Supplementary Information

Synthesis, crystal structure and fluorescence spectrum of some new 1,2,3-triazol-xanthen-3-one derivatives

Hong-Ru Dong*, Chi-Qiong Jin & Zi-Bao Chen
School of Chemical Engineering, Lanzhou University of Arts and Science, Lanzhou, Gansu 730000, P. R. China
E-mail: 1000467@luas.edu.cn; donghr12@lzu.edu.cn

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Contents

I Experimental Section

Melting points were determined on an XT_4-100X microscopic melting point apparatus (The melting point of this series compounds are more than 300 °C, melting point was measured by domestic XT_4-100X microscopic melting point instrument.). IR spectra were obtained in KBr pellets on a Nicolet 170SX FT-IR spectrometer. The high resolution mass spectrometry was measured with MICRO-TOF QⅡ (ESI). ^{1}H NMR spectroscopy was recorded at Varian Mercury Plus-300NMR instrument with TMS as an internal standard.

2. 2 Synthetic procedure of the target compound

Preparation of 1-aryl-5-methyl-1,2,3-triazol-4-carboxylic acid (4a-j) was following methods in the literature.

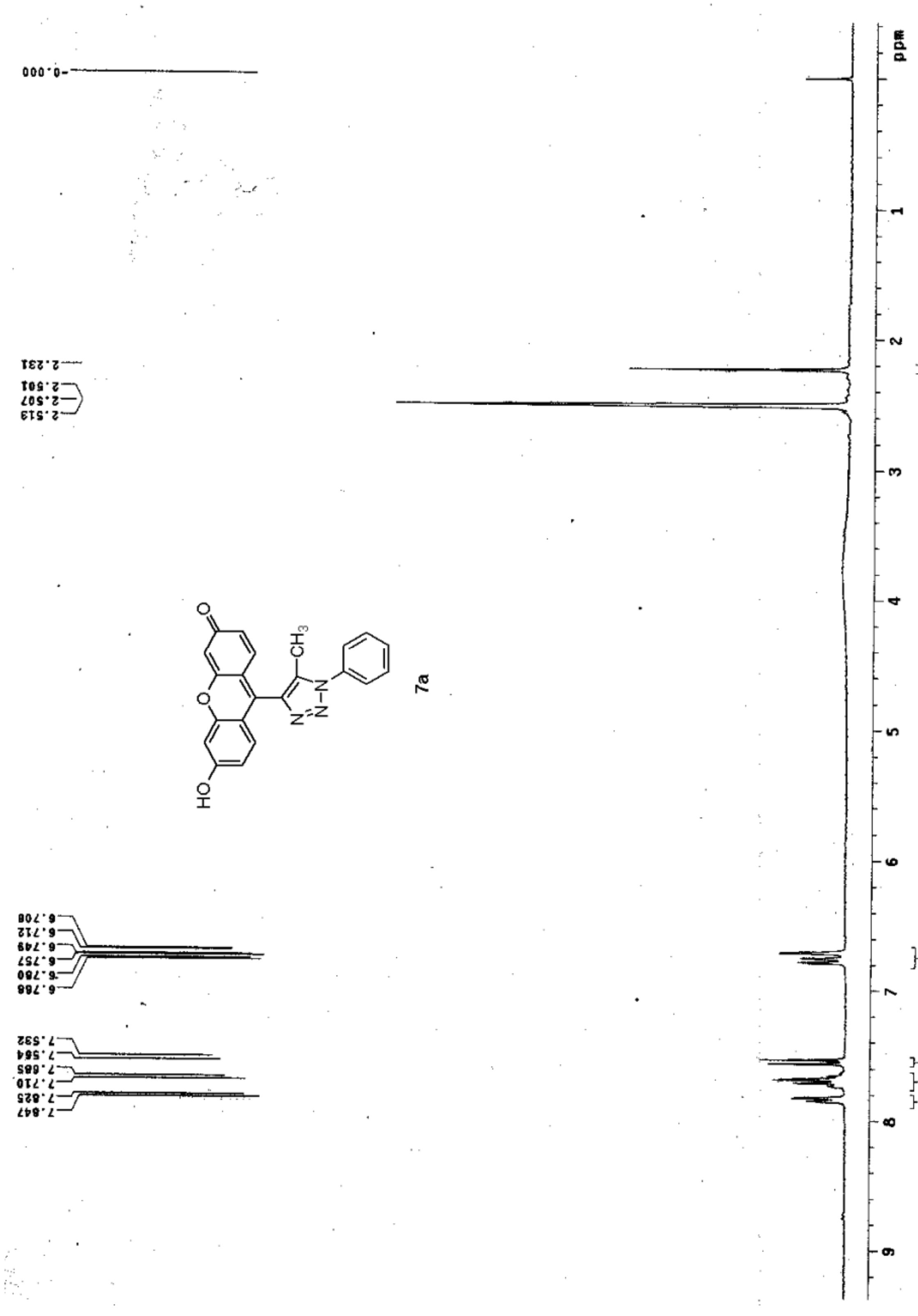
Preparation of 1-aryl-5-methyl-1,2,3-triazol-4-carbonyl chloride 5a-j was following methods in the literature.

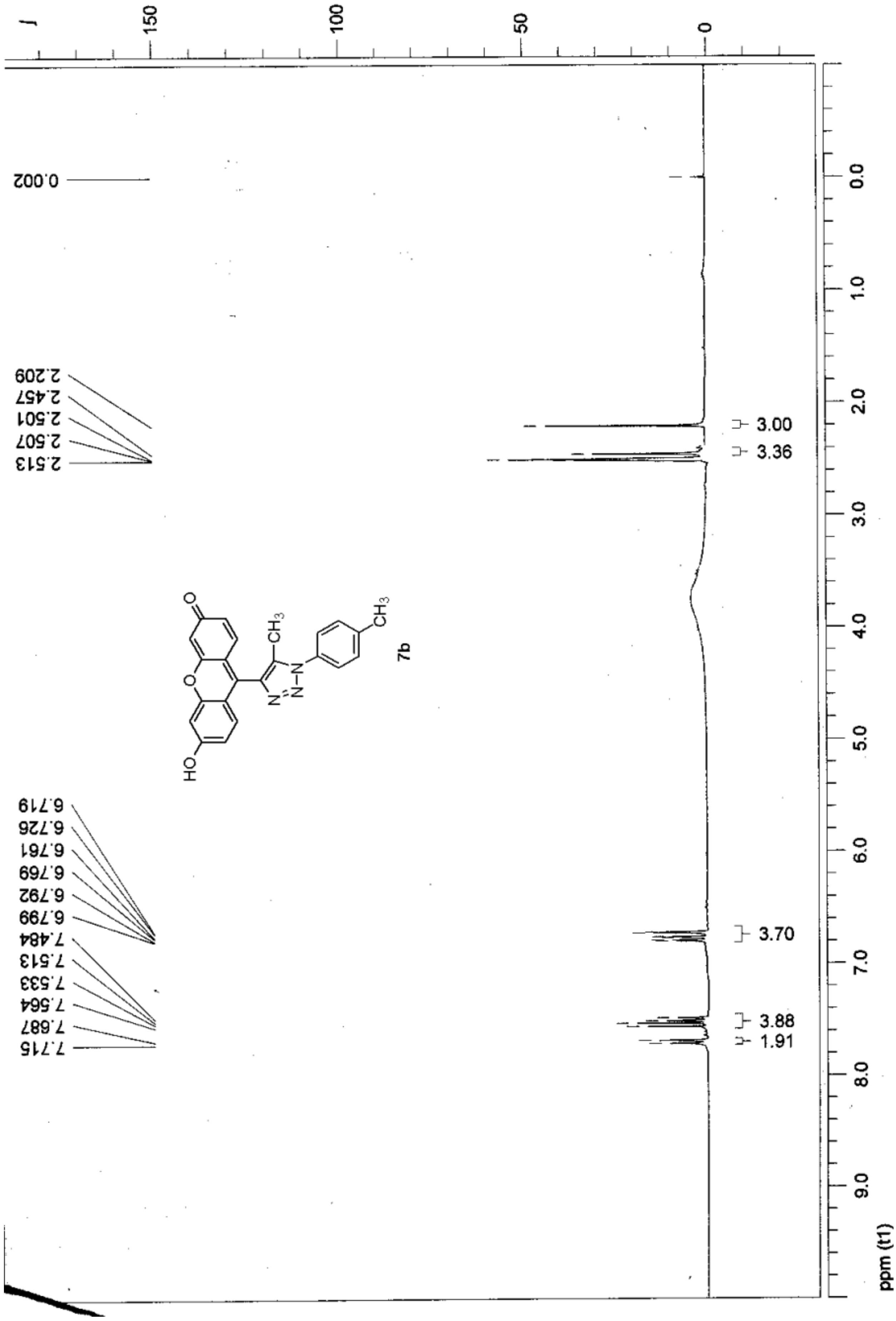
General procedure of preparation of (2,4-dihydroxy- phenyl)-(1-aryl-5-methyl-1*H*-1,2,3-triazol-4-yl)-methanone 6a~j following methods in the literature.

General preparation procedure of 9-(1-aryl-5-methyl-1*H*- 1,2,3-triazol-4-yl)-6-hydroxy-3*H*-xanthen-3-one derivatives 7a~j following the procedure method.

A solution of (1-aryl-5-methyl-1*H*-1,2,3-triazol-4-yl)-(2,4- dihydroxy-phenyl)-methanone **6a~j** (0.0015 mol) and resorcinol (0.0018mol) and 4-methylbenzenesulfonic acid (0.011 mol) with stirring in 25mL round bottomed flask at 110 °C under argon for 6-8 hours. Then reaction mixture was cooled to room temperature, a solution of 2g NaOH in 25mL water was added under acutely stirred. The reaction mixture was heated to solution of solid and was poured into 25mL water. The pH of the reaction mixture was regulated to pH = 5 by glacial acetic acid. The red precipitation was separation, filtered, washed with water and recrystallized from ethanol to give **7a-j**.

II. ^{1}**H NMR** spectroscopy of **7a-j**

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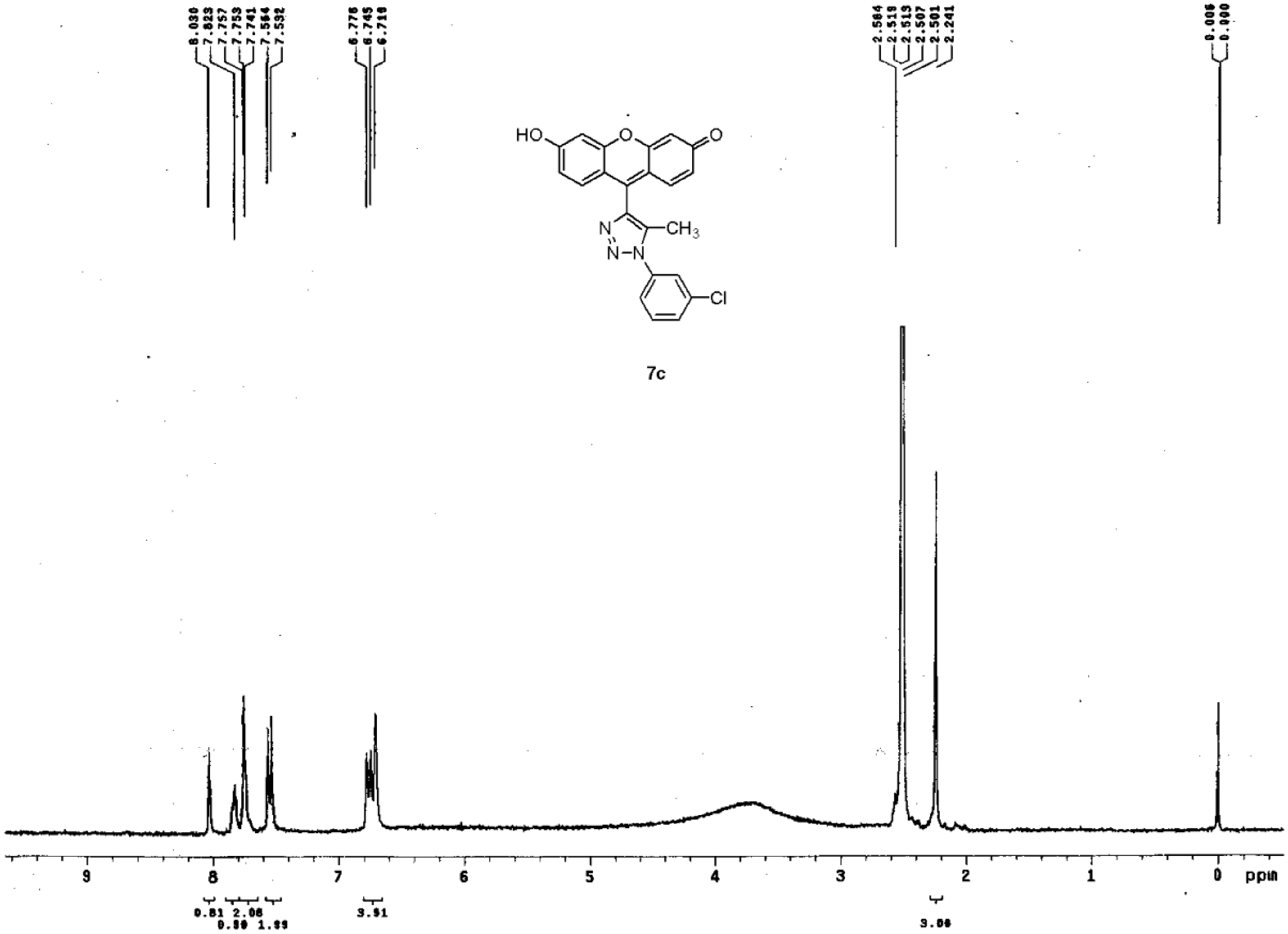
6.792
6.799
7.484
7.513
7.533
7.564
7.687
7.715
3.00
3.36
3.70
3.88
1.91
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)
HO
O
CH3
N
7b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2.513
2.507
2.501
2.241
0.006
0.000
HO
O
CH3
N
N
N
Cl
9
8
7
6
5
4
3
2
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ppm
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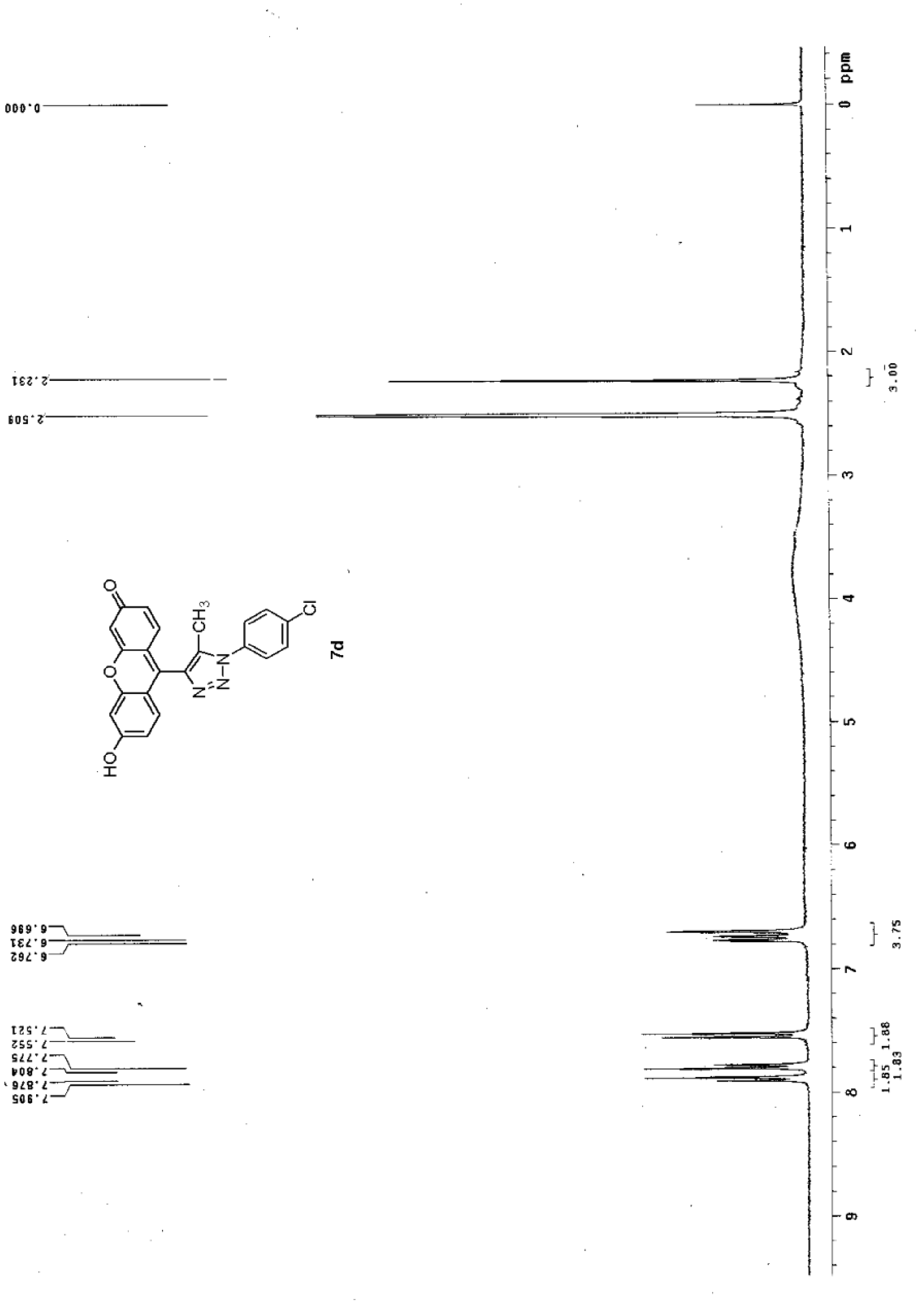
0.80
1.99
3.91
3.00

7c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8
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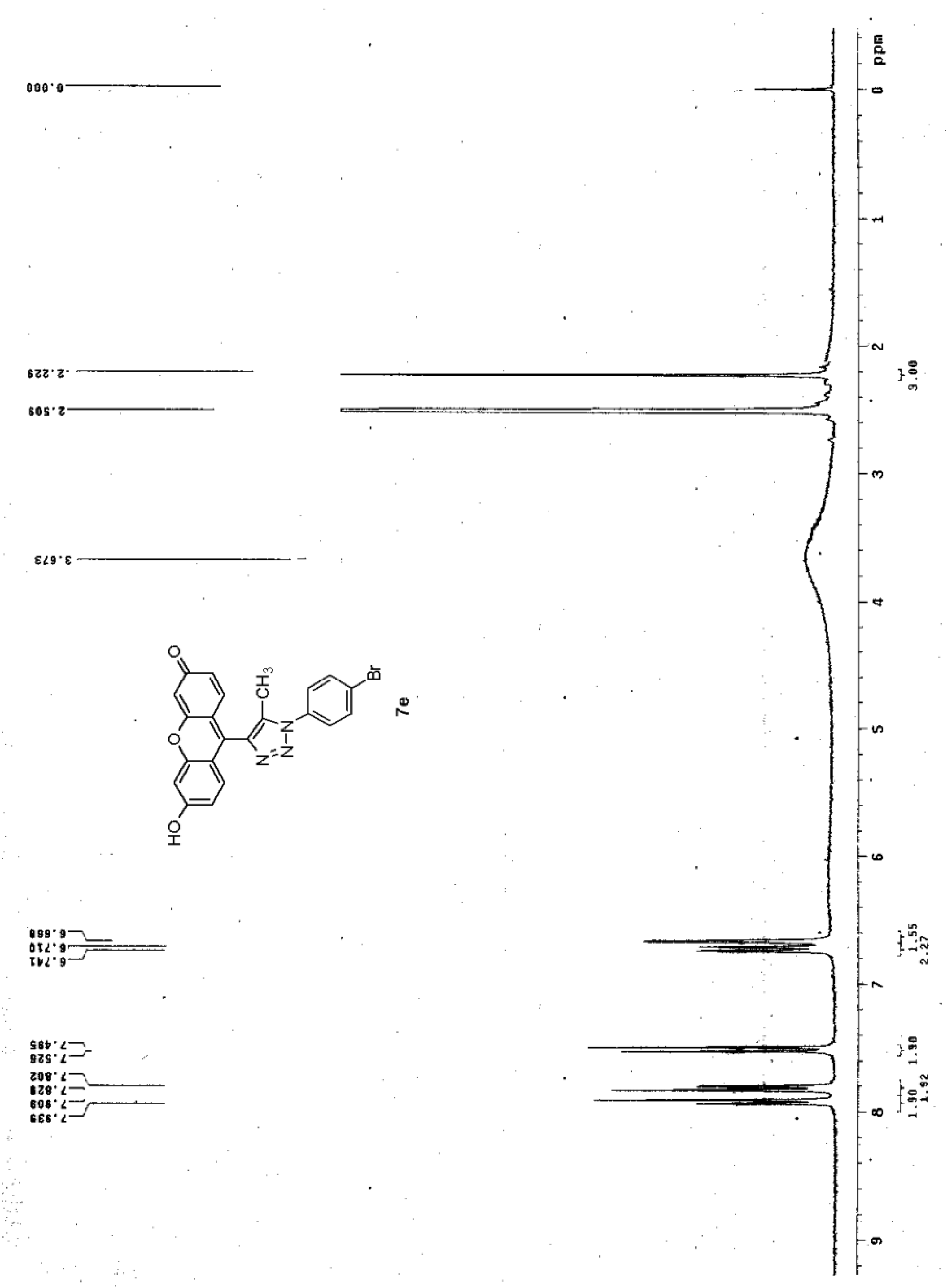
N
Cl
7d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CH3
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N
O
HO
7e
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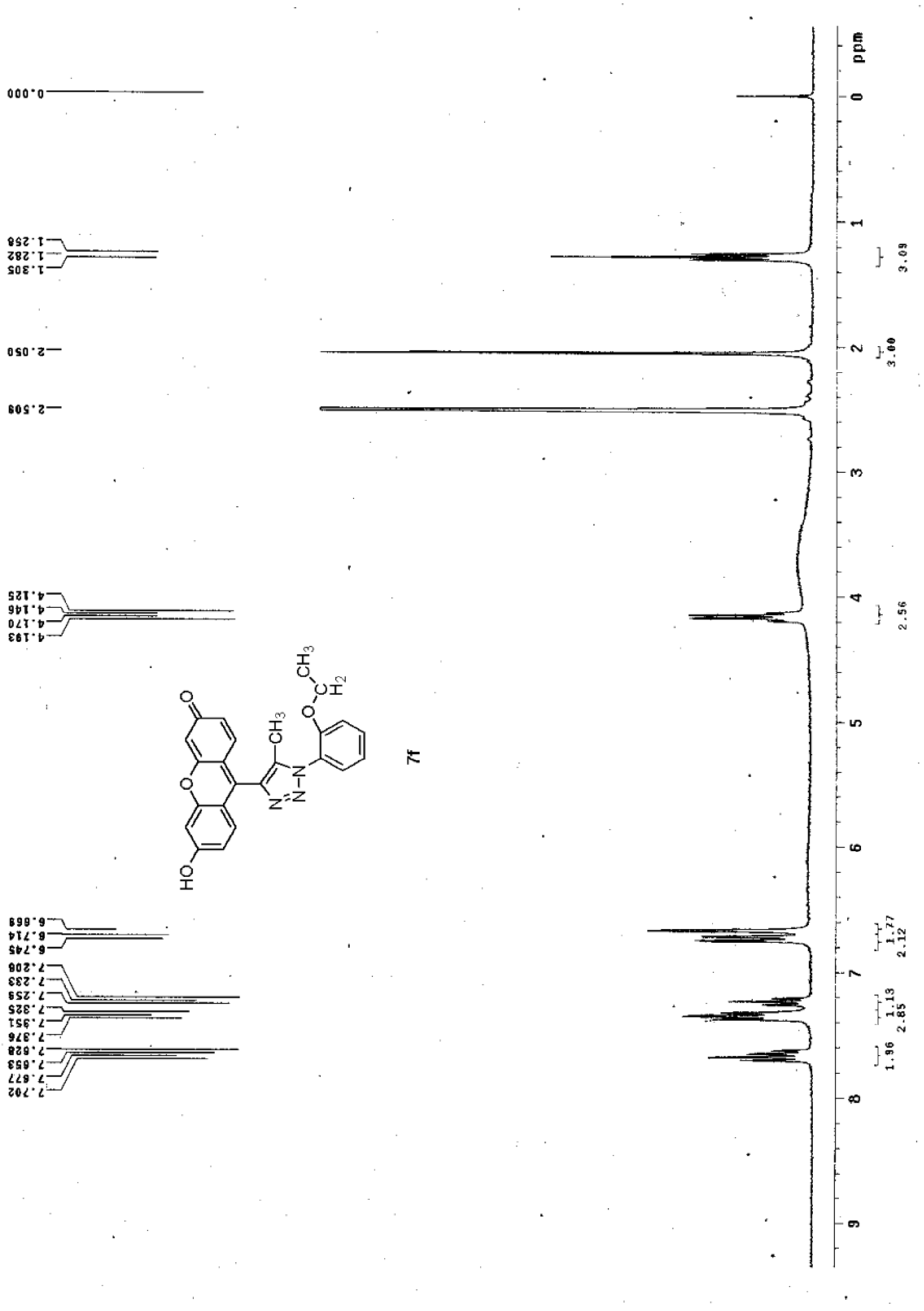
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7.351
7.376
7.628
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7.677
7.702
HO
O
CH_3
N
N–N
O
C
H_2
CH_3
7f
3.09
3.00
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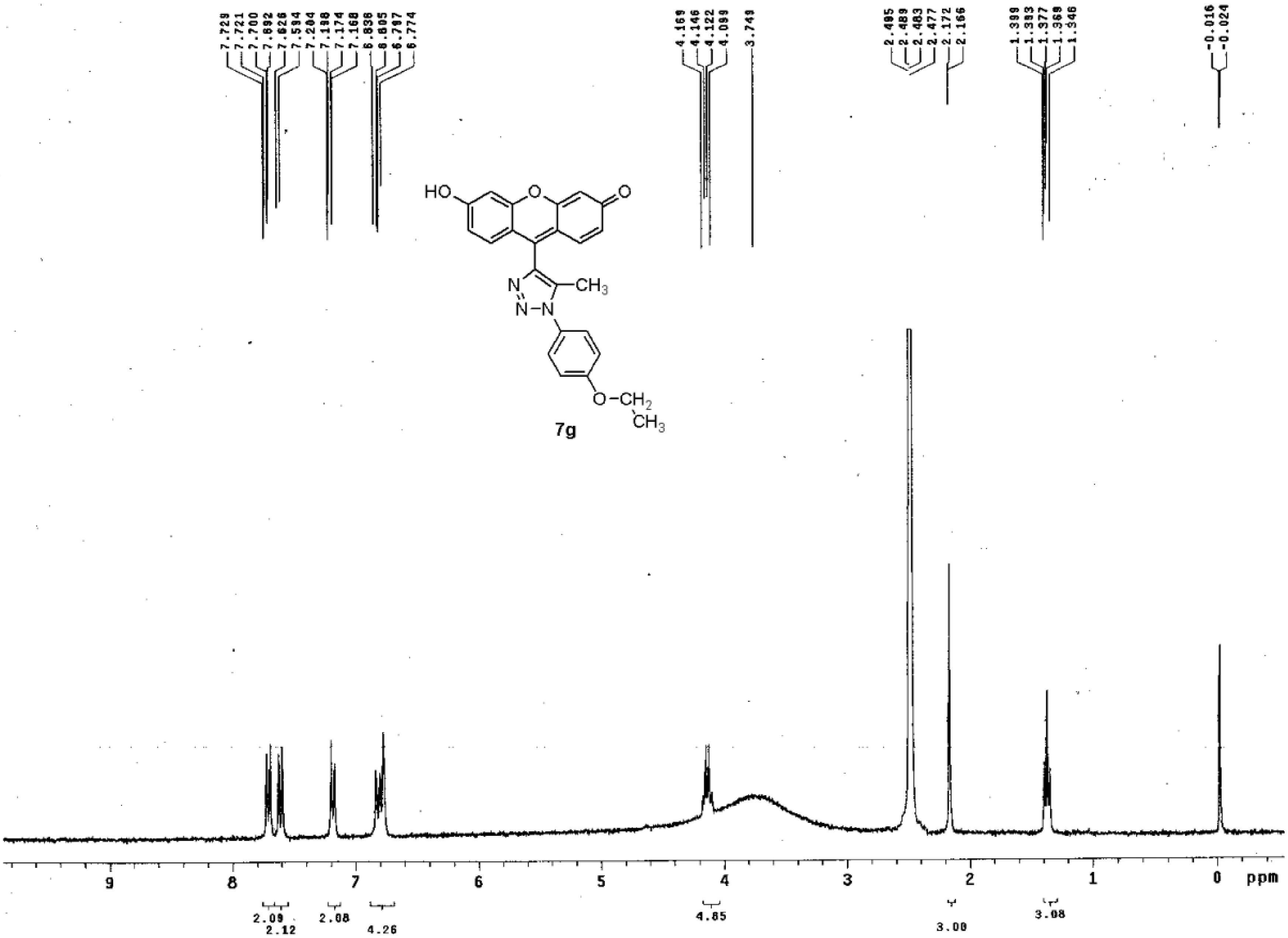
1
2
3
4
5
6
7
8
9
ppm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6.774
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2.166
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HO
O
N
N
N
CH3
O−CH2
CH3
9
8
7
6
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4
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2
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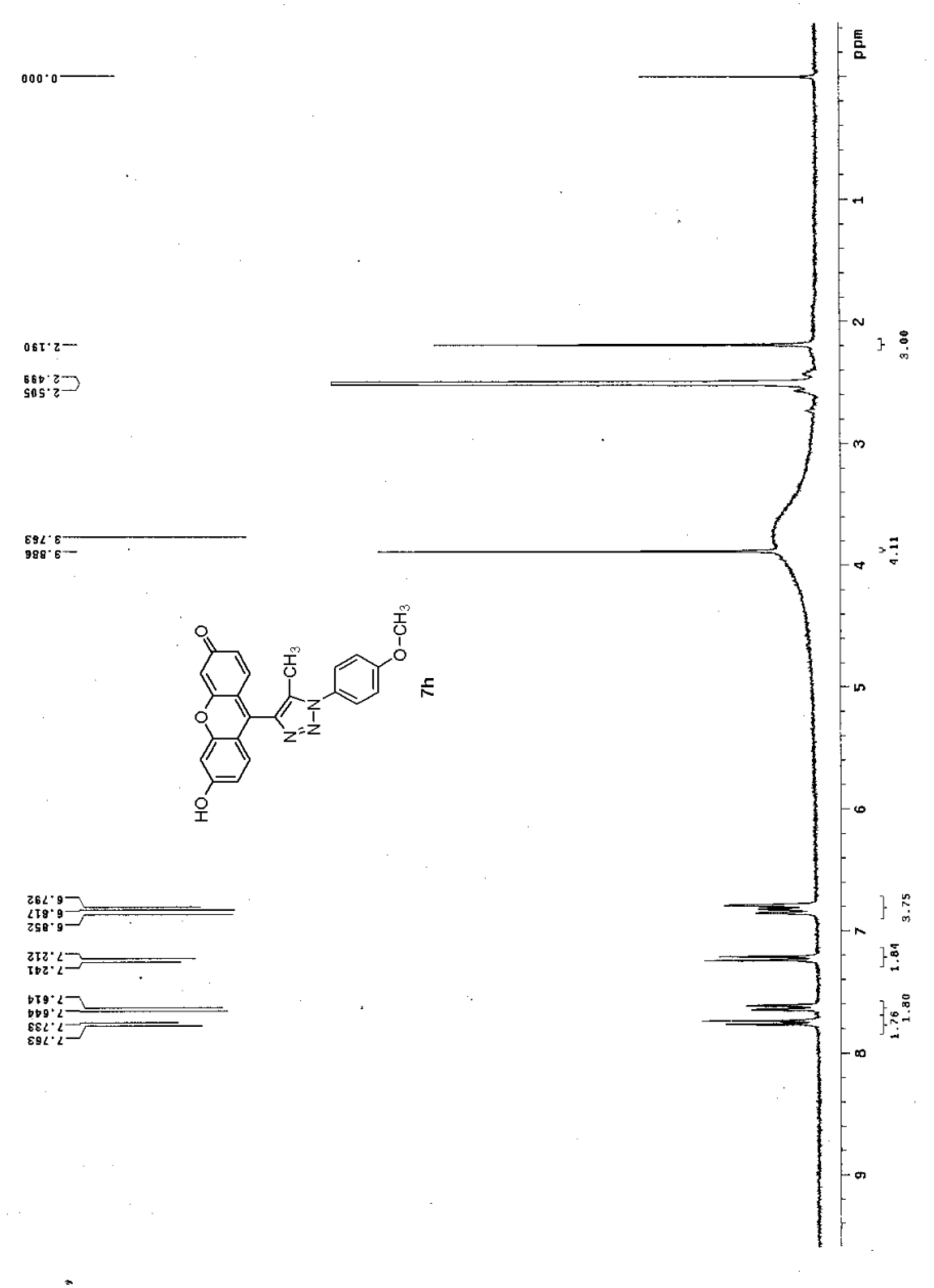
3.08

7g



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7.763
HO
O
N
N–N
CH3
O–CH3
ppm
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2
3
4
5
6
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8
9
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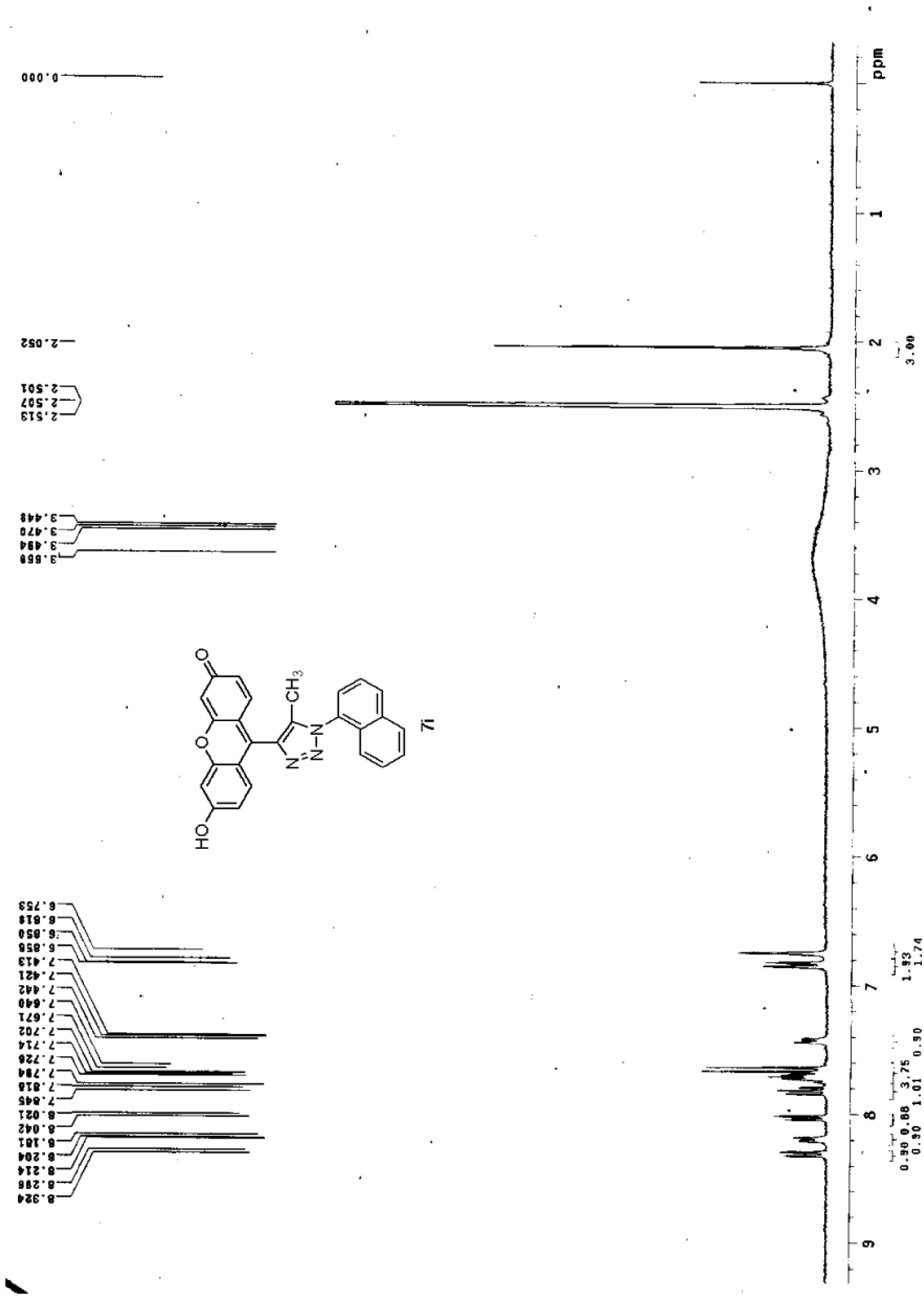
1.76
1.80

7h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O
CH3
HO
O
N
N
N
7i
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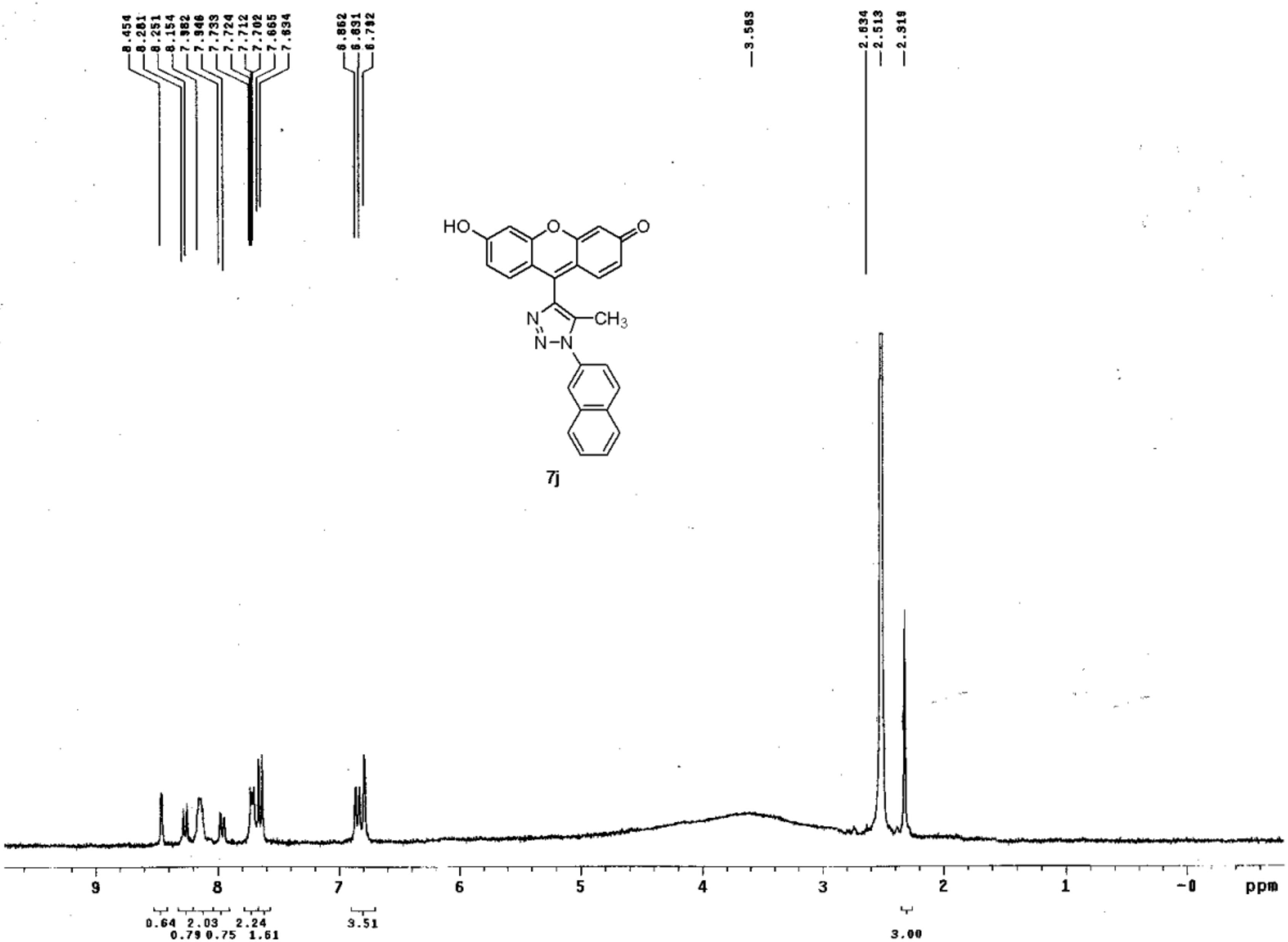
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2.319
HO
O
O
N
N
N
CH$_3$
9
8
7
6
5
4
3
2
1
-0
ppm
0.64
0.79
2.03
0.75
2.24
1.61
3.51
3.00

7j

III. The crystal structure and conformation of compound 7c

The colorless transparent crystal of compound **7c** (**Fig. 1**) with a size of 0.40 mm× 0.35 mm×0.30 mm was selected for X-ray diffraction analysis. APEX2 was applied for data collection [1]. SAINT was applied for cell refinement and data reduction. The SHELXS-97 program was applied for the structure analysis according to reported methods [2]. All measurements were made on a Bruker D_8 Smart Apex II diffractometer with graphite-monochromatic Mo$K\alpha$ radiation (λ = 0.71073 Å) at 567(2) K. A total of 7072 integrated reflections in the range of $1.77 \leq \theta \leq 25.50°$ (index ranges: $-10 \leq h \leq 9$, $-11 \leq k \leq 11$, $-12 \leq l \leq 14$) were collected with 2160 unique ones (Rint = 0.0255). All of the non-hydrogen atoms were located with successive difference Fourier syntheses by full-matrix least-squares and the final refinement gave $R = 0.0597$, $wR = 0.1481$ ($w = 1/[\sigma^2(Fo^2) + (0.0748P)^2 + 0.3408P]$, where $P = (Fo^2 + 2Fc^2)/3$, $Fc^* = \mathrm{k}Fc[1 + 0.001\mathrm{x}Fc^2\lambda^3/\sin(2\theta)]^{-1/4}$ (Extinction-coef 0.006(3)) and $S = 1.046$ by using the SHELXL program [3], and the hydrogen atoms were added from difference Fourier map and refined freely.

The structure of the title compound **7c** is shown in **Fig. 1**.

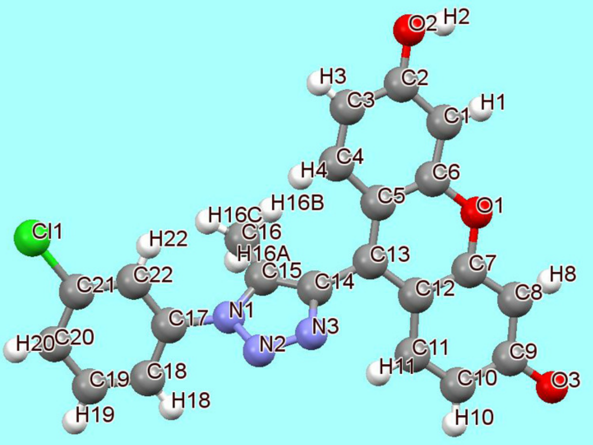

Fig. 1 Mercury view of the molecular structure for the title compound 7c showing the atom numbering scheme

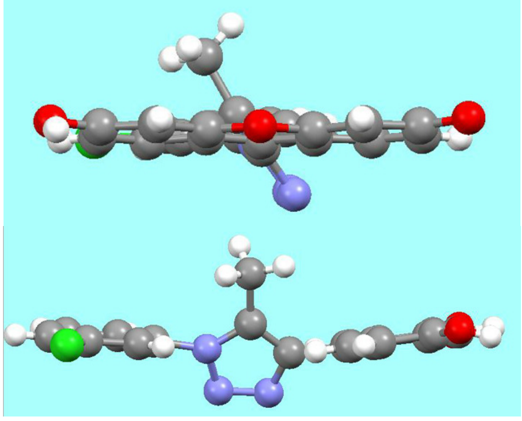

Fig. 2 The title compound 7c showing tri-ring plane

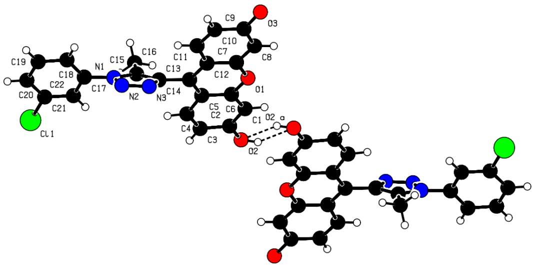

Fig. 3 The H-bond structure of the compound 7c (PWT drawing for the Platon)

Table I — Crystal data and summary of data collection and structure refinement

Compound	$C_{22}H_{14}C1N_3O_3$
CCDC deposit No	2034640
Color	Reddish brown
Formula weight	403.81
Temperature,℃	21(294K)
Crystal system	Triclinic
Space group	P-1
Unit-Cell dimensions	
	a = 8.296(4) Å
	b = 9.726(5)Å
	c = 11.976(6)Å
	α = 90.953(7)°
	β = 105.081(7)°
	γ = 100.693(8)°
Volume($Å^3$)	914.7(8)
Z	2
D_{calc}, g cm^{-3}	1.466
F(000)	416
Absorption coefficient, mm^{-1}	0.240
Diffractometer/Scan	CCD area detector, ω /2 θ
Radiation/λ	Mo$k\alpha$(graphite monochromator)/ 0.71073Å
θ min, θ max, (°)	1.77-25.50
Reflections measured	3333
Independent/observedreflections	2160
Data/restraints/parameters	7072/0/265
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.046
shift/su_max	0.000
Final R indices	R_1=0.0597,wR2=0.1481
R indices[I>2σ(I)]	R_1=0.0947,wR2=0.1738
Extinction coefficient	0.006(3)
Largest diff. Peak and hole	0.314and-0.384 e $Å^{-3}$

Table II — Selected Bond Lengths (Å) and Bond Angles (°) for the Target Compound 7c

Bond	Dist. (**Å**)	Bond	Dist. (**Å**)	Bond	Dist. (**Å**)
N(1)–N (2)	1.361(3)	N(1)–C(15)	1.365(3)	N(1)–C(17)	1.429(4)
N(2)–N(3)	1.301(3)	N(3)–C(14)	1.373(3)	C(14)–C(15)	1.372(4)
C(15)–C(16)	1.490(4)	C(13)–C(14)	1.479(4)	C(6)–O(1)	1.366(3)
C(7)–O(1)	1.368(3)	C(2)–O(2)	1.295(3)	O(3)–C(9)	1.298(4)
Cl(1)–C(21)	1.725(4)				
Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
C(15)–N(1)–N(2)	111.2(2)	C(15)–N(1)–C(17)	131.4(3)	N(2)–N(1)–C(17)	117.2(2)
N(1)–N(2)–N(3)	107.3(2)	N(2)–N(3)–C(14)	108.7(2)	N(1)–C(15)–C(14)	103.3(2)
N(1)–C(15)–C(16)	123.4(3)	N(3)–C(14)–C(13)	119.3(2)	N(3)–C(14)–C(15)	109.5(2)
N(1)–C(17)–C(18)	119.2(3)	N(1)–C(17)–C(22)	119.1(3)	O(1)–C(6)–C(1)	116.2(2)
O(1)–C(6)–C(5)	120.4(2)	O(1)–C(7)–C(12)	120.2(2)	O(1)–C(7)–C(8)	116.5(2)
O(2)–C(2)–C(1)	123.3(3)	O(2)–C(2)–C(3)	118.9(3)	O(3)–C(9)–C(8)	120.8(3)
O(3)–C(9)–C(10)	120.2(3)	C(6)–O(1)–C(7)	121.0(2)	C(13)–C(14)–C(15)	131.1(3)
C(14)–C(15)–C(16)	133.0(3)	Cl(1)–C(21)–C(20)	119.1(3)	Cl(1)–C(21)–C(22)	119.6(3)

Table III — Selected Dihedral Bond Torsion Angles (°)

Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
C(18)-C(17)-N(1)-N(2)	58.3 (4)	C(22)-C(17)-N(1)-N(2)	116.4 (3)	C(18)-C(17)-N(1)-C(15)	128.0 (4)
C(22)-C(17)-N(1)-C(15)	-57.3 (5)	C(12)-C(13)-C(14)-C(15)	124.8 (3)	C(5)-C(13)-C(14)-C(15)	55.4 (4)
C(12)-C(13)-C(14)-N(3)	53.3 (4)	C(5)-C(13)-C(14)-N(3)	-126.4 (3)		

[1] APEX2 (Version 2.1), SAINT Plus, Data Reduction and Correction Program (Version 7.31A, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA, **2006**.

[2] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97: a new tool for crystal structure determination and refinement. *J. Appl. Crystallogr.* **1999**, 32, 115-119.

[3] Sheldrick, G. M. *SHELXL-97. Program for the Solution of Crystal Structures*. University of Gottingen, Germany **1997**.

IV. The fluorescence excitation and emission spectrum determinations of the title compounds 7a-j

Table IV — The fluorescence spectrum of compounds 7a-j in EtOH solution

No.	Fluorescence intensity	Emission $\lambda_{\max}$ (nm)	Fluorescence intensity	Excitation $\lambda_{\max}$ (nm)
7a	202.089096	544	204.261061	527.5
7b	197.824126	544	197.336660	526.5
7c	187.988638	547.5	187.078361	529.5
7d	207.042994	546	202.841994	526
7e	206.218207	546	204.472257	526.5
7f	213.492686	544.5	213.820350	529
7g	212.742000	543.5	210.885213	527
7h	214.532625	543.5	209.740502	526.5
7i	204.040523	545.5	204.688328	529
7j	203.679487	544.5	203.728328	527
fluorescein	102.307932	522.5	101.145666	503.5

Table V — The fluorescence spectrum of compounds 7a-j in 0.1 NaOH solution(pH=13.0)

No.	Fluorescence intensity	Emission λ_{max} (nm)	Fluorescence intensity	Excitation λ_{max} (nm)
7a	341.245994	536.5	163.636216; 341.356010; 258.480255	335.5; 479; 524
7b	342.614096	537	183.759000; 344.961000; 255.575000	336; 479.5; 524.5
7c	330.418445	536.5	160.465428; 331.299432; 254.266458	334; 479; 522.5
7d	332.156990	537	162.015311; 329.752474; 249.788458	338; 481; 523.5
7e	343.254649	536	148.772855; 338.102153; 273.699055	338; 480; 519.5
7f	358.930936	536.5	152.005473; 354.039621; 268.619979	340.5; 479.5; 522
7g	353.395549	536	157.066499; 353.844773; 267.528411	338; 480; 523.5
7h	366.804857	535	161.705018; 361.834896; 278.048805	341; 480.5; 521
7i	346.120200	536.5	164.754001; 341.011580; 262.653589	334; 480; 523
7j	345.875883	536	161.240417; 344.046410; 266.851265	335; 478.5; 521
fluorescein	486.752493	523.5	289.388562; 487.113303; 369.071597	328.5; 461; 509

V. The ultraviolet-visible spectra determinations of the title compounds 7a-j

Table VI — The ultraviolet-visible spectra of compounds 7a-j

No.	Absorbance Intensity(EtOH)	Emission λ_{max} (nm)	Absorbance intensity(pH=13.0)	Excitation λ_{max} (nm)
7a	1.103335	522	2.345344	508
7b	0.822615	521	2.657693	508
7c	1.660779	522	2.275287	509
7d	0.851299	523	2.265751	509
7e	1.150787	523	1.850194	509
7f	1.368708	521	2.23231	509
7g	0.910134	522	2.196458	508
7h	0.765416	522	2.126223	508
7i	1.01219	523	2.042579	510
7j	0.767363	522	2.104516	509
fluorescein	0.245803	497	2.855093	488