Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis of Heterocyclic-Fused Benzofurans via C–H Functionalization of Flavones and Coumarins

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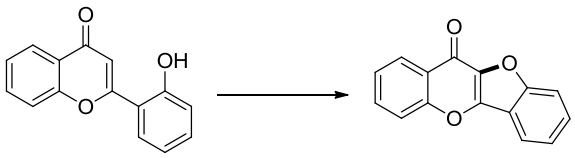
Appendix I

I. General Methods and Materials. Unless stated otherwise, reactions were performed in flame-dried glassware. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F^{254} plates and visualization on TLC was achieved by UV light (254 and 365 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). ^{1}H NMR was recorded on 400 MHz and chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, td = doublet of triplet, ddd = doublet of doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on 100 MHz and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of Chloroform-d. Mass spectral data were obtained from the KAIST Basic Science Institute by using ESI method. Dichloromethane was distilled from calcium hydride. Commercial grade reagents and solvents were used without further purification except as indicated below.

II. Optimization Study

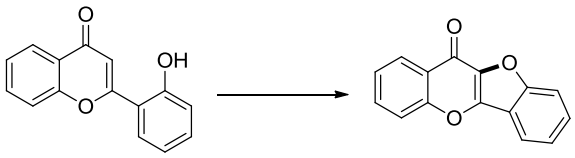
Table S1. Optimization of catalytic Cu system.[a]



Entry	Cu(II) (equiv)	Solvent	Oxidant (equiv)	Additive (equiv)	Yield (%)[b]
1	$Cu(OAc)_2$ (0.3)	DMSO	$PhI(OAc)_2$ (1.5)		-
2	$Cu(OAc)_2$ (0.3)	DMSO	$PhI(OTFA)_2$ (1.5)		-
3	$Cu(OAc)_2$ (0.3)	DMSO	Ag_2CO_3 (1.5)		27
4	$Cu(OAc)_2$ (0.3)	DMSO	$K_2S_2O_8$ (3)		-
5	$Cu(OAc)_2$ (0.3)	DMSO	BQ (1.5)		trace
6	$Cu(OAc)_2$ (0.3)	DMSO	O_2		9
7	$Cu(OAc)_2$ (0.3)	PhMe/DMSO(20:1)	O_2		11
8	$Cu(OAc)_2$ (0.3)	PhMe/DMSO(20:1)	O_2	$Zn(OTf)_2$ (0.2)	65
9	$Cu(OAc)_2$ (0.3)	PhMe/DMSO(20:1)	O_2	$Zn(OTf)_2$ (0.7)	80
10	**$Cu(OAc)_2$ (0.3)**	**PhMe/DMSO(20:1)**	**O_2**	**$Zn(OTf)_2$ (1.0)**	**82**
11	$Cu(OAc)_2$ (0.3)	PhMe/DMSO(20:1)	O_2	$Zn(OTf)_2$ (1.2)	77
12	$Cu(OAc)_2$ (0.3)	PhMe/DMSO(20:1)	O_2	$Zn(OTf)_2$ (2.0)	75

[a] Reactions were conducted at 120 °C for 24 h.

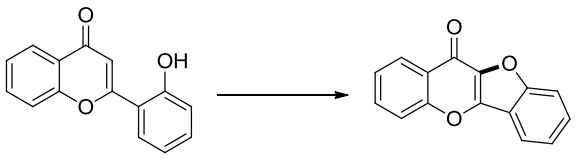
Table S2. Screen of solvents and additives.[a]



Entry	Cu(II) (equiv)	Solvent	Additive (equiv)	Yield (%)[b]
1	$Cu(OAc)_2$ (1.2)	DMF	-	19
2	$Cu(OAc)_2$ (1.2)	DMSO	-	56
3	$Cu(OAc)_2$ (1.2)	PhMe	-	15
4	$Cu(OAc)_2$ (1.2)	DMSO	K_2CO_3 (1.5)	40
5	$Cu(OAc)_2$ (1.2)	DMSO	TEA (1.5)	41
6	$Cu(OAc)_2$ (1.2)	DMSO	pyridine (1.5)	42
7	$Cu(OAc)_2$ (1.2)	DMSO	TFA (2)	-
8	$Cu(OAc)_2$ (1.2)	DMSO	AcOH (2)	34
9	$Cu(OAc)_2$ (1.2)	DMSO	PivOH (2)	9
10	$Cu(OAc)_2$ (1.2)	DMF/DMSO(20:1)	-	54
11	$Cu(OAc)_2$ (1.2)	PhMe/DMSO(20:1)	-	71
12	$Cu(OAc)_2$ (1.2)	Dioxane/DMSO(20:1)	-	34
13	$Cu(OAc)_2$ (1.2)	DME/DMSO(20:1)	-	trace
14	$Cu(OAc)_2$ (1.2)	DCE/DMSO(20:1)	-	24
15	$Cu(OAc)_2$ (1.2)	MeCN/DMSO(20:1)	-	26
16	$Cu(OAc)_2$ (1.2)	Xylene/DMSO(20:1)	-	38
17	$Cu(OTf)_2$ (1.2)	PhMe/DMSO(20:1)	-	-
18	$Cu(OPiv)_2$ (1.2)	PhMe/DMSO(20:1)	-	31
19	$Cu(TFA)_2$ (1.2)	PhMe/DMSO(20:1)	-	22
20	$Cu(OMe)_2$ (1.2)	PhMe/DMSO(20:1)	-	59
21	**$Cu(OAc)_2$ (1.2)**	PhMe/DMSO(20:1)	**$Zn(OTf)_2$ (0.2)**	**87**

[a] Reactions were conducted at 120 °C for 24 h.

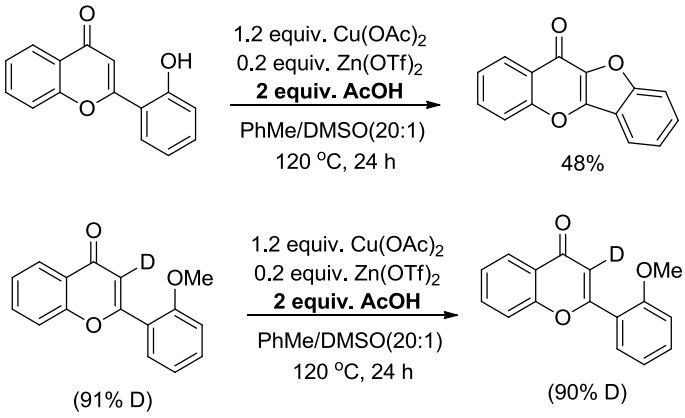
Table S3. Screen of Lewis acids.[a]



Entry	Cu(II) (equiv)	Solvent	Additive (equiv)	Yield (%)[b]
1	$Cu(OAc)_2$ (1.2)	PhMe/DMSO(20:1)	$Zn(OAc)_2$ (0.2)	35
2	**$Cu(OAc)_2$ (1.2)**	**PhMe/DMSO(20:1)**	**$Zn(OTf)_2$ (0.2)**	**87**
3	$Cu(OAc)_2$ (1.2)	PhMe/DMSO(20:1)	$ZnBr_2$ (0.2)	77
4	$Cu(OAc)_2$ (1.2)	PhMe/DMSO(20:1)	ZnI_2 (0.2)	38
5	$Cu(OAc)_2$ (1.2)	PhMe/DMSO(20:1)	LiOTf (0.2)	63
6	$Cu(OAc)_2$ (1.2)	PhMe/DMSO(20:1)	KOTf (0.2)	75
7	$Cu(OAc)_2$ (1.2)	PhMe/DMSO(20:1)	AgOTf (0.2)	71
8	$Cu(OAc)_2$ (1.2)	PhMe/DMSO(20:1)	$Bi(OTf)_3$ (0.2)	26
9	$Cu(OAc)_2$ (1.2)	PhMe/DMSO(20:1)	$In(OTf)_3$ (0.2)	81
10	$Cu(OAc)_2$ (1.2)	PhMe/DMSO(20:1)	$Sm(OTf)_3$ (0.2)	69
11	$Cu(OAc)_2$ (1.2)	PhMe/DMSO(20:1)	$Yb(OTf)_3$ (0.2)	48
12	$Cu(OAc)_2$ (1.2)	PhMe/DMSO(20:1)	$Sn(OTf)_2$ (0.2)	67

[a] Reactions were conducted at 120 °C for 24 h.

The exposure of C3-deuteriated 2-methoxyphenyl chromone to the catalytic conditions did not induce H/D scrambling, indicating that the important role of the phenolic OH directing group coordination during the C-H functionalization.



Scheme 1S. H/D exchange experiments.

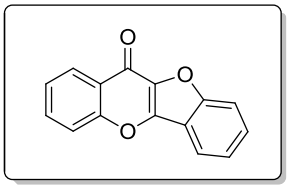
III. Experimental Procedure

General procedure (GPI) for intramolecular C-O coupling reaction:

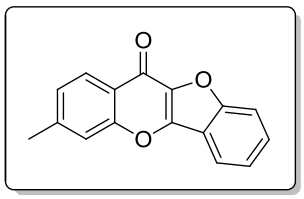
2-(2-hydroxyphenyl)flavone (0.063 mmol), $Cu(OAc)_2$ (1.2 eq) and $Zn(OTf)_2$ (0.2 eq) were combined in PhMe/DMSO(20:1) mixture (0.84 mL) in a cap test tube. The reaction mixture was heated to 120 °C. The reaction

was stirred for 12-24 hours. The mixture was monitored by TLC using EtOAc and *n*-hexane = 1 : 1 as the mobile phase and stirred until starting material disappeared. After cooled to RT, the mixture solvent was removed under reduced pressure. The reaction mixture was diluted with CH_2Cl_2 and the residue was extracted with aqueous NH_4Cl (3 × 30 ml). The organic layer was dried over $MgSO_4$. After removal of solvent, the residue was purified by flash chromatography on silica gel to give desired product.

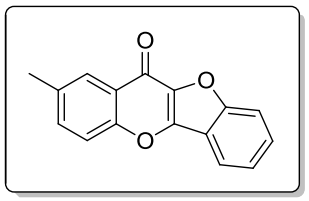
IV. Compound Characterizations :



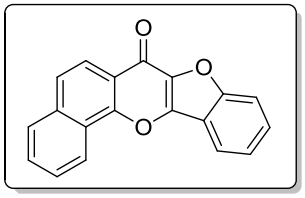
11H-benzofuro[3,2-b]chromen-11-one (2a). Yield 87 % (13.0 mg). mp 187–189 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.44 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.95 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.76 – 7.57 (m, 4H), 7.49 – 7.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 155.8, 155.0, 149.0, 137.3, 133.4, 130.5, 126.5, 125.1, 124.8, 124.2, 120.5, 118.3, 118.0, 113.4. HRMS (ESI^+) m/z calcd. for $C_{15}H_8NaO_3^+$ $[M+Na]^+$: 259.0366, found: 259.0368.



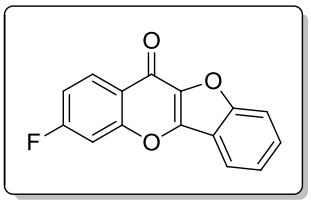
3-methyl-11H-benzofuro[3,2-b]chromen-11-one (2b). Yield 84% (13.4 mg). mp 203–205 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.32 (d, *J* = 8.2 Hz, 1H), 7.94 (ddd, *J* = 7.9, 1.3, 0.8 Hz, 1H), 7.66 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.60 (ddd, *J* = 8.5, 7.0, 1.3 Hz, 1H), 7.46 (s, 1H), 7.42 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.29 – 7.25 (m, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 156.0, 155.0, 148.8, 144.8, 137.3, 130.2, 126.4, 126.2, 124.1, 122.8, 120.5, 118.1, 118.1, 113.4, 21.8. HRMS (ESI^+) m/z calcd. for $C_{16}H_{10}NaO_3^+$ $[M+Na]^+$: 273.0522, found: 273.0503.



2-methyl-11H-benzofuro[3,2-b]chromen-11-one (2c). Yield 96% (15.2 mg). mp 222–224 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.23 (d, *J* = 0.7 Hz, 1H), 7.95 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.65 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.63 – 7.50 (m, 3H), 7.42 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 155.0, 154.1, 149.0, 137.3, 134.9, 134.6, 130.3, 125.9, 124.8, 124.1, 120.5, 118.1, 118.0, 113.4, 20.9. HRMS (ESI^+) m/z calcd. for $C_{16}H_{10}NaO_3^+$ $[M+Na]^+$: 273.0522, found: 273.0514.

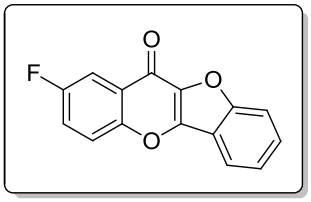


7H-benzo[h]benzofuro[3,2-b]chromen-7-one (2d). Yield 85% (15.3 mg). mp 225–227 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.70 – 8.63 (m, 1H), 8.35 (d, *J* = 8.7 Hz, 1H), 8.05 (ddd, *J* = 7.9, 1.4, 0.7 Hz, 1H), 7.94 – 7.89 (m, 1H), 7.79 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.73 – 7.66 (m, 3H), 7.62 (ddd, *J* = 8.5, 7.1, 1.3 Hz, 1H), 7.47 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 154.9, 153.0, 148.2, 138.2, 135.7, 130.2, 129.3, 128.1, 127.3, 125.1, 124.2, 124.1, 122.3, 121.4, 121.2, 120.3, 118.0, 113.5. HRMS (ESI^+) m/z calcd. for $C_{19}H_{10}NaO_3^+$ $[M+Na]^+$: 309.0522, found: 309.0511.

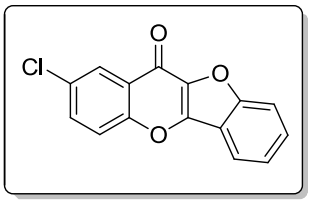


3-fluoro-11H-benzofuro[3,2-b]chromen-11-one (2e). Yield 78% (12.4 mg). mp 224–226 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.47 (dd, *J* = 8.9, 6.3 Hz, 1H), 7.96 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.68 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.63 (ddd, *J* = 8.5, 7.0, 1.3 Hz, 1H), 7.46 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.37 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.24 – 7.19 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 166.5, 165.4 (d, J_{CF} = 255.1 Hz), 156.8 (d, J_{CF} = 13.1

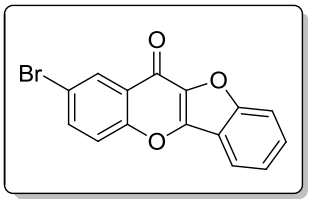
Hz), 155.0 , 149.3 (d, J_{CF} = 1.6 Hz), 137.2 , 130.6 , 128.9 (d, J_{CF} = 10.6 Hz), 124.3 , 122.0 (d, J_{CF} = 2.5 Hz), 120.5 , 117.8 , 113.7 (d, J_{CF} = 22.7 Hz), 113.5 , 105.2 (d, J_{CF} = 25.7 Hz). HRMS (ESI^+) m/z calcd. for $C_{15}H_7FNaO_3^+$ $[M+Na]^+$: 277.0271, found: 277.0266.



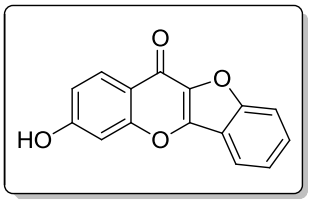
2-fluoro-11H-benzofuro[3,2-b]chromen-11-one (2f). Yield 72% (11.4 mg). mp 217–219 °C. white solid. ^1H NMR (400 MHz, Chloroform-d) δ 8.09 (dd, *J* = 8.4, 3.1 Hz, 1H), 7.97 (ddd, *J* = 7.9, 1.3, 0.8 Hz, 1H), 7.71 – 7.61 (m, 3H), 7.49 – 7.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3 (d, J_{CF} = 2.3 Hz), 159.4 (d, J_{CF} = 246.9 Hz), 155.2 , 151.9 (d, J_{CF} = 1.8 Hz), 149.4 , 136.8 , 130.8 , 126.5 (d, J_{CF} = 7.5 Hz), 124.3 , 121.5 (d, J_{CF} = 25.4 Hz), 120.6 , 120.2 (d, J_{CF} = 8.1 Hz), 117.8 , 113.5 , 111.6 (d, J_{CF} = 24.4 Hz). HRMS (ESI^+) m/z calcd. for $C_{15}H_7FNaO_3^+$ $[M+Na]^+$: 277.0271, found: 277.0273.



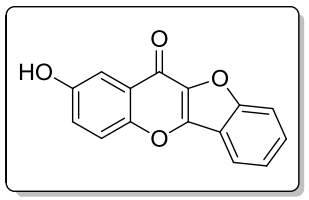
2-chloro-11H-benzofuro[3,2-b]chromen-11-one (2g). Yield 71% (12.0 mg). mp 273–275 °C. white solid. ^1H NMR (400 MHz, Chloroform-d) δ 8.43 (dd, *J* = 2.4, 0.6 Hz, 1H), 7.97 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.70 – 7.61 (m, 4H), 7.46 (ddd, *J* = 8.0, 6.8, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 155.2, 154.1, 149.4, 137.1, 133.6, 131.0, 130.8, 126.3, 126.0, 124.4, 120.6, 119.9, 117.8, 113.5. HRMS (ESI^+) m/z calcd. for $C_{15}H_7ClNaO_3^+$ $[M+Na]^+$: 292.9976, found: 292.9952.



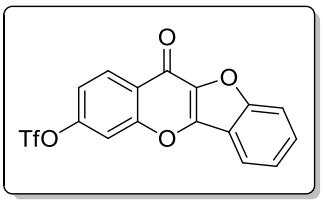
2-bromo-11H-benzofuro[3,2-b]chromen-11-one (2h). Yield 45% (9.0 mg). mp 271–273 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.59 (d, *J* = 2.5 Hz, 1H), 7.97 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.82 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.46 (ddd, *J* = 8.0, 6.7, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 155.3, 154.6, 149.4, 137.1, 136.4, 130.9, 129.2, 126.6, 124.4, 120.6, 120.2, 118.5, 117.8, 113.5. HRMS (ESI^+) m/z calcd. for $C_{15}H_7BrNaO_3^+$ $[M+Na]^+$: 336.9471, found: 336.9444.



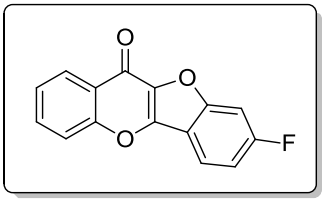
3-hydroxy-11H-benzofuro[3,2-b]chromen-11-one (2i). Yield 63% (10.0 mg). mp 315–317 °C. orange solid. ^{1}H NMR (400 MHz, Dimethyl sulfoxide-d_6) δ 10.99 (s, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 8.09 (ddd, *J* = 7.9, 1.3, 0.7 Hz, 1H), 7.87 (dt, *J* = 8.5, 0.8 Hz, 1H), 7.73 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.54 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H), 7.11 (d, *J* = 2.2 Hz, 1H), 7.02 (dd, *J* = 8.8, 2.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.9, 162.8, 157.3, 154.0, 147.9, 136.6, 130.4, 127.3, 124.5, 120.5, 117.6, 117.1, 114.8, 113.3, 102.9. HRMS (ESI^+) m/z calcd. for $C_{15}H_8NaO_4^+$ $[M+Na]^+$: 275.0315, found: 275.0287.



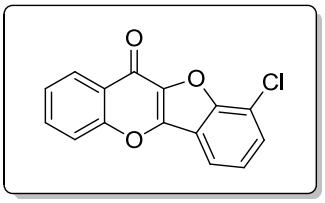
2-hydroxy-11H-benzofuro[3,2-b]chromen-11-one (2j). Yield 72% (11.5 mg). mp 296-298 °C. white solid. ^{1}H NMR (400 MHz, Dimethyl sulfoxide-d_6) δ 10.12 (s, 1H), 8.04 (ddd, *J* = 7.9, 1.4, 0.7 Hz, 1H), 7.84 (dt, *J* = 8.5, 0.8 Hz, 1H), 7.75 – 7.68 (m, 2H), 7.56 – 7.47 (m, 2H), 7.29 (dd, *J* = 9.0, 3.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 154.7, 154.2, 148.9, 148.4, 136.3, 130.8, 125.5, 124.5, 122.8, 120.6, 119.8, 117.5, 113.3, 108.4. HRMS (ESI^+) m/z calcd. for $C_{15}H_8NaO_4^+$ $[M+Na]^+$: 275.0315, found: 275.0287.



11-oxo-11H-benzofuro[3,2-b]chromen-3-yl trifluoromethanesulfonate (2k). Yield 82% (19.5 mg). mp 161-163 ^{o}C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.57 (d, *J* = 8.9 Hz, 1H), 7.97 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.73 – 7.62 (m, 3H), 7.48 (ddd, *J* = 8.0, 6.6, 1.5 Hz, 1H), 7.40 (dd, *J* = 8.9, 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 155.9, 155.3, 151.9, 149.7, 137.2, 131.1, 129.1, 125.1, 124.6, 123.5, 120.6, 120.3, 118.3, 117.6, 117.1, 113.9, 113.6, 111.8. HRMS (ESI^{+}) m/z calcd. for $C_{16}H_7F_3NaO_6S^{+}$ $[M+Na]^{+}$: 406.9808, found: 406.9822.

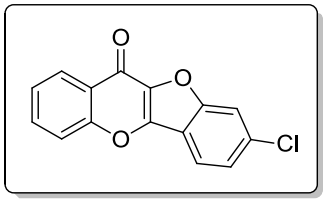


8-fluoro-11H-benzofuro[3,2-b]chromen-11-one (2l). Yield 69% (10.9 mg). mp 226–228 ^{o}C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.45 (ddd, *J* = 8.0, 1.7, 0.5 Hz, 1H), 7.94 (ddd, *J* = 8.7, 5.3, 0.5 Hz, 1H), 7.75 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.67 (ddd, *J* = 8.5, 1.3, 0.5 Hz, 1H), 7.49 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.37 (ddd, *J* = 8.6, 2.2, 0.5 Hz, 1H), 7.25 – 7.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8 , 164.3 (d, J_{CF} = 251.4 Hz), 155.8 , 155.6 (d, J_{CF} = 13.9 Hz), 148.7 , 138.1 (d, J_{CF} = 3.3 Hz), 133.5 , 126.6 , 125.0 , 121.7 (d, J_{CF} = 10.7 Hz), 118.2 , 114.6 (d, J_{CF} = 1.8 Hz), 113.5 (d, J_{CF} = 25.0 Hz), 101.1 (d, J_{CF} = 26.9 Hz). HRMS (ESI^{+}) m/z calcd. for $C_{15}H_7FNaO_3^{+}$ $[M+Na]^{+}$: 277.0271, found: 277.0241.

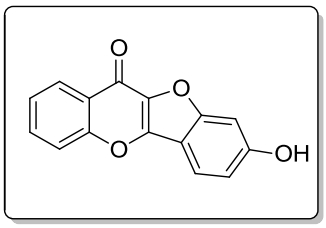


9-chloro-11H-benzofuro[3,2-b]chromen-11-one (2m). Yield 77% (13.0 mg). mp 264–266 ^{o}C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.47 (ddd, *J* = 8.0, 1.7, 0.5 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.76 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.68 (dd, *J* = 8.5, 0.8 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.49 (ddd, *J* = 8.1, 7.0, 1.2 Hz,

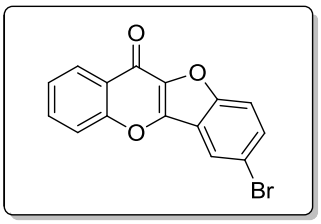
1H), 7.39 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 155.8, 150.8, 148.7, 137.8, 133.7, 130.3, 126.7, 125.2, 125.1, 125.0, 119.8, 119.2, 119.0, 118.3. HRMS (ESI$^+$) m/z calcd. for $C_{15}H_7ClNaO_3^+$ $[M+Na]^+$: 292.9976, found: 292.9957.



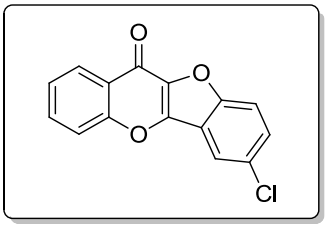
8-chloro-11H-benzofuro[3,2-b]chromen-11-one (2n). Yield 65% (11.0 mg). mp 211–213 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.46 (ddd, *J* = 8.0, 1.7, 0.5 Hz, 1H), 7.90 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.76 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.49 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.44 (dd, *J* = 8.5, 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 155.8, 155.0, 148.5, 137.8, 136.6, 133.6, 126.6, 125.3, 125.1, 125.1, 121.2, 118.3, 116.8, 114.0. HRMS (ESI$^+$) m/z calcd. for $C_{15}H_7ClNaO_3^+$ $[M+Na]^+$: 292.9976, found: 292.9950.



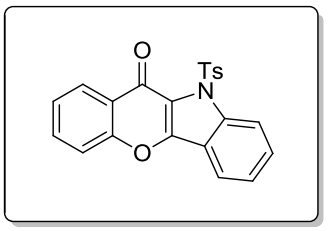
8-hydroxy-11H-benzofuro[3,2-b]chromen-11-one (2o). Yield 76% (12.0 mg). mp 295-297 °C. light yellow solid. ^{1}H NMR (400 MHz, Dimethyl sulfoxide-d_6) δ 10.66 (s, 1H), 8.32 – 8.20 (m, 1H), 7.93 – 7.79 (m, 3H), 7.61 – 7.50 (m, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 7.02 (dd, *J* = 8.6, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.8, 161.2, 156.5, 155.0, 149.4, 135.7, 133.5, 125.5, 125.1, 124.6, 121.4, 118.4, 114.9, 109.1, 98.6. HRMS (ESI$^+$) m/z calcd. for $C_{15}H_8NaO_4^+$ $[M+Na]^+$: 275.0315, found: 275.0286.



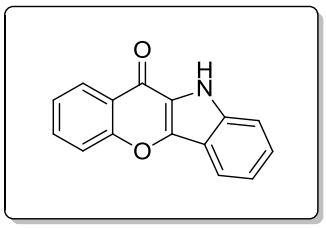
7-bromo-11H-benzofuro[3,2-b]chromen-11-one (2p). Yield 77% (15.3 mg). mp 262–264 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.45 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 7.76 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.49 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 155.8, 153.6, 147.7, 138.1, 133.8, 133.4, 126.6, 125.1, 125.1, 123.2, 119.8, 118.3, 117.3, 115.0. HRMS (ESI^+) m/z calcd. for $C_{15}H_7BrNaO_3^+$ $[M+Na]^+$: 336.9471, found: 336.9454.



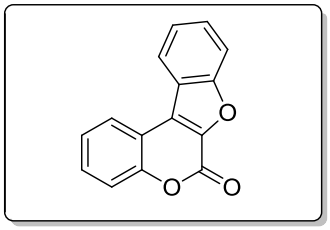
7-chloro-11H-benzofuro[3,2-b]chromen-11-one (2q). Yield 62% (10.5 mg). mp 254–256 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.45 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.96 (d, *J* = 2.1 Hz, 1H), 7.76 (ddd, *J* = 8.7, 7.0, 1.7 Hz, 1H), 7.67 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.56 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.49 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 155.8, 153.3, 147.9, 138.3, 133.7, 130.7, 130.0, 126.6, 125.1, 120.1, 119.3, 118.3, 114.7. HRMS (ESI^+) m/z calcd. for $C_{15}H_7ClNaO_3^+$ $[M+Na]^+$: 292.9976, found: 292.9950.



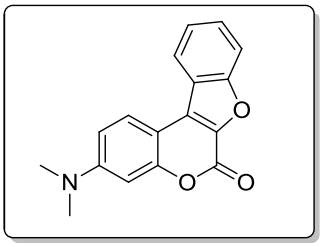
10-tosylchromeno[3,2-b]indol-11(10H)-one (2r). Yield 82% (13.0 mg). mp 244–246 °C. light yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.49 (d, *J* = 8.7 Hz, 1H), 8.35 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 154.7, 150.0, 144.8, 138.6, 136.7, 133.2, 130.6, 129.5, 127.8, 126.9, 124.8, 124.7, 124.1, 120.3, 120.0, 118.8, 117.7, 116.2, 21.7. HRMS (ESI^+) m/z calcd. for $C_{22}H_{15}NNaO_4S^+$ $[M+Na]^+$: 412.0614, found: 412.0601.



chromeno[3,2-b]indol-11(10H)-one (2s). Yield 74% (11.0 mg). mp 279-281 °C. light yellow solid. ^{1}H NMR (400 MHz, Dimethyl sulfoxide-d_6) δ 12.17 (s, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.59 – 7.49 (m, 3H), 7.26 (ddd, *J* = 8.0, 6.6, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.4, 155.3, 143.8, 137.0, 133.3, 128.0, 125.4, 124.2, 123.2, 120.9, 120.4, 119.4, 118.4, 114.7, 113.2. HRMS (ESI$^+$) m/z calcd. for $C_{15}H_9NNaO_2^+$ $[M+Na]^+$: 258.0525, found: 258.0507.

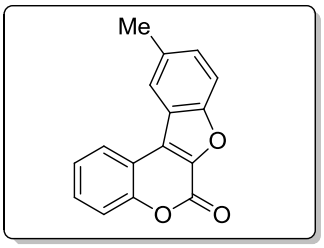


6H-benzofuro[2,3-c]chromen-6-one (4a). Yield 46% (6.8 mg). mp 165–167 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.16 (d, *J* = 8.0 Hz, 1H), 8.10 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.62 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.55 – 7.39 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 153.6, 152.1, 138.5, 129.8, 127.4, 124.9, 124.8, 124.0, 122.9, 122.4, 117.6, 116.8, 113.4. HRMS (ESI$^+$) m/z calcd. for $C_{15}H_8NaO_3^+$ $[M+Na]^+$: 259.0366, found: 259.0398.

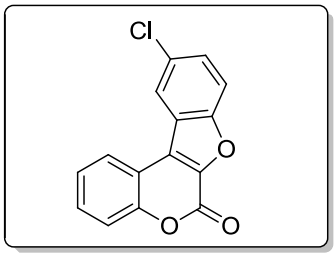


3-(dimethylamino)-6H-benzofuro[2,3-c]chromen-6-one (4b). Yield 52% (8.8 mg). mp 204–206 °C. light yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.12 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.58 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.48 – 7.40 (m, 1H), 6.75 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.66 (d, *J* = 2.5 Hz, 1H), 3.04 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 154.4, 154.3, 151.4, 136.1, 129.5, 128.7, 124.5, 124.2,

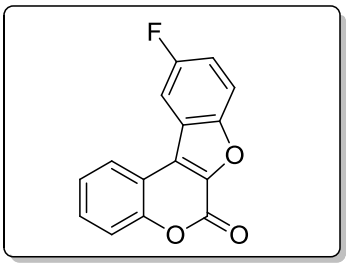
123.1, 122.7, 113.2, 109.7, 105.5, 99.3, 40.2. HRMS (ESI$^+$) m/z calcd. for $C_{17}H_{13}NNaO_3^+$ $[M+Na]^+$: 302.0788, found: 302.0797.



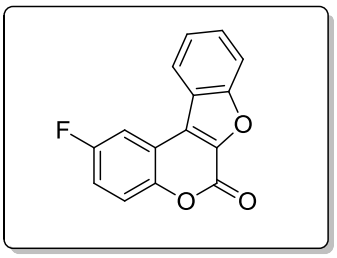
10-methyl-6H-benzofuro[2,3-c]chromen-6-one (4c). Yield 44% (8.8 mg). mp 188–190 ^oC. white solid. ^1H NMR (400 MHz, Chloroform-d) δ 8.15 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.99 – 7.95 (m, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.46 – 7.41 (m, 2H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 153.7, 152.1, 138.7, 134.7, 131.3, 129.7, 127.2, 124.9, 124.1, 122.5, 122.5, 117.6, 117.0, 112.9, 21.5. HRMS (ESI$^+$) m/z calcd. for $C_{16}H_{10}NaO_3^+$ $[M+Na]^+$: 273.0522, found: 273.0525.



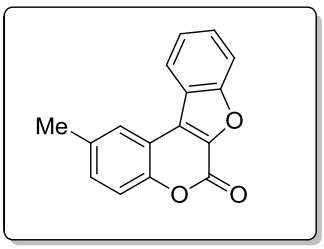
10-chloro-6H-benzofuro[2,3-c]chromen-6-one (4d). Yield 51% (11.0 mg). mp 219–221 ^oC. white solid. ^1H NMR (400 MHz, Chloroform-d) δ 8.15 (dd, *J* = 2.2, 0.6 Hz, 1H), 8.06 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.67 (dd, *J* = 9.0, 0.6 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.52 – 7.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 153.2, 152.1, 139.6, 130.6, 130.1, 126.7, 125.1, 123.9, 123.7, 122.5, 117.7, 116.3, 114.5. HRMS (ESI$^+$) m/z calcd. for $C_{15}H_7ClNaO_3^+$ $[M+Na]^+$: 292.9976, found: 292.9958.



10-fluoro-6H-benzofuro[2,3-c]chromen-6-one (4e). Yield 50% (10.2 mg). mp 225–227 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.03 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.83 (dd, *J* = 8.1, 2.5 Hz, 1H), 7.73 – 7.66 (m, 1H), 7.59 – 7.41 (m, 3H), 7.38 (td, *J* = 8.9, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (d, J_{CF} = 243.3 Hz), 153.4 (d, J_{CF} = 24.3 Hz), 152.1 , 140.0 , 130.0 , 127.3 (d, J_{CF} = 4.5 Hz), 125.1 , 123.7 , 123.0 (d, J_{CF} = 10.6 Hz), 118.1 (d, J_{CF} = 26.4 Hz), 117.7 , 116.4 , 114.5 (d, J_{CF} = 9.4 Hz), 108.5 (d, J_{CF} = 25.6 Hz). HRMS (ESI^{+}) m/z calcd. for $C_{15}H_7FNaO_3^{+}$ $[M+Na]^{+}$: 277.0271, found: 277.0270.



2-fluoro-6H-benzofuro[2,3-c]chromen-6-one (4f). Yield 48% (7.6 mg). mp 210–212 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.18 – 8.12 (m, 1H), 7.82 – 7.71 (m, 2H), 7.66 (ddt, *J* = 8.5, 7.5, 1.3 Hz, 1H), 7.57 – 7.44 (m, 2H), 7.30 – 7.21 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 159.2 (d, J_{CF} = 244.9 Hz), 157.4 , 153.2 , 148.4 (d, J_{CF} = 2.3 Hz), 139.1 , 130.1 , 126.8 (d, J_{CF} = 3.0 Hz), 125.1 , 122.6 , 122.1 , 119.1 (d, J_{CF} = 8.8 Hz), 117.7 (d, J_{CF} = 9.6 Hz), 117.1 (d, J_{CF} = 24.3 Hz), 113.6 , 110.0 (d, J_{CF} = 25.0 Hz). HRMS (ESI^{+}) m/z calcd. for $C_{15}H_7FNaO_3^{+}$ $[M+Na]^{+}$: 277.0271, found: 277.0273.



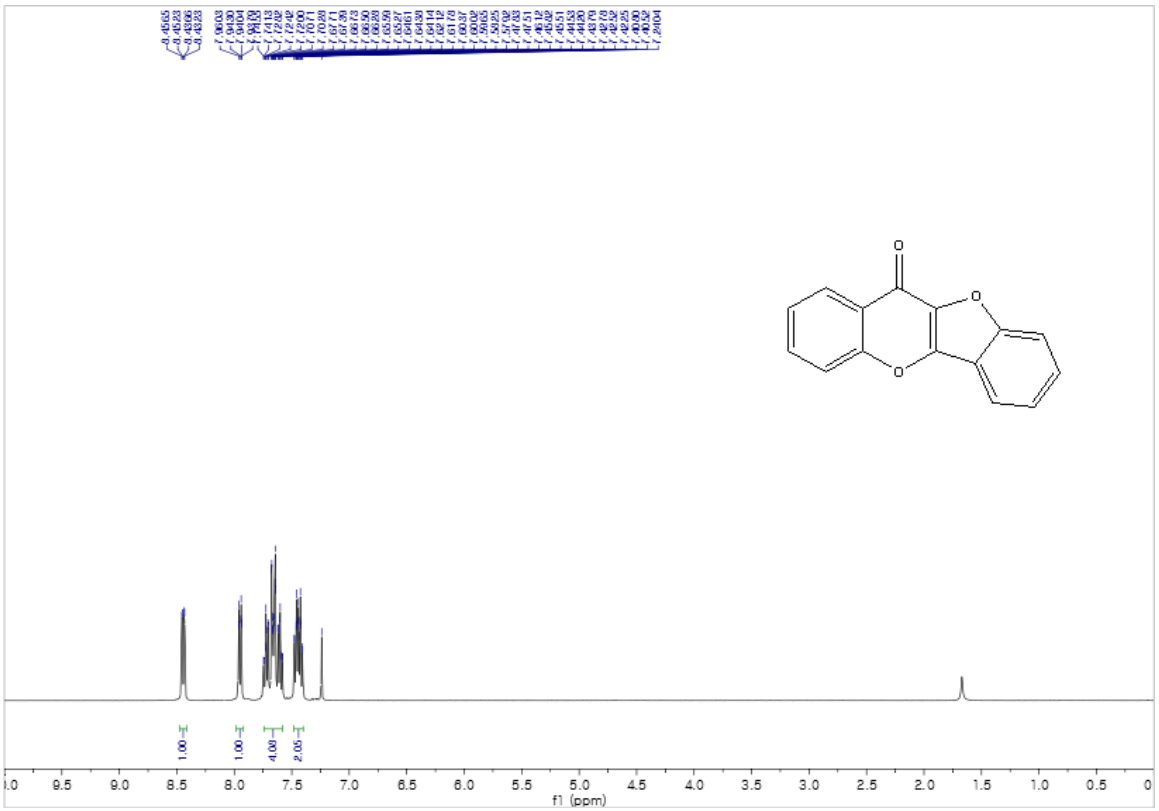
2-methyl-6H-benzofuro[2,3-c]chromen-6-one (4g). Yield 47% (9.2 mg). mp 196–198 °C. white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.16 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.69 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.61 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.48 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.35 – 7.27 (m, 2H), 2.49 (s, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 157.2, 153.7, 150.2, 138.6, 134.7, 130.7, 129.7, 127.3, 124.7, 123.9, 123.0, 122.4, 117.2, 116.5, 113.3, 21.1. HRMS (ESI^+) m/z calcd. for $C_{16}H_{10}NaO_3^+$ $[M+Na]^+$: 273.0522, found: 273.0515.

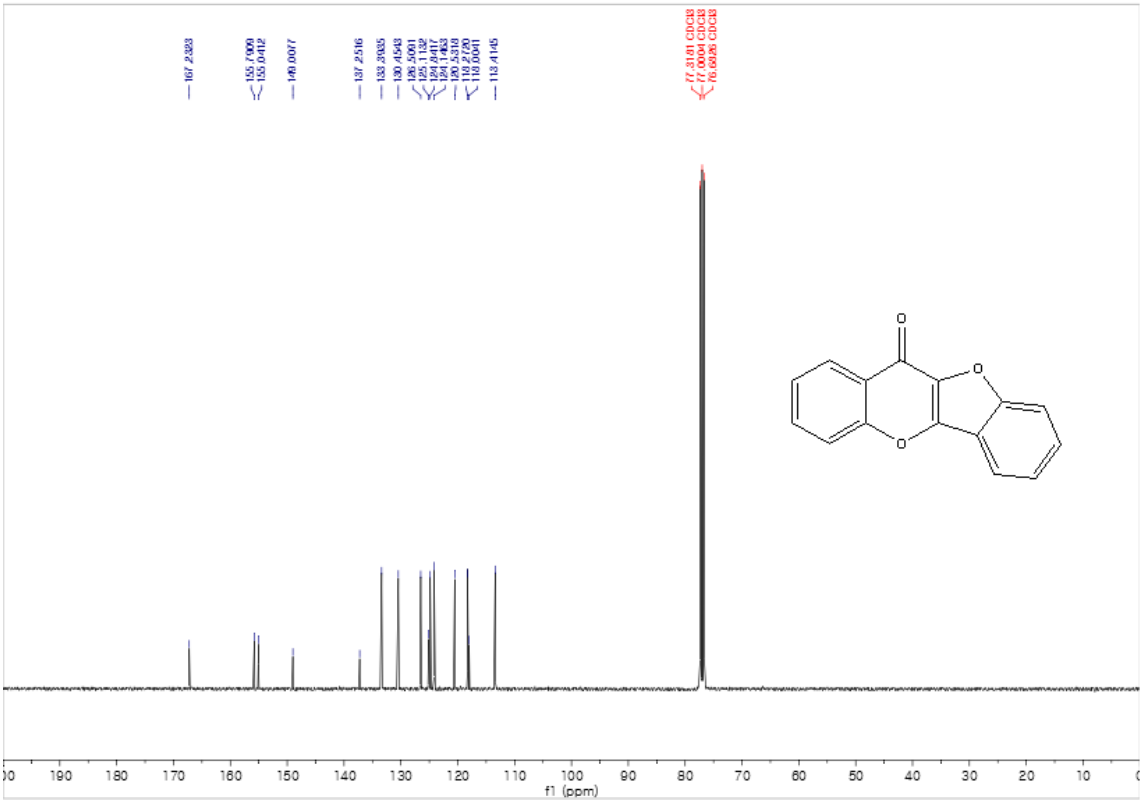
Appendix Ⅰ

Spectral Copies of ^{1}H and ^{13}C NMR Data Obtained in this Study

11H-benzofuro[3,2-b]chromen-11-one (2a)

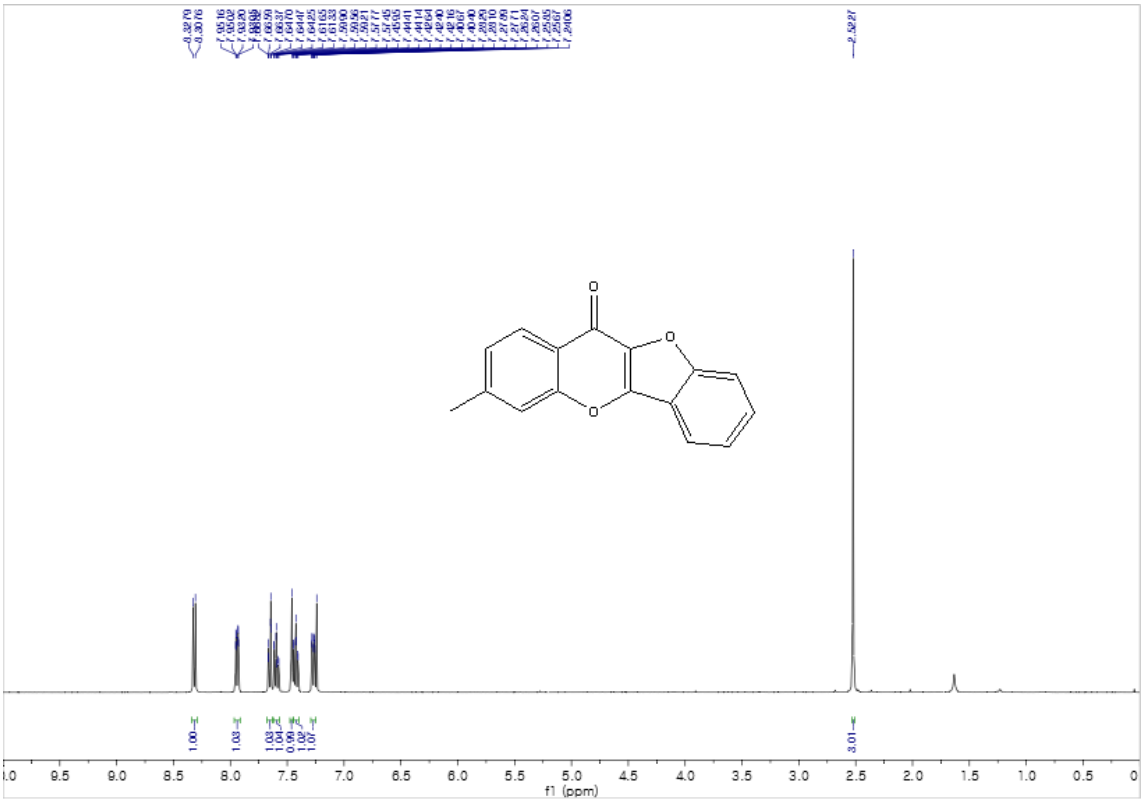


400 MHz, ^{1}H NMR in $CDCl_3$

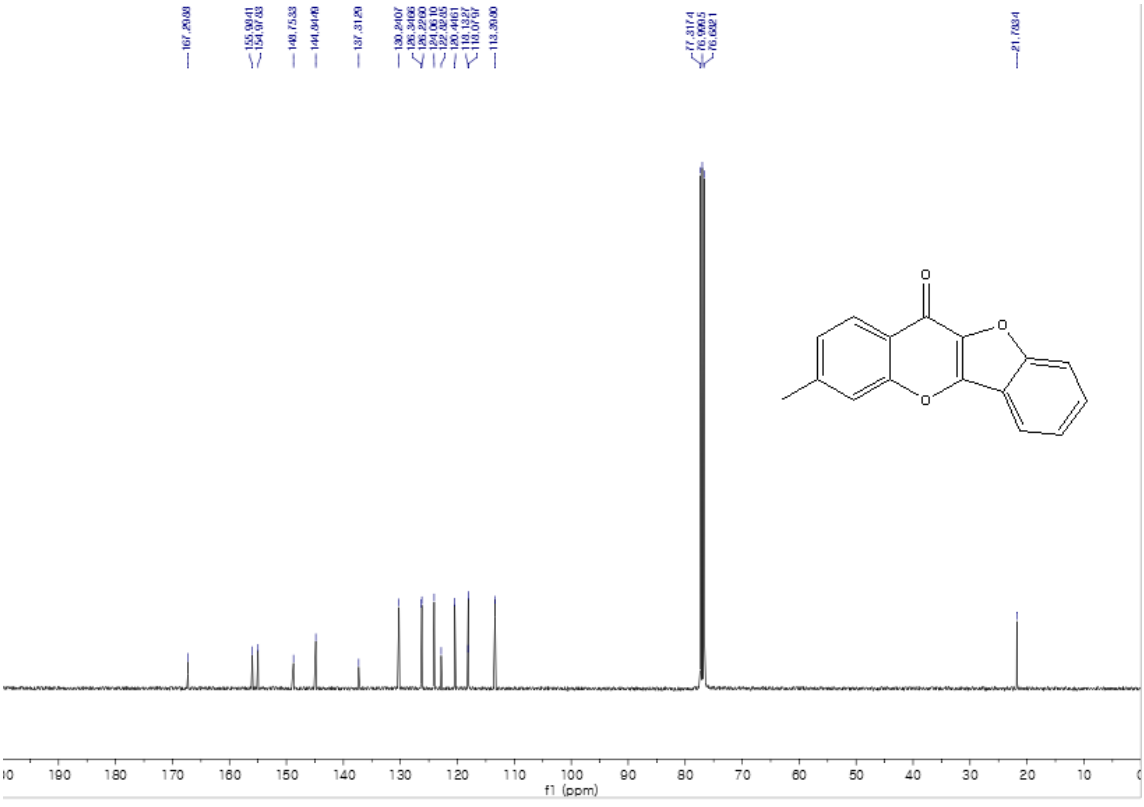


100 MHz, ^{13}C NMR in $CDCl_3$

3-methyl-11H-benzofuro[3,2-b]chromen-11-one (2b)

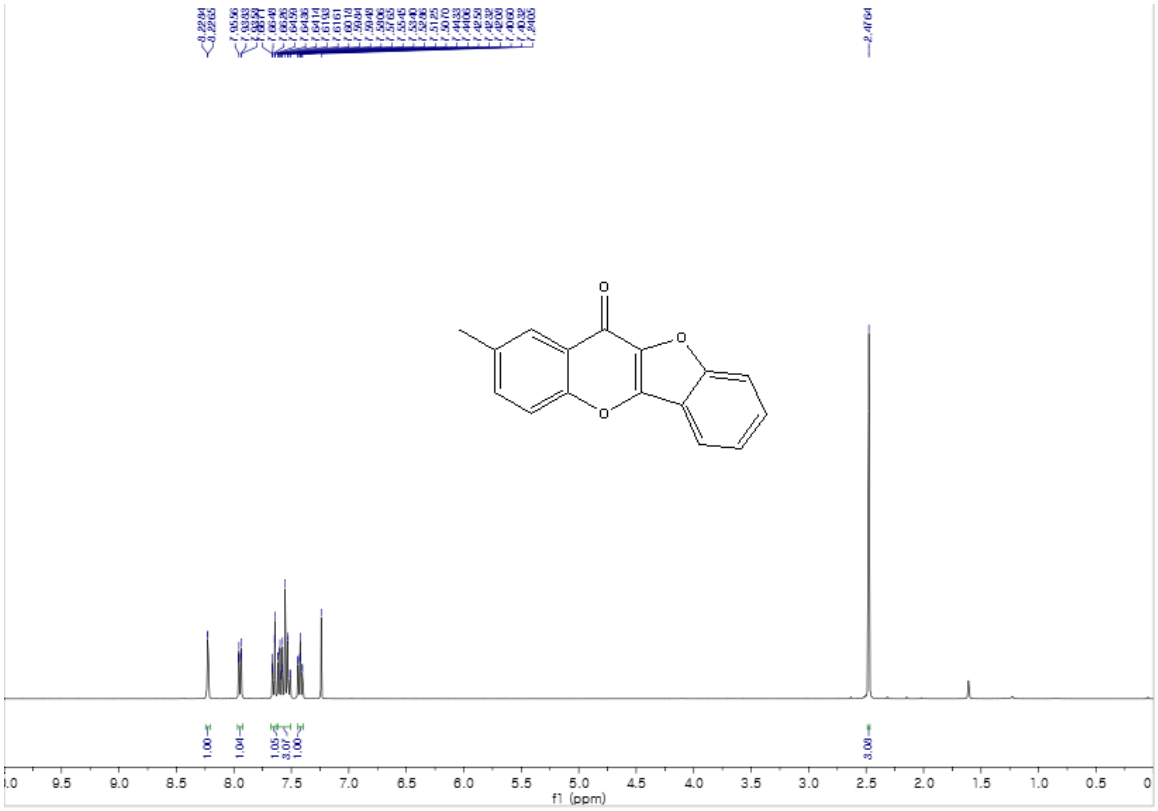


400 MHz, ^{1}H NMR in $CDCl_3$

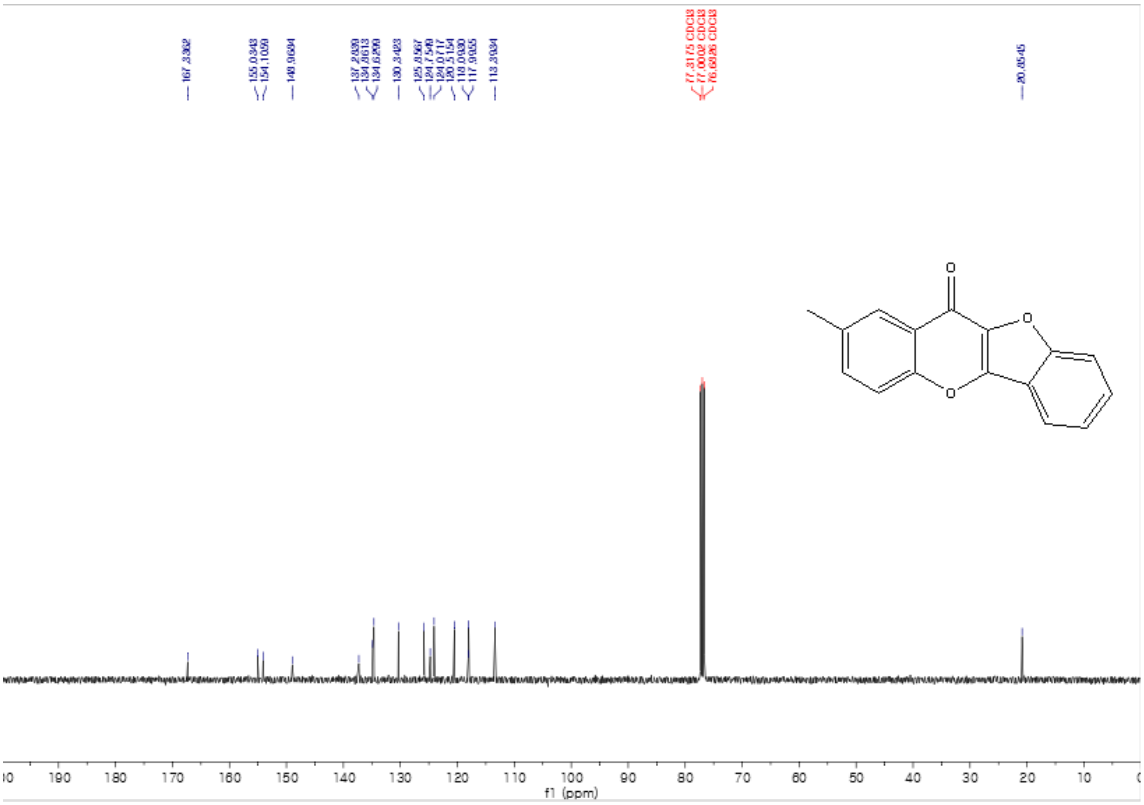


100 MHz, ^{13}C NMR in $CDCl_3$

2-methyl-11H-benzofuro[3,2-b]chromen-11-one (2c)

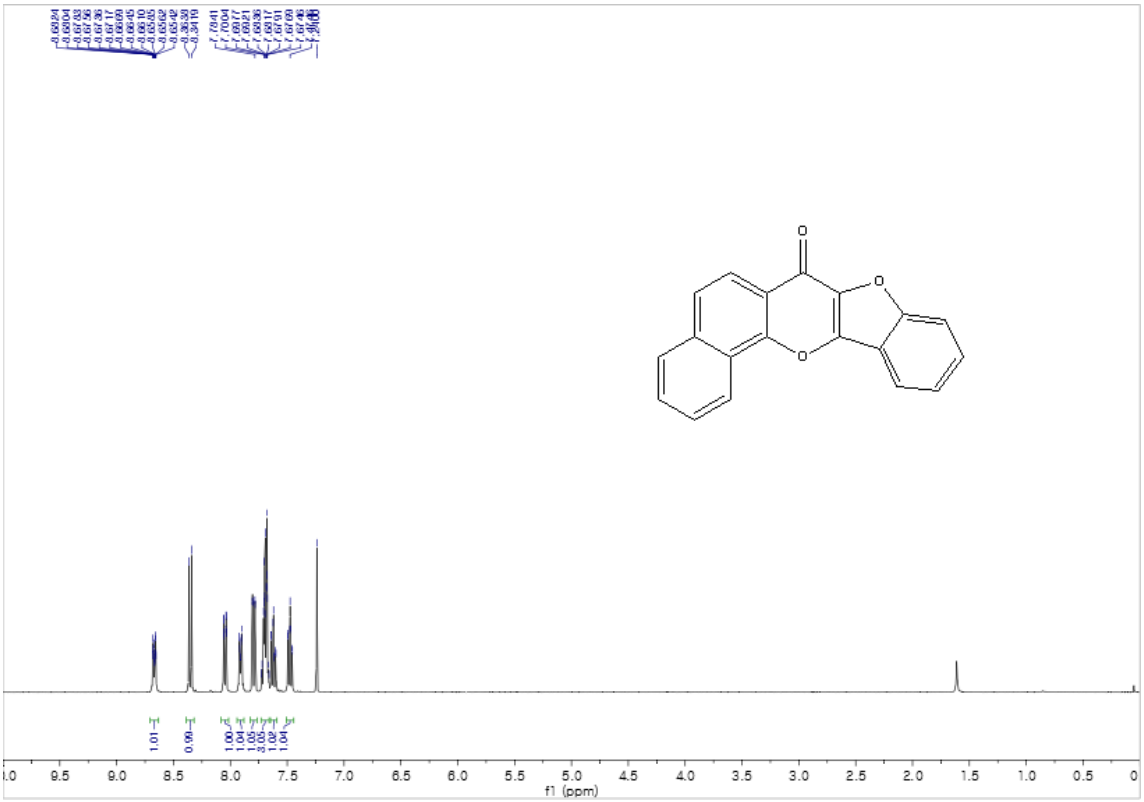


400 MHz, ^{1}H NMR in $CDCl_3$

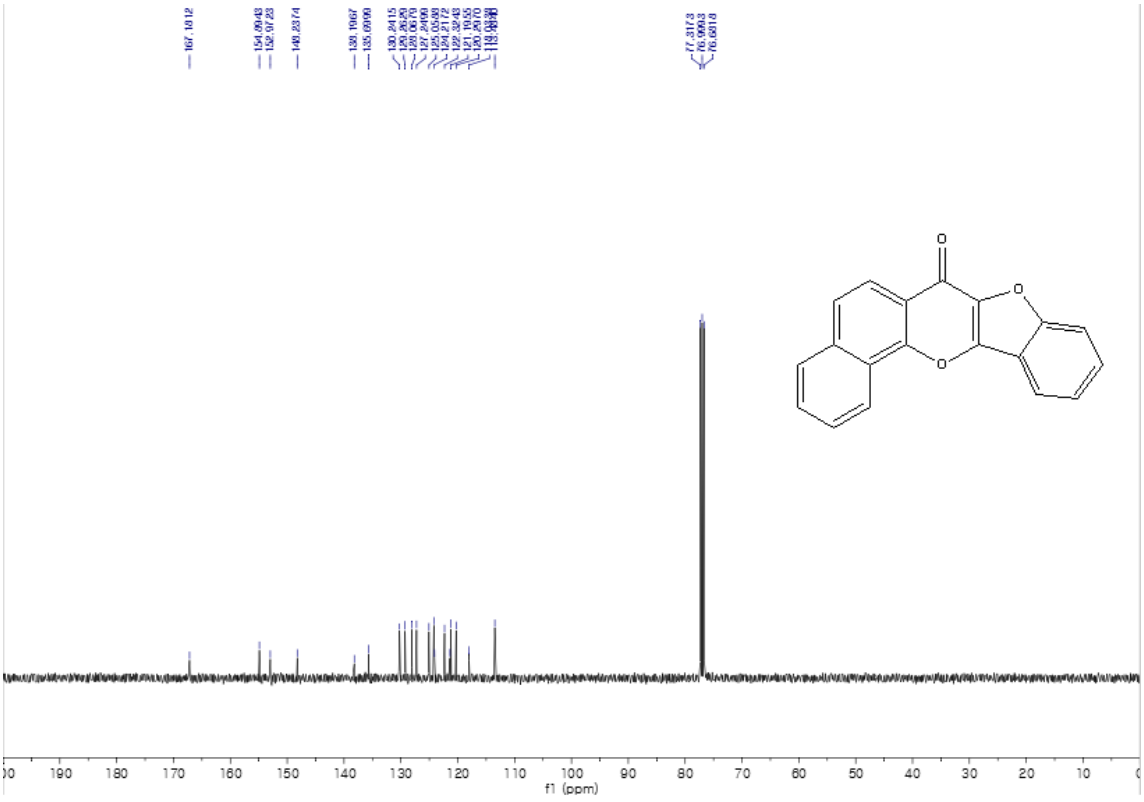


100 MHz, ^{13}C NMR in $CDCl_3$

7H-benzo[h]benzofuro[3,2-b]chromen-7-one (2d)

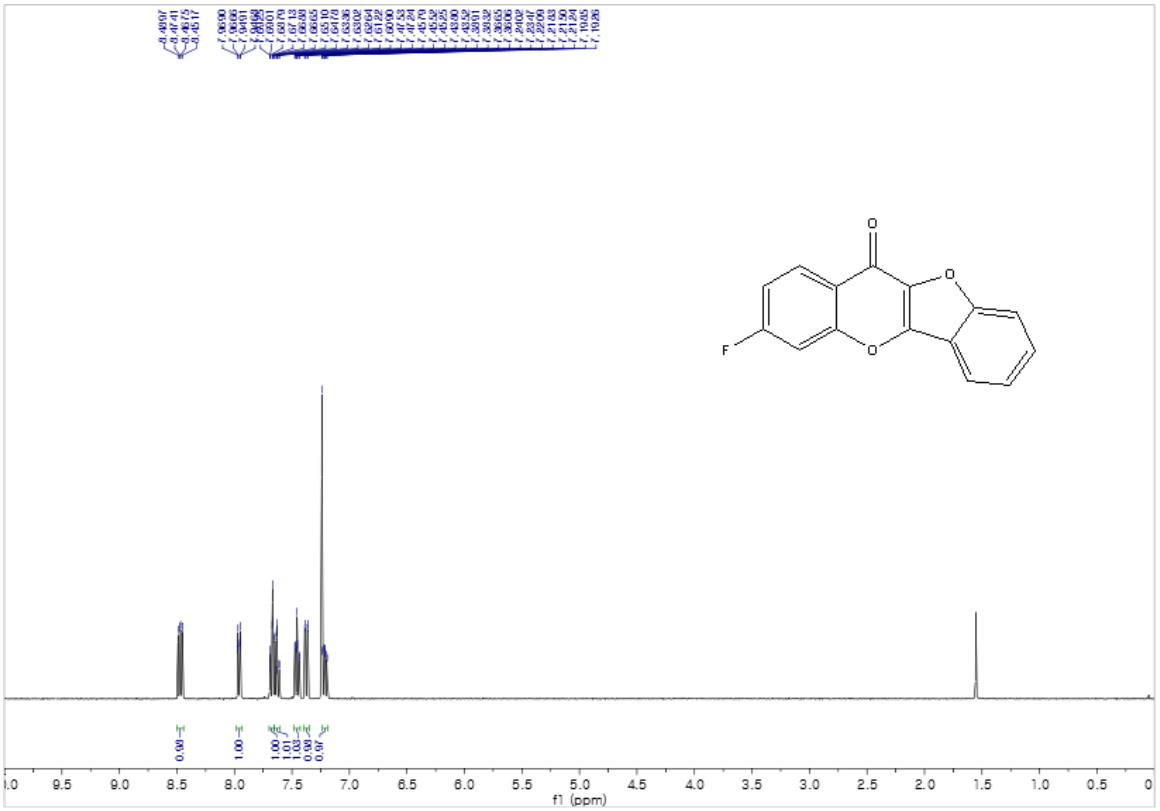


400 MHz, ^{1}H NMR in $CDCl_3$

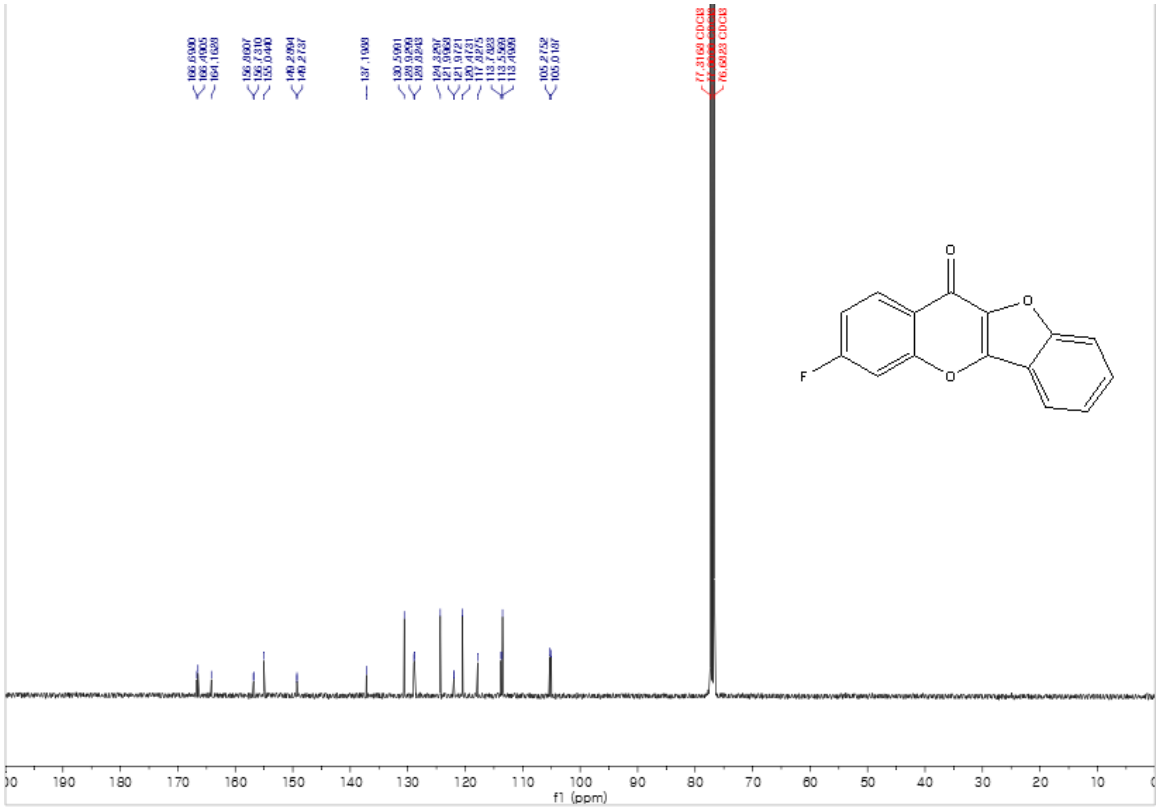


100 MHz, ^{13}C NMR in $CDCl_3$

3-fluoro-11H-benzofuro[3,2-b]chromen-11-one (2e)

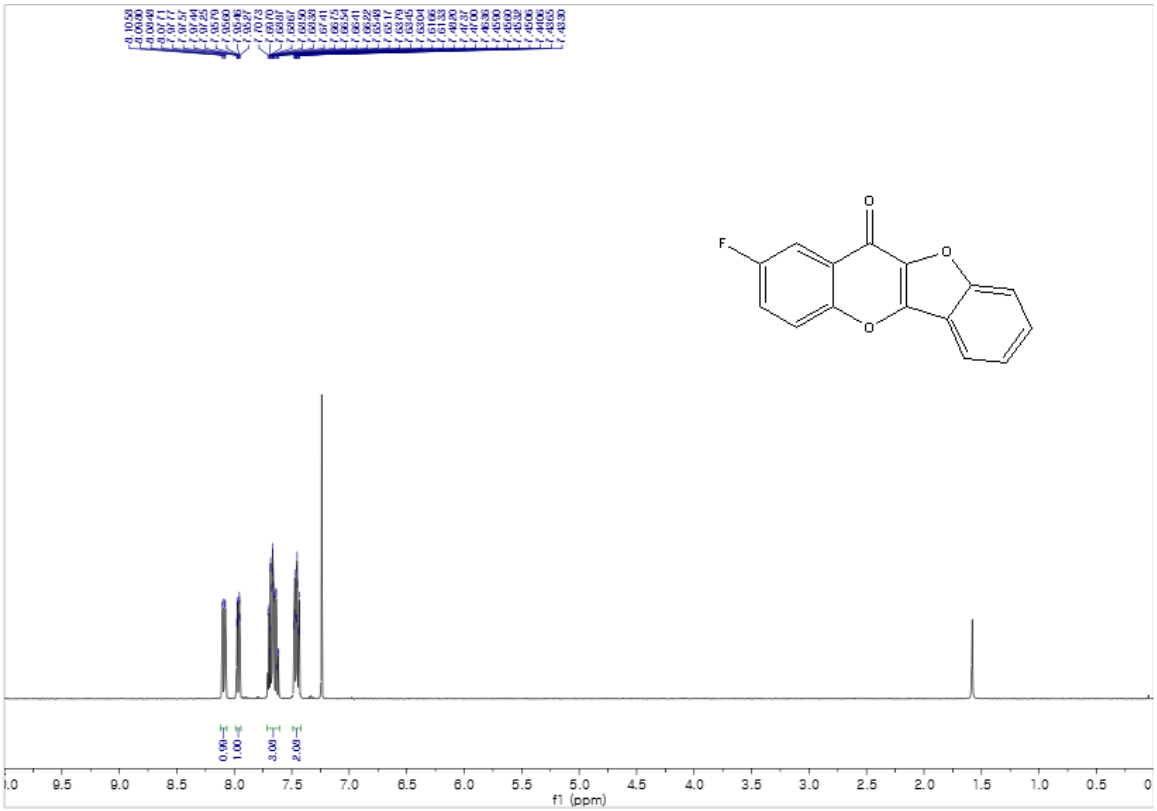


400 MHz, ^{1}H NMR in $CDCl_3$

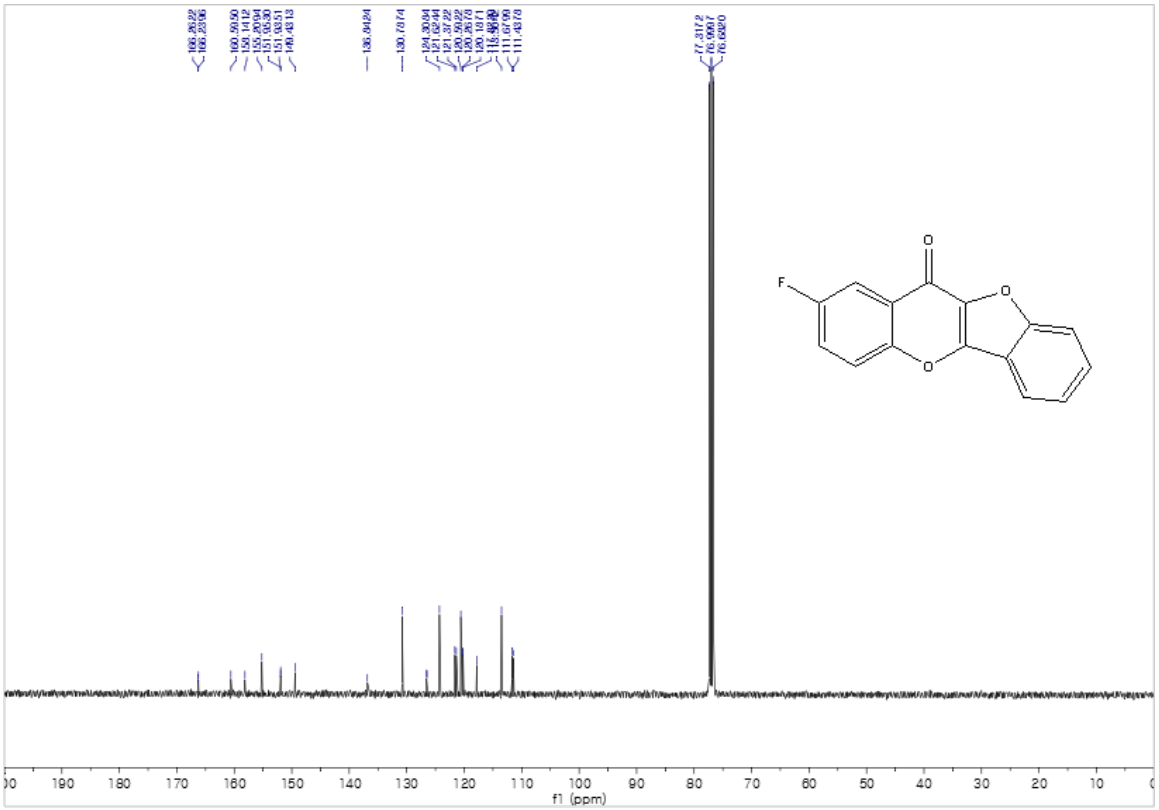


100 MHz, ^{13}C NMR in $CDCl_3$

2-fluoro-11H-benzofuro[3,2-b]chromen-11-one (2f)

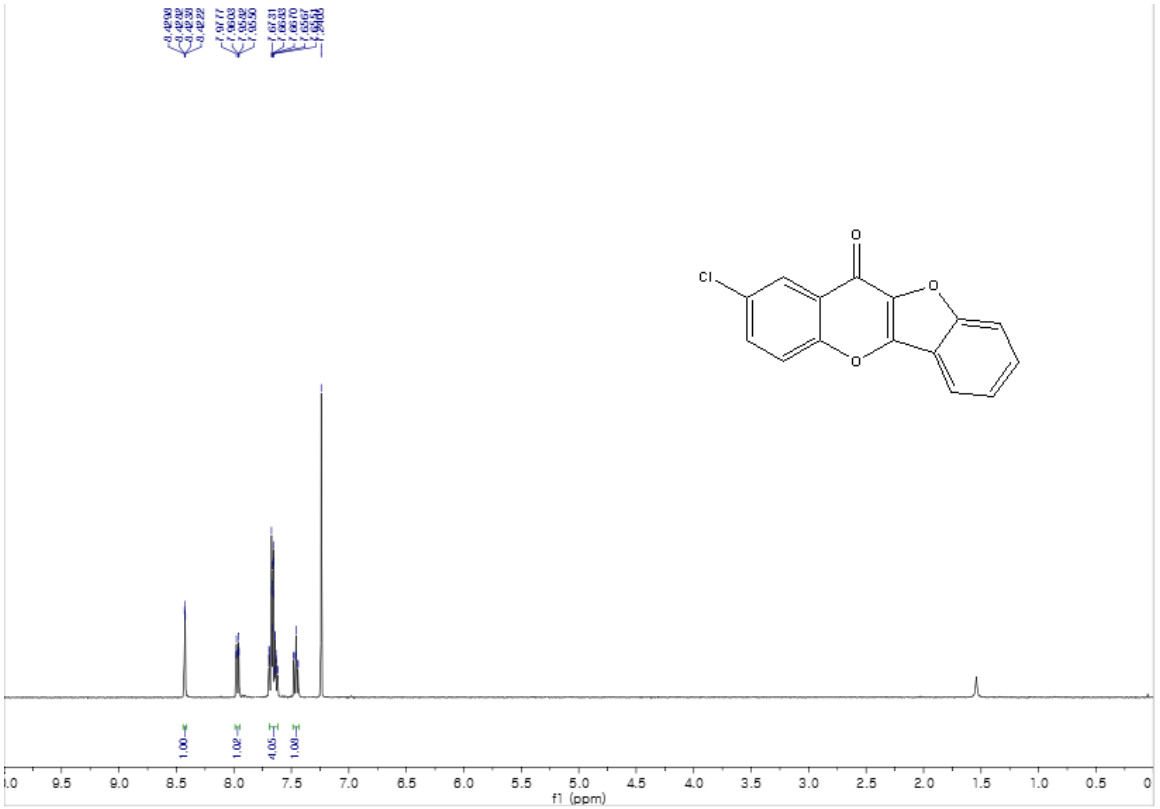


400 MHz, ^{1}H NMR in $CDCl_3$

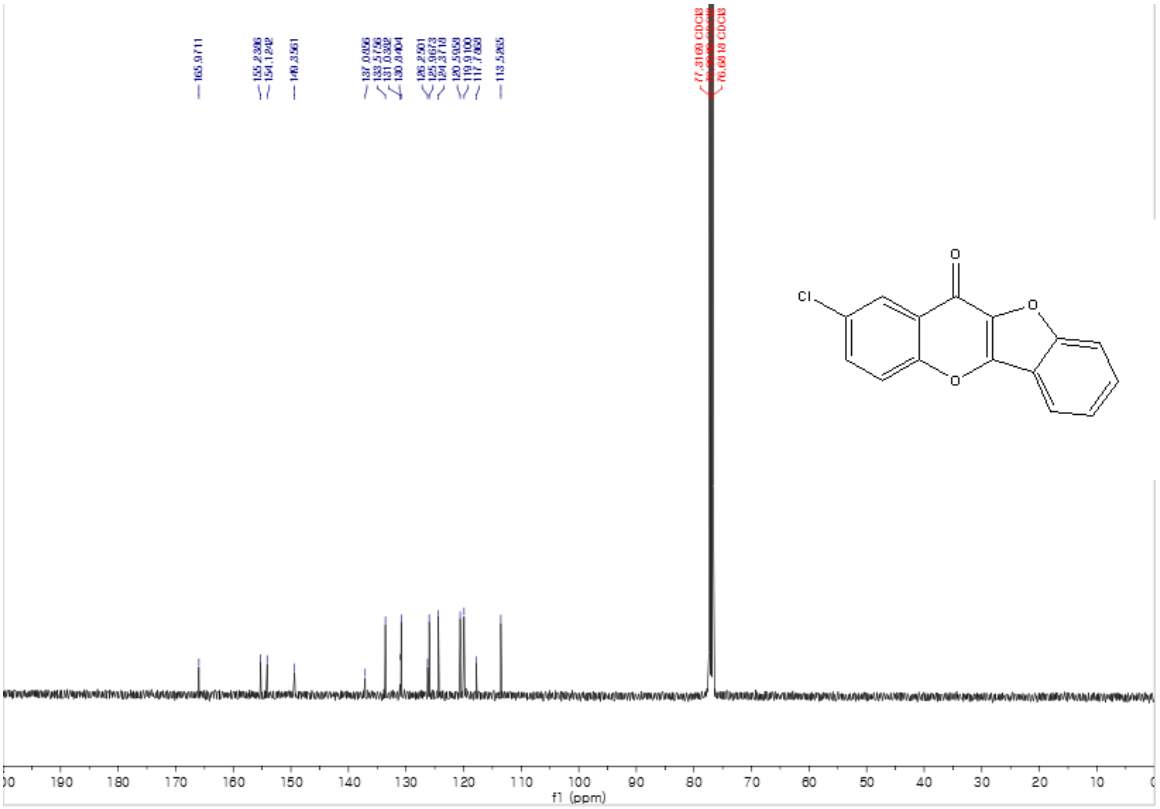


100 MHz, ^{13}C NMR in $CDCl_3$

2-chloro-11H-benzofuro[3,2-b]chromen-11-one (2g)

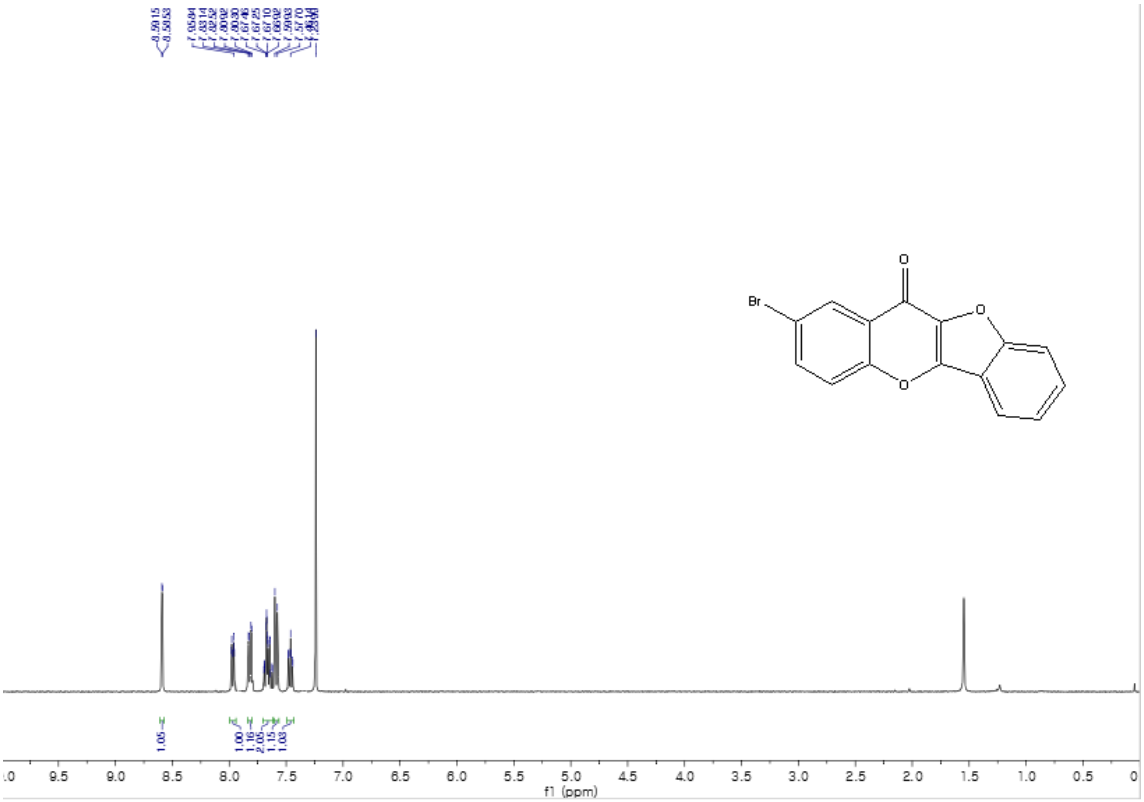


400 MHz, ^{1}H NMR in $CDCl_3$

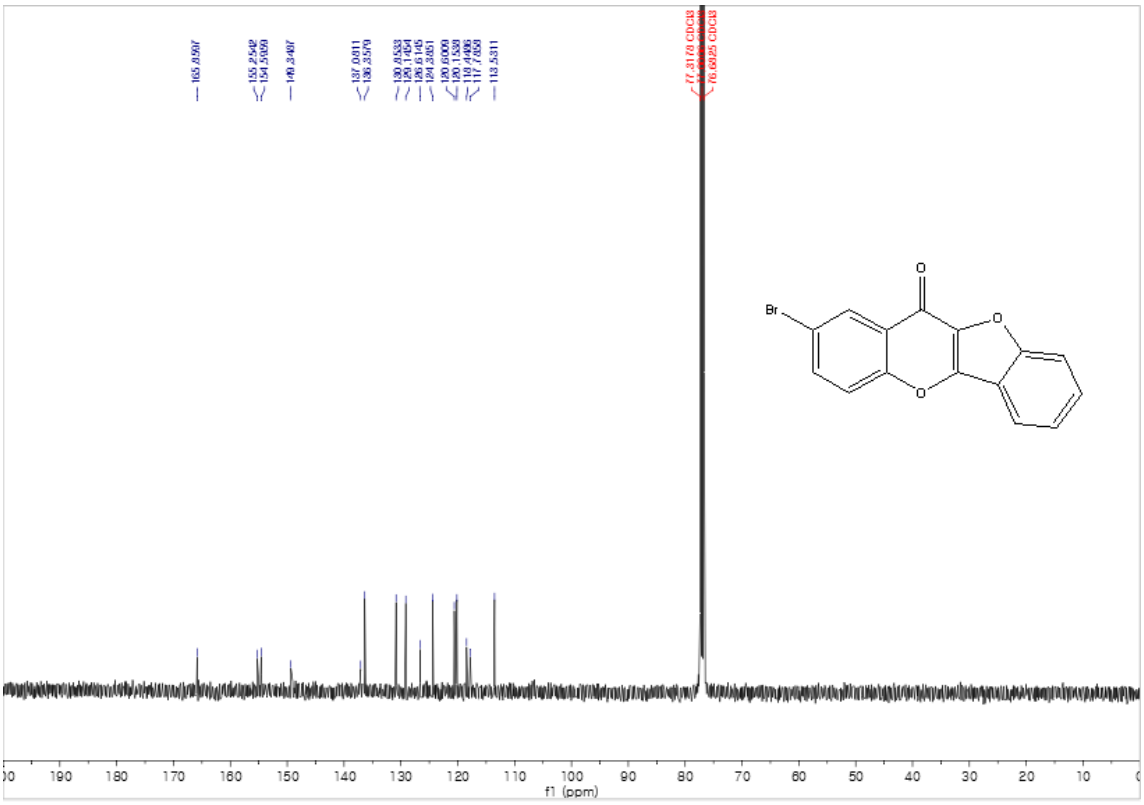


100 MHz, ^{13}C NMR in $CDCl_3$

2-bromo-11H-benzofuro[3,2-b]chromen-11-one (2h)

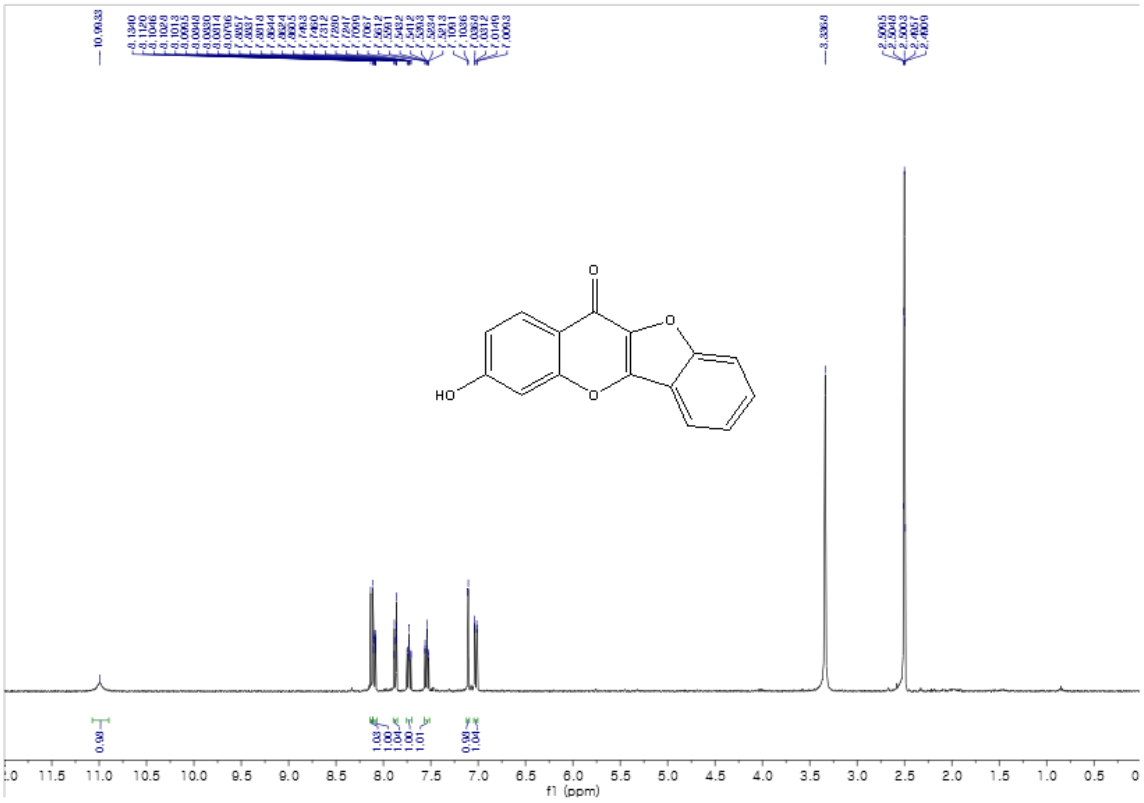


400 MHz, ^{1}H NMR in $CDCl_3$

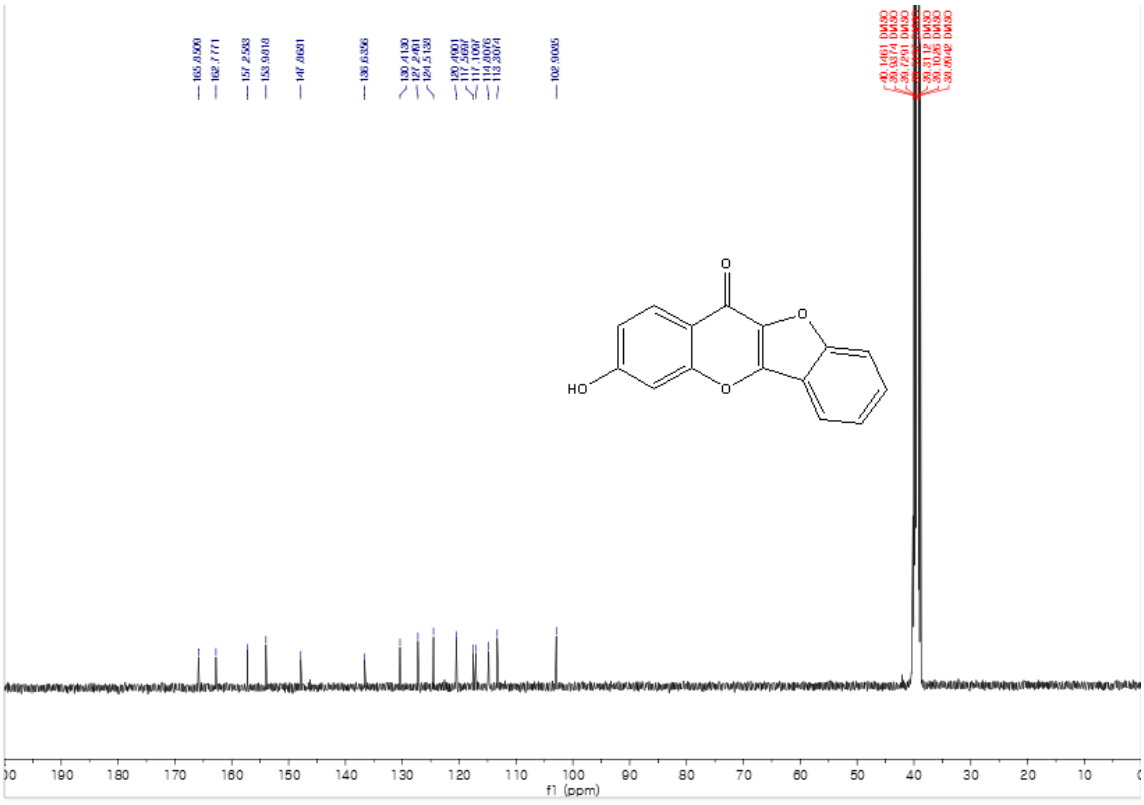


100 MHz, ^{13}C NMR in $CDCl_3$

3-hydroxy-11H-benzofuro[3,2-b]chromen-11-one (2i)

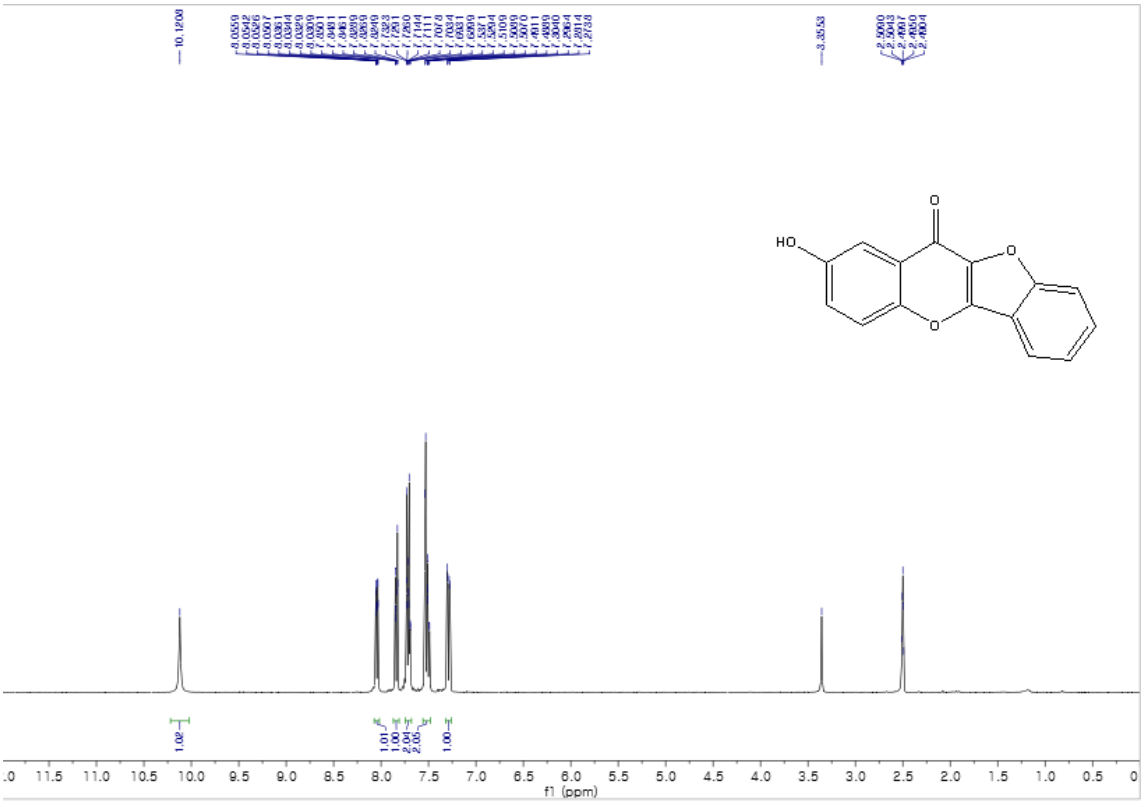


400 MHz, ^{1}H NMR in DMSO-d$_6$

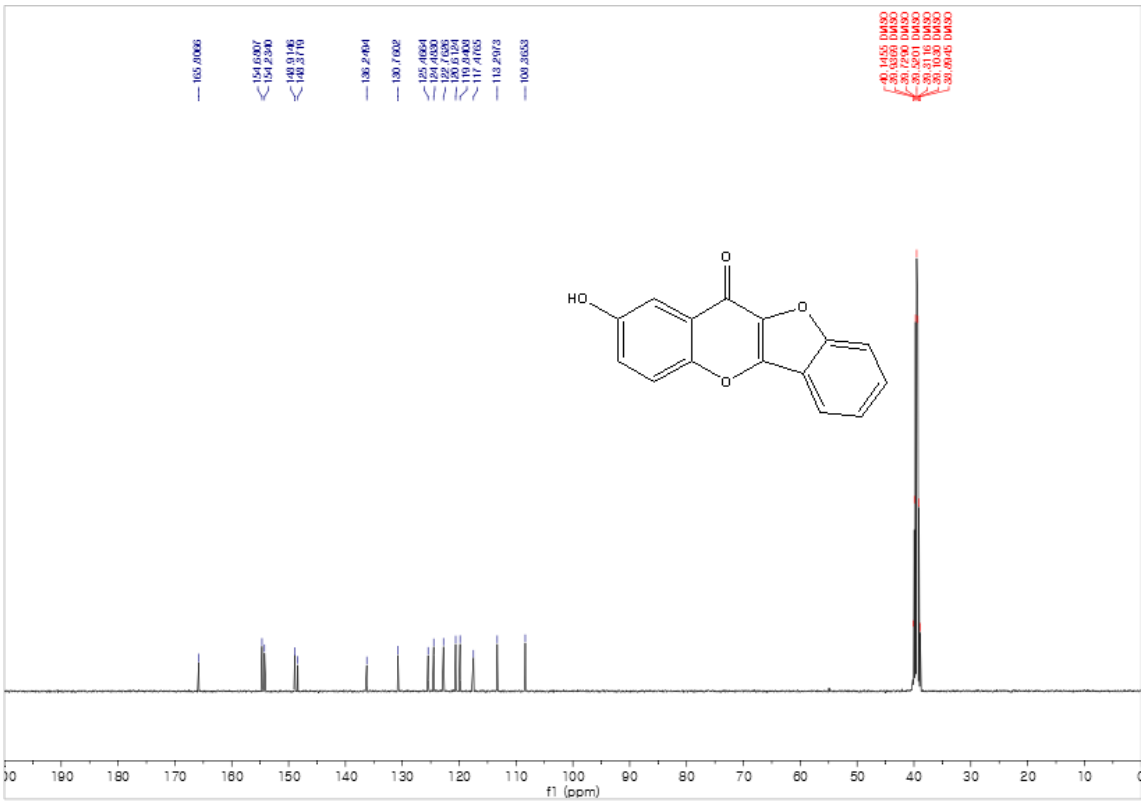


100 MHz, ^{13}C NMR in DMSO-d$_6$

2-hydroxy-11H-benzofuro[3,2-b]chromen-11-one (2j)

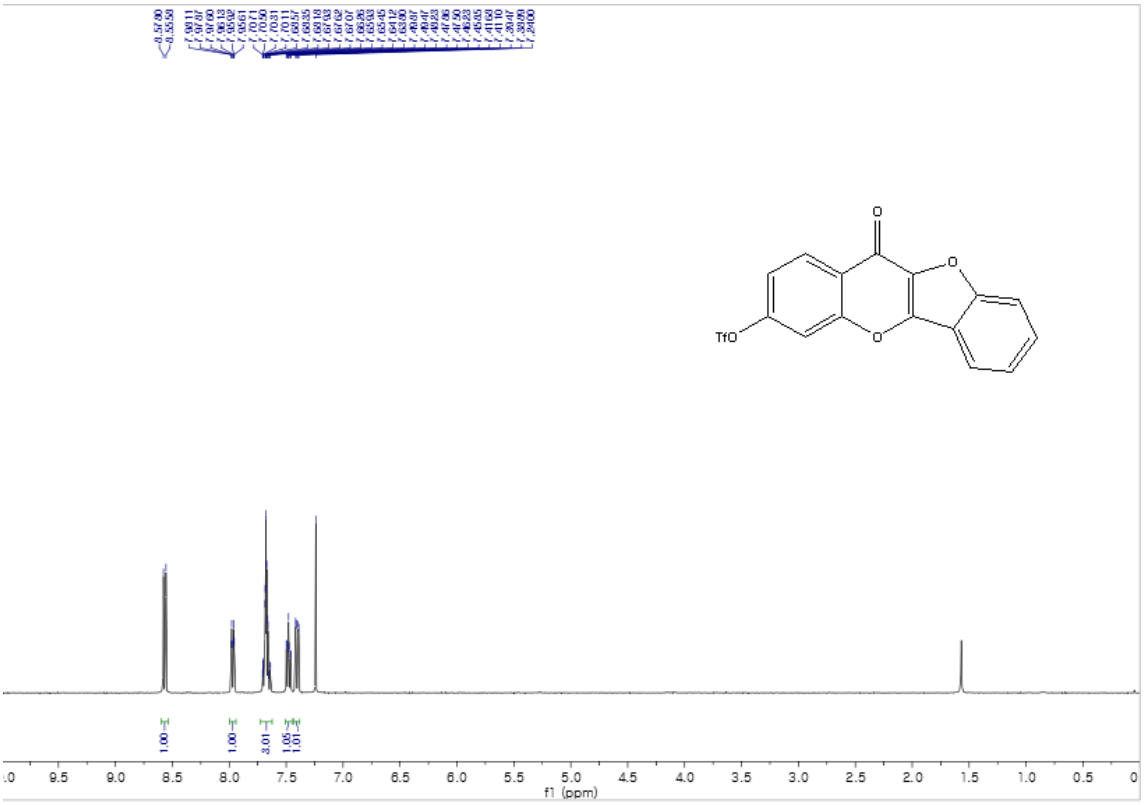


400 MHz, ^{1}H NMR in DMSO-d$_6$

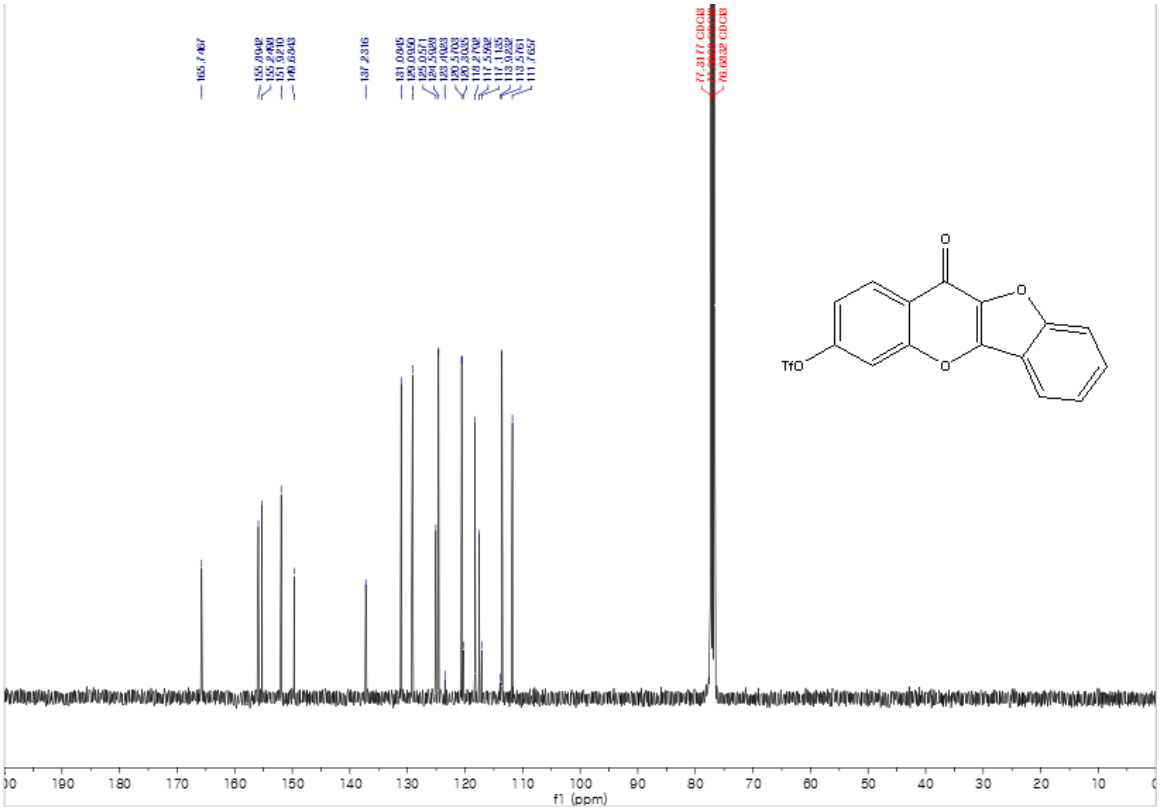


100 MHz, ^{13}C NMR in DMSO-d$_6$

11-oxo-11H-benzofuro[3,2-b]chromen-3-yl trifluoromethanesulfonate (2k)

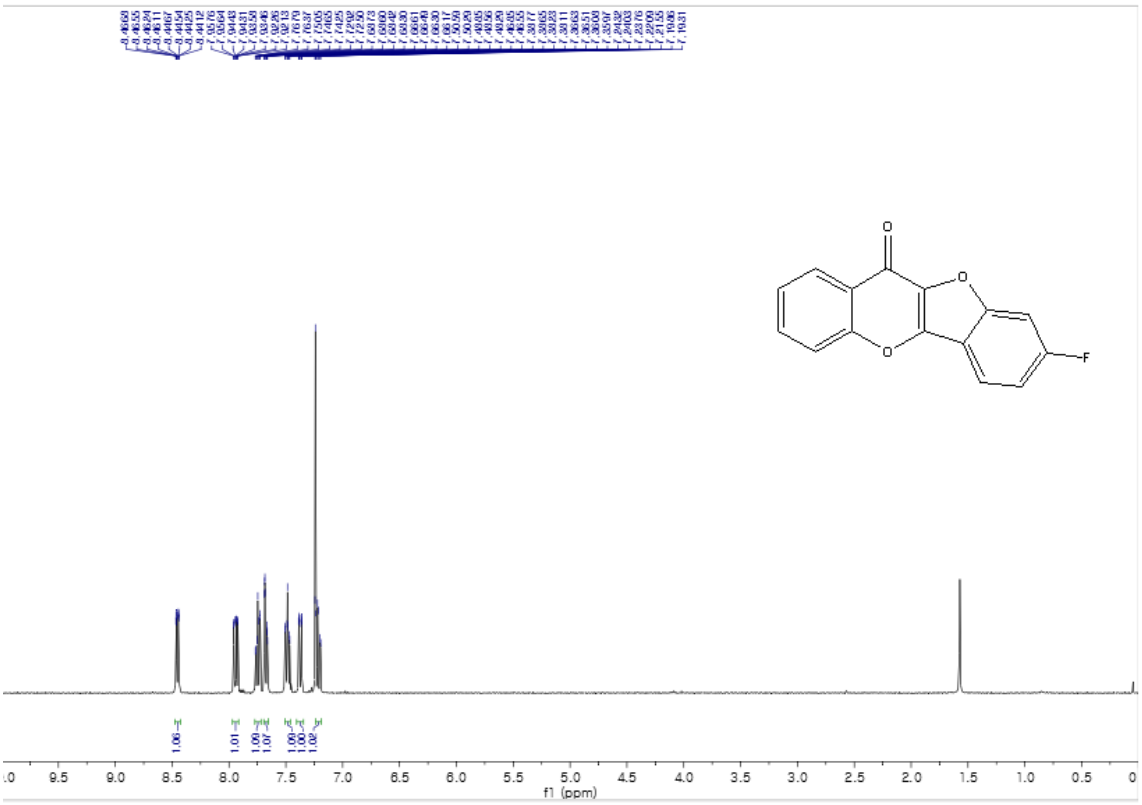


400 MHz, ^{1}H NMR in $CDCl_3$

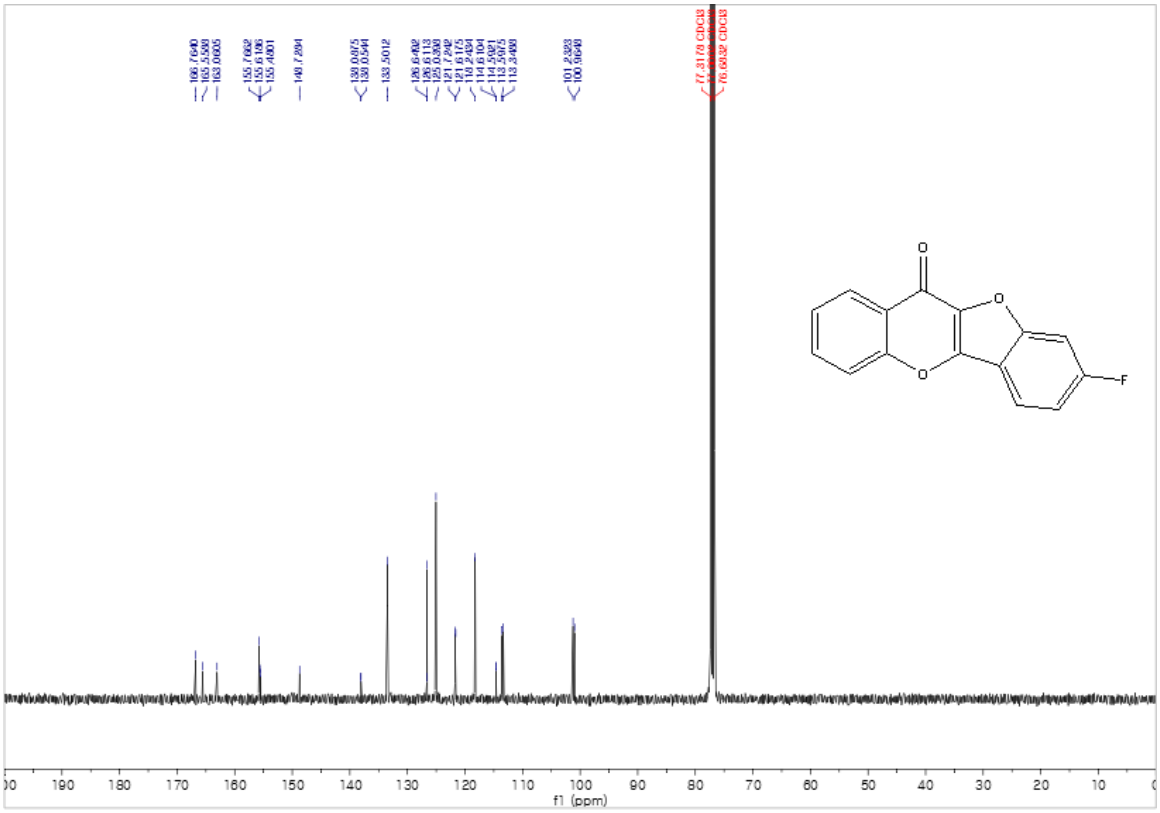


100 MHz, ^{13}C NMR in $CDCl_3$

8-fluoro-11H-benzofuro[3,2-b]chromen-11-one (2l)

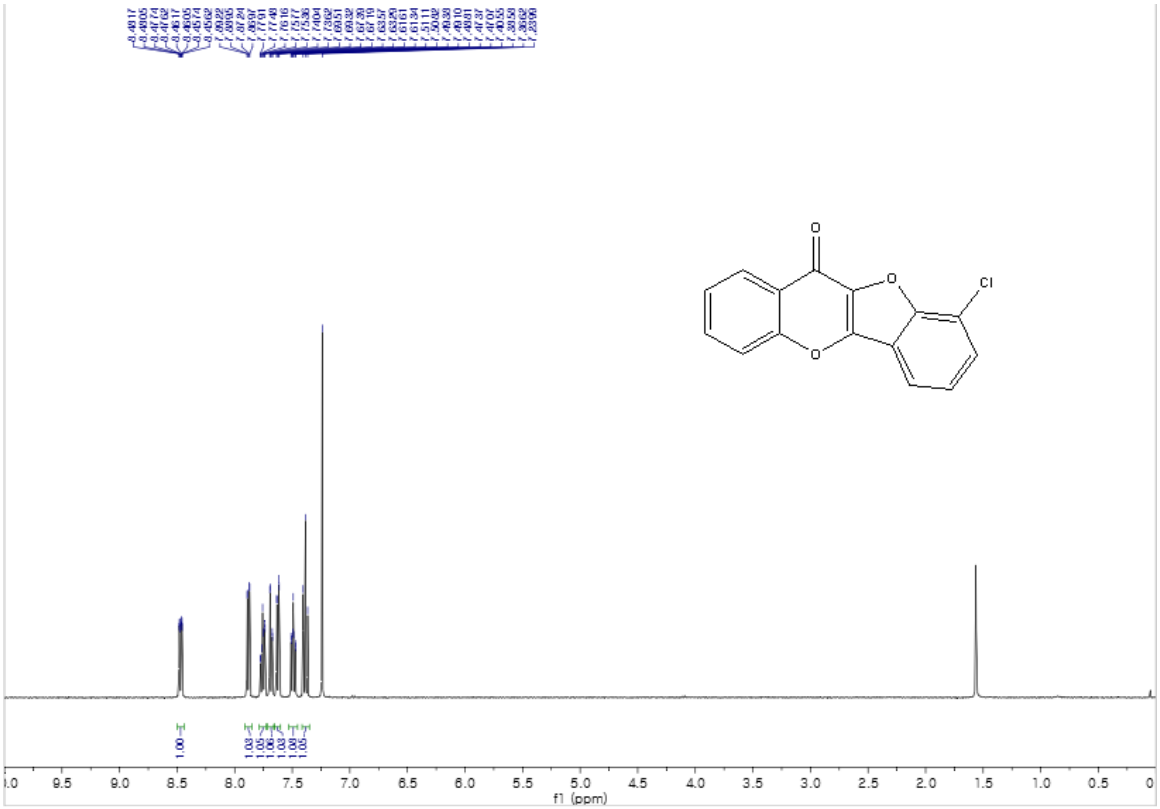


400 MHz, ^{1}H NMR in $CDCl_3$

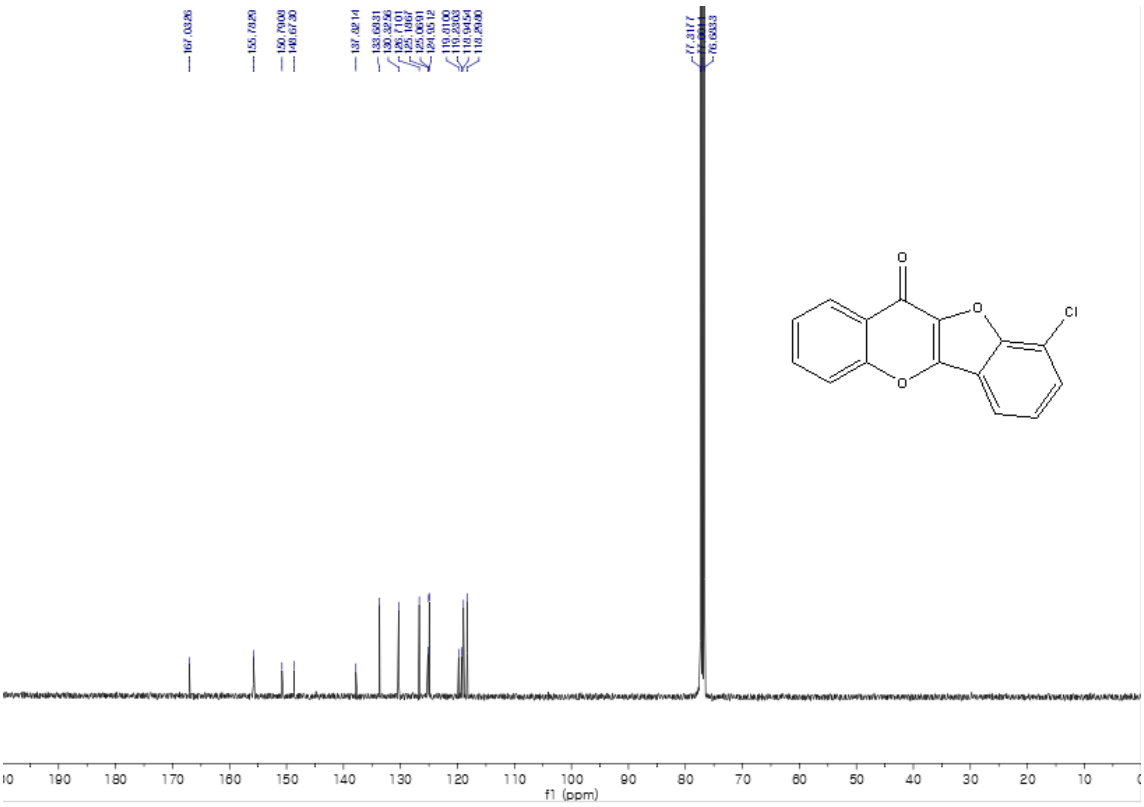


100 MHz, ^{13}C NMR in $CDCl_3$

9-chloro-11H-benzofuro[3,2-b]chromen-11-one (2m)

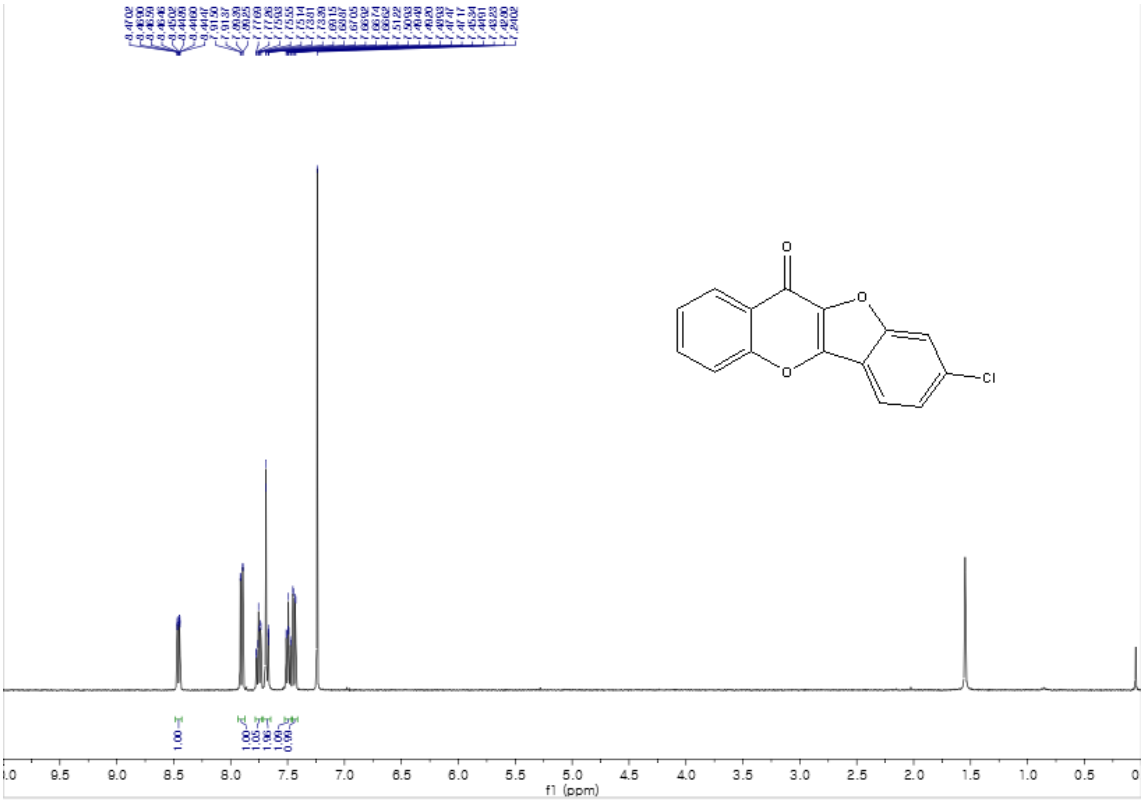


400 MHz, ^{1}H NMR in $CDCl_3$

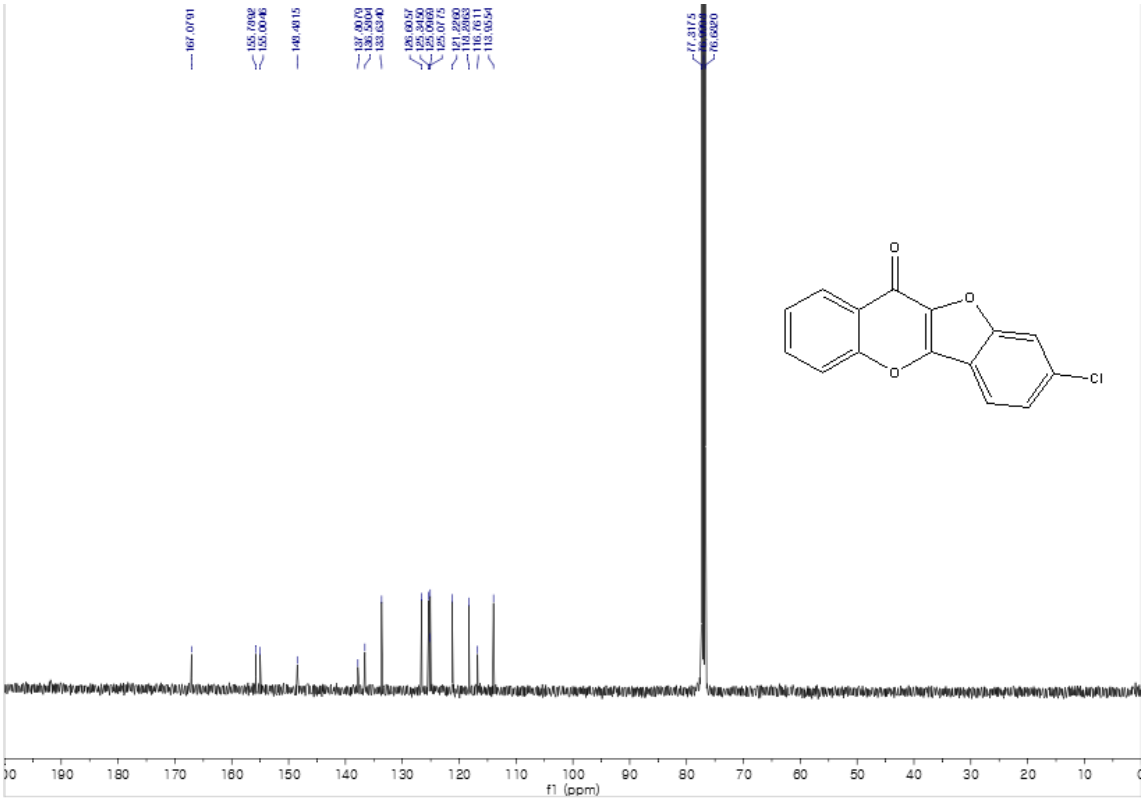


100 MHz, ^{13}C NMR in $CDCl_3$

8-chloro-11H-benzofuro[3,2-b]chromen-11-one (2n)

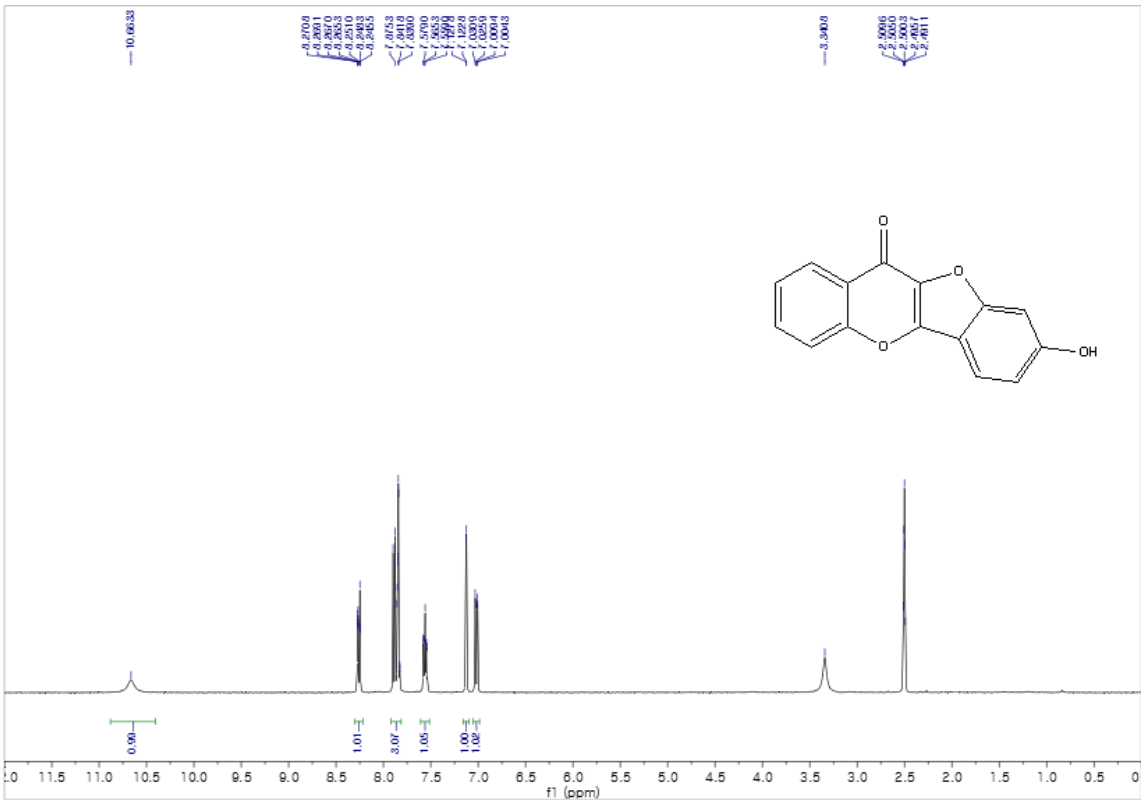


400 MHz, ^{1}H NMR in $CDCl_3$

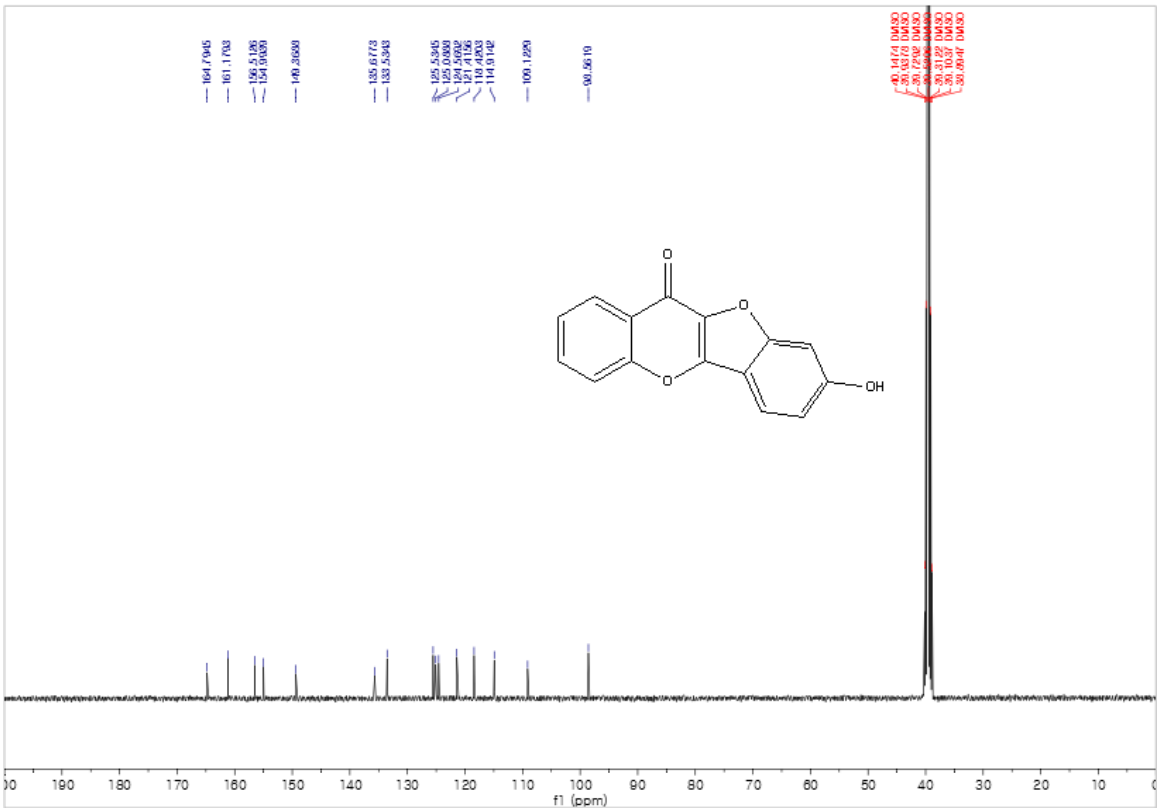


100 MHz, ^{13}C NMR in $CDCl_3$

8-hydroxy-11H-benzofuro[3,2-b]chromen-11-one (2o)

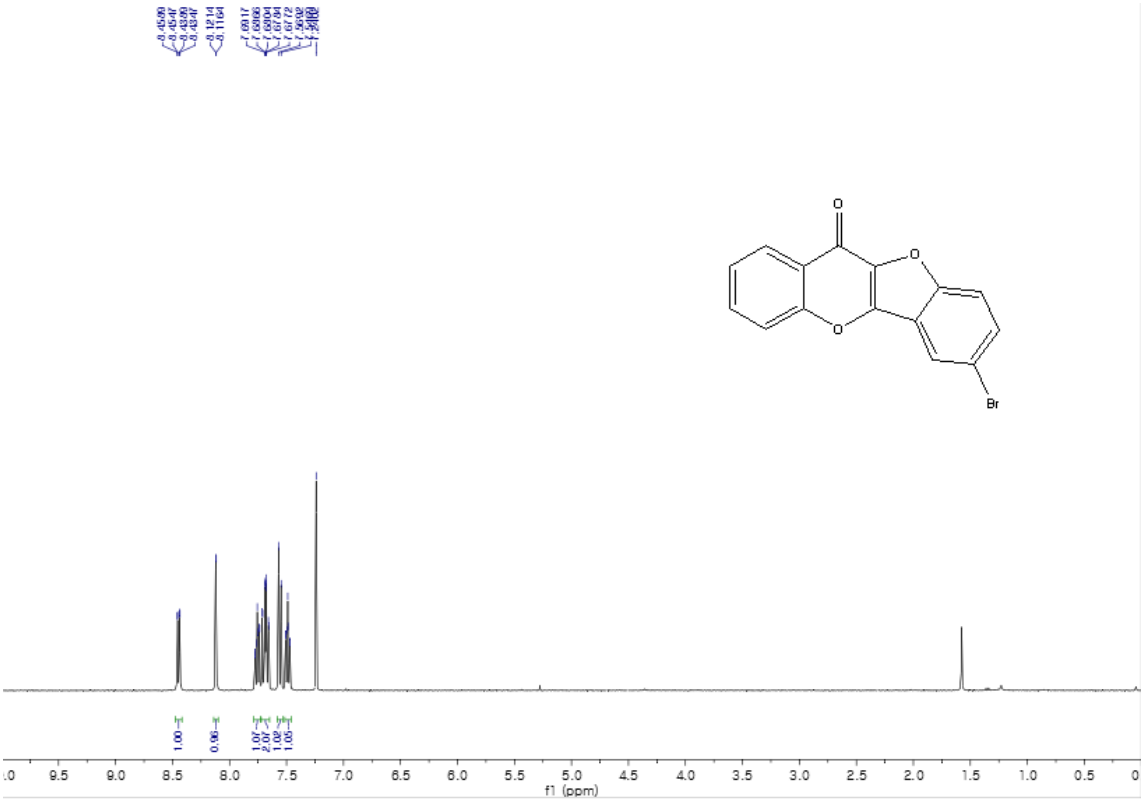


400 MHz, ^{1}H NMR in DMSO-d$_6$

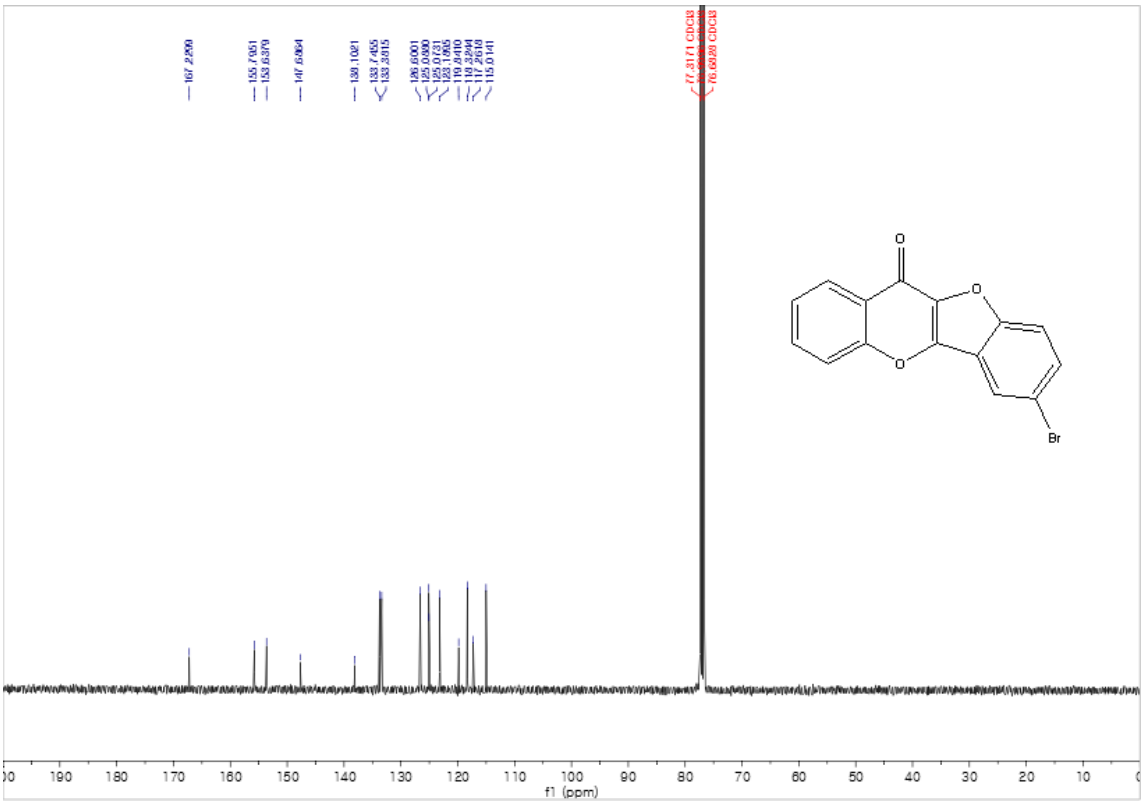


100 MHz, ^{13}C NMR in DMSO-d$_6$

7-bromo-11H-benzofuro[3,2-b]chromen-11-one (2p)

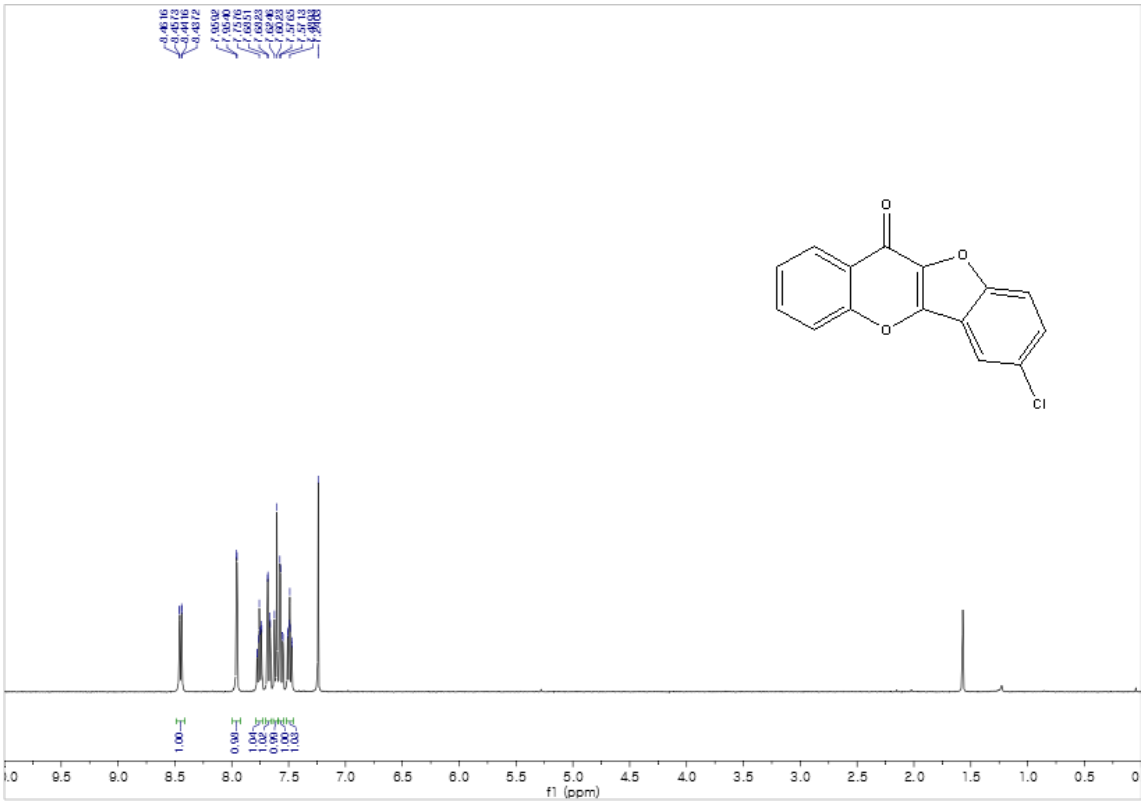


400 MHz, ^{1}H NMR in $CDCl_3$

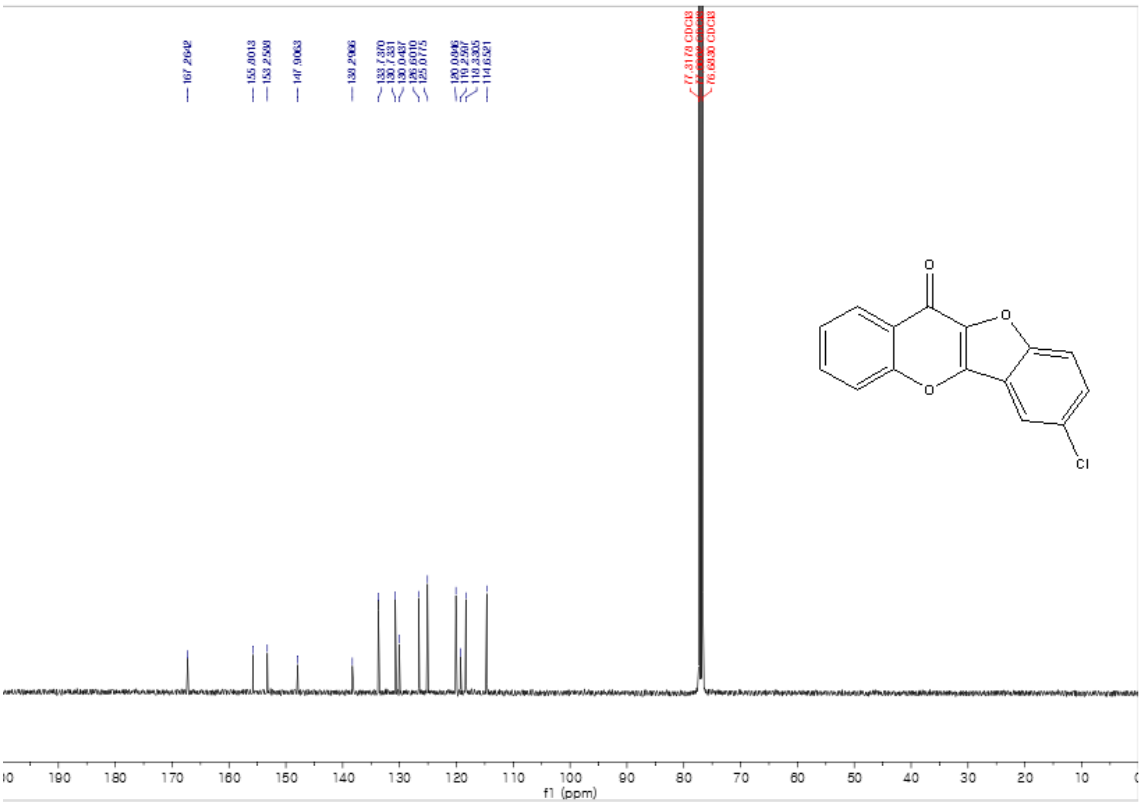


100 MHz, ^{13}C NMR in $CDCl_3$

7-chloro-11H-benzofuro[3,2-b]chromen-11-one (2q)

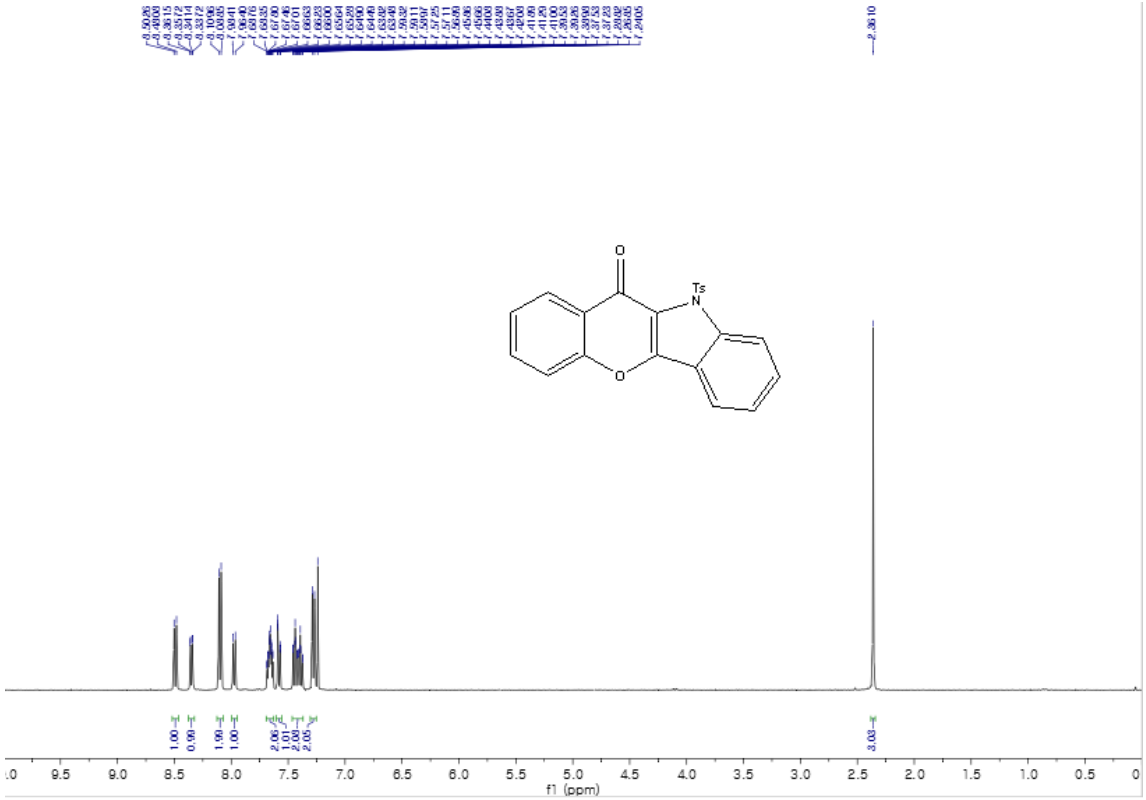


400 MHz, ^{1}H NMR in $CDCl_3$

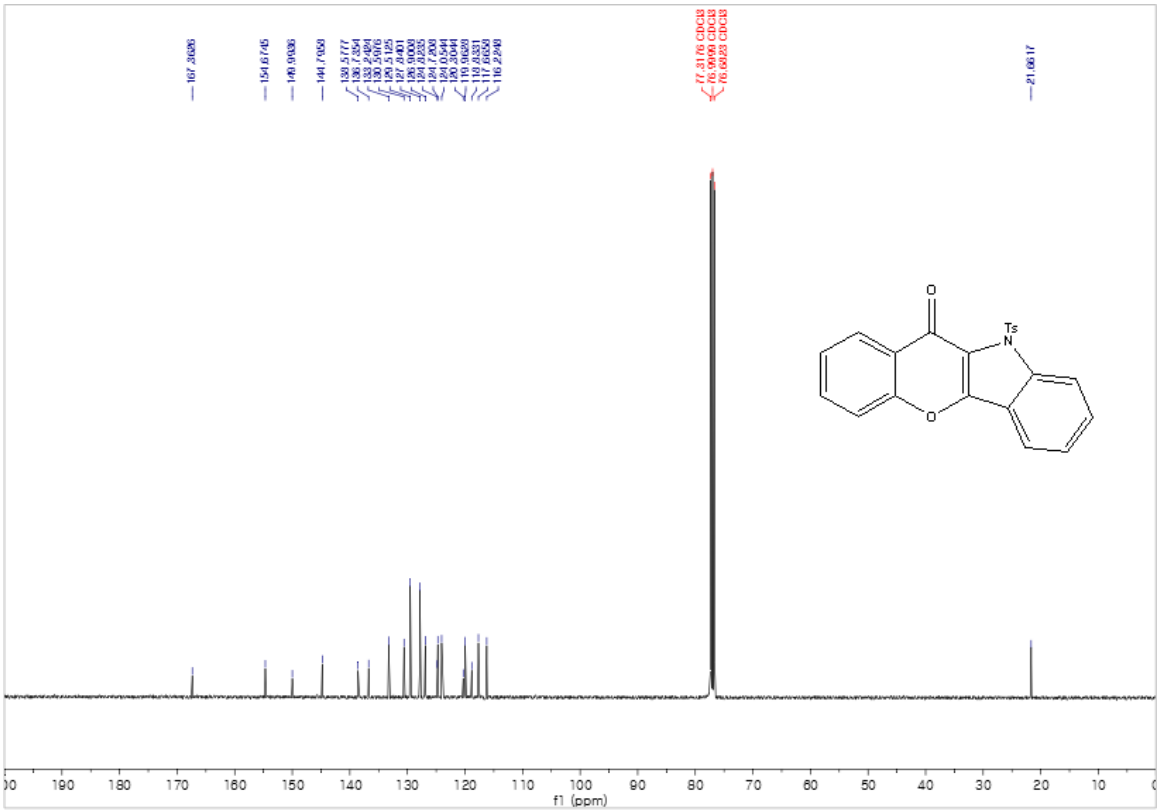


100 MHz, ^{13}C NMR in $CDCl_3$

10-tosylchromeno[3,2-b]indol-11(10H)-one (2r)

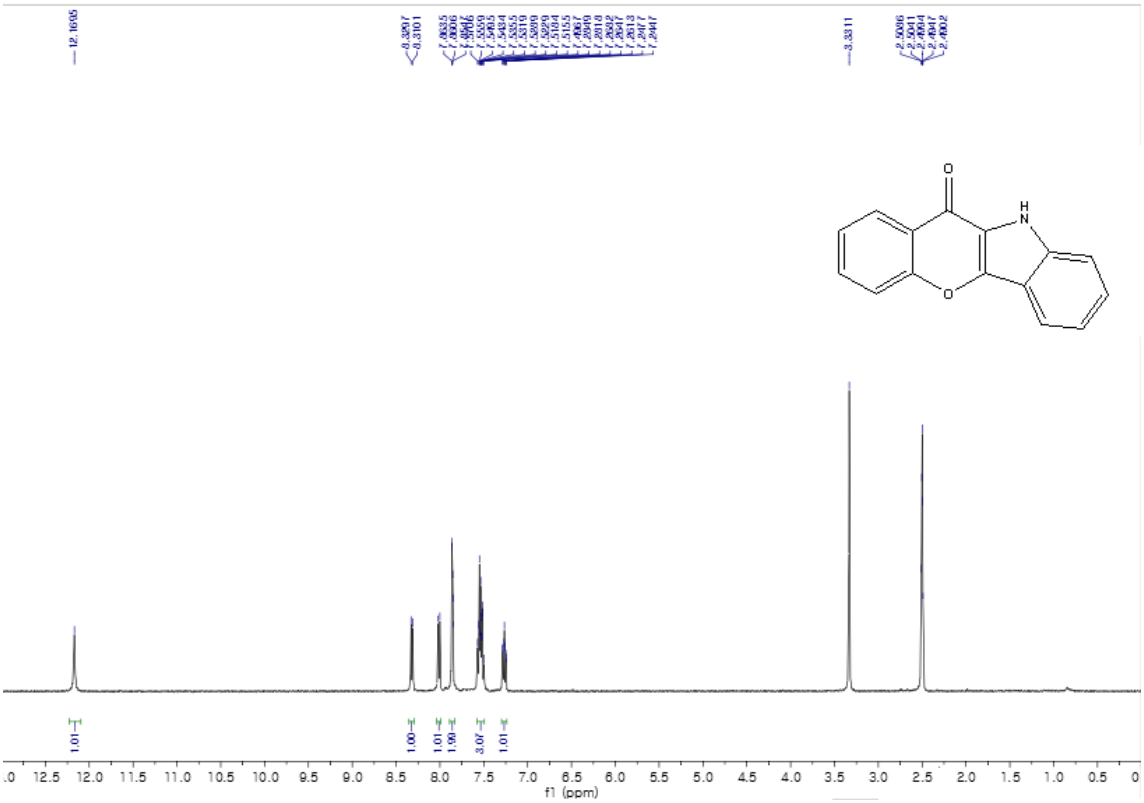


400 MHz, ^{1}H NMR in $CDCl_3$

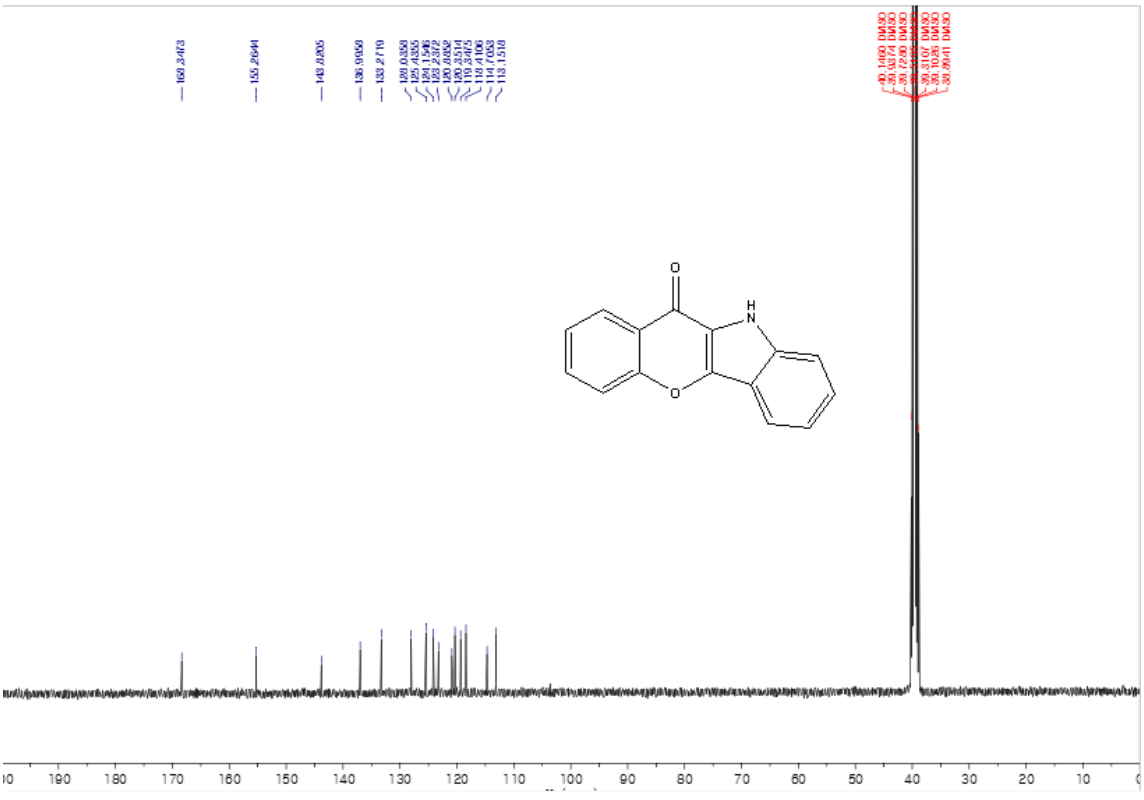


100 MHz, ^{13}C NMR in $CDCl_3$

chromeno[3,2-b]indol-11(10H)-one (2s)

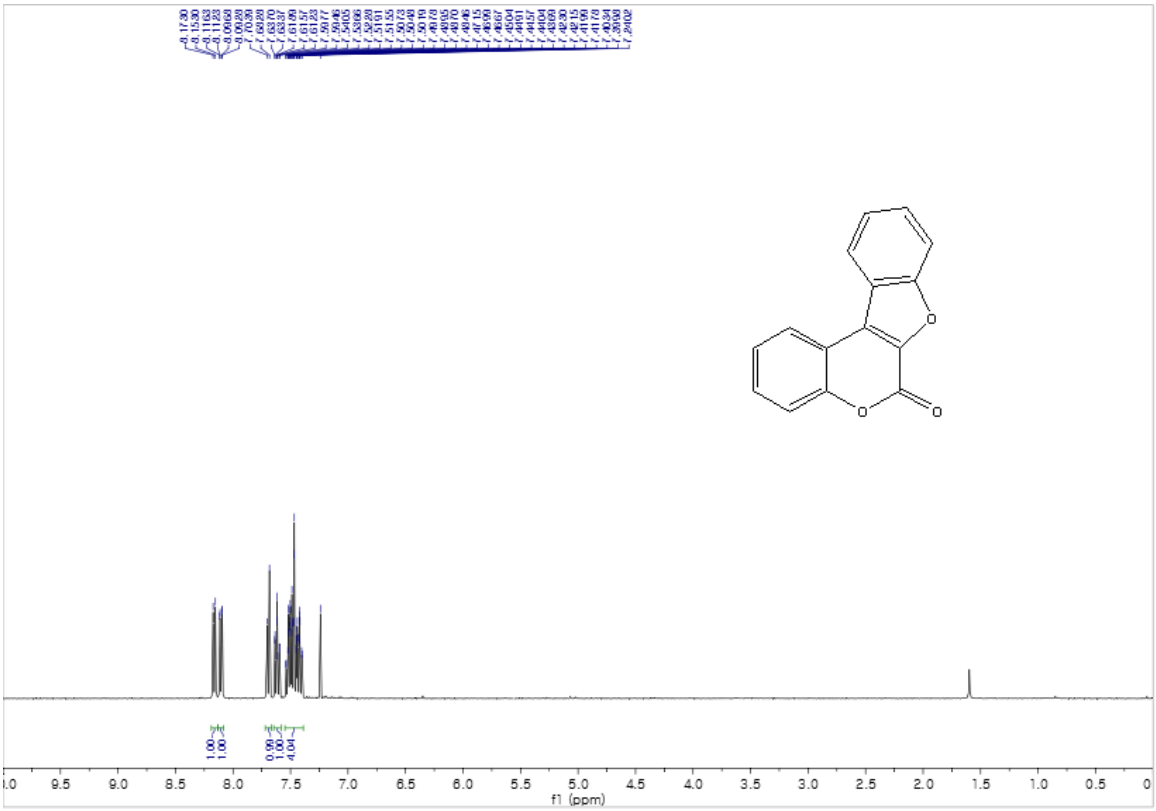


400 MHz, ^{1}H NMR in DMSO-d$_6$

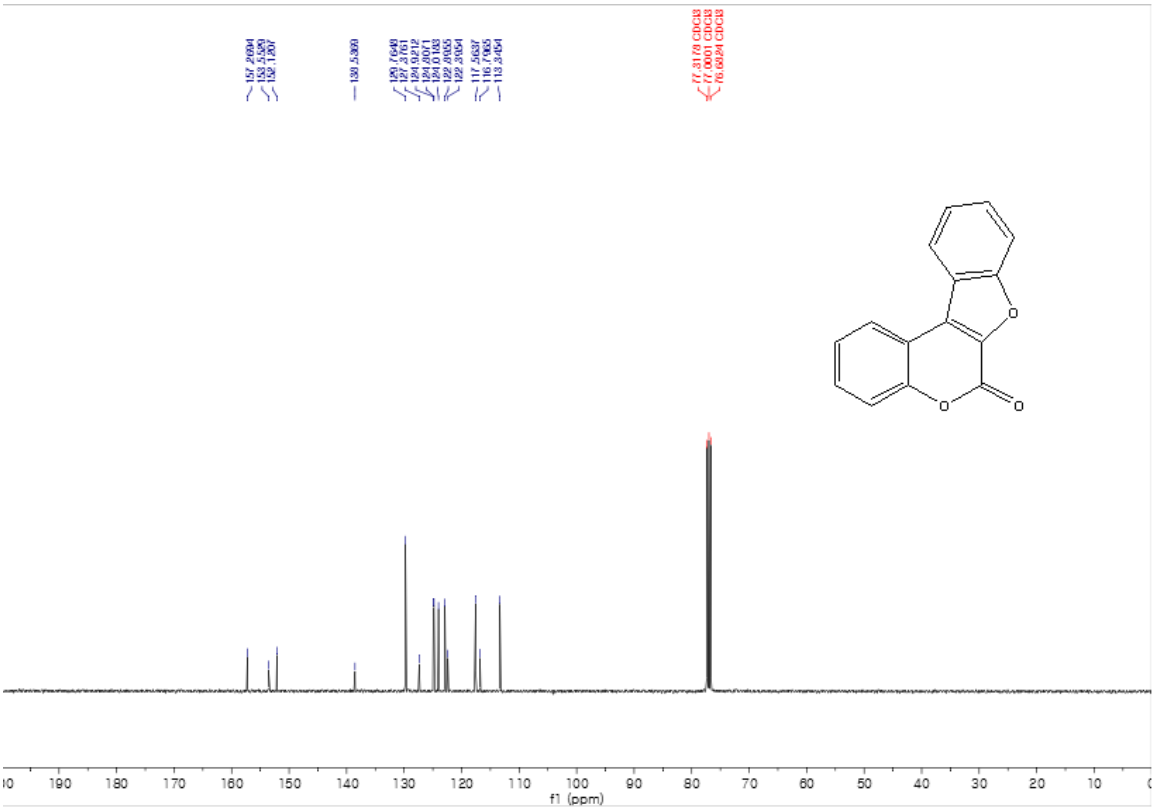


100 MHz, ^{13}C NMR in DMSO-d$_6$

6H-benzofuro[2,3-c]chromen-6-one (4a)

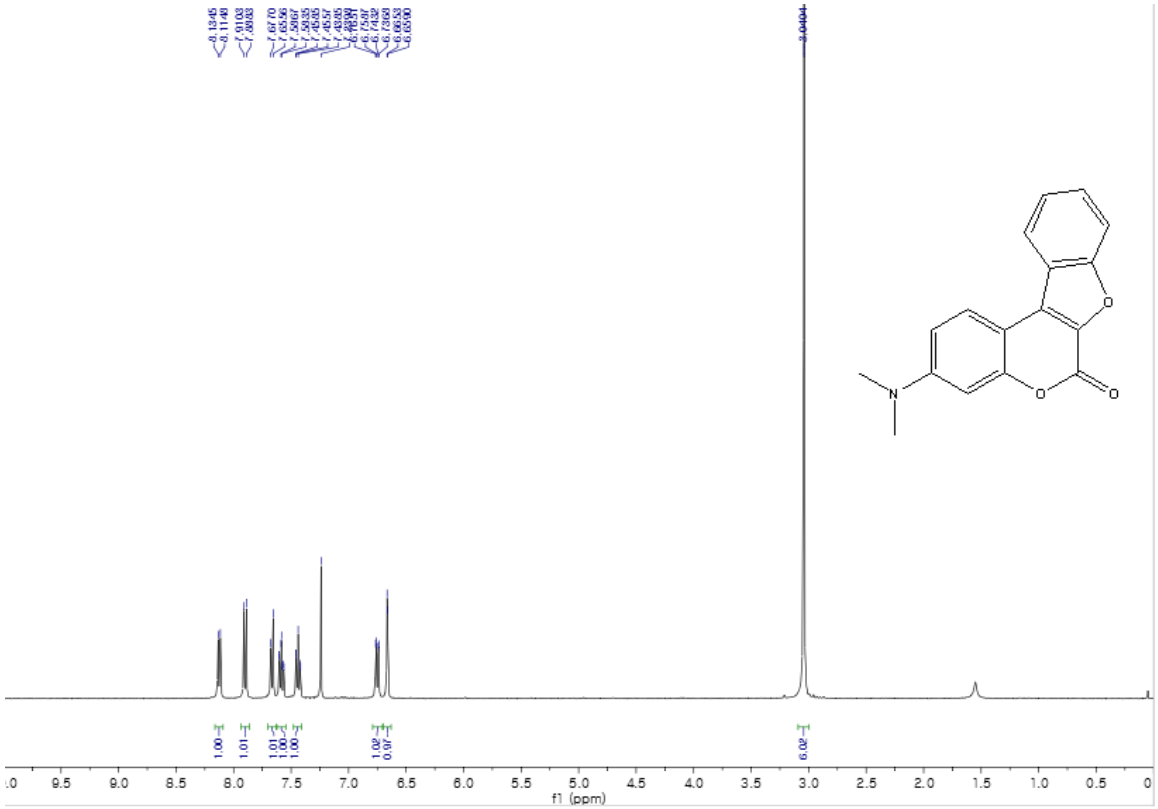


400 MHz, ^{1}H NMR in $CDCl_3$

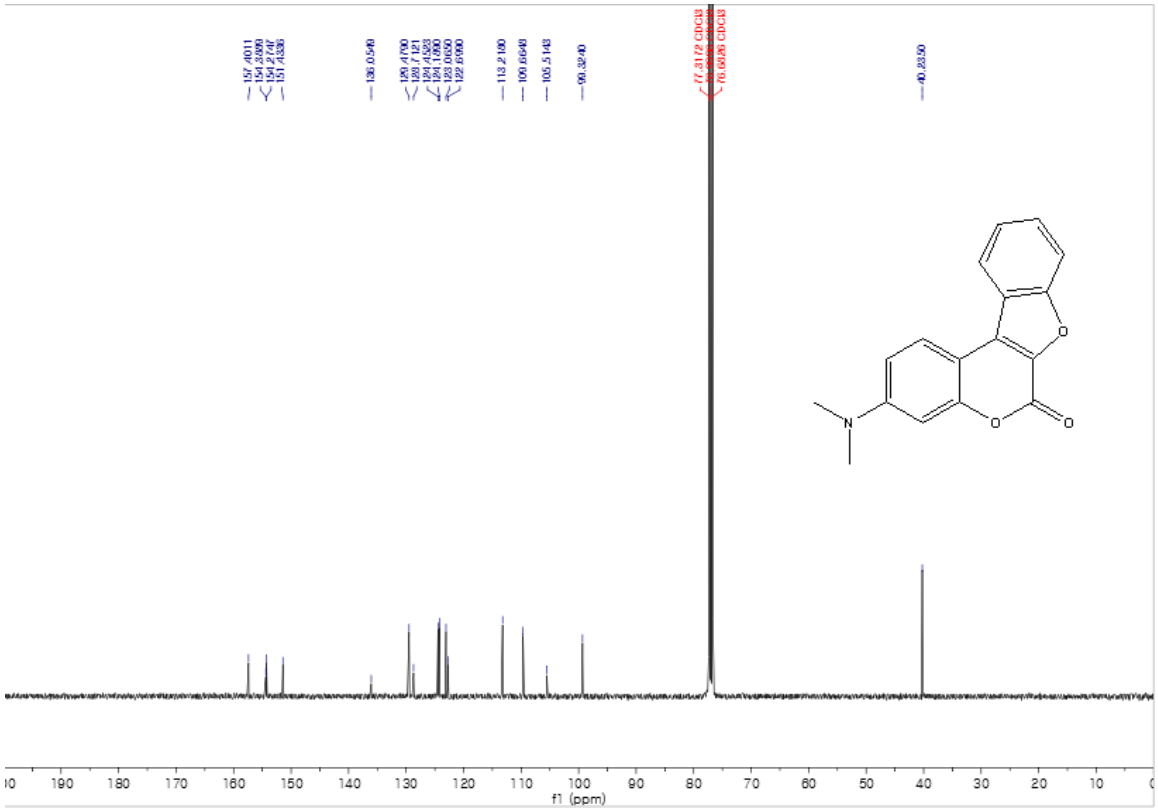


100 MHz, ^{13}C NMR in $CDCl_3$

3-(dimethylamino)-6H-benzofuro[2,3-c]chromen-6-one (4b)

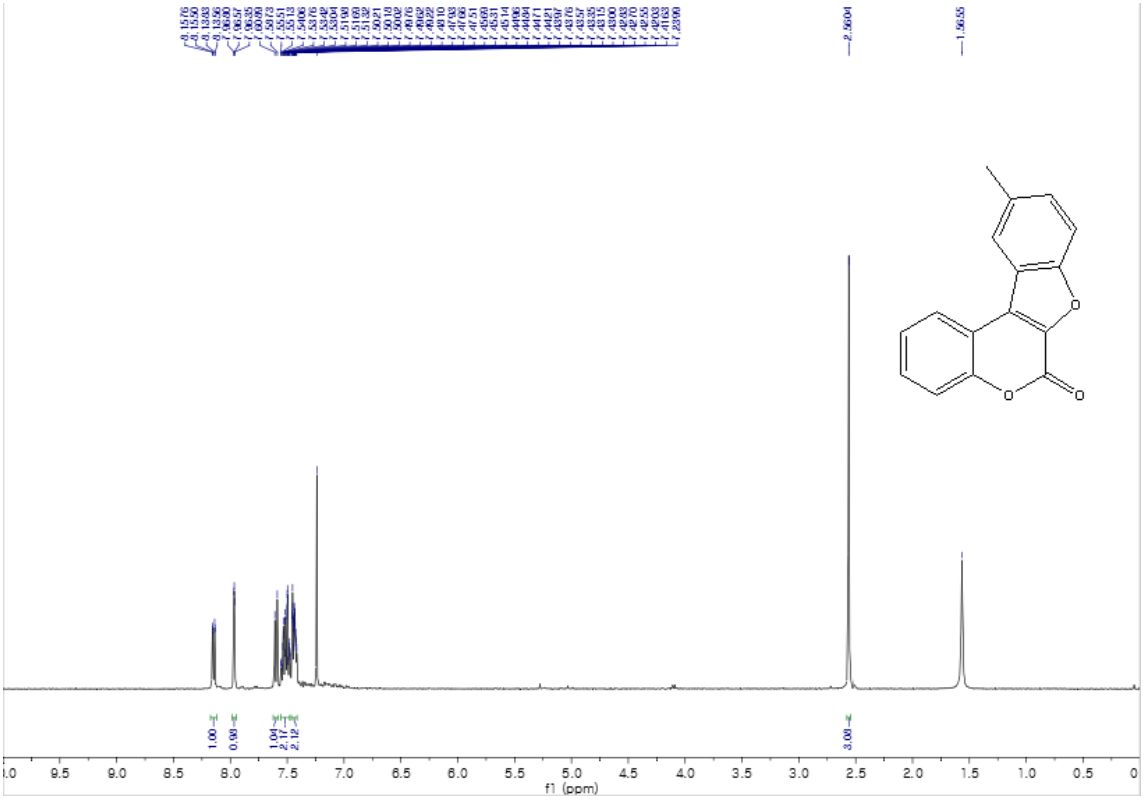


400 MHz, ^{1}H NMR in $CDCl_3$

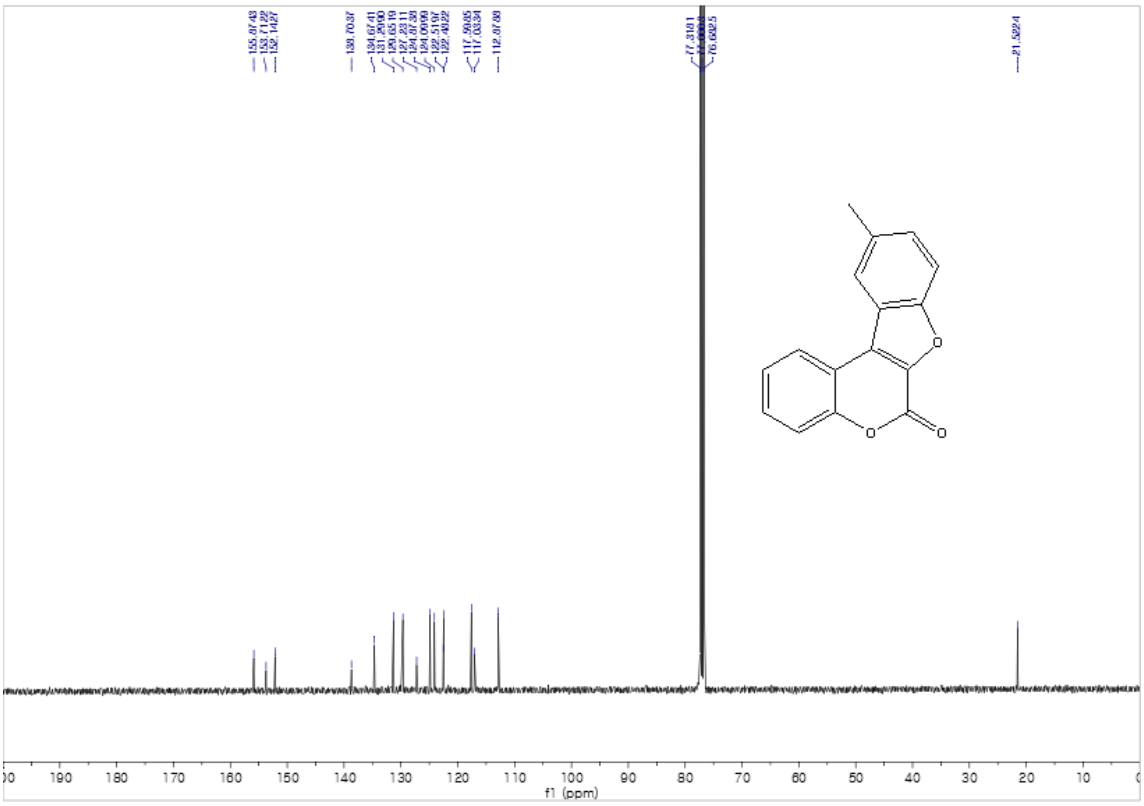


100 MHz, ^{13}C NMR in $CDCl_3$

10-methyl-6H-benzofuro[2,3-c]chromen-6-one (4c)

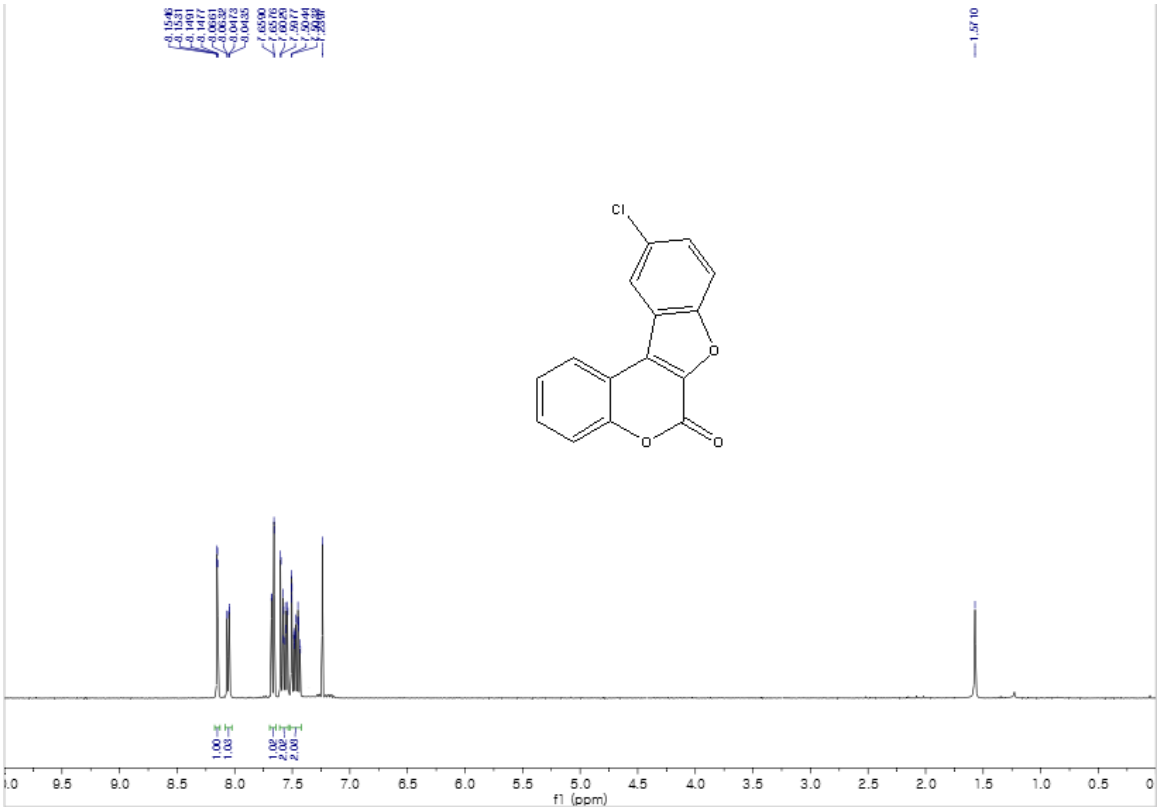


400 MHz, ^{1}H NMR in $CDCl_3$

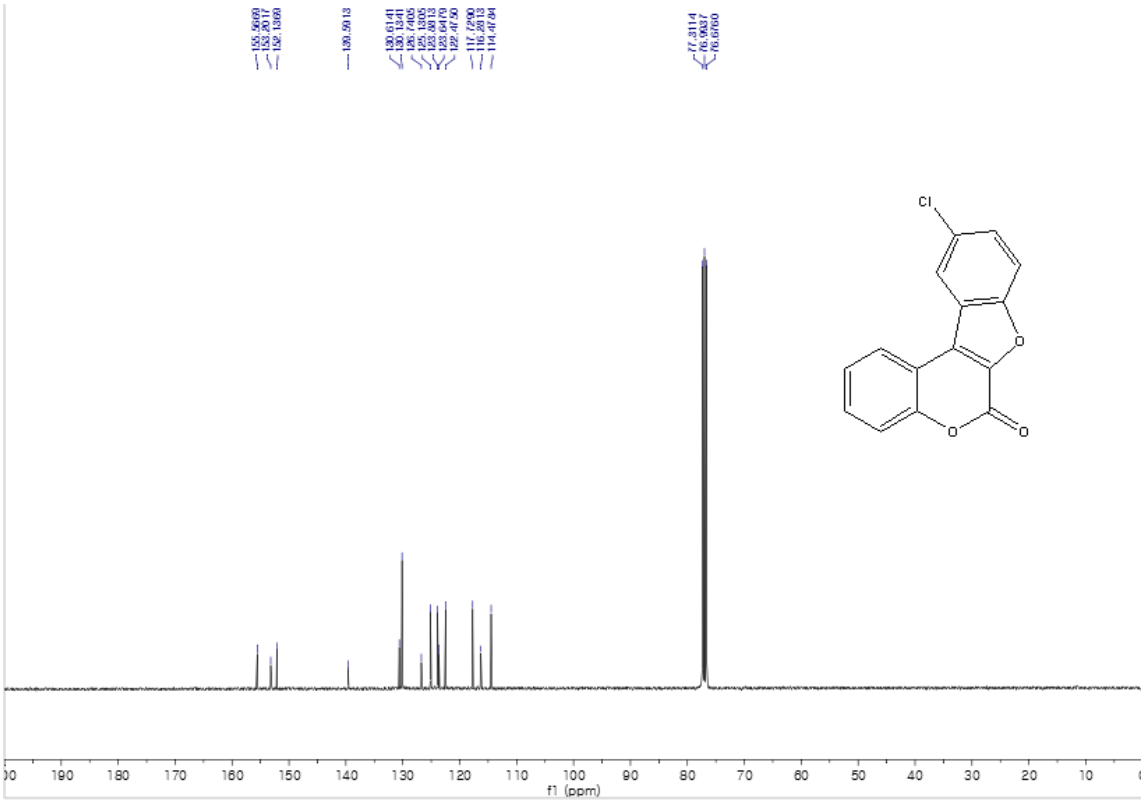


100 MHz, ^{13}C NMR in $CDCl_3$

10-chloro-6H-benzofuro[2,3-c]chromen-6-one (4d)

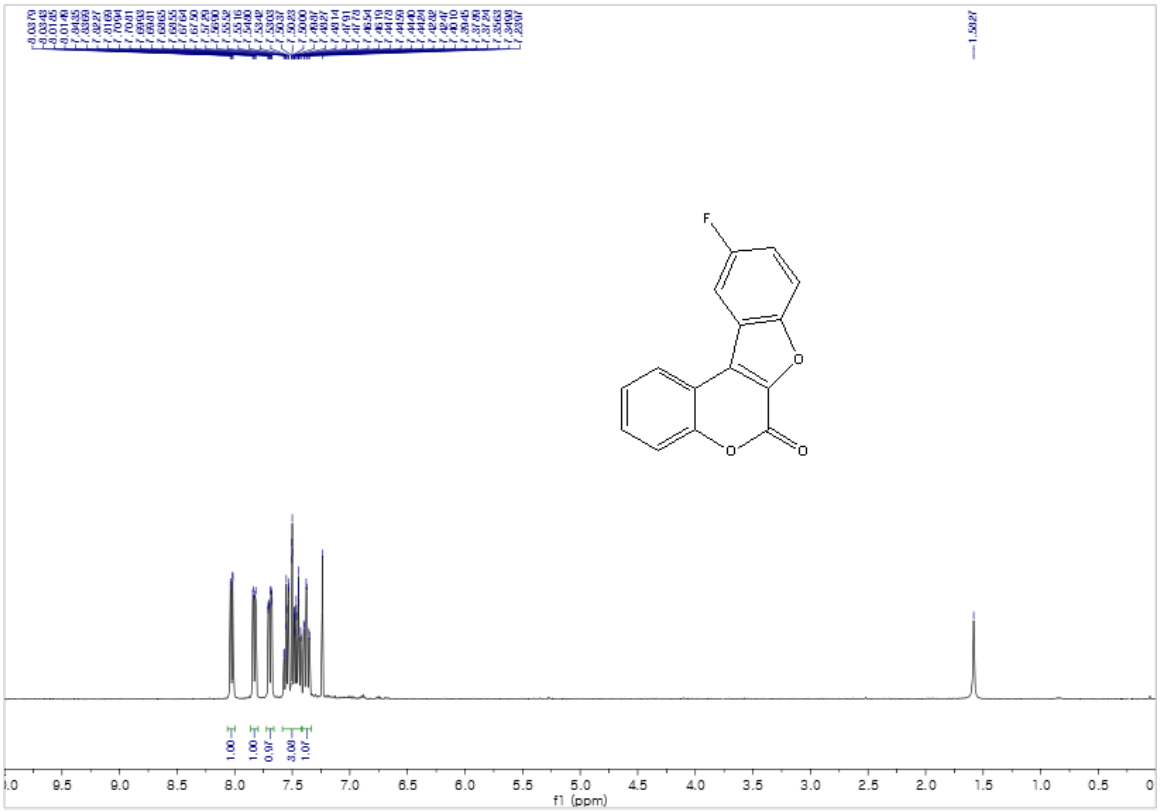


400 MHz, ^{1}H NMR in $CDCl_3$

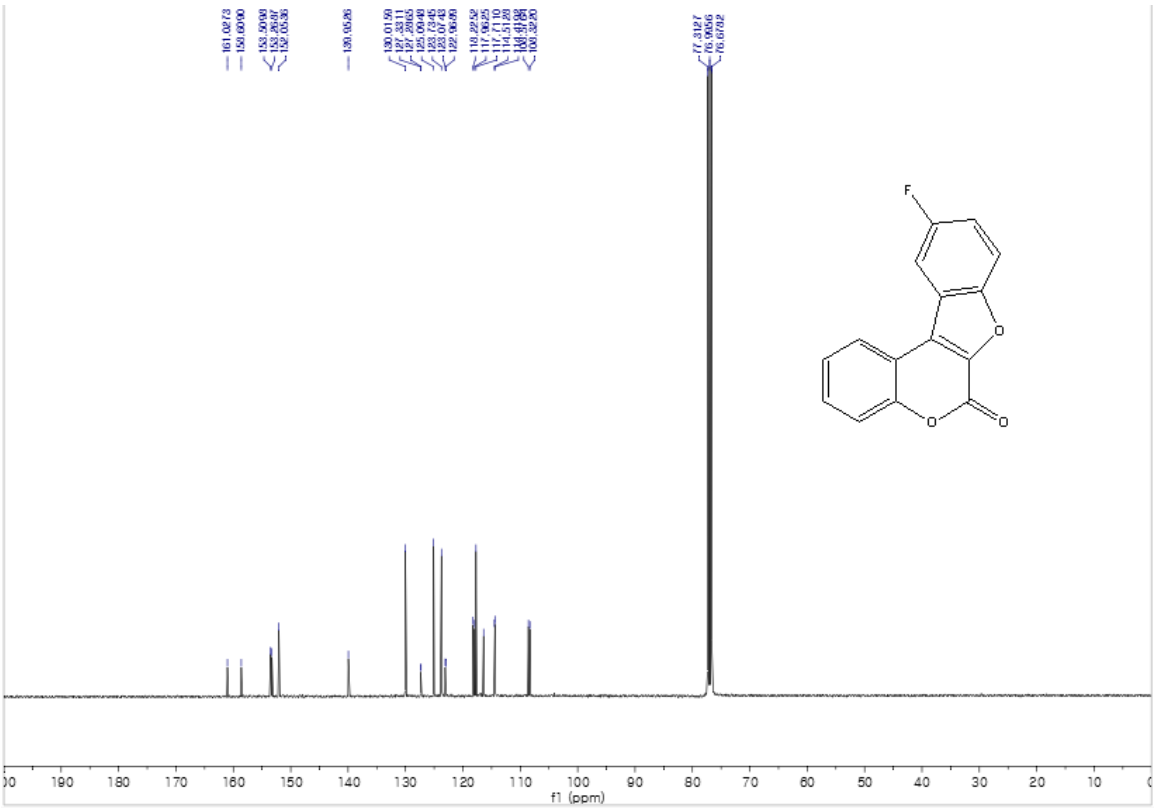


100 MHz, ^{13}C NMR in $CDCl_3$

10-fluoro-6H-benzofuro[2,3-c]chromen-6-one (4e)

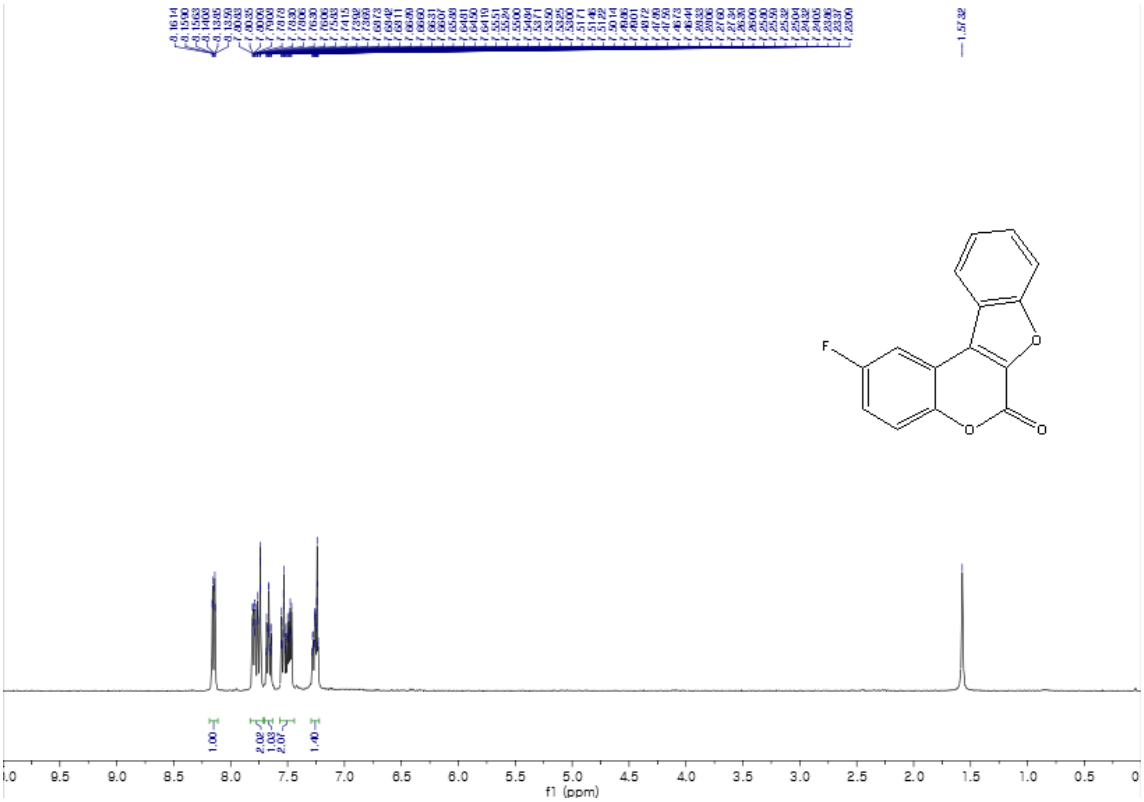


400 MHz, ^{1}H NMR in $CDCl_3$

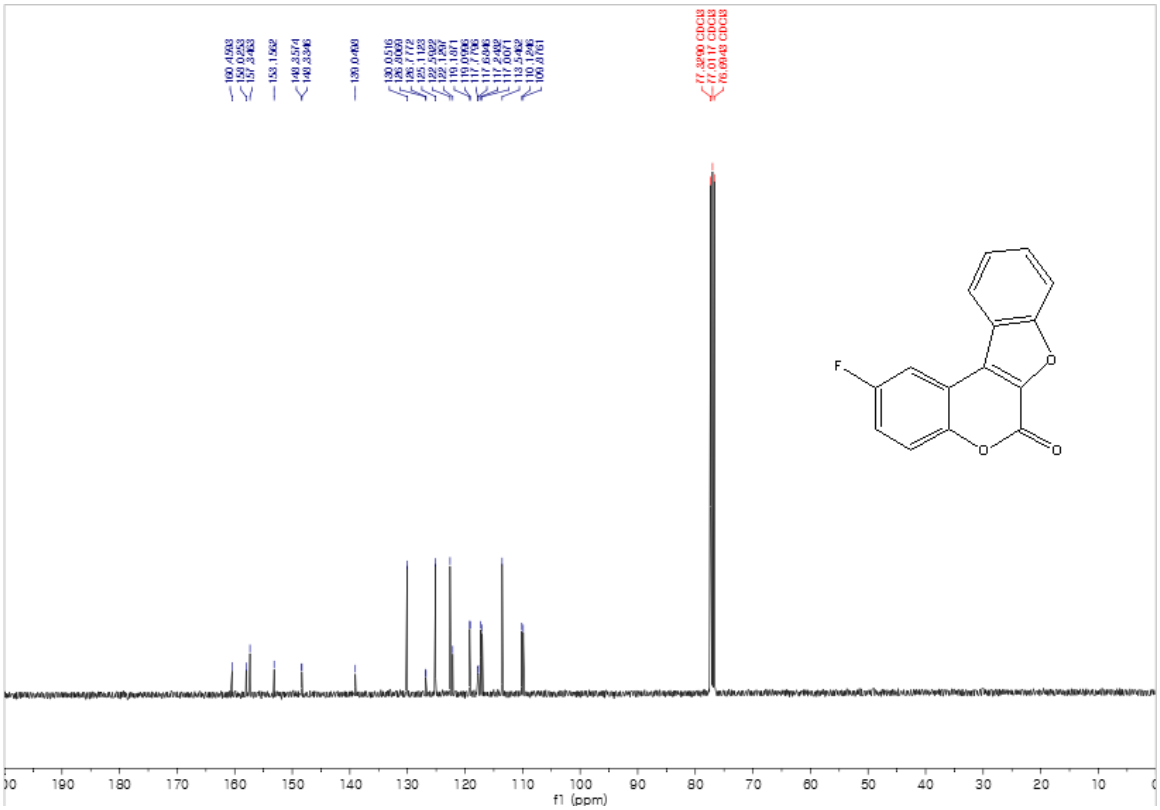


100 MHz, ^{13}C NMR in $CDCl_3$

2-fluoro-6H-benzofuro[2,3-c]chromen-6-one (4f)

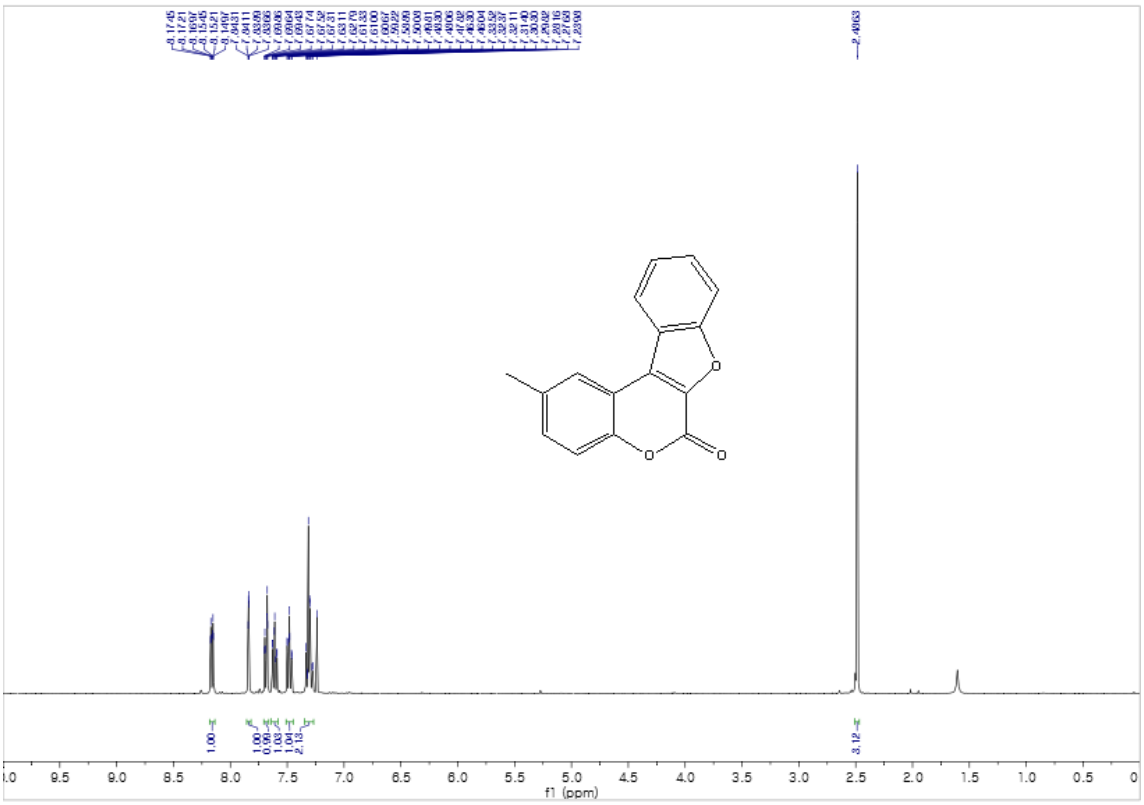


400 MHz, ^{1}H NMR in $CDCl_3$

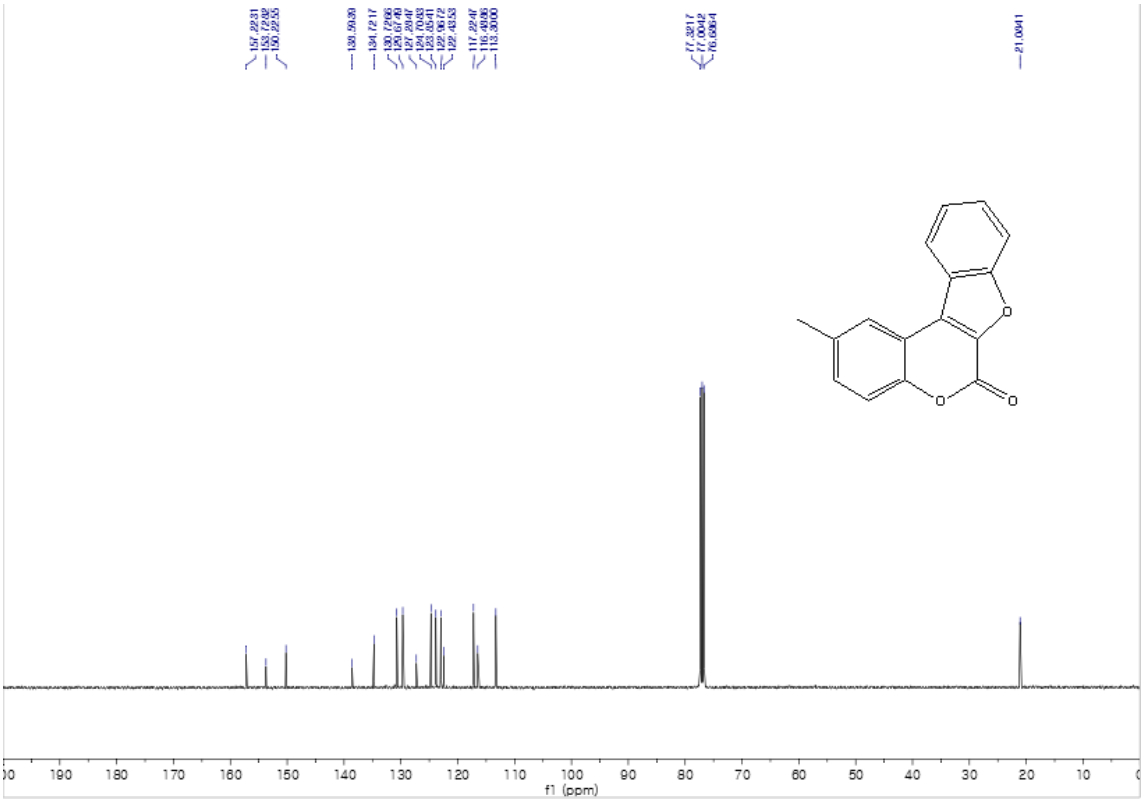


100 MHz, ^{13}C NMR in $CDCl_3$

2-methyl-6H-benzofuro[2,3-c]chromen-6-one (4g)



400 MHz, ^{1}H NMR in $CDCl_3$



100 MHz, ^{13}C NMR in $CDCl_3$