

## Supporting Information

### Tetramethylguanidium-based ionic liquids as efficient and reusable catalyst for the synthesis of biscoumarin at room temperature

Anlian Zhu, Mingyue Wang, Xiaowei Li, Mingming Han, Lingjun Li, Jianji Wang\*

Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine

Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of

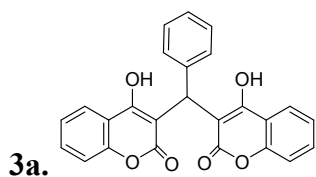
Education, School of Chemistry and Chemical Engineering, Henan Normal

University, Xinxiang, Henan 453007, P. R. China

Telephone: +86-0373-3325805; Fax: +86-0373-3329030

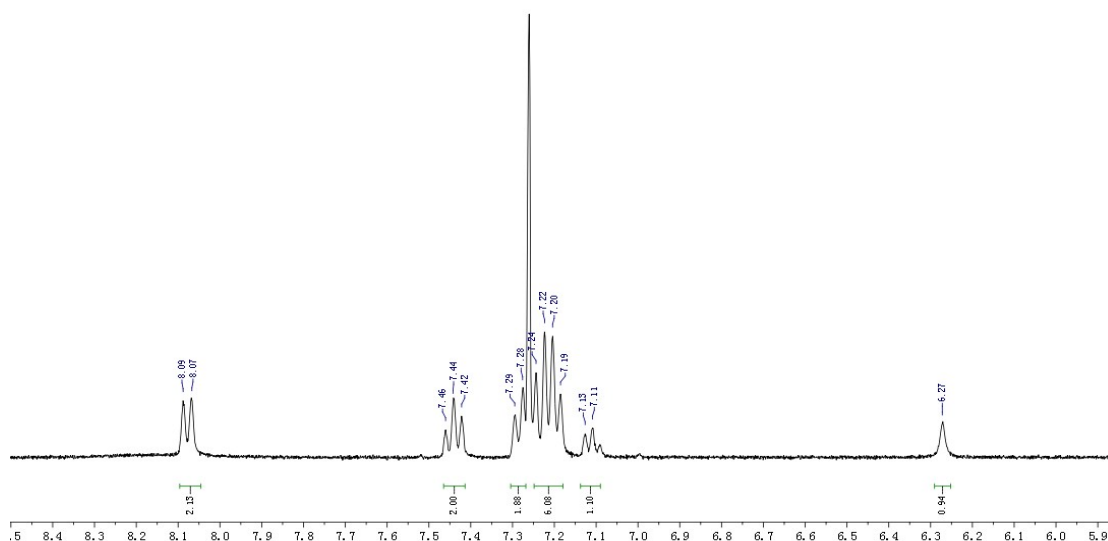
jwang@htu.cn

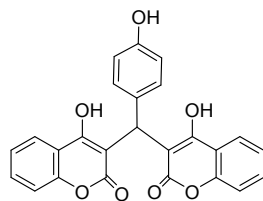
<sup>1</sup>H-NMR spectra were recorded on a BRUKER AV-400 instrument at room temperature. Chemical shifts ( $\delta$ ) are expressed in ppm from the internal standard tetramethylsilane and coupling constants ( $J$ ) are given in Hz.



3,3'-(Phenylmethylene)bis-(4-hydroxy-2H-chromen-2-one)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (d,  $J$  = 8.4 Hz, 2H), 7.44 (t,  $J$  = 7.7 Hz, 2H), 7.29 (d,  $J$  = 7.5 Hz, 2H), 7.21 (dd,  $J$  = 15.5, 7.9 Hz, 6H), 7.12 (d,  $J$  = 7.0 Hz, 1H), 6.27 (s, 1H).

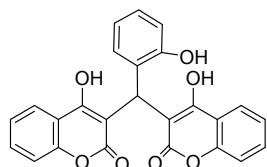
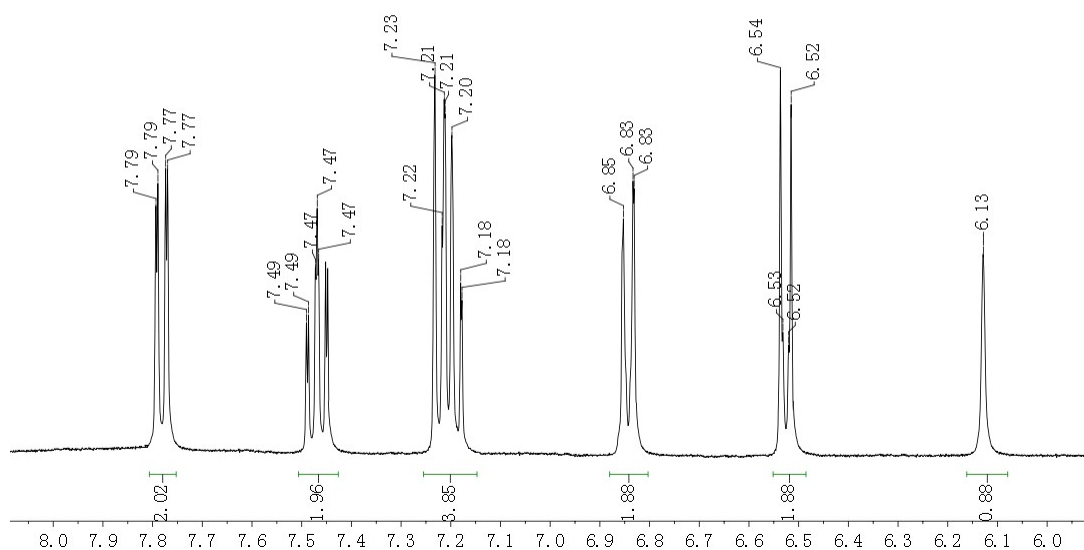




**3b.**

3,3'-(4-Hydroxyphenylmethylene)bis-(4-hydroxy-2H-chromen-2-one)

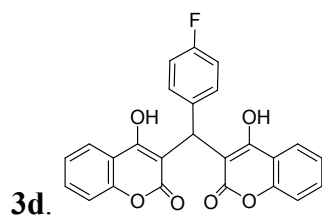
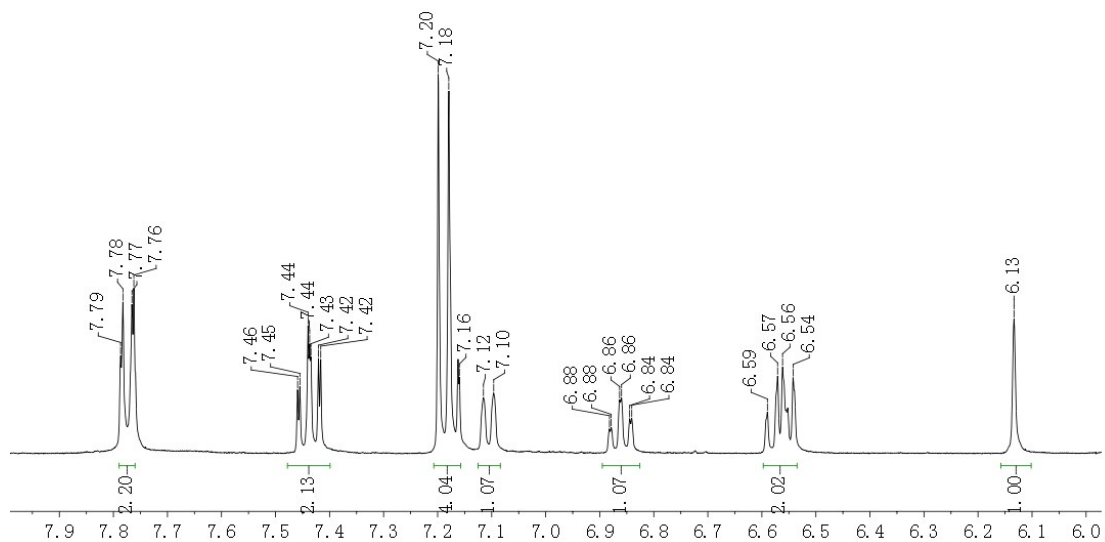
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.78 (dd,  $J = 7.8, 1.6$  Hz, 2H), 7.50 – 7.43 (m, 2H), 7.24 – 7.17 (m, 4H), 6.84 (d,  $J = 7.8$  Hz, 2H), 6.53 (d,  $J = 8.6$  Hz, 2H), 6.13 (s, 1H).



**3c.**

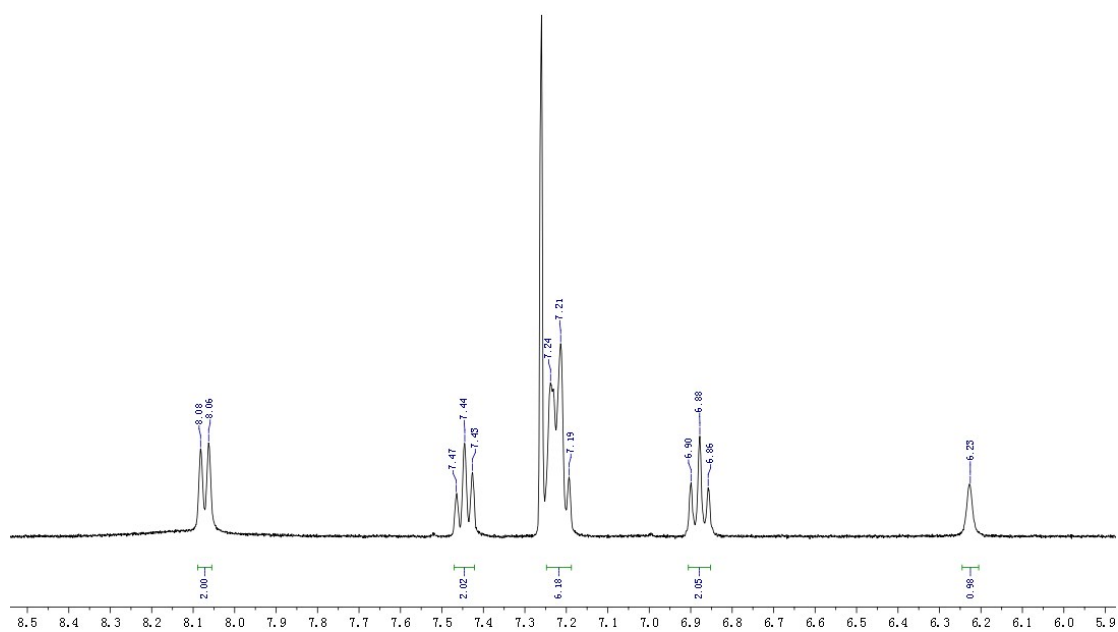
3,3'-(2-Hydroxyphenylmethylene)bis-(4-hydroxy-2H-chromen-2-one)

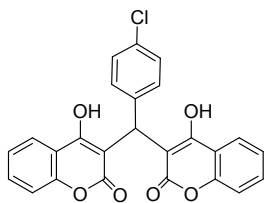
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.77 (dd,  $J = 8.3, 1.6$  Hz, 2H), 7.48 – 7.40 (m, 2H), 7.18 (t,  $J = 7.8$  Hz, 4H), 7.11 (d,  $J = 7.6$  Hz, 1H), 6.86 (td,  $J = 7.5, 1.4$  Hz, 1H), 6.57 (dd,  $J = 11.4, 7.7$  Hz, 2H), 6.13 (s, 1H).



3,3'-(4-Fluorophenylmethylene)bis(4-hydroxy-2H-chromen-2-one)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 7.8$  Hz, 2H), 7.45 (t,  $J = 7.8$  Hz, 2H), 7.22 (t,  $J = 8.9$  Hz, 6H), 6.88 (t,  $J = 8.3$  Hz, 2H), 6.23 (s, 1H).

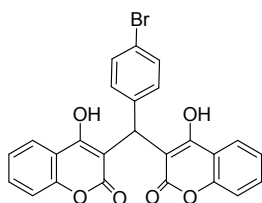
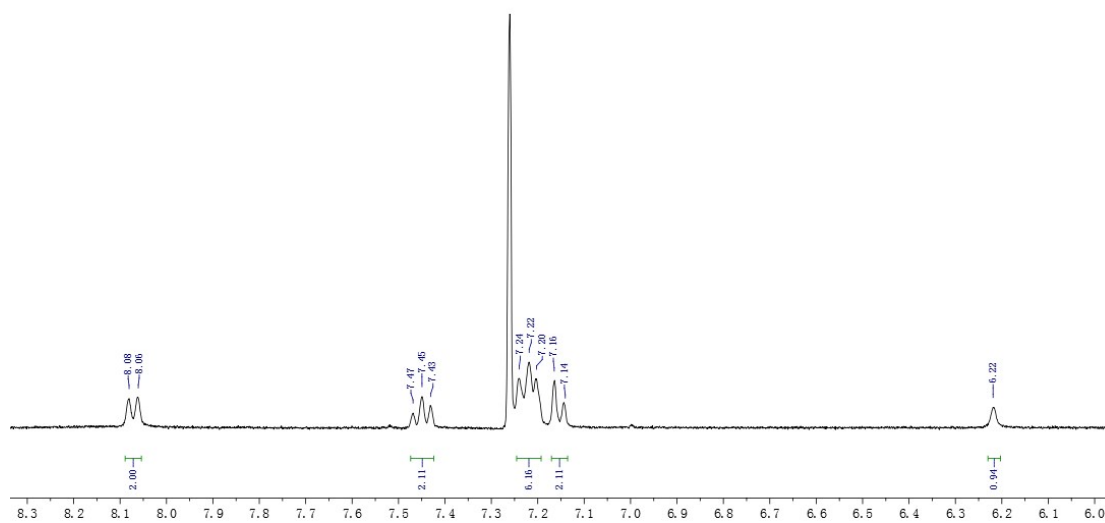




**3e.**

3,3'-(4-Chlorophenylmethylene)bis-(4-hydroxy-2H-chromen-2-one)

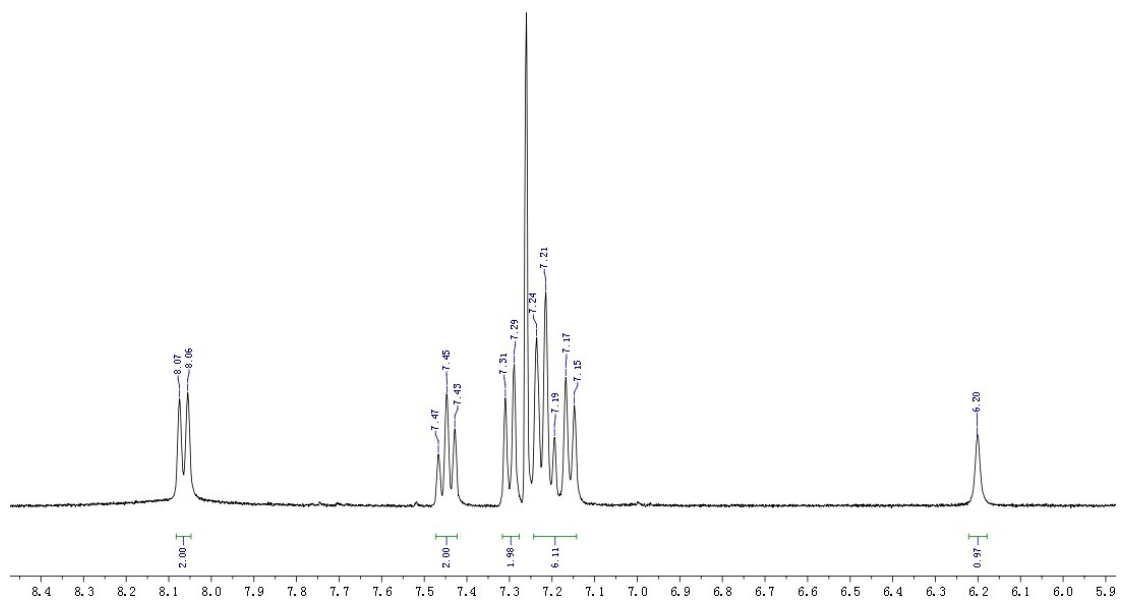
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 7.9$  Hz, 2H), 7.45 (t,  $J = 7.7$  Hz, 2H), 7.25 – 7.19 (m, 6H), 7.15 (d,  $J = 9.5$  Hz, 2H), 6.22 (s, 1H).



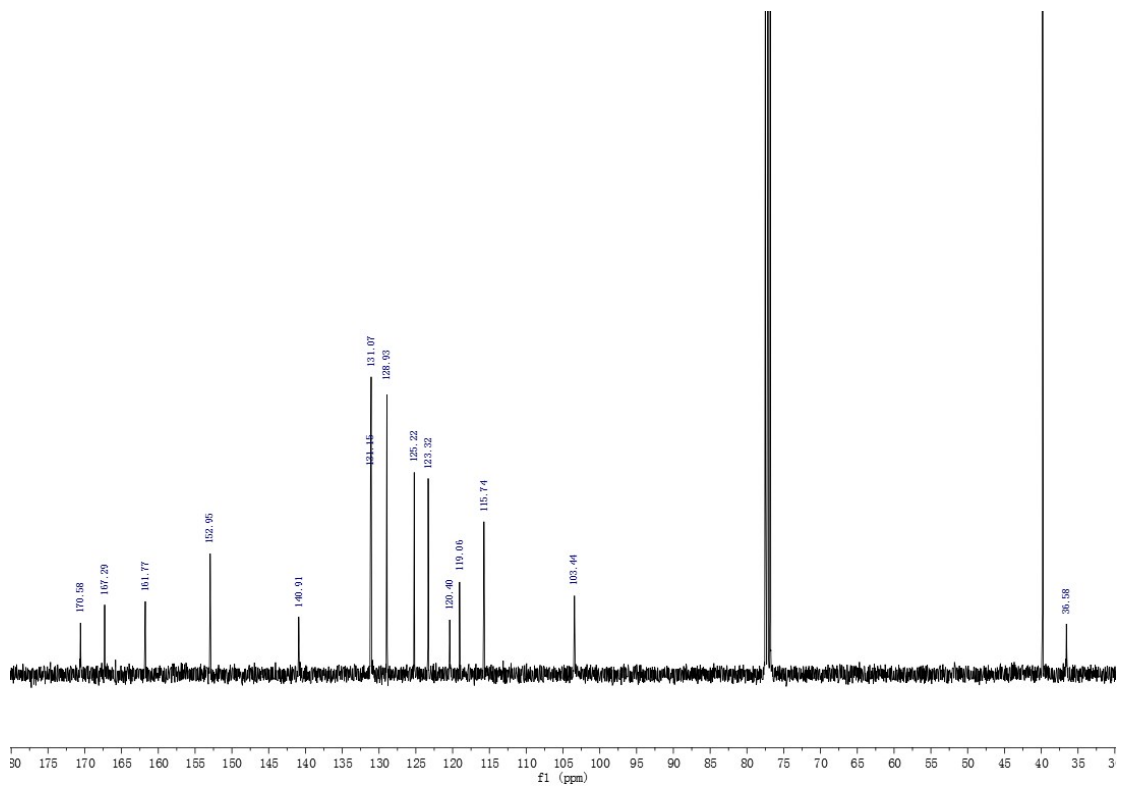
**3f.**

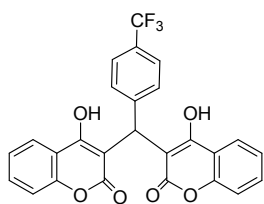
3,3'-(4-Bromophenylmethylene)bis-(4-hydroxy-2H-chromen-2-one)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 7.8$  Hz, 2H), 7.45 (t,  $J = 7.7$  Hz, 2H), 7.30 (d,  $J = 8.3$  Hz, 2H), 6.20 (s, 1H).



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 170.58, 167.29, 161.77, 152.95, 140.91, 131.15, 131.07, 128.93, 125.22, 123.32, 120.40, 119.06, 115.74, 103.44, 36.58.

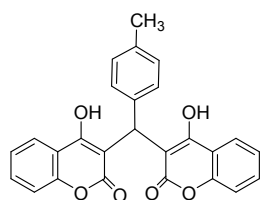
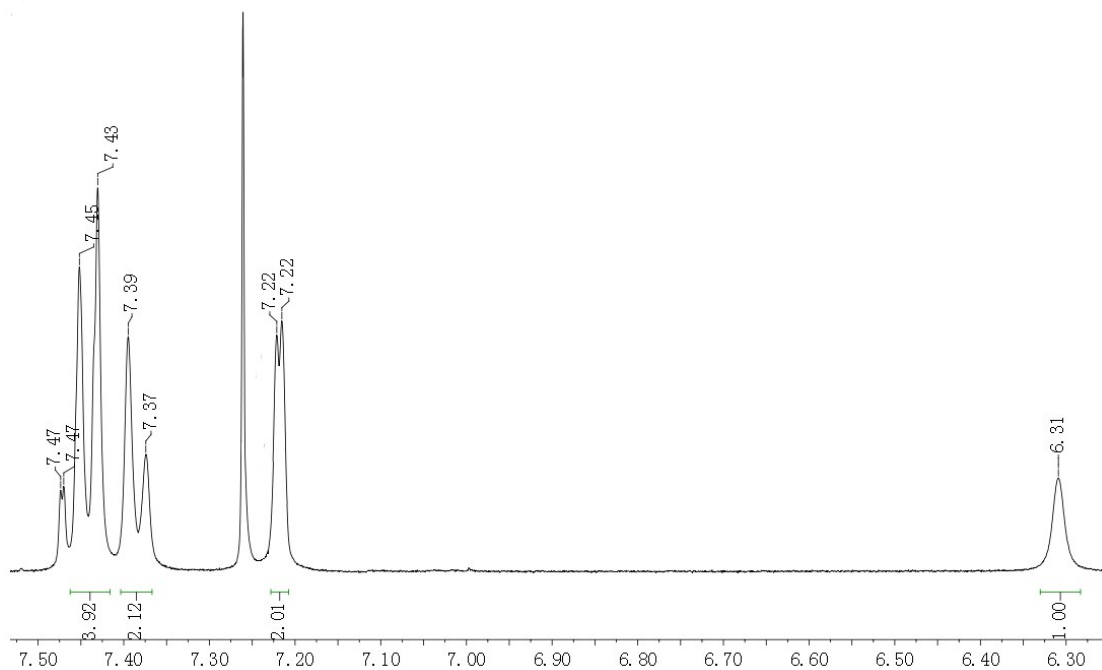




**3g.**

3,3'-(4-Trifluoromethylphenylmethylene)bis-(4-hydroxy-2H-chromen-2-one)

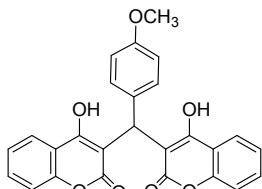
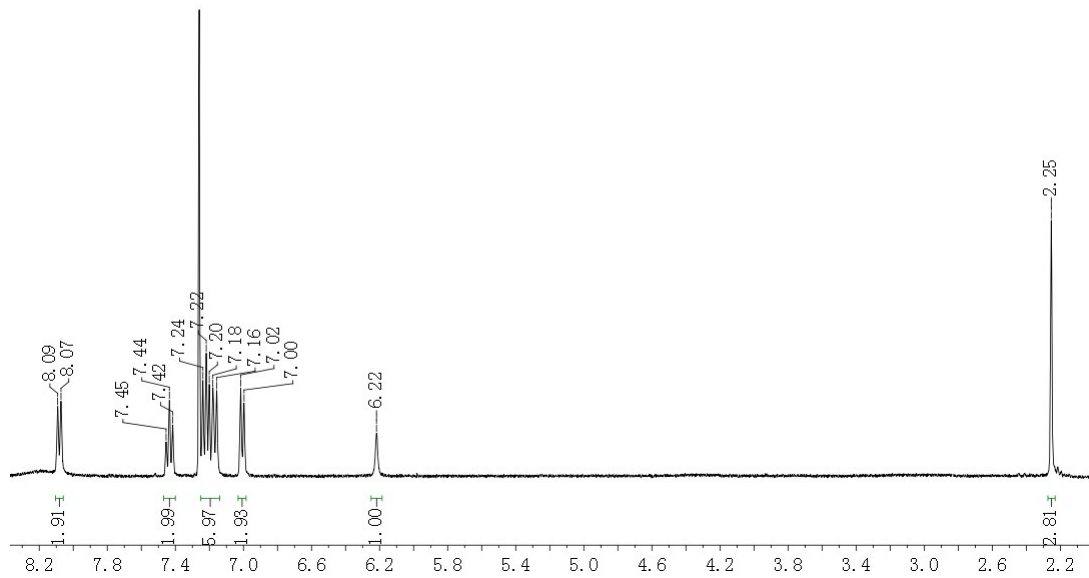
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J = 7.9$  Hz, 4H), 7.44 (d,  $J = 8.5$  Hz, 4H), 7.38 (d,  $J = 8.2$  Hz, 2H), 7.22 (d,  $J = 2.4$  Hz, 2H), 6.31 (s, 1H).



**3h.**

3,3'-(4-Methylphenylmethylene)bis-(4-hydroxy-2H-chromen-2-one)

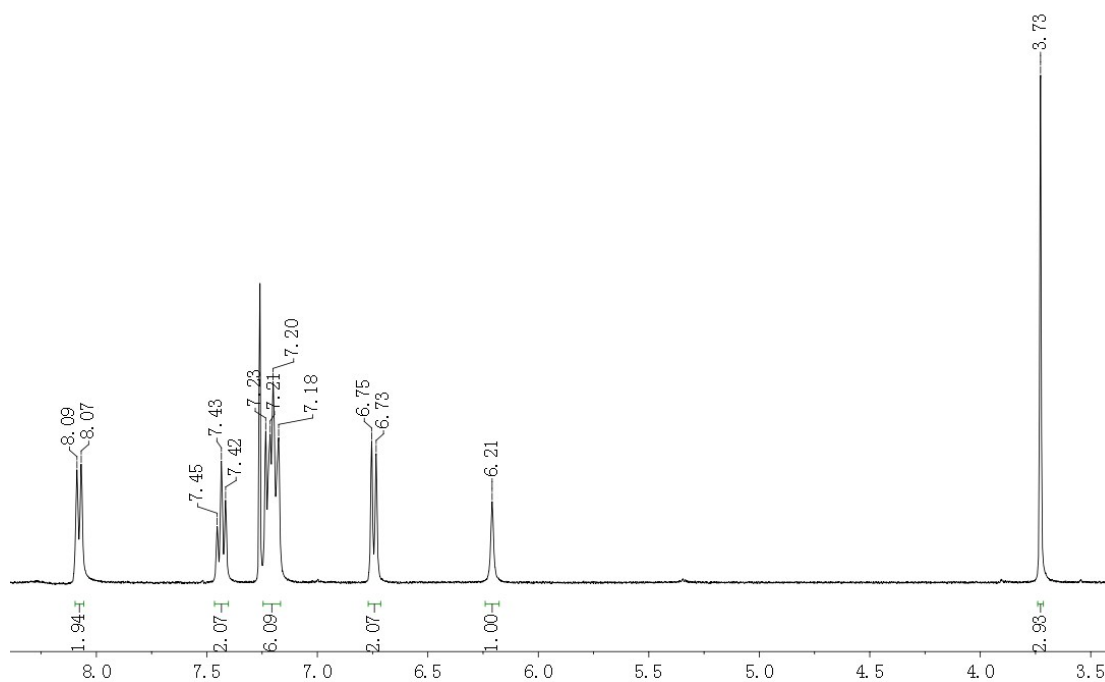
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 7.9$  Hz, 2H), 7.44 (t,  $J = 7.8$  Hz, 2H), 7.25 – 7.14 (m, 6H), 7.01 (d,  $J = 7.9$  Hz, 2H), 6.22 (s, 1H), 2.25 (s, 3H).

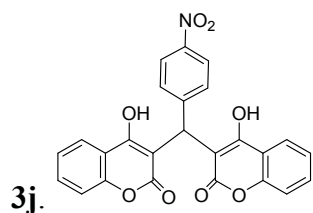


**3i.**

3,3'-(4-Methoxyphenylmethylene)bis(4-hydroxy-2H-chromen-2-one)

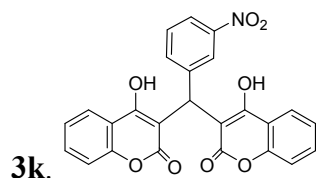
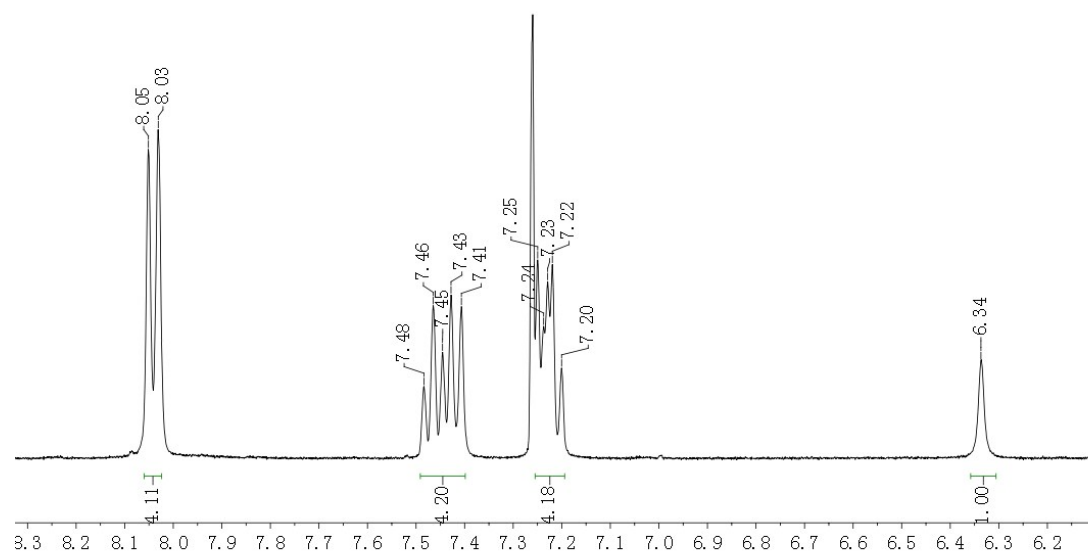
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 7.6$  Hz, 2H), 7.43 (t,  $J = 7.7$  Hz, 2H), 7.21 (dd,  $J = 14.3, 9.1$  Hz, 6H), 6.74 (d,  $J = 8.1$  Hz, 2H), 6.21 (s, 1H), 3.73 (s, 3H).





3,3'-(4-Nitrophenylmethylene)bis-(4-hydroxy-2H-chromen-2-one)

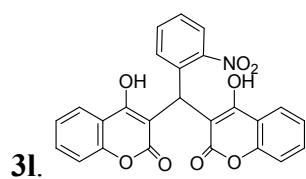
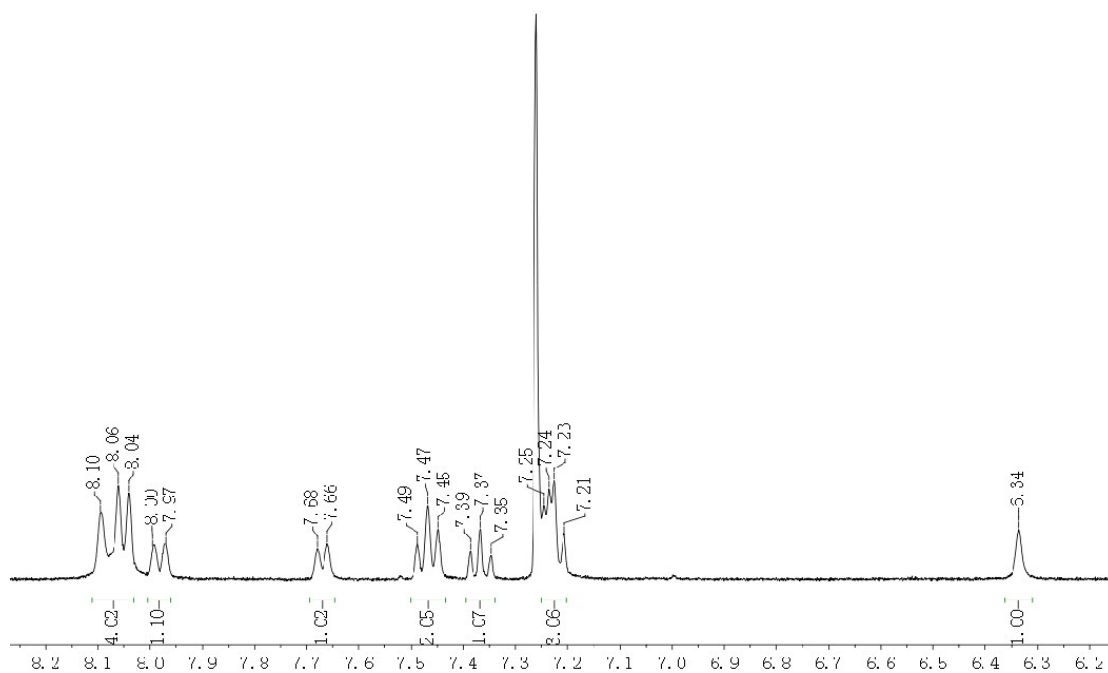
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 8.1$  Hz, 4H), 7.49 – 7.40 (m, 4H), 7.25 – 7.19 (m, 4H), 6.34 (s, 1H).



3,3'-(3-Nitrophenylmethylene)bis-(4-hydroxy-2H-chromen-2-one)

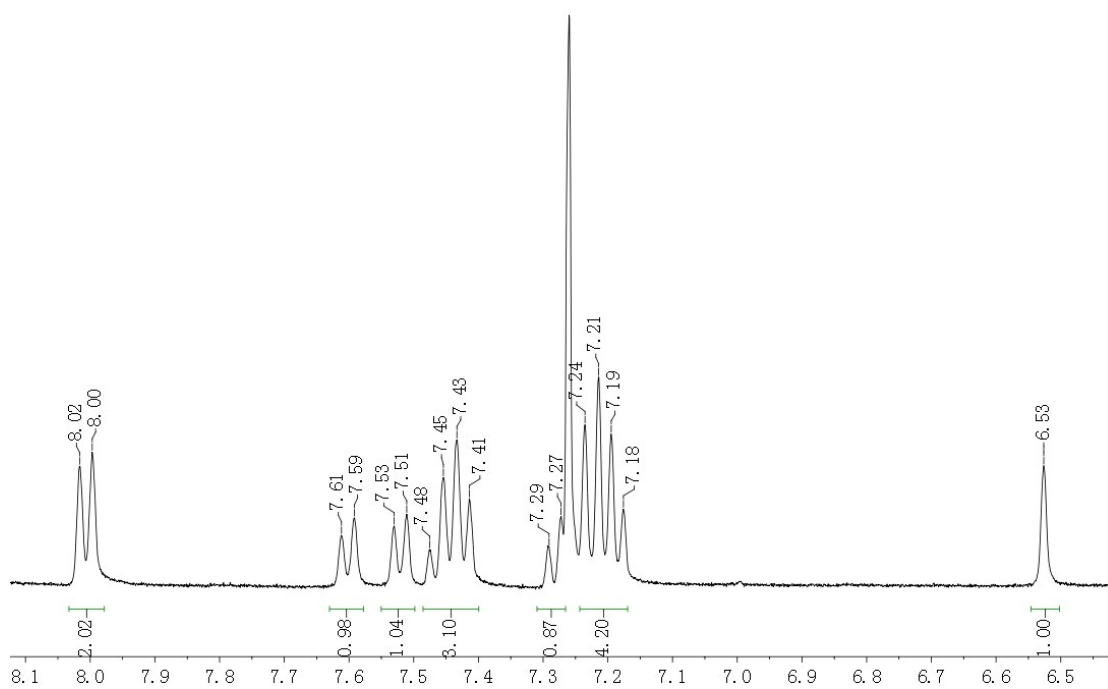
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 – 8.03 (m, 4H), 7.98 (d,  $J = 10.0$  Hz, 1H), 7.67 (d,  $J = 7.8$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 7.37 (t,  $J = 8.0$  Hz, 1H), 7.23 (dd,  $J = 9.8$ , 6.0 Hz, 3H), 6.34 (s, 1H).

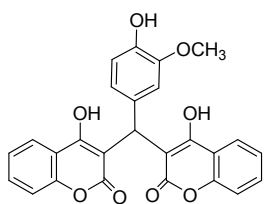




**3,3'-(2-Nitrophenylmethylene)bis-(4-hydroxy-2H-chromen-2-one)**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 7.7$  Hz, 2H), 7.60 (d,  $J = 8.1$  Hz, 1H), 7.52 (d,  $J = 7.8$  Hz, 1H), 7.44 (dd,  $J = 16.5, 8.1$  Hz, 3H), 7.28 (d,  $J = 7.4$  Hz, 1H), 7.20 (dd,  $J = 15.8, 8.0$  Hz, 4H), 6.53 (s, 1H).

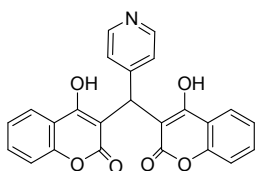
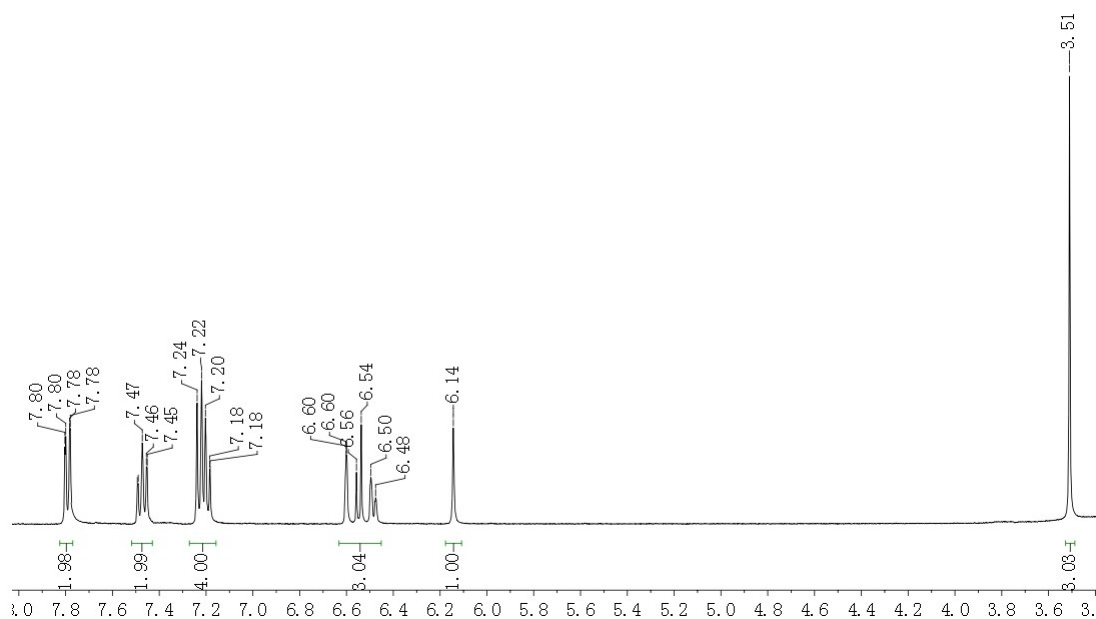




**3m.**

3,3'-(4-Hydroxy-3-methoxyphenylmethylene)bis-(4-hydroxy-2H-chromen-2-one)

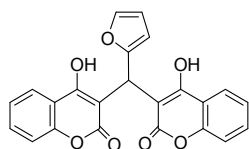
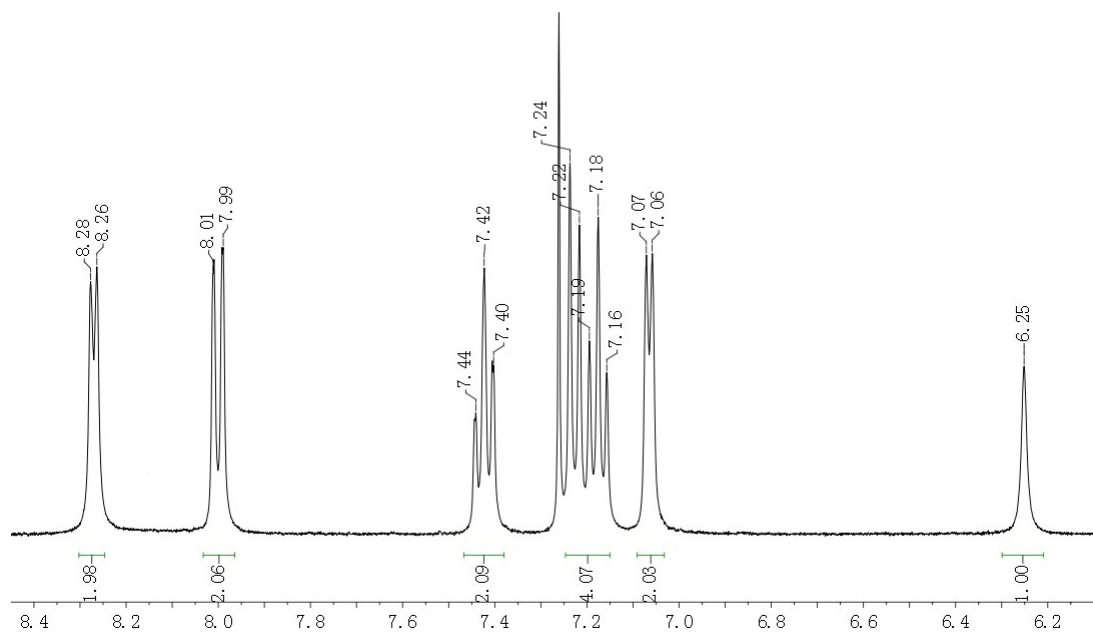
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.79 (dd,  $J = 7.8, 1.4$  Hz, 2H), 7.52 – 7.43 (m, 2H), 7.27 – 7.16 (m, 4H), 6.63 – 6.45 (m, 3H), 6.14 (s, 1H), 3.51 (s, 3H).



**3n.**

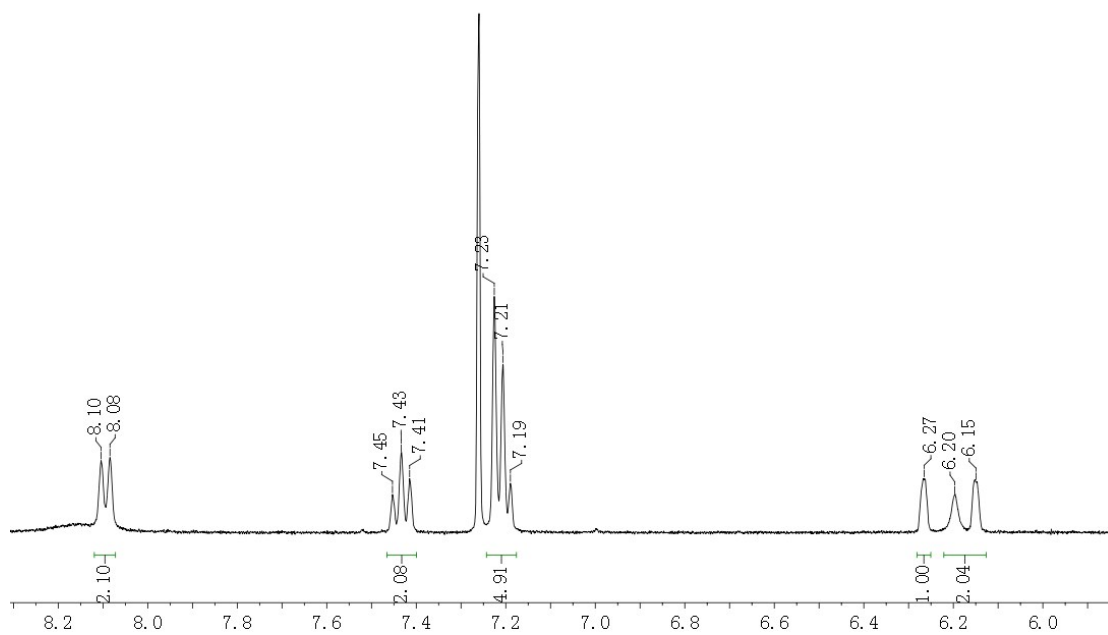
3,3'-(N-pyridylmethylene)bis-(4-hydroxy-2H-chromen-2-one)

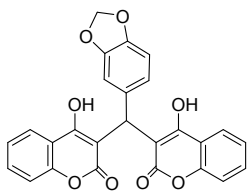
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (d,  $J = 5.5$  Hz, 2H), 8.00 (d,  $J = 8.9$  Hz, 2H), 7.42 (t,  $J = 7.7$  Hz, 2H), 7.25 – 7.15 (m, 4H), 7.06 (d,  $J = 5.1$  Hz, 2H), 6.25 (s, 1H).



3,3'-(furan-2-ylmethylene)bis(4-hydroxy-2H-chromen-2-one)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J = 7.9$  Hz, 2H), 7.43 (t,  $J = 7.7$  Hz, 2H), 7.24 – 7.18 (m, 5H), 6.27 (s, 1H), 6.17 (d,  $J = 19.0$  Hz, 2H).

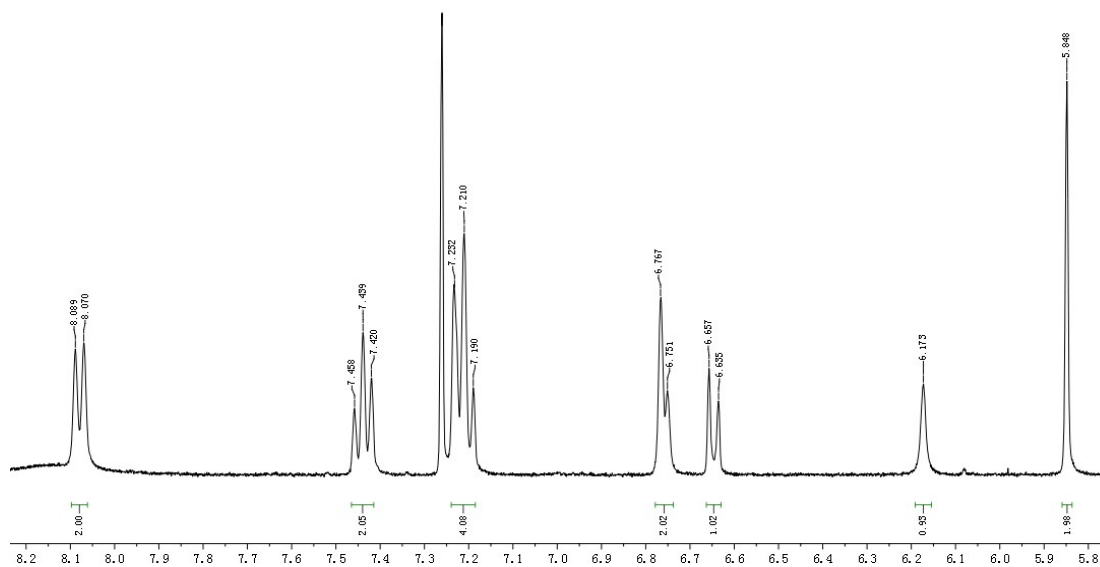




**3p.**

3,3'-(benzo[d][1,3]dioxol-5-ylmethylene)bis(4-hydroxy-2H-chromen-2-one)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 7.6$  Hz, 2H), 7.44 (t,  $J = 7.6$  Hz, 2H), 7.21 (t,  $J = 8.5$  Hz, 4H), 6.76 (d,  $J = 6.2$  Hz, 2H), 6.65 (d,  $J = 8.6$  Hz, 1H), 6.17 (s, 1H), 5.85 (s, 2H).



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 170.77, 167.44, 161.80, 152.84, 147.55, 145.22, 135.50, 130.95, 125.30, 123.18, 120.48, 119.55, 115.58, 107.79, 107.70, 103.76, 100.61, 36.61.

