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

Supporting Information

*Kesavapillai Sreenath, Ronald J. Clark, and Lei Zhu**

Department of Chemistry and Biochemistry

Florida State University, 95 Chieftan Way

Tallahassee, Florida 32306-4390

lzhu@chem.fsu.edu

Table of Contents

I. Additional Figures

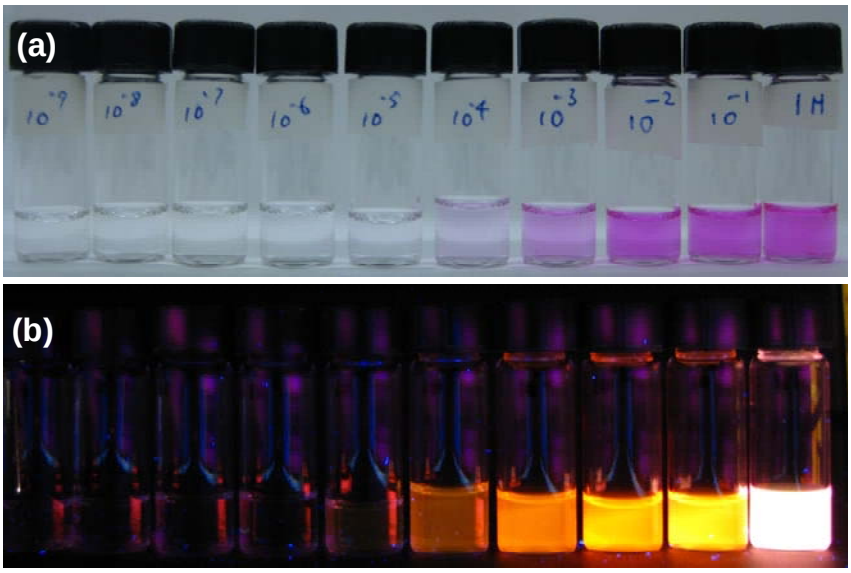


Figure S1. Visual appearance of **2** (10 μM) in CH_3CN upon increasing $Zn(ClO_4)_2$ concentration from 1 nM to 1 M (left to right) under (a) ambient light, and (b) upon illumination using a handheld UV lamp (λ_{ex} = 365 nm).

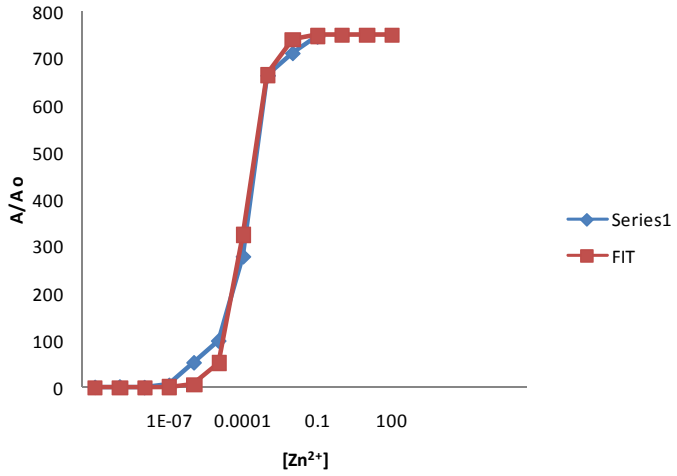


Figure S2. Absorbance increase (A/A_0 at 568 nm) of **2** (10 μM), with increasing [$Zn(ClO_4)_2$]. The brown line is the fitting curve of A/A_0 *vs* [Zn^{2+}] based on a 1:1 binding isotherm equation.[1] Dissociation constant of the putative 1:1 (ligand/Zn^{2+}) complex K_d = 0.1 mM.

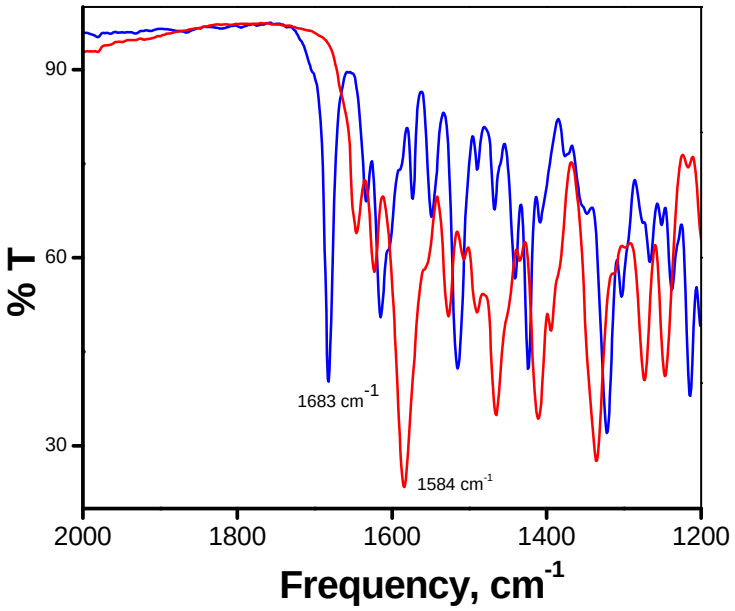


Figure S3. IR spectra of **3** (blue) and [Zn(**3**)]$(ClO_4)_2$.

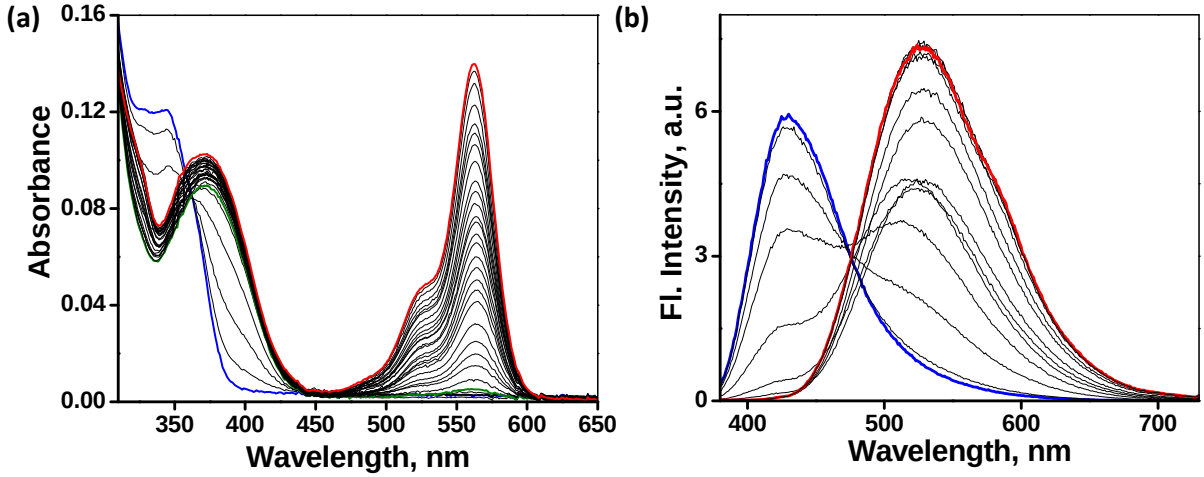


Figure S4. (a) Effect of addition of $Zn(ClO_4)_2$ (0-60 μM) on the absorption spectrum of the mixture of **1** (3.0 μM) and **2** (3.0 μM) in CH_3CN. (b) Corresponding changes of the emission spectrum (λ_{ex} = 370 nm).

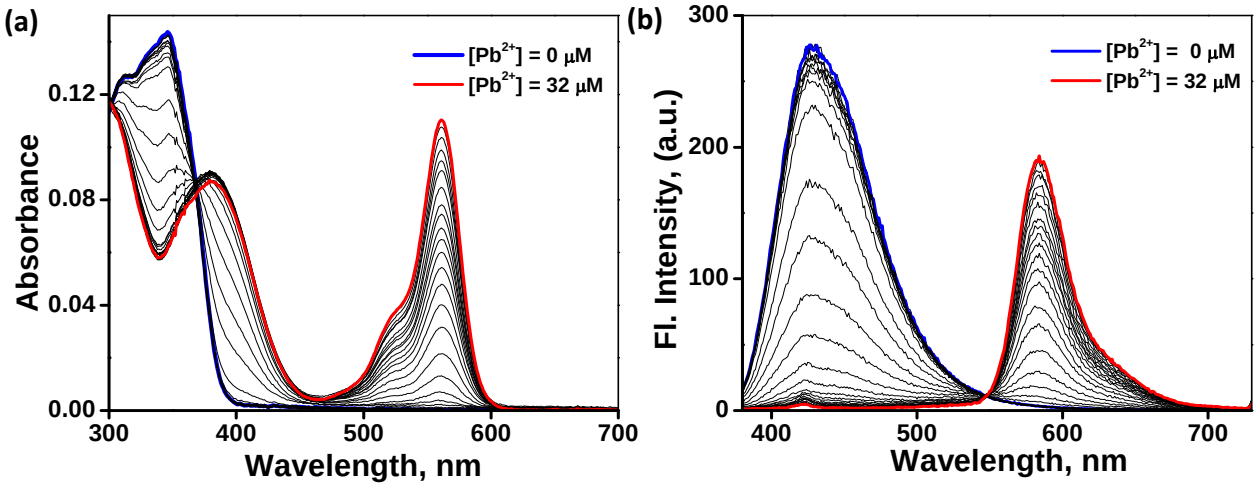


Figure S5. (a) Effect of addition of $Pb(ClO_4)_2$ (0-32 μM) on the absorption spectrum of compound **4** (3.1 μM) in CH_3CN. (b) Corresponding changes of the emission spectrum (λ_{ex} = 370 nm).

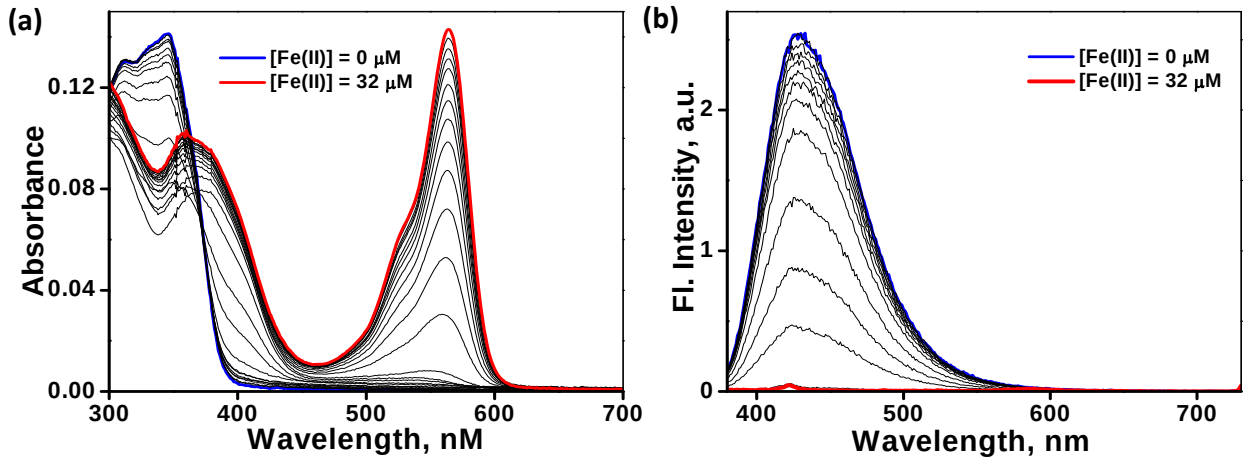


Figure S6. (a) Effect of addition of $Fe(ClO_4)_2$ (0-32 μM) on the absorption spectrum of compound **4** (3.1 μM) in CH_3CN. (b) Corresponding changes of the emission spectrum (λ_{ex} = 370 nm).

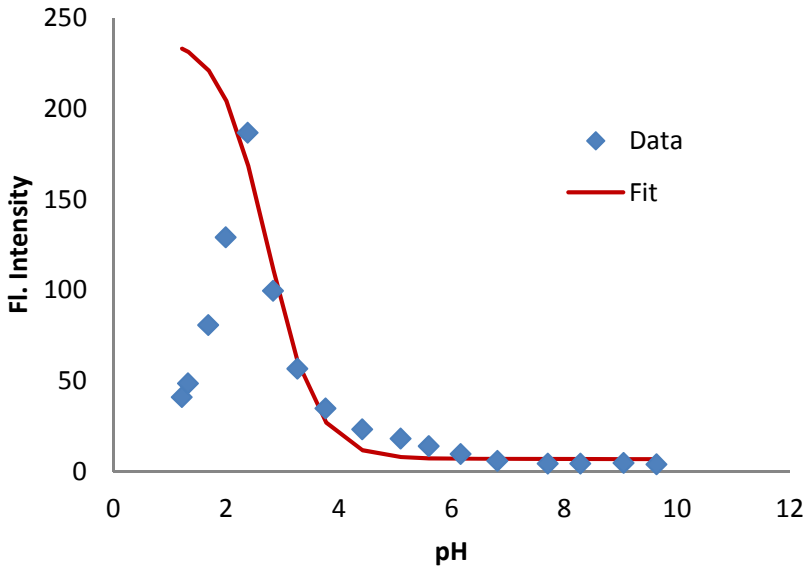


Figure S7. Variation of fluorescence intensity of **2** at 588 nm *vs.* pH (λ_{ex} = 570 nm). The purple line is the fitting curve based on a modified Henderson–Hasselbalch equation.[2] pK_a ~ 2.8.

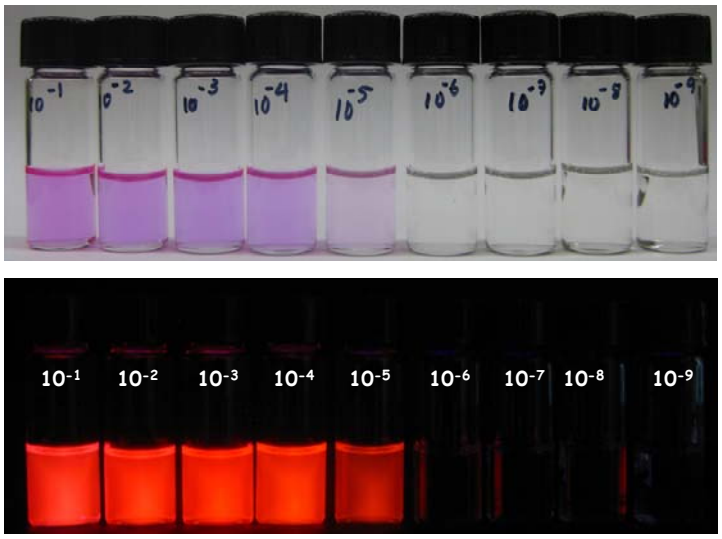


Figure S8. Visual appearance of **5** (10 μM) in CH_3CN upon increasing $Zn(ClO_4)_2$ concentration from 1 nM to 0.1 M (right to left) under (a) ambient light, and (b) upon illumination using a handheld UV lamp (λ_{ex} = 365 nm).

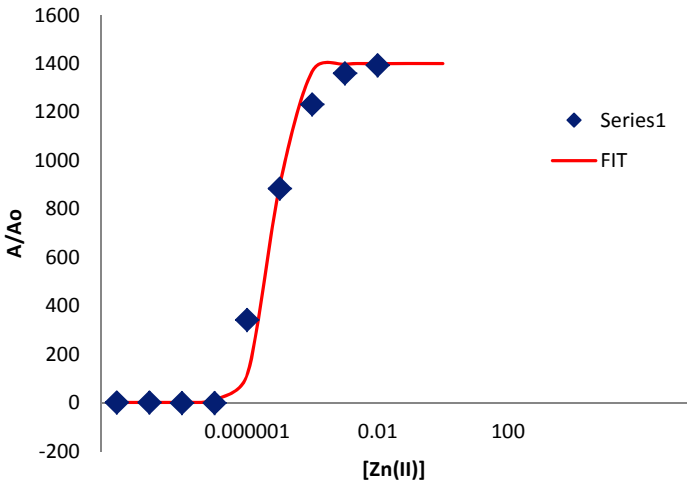


Figure S9. Absorbance increase (A/A_0 at 584 nm) of **5** (10 μM) with increasing [$Zn(ClO_4)_2$]. The red line is the fitting curve of A/A_0 *vs* [Zn^{2+}] based on a 1:1 binding isotherm equation.[1] Dissociation constant of the putative 1:1 complex (ligand/Zn^{2+}) K_d = 20 μM.

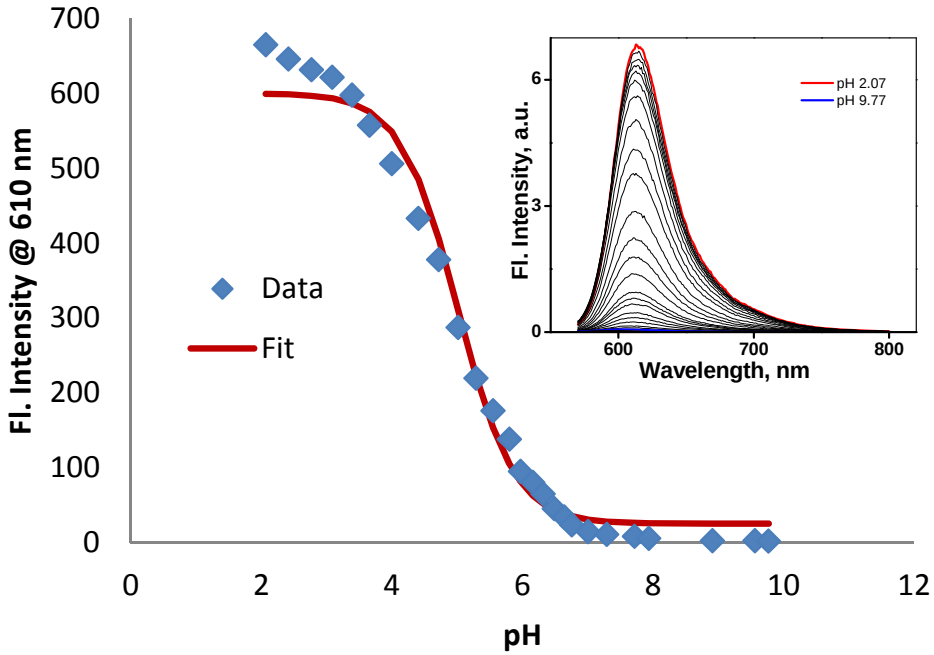


Figure S10. Variation of fluorescence intensity of **5** at 610 nm *vs.* pH (λ_{ex} = 570 nm). Inset shows the emission spectra of **5** at various pH (red line at pH = 2.07 and blue line at pH = 9.77). pK_a = 5.0.

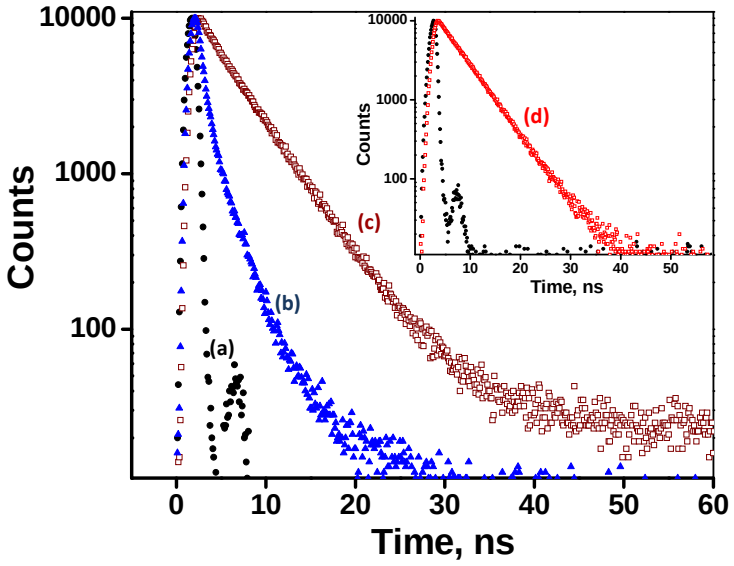


Figure S11. Fluorescence decay profiles monitored at 520 nm (▲) and 610 nm (□) by exciting samples using a 370 nm nanoLED excitation source, (a) IRF (●), (b) the monozinc complex of **6** (▲, blue), (c) **6** in the presence of 10 equiv of $Zn(ClO_4)_2$ (□, wine). Inset: (d) **5** in the presence of 10 equiv of $Zn(ClO_4)_2$ (□, red) in CH_3CN excited at 560 nm.

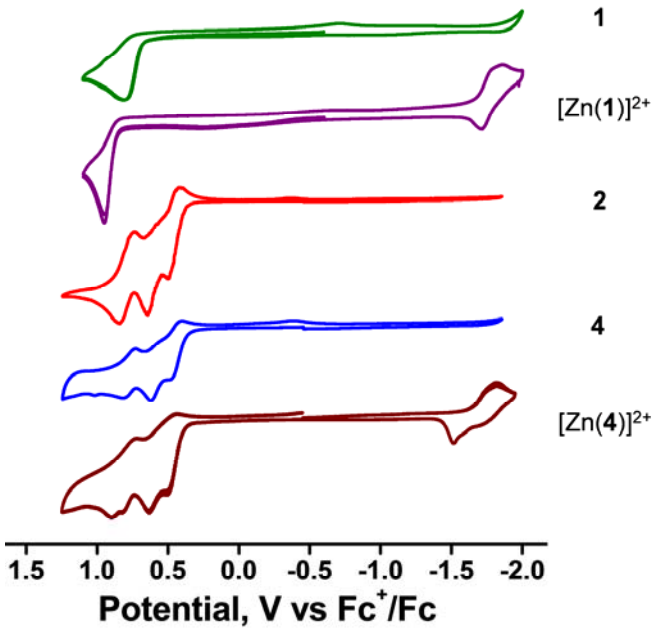


Figure S12. Cyclic voltammograms of **1** (green), $[Zn(\mathbf{1})]^{2+}$ (violet), **2** (red), **4** (blue), and $[Zn(\mathbf{4})]^{2+}$ (brown) in 0.1 M Bu_4NPF_6/CH_3CN at a sweep rate of 100 mV/s.

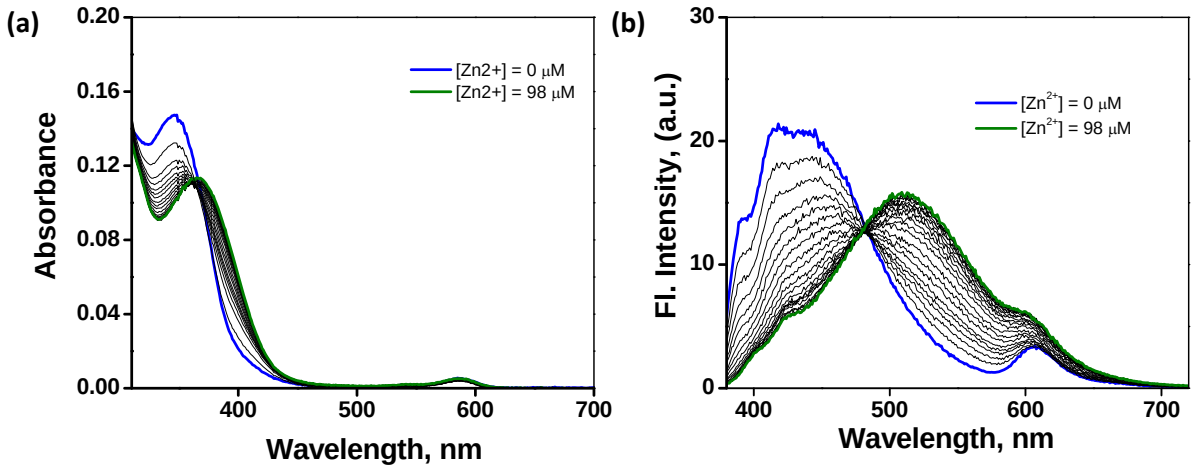


Figure S13. (a) Effect of addition of $ZnCl_2$ (0-98 μM) on the absorption spectrum of compound **6** (5 μM) in a 1:1 CH_3CN/HEPES buffer (50 mM HEPES, 50 mM NaCl, pH 7.2) solution. (b) Corresponding changes of the emission spectrum (λ_{ex} = 370 nm).

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

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

[a] Lowest oxidation potential, [b] of monozinc complex.

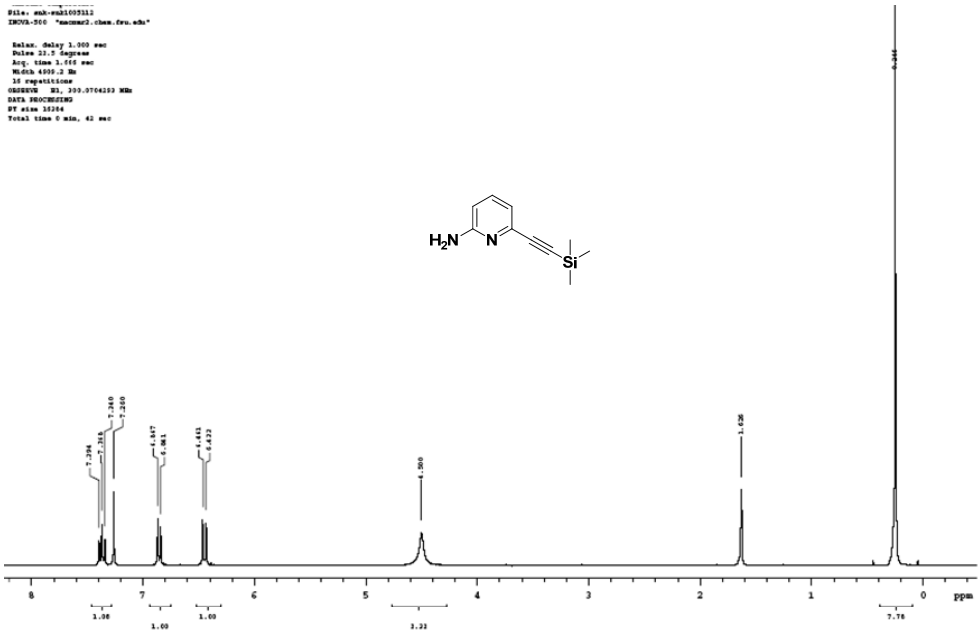
II. References

(1) Zhu, L.; Zhong, Z.; Anslyn, E. V. *J. Am. Chem. Soc.* **2005**, *127*, 4260-4269.

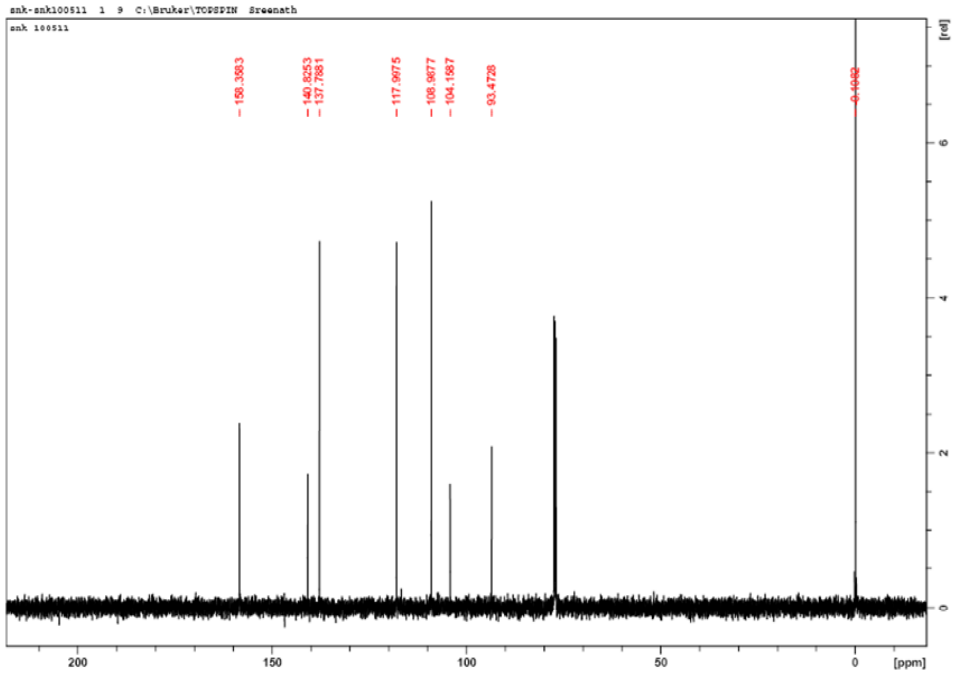
(2) Kuang, G.-C.; Allen, J. R.; Baird, M. A.; Nguyen, B. T.; Zhang, L.; Morgan, T. J. Jr.; Levenson, C. W.; Davidson, M. W.; Zhu, L. *Inorg. Chem.* **2011**, *50*, 10493-10504.

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

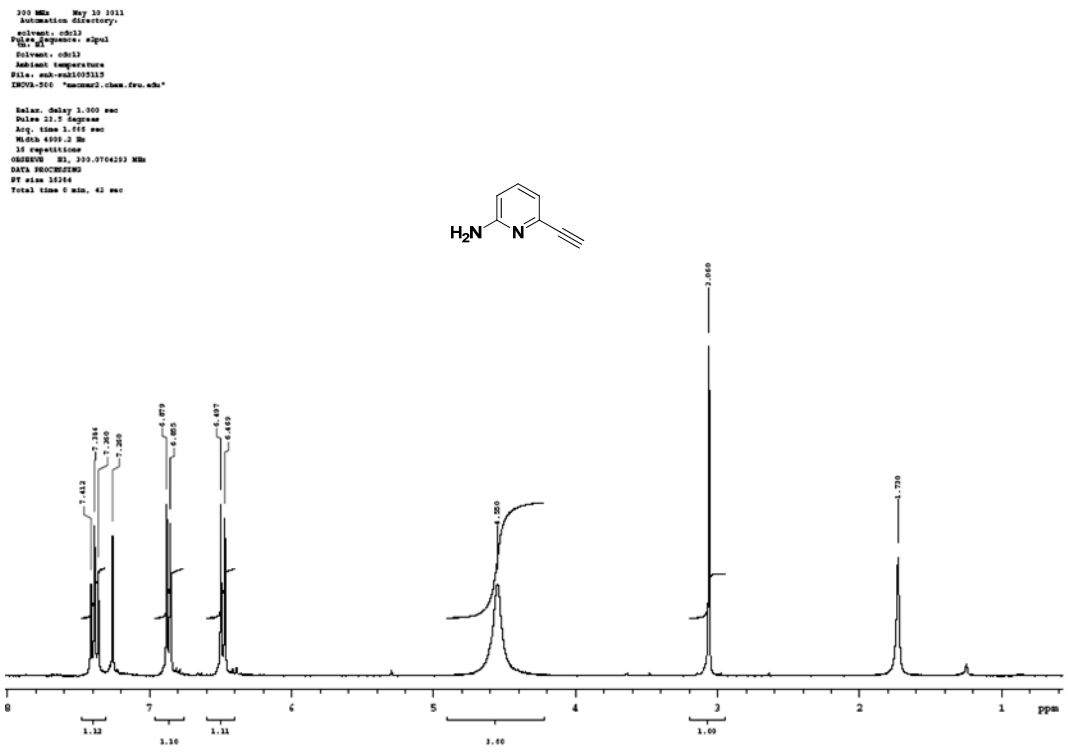
^{1}H NMR (300 MHz, $CDCl_3$) of 2-amino-6[(trimethylsilyl)ethynyl]pyridine



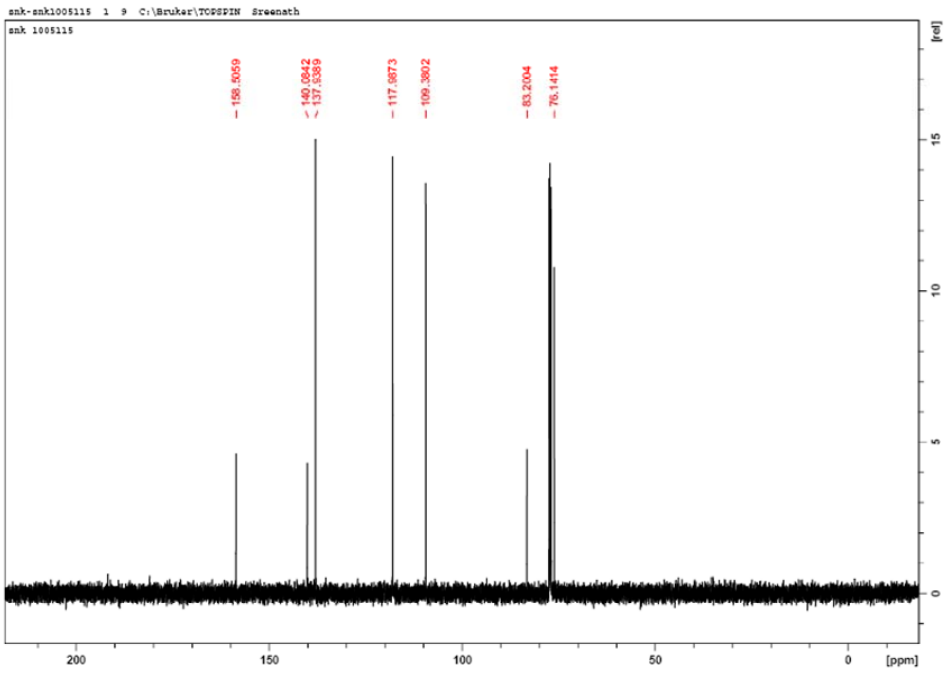
^{13}C NMR (125 MHz, $CDCl_3$) of 2-amino-6[(trimethylsilyl)ethynyl]pyridine



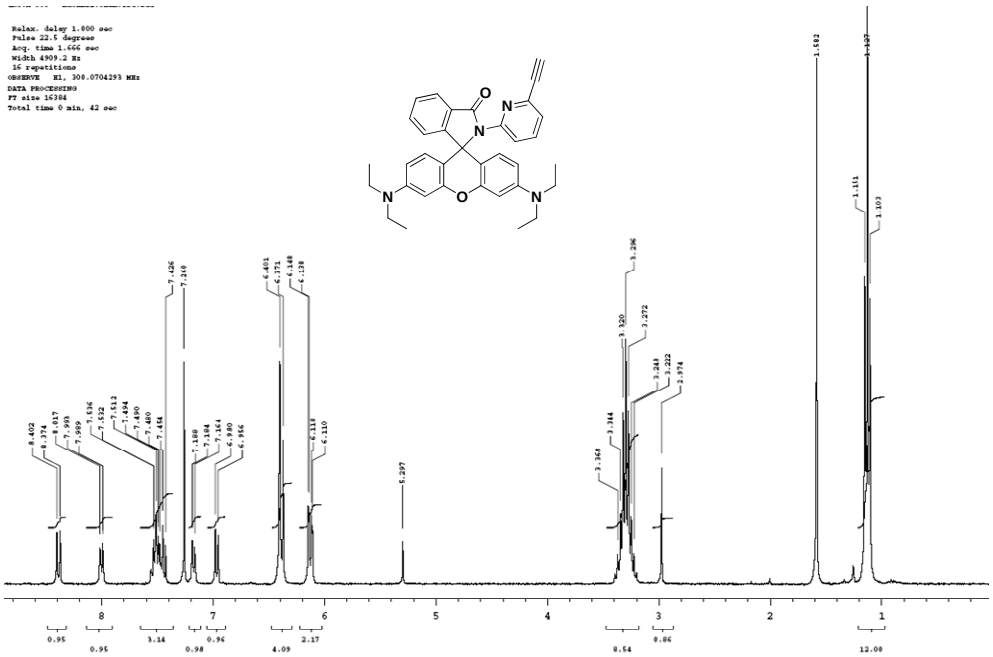
^{1}H NMR (300 MHz, $CDCl_3$) of 2-amino-6-ethynylpyridine



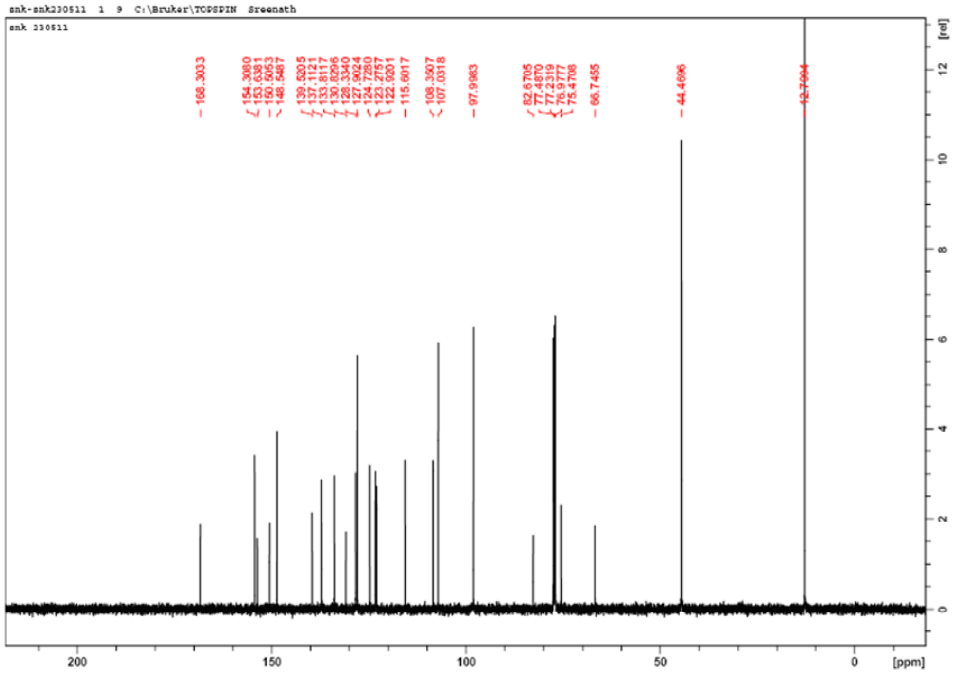
^{13}C NMR (125 MHz, $CDCl_3$) of 2-amino-6-ethynylpyridine



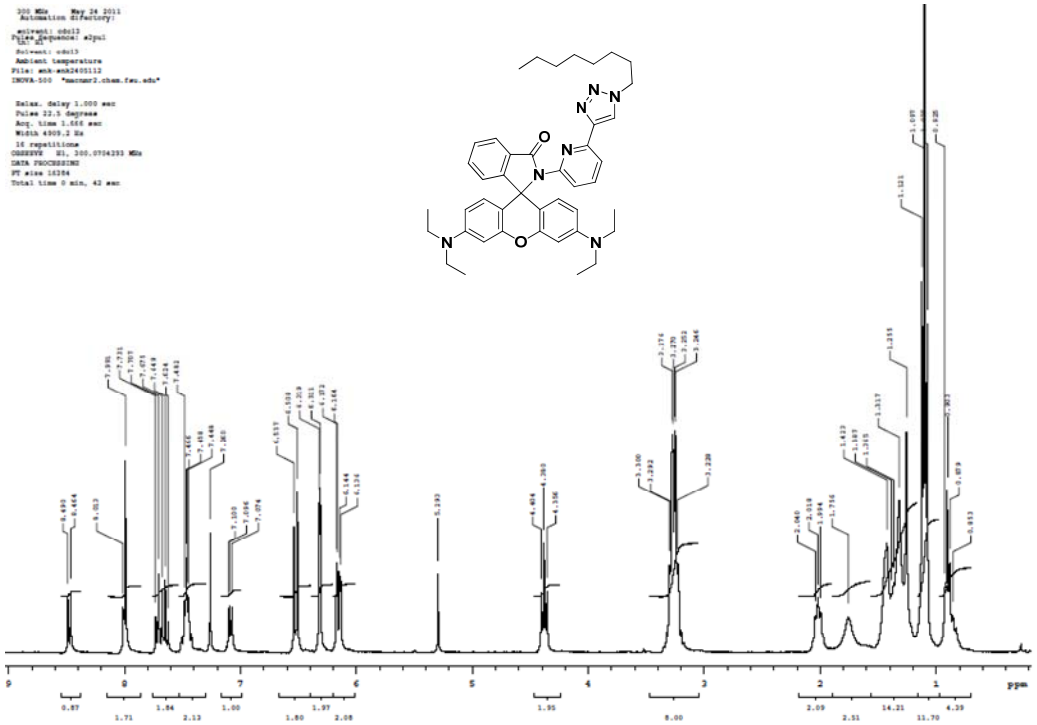
^{1}H NMR (300 MHz, $CDCl_3$) of compound **7**



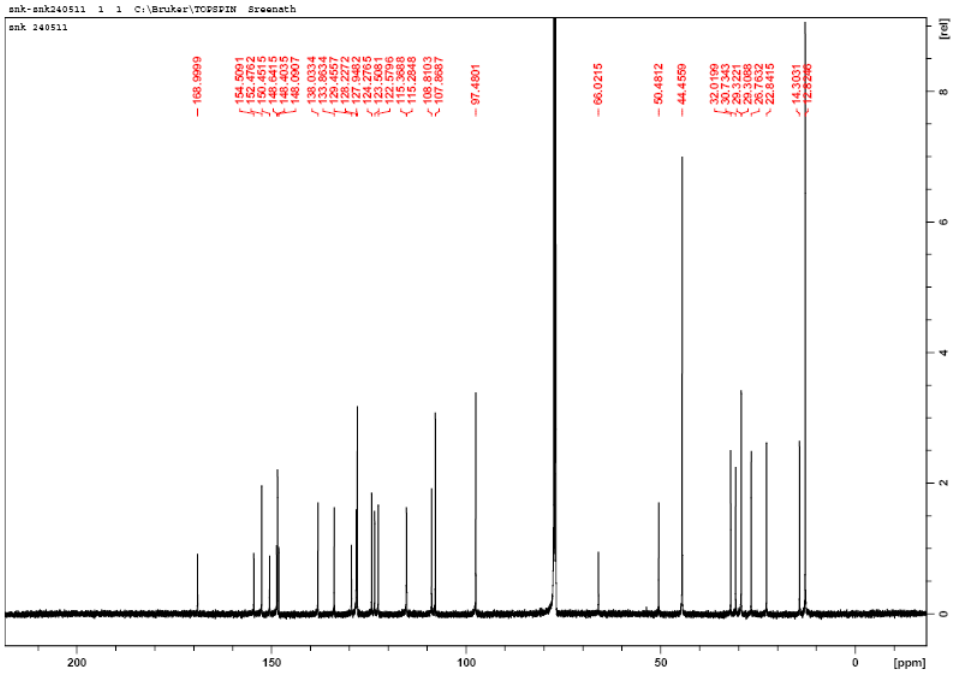
^{13}C NMR (125 MHz, $CDCl_3$) of compound **7**



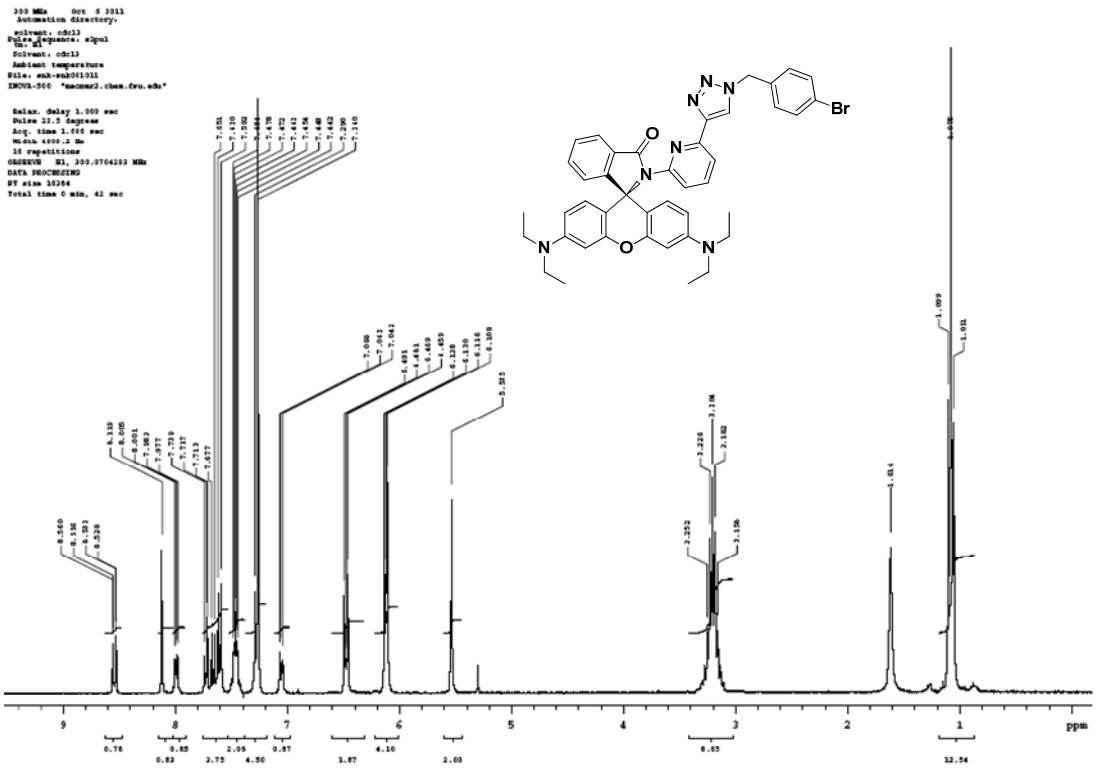
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2**



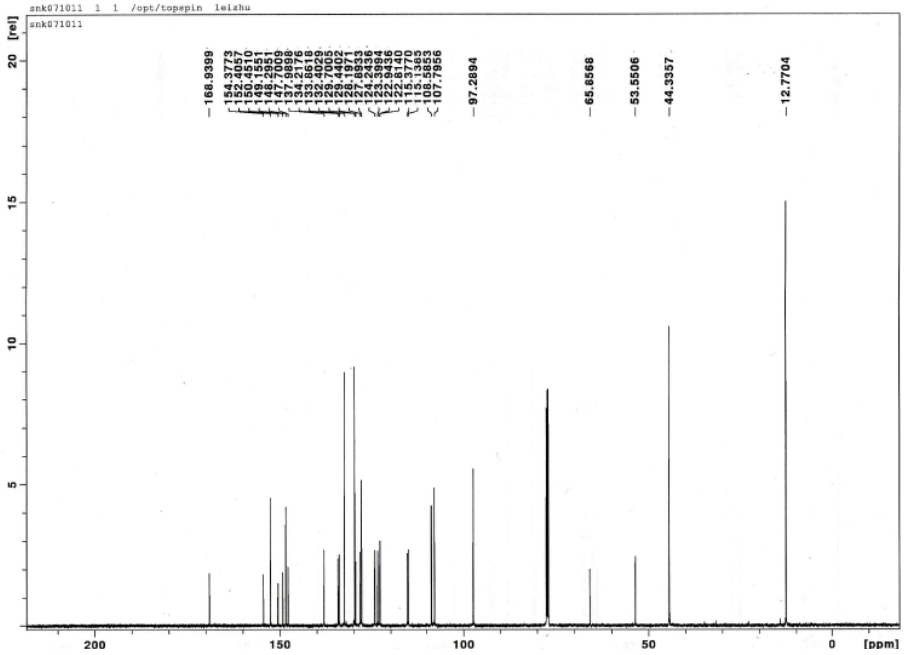
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2**



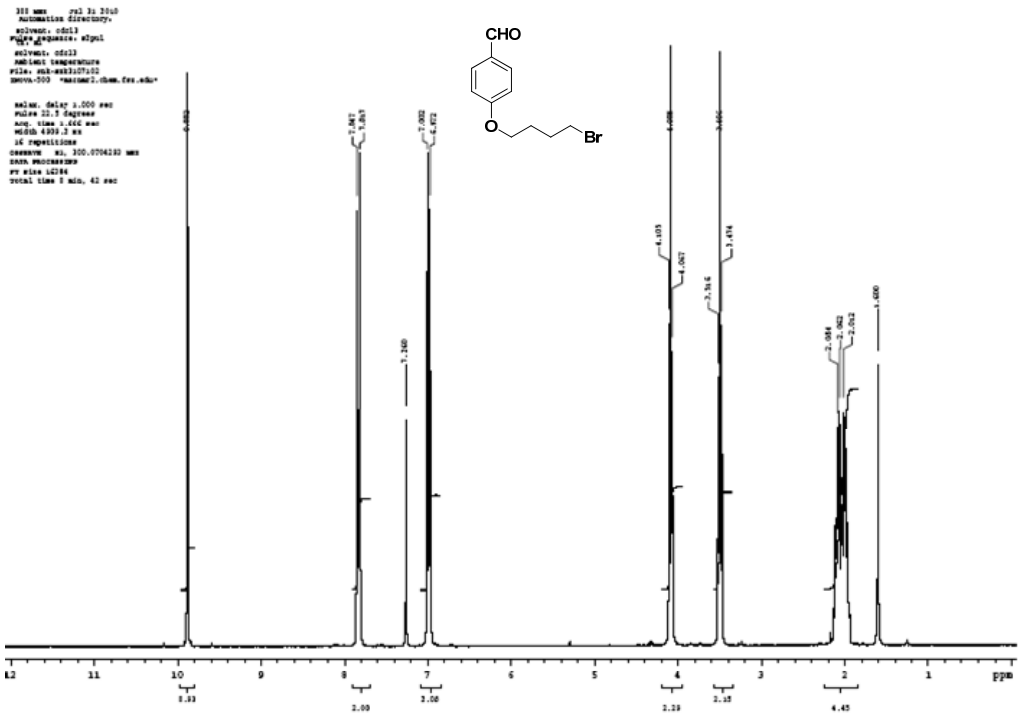
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3**



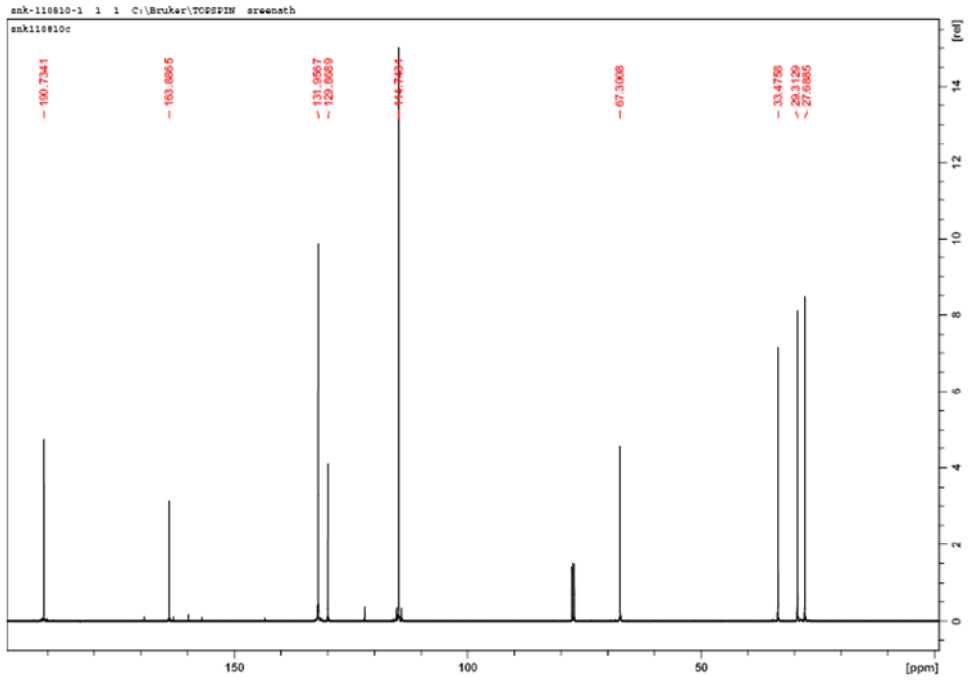
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3**



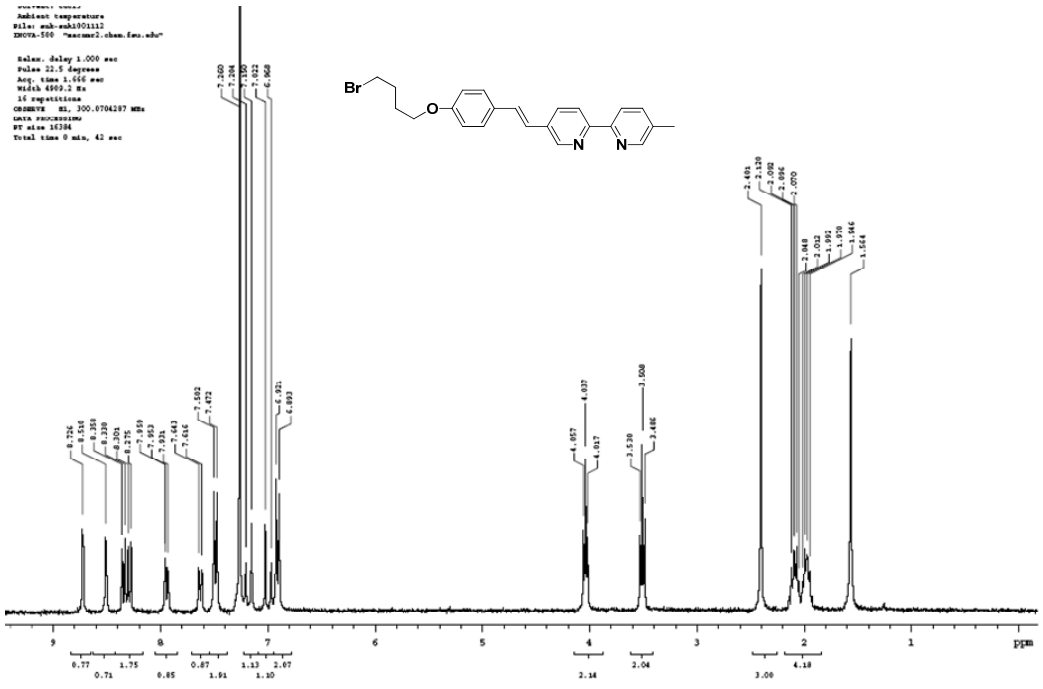
^{1}H NMR (300 MHz, $CDCl_3$) of compound **8**



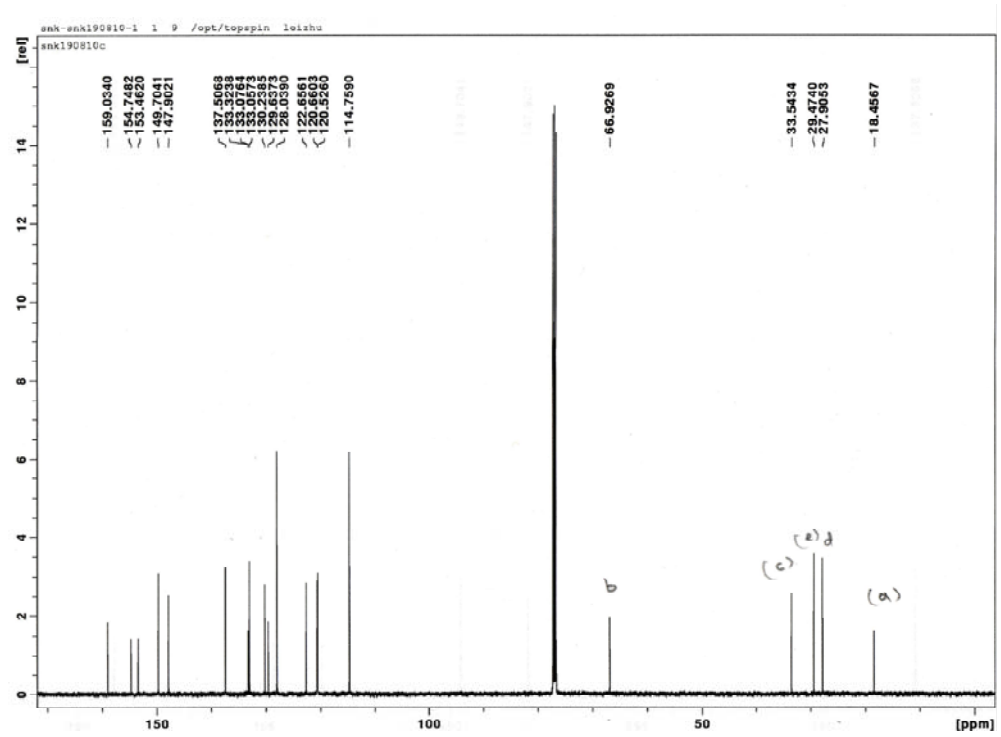
^{13}C NMR (125 MHz, $CDCl_3$) of compound **8**



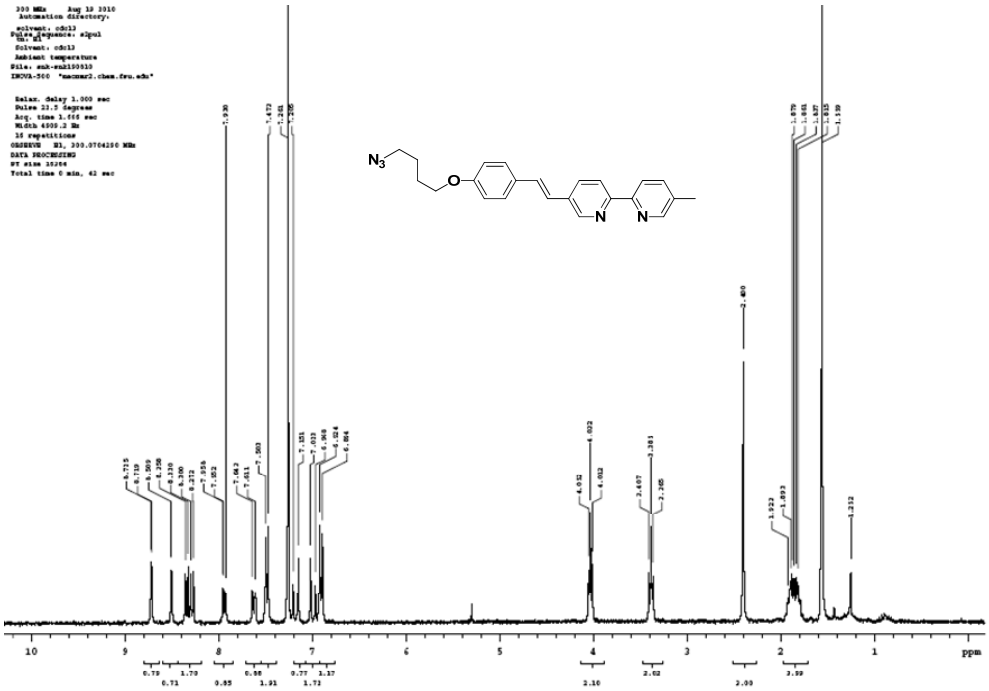
^{1}H NMR (300 MHz, $CDCl_3$) of compound **10**



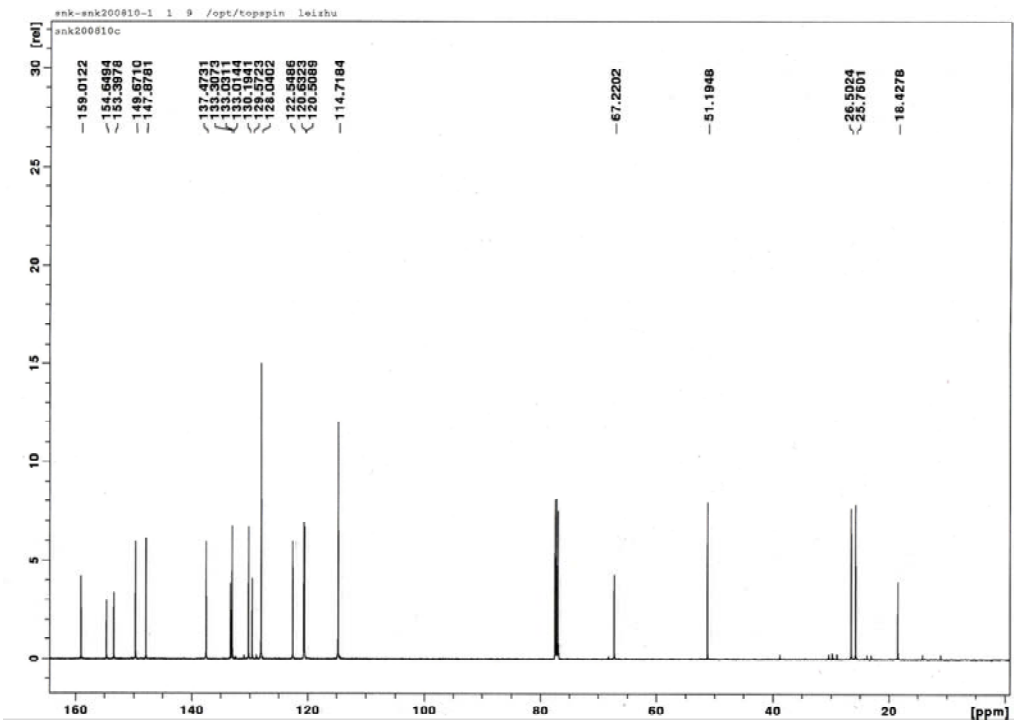
^{13}C NMR (125 MHz, $CDCl_3$) of compound **10**



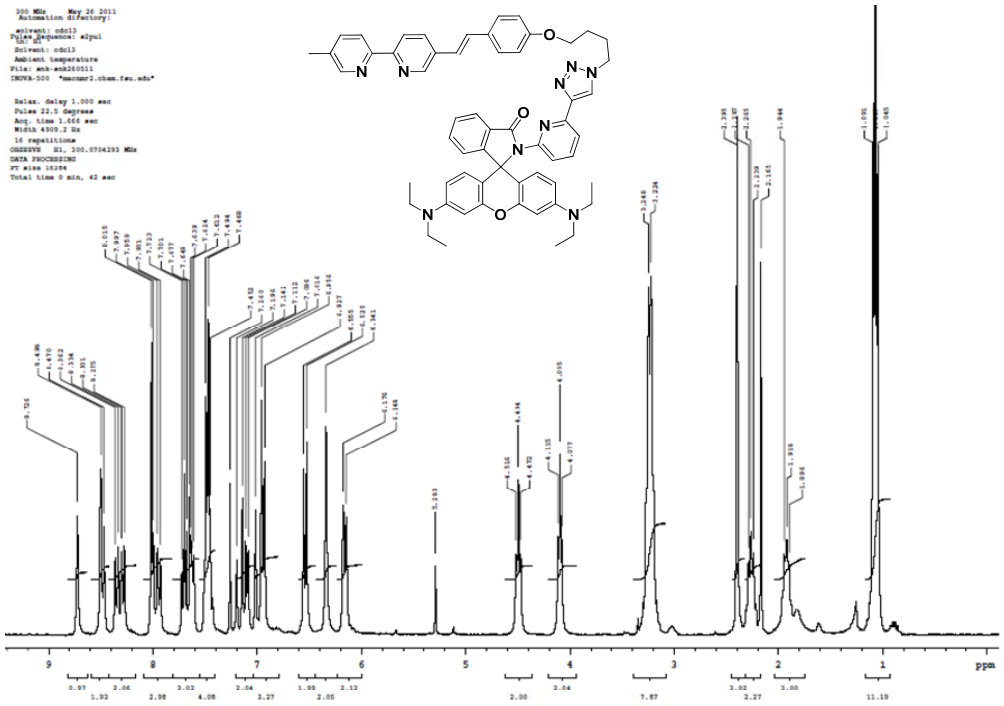
^{1}H NMR (300 MHz, $CDCl_3$) of compound **11**



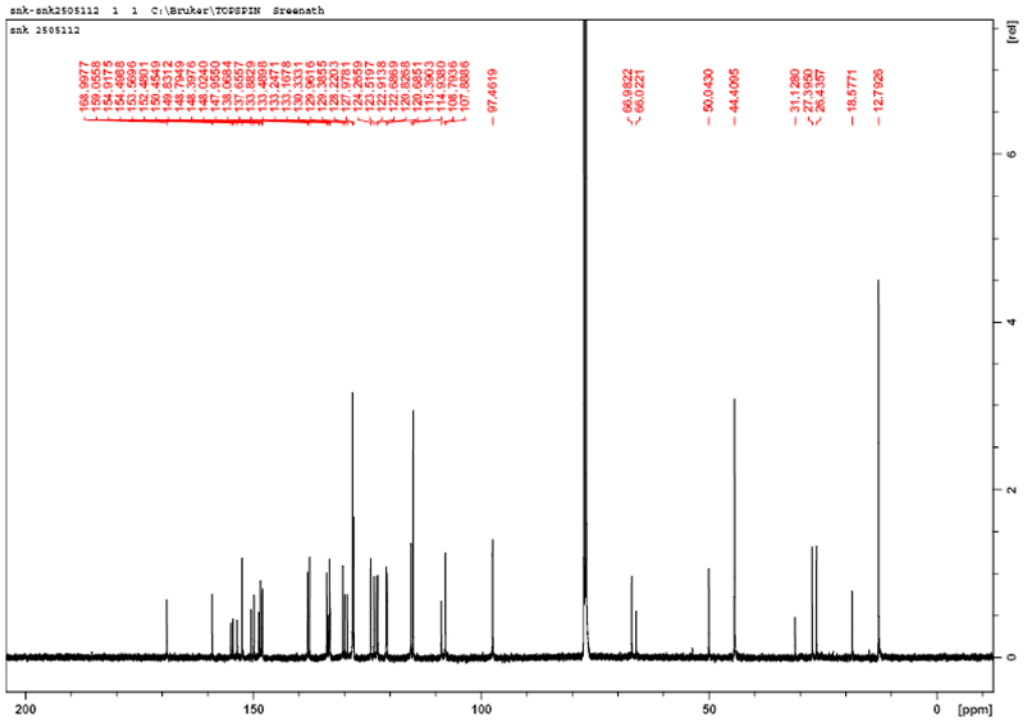
^{13}C NMR (125 MHz, $CDCl_3$) of compound **11**



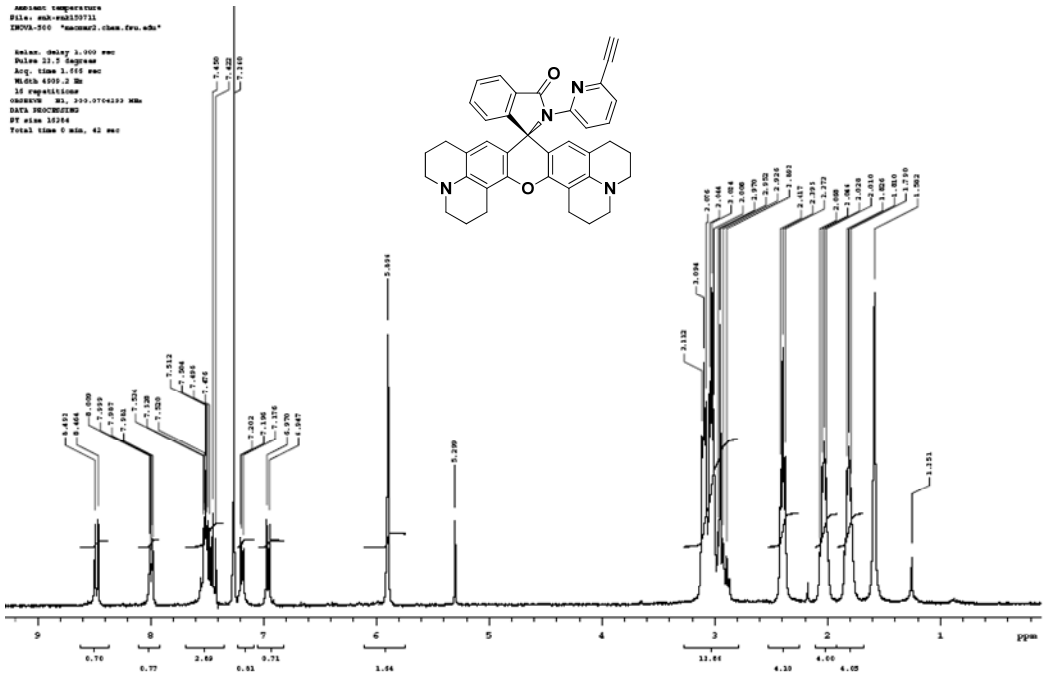
^{1}H NMR (300 MHz, $CDCl_3$) of compound **4**



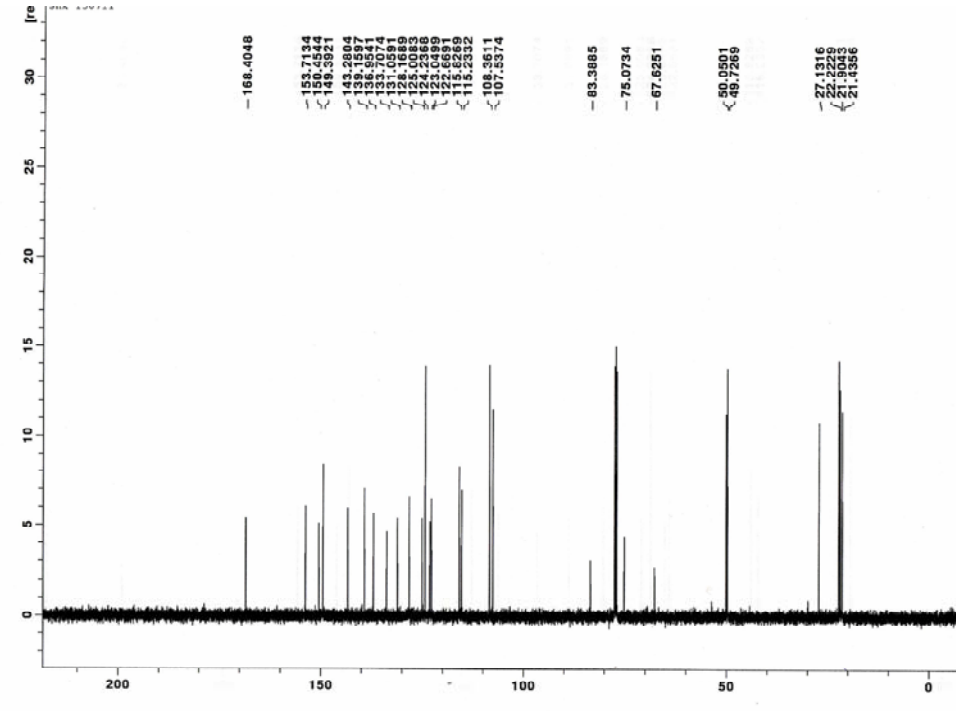
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4**



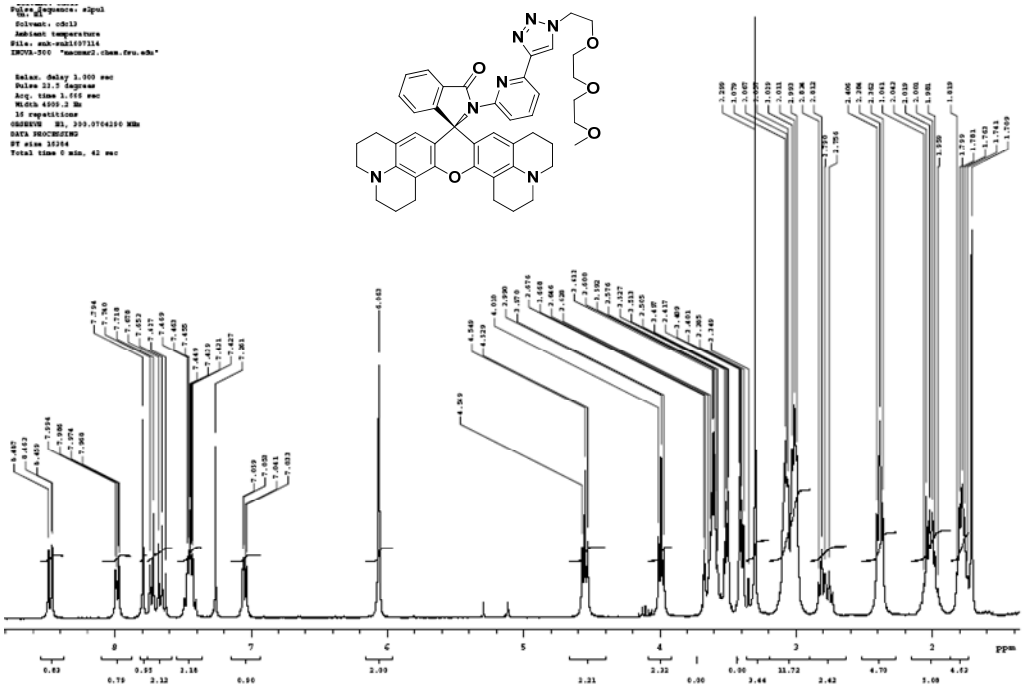
^{1}H NMR (300 MHz, $CDCl_3$) of compound **12**



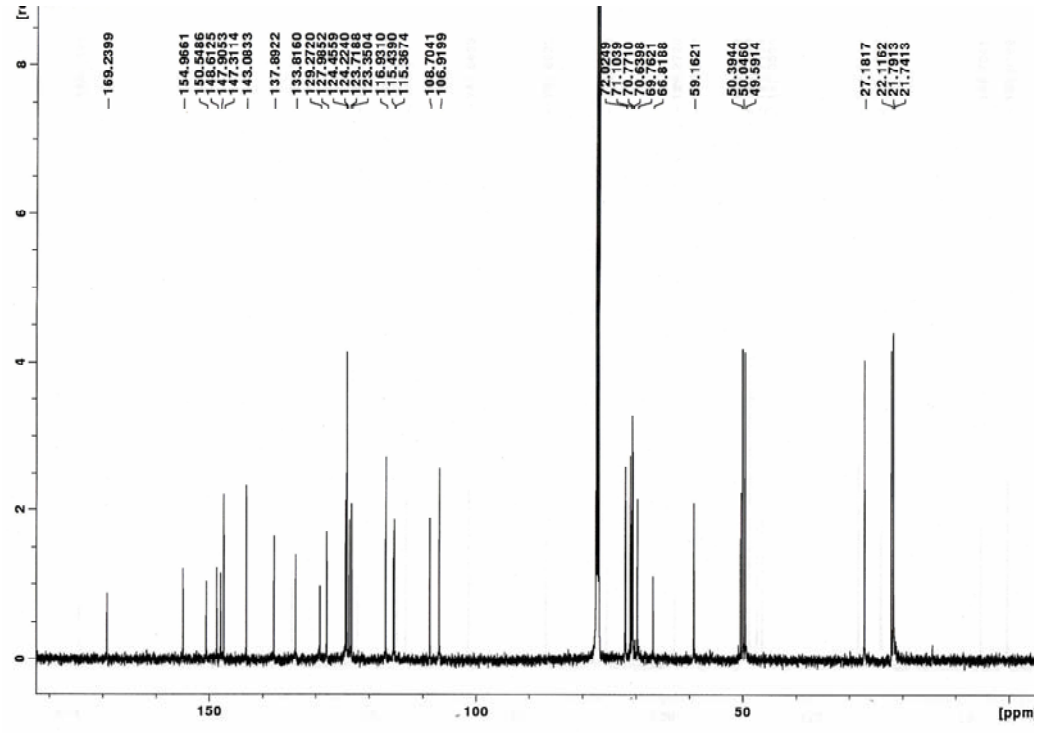
^{13}C NMR (125 MHz, $CDCl_3$) of compound **12**



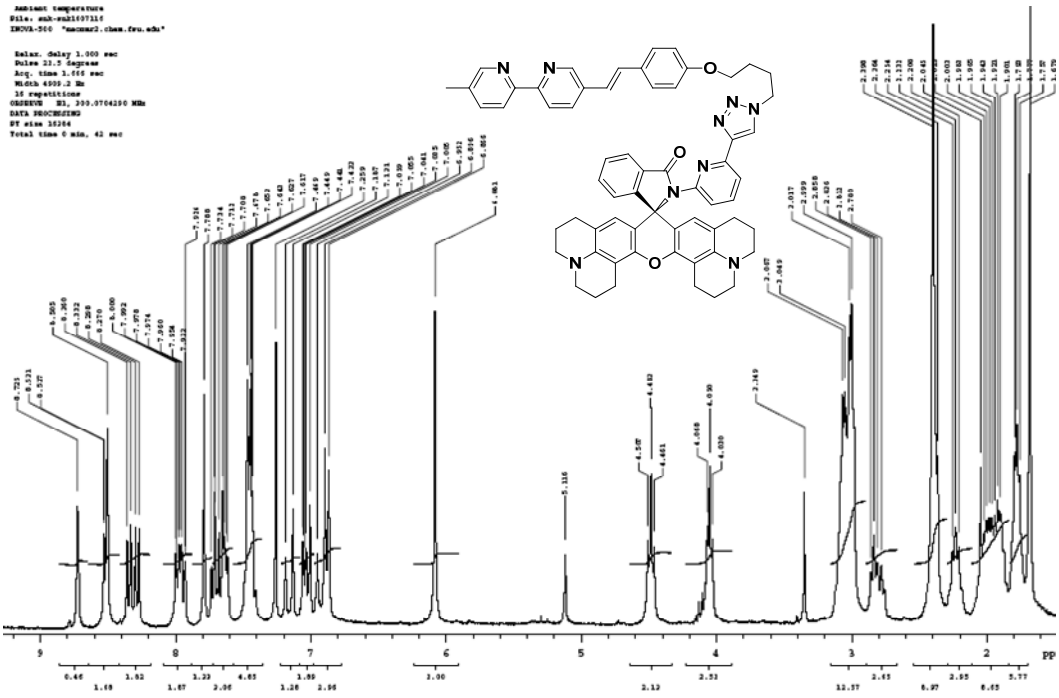
^{1}H NMR (300 MHz, $CDCl_3$) of compound **5**



^{13}C NMR (125 MHz, $CDCl_3$) of compound **5**



^{1}H NMR (300 MHz, $CDCl_3$) of compound **6**



^{13}C NMR (125 MHz, $CDCl_3$) of compound **6**