Enhancing the Photostability of Arylvinylbipyridyl Compounds as Fluorescent Indicators for Intracellular Zinc(II) Ions

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Supporting Information

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(a) Excitation spectra of compound **2** in different solvents at different emission wavelengths

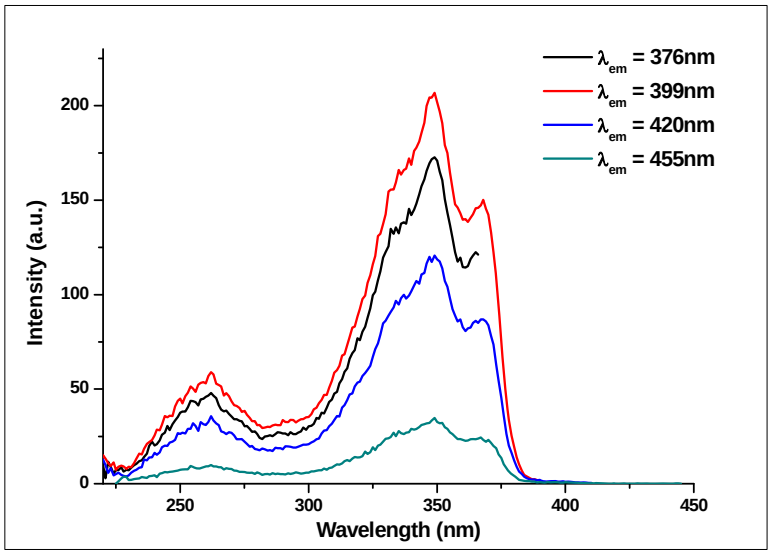

Figure S1. Excitation spectra of compound **2** (2.2 μM, λ_{em} = 376, 399, 420 and 455 nm) in hexanes.

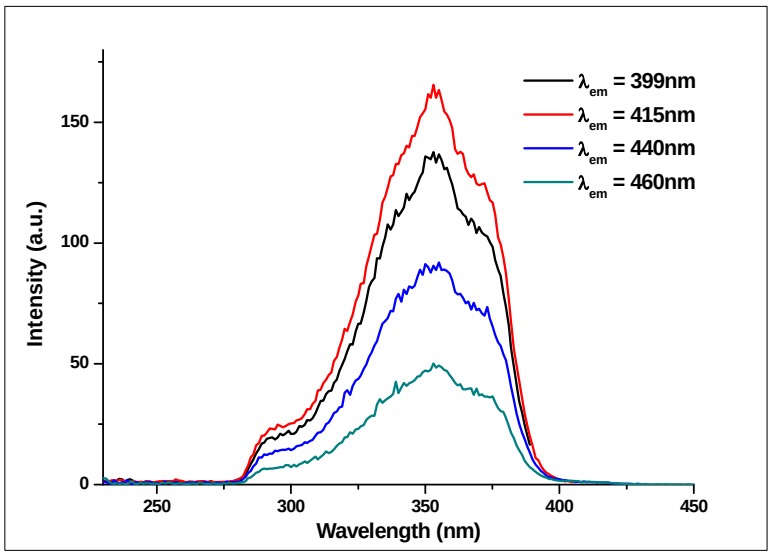

Figure S2. Excitation spectra of compound **2** (2.2 μM, λ_{em} = 399, 415, 440 and 460 nm) in toluene.

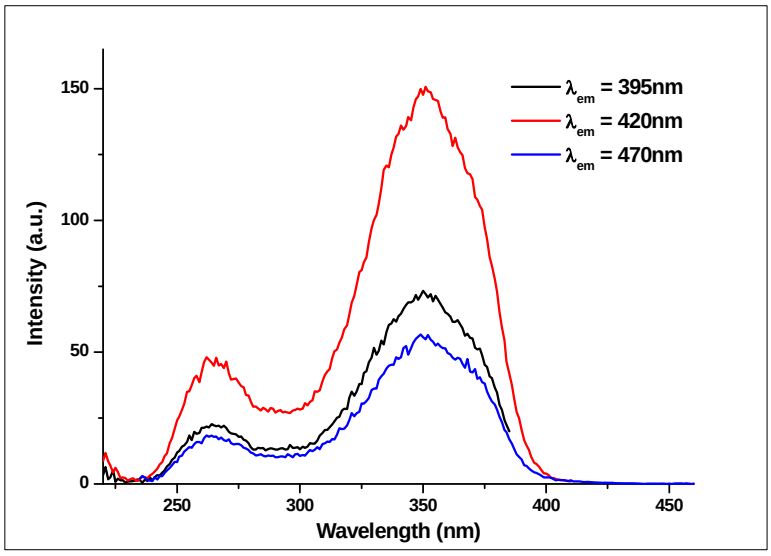

Figure S3. Excitation spectra of compound **2** (2.2 μM, λ_{em} = 395, 420 and 470 nm) in chloroform.

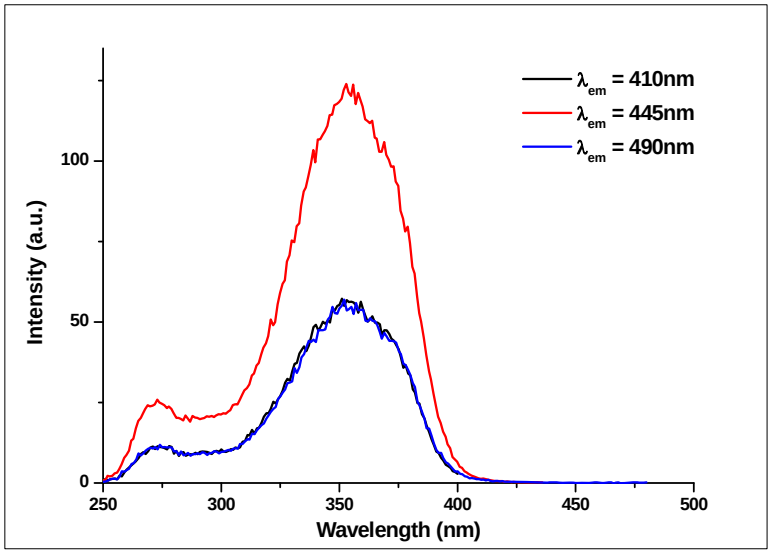

Figure S4. Excitation spectra of compound **2** (2.2 μM, λ_{em} = 410, 445 and 490 nm) in DMSO.

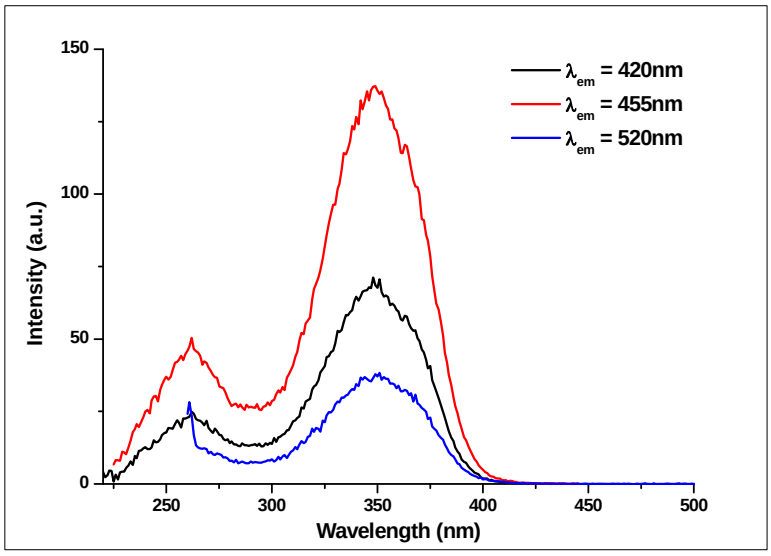

Figure S5. Excitation spectra of compound **2** (2.2 μM, λ_{em} = 420, 455 and 520 nm) in methanol.

(b) Absorption and Emission spectra of **L** and **ZnL** in CH_3CN (L = **2** or **4**)

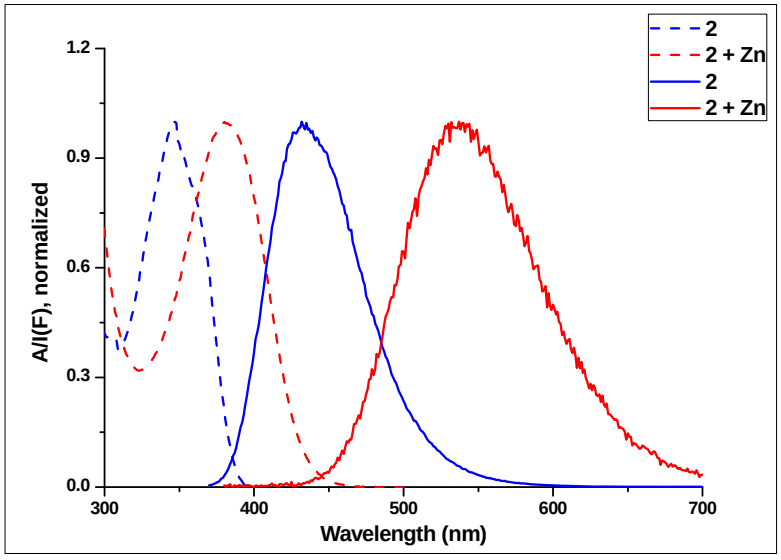

Figure S6. Normalized absorption and emission spectra of compound **2** (4.4 µM, λ_{ex} = 360 nm) in the absence or presence of $Zn(ClO_4)_2$ (50 µM) in acetonitrile.

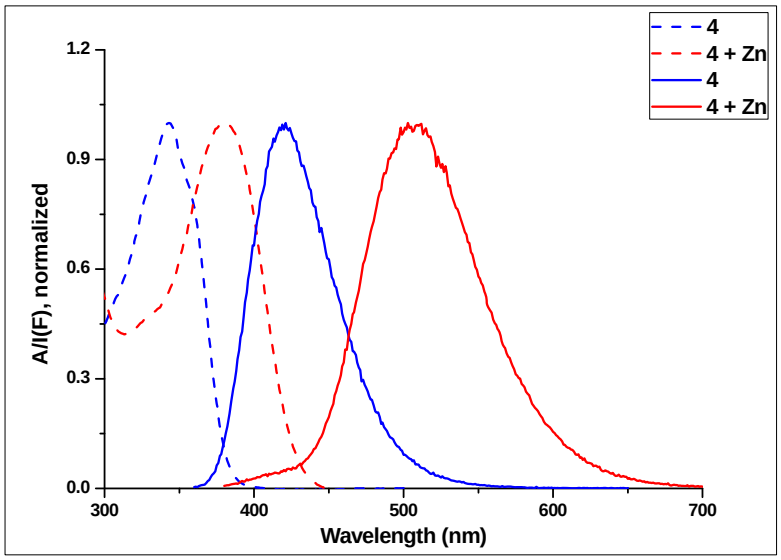

Figure S7. Normalized absorption and emission spectra of compound **4** (5.0 μM, λ_{ex} = 364 nm) in the absence or presence of $Zn(ClO_4)_2$ (50 μM) in acetonitrile.

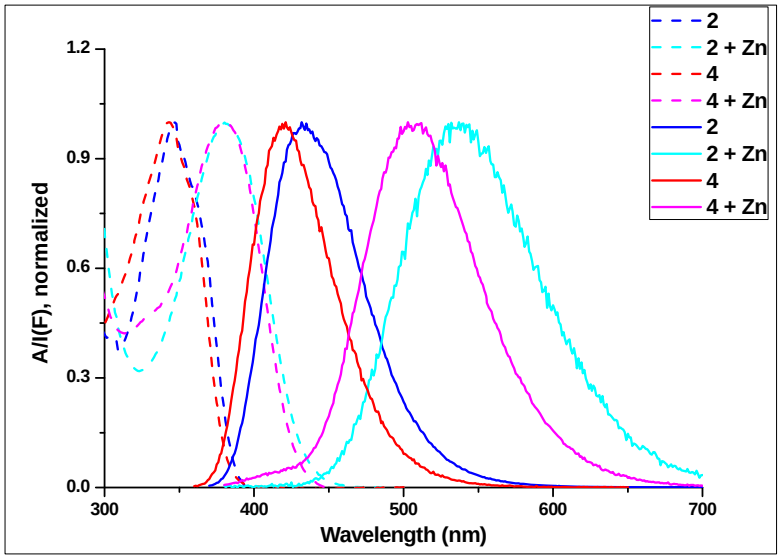

Figure S8. Combined normalized absorption and emission spectra of compound **2** and **4** as well as their Zinc complexes in acetonitrile.

(c) Zn(II) titration data of compounds **1**, **3**, and **4** in neutral aqueous solutions

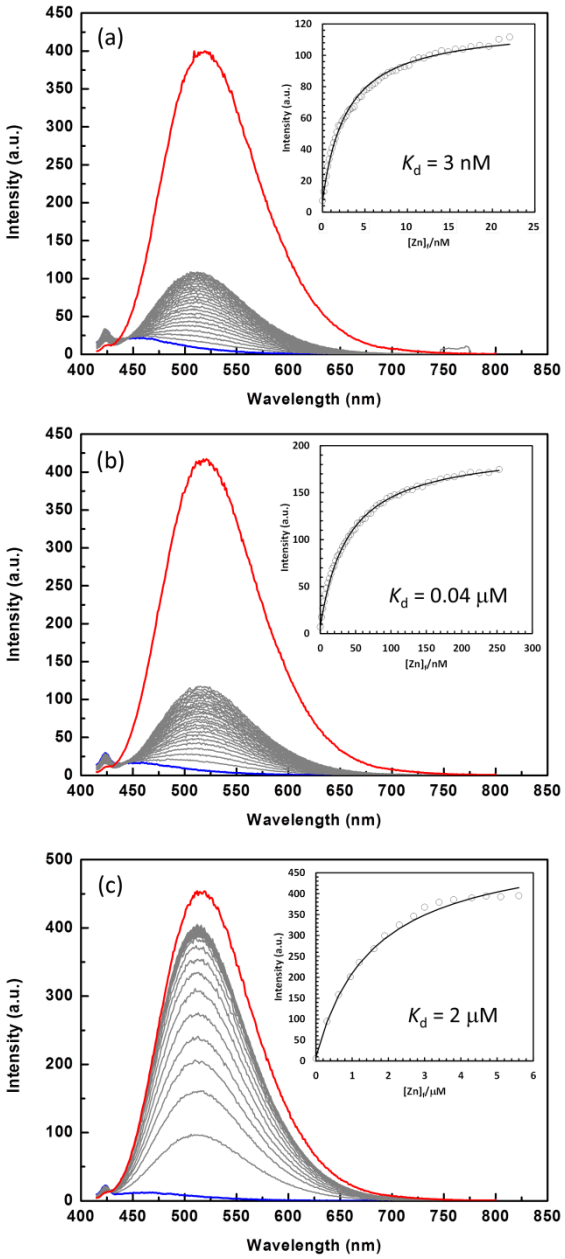

Figure S9. Fluorescence spectra of **1** (2.5 μM, λ_{ex} = 405 nm) in the presence of $Zn(ClO_4)_2$ (0-2 mM) in an aqueous solution ([HEPES] = 100 mM, [metal buffer] = 1 mM, [KNO_3] = 100 mM, pH 7.4). Metal buffer = NTA (a); ADA (b); and citrate (c). The initial zinc(II)-free and the final zinc(II)-saturated spectra of each titration experiment are coded blue and red, respectively. Insets: fluorescence intensity at indicated emission wavelength vs free zinc(II) concentration $[Zn]_f$. The solid lines are fitting curves using a 1:1 binding model.

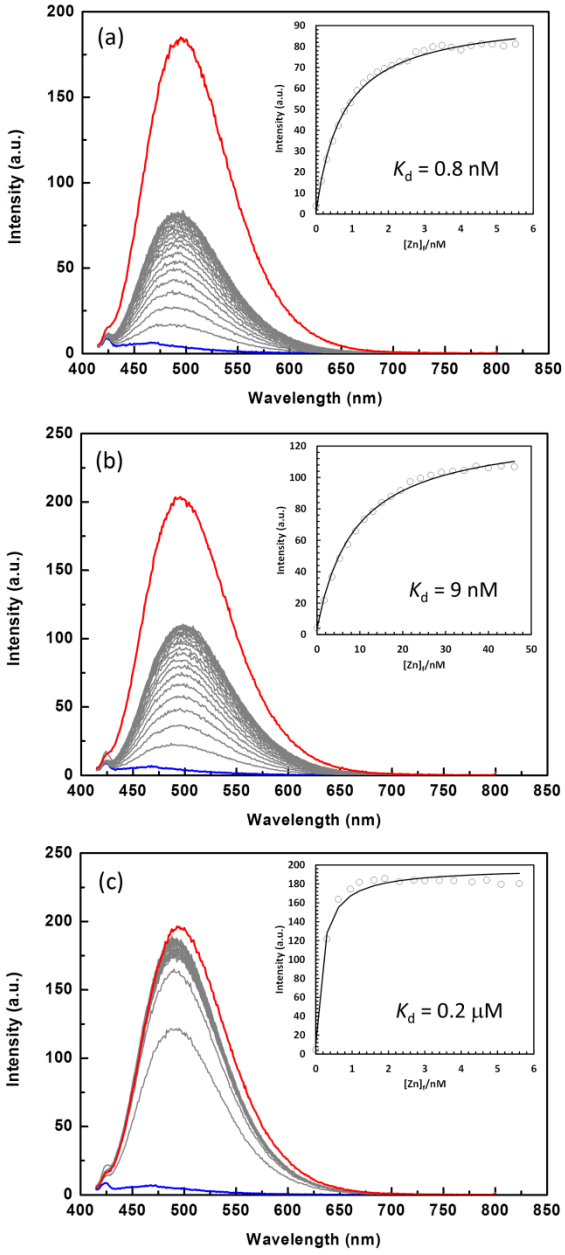

Figure S10. Fluorescence spectra of **3** (2.5 μM, λ_{ex} = 405 nm) in the presence of $Zn(ClO_4)_2$ (0-2 mM) in an aqueous solution ([HEPES] = 100 mM, [metal buffer] = 1 mM, [KNO_3] = 100 mM, pH 7.4). Metal buffer = NTA (a); ADA (b); and citrate (c). The initial zinc(II)-free and the final zinc(II)-saturated spectra of each titration experiment are coded blue and red, respectively. Insets: fluorescence intensity at indicated emission wavelength vs free zinc(II) concentration $[Zn]_f$. The solid lines are fitting curves using a 1:1 binding model.

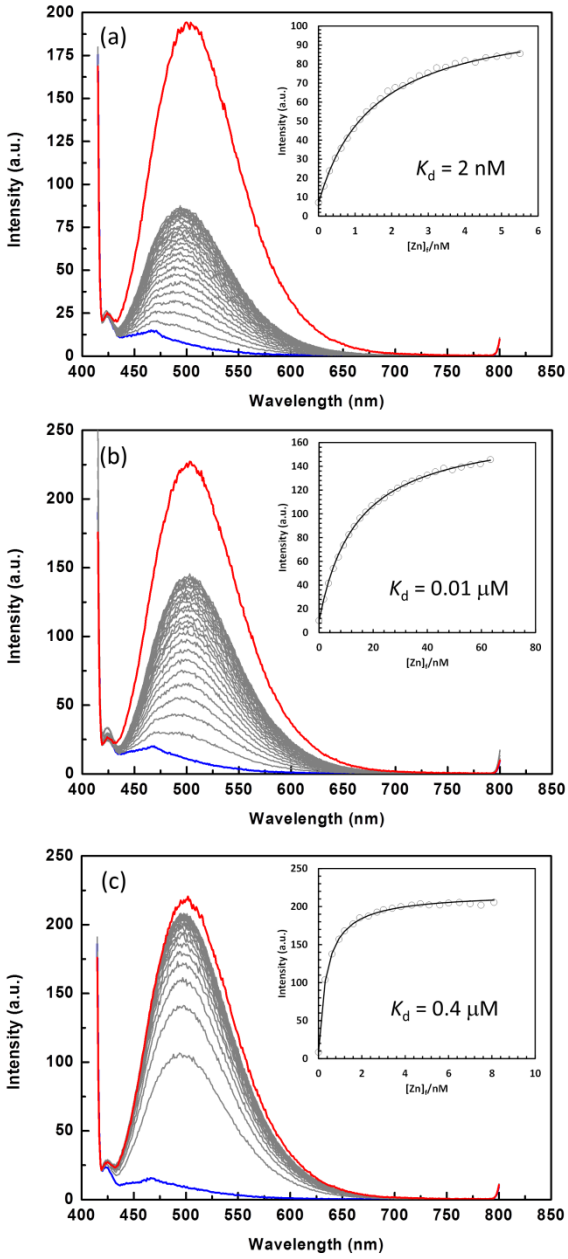

Figure S11. Fluorescence spectra of **4** (2.5 μM, λ_{ex} = 405 nm) in the presence of $Zn(ClO_4)_2$ (0-2 mM) in an aqueous solution ([HEPES] = 100 mM, [metal buffer] = 1 mM, [KNO_3] = 100 mM, pH 7.4). Metal buffer = NTA (a); ADA (b); and citrate (c). The initial zinc(II)-free and the final zinc(II)-saturated spectra of each titration experiment are coded blue and red, respectively. Insets: fluorescence intensity at indicated emission wavelength vs free zinc(II) concentration $[Zn]_f$. The solid lines are fitting curves using a 1:1 binding model.

(d) Metal ion selectivity of **2** and **4** in neutral aqueous solutions

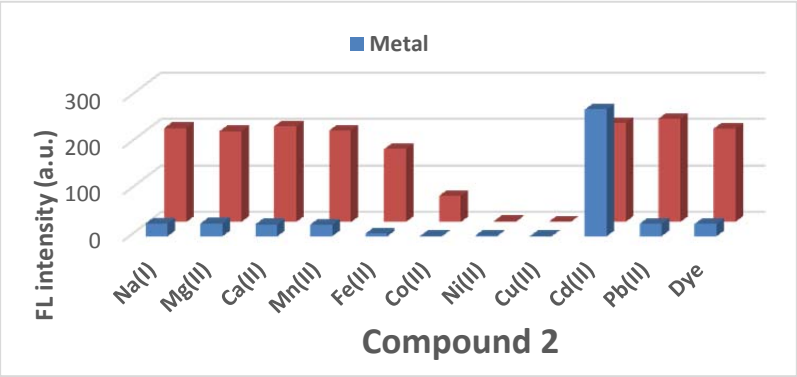

Figure S12. Fluorescence spectroscopic responses of compound **2** (5 µM, λ_{ex} = 405 nm) to various metal ions in HEPES buffer solution at pH 7.4 (HEPES 100 mM, KCl 100 mM). Blue bars represent the fluorescence intensity at 524 nm in the presence of various metal ions (chloride salts). Metal ion concentrations of Na(I), Ca(II), Mg(II) were 1 mM, and for other ions 100 µM. Orange bars represent the intensity at 524 nm following the addition of $ZnCl_2$ (100 µM).

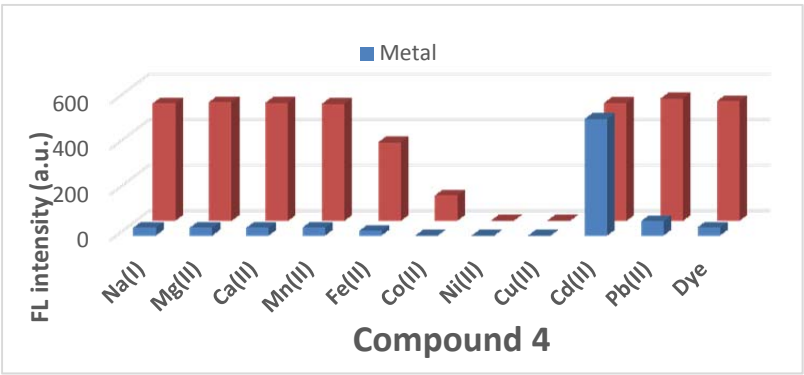

Figure S13. Fluorescence spectroscopic responses of compound **4** (5 µM, λ_{ex} = 405 nm) to various metal ions in HEPES buffer solution at pH 7.4 (HEPES 100 mM, KCl 100 mM). Blue bars represent the fluorescence intensity at 495 nm in the presence of various metal ions (chloride salts). Metal ion concentrations of Na(I), Ca(II), Mg(II) were 1 mM, and for other ions 100 µM. Orange bars represent the intensity at 495 nm following the addition of $ZnCl_2$ (100 µM).

(e) ^{1}H and ^{13}C NMR Spectra

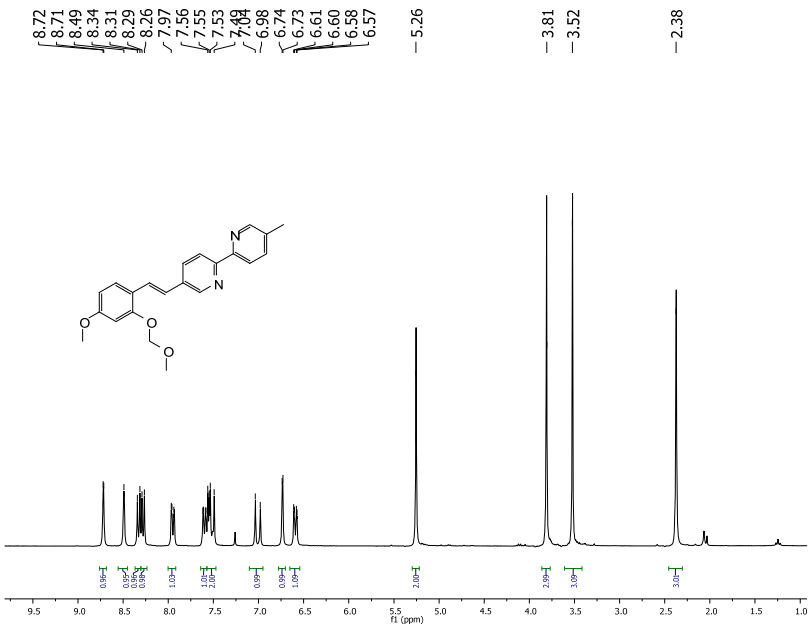

Figure S14. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound **7**.

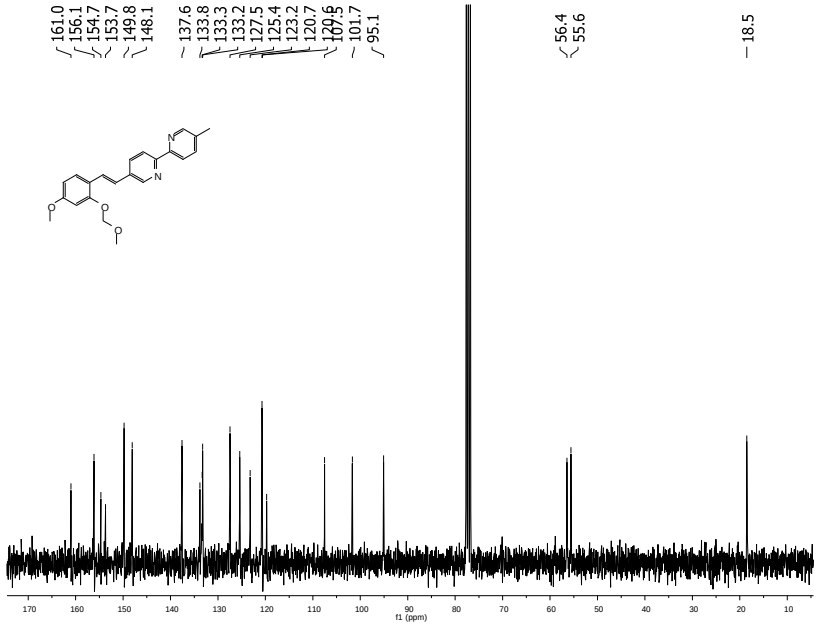

Figure S15. ^{13}C NMR (75 MHz, $CDCl_3$) of Compound **7**.

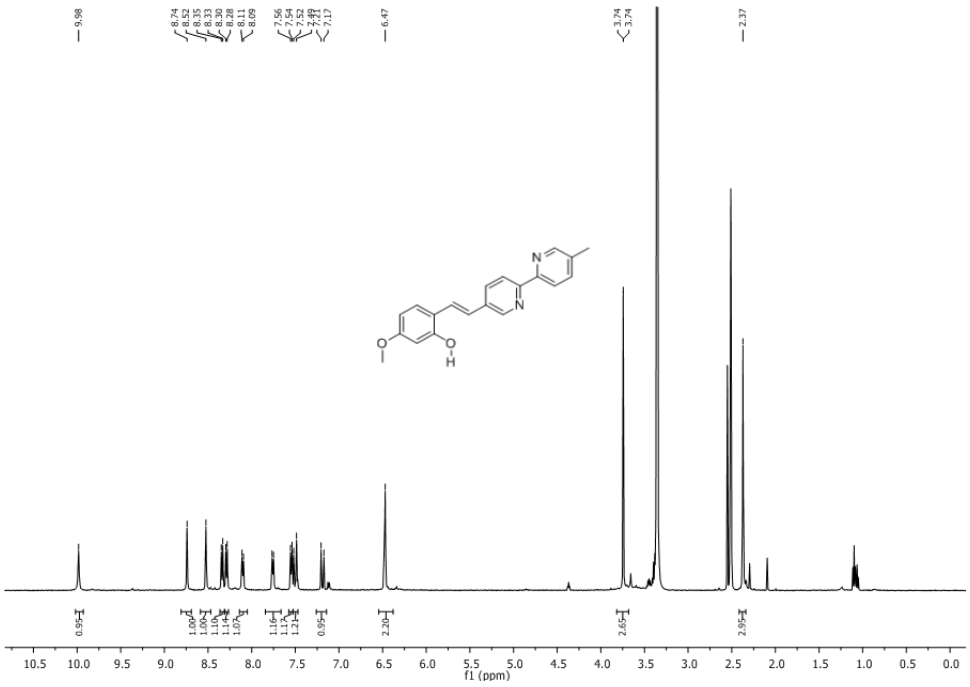

Figure S16. ^{1}H NMR (500 MHz, DMSO-d_6) of Compound **8**.

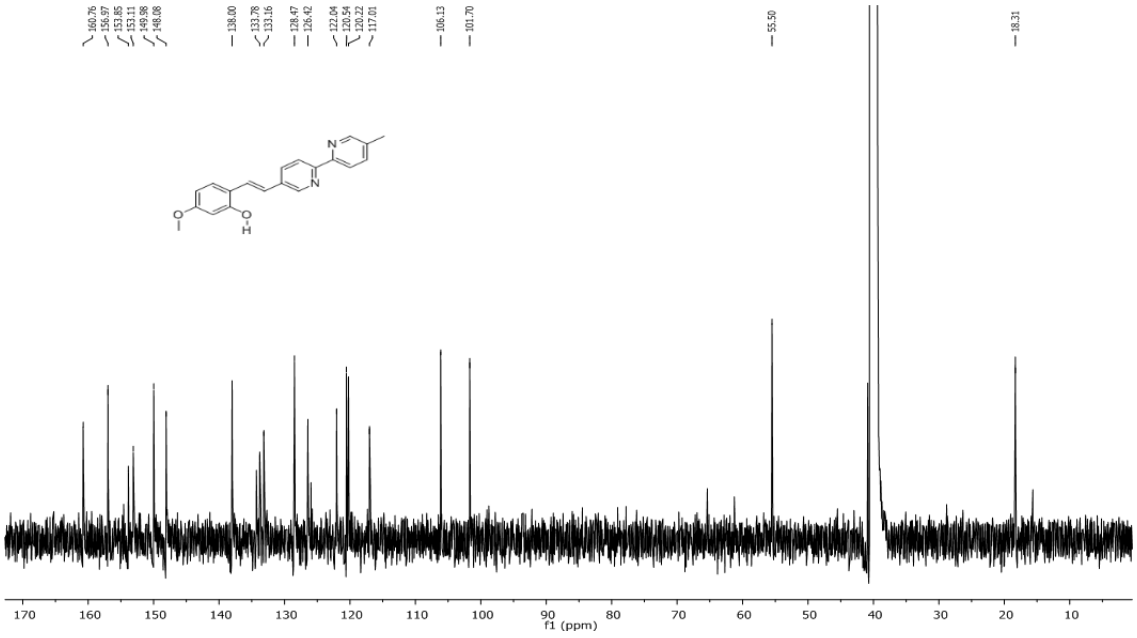

Figure S17. ^{13}C NMR (125 MHz, DMSO-d_6) of Compound **8**.

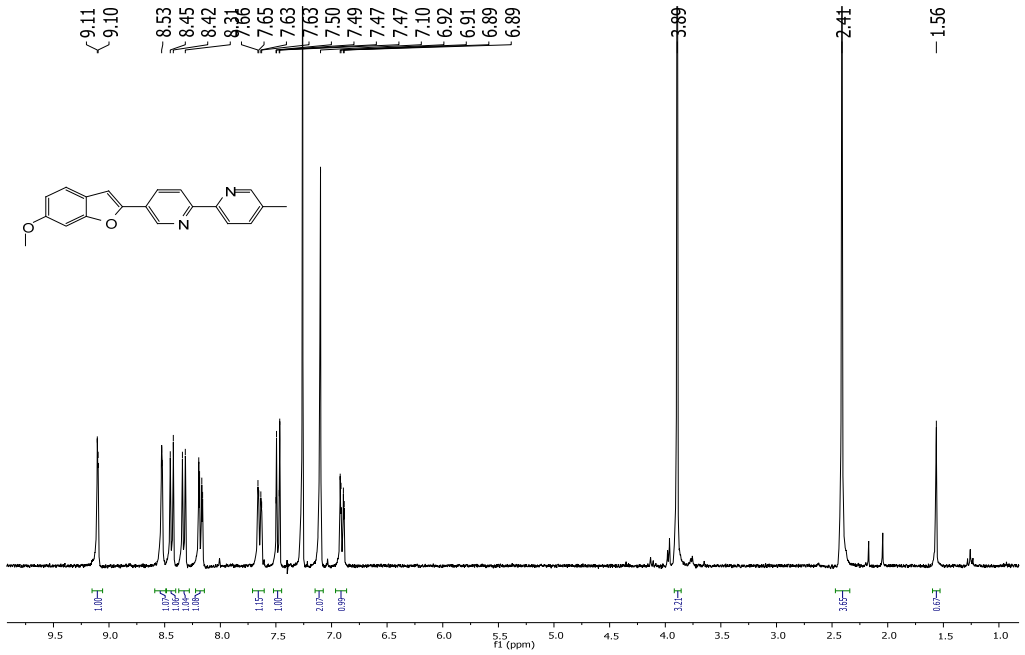

Figure S18. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound **2**.

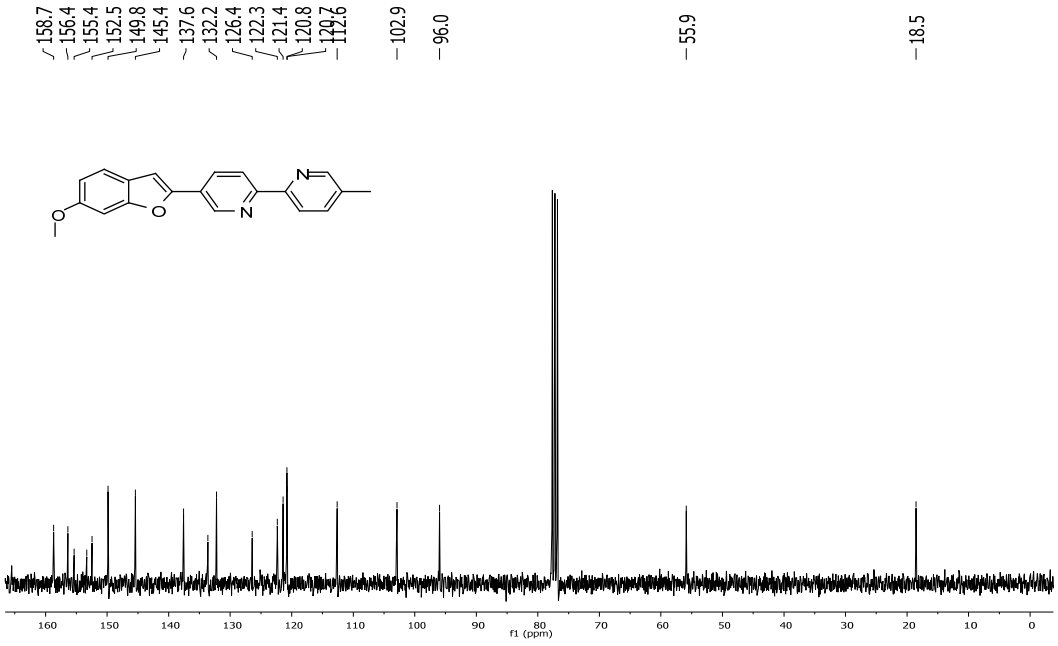

Figure S19. ^{13}C NMR (75 MHz, $CDCl_3$) of Compound **2**.

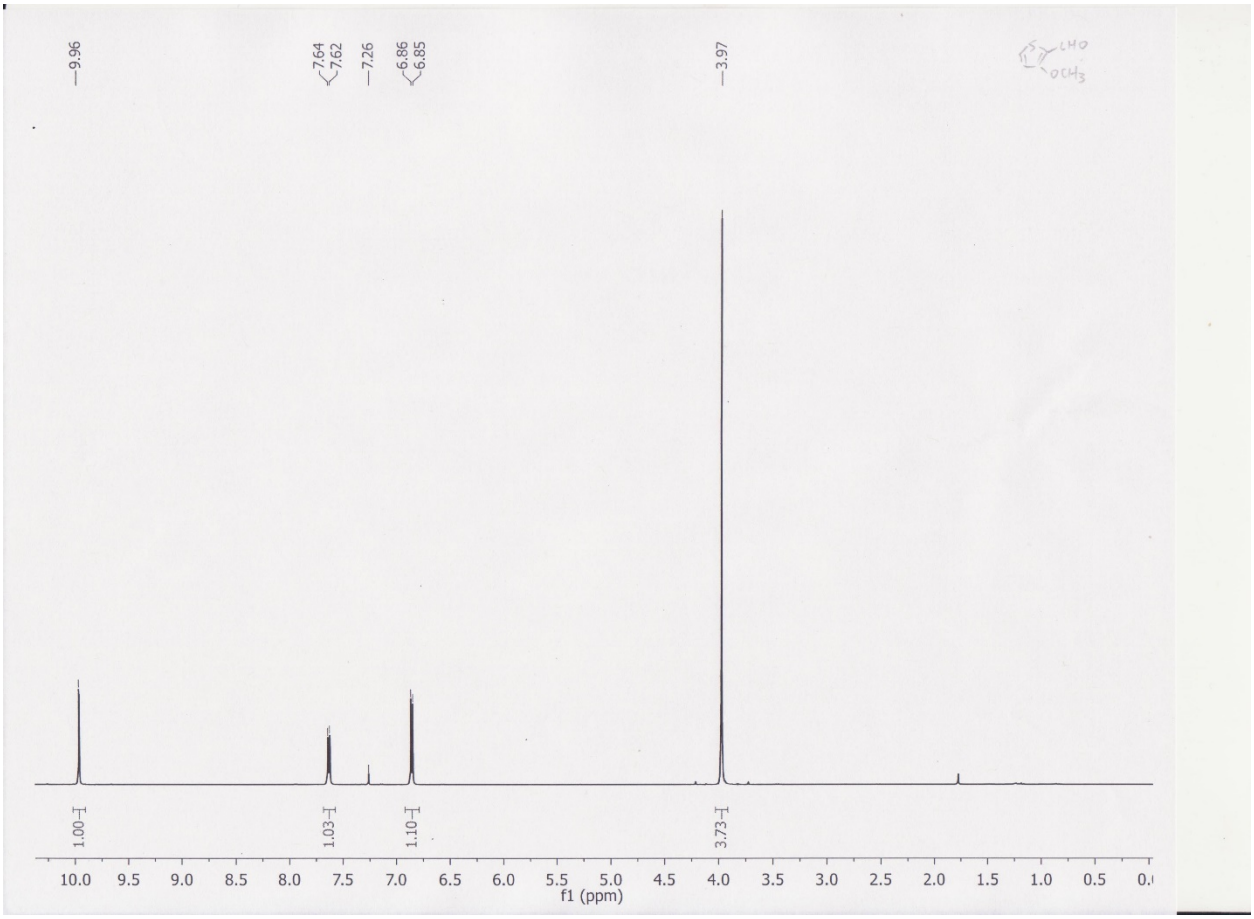

Figure S20. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound **10**.

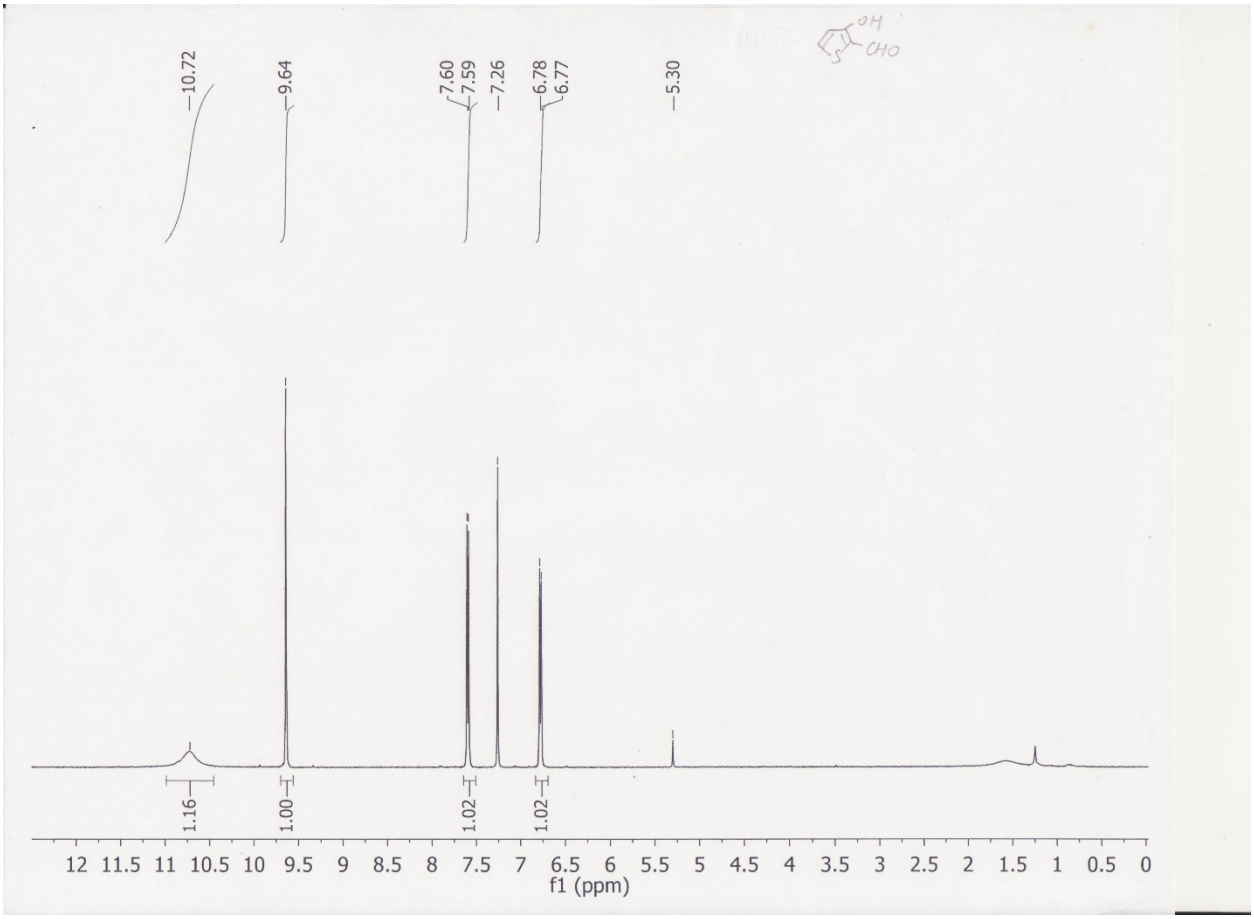

Figure S21. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound **11**.

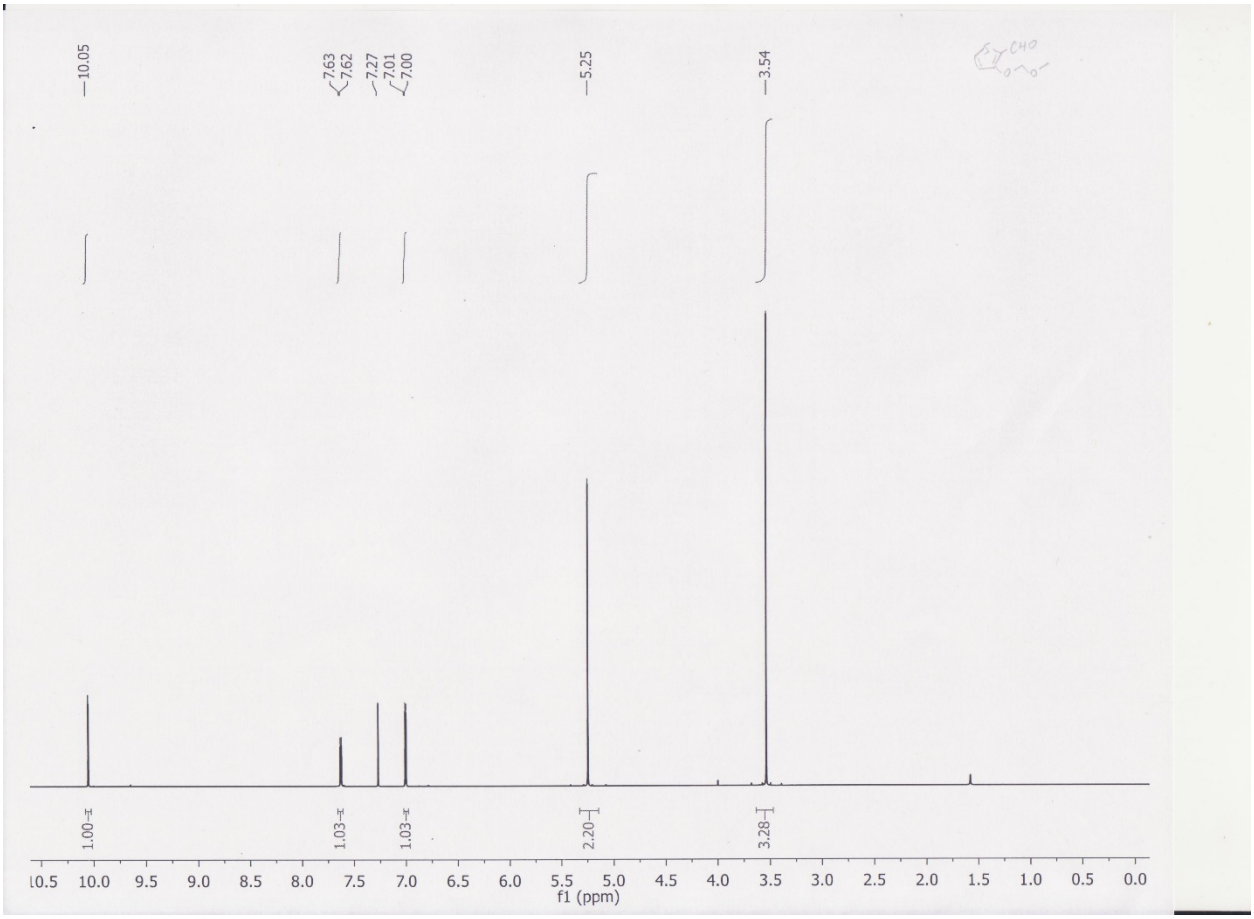

Figure S22. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **12**.

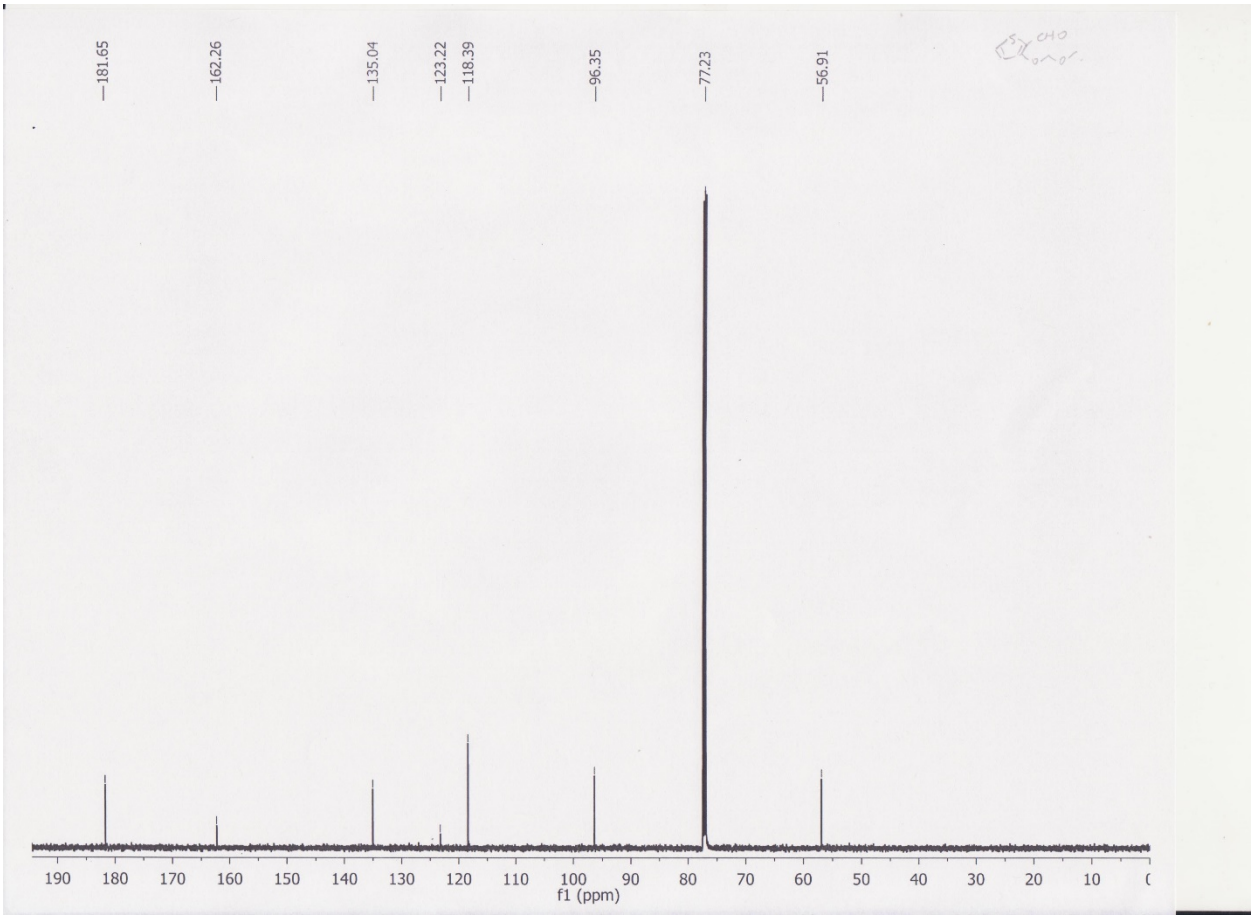

Figure S23. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **12**.

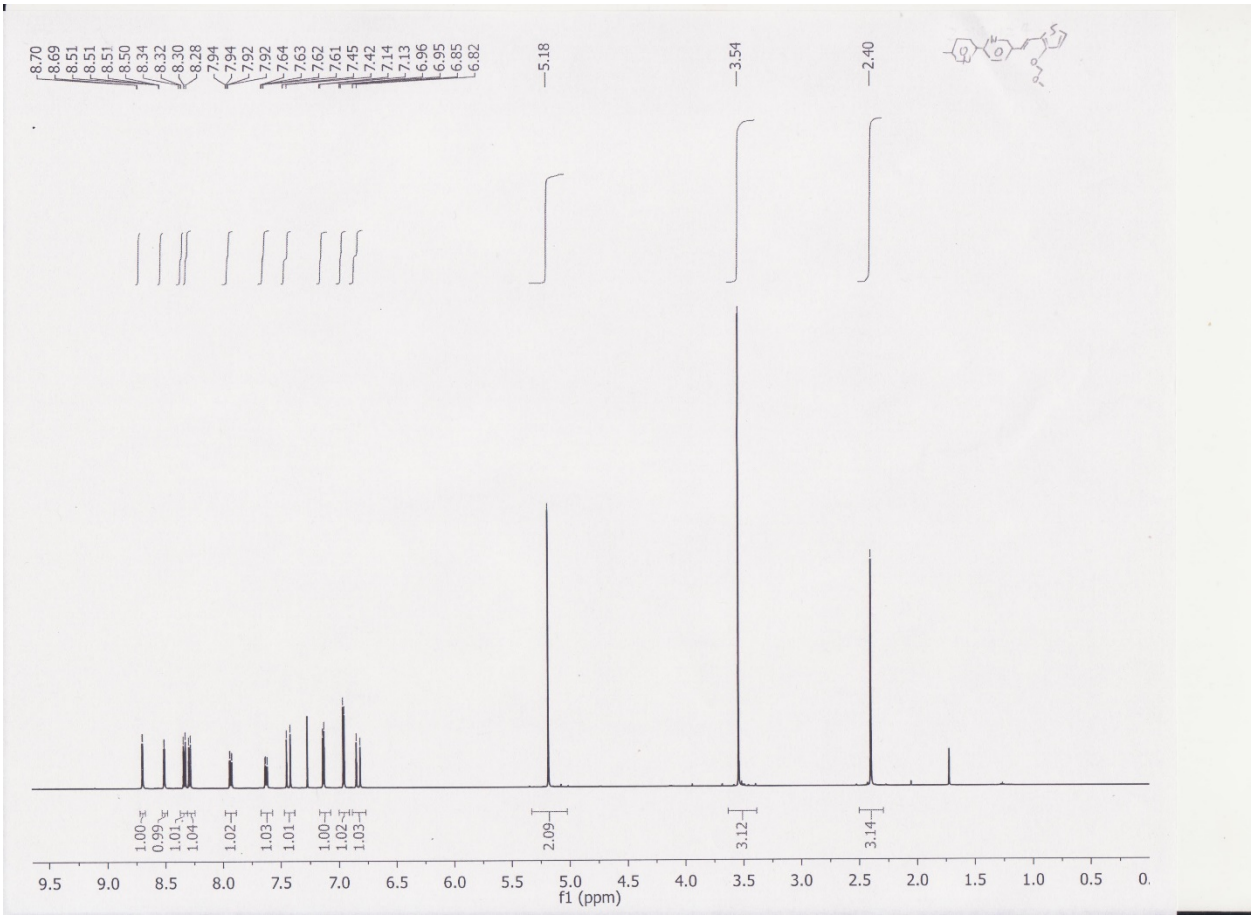

Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **13**.

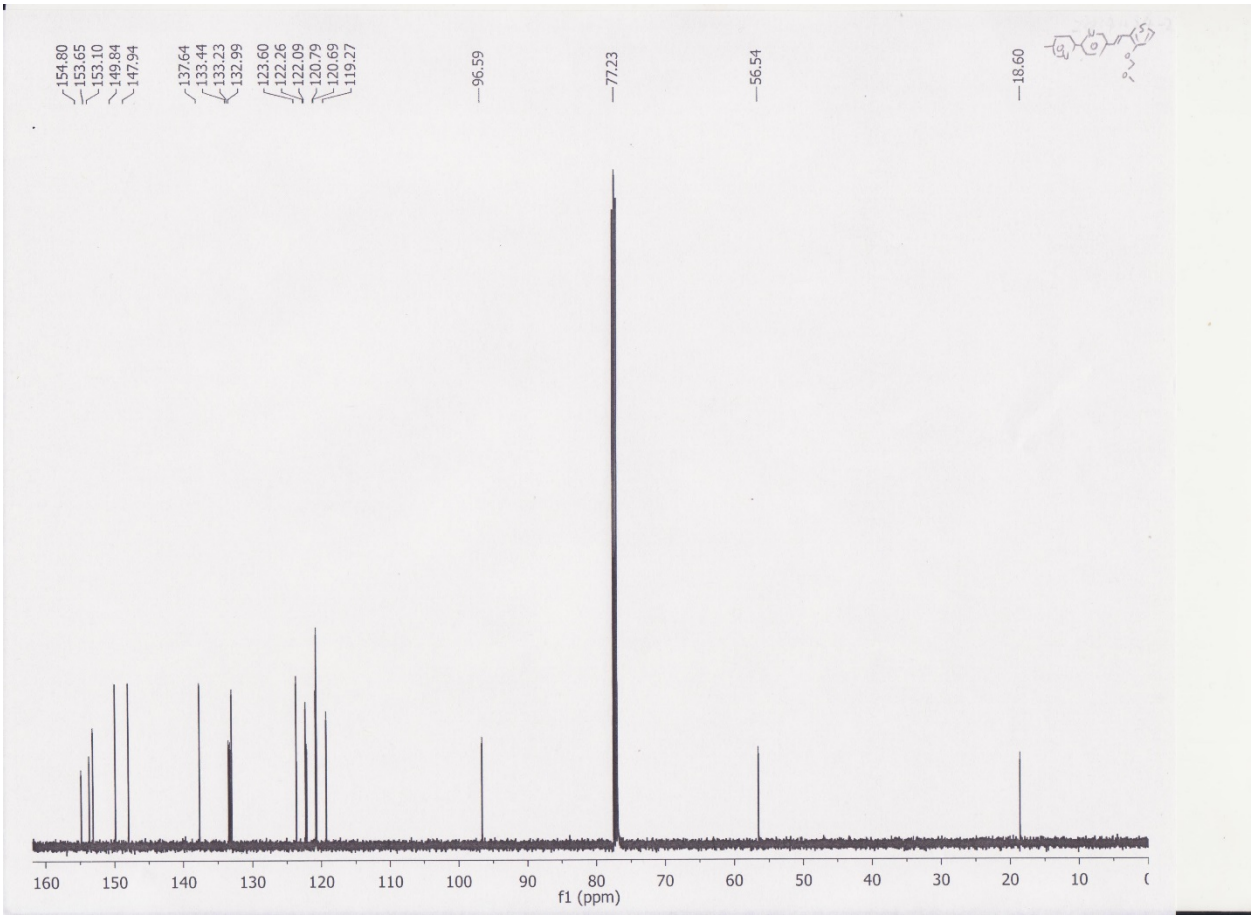

Figure S25. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **13**.

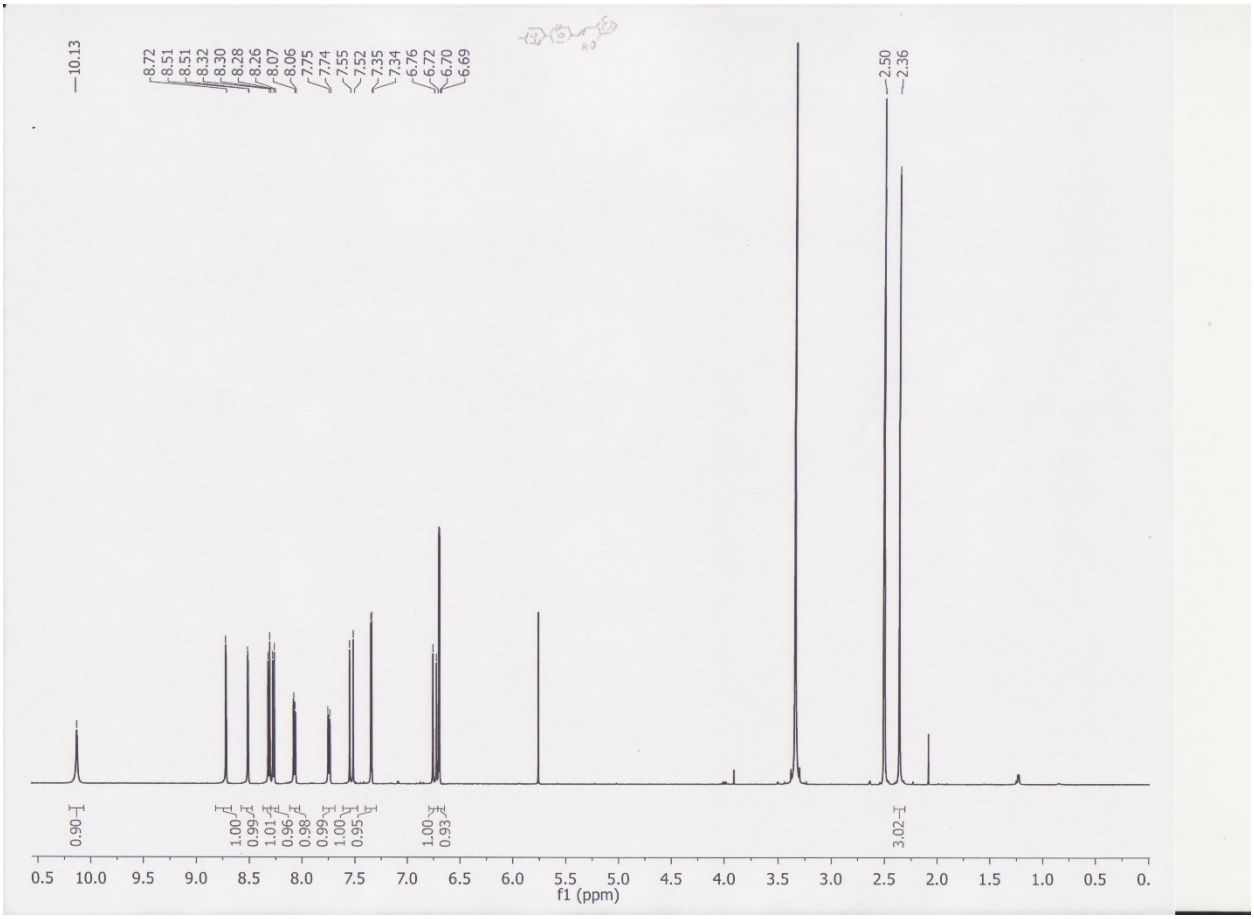

Figure S26. ^{1}H NMR (500 MHz, DMSO-d_6) of Compound **14**.

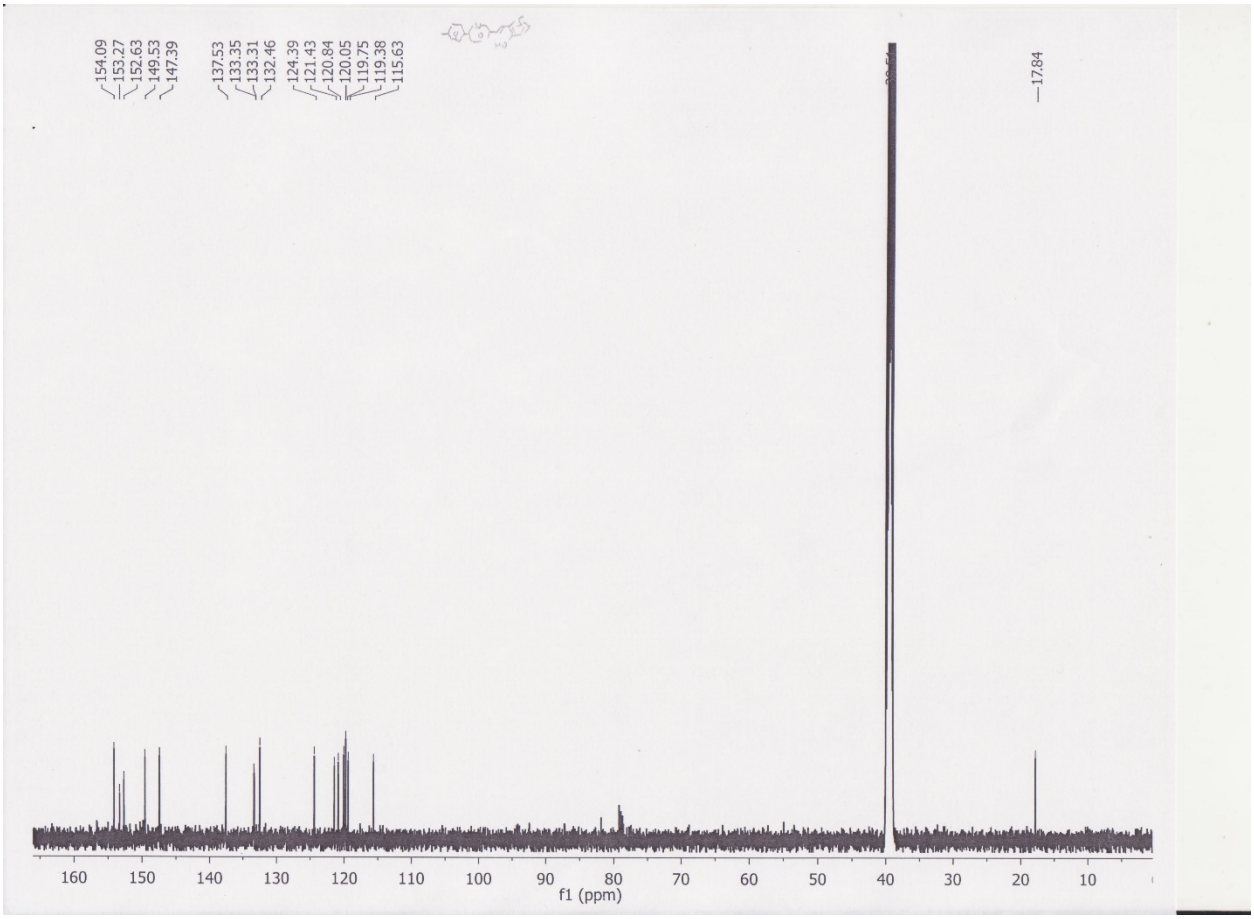

Figure S27. ^{13}C NMR (125 MHz, DMSO-d_6) of Compound **14**.

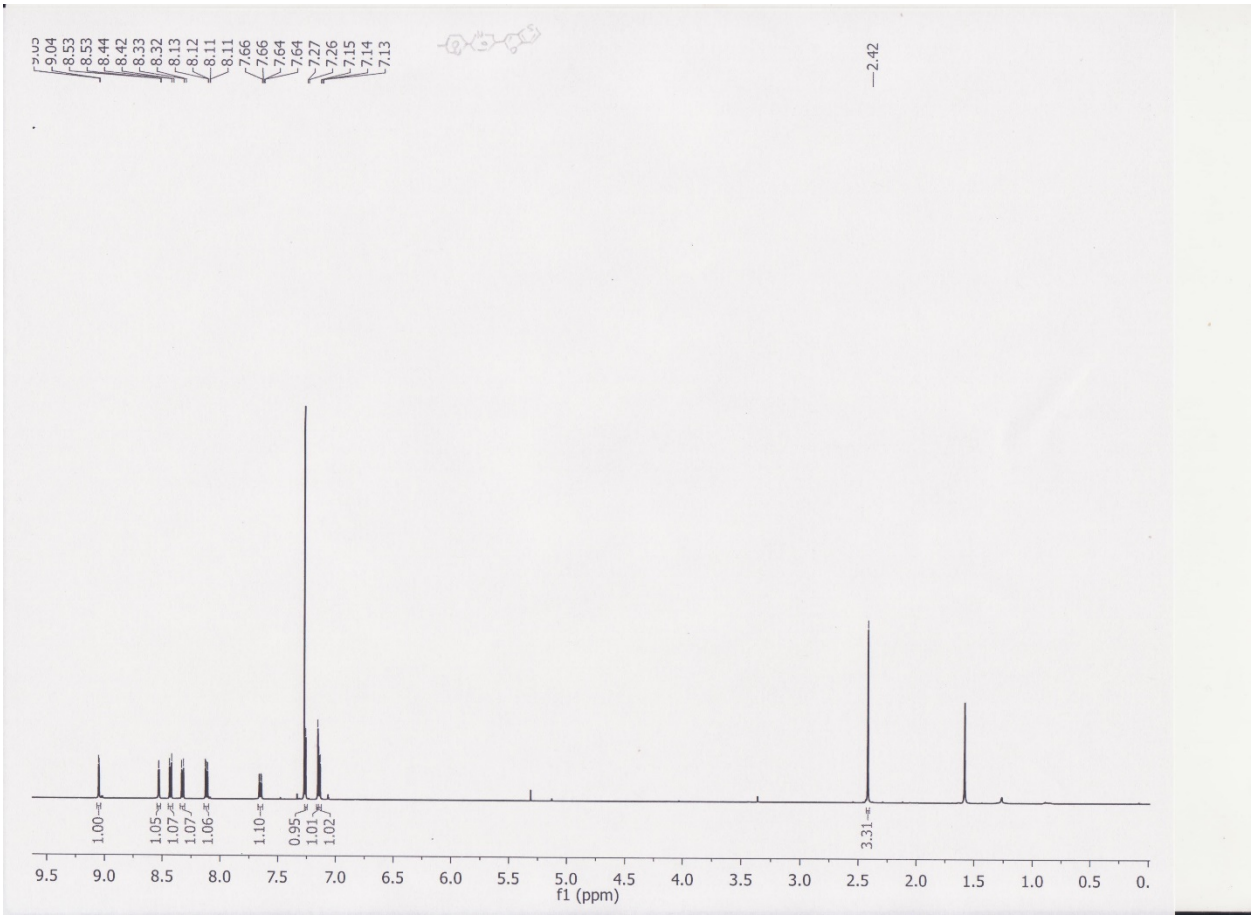

Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **4**.

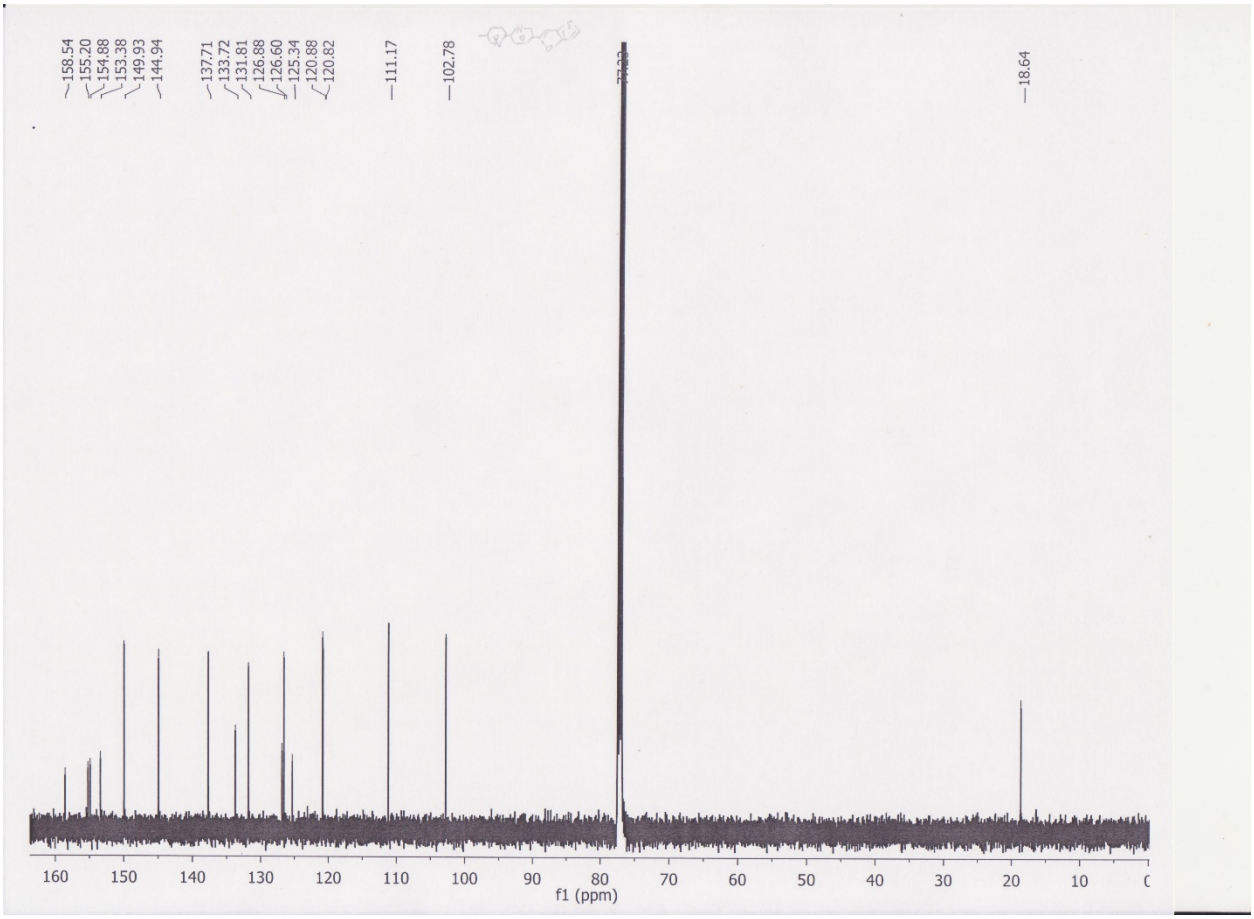

Figure S29. ^{13}C NMR (75 MHz, $CDCl_3$) of Compound **4**.