Supplementary Material

Synthesis and characterization of a new hydrazone-coumarin chemosensor for Fe^{3+} in a water-acetonitrile mixture

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Appendix A: Proton NMR

The first step involved the dissolution of 37 g of powdered resorcinol in 45 ml of ethyl acetoacetate until a complete solution was obtained. This solution was then slowly added to a cold 150 ml solution of H_2SO_4, while maintaining the temperature below 10°C. The resulting mixture was stirred for 0.5 hours. Afterward, the mixture was poured into ice-cold water, and the solid product, 7-hydroxy-4-methyl-2H-chromen-2-one, was separated, filtered, and dried. Yield: 85%. M.p 157-167^{o}C. ^{1}H NMR (400 MHz, DMSO) 9.54 (1 H, s), 6.62 (1 H, d, *J* 8.6), 5.86 – 5.79 (1 H, m), 5.72 (1 H, s), 5.15 (1 H, s), 1.39 (3 H, s). ^{13}C NMR (400 MHz, DMSO) 158.56, 154.05, 152.85, 146.11, 128.60 , 113.54, 112.48, 111.68, 18.73.

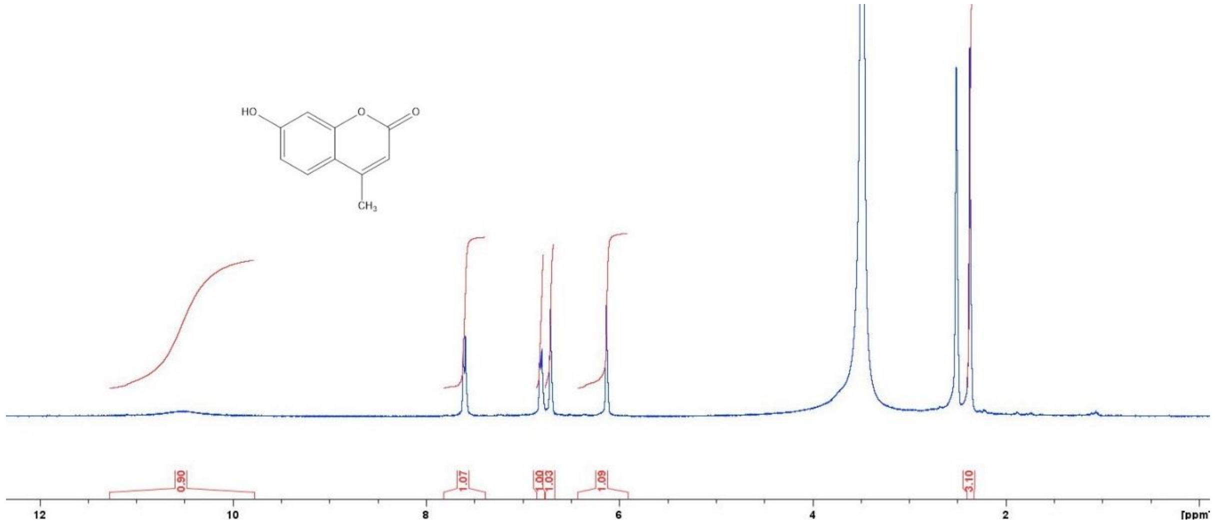


Figure S1. ^{1}H NMR spectra for 7-hydroxy-4-methyl-2H-chromen-2-one in DMSO.

7-hydroxy-4-methyl-2H-chromen-2-one was subjected to nitration using concentrated nitric acid and sulfuric acid at 5°C, resulting in the formation of two nitro isomers. The isomers were added to hot ethanol, and the filtrate was cooled in an ice bath to crystallize the product, 7-hydroxy-4-methyl-8-nitro-2H-chromen-2-one. The obtained product was then recrystallized from ethanol to ensure purity. Yield: 75%. M.p 109-117^{o}C. ^{1}H NMR (400 MHz, DMSO) 15.82, 12.17, 10.53, 8.29, 8.10, 7.82, 7.79, 7.61, 7.59, 7.07, 7.05, 7.00, 6.82, 6.80, 6.71, 6.31, 6.13, 5.90, 3.36, 2.68, 2.57, 2.51, 2.41, 2.37, 2.33, 2.25, 1.91, 1.06.^{13}C NMR (400 MHz, DMSO) 158.56, 154.05, 152.85, 146.11, 128.60 , 113.54, 112.48, 111.68, 18.73. FT-IR V/cm 3040 (OH), 1702 (C=O).

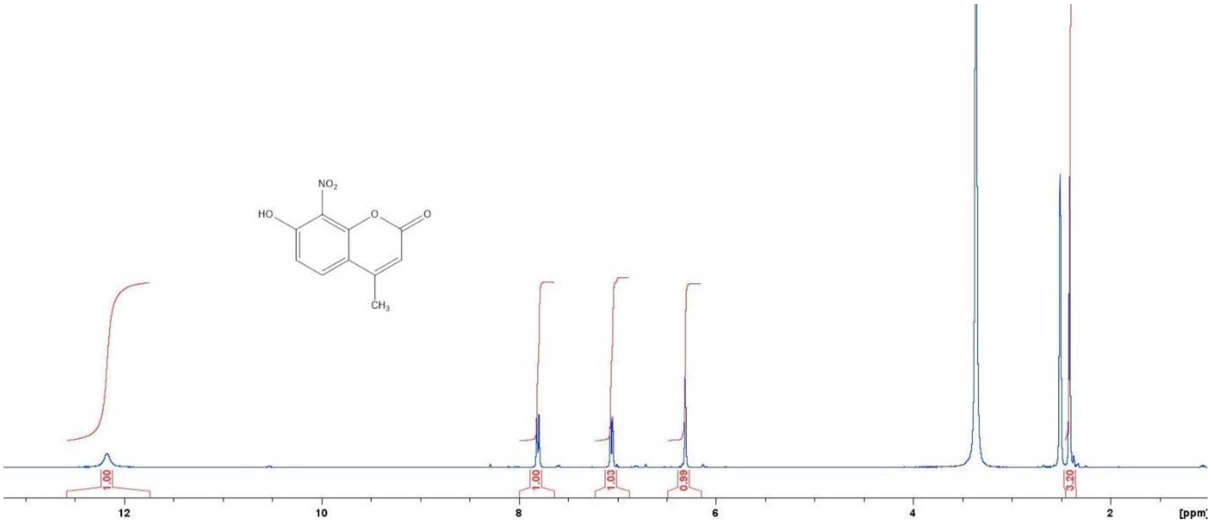


Figure S2. ^{1}H NMR spectra for 7-hydroxy-4-methyl-8-nitro-2H-chromen-2-one in DMSO.

Compound **(1)** was synthesis from literature proceeding [32].
Yield 67%. M.p 112-127 ^{o}C. ^{1}H NMR (400 MHz, DMSO) δ 11.71 (s, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.23 (s, 1H), 2.39 (s, 3H). ^{13}C (400 MHz, DMSO) 160.80, 154.56, 148.04, 141.75, 124.01, 112.89, 111.66, 110.39, 18.68. FT-IR V/cm 3040 (OH), 2380 (NH2), 1702 (C=O).

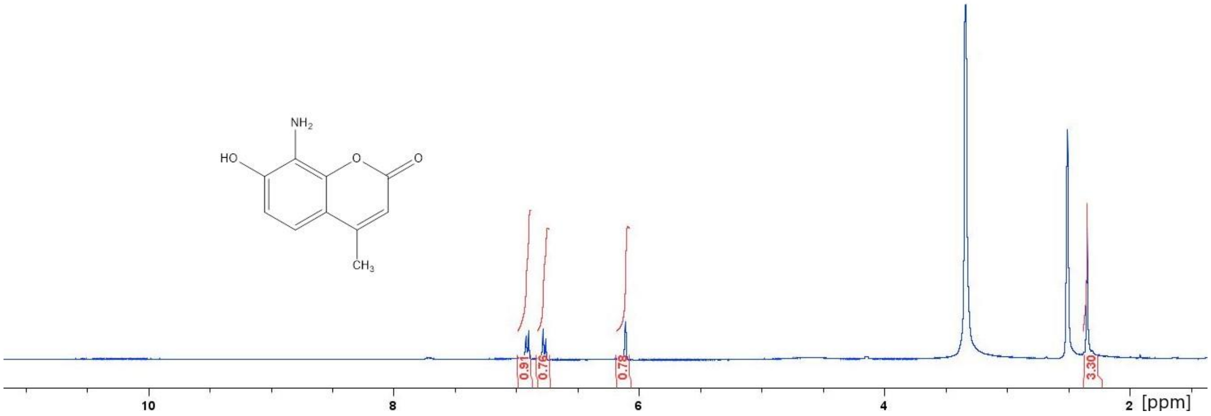


Figure S3. ^{1}H NMR spectra for 8-amino-7-hydroxy-4-methyl-2H-chromen-2-one (**1**) in DMSO.

Coumarin derivative (**2**) was synthesised by adding a solution mixture of 20 ml EtOH and 30 ml HCl (1M) to 1 (1.00 g, 5.70 mmol. The mixture was kept in ice until its temperature was below 5^{o}C. To the cooled mixture, $NaNO_2$ (2.00 g, 28.50 mmol) was added and the mixture stirred for 0.5 h to allow the reaction to take place. After 30 min of stirring, the resulted precipitate was filtered off, washed with water and dried under reduced pressure to afford the reddish brown azide -functionalized product 2. 63% yield. M.p 102-107^{o}C. ^{1}H NMR (400 MHz, DMSO) δ 7.75 (d, *J* = 8.3 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 1H), 6.12 (s, 1H), 2.39 (s, 3H).

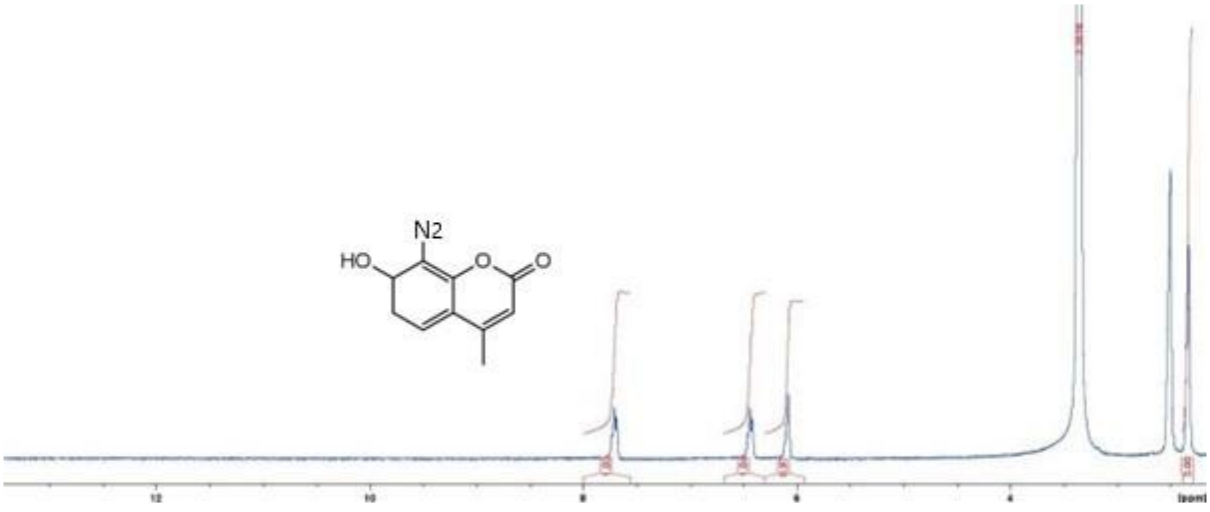


Figure S4. ^{1}H NMR spectra for (**2)** in DMSO.

Compound (**3**) was synthesised by adding compound **2** (0,5 g), but-3-yn-2-ol (2 mol eq), Cu_2SO_4 (0.02g, 0.054 mmol), sodium ascorbate (0.03 g, 0.15 mmol), and PMDETA (0.03 g, 0.15 mmol) were added to Tetrahydrofuran (THF) (20 mL) and stirred for 72 hours. THF was removed under reduced pressure and the resultant crude product was purified by column chromatography over silica gel (Hexane: Ethyl acetate, 70:30) to yield compound **3** as a yellow solid in 75% yield. m.p. 125–130 °C. IR vmax (cm− 1): 3393 (O-H), 3302 (≡ C-H), 1683 (C = O), 1601 (C = C). ^{1}H NMR (DMSO, 400 MHz): 10.88 (s, OH), 7.43 (s, 1H), 7.15 (d, *J* = 8.7 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.17 (s, 1NH), 4.46 (t, *J* = 6.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.37 (s, 2H).

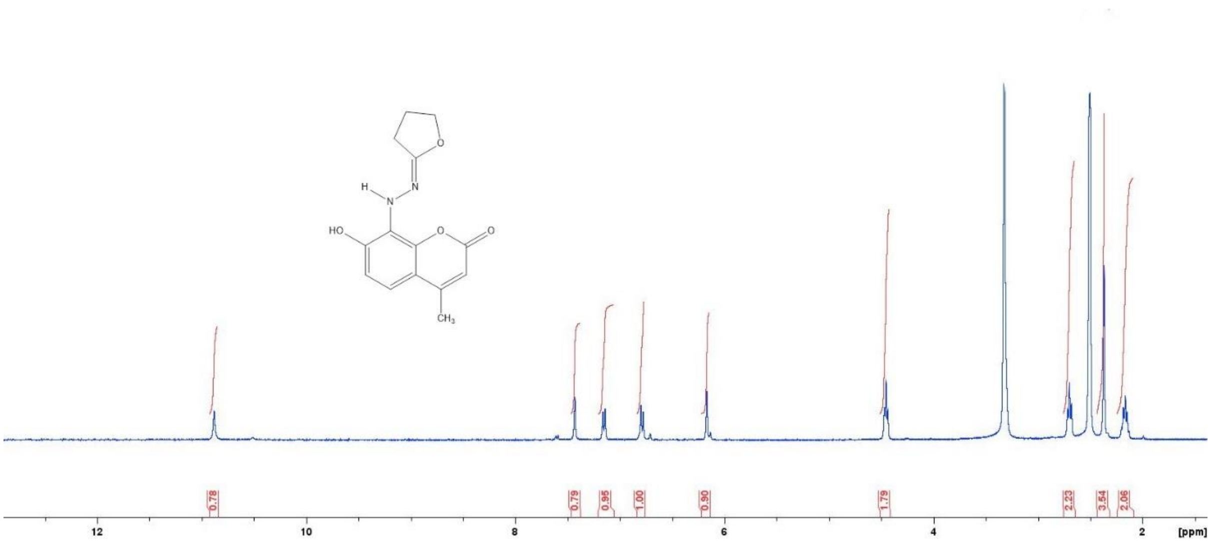


Figure S5. ^{1}H NMR spectra for (E)-8-(2-(dihydrofuran-2(3H)-ylidene)hydrazinyl)-7-hydroxy-4-methyl-2H-chromen-2-one (**3**) in DMSO.

Appendix A: Carbon NMR

63% yield. M.p 102-107°C. ^{1}H NMR (400 MHz, DMSO) δ 7.75 (d, *J* = 8.3 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 1H), 6.12 (s, 1H), 2.39 (s, 3H).

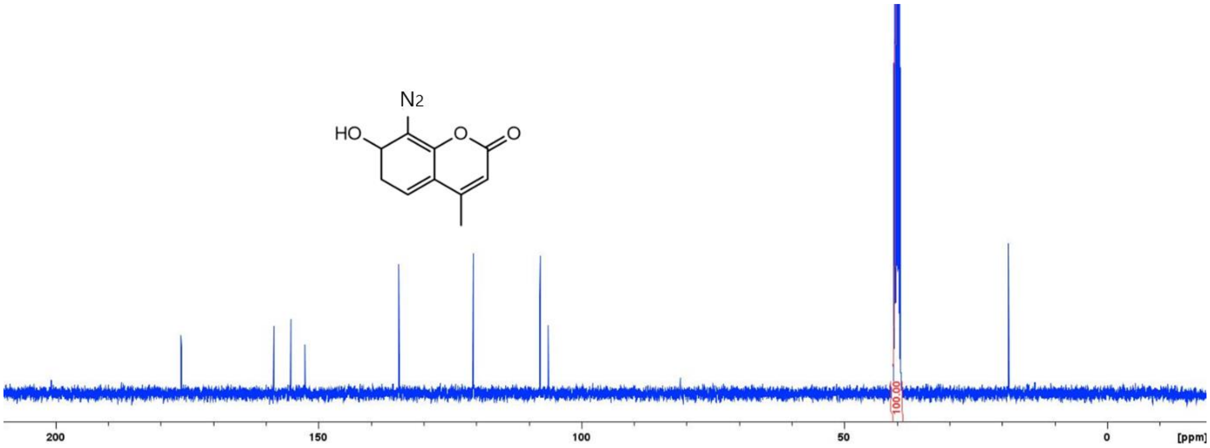


Figure S6. ^{13}C NMR spectra for (**2**) in DMSO.

^{13}C NMR (CDCl3, 400 MHz): δ = 162.06, 155.90, 150.64, 139.76, 129.11, 120.75, 109.07, 108.11, 97.17, 80.44, 71.26, 69.14, 44.82, 26.48, 12.42.

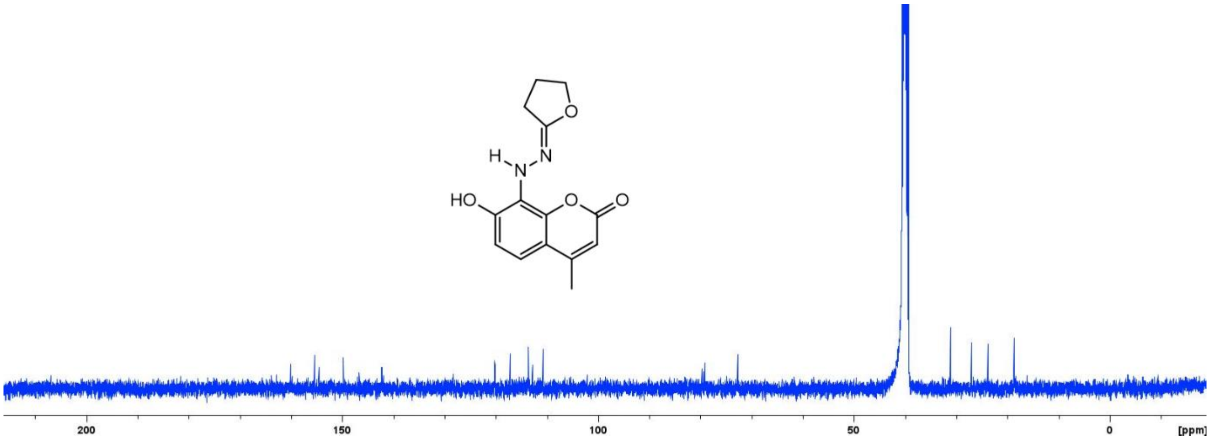


Figure S7. ^{13}C NMR spectra for (E)-8-(2-(dihydrofuran-2(3H)-ylidene)hydrazinyl)-7-hydroxy-4-methyl-2H-chromen-2-one (**3**) in DMSO.

Appendix B: IR-FT Spectra

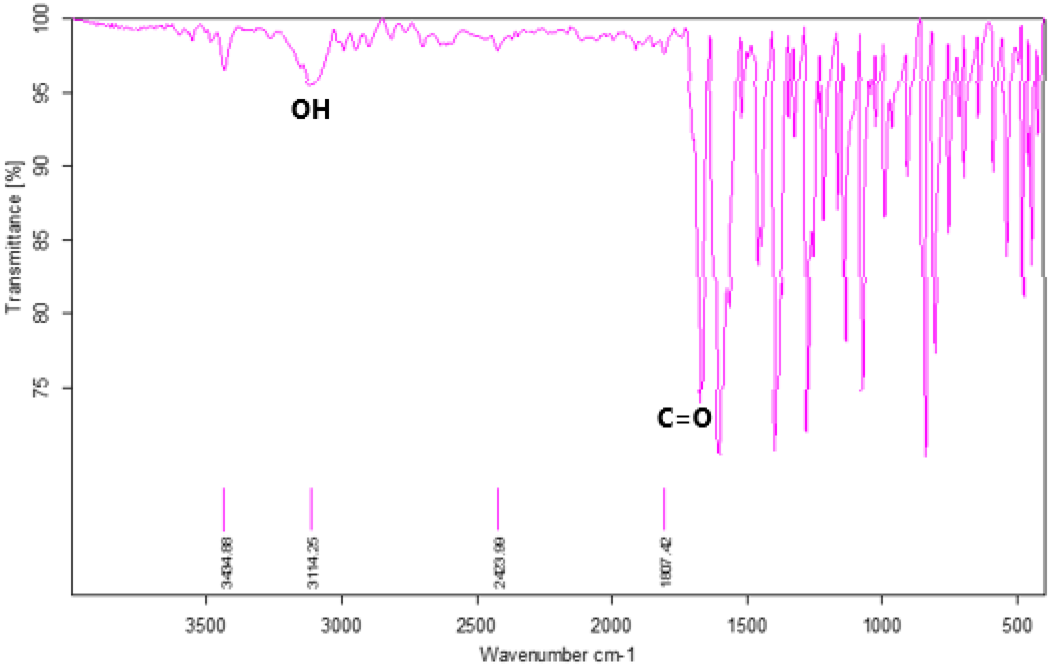


Figure S.8. FT-IR for spectra 7-hydroxy-4-methyl-2H-chromen-2-one.

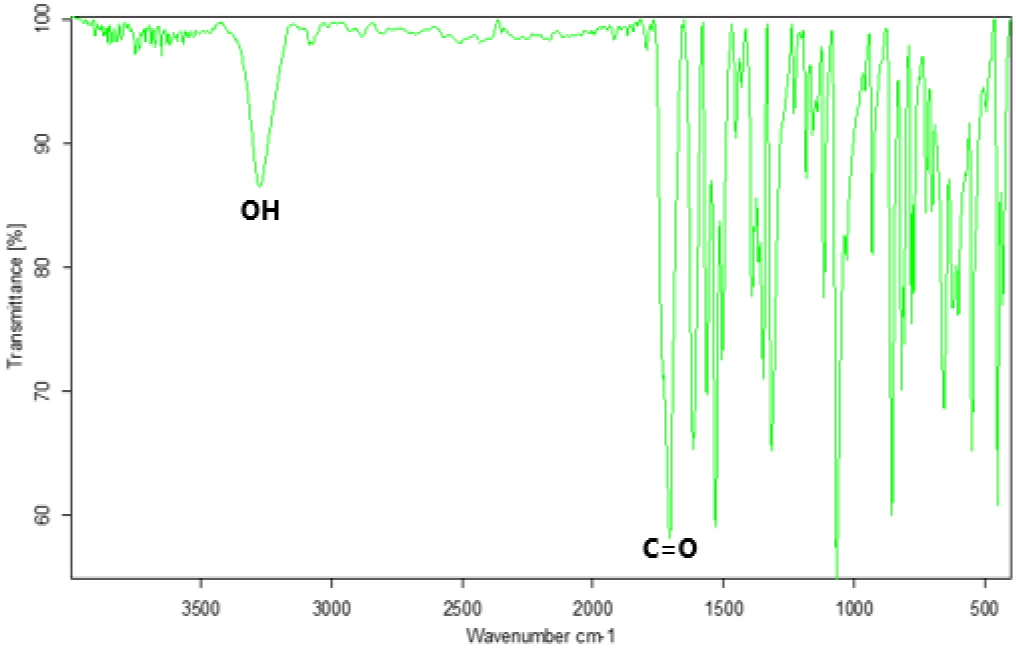


Figure S.9. FT-IR spectra for 7-hydroxy-4-methyl-8-nitro-2H-chromen-2-one.

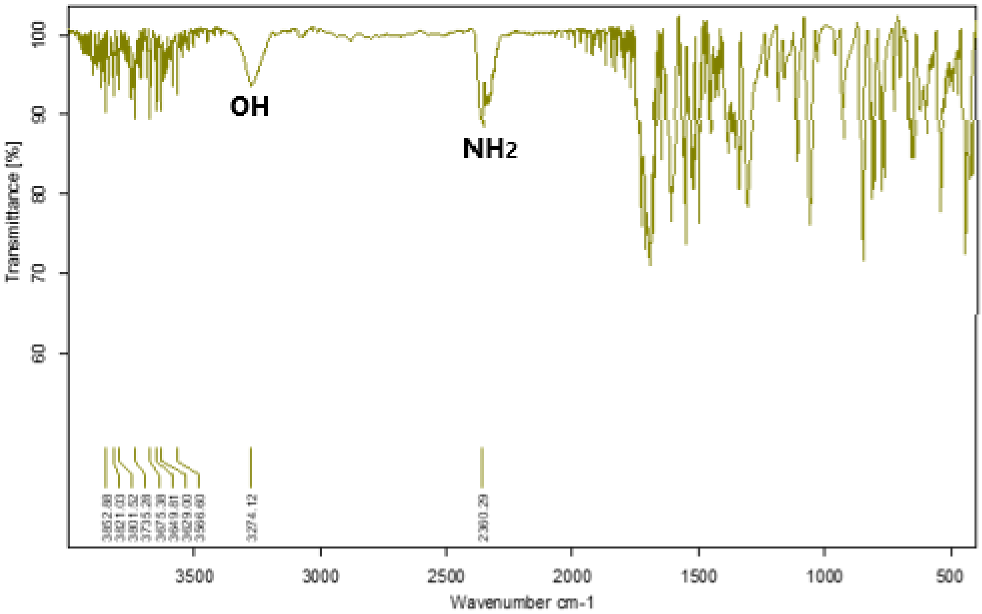


Figure S10. FT-IR spectra for 8-amino-7-hydroxy-4-methyl-2H-chromen-2-one (**1**).

FT-IR V/cm 2127 (N_2), 1702 (C=O).

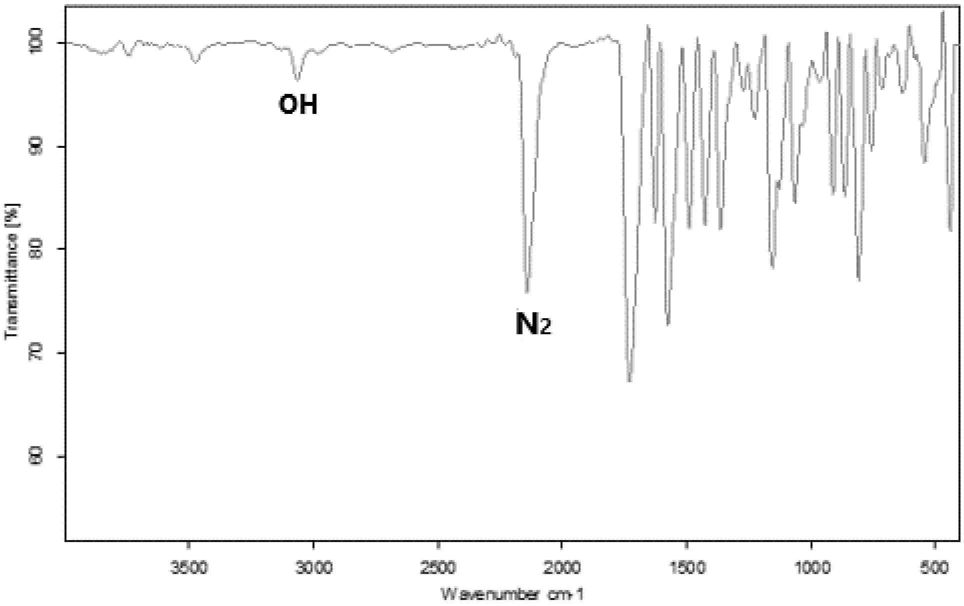


Figure S11. FT-IR spectra for 8-azido-7-hydroxy-4-methyl-6,7-dihydro-2H-chromen-2-one (**2**).

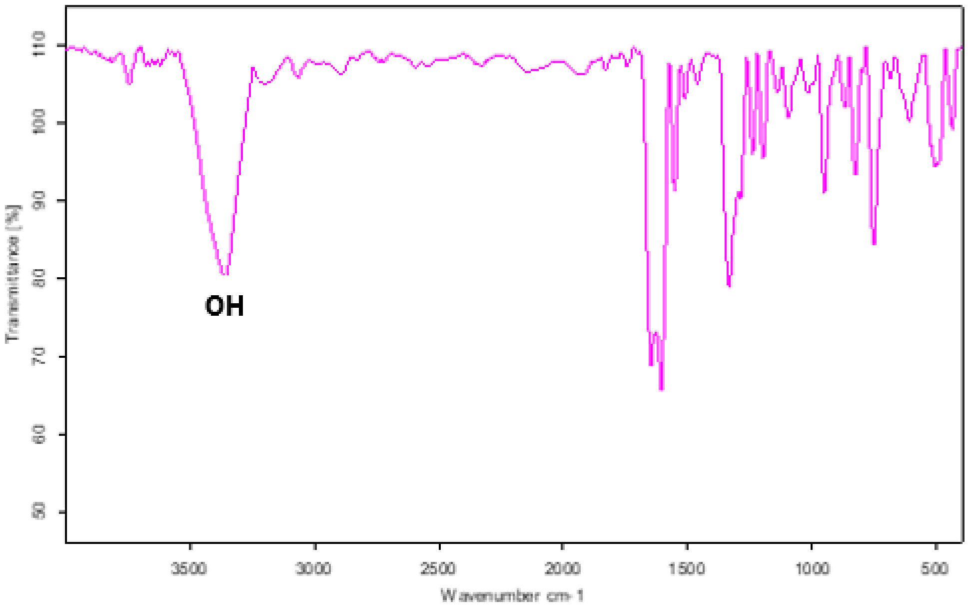
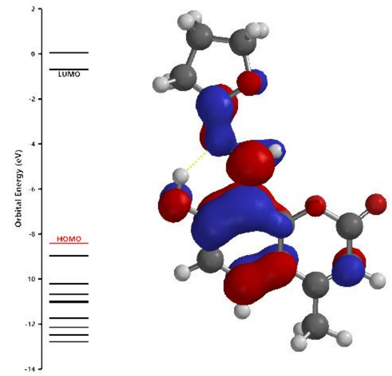


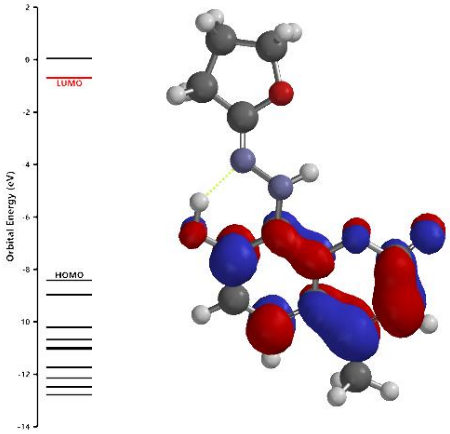
Figure S12. FT-IR spectra for (E)-8-(2-(dihydrofuran-2(3H)-ylidene)hydrazinyl)-7-hydroxy-4-methyl-2H-chromen-2-one (**3**).

Appendix C: Molecular modelling

In addition, in order to further study the ground state geometry and charge transfer of 3, sensors in gas phases were calculated on molecular mechanics level (MMFF), and semiempirical level (PM3) using Spartan ‘10 molecular modelling software.



HOMO (-8.4 eV)



LUMO (-0.7 eV)

Figure S13. Molecular modelling structure of HOMO and LUMO of 3.