

## Supporting Information

# Natural Phosphate-Supported Cu(II), an Efficient and Recyclable Catalyst for Synthesis of Xanthene and 1,4-Disubstituted 1,2,3-Triazole Derivatives

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## 1. General details

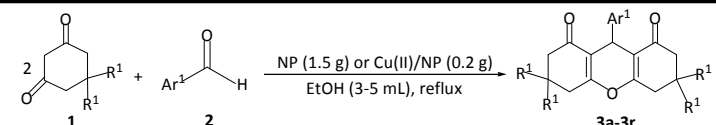
All chemicals were purchased from Merck and Sigma Aldrich. All products were known and their structures were identified by comparing their melting points and spectral data with the authentic samples. FTIR spectra were recorded on a Bruker Tensor 27 spectrometer, using KBr pellets for solids.  $^1\text{H}$  and  $^{13}\text{C}$  Nuclear Magnetic Resonance (NMR) spectra were recorded using a Bruker Advance DRX spectrometer at 400 MHz in  $\text{DMSO-d}_6$  and  $\text{CDCl}_3$  with tetramethylsilane as the internal reference.

## 2. Results and discussion

### 2.1. Coupling reaction-based synthesis of xanthenes

In our previous study on natural phosphate (NP), we used NP for the synthesis of xanthene derivatives; the results are shown in Table 1, NO 1. In order to improve the catalytic activity of NP, we prepared different catalyst and tested them for the synthesis of xanthene (please refer to Table 2 in the article text).  $\text{Cu(II)/NP}$  showed the best result. To investigate the application scope of  $\text{Cu(II)/NP}$  as an efficient catalyst, various aryl aldehydes (**2**) were chosen to react with 1,3-diketones ( $\text{R}_1 = \text{H}, \text{CH}_3$ ) in refluxing ethanol to give different xanthene derivatives (Table 1). Both aryle aldehydes, bearing electron-withdrawal (Table 1, entries 1-3,5, 9-12, 17 and 18) and electron-donating (Table 1, entries 4, 6, 7, 13, 14 and 16) substituents, readily participated in the reactions and formed the desired products in high yields. The nature of substituents on 1,3-diketone did not affect the reactions significantly.

**Table 1.** Synthesis of various xanthenes **3** catalysed by NP and  $\text{Cu(II)/NP}$



Entry	$\text{R}^1$	$\text{Ar}^1$	Product <b>3</b>	NO 1. NP		NO 2. $\text{Cu(II)/NP}$	
				Time (h)	Yield <b>3</b> (%)	Time (h)	Yield <b>3</b> (%)
1	$\text{CH}_3$	4-Cl- $\text{C}_6\text{H}_4$	3a	6.5	90	2.5	97
2	$\text{CH}_3$	4-Br- $\text{C}_6\text{H}_4$	3b	7.0	93	2	96
3	$\text{CH}_3$	4-CN- $\text{C}_6\text{H}_4$	3c	7.0	91	2	94
4	$\text{CH}_3$	4-OMe- $\text{C}_6\text{H}_4$	3d	8.0	85	2.5	85
5	$\text{CH}_3$	2,4-di-Cl- $\text{C}_6\text{H}_3$	3e	8.0	91	2	97
6	$\text{CH}_3$	2-OH- $\text{C}_6\text{H}_4$	3f	8.0	85	2.5	94
7	$\text{CH}_3$	4-Me- $\text{C}_6\text{H}_4$	3g	8.5	84	2.5	85
8	$\text{CH}_3$	$\text{C}_6\text{H}_5$	3h	8.5	86	2.5	87
9	$\text{CH}_3$	4- $\text{NO}_2$ - $\text{C}_6\text{H}_4$	3i	6.5	95	2	97
10	H	4-Cl- $\text{C}_6\text{H}_4$	3j	6.5	92	2	93
11	H	4-CN- $\text{C}_6\text{H}_4$	3k	7.0	93	2.5	94
12	H	2,4-di-Cl- $\text{C}_6\text{H}_3$	3l	8.0	90	2	92
13	H	2-OH- $\text{C}_6\text{H}_4$	3m	8.0	87	2.5	88
14	H	4-Me- $\text{C}_6\text{H}_4$	3n	8.5	85	2.5	86
15	H	$\text{C}_6\text{H}_5$	3o	8.5	84	2.5	85
16	H	4-OMe- $\text{C}_6\text{H}_4$	3p	8.0	84	3	85
17	H	4- $\text{NO}_2$ - $\text{C}_6\text{H}_4$	3q	6.5	94	2	95
18	H	4-Br- $\text{C}_6\text{H}_4$	3r	6.5	91	2	92

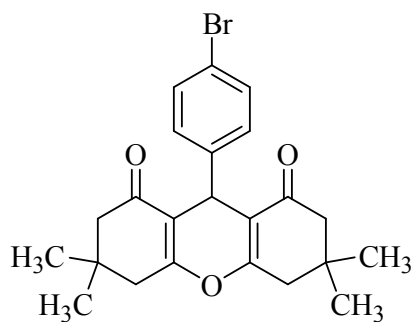
### 3. Spectral data of selected compounds

#### 3.1. 9-(4-Bromo-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3b**)

White solid; mp = 240-242°C [1], IR (KBr, cm<sup>-1</sup>):  $\nu$  = 2952.5, 2875.3, 1658.5, 1361.5, 1197.6, 1004.7.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.35 (d, 2H, J = 6.4 Hz, H-Ar), 7.20 (d, 2H, J = 8.8 Hz, H-Ar), 4.71 (s, 1H, H<sub>9</sub>), 2.47 (t, 4H, 2CH<sub>2</sub>), 2.21 (q, 4H, 2CH<sub>2</sub>), 1.11 (s, 6H, 2Me), 1.00 (s, 6H, 2Me). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 196.3, 162.4, 143.2, 131.1, 130.2, 120.2, 115.2, 50.7, 40.8, 32.2, 31.6, 29.3, 27.3 ppm.

Calculated for C<sub>23</sub>H<sub>25</sub>BrO<sub>3</sub>: C, 64.34; H, 5.87; Br, 18.16. Found: C, 64.32, H, 5.85; Br, 18.59.



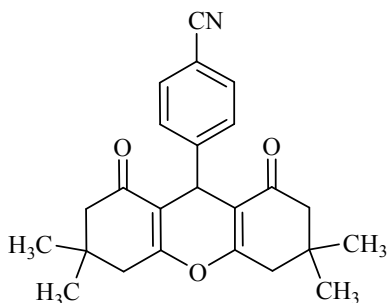
(**3b**)

#### 3.2. 4-(3,3,6,6-Tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl) benzonitrile (**3c**)

White solid; mp = 222-224°C [2], IR (KBr, cm<sup>-1</sup>):  $\nu$  = 2952.5, 2875.3, 2260.5, 1660.4, 1471.4,

1361.5, 1197.6, 1151.3, 1004.7, 844.7. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.53 (d, 2H, J = 8.0 Hz, H-Ar), 7.43 (d, 2H, J = 8.0 Hz, H-Ar), 4.78 (s, 1H, H-9), 2.50 (brs, 4H, 2CH<sub>2</sub>), 2.25 (d, 2H, J = 16 Hz, CH<sub>2</sub>),  $\delta$  = 2.15 (d, 2H, J = 16 Hz, CH<sub>2</sub>), 1.13 (s, 6H, 2Me), 1.00 (s, 6H, 2Me). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 196.4, 162.4, 142.7, 132.0, 129.8, 128.2, 115.2, 50.7, 40.8, 32.2, 31.5, 29.33, 27.3

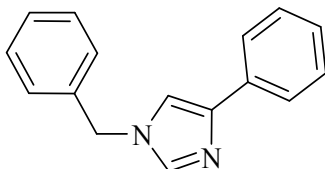
ppm. Calculated for C<sub>24</sub>H<sub>25</sub>NO<sub>3</sub>: C, 76.77; H, 6.71; N, 3.73. Found: C, 76.71, H, 6.69; N, 3.71.



(**3c**)

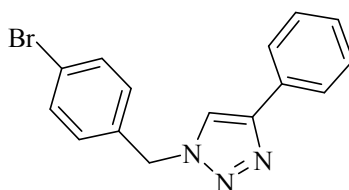
3.3. 1-benzyl-4-phenyl-1H-1,2,3-triazole (**8a**)

mp = 133-134°C [3],  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.82 (d,  $J=7.2$  Hz, 2H), 7.70 (s, 1H), 7.44-7.32 (m, 8H), 5.60 (s, 2H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 148.1, 134.7, 130.5, 129.1, 128.74, 128.7, 128.1, 128.0, 125.6, 119.5, 54.1. ppm.



3.4. 1-(4-bromobenzyl)-4-phenyl-1H-1,2,3-triazole (**8b**)

mp = 156-158°C [3],  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.83 (d,  $J = 7.2$  Hz, 2H), 7.73 (s, 1H), 7.53 (d,  $J = 8.4$  Hz, 2H), 7.43 (t,  $J = 7.4$  Hz, 2H), 7.34 (t,  $J = 7.4$  Hz, 1H), 7.20 (d,  $J = 8.4$  Hz, 2H), 5.54 (s, 2H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.5, 147.9, 141.7, 130.0, 128.82, 128.5, 128.4, 125.64, 124.2, 119.8, 53.0 ppm.

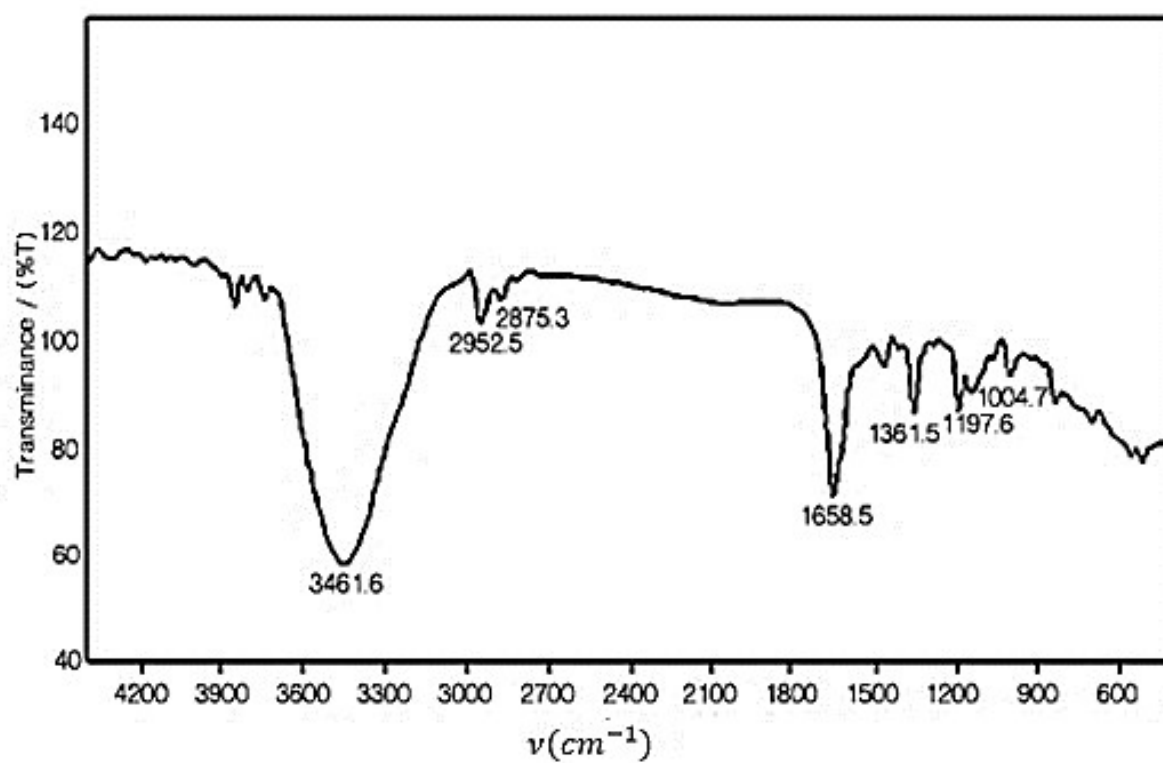
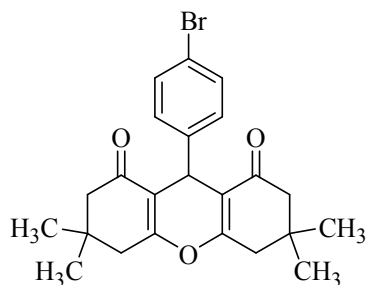


**(8b)**

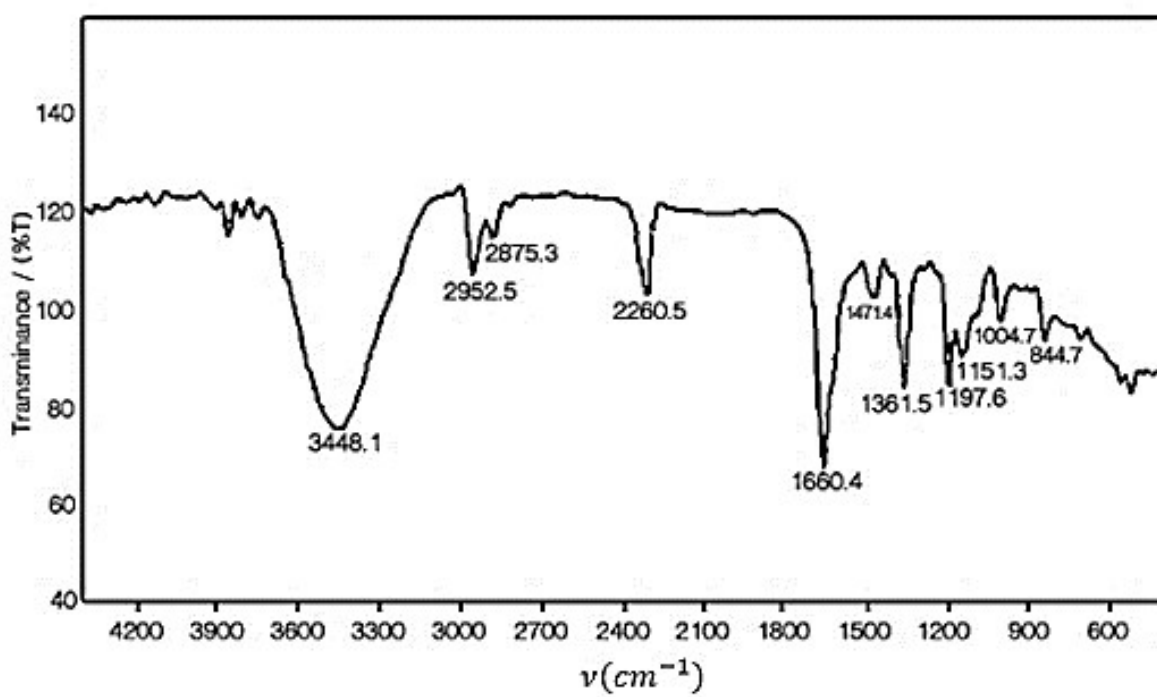
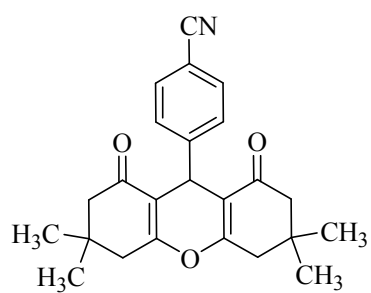
#### 4. FTIR, $^1\text{H}$ and $^{13}\text{C}$ NMR of selected xanthene

##### 4.1. FTIR

9-(4-Bromo-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3b**)

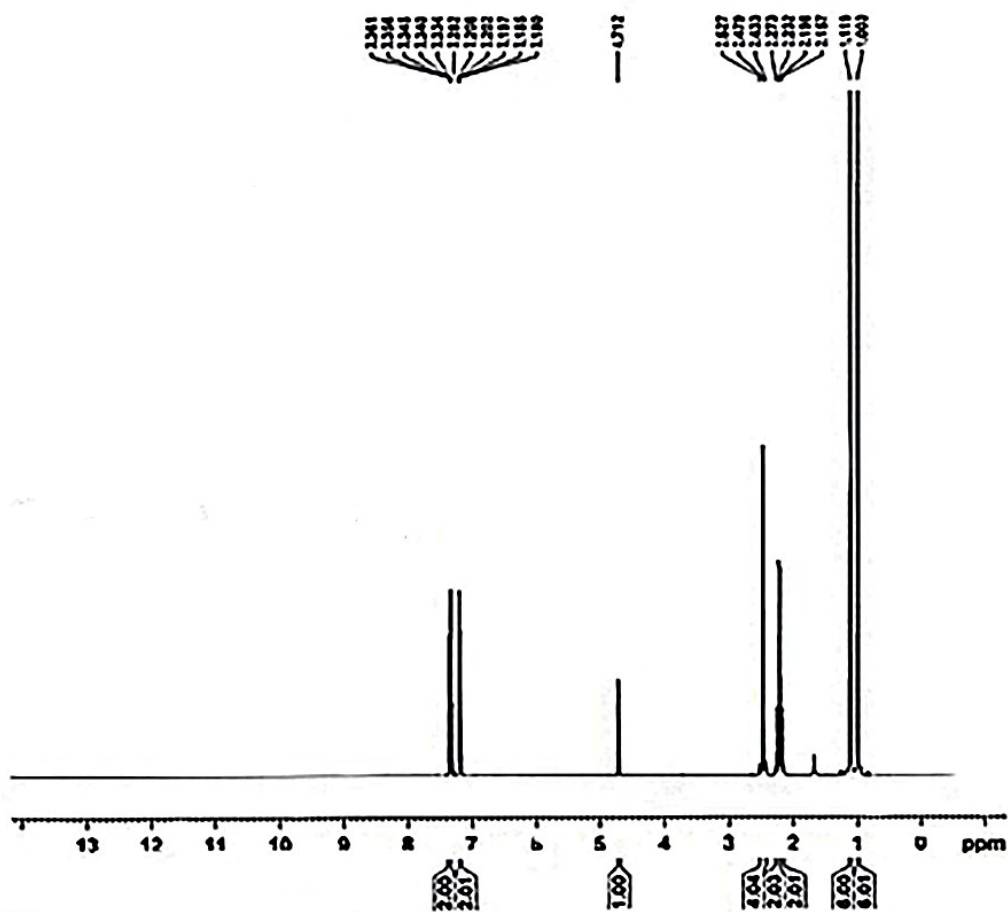


4-(3,3,6,6-Tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl) benzonitrile(**3c**)

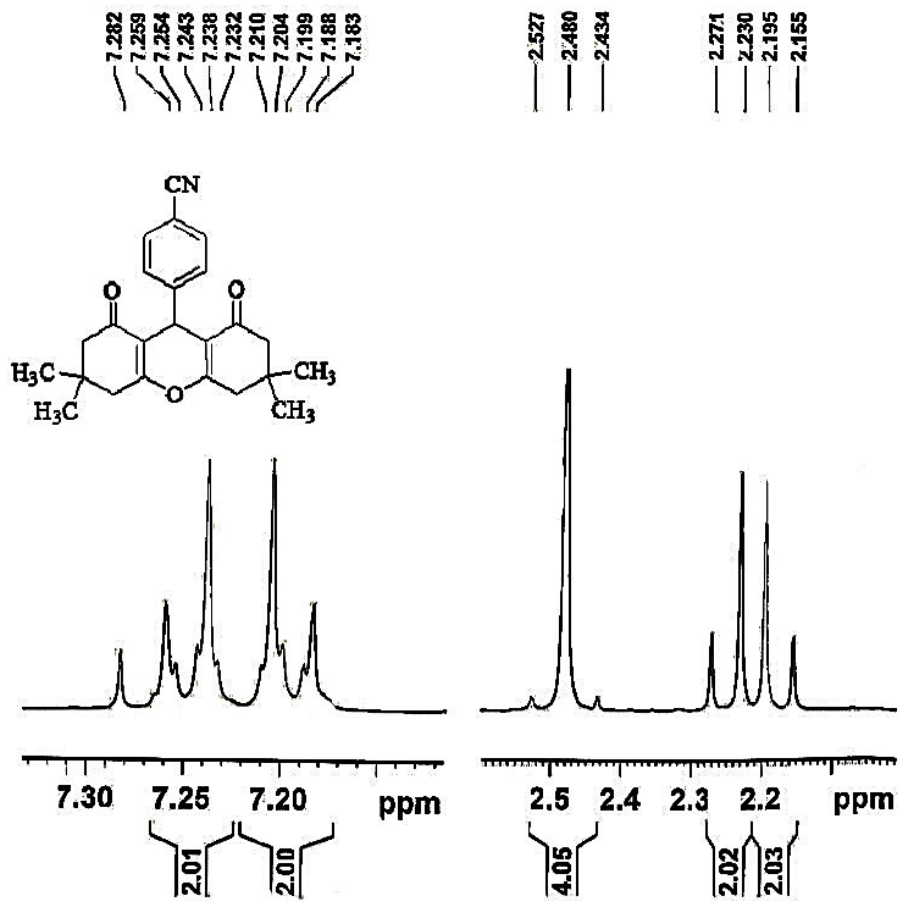


#### 4.2. <sup>1</sup>H NMR

9-(4-Bromo-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3b**)



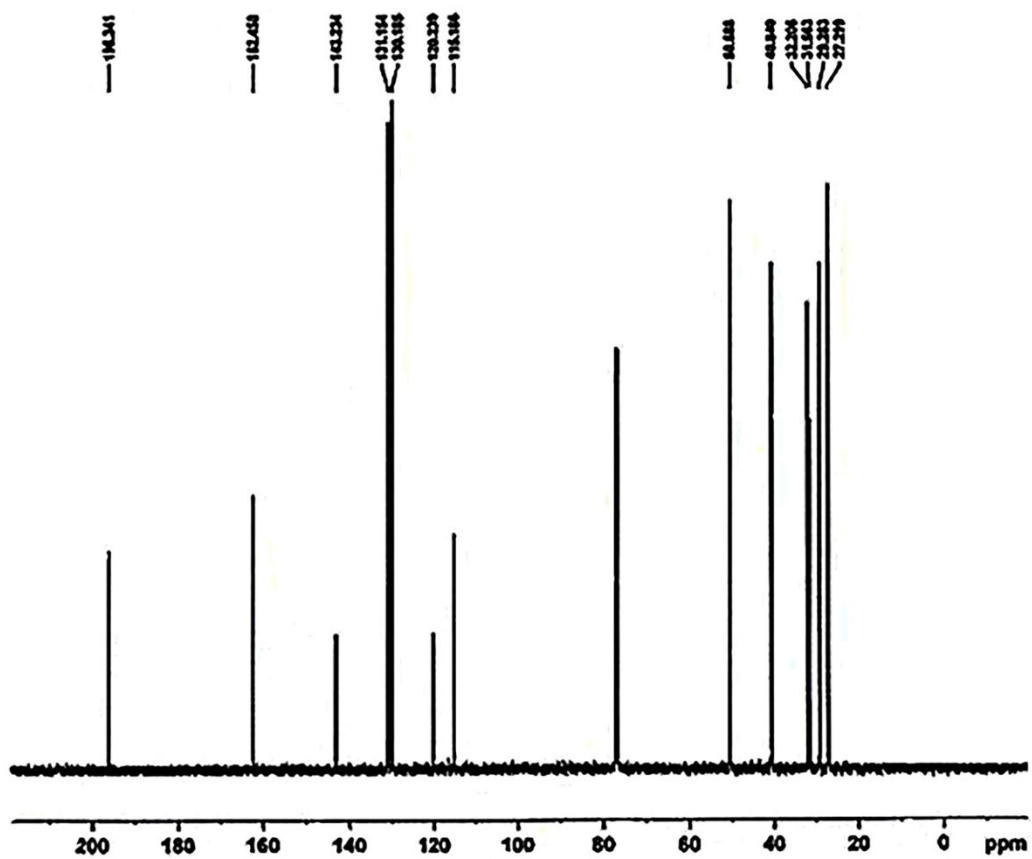
4-(3,3,6,6-Tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl) benzonitrile  
(3c)



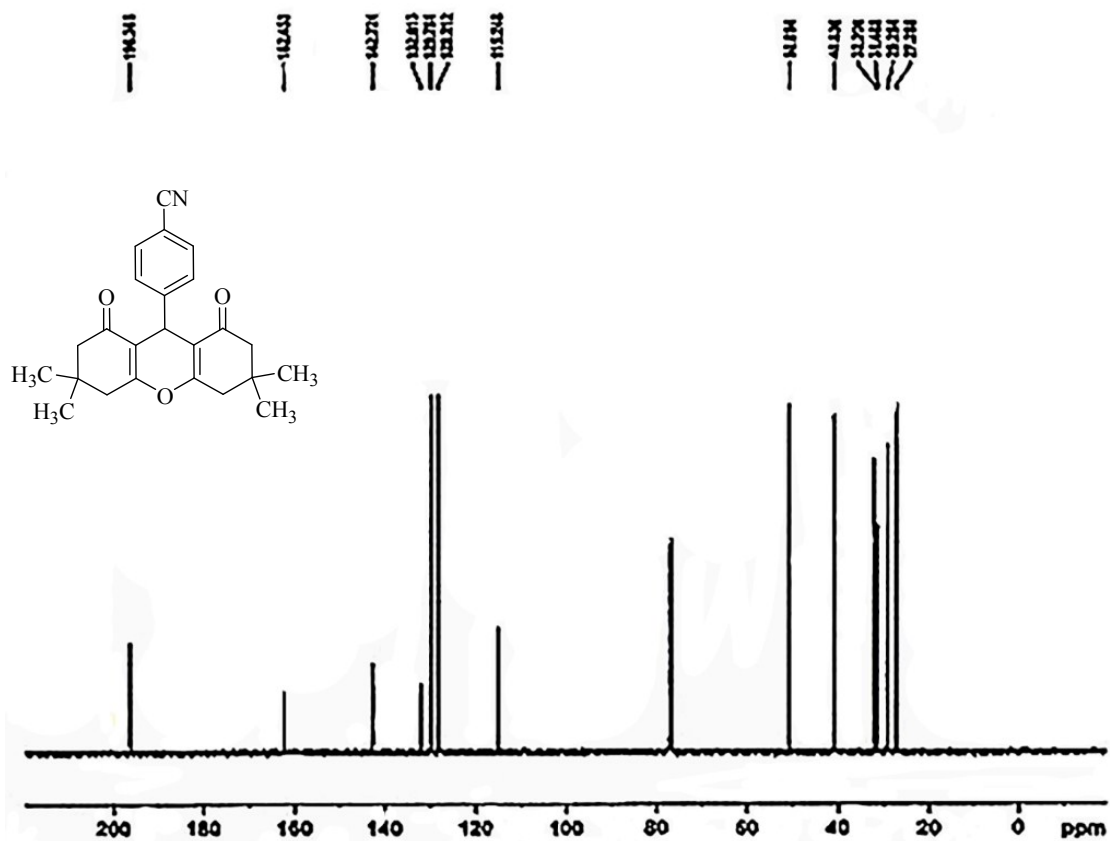


### 4.3. <sup>13</sup>C NMR

9-(4-Bromo-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3b**)



4-(3,3,6,6-Tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl) benzonitrile  
(3c)





1-(4-bromobenzyl)-4-phenyl-1H-1,2,3-triazole (**8b**)

