Supplementary Material (ESI) for Chemical Communications

Synthesis of chromanones: a novel palladium-catalyzed Wacker-type oxidative cyclization involving 1,5-hydride alkyl to palladium migration

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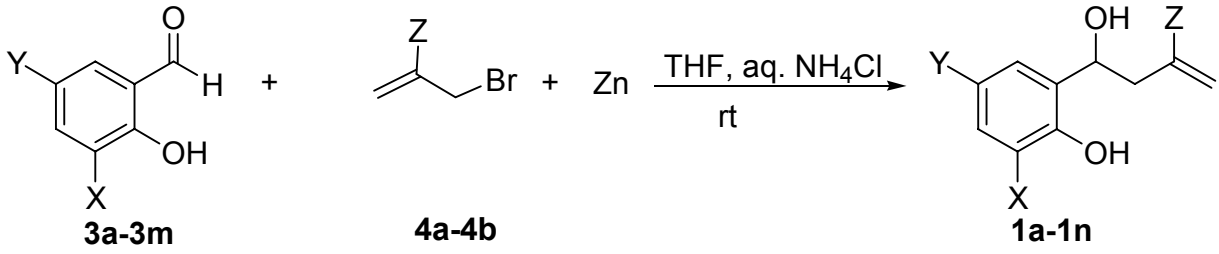
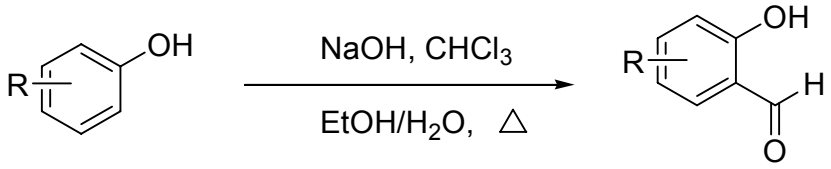
Synthesis of substances 1a-1n (Scheme SI-1).[1]

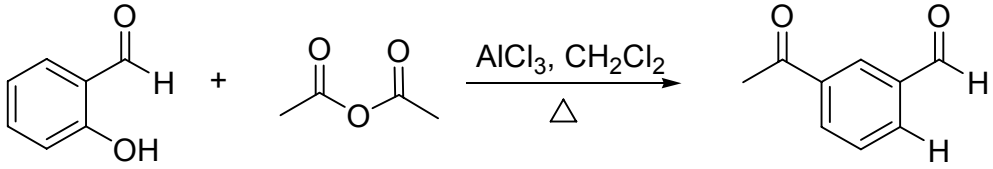


Scheme SI-1. Synthesis of **1a-1n**.

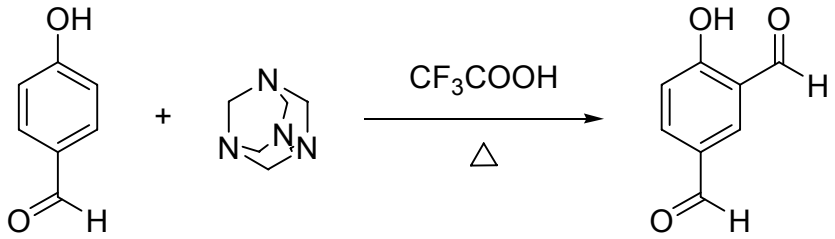
3a, 3b, 3e, 3g, **3k, 4a** and **4b** are commercially available, **3c, 3d, 3f, 3h** and **3i** were synthesized by Reimer-Tiemann reaction as shown in Scheme SI-2. The syntheses of **3j** and **3m** were showed in Scheme SI-3 and Scheme SI-4. **1l** was synthesized by the reduction of **1j** with $NaBH_4$ in EtOH.



Scheme SI-2. General procedure for Reimer-Tiemann reaction.



Scheme SI-3. The synthesis of **3j**.[2]



Scheme SI-4. The synthesis of **3m**.[3]

General experimental procedure for Reimer-Tiemann reaction:

To a solution of the corresponding phenol (10 mmol) in 10 mL of ethanol was added 3.0 g of

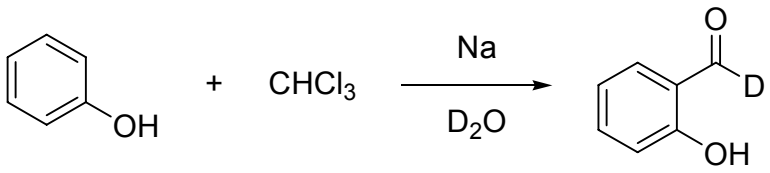
NaOH (75 mmol) in 15 mL of water. When the reaction mixture was heated to 80°C, the dropwise addition of chloroform was started. After the reaction was carried out for 5 min, a total of 2.36 g. (20 mmol) of chloroform was added dropwise so as to maintain a gentle refluxing. Stirring was continued for 1 hour after the chloroform addition was finished. The ethanol was removed by reduced pressure and 1 M HCl was added to neutralize the excess NaOH until PH = 2-3. The solution was then extracted with ethyl acetate for three times. The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was then purified by column chromatography over silica gel to afford **3** with high purity.

1 C. Einhorn, J.-L. Luche, *J. Organoment. Chem.* 1987, **322**, 177.

2 P. Kahnberg, C. W. Lee, R. H.Grubbs, *Telehedron* 2002, **58**, 5203.

3 J. R. Still, J. A. Ward, C. Leffelman, K. A. Sullivan, *Telehedron Lett.* 1996, **52**, 9267.

Typical experimental procedure for the synthesis of deuterium 2-(1-hydroxybut-3-enyl)phenol 1a-*d* (Scheme SI-5)[1]

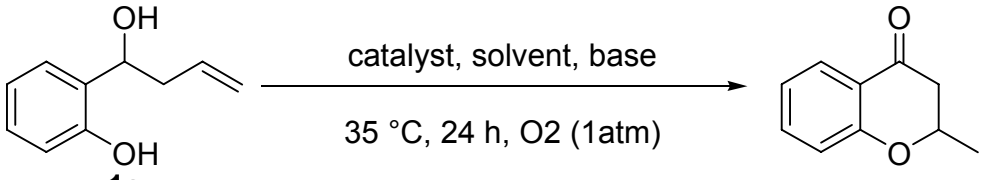


Scheme SI-5.

1 D. S. Kemp, *J. Org. Chem.*1971, **36**, 202.

Optimization of reaction conditions.（Table SI-1 and Table SI-2）

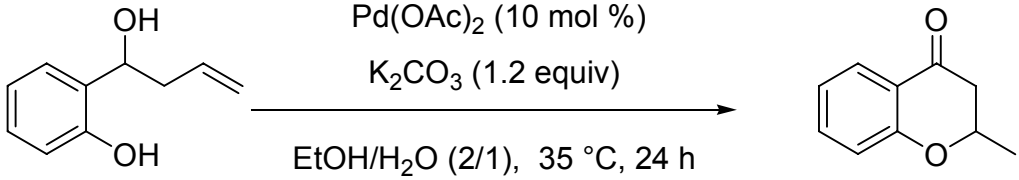
Table SI-1. Screen for different catalyst, base (acid) and solvent.



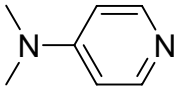
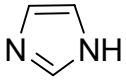
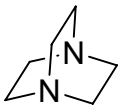
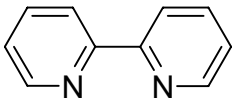
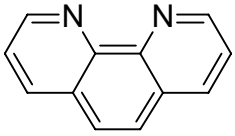
1a **2a**

entry	catalyst	solvent	base (acid)	isolated yield (%)
1	$Pd(OAc)_2$	DMSO	K_2CO_3	18
2	$Pd(OAc)_2$	DMF	K_2CO_3	trace
3	$Pd(OAc)_2$	Tol(dry)	K_2CO_3	trace
4	$Pd(OAc)_2$	Tol(wet)	K_2CO_3	22
5	$Pd(OAc)_2$	CH_3CN	K_2CO_3	16
6	$Pd(OAc)_2$	THF	K_2CO_3	15
7	$Pd(OAC)_2$	MeOH	K_2CO_3	30
8	$Pd(OAc)_2$	EtOH	K_2CO_3	24
9	$Pd(OAc)_2$	i-PrOH	K_2CO_3	trace
10	$Pd(OAc)_2$	DMSO/H_2O (2/1)	K_2CO_3	36
11	$Pd(OAc)_2$	MeOH/H_2O (2/1)	K_2CO_3	57
12	$Pd(OAc)_2$	EtOH/H_2O (2/1)	K_2CO_3	67
13	$Pd(OAc)_2$	EtOH/H_2O (9/1)	K_2CO_3	52
14	$Pd(OAc)_2$	EtOH/H_2O (1/1)	K_2CO_3	60
15	$Pd(OAc)_2$	H_2O	K_2CO_3	trace
16	$Pd(OAc)_2$	EtOH/H_2O (2/1)	Na_2CO_3	65
17	$Pd(OAc)_2$	EtOH/H_2O (2/1)	$KHCO_3$	55
18	$Pd(OAc)_2$	EtOH/H_2O (2/1)	NaOH	53
19	$Pd(OAc)_2$	EtOH/H_2O (2/1)	-	trace
20	$Pd(OAc)_2$	EtOH/H_2O (2/1)	Et_3N	54
21	$PdCl_2$	EtOH/H_2O (2/1)	K_2CO_3	58
22	$Pd(CH_3CN)_2Cl_2$	EtOH/H_2O (2/1)	K_2CO_3	61
23	$Pd(OAc)_2$, TBAB	EtOH/H_2O (2/1)	K_2CO_3	36
24	$Pd(OAc)_2$, LiCl	EtOH/H_2O (2/1)	K_2CO_3	63
25	$Pd(OAc)_2$	EtOH/H_2O (2/1)	HOAc	no product
26	$Pd(OAc)_2$	EtOH/H_2O (2/1)	HCl	no product

Table SI-2. Screen for different oxidant and ligand.



1a **2a**

entry	oxidant	ligand	isolated yield (%)
1	air	-	60
2	O_2 (1 atm)	-	67
3	N_2 (1 atm)	-	11
4	$CuCl_2$ (10 mol %)	-	60
5	$CuCl_2$ (1 equiv)	-	8
6	benzoquinone (1 equiv)	-	57
7	O_2 (1 atm)		62
8	O_2 (1 atm)		trace
9	O_2 (1 atm)		64
10	O_2 (1 atm)		trace
11	O_2 (1 atm)		trace

Determination of the absolute stereochemistry and enantiomeric excess of 1a and 2a

(*S*)-**1a** (*ee* = 63 %) and (*R*)-**1a** (*ee* = 33 %) were synthesized as showed in Scheme SI-6.[1] (*Note:* After completing of the reaction, 1 M HCl was added to neutralize the excess NaOH until PH = 2-3) The Absolute Stereochemistry of **1a** was determined by its ramification (Scheme SI-7). (*S*)-**2a** (*ee* % = 66 %) was obtained had $[\alpha]_D^{20}$ = -31.6°(*c* = 2.0, $CHCl_3$) and (*R*)-**2a** (*ee* % = 34 %) was obtained had $[\alpha]_D^{20}$ = +16.9°(*c* = 2.0, $CHCl_3$).[2] (*S*)-**5a** (*ee* % = 63 %) was obtained had $[\alpha]_D^{20}$ = -55.3°(*c* = 1.0, C_6H_6).[3]

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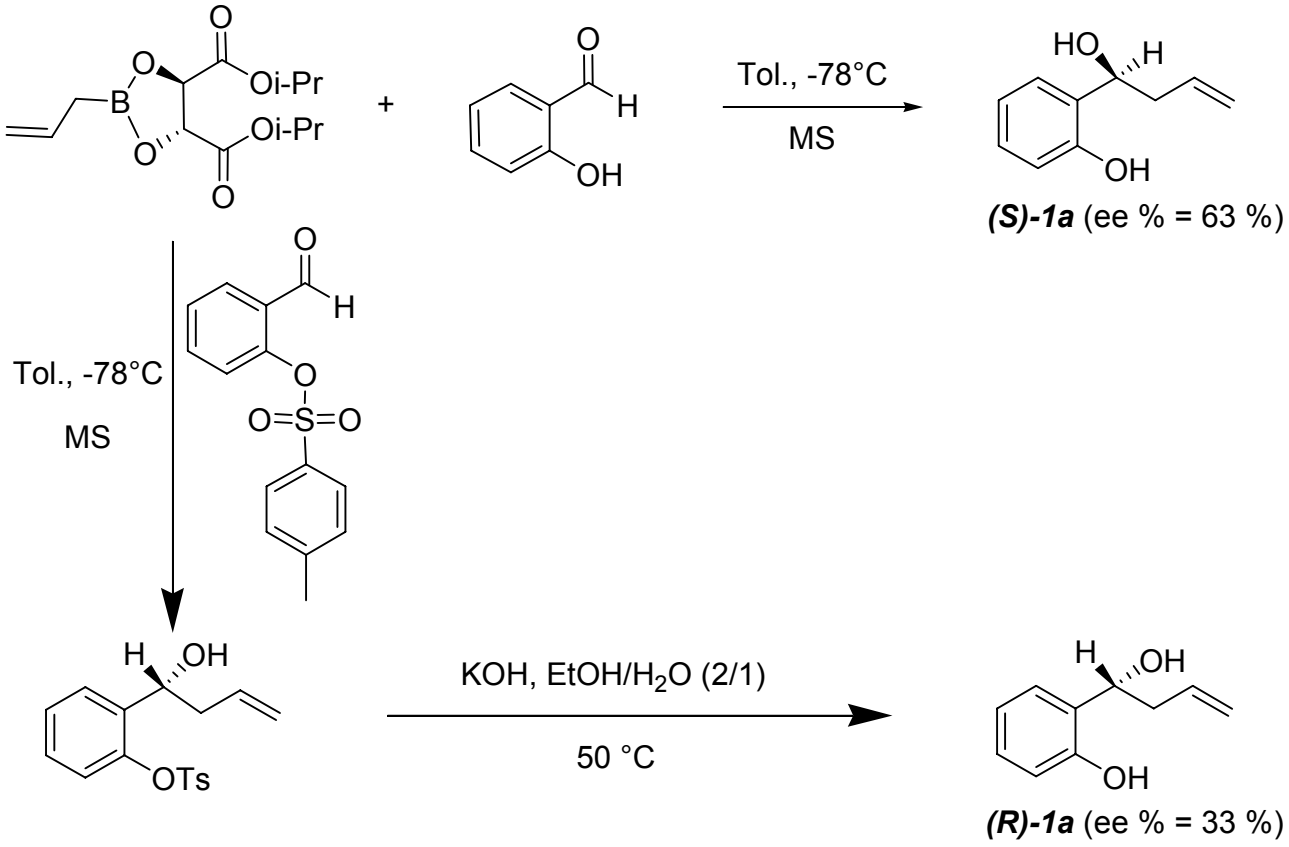
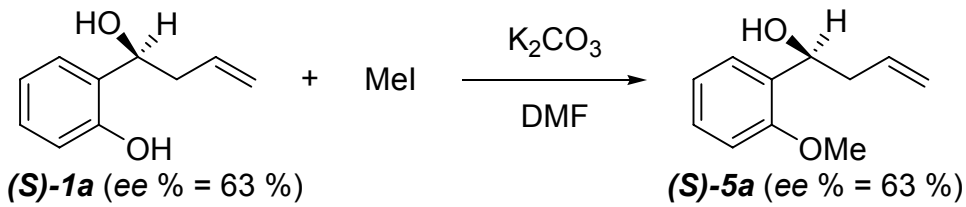
1 W. R. Roush, A. E. Walts, L. K. Hoong *J. Am. Chem. Soc.* 1985, **107**, 8186

2 (a) S. T. Saengchantara, T. W. Wallace, *Tetrahedron* 1990, **46**, 6553; (b) K. J. Hodgetts, *Tetrahedron Lett.* 2001, **42**, 3763.

3 T. Shimada, A. Kina, T. Hayashi, *J. Org. Chem.* 2003, **68**, 6329.

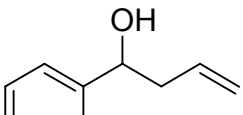


Scheme SI-6. Synthesis of **(*S*)-1a** (*ee* % = 63 %) and **(*R*)-1a** (*ee* % = 33 %).

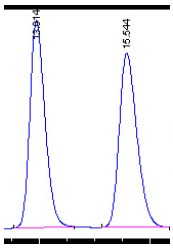


Scheme SI-7. Synthesis the **(*S*)-5a.**

The *ee* of **(*S*)-1a** (*ee* %= 63 %), **(*R*)-1a** (*ee* % = 33 %), **(*S*)-2a** (*ee* % = 66 %), **(*R*)-2a** (*ee* % = 34 %) and **(*S*)-5a** (*ee* % = 63 %) were determined by chiral HPLC analysis using a CHIRALCEL OD-H column.



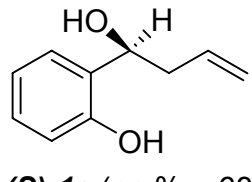
Racemic-1a



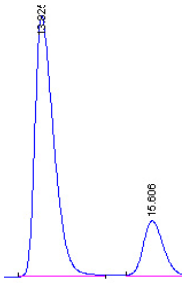
HPLC Condition:

Chiralcel OD-H, Hex/*i*-PrOH = 90/10, 0.5 mL/min

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.914	BB	0.2917	3312.50977	174.32845	50.3589
2	15.544	BB	0.3437	3265.29907	146.67509	49.6411



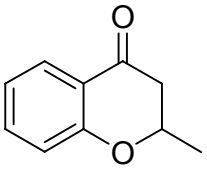
(S)-1a (*ee* % = 63 %)



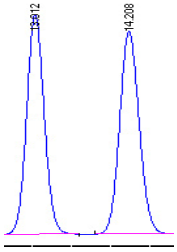
HPLC Condition:

Chiralcel OD-H, Hex/*i*-PrOH = 90/10, 0.5 mL/min

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.825	BB	0.3216	9200.84277	433.49365	81.2733
2	15.606	BB	0.3526	2120.02417	92.78915	18.7267



Racemic-2a



HPLC Condition:

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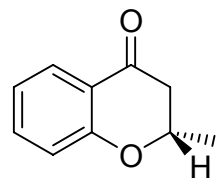
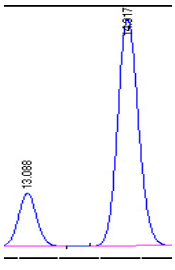


(S)-2a (ee % = 66 %)



HPLC Condition:

Chiralcel OD-H, Hex/*i*-PrOH = 97/3, 0.5 mL/min

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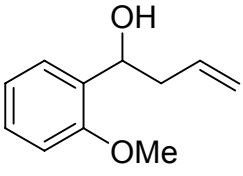
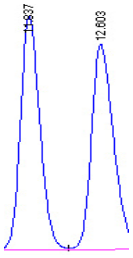
1	13.088	BB	0.2422	2128.97827	136.34039	16.9781
2	14.317	BB	0.2779	1.04106e4	584.30750	83.0219



Racemic-5a



HPLC Condition:

Chiralcel OD-H, Hex/*i*-PrOH = 90/10, 0.5 mL/min

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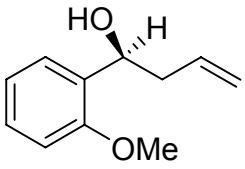
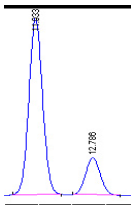
1	11.837	BV	0.2215	4566.81543	318.04712	49.7939
2	12.603	VB	0.2549	4604.61572	278.48154	50.2061



(S)-5a (*ee* % = 63 %)



HPLC Condition:

Chiralcel OD-H, Hex/*i*-PrOH = 90/10, 0.5 mL/min

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.933	BB	0.2195	773.97052	54.55669	81.4093
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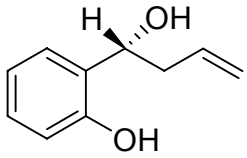
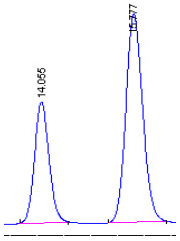


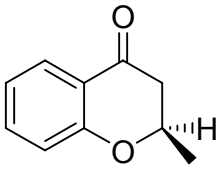
(R)-1a (*ee* % = 33 %)



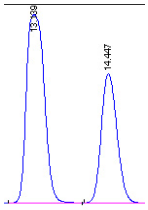
HPLC Condition:

Chiralcel OD-H, Hex/*i*-PrOH = 90/10, 0.5 mL/min

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.055	BB	0.2919	731.79041	38.81956	33.3836
2	15.777	BB	0.3394	1460.27673	66.71751	66.6164



(R)-2a (ee % = 34 %)

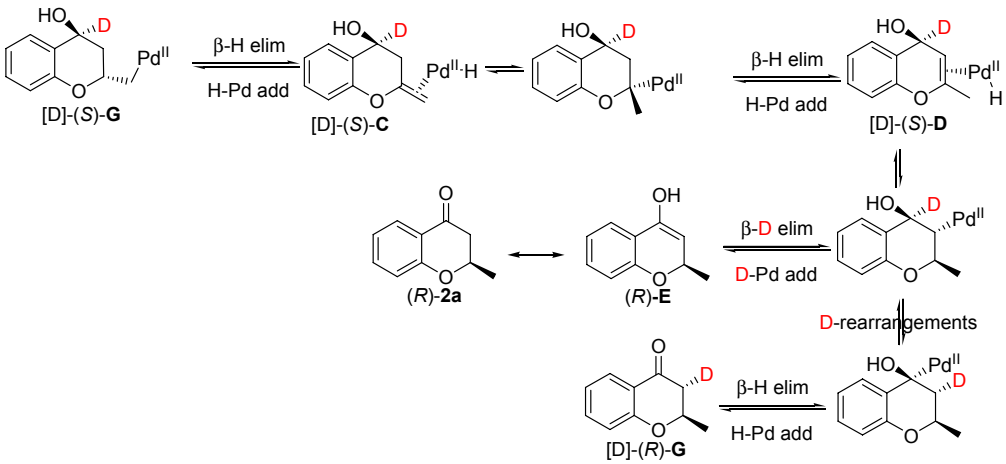


HPLC Condition:

Chiralcel OD-H, Hex/*i*-PrOH = 97/3, 0.5 mL/min

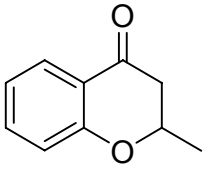
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.139	BB	0.3552	1.50302e4	687.08197	62.3845
2	14.447	BB	0.3040	9062.60254	471.97867	37.6155

Proposed mechanism for pathway B.[1]



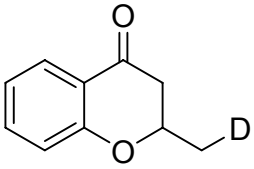
1 (a) T. Hayashi, K. Yamasaki, M. Mimura, Y. Uozumi, *J. Am. Chem. Soc.* 2004, **126**, 3036;
(b) R. M. Trend, Y. K. Ramtohul, B. M. Stoltz, *J.Am.Chem. Soc.* 2005, **127**, 17778;
(c) J. A. Keith, J. Oxgaard, W.A. Goddard, III, *J. Am. Chem. Soc.* 2006, **128**, 3132.

Characterization data for the products



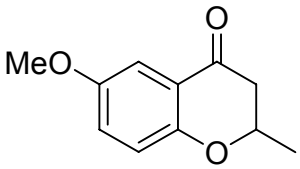
2,3-dihydro-2-methylchromen-4-one (2a)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.88 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 7.50-7.44 (m, 1 H), 7.03-6.95 (m, 2 H), 4.63-4.56 (m, 1 H), 2.68 (d, J = 7.8 Hz, 2 H), 1.52 (d, J = 6.3 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 192.5, 161.7, 136.0, 127.0, 121.2, 120.9, 117.9, 74.3, 44.6, 21.0. IR (KBr film, cm^{-1}): v = 2926, 1695, 1609, 1464, 1385, 1308, 1230, 1122, 1036, 949, 764, 569. HRMS calc. $C_{10}H_{10}O_2$ (M^+): 162.0681. Found: 162.0703.



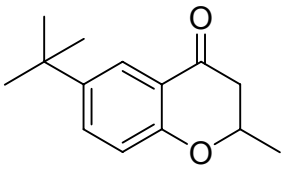
2,3-dihydro-2-methylchromen-4-one (2a-*d*)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.88 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 7.50-7.44 (m, 1 H), 7.03-6.95 (m, 2 H), 4.62-4.57 (m, 1 H), 2.68 (d, J = 7.8 Hz, 2 H), 1.53-1.49 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 192.5, 161.8, 136.0, 127.0, 121.3, 120.9, 118.0, 74.4, 74.3, 44.7, 20.8 (t, J = 19.7 Hz). IR (KBr film, cm^{-1}): v = 2940, 1694, 1607, 1473, 1464, 1309, 1229, 1115, 765. HRMS calc. $C_{10}H_{19}DO_2$ (M^+): 163.0741. Found: 163.0744.



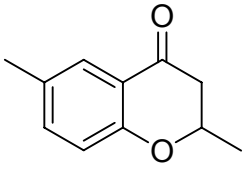
2,3-dihydro-6-methoxy-2-methylchromen-4-one (2b)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.31 (d, J = 3.0 Hz, 1 H), 7.09 (dd, J = 9.0 Hz, 3.0 Hz), 6.90 (d, J = 9.0 Hz, 1 H), 4.58-4.51 (m, 1 H), 3.80 (s, 3 H), 2.66 (d, J = 7.8 Hz, 2 H), 1.51 (d, J = 6.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 192.5, 156.5, 154.0, 125.2, 120.7, 119.2, 107.4, 74.4, 55.8, 44.6, 21.0. IR (KBr film, cm^{-1}): v = 2980, 2838, 1682, 1620, 1487, 1433, 1386, 1285, 1218, 1173, 1127, 1033, 945, 867, 821, 797, 701. HRMS calc. $C_{11}H_{12}O_3$ (M^+): 192.0786. Found: 192.0777.



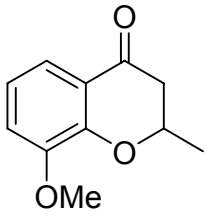
6-tert-butyl-2,3-dihydro-2-methylchromen-4-one (2c)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.88 (d, J = 2.4 Hz, 1 H), 7.53 (dd, J = 8.7 Hz, 2.4 Hz, 1 H), 6.91 (d, J = 8.7 Hz, 1 H), 4.58-4.55 (m, 1 H), 2.68-2.65 (m, 2 H), 1.50 (d, J = 6.3 Hz, 3 H), 1.31 (s, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 192.7, 159.7, 144.1, 133.7, 122.9, 120.1, 117.6, 74.2, 44.8, 34.3, 31.4, 21.1. IR (KBr film, cm^{-1}): v = 1694, 1614, 1491, 1421, 1297, 1140, 1032, 949, 866, 832, 573. HRMS calc. $C_{14}H_{18}O_2$ (M^+): 218.1307. Found: 218.1310.



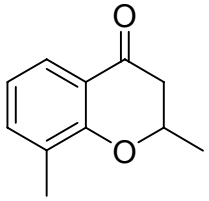
2,3-dihydro-2,6-dimethylchromen-4-one (2d)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.67 (s, 1 H), 7.30-7.25 (m, 1 H), 6.88-6.84 (m, 1 H), 4.59-4.51 (m, 1 H), 2.67-2.63 (m, 2 H), 2.30 (s, 3 H), 1.51-1.48 (m, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 192.7, 159.8, 137.0, 130.6, 126.5, 120.5, 117.7, 74.3, 44.7, 21.0, 20.4. IR (KBr film, cm^{-1}): v = 2980, 2910, 1694, 1620, 1490, 1420, 1392, 1292, 1224, 1030, 948, 823, 789. HRMS calc. $C_{11}H_{12}O_2$ (M^+): 176.0837. Found: 176.0841.



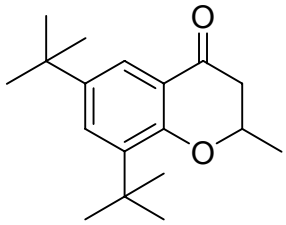
2,3-dihydro-8-methoxy-2-methylchromen-4-one (2e)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.49 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 7.05 (dd, J = 7.8 Hz, 1.2Hz, 1 H), 6.94 (t, J = 7.8 Hz, 1 H). 4.67-465 (m, 1 H), 3.90 (s, 3 H), 2.72-2.69 (m, 2 H), 1.59 (d, J = 6.3 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 192.5, 151.8, 149.0, 121.7, 120.7, 118.3, 116.9, 75.0, 56.4, 44.5, 21.0. IR (KBr film, cm^{-1}): ν = 2972, 1688, 1603, 1582, 1488, 1451, 1302, 1262, 1049, 948, 865, 785, 737, 572. HRMS calc. $C_{11}H_{12}O_3$ (M^+): 192.0786. Found: 192.0787.



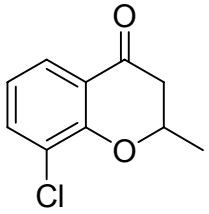
2,3-dihydro-2,8-dimethylchromen-4-one (2f)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.73 (d, J = 7.5 Hz, 1 H), 7.32 (d, J = 6.6 Hz, 1 H), 6.89 (t, J = 7.5 Hz, 1 H), 4.61-4.54 (m, 1 H), 2.68-2.65 (m, 2 H), 2.24 (s, 3 H), 1.53 (d, J = 6.3 Hz,3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 192.9, 160.0, 136.8, 127.1, 124.5, 120.54, 120.49, 74.1, 44.5, 21.0, 15.6. IR (KBr film, cm^{-1}): ν = 2977, 1687, 1599, 1478, 1385, 1223, 1030, 949, 870, 787, 745, 579. HRMS calc. $C_{11}H_{12}O_2$ (M^+): 176.0837. Found: 176.0843.



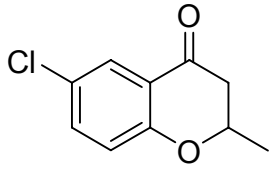
6,8-di-tert-butyl-2,3-dihydro-2-methylchromen-4-one (2g)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.79 (d, J = 2.7 Hz, 1 H), 7.54 (d, J = 2.7 Hz, 1 H), 4.55-4.50 (m, 1 H), 2.67-2.65 (m, 2 H), 1.54 (d, J = 6.3 Hz, 3 H), 1.40 (s, 9 H), 1.31 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 193.6, 158.8, 143.2, 138.3, 130.7, 121.0, 74.0, 44.8, 35.1, 34.6, 31.5, 29.8, 21.2. IR (KBr film, cm^{-1}): ν = 2962, 1695, 1604, 1476, 1444, 1363, 1387, 1364, 1277, 1248, 1034, 891, 579. HRMS calc. $C_{18}H_{26}O_2$ (M^+): 274.1933. Found: 274.1942.



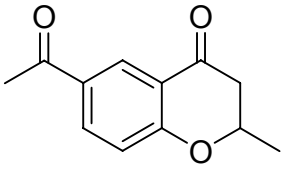
8-chloro-2,3-dihydro-2-methylchromen-4-one (2h)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.80 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 7.55 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 6.95 (t, J = 7.8 Hz, 1 H), 4.72-4.65 (m, 1 H), 2.74-2.71 (m, 2 H), 1.59 (d, J = 5.7 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 191.6, 157.3, 136.1, 125.6, 122.9, 122.2, 121.3, 75.3, 44.3, 20.9. IR (KBr film, cm^{-1}): ν = 2981, 1696, 1597, 1469, 1442, 1391, 1292, 1243, 1138, 1022, 944, 883, 777, 577. HRMS calc. $C_{10}H_9ClO_2$ (M^+): 196.0291. Found: 196.0286.



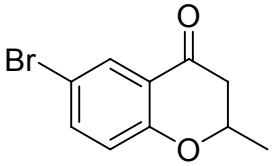
6-chloro-2,3-dihydro-2-methylchromen-4-one (2i)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.83 (d, J = 2.6 Hz, 1 H), 7.40 (dd, J = 8.8 Hz, 2.6 Hz, 1 H), 6.93 (d, J = 8.3 Hz, 1 H), 4.62-4.55 (m, 1 H), 2.73-2.66 (m, 2 H), 1.52 (d, J = 6.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 191.3, 160.2, 135.8, 126.8, 126.4, 121.7, 119.8, 74.7, 44.3, 20.9. IR (KBr film, cm^{-1}): ν = 2963, 1684, 1599, 1468, 1421, 1387, 1276, 1180, 1022, 949, 826, 574. HRMS calc. $C_{10}H_9ClO_2$ (M^+): 196.0291. Found: 196.0292.



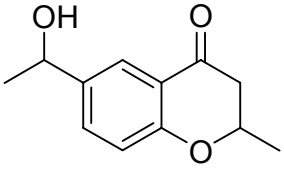
6-acetyl-2,3-dihydro-2-methylchromen-4-one (2j)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.46 (d, J = 2.1 Hz, 1 H), 8.15-8.11 (m, 1 H), 7.04 (d, J = 8.7 Hz, 1 H), 4.68 (m. 1H), 2.75-2.72 (m, 2 H), 2.60 (d, J = 0.9 Hz, 3 H), 1.57 (dd, J = 6.6 Hz, 0.9 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 196.3, 191.6, 165.1, 135.4, 130.8, 128.6, 120.0, 118.8, 75.0, 44.3, 26.5, 20.9. IR (KBr film, cm^{-1}): v = 1694, 1682, 1568, 1487, 1426, 1361, 1257, 1129, 947, 837, 571. HRMS calc. $C_{12}H_{12}O_3$ (M^+): 204.0786. Found: 204.0783.



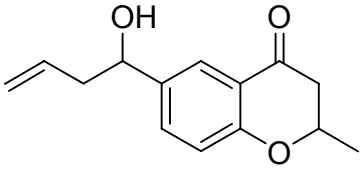
6-bromo-2,3-dihydro-2-methylchromen-4-one (2k)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.98 (d, J = 2.4 Hz, 1 H), 7.54 (dd, J = 9.0 Hz, 2.4 Hz, 1 H), 6.87 (d, J = 9.0 Hz, 1 H), 4.62-4.55 (m, 1 H), 2.69-2.66 (m, 2 H), 1.52 (d, J = 6.3 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 191.3, 160.7, 138.7, 129.6, 122.2, 120.2, 114.0, 74.7, 44.3, 21.0. IR (KBr film, cm^{-1}): v = 2961, 1683, 1596, 1466, 1417, 1389, 1275, 1226, 1181, 1023, 823, 572. HRMS calc. $C_{10}H_9BrO_2$ (M^+): 239.9786. Found: 239.9790.



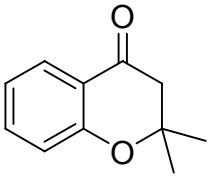
2,3-dihydro-6-(1-hydroxyethyl)-2-methylchromen-4-one (2l)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.80 (s, 1H), 7.53 (d, J = 8.7 Hz, 1 H), 6.94 (d, J = 8.7 Hz, 1 H), 4.88-4.82 (m, 1 H), 4.59-4.52 (m, 1 H), 2.66-2.63 (m, 2 H), 2.46 (s, 1 H), 1.51-1.45 (m, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 192.7, 161.1, 139.0, 133.65, 133.64, 123.71, 123.68, 120.4, 118.2, 74.4, 69.5, 44.60, 44.58, 25.1, 21.0. IR (KBr film, cm^{-1}): 3424, 2975, 1690, 1617, 1490, 1387, 1276, 1229, 1176, 949, 833, 570. HRMS calc. $C_{12}H_{14}O_3$ (M^+): 206.0943. Found: 206.0950.



2,3-dihydro-6-(1-hydroxybut-3-enyl)-2-methylchromen-4-on e (2m)

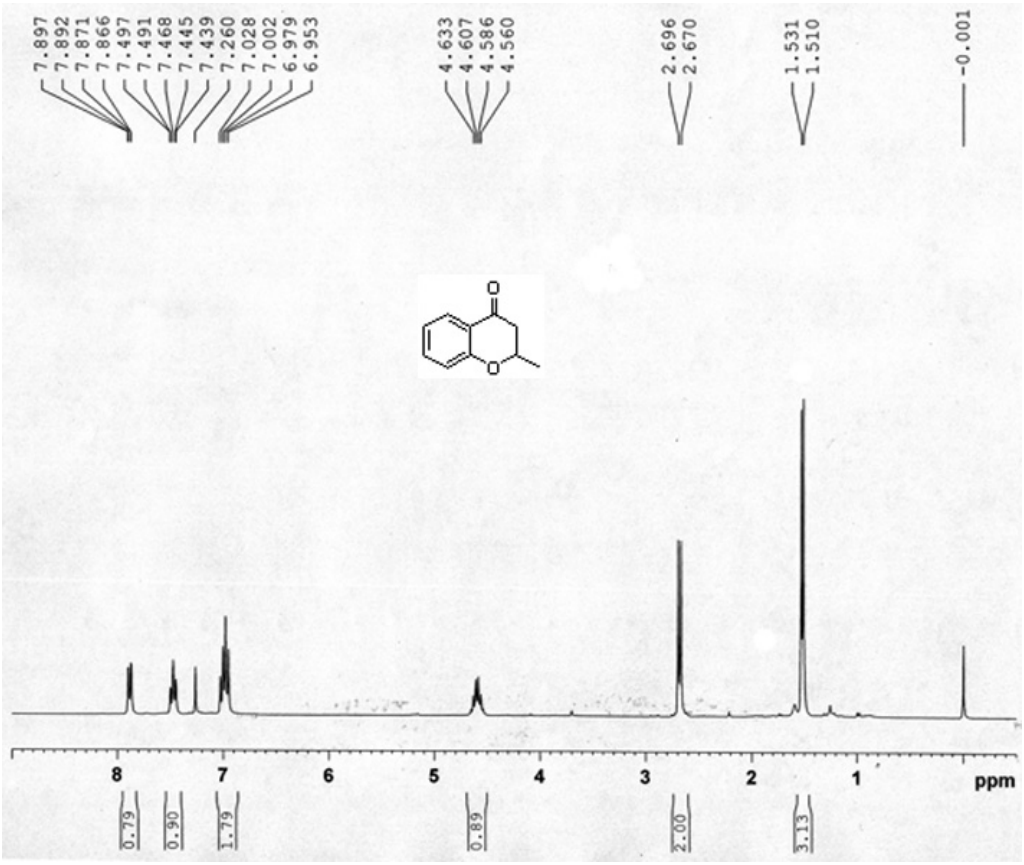
^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.83 (s, 1 H), 7.54-7.50 (m, 1 H), 6.96 (d, J = 8.7 Hz, 1 H), 5.83-5.74 (m, 1 H), 5.18-5.12 (m, 2 H), 4.71 (d, J = 6.0 Hz, 1 H), 4.62-4.55 (m, 1 H), 2.67 (d, J = 7.2 Hz, 2 H), 2.51-2.46 (m, 2 H), 2.16 (s, 1 H), 1.52 (d, J = 6.3 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 192.6, 161.1, 137.1, 134.2, 133.92, 133.89, 124.26, 124.21, 120.3, 118.5, 118.1, 74.4, 72.6, 44.56, 44.54 43.6, 21.0. IR (KBr film, cm^{-1}): 3435, 2978, 1692, 1617, 1489, 1435, 1387, 1296, 1230, 1172, 1132, 1033, 918, 835, 570. HRMS calc. $C_{14}H_{16}O_3$ (M^+): 232.1099. Found: 232.1112.



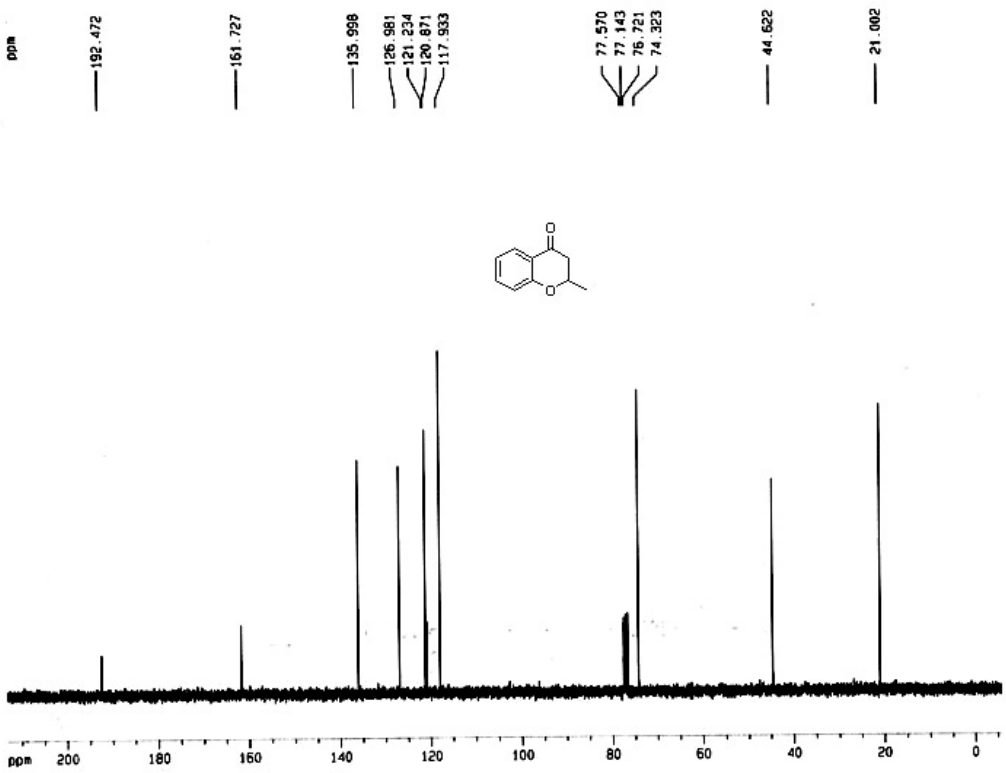
2,3-dihydro-2,2-dimethylchromen-4-one (2n)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.86 (dd, J = 7.7 Hz, 1.2 Hz, 1 H), 7.50-7.44 (m, 1 H), 7.00-6.91 (m, 2 H), 2.73 (s, 2H), 1.46 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ =192.6, 160.1, 136.2, 126.6, 120.8, 120.3, 118.4, 79.2, 49.0, 26.7. IR (KBr film, cm^{-1}): 2977, 2933, 1688, 1605, 1457, 1371, 1328, 1247, 1119, 1024, 928, 896, 765, 572. HRMS calc. $C_{11}H_{12}O_2$ (M^+): 17600837. Found: 1760.0850.

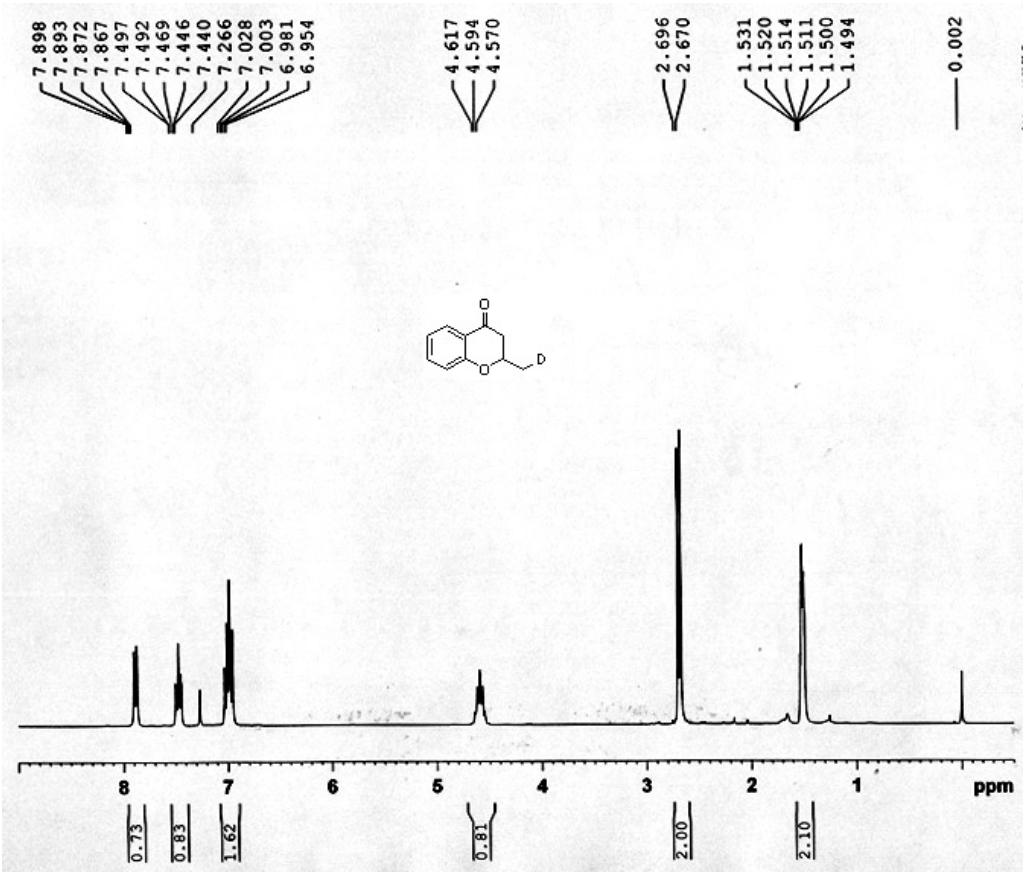
2a (^{1}H NMR)



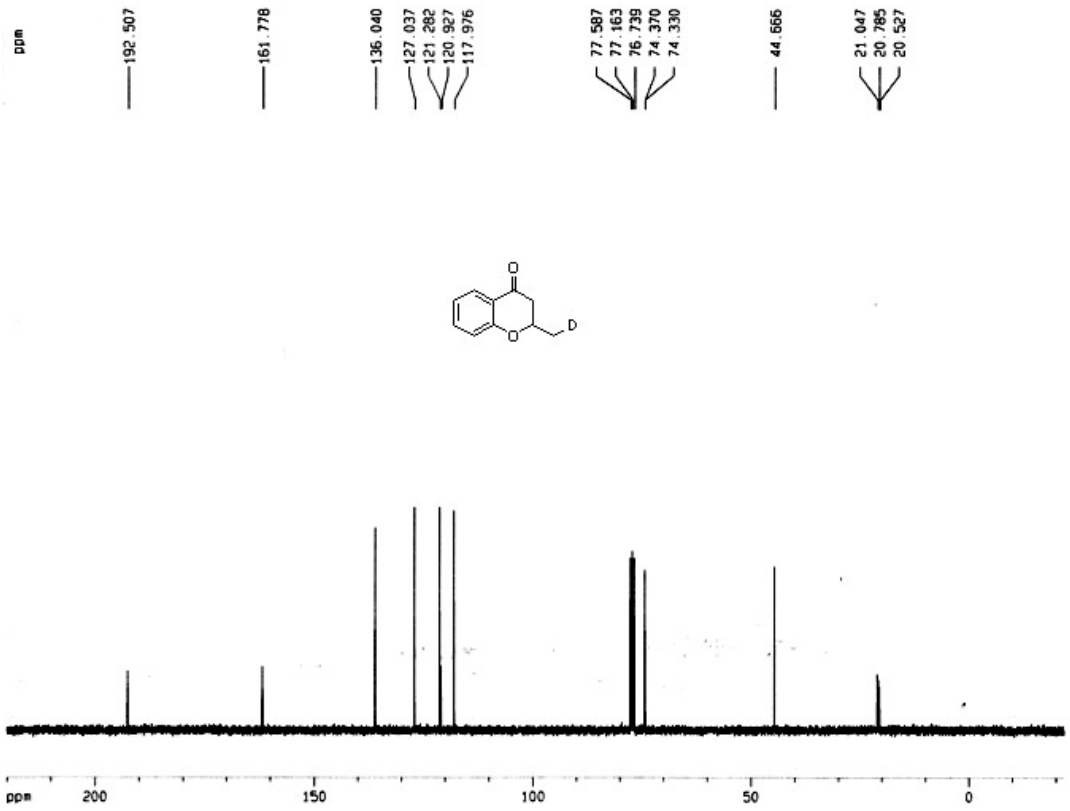
2a (^{13}C NMR)



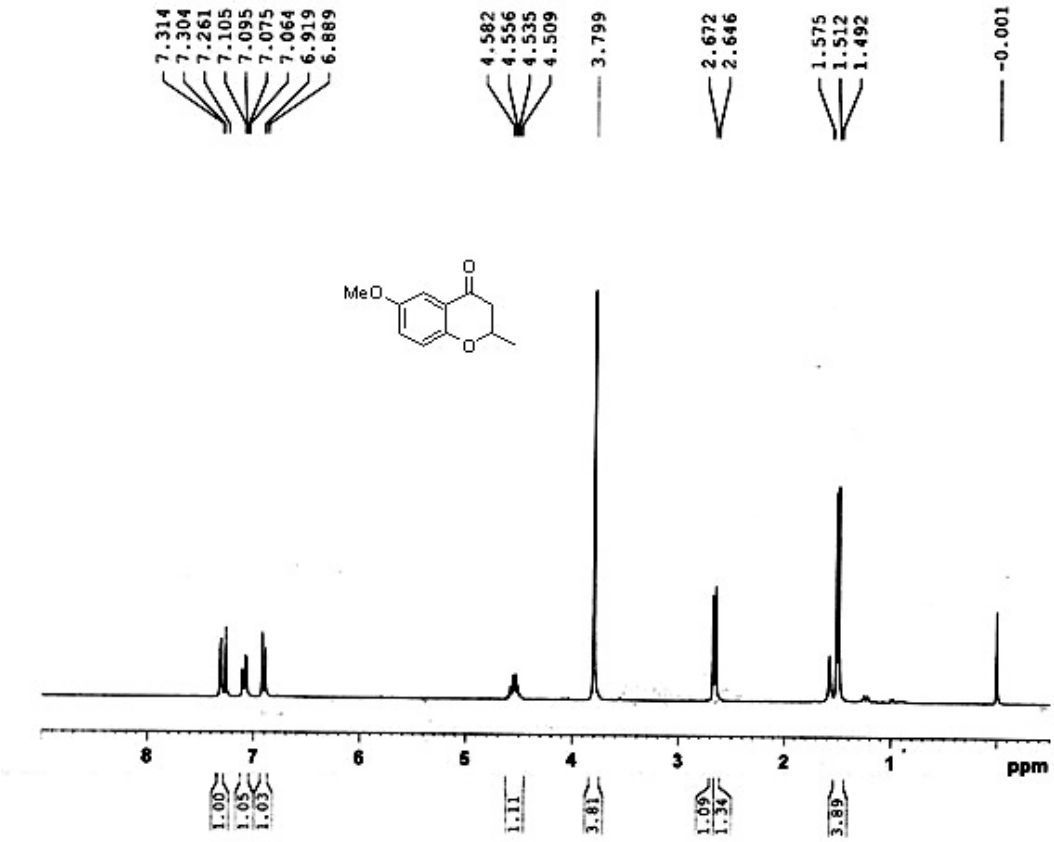
2a-*d* (^{1}H NMR)



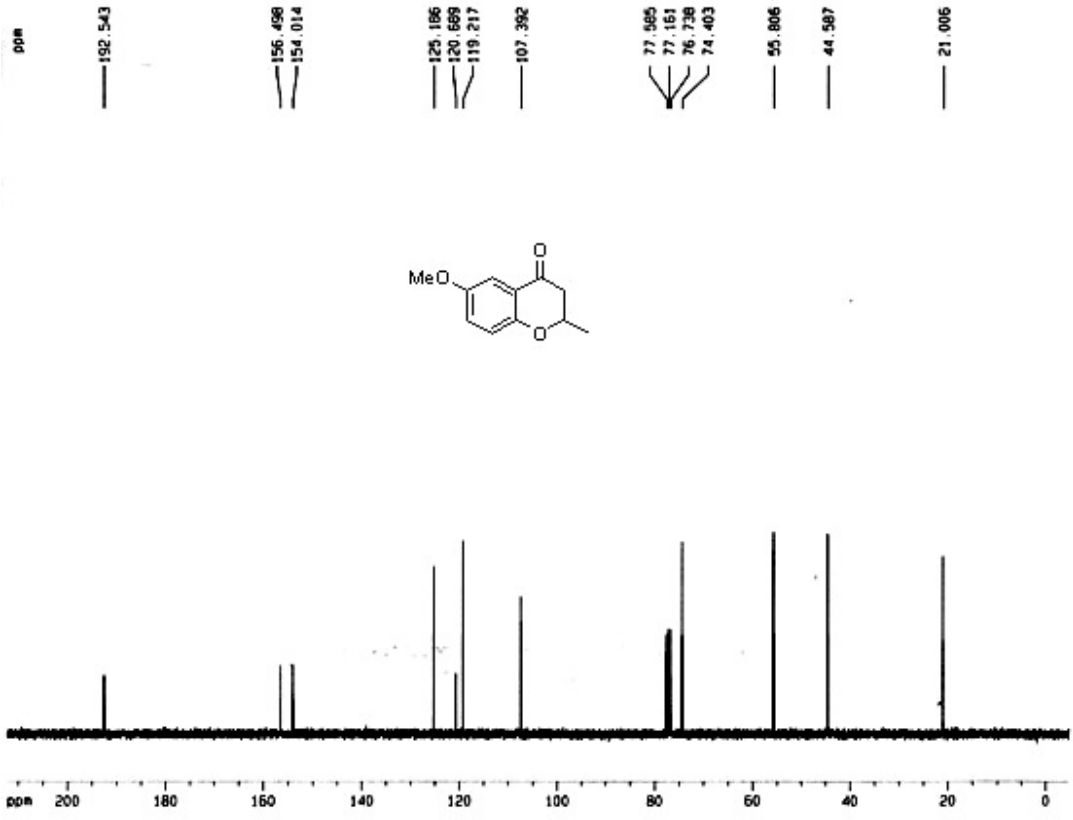
2a-*d* (^{13}C NMR)



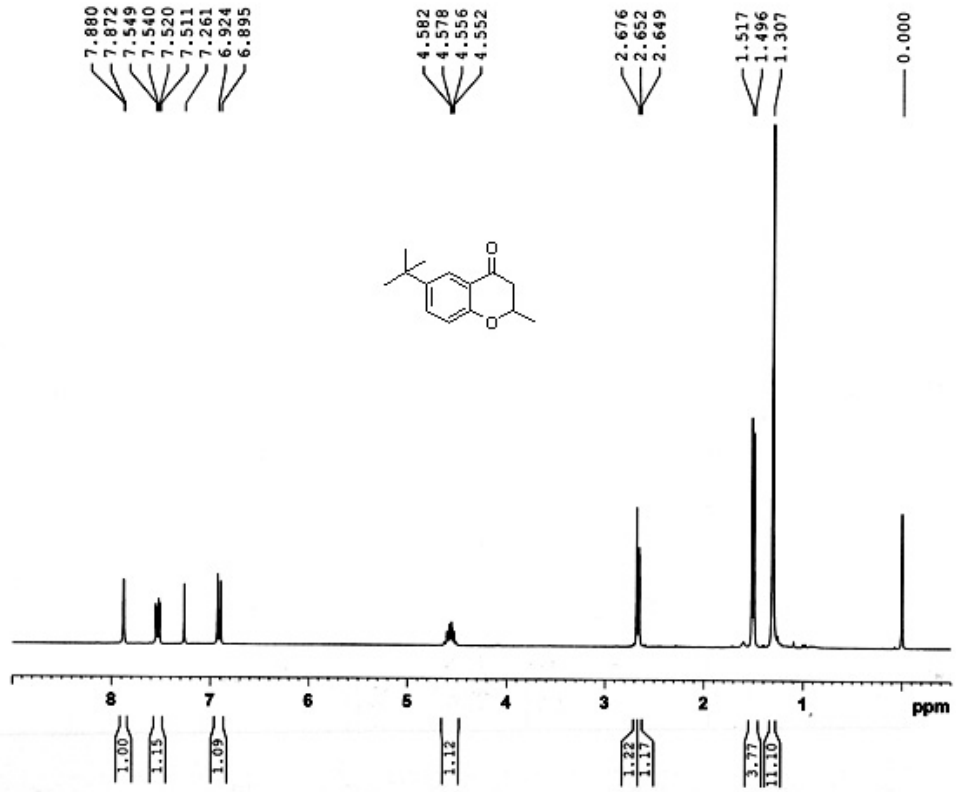
2b (^{1}H NMR)



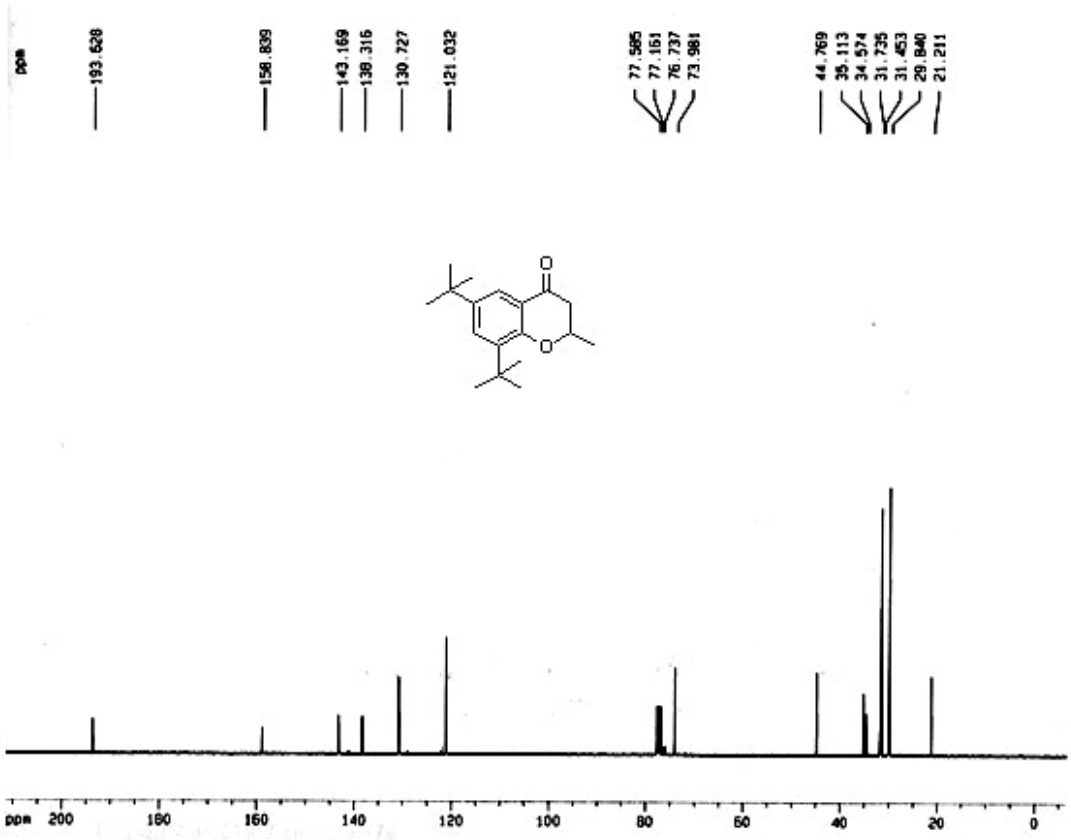
2b (^{13}C NMR)



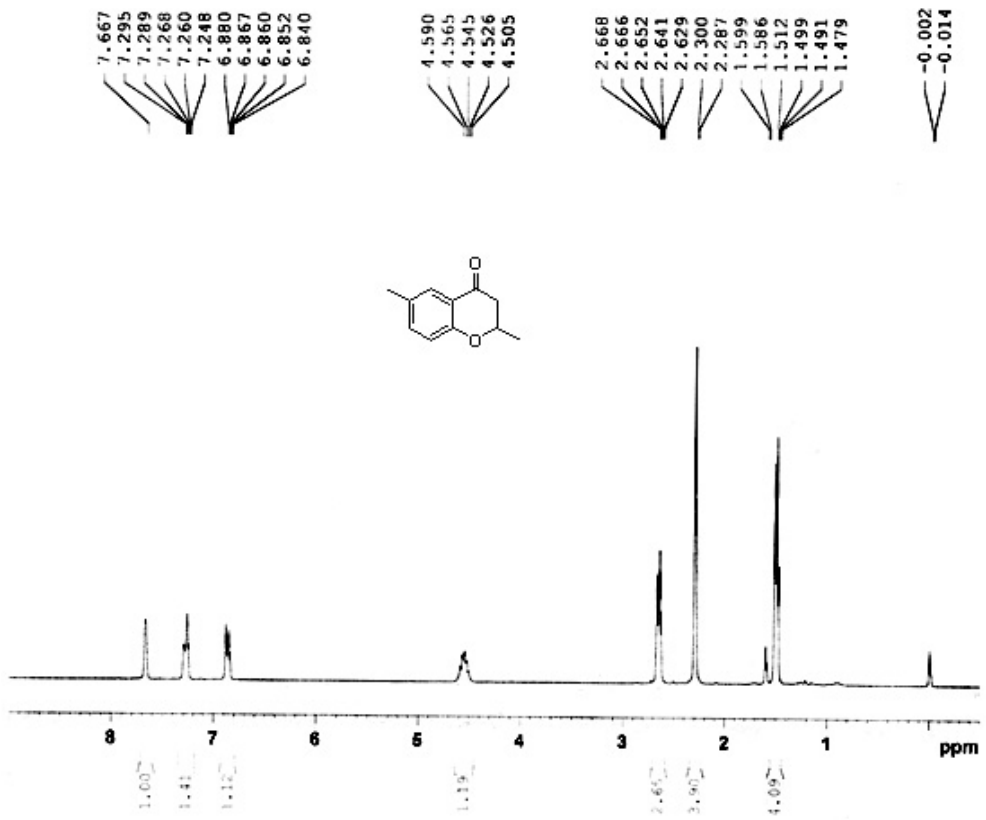
2c (^{1}H NMR)



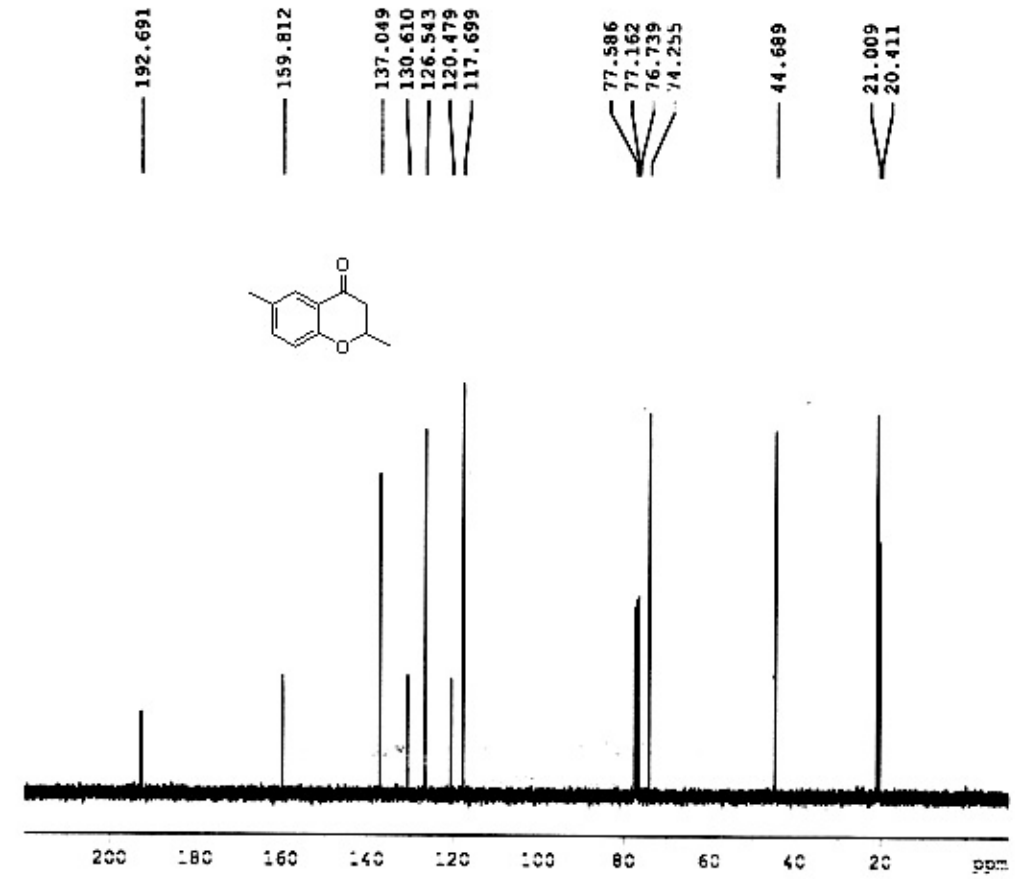
2c (^{13}CNMR)



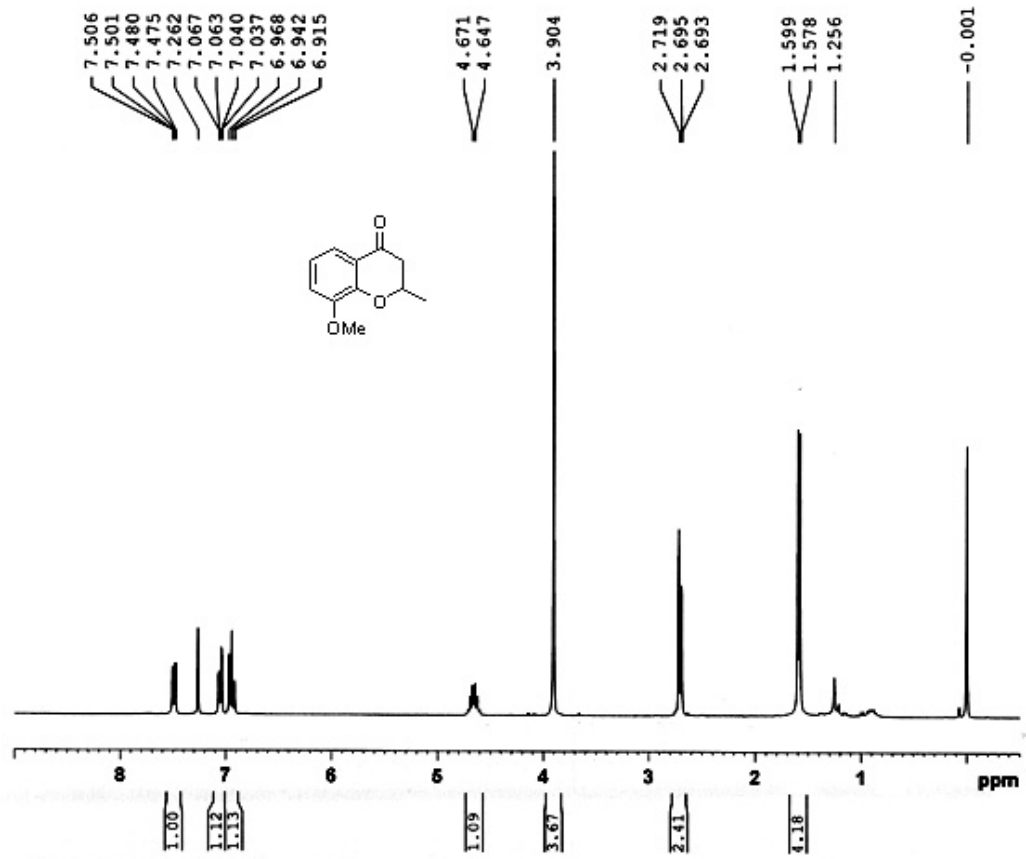
2d (^{1}HNMR)



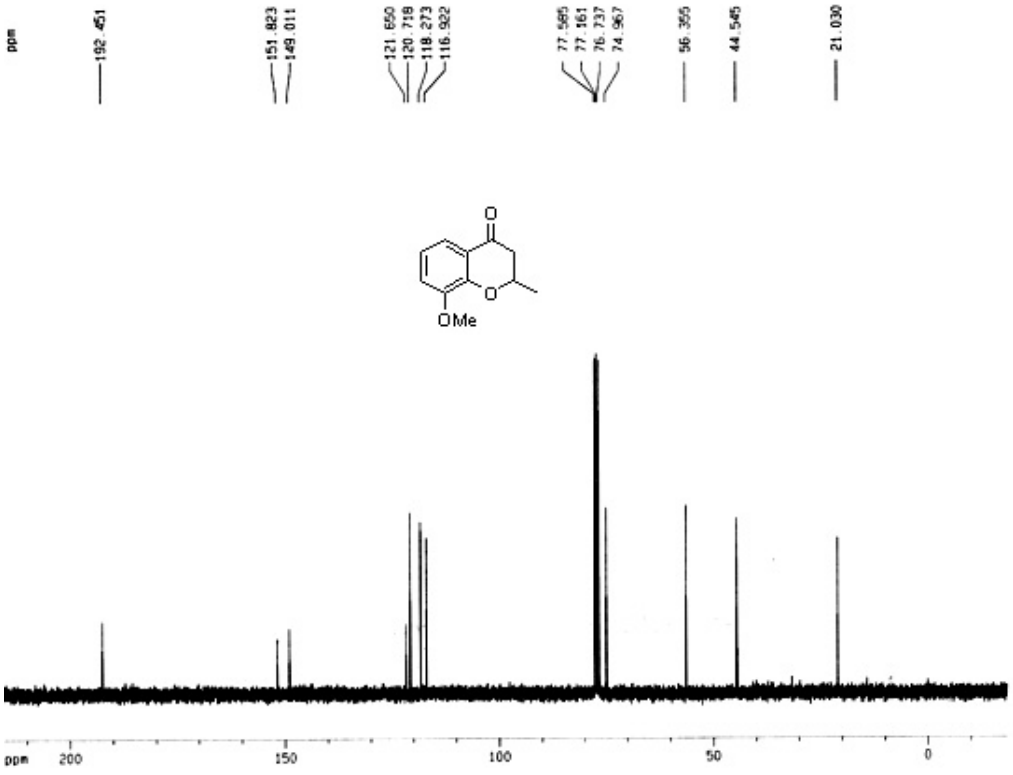
2d (^{13}C NMR)



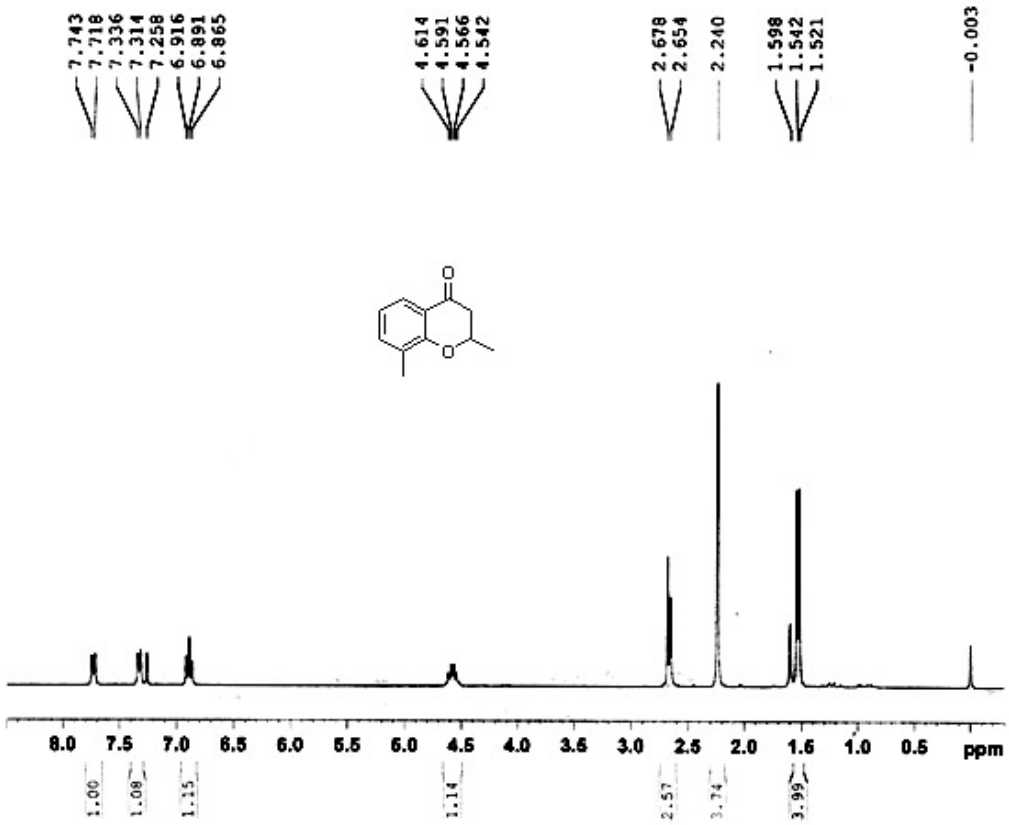
2e (^{1}H NMR)



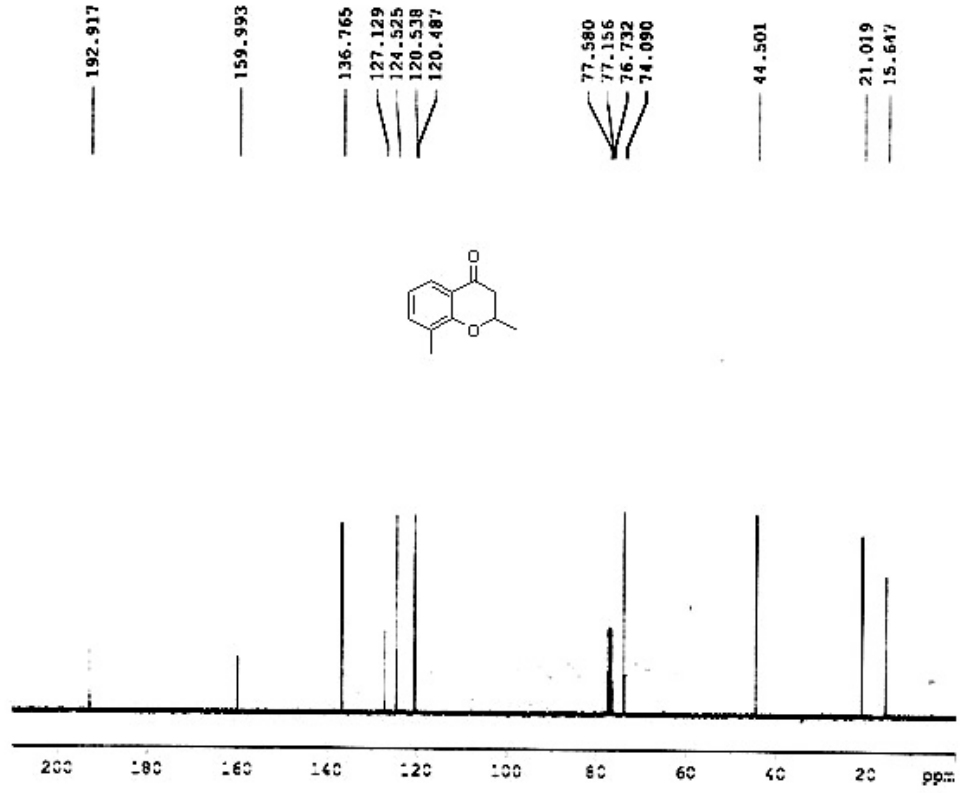
2e (^{13}C NMR)



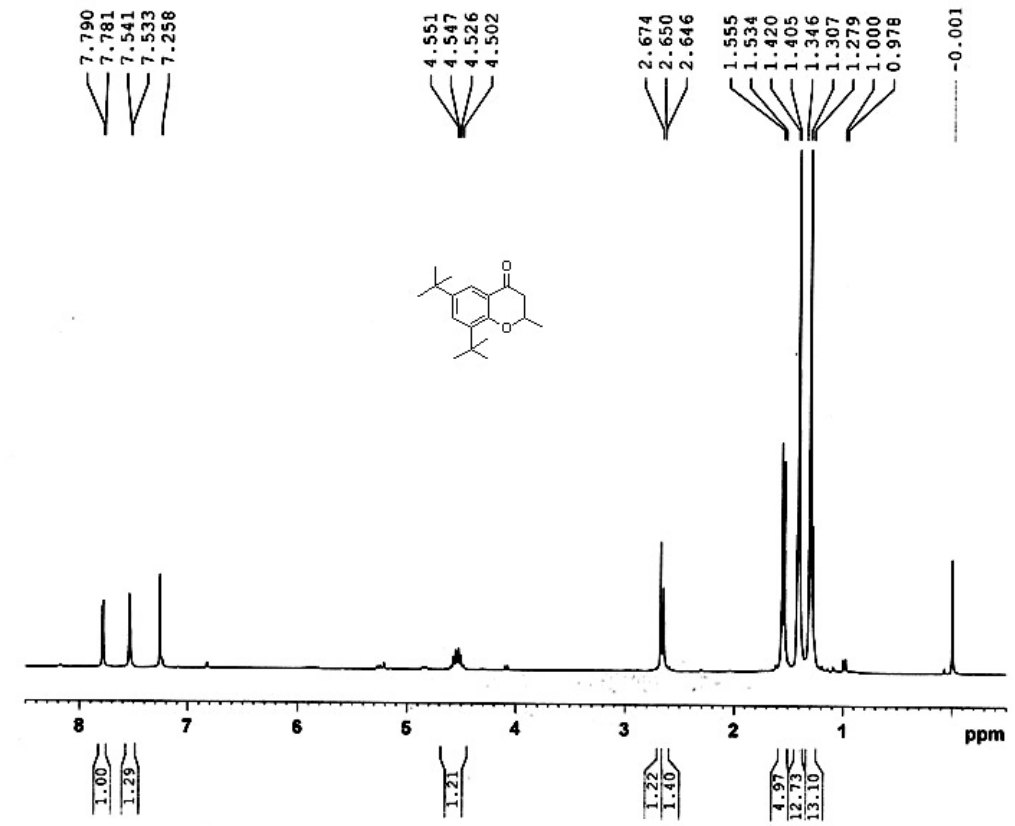
2f (^{1}H NMR)



2f (^{13}C NMR)



2g (^{1}H NMR)



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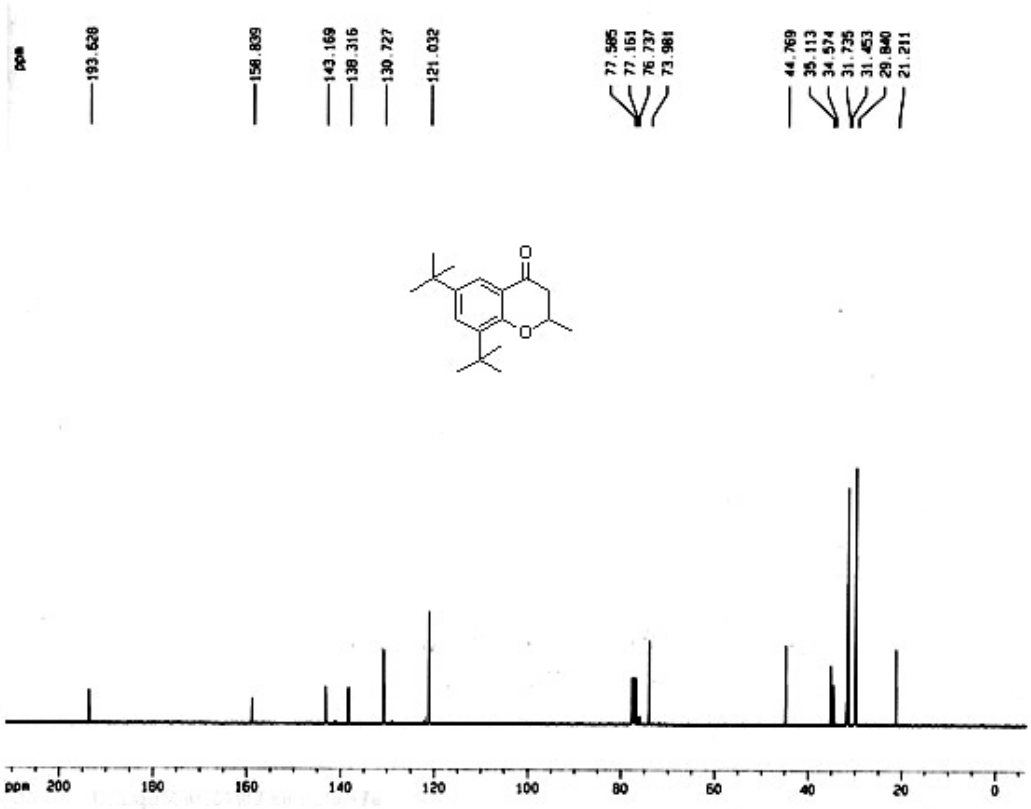
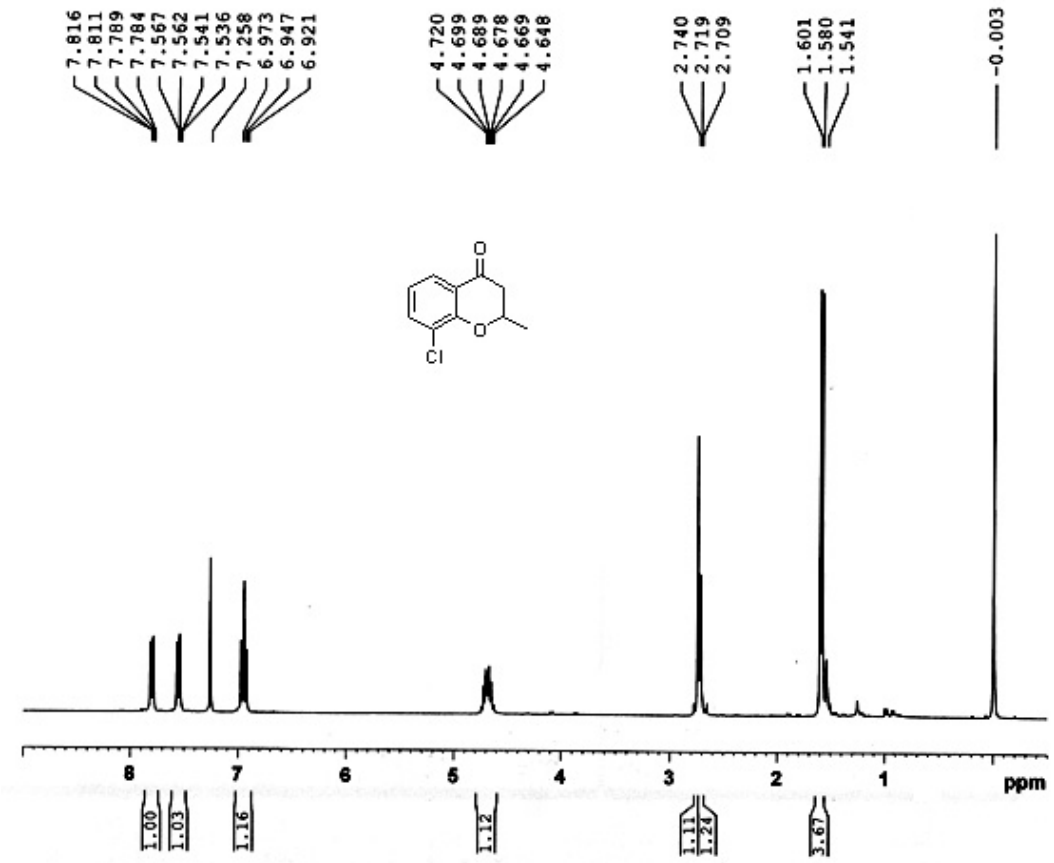
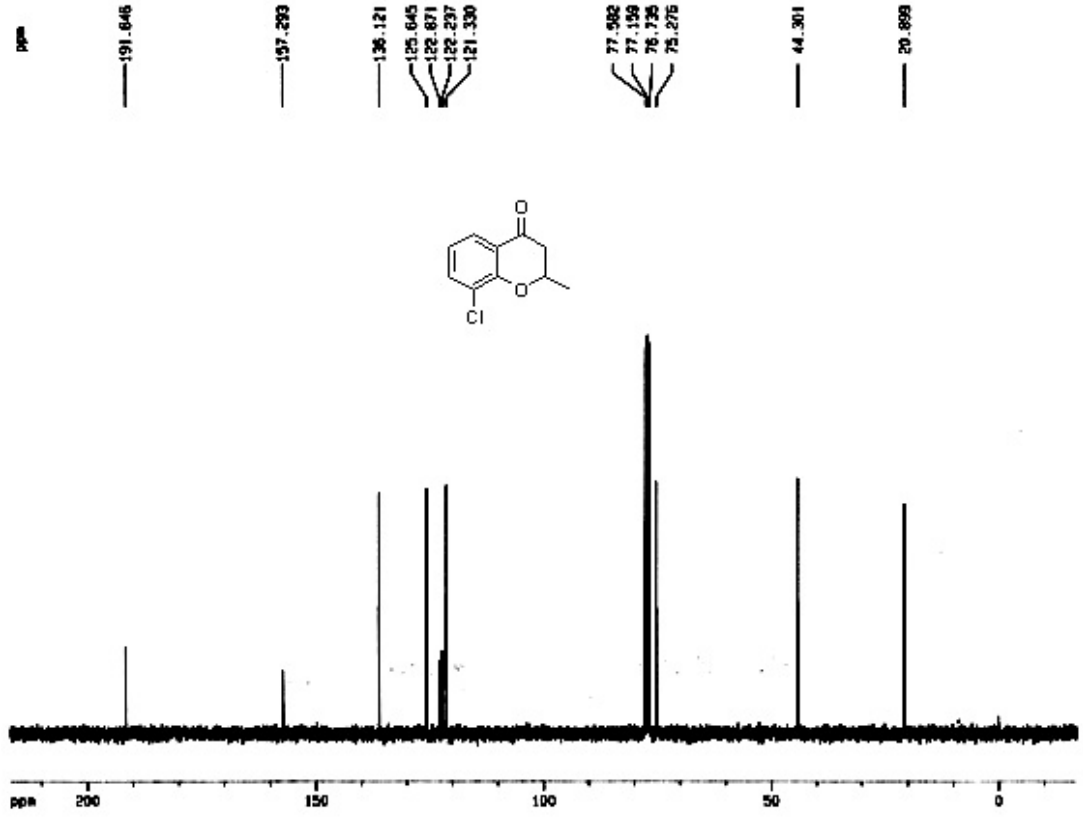


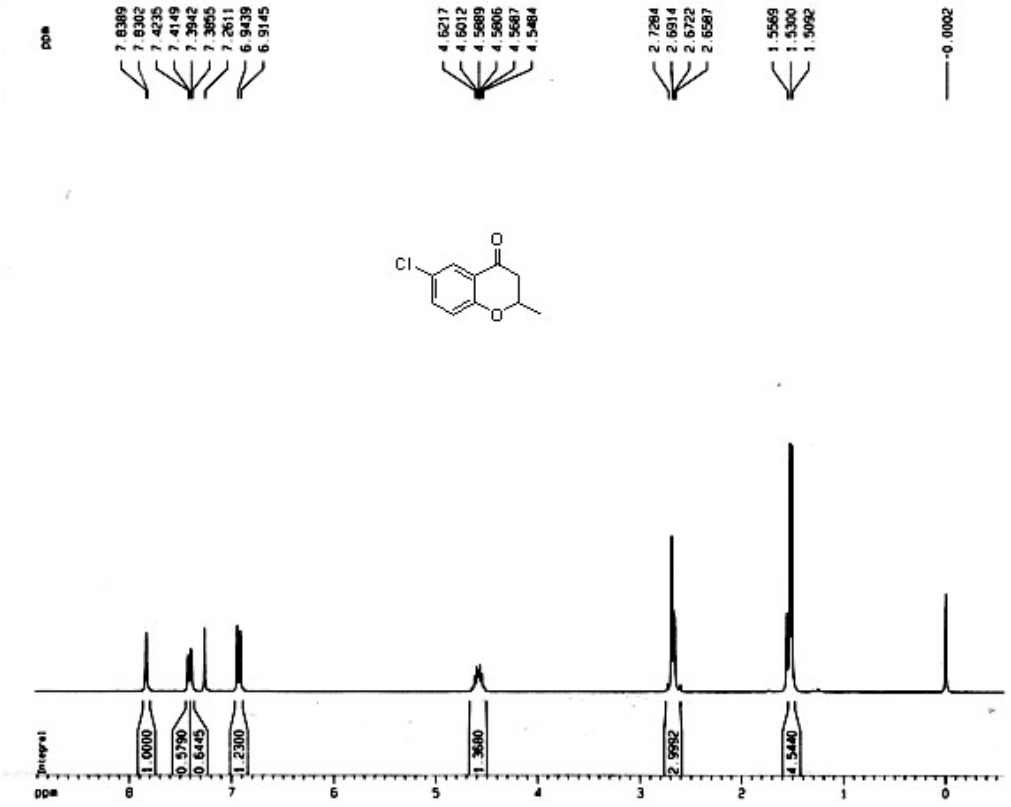
2h (^{1}H NMR)



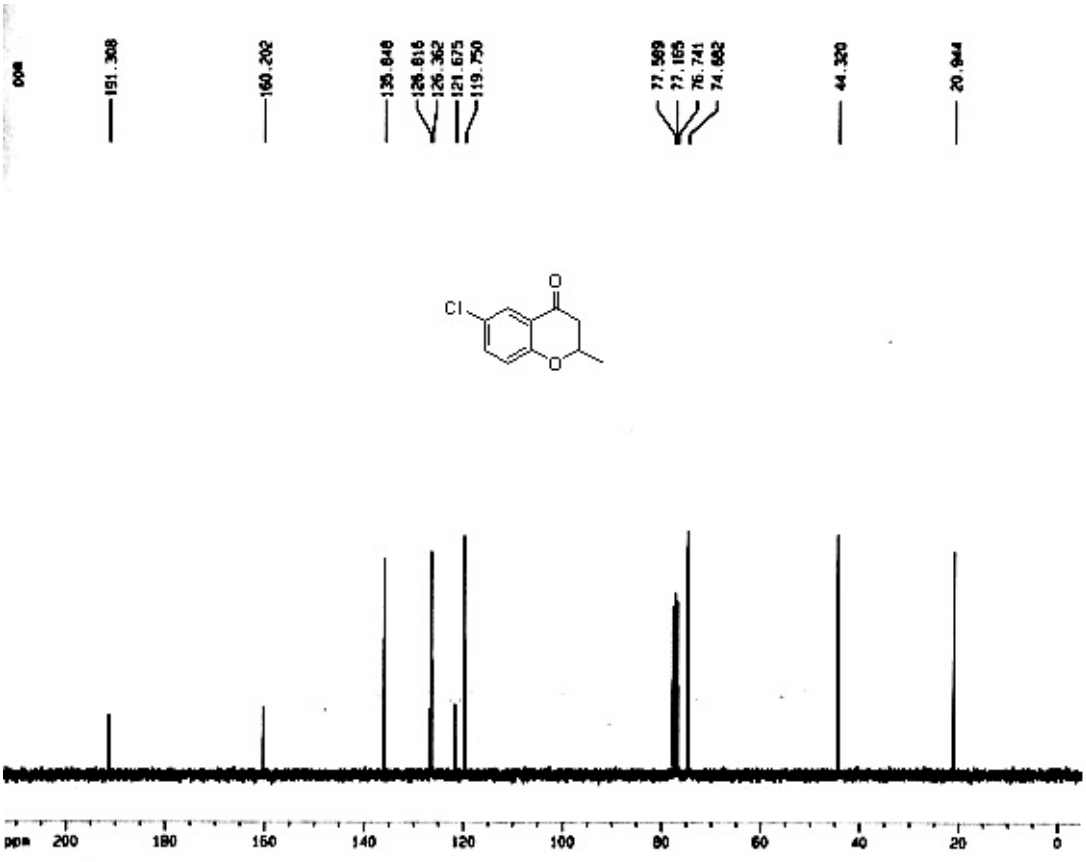
2h (^{13}C NMR)



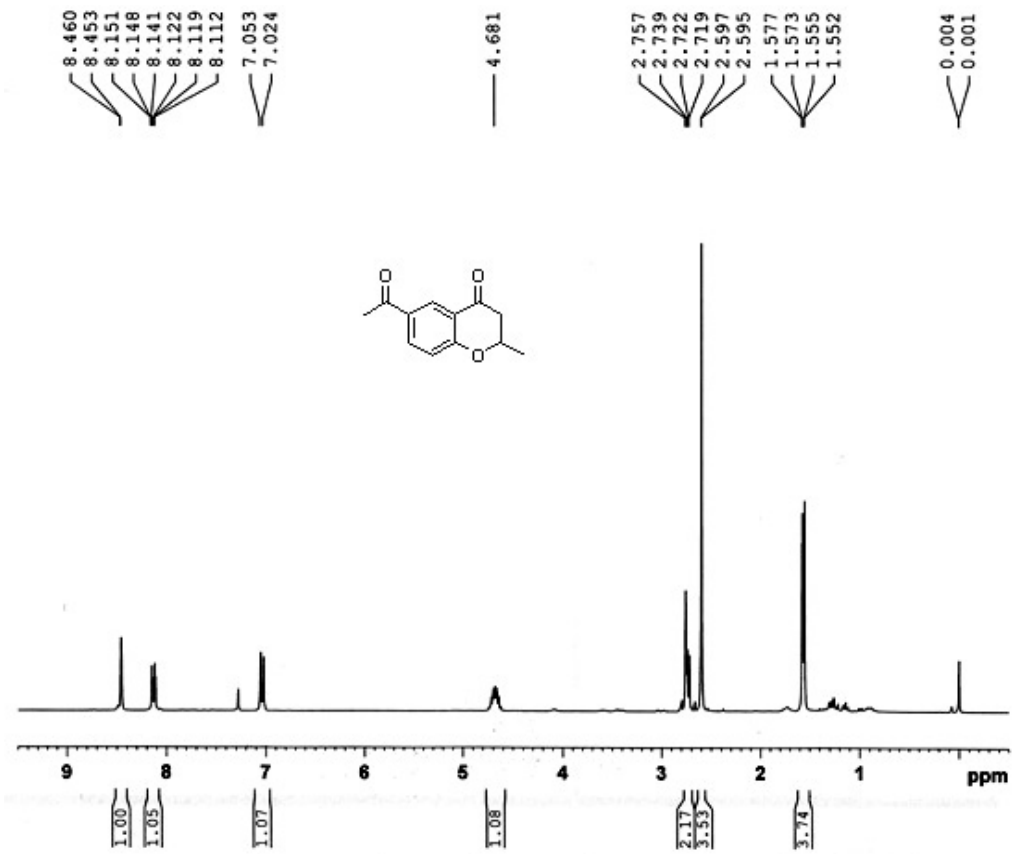
2i (^{1}H NMR)



2i (^{13}C NMR)



2j (^{1}H NMR)



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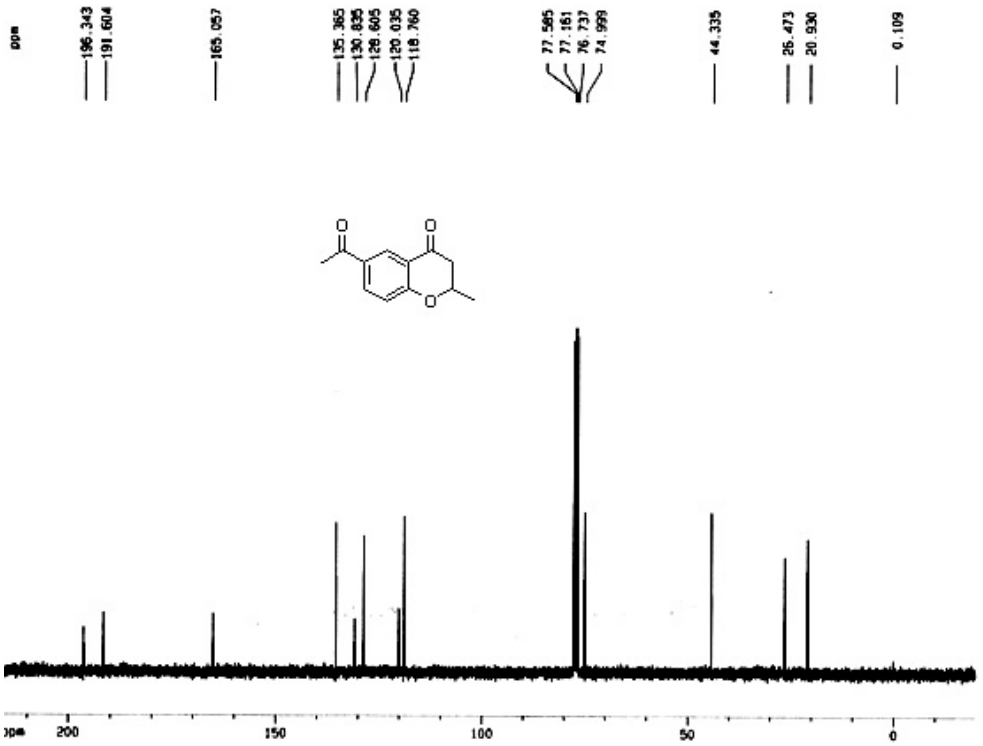

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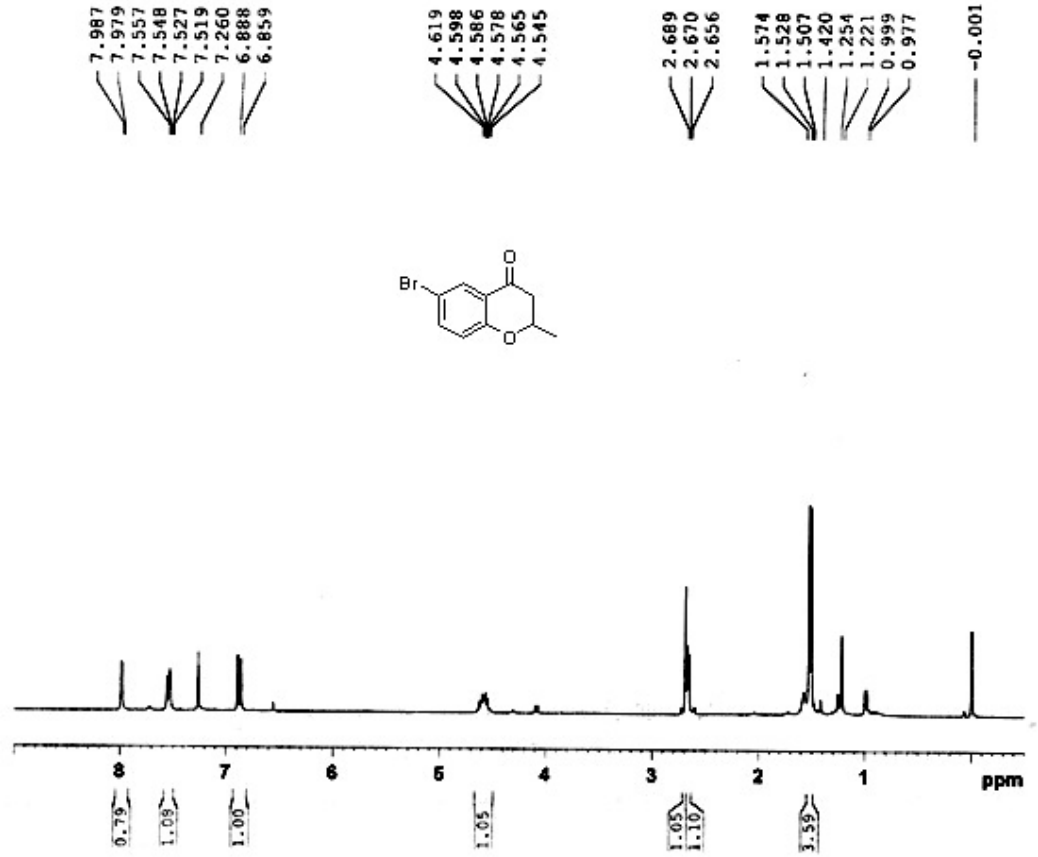

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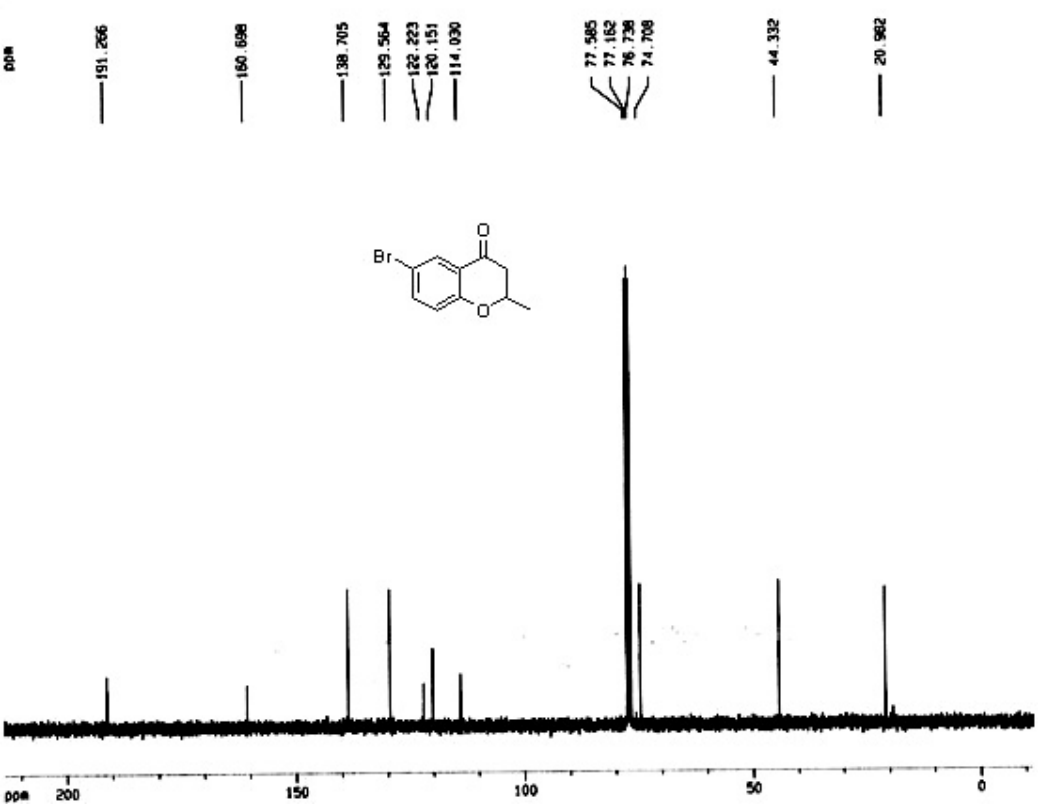

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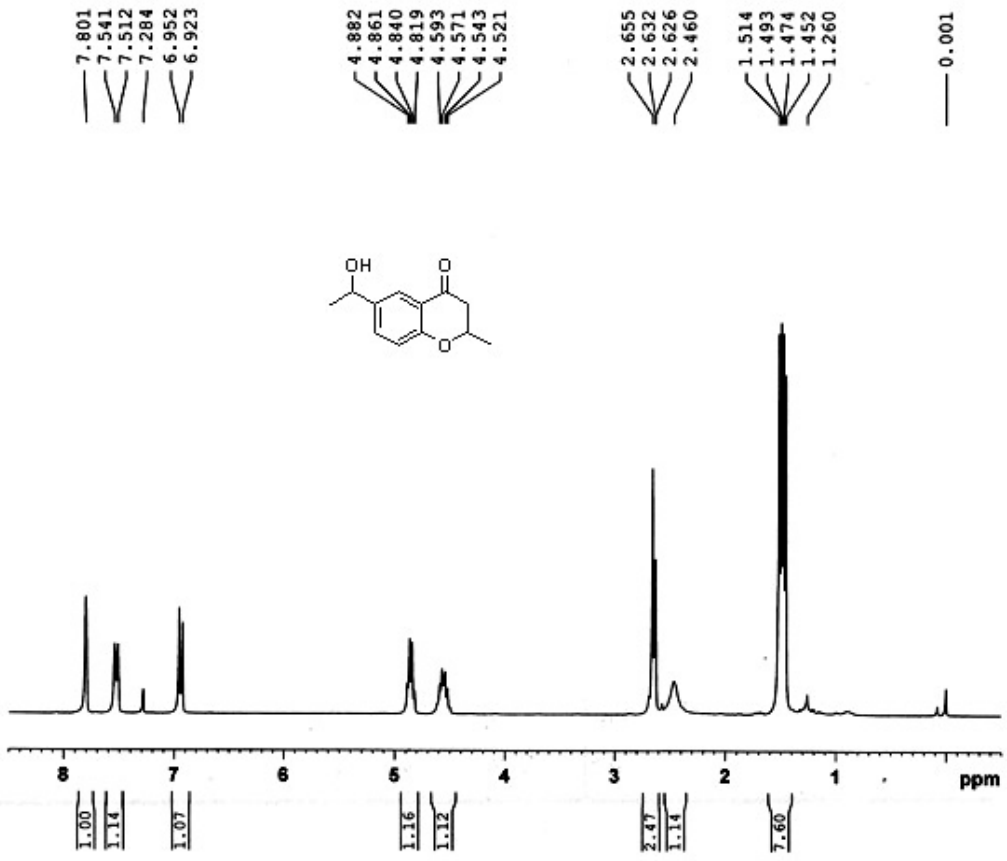

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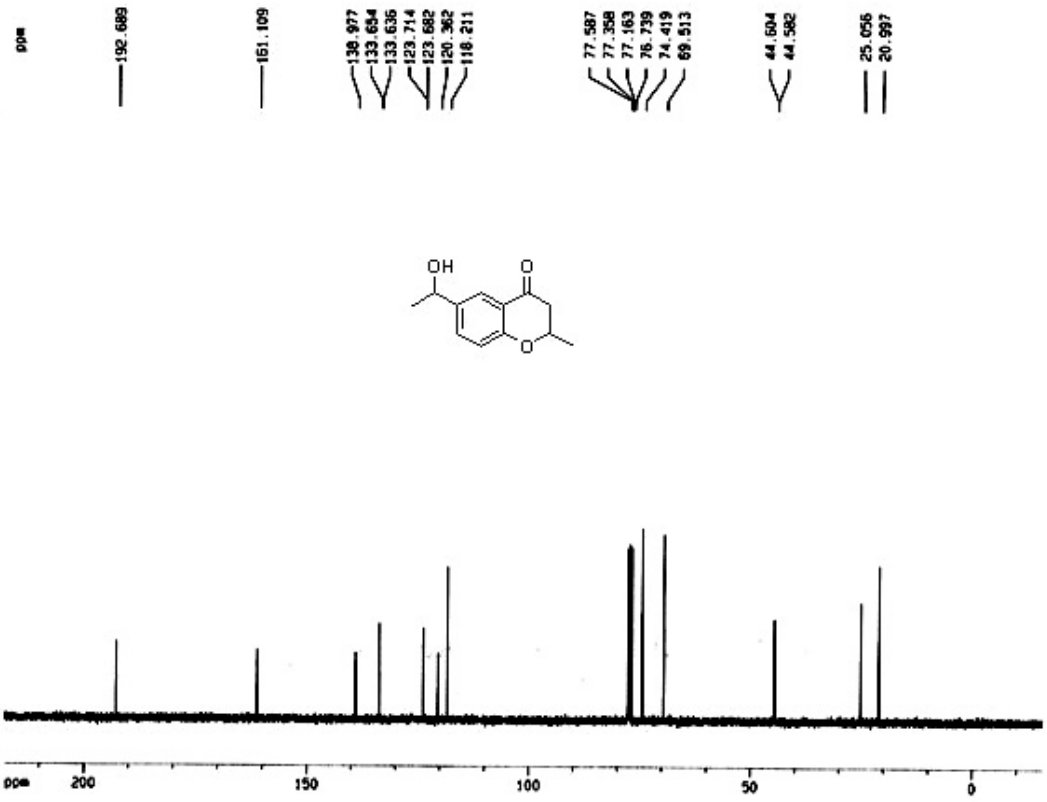
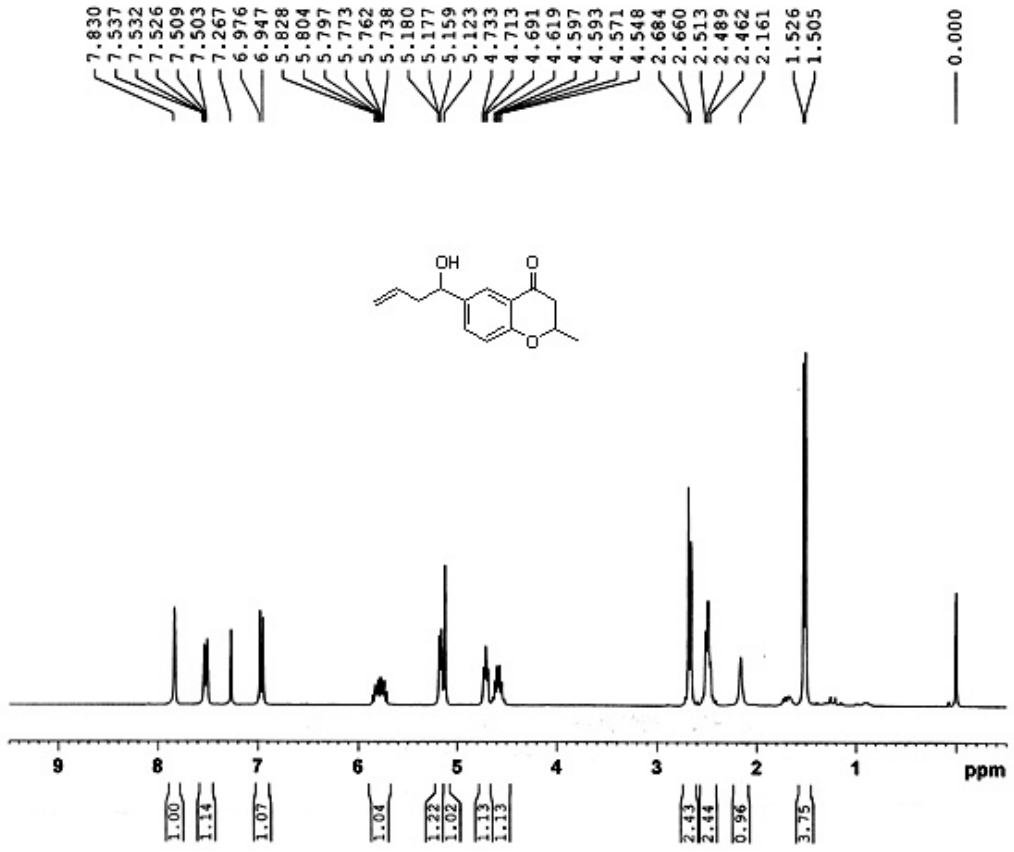
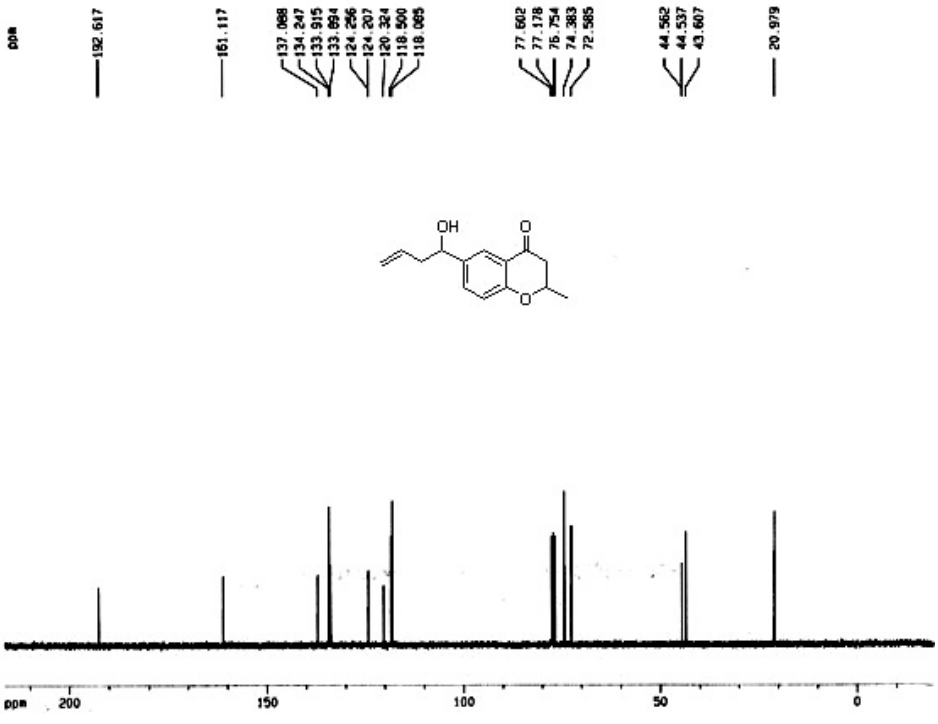


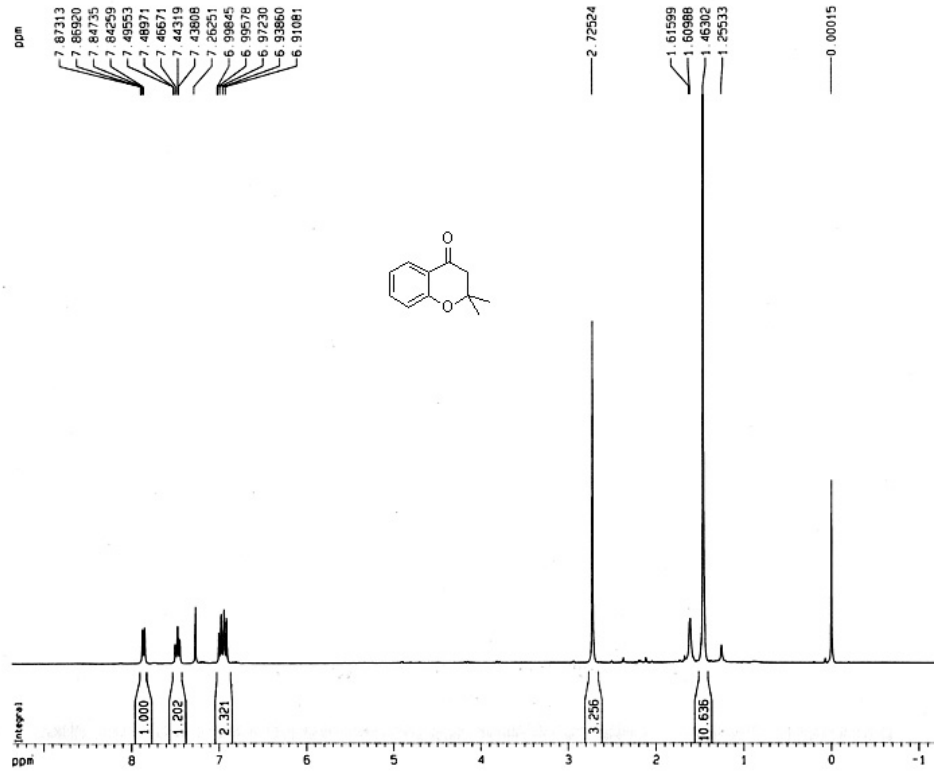
2m (^{1}H NMR)



2m (^{13}C NMR)



2n (^{1}H NMR)



2n (^{13}C NMR)