Electronic supplementary information

Solid-State Emissive O-BODIPY Dyes with Bimodal Emissions across red and near infrared region

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Synthetic procedure for 4,4-Difluoro-1,3,5,7,8-pentamethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene. 1

A solution of acetyl chloride **(**5.39 mL, 75.76 mmol) was added drop-wise to a stirred solution of 3-ethyl-2,4-dimethylpyrrole (4.381 mL, 32.48 mmol) in dry dichloromethane (20 mL), over a period of 15 mints. The reaction mixture was heated (40 C, 1hour), cooled to room temperature, diluted with petroleum ether (232 mL), and triturated for 12 hours. The solvent was evaporated under reduced pressure, the residue was suspended in dry toluene (400 mL), followed by addition of dry triethylamine (8.539 mL, 63.91 mmol).

The mixture was stirred for 15 minutes and boron trifluoride etherate (10.88 mL, 88.8 mmol) was added drop-wise with stirring as a green fluorescence developed. The reaction mixture was heated (50C, 60 minutes), cooled to 40 C, washed with water (3 x 100mL), and dried (sodium anhydrous sulfate). The solvent was removed under reduced pressure to give the crude products as a dark brown solid. The crude material was purified by chromatography (silica gel) (DCM/ n-Hexane 1;1) to give the pure product as an orange solid (4 g, 77.45 %).^{1}H NMR δ_H(400 MHz, CDCl3) 2.56 (s, 3H), 2.45 (s, 6H), 2.35 (q, J =7.5, 4H), 2.29 (s, 6H), 1.00 (t, J = 7.5, 6H) ^{13}C NMR ; δC (125 MHz, CDCl3) 152.0, 139.9, 136.5, 132.6,131.9, 17.4, 17.2, 15.1, 14.6, 12.61; ^{11}B NMR δB (160 MHz, CDCl3) 0.46 (t, J = 32); MS: *m/z* calcd for $[C_{18}H_{25}BF_2N_2]^+$: 318.22; found: 318.30, $[M]^+$.

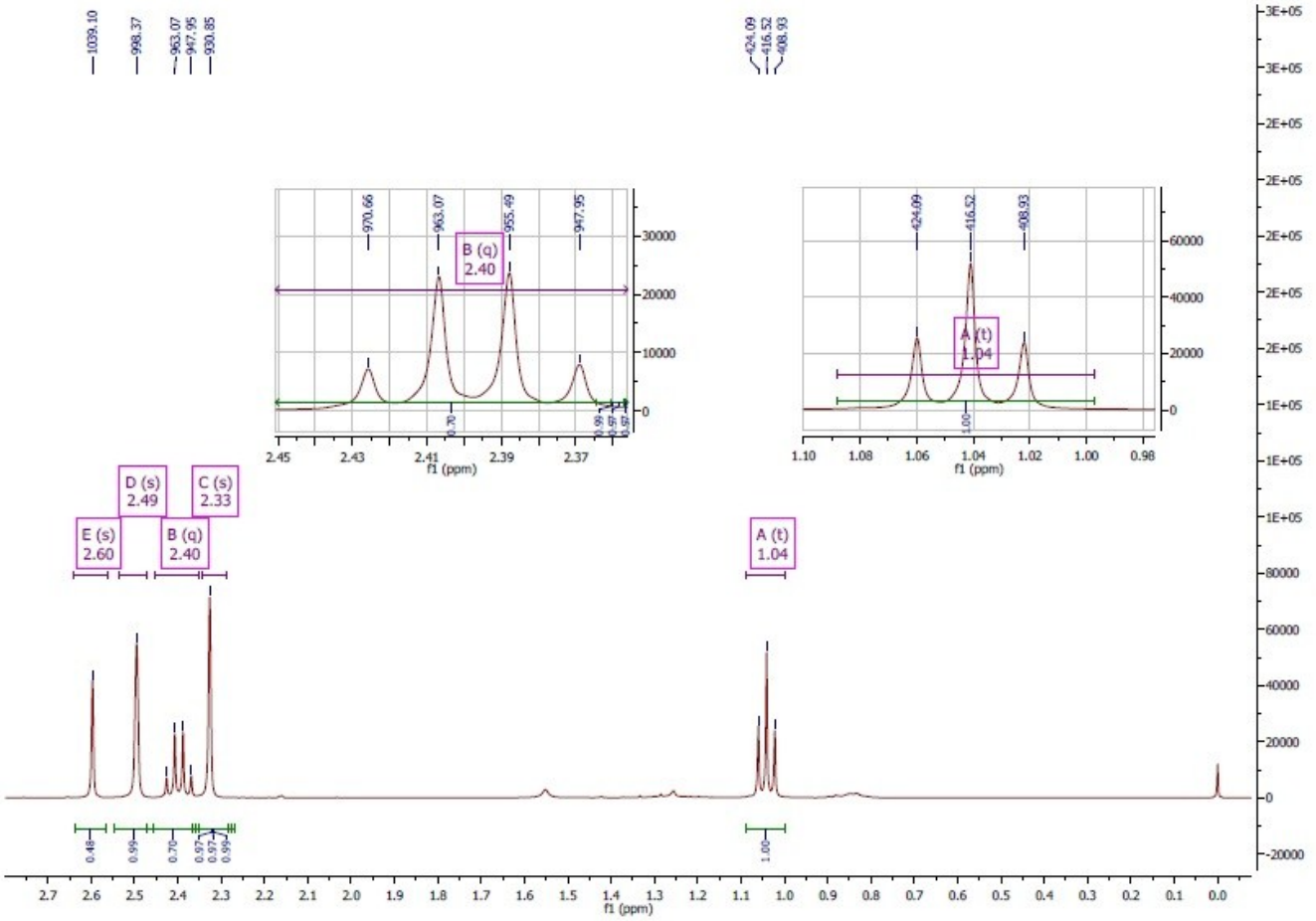

Figure S-1. ^{1}H-NMR of compound 1 in $CDCl_3$

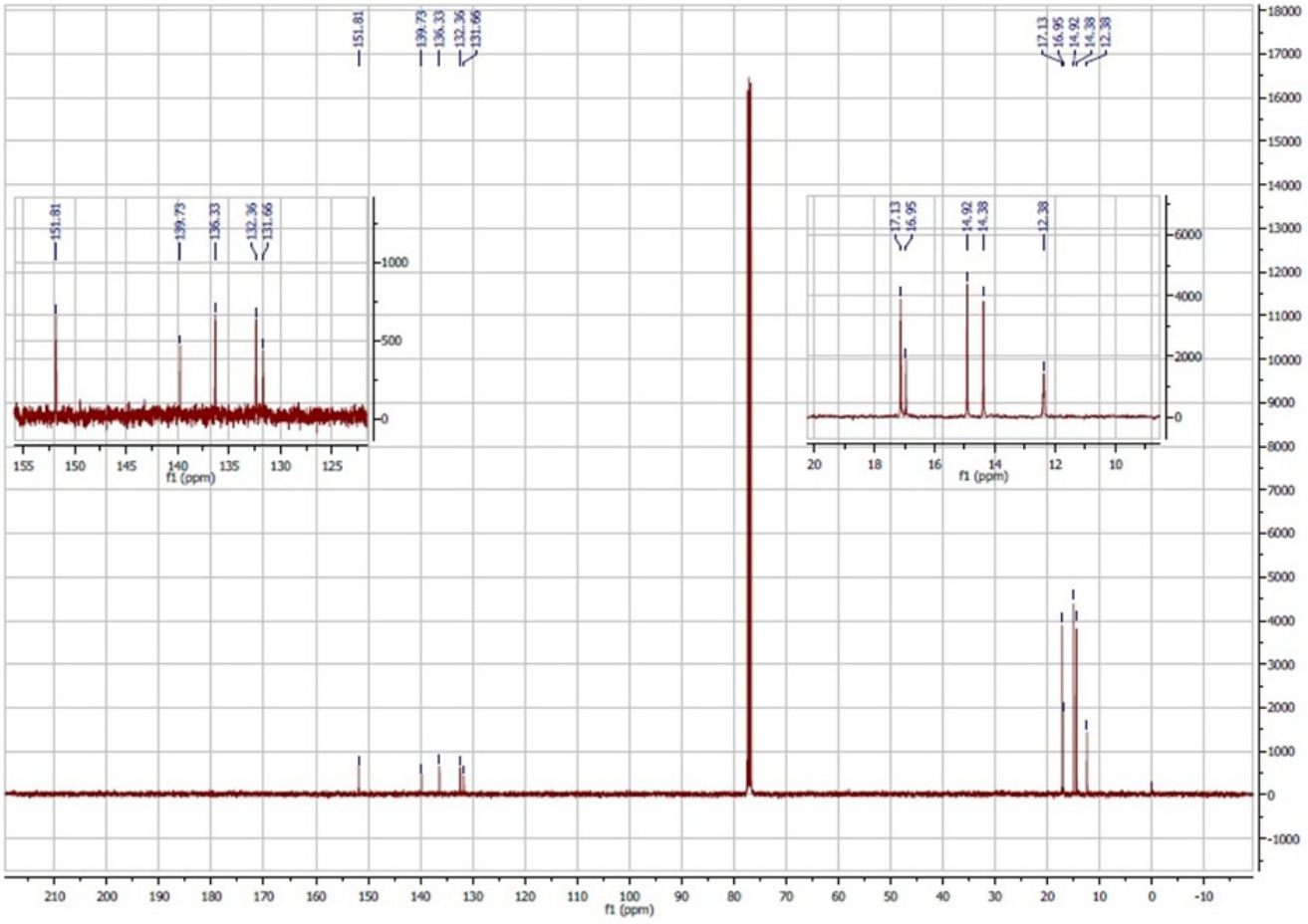

Figure S-2. ^{13}C-NMR of compound 1 in $CDCl_3$

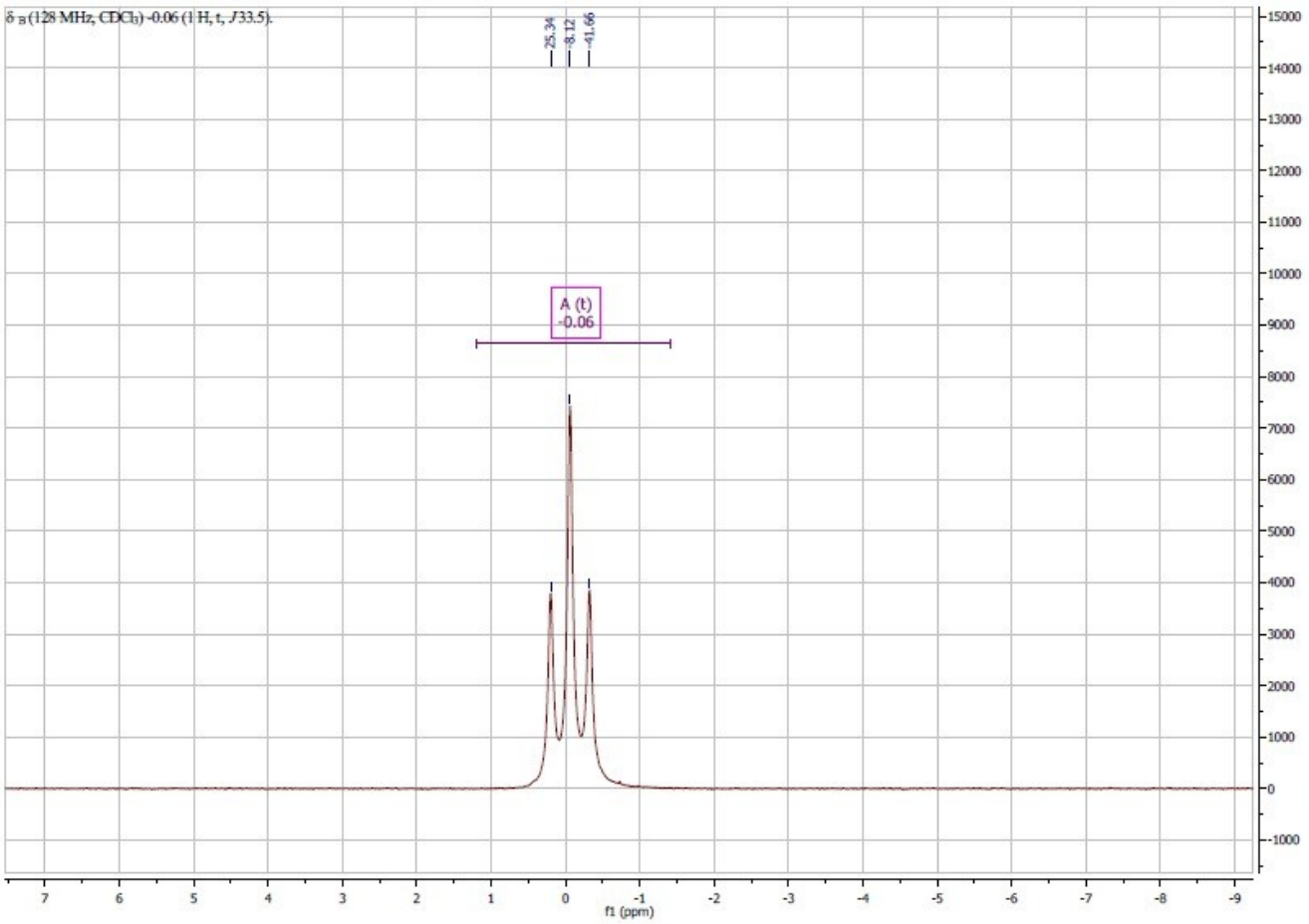

Figure S-3. ^{11}B-NMR of compound 1 in $CDCl_3$.

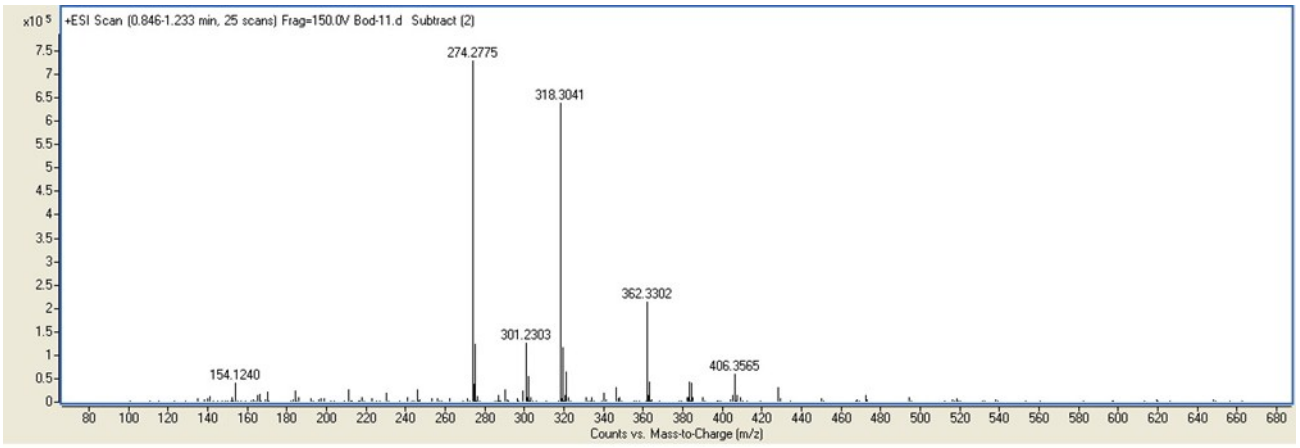

Figure S-4. HRMS spectrum of compound 1

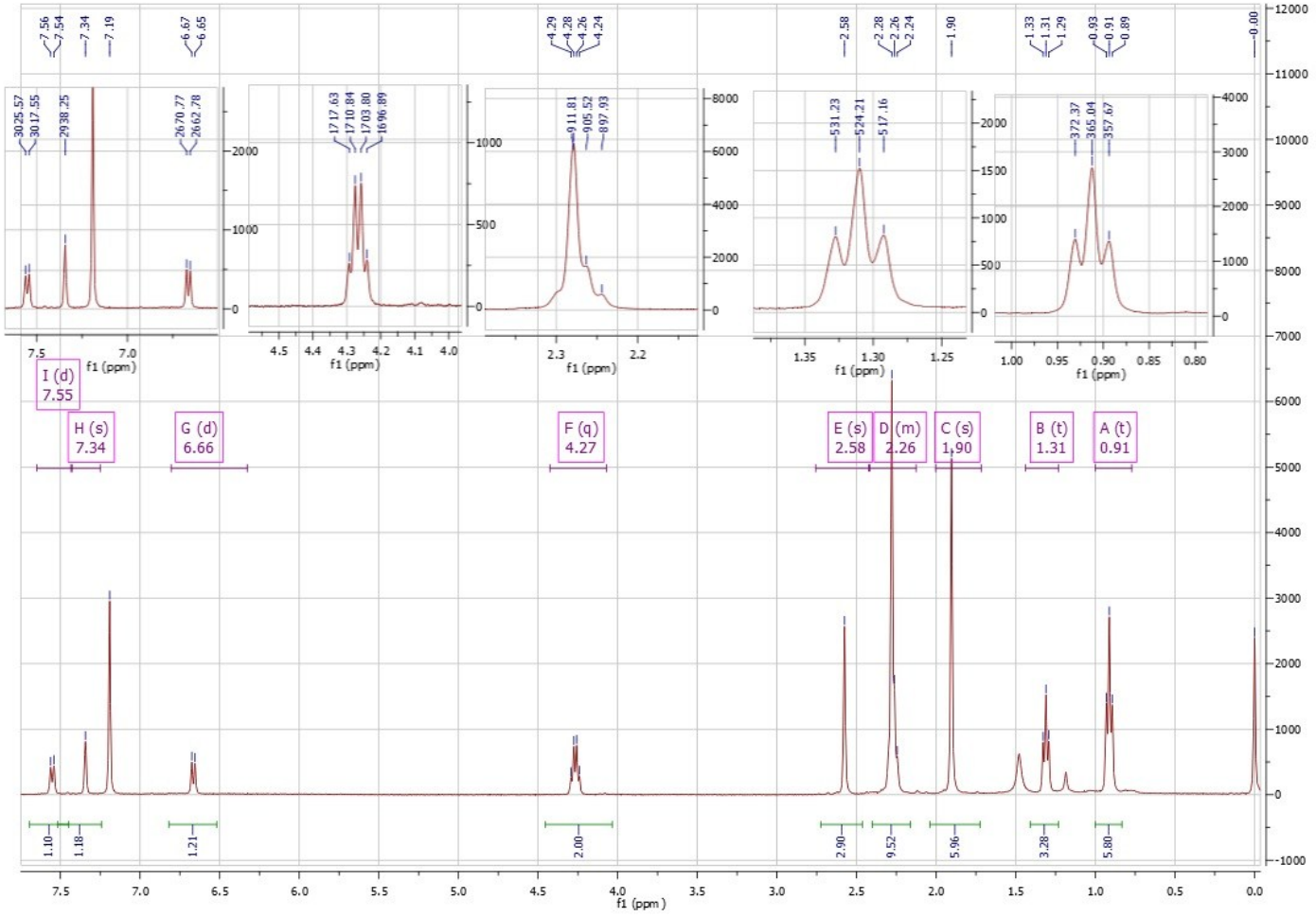

Figure S-5. ^{1}H-NMR of compound 2a in $CDCl_3$.

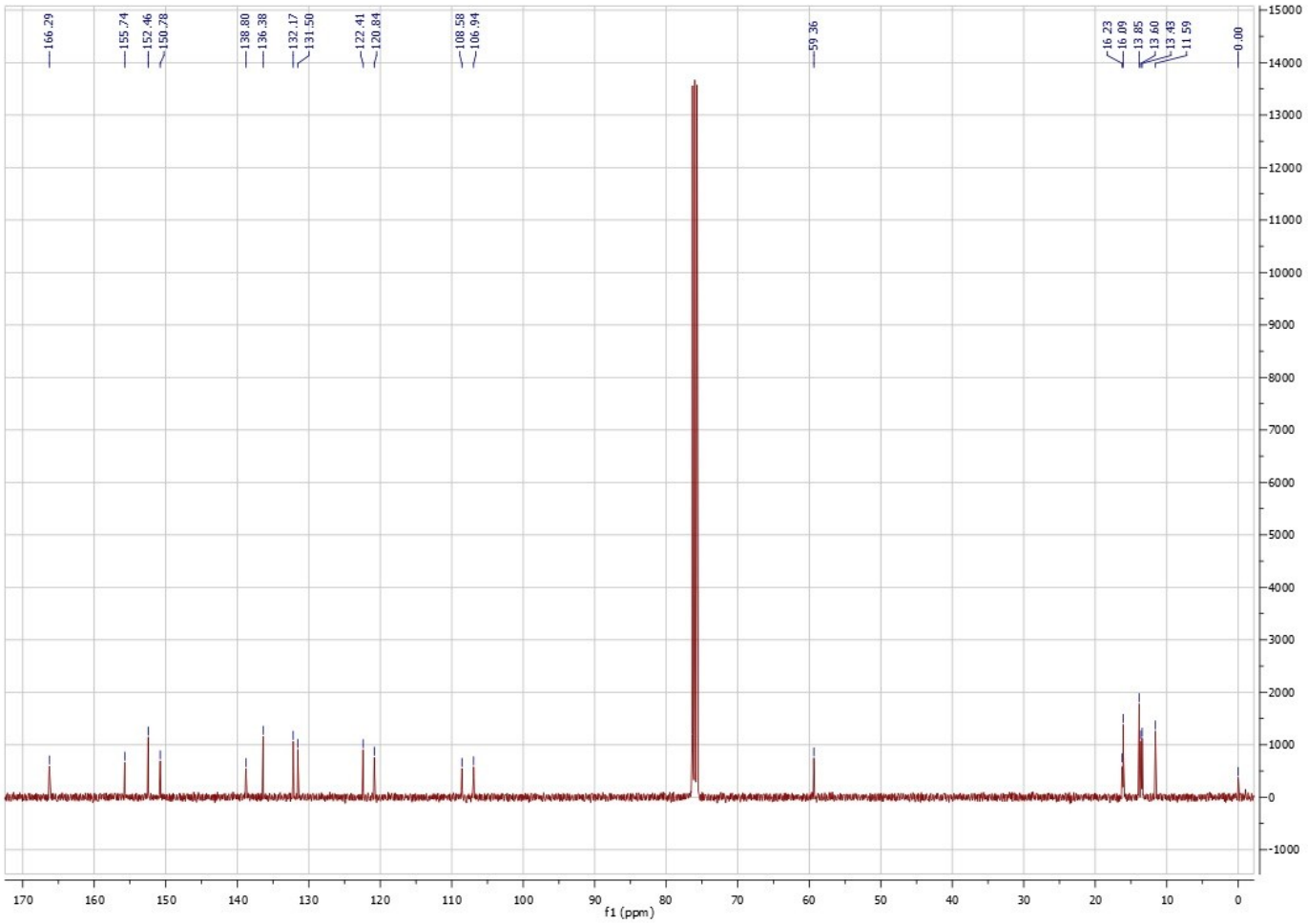

Figure S-6. ^{13}C-NMR of compound 2a in $CDCl_3$.

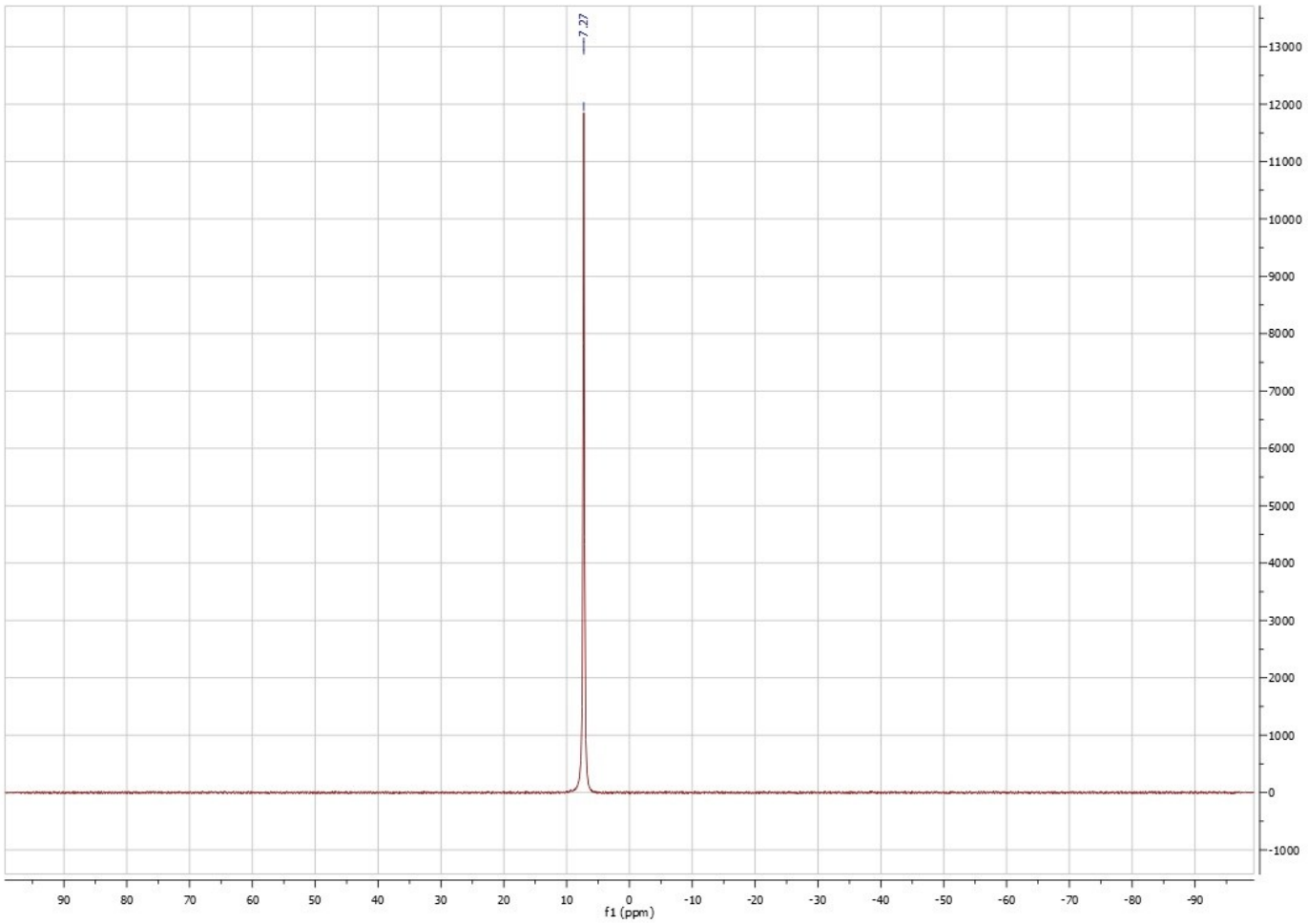

Figure S-7. ^{11}B-NMR of compound 2a in $CDCl_3$.

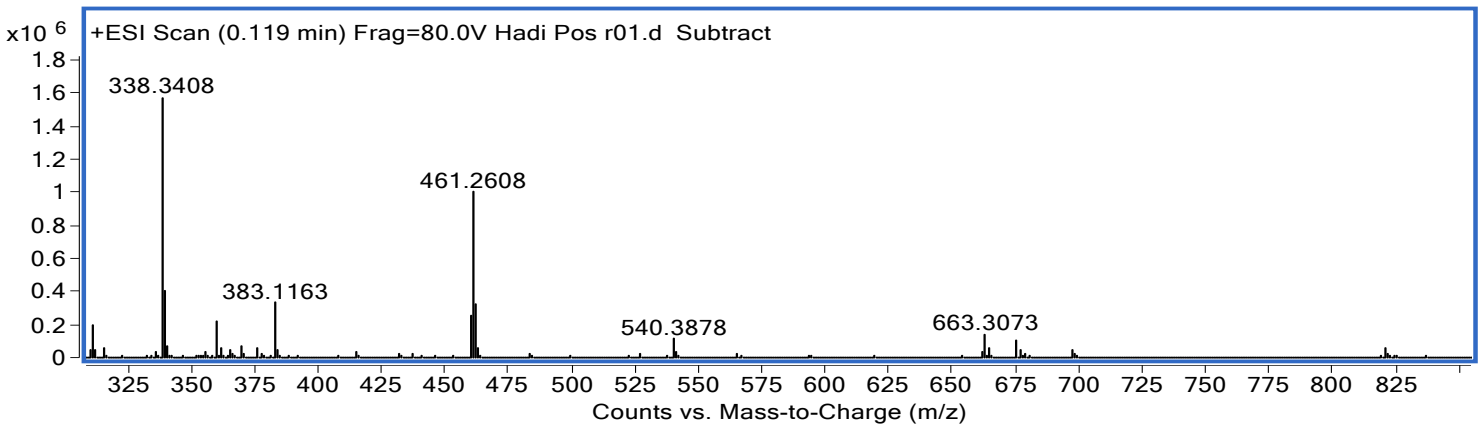

Figure S-8. HRMS spectrum of compound 2a

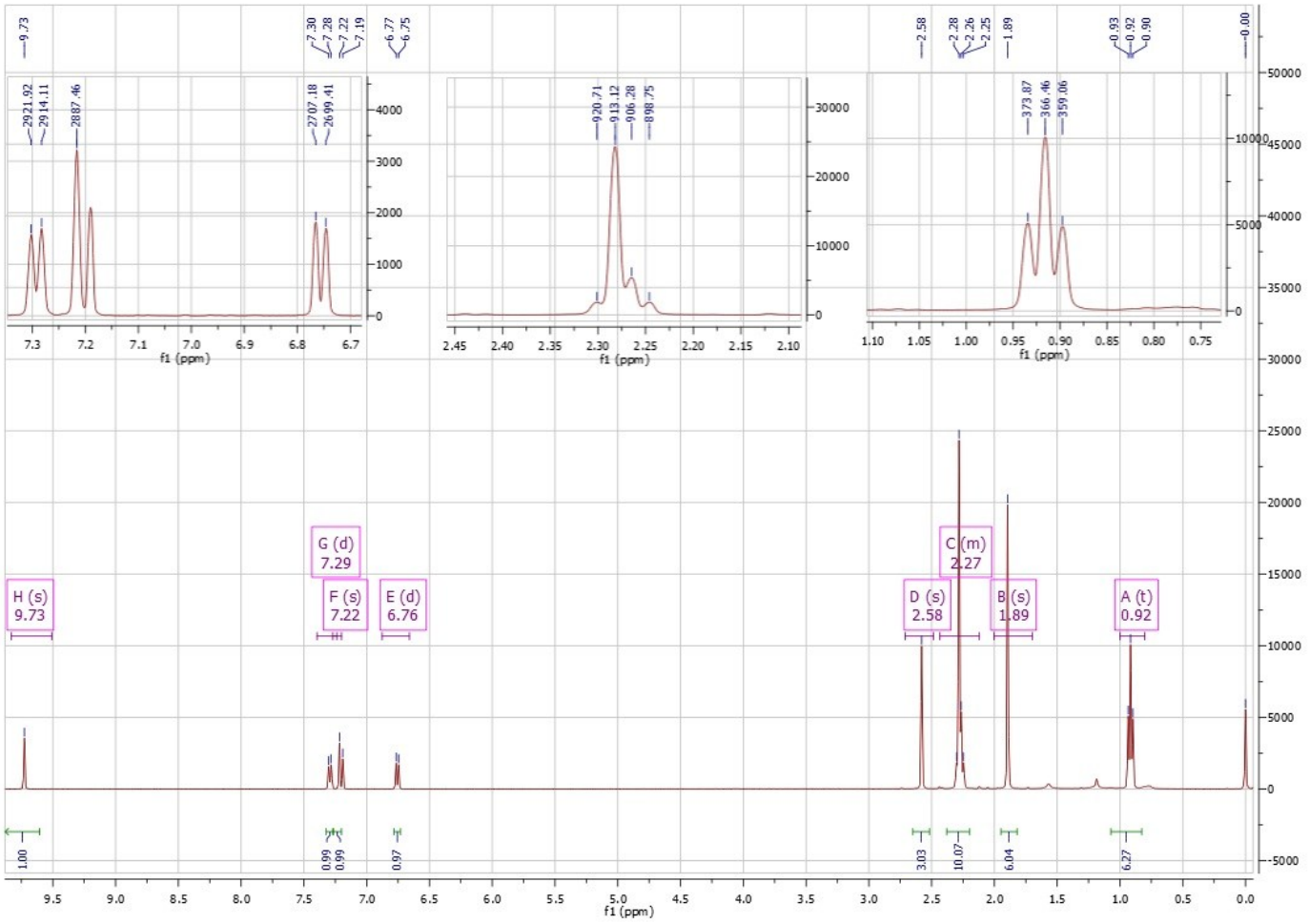

Figure S-9. ^{1}H-NMR of compound 2b in $CDCl_3$.

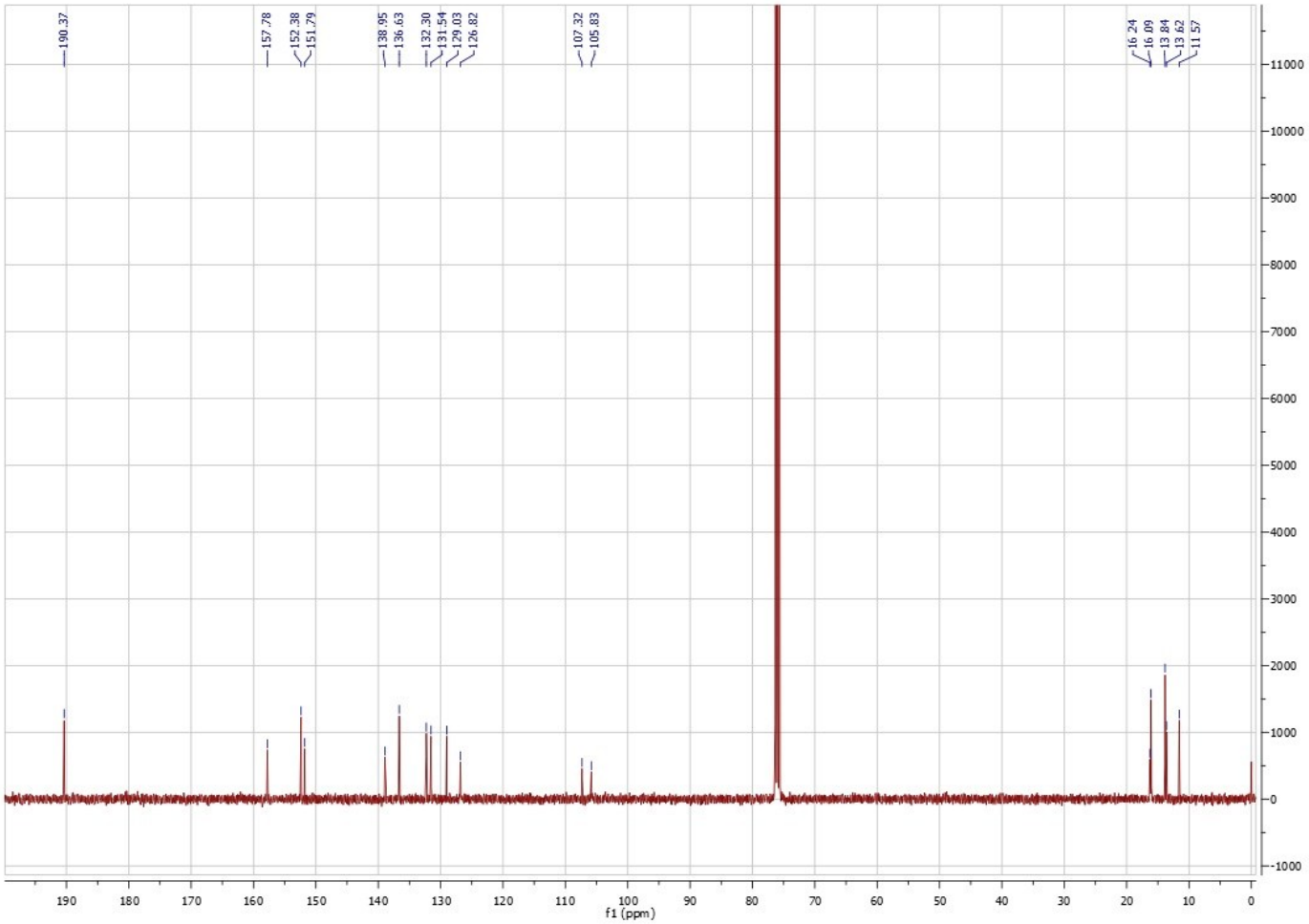

Figure S-10. ^{13}C-NMR of 2b in $CDCl_3$.

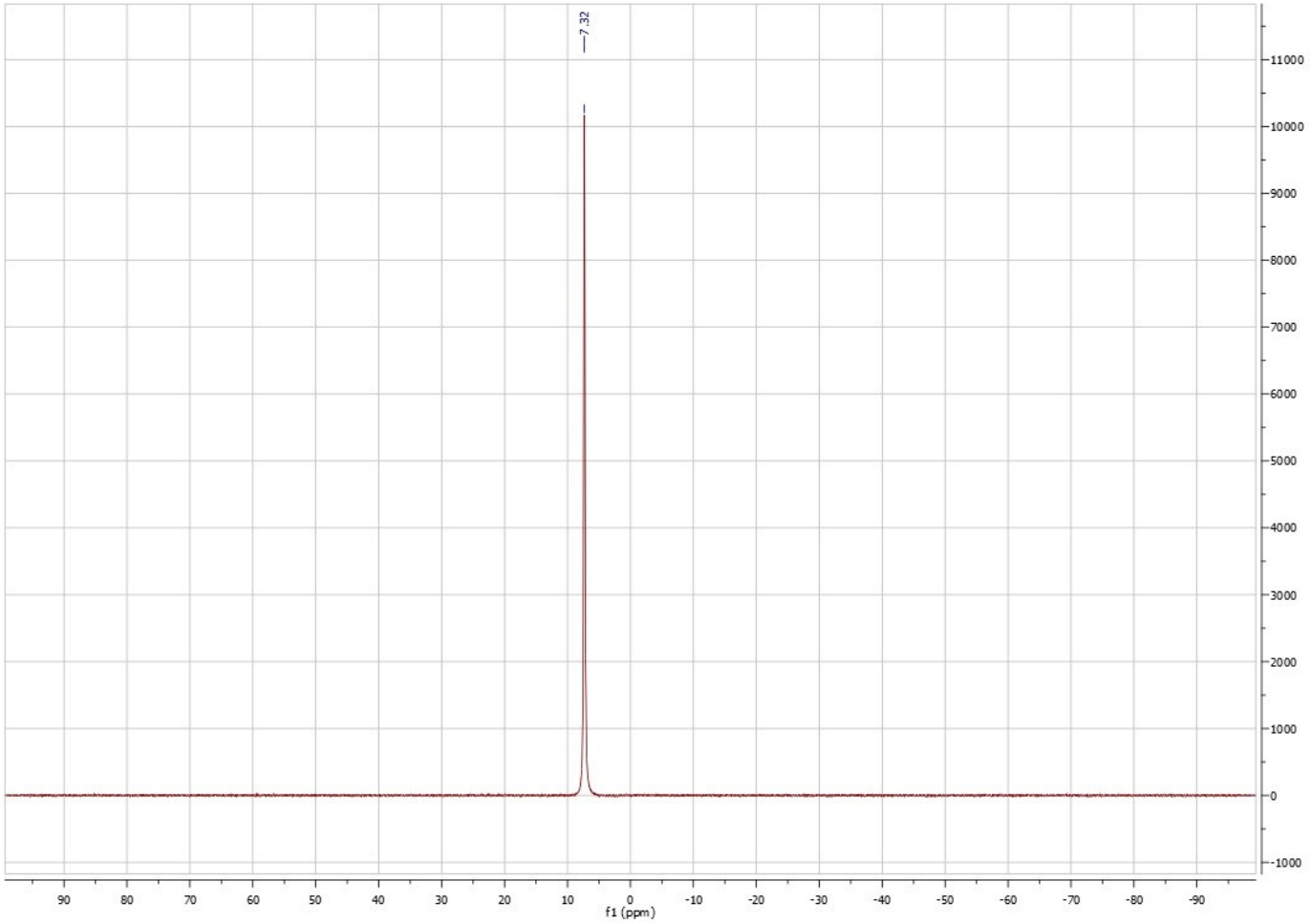

Figure S-11 ^{11}B-NMR of 2b in $CDCl_3$.

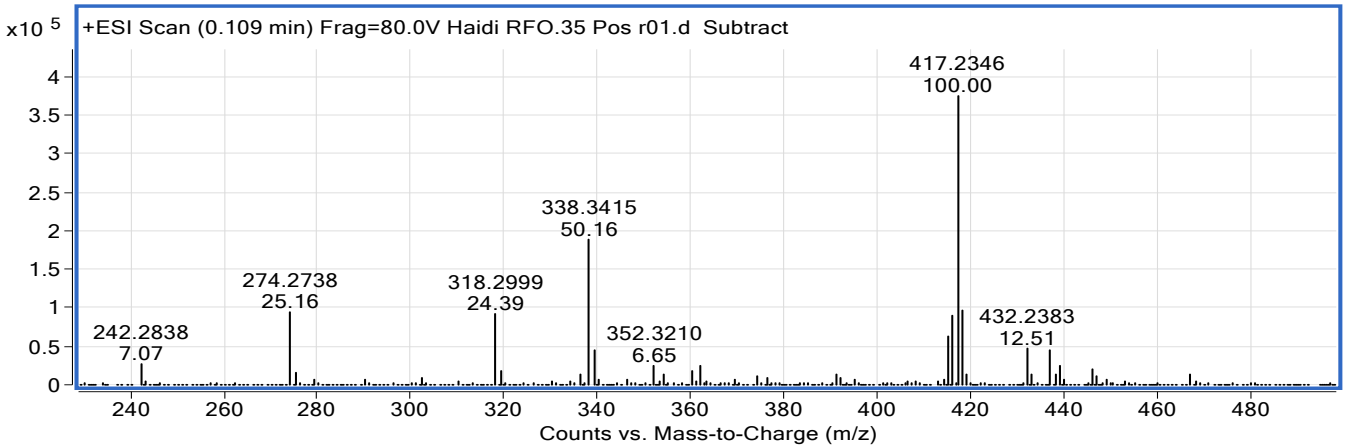

Figure S-12 HRMS spectrum of 2b.

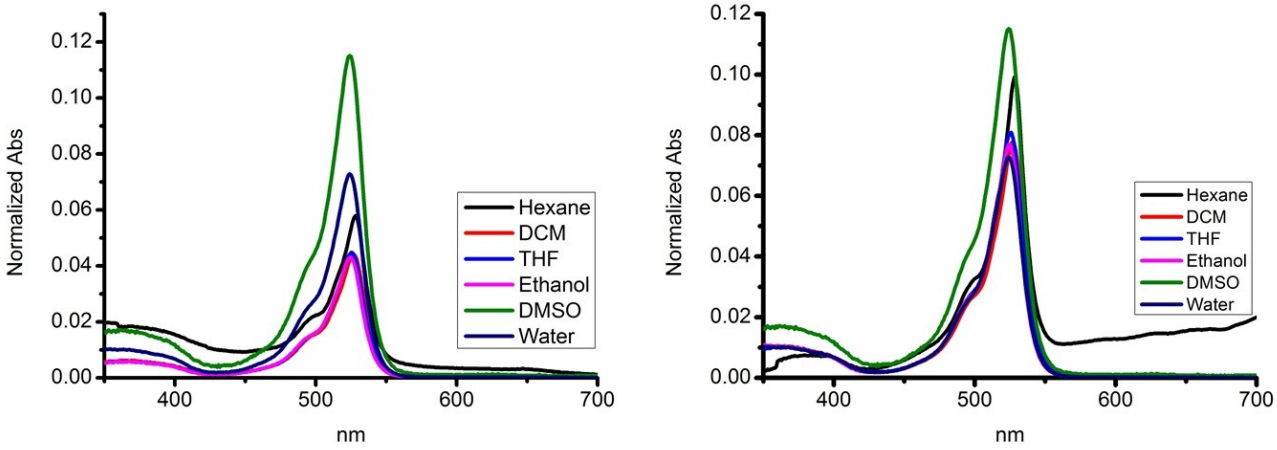

Figure S-13. Normalized absorption spectra of 10 μM in different solvents (Left) 2a, (Right) 2b.

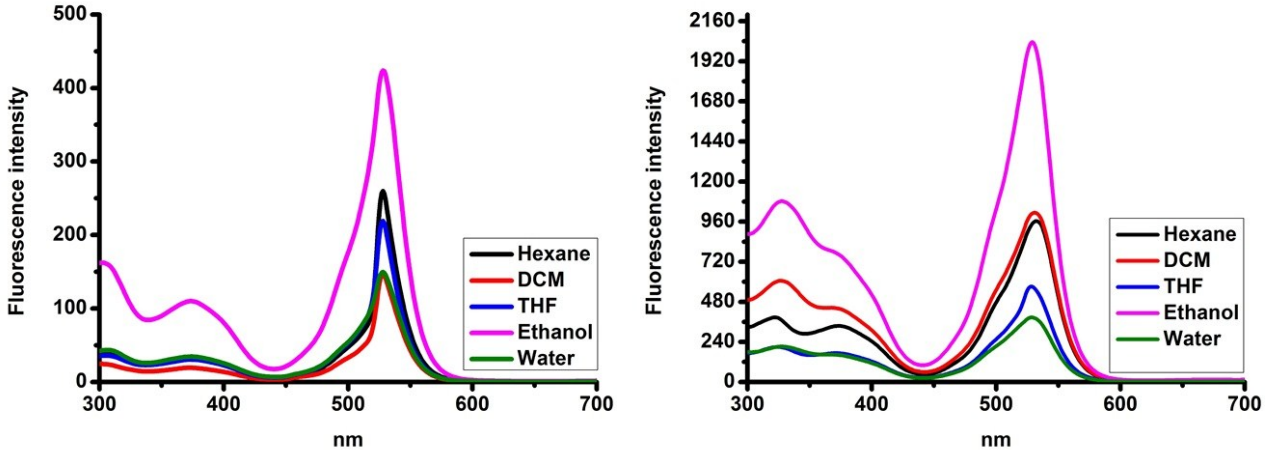

Figure S-14. Excitation spectra of 10 μM in different solvents, slit width 5nm, PMT voltage 700, (Left) 2a, (Right) 2b.

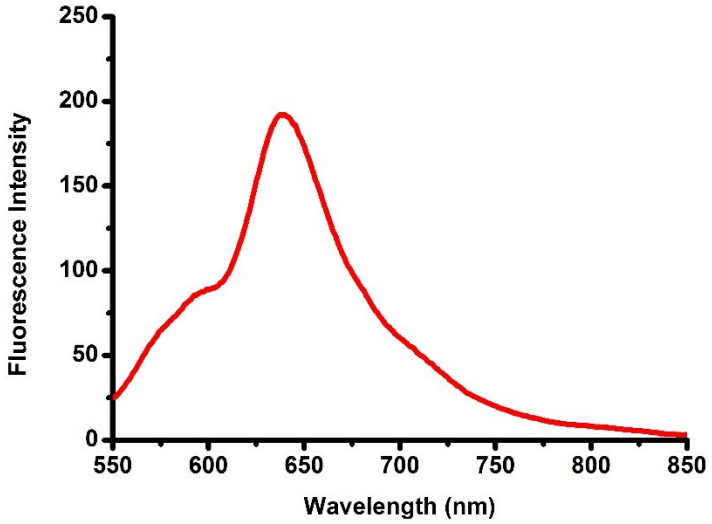

Figure S-15. Solid state fluorescence spectrum of F-Bodipy , slit width 5nm, PMT voltage 700.

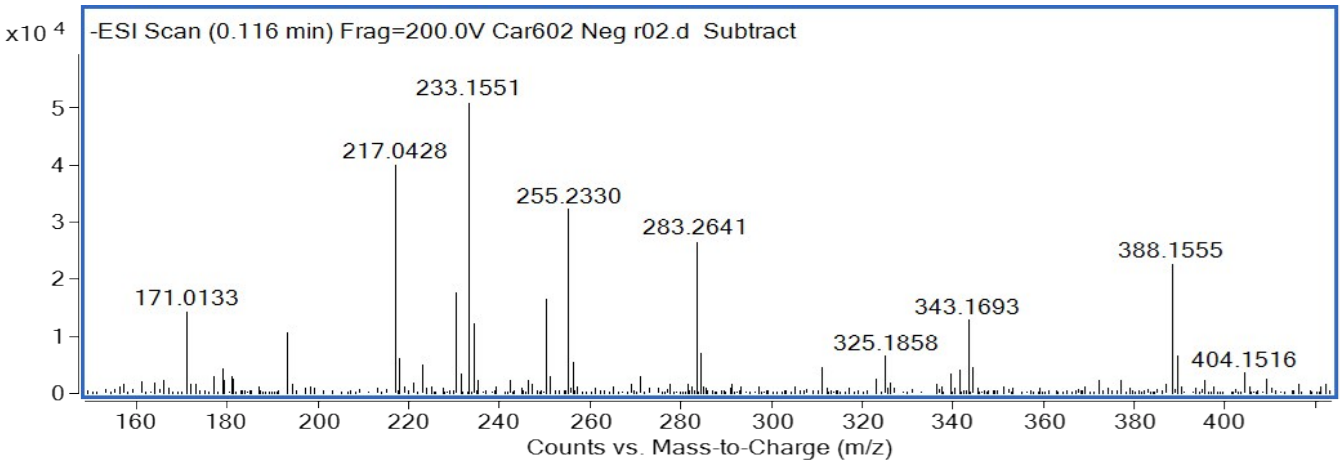

Figure S-16. HRMS spectrum for reaction mixture of 2a 10 μM and PLE enzyme 1 U/ml in phosphate buffer solution 100mM pH 7.4.

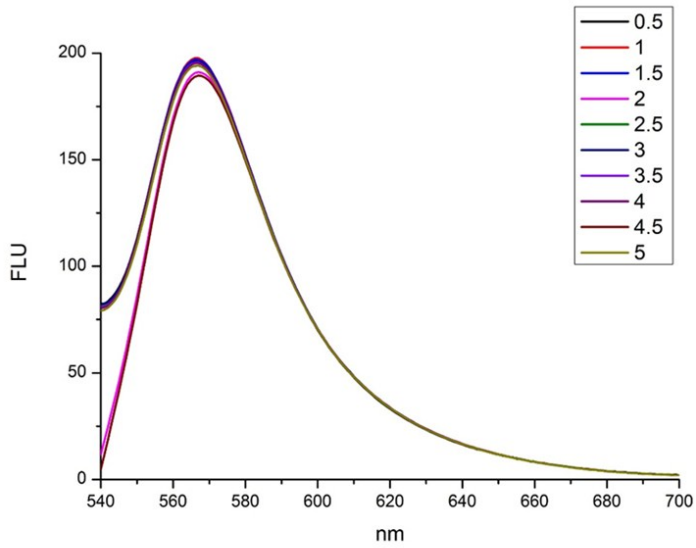

Figure S-17. emission spectra changing with time for probe 10 μM and PLE enzyme 1 U/ml in phosphate buffer solution 100mM pH 7.4 , 510 nm has been used for excitation.

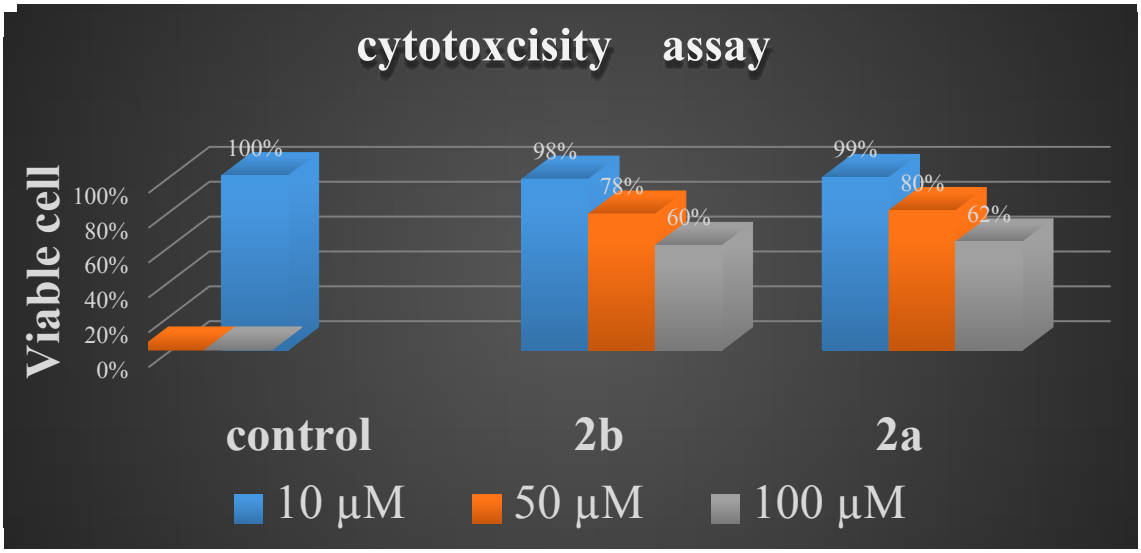

Figure S-18. MTT assay for 2a and 2b with concentrations 10 μM , 50 μM and 100 μM in HeLa cell after incubation for 24h.

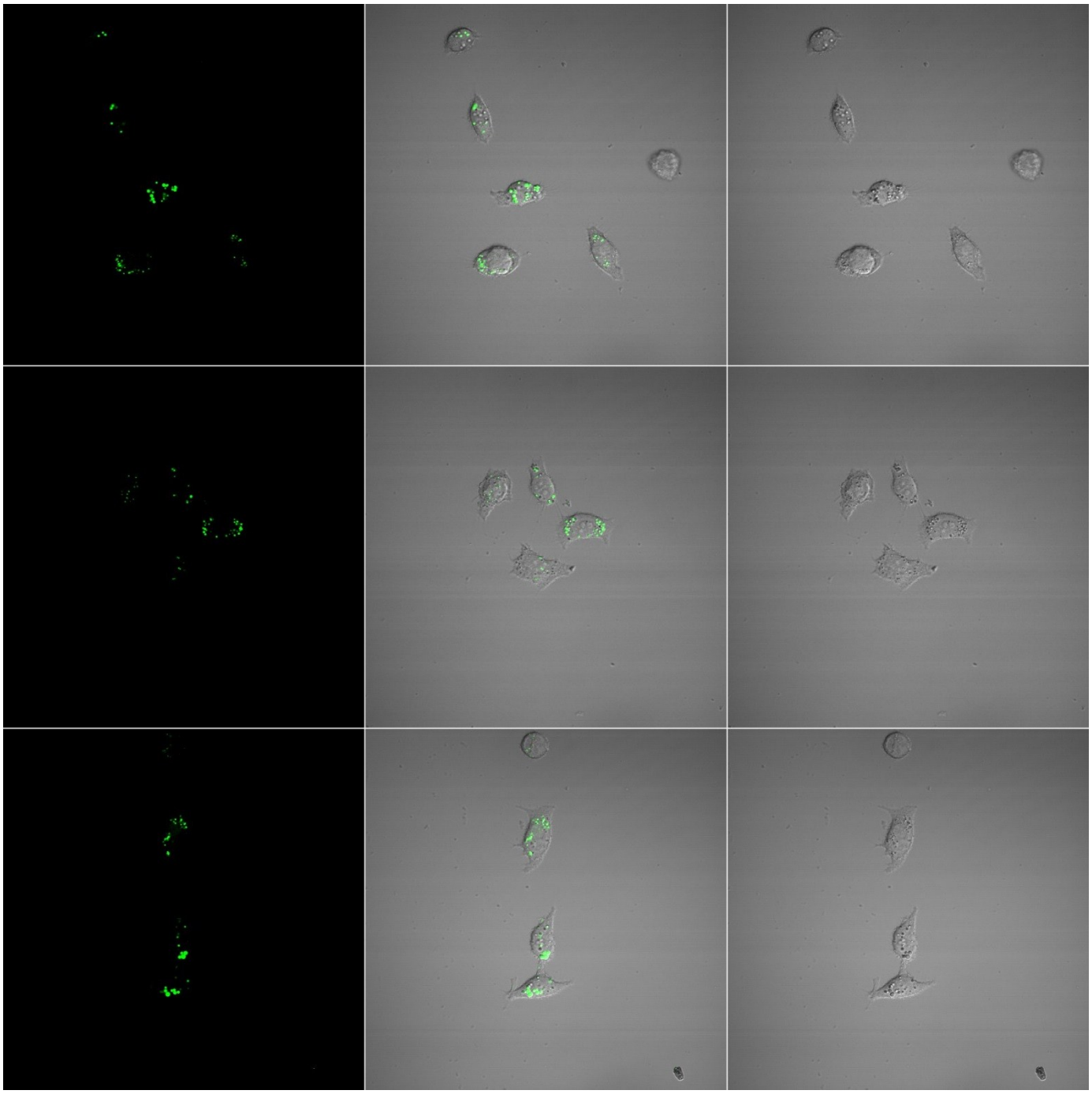

Figure S-19. Different images taken by fluorescent microscope after stunning HeLa cells with 1 nM of compound 2a for 20 mints (Left) green channel, (middle) overlay and (Right) Bright field

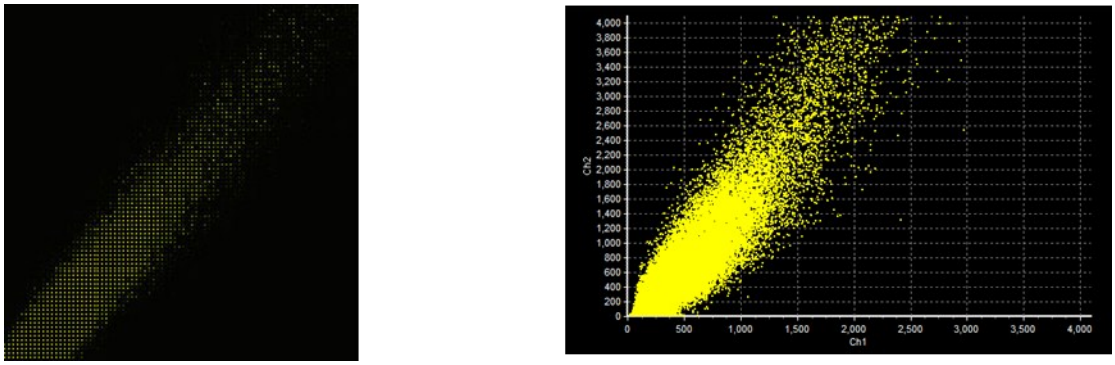

Figure S-20. Left) scatter plot of 2a by using the software Imagej, Right) scatter plot of 2b.

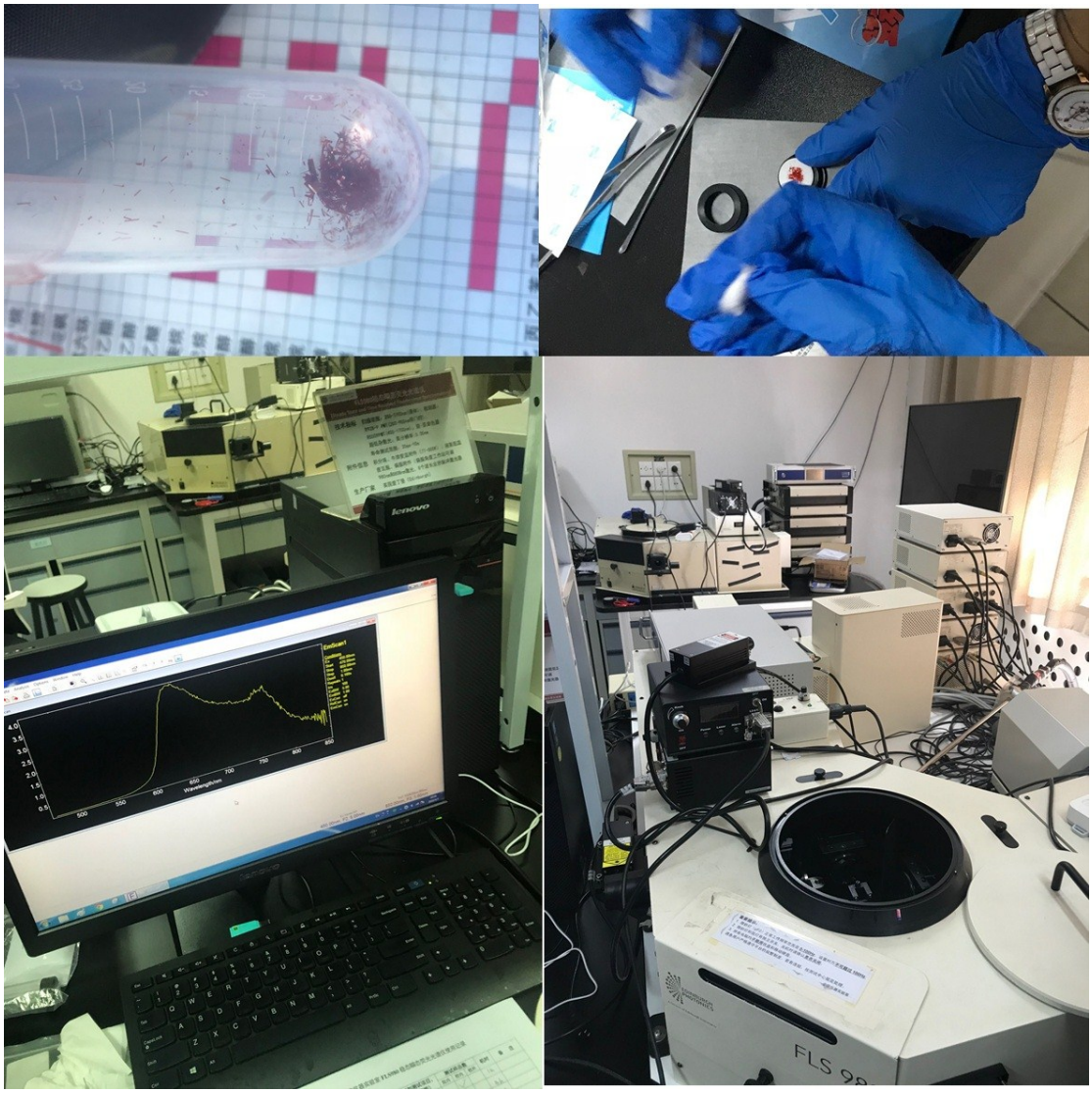

Figure S-21. Different pictures illustrate the process of measuring solid-state fluorescence spectra.