Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

A facile route to flavone and neoflavone backbones via a regioselective palladium catalyzed oxidative Heck reaction

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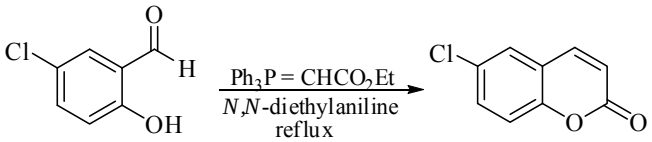
1 General remarks

All commercially available reagents were used without further purification. Solvents were dried and distilled by standard procedures. Coumarines, Palladium (II) and other reagents were purchased from Acros Organics. 6-Chlorocoumarin and chromenone derivatives were synthesized according to the reported methods.[1,2] Column chromatography was carried out on silica gel. TLC was conducted on silica gel 250 micron, F_{254} plates. ^{1}H NMR spectra were recorded on a Bruker 500 MHz NMR instrument. Chemical shifts are reported in ppm with TMS as an internal standard (TMS: δ 0.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), integration and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Bruker 125 MHz NMR spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent as internal standard ($CDCl_3$: δ = 77.0 ppm; DMSO-d_6: δ = 39.5 ppm).

2 General experimental details

2-1 Synthesis of coumarin 1g

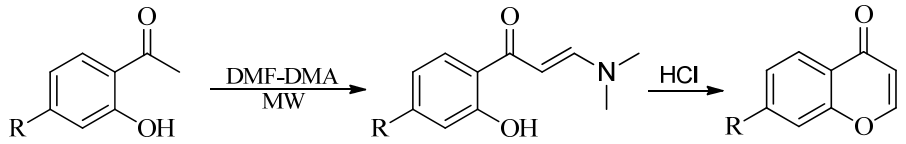


1g

6-chloro-2*H*-chromen-2-one **1g** was synthesized by the Wittig reaction of 6-chloro-2-hydroxybenzaldehyde with the Wittig reagent, ethyl(triphenylphosphoranylidene)acetate in *N,N'*-diethylaniline under reflux. 6-chloro-2-hydroxybenzaldehyde (1 mmol) and ethyl(triphenylphosphoranylidene)acetate (1.2 mmol) were dissolved in *N,N'*-diethylaniline (15 ml) and the resulting mixture was stirred at reflux for 4 h. The solvent was removed under reduced pressure and the resulting brown oil was purified by column chromatography (EtOAc/hexanes)[1].

[1] D. Maes, M. Eugenia Riveiro, C. Shayo, C. Davio, S. Debenedetti, N. De Kimpe, Tetrahedron 64 (**2008**) 4438-4443.

2-2 Synthesis of chromenones



8a-8b
R= H, OH

9a-9c
R= H, OH, OMe

6a-6b
R= H, OMe

A mixture of 2-hydroxyacetophenone (5 mmol, 0.6 mL) and *N*,*N*-dimethylformamide-dimethylacetal (1 equiv, 0.66 mL) was irradiated under microwave for 15 s (300 W max, T=115 ^{o}C). The resulting mixture was cooled at room temperature and crystallized in hexane to give the enamine intermediate **9** (red crystals). When the reaction was performed in the presence of 2,4-dihydroxyacetophenone, an additional O-methylation of hydroxyl group was happened[2].

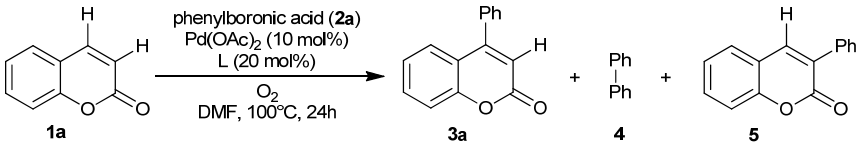
To the solution of the enamine **9** (1 g, 5.24 mmol) in methylene chloride (40 mL) was added concentrated HCl (4 mL). The resulting mixture was refluxed for 1 h. After cooling, the mixture was extracted with methylene chloride (3×40 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution, then with brine, dried over $MgSO_4$, filtered and concentrated to afford corresponding chromenone **6**.[2]

[2] M. Spadafora, V. Y. Postupalenko, V. V. Shvadchak, A. S. Klymchenko, Y. Me´ly, A. Burger, R. Benhida, Tetrahedron 65 (**2009**) 7809–7816

3 Oxidative Heck Reaction

3-1 Screening of reaction conditions

Table S1. Effect of Ligands on the Cross-Coupling Reaction of Phenylboronic acid with Coumarin **1a**



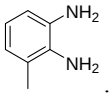
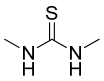
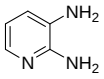
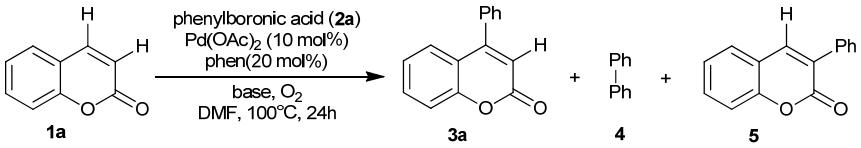
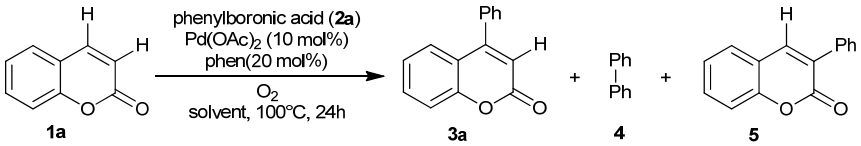
Entry	Ligand 20 mol%	Yield **3a**	**5**	**4**
1	phen.	85	0	10
2	dmphen	15	0	70
3	dmap	40	0	20
4	bpy	62	0	30
5	PPh_3	10	0	25
6		0	0	73
7		0	0	8
8		0	0	64

Table S2. Effect of Bases on the Cross-Coupling Reaction of Phenylboronic acid with Coumarin **1a**



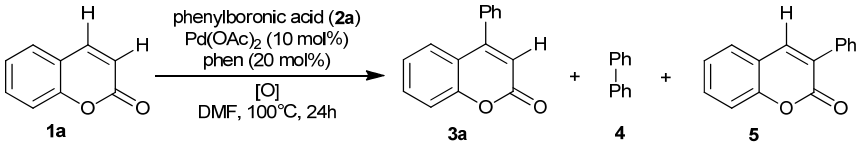
Entry	Base (2.0 equiv)	Yield **3a**	**5**	**4**
1	—	85	0	10
2	K_2CO_3	5	0	85
3	KOAc	5	0	90
4	Na_2CO_3	0	0	80
5	KF	0	0	92
6	K_2HPO_4	5	0	90
7	DABCO	5	0	80

Table S3. Effect of Solvents on the Cross-Coupling Reaction of Phenylboronic acid with Coumarin **1a**



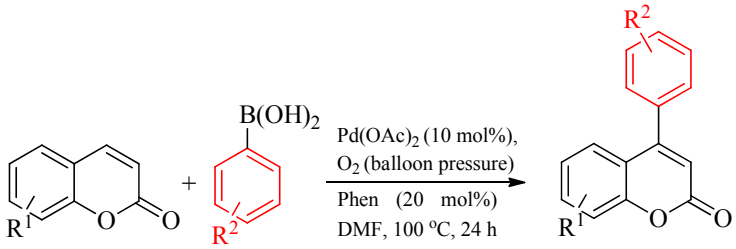
Entry	Solvent	Yield		
		3a	**5**	**4**
1	DMF	85	0	10
2	Dioxone	68	0	15
3	toluene	No Reaction		
4	TFA	No Reaction		
5	ACN	14	0	0
6	DMF/TFA 2.5/0.5	No Reaction		
7	AcOH	No Reaction		
4	TFA	No Reaction		
8	DMF/TFA 2.5/0.5	0	0	73

Table S4. Effect of Oxidant on the Cross-Coupling Reaction of Phenylboronic acid with Coumarin **1a**



Entry	Oxidant	Yield		
		3a	**5**	**4**
1	O_2	85	0	10
2	$Na_2S_2O_8$ (3 eq)	0	0	90
3	BQ (3 eq)	0	0	20
4	$Cu(OAc)_2$ (3 eq)	15	0	10

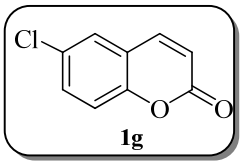
3-2 General procedure for direct arylation of coumarins and chromenones



Coumarin (0.20 mmol), $Pd(OAc)_2$ (10 mol%) and 1,10-phenanthroline (6 mg, 0.02 mmol) were combined in dried DMF (0.15 mL) under O_2 and stirred for 5 min (*Note: DMF was dried over calcium hydride for 24 hours and then distilled under vacuum*). The reaction mixture was heated to 100 ^{o}C and the aryl boronic acid (0.1 mmol) in DMF (0.10 mL) was added slowly over 2 h (every 30 minutes) to reduce the homo-coupling product of aryl boronic acid. The reaction was stirred and monitored by TLC using EtOAc: petroleum ether (2:8) as the mobile phase. After completion, the reaction mixture was diluted with EtOAc (8 mL). After stirring this mixture for 5 min the precipitate was filtered over Celite using EtOAc as the eluent. The filtrate was concentrated and purified by chromatography on silica gel (EtOAc/hexanes).

4 Experimental characterization data

4-1 Starting materials



1g

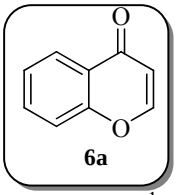
6-chloro-2*H*-chromen-2-one (1g). mp 153–155 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.48 (d, 1H, *J*= 9.5 Hz, H_3), 7.29 (d, 1H, *J*=7.0 Hz, H_8), 7.48-7.50 (m, 2H, $H_{5,7}$), 7.65 (d, 1H, *J*= 9.5 Hz, H_4). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 117.3, 117.8, 119.3, 126.6, 129.2, 131.3, 141.7, 151.9, 159.5.

(*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)-prop-2-en-1-one (9)

mp 130–131 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.95 (s, 3H, N-Me), 3.17 (s, 3H, N-Me), 5.76 (d, 1H, *J*= 12.1 Hz), 6.81 (dt, 1H, *J*=1.0 and 7.1 Hz), 6.92 (dd, 1H, *J*= 0.9 and 8.4 Hz), 7.30 (dt, 1H, *J*= 1.5 and 8.4 Hz), 7.69 (dd, 1H, *J*= 1.4 and 8.0 Hz), 7.87 (d, 1H, *J*= 12.0 Hz), 13.99 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.5, 45.5, 90.1, 118.1, 118.3, 120.4, 128.3, 134.0, 154.9, 163.0, 191.6.

(*E*)-3-dimethylamino-1-(2-hydroxy-4-methoxy)-phenylpropenone (10)

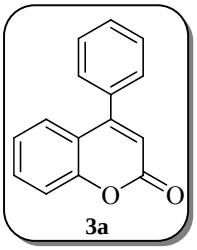
mp 130–133 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, 1H, *J* = 12.0 Hz, CH=CH), 7.61 (d, 1H, *J* = 9.2 Hz, Ph), 6.41 (d, 1H, *J* = 2.4 Hz, Ph), 6.38 (dd, 1H, *J* = 2.4 and 9.2 Hz, Ph), 5.68 (d, 1H, *J* = 12.0 Hz, CH=CH), 3.82 (s, 3H, O-CH_3), 3.18 (s, 3H, N-CH_3), 2.96 (s, 3H, N-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.4, 45.4, 55.4, 89.8, 101.0, 106.4, 113.8, 129.7, 154.0, 164.3, 165.5, 190.6.



6a

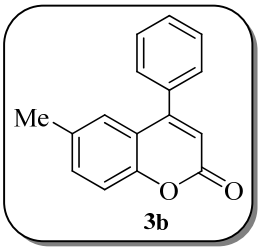
4*H*-chromen-4-one (6a). Yield 90%; mp 52–54 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.31 (d, 1H, *J*= 6.0 Hz), 7.33–7.44 (m, 2H), 7.63 (ddd, 1H, *J*= 1.8, 7.1 and 8.4 Hz), 7.83 (d, 1H, *J*= 6.0 Hz), 8.18 (dd, 1H, *J*= 1.5 and 7.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 113.1, 118.3, 125.0, 125.3, 125.9, 133.8, 155.4, 156.6, 177.7.

4-2 Coumarins 3a-3n



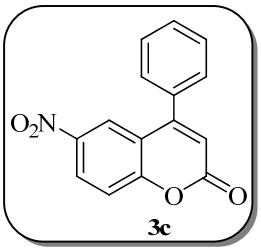
3a

4-phenyl-2*H*-chromen-2-one (3a). Yield 75%; Oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.39 (s, 1H, H_3 coumarin), 7.24 (t, 1H, *J* = 7.4 Hz, H_6 coumarin), 7.40-7.57 (m, 8H, H Ph and H coumarin); ^{13}C NMR (125 MHz, $CDCl_3$) δ 115.1, 117.3, 124.2, 126.9, 128.4, 128.9, 129.7, 130.9, 131.9, 135.2, 154.2, 155.7, 160.8; IR (KBr): 1730 (C=O) cm^{-1}. Anal.Calcd for $C_{15}H_{10}O_2$: C, 81.07; H, 4.54. Found: C, 81.31; H, 4.20.



3b

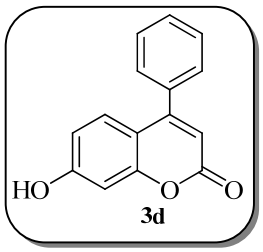
6-methyl-4-phenyl-2*H*-chromen-2-one (3b). Yield 88%; Oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.35 (s, 3H, CH_3), 6.37 (s, 1H, H_3 coumarin), 7.27 (d, 1H, *J* = 1.8 Hz, H_5 coumarin), 7.31 (d, 1H, *J*= 8.4 Hz, H_8 coumarin), 7.36 (dd, 1H, *J* = 1.8, *J* = 8.4 Hz, H_7 coumarin), 7.48-7.43 (m, 2H, H Ph), 7.56-7.53 (m, 3H, H Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.9, 115.1, 117.0, 118.6, 126.7, 128.4, 128.8, 129.6, 132.9, 133.9, 135.3, 152.3, 155.6, 160.9; IR (KBr): 1732 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.19; H, 5.38.



3c

6-nitro-4-phenyl-2*H*-chromen-2-one (3c). Yield 72%, mp 208-210 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.53 (s, 1H, H_3 coumarin), 7.47-7.49 (m, 3H, H Ph), 7.47-7.49 (m, 5H, H Ph), 7.60 (dd, 1H, *J* = 2.2, *J* = 6.0 Hz, H_8 coumarin), 8.42-8.44 (m, 2H, $H_{5,7}$ coumarin); ^{13}C NMR (125 MHz,

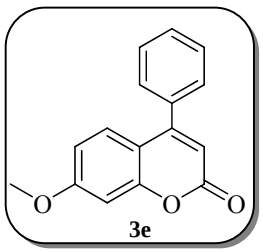
$CDCl_3$) δ 158.0, 157.7, 154.6, 143.9, 133.7, 130.5, 129.4, 128.2, 126.7, 123.0, 118.5, 116.7; IR (KBr): 1731 (C=O), 1333 and 1516 (NO_2); MS, *m/z* (%) 267 ($M^{\bullet+}$, 100), 239 (66), 193 (40), 165 (98); Anal. Calcd for $C_{15}H_9NO_4$: C, 67.42; H, 3.39; N, 5.24. Found: C, 67.13; H, 3.54; N, 5.06.



3d

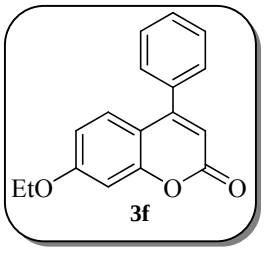
7-hydroxy-4-phenyl-2*H*-chromen-2-one (3d)

Yield 68%, mp 210-212 ºC; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 6.15 (s, 1H, H_3 coumarin), 6.79 (m, 2H, H_6 and H_8 coumarin), 7.27 (d, 1H, *J* = 7.8 Hz, H_5 coumarin), 7.51-7.56 (m, 5H, H Ph), 10.64 (s, 1H, OH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 102.6, 110.3, 110.6, 113.2, 128.0, 128.3, 128.7, 129.5, 135.1, 155.3, 155.5, 160.0, 161.3; IR (KBr): 3445 (OH), 1694 (C=O) cm^{-1} . Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.37; H, 4.59.



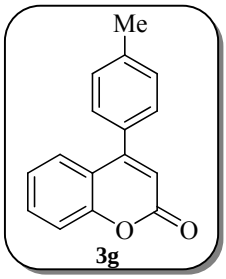
3e

7-methoxy-4-phenyl-2*H*-chromen-2-one (3e). Yield 70%, mp 114-116 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.89 (s, 3H, O-CH_3), 6.22 (s, 1H, H_3 coumarin), 6.79 (dd, 1H, *J* = 2.6, 8.8 Hz, H_6 coumarin), 6.90 (d, 1H, *J*= 2.6 Hz, H_8 coumarin), 7.38 (d, 1H, *J* = 8.8 Hz, H_5 coumarin), 7.45-7.42 (m, 2H, H Ph), 7.53-7.50 (m, 3H, H Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.8. 101.1, 111.8, 112.3, 127.9, 128.3, 128.8, 129.6, 130.9, 132.3, 135.6, 155.8, 161.2, 162.8; IR (KBr): 1731 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: 76.32; H, 4.56.



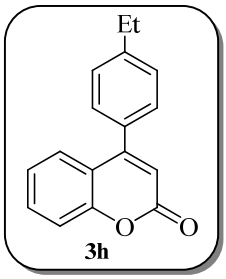
3f

7-ethoxy-4-phenyl-2*H*-chromen-2-one (3f).Yield 74%, mp 146-148 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (t, 3H, *J* = 4.5 Hz, CH_3), 4.11 (q, 2H, *J* = 4.5 Hz, O-CH_2), 6.23 (s, 1H, H_3 coumarin), 6.79 (dd, 1H, *J* = 2.5, 8.9 Hz, H_6 coumarin), 6.88 (d, 1H, *J*= 2.5 Hz, H_8 coumarin), 7.39 (d, 1H, *J* = 8.9 Hz, H_5 coumarin), 7.46-7.44 (m, 2H, H Ph), 7.53-7.52 (m, 3H, H Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.6, 64.2, 101.5, 111.7, 112.3, 112.7, 127.9, 128.4, 128.8, 129.5, 135.6, 155.9, 156.0, 161.3, 162.2; IR (KBr): 1730 (C=O) cm^{-1}; MS, *m/z* (%) 266 ($M^{\bullet+}$, 98), 238 (40), 210 (100), 181 (32); Anal. Calcd for $C_{17}H_{14}O_3$ (266.29): C, 76.68; H, 5.30. Found: 76.44; H, 5.19.



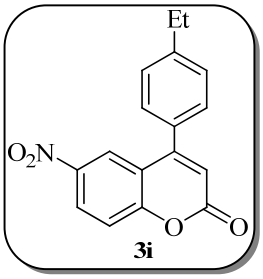
3g

4-*p*-tolyl-2*H*-chromen-2-one (3g). Yield 73%, mp 79-81 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.46 (s, 3H, CH_3), 6.38 (s, 1H, H_3 coumarin), 7.24 (t, 1H, *J* = 7.5 Hz, H_6 coumarin), 7.33-7.37 (m, 4H, H Ph), 7.42 (d, 1H, *J* = 8.1 Hz, H_8 coumarin), 7.53-7.57 (m, 2H, H_5 and H_7 coumarin); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 114.8, 117.3, 119.0, 124.1, 127.0, 128.4, 129.5, 131.8, 132.3, 139.9, 154.2, 155.7, 160.8; IR (KBr): 1733 (C=O) cm^{-1}. Anal.Calcd for $C_{16}H_{12}O_2$ (236.27): C, 81.34; H, 5.12. Found: C, 81.63; H, 5.32.



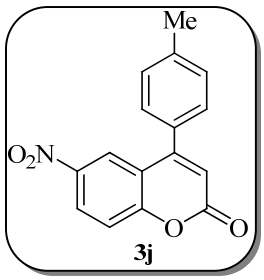
3h

4-(4-ethylphenyl)-2*H*-chromen-2-one (3h). Yield 76%; Oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (t, 3H, *J*= 7.6 Hz , CH_3), 2.77 (q, 2H, *J*= 7.6 Hz, CH_2), 6.38 (s, 1H, H_3 coumarin), 7.24 (dt, 1H, *J*= 1.2, *J* = 8.4 Hz, H_6 coumarin), 7.35-7.41 (m, 4H, H Ph), 7.42 (dd, 1H, *J* = 1.2, *J* = 8.4 Hz, H_8 coumarin), 7.54-7.57 (m, 2H, H_5 and H_7 coumarin); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.4, 28.7, 114.9, 117.3, 119.0, 124.0, 127.0, 128.3, 128.5, 131.8, 132.5, 146.2, 154.2, 155.7, 160.9; IR (KBr): 1733 (C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.37; H, 5.38.



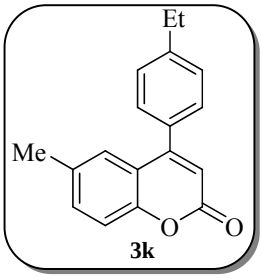
3i

4-(4-ethylphenyl)-6-nitro-2*H*-chromen-2-one (3i). Yield 68%; Oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (t, 3H, *J*= 7.6 Hz, CH_3), 2.80 (q, 2H, *J*= 7.6 Hz, CH_2), 6.51 (s, 1H, H_3 coumarin), 7.39-7.44 (m, 4H, H Ph), 7.54 (d, 1H, *J* = 9.0 Hz, H_8 coumarin), 8.42 (dd, 1H, *J* = 2.6, 9.0 Hz, H_7 coumarin), 8.49 (d, 1H, *J* = 2.6 Hz, H_5 coumarin); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.3, 28.7, 116.3, 118.4, 119.4, 123.1, 126.5, 128.3, 128.9, 131.0, 143.9, 147.1, 154.7, 157.7, 159.0; IR (KBr): 1730 (C=O), 1337 and 1505 (NO_2) cm^{-1}; MS, *m/z* (%) 295 ($M^{\bullet+}$, 91), 266 (95), 252 (38), 149 (100), 43 (71); Anal. Calcd for $C_{17}H_{13}NO_4$ (295.29): C, 69.15; H, 4.44; N, 4.74. Found: C, 69.44; H, 4.27; N, 4.59.



3j

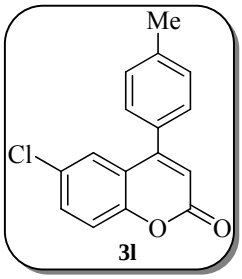
6-nitro-4-p-tolyl-2*H*-chromen-2-one (3j). Yield 77%, mp 214-217 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50 (s, 3H, CH_3), 6.51 (s, 1H, H_3 coumarin), 7.37 (d, 2H, *J*= 8.2 Hz, H Ph), 7.41 (d, 2H, *J*= 8.2 Hz, H Ph), 7.54 (d, 1H, *J* = 9.0 Hz, H_8 coumarin), 8.42 (dd, 1H, *J* = 2.6, 9.0 Hz, H_7 coumarin), 8.47 (d, 1H, *J* = 2.6 Hz, H_5 coumarin); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 116.3, 118.4, 119.4, 123.1, 126.6, 128.2, 130.1, 130.8, 140.9, 143.9, 154.7, 157.7, 159.0; IR (KBr): 1731 (C=O), 1338 and 1516 (NO_2) cm^{-1}. Anal. Calcd for $C_{16}H_{11}NO_4$: C, 68.32; H, 3.94; N, 4.98. Found: C, 68.20; H, 3.75; N, 5.11.



3k

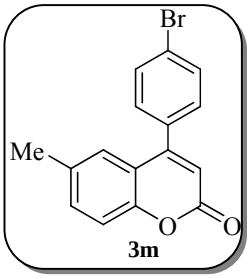
4-(4-ethylphenyl)-6-methyl-2*H*-chromen-2-one (3k). Yield 84%, mp 41-44 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (t, 3H, *J* = 7.5 Hz, $\underline{CH_3}$-CH_2), 2.35 (s, 3H, CH_3), 2.77 (q, 2H, *J* = 7.5 Hz, $\underline{CH_2}$-CH_3), 6.35 (s, 1H, H_3 coumarin), 7.30-7.31 (d, *J* = 8.3 Hz, 2H, H Ph), 7.35-7.40 (m, 5H, 2H

Ph and $H_{5,7,8}$ coumarin). ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.3, 20.9, 28.4, 114.8, 117.0, 118.7, 126.7, 127.3, 128.5, 128.6, 132.7, 133.6, 146.0, 152.3, 155.7, 161.1; IR (KBr): 1737 (C=O) cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.47; H, 6.28.



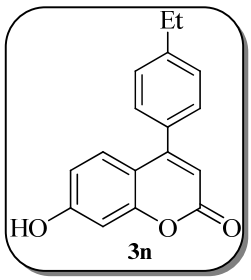
3l

6-chloro-4-p-tolyl-2*H*-chromen-2-one (3l).Yield 82%, 156-159 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 2.48 (s, 3H, CH_3), 6.40 (s, 1H, H_3 coumarin), 7.34-7.38 (m, 5H, 4H Ph and H_8 coumarin), 7.49-7.52 (m, 2H, H_5 and H_7 coumarin); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 115.7, 118.7, 120.2, 126.3, 128.2, 129.5, 129.7, 131.6, 131.7, 140.2, 152.5, 154.7, 160.2; IR (KBr): 1734 (C=O) cm^{-1}; MS, *m/z* (%) 272 ($M^{\bullet+}$+2, 38), 270 ($M^{\bullet+}$, 100), 255 (60), 242 (89), 178 (53); Anal.Calcd for $C_{16}H_{11}ClO_2$: C, 70.99; H, 4.10. Found: C, 70.75; H, 4.33.



3m

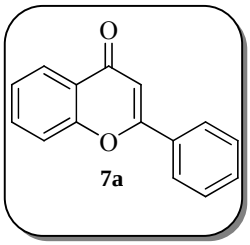
4-(4-bromophenyl)-6-methyl-2*H*-chromen-2-one (3m).Yield 80%, mp 104-106 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 2.35 (s, 3H, CH_3), 6.34 (s, 1H, H_3 coumarin), 7.19 (s, 1H, H_5 coumarin), 7.31-7.39 (m, 4H, 2H Ph and H_7 and H_8 coumarin), 7.68 (d, 2H, *J* = 8.1 Hz, , H Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.4, 114.8, 116.7, 117.8, 123.5, 125.8, 129.5, 13.6, 132.6, 133.5, 133.7, 151.8, 153.9, 160.2; IR (KBr): 1725 (C=O) cm^{-1}; MS, *m/z* (%) 313 ($M^{\bullet+}$+2, 100), 311 ($M^{\bullet+}$, 98), 288 (83), 284 (80), 235 (19), 178 (59); Anal. Calcd for $C_{16}H_{11}BrO_2$: C, 60.98; H, 3.52. Found: C, 60.71; H, 3.39.



3n

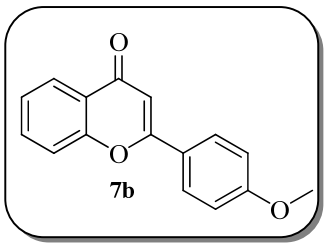
4-3 Chromenones 7a-7i

4-(4-ethylphenyl)-7-hydroxy-2H-chromen-2-one (3n). Yield 68%, mp 174-177 ºC; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.24 (t, 3H, *J* = 7.6 Hz, CH_3), 2.70 (q, 2H, *J* = 7.6 Hz, CH_2), 6.13 (s, 1H, H_3 coumarin), 6.77-6.80 (m, 2H, H_6 and H_8 coumarin), 7.32 (d, 1H, *J* = 8.6 Hz, H_5 coumarin), 7.39-7.44 (m, 4H, H Ph), 11.34 (s, 1H, OH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 15.4, 27.9, 102.6, 110.0, 110.6, 113.1, 128.2, 128.4, 132.5, 145.4, 155.4, 155.5, 160.1, 161.3; IR (KBr): 3443 (OH), 1695 (C=O) cm^{-1}; MS, *m/z* (%) 238 ($M^{\bullet+}$, 94), 210 (100), 181 (37); Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.81; H, 5.19.



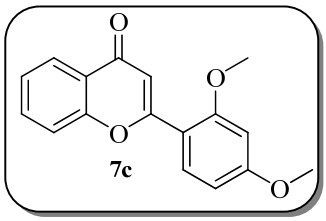
7a

2-phenyl-4*H*-chromen-4-one (7a). Yield 86%, mp 96-98 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (s, 1H, H_3 chromenone), 7.44 (dt, 1H, *J* = 7.4, 1.1 Hz, H_6 chromenone), 7.56-7.54 (m, 3H, H Ph), 7.58 (d, 1H, *J* = 7.7 Hz, H_8 chromenone), 7.70 (dt, 1H, *J* = 1.7, 7.1 Hz, H_7 chromenone), 7.94-7.96 (m, 2H, H Ph), 8.25 (dd, 1H, *J* = 1.5, 7.9 Hz, H_5 chromenone); ^{13}C NMR (125 MHz, $CDCl_3$) δ, 107.5, 118.0, 125.2, 125.7, 126.3, 129.0, 131.6, 133.3, 133.8, 154.6, 156.2, 163.5, 178.4; IR (KBr): 1642 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{10}O_2$ (222.24): C, 81.07; H, 4.54. Found: C, 81.30; H, 4.33.

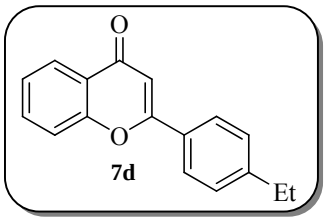


7b

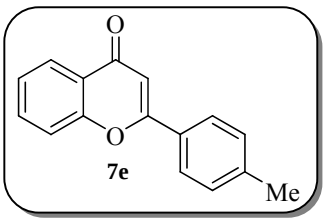
2-(4-methoxyphenyl)-4*H*-chromen-4-one (7b). Yield 80%, mp 124-126 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 3H, O-CH_3), 6.81 (s, 1H, H_3 chromenone), 7.03 (d, 2H, *J* = 8.6 Hz, H Ph), 7.43 (t, 1H, *J*= 8.8 Hz, H_6 chromenone), 7.56 (d, 1H, *J* = 8.3 Hz, H_8 chromenone), 7.70 (t, 1H, *J* = 7.4, H_7 chromenone), 7.90 (d, 2H, *J* = 8.6 Hz, H Ph), 8.23 (d, 1H, *J* = 7.6 Hz , H_5 chromenone); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.6, 105.9, 114.5, 117.9, 123.7, 123.9, 125.2, 125.6, 128.1, 133.7, 156.2, 162.5, 163.7, 178.4; IR (KBr): 1649 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.02; H, 4.66.



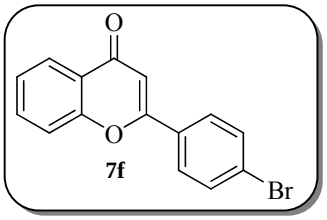
2-(2,4-dimethoxyphenyl)-4*H*-chromen-4-one (7c). Yield 88%, mp 127-129 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.89 (s, 3H, O-CH_3), 3.93 (s, 3H, O-CH_3), 6.56 (d, 1H, *J* = 2.4 Hz, H_3 Ph), 6.65 (dd, 1H, *J* = 2.4, *J* = 8.8 Hz, H_5 Ph), 7.15 (s, 1H, H_3 chromenone), 7.39 (dt, 1H, *J* = 1.6, *J* = 8.0 Hz, 1H, H_6 chromenone), 7.51 (d, 1H, *J* = 8.3 Hz, H_8 chromenone), 7.66 (dt, 1H, *J* = 1.6, *J* = 7.4 Hz, H_7 chromenone), 7.91 (d, 1H, *J* = 8.7 Hz, H_6 Ph), 8.23 (dd, 1H, *J* = 1.4, *J* = 7.6 Hz, H_5 chromenone). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5, 55.6, 98.9, 105.3, 111.3, 113.0, 117.9, 124.7, 125.2, 125.6, 130.4, 133.3, 156.4, 159.6, 160.8, 163.2, 178.9; IR (KBr): 1650 (C=O) cm^{-1}.Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.57; H, 5.22.



2-(4-ethylphenyl)-4*H*-chromen-4-one (7d).Yield 92%, mp 47-49 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29 (t, 3H, *J* = 7.6 Hz, CH_3), 2.73 (q, 2H, *J* = 7.6 Hz, CH_2), 7.27 (s, 1H, H_3 chromenone), 7.36 (d, 2H, *J* = 8.4 Hz, H Ph), 7.42 (dt, 1H, *J*= 1.0, *J*= 7.6 Hz, H_6 chromenone), 7.57 (dd, 1H, *J* = 1.0, *J*= 7.8 Hz, H_8 chromenone), 7.70 (td, 1H, *J* = 1.6, *J*= 7.8 Hz, H_7 chromenone), 7.86 (d, 2H, *J* = 8.4 Hz, H Ph), 8.24 (dd, 1H, *J* = 1.6, 7.6 Hz, H_5 chromenone); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.2, 28.8, 106.9, 118.0, 123.9, 125.1, 125.6, 126.3, 128.6, 129.1, 133.7, 148.5, 156.2, 163.6, 178.5; IR (KBr): 1644 (C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_2$ (250.29): C, 81.58; H, 5.64. Found: C, 81.26; H, 5.89.

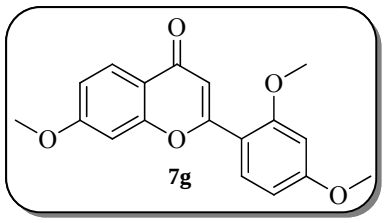


2-*p*-tolyl-4*H*-chromen-4-one (7e). Yield 90%, mp 85-87 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (t, 3H, *J* = 7.7 Hz, CH_3), 6.82 (s, 1H, H_3 chromenone), 7.32 (d, 2H, *J* = 8.4 Hz, H Ph), 7.42 (dt, 1H, *J*= 7.1, *J*= 1.0 Hz, H_6 chromenone), 7.57 (d, 1H, *J* = 7.3, 1 Hz, H_8 chromenone), 7.69 (dt, 1H, *J* = 1.6, 7.7 Hz, H_7 chromenone), 7.82 (d, 2H, *J* = 8.3 Hz, H Ph), 8.23 (dd, 1H, *J* = 1.6, 7.6 Hz, H_5 chromenone); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 106.9, 118.0, 123.9, 125.1, 125.6, 126.2, 128.8, 129.7, 133.6, 142.3, 156.2, 163.6, 178.5; IR (KBr): 1643 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.58; H, 5.22.



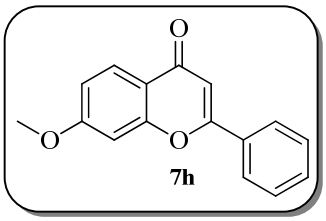
7f

2-(4-bromophenyl)-4*H*-chromen-4-one (7f).Yield 85%, mp 173-176 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (s, 1H, H_3 chromenone), 7.45 (t, 1H, *J*= 7.5 Hz, H_6 chromenone), 7.57 (d, 1H, *J* = 8.3 Hz, H_8 chromenone), 7.81 (d, 2H, *J* = 8.5 Hz, H Ph), 7.73 (t, 1H, *J* = 8.2 Hz, H_7 chromenone), 7.86 (d, 2H, *J* = 8.5 Hz, H Ph), 8.24 (d, 1H, *J* = 7.5 Hz, H_5 chromenone); ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.7, 118.0, 123.9, 125.4, 125.7, 126.3, 127.7, 130.7, 132.3, 133.9, 156.1, 162.3, 178.3; IR (KBr): 1663 (C=O) cm^{-1}; MS, *m/z* (%) 302 ($M^{\bullet+}$+2, 98), 300 ($M^{\bullet+}$, 100), 274 (30), 272 (30), 221 (63); Anal. Calcd for $C_{15}H_9BrO_2$: C, 59.83; H, 3.01. Found: C, 59.52; H, 3.29.



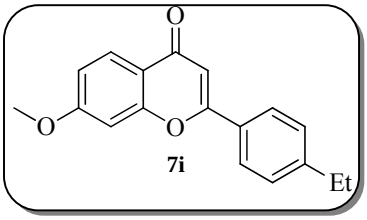
7g

2-(2,4-dimethoxyphenyl)-7-methoxy-4*H*-chromen-4-one (7g). Yield 91%, mp 118-120 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.95-3.80 (m, 9H, O-CH_3), 6.56 (s, 1H, H_3 chromenone), 6.62 (d, 1H, *J*= 8.8 Hz, H_5 Ph), 6.92 (s, 1H, H_3 Ph), 6.95 (d, 1H, *J*= 8.8 Hz, H_6 Ph), 7.08 (s, 1H, H_8 chromenone), 7.88 (d, 1H, *J* = 8.8 Hz, H_6 chromenone), 8.12 (d, 1H, *J* = 8.8 Hz, H_5 chromenone); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.1, 55.2, 55.3, 98.3, 99.7, 104.7, 110.7, 113.1, 113.5, 117.1, 126.4, 129.8, 157.6, 159.0, 159.9, 162.6, 163.4, 177.9; IR (KBr): 1627 (C=O) cm^{-1}; MS, *m/z* (%) 312 ($M^{\bullet+}$, 8), 281 (13), 221 (21), 176 (100), 149 (84); Anal. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16. Found: C, 69.41; H, 5.01.



7h

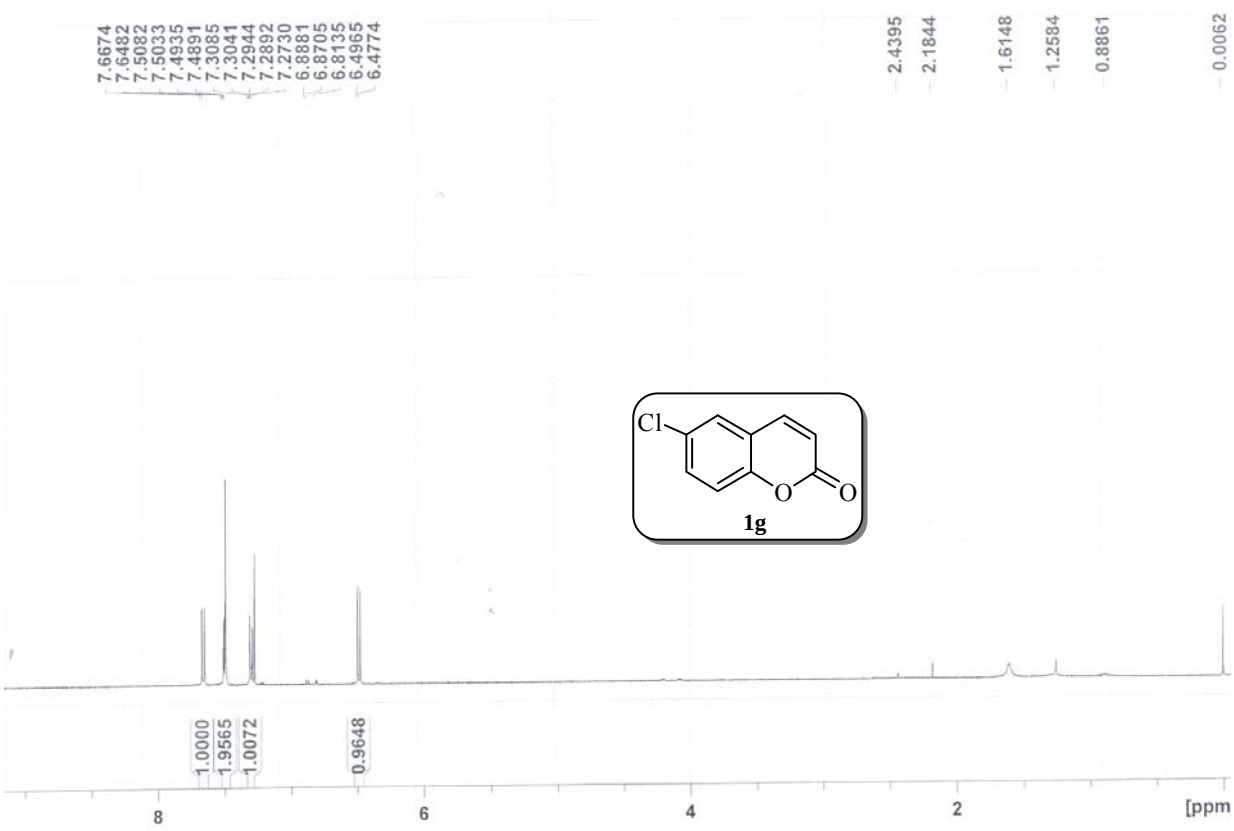
7-methoxy-2-phenyl-4*H*-chromen-4-one (7h). Yield 81%, mp 83-85 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94 (s, 3H, O-CH_3), 6.79 (s, 1H, H_3 chromenone), 6.96-7.01 (m, 2H, $H_{6,8}$ chromenone), 7.51-7.55 (m, 3H, H Ph), 7.93-7.90 (m, 2H, H Ph), 8.13 (d, 1H, *J* = 8.6 Hz, H_5 chromenone); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.8, 100.3, 107.4, 114.4, 117.8, 126.1, 127.0, 128.9, 131.4, 131.8, 157.9, 163.0, 164.2, 177.8; IR (KBr): 1625 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.41; H, 4.60.

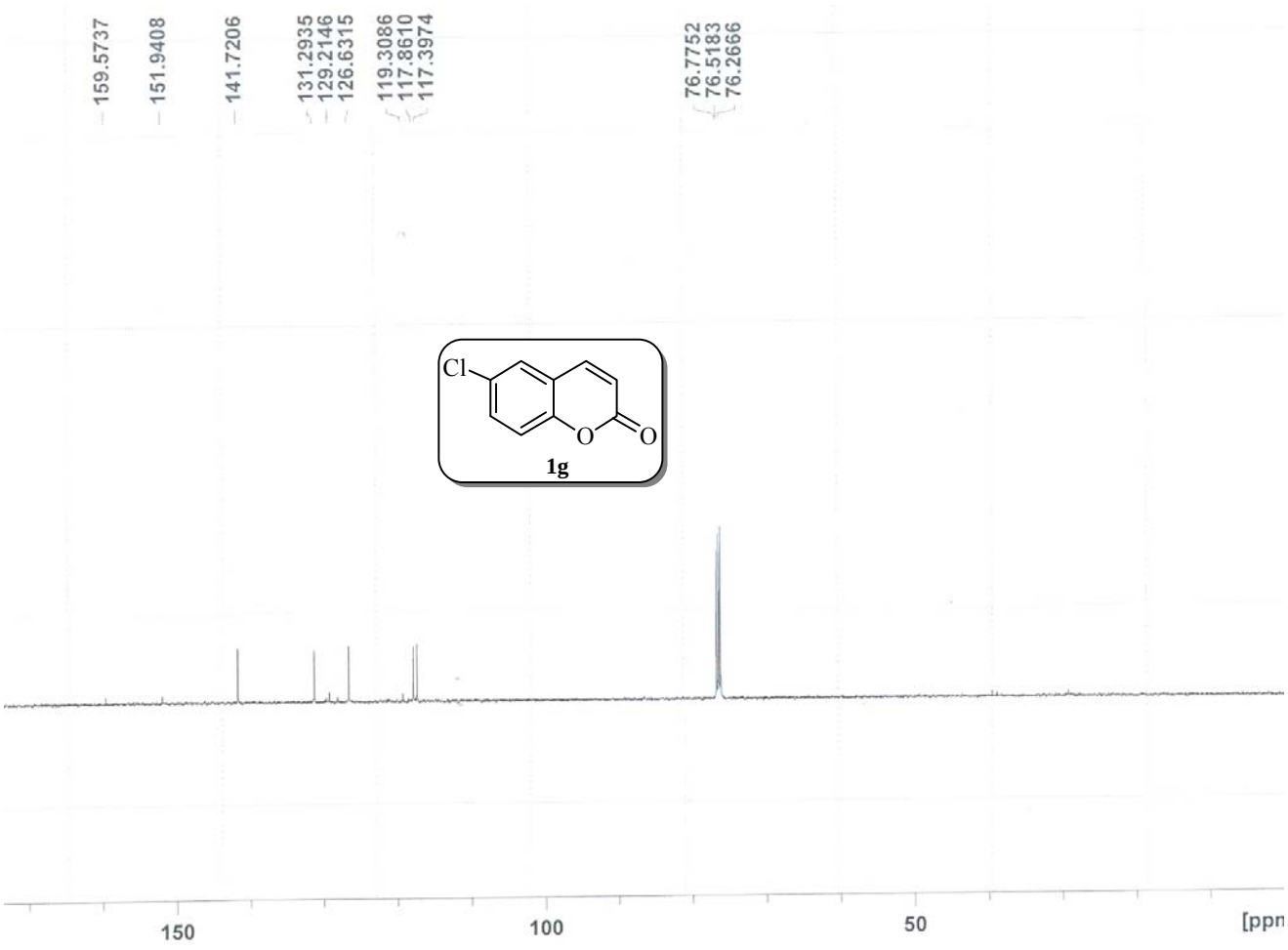


7i

2-(4-ethylphenyl)-7-methoxy-4*H*-chromen-4-one (7i). Yield 77%, mp 160-163 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (t, 3H, *J* = 7.6 Hz, CH_3), 2.75 (q, 2H, *J* = 7.6 Hz, CH_2), 3.96 (s, 3H, OCH_3), 6.88 (s, 1H, H_3 chromenone), 7.00-7.03 (m, 2H, $H_{6,8}$ chromenone), 7.36 (d, 2H, *J*= 7.8 Hz, H Ph), 7.87 (d, 2H, *J*= 7.8 Hz, H Ph), 8.15 (d, 1H, *J* = 8.6 Hz, H_5 chromenone); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.3, 28.8, 55.8, 100.4, 106.7, 114.5, 117.5, 126.3, 127.0, 128.6, 129.1, 148,5, 158.0, 163.7, 164.3, 177.9; IR (KBr): 1615 (C=O) cm^{-1}; MS, *m/z* (%) 280 ($M^{\bullet+}$, 100), 265 (56), 236 (50), 221 (41); Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.33; H, 5.57.

5 ^{1}H and ^{13}C NMR Spectra

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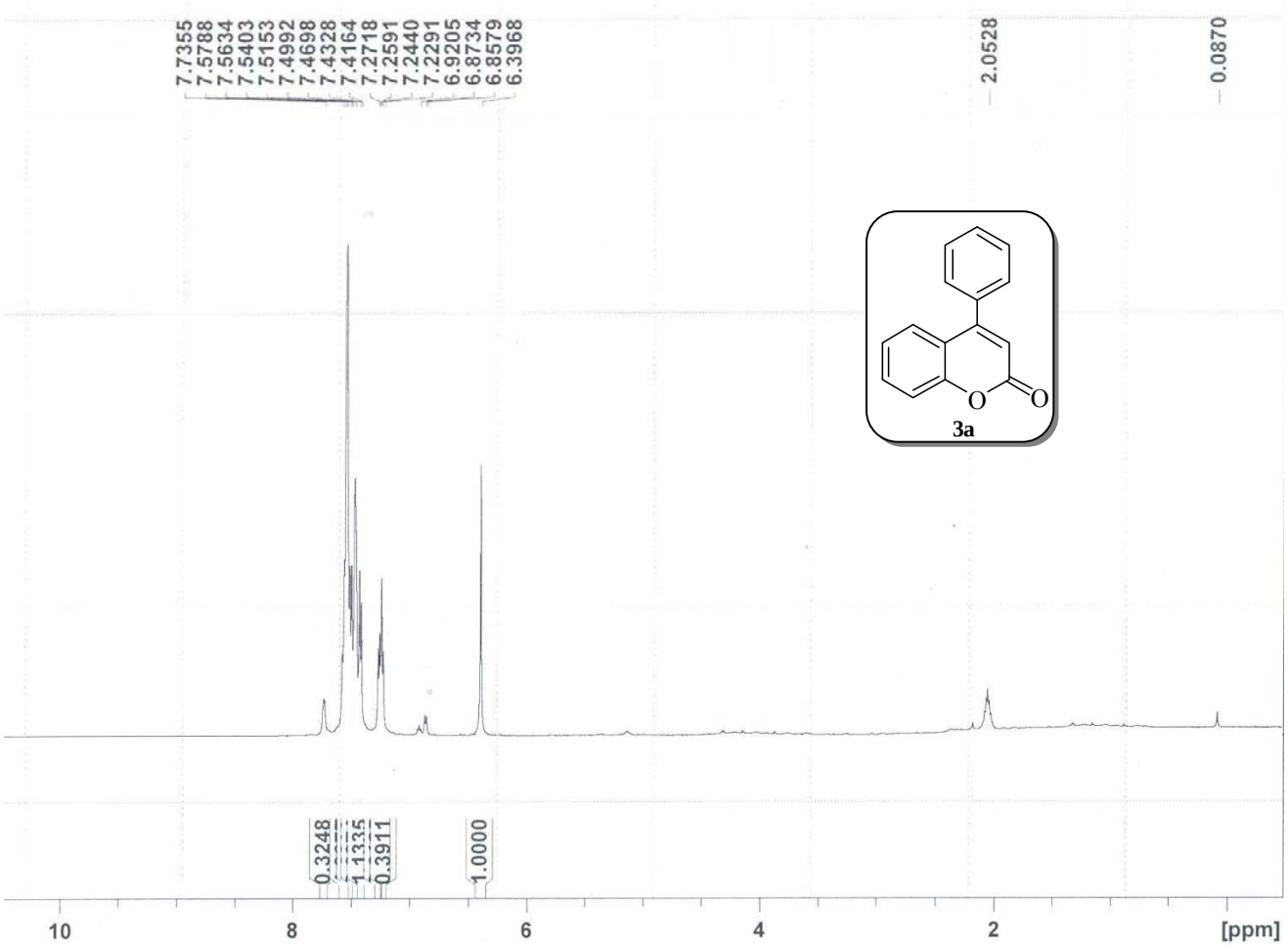

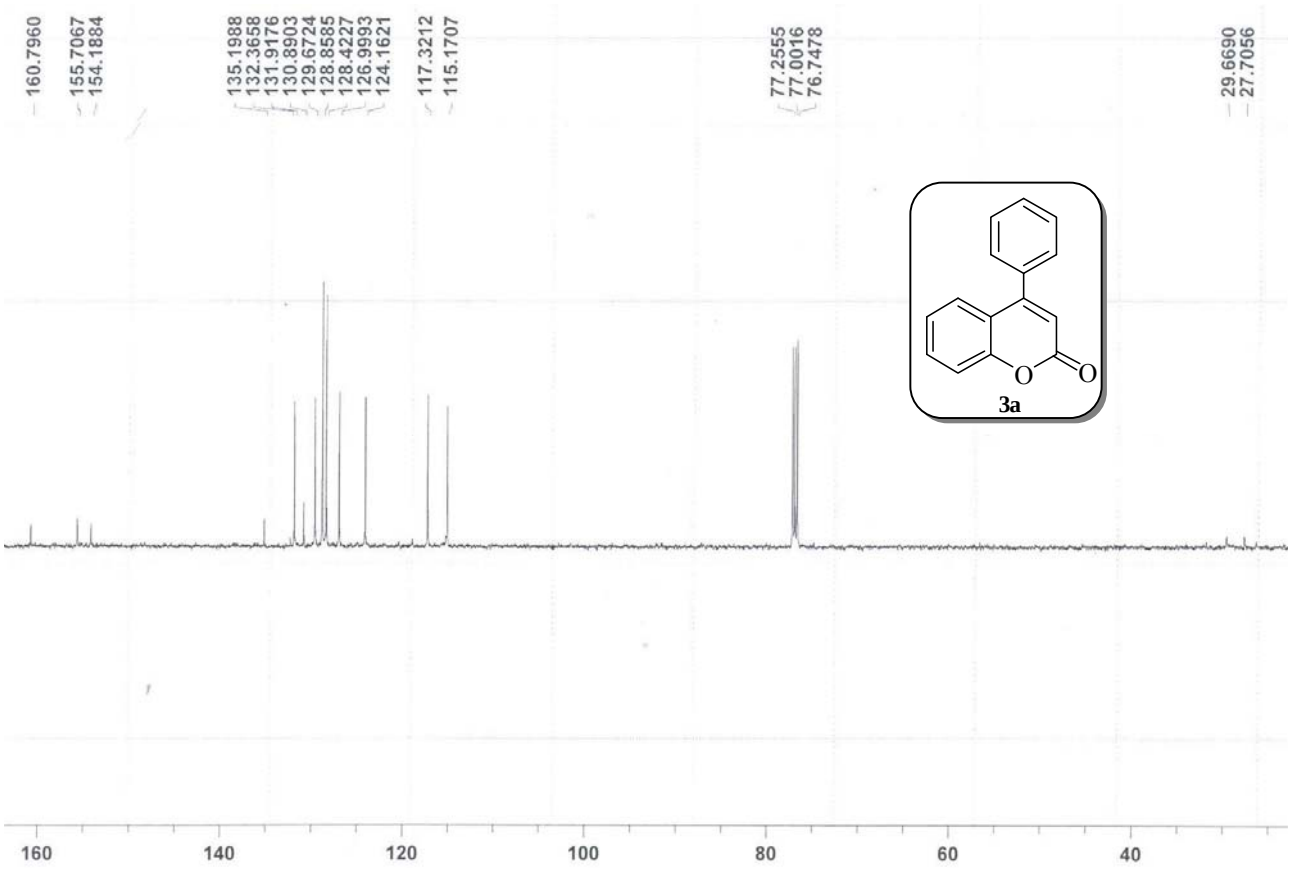
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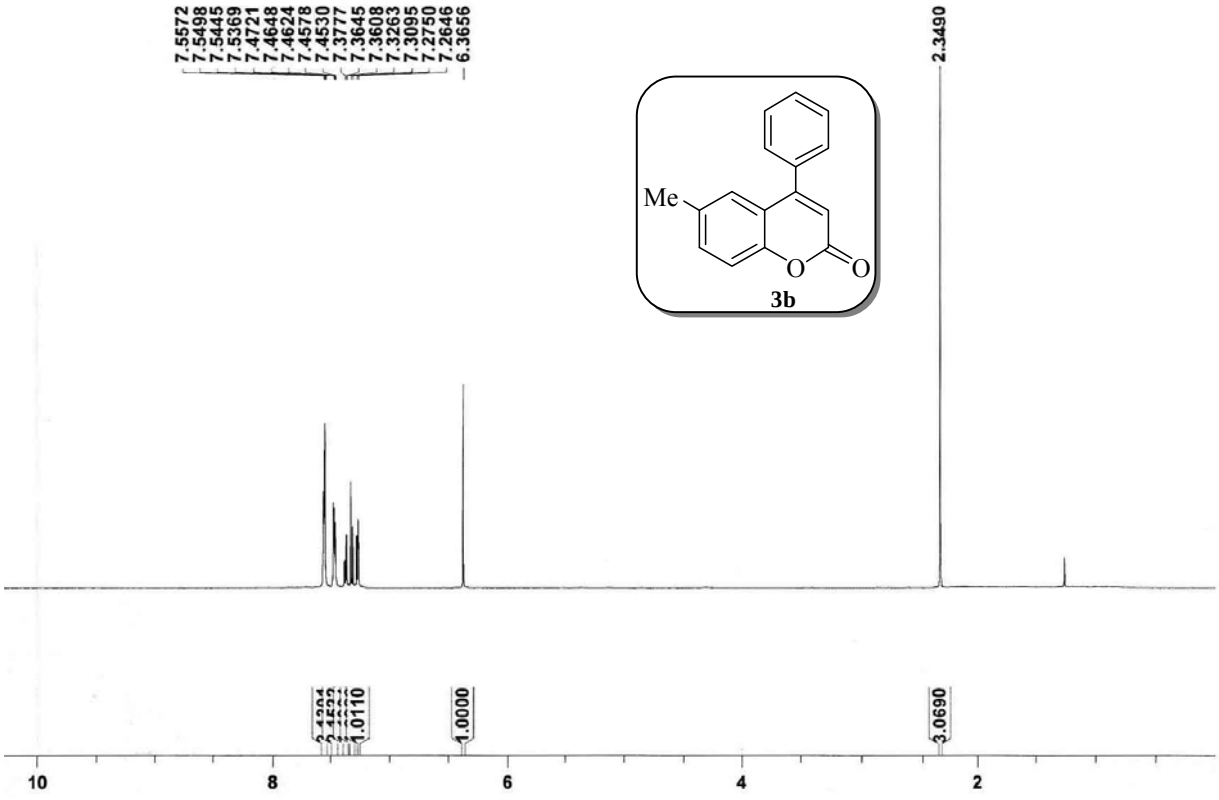
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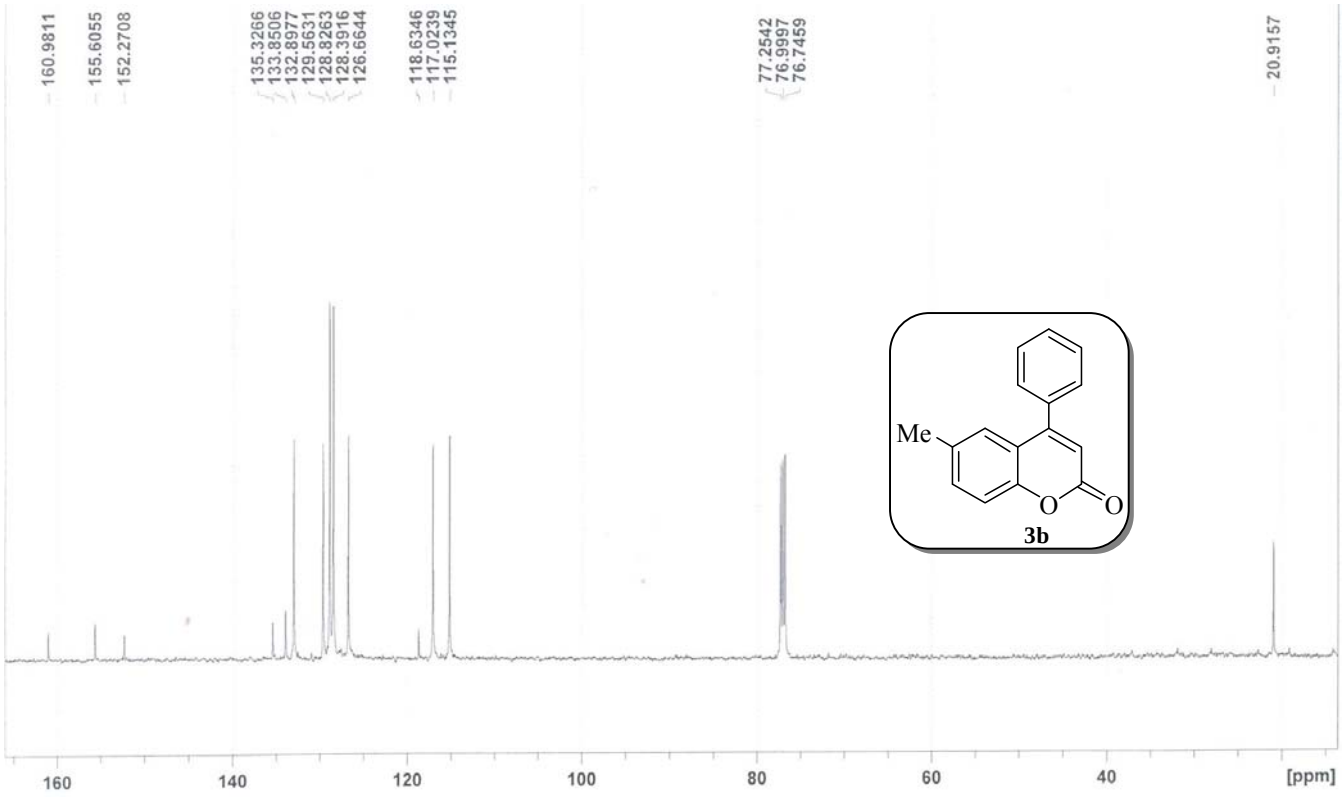
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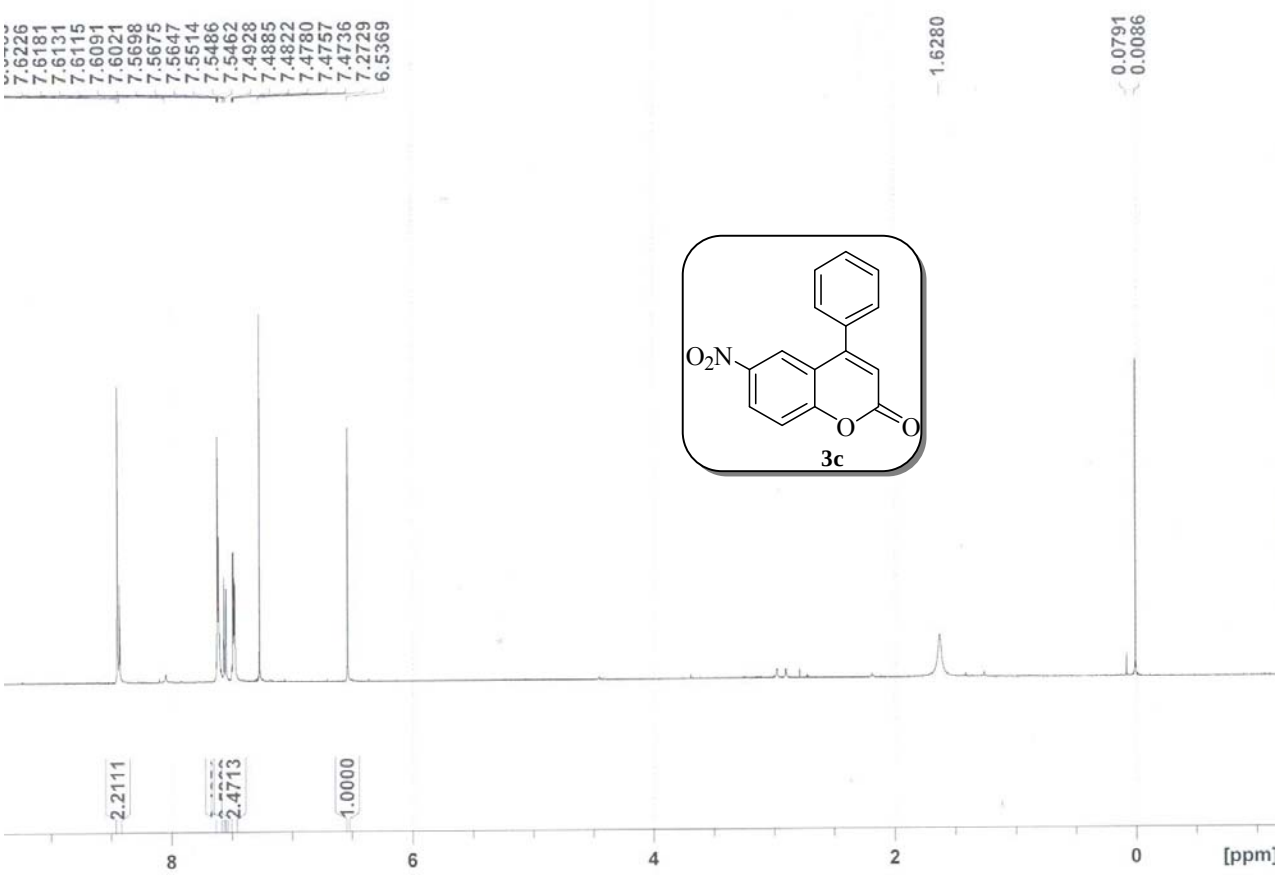
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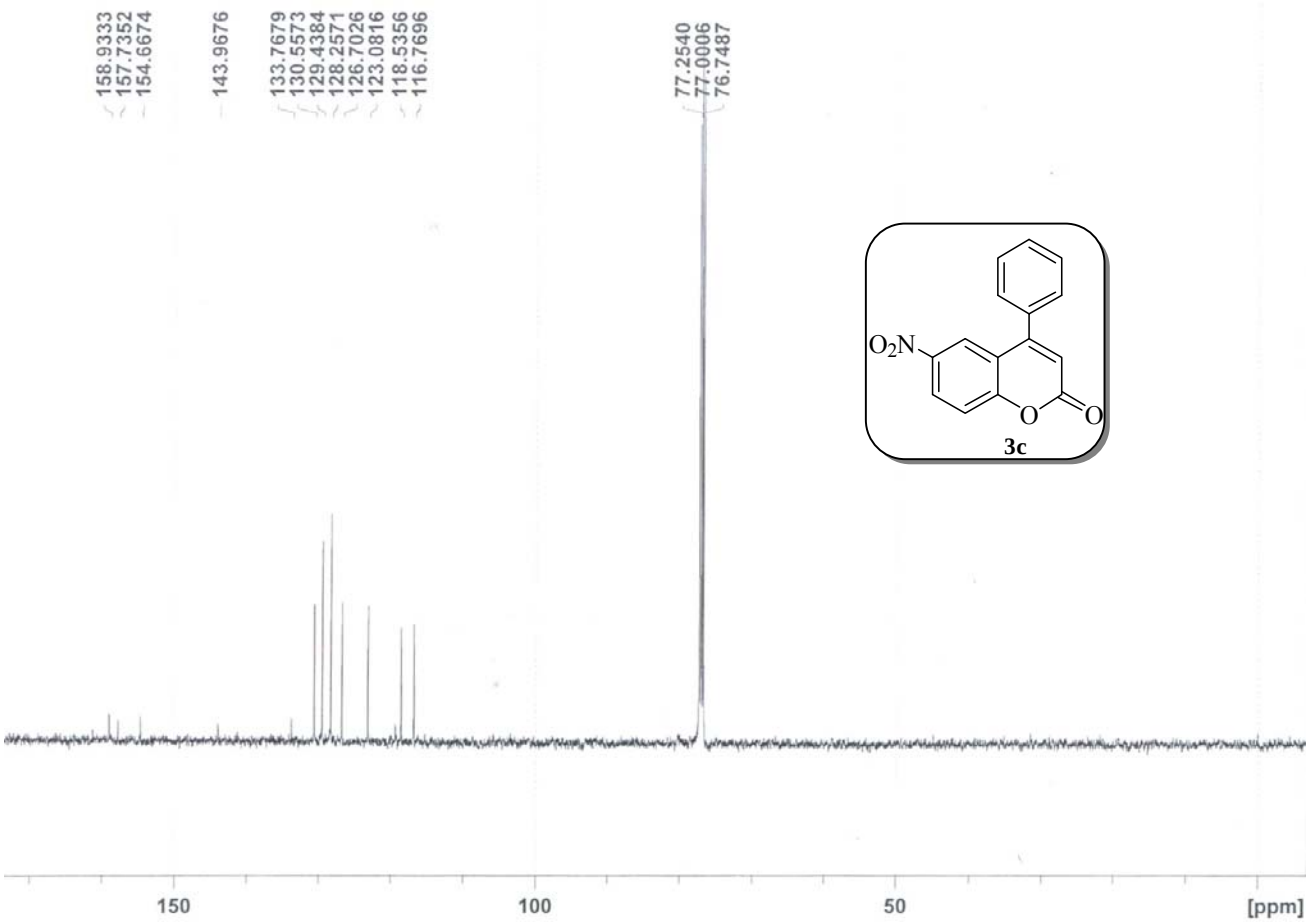
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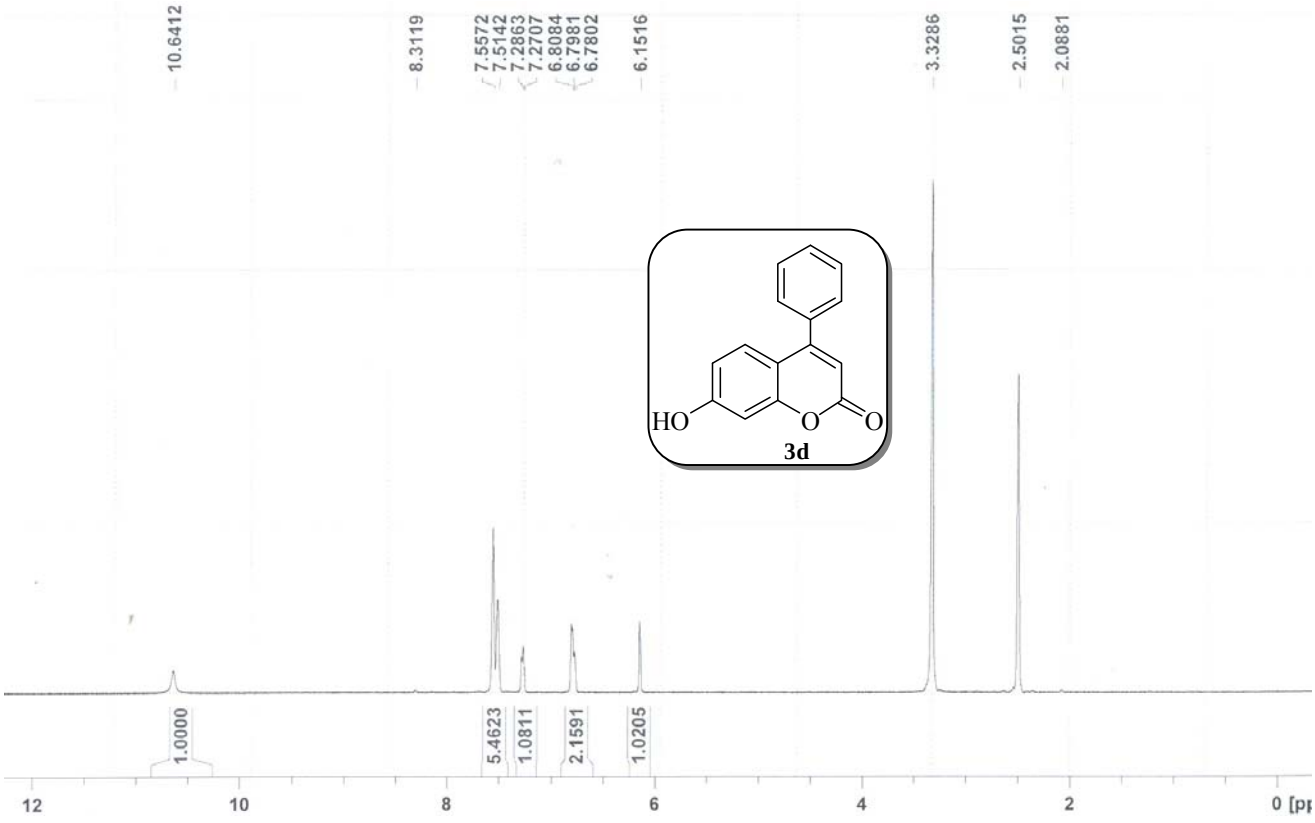
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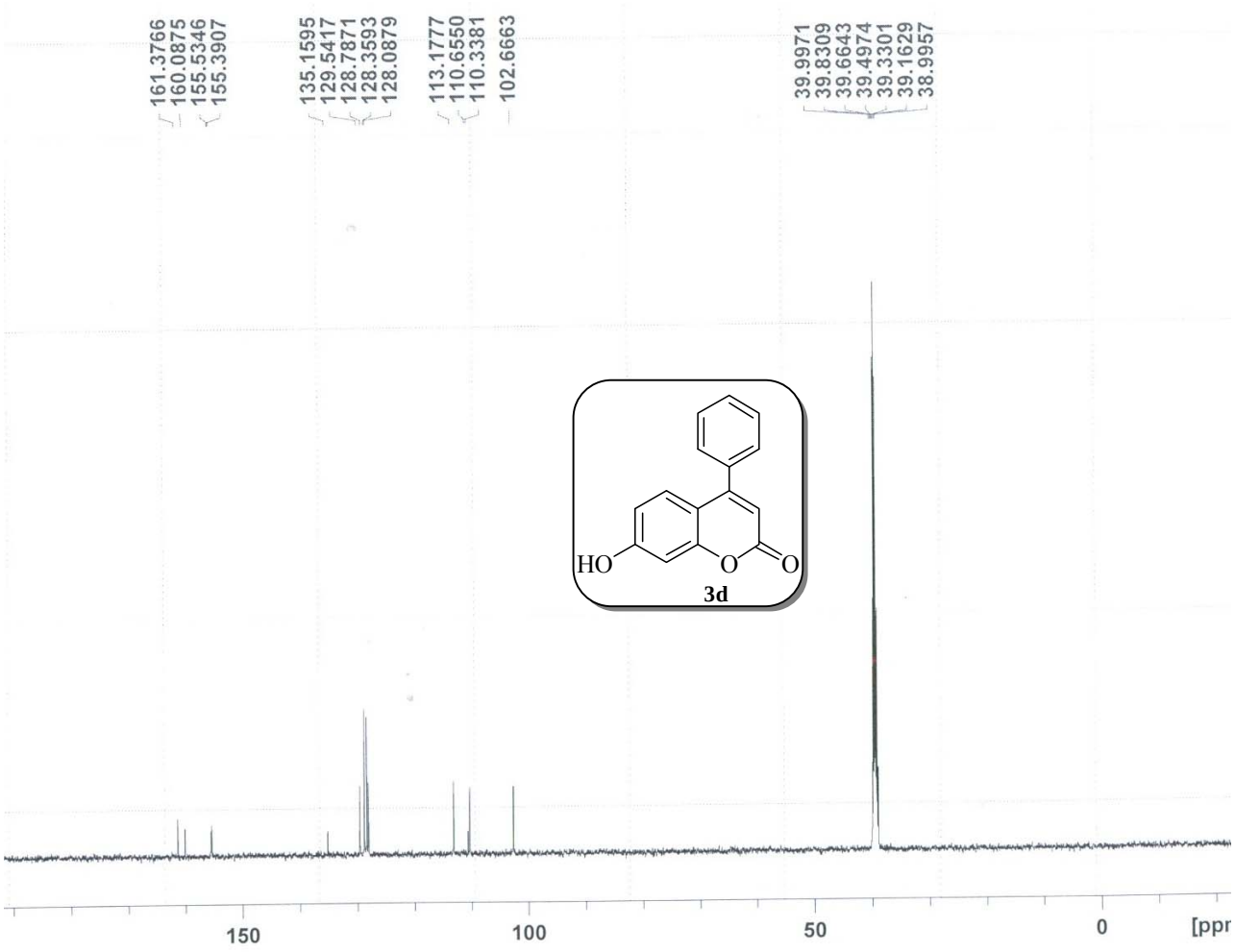
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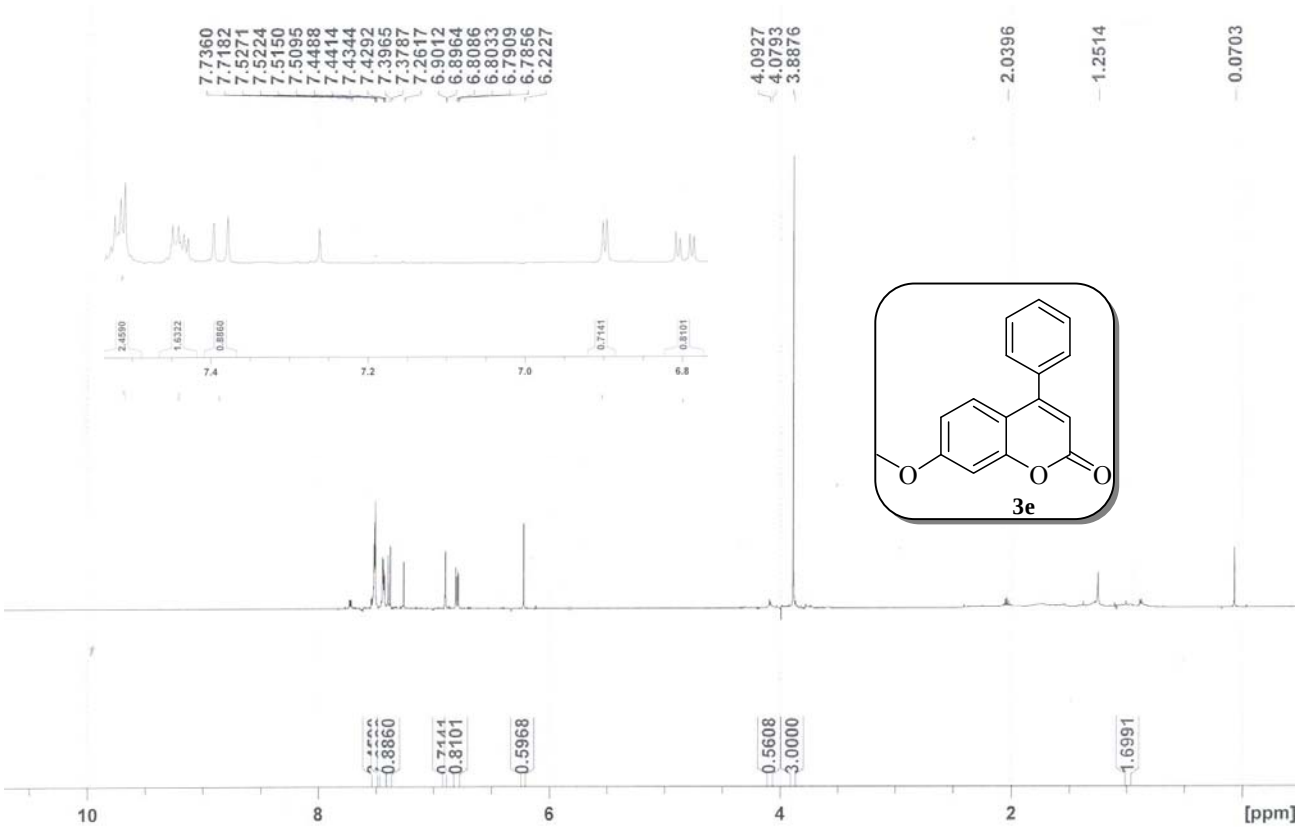
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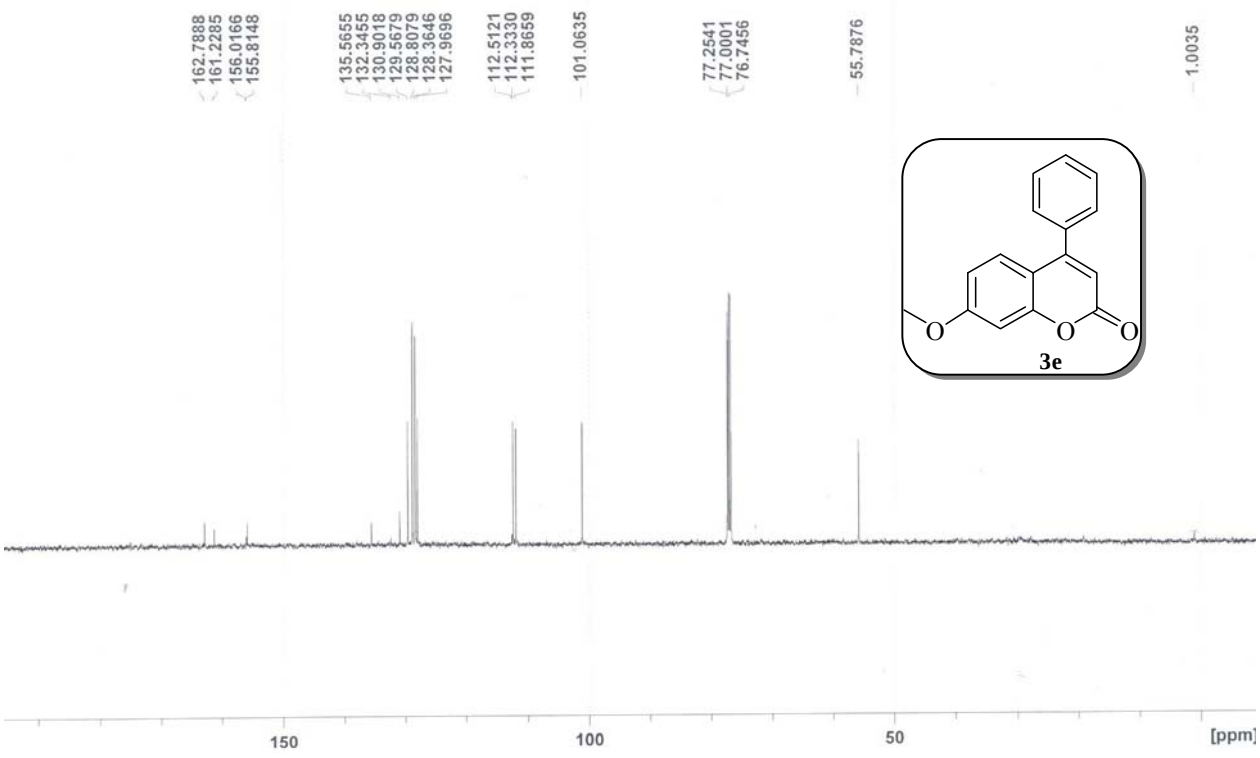
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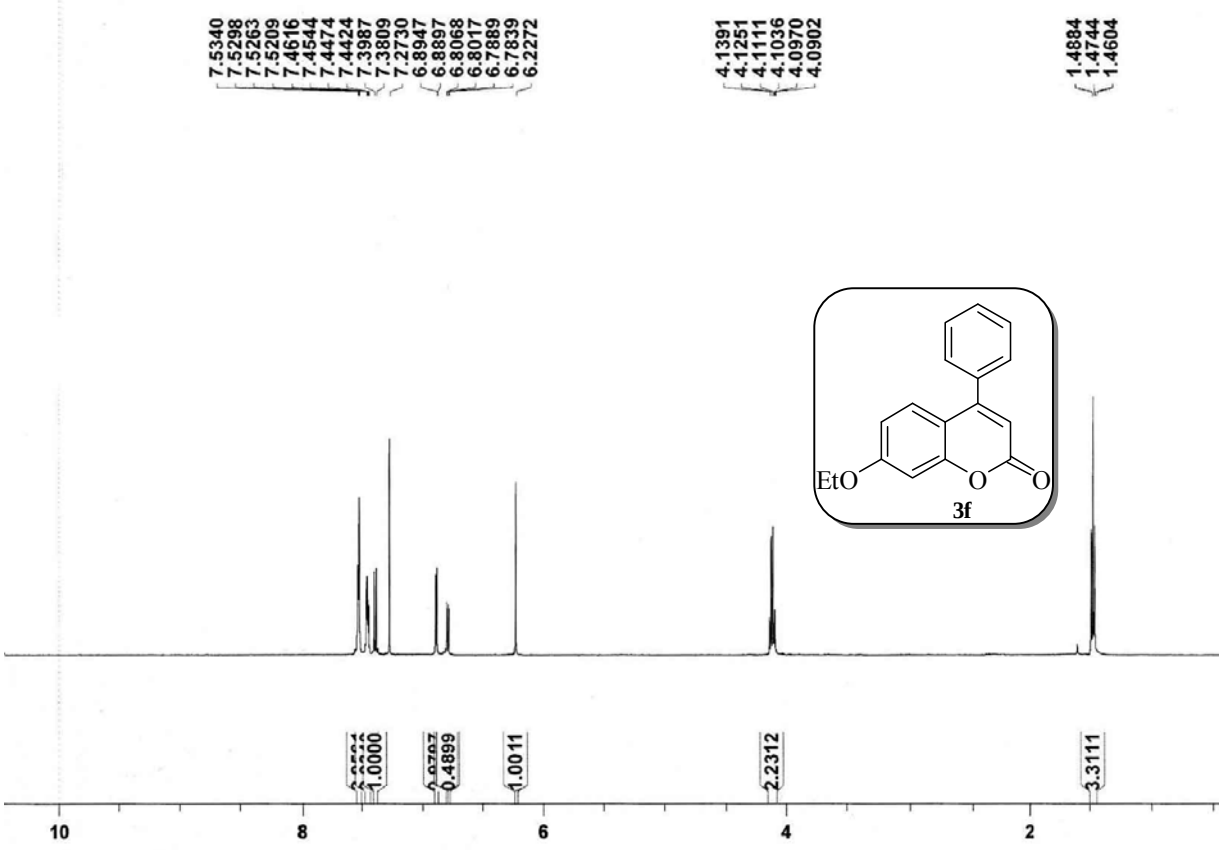
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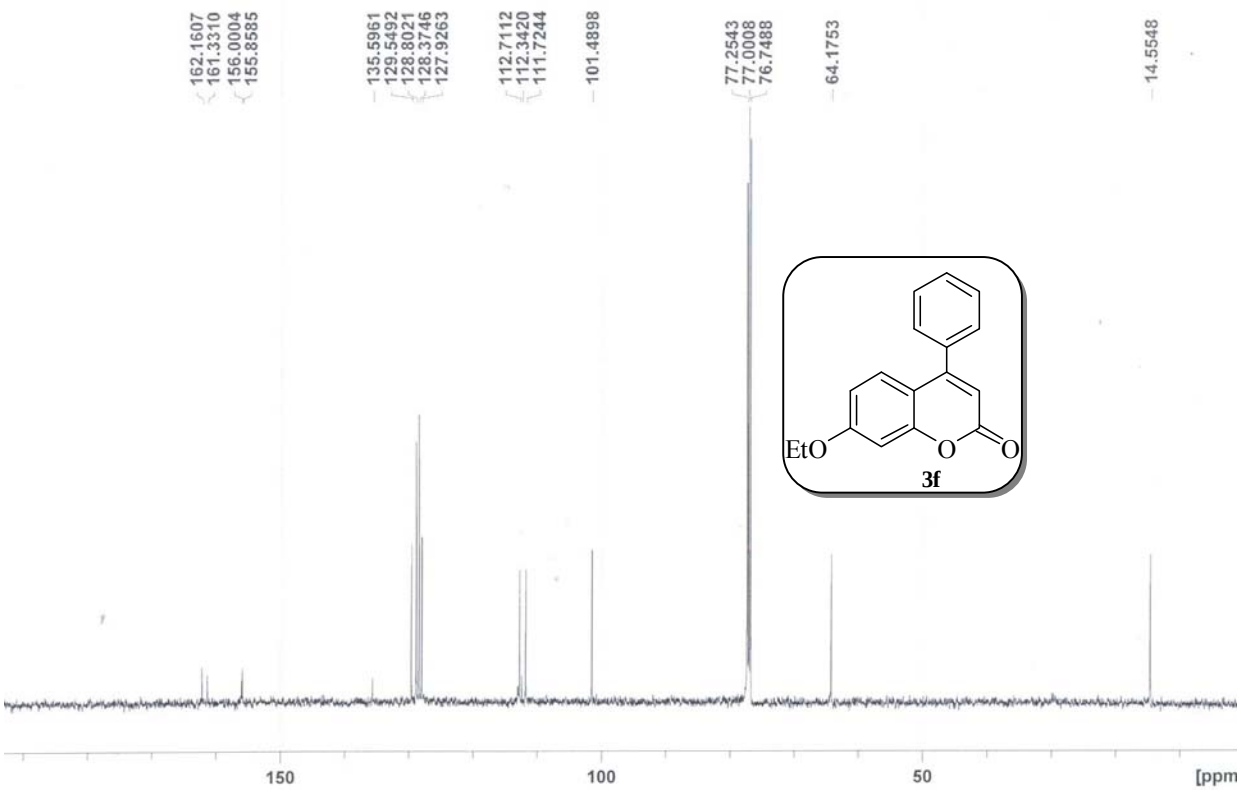
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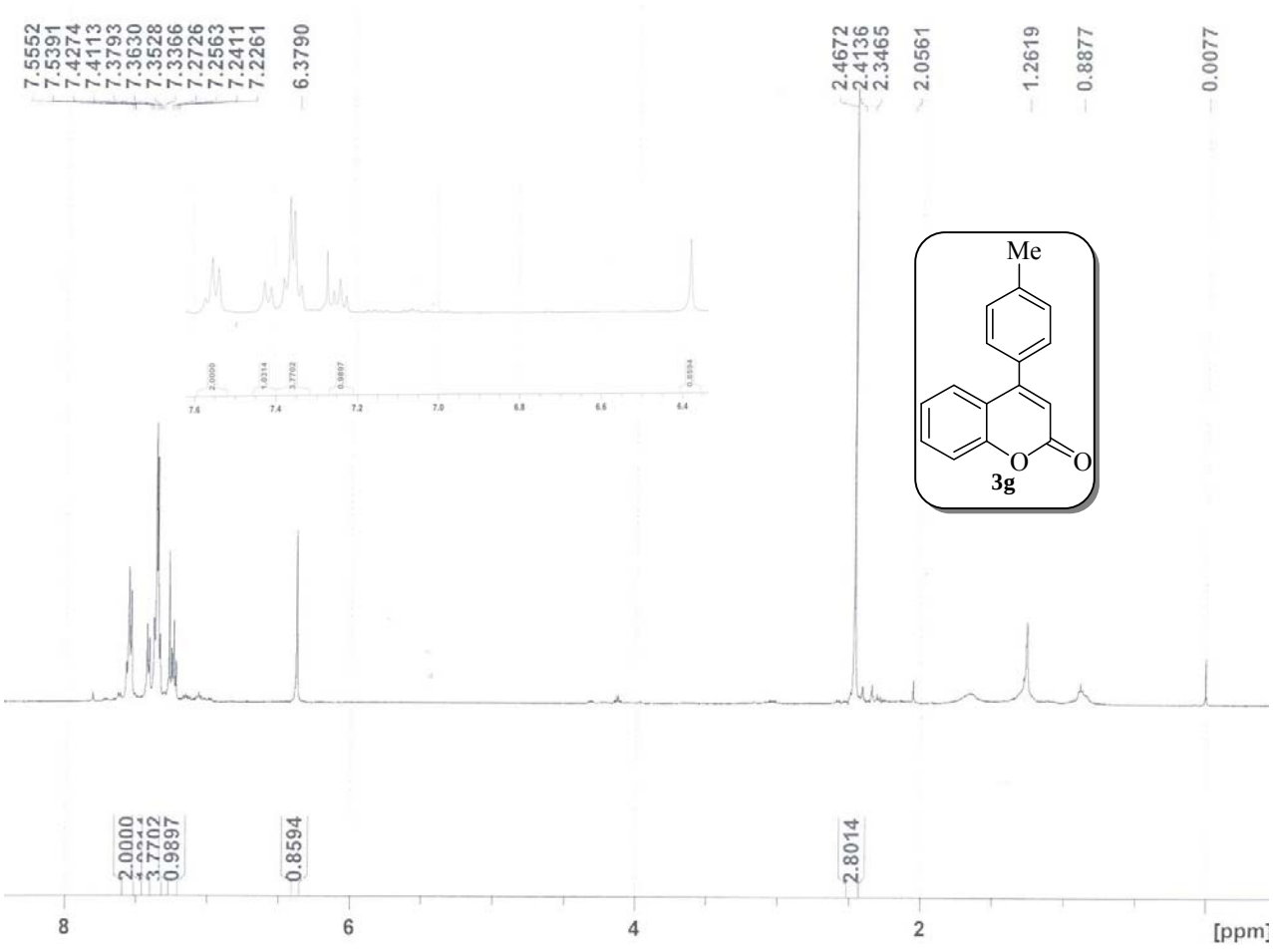
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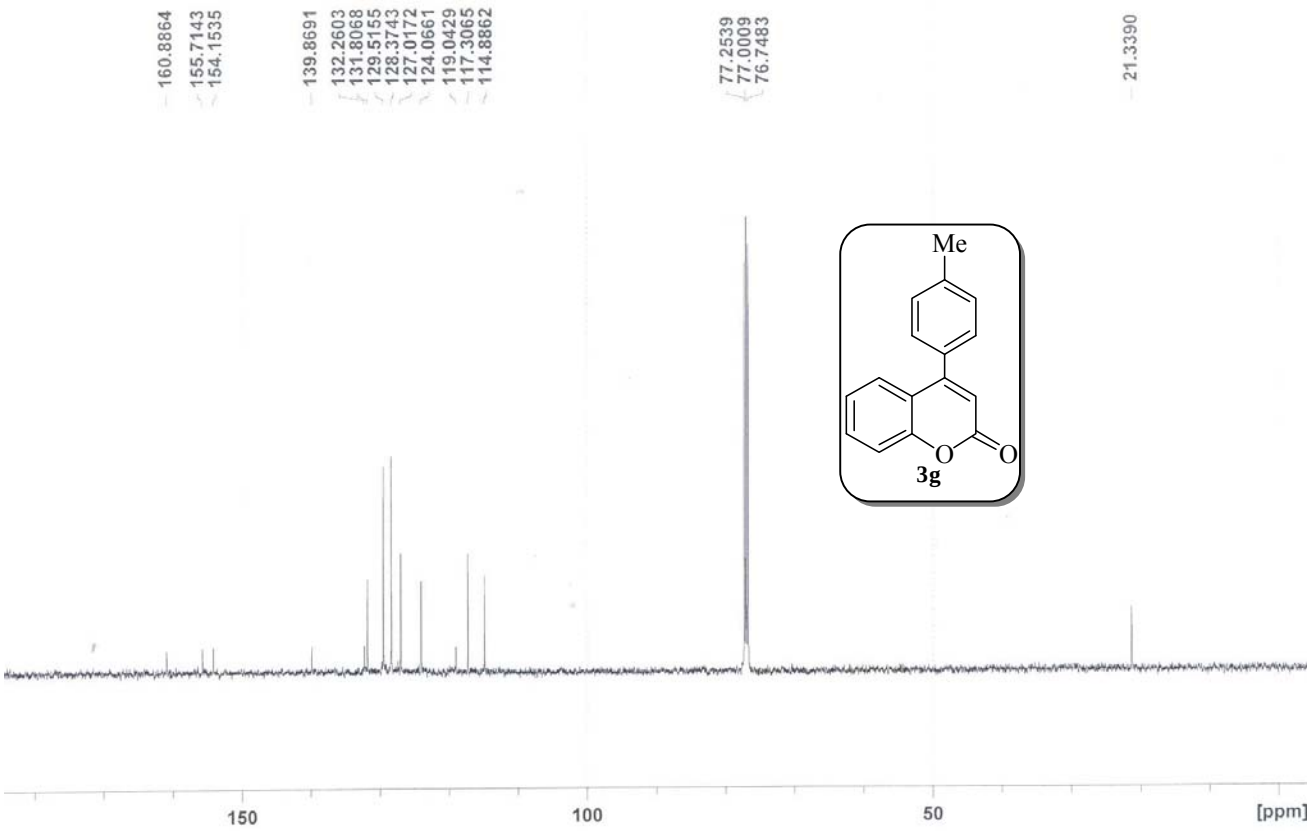
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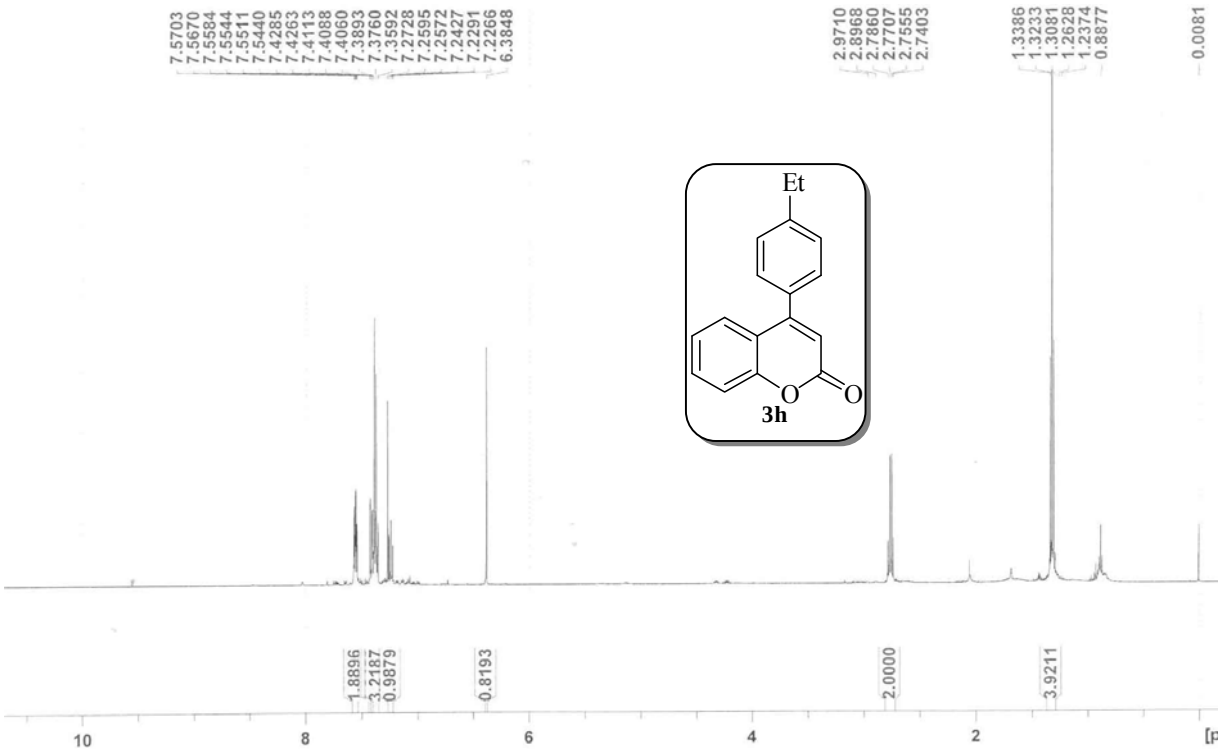
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7.2595
7.2572
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7.2291
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2.7403
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1.2628
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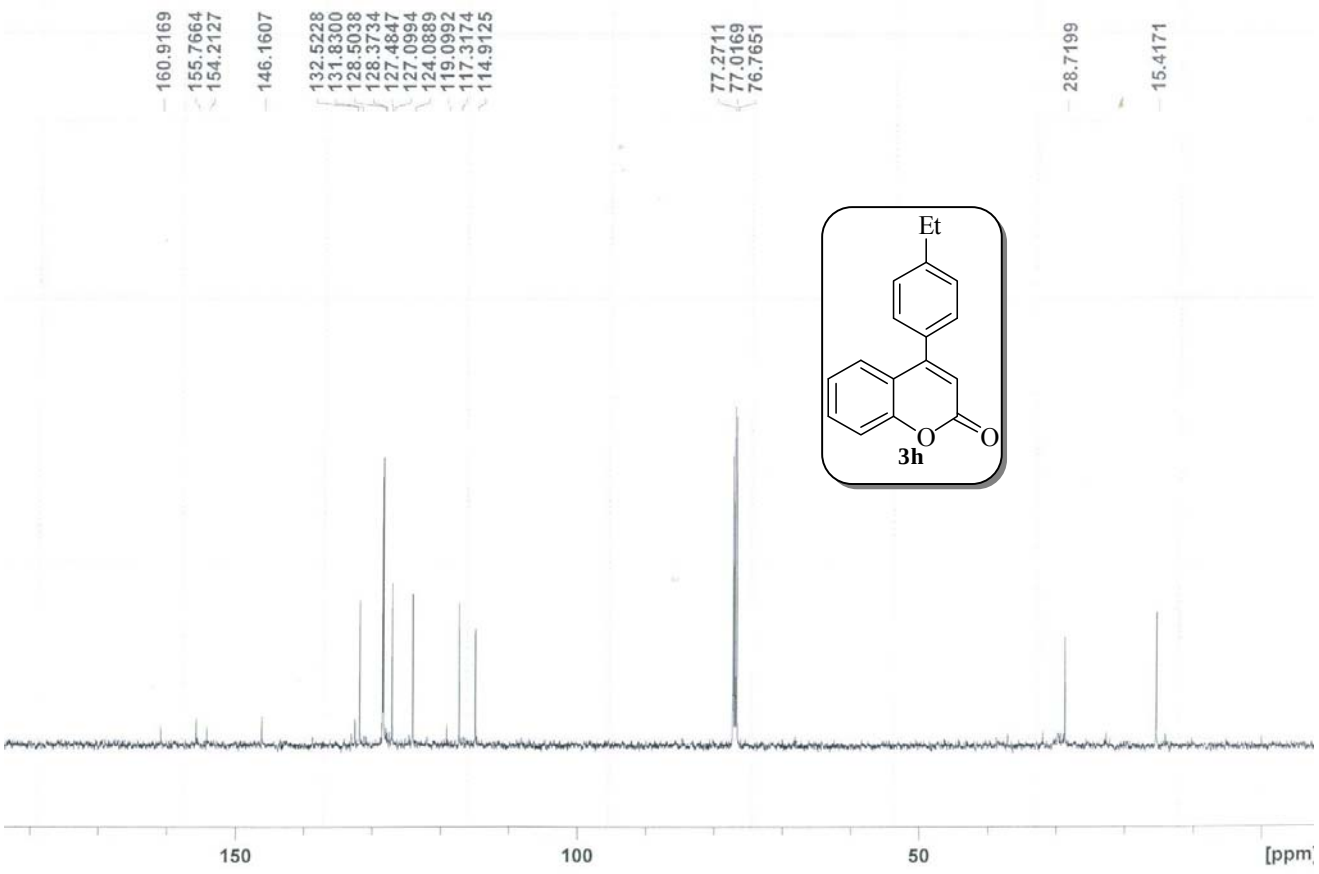
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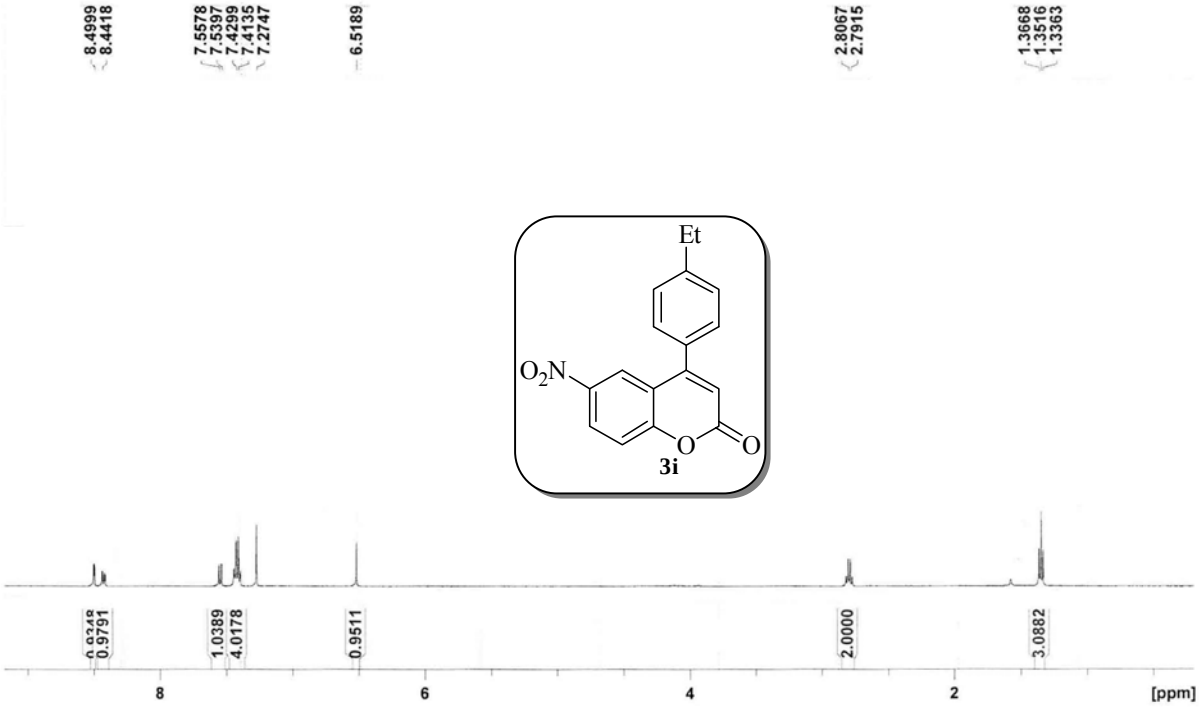
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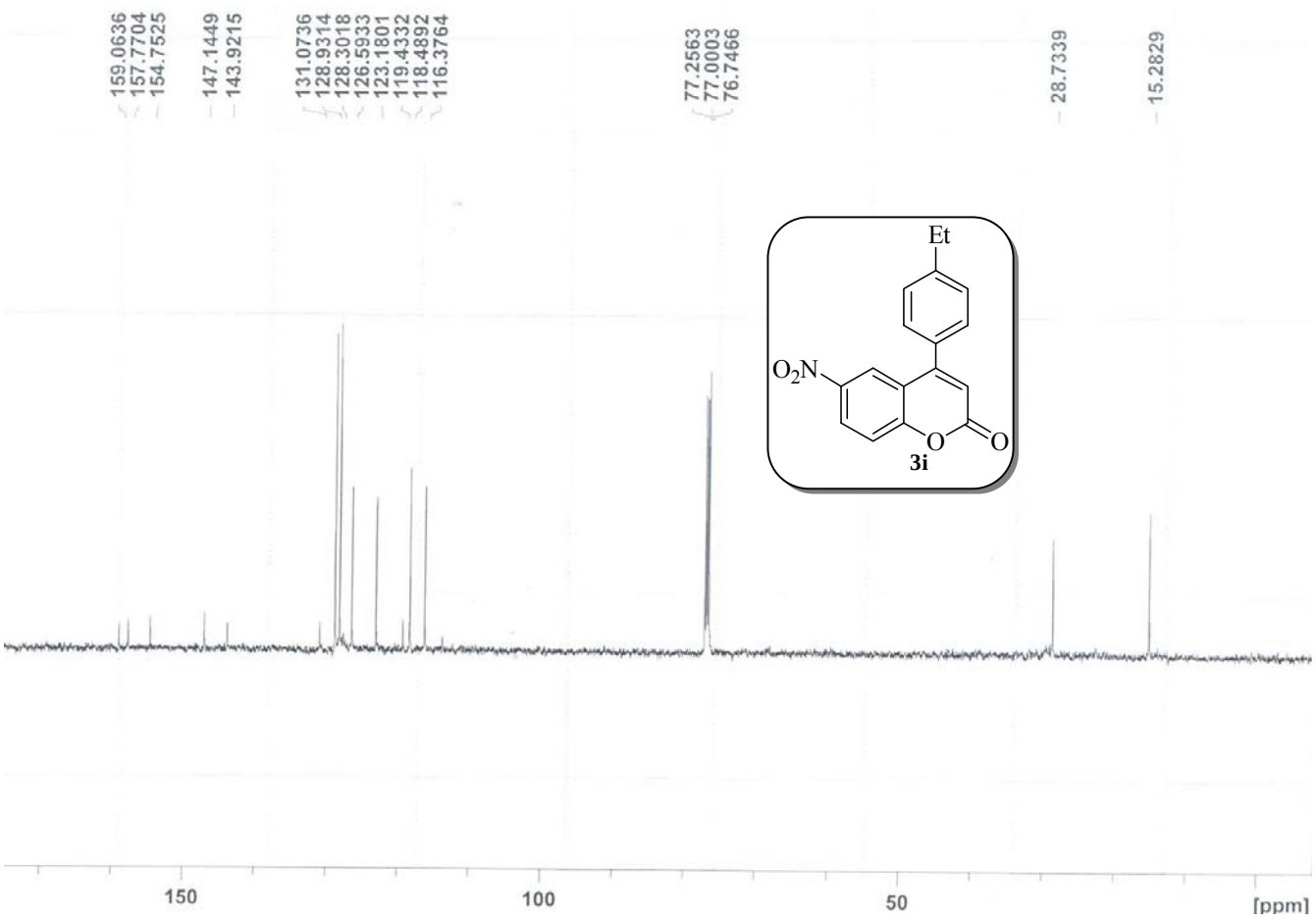
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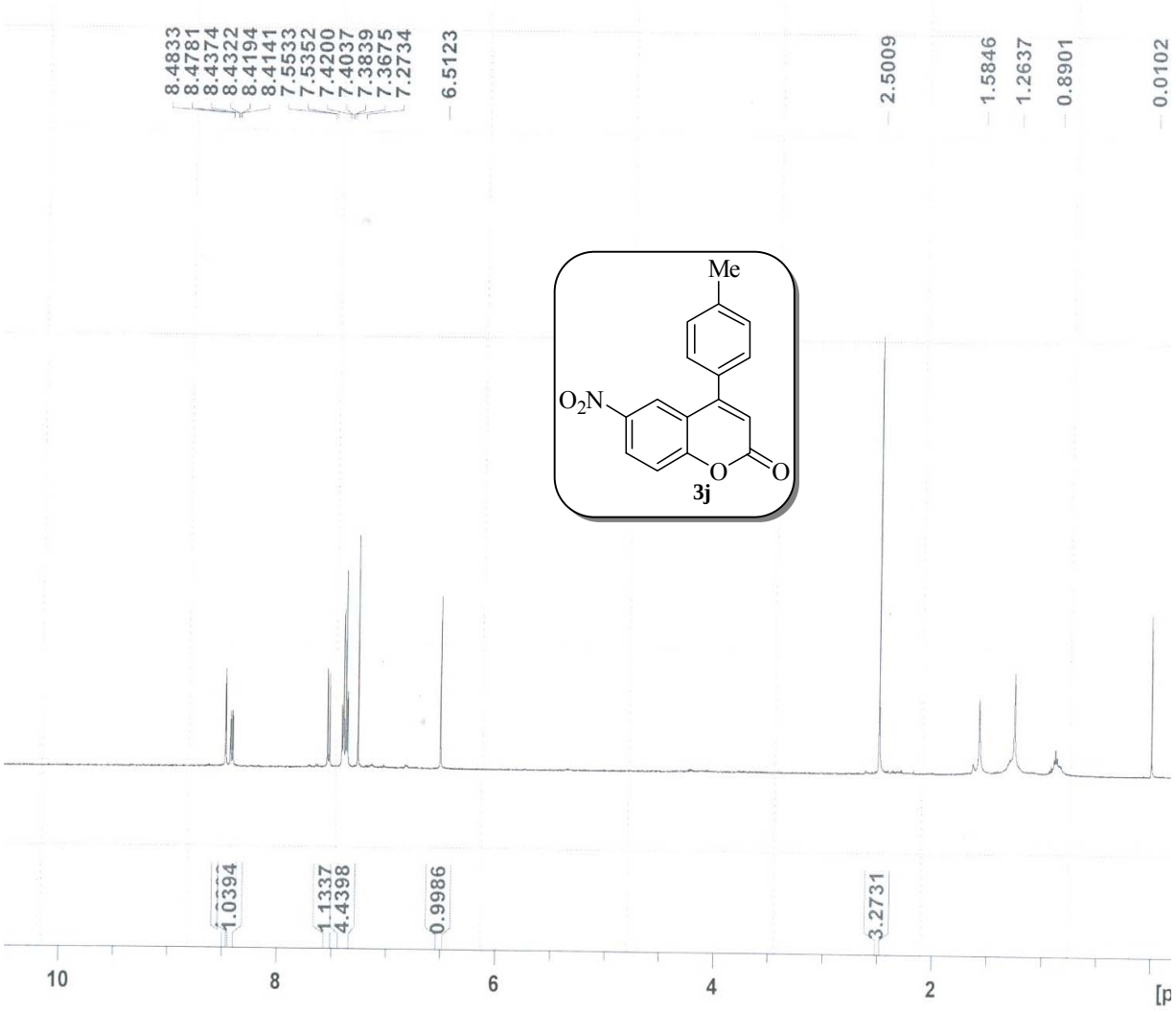
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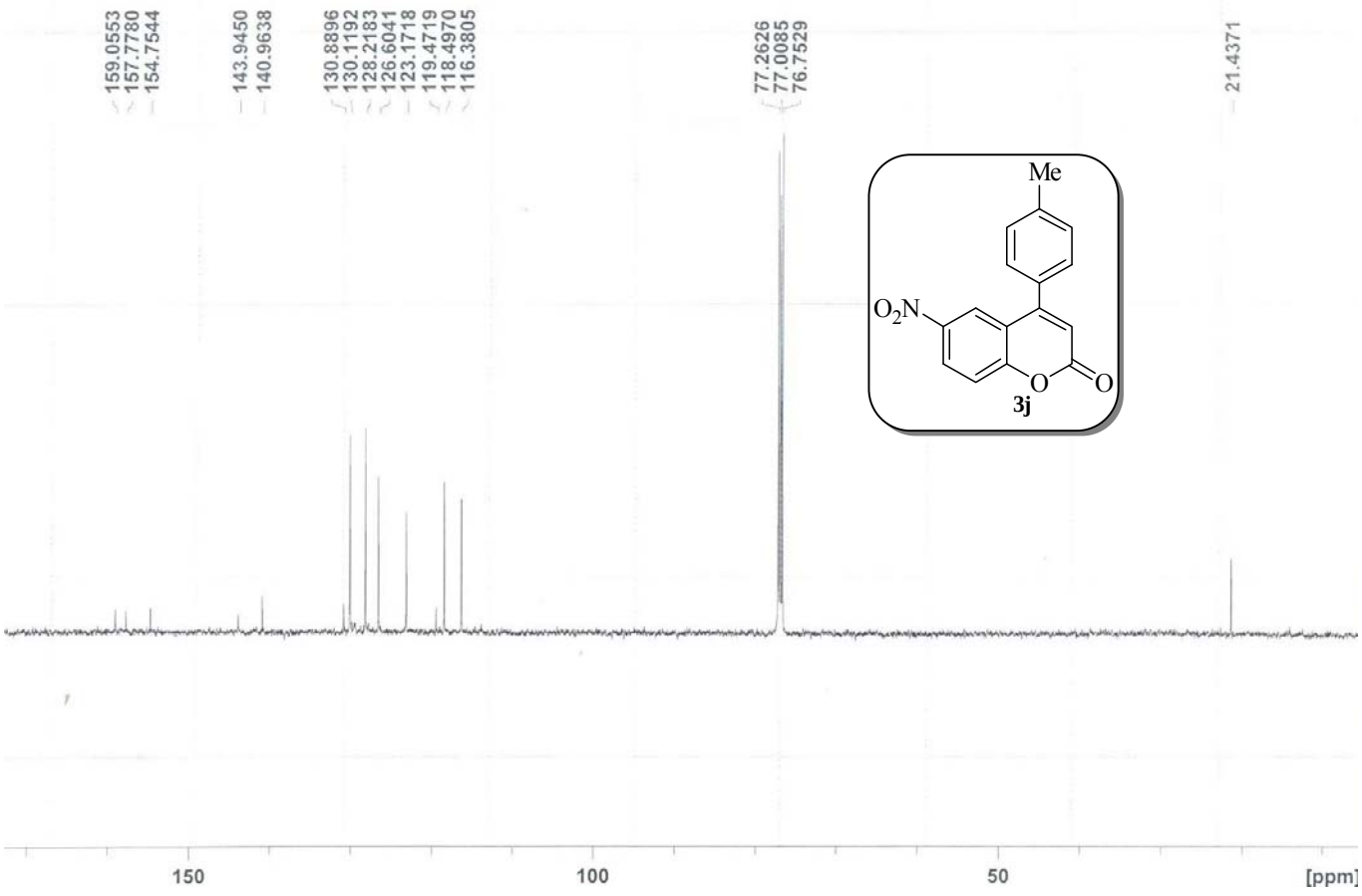

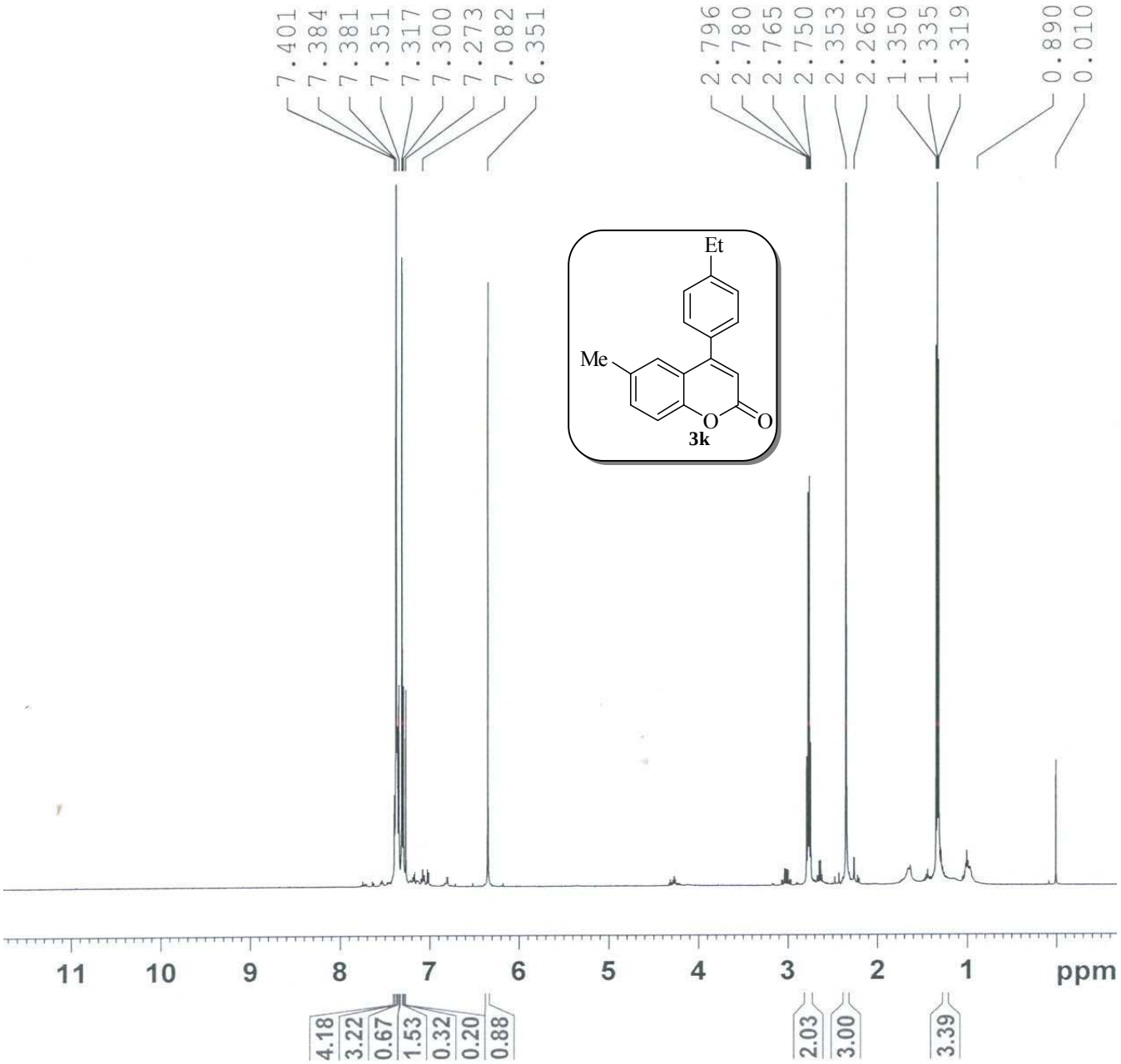
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3k
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8
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6
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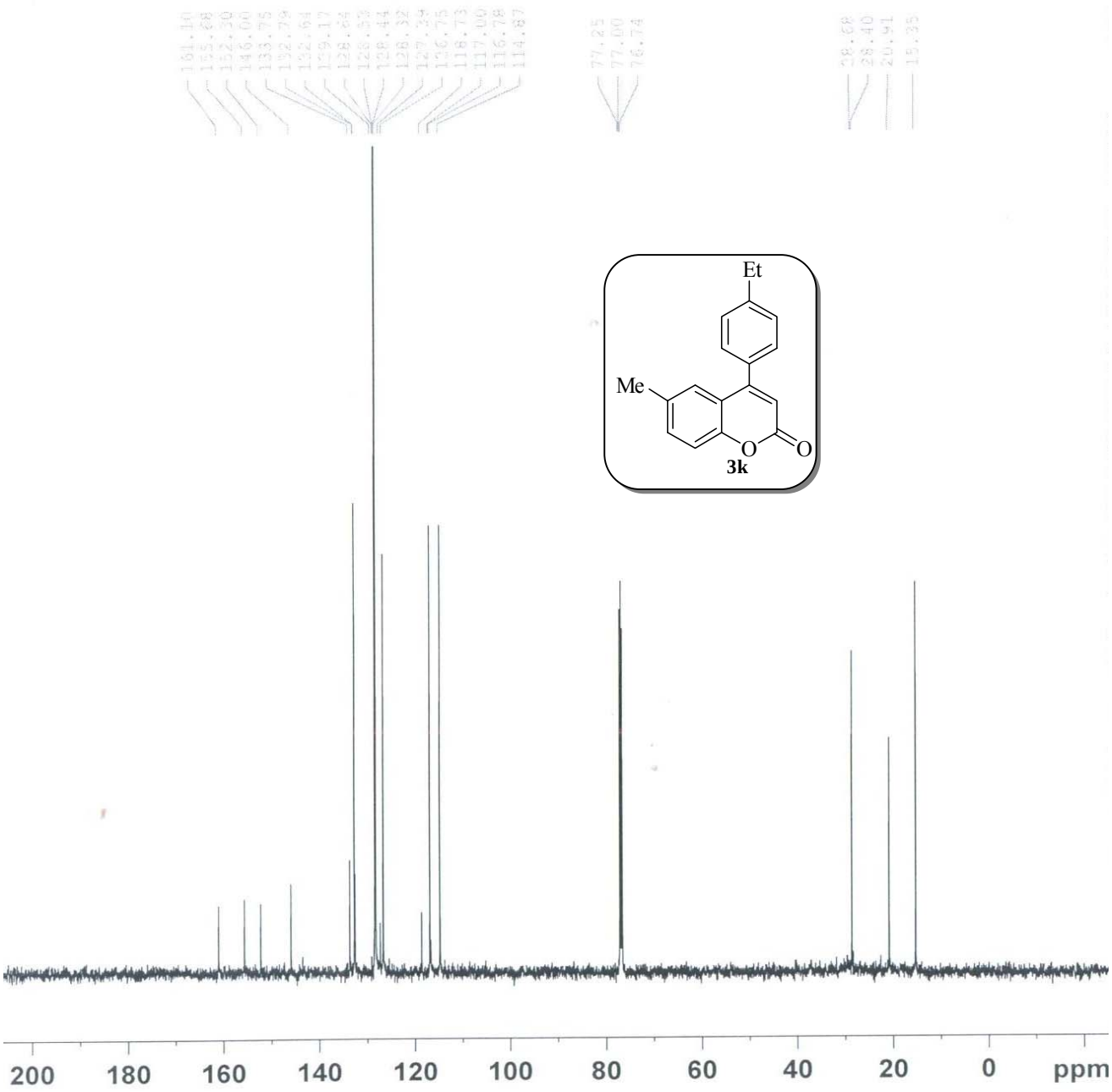
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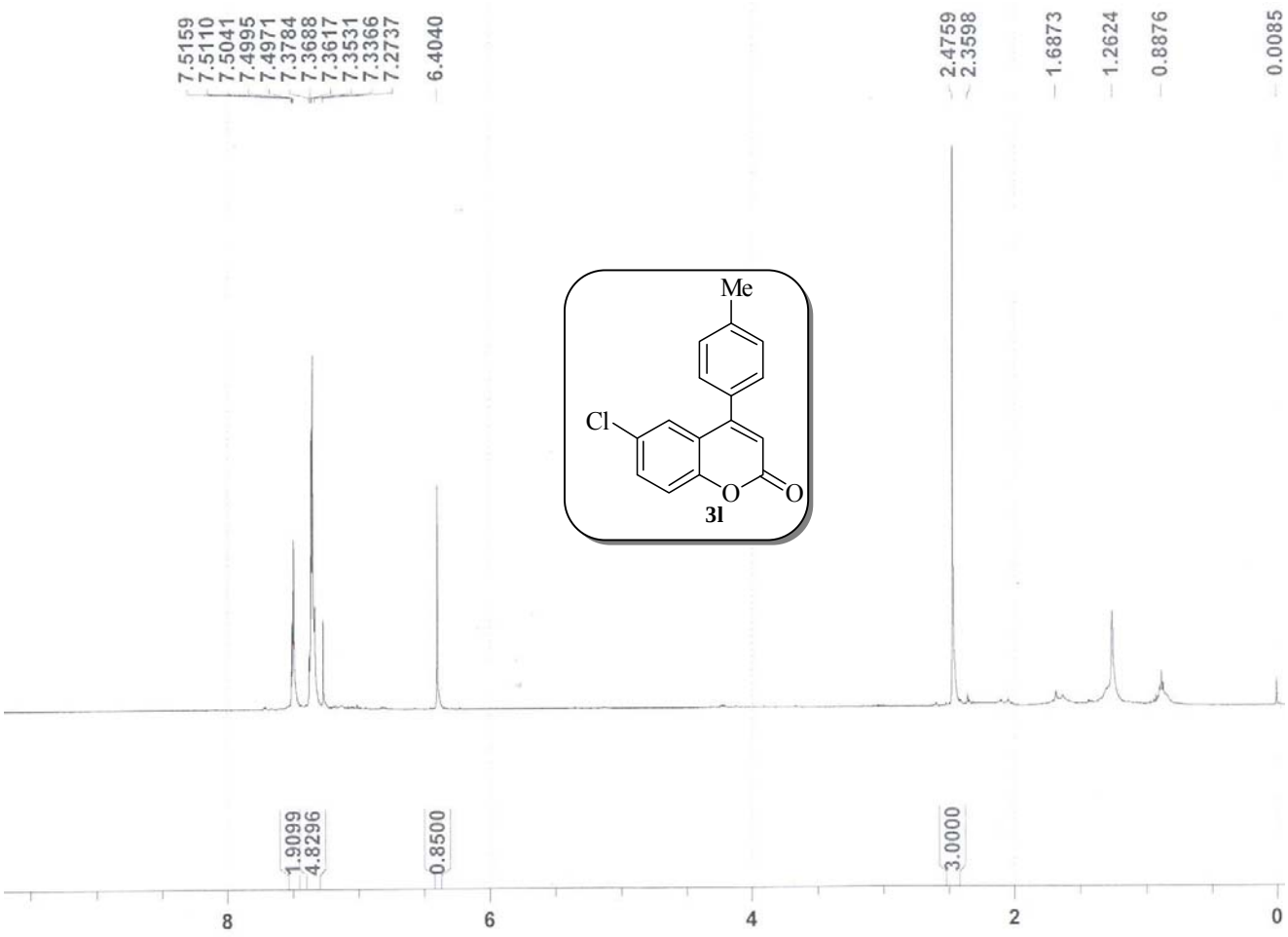

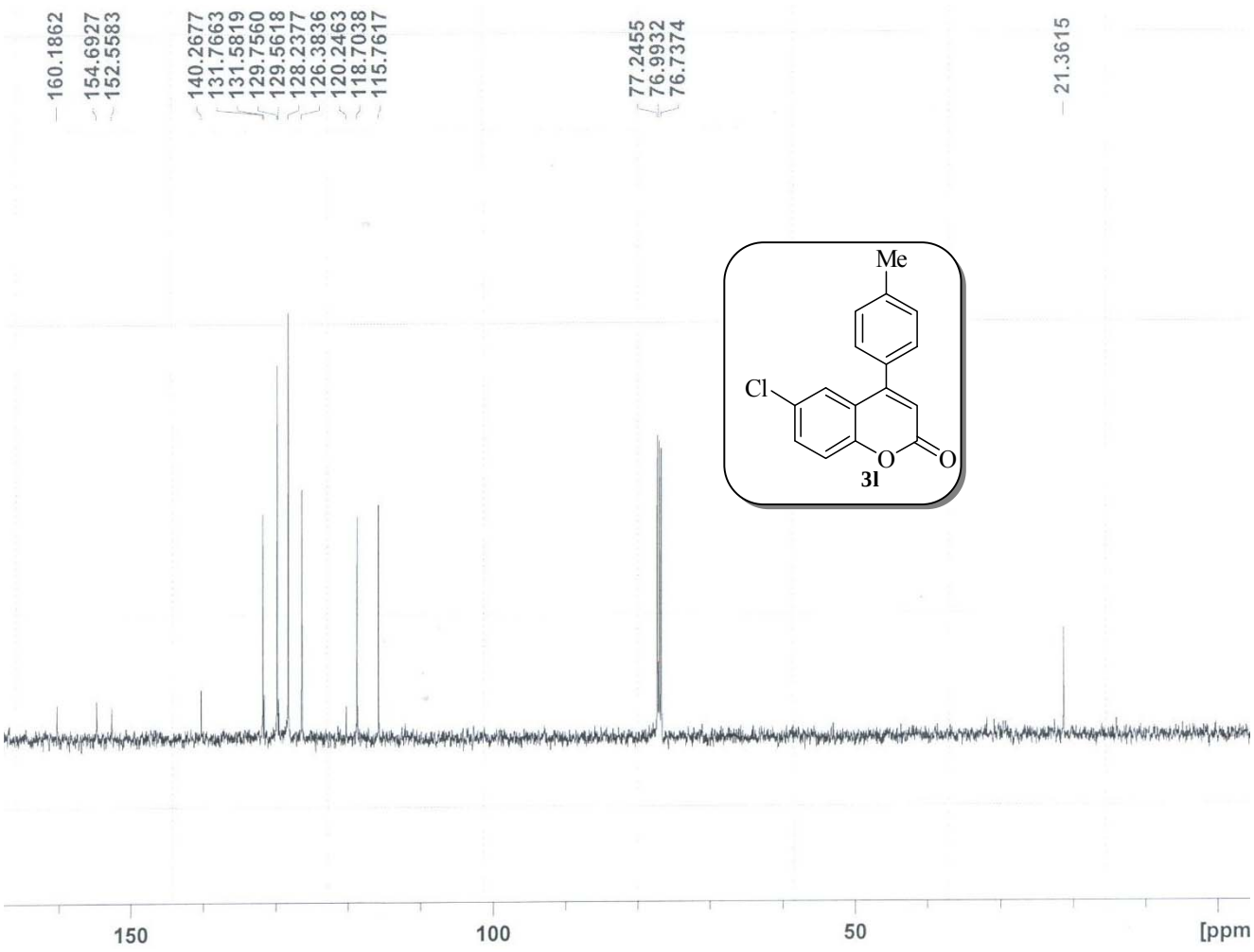
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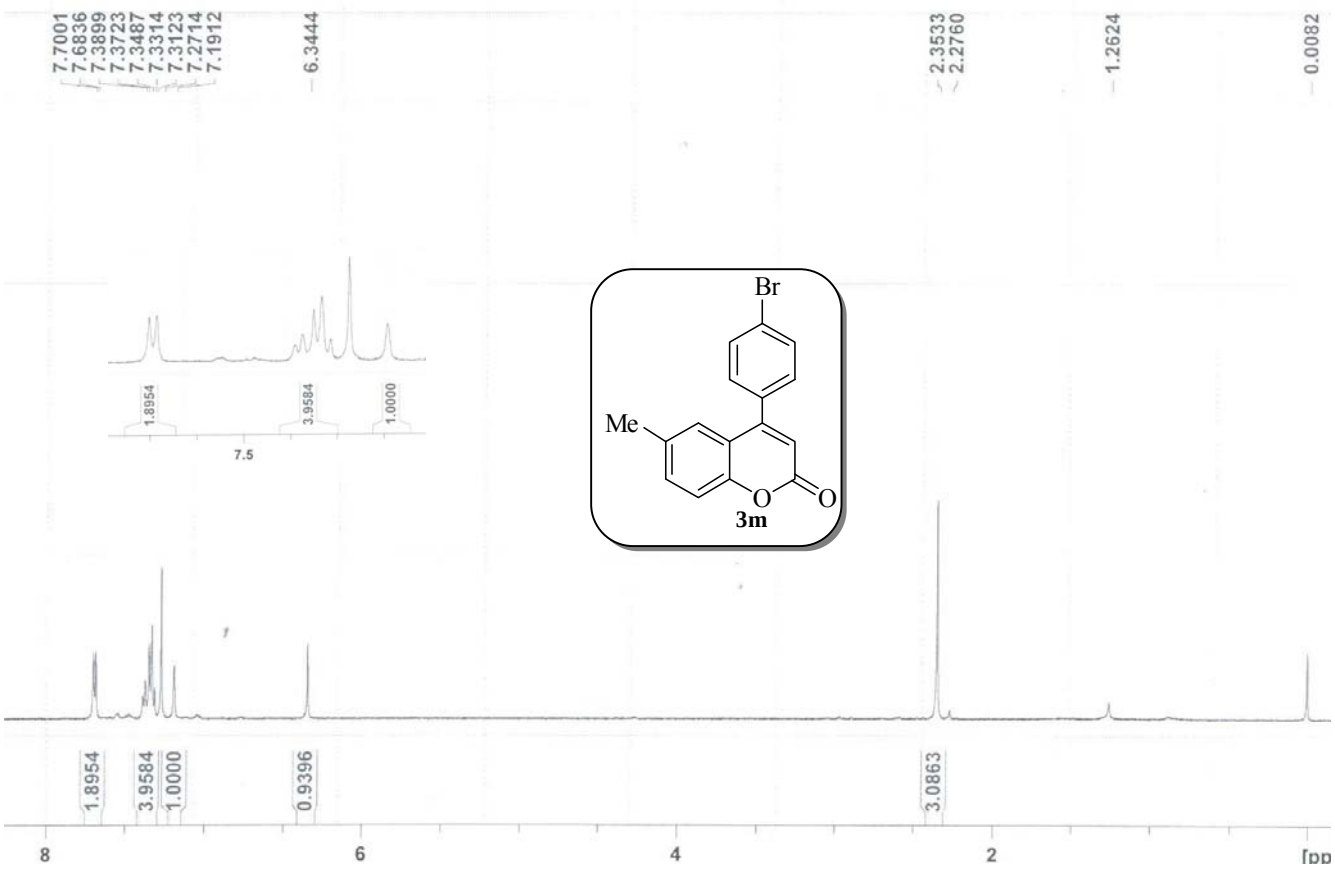
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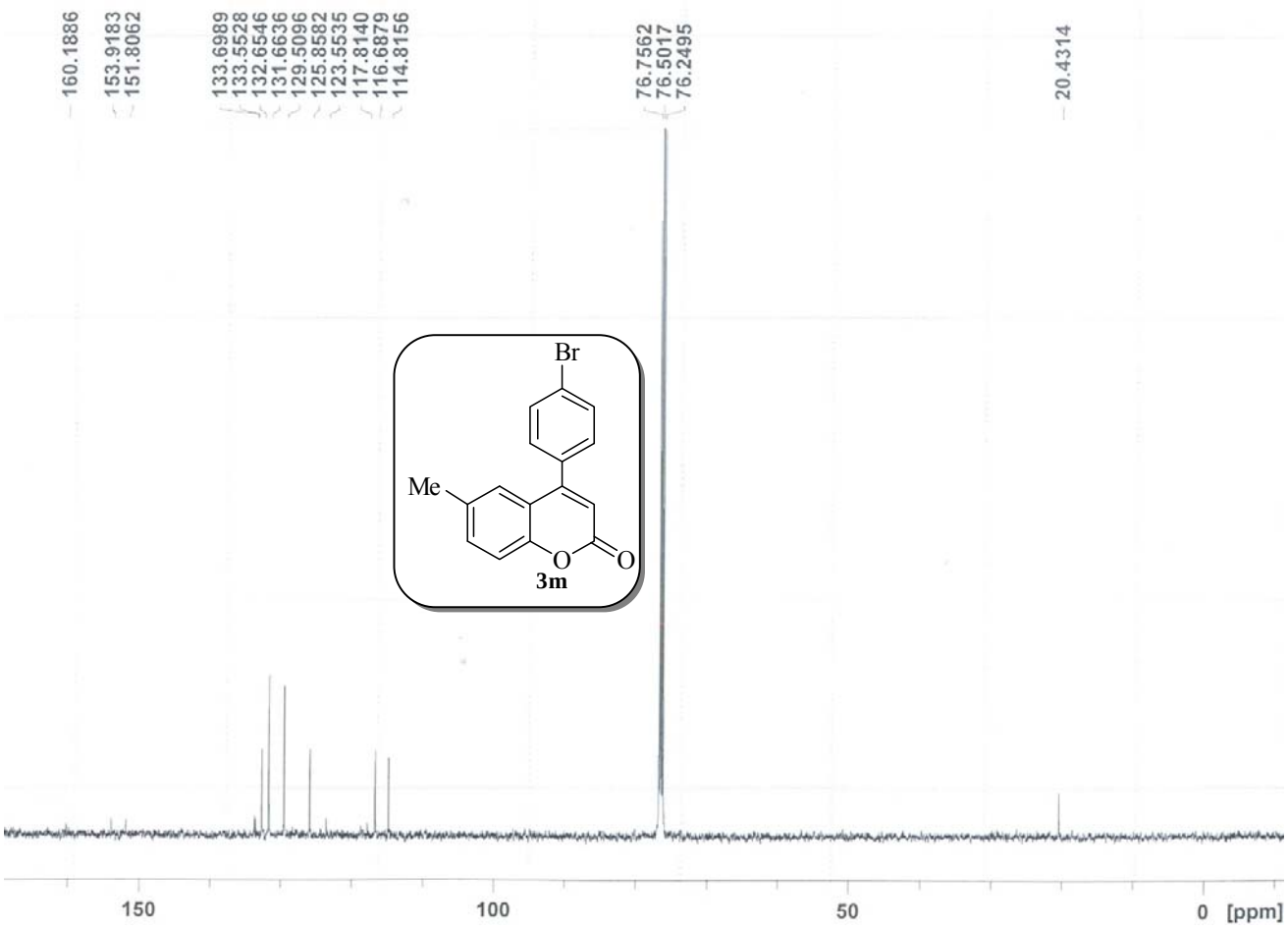
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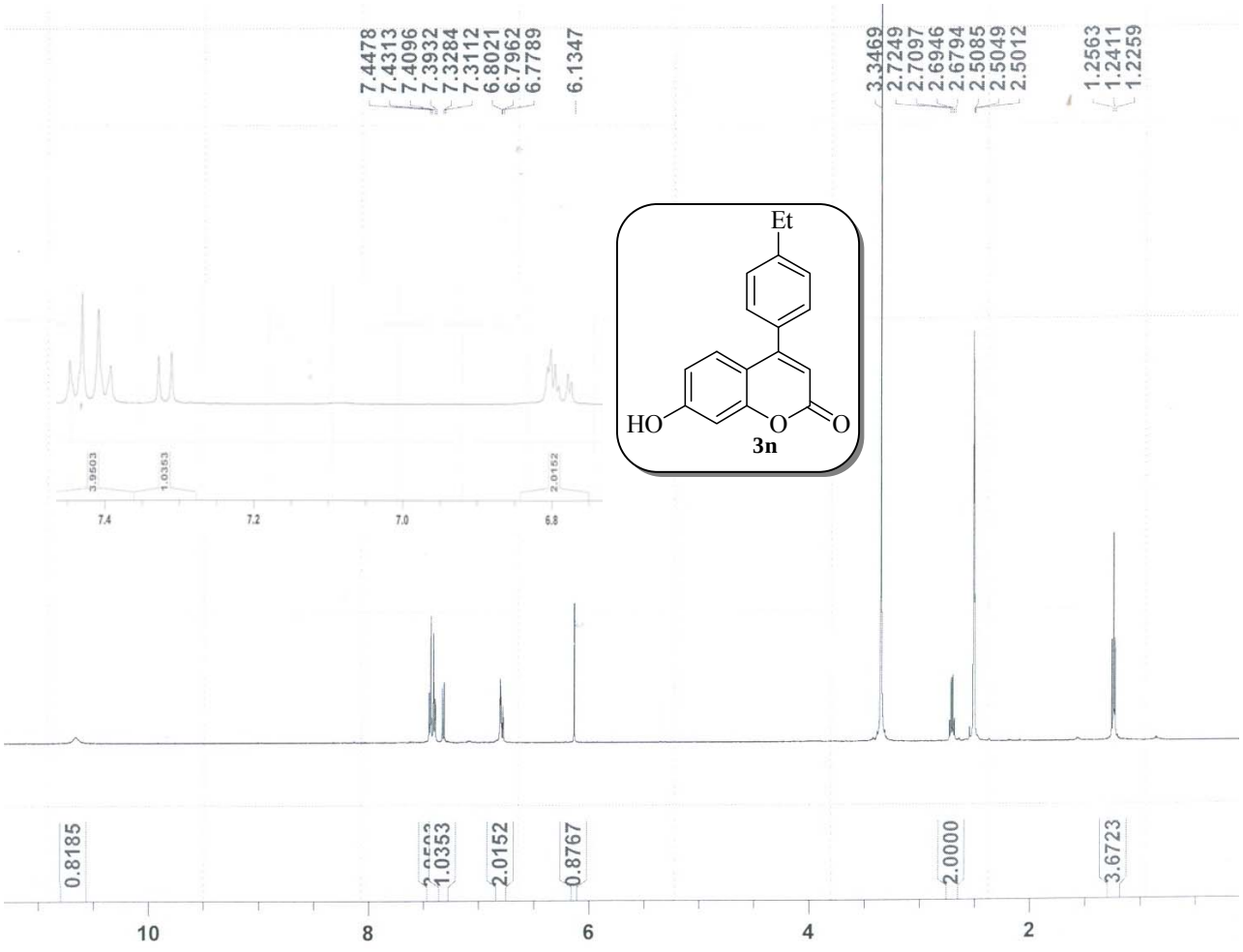
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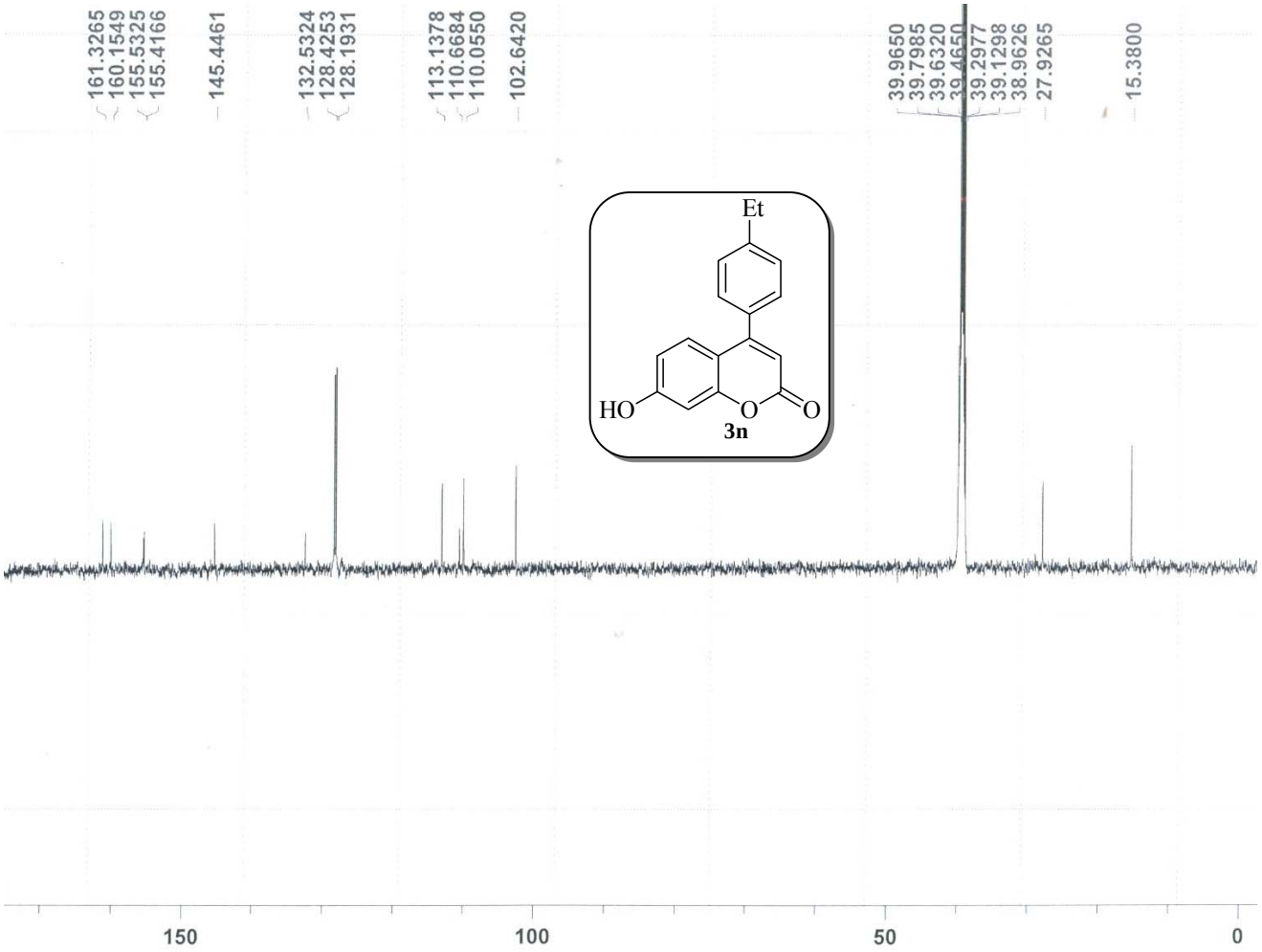
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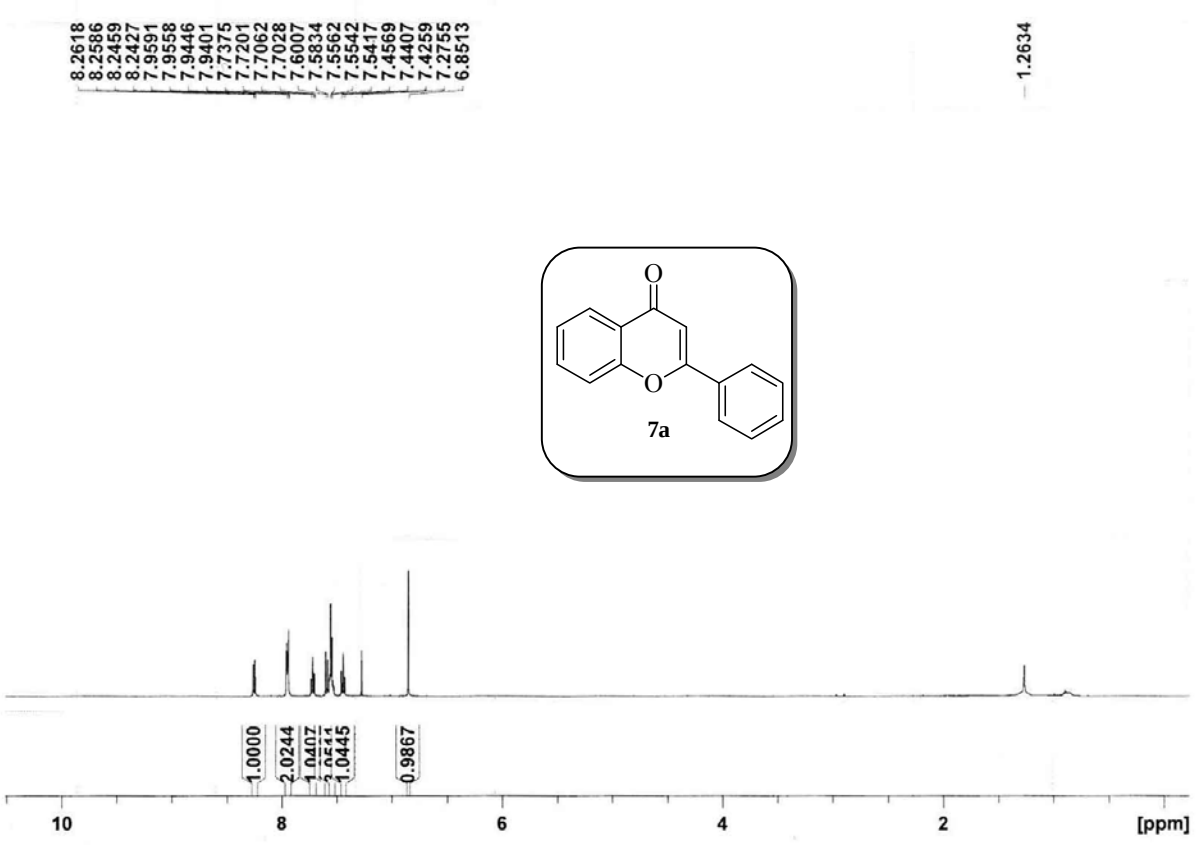
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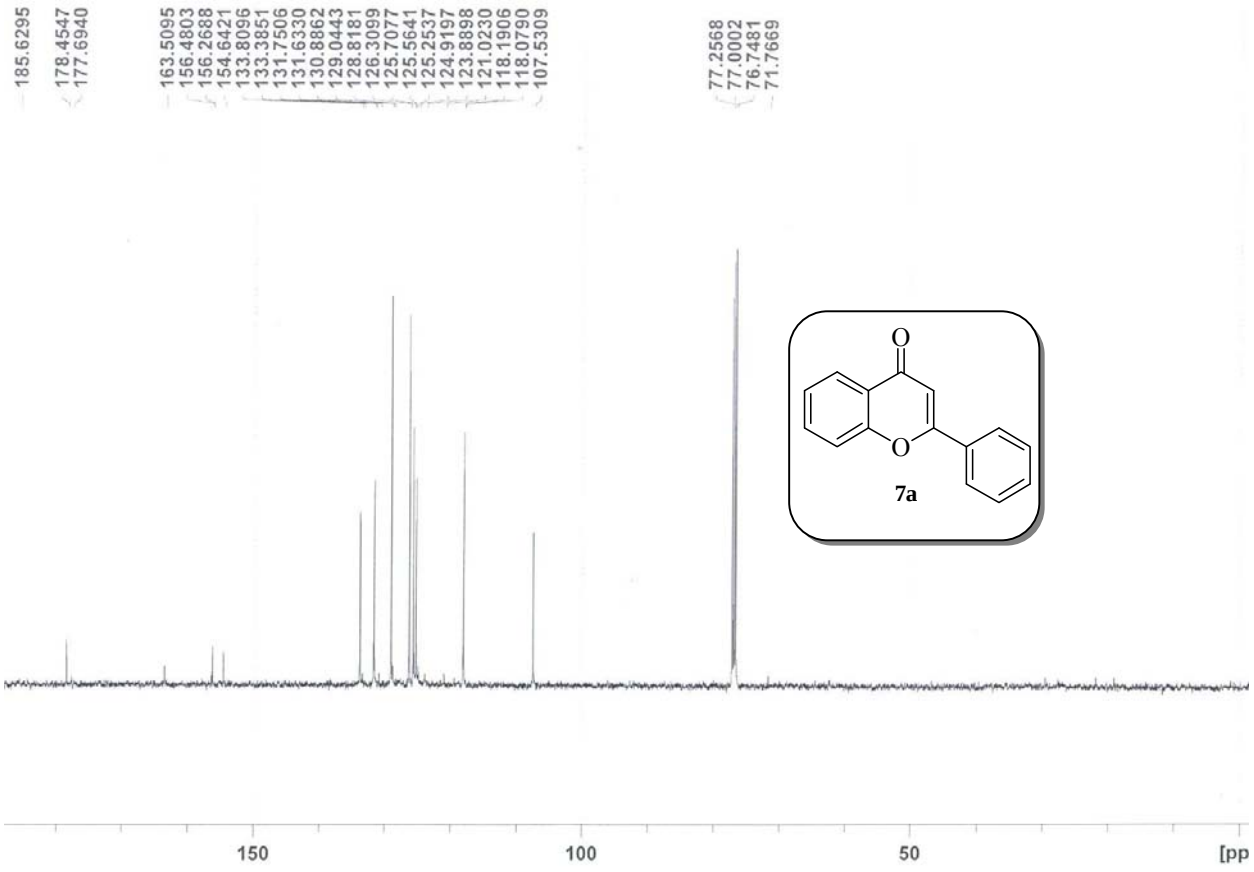
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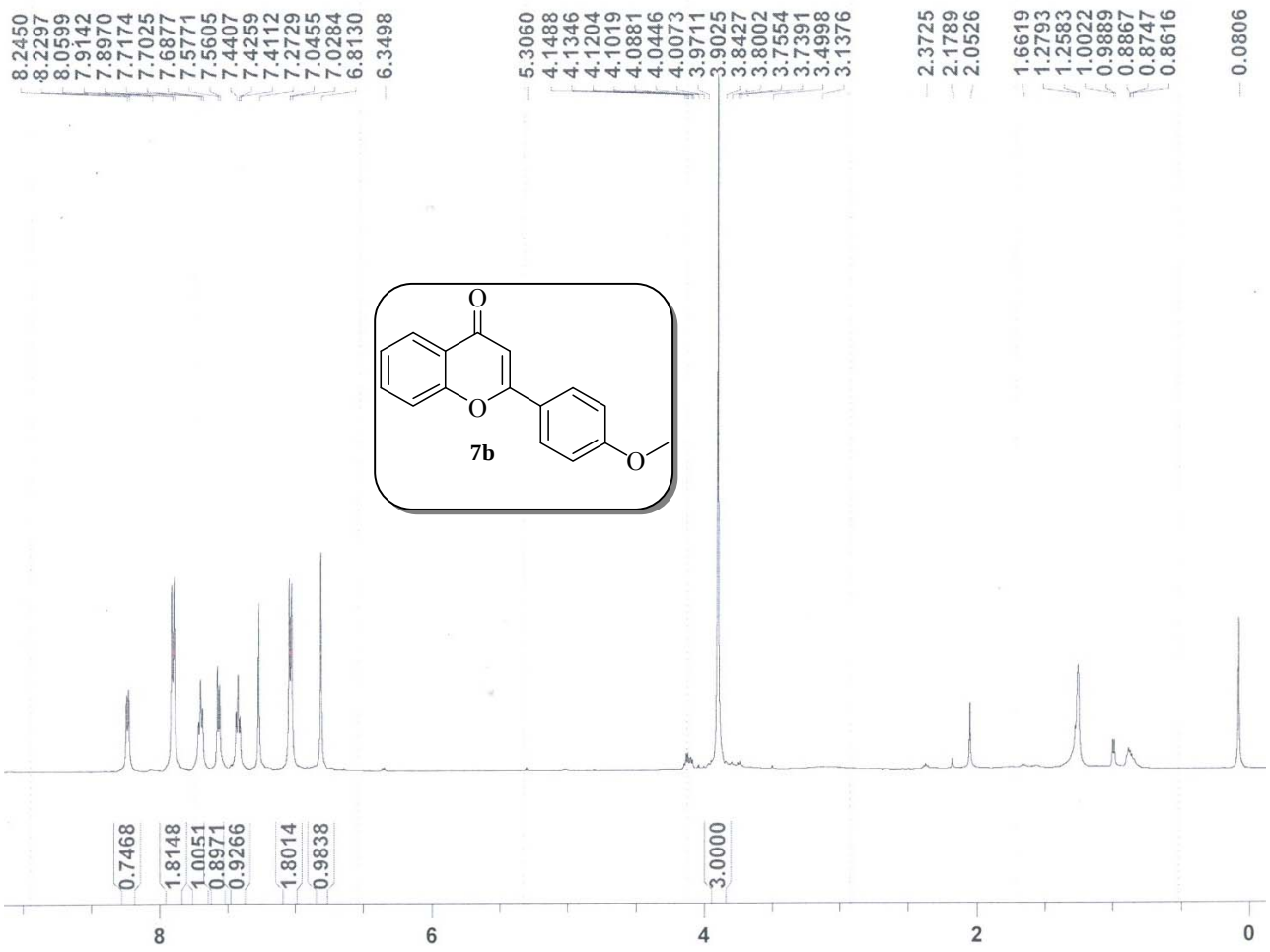
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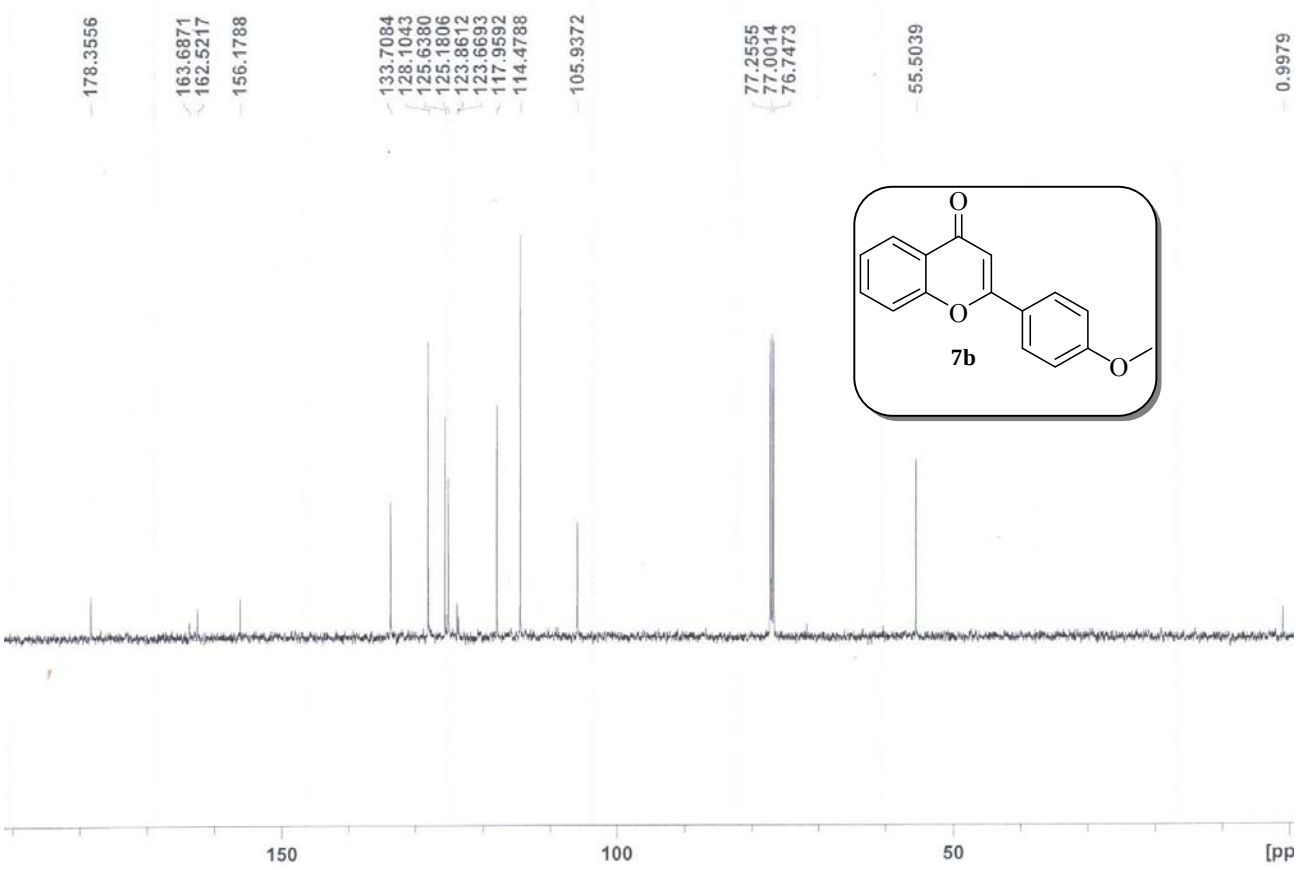
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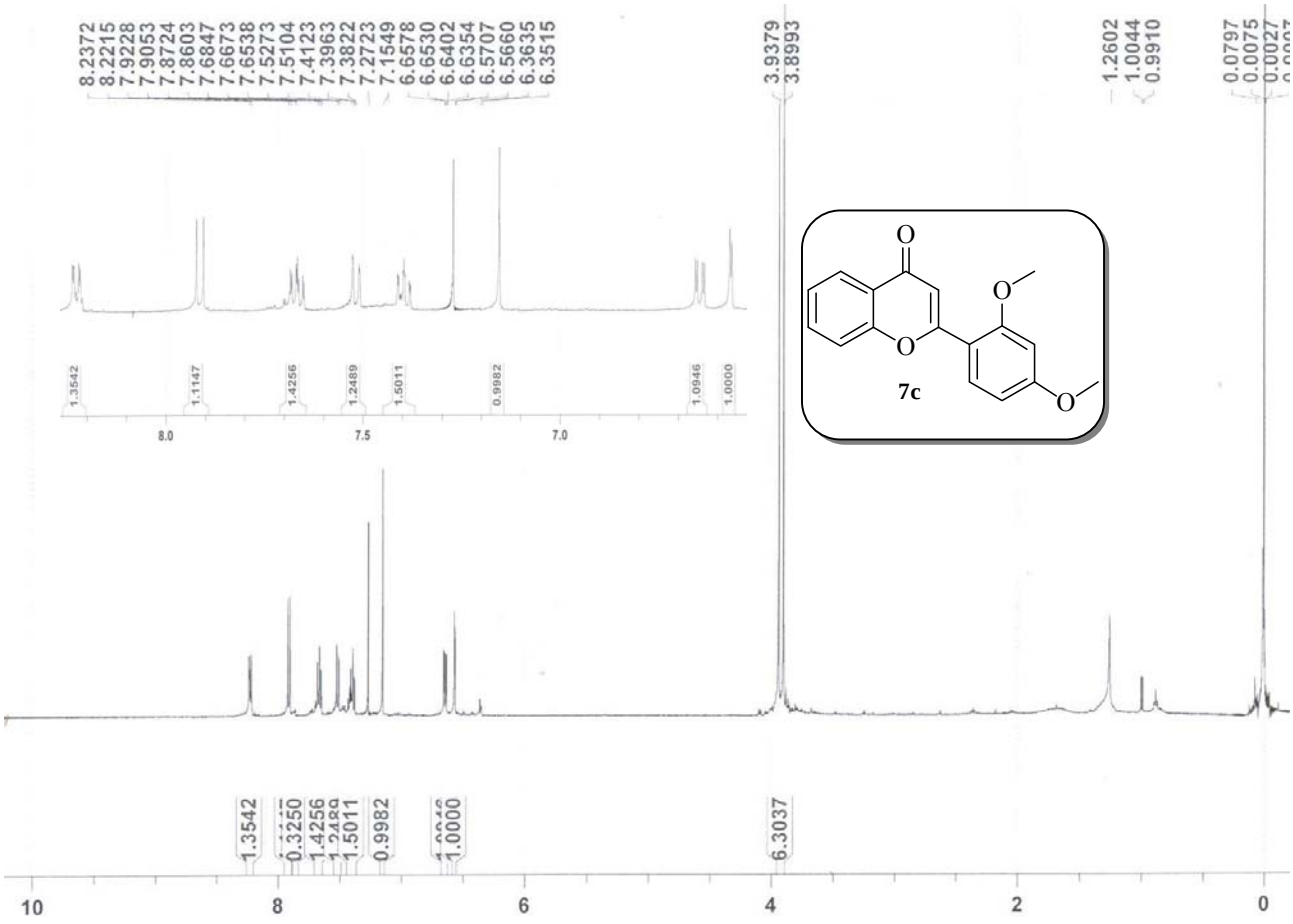
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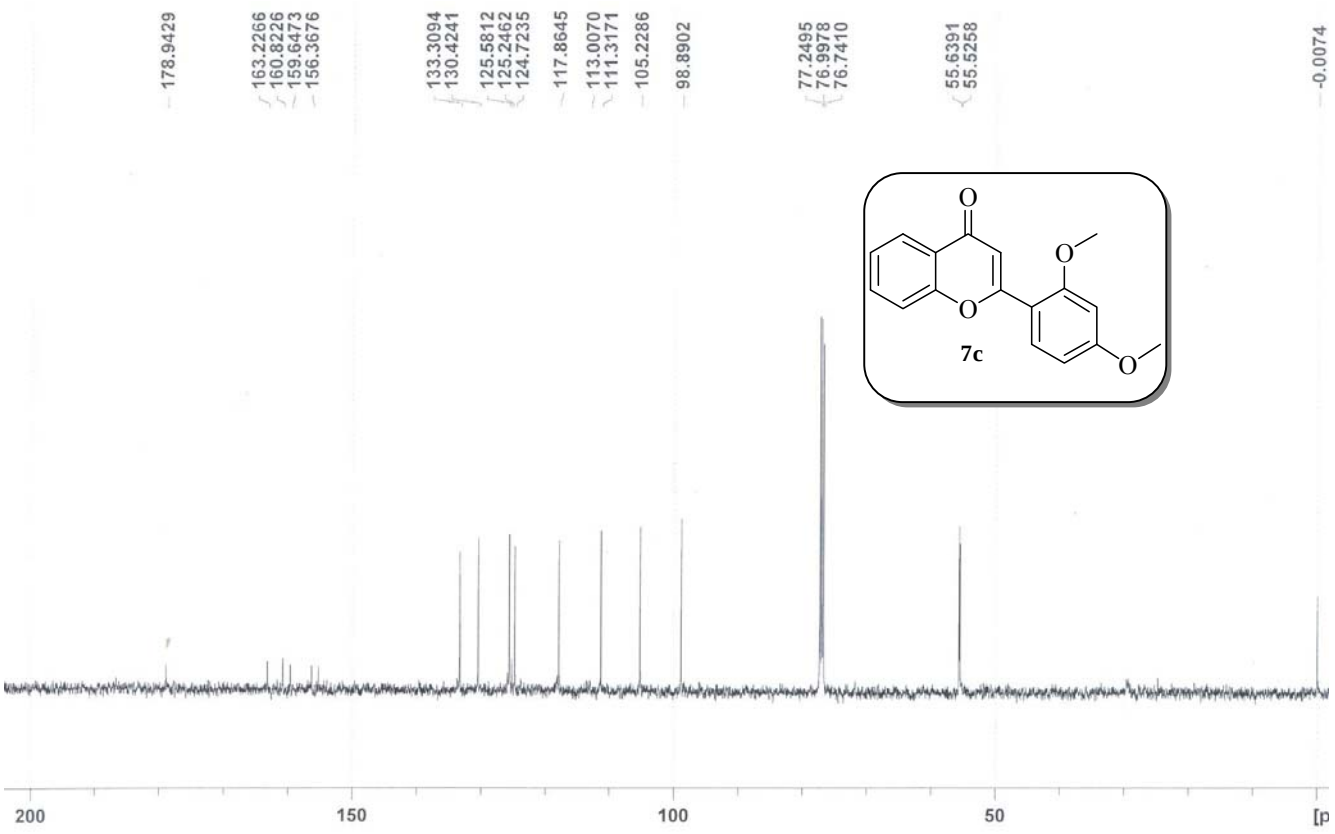
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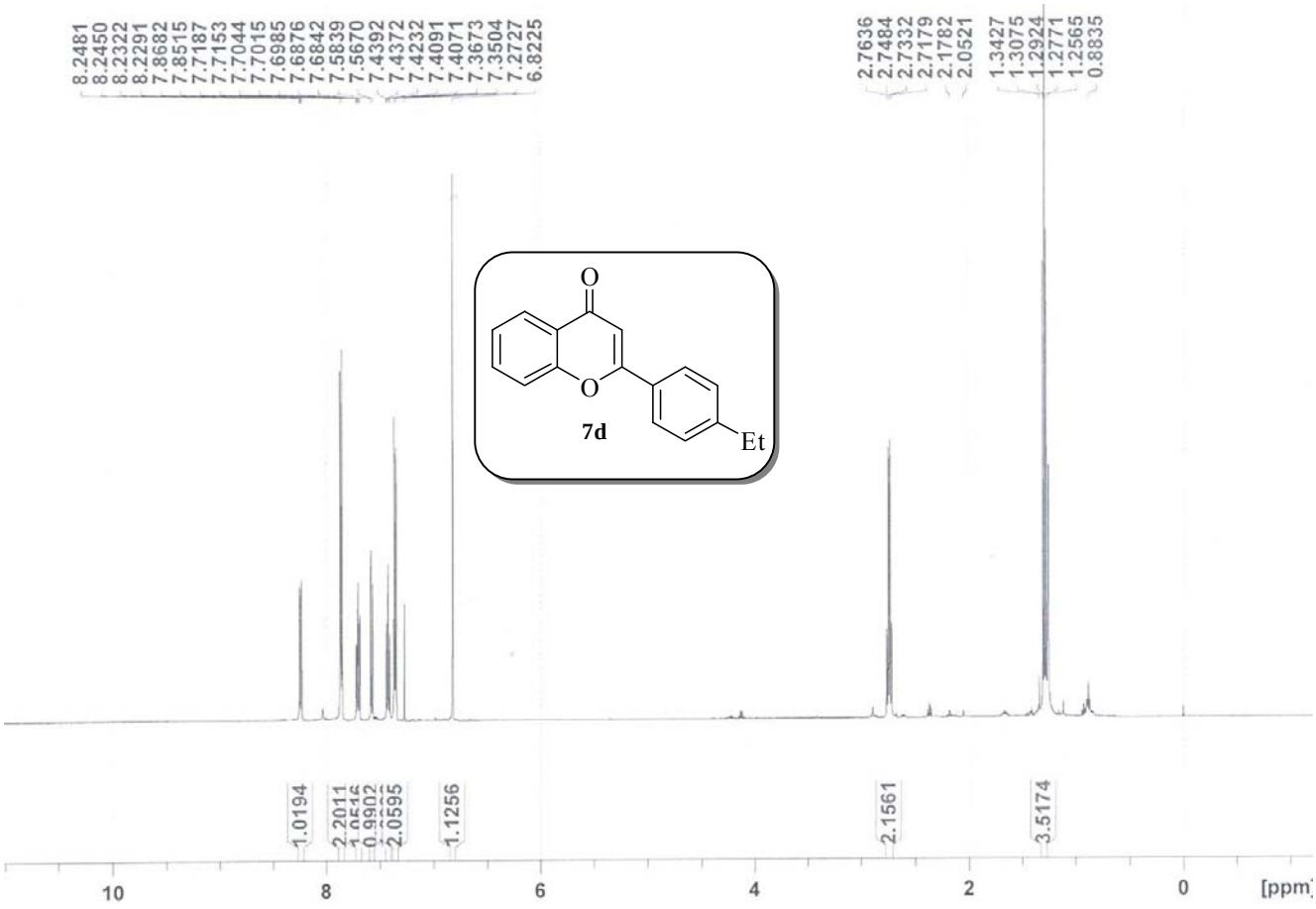

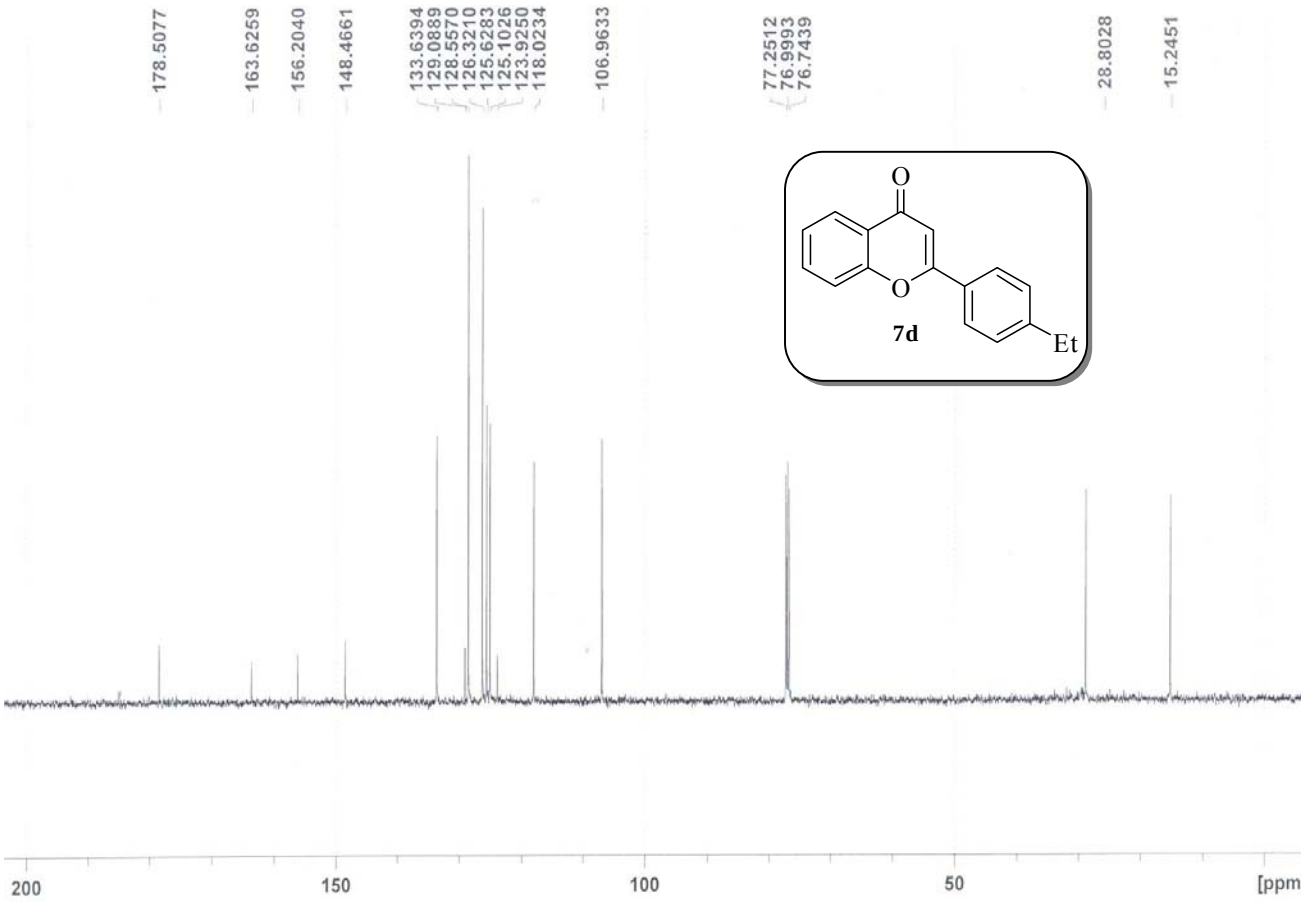
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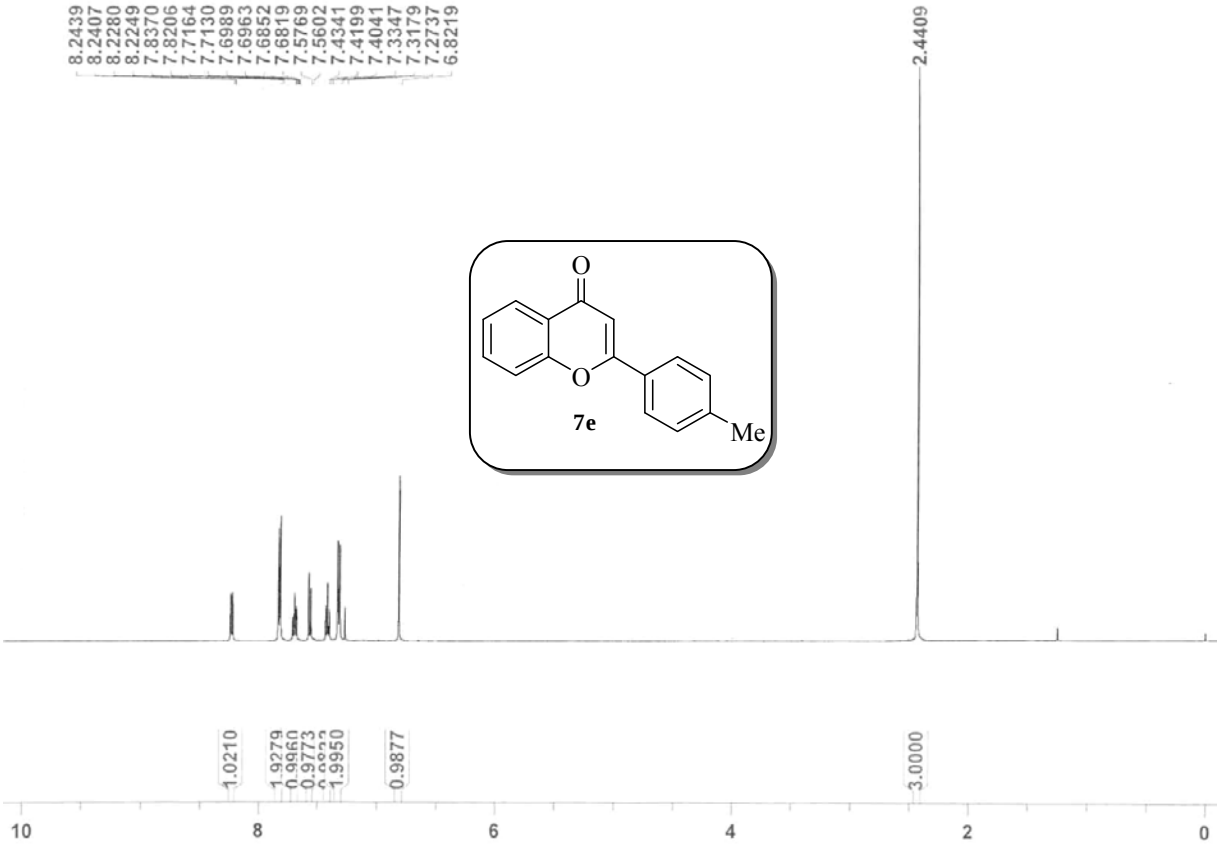
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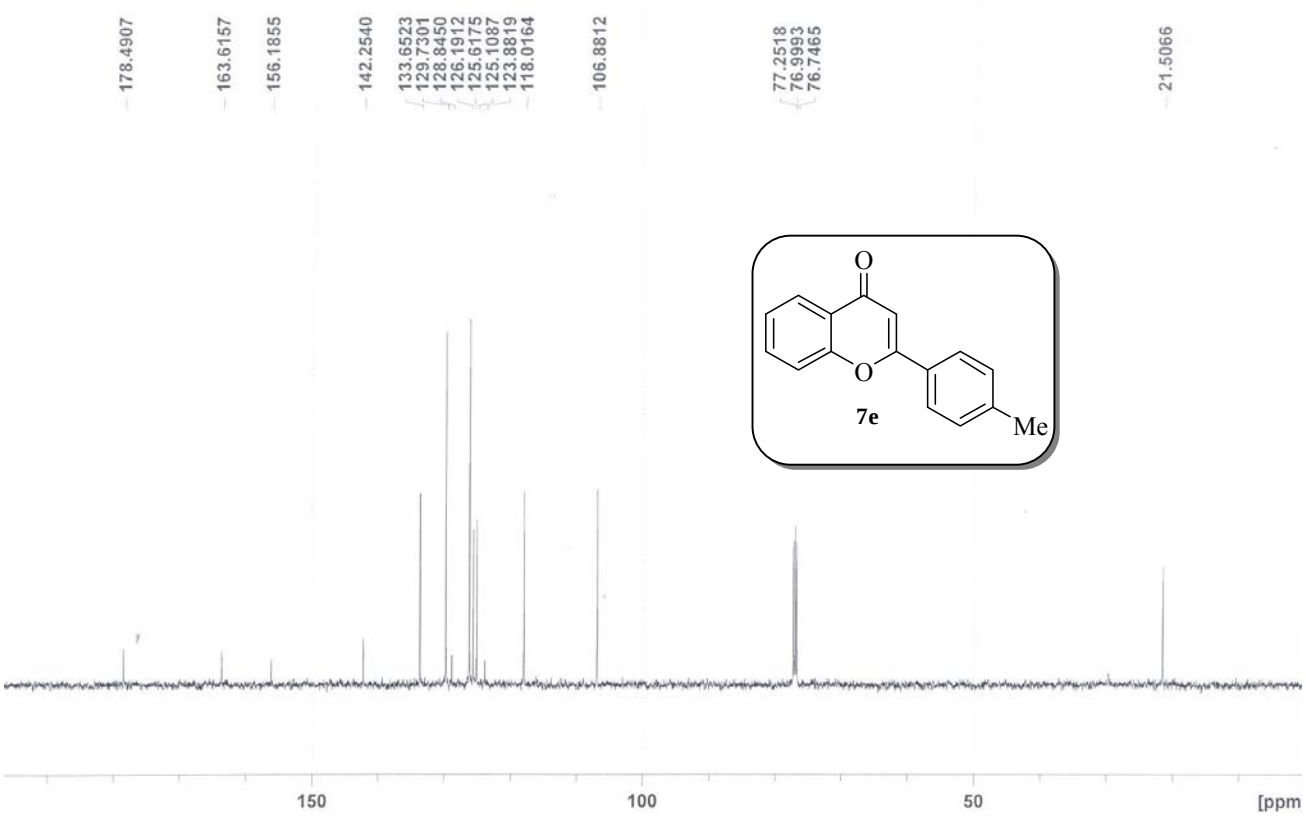
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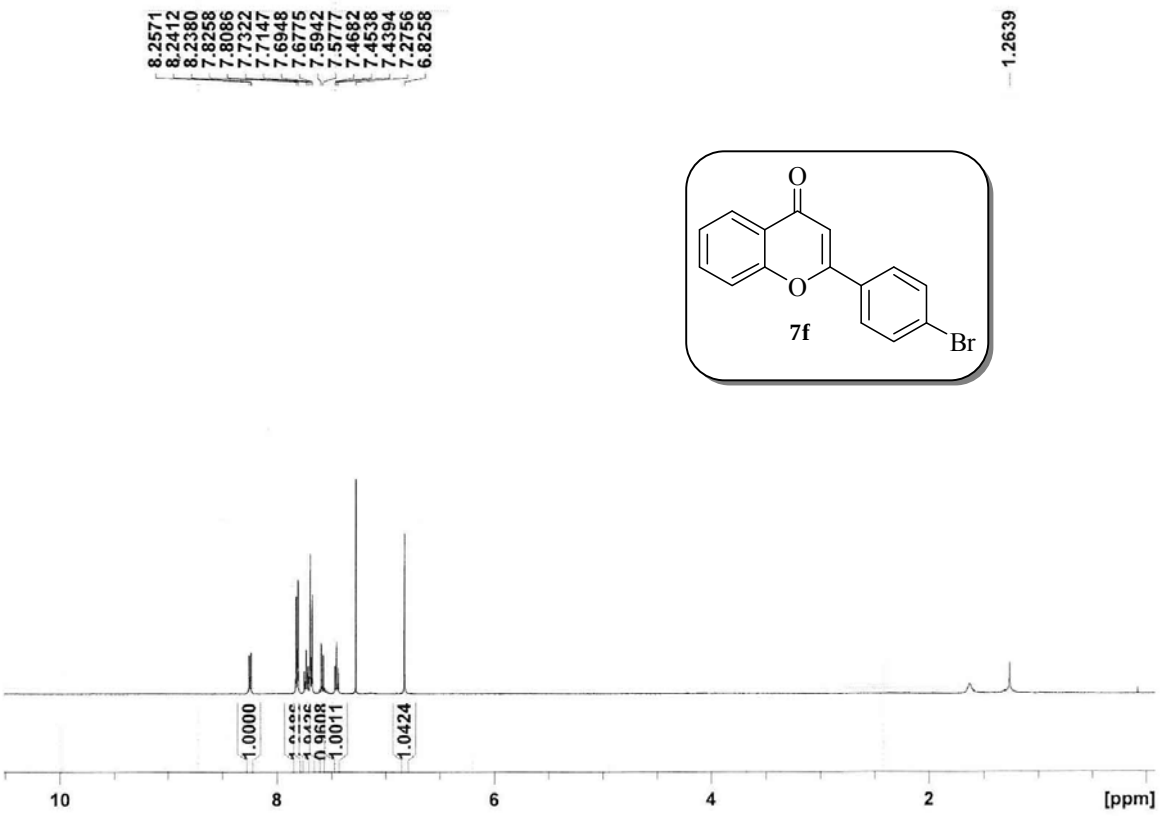
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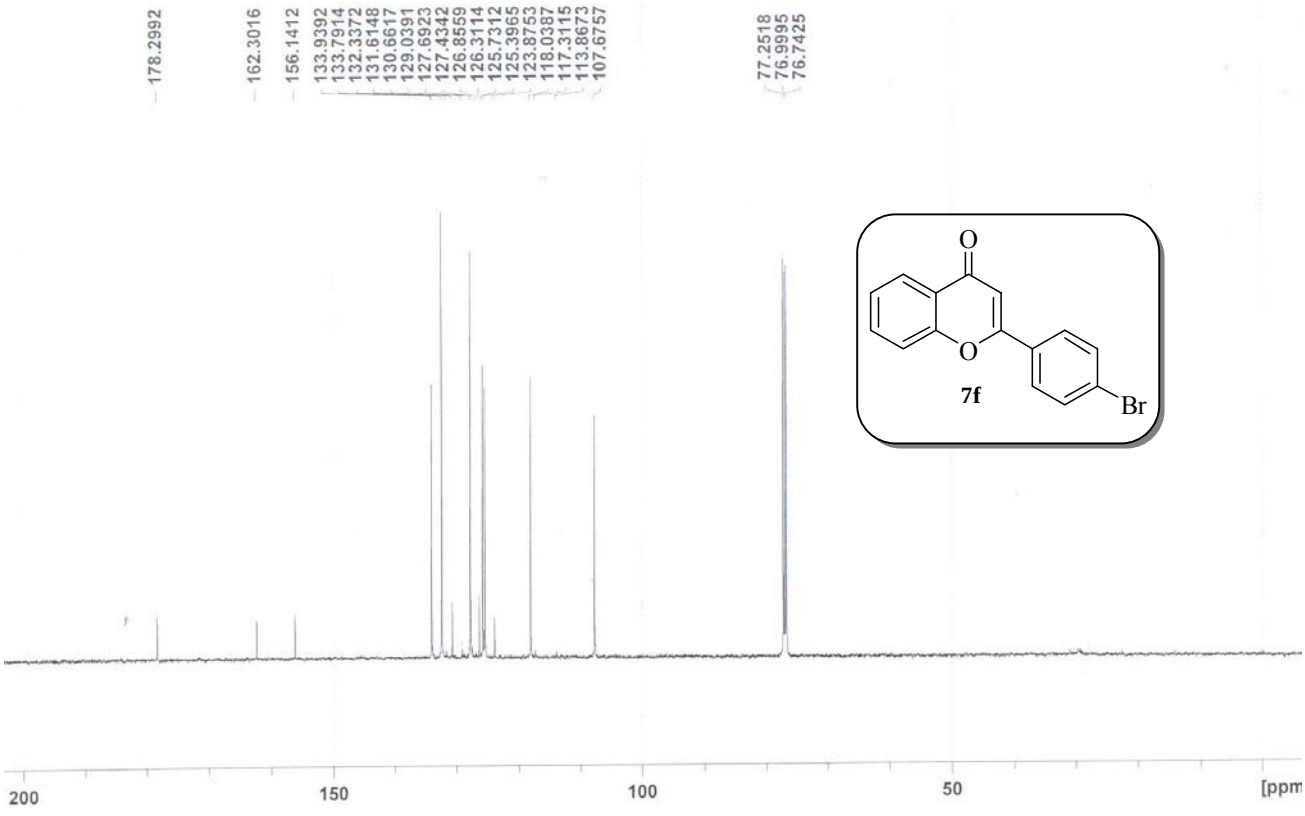
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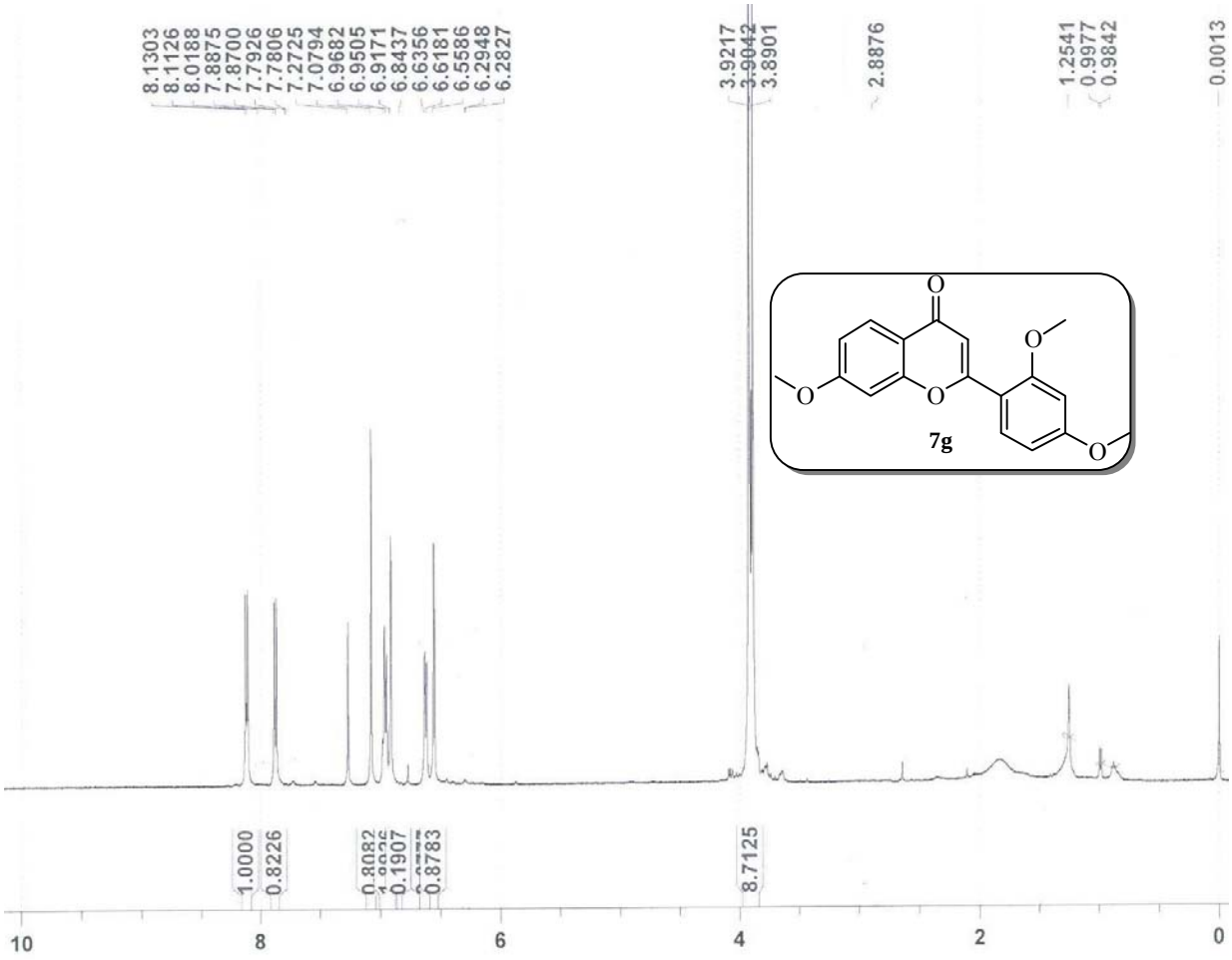
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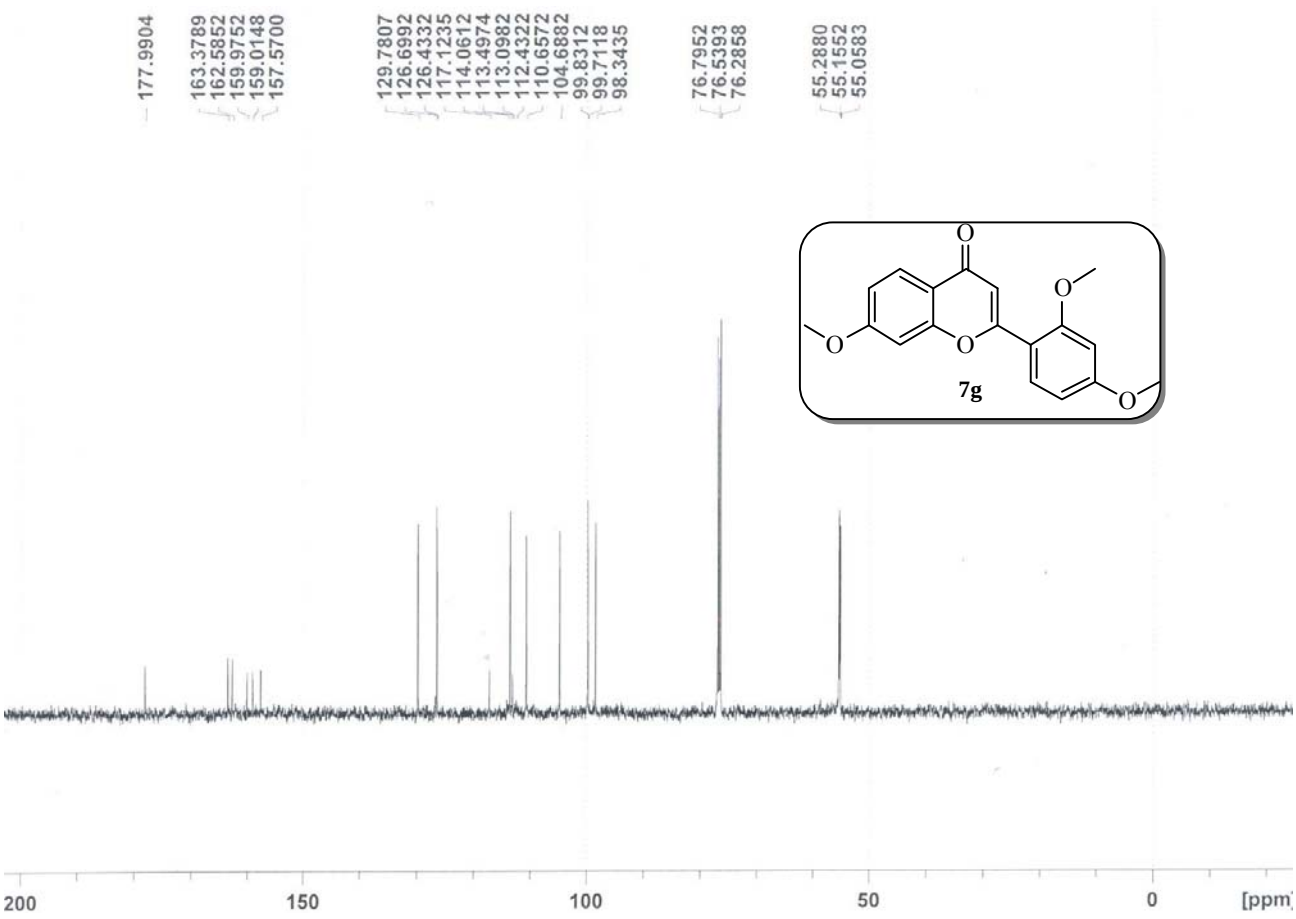
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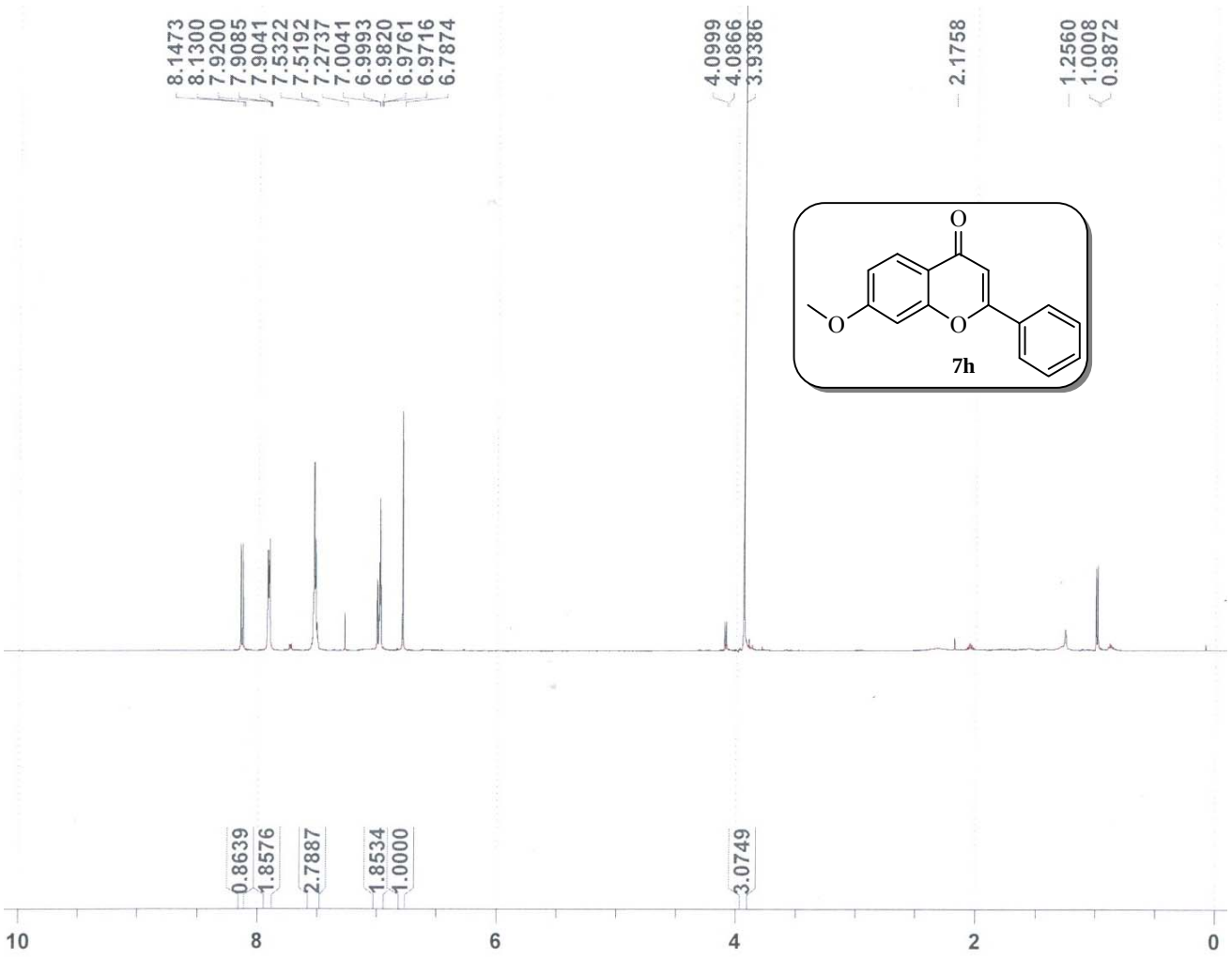
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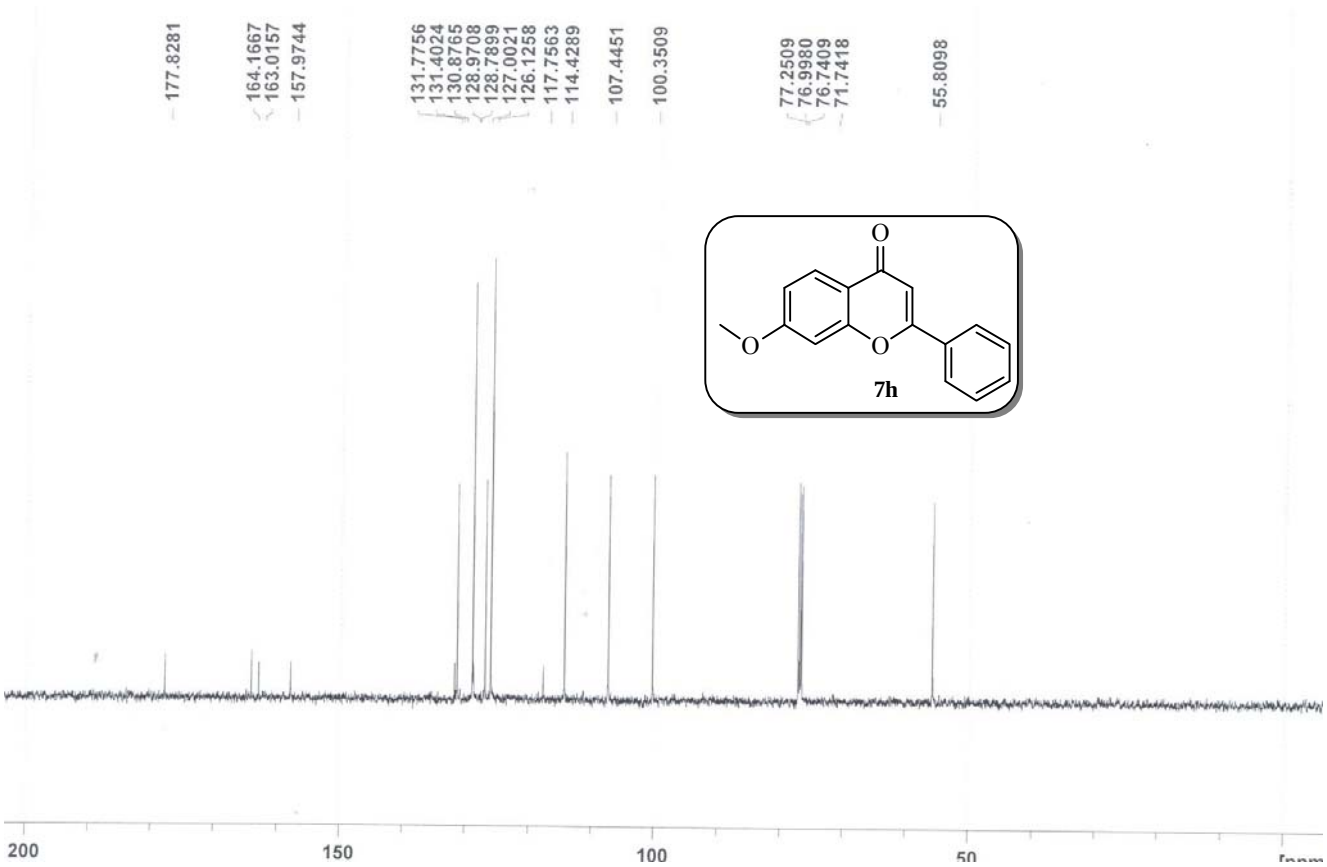
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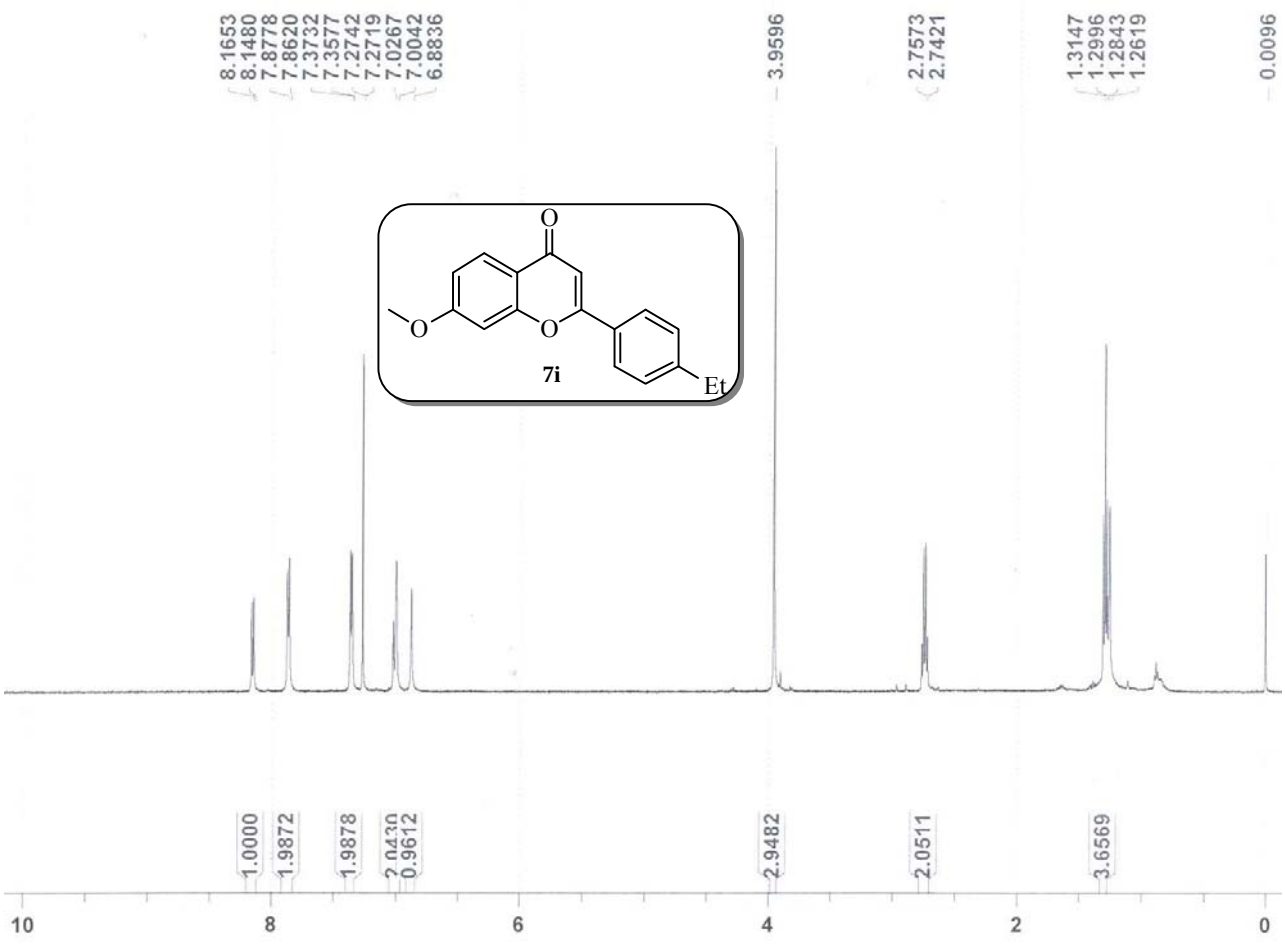
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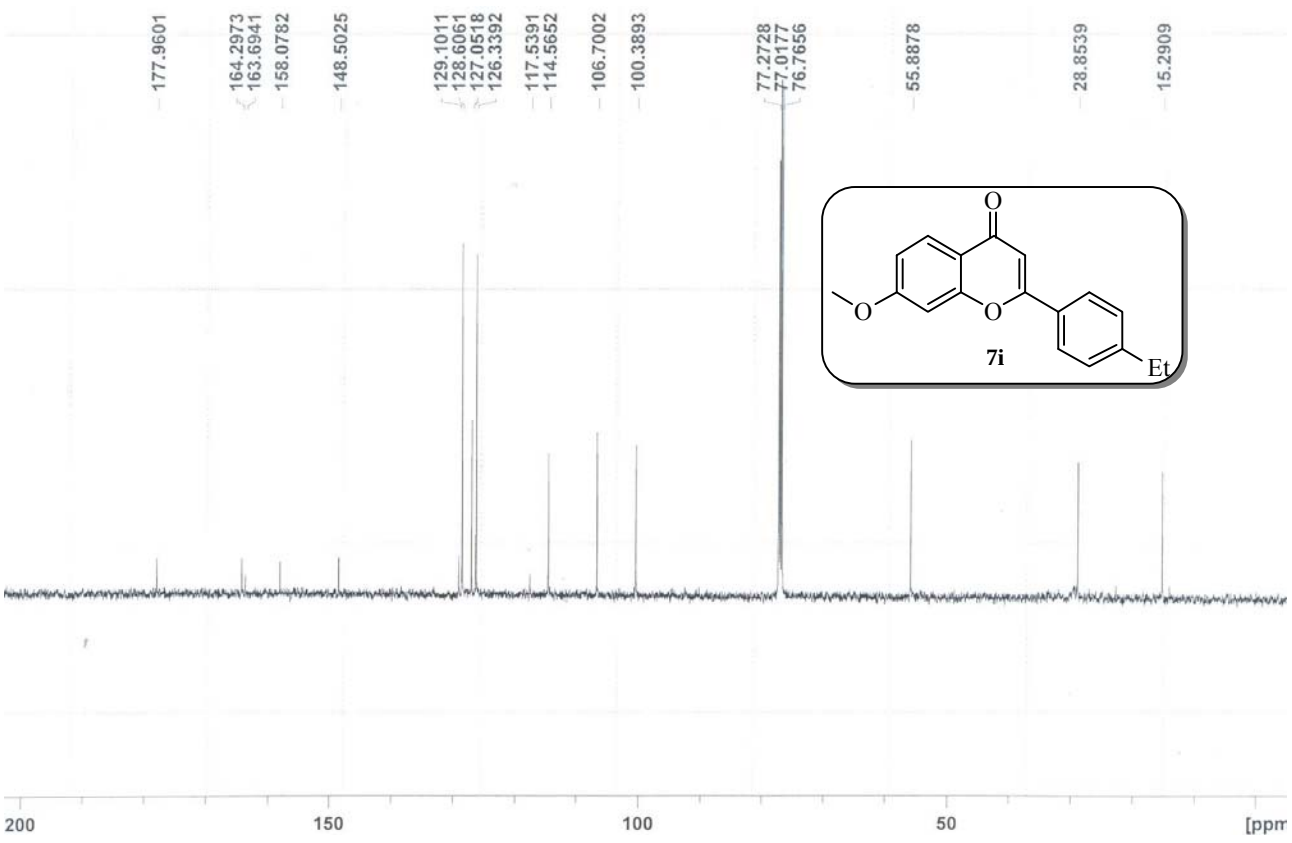
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