ChemistryOPEN

Supporting Information

Acid-Responsive Absorption and Emission of 5-*N*-Arylaminothiazoles: Emission of White Light from a Single Fluorescent Dye and a Lewis Acid

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Contents

General Remarks.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_3OH. Chemical shifts of protons are reported in δ values referenced to tetramethylsilane as an internal standard in $CDCl_3$, and the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. All spectra were acquired in the proton-decoupled mode. HRMS were recorded on a double-focusing mass spectrometer (EI). IR spectra were obtained using KBr pellets or neat films. UV−vis absorption, fluorescence, and absolute fluorescence quantum yields were obtained on the respective spectrometers. Toluene was distilled from sodium metal. All other chemicals were used without further purification. Column chromatography was performed on silica gel 60 N (Spherical Neutral, 100−210 μm). All manipulations of synthesis were carried out under an argon atmosphere. All measurements were carried out under atmosphere at 23 ℃.

Materials.

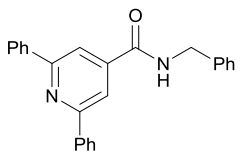
2,6-Diphenylisonicotinic acid, Lawesson's reagent and deuterated solvents were purchased from Aldrich Chemical Company, Inc. Dichloromethane (for synthesis), ethyl acetate, hexane, iodine, methanol, THF and silica gel 60N (Spherical Neutral, 100−210 μm) were purchased from Kanto Chemical Co., Inc. Acetonitrile, benzylamine, dichloromethane (for measurements), diethyl ether, $Na_2S_2O_3$, $MgSO_4$, toluene and 3 Å molecular sieve were purchased from Nakarai Tesque Inc. *n*-BuLi was purchased from Mitsuwa Chemical, Ltd. The compounds **1**, **2**, thioamides and thioformamides were prepared according to literature procedures.[1]

Instruments.

^{1}H and ^{13}C NMR spectra were measured on a JNM-α400 spectrometer. The mass spectra (MS) and high resolution mass spectra (HRMS) were taken on JMS-700 mass spectrometers. The IR spectra were obtained on a JASCO-FT-IR 410 spectrophotometer. UV-vis spectra were measured on a HITACHI U-4100 spectrophotometer. Fluorescence spectra were measured on a HORIBA FluoroMax-4. Excited and fluorescence spectra were measured on a JASCO spectrofluorometer FP-8600. Fluorescent quantum yields were measured on a HAMAMATSU absolute PL quantum yield spectrometer C11347-01. Fluorescence lifetimes were measured on a HAMAMATSU compact fluorescence lifetime spectrometer C11367.

Synthesis of thioamide

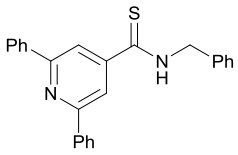
***N*-Phenylmethyl-3,5-diphenyl-4-pyridincarboamide**



The 2,6-diphenylisonicotinic acid (0.826 g, 3.0 mmol) and 3 Å MS (0.27 g) was added benzylamine (0.33 mL, 3.0 mmol) at room temperature, and the mixture was stirred for 46.5 h at 160 ℃. The resulting mixture was filtered, and extracted with methanol. The residue was purified by column chromatography (SiO_2, CH_2Cl_2) and recrystallized from CH_2Cl_2/hexane to give amide (0.922 g, 84%) as a white solid. (m.p. 178−180 ℃); IR (KBr) 3285, 3031, 1638, 1537, 1495, 1455, 1404, 1371, 1344, 1274, 1244, 1179, 1072, 918, 784, 683

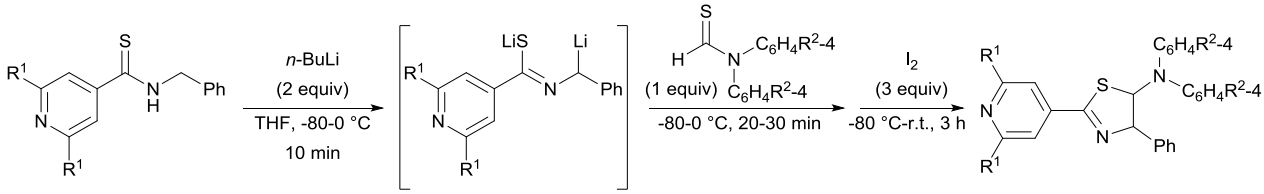
cm^{-1}; ^{1}H NMR (400 MHz, CD_3OH) δ 4.64 (d, *J* = 8.0 Hz, 2H, CH_2), 6.57 (br, 1H, NH), 7.28−7.45 (m, 12H, Ar), 7.82 (s, 2H, Py), 8.09−8.11 (m, 3H, Ar); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 44.2 (CH_2), 115.9, 127.1, 127.8, 128.0, 128.7, 128.8, 128.9, 129.5, 129.9, 137.0, 137.6, 138.6, 143.3, 157.8, 166.2 (Ar), ; MS (EI) *m*/*z* 364 (M^+); HRMS (EI) Calcd for $C_{25}H_{20}N_2O$: 364.1576; found : 364.1588.

_N_-Phenylmethyl-3,5-diphenyl-4-pyridincarbothioamide



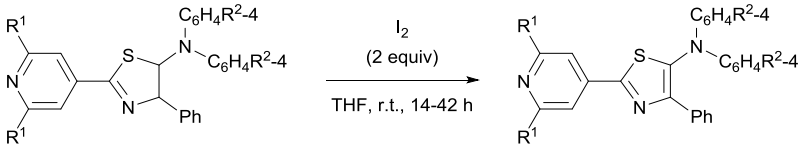
To a solution of *N*-phenylmethyl-3,5-diphenyl-4-pyridincarboamide (0.364 g, 1.0 mmol) in toluene (5.0 mL) was added Lawesson's reagent (0.809 g, 2.0 mmol) at room temperature, and the mixture was stirred for 6 h at 115 ℃. The resulting mixture was concentrated in vacuo. The residue was purified by column chromatography (SiO_2, CH_2Cl_2, methanol and hexane : EtOAc = 5 : 1) to give thioamide (0.269 g, 71%) as a yellow solid. (m.p. 166−167 ℃); IR (KBr) 3177, 3030, 2916, 1603, 1549, 1495, 1391, 1329, 1259, 1197, 1077, 992, 962, 660 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 (d, *J* = 4.0 Hz, 2H, CH_2), 7.38−7.50 (m, 11H, Ar), 7.89 (m, 3H, NH, Py), 8.12 (d, *J* = 8.0 Hz, 4H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.1 (CH_2), 115.7, 127.2, 128.6, 128.6, 128.9, 129.3, 129.6, 135.8, 138.7, 150.3, 157.7 (Ar), 197.5 (S=C); MS (EI) *m*/*z* 380 (M^+); HRMS (EI) Calcd for $C_{25}H_{20}N_2S$: 380.1347; found : 380.1350.

General Procedure for the Preparation of Thiazolines.



To a solution of thioamide (1 equiv) in THF was added slowly a 1.25 M solution of *n*-butyllithium in *n*-hexane (2 equiv) at -80−0 ℃, and the mixture was stirred for 10 min at this temperature. To this was added thioformamide (1 equiv) at -80−0 ℃, and the mixture was stirred for 20−30 min at this temperature. To this was added iodine (3 equiv) at -80−0 ℃, and the mixture was stirred for 3 h at -80 ℃ to room temperature. The resulting mixture was poured into a saturated aqueous solution of $Na_2S_2O_3$, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (SiO_2) to give the corresponding thiazolines.

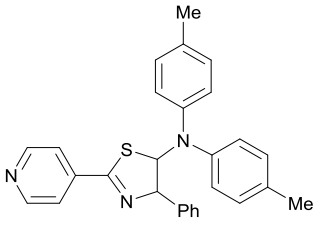
General Procedure for the Preparation of Thiazoles.



To a solution of thiazoline (1 equiv) in THF was added iodine (2 equiv) at room temperature, and the mixture was stirred for 14−42 h at room temperature. The resulting mixture was poured into a saturated

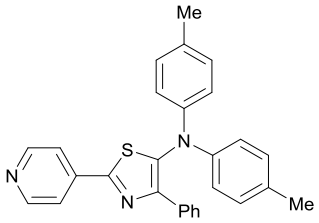
aqueous solution of $Na_2S_2O_3$, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (SiO_2) to give the corresponding thiazoles.

(4R*,5S*)-4,5-Dihydro-2-(4-pyridyl)-4-phenyl-*N*,*N*-bis(4-methylphenyl)-5-thiazolamine



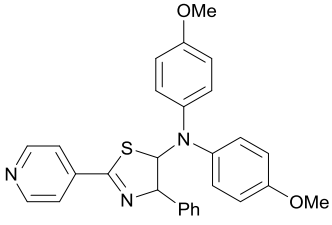
According to the general procedure for thiazolines, the crude material was purified by column chromatography (SiO_2, hexane : EtOAc = 5 : 1) to give the corresponding thiazoline (0.156 g, 72%) as a yellow oil. : IR (KBr) 3028, 2920, 2859, 1592, 1508, 1407, 1237, 1034, 962, 824, 730, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 6H, Me), 6.00 (d, *J* = 4.0 Hz, 1H, SCH), 6.34 (d, *J* = 4 Hz, 1H, NCH), 6.91 (d, *J* = 8 Hz, 4H, Ar), 7.06 (d, *J* = 8 Hz, 4H, Ar), 7.28−7.35 (m, 5H, Ar), 7.63−7.64 (m, 2H, Ar), 7.67−7.68 (m, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6, 85.4, 85.5, 124.9, 126.2, 129.2, 131.0, 131.8, 132.9, 136.4, 142.4, 143.5, 146.1, 153.2 169.9; MS (EI) *m*/*z* 435 (M^+); HRMS (EI) Calcd for $C_{28}H_{25}N_3OS$: 435.1769; found : 435.1761.

2-(4-Pyridyl)-4-phenyl-*N*,*N*-bis(4-methylphenyl)-5-thiazolamine (**3**)



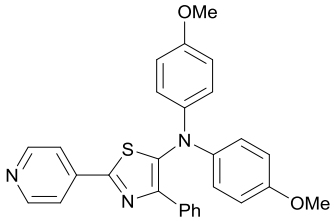
According to the general procedure for thiazoles, compound **3** was prepared. The crude material was purified by column chromatography (SiO_2, hexane : EtOAc = 3 : 1) to give thiazole **3** (0.09 g, 63%) as an orange oil.: IR (KBr) 3027, 2919, 1595, 1505, 1444, 1345, 1286, 995, 909, 812, 727, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 6H, OMe), 6.97−7.03 (m, 7H, Ar), 7.21−7.29 (m, 4H, Ar), 7.79−7.80 (m, 2H, Ar), 7.92−7.94 (m, 2H, Ar), 8.66−8.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6 (Me), 122.8, 123.3, 124.5, 130.3, 131.0, 131.1, 132.8, 135.9, 139.6, 143.7, 147.1, 151.5, 153.3 (Ar), 162.3 (SC=N); MS (EI) *m*/*z* 433 (M^+); HRMS (EI) Calcd for $C_{28}H_{23}N_3S$: 433.1613; found : 433.1611.

(4R*,5S*)-4,5-Dihydro-2-(4-pyridyl)-4-phenyl-*N*,*N*-bis(4-methoxyphenyl)-5-thiazolamine



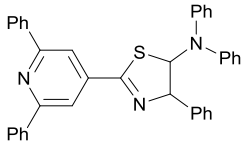
According to the general procedure for thiazolines, the crude material was purified by column chromatography (SiO_2, hexane : EtOAc = 10 : 1 and 5 : 1) to give the corresponding thiazoline (0.189 g, 81%) as a yellow oil. : IR (KBr) 3037, 2998, 2930, 2832, 1591, 1506, 1242, 1032, 961, 823, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 6H, OMe), 6.00 (d, *J* = 4.0 Hz, 1H, SCH), 6.31 (d, *J* = 4 Hz, 1H, NCH), 6.79−6.82 (m, 4H, Ar), 6.95−6.98 (m, 4H, Ar), 7.31−7.35 (m, 5H, Ar), 7.64−7.66 (m, 2H, Ar), 7.68 (d, 4.0 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 58.3, 58.4, 85.6, 86.3, 117.6, 125.1, 127.6, 129.1, 129.3, 131.1, 131.6, 142.1, 152.9, 153.0, 159.1, 169.7; MS (EI) *m*/*z* 465 (M^+, -2H); HRMS (EI) Calcd for $C_{28}H_{25}N_3O_2S$: 467.1667; found : 467.1646.

2-(4-Pyridyl)-4-phenyl-*N*,*N*-bis(4-methoxyphenyl)-5-thiazolamine (**4**)



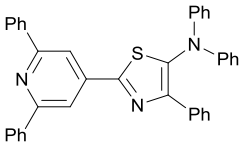
According to the general procedure for thiazoles, compound **4** was prepared. The crude material was purified by column chromatography (SiO_2, hexane : EtOAc = 3 : 1) to give thiazole **4** (0.05 g, 44%) as a brown oil.: IR (KBr) 2929, 1593, 1504, 1443, 1241, 1779, 1033, 823, 696, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 6H, OMe), 6.77−6.79 (m, 4H, Ar), 7.01−7.03 (m, 4H, Ar), 7.21−7.29 (m, 3H, Ar), 7.79−7.81 (m, 2H, Ar), 7.93−7.95 (m, 2H, Ar), 8.68−8.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 55.9 (OMe), 114.8, 114.9, 120.1, 123.1, 123.4, 127.7, 128.4, 133.4, 140.8, 141.1, 143.9, 148.0, 150.7, 150.9, 156.1 (Ar), 159.0 (SC=N); MS (EI) *m*/*z* 465 (M^+); HRMS (EI) Calcd for $C_{28}H_{23}N_3O_2S$: 465.1511; found : 465.1530.

(4R*,5S*)-4,5-Dihydro-2-(3,5-diphenyl-4-pyridyl)-4-phenyl-*N*,*N*-diphenyl-5-thiazolamine



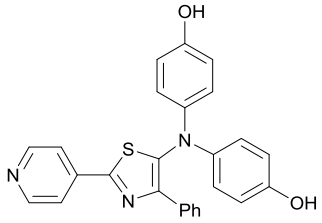
According to the general procedure for thiazolines, the crude material was purified by column chromatography (SiO_2, hexane : EtOAc = 20 : 1) to give the corresponding thiazoline (0.136 g, 49%) as a pale yellow solid. (m.p. 87−90 ℃) : IR (KBr) 3429, 3033, 1592, 1578, 1551, 1492, 1449, 1405, 1352, 1248, 1206, 1179, 1032, 906, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.11 (d, *J* = 4.0 Hz, 1H, SCH), 6.41 (d, *J* = 4.0 Hz, 1H, NCH), 7.07−7.12 (m, 6H, Ar), 7.28−7.38 (m, 8H, Ar), 7.42−7.52 (m, 7H, Ar), 8.05 (s, 2H, Py), 8.19 (d, *J* = 4.0 Hz, 4H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.0, 82.7, 117.1, 123.5, 124.1, 126.4, 127.1, 128.2, 128.7, 129.0, 129.3, 129.5, 138.8, 139.3, 142.2, 145.5, 157.6 (Ar), 167.5 (SC=N); MS (EI) *m*/*z* 559 (M^+); HRMS (EI) Calcd for $C_{38}H_{29}N_3S$: 559.2082; found : 559.2077.

2-(3,5-Diphenyl-4-Pyridyl)-4-phenyl-*N*,*N*-diphenyl-5-thiazolamine (**6**)



According to the general procedure for thiazoles, compound **6** was prepared. The crude material was purified by column chromatography (SiO_2, hexane : EtOAc = 20 : 1) and GPC to give thiazole **6** (0.05 g, 65%) as a yellow solid. (m.p. 240−242 ℃): IR (KBr) 3435, 1595, 152, 1524, 1488, 1443, 1352, 1306, 1271, 1154, 1072, 908, 777, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.02 (t, *J* = 4.0 Hz, 2H, Ar), 7.14−7.16 (m, 4H, Ar), 7.23−7.29 (m, 7H, Ar), 7.45−7.47 (m, 2H, Ar), 7.49−7.53 (m, 4H, Ar), 7.94−7.96 (m, 2H, Ar), 8.20−8.23 (m, 6H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.2, 121.8, 123.6, 127.2, 127.6, 128.4, 128.8, 129.5, 133.1, 139.1, 142.0, 142.5, 146.5, 148.9, 149.2, 157.9, 159.4 (Ar), 160.8 (SC=N); MS (EI) *m*/*z* 557 (M^+); HRMS (EI) Calcd for $C_{38}H_{27}N_3S$: 557.1926; found : 557.1923.

2-(4-Pyridyl)-4-phenyl-*N*,*N*-bis(4-hydroxyphenyl)-5-thiazolamine (**5**)

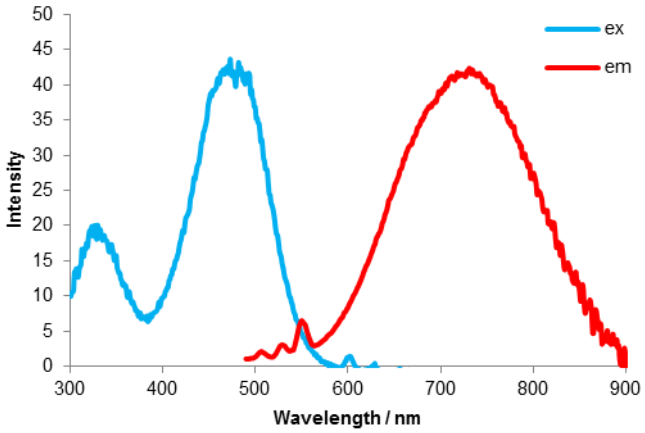


To a 5-*N*,*N*-bis(4-methoxyphenyl)thiazole **4** (0.028 g, 0.06 mmol) was added HBr (0.1 mL) at room temperature, and the mixture was stirred for 13 h at 100 ℃. The resulting mixture was poured into a saturated aqueous solution of K_2CO_3, and extracted with EtOAc. The organic layer was dried over Na_2SO_4

and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, 5−7% MeOH in CH_2Cl_2) to give thiazole **5** (0.023 g, 90%) as a yellow solid. (m.p. 272−274 ℃); IR (KBr) 3391, 3233, 3043, 3025, 2796, 1602, 1507, 1441, 1242, 1213, 830, 695 cm^{-1}; ^1H NMR (400 MHz, CD_3OH) δ 6.62−6.65 (m, 4H, Ar), 6.85−6.87 (m, 4H, Ar), 7.18−7.23 (m, 3H, Ar), 7.82−7.84 (m, 2H, Ar), 7.88−7.90 (m, 2H, Ar), 8.57−8.59 (m, 2H, Ar) The protons due to OH were not observed.; ^{13}C NMR (100 MHz, CD_3COCD_3) δ 116.6, 117.4, 120.9, 124.7, 128.8, 129.3, 129.5, 134.9, 141.3, 148.0, 152.1, 155.2, 159.5, 165.2; MS (EI) *m/z* 437 (M^+); HRMS (EI) Calcd for $C_{26}H_{19}N_3O_2S$: 437.1198; found : 437.1212.

Photophysical properties and spectra (The addition of Brønsted acids)

Fig. S1 The excitation and fluorescent spectra of **7** with TfOH in CH_3CN



Spectra of thiazole **3**−**6** and **8**−**11** were measured in Et_2O (Table 2). Fluorescent spectra of **8**−**10** were not observed because of their weak fluorescent intensities.

Fig. S2 Absorption spectra of **3** and **8**

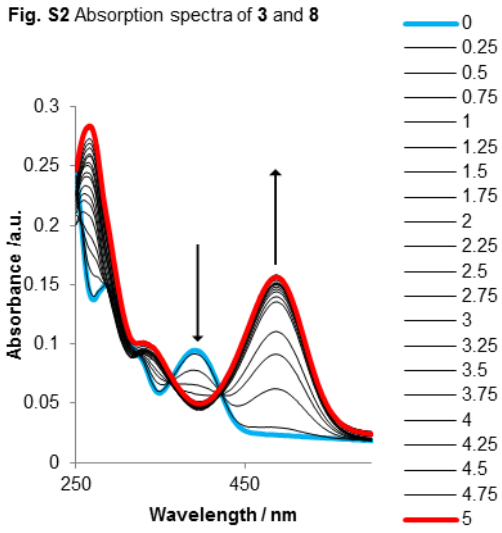


Fig. S3 Fluorescent spectra of **3** and **8**

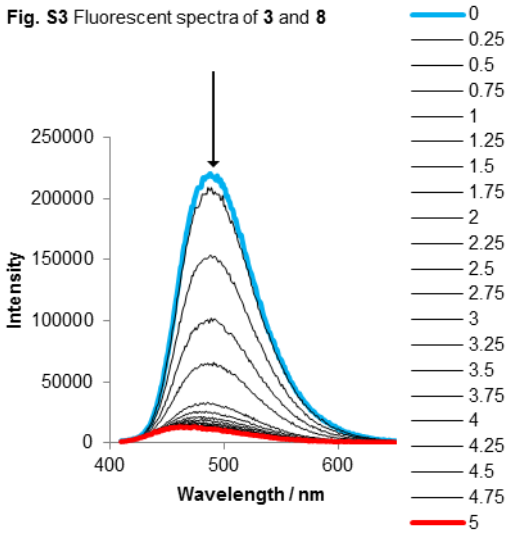


Fig. S4 Absorption spectra of **4** and **9**

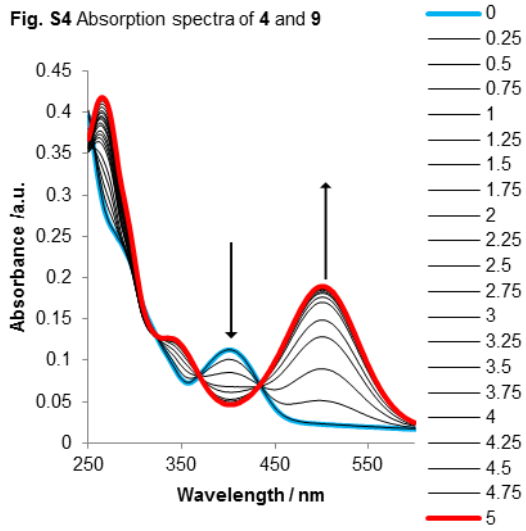


Fig. S5 Fluorescent spectra of **4** and **9**

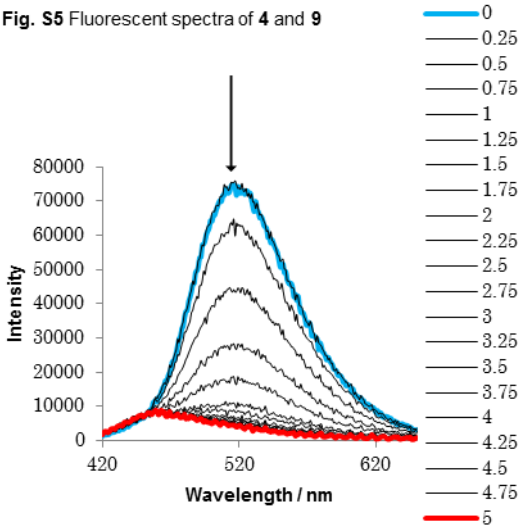


Fig. S6 Absorption spectra of **5** and **10**

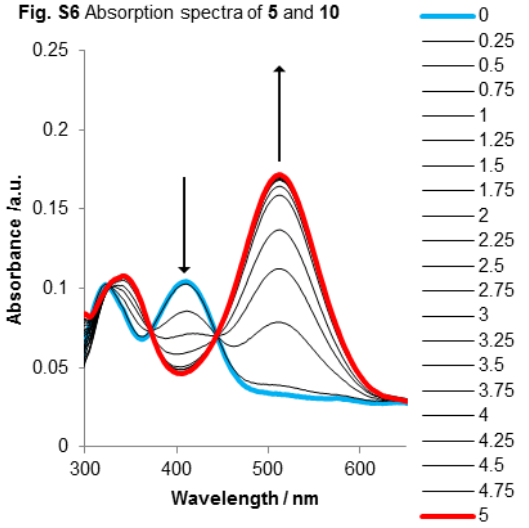


Fig. S7 Fluorescent spectra of **5** and **10**

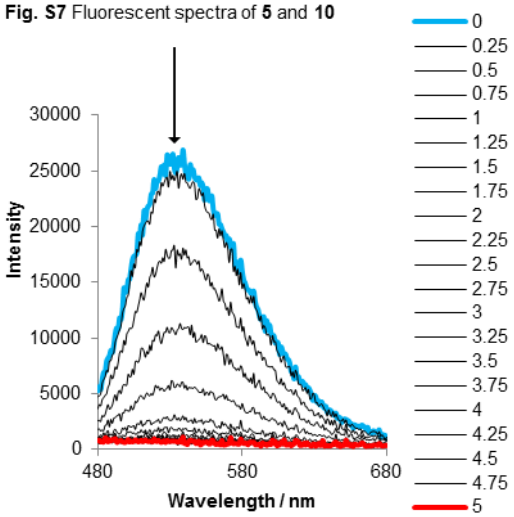


Fig S8. Absorption spectra of **6** and **11**

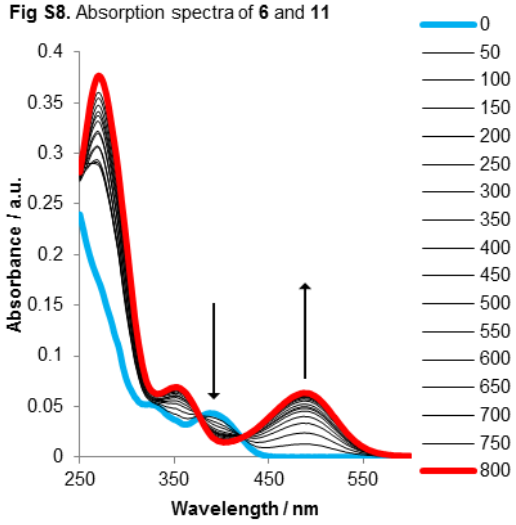


Fig. S9 Fluorescent spectra of **6** and **11**

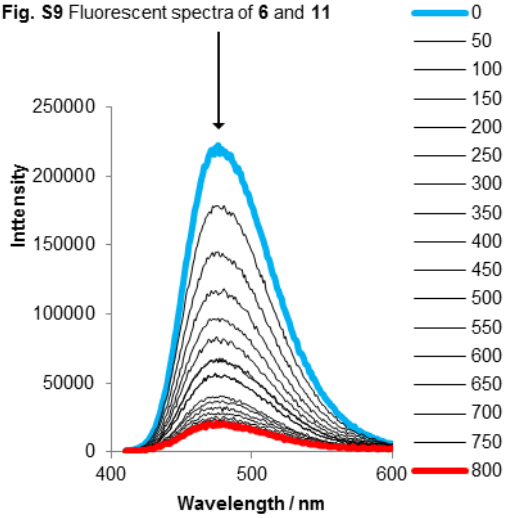
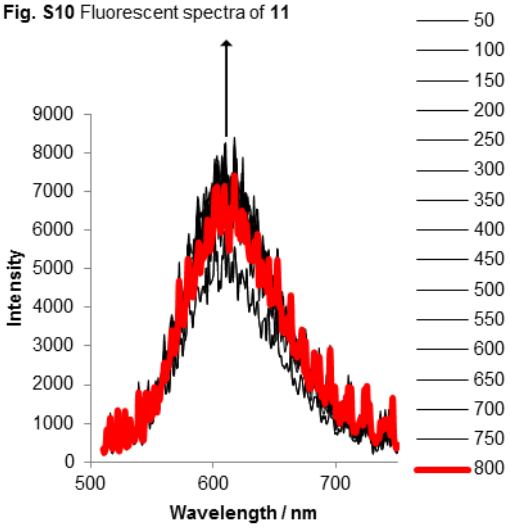
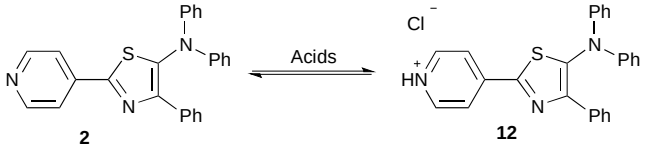


Fig. S10 Fluorescent spectra of **11**



The addition of HCl to thiazole **2**, shifted its wavelengths of absorption and emission to longer wavelengths by 83 nm and 108 nm, respectively (Table S1, entry 1). However, **2** did not show any changes when adding TFA and CH_3COOH (entries 2 and 3).

Table S1. Photophysical properties of thiazole **2** and **12**[a]



entry	λ_{abs} (nm)	λ_{em} (nm)[b]	acid	IP[c] (nm)		λ_{abs} (nm)	λ_{em} (nm)[b]
1	382	472	HCl	412	**12**	465	580
2	382	472	TFA	-	-	-	
3	382	472	CH_3COOH	-	-	-	

[a]In Et_2O, c = 10^{-5} M. [b]Excited at wavelength of maximum absorption. [c]IP stands for isosbestic point.

Fig. S11 Absorption spectra of **2** with HCl

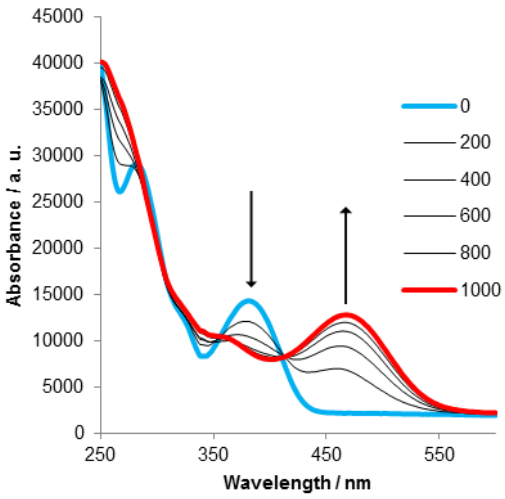


Fig. S12 Fluorescent spectra of **2** with HCl

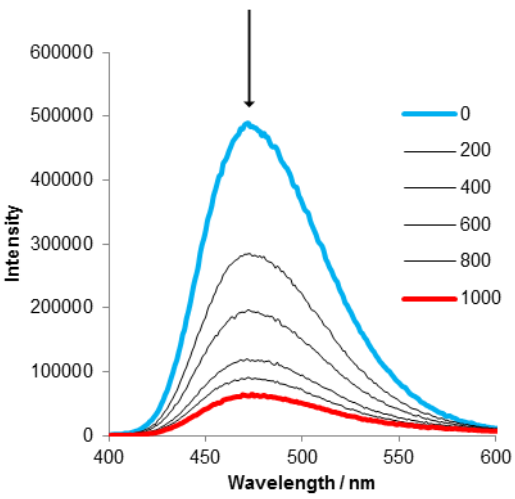
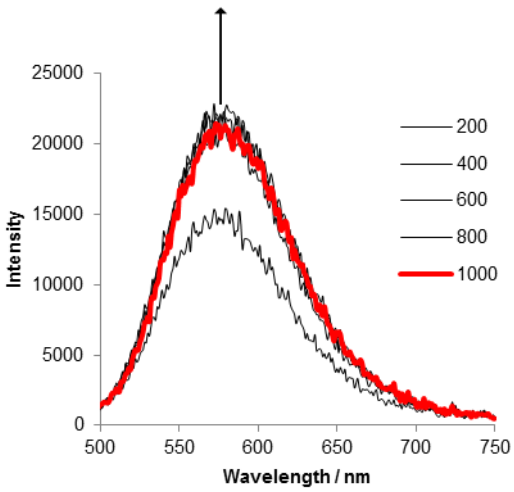


Fig. S13 Fluorescent spectra of **12**



Photophysical properties and spectra (The addition of Lewis acids)

Fig. S14 Absorption spectra of **2**·BCl_3

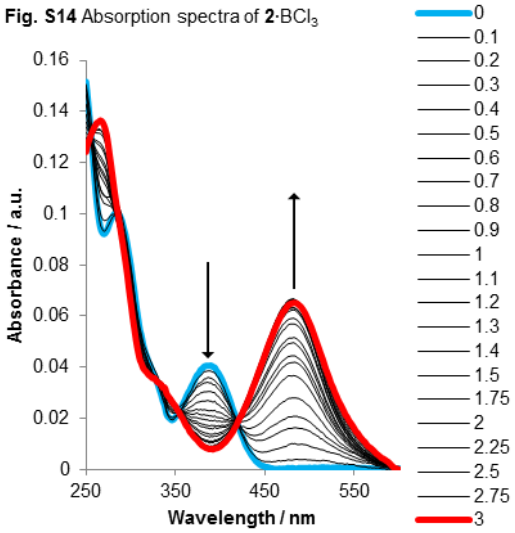


Fig. S15 Fluorescent spectra of **2** with BCl_3

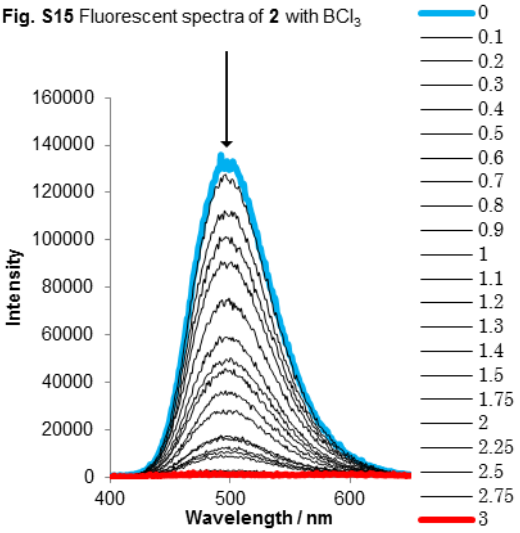


Fig. S16 Fluorescent spectra of **2**·BCl_3

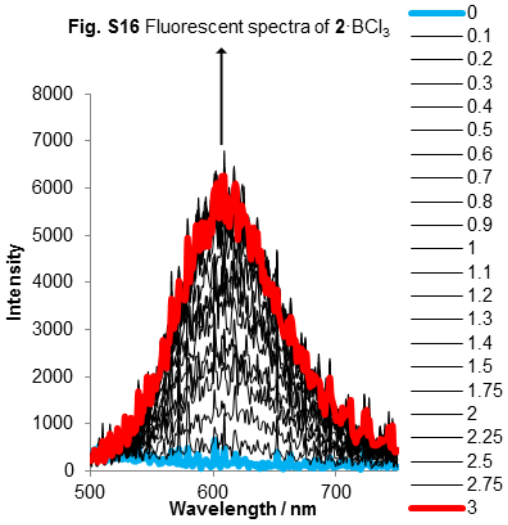


Fig. S17 Absorption spectra of **2**·$AlCl_3$

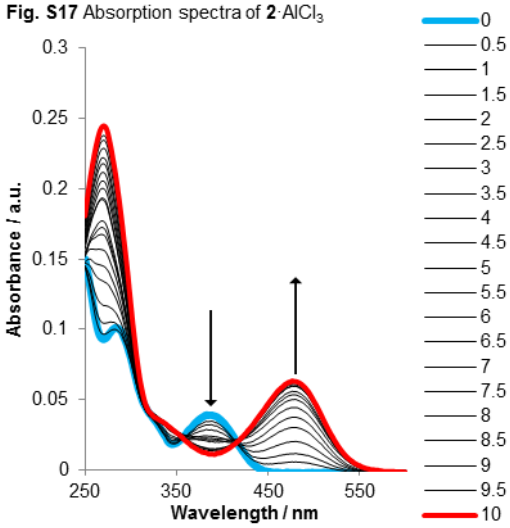


Fig. S18 Fluorescent spectra of **2** with $AlCl_3$

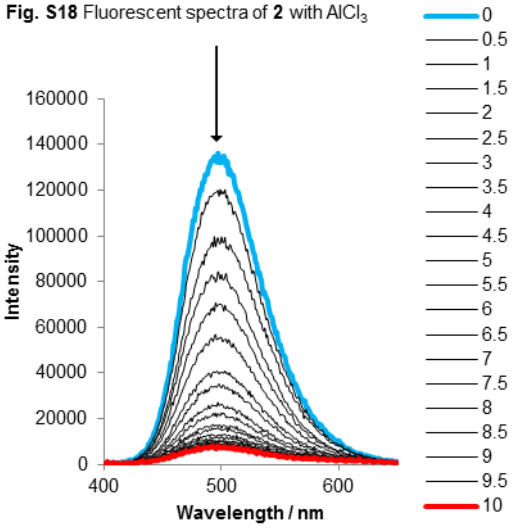


Fig. S19 Fluorescent spectra of **2**·$AlCl_3$

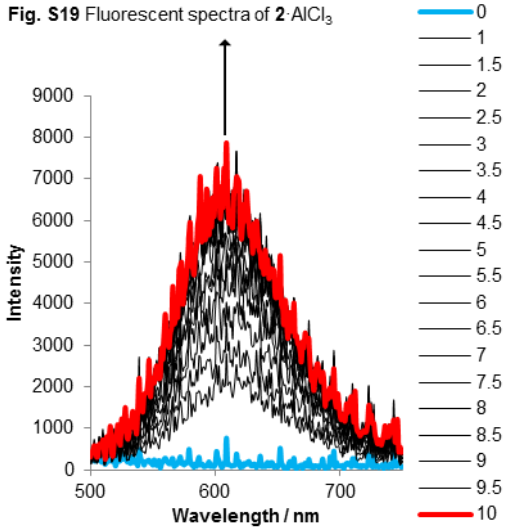


Fig. S20 Absorption spectra of **2**·$GaCl_3$

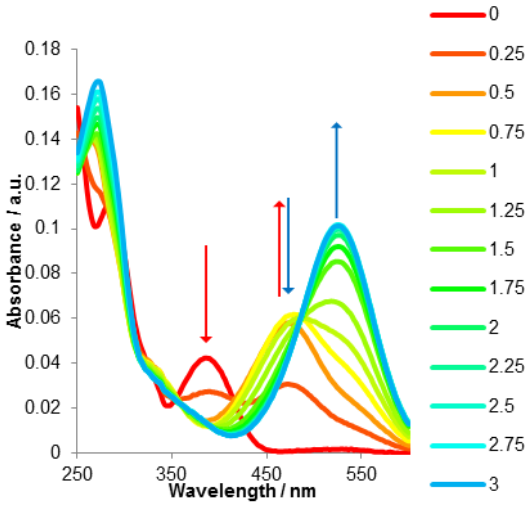


Fig. S21 Fluorescent spectra of **2** with $GaCl_3$

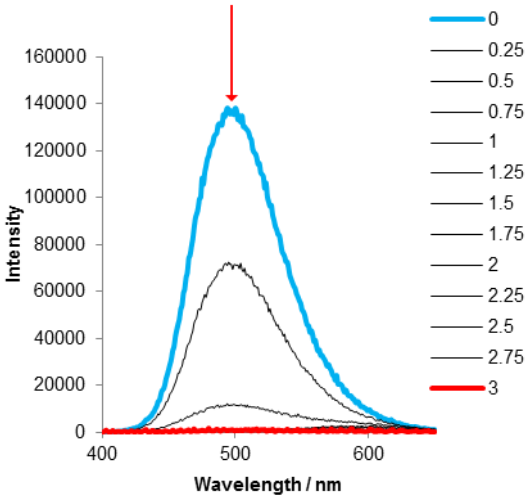


Fig. S22 Fluorescent spectra of **2**·$GaCl_3$

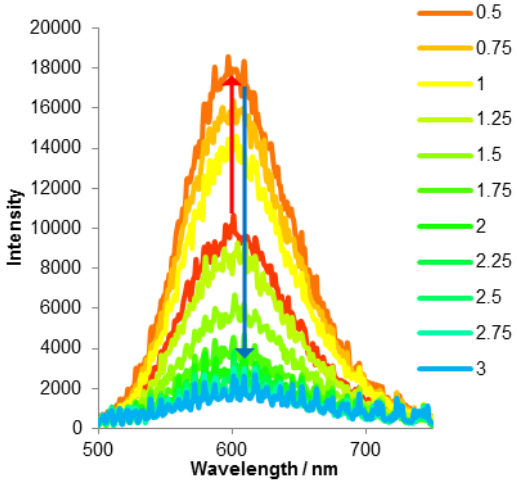
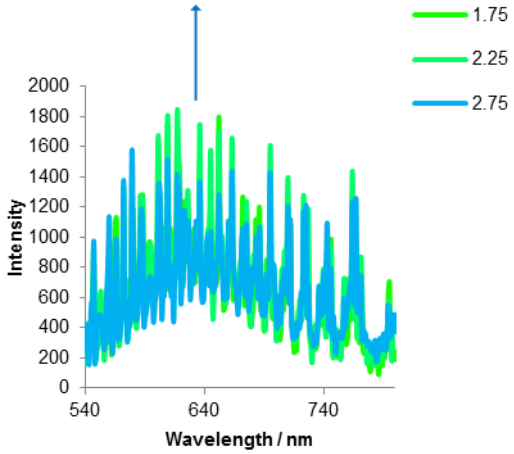


Fig. S23 Fluorescent spectra of **2**·$GaCl_3$



Photophysical properties of the mixture of thiazole **2** and Lewis acids were measured in CH_2Cl_2. The reaction of **2** and $GaCl_3$ passed through two steps (0.25−0.5 equiv. and 0.75−3 equiv. of $GaCl_3$). The red arrow indicates the equivalents of $GaCl_3$ from 0.25 to 0.5 equiv. While, the blue arrow indicates the equivalents of $GaCl_3$ from 0.75 to 3 equiv.

Fig. S24 Absorption spectra of **2**·$B(C_6F_5)_3$

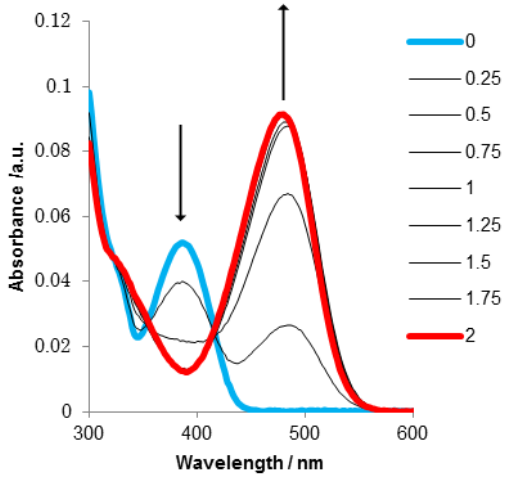


Fig. S25 Fluorescent spectra of **2** with $B(C_6F_5)_3$

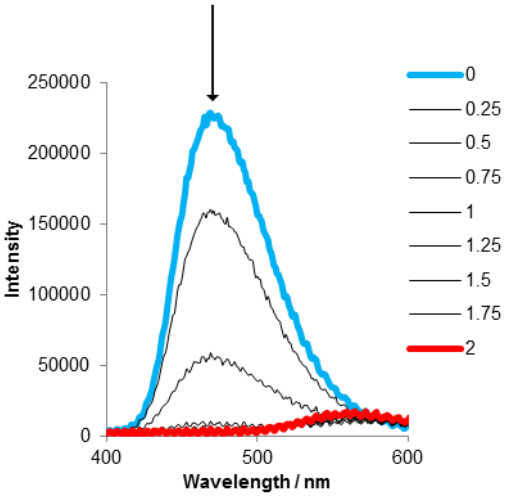


Fig. S26 Fluorescent spectra of **2**·$B(C_6F_5)_3$

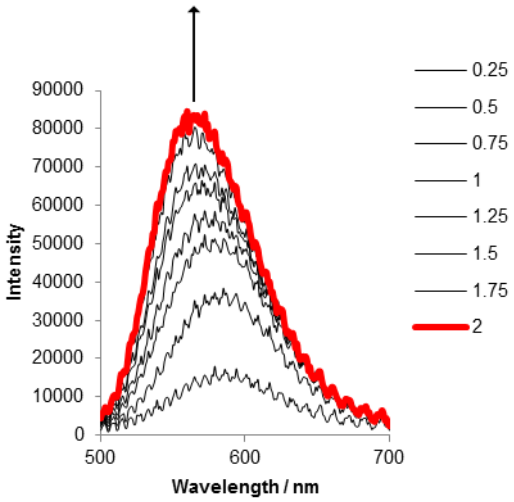


Fig. S27 Absorption spectra of **6**·$B(C_6F_5)_3$

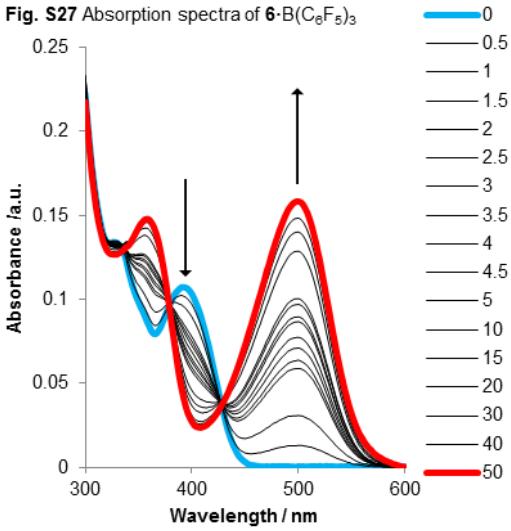


Fig. S28 Fluorescent spectra of **6** with $B(C_6F_5)_3$

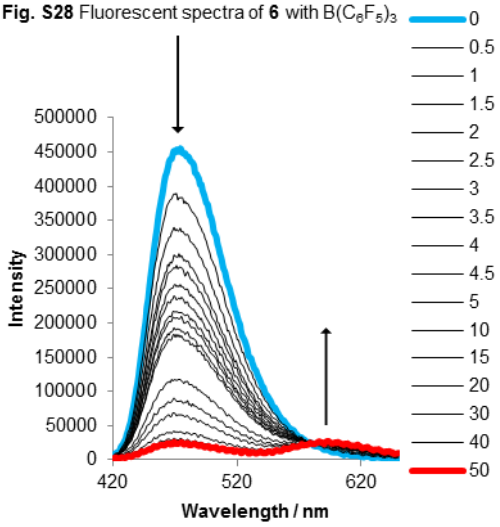
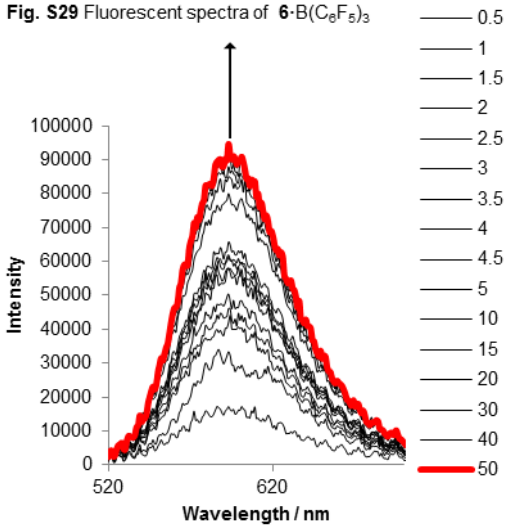


Fig. S29 Fluorescent spectra of **6**·$B(C_6F_5)_3$



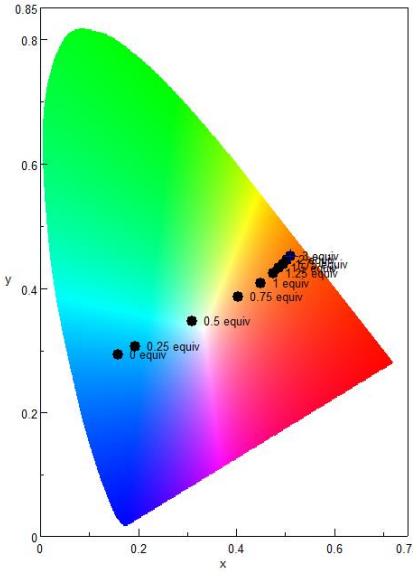
The spectra of absorption and emission of **2** and **6** changed by adding $B(C_6F_5)_3$.

CIE coordinates

Table S2. CIE data of **2** with 0-3 equivalents of $B(C_6F_5)_3$[a]

equiv[b]	x	y
0	0.16	0.29
0.25	0.19	0.31
0.5	0.31	0.35
0.75	0.40	0.38
1	0.45	0.41
1.25	0.47	0.42
1.5	0.49	0.43
1.75	0.49	0.44
2	0.50	0.44
3	0.51	0.45

[a]In toluene, c = 10^{-5} M. Excited at 365 nm.
[b]Equivalents of $B(C_6F_5)_3$



CIE coordinates of solution **2** and $B(C_6F_5)_3$ were plotted from the emission spectra (Figure 3 (b), Table S2). The color of the solution changed more drastically than that of **6**. The solution **2** showed bluish white emission when 0.5 equivalents of $B(C_6F_5)_3$ were added.

Fig. S30 Fluroescent spectra of **6**·$B(C_6F_5)_3$ for CIE

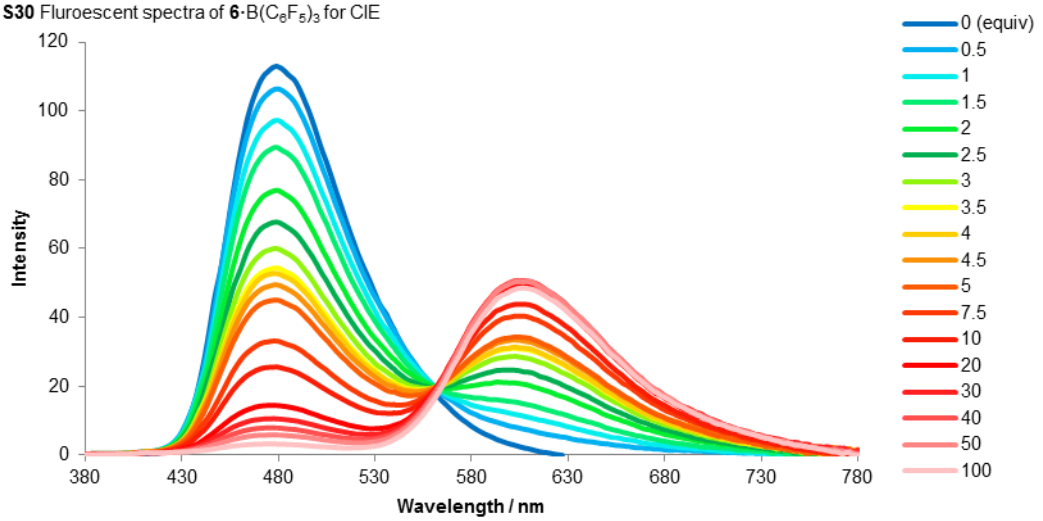
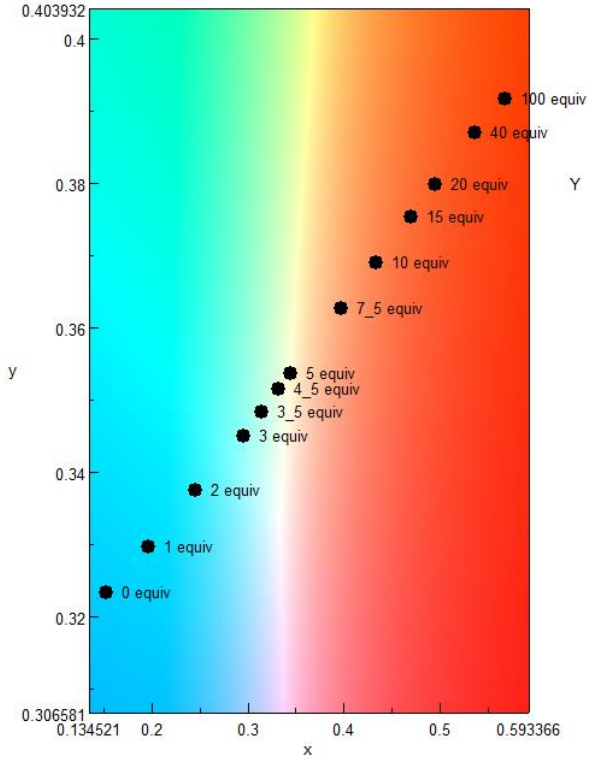


Table S3. CIE data of **6** with 0-100 equivalents of $B(C_6F_5)_3$[a]

equiv[b]	x	y
0	0.15	0.32
0.5	0.18	0.33
1	0.20	0.33
1.5	0.21	0.33
2	0.25	0.34
2.5	0.27	0.34
3	0.30	0.34
3.5	0.31	0.35
4	0.32	0.35
4.5	0.33	0.35
5	0.35	0.35
7.5	0.40	0.36
10	0.43	0.37
20	0.50	0.38
30	0.52	0.38
40	0.54	0.39
50	0.55	0.39
100	0.58	0.39

[a]In toluene, c = 10^{-5} M. Excited at 365 nm.

[b]Equivalents of $B(C_6F_5)_3$



CIE calculated from emission spectra of solution **6** and $B(C_6F_5)_3$ (Figure S31, Table S3). The emission color of solution **6** and $B(C_6F_5)_3$ gradually changed from blue to white and orange.

DFT calculations

All calculations were carried out using the GAUSSIAN 09 program.[2] Geometry optimization was performed with hybrid density functional theory (DFT) at the B3LYP[3] level, by using the 6-31+G(d,p) basis set for all atoms. The UV/Vis absorption spectra of optimized geometries were calculated with the time dependent (TD) DFT method at CAM-B3LYP[4] level. Solvent effects were taken into account by means of polarized continuum model (PCM)[5] calculations. The results for **2** and **7** are shown in Figures S31 and S32 respectively, and the energy levels of their HOMO and LUMO, and NBO charges are summarized in Table S4. XYZ Coordinates are uploaded as a separate Supporting Information.

Figure. S31 Results of DFT calcualtionof **2**

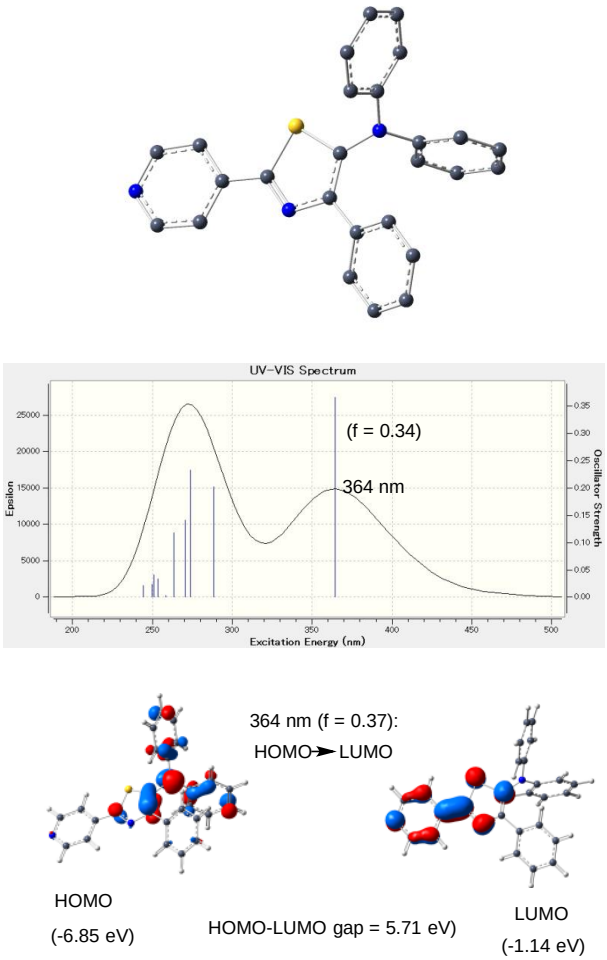


Figure. S32 Results of DFT calcualtionof **7•H_2O**

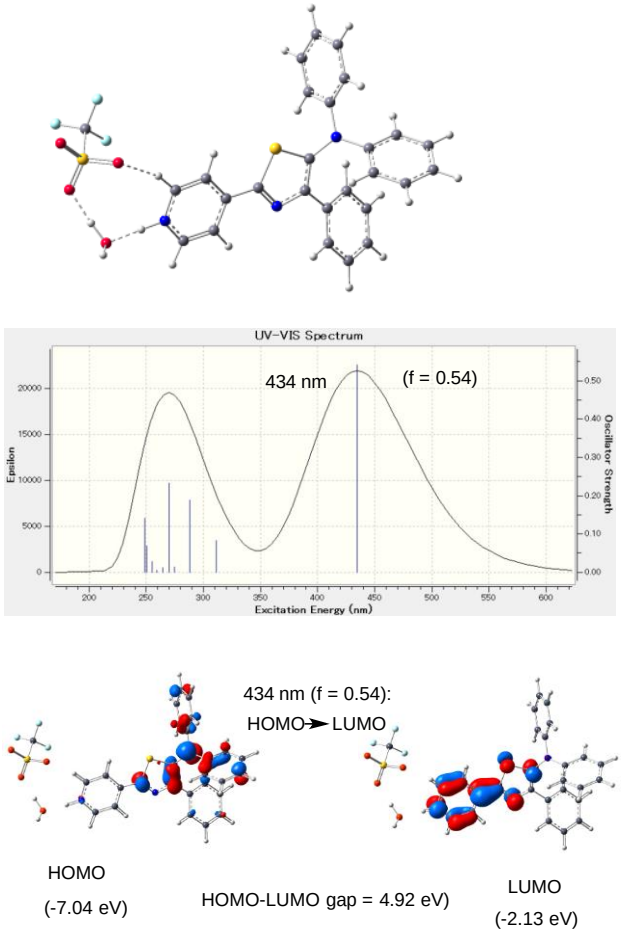


Table S4. Summary of energy and eneryg gaps of HOMO and LUMO of **2** and **7•H_2O**

	HOMO (eV)	LUMO (eV)	HOMO-LUMO gap (eV)
2	-6.85	-1.14	5.71
7•H_2O	-7.05 (0.2 down)	-2.13 (0.99 down)	4.92

The calculated UV-vis absorption spectra for **2** and **7** at CAM-B3LYP level show a red shift of 70 nm in absorption maximum from 364 nm in **2** to 434 nm in **7** after protonation, which is consistent with the experimental results in Table 1 exhibiting a substantial red shift of 93 nm from 382 nm in **2** to 475 nm in protonated **7**. To find possible origins of such remarkably red-shifted absorption of **7**, we investigated their electronic properties in details. TD-DFT results indicated that the maximum absorption is mainly assigned to HOMO-LUMO transition for both of **2** and **7**, as shown in Fig. S32 and S33. Interestingly, LUMO orbital has a great contribution from the pyridyl group, whereas HOMO orbital is basically from aminothiazole fragment and almost none from the pyridyl group. It is noticed that protonation of **2** leads to lowering of both HOMO and LUMO orbitals. But LUMO orbital is much more strongly lowered by 0.99 eV in energy, compared with HOMO orbital with lowering of 0.2 eV, as shown in Table S4. Consequently, the HOMO-LUMO electronic band gap significantly drops down by 0.79 eV from 5.71 eV to 4.92 eV, which is probably the origin for the intense red-shifted absorption in **7**.

X-ray structure analyses

The X-ray quality crystals were obtained by slow diffusion of hexane into CH_2Cl_2 solutions of **2** and **7**. The crystal was cut from the grown crystals and was mounted on a glass fiber. Intensity data were collected on a RIGAKU Saturn70 CCD system with VariMax Mo Optic using MoKα radiation (λ = 0.71075 Å). X-ray absorption was corrected by multi-scan methods.[6], [7] The structures were solved by direct method using SHELXS-97 and refined by the full-matrix least-squares method on F^2 using SHLEXL-97.[8] Structure determination was carried out using the free GUI software of Yadokari-XG 2009.[9] Crystal data and structure refinement are summarized in the Tables S5 and S6.

Crystal data and structure refinement

Table S5. Crystal data and structure refinement for **2**

Empirical formula	$C_{26}H_{19}N_3S$	
Formula weight	405.50	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Crystal system	Orthorhombic	
Space group	*P*bca	
Unit cell dimensions	a = 7.4437(4) Å	a= 90°
	b = 20.0110(11) Å	b= 90°
	c = 26.7323(16) Å	g= 90°
Volume	3981.9(4) $Å^3$	
Z	8	
Density (calculated)	1.353 Mg/m^3	
Absorption coefficient	0.181 mm^{-1}	
F(000)	1696	
Crystal size	0.08 x 0.02 x 0.01 mm^3	
Theta range for data collection	1.52 to 25.50°	
Index ranges	-8<=h<=9, -24<=k<=23, -32<=l<=32	
Reflection collected	50863	
Independent reflections	3703 [*R*(int) = 0.2451]	
Completeness to theta = 27.50°	100.0%	
Max. min. transmission	0.9982 and 0.9857	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3703 / 0 / 271	
Goodness-of-fit on F^2	1.046	
Final R indices [*I*>2sigma(*I*)]	R_1 = 0.0739, wR_2 = 0.1698	
R indices (all data)	R_1 = 0.1386, wR_2 = 0.2148	
Largest diff. peak and hole	0.524 and -0.640 e.$Å^{-3}$	

Table S6. Crystal data and structure refinement for **7**

Empirical formula	$C_{27}H_{22}F_3N_3O_4S_2$	
Formula weight	573.60	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.8558(6) Å	a= 90°
	b = 6.8270(3) Å	b= 90.959°
	c = 31.3378(18) Å	g= 90°
Volume	2536.1(2) $Å^3$	
Z	4	
Density (calculated)	1.502 Mg/m^3	
Absorption coefficient	0.273 mm^{-1}	
F(000)	1184	
Crystal size	0.08 x 0.04 x 0.01 mm^3	
Theta range for data collection	1.83 to 25.50°	
Index ranges	-14<=h<=14, -8<=k<=8, -37<=l<=37	
Reflection collected	22829	
Independent reflections	4583 [*R*(int) = 0.1152]	
Completeness to theta = 27.50°	97.0%	
Max. min. transmission	0.9973 and 0.9785	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4583 / 4 / 358	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R_1 = 0.0720, wR_2 = 0.1577	
R indices (all data)	R_1 = 0.1624, wR_2 = 0.2070	
Largest diff. peak and hole	0.977 and -0.368 e.$Å^{-3}$	

Planes for the calculations of dihedral angles **A-2**, **A-4**, and **A-5** of **2** and **7** are shown in Figures S33–S38.

Figure. S33 Two planes for the calcuation of dihedorak angle **A-2** of **2**

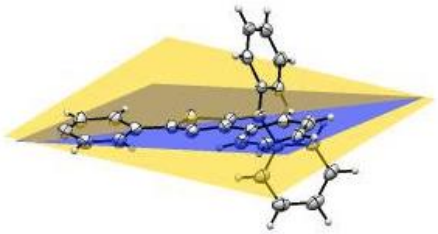


Figure. S34 Two planes for the calcuation of dihedorak angle **A-4** of **2**

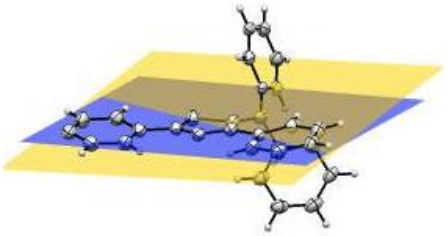


Figure. S35 Two planes for the calcuation of dihedorak angle **A-5** of **2**

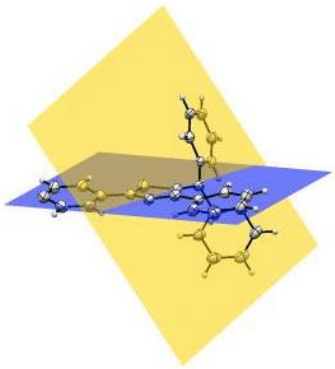


Figure. S36 Two planes for the calcuation of dihedorak angle **A-2** of **7**

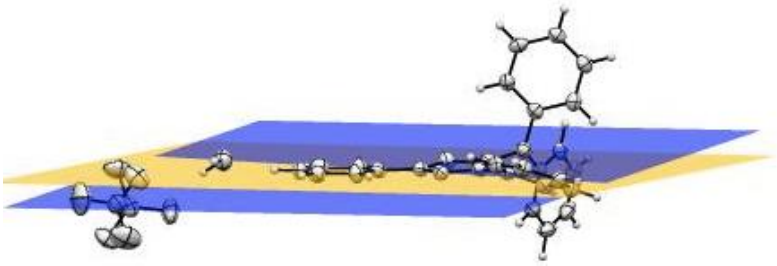


Figure. S37 Two planes for the calcuation of dihedorak angle **A-4** of **7**

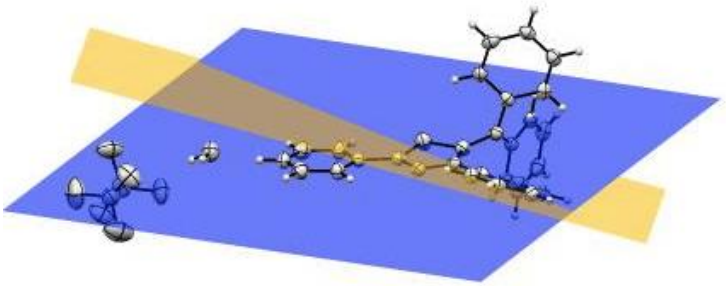
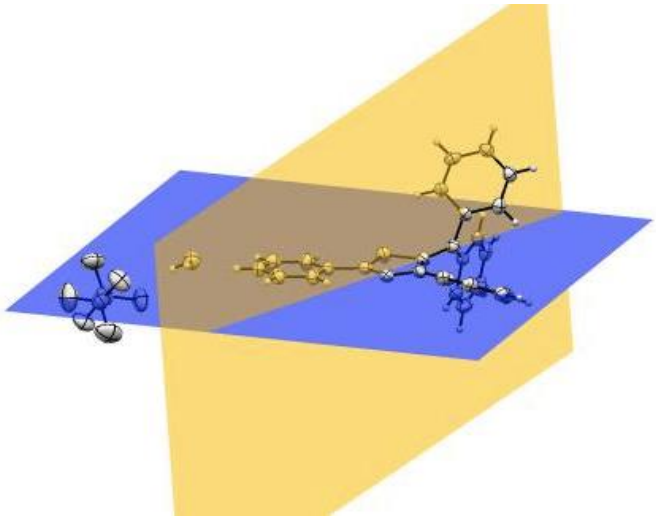


Figure. S38 Two planes for the calcuation of dihedorak angle **A-5** of **7**



References.

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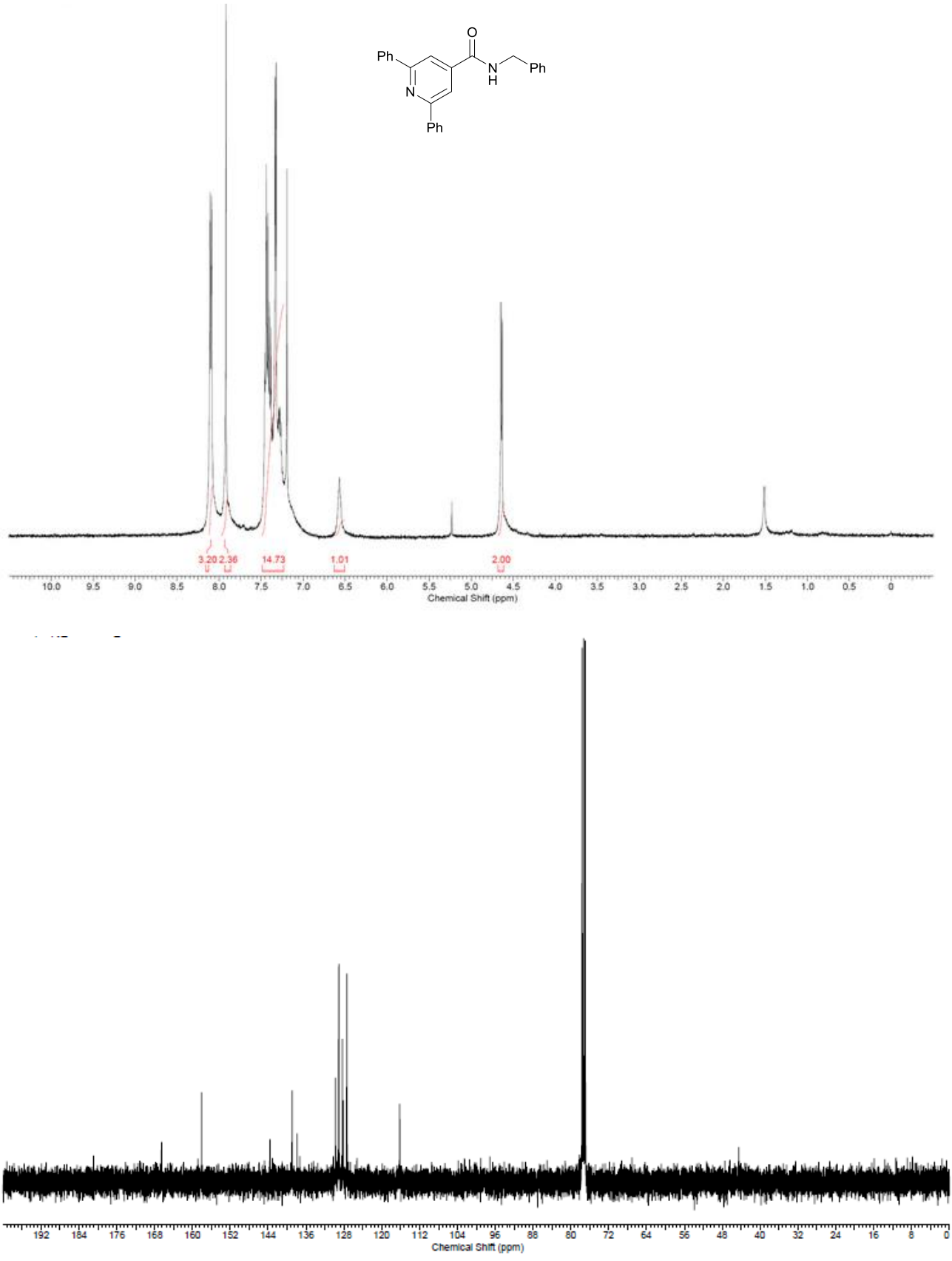
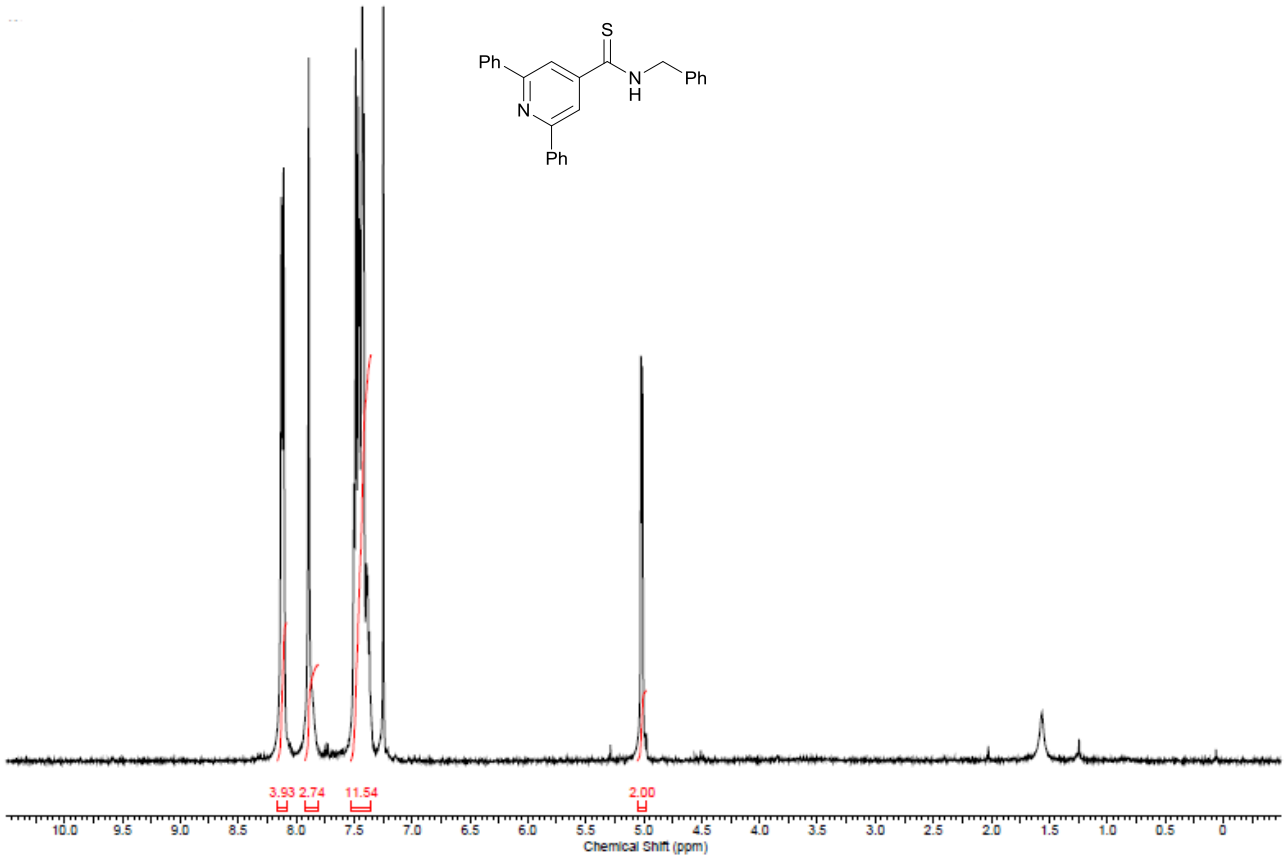
^{1}H and ^{13}C NMR spectra

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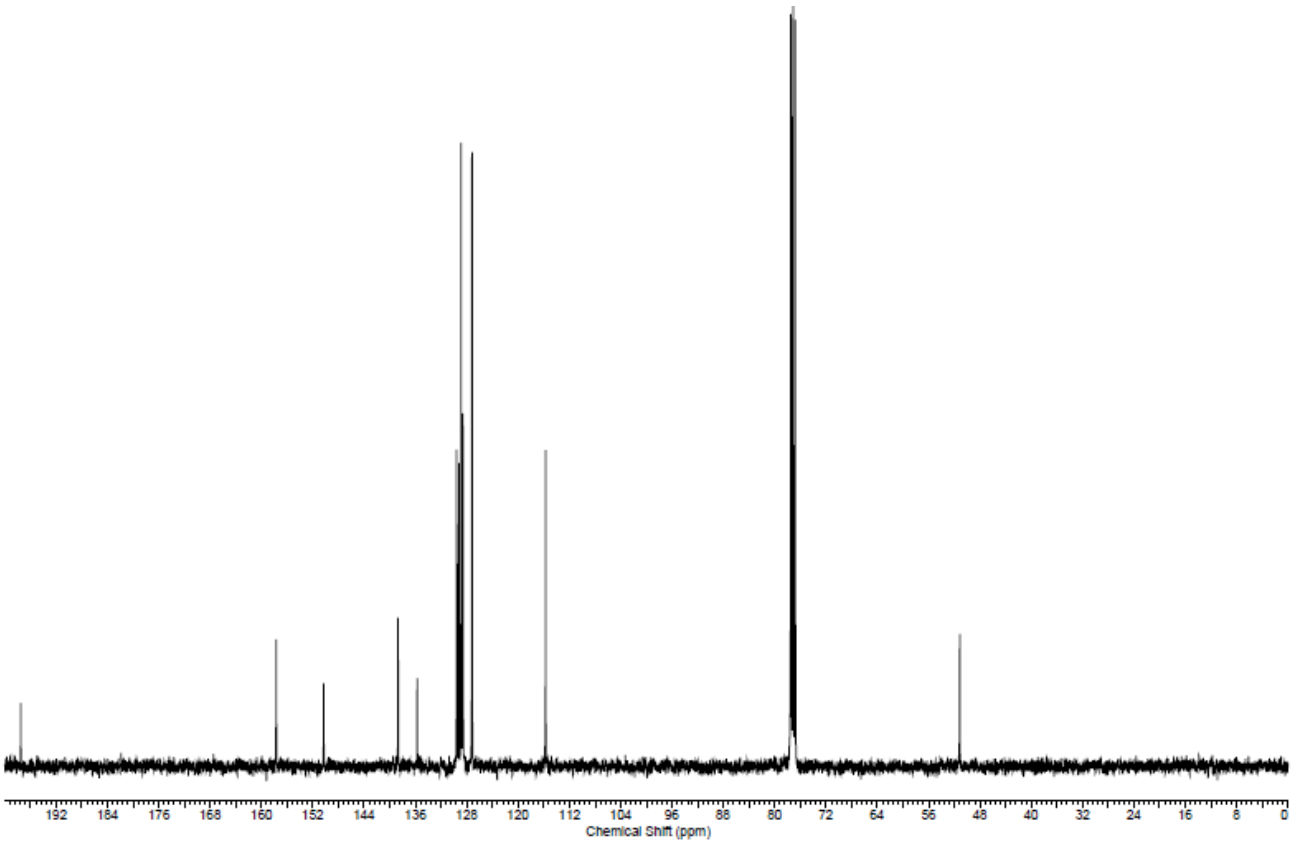
Ph
N
H
Ph
Ph
3.93
2.74
11.54
2.00
Chemical Shift (ppm)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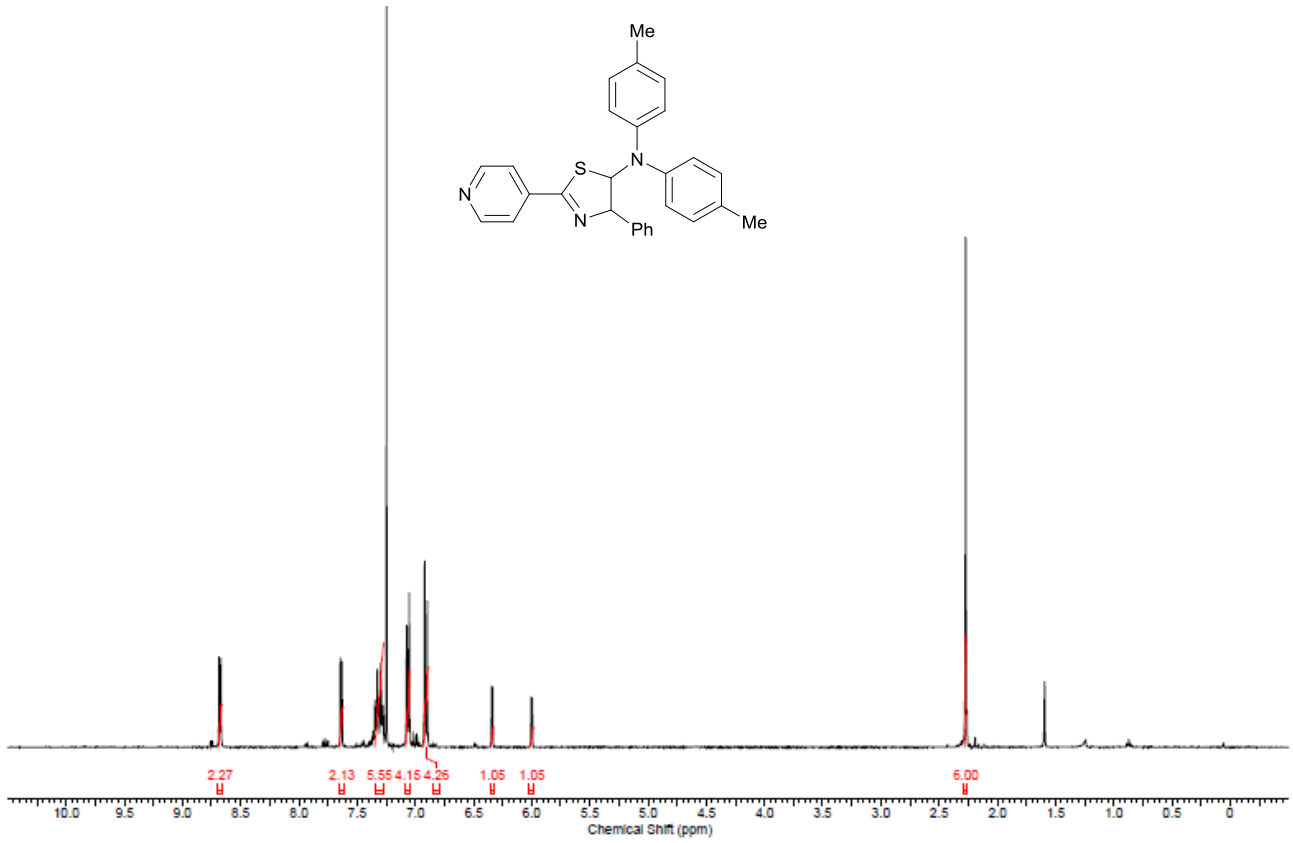
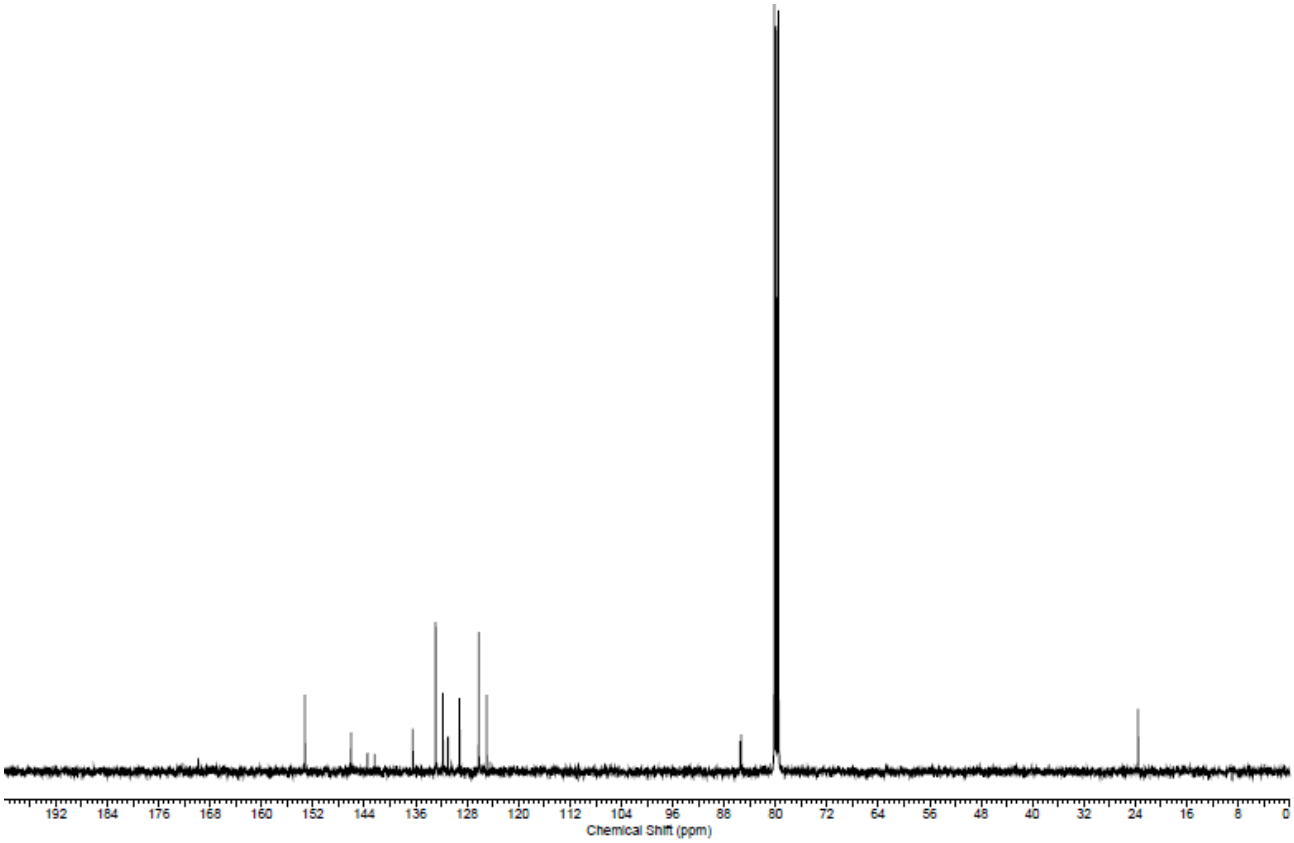

Me
S
N
N
N
Ph
Me
2.27
2.13
5.55
4.15
4.26
1.05
1.05
6.00
Chemical Shift (ppm)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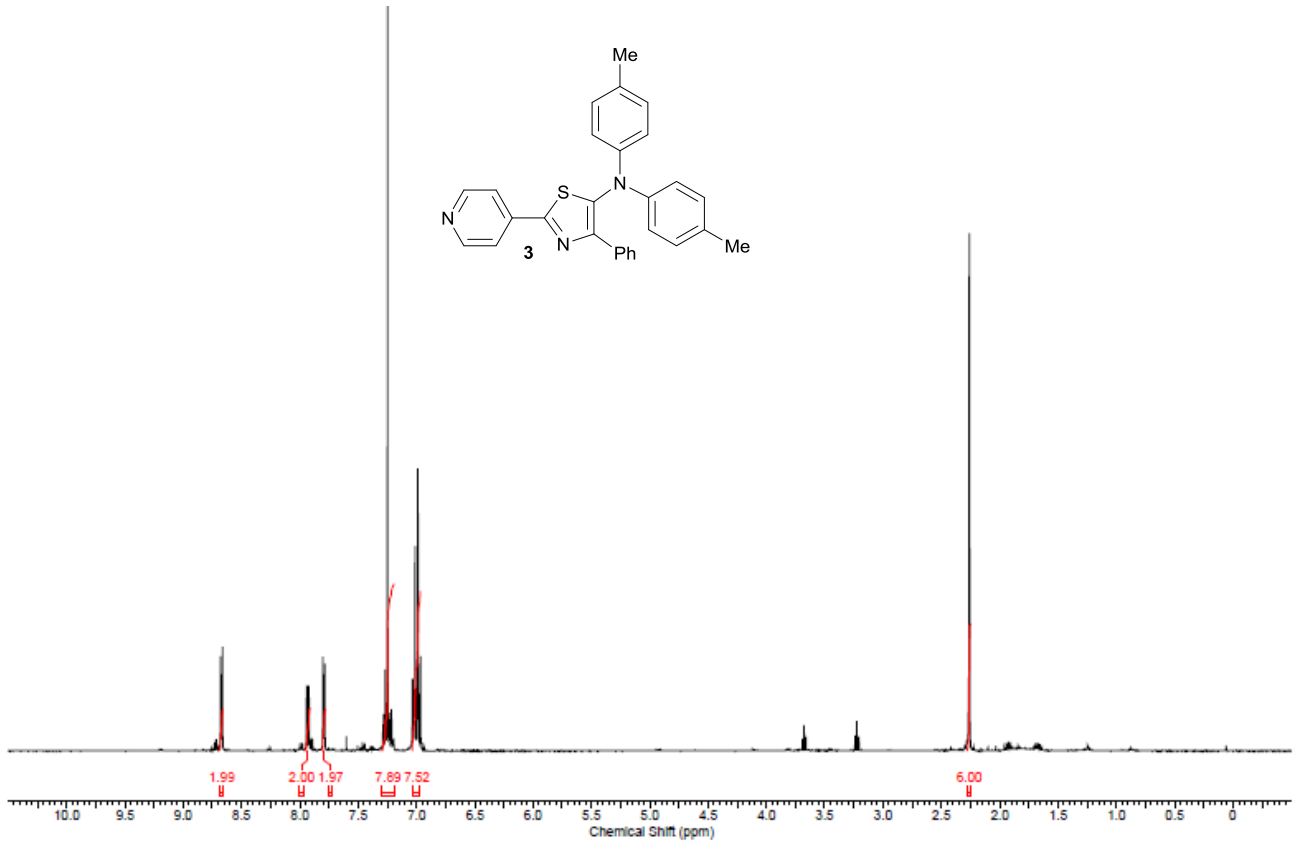
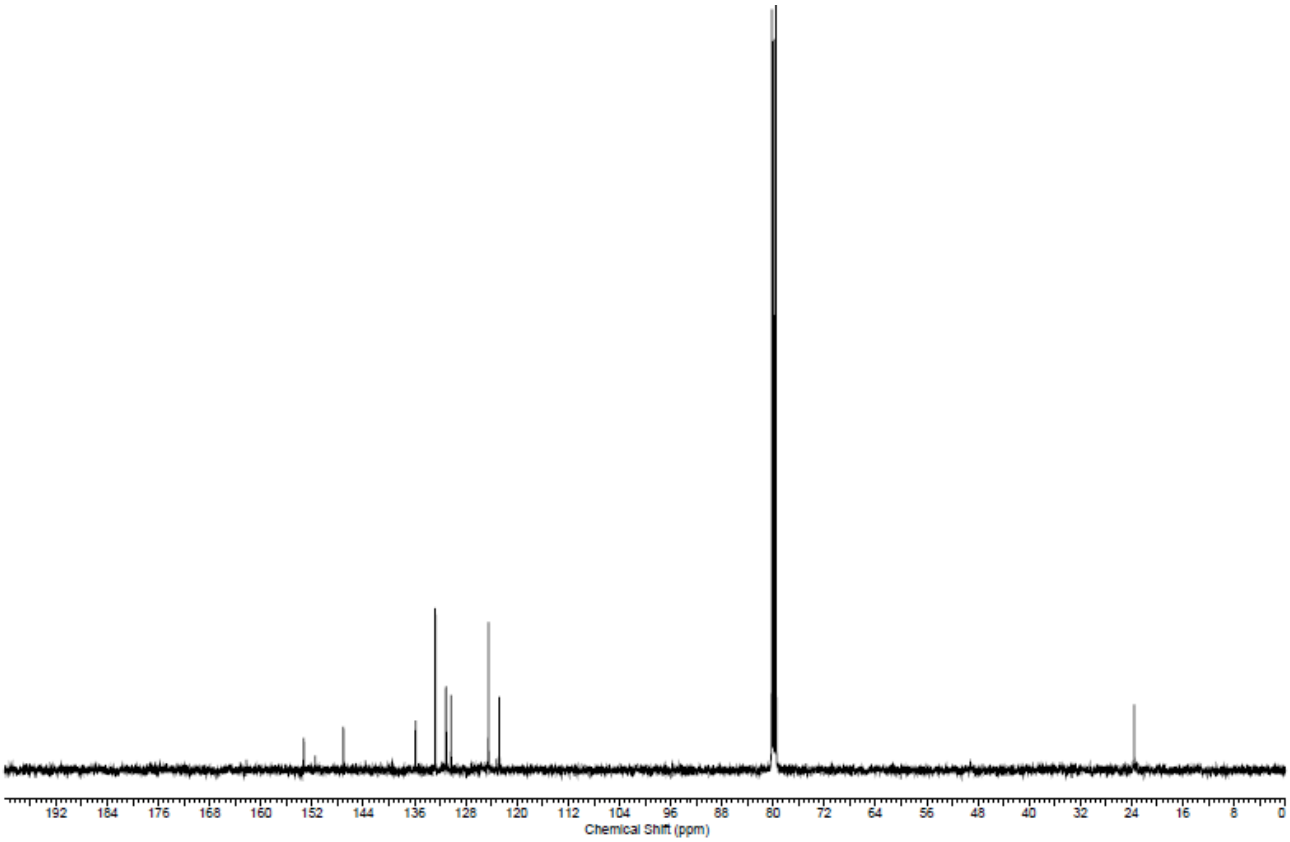

Me
S
N
N
N
Ph
Me
3
1.99
2.00
1.97
7.89
7.52
6.00
Chemical Shift (ppm)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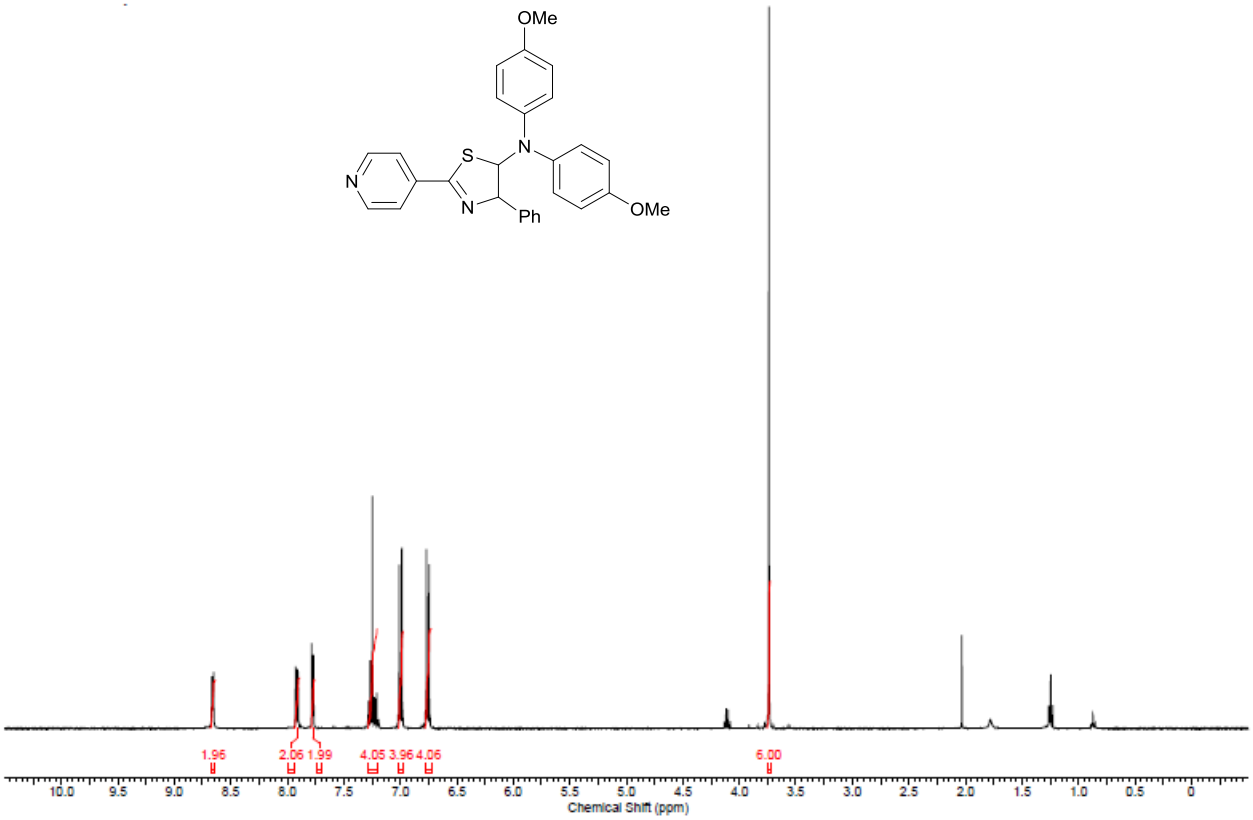
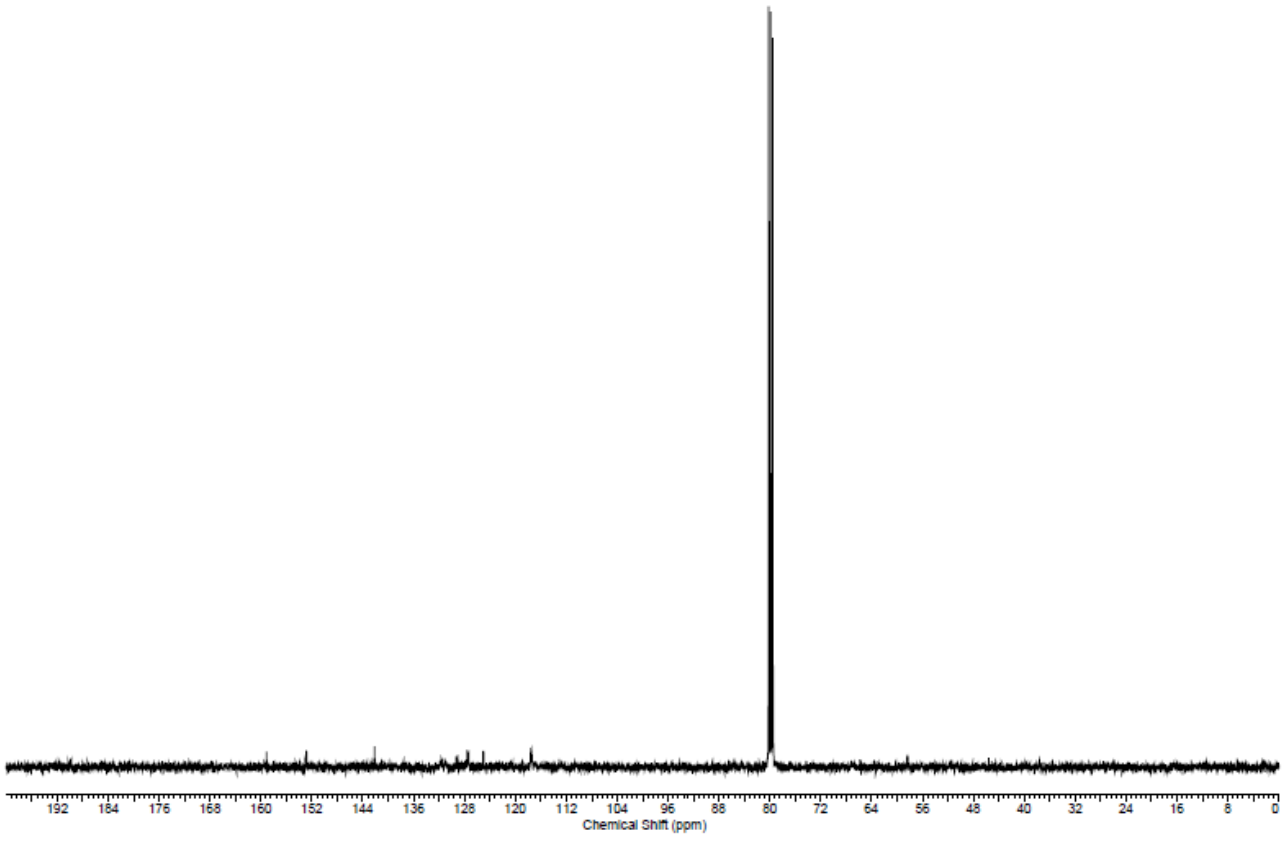

OMe
N
S
N
N
Ph
OMe
1.96
2.06
1.99
4.05
3.96
4.06
6.00
Chemical Shift (ppm)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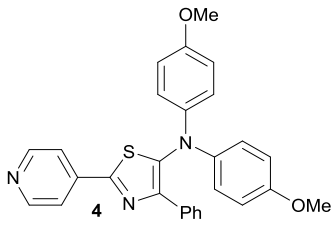
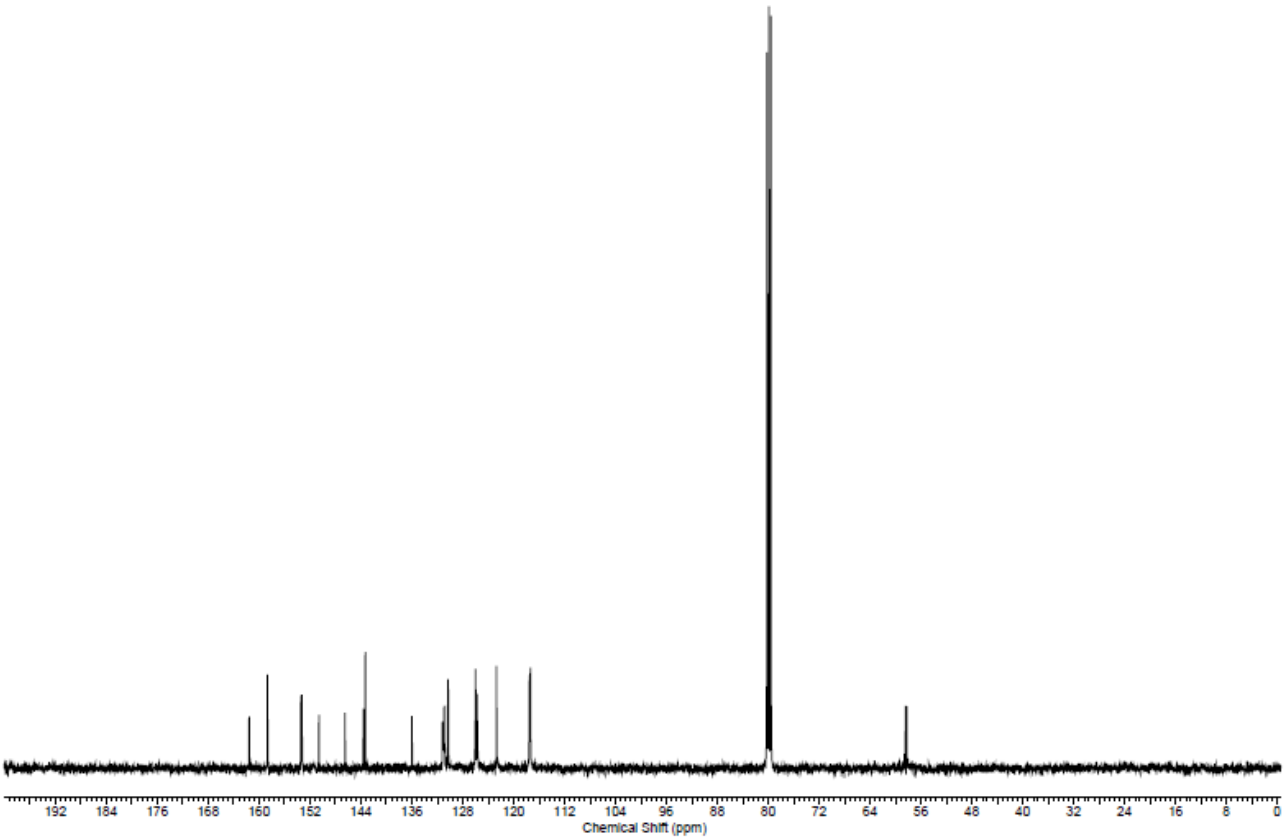

OMe
N
S
N
N
Ph
OMe

4

2.01
2.11
2.05
4.44
4.21
4.22
6.00
Chemical Shift (ppm)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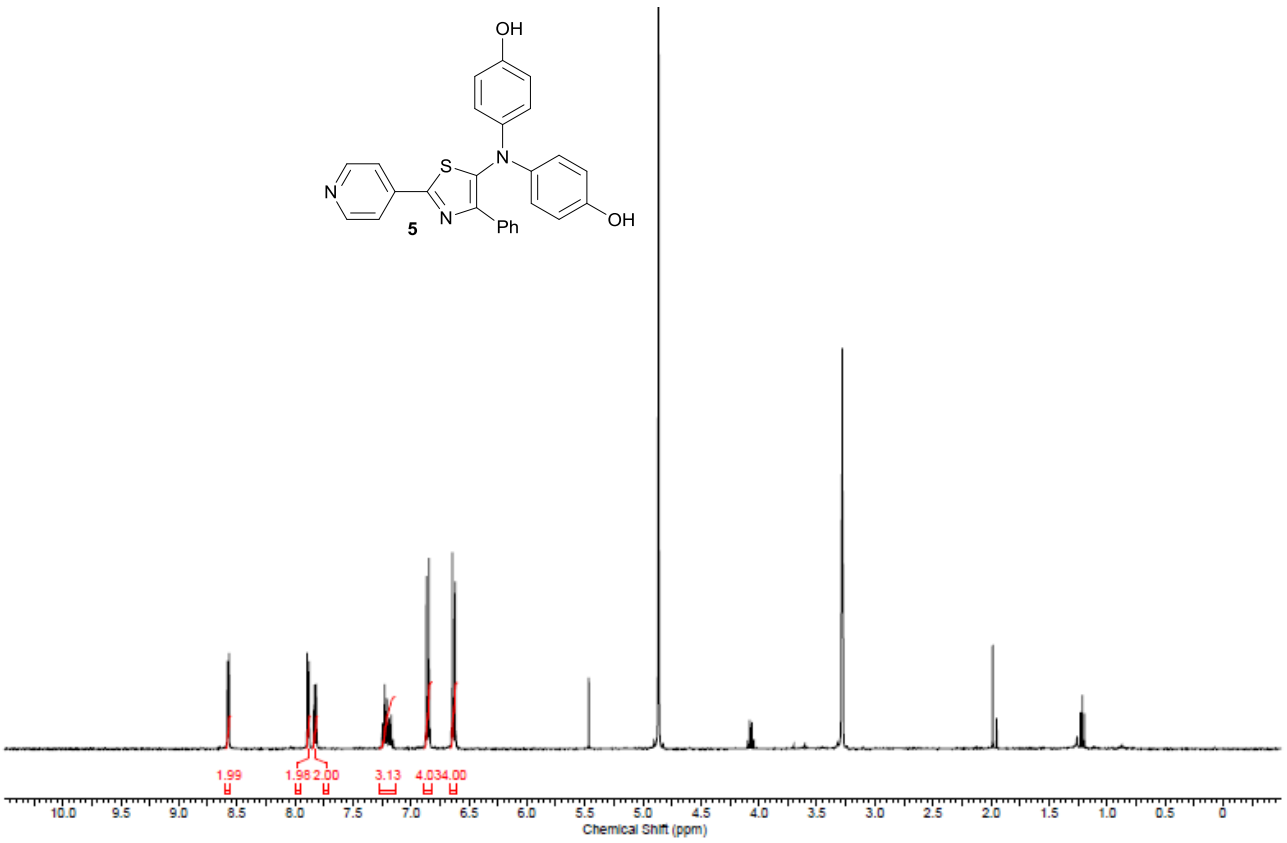
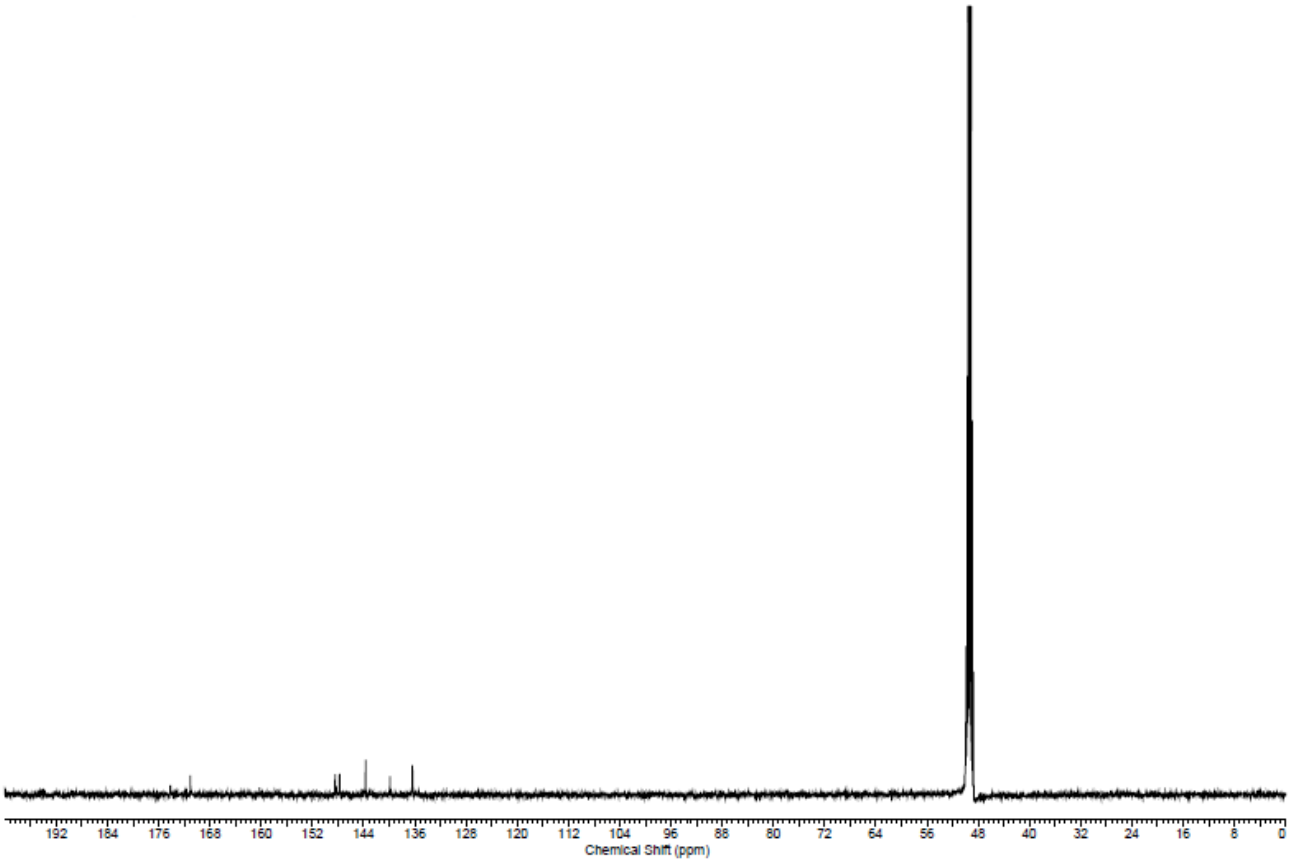
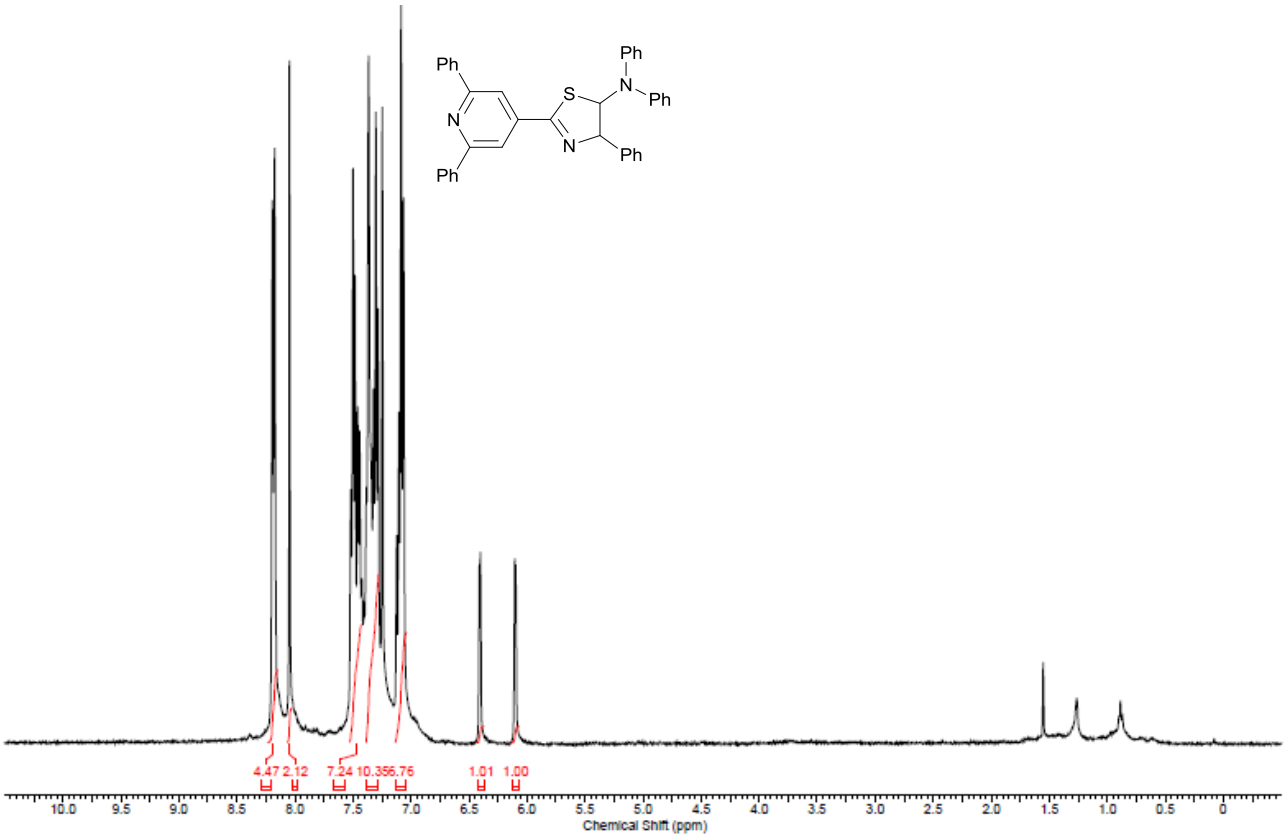
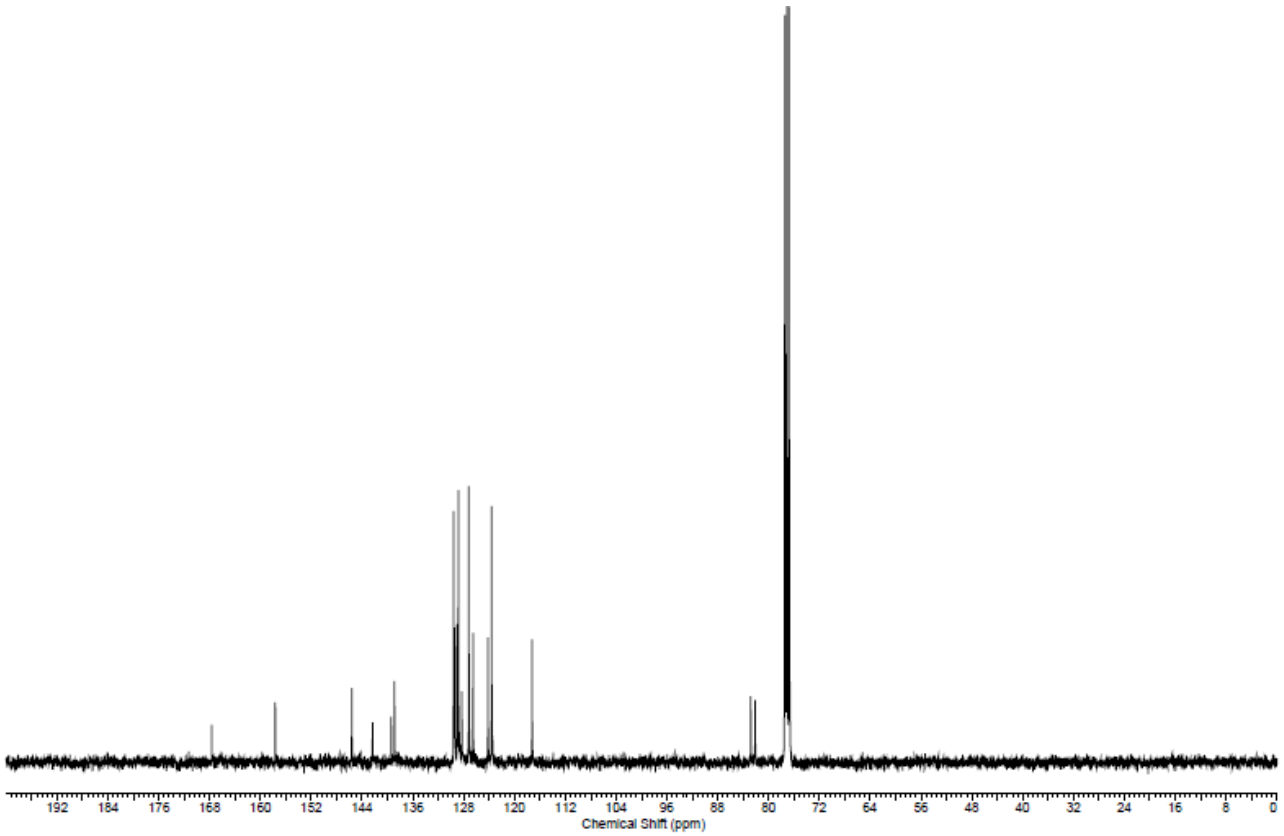
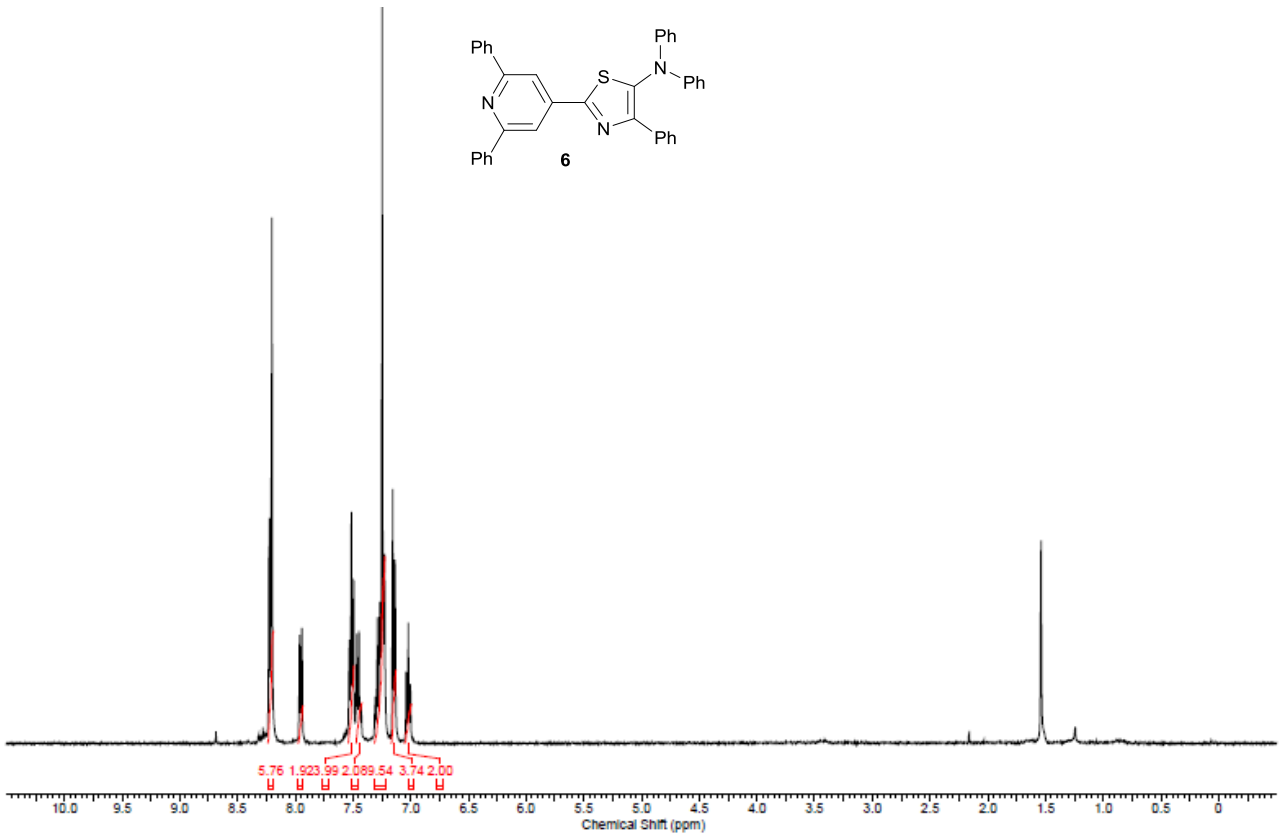
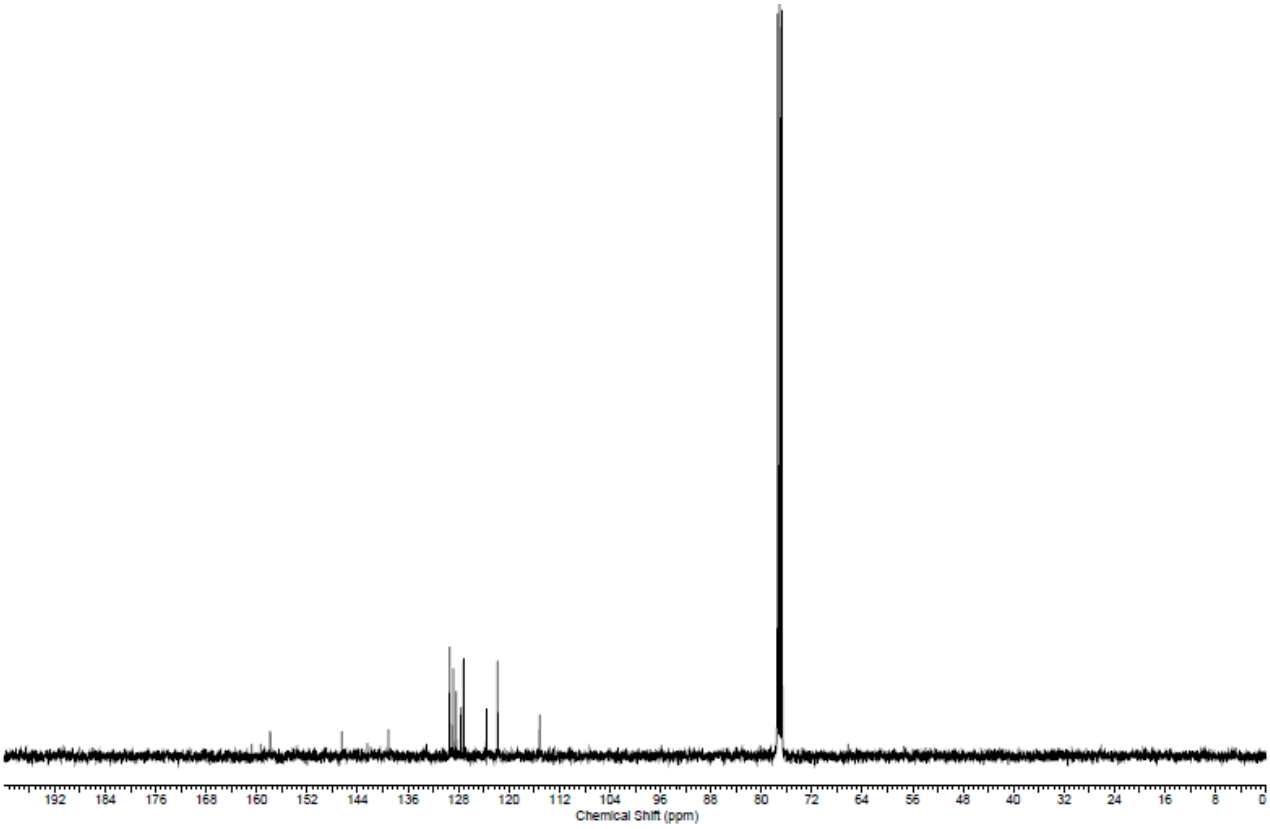

OH
S
N
N
N
Ph
OH
5
1.99
1.98
2.00
3.13
4.03
4.00
Chemical Shift (ppm)


Chemical Shift (ppm)


Ph
N
Ph
S
N
Ph
Ph
Ph
4.47 2.12 7.24 10.35 6.76 1.01 1.00
Chemical Shift (ppm)


Chemical Shift (ppm)


Ph
Ph
N
Ph
S
N
Ph
N
Ph
Ph
6
5.76 1.92 3.99 2.08 9.54 3.74 2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)