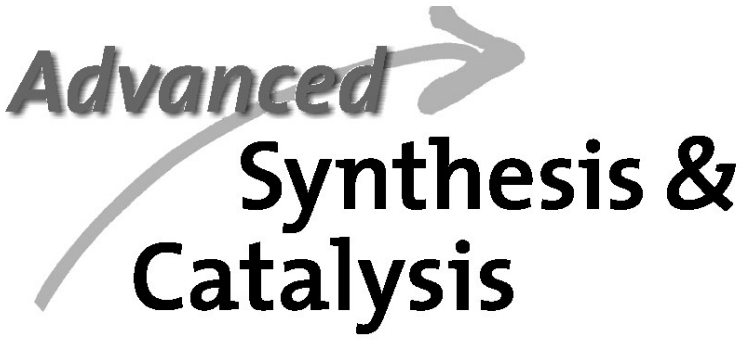


Supporting Information

Supporting Information For

A Selective Transformation of Flavanones to 3-Bromoflavones and Flavones Under Microwave Irradiation

Zhongzhen Zhou, Peiliang Zhao, Wei Huang, and Guangfu Yang *

Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan, 430079, P. R. China,
Fax: *+ 86(27) 67867141*
E-mail: *gfyang@mail.ccnu.edu.cn*

Experimental Section

Melting points were uncorrected. Mass spectroscopy was measured on a Finnigan Trace MS spectrometer. NMR were recorded in CDCl3 on a Varian Mercury 400 spectrometer and resonances are given in ppm (d) relative to TMS. HPLC were performed on an Agilent 1100 MWD instrument. Elementary analyses were performed on a Vario EL III elementary analysis instrument. Microwave irradiation reactions were carried out on a SmithsynthesizerTM instrument (Fig.1)

Fig.1 Microwave Reactor from Personal Chemistry

Traditional Preparation of Flavone 2 and 3-Bromoflavone 3. NBS (1 mmol) and a catalytic amount of AIBN were added to a solution of flavanone **1** (1 mmol) in anhydrous CCl_4 (5 mL). The resulting solution was refluxed and traced by TLC. After refluxing for 12 h, the reaction mixture was filtered. The filtrate was condensed under reduced pressure and the residue was chromatographed to give flavone **2** and a samll amount of 3-bromoflavone **3**.

Microwave irradiation Preparation of Flavone 2. NBS (1 mmol) and a catalytic amount of AIBN were added to a solution of flavanone **1** (1 mmol) in anhydrous CCl_4 (5 mL) in a microwave tube. The sealed tube was placed in a SmithsynthesizerTM and irradiated at 100 °C for 10 min. The resulting mixture was filtered. The filtrate was condensed under reduced pressure and the residue was chromatographed or recrystallized to give flavone **2**.

Traditional Preparation of 3-Bromoflavone 3. NBS (3 mmol) and a catalytic amount of AIBN were added to a solution of flavanone **1** (1 mmol) in anhydrous CCl_4 (5 mL). The resulting solution was refluxed and traced by TLC. After refluxing for 24 h, the reaction mixture was filtered. The filtrate was condensed under reduced pressure and the residue was chromatographed to give 3-bromoflavone **3** and a small amount of flavone **2**.

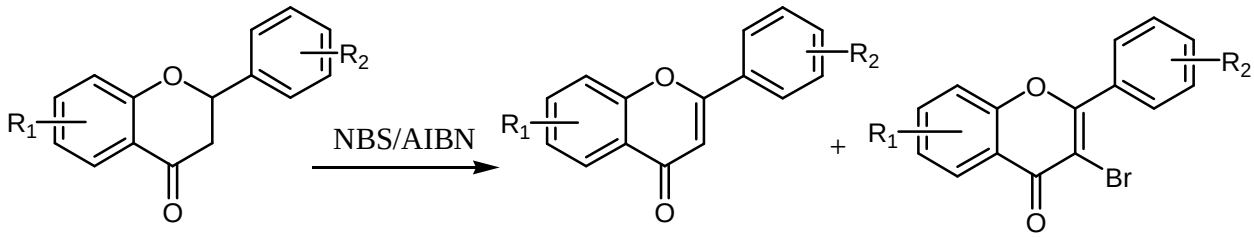
Solvent-free Microwave irradiation Preparation of 3-Bromoflavone 3. NBS powder (3 mmol), a catalytic amount of AIBN and flavanone **1** powder (1 mmol) were mixed and added into a microwave tube. The sealed tube was placed in a SmithsynthesizerTM and irradiated at 140 °C for 10 min. The resulting mixture was chromatographed or recrystallized to give 3-bromoflavone **3**.

Table 1 Optimization of Solvent for Synthesis of 2a Under Microwave Irradiation

No.	Flavanone/ NBS	Temperature (°C)	Time (min)	Solvent	Yield (%)[a]
					2a
1	1:1	100	10	CH_2Cl_2	53
2	1:1	100	10	$CHCl_3$	76
3	1:1	100	10	CCl_4	90
4	1:1	100	10	free	0
5	1:1	140	10	free	complex

[a] the yield was measured by HPLC

Table 2 Results of Solvent-Free Synthesis of 2

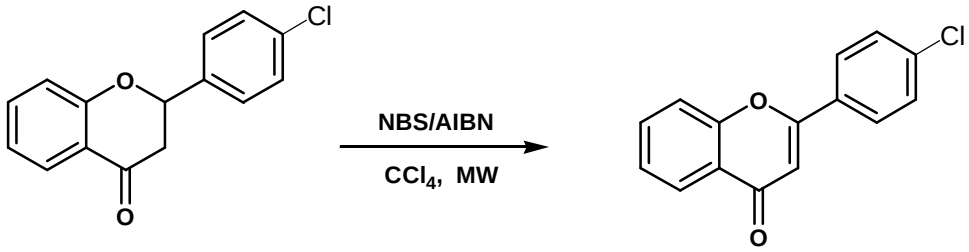


1 2 3

No	(1)/ NBS	R1	R2	P (W)	T(?)	t(min)	Yield (%)[a]		
							1	2	3
1a	1:1	H	H	150 ~ 300	140	10	43	15	41
1b	1:1	H	3’-Cl	150 ~ 300	140	10	56	31	12
1c	1:1	H	4’-Cl	150 ~ 300	140	10	34	25	41
1d	1:1	H	3’-Br	150 ~ 300	140	10	54	24	21
1e	1:1	H	4’-MeO	150 ~ 300	140	10	30	58	11
1f	1:1	7-MeO	H	150 ~ 300	140	10	34	49	17
1g	1:1	6-Cl	H	150 ~ 300	140	10	37	26	38
1h	1:1	7-MeO	4’-Cl	150 ~ 300	140	10	40	55	5

[a] the yield was measured by HPLC

Table 3 Optimization for the bromination of 4'-chloroflavanone

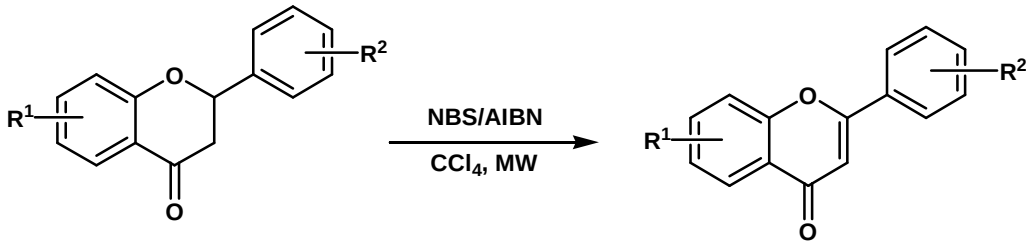


1C 2C

No	Temp. (°C)	Time (min)	Yield (%)[a]
			2c
1	80	10	4
2	90	10	34
3	100	10	96
4	110	10	95
5	120	10	95
6	130	10	95
7	100	5	70
8	100	15	95
9	100	20	96

[a] the yield was measured by HPLC

Table 4 Microwave-assisted Dehydrogenation of Flavanones with NBS



1 2

No	R^1	R^2	Microwave irradiation		Traditional heating	
			Time (min)	Yield (%)[a]	Time (h)	Yield (%)[a]
1	H	H	10	90 (88)	16	65 (61)
2	H	3'-Cl	10	98 (95)	12	74 (70)
3	H	4'-Cl	10	95 (92)	12	79 (74)
4	H	4'-Me	10	73 (69)	12	60 (55)
5	H	3'-Br	10	97 (94)	12	75 (70)
6	H	4'-MeO	10	89 (85)	12	62 (58)
7	7-MeO	H	10	89 (87)	12	65 (62)
8	6-Me	H	10	73 (69)	12	62 (59)
9	6-Cl	H	10	97 (95)	12	64 (60)
10	7-MeO	4'-Cl	10	97 (94)	12	66 (63)

[a] the yield was measured by HPLC; the value in parentheses is the isolated yield.

Table 5 Optimization of Brominating Reagent for Synthesis of 3a Under Microwave Irradiation

No	Brominating reagent	Flavanone/brominating reagent	Solvent	Yield (%)[a]	
				2a	**3a**
1	$CuBr_2$	1:4	CH_2Cl_2	0	0
2	$CuBr_2$	1:2	CH_2Cl_2	0	0
3	PHPB	1:1	CH_2Cl_2	1	41
4	PHPB	1:2	CH_2Cl_2	2	30
5	PHPB	1:3	CH_2Cl_2	1	21
6	TCH	1:1	CH_2Cl_2	0	0
7	TCH	1:2	CH_2Cl_2	0	0
8	TCH	1:3	CH_2Cl_2	0	0
9	NBS/AIBN	1:1	CH_2Cl_2	55	4
10	NBS/AIBN	1:2	CH_2Cl_2	64	30
11	NBS/AIBN	1:3	CH_2Cl_2	36	58
12	Br_2/Py	1:1	CH_2Cl_2	0	0
13	Br_2/Py	1:2	CH_2Cl_2	0	0

[a] the yield was measured by HPLC

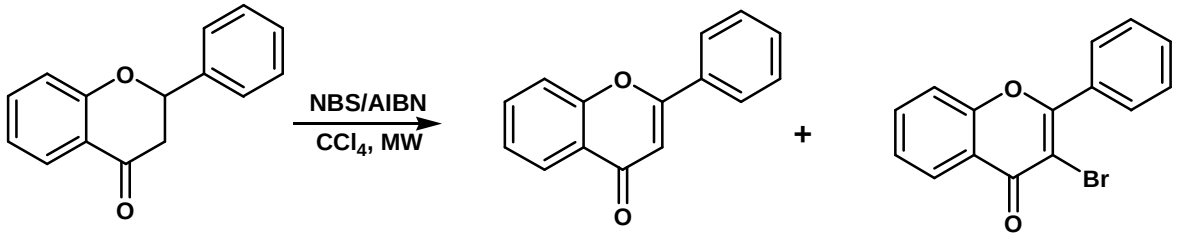
[b] PHPB: pyridinium bromide petromide, TCH: 2,4,4,6-tetroabromo-2,5-cyclohexadienone.

Table 6 Optimization of Solvent for Synthesis of 3a Under Microwave Irradiation

No.	Flavanone/ NBS	Temperature (°C)	Time (min)	Solvent	Yield (%)[a]	
					2a	3a
1	1:3	100	10	CH_2Cl_2	6	54
2	1:3	100	10	$CHCl_3$	4	89
3	1:3	100	10	CCl_4	1	96
4	1:3	140	10	free	0	100

[a] the yield was measured by HPLC

Table 7 Optimization of Temperature and Time for Synthesis of 3a

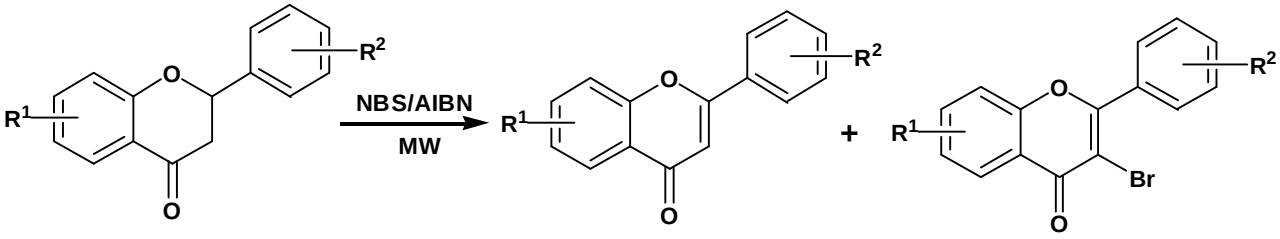


1a **2a** **3a**

No	Temperature	Time (min)	Yield (%)[a]	
			2a	**3a**
1	100	15	100	0
2	120	15	95	4
3	140	15	6	93
4	160	15	10	89
5	140	10	11	89
6	140	25	8	92

[a] the yield was measured by HPLC

Table 8 Microwave-assisted Preparation of 3-Bromoflavone 3



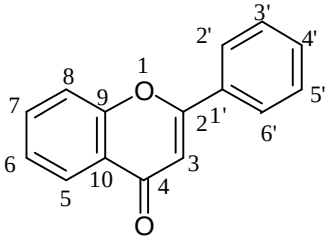
1 **2** **3**

No.	R^1	R^2	Solvent-free Microwave [a]				Conventional Refluxing		
			Temp. (^{0}C)	Time (min)	Yield (%)[b] **2**	**3**	Time (h)	Yield (%)[b] **2**	**3**
1a	H	H	140	10	0	100(98)	24	10	70(65)
1b	H	3'-Cl	140	10	7	93(90)	24	28	54(51)
1c	H	4'-Cl	140	10	6	94(91)	24	8	80(77)
1d	H	3'-Br	140	10	2	98(95)	24	30	52(50)
1e	H	4'-MeO	140	10	6	94(93)	24	26	55(51)
1f	7-MeO	H	140	10	9	91(87)	24	15	61(58)
1g	6-Cl	H	140	10	5	95(94)	24	18	66(64)
1h	7-MeO	4'-Cl	140	10	9	91(89)	24	16	65(63)

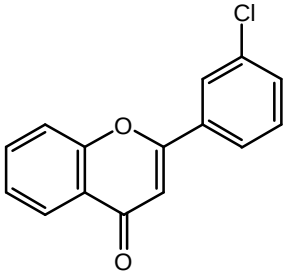
[a] the irradiation power is 150~300 w;

[b] the yield was measured by HPLC; the value in parentheses is the isolated yield

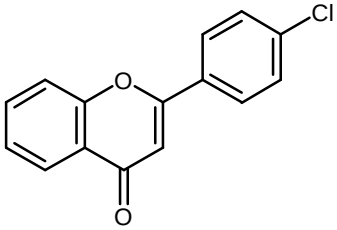
Data for Characterization of 2 and 3:



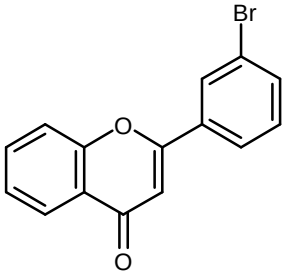
Flavone 2a: Mp 101 ~ 102 ? (Lit.[2a] 98 ?); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.93 (s, 1H), 7.44 ~ 7.60 (m, 5 H), 7,72 (m, 1H), 7.90 ~ 7.96 (m, 2H), 8.22 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.4 (C - 3), 118.0 (C - 8) , 123.7 (C - 10), 125.1 and 125.5 (C – 6 or C – 5), 126.1 (C –2' and C – 6'), 128.9 (C - 3' and C- 5'), 131.5 (C – 1' and C - 4'), 133.7 (C - 7), 156.1 (C - 9), 163.2 (C - 2), 178.4 (C=O); Anal. calcd for $C_{15}H_{10}O_2$: C, 81.07, H, 4.54. Found: C, 80.99, H, 4.24.



3'-Chloroflavone 2b: Mp 109 ~ 110 ? ; ^{1}H NMR (300 MHz, $CDCl_3$)**:** δ = 6.81 (s, 1H), 7.43 ~ 7.48 (m, 2H), 7.51(d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.71 ~ 7.74 (m, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.94 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.0 (C – 3), 118.0 (C – 8), 123.7 (C – 10), 124.3 (C – 6'), 125.4 and 125.6 (C – 6 or C – 5), 126.2 (C – 2'), 130.3 (C – 5'), 131.4 (C – 4'), 133.4 and 133.9 (C – 1' or C – 7), 135.1 (C-Cl), 156.0 (C – 9), 161.5 (C – 2), 178.2 (C=O); Anal. calcd for $C_{15}H_9ClO_2$: C 70.19, H 3.53, Found: C, 69.99, H, 3.42.

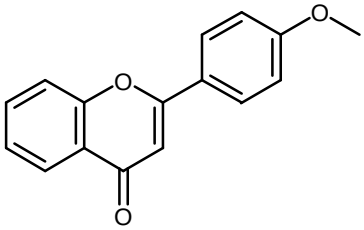


4'-Chloroflavone 2c: Mp 188 ~ 189 ? (Lit. [2b] 188 ~ 189?); ^{1}H NMR (300 MHz, $CDCl_3$)**:** δ = 6.80 (s, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.71 (t, *J* = 7.2 Hz, 1H), 7.88 (d, *J* = 9 Hz, 2H), 8.24 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 107.6 (C – 3), 118.0 (C – 8), 123.7 (C – 10) , 125.4 (C – 6), 125.70 (C – 5), 127.5 (C –2' and C – 6'), 129.3 (C - 3' and C- 5') , 130.1 (C – 1'), 133.9 (C – 7) 137.8 (C-Cl), 156.1 (C – 9), 162.2 (C – 2), 178.3 (C=O); Anal. calcd for $C_{15}H_9ClO_2$: C 70.19, H 3.53, Found: C, 70.38, H, 3.30.

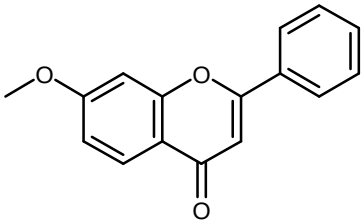


3'-bromoflavone 2d: Mp 114 ~ 115 ? ; ^{1}H NMR (300 MHz, $CDCl_3$)**:** δ = 6.80 (s, 1H), 7.40 ~ 7.45 (m, 2H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.72 (m, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 8.09 (s, 1H), 8.24 (d, *J* = 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.0 (C – 3), 118.1 (C – 8), 123.1 and 123.7 (C – 10 or C – 6'), 124.80 (C – 6), 125.4 and 125.6 (C – 2' or C – 5), 129.1 (C – 5'),

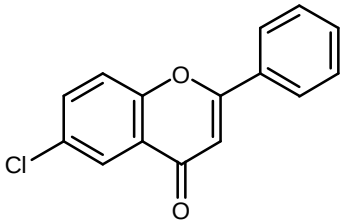
130.5 (C – 4'), 133.6 (C – 1'), 134.0 and 134.4 (C – 7 or C-3'), 156.0 (C – 9), 161.6 (C – 2), 178.2 (C=O); Anal. calcd for $C_{15}H_9BrO_2$: C, 60.11, H, 2.90. Found: C, 59.83, H, 3.01



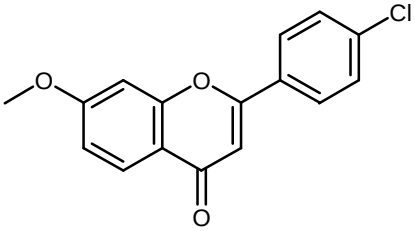
4'-methoxylflavone 2e: Mp 160~161? (Lit.[2a] 156 ?); ^{1}H NMR (300 MHz, $CDCl_3$)**:** δ = 3.90 (s, 3H), 6.75 (s, 1H), 7.04 (d, *J* = 9 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 9 Hz, 2H), 8.23 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5 (CH_3-O), 106.0 (C – 3), 114.4 (C - 3' and C- 5'), 117.9 (C – 8), 123.8 and 123.9 (C –1' or C - 10) , 125.0 and 125.5 (C – 6 or C – 5), 127.9 (C - 2' and C - 6'), 133.5 (C – 7), 156.1 (C – 9), 162.3 (C – 2), 163.4 (C - 4'), 178.4 (C=O); Anal. calcd for $C_{16}H_{12}O_3$: C, 76.18, H 4.79, Found: C, 75.70, H, 4.40.



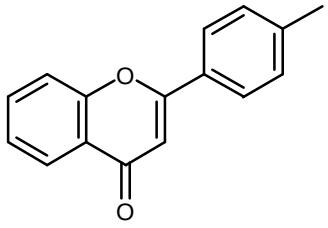
7-methoxylflavone 2f: Mp 110 ~ 112 ? (Lit.[2d, e] 105 ~ 106 ?); ^{1}H NMR (300 MHz, $CDCl_3$)**:** δ = 3.92 (s, 3H), 6.75 (s, 1H), 6.90 ~ 7.00(m, 2H), 7.50 ~ 7.51 (m, 3H), 7.87 ~ 7.90 (m, 2H), 8.12 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.8 (CH_3-O), 100.3 (C – 8), 107.4 (C – 3), 114.4 (C – 6), 117.6 (C – 10), 126.1 and 126.9 ((C – 2' and C – 6') or C – 5) , 128.9 (C – 3' and C – 5'), 131.4 and 131.7 (C - 1' or C – 4'), 157.9 (C – 9), 162.9 (C – 2), 164.1 (C – 7), 177.8 (C=O); Anal. calcd for $C_{16}H_{12}O_3$: C, 76.18, H 4.79, Found: C,76.13, H, 4.36.



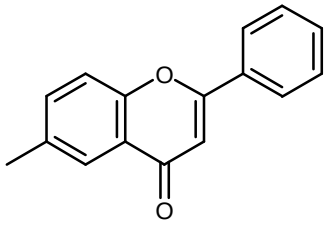
6-Chloroflavone 2g: Mp 183 ~ 184 ? (Lit.[2g] 182 ~ 184?); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.81 (s, 1H), 7.50 ~ 7.53 (m, 2H), 7.60 ~ 7.90 (m, 5H), 8.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.6 (C – 3), 119.9 (C – 8), 123.7 (C – 5), 125.2 (C – 10), 126.6 (C – 2' and C – 6'), 129.2 (C – 3' and C – 5'), 131.2 and 131.5 (C – 6 or C – 1'), 132.0 (C – 4'), 134.1(C – 7), 154.6 (C – 9), 162.5 (C – 2),178.6 (C=O) ; Anal. calcd for $C_{15}H_9ClO_2$: C, 70.19, H, 3.53, Found: C, 70.33, H, 3.22



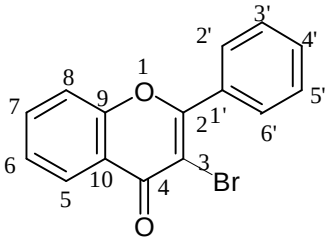
7-methoxy-4'-choroflavone 2h: Mp 159 ~ 161? ; ^{1}H NMR (300 MHz, CDCl3): δ = 3.99 (s, 3H), 6.78 (s, 1H), 7.00 ~ 7.10 (m, 2H), 7.45 ~ 7.90 (m, 4H), 8.18 (d, *J* = 8.1Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.8 (CH_3-O), 99.8 (C – 8), 107.7 (C- 3), 114.4 (C – 6), 117.5 (C – 10), 126.8 (C – 5), 129.0 (C – 2' and C – 6'), 131.2 and 131.6 ((C – 3'and C – 5') or C – 1'), 134.7 (C – 4'), 157.9 (C - 9), 162.8 (C - 2), 164.4 (C- 7), 178.8 (C=O); Anal. calcd for $C_{16}H_{11}ClO_3$: C, 67.03, H, 3.87, Found: C, 67.34, H, 3.56.



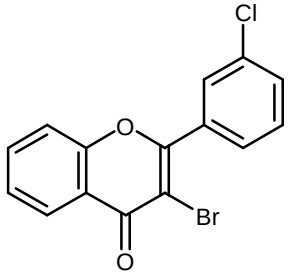
4'-methylflavone 2i: Mp 111 ~ 113 ? (Lit.[2c] 110 ~ 112?); ^{1}H NMR (300 MHz, $CDCl_3$)**:** δ = 2.44 (s, 3H), 6.83 (s, 1H), 7.26 ~ 7.84 (m, 7H), 8.24 (d, *J* = 6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (CH_3), 106.7 (C – 3), 117.9 (C – 8), 123.7 (C – 10), 125.2 and 125.5 (C – 6 or C – 5), 126.60 (C – 3' and C – 5'), 127.2(C – 2' and C – 6'), 129.6 (C – 1'), 133.6 (C - 7), 141.2 (C - 4'), 156.1 (C - 9), 163.4 (C - 2), 178.4 (C=O); Anal. calcd for $C_{16}H_{12}O_2$: C, 81.34, H, 5.12, Found: C 81.11, H, 5.01.



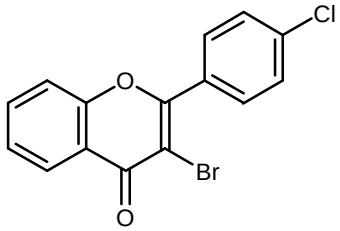
6-methylflavone 2j: Mp 123 ~ 124 ? (Lit.[2f] 121 ~ 122 ?); ^{1}H NMR (300 MHz, $CDCl_3$)**:** δ = 2.45 (s, 3H), 6.86 (s, 1H), 6.90 ~ 7.00 (m, 2H), 7.5 ~ 7.8 (m, 5H), 8.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$: δ = 21.0 (CH_3), 107.6 (C – 3), 118.9 (C – 8), 123.7 (C – 10), 124.9 (C – 5), 128.0 (C – 2' and C – 6'), 129.4 (C – 3' and C – 5'), 131.2 and 131.8 (C – 4' or C – 1'), 135.2 (C - 6), 137.3 (C - 7), 156.3 (C - 9), 163.7 (C - 2), 177.9 (C=O); Anal. calcd for $C_{16}H_{12}O_2$: C, 81.34, H, 5.12, Found: C 81.06, H, 4.89.



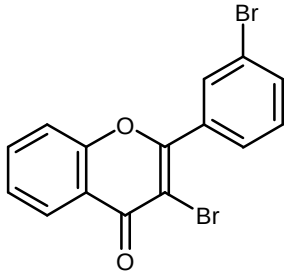
3-bromoflavone 3a: mp 125 ~ 126 ? (Lit.[3] 126 ?); ^{1}H NMR (400 MHz, $CDCl_3$): d 7.46 ~ 7.57 (m, 5 H), 7.71 ~ 7.75 (m, 1H), 7.87 (dd, *J* = 7.4 Hz, 2.2 Hz, 2 H), 8.29 (dd, *J* = 8 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): d 109.3 (C – 3), 117.9 (C – 8), 121.8 (C – 10), 125.7 (C – 5), 126.6 (C – 6), 128.3 (C – 2' and C – 6'), 129.3(C – 1'), 131.17 (C – 3' and C – 5'), 132.9 (C – 4'), 134.2 (C – 7), 155.6 (C – 9), 162.1 (C – 2), 173.2 (C=O); EI - Ms (*m/z*) 303 ($(M + 1)^+$), 300 ($(M -1)^+$); Anal. calcd for $C_{15}H_9BrO_2$: C, 59.83, H, 3.01.Found: C, 60.14 H, 3.21.



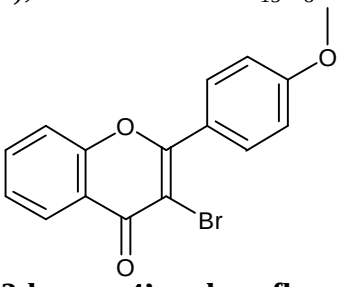
3-bromo-3'-chloro-flavone 3b: mp 173 ~ 175 ? ; ^{1}H NMR (400 MHz, $CDCl_3$): d 7.47 ~ 7.55 (m, 4 H), 7.72 ~ 7.78 (m, 2 H), 7.83 (t, *J* = 1.6 Hz, 1H), 8.29 (dd, *J* = 8 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): d 109.6 (C – 3), 117.9 (C – 8), 121.7(C – 10), 125.9 and 126.6 (C – 5 or C – 6'), 127.6 (C – 6), 129.3 and 129.7 (C – 1' or C – 2'), 131.2 (C – 5'), 132.3 (C – 4'), 133.8 and 134.4 (C – 7 or C – 3'), 155.5 (C – 9), 160.4 (C – 2), 172.9 (C=O); EI - Ms (*m/z*) 336 (M^+), 334 ($(M - 2)^+$); Anal. calcd for $C_{15}H_8BrClO_2$: C, 53.69, H, 2.40. Found: C, 53.86, H, 2.44.



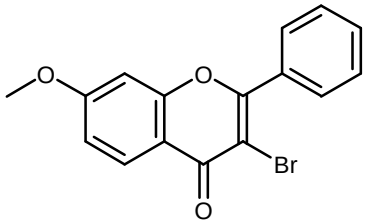
3-bromo-4'-chloroflavone 3c: mp 178 ~ 179 ? (Lit.[4] 179 ~ 180 ?); ^{1}H NMR (400 MHz, $CDCl_3$): d 7.46 ~ 7.54 (m, 4H), 7.71 ~ 7.76 (m, 1H), 7.81 ~ 7.84 (m, 2H), 8.29 (dd, *J* = 8 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): d 109.4 (C – 3), 117.8 (C – 8), 121.7 (C – 10), 125.9 and 126.6 (C – 6 or C - 5), 128.7(C – 2' and C – 6'), 130.8 and 131.2 (C – 1' or (C – 3' and C – 5')), 134.3 (C – 7), 137.4 (C – 4'), 155.5 (C – 9), 160.8 (C – 2), 173.0 (C=O); EI - Ms (*m/z*) 336 (M^+), 334((M - 2)$^+$); Anal. calcd for $C_{15}H_8BrClO_2$: C, 53.69, H, 2.40. Found: C, 53.46, H, 2.34.



3,3'-dibromoflavone 3d: mp 178 ~ 179? ; ^{1}H NMR (400 MHz, $CDCl_3$): d 7.40 ~7.53 (m, 4H), 7.68 ~ 7.83 (m, 2H), 7.99 (t, *J* = 1.8 Hz, 1H), 8.31 (dd, *J* = 8.2 Hz, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): d 109. 7 (C – 3), 117.9 (C – 8), 121.7 and 122.3 (C – 5 or C – 10), 125.8 and 126.4 (C –6' or C – 6), 128.0 (C – 2'), 129.9 (C – 1'), 131.9 and 132.1 (C – 4' or C – 5'), 134.1 and 134.4 (C – 3' or C – 7), 155.6 (C – 9), 160.3 (C – 10), 172.9 (C=O); EI - Ms (*m/z*) 382 ((M + 2) $^+$), 380 (M^+), 378 ((M - 2) $^+$); Anal. calcd for $C_{15}H_8Br_2O_2$: C, 47.41, H, 2.12. Found: C, 47.61, H, 2.10.

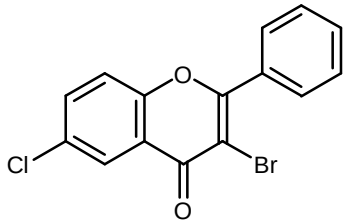


3-bromo-4'methoxyflavone 3e: mp 141 ~ 143? (Lit.[5] 140 ?); ^{1}H NMR (400 MHz, $CDCl_3$): d 3.91 (s, 3H), 7.03 (d, *J* = 8.8 Hz, 2H), 7.44~7.51 (m, 2H), 7.69 ~ 7.73 (m, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 8.28 (d, *J* = 8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): d 55.49 (CH_3-O), 108.5 (C – 3), 113.6 (C 3' and C – 5'), 117.8 (C – 8), 121.7 and 122.4 (C –1' or C – 10), 125.60 (C – 5), 126.5 (C – 6), 131.1(C – 2' and C - 6'), 134.0 (C – 7), 155.5 (C – 9), 161.7 (C – 2), 163.7 (C – 4'), 173.2 (C=O); EI - Ms (*m/z*) 332 ((M + 1) $^+$), 330 ((M - 1) $^+$); Anal. calcd for $C_{16}H_{11}BrO_2$: 58.03, H 3.35. Found: C, 58.19, H, 3.21.

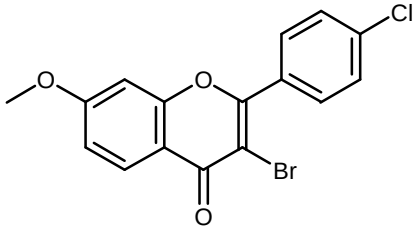


3-bromo-7-methoxyflavone 3f: mp 125 ~ 126 ? (Lit.[4] 124~125 ?); ^{1}H NMR (400 MHz, $CDCl_3$): d= 3.90 (d, *J* = 2.4 Hz, 3H), 6.89 (d, *J* = 3.2 Hz, 1H), 7.00 ~ 7.04 (m, 1H), 7.54 ~ 7.55 (m, 3H), 7.86 (dd, *J* = 5.6 Hz, 2 Hz, 2H), 8.20 (dd, *J* = 8.8 Hz, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): d 55.92 (CH_3-O), 99.8 (C – 8), 109.3 (C – 3), 115.3 and 115.6 (C – 6 or C – 10), 127.9 (C – 5), 128.3 (C – 2' and C – 6'), 129.3 (C – 1'), 131.0 (C – 3'and C – 5'), 132.9(C – 4'), 157.40 (C - 9), 161.5 (C - 10), 164.4 (C- 7), 172.4 (C=O); EI - Ms (*m/z*) 332 ((M + 1) $^+$), 330 ((M - 1) $^+$); Anal. calcd for $C_{16}H_{11}BrO_2$:

C, 58.03, H, 3.35. Found: C, 58.22, H, 3.18.



3-bromo-6-chloroflavone 3g: mp 190 ~ 191 ? (Lit.[5] 187 ~ 189?); ^{1}H NMR (400 MHz, $CDCl_3$): d 7.46 ~7.68 (m, 5H), 7.84 (dd, *J* = 7.8 Hz, 1.4 Hz, 2H), 8.25 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, DCl_3): d= 109.1 (C – 3), 119.6 (C – 8), 122.6 (C – 5), 125.7 (C – 10), 128.3 (C – 2' and C - 6'), 129.3 (C – 1'), 131.3 and 131.6 (C - 6 or (C – 3' and C – 5')), 132.5 (C – 4'), 134.4 (C – 7), 153.9 (C – 9), 162.2 (C – 2), 172.1 (C=O); EI - Ms (*m/z*) 336 (M^+), 334 ((M - 2) $^+$); Anal. calcd for $C_{15}H_8BrClO_2$: C, 53.69, H, 2.40. Found: C, 53.87, H, 2.66.



3-bromo-4'-chloro-7-methoxyflavone 3h: mp 188 ~ 189 ? ; ^{1}H NMR (400 MHz, CDCl3): d 3.91 (s, 3H), 6.85 (d, *J* = 2.0 Hz, 1H), 7.03 (dd, *J* = 9.0 Hz, 2.6 Hz, 1H), 7.50 (dd, *J* = 6.8 Hz, 2 Hz, 2H), 7.80 (dd, *J* = 6.6 Hz, 1.8 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): d 55.9(CH_3 - O), 99.8 (C – 8), 109.5 (C - 3), 115.3 and 115.5 (C – 6 or C – 10), 127.9 (C – 5), 128.6 (C – 2' and C – 6'), 130.6 (C – 3'and C – 5'), 131.2 (C – 1'), 137.2 (C – 4'), 157.3 (C - 9), 160.2 (C - 2), 164.5 (C - 7), 172.2 (C=O); EI - Ms (*m/z*) 366 (M^+), 364 ((M - 2)$^+$); Anal. calcd for $C_{16}H_{10}BrClO_3$: C, 52.56, H 2.76. Found: C, 52.36, H, 2.59

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[2] a) M. S. Mahal, H. S. Rai, K. Venkataraman, *J Chem. Soc.* **1935**, 866. b) W. Baker; J. B. Harbone, W. D. Ollis, *J. Chem. Soc.* **1952**, 1294. c) U. K. Mallik, M. M. Saha, A. K. Mallik, *Indian J. Chem. Soc.* **1989**, *20B*, 970; d) A. Nishinaga, H. Ando, K. Maruyama, T. Mashino, *Synthesis* **1992**, *9*, 839. e) P. G. Ciattini, E. Morera, G. Ortar, S. S. Rossi, *Tetrahedron* **1991**, *47(32)*, 6449. f) O. Dann, G. Mylius, *Justus Liebigs Ann. Chem.* **1954**, *587*, 1. g) S. Hatori, *Bull. Chem. Soc. Jpn.*, **1927**, *2*, 171.

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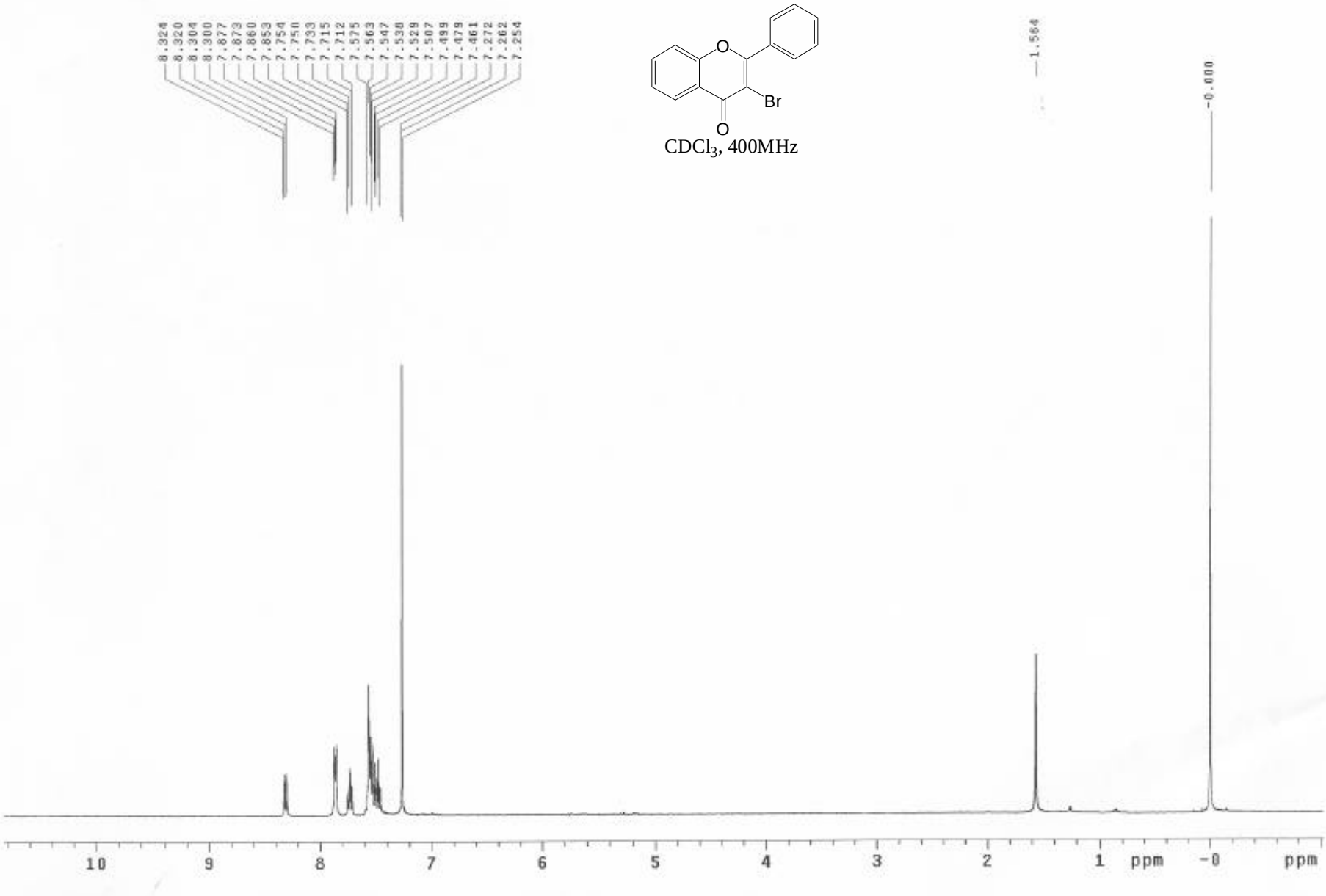
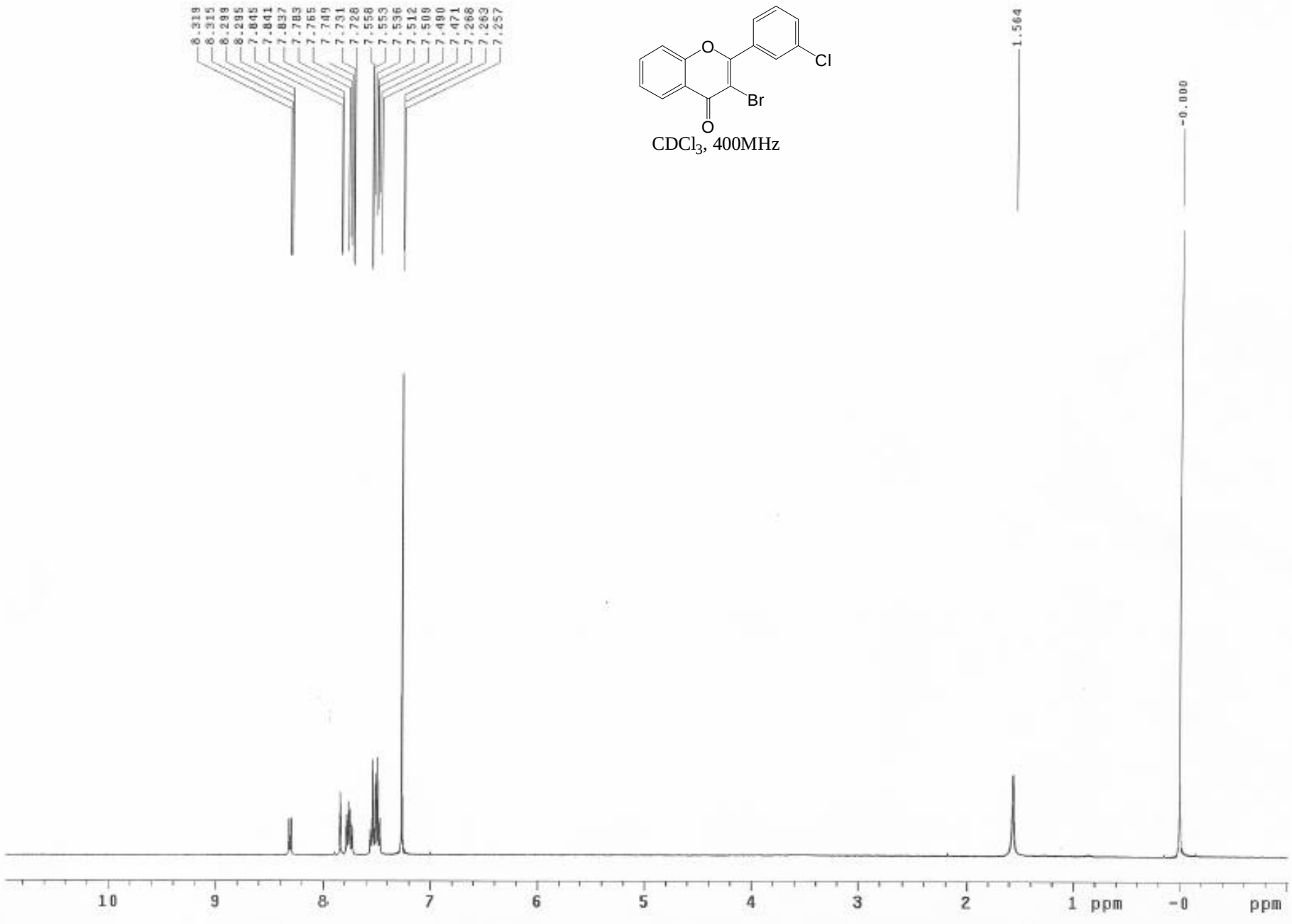


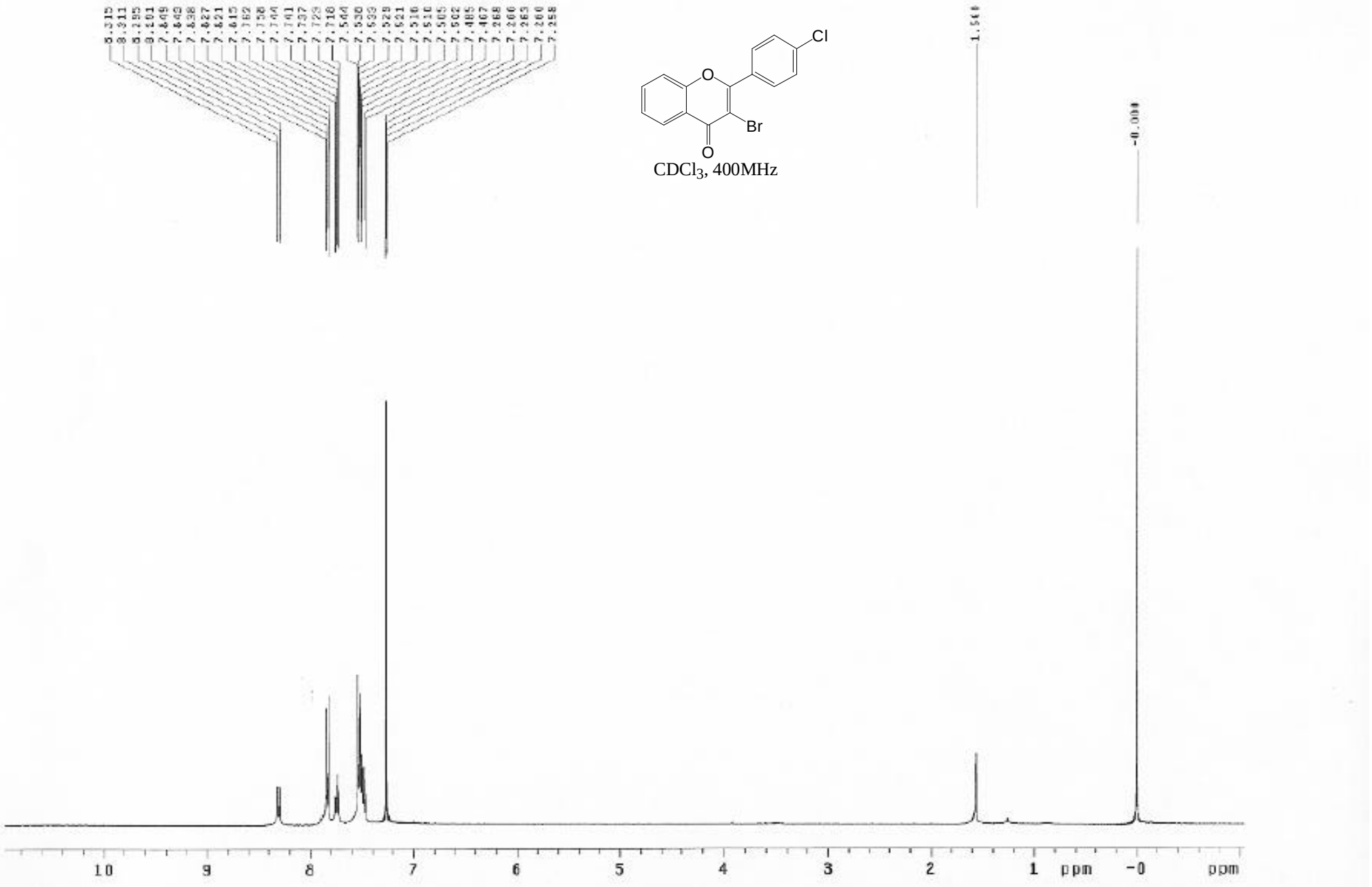
$CDCl_3$, 400MHz

^1H NMR of 3a



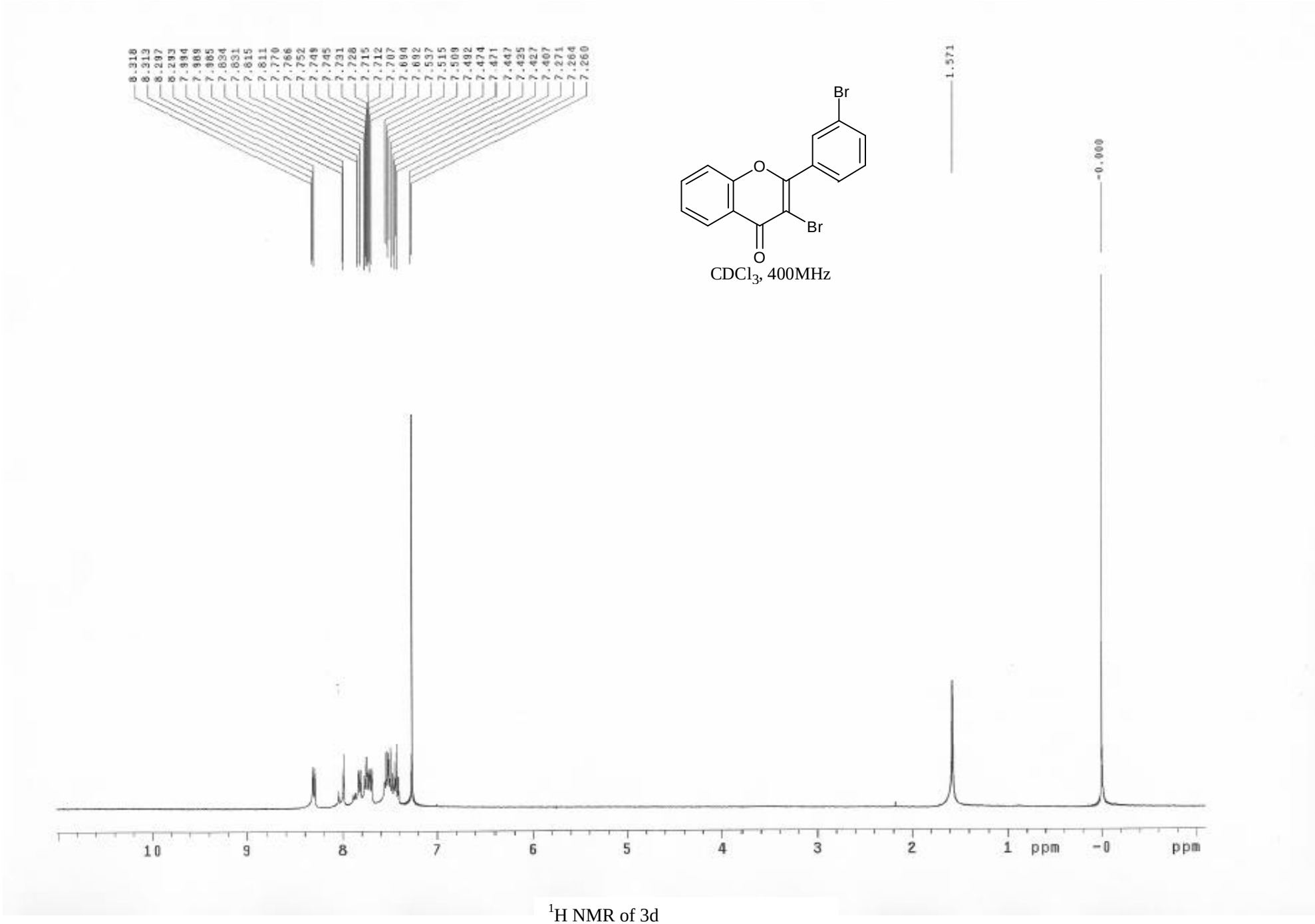
$CDCl_3$, 400MHz

^{1}H NMR of 3b



$CDCl_3$, 400MHz

^{1}H NMR of 3c


8.318
8.313
8.297
8.293
7.994
7.989
7.985
7.834
7.831
7.815
7.811
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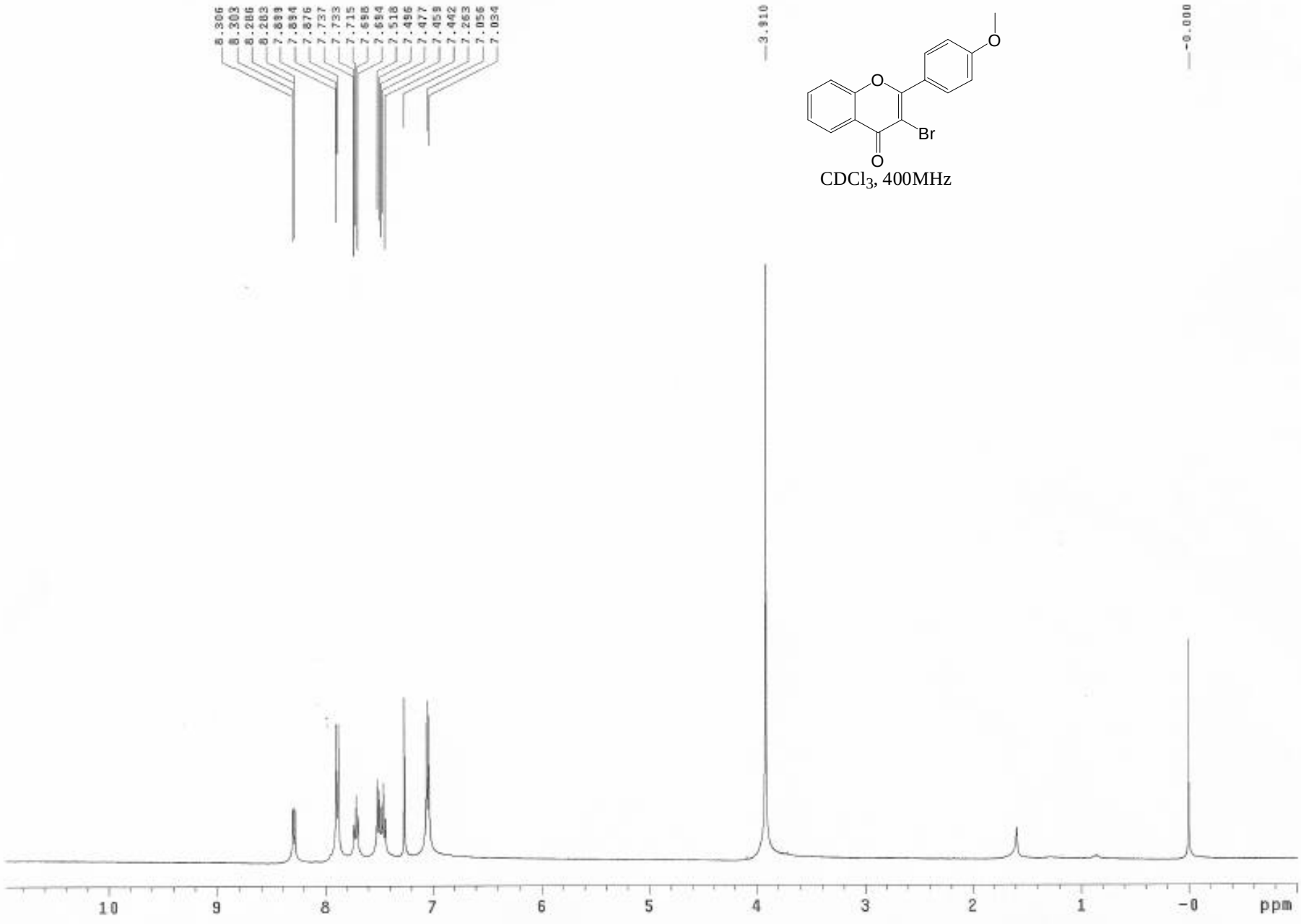
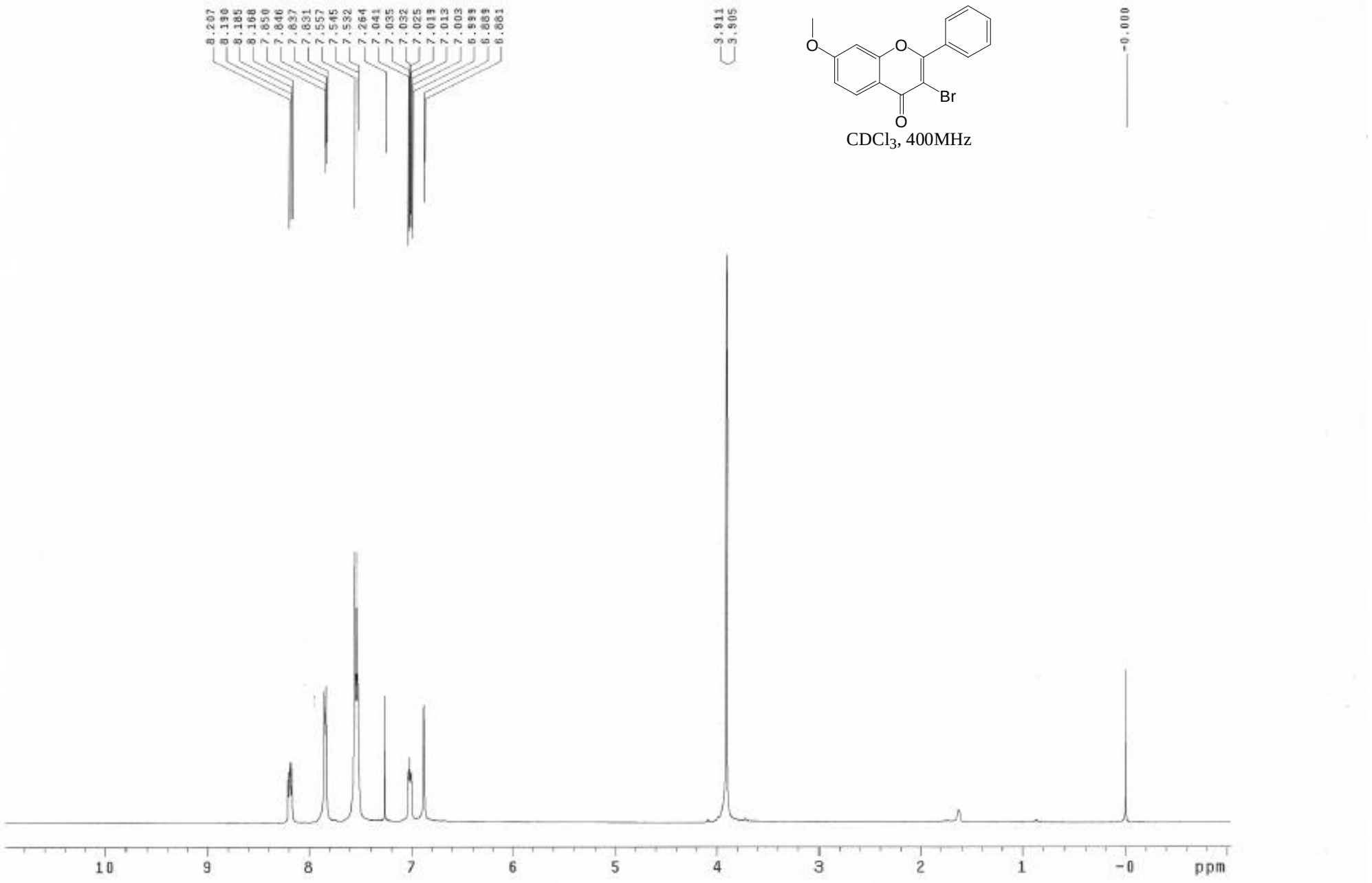
7.766
7.752
7.749
7.745
7.731
7.728
7.715
7.712
7.707
7.694
7.692
7.537
7.515
7.509
7.492
7.474
7.471
7.447
7.425
7.427
7.407
7.271
7.264
7.260
Br
O
Br
O
1.571
0.000
CDCl3, 400MHz
10
9
8
7
6
5
4
3
2
1 ppm
0 ppm

^{1}H NMR of 3d



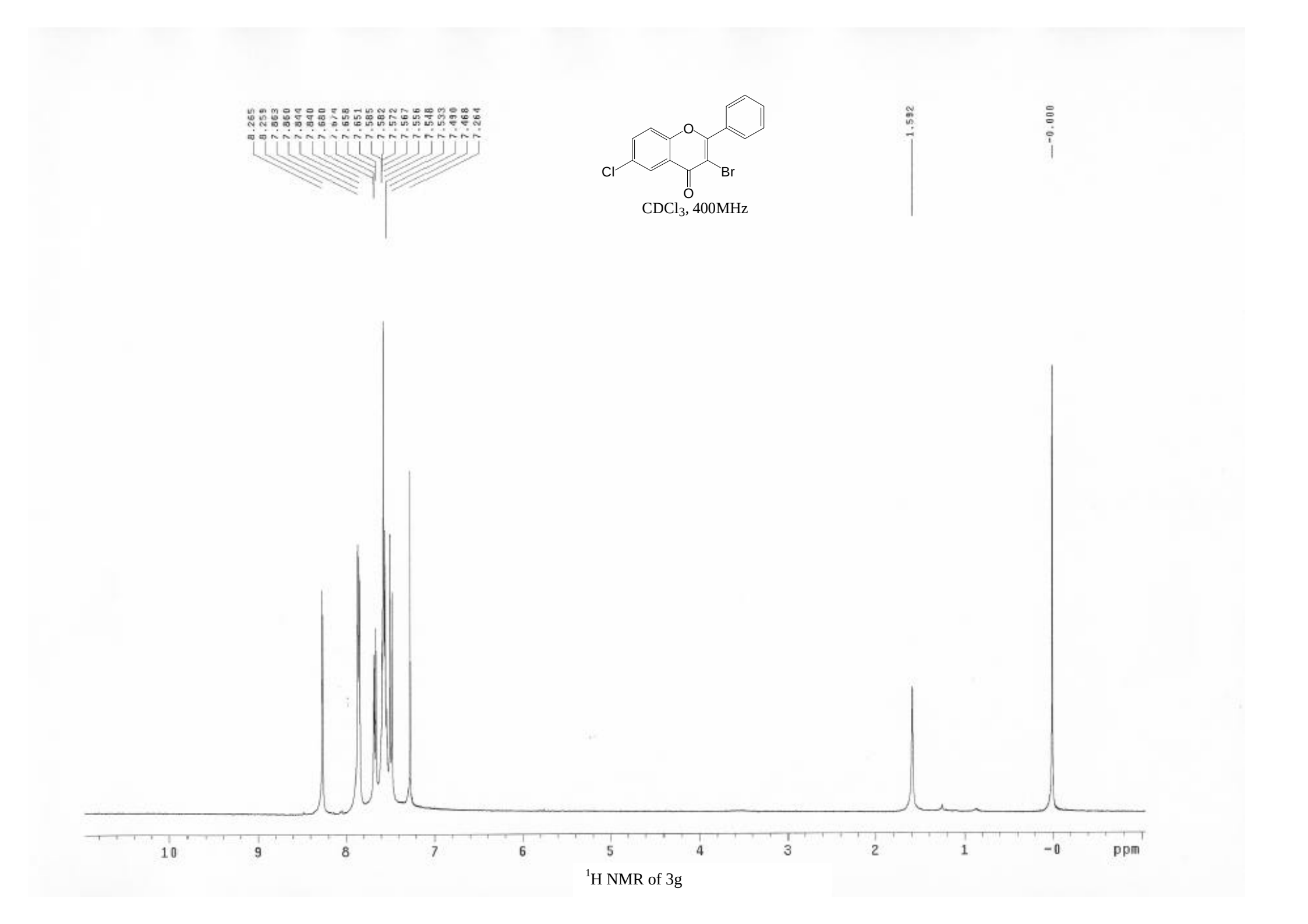
$CDCl_3$, 400MHz

^{1}H NMR of 3e



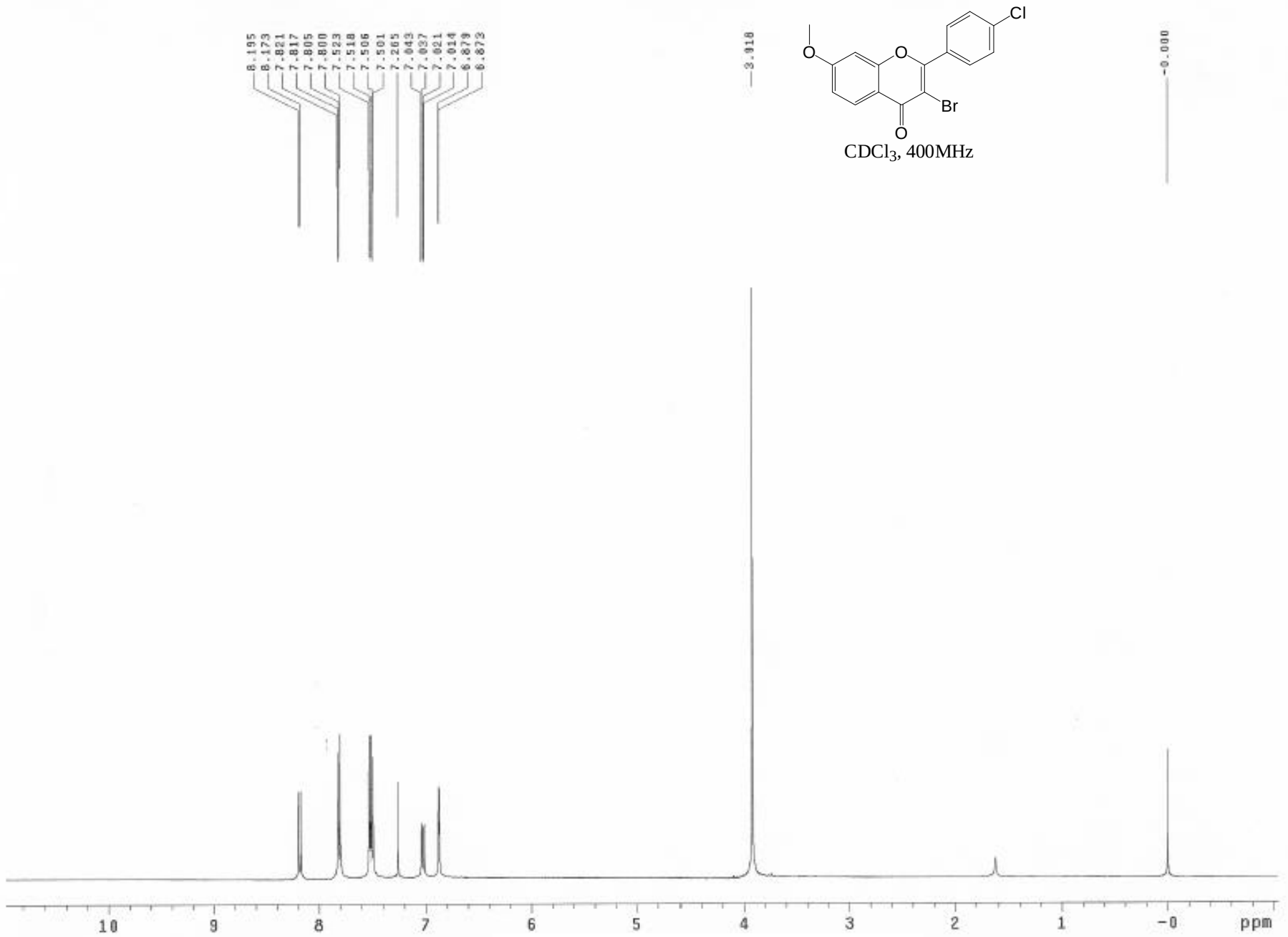
$CDCl_3$, 400MHz

^{1}H NMR of 3f



$CDCl_3$, 400MHz

^1H NMR of 3g



$CDCl_3$, 400MHz

^1H NMR of 3h