Supporting Information

Synthesis of a [2]Rotaxane Operated in basic Environment

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§1. Materials

Unless stated otherwise, all reagents and anhydrous solvents were purchased from Aldrich Chemicals and used without further purification.

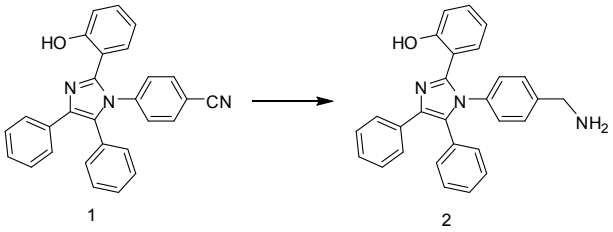
§2. Instruments

Column chromatography: SiO_2 (200–300 mesh). TLC glass plates coated with SiO_2 F254 were visualized by UV light. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 or 600 MHz instrument at a constant temperature of 298 K. Chemical

shifts are reported in parts per million from low to high field and referenced to TMS. MALDI-TOF mass spectra were recorded on a Bruker Biflex III MALDI-TOF spectrometer. UV/Vis spectra were measured on a Hitachi U-3010 spectrometer. Fluorescence excitation and emission spectra were recorded using a Hitachi F-4500 FL fluorimeter at a constant temperature of 298 K.

§3. Synthetic route

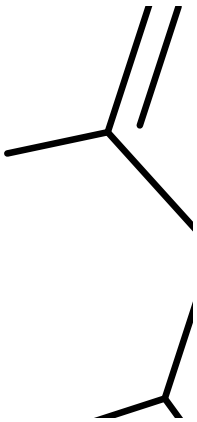
§4. Synthesis and characterization data of all compounds



1 2

Compound **1**: compound **1** was synthesized according to reference S1. M.p. = 174-175 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.65 (m, 2 H), 7.51 (m, 2 H), 7.25-7.50 (m, 7H), 7.23 (m, 1H), 7.08 (m, 3H), 6.50 (m, 1H), 6.43 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 158.36, 144.86, 141.16, 136.09, 133.53, 132.65, 131.34, 130.54, 130.09, 129.70, 129.23, 129.08, 128.94, 128.81, 128.46, 127.98, 127.44, 126.99, 126.13, 118.28, 118.07, 117.64, 113.23, 112.43 ppm; EI-MS: m/z 413.4; elemental analysis (%) calcd for $C_{28}H_{19}N_3O$: C 81.34, H 4.63, N 10.16; found: C 81.66, H 4.64, N 10.12.

Compound **2**: $LiAlH_4$ (0.74 g, 20 mmol) was added slowly to a solution of the compound 1 (2 g, 4.8 mmol) in anhydrous THF at 0 ℃. After being at room temperature overnight, the mixture was quenched with aqueous Na_2SO_4. After filtration, the solvent was evaporated off, and the residue was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4. After concentrated in vacuo, the crude product was purified by chromatography (SiO_2: CH_2Cl_2/MeOH, 20:1) to afford compound **2** as slightly yellow oil in 58% yield. M.p. = 141-142 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.54 (m, 2 H), 7.06-7.36 (m, 14 H), 6.57 (m, 1 H), 6.46 (m, 1 H), 3.92 ppm (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 158.55, 145.08, 144.23, 141.81, 135.80, 135.73, 135.26, 133.23, 131.46, 130.64, 129.98, 129.18, 128.75, 128.60, 128.39, 128.25, 128.17, 127.10, 127.01, 126.13, 118.02, 117.77, 113.16, 45.78 ppm; EI-MS: m/z 417; elemental analysis (%) calcd for $C_{28}H_{23}N_3O$: C 80.55, H 5.55, N 10.06; found: C 80.79, H 5.52, N 10.10.



Compound **5**: A solution of the compound **2** (0.418 g, 1 mmol) and **3** (0.16 g, 1 mmol) in toluene (50 mL) was heated under reflux overnight by using a Dean-Stark apparatus. The solvent was removed under reduced pressure after the reaction was cooled to room temperature. The residue was dissolved in THF (50 mL), then $NaBH_4$ (0.4 g, 10.5 mmol) was added cautiously at 0 ℃. The mixture was stirred at room temperature for a further 4 h. Water was added to quench the excess $NaBH_4$. The solvent was evaporated off, and the residue was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4. After concentrated in vacuo, the crude product compound **4** (300 mg, 0.53 mmol) was dissolved in acetone and a few drops of trifluroacetic acid were added. After 0.5 hour, the solvent was removed under vacuo. The residue was dissolved in a mixture of acetone and water. Then the aqueous of NH_4PF_6 (122 mg, 0.75 mmol) was added. The mixture was stirred for 1 h and then the acetone was evaporated off. The aqueous solution was extracted with CH_2Cl_2 several times. The collected organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo to yield **5** as a yellow solid (600 mg, 85%). M.p. = 115-116 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.53 (m, 2 H), 7.46 (m, 2 H), 7.16-7.38 (m, 10 H), 6.95-6.99 (m, 4 H), 6.65 (m, 1 H), 6.45 (m, 1 H), 4.78 (s, 2 H), 3.81 (s, 2 H), 3.67 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 158.49, 157.03, 144.22, 136.5, 132.89, 132.22, 131.96, 131.62, 131.19, 130.69, 129.69, 128.75, 127.56, 122.7, 119.22, 117.89, 115.47, 114.98, 111.17, 78.06, 76.15, 55.77 ppm; MS (MALDI-TOF): m/z 562.3; elemental analysis (%) calcd for $C_{38}H_{31}N_3O_2$: C 81.26, H 5.56, N 7.48; found: C 81.59, H 5.53, N 7.51.

Rotaxane **R-1-a**: A mixture of compound 5 (354 mg, 0.50 mmol), compound **6** (117 mg, 0.50 mmol) , macrocycle DB24C8 (211 mg, 0.48 mmol), and $[Cu(MeCN)_4]PF_6$ (175 mg, 0.47 mmol) was stirred in dry CH_2Cl_2 at room temperature under nitrogen for 24 h. After removal of the solvent, the crude product was purified by column chromatography (SiO_2: CH_2Cl_2/MeOH 60:1) to afford rotaxane R-1-a (845 mg, 68%). M.p. = 139-140 ℃. ^{1}H NMR (CD_3CN, 400 MHz, 298 K): δ = 8.56 (s, 1 H), 8.36 (m, 2H), 8.06 (m, 2H), 7.52 (m, 2H), 7.19-7.46 (m, 17H), 7.15 (m, 1H), 7.01 (m, 1H), 6.98 (m, 2H), 6.88 (m, 4H), 6.72 (m, 4H), 6.68 (m, 2H), 6.42 (m, 1H), 6.27 (m, 1H), 4.92 (s, 2H), 4.61 (s, 2H), 4.20 (s, 2H), 4.08 (m, 4H), 3.99 (m, 4H), 3.59 (m, 8H), 3.33 (m, 4H), 3.28 ppm (m, 4H); ^{13}C NMR (CD_3CN, 100 MHz, 298 K) δ = 160.22, 159.75, 150.04, 148.83, 146.26, 144.78, 138.93, 136.22, 135.87, 134.58, 133.23, 132.94, 132.61, 132.5, 132.13, 131.85, 131.72, 131.35, 131.02, 130.81, 130.64, 130.43, 130.19, 129.92, 128.91, 127.82, 127.44, 126.96, 126.61, 124.94, 124.87, 124.75, 122.83, 116.56, 115.78, 114.43, 114.12, 71.94, 71.39, 69.46, 62.51, 53.67, 52.59, 47.49 ppm; MS (MALDI-TOF): m/z: 1243.5 $[M]^+$, 1275.5 $[M+O_2]^+$; elemental analysis (%) calcd for $C_{77}H_{75}N_6F_6O_{10}P$: C 66.56, H 5.44, N 6.05; found: C 66.78, H 5.42, N 6.09.

Thread **T-1-a**: A mixture of compound **5** (354 mg, 0.50 mmol), compound **6** (117 mg, 0.47 mmol), and $[Cu(MeCN)_4]PF_6$ (175 mg, 0.47 mmol) was stirred in dry CH_2Cl_2 at room temperature under nitrogen for 24 h. After removal of the solvent, the crude product was purified by column chromatography (SiO_2: CH_2Cl_2/MeOH 30:1) to afford Thread **T-1-a** (700 mg, 88%). M.p. = 132-133 ℃. ^{1}H NMR (CD_3CN, 400 MHz, 298 K): δ = 8.69 (s, 1 H), 8.49 (d, 2H, *J* = 8.87 Hz), 8.15 (d, 2H, *J* = 8.38 Hz), 7.64-7.68 (m, 3H), 7.58-7.60 (m, 2H), 7.25-7.55 (m, 17H), 7.20 (t, 1H, *J* = 9.72, 7.22 Hz), 7.03 (d, 1H, *J* = 8.12 Hz), 6.98 (d, 2H, *J* = 7.52 Hz), 6.77-6.80 (m, 8H), 6.61 (s, 2H), 6.53-6.55 (m, 3H), 6.42 (t, 1H, *J* = 7.10 Hz), 4.99 (s, 2H), 3.88 (s ,2H), 3.77 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ = 159.71, 144.88, 143.55, 137.72, 135.36, 132.93, 131.39, 131.20, 131.05, 130.73, 130.34, 129.62, 129.55, 129.20, 128.54, 128.35, 127.77, 127.15, 126.86, 125.93, 125.44, 123.56, 122.87, 118.01, 117.79, 115.05, 112.85, 61.24, 50.25, 50.03, 46.57 ppm; MS (MALDI-TOF): m/z: 795.3 $[M]^+$; elemental analysis (%) calcd for $C_{53}H_{43}N_6F_6O_2P$: C 67.65, H 4.61, N 8.93; found: C 67.93, H 4.58, N 8.97.

Rotaxane **R-2-a**: Rotaxane **R-1-a** (100 mg, 0.08 mmol) was dissolved in iodomethane (2 mL) and the mixture was stirred for 24 h at 40 ℃. Then iodomethane was evaporated and the solid was washed with Et_2O to give an orange solid. Then, to a suspension of the previous solid in H_2O (10 mL) were added NH_4PF_6 (16.3 mg, 0.1 mmol) and CH_2Cl_2 (15 mL). Then the resulted bilayer solution was vigorously stirred for 1h. After separation, the aqueous layer was extracted with CH_2Cl_2 (x3). The organic layers were combined, dried over Na_2SO_4, and concentrated to obtain quantitatively the rotaxane **R-2-a** (123 mg) as a yellow solid. M.p. = 128-129 ℃. ^{1}H NMR (CD_3CN, 400 MHz, 298 K): δ = 8.85 (s, 1 H), 8.36 (d, 2H, *J* = 9.14 Hz), 8.24 (m, 3H), 7.74 (t, 2H, *J* = 6.81, 7.62 Hz), 7.65 (t, 2H, *J* = 7.84, 6.81 Hz), 7.52-7.55 (m, 4H), 7.49 (m, 2H), 7.38 (d, 1H, *J* = 8.33 Hz), 7.27-7.32 (m, 7H), 7.19 (m, 1H), 7.09 (d, 2H, *J* = 8.65 Hz), 7.03 (m, 1H), 6.78-6.84 (m, 10H), 6.57 (m, 1H), 6.54 (d, 2H, *J* = 8.62 Hz), 6.44 (m, 1H), 4.95 (s, 2H), 4.75 (m, 2H), 4.42 (m, 2H), 4.16 (s, 3H), 4.05-4.09 (m, 4H), 3.93-3.96 (m 4H), 3.65-3.68 (m, 8H), 3.51-3.55 (m, 4H), 3.31-3.35 ppm (m, 4H); ^{13}C NMR (CD_3CN, 100 MHz, 298 K) δ = 159.20, 158.30, 149.52, 148.28, 148.15, 145.67, 140.53, 139.54, 132.64, 132.36, 132.18, 132.15, 131.21, 130.49, 130.17, 129.97, 129.58, 129.35, 129.07, 127.20, 126.68, 115.44, 115.25, 113.83, 113.63, 71.46, 71.29, 70.92, 70.74, 69.85, 69.52, 68.88, 58.77, 52.96, 52.19, 50.98, 39.60 ppm; MS (MALDI-TOF): m/z: 1257.6 $[M-H]^+$; elemental analysis (%) calcd for $C_{78}H_{78}N_6F_{12}O_{10}P_2$: C 60.46, H 5.07, N 5.42; found: C 60.69, H 5.04, N

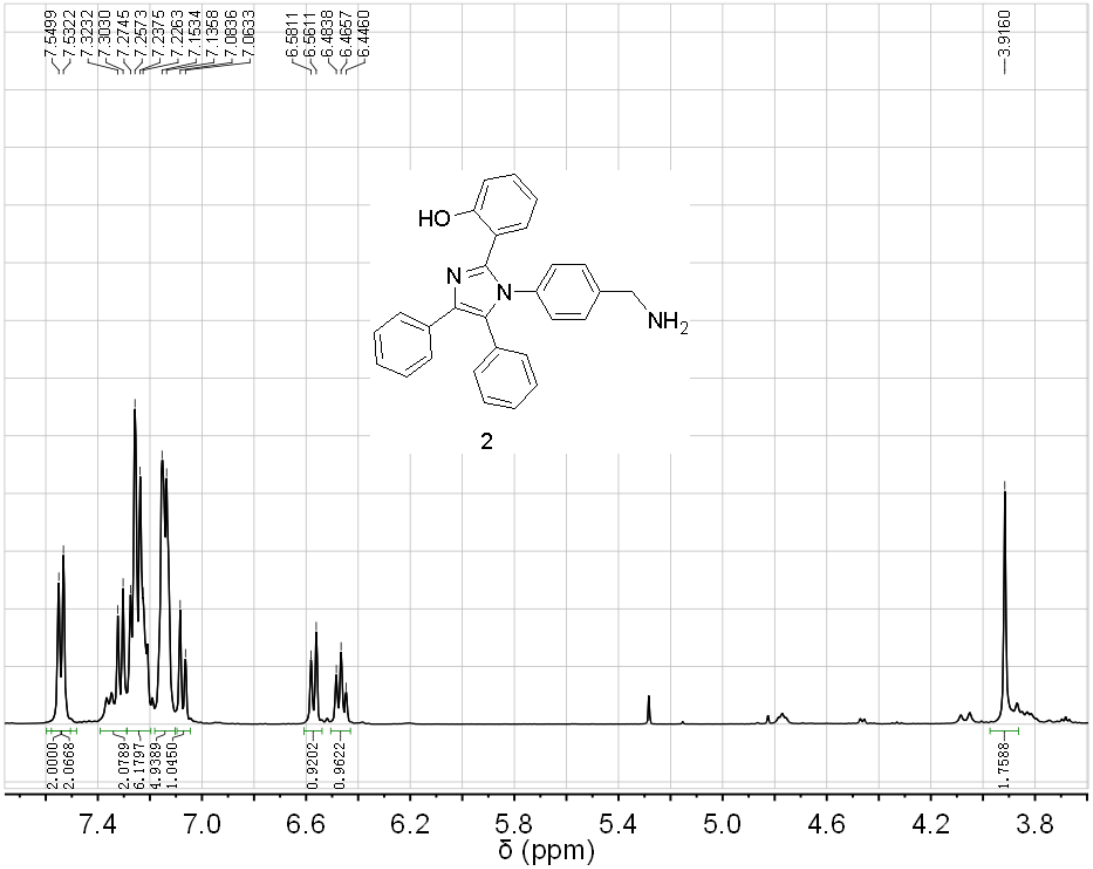
5.44.

Thread **T-2-a**: Thread **T-2-a** was synthesized by using the same procedure as described for the preparation of rotaxane **R-2-a**. M.p. = 121-122 ℃. ^{1}H NMR (CD_3CN, 400 MHz, 298 K): δ = 8.81 (s, 1 H), 8.33 (d, 2H, *J* = 8.88 Hz), 8.24 (m, 3H), 7.71 (m, 2H), 7.63 (m, 2H), 7.62 (m, 3H), 7.18-7.52 (m, 16H), 6.93-7.01(m, 4H), 6.75 (s, 2H), 6.57 (m, 1H), 6.45 (m, 1H), 5.16 (s, 2H), 4.17 (s, 3H), 3.93 (s, 2H), 3.84 ppm (s, 2H); ^{13}C NMR (CD_3CN, 100 MHz, 298 K) δ = 159.21, 145.75, 135.74, 135.22, 132.47, 132.37, 132.16, 132.06, 130.73, 130.51, 130.20, 129.48, 129.38, 129.06, 126.65, 118.38, 116.37, 115.92, 115.80, 59.04, 55.26, 51.01, 39.57 ppm; MS (MALDI-TOF): m/z: 812.4 $[M+H]^+$; elemental analysis (%) calcd for $C_{54}H_{46}N_6F_{12}O_2P_2$: C 58.91, H 4.21, N 7.63; found: C 59.12, H 4.19, N 7.65.

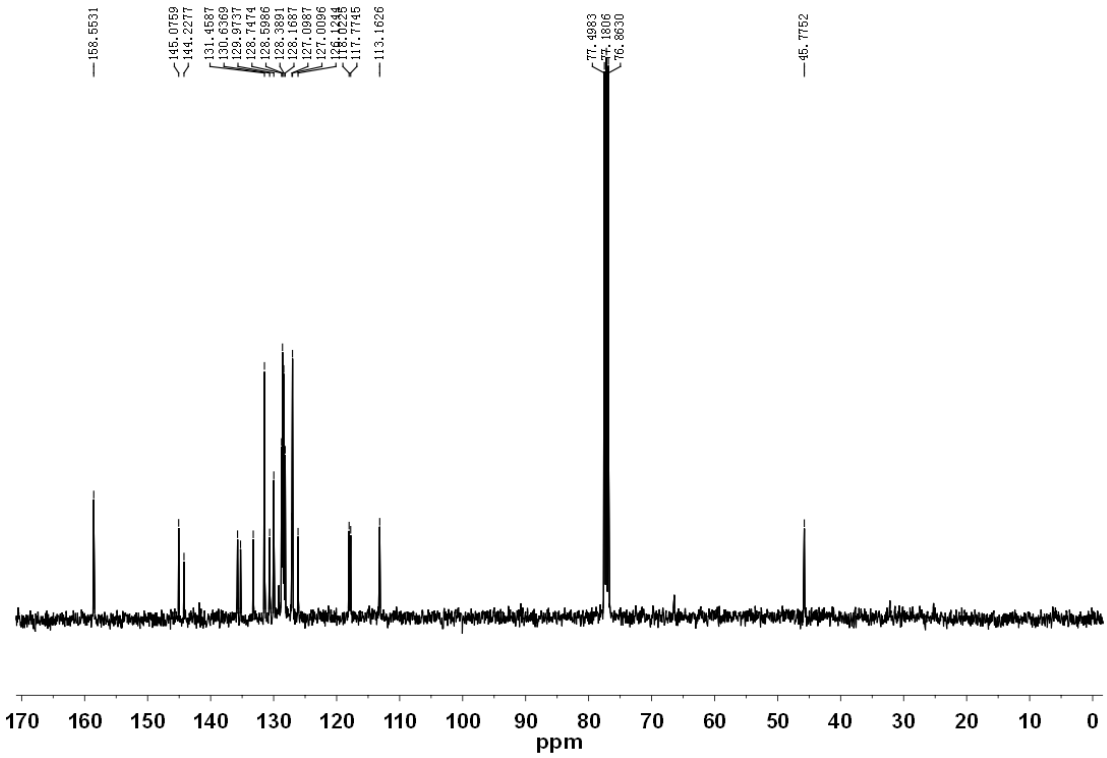
deprotonation procedure:
To a solution of the rotaxane **R-1(2)-a** or thread **T-1(2)-a** (1 equiv) in acetone was added a large excess of DIEA (100 equiv) and the mixture was stirred for 1h. After evaporation, and in order to remove the diisopropylethylammonium hexafluorophosphate, the crude was diluted with CH_2Cl_2 and water was added. The aqueous layer was extracted with CH_2Cl_2 (x3) then the organic layers were combined, dried over Na_2SO_4 and concentrated. Et_2O was added to dissolve the excess of DIEA then removed to obtain the rotaxane **R-1(2)-b** or thread **T-1(2)-b**.

§5. NMR and MS spectra

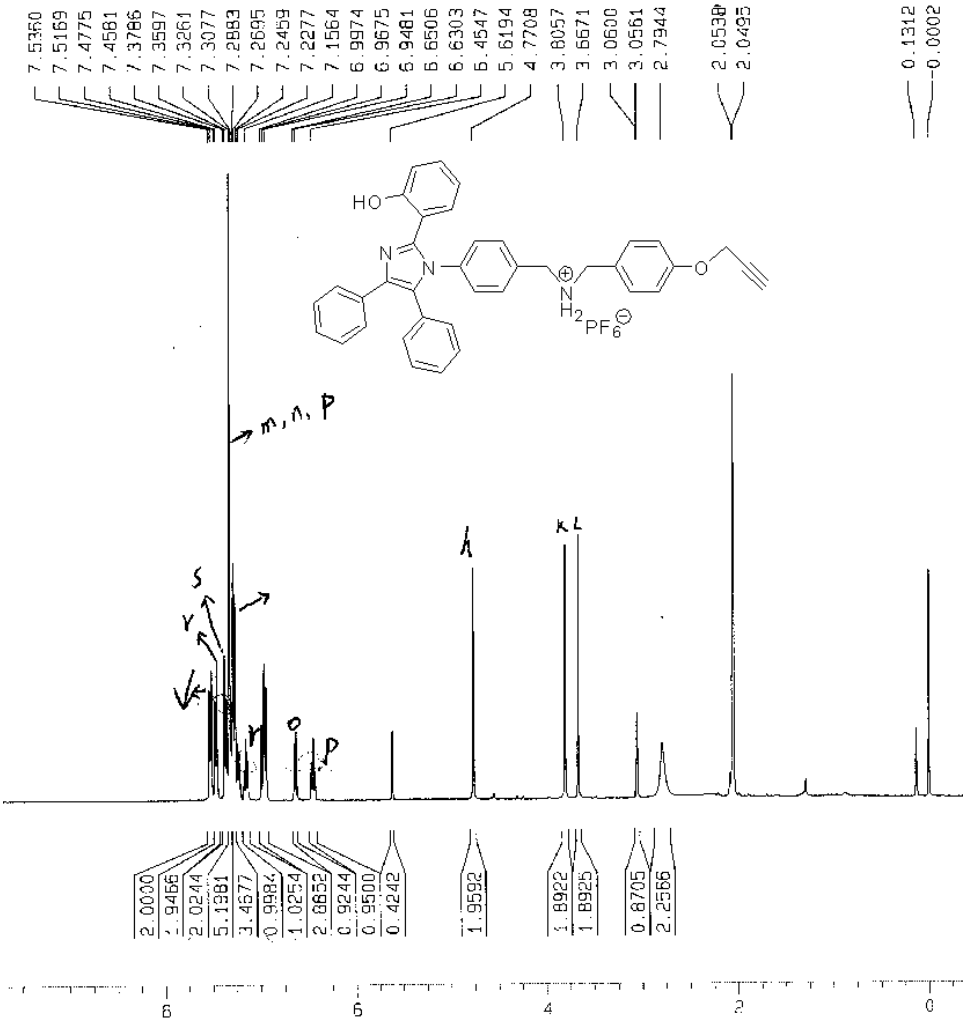
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **2**



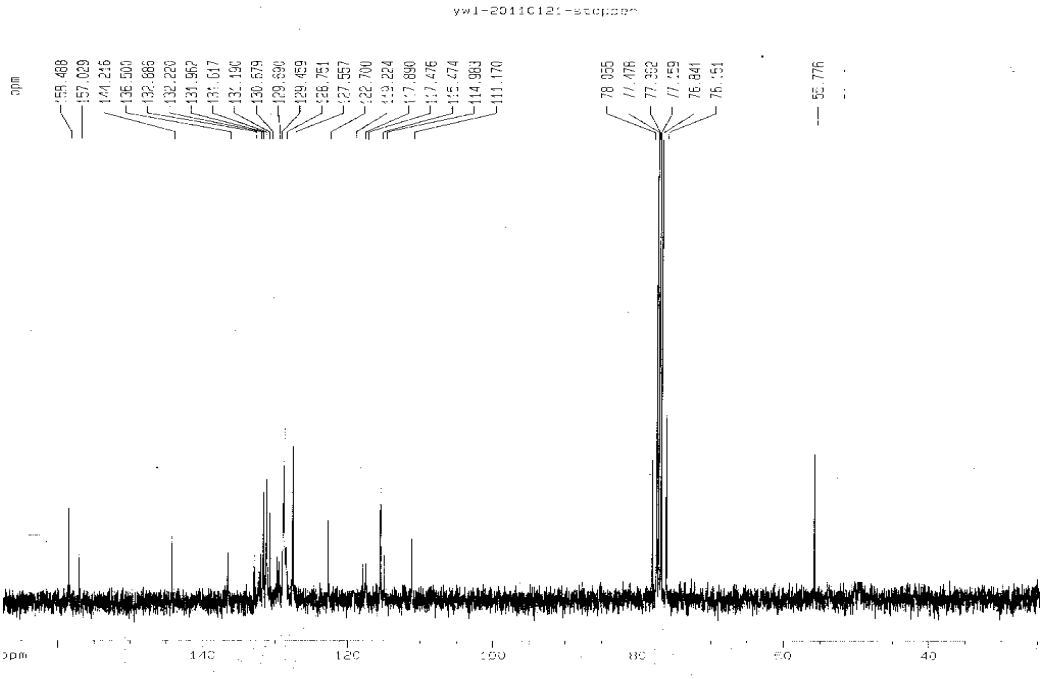
^{13}C NMR ($CDCl_3$, 100 MHz) of compound **2**



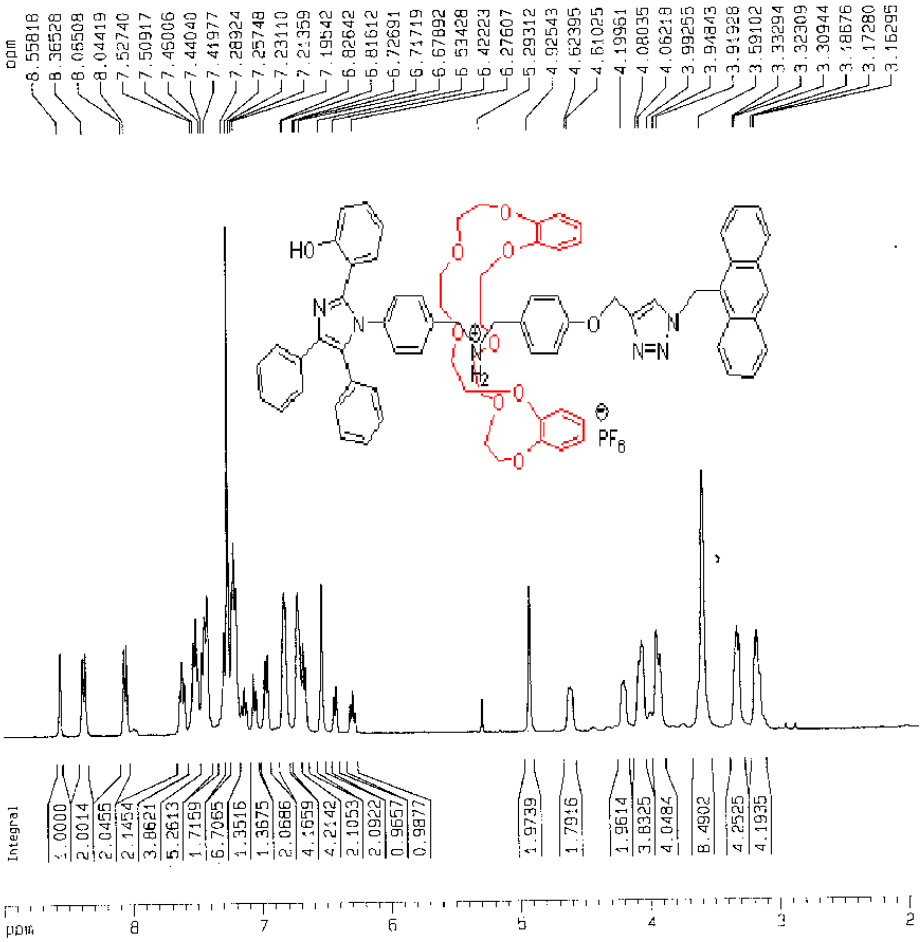
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **5**



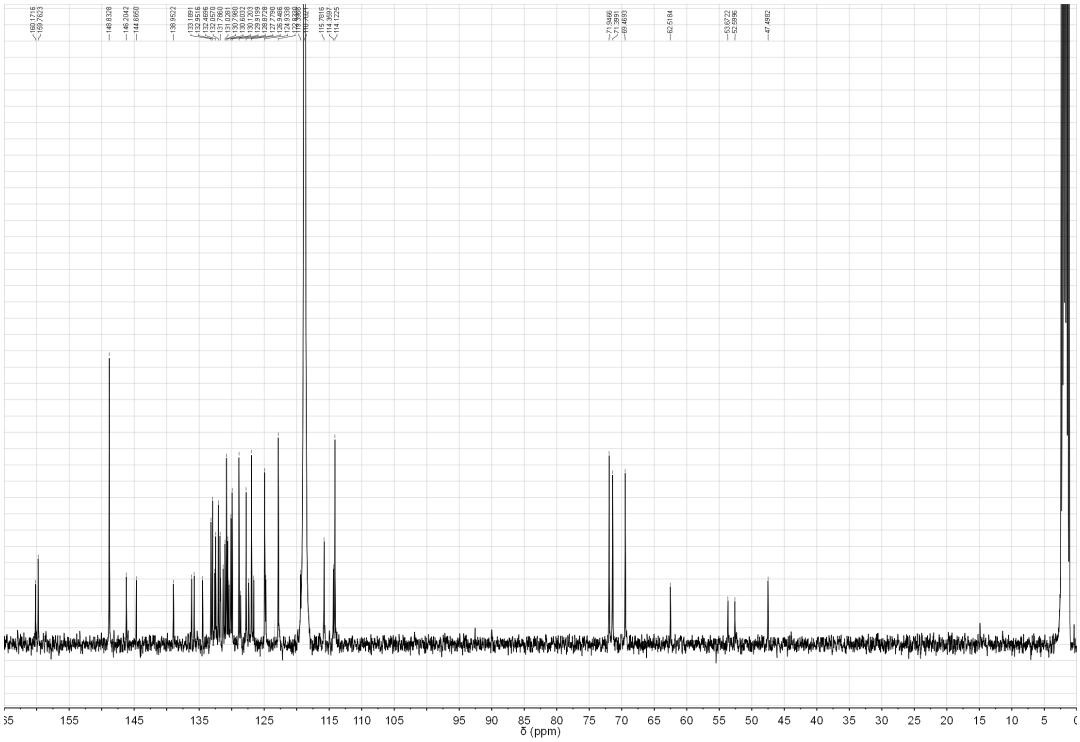
^{13}C NMR ($CDCl_3$, 100 MHz) of compound **5**



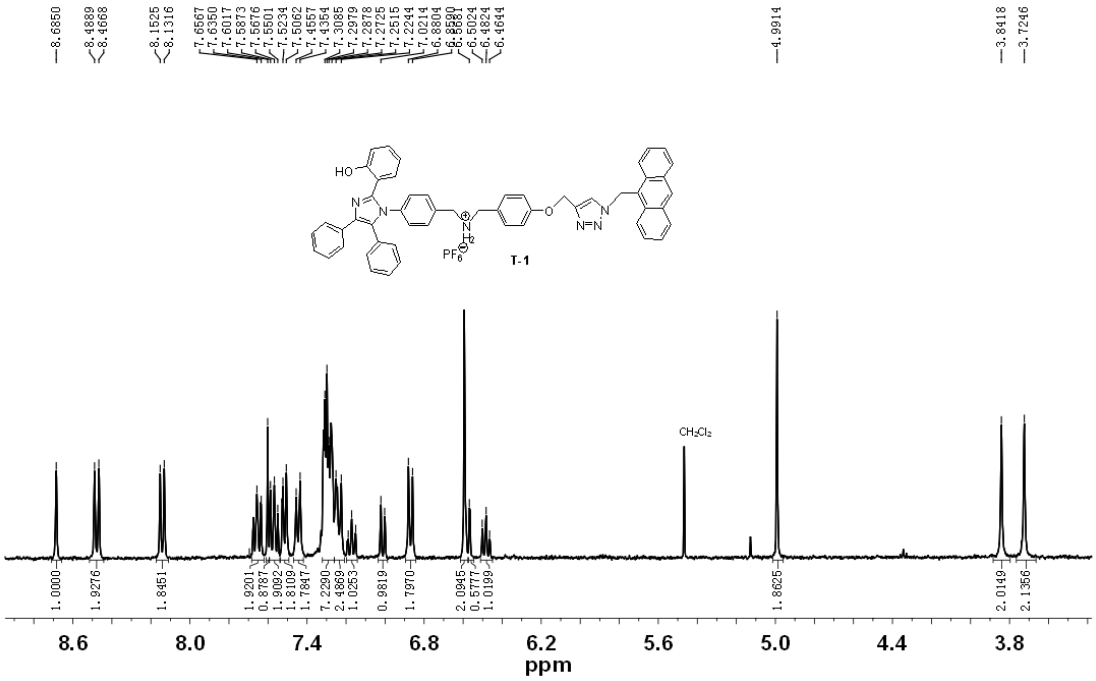
^{1}H NMR ($CDCl_3$, 400 MHz) of **R-1-a**



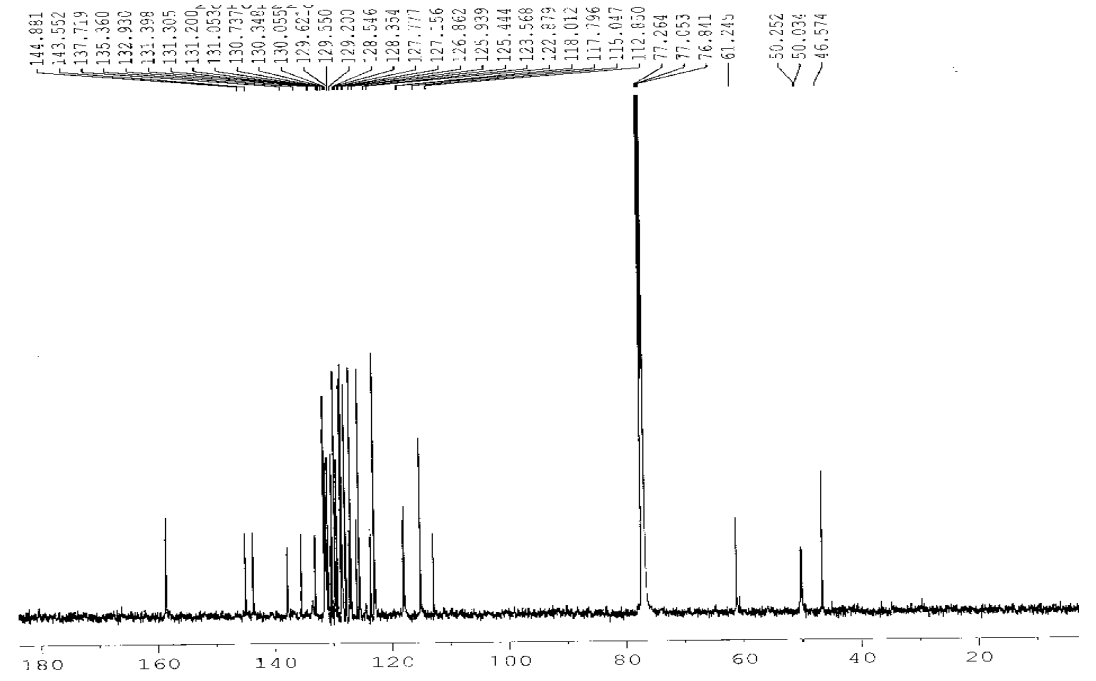
^{13}C NMR ($CDCl_3$, 100 MHz) of **R-1-a**



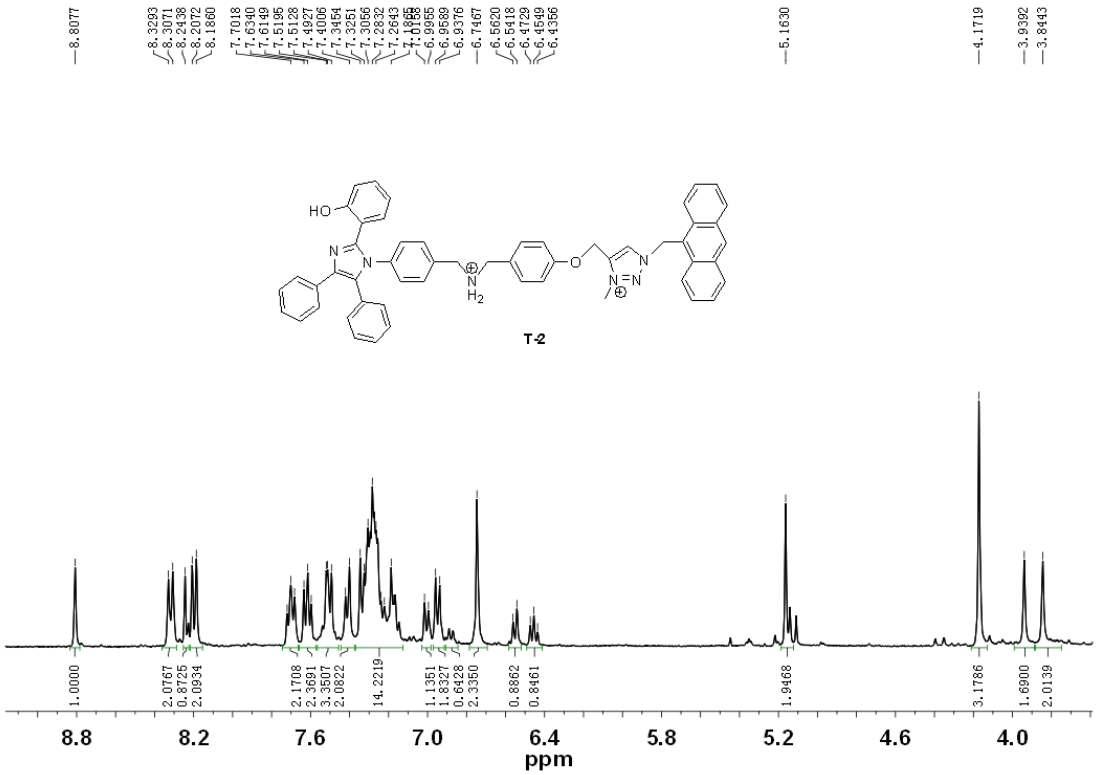
^{1}H NMR ($CDCl_3$, 400 MHz) of **T-1-a**



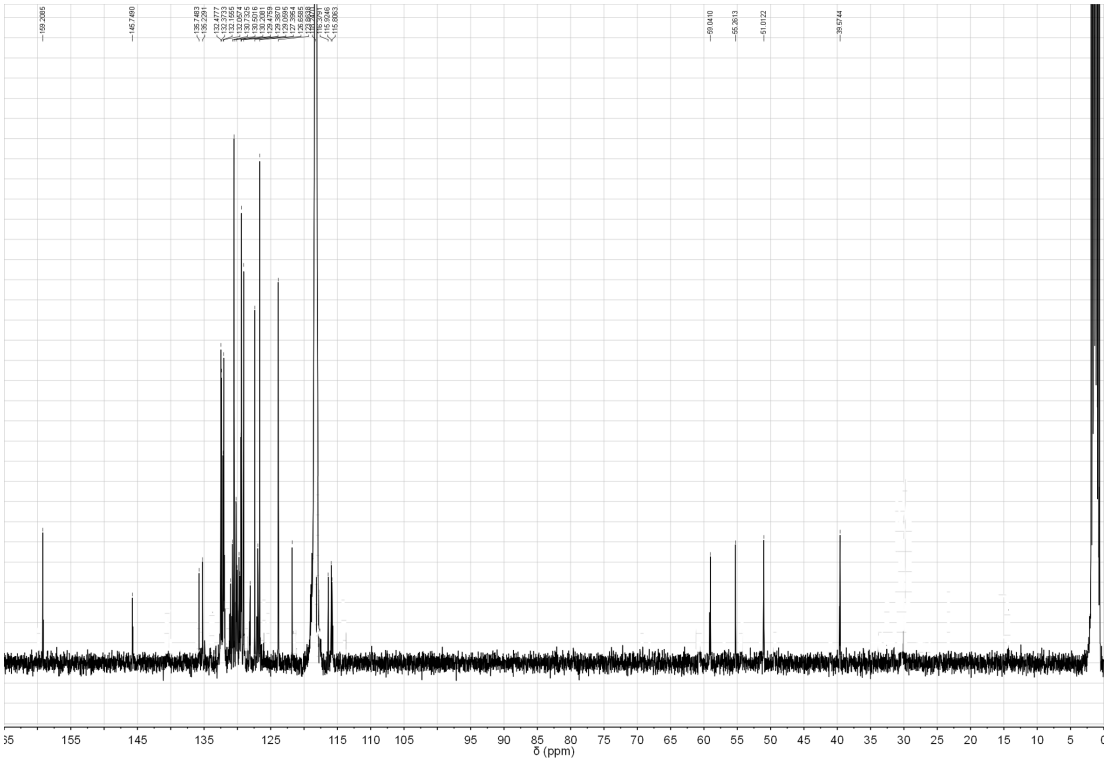
^{13}C NMR ($CDCl_3$, 100 MHz) of **T-1-a**



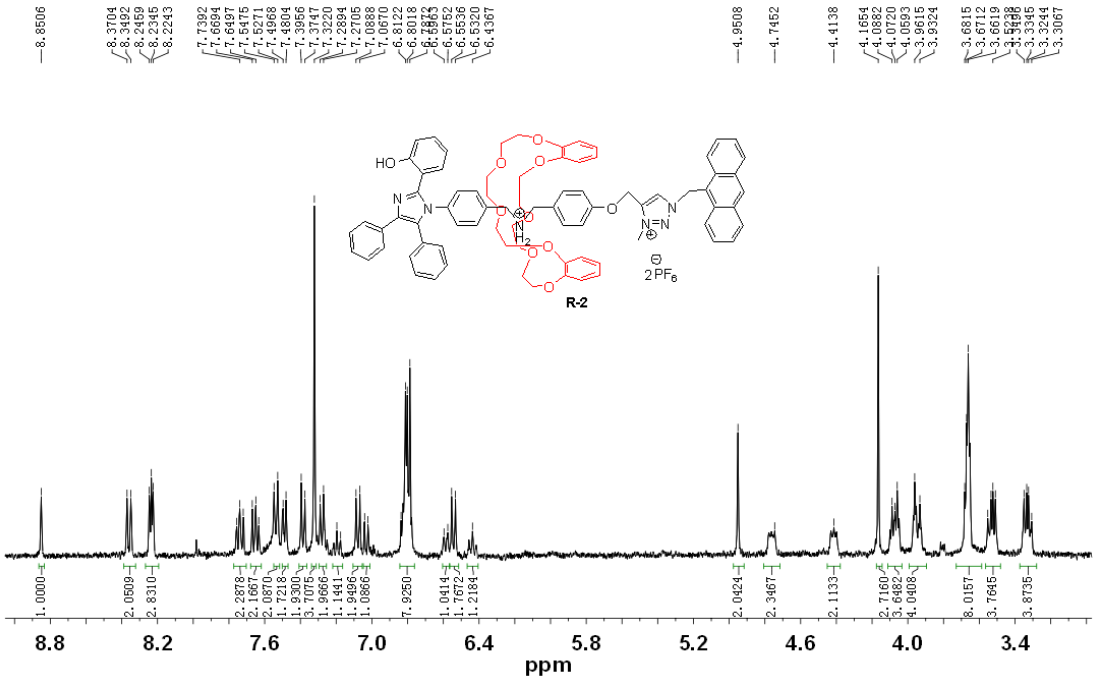
^{1}H NMR ($CDCl_3$, 400 MHz) of **T-2-a**



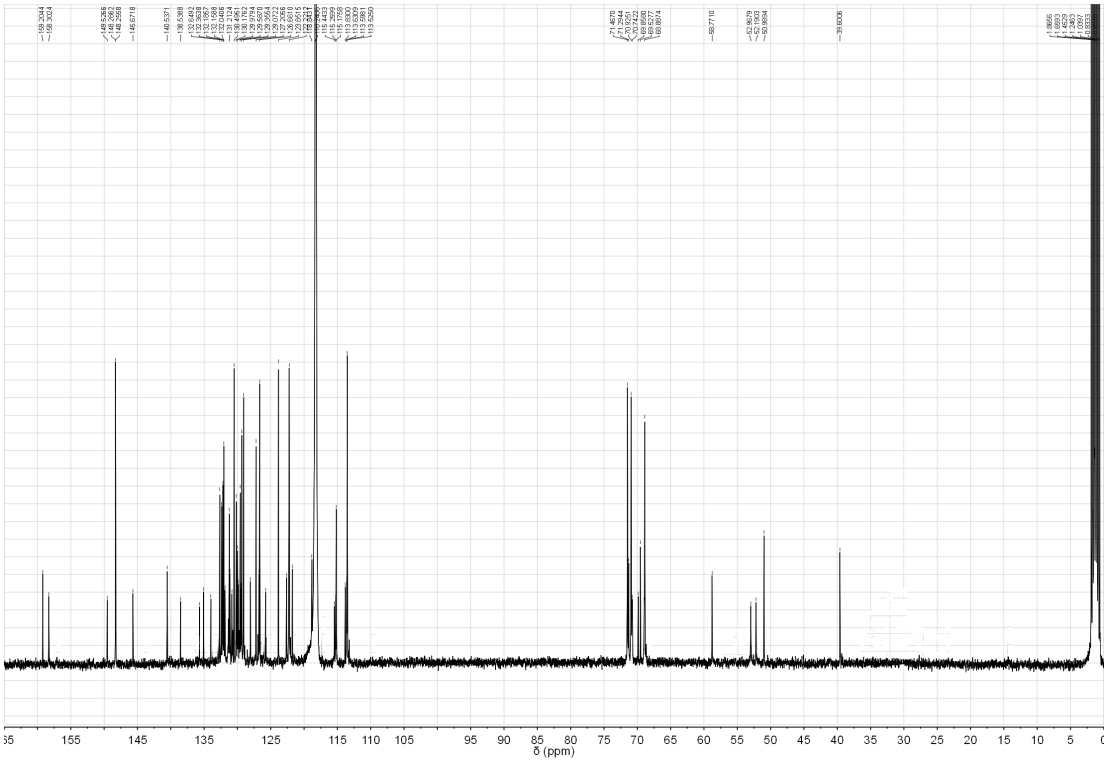
^{13}C NMR ($CDCl_3$, 100 MHz) of **T-2-a**



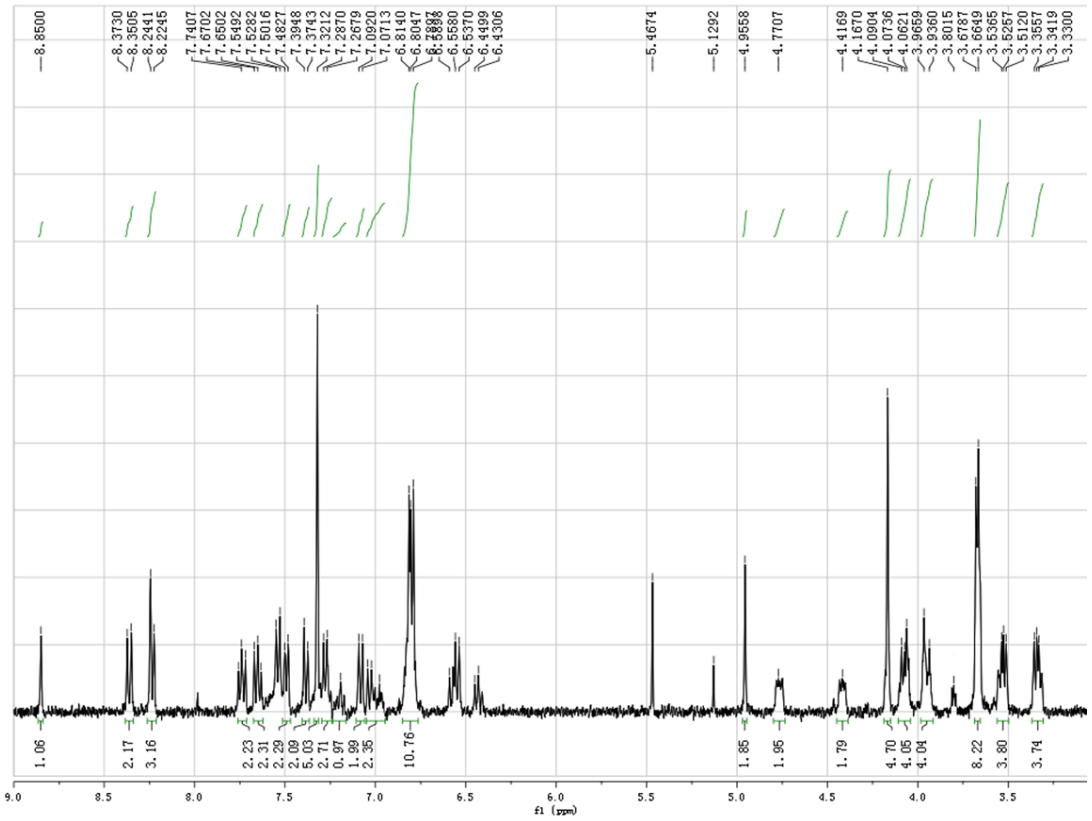
^{1}H NMR (CD_3CN, 400 MHz) of **R-2-a**



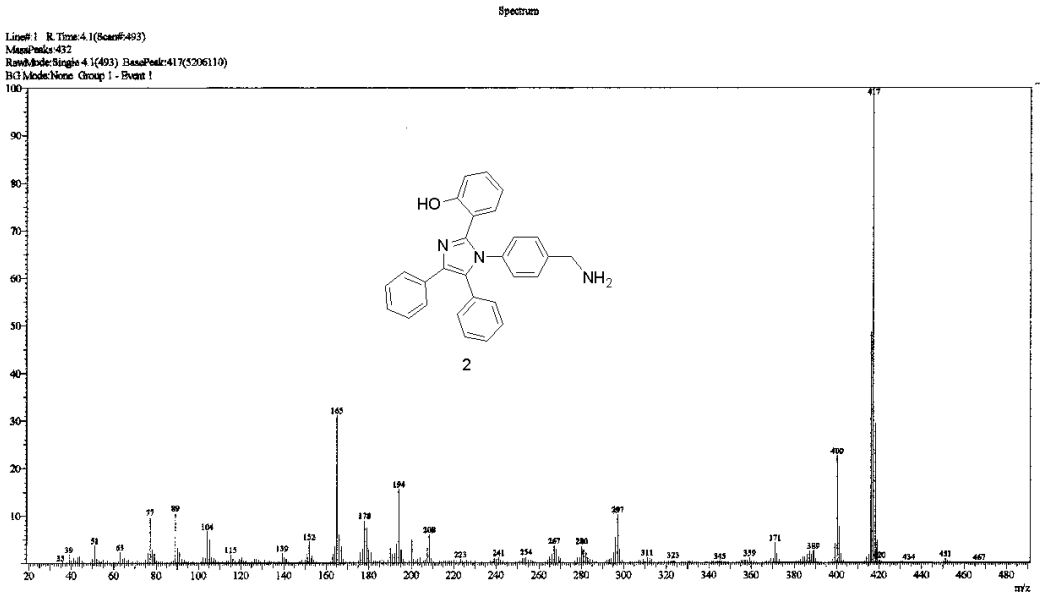
^{13}C NMR (CD_3CN, 100 MHz) of **R-2-a**



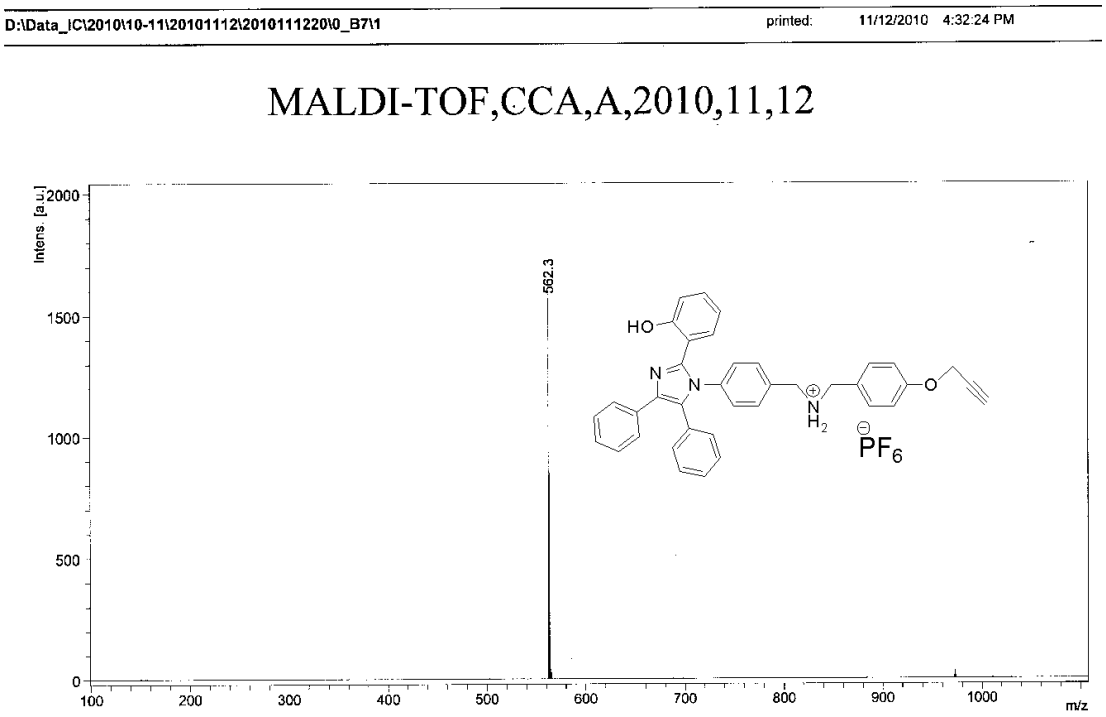
^{1}H NMR (CD_3CN, 400 MHz) of **R-2-b**



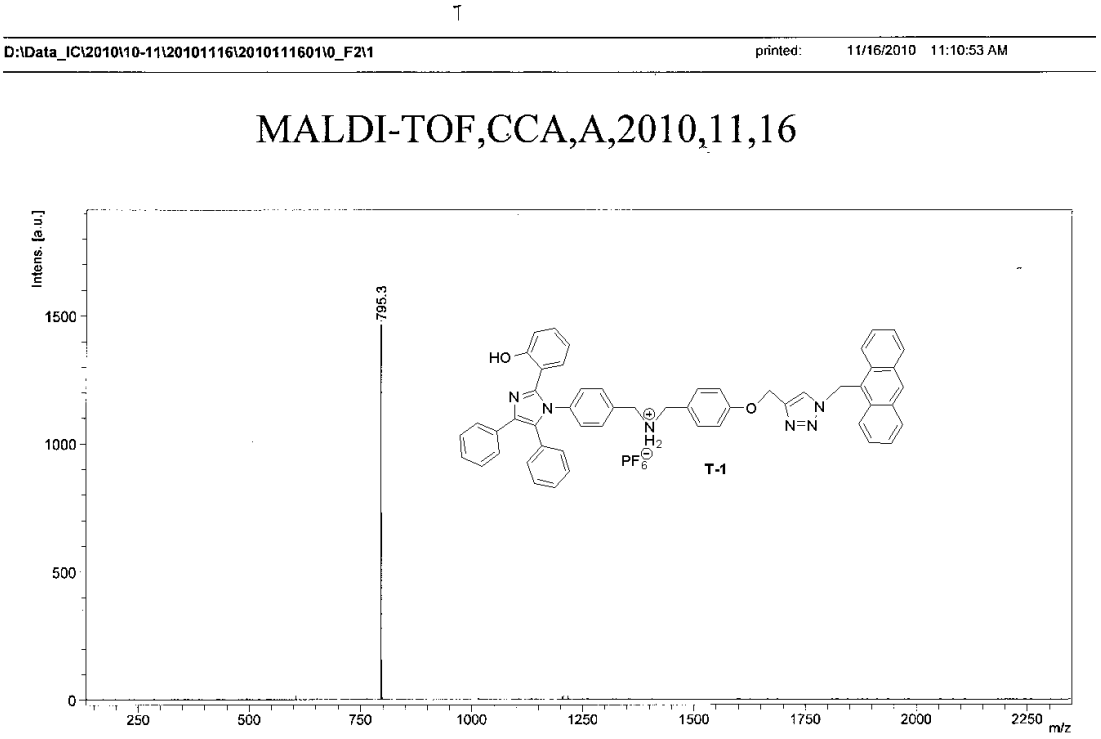
MS of compound **2**



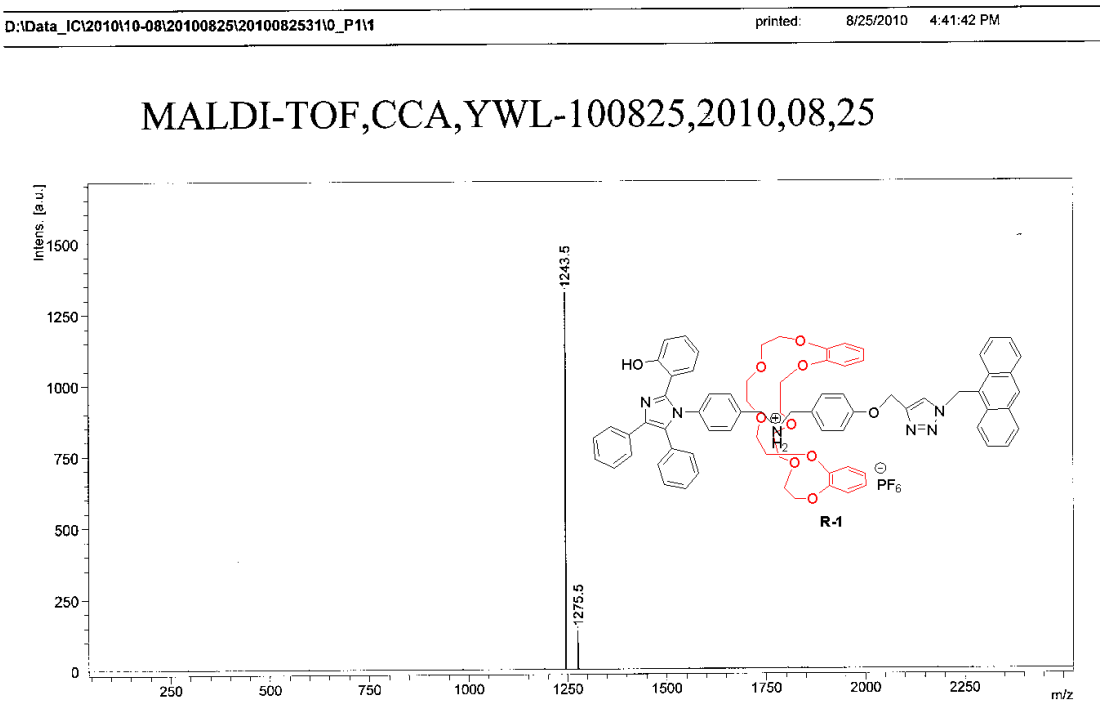
MALDI-TOF of compound **5**



MALDI-TOF of **T-1-a**



MALDI-TOF of **R-1-a**



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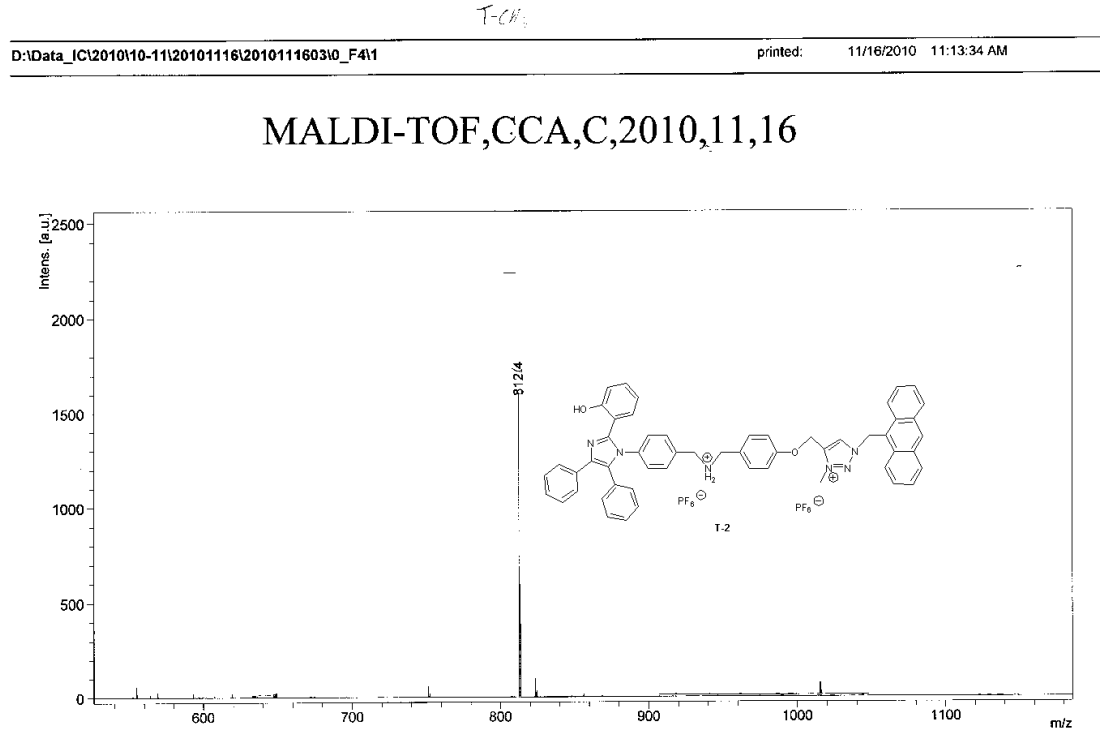
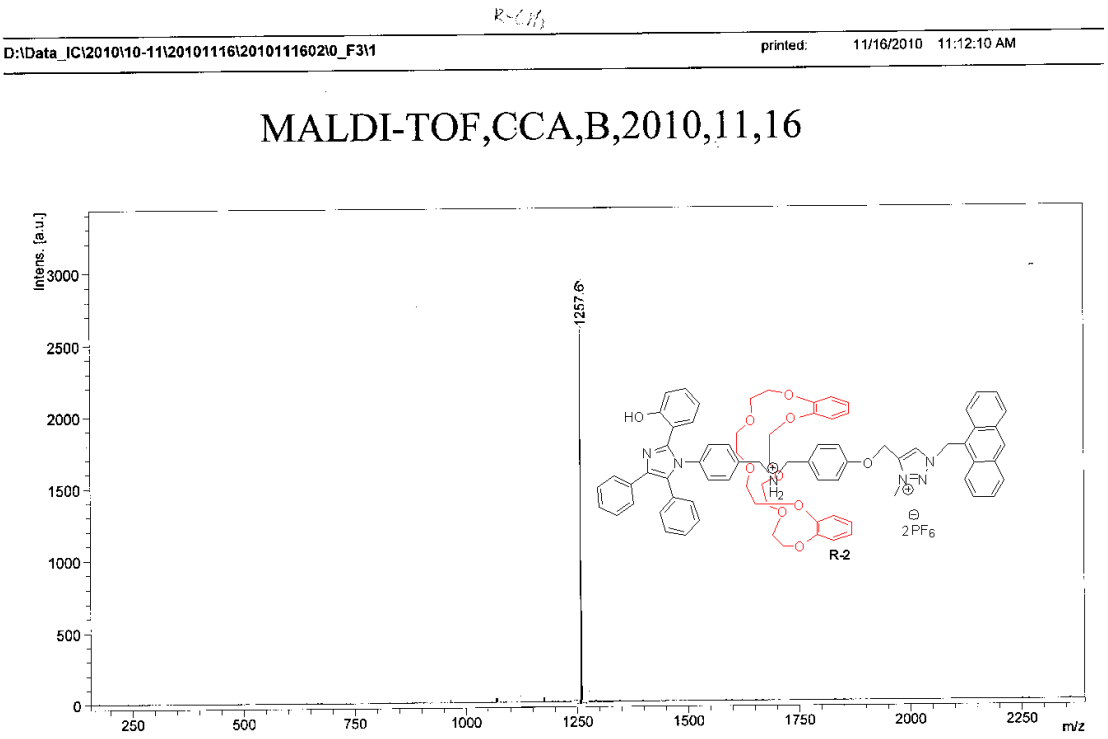


MALDI-TOF of **R-2-a**



§6. COSY-NMR spectra of R-2-a

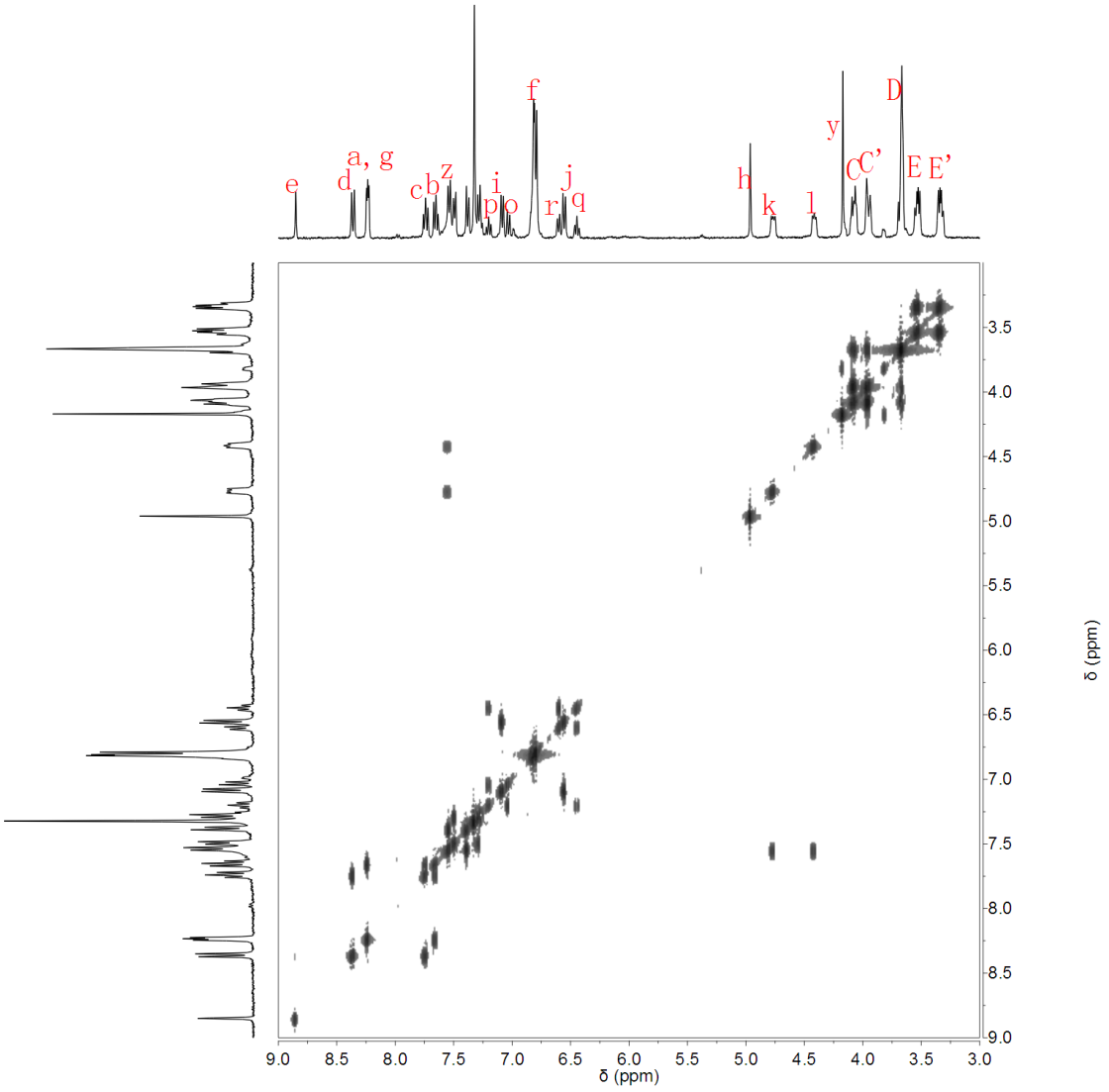


Figure S0. The COSY-NMR spectra (600 MHz, CD_3CN, 298 K) of **R-2-a**.

§7. UV/Vis and FL spectra and titrational 1H NMR spectra of R-2-b

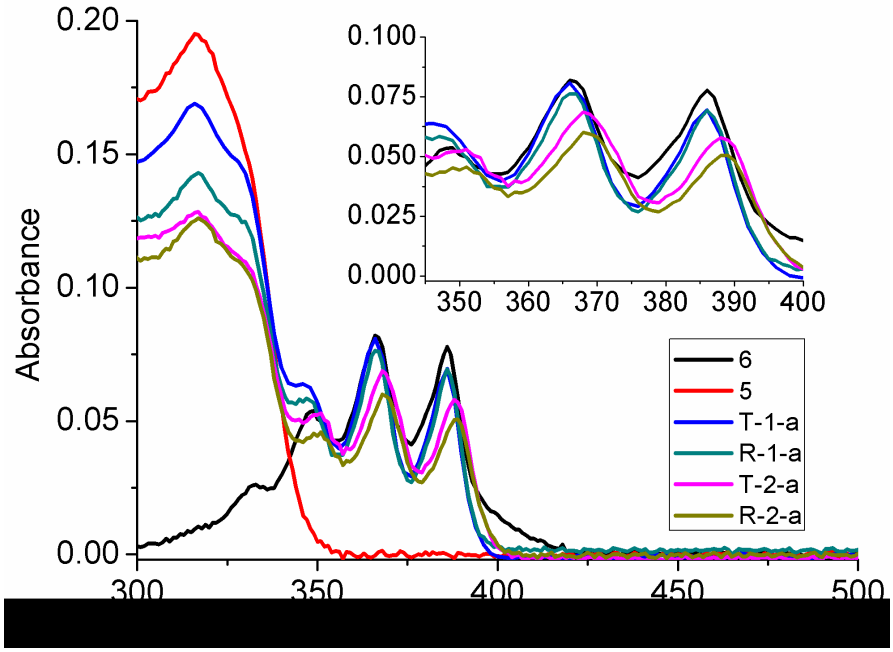


Fig. S1. Absorption spectra of compound **6**, **5**, **T-1-a**, **T-2-a**, **R-1-a** and **R-2-a** (1×10^{-5} M, 298 K) in CH_3CN.

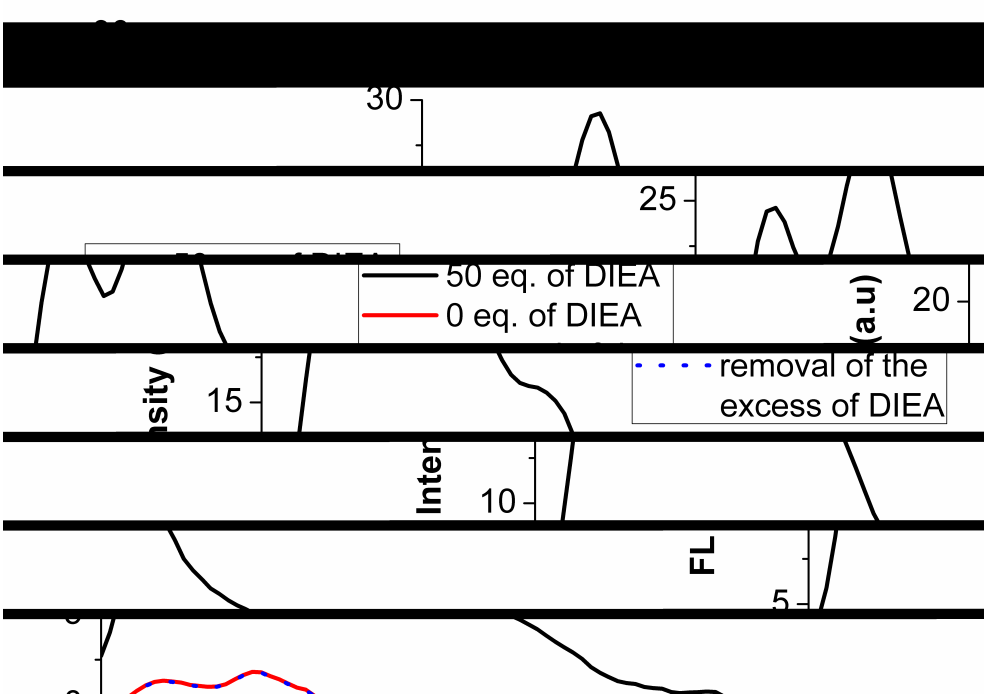


Fig. S2. Fluorescence spectra of **R-2-b** (λ_{exc} = 370 nm, 1×10^{-5} M) in CH_3CN (addition and removal of DIEA).

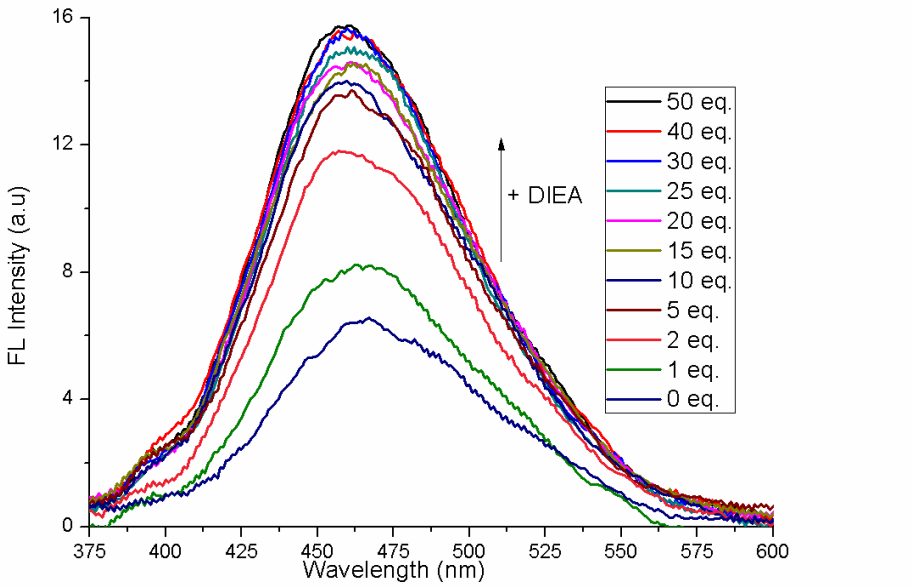


Fig. S3. Fluorescence spectra of **R-2-b** (λ_{exc} = 310 nm, 1×10^{-5} M) in CH_3CN with various equivalents of DIEA (0 equiv to 50 equiv).

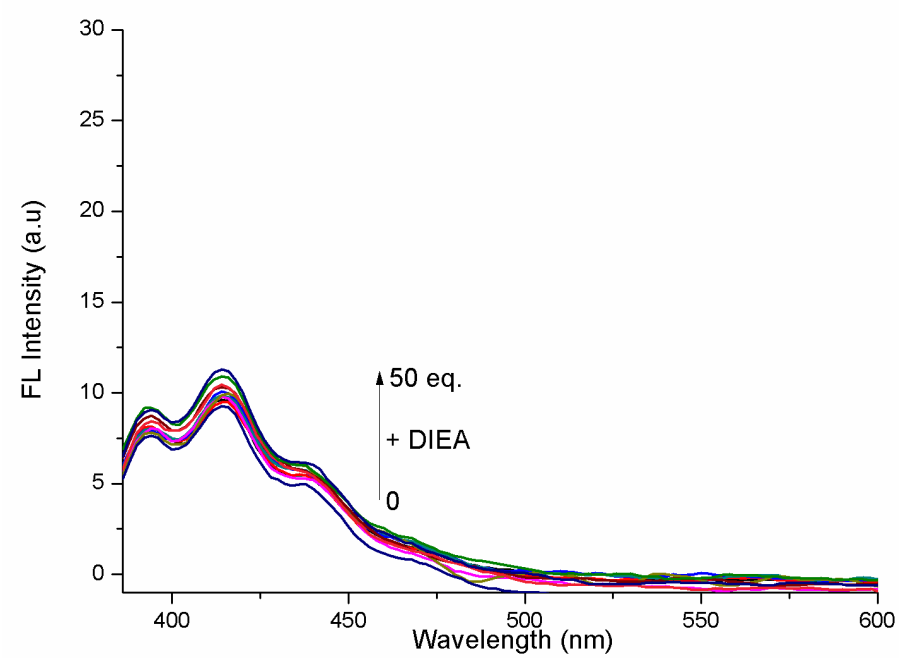


Fig. S4. Fluorescence spectra of **T-2-b** (λ_{exc} = 370 nm, 1×10^{-5} M) in CH_3CN with various equivalents of DIEA (0 equiv to 50 equiv).

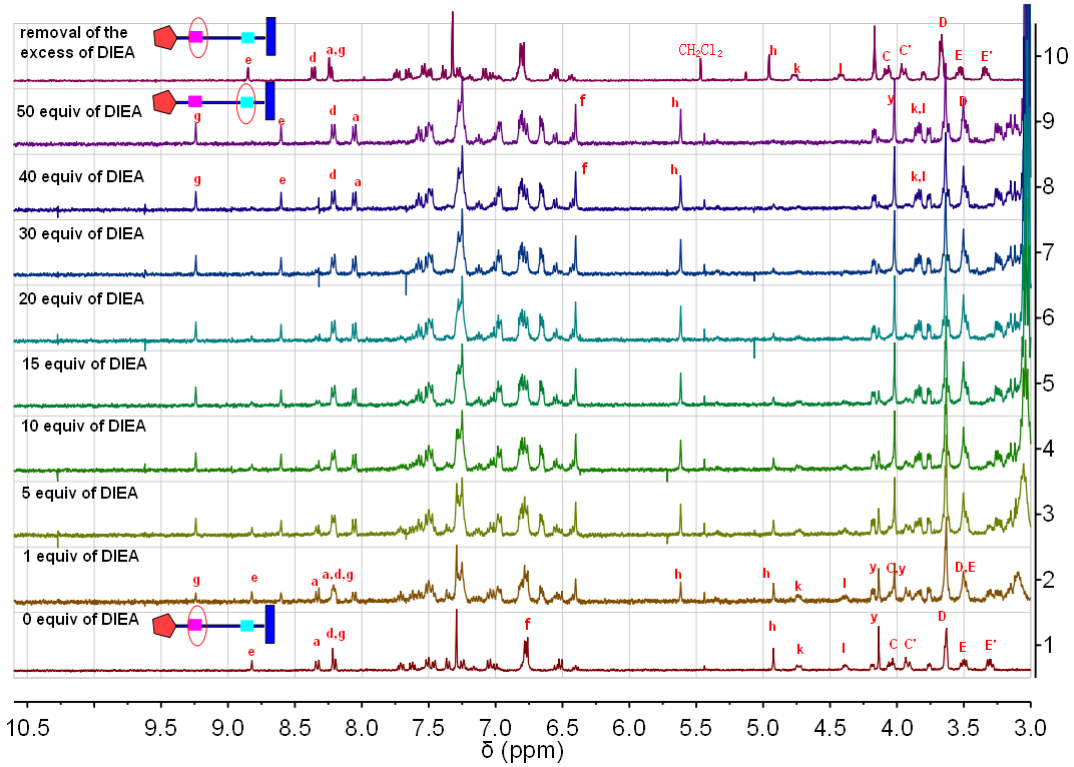


Fig. S5 ^{1}H NMR spectra of **R-2-b** in CD_3CN at 298 K upon titrational addition of DIEA

Reference:

S1. Park S.; Kwon O-H.; Lee Y-S.; Jang D-J.; Park S. Y. *J. Phys. Chem. A* **2007,** *111,* 9649-9653