

Supporting Information

Rh-catalyzed direct synthesis of 2,2'-dihydroxybenzophenones and xanthones

Maddali L. N. Rao^{*} and Boddu S. Ramakrishna

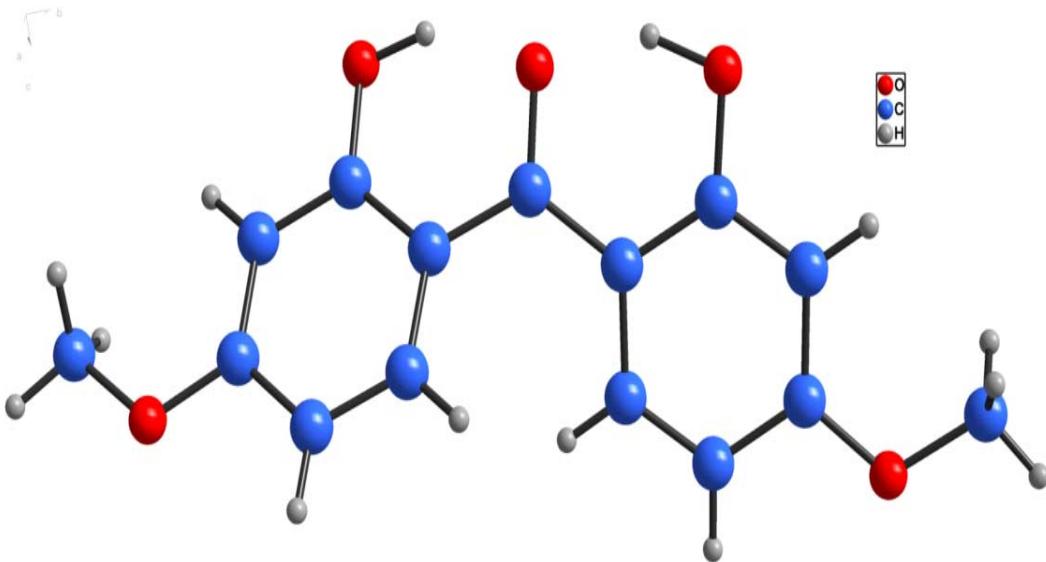
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Contents

1. Crystallographic data for Compound **2.2** (CCDC-1480785).....S2-S3
2. Copies of ¹H NMR, ¹³C NMR and HRMS spectra of Compound **2.1** to **2.11** (Table 2).....S4-S36
3. Copies of ¹H NMR, ¹³C NMR and HRMS spectra of Compound **3.1** to **3.10** (Table 3).....S37-S66
4. Copies of ¹H NMR, ¹³C NMR and HRMS spectra of Compound **4** (Scheme 2).....S67-S69

1. Crystallographic data for Compound 2.2 (CCDC-1480785):



Crystal data and structure refinement for 2marb_0m.

Identification code 2marb_0m

Empirical formula C15 H14 O5

Formula weight 274.26

Temperature 298(2) K

Wavelength 0.71073 Å

Crystal system Monoclinic

Space group P21/n

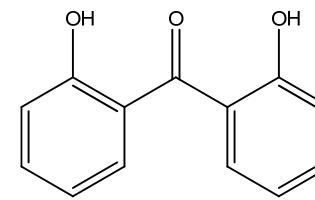
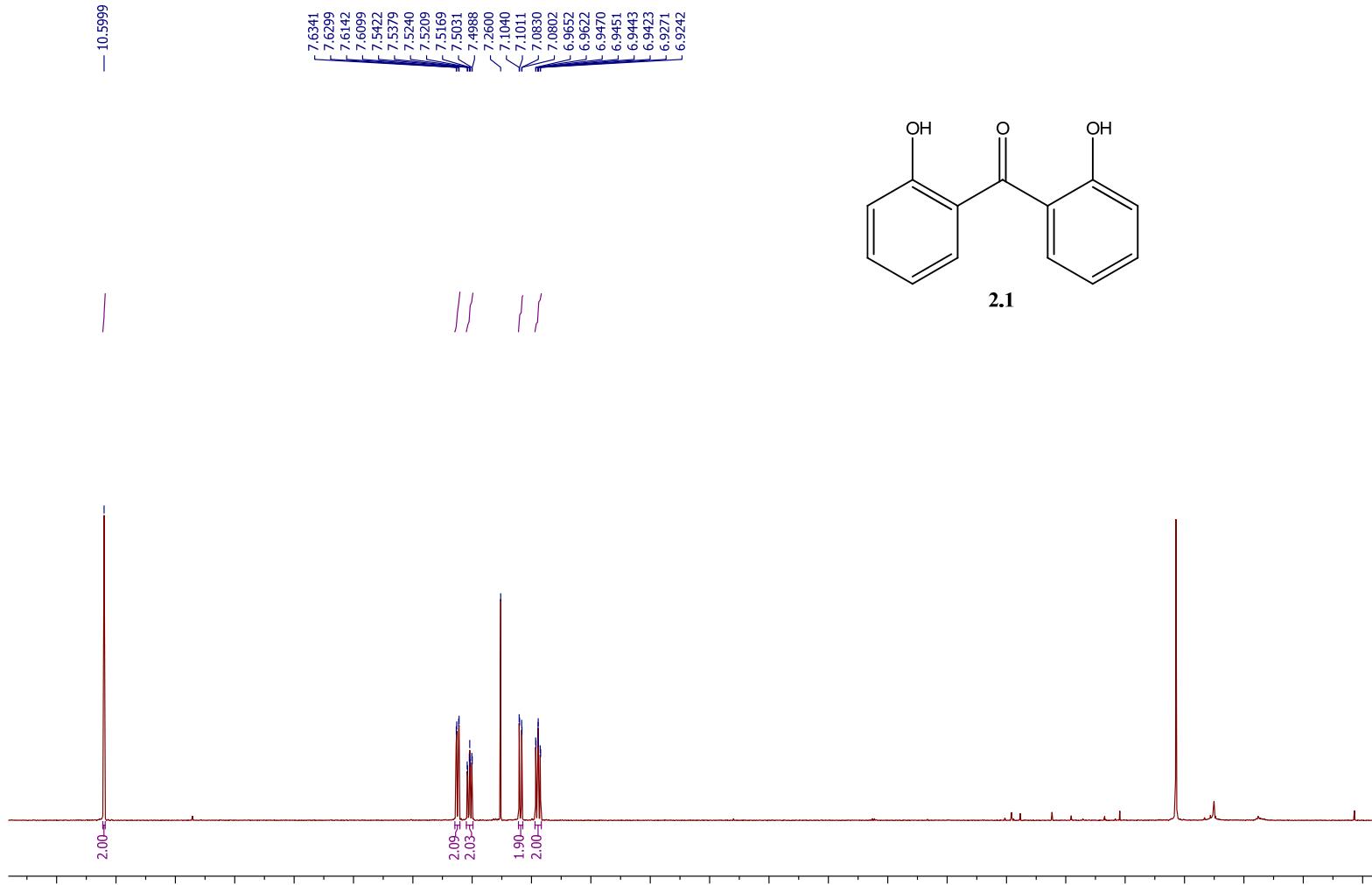
Unit cell dimensions $a = 3.8416(3)$ Å $a = 90^\circ$.

$b = 25.1212(16)$ Å $b = 92.567(2)^\circ$.

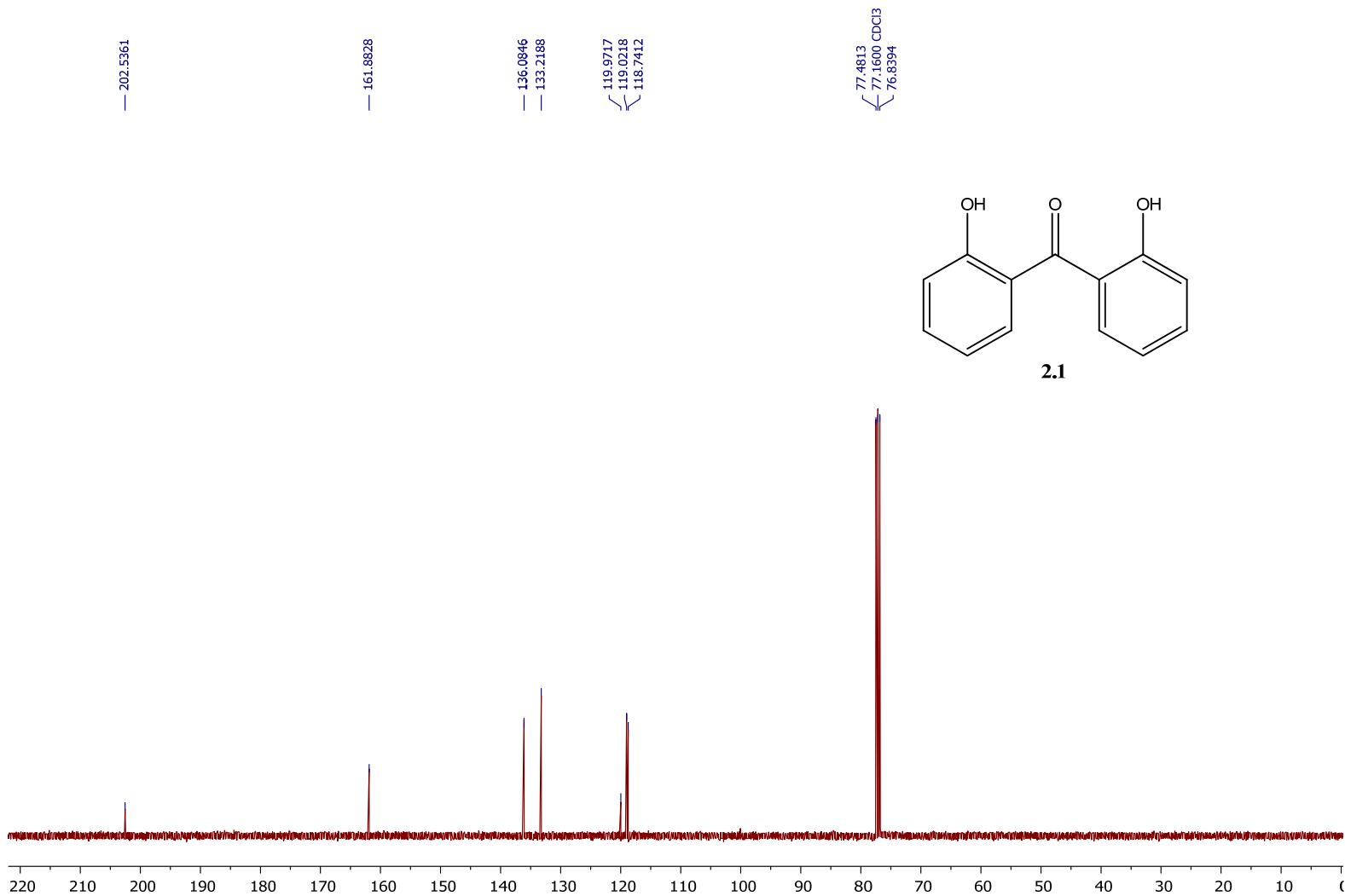
$c = 12.9636(9)$ Å $g = 90^\circ$.

Volume	1249.80(15) Å ³
Z	4
Density (calculated)	1.458 Mg/m ³
Absorption coefficient	0.110 mm ⁻¹
F(000)	576
Crystal size	0.16 x 0.13 x 0.12 mm ³
Theta range for data collection	2.26 to 28.35°
Index ranges	-5<=h<=5, -33<=k<=33, -13<=l<=17
Reflections collected	12538
Independent reflections	3107 [R(int) = 0.0674]
Completeness to theta = 28.35°	99.8 %
Absorption correction	Empirical
Max. and min. transmission	0.987 and 0.983
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3107 / 0 / 190
Goodness-of-fit on F ²	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0581, wR2 = 0.1219
R indices (all data)	R1 = 0.1180, wR2 = 0.1535
Largest diff. peak and hole	0.292 and -0.362 e.Å ⁻³

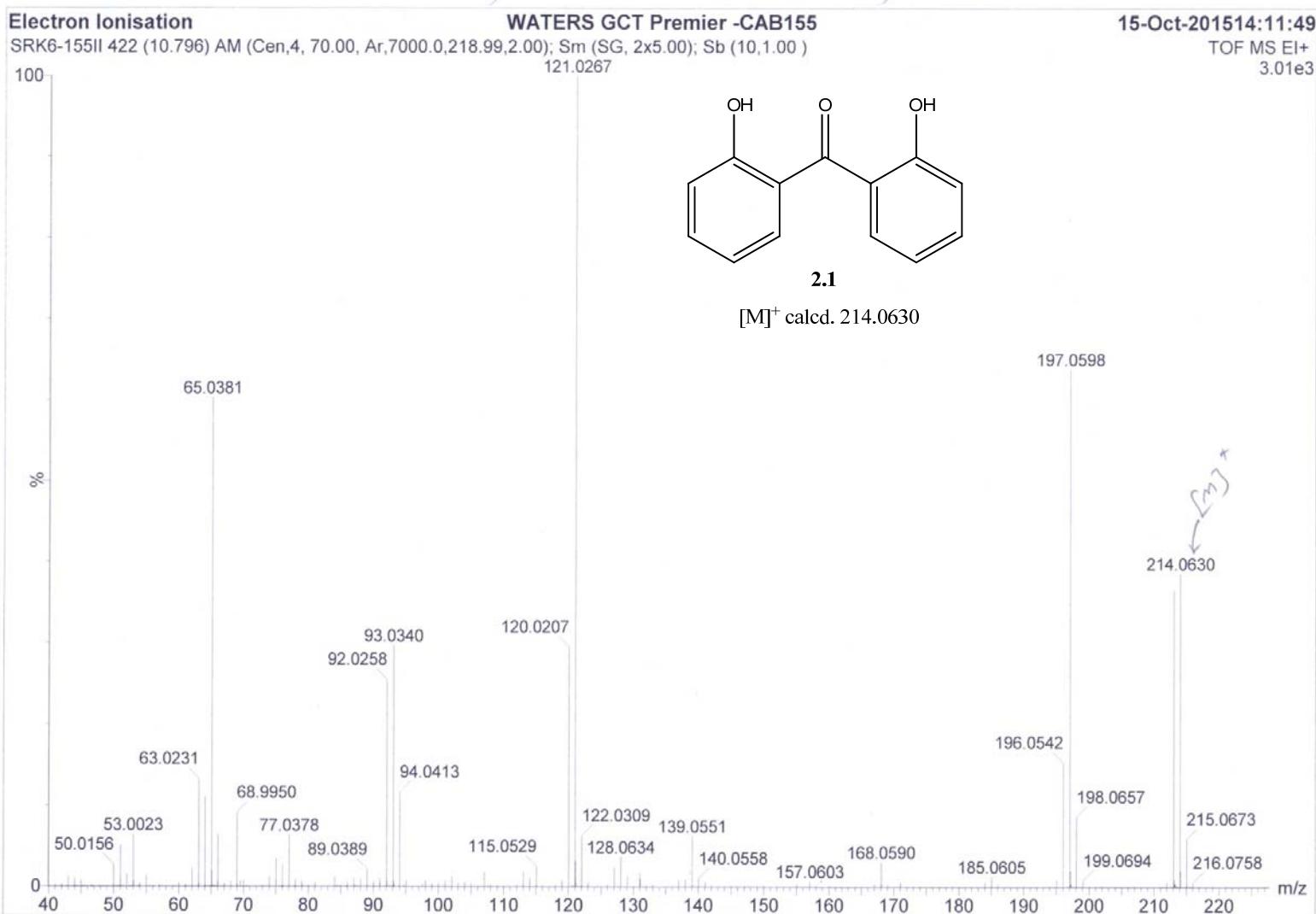
2. Copies of ^1H NMR, ^{13}C NMR and HRMS spectra of Compound 2.1 to 2.11 (Table 2):



^1H NMR (400 MHz, CDCl_3) spectrum of bis(2-hydroxyphenyl)methanone (**2.1**)

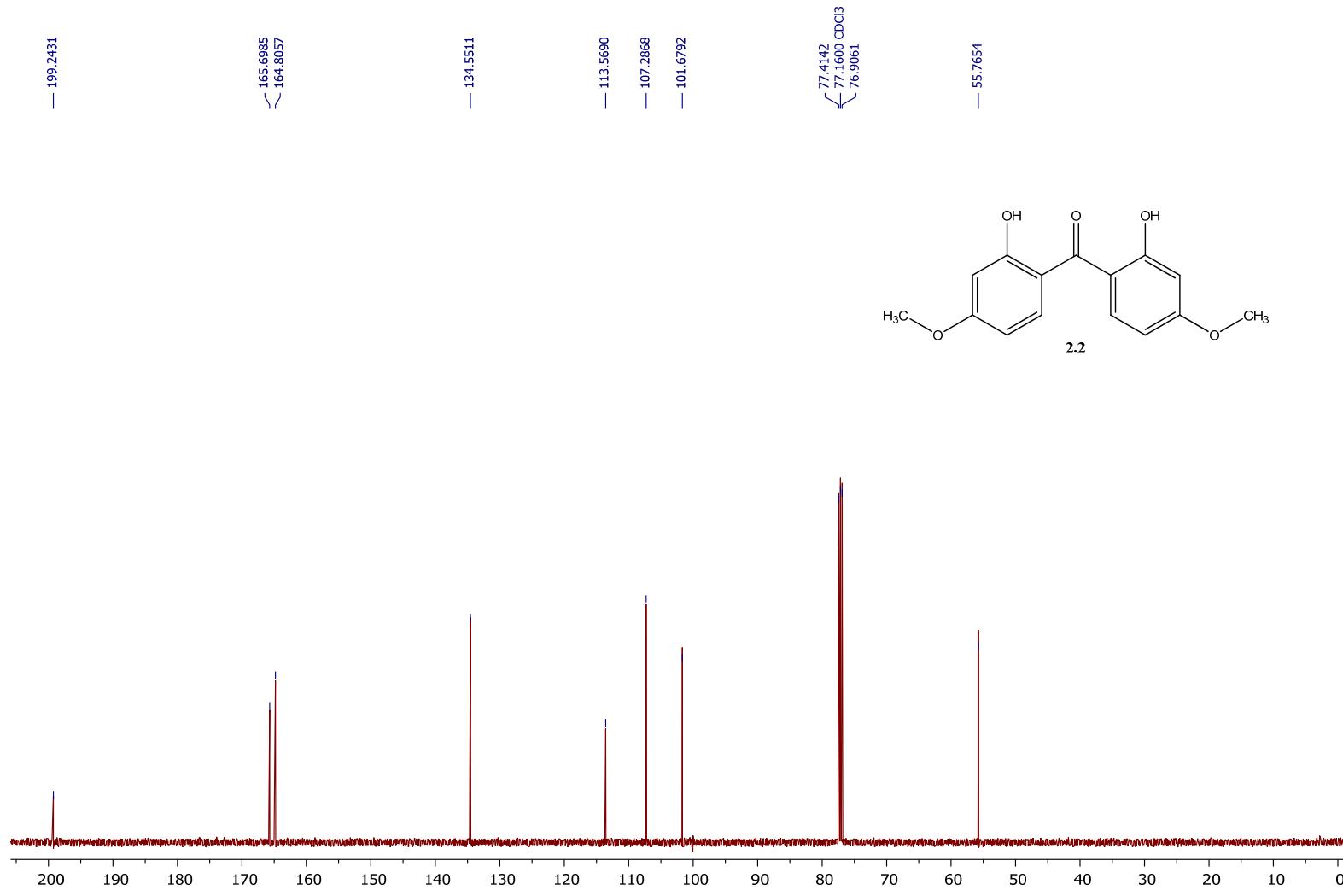


^{13}C NMR (100 MHz, CDCl₃) spectrum of bis(2-hydroxyphenyl)methanone (**2.1**)

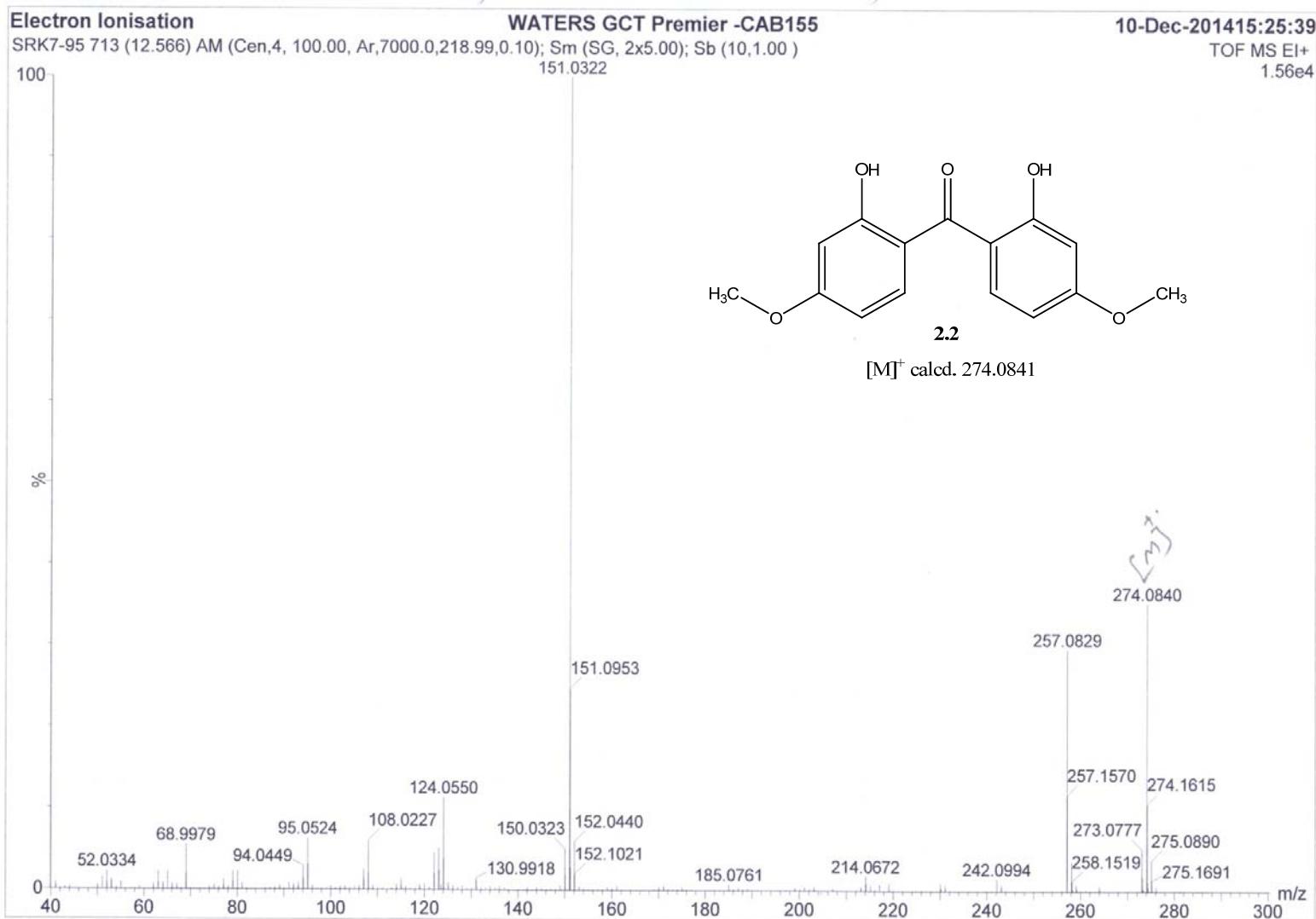


EI(HRMS) spectrum of bis(2-hydroxyphenyl)methanone (**2.1**)

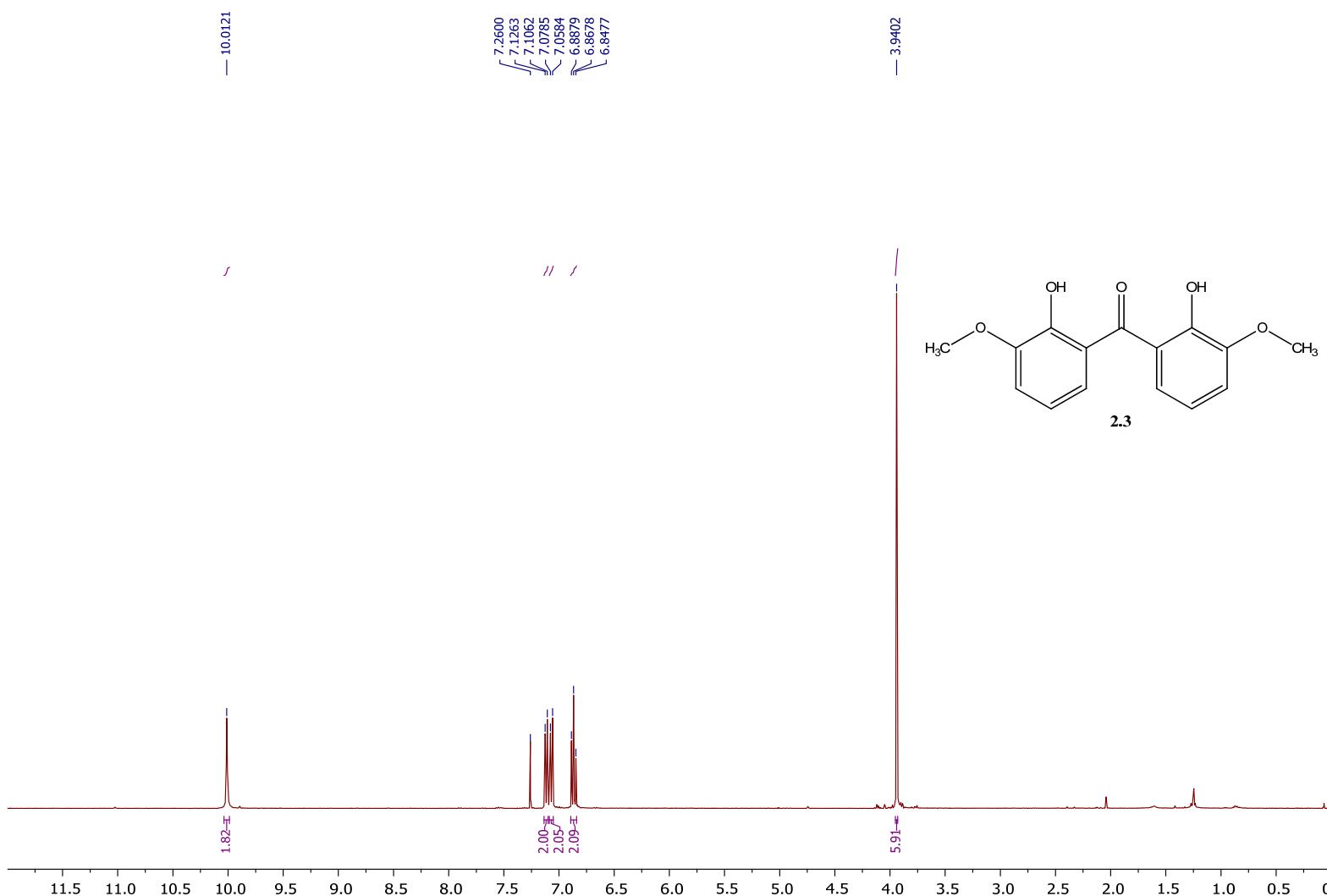




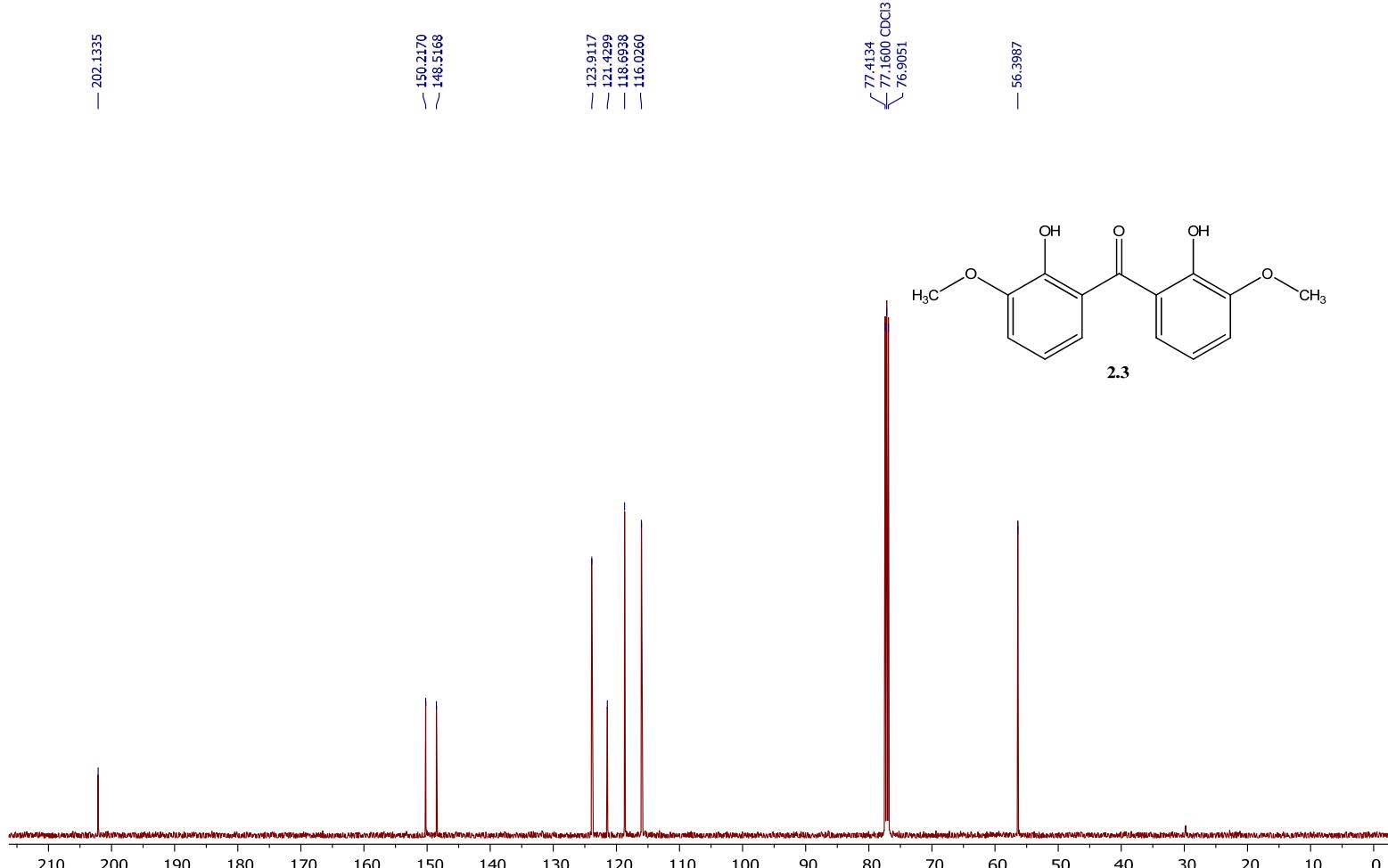
¹³C NMR (125 MHz, CDCl₃) spectrum of bis(2-hydroxy-4-methoxyphenyl)methanone (**2.2**)

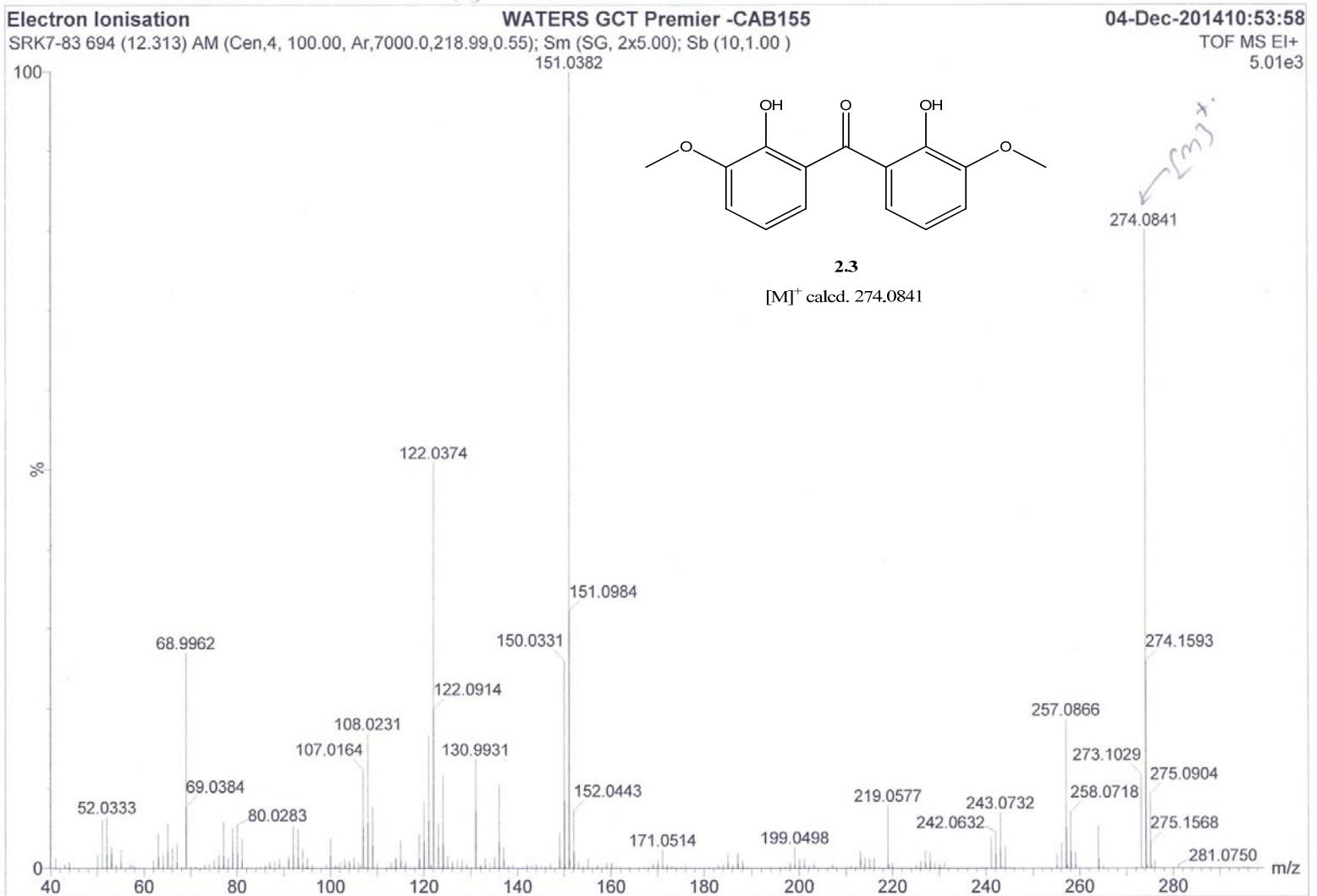


EI(HRMS) spectrum of bis(2-hydroxy-4-methoxyphenyl)methanone (**2.2**)

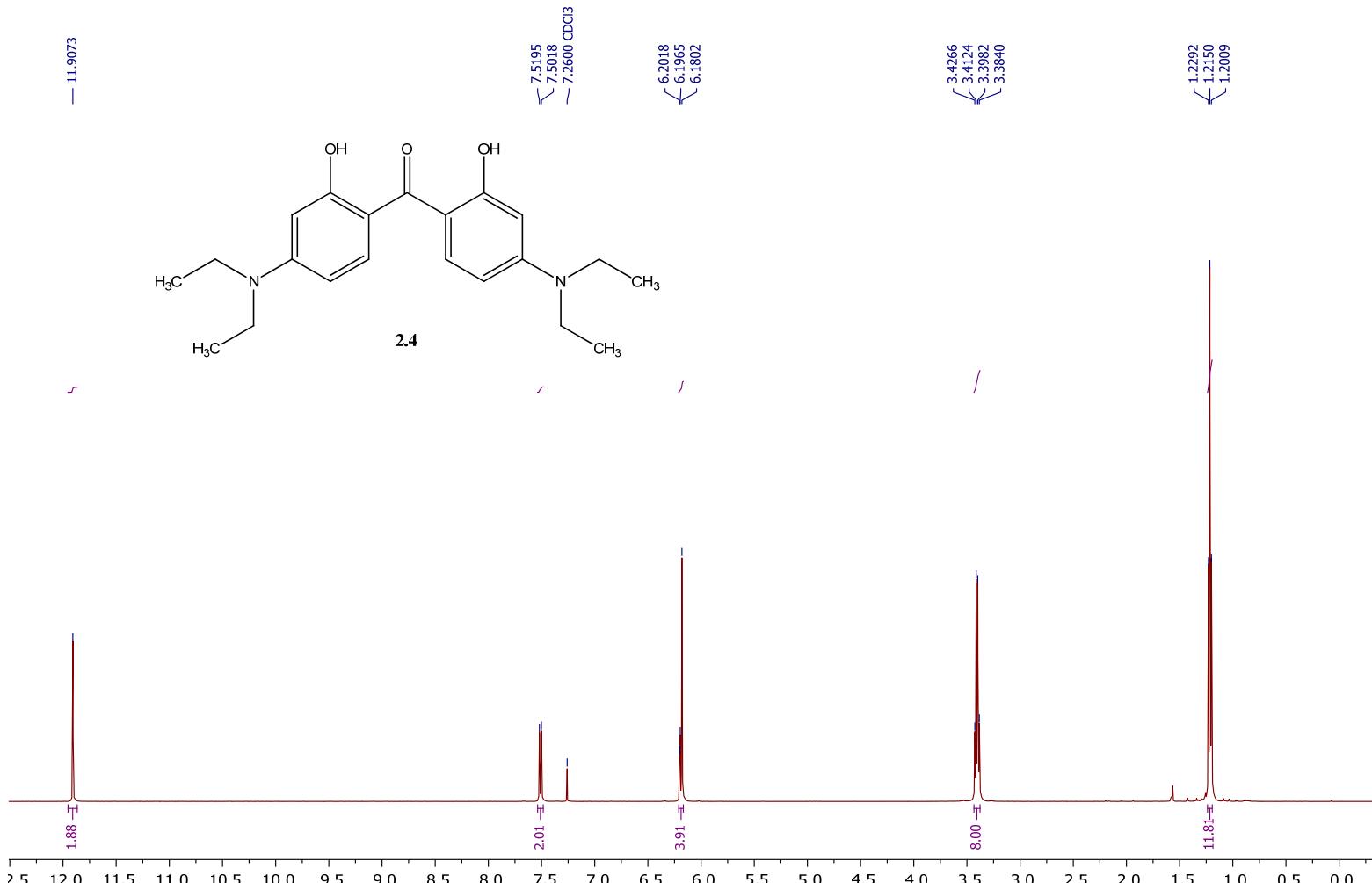


^1H NMR (400 MHz, CDCl_3) spectrum of bis(2-hydroxy-3-methoxyphenyl)methanone (**2.3**)

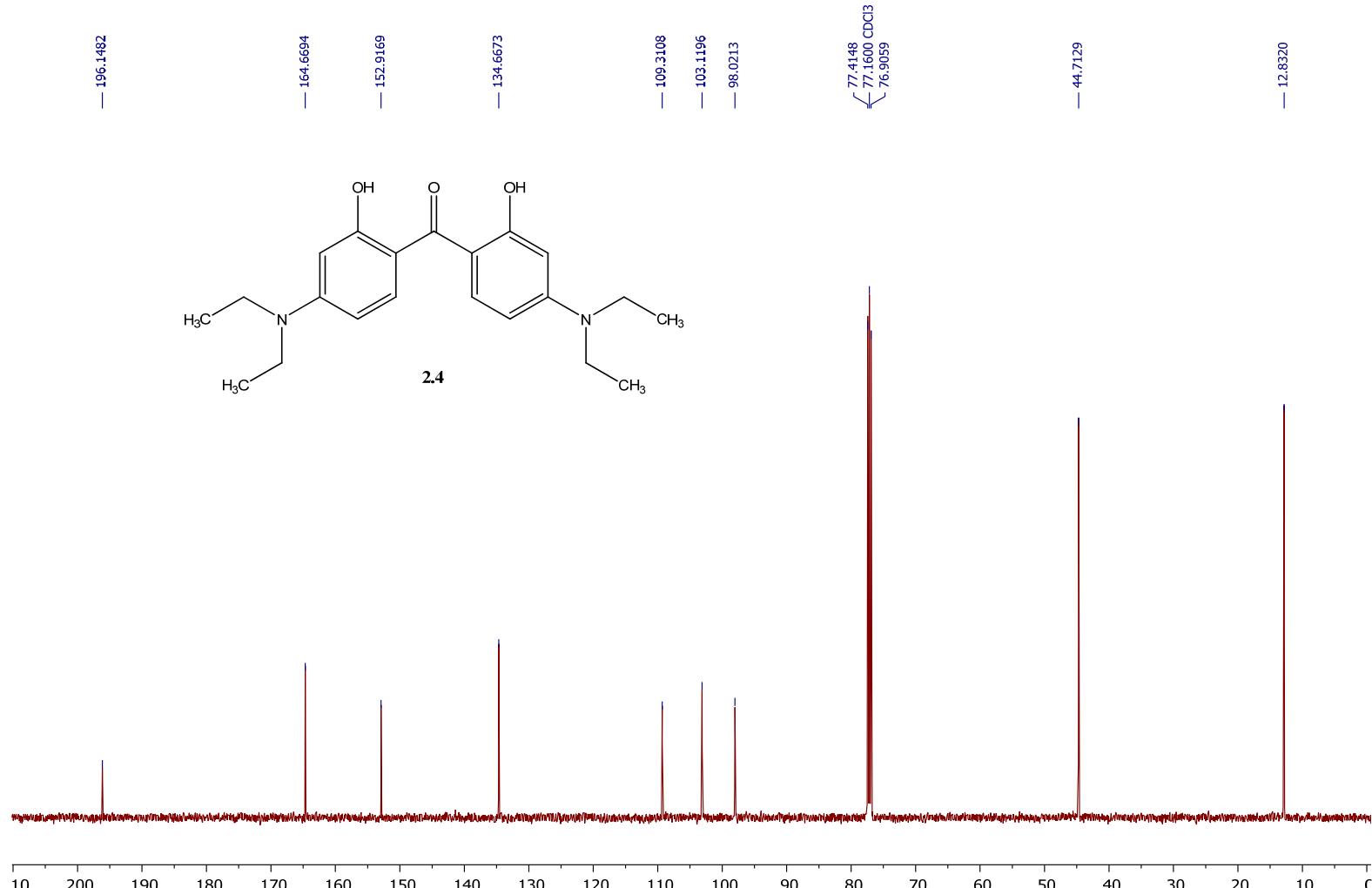




EI(HRMS) spectrum of bis(2-hydroxy-3-methoxyphenyl)methanone (**2.3**)



^1H NMR (500 MHz, CDCl₃) spectrum of bis(4-(diethylamino)-2-hydroxyphenyl)methanone (**2.4**)



^{13}C NMR (125 MHz, CDCl₃) spectrum of bis(4-(diethylamino)-2-hydroxyphenyl)methanone (**2.4**)

Electrospray Ionisation -MS

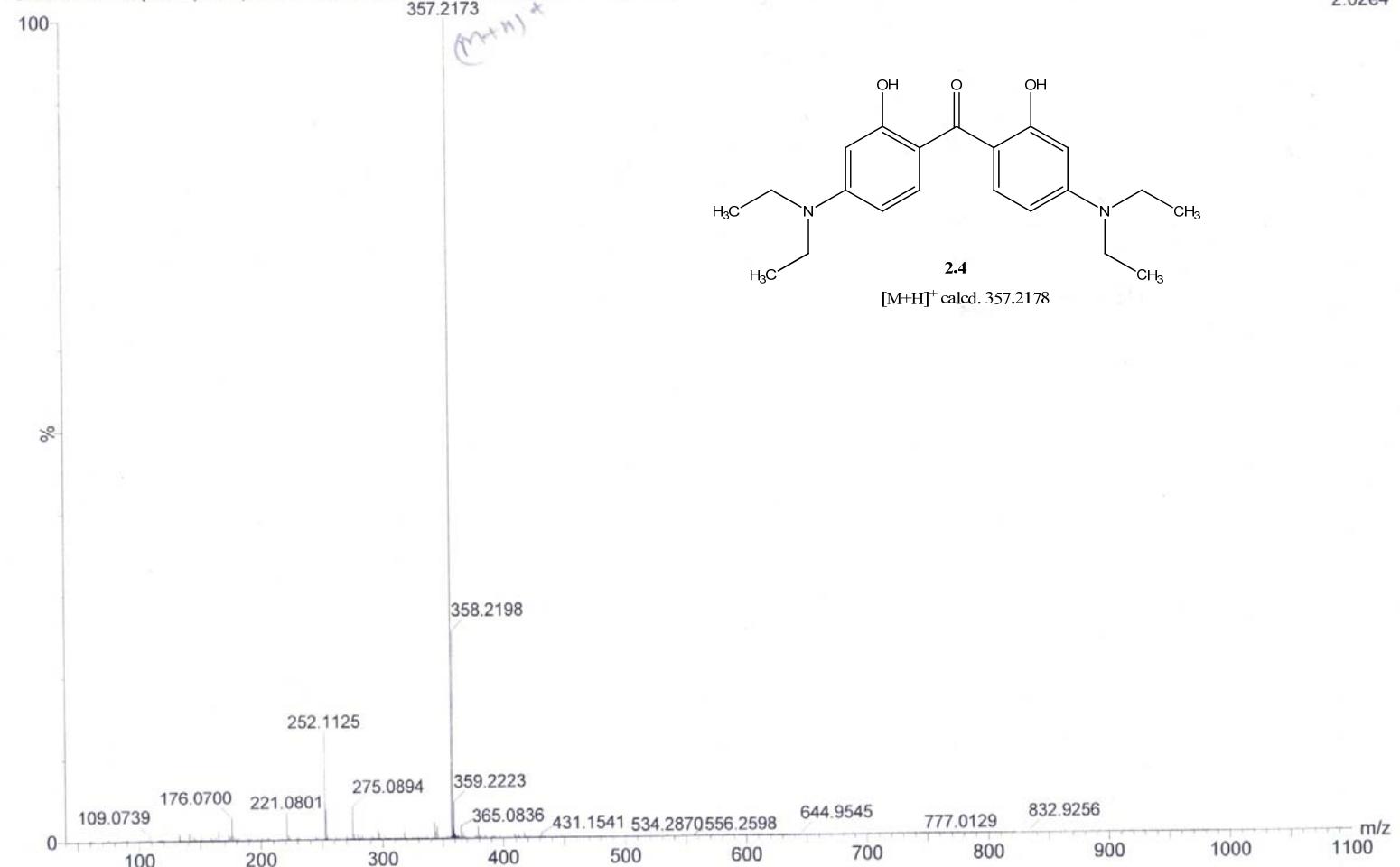
WATERS Q-TOF Premier-HAB213

27-Nov-2015

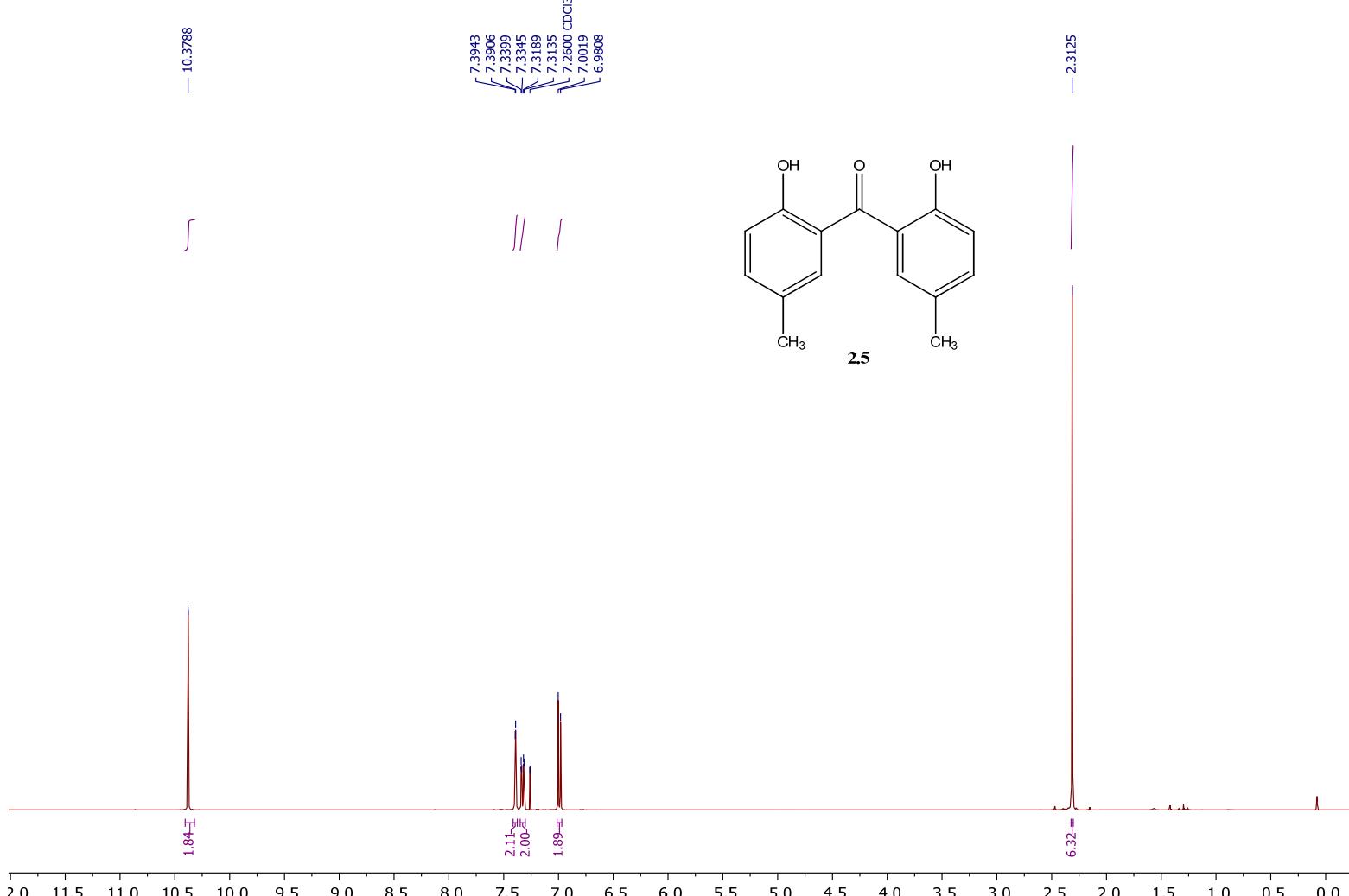
16:39:35

1: TOF MS ES+
2.02e4

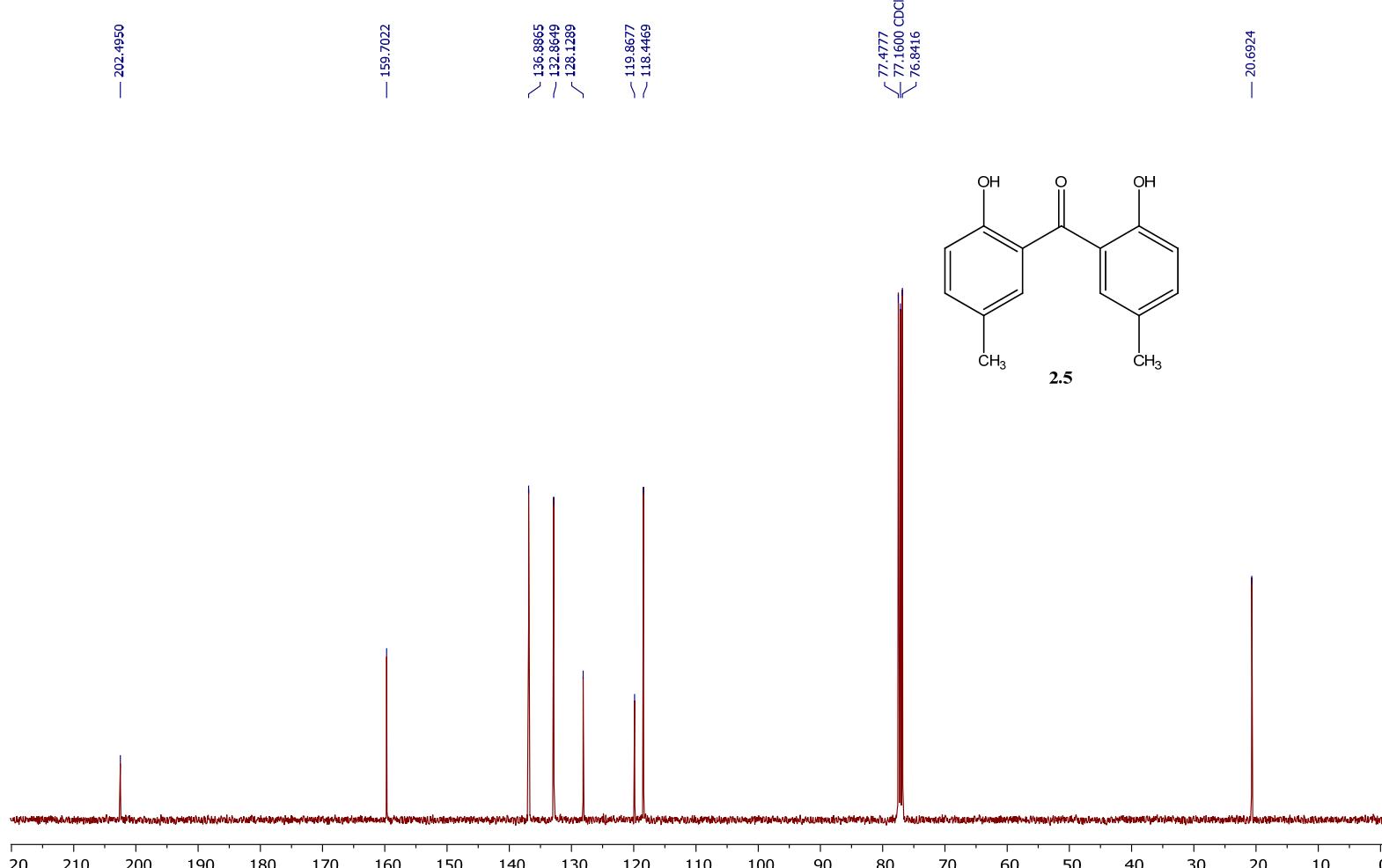
SRK-8-193 10 (0.222) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.25,LS 10); Sm (SG, 1x5.00); Sb (10,1.00); Cm (10:20-41:52)



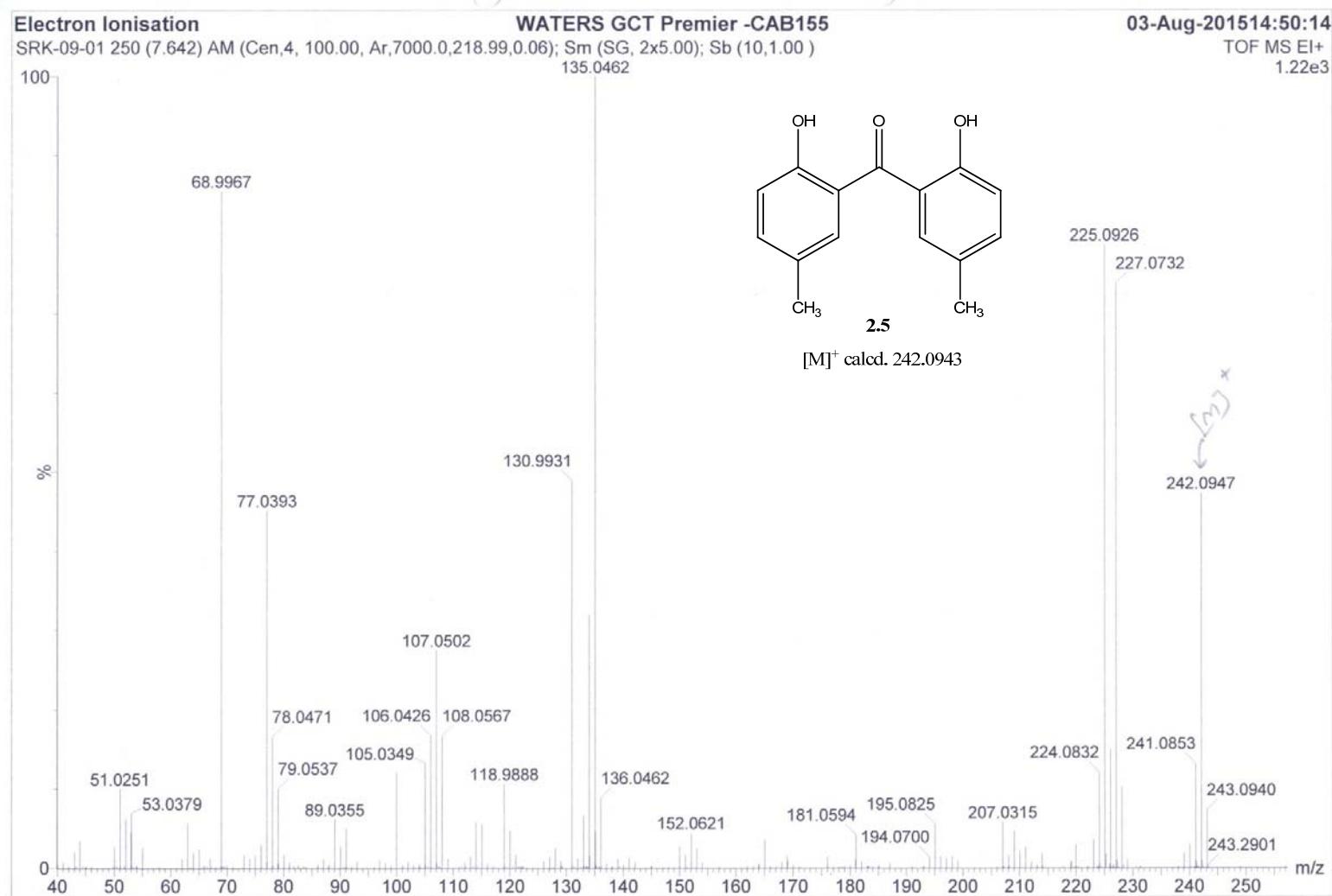
ESI(HRMS) spectrum of bis(4-(diethylamino)-2-hydroxyphenyl)methanone (**2.4**)



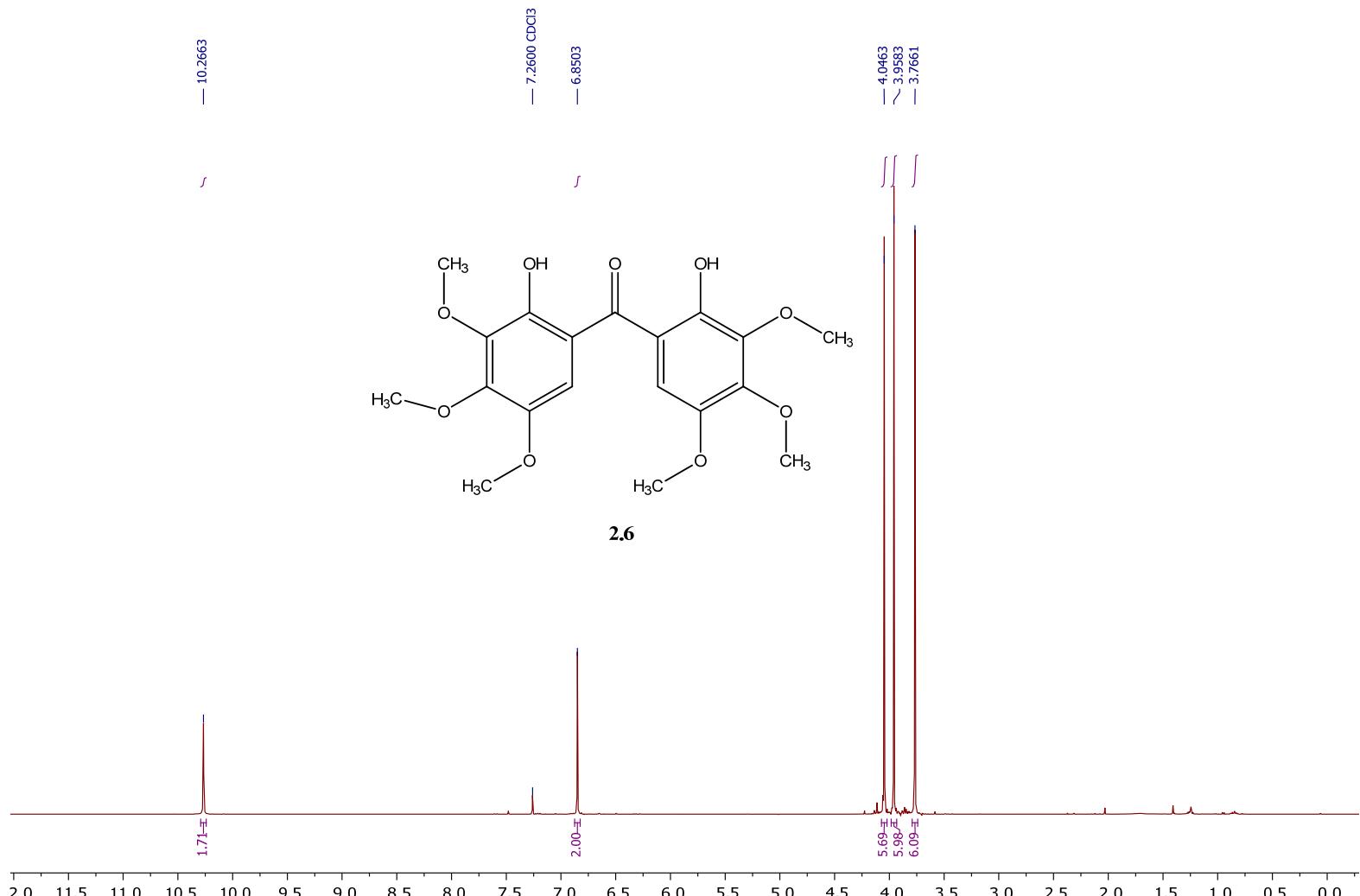
¹H NMR (400 MHz, CDCl₃) spectrum of bis(2-hydroxy-5-methylphenyl)methanone (**2.5**)



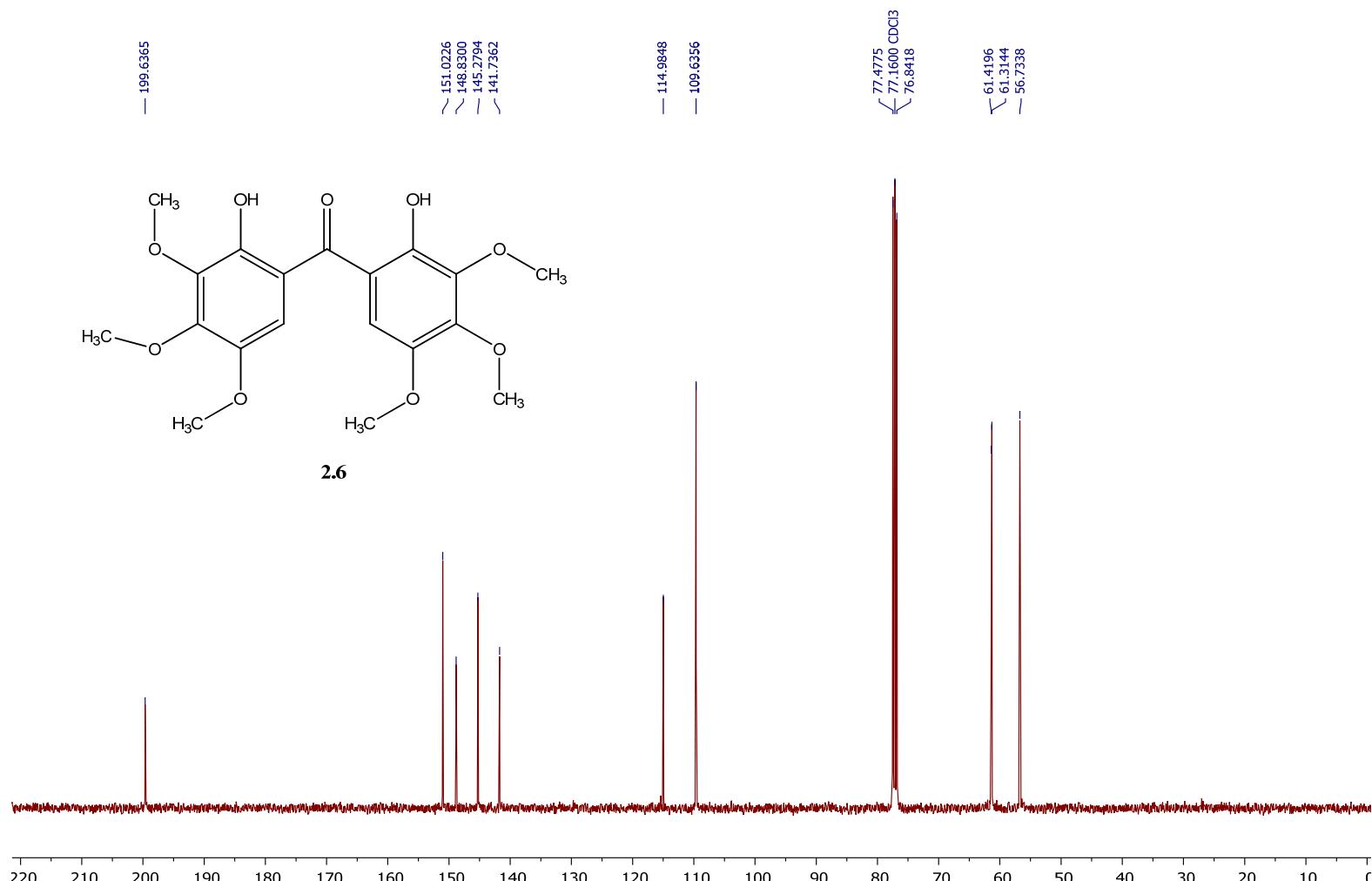
¹³C NMR (100 MHz, CDCl₃) spectrum of bis(2-hydroxy-5-methylphenyl)methanone (**2.5**)



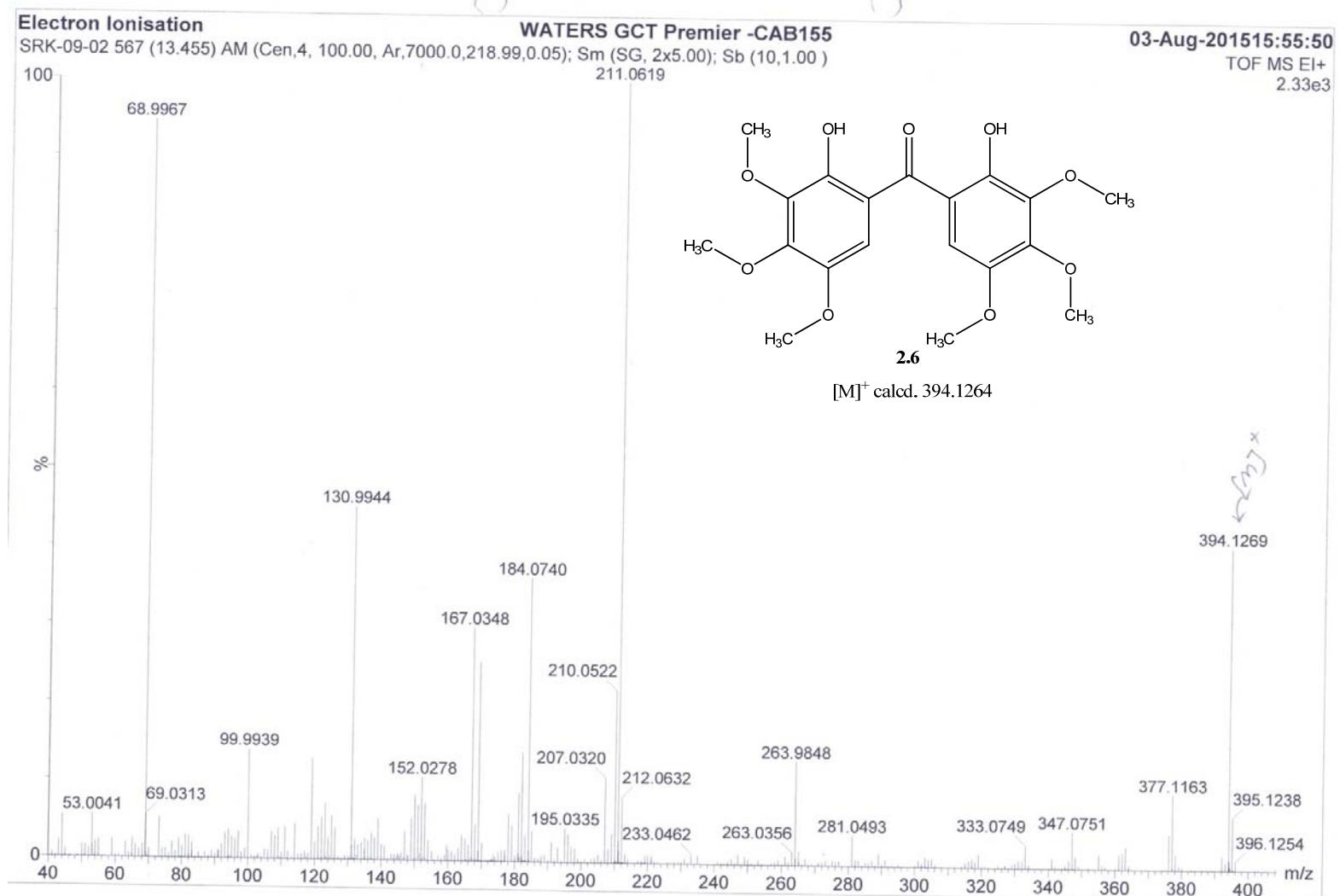
EI(HRMS) spectrum of bis(2-hydroxy-5-methylphenyl)methanone (**2.5**)



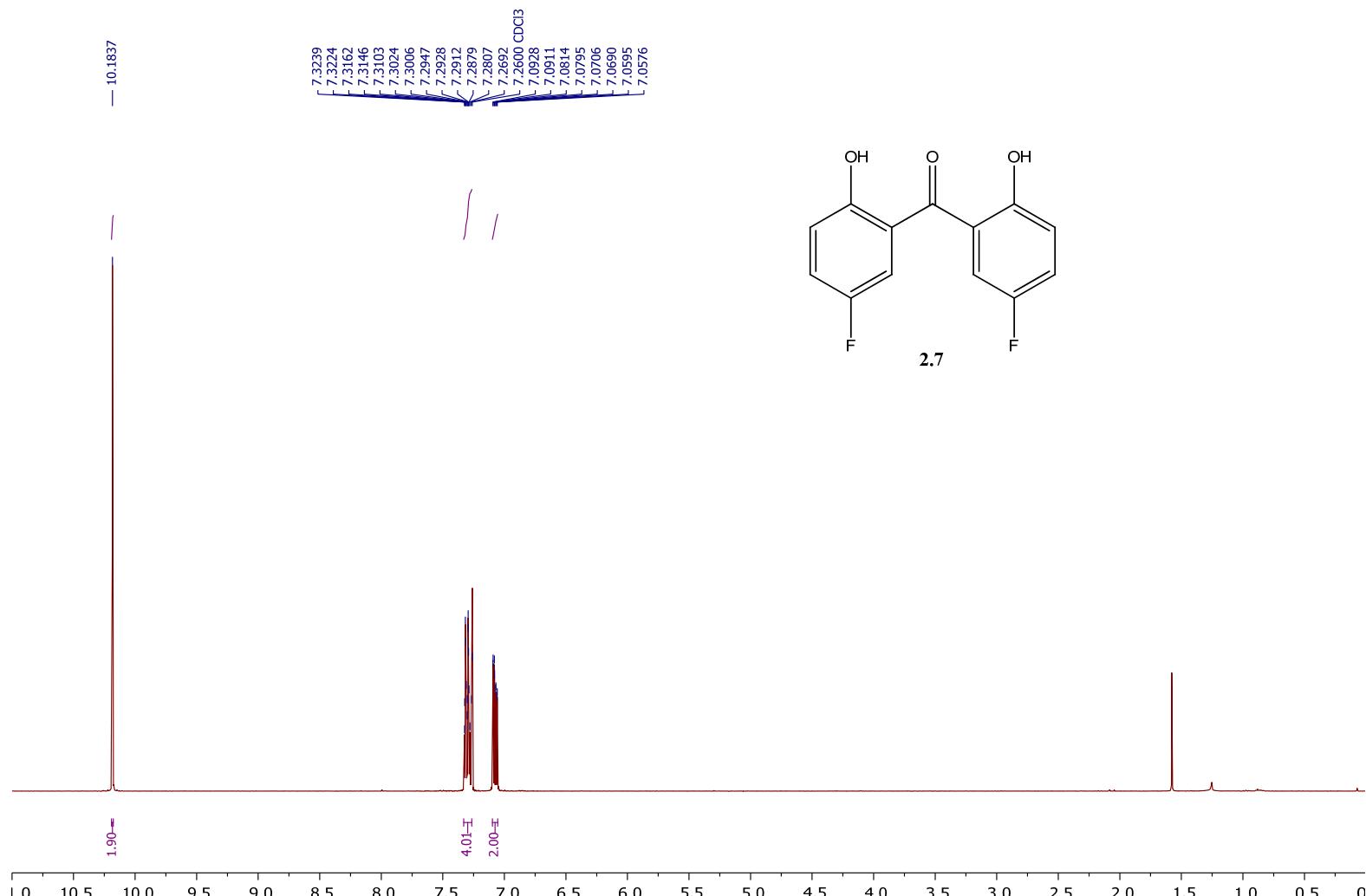
^1H NMR (400 MHz, CDCl₃) spectrum of bis(2-hydroxy-3,4,5-trimethoxyphenyl)methanone (**2.6**)



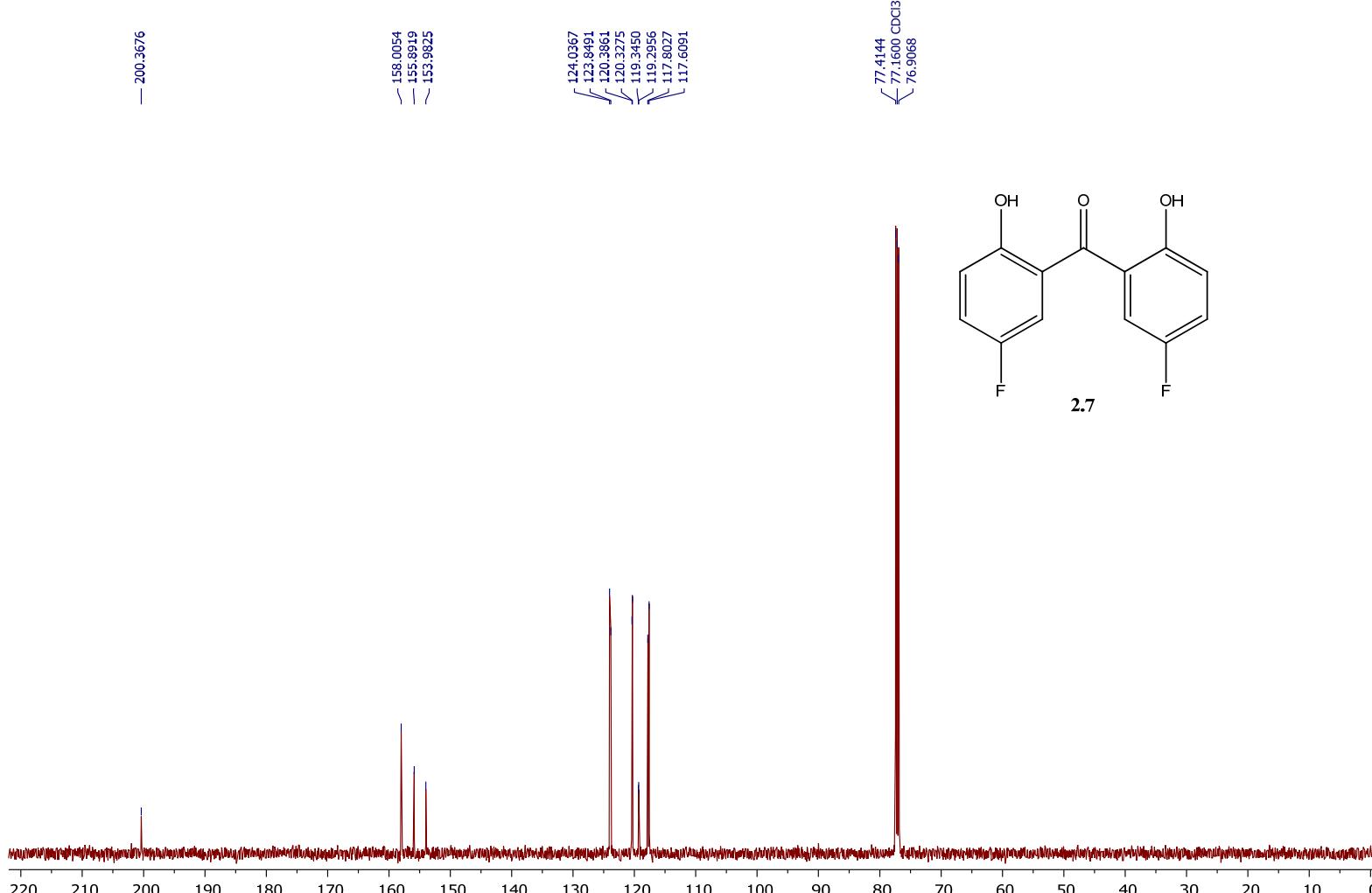
^{13}C NMR (100 MHz, CDCl₃) spectrum of bis(2-hydroxy-3,4,5-trimethoxyphenyl)methanone (**2.6**)



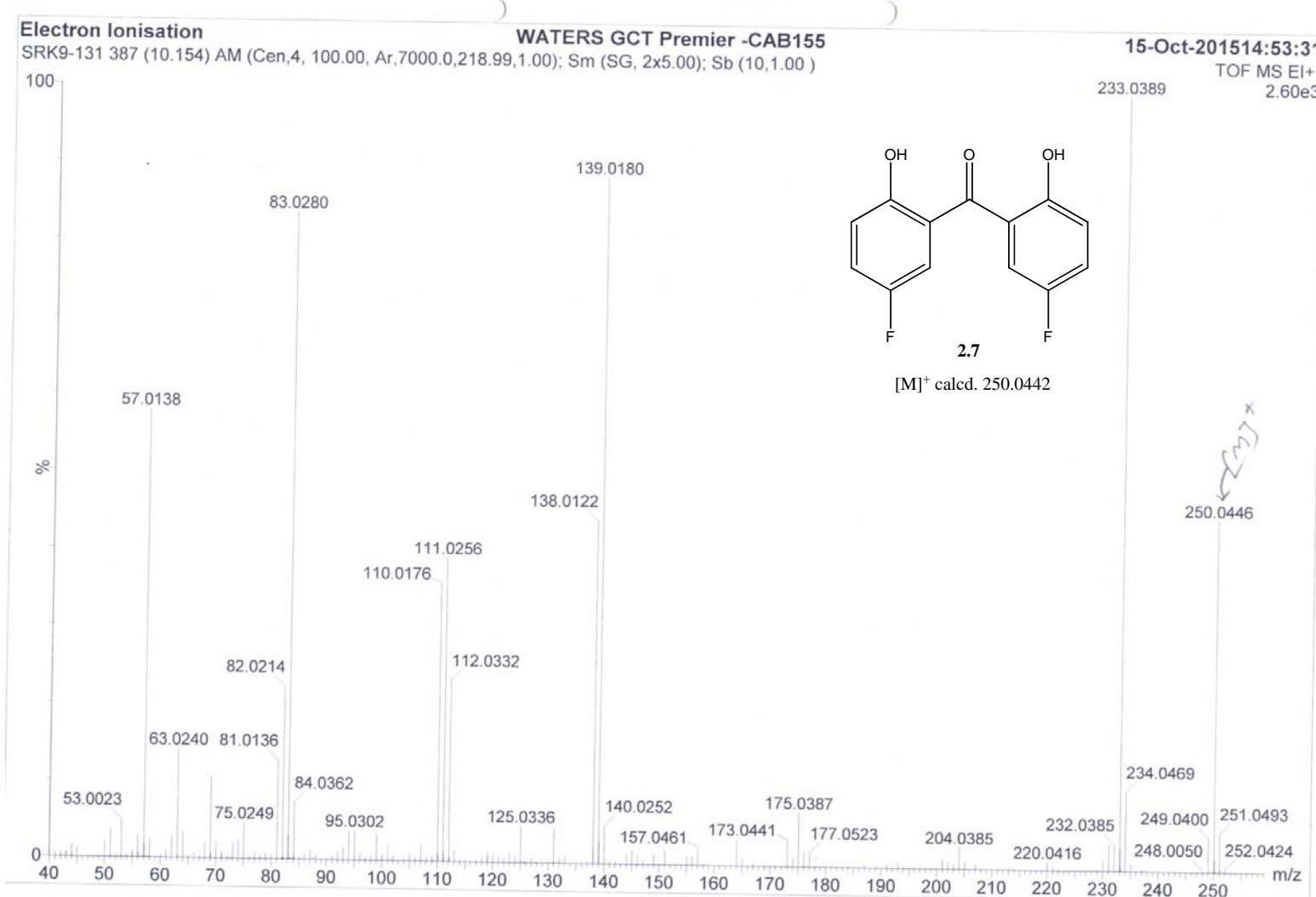
EI(HRMS) spectrum of bis(2-hydroxy-3,4,5-trimethoxyphenyl)methanone (**2.6**)



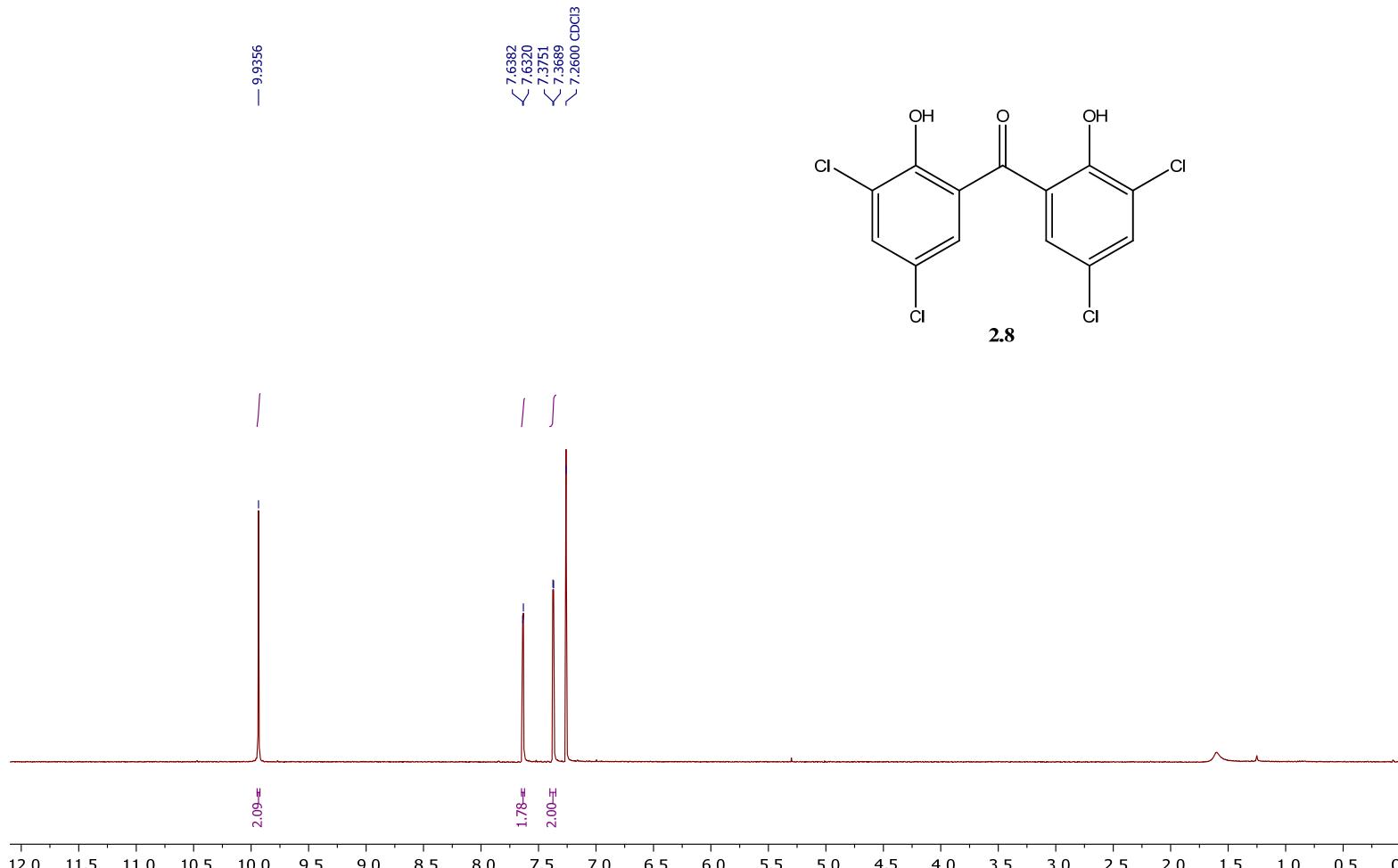
¹H NMR (400 MHz, CDCl₃) spectrum of bis(5-fluoro-2-hydroxyphenyl)methanone (**2.7**)



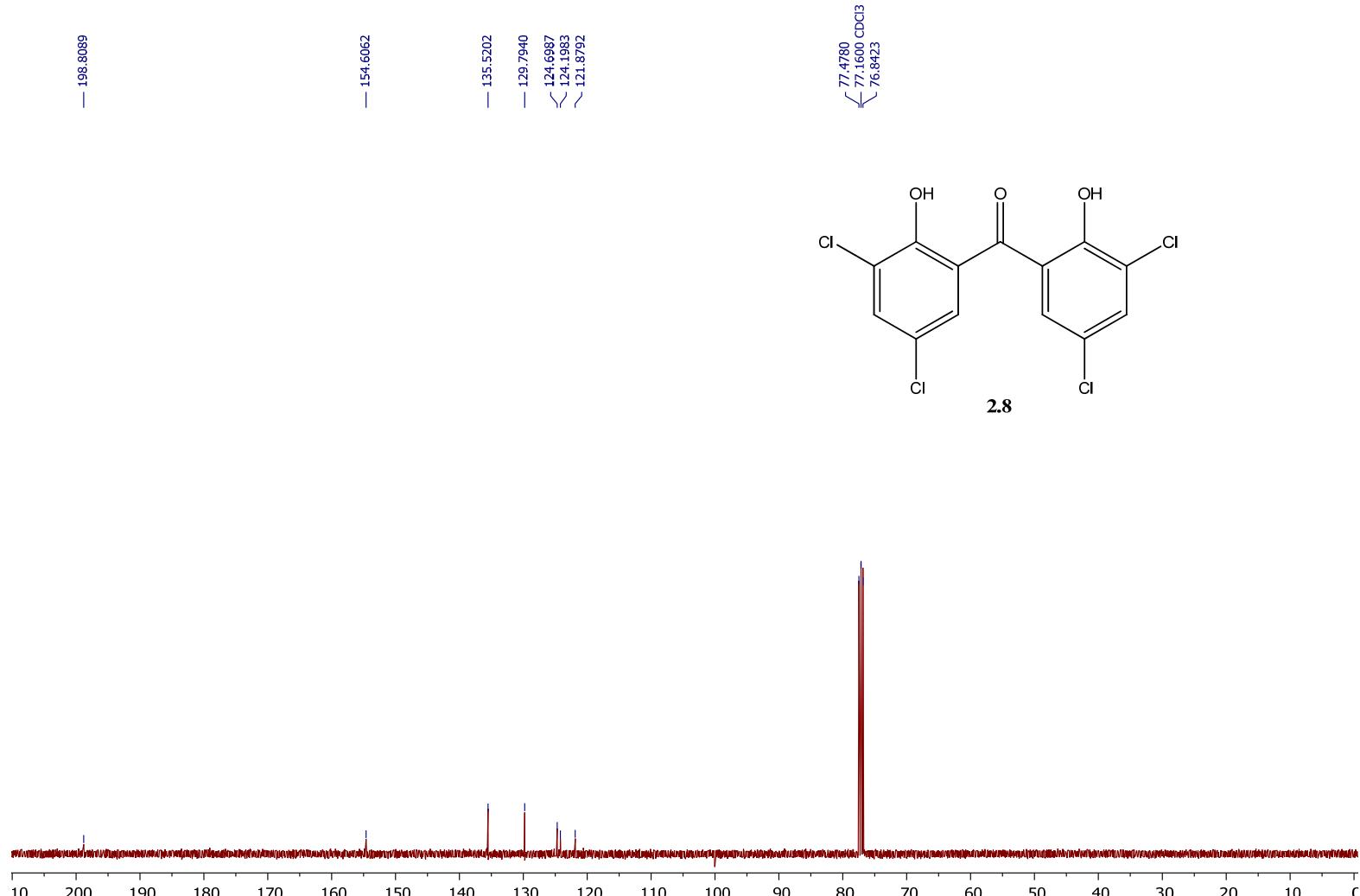
¹³C NMR (125 MHz, CDCl₃) spectrum of bis(5-fluoro-2-hydroxyphenyl)methanone (**2.7**)



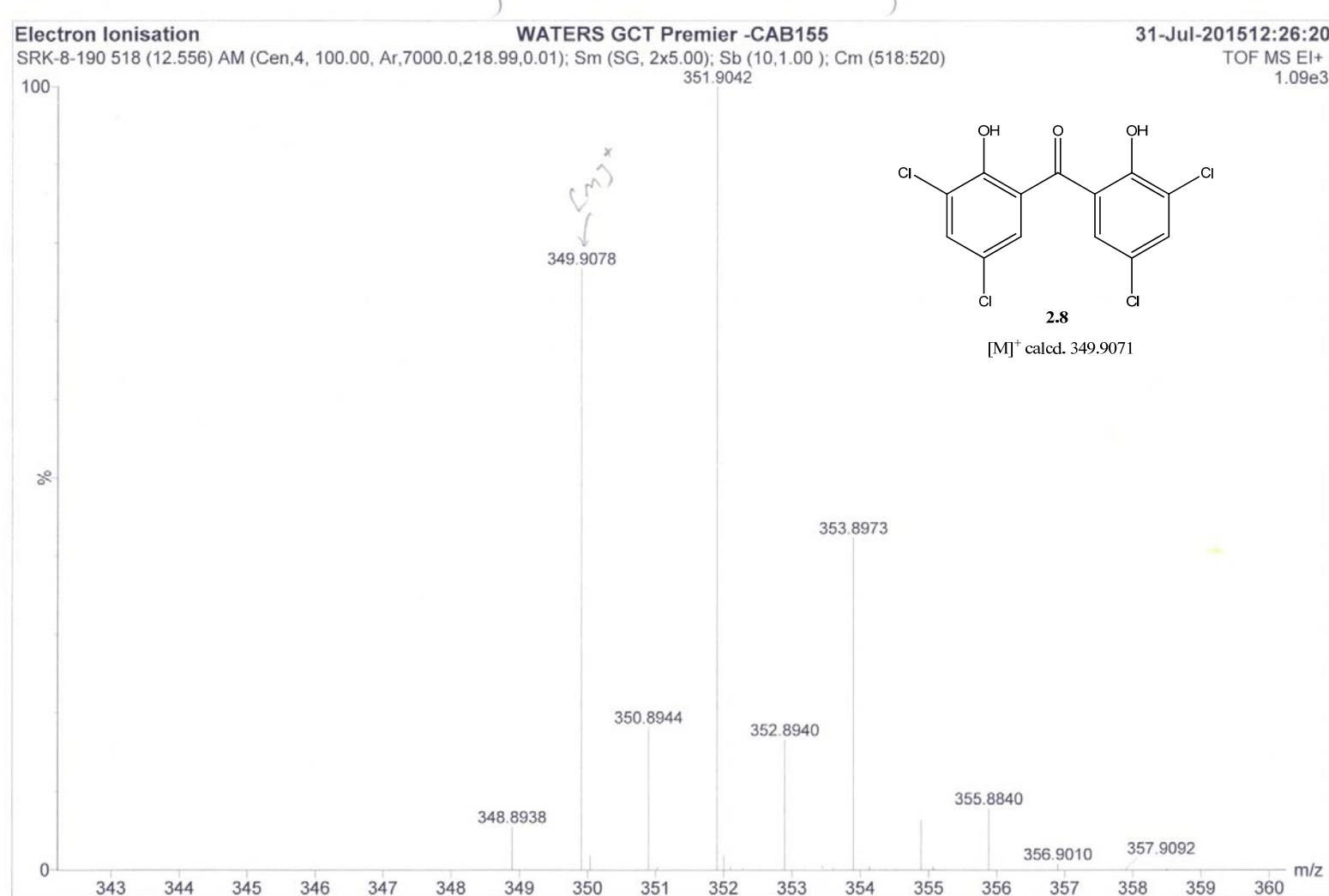
EI(HRMS) spectrum of bis(5-fluoro-2-hydroxyphenyl)methanone (**2.7**)



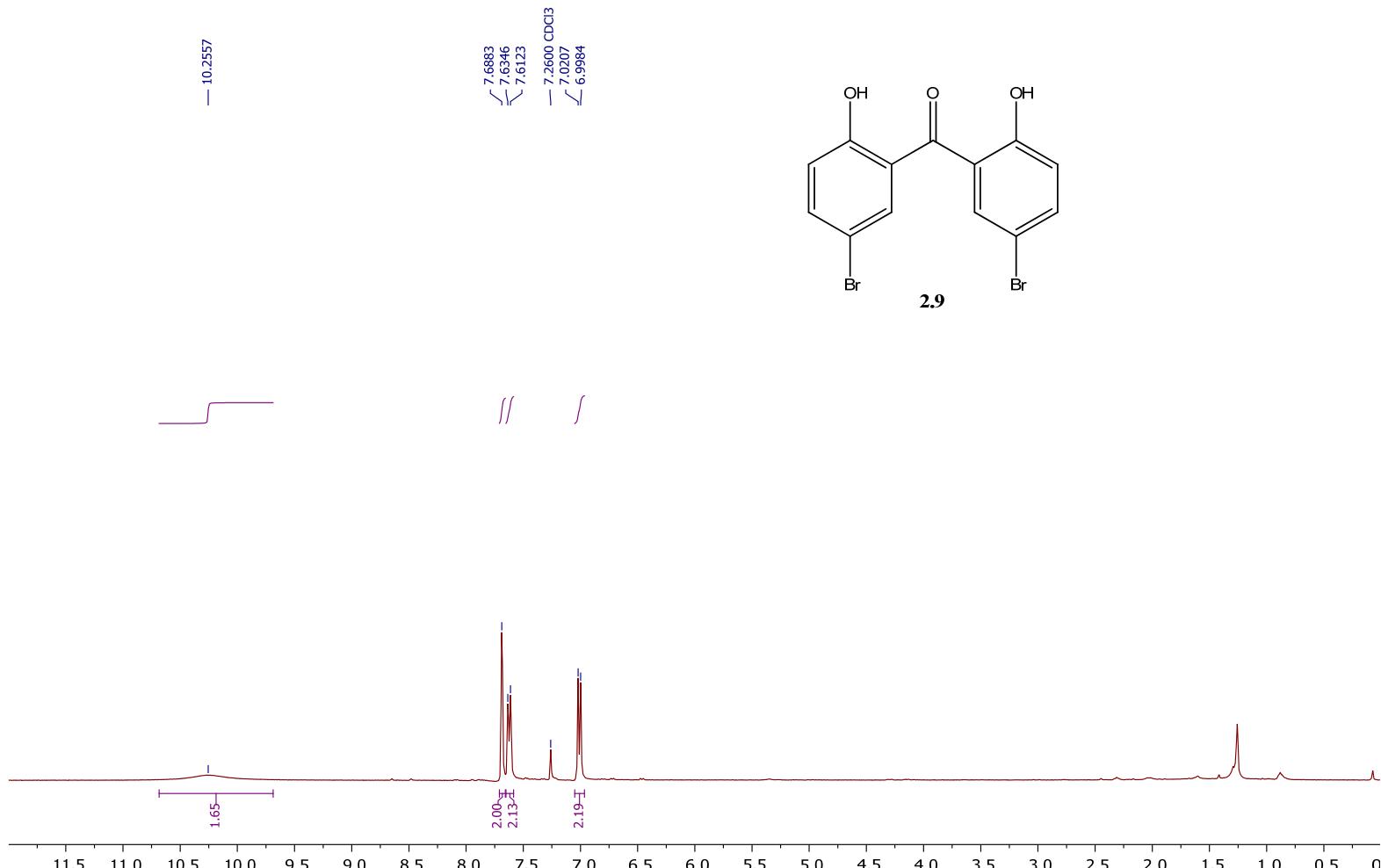
^1H NMR (400 MHz, CDCl₃) spectrum of bis(3,5-dichloro-2-hydroxyphenyl)methanone (**2.8**)



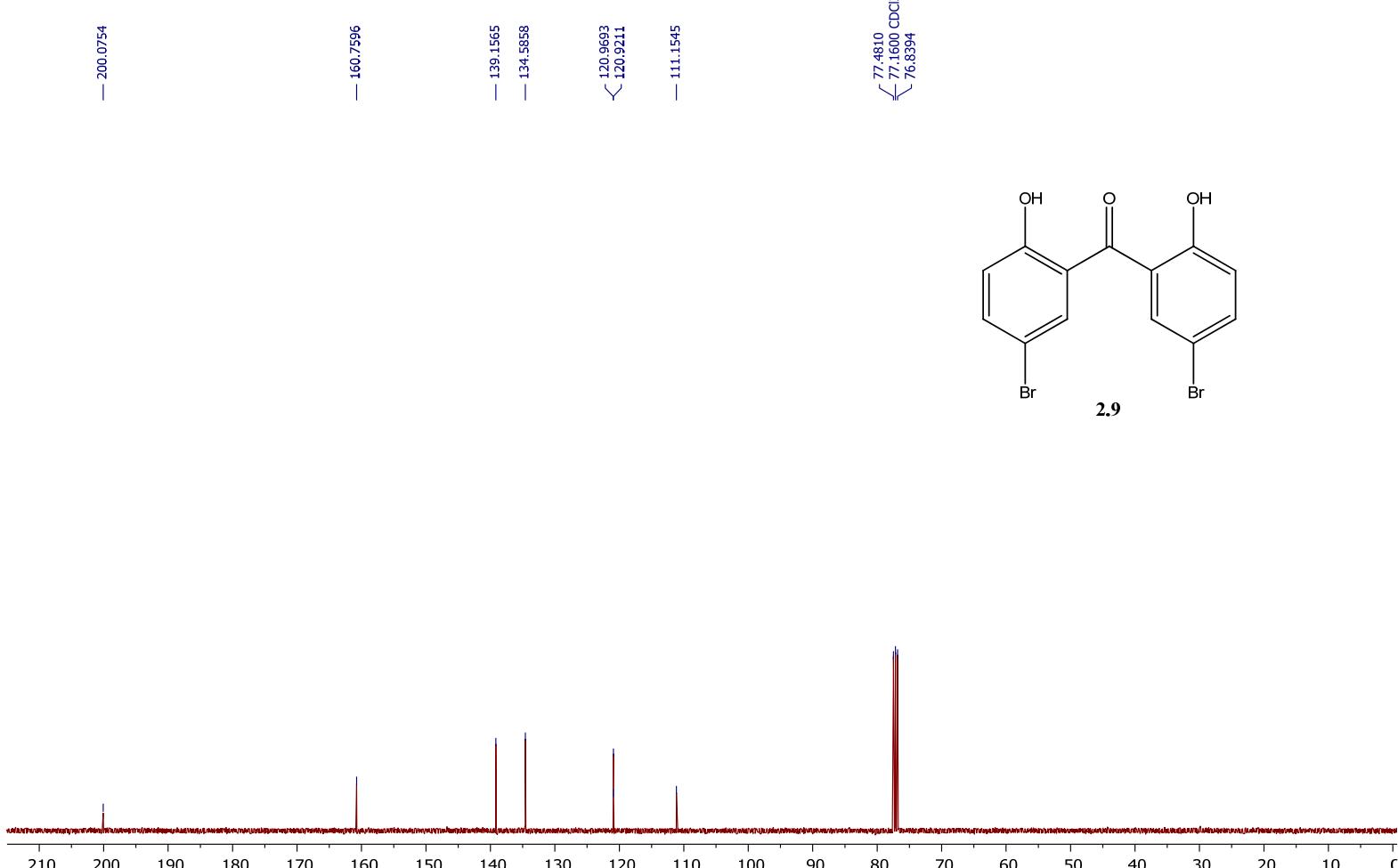
^{13}C NMR (100 MHz, CDCl₃) spectrum of bis(3,5-dichloro-2-hydroxyphenyl)methanone (**2.8**)



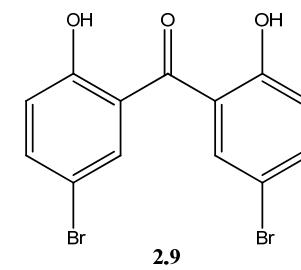
EI(HRMS) spectrum of bis(3,5-dichloro-2-hydroxyphenyl)methanone (**2.8**)



^1H NMR (400 MHz, CDCl_3) spectrum of bis(5-bromo-2-hydroxyphenyl)methanone (**2.9**)



¹³C NMR (100 MHz, CDCl₃) spectrum of bis(5-bromo-2-hydroxyphenyl)methanone (**2.9**)



Electrospray ionisation -MS

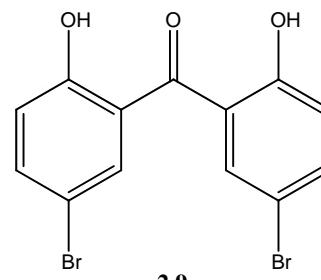
WATERS Q-TOF Premier-HAB213

26-Oct-2015
10:09:23

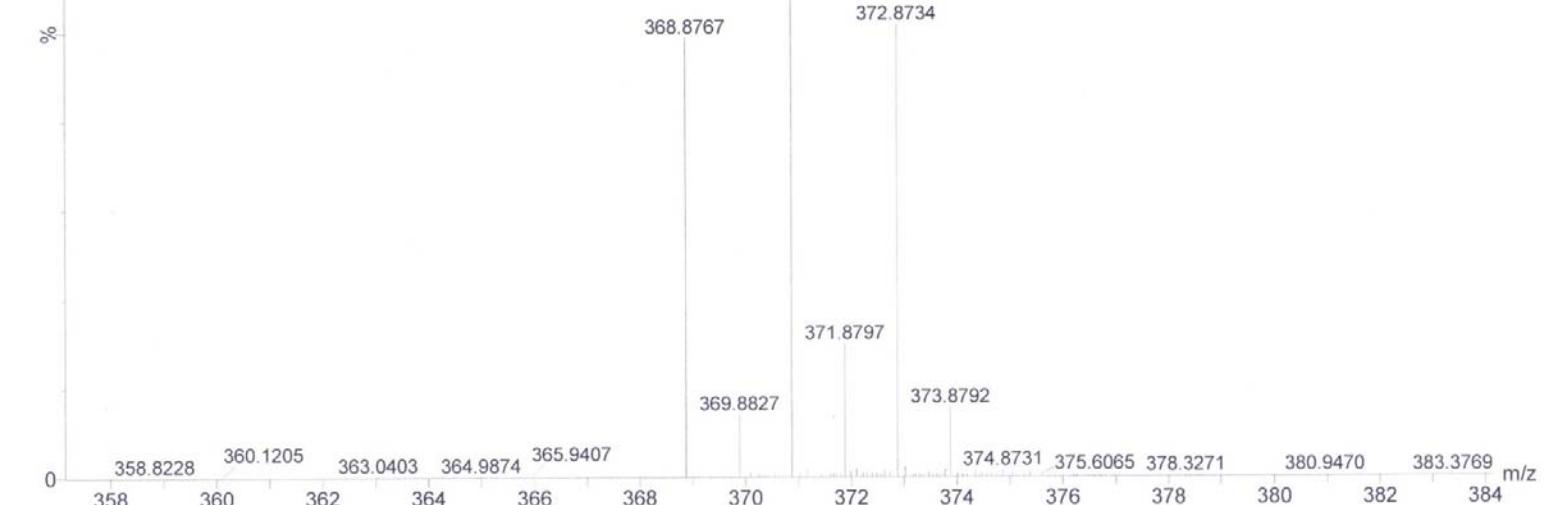
SRK8-184-II- 23 (0.480) AM (Cen,4, 70.00, Ar,10000.0,554.26,1.00,LS 10); Sm (SG, 1x5.00); Sb (15,10.00); Cm (23:24-101:104)
370.8746

1: TOF MS ES-
8.04e3

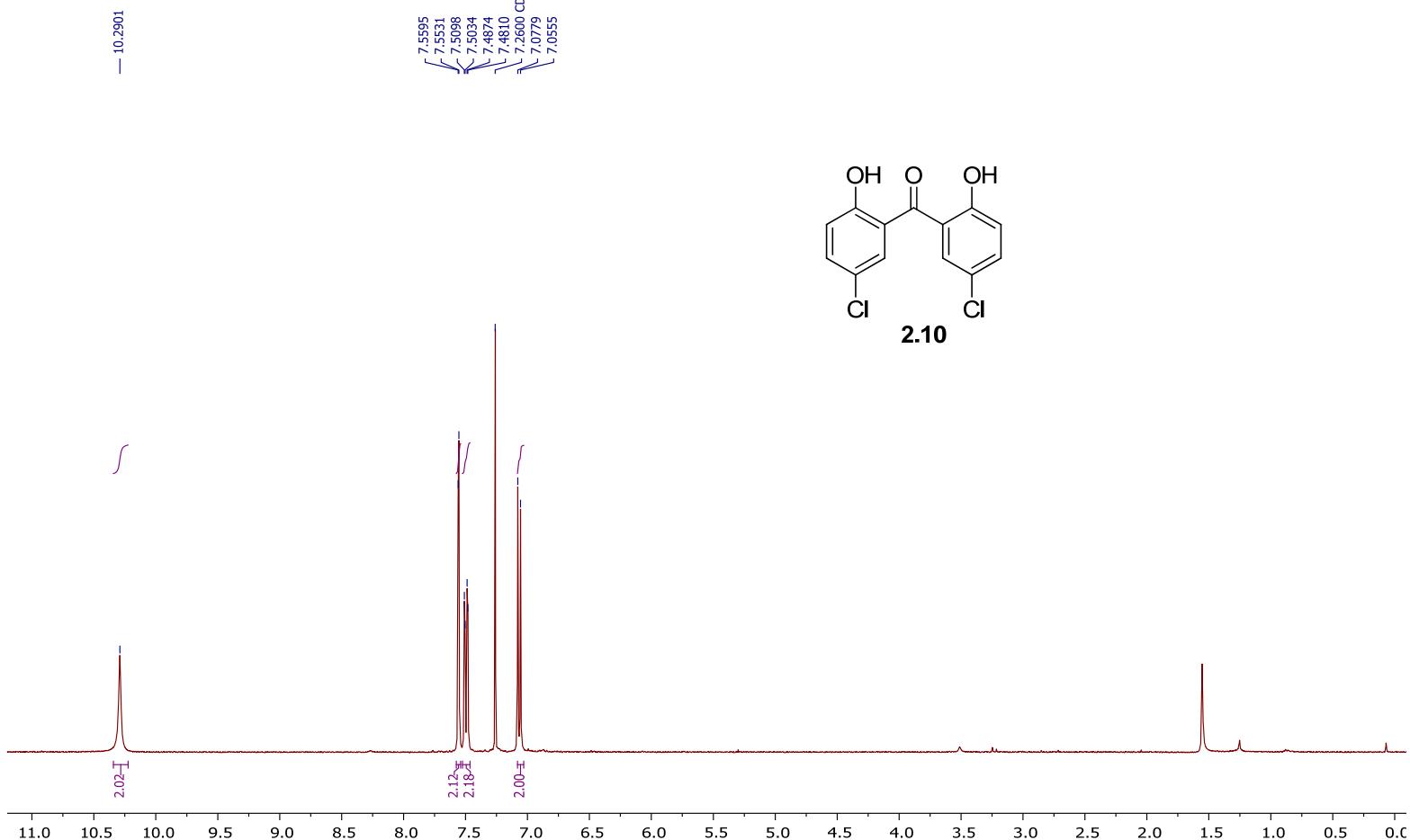
100

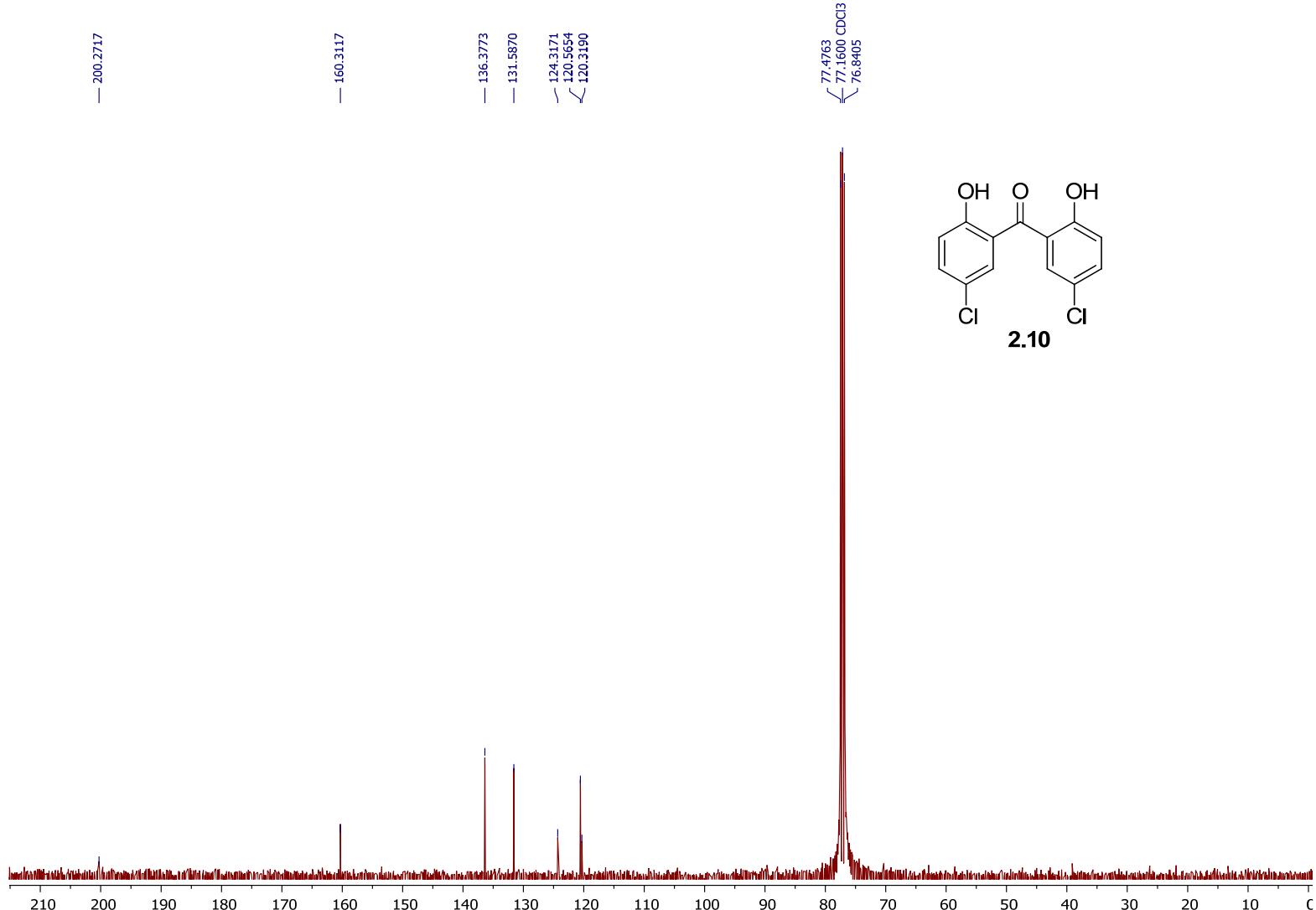


[M-H]⁻ calcd. 368.8762



ESI(HRMS) spectrum of bis(5-bromo-2-hydroxyphenyl)methanone (**2.9**)





¹³C NMR (100 MHz, CDCl₃) spectrum of bis(5-chloro-2-hydroxyphenyl)methanone (**2.10**)

Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

19-Apr-2016
12:20:39

1: TOF MS ES-
1.12e4

SRK10-190- 24 (0.498) AM (Cen,4, 100.00, Ar,8500.0,554.26,5.00,LS 10); Sm (SG, 2x5.00); Sb (10,1.00); Cm (24:26-1:4)

280.9776

100

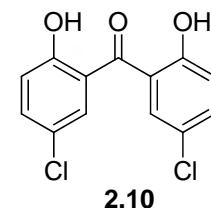
80

60

40

20

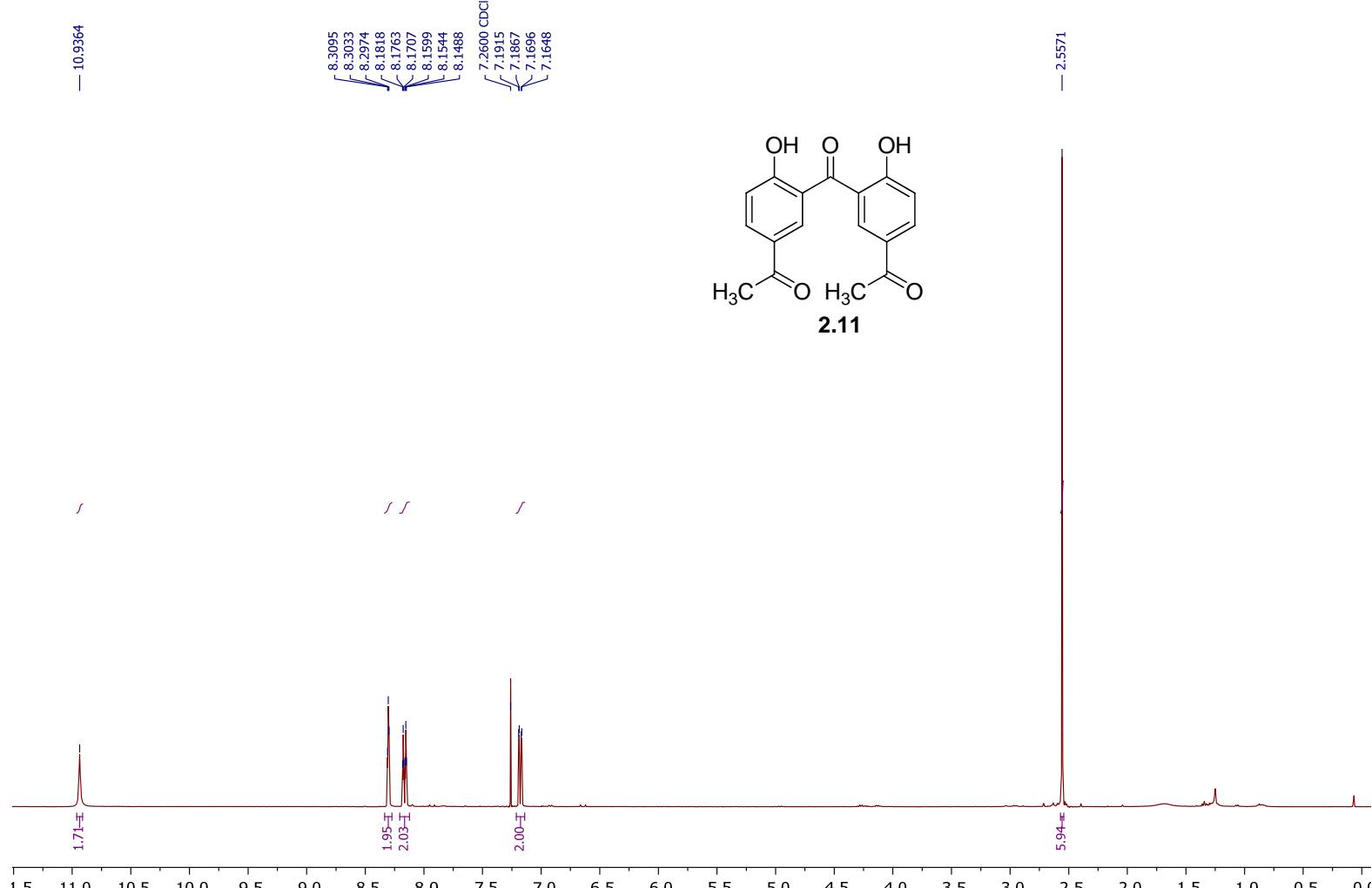
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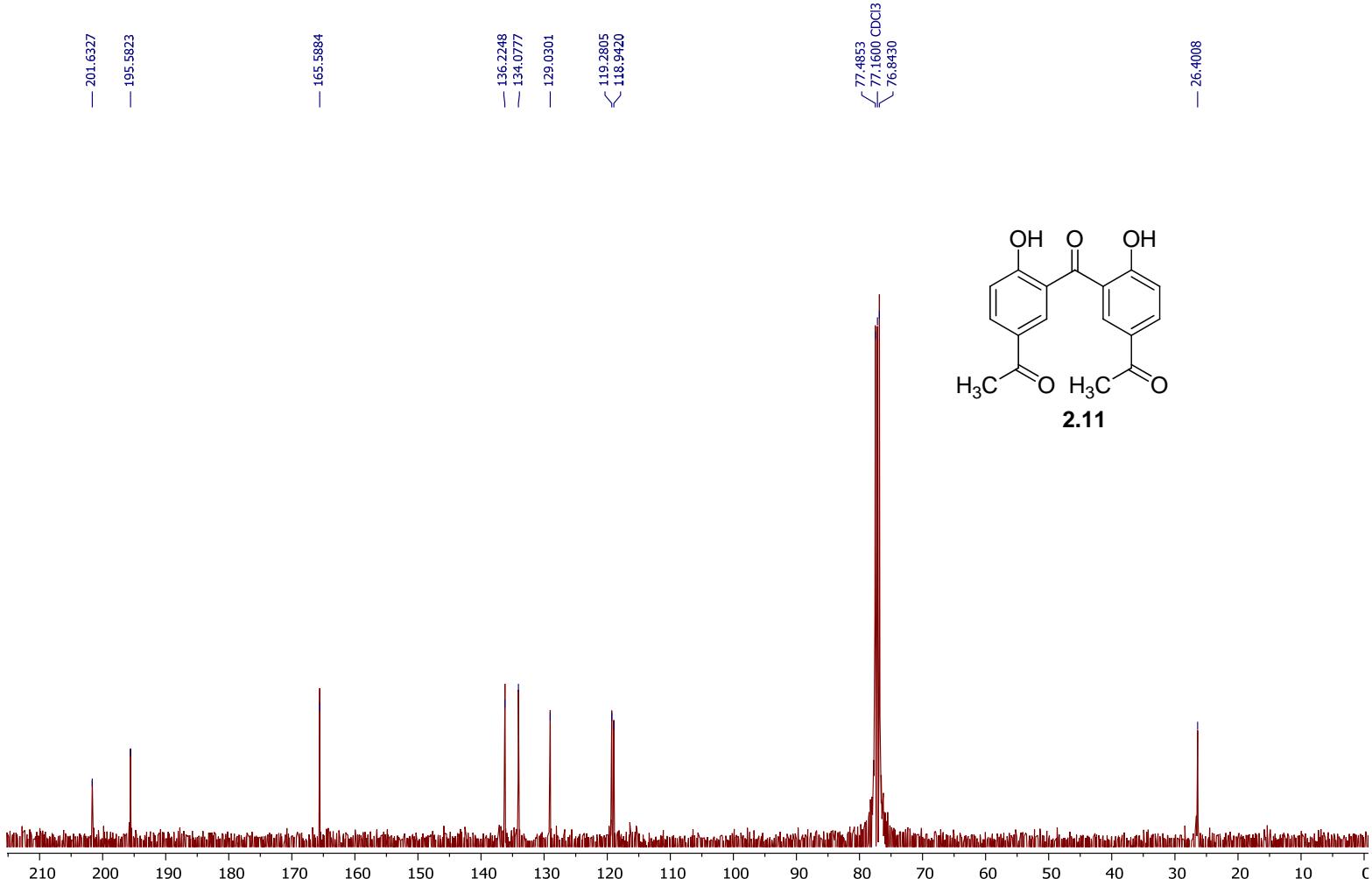
[M-H]⁻ calcd. 280.9772

272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 m/z

ESI(HRMS) spectrum of bis(5-chloro-2-hydroxyphenyl)methanone (**2.10**)



¹H NMR (400 MHz, CDCl₃) spectrum of 1,1'-(3,3'-carbonylbis(4-hydroxy-3,1-phenylene))diethanone (**2.11**)



^{13}C NMR (100 MHz, CDCl_3) spectrum of 1,1'-(3,3'-carbonylbis(4-hydroxy-3,1-phenylene))diethanone (**2.11**)

Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

19-Apr-2016

09:49:36

1: TOF MS ES+

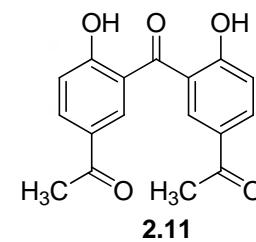
1.09e4

SRK10-195 23 (0.476) AM (Cen,4, 100.00, Ar,8500.0,556:28,5.00,LS 10); Sm (SG, 2x5.00); Sb (10,1.00); Cm (23:24-1:3)

100

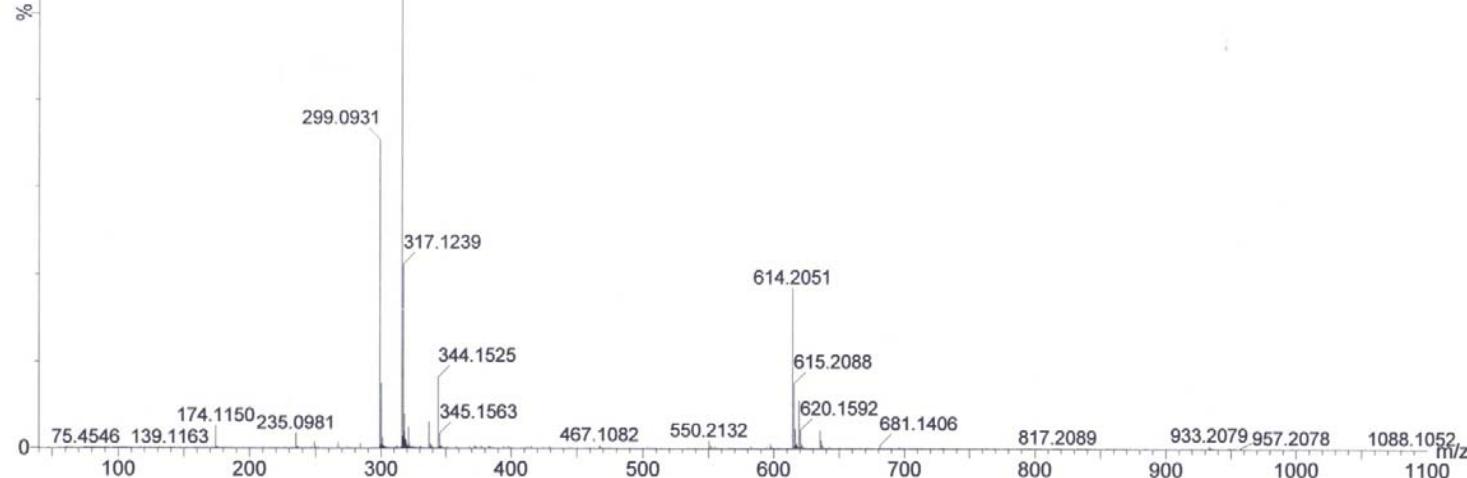
316.1184

$\text{M} + \text{NH}_4^+$



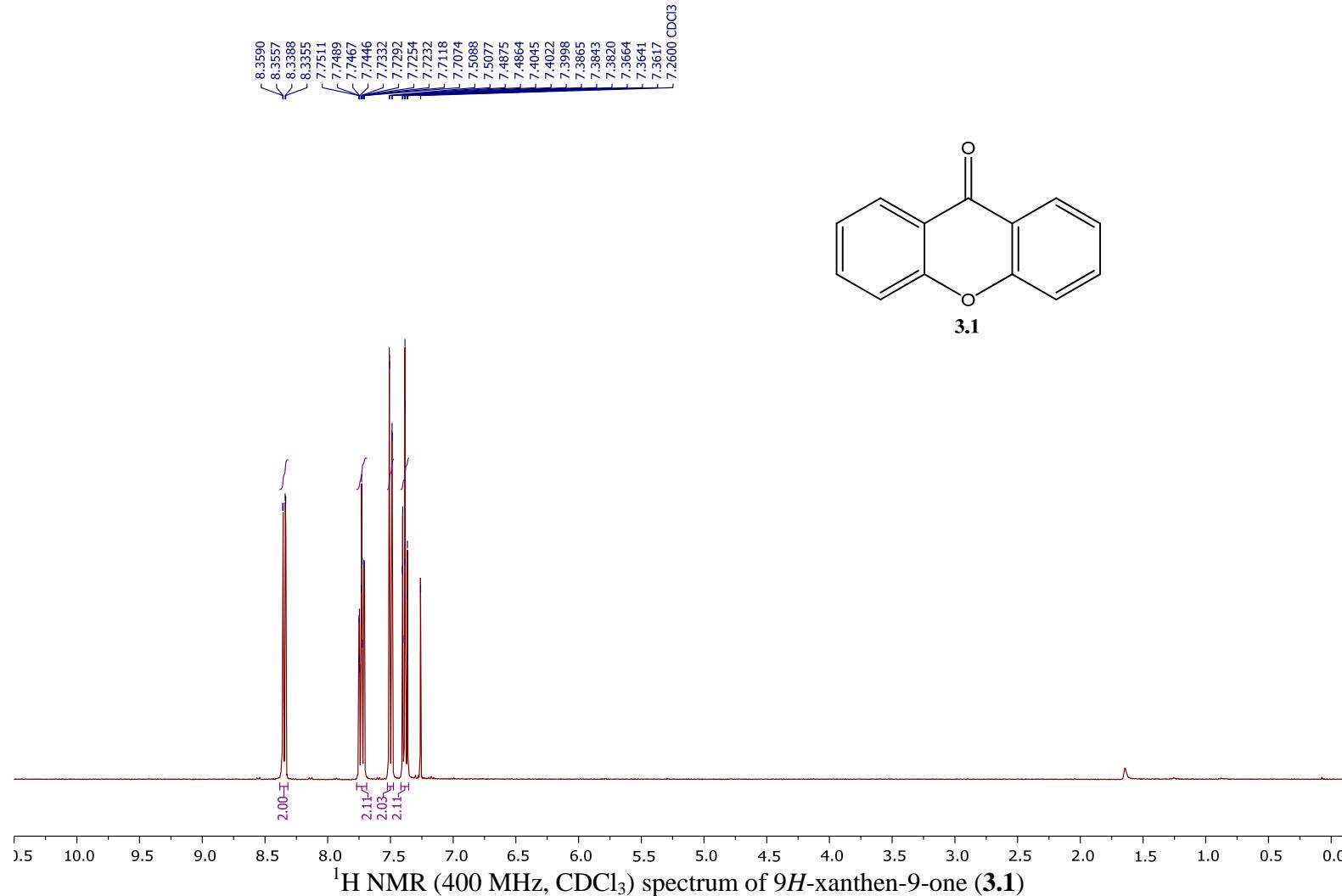
2.11

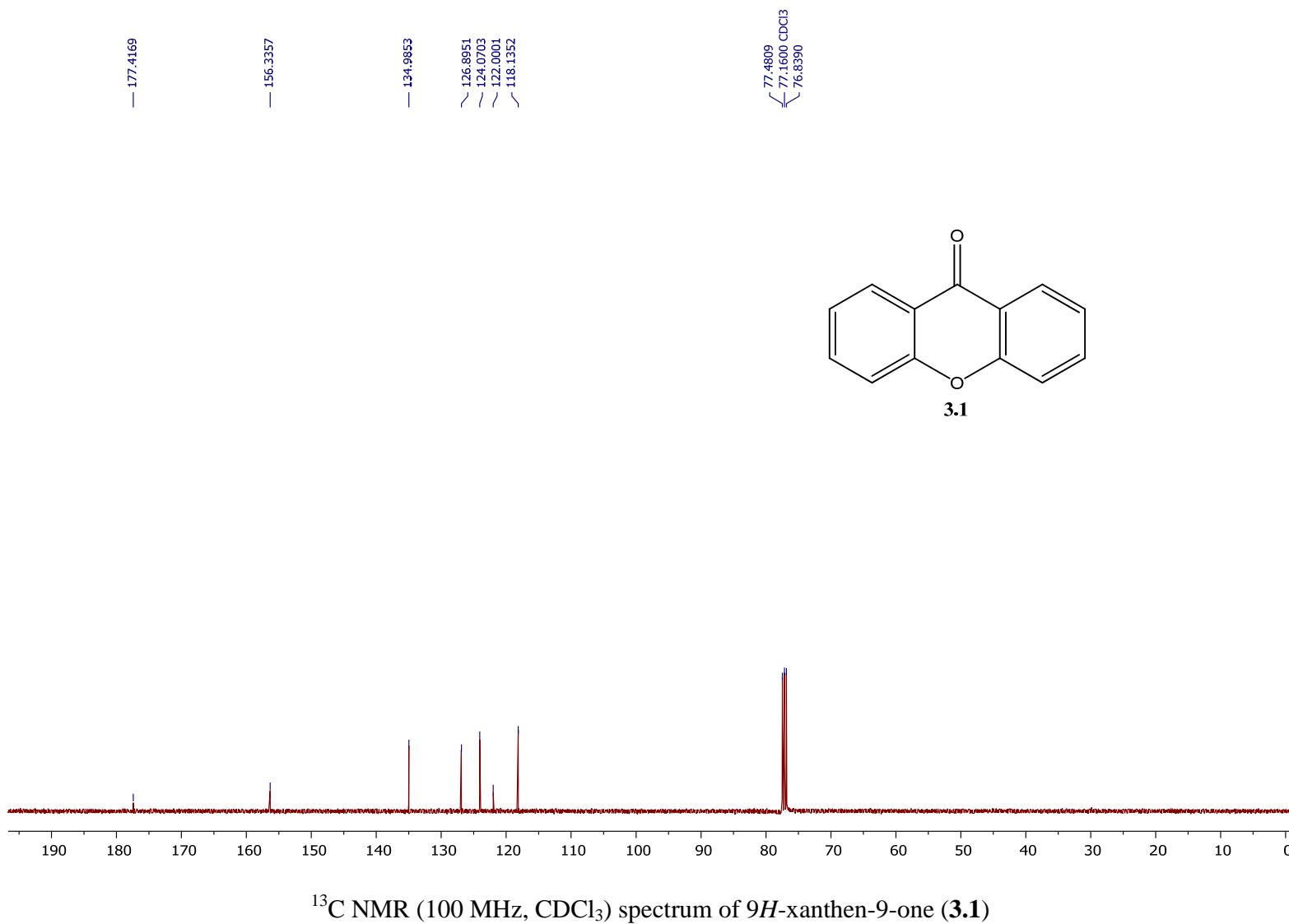
$[\text{M} + \text{NH}_4]^+$ calcd. 316.1185



ESI(HRMS) spectrum of 1,1'-(3,3'-carbonylbis(4-hydroxy-3,1-phenylene))diethanone (**2.11**)

3. Copies of ^1H NMR, ^{13}C NMR and HRMS spectra of Compound 3.1 to 3.10 (Table 3):





Electrospray ionisation-MS

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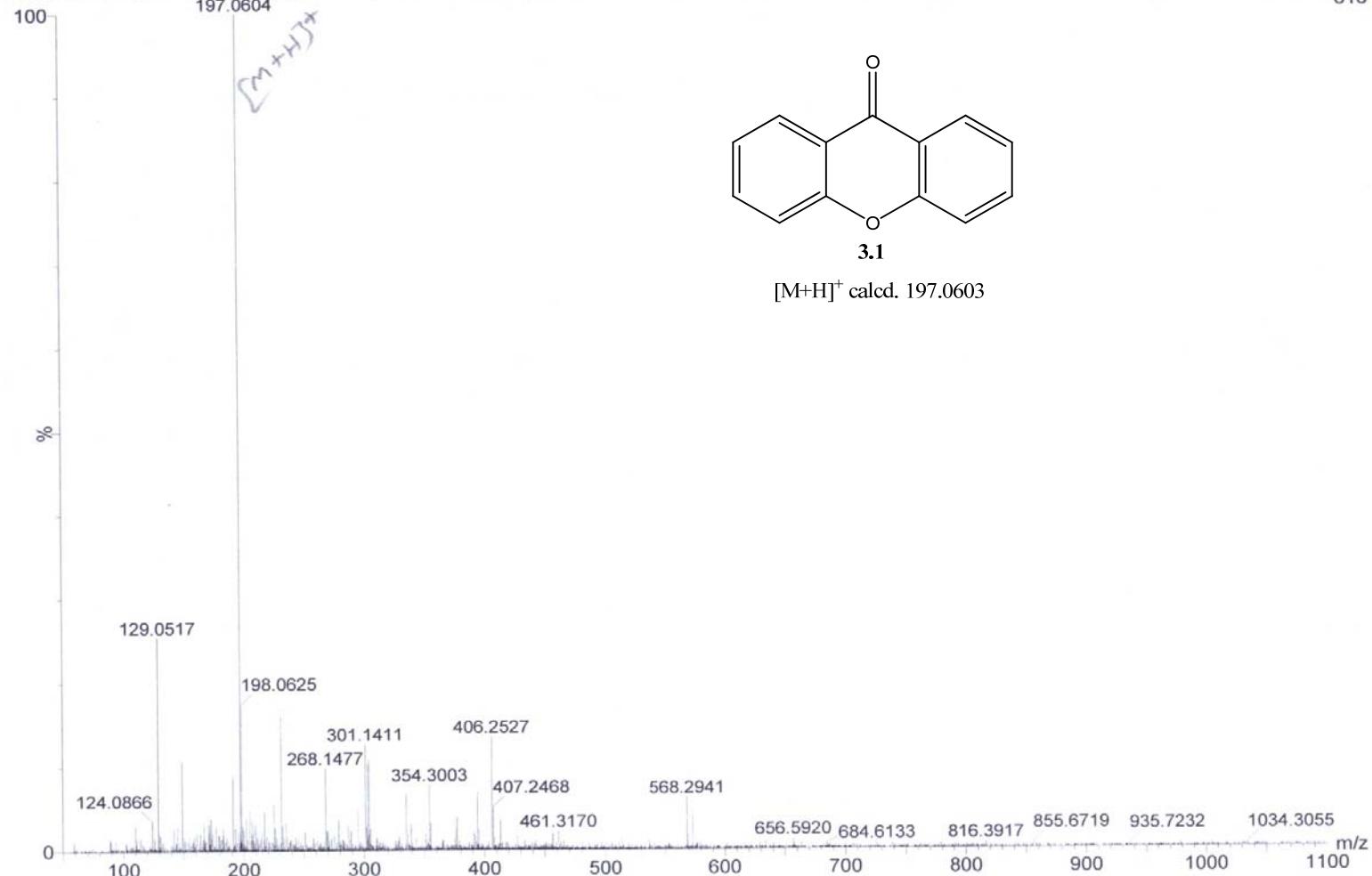
WATERS-Q-ToF Premier-HAB21

197.0604

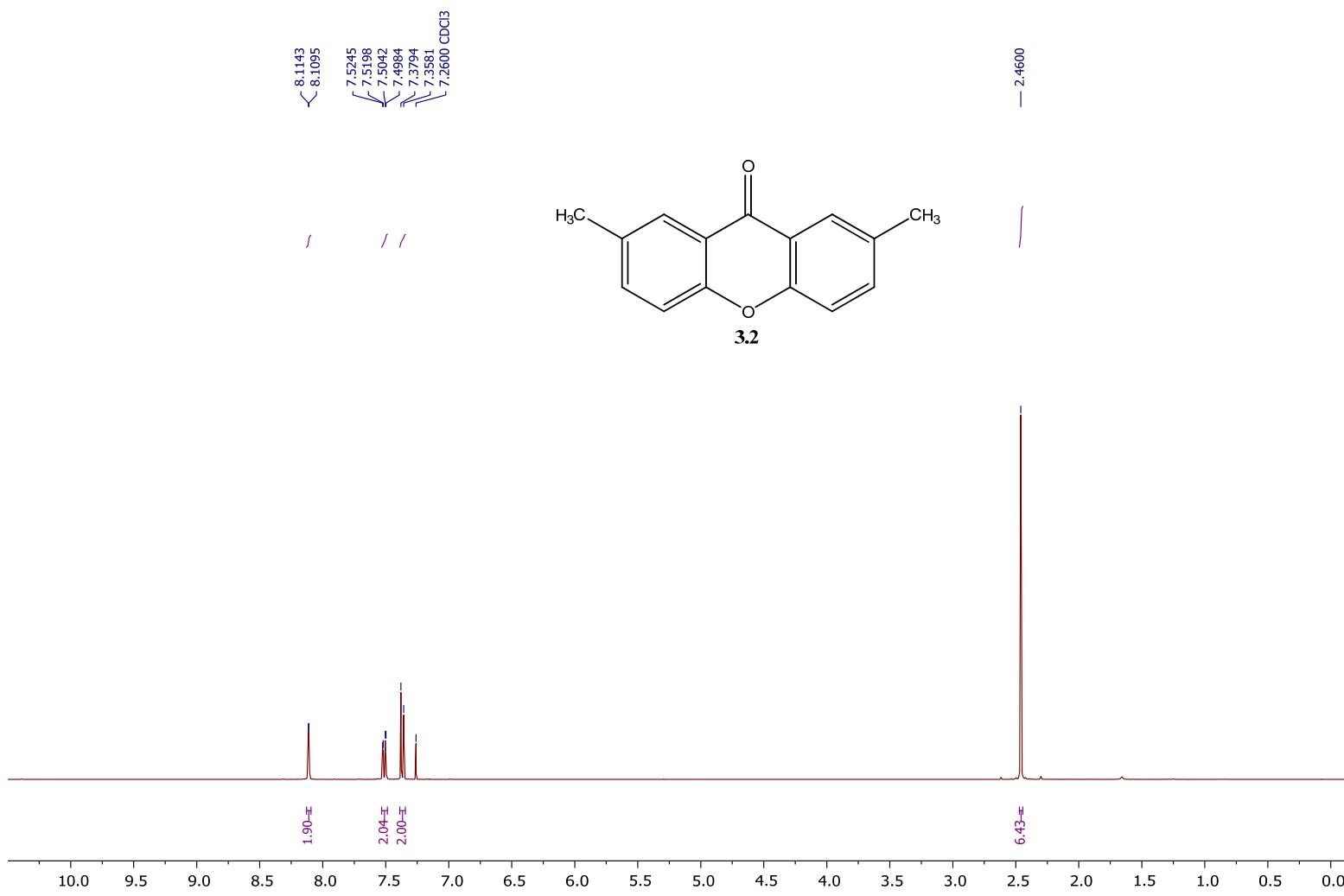
14:30:31 10-Sep-2014

1: TOF MS ES+

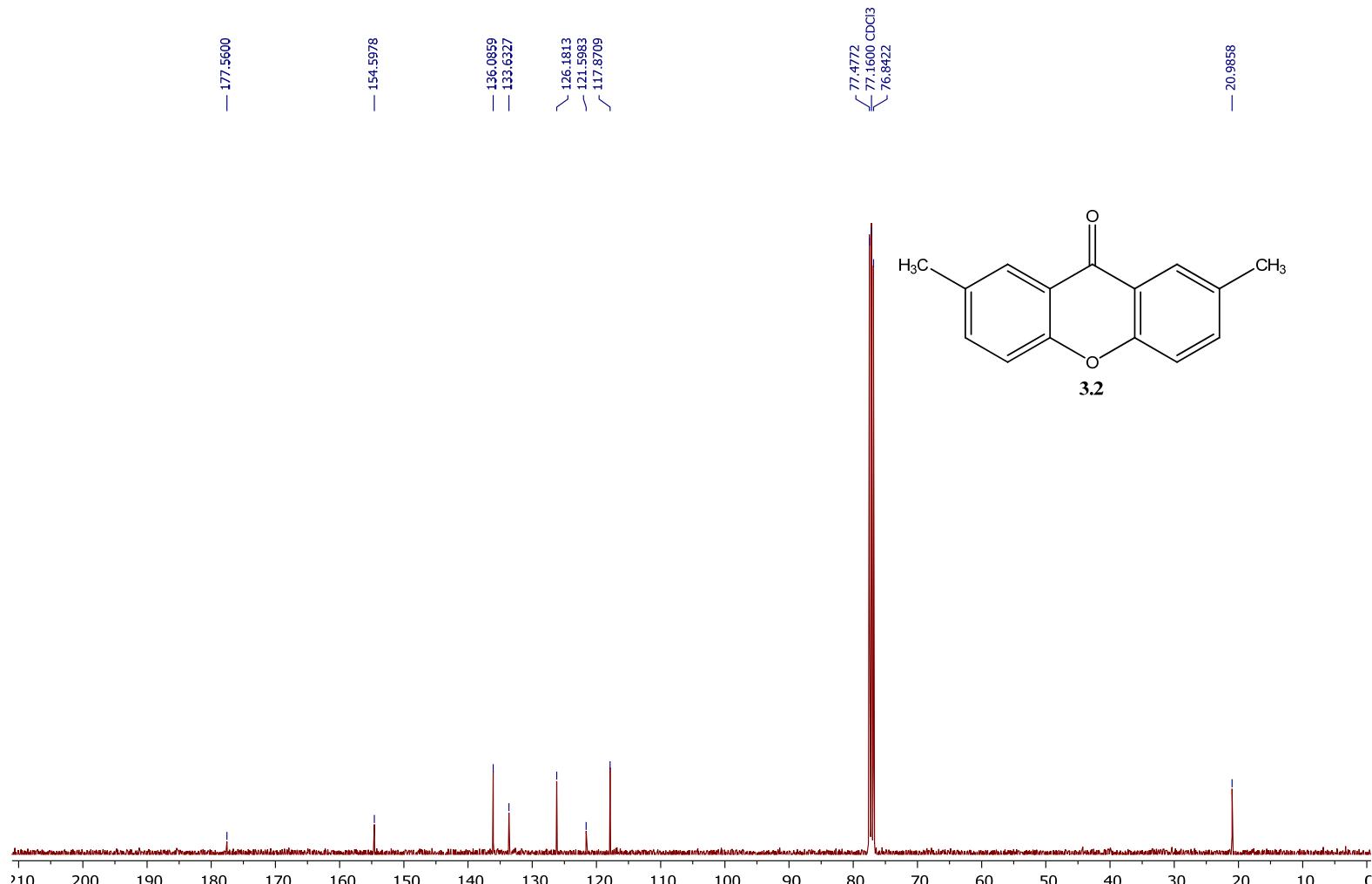
616



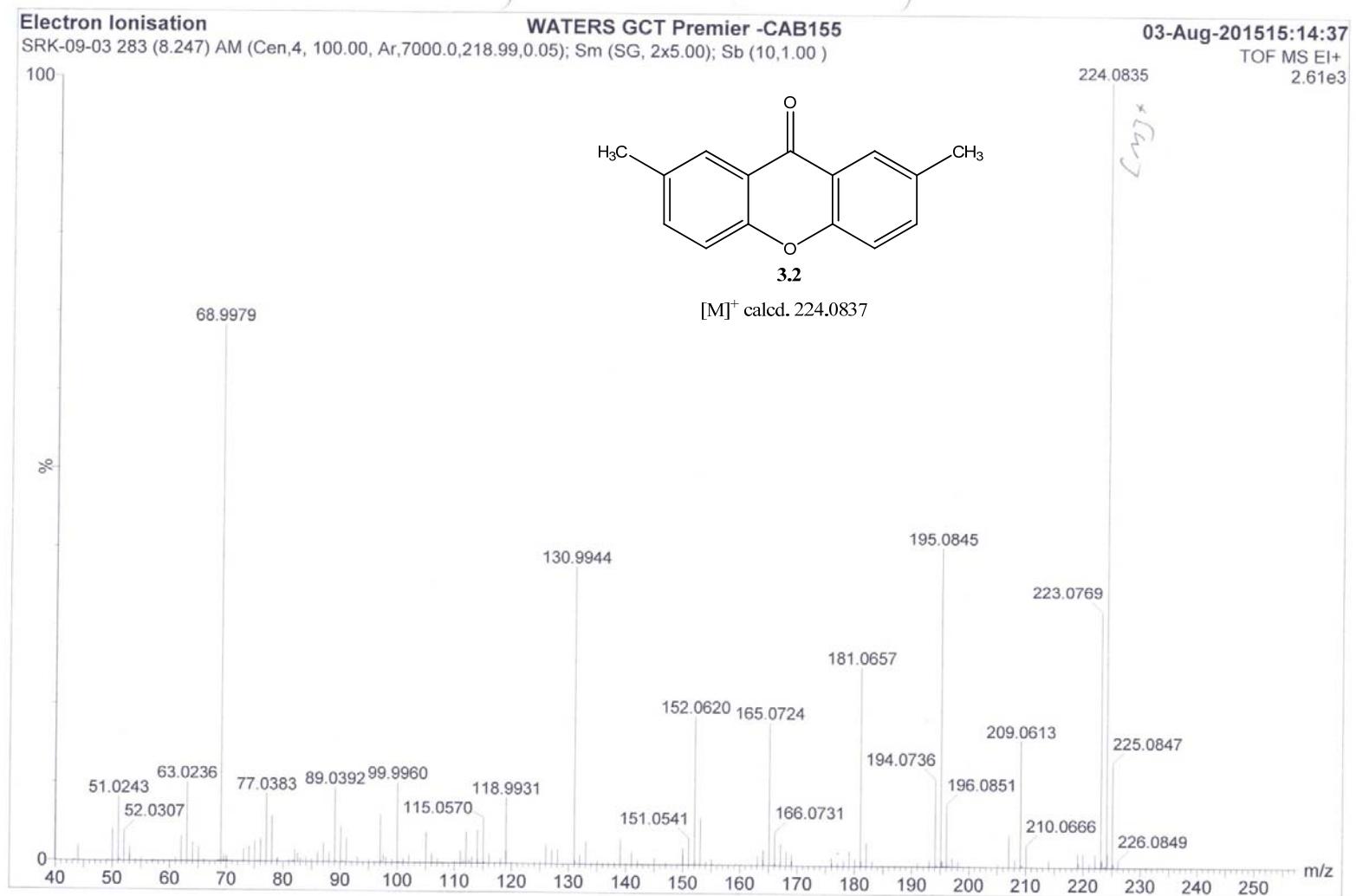
ESI(HRMS) spectrum of 9H-xanthen-9-one (**3.1**)



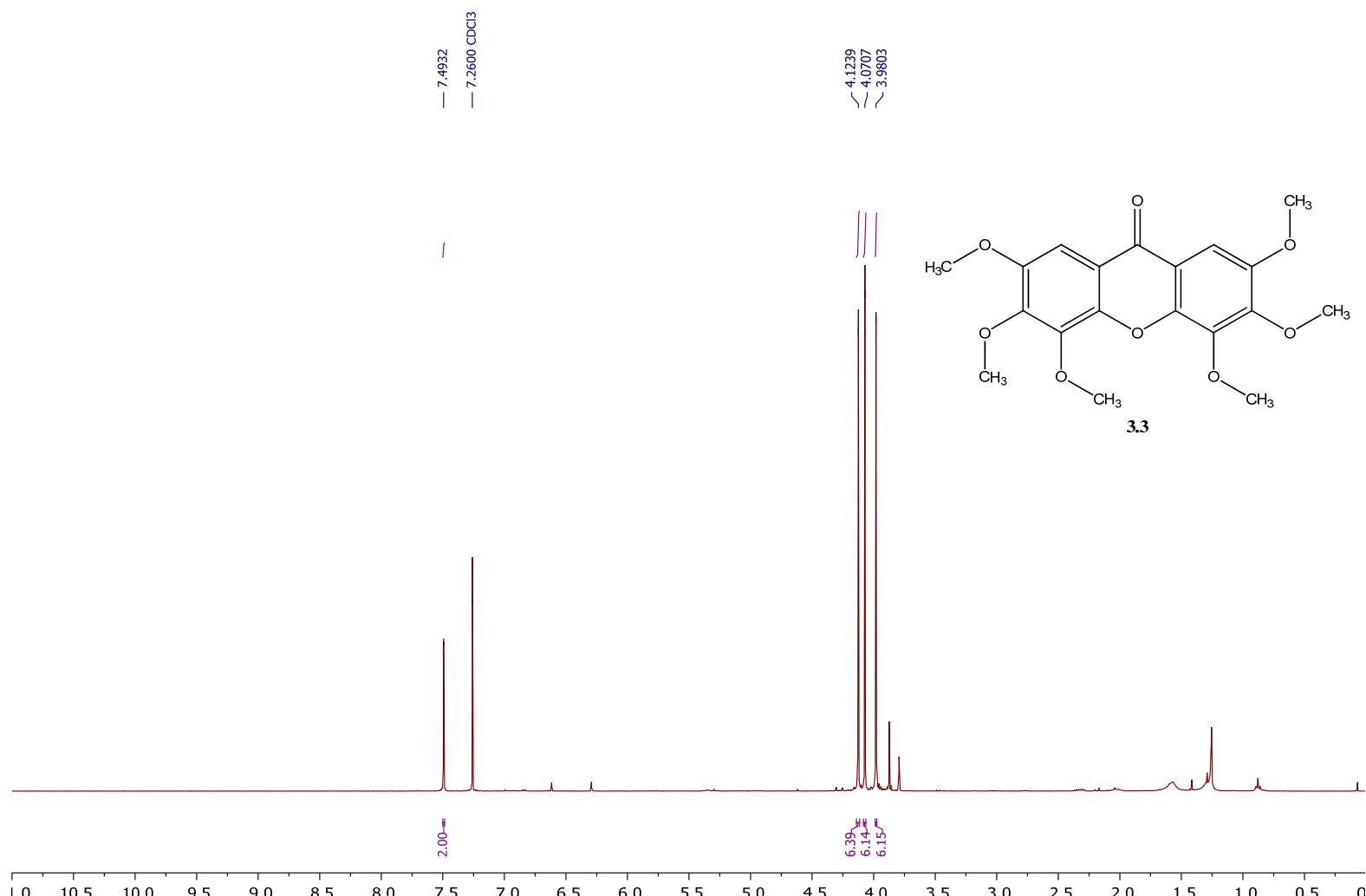
¹H NMR (400 MHz, CDCl₃) spectrum of 2,7-dimethyl-9H-xanthen-9-one (**3.2**)



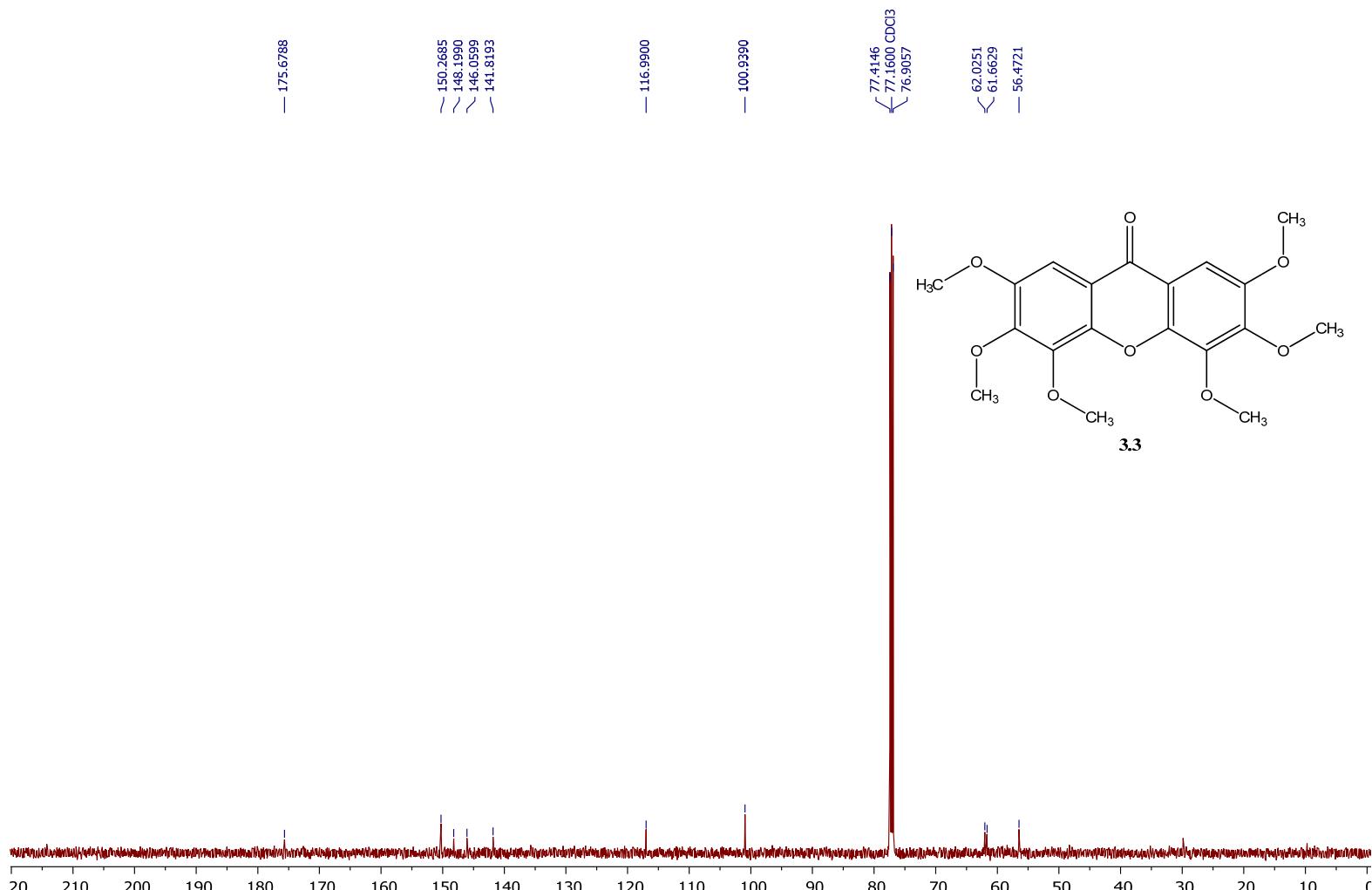
¹³C NMR (100 MHz, CDCl₃) spectrum of 2,7-dimethyl-9*H*-xanthen-9-one (**3.2**)



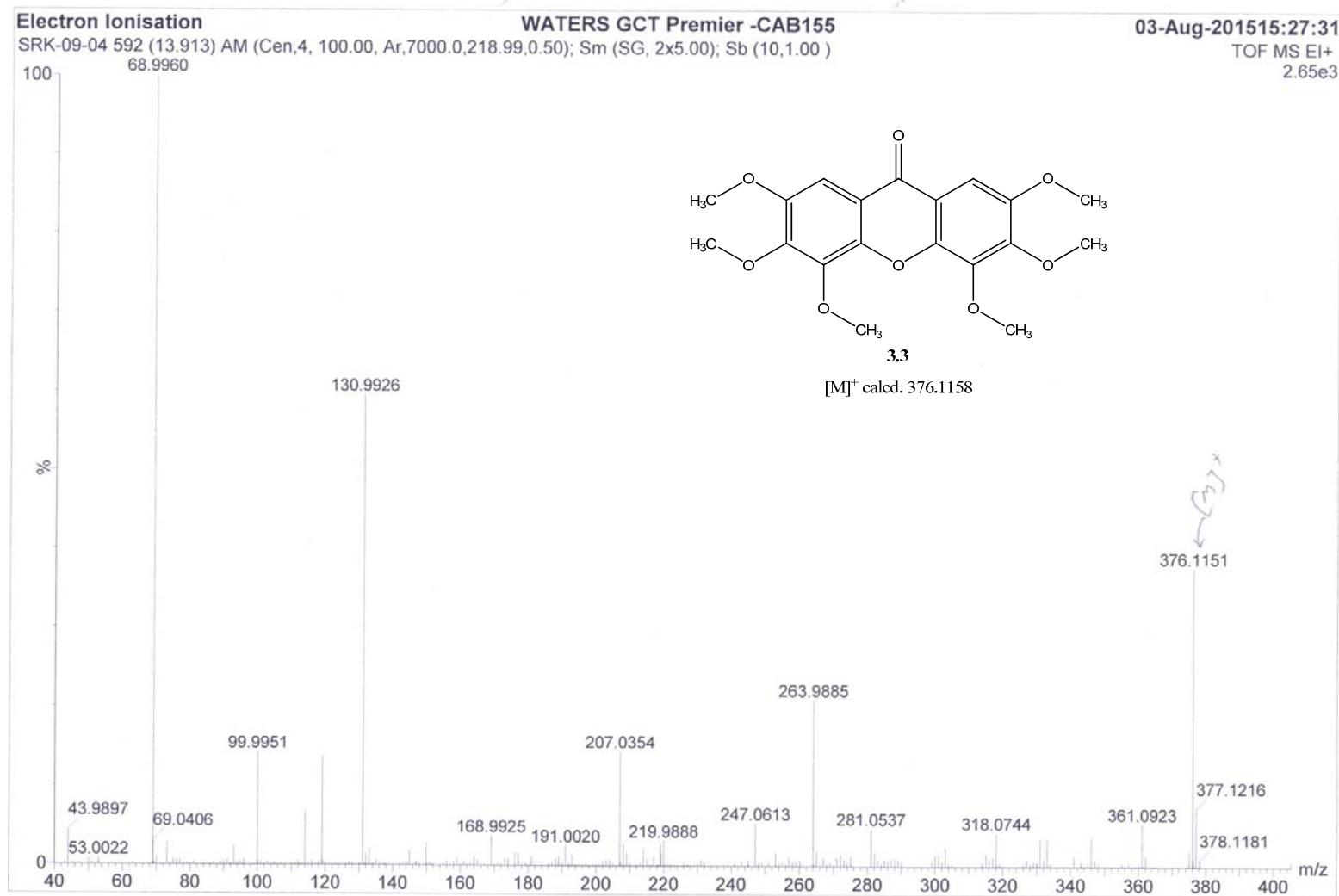
EI(HRMS) spectrum of 2,7-dimethyl-9*H*-xanthen-9-one (**3.2**)



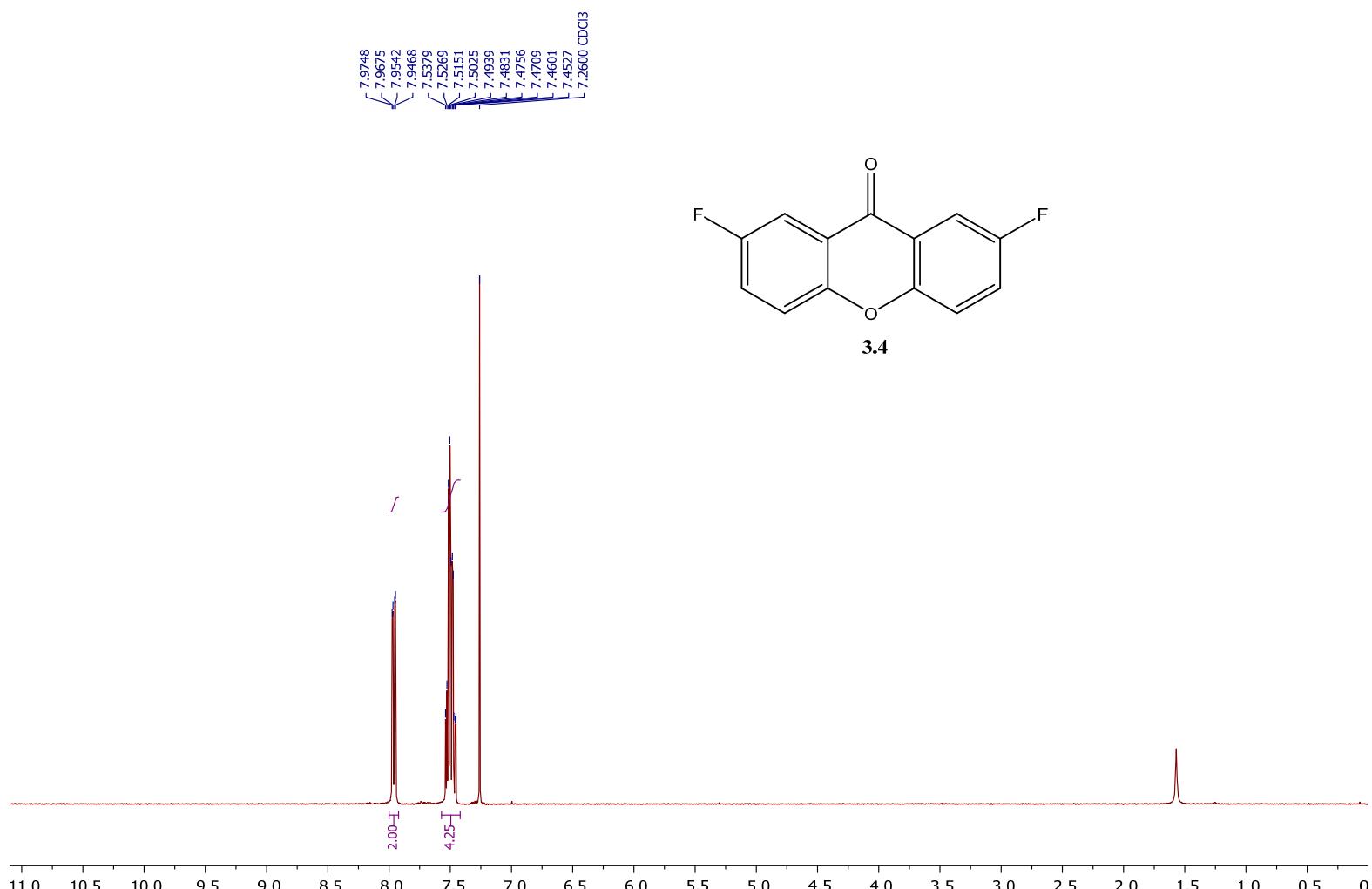
^1H NMR (400 MHz, CDCl_3) spectrum of 2,3,4,5,6,7-hexamethoxy-9*H*-xanthen-9-one (**3.3**)



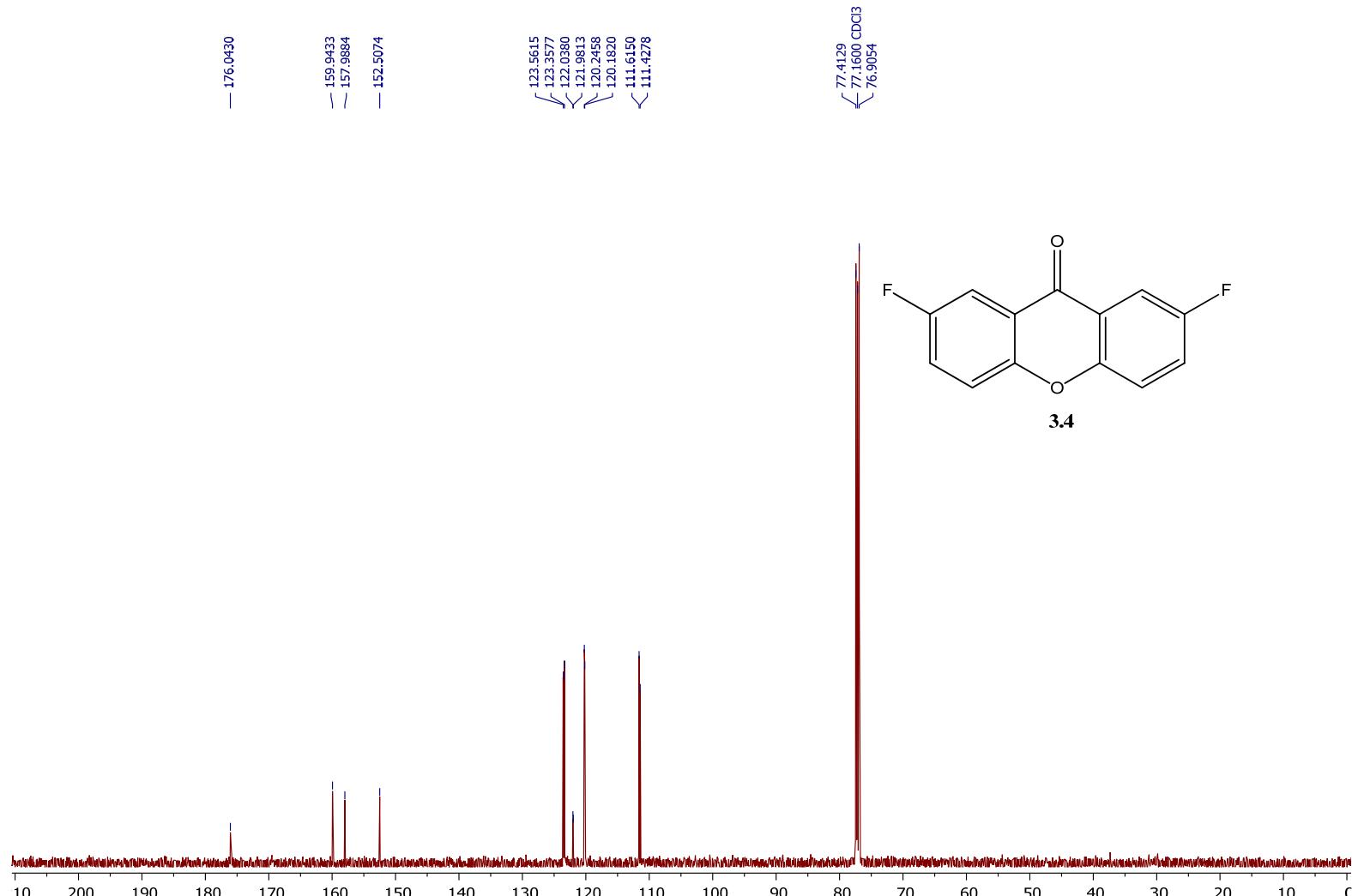
^{13}C NMR (125 MHz, CDCl₃) spectrum of 2,3,4,5,6,7-hexamethoxy-9*H*-xanthen-9-one (**3.3**)



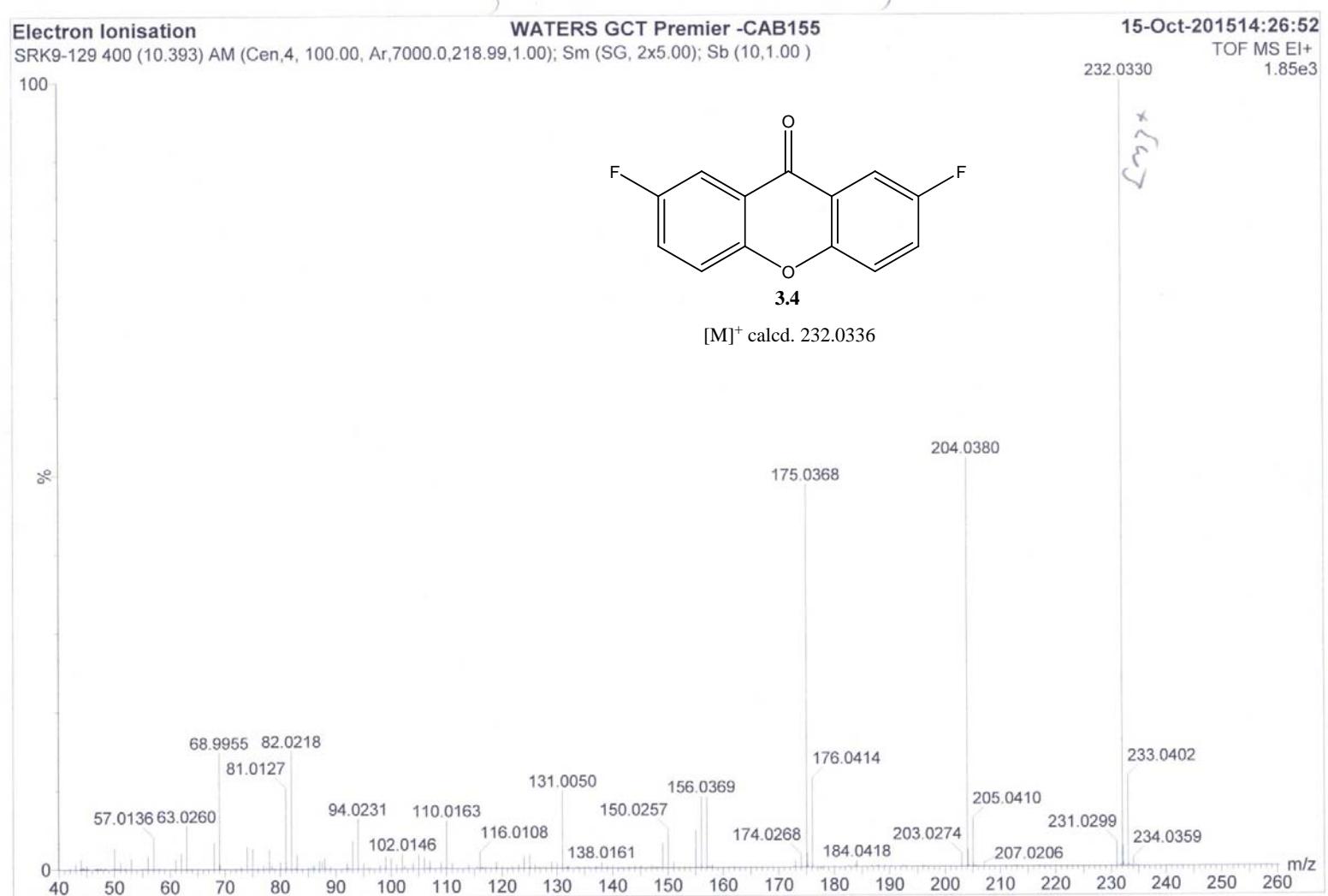
EI(HRMS) spectrum of 2,3,4,5,6,7-hexamethoxy-9*H*-xanthen-9-one (**3.3**)



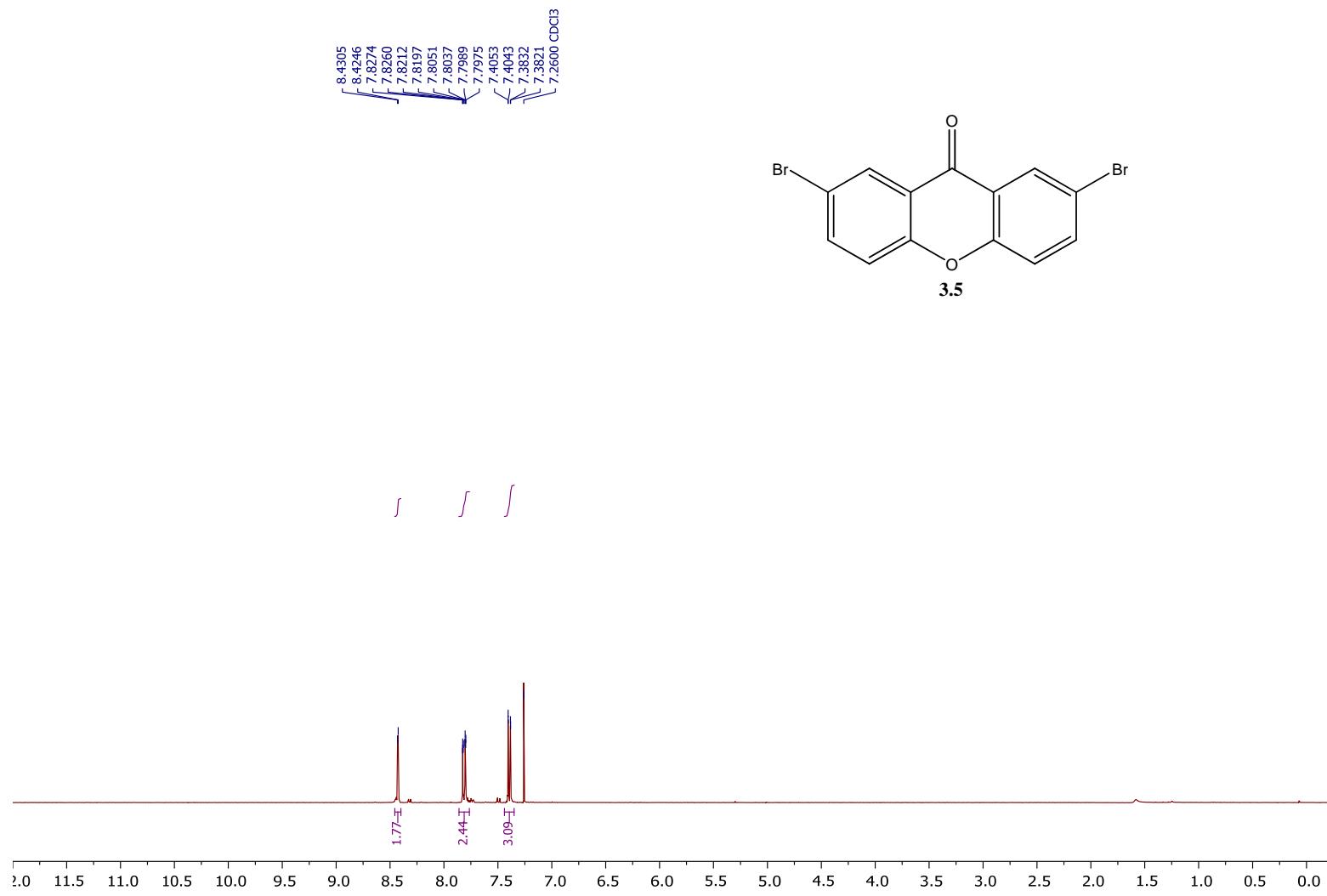
^1H NMR (400 MHz, CDCl_3) spectrum of 2,7-difluoro-9*H*-xanthen-9-one (**3.4**)

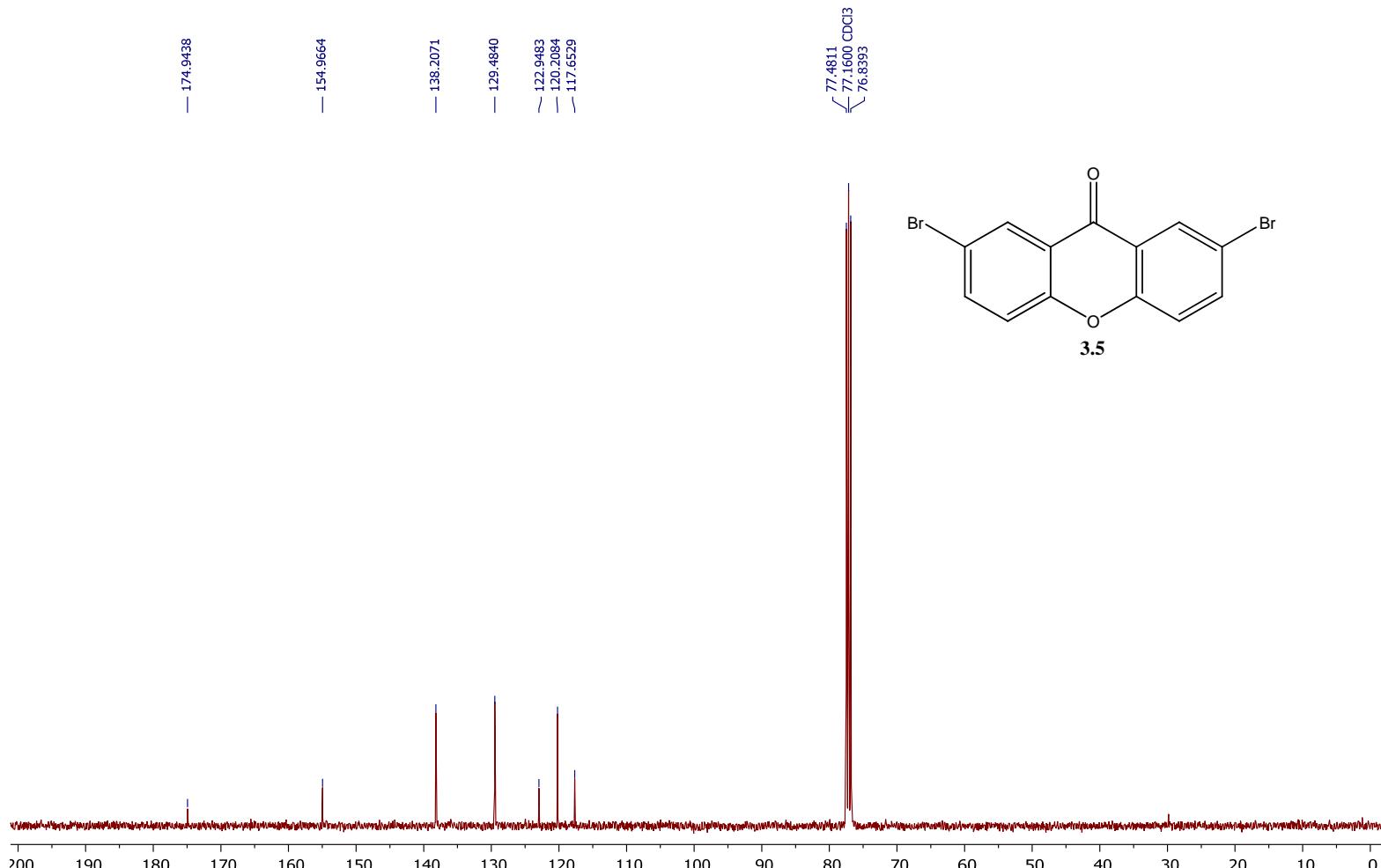


^{13}C NMR (125 MHz, CDCl₃) spectrum of 2,7-difluoro-9*H*-xanthen-9-one (**3.4**)

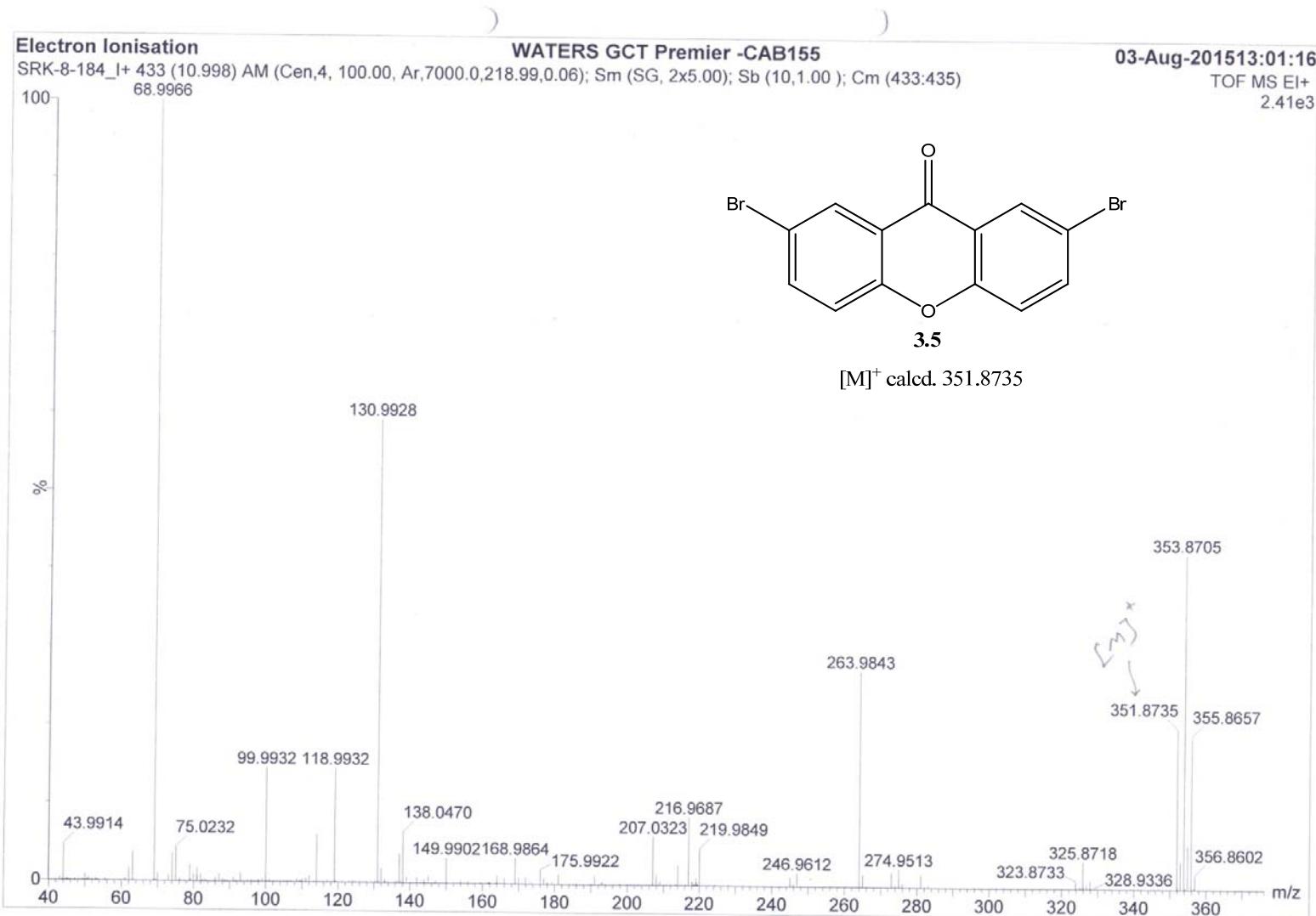


EI(HRMS) spectrum of 2,7-difluoro-9*H*-xanthen-9-one (**3.4**)

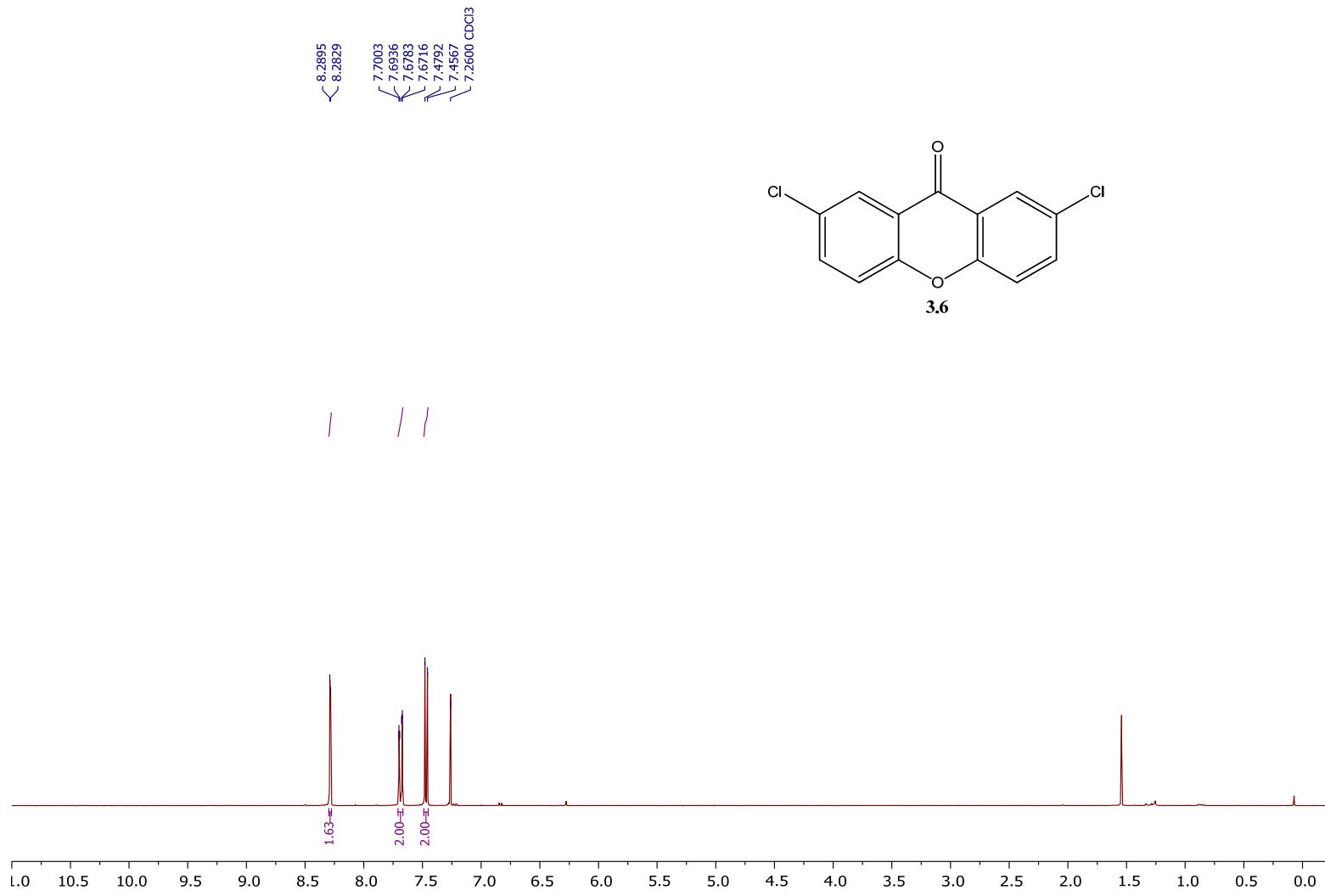




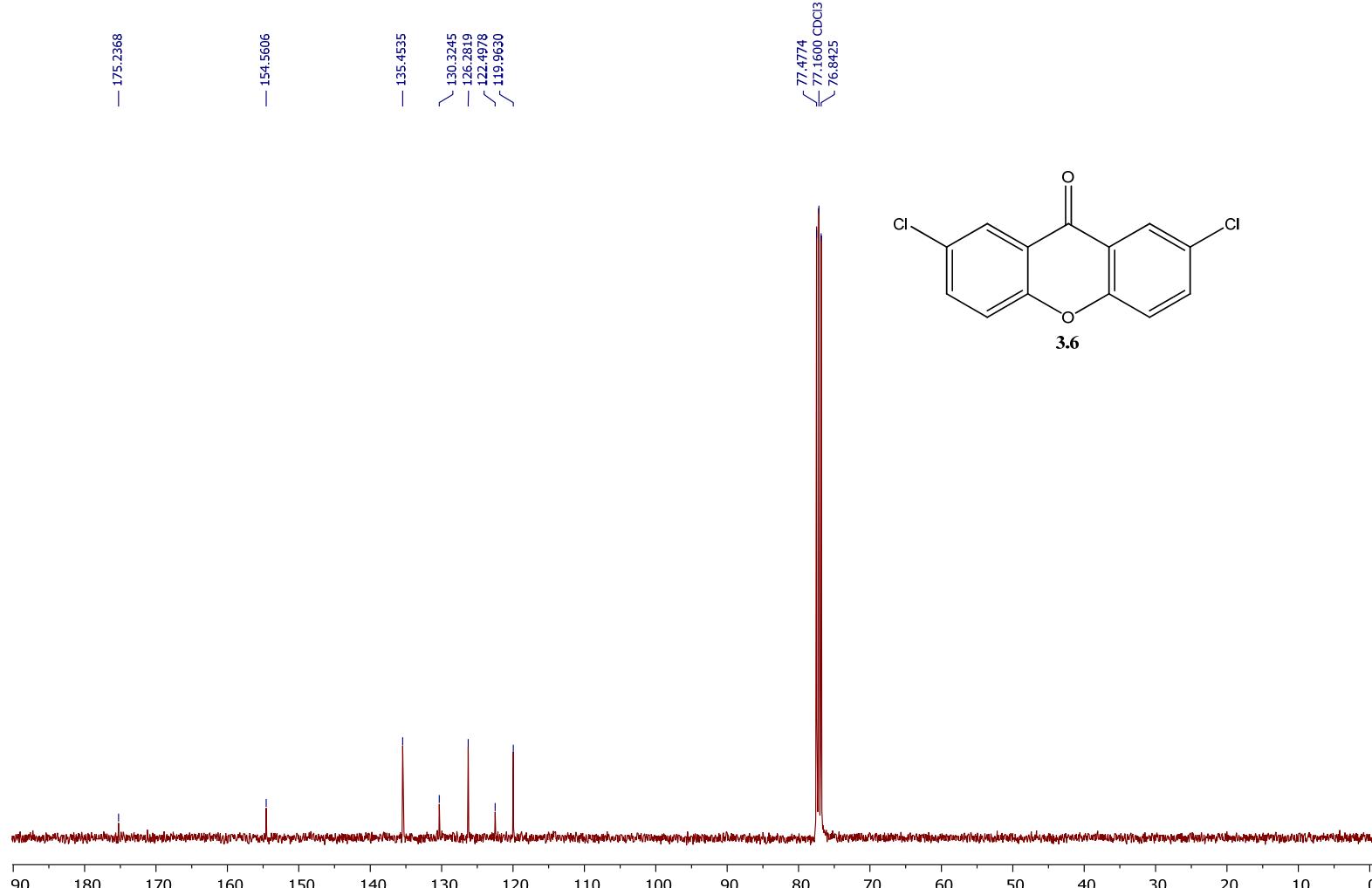
^{13}C NMR (100 MHz, CDCl₃) spectrum of 2,7-dibromo-9*H*-xanthen-9-one (**3.5**)



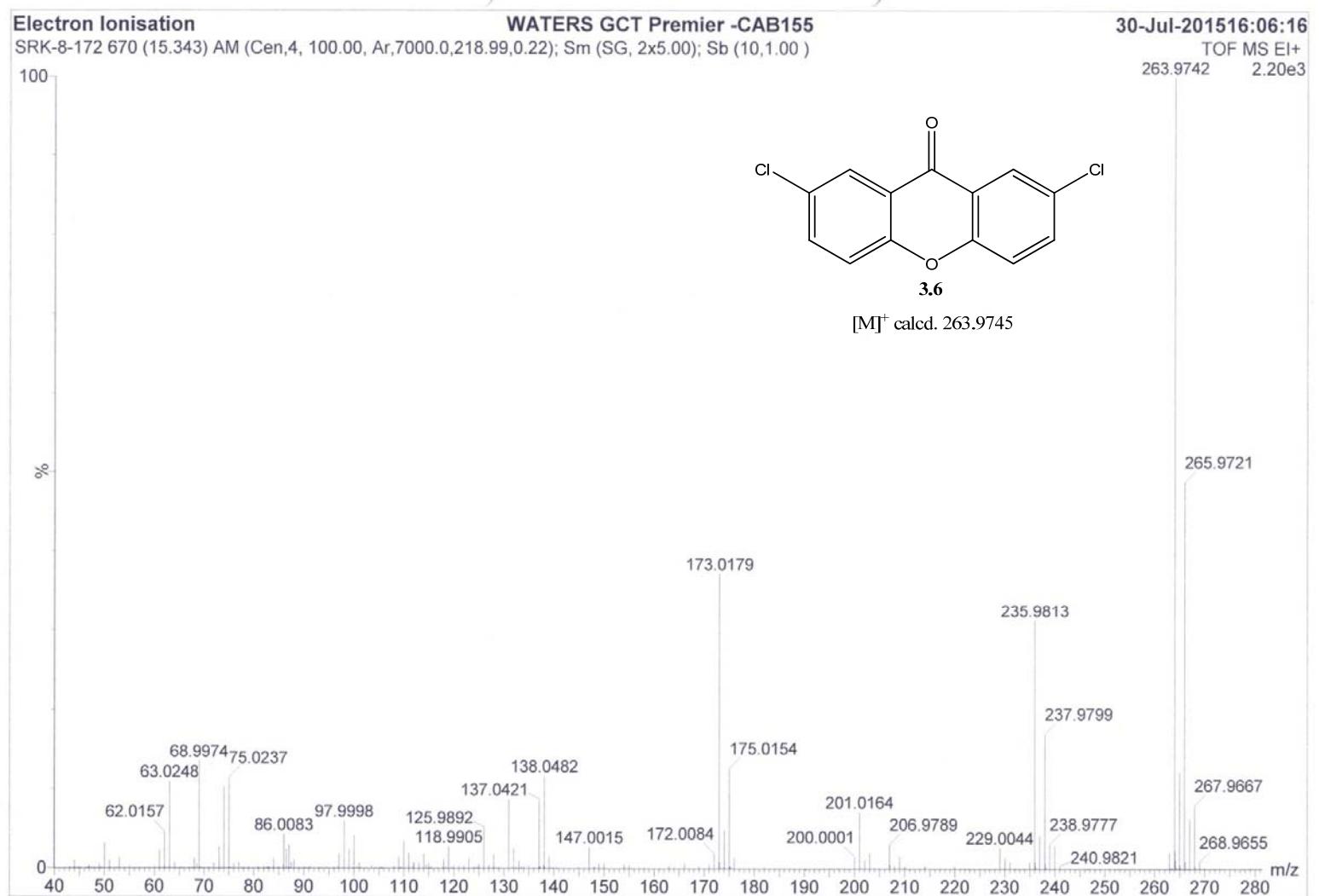
EI(HRMS) spectrum of 2,7-dibromo-9*H*-xanthen-9-one (**3.5**)



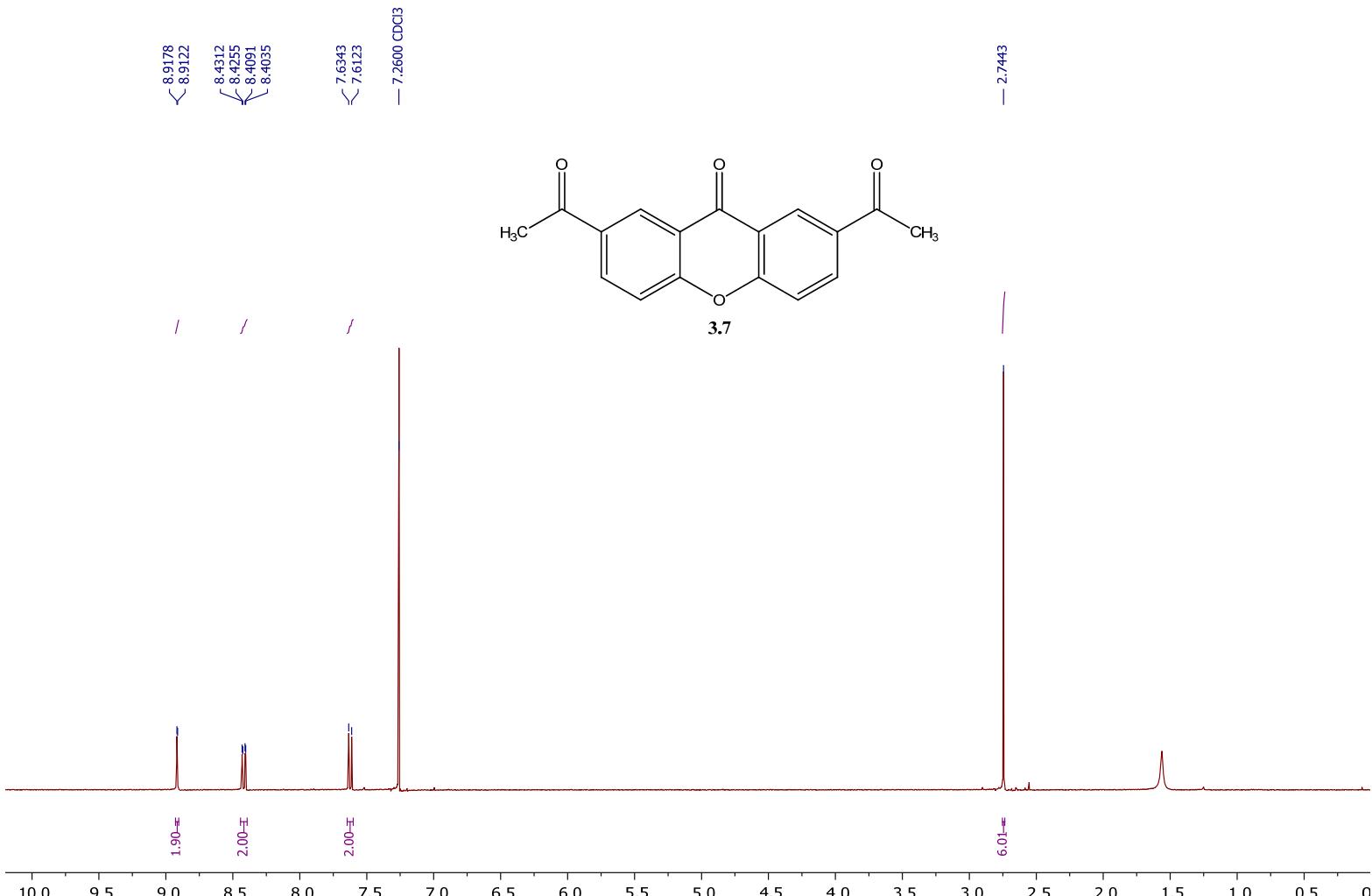
¹H NMR (400 MHz, CDCl₃) spectrum of 2,7-dichloro-9*H*-xanthen-9-one (**3.6**)

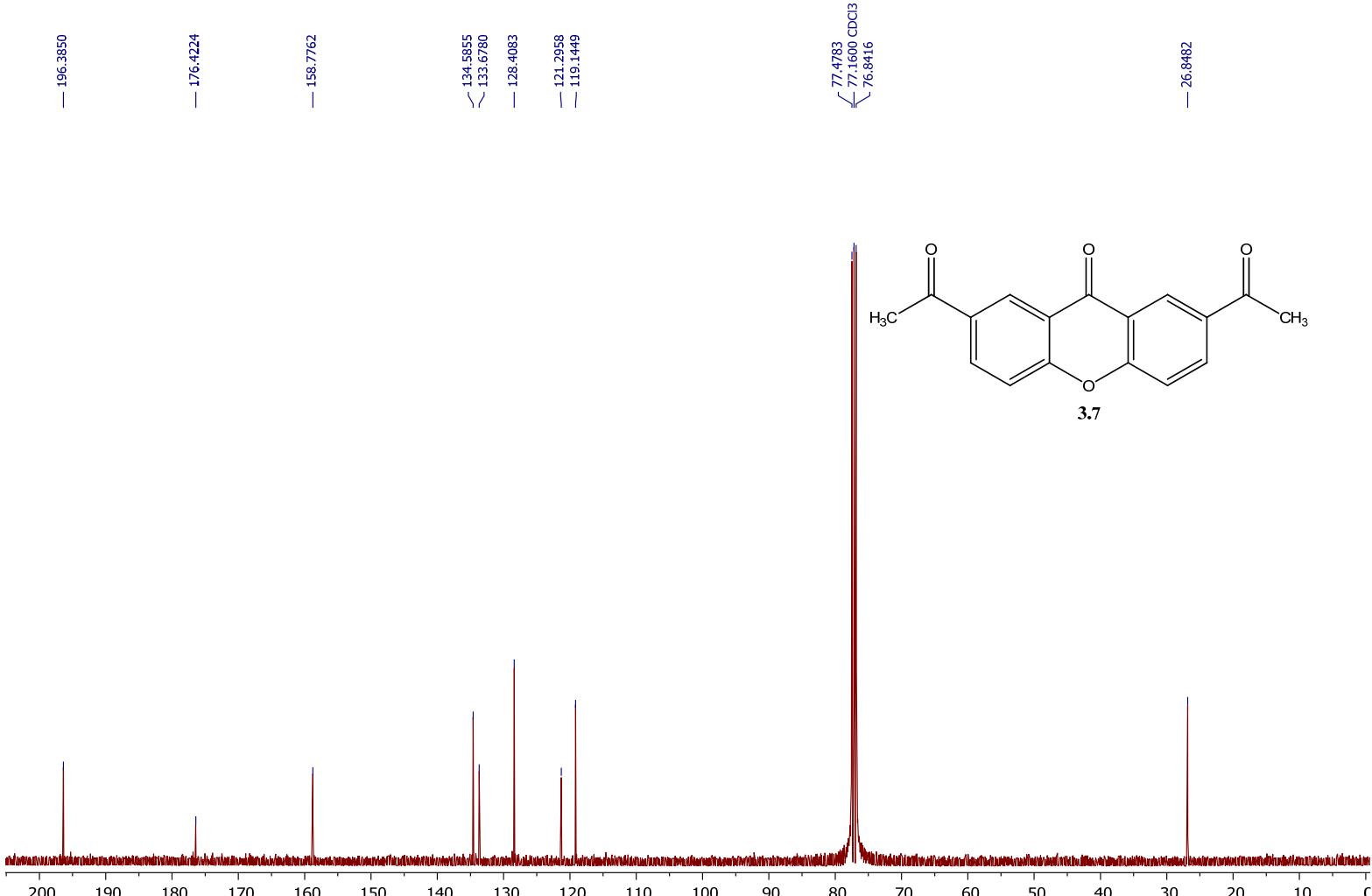


^{13}C NMR (100 MHz, CDCl₃) spectrum of 2,7-dichloro-9*H*-xanthen-9-one (**3.6**)

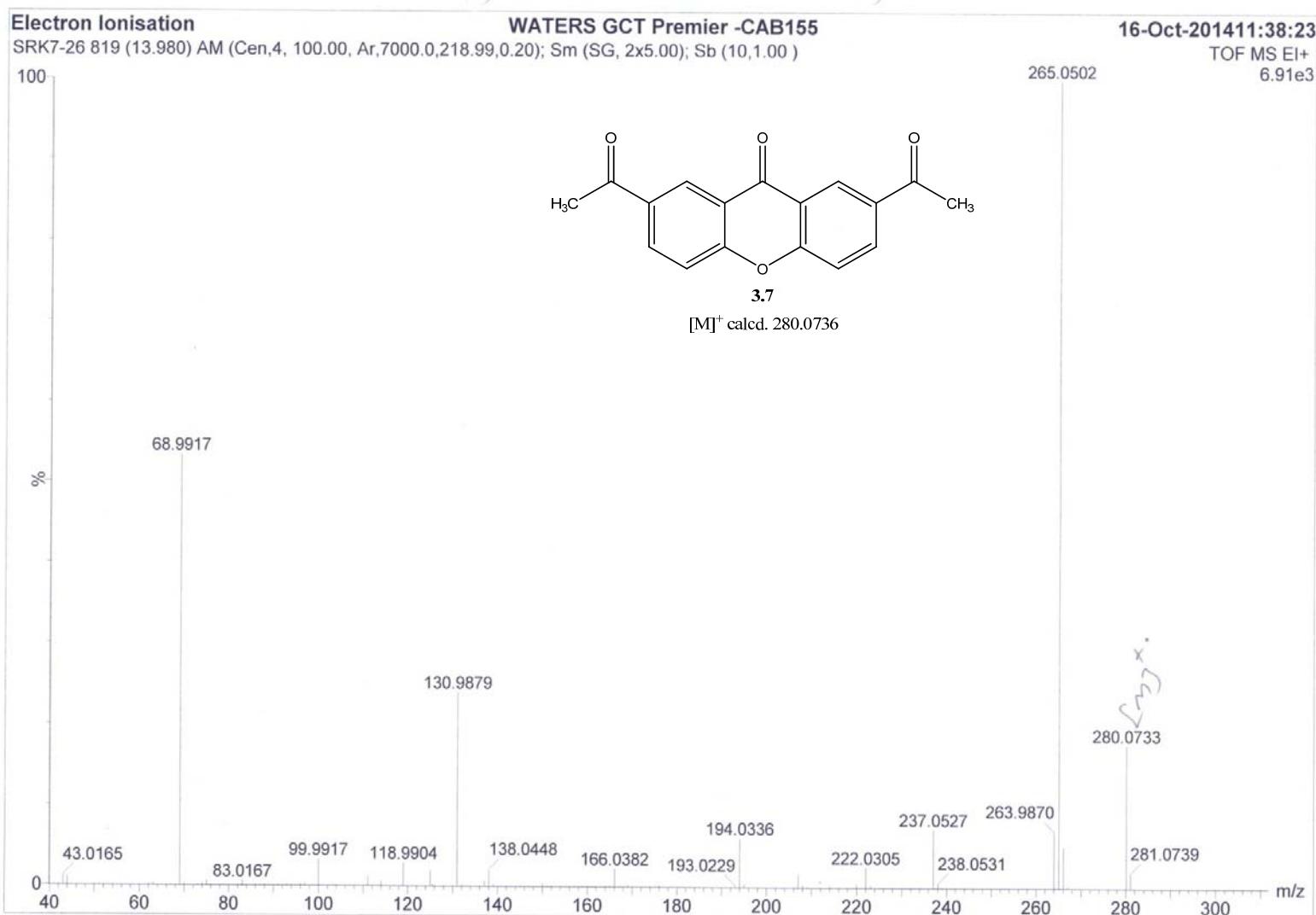


EI(HRMS) spectrum of 2,7-dichloro-9*H*-xanthen-9-one (**3.6**)

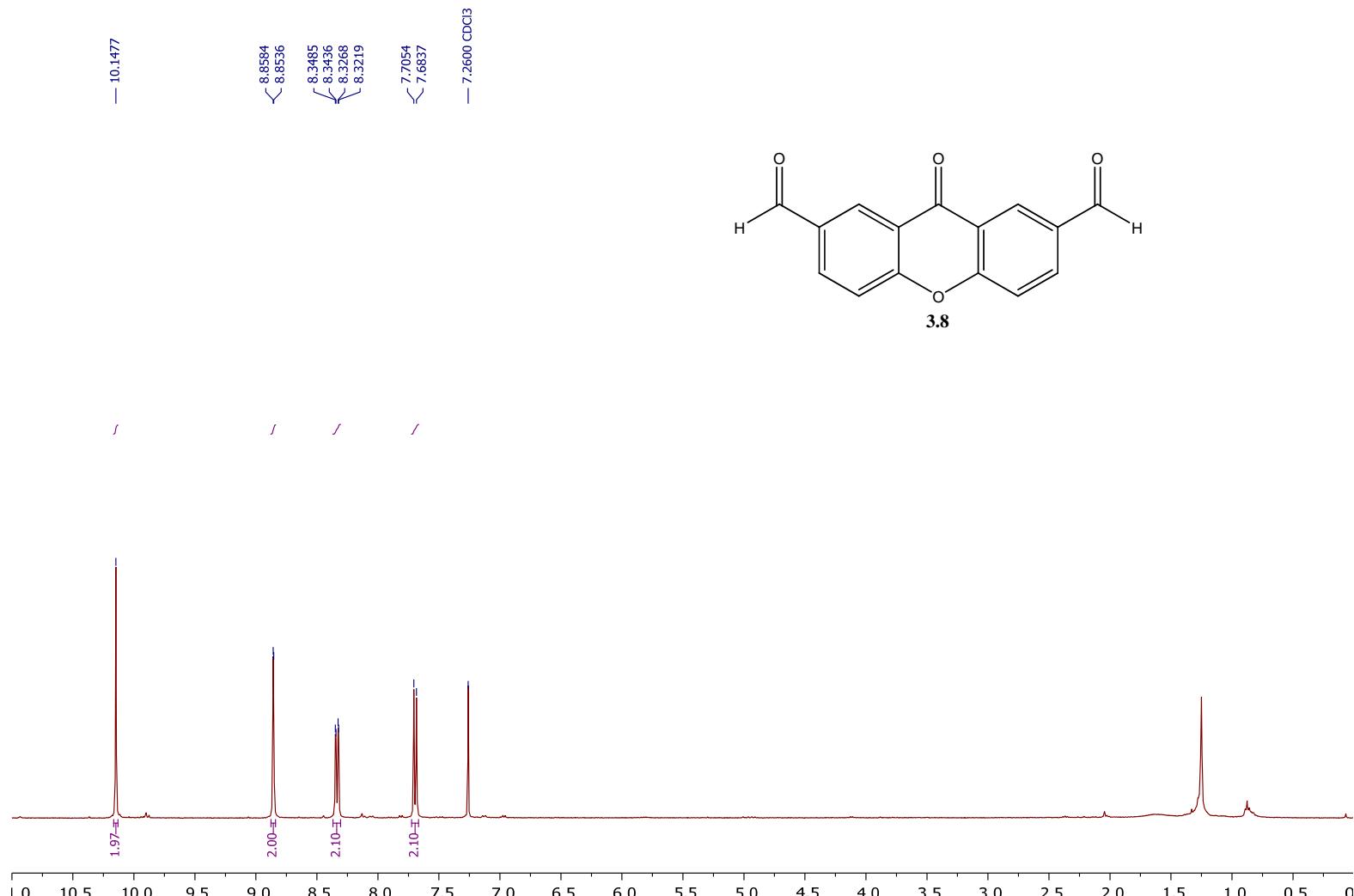


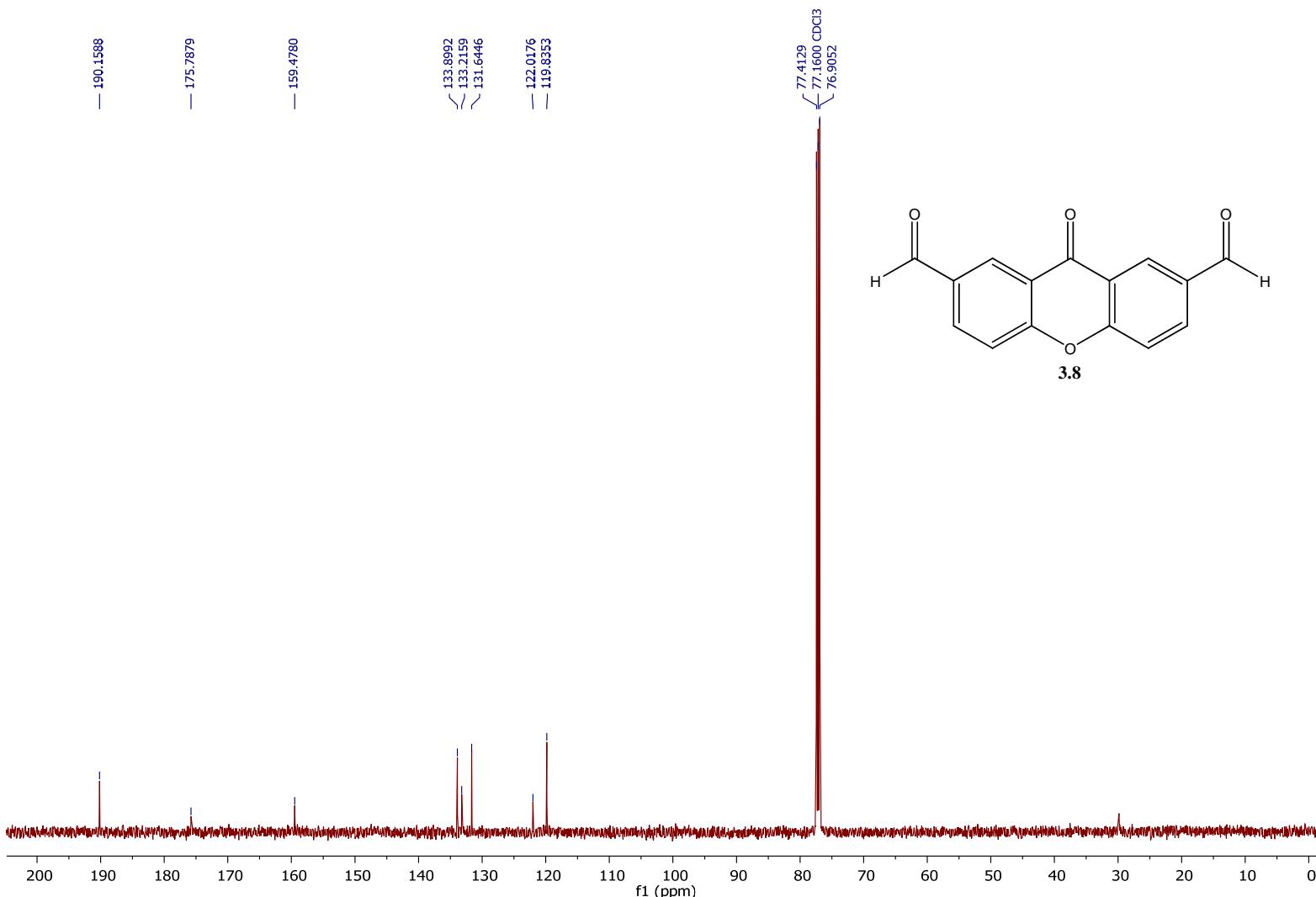


¹³C NMR (100 MHz, CDCl₃) spectrum of 1,1'-(9-oxo-9*H*-xanthene-2,7-diyl)diethanone (**3.7**)



EI(HRMS) spectrum of 1,1'-(9-oxo-9*H*-xanthene-2,7-diyl)diethanone (**3.7**)





^{13}C NMR (125 MHz, CDCl₃) spectrum of 9-oxo-9*H*-xanthene-2,7-dicarbaldehyde (**3.8**)

Electron Ionisation

WATERS GCT Premier -CAB155

SRK7-94 729 (12.779) AM (Cen,4, 100.00, Ar,7000.0,218.99,0.25); Sm (SG, 2x5.00); Sb (10,1.00)

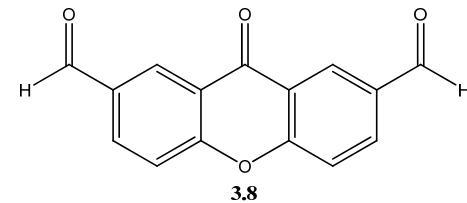
12-Dec-2014 15:55:32

TOF MS EI+
251.0366 2.83e3

100

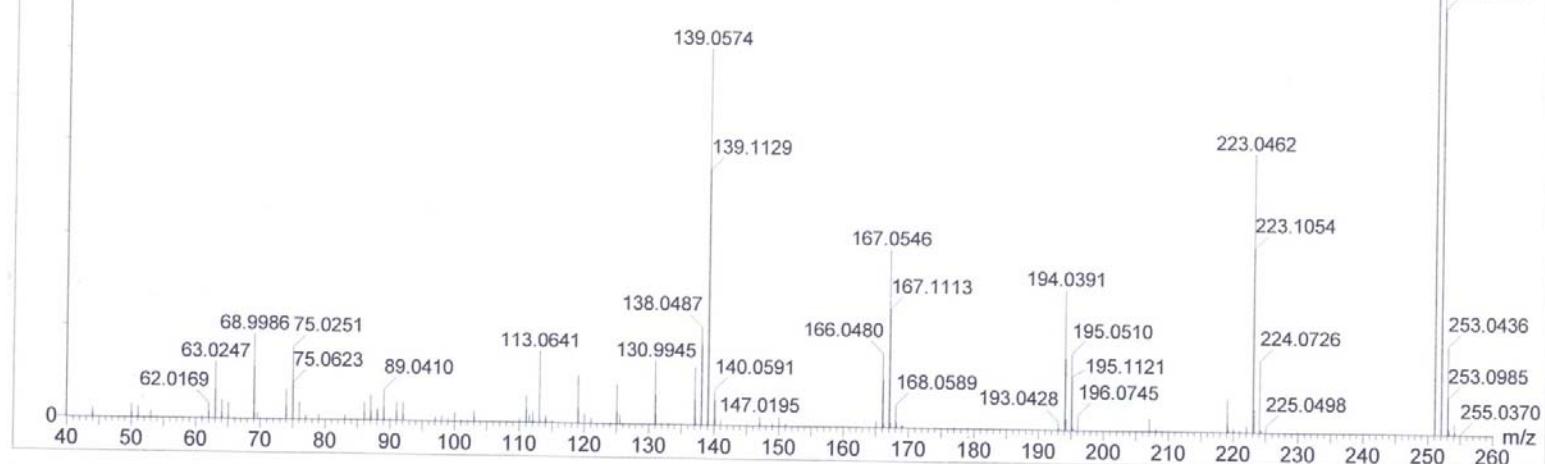
%

0

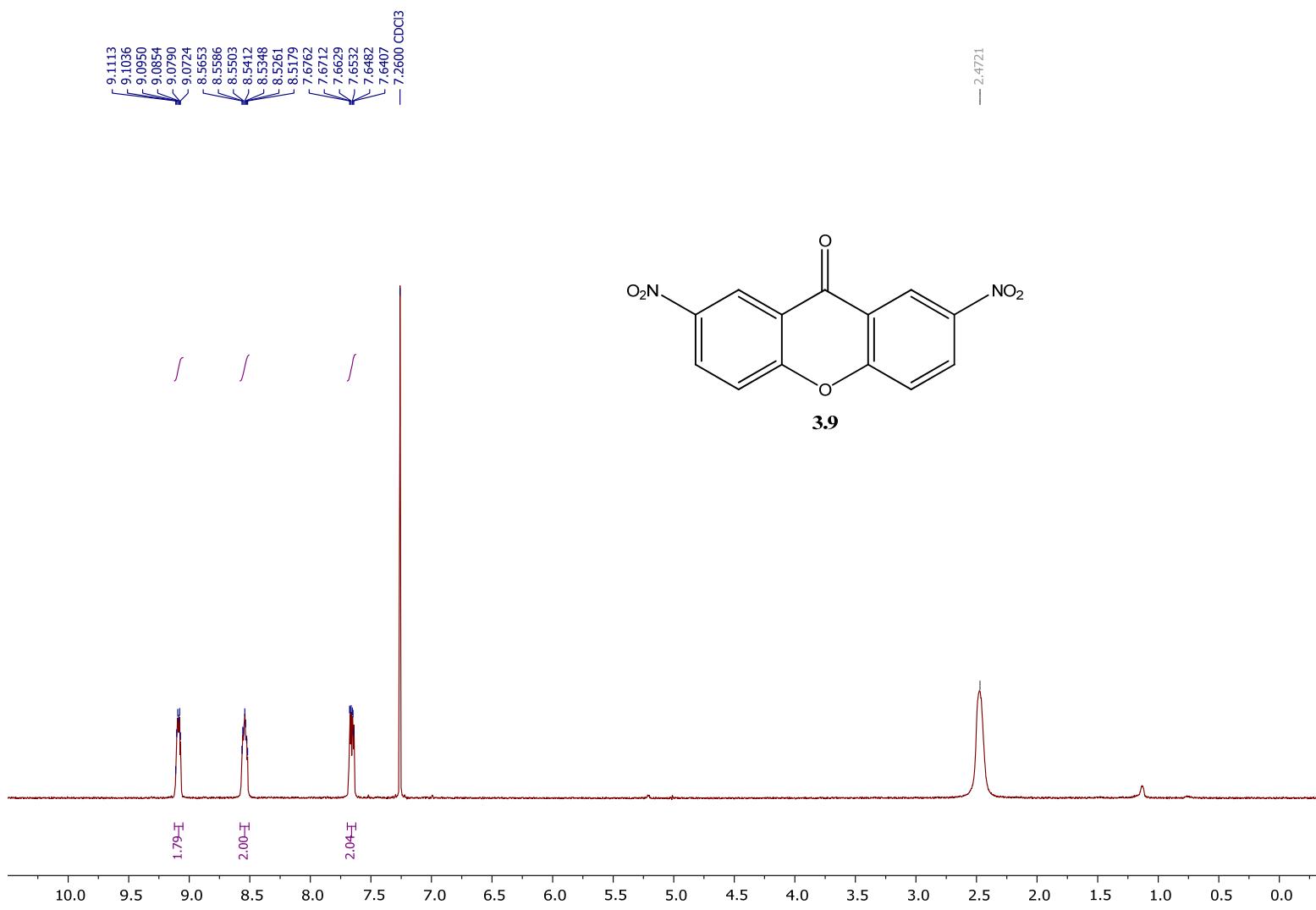


3.8

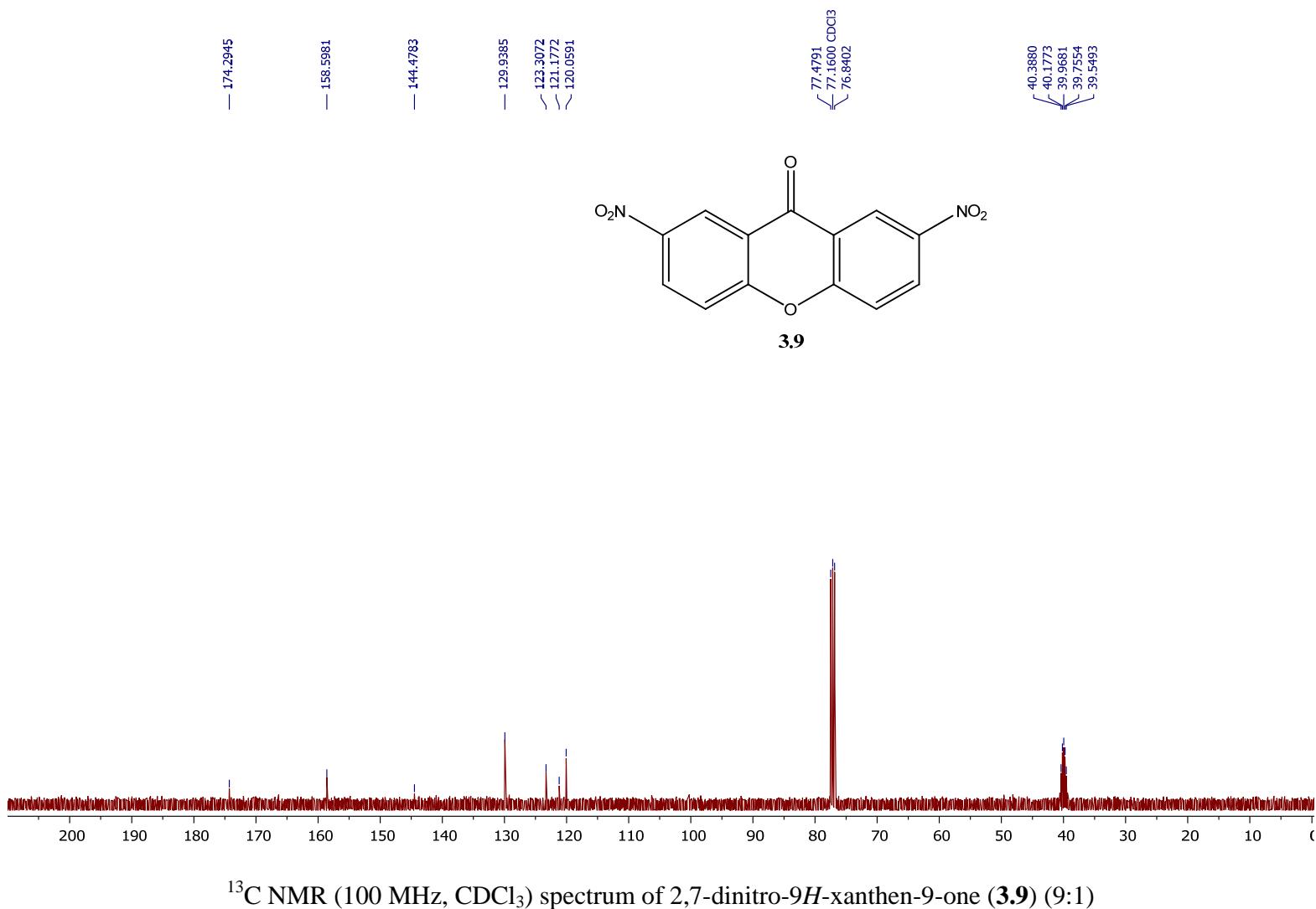
[M]⁺ calcd. 252.0423

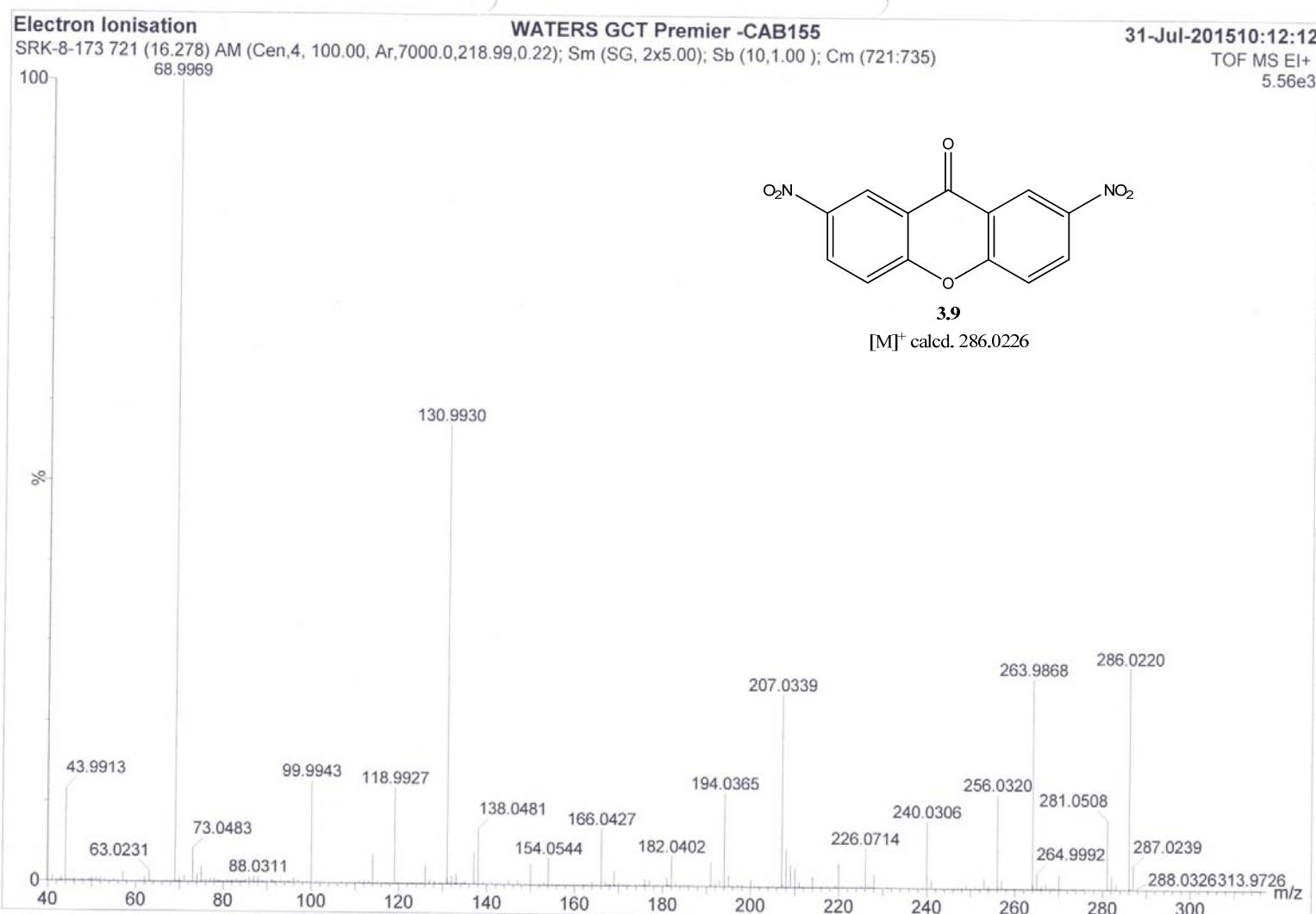


EI(HRMS) spectrum of 9-oxo-9H-xanthene-2,7-dicarbaldehyde (**3.8**)

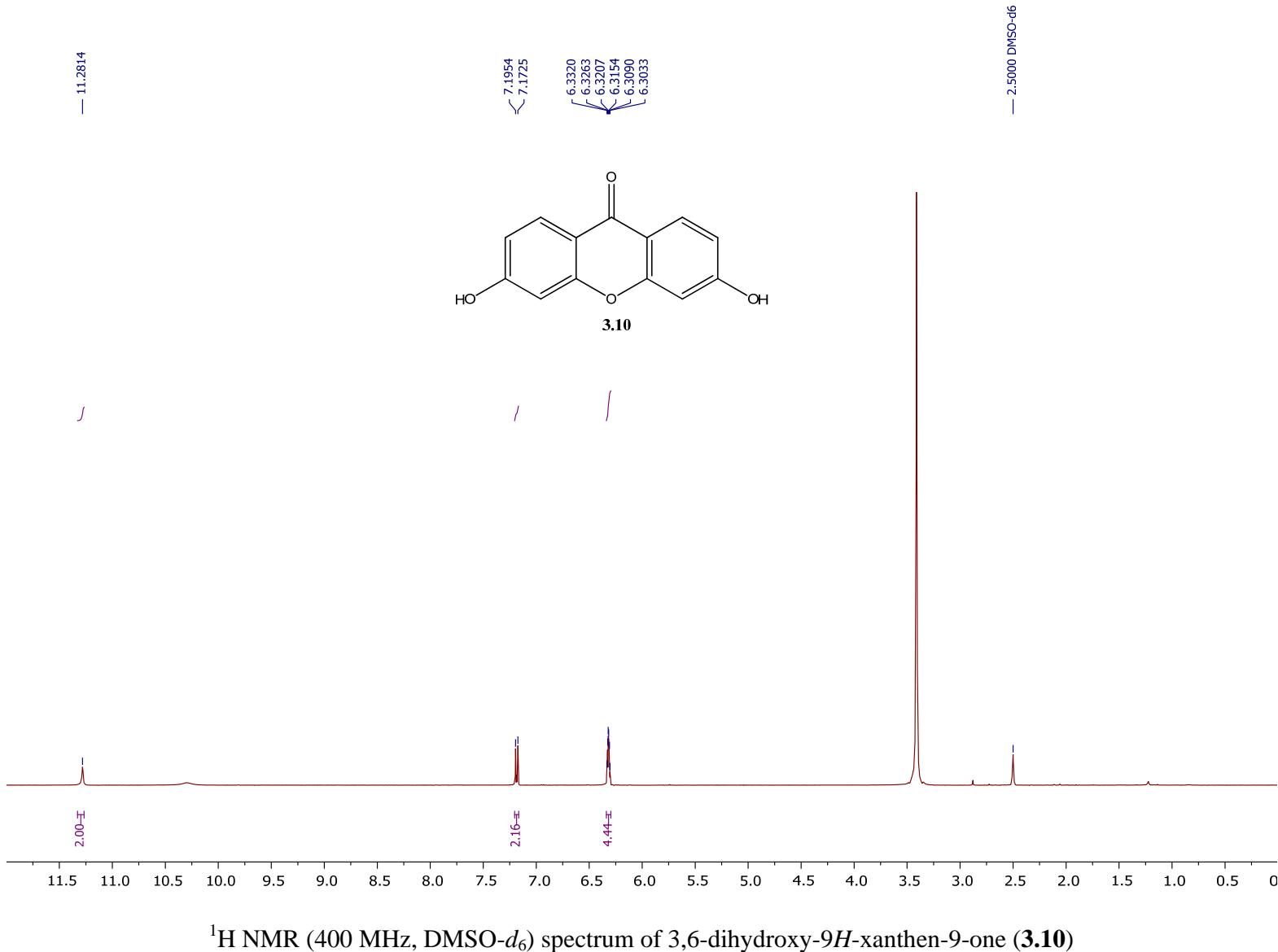


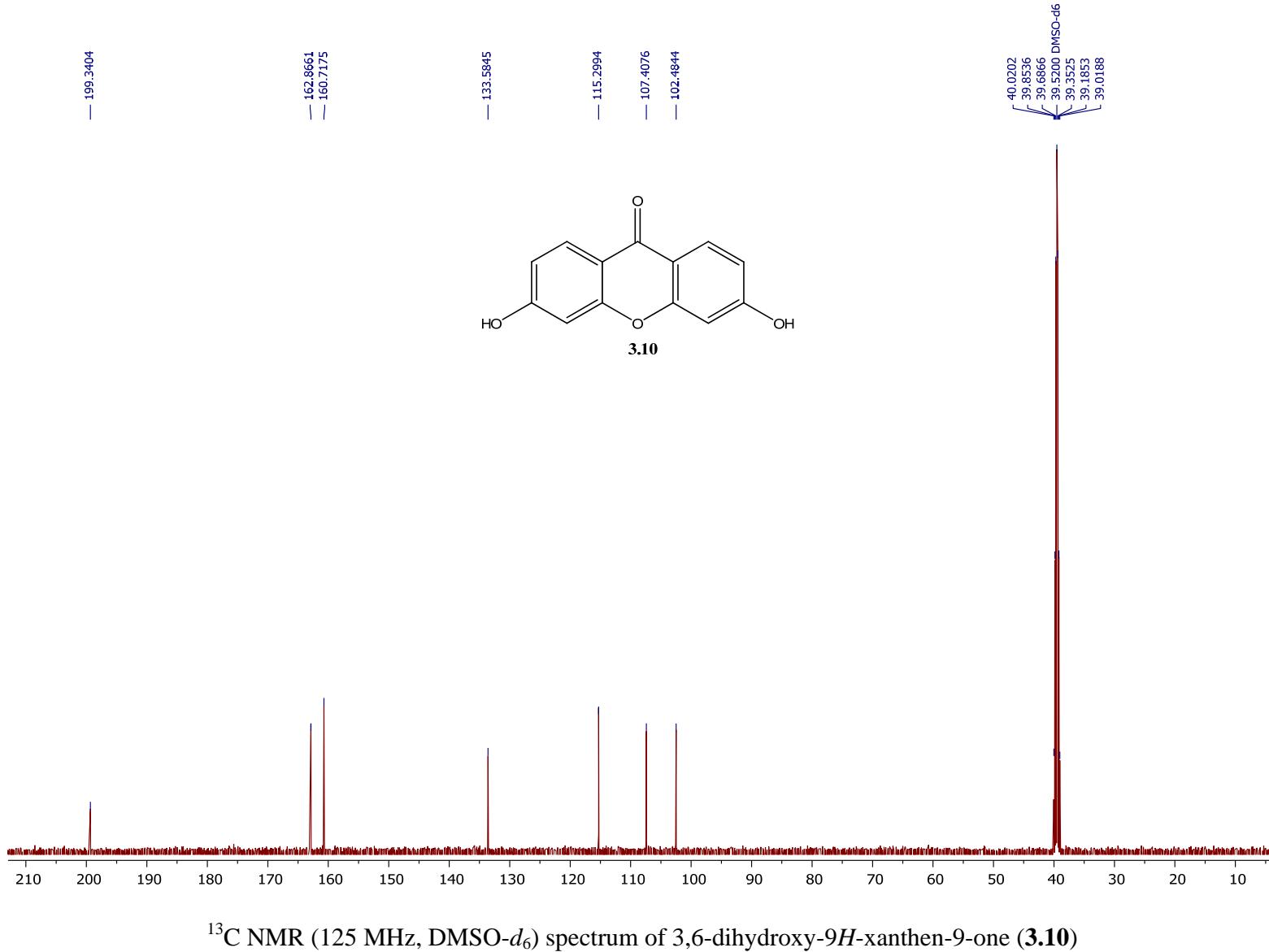
^1H NMR (400 MHz, CDCl₃) spectrum of 2,7-dinitro-9*H*-xanthen-9-one (**3.9**) (9:1)





EI(HRMS) spectrum of 2,7-dinitro-9*H*-xanthen-9-one (**3.9**)





Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

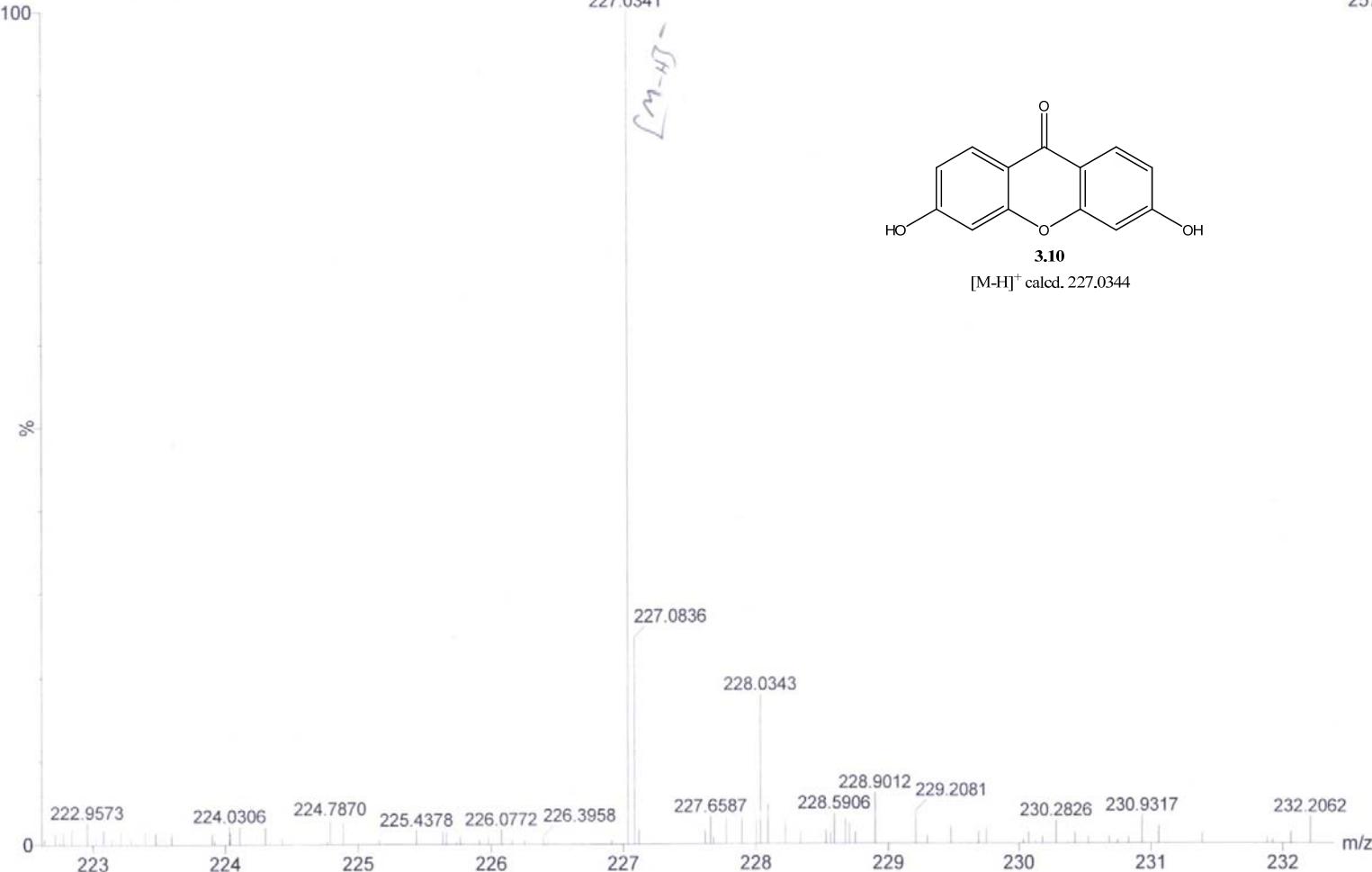
24-Nov-2015

11:55:28

1: TOF MS ES-
257

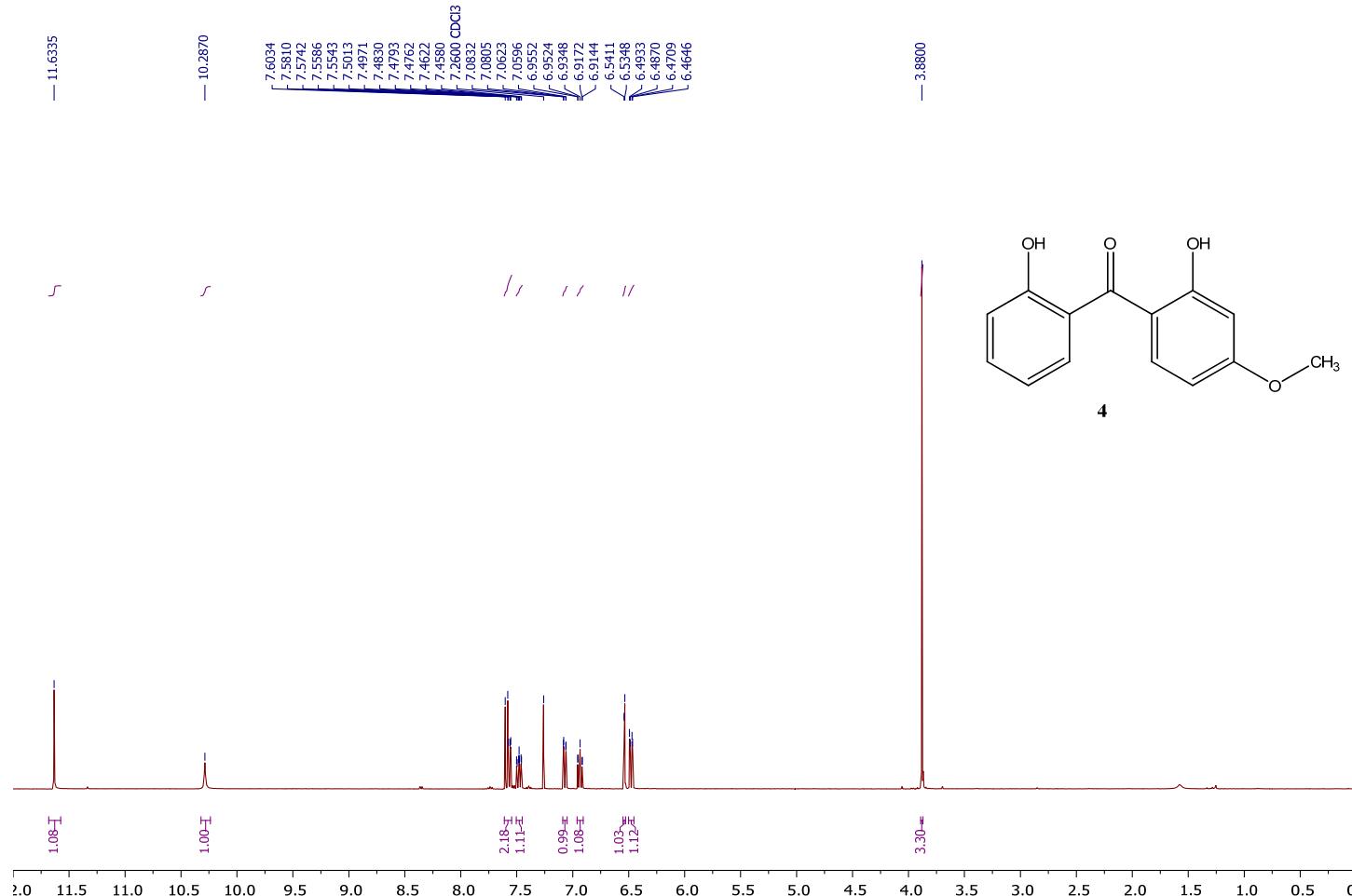
SRK10-02- 30 (0.627) AM (Cen,4, 100.00, Ar,8500.0,554.26,1.00,LS 10); Sm (SG, 1x5.00); Sb (10,1.00); Cm (30:33:1:4)

227.0341

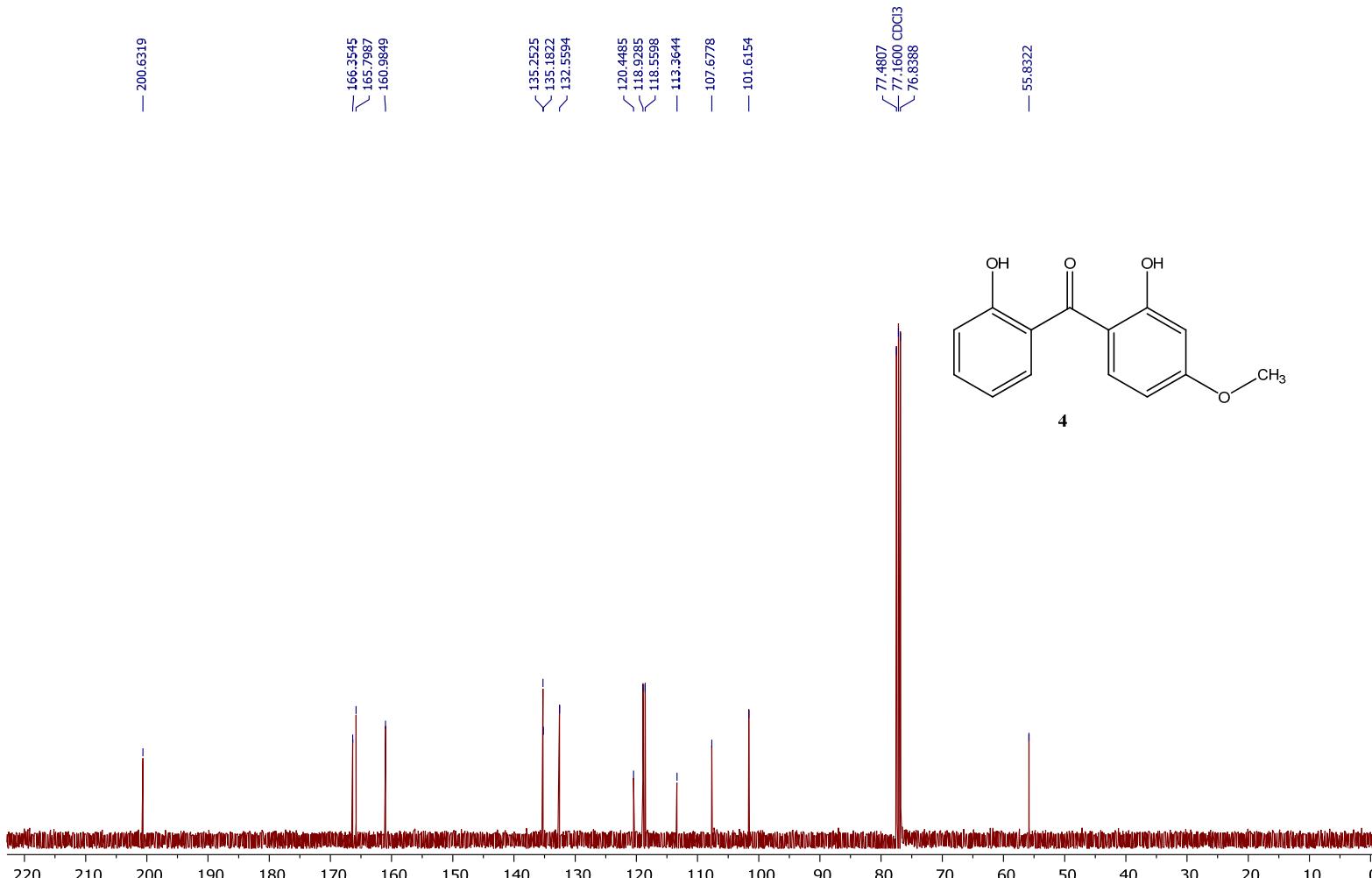


ESI(HRMS) spectrum of 3,6-dihydroxy-9*H*-xanthen-9-one (**3.10**)

4. Copies of ^1H NMR, ^{13}C NMR and HRMS spectra of Compound 4 (Scheme 2):



^1H NMR (400 MHz, CDCl₃) spectrum of (2-hydroxy-4-methoxyphenyl)(2-hydroxyphenyl)methanone (**4**)



^{13}C NMR (100 MHz, CDCl_3) spectrum of (2-hydroxy-4-methoxyphenyl)(2-hydroxyphenyl)methanone (**4**)

Electrospray ionisation-MS

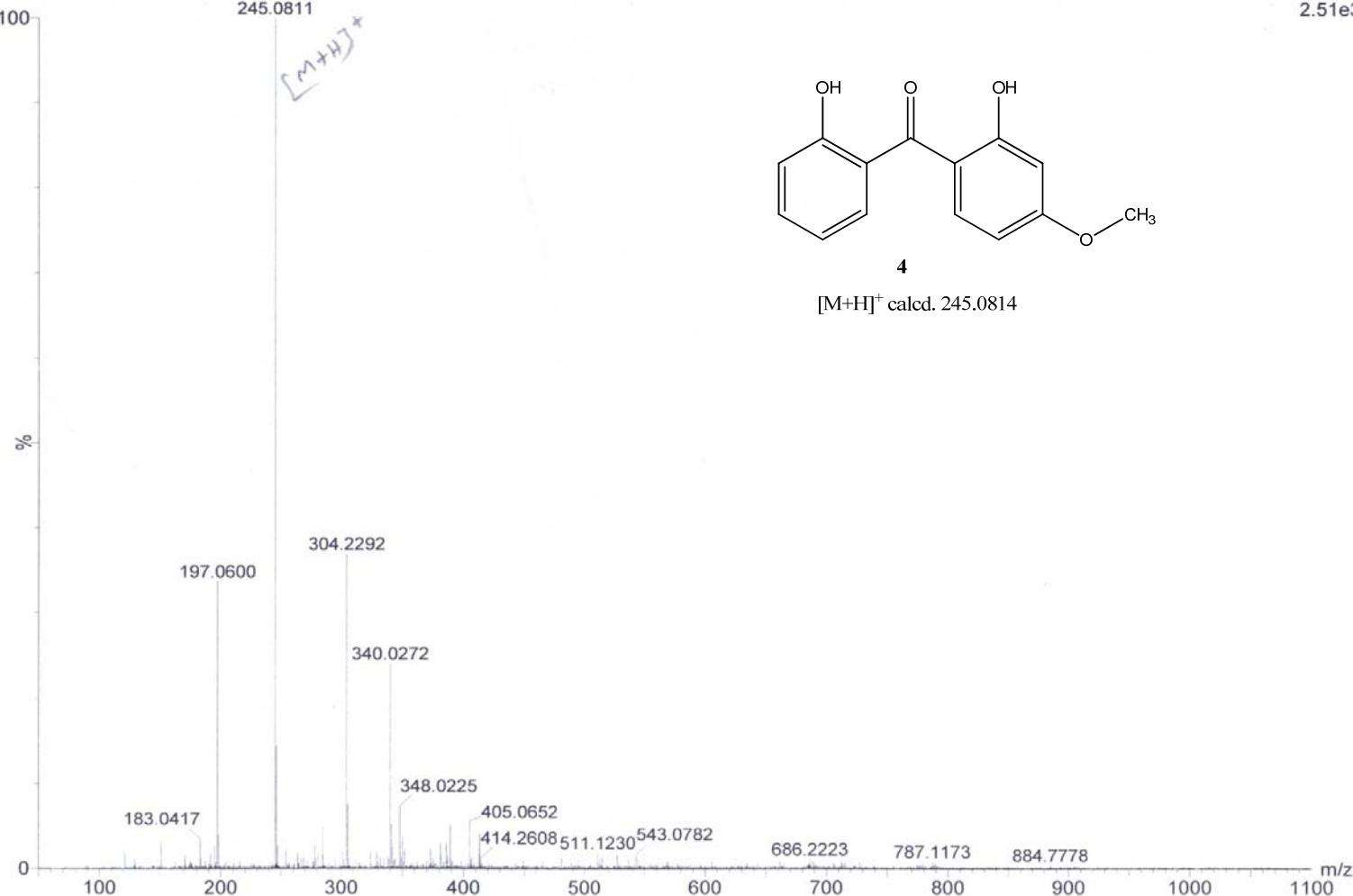
SRK6-168 15 (0.314) AM (Cen,4, 100.00, Ar,8500.0,556.28,5.00,LS 10); Sm (SG, 2x5.00); Sb (10,1.00); Cm (15:17-1:5)

WATERS-Q-ToF Premier-HAB21

245.0811

14:28:04 10-Sep-2014

1: TOF MS ES+
2.51e3



ESI(HRMS) spectrum of (2-hydroxy-4-methoxyphenyl)(2-hydroxyphenyl)methanone (**4**)