Electronic Supplementary Information

A selective fluorescent sensor for Zn^{2+} based on aggregation-induced emission (AIE) activity and metal chelating ability of bis(2-pyridyl)diphenylethylene

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Contents

Experimental:

All commercially available starting materials, reagents, and solvents were used as supplied, unless otherwise stated. Reported yields are isolated yields. Purification of all final products was accomplished by silica gel flash column chromatography. Chloroform : methanol or hexane : ethyl acetate were used as elution solvents. Proton (^{1}H) and carbon (^{13}C) NMR were collected on Bruker NMR spectrometers at 300 MHz or 400 MHz for ^{1}H and 75 MHz or 100 MHz for ^{13}C. Chemical shifts (δ) are reported in parts-per million (ppm) relative to residual undeuterated solvent. Melting points were recorded using a capillary melting point apparatus and are uncorrected. High resolution mass spectra were obtained in positive ion mode using electron spray ionization (ESI) on a double-focusing magnetic sector mass spectrometer. UV-visible spectra were obtained using quartz cuvettes on a Varian Cary 100-Scan dual-beam spectrophotometer. Each measurement was done in duplicate and compared to solvent blank. Blank samples were prepared using HPLC grade acetonitrile. Fluorescence spectra were obtained in air at room temperature using a Horiba Jobin Yvon Fluoromax-4 spectrofluorimeter using 3 mL quartz cuvettes. Samples were prepared using HPLC grade solvents. X-Ray diffraction data were collected on a Nonius Kappa CCD diffractometer equipped with Mo Kα radiation with λ = 0.71073 °A. Structures were solved by direct methods and data was refined by full-matrix least squares refinement on F^2 against all reflections.

2,2'-(2,2-Dibromoethene-1,1-diyl)dipyridine (3)

Di(2-pyridyl) ketone (368 mg, 2.00 mmol) was dissolved in chlorobenzene (50 mL). Carbon tetrabromide (1.33 g, 4.00 mmol) and PPh_3 (2.1 g, 8.00 mmol) were added and the reaction mixture was heated to reflux and maintained for 3 d. After this time the reaction mixture was allowed to cool to rt and insoluble material was removed by filtration. The filtrate was treated with 50 mL of 1 M aq. HCl. The aqueous layer was separated and basified with 1 M aq. NaOH until pH 12. The aqueous phase was extracted with CH_2Cl_2 (2×50 mL), and the combined organic fractions were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography using ethyl acetate/hexane 1:1 as eluent to yield **3** (482 mg, 71%) as off-white solid. Mp 161-163°C. ^{1}H NMR (300 MHz, C*D*Cl_3) δ 7.15-7.19 (m, 2H), 7.54-7.56 (m, 2H), 7.65-7.70 (m, 2H), 8.55 (d, 2H, *J* = 5.9 Hz). ^{13}C NMR (75 MHz, C*D*Cl_3) δ 98.2, 125.5, 127.3, 139.2, 149.1, 152.2, 160.2. HRMS (ESI): calcd for $C_{12}H_9N_2Br_2$ $[M+H]^+$, 338.9132; found, 338.9131.

2,2'-(2,2-Diphenylethene-1,1-diyl)dipyridine (4)

Compound **3** (340 mg, 1.00 mmol) was dissolved in 50 mL of dioxane : water (4 : 1). The flask was charged with Na_2CO_3 (690 mg, 5.00 mmol), $Pd(OAc)_2$ (28 mg, 0.12 mmol), PPh_3 (130 mg, 0.50 mmol) and phenylboronic acid (610 mg, 5.00 mmol). The reaction was heated to reflux under argon overnight. After cooling, the reaction mixture was diluted with water and extracted with ethyl acetate (3 × 50 mL) and the combined organic fractions were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography using ethyl acetate/hexane 1:1 and 2:1 as eluent to yield **4** (204 mg, 61%) as a yellowish white solid. Mp 185-187°C.

^{1}H NMR (300 MHz, C*D*Cl$_3$) δ 7.01-7.18 (m, 10H), 7.39-7.58 (m, 4H), 7.69-7.76 (m, 2H), 8.54 (d, 2H, *J* = 5.3 Hz). ^{13}C NMR (75 MHz, C*D*Cl$_3$) δ 123.9, 129.4, 129.9, 130.5, 131.3, 133.6, 134.7, 138.4, 145.1, 151.9, 163.9. HRMS (ESI): calcd for $C_{24}H_{19}N_2$ $[M+H]^+$, 335.1548; found, 335.1543.

4·Zn(OAc)$_2$

To a solution of **4** (20 mg, 0.06 mmol) in methanol (4 ml), Zn(OAc)$_2$ (13 mg, 0.06 mmol) was added and the white precipitate formed was filtered off. The filtrate was allowed to slowly evaporate to give **4**·Zn(OAc)$_2$ (26 mg, 85%) as colorless crystals. Mp >200°C.

2,2'-(2,2-Bis(4-methoxyphenyl)ethene-1,1-diyl)dipyridine (5)

Using the procedure given for the preparation of **4**, **3** (340 mg, 1 mmol) and 4-methoxyphenylboronic acid (760 mg, 5.0 mmol) were coupled to give **5** (295 mg, 75%) as orange-yellow solid. Mp 152-153°C. ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ 3.75 (s, 6H), 6.65 (d, 4H, *J* = 8.1 Hz), 6.93-7.14 (m, 10H), 8.17 (d, 2H, *J* = 7.9 Hz). ^{13}C NMR (100 MHz, acetone-d*6*) δ 55.6, 114.0, 114.2, 122.0, 127.8, 133.3, 136.1, 136.5, 136.6, 149.6, 160.1, 162.8. HRMS (ESI): calcd for $C_{26}H_{23}N_2O_2$ $[M+H]^+$, 395.1760; found, 395.1759.

2,2'-(2,2-Bis(dibenzo[*b,d*]thiophen-4-yl)ethene-1,1-diyl)dipyridine (6)

Using the procedure given for the preparation of **4**, **3** (340 mg, 1 mmol) and dibenzothiophene-4-boronic acid (1.140 g, 5.0 mmol) were coupled to give **6** (366 mg, 67%) as yellow solid. Mp 177-179°C. ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ 7.26-7.33 (m, 4H), 7.43-7.53 (m, 6H), 7.65-7.70 (m, 6H), 8.02-8.06 (m, 4H), 8.53 (d, 2H, *J* = 5.3 Hz). ^{13}C NMR (100 MHz, C*D*Cl$_3$) δ121.6, 122.5, 123.6, 125.2, 125.3, 127.2, 127.7, 129.5, 129.6, 133.0, 133.1, 133.2, 134.1, 136.8, 137.5, 140.9, 142.6, 150.4, 161.3. HRMS (ESI): calcd for $C_{36}H_{23}N_2S_2$ $[M+H]^+$, 547.1303; found, 547.1303.

3,3'-(2,2-Dibromoethene-1,1-diyl)dipyridine (7)

Using the procedure given for the preparation of **3**, di(3-pyridyl) ketone[1] (368 mg, 2.00 mmol) was converted into **7** (381 mg, 56%) as pale yellow solid. Mp 140-142°C. ^{1}H NMR (300 MHz, acetone-d*6*) δ 7.44-7.48 (m, 2H), 7.82-7.86 (m, 2H), 8.62 (d, 2H, *J* = 5.1 Hz), 8.72 (s, 2H). ^{13}C NMR (75 MHz, acetone-d*6*) δ 96.3, 126.2, 138.6, 139.5, 145.1, 151.9, 152.1. HRMS (ESI): calcd for $C_{12}H_9N_2Br_2$ $[M+H]^+$, 338.9132; found, 338.9139.

4,4'-(2,2-Dibromoethene-1,1-diyl)dipyridine (8)

Using the procedure given for the preparation of **3**, di(4-pyridyl) ketone[2] (368 mg, 2.00 mmol) was converted into **8** (435 mg, 64%) as dark yellow solid. Mp 163-164°C. ^{1}H NMR (400 MHz, C*D*Cl$_3$) 7.06 (d, 4H, *J* = 5.2 Hz), 8.46 (d, 4H, *J* = 5.2 Hz). ^{13}C NMR (75 MHz, C*D*Cl$_3$) δ 97.0, 125.8, 145.4, 150.1, 152.9. HRMS (ESI): calcd for $C_{12}H_9N_2Br_2$ $[M+H]^+$, 338.9132; found, 338.9136.

1,1,2,2-Tetra(pyridin-3-yl)ethene (9)

Using the procedure given for the preparation of **4**, **7** (340 mg, 1 mmol) and 3-pyridineboronic acid (615 mg, 5.0 mmol) were coupled to give **9** (182 mg, 54%) as yellowish white solid. The crude product was purified by flash column chromatography using 100 % ethyl acetate, followed by chloroform/methanol 3:1 as eluent. Mp 189-191°C. ^{1}H NMR (400 MHz, methanol-d*4*) 7.32-7.35 (m, 4H), 7.60-7.63 (m, 4H), 8.30

(s, 4H), 8.38 (d, 4H, *J* = 4.5 Hz). ^{13}C NMR (75 MHz, methanol-d*4*) δ 126.4, 140.4, 140.5, 141.8, 150.4, 153.4.HRMS (ESI): calcd for $C_{22}H_{17}N_4$ $[M+H]^+$, 337.1453; found, 337.1457.

1,1,2,2-Tetra(pyridin-4-yl)ethene (10)

Using the procedure given for the preparation of **4**, **8** (340 mg, 1 mmol) and 4-pyridineboronic acid (615 mg, 5.0 mmol) were coupled to give **10** (229 mg, 68%) as off-white solid. The crude product was purified by flash column chromatography using 100 % ethyl acetate, followed by chloroform/methanol 3:1 as eluent. Mp 195-196°C. ^{1}H NMR (300 MHz, methanol-d*4*) 7.23 (d, 4H, *J* = 5.1 Hz), 8.47 (d, 4H, *J* = 5.1 Hz). ^{13}C NMR (75 MHz, methanol-d*4*) δ 128.2, 142.9, 151.6, 151.8. HRMS (ESI): calcd for $C_{22}H_{17}N_4$ $[M+H]^+$, 337.1453; found, 337.1458.

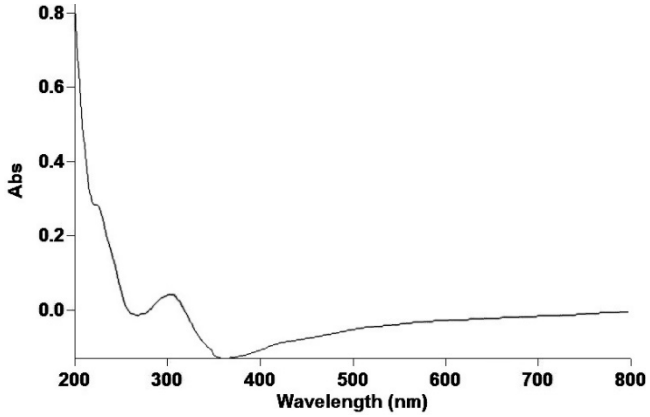


Figure S1. UV-vis absorption spectrum of **4** (CH_3CN, 25 µM).

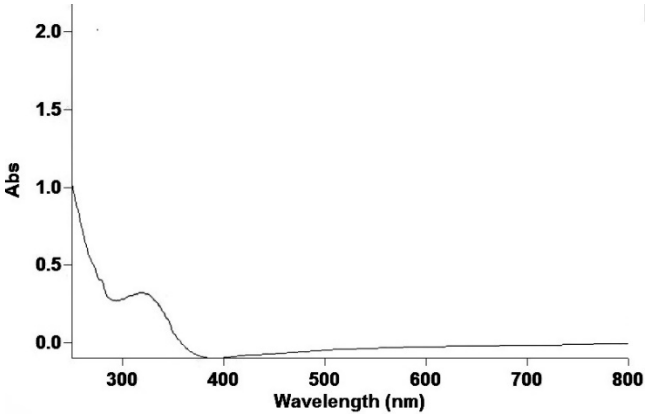


Figure S2. UV-vis absorption spectrum of **5** (CH_3CN, 50 µM).

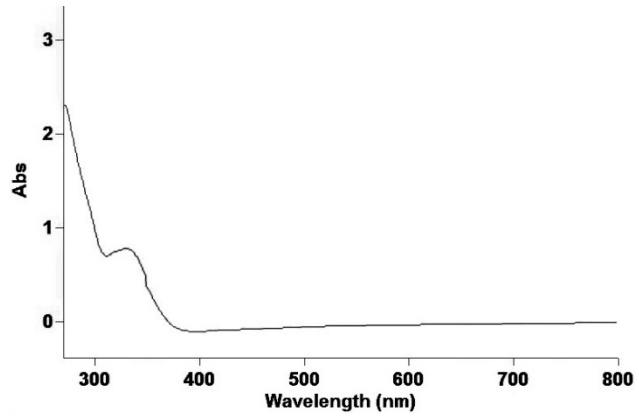


Figure S3. UV-vis absorption spectrum of **6** (CH_3CN, 50 μM).

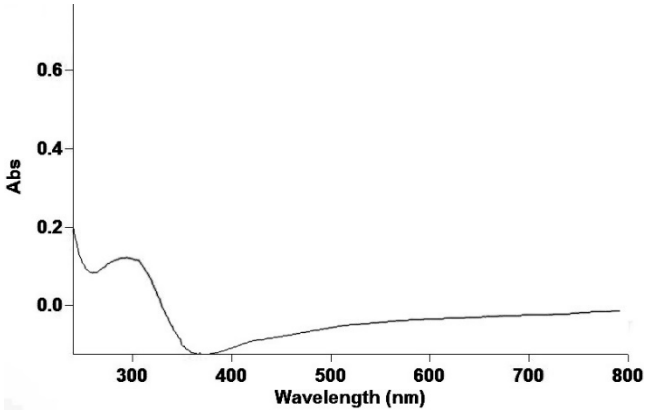


Figure S4. UV-vis absorption spectrum of **9** (CH_3CN, 50 μM).

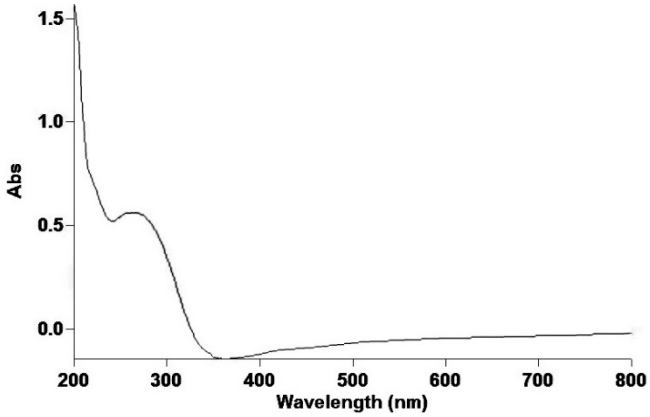


Figure S5. UV-vis absorption spectrum of **10** (CH_3CN, 50 μM).

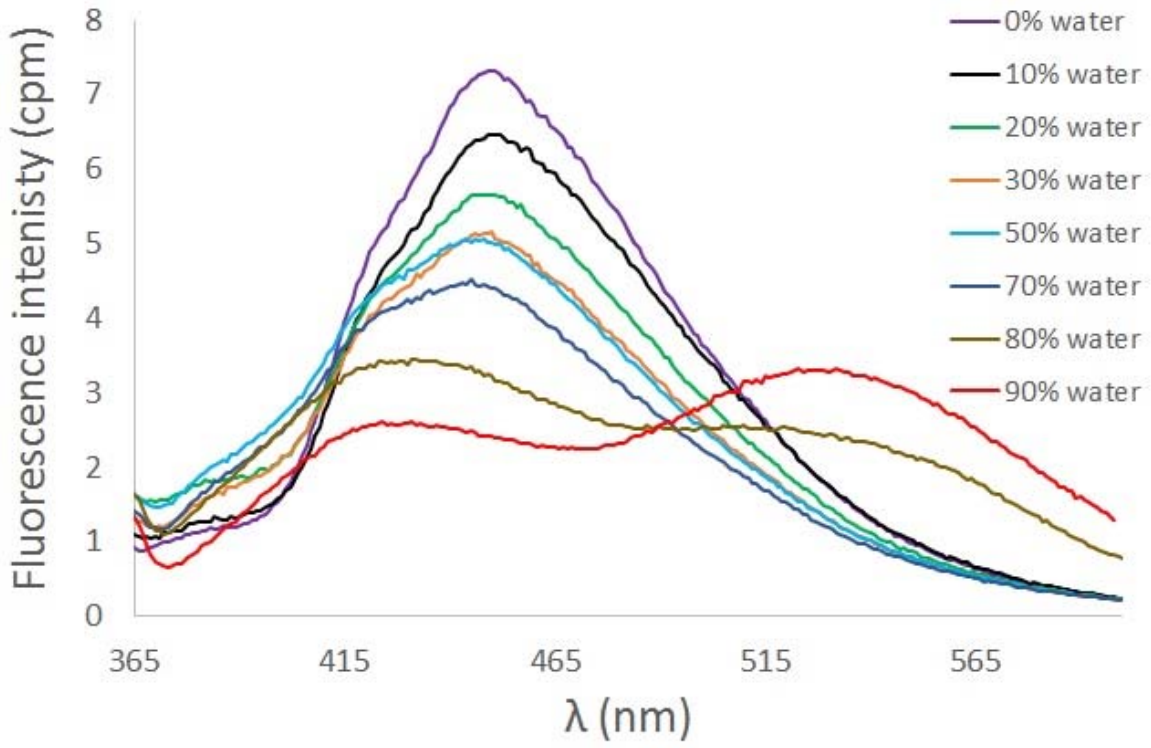


Figure S6. AIE profile of **5** in CH_3CN/H_2O mixtures. λ_{ex} = 331 nm, [**5**] = 10 μM.

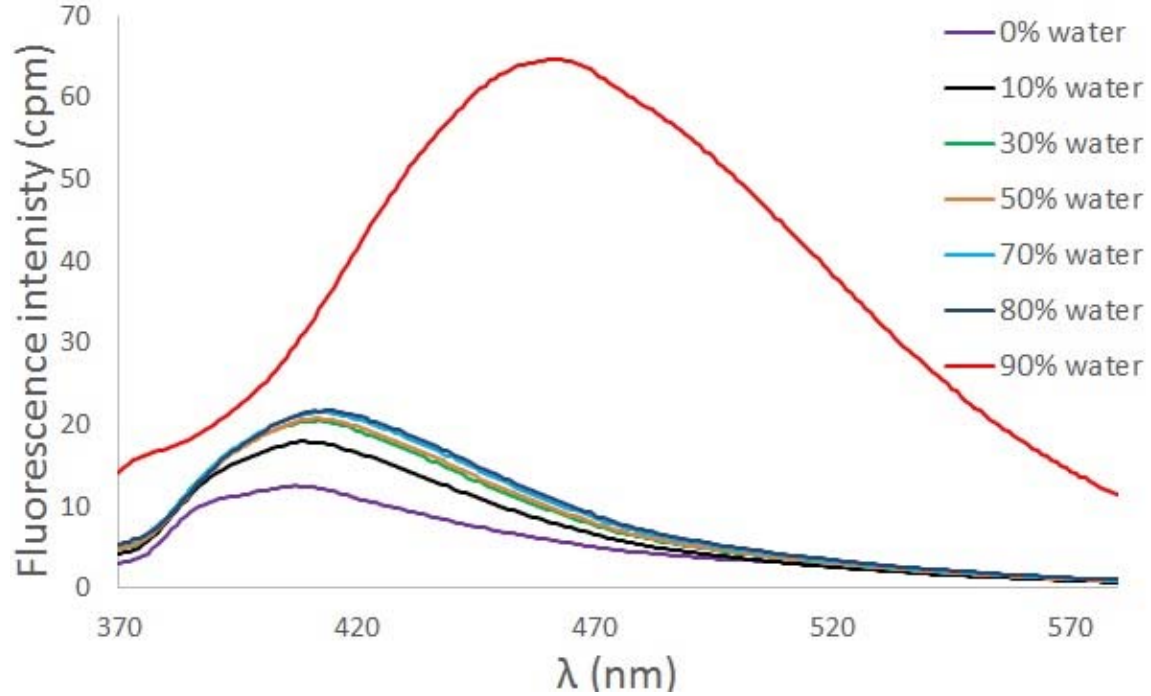
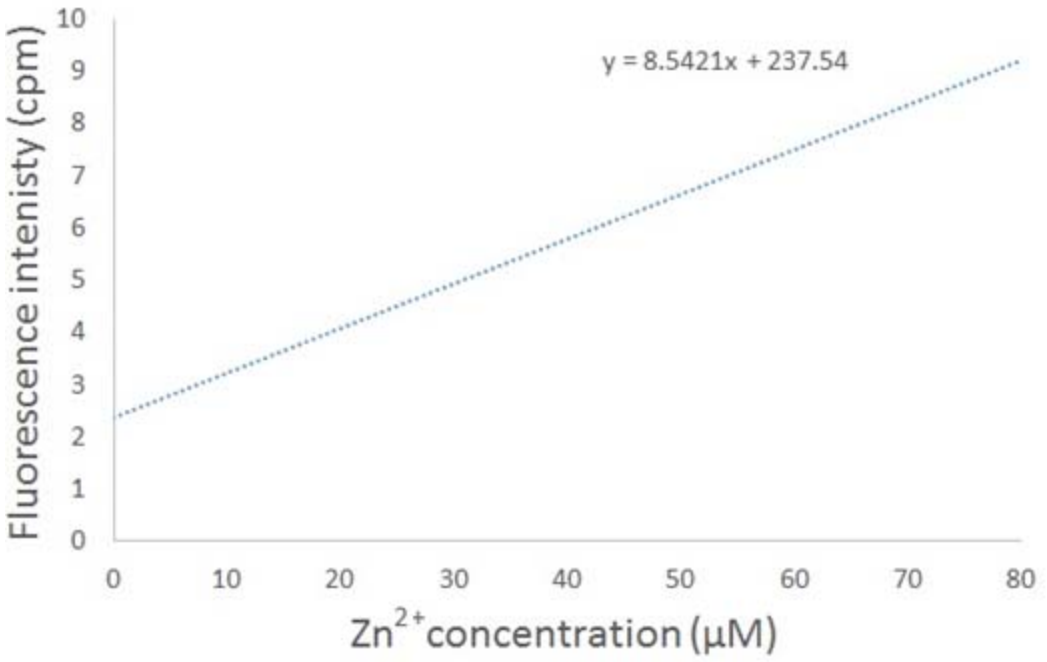


Figure S7. AIE profile of **6** in CH_3CN/H_2O mixtures. λ_{ex} = 337 nm, [**6**] = 10 μM



LOD = 3.3(S.D./S) = 94.1 nM;

S.D. = standard deviation of the response of the curve; S= the slope of the calibration curve

Figure S8. Determination of limit of detection (LOD) of **4** for $Zn(ClO_4)_2$.

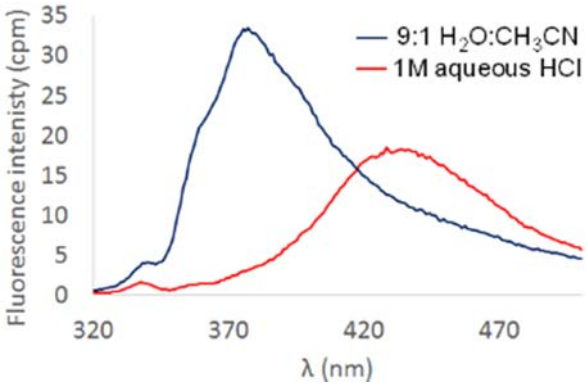


Figure S9. Comparison of the fluorescence spectrum of **4** in 9:1 H_2O:CH_3CN and 1 M aqueous HCl. λ_{ex} = 317 nm, [**4**] = 10 μM.

Job plot

A Job plot was constructed to determine the binding stoichiometry between **4** and $Zn(ClO_4)_2$ using ^1H NMR titrations by monitoring the change in chemical shift ($\Delta\delta$) of the most downfield pyridine hydrogen as a function of **4**/Zn^{2+} mole fraction. Stock solutions (5 mM each) of **4** and $Zn(ClO_4)_2$ were prepared in D_2O:C*D*$_3$CN (1:1). NMR samples were prepared with different mole fractions of **4** and $Zn(ClO_4)_2$ while maintaining the total concentration of ([**4**] + [$Zn(ClO_4)_2$]) for each sample at 5 mM.

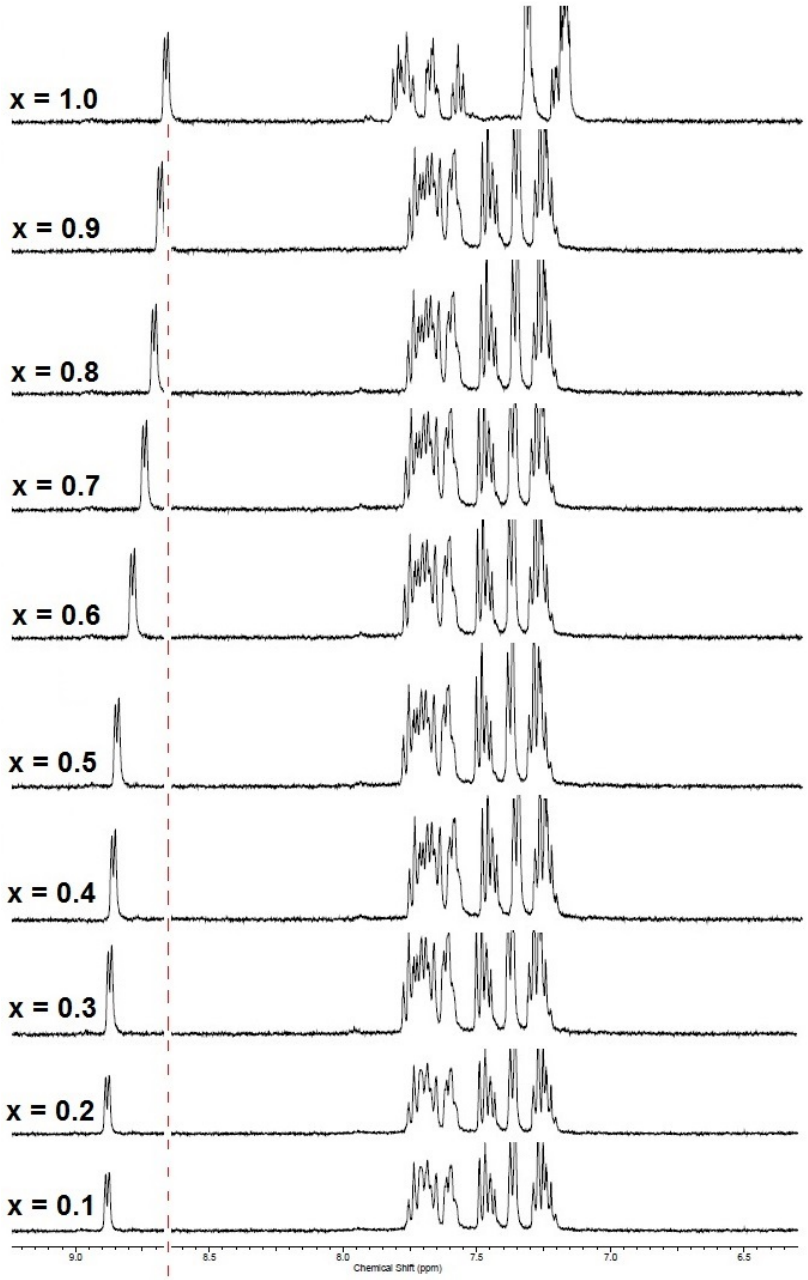


Figure S10. ^1H NMR spectra of **4** + $Zn(ClO_4)_2$ at different relative mole fractions (x = mole fraction **4**) in D_2O:C*D*$_3$CN (1:1). Total concentration of ([**4**] + [$Zn(ClO_4)_2$]) = 5.0 mM in all spectra.

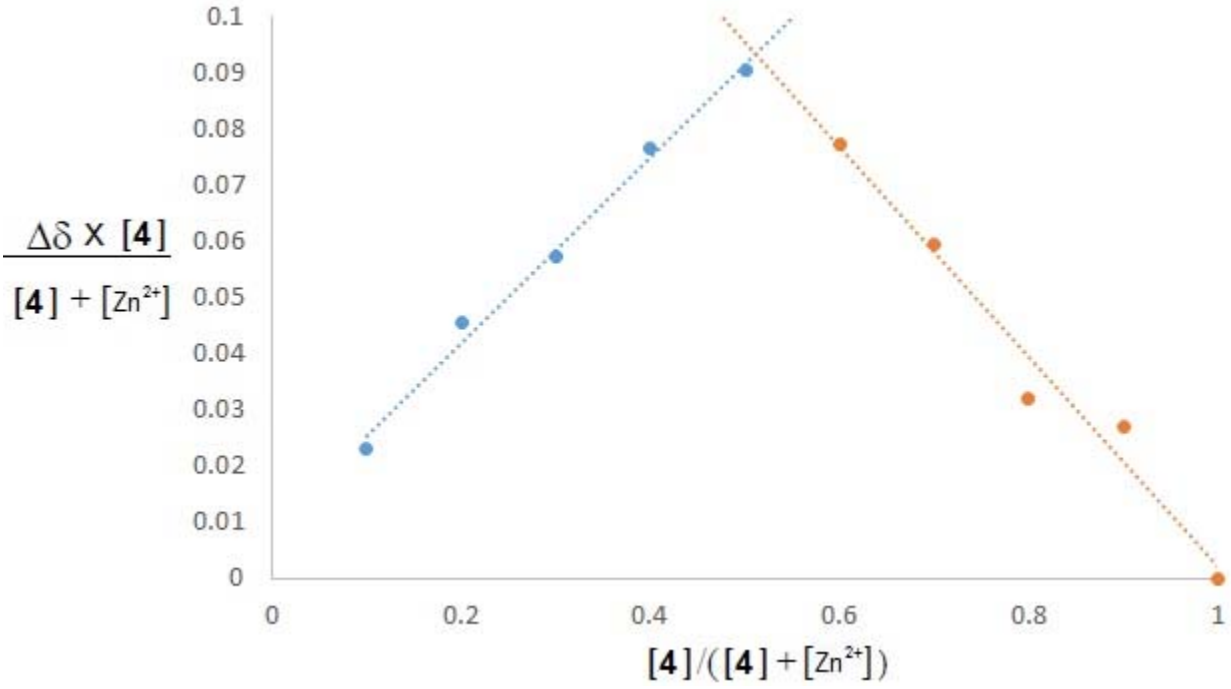


Figure S11. NMR Job plot of **4** with $Zn(ClO_4)_2$ in D_2O:C*D*$_3$CN (1:1) showing maximum $\Delta\delta$ at 0.5 mole fraction **4** (1:1 binding stoichiometry).

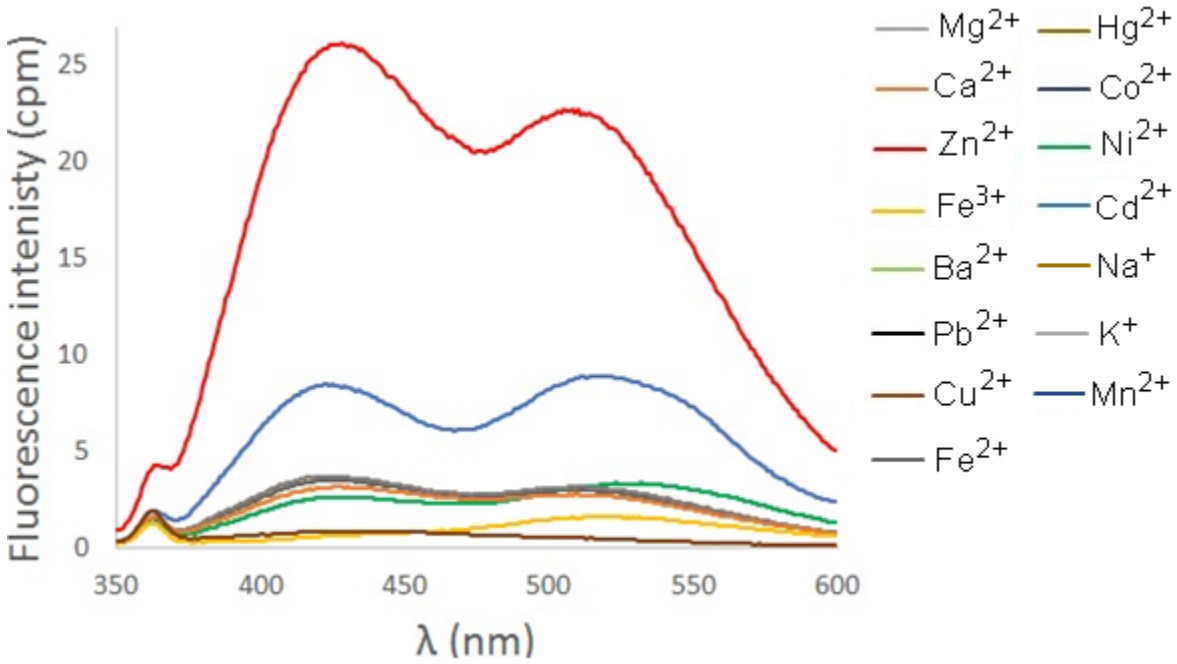


Figure S12. Fluorescence spectra of **5** in the presence of various metal ions (2 equivalents). 9:1 H_2O:CH_3CN, λ_{ex} = 331 nm, [**5**] = 10 μM.

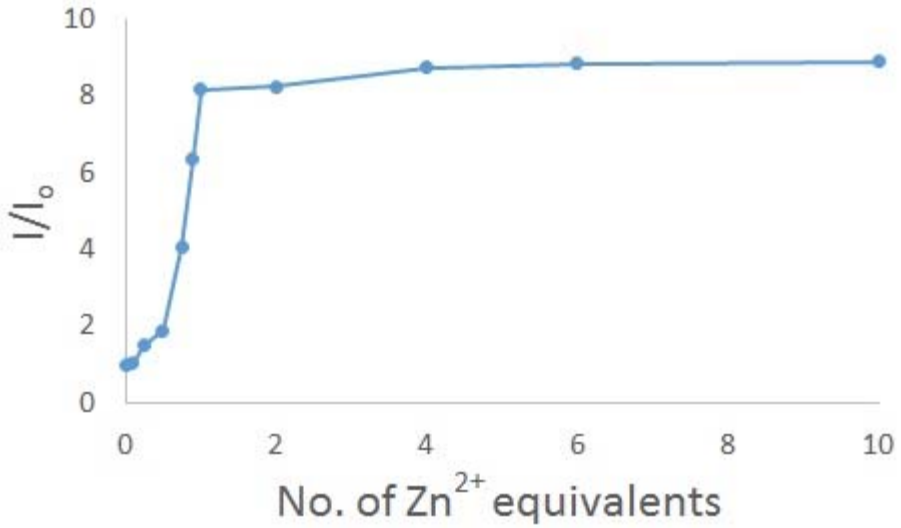


Figure S13. Change in fluorescence intensity of **5** (I/I_o) at 427 nm as a function of added Zn^{2+} in 9:1 H_2O:CH_3CN. λ_{ex} = 331 nm, [**5**] = 10 μM.

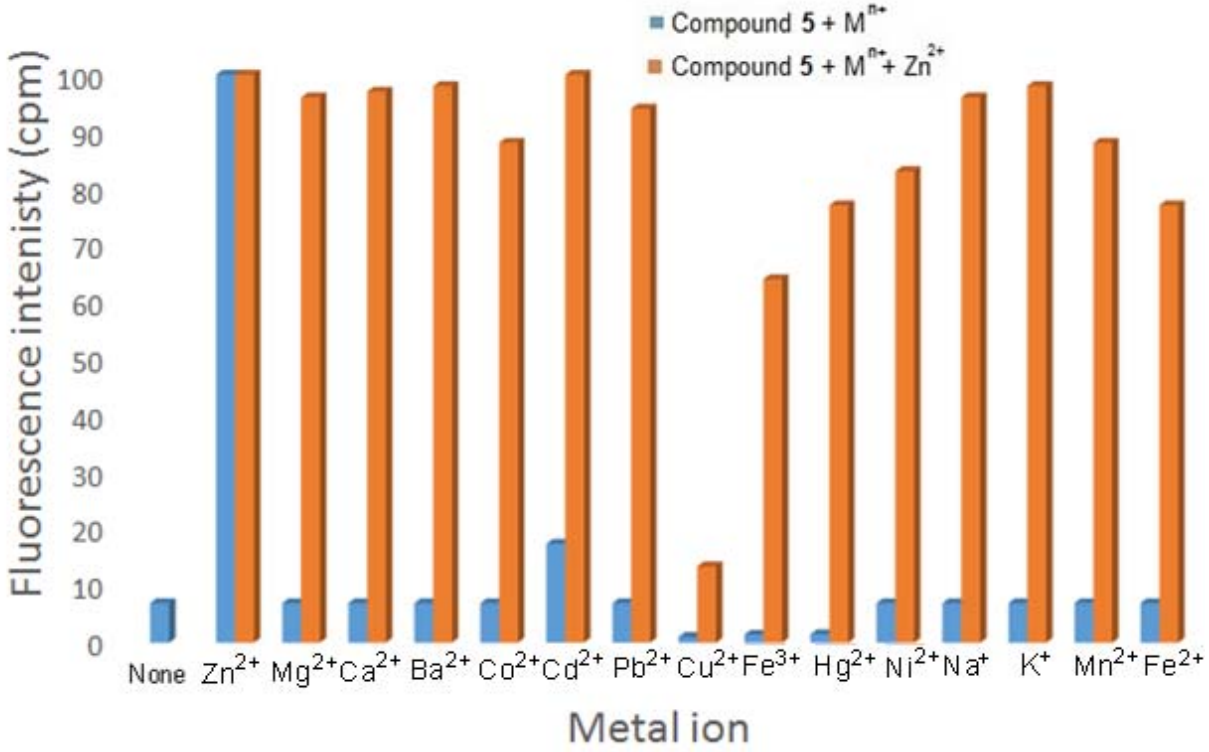


Figure S14. Emission of **5** in the presence of various metal ions and Zn^{2+}+metal ion combinations (normalized to emission in the presence of Zn^{2+} alone). 9:1 H_2O:CH_3CN, λ_{ex} = 331 nm, [**5**] = 10 μM.

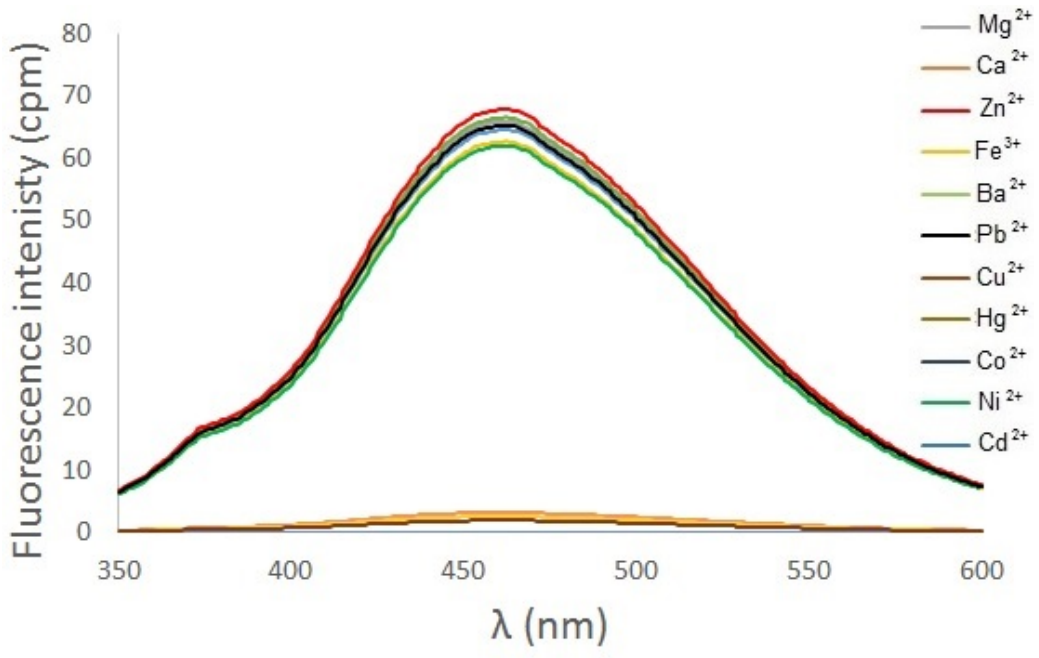


Figure S15. Fluorescence spectra of **6** in the presence of various metal ions (2 equivalents). 9:1 H_2O:CH_3CN, λ_{ex} = 337 nm, [**6**] = 10 μM.

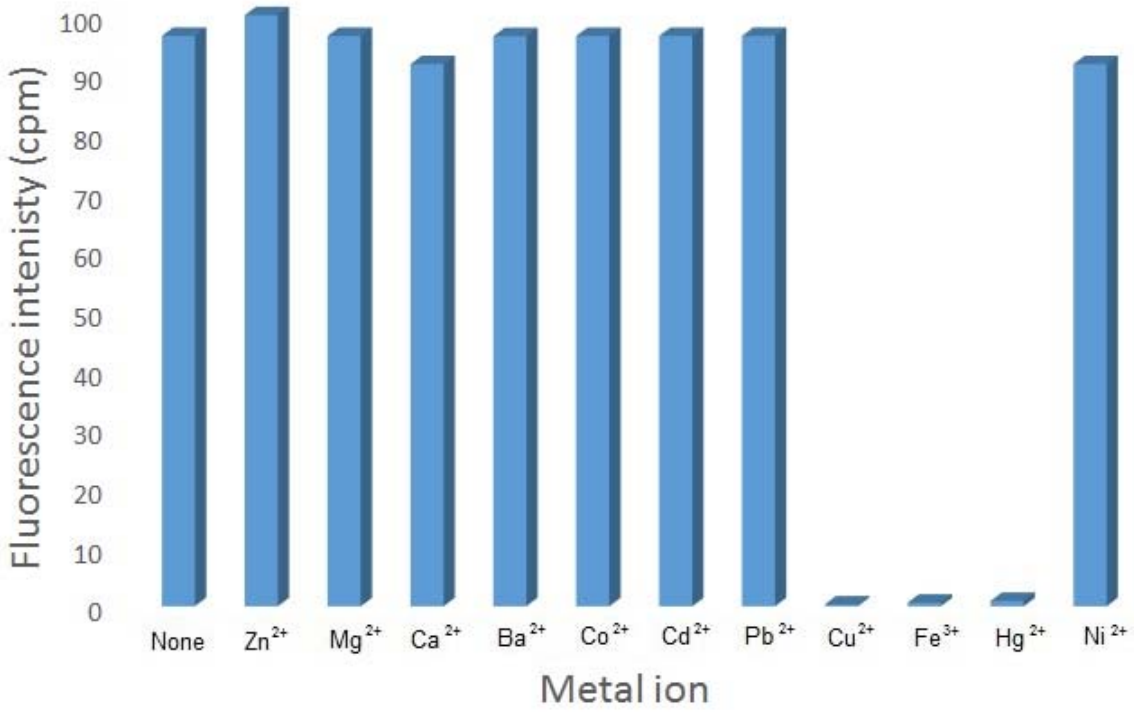


Figure S16. Emission of **6** in the presence of 2 equivalents of metal ions (normalized to emission in the presence of Zn^{2+}). 9:1 H_2O:CH_3CN, λ_{ex} = 337 nm, [**6**] = 10 μM.

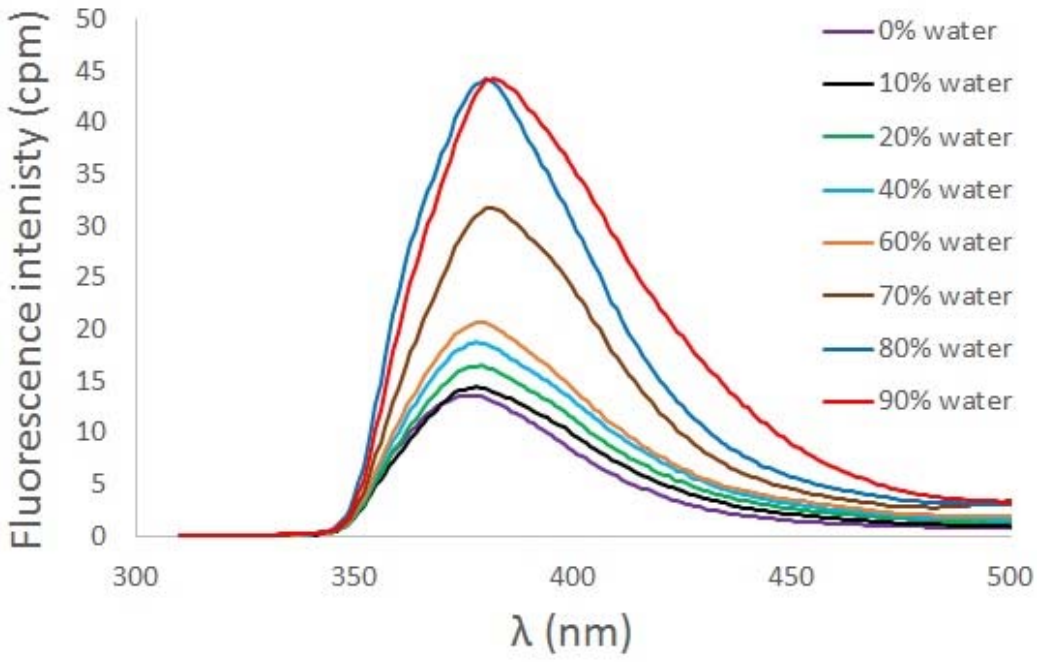


Figure S17. AIE profile of **9** in CH_3CN/H_2O mixtures. λ_{ex} = 305 nm, [**9**] = 10 μM.

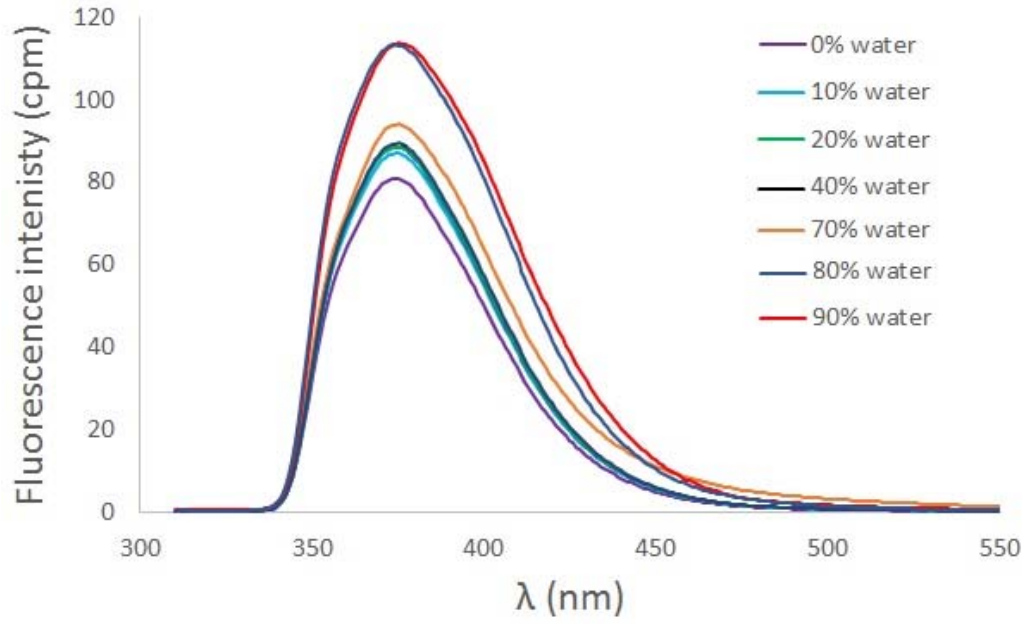


Figure S18. AIE profile of **10** in CH_3CN/H_2O mixtures. λ_{ex} = 290 nm, [**10**] = 10 μM.

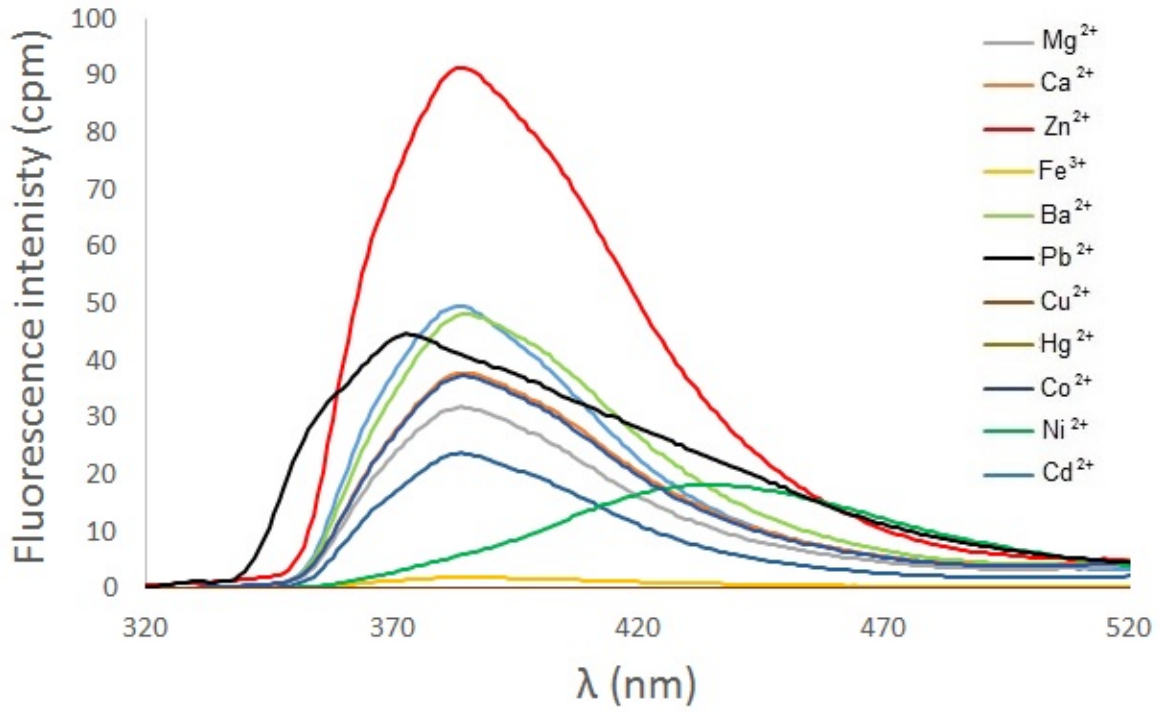


Figure S19. Fluorescence spectra of **9** in the presence of various metal ions (4 equivalents) in 9:1 H_2O:CH_3CN. λ_{ex} = 305 nm, [**9**] = 10 μM.

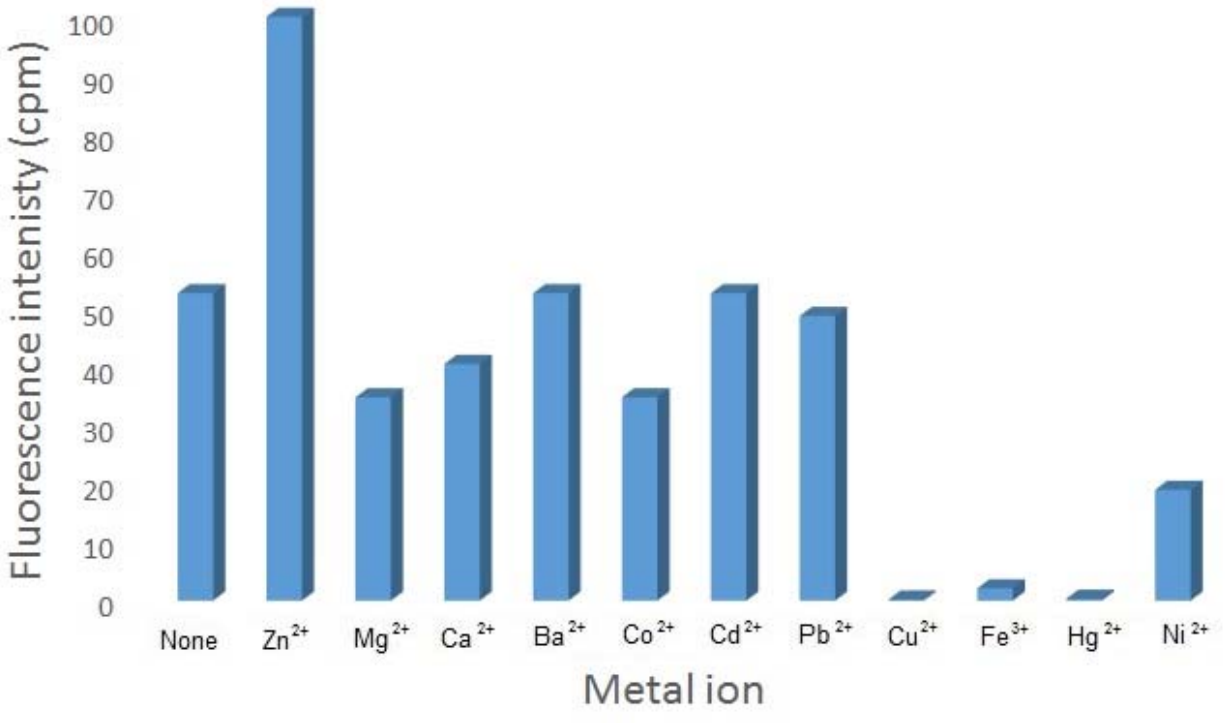


Figure S20. Emission of **9** in the presence of 4 equivalents of metal ions (normalized to emission in the presence of Zn^{2+}) in 9:1 H_2O:CH_3CN. λ_{ex} = 305 nm, [**9**] = 10 μM.

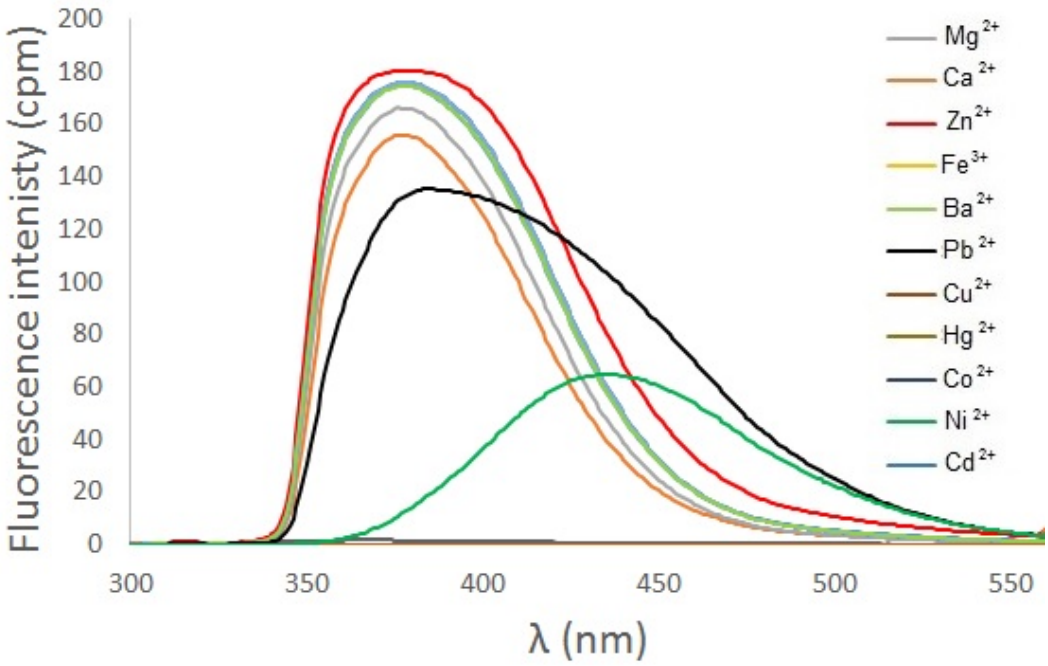


Figure S21. Fluorescence spectra of **10** in the presence of various metal ions (4 equivalents) in 9:1 H_2O:CH_3CN. λ_{ex} = 290 nm, [**10**] = 10 μM.

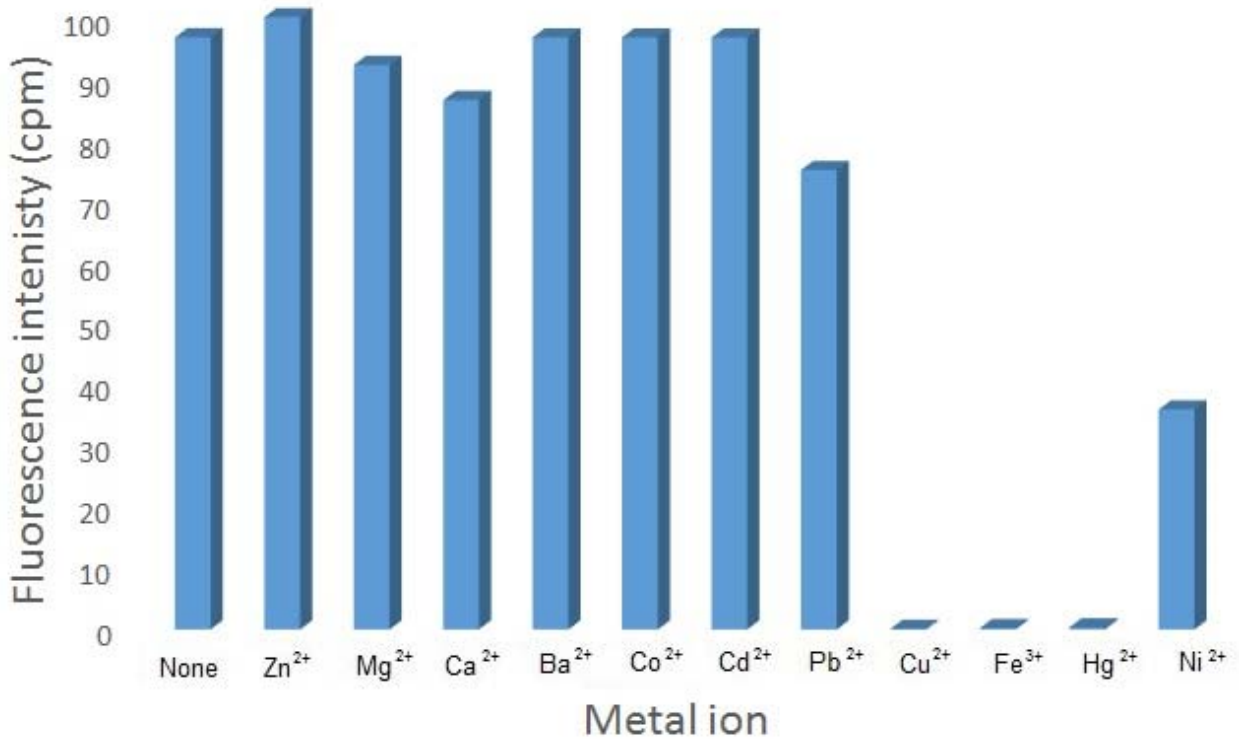
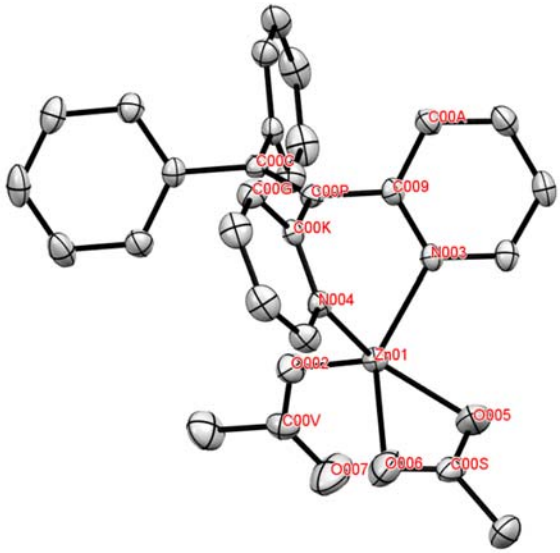


Figure S22. Emission of **10** in the presence of 4 equivalents of metal ions (normalized to emission in the presence of Zn^{2+}) in 9:1 H_2O:CH_3CN. λ_{ex} = 290 nm, [**10**] = 10 μM.

Table S1. Crystallographic data for **4**·$Zn(OAc)_2$.

Formula	$C_{28}H_{24}N_2O_4Zn$
FW	517.86
Crystal System	Monoclinic
Space group	$P2_1/c$
a/Å	8.5965(9)
b/Å	18.1619(18)
c/Å	15.3006(15)
α/°	90
β/°	90.404(4)
γ/°	90
V/Å^3	2388.8(4)
Z	4
D_{calc}	1.440
μ (mm^{-1})	1.066
T/K	190(2)
No. of reflections	27531
No. of unique reflections	5451
No. of reflections with $I > 2\sigma(I)$	4688
No. of parameters	318
R_1 [$I > 2\sigma(I)$]	0.0285
wR_2	0.0770
CCDC No.	1486438

Table S2. ORTEP Plot and selected bond lengths and angles in **4**·$Zn(OAc)_2$ (hydrogens omitted).



Selected bond distances (Å) and angles (°):

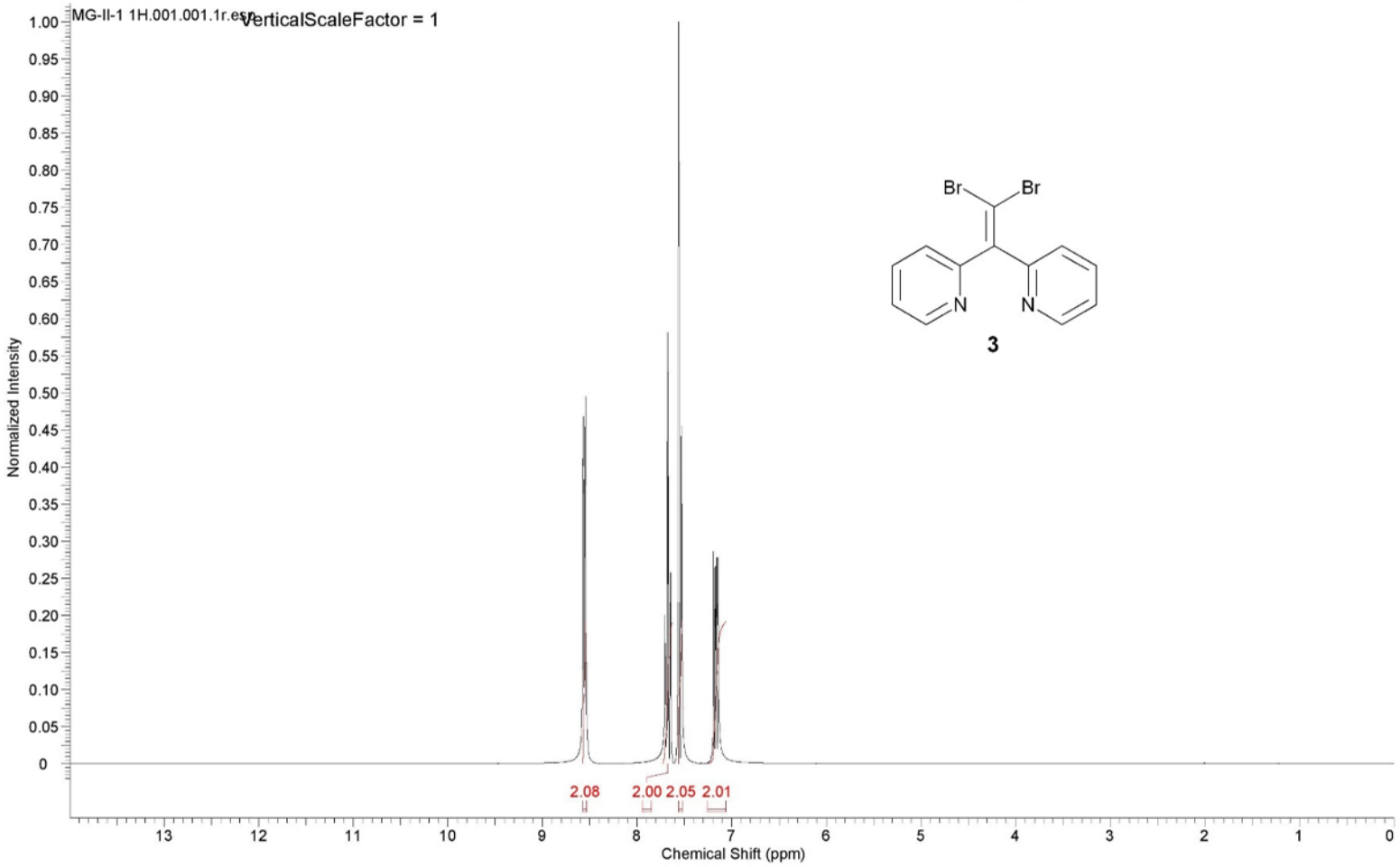
Zn(01)-N(0003)	2.093	N(004)-Zn(01)-N(003)	88.60
Zn(01)-N(004)	2.088	N(004)-Zn(01)-O(002)	99.54
Zn(01)-O(002)	1.937	N(004)-Zn(01)-O(005)	128.93
Zn(01)-O(005)	2.032	N(003)-Zn(01)-O(002)	107.30
Zn(01)-O(006)	2.313	N(003)-Zn(01)-O(005)	92.40
C(00S)-O(005)	1.245	O(002)-Zn(01)-O(005)	128.32
C(00S)-O(006)	1.243	C(00G)-C(00K)-C(00P)-C(00C)	53.80
C(00V)-O(002)	1.266	C(00A)-C(009)-C(00P)-C(00C)	57.25
C(00V)-O(007)	1.221		

References:

1. B. S. Park, S. W. Lee, I. T. Kim, J. S. Tae and S. H. Lee, *Heteroatom Chemistry*, 2012, **23**, 66-73.
2. *n*-Butyllithium (14.2 mL, 23 mmol, 1.6 M solution in THF) was added dropwise to a solution of 4-iodopyridine (3.89 g, 19 mmol) in diethyl ether (40 mL) at -78 °C and stirred for 15 min. A solution of methyl isonicotinate (2.6 g, 19 mmol) in diethyl ether (10 mL) was added dropwise to the reaction mixture at -78 °C and stirred for 4 h at the same temperature. The reaction was quenched with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 50 mL) and the combined organic fractions were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography using ethyl acetate/hexane 1:1 and 2:1 as eluent to yield pure product (1.32 g, 38%) as a yellow solid.

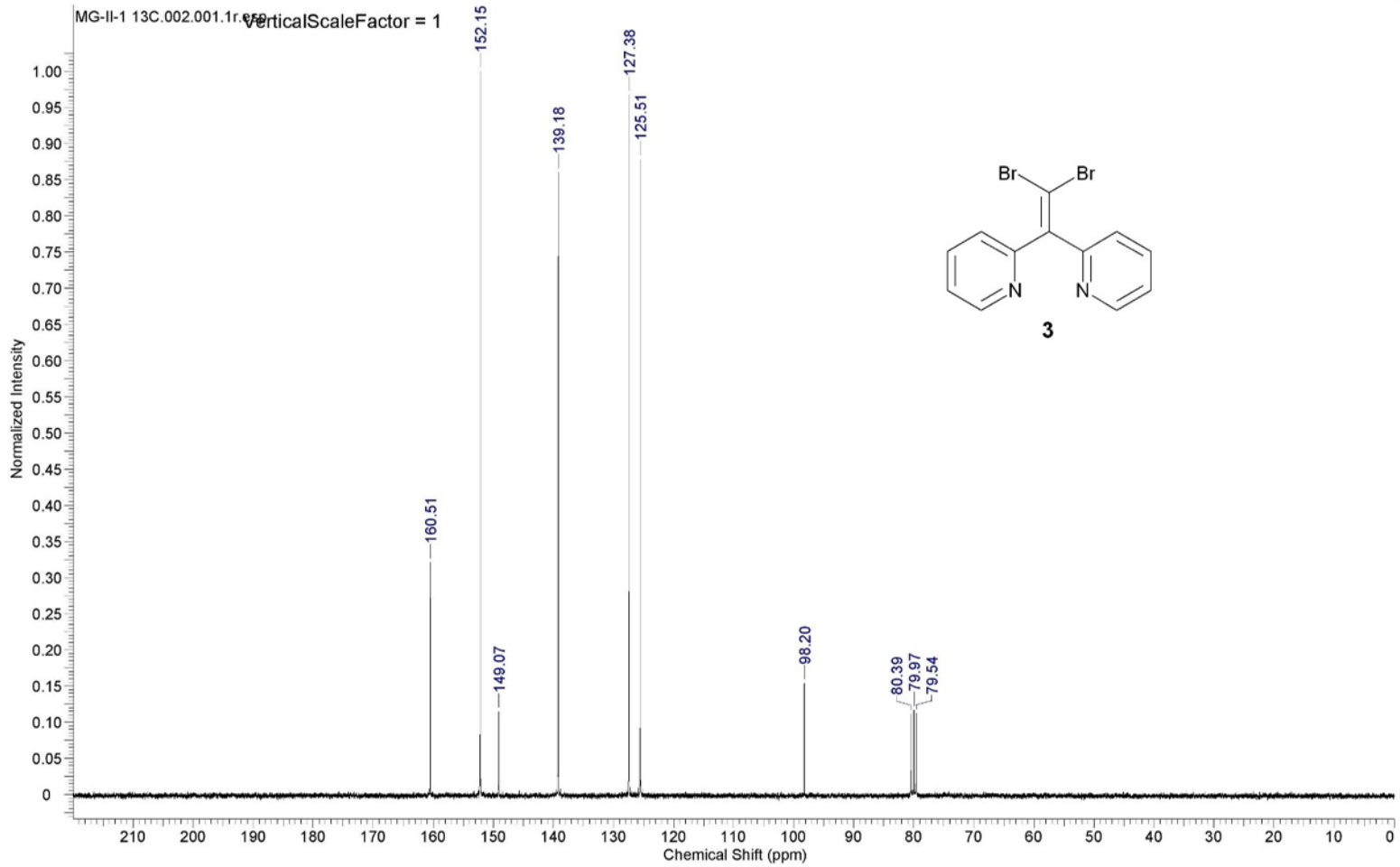
5/8/2016 3:03:03 PM

Acquisition Time (sec)	5.3084	***Comment***	1H	Av-300 TopSpin 1.3		***Date***	21 Dec 2015 13:58:56
Date Stamp	21 Dec 2015 13:58:56			***File Name***	E:\OLD NMR 300\MG-II-1 1H\1\pdata\1\1r		
Frequency (MHz)	300.13	***Nucleus***	1H	***Number of Transients***	16	***Origin***	spect
Original Points Count	32768	***Owner***	root	***Points Count***	65536	***Pulse Sequence***	zg30
Receiver Gain	322.50	***SW(cyclical) (Hz)***	6172.84	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2413.5735	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	6172.75	***Temperature (degree C)***	23.660



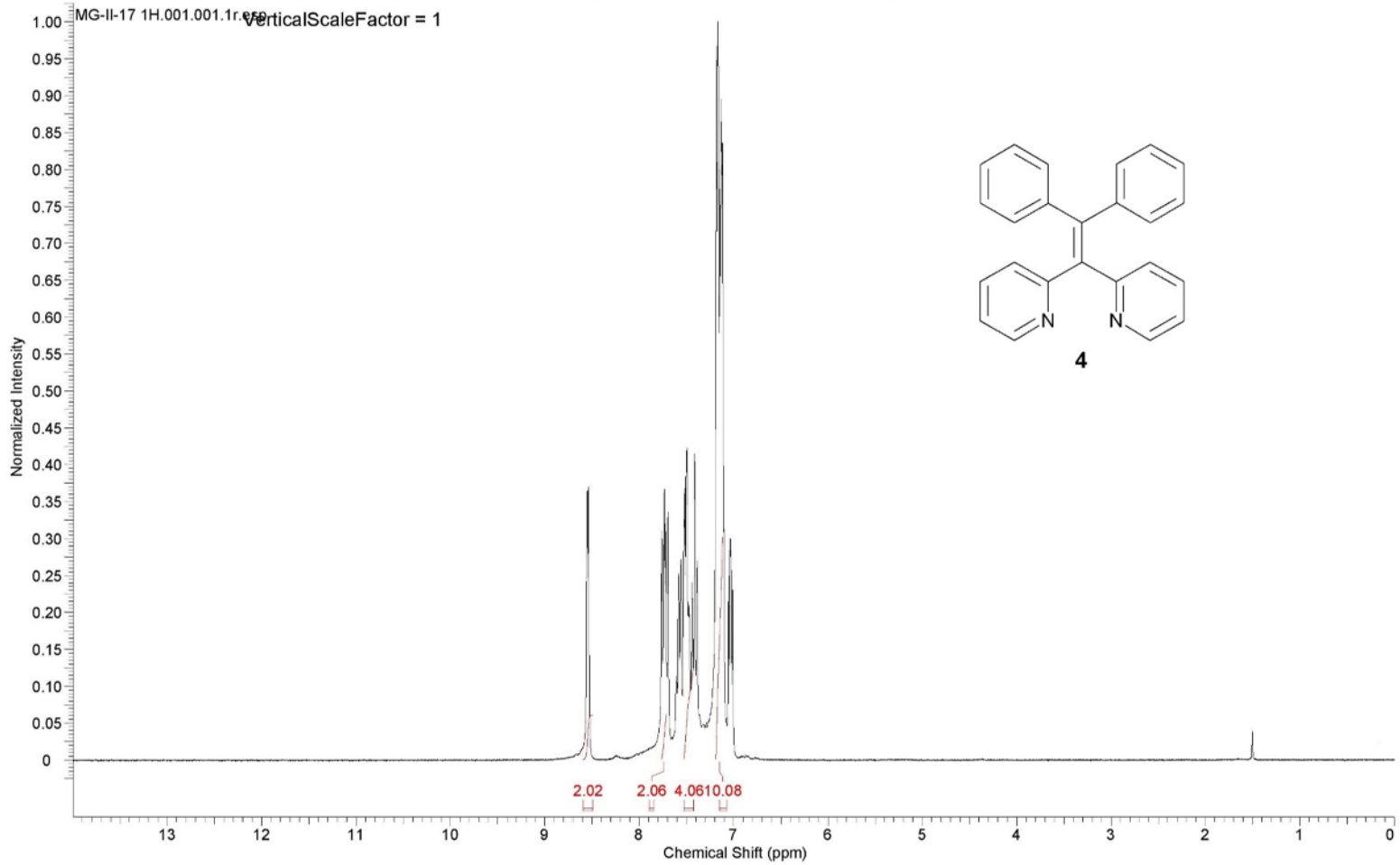
5/8/2016 3:05:14 PM

Acquisition Time (sec)	1.6417	***Comment***	13C TopSpin 1.3 Avance-300 NS = 200			***Date***	21 Dec 2015 14:16:00
Date Stamp	21 Dec 2015 14:16:00			***File Name***	E:\OLD NMR 300\MG-II-1 13C\2\pdata\1\1r		
Frequency (MHz)	75.47	***Nucleus***	13C	***Number of Transients***	450	***Origin***	spect
Original Points Count	32768	***Owner***	root	***Points Count***	131072	***Pulse Sequence***	zgdc30
Receiver Gain	46341.00	***SW(cyclical) (Hz)***	19960.08	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	7747.7314	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	19959.93	***Temperature (degree C)***	24.560



6/11/2016 5:09:56 PM

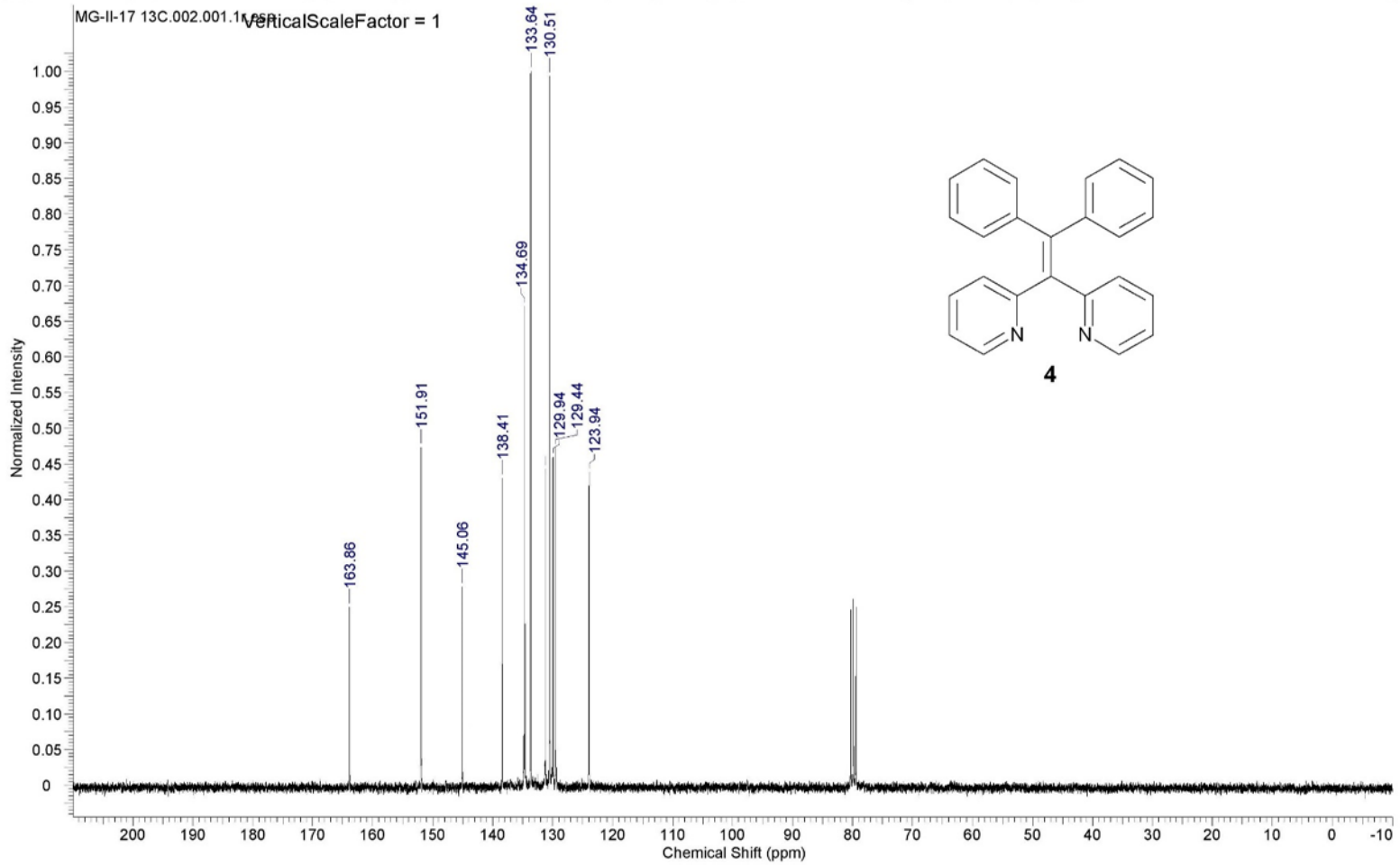
Acquisition Time (sec)	5.3084	***Comment***	1H Av-300 TopSpin 1.3			***Date***	24 Dec 2015 12:22:56
Date Stamp	24 Dec 2015 12:22:56			***File Name***	E:\OLD NMR 300\MG-II-17 1H\1\pdata\1\1r		
Frequency (MHz)	300.13	***Nucleus***	1H	***Number of Transients***	10	***Origin***	spect
Original Points Count	32768	***Owner***	root	***Points Count***	65536	***Pulse Sequence***	zg30
Receiver Gain	322.50	***SW(cyclical) (Hz)***	6172.84	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2413.5735	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	6172.75	***Temperature (degree C)***	23.660



4

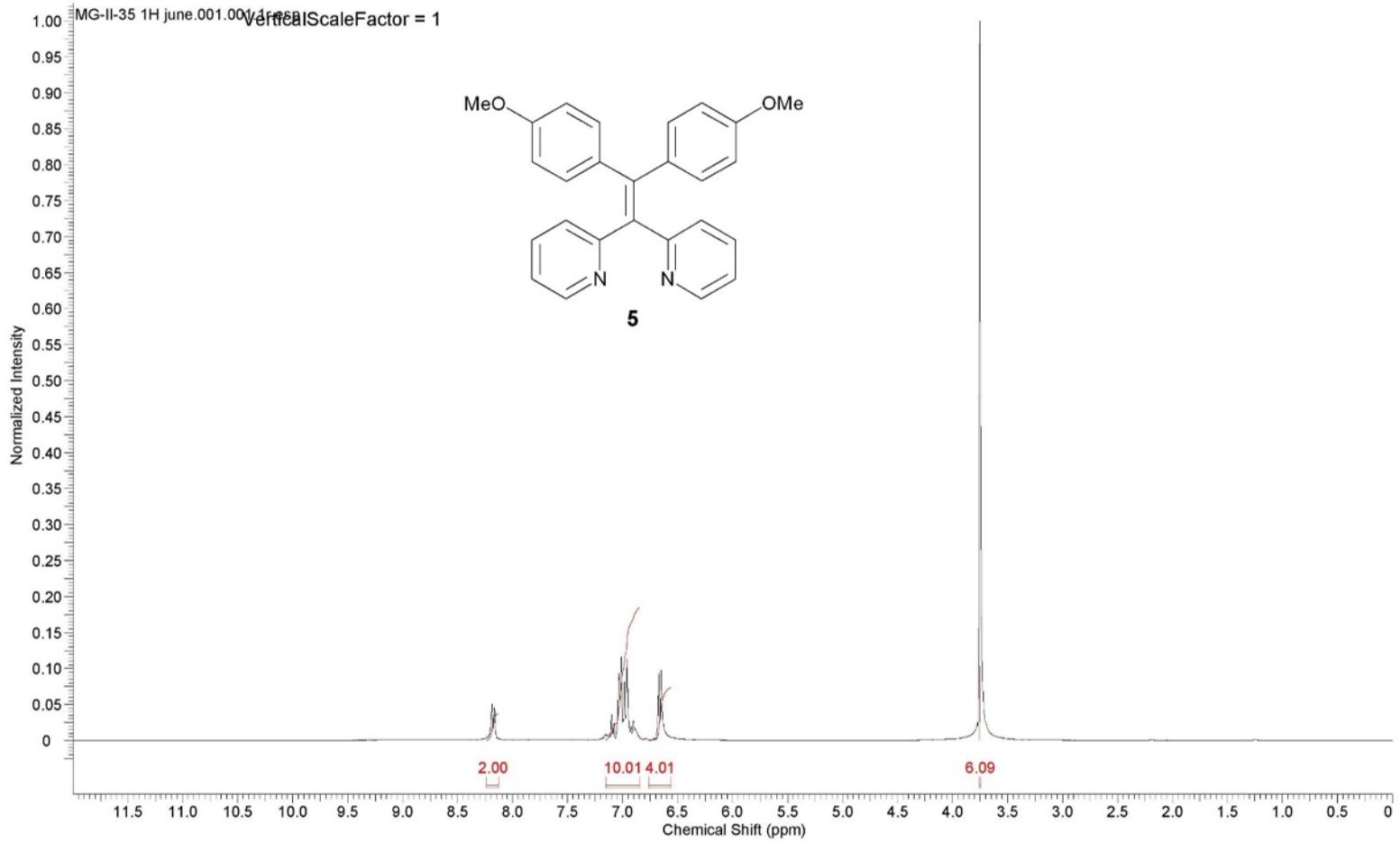
6/11/2016 5:03:12 PM

Acquisition Time (sec)	1.6417	***Comment***	13C TopSpin 1.3 Avance-300 NS = 200			***Date***	24 Dec 2015 12:46:24
Date Stamp	24 Dec 2015 12:46:24			***File Name***	E:\OLD NMR 300\MG-II-17 13C\2\pdata\1\1r		
Frequency (MHz)	75.47	***Nucleus***	13C	***Number of Transients***	600	***Origin***	spect
Original Points Count	32768	***Owner***	root	***Points Count***	131072	***Pulse Sequence***	zgdc30
Receiver Gain	46341.00	***SW(cyclical) (Hz)***	19960.08	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	7747.7314	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	19959.93	***Temperature (degree C)***	24.660



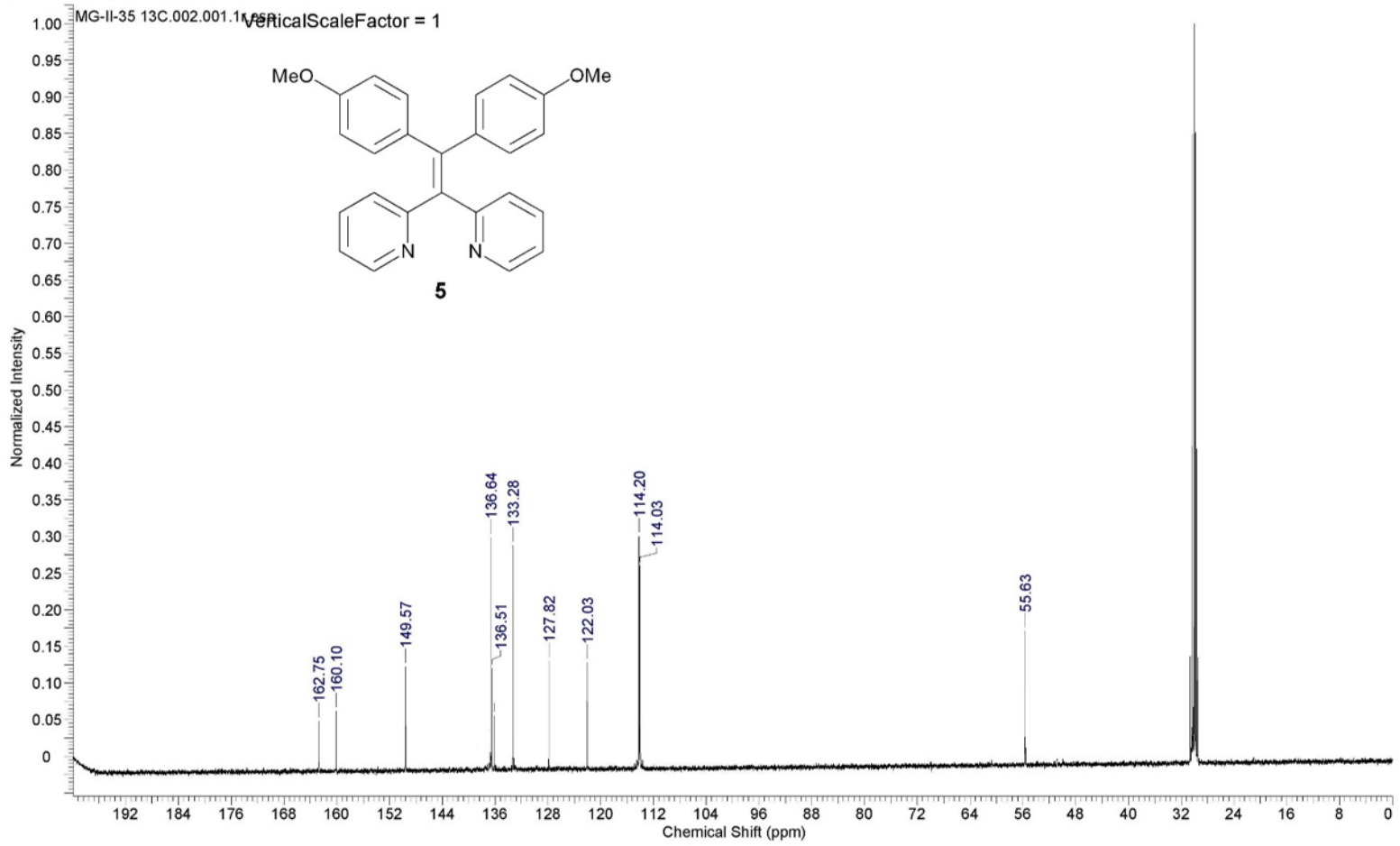
6/21/2016 8:37:27 AM

Acquisition Time (sec)	2.0447	***Comment***	1H Sugar/D2O DRX-400 1H_training Sep 11 2014 Shim update- May 28, 2014				
Date	13 Jun 2016 13:33:36			***Date Stamp***	13 Jun 2016 13:33:36		
File Name	E:\June 2016 NMR\MG-II-35 1H june\1\pdata\1\1r			***Frequency (MHz)***	400.13	***Nucleus***	1H
Number of Transients	4	***Origin***	spect	***Original Points Count***	16384	***Owner***	root
Points Count	131072	***Pulse Sequence***	zg30	***Receiver Gain***	406.40	***SW(cyclical) (Hz)***	8012.82
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	3193.2092	***Spectrum Type***	STANDARD
Sweep Width (Hz)	8012.76	***Temperature (degree C)***	23.160				



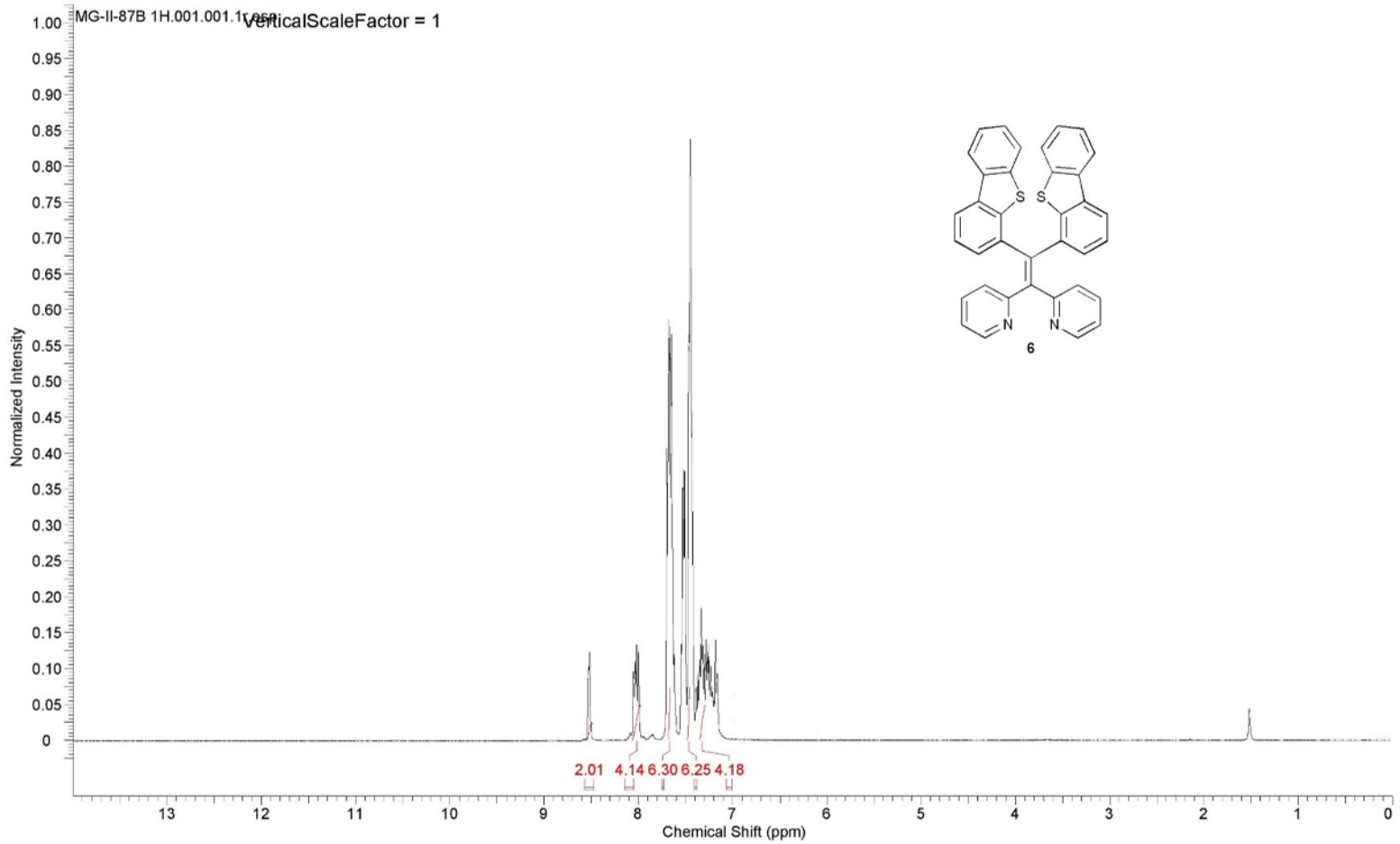
6/11/2016 5:20:53 PM

Acquisition Time (sec)	1.2485	***Comment***	13C DRX-400 13C_training PrOH/DMSO Sep 11, 2014				
Date	11 Jan 2016 11:18:56			***Date Stamp***	11 Jan 2016 11:18:56		
File Name	E:\OLD NMR\MG-II-35 13C\2\pdata\1\1r			***Frequency (MHz)***	100.61	***Nucleus***	13C
Number of Transients	550	***Origin***	spect	***Original Points Count***	32768	***Owner***	root
Points Count	131072	***Pulse Sequence***	zgdc30	***Receiver Gain***	362.00	***SW(cyclical) (Hz)***	26246.72
Solvent	Acetone	***Spectrum Offset (Hz)***	7026.2886	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	26246.52
Temperature (degree C)	24.160						



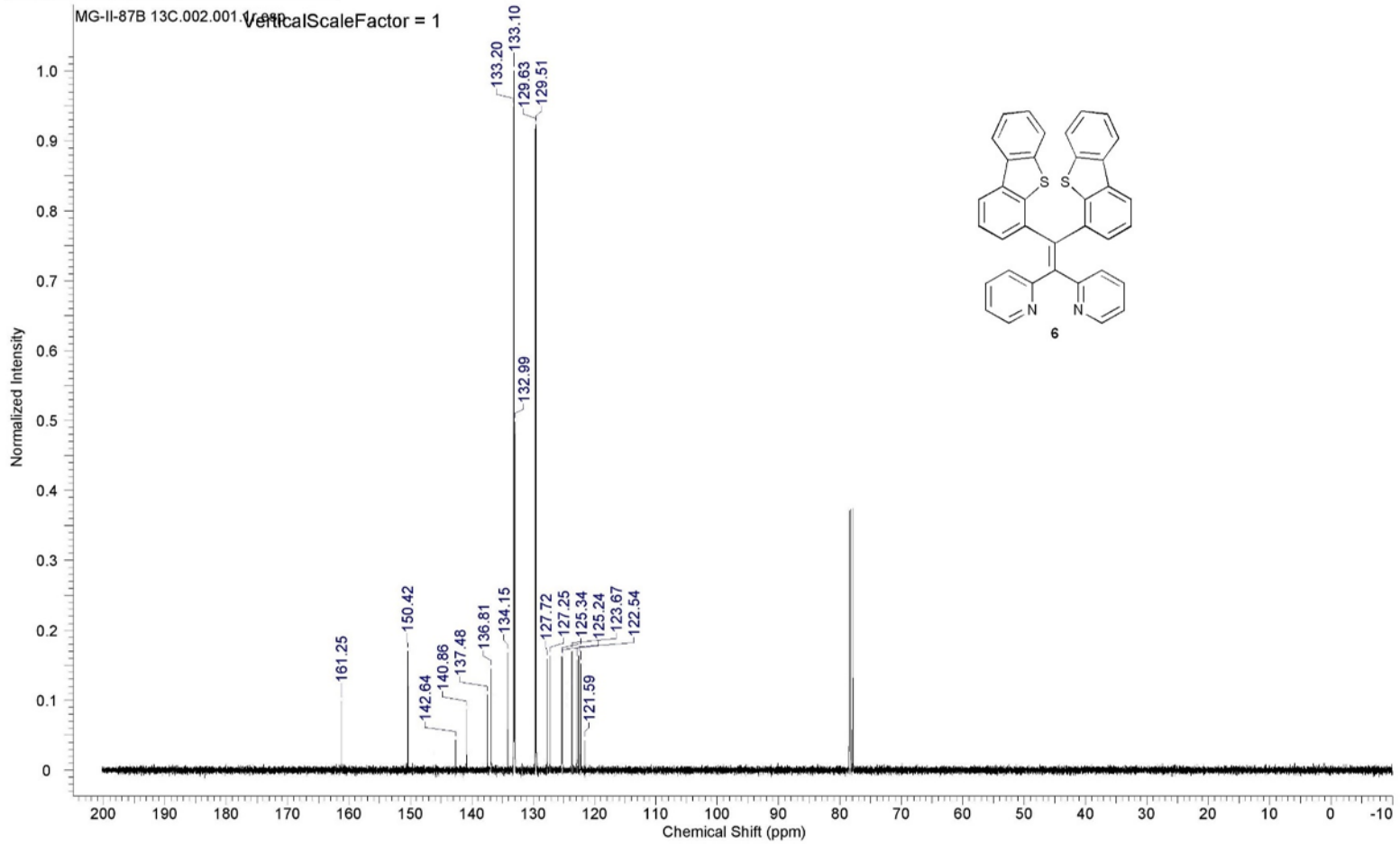
6/11/2016 5:59:27 PM

Acquisition Time (sec)	2.0447	***Comment***	1H Sugar/D2O DRX-400 1H_training Sep 11 2014 Shim update- May 28, 2014				
Date	24 Feb 2016 16:43:12			***Date Stamp***	24 Feb 2016 16:43:12		
File Name	E:\OLD NMR\MG-II-87B 1H\1\pdata\1\1r			***Frequency (MHz)***	400.13	***Nucleus***	1H
Number of Transients	4	***Origin***	spect	***Original Points Count***	16384	***Owner***	root
Points Count	131072	***Pulse Sequence***	zg30	***Receiver Gain***	71.80	***SW(cyclical) (Hz)***	8012.82
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	3193.2092	***Spectrum Type***	STANDARD
Sweep Width (Hz)	8012.76	***Temperature (degree C)***	24.160				



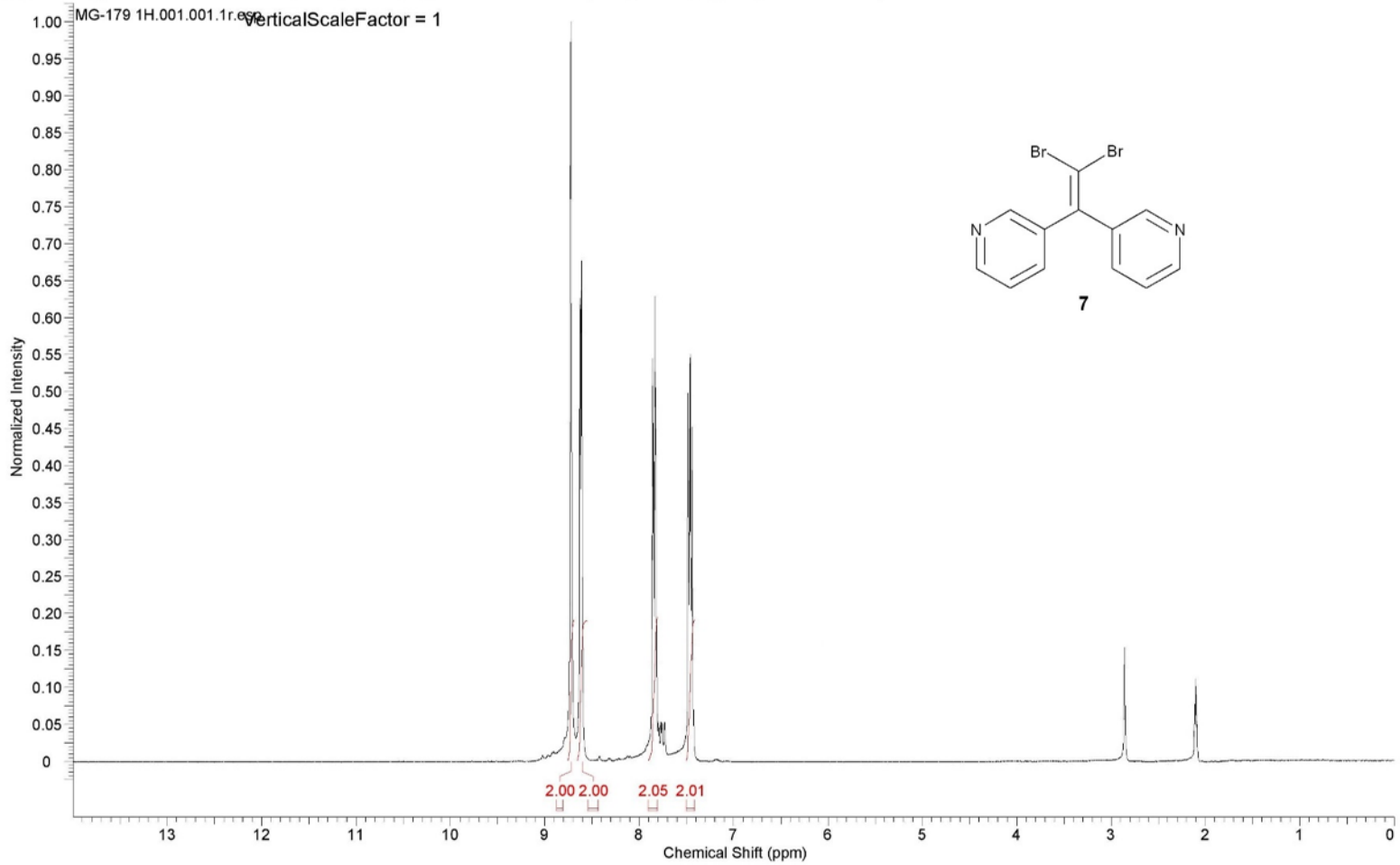
6/11/2016 5:53:13 PM

Acquisition Time (sec)	1.2485	***Comment***	13C Sucrose/D2O DRX-400 After magnet-rebuild- Sep 2013 Sample breakage-April 2014 May 28 after probe repair				
Date	24 Feb 2016 16:58:08			***Date Stamp***	24 Feb 2016 16:58:08		
File Name	E:\OLD NMR\MG-II-87B 13C\2\pdata\1\1r			***Frequency (MHz)***	100.61	***Nucleus***	13C
Number of Transients	400	***Origin***	spect	***Original Points Count***	32768	***Owner***	root
Points Count	131072	***Pulse Sequence***	zgdc30	***Receiver Gain***	362.00	***SW(cyclical) (Hz)***	26246.72
Solvent	CHLOROFORM-d	***Spectrum Offset (Hz)***	7026.2886	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	26246.52
Temperature (degree C)	24.160						



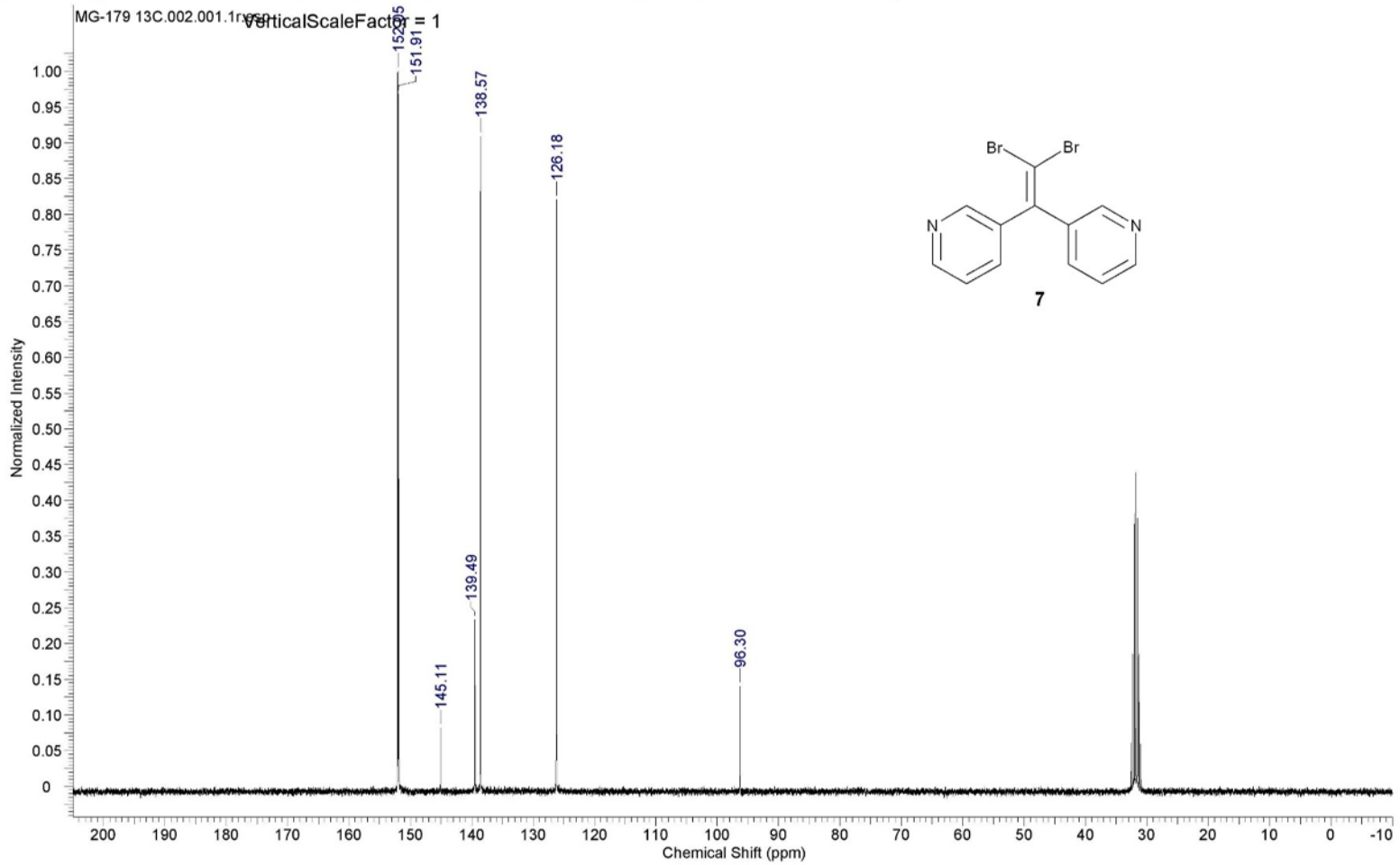
6/11/2016 4:51:55 PM

Acquisition Time (sec)	5.3084	***Comment***	1H Av-300 TopSpin 1.3			***Date***	27 Aug 2015 15:20:16
Date Stamp	27 Aug 2015 15:20:16			***File Name***	E:\OLD NMR 300\MG-179 1H\1\pdata\1\1r		
Frequency (MHz)	300.13	***Nucleus***	1H	***Number of Transients***	16	***Origin***	spect
Original Points Count	32768	***Owner***	root	***Points Count***	65536	***Pulse Sequence***	zg30
Receiver Gain	406.40	***SW(cyclical) (Hz)***	6172.84	***Solvent***	Acetone	***Spectrum Offset (Hz)***	2413.5735
Spectrum Type	STANDARD	***Sweep Width (Hz)***	6172.75	***Temperature (degree C)***	23.460		



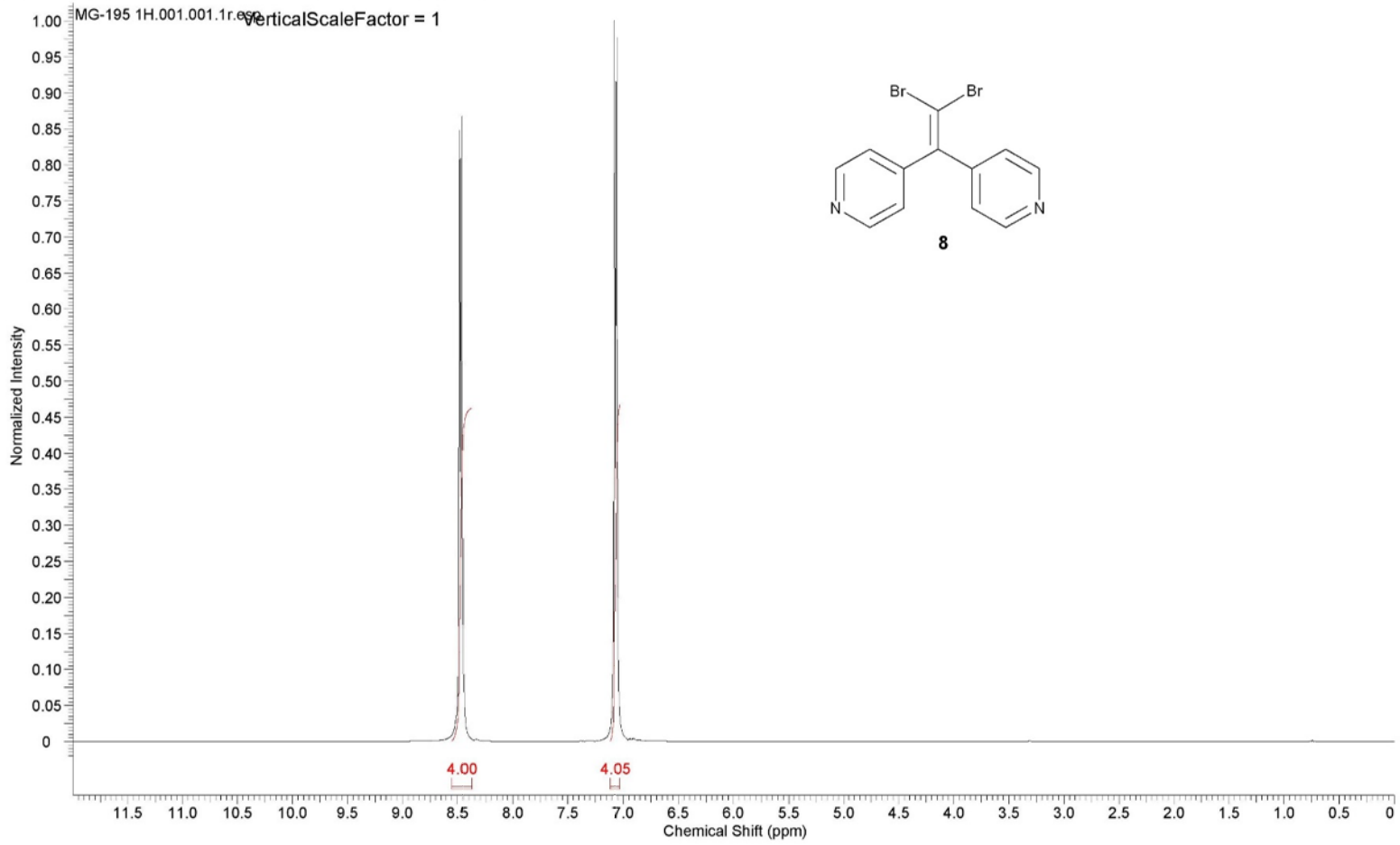
6/11/2016 4:56:06 PM

Acquisition Time (sec)	1.6417	***Comment***	13C TopSpin 1.3 Avance-300 NS = 200			***Date***	27 Aug 2015 15:43:44
Date Stamp	27 Aug 2015 15:43:44			***File Name***	E:\OLD NMR 300\MG-179 13C\2\pdata\1\1r		
Frequency (MHz)	75.47	***Nucleus***	13C	***Number of Transients***	600	***Origin***	spect
Original Points Count	32768	***Owner***	root	***Points Count***	131072	***Pulse Sequence***	zgdc30
Receiver Gain	26008.00	***SW(cyclical) (Hz)***	19960.08	***Solvent***	Acetone	***Spectrum Offset (Hz)***	7747.7314
Spectrum Type	STANDARD	***Sweep Width (Hz)***	19959.93	***Temperature (degree C)***	24.560		



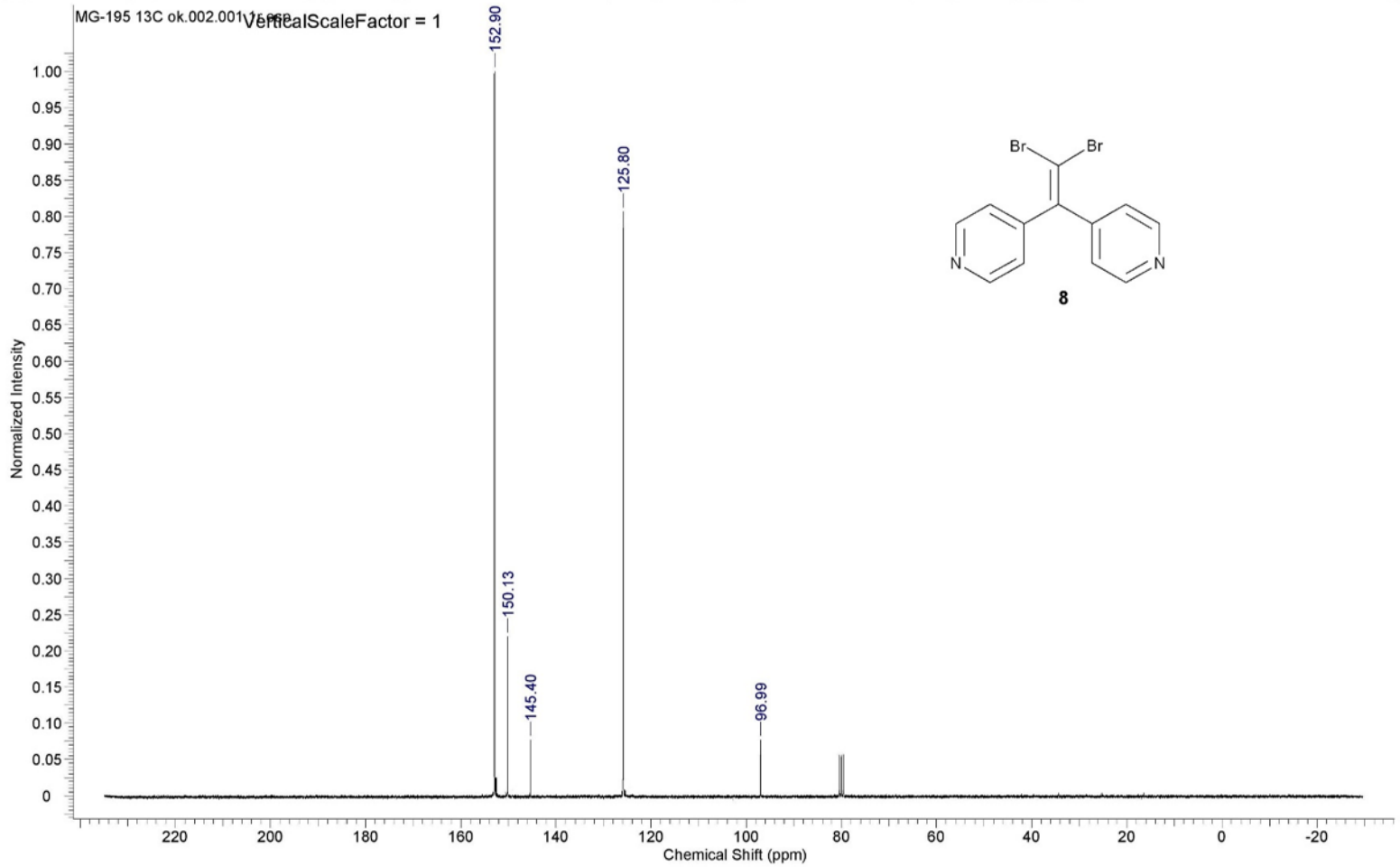
6/11/2016 4:31:18 PM

Acquisition Time (sec)	2.0447	*Comment*	1H Sugar/D2O DRX-400 1H_training Sep 11 2014 Shim update- May 28, 2014				
Date	16 Sep 2015 11:02:08			*Date Stamp*	16 Sep 2015 11:02:08		
File Name	E:\OLD NMR\MG-195 1H\1\pdata\1\1r			*Frequency (MHz)*	400.13	*Nucleus*	1H
Number of Transients	4	*Origin*	spect	*Original Points Count*	16384	*Owner*	root
Points Count	131072	*Pulse Sequence*	zg30	*Receiver Gain*	35.90	*SW(cyclical) (Hz)*	8012.82
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	3193.2092	*Spectrum Type*	STANDARD
Sweep Width (Hz)	8012.76	*Temperature (degree C)*	23.160				



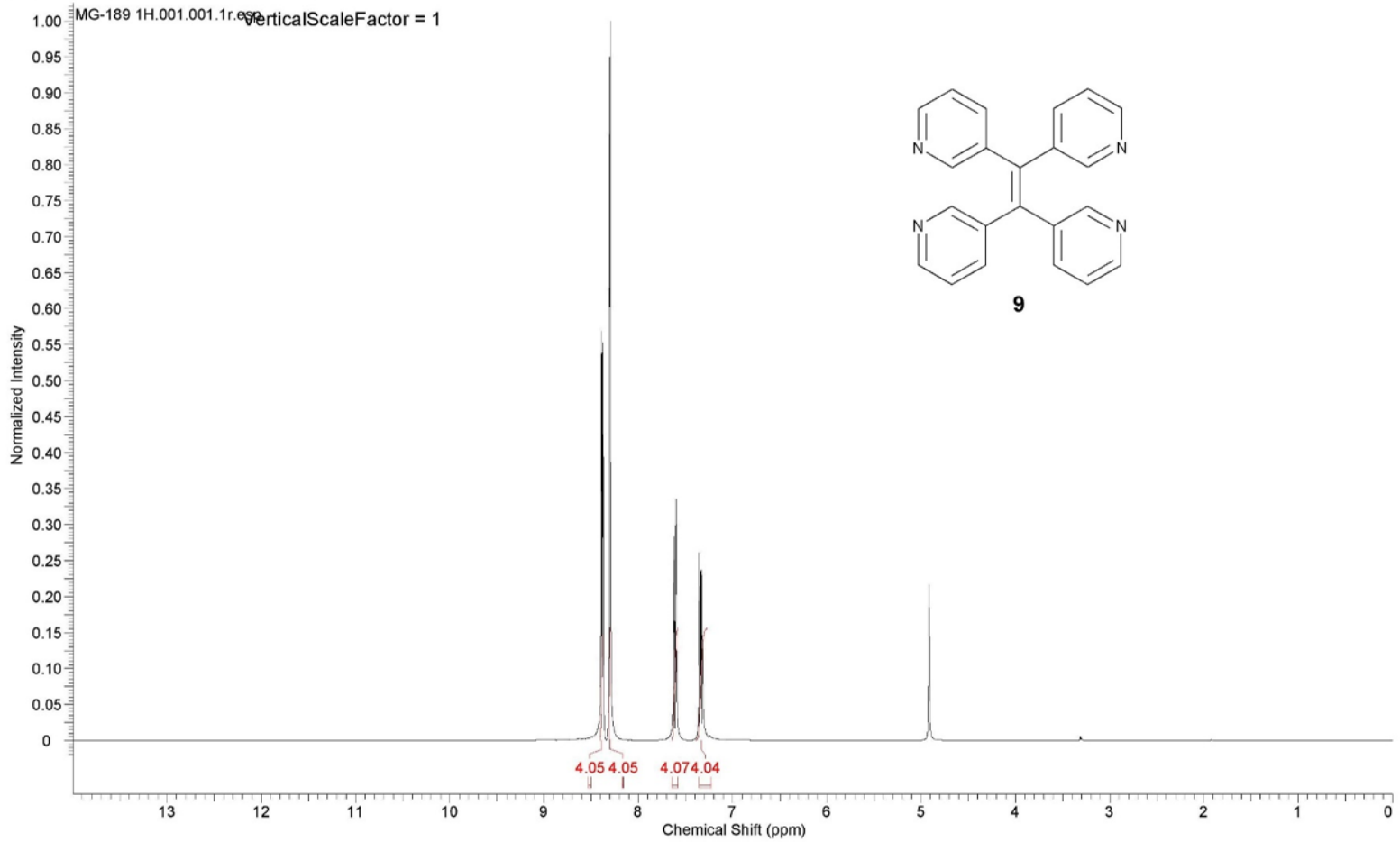
6/11/2016 4:42:14 PM

Acquisition Time (sec)	1.6417	***Comment***	13C TopSpin 1.3 Avance-300 NS = 200			***Date***	16 Sep 2015 11:25:36
Date Stamp	16 Sep 2015 11:25:36			***File Name***	E:\OLD NMR 300\MG-195 13C ok\2\pdata\1\1r		
Frequency (MHz)	75.47	***Nucleus***	13C	***Number of Transients***	400	***Origin***	spect
Original Points Count	32768	***Owner***	root	***Points Count***	131072	***Pulse Sequence***	zgdc30
Receiver Gain	46341.00	***SW(cyclical) (Hz)***	19960.08	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	7747.7314	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	19959.93	***Temperature (degree C)***	24.560



5/8/2016 2:35:16 PM

Acquisition Time (sec)	2.0447	*Comment*	1H Sugar/D2O DRX-400 1H_training Sep 11 2014 Shim update- May 28, 2014				
Date	02 Sep 2015 19:06:24			*Date Stamp*	02 Sep 2015 19:06:24		
File Name	E:\OLD NMR\MG-189 1H\1\pdata\1\1r			*Frequency (MHz)*	400.13	*Nucleus*	1H
Number of Transients	4	*Origin*	spect	*Original Points Count*	16384	*Owner*	root
Points Count	131072	*Pulse Sequence*	zg30	*Receiver Gain*	64.00	*SW(cyclical) (Hz)*	8012.82
Solvent	METHANOL-d4	*Spectrum Offset (Hz)*	3193.2092	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	8012.76
Temperature (degree C)	23.160						



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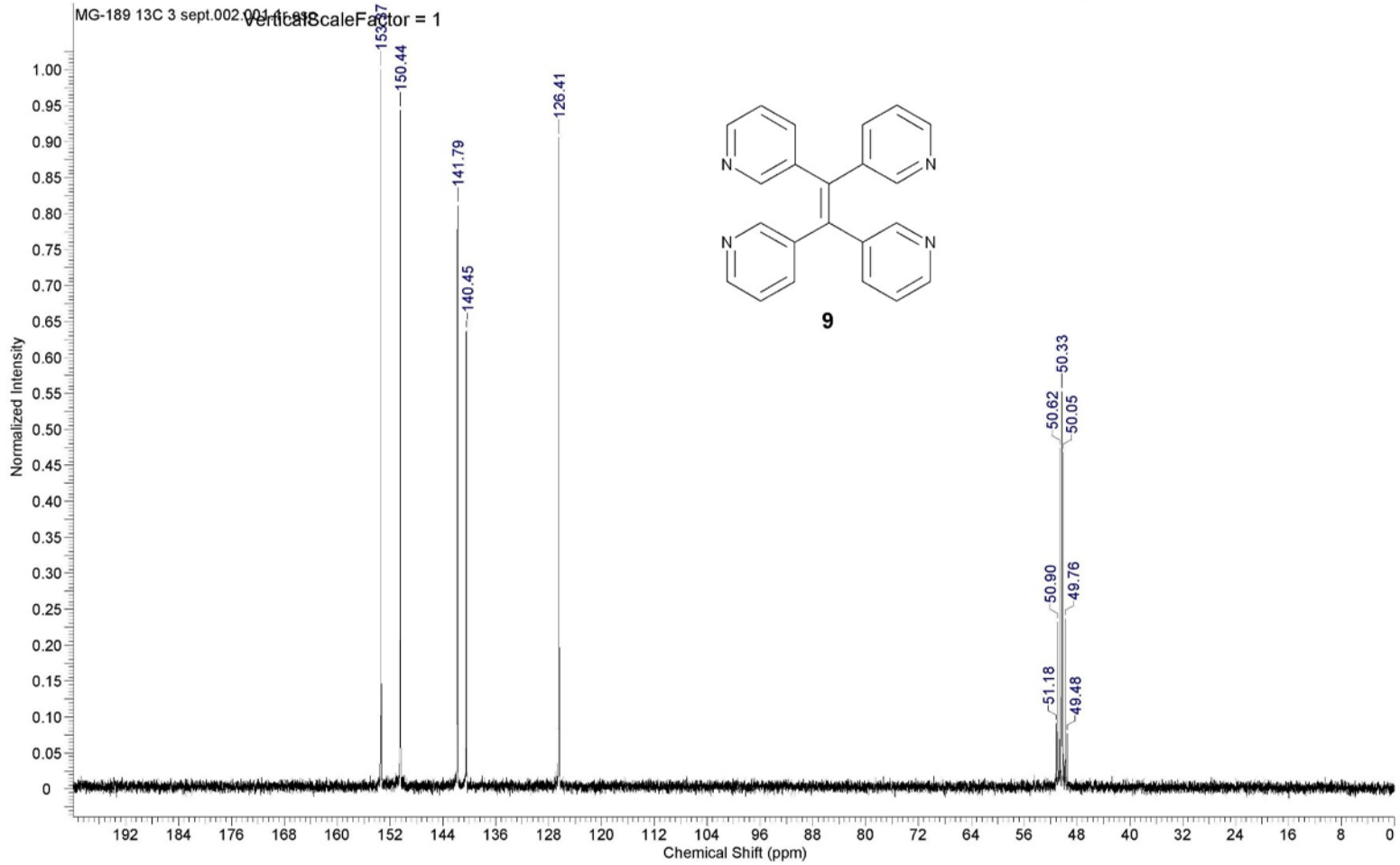
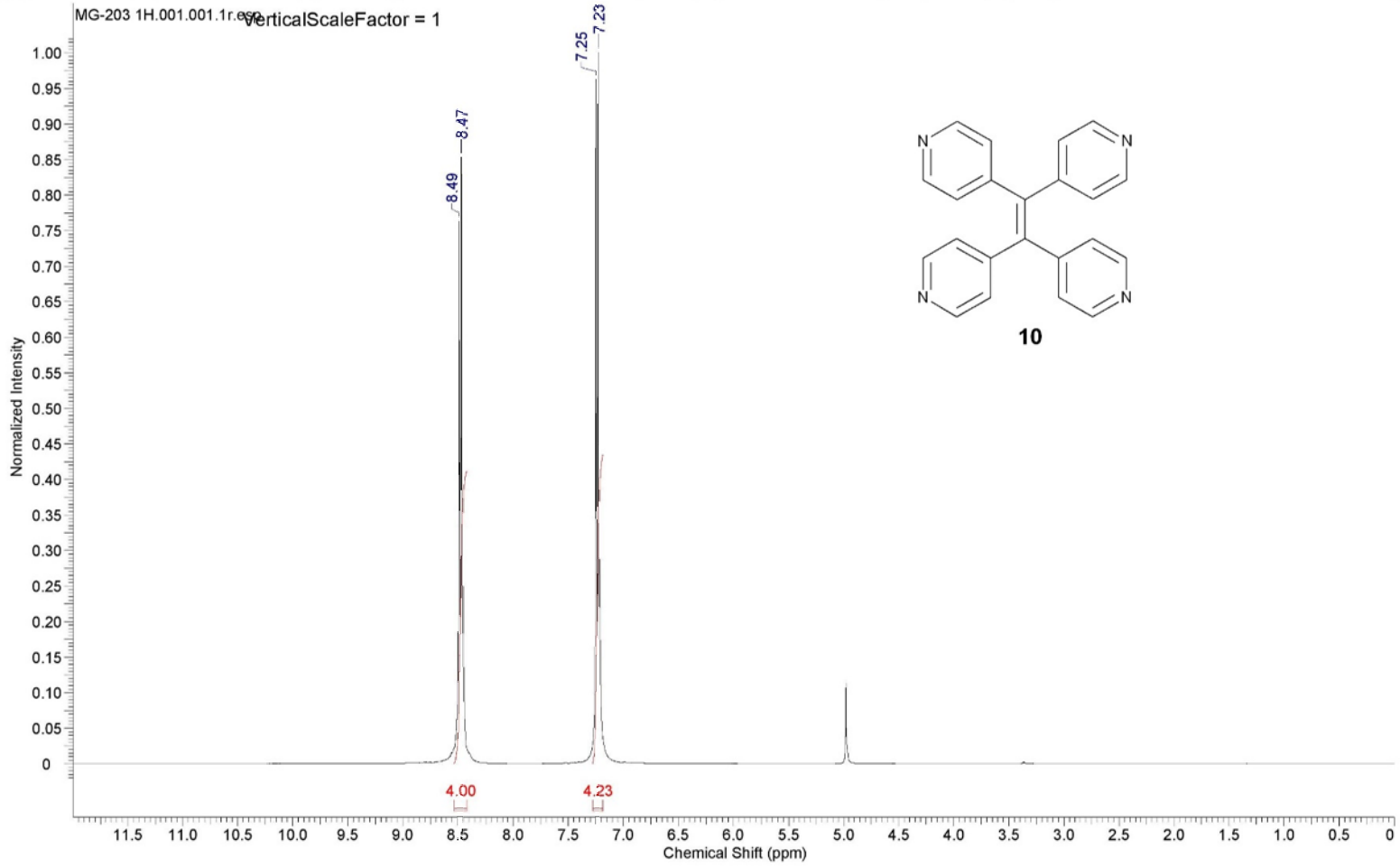
5/8/2016 2:27:53 PM

Acquisition Time (sec)	1.6417	***Comment***	13C TopSpin 1.3 Avance-300 NS = 200			***Date***	03 Sep 2015 15:52:16
Date Stamp	03 Sep 2015 15:52:16			***File Name***	E:\OLD NMR 300\MG-189 13C 3 sept\2\pdata\1\1r		
Frequency (MHz)	75.47	***Nucleus***	13C	***Number of Transients***	700	***Origin***	spect
Original Points Count	32768	***Owner***	root	***Points Count***	131072	***Pulse Sequence***	zgdc30
Receiver Gain	46341.00	***SW(cyclical) (Hz)***	19960.08	***Solvent***	METHANOL-d4		
Spectrum Offset (Hz)	7747.7314	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	19959.93	***Temperature (degree C)***	24.660



2/26/2016 6:39:56 PM

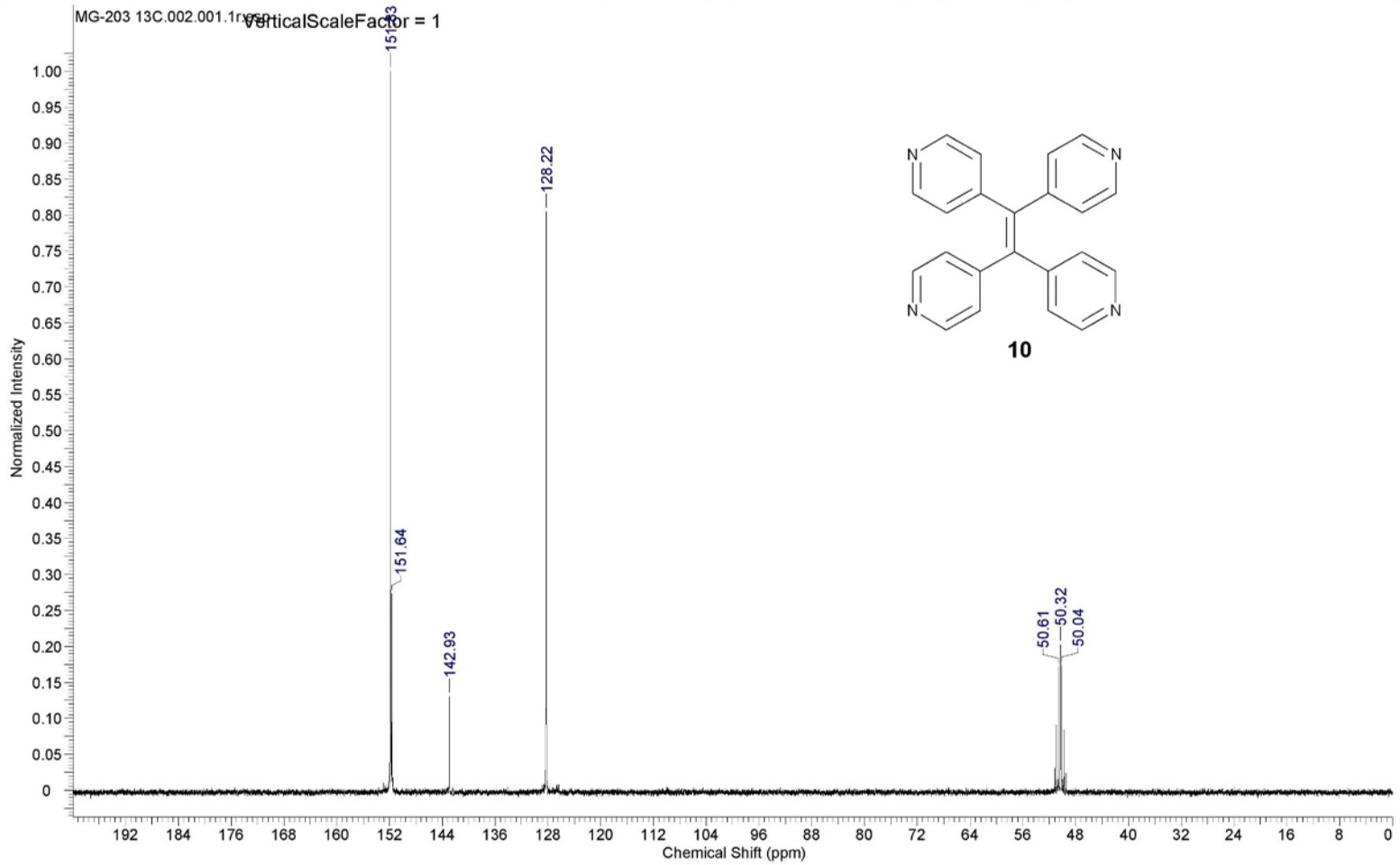
Acquisition Time (sec)	5.3084	***Comment***	1H	Av-300 TopSpin 1.3		***Date***	22 Sep 2015 16:39:12
Date Stamp	22 Sep 2015 16:39:12			***File Name***	E:\Feb. 2016\MG-203 1H\1\pdata\1\1r		
Frequency (MHz)	300.13	***Nucleus***	1H	***Number of Transients***	10	***Origin***	spect
Original Points Count	32768	***Owner***	root	***Points Count***	65536	***Pulse Sequence***	zg30
Receiver Gain	456.10	***SW(cyclical) (Hz)***	6172.84	***Solvent***	METHANOL-d4		
Spectrum Offset (Hz)	2413.5735	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	6172.75	***Temperature (degree C)***	23.560



10

5/8/2016 2:26:02 PM

Acquisition Time (sec)	1.6417	***Comment***	13C TopSpin 1.3 Avance-300 NS = 200			***Date***	22 Sep 2015 17:00:32
Date Stamp	22 Sep 2015 17:00:32			***File Name***	E:\OLD NMR 300\MG-203 13C\2\pdata\1\1r		
Frequency (MHz)	75.47	***Nucleus***	13C	***Number of Transients***	550	***Origin***	spect
Original Points Count	32768	***Owner***	root	***Points Count***	131072	***Pulse Sequence***	zgdc30
Receiver Gain	46341.00	***SW(cyclical) (Hz)***	19960.08	***Solvent***	METHANOL-d4		
Spectrum Offset (Hz)	7747.7314	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	19959.93	***Temperature (degree C)***	24.560



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