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Fluorescent β-ketothiolester boron complex: substitution based "turn-off" or "ratiometric" sensor for diamine

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I. NMR spectra of Compounds 3a-b

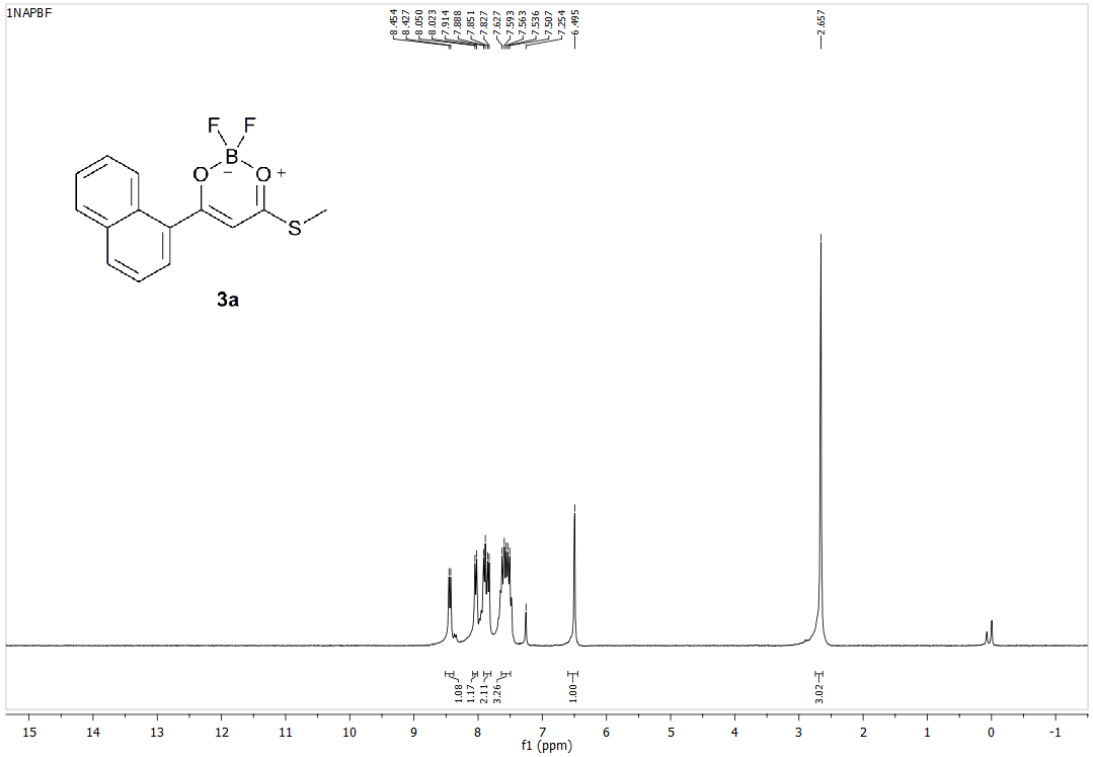

Fig. S1 ^{1}H NMR Spectrum of **3a**

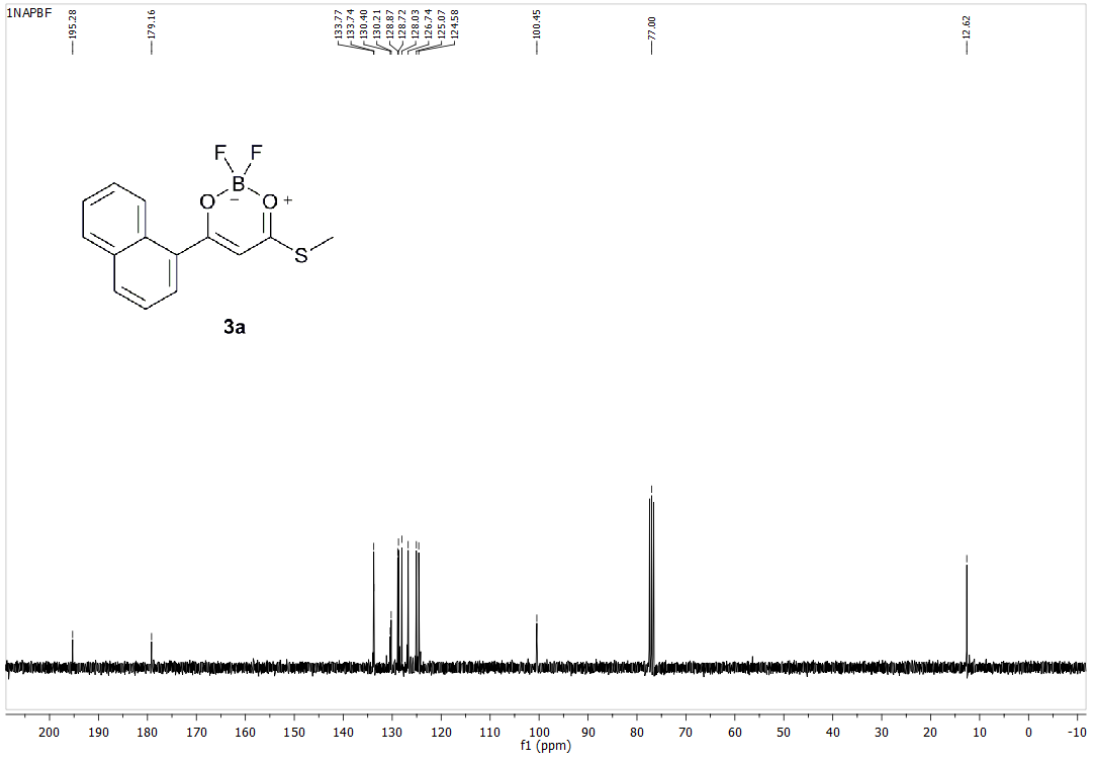

Fig. S2 ^{13}C NMR Spectrum of **3a**

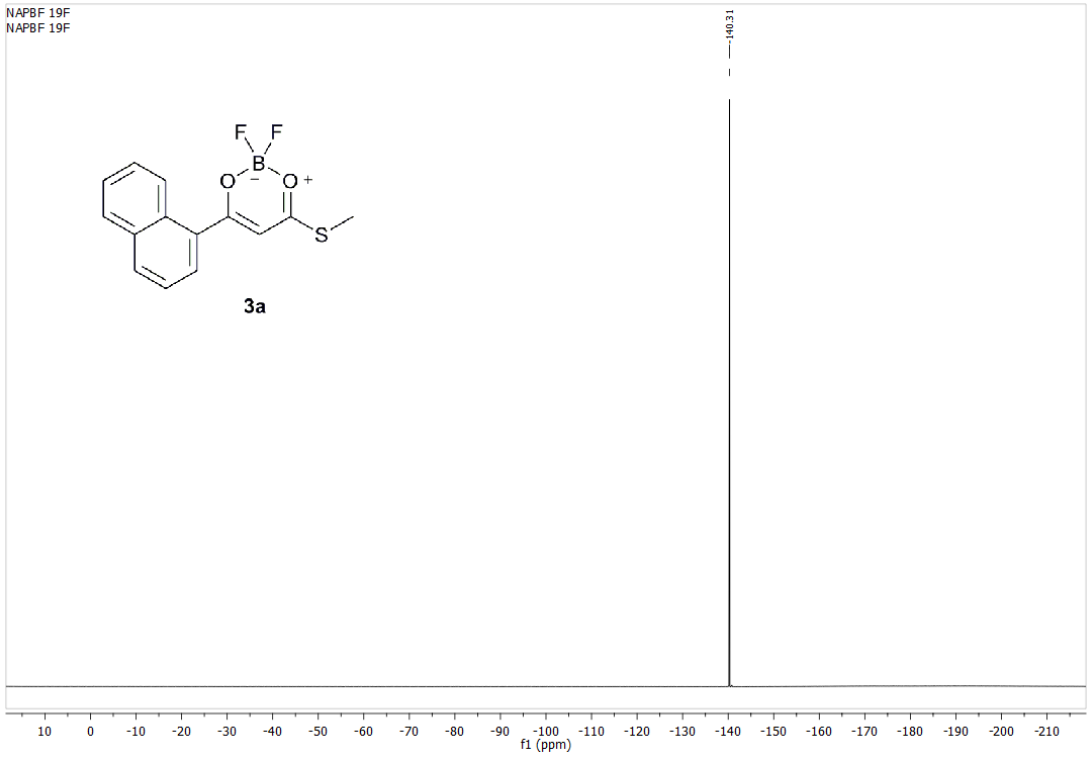

Fig. S3 ^{19}F NMR Spectrum of **3a**

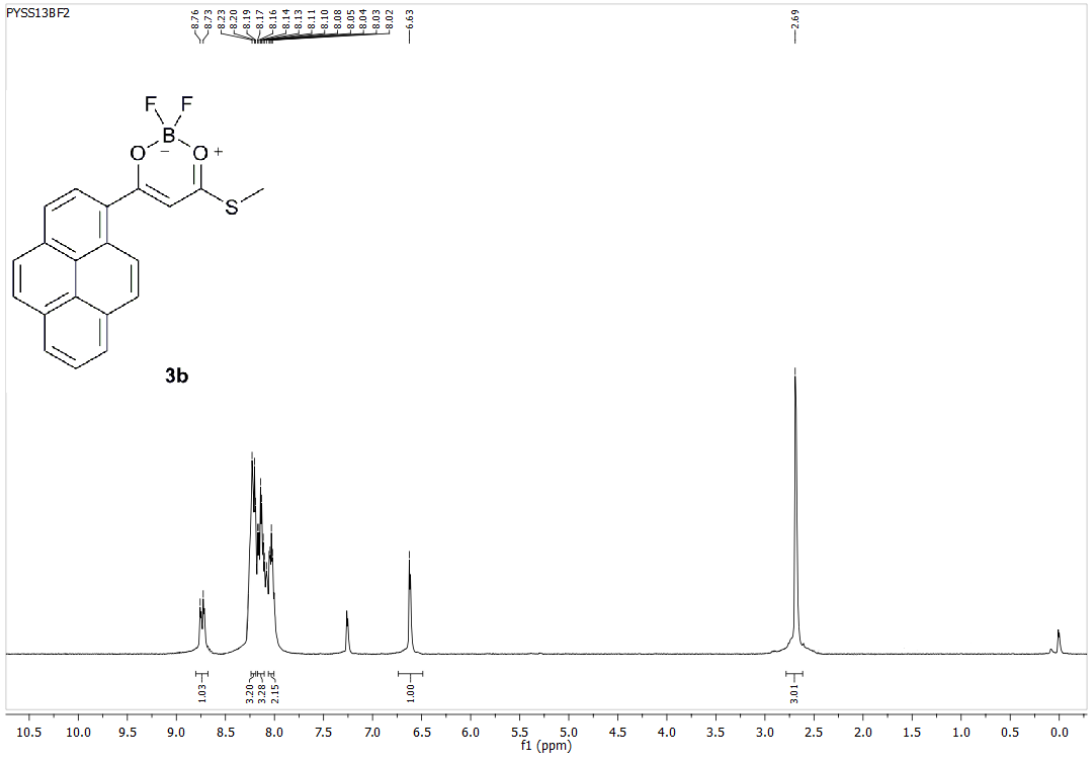

Fig. S4 ^{1}H NMR Spectrum of **3b**

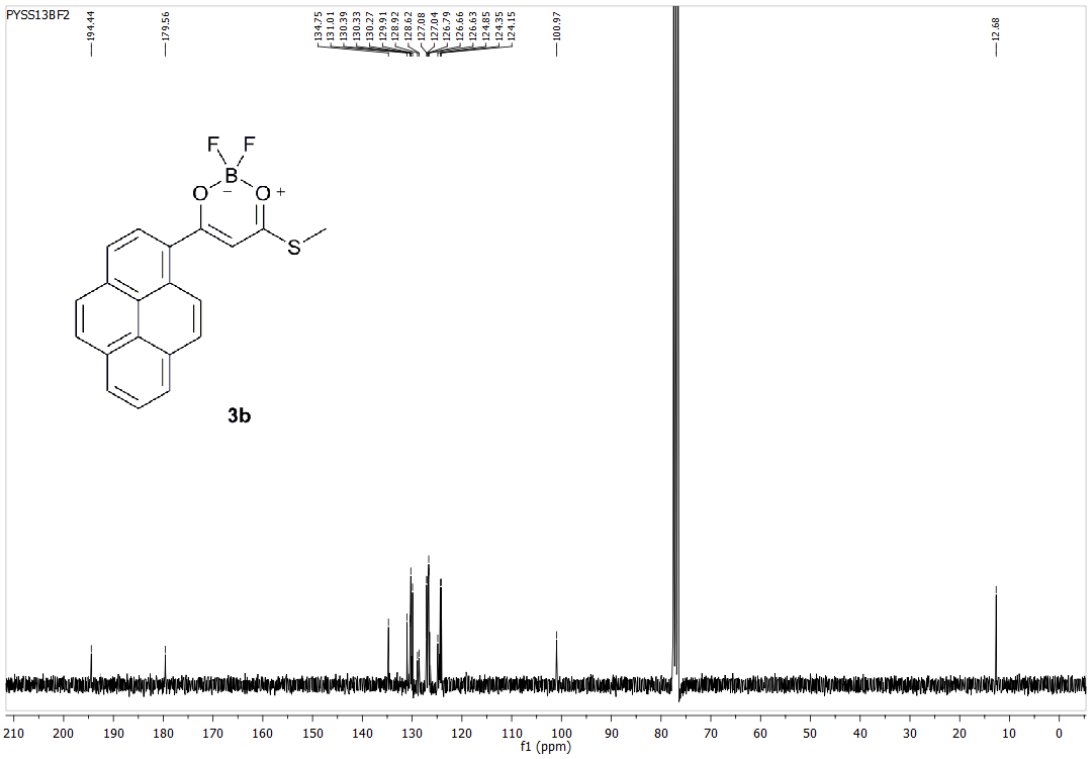

Fig. S5 ^{13}C NMR Spectrum of **3b**

II. Photophysical properties of 3a-b

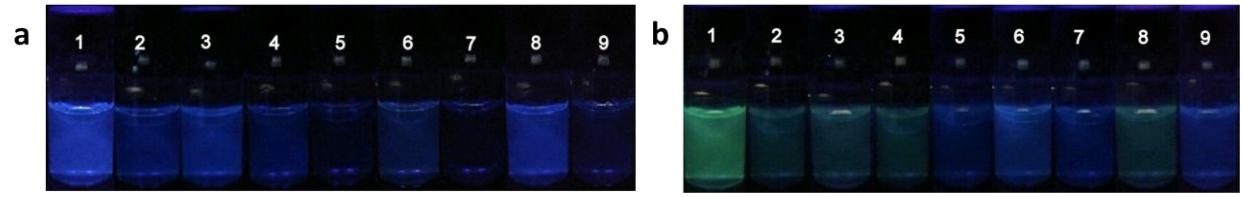

Fig. S6 photography of solution of probes **3a** (a) and **3b** (b) in $CHCl_3$ (1×10^{-5} M) up on addition of amines 1 µM (left to right); probe reference (1), Aniline (2), Diisopropyl ethylamine (3), Dimethylaniline (4), Morpholine (5), Benzylamine (6), n-Butylamine (7), triethylamine (8), Ethylenediamine (9).

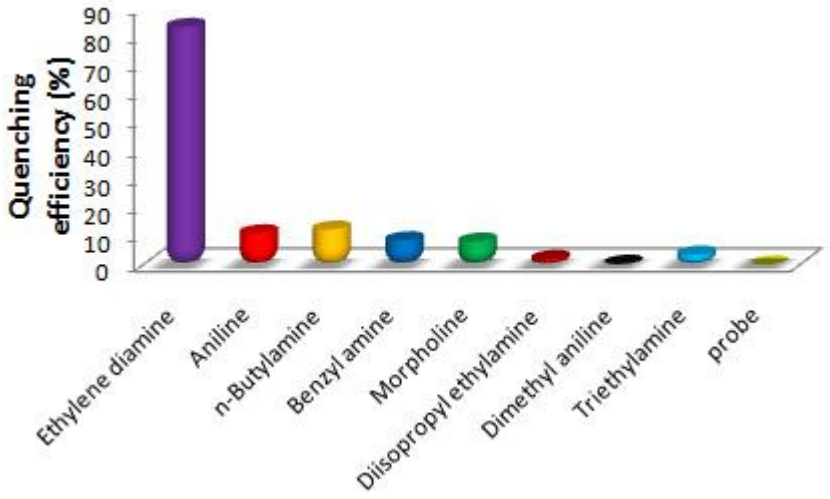

Fig. S7 Relative fluorescence quenching of **3a** (1×10^{-5} M) in $CHCl_3$ upon addition of various amines (100 equiv)

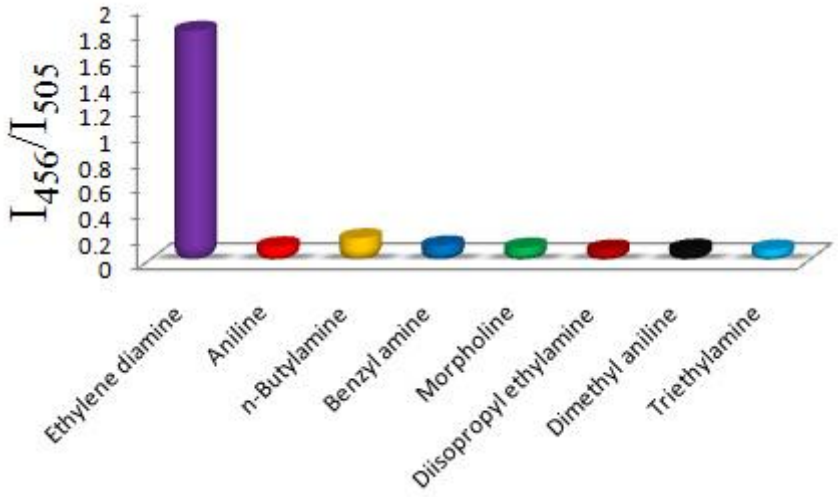

Fig. S8 Relative fluorescence intensity changes (I_{456}/I_{505}) of **3b** (1×10^{-5} M) in $CHCl_3$ upon addition of various amines (100 equiv)

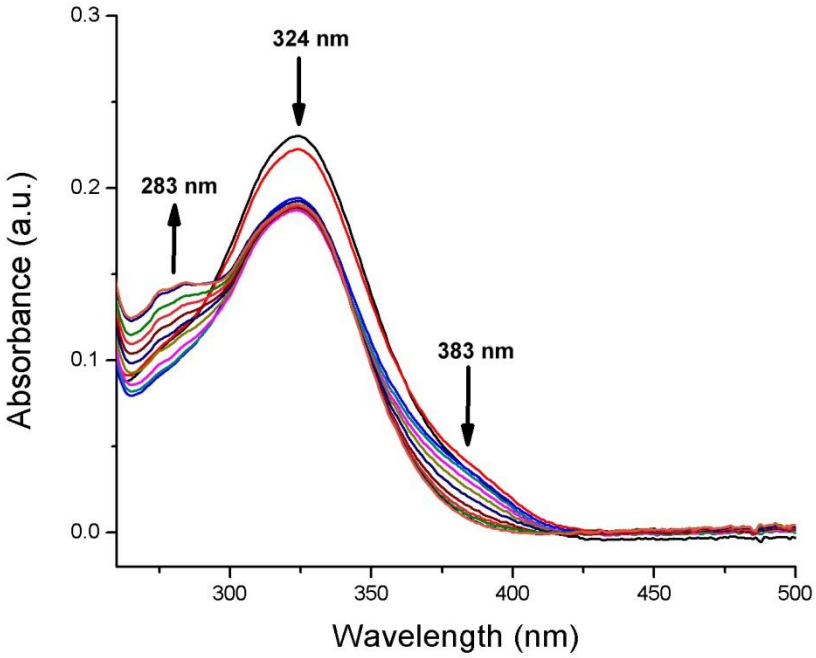

Fig. S9 Absorption Spectral change of probe **3a** (1×10^{-5} M) containing a different concentration of En (0-12 equivalent) in $CHCl_3$ solution

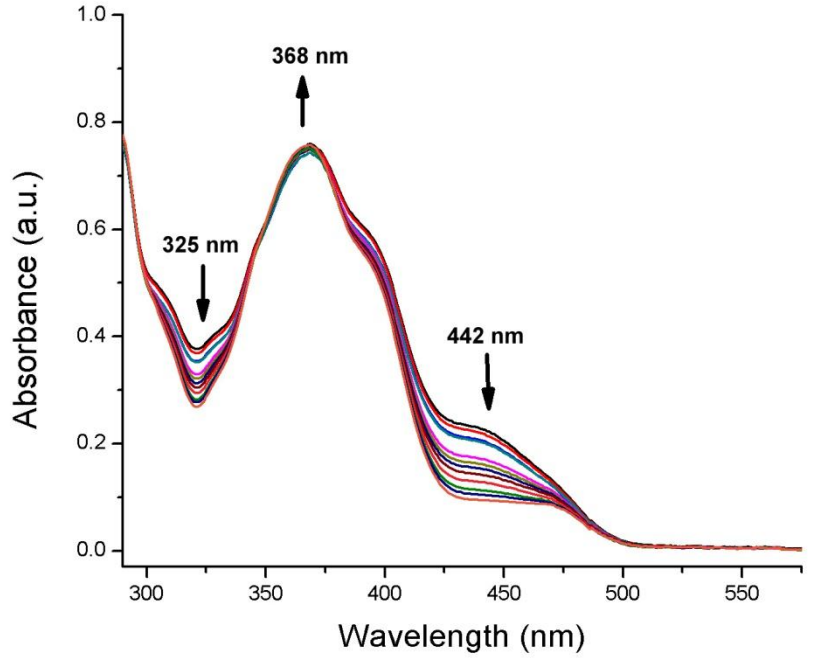

Fig. S10 Absorption Spectral change of probe **3b** (1×10^{-5} M) containing a different concentration of En (0-12 equivalent) in $CHCl_3$ solution

Fig. S11 Calorimetric change upon addition of En 12 equivalent in **3b** (1×10^{-5} M) in $CHCl_3$ under visible light, (left) before addition, (right) after addition

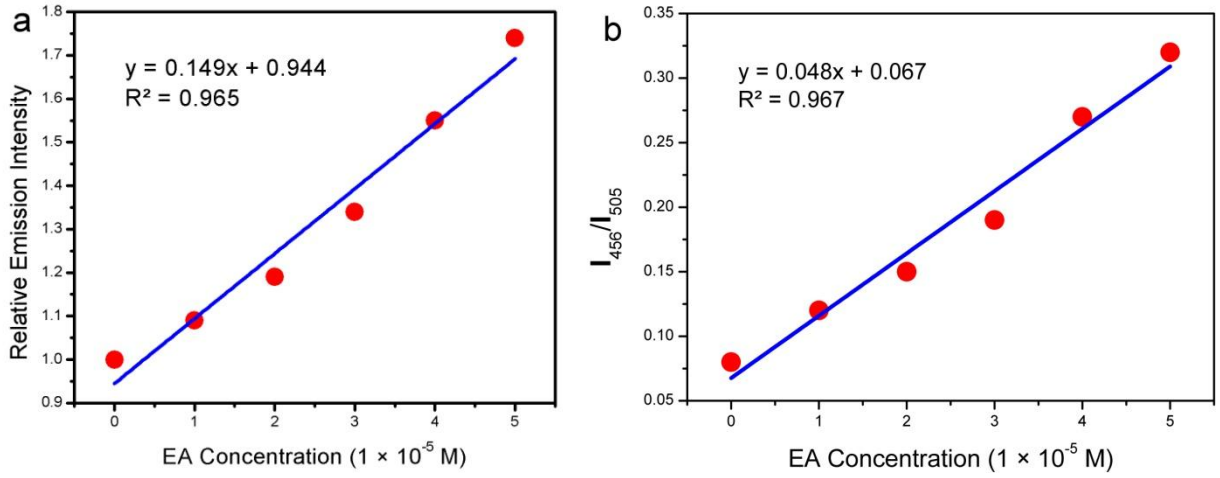

Fig. S12 Calibration plot for detection limit (LOD) in **3a** (a) and **3b** (b). The LOD was derived by using the formula 3σ/slope, where σ is the standard deviation of the blank (5 samples) and slope was obtained from linear calibration curve.

III. NMR and Mass spectra of Compounds 3a + En and 3b + En

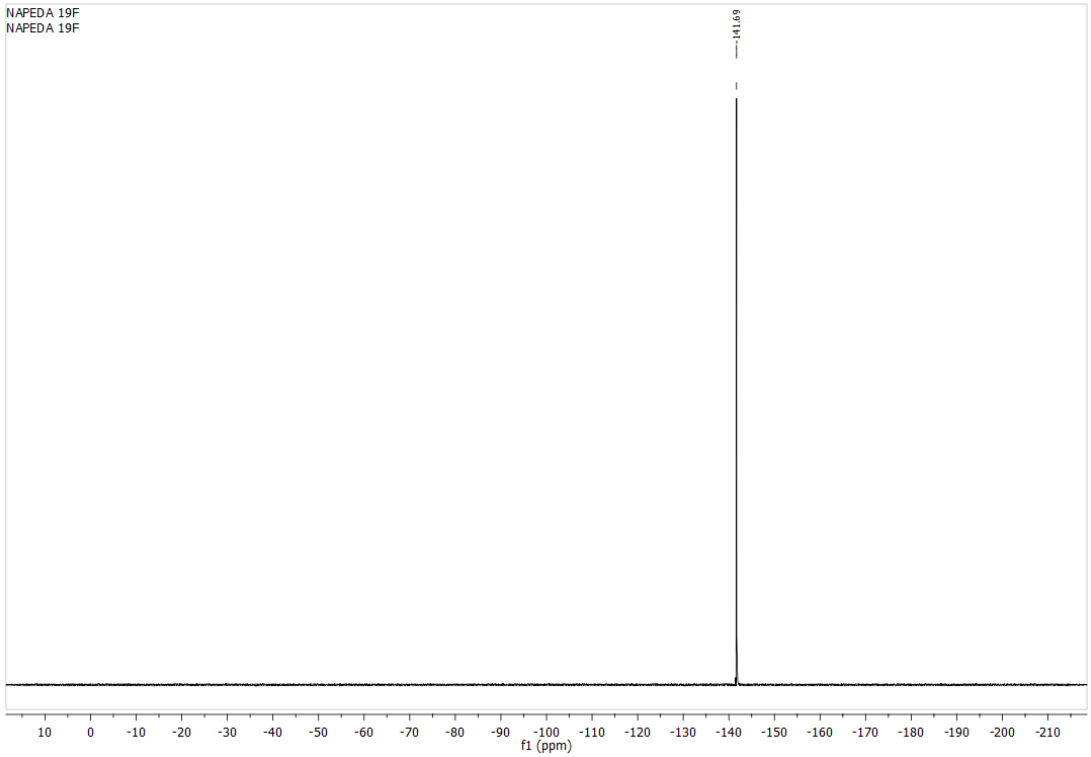

Fig. S13 ^{19}F NMR Spectrum of **3a** after addition of **En**

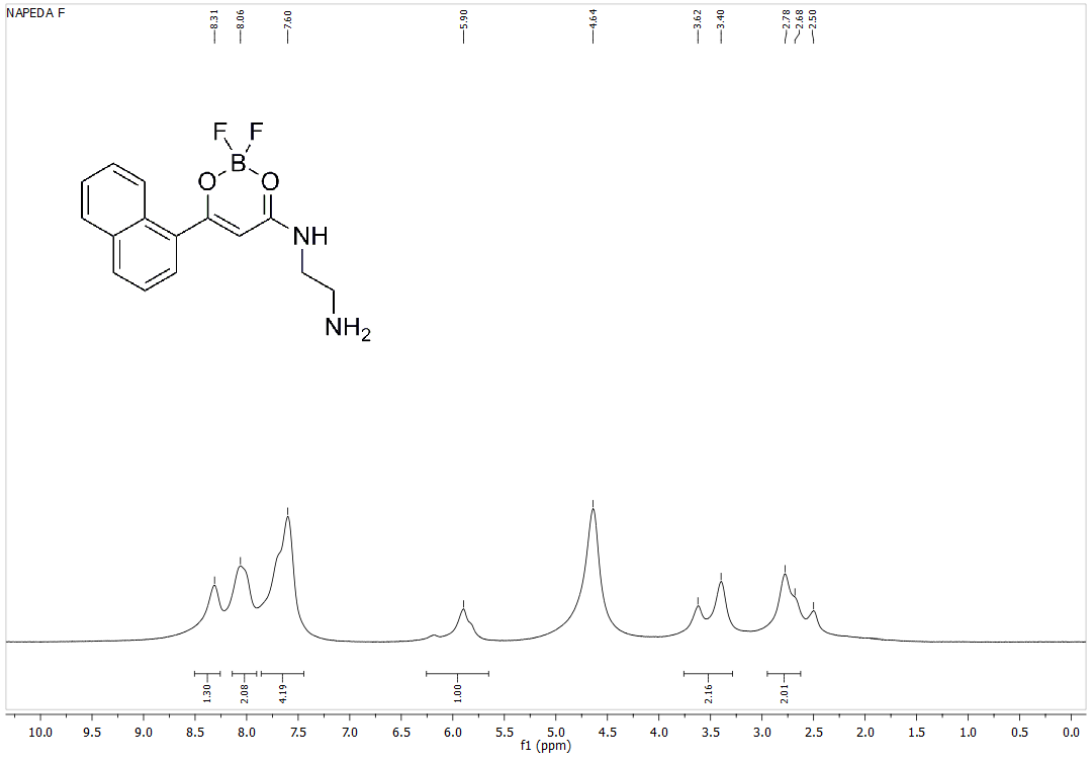

Fig. S14 ^{1}H NMR Spectrum of **3a + En**

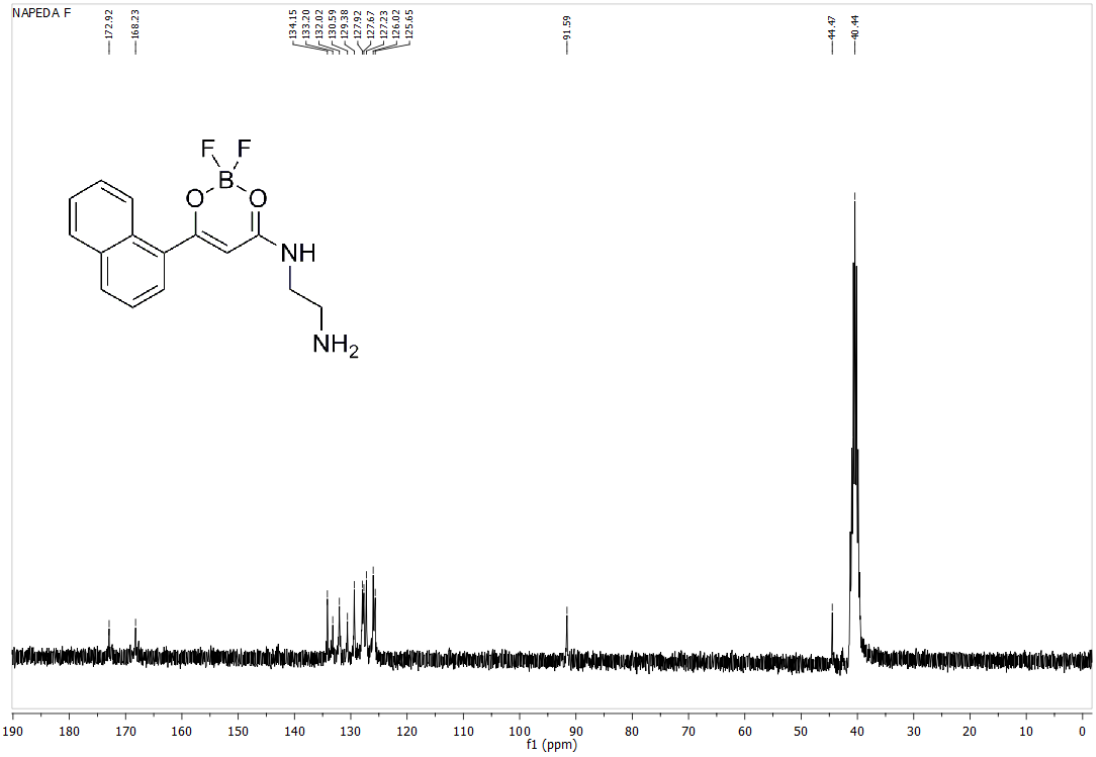

Fig. S15 ^{13}C NMR Spectrum of **3a + En**

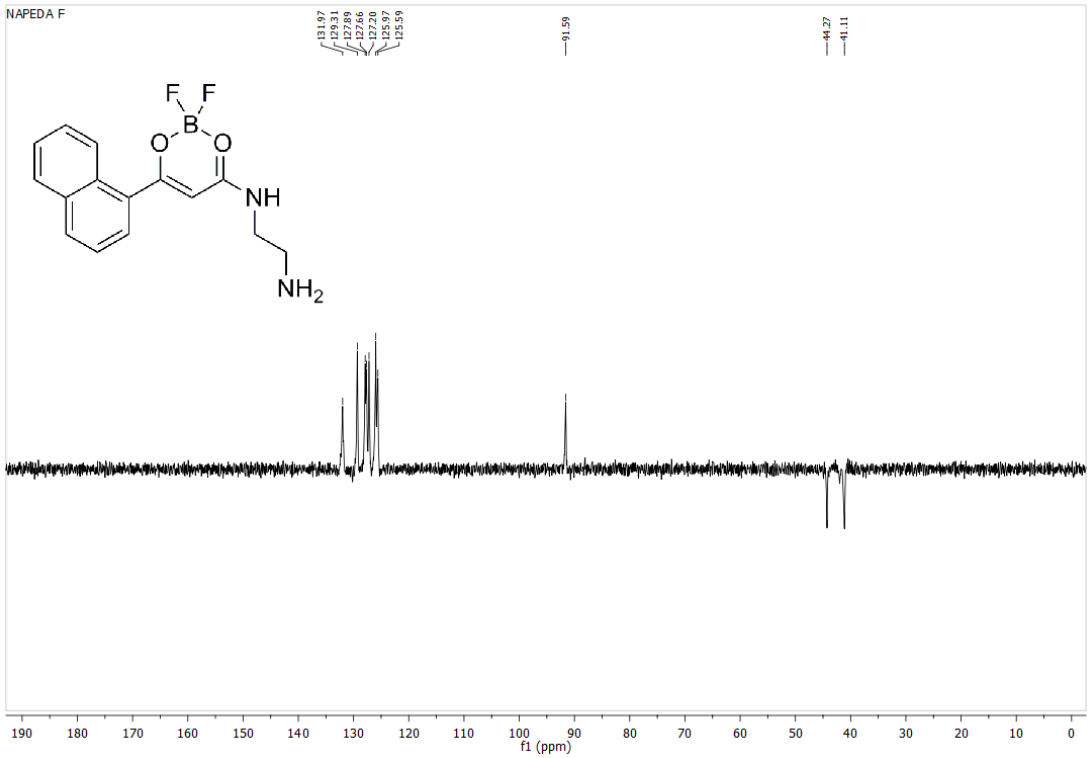

Fig. S16 DEPT-135 NMR Spectrum of **3a + En**

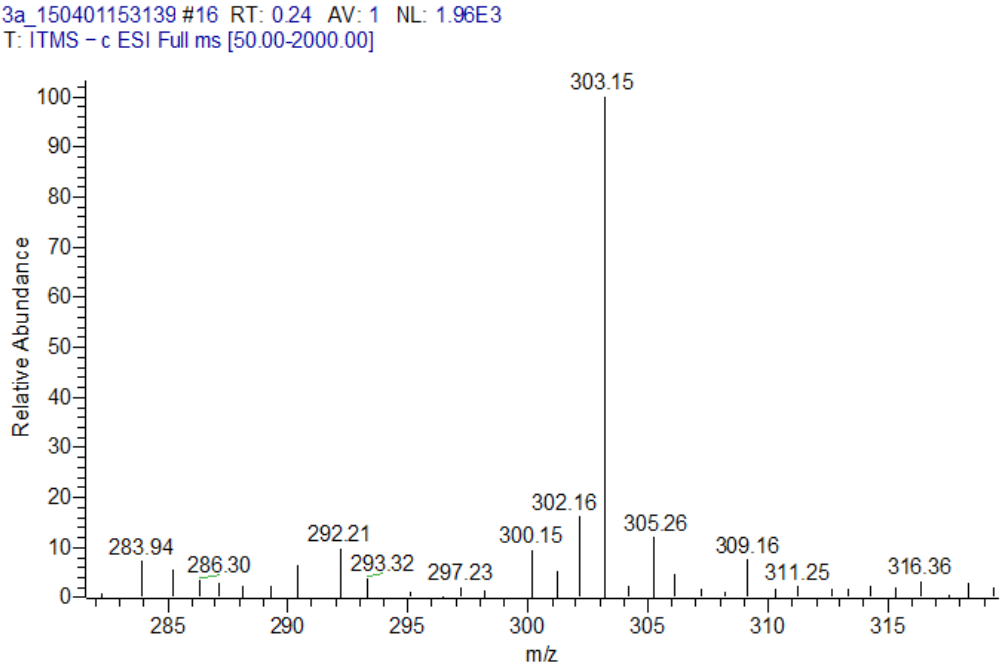

Fig. S17 Mass Spectrum of **3a + En**

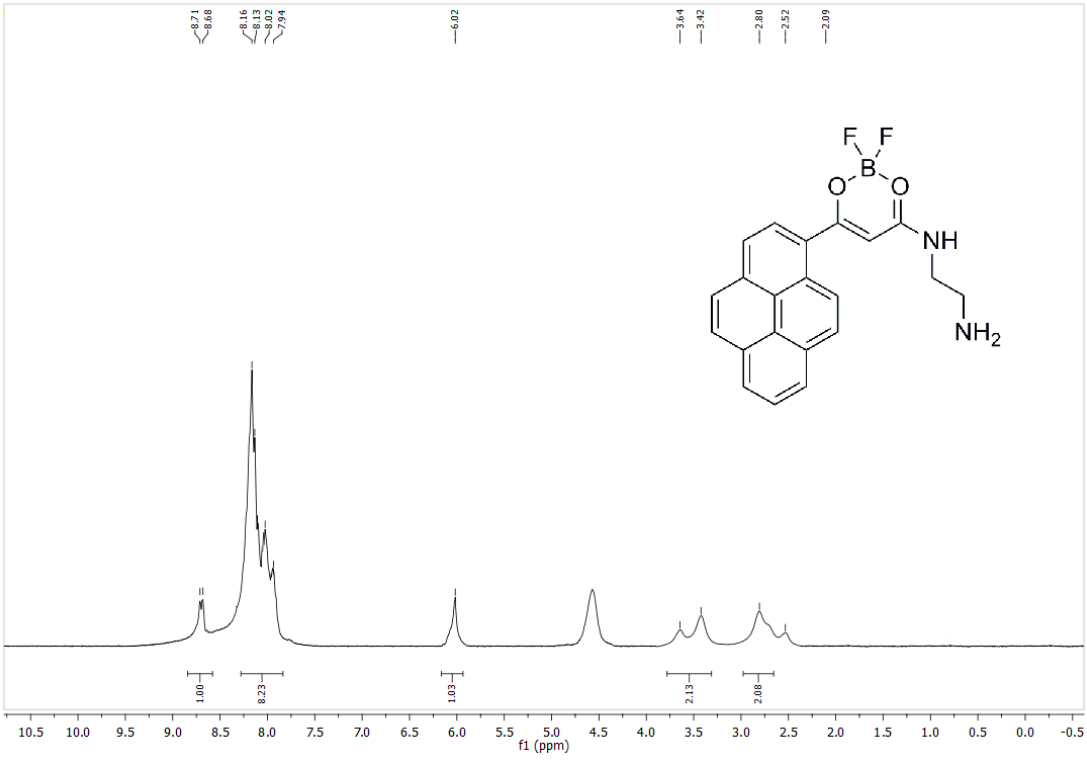

Fig. S18 ^{1}H NMR Spectrum of **3b + En**

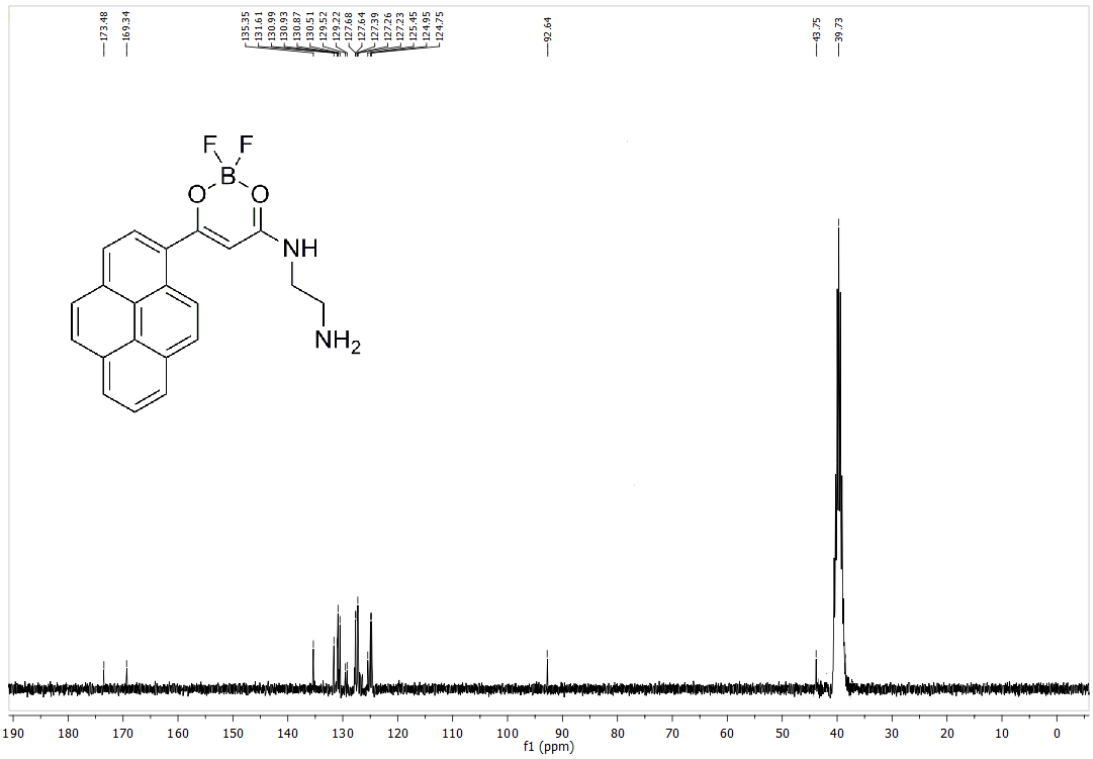

Fig. S19 ^{13}C NMR Spectrum of **3b + En**

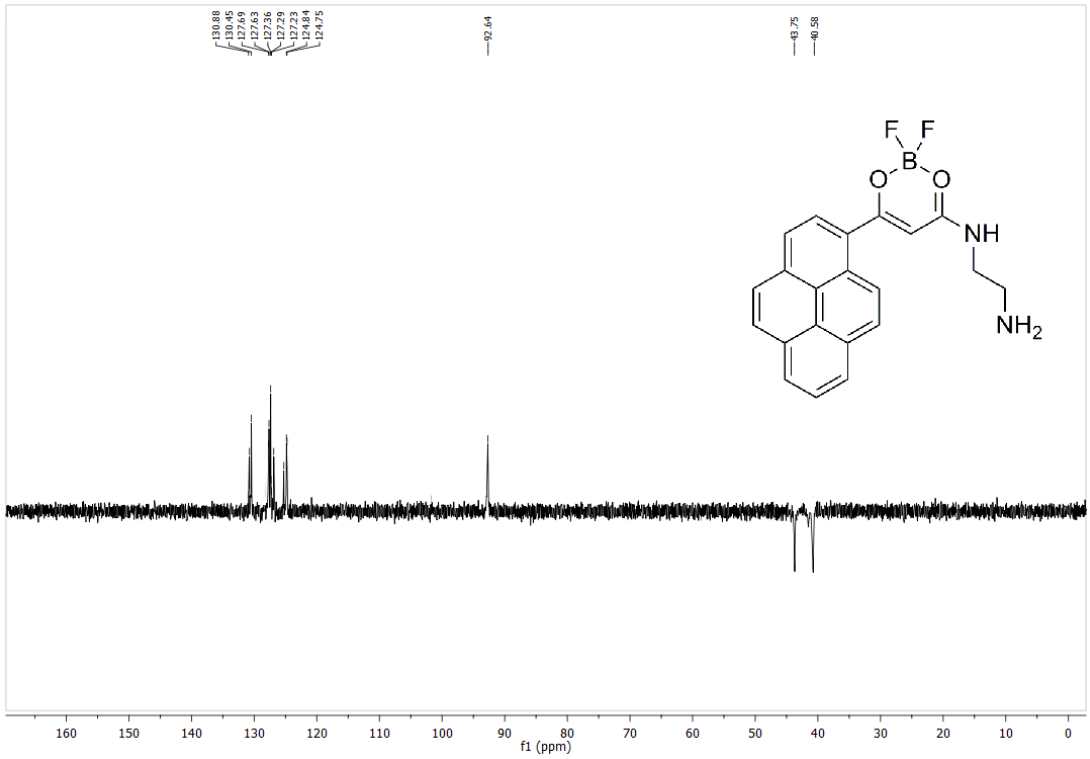

Fig. S20 DEPT-135 NMR Spectrum of **3b + En**

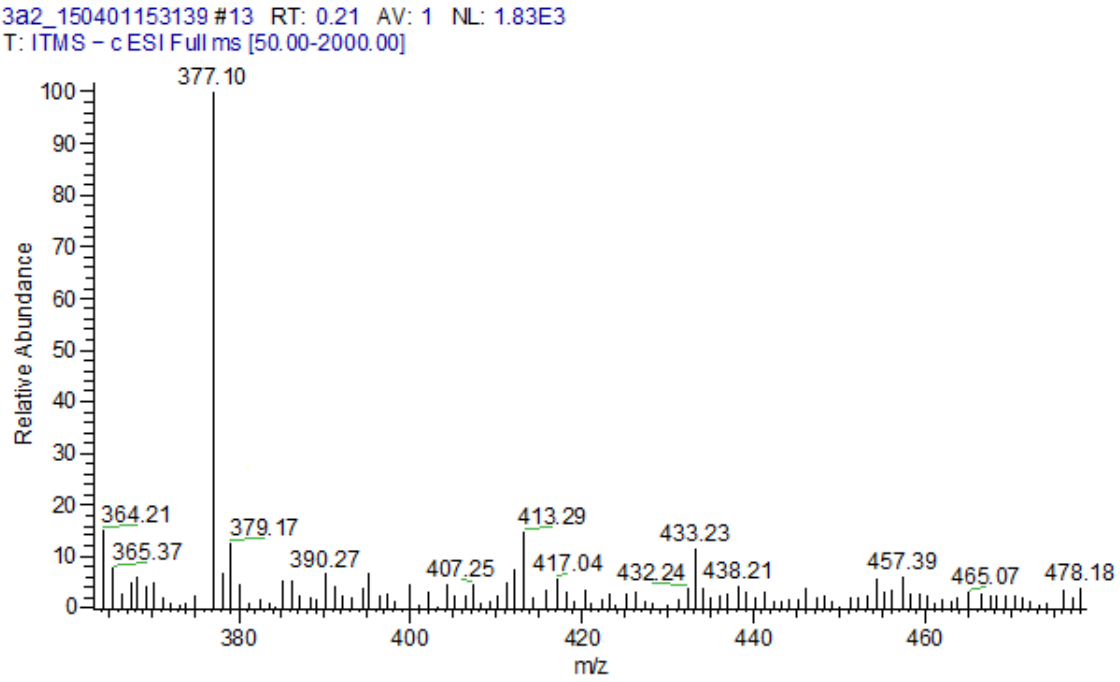

Fig. S21 Mass Spectrum of **3b + En**

IV. Kinetics studies of 3a and 3b with En

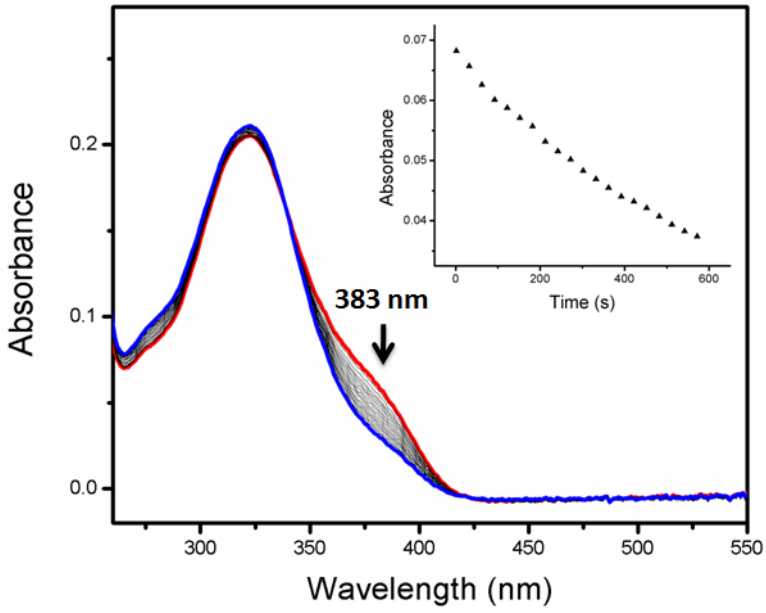

Fig. S22 The kinetics of En sensing by the reaction of **3a** (1×10^{-5} M) with three equivalent of En in $CHCl_3$ at 25 °C. Insert: plot of Absorption *vs* Time.

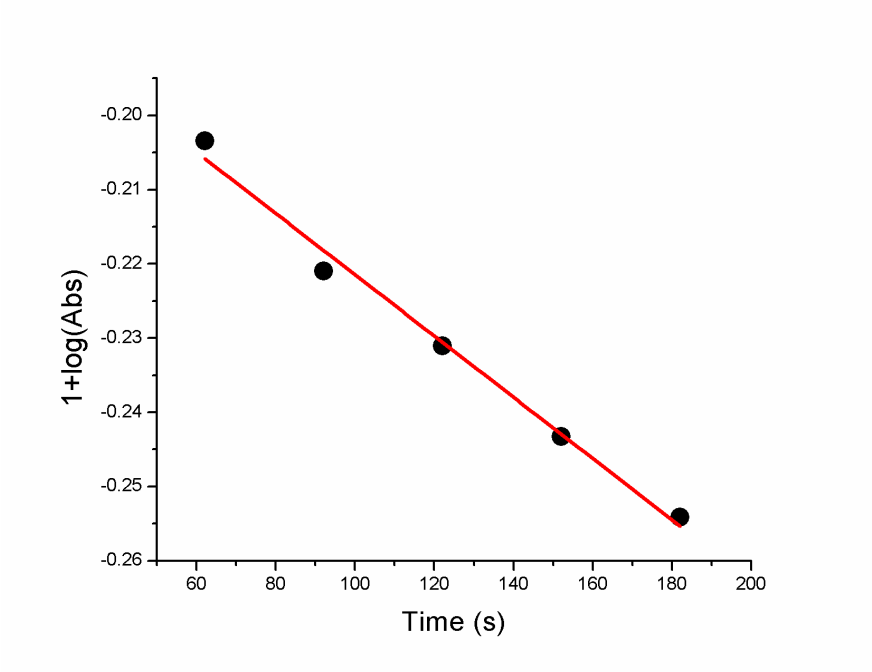

Fig. S23 Plot of [1+log(Abs)] *vs* Time by the reaction of **3a** (1×10^{-5} M) with three equivalent of En in $CHCl_3$ at 25 °C.

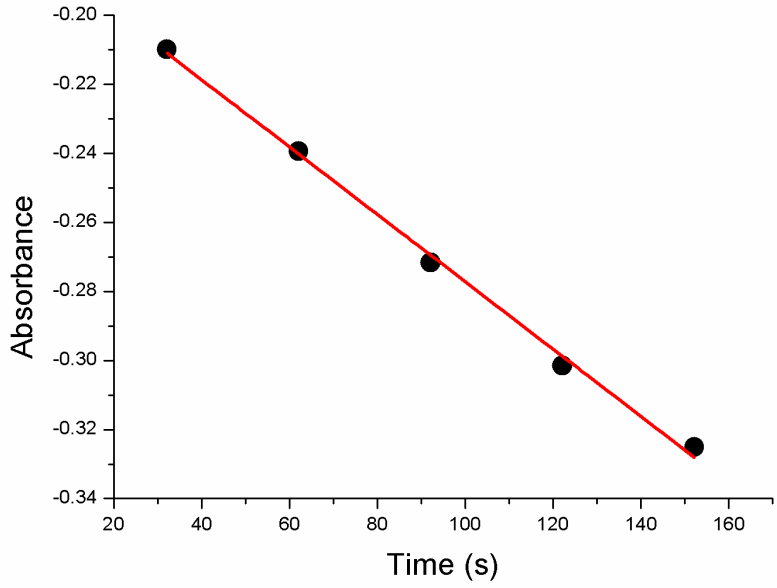

Fig. S24 Plot of [1+log(Abs)] *vs* Time by the reaction of **3a** (1×10^{-5} M) with six equivalent of En in $CHCl_3$ at 25 °C.

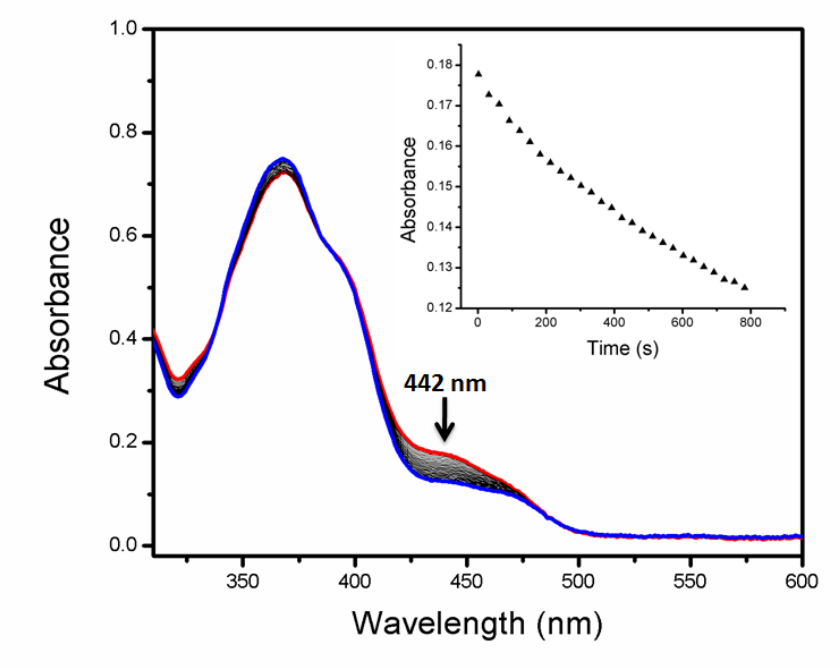

Fig. S25 The kinetics of En sensing by the reaction of **3b** (1×10^{-5} M) with three equivalent of En in $CHCl_3$ at 25 °C. Insert: plot of Absorption *vs* Time.

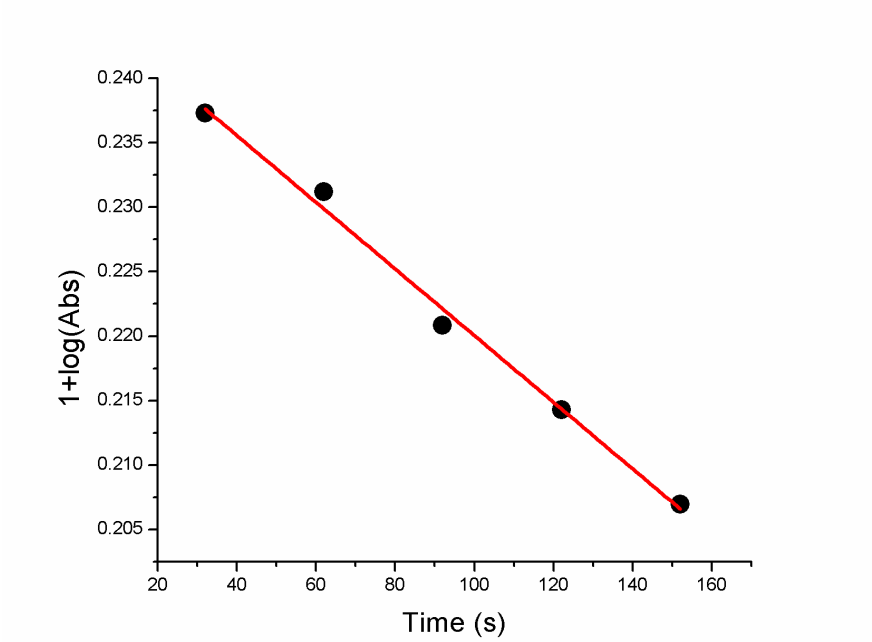

Fig. S26 Plot of [1+log(Abs)] *vs* Time by the reaction of **3b** (1×10^{-5} M) with three equivalent of En in $CHCl_3$ at 25 °C.

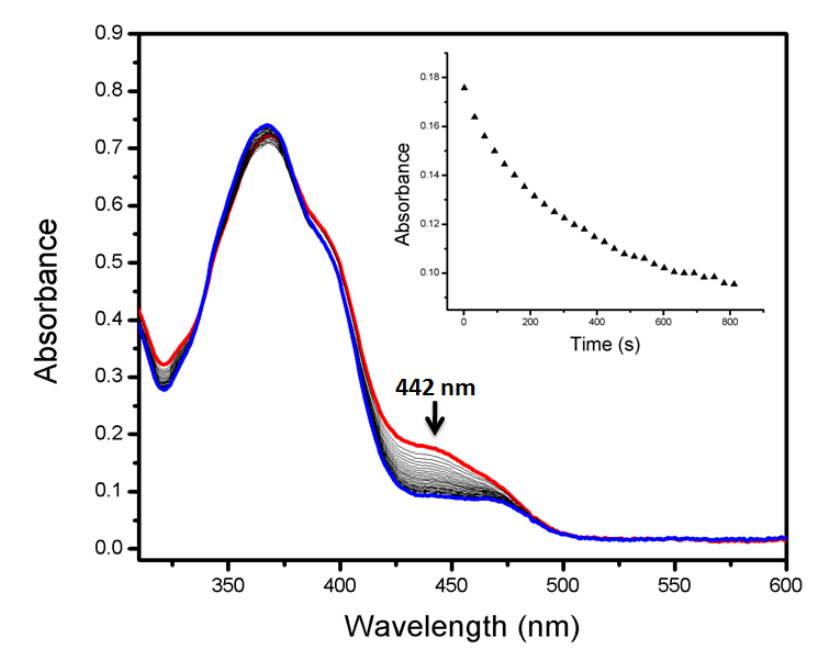

Fig. S27 The kinetics of En sensing by the reaction of **3b** (1×10^{-5} M) with six equivalent of En in $CHCl_3$ at 25 °C. Insert: plot of Absorption *vs* Time.

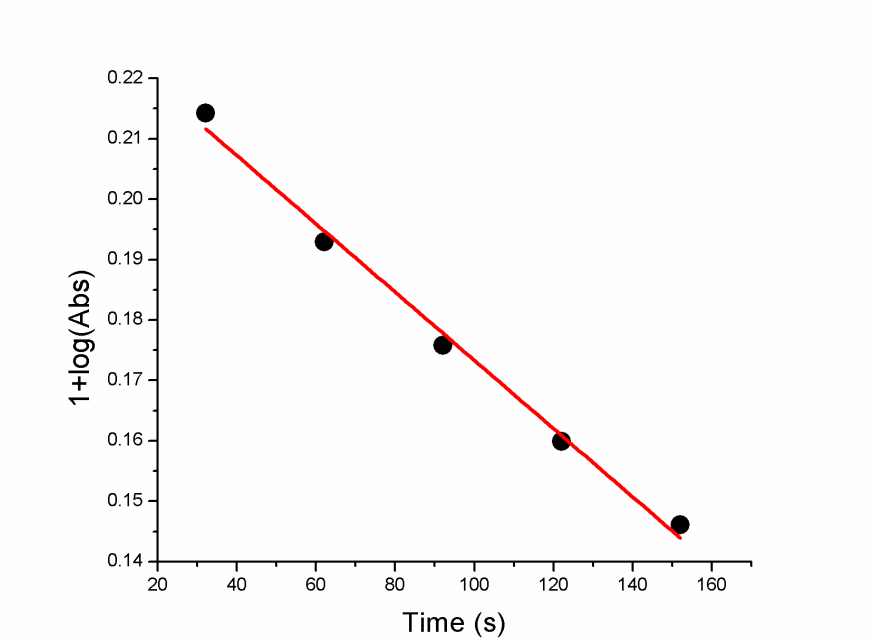

Fig. S28 Plot of [1+log(Abs)] *vs* Time by the reaction of **3b** (1×10^{-5} M) with six equivalent of En in $CHCl_3$ at 25 °C.

V. Sensing of diamines with 3a and 3b

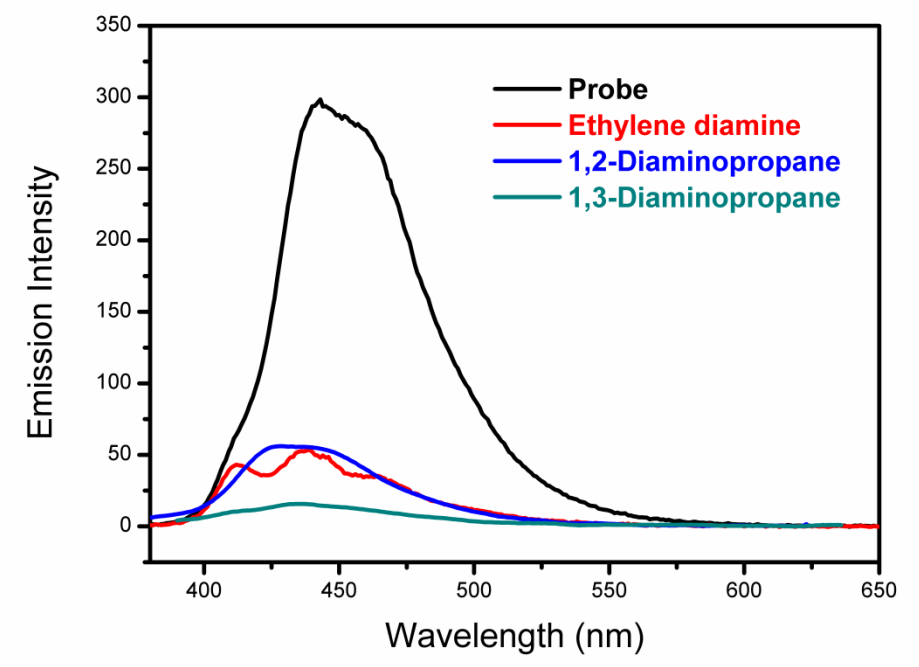

Fig. S29 Emission spectral change of **3a** in $CHCl_3$ (1×10^{-5} M) in the presence of 20 equivalent addition of diamine.

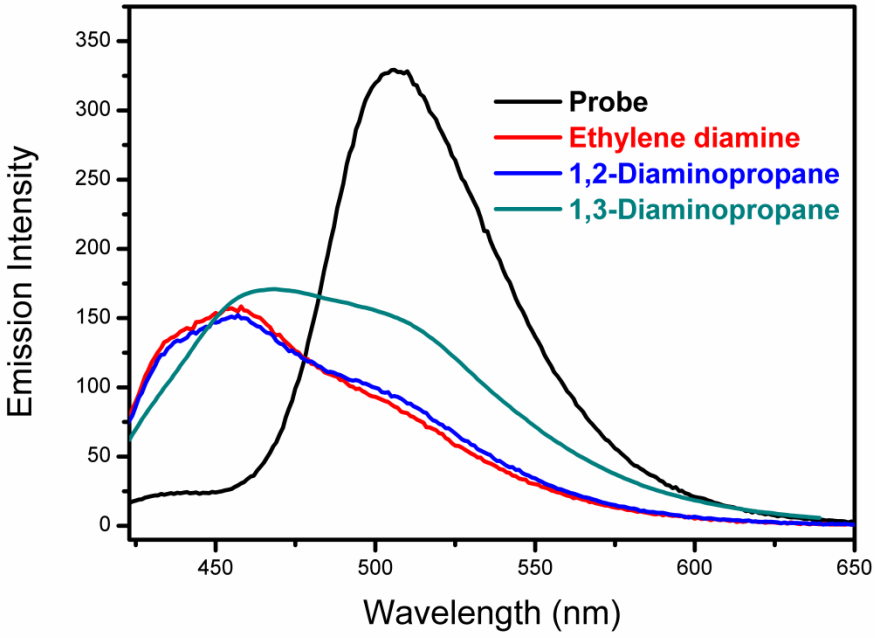

Fig. S30 Emission spectral change of **3b** in $CHCl_3$ (1×10^{-5} M) in the presence of 20 equivalent addition of diamine.

Table S1 Quantum yield of **3a** and **3b** with diamines in $CHCl_3$.[a]

S.No	Dye + Diamine	ϕ_f[b]
1	3a + Ethylenediamine	0.12
2	3a + 1,2-diaminopropane	0.13
3	3a + 1,3-diaminopropane	0.04
4	3b + Ethylenediamine	0.49
5	3b + 1,2-diaminopropane	0.50
6	3b + 1,3-diaminopropane	0.64

(a) The measured concentration 1×10^{-5} M at 25 °C. (b) Determined by comparison with quinine sulfate.

VI. HRMS spectra of 3a and 3b

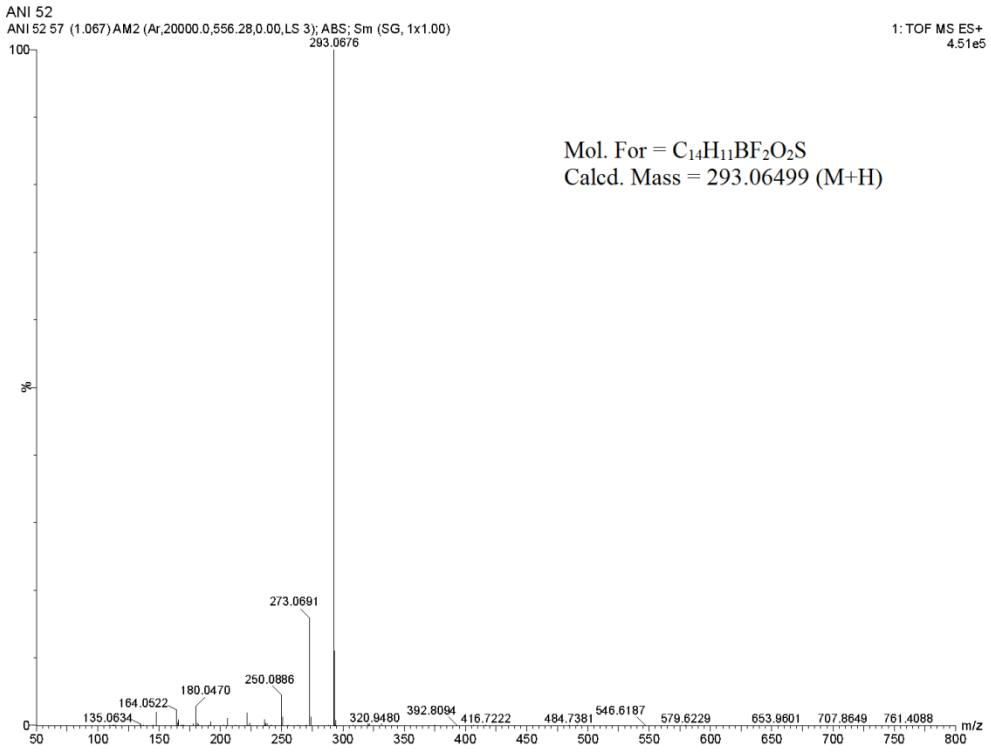

Fig. S31 HRMS Spectrum of **3a**

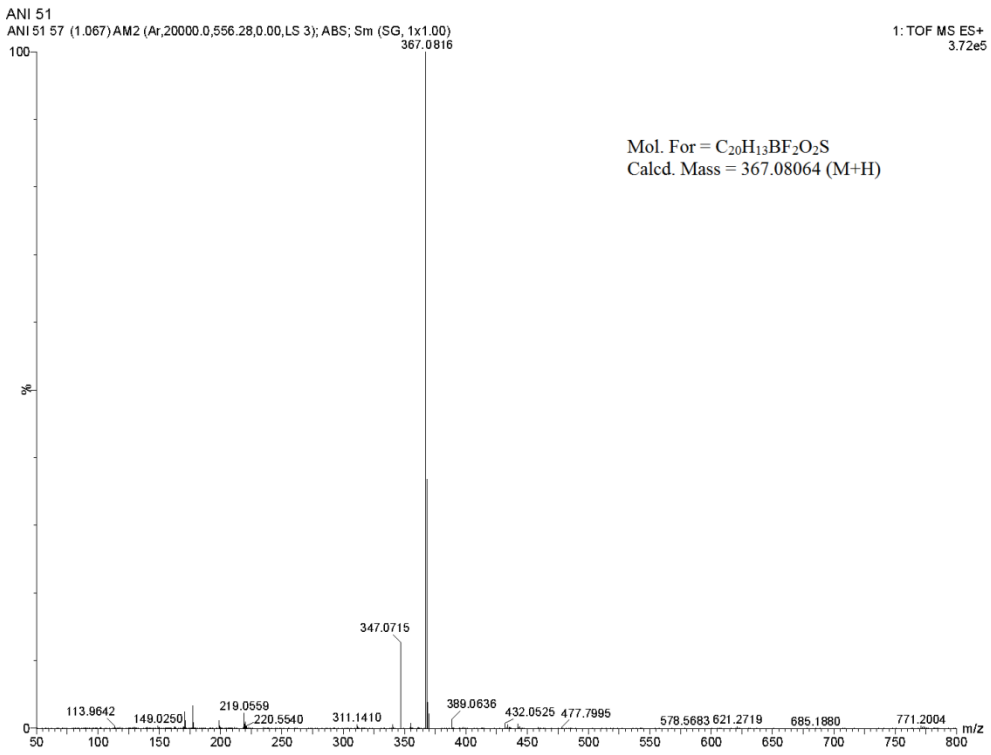

Fig. S32 HRMS Spectrum of **3b**

VII. DFT Calculation of 3a and 3a+En

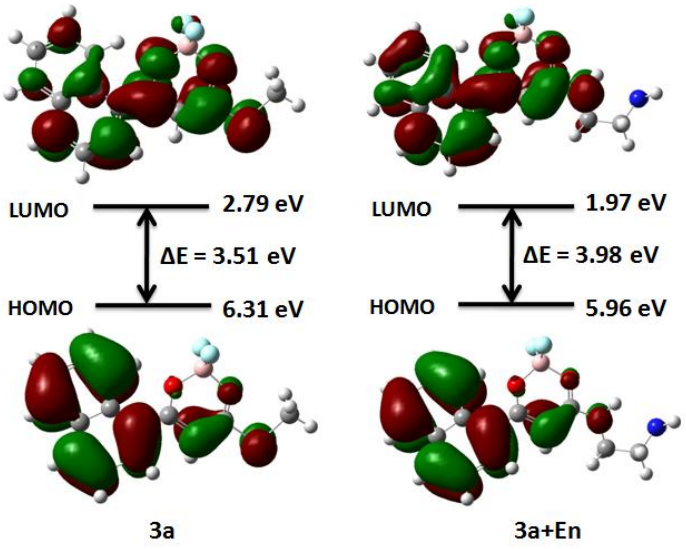

Fig. S33 HOMO and LUMO energy levels of **3a** and **3a+En** calculated using TD-DFT/B3LYP/6-31G basic set.