Supporting Information

Design and Synthesis of Triazolyl Coumarin as a Selective Fluorescent Chemosensor for Hg^{2+}

I-Ting Ho,† Ting-Ling Lai † Ren-Tsung Wu,† Ming-Tsung Tsai, Chun-Ming Wu and Wen-Sheng Chung*

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050
E-mail: wschung@nctu.edu.tw
†Coauthors contributed equally to this work.

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Experimental section

General methods

^{1}H NMR spectra were measured with either a 300 MHz or 600 MHz spectrometers. Natural abundance ^{13}C NMR spectra were measured using pulse Fourier transform, with a 300 MHz NMR spectrometer operating at 75.4 MHz. All reported yields were from an average of three runs and were based on uncovered starting materials.

Synthetic procedures

*Synthesis of 3-(4-((4-tert-butylphenoxy)methyl)-1H-1,2,3-triazol-1-yl)-7-methoxycoumarin (**L1**).*

A mixture of 4-*tert*-butylphenyl propargyl ether (75 mg, 0.40 mmol) and coumarin **1** (90 mg, 0.41 mmol) in THF and water (v/v = 2:1, 30 mL) was added CuI (5 mg, 0.03 mmol). The heterogeneous mixture was stirred vigorously for 24 h. The solvent was removed under a vacuum, and the residue was re-dissolved in chloroform and washed with water. The chloroform solution was dried over $MgSO_4$ and evaporated to give the solid crude product. Column chromatography on silica gel eluting with hexane/ethyl acetate (v/v = 1/1) as eluent to give 87 mg (52%) of **L1**: mp 183-185 °C; R_f 0.30 (hexane/ethyl acetate = 4/1); ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H 8.68 (s, 1H; coumarin-*H*), 8.53 (s, 1H; C*H* of triazole), 7.57 (d, J = 8.7 Hz, 1H; coumarin-*H*), 7.35–7.29 (m, 2H; Ph-H), 7.01–6.88 (m, 4H; Ph-*H* and coumarin-*H*), 5.27 (s, 2H; CH_2-O), 3.92 (s, 3H; OCH_3), 1.30 (s, 9H; $C(CH_3)_3$); ^{13}C-NMR (75.4MHz, $CDCl_3$) δ_C 163.8 (Cq), 155.7 (Cq), 156.1 (Cq), 155.9 (Cq), 154.7 (Cq), 144.4 (Cq), 143.9 (Cq), 133.9 (CH), 129.9 (CH), 126.3 (CH), 123.8 (CH), 120.2 (Cq), 114.2 (Cq), 114.0 (CH), 111.4 (Cq), 100.7 (CH), 61.7 (CH_2), 56.0 (CH_3), 34.1 (Cq), 31.5 (CH_3); EI-MS m/z 405 $[M]^+$; HRMS (EI) calcd for $C_{23}H_{23}N_3O_4$ 405.1689, found 405.1690.

X-ray crystal data. $C_{23}H_{23}N_3O_4$; M = 405.44; T = 100(2) K; triclinic; a = 5.933(3) Å, b = 11.085(6) Å, c = 15.588(8) Å, α = 93.50(2)°, β = 92.85(2)°, γ = 93.01(2)°, V = 1020.4(9) Å^3; space group P$\bar{1}$; Z = 2; ρ_{calcd} = 1.320 mg m^{-3}; crystal dimensions 0.17 × 0.15 × 0.06 mm^3; λ (Mo K$_\alpha$) = 0.71073 Å; μ = 0.092 mm^{-1}; 13644 reflections collected; 4137 independent reflections [R_{int} = 0.0764]; 275 parameter refined on F^2; R_1 = 0.0763, wR2[F^2] = 0.1373 (all data); GOF on F^2 0.973, $\Delta\rho_{max}$ = 0.373 eÅ^{-3}. CCDC 870923 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

*Synthesis of 3-azidomethyl-7-methoxycoumarin (**3**).*

To a solution of 3-bromomethyl-7-methoxycoumarin **2** (270 mg, 1 mmol) in acetone (15 mL) was added NaN_3 (131 mg, 2 mmol). The reaction mixture was refluxed for 1 h. The residual NaN_3 was filtered out and the filtrate was washed with water and extracted with $CHCl_3$ (10 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and evaporated to dryness affording 226 mg (98%) of **3** as a cream-color solid: mp 104–105 °C; R_f 0.19 (CH_2Cl_2/n-Hexane = 2:1); ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.69 (s, 1H; coumarin-*H*), 7.41 (d, *J* = 8.5 Hz, 1H; coumarin-*H*), 6.90–6.84 (m, 2H; coumarin-*H*), 4.34 (2H; C*H*$_2$-N_3), 3.89 (s, 3H; OC*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_c 162.9 (Cq), 160.9 (Cq), 155.3 (Cq), 140.4 (CH), 128.9 (CH), 120.0 (Cq), 113.0 (CH), 112.3 (Cq), 100.6 (CH), 55.8 (CH_3), 50.0 (CH_2); EI-MS m/z 231 $[M]^+$; HRMS (EI) calcd for $C_{11}H_9N_3O_3$ 231.0644, found 231.0652.

*Synthesis of 3-((4-((4-tert-butylphenoxy)methyl)-1H-1,2,3-triazol-1-yl)methyl)-7- methoxy-courmarin (**L2**).*

3-Azidomethyl-7-methoxycoumarin **3** (231 mg, 1 mmol) was added to the suspension of 4-*tert*-butylphenyl propargyl ether (188 mg, 1 mmol) and CuI (20 mg, 0.11 mmol) in THF/H_2O (8 mL, v/v = 3:1). The reaction mixture was vigorously stirred at 40 °C for 3 h. Acetone (20 mL) was added to the resulting suspension for dissolving organic compound, and the insoluble inorganic precipitate was then filtered out. The filtrate was washed with water (20 mL) and extracted with $CHCl_3$ (15 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and evaporated to give a pale gray solid. The crude product was further purified by column chromatography on silica gel (Et_2O/CH_2Cl_2 = 1:15) to afford 360 mg (85%) of **L2** as a white solid: mp 145–147 °C; R_f 0.47 (Et_2O/CH_2Cl_2 = 1:5); ^1H NMR($CDCl_3$, 300 MHz) δ_H 7.91 (s, 1H; C*H* of triazole), 7.66 (s, 1H; coumarin-*H*), 7.36 (d, *J* = 8.6 Hz, 1H; coumarin-*H*), 7.32–7.29 (m, 2H; Ph-*H*), 6.95–6.90 (m, 2H; Ph-*H*), 6.86 (dd, J_1 = 8.6 Hz, J_2 = 2.4 Hz, 1H; coumarin-*H*), 6.82 (d, *J* = 2.4 Hz, 1H; coumarin-*H*), 5.44 (s, 2H; C*H*$_2$-O), 5.19 (s, 2H; C*H*$_2$-triazole), 3.88 (s, 3H; OCH_3), 1.27 (s, 9H; C(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_c 163.4 (Cq), 161.1 (Cq), 155.9 (Cq), 155.7 (Cq), 143.9 (Cq), 142.7 (CH), 129.3 (CH), 126.3 (CH), 118.9 (Cq), 114.2 (CH), 113.2 (CH), 112.1 (Cq), 100.7 (CH), 62.0 (CH_2), 55.9 (CH_3), 49.2 (CH_2), 34.1 (Cq), 31.5 (CH_3); EI-MS m/z 419 $[M]^+$; HRMS (EI) calcd for $C_{24}H_{25}N_3O_4$ 419.1845, found 419.1844.

Synthesis of 3-azidoacetyl-7-methoxycoumarin (5).

A solution of 3-bromoacetyl-7-methoxycoumarin **4** (297 mg, 1 mmol) in acetone (75 mL) was treated with NaN_3 (195 mg, 3 mmol). The reaction mixture was refluxed for 2.5 h. The residual NaN_3 was subsequently filtered off, and the filtrate was concentrated under reduced pressure to give a dark brown solid. It was re-dissolved with $CHCl_3$ (25 mL) and washed with water (10 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and evaporated into dryness to yield a brown solid. The crude product was then washed with an appropriate amount of MeOH to afford 226 mg (87%) of **5** as a pale brown solid: mp 158–160 °C ($CHCl_3$); R_f 0.21 (CH_2Cl_2/n-Hexane = 2:1); ^1H NMR ($CDCl_3$, 300 MHz) δ_H 8.65 (s, 1H; coumarin-*H*), 7.60 (d, *J* = 8.8 Hz, 1H; coumarin-*H*), 6.94 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H;

coumarin-*H*), 6.84 (d, *J* = 2.4 Hz, 1H; coumarin-*H*), 4.70 (s, 2H; CH_2-N_3), 3.93 (s, 3H; OCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_c 191.0 (Cq), 166.0 (Cq), 159.5 (Cq), 158.0 (Cq), 149.4 (CH), 131.9 (CH), 118.0 (Cq), 114.4 (CH), 111.9 (Cq), 100.4 (CH), 58.6 (CH_2), 56.2 (CH_3); EI-MS m/z 259 $[M]^+$; HRMS (EI) calcd for $C_{12}H_9N_3O_4$ 259.0593, found 259.0598.

*Synthesis of 3-(2-(4-((4-tert-butylphenoxy)methyl)-1H-1,2,3-triazol-1-yl)acetyl)-7-methoxy-coumarin (**L3**).*

3-Azidoacetyl-7-methoxycoumarin **5** (259 mg, 1 mmol) was added to the suspension of 4-*tert*-butylphenyl propargyl ether (188 mg, 1 mmol) and CuI (20 mg, 0.11 mmol) in THF/H_2O (8 mL, v/v = 3:1). The reaction mixture was vigorously stirred at 40 °C for overnight. Hot $CHCl_3$ (50 mL) was added to the resulting suspension for dissolving the organic compound. The insoluble inorganic precipitate was filtered off in vacuum, and the filtrate was then washed with water (10 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give a pale yellow solid. The crude product was further purified by column chromatography on silica gel (Et_2O/CH_2Cl_2 = 1:9) to give 319 mg (71%) of **L3** as a milk white solid: mp 260–262 °C; R_f 0.40 (Et_2O/CH_2Cl_2 = 1:9); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 8.63 (s, 1H; H_e), 7.71 (s, 1H; H_g), 7.61 (d, *J* = 8.8, 1H; H_d), 7.33–7.26 (m, 2H; H_i), 6.98–6.93 (m, 3H; H_c and H_j), 6.88 (d, *J* = 2.3, 1H; H_f), 5.94 (s, 2H; H_b), 5.25 (s, 2H; H_h), 3.95 (s, 3H; H_a), 1.28 (s, 9H; C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_c 188.4 (Cq), 166.4 (Cq), 159.8 (Cq), 158.2 (Cq), 156.0 (Cq), 150.0 (CH), 143.9 (Cq), 132.1 (CH), 126.3 (CH), 117.5 (Cq), 114.6 (CH), 114.2 (CH), 111.9 (Cq), 100.5 (CH), 62.1 (CH_2), 58.9 (CH_2), 56.2 (CH_3), 34.1 (Cq), 31.5 (CH_3); EI-MS m/z 447 $[M]^+$; HRMS (EI) calcd for $C_{25}H_{25}N_3O_5$ 447.1794, found 447.1797.

X-ray crystal data. $C_{25}H_{25}N_3O_5$; M = 447.48; T = 220(2) K; triclinic; a = 5.7298(4) Å, b = 11.4420(8) Å, c = 17.7012(13) Å, α = 96.531(2)°, β = 96.165(2)°, γ= 93.056(2)°, V = 1143.77(14) Å^3; space group $P\bar{1}$; Z = 2; ρ_{cald} = 1.299 mg m^{-3}; crystal dimensions 0.60 × 0.10 × 0.04 mm^3; l (Mo K) = 0.71073 Å; μ= 0.092 mm^{-1}; 10379 reflections collected; 4027 independent reflections [R_{int} = 0.0393]; 303 parameter refined on F^2; R_1 = 0.0805, wR2[F^2] = 0.1918 (all data); GOF on F^2 1.106; $\Delta\rho_{max}$ = 0.784 eÅ^{-3}. CCDC 870924 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

*Synthesis of 3-(2-(4-benzyl-1H-1,2,3-triazol-1-yl)acetyl)-7-methoxy-coumarin (**L4**).*

The synthetic procedure was adapted from that used for **L3**. 3-Azidoacetyl-7-methoxycoumarin **5** (102 mg, 0.39 mmol) and prop-2-ynylbenzene (45 mg, 0.39 mmol) were used. The reaction mixture was separated by column chromatography to give 79 mg (50%) of **L4** as a pale yellow solid: mp 262–264 °C ($CHCl_3$); R_f 0.43

(CH_2Cl_2/Et_2O = 5:1); ^{1}H NMR (D_6-DMSO, 300 MHz) δ_H 8.79 (s, 1H; H_e), 7.94 (d, J = 8.7 Hz, 1H; H_d), 7.77 (s, 1H; H_g), 7.31–7.21 (m, 5H; Ph-*H*), 7.15 (d, J = 2.3 Hz, 1H; H_f), 7.07 (dd, J_1 = 8.7 Hz, J_2 = 2.3 Hz, 1H; H_c), 5.91 (s, 2H; H_b), 4.04 (s, 2H; H_h), 3.92 (s, 3H; H_a); ^{13}C NMR (D_6-DMSO, 75 MHz) δ_c 189.4 (Cq), 165.6 (Cq), 159.1 (Cq), 157.5 (Cq), 149.1 (CH), 145.9 (Cq), 139.7 (Cq), 132.8 (CH), 128.6 (CH), 128.5 (CH), 126.2 (CH), 124.3 (CH), 118.2 (Cq), 114.0 (CH), 111.9 (Cq), 100.5 (CH), 69.9 (CH_2), 58.2 (CH_2), 56.5 (CH_3); EI-MS m/z 375 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{17}N_3O_4$: 375.1219, found 375.1222.

General procedures for the UV-Vis and fluorescence experiments.

UV-vis spectra were recorded on a spectrophotometer with a diode array detector, and the resolution was set at 1 nm. Fluorescence spectra were recorded on a luminescence spectrophotometer. For all measurements of fluorescence spectra, excitation was at 308 nm with the excitation and emission slit width at 4.0 nm. UV-Vis and fluorescence titration experiments were performed with 20 μM solutions of coumarins **L1–L4** and varying concentrations of metal perchlorate in MeOH-$CHCl_3$ (9:1, v/v). During the measurements the temperature of the quartz sample cell and chamber was kept at 25 °C.

General procedures for quantum yield measurements.

The relative fluorescence quantum yields were determined by comparison of the integrated area of the emission spectra of the samples with respect to anthracene in EtOH (Φ = 0.27). For the metal-free studies, coumarin **L3** and **L4** were prepared in 20 μM in MeOH-$CHCl_3$ (9:1, v/v). For the metal-bound studies, 10 equiv $Hg(ClO_4)_2$ were added to coumarin **L3** and **L4** (20 μM) in MeOH-$CHCl_3$ (9:1, v/v). Emission spectra of these samples were integrated from 350 to 600 nm with excitation at 374 nm. The relative fluorescence quantum yields were calculated using the equation: $\Phi = (A_{ref}/A)*(F/F_{ref})*(n_{MeOH}^2/n_{EtOH}^{\ 2})*\ \Phi_{ref}$, where A is the absorbance at the excitation wavelength, F is the integrated emission area and n is the refractive index of the solvent (n_{MeOH} = 1.3282, n_{EtOH} = 1.3640 at 25 °C).

General procedures for fluorescence lifetime measurements.

The fluorescence lifetime was measured by computer controlled Time Correlated Single Photon Counting (TCSPC) spectrometer with sub-nanosecond pulse LED at 375 nm excitation wavelength. LED was driven by an oscillator module (PDL 200-B, Picoquant, Germany) at a repetition rate of 8 MHz. The fluorescence lifetime measurements were performed with 20 μM solutions of coumarins (**L3** and **L4**) and varying concentrations of $Hg(ClO_4)_2$ in MeOH-$CHCl_3$ (9:1, v/v) at room temperature. The sample was degassed by bubbling of N_2 (g) through the solution for 2 min. Fluorescence lifetime data were analyzed using the software provided by FluoroFit (Picoquant, Germany) which is based on re-convolution technique using iterative non-linear least-square methods.

General procedures for the ^{1}H-NMR titration experiments.

^{1}H-NMR titration spectra were recorded at 300 or 600 MHz with tetramethylsilane (TMS) in a coaxial capillary tube as an external standard. Experiments were performed with 2.5 mM solutions of **L3** and **L4** in $CD_3OD–CDCl_3$ (1:1, v/v) by adding various concentrations of $Hg(ClO_4)_2$ at 25 °C.

General procedures for the detection limit measurements.

The detection limit (C_{DL}) of Hg^{2+} by **L3** and **L4** (20 μM) in MeOH-$CHCl_3$ (9:1, v/v) was determined using the equation: $C_{DL}= k_D*S_b/m$, where S_b denotes the standard deviation of blank solution (without analyte), *m* is the sensitivity that agrees with the slope of the calibration curve. For k_D, a value of 3 is recommended. The S_b was obtained from the results of 20 separate measurements.

Ligand	Slope, *m*	R^2	Standard deviation, S_b	Detection limit, C_{DL}
L3	306676	0.988	0.0205	2.00×10^{-7} M
L4	150185	0.9896	0.0158	3.15×10^{-7} M

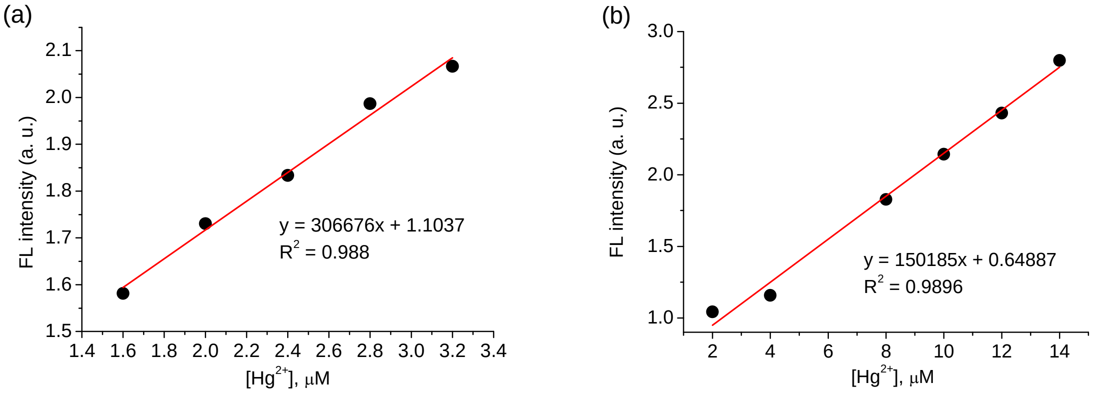

Figure Sa. Calibration curve of (a) **L3** and (b) **L4** (20 μM) in MeOH-$CHCl_3$ (9:1, v/v). Excitation wavelength was 367 nm. The fluorescence intensities of **L3** and **L4** were recorded at 423 nm and 427 nm, respectively.

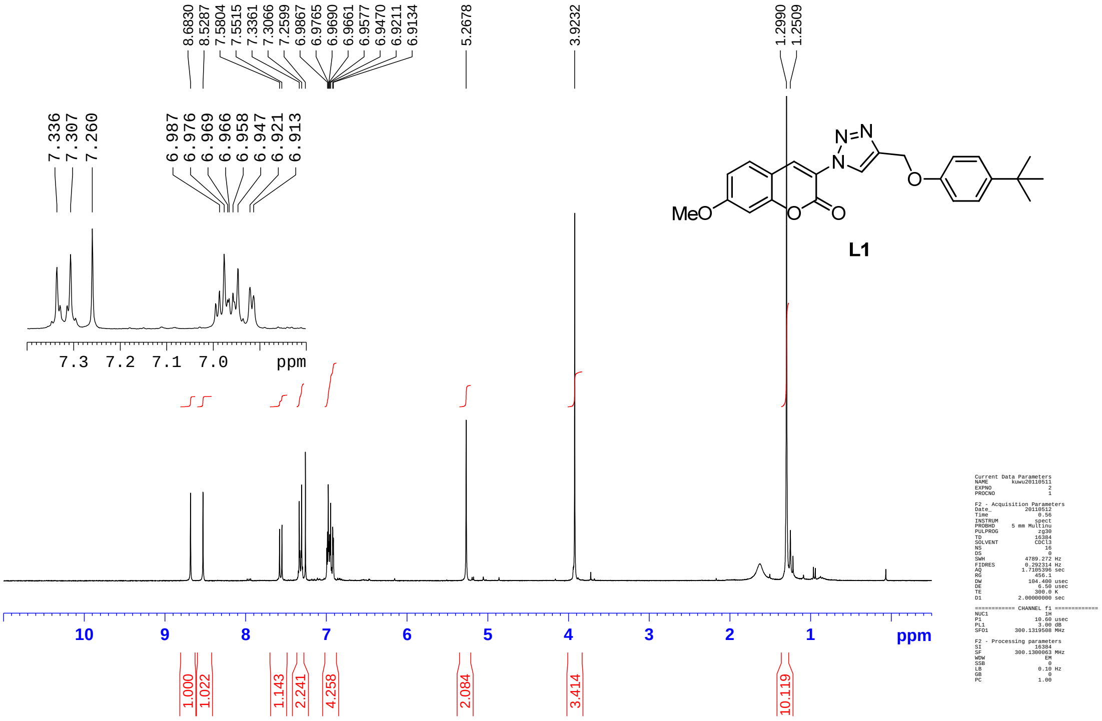

Figure S1. ^{1}H-NMR (300 MHz, $CDCl_3$) of spectrum 3-(4-((4-tert-butylphenoxy)-methyl)-1*H*-1,2,3-triazol-1-yl)-7-methoxycoumarin **L1**.

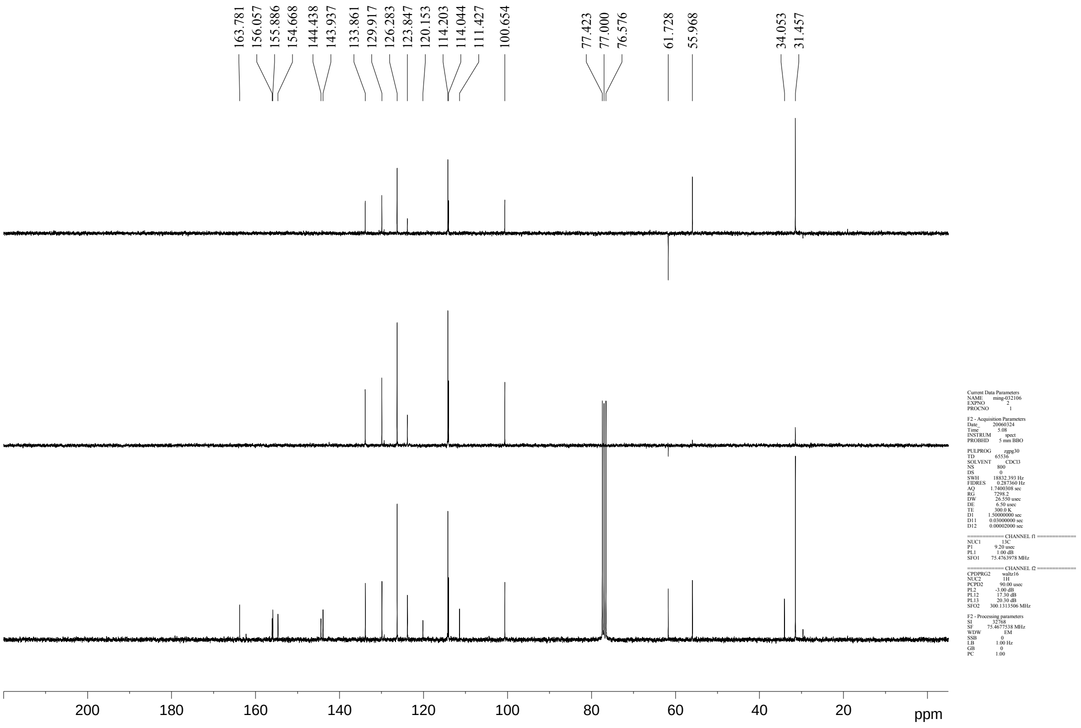

Figure S2. ^{13}C-NMR and DEPT (300 MHz, $CDCl_3$) of spectra of 3-(4-((4-tert-butyl-phenoxy) -methyl)-1*H*-1,2,3-triazol-1-yl)-7-methoxycoumarin **L1**.

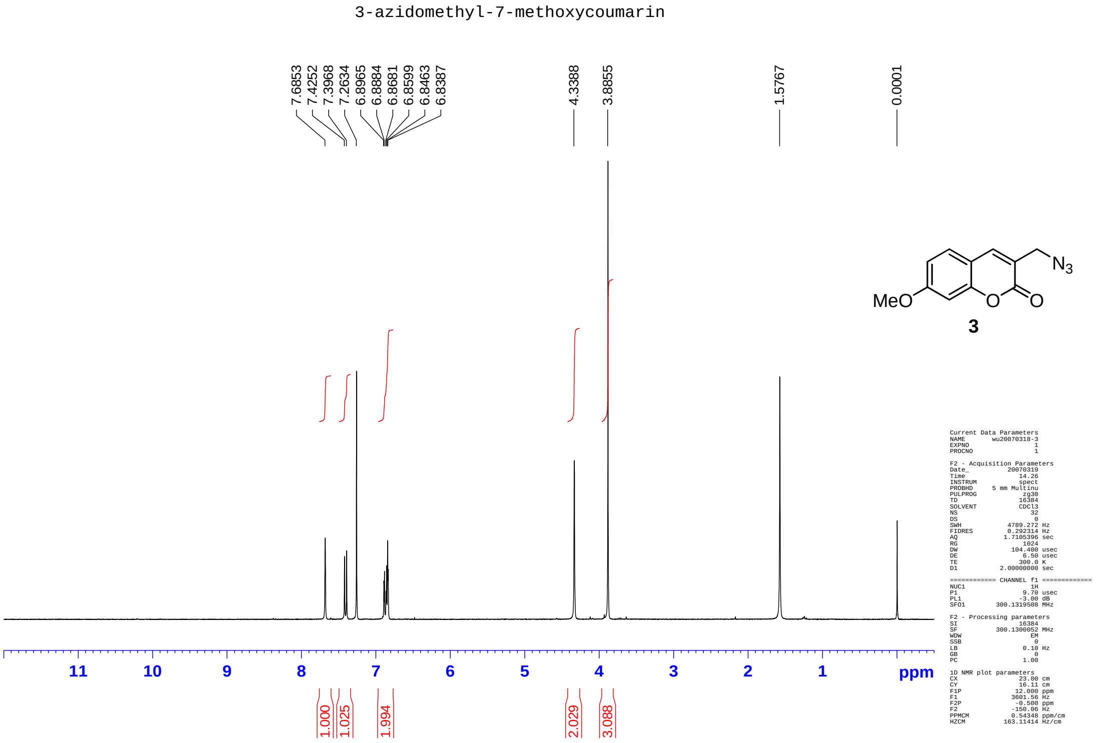

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Figure S3. ^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 3-azidomethyl-7-methoxycoumarin **3**.

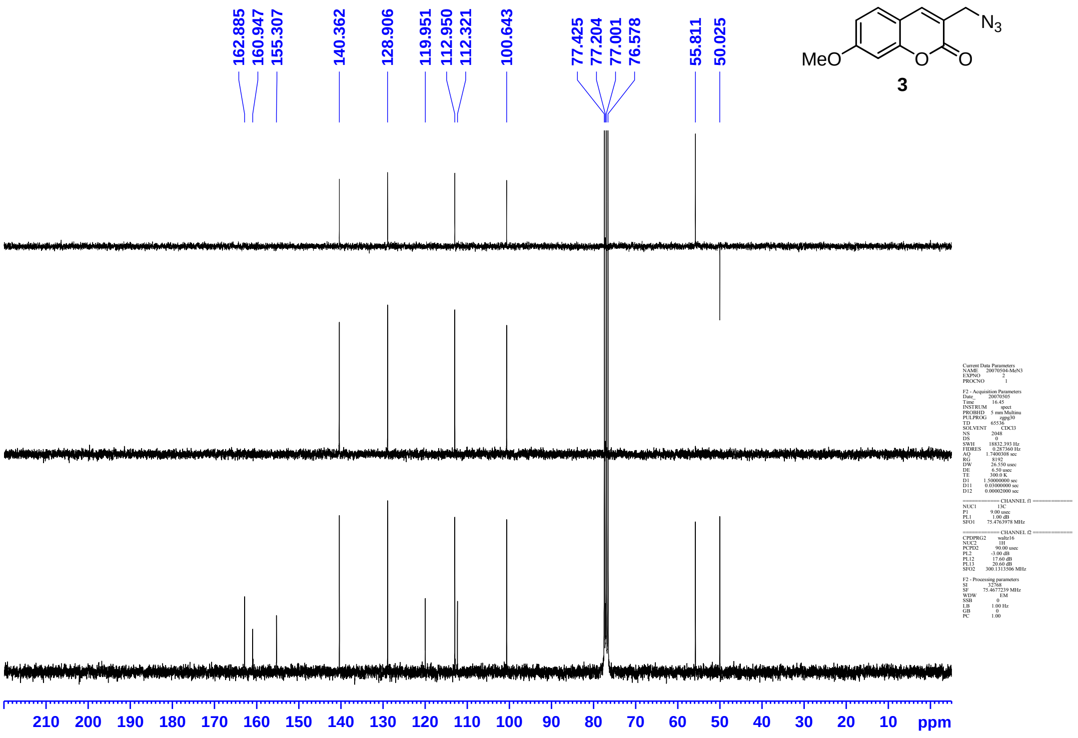

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Figure S4. ^{13}C-NMR and DEPT ($CDCl_3$, 75 MHz) spectra of 3-azidomethyl-7-methoxy-coumarin **3**.

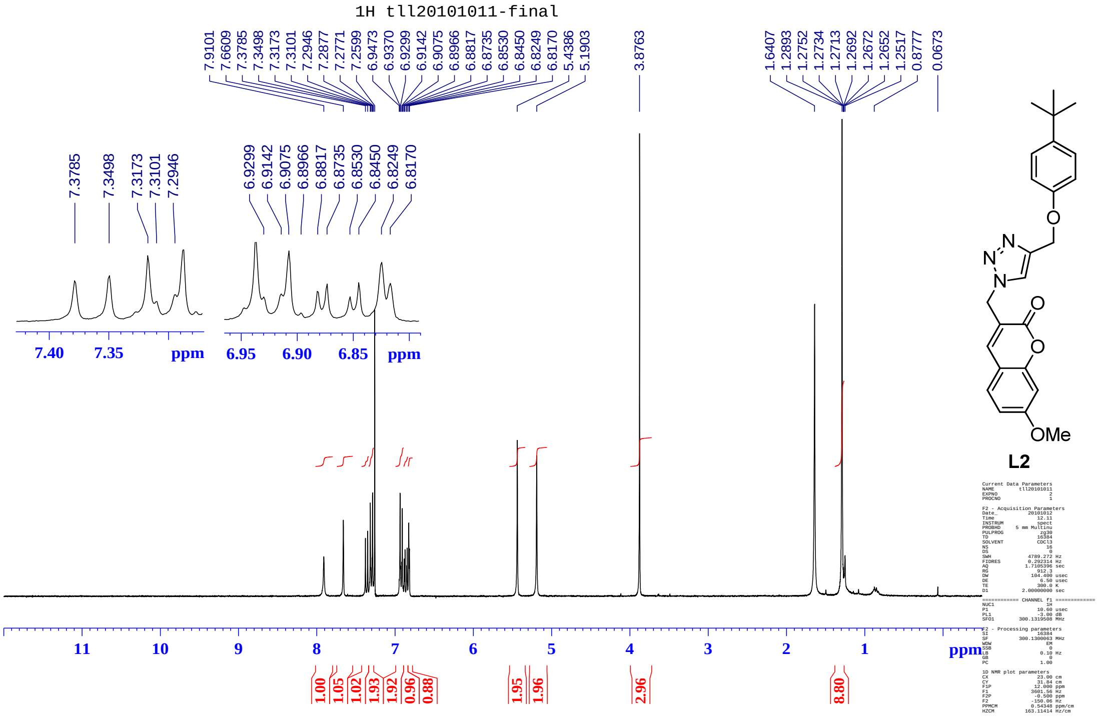

Figure S5. ^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 3-((4-((4-*tert*-butylphenoxy)-methyl)-1H-1,2,3-triazol-yl)methyl)-7-methoxycourmarin **L2**.

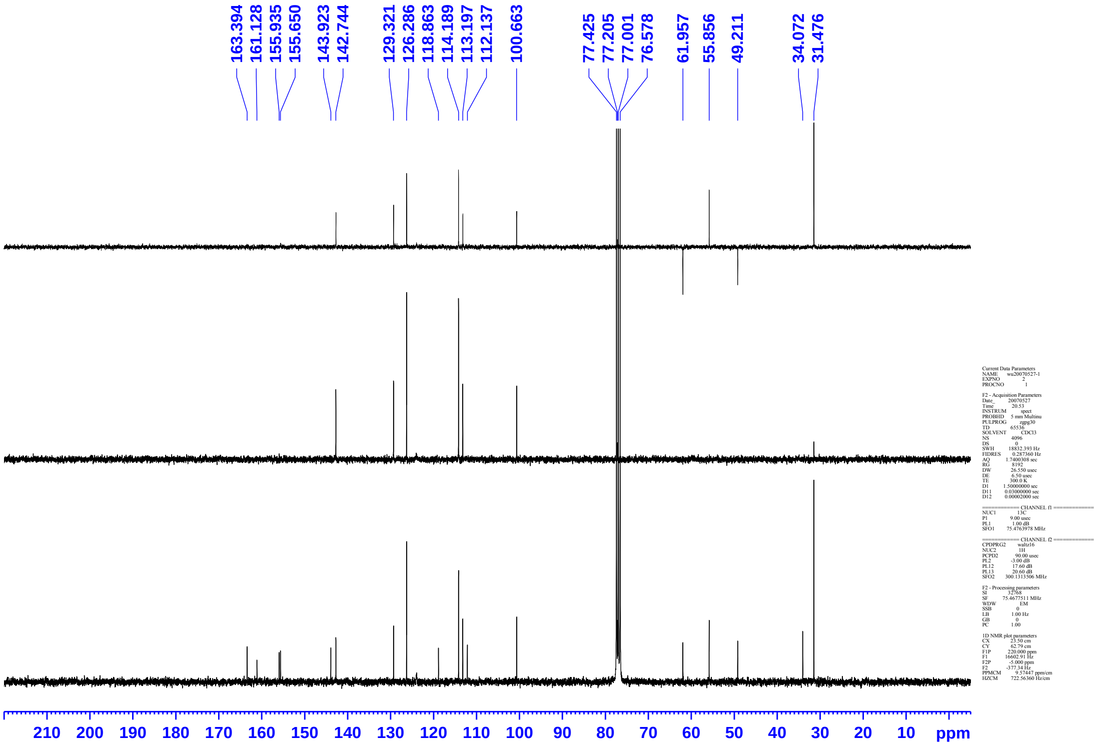

Figure S6. ^{13}C-NMR and DEPT ($CDCl_3$, 75 MHz) spectra of 3-((4-((4-*tert*-butyl-phenoxy)methyl)-1*H*-1,2,3-triazol-1-yl)-methyl)-7-methoxycourmarin **L2**.

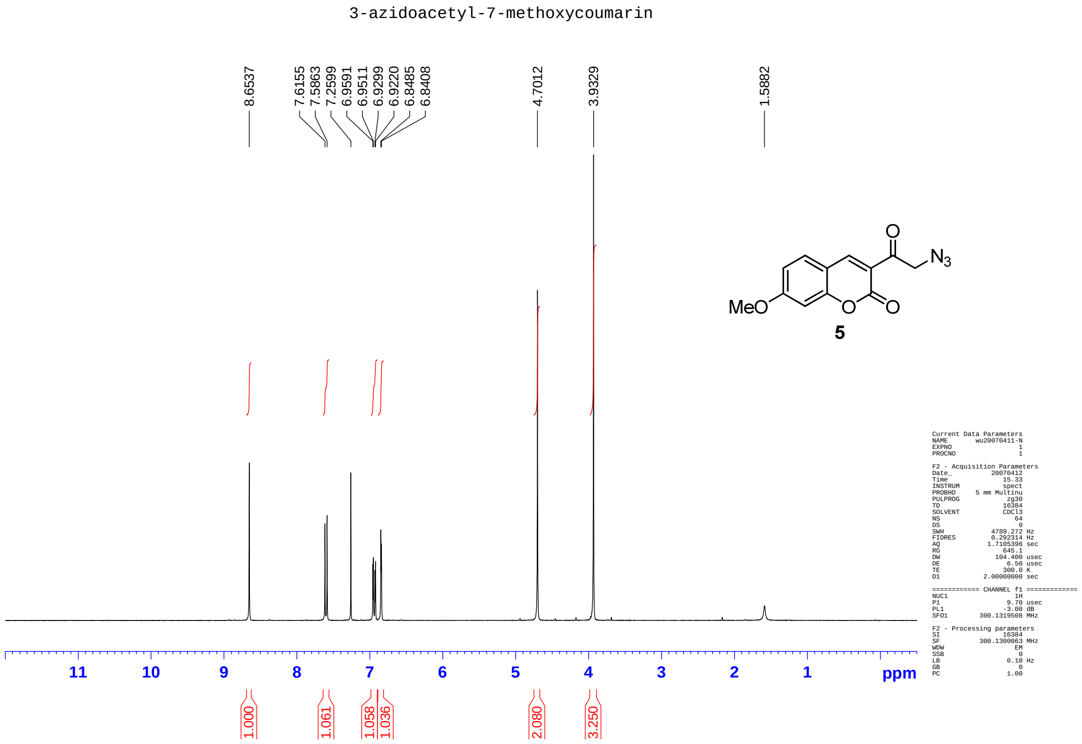

Figure S7. ^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 3-azidoacetyl-7-methoxycoumarin **5**.

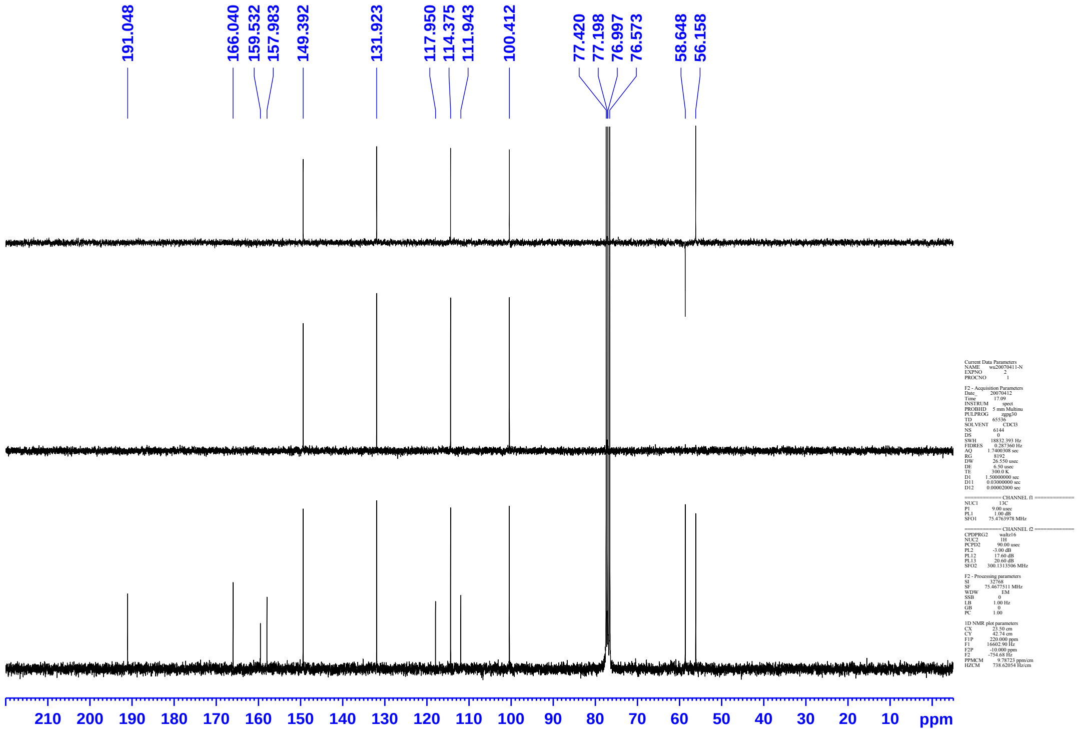

Figure S8. ^{13}C-NMR and DEPT ($CDCl_3$, 75 MHz) spectra of 3-azidoacetyl-7-methoxy-coumarin **5**.

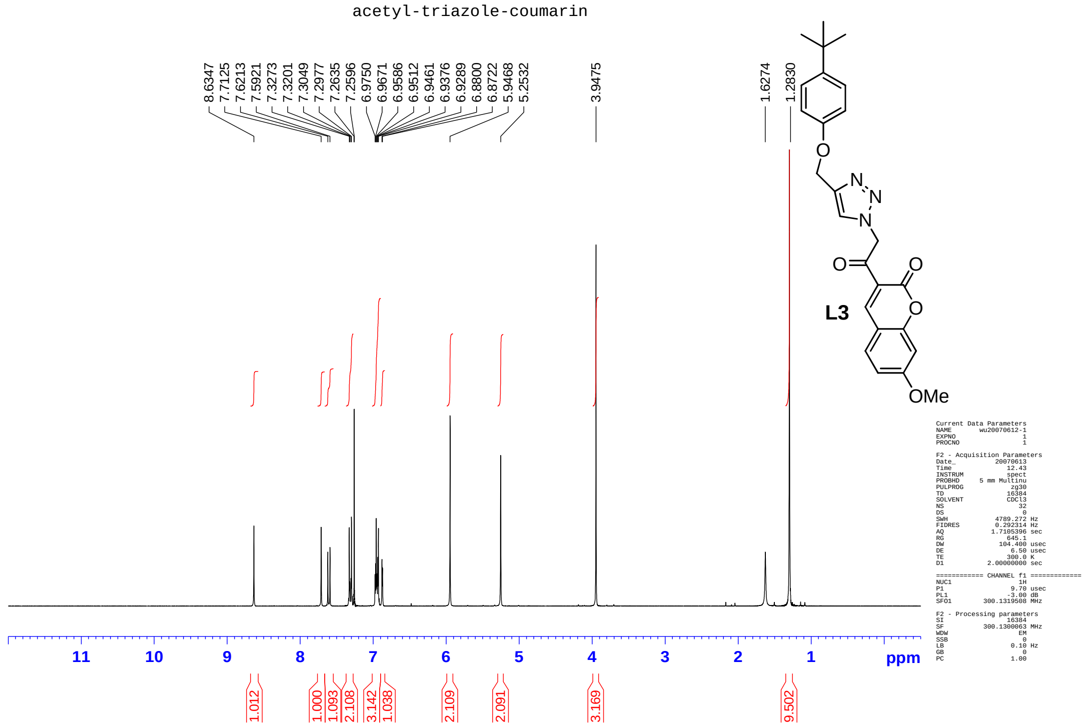

Figure S9. ^{1}H-NMR (CDCl$_3$, 300 MHz) spectrum of 3-(2-(4-((4-*tert*-butylphenoxy) methyl)-1*H*-1,2,3-triazol-1-yl)acetyl)-7-methoxycoumarin **L3**.

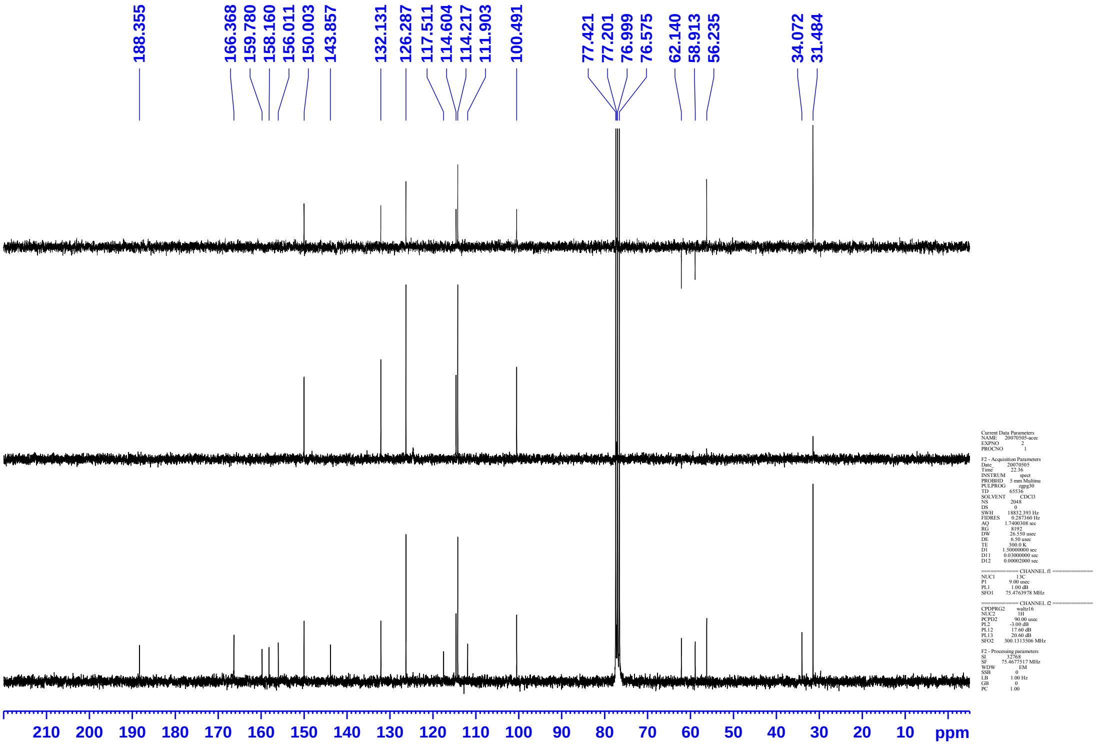

Figure S10. ^{13}C-NMR and DEPT (CDCl$_3$, 75 MHz) spectra of 3-(2-(4-((4-*tert*-butyl-phenoxy)methyl)-1*H*-1,2,3-triazol-1-yl)acetyl)-7-methoxycoumarin **L3**.

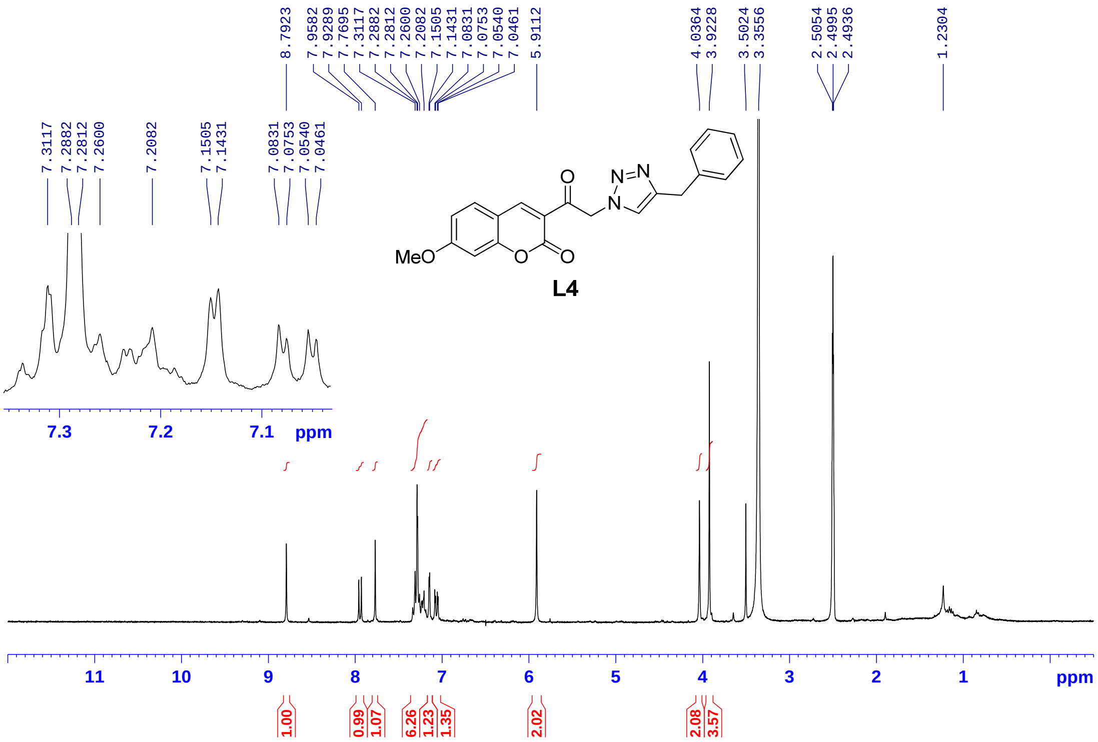

Figure S11. ^{1}H-NMR (D_6-DMSO, 300 MHz) spectrum of 3-(2-(4-benzyl-1H-1,2,3-triazol-1-yl)acetyl)-7-methoxycoumarin **L4**.

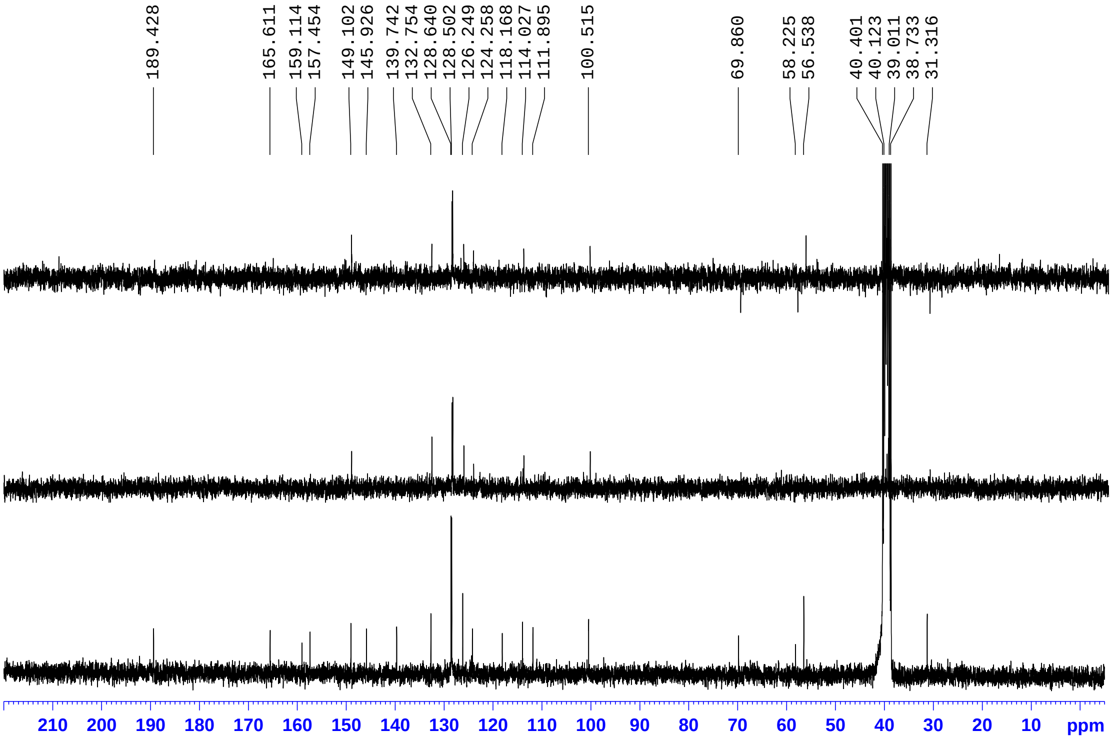

Figure S12. ^{13}C-NMR and DEPT (D_6-DMSO, 75 MHz) spectra of 3-(2-(4-benzyl-1*H*-1,2,3-triazol-1-yl)acetyl)-7-methoxycoumarin **L4**.

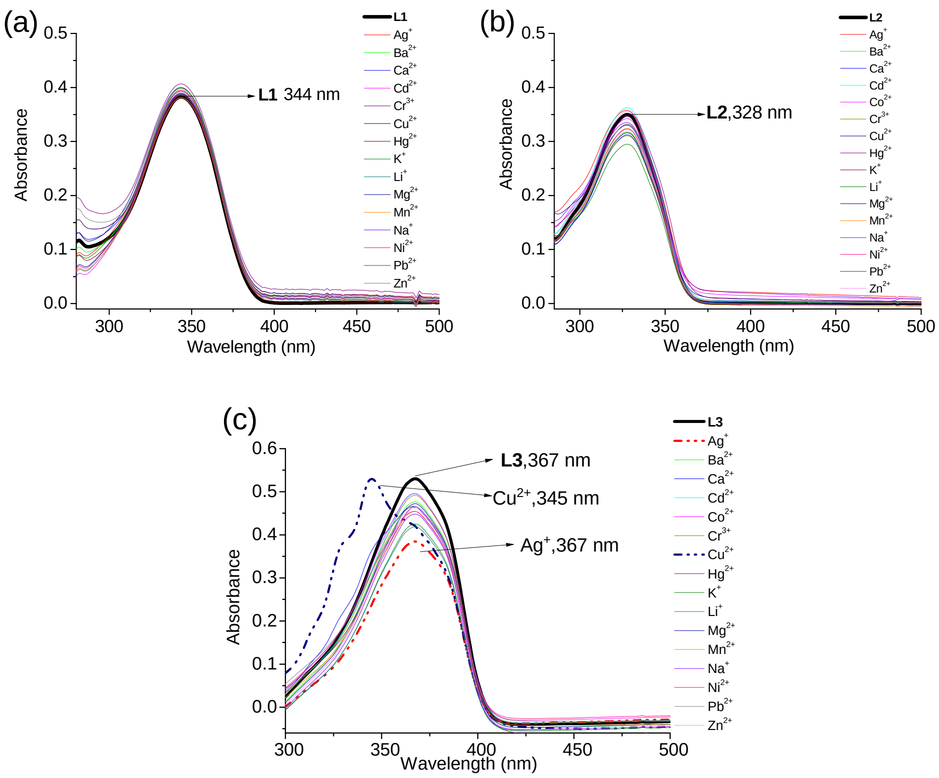

Figure S13. UV-Vis spectrum of (a) **L1**, (b) **L2** and (c) **L3** (20 μM) by the addition of 10 equiv of various metal perchlorates (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Ni^+, Cu^{2+}, Zn^{2+}, Hg^{2+}, Ag^+, Cd^{2+}, and Pb^{2+}) in MeOH-$CHCl_3$ (9:1, v/v).

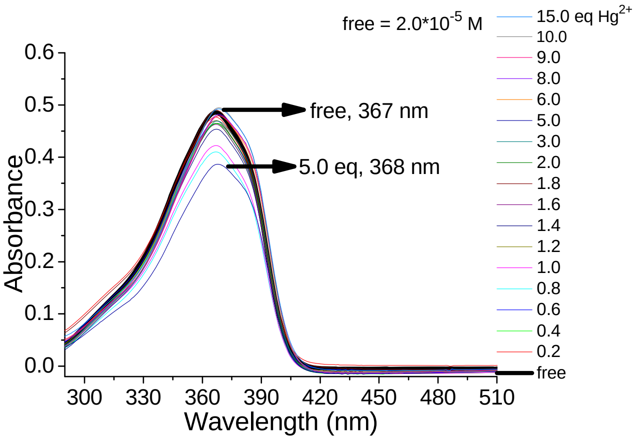

Figure S14. UV-Vis spectrum of **L3** (20 μM) with various equiv of $Hg(ClO_4)_2$ in MeOH-$CHCl_3$ (9:1, v/v).

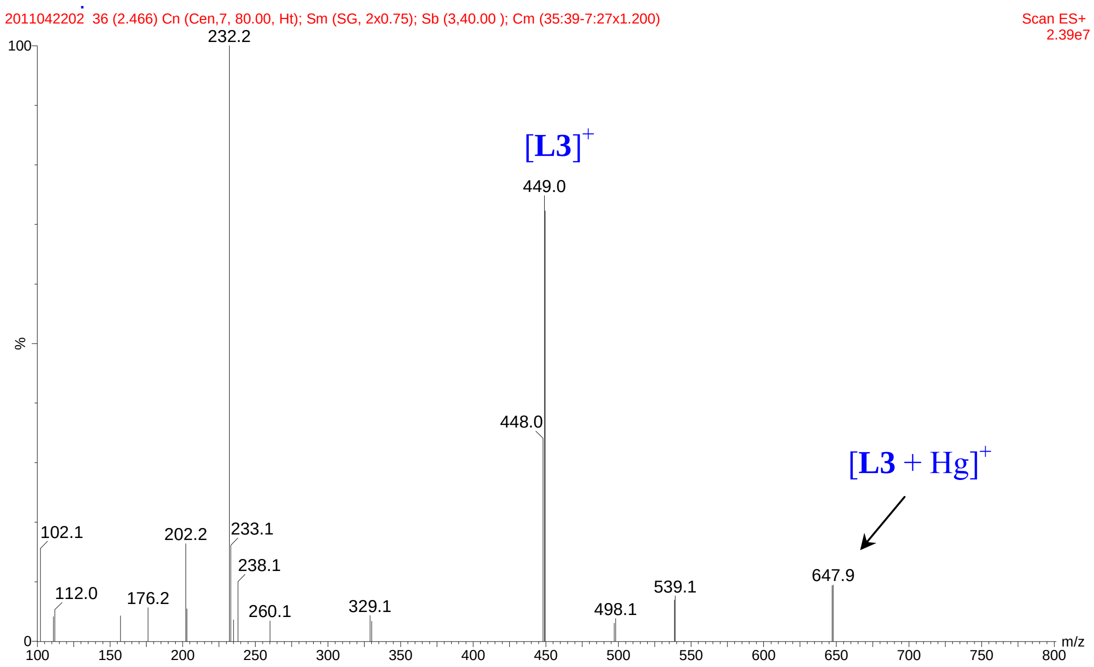

Figure S15. The ESI-MS spectrum of **L3** by adding 1 equiv of $Hg(ClO_4)_2$.

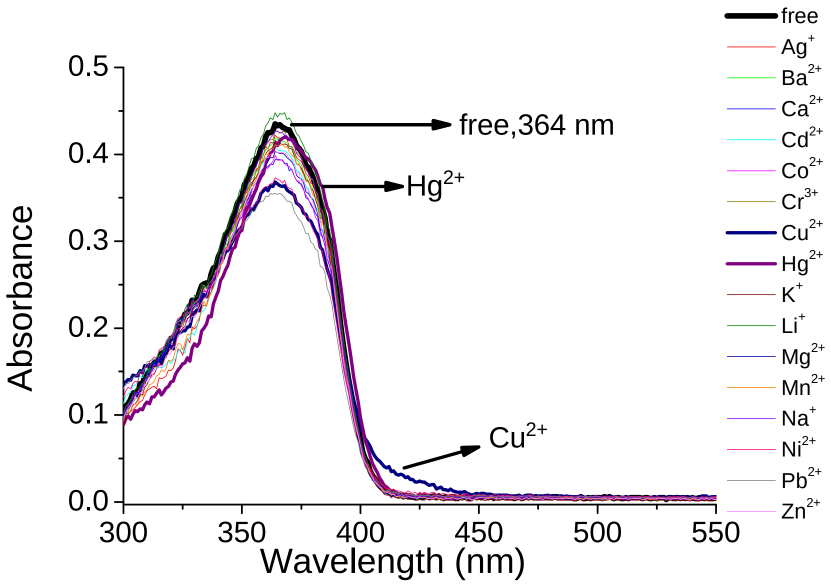

Figure S16. UV-Vis spectrum of **L4** (20 μM) by the addition of 10 equiv of various metal perchlorates (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Ni^+, Cu^{2+}, Zn^{2+}, Hg^{2+}, Ag^+, Cd^{2+}, and Pb^{2+}) in $MeOH-CHCl_3$ (9:1, v/v).

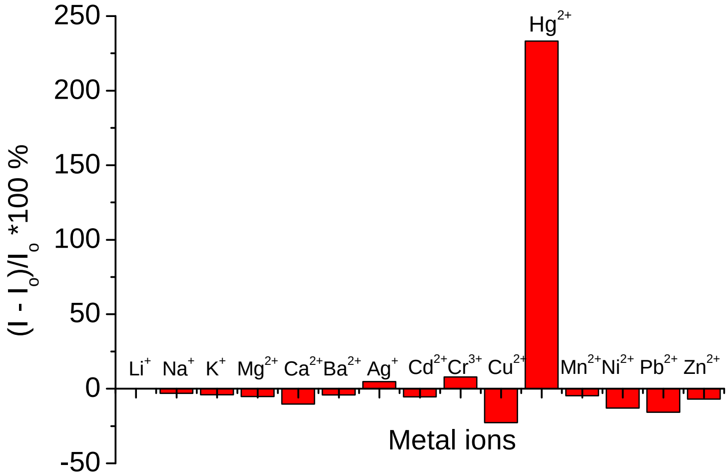

Figure S17. Percentage fluorescence intensity changes of **L4** by the addition of 10 equiv of various metal perchlorates (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Ni^+, Cu^{2+}, Zn^{2+}, Hg^{2+}, Ag^+, Cd^{2+}, and Pb^{2+}) in MeOH/$CHCl_3$ (9:1, v/v). Excitation wavelength was 367 nm. The fluorescence intensities of **L4** was recorded at 427 nm.

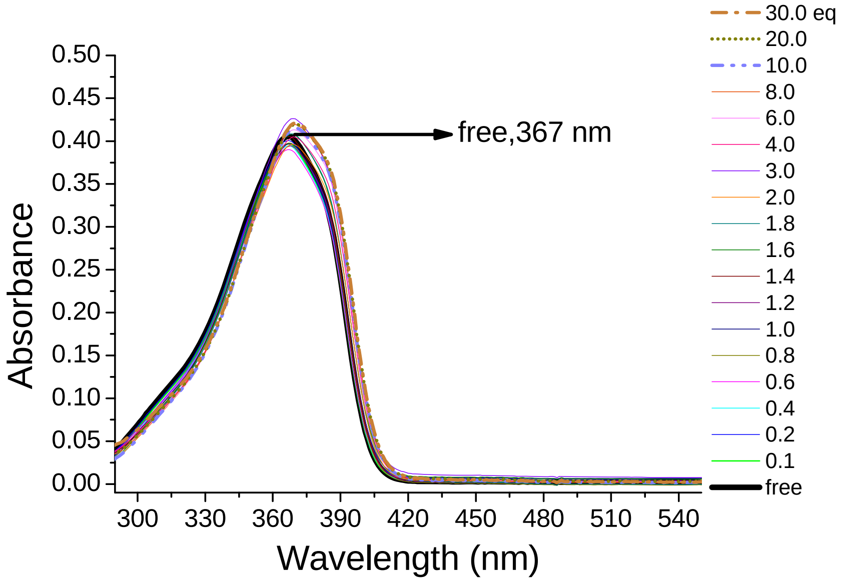

Figure S18. UV-Vis spectrum of **L4** (20 μM) with various equiv of $Hg(ClO_4)_2$ in MeOH-$CHCl_3$ (9:1, v/v).

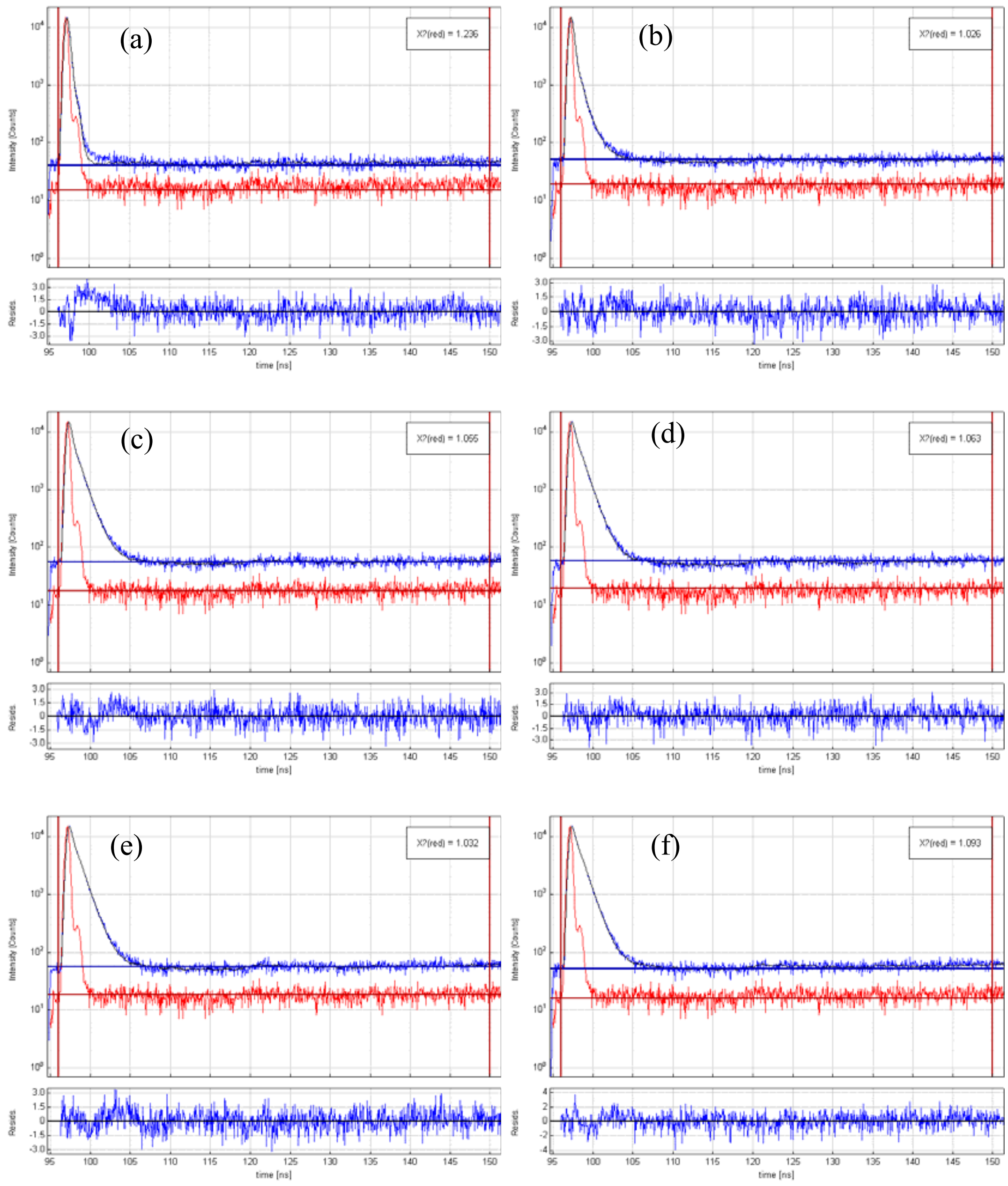

Figure S19. Fluorescence decay profiles and the distribution of weighted residuals for the single or bi-exponential function of **L3** (20 μM, λ_{ex} = 375 nm LED, monitored at 423 nm) with (a) 0, (b) 1, (c) 2, (d) 5, (e) 10 and (f) 20 equiv. of $Hg(ClO_4)_2$ in cosolvent MeOH/$CHCl_3$ (9:1, v/v). IRF means the instrument response function (IRF), which was obtained by the detection of Rayleigh scattered light in a scattering solution.

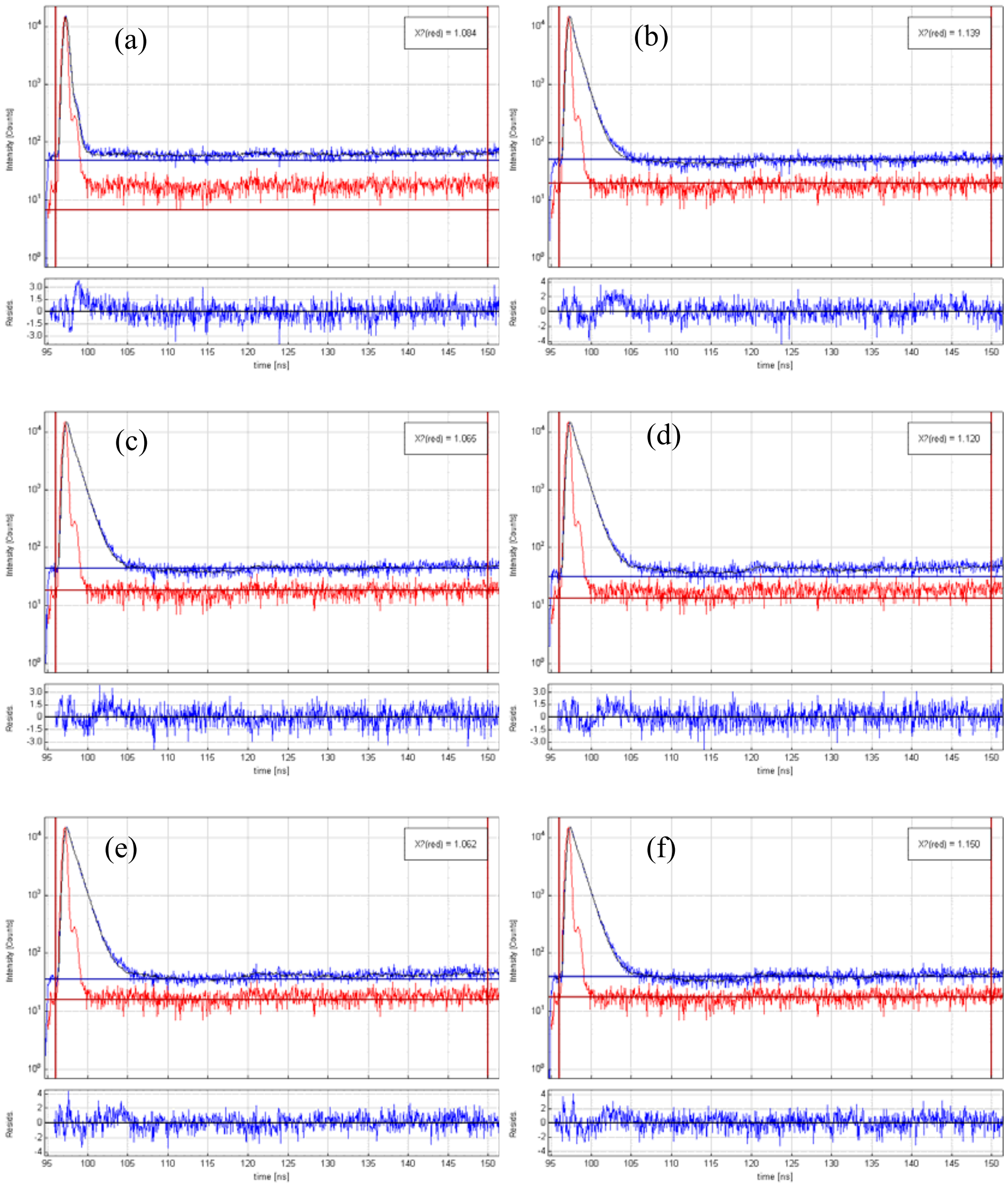

Figure S20. Fluorescence decay profiles and the distribution of weighted residuals for the single or bi-exponential function of **L4** (20 μM, λ_{ex} = 375 nm LED, monitored at 427 nm) with (a) 0, (b) 1, (c) 2, (d) 5, (e) 10 and (f) 20 equiv. of $Hg(ClO_4)_2$ in cosolvent MeOH/$CHCl_3$ (9:1, v/v). IRF means the instrument response function (IRF), which was obtained by the detection of Rayleigh scattered light in a scattering solution.

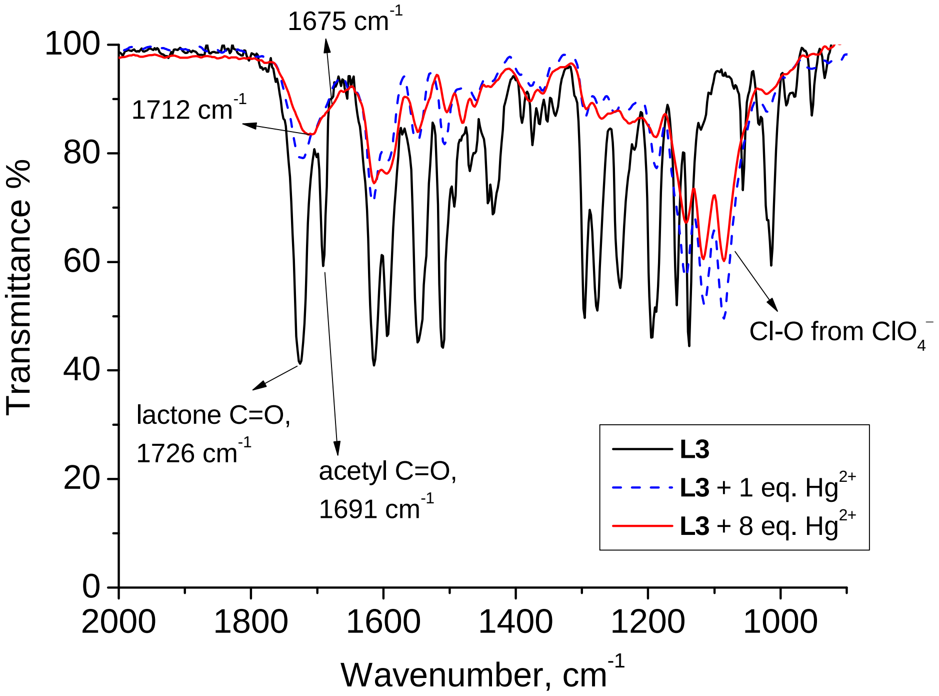

Figure S21. The FT-IR spectrum of **L3** (solid line) and its complex with Hg$(ClO_4)_2$ (dashed blue and solid red lines).

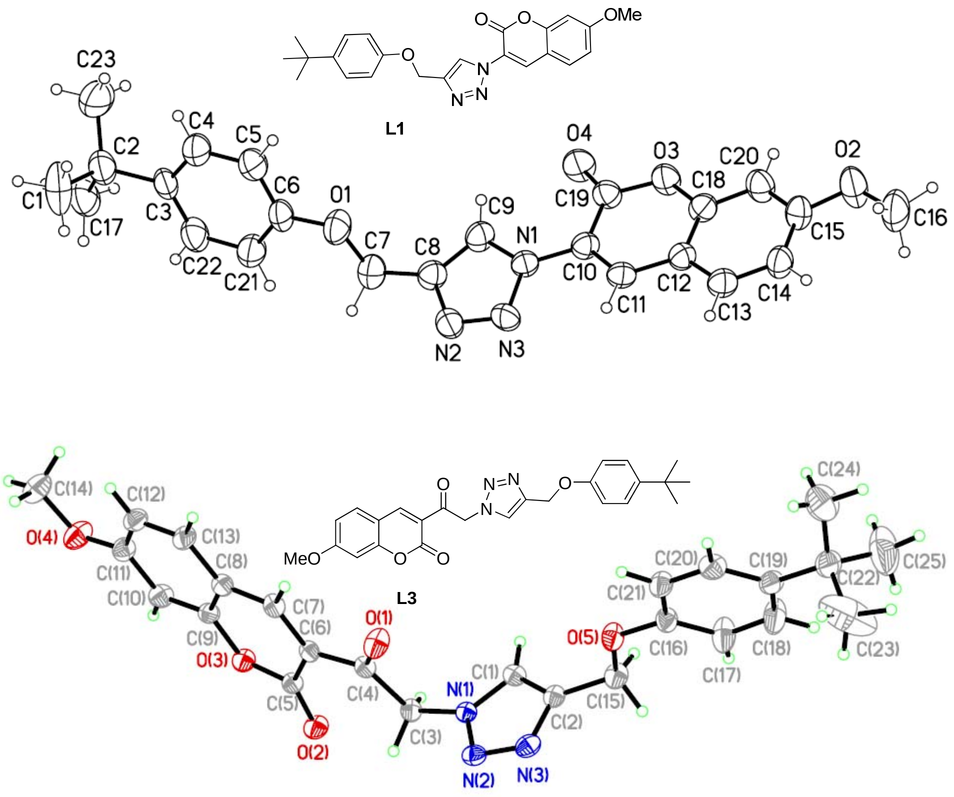

Figure S22. The X-ray crystal structures of **L1** (110634LT_0m) and **L3** (IC12713).

Table S2. Crystal data and structure refinement for 110634LT_0m.

Identification code	110634lt_0m	
Empirical formula	C23 H23 N3 O4	
Formula weight	405.44	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.933(3) Å	= 93.50(2)°.
	b = 11.085(6) Å	= 92.85(2)°.
	c = 15.588(8) Å	= 93.01(2)°.
Volume	1020.4(9) Å^3	
Z	2	
Density (calculated)	1.320 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	428	
Crystal size	0.17 x 0.15 x 0.06 mm^3	
Theta range for data collection	1.31 to 26.56°.	
Index ranges	-7<=h<=6, -13<=k<=13, -19<=l<=19	
Reflections collected	13644	
Independent reflections	4137 [R(int) = 0.0764]	
Completeness to theta = 26.56°	97.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9486 and 0.7632	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4137 / 0 / 275	
Goodness-of-fit on F^2	0.973	
Final R indices [I>2sigma(I)]	R1 = 0.0763, wR2 = 0.2076	
R indices (all data)	R1 = 0.1373, wR2 = 0.2611	
Largest diff. peak and hole	0.373 and -0.455 e.Å^{-3}	

Table S3. Crystal data and structure refinement for ic12713.

Identification code	ic12713	
Empirical formula	$C25 H25 N3 O5$	
Formula weight	447.48	
Temperature	220(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.7298(4) Å	= 96.531(2)°.
	b = 11.4420(8) Å	= 96.165(2)°.
	c = 17.7012(13) Å	= 93.056(2)°.
Volume	1143.77(14) Å^3	
Z	2	
Density (calculated)	1.299 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	472	
Crystal size	0.60 x 0.10 x 0.04 mm^3	
Theta range for data collection	1.17 to 25.00°.	
Index ranges	-6<=h<=6, -13<=k<=13, -21<=l<=20	
Reflections collected	10379	
Independent reflections	4027 [R(int) = 0.0393]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9963 and 0.9470	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4027 / 0 / 303	
Goodness-of-fit on F^2	1.106	
Final R indices [I>2sigma(I)]	R1 = 0.0805, wR2 = 0.1918	
R indices (all data)	R1 = 0.1129, wR2 = 0.2179	
Extinction coefficient	0.037(5)	
Largest diff. peak and hole	0.784 and -0.377 e.Å^{-3}	