

Tricolor Emission of a Fluorescent Heteroditopic Ligand over a Concentration Gradient of Zinc(II) Ions

Supporting Information

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Table of Contents

No.	Title	Page No.
I	Additional Figures	S4-S8
	Figure S1. Visual appearance of 2 (10 μM) in CH_3CN upon increasing $\text{Zn}(\text{ClO}_4)_2$ concentration from 1 nM to 1 M under ambient light, and upon illumination using a handheld UV lamp.	S4
	Figure S2. Absorbance increase (A/A_0 at 568 nm) of 2 (10 μM), with increasing $[\text{Zn}(\text{ClO}_4)_2]$ and fitting curve of A/A_0 vs $[\text{Zn}^{2+}]$ based on a 1:1 binding isotherm equation.	S4
	Figure S3. IR spectra of 3 (blue) and $[\text{Zn}(\mathbf{3})](\text{ClO}_4)_2$.	S5
	Figure S4. Effect of addition of $\text{Zn}(\text{ClO}_4)_2$ (0-60 μM) on absorption spectrum of the mixture of 1 (3.0 μM) and 2 (3.0 μM) in CH_3CN , and corresponding changes of the emission spectrum.	S5
	Figure S5. Effect of addition of $\text{Pb}(\text{ClO}_4)_2$ (0-32 μM) on the absorption spectrum of compound 4 (3.1 μM) in CH_3CN , and corresponding changes of the emission spectrum.	S6
	Figure S6. Effect of addition of $\text{Fe}(\text{ClO}_4)_2$ (0-32 μM) on the absorption spectrum of compound 4 (3.1 μM) in CH_3CN , and corresponding changes of the emission spectrum.	S6
	Figure S7. Variation of fluorescence intensity of 2 at 588 nm vs. pH, and the fitting curve based on a modified Henderson–Hasselbalch equation.	S7
	Figure S8. Visual appearance of 5 (10 μM) in CH_3CN upon increasing $\text{Zn}(\text{ClO}_4)_2$ concentration from 1 nM to 0.1 M under ambient light, and upon illumination using a handheld UV lamp.	S7
	Figure S9. Absorbance increase (A/A_0 at 584 nm) of 5 (10 μM) with increasing $[\text{Zn}(\text{ClO}_4)_2]$, and the fitting curve of A/A_0 vs $[\text{Zn}^{2+}]$ based on	S8

a 1:1 binding isotherm equation.

Figure S10. Variation of fluorescence intensity of **5** at 610 nm vs. pH. **S8**

Figure S11. Fluorescence decay profiles of **5** and **6** in the presence of $\text{Zn}(\text{ClO}_4)_2$ monitored in CH_3CN . **S9**

Figure S12. Cyclic voltammograms. **S9**

Figure S13. Effect of addition of ZnCl_2 (0-98 μM) on the absorption and emission spectra of compound **6** (5 μM) in a 1:1 CH_3CN /HEPES buffer (50 mM HEPES, 50 mM NaCl, pH 7.2) solution. **S10**

Table S1. Electrochemical data. **S10**

II **References** **S10**

III **Copies of ^1H and ^{13}C NMR Spectra** **S11-S22**

^1H and ^{13}C NMR of 2-amino-6[(trimethylsilyl)ethynyl]pyridine **S11**

^1H and ^{13}C NMR of 2-amino-6-ethynylpyridine **S12**

^1H and ^{13}C NMR of compound **7** **S13**

^1H and ^{13}C NMR of compound **2** **S14**

^1H and ^{13}C NMR of compound **3** **S15**

^1H and ^{13}C NMR of compound **8** **S16**

^1H and ^{13}C NMR of compound **10** **S17**

^1H and ^{13}C NMR of compound **11** **S18**

^1H and ^{13}C NMR of compound **4** **S19**

^1H and ^{13}C NMR of compound **12** **S20**

^1H and ^{13}C NMR of compound **5** **S21**

^1H and ^{13}C NMR of compound **6** **S22**

I. Additional Figures

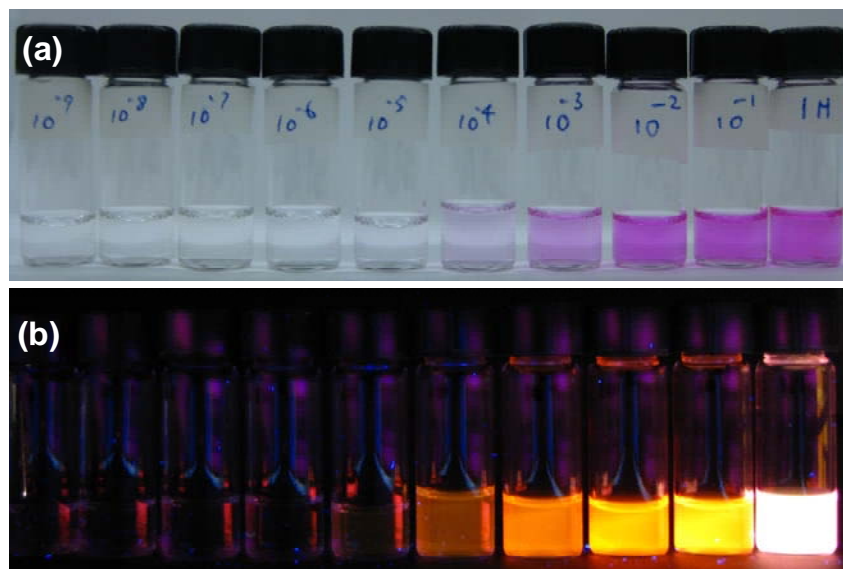


Figure S1. Visual appearance of **2** (10 μ M) in CH_3CN upon increasing $Zn(ClO_4)_2$ concentration from 1 nM to 1 M (left to right) under (a) ambient light, and (b) upon illumination using a handheld UV lamp ($\lambda_{ex} = 365$ nm).

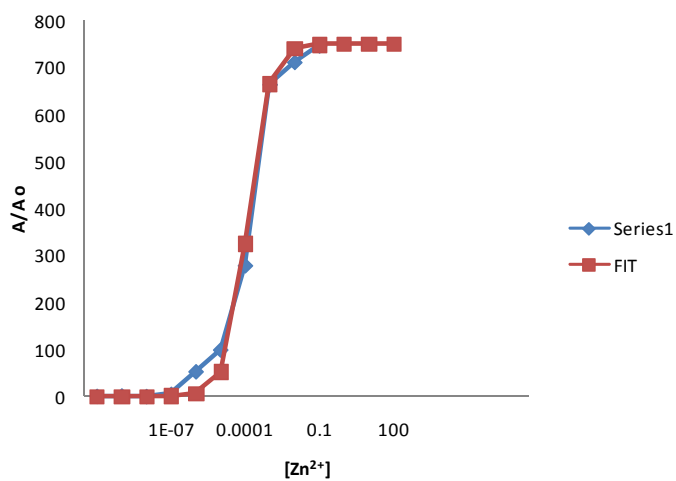


Figure S2. Absorbance increase (A/A_0 at 568 nm) of **2** (10 μ M), with increasing $[Zn(ClO_4)_2]$. The brown line is the fitting curve of A/A_0 vs $[Zn^{2+}]$ based on a 1:1 binding isotherm equation.¹ Dissociation constant of the putative 1:1 (ligand/ Zn^{2+}) complex $K_d = 0.1$ mM.

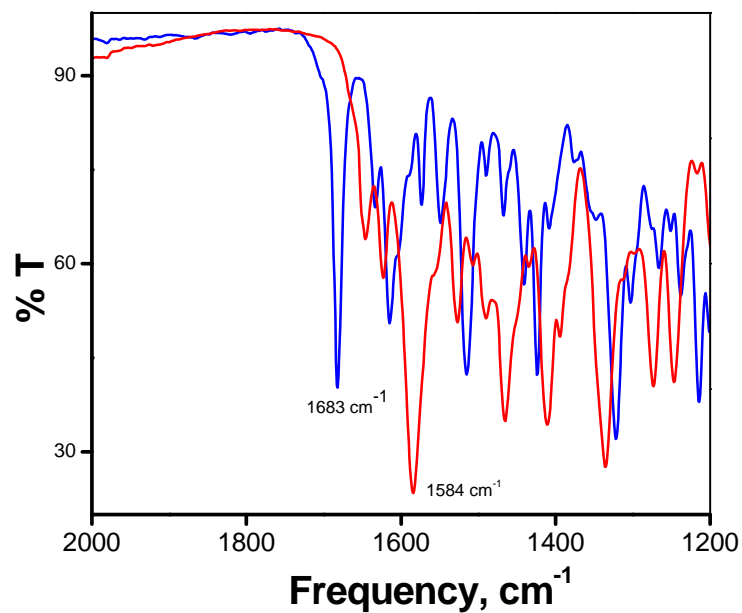


Figure S3. IR spectra of **3** (blue) and $[\text{Zn}(\mathbf{3})](\text{ClO}_4)_2$.

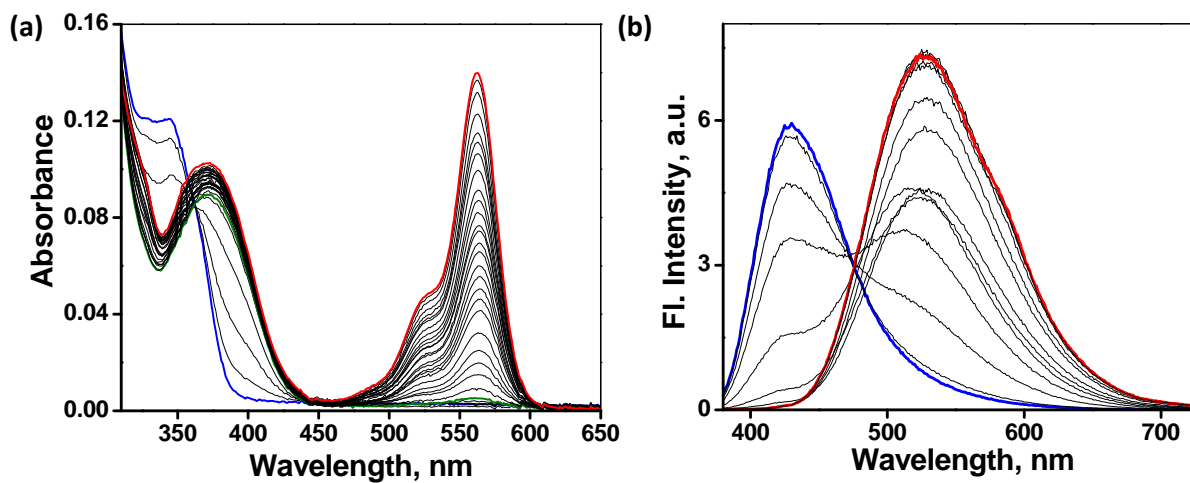


Figure S4. (a) Effect of addition of $\text{Zn}(\text{ClO}_4)_2$ (0-60 μM) on the absorption spectrum of the mixture of **1** (3.0 μM) and **2** (3.0 μM) in CH_3CN . (b) Corresponding changes of the emission spectrum ($\lambda_{\text{ex}} = 370 \text{ nm}$).

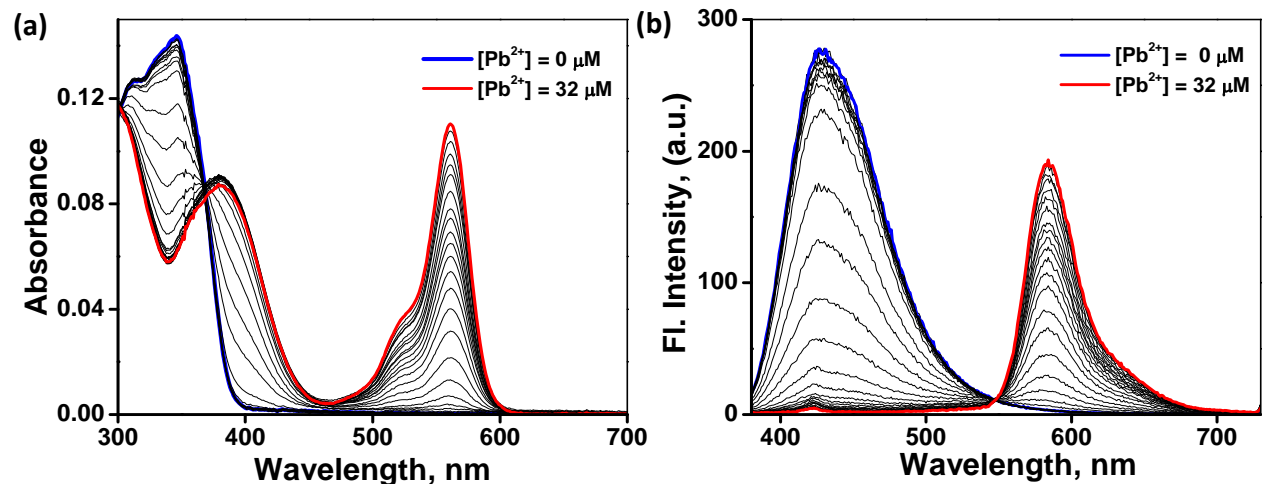


Figure S5. (a) Effect of addition of $\text{Pb}(\text{ClO}_4)_2$ (0-32 μM) on the absorption spectrum of compound **4** (3.1 μM) in CH_3CN . (b) Corresponding changes of the emission spectrum ($\lambda_{\text{ex}} = 370$ nm).

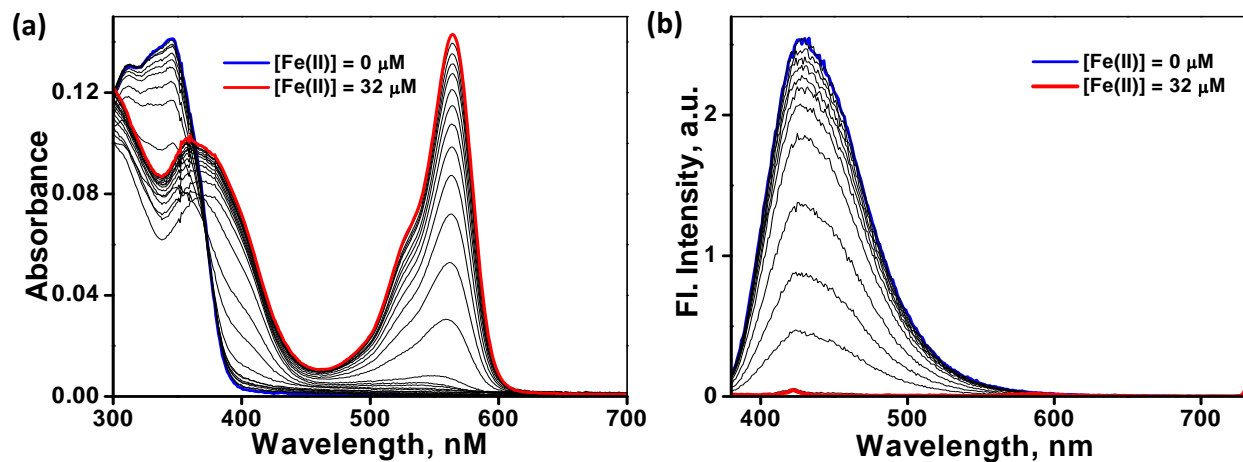


Figure S6. (a) Effect of addition of $\text{Fe}(\text{ClO}_4)_2$ (0-32 μM) on the absorption spectrum of compound **4** (3.1 μM) in CH_3CN . (b) Corresponding changes of the emission spectrum ($\lambda_{\text{ex}} = 370$ nm).

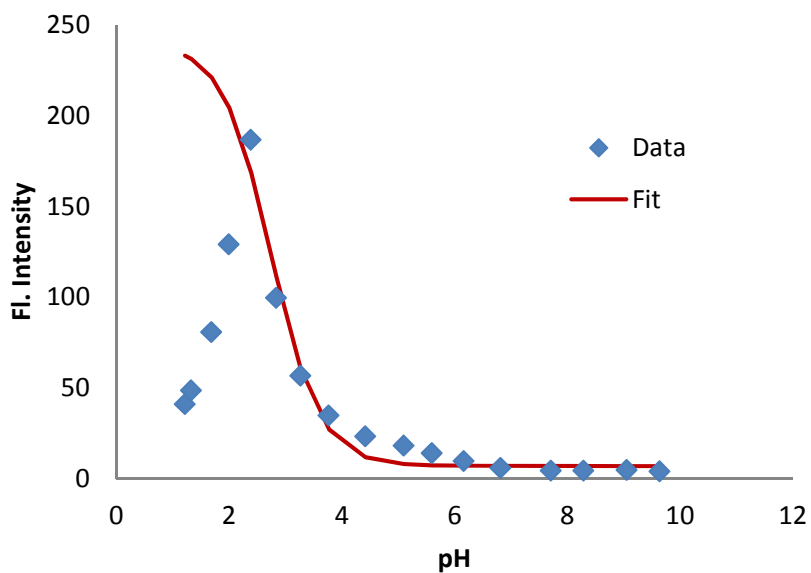


Figure S7. Variation of fluorescence intensity of **2** at 588 nm vs. pH ($\lambda_{\text{ex}} = 570$ nm). The purple line is the fitting curve based on a modified Henderson–Hasselbalch equation.² $\text{pK}_{\text{a}} \sim 2.8$.

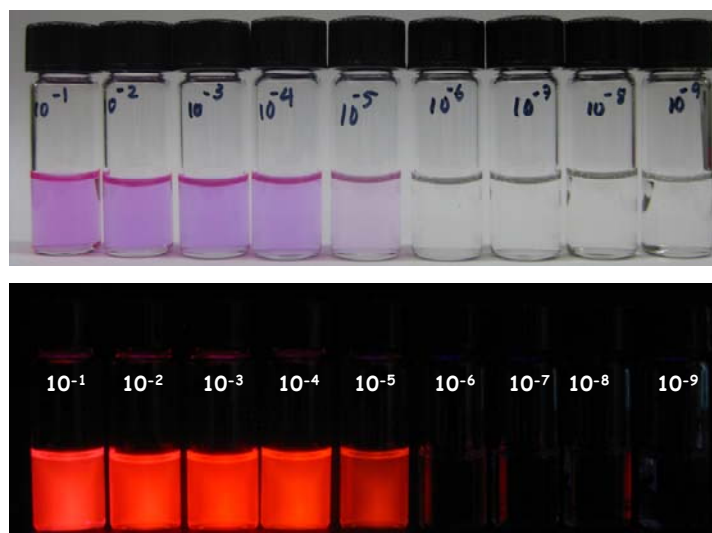


Figure S8. Visual appearance of **5** ($10 \mu\text{M}$) in CH_3CN upon increasing $\text{Zn}(\text{ClO}_4)_2$ concentration from 1 nM to 0.1 M (right to left) under (a) ambient light, and (b) upon illumination using a handheld UV lamp ($\lambda_{\text{ex}} = 365$ nm).

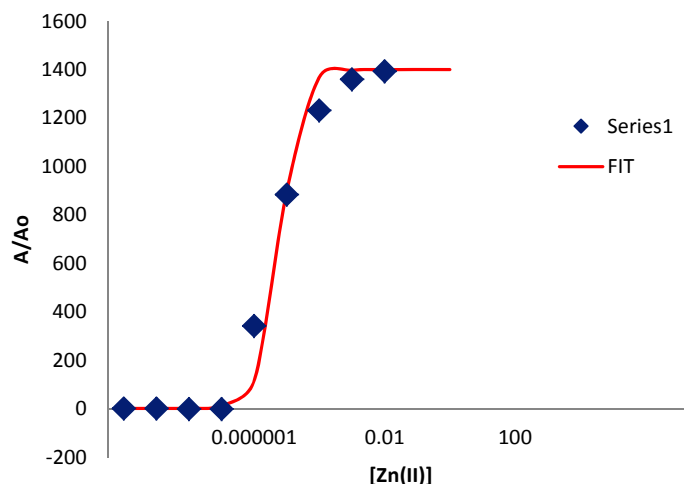


Figure S9. Absorbance increase (A/A_0 at 584 nm) of **5** (10 μM) with increasing $[\text{Zn}(\text{ClO}_4)_2]$. The red line is the fitting curve of A/A_0 vs $[\text{Zn}^{2+}]$ based on a 1:1 binding isotherm equation.¹ Dissociation constant of the putative 1:1 complex (ligand/ Zn^{2+}) $K_d = 20 \mu\text{M}$.

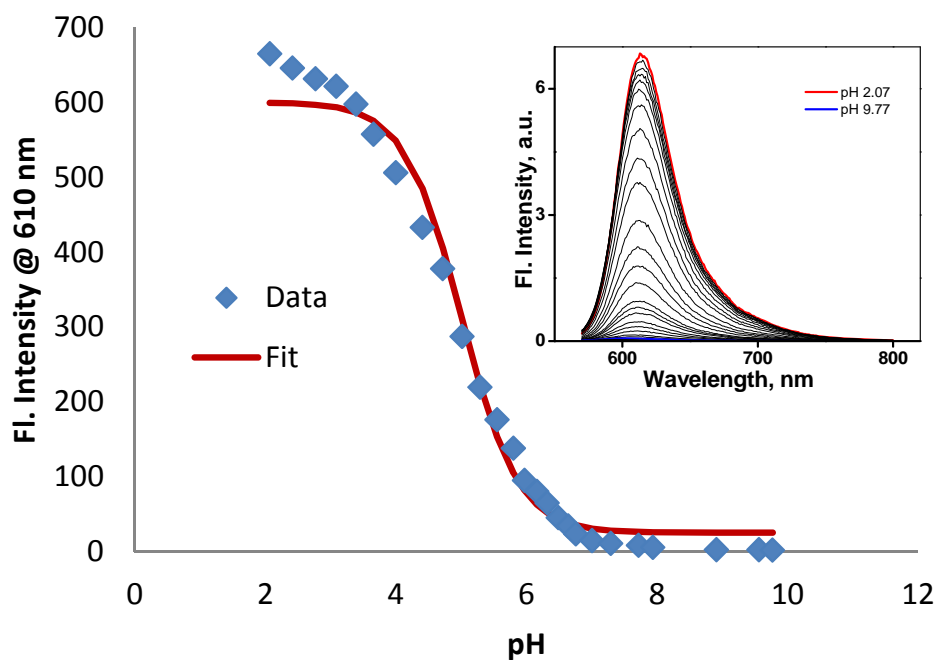


Figure S10. Variation of fluorescence intensity of **5** at 610 nm vs. pH ($\lambda_{\text{ex}} = 570 \text{ nm}$). Inset shows the emission spectra of **5** at various pH (red line at pH = 2.07 and blue line at pH = 9.77). $\text{p}K_a = 5.0$.

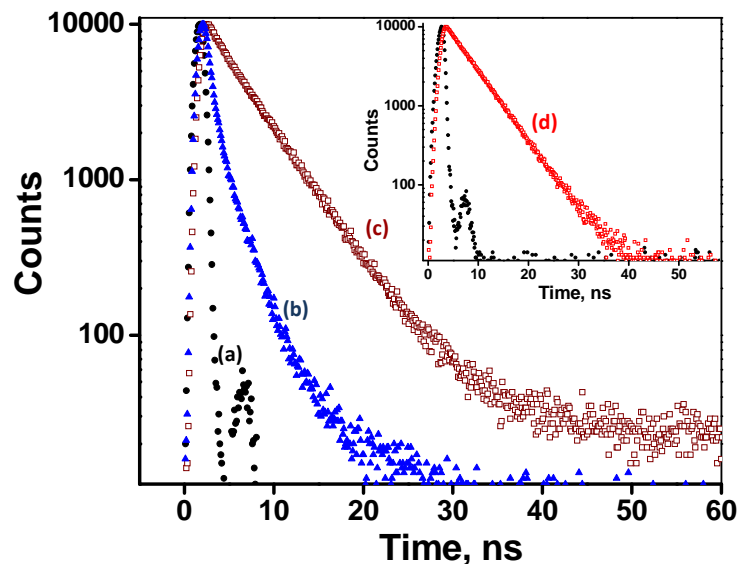


Figure S11. Fluorescence decay profiles monitored at 520 nm (\blacktriangle) and 610 nm (\square) by exciting samples using a 370 nm nanoLED excitation source, (a) IRF (\bullet), (b) the monozinc complex of **6** (\blacktriangle , blue), (c) **6** in the presence of 10 equiv of $\text{Zn}(\text{ClO}_4)_2$ (\square , wine). Inset: (d) **5** in the presence of 10 equiv of $\text{Zn}(\text{ClO}_4)_2$ (\square , red) in CH_3CN excited at 560 nm.

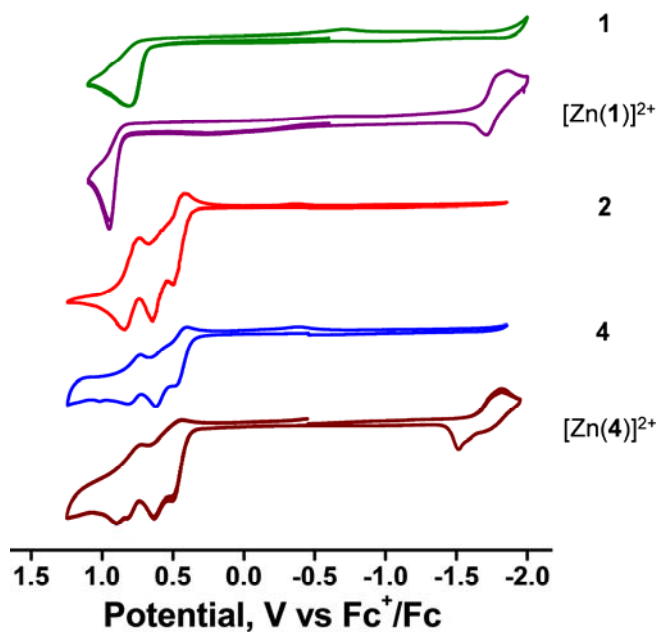


Figure S12. Cyclic voltammograms of **1** (green), $[\text{Zn}(\mathbf{1})]^{2+}$ (violet), **2** (red), **4** (blue), and $[\text{Zn}(\mathbf{4})]^{2+}$ (brown) in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ at a sweep rate of 100 mV/s.

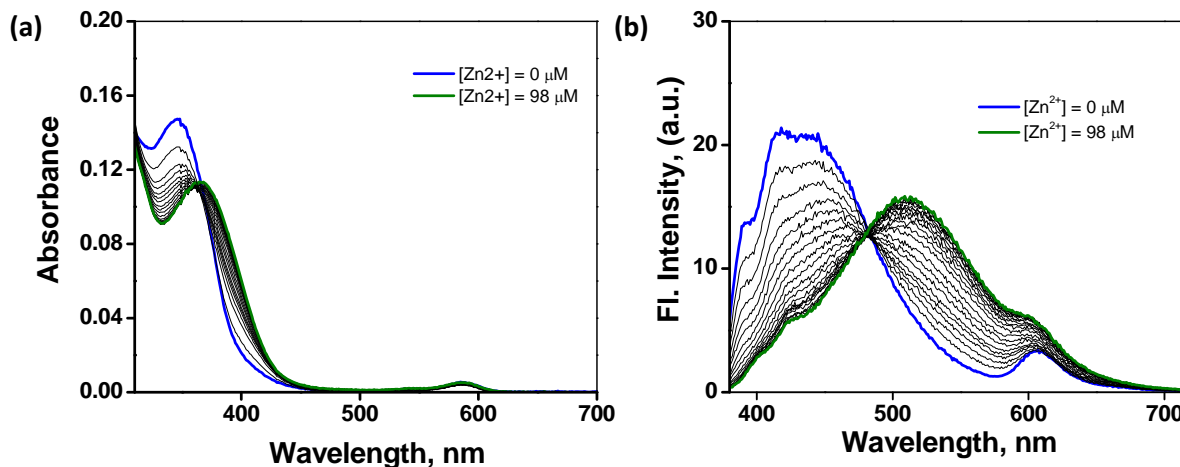


Figure S13. (a) Effect of addition of ZnCl_2 (0-98 μM) on the absorption spectrum of compound **6** (5 μM) in a 1:1 $\text{CH}_3\text{CN}/\text{HEPES}$ buffer (50 mM HEPES, 50 mM NaCl, pH 7.2) solution. (b) Corresponding changes of the emission spectrum ($\lambda_{\text{ex}} = 370$ nm).

Table S1. Electrochemical data of **1**, $[\text{Zn}(\mathbf{1})]^{2+}$, **2**, **4**, and $[\text{Zn}(\mathbf{4})]^{2+}$.

Compound	^a E_{ox} , V vs Fc^+/Fc	E_{red} , V vs Fc^+/Fc
1	0.80	-
^b $[\text{Zn}(\mathbf{1})]^{2+}$	0.96	-1.73
2	0.47	-
4	0.47	-
^b $[\text{Zn}(\mathbf{4})]^{2+}$	0.48	-1.77

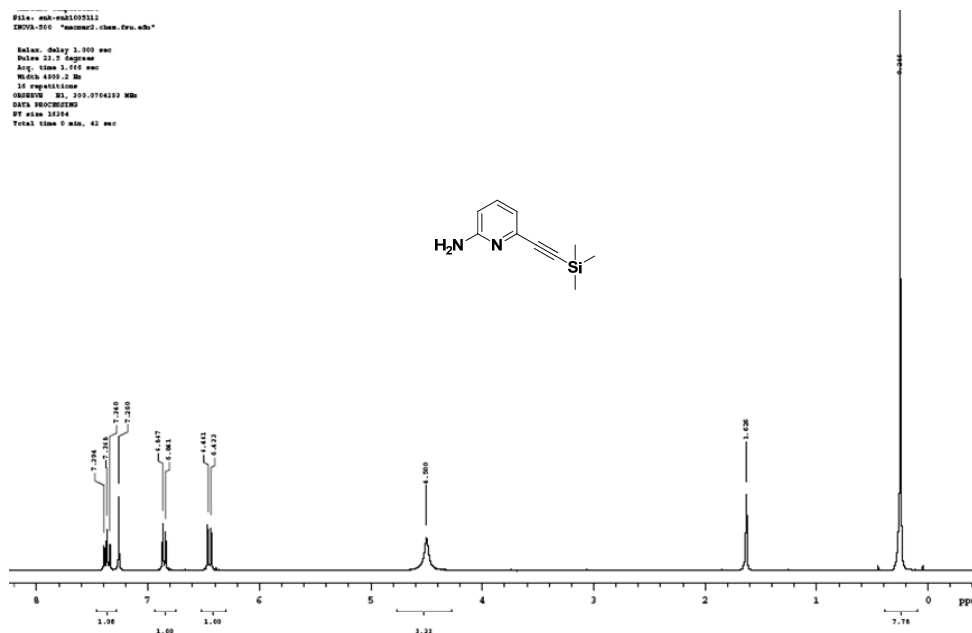
^a Lowest oxidation potential, ^b of monozinc complex.

II. References

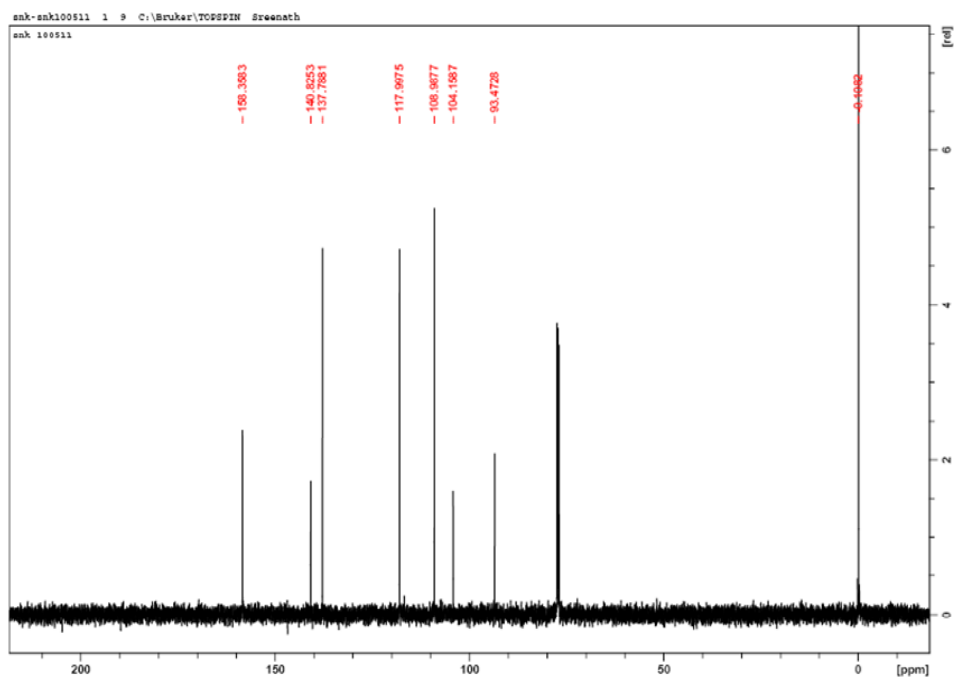
- (1) Zhu, L.; Zhong, Z.; Anslyn, E. V. *J. Am. Chem. Soc.* **2005**, *127*, 4260-4269.
- (2) Kuang, G.-C.; Allen, J. R.; Baird, M. A.; Nguyen, B. T.; Zhang, L.; Morgan, T. J. Jr.; Levenson, C. W.; Davidson, M. W.; Zhu, L. *Inorg. Chem.* **2011**, *50*, 10493-10504.

III. Copies of ^1H and ^{13}C NMR of Compounds

^1H NMR (300 MHz, CDCl_3) of 2-amino-6[(trimethylsilyl)ethynyl]pyridine



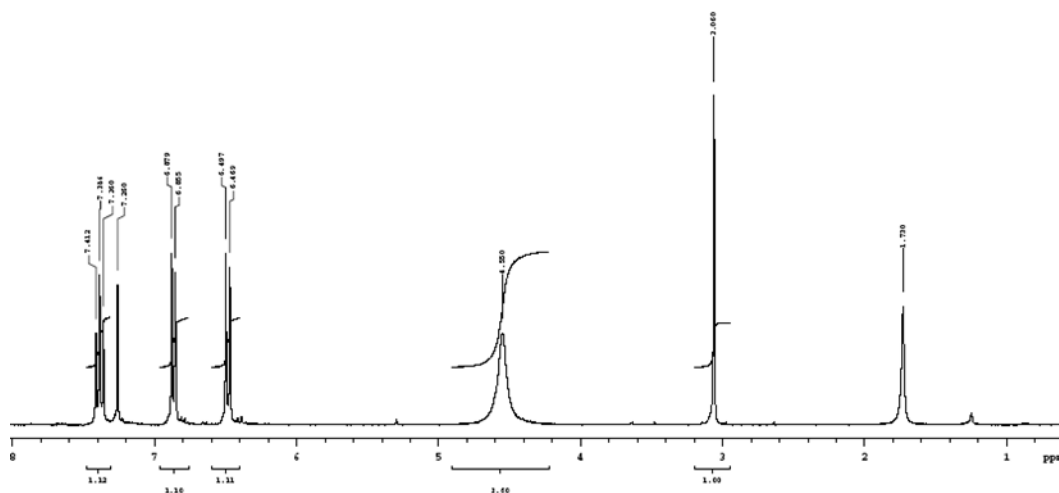
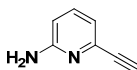
^{13}C NMR (125 MHz, CDCl_3) of 2-amino-6[(trimethylsilyl)ethynyl]pyridine



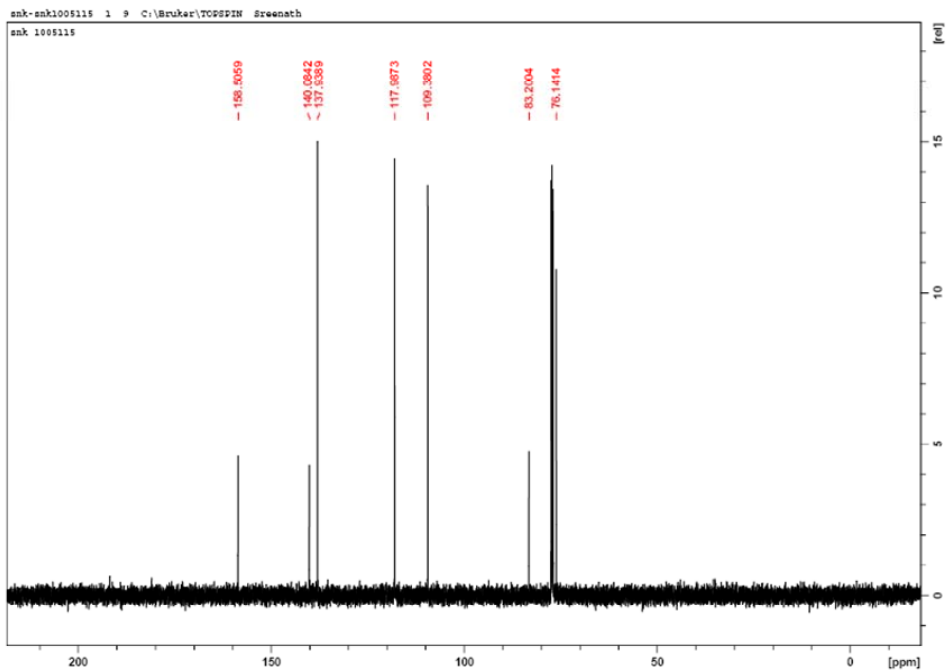
^1H NMR (300 MHz, CDCl_3) of 2-amino-6-ethynylpyridine

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300 MHz   May 10 2011
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pc1magr_00133
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Solvent: cdcl3
Acquisition temperature
File: snk-0011005115
INOVA-500 "nucmer2.chem.fsu.edu"

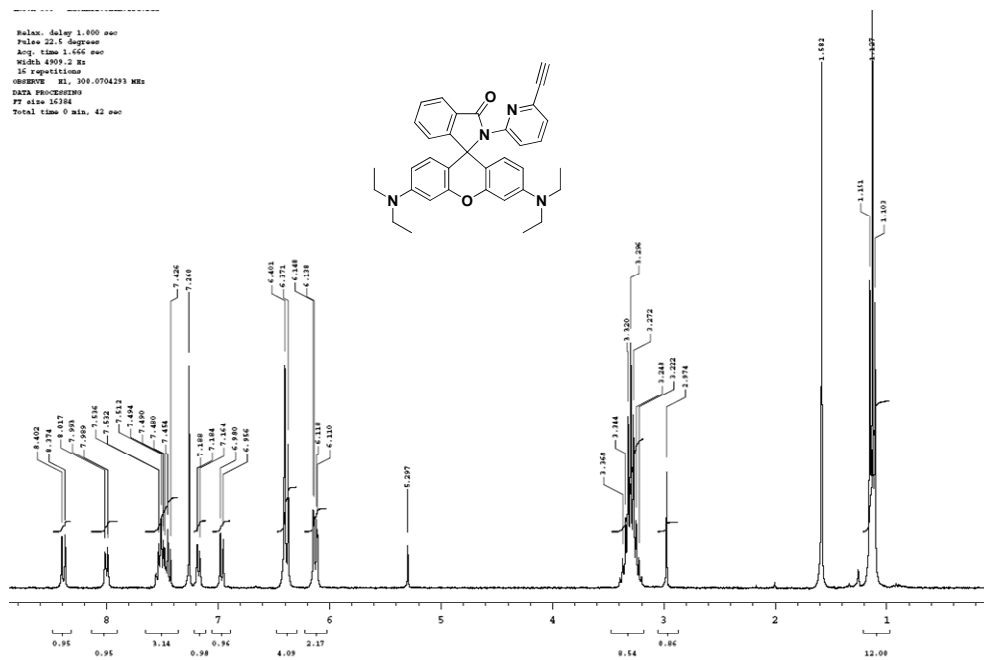
Delay: 1.000 sec
Pulse: 23.5 degree
Acq. time: 3.161 sec
NUC1: 13C 125.0 MHz
15 repetitions
OBSERVED: 83, 300.0704200 MHz
DATA PROCESSING
PT: 1000 1024
Total time 0 min, 41 sec
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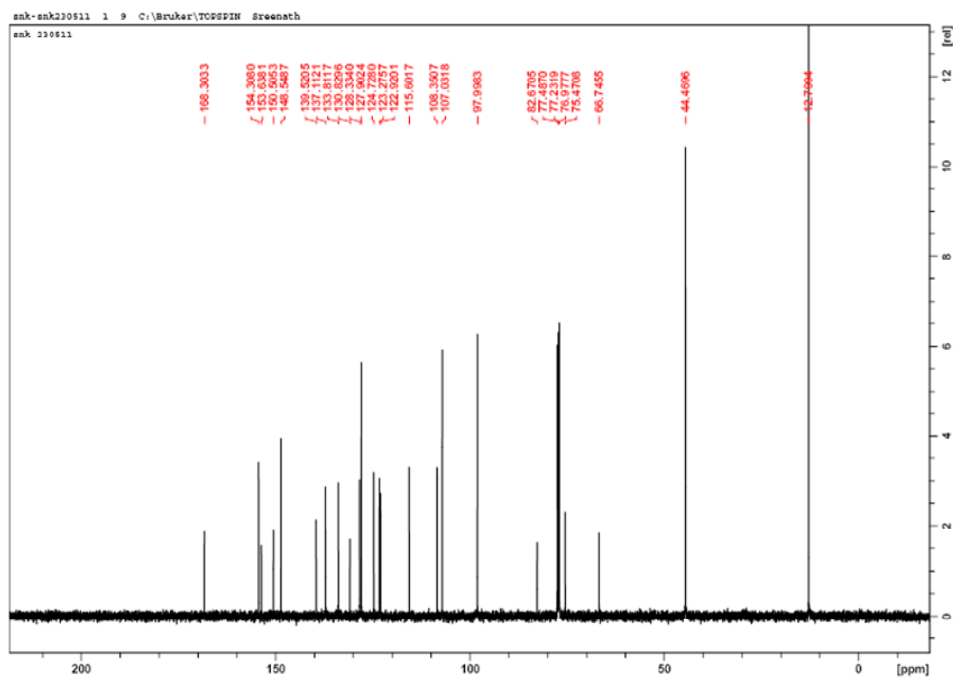
^{13}C NMR (125 MHz, CDCl_3) of 2-amino-6-ethynylpyridine



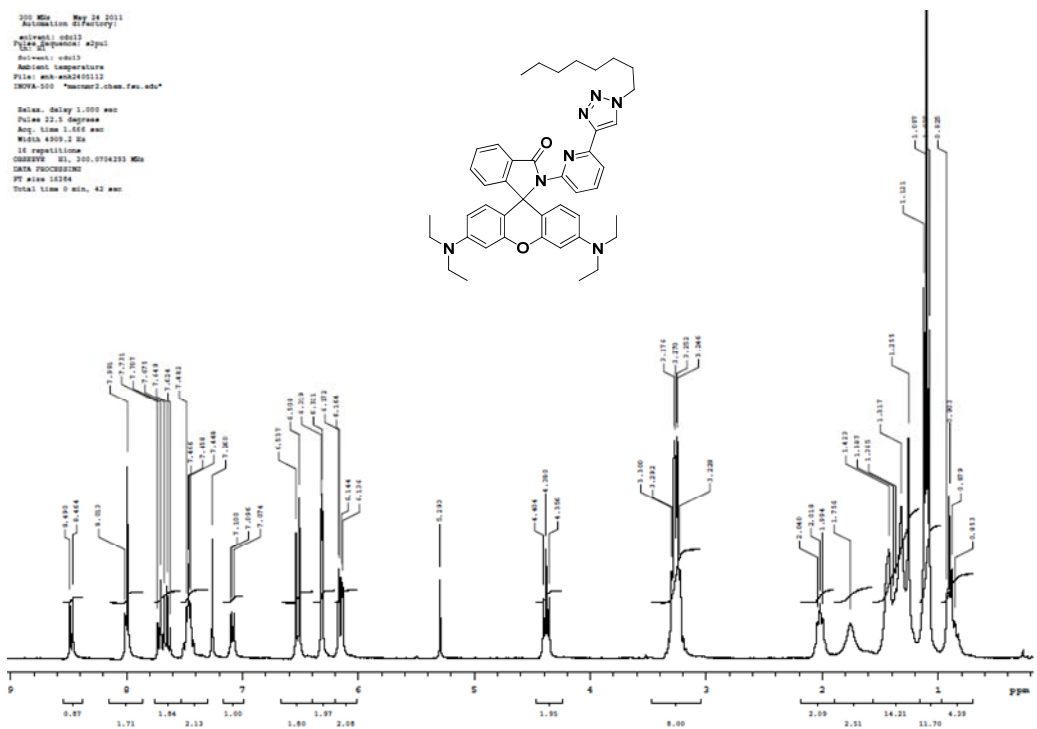
¹H NMR (300 MHz, CDCl₃) of compound **7**



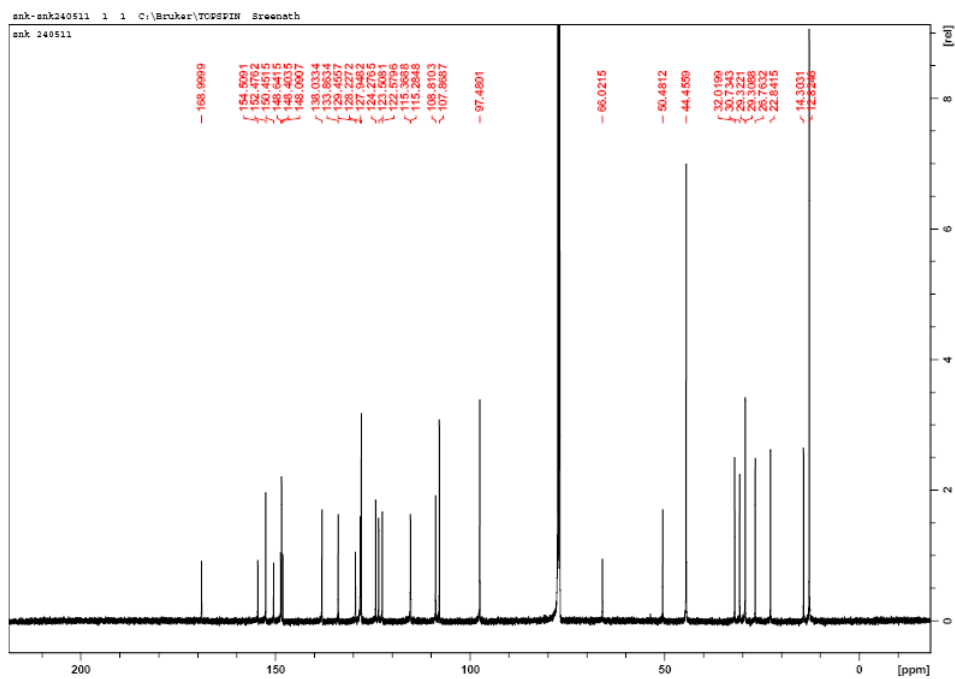
¹³C NMR (125 MHz, CDCl₃) of compound **7**



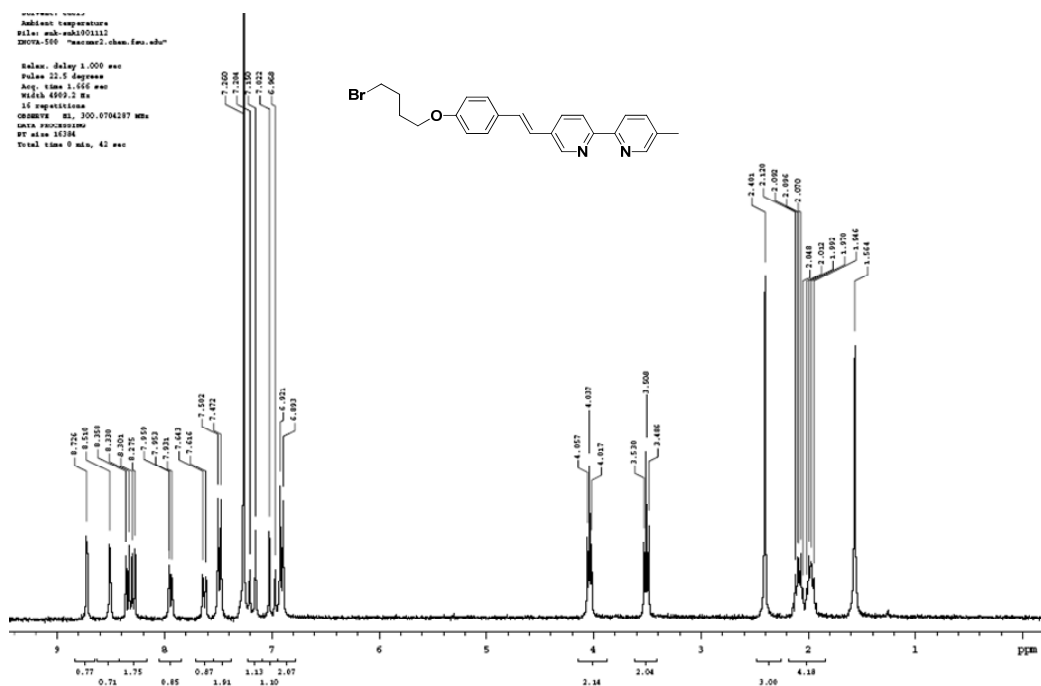
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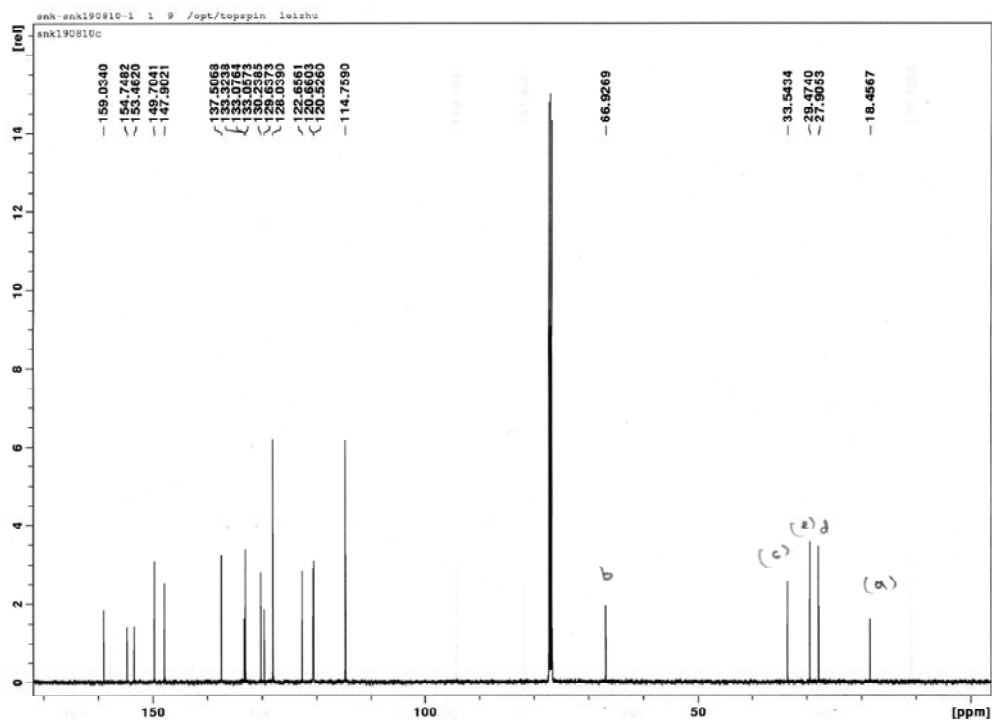
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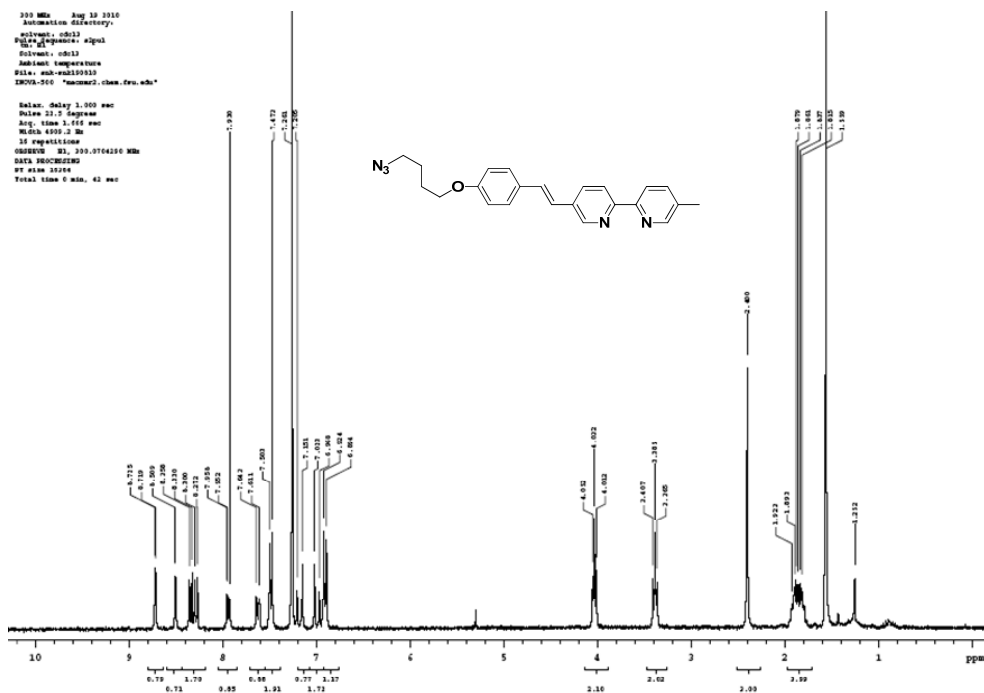
^1H NMR (300 MHz, CDCl_3) of compound **10**



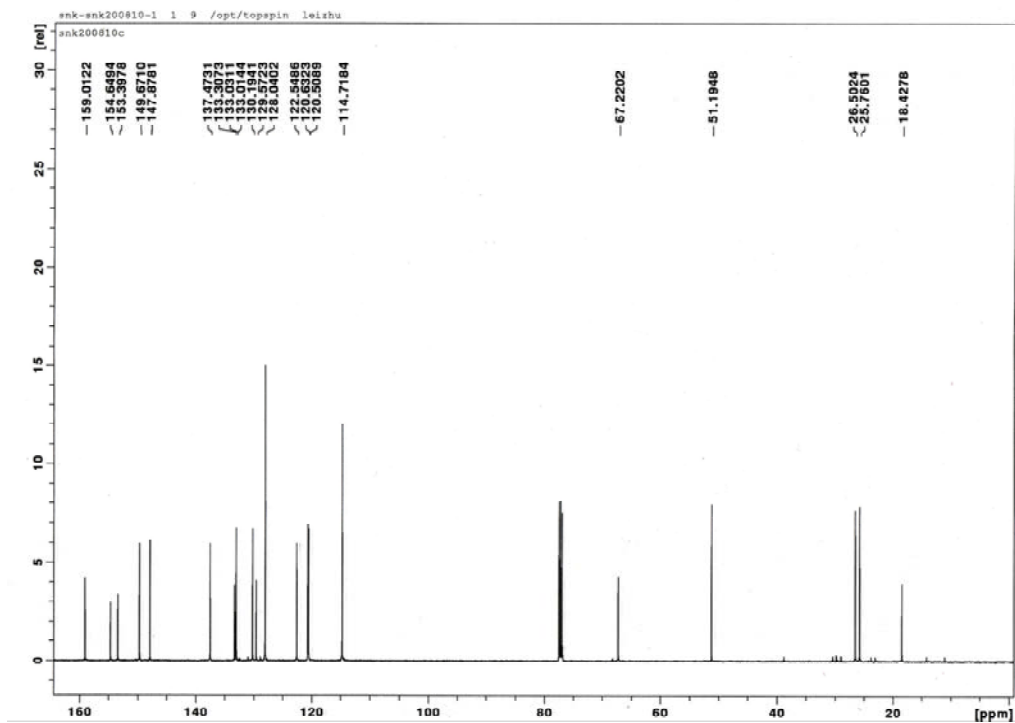
^{13}C NMR (125 MHz, CDCl_3) of compound **10**



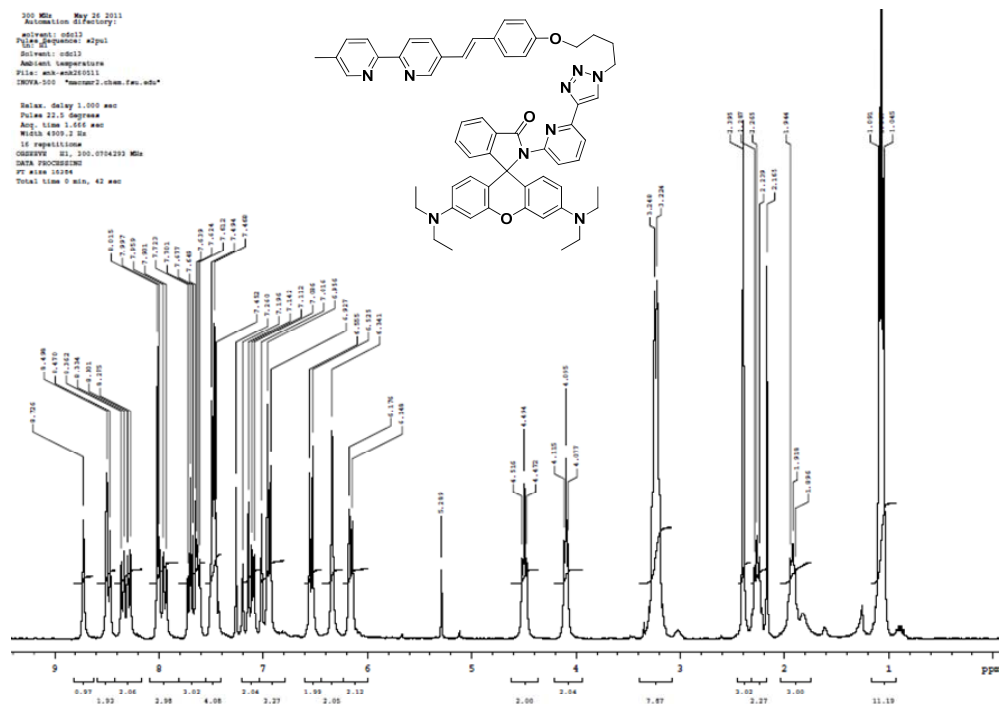
^1H NMR (300 MHz, CDCl_3) of compound **11**



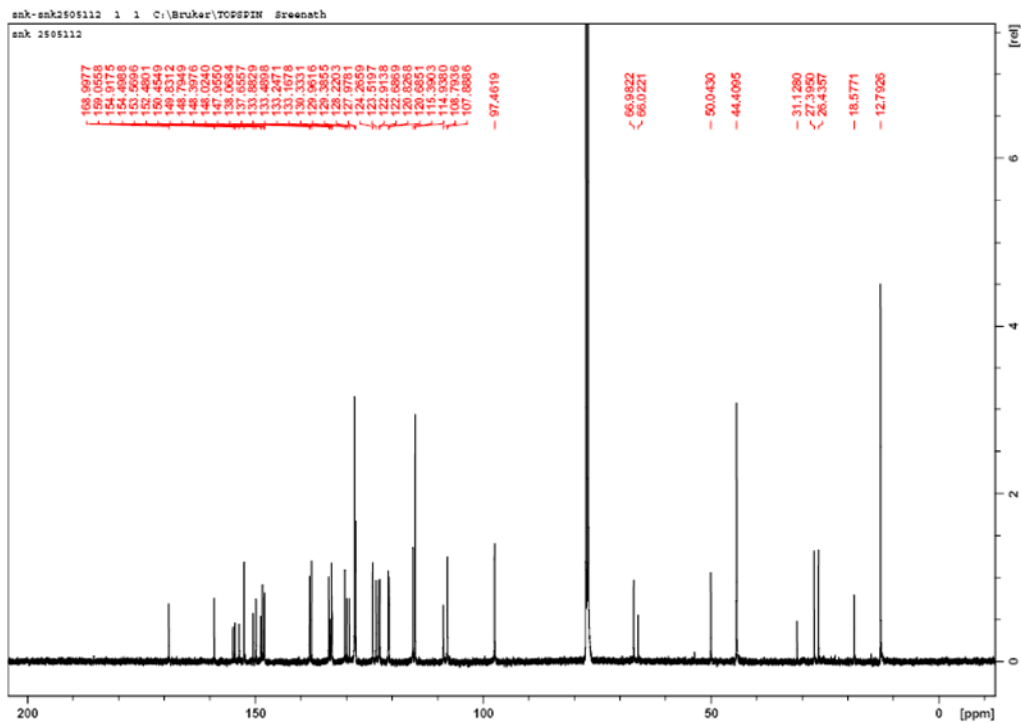
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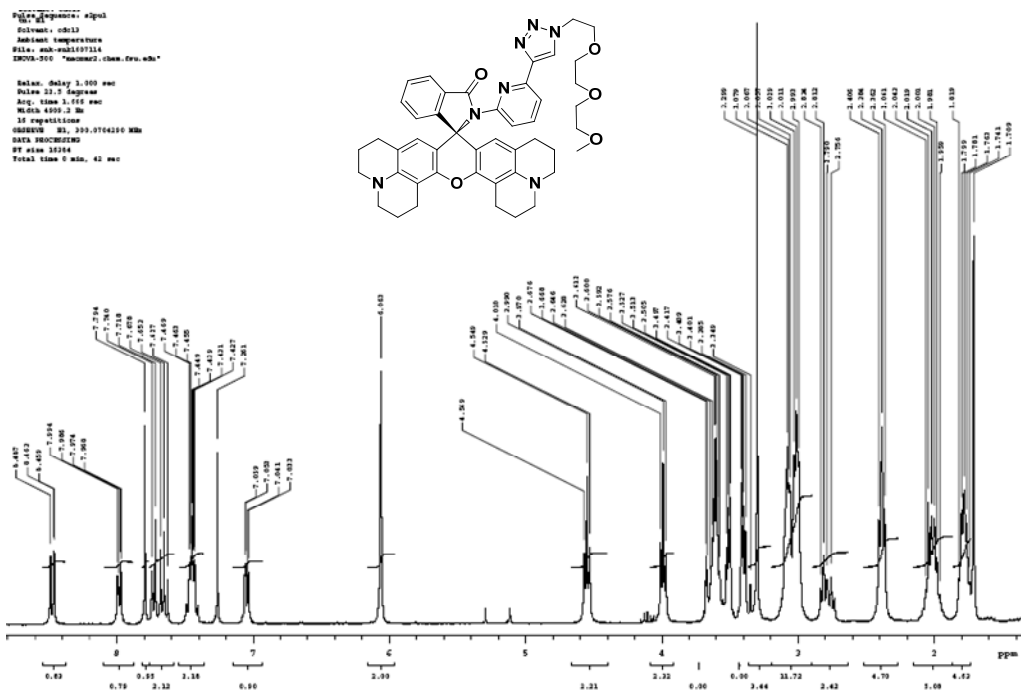
¹H NMR (300 MHz, CDCl₃) of compound 4



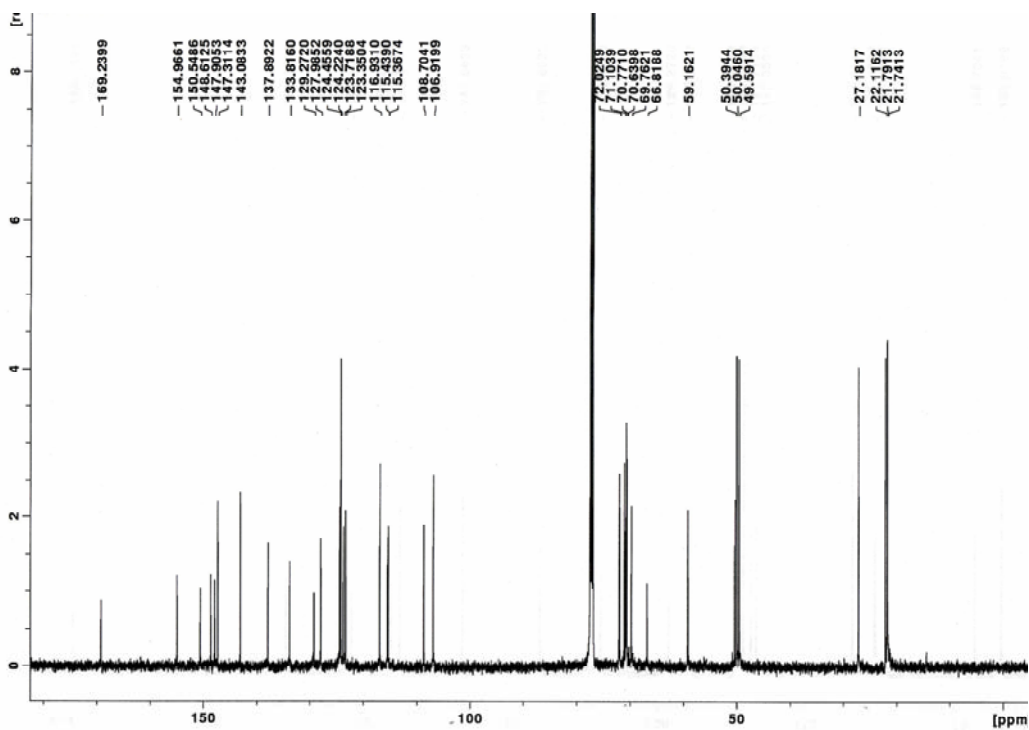
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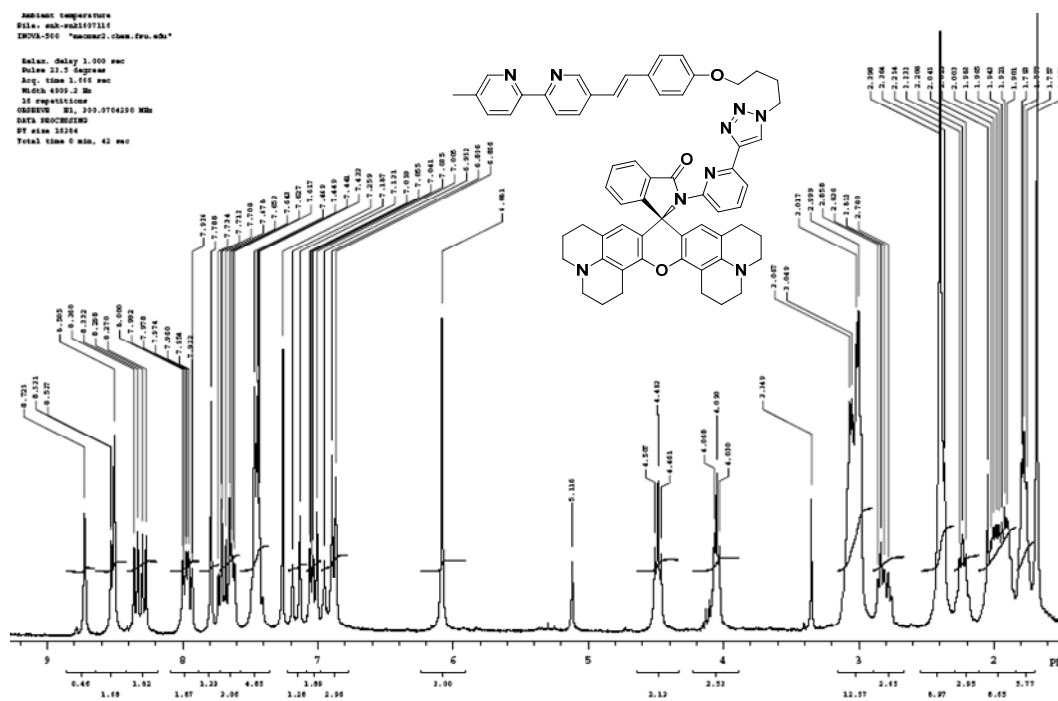
¹H NMR (300 MHz, CDCl₃) of compound **5**



¹³C NMR (125 MHz, CDCl₃) of compound **5**



¹H NMR (300 MHz, CDCl₃) of compound 6



¹³C NMR (125 MHz, CDCl₃) of compound 6

