Supporting information

Title: A coumarin-based fluorescent chemosensor as Sn indicator and a fluorescent cellular imaging agent

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Characterization of 1

Mp. = 211 - 213 ^{o}C; calculated MW = 334.05; ESI-MS *m/z* = 334, 120, 92; FT-IR (KBr, ν/cm^{-1}): 3400 (OH stretch), 1697 (C=O stretch); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 12.51 (s, 2H), 7.80 (d.d, *J*= 8.00, 1.5Hz, 2H), 7.34 (d.t, *J*= 7.75, 1.5Hz, 2H), 7.35 (d, *J*= 7.35Hz, 2H), 7.33 (t, *J*= 7.33Hz, 2H), 5.60 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 166.1, 162.3, 154.0, 133.2, 124.3, 123.6, 116.8, 116.3, 91.5, 19.1; Anal. Calcd. For $C_{19}H_{12}O_6$(%): C, 67.86; H, 3.60. Found: C, 67.84; H, 3.61.

Characterization of 2a

Mp=184-186^{o}C; calculated MW = 360; ESI-MS *m/z* = 360, 120, 92; FT-IR (KBr, ν/cm^{-1}): 3230 (OH Stretch), 1718 (C=O stretch); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.97 (t, *J*= 9.00Hz, 2H), 7.60 (t, *J*= 7.75Hz, 1H), 7.39 (t, *J*= 7.75Hz, 1H), 7.38 (t, *J*= 6.50Hz, 2H), 7.29 (d, *J*= 8.00Hz, 2H), 7.27 (d, *J*= 8.50Hz, 2H), 3.70 (bs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 163.2, 152.6, 152.2, 132.3, 131.9, 124.5, 123.9, 123.1, 116.8, 116.1, 101.8, 25.0; Anal. Calcd. For $C_{21}H_{12}O_6$ (%): C, 70.00; H, 3.36. Found: C, 69.78; H, 3.39.

Characterization of 2b

Mp=230-232 ^{o}C; calculated MW = 378; ESI-MS *m/z* = 378, 120, 92; FT-IR (KBr, ν/cm^{-1}): 3492, 3238 (OH Stretch), 1717, 1671 (C=O stretch); ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 11.62 (s, 1H), 8.00 (d, *J*= 8.00Hz, 1H), 7.88 (d, *J*=7.50Hz, 1H), 7.64 (t, *J*= 8.50Hz, 1H), 7.61 (t, *J*= 8.00Hz, 1H), 7.42- 7.36 (m, 6H), 5.63 (t, 3.00Hz, 1H), 4.42 (s, 1H), 2.32 (d.d.d, *J*= 10.50, 2.50, 1.50Hz, 1H), 2.17 (bs, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 165.7, 160.9, 160.7, 157.1, 152.3, 152.3, 132.3(2C), 124.7, 124.3, 123.7, 122.7, 116.7 (2C), 116.7, 115.8, 106.4, 104.5, 100.2, 56.6, 30.7; Anal. Calcd. For $C_{21}H_{14}O_7$ (%): C, 67.67; H, 3.73. Found: C, 67.70; H, 3.71.

Characterization of 3

Mp= 245-248 ^{o}C; calculated Mw= 360; ESI-MS *m/z* = 360, 120, 92; FT-IR (KBr, ν/cm^{-1}): 3467 (OH Stretch), 1718, 1636 (C=O stretch), 1616 (C=C Stretch); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 12.54 (s, 1H), 8.96 (t, *J*= 13.50Hz, 1H), 8.18 (d, *J*=14.00Hz, 1H), 7.95 (d, *J*= 7.50Hz, 1H), 7.67-7.59 (m, 2H), 7.42- 7.23 (m, 5H), 5.60 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 177.9, 166.1, 162.5, 162.3, 161.1, 154.6, 154.0, 134.3(2C), 133.1, 126.5(2C), 124.4, 124.0, 123.7, 121.4, 120.8, 117.1, 116.8, 107.0, 91.5; Anal. Calcd. For $C_{21}H_{12}O_6$ (%): C, 70.0; H, 3.36. Found: C, 70.06; H, 3.31.

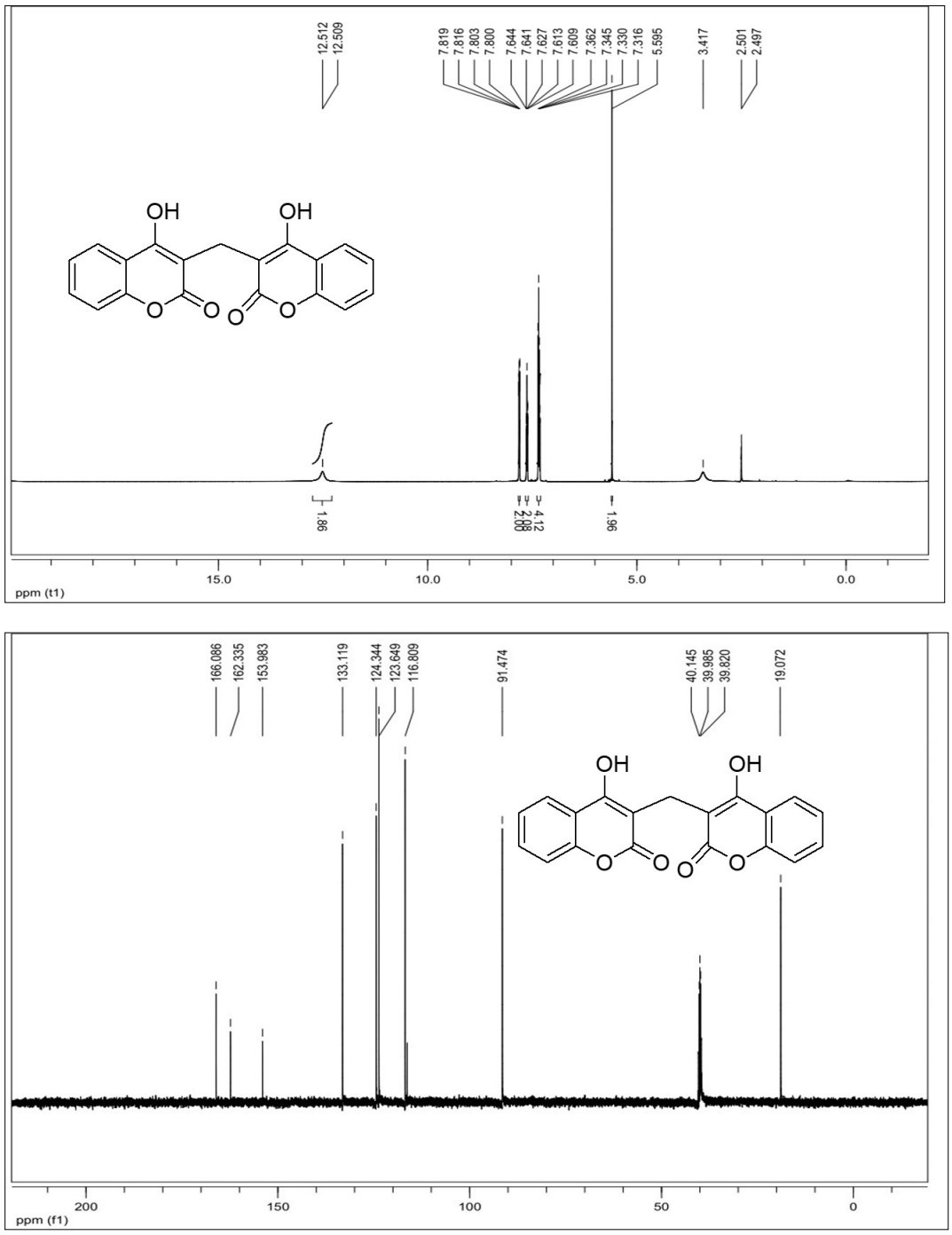


Figure A.1 ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **1**

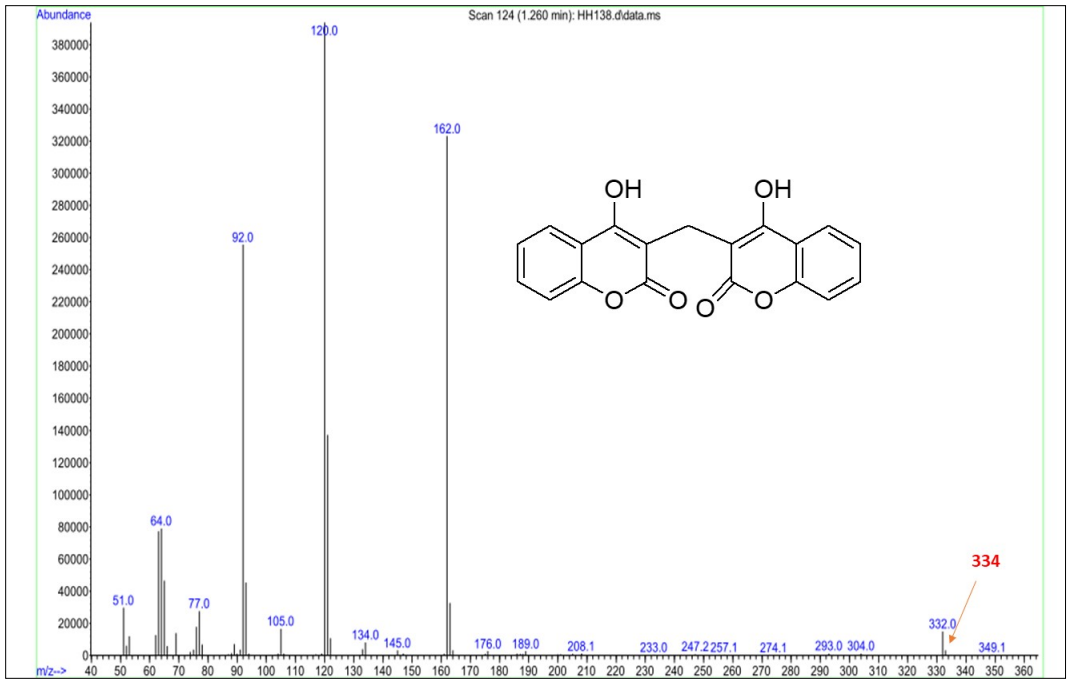


Figure A.2 Mass spectrum of **1**

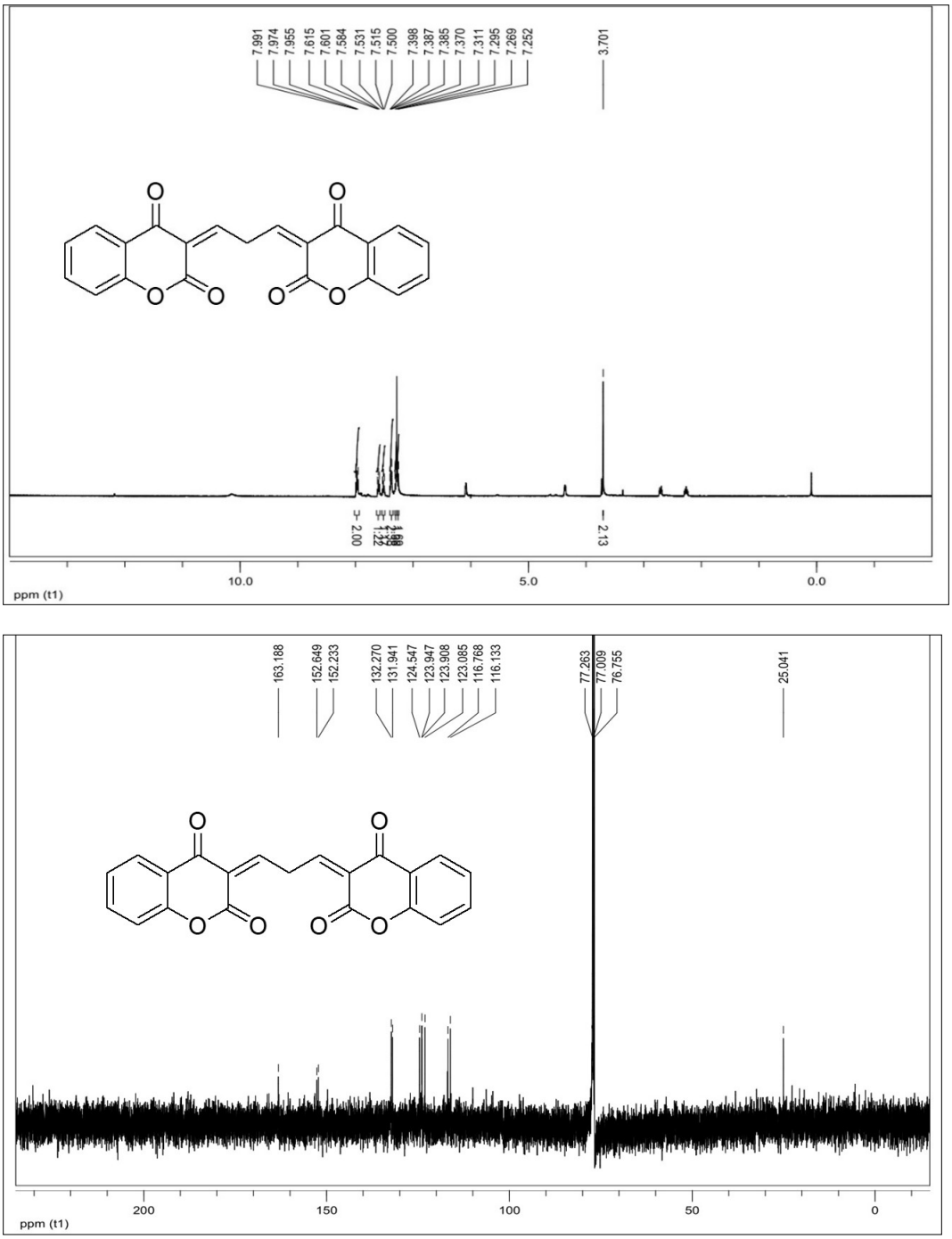


Figure B.1 ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2a**

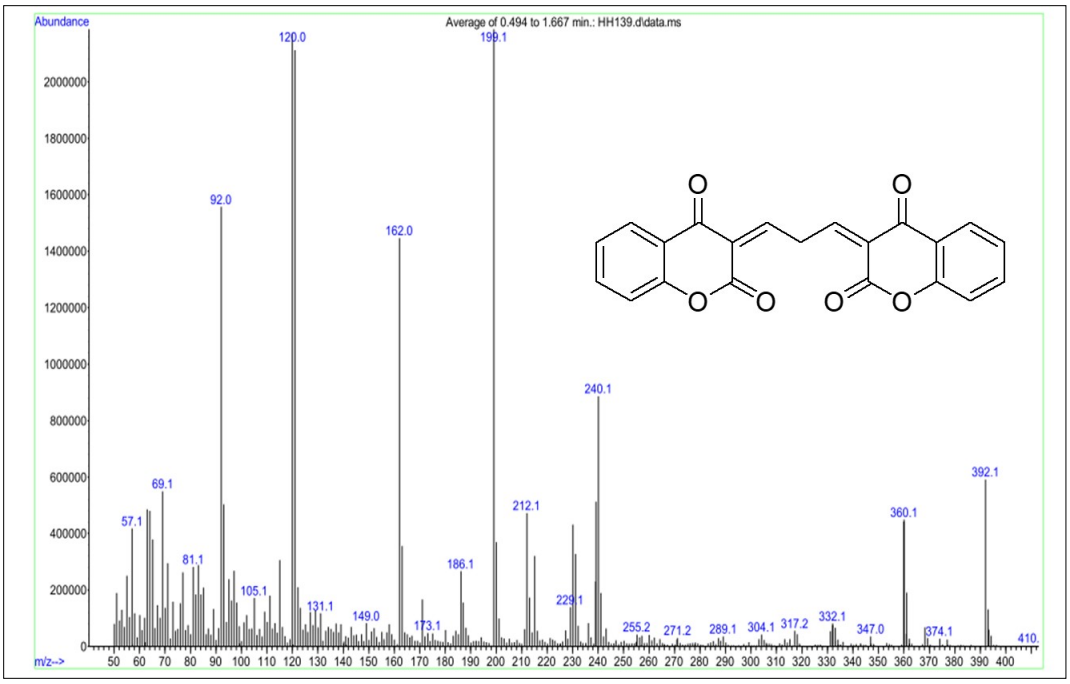


Figure B.2 Mass spectrum of **2a**

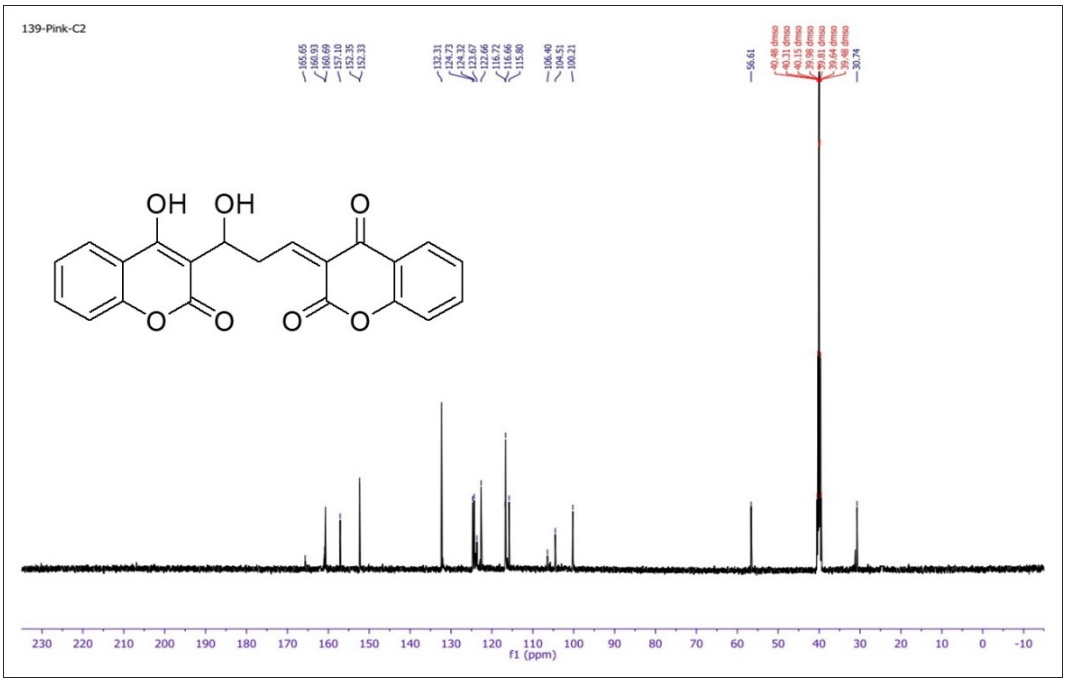


Figure C.1 ^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of **2b**

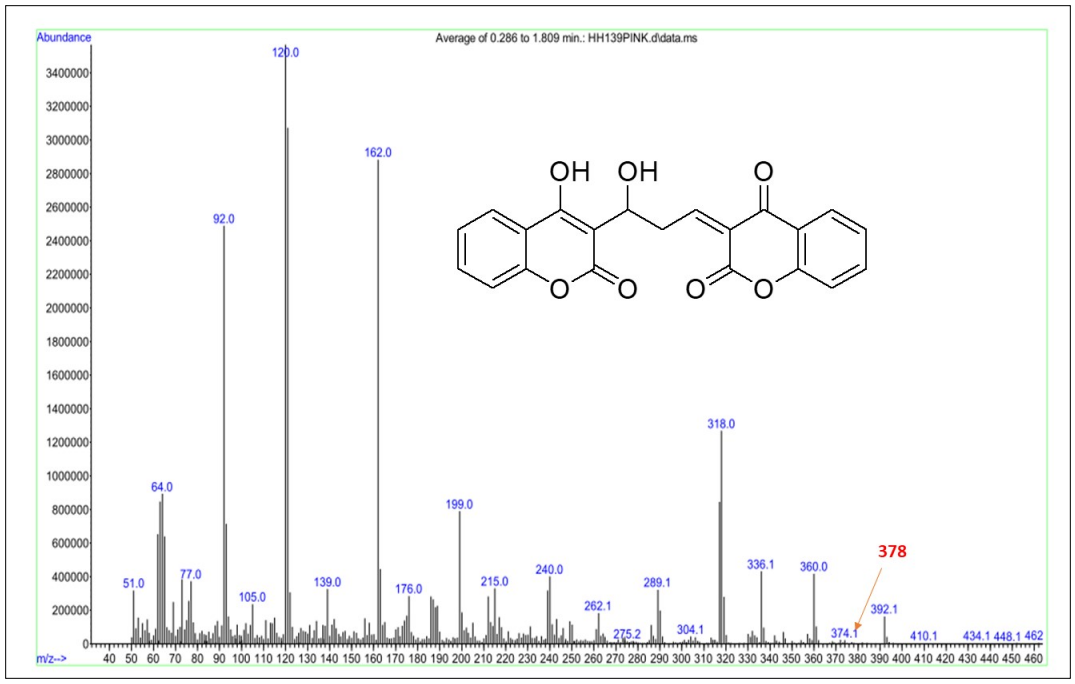
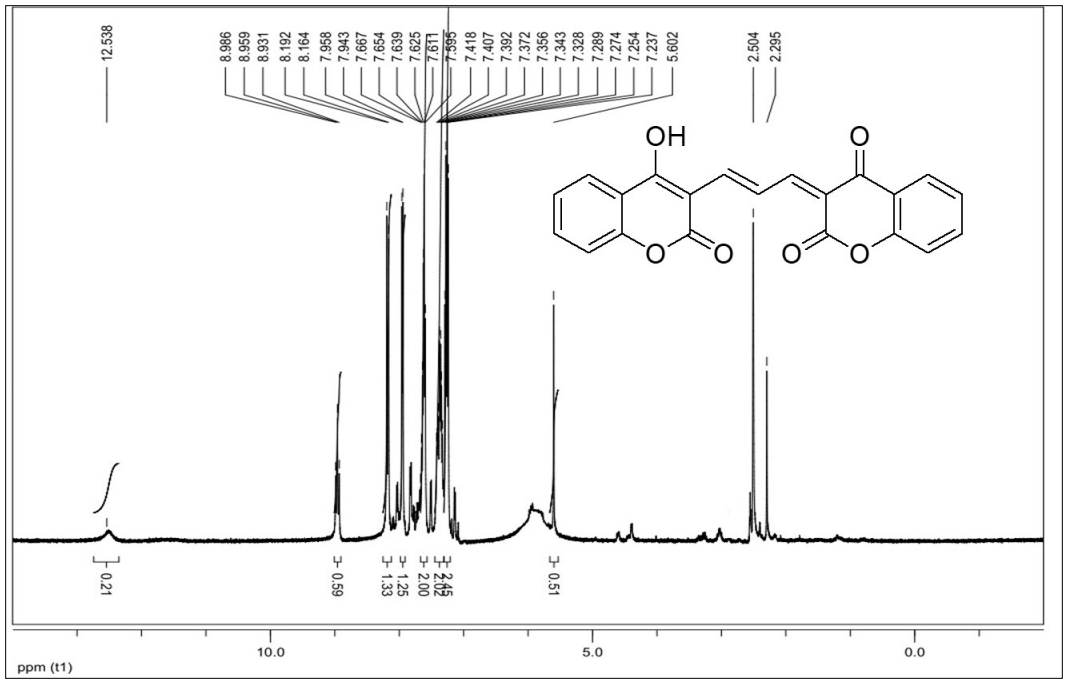


Figure C.2 Mass spectrum of **2b**



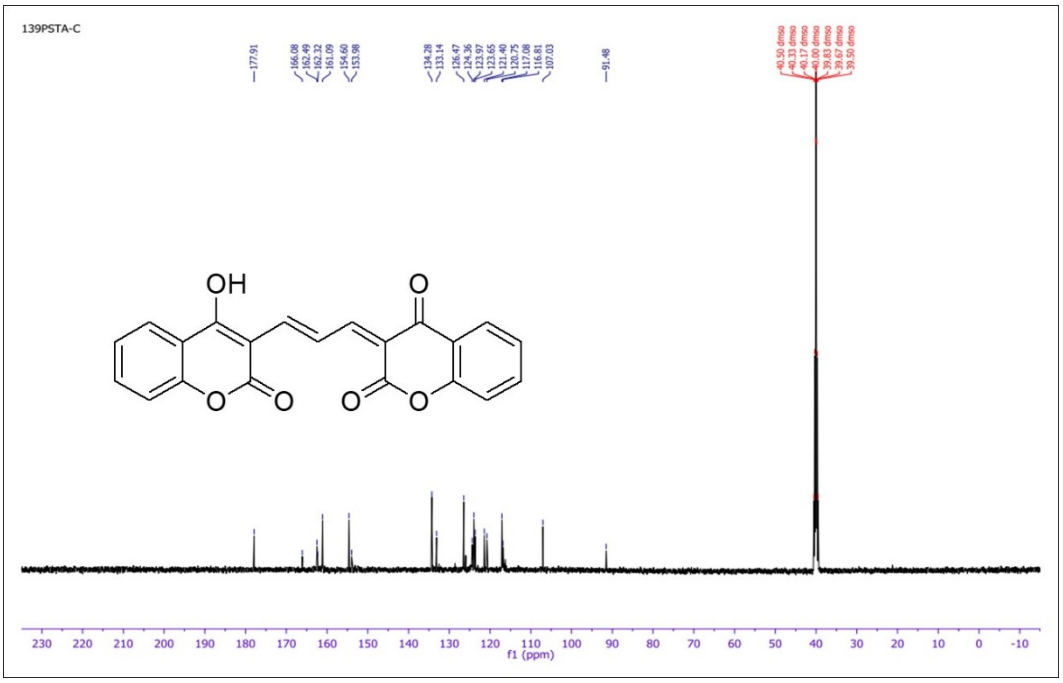


Figure D.1 ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra of **3**

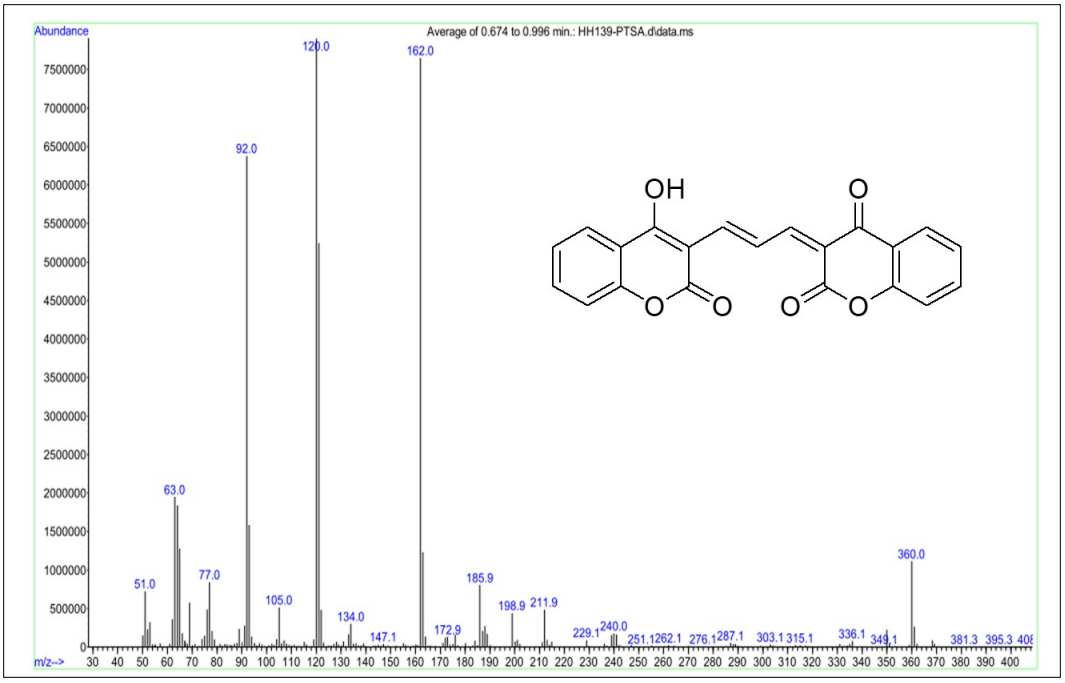
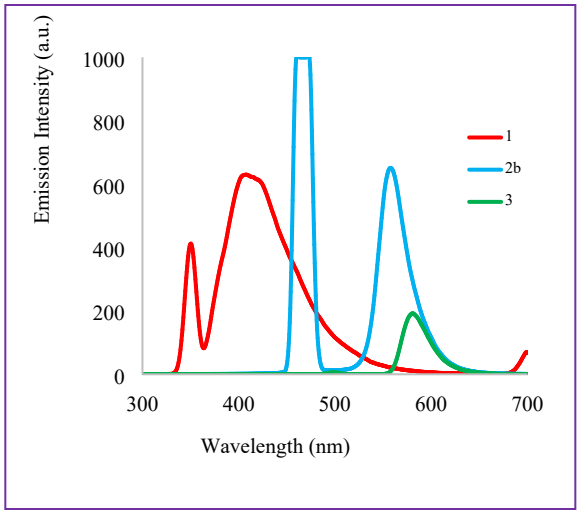


Figure D.2 Mass spectrum of **3**

A: 

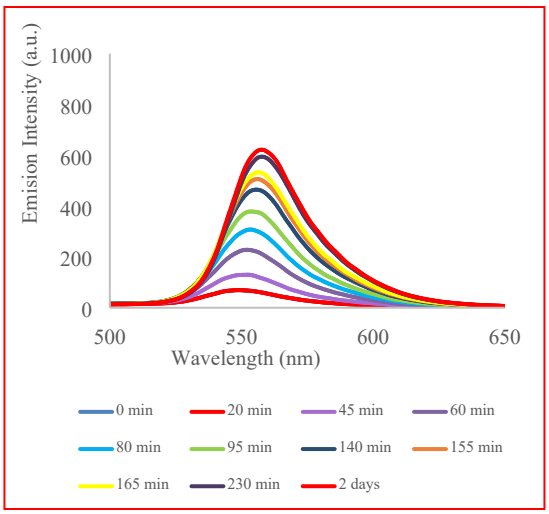
B 

Figure E.1 (A) Fluorescence spectrum of the synthesized compounds, (B) fluorescence change of 2a (0 min) converting to 2b (λ_{ex}= 470 nm, λ_{em}= 557 nm)

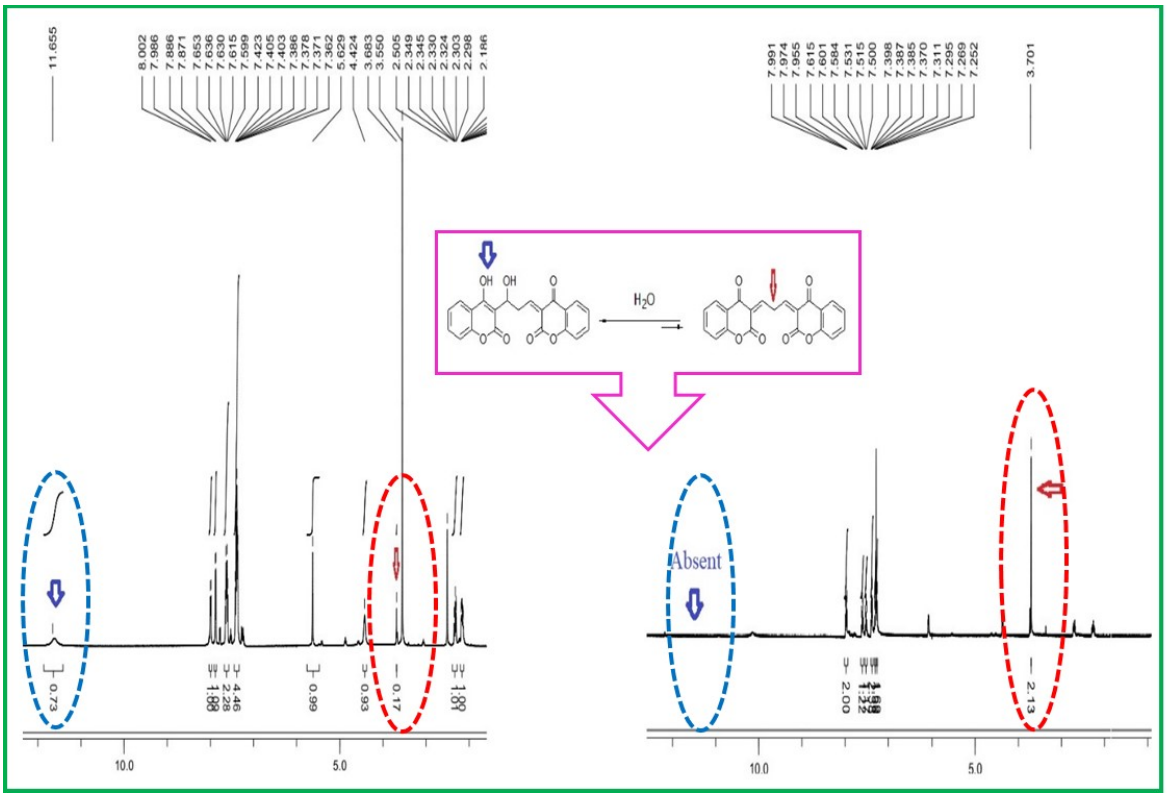
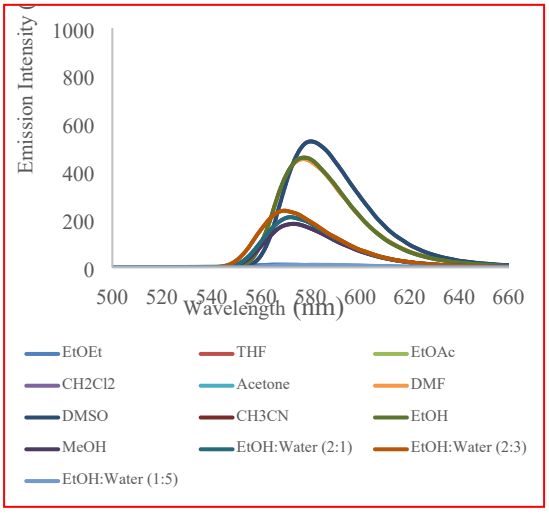


Figure F.1 [1]H NMR spectroscopy of compound **2a** (right) compared to compound **2b** (left)

A: 

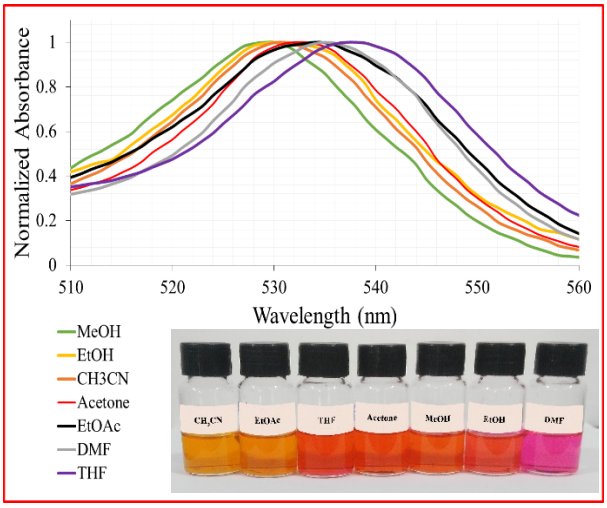
B: 

Figure G.1. solvatochromic effect of **3** (5.0×10^{-5} M) investigated via A) fluorescence emission (λ_{ex} = 480 nm) and B) UV-Vis absorption in different solvents; Inset: digital photographs of solvent-dependent color change.

A:

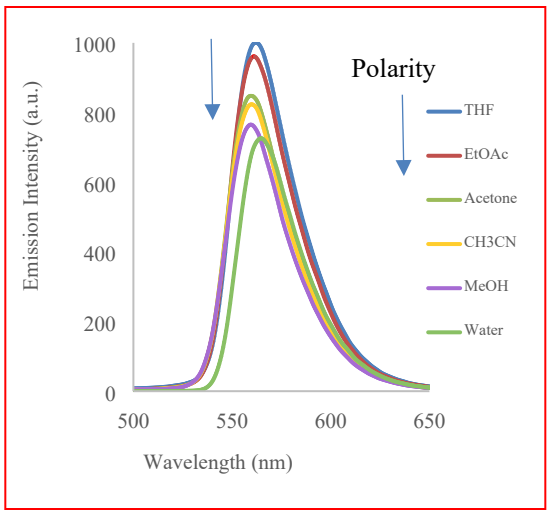
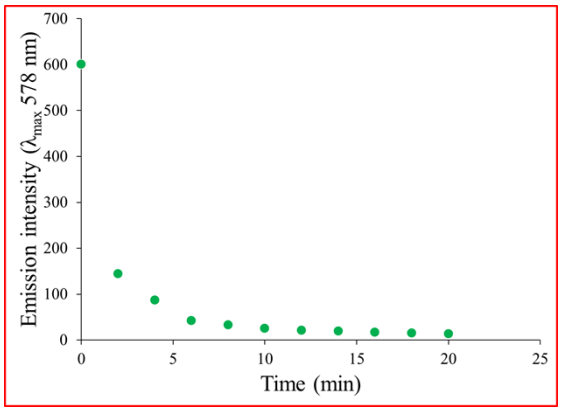


Figure G.2. Fluorescence emission of 2b (5.0×10^{-5} M) in different solvents (λ_{ex} = 470 nm)

A: 

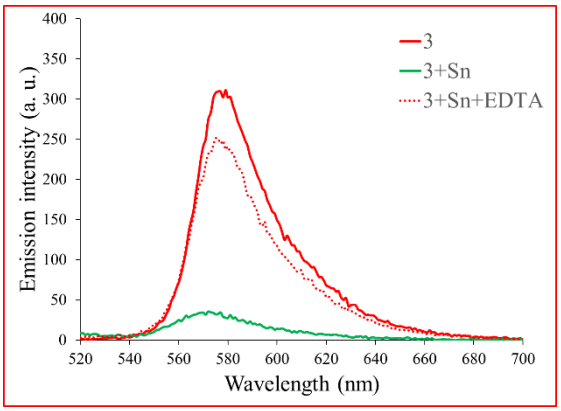
B: 

Figure H.1 A) Response time and B) Reversibility of 3 by the addition of EDTA to the 3+Sn^{2+} complex

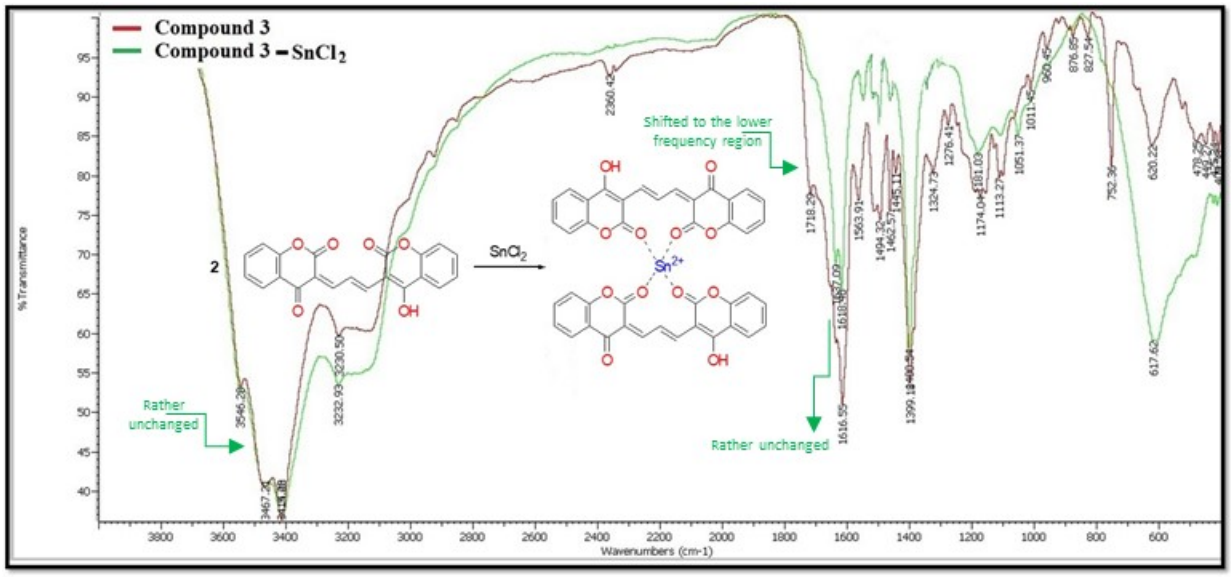
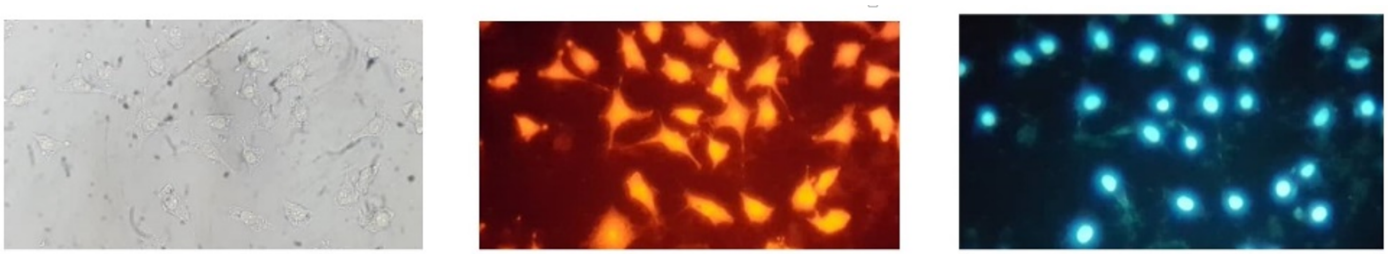


Figure I.1. The possible complex structure of compound **3** with Sn^{2+}



1 **2** **3**

Figure J.1. Microscopy images of the probe in MCF7 cells. The cells were incubated with probe (2.5×10-5 M) for 60 min at 37 °C, and washed with PBS for 3 times.

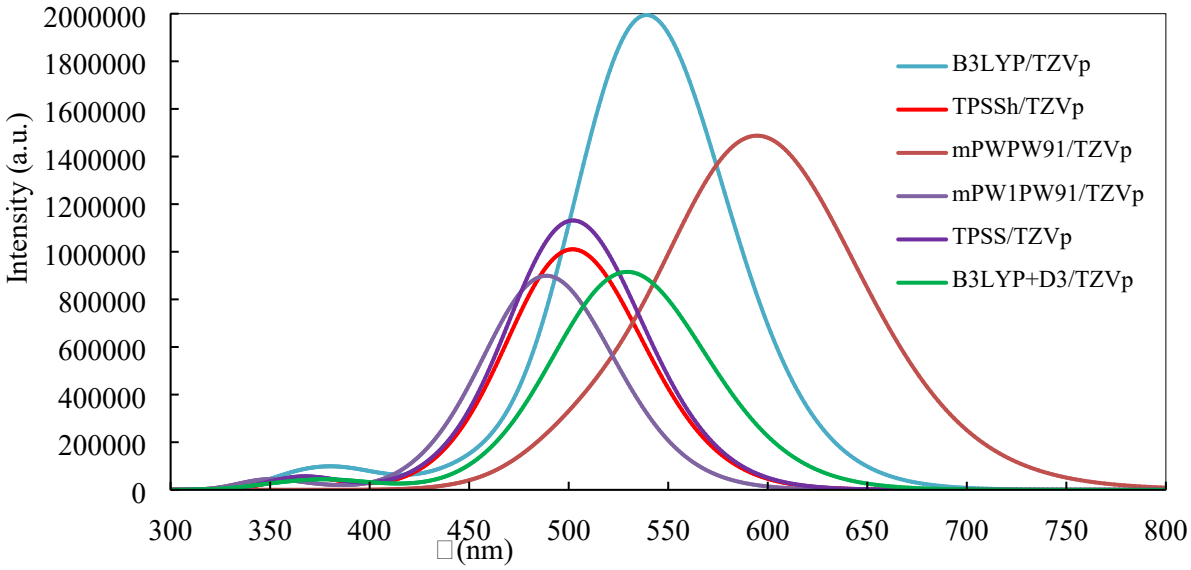
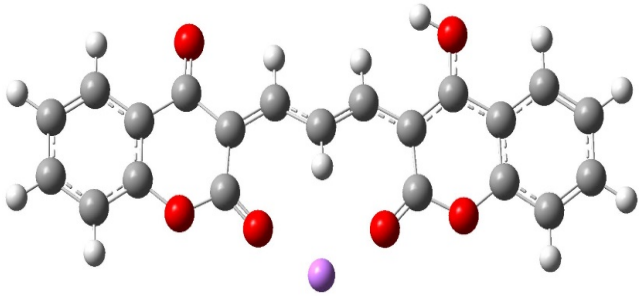
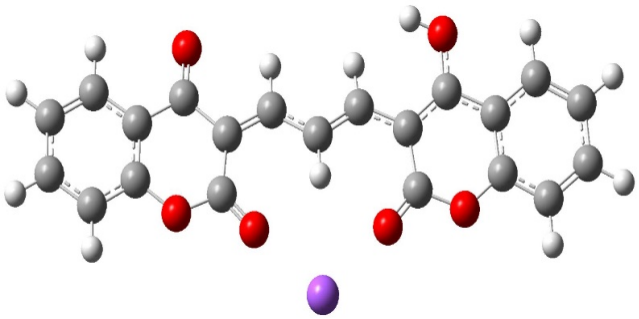


Figure K1. Fluorescence spectra of compound **3** at different levels of theory.



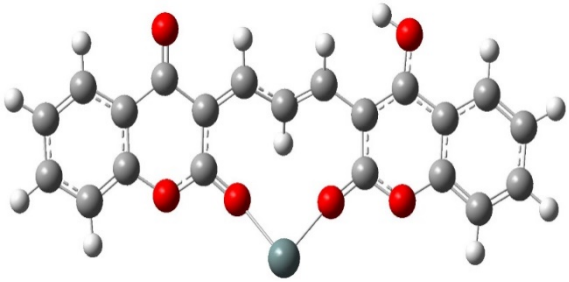
3-Li^{+}

E_{ads}= -7.38 kcal mol^{-1}



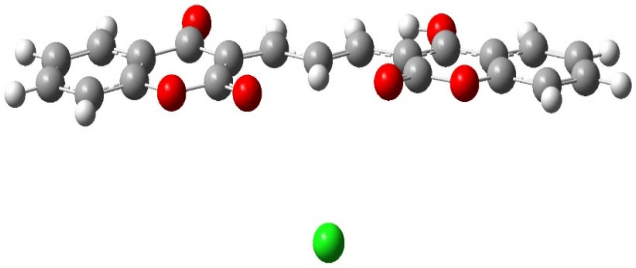
3-Na^{+}

E_{ads}= -9.27 kcal mol^{-1}



3-Sn^{2+}

E_{ads}= -73.41 kcal mol^{-1}



3-Cl^{-}

E_{ads}= -0.69 kcal mol^{-1}

Figure L.1 The most **s**table configurations for the adsorption of Sn^{+2}, Li^{+}, Na^{+}, and Cl^{-} over compound **3** in the EtOH-H_2O (2/3) medium.