Electronic Supplementary Material (ESI) for RSC Advances.

Pyridinium 5-Aminothiazoles: Specific Photophysical Properties and Vapochlormism in Halogenated Solvents

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General Remarks.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO. 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 and 40−50 μm).

Materials.

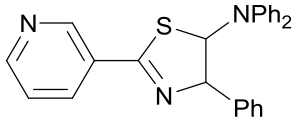
Carbon tetrachloride, methyl trifluoromethanesulfonate, 1,1,2,2-tetrachloroethane, and deuterated solvents were purchased from Aldrich Chemical Company, Inc. Benzyl bromide, butyl trifluoromethanesulfonate, dichloromethane (for synthesis), ethyl acetate, hexane, iodine, methanol, THF, and silica gel 60N (Spherical Neutral, 100−210 and 40−50 μm) were purchased from Kanto Chemical Co., Inc. Acetone, acetonitrile, benzylamine, bromoform, chloroform, 1,2-dichloroethane, dichloromethane (for measurements), diethyl ether, diisopropylamine, $Na_2S_2O_3$, methanol (for measurements), $MgSO_4$, THF (for measurements), toluene, and 3 Å molecular sieve were purchased from Nakarai Tesque Inc. *n*-BuLi was purchased from Mitsuwa Chemical, Ltd. Methyl methacrylate polymer, 1,1,1,3,3-pentafluorobutane and 3-pyridinecarbaldehyde was purchased from Wako, Ltd. The compounds **1**[1], **2**[2], **4**,[3] and benzyl iodide[4] were prepared according to literature procedures.

Instruments.

^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-AL400 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 and fluorescent quantum yield were measured on a JASCO spectrofluorometer FP-8500. The PMMA films were prepared with an Aiden Spincoater TYPE SC8001. Powder X-Ray diffraction patterns were recorded with a reflection method, using a Rigaku RINT2100-Ultima+ operated at a 40-kV accelerating potential and a 30-mA emission current. CuKα radiation was used and the diffracted intensities were detected by a scintillation counter as a function of diffraction angle (2θ), with divergence and scattering slits of 1° and the receiving slit of 0.15 mm. The accuracy and precision of the diffraction angle were both within ±0.01° by use of a Si polycrystalline standard at 298 K.

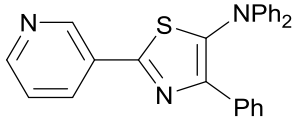
Synthesis of starting materials

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



For the preparation of lithium di(isopropyl)amide (LDA), a solution of diisopropylamine (0.15 mL, 1.1 mmol) in THF (2.6 mL) was added slowly to a 1.25 M solution of *n*-butyllithium in *n*-hexane (0.63 mL, 1.0 mmol) at -20 °C, and the resulting solution was stirred at this temperature for 30 min. To a solution of *N*-phenylmethyl-3-pyridinecarbothioamide (0.11 g, 0.5 mmol) in THF (3.0 mL) was added THF solution of LDA at -20 °C, and the mixture was stirred for 10 min at this temperature. The resulting mixture was poured into a saturated aqueous solution of $Na_2S_2O_3$, and it was 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, hexane : EtOAc = 20 : 1, 8 : 1 and 3 : 1) to give the corresponding thiazoline (0.12 g, 82%) as a pale yellow solid. (mp. 154−159 °C): IR (KBr) 2923, 1602, 1491, 1239, 1034, 1024, 953, 591 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.95 (d, *J* = 3.4 Hz, 1H, SCH), 6.29 (d, *J* = 3.9 Hz, 1H, NCH), 6.95−7.03 (m, 7H, Ar), 7.17−7.30 (m, 9H, Ar), 7.99−8.02 (m, 1H, Ar), 8.61 (m, 1H, Ar), 8.94 (m, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.2, 82.7, 123.5, 123.6, 124.1, 126.5, 128.2, 129.0, 129.5, 129.7, 135.5, 139.7, 145.7, 150.0, 152.1, 165.9; MS (EI) *m*/*z* 407 (M^+); HRMS (EI) Calcd for $C_{26}H_{21}N_3S$: 407.1456; found : 407.1436.

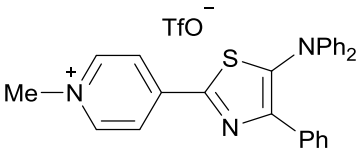
2-(3-Pyridyl)-4-phenyl-*N*,*N*-diphenyl-5-thiazolamine (**3**)



To a solution of the corresponding thiazoline (0.12 g, 0.3 mmol) in THF (3.0 mL) was added iodine (0.16 g, 0.6 mmol) at room temperature, and the mixture was strred for 17 h. The resulting mixture was poured into a saturated aqueous solution of $Na_2S_2O_3$ and water, and it was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude material was purified by column chromatography (SiO_2, hexane : EtOAc = 20 : 1 and 8 : 1) to give thiazole **3** (0.07 g, 59%) as a yellow solid. (mp. 144−147 °C): IR (KBr) 2926, 1586, 1491, 1264, 1024, 761, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.98−7.02 (m, 2H, Ar), 7.12−7.14 (m, 5H, Ar), 7.20−7.29 (m, 7H, Ar), 7.34−7.37 (m, 1H, Ar), 7.92−7.96 (m, 2H, Ar), 8.24−8.27 (m, 1H, Ar), 9.16 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.6, 123.5, 123.8, 127.6, 128.3, 128.4, 129.4, 130.1, 133.1, 133.4, 141.0, 146.5, 147.5, 149.1, 150.8, 160.0; MS (EI) *m*/*z* 405 (M^+); HRMS (EI) Calcd for $C_{26}H_{19}N_3S$: 405.1300; found : 405.1295.

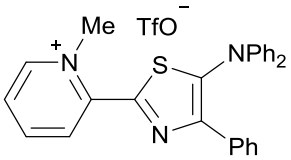
Synthesis of pyridinium thiazoles

2-(4-Methylpyridinium)-4,*N*,*N*-triphenyl-5-thiazolamine trifluoromethanesulfonate (5)



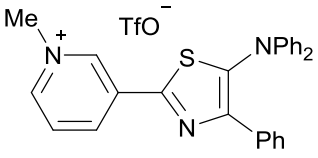
To a solution of 2-(4-pyridyl)-4,*N*,*N*-triphenyl-5-thiazolamine (0.101 g, 0.25 mmol) in CH_2Cl_2 (3.0 mL) was added methyl trifluoromethanesulfonate (55 μL, 0.5 mmol) at room temperature, and the mixture was stirred for 24 h at room temperature. The resulting mixture was concentrated in vacuo. The residue was purified by column chromatography (SiO_2, EtOAc, CH_2Cl_2 and 6%MeOH in CH_2Cl_2) to give thiazole (0.14 g, 97%) as a yellow solid. (mp. 225 °C): IR (KBr) 3051, 1644, 1490, 1262, 1164, 1029, 696, 637 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.44 (s, 3H, Me), 7.03−7.08 (m, 6H, Ar), 7.20−7.25 (m, 7H, Ar), 7.71−7.74 (m, 2H, Ar), 8.26 (d, *J* = 4.0 Hz, 2H, Ar), 8.79 (d, *J* = 8.0 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.2, 117.5, 122.7, 124.8, 127.6, 128.2, 128.7, 129.6, 132.1, 139.9, 145.5, 146.0, 147.6, 149.6, 151.3; Anal. Calcd. for $C_{28}H_{22}F_3N_3O_3S_2 \cdot 0.25CH_2Cl_2$ H, 3.84; C, 57.43; N, 7.11. Found: H, 3.64; C, 57.44; N, 7.10.

2-(2-Methylpyridinium)-4,*N*,*N*-triphenyl-5-thiazolamine trifluoromethanesulfonate (6)



To a solution of 2-(2-pyridyl)-4,*N*,*N*-triphenyl-5-thiazolamine (0.101 g, 0.25 mmol) in CH_2Cl_2 (3.0 mL) was added methyl trifluoromethanesulfonate (55 μL, 0.5 mmol) at room temperature, and the mixture was stirred for 43 h at room temperature. The resulting mixture was concentrated in vacuo. The residue was purified by column chromatography (SiO_2, EtOAc, CH_2Cl_2 and 6%MeOH in CH_2Cl_2) to give thiazole (0.09 g, 65%) as a yellow solid. (mp. 193 °C): IR (KBr) 3060, 1587, 1490, 1273, 1153, 1029, 697, 636 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.84 (s, 3H, Me), 7.10−7.12 (m, 6H, Ar), 7.23−7.29 (m, 7H, Ar), 7.69−7.70 (m, 2H, Ar), 8.02−8.04 (m, 1H, Ar), 8.18 (d, *J* = 8.0 Hz, 1H, Ar), 8.41−8.43 (m, 1H, Ar), 9.21 (d, *J* = 8.0 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.8, 122.7, 124.9, 126.1, 127.1, 127.4, 128.3, 128.8, 128.9, 129.7, 131.8, 144.9, 145.9, 148.4, 148.6, 149.4, 152.2; Anal. Calcd. for $C_{28}H_{22}F_3N_3O_3S_2 \cdot 0.6CH_2Cl_2$ H, 3.77; C, 55.35; N, 6.77. Found: H, 3.77; C, 55.33; N, 6.61.

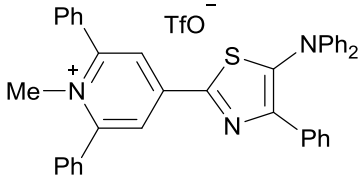
2-(3-Methylpyridinium)-4,*N*,*N*-triphenyl-5-thiazolamine trifluoromethanesulfonate (7)



To a solution of 2-(3-pyridyl)-4,*N*,*N*-triphenyl-5-thiazolamine (0.101 g, 0.25 mmol) in CH_2Cl_2 (3.0 mL) was added methyl trifluoromethanesulfonate (55 μL, 0.5 mmol) at room temperature, and the mixture was stirred for 62 h at room temperature. The resulting mixture was concentrated in vacuo. The residue was purified by column chromatography (SiO_2, EtOAc, CH_2Cl_2 and 6%MeOH in CH_2Cl_2) to give thiazole (0.12 g, 86%) as a yellow solid. (mp. 243−245 °C): IR (KBr) 3071, 2924, 1491, 1268, 1163, 1031,

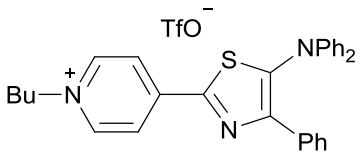
638 cm^{-1}; ^{1}H NMR (400 MHz, DMSO) δ 4.40 (s, 3H, Me), 7.03−7.08 (m, 6H, Ar), 7.26−7.33 (m, 7H, Ar), 7.91−7.92 (m, 2H, Ar), 8.16−8.19 (m. 1H, Ar), 8.98−9.00 (m, 2H, Ar), 9.58 (s, 1H, Ar); ^{13}C NMR (100 MHz, DMSO) δ 48.8, 122.1, 124.5, 127.6, 128.5, 129.0, 129.2, 130.3, 132.6, 133.0, 141.4, 143.6, 144.0, 146.3, 146.4, 148.4, 155.4; Anal. Calcd. for $C_{28}H_{22}F_3N_3O_3S_2$ H, 3.89; C, 59.04; N, 7.38. Found: H, 3.85; C, 58.85; N, 7.15.

2-(3,5-Diphenyl-4-methylpyridinium)-4,*N*,*N*-triphenyl-5-thiazolamine trifluoromethanesulfonate (8)



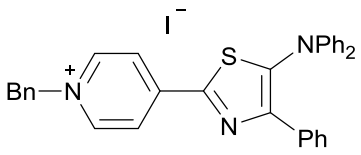
To a solution of 2-(3,5-diphenyl-4-pyridyl)-4,*N*,*N*-triphenyl-5-thiazolamine (0.139 g, 0.25 mmol) in CH_2Cl_2 (5.5 mL) was added methyl trifluoromethanesulfonate (55 μL, 0.5 mmol) at room temperature, and the mixture was stirred for 45 h at room temperature. The resulting mixture was concentrated in vacuo. The residue was purified by column chromatography (SiO_2, EtOAc) to give thiazole (0.13 g, 73%) as a yellow solid. (mp. 136−139 °C): IR (KBr) 3059, 1623, 1489, 1442, 1357, 1262, 1154, 1030, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H, Me), 7.02−7.07 (m, 6H, Ar), 7.16−7.26 (m, 7H, Ar), 7.58−7.60 (m, 6H, Ar), 7.69−7.71 (m, 2H, Ar), 7.78−7.80 (m, 4H, Ar), 8.11 (s, 2H, Py); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.2, 122.9, 123.5, 124.6, 127.6, 128.1, 128.6, 129.2, 129.5, 131.4, 132.2, 132.5, 146.1, 146.4, 148.4, 149.5, 152.1, 153.7, 157.5; Anal. Calcd. for $C_{40}H_{30}F_3N_3O_3S_2 \cdot 1.08CH_2Cl_2$ H, 3.98; C, 60.63; N, 5.16. Found: H, 3.85; C, 60.56; N, 5.15.

2-(4-Butylpyridinium)-4,*N*,*N*-triphenyl-5-thiazolamine trifluoromethanesulfonate (9)



To a solution of 2-(4-pyridyl)-4,*N*,*N*-triphenyl-5-thiazolamine (0.101 g, 0.25 mmol) in CH_2Cl_2 (3.0 mL) was added butyl trifluoromethanesulfonate (82 μL, 0.5 mmol) at room temperature, and the mixture was stirred for 18 h at 40 °C. The resulting mixture was concentrated in vacuo. The residue was purified by column chromatography (SiO_2, EtOAc, CH_2Cl_2 and 6%MeOH in CH_2Cl_2) to give thiazole (0.06 g, 36%) as a dark red solid. (mp. 201 °C): IR (KBr) 3058, 2963, 1638, 1490, 1260, 1161, 1029, 693, 638 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (m, 3H, CH_3), 1.32 (m, 2H, CH_2), 1.73 (m, 2H, CH_2), 4.57 (m, 2H, CH_2), 7.01 (d, J = 7.3 Hz, 6H, Ar), 7.17−7.19 (m, 7H, Ar), 7.67 (m, 2H, Ar), 8.23 (m, 2H, Ar), 8.79 (m, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 19.3, 33.3, 61.4, 122.6, 122.8, 124.7, 125.8, 127.0, 127.6, 128.2, 128.4, 128.7, 129.6, 132.1, 144.7, 145.9, 147.6; Anal. Calcd. for $C_{31}H_{28}F_3N_3O_3S_2 \cdot 0.3CH_2Cl_2 \cdot 0.3MeOH$ H, 4.65; C, 58.45; N, 6.46. Found: H, 4.62; C, 58.49; N, 6.51.

2-(4-Benzylpyridinium)-4,*N*,*N*-triphenyl-5-thiazolamine iodide (10)



To a solution of 2-(4-pyridyl)-4,*N*,*N*-triphenyl-5-thiazolamine (0.101 g, 0.25 mmol) in CH_2Cl_2 (3.0 mL) was added benzyl iodide (0.109 g, 0.5 mmol) at room temperature, and the mixture was stirred for 27 h under dark condition. The resulting mixture was concentrated in vacuo. The residue was purified by column chromatography (SiO_2, EtOAc, CH_2Cl_2 and 6%MeOH in CH_2Cl_2) to give thiazole (0.12 g, 72%) as a dark red solid. (mp. 120−123 °C): IR (KBr) 3026, 2928, 1632, 1487, 1352, 1153, 753, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.06 (s, 2H, CH_2), 7.08 (d, *J* = 7.7 Hz, 6H, Ar), 7.21−7.26 (m, 7H, Ar), 7.42−7.45 (m, 3H, Ar), 7.59−7.61 (m, 2H, Ar), 7.71−7.73 (m, 2H, Ar), 8.30 (d, *J* = 7.2 Hz, 2H, Ar), 9.17 (d, *J* = 6.7 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.9, 122.7, 124.9, 127.7, 128.3, 128.8, 129.8, 129.7, 129.8, 129.9, 130.2, 132.2, 132.4, 139.8, 144.8, 145.0, 146.0, 149.7, 169.9; Anal. Calcd. for $C_{33}H_{26}IN_3S·0.3CH_2Cl_2·0.2MeOH$ H, 4.21; C, 61.16; N, 6.38. Found: H, 4.24; C, 61.12; N, 6.21.

X-ray structure analyses

The X-ray quality crystals were obtained by slow diffusion of hexane into CH_2Cl_2 solution of **5** or into THF solution of **5**. 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.[5, 6] 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.[7] Structure determination was carried out using the free GUI software of Yadokari-XG 2009.[8] Crystal data and structure refinement are summarized in the Tables S1 and S2.

Table S1. Crystal data and structure refinement for **5**

Empirical formula	$C_{28}H_{22}F_3N_3O_3S_2$	
Formula weight	569.60	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 7.14530(10) Å	α= 83.2770(10)°
	b = 9.8932(2) Å	β= 84.6600(10)°
	c = 19.2696(4) Å	γ= 73.9710(10)°
Volume	1297.57(4) Å^3	
Z	2	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	0.264 mm^{-1}	
F(000)	588	
Crystal size	0.20 x 0.10 x 0.05 mm^3	
Theta range for data collection	1.07 to 29.17°	
Index ranges	-9<=h<=9, -13<=k<=13, -26<=l<=26	
Reflection collected	35355	
Independent reflections	6976 [*R*(int) = 0.0368]	
Completeness to theta = 27.50°	99.6%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6976 / 319 / 502	
Goodness-of-fit on F^2	1.025	
Final R indices [*I*>2sigma(*I*)]	R_1 = 0.0517, wR_2 = 0.1350	
R indices (all data)	R_1 = 0.0607, wR_2 = 0.1436	
Largest diff. peak and hole	1.012 and -0.533 e.Å^{-3}	

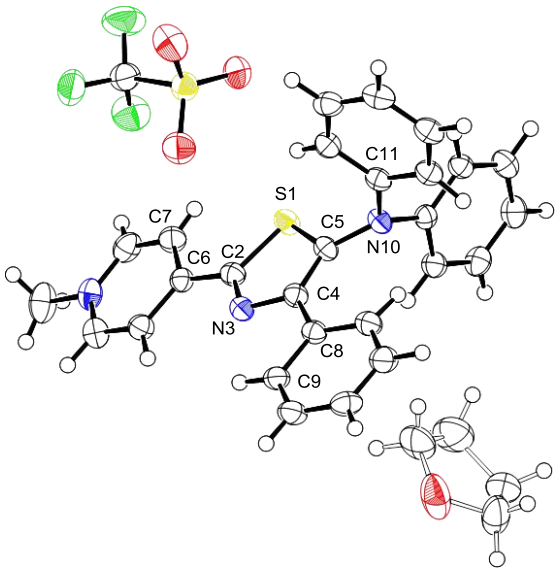


Fig. S1 The molecular structure for **5** with THF with thermal displacement parameters set at 50% probability. Selected dihedral angles (°) and bond lengths (Å): S1-C2-C6-C7 7.0(5), N3-C4-C8-C9 1.4(5), S1-C5-N10-C11 55.5(4), C2-C6 1.470(5), C4-C8 1.478(5), C5-N10 1.412(4), N10-C11 1.431(4).

Table S2. Crystal data and structure refinement for **5** with THF

Empirical formula	$C_{30}H_{26}F_3N_3O_{3.5}S_2$	
Formula weight	605.66	
Temperature	153(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	*C*2/c (#15)	
Unit cell dimensions	a = 44.6818(13) Å	α= 90°
	b = 7.1241(3) Å	β= 111.2048(16)°
	c = 18.7470(10) Å	γ= 90°
Volume	5563.5(4) $Å^3$	
Z	8	
Density (calculated)	1.446 Mg/m^3	
Absorption coefficient	0.252 mm^{-1}	
F(000)	2512	
Crystal size	0.18 x 0.08 x 0.05 mm^3	
Theta range for data collection	2.33 to 26.99°	
Index ranges	-55<=h<=56, -8<=k<=8, -23<=l<=23	
Reflection collected	40988	
Independent reflections	5995 [*R*(int) = 0.0604]	
Completeness to theta = 27.50°	99.0%	
Max. min. transmission	0.9875 and 0.9560	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5995 / 32 / 485	
Goodness-of-fit on F^2	1.077	
Final R indices [*I*>2sigma(*I*)]	R_1 = 0.0754, wR_2 = 0.2127	
R indices (all data)	R_1 = 0.0892, wR_2 = 0.2255	
Largest diff. peak and hole	0.491 and -0.437 e.$Å^{-3}$	

Photophysical properties.

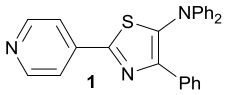
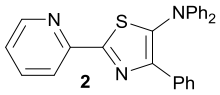
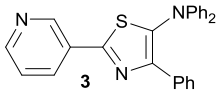
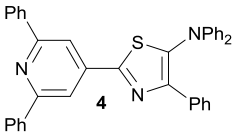
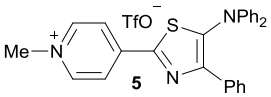
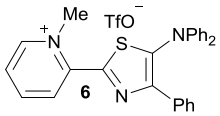
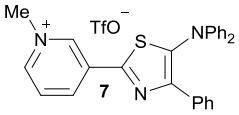
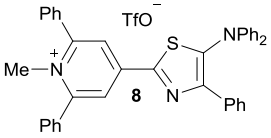
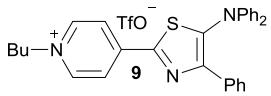
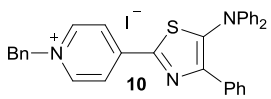
compounds		UV-vis		Fluorescence		
		λ_{abs} /nm	logε	λ_{em} /nm[a]	Φ_F[b]	Stokes shift /cm^{-1}
 **1**	$CHCl_3$	394	4.44	500	0.52	5380 [106 nm]
	THF	385	3.89	495	0.48	5772 [110 nm]
	solid			465	0.21	
 **2**	$CHCl_3$	386	4.14	489	0.57	5457 [103 nm]
	THF	379	3.77	482	0.15	5638 [103 nm]
	solid			463	0.16	
 **3**	$CHCl_3$	376	3.99	480	0.56	5762 [104 nm]
	THF	372	3.97	478	0.46	5961 [106 nm]
	solid			451	0.15	
 **4**	$CHCl_3$	394	3.75	497	0.51	5260 [103 nm]
	THF	390	4.12	500	0.58	5641 [110 nm]
	solid			488	0.13	
 **5**	$CHCl_3$	510	4.32	650	0.05	4223 [140 nm]
	THF	478	3.94	663	0.05	5838 [185 nm]
	solid			596	0.13	
 **6**	$CHCl_3$	482	4.15	645	0.03	5243 [163 nm]
	THF	451	3.94	629	0.02	6275 [178 nm]
	solid			574	0.15	
 **7**	$CHCl_3$	448	3.72	625	0.02	6321 [177 nm]
	THF	412	3.60	528	0.02	5332 [116 nm]
	solid			505	0.05	
 **8**	$CHCl_3$	507	4.07	677	0.03	4953 [170 nm]
	THF	492	3.88	697	0.01	5978 [205 nm]
	solid			675	0.08	
 **9**	$CHCl_3$	510	4.25	654	0.05	4317 [144 nm]
	THF	479	3.85	672	0.02	5996 [193 nm]
	solid			662	0.05	
 **10**	$CHCl_3$	517	4.19	647	0.04	3886 [130 nm]
	THF	493	3.81	562	0.05	2490 [69 nm]
	solid			675	0.02	

Table S3 Photophysical properties of **1**−**10**. [**1**−**10**] = 1×10^{-5} M. [a] Excited at excitation wavelengths. [b] Absolute fluorescence quantum yield.

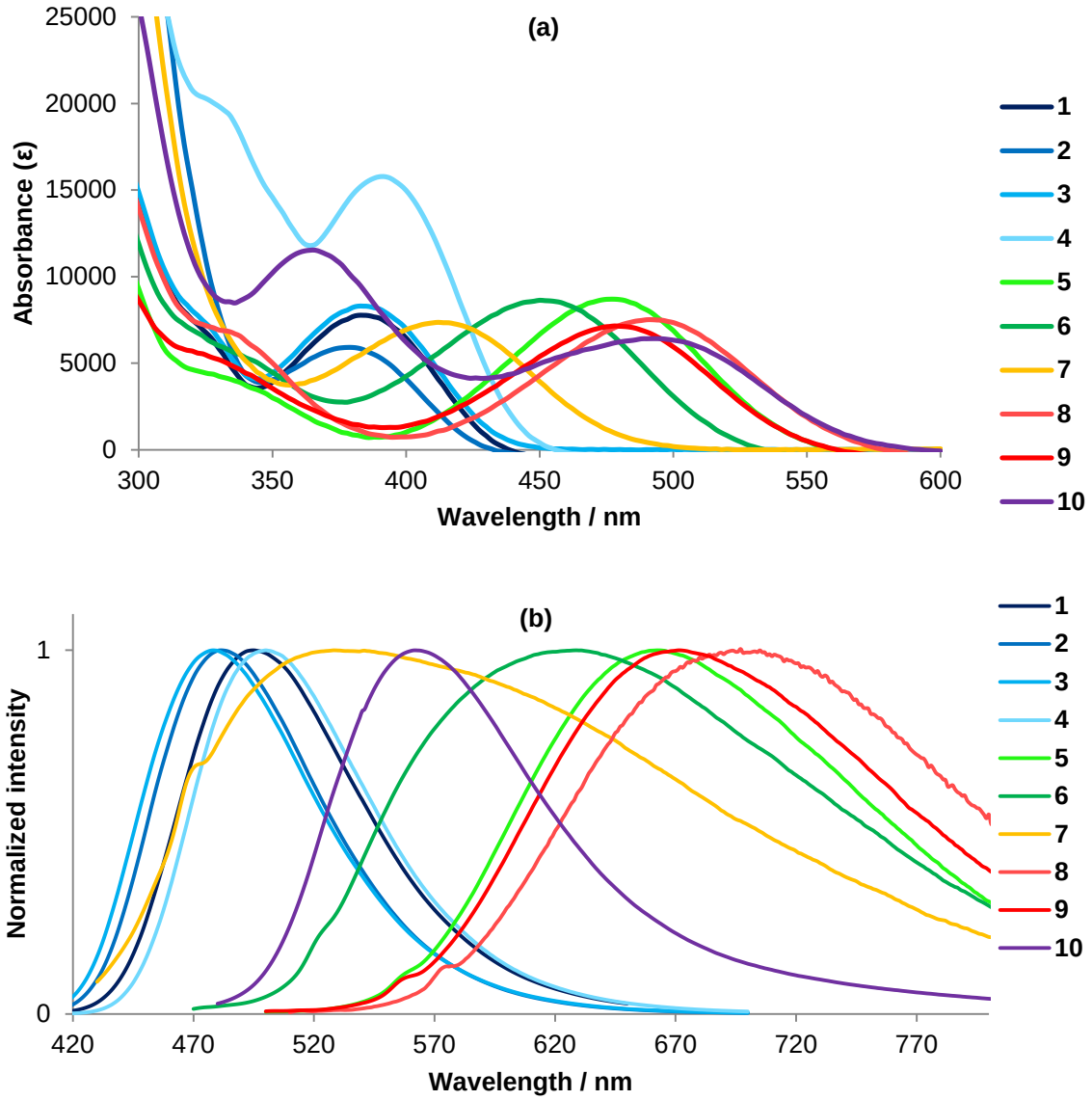


Fig. S2 (a) UV-vis absorption spectra of **1**−**10**. (b) Emission spectra of **1**−**10**. [**1**−**10**] = 1×10^{-5} M, in THF.

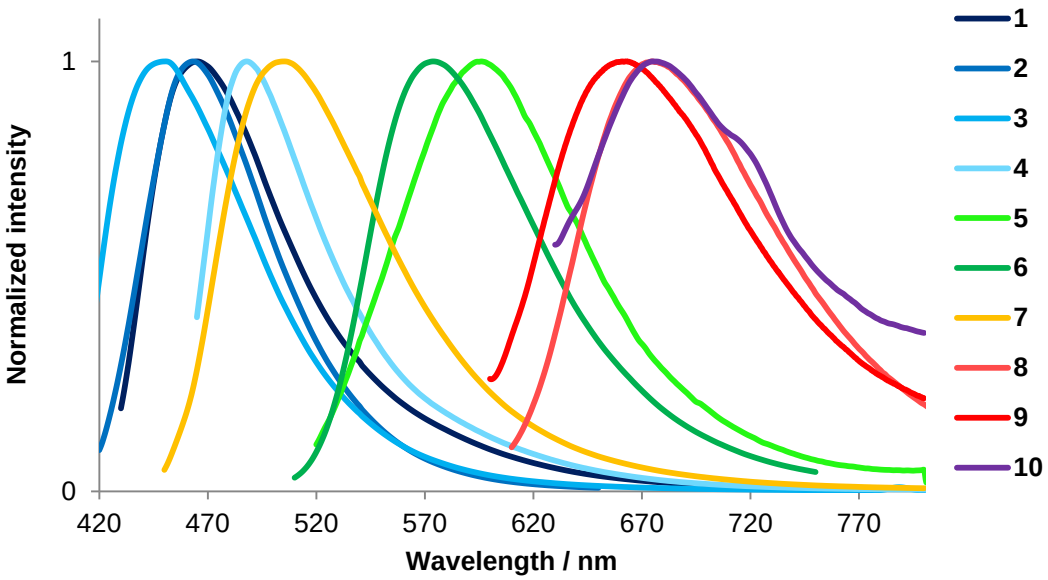


Fig. S3 Emission spectra of **1**−**10** as the solid state.

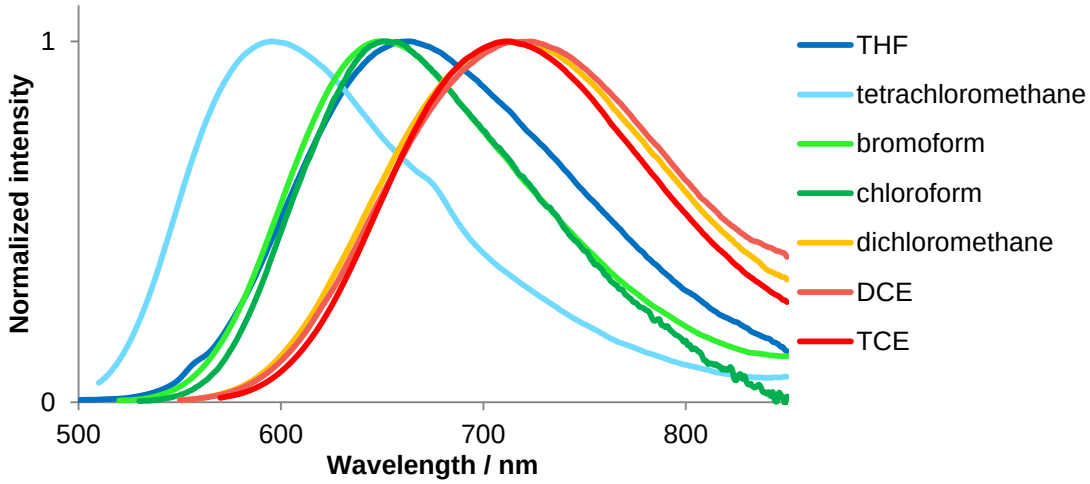


Fig. S4 Emission spectra of **5** in various solvents. [**5**] = 1×10^{-5} M.

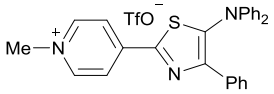
compounds	UV-vis		Fluorescence		
	λ_{abs} /nm	logε	λ_{em} /nm[a]	Φ_F[b]	Stokes shift /cm^{-1}
	507	4.05	648	0.05	4292 [141 nm]

Table S4 Photophysical properties of **5** in chlorobenzene; [**5**] = 1×10^{-5} M; [a] excited at the excitation wavelengths; [b] absolute fluorescence quantum yield.

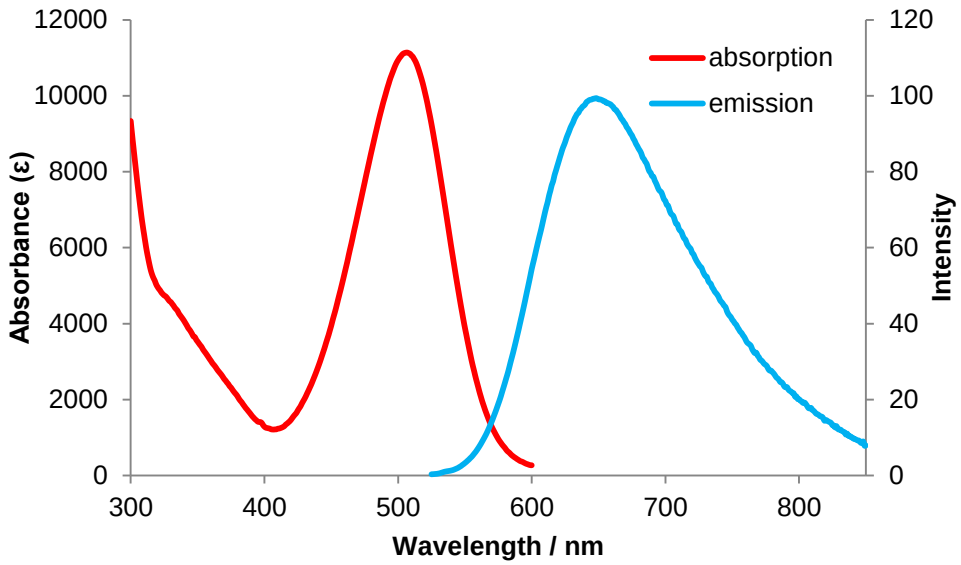


Fig. S5 Absorption and emission spectra of **5** in chlorobenzene; [**5**] = 1×10^{-5} M.

Chlorobenzene was used as an aromatic halogenated solvent and also changed absorption and emission wavelengths to the longer wavelengths.

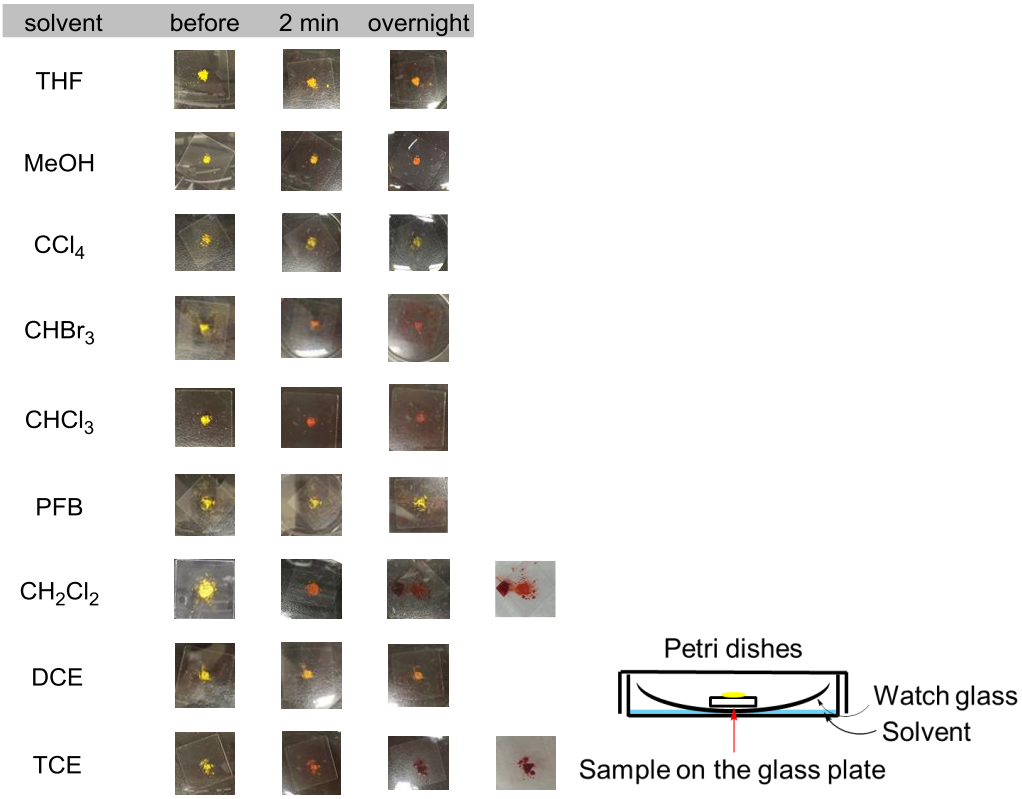


Table S5 Vapochromism with various solvents. The petri dishes sealed by using silicone grease.

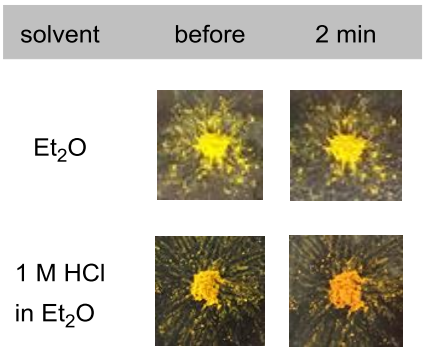


Table S6 Vapochromism with HCl.

The vapor of Et_2O did not change the color of **5**. In contrast, the vapor of 1 M HCl in Et_2O changed color of **5** from yellow to orange.

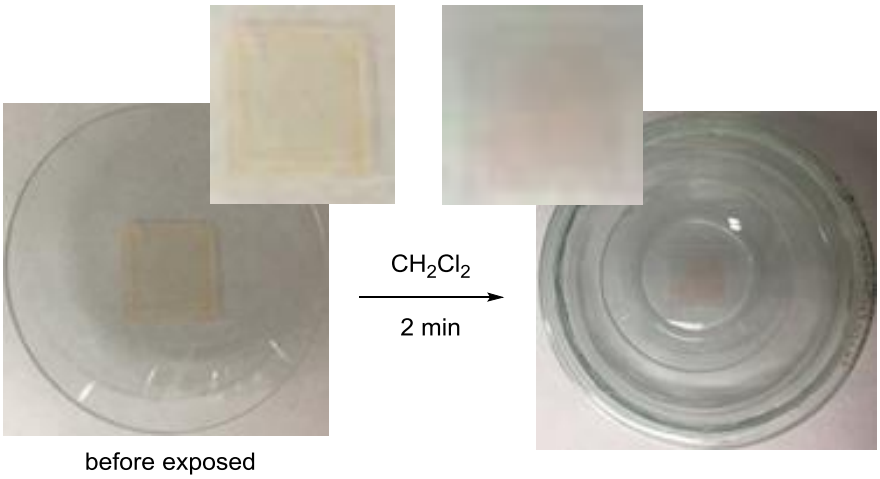


Fig. S6 Photographs of PMMA film of **5** with CH_2Cl_2 vapor in sealed glass cases.

The method of preparation of PMMA film: To a solution of methyl methacrylate polymer (0.1 g) in acetone (1.0 mL) was added **5** (0.006 g, 0.01 mmol). This solution was put on the crystal glass plate (18×18×t0.3 mm), and was spread evenly by spin coater (3000 rpm, 1 min). The resulting plate dried under reduced pressure at 50 °C.

The detection limits of these color changes are 50% of halogenated solvents (vapochlormism) and 30% of halogenated solvents (casting method).

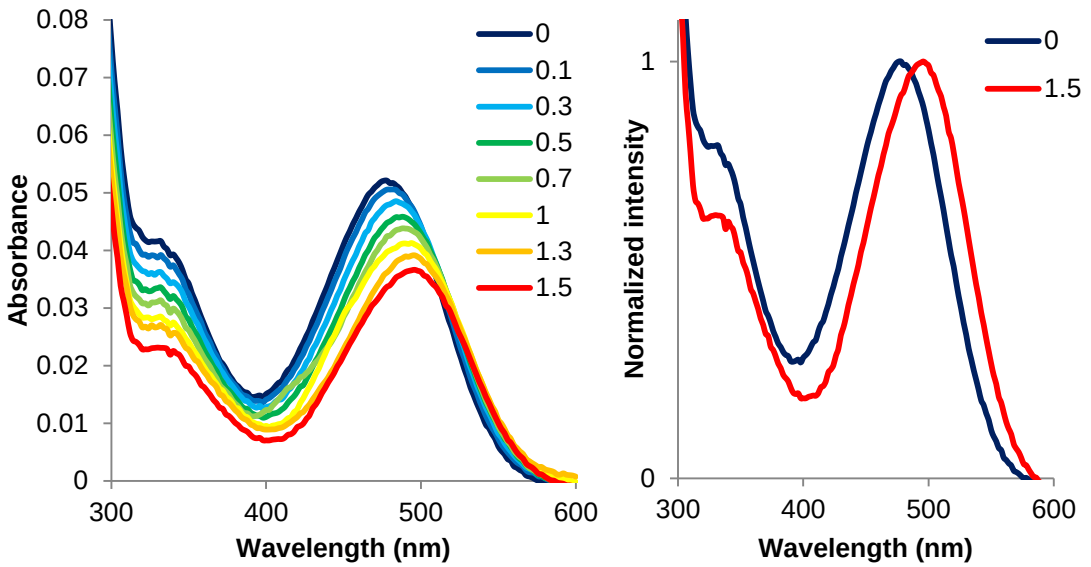


Fig. S7 UV-vis absorption spectroscopic titration of **5** with 0−1.5 mL of $CHCl_3$. [**5**] = 1×10^{-5} M, in THF. 0.1 mL of $CHCl_3$ is about 46.6 equiv.

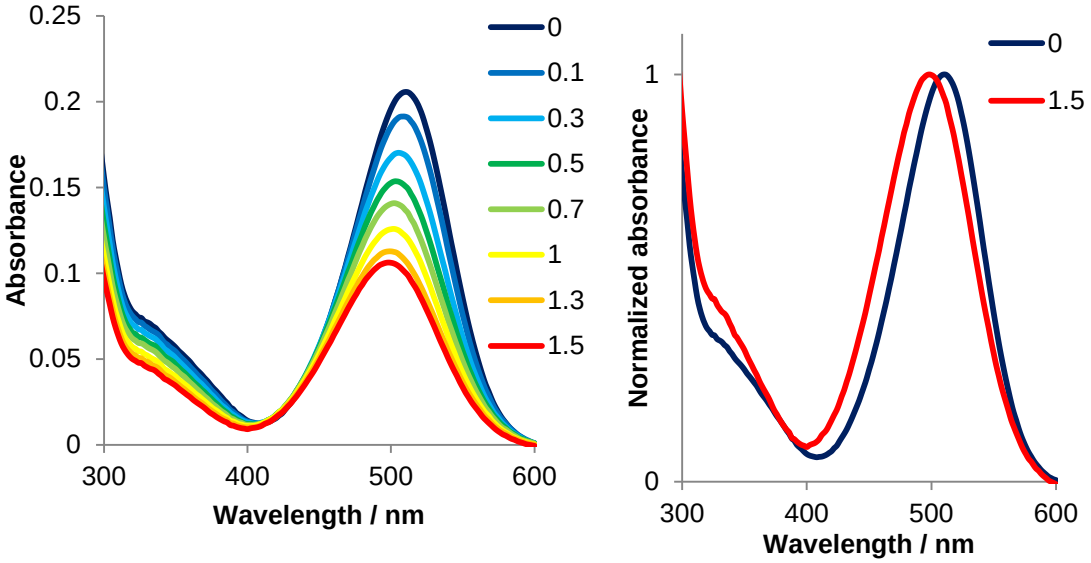


Fig. S8 UV-vis absorption spectroscopic titration of **5** with 0−1.5 mL of THF. [**5**] = 1×10^{-5} M, in $CHCl_3$. 0.1 mL of THF is about 46.3 equiv.

The powder X-ray diffraction pattern.

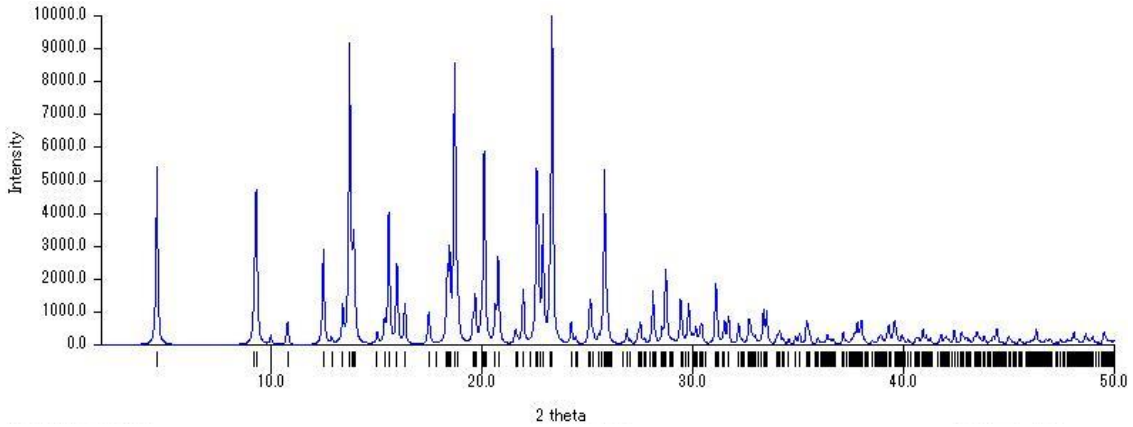


Fig. S9 The simulation signals of powder X-ray diffraction pattern from X-ray structure analysis of **5** obtained from hexane/CH_2Cl_2 solution (Figure S1). The simulation signals were calculated by Mercury.

simulation (2 theta / degree)	4.63	9.36	10.1	10.84	12.53	13.81	15.64	16.04
obtained (dichloromethane)	4.92	8.9	10		12.5	14.86	15.42	15.7
obtained (yellow solid)	4.58	9.16		10.62		13.66	15.5	16.14
simulation (2 theta / degree)	16.44	17.53	18.54	18.74	19.75	20.16	20.84	22
obtained (dichloromethane)	16.9	17.46	18.58	19.2	19.74		21.34	22
obtained (yellow solid)	16.3	17.36	18.4		19.8		20.46	22.24
simulation (2 theta / degree)	22.66	22.99	23.4	25.22	25.9	27.59	28.8	29.48
obtained (dichloromethane)		23.76	24.76	25.6	26.02	27.26	29.2	29.54
obtained (yellow solid)		22.86		25.26		27.22	27.92	28.44

Table S7 The signals of powder X-ray diffraction pattern of simulation (black), CH_2Cl_2 (red), and yellow solid (green).

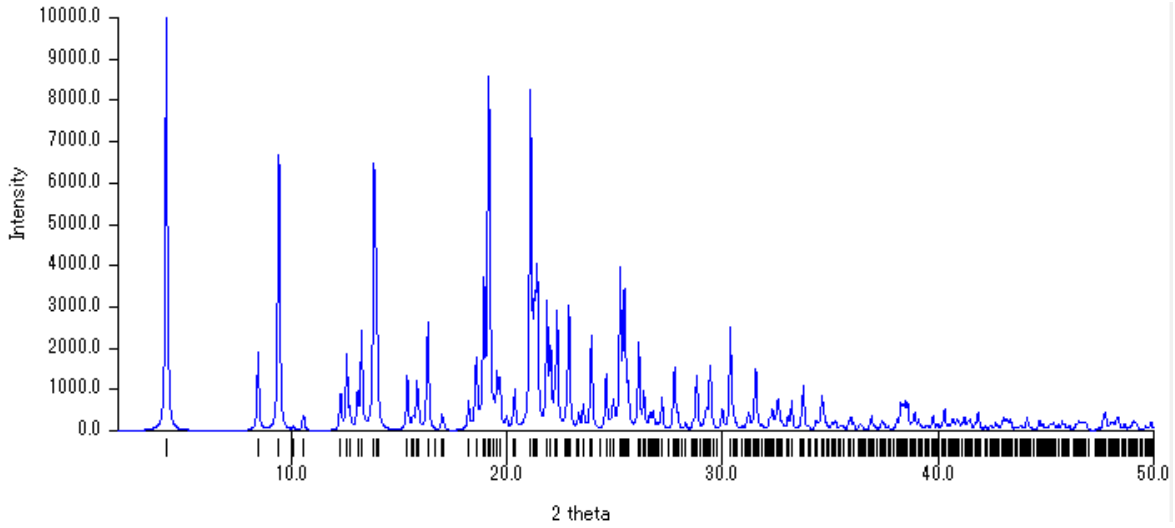


Fig. S10 The simulation signals of powder X-ray diffraction pattern from X-ray structure analysis of **5** obtained from hexane/THF solution (Figure S2). The simulation signals were calculated by Mercury.

simulation (2 theta / degree)	4.26	8.56	9.53	10.64	12.33	12.6	13.27	13.88
obtained (THF)	4.18	8.22	9.3		12.4			13.74
simulation (2 theta / degree)	15.43	15.9	16.38	17.05	18.27	18.61	19.08	19.21
obtained (THF)	15.68	15.92	16.6			18.58	18.8	19.26
simulation (2 theta / degree)	19.69	20.43	21.17	21.44	21.92	22.39	22.93	23.94
obtained (THF)		20.42	20.82	21.54	22.02	22.52	23.02	23.34
simulation (2 theta / degree)	24.62	25.29	25.49	26.17	26.44	27.79	27.27	29.48
obtained (THF)		25.04					28.3	

Table S8 The signals of powder X-ray diffraction pattern of simulation (black) and THF (blue).

The crystal packing structures.

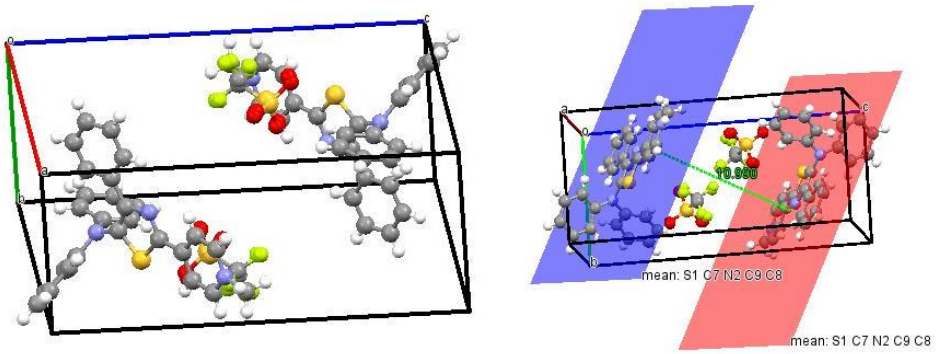


Fig. S11 The crystal structure of **5** obtained from hexane/CH_2Cl_2 solution (Table S1). The distance between the planes of five membered rings was 10.990 Å.

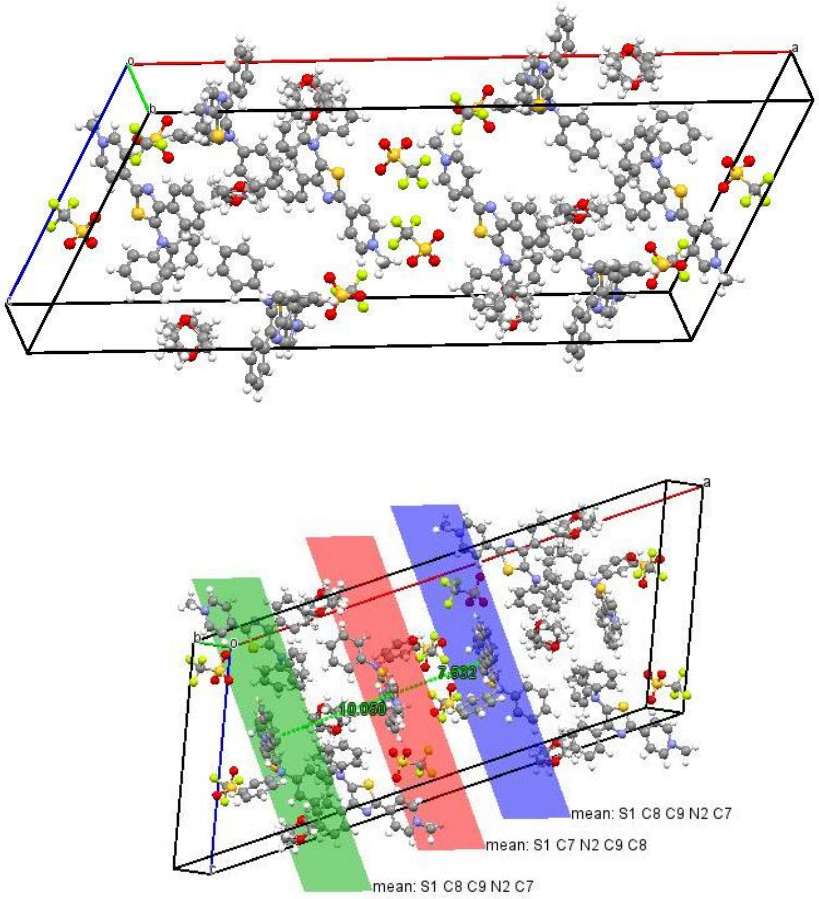


Fig. S12 The crystal structure of **5** obtained from hexane/THF solution (Table S2). The distance between the planes of five-membered rings holding TfO^- anions was 7.532 Å. The distance between the planes of five-membered rings holding THF molecules was 10.050 Å. Additionally, thiazole molecules located around a THF molecule.

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

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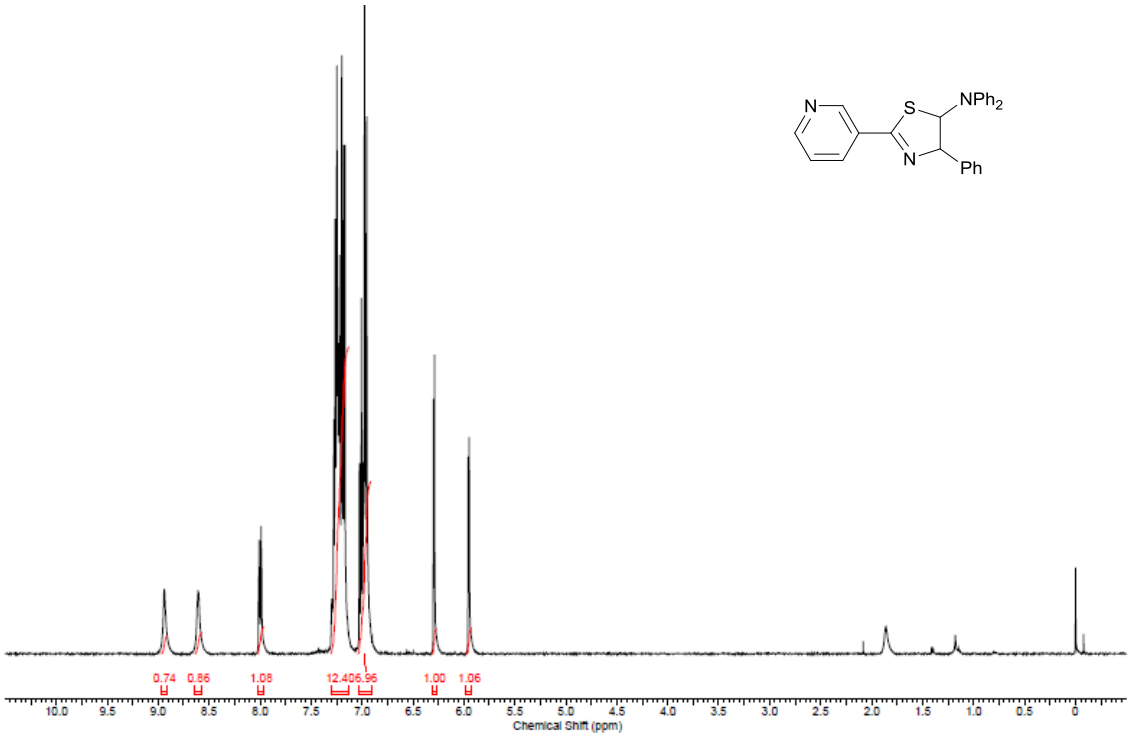
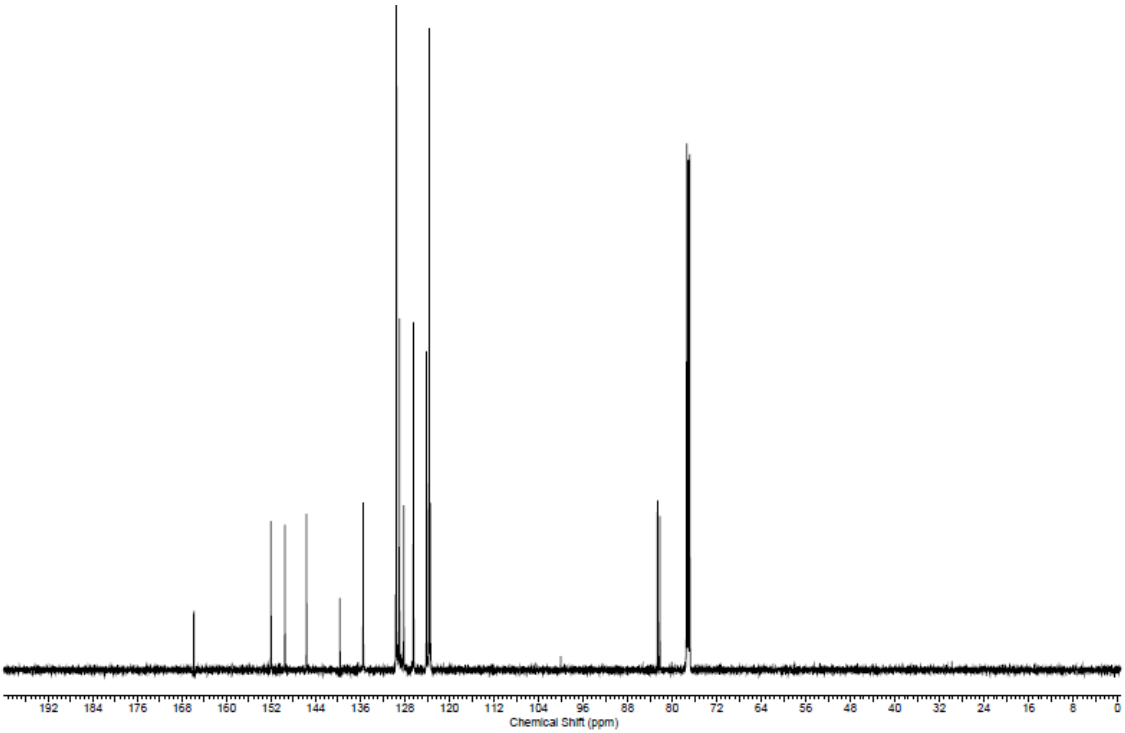
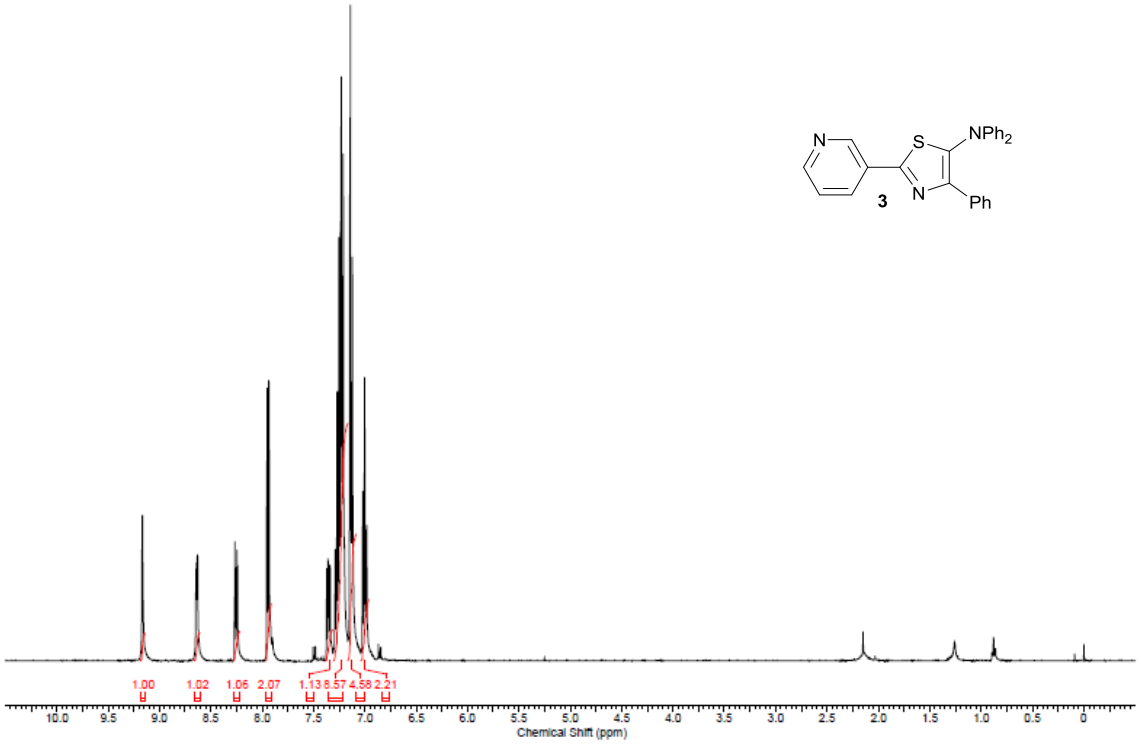
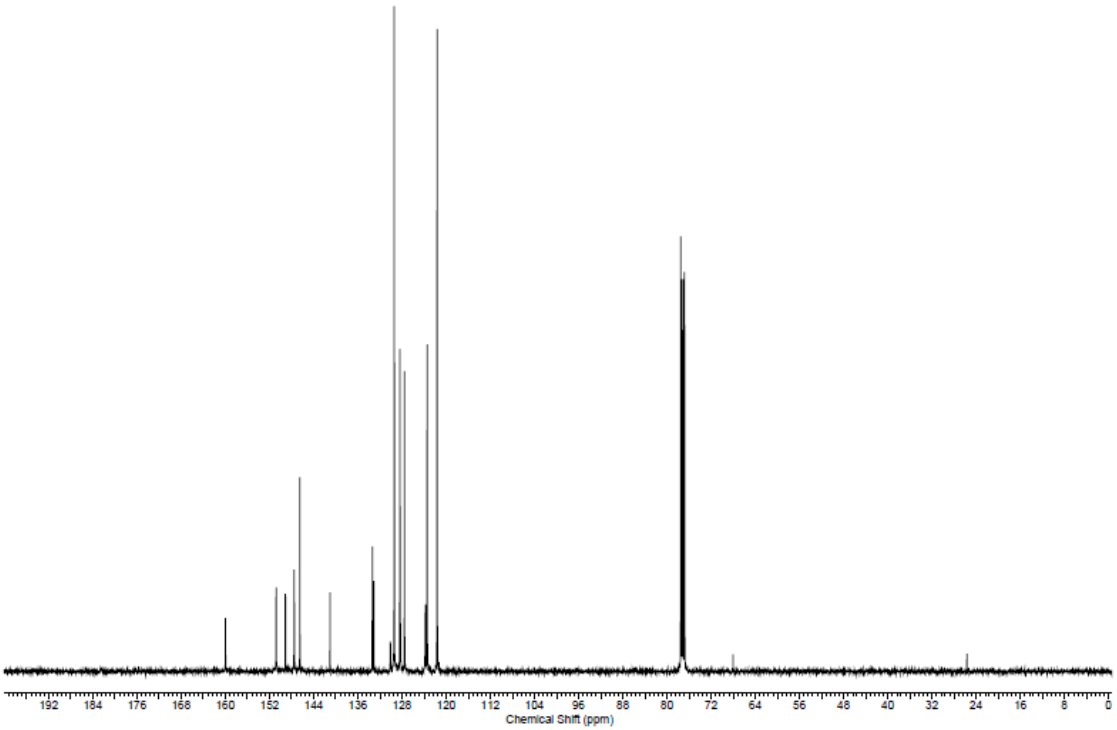


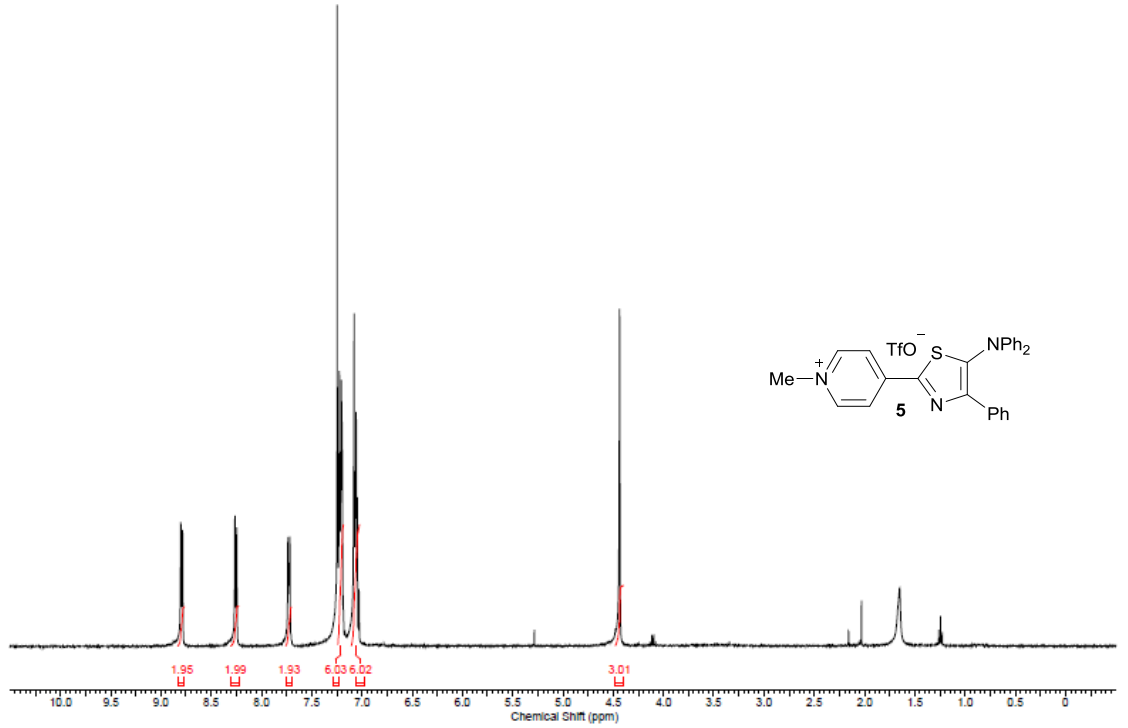


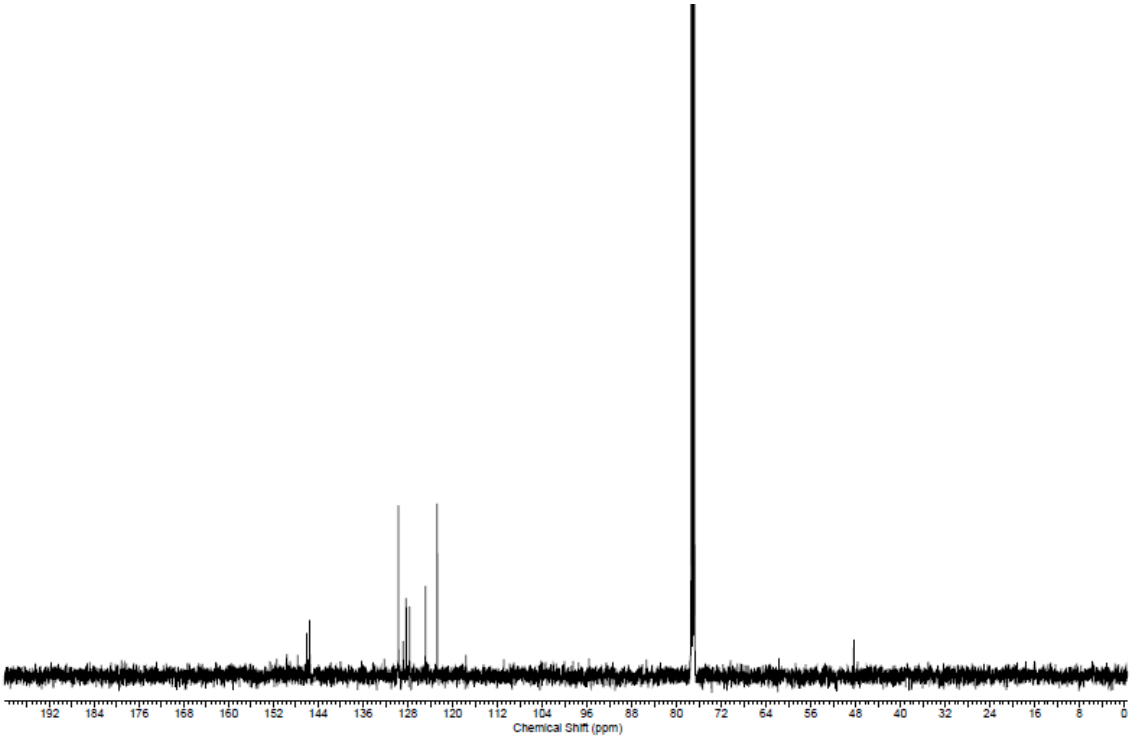
2-(3-Pyridyl)-4-phenyl-*N*,*N*-diphenyl-5-thiazolamine (3)





2-(4-Methylpyridinium)-4,*N*,*N*-triphenyl-5-thiazolamine trifluoromethanesulfonate (5)





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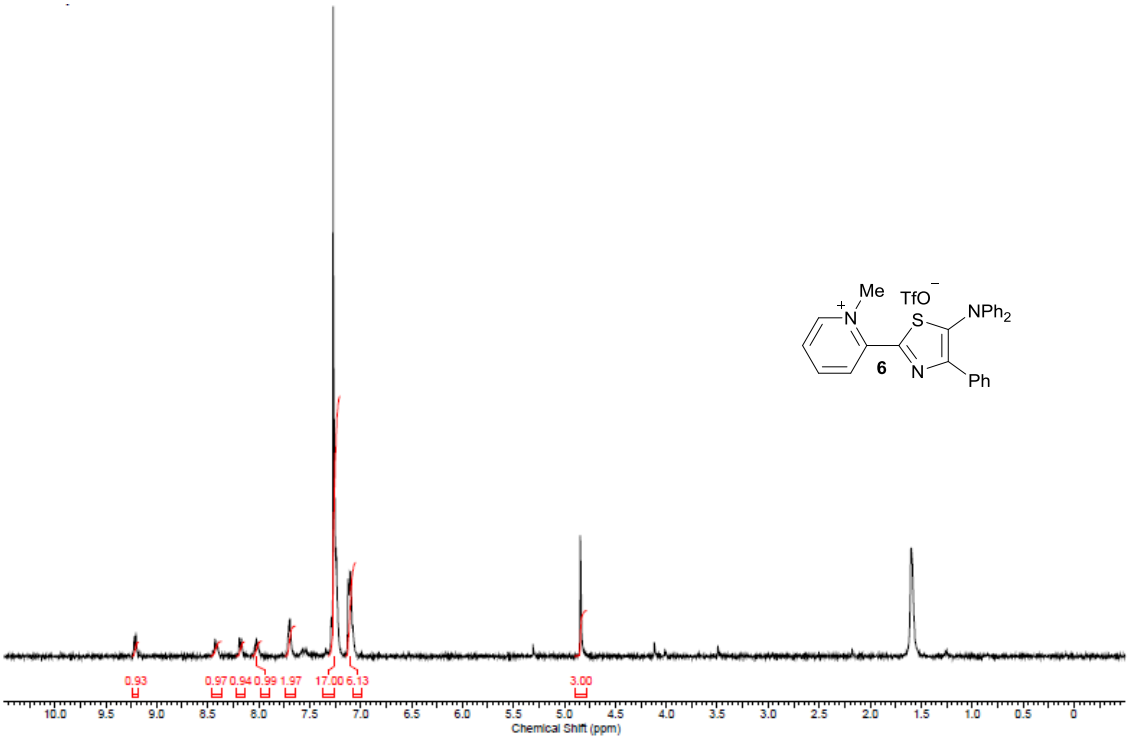

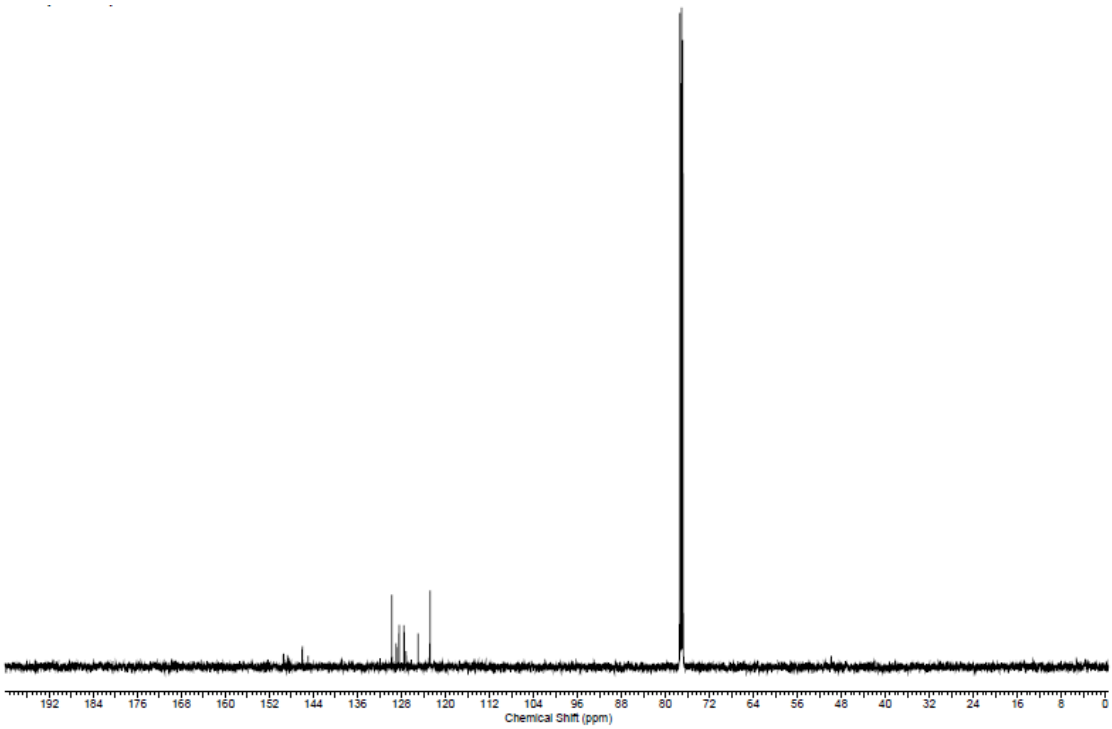

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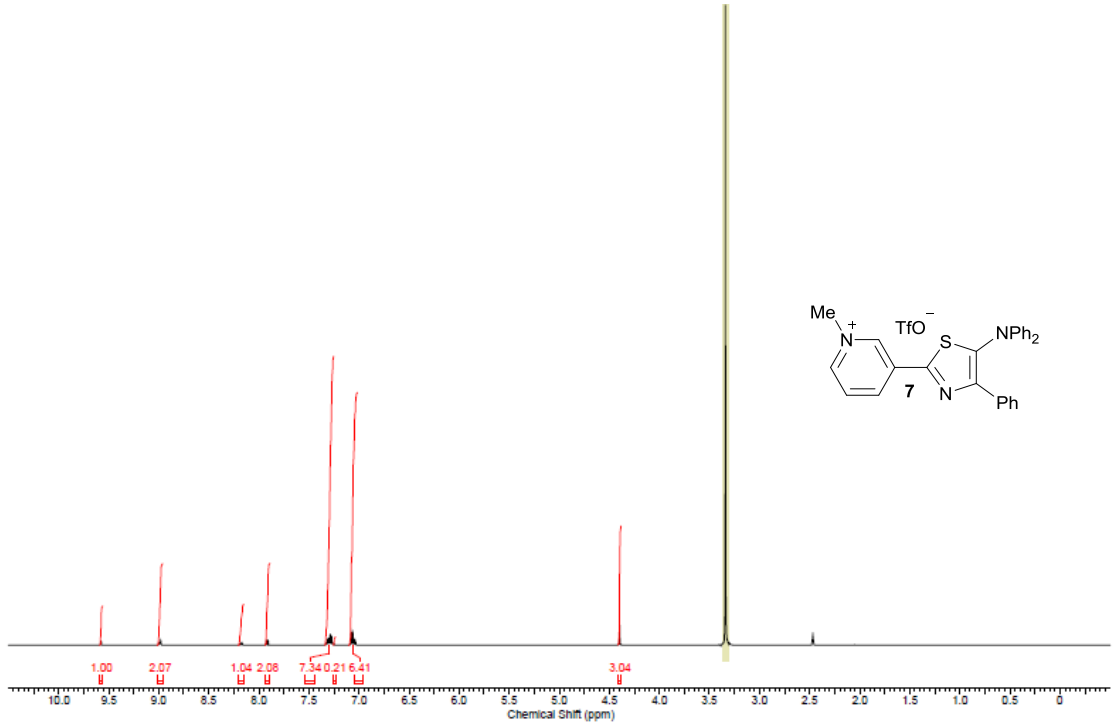
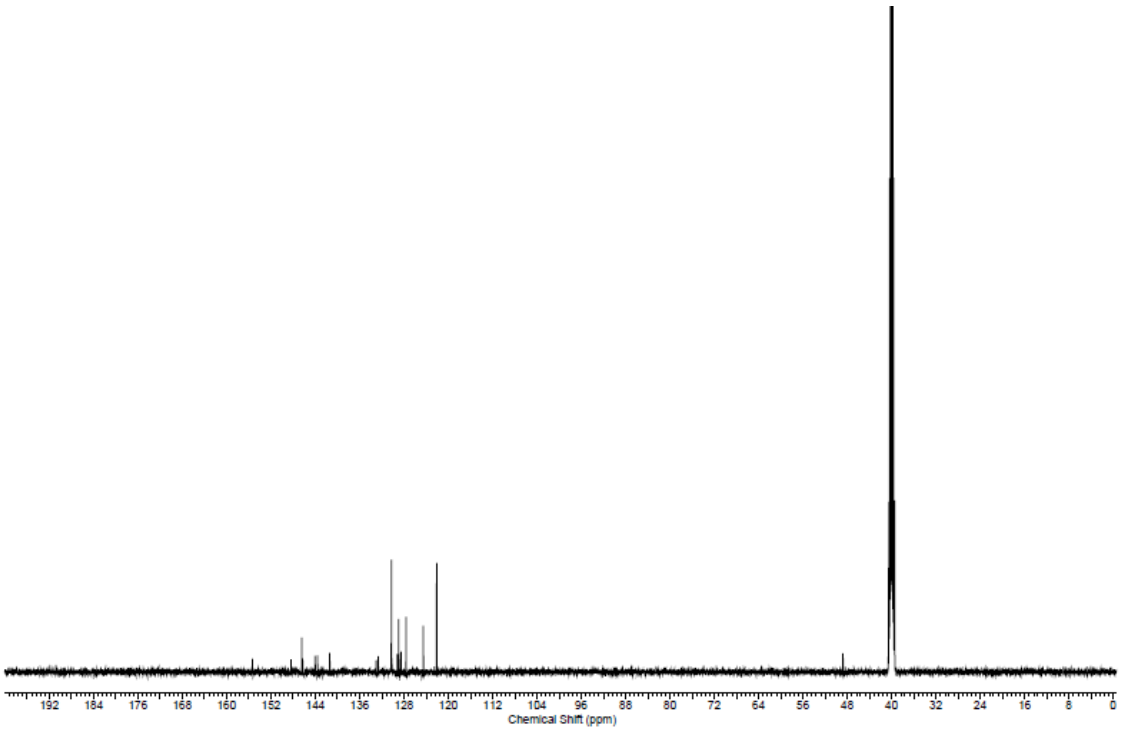
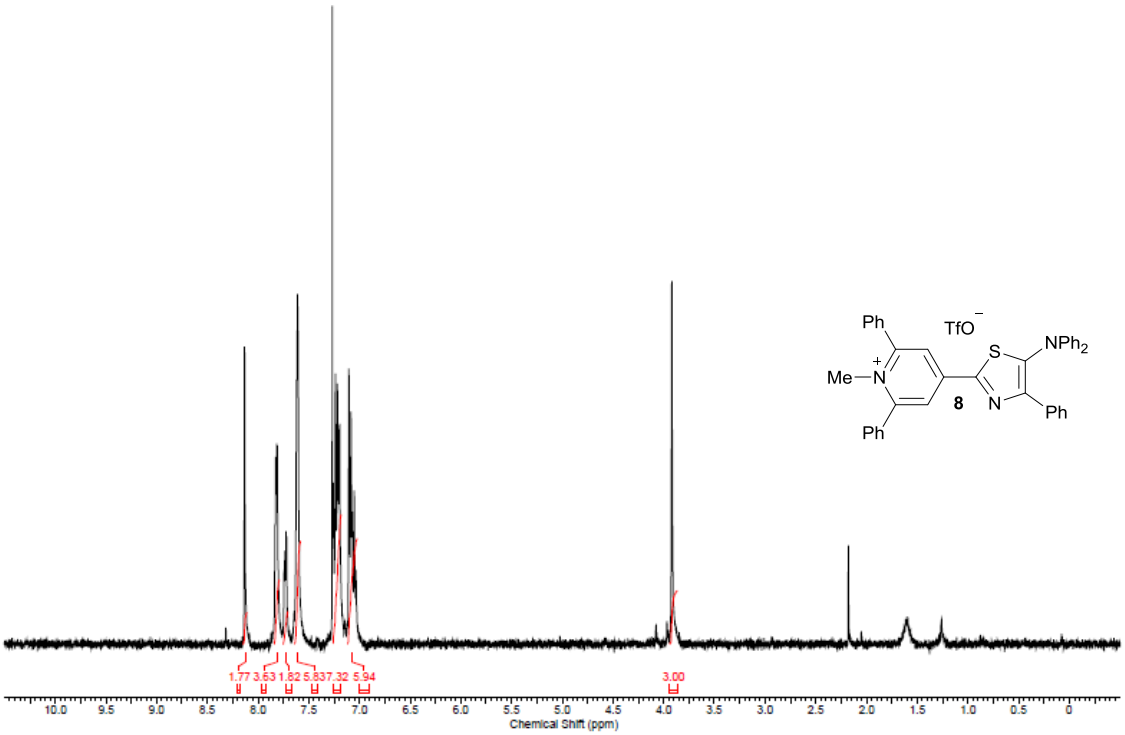
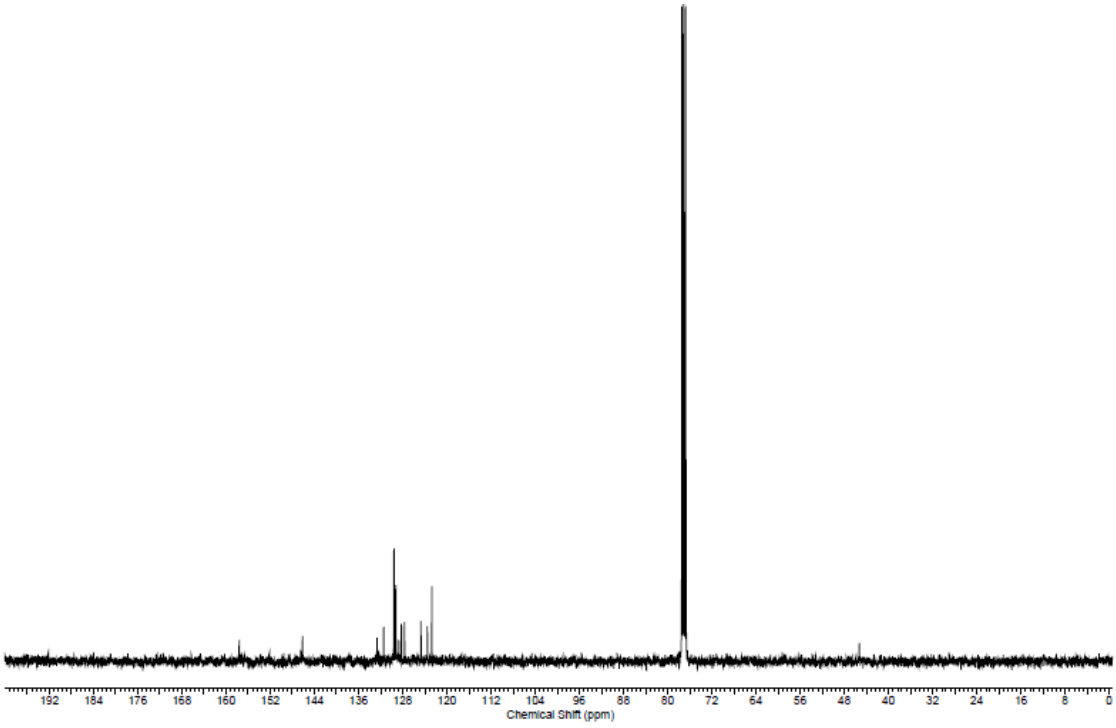




2-(3,5-Diphenyl-4-methylpyridinium)-4,*N*,*N*-triphenyl-5-thiazolamine trifluoromethanesulfonate (8)





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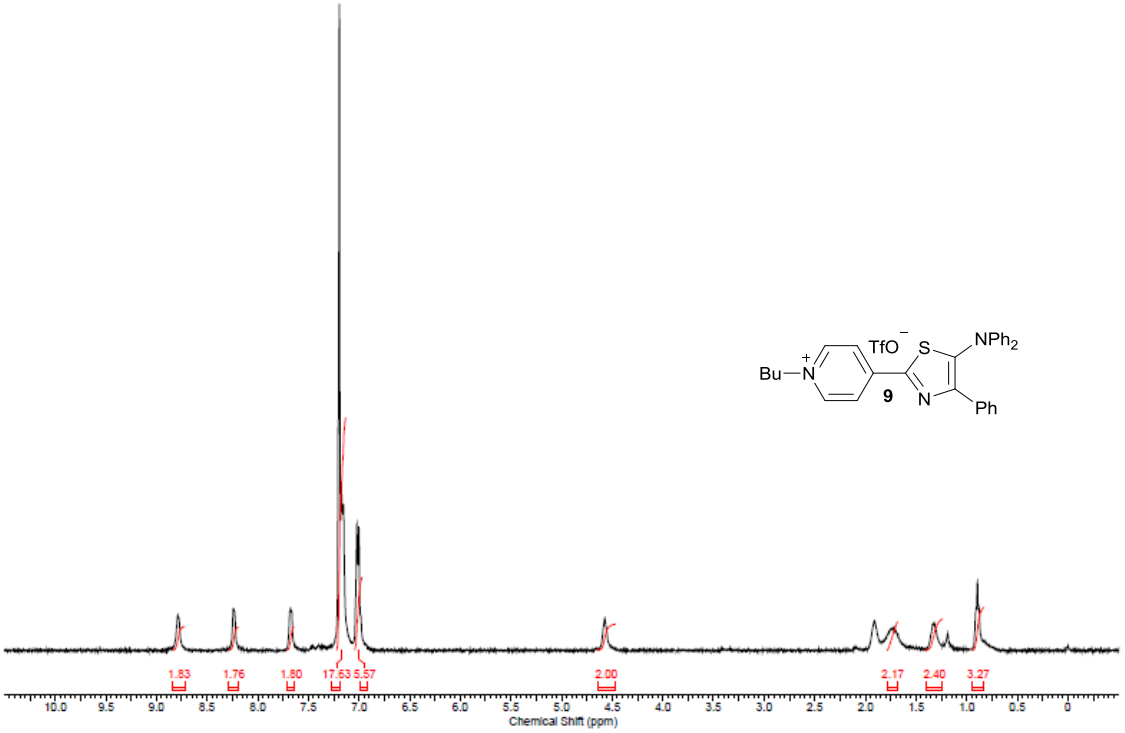

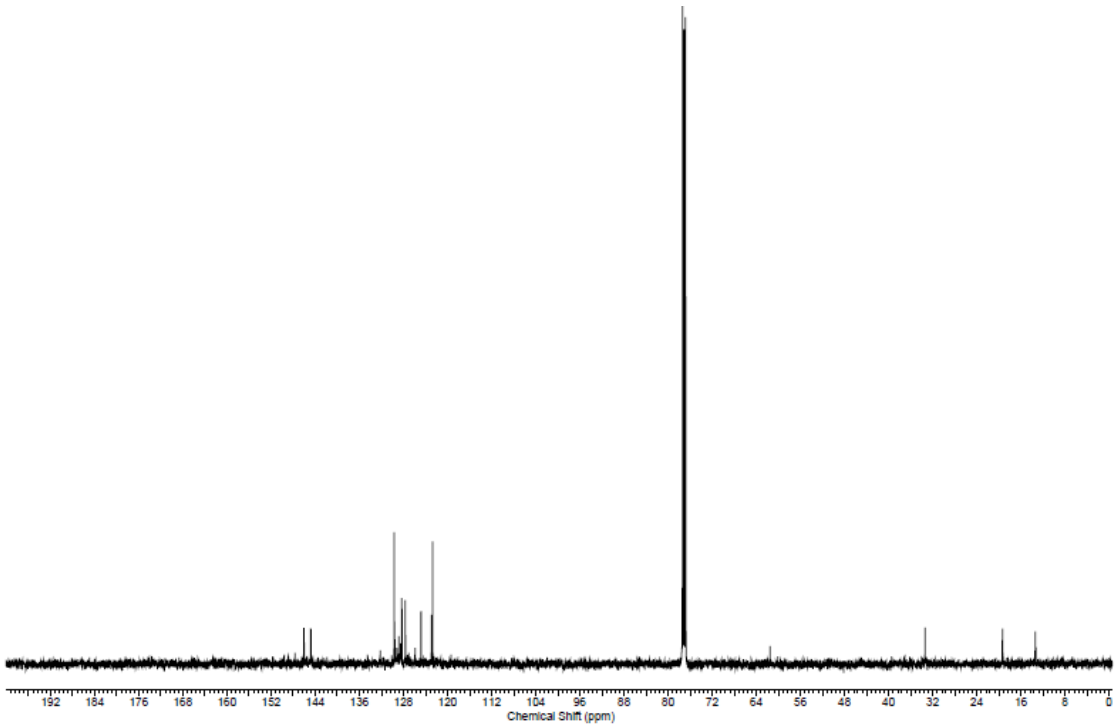

2-(4-Benzylpyridinium)-4,*N*,*N*-triphenyl-5-thiazolamine iodide (10)