Supporting Information

Synthesis of Heterocyclic-Fused Benzopyrans via the Pd(II)-Catalyzed C–H Alkenylation/C–O Cyclization of Flavones and Coumarins

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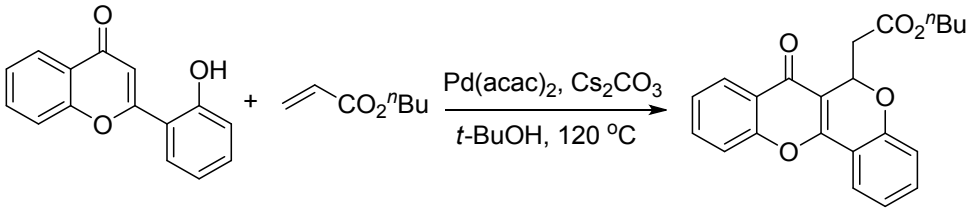
I. Optimization Study

Appendix I

Spectral Copies of 1H- and 13C-NMR Data Obtained in this Study

I. Optimization Study

Table S1. Oxidant screening.[a]

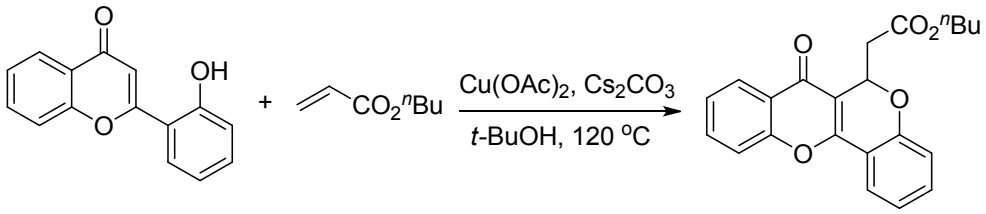


Entry	Oxidant (equiv)	Time	Yield (%)
1	AgOAc (2)	3h	-
2	$Cu(OAc)_2 \cdot H_2O$ (3)	3h	53%
3	CuOAc (3)	5h	56%
4	$Cu(TFA)_2 \cdot nH_2O$ (3)	11h	> 10%
5	$Cu(OTf)_2$ (3)	3h	-
6	$Cu(OPiv)_2$ (3)	3h	-
7	$CuCO_3 \cdot Cu(OH)_2$ (3)	11h	> 10%
8	CuO (3)	11h	> 10%
9	$Cu(acac)_2$ (3)	11h	> 10%
10	$K_2S_2O_8$ (3)	19h	trace
11	$Ce(SO_4)_2$ (3)	19h	trace
12	$Mn(OAc)_3 \cdot 2H_2O$ (2)	6h	38%
13	$PhI(OAc)_2$ (2)	3h	-
14	CAN (2)	19h	trace
15	Oxone (2)	19h	12%
16	$FeCl_3$ (3)	3h	-
17	DDQ (2)	3h	-
18	TEMPO (2)	3h	-
19	$PhCO_3tBu$ (2)	3h	12%
20	MnO_2 (2)	7h	11%
21	$MnCl_2$ (3)	7h	13%
22	CuF_2 (3)	11h	10%

23	$CuCl_2$ (3)	3h	trace
24	$CuBr_2$ (3)	24h	31%
25	CuCl (3)	24h	17%
26	CuBr (3)	11h	21%
27	CuI (3)	24h	20%

[a] Reactions were conducted with flavone, butyl acrylate (2 equiv), Pd catalyst (0.2 equiv), oxidant, and base (2 equiv) in *t*-BuOH at 120 ºC.

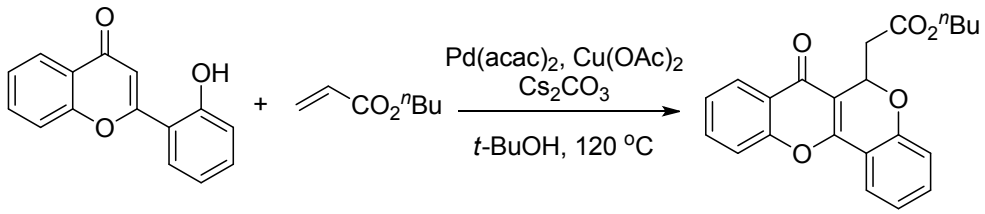
Table S2. Pd screening.[a]



Entry	Oxidant (equiv)	Time	Yield (%)[b]
1	$Pd(TFA)_2$ (0.2)	3h	42%
2	$Pd(OPiv)_2$ (0.2)	3h	53%
3	$Pd(acac)_2$ (0.2)	3h	60%
4	$Pd(SO_4)_2$ (0.2)	3h	39%
5	$Pd(NO_3)_2 \cdot nH_2O$ (0.2)	3h	32%
6	$PdCl_2(TMEDA)_2$ (0.2)	3h	-
7	$Pd(HFac)_2$ (0.2)	3h	48%
8	$Pd(MeCN)_4(BF_4)_2$ (0.2)	3h	48%
9	$PdCl_2$ (0.2)	2.5h	15%
10	$Pd_2(dba)_3$ (0.1)	2.5h	30%
11	$PdCl_2(PPh_3)_2$ (0.1)	2.5h	35%
12	$Pd(dppf)Cl_2$ (0.1)	6h	59%
13	$Pd(PPh_3)_4$ (0.1)	2.5h	45%

[a] Reactions were conducted with flavone, butyl acrylate (2 equiv), Pd catalyst, oxidant (3 equiv), and base (2 equiv) in *t*-BuOH at 120 ºC.

Table S3. Additive screening. [a]



Entry	Additive (0.2 equiv)	Yield (%)[b]
1	Al_2O_3	74%
2	V_2O_5	57%
3	$ZnBr_2$	56%
4	$Co(OAc)_2$	56%
5	MnO_2	60%
6	$Mn(OAc)_2{\cdot}3H_2O$	64%
7	LiOTf	65%
8	KOTf	58%
9	$Sm(OTf)_3$	59%
10	$In(OTf)_3$	58%
11	$Sn(OTf)_2$	63%
12	4A MS	43%
13	silica gel	50%

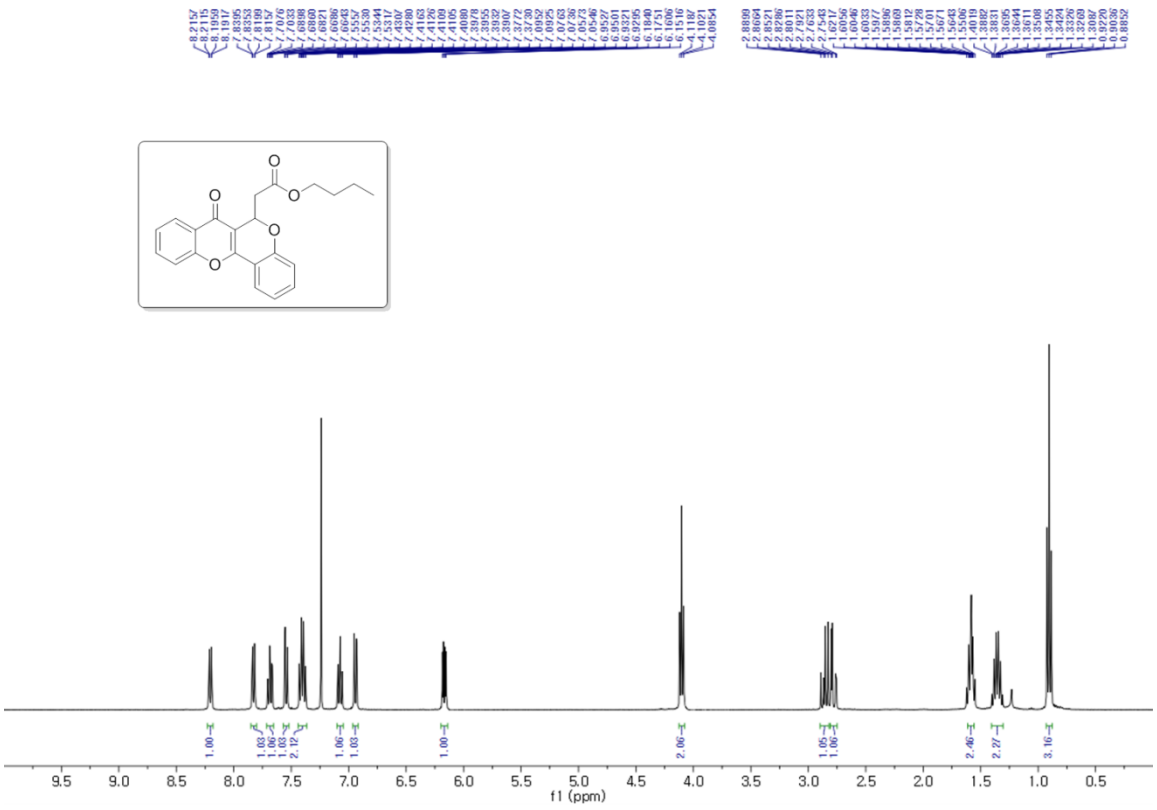
[a] Reactions were conducted with flavone, butyl acrylate (2 equiv), Pd catalyst (0.2 equiv), oxidant (3 equiv), additive (0.2 equiv), and base (2 equiv) in *t*-BuOH at 120 ºC.

Appendix I

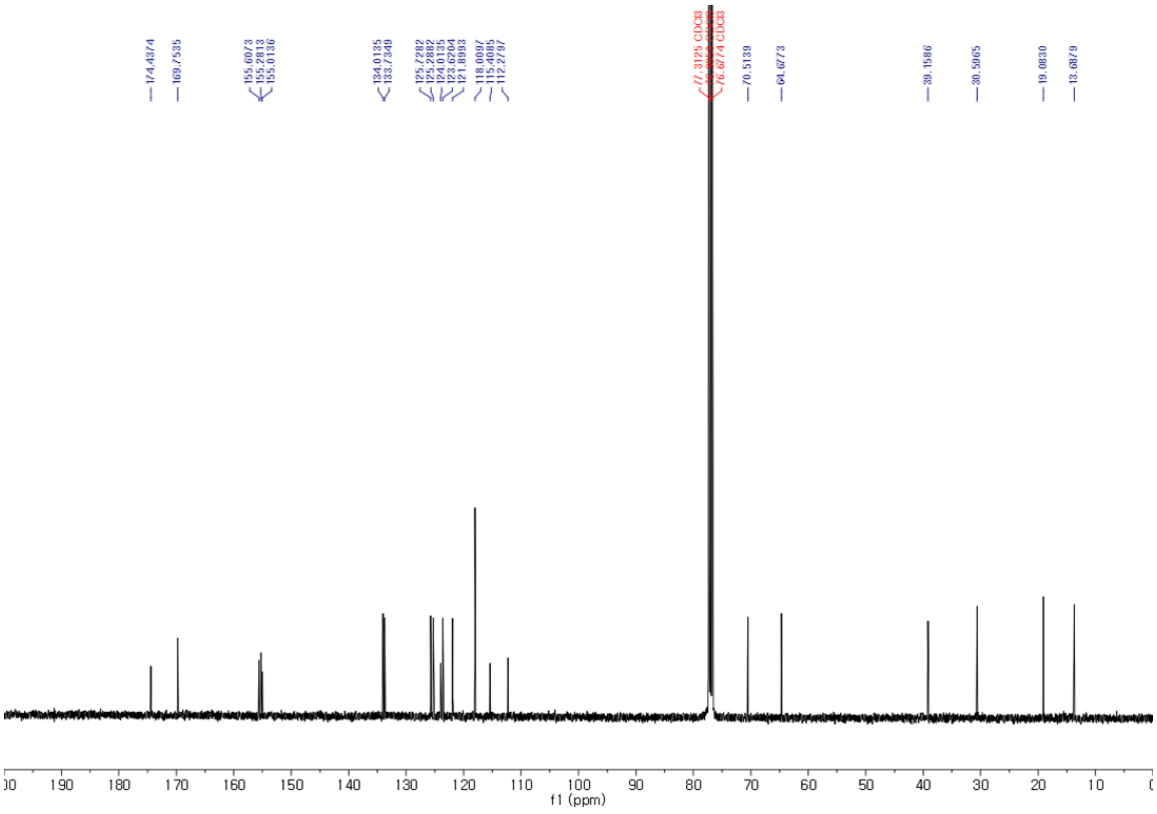
Spectral Copies of ^{1}H and ^{13}C NMR Data

Obtained in this Study

Butyl 2-(7-Oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetate (3a)

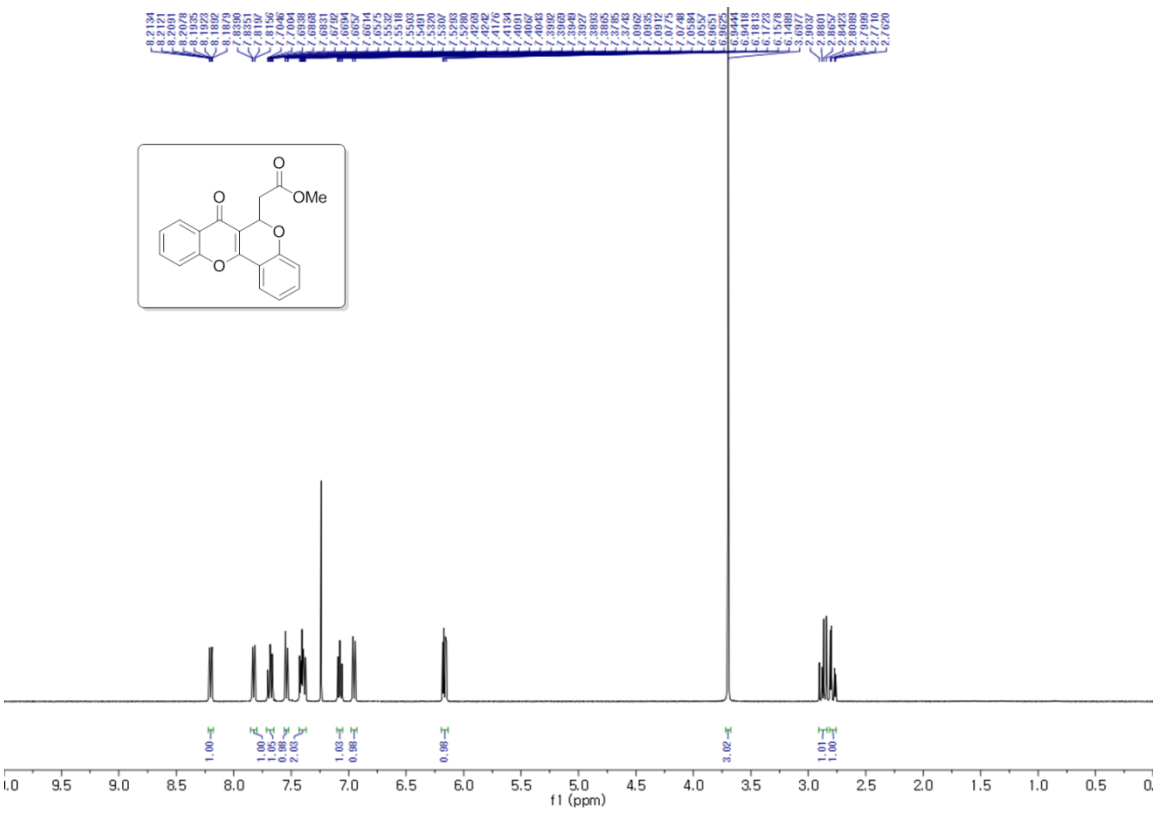


400 MHz, ^{1}H NMR in $CDCl_3$

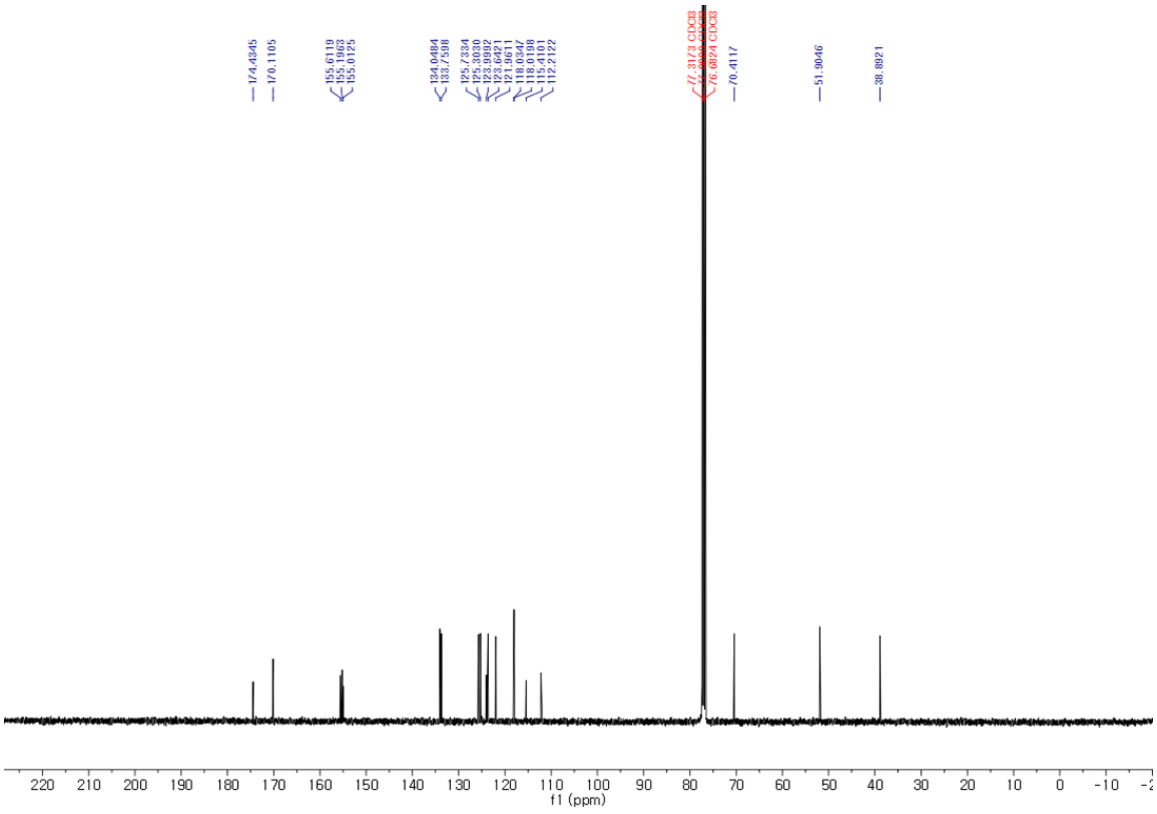


100 MHz, ^{13}C NMR in $CDCl_3$

Methyl 2-(7-Oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetate (3b)

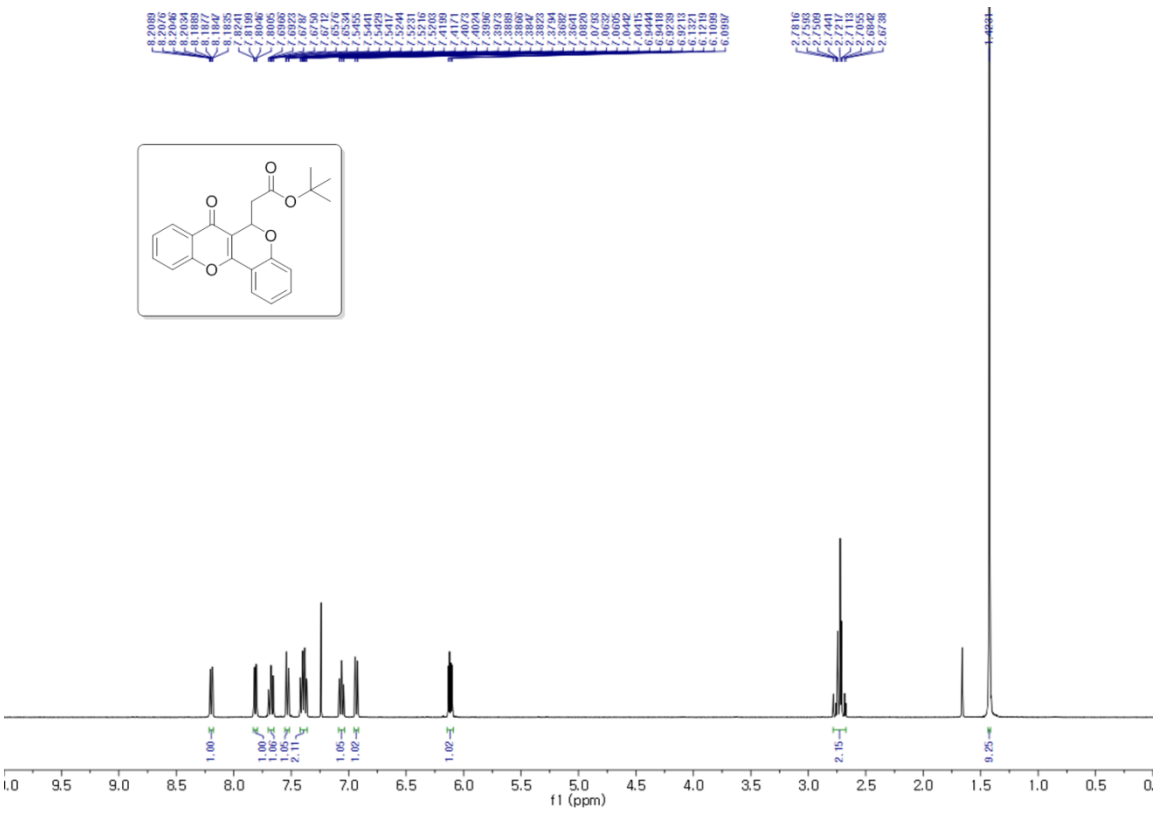


400 MHz, ^{1}H NMR in $CDCl_3$

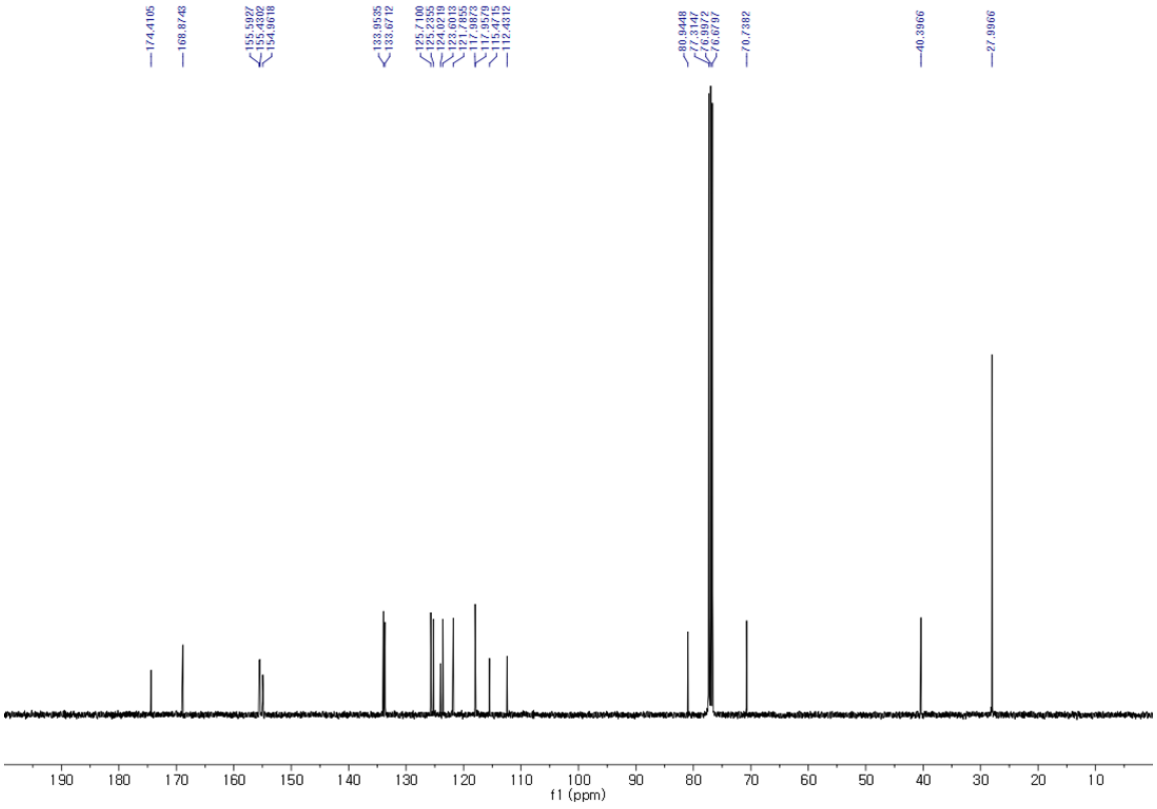


100 MHz, ^{13}C NMR in $CDCl_3$

tert-Butyl 2-(7-Oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetate (3c)

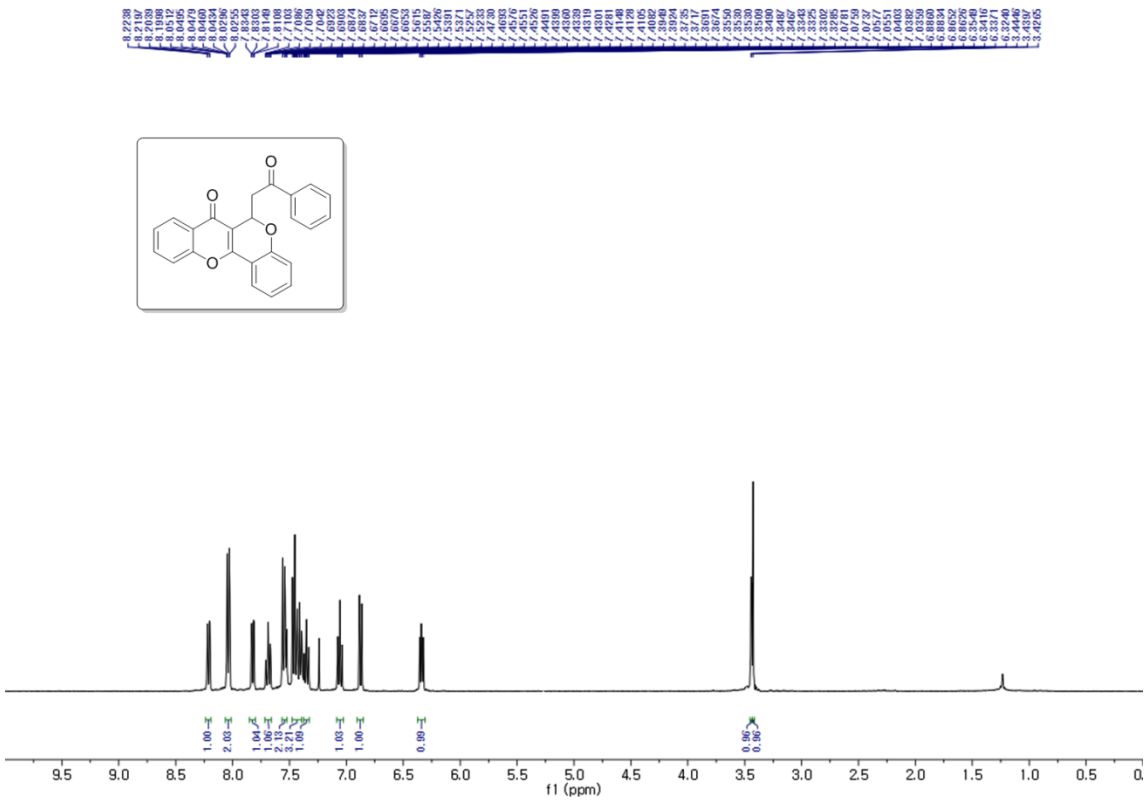


400 MHz, ^{1}H NMR in $CDCl_3$

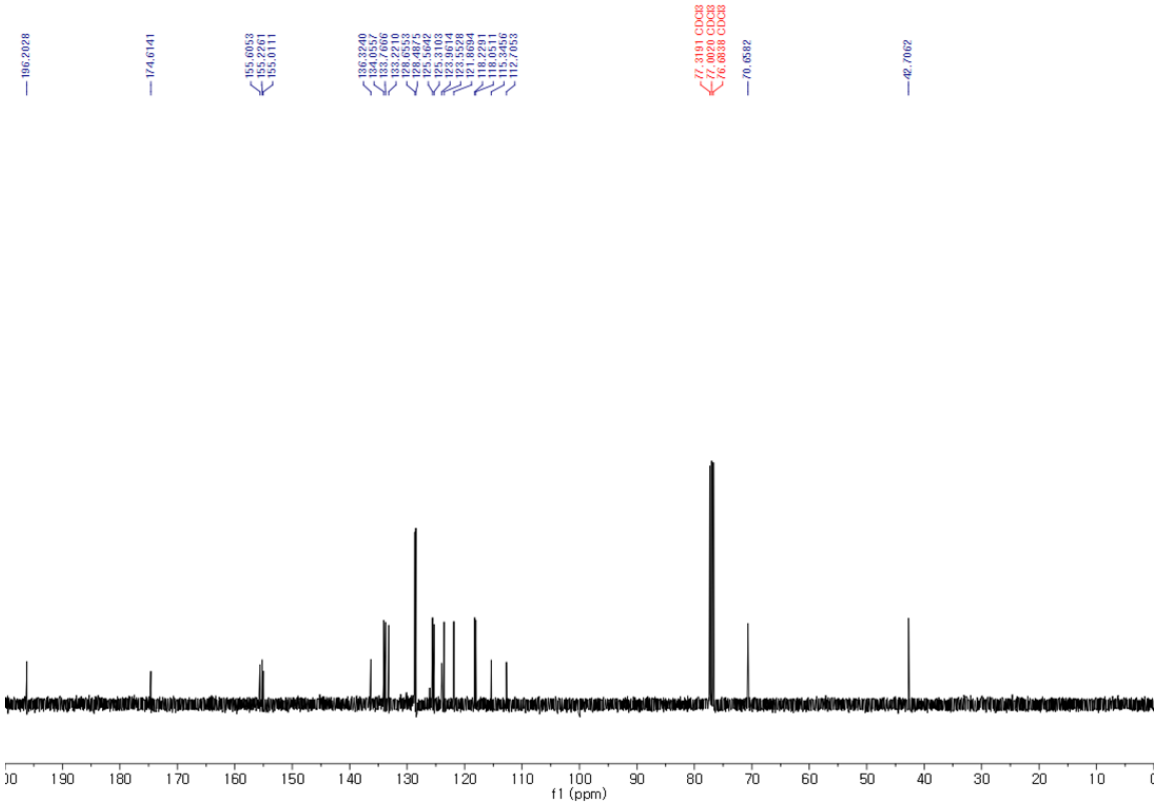


100 MHz, ^{13}C NMR in $CDCl_3$

6-(2-Oxo-2-phenylethyl)chromeno[4,3-b]chromen-7(6H)-one (3d)

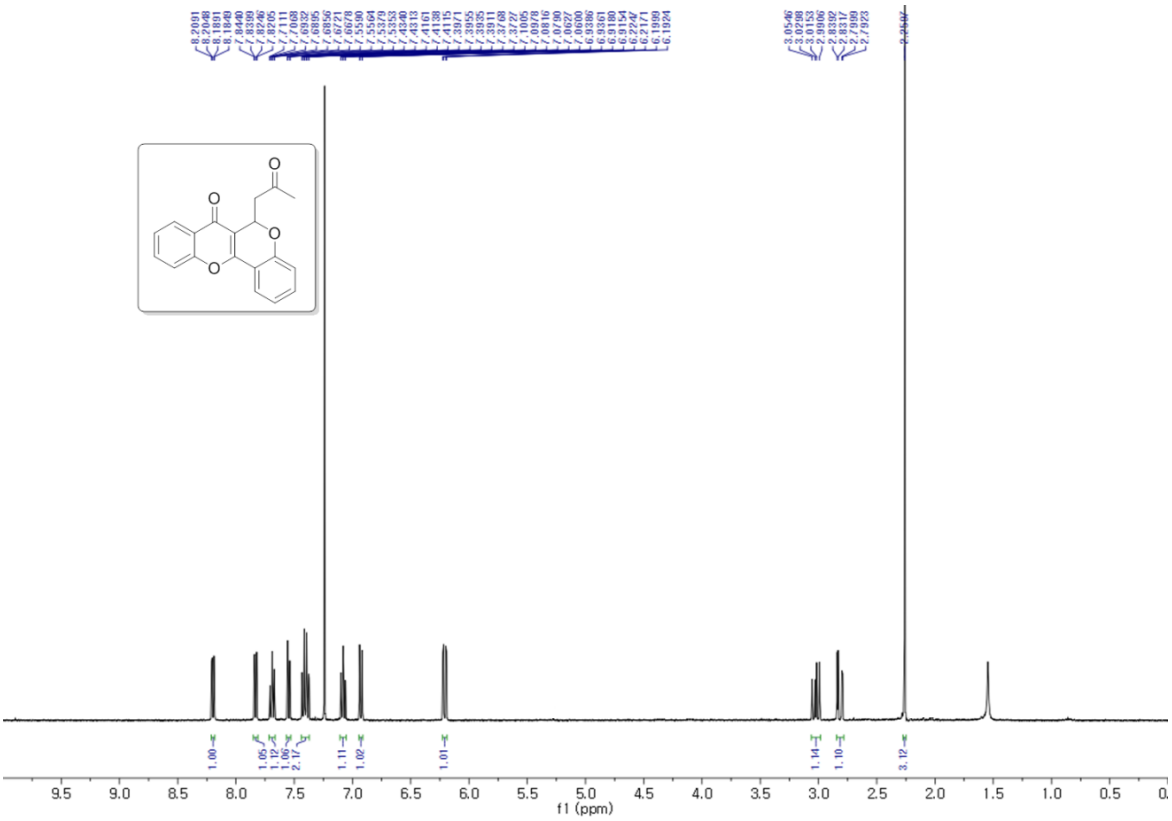


400 MHz, ^{1}H NMR in $CDCl_3$

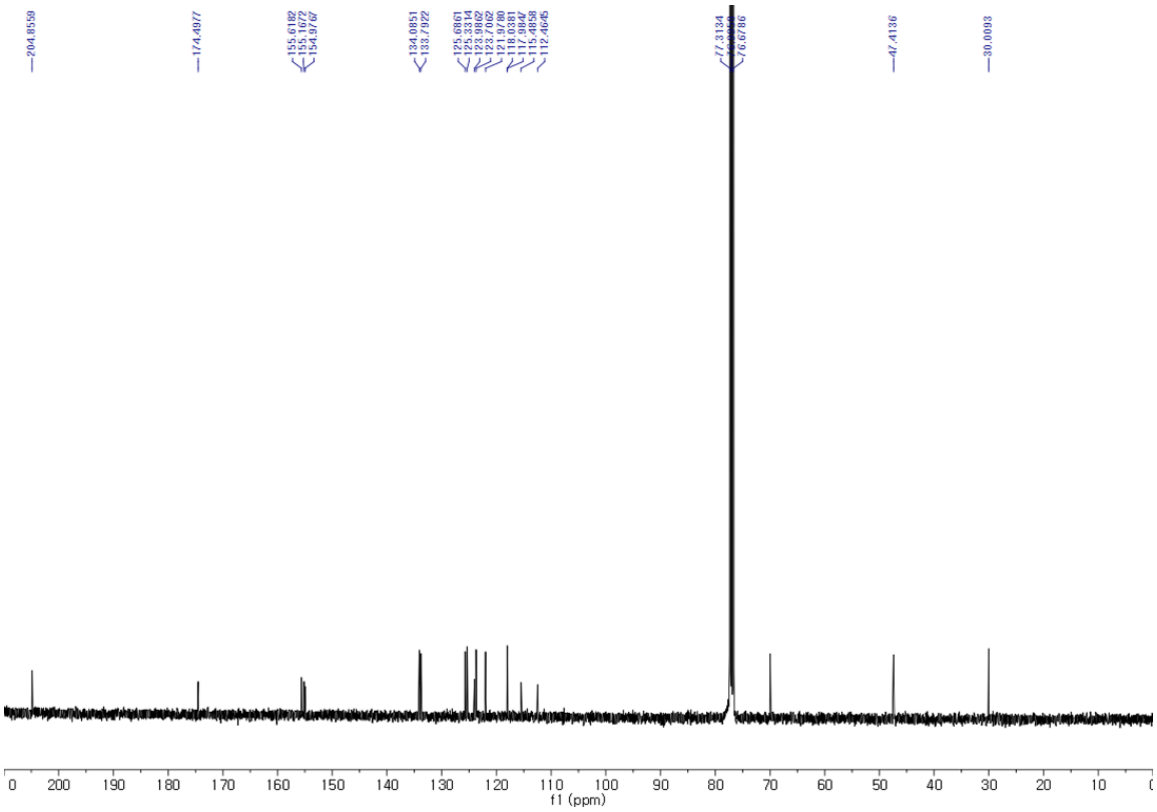


100 MHz, ^{13}C NMR in $CDCl_3$

6-(2-Oxopropyl)chromeno[4,3-b]chromen-7(6H)-one (3e)

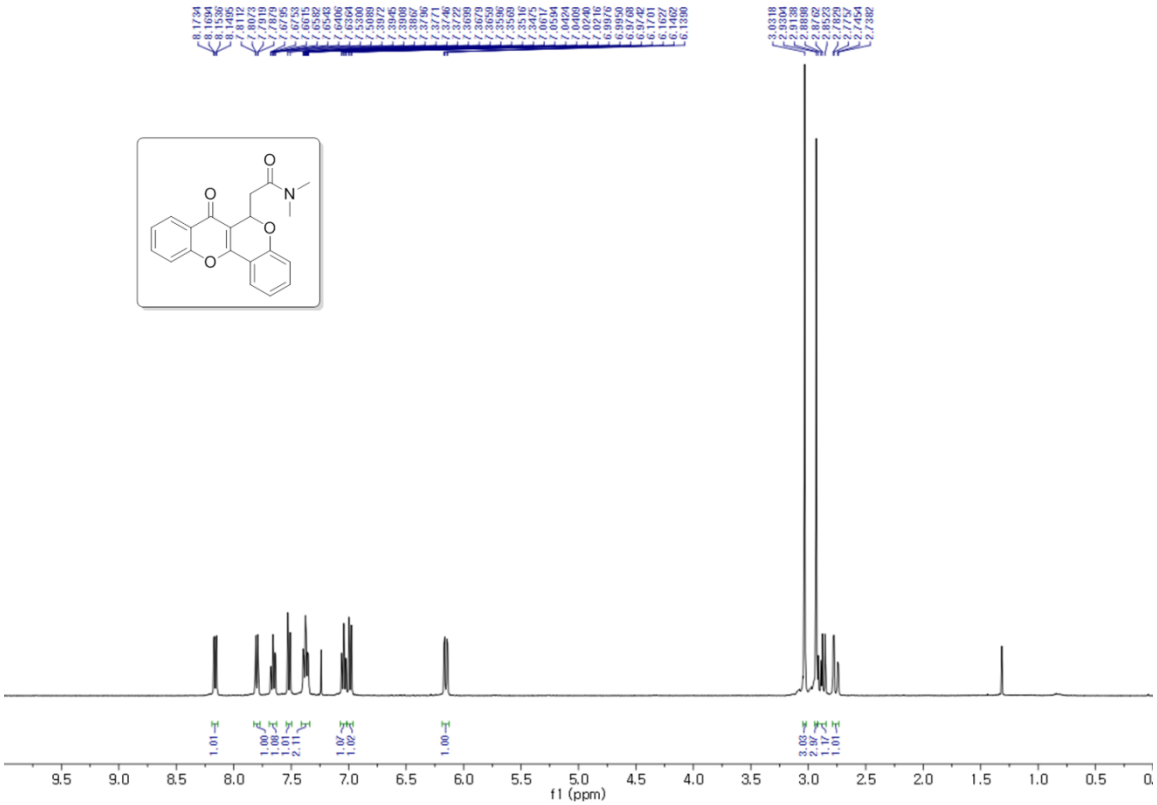


400 MHz, ^{1}H NMR in $CDCl_3$

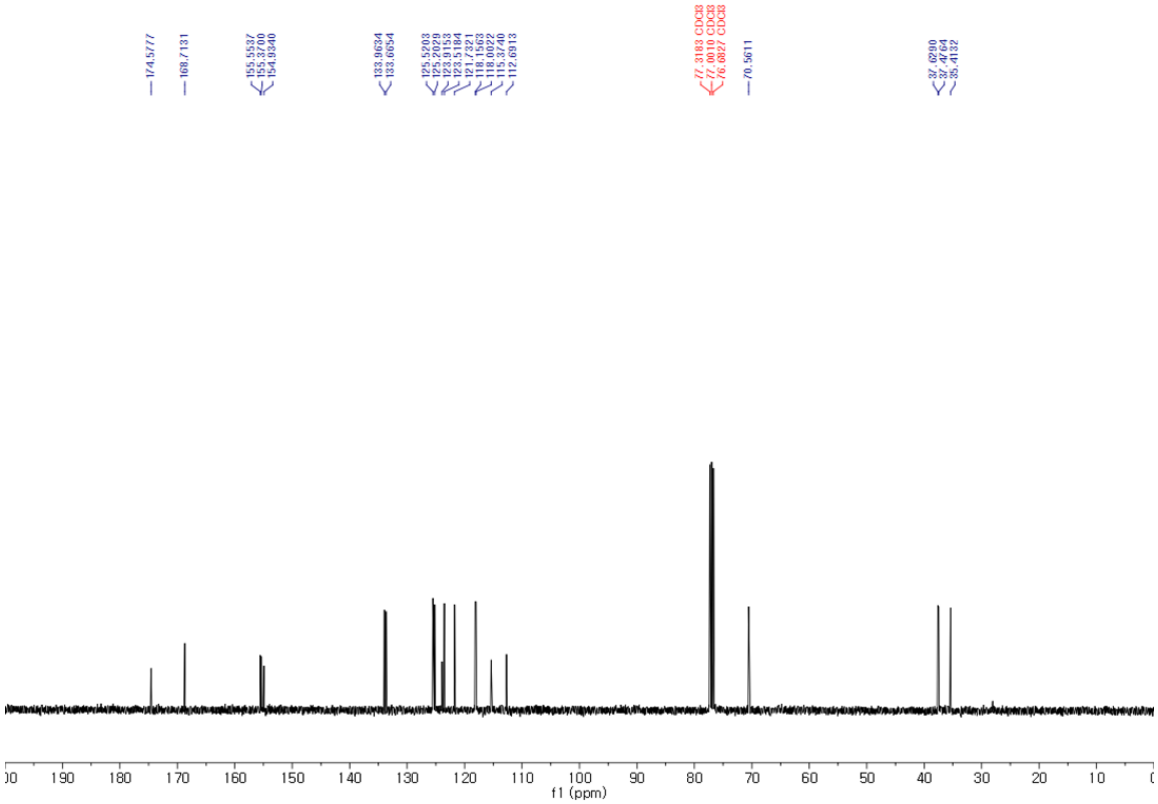


100 MHz, ^{13}C NMR in $CDCl_3$

N,N-Dimethyl-2-(7-oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetamide (3f)

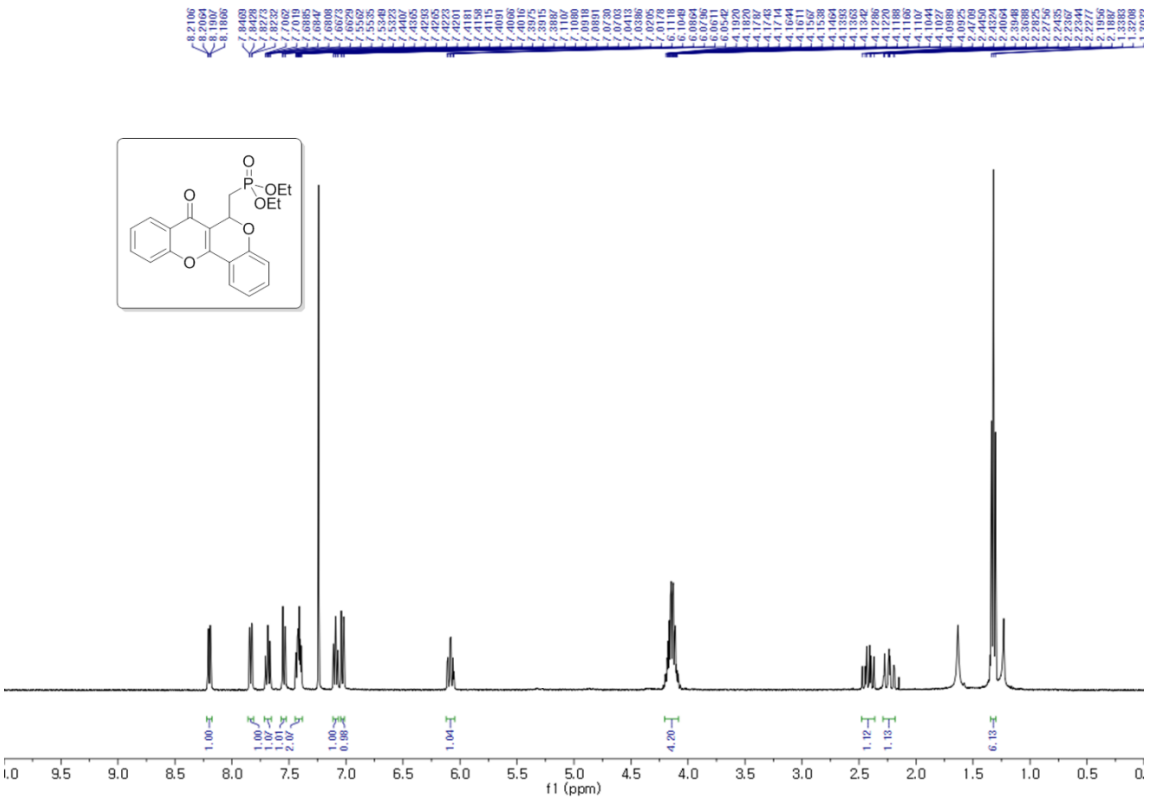


400 MHz, ^{1}H NMR in $CDCl_3$

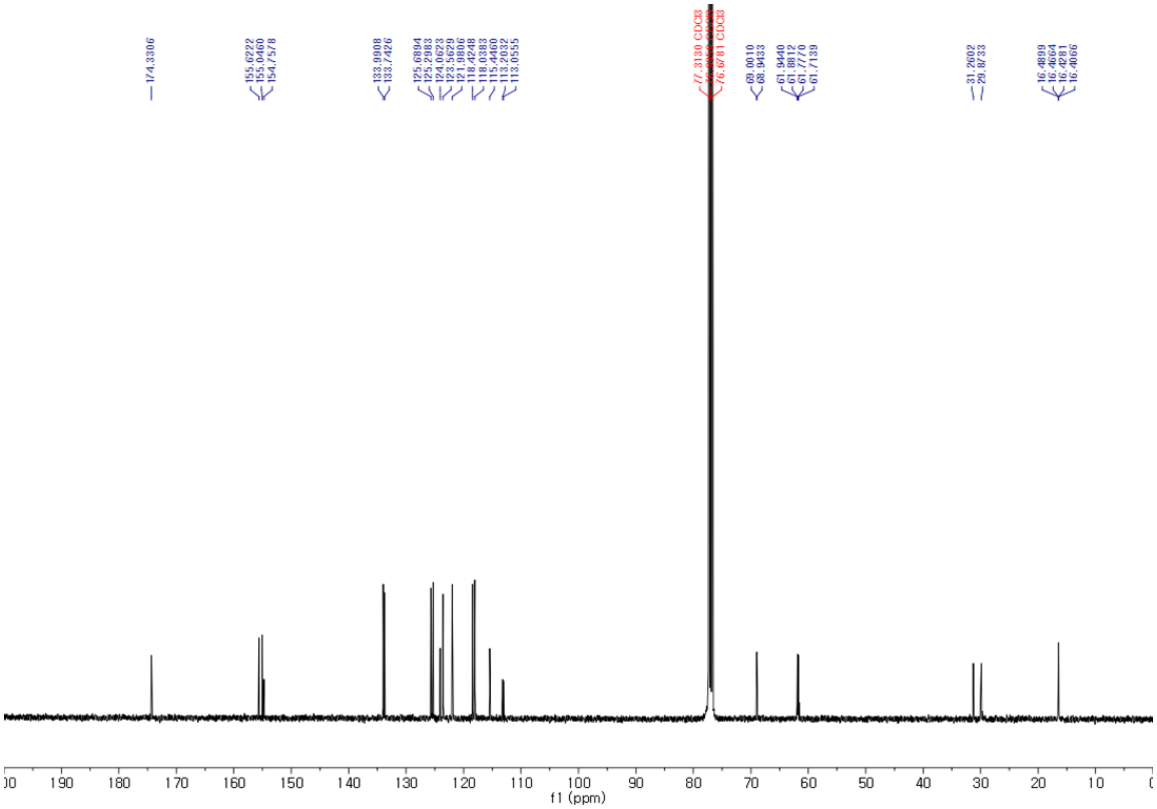


100 MHz, ^{13}C NMR in $CDCl_3$

Diethyl ((7-Oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)methyl)phosphonate (3g)

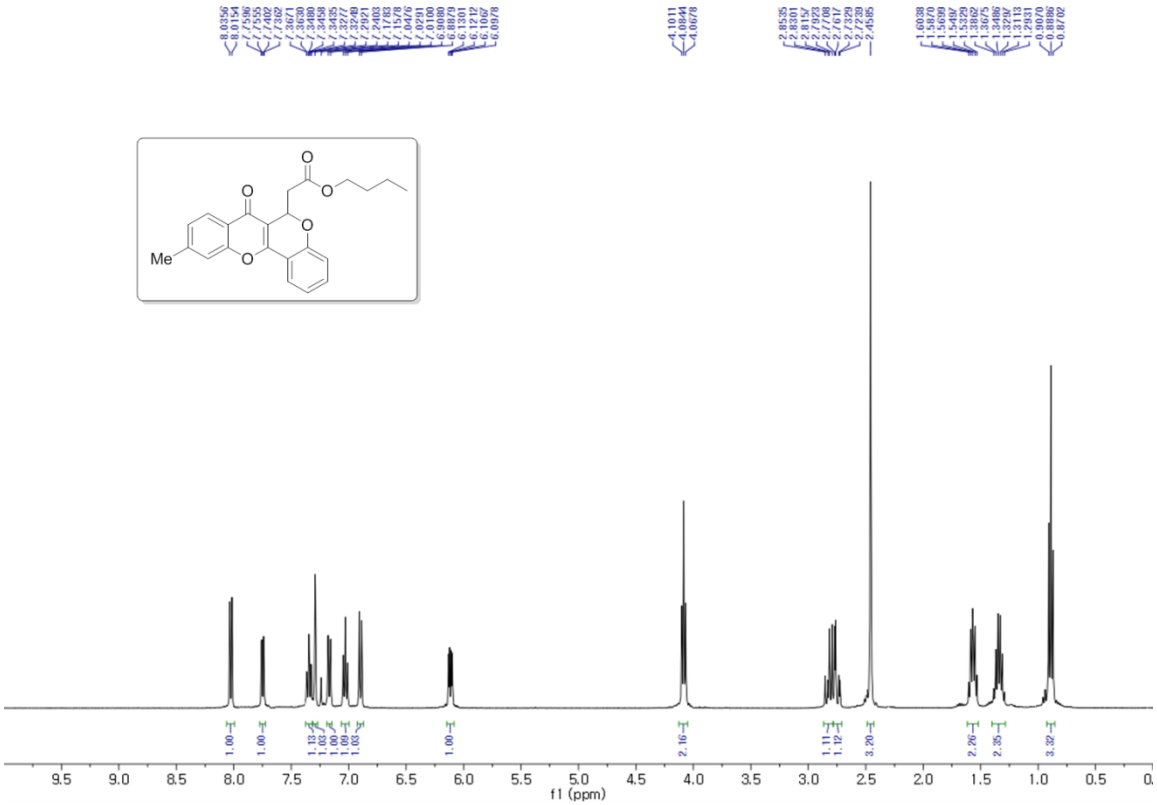


400 MHz, ^{1}H NMR in $CDCl_3$

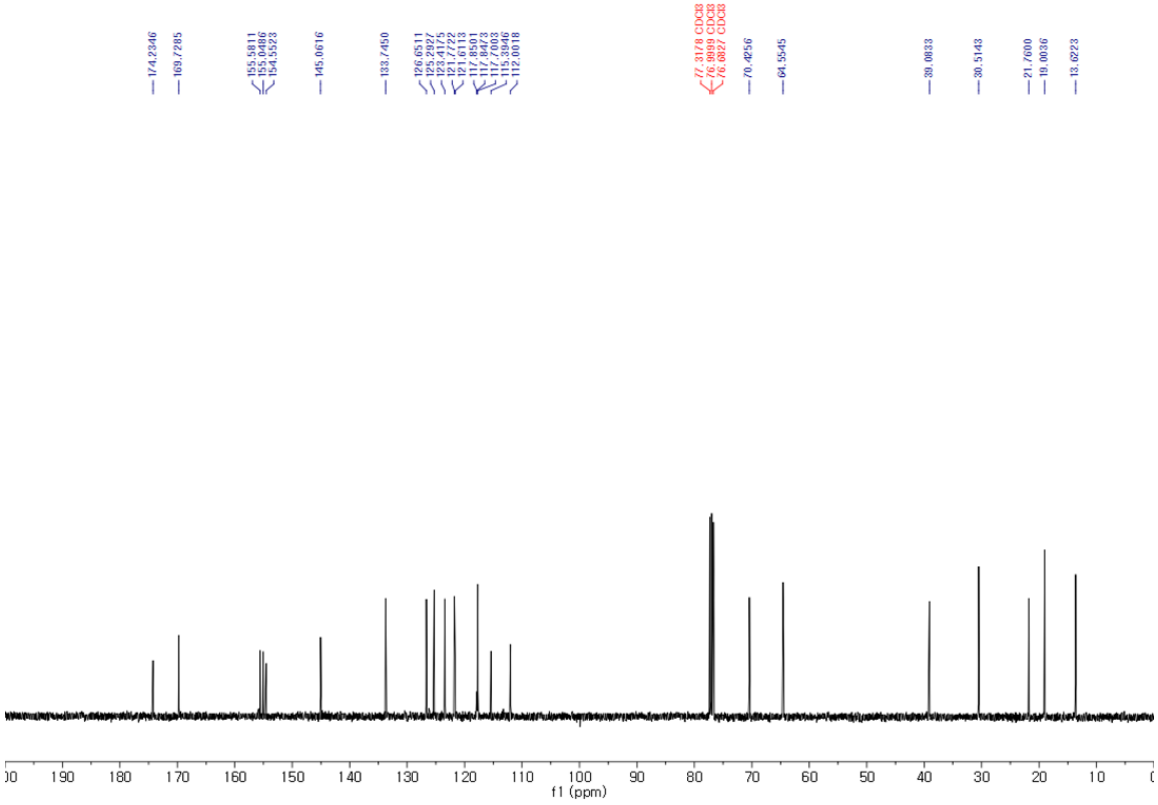


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(10-Methyl-7-oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetate (3h)

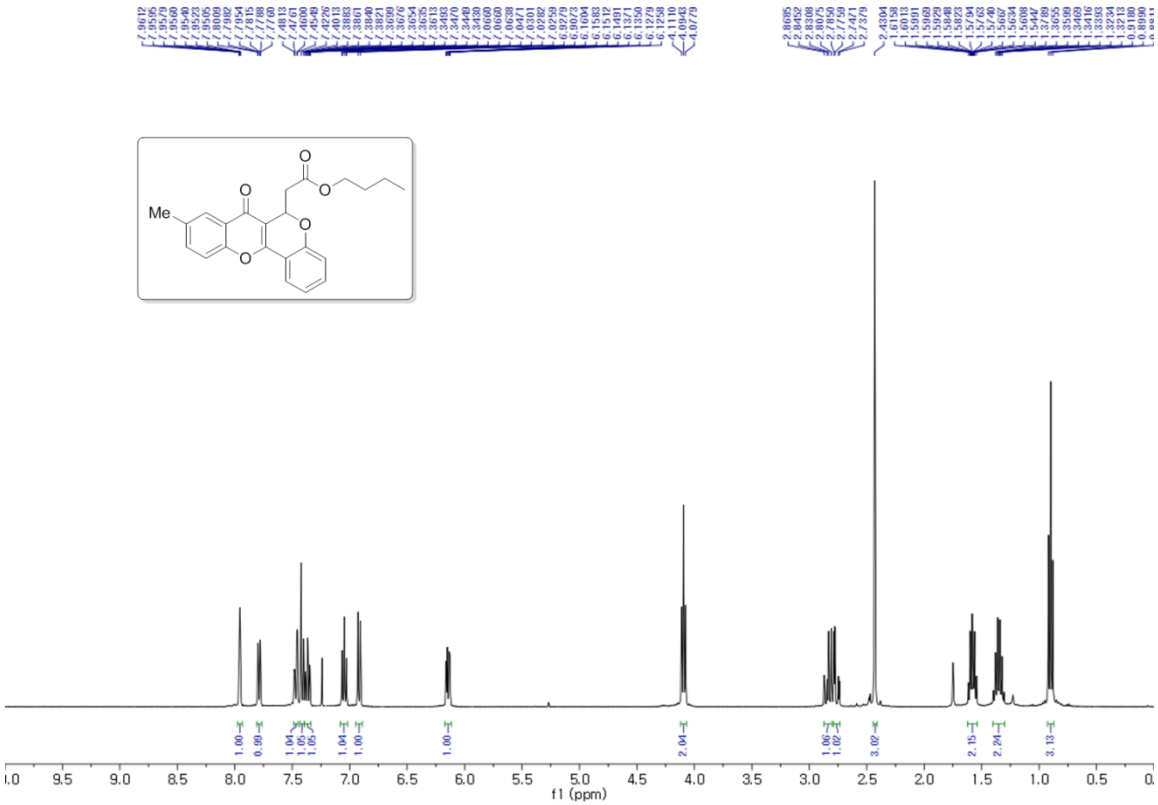


400 MHz, ^{1}H NMR in $CDCl_3$

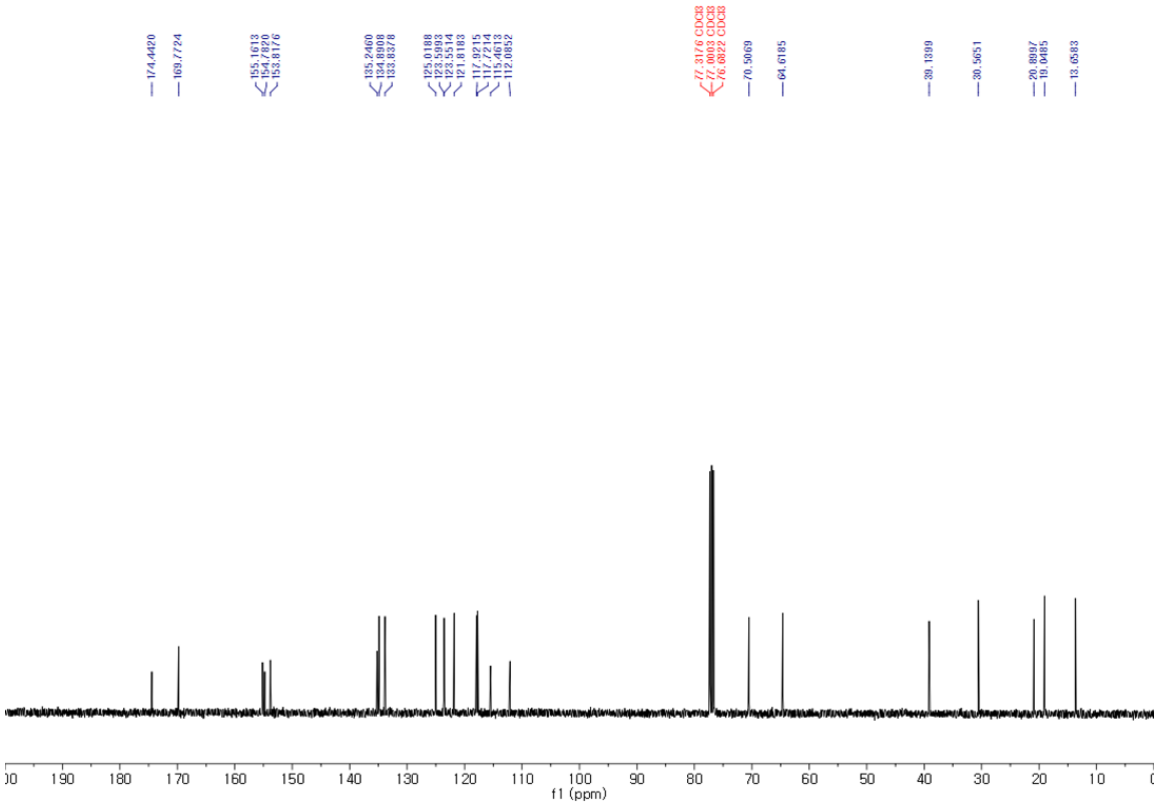


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(9-Methyl-7-oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetate (3i)

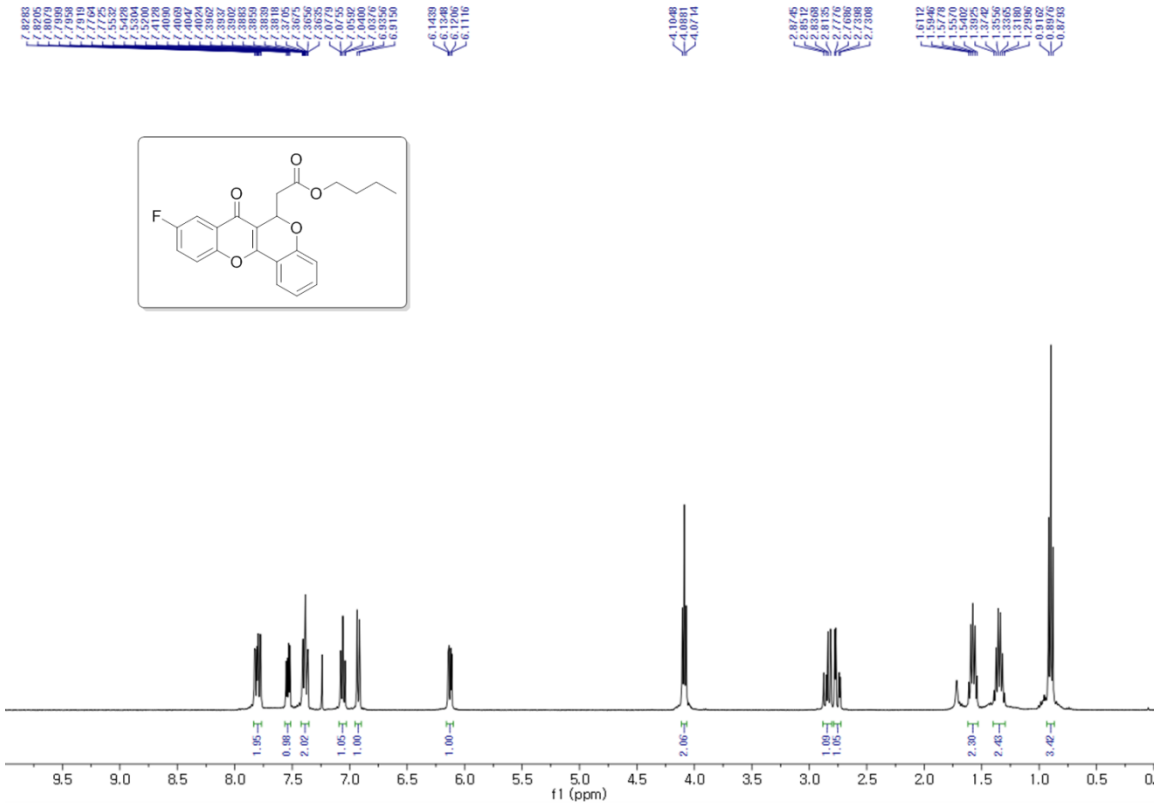


400 MHz, ^{1}H NMR in $CDCl_3$

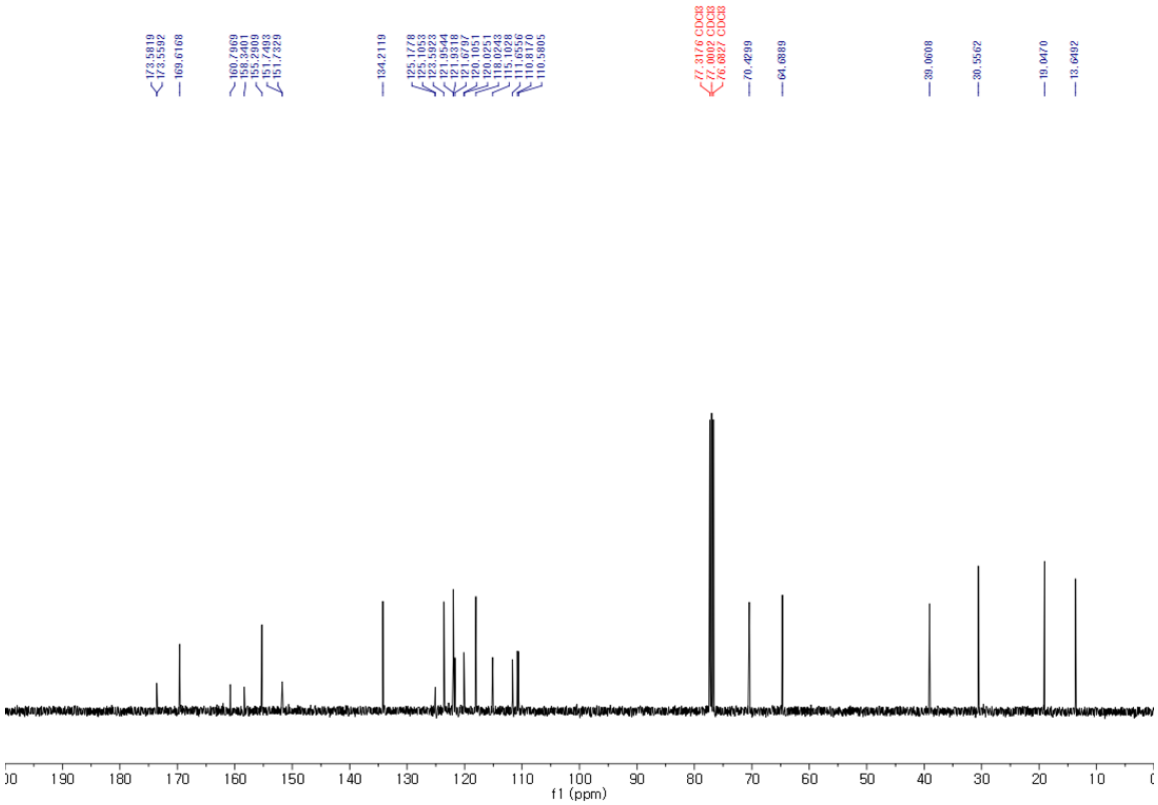


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(9-Fluoro-7-oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetate (3j)

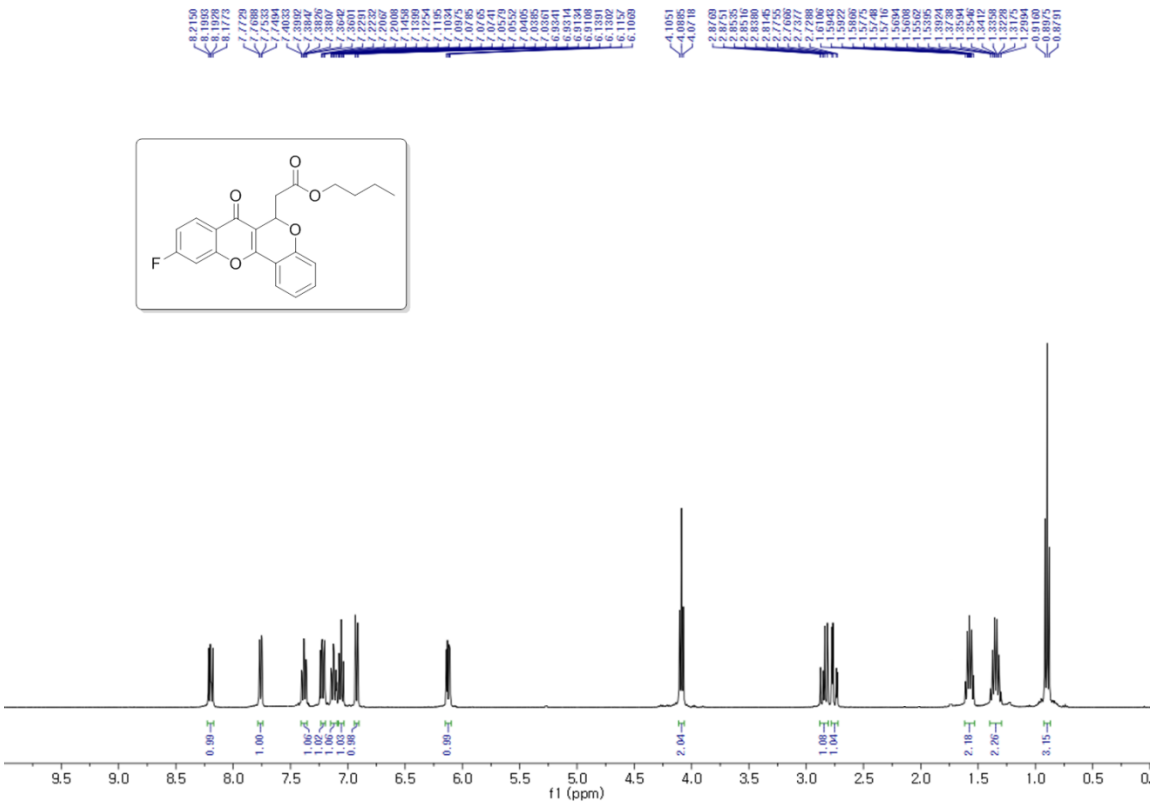


400 MHz, ^{1}H NMR in $CDCl_3$

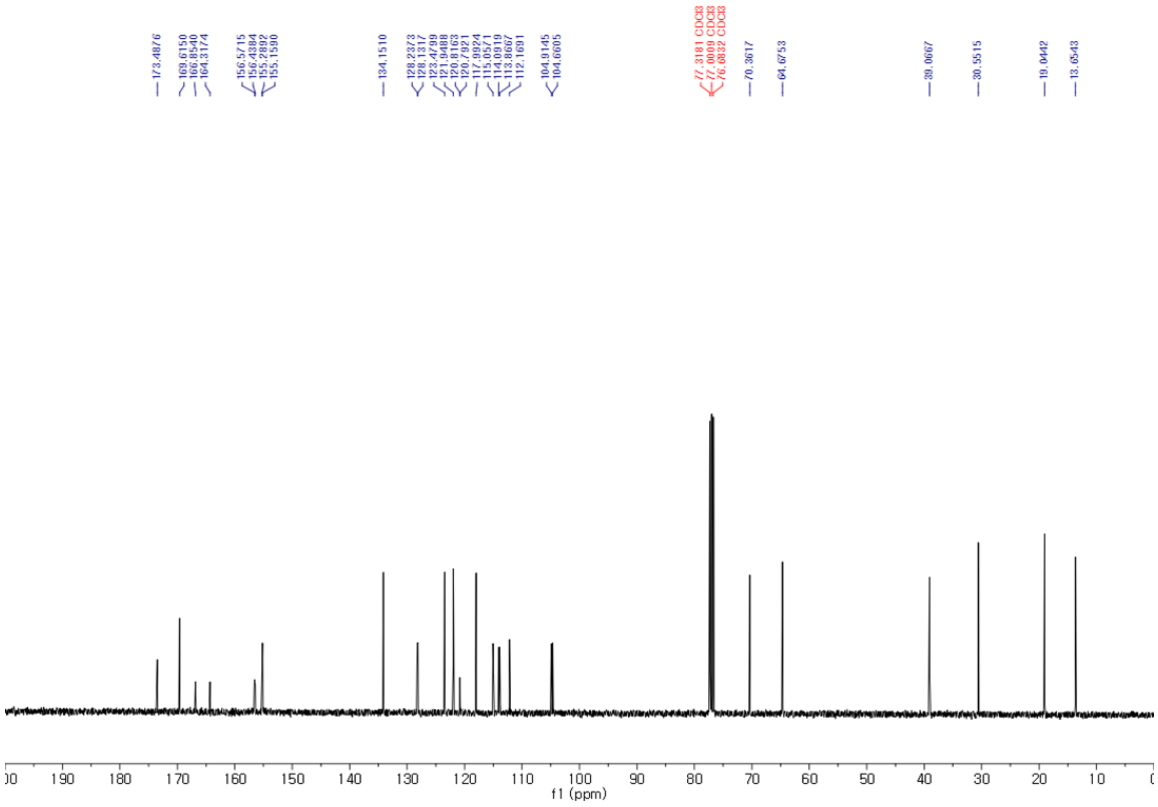


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(10-Fluoro-7-oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetate (3k)

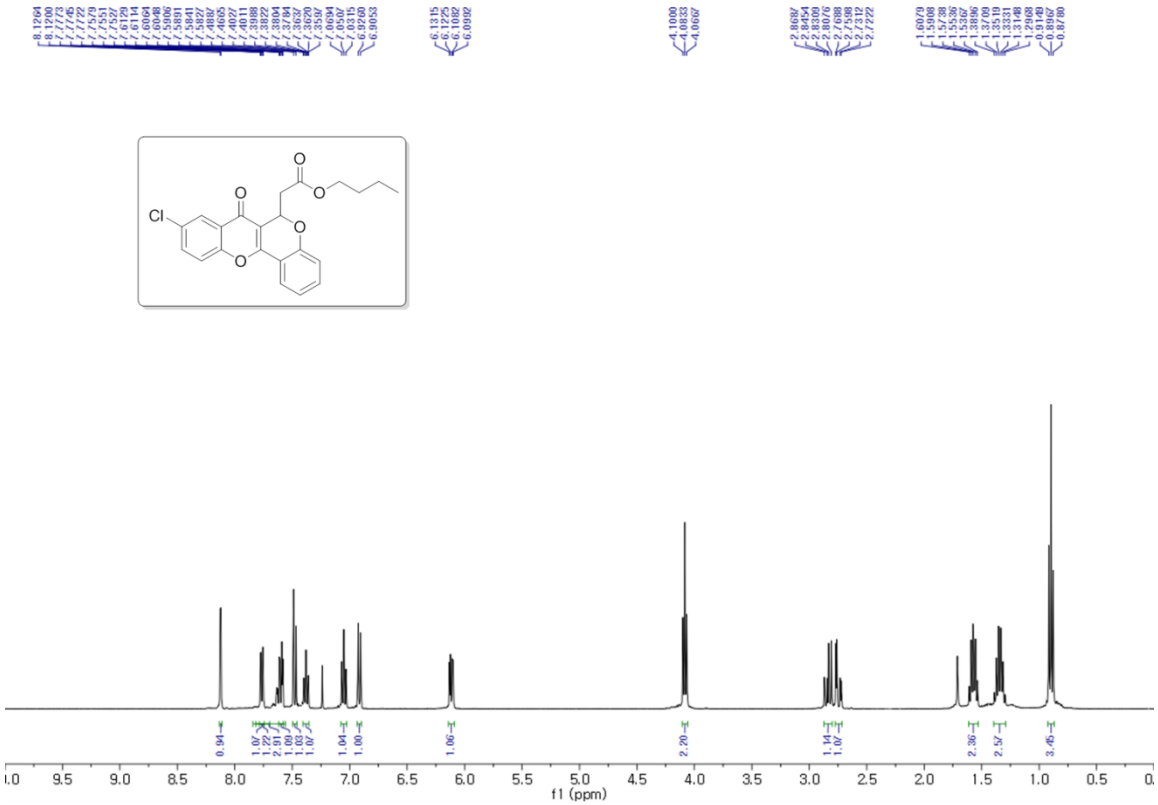


400 MHz, ^{1}H NMR in $CDCl_3$

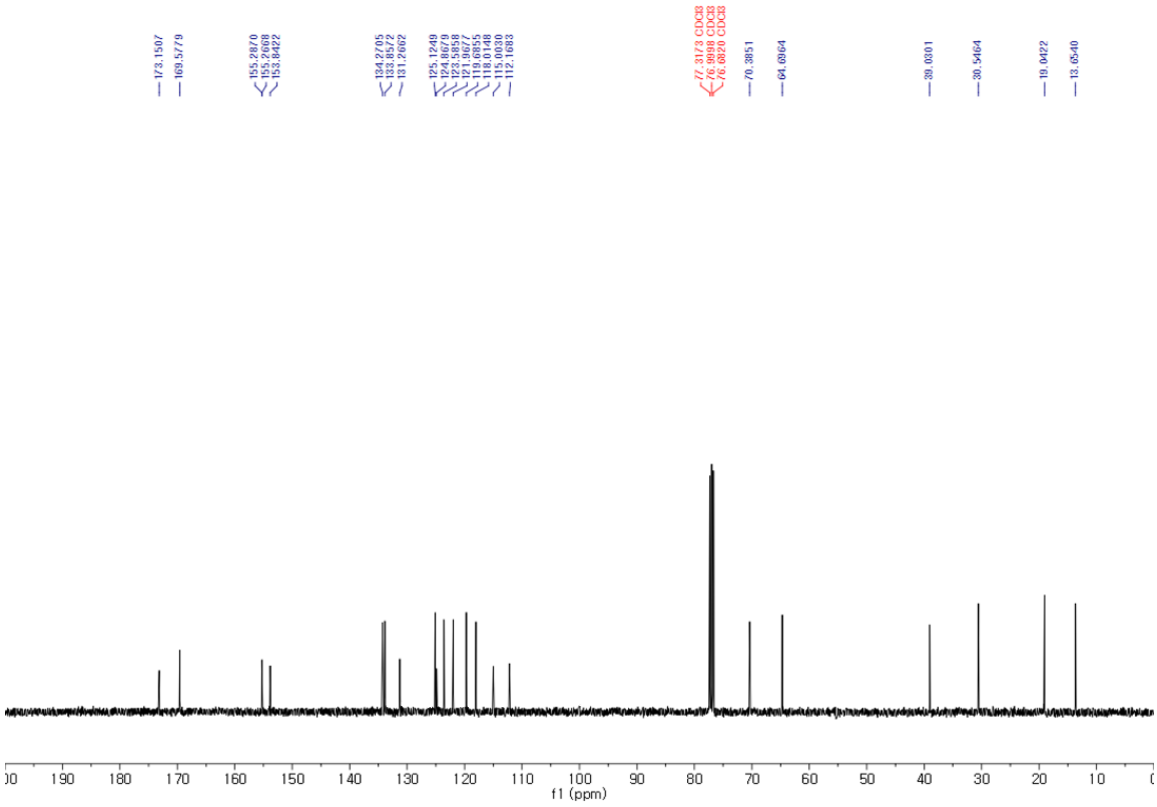


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(9-Chloro-7-oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetate (3l)

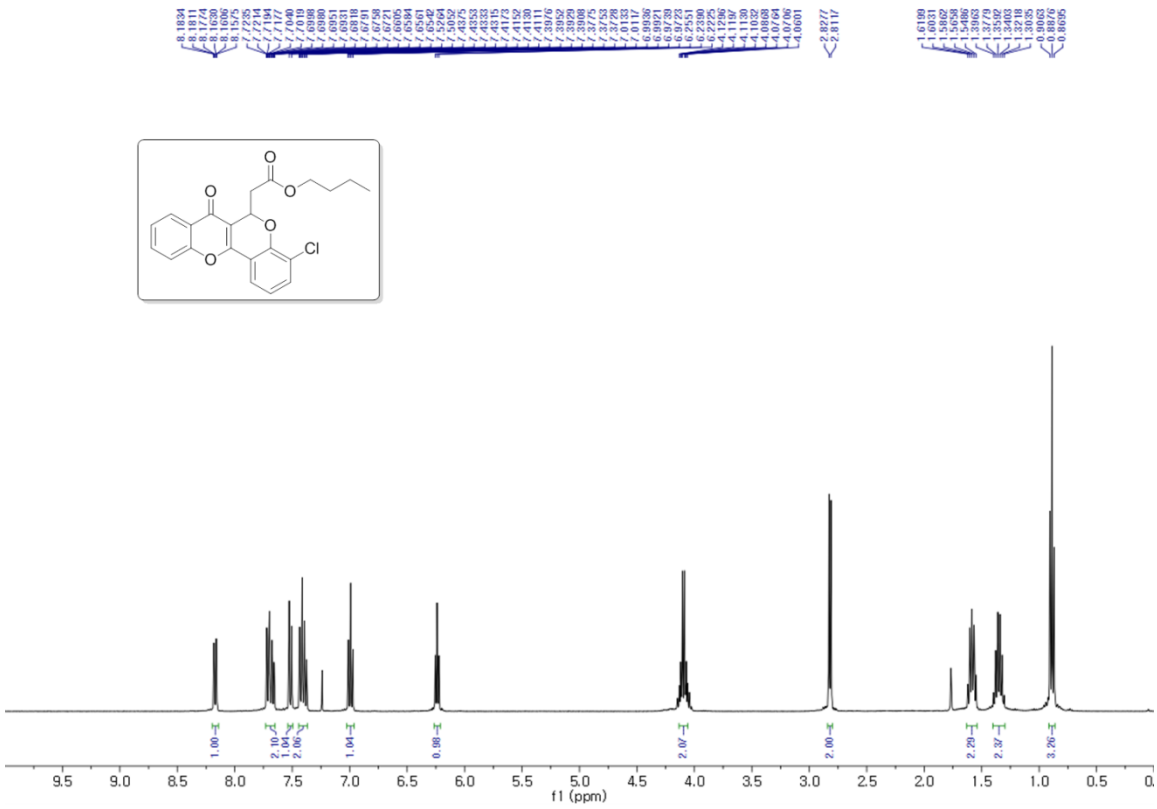


400 MHz, ^{1}H NMR in $CDCl_3$

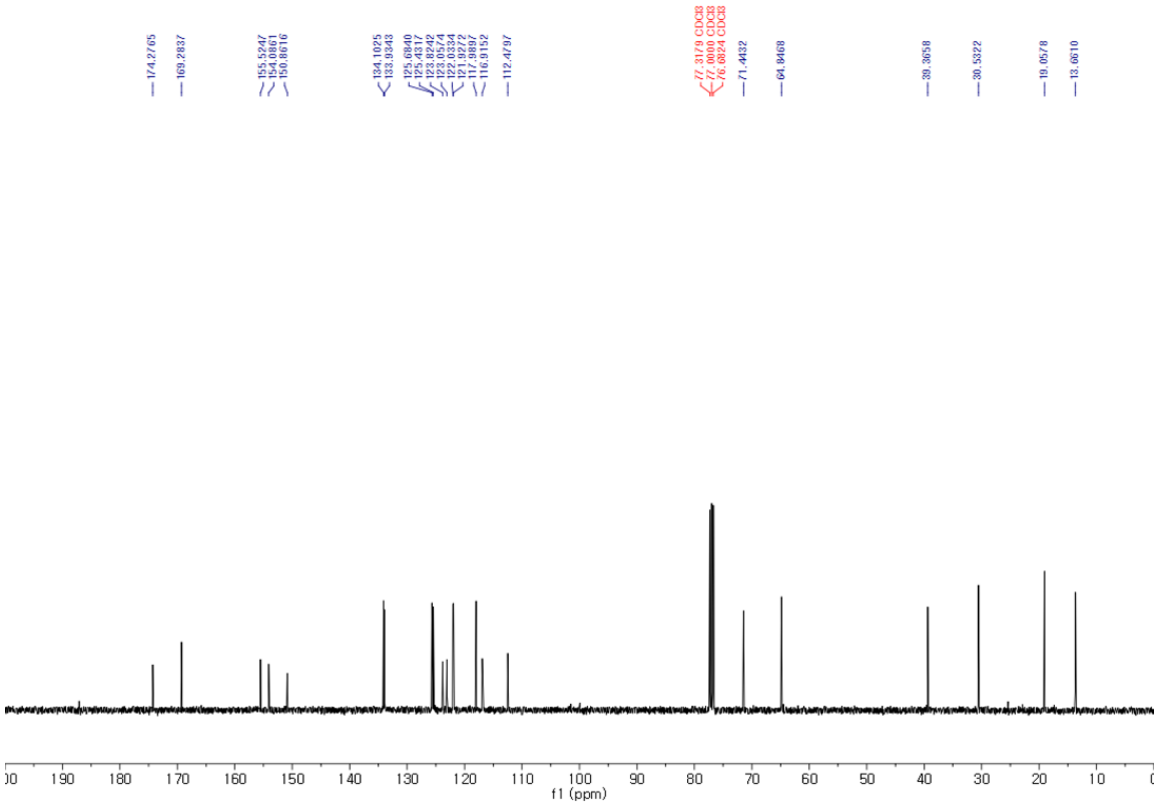


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(4-Chloro-7-oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetate (3m)

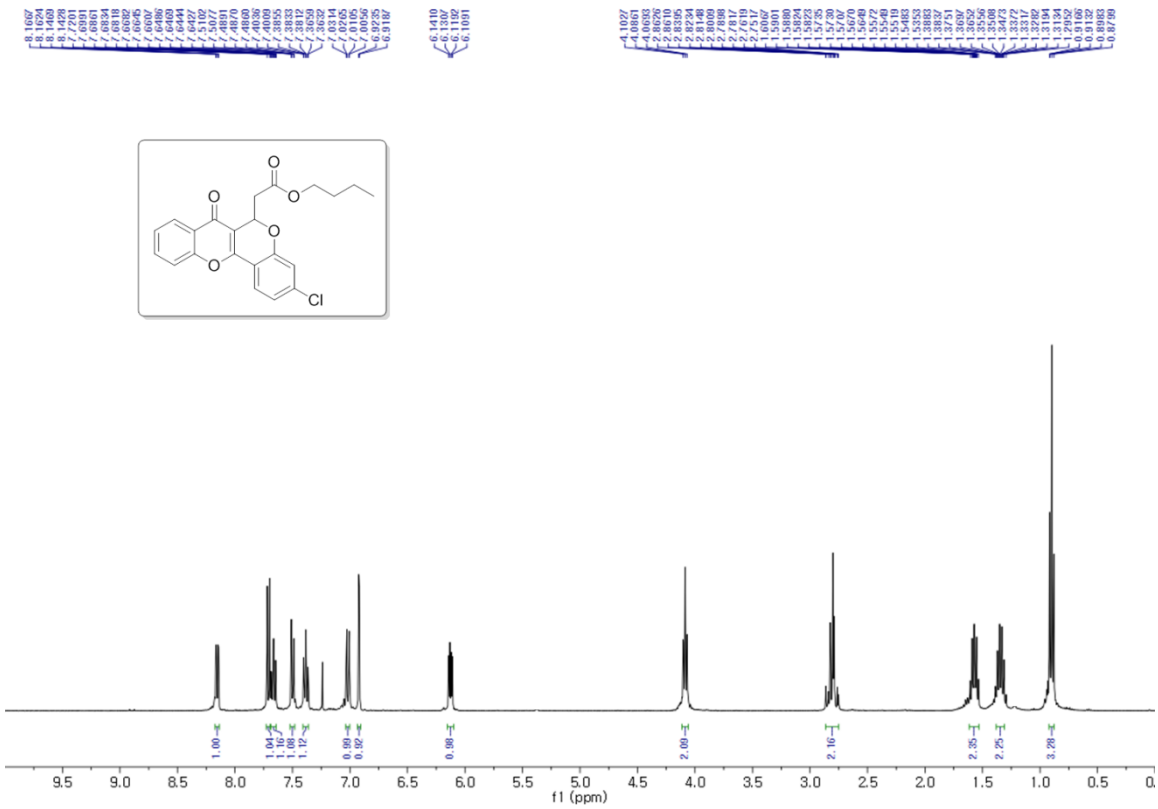


400 MHz, ^{1}H NMR in $CDCl_3$

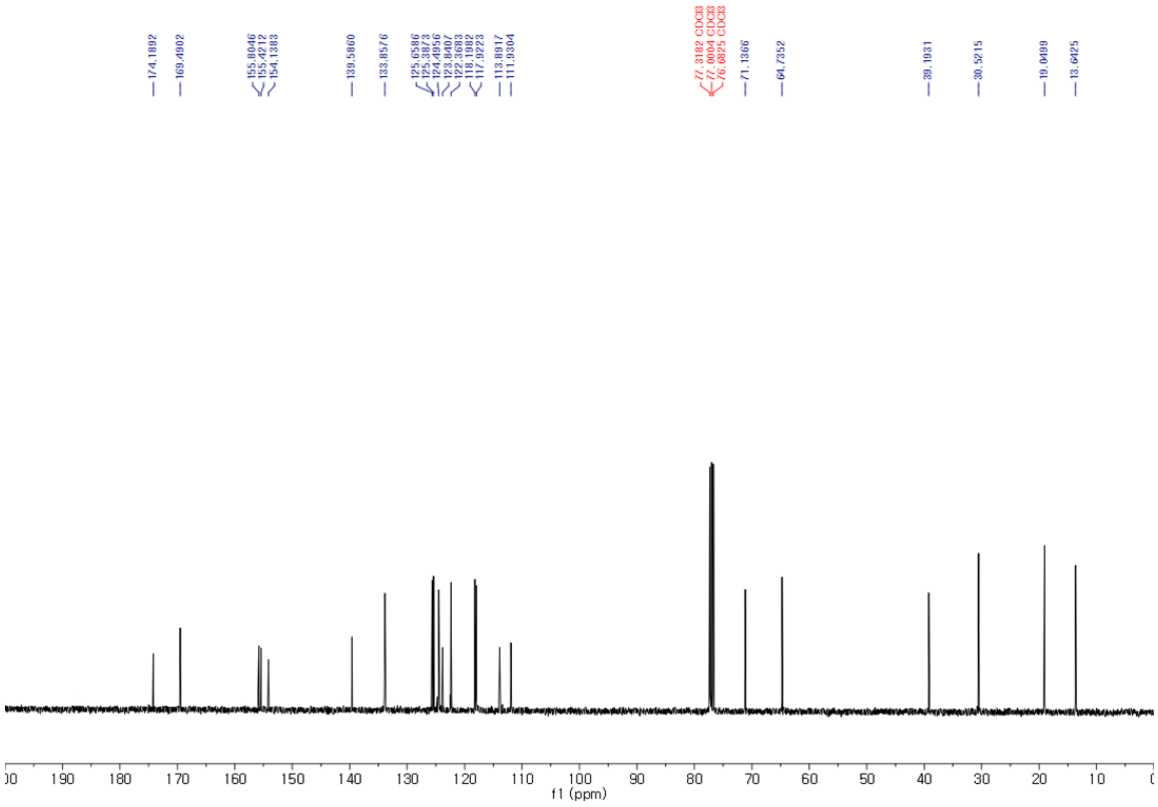


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(3-Chloro-7-oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetate (3n)

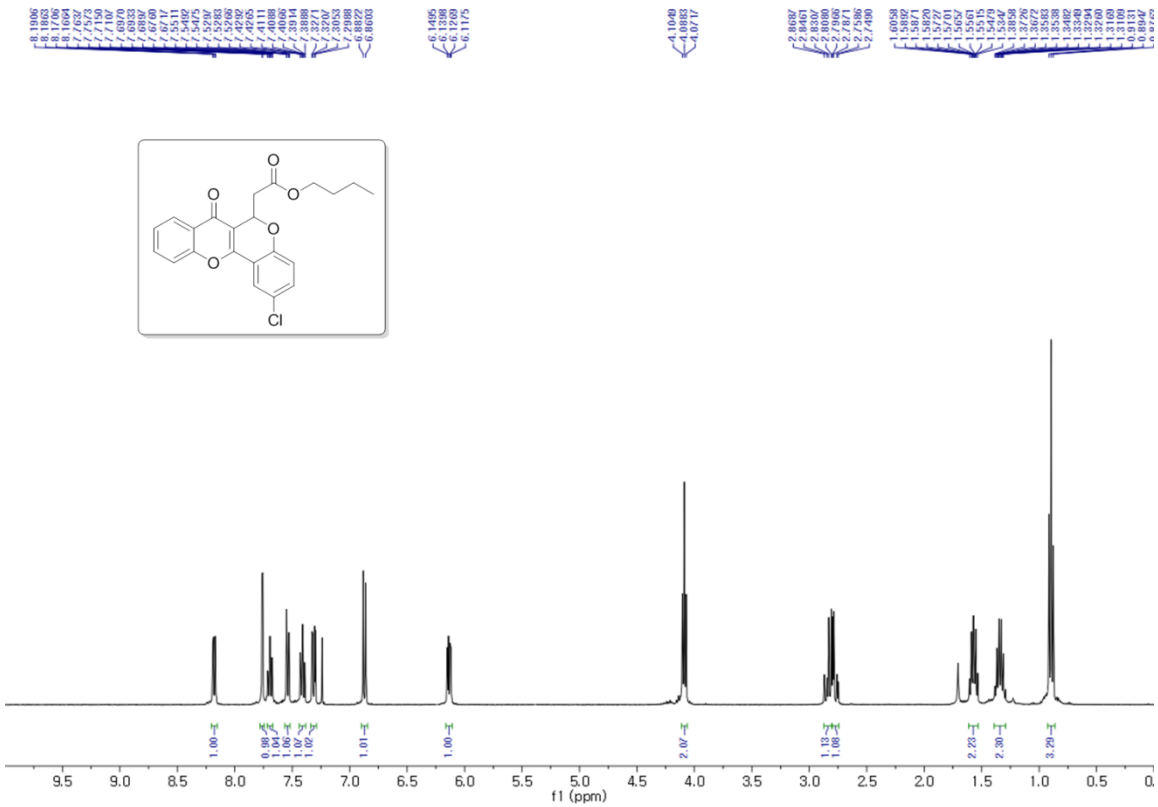


400 MHz, ^{1}H NMR in $CDCl_3$

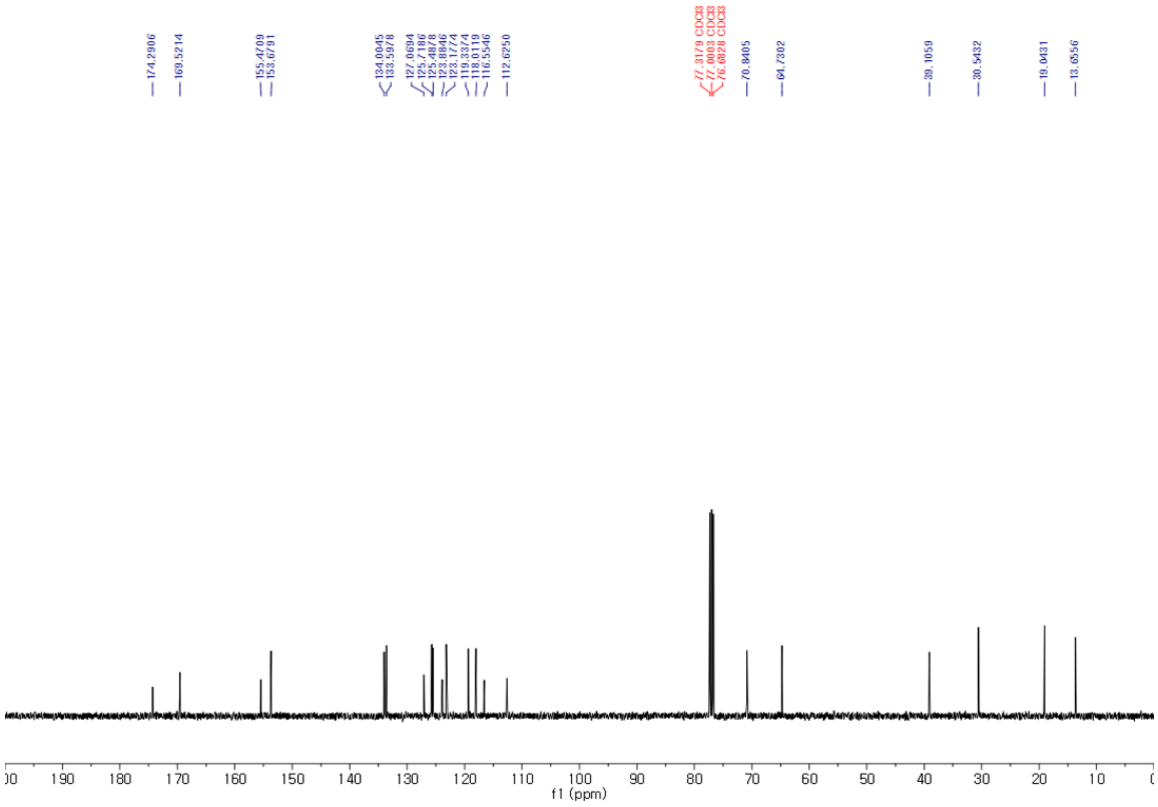


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(2-Chloro-7-oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetate (3o)

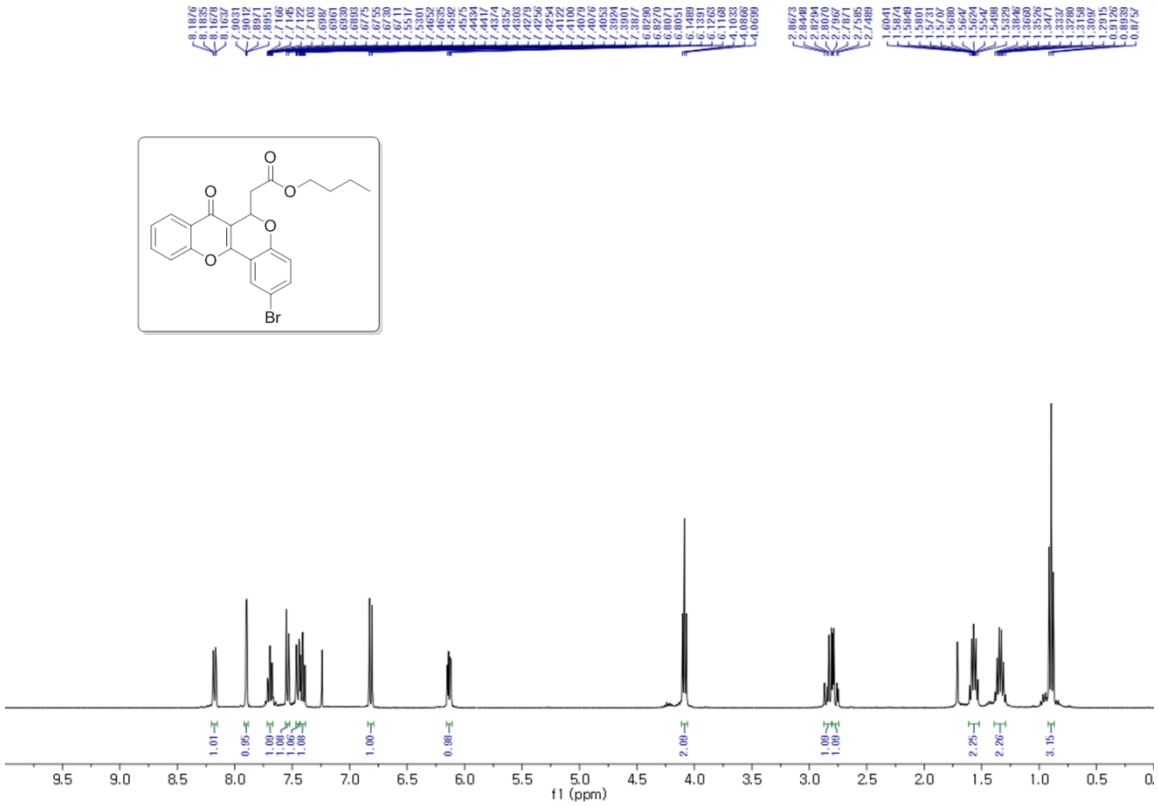


400 MHz, ^{1}H NMR in $CDCl_3$

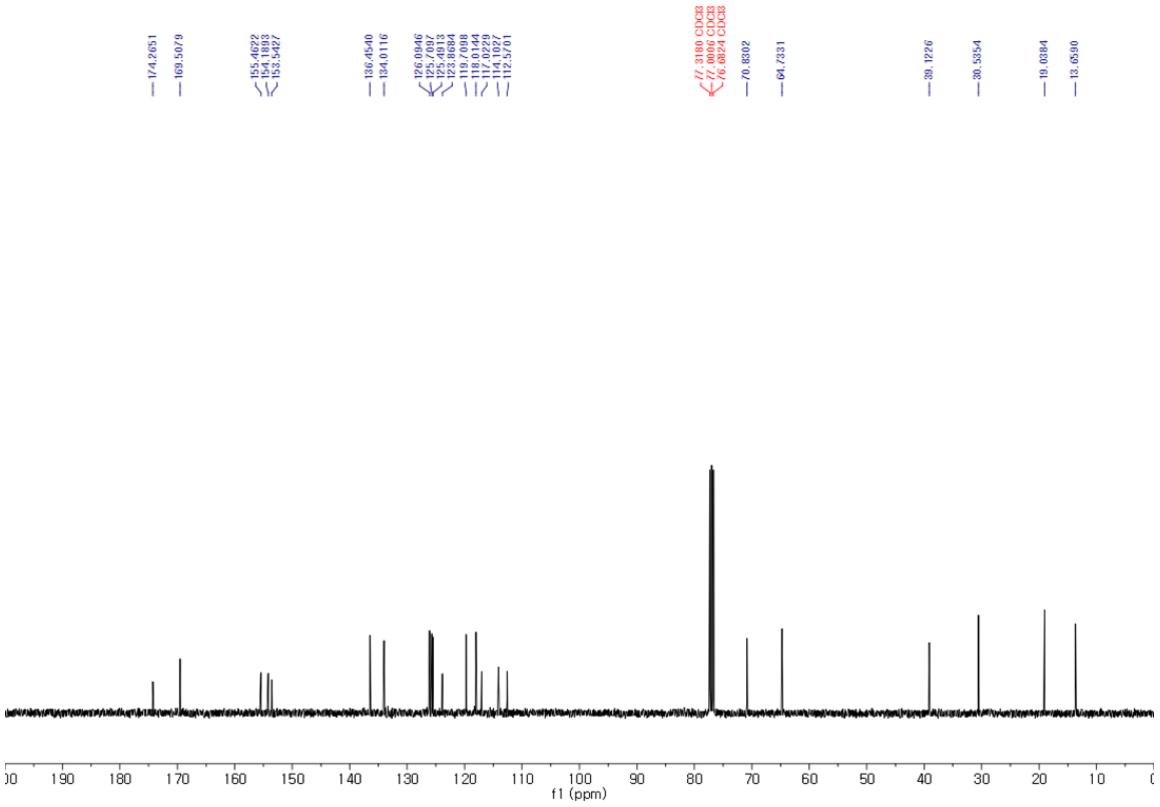


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(2-Bromo-7-oxo-6,7-dihydrochromeno[4,3-b]chromen-6-yl)acetate (3p)

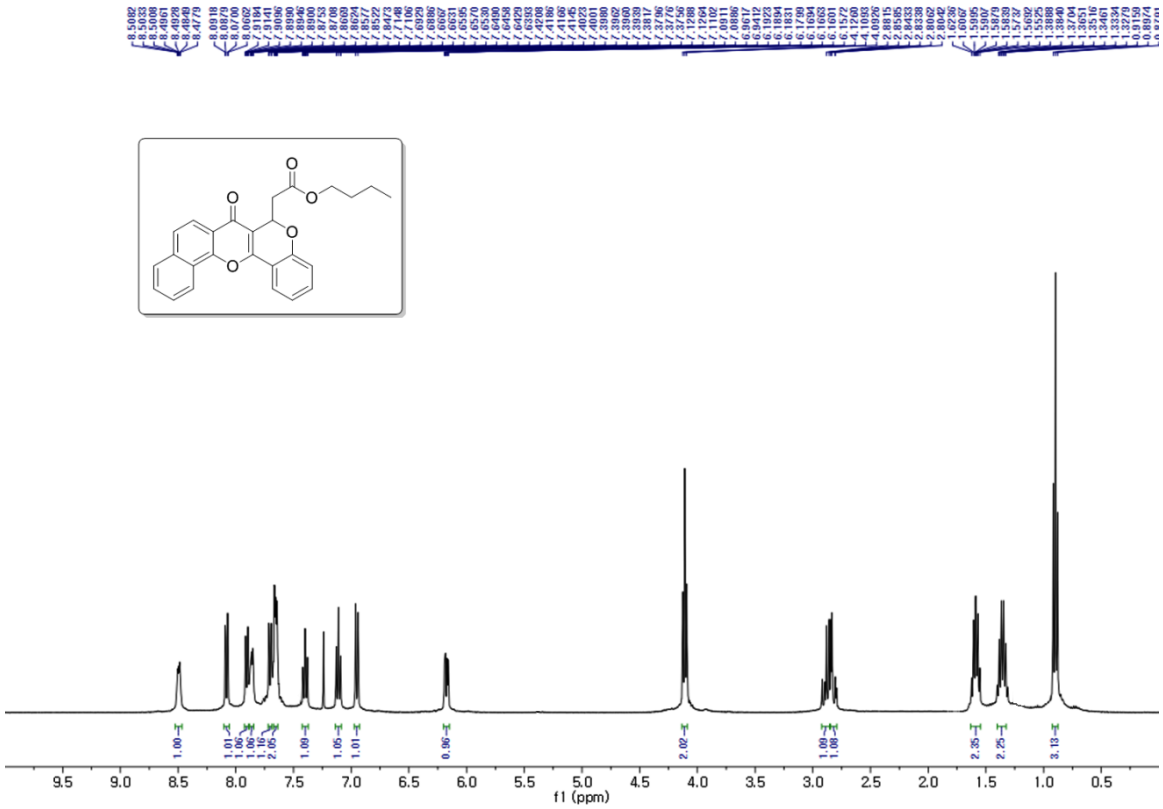


400 MHz, ^{1}H NMR in $CDCl_3$

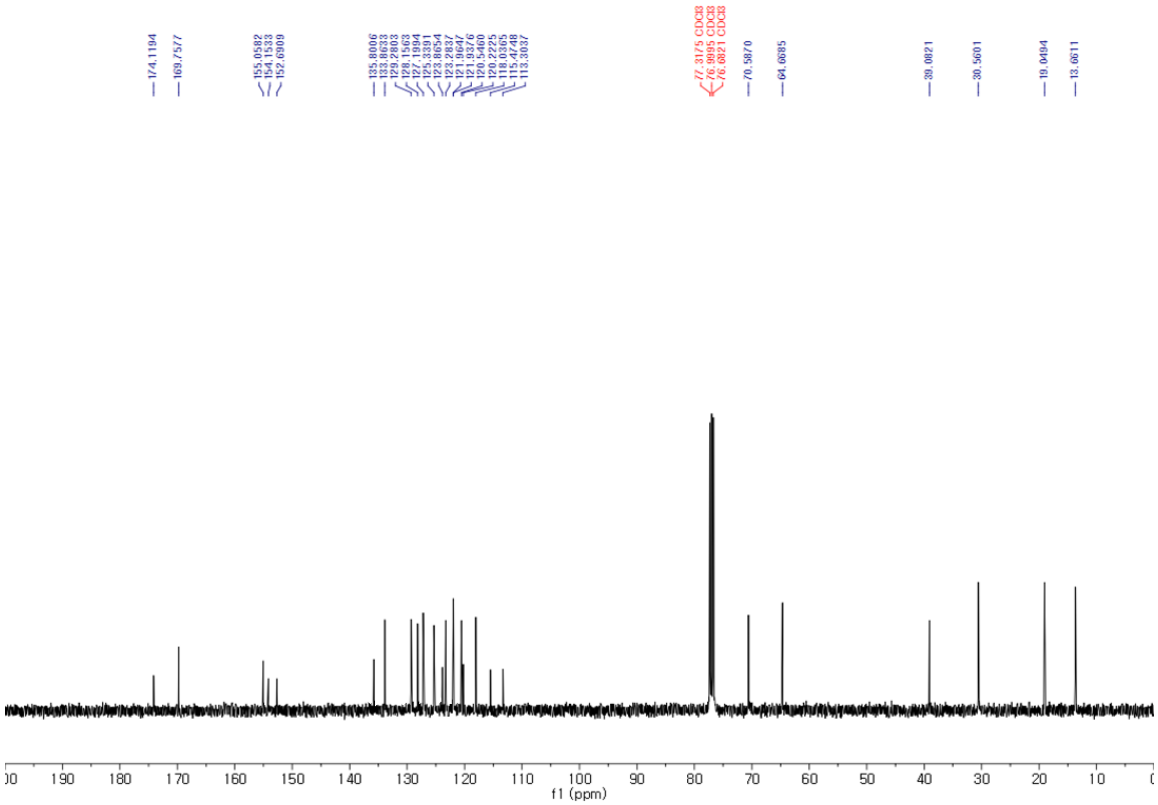


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(7-Oxo-6,7-dihydrobenzo[h]chromeno[4,3-b]chromen-6-yl)acetate (3q)

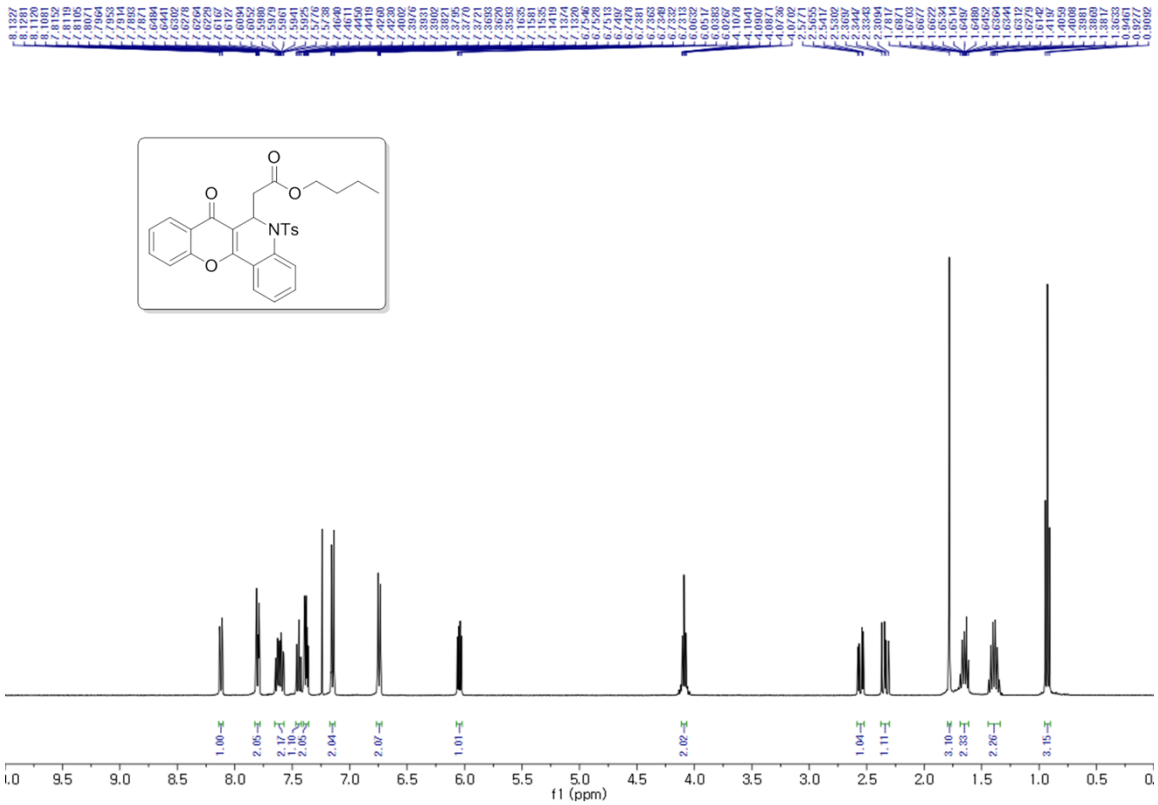


400 MHz, ^{1}H NMR in $CDCl_3$

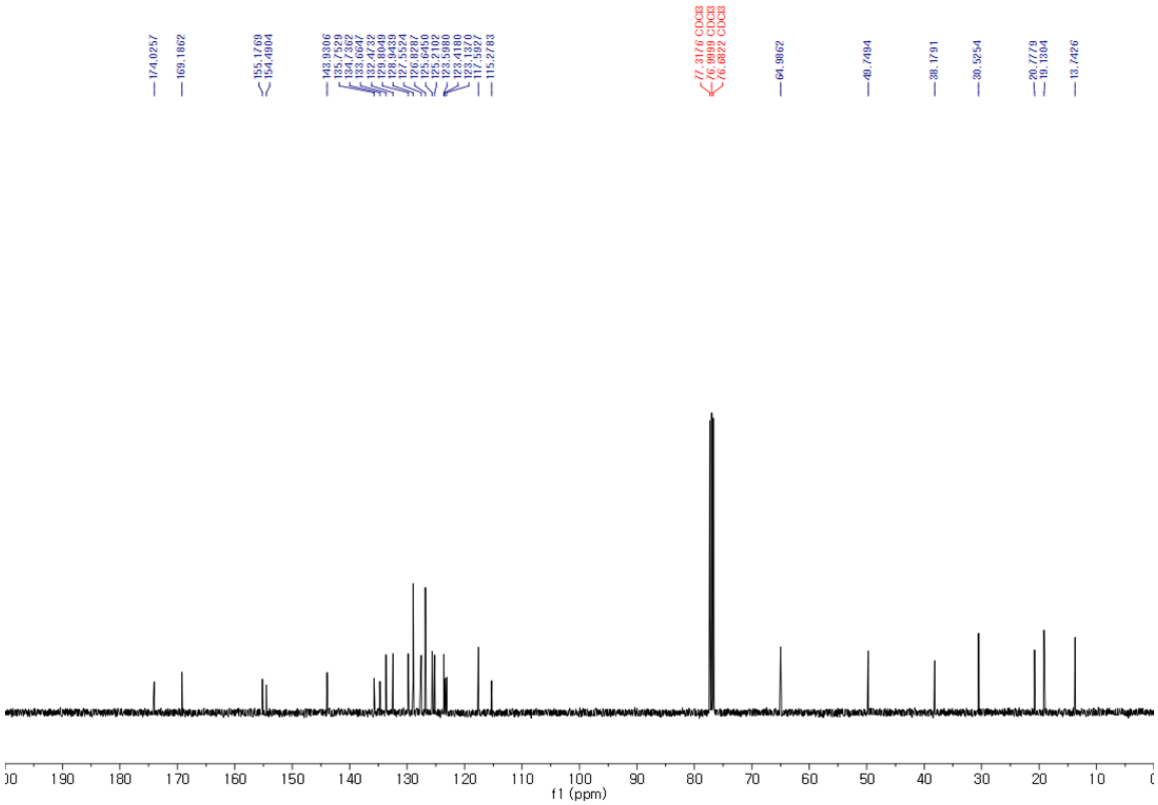


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(7-Oxo-5-tosyl-6,7-dihydro-5H-chromeno[3,2-c]quinolin-6-yl)acetate (3r)

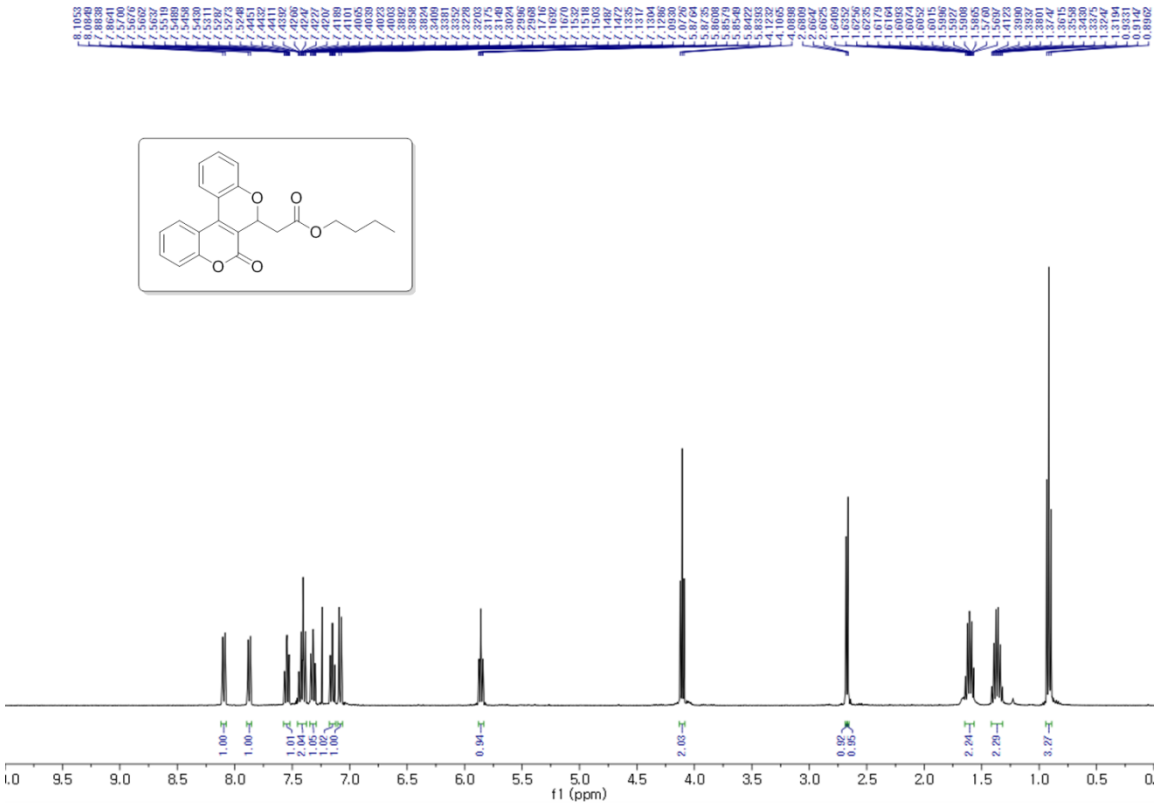


400 MHz, ^{1}H NMR in $CDCl_3$

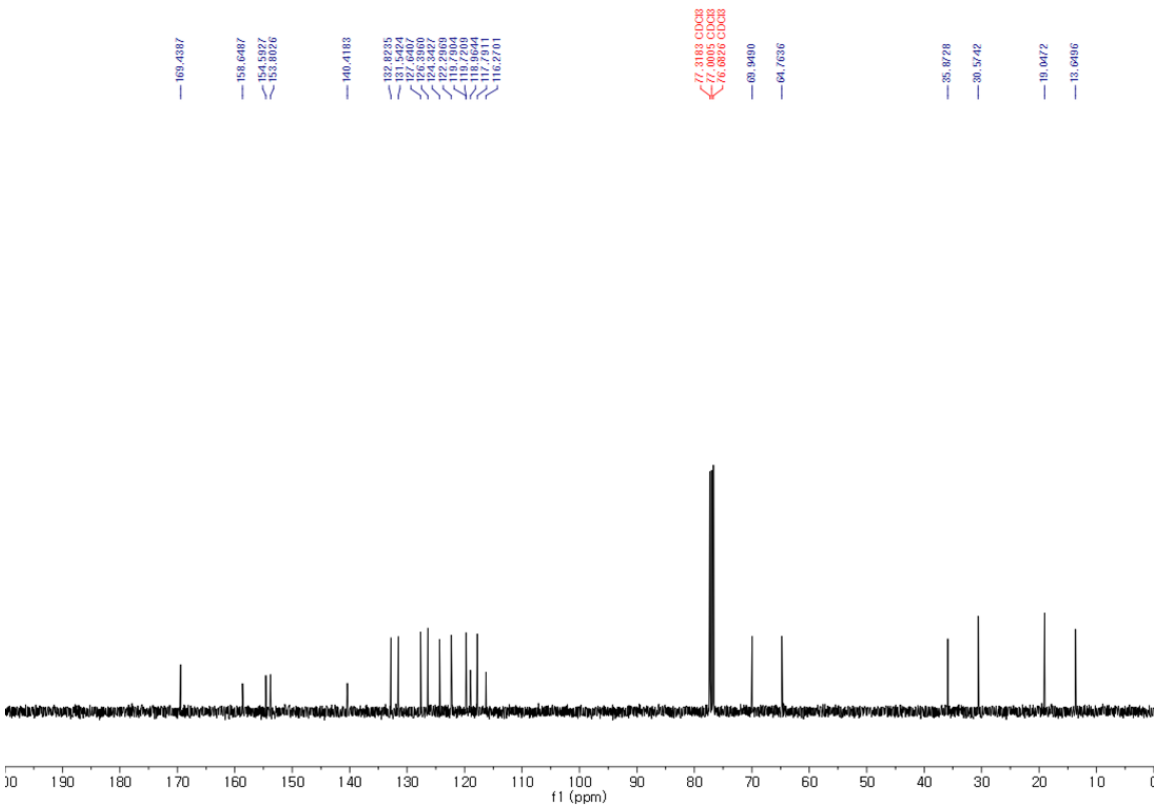


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(7-Oxo-6,7-dihydrochromeno[3,4-c]chromen-6-yl)acetate (5a)

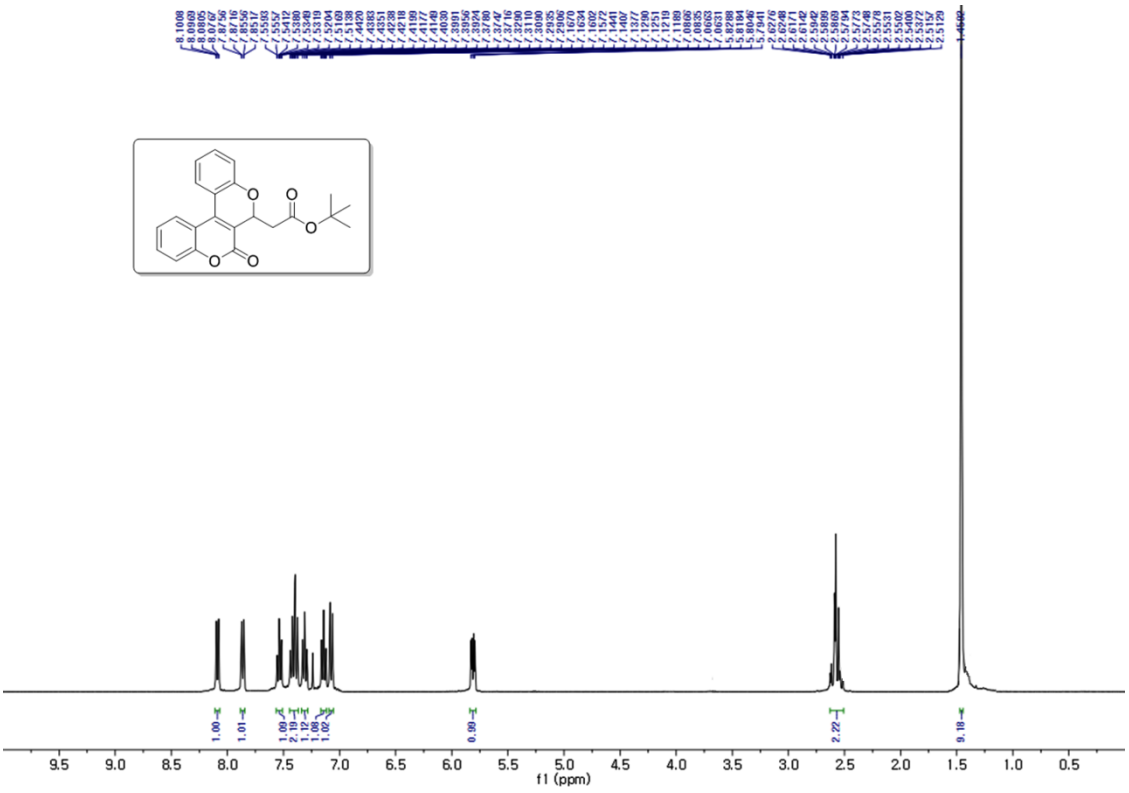


400 MHz, ^{1}H NMR in $CDCl_3$

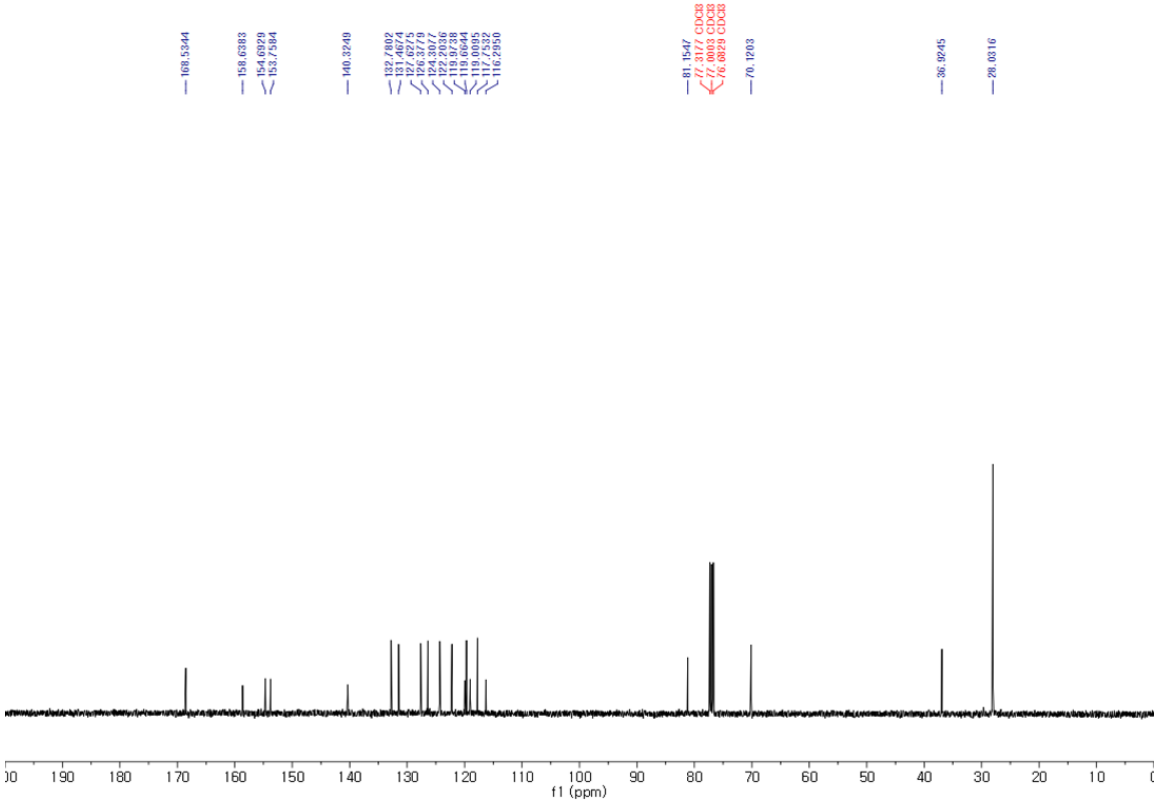


100 MHz, ^{13}C NMR in $CDCl_3$

tert-Butyl 2-(7-Oxo-6,7-dihydrochromeno[3,4-c]chromen-6-yl)acetate (5b)

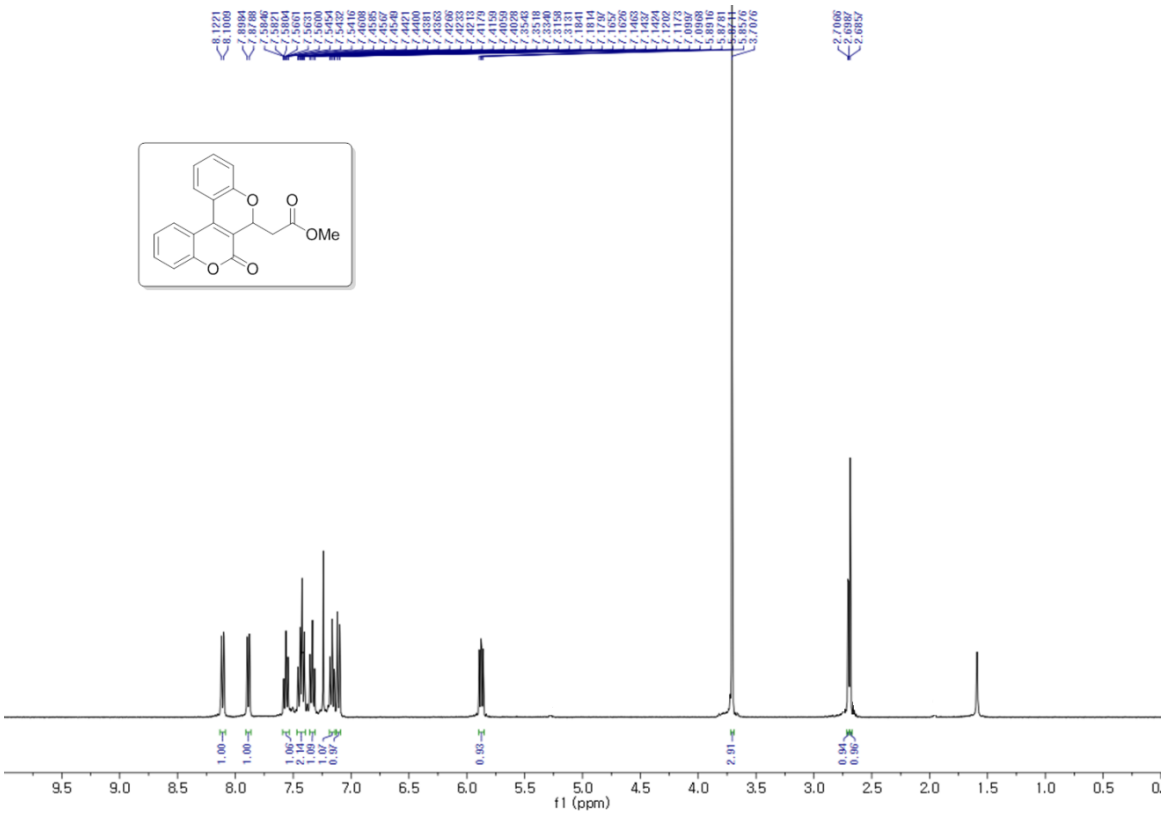


400 MHz, ^{1}H NMR in $CDCl_3$

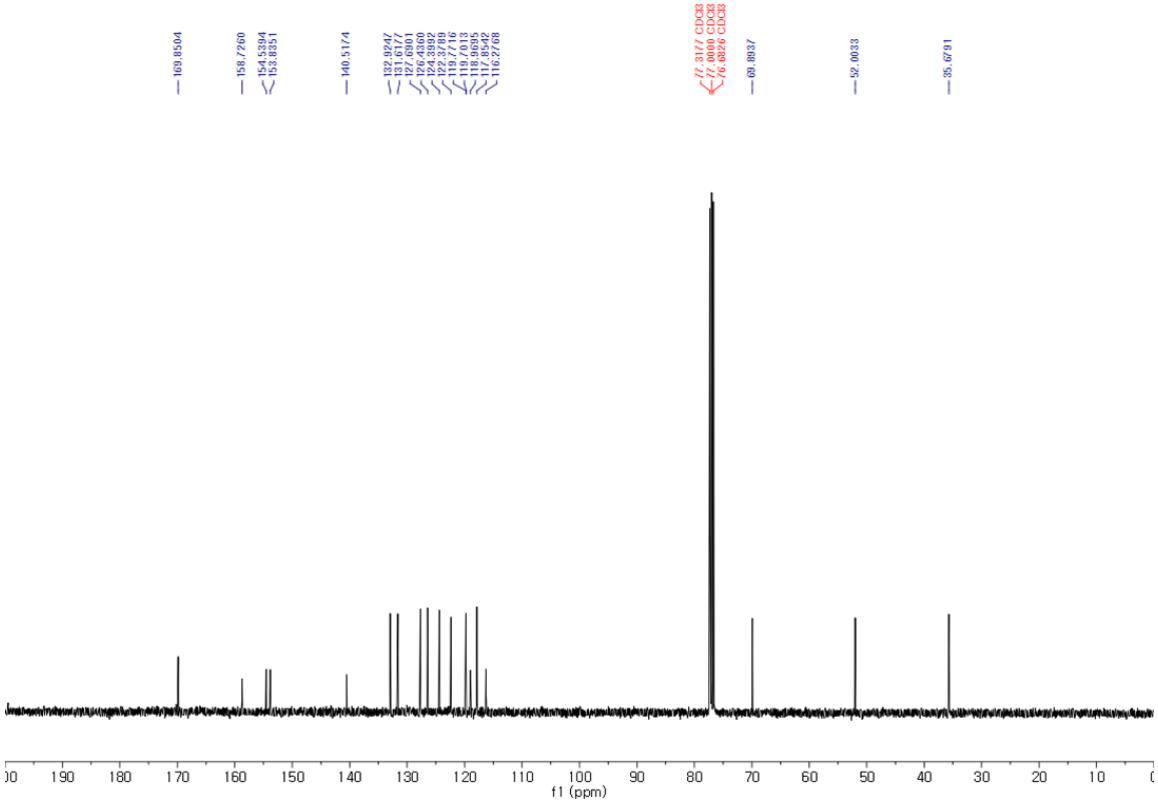


100 MHz, ^{13}C NMR in $CDCl_3$

Methyl 2-(7-Oxo-6,7-dihydrochromeno[3,4-c]chromen-6-yl)acetate (5c)

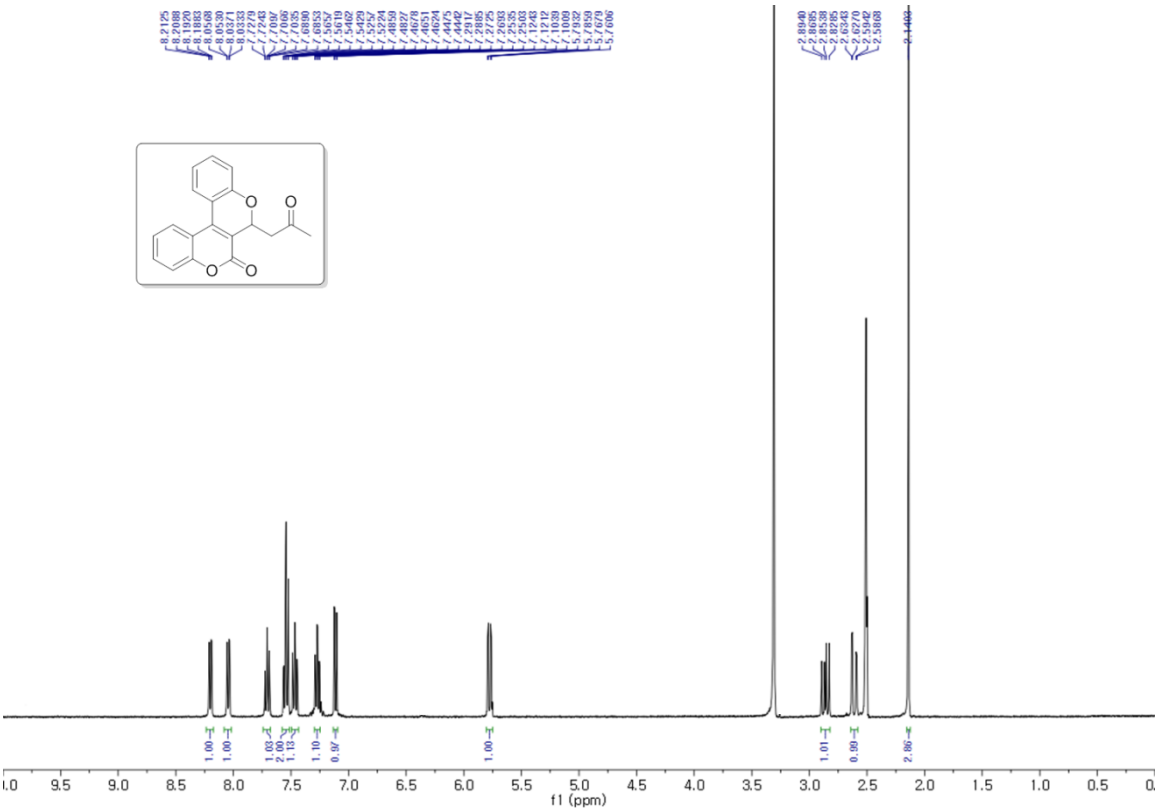


400 MHz, ^{1}H NMR in $CDCl_3$

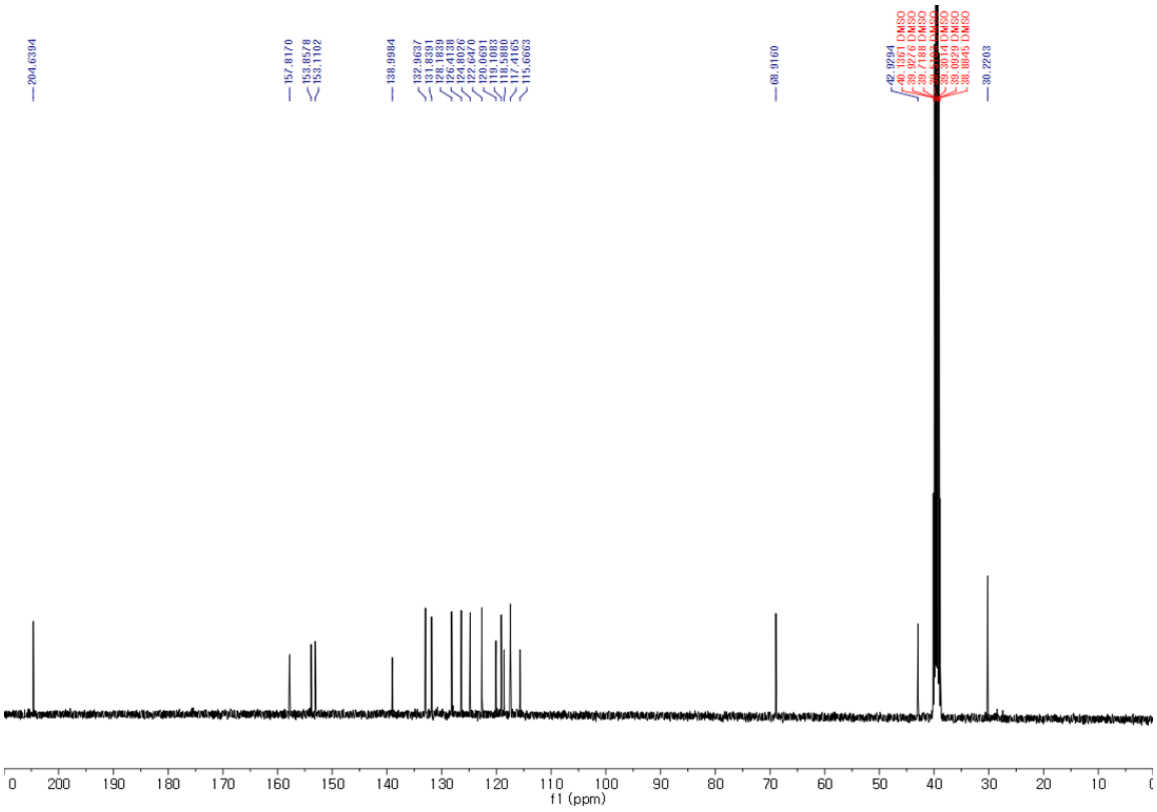


100 MHz, ^{13}C NMR in $CDCl_3$

7-(2-Oxopropyl)chromeno[3,4-c]chromen-6(7H)-one (5d)

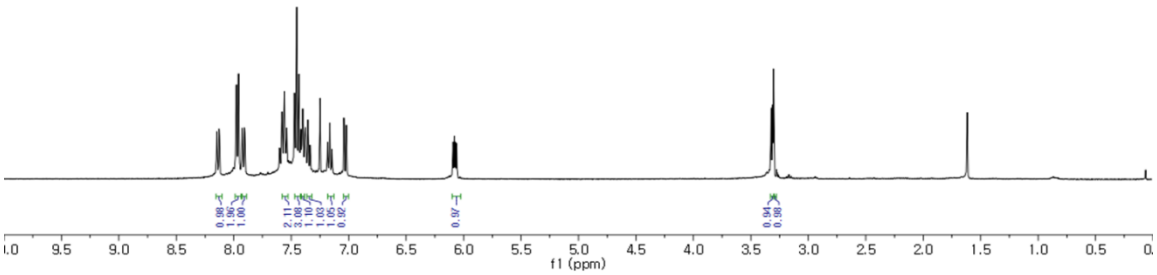


400 MHz, ^{1}H NMR in $CDCl_3$

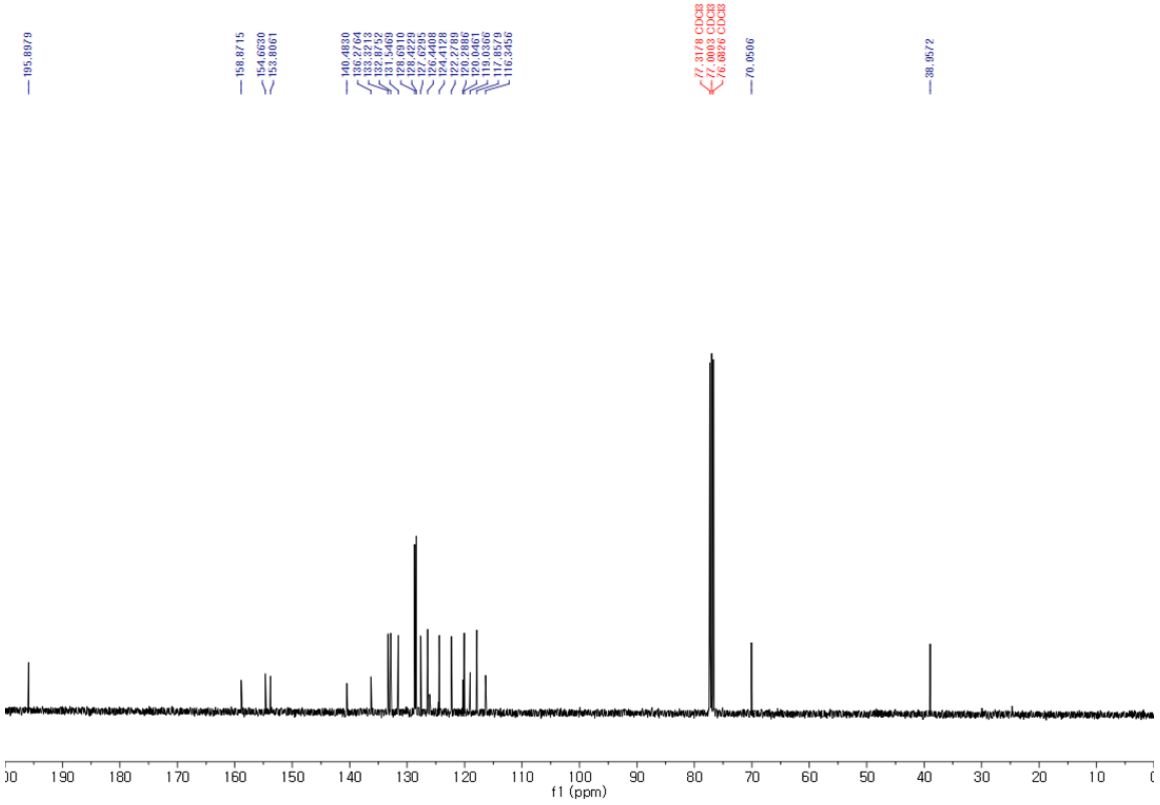


100 MHz, ^{13}C NMR in $CDCl_3$

7-(2-Oxo-2-phenylethyl)chromeno[3,4-c]chromen-6(7H)-one (5e)

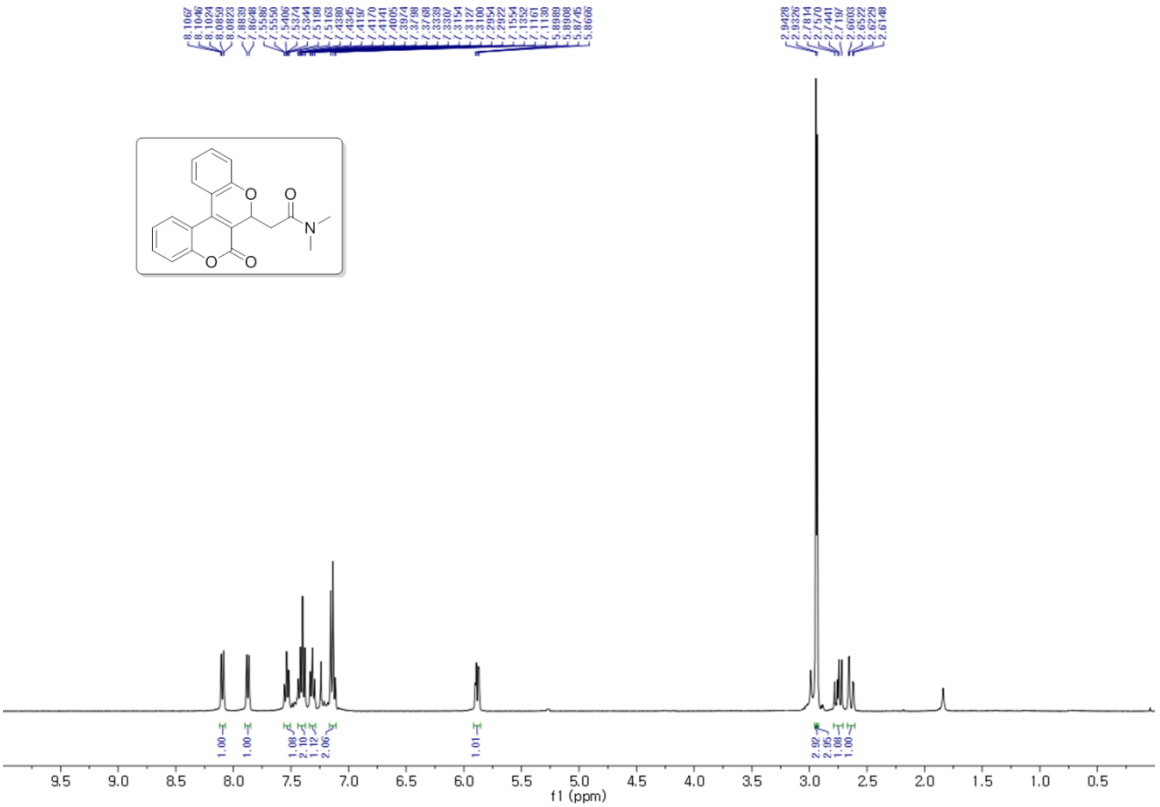


400 MHz, ^{1}H NMR in $CDCl_3$

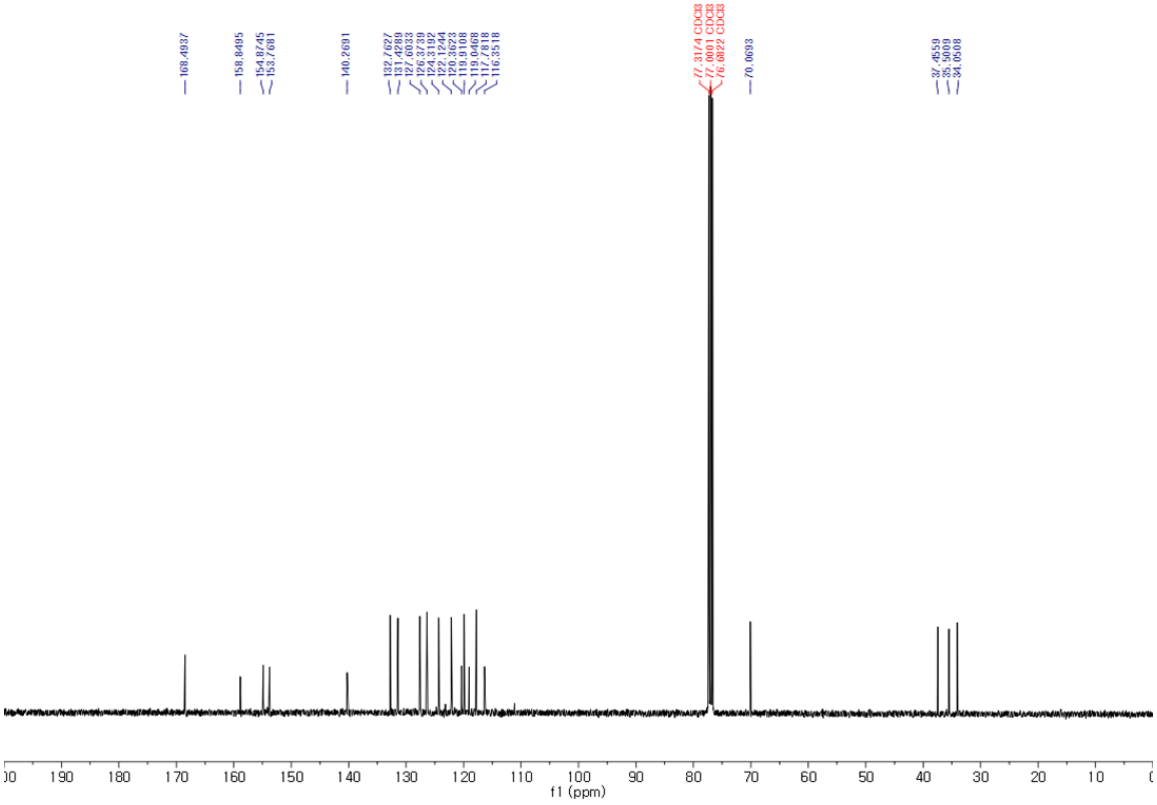


100 MHz, ^{13}C NMR in $CDCl_3$

N,N-Dimethyl-2-(7-oxo-6,7-dihydrochromeno[3,4-c]chromen-6-yl)acetamide (5f)

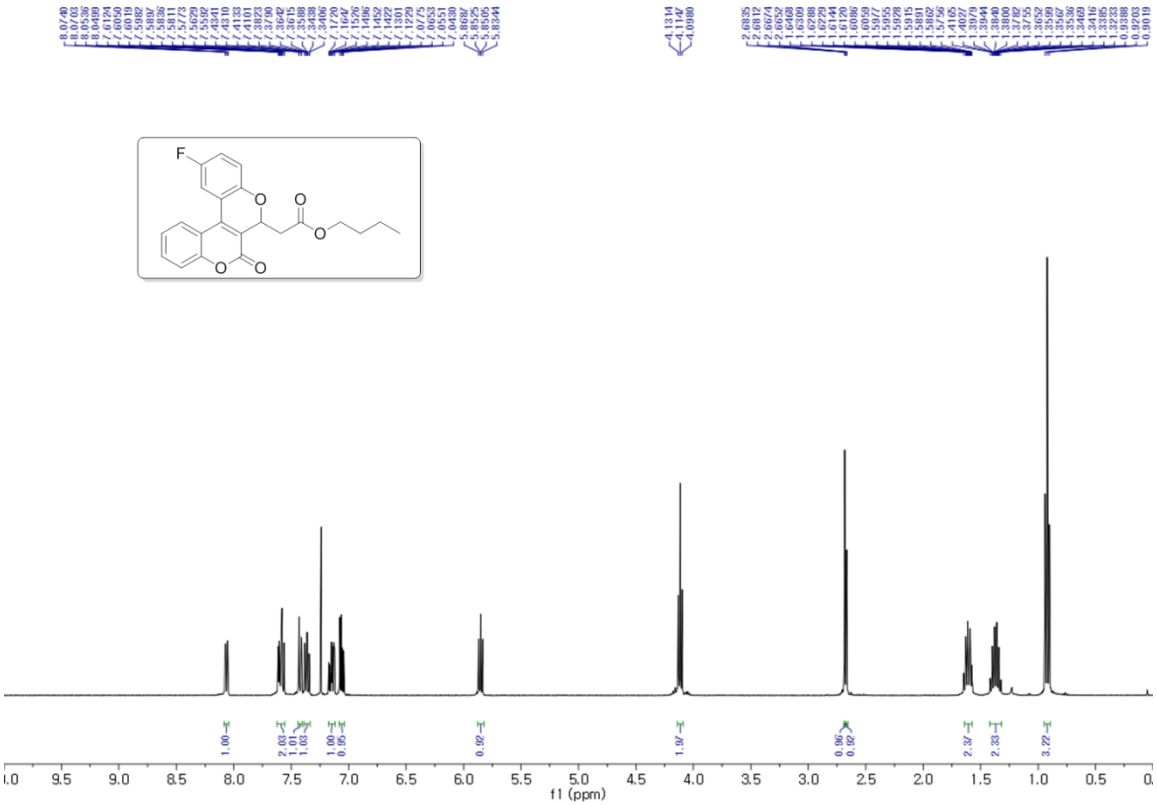


400 MHz, ^{1}H NMR in $CDCl_3$

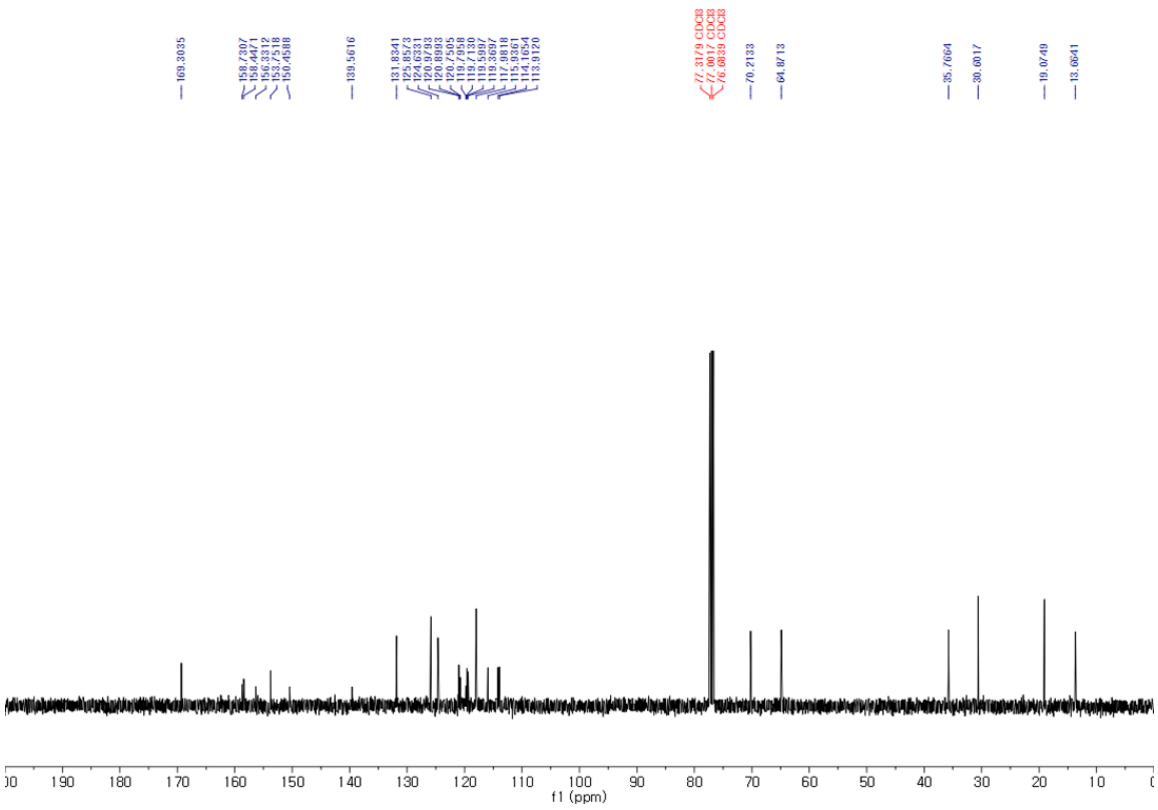


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(2-Fluoro-7-oxo-6,7-dihydrochromeno[3,4-c]chromen-6-yl)acetate (5g)

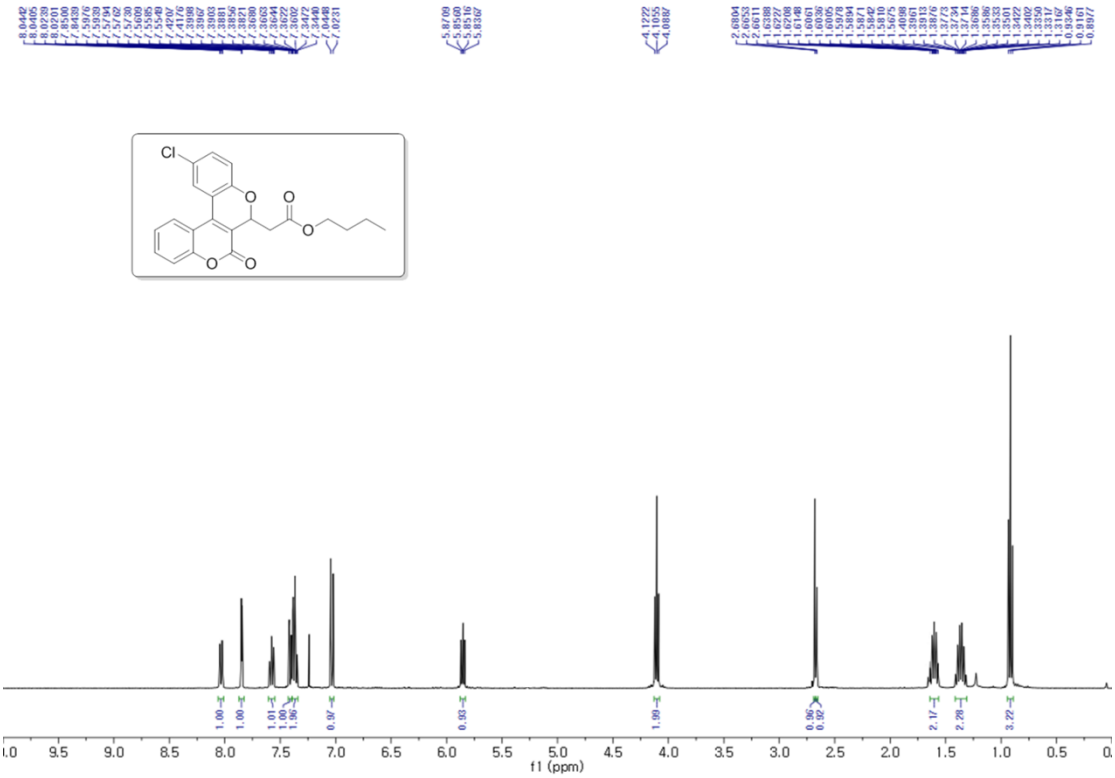


400 MHz, ^{1}H NMR in $CDCl_3$

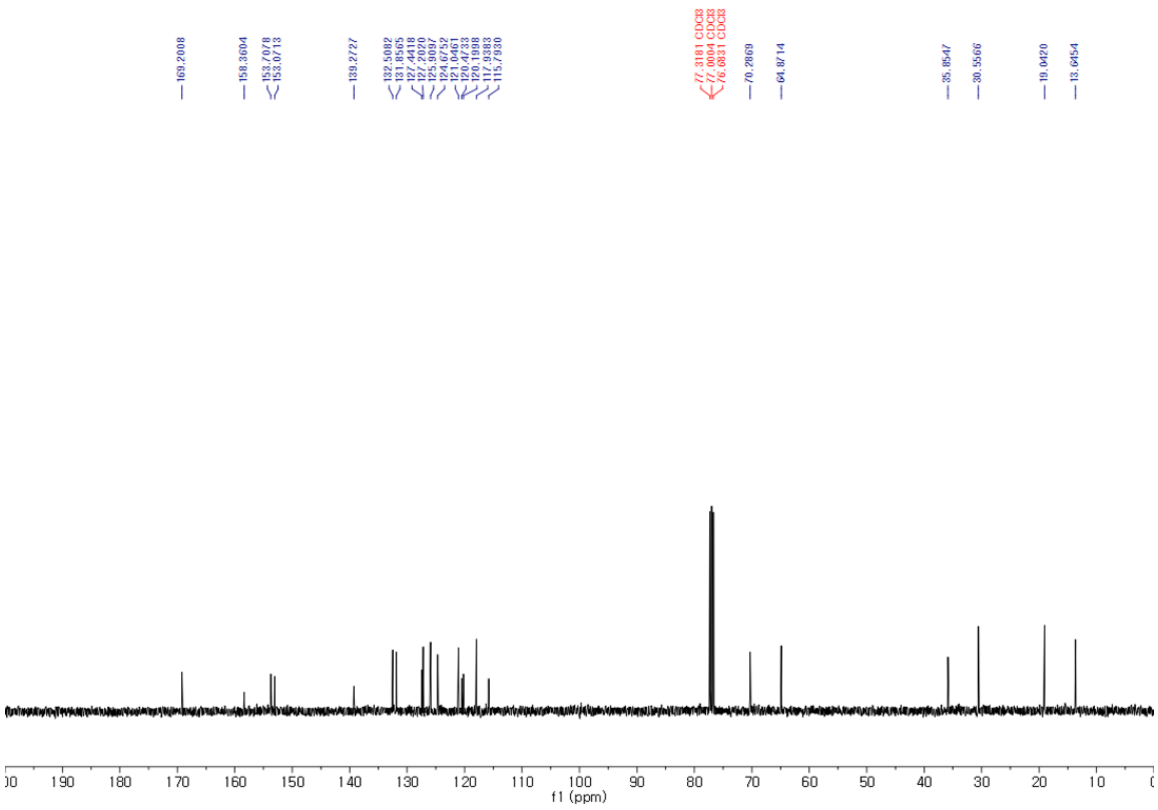


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(2-Chloro-7-oxo-6,7-dihydrochromeno[3,4-c]chromen-6-yl)acetate (5h)

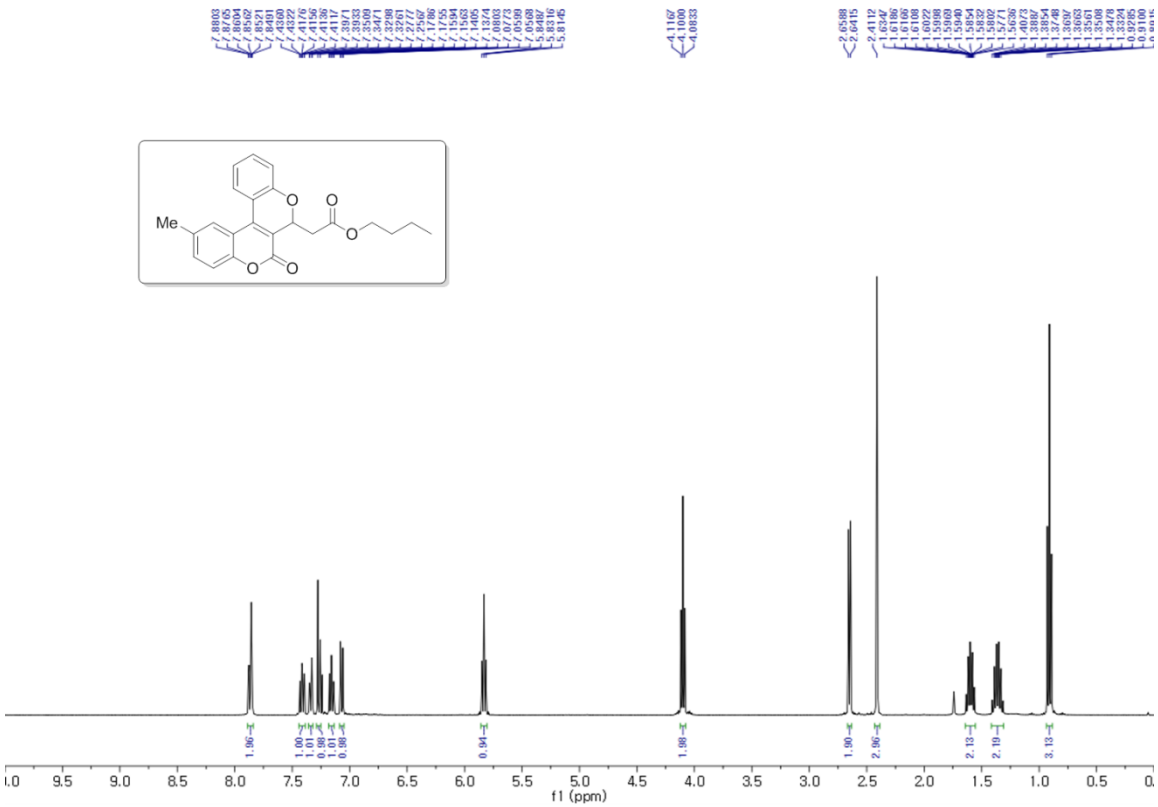


400 MHz, ^{1}H NMR in $CDCl_3$

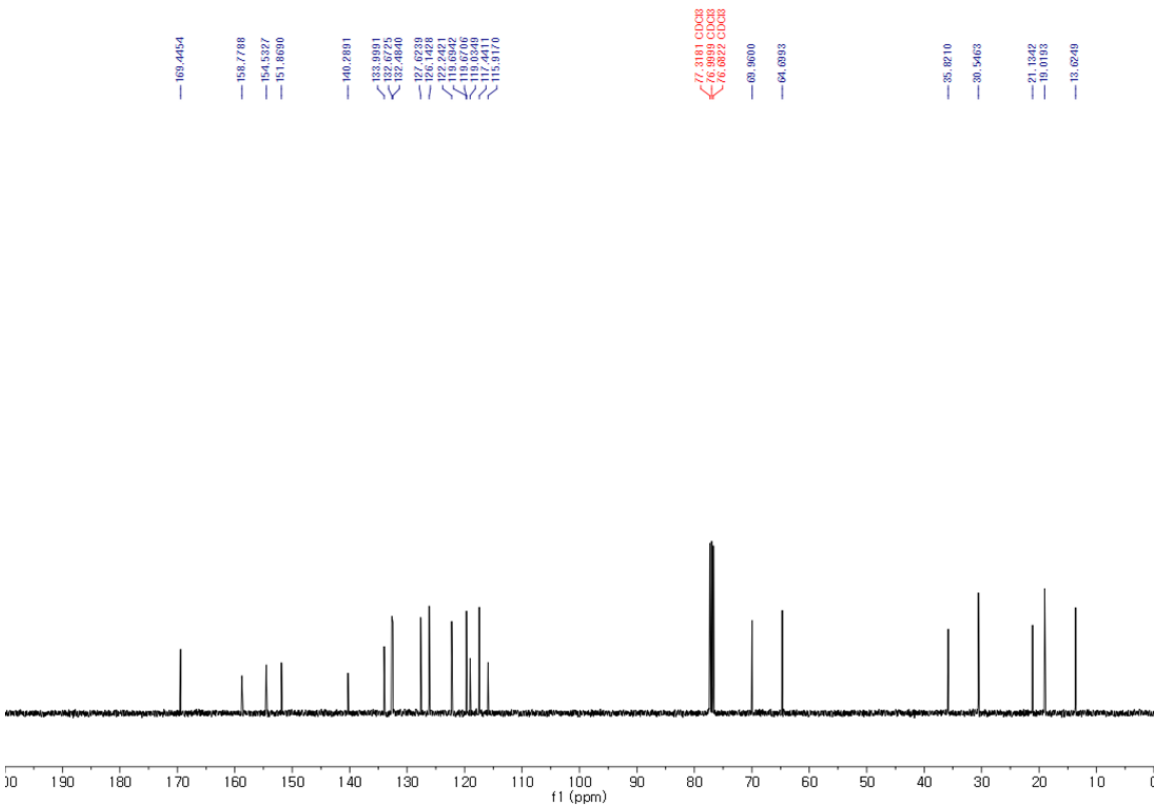


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(11-Methyl-7-oxo-6,7-dihydrochromeno[3,4-c]chromen-6-yl)acetate (5i)

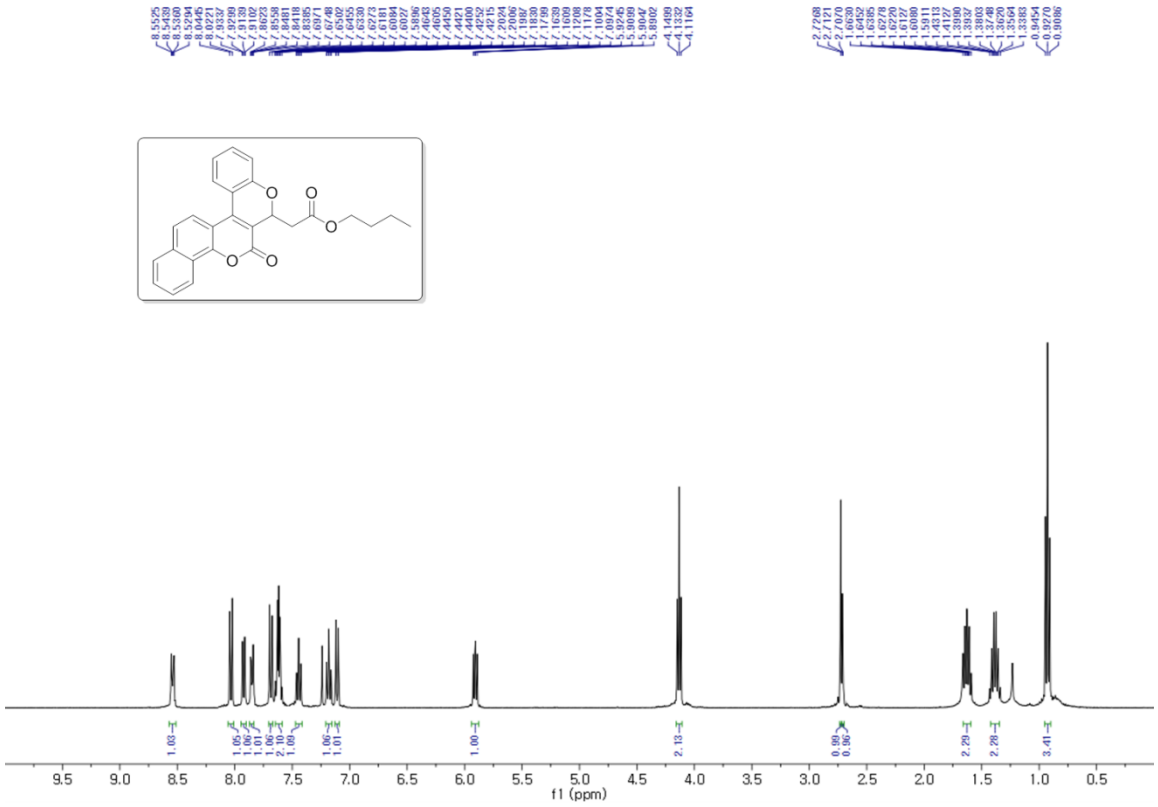


400 MHz, ^{1}H NMR in $CDCl_3$

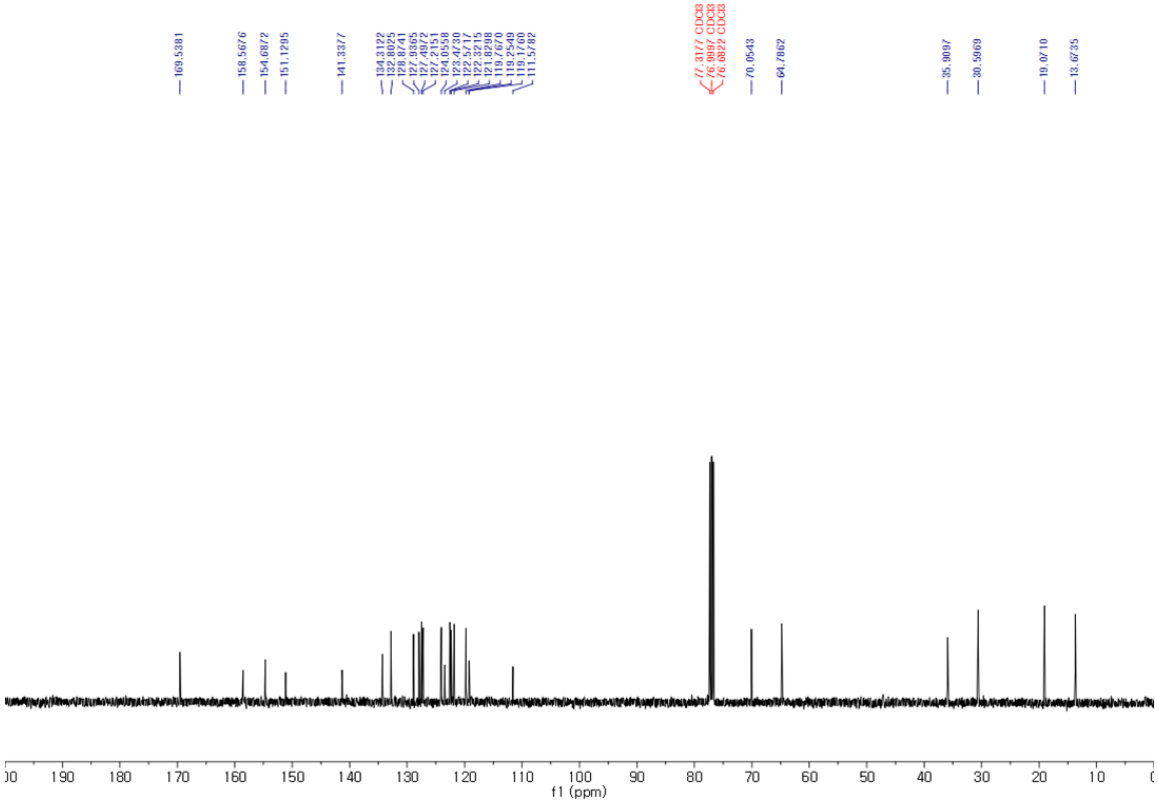


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(14-Oxo-1,14-dihydrobenzo[h]chromeno[3,4-c]chromen-1-yl)acetate (5j)

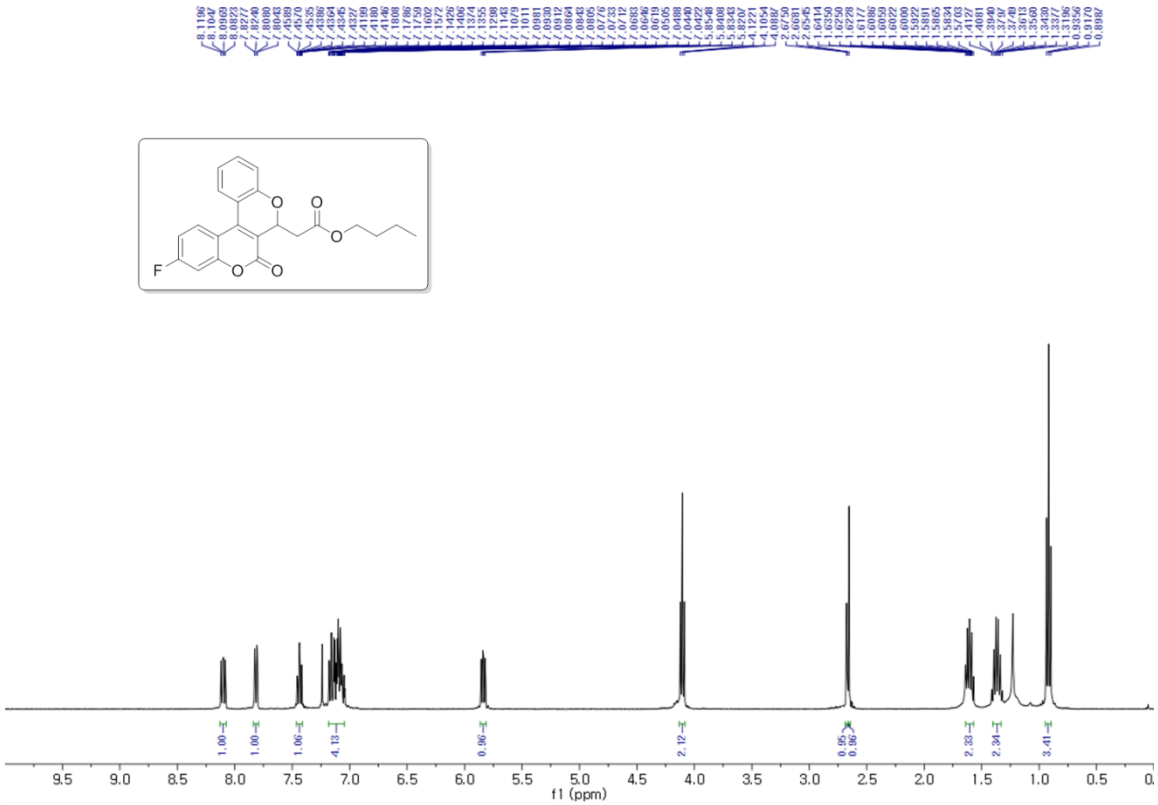


400 MHz, ^{1}H NMR in $CDCl_3$

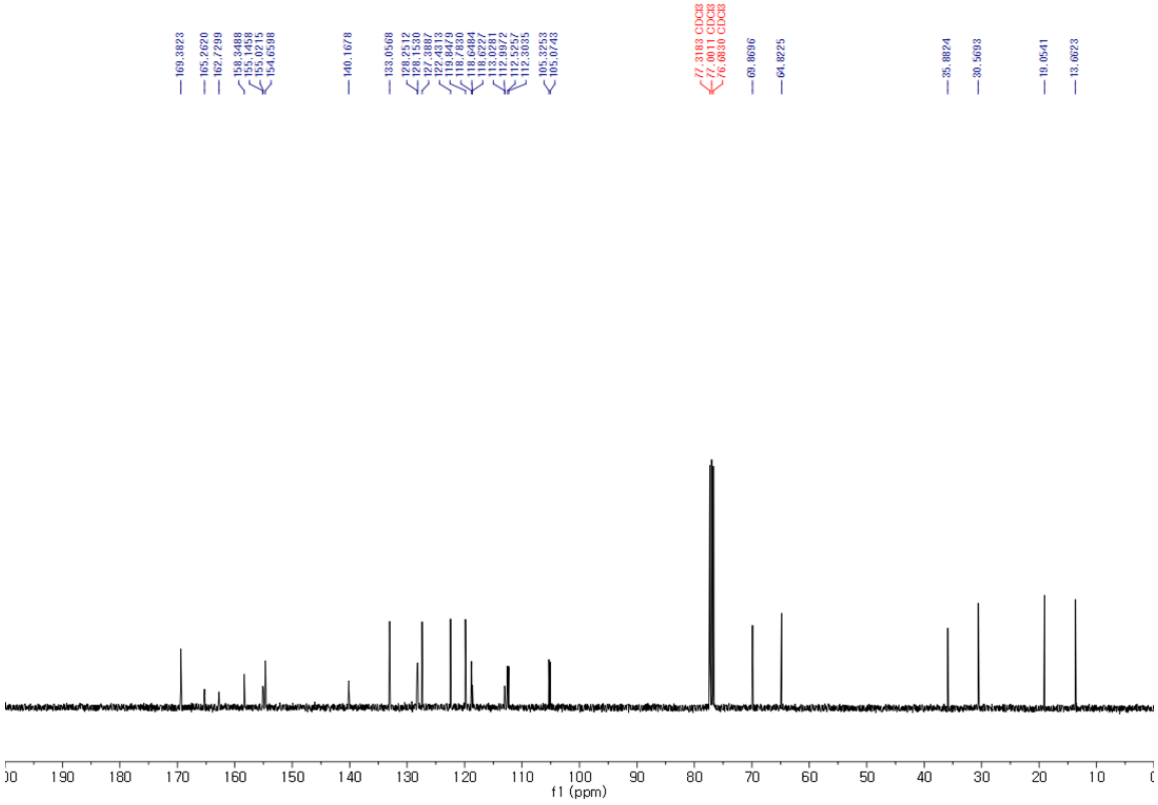


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(10-Fluoro-7-oxo-6,7-dihydrochromeno[3,4-c]chromen-6-yl)acetate (5k)

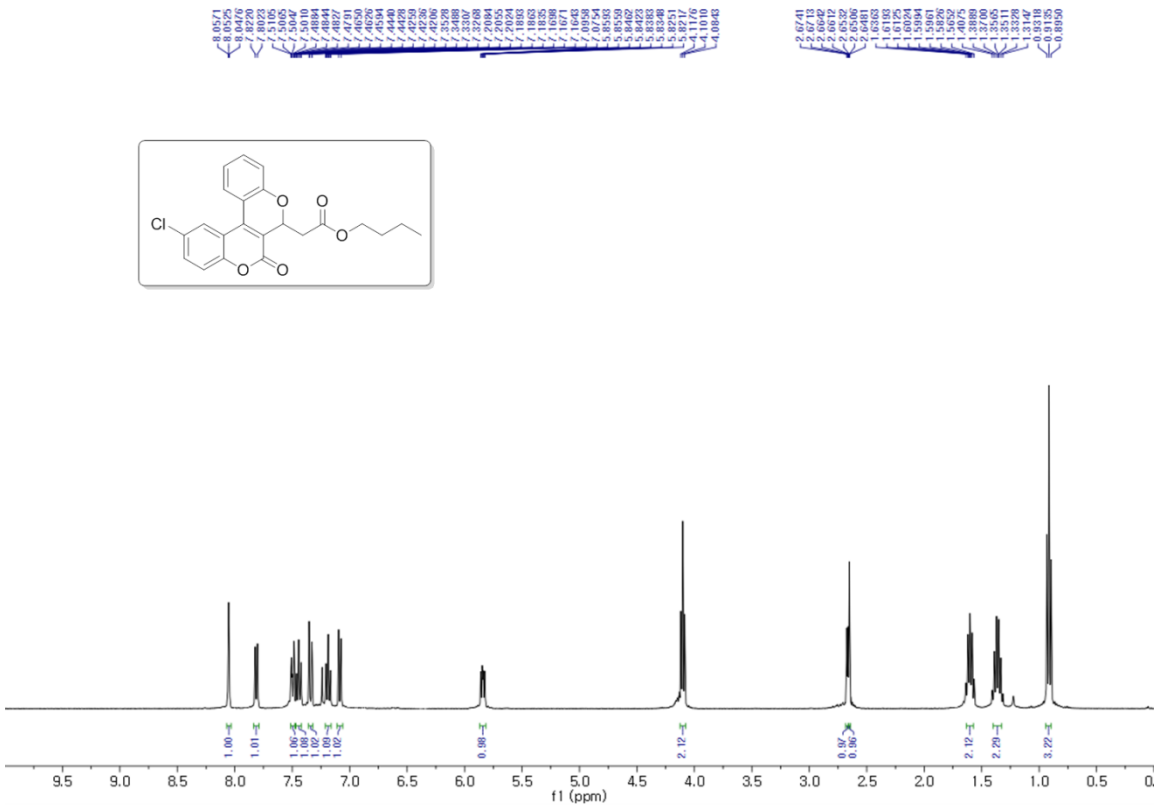


400 MHz, ^{1}H NMR in $CDCl_3$

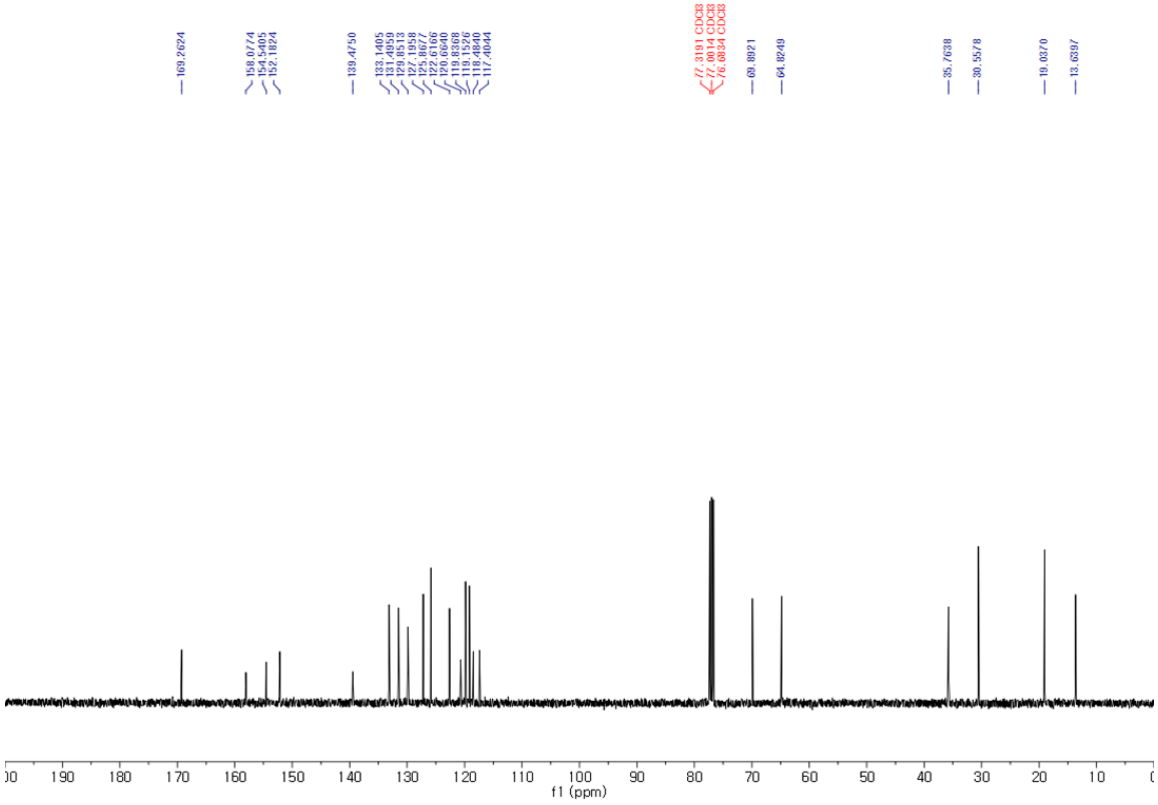


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(11-Chloro-7-oxo-6,7-dihydrochromeno[3,4-c]chromen-6-yl)acetate (5l)

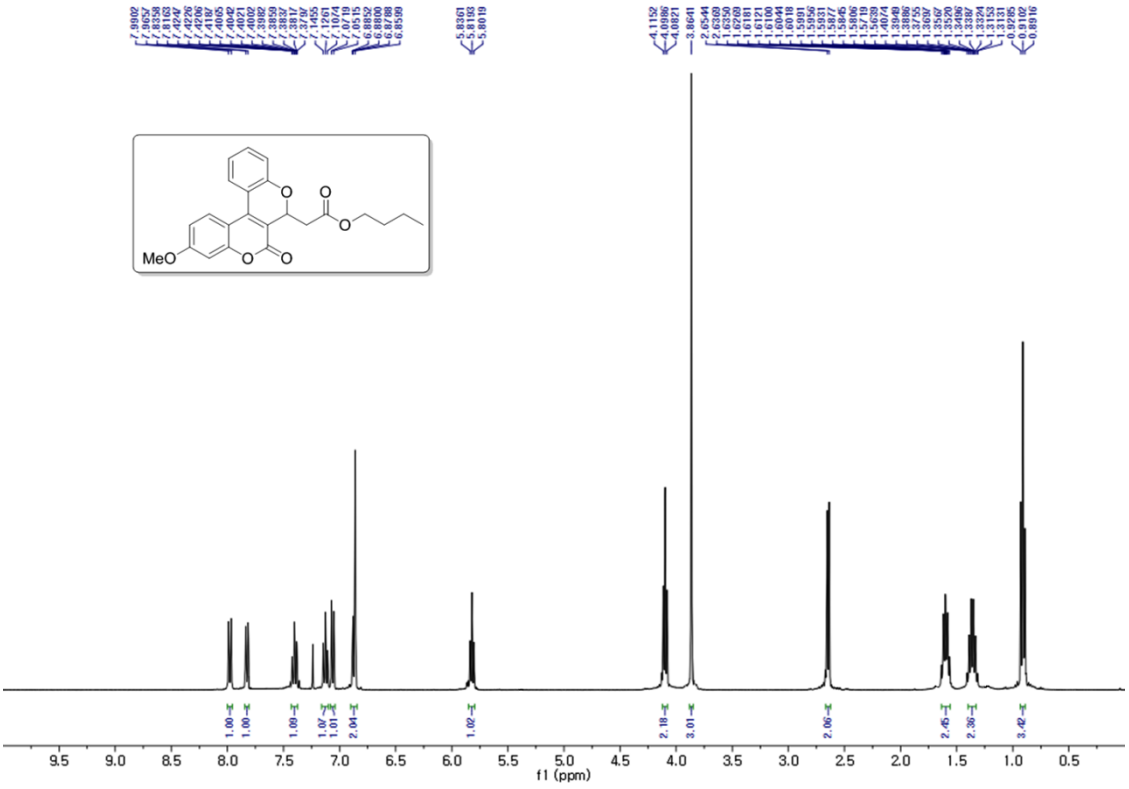


400 MHz, ^{1}H NMR in $CDCl_3$

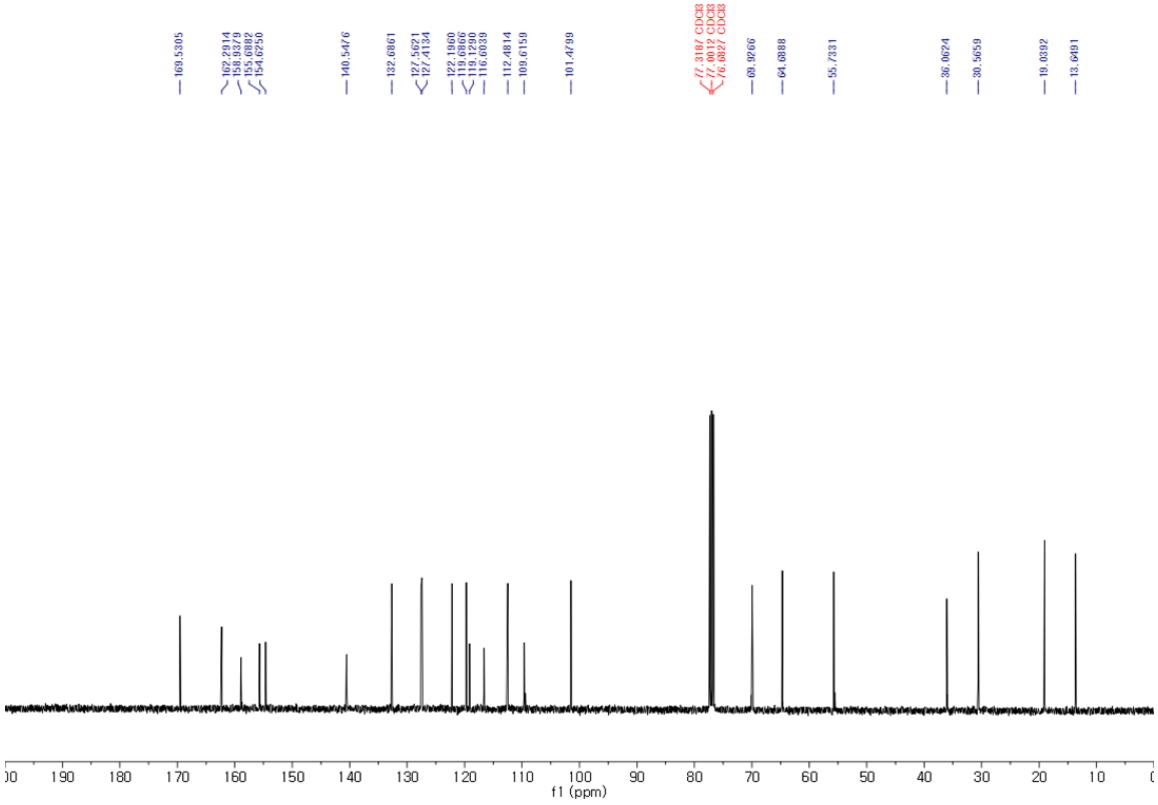


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(10-Methoxy-7-oxo-6,7-dihydrochromeno[3,4-c]chromen-6-yl)acetate (5m)

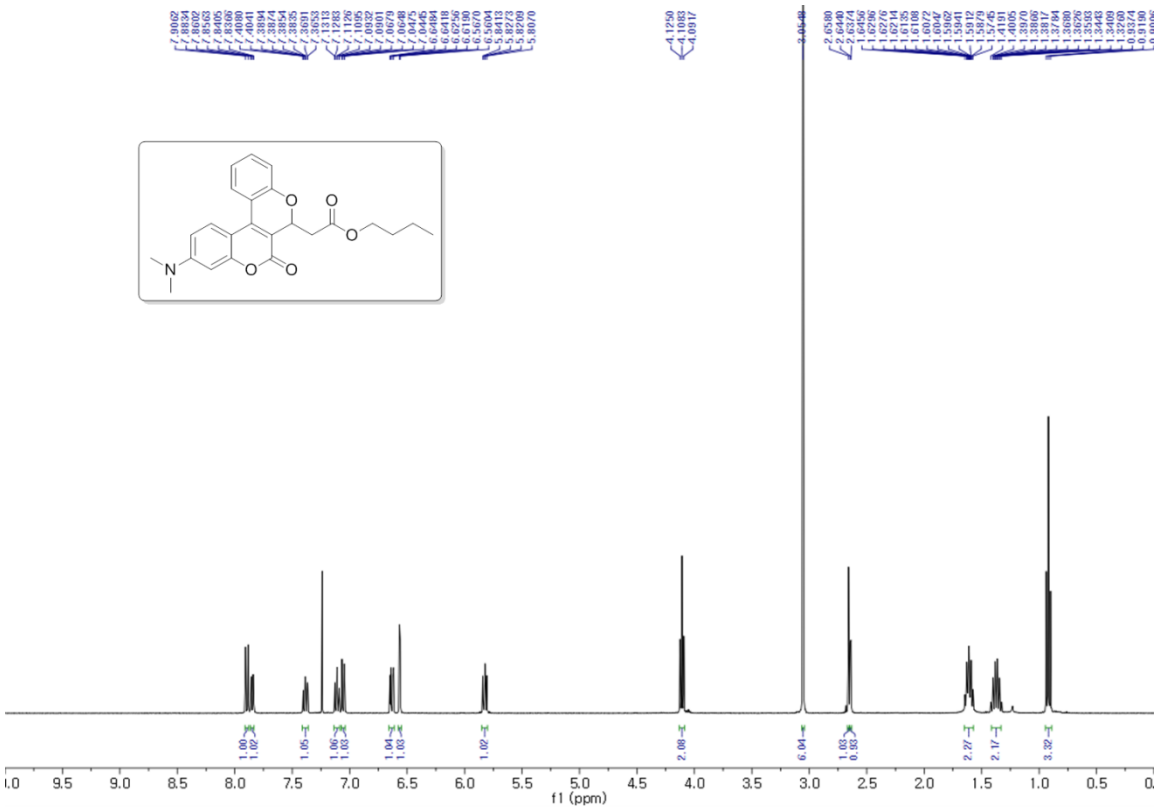


400 MHz, ^{1}H NMR in $CDCl_3$

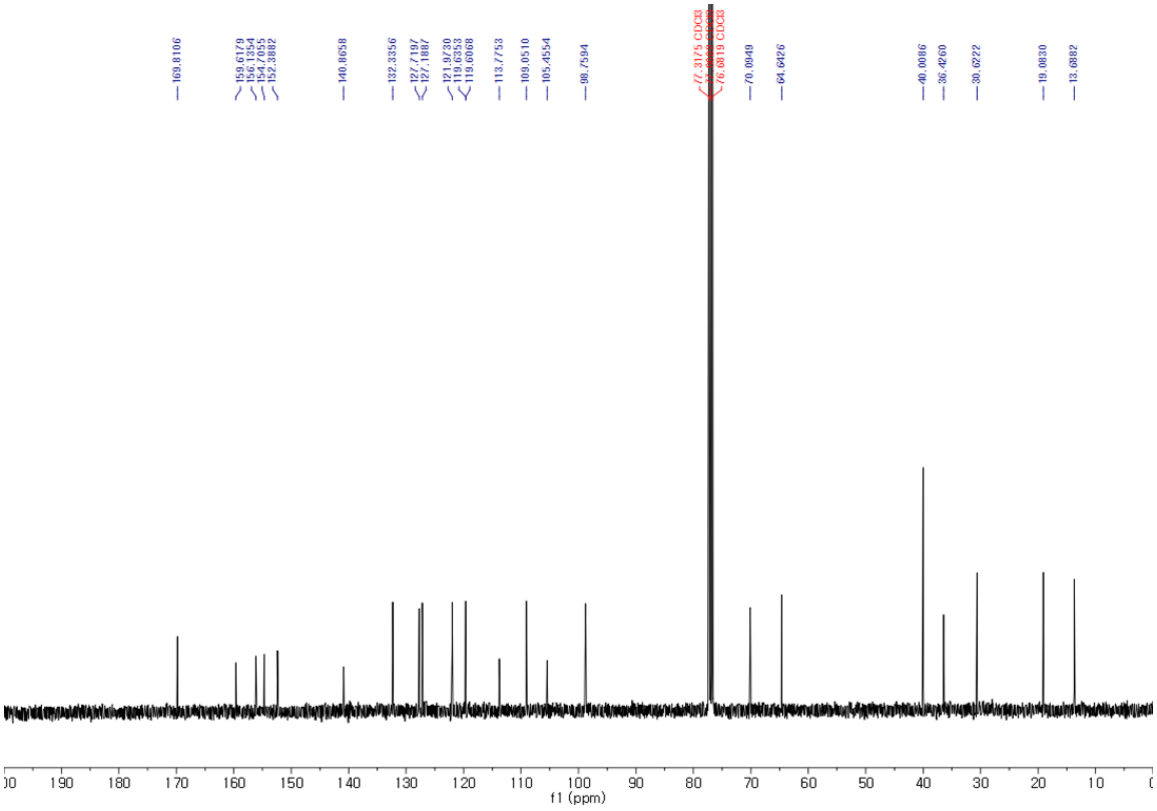


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(10-(Dimethylamino)-7-oxo-6,7-dihydrochromeno[3,4-c]chromen-6-yl)acetate (5n)

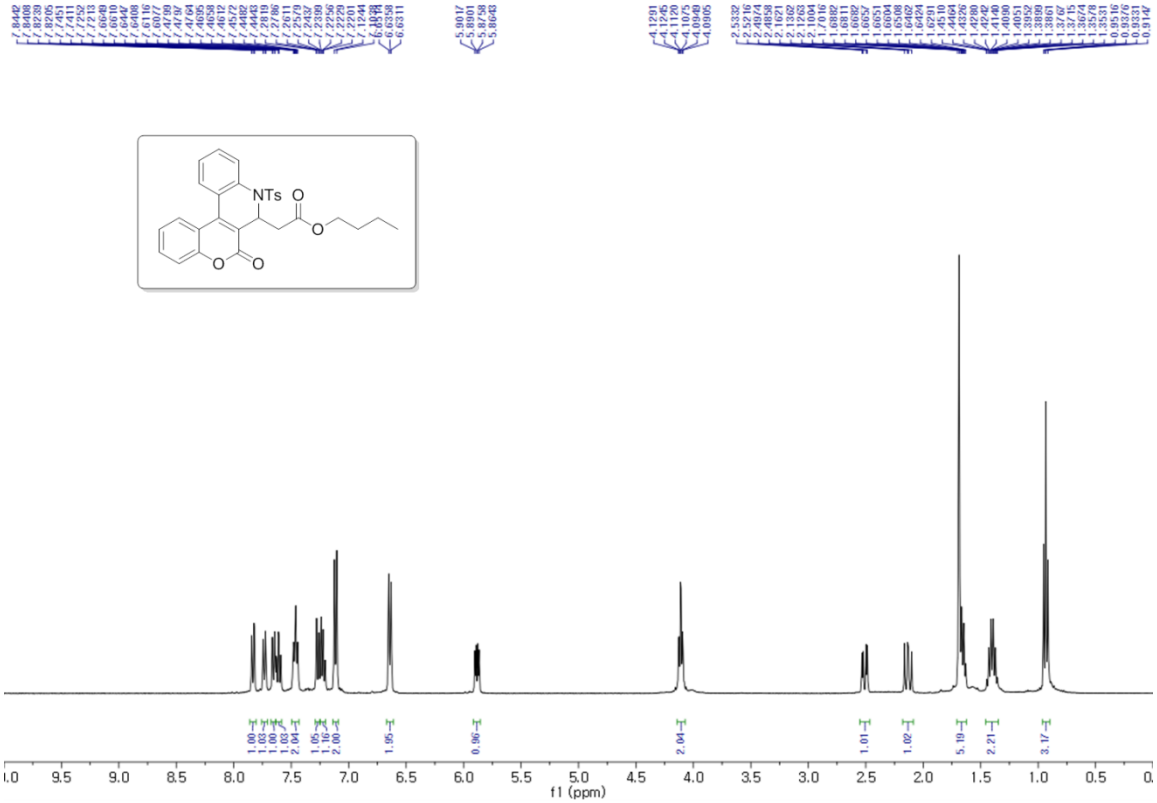


400 MHz, ^{1}H NMR in $CDCl_3$

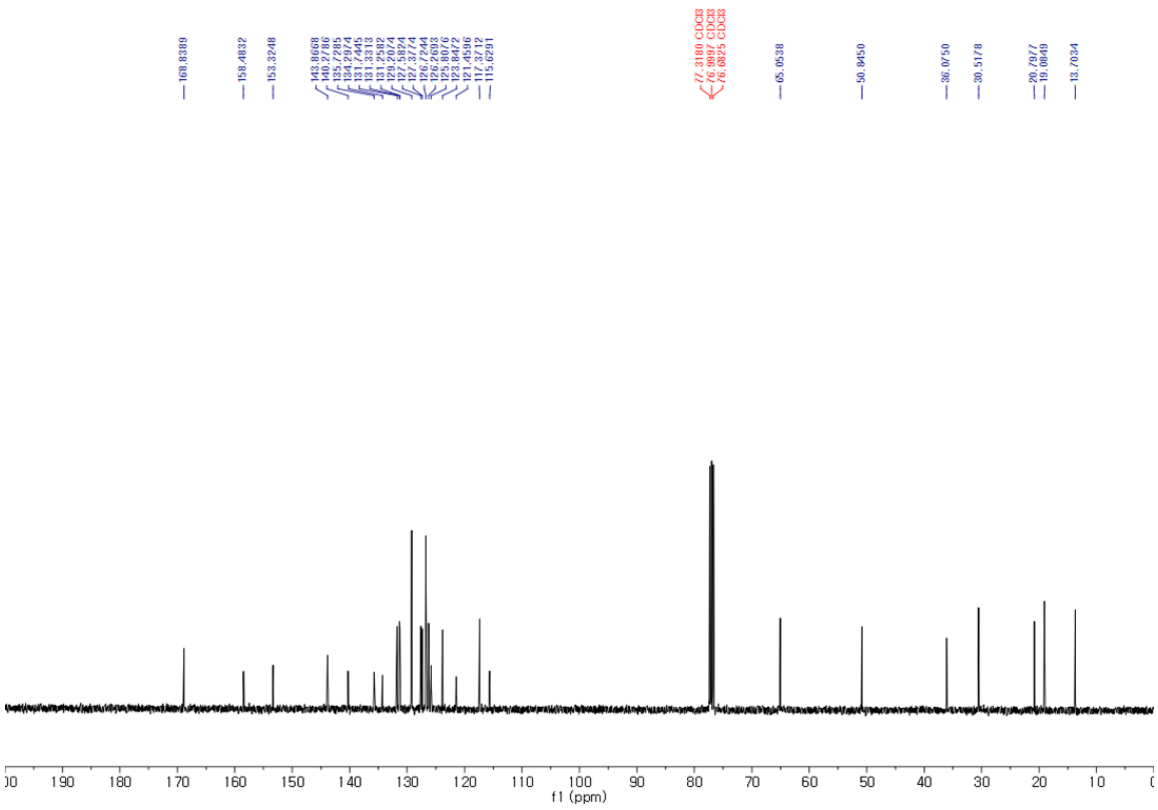


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-(6-Oxo-8-tosyl-7,8-dihydro-6H-chromeno[3,4-c]quinolin-7-yl)acetate (5o)



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



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