

Supporting Information

A versatile approach to flavones *via* one-pot Pd(II)-catalyzed dehydrogenation/oxidative boron-Heck coupling sequence of chromanones

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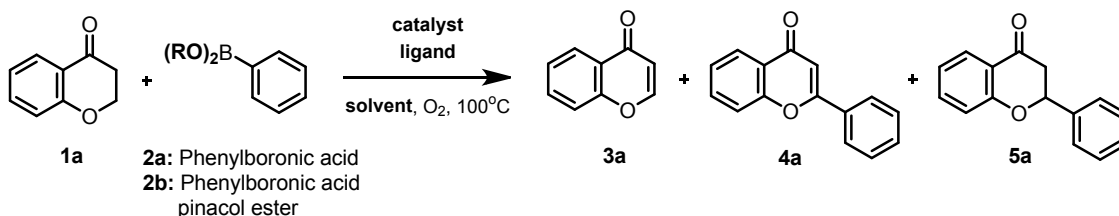
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Detailed Optimization

Table S1. Additional Optimization for Pd (II)-Catalyzed Dehydrogenation/Oxidative Heck Coupling Sequence of chromanone **1a**^a



entry	2a or 2b (equiv)	catalyst (equiv)	ligand (equiv)	solvent	Isolated Yield(%)		
					3a	4a	5a
1	2a (3)	Pd(TFA) ₂ (0.15)		AcOH	0	0	0
2	2a (3)	Pd(TFA) ₂ (0.15)	DMSO (0.3)	AcOH	34	13	9
3	2a (3)	Pd(TFA) ₂ (0.15)		DMSO	43	0	0
4	2a (3)	Pd(TFA) ₂ (0.15)	pyridine (0.3)	DMSO	76	2	0
5	2a (3)	Pd(TFA) ₂ (0.15)	DMAP (0.3)	DMSO	70	2	0
6	2a (3)	Pd(TFA) ₂ (0.15)	bipyridine (0.3)	DMSO	35	11	11
7	2a (3)	Pd(TFA) ₂ (0.15)	phenanthroline (0.3)	DMSO	24	19	9
8	2a (3)	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	DMSO	1	42	25
9	2a (3)	Pd(TFA) ₂ (0.15)	DMSO (0.3)	DMF	0	0	0
10	2a (3)	Pd(TFA) ₂ (0.15)	DMAP (0.3)	DMF	0	0	0
11	2a (3)	Pd(TFA) ₂ (0.15)	Bipyridine (0.3)	DMF	0	21	3
12	2a (3)	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	DMF	0	13	4
13	2a (3)	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	DMF	0	35	0
14	2b (3)	Pd(TFA) ₂ (0.05)	5-NO ₂ -phenanthroline (0.1)	DMSO	36	52	3
15	2b (3)	Pd(TFA) ₂ (0.1)	5-NO ₂ -phenanthroline (0.2)	DMSO	13	72	1
16	2b (3)	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	DMSO	0	93	1
17	2b (3)	Pd(TFA) ₂ (0.2)	5-NO ₂ -phenanthroline (0.4)	DMSO	0	96	0
18	2b (1.5)	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	DMSO	0	72	0
19	2b (3)	Pd(TFA) ₂ (0.05)	5-NO ₂ -phenanthroline (0.1)	DMF	24	48	5
20	2b (3)	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	DMF	0	70	0
21	2b (3)	Pd(TFA) ₂ (0.2)	5-NO ₂ -phenanthroline (0.4)	DMF	0	78	0
22	2b (1.5)	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	DMF	26	39	0
23	2b (3)	Pd(OAc) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	DMSO	0	70	1
24	2b (3)	Pd(OAc) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	DMF	34	40	0

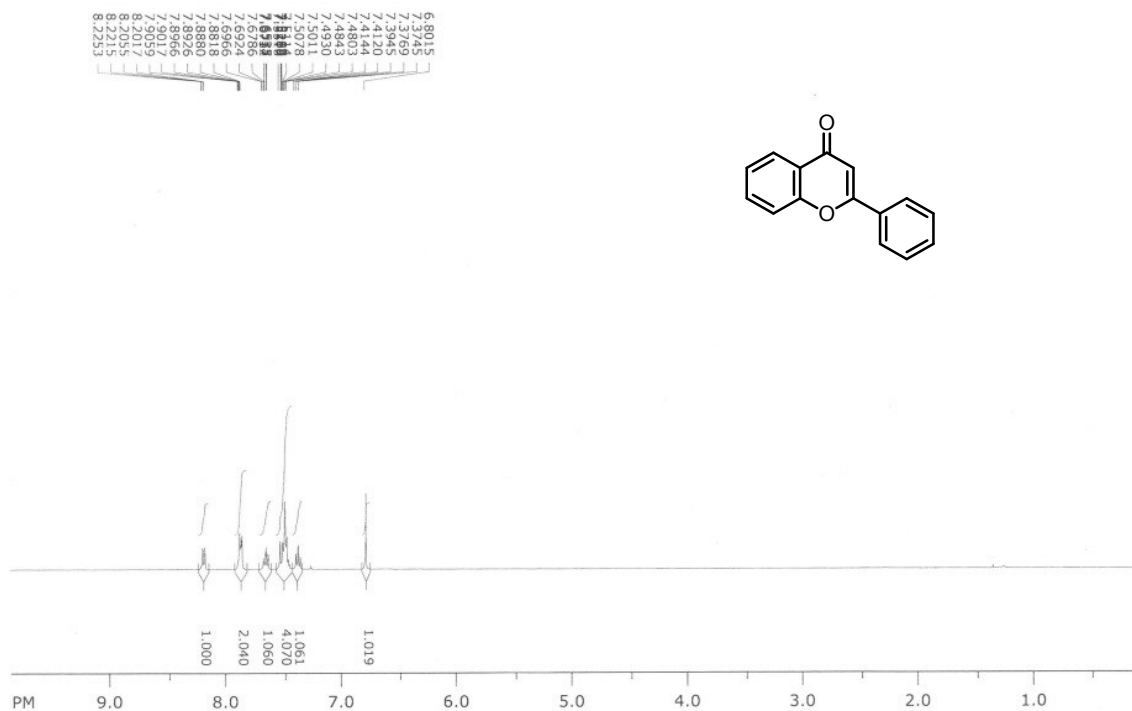
25	2b (3)	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	toluene	57	2	3
26	2b (3)	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	CH ₃ CN ^b	52	4	13
27	2b (3)	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	Dioxane	51	1	1
28	2b (3)	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	THF ^b	72	3	3
29	2a (1.5) ^c	Pd(TFA) ₂ (0.15)	DMSO(0.3)	AcOH	0	0	0
30	2a (1.5) ^c	Pd(TFA) ₂ (0.1)	phenanthroline(0.2)	DMF	26	13	22
31	2a (1.5) ^c	Pd(TFA) ₂ (0.15)	phenanthroline(0.3)	DMF	5	43	20
32	2a (1.5) ^c	Pd(TFA) ₂ (0.2)	phenanthroline(0.4)	DMF	3	49	1
33	2a (3) ^c	Pd(TFA) ₂ (0.15)	phenanthroline(0.3)	DMF	14	33	25
34	2a (1.5) ^c	Pd(TFA) ₂ (0.2)	2,9-dimethyl-1,10-phenanthroline(0.4)	DMF	12	0	0
35	2a (1.5) ^c	Pd(TFA) ₂ (0.2)	4,7-dihydroxy-1,10-phenanthroline(0.4)	DMF	0	0	0
36	2a (1.5) ^c	Pd(TFA) ₂ (0.2)	bipyridine(0.4)	DMF	0	44	6
37	2a (1.5) ^c	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	DMF	10	45	5
38	2a (3) ^c	Pd(TFA) ₂ (0.15)	5-NO ₂ -phenanthroline (0.3)	DMF	4	55	4
39	2a (3) ^c	Pd(TFA) ₂ (0.2)	5-NO ₂ -phenanthroline (0.4)	DMF	0	66	13
40	2a (1.5) ^c	Pd(OAc) ₂ (0.15)	phenanthroline(0.3)	DMF	13	15	5
41	2a (1.5) ^c	Pd(TFA) ₂ (0.2)	phenanthroline(0.4)	DMSO	63	21	3
42	2a (1.5) ^c	Pd(TFA) ₂ (0.2)	phenanthroline(0.4)	Dioxane	16	3	20
43	2a (1.5) ^c	Pd(TFA) ₂ (0.2)	phenanthroline(0.4)	AcOH	0	0	0
44	2a (1.5) ^c	Pd(TFA) ₂ (0.2)	phenanthroline(0.4)	toluene	3	5	32
45	2a (1.5) ^c	Pd(TFA) ₂ (0.2)	phenanthroline(0.4)	CH ₃ CN ^b	41	0	23
46	2a (1.5) ^c	Pd(TFA) ₂ (0.2)	phenanthroline(0.4)	HMPA	0	12	0
47	2b (3) ^c	Pd(TFA) ₂ (0.15)	Phenanthroline(0.3)	DMF	0	79	0

^aReaction conditions: To a solution of Pd catalyst, and ligand in anhydrous solvent (1mL) were added chromanone (**1a**) and phenyl boronic acid (**2a**) or its pinacol ester (**2b**) under O₂ atmosphere. The reaction mixture was stirred at 100°C until complete consumption of the starting material on TLC. Then, the reaction mixture was diluted with EtOAc and filtered through a pad of celite. The filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel (EtOAc/Hexanes). ^bReflux condition. ^cReagent **2** was added to reaction mixture after 24h.

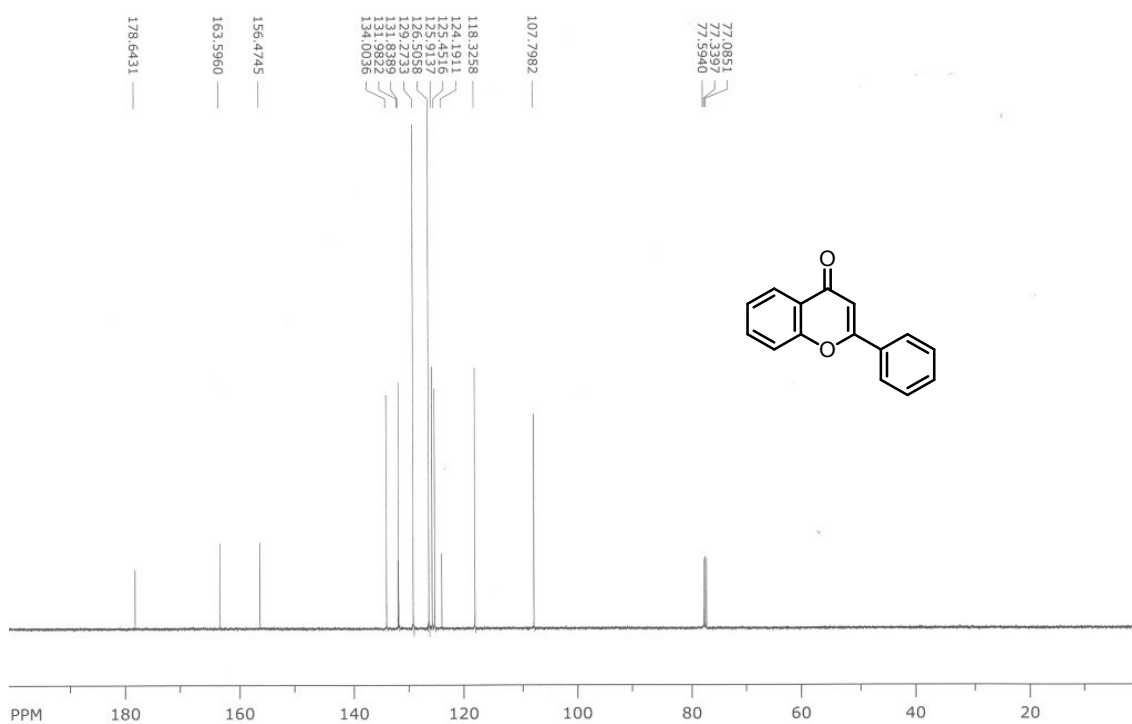
^1H NMR and ^{13}C NMR spectra

Compound 4a

▼ ^1H -NMR (CDCl_3 , 400 MHz)

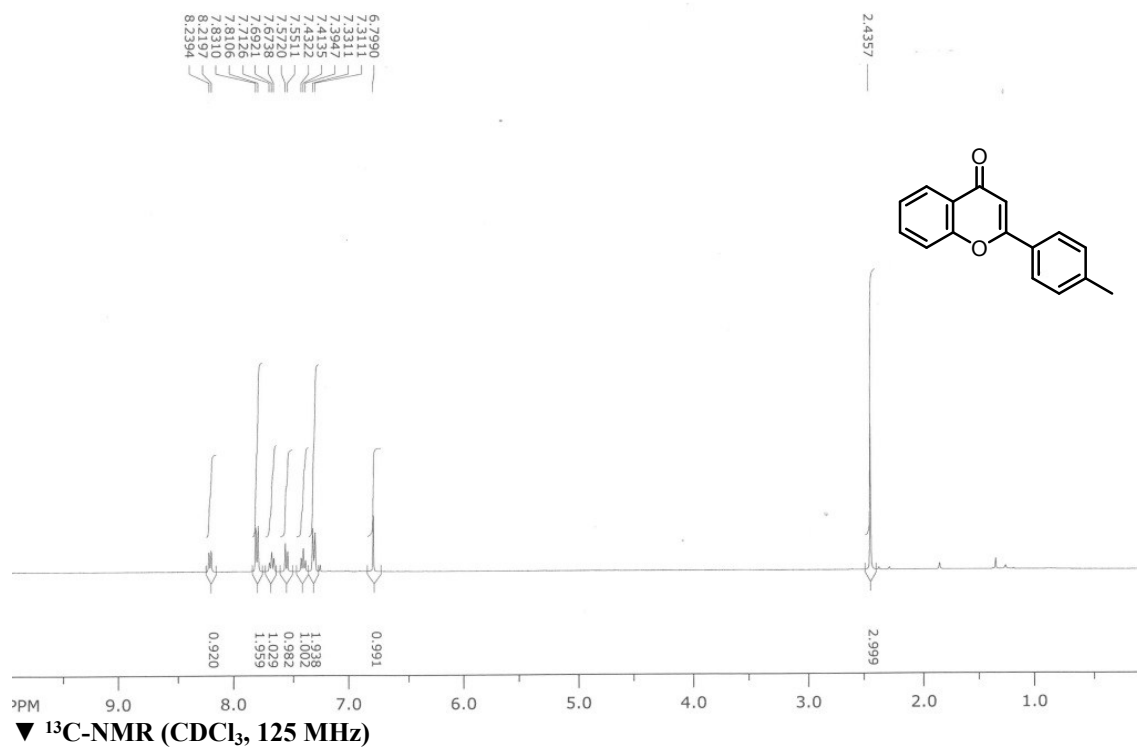


▼ ^{13}C -NMR (CDCl_3 , 125 MHz)

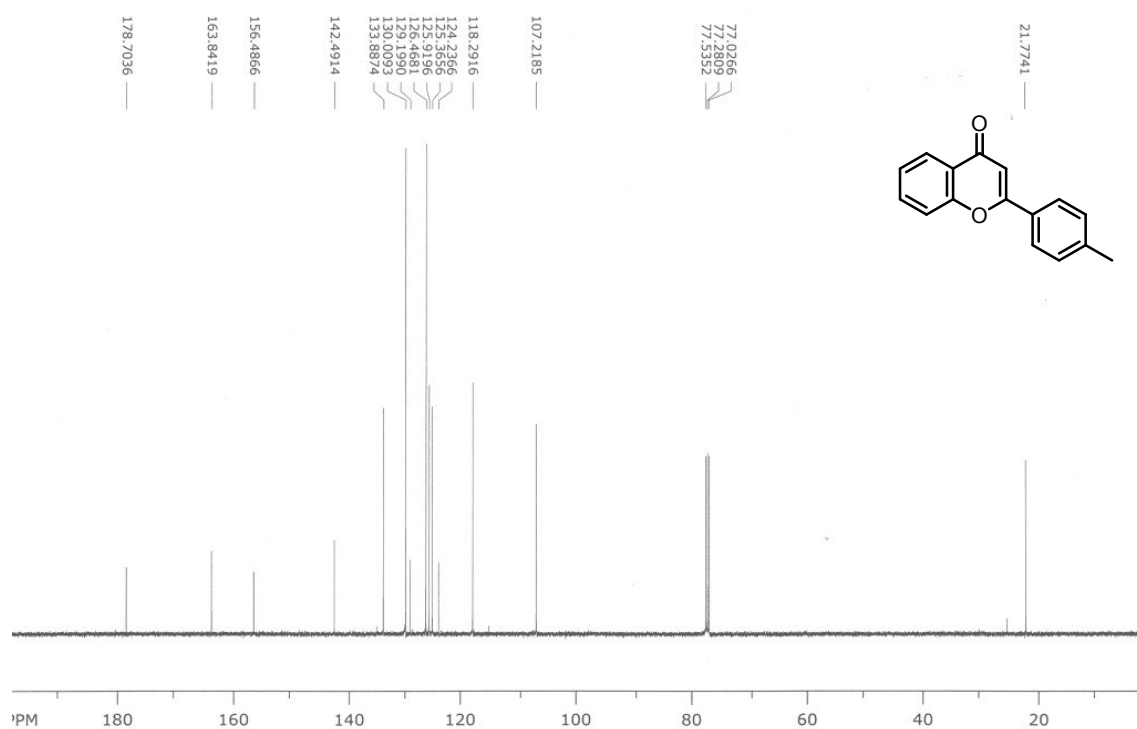


Compound 4b

▼ ¹H-NMR (CDCl₃, 400 MHz)

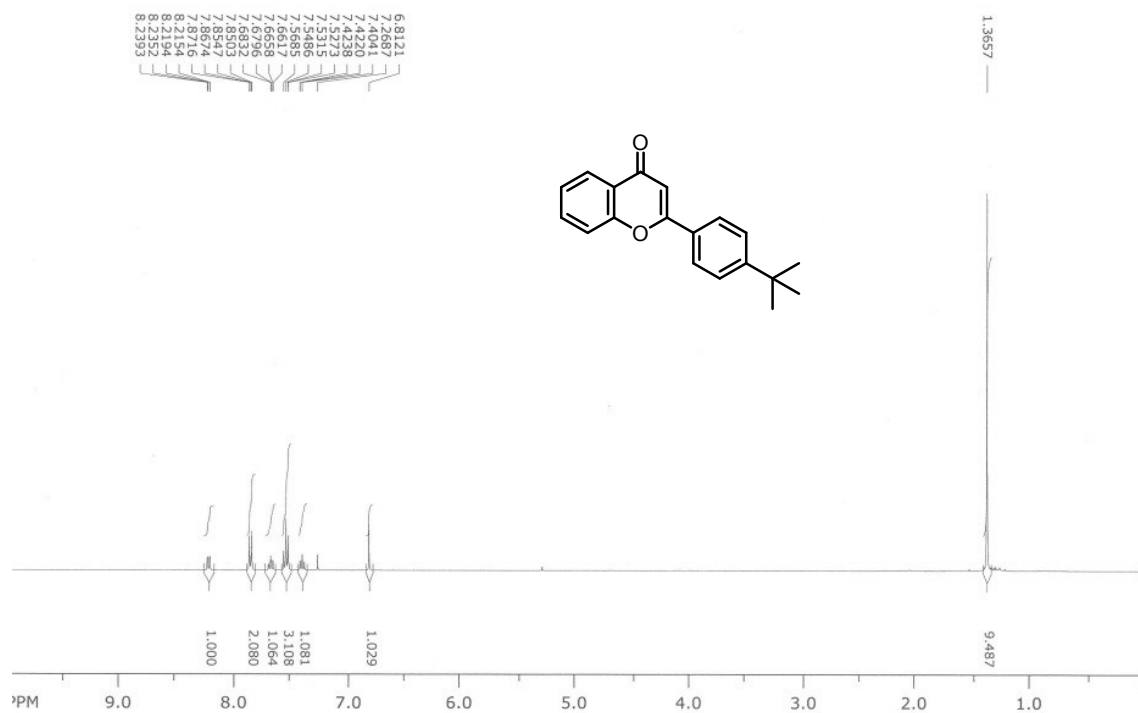


▼ ¹³C-NMR (CDCl₃, 125 MHz)

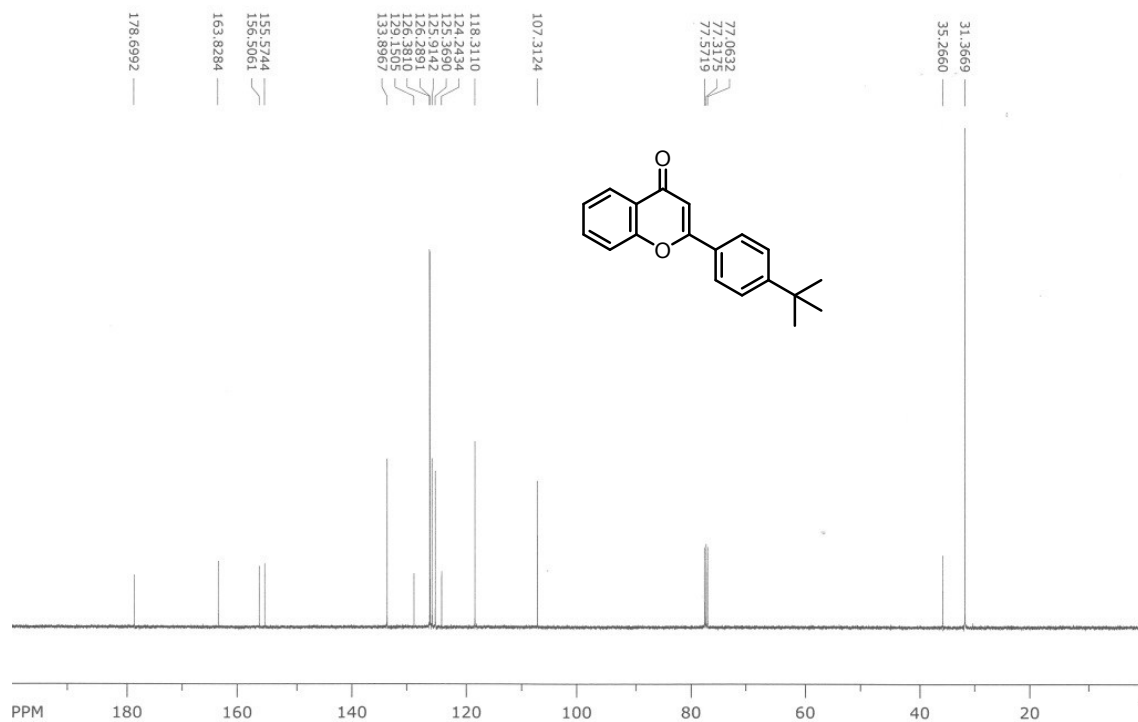


Compound 4c

▼ ¹H-NMR (CDCl₃, 400 MHz)

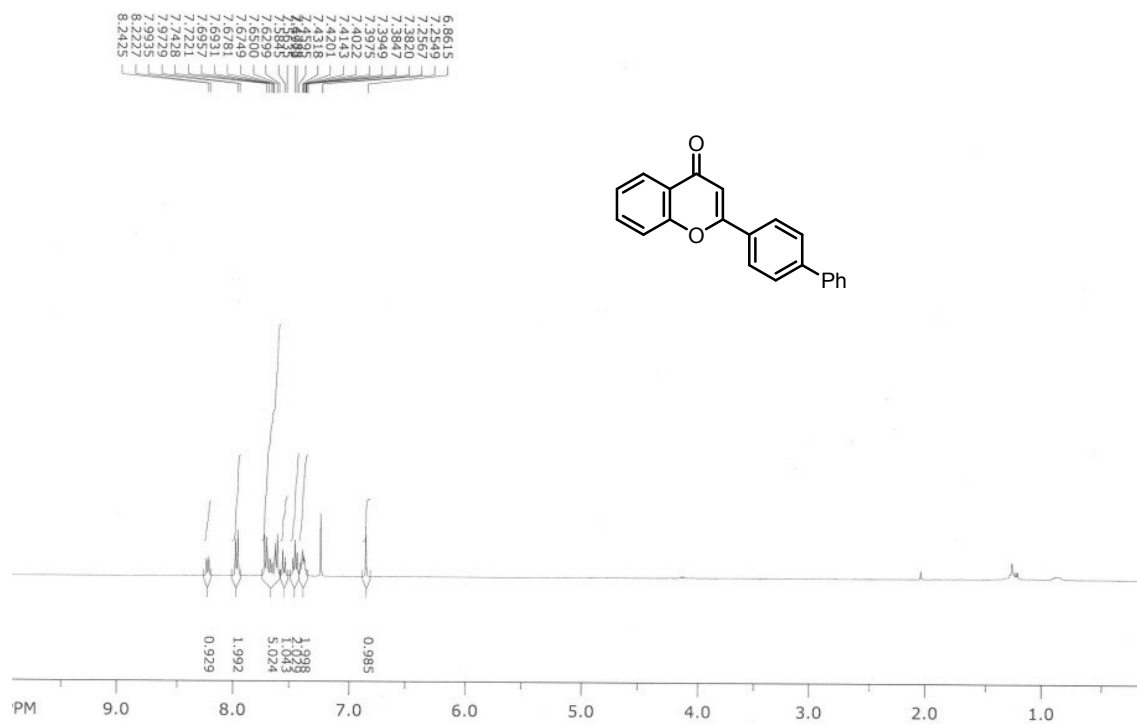


▼ ¹³C-NMR (CDCl₃, 125 MHz)

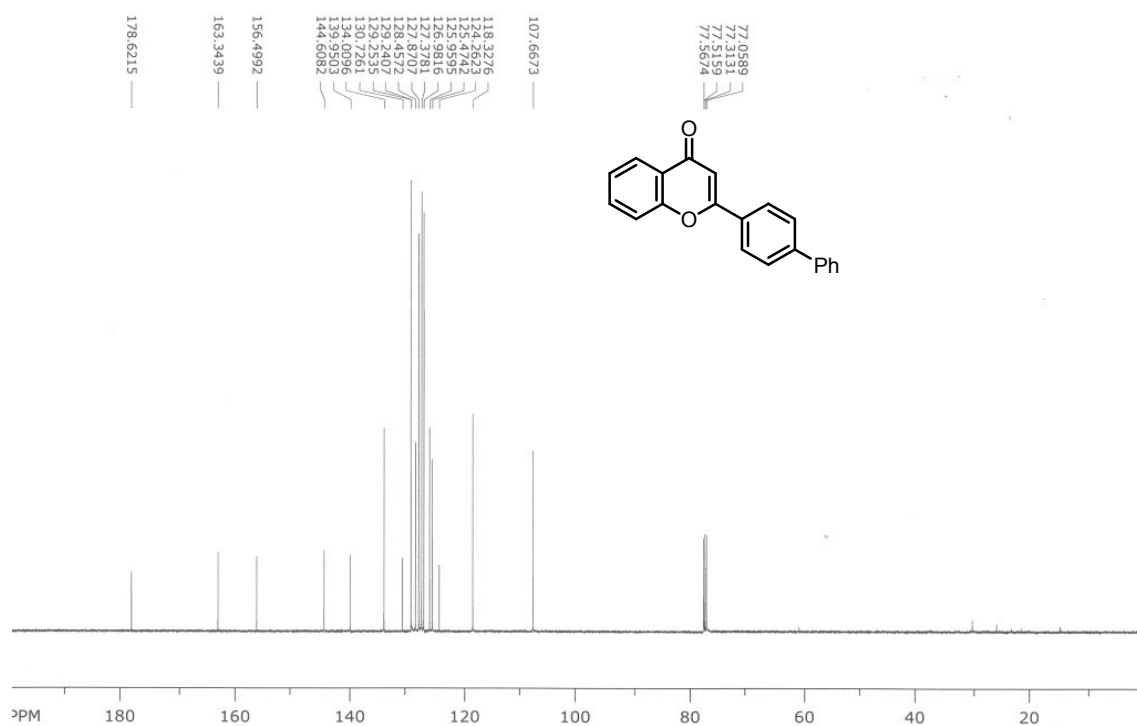


Compound 4d

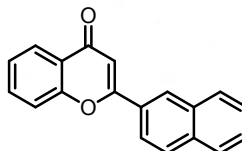
▼ ¹H-NMR (CDCl₃, 400 MHz)



▼ ¹³C-NMR (CDCl₃, 125 MHz)

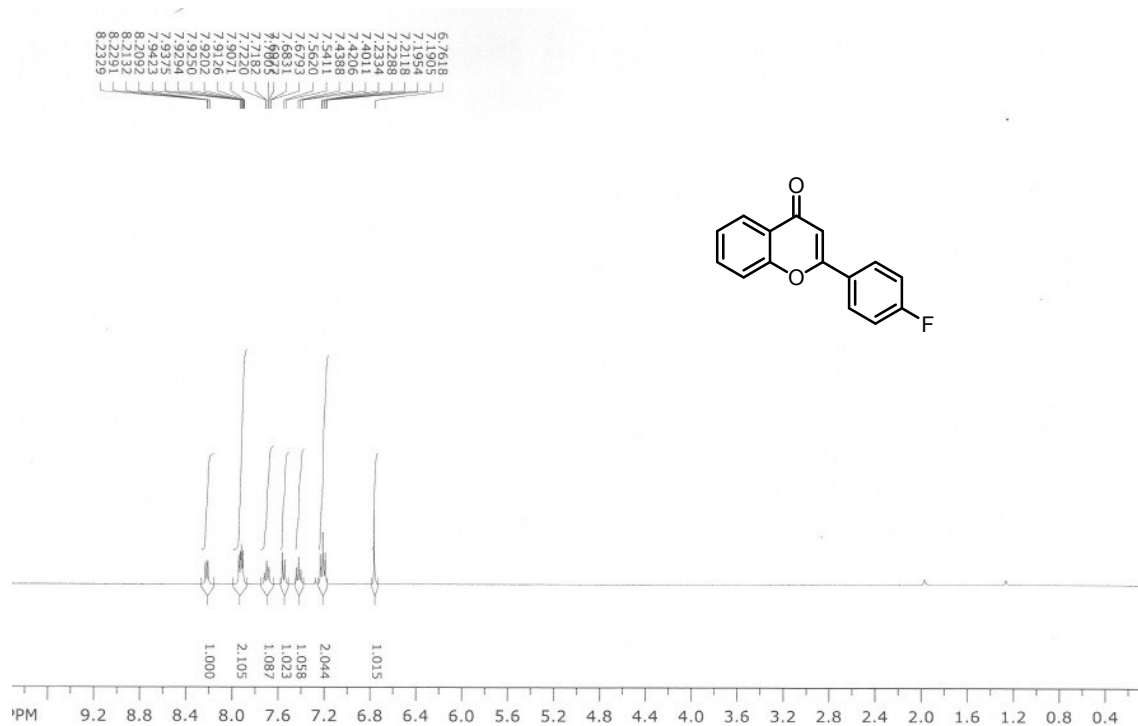


▼ ¹H-NMR (CDCl₃, 400 MHz)

[illegible]

Compound 4f

▼ ¹H-NMR (CDCl₃, 400 MHz)

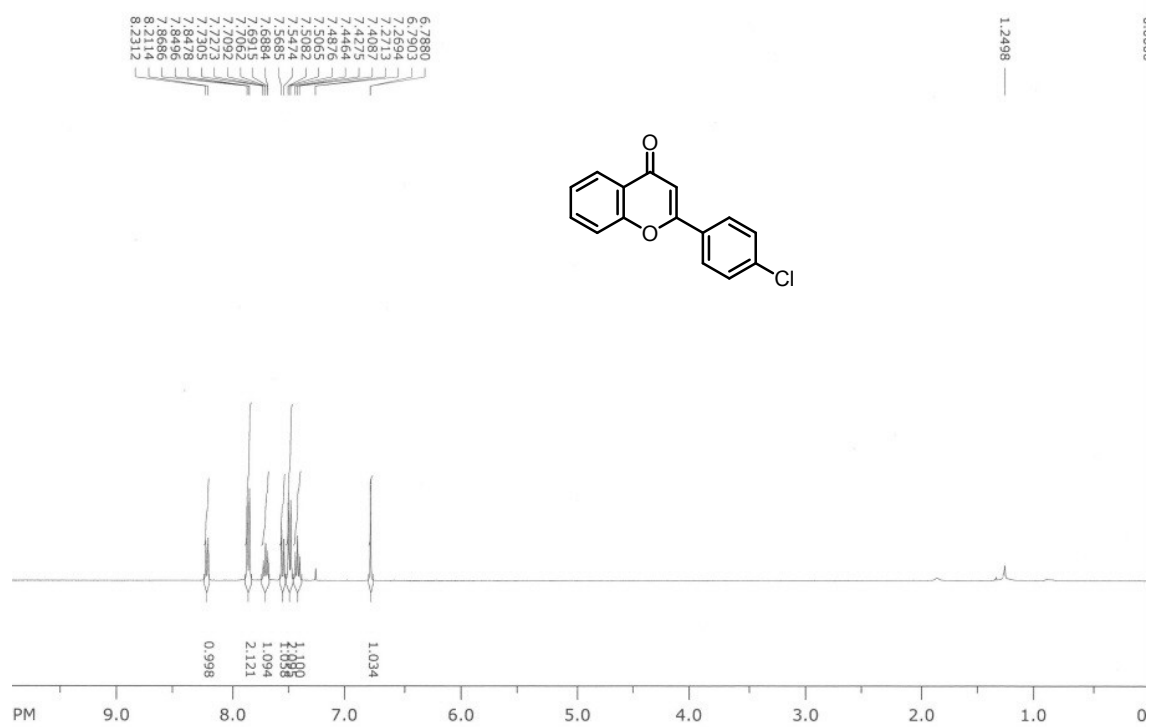


▼ ¹³C-NMR (CDCl₃, 125 MHz)

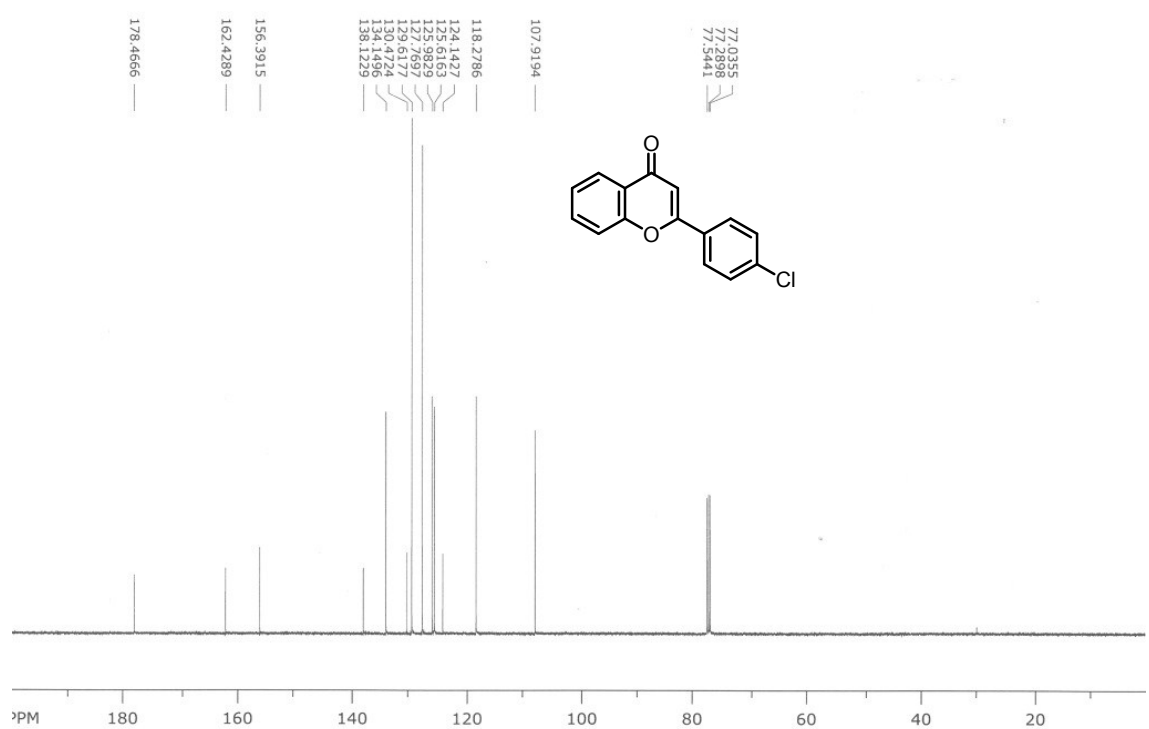


Compound 4g

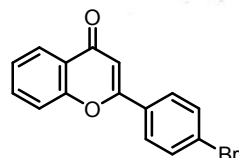
▼ ¹H-NMR (CDCl₃, 400 MHz)



▼ ¹³C-NMR (CDCl₃, 125 MHz)



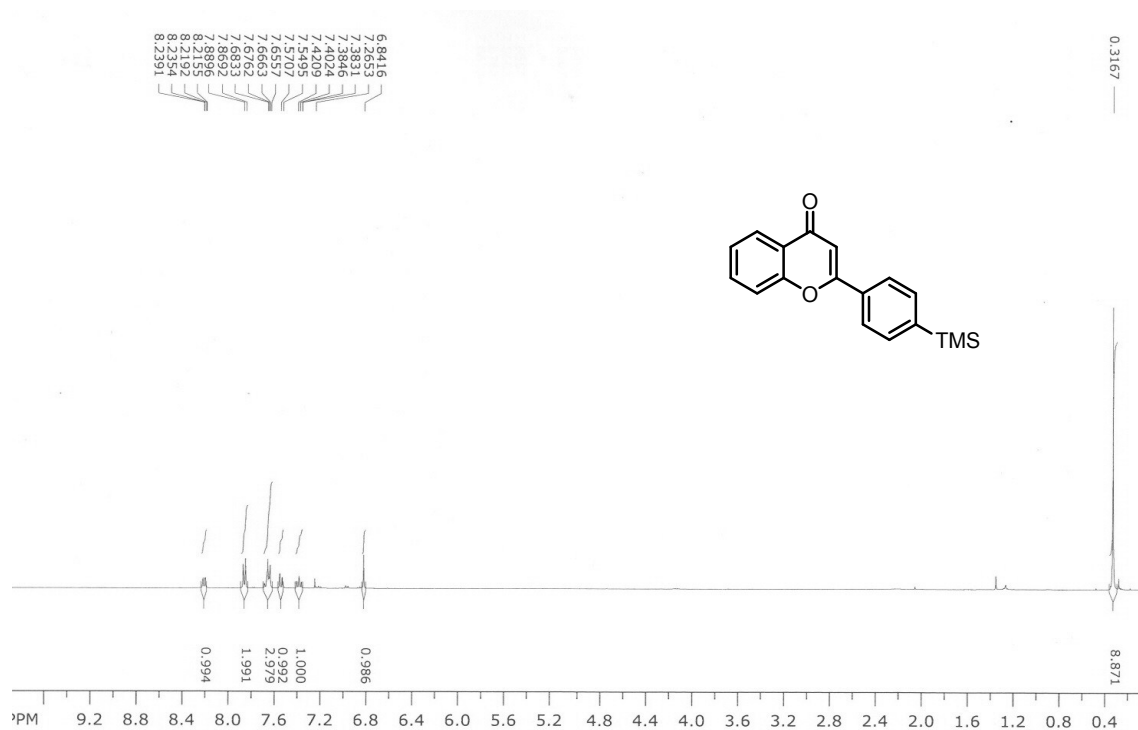
▼ ¹H-NMR (CDCl₃, 400 MHz)



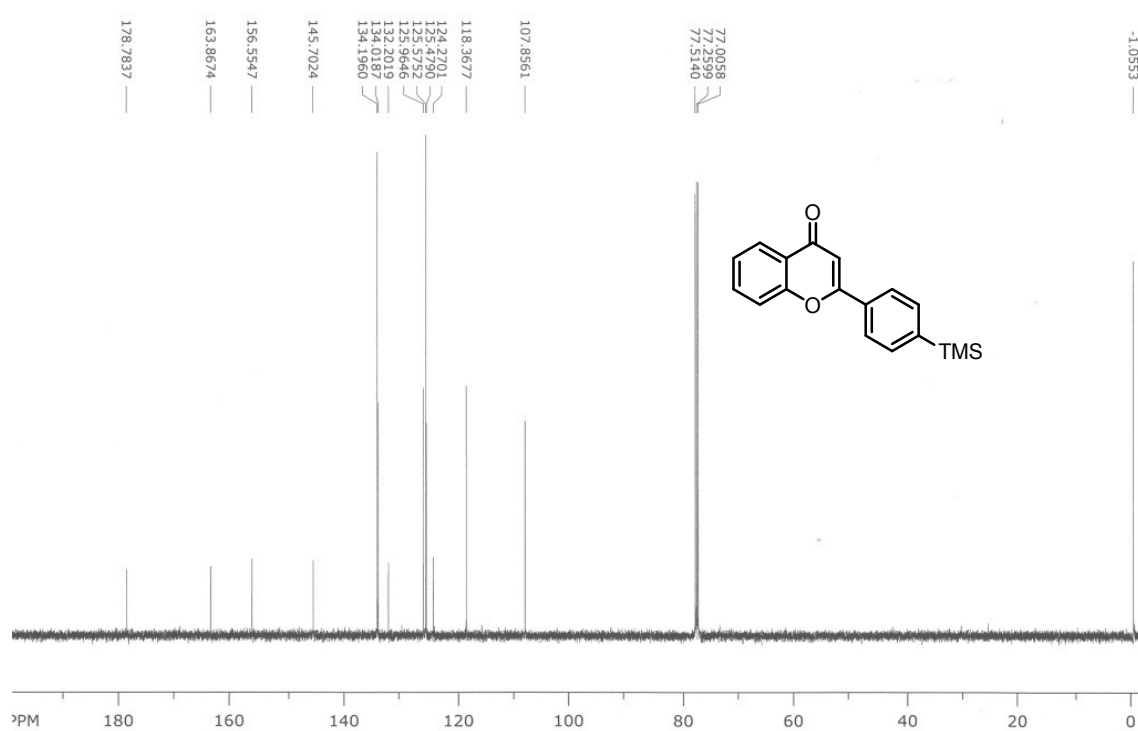
Chemical structure of 6-bromo-2-phenylisobenzofuran-1-one is shown. The ¹³C NMR spectrum (CDCl₃) displays peaks at 178.4726, 162.5127, 156.4018, 147.9889, 147.9371, 147.8990, 147.8536, 147.8093, 147.7656, 147.7236, 147.6816, 147.6396, 147.5976, 147.5556, 147.5136, 147.4716, 147.4296, 147.3876, 147.3456, 147.3036, 147.2616, 147.2196, 147.1776, 147.1356, 147.0936, 147.0516, 147.0096, 146.9676, 146.9256, 146.8836, 146.8416, 146.7996, 146.7576, 146.7156, 146.6736, 146.6316, 146.5896, 146.5476, 146.5056, 146.4636, 146.4216, 146.3796, 146.3376, 146.2956, 146.2536, 146.2116, 146.1696, 146.1276, 146.0856, 146.0436, 146.0016, 145.9596, 145.9176, 145.8756, 145.8336, 145.7916, 145.7496, 145.7076, 145.6656, 145.6236, 145.5816, 145.5396, 145.4976, 145.4556, 145.4136, 145.3716, 145.3296, 145.2876, 145.2456, 145.2036, 145.1616, 145.1196, 145.0776, 145.0356, 144.9936, 144.9516, 144.9096, 144.8676, 144.8256, 144.7836, 144.7416, 144.6996, 144.6576, 144.6156, 144.5736, 144.5316, 144.4896, 144.4476, 144.4056, 144.3636, 144.3216, 144.2796, 144.2376, 144.1956, 144.1536, 144.1116, 144.0696, 144.0276, 143.9856, 143.9436, 143.9016, 143.8596, 143.8176, 143.7756, 143.7336, 143.6916, 143.6496, 143.6076, 143.5656, 143.5236, 143.4816, 143.4396, 143.3976, 143.3556, 143.3136, 143.2716, 143.2296, 143.1876, 143.1456, 143.1036, 143.0616, 143.0196, 142.9776, 142.9356, 142.8936, 142.8516, 142.8096, 142.7676, 142.7256, 142.6836, 142.6416, 142.5996, 142.5576, 142.5156, 142.4736, 142.4316, 142.3896, 142.3476, 142.3056, 142.2636, 142.2216, 142.1796, 142.1376, 142.0956, 142.0536, 142.0116, 141.9696, 141.9276, 141.8856, 141.8436, 141.8016, 141.7596, 141.7176, 141.6756, 141.6336, 141.5916, 141.5496, 141.5076, 141.4656, 141.4236, 141.3816, 141.3396, 141.2976, 141.2556, 141.2136, 141.1716, 141.1296, 141.0876, 141.0456, 141.0036, 140.9616, 140.9196, 140.8776, 140.8356, 140.7936, 140.7516, 140.7096, 140.6676, 140.6256, 140.5836, 140.5416, 140.4996, 140.4576, 140.4156, 140.3736, 140.3316, 140.2896, 140.2476, 140.2056, 140.1636, 140.1216, 140.0796, 140.0376, 140.000, 139.960, 139.920, 139.880, 139.840, 139.800, 139.760, 139.720, 139.680, 139.640, 139.600, 139.560, 139.520, 139.480, 139.440, 139.400, 139.360, 139.320, 139.280, 139.240, 139.200, 139.160, 139.120, 139.080, 139.040, 139.000, 138.960, 138.920, 138.880, 138.840, 138.800, 138.760, 138.720, 138.680, 138.640, 138.600, 138.560, 138.520, 138.480, 138.440, 138.400, 138.360, 138.320, 138.280, 138.240, 138.200, 138.160, 138.120, 138.080, 138.040, 138.000, 137.960, 137.920, 137.880, 137.840, 137.800, 137.760, 137.720, 137.680, 137.640, 137.600, 137.560, 137.520, 137.480, 137.440, 137.400, 137.360, 137.320, 137.280, 137.240, 137.200, 137.160, 137.120, 137.080, 137.040, 137.000, 136.960, 136.920, 136.880, 136.840, 136.800, 136.760, 136.720, 136.680, 136.640, 136.600, 136.560, 136.520, 136.480, 136.440, 136.400, 136.360, 136.320, 136.280, 136.240, 136.200, 136.160, 136.120, 136.080, 136.040, 136.000, 135.960, 135.920, 135.880, 135.840, 135.800, 135.760, 135.720, 135.680, 135.640, 135.600, 135.560, 135.520, 135.480, 135.440, 135.400, 135.360, 135.320, 135.280, 135.240, 135.200, 135.160, 135.120, 135.080, 135.040, 135.000, 134.960, 134.920, 134.880, 134.840, 134.800, 134.760, 134.720, 134.680, 134.640, 134.600, 134.560, 134.520, 134.480, 134.440, 134.400, 134.360, 134.320, 134.280, 134.240, 134.200, 134.160, 134.120, 134.080, 134.040, 134.000, 133.960, 133.920, 133.880, 133.840, 133.800, 133.760, 133.720, 133.680, 133.640, 133.600, 133.560, 133.520, 133.480, 133.440, 133.400, 133.360, 133.320, 133.280, 133.240, 133.200, 133.160, 133.120, 133.080, 133.040, 133.000, 132.960, 132.920, 132.880, 132.840, 132.800, 132.760, 132.720, 132.680, 132.640, 132.600, 132.560, 132.520, 132.480, 132.440, 132.400, 132.360, 132.320, 132.280, 132.240, 132.200, 132.160, 132.120, 132.080, 132.040, 132.000, 131.960, 131.920, 131.880, 131.840, 131.800, 131.760, 131.720, 131.680, 131.640, 131.600, 131.560, 131.520, 131.480, 131.440, 131.400, 131.360, 131.320, 131.280, 131.240, 131.200, 131.160, 131.120, 131.080, 131.040, 131.000, 130.960, 130.920, 130.880, 130.840, 130.800, 130.760, 130.720, 130.680, 130.640,

Compound 4i

▼ ¹H-NMR (CDCl₃, 400 MHz)

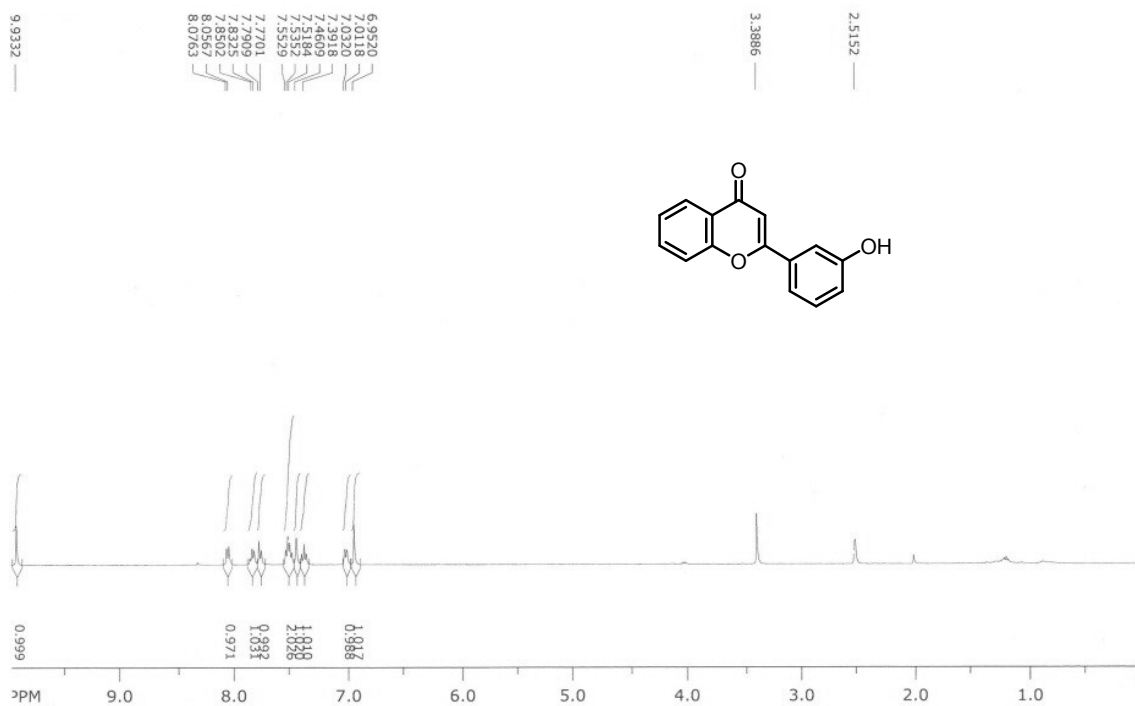


▼ ¹³C-NMR (CDCl₃, 125 MHz)

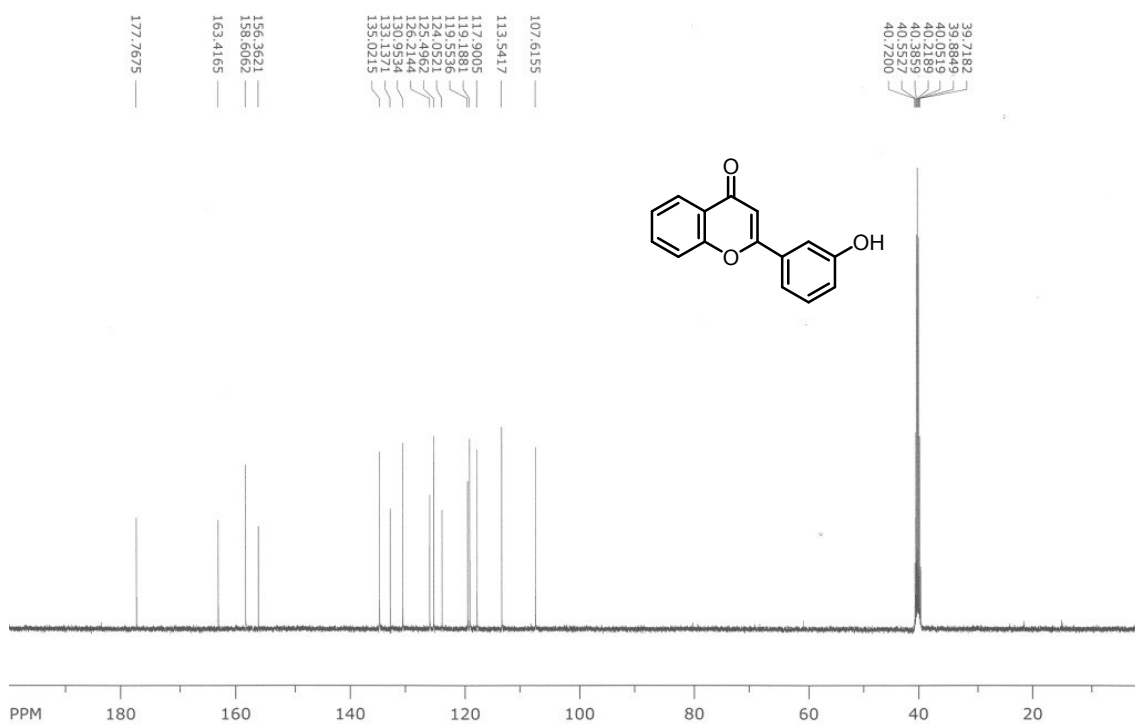


Compound 4j

▼ ¹H-NMR (DMSO-d₆, 400 MHz)

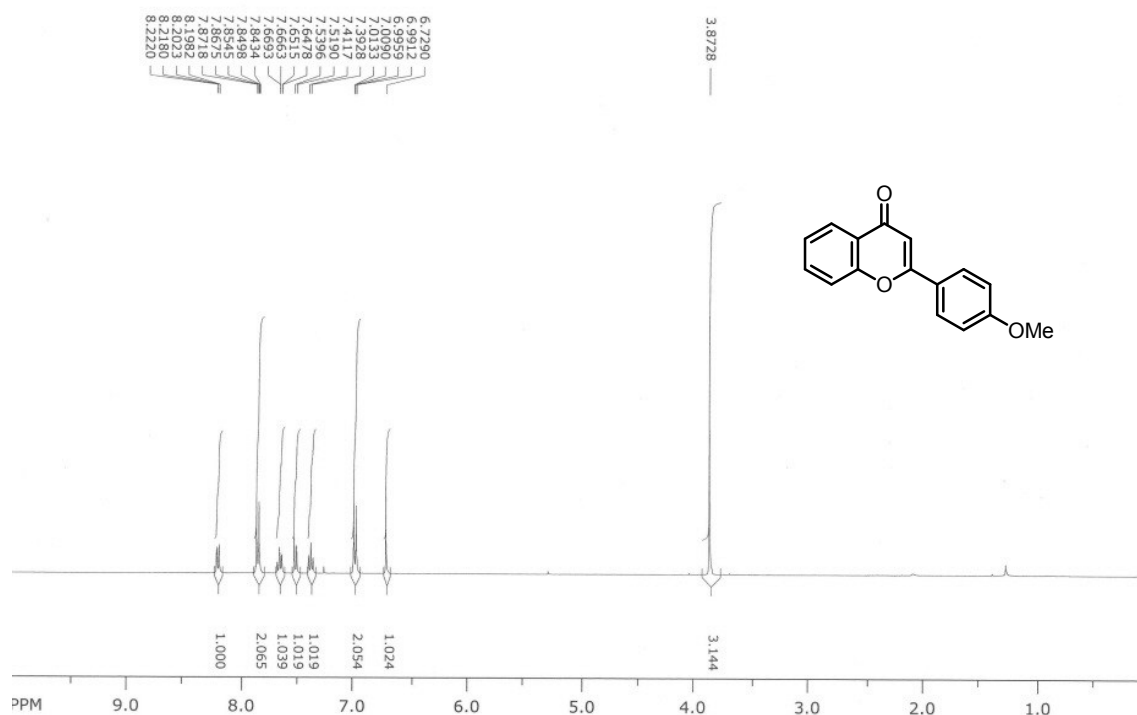


▼ ¹³C-NMR (DMSO-d₆, 125 MHz)

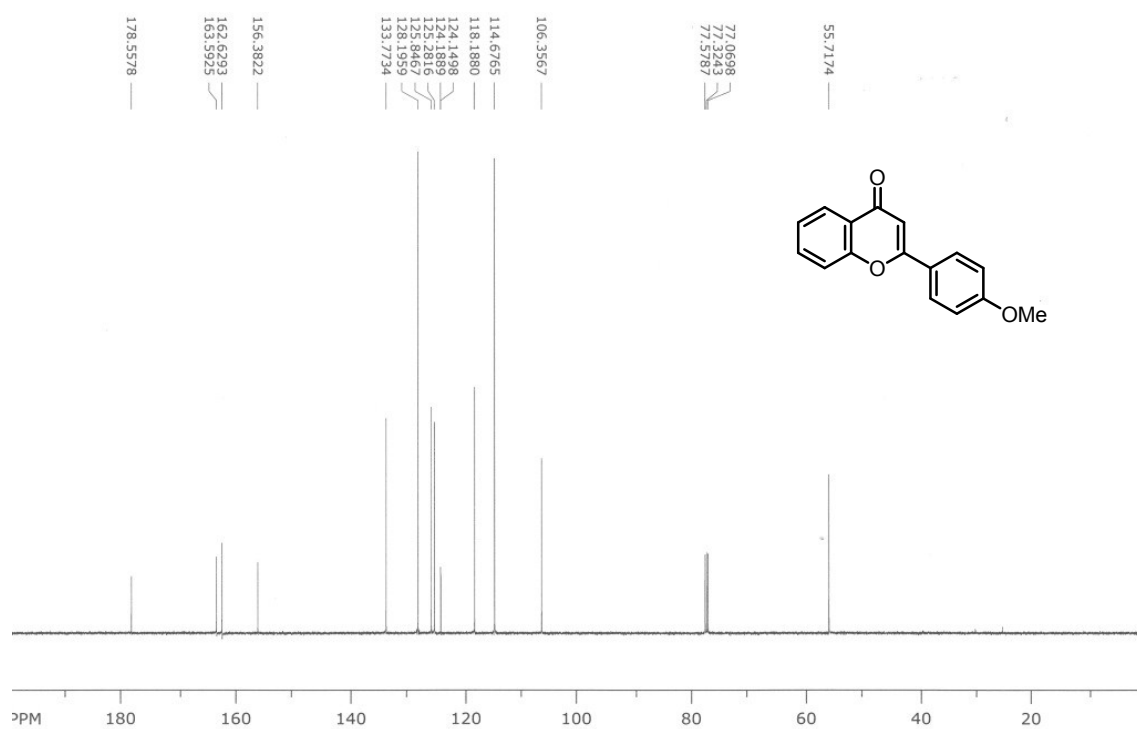


Compound 4k

▼ ¹H-NMR (CDCl₃, 400 MHz)

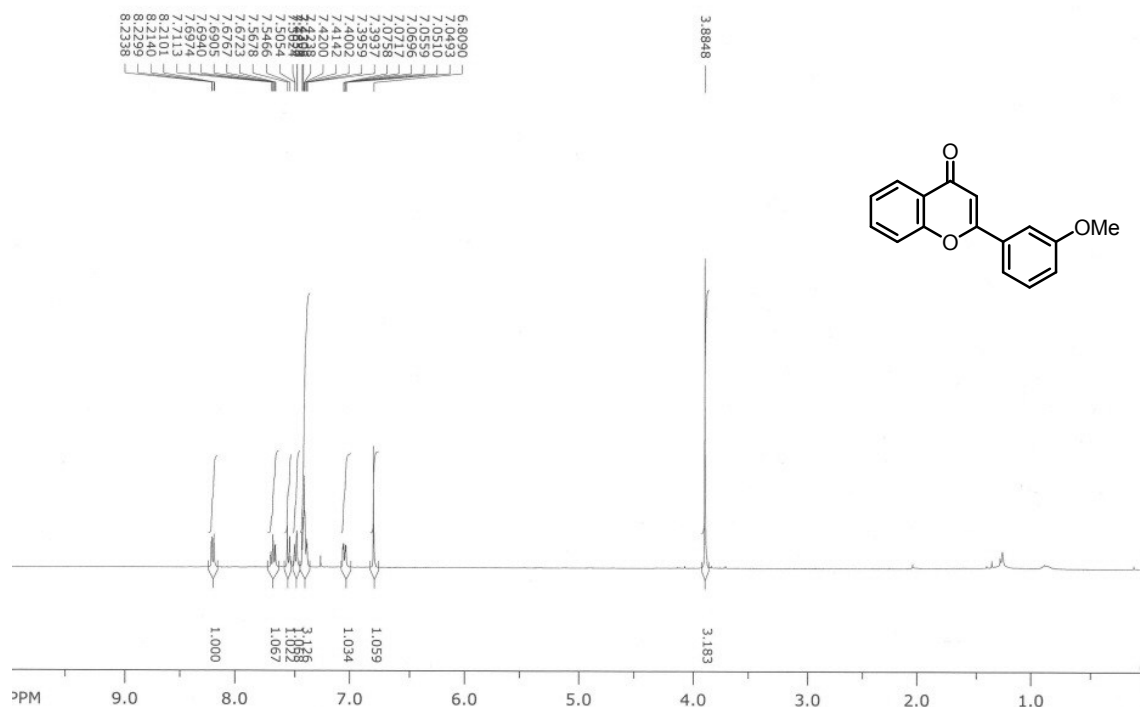


▼ ¹³C-NMR (CDCl₃, 125 MHz)

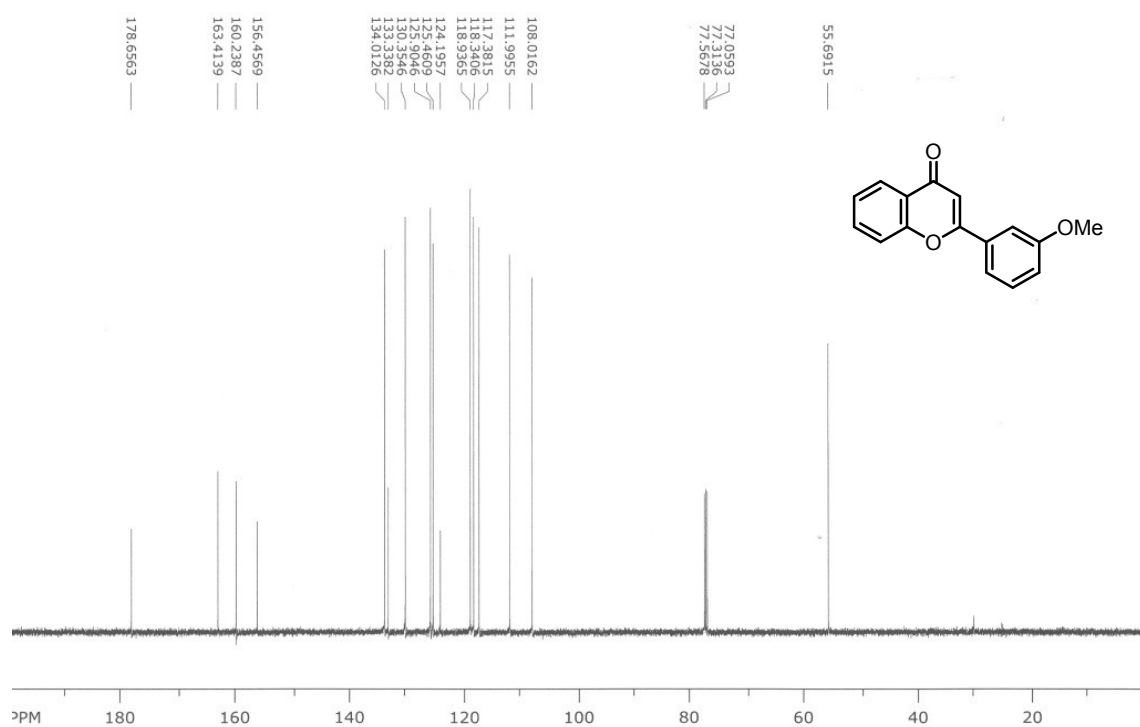


Compound 4l

▼ ¹H-NMR (CDCl₃, 400 MHz)

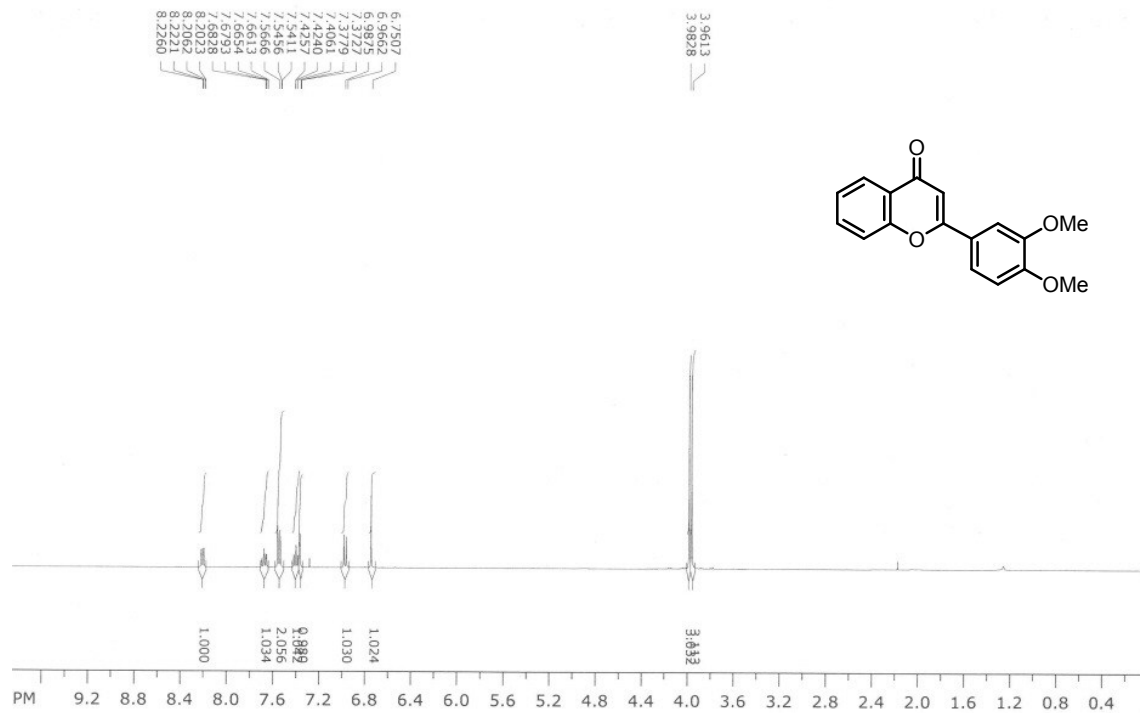


▼ ¹³C-NMR (CDCl₃, 125 MHz)

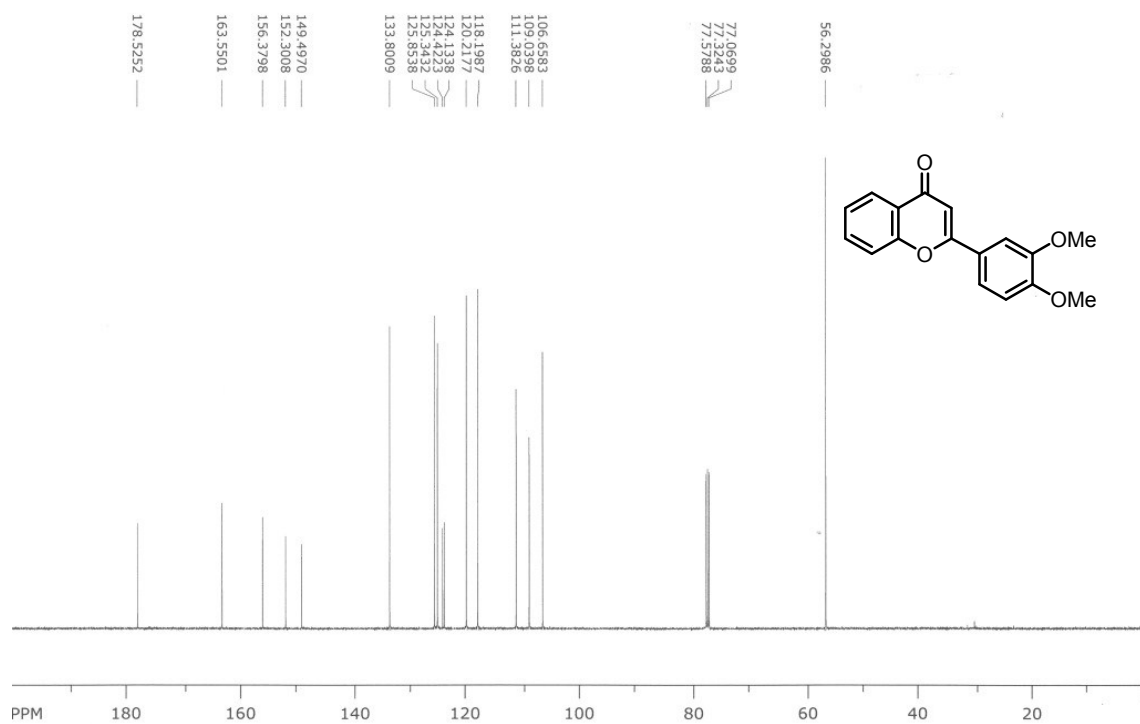


Compound 4m

▼ ¹H-NMR (CDCl₃, 400 MHz)

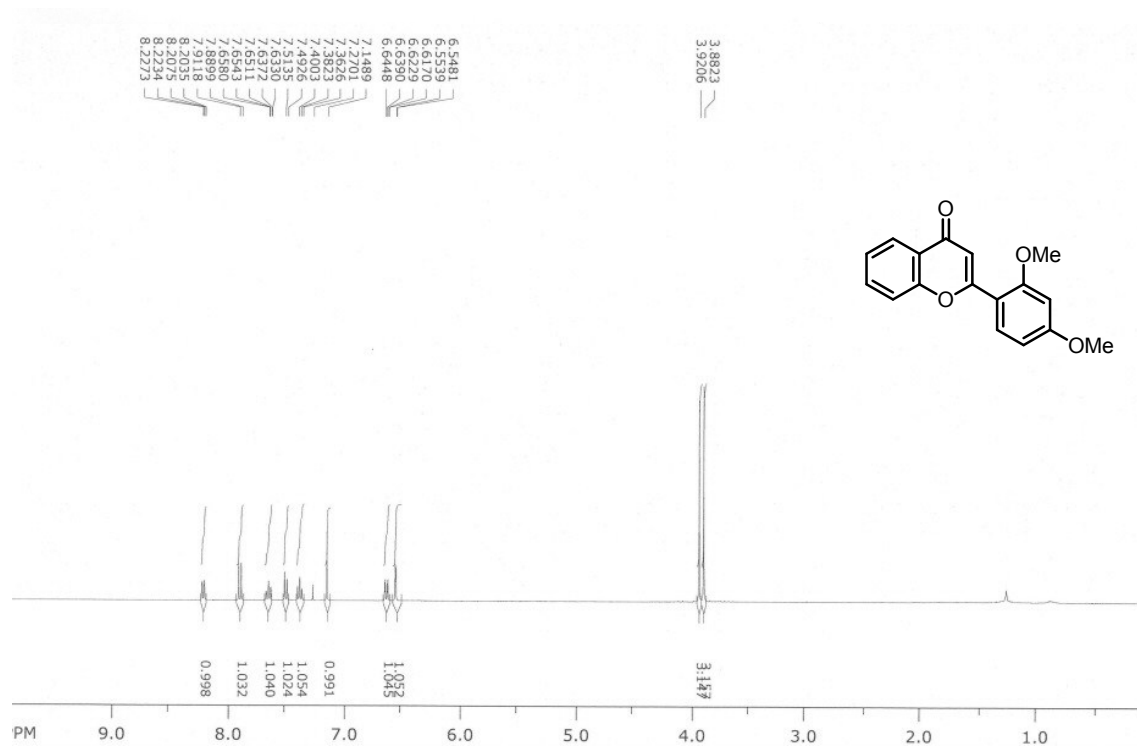


▼ ¹³C-NMR (CDCl₃, 125 MHz)

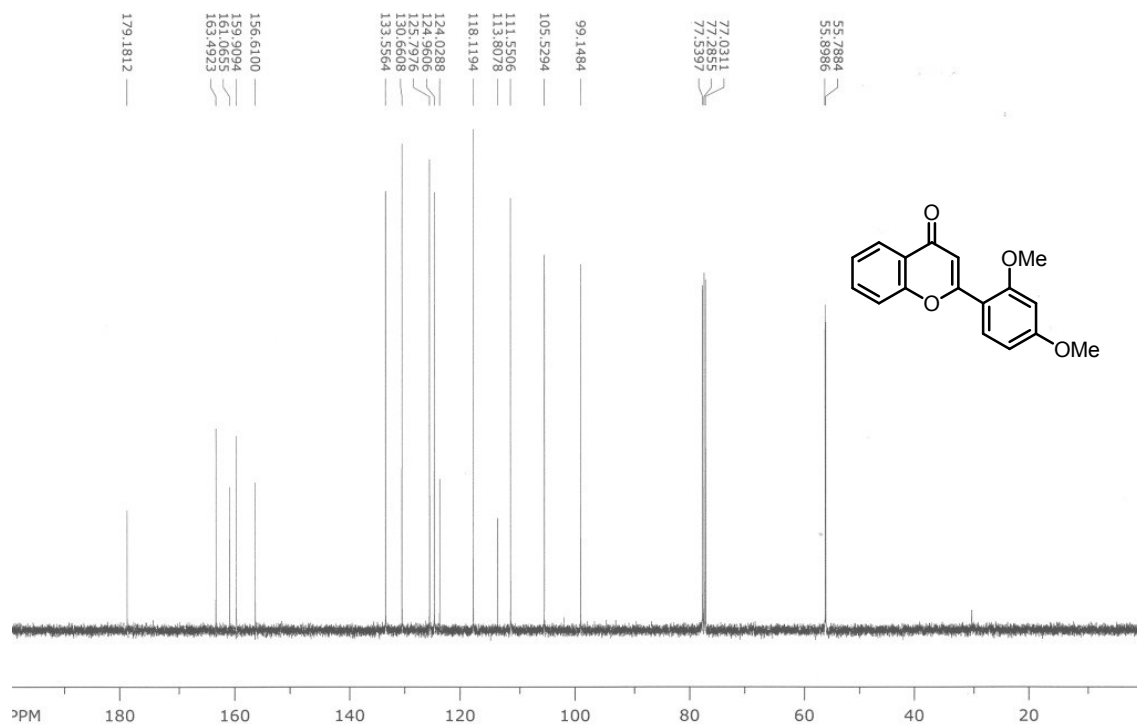


Compound 4n

▼ ¹H-NMR (CDCl₃, 400 MHz)



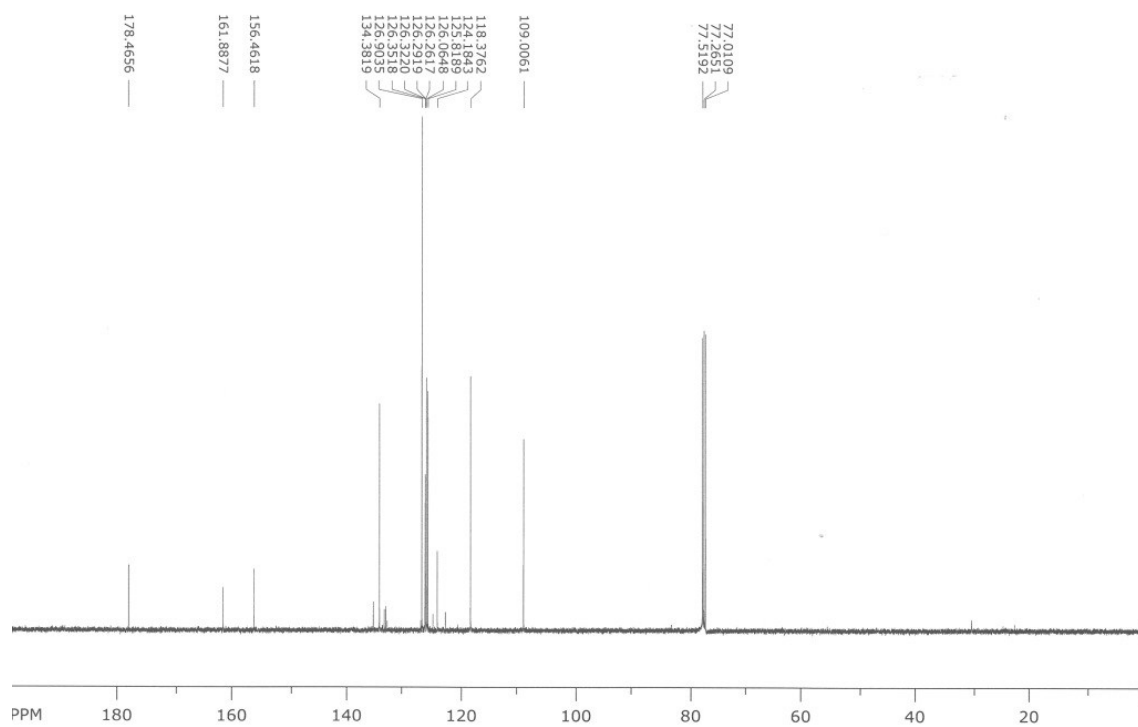
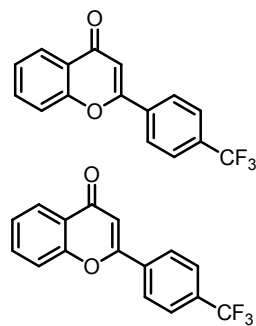
▼ ¹³C-NMR (CDCl₃, 125 MHz)



Compound 4o

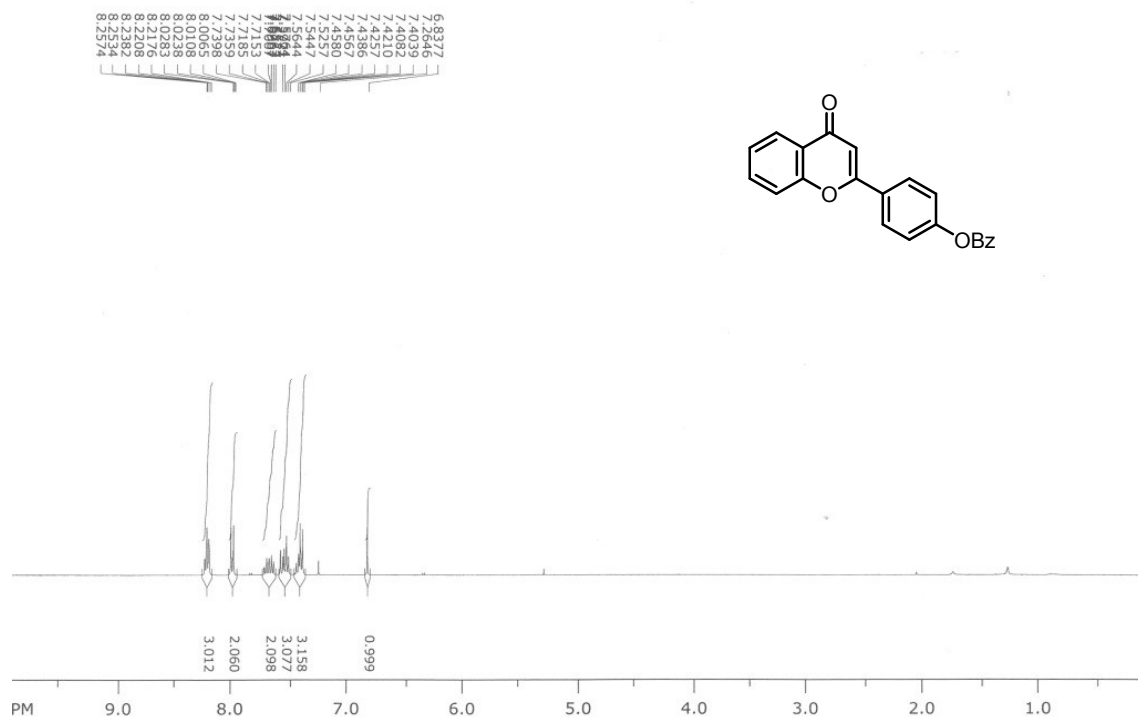
▼ ¹H-NMR (CDCl₃, 400 MHz)

▼ ¹³C-NMR (CDCl₃, 125 MHz)

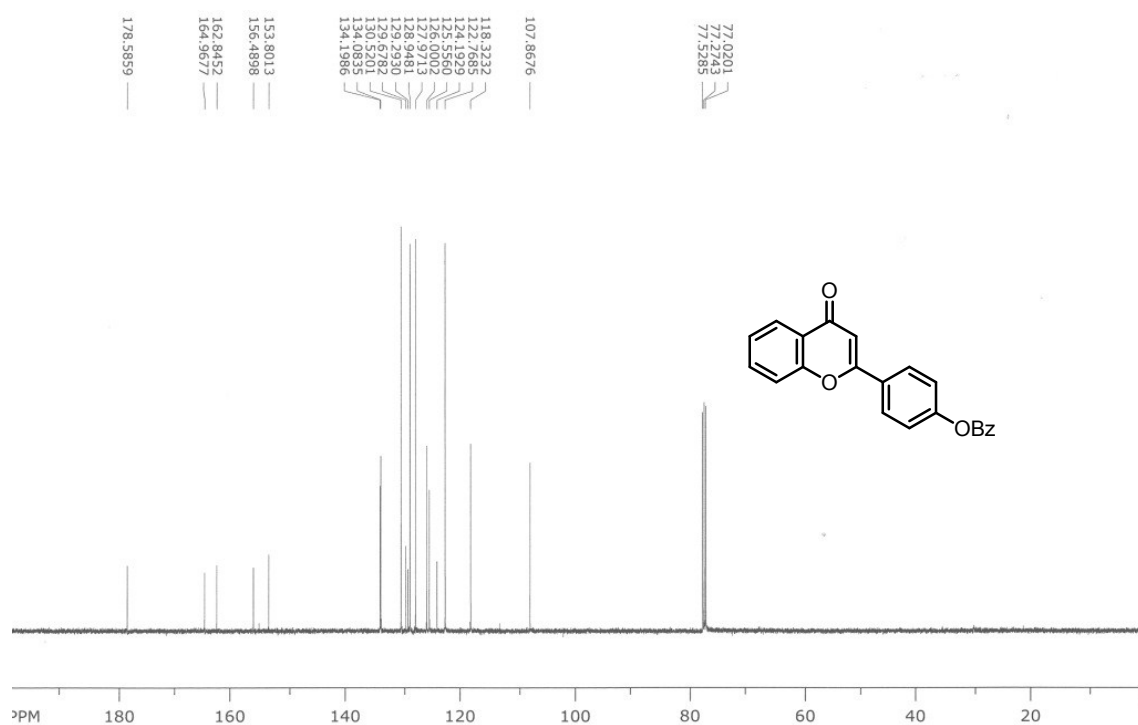


Compound 4p

▼ ¹H-NMR (CDCl₃, 400 MHz)

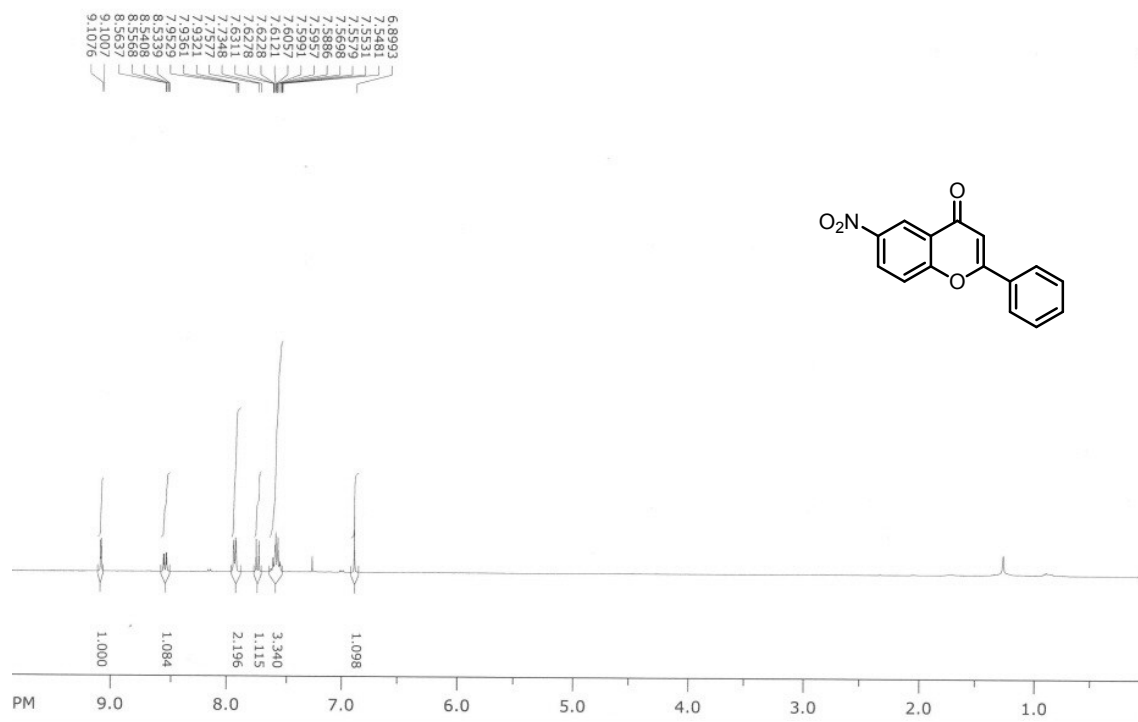


▼ ¹³C-NMR (CDCl₃, 100 MHz)

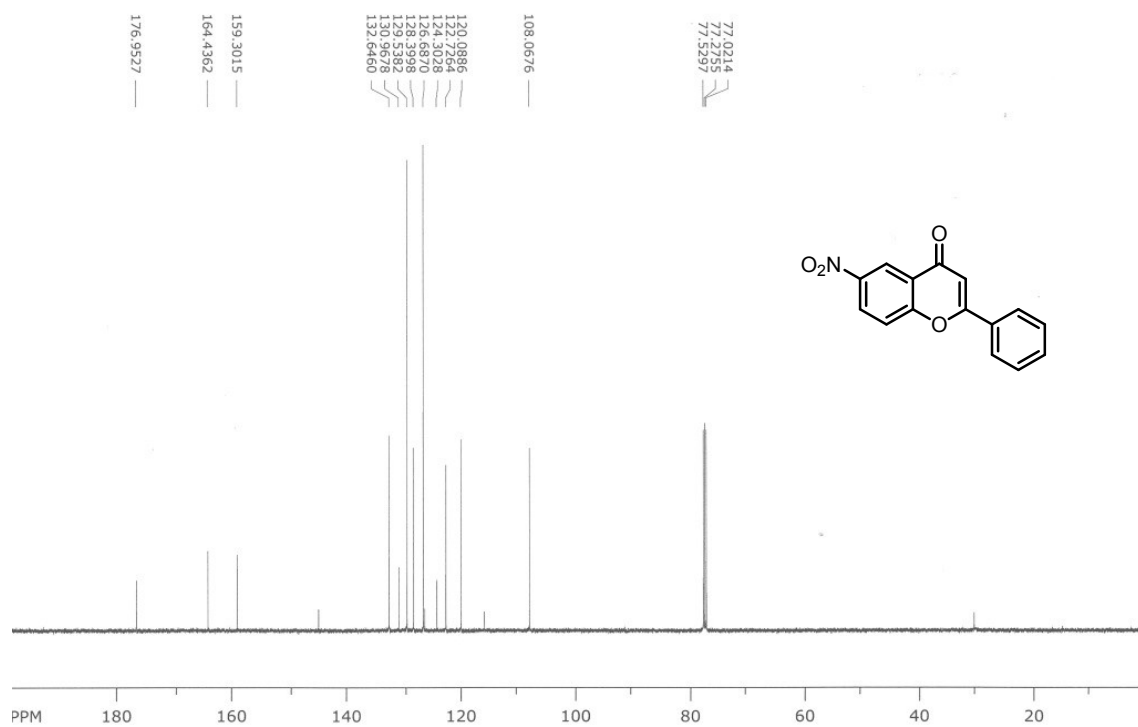


Compound 4q

▼ ¹H-NMR (CDCl₃, 400 MHz)

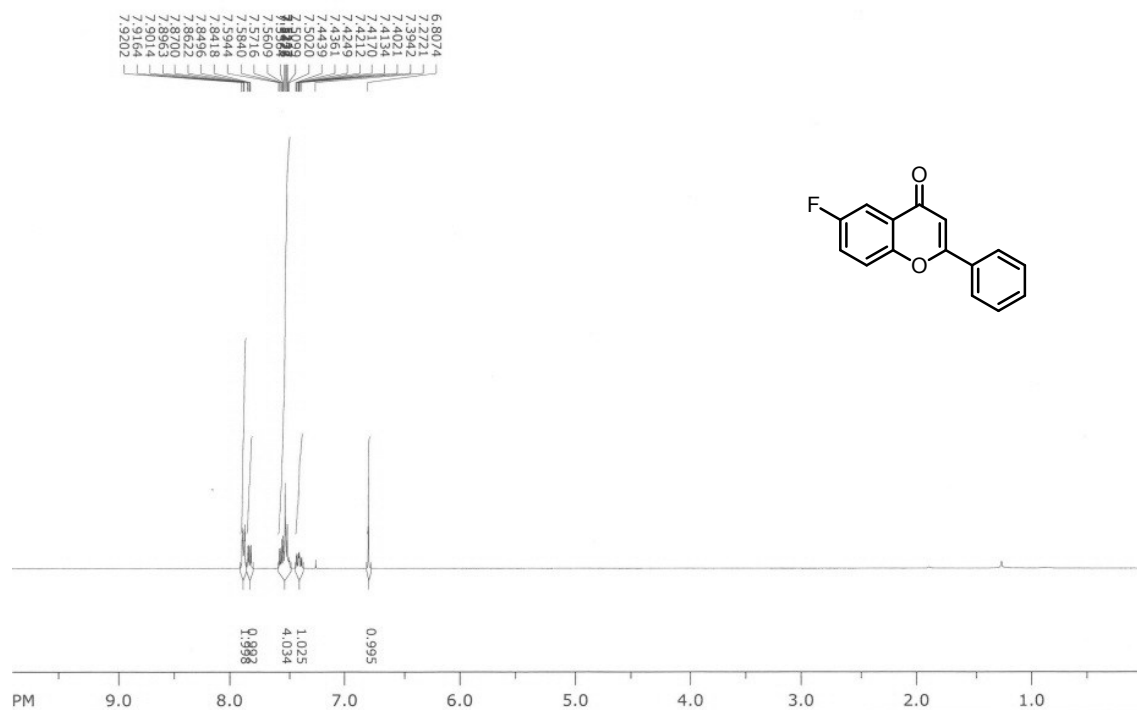


▼ ¹³C-NMR (CDCl₃, 125 MHz)

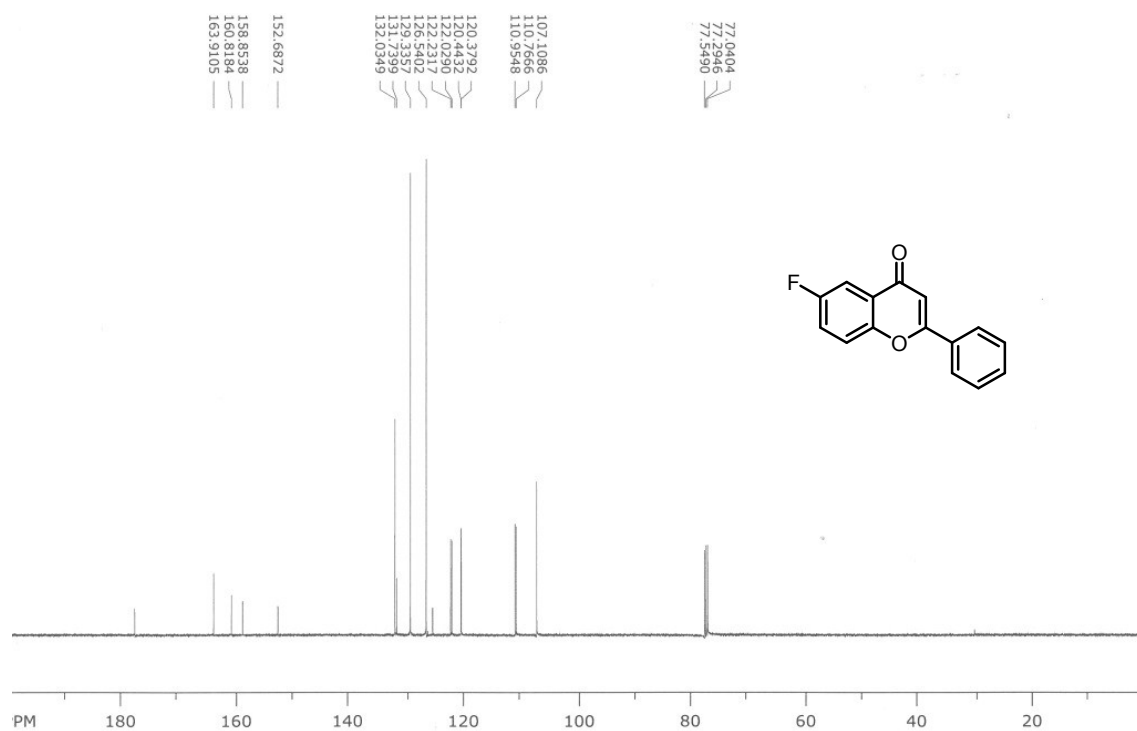


Compound 4r

▼ ¹H-NMR (CDCl₃, 400 MHz)

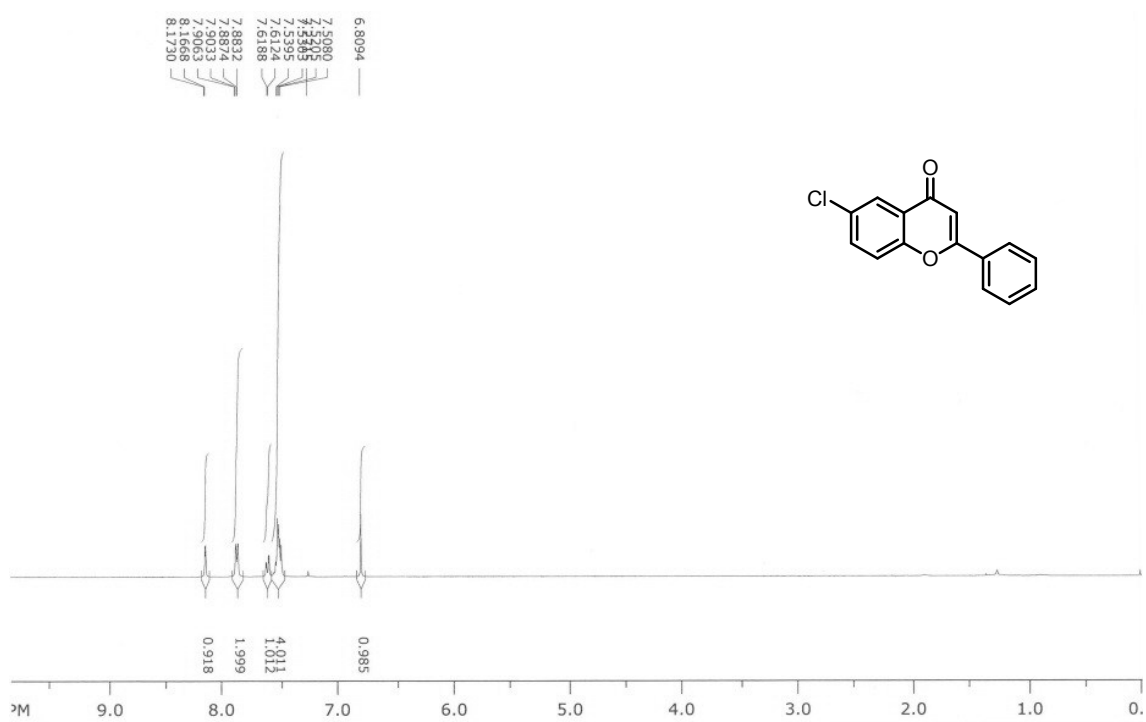


▼ ¹³C-NMR (CDCl₃, 125 MHz)

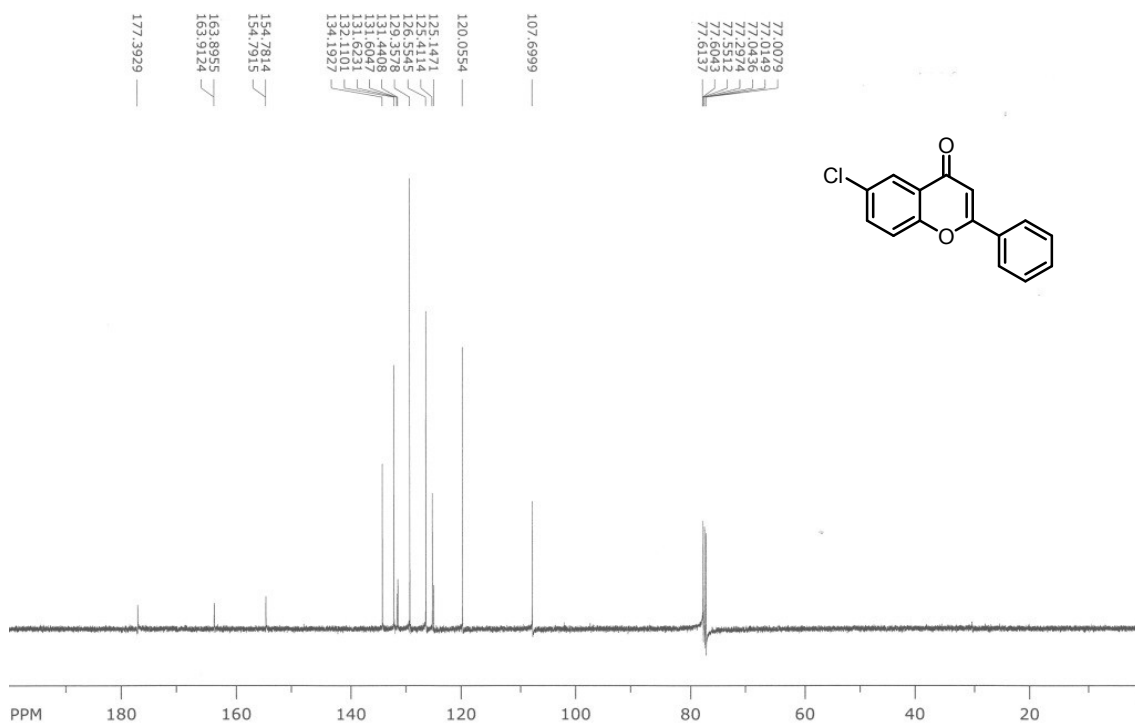


Compound 4s

▼ ¹H-NMR (CDCl₃, 400 MHz)

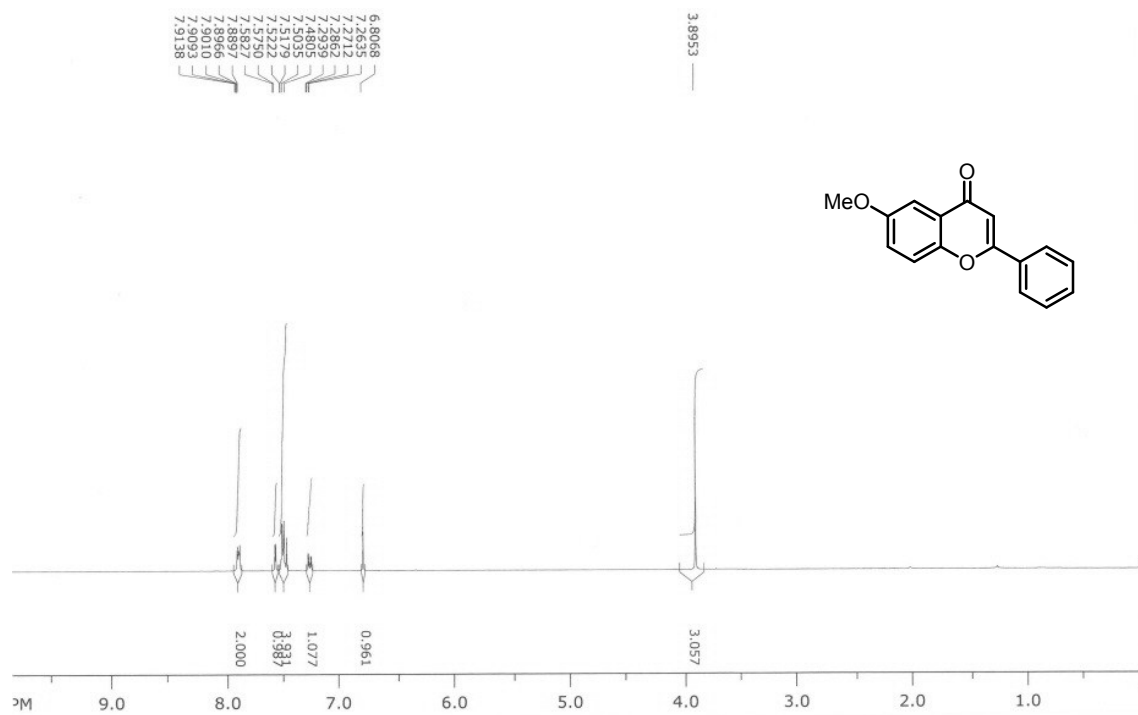


▼ ¹³C-NMR (CDCl₃, 125 MHz)

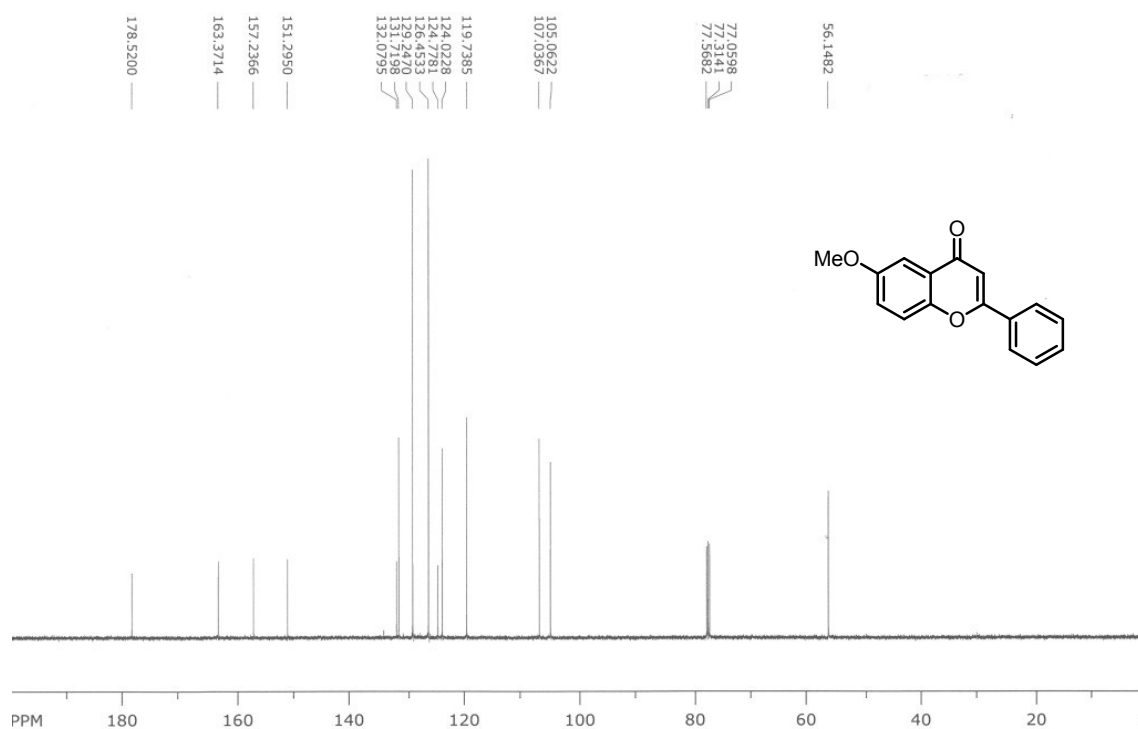


Compound 4t

▼ ¹H-NMR (CDCl₃, 400 MHz)

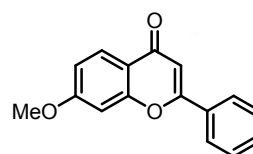
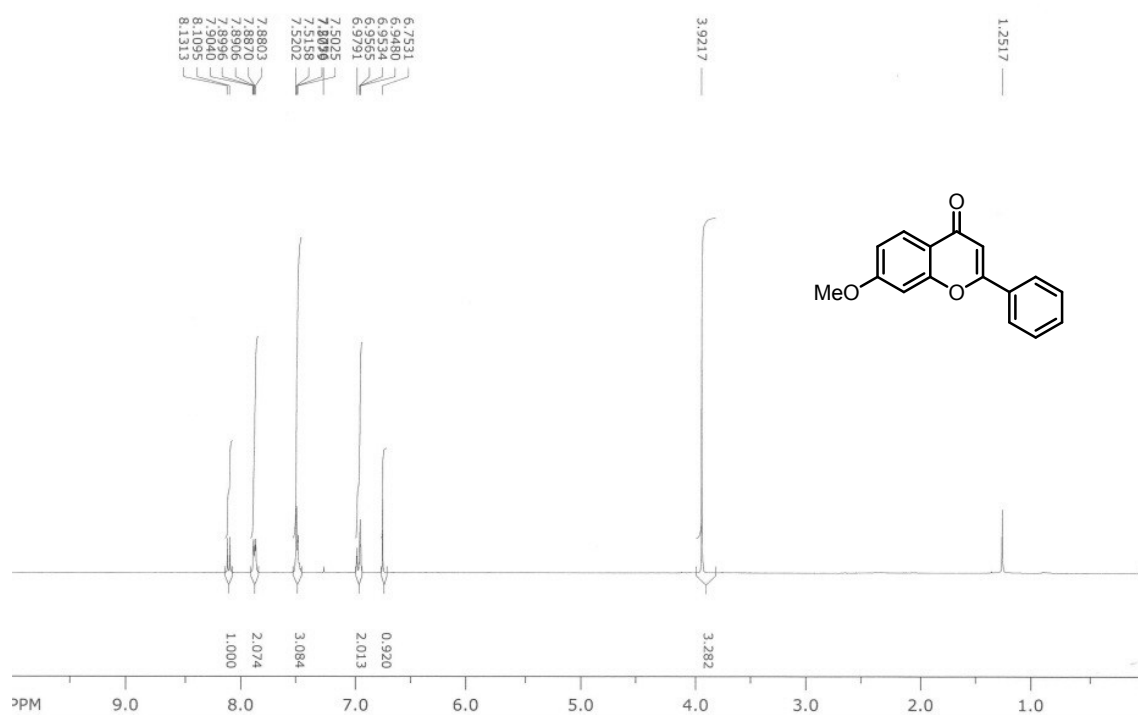


▼ ¹³C-NMR (CDCl₃, 125 MHz)

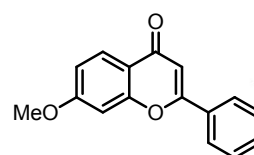
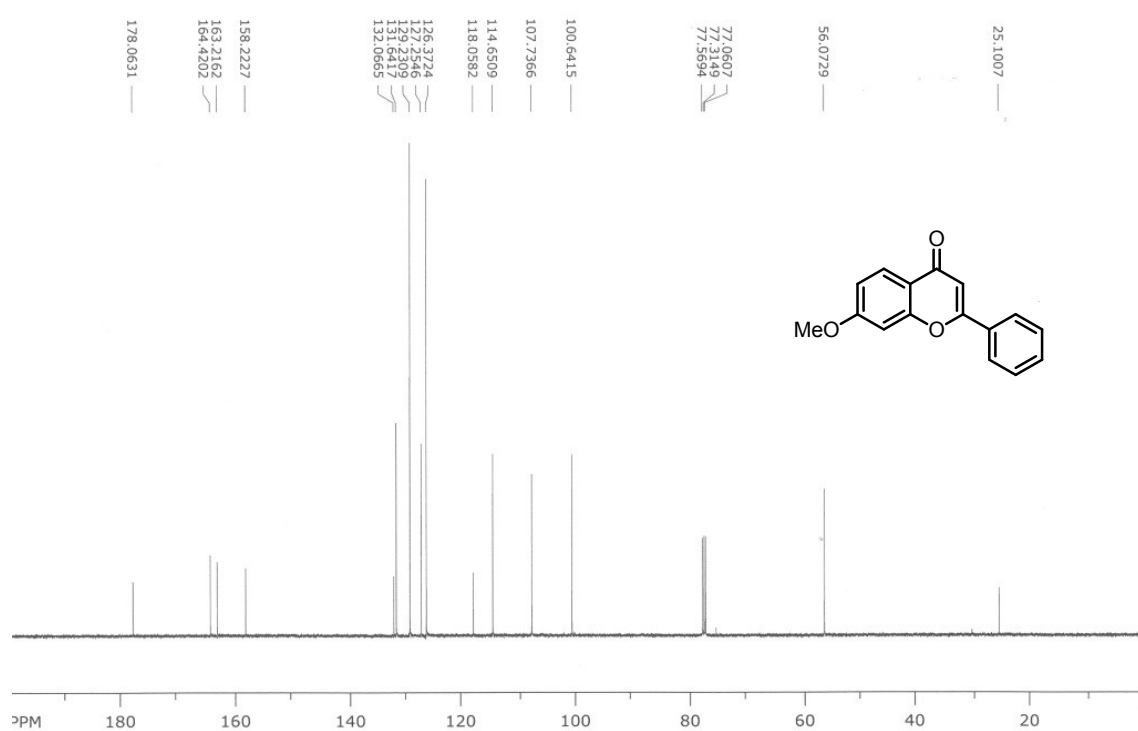


Compound 4u

▼ ¹H-NMR (CDCl₃, 400 MHz)

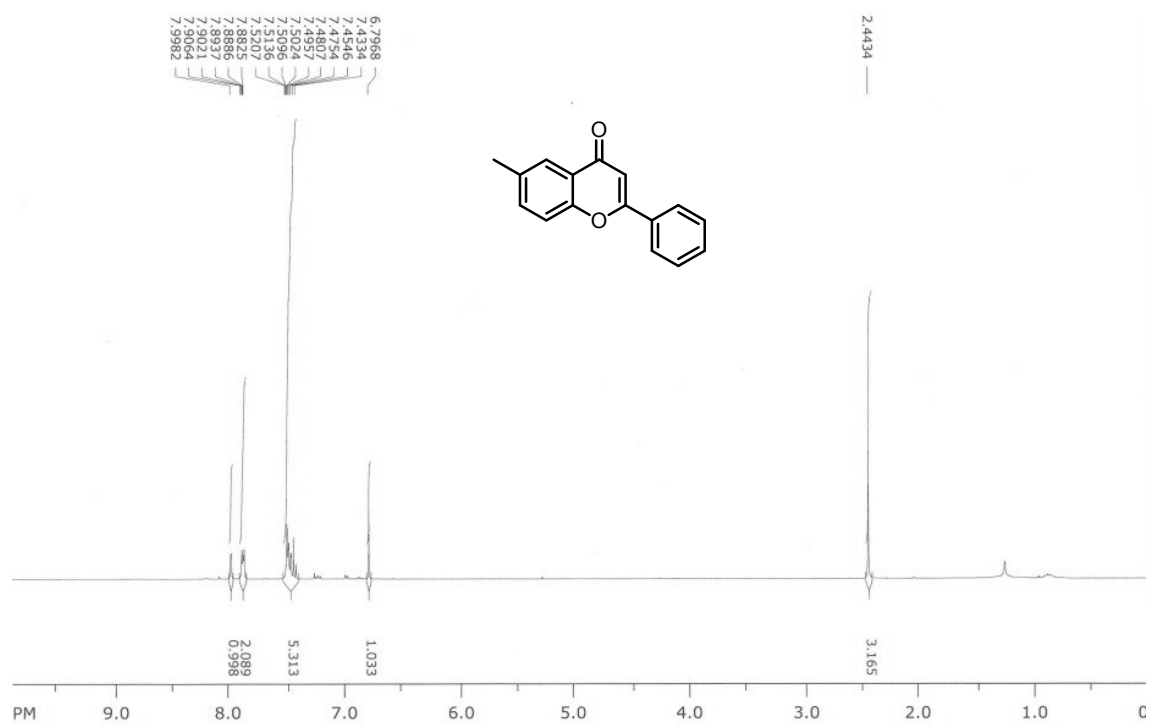


▼ ¹³C-NMR (CDCl₃, 125 MHz)

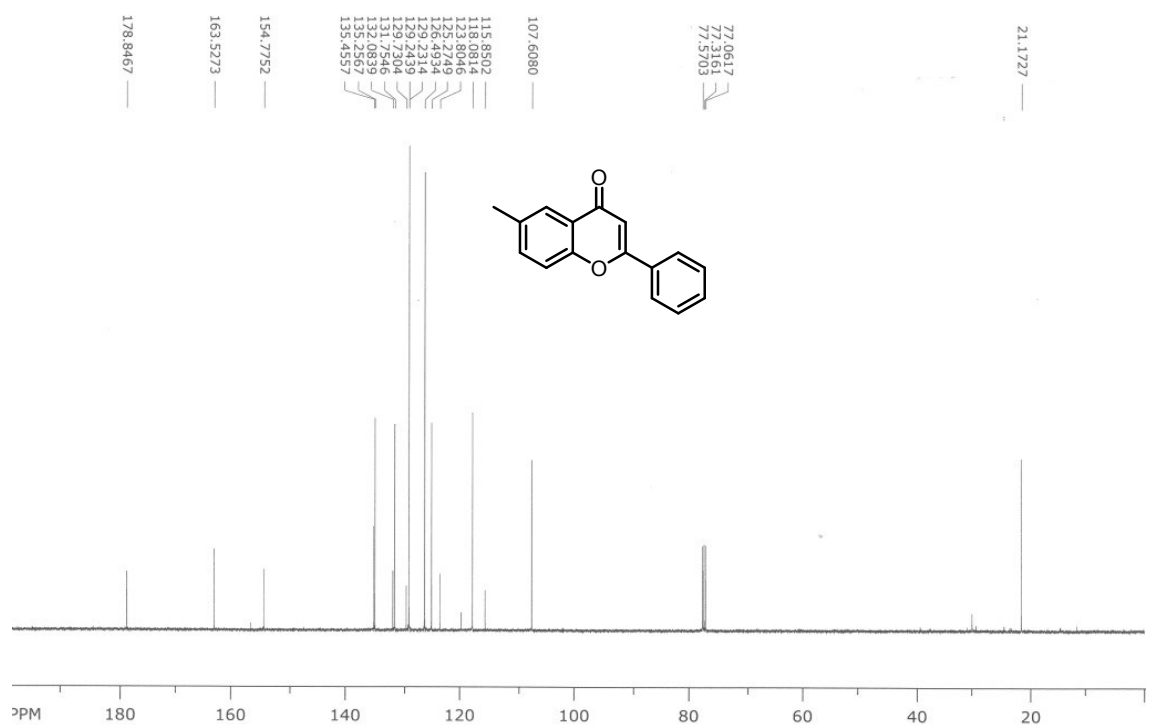


Compound 4v

▼ ¹H-NMR (CDCl₃, 400 MHz)

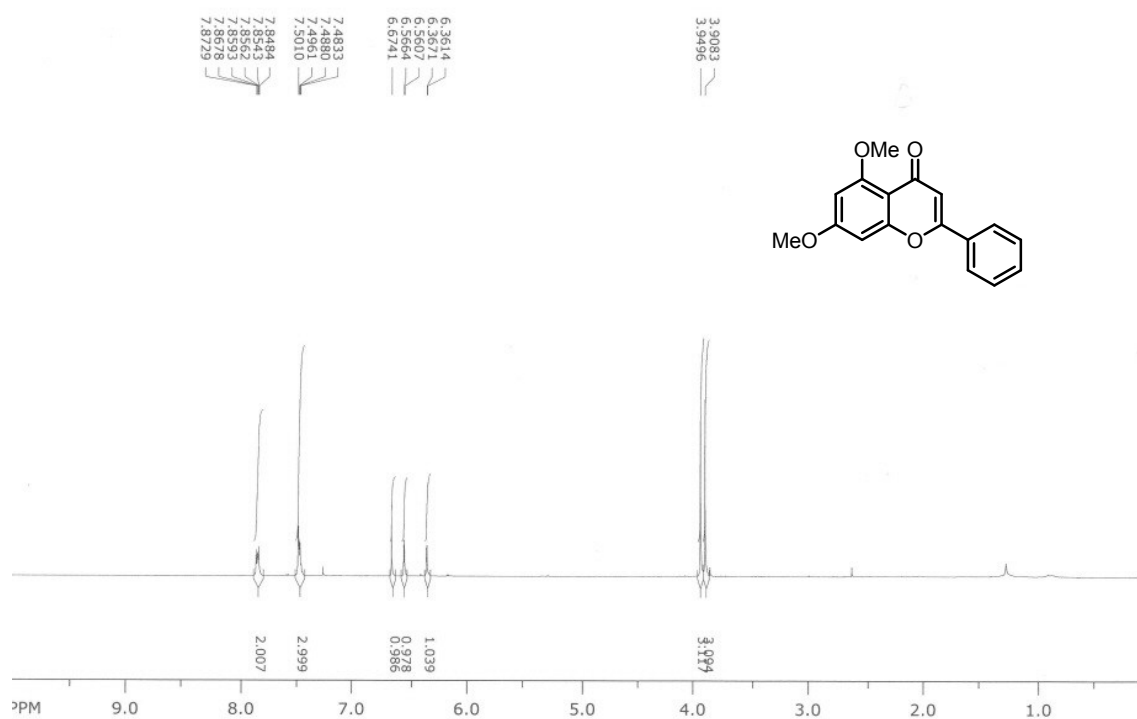


▼ ¹³C-NMR (CDCl₃, 125 MHz)

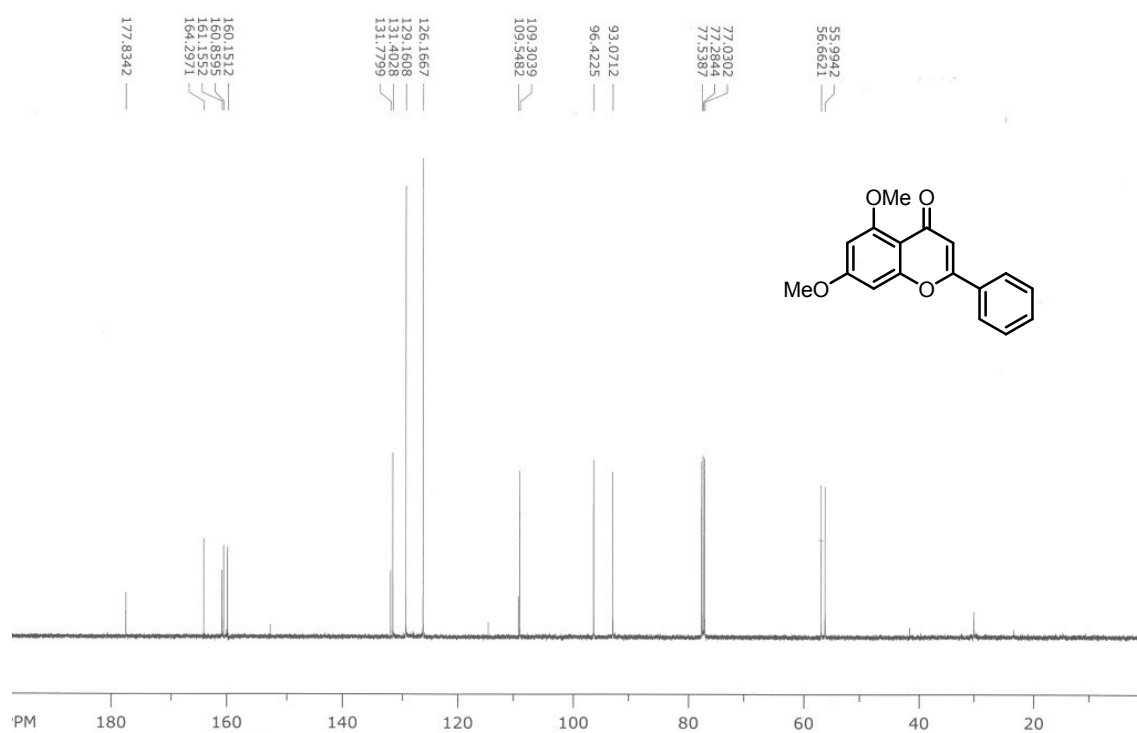


Compound 4w

▼ ¹H-NMR (CDCl₃, 400 MHz)



▼ ¹³C-NMR (CDCl₃, 125 MHz)

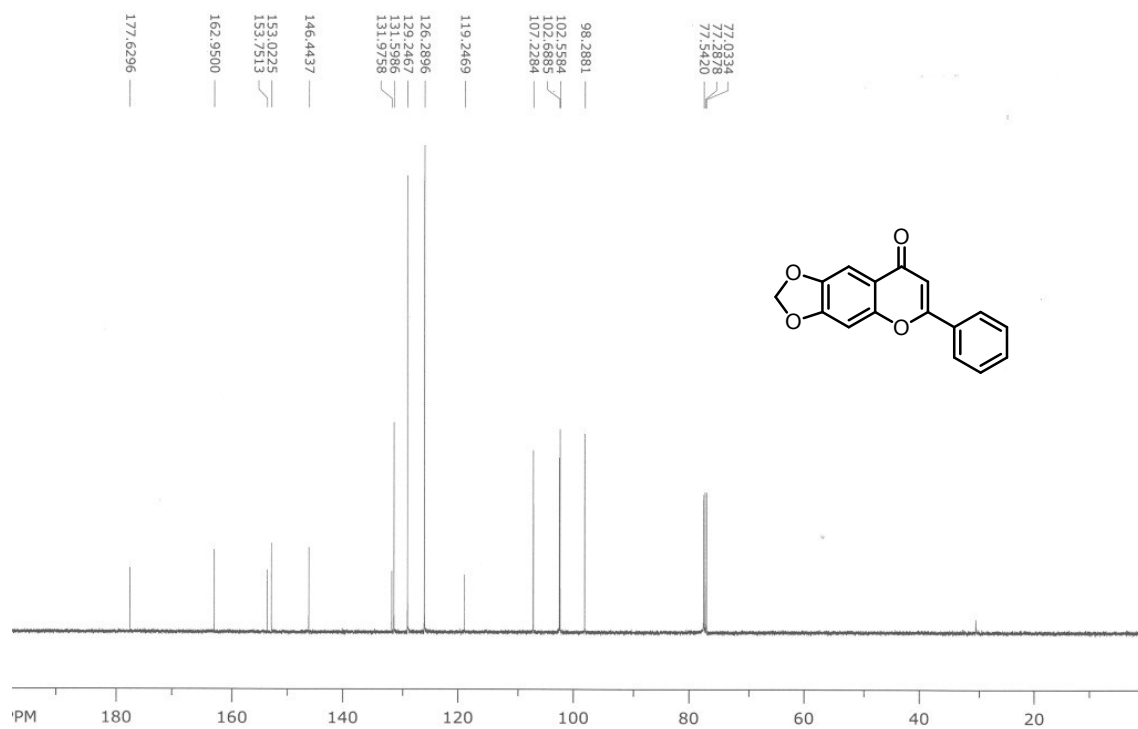


Compound 4x

▼ ¹H-NMR (CDCl₃, 400 MHz)

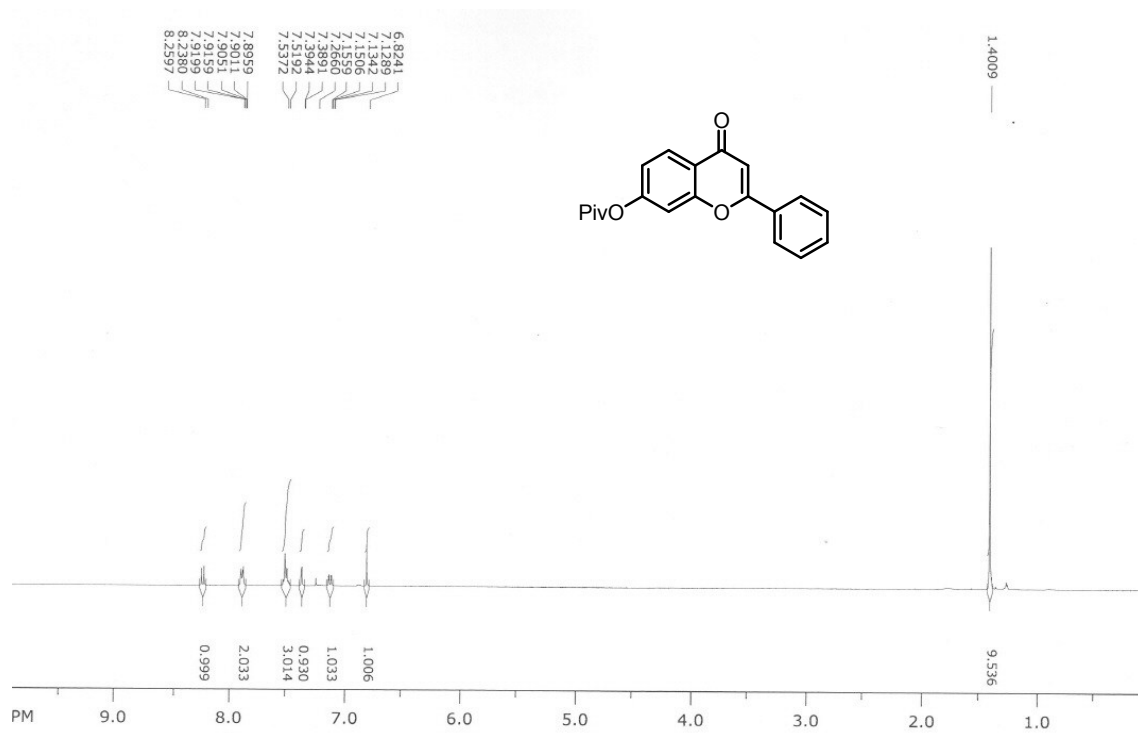


▼ ¹³C-NMR (CDCl₃, 125 MHz)

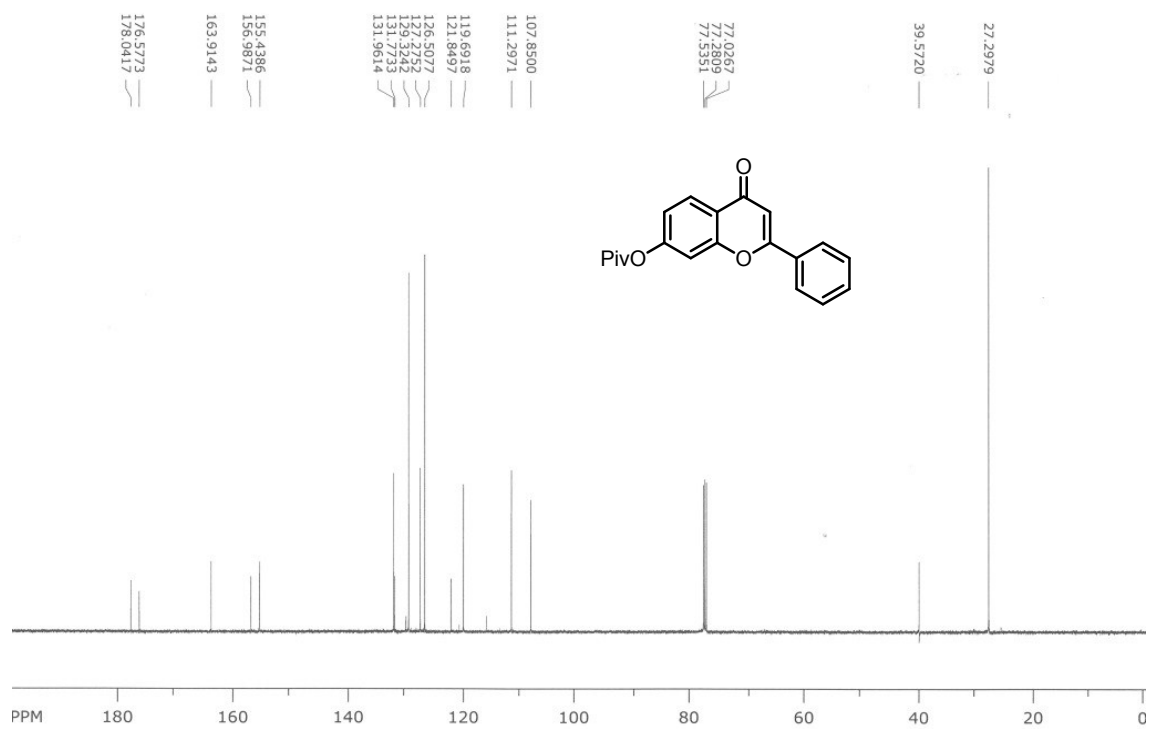


Compound 4y

▼ ¹H-NMR (CDCl₃, 400 MHz)

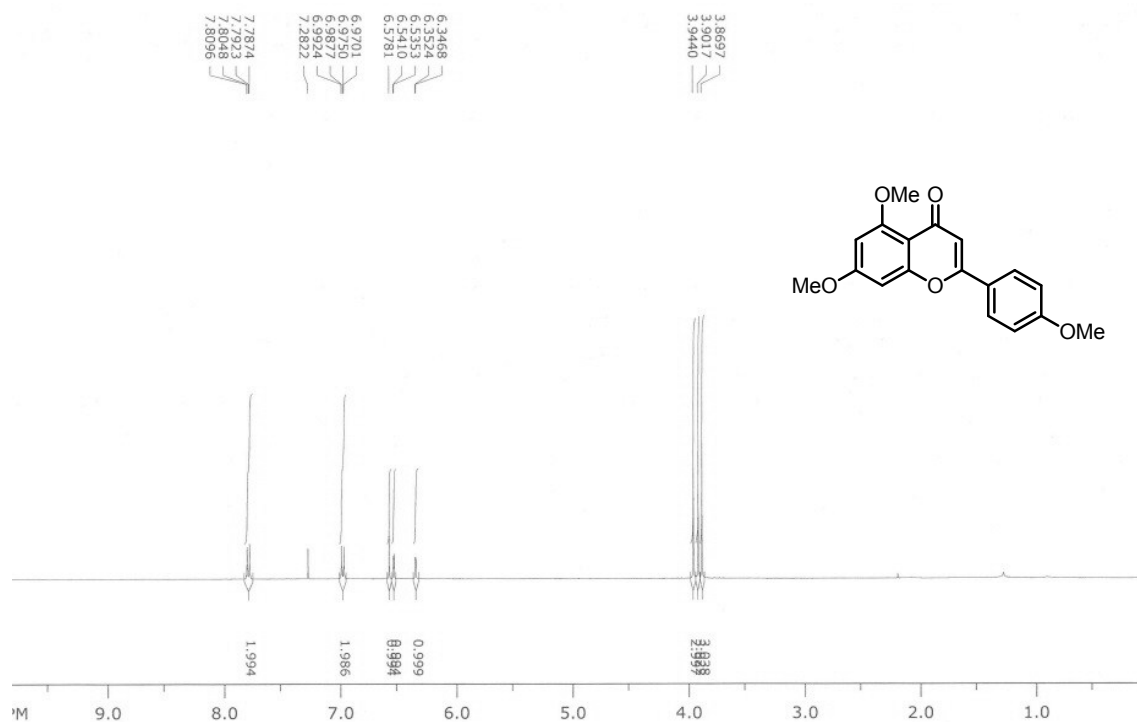


▼ ¹³C-NMR (CDCl₃, 125 MHz)

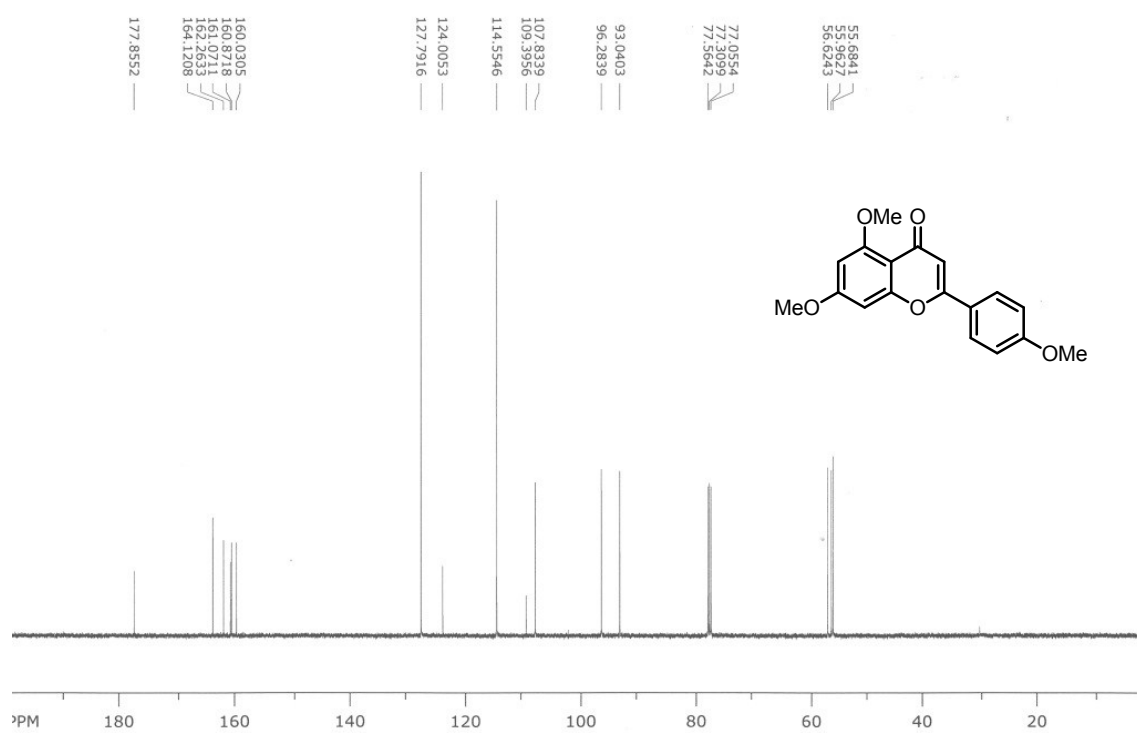


Compound 7

▼ ¹H-NMR (CDCl₃, 400 MHz)

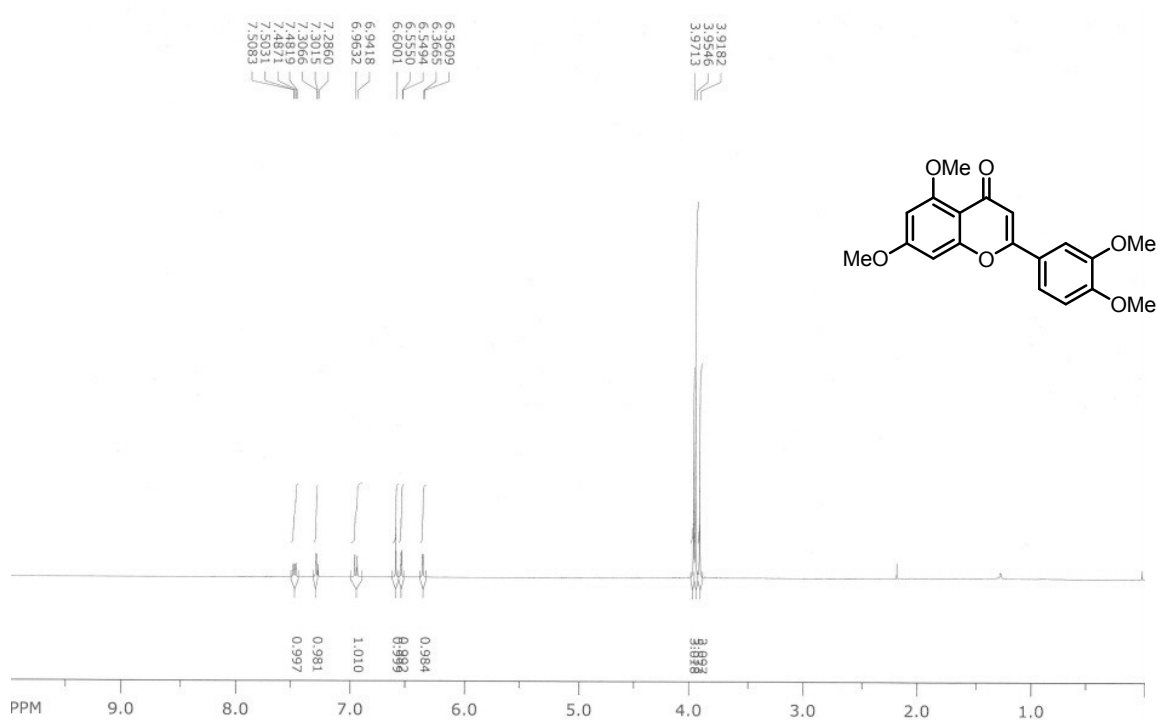


▼ ¹³C-NMR (CDCl₃, 100 MHz)



Compound 9

▼ ¹H-NMR (CDCl₃, 400 MHz)



▼ ¹³C-NMR (CDCl₃, 100 MHz)

