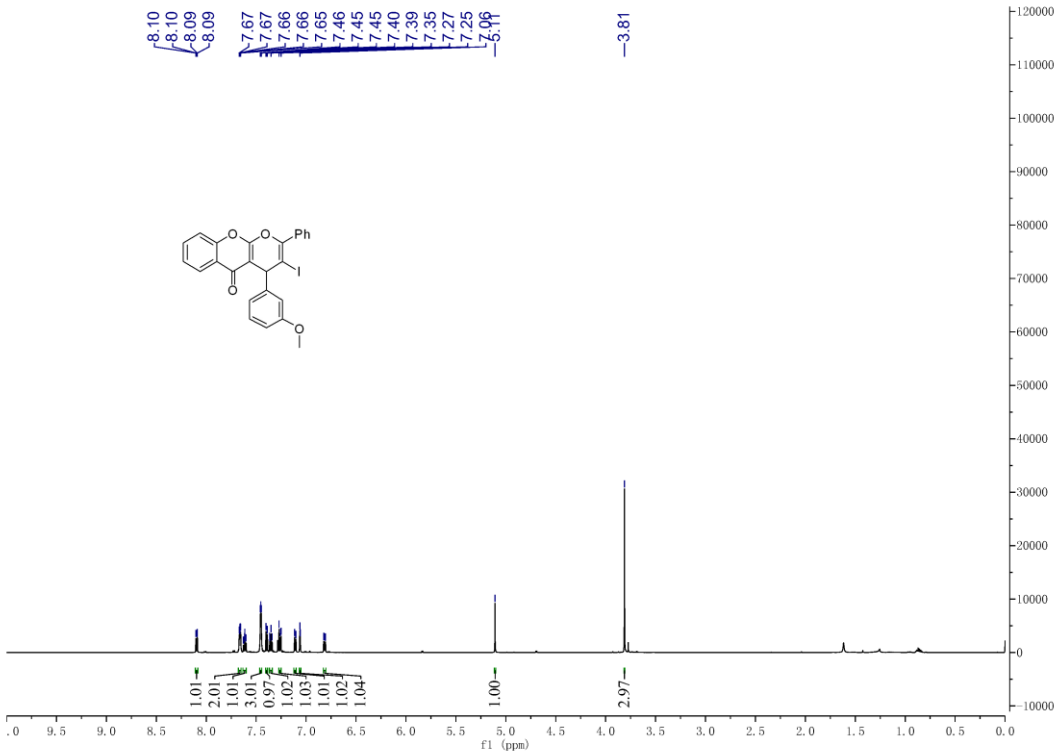
^{13}C NMR spectrum of **5g** (151 MHz, $CDCl_3$)



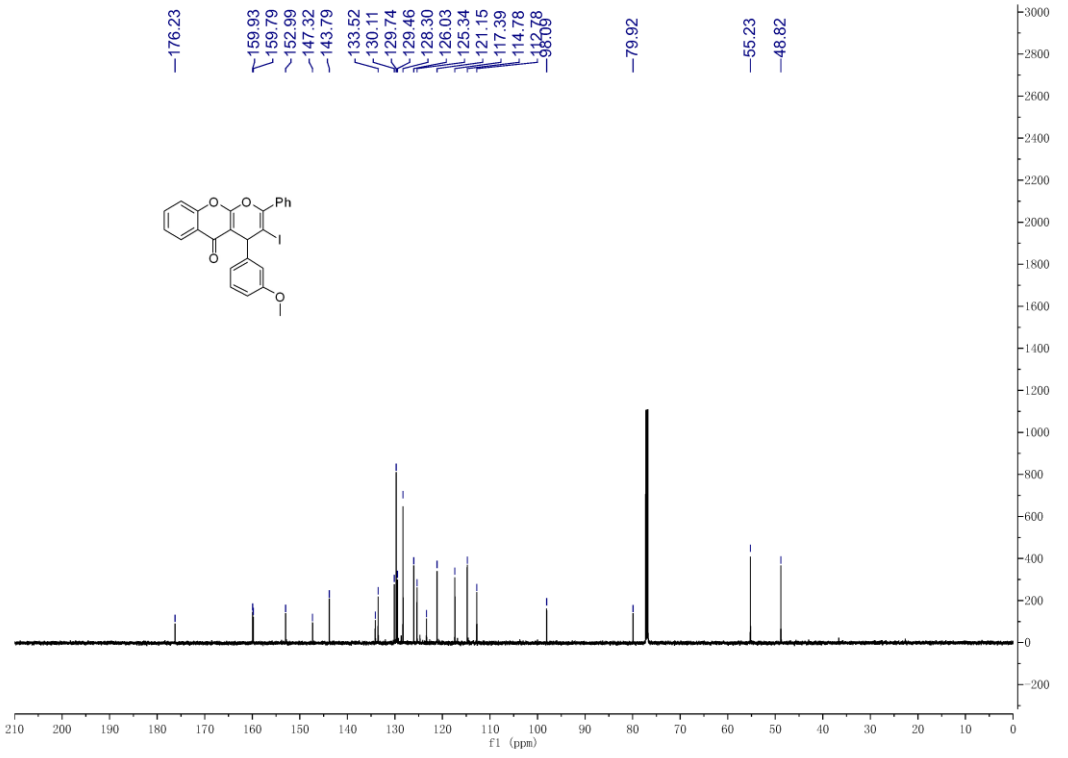
^{1}H NMR spectrum of **5h** (600MHz, $CDCl_3$)



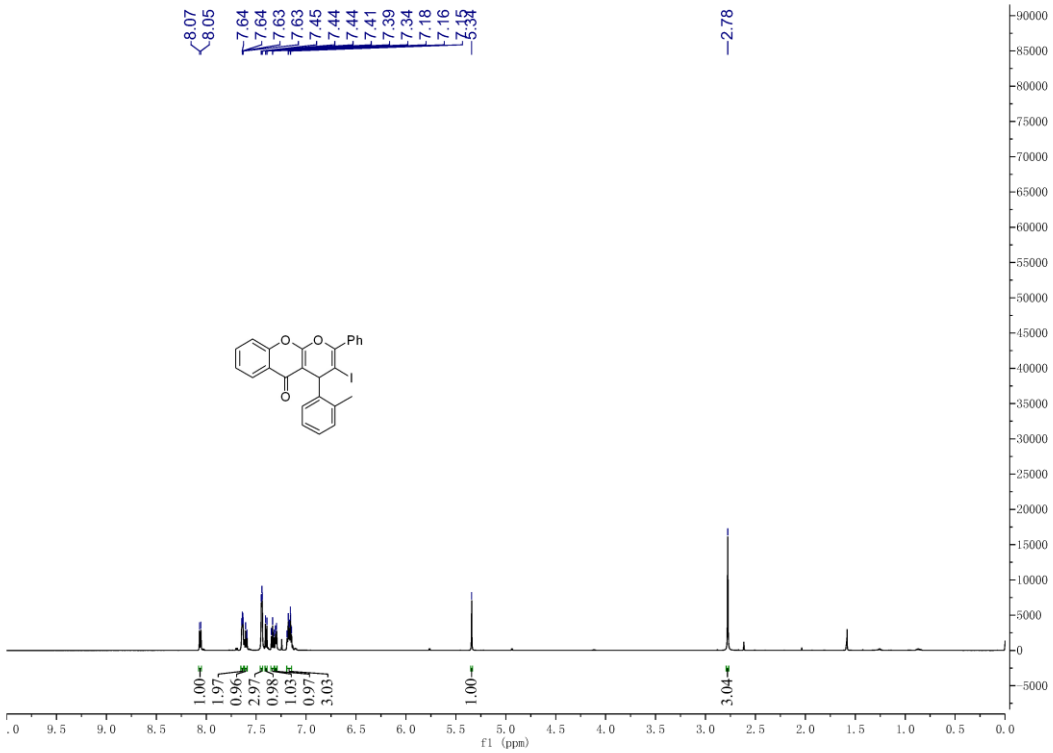
^{13}C NMR spectrum of **5h** (151 MHz, $CDCl_3$)



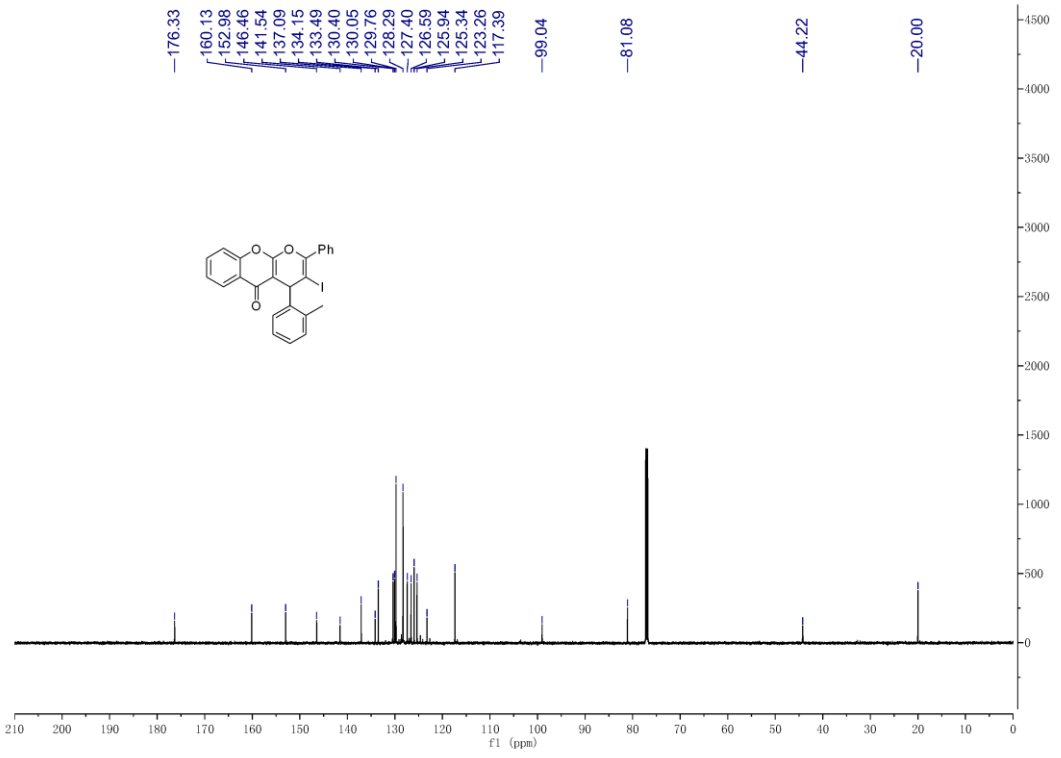
^{1}H NMR spectrum of **5i** (600MHz, $CDCl_3$)



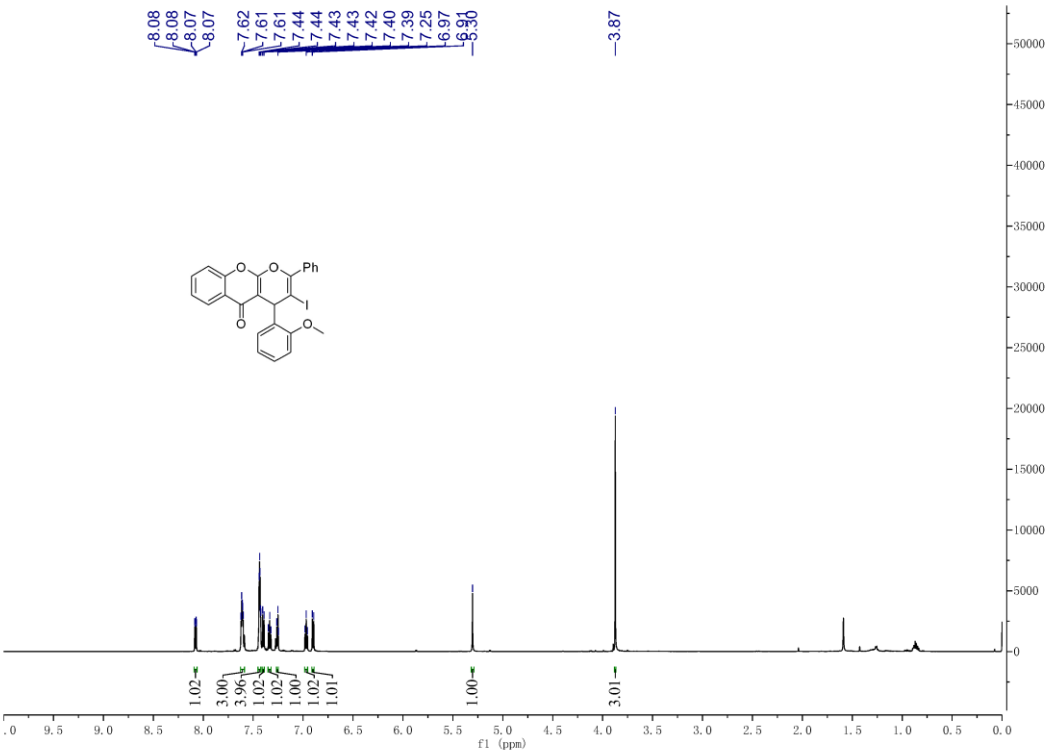
^{13}C NMR spectrum of **5i** (151 MHz, $CDCl_3$)



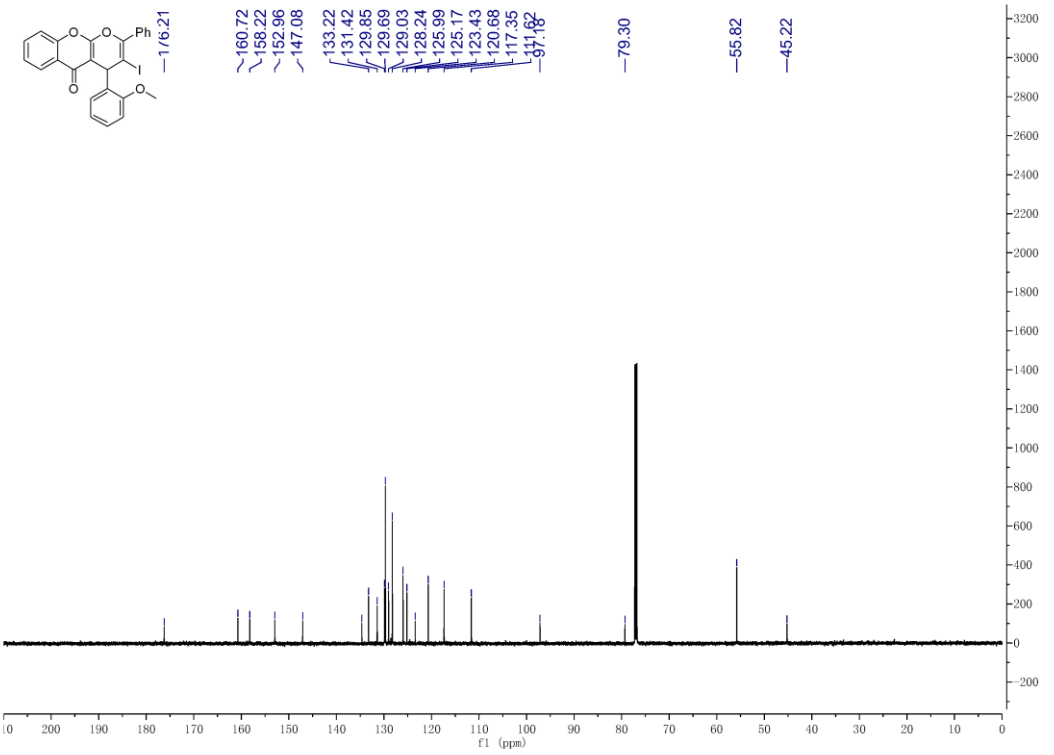
^{1}H NMR spectrum of **5j** (600MHz, $CDCl_3$)



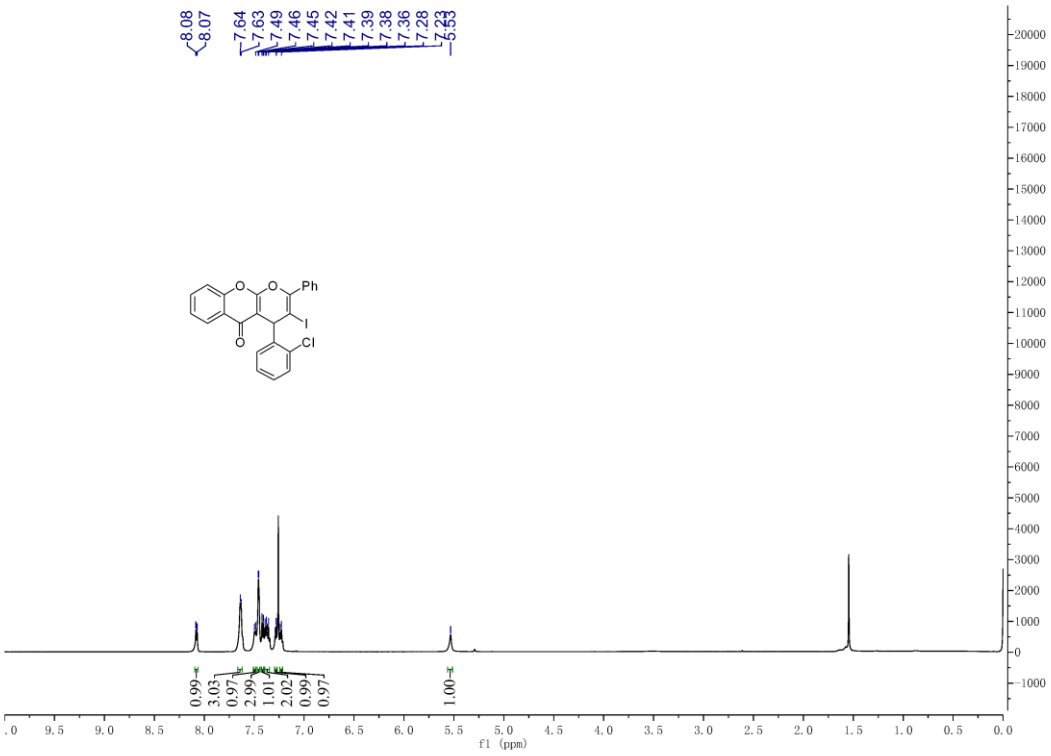
^{13}C NMR spectrum of **5j** (151 MHz, $CDCl_3$)



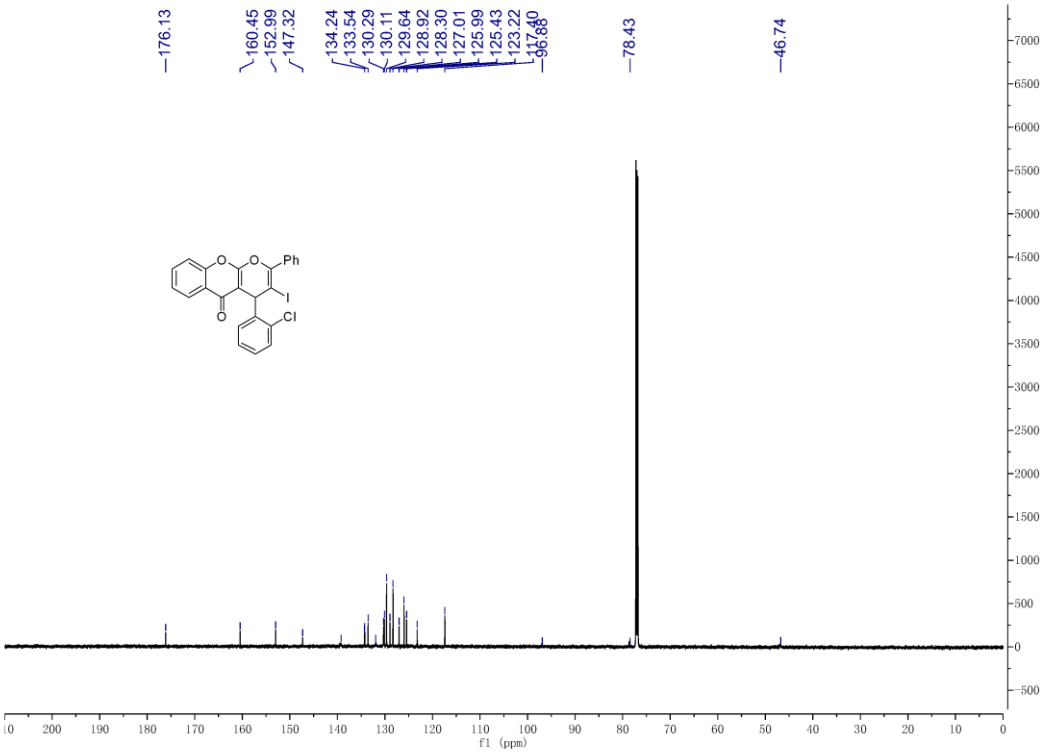
^{1}H NMR spectrum of **5k** (600MHz, $CDCl_3$)



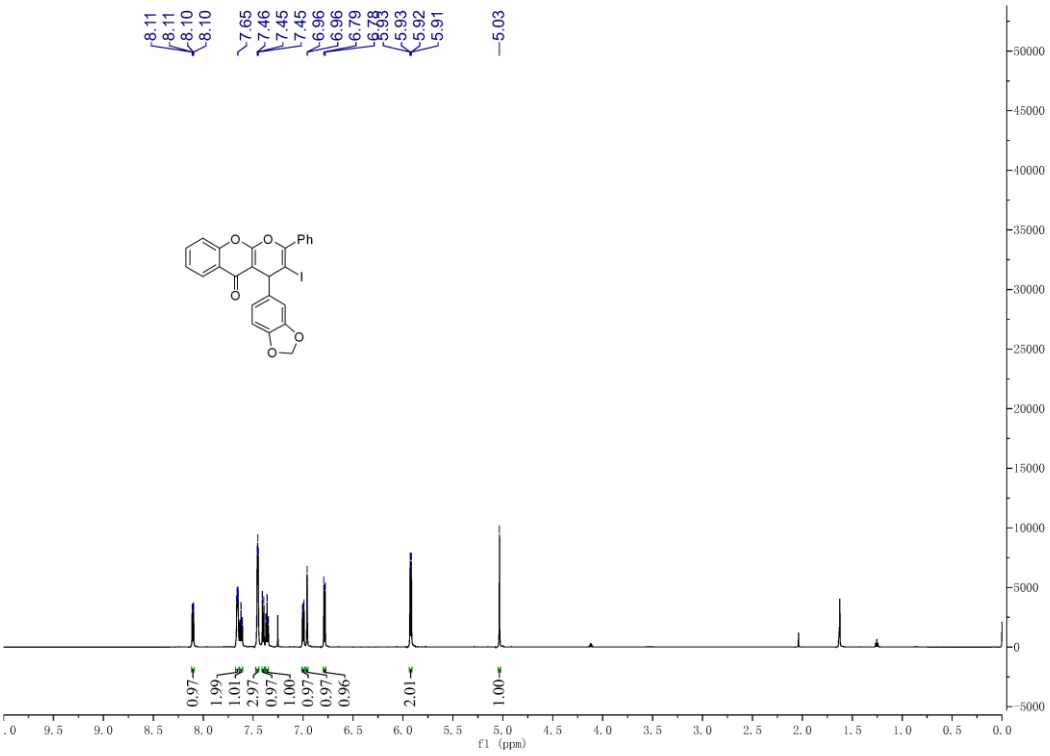
^{13}C NMR spectrum of **5k** (151 MHz, $CDCl_3$)



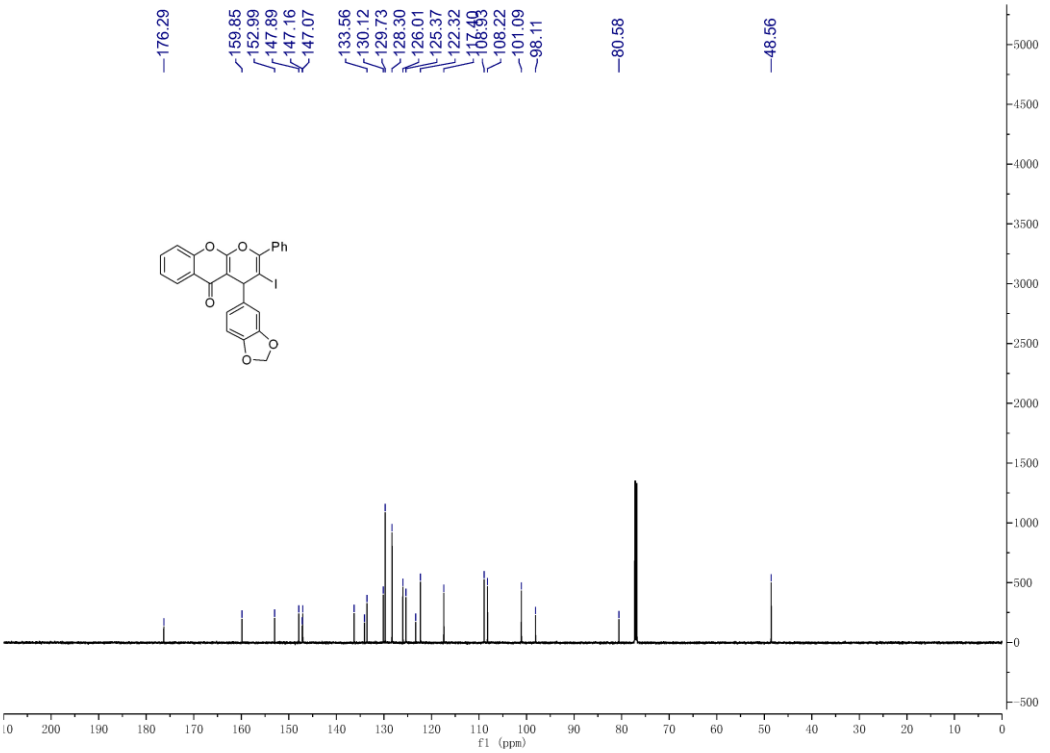
^{1}H NMR spectrum of **5l** (600MHz, $CDCl_3$)



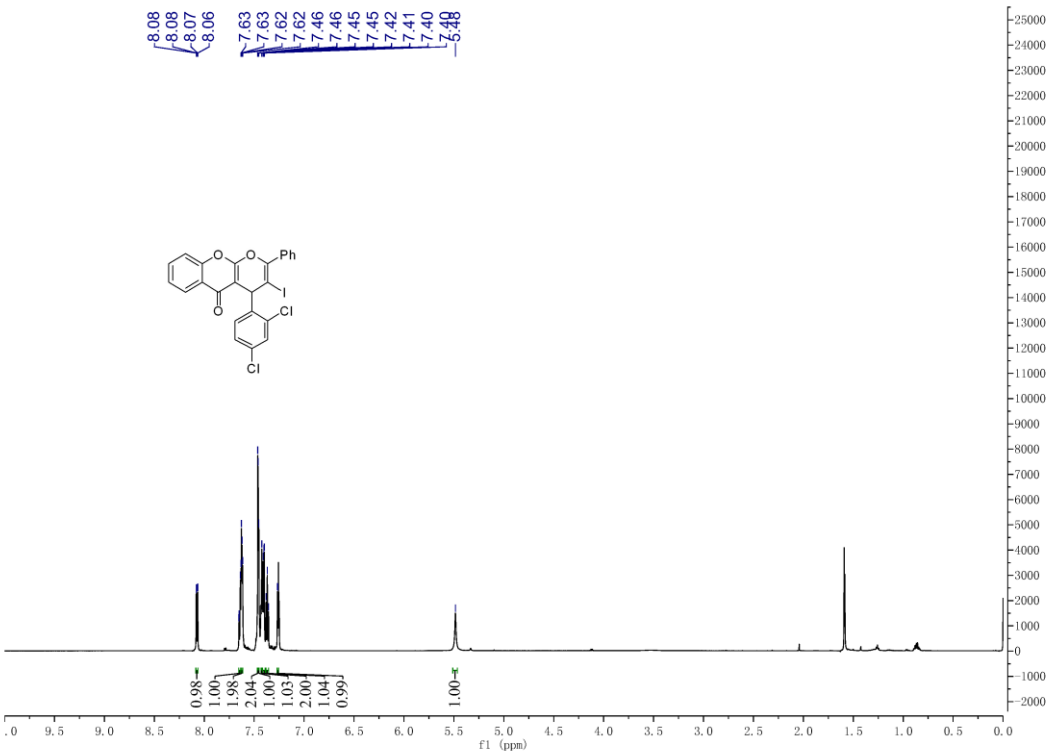
^{13}C NMR spectrum of **5l** (151 MHz, $CDCl_3$)



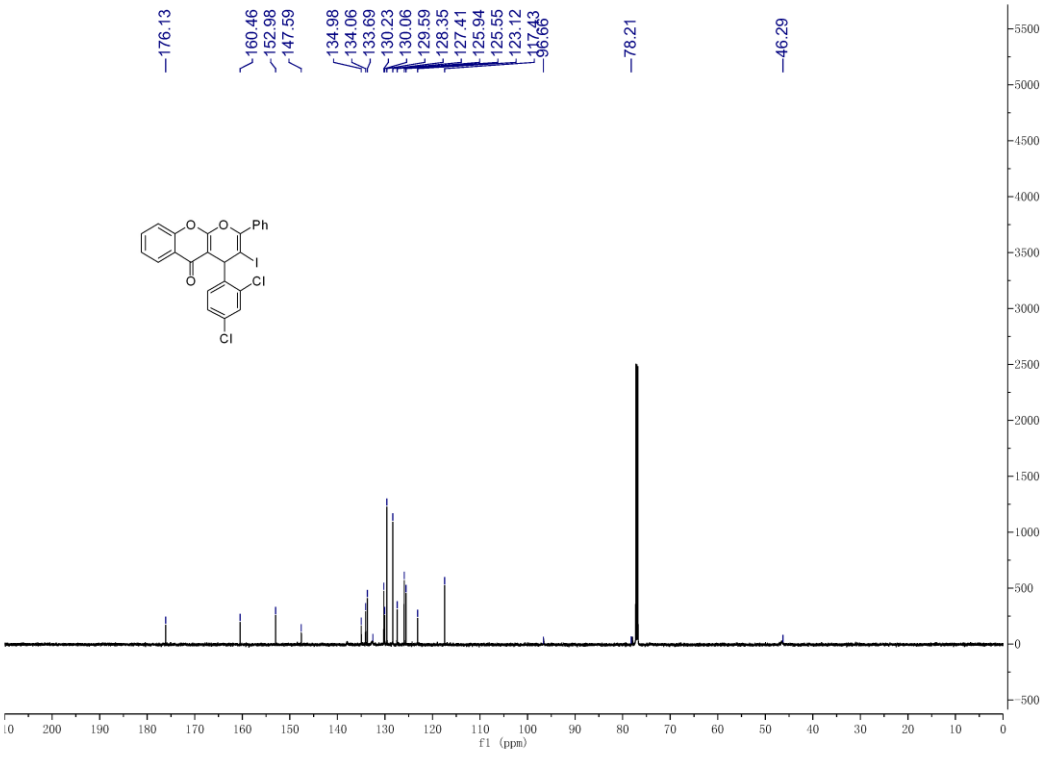
^{1}H NMR spectrum of **5m**(600MHz, $CDCl_3$)



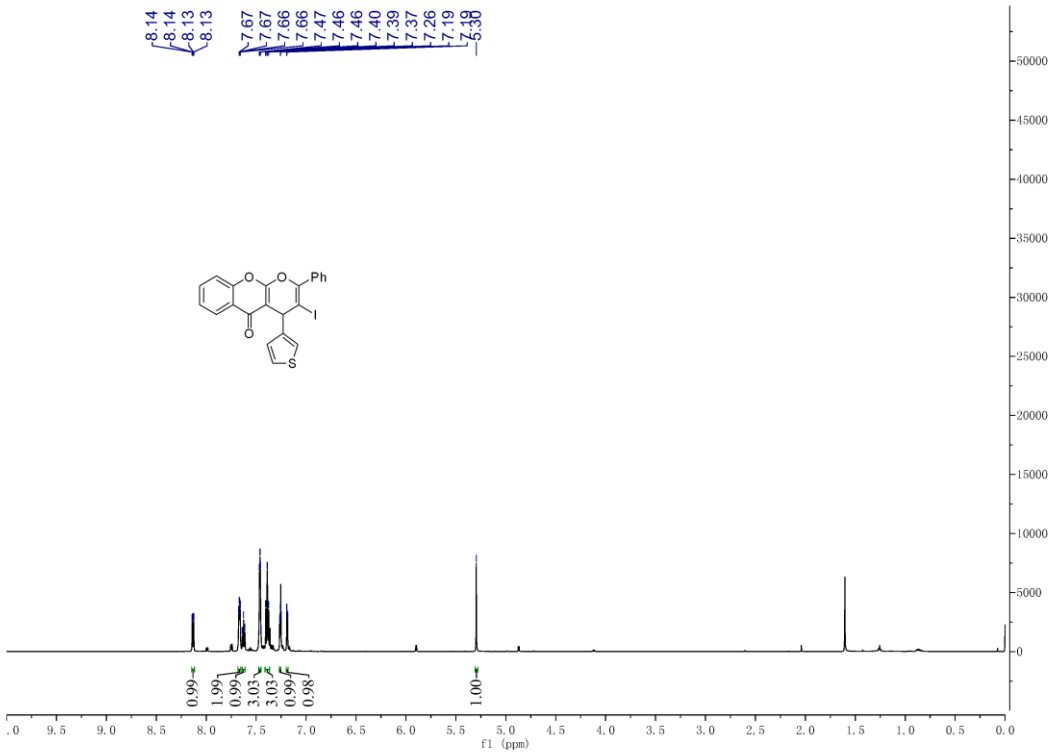
^{13}C NMR spectrum of **5m** (151 MHz, $CDCl_3$)



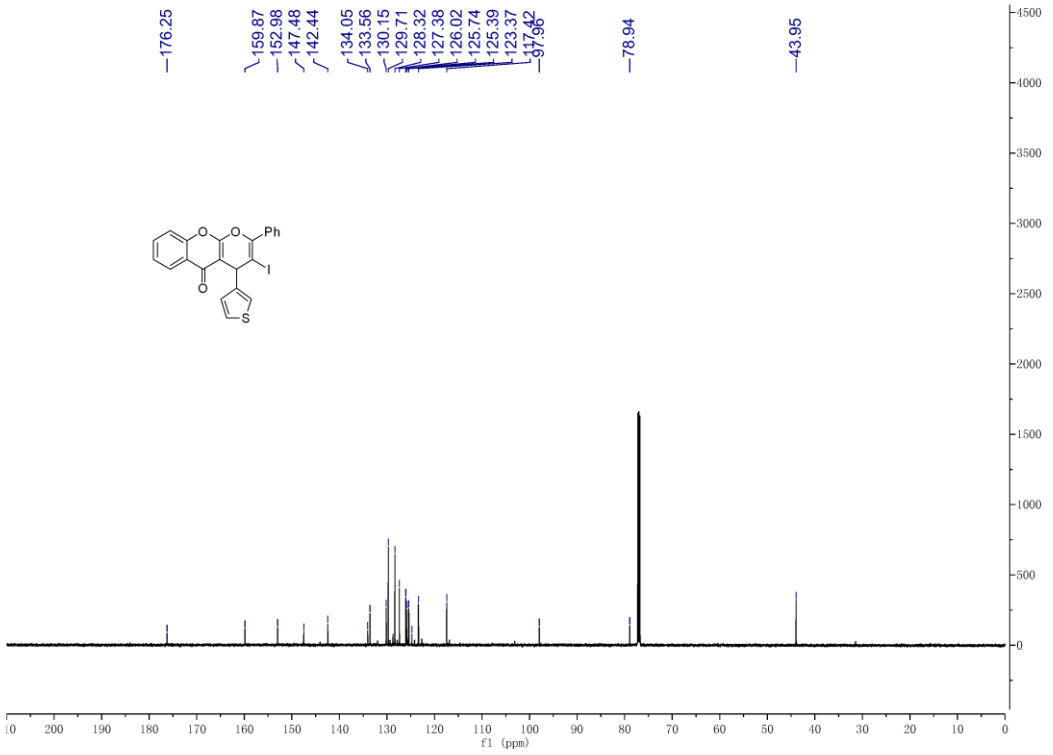
^{1}H NMR spectrum of **5n** (600MHz, $CDCl_3$)



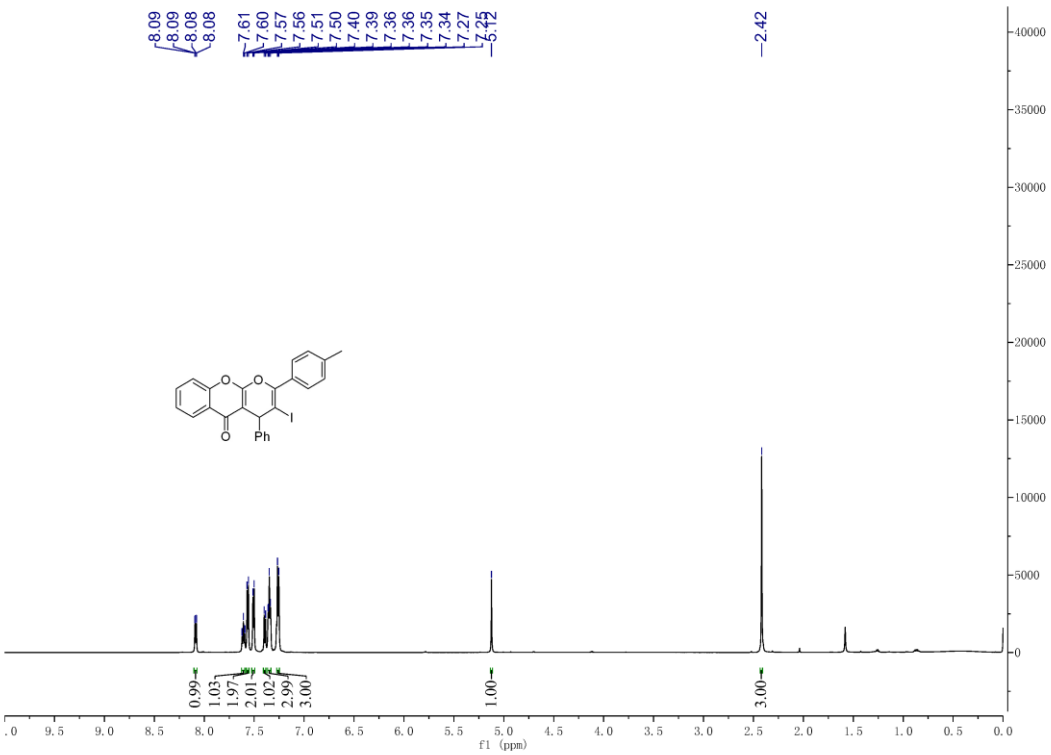
^{13}C NMR spectrum of **5n** (151 MHz, $CDCl_3$)



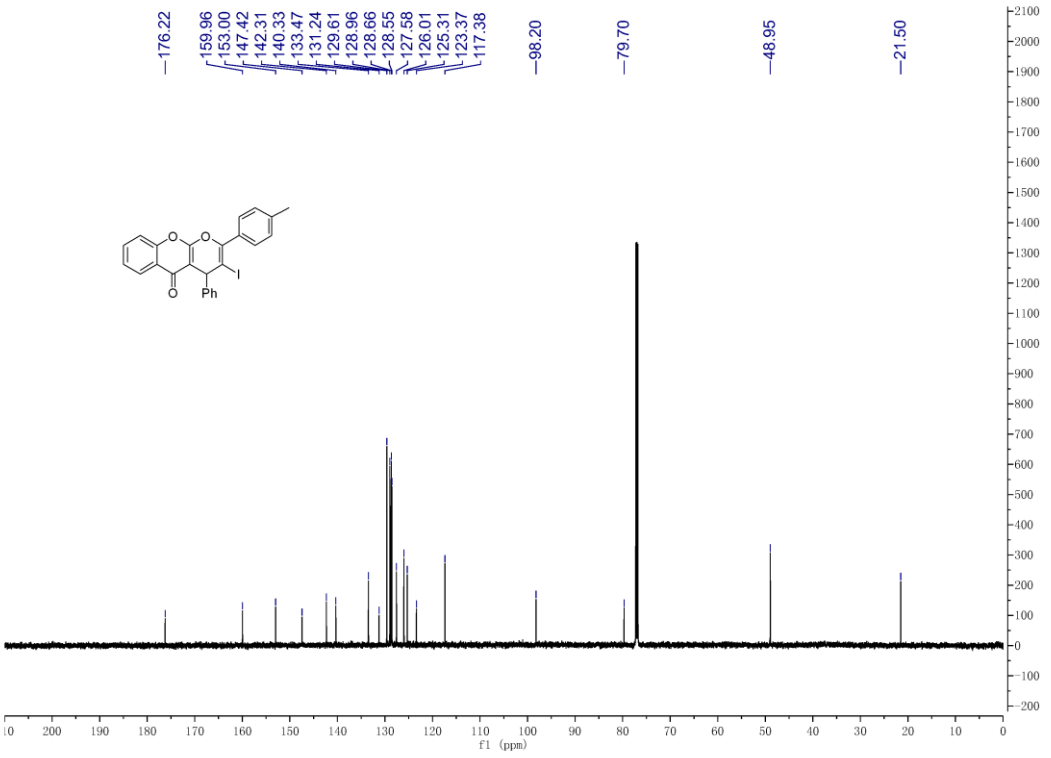
^{1}H NMR spectrum of **5o** (600MHz, $CDCl_3$)



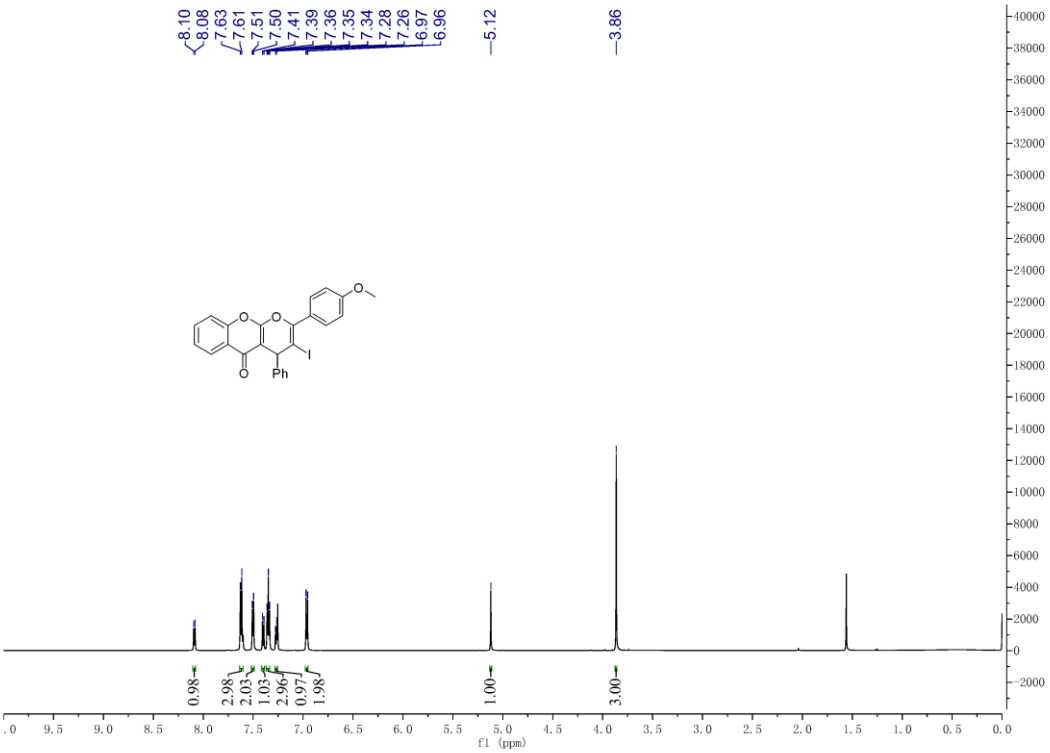
^{13}C NMR spectrum of **5o** (151 MHz, $CDCl_3$)



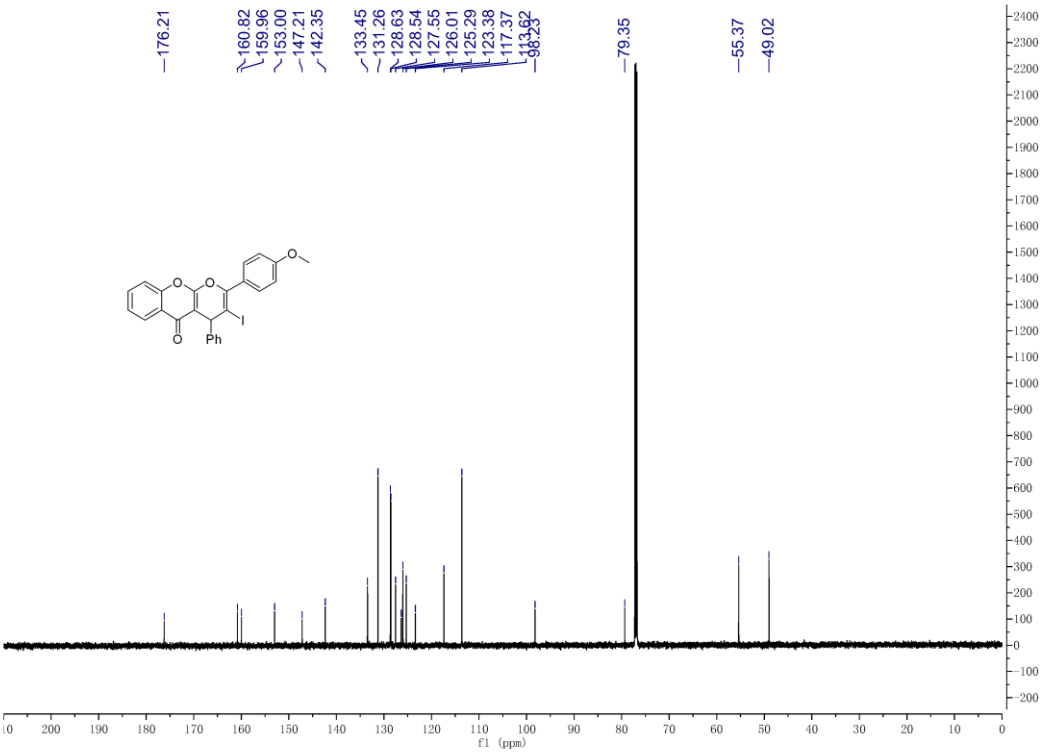
^{1}H NMR spectrum of **5p** (600MHz, $CDCl_3$)



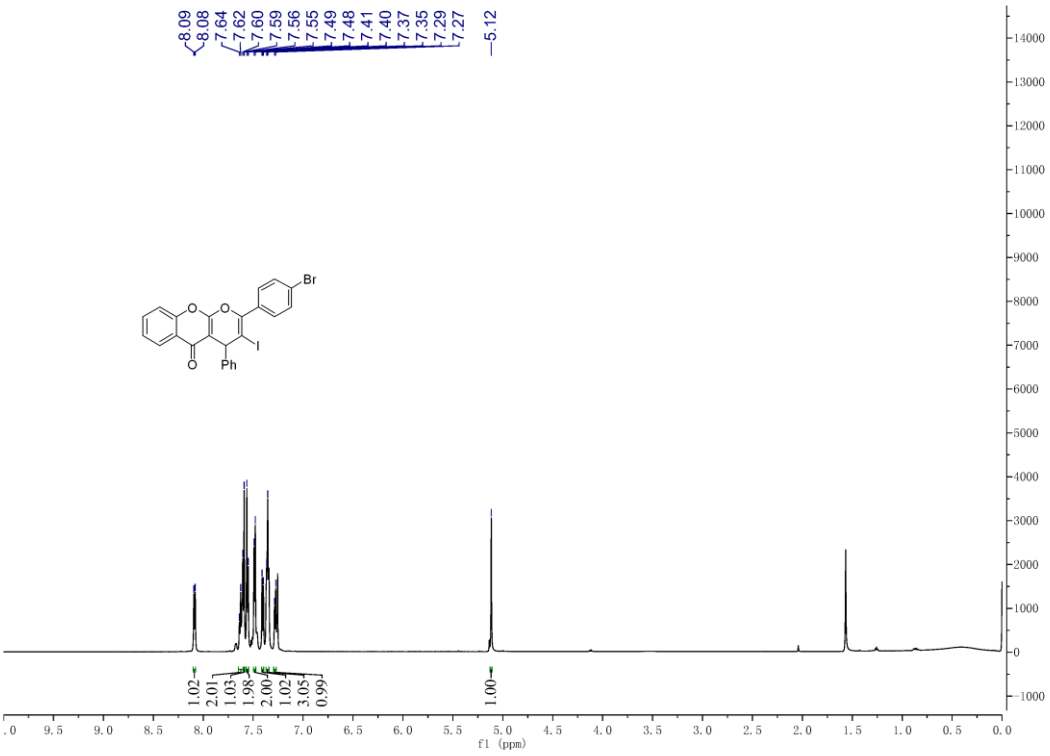
^{13}C NMR spectrum of **5p** (151 MHz, $CDCl_3$)



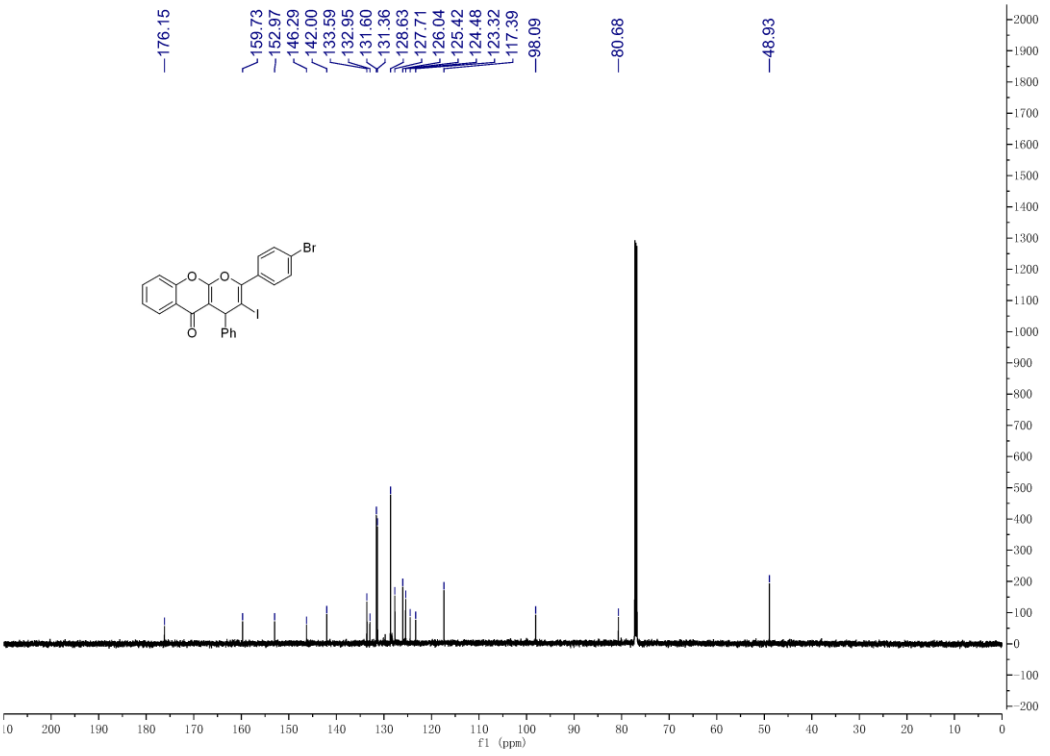
^{1}H NMR spectrum of **5q** (600MHz, $CDCl_3$)



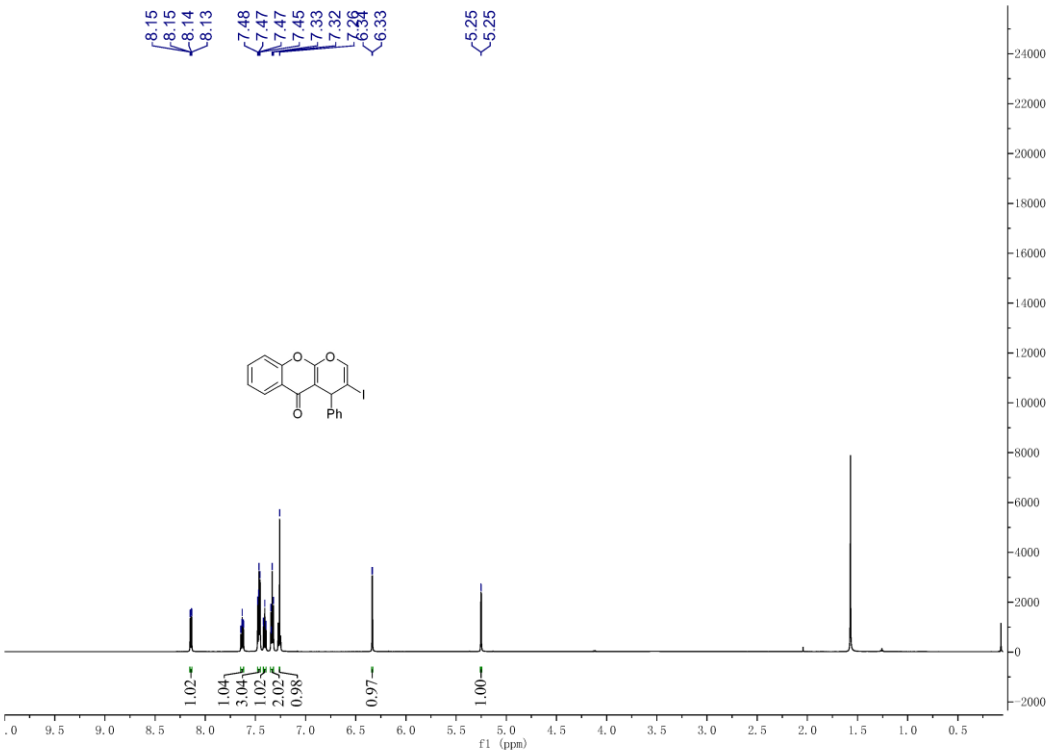
^{13}C NMR spectrum of **5q** (151 MHz, $CDCl_3$)



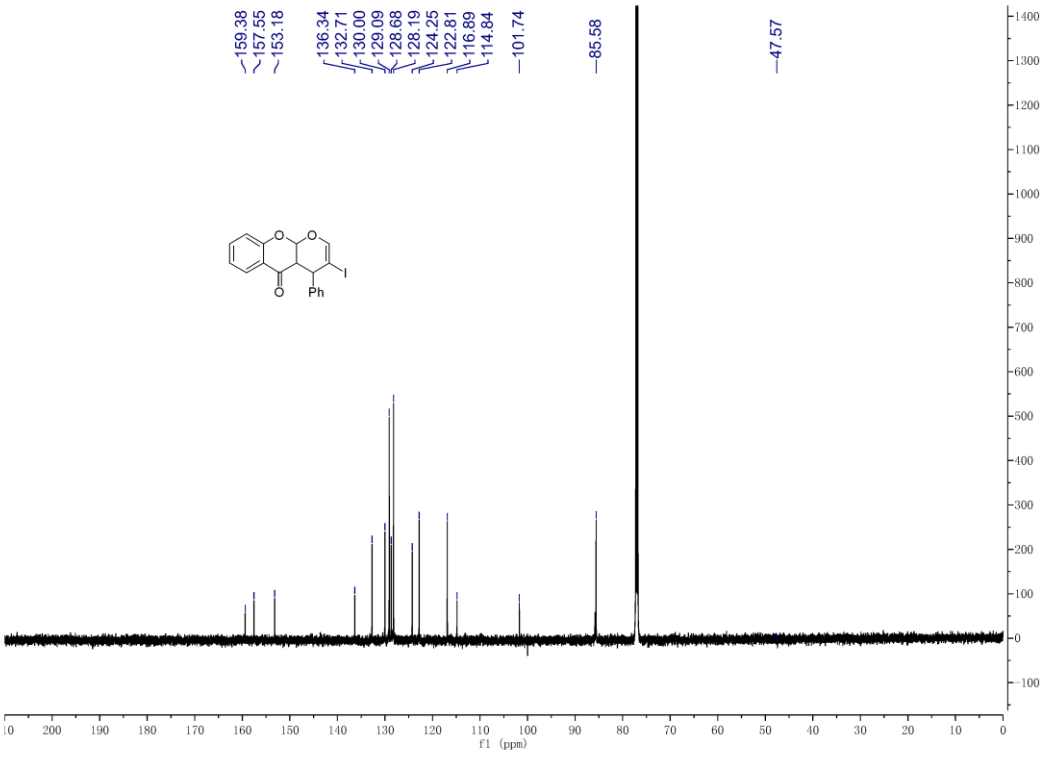
^{1}H NMR spectrum of **5r** (600MHz, $CDCl_3$)



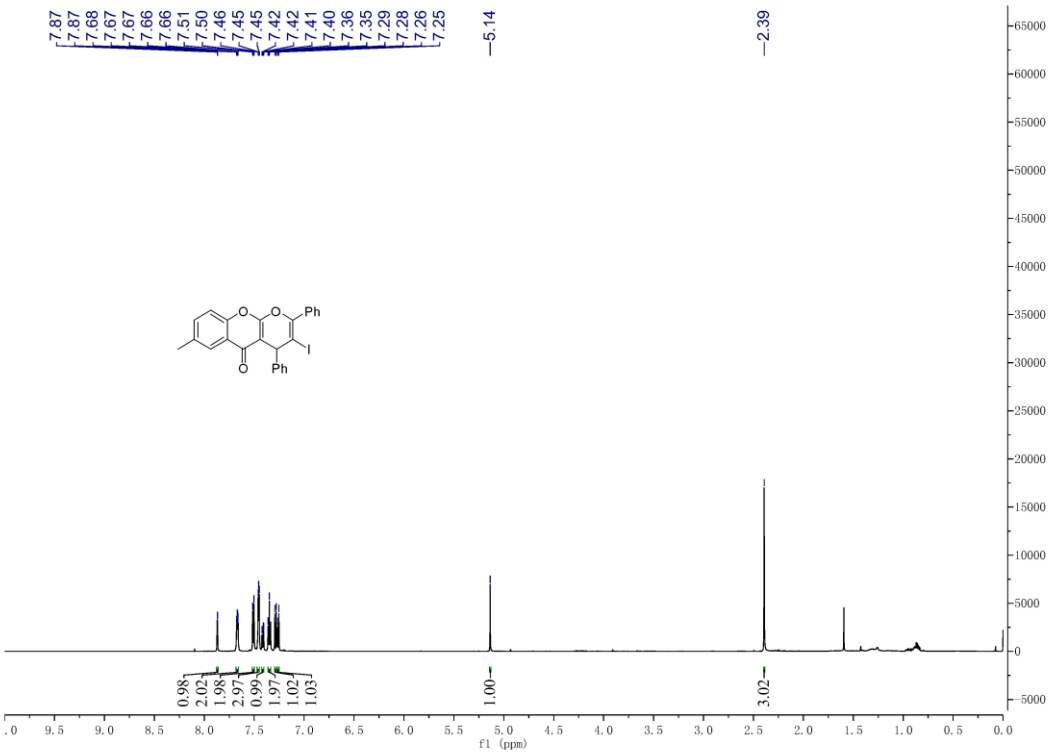
^{13}C NMR spectrum of **5r** (151 MHz, $CDCl_3$)



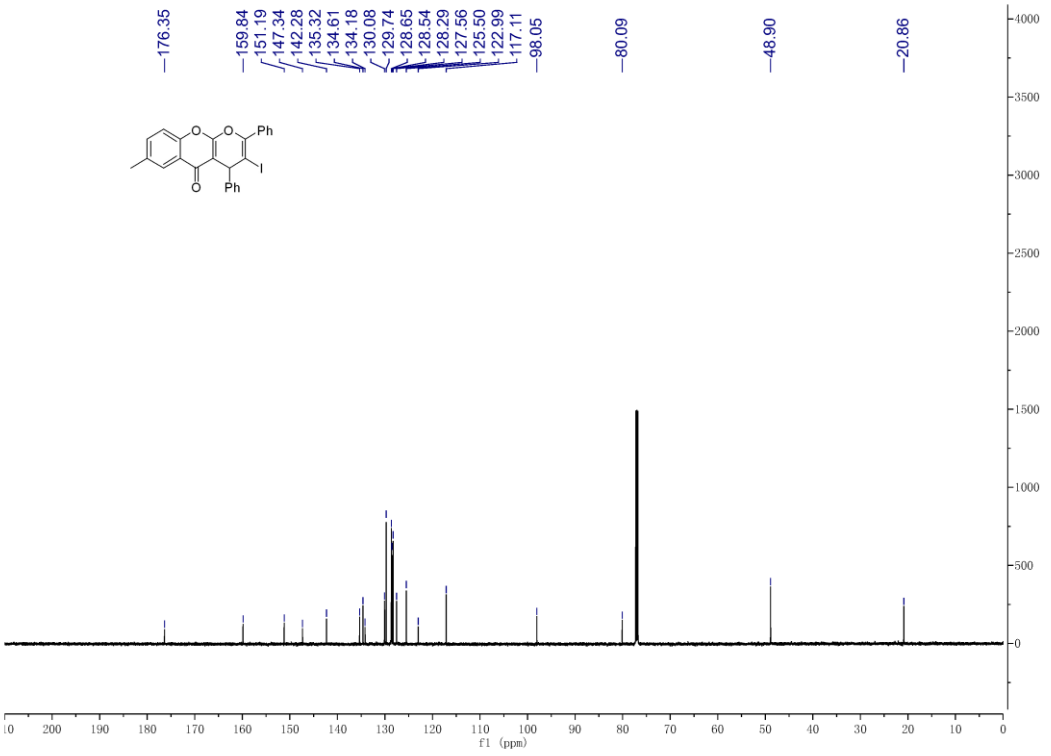
^{1}H NMR spectrum of **5s** (600MHz, $CDCl_3$)



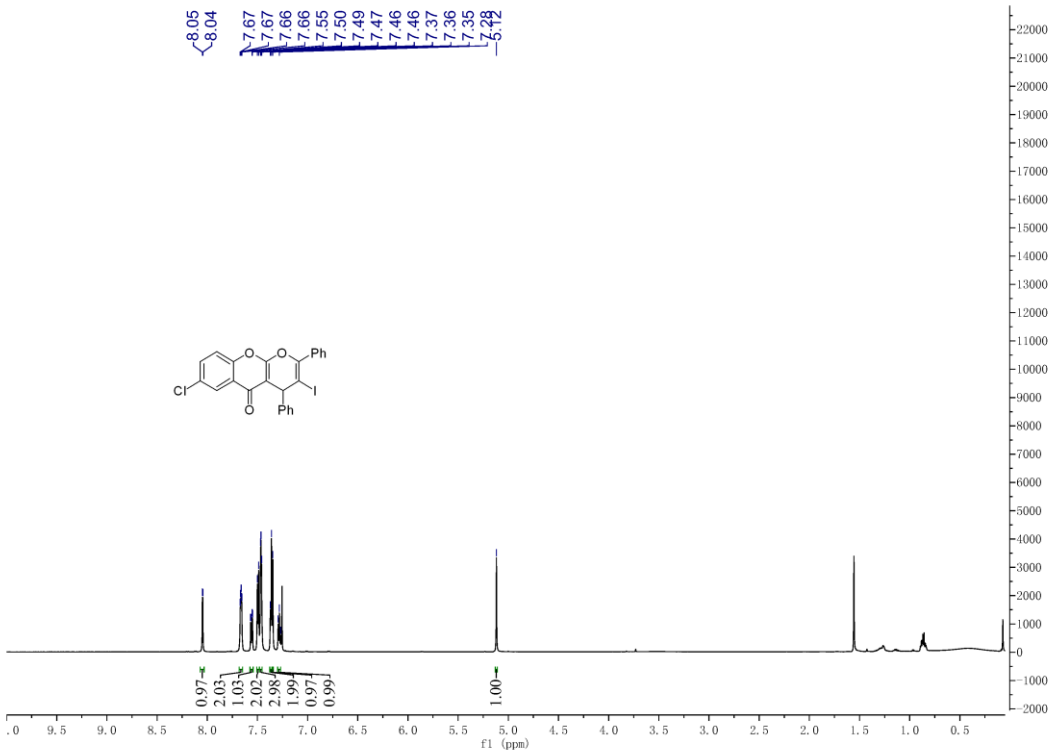
^{13}C NMR spectrum of **5s** (151 MHz, $CDCl_3$)



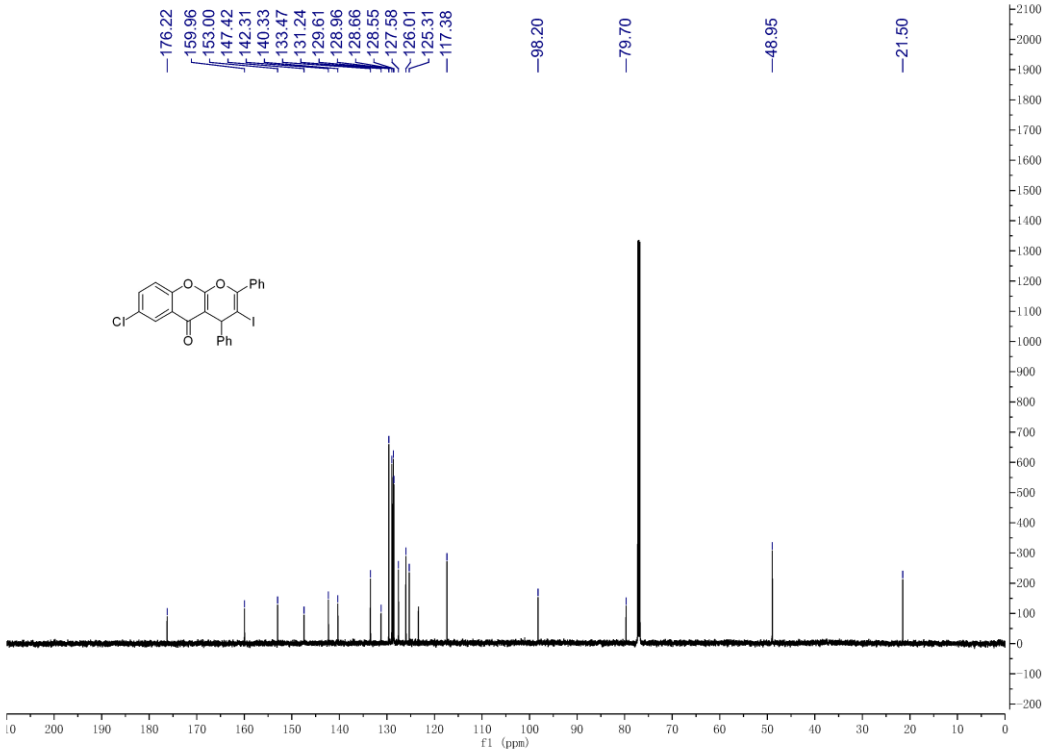
^{1}H NMR spectrum of **5t** (600MHz, $CDCl_3$)



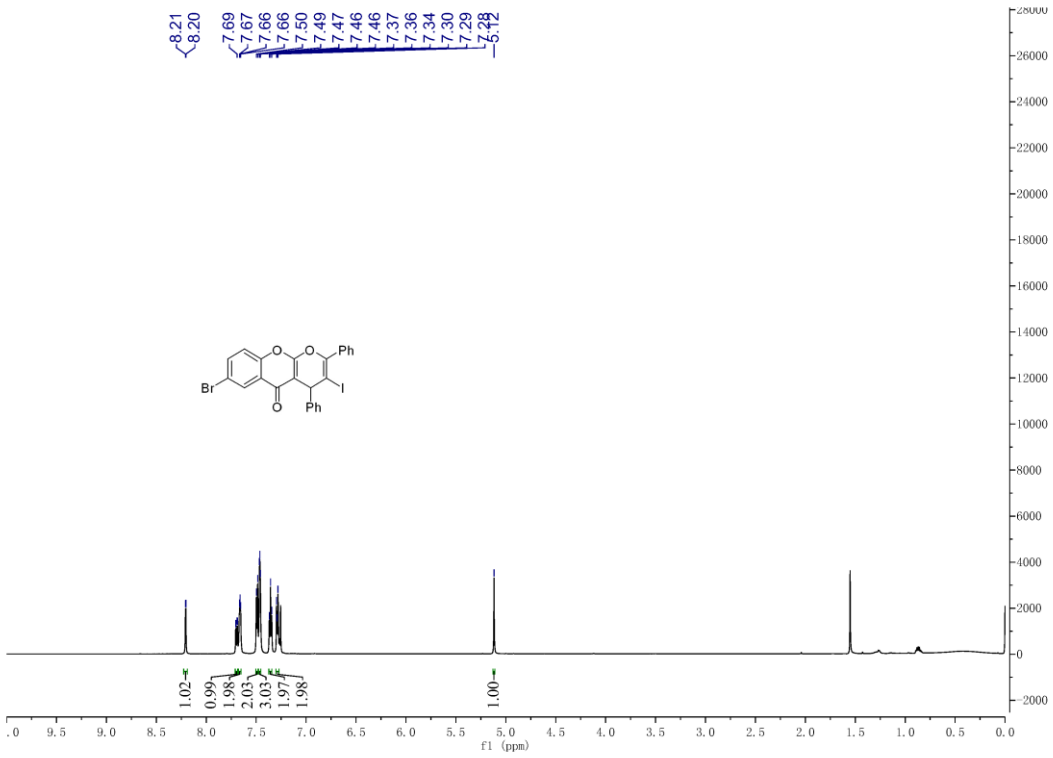
^{13}C NMR spectrum of **5t** (151 MHz, $CDCl_3$)



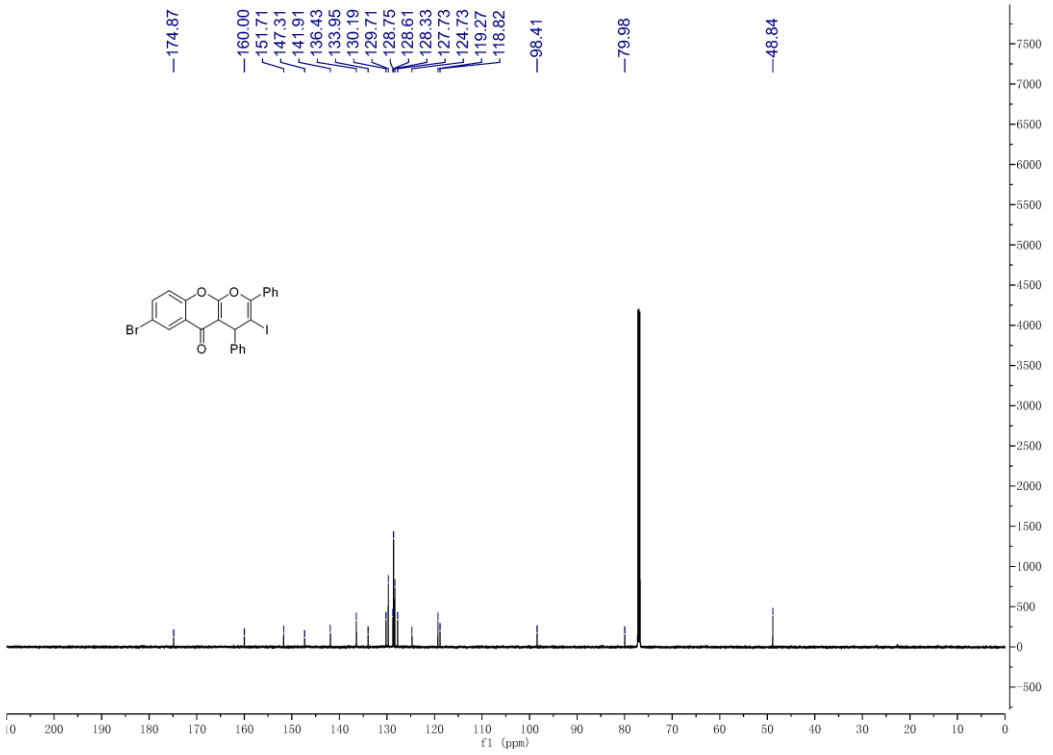
^{1}H NMR spectrum of **5u** (600MHz, $CDCl_3$)



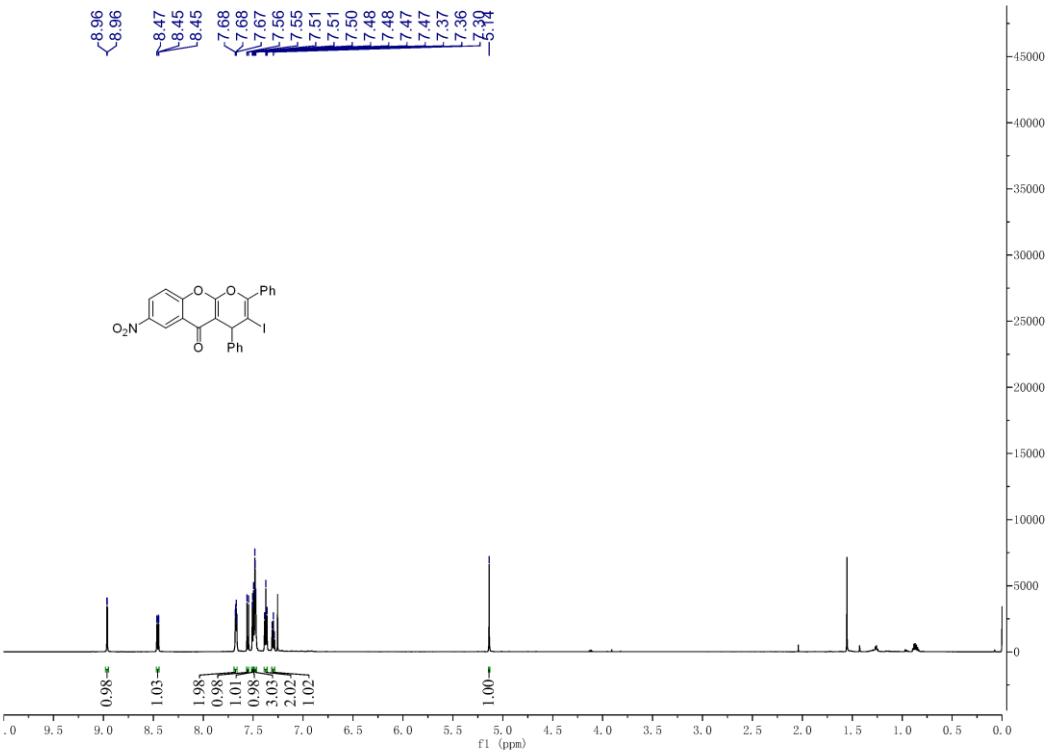
^{13}C NMR spectrum of **5u** (151 MHz, $CDCl_3$)



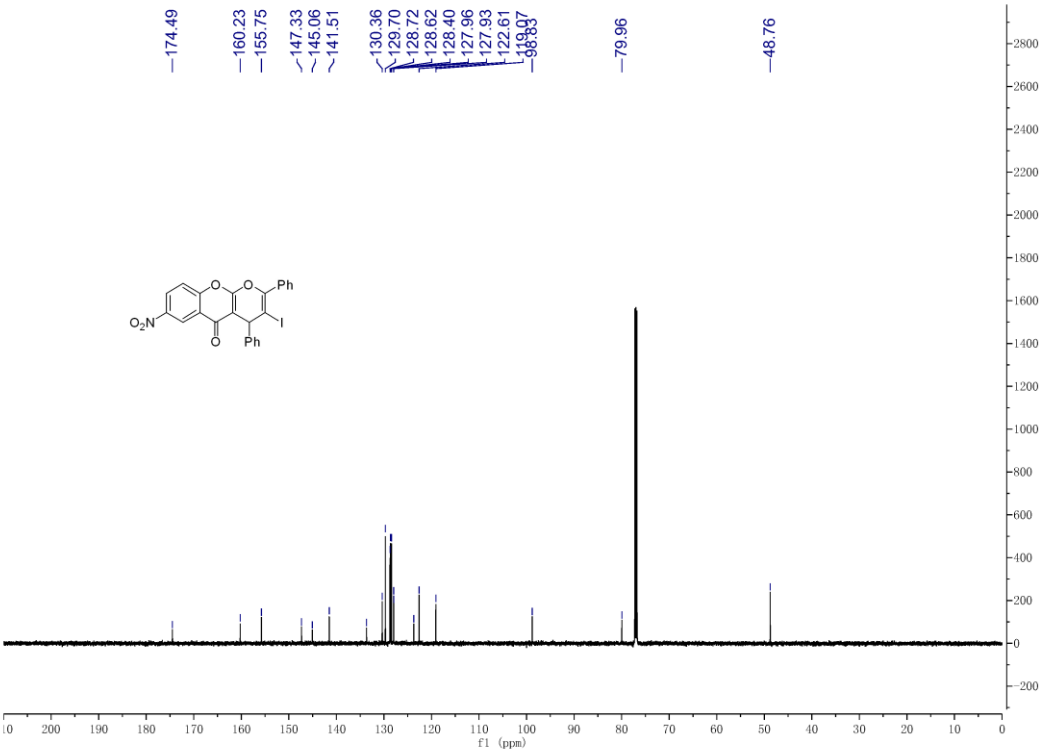
^{1}H NMR spectrum of **5v** (600MHz, $CDCl_3$)



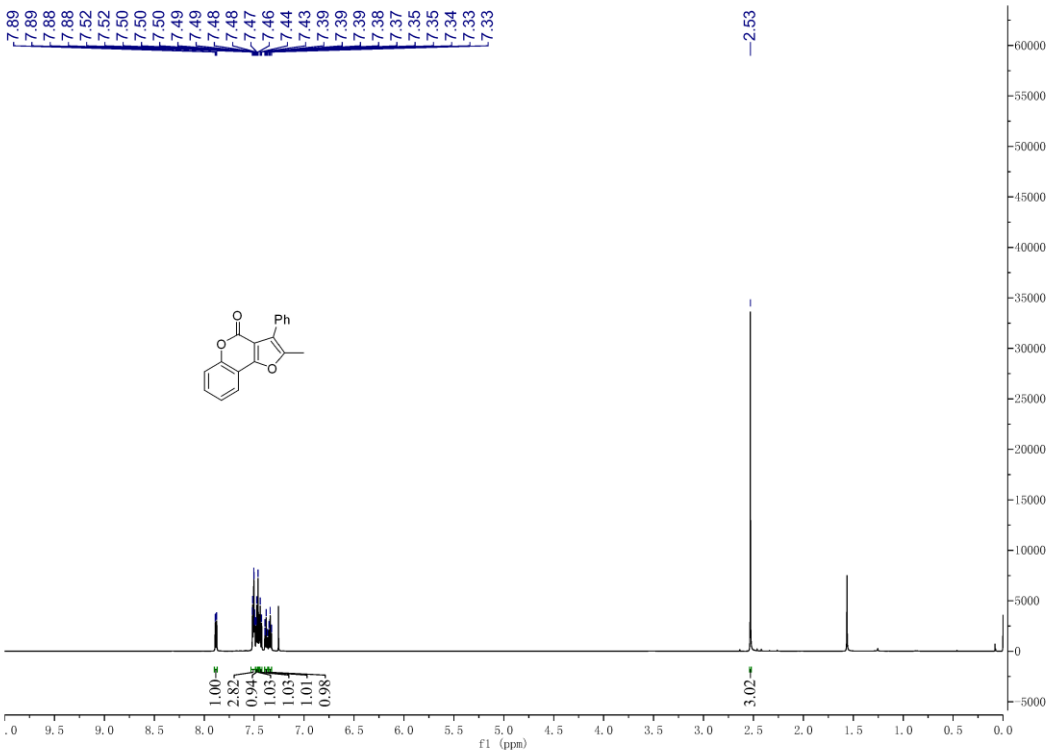
^{13}C NMR spectrum of **5v** (151 MHz, $CDCl_3$)



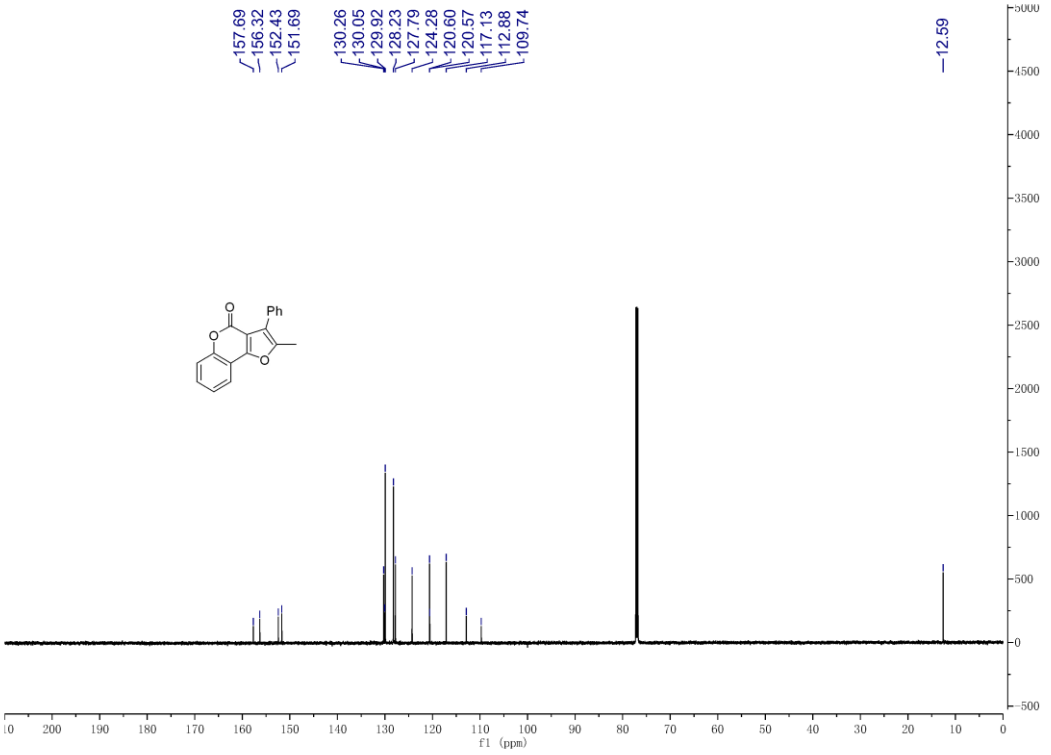
^{1}H NMR spectrum of **5w** (600MHz, $CDCl_3$)



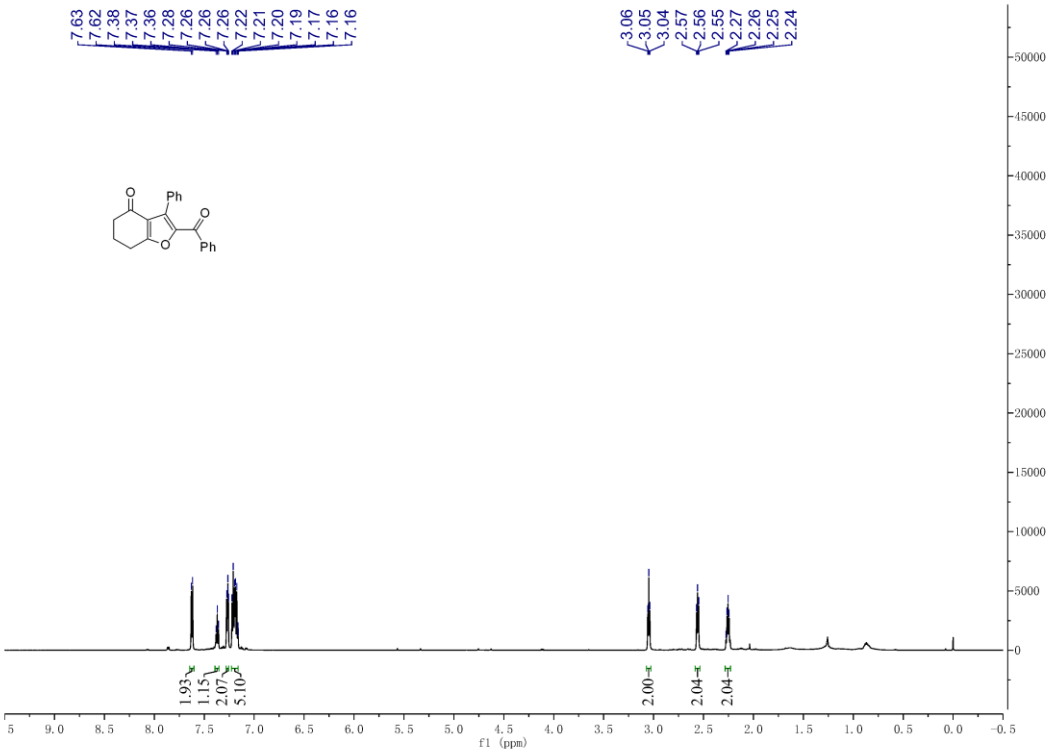
^{13}C NMR spectrum of **5w** (151 MHz, $CDCl_3$)



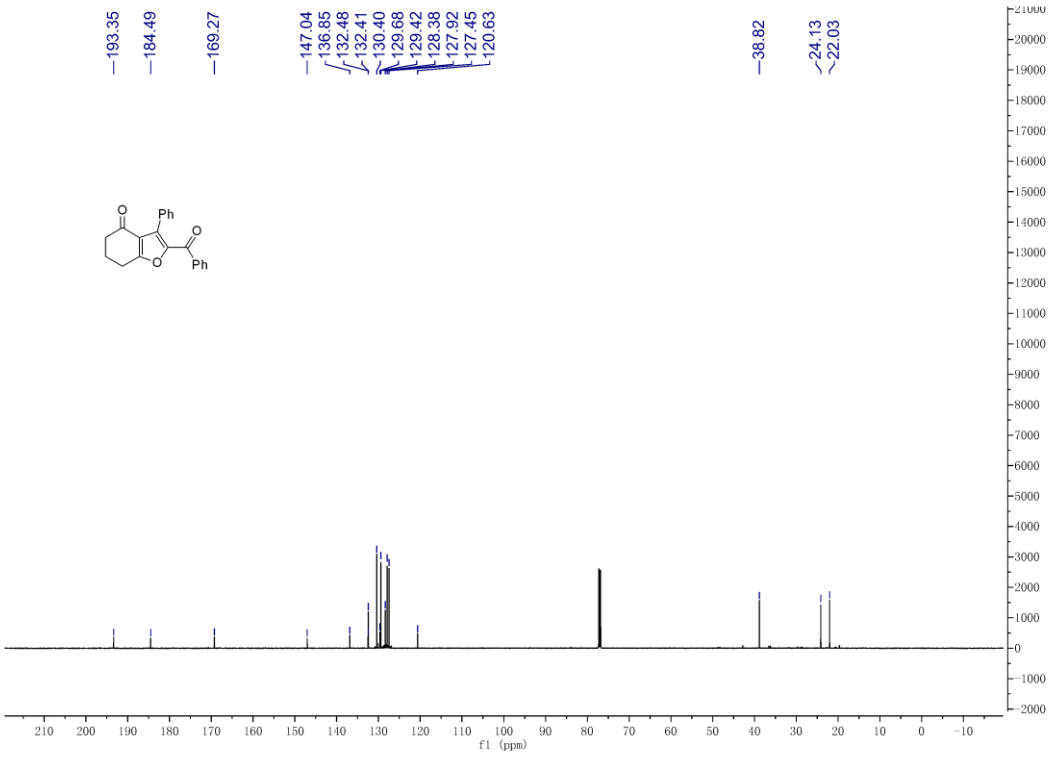
^{1}H NMR spectrum of **5x**(600MHz, $CDCl_3$)



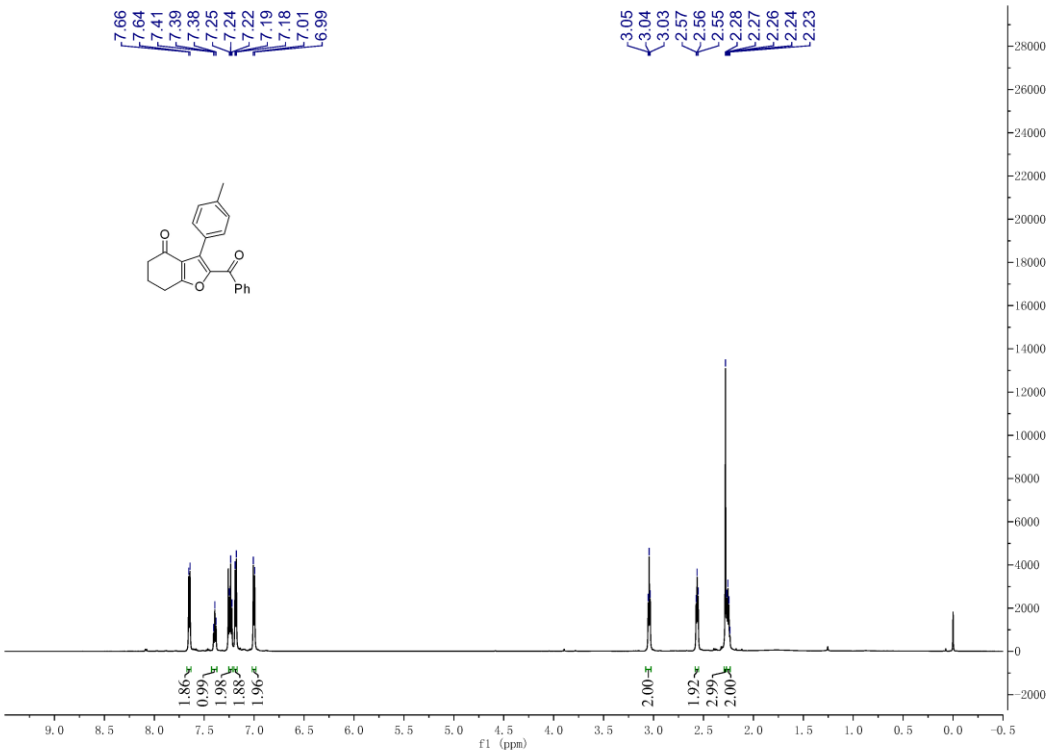
^{13}C NMR spectrum of **5x** (151 MHz, $CDCl_3$)



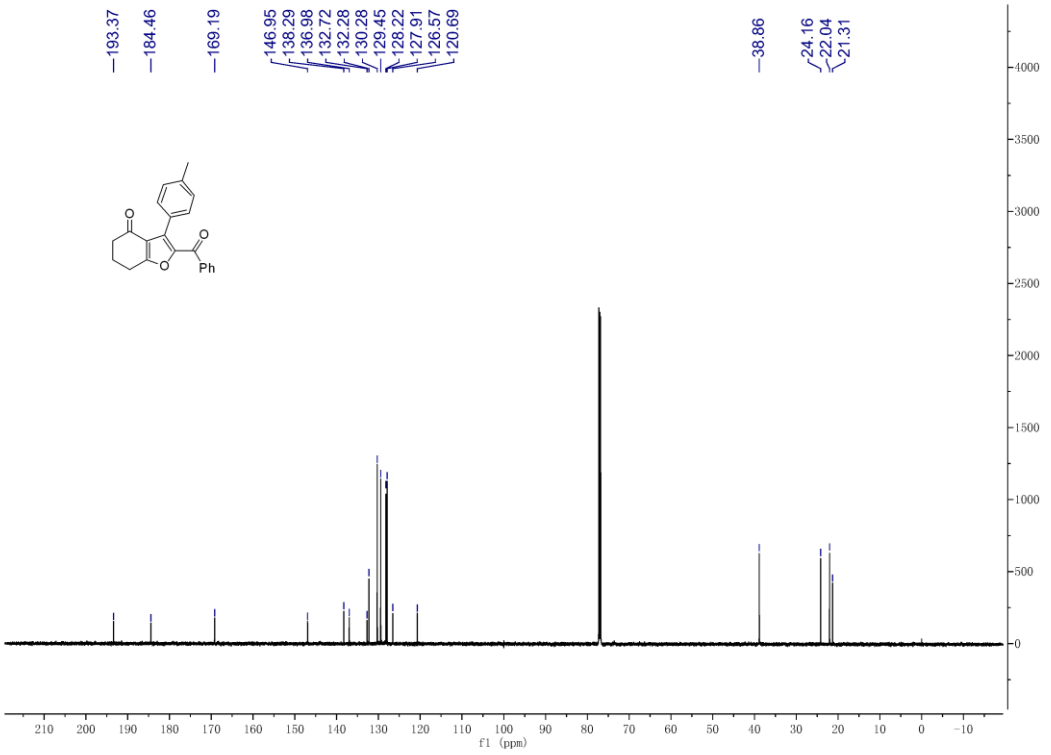
^{1}H NMR spectrum of **6a** (600MHz, $CDCl_3$)



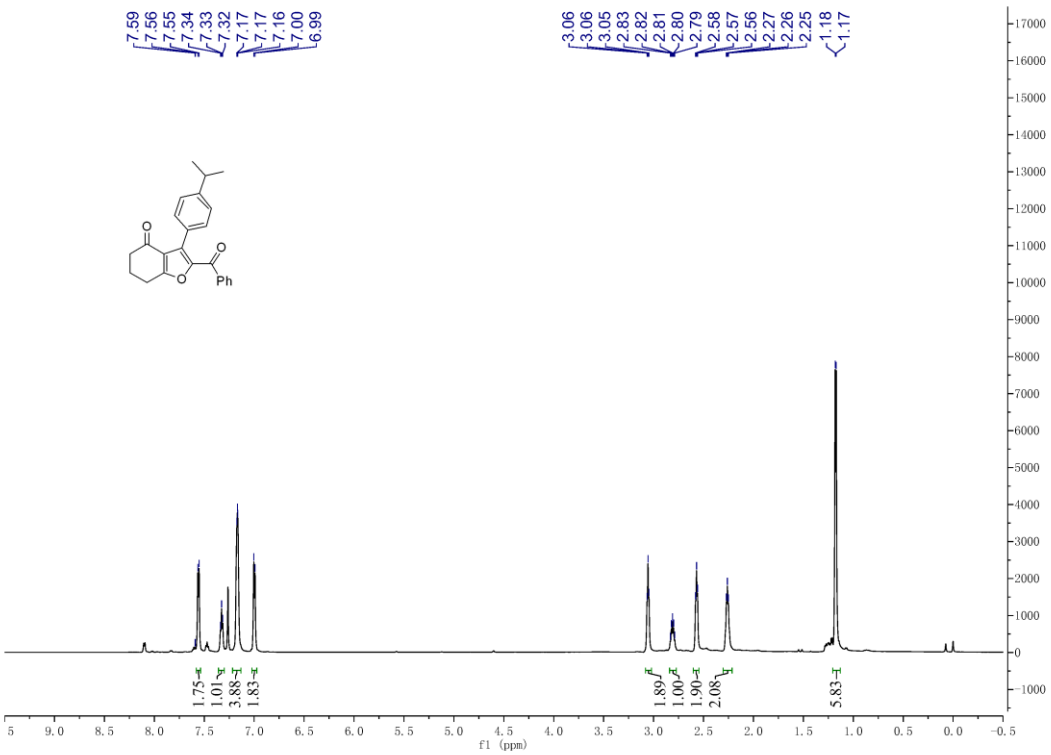
^{13}C NMR spectrum of **6a** (151 MHz, $CDCl_3$)



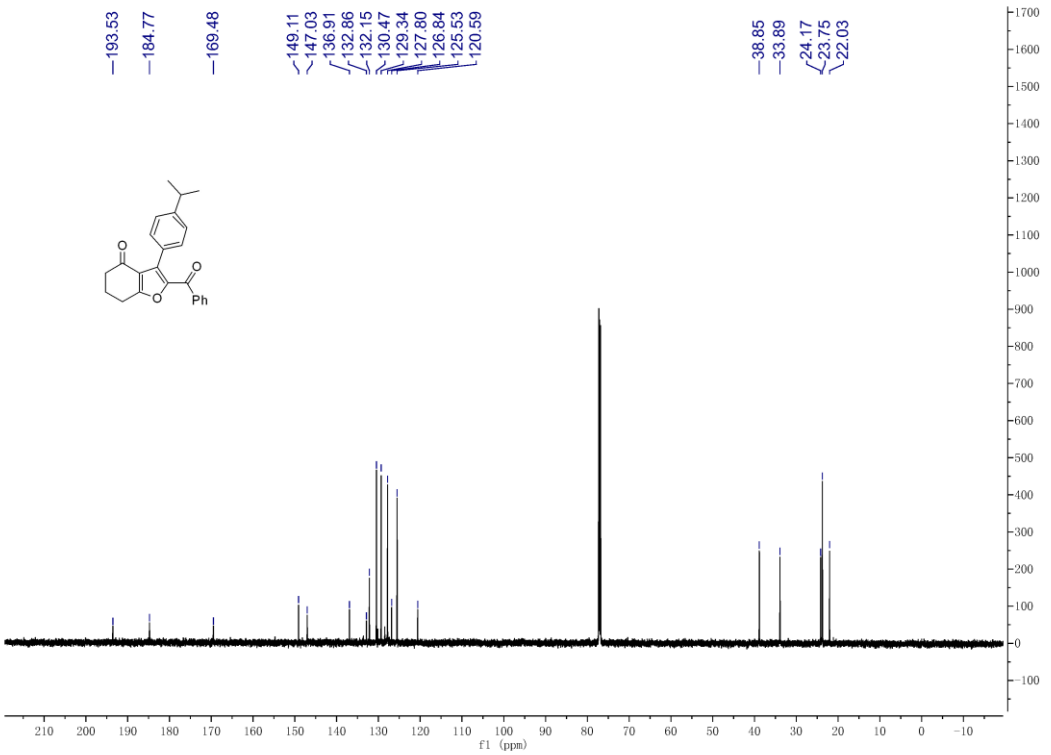
^{1}H NMR spectrum of **6b** (600MHz, $CDCl_3$)



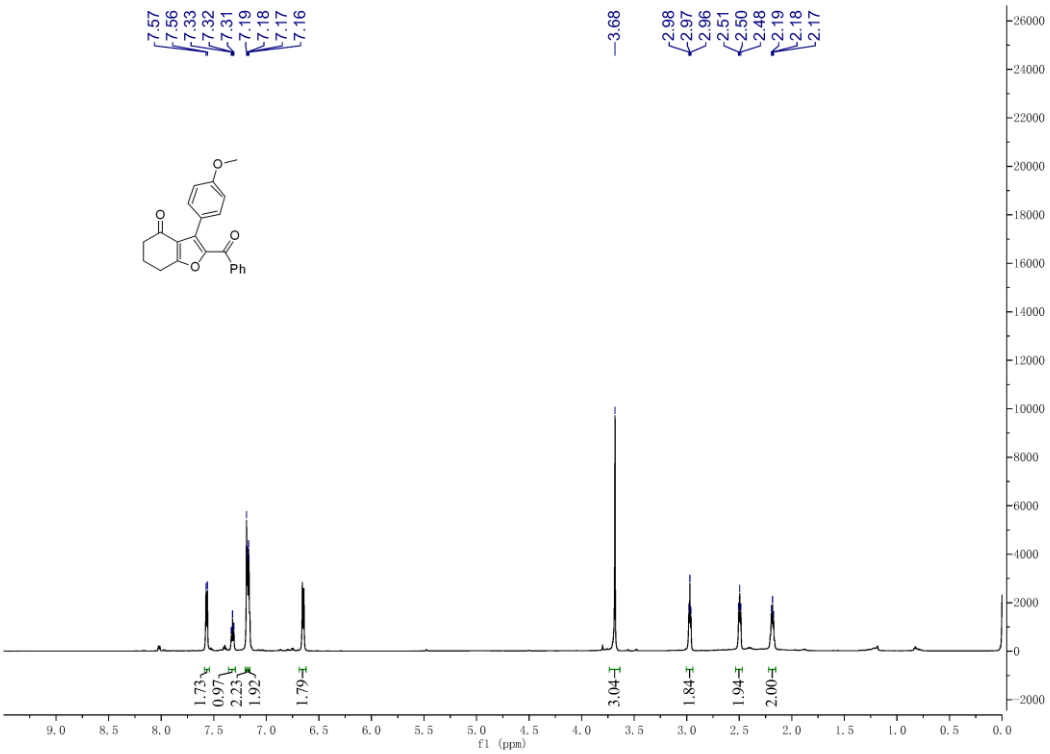
^{13}C NMR spectrum of **6b** (151 MHz, $CDCl_3$)



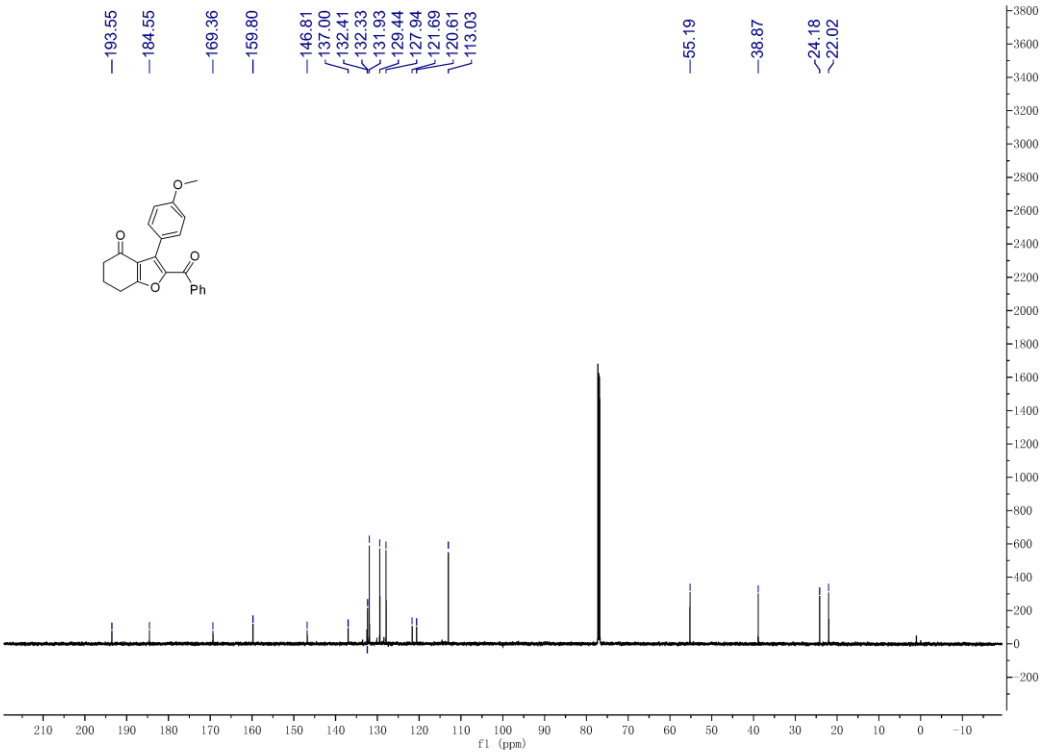
^{1}H NMR spectrum of **6c** (600MHz, $CDCl_3$)



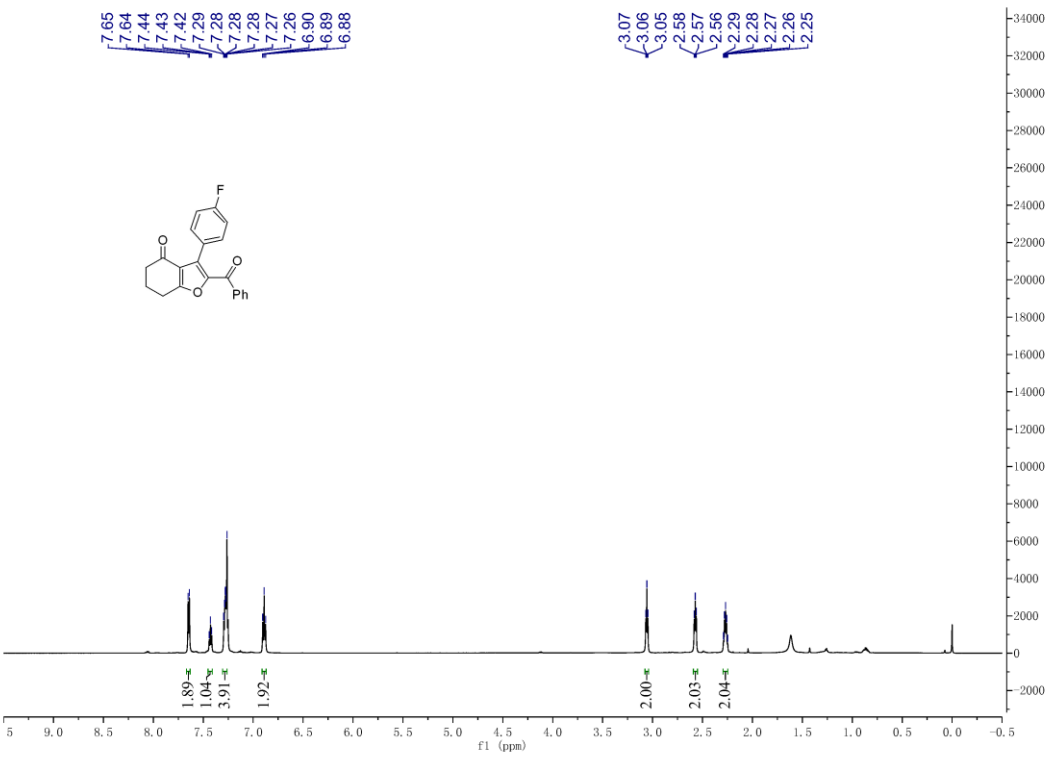
^{13}C NMR spectrum of **6c** (151 MHz, $CDCl_3$)



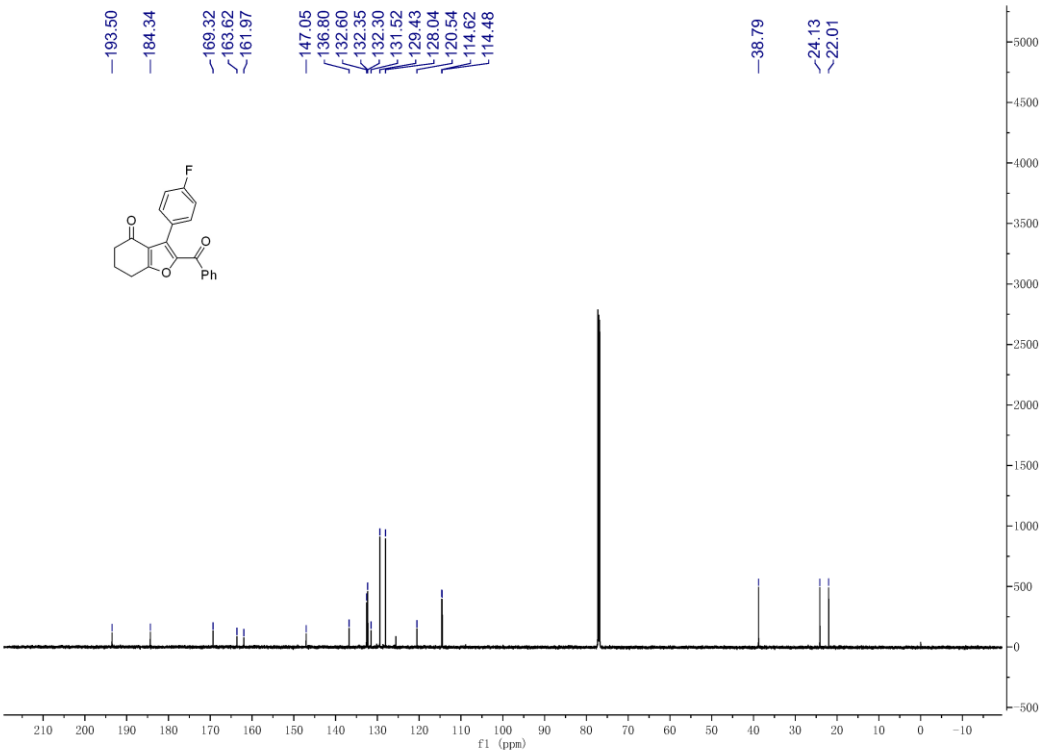
^{1}H NMR spectrum of **6d** (600MHz, $CDCl_3$)



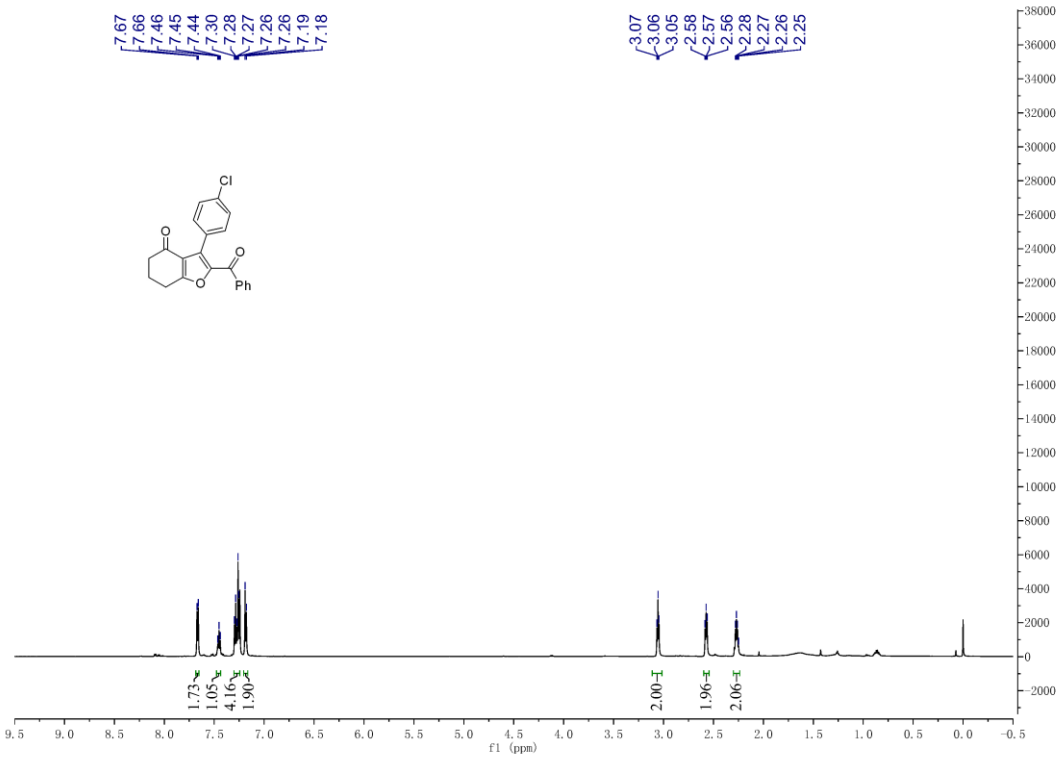
^{13}C NMR spectrum of **6d** (151 MHz, $CDCl_3$)



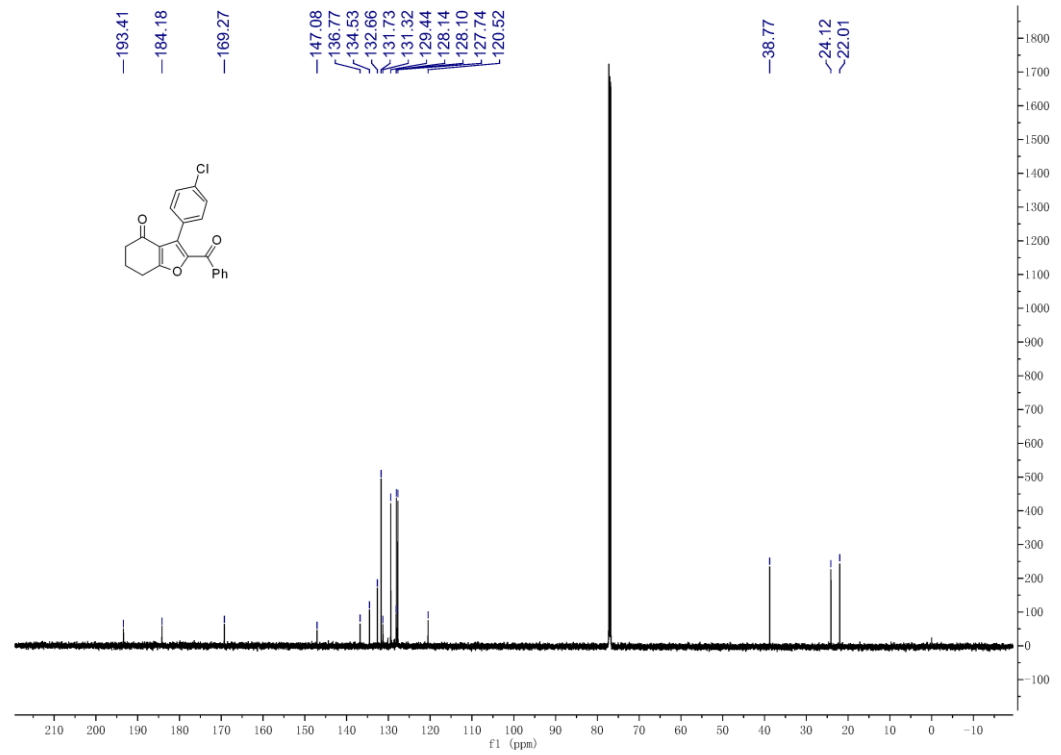
^{1}H NMR spectrum of **6e** (600MHz, $CDCl_3$)



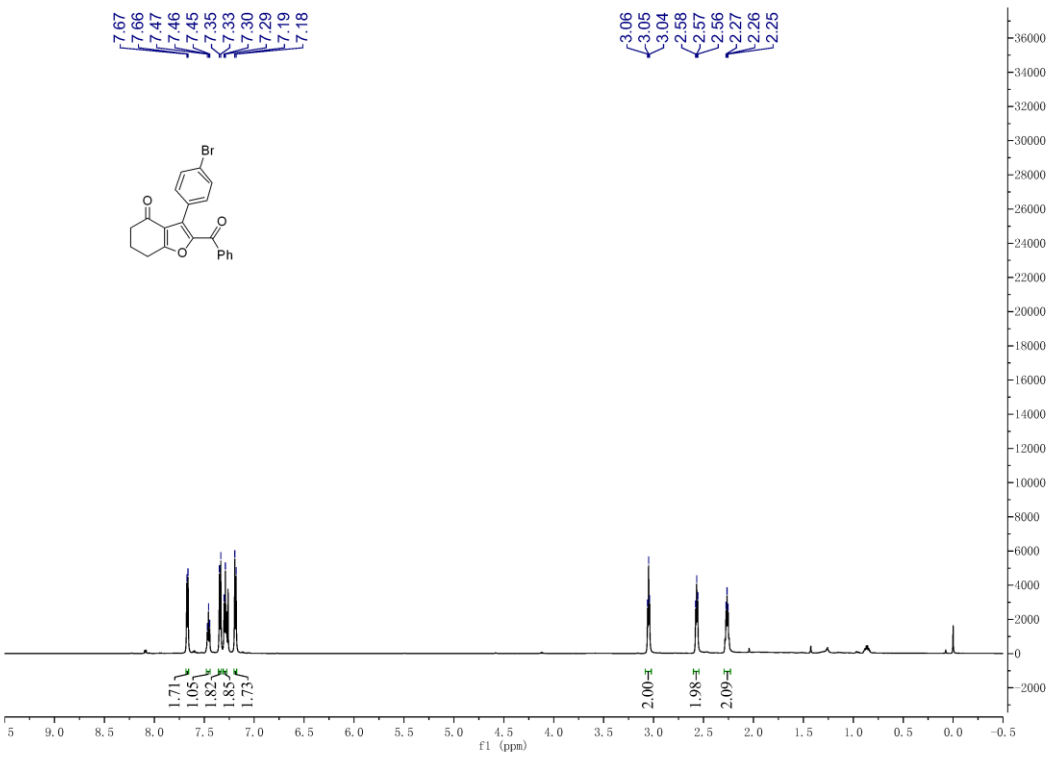
^{13}C NMR spectrum of **6e** (151 MHz, $CDCl_3$)



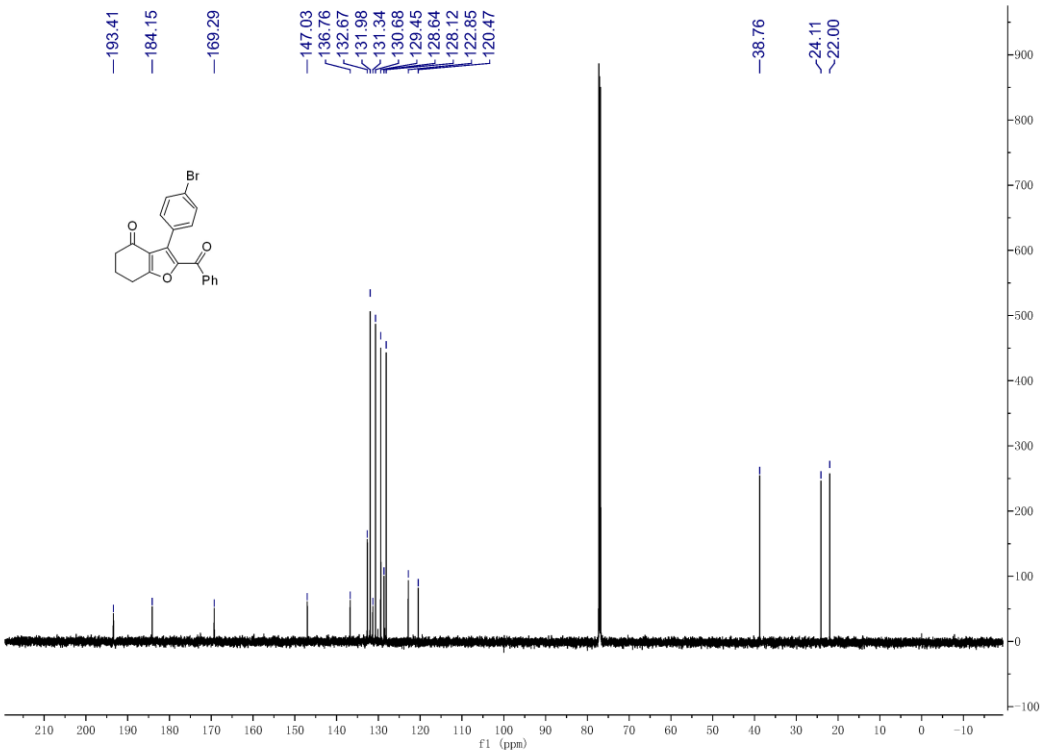
^{1}H NMR spectrum of **6f** (600MHz, $CDCl_3$)



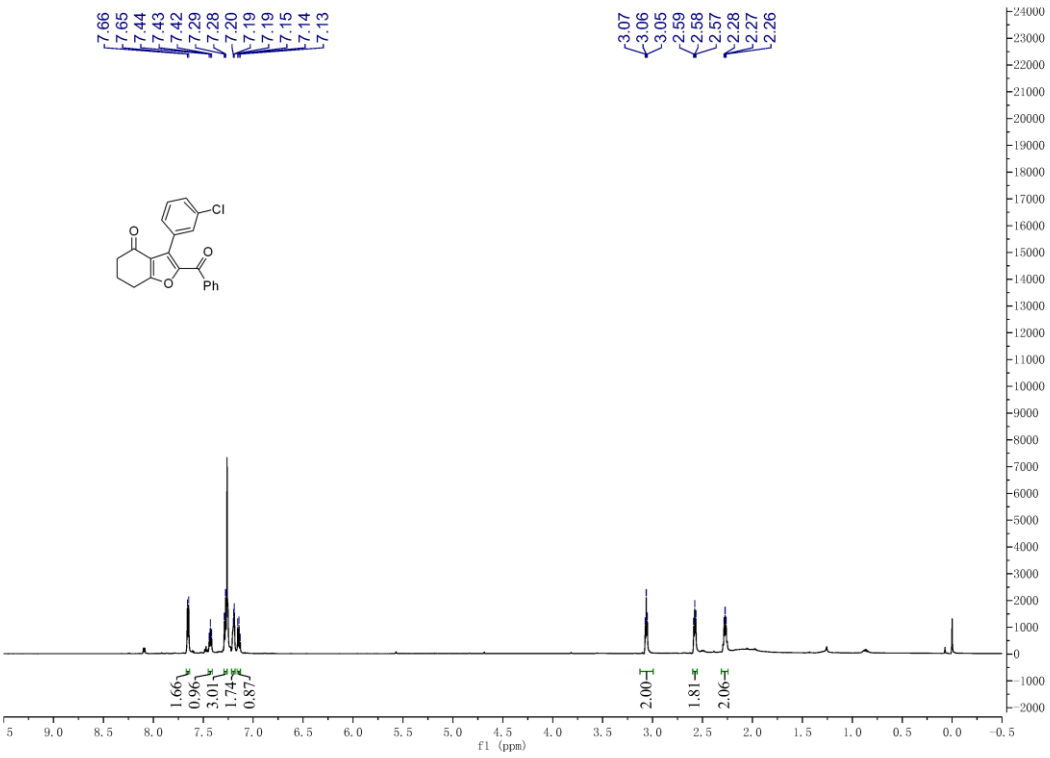
^{13}C NMR spectrum of **6f** (151 MHz, $CDCl_3$)



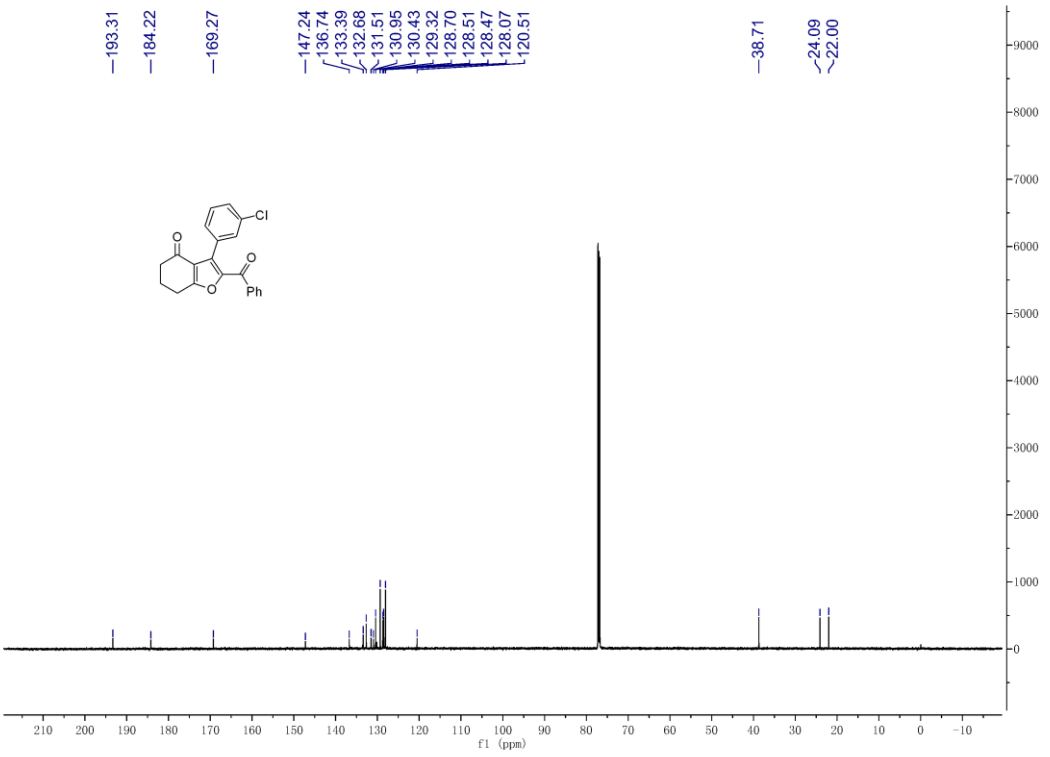
^{1}H NMR spectrum of **6g** (600MHz, $CDCl_3$)



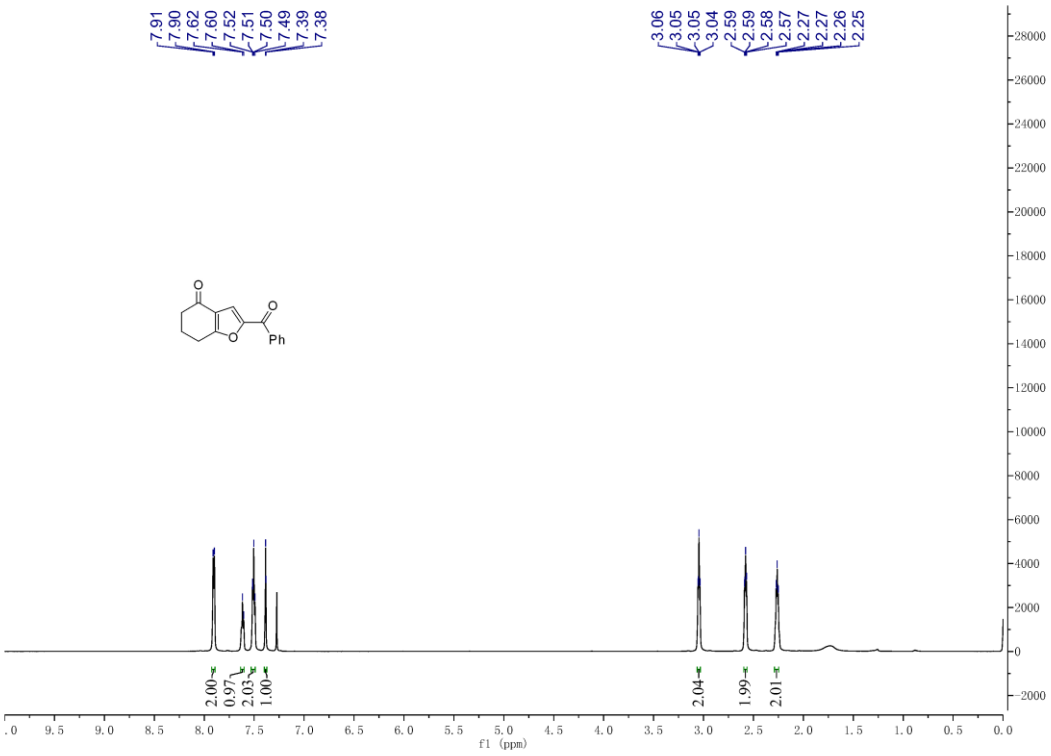
^{13}C NMR spectrum of **6g** (151 MHz, $CDCl_3$)



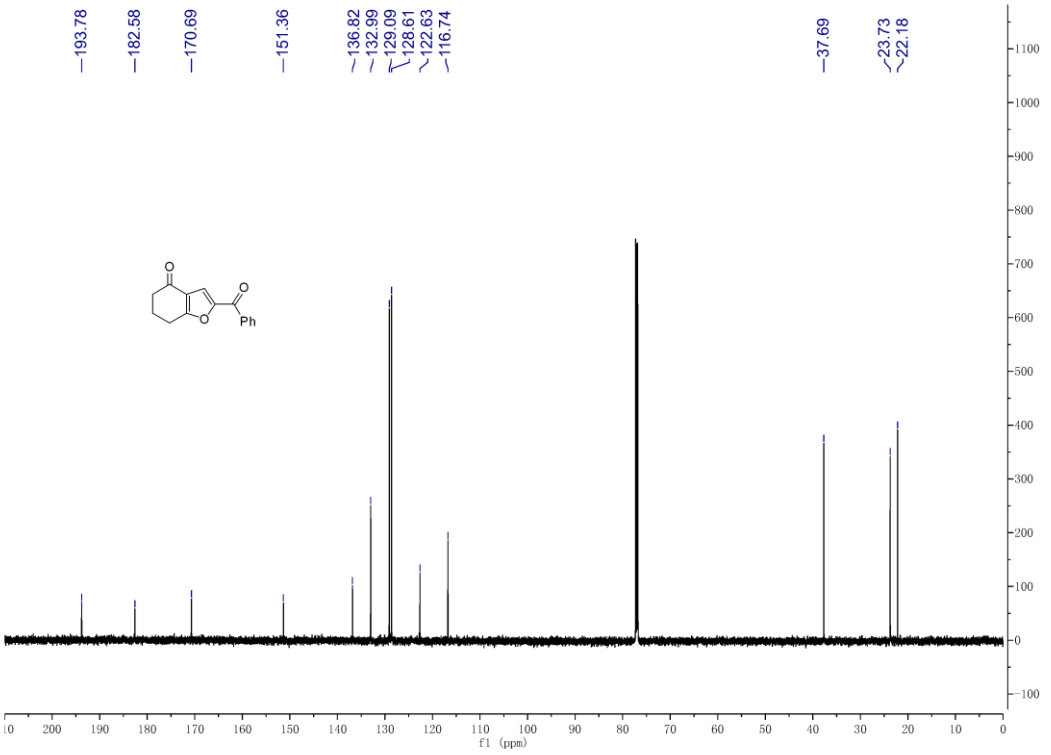
^{1}H NMR spectrum of **6h** (600MHz, $CDCl_3$)



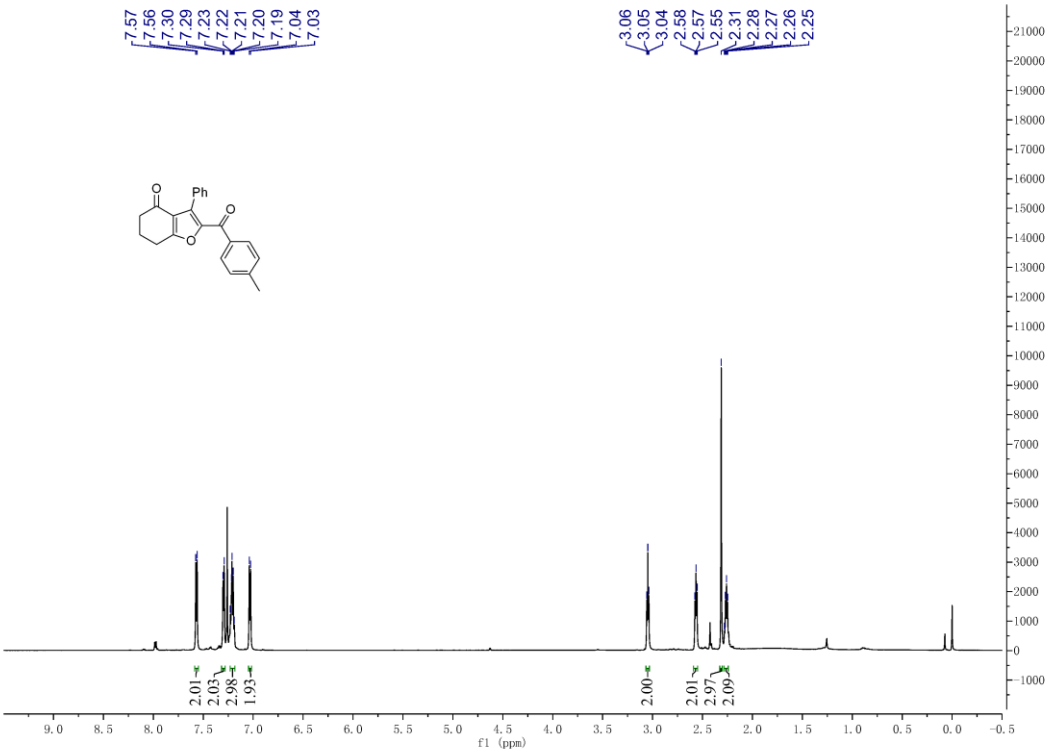
^{13}C NMR spectrum of **6h** (151 MHz, $CDCl_3$)



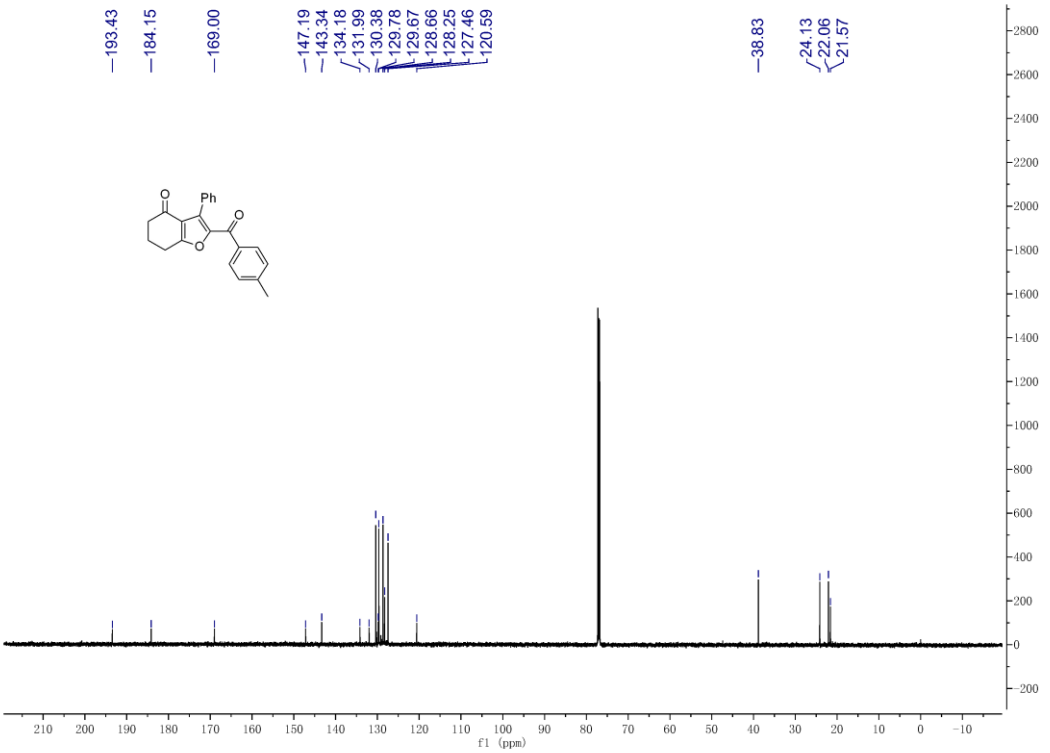
^{1}H NMR spectrum of **6i** (600MHz, $CDCl_3$)



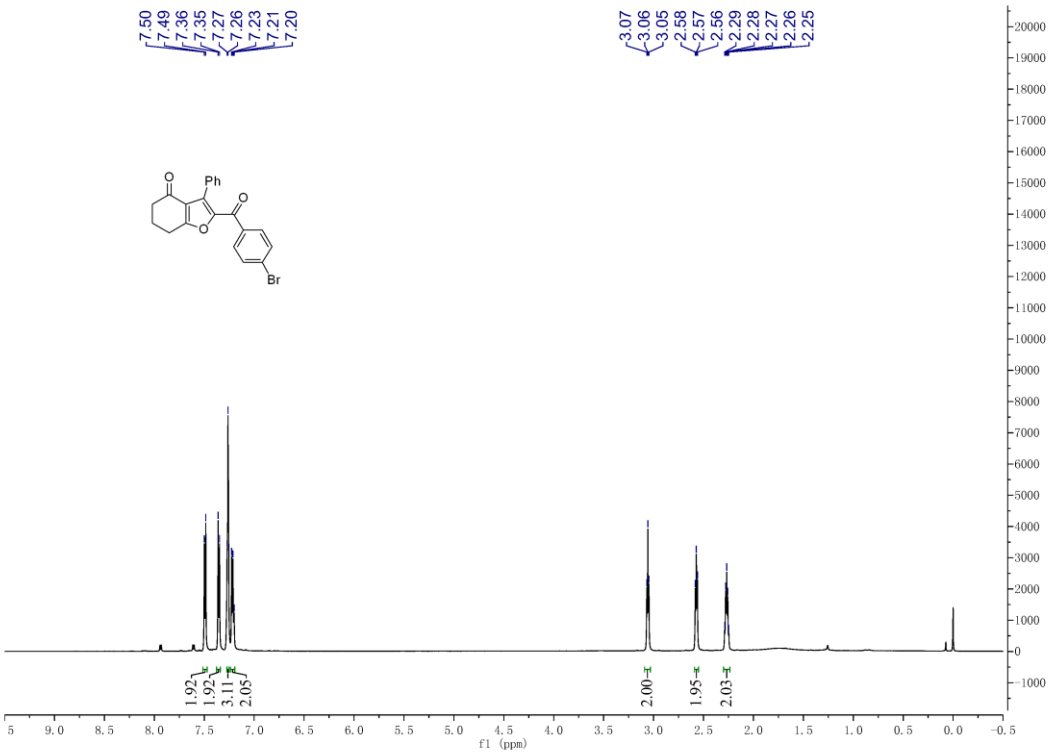
^{13}C NMR spectrum of **6i** (151 MHz, $CDCl_3$)



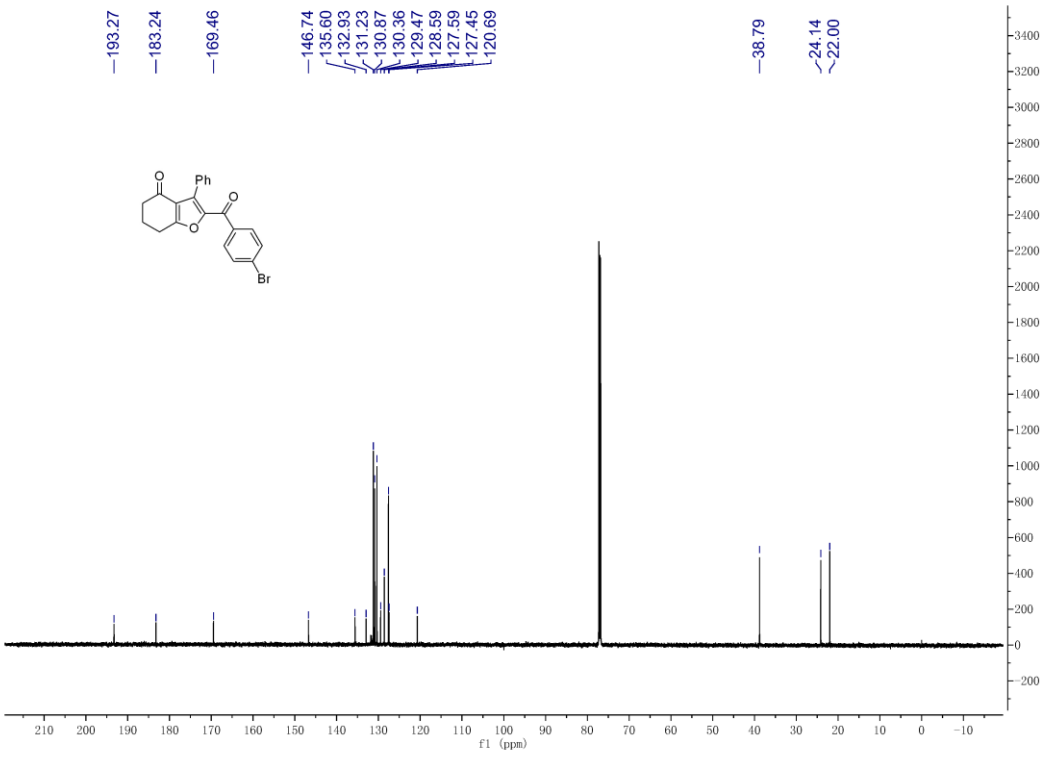
^{1}H NMR spectrum of **6j** (600MHz, $CDCl_3$)



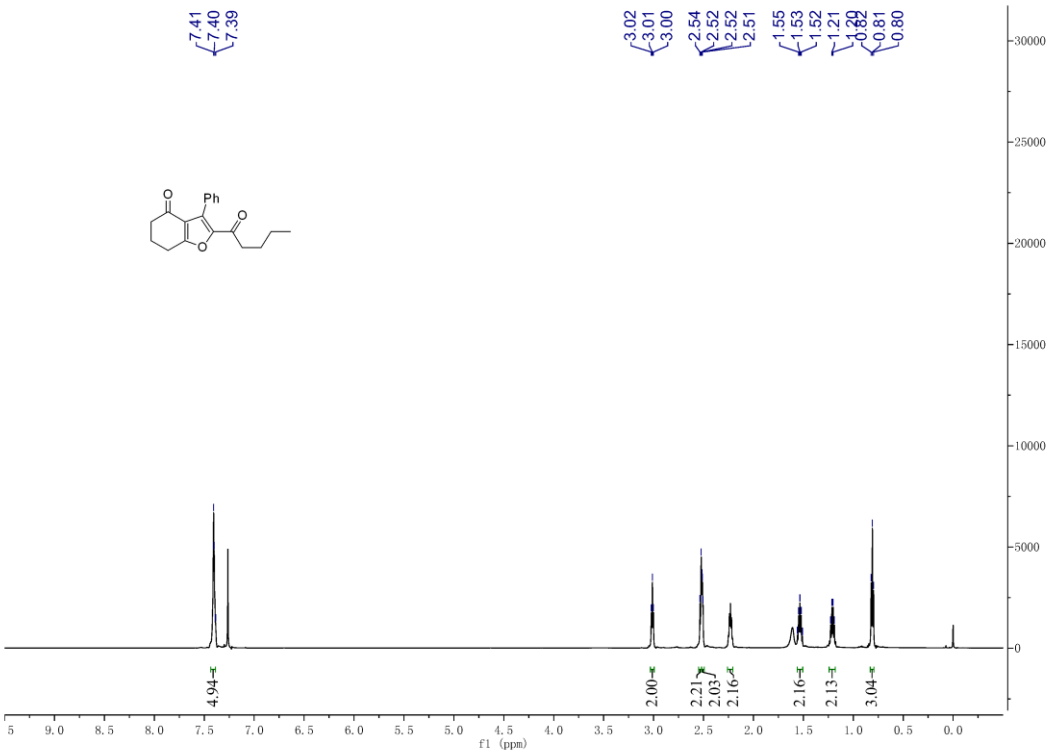
^{13}C NMR spectrum of **6j** (151 MHz, $CDCl_3$)



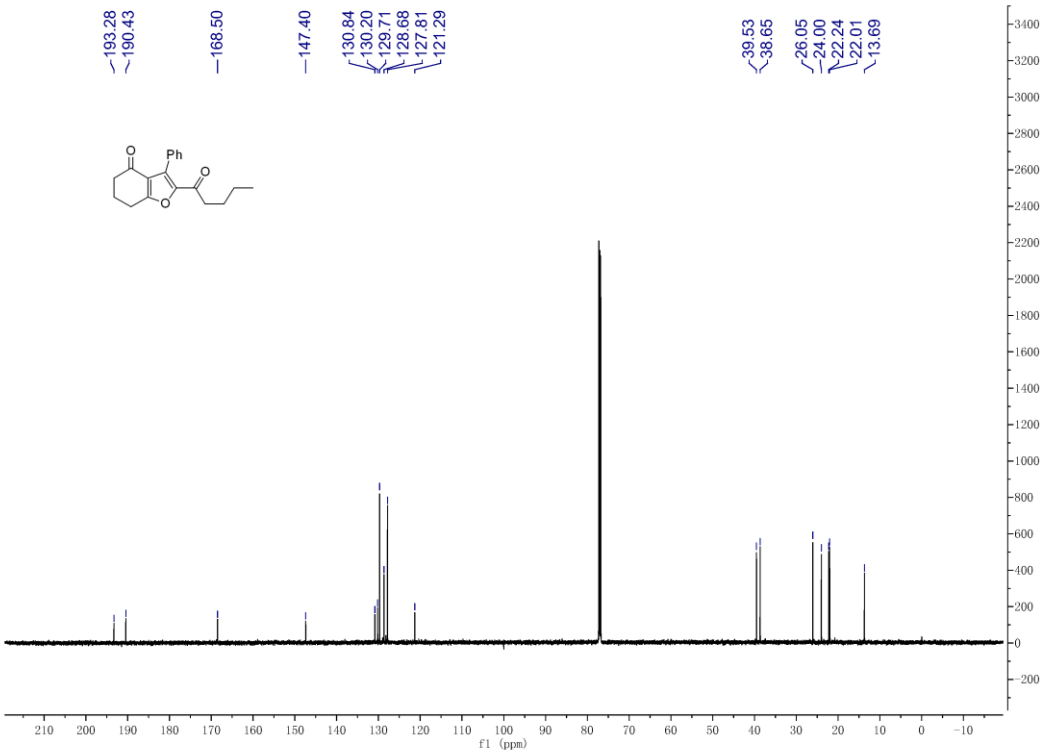
^{1}H NMR spectrum of **6k** (600MHz, $CDCl_3$)



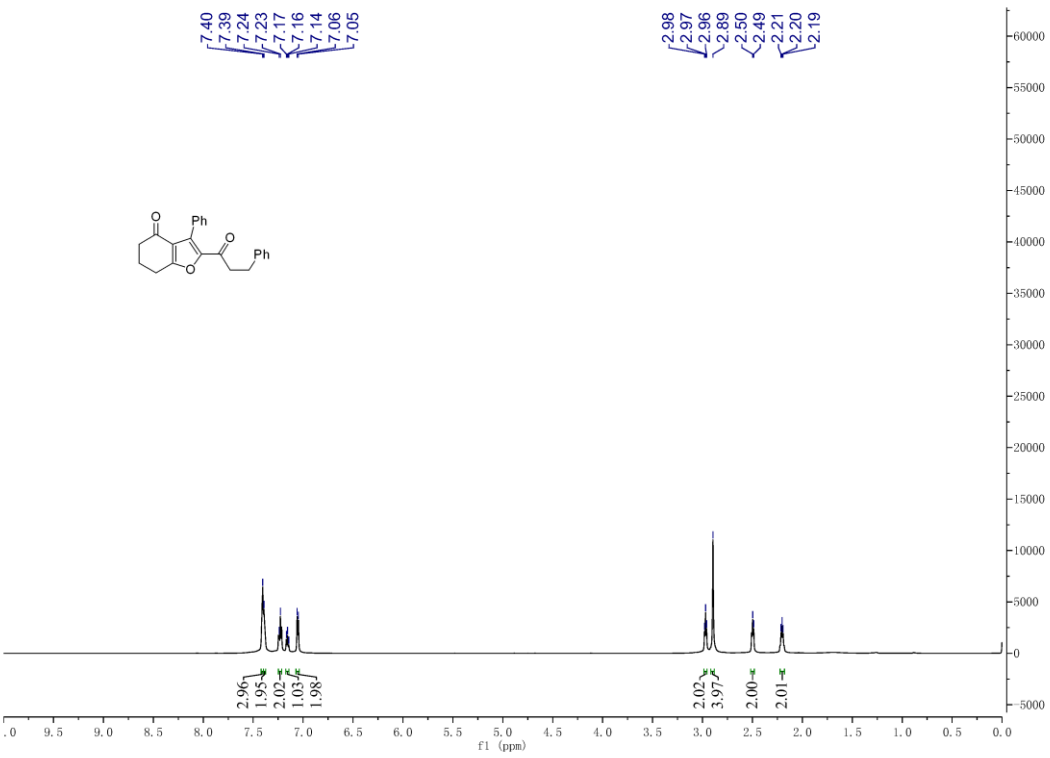
^{13}C NMR spectrum of **6k** (151 MHz, $CDCl_3$)



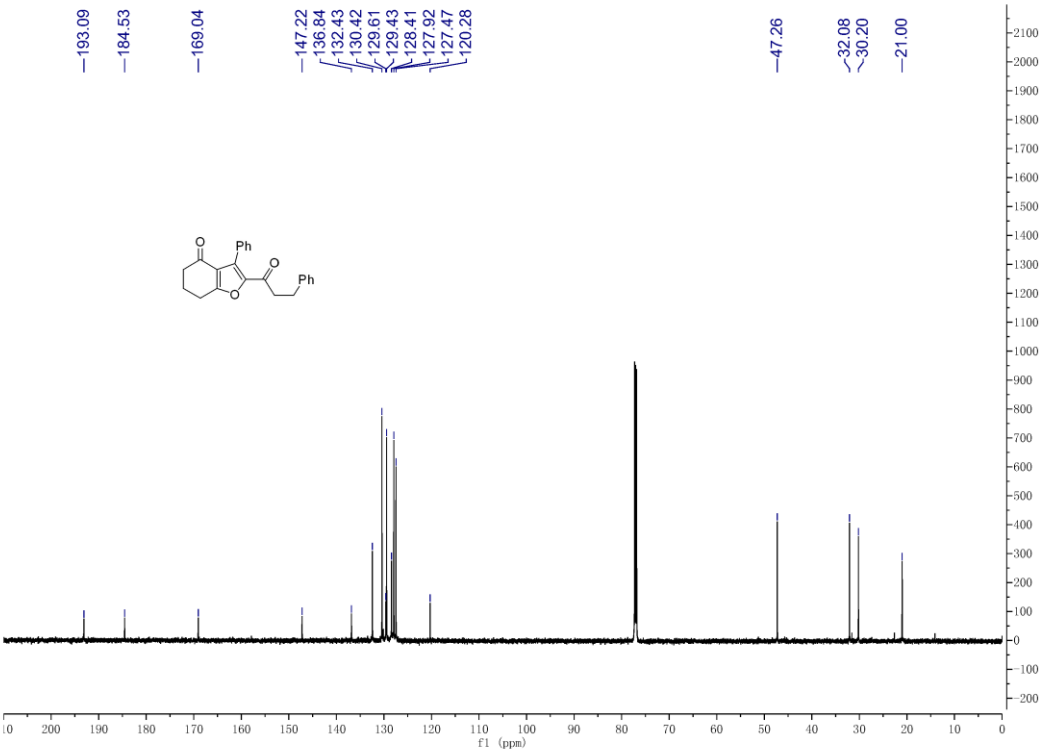
^{1}H NMR spectrum of **6l** (600MHz, $CDCl_3$)



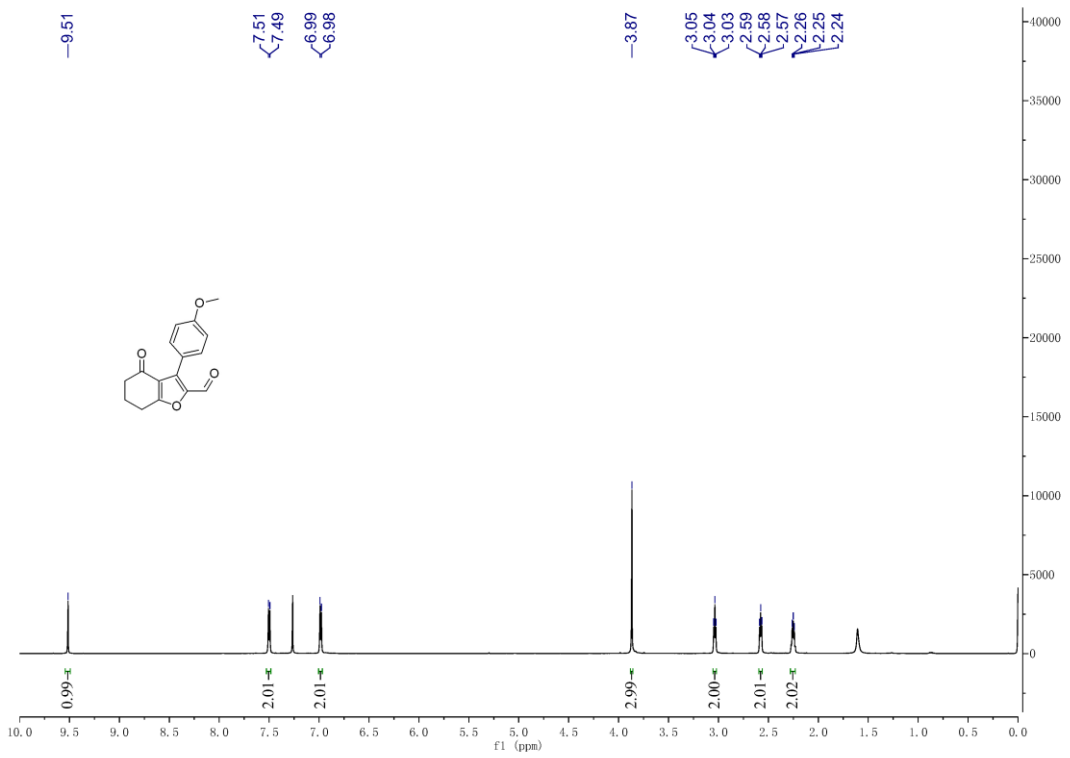
^{13}C NMR spectrum of **6l** (151 MHz, $CDCl_3$)



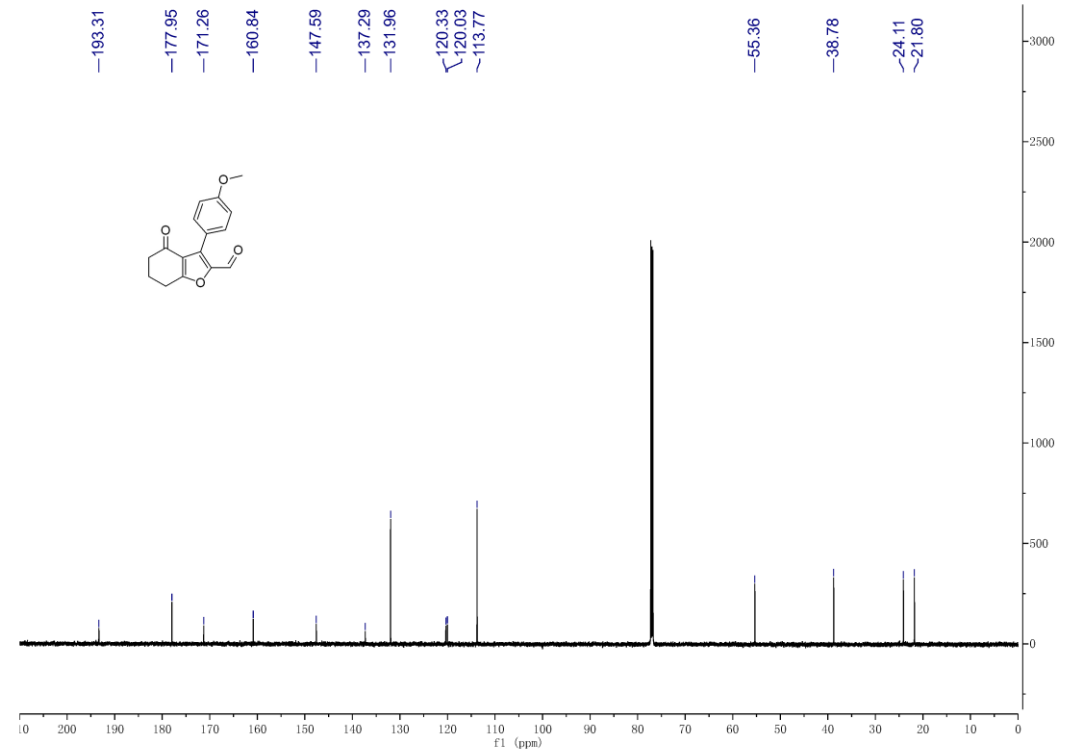
^{1}H NMR spectrum of **6m** (600MHz, $CDCl_3$)



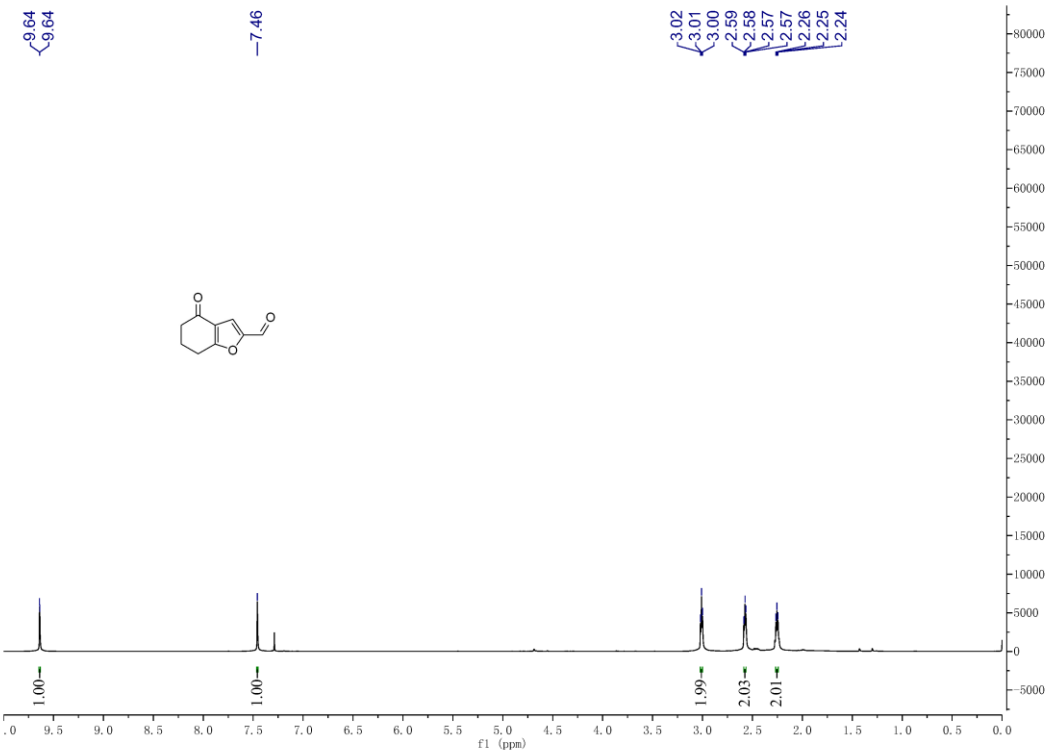
^{13}C NMR spectrum of **6m** (151 MHz, $CDCl_3$)



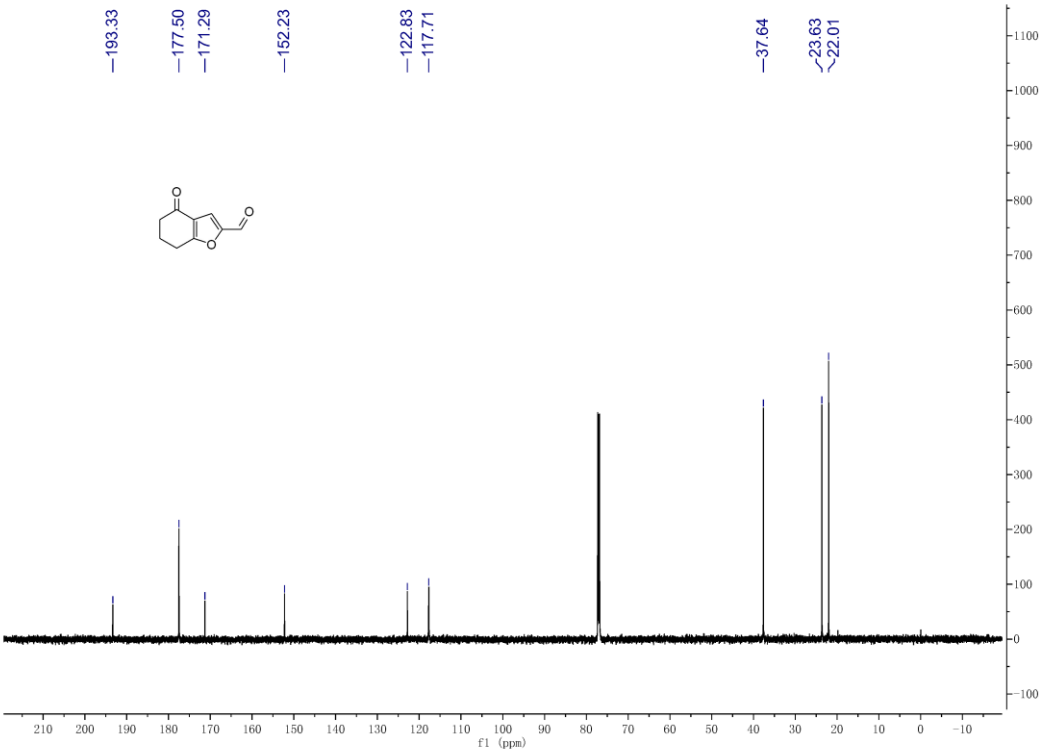
^{1}H NMR spectrum of **6n** (600MHz, $CDCl_3$)



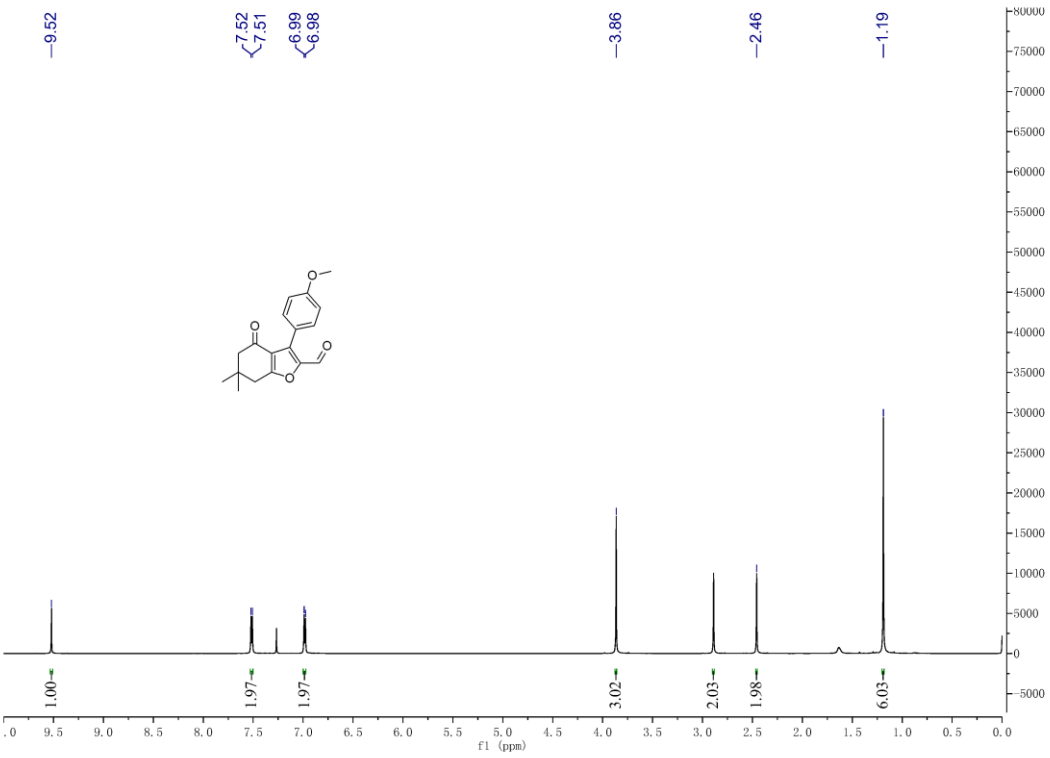
^{13}C NMR spectrum of **6n** (151 MHz, $CDCl_3$)



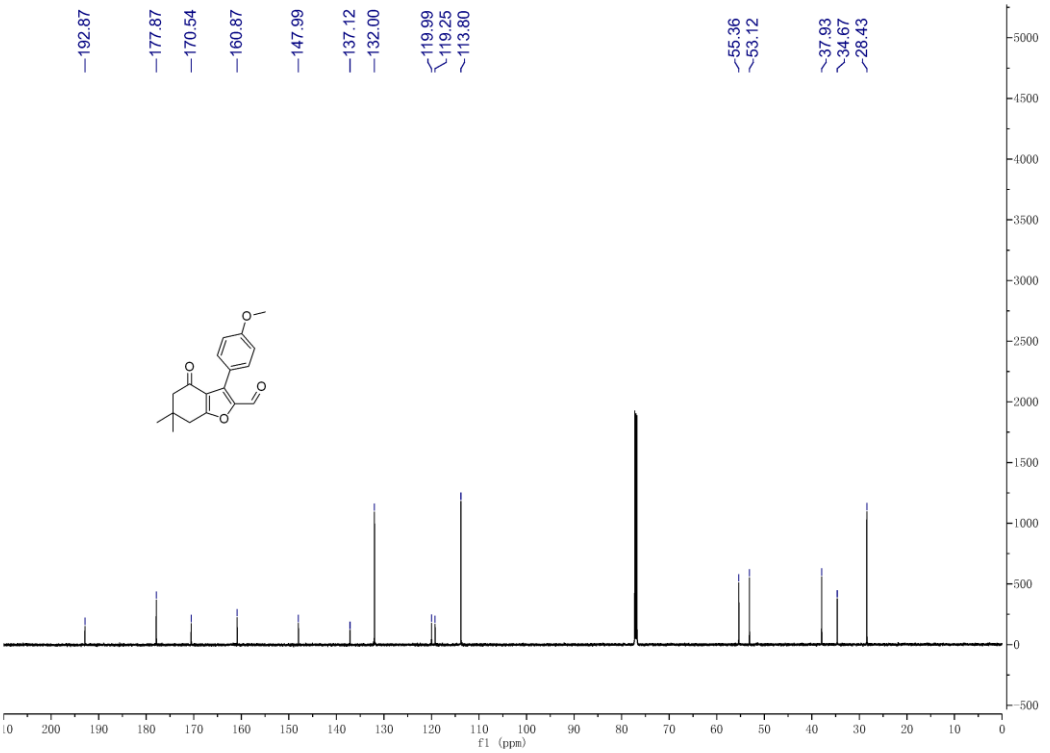
^{1}H NMR spectrum of **6o** (600MHz, $CDCl_3$)



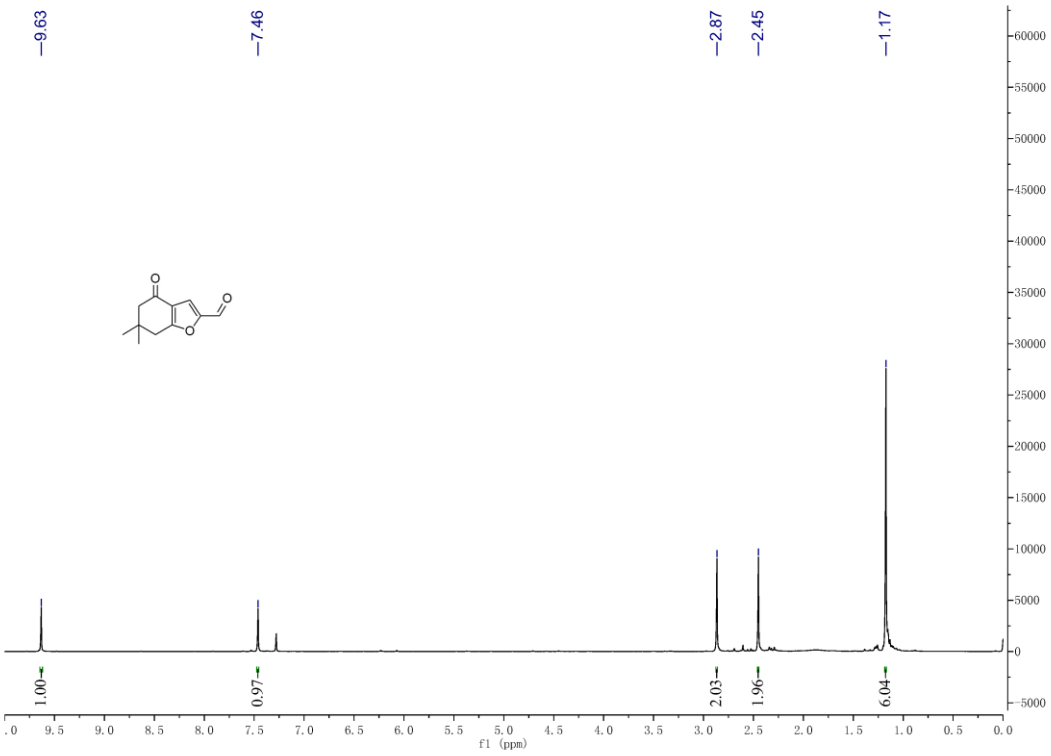
^{13}C NMR spectrum of **6o** (151 MHz, $CDCl_3$)



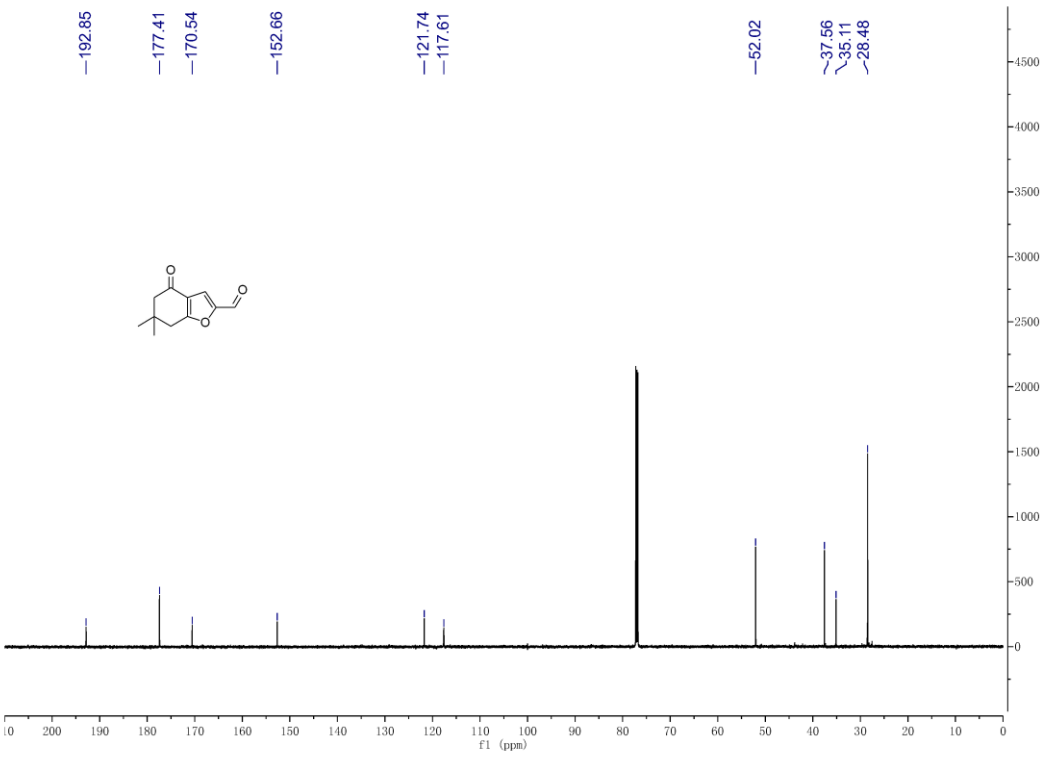
^{1}H NMR spectrum of **6p** (600MHz, $CDCl_3$)



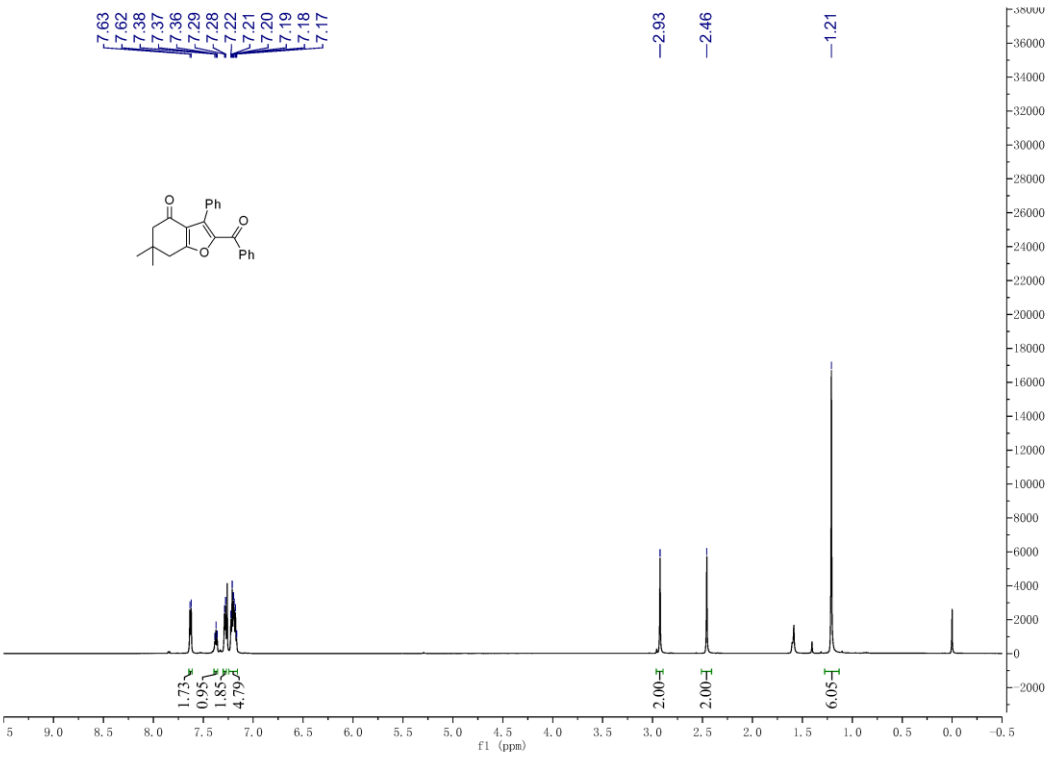
^{13}C NMR spectrum of **6p** (151 MHz, $CDCl_3$)



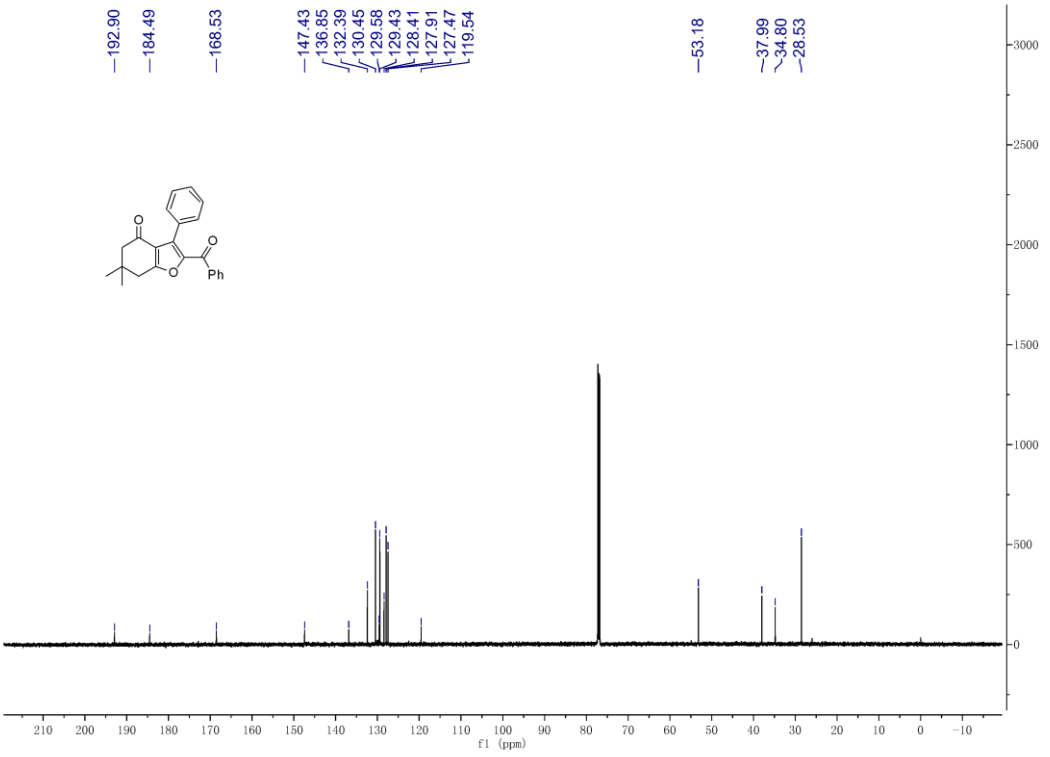
^{1}H NMR spectrum of **6q** (600MHz, $CDCl_3$)



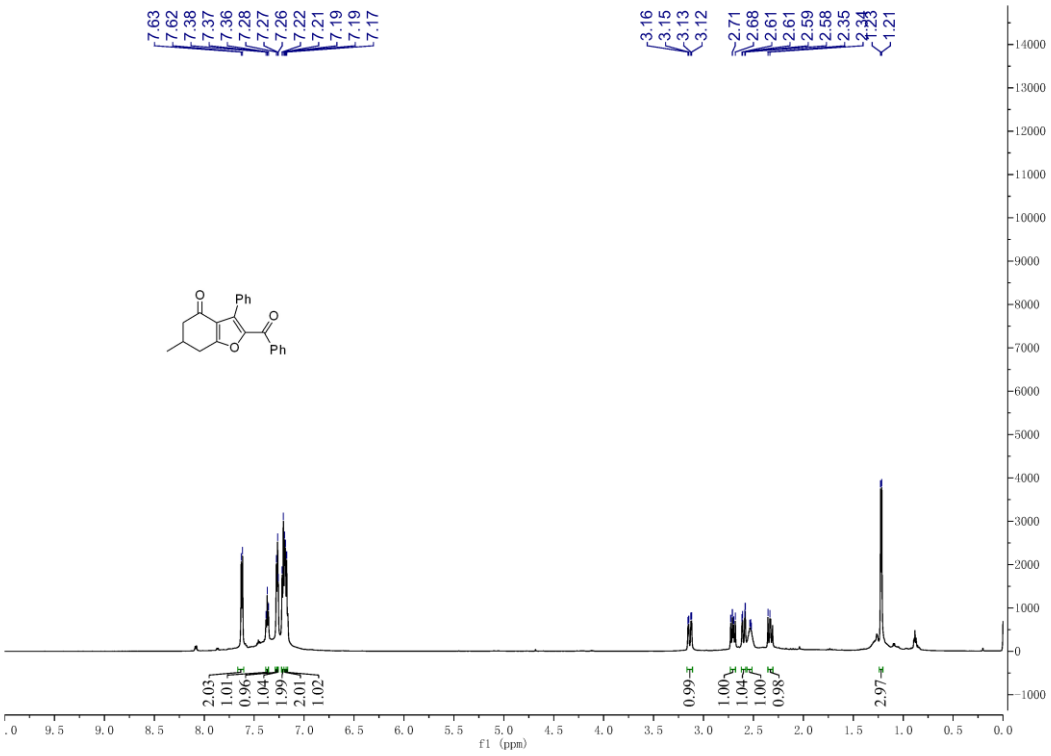
^{13}C NMR spectrum of **6q** (151 MHz, $CDCl_3$)



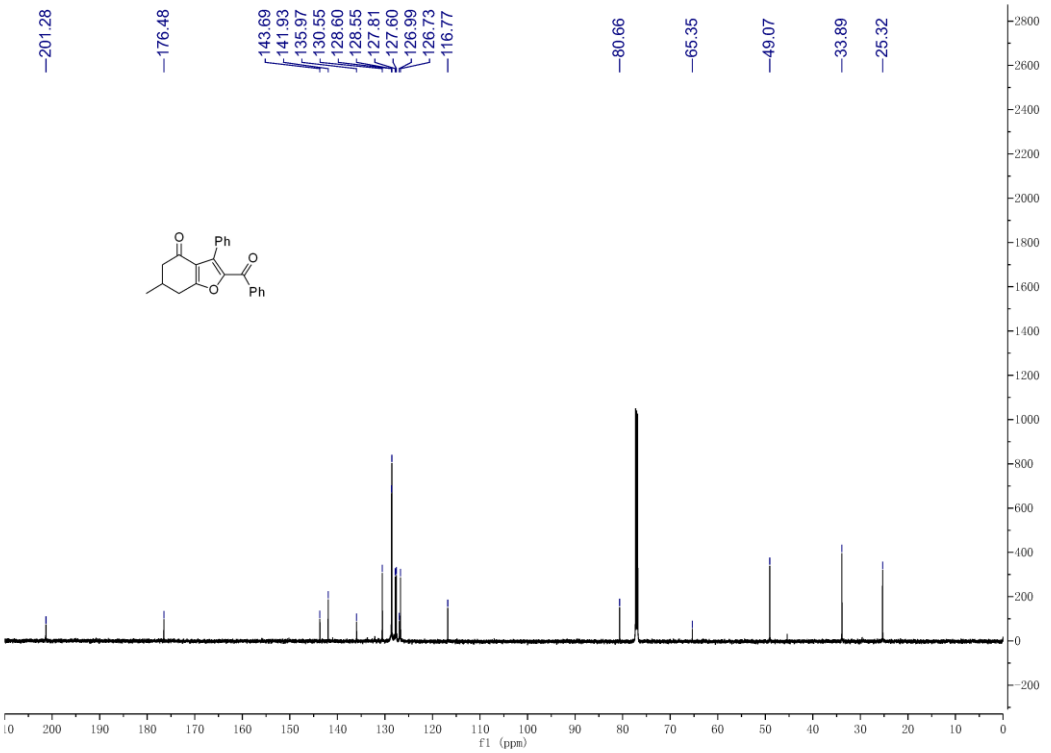
^{1}H NMR spectrum of **6r** (600MHz, $CDCl_3$)



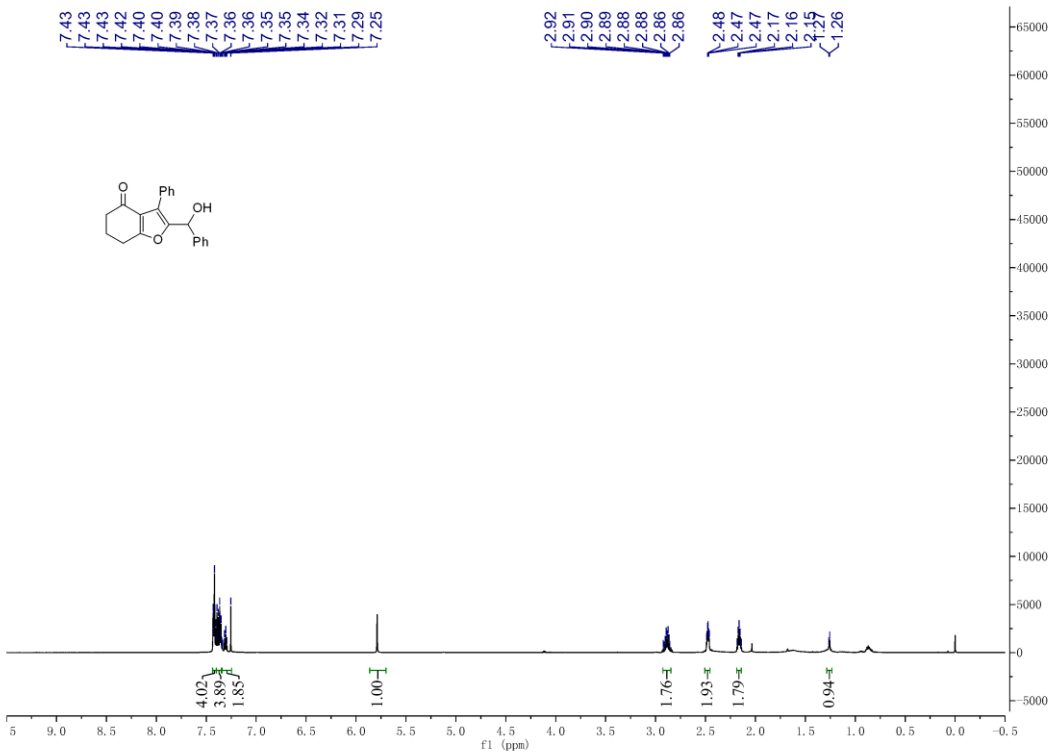
^{13}C NMR spectrum of **6r** (151 MHz, $CDCl_3$)



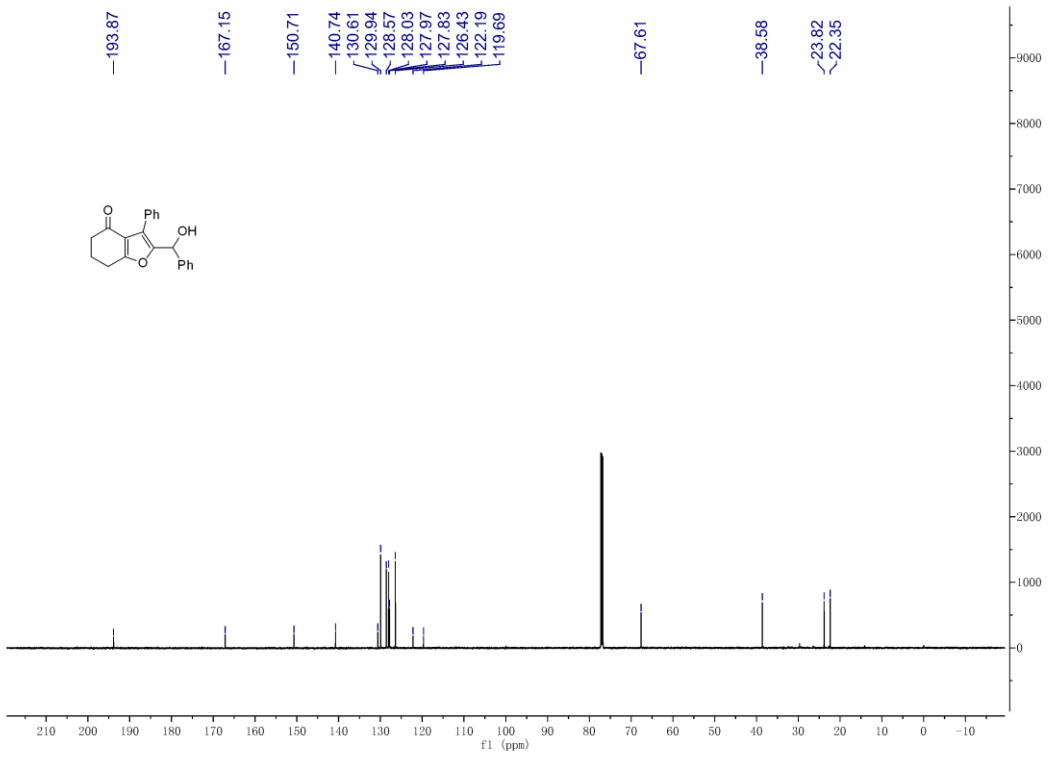
^{1}H NMR spectrum of **6s** (600MHz, $CDCl_3$)



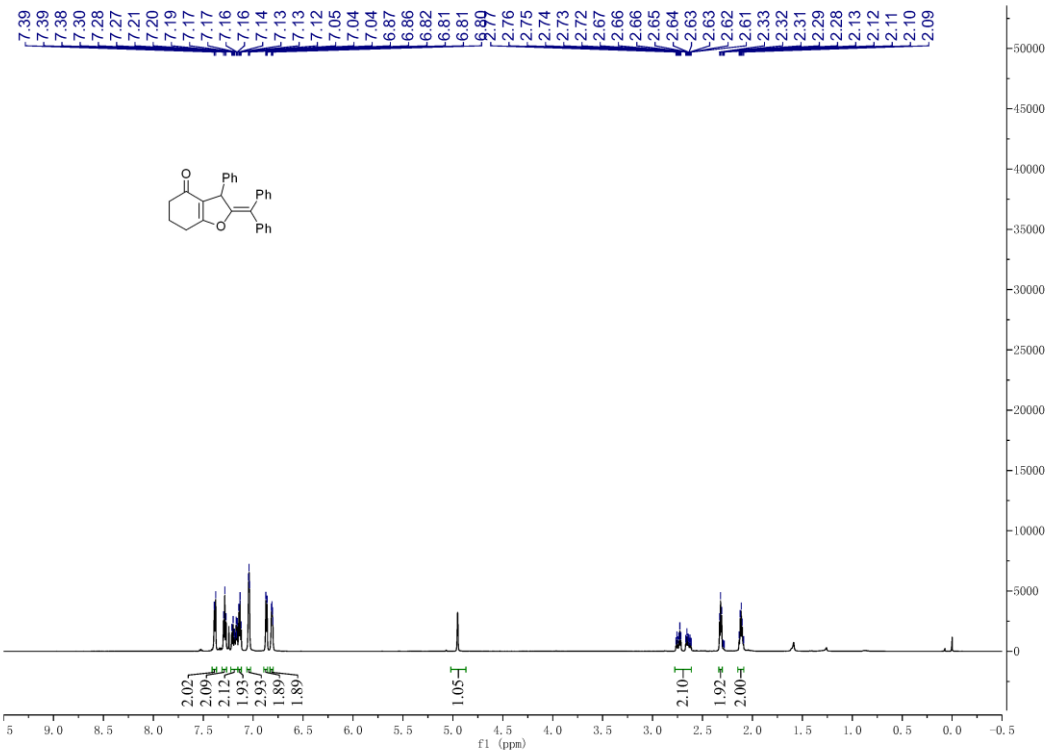
^{13}C NMR spectrum of **6s** (151 MHz, $CDCl_3$)



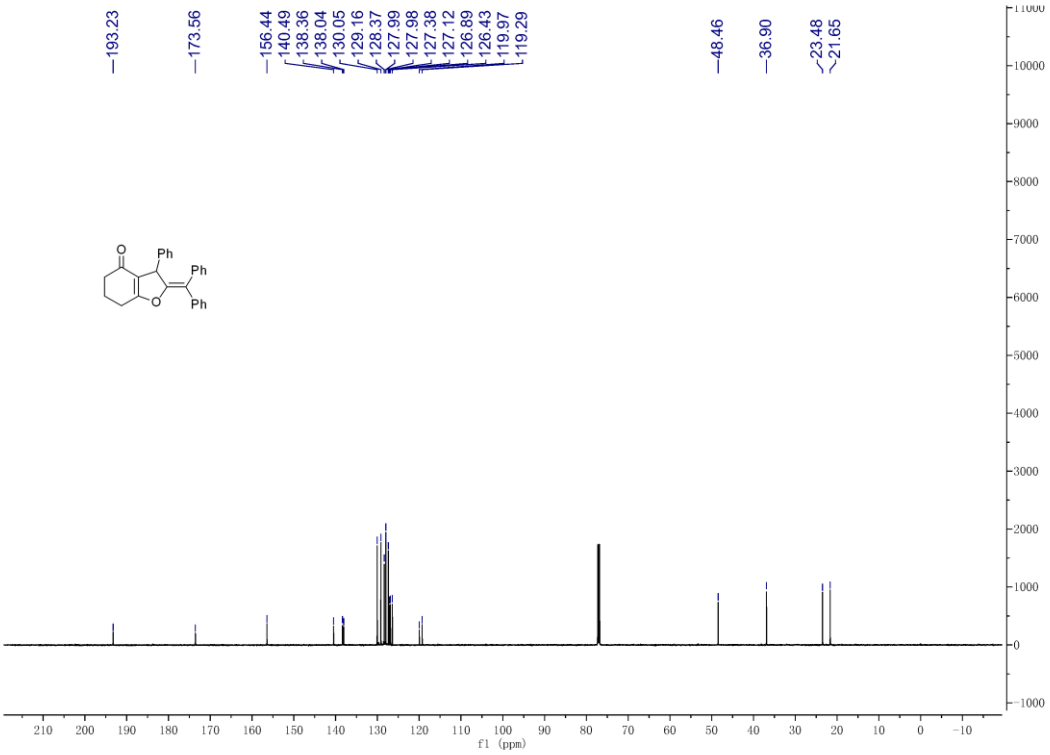
^{1}H NMR spectrum of **7** (600MHz, $CDCl_3$)



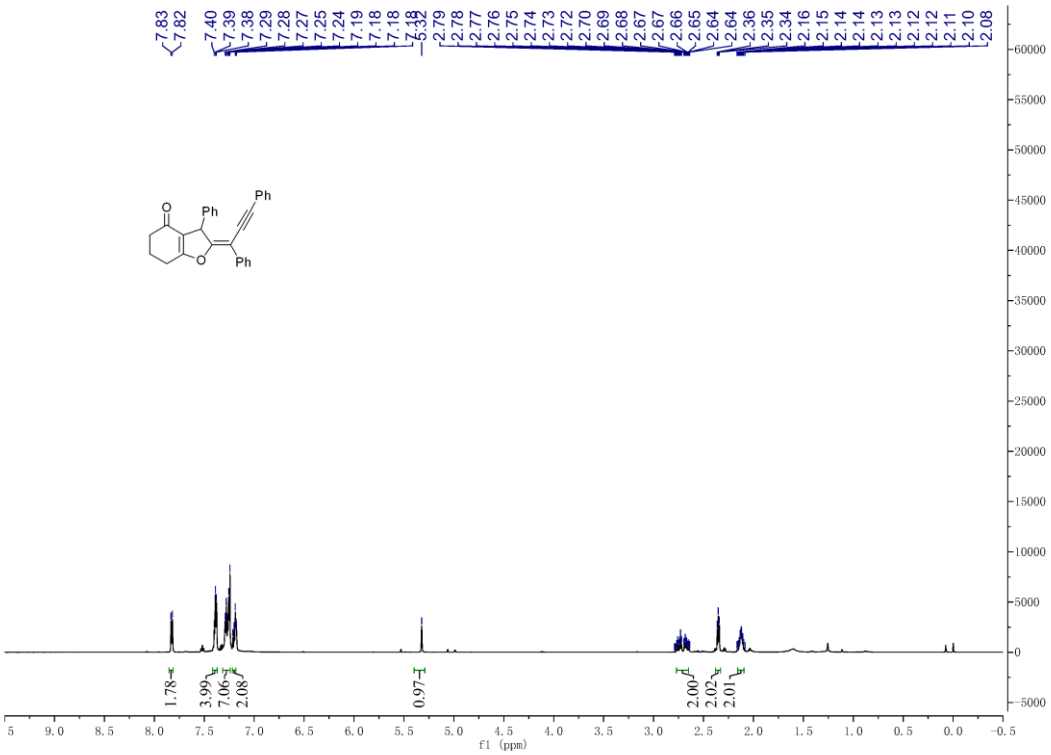
^{13}C NMR spectrum of **7** (151 MHz, $CDCl_3$)



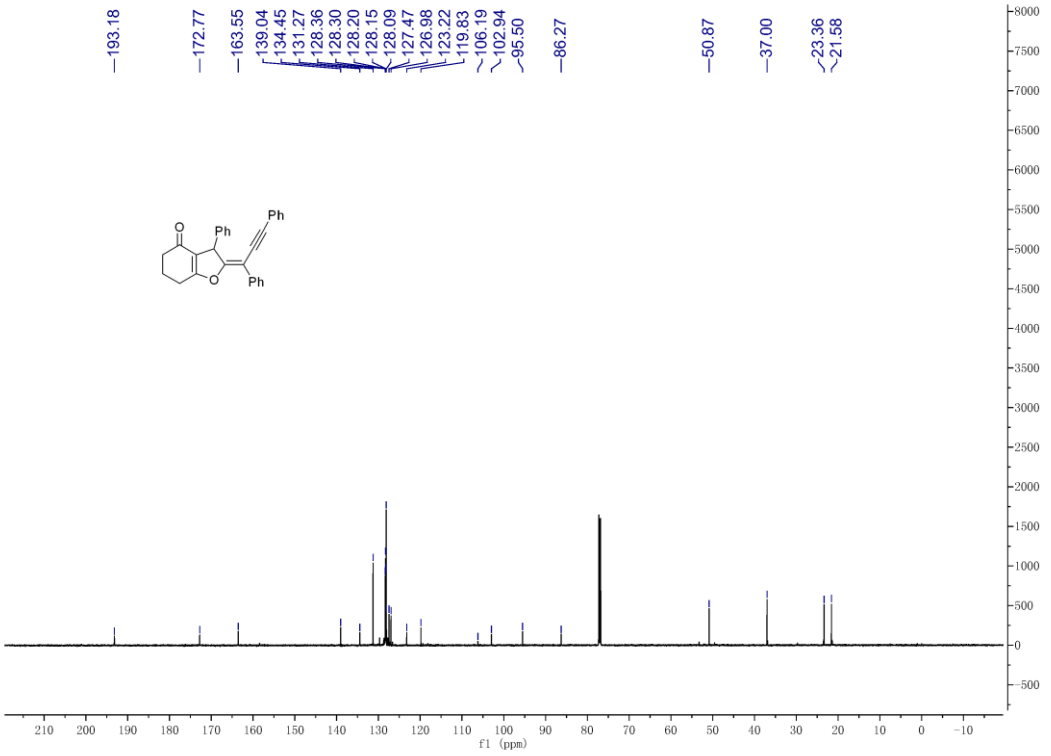
^{1}H NMR spectrum of **8** (600MHz, $CDCl_3$)



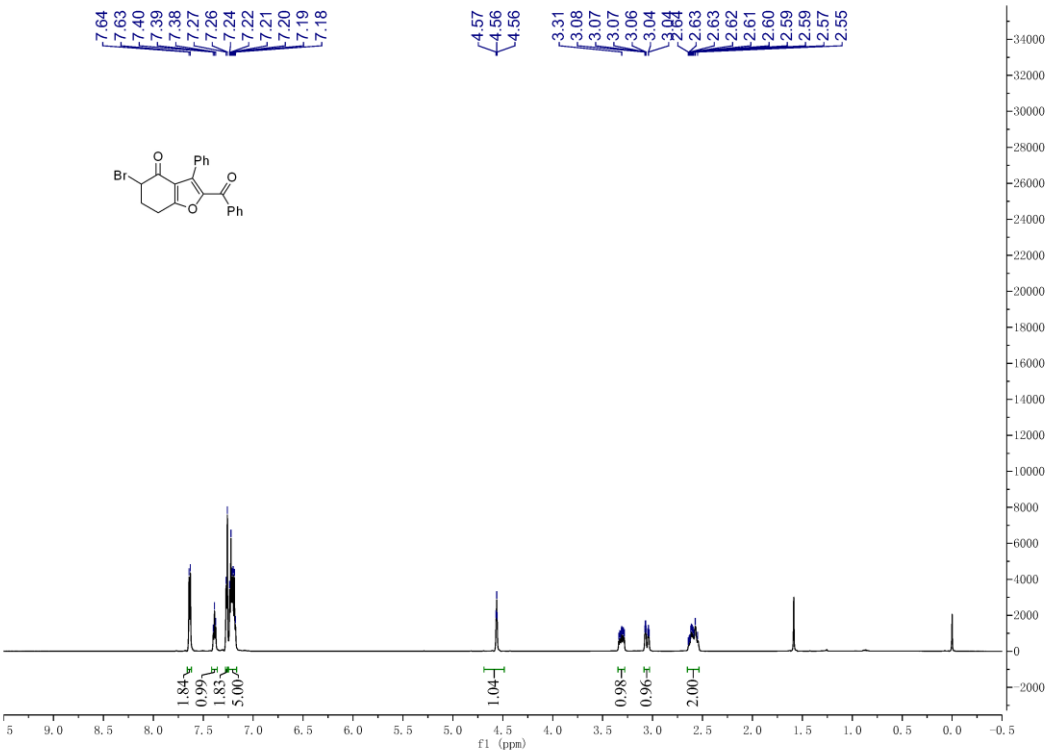
^{13}C NMR spectrum of **8** (151 MHz, $CDCl_3$)



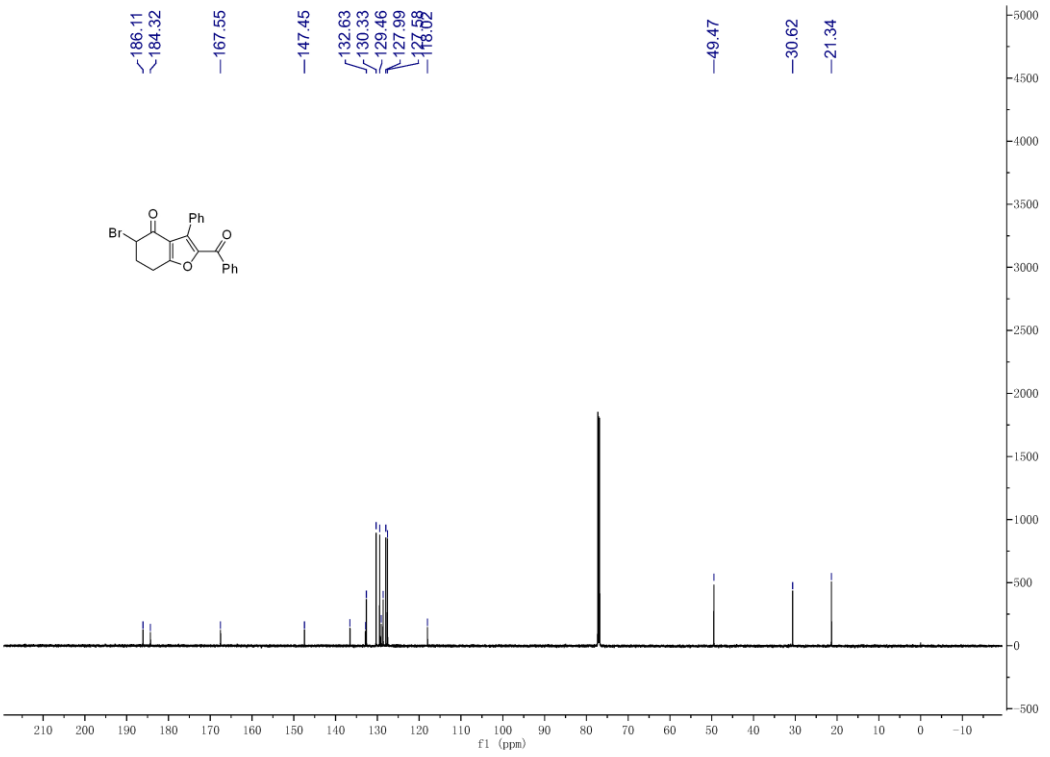
^{1}H NMR spectrum of **8** (600MHz, $CDCl_3$)



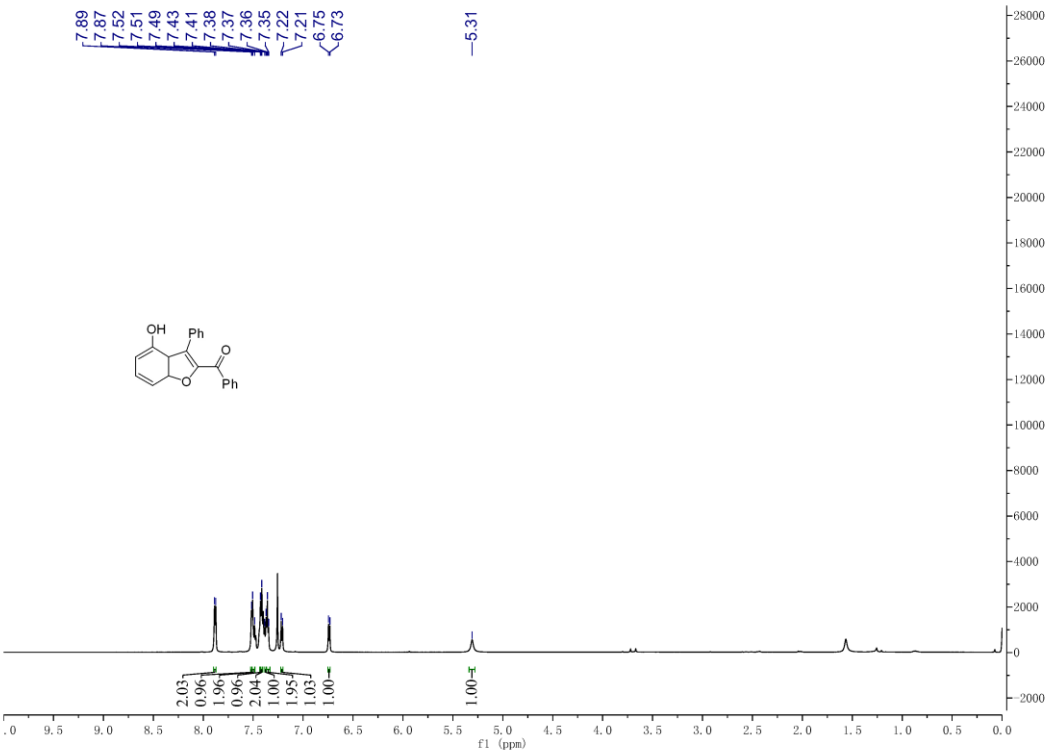
^{13}C NMR spectrum of **9** (151 MHz, $CDCl_3$)



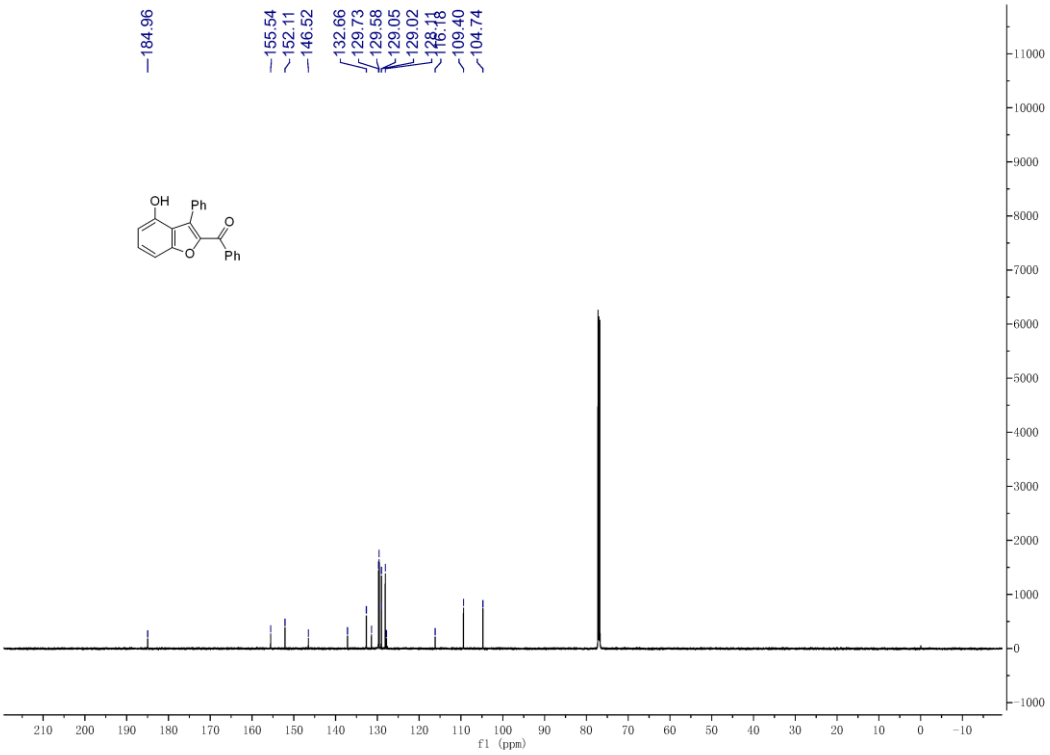
^{1}H NMR spectrum of **10** (600MHz, $CDCl_3$)



^{13}C NMR spectrum of **10** (151 MHz, $CDCl_3$)



^{1}H NMR spectrum of **11** (600MHz, $CDCl_3$)



^{13}C NMR spectrum of **11** (151 MHz, $CDCl_3$)