Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Synthetic Approach to Flavanones and Flavones via Ligand-Free Palladium(II)-Catalyzed Conjugate Addition of Arylboronic Acids to Chromones

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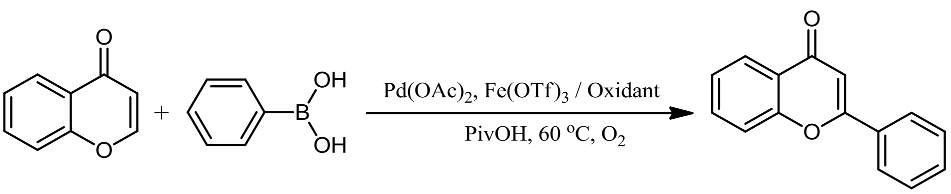
Appendix I

I. General Methods and Materials

Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of oxygen. Solvents were used without purification or degassing. 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 354 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. 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. High-resolution mass spectrometry (HRMS) data were recorded on LC-TOF. Commercial grade reagents and solvents were used without further purification except as indicated below. Unless otherwise stated, all commercial reagents and solvents were used without additional purification.

II. Optimization Study

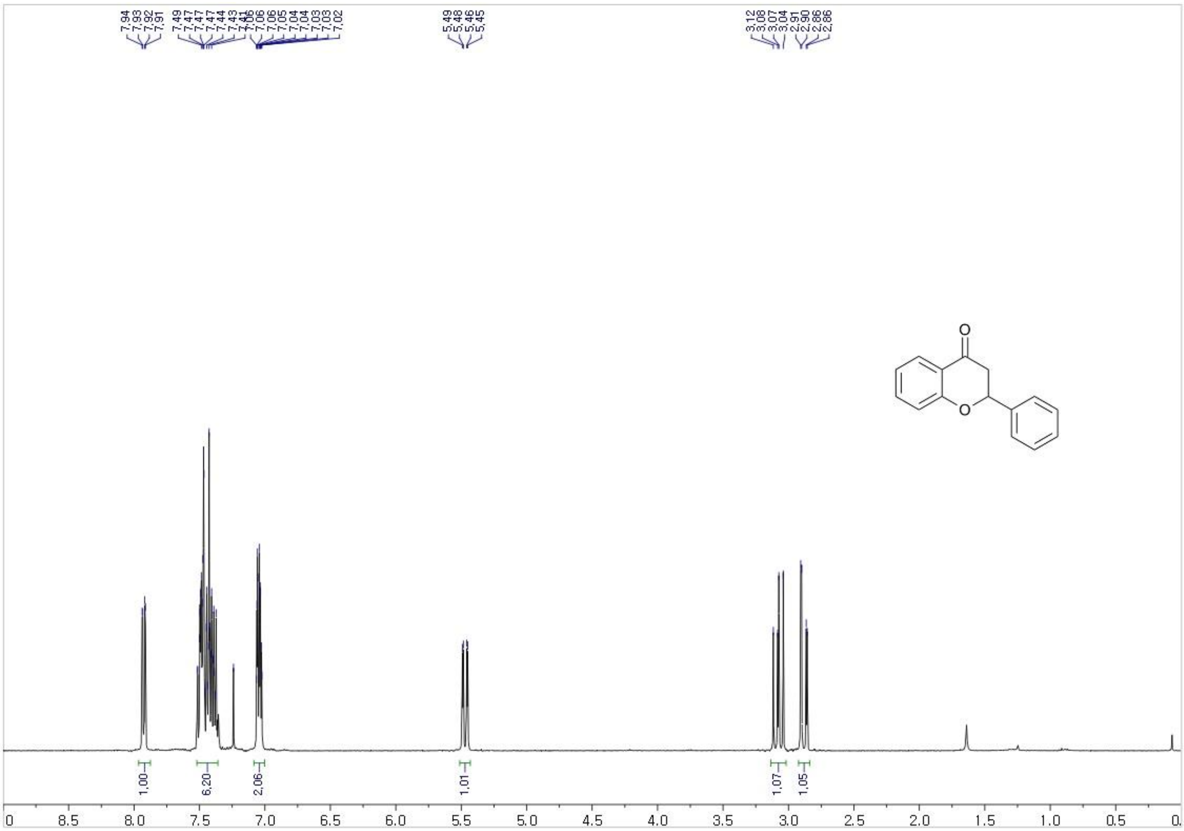
Table 1S. Screening of Oxidants



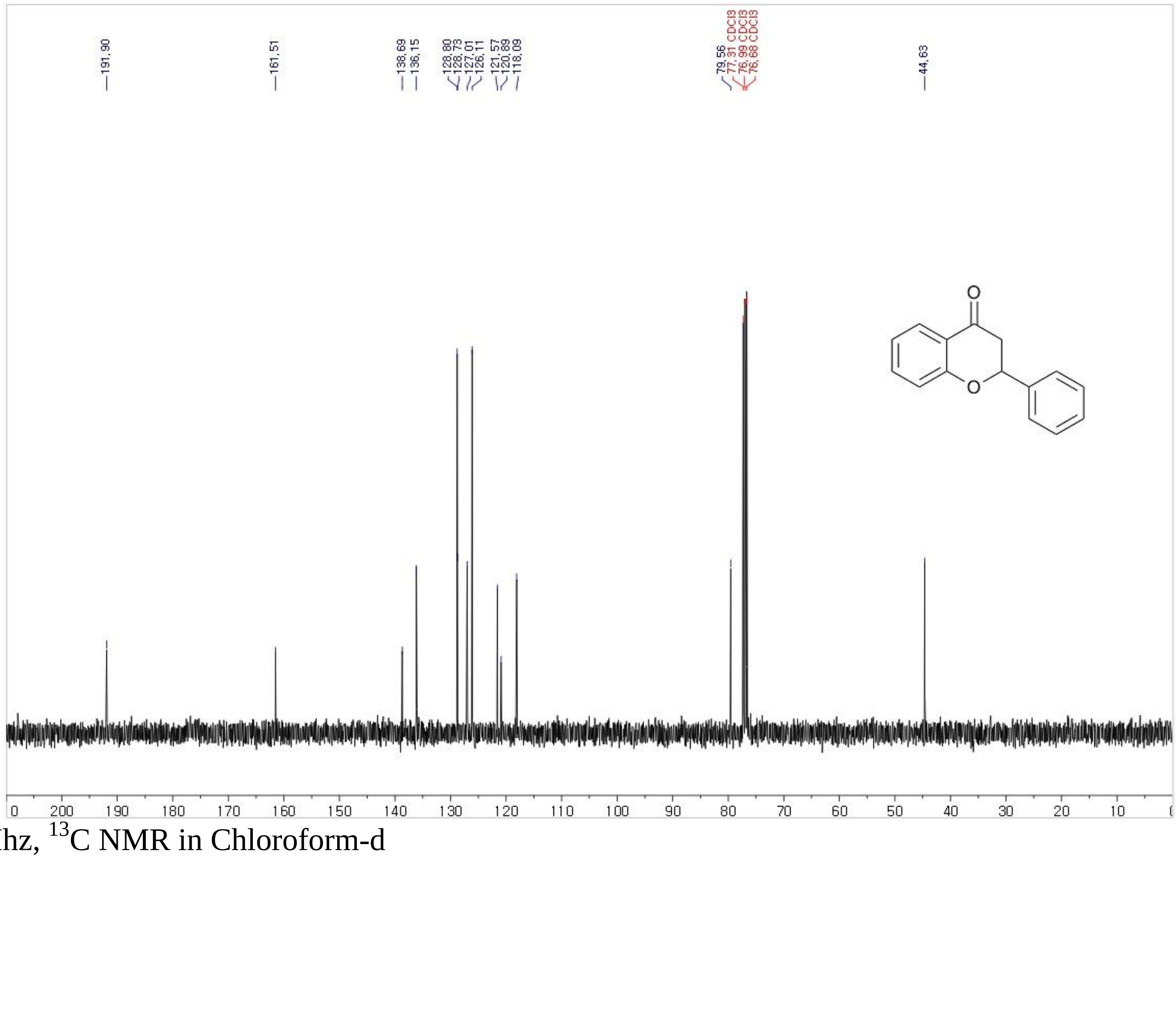
entry	oxidant	yield (%)
1	$Pb(OAc)_4$	-
2	MnO_2	8
3	CAN	-
4	CrO_3	71

5	PDC	-
6	BQ	trace
7	Oxone®	55
8	I_2	-
9	$Tl(OTf)_3$	-
10	SeO_2	-
11	IBX	-
12	*m*-CPBA	30
13	$(BzO)_2$	62
14	*t*-BuOOH	-
15	$(t\text{-BuO})_2$	-
16	TEMPO	20
17	DDQ	35
18	DDQ, KNO_2	97

2-Phenylchroman-4-one (3a)

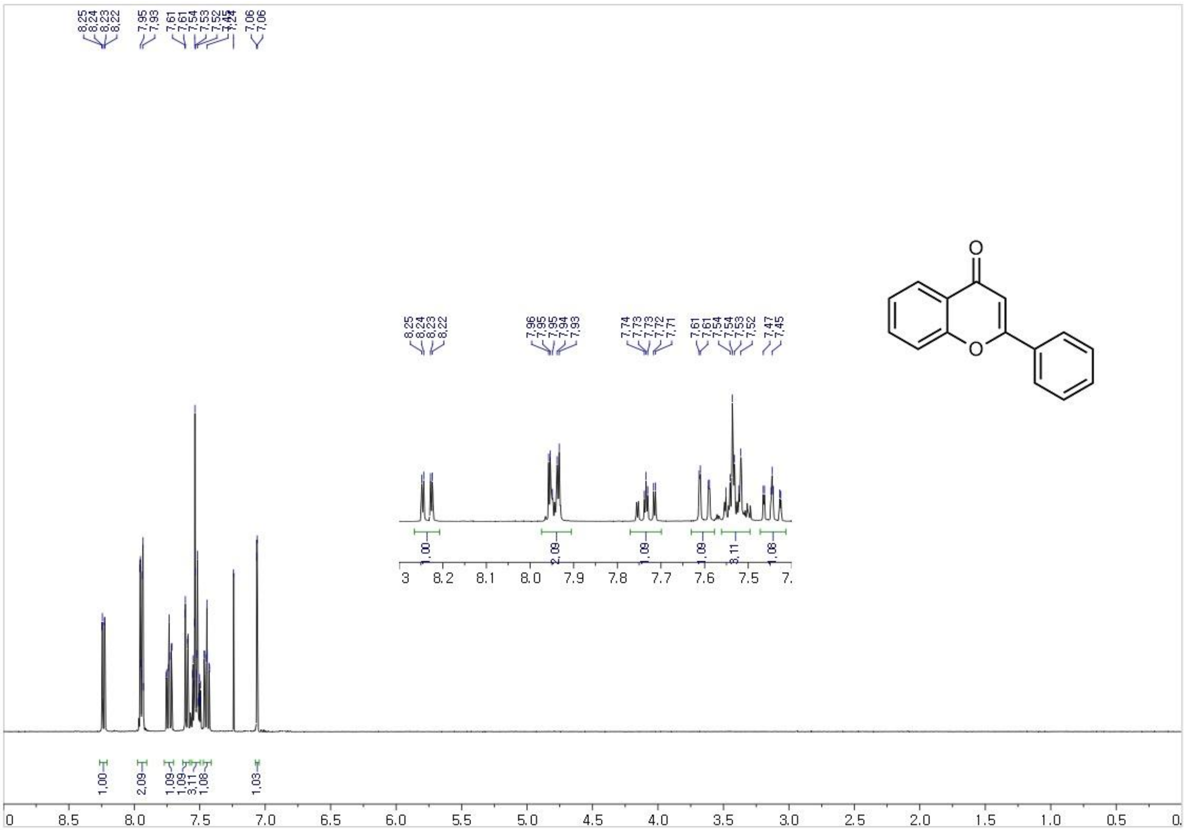


400 Mhz, ^{1}H NMR in Chloroform-d

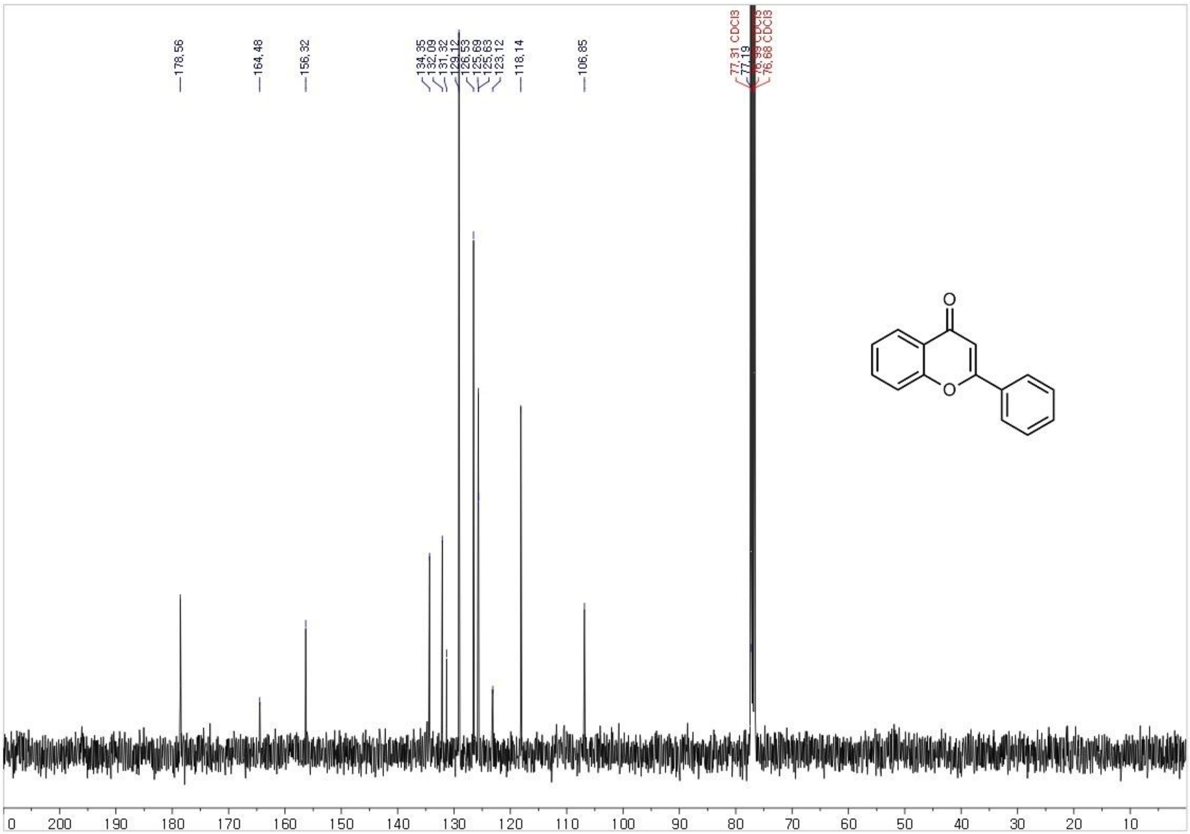


100 Mhz, ^{13}C NMR in Chloroform-d

2-Phenyl-4H-chromen-4-one (4a)

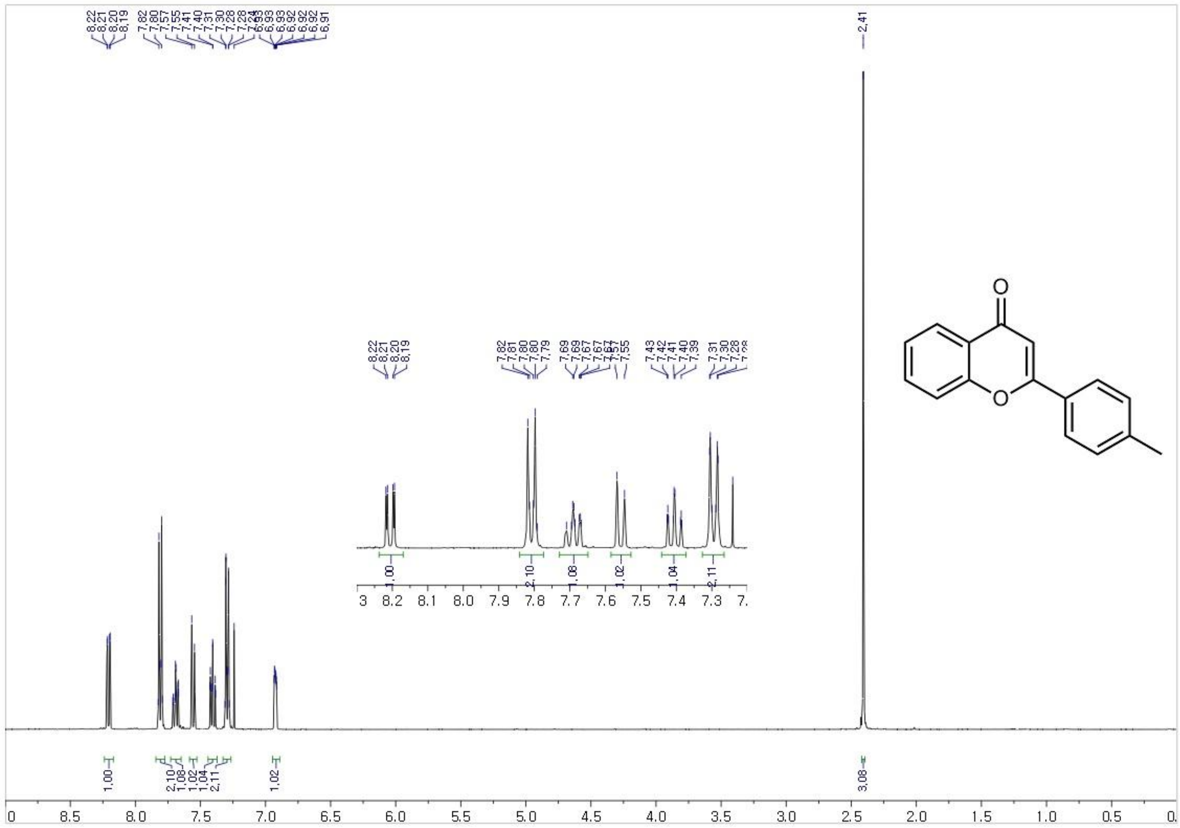


400 Mhz, ^{1}H NMR in Chloroform-d

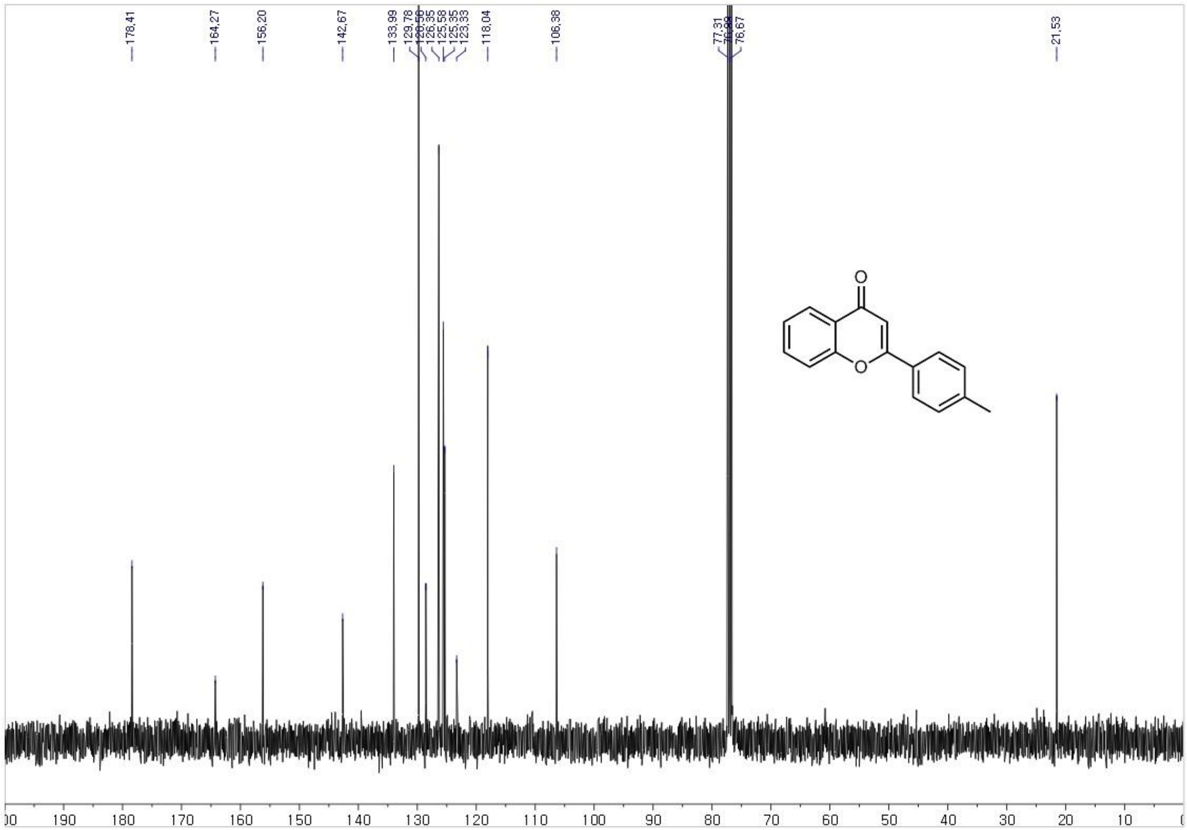


100 Mhz, ^{13}C NMR in Chloroform-d

2-(*p*-tolyl)-4H-chromen-4-one (4b)

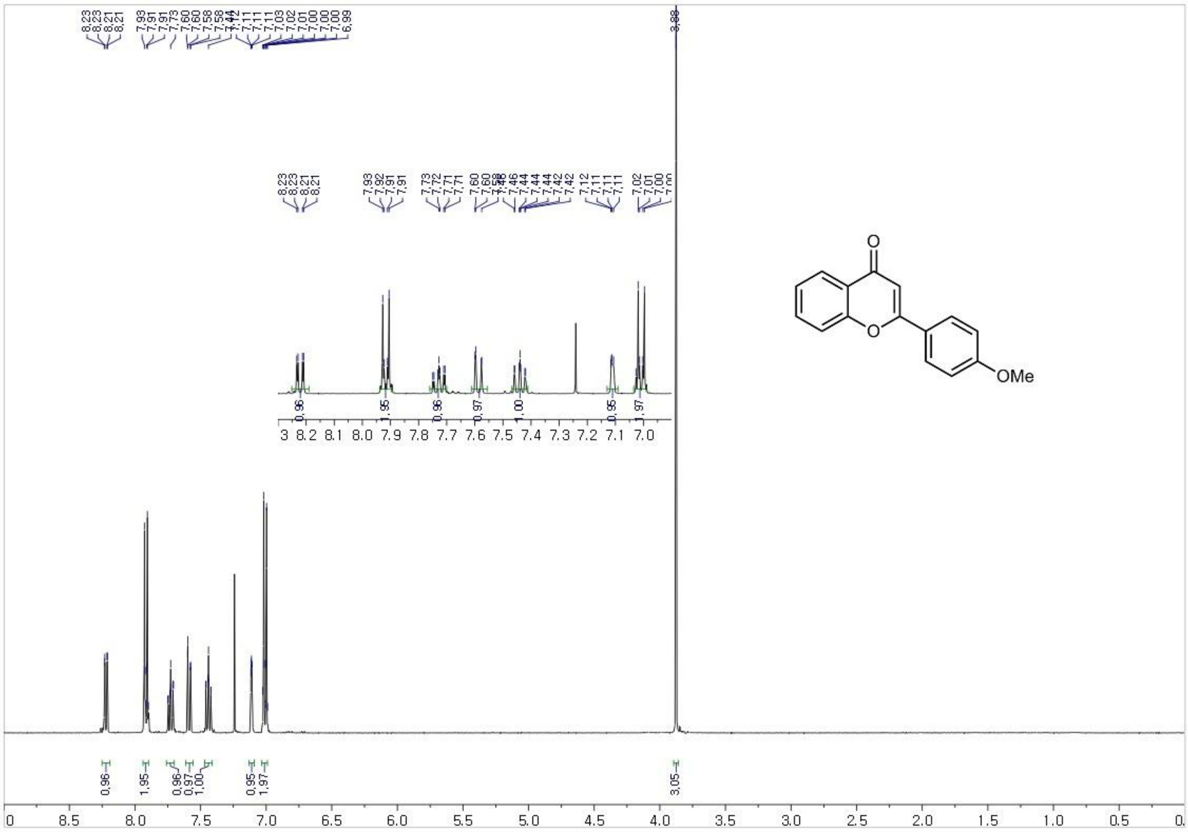


400 Mhz, ^{1}H NMR in Chloroform-d

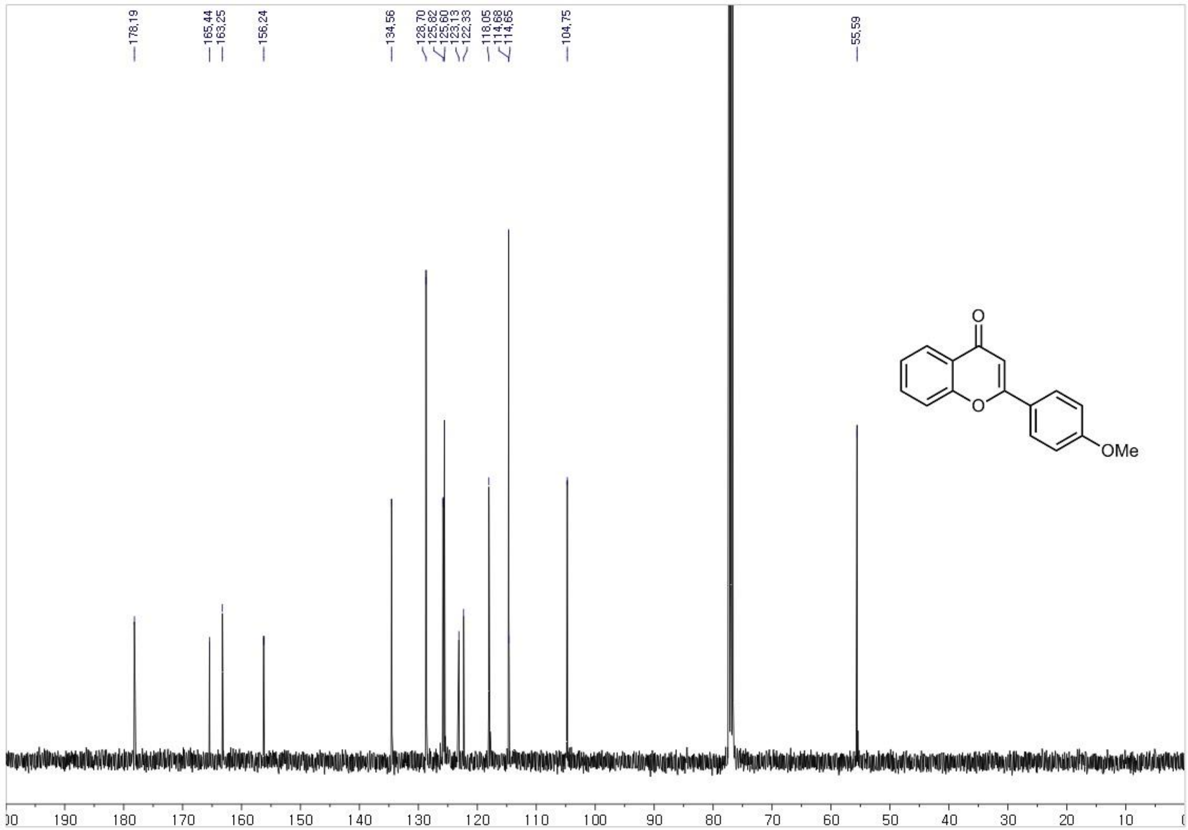


100 Mhz, ^{13}C NMR in Chloroform-d

2-(4-methoxyphenyl)-4H-chromen-4-one (4c)

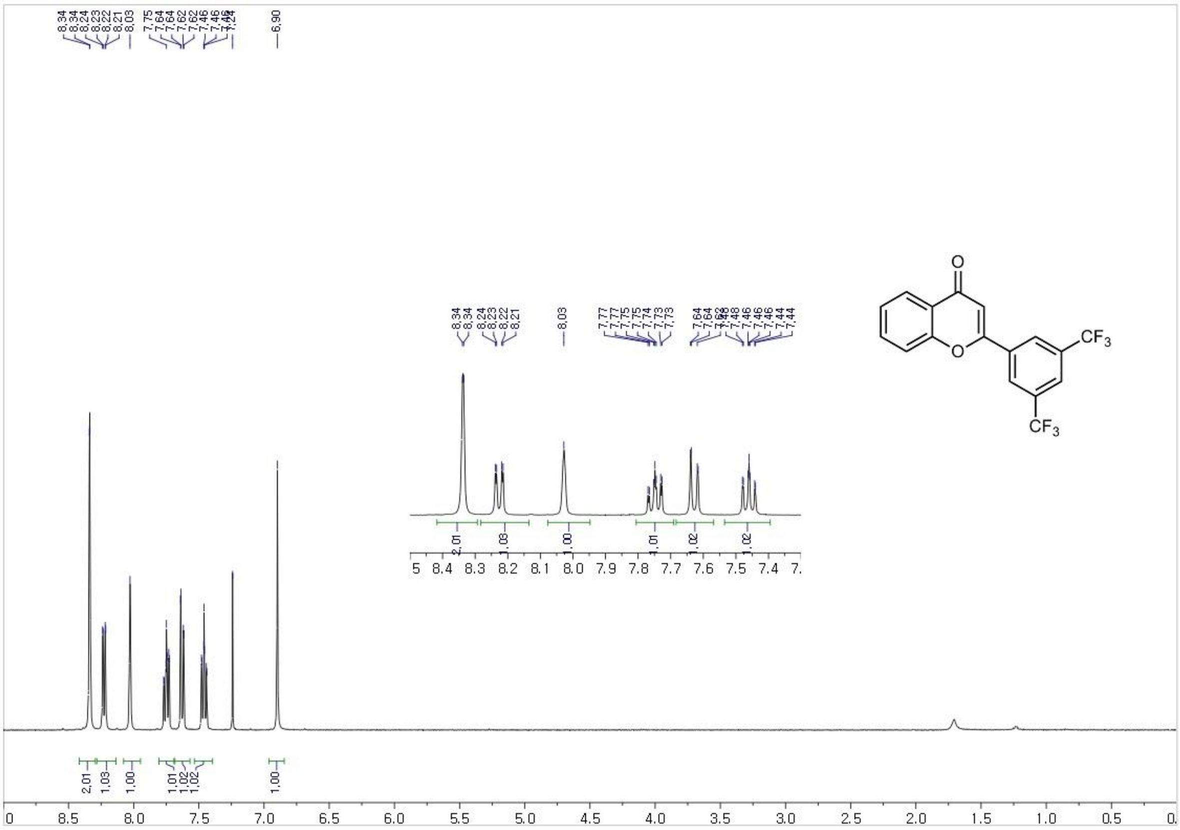


400 Mhz, ^{1}H NMR in Chloroform-d

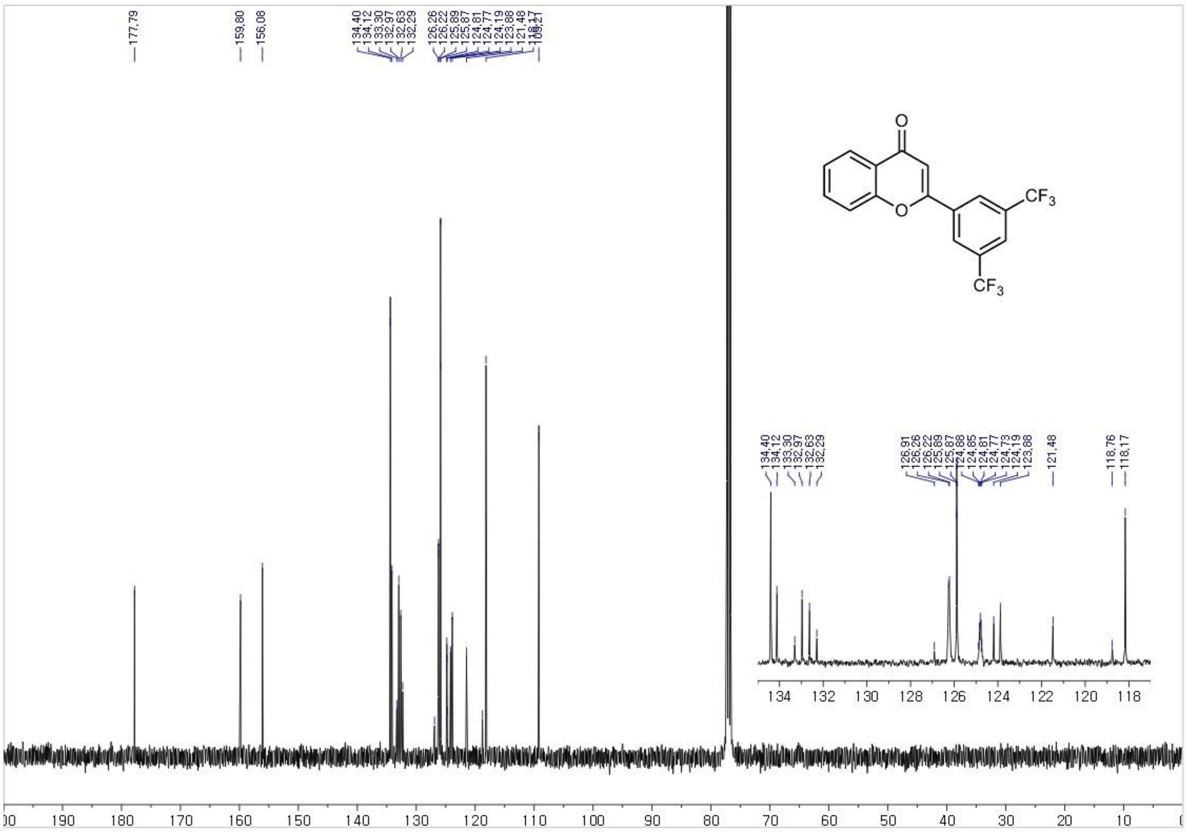


100 Mhz, ^{13}C NMR in Chloroform-d

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

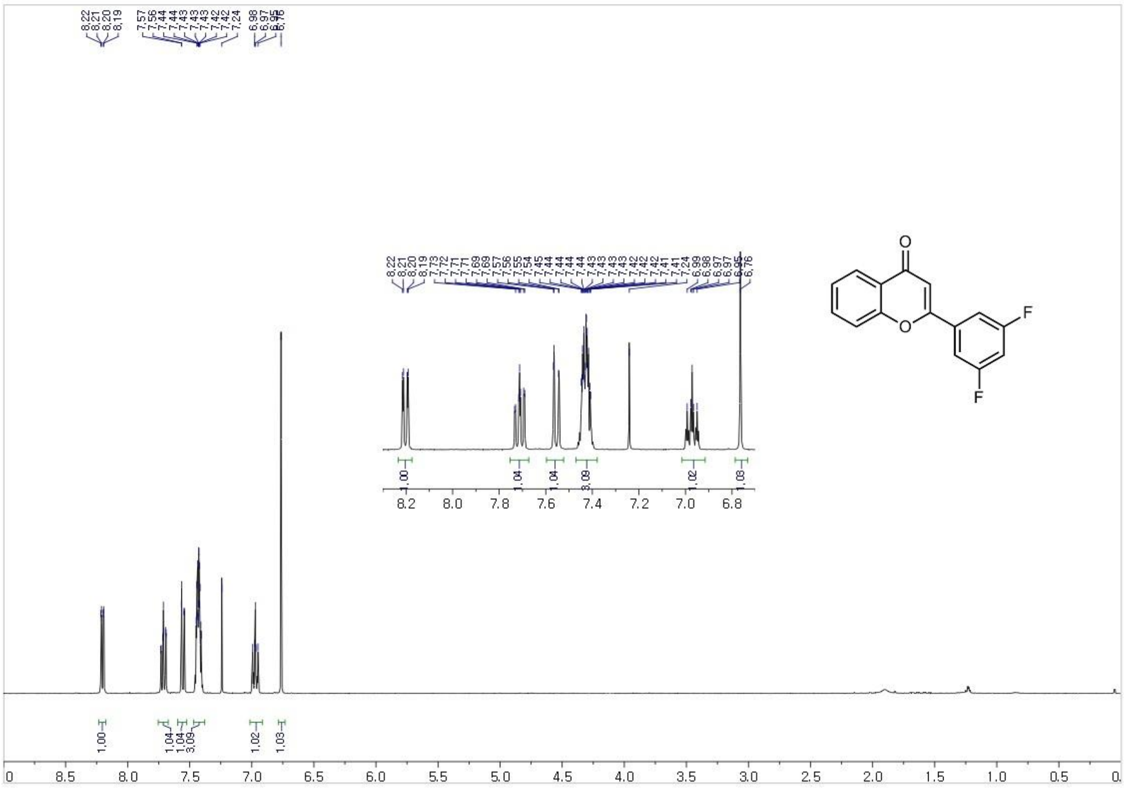


400 Mhz, ^{1}H NMR in Chloroform-d

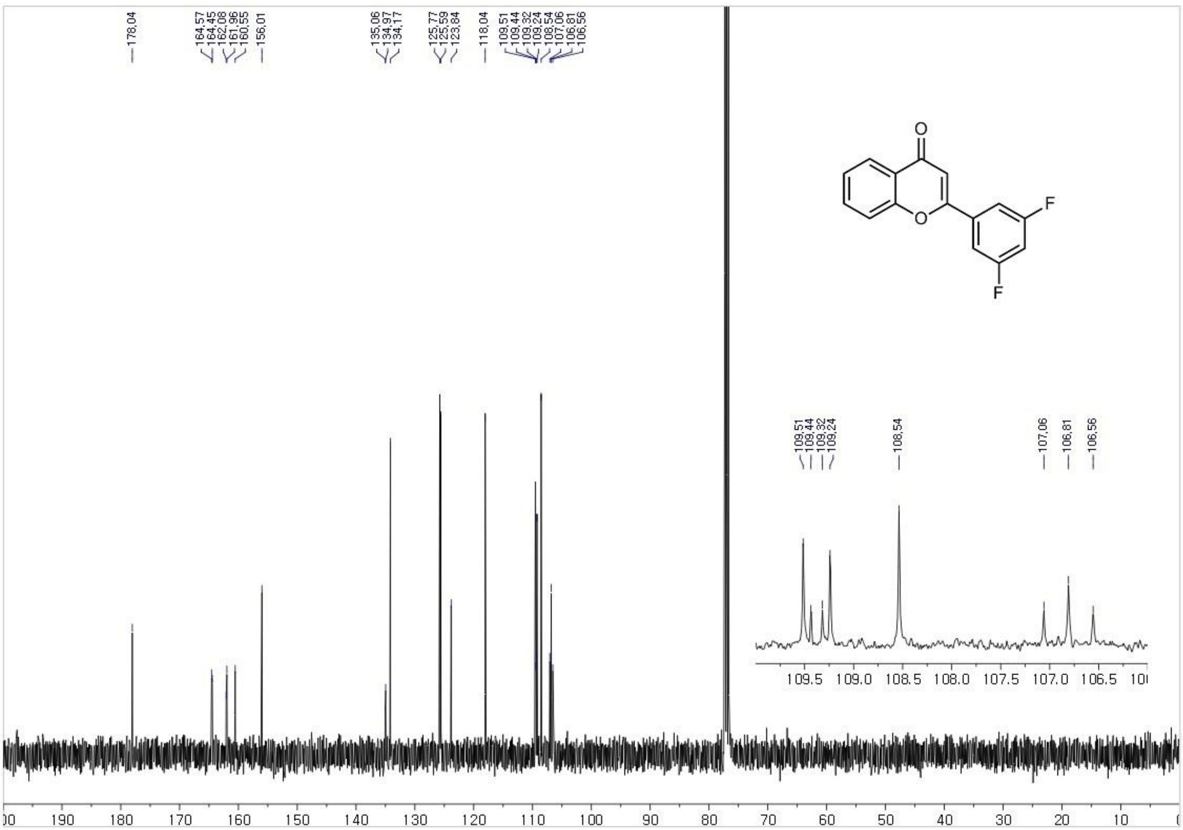


100 Mhz, ^{13}C NMR in Chloroform-d

2-(3,5-difluorophenyl)-4H-chromen-4-one (4e).

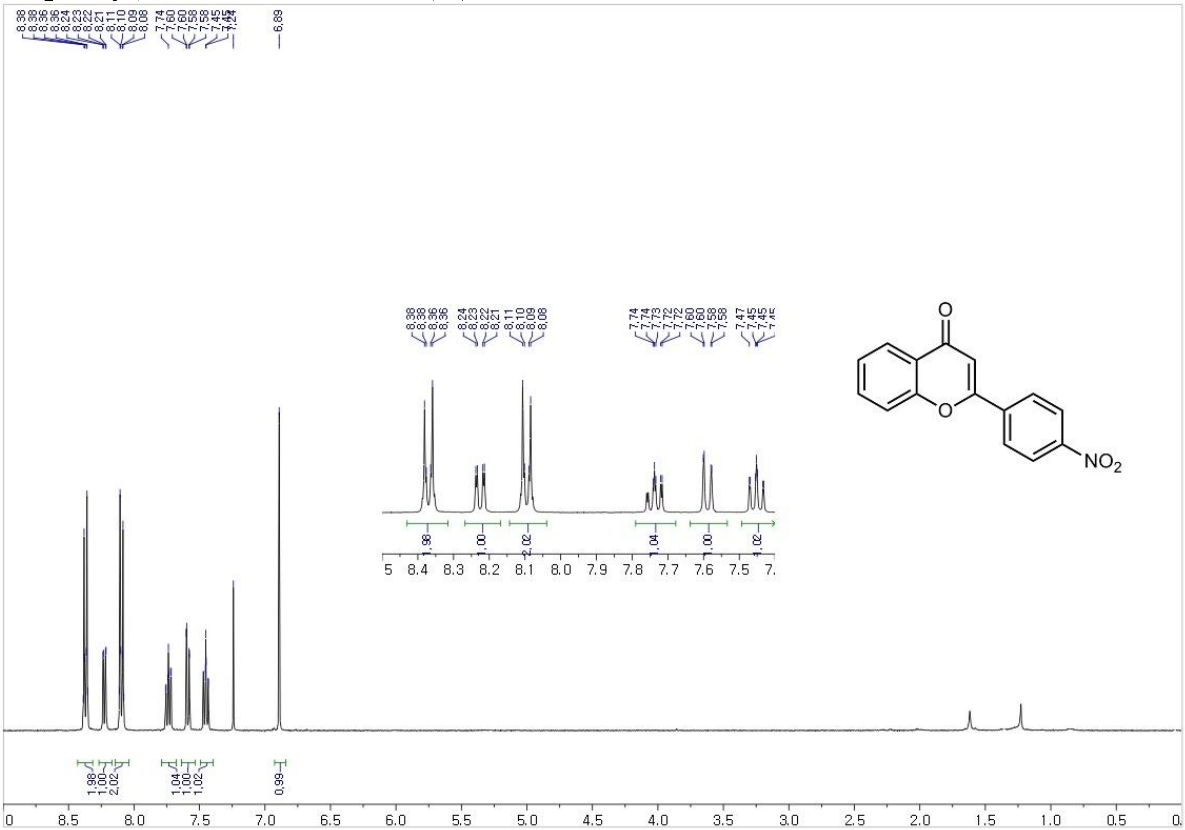


400 Mhz, ^{1}H NMR in Chloroform-d

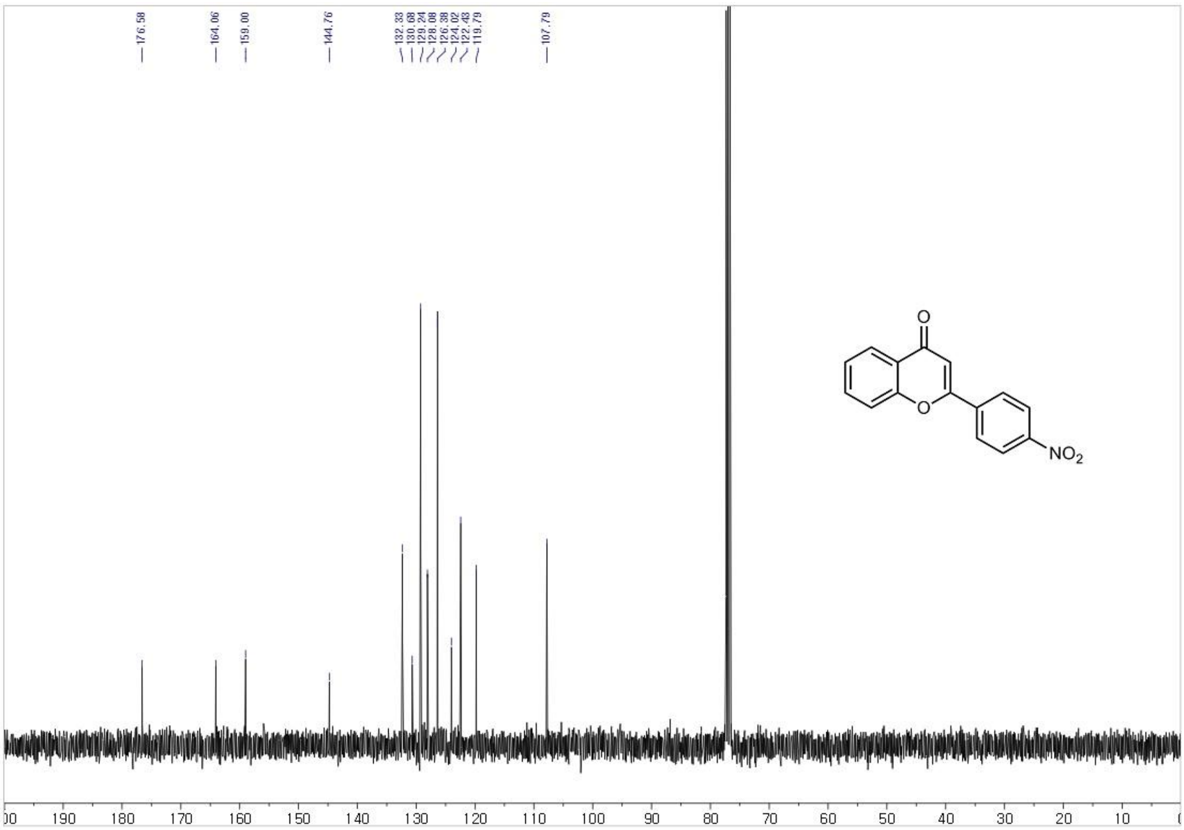


100 Mhz, ^{13}C NMR in Chloroform- d

2-(4-nitrophenyl)-4H-chromen-4-one (4f)

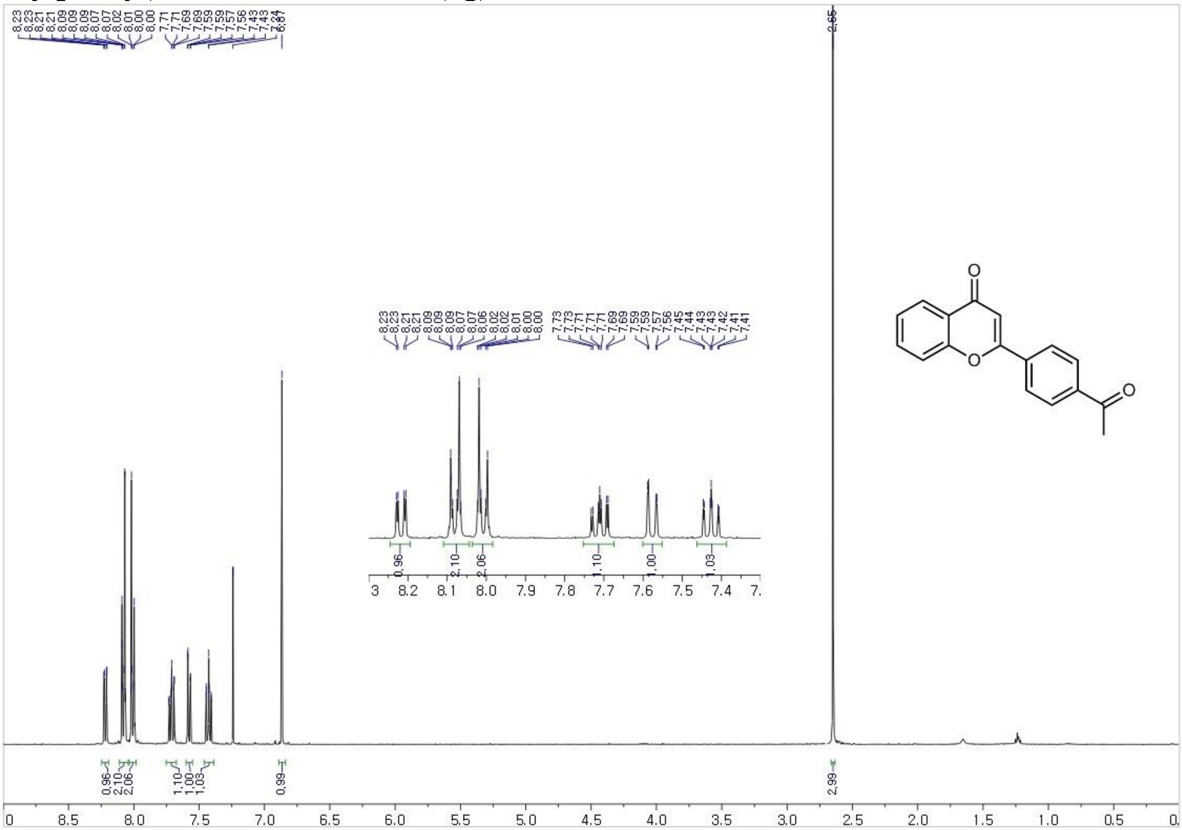


400 Mhz, ^{1}H NMR in Chloroform-d

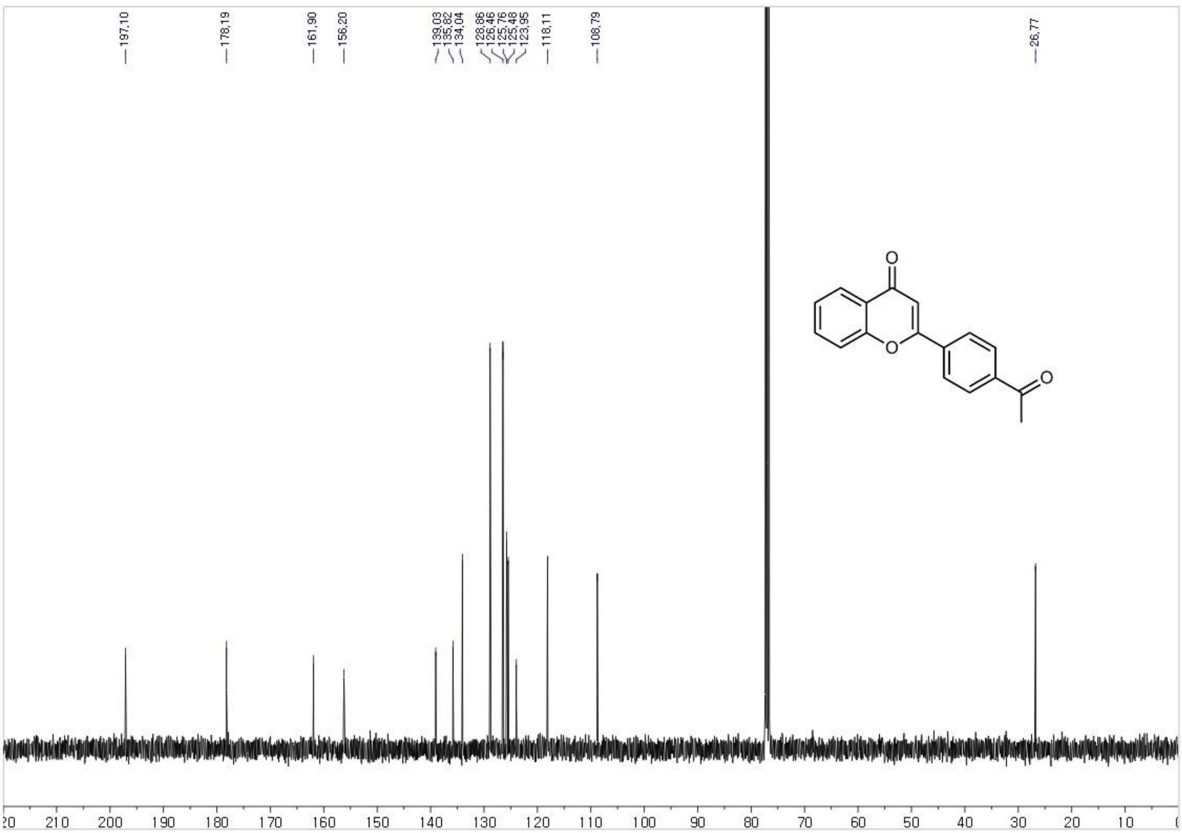


100 Mhz, ^{13}C NMR in Chloroform-d

2-(4-acetylphenyl)-4H-chromen-4-one (4g)

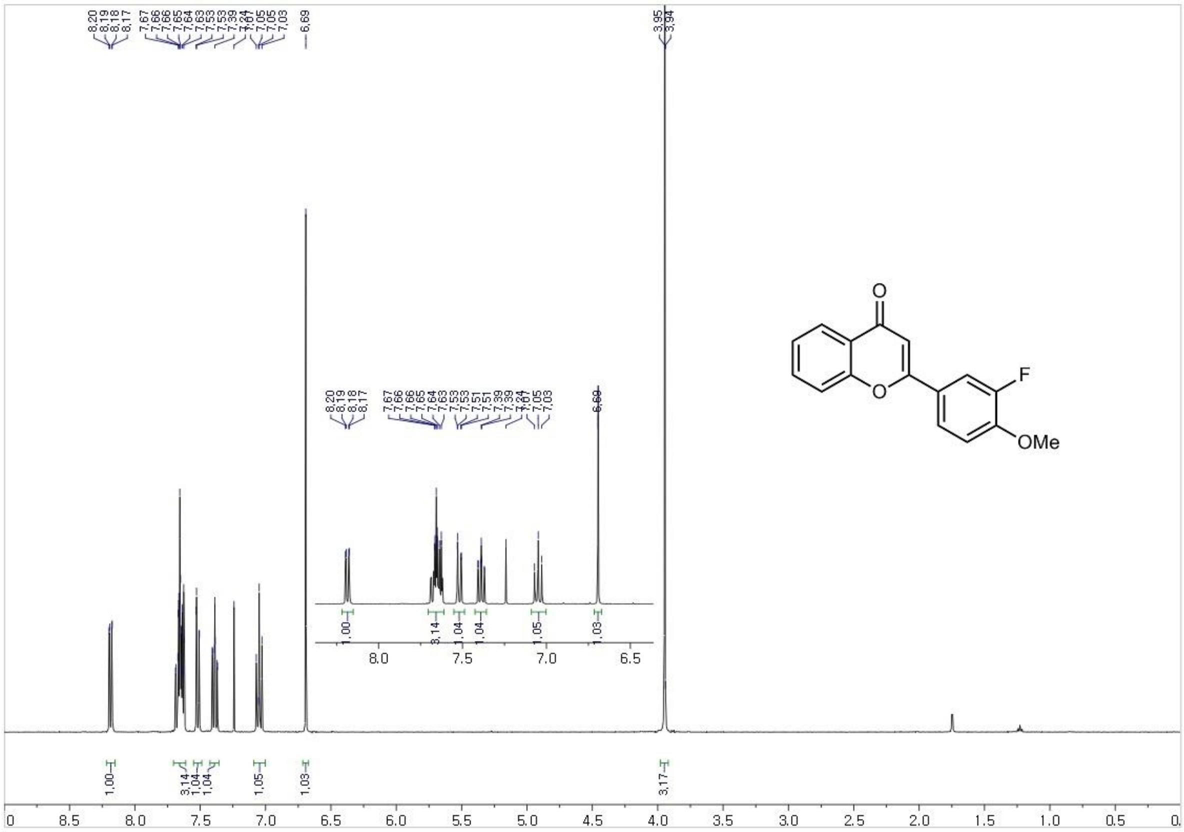


400 Mhz, ^{1}H NMR in Chloroform-d

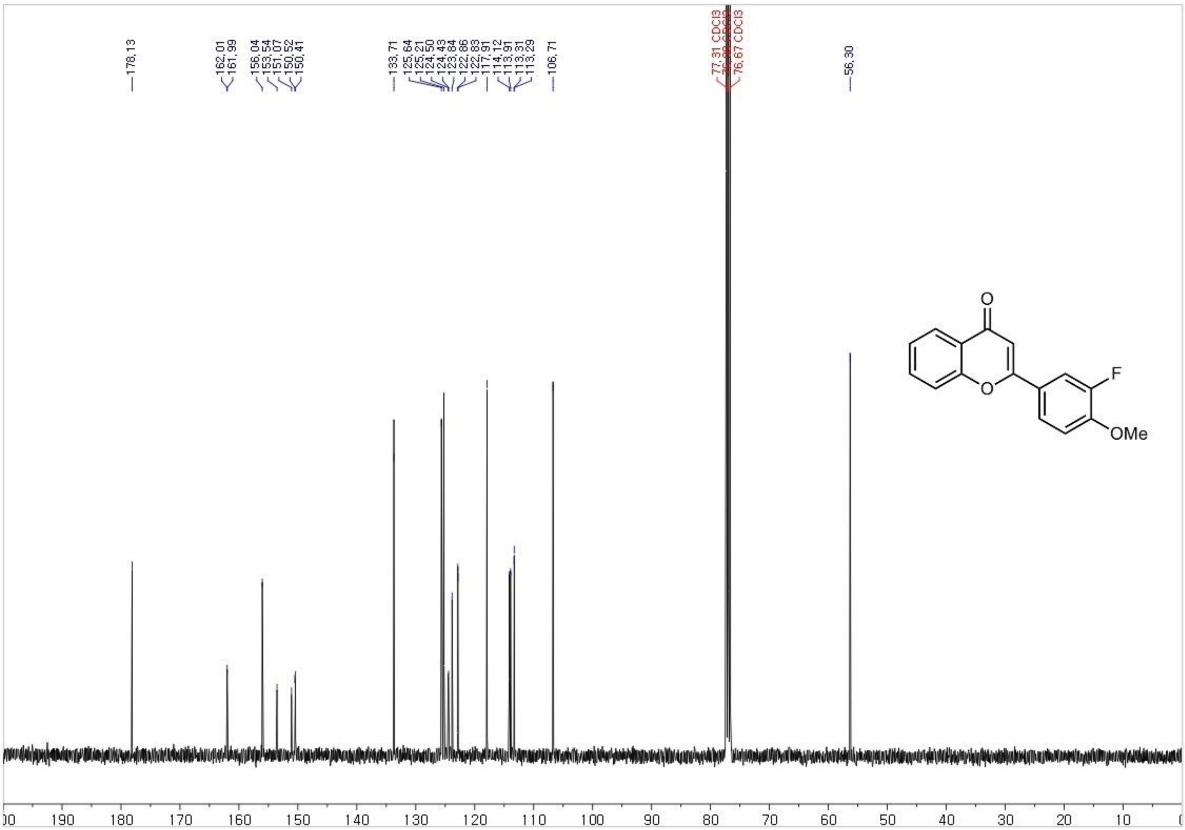


100 Mhz, ^{13}C NMR in Chloroform-d

2-(3-fluoro-4-methoxyphenyl)-4H-chromen-4-one (4h)

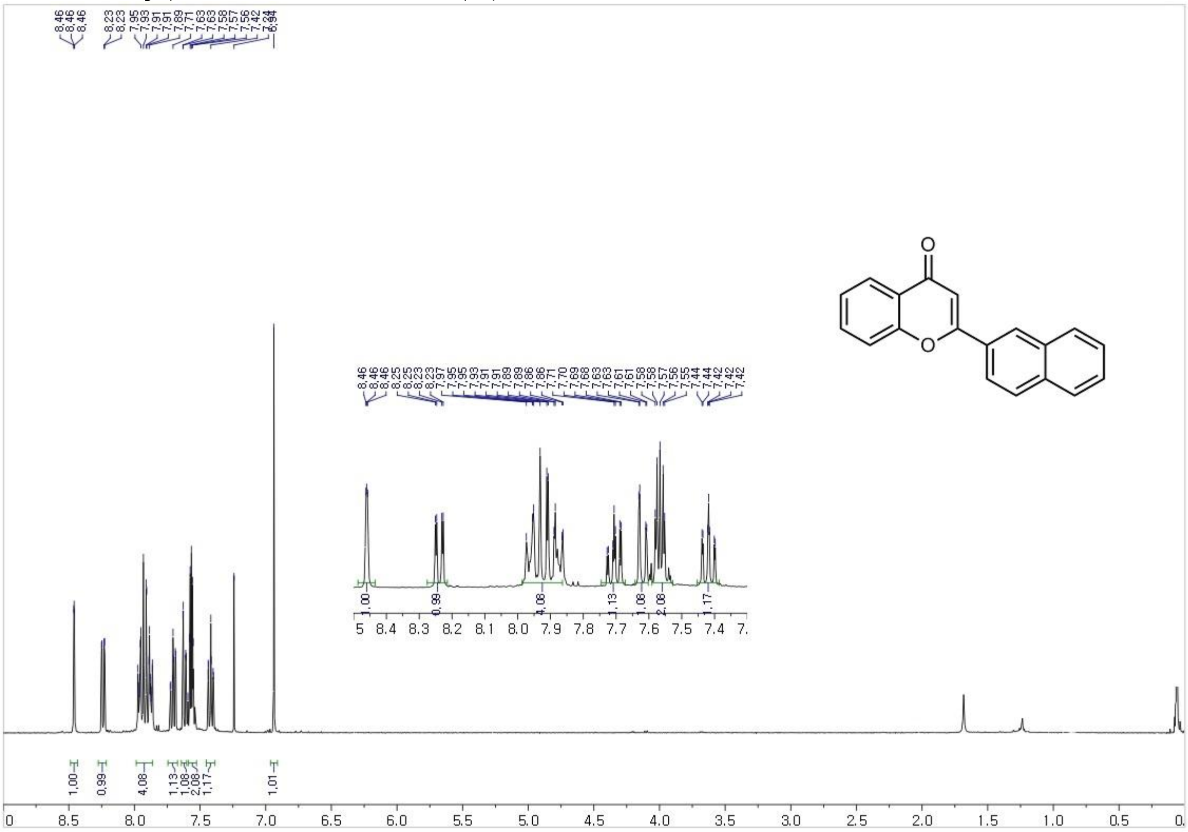


400 Mhz, ^{1}H NMR in Chloroform-d

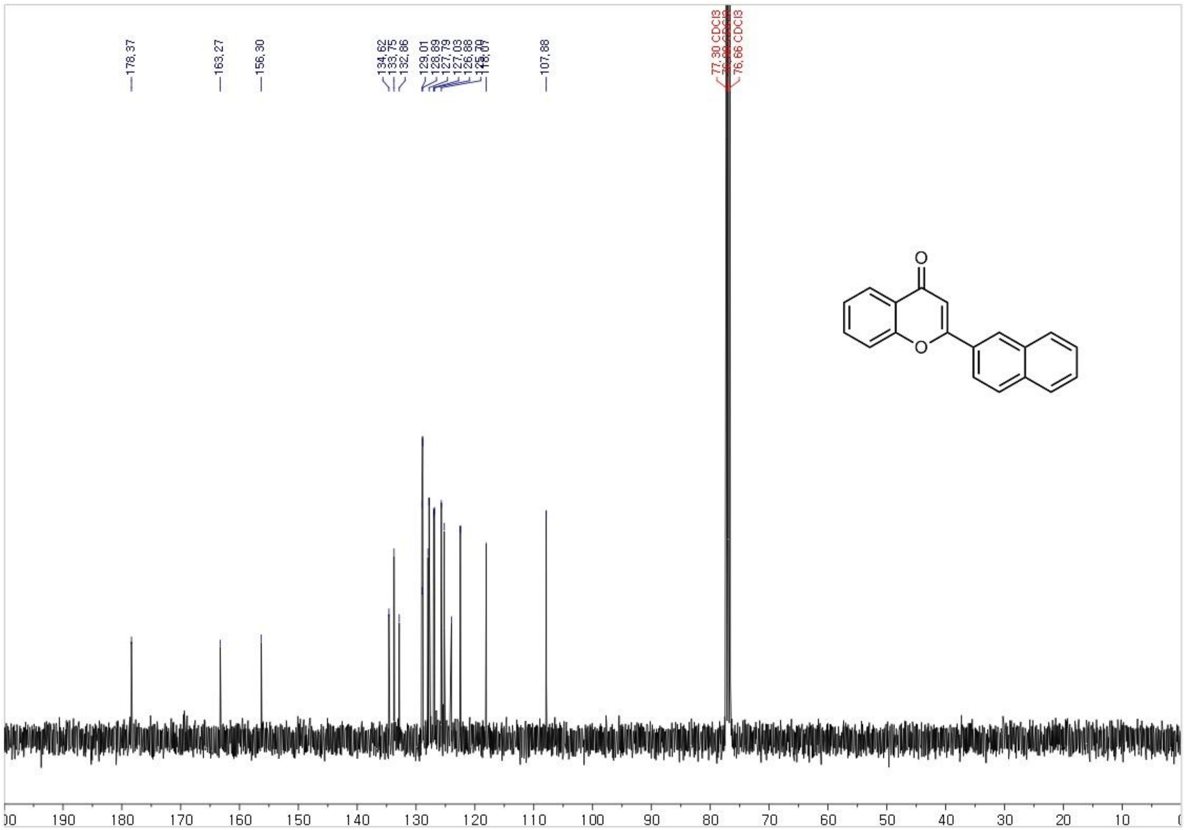


100 Mhz, ^{13}C NMR in Chloroform-d

2-(naphthalen-2-yl)-4H-chromen-4-one (4i)

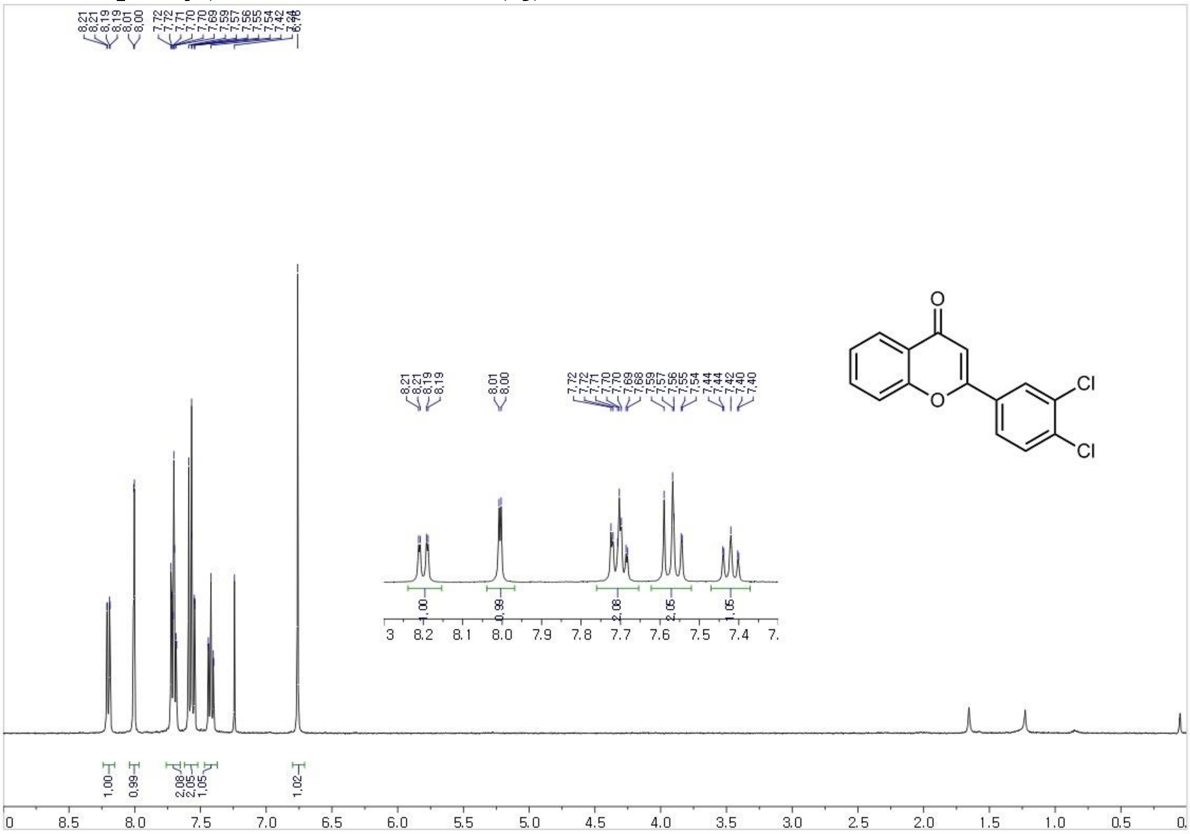


400 Mhz, ^{1}H NMR in Chloroform-d

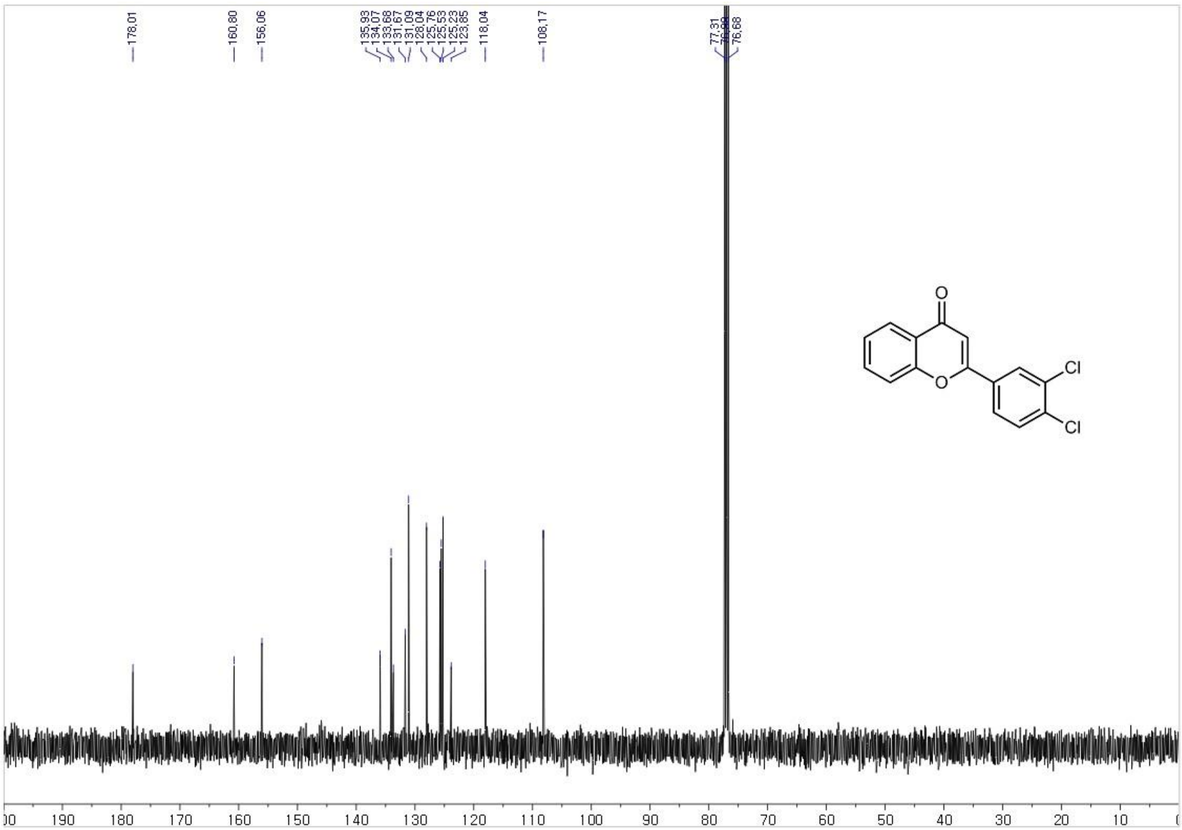


100 Mhz, ^{13}C NMR in Chloroform-d

2-(3,4-dichlorophenyl)-4H-chromen-4-one (4j)

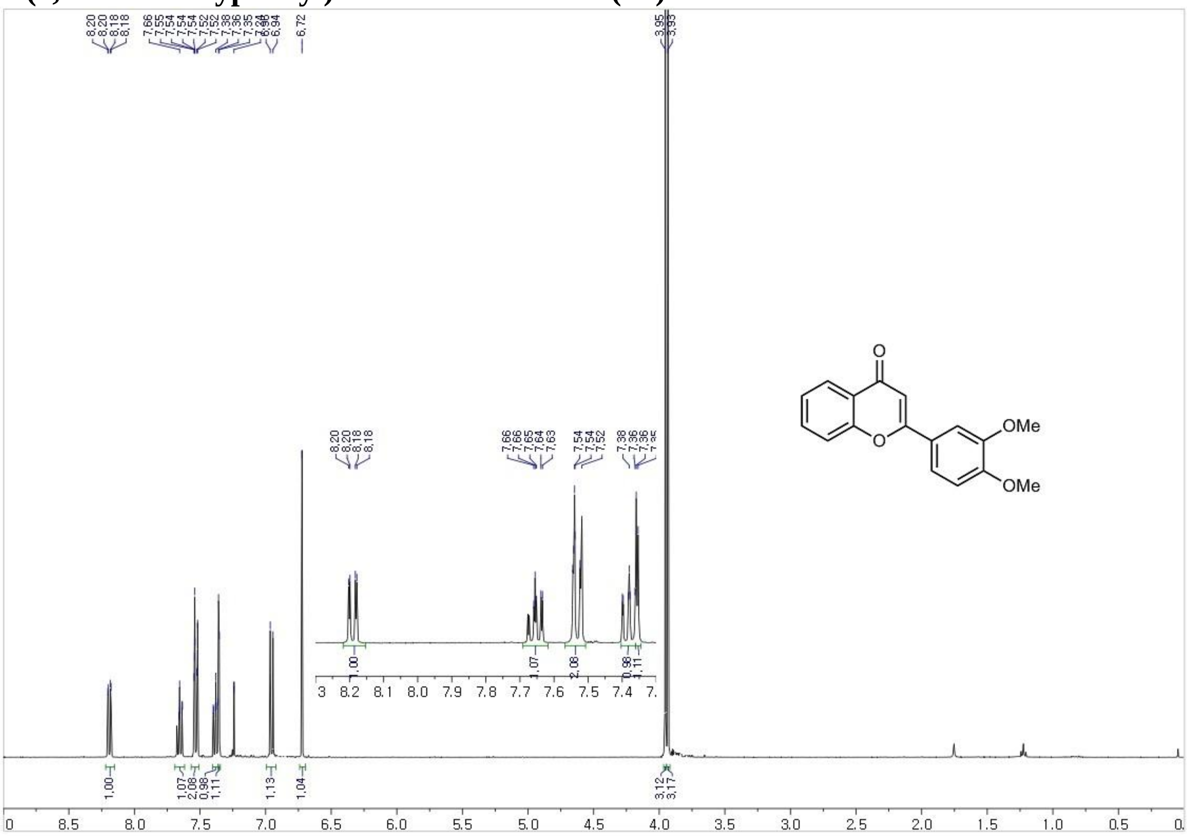


400 Mhz, ^{1}H NMR in Chloroform-d

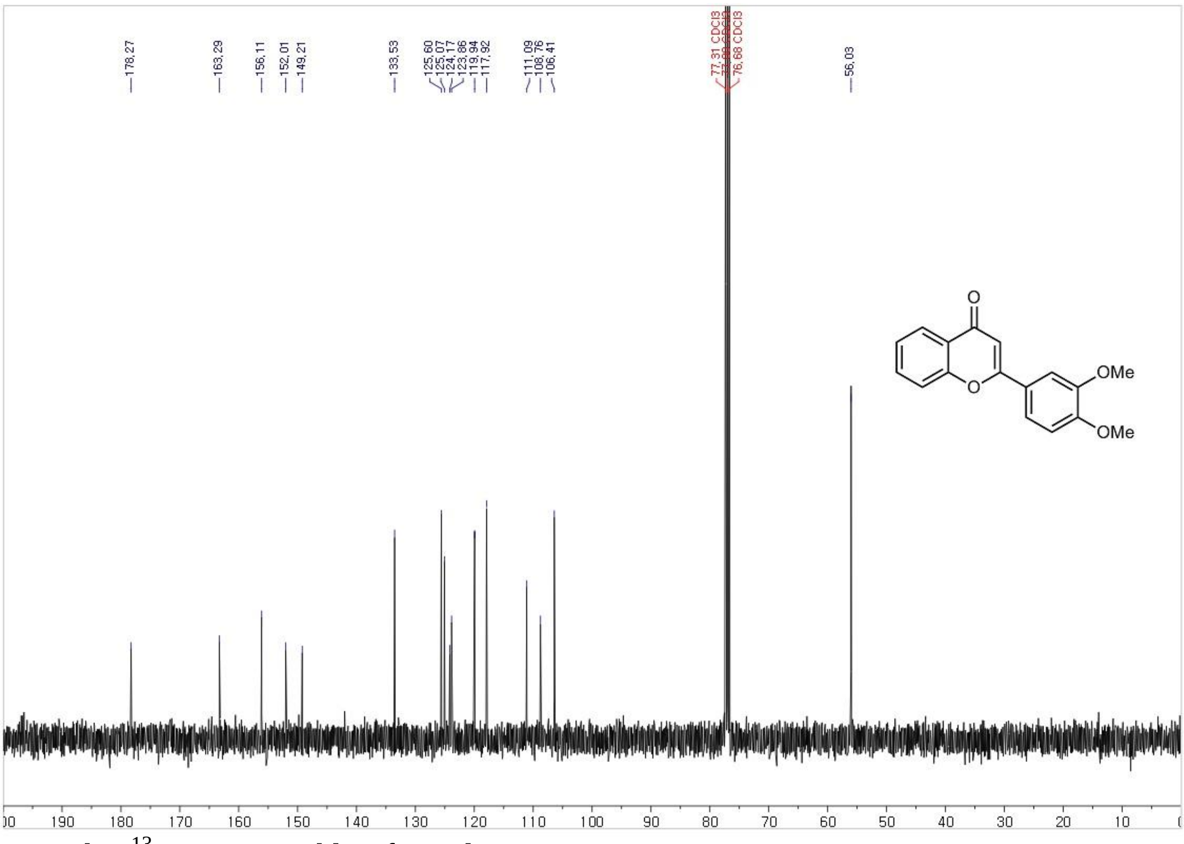


100 Mhz, ^{13}C NMR in Chloroform-d

2-(3,4-dimethoxyphenyl)-4H-chromen-4-one (4k)

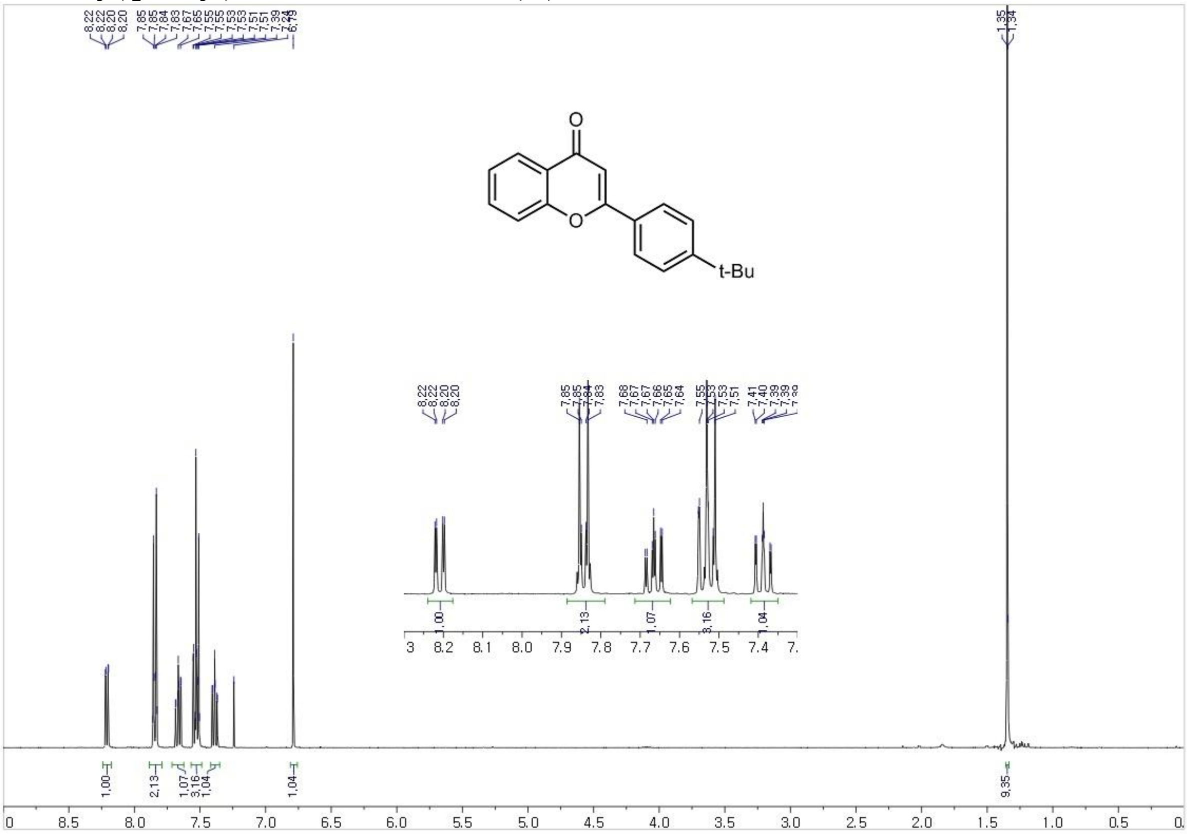


400 Mhz, ^{1}H NMR in Chloroform-d

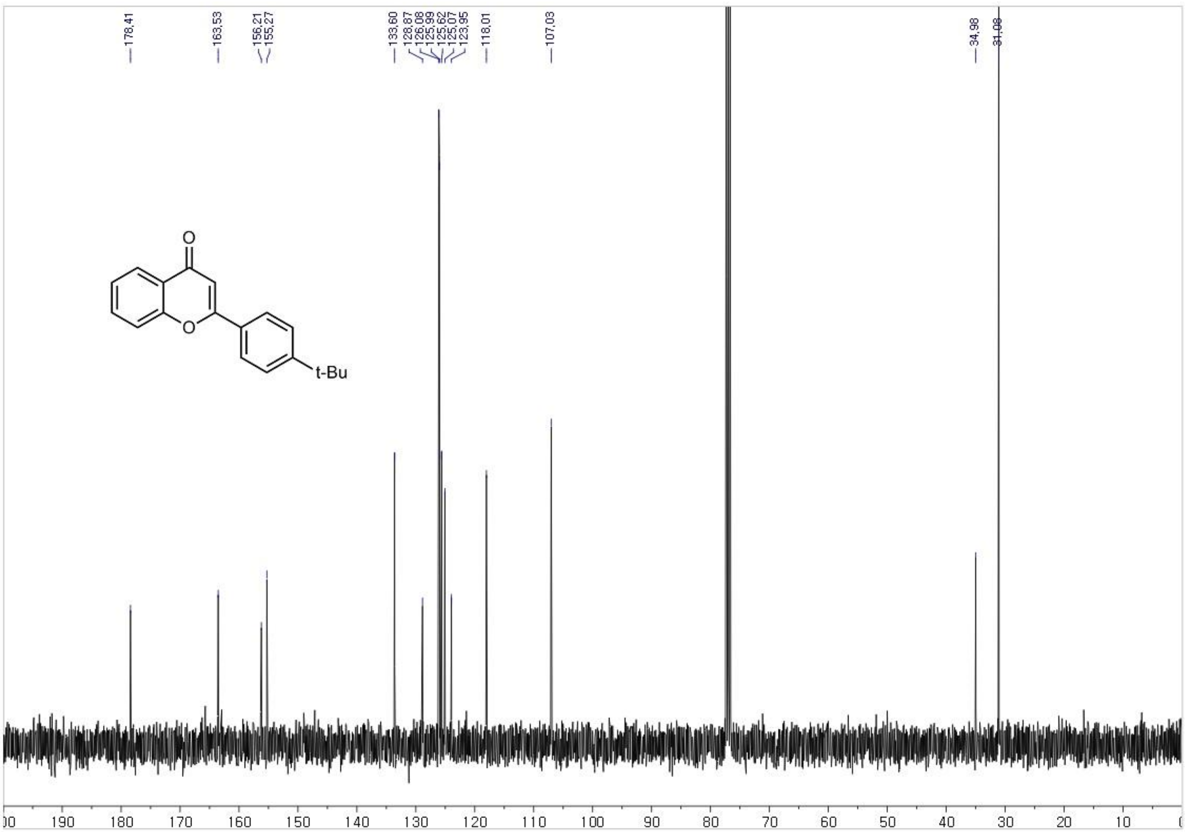


100 Mhz, ^{13}C NMR in Chloroform-d

2-(4-(tert-butyl)phenyl)-4H-chromen-4-one (4l)

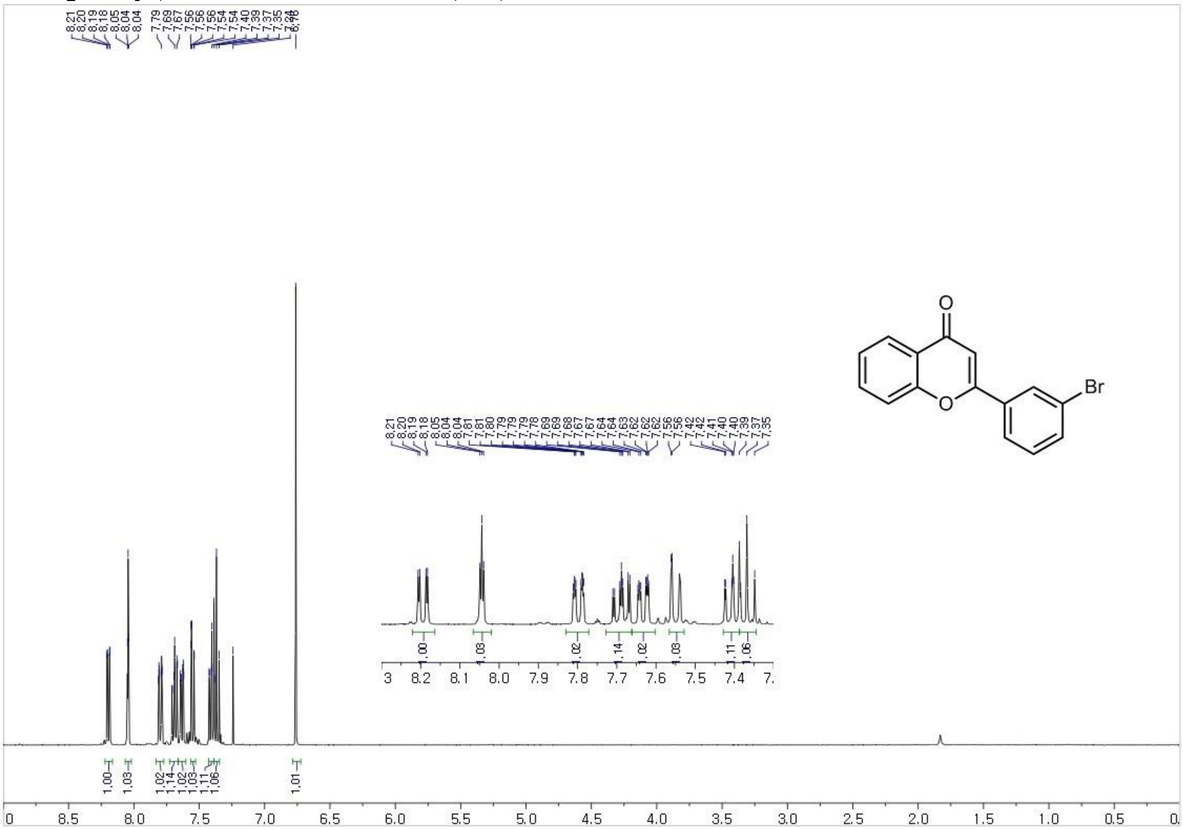


400 Mhz, ^{1}H NMR in Chloroform-d

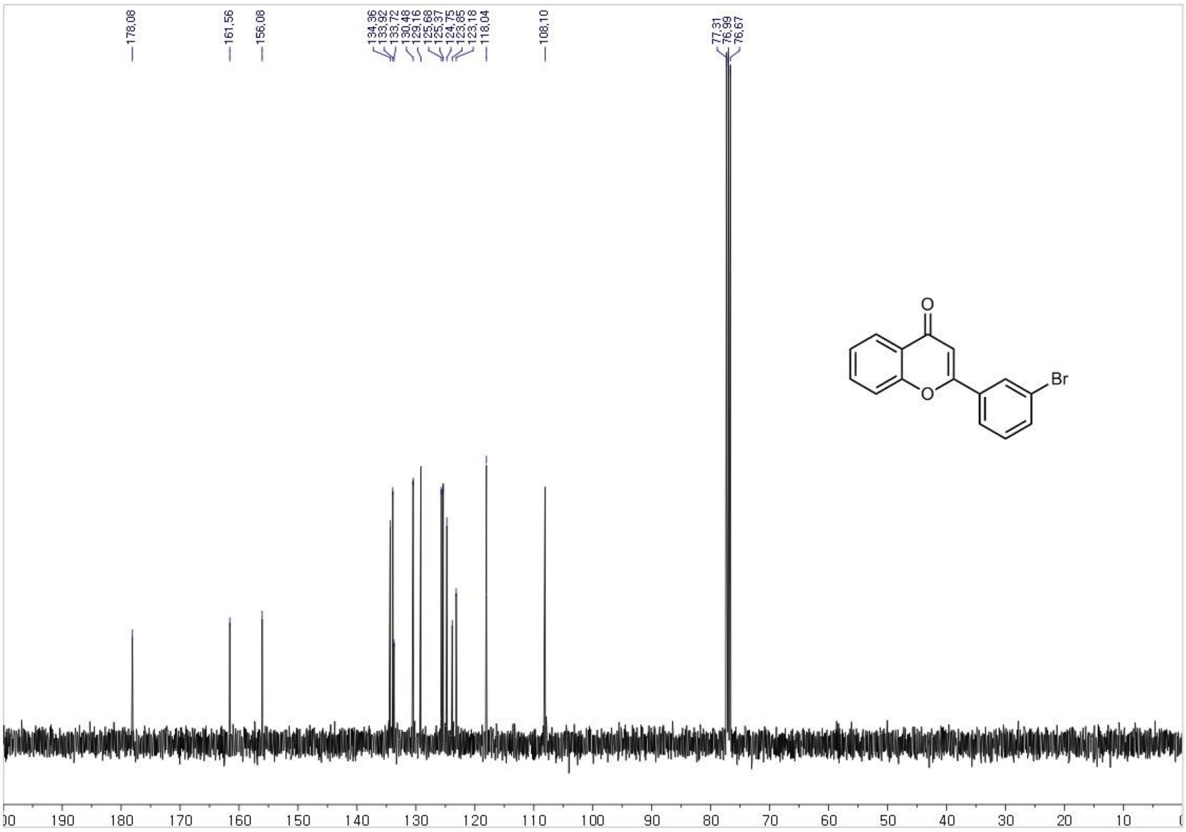


100 Mhz, ^{13}C NMR in Chloroform-d

2-(3-bromophenyl)-4H-chromen-4-one (4m)

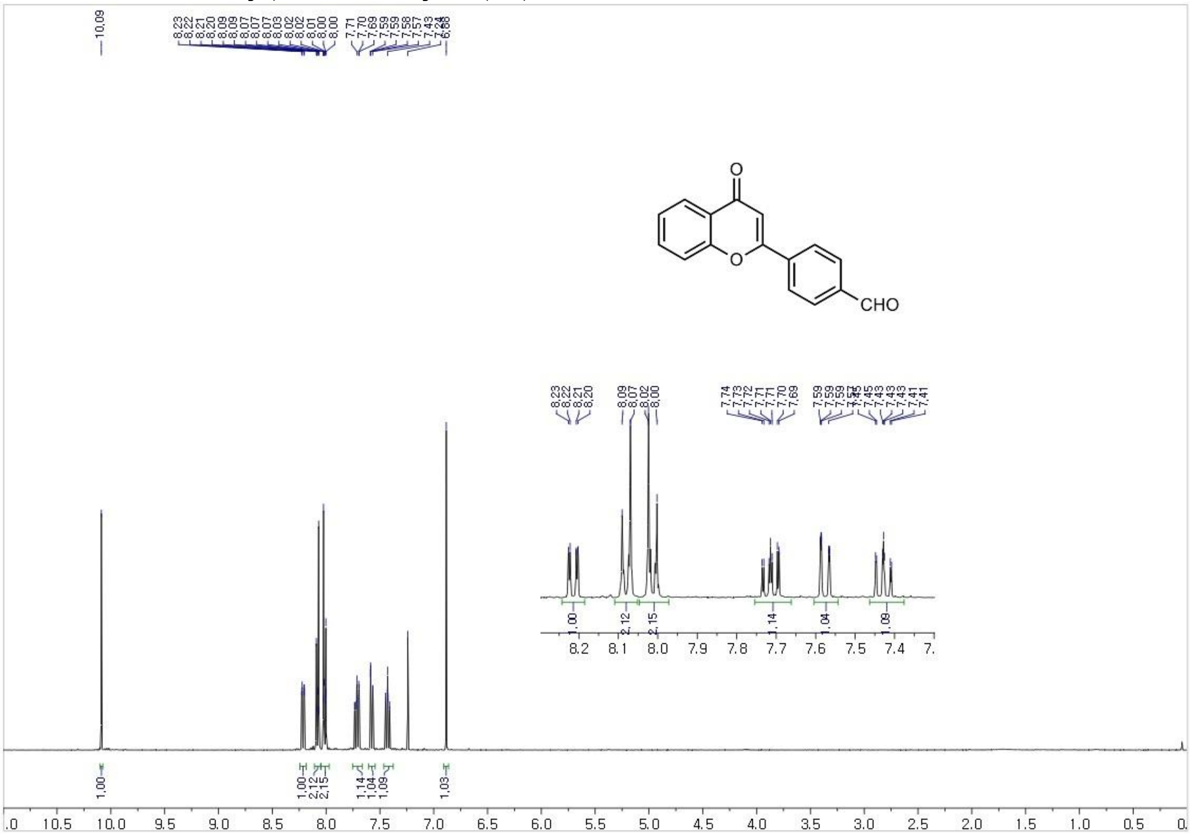


400 Mhz, ^{1}H NMR in Chloroform-d

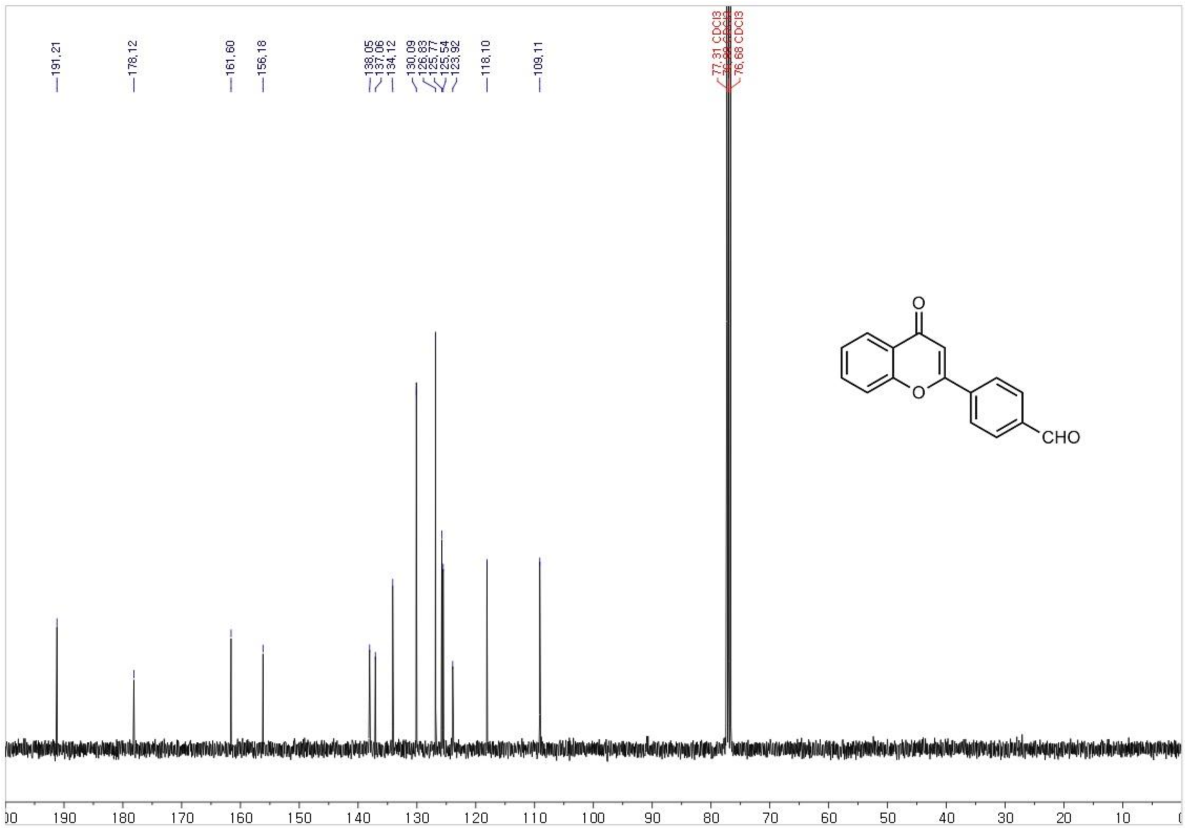


100 Mhz, ^{13}C NMR in Chloroform-d

4-(4-oxo-4H-chromen-2-yl)benzaldehyde (4n)

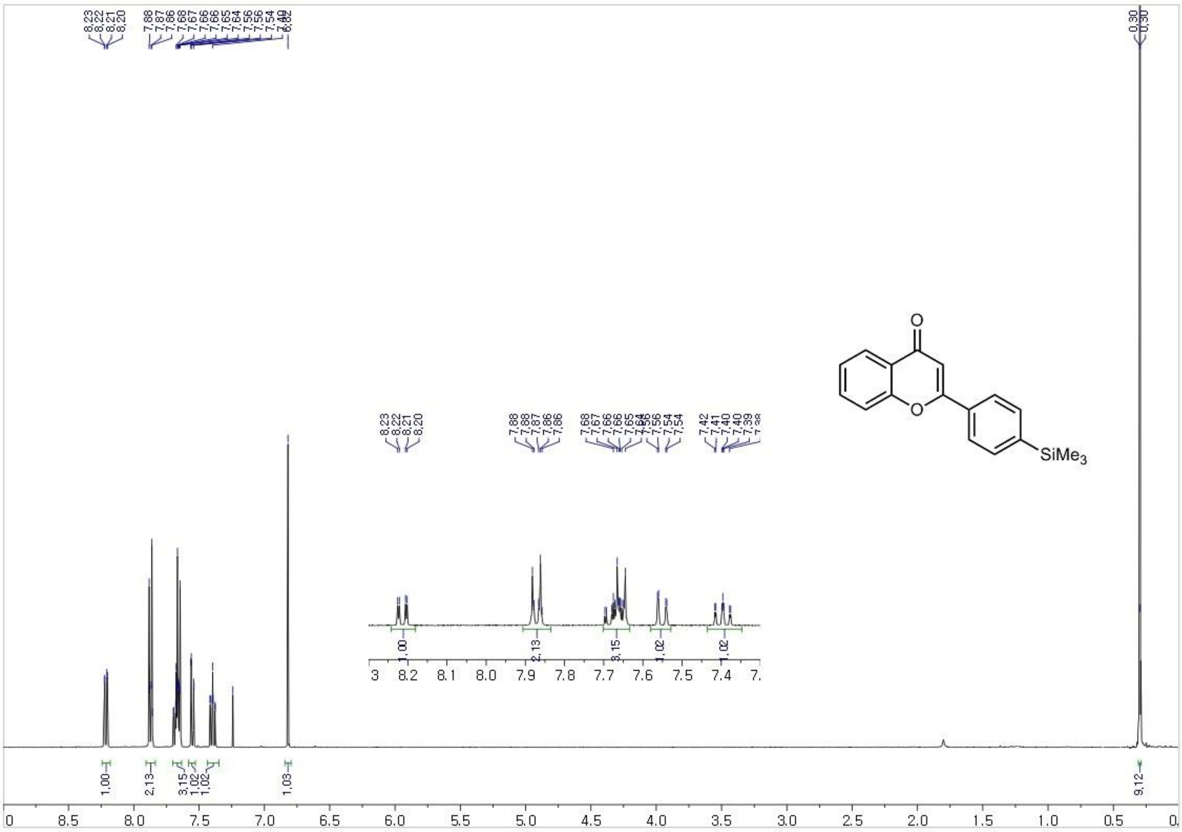


400 Mhz, ^{1}H NMR in Chloroform-d

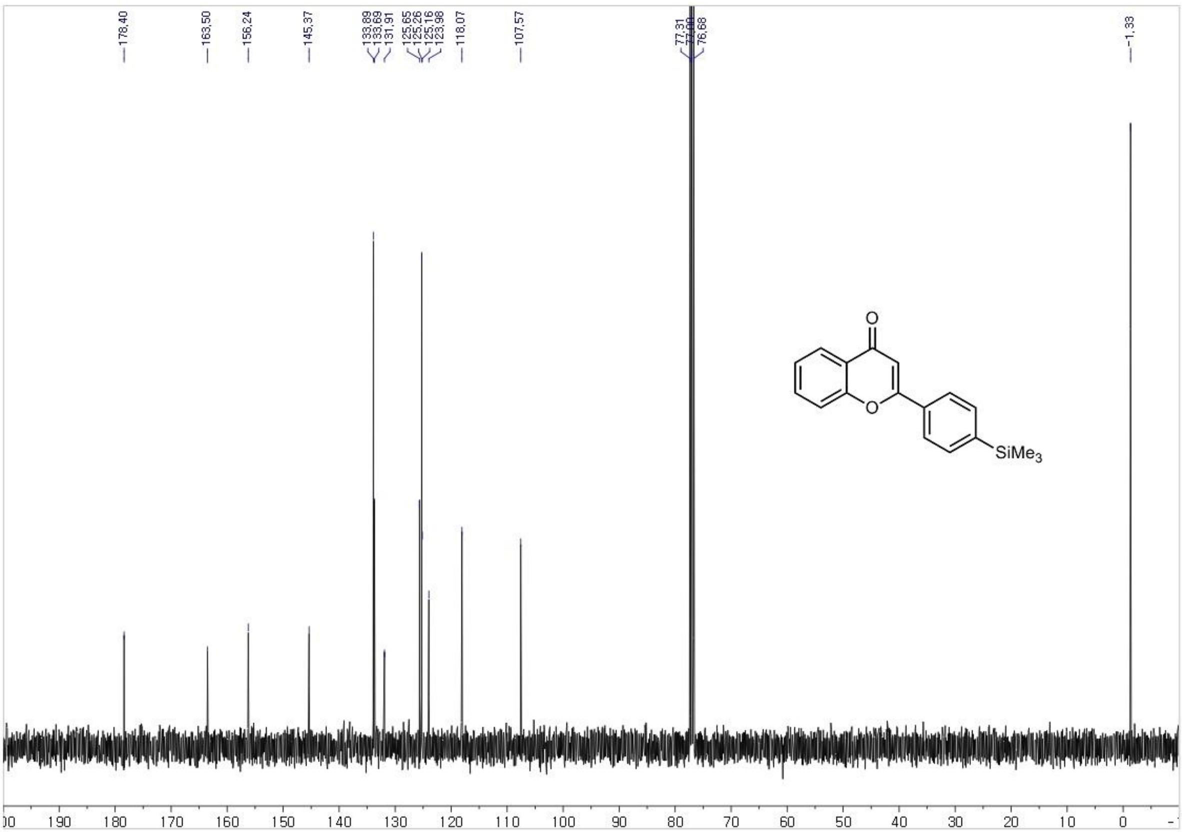


100 Mhz, ^{13}C NMR in Chloroform-d

2-(4-(trimethylsilyl)phenyl)-4H-chromen-4-one (4o)

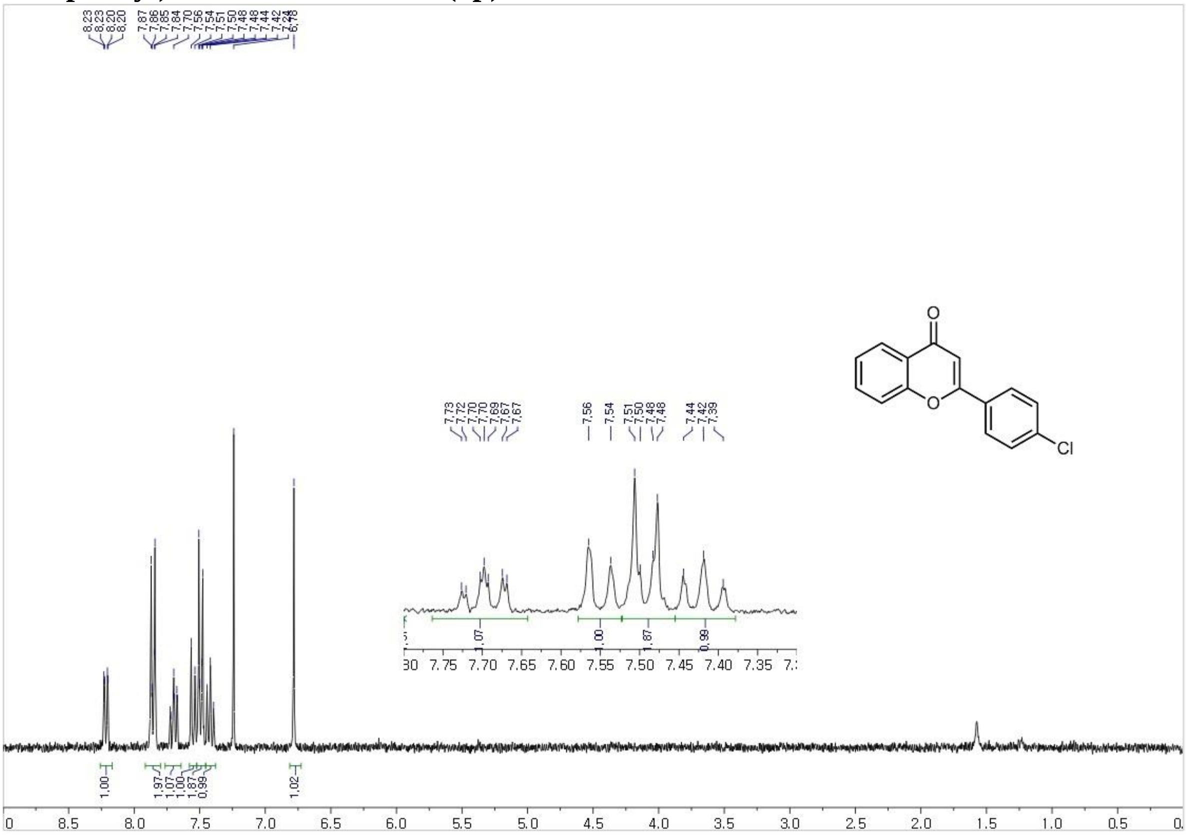


400 Mhz, ^{1}H NMR in Chloroform-d

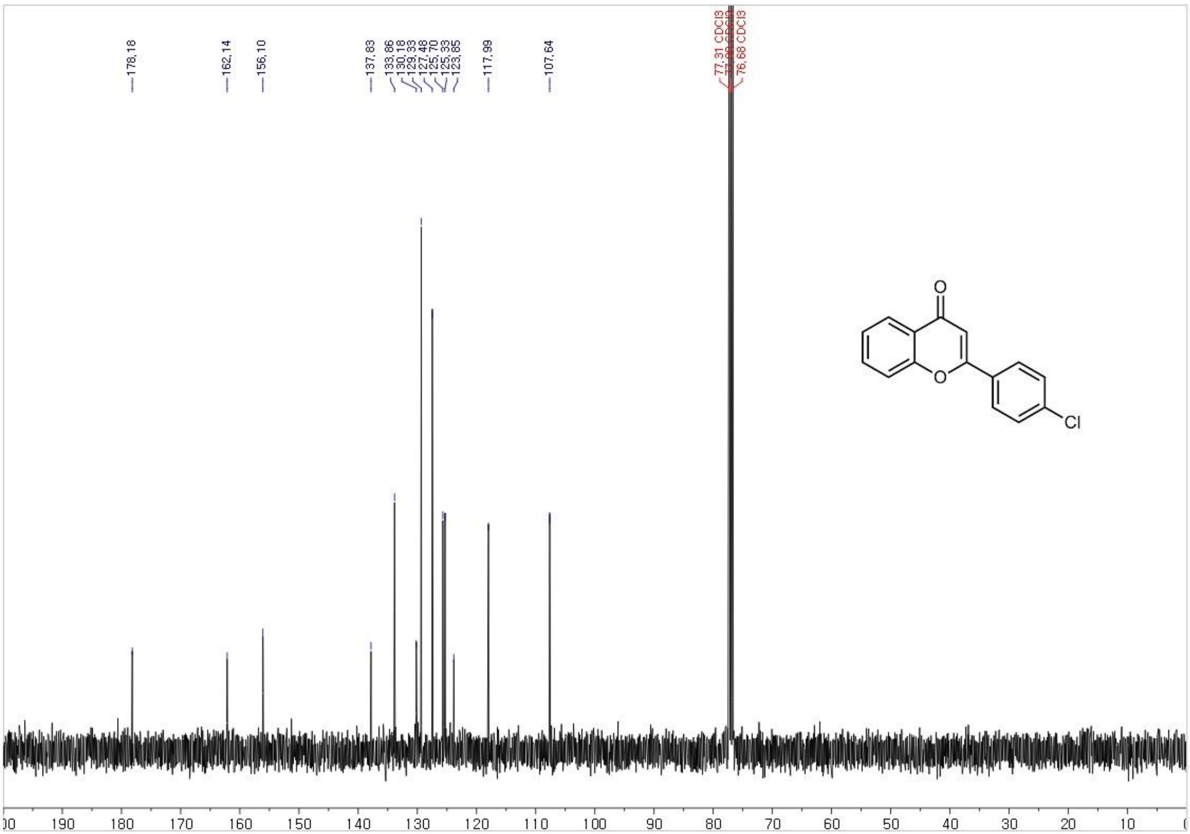


100 Mhz, ^{13}C NMR in Chloroform-d

2-(4-chlorophenyl)-4H-chromen-4-one (4p)

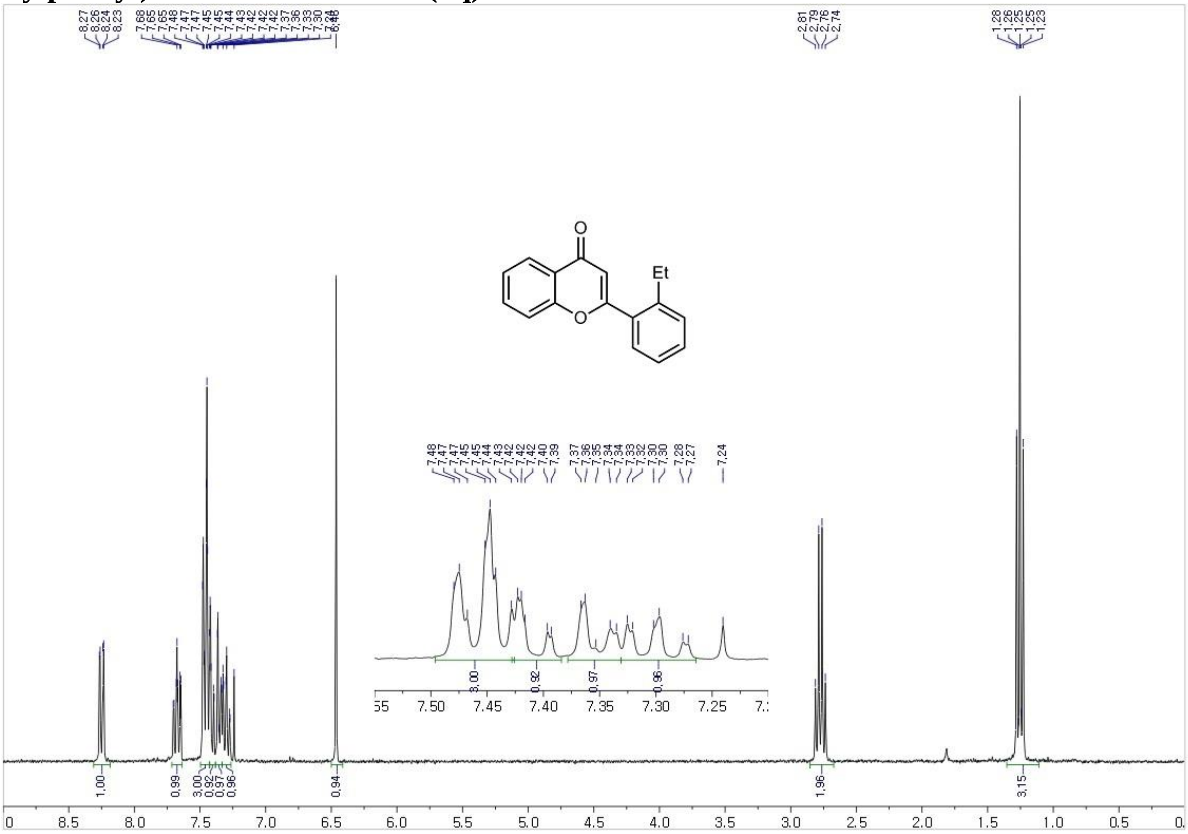


400 Mhz, ^{1}H NMR in Chloroform-d

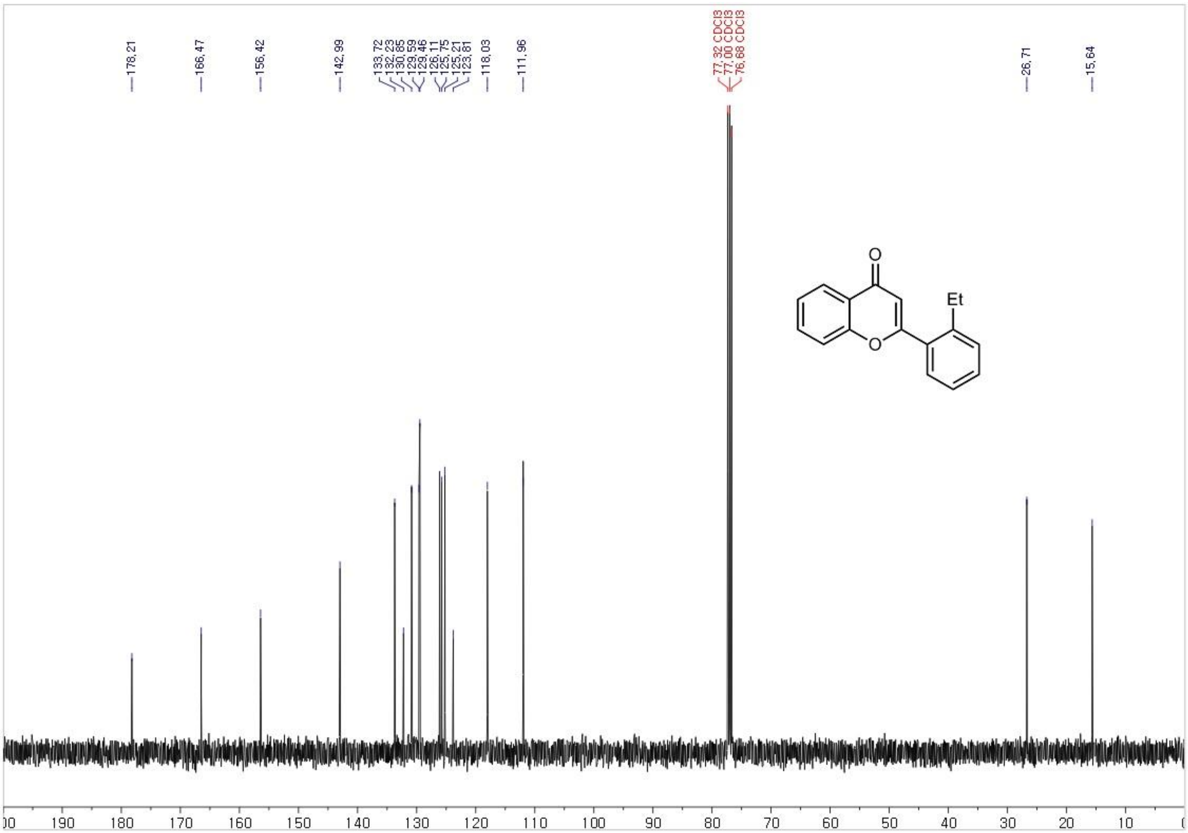


100 Mhz, ^{13}C NMR in Chloroform-d

2-(2-ethylphenyl)-4H-chromen-4-one (4q)

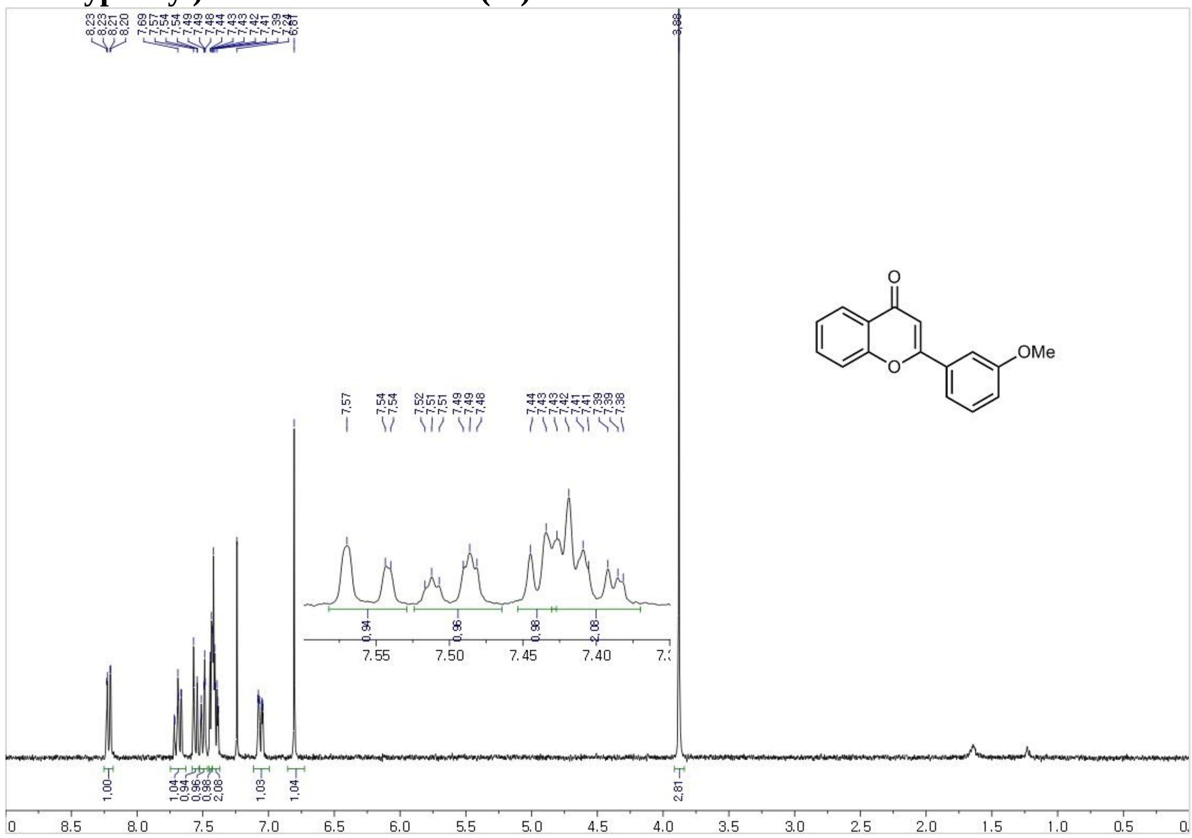


400 Mhz, ^{1}H NMR in Chloroform-d

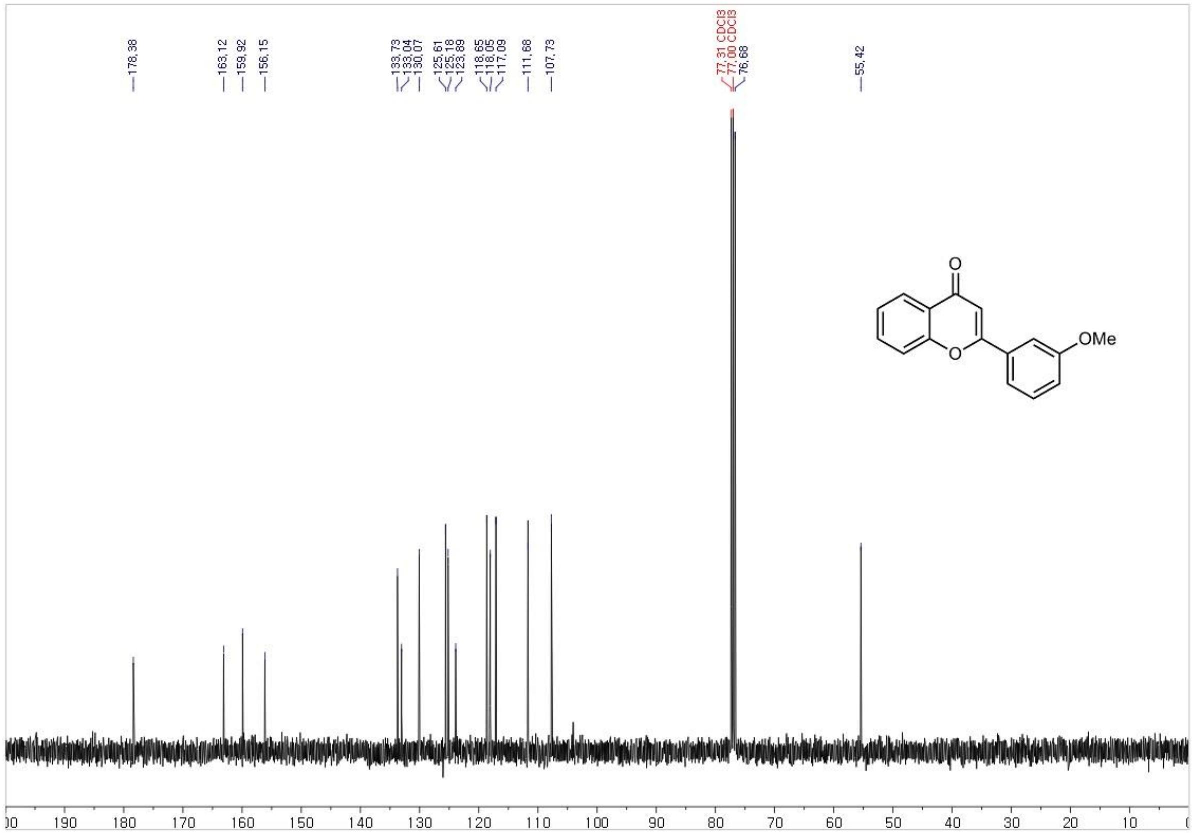


100 Mhz, ^{13}C NMR in Chloroform-d

2-(3-methoxyphenyl)-4H-chromen-4-one (4r)

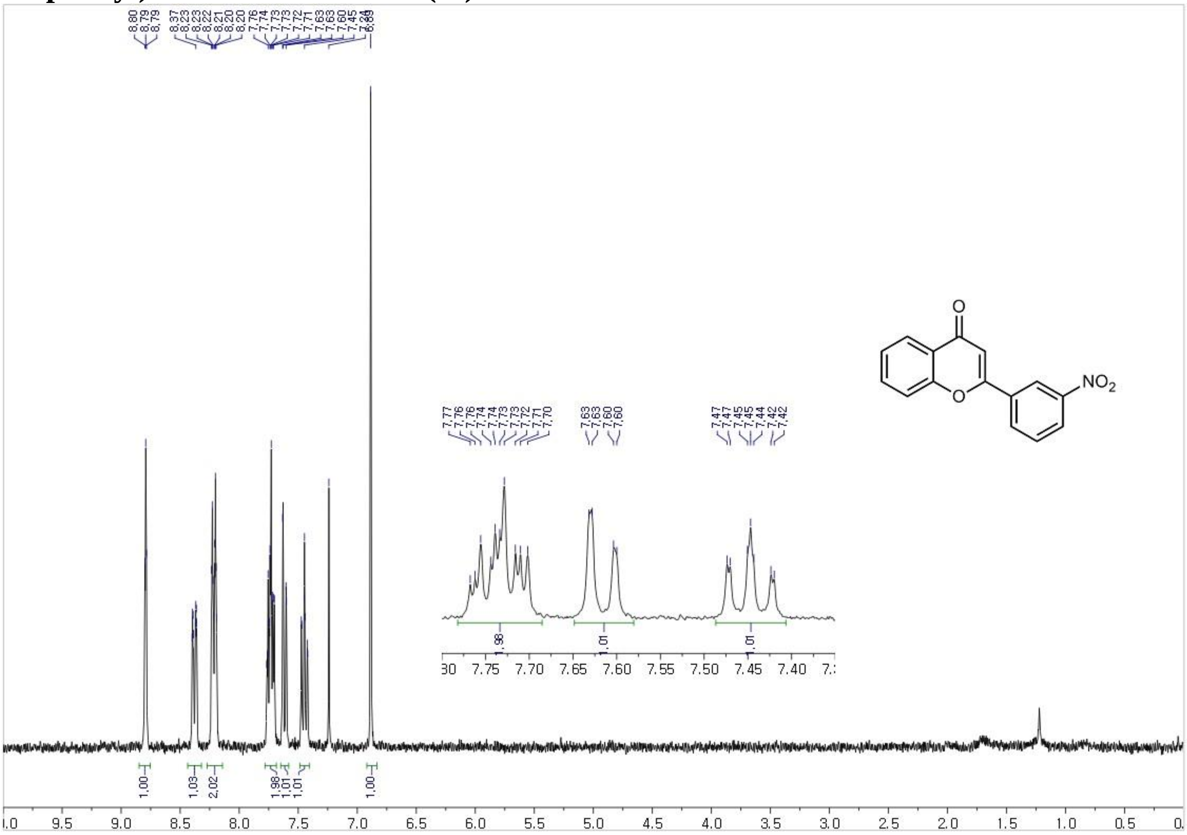


400 Mhz, ^{1}H NMR in Chloroform-d

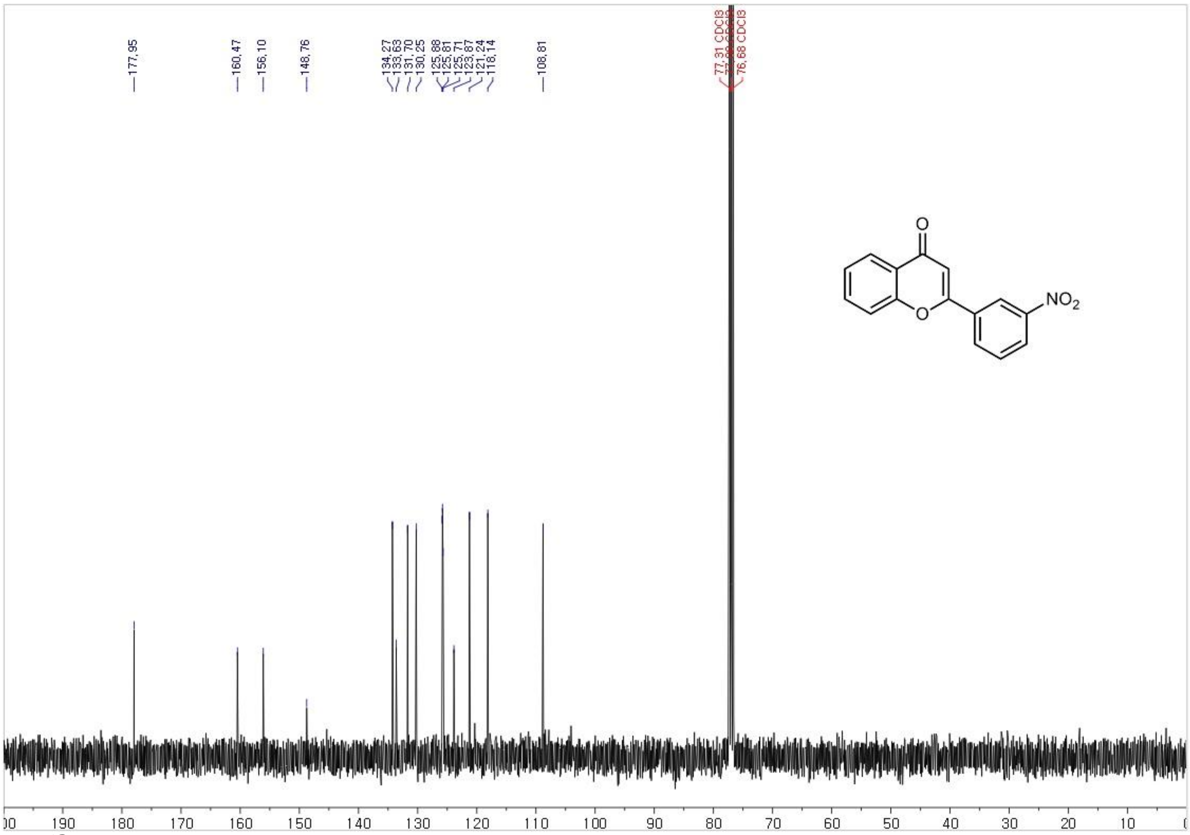


100 Mhz, ^{13}C NMR in Chloroform-d

2-(3-nitrophenyl)-4H-chromen-4-one (4s)

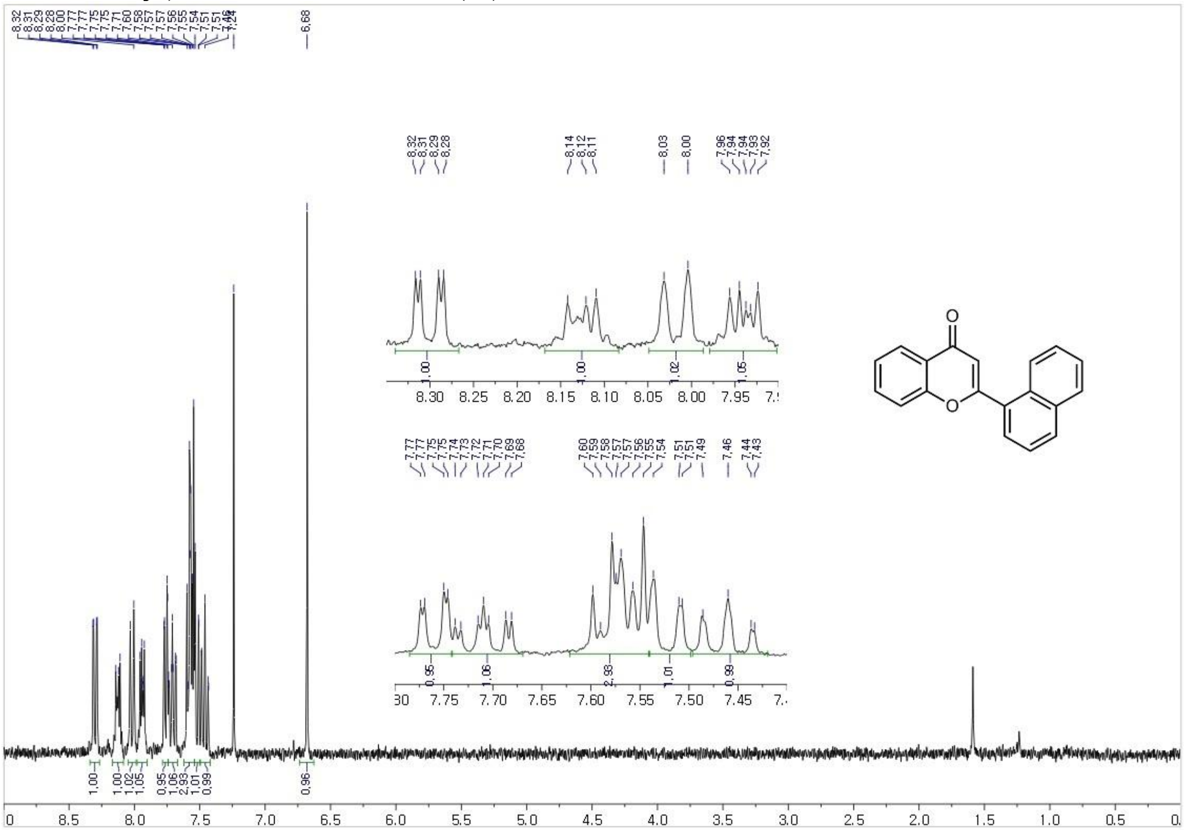


400 Mhz, ^{1}H NMR in Chloroform-d

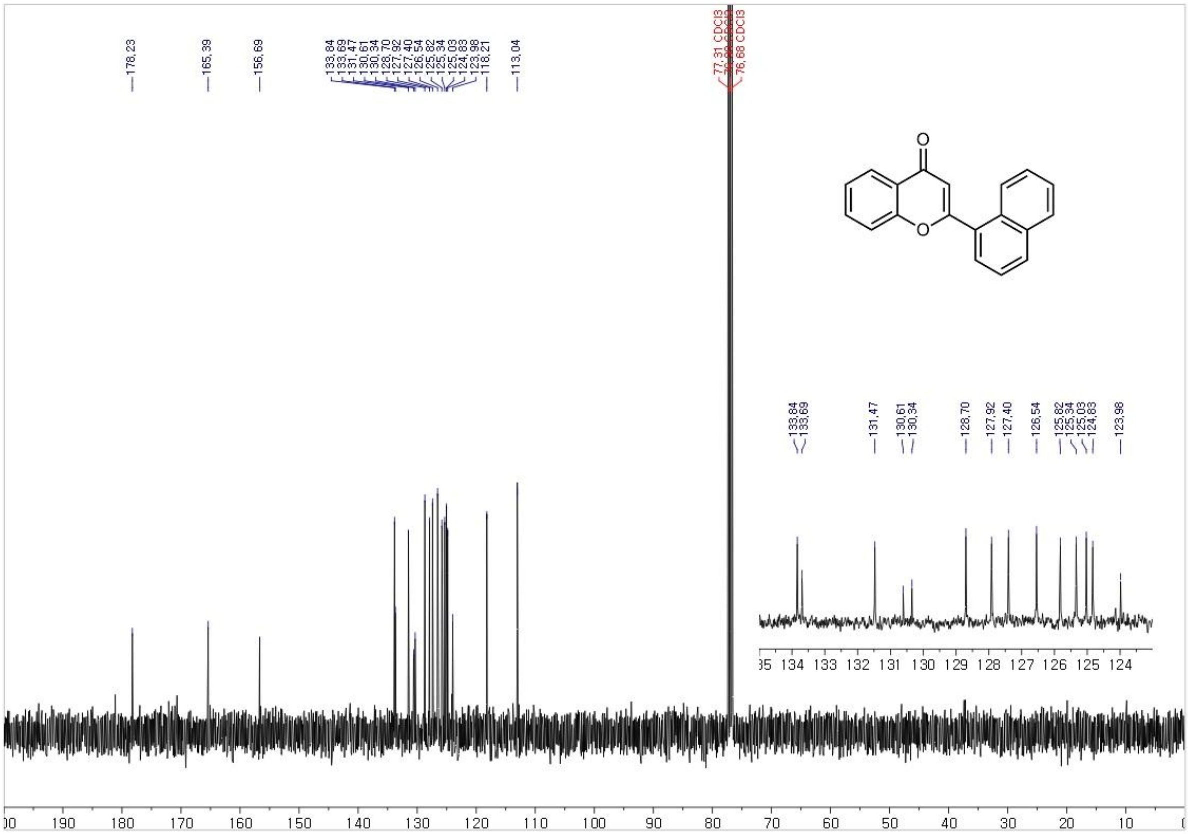


100 Mhz, ^{13}C NMR in Chloroform-d

2-(naphthalen-1-yl)-4H-chromen-4-one (4t)



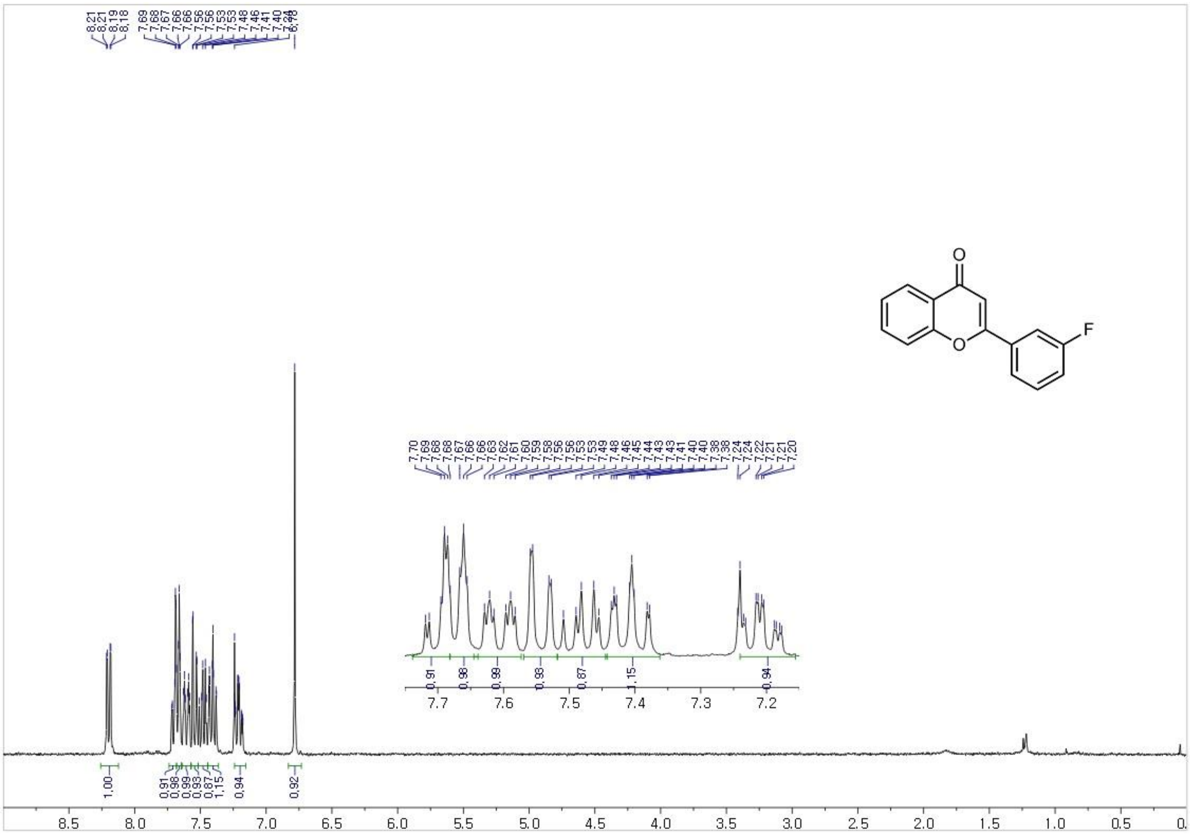
400 Mhz, ^{1}H NMR in Chloroform-d



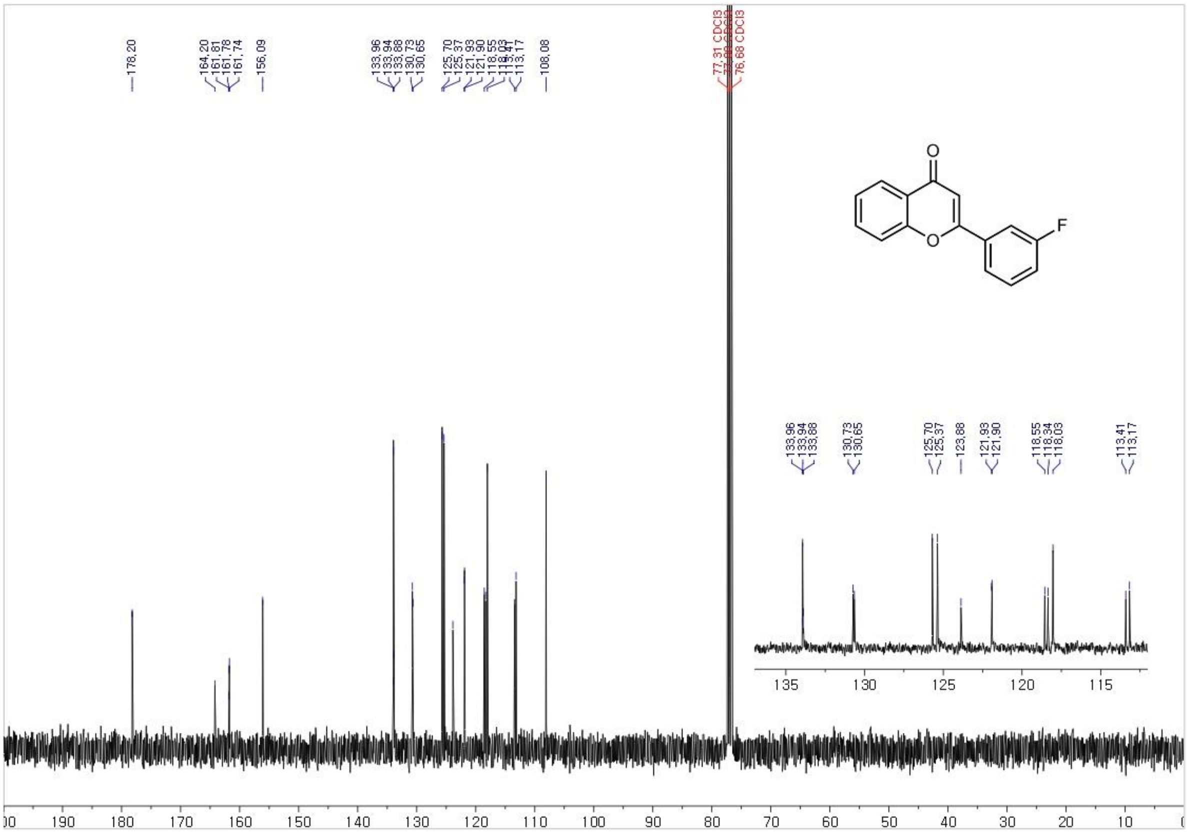
100 Mhz, ^{13}C NMR in Chloroform-d

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

2-(3-fluorophenyl)-4H-chromen-4-one (4u)

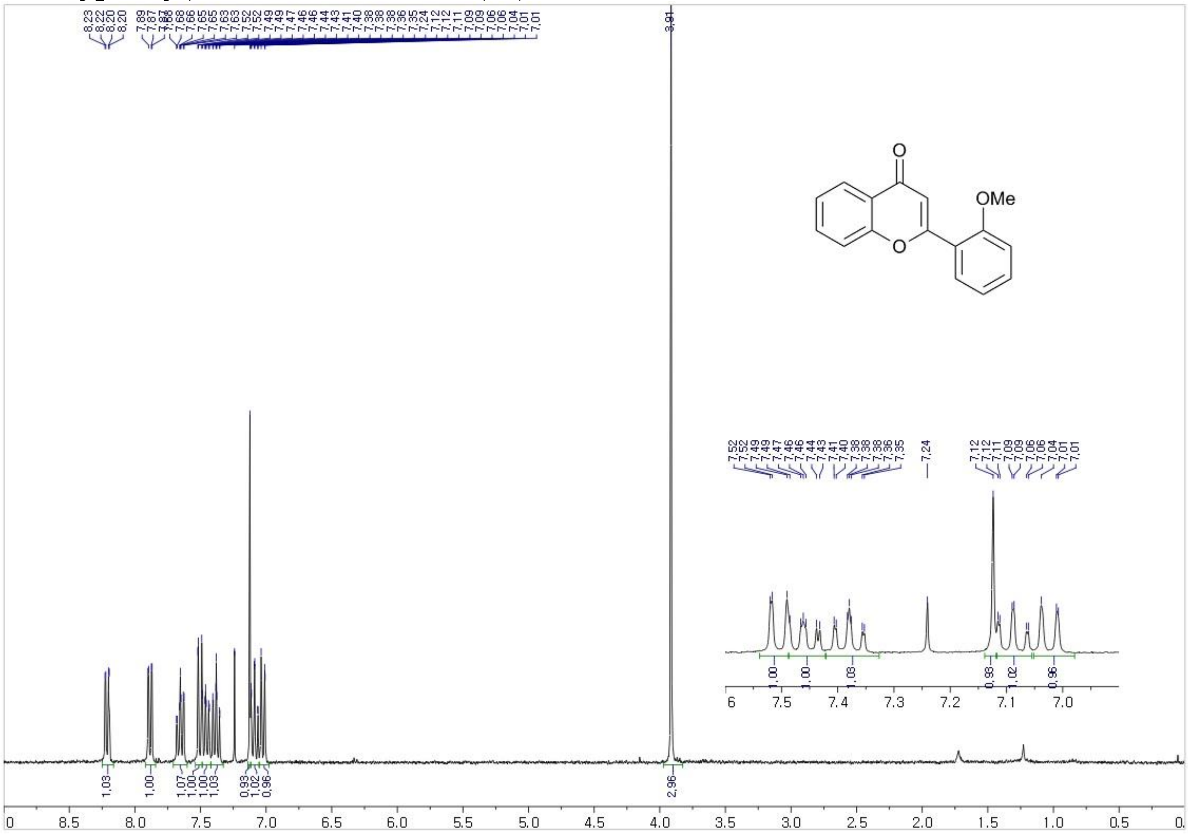


400 Mhz, ^{1}H NMR in Chloroform-d

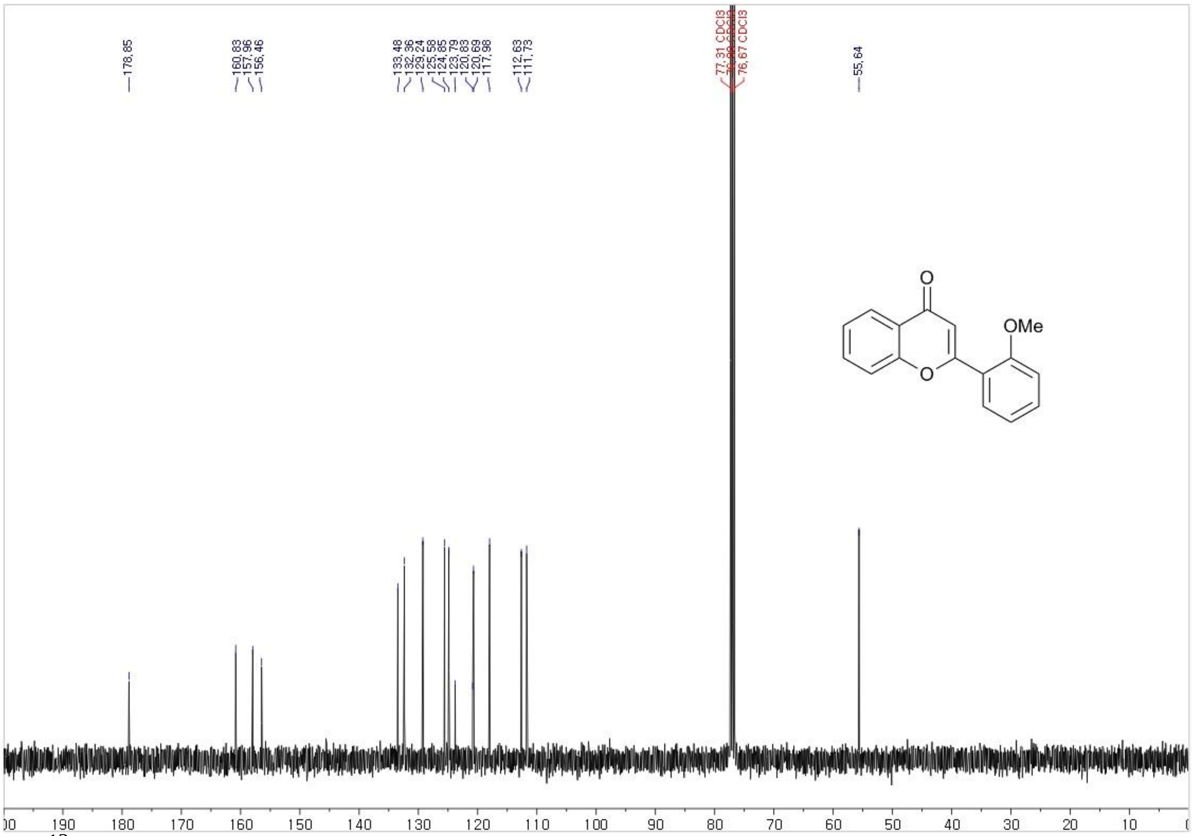


100 Mhz, ^{13}C NMR in Chloroform-d

2-(2-methoxyphenyl)-4H-chromen-4-one (4v)

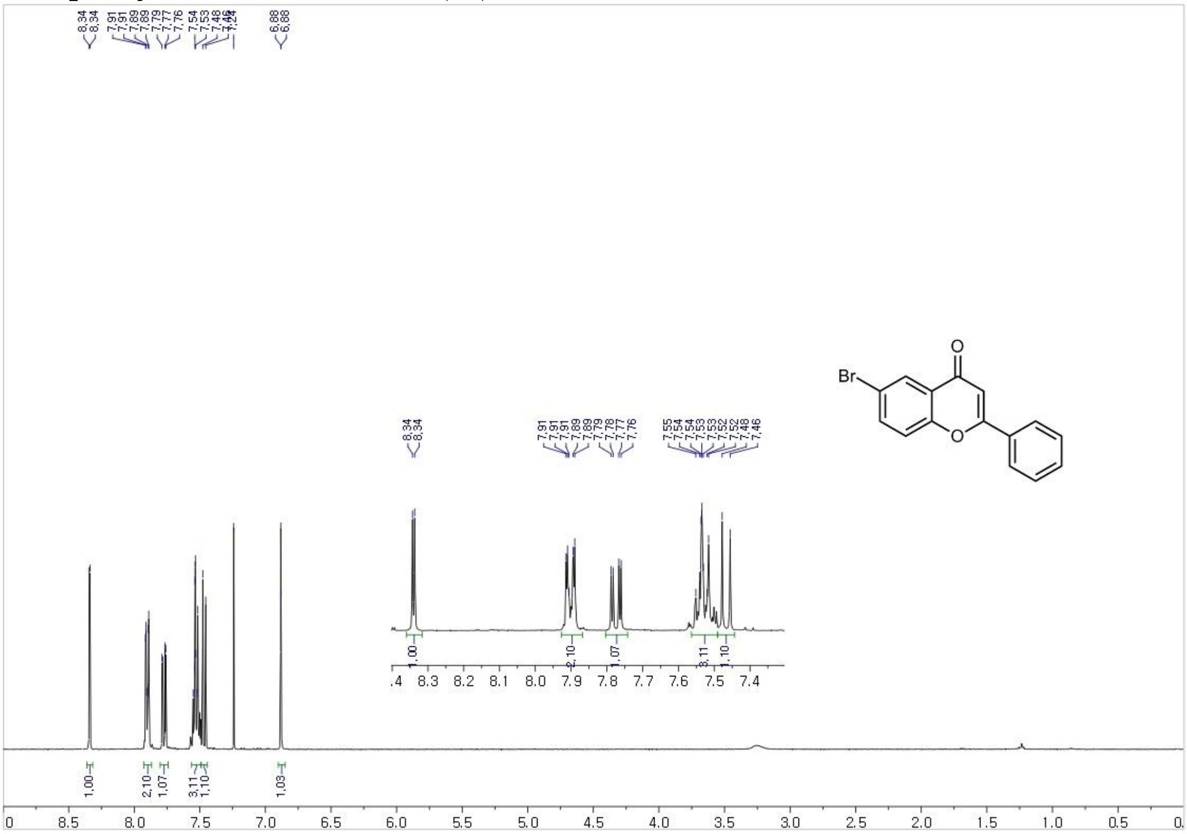


400 Mhz, ^{1}H NMR in Chloroform-d

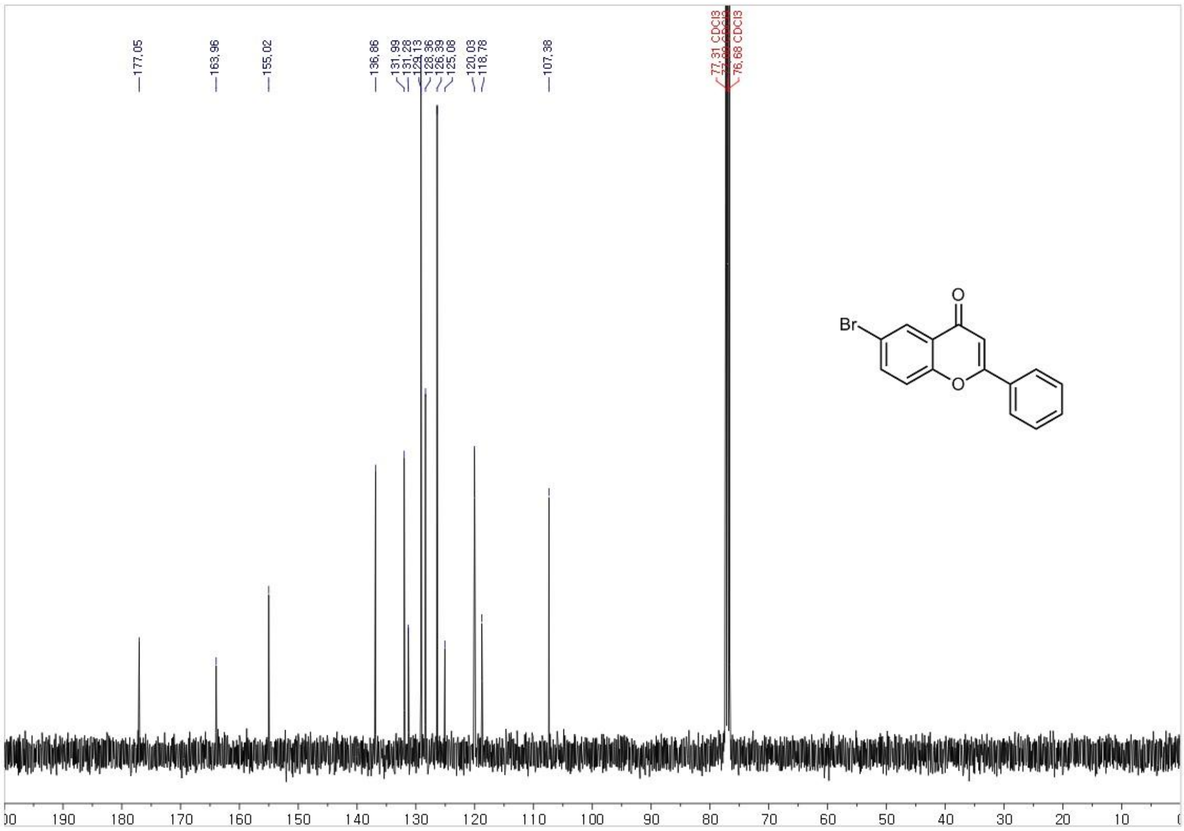


100 Mhz, ^{13}C NMR in Chloroform-d

6-bromo-2-phenyl-4H-chromen-4-one (5a)

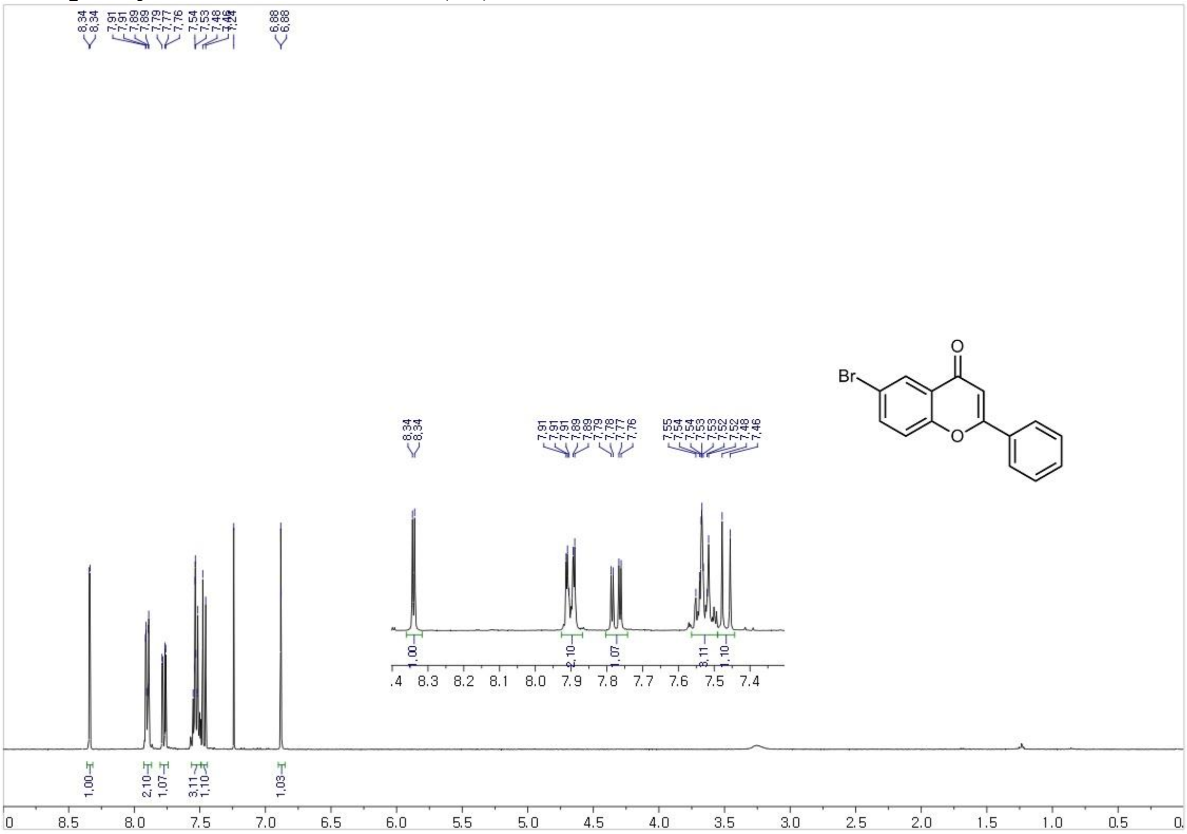


400 Mhz, ^{1}H NMR in Chloroform-d

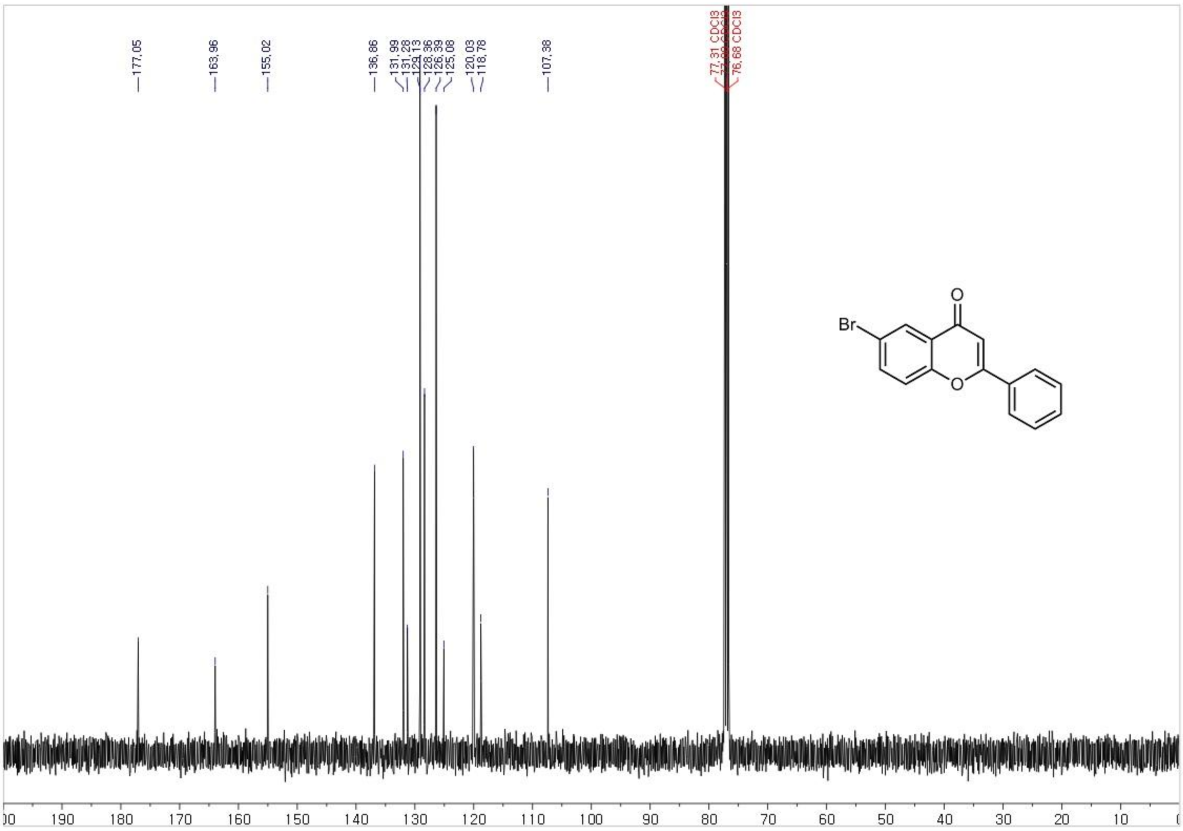


100 Mhz, ^{13}C NMR in Chloroform-d

6-bromo-2-phenyl-4H-chromen-4-one (5b)

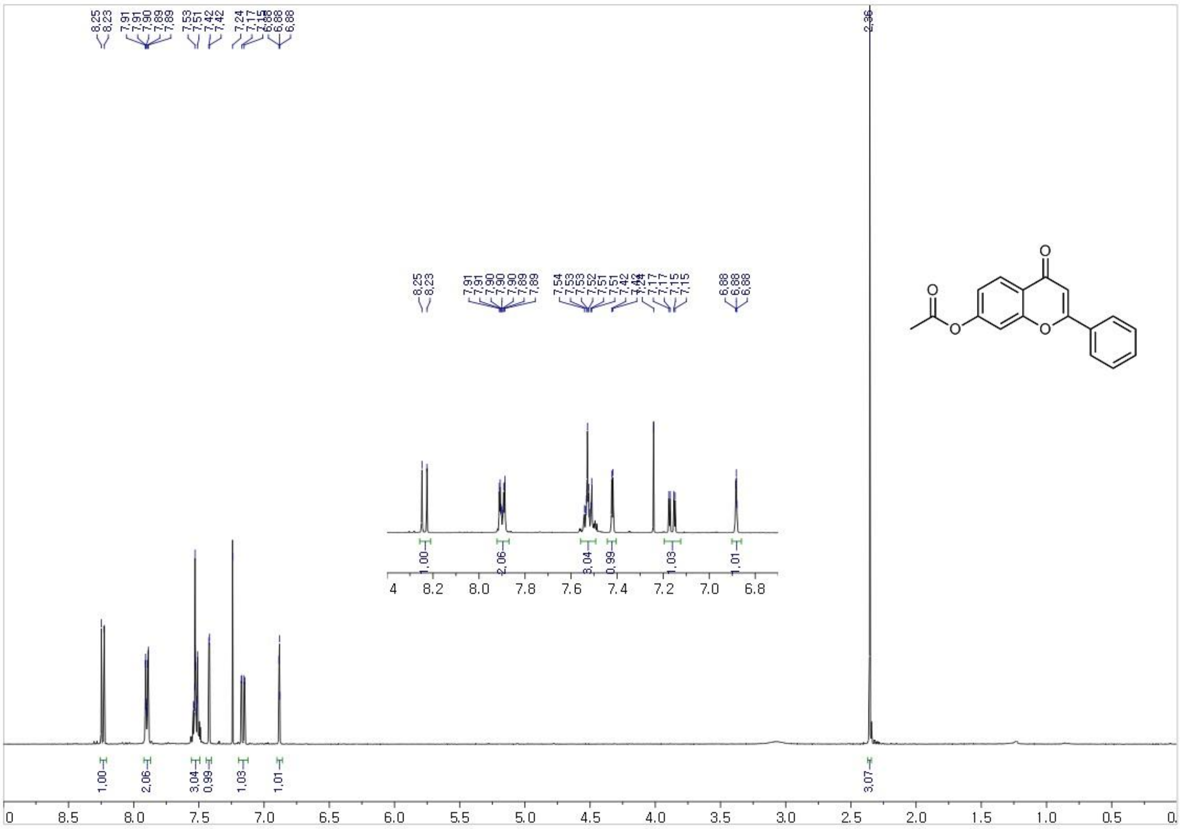


400 Mhz, ^{1}H NMR in Chloroform-d

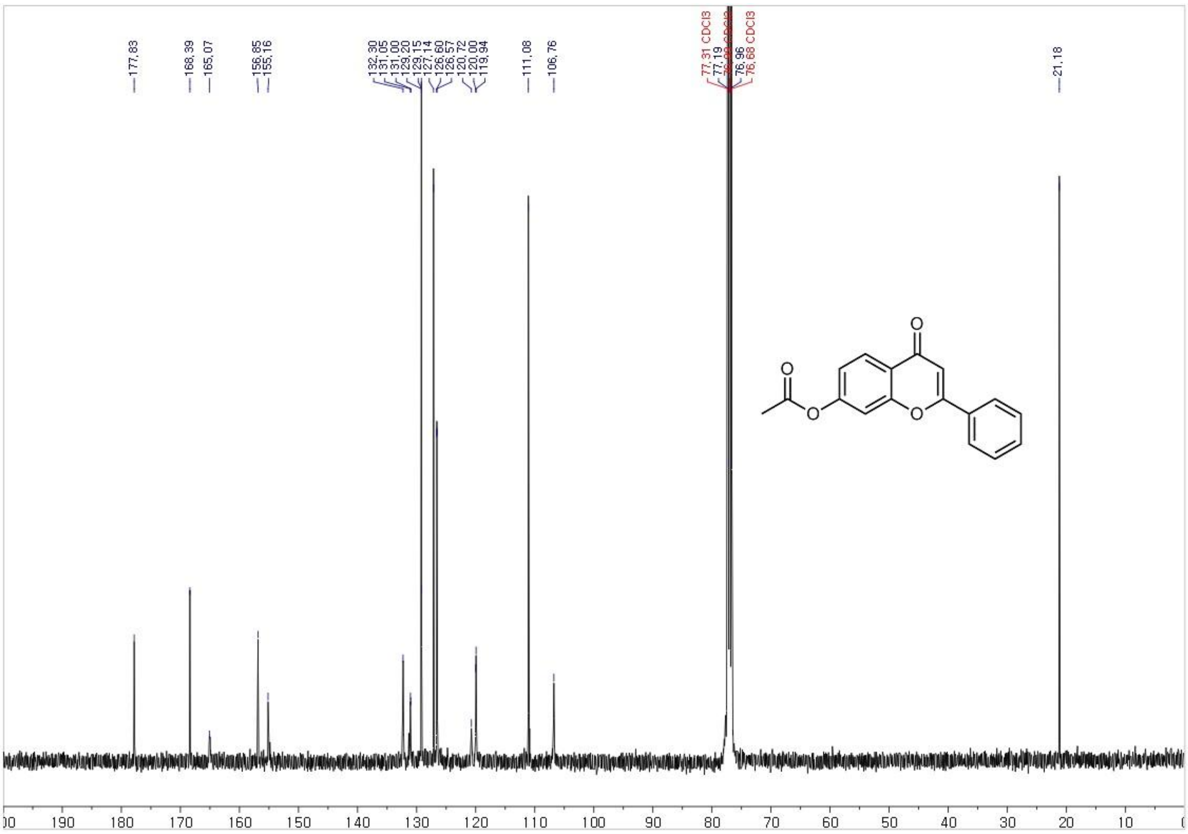


100 Mhz, ^{13}C NMR in Chloroform-d

4-oxo-2-phenyl-4H-chromen-7-yl acetate (5c)

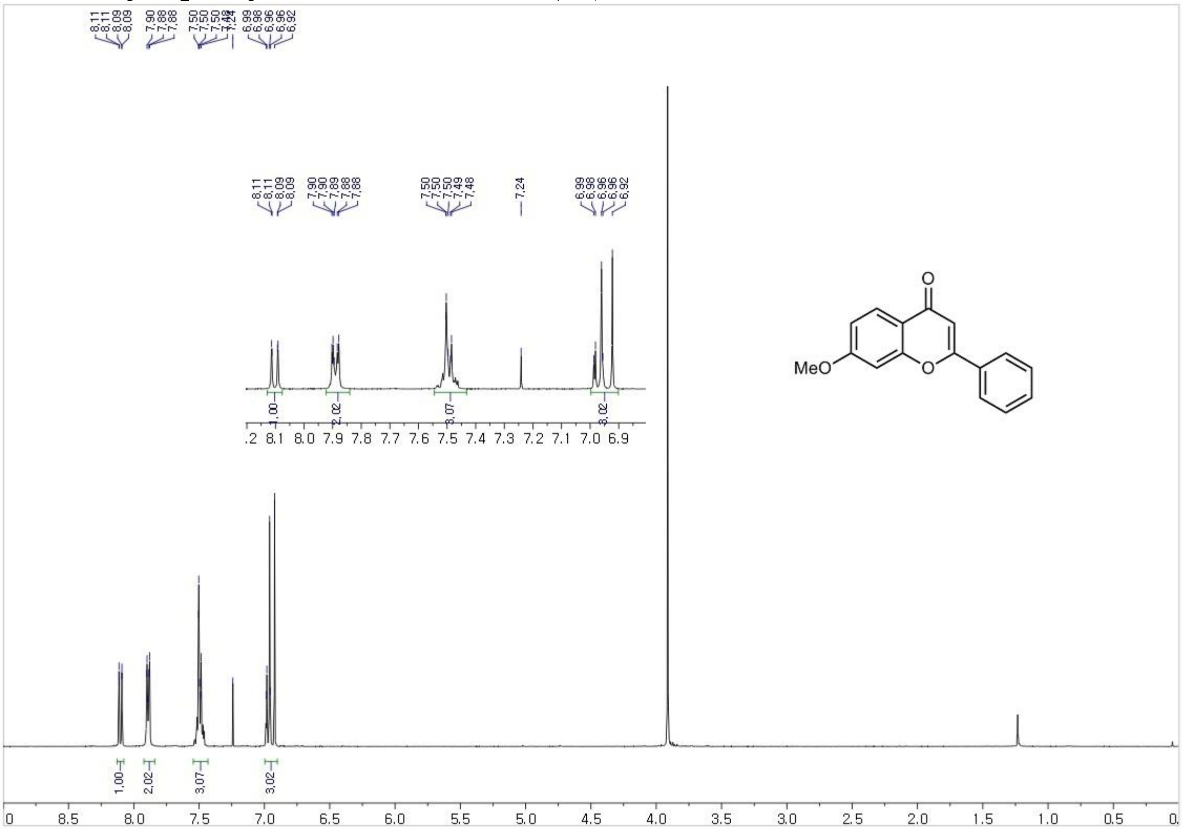


400 Mhz, ^{1}H NMR in Chloroform-d

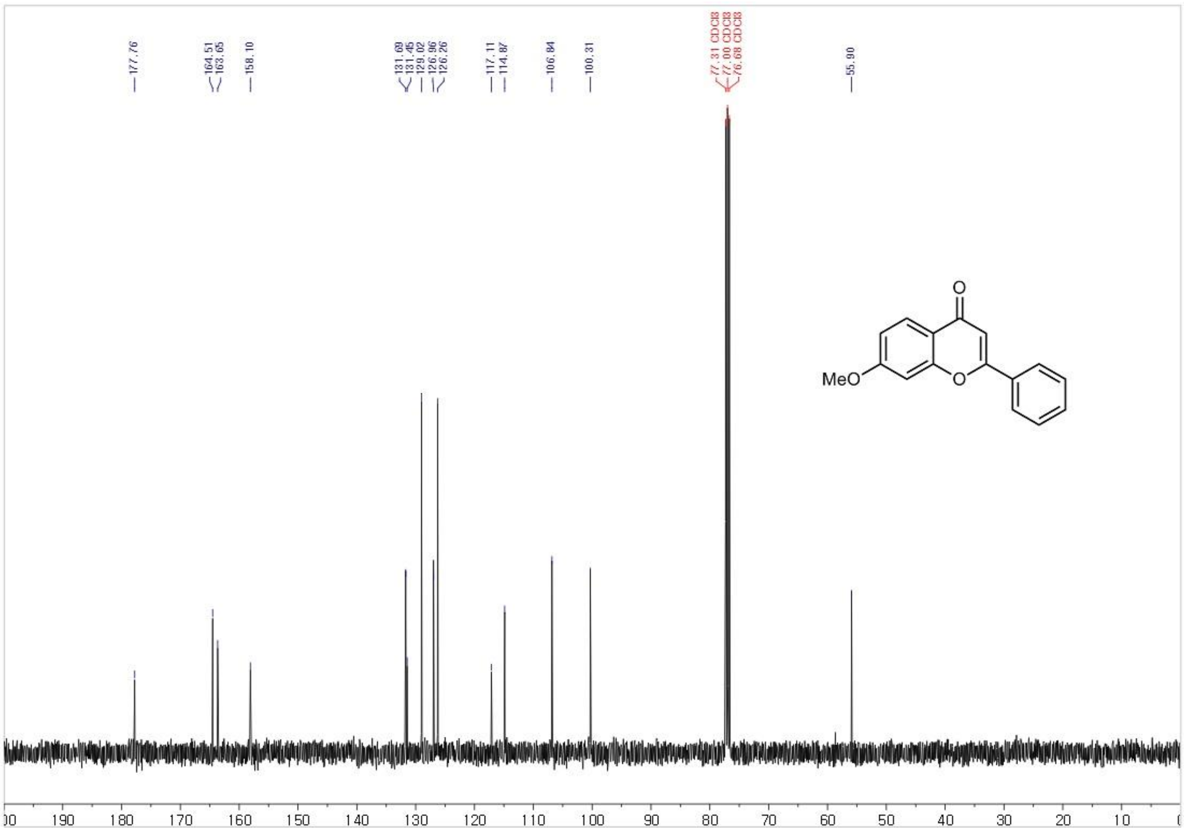


100 Mhz, ^{13}C NMR in Chloroform-d

7-methoxy-2-phenyl-4H-chromen-4-one (5d)

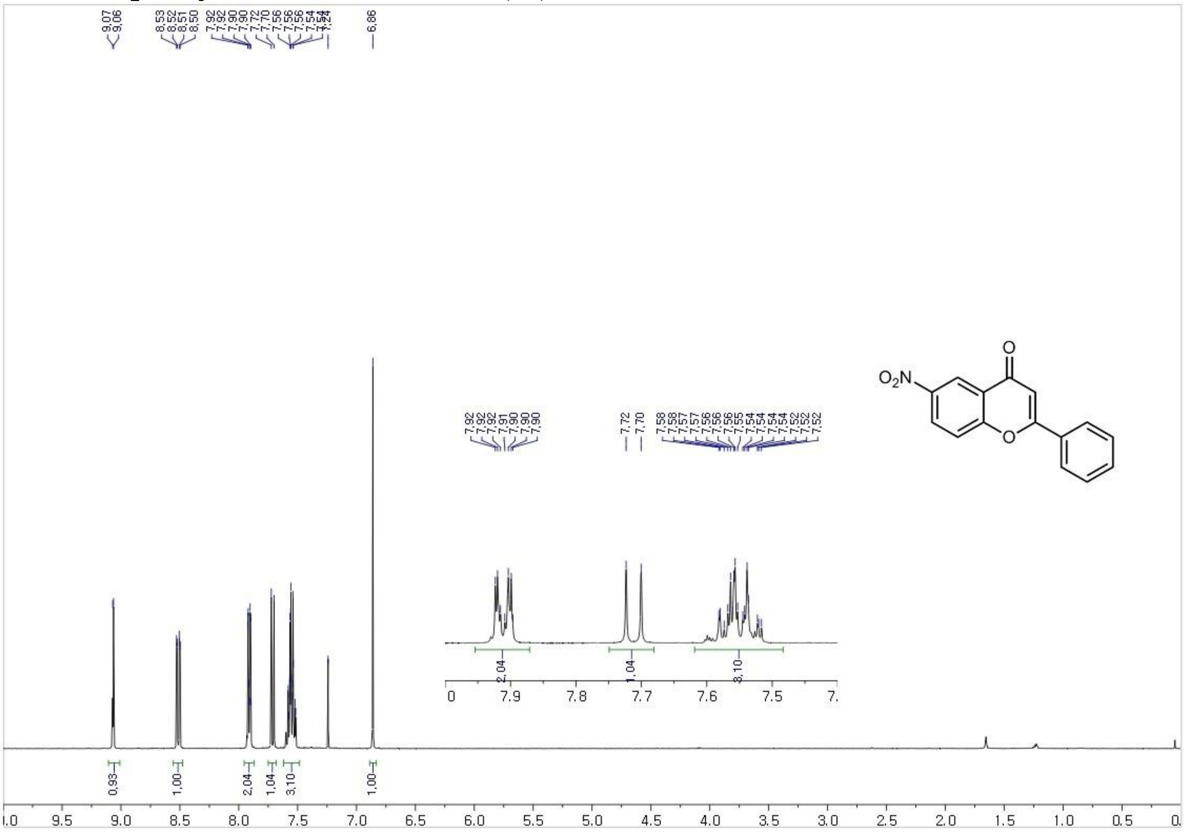


400 Mhz, ^{1}H NMR in Chloroform-d

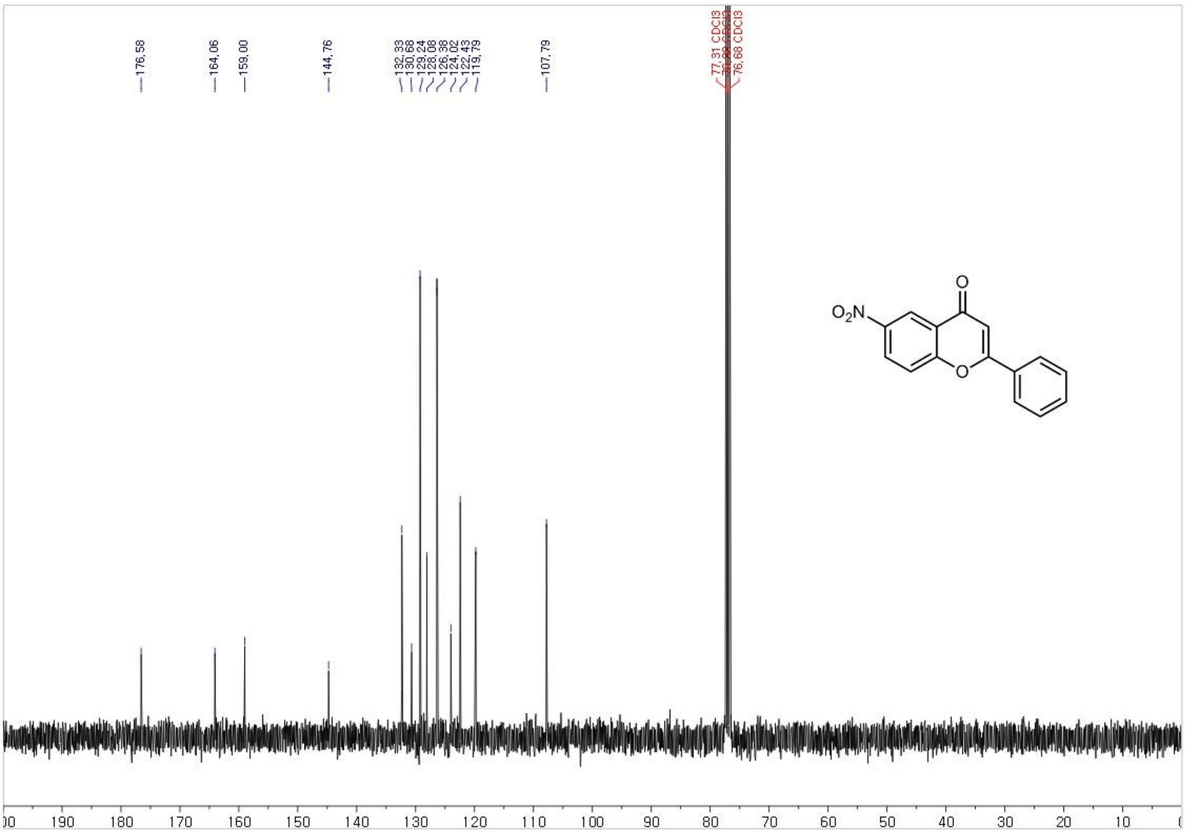


100 Mhz, ^{13}C NMR in Chloroform-d

6-nitro-2-phenyl-4H-chromen-4-one (5e)

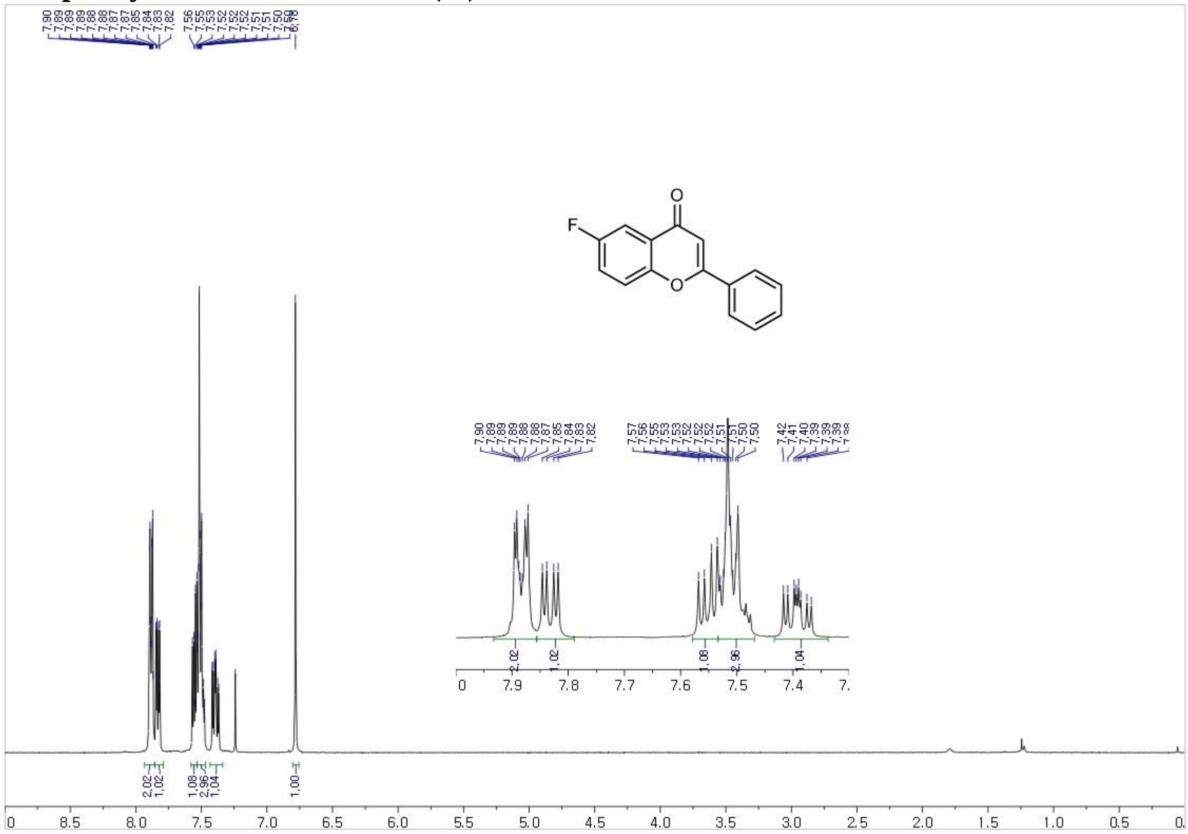


400 Mhz, ^{1}H NMR in Chloroform-d

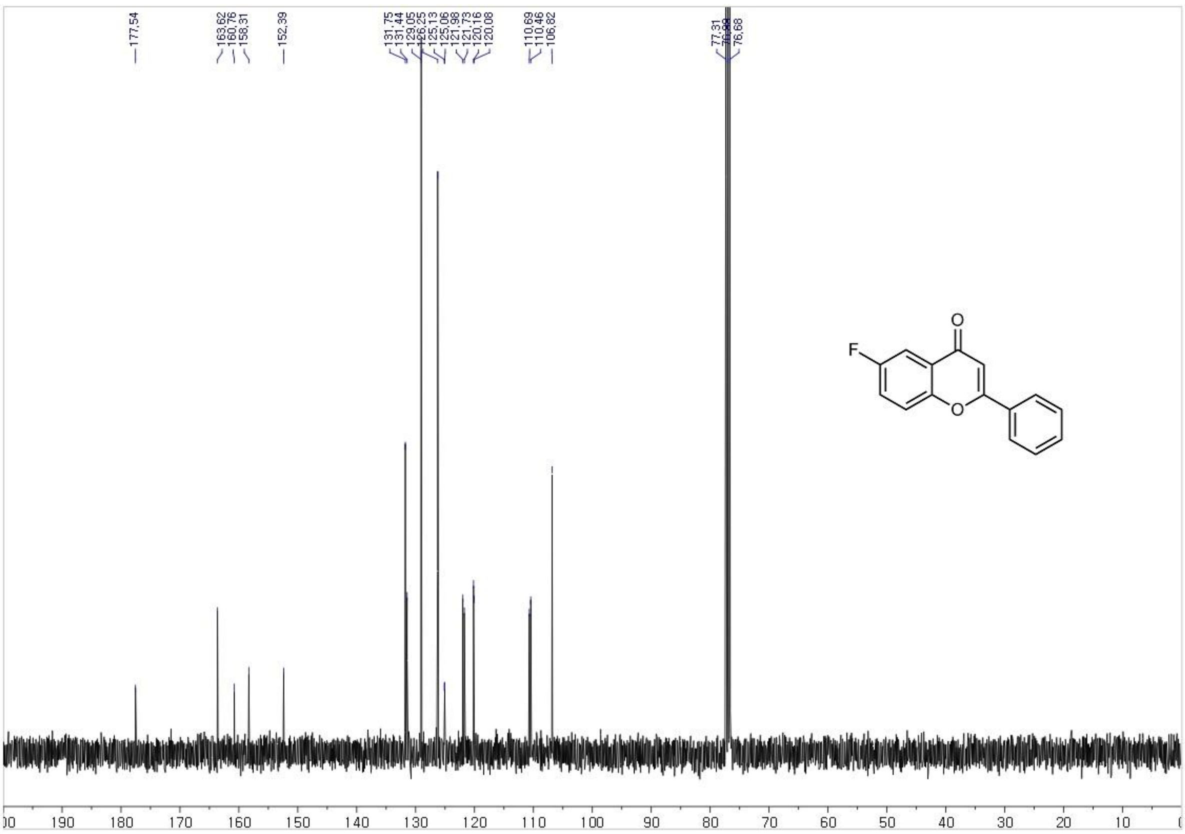


100 Mhz, ^{13}C NMR in Chloroform-d

6-fluoro-2-phenyl-4H-chromen-4-one (5f)

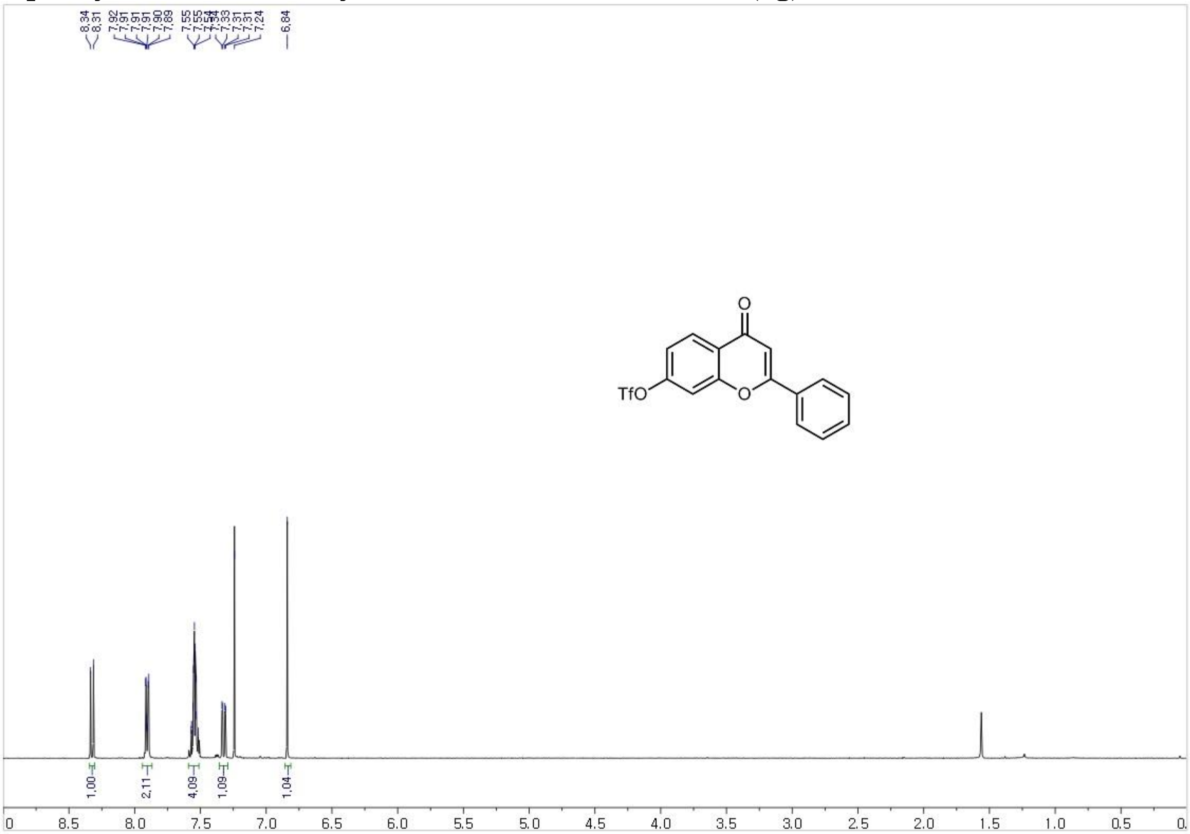


400 Mhz, ^{1}H NMR in Chloroform-d

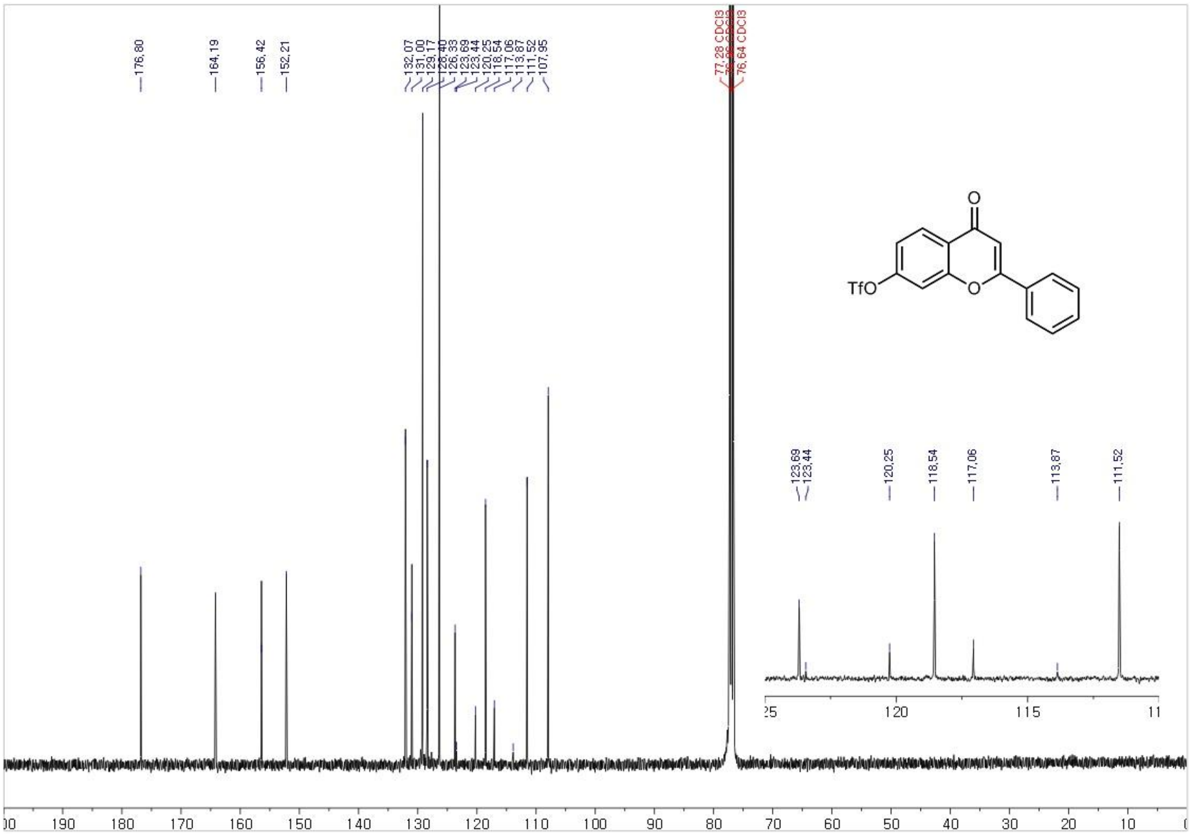


100 Mhz, ^{13}C NMR in Chloroform-d

4-oxo-2-phenyl-4H-chromen-7-yl trifluoromethanesulfonate. (5g)

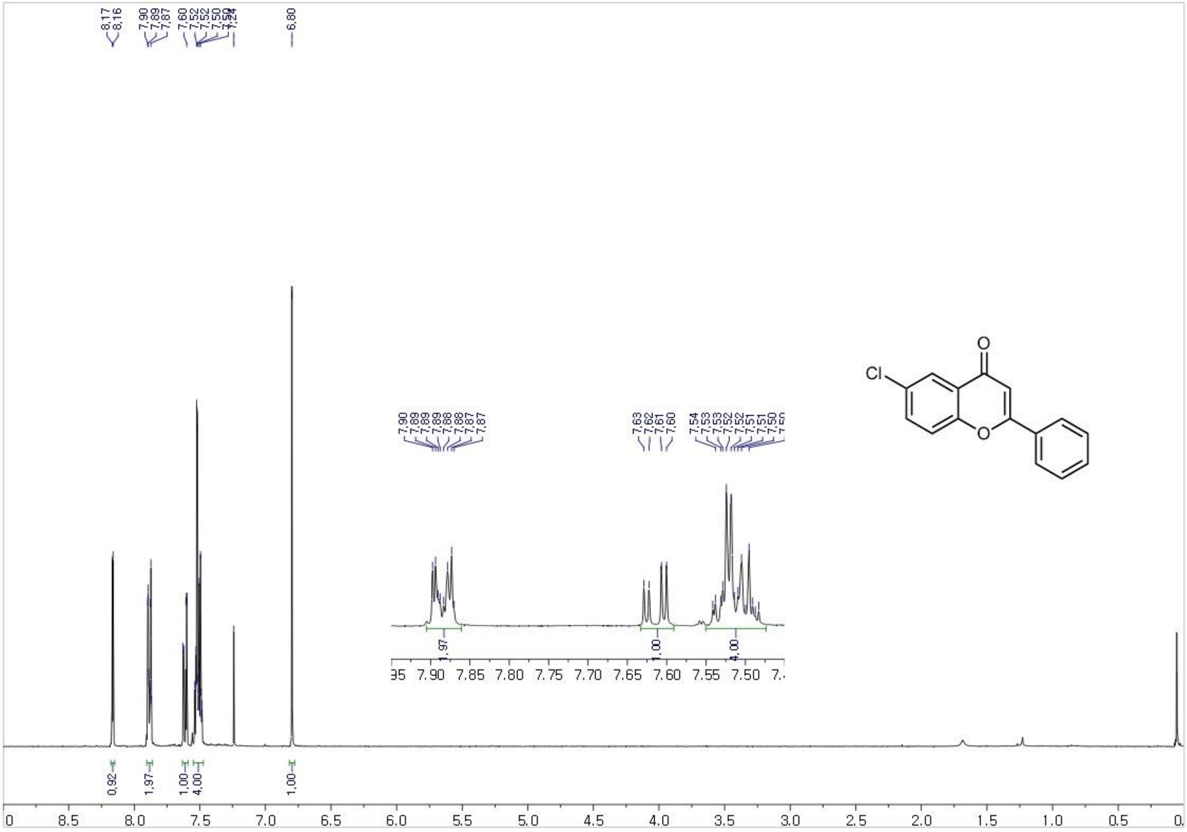


400 Mhz, ^{1}H NMR in Chloroform-d

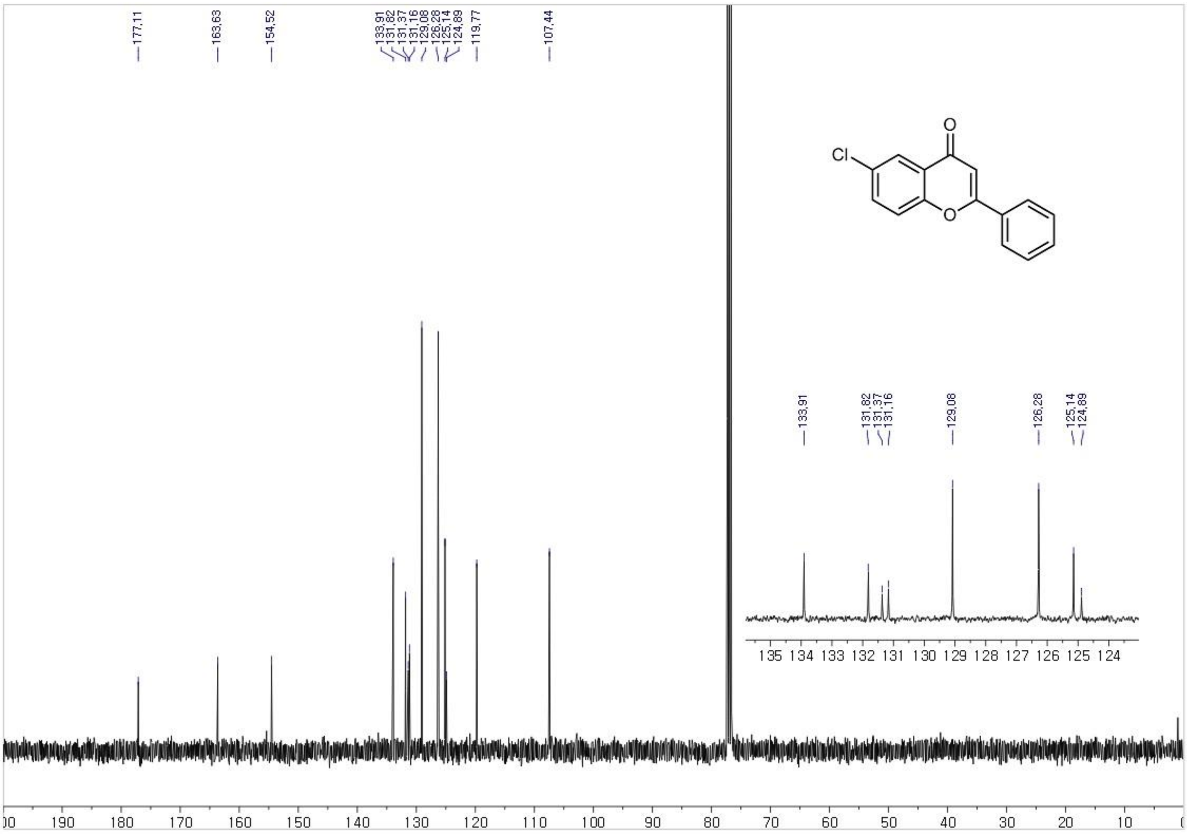


100 Mhz, ^{13}C NMR in Chloroform-d

6-chloro-2-phenyl-4H-chromen-7-one (5h)



400 Mhz, ^{1}H NMR in Chloroform-d



100 Mhz, ^{13}C NMR in Chloroform-d