

Creation of Excitation-Driven Hypervalent Tin(IV) Compounds For Aggregation-Induced Emission and Application to Thermoresponsive Luminescent Films below Freezing Point

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Abstract

Although many researchers have devoted their much effort to establish the strategy for developing a stimuli-responsive molecule and tuning of their properties according to the preprogrammed design, it is still challenging to create desired molecules from the scratch. We recently demonstrated that the molecules with a large structural difference between the theoretically optimized structures in the ground and excited states have a potential to exhibit stimuli-responsive luminescent properties. We defined these molecules as an excitation-driven molecule and have shown that they are a versatile platform for designing stimuli-responsive luminescent molecules. Herein, based on the concept of excitation-driven molecules, we show that the hypervalent tin-fused azomethine (TAm) compounds possessing aggregation-induced emission (AIE) properties can be obtained by simple chemical modification with a methyl group although conventional TAm derivatives are well known to be highly luminescent compounds in solution. Furthermore, by combining the solid-state luminescence property of AIE and the coordination number shifts of the hypervalent tin atom, the thermoresponsive films operating below the freezing point are fabricated with the polymer. In this study, we apply the concept of excitation-driven molecules to the hypervalent compounds and demonstrate to obtain the novel functional materials.

Introduction

Stimuli-responsive materials can covert information on the micro environment into easily observable signals with detectors or human eyes.^[1] Therefore, the design and development of stimuli-responsive materials are relevant topics in the information society, where the acquisition and analysis of information create great values.^[2] In particular, in the case of organic luminescent molecules, it is possible to tune the target recognition through the molecular design owing to wide structural variety.^[3] Moreover, stimuli-responsive materials that undergo irreversible changes, such as chemical or physical reactions, can keep history of their responses without an electrical power source.^[4] On the other hand, despite the fact that many researchers have made great efforts to establish strategies to develop stimuli-responsive molecules and tune their properties according to preprogrammed designs, it is still challenging to create desired functional molecules from scratch.

Recently, we have found that certain boron complexes exhibit stimuli-responsive luminescent properties^[5,6] such as aggregation-induced emission (AIE),^[7–9] crystallization-induced emission enhancement (CIEE),^[10–15] and viscous-response intramolecular charge transfer (ICT) emission.^[16] In AIE^[17,18] and CIEE,^[19] the dyes hardly show emission in solution and amorphous states, while the emission is recovered in aggregated and crystalline states, respectively, by the restriction of molecular motions in the condensed state. In viscous-response ICT emission, the boron–nitrogen coordination bond in borafluorene is cleaved in the excited state, and the degree of the release of nitrogen coordination for the ICT emission can be modulated by the solvent

viscosity. By exploring the common features of these stimuli-responsive molecules, we found that they exhibit a large structural relaxation in the excited states. Based on these insights, we hypothesized that the theoretical exploration of the molecule that shows a large structural difference between the ground and excited states should lead to the creation of unique stimuli-responsive molecules through the modulation of molecular motions. We defined such molecules as excitation-driven molecules and proposed them as the new class of the molecular scaffolds for creating stimuli-responsive luminescent materials.^[20] The importance of considering the excited state in elucidating the mechanism of stimuli-responsive luminescence properties has also been suggested.^[21–27]

Hypervalent tin-fused azomethine (TAm) compounds are known to exhibit intense luminescence in solution.^[28–30] Therefore, TAm compounds have been used for bioimaging probes,^[31–34] light sources in organic light-emitting diodes (OLEDs),^[35] and dyes in organic solar cells.^[36] We also recently demonstrated that hypervalent tin-fused azobenzene (TAz) compounds^[37] exhibit the deep red to near-infrared (NIR) luminescence owing to their narrow energy gap originating from the low lowest unoccupied molecular orbital (LUMO) and the high highest occupied molecular orbital (HOMO) energy levels caused by the tin–nitrogen coordination bond and the polarized three-center four-electron (3c-4e) bond, respectively.^[38–40] Furthermore, we have shown that the coordination number shifts of tin induced by the addition of ligands are applicable for modulating the electronic properties of the directly-linked π -conjugated systems.^[38] Based on the unique reactivity of the hypervalent tin, vapo-chromic films consisting of π -conjugated polymers were developed.^[41,42] On the other hand, aggregation-caused

quenching (ACQ) in polymer films remains a serious problem to be solved. To overcome this problem, it is necessary to develop solid-state luminescent polymers that contain stimuli-responsive hypervalent tin moieties in the polymer main chains for obtaining light-emitting film materials.

In this study, we initially demonstrate to convert TAm compounds into excitation-driven molecules with excellent solid-state luminescence. From the results of quantum chemical calculations, it was presumed that the excitation-driven property can be induced simply by modifying the azomethine moiety with a methyl group. Consequently, it was shown that the luminescence behavior can be reversed from ACQ to AIE by the methyl substitution as the theoretical suggestion. Furthermore, taking advantage of the solid-state emission, the AIE-active π -conjugated polymers were created. The synthesized polymers were used for thermoresponsive luminescent materials and the operating temperature range was tunable by the coordination strength between tin and the ligand to form the seven-coordinated tin center. In particular, by using the ligand with weak coordination ability, the luminescence color change was inducible even below the freezing point. Our results, based on the design strategy of excitation-driven molecules, offer the possibility of freely creating stimulus-responsive molecules from scratch even with minimal molecular modification.

Results and Discussion

Molecular Designs from DFT calculations

The excitation-driven compounds for solid-state luminescent materials were designed by quantum chemical calculations with density functional theory (DFT). The detail calculation methods are shown in the Supporting Information. First, we explored for the TAm derivatives with large structural changes between the optimized structures in the ground and the excited states (Figure 1). It is known that the **TAmH** analogs show efficient emission in solution.^[28–36] Therefore, we introduced a phenyl group at the carbon of the azomethine moiety by referring to the structure of tetraphenylethene (TPE), which shows AIE because of the rotatable sterically-interacted phenyl rings.^[43] The bromine group was added to increase the crystallinity even with the twisted π -conjugated system. As a result, the structural changes between in the ground and the excited states were clearly shown in the dihedral angle of C(1)-N(1)-C(13)-H(4) for **TAmH** and C(1)-N(1)-C(13)-C(26) for **TAmPh**. In **TAmH**, the change in the dihedral angle of C(1)-N(1)-C(13)-H(4) between in the ground and the excited states was 2.5°. On the other hand, the larger alteration in the dihedral angle of C(1)-N(1)-C(13)-C(26) was proposed in **TAmPh** (15.3°). This should be because of the steric repulsion with surrounding atoms derived from the larger size of the phenyl ring compared to that of the hydrogen atom.

To evaluate the substituent effect on the large structural deformation in the excited state, we also designed **TAmMe** in which the phenyl group in **TAmPh** was replaced by a methyl group. Consequently, in **TAmMe**, the variation in the dihedral angle of C(1)-N(1)-C(13)-C(26) between in the ground and the excited states was 8.0°. Although the difference of the dihedral angle in **TAmMe** was smaller than that in **TAmPh**, the dihedral angle in the excited state of **TAmMe** was 21.2°, which was comparable to that of **TAmPh**

(23.4°). This indicates that the structure of **TAmMe** is highly twisted in the excited state, and it is suggested that the creation of excitation-driven compounds should be possible even with the introduction of a simple methyl group.

The degree of structural changes after photo-excitation can be estimated by the width of the Stokes shift which is defined as the energy difference between $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_0$ transitions. According to the calculated transition energies, the Stokes shifts were estimated to be 5,700 cm^{-1} (154 nm) for **TAmH**, 7,300 cm^{-1} (206 nm) for **TAmMe**, and 8100 cm^{-1} (256 nm) for **TAmPh** (Figure S1 and Table S1). This also implies that the introduction of the methyl and phenyl groups has a potential to enhance structural changes between the ground and excited states. From these results, **TAmMe** and **TAmPh** are selected as a candidate of excitation-driven molecules, and their twisted structures could be favorable for exhibiting solid-state emission. Therefore, we synthesized **TAmH**, **TAmMe**, and **TAmPh** to investigate their optical properties for evaluating validity of calculation data.

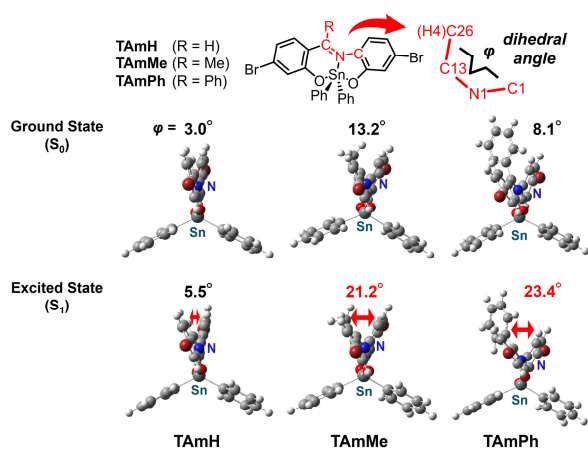
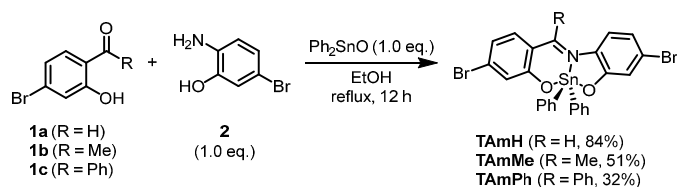


Figure 1. Dihedral angles (φ) of C(1)-N(1)-C(13)-H(4) for **TAmH** or C(1)-N(1)-C(13)-C(26) for **TAmMe** and **TAmPh** of the optimized structures in the ground and excited states (S_0 and S_1).

Synthetic procedures for TAm derivatives

Scheme 1 shows the synthesis of **TAmH**, **TAmMe**, and **TAmPh**. 4-Bromo-2-hydroxybenzaldehyde (**1a**), 4-bromo-2-hydroxyacetaldehyde (**1b**), and 4-bromo-2-hydroxybenzophenone (**1c**) were reacted with 4-bromo-2-hydroxybenzaldehyde (**2**) and diphenyltin(IV) oxide in ethanol (EtOH) at reflux condition, and **TAmH**, **TAmMe**, and **TAmPh** were obtained in 84, 51, and 32% isolated yields, respectively. The synthesized TAm derivatives were characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{119}Sn NMR spectroscopy and high-resolution mass spectrometry (HRMS). From these characterization data, it was confirmed that they had the designed structures and enough purity to evaluate optical properties.

Scheme 1. Synthesis of TAmH, TAmMe, and TAmPh



Crystal structures

The crystal structures of **TAmH**, **TAmMe**, and **TAmPh** were revealed by the single crystal X-ray diffraction analysis (Figure 2). The detailed crystallographic data are shown in Tables S2–S4 and Figures S2–S4. All TAm derivatives formed five-coordinated hypervalent compounds. The tendency of the magnitude of the distortion around the azomethine moiety was in good agreement with the optimized S_0 structure obtained from the quantum chemical calculation. **TAmH** had the highly planar π -conjugated system including the azomethine moiety with the absolute value of the C(1)-N(1)-C(13)-H(4) dihedral angle of 0.57° (Figure 2a). In addition, the π -plane was largely overlapped with the neighbor molecule in the packing structure. On the other hand, the π -conjugated systems in **TAmMe** and **TAmPh** were slightly twisted by the steric repulsion of the methyl and phenyl groups at the azomethine moiety with the hydrogen atoms in both sides of the benzene rings, respectively (Figures 2b and 2c). The absolute values of the C(1)-N(1)-C(13)-C(26) dihedral angles were 8.56° for **TAmMe** and 6.50° for **TAmPh**. Moreover, the π -planes of **TAmMe** and **TAmPh** in the packing structures were less overlapped than that of **TAmH** because of the distorted π -conjugated system and steric hindrance of the substituents at the azomethine moieties. Therefore, in **TAmMe** and **TAmPh**, the formation of intermolecular π - π interactions leading to ACQ should be disturbed. In other words, **TAmMe** and **TAmPh** have a potential to show solid-state emission with AIE.

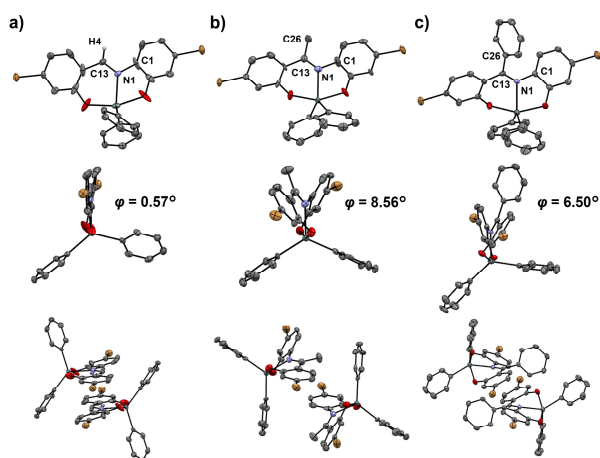


Figure 2. Top view (upper), side view (middle), and packing structures (lower) of ORTEP drawings of a) **TAmH**, b) **TAmMe**, and c) **TAmPh** with the dihedral angles (φ) in C(1)-N(1)-C(13)-H(4) for **TAmH** and C(1)-N(1)-C(13)-C(26) for **TAmMe** and **TAmPh**. Hydrogen atoms except for H(4) in **TAmH** and a minor conformation of **TAmH** are omitted to clarity.

Optical properties of **TAmH**, **TAmMe**, and **TAmPh**

To evaluate the optical properties of the synthesized TAM derivatives, we measured UV-vis absorption and photoluminescence (PL) spectra in solution (1.0×10^{-5} M in CHCl_3) and solid. As we expected, **TAmMe**, and **TAmPh** clearly showed AIE, while **TAmH** exhibited ACQ (Figure 3 and Table 1). The absorption bands of **TAmMe** and **TAmPh** exhibited hypsochromic shifts compared to that of **TAmH**. This should be caused by the twisted π -conjugated systems of **TAmMe** and **TAmPh**, which prevent the delocalization of the π -electron. On the other hand, larger bathochromic shifts in the PL

spectra were observed in **TAmMe** and **TAmPh** compared to that in **TAmH**. The Stokes shifts ($\Delta\nu$) were calculated to be 4,330 cm^{-1} (114 nm) for **TAmH**, 6,890 cm^{-1} (174 nm) for **TAmMe**, and 7,210 cm^{-1} (202 nm) for **TAmPh**, and the tendency was identical to the results of the quantum chemical calculation.

TAmH showed highly efficient emission in solution ($\Phi_{\text{PL}} = 34.5\%$), whereas the critical ACQ was observed in the solid sample ($\Phi_{\text{PL}} = 8.3\%$). In contrast, **TAmMe** and **TAmPh** hardly showed emission in solution ($\Phi_{\text{PL}} < 1\%$), meanwhile the emission intensities were enhanced in solid ($\Phi_{\text{PL}} = 20.3\%$ for **TAmMe** and $\Phi_{\text{PL}} = 21.1\%$ for **TAmPh**) accompanied by the hypochromic shifts of emission bands. The emission enhancement was also observed in the 1 wt% dye-dispersed polymer film (Figure S5 and Table S5). These are the typical behavior of AIE, where the structural relaxation is strongly restricted in solid and the polymer matrix with multiple intermolecular interactions. From the PL lifetime measurement, the radiative and nonradiative constants (k_r and k_{nr}) of **TAmH** in solid decreased and increased compared to those in solution, respectively (Figure S6 and Table S5). This should be caused by the strong intermolecular π - π interaction leading to ACQ such as H-aggregation.^[44] In contrast, owing to the few intermolecular π - π interactions, the k_r and k_{nr} of **TAmMe** and **TAmPh** in solid increased and decreased compared to those of **TAmH**, respectively. The elevation of the k_r values in crystal might be derived from the high refractive indices in organic crystal including heavy elements.^[44,45] In addition, the reduction of k_{nr} was attributed to the significant restriction of the molecular motions through multiple intermolecular interactions in crystal. From these optical properties, it can be said that we were able to design and create

excitation-driven molecules with efficient solid-state emission from scratch with quantum chemical calculations.

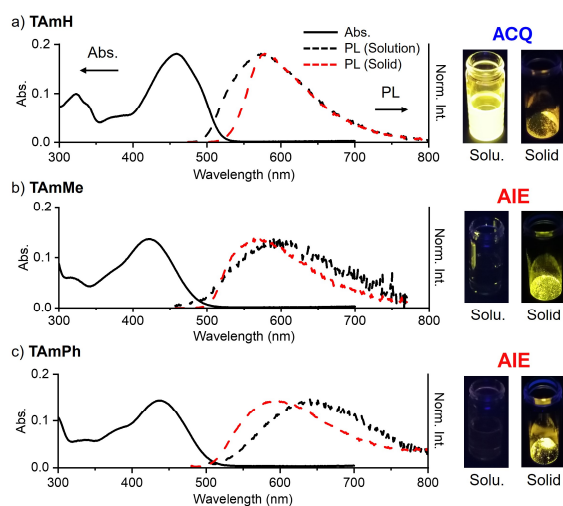


Figure 3. UV–vis absorption and PL spectra of a) **TAmH**, b) **TAmMe**, and c) **TAmPh** in solution (1.0×10^{-5} M in CHCl_3) and solid, excited at the absorption maximum wavelength in solution. Photographs under UV irradiation (365 nm) in solution (Solu.) and solid (Solid).

Table 1. Optical data of **TAmH**, **TAmMe**, and **TAmPh**

		$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{PL}}^b / \text{nm}$	$\Delta\nu / \text{cm}^{-1} (\Delta\lambda / \text{nm})^c$	$\Phi_{\text{PL}}^{b,d} / \%$
TAmH	CHCl_3^a	459	573	4330 (114)	34.5
	Solid	– ^e	580	– ^e	8.3
TAmMe	CHCl_3^a	423	597	6890 (174)	<1
	Solid	– ^e	561	– ^e	20.3
TAmPh	CHCl_3^a	438	640	7210 (202)	<1
	Solid	– ^e	597	– ^e	21.1

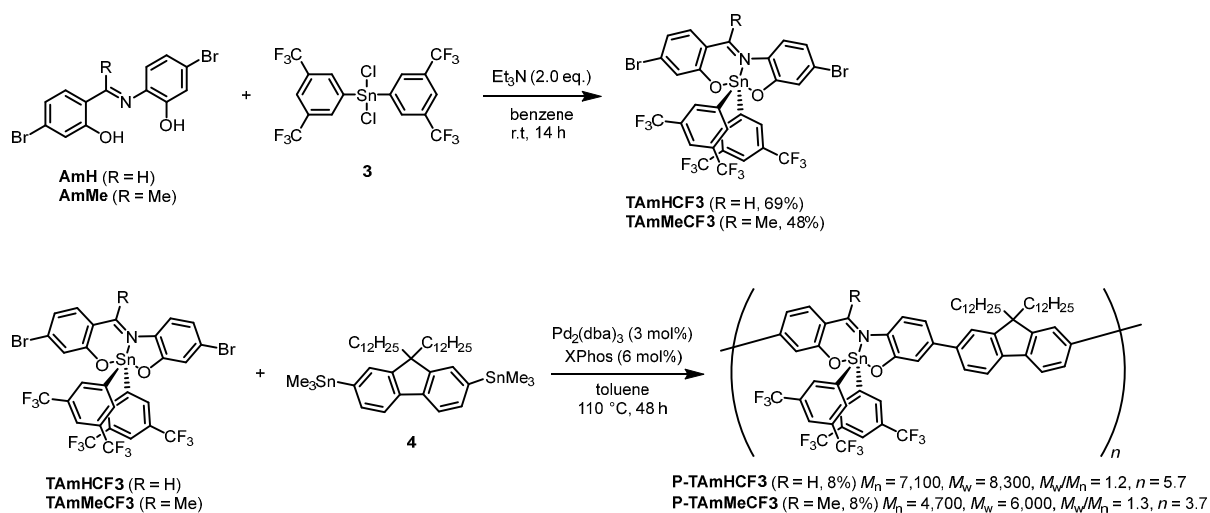
^a 1.0×10^{-5} M, ^b excited at λ_{abs} in CHCl_3 , ^c Stokes shift ($\Delta\nu$) = $(1/\lambda_{\text{abs}} - 1/\lambda_{\text{PL}}) \times 10^7$ and $\Delta\lambda = \lambda_{\text{PL}} - \lambda_{\text{abs}}$, ^d absolute PL quantum yield, ^e not measured.

Synthesis of stimuli-responsive materials

It was revealed that the introduction of the methyl group at the azomethine moiety is effective for obtaining solid-state emission. Next, to load stimuli-responsiveness through the coordination number shifts at the hypervalent tin center, the monomers, **TAmHCF3** and **TAmMeCF3**, were designed. In these compounds, to realize the stimuli-responsiveness with high sensitivity, the Lewis acidity of the tin center was enhanced by the introduction of electron-withdrawing trifluoromethyl groups. The synthesis was performed according to Scheme 2. The reactions with di-[3,5-(trifluoromethyl)phenyl]dichlorostannane (**3**) and the corresponding azomethine ligands (**AmH** and **AmMe**) were conducted in the presence of triethylamine (Et_3N) to trap the eliminated hydrogen chloride (HCl). **TAmHCF3** and **TAmMeCF3** were afforded in 69 and 48% isolated yields, respectively.

To prepare the stimuli-responsive polymeric materials with intense luminescence and good film-formability, copolymerization was carried out in the Migita–Kosugi–Stille cross-coupling reaction^[46,47] with **TAmHCF3** and **TAmMeCF3** and a fluorene comonomer (**4**) in the presence of $\text{Pd}_2(\text{dba})_3$ (dba = dibenzylideneacetone) and XPhos (2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl). Due to the low reactivity of the monomers, the low molecular weight products remained after the reaction. Therefore, the high molecular weight parts of the synthesized polymers (**P-TAmHCF3** and **P-**

TAmMeCF3) were separated by high performance liquid chromatography (HPLC) (**P-TAmHCF3**: $M_n = 7,100$, $M_w = 8,300$, $M_w/M_n = 1.2$, $n = 5.7$, 8% isolated yield, and **P-TAmMeCF3**: $M_n = 4,700$, $M_w = 6,000$, $M_w/M_n = 1.3$, $n = 3.7$, 8% isolated yield). Number and weight average molecular weights (M_n and M_w) were determined by gel permeation chromatography (GPC) using polystyrene standards and CHCl_3 as eluent. According to these polymer properties, we concluded that the products should have enough length to exhibit luminescence originating from the extended π -conjugation and have film-formability for evaluating stimuli-responsiveness of polymer films. All products were characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{119}Sn NMR spectra and high-resolution mass spectrometry (HRMS). From these characterization data, it was confirmed that the synthesized compounds had enough purity to conduct optical measurements.



Scheme 2. Synthesis of TAm monomers and their copolymers. The regiorandom polymers were obtained, and this certain structure is shown here.

Optical properties for monomers and polymers

The optical properties of the synthesized monomers and polymers were investigated by UV–vis absorption and PL spectra measurements (Figures 4 and S7 and Table 2). Consequently, **TAmHCF3** and **TAmMeCF3** exhibited ACQ and AIE, respectively, similarly to **TAmH** and **TAmMe**. This indicates that the optical features in the main π -conjugated system were retained regardless of the substituents at tin. The ACQ and AIE properties of the monomers were able to be taken over the properties of the polymers. **P-TAmHCF3** showed bathochromic shifts of absorption and emission bands with the high emission efficiency. This is because of the extension of π -conjugation through the polymer main chain including multiple TAm units.^[48] On the other hand, the emission was crucially quenched in film due to ACQ. Although the bathochromic shifts of absorption and emission bands were also observed in **P-TAmMeCF3**, the emission efficiency was still low. In contrast to **P-TAmHCF3**, the emission efficiency was clearly enhanced in film. From the analysis with the PL lifetime measurements, the emission enhancement of the π -conjugated polymer was attributed to the increase in the k_r value (Figure S8 and Table S6). Although the PL lifetime of **P-TAmHCF3** was not detected in solution, the AIE property of the film should be derived from the large decrease in k_{nr} by suppressing molecular motions. The resulting absolute PL quantum yields of the polymers in film were the same, and we used **P-TAmMeCF3** for stimuli-responsive tests because of its high solubility and processability, and higher chemical stability against a nucleophilic attack of the ketimine moiety in **P-TAmMeCF3** compared to the aldimine one in **P-TAmHCF3**.

Table 2. Optical data of TAm monomers and polymers

		λ_{abs} / nm	λ_{PL} ^b / nm	Φ_{PL} ^{b,c} / %
TAmHCF3	In CHCl ₃ ^a	456	570	31.7
	Solid	– ^d	562	8.1
TAmMeCF3	In CHCl ₃ ^a	417	574	<1
	Solid	– ^d	557	11.6
P-TAmHCF3	In CHCl ₃ ^a	498	575, 618	49.1
	Film ^e	505	591, 633	4.7
P-TAmMeCF3	In CHCl ₃ ^a	457	618	1.0
	Film ^e	465	624	4.7

^a 1.0×10^{-5} M for monomers and 1.0×10^{-5} M per repeating unit for polymers, ^b excited at λ_{abs} in CHCl₃, ^c absolute PL quantum yield, ^d not measured, ^e spin-coated film (1000 rpm, 30 s) on the quartz substrate (0.9 cm $\times$ 2.5 cm) from the polymer solution (polymer (1.0 mg) / CHCl₃ (300 μ L)).

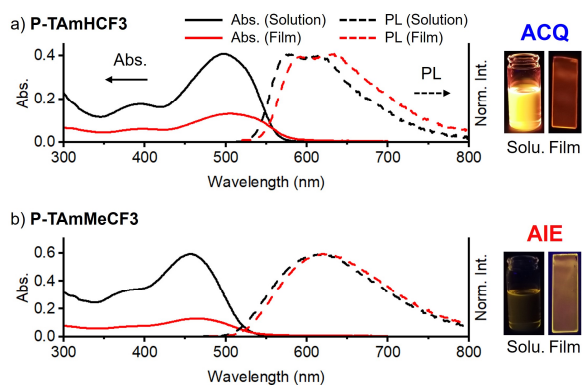


Figure 4. UV–vis absorption and PL spectra of a) **P-TAmHCF3** and b) **P-TAmMeCF3** in CHCl₃ (1.0×10^{-5} M per repeating unit) and film, excited at the absorption maximum wavelength in CHCl₃. Photographs under UV irradiation (365 nm) in solution (Solu.) and film (Film).

Binding constants

Before the stimuli-responsive tests based on the coordination number shifts of the hypervalent tin center, we estimated a binding constant (K) which should be enhanced by the electron-withdrawing substituents at tin. The details of the estimation method are shown in the Supporting Information (Figure S9). Previously, we revealed that the similar hypervalent tin compounds can form the robust seven coordination state with 1,10-phenanthroline (**phen**).^[42] In the titration experiments with the UV-vis absorption measurement of **TAmMe**, the spectral changes were observed with the addition of 20 eq. **phen** (Figure 5a). In **TAmMeCF3**, interestingly, the similar changes were induced with the only 0.2 eq. **phen** (Figure 5b). From these data, the estimated binding constants were determined as $6.1 \times 10^2 \text{ M}^{-1}$ for **TAmMe** and $4.1 \times 10^5 \text{ M}^{-1}$ for **TAmMeCF3**. By introducing trifluoromethyl groups at the tin moiety, about 700 times increase in the binding constant was achieved. The electron density at the tin center was lowered by electron-withdrawing substituents, and subsequently the Lewis acidity of tin atom was improved. The binding constant of 2,2'-bipyridyl (**bipy**) with **TAmMeCF3** was reduced to be $4.2 \times 10^2 \text{ M}^{-1}$ due to the rotatable structural flexibility of **bipy**. We constructed the stimuli-responsive materials based on these differences in the binding constants.

The coordination number shifts of the tin center from five to seven upon addition of the ligands (**phen** and **bipy**) were confirmed by ^{119}Sn NMR spectroscopy. It is known that more than 200 ppm upfield chemical shift is observed by the coordination number shifts from five to seven.^[42,49] According to the spectrum of **TAmMeCF3**, about 250 ppm upfield chemical shift was detected upon the addition of 8 eq **phen**, which was the enough

amount of the formation of the seven coordination in solution (Figure S10a). On the other hand, upon the addition of 10 eq **bipy**, which was not the enough amount of the formation of the seven coordination in solution, the sharp signal with about 260 ppm up-field chemical shift was observed at 225 K (Figure S10b), although the broadened signal was detected at room temperature (298 K) (Figure S10c). From these results, not only the strength of the coordination but also the temperature are significant to keep the seven coordination state.

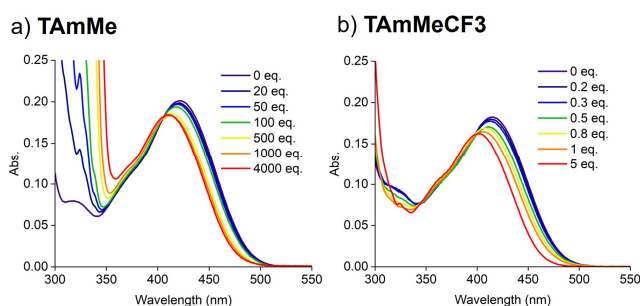


Figure 5. UV-vis absorption titration spectra of a) **TAmMe** and b) **TAmMeCF3** in toluene (1.0×10^{-5} M) with various equivalent of **phen** (0, 20, 50, 100, 200, 500, 1000, and 4000 eq. for **TAmMe** and 0, 0.2, 0.3, 0.5, 0.8, 1, and 5 eq. for **TAmMeCF3**).

Thermoresponsive luminescent polymer films

We attempted to apply **P-TAmMeCF3** for thermoresponsive luminescent materials based on the coordination number shifts at the TAm moieties in the polymer main chain. The polymer films were prepared from the mixed solution of **P-TAmMeCF3** and ligands (**phen** and **bipy**) with maintaining the coordination between tin and the ligands. The

details of the film preparation methods are shown in the Supporting Information. The film was then heated to eliminate the ligands. The temperature-variable (VT) PL spectra were measured while heating the films, and the elimination of the ligands was confirmed by the alteration of emission intensity and the shift of peak wavelength.

First, **phen** was selected as the ligand because of its strong coordination ability. The polymer thin film was prepared by a spin-coating method on the quartz substrate, and the VT-PL spectra were monitored from 300 to 500 K. As a result, the bathochromic shift accompanied by increase in emission was observed from 375 to 425 K (Figure 6). This result suggests that **phen** was removed from the tin center from 375 K, and the coordination number of the tin atom was changed from seven to five. Previously, we observed the similar tendency in the spectral change with the π -conjugated polymer films involving TAZ moieties, and **phen** remained in the film after the dissociation of the coordination with tin.^[42] After heating to 500 K, the spectrum was not recovered to the original state even cooling to 300 K (Figure S11). This fact suggests that once **phen** was eliminated from the tin center, re-coordination hardly occurs by cooling the film. Therefore, **P-TAmMeCF3** can be used as an irreversible thermosensor which is able to memorize a past temperature increase. In **P-TAmMeCF3**, by selecting the ligands with adequate coordination ability, the energy required for desorption should be modulated. This can lead to control of the sensing temperature range.

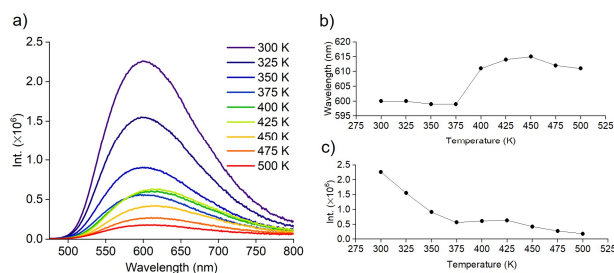


Figure 6. a) VT-PL spectra of the film including **P-TAmMeCF3** and **phen** from 300 to 500 K, excited at 465 nm. b) Relationship of temperature and the peak wavelength. c) Relationship of temperature and PL intensity.

Next, **bipy**, which has a lower coordination ability than **phen**, was selected for sensing in the lower temperature range. Due to the low coordination ability of **bipy**, it was difficult to fabricate the film by the spin-coating method performed at room temperature. Therefore, we placed a mixed solution of **P-TAmMeCF3** and **bipy** in the measurement vessel and prepared the film in a vacuum at 225 K (Figure S12). After that, VT-PL spectra were measured from 225 to 375 K. Consequently, bathochromic shifts of the emission band were observed from 250 to 350 K (Figure 7). Similarly to **phen**, this suggests that **bipy** was eliminated from the tin atoms in this temperature range. In other words, the operating temperature range can be controlled by selecting the ligands with different coordination ability. From the differential scanning calorimetry (DSC) measurement, glass transition in the **P-TAmMeCF3** film was hardly observed from 220 to 400 K (Figure S13). This indicates that the spectral shift was attributed not to the motion of the polymer chain but to the dissociation of the coordination between tin and

the ligand. In addition, the film was re-cooled to 225 K after heated to 375 K, the spectrum did not recover the original state (Figure S14). This indicates that **P-TAmMeCF3** can also work as an irreversible thermosensor. Conventional irreversible sensors are mainly operated in high temperature region, and irreversible sensors which can be used in the low temperature range are still limited.^[50–53] It should be emphasized that we accomplished to obtain the irreversible temperature sensor which can work below the freezing point (273 K). Such films might be applicable to sensors which record unexpected temperature increases and provide quality assurance for materials such as COVID-19 vaccine that must be stored at low temperatures.

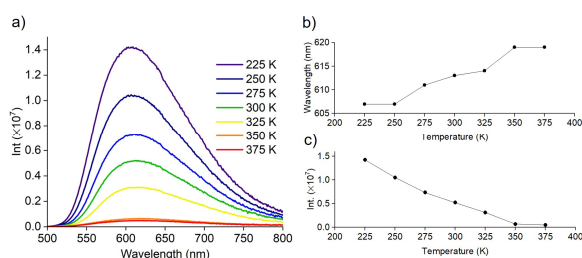


Figure 7. a) VT-PL spectrum of the film containing **PTAmMeCF3** and **bipy** from 225 to 375 K, excited at 465 nm. b) Relationship of temperature and the peak wavelength. c) Relationship of temperature and PL intensity.

As the control tests, VT-PL spectra were measured by using the films prepared from the pure **P-TAmMeCF3** solution and the mixed solution of **P-TAmMeCF3** and non-coordinating solid amine (diphenylamine (**DPA**)). Accordingly, the spectral changes were hardly observed in these films (Figures S15–S17), not likely to the films using **phen**

and **bipy**. Therefore, we confirmed that the spectral alteration should be attributed not to the annealing of the film and coexistence of solid amine but to the coordination number shifts at the tin center from seven to five upon heating.

Conclusion

We can logically design stimuli-responsive molecules with DFT calculations based on the concept of the excitation-driven molecules. Consequently, it was predicted that simple chemical modification with a methyl group induces significant structural changes between the optimized structures in the ground and excited states. Indeed, as we expected, the methyl-substituted TAm compound (**TAmMe**) clearly showed AIE. Moreover, the AIE property was retained even after the chemical modification of the electron-withdrawing substituents at tin, which enables to increase the Lewis acidity of the hypervalent tin center. Taking advantage of the AIE and the coordination number shifts of the tin center, the thermoresponsive luminescent films were fabricated with the polymers. Furthermore, originating from the binding strength between the tin and the additional ligand to form seven-coordinated tin center, the operating temperature range was able to be modulated even below freezing point. Significantly, these binding constants are also predictable by the quantum calculation. The molecular design based on the concept of excitation-driven molecules is a novel strategy for creating various functional materials from the organic scaffold from scratch.

Conflicts of interest

There are no conflicts to declare.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Deposition Number(s) [2380540](https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/asia.202401094) (for **TAmH**), [2380541](https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/asia.202401094) (for **TAmMe**), [2380542](https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/asia.202401094) (for **TAmPh**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe [Access Structures service](http://www.ccdc.cam.ac.uk/structures).

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Supporting Information

Creation of Excitation-Driven Hypervalent Tin(IV) Compounds For Aggregation-Induced Emission and Application to Thermoresponsive Luminescent Films below Freezing Point

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General

^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{119}Sn NMR spectra were recorded on a JEOL ECZ400 instrument at 400, 100 and 149 MHz, respectively. Samples were analyzed in CDCl_3 , CD_2Cl_2 , and $\text{DMSO}-d_6$. The chemical shift values were expressed relative to Me_4Si as an internal standard in CDCl_3 for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR. In CD_2Cl_2 , and $\text{DMSO}-d_6$, the chemical shift values were expressed relative to the solvent signals for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR. In ^{119}Sn NMR, the chemical shift values were expressed relative to Me_4Sn as an external capillary standard. High-resolution mass spectrometry (HRMS) was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer for electrospray ionization (ESI). UV-vis spectra were recorded on a SHIMADZU UV-3600i Plus spectrophotometer, and samples were analyzed at room temperature. HORIBA JOBIN YVON Fluorolog-3 was used for PL spectra at room temperature or VT with an Oxford Optistat DN2. Absolute photoluminescence quantum efficiency (Φ_{PL}) was recorded on a Hamamatsu Photonics Quantaaurus-QY Plus C13534-01 with an integral sphere. PL lifetime measurement was performed on a Horiba DeltaFlex spectrofluorometer system; excitation was carried out by using visible diode lasers (DeltaDiode DD-375L, Peak Wavelength: 375 nm, Pulse Width Typical: 45 ps). Recyclable preparative high-performance liquid chromatography (HPLC) was carried out on a Japan Analytical Industry Model LaboACE LC-5060 (JAIGEL-2.5HR Plus and 3HR Plus columns) using CHCl_3 as an eluent at room temperature for separation of the high molecular weight part of polymers. Gel permeation chromatography (GPC) was carried out on a Shimadzu Prominence system equipped with three consecutive polystyrene gel columns (TOSOH TSKgel: G4000H_{XL}, G3000H_{XL}, G2500H_{XL}) using chloroform as an eluent after calibration with standard polystyrene samples. X-ray crystallographic analysis was carried out by Rigaku Saturn 724+ with MicroMax-007HF CCD diffractometer with Varimax Mo optics using graphite-monochromated MoK α radiation. A symmetry-related absorption correction was carried out by using the program ABSCOR.^[1] The analysis was carried out with direct methods (SHELX-97^[2]) using Yadokari-XG.^[3] The program ORTEP3^[4] and Mercury-4.2.0 were used to generate the X-ray structural diagram. Differential scanning calorimetry (DSC) was recorded on a Hitachi High-Tech Science Corporation DSC7020.

Materials

Commercially available compounds used without purification:

4-Bromo-2-hydroxybenzaldehyde (**1a**) (Angene International Limited)
4-Bromo-2-hydroxyacetaldehyde (**1b**) (Tokyo Chemical Industry Co, Ltd.)
4-Iodophenol (FUJIFILM Wako Pure Chemical Corporation)
Na₂CO₃ (FUJIFILM Wako Pure Chemical Corporation)
PdCl₂ (Tokyo Chemical Industry Co, Ltd.)
2-Amino-5-bromophenol (**2**) (Angene International Limited)
Ph₂SnO (Sigma-Aldrich)
Piperidine (FUJIFILM Wako Pure Chemical Corporation)
CH(OEt)₃ (FUJIFILM Wako Pure Chemical Corporation)
SnCl₄ (Nacalai Tesque Inc.)
Et₃N (FUJIFILM Wako Pure Chemical Corporation)
Pd₂(dba)₃ (dba = dibenzylideneacetone) (Tokyo Chemical Industry Co, Ltd.)
2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) (Strem Chemicals, Inc.)
1,10-Phenanthroline (FUJIFILM Wako Pure Chemical Corporation)
2,2'-Bipyridyl (Tokyo Chemical Industry Co, Ltd.)
Diphenylamine (Tokyo Chemical Industry Co, Ltd.)
Polystyrene (FUJIFILM Wako Pure Chemical Corporation)

Commercially available solvents:

Toluene (deoxidized grade), ethanol (EtOH, deoxidized grade), benzene (super dehydrated grade), and hexane (super dehydrated grade) were purchased from FUJIFILM Wako Pure Chemical Corporation and used without purification. Triethylamine (Et₃N) (Kanto Chemical Co., Inc.) and diethyl ether (Et₂O, super dehydrated grade, FUJIFILM Wako Pure Chemical Corporation) was purified by passage through solvent purification columns under N₂ pressure.^[5]

Compounds prepared as described in the literatures:

4-Bromo-2-hydroxybenzophenone (**1c**)^[6]

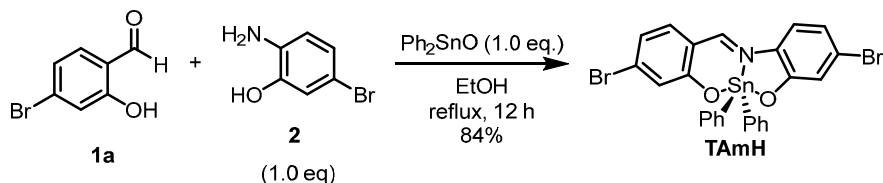
Tetrakis[3,5-bis(trifluoromethyl)phenyl]stannane^[7]

Di-[3,5-(trifluoromethyl)phenyl]dichlorostannane (**3**)^[8]

1,1'-(9,9-Didodecyl-9*H*-fluorene-2,7-diyl)bis[1,1,1-trimethylstannane] (**4**)^[8]

Synthetic procedures and characterization

Synthesis of TAmH



A mixture of 4-bromo-2-hydroxybenzaldehyde (**1a**) (1.01 g, 5.00 mmol, 1.00 eq.), 2-amino-5-bromophenol (**2**) (0.940 g, 5.00 mmol, 1.00 eq.), and Ph_2SnO (1.45 g, 5.00 mmol, 1.00 eq.) in EtOH (100 mL) were stirred at reflux temperature for 12 h. After the reaction, the product was dissolved in CHCl_3 and filtered. The solvents of the filtrate were removed under reduced pressure. The resulting solid was washed in Et_2O by sonication, and filtered to afford **TAmH** (2.70 g, 4.21 mmol, 84%) as an orange solid.

Characterization:

^1H NMR (CHCl_3 , 400 MHz) δ 8.63–8.50 (t, $J_{\text{H-Sn}} = 27.6$ Hz, 1H), 7.89–7.86 (m, $J_{\text{H-Sn}} = 40.7$ Hz, 4H), 7.45–7.37 (m, 6H), 7.33 (d, $J = 1.83$ Hz, 1H), 7.28 (d, $J = 1.83$ Hz, 1H), 7.15 (d, $J = 8.69$ Hz, 1H), 7.07 (d, $J = 8.23$ Hz, 1H), 6.91 (dd, $J = 8.23, 1.83$ Hz, 1H), 6.83 (dd, $J = 8.69, 2.29$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 169.3, 160.8, 159.6, 138.9, 136.4 (t, $J_{\text{C-Sn}} = 26.8$ Hz), 136.1, 132.7, 130.6 (t, $J_{\text{C-Sn}} = 8.7$ Hz), 130.3, 128.9 (t, $J_{\text{C-Sn}} = 43.7$ Hz), 125.7, 124.1, 122.1, 121.4, 120.0, 116.8, 115.7 ppm; ^{119}Sn NMR (CDCl_3 , 149 MHz) δ –324.3 ppm; HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{17}\text{Br}_2\text{NO}_2\text{SnCl}$ $[\text{M}+\text{Cl}]^-$: 675.8316, found: 675.8324.

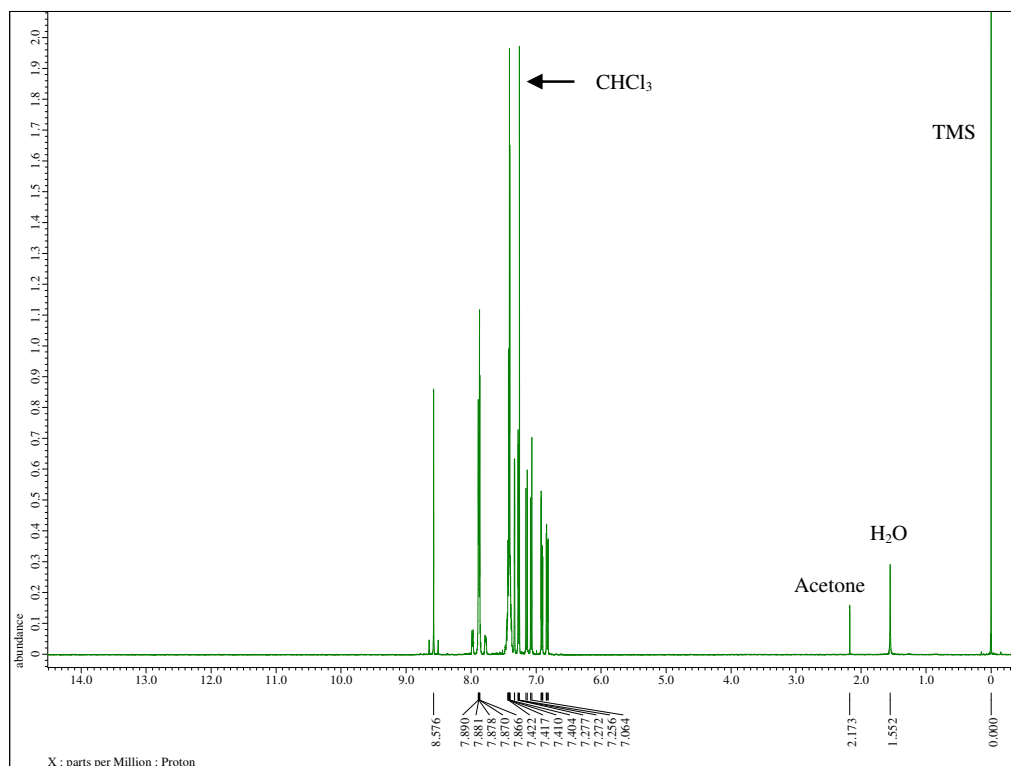


Chart S1. ^1H NMR spectrum of **TAmH** in CDCl_3 at 400 MHz.

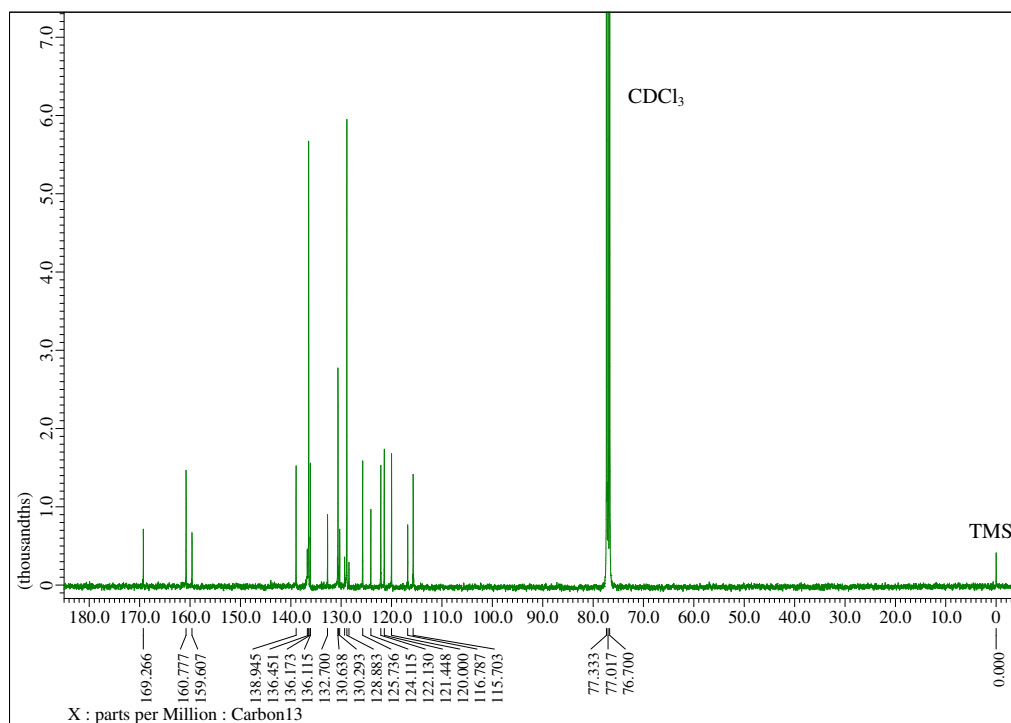


Chart S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **TAmH** in CDCl_3 at 100 MHz.

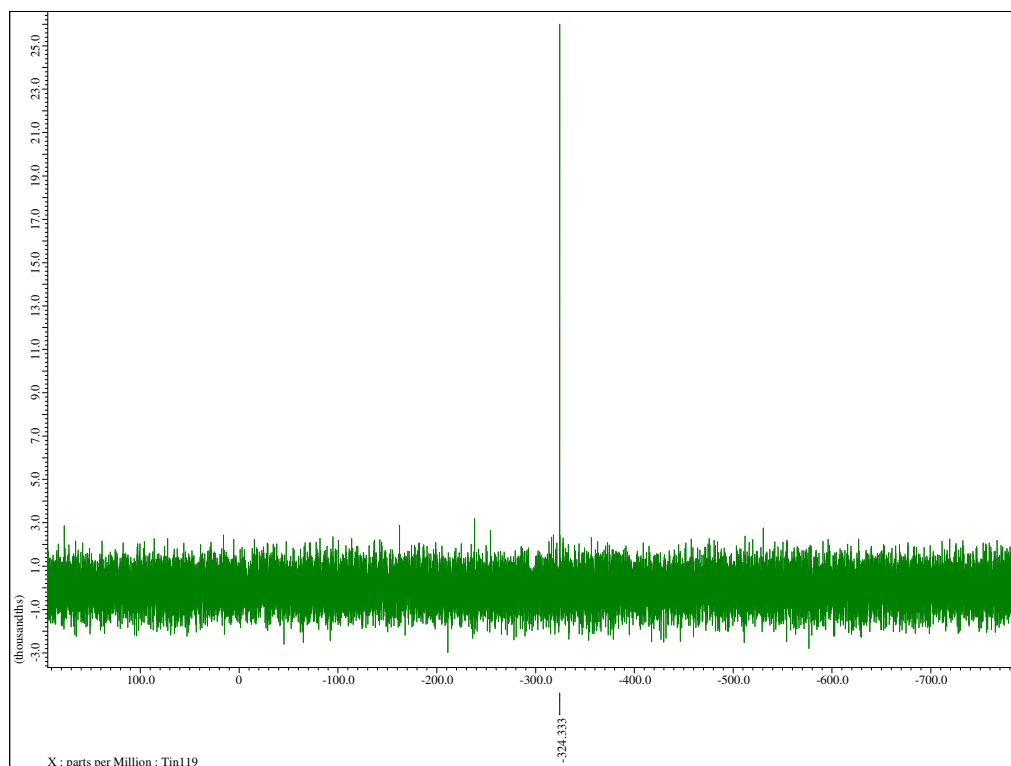
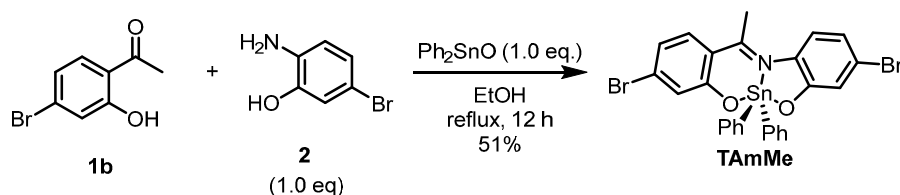


Chart S3. ^{119}Sn NMR spectrum of **TAmH** in CDCl_3 at 149 MHz.

Synthesis of TAmMe



A mixture of 4-bromo-2-hydroxyacetaldehyde (**1b**) (0.258 g, 1.20 mmol, 1.00 eq.), 2-amino-5-bromophenol (**2**) (0.226 g, 1.20 mmol, 1.00 eq.), and Ph_2SnO (0.347 g, 1.20 mmol, 1.00 eq.) in EtOH (24 mL) were stirred at reflux temperature for 12 h. After the reaction, the product was dissolved in CHCl_3 and filtered. The solvents of the filtrate were removed under reduced pressure. The resulting solid was dissolved in CH_2Cl_2 and precipitated in MeOH to afford **TAmMe** (0.405 g, 0.617 mmol, 51%) as a yellow solid.

Characterization:

^1H NMR (CHCl_3 , 400 MHz) δ 7.83–7.80 (m, $J_{\text{H-Sn}} = 39.0$ Hz, 4H), 7.47 (d, $J = 9.15$ Hz, 1H), 7.40–7.38 (m, 7H), 7.28 (d, $J = 1.83$ Hz, 1H), 6.90 (dd, $J = 8.92, 2.29$ Hz, 1H), 6.86–6.79 (dd, m, 2H), 2.78 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 Hz) δ 175.6, 168.8, 160.0, 137.7, 136.5 (t, $J_{\text{C-Sn}} = 26.9$ Hz), 132.0, 130.9, 130.8, 130.6 (t, $J_{\text{C-Sn}} = 8.6$ Hz), 128.8 (t, $J_{\text{C-Sn}} = 42.2$ Hz), 127.1, 124.2 (t, $J_{\text{C-Sn}} = 8.6$ Hz), 123.1, 121.8, 121.2, 119.1, 118.8, 21.3 ppm; ^{119}Sn NMR (CDCl_3 , 149 MHz) δ –314.7 ppm; HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{19}\text{Br}_2\text{NO}_2\text{SnNa}$ $[\text{M}+\text{Na}]^+$: 677.8670, found: 677.8679.

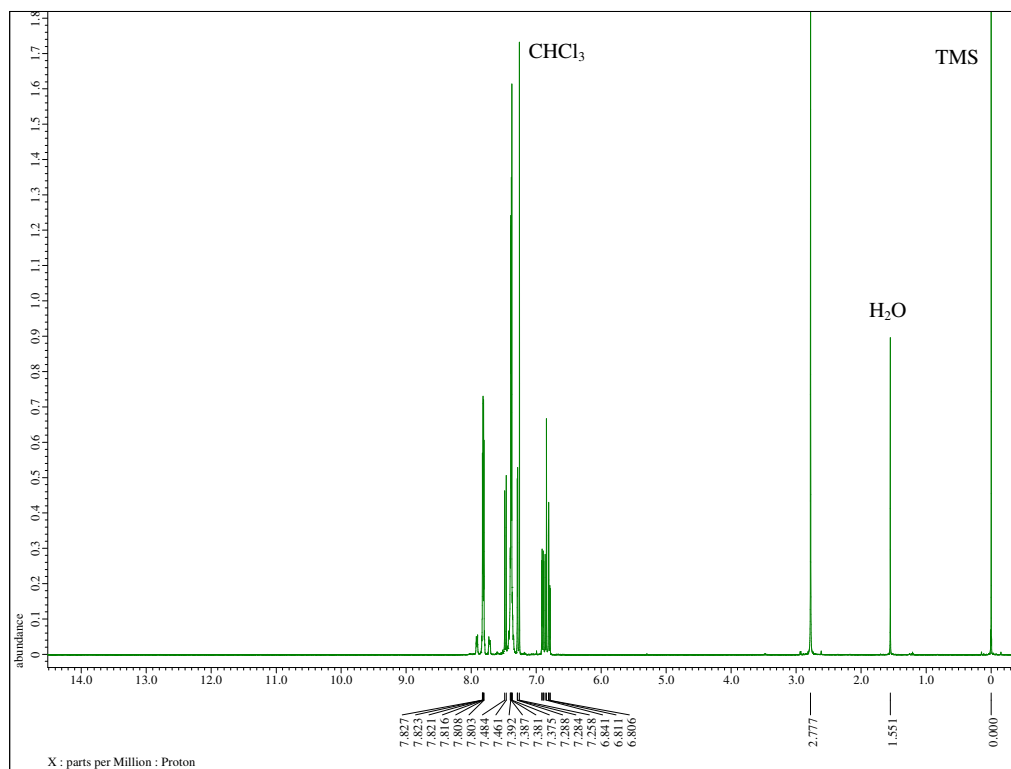


Chart S4. ¹H NMR spectrum of TAmMe in CDCl₃ at 400 MHz.

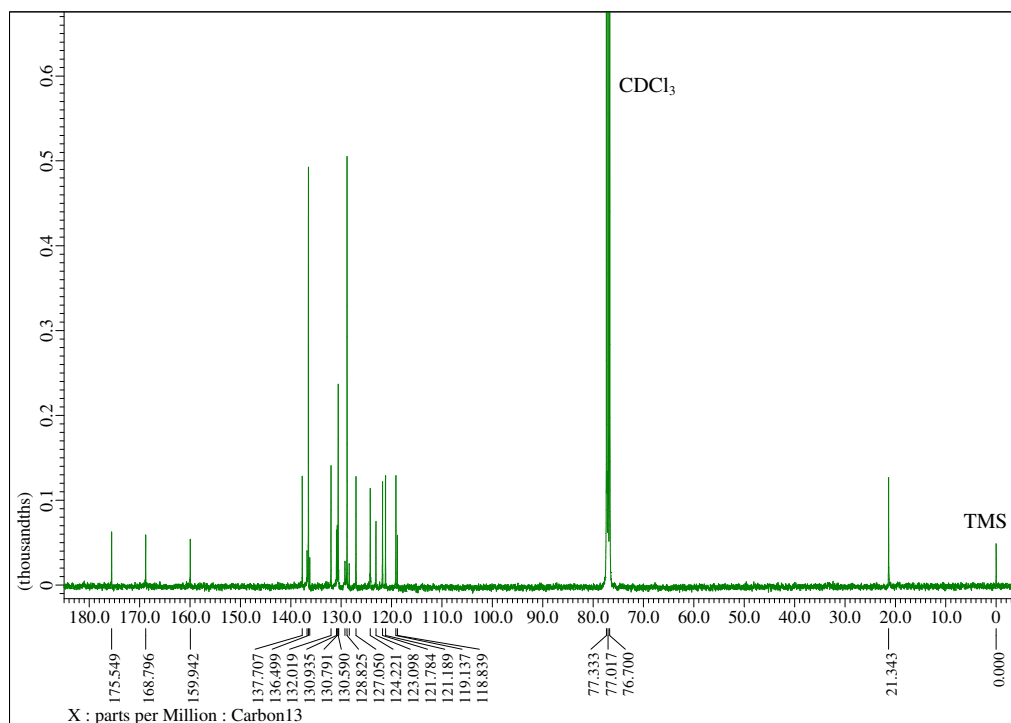


Chart S5. ¹³C{¹H} NMR spectrum of TAmMe in CDCl₃ at 100 MHz.

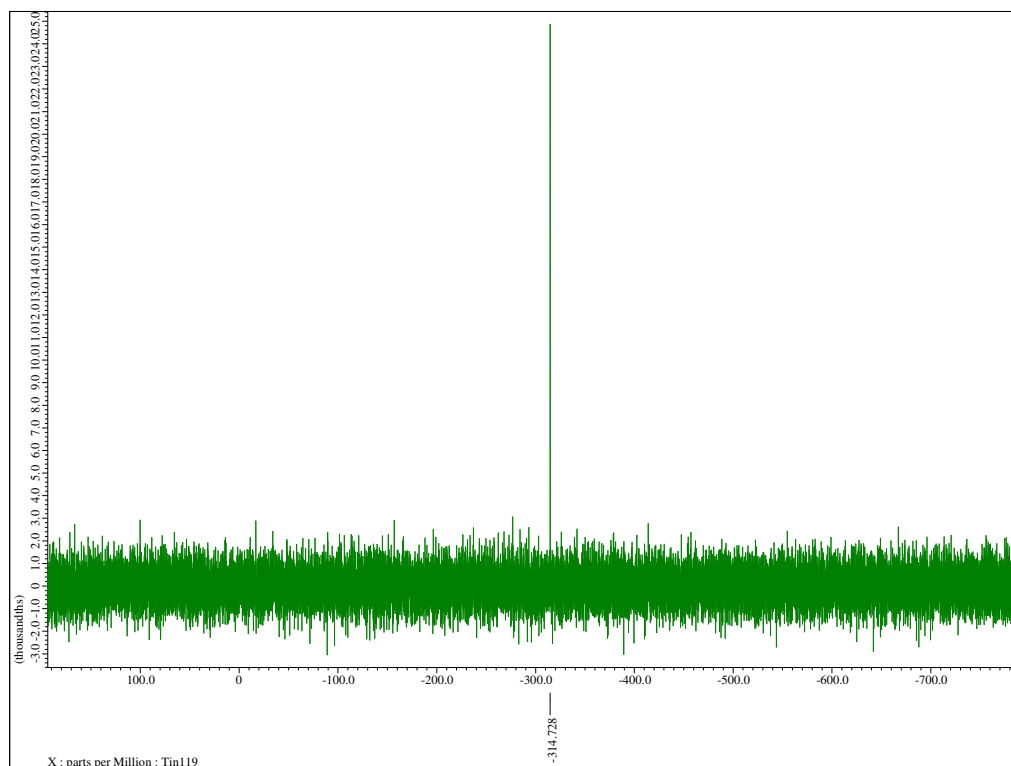
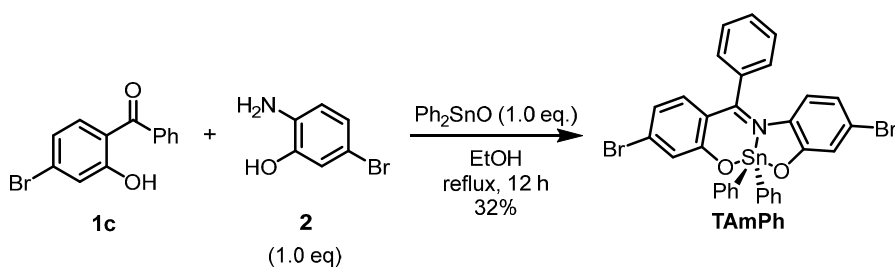


Chart S6. ^{119}Sn NMR spectrum of **TAmMe** in CDCl_3 at 149 MHz.

Synthesis of TAmPh



A mixture of 4-bromo-2-hydroxybenzophenone (**1c**) (1.11 g, 4.00 mmol, 1.00 eq.), 2-amino-5-bromophenol (**2**) (0.752 g, 4.00 mmol, 1.00 eq.), and Ph_2SnO (1.16 g, 4.00 mmol, 1.00 eq.) in EtOH (80 mL) were stirred at reflux temperature for 12 h. After the reaction, the product was dissolved in CHCl_3 and filtered. The solvents of the filtrate were removed under reduced pressure. The resulting solid was dissolved in CH_2Cl_2 and precipitated in MeOH to afford **TAmPh** (0.927 g, 1.29 mmol, 32%) as an orange solid.

Characterization:

^1H NMR (CHCl_3 , 400 MHz) δ 7.88–7.85 (m, $J_{\text{H-Sn}} = 39.8$ Hz, 4H), 7.49–7.35 (m, 10H), 7.22–7.16 (m, 3H), 6.69–6.63 (m, 2H), 6.29 (dd, $J = 8.69, 2.29$ Hz, 1H), 5.92 (d, $J = 8.69$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 174.4, 169.6, 160.1, 137.4, 136.5 (t, $J_{\text{C-Sn}} = 26.9$ Hz), 135.4, 135.1, 131.0, 130.6 (t, $J_{\text{C-Sn}} = 8.6$ Hz), 130.6, 129.2, 129.1, 128.8 (t, $J_{\text{C-Sn}} = 41.2$ Hz), 126.4, 123.7 (t, $J_{\text{C-Sn}} = 7.7$ Hz), 122.6, 121.5, 120.8, 119.6, 119.0 ppm; ^{119}Sn NMR (CDCl_3 , 149 MHz) δ –323.5 ppm; HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{21}\text{Br}_2\text{NO}_2\text{SnNa}$ $[\text{M}+\text{Na}]^+$: 739.8827, found: 739.8837.

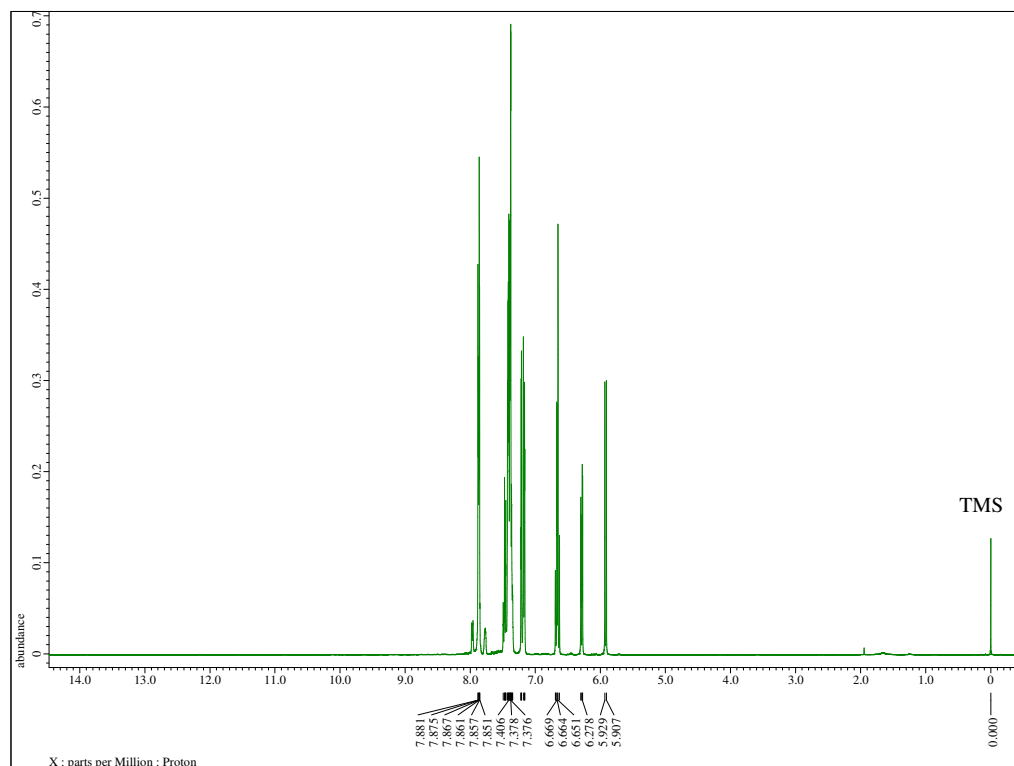


Chart S7. ¹H NMR spectrum of TAmPh in CDCl₃ at 400 MHz.

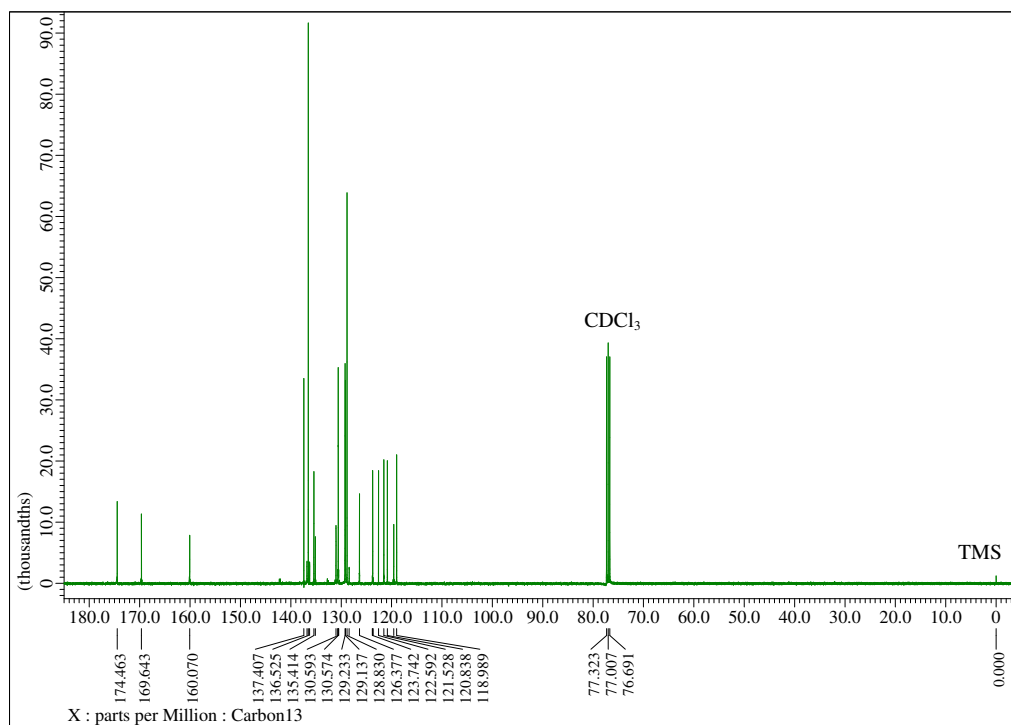


Chart S8. ¹³C{¹H} NMR spectrum of TAmPh in CDCl₃ at 100 MHz.

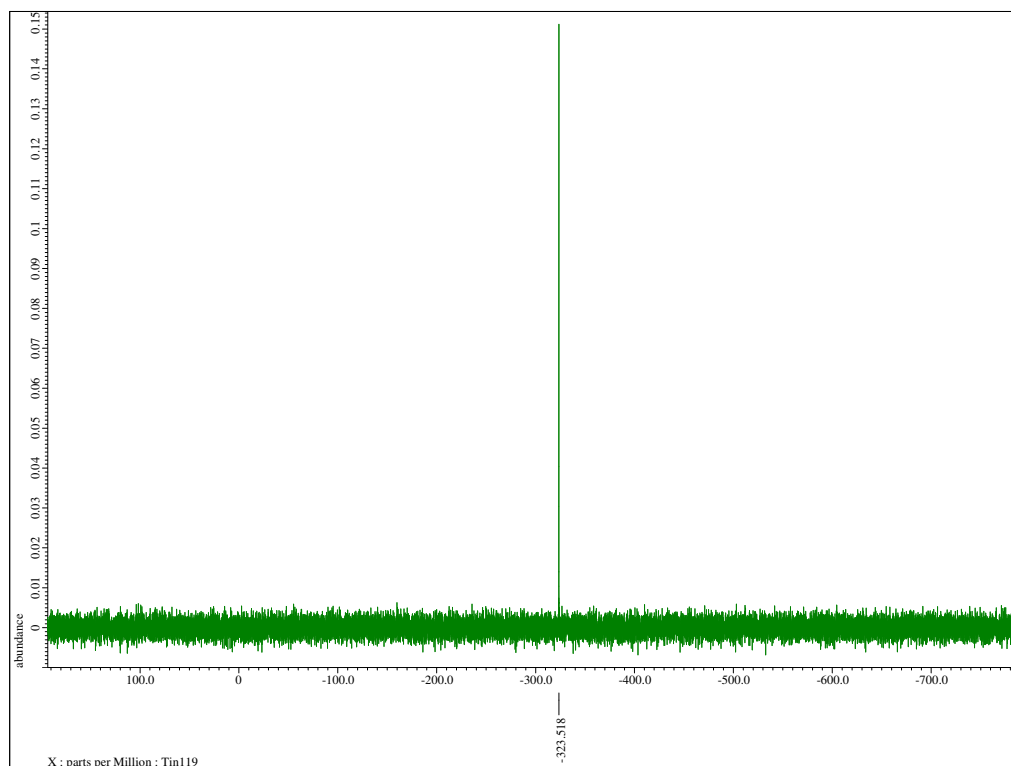
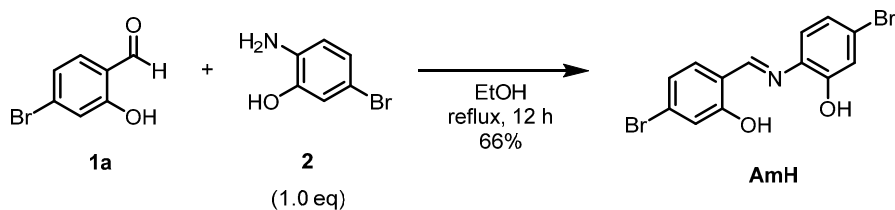


Chart S9. ^{119}Sn NMR spectrum of **TAmPh** in CDCl_3 at 149 MHz.

Synthesis of Am



A mixture of 4-bromo-2-hydroxybenzaldehyde (**1a**) (2.01 g, 10.0 mmol, 1.0 eq.) and 2-amino-5-bromophenol (**2**) (1.88 g, 10.0 mmol, 1.0 eq.) in EtOH (50 mL) were stirred at reflux temperature for 12 h. After the reaction, the product was cooled to $-20\text{ }^{\circ}\text{C}$, and the precipitate was filtered to afford **AmH** (2.46 g, 6.63 mmol, 66%) as an orange solid.

Characterization:

^1H NMR (DMSO- d_6 , 400 MHz) δ 14.06 (br, 1H), 10.39 (br, 1H), 9.00 (s, 1H), 7.57 (d, $J = 8.00$ Hz, 1H), 7.36 (d, $J = 8.80$ Hz, 1H), 7.16–7.12 (m, 3H), 7.07 (dd, $J = 8.00, 1.60$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 100 MHz) δ 161.9, 161.0, 152.2, 133.8, 133.7, 126.3, 122.3, 121.8, 121.0, 119.9, 199.7, 119.0, 118.6 ppm; HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_8\text{Br}_2\text{NO}_2$ $[\text{M}-\text{H}]^-$: 367.8927, found: 367.8926.

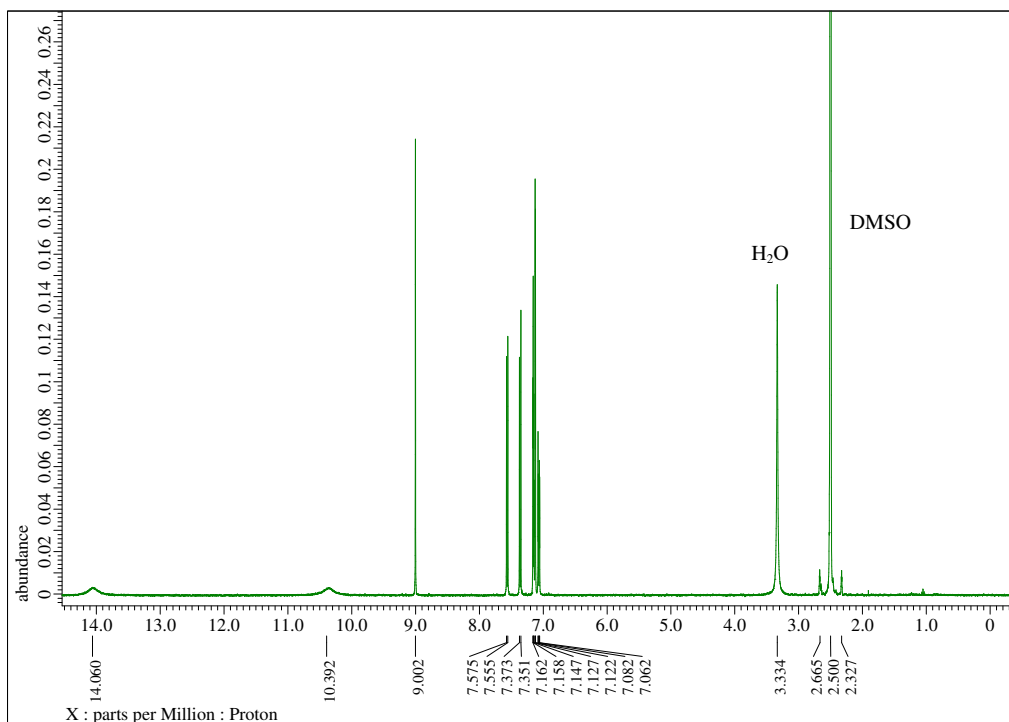


Chart S10. ¹H NMR spectrum of **AmH** in DMSO-*d*₆ at 400 MHz.

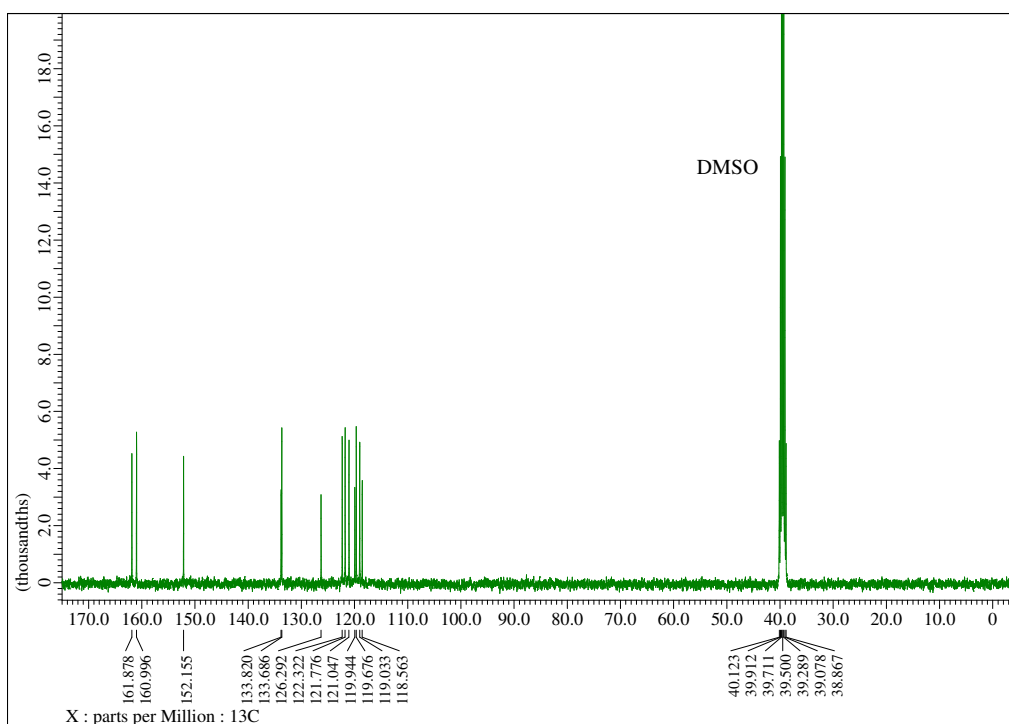
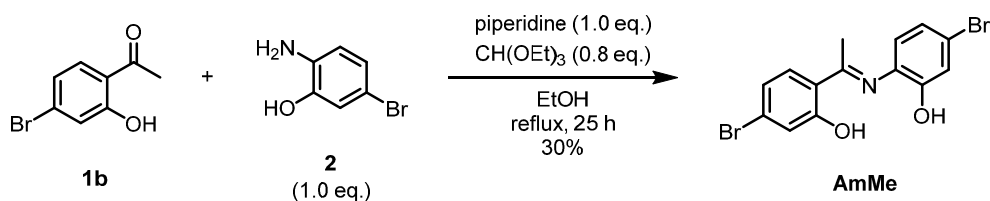


Chart S11. ¹³C{¹H} NMR spectrum of **AmH** in DMSO-*d*₆ at 100 MHz.

Synthesis of AmMe



A mixture of 4-bromo-2-hydroxyacetaldehyde (**1b**) (1.94 g, 9.00 mmol, 1.00 eq.), 4-bromo-2-hydroxyaniline (**2**) (1.69 g, 9.00 mmol, 1.00 eq.), piperidine (0.890 mL, 9.00 mmol, 1.00 eq.), and CH(OEt)₃ (1.20 mL, 7.20 mmol, 0.800 eq.) in EtOH (18 mL) were stirred at reflux temperature for 25 h. After the reaction, the product was filtered, and the solvent was removed under reduced pressure. The residue was purified by short column chromatography (CH₂Cl₂) and recrystallization with CHCl₃ twice to afford **AmMe** (1.03 g, 2.67 mmol, 30%) as a yellow solid.

Characterization:

¹H NMR (DMSO-*d*₆, 400 MHz) δ 15.19 (s, 1H), 10.16 (s, 1H), 7.70 (d, *J* = 8.69 Hz, 1H), 7.12 (dd, *J* = 13.04, 2.29 Hz, 2H), 7.09 (dd, *J* = 8.16, 2.29 Hz, 1H), 7.03 (dd, *J* = 8.23, 1.83 Hz, 1H), 6.89 (d, *J* = 8.23 Hz, 1H), 2.28 (s, 3H) ppm; ¹³C{¹H} NMR (DMSO-*d*₆, 100 MHz) δ 173.0, 162.5, 149.5, 132.8, 131.4, 126.1, 124.3, 122.0, 121.7, 120.2, 118.7, 117.8, 17.5 ppm; HRMS (ESI) calcd. for C₁₄H₁₂Br₂NO₂ [M+H]⁺: 383.9229, found: 383.9230.

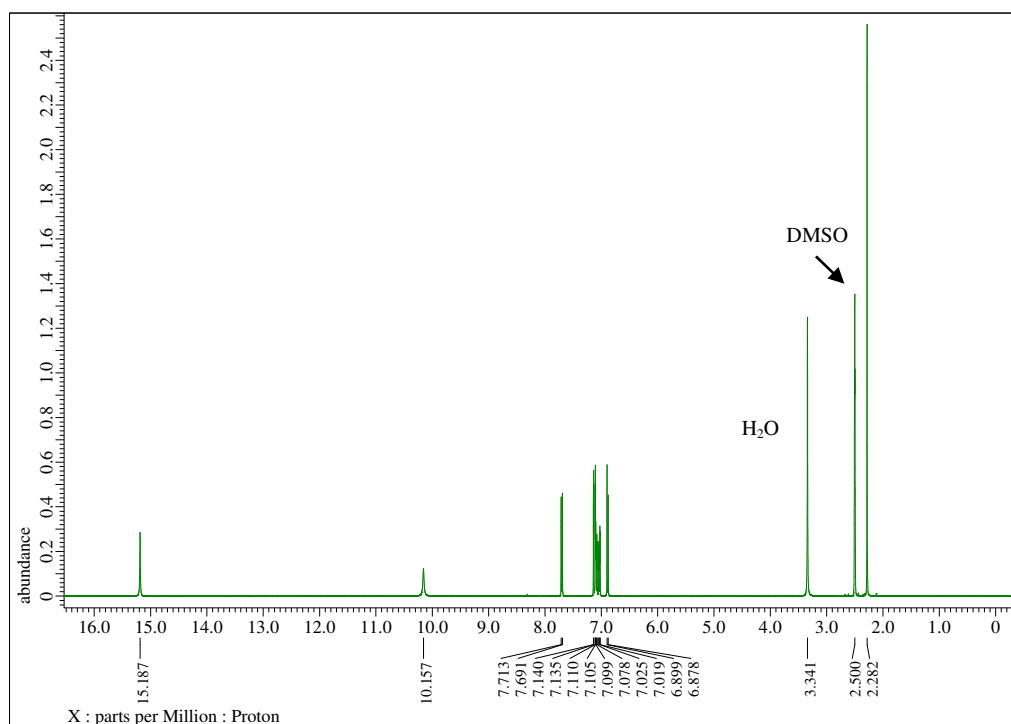


Chart S12. ¹H NMR spectrum of **AmMe** in DMSO-*d*₆ at 400 MHz.

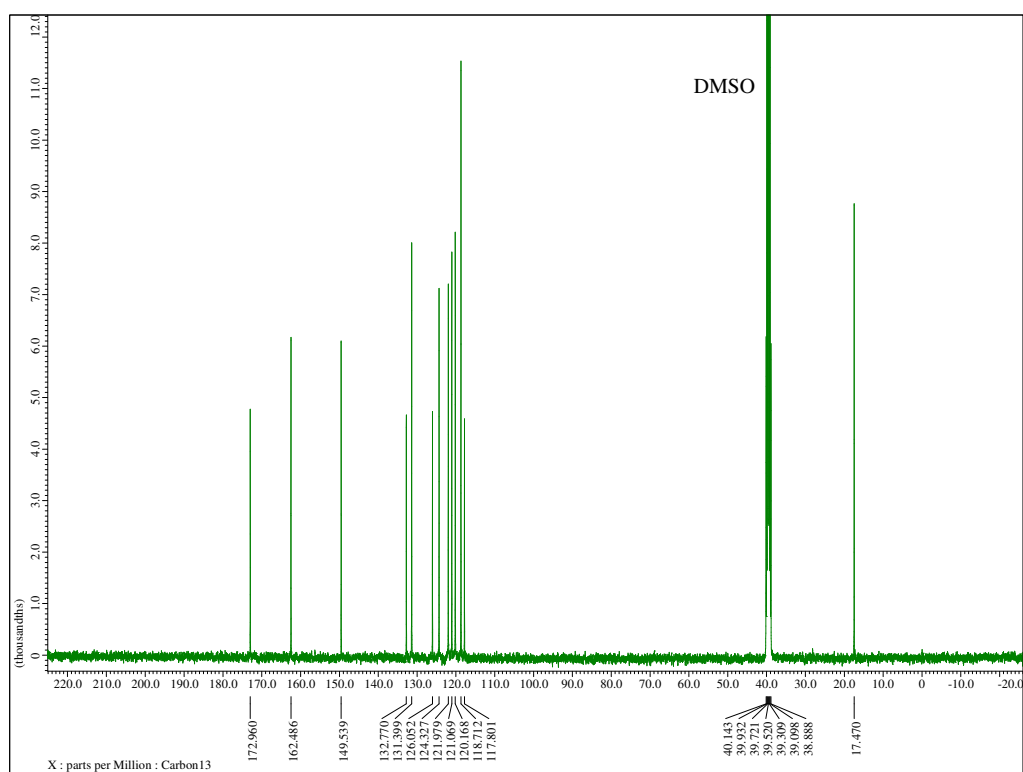
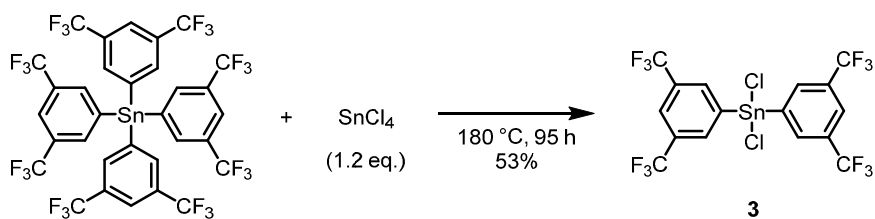


Chart S13. ¹³C{¹H} NMR spectrum of **AmMe** in DMSO-*d*₆ at 100 MHz.

Synthesis of **3**



Tetrakis[3,5-bis(trifluoromethyl)phenyl]stannane (2.91 g, 3.00 mmol, 1.00 eq.) was added to an oven dried 100 mL Schlenk flask under N_2 atmosphere. Via syringe, SnCl_4 (0.938 mg, 3.60 mmol, 1.20 eq.) was slowly added to the flask. The flask was placed under static vacuum at 77 K for 30 min and sealed with J. Young PTFE stopcock. The sealed flask was entirely immersed in an oil bath and heated at $180\text{ }^\circ\text{C}$ for 95 h. After completion of the reaction, a light yellow mixture was obtained. The product was dissolved in dry CH_2Cl_2 and the undissolved solid was removed by $0.20\text{ }\mu\text{m}$ PTFE filter. The filtrate was concentrated with a rotary evaporator and the solid was recrystallization with dry hexane to obtain **3** as a colorless crystal (1.96 g, 3.18 mmol, 53%).

Characterization:

^1H NMR (CHCl_3 , 400 MHz) δ 8.16 (s, 4H), 8.10 (s, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 138.4, 134.9 (t, $J_{\text{C-Sn}} = 32.60$ Hz), 133.1 (q, $J_{\text{C-F}} = 34.04$ Hz), 126.3 (m), 122.8 (q, $J_{\text{C-F}} = 273.58$ Hz) ppm; ^{119}Sn NMR (CDCl_3 , 149 MHz) δ -35.7 ppm. HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_6\text{Cl}_3\text{F}_{12}\text{Sn}$ $[\text{M}+\text{Cl}]^-$: 650.8371, found: 650.8351.

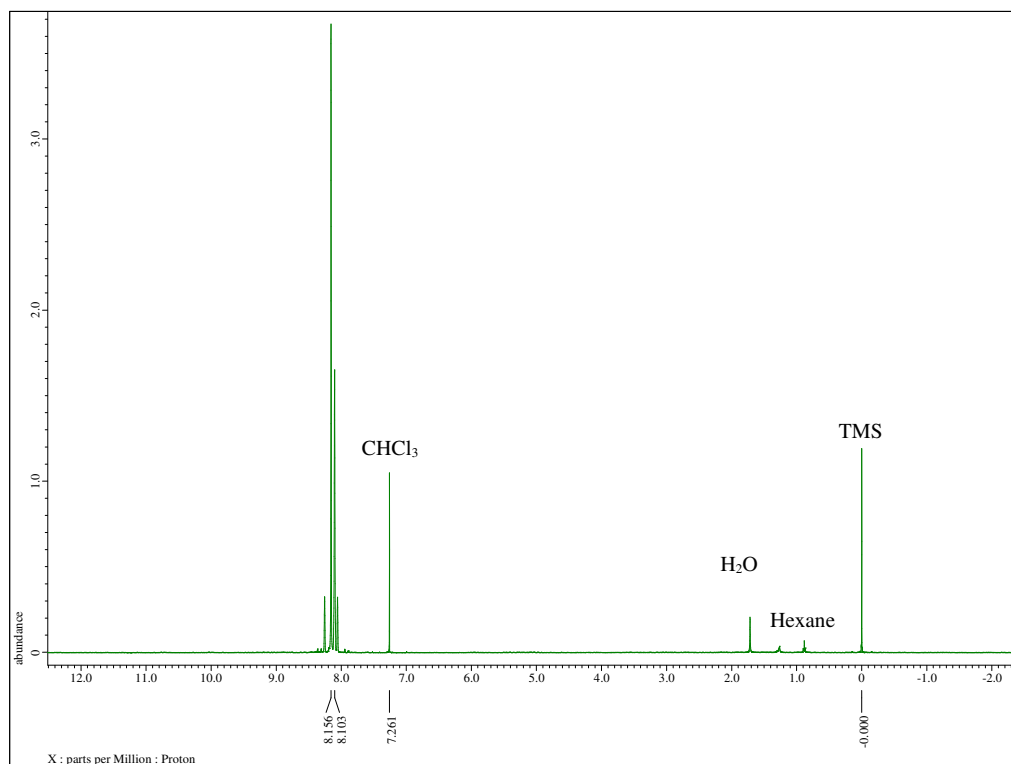


Chart S14. ¹H NMR spectrum of **3** in CDCl₃ at 400 MHz.

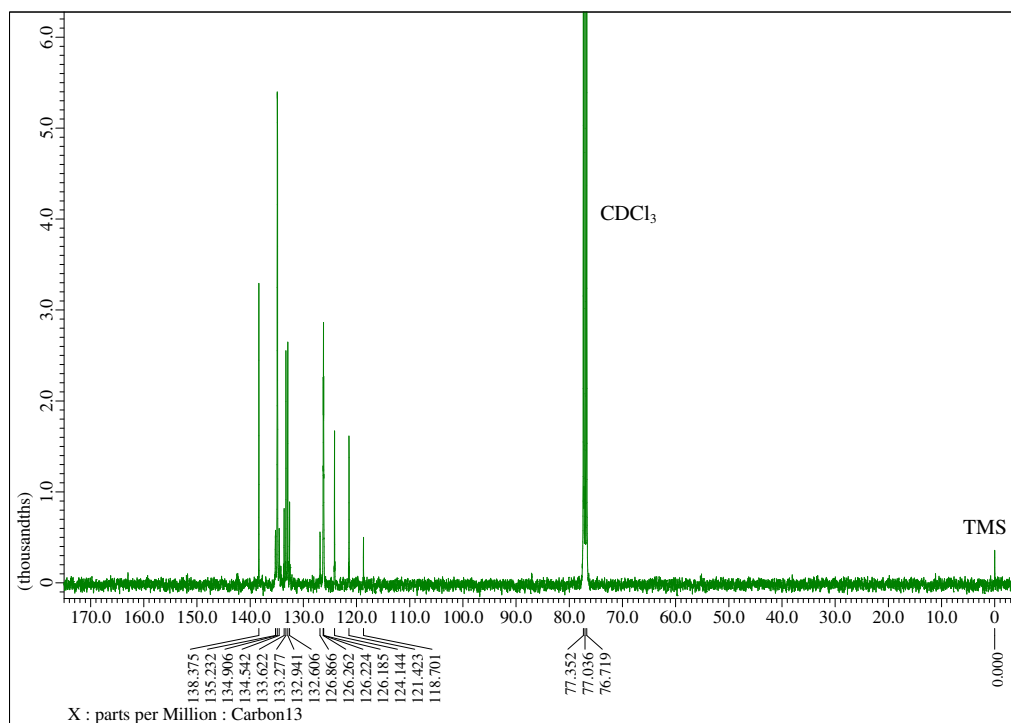


Chart S15. ¹³C{¹H} NMR spectrum of **3** in CDCl₃ at 100 MHz.

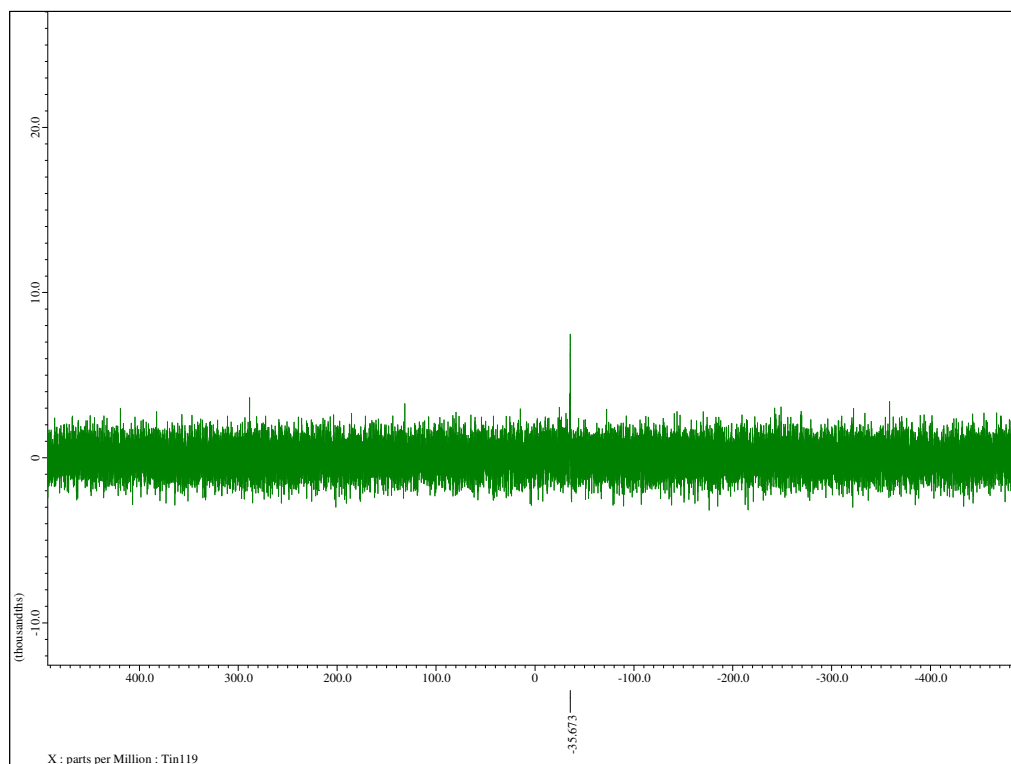
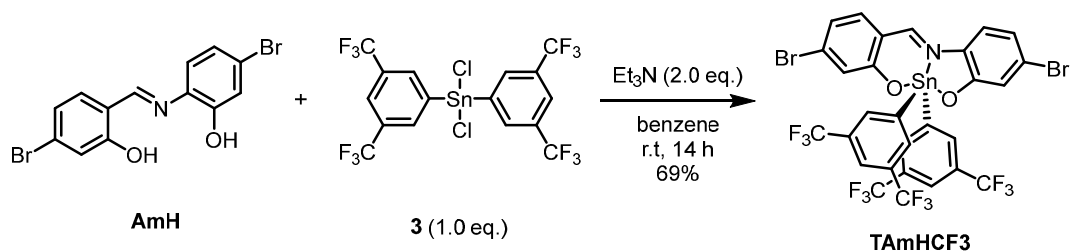


Chart S16. ^{119}Sn NMR spectrum of **3** in CDCl_3 at 149 MHz.

Synthesis of TAmHCF3



A mixture of **AmH** (0.557 g, 1.50 mmol, 1.00 eq.), **3** (0.924 g, 1.50 mmol, 1.00 eq.), and Et₃N (0.420 mL, 3.00 mmol, 2.00 eq.) in benzene (45 mL) were stirred at room temperature for 14 h. After the reaction, the product was filtered, and the solvent was removed under reduced pressure. The residue was precipitated by THF/EtOH to afford **TAmHCF3** (0.951 g, 69%) as an orange solid.

Characterization:

¹H NMR (CHCl₃, 400 MHz) δ 8.68 (t, $J_{\text{H-Sn}}$ = 32.24 Hz, 1H), 8.33 (t, $J_{\text{H-Sn}}$ = 39.40 Hz, 4H), 7.92 (s, 2H), 7.42 (d, J = 1.37 Hz, 1H), 7.37 (d, J = 2.29 Hz, 1H), 7.21 (d, J = 8.69 Hz, 1H), 7.15 (d, J = 8.23 Hz, 1H), 7.06 (d, J = 1.37 Hz, 1H), 7.04 (d, J = 1.83 Hz, 1H), 6.94 (dd, J = 8.69, 2.29 Hz, 1H) ppm; ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 168.5, 161.6, 158.5, 141.2, 136.4, 136.3, 134.3, 132.2 (q, $J_{\text{C-F}}$ = 33.39 Hz), 129.5, 125.8, 125.2, 124.9 (m), 123.2, 123.3 (q, $J_{\text{C-F}}$ = 272.10 Hz), 122.5, 121.6, 116.9, 115.7 ppm; ¹¹⁹Sn NMR (CDCl₃, 149 MHz) δ -335.6 ppm; HRMS (ESI) calcd. for C₂₉H₁₄Br₂F₁₂NO₂SnCl [M+Cl]⁻: 947.7811, found: 947.7820.

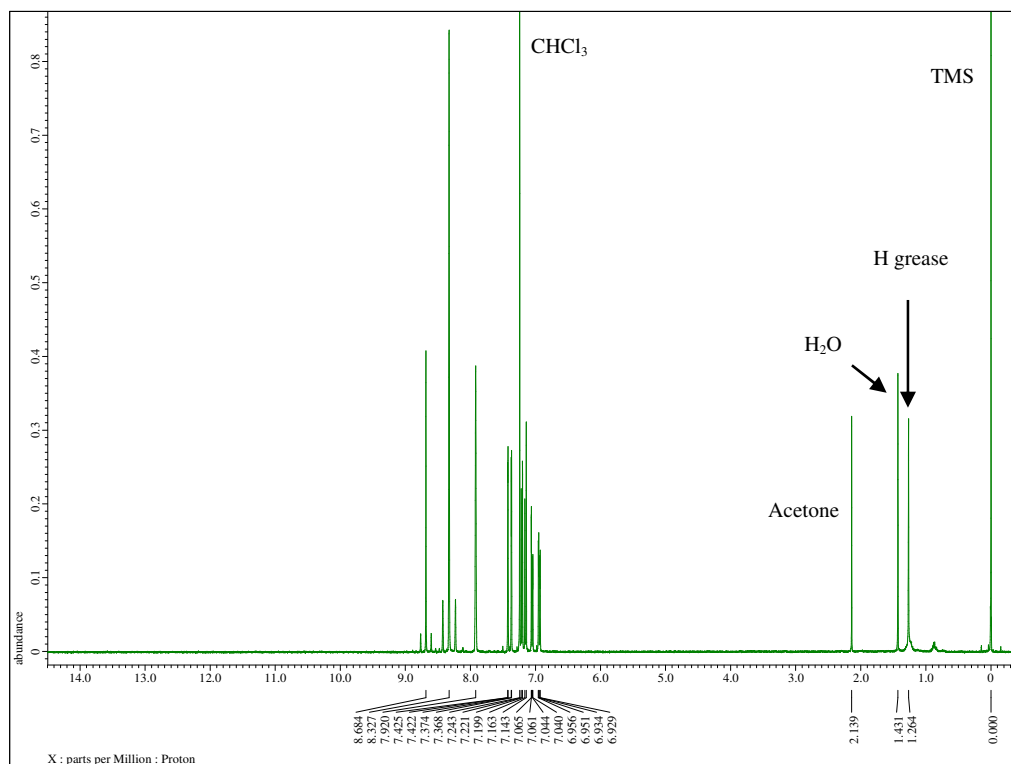


Chart S17. ^1H NMR spectrum of **TAmHCF3** in CDCl_3 at 60 °C at 400 MHz.

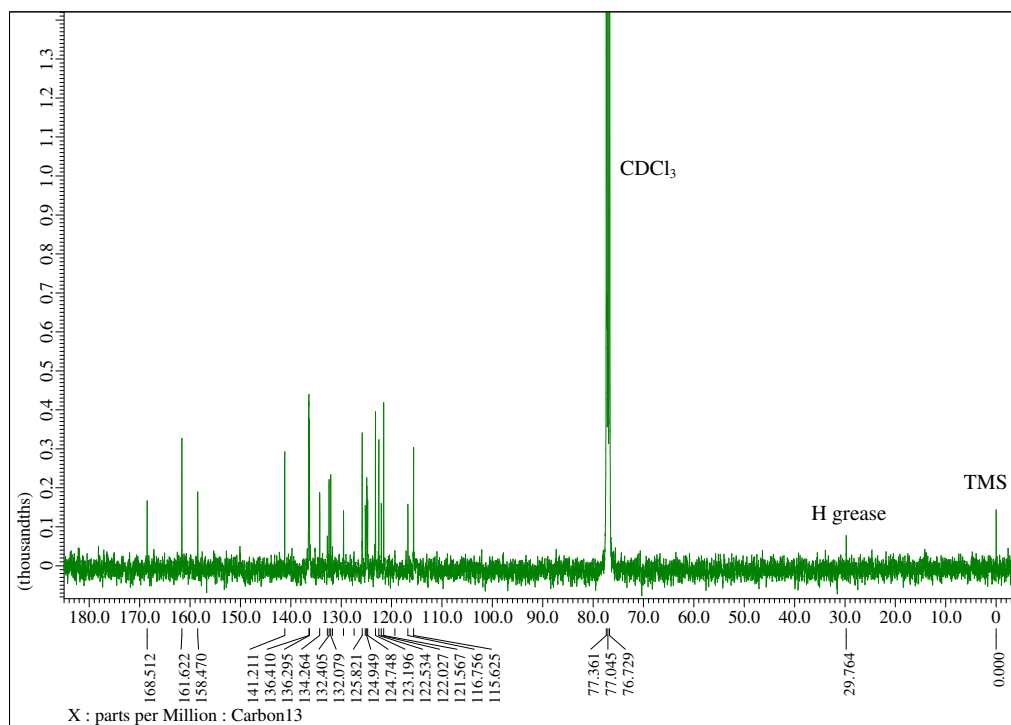


Chart S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **TAmHCF3** in CDCl_3 at 60 °C at 100 MHz.

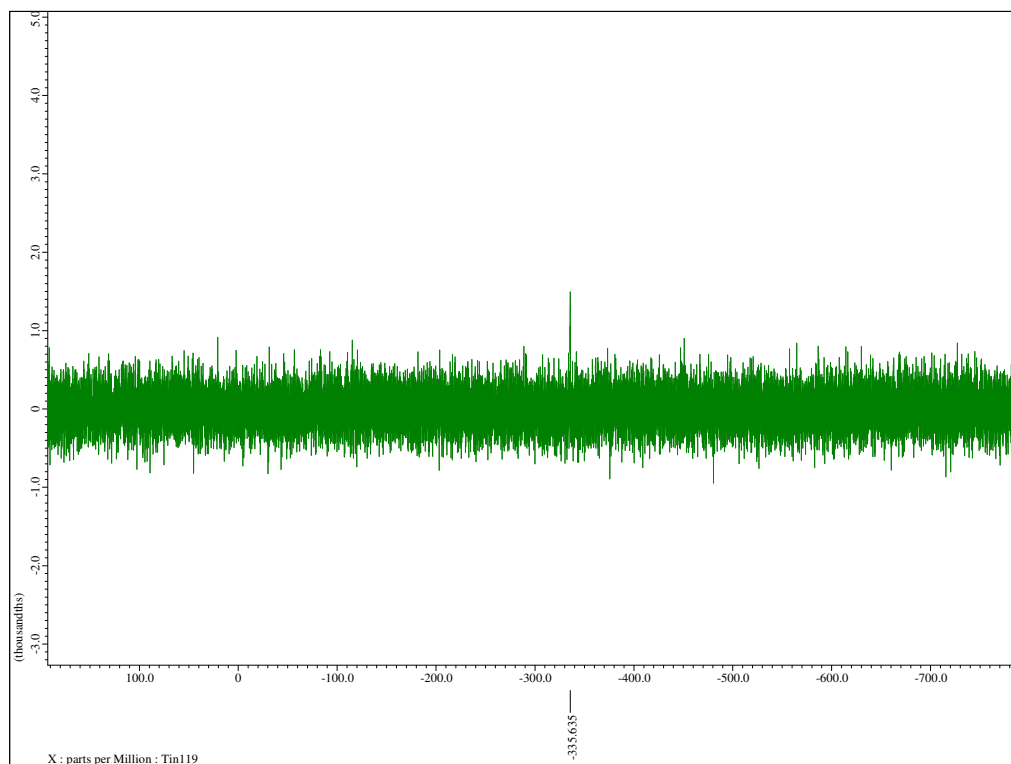
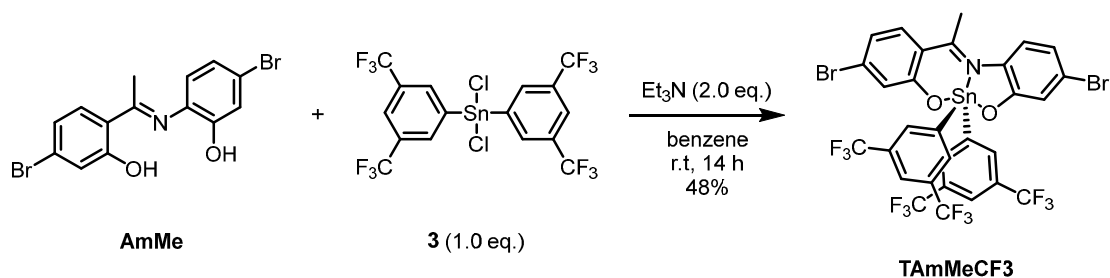


Chart S19. ^{119}Sn NMR spectrum of **TAmHCF3** in CDCl_3 at 60 °C at 149 MHz.

Synthesis of TAmMeCF3



A mixture of **AmMe** (0.193 g, 0.500 mmol, 1.00 eq.), **3** (0.308 g, 0.500 mmol, 1.00 eq.), and Et₃N (0.140 mL, 1.00 mmol, 2.00 eq.) in benzene (15 mL) were stirred at room temperature for 14 h. After the reaction, the product was filtered, and the solvent was removed under reduced pressure. The residue was precipitated by EtOH/hexane to afford **TAmMeCF3** (0.589 g, 48%) as a yellow solid.

Characterization:

¹H NMR (CHCl₃, 400 MHz) δ 8.30 (t, $J_{\text{H-Sn}}$ = 38.00 Hz, 4H), 7.90 (s, 2H), 7.54 (d, J = 9.15 Hz, 1H), 7.50 (d, J = 1.83 Hz, 1H), 7.37 (d, J = 1.83 Hz, 1H), 7.02 (dd, J = 8.92, 2.29 Hz, 1H), 6.96–6.89 (m, 2H) ppm; ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 176.8, 167.6, 158.6, 139.5, 136.6 (t, $J_{\text{C-Sn}}$ = 28.06 Hz), 132.2, 132.0, 131.8 (q, $J_{\text{C-F}}$ = 32.70 Hz), 130.0, 127.1, 124.8 (m), 124.2, 124.0, 123.2 (q, $J_{\text{C-F}}$ = 272.40 Hz) 122.7, 122.0, 120.5, 118.6, 21.4 ppm; ¹¹⁹Sn NMR (CDCl₃, 149 MHz) δ -327.4 ppm; HRMS (ESI) calcd. for C₃₀H₁₄Br₂F₁₂NO₂Sn [M-H]⁻: 925.8201, found: 925.8204.

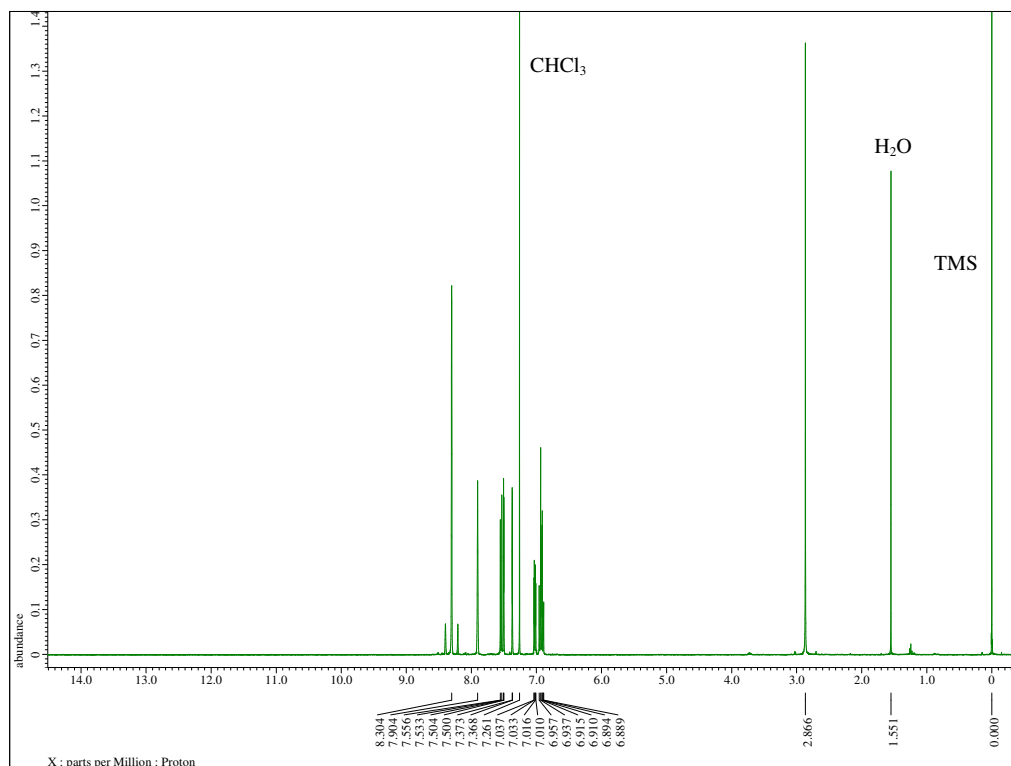


Chart S20. ¹H NMR spectrum of **TamMeCF₃** in CDCl₃ at 400 MHz.

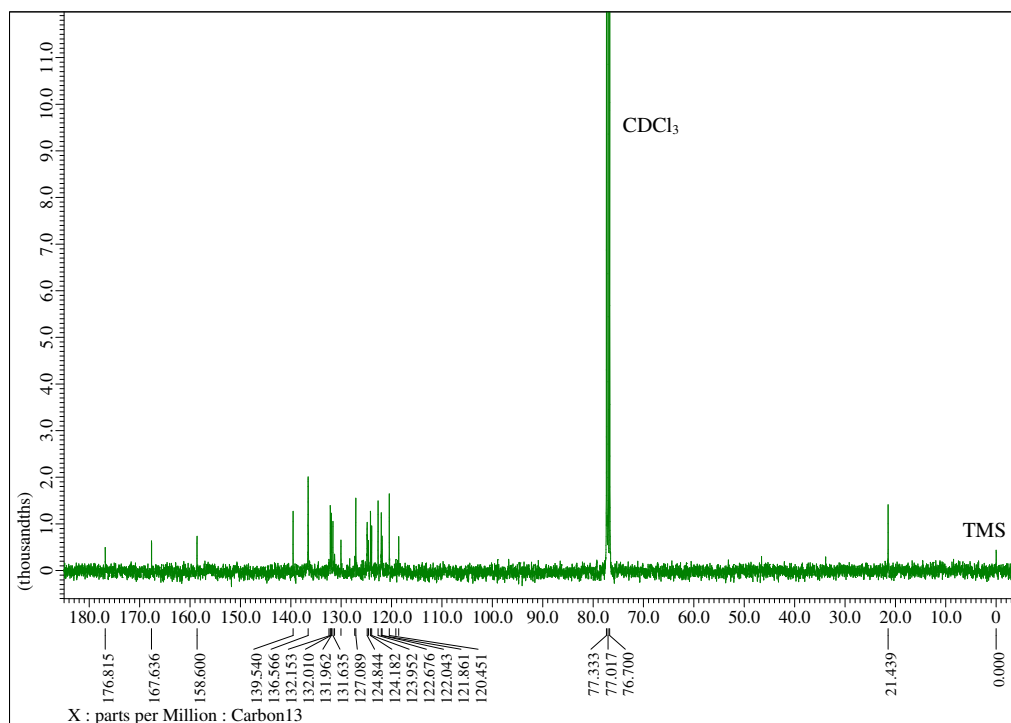


Chart S21. ¹³C{¹H} NMR spectrum of **TamMeCF₃** in CDCl₃ at 100 MHz.

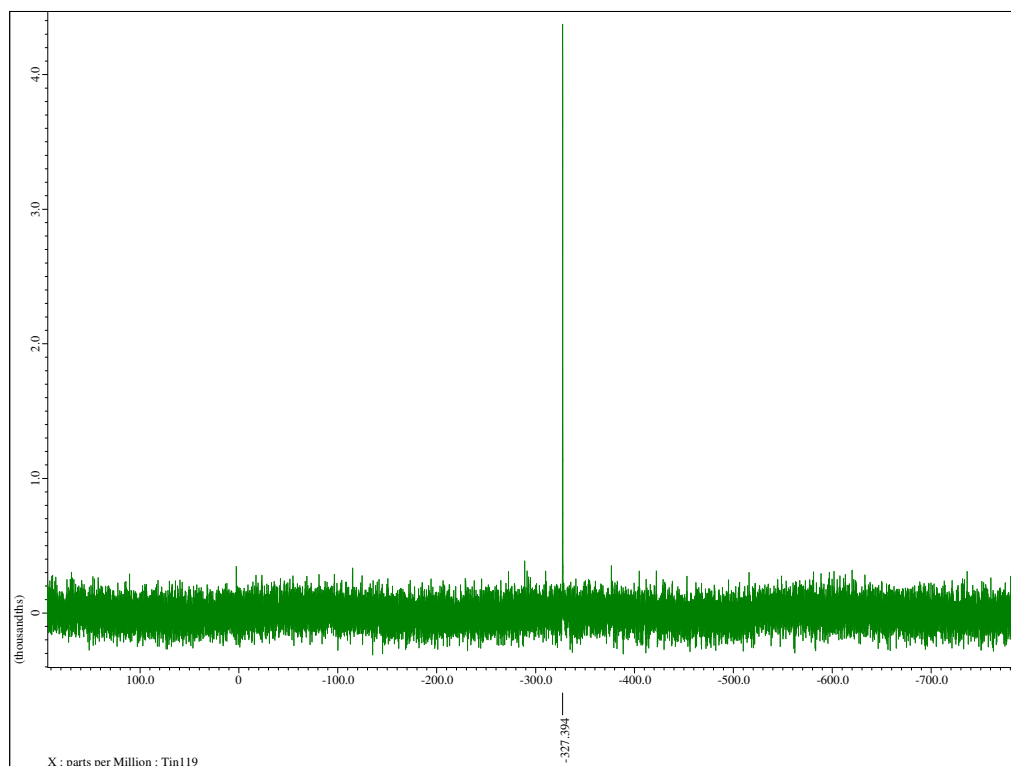
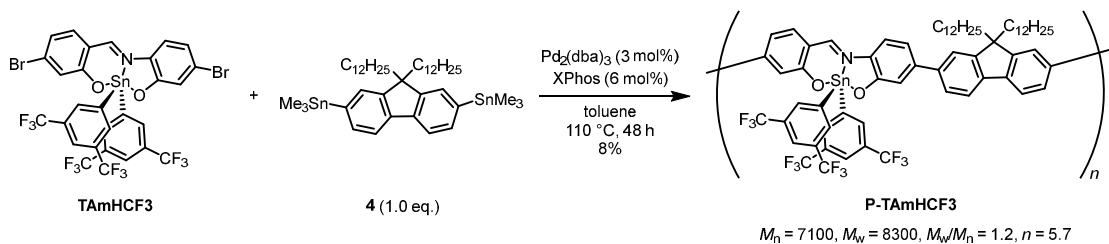


Chart S22. ^{119}Sn NMR spectrum of **TAmMeCF3** in CDCl_3 at 149 MHz.

Synthesis of P-TAmHCF3



A mixture of **TAmHCF3** (0.183 g, 0.200 mmol, 1.00 eq.), **4** (0.166 g, 0.200 mmol, 1.00 eq.), $\text{Pd}_2(\text{dba})_3$ (0.0055 g, 0.0060 mmol, 0.03 eq.), XPhos (0.0057 g, 0.012 mmol, 0.06 eq.) in toluene (4.0 mL) was stirred at 110 °C for 48 h under N_2 atmosphere. After cooling to room temperature, the solution was poured into a large amount of MeCN to collect the polymer by filtration. The polymer was separated the high molecular weight part by HPLC to afford **P-TAmHCF3** (0.0193 g, 8%) as a red solid.

Characterization:

^1H NMR (CHCl_3 , 400 MHz) δ 9.08 (br), 8.81 (br), 8.63 (br), 8.53 (br), 8.09 (br), 7.94 (br), 7.90 (br), 7.84 (br), 7.78 (br), 7.71 (br), 7.66 (br), 7.57 (br), 7.49 (br), 7.37 (br), 7.18 (br), 2.12 (br), 2.04 (br), 1.25 (br), 1.15 (br), 0.83 (br), 0.42 (br), 0.36 (br), 0.35 (br), 0.34 (br), 0.32 (br) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 141.7, 136.6, 124.7, 121.4, 120.2, 31.9, 30.1, 29.6, 29.3, 23.8, 22.7, 14.1 ppm. The other $^{13}\text{C}\{^1\text{H}\}$ signals were not detected because of broadening peaks in a polymer. ^{119}Sn NMR signal was not detected because of broadening peaks in a polymer.

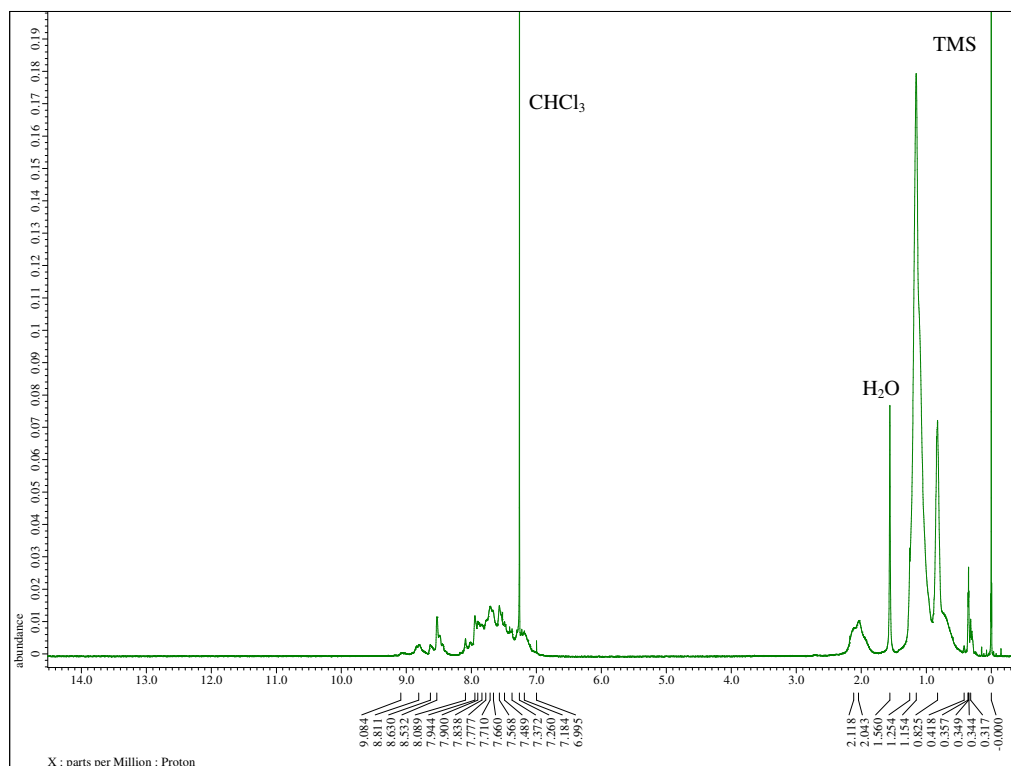


Chart S23. ^1H NMR spectrum of **P-TAmHCF3** in CDCl_3 at 400 MHz.

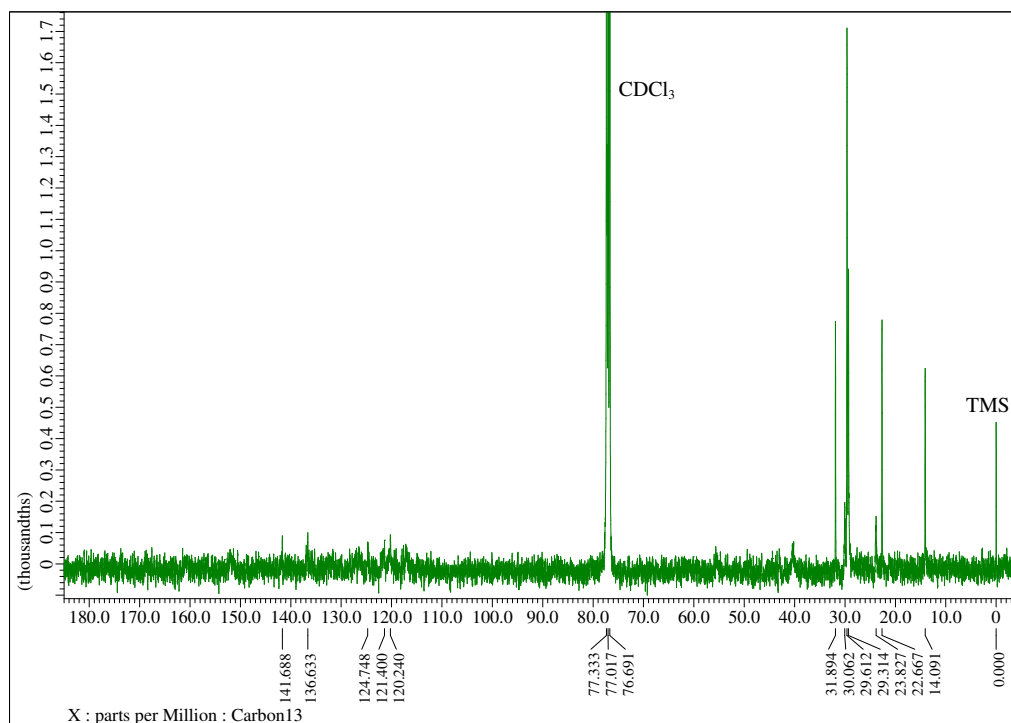


Chart S24. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P-TAmHCF3** in CDCl_3 at 100 MHz.

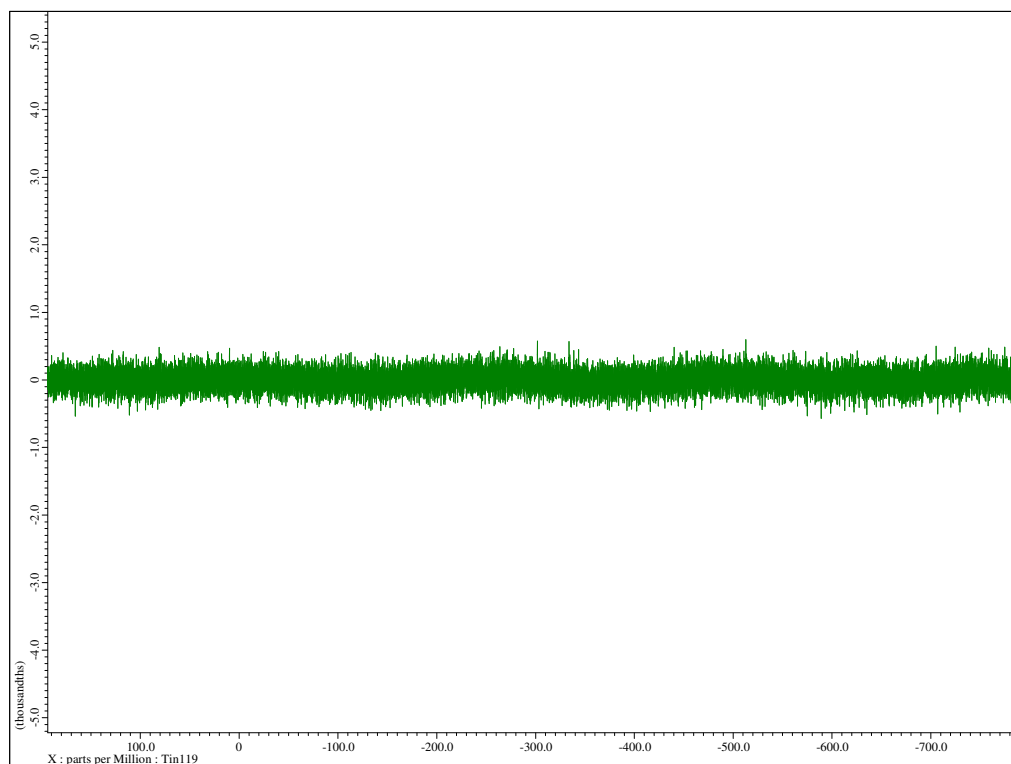
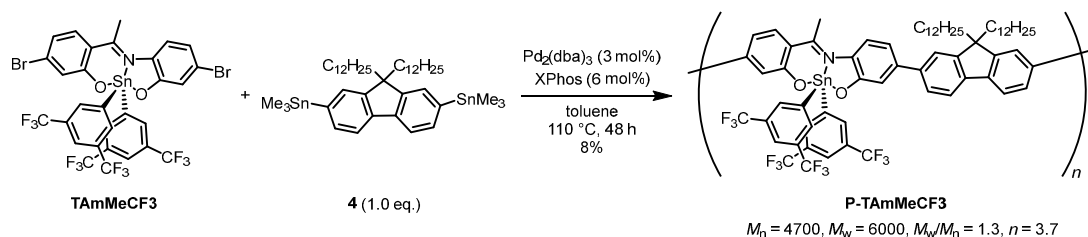


Chart S25. ^{119}Sn NMR spectrum of **P-TAmHCF3** in CDCl_3 at 149 MHz.

Synthesis of P-TAmMeCF3



A mixture of **TAmMeCF3** (0.185 g, 0.200 mmol, 1.00 eq.), **4** (0.166 g, 0.200 mmol, 1.00 eq.), $\text{Pd}_2(\text{dba})_3$ (0.0055 g, 0.0060 mmol, 0.03 eq.), XPhos (0.0057 g, 0.012 mmol, 0.06 eq.) in toluene (4.0 mL) was stirred at 110 °C for 48 h under N_2 atmosphere. After cooling to room temperature, the solution was poured into a large amount of MeCN to collect the polymer by filtration. The polymer was separated the high molecular weight part by HPLC to afford **P-TAmMeCF3** (0.0210 g, 8%) as a red solid.

Characterization:

^1H NMR (CHCl_3 , 400 MHz) δ 8.50 (br), 7.90 (br), 7.84 (br), 7.76 (br), 7.67 (br), 7.62 (br), 7.60 (br), 7.56 (br), 7.48 (br), 7.46 (br), 7.22 (br), 7.12 (br), 7.00 (br), 3.14 (br), 3.02 (br), 2.06 (br), 1.95 (br), 1.16 (br), 0.83 (br), 0.73 (br), 0.36 (br) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 31.9, 29.6, 29.3, 22.7, 14.1 ppm. The other $^{13}\text{C}\{^1\text{H}\}$ signals were not detected probably because of broadening peaks in a polymer. ^{119}Sn NMR signal was not detected because of broadening peaks in a polymer.

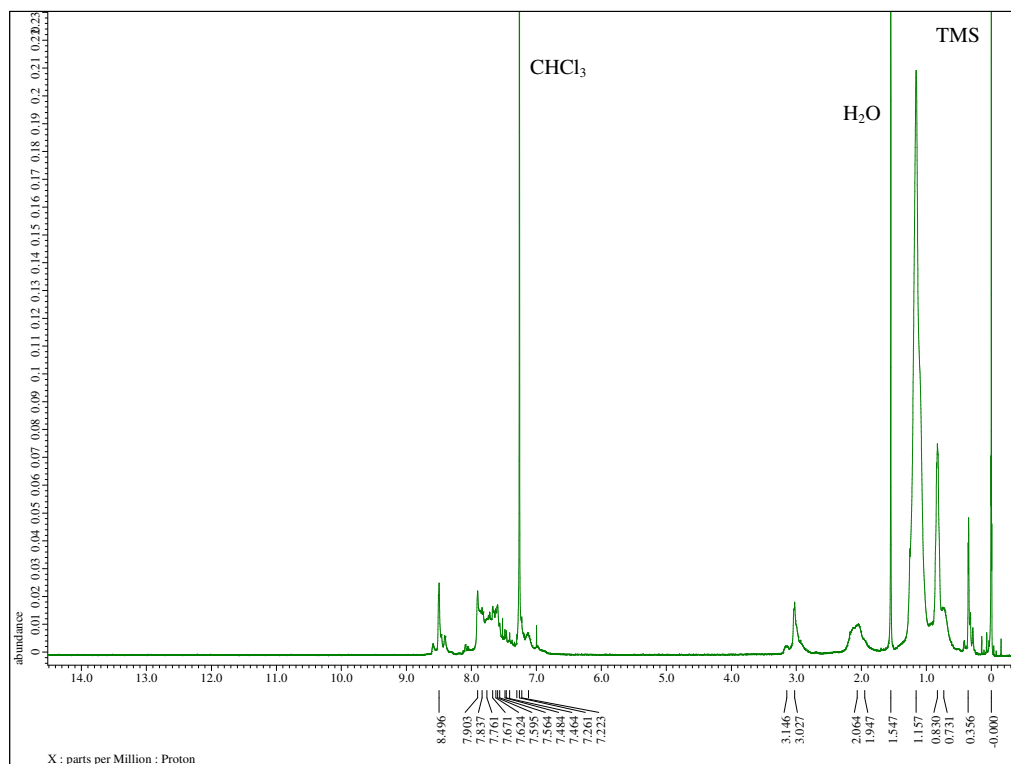


Chart S26. ¹H NMR spectrum of **P-TAmMeCF₃** in CDCl₃ at 400 MHz.

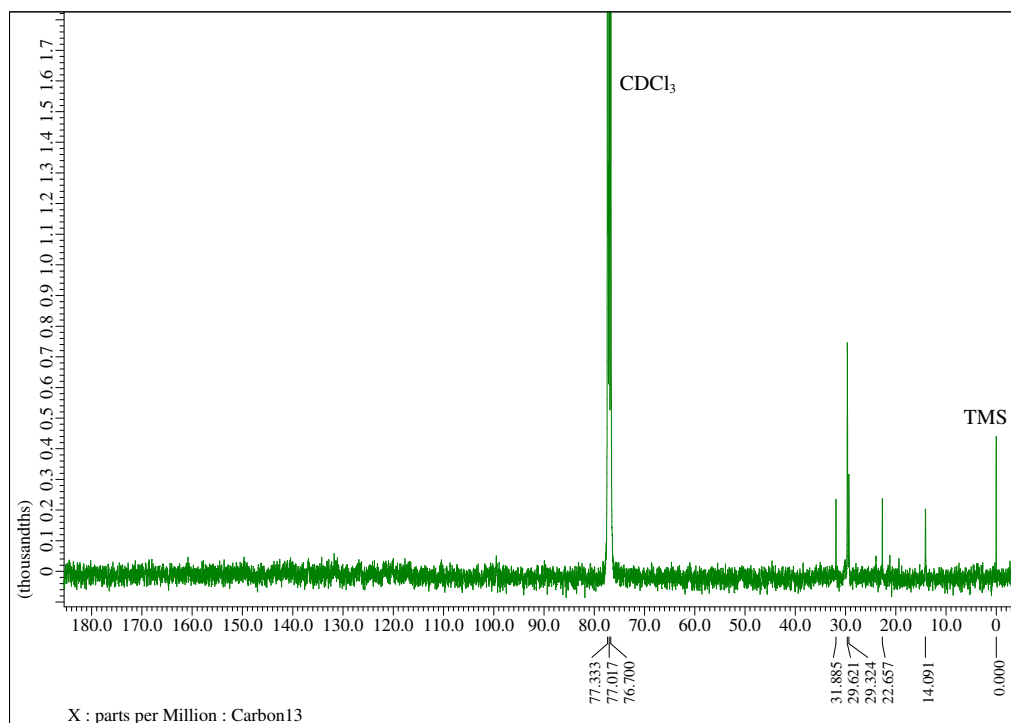


Chart S27. ¹³C{¹H} NMR spectrum of **P-TAmMeCF₃** in CDCl₃ at 100 MHz.

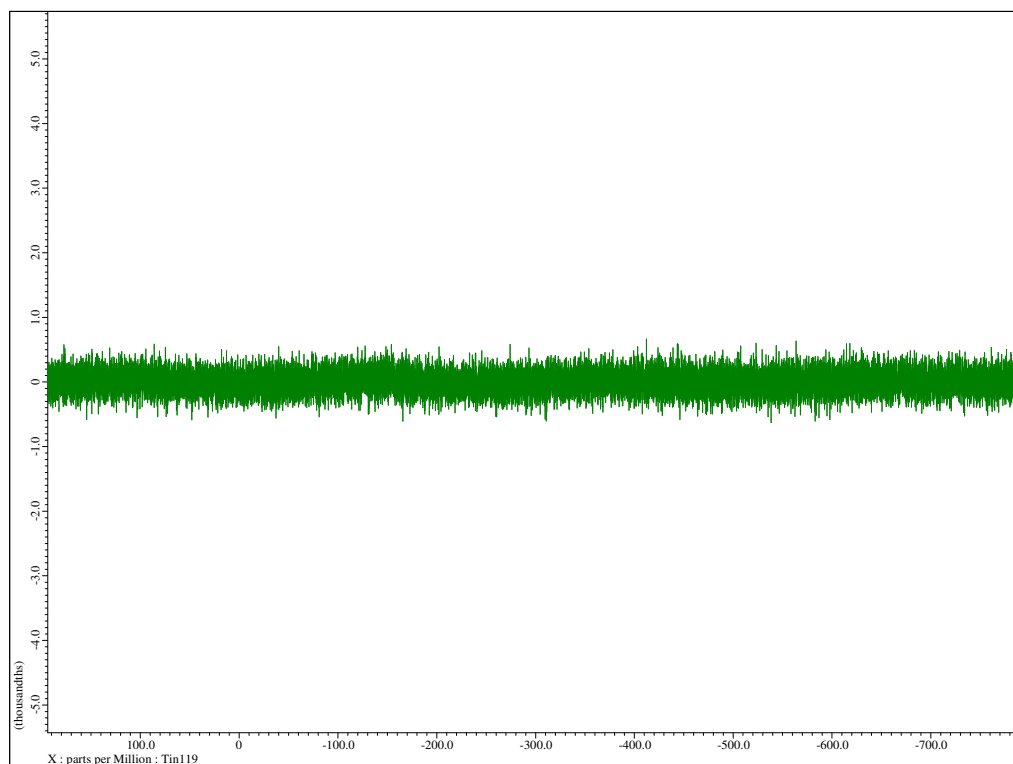


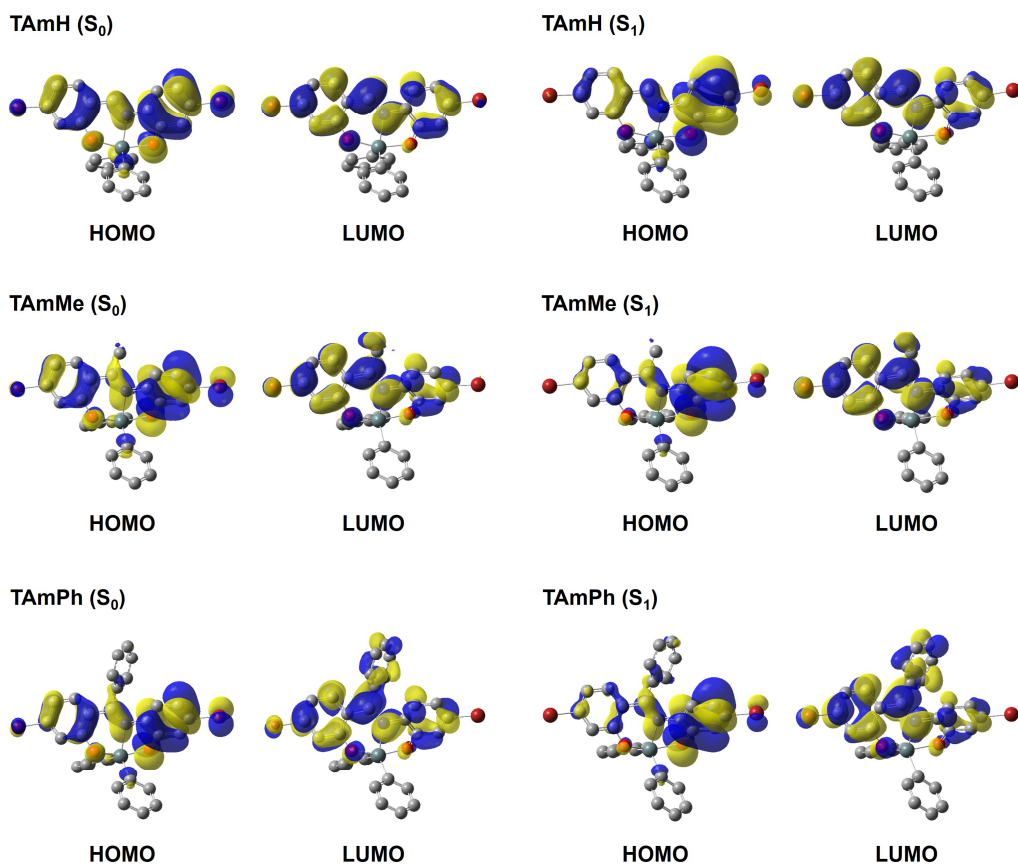
Chart S28. ^{119}Sn NMR spectrum of **P-TAmMeCF3** in CDCl_3 at 149 MHz.

Computational details for theoretical calculation

The Gaussian 16 program package^[9] was used for computation of single molecules. We optimized the structures of **TAmH**, **TAmMe**, **TAmPh** in the ground state (S_0) and in the first excited state (S_1) with a density functional theory (DFT) and a time-dependent DFT (TD-DFT), respectively. The optimized structure in the S_0 was calculated at the B3LYP/LanL2DZ level for Br, Sn and the B3LYP/6-31+G(d,p) level for the other elements. By using the optimized structure in the S_0 as the initial structure, the optimized structure in the S_1 was calculated at the TD-B3LYP/LanL2DZ level for Br, Sn and the TD-B3LYP/6-31+G(d,p) level for the other elements. We calculated the transition energies of the $S_0 \rightarrow S_1$ in the S_0 geometry and $S_1 \rightarrow S_0$ in the S_1 geometry at the TD-B3LYP/LanL2DZ level for Br, Sn and the TD-B3LYP/6-31+G(d,p) level for the other elements.

Table S1. Results of representative transitions from TD-DFT calculations of TAm derivatives

	Energy gap	Wavelength	Stokes shift	Oscillator	transition	Assignment (Weight)
	/ eV	/ nm	/ cm ⁻¹	Strength		
TAmH (S ₀)	2.7496	450.91	5653.1	0.3645	S ₀ → S ₁	HOMO → LUMO (0.69831)
TAmH (S ₁)	2.0488	605.17		0.1815	S ₁ → S ₀	LUMO → HOMO (0.70062)
TAmMe (S ₀)	2.8337	437.54	7327.3	0.2791	S ₀ → S ₁	HOMO → LUMO (0.69881)
TAmMe (S ₁)	1.9252	644.01		0.1260	S ₁ → S ₀	LUMO → HOMO (0.70302)
TAmPh (S ₀)	2.7589	449.41	8076.0	0.2600	S ₀ → S ₁	HOMO → LUMO (0.69913)
TAmPh (S ₁)	1.7575	705.45		0.1026	S ₁ → S ₀	LUMO → HOMO (−0.70376)

**Figure S1.** Selected Kohn–Sham orbitals of TAmH, TAmMe, and TAmPh obtained with DFT calculations (isovalue = 0.02). Hydrogen atoms are omitted for clarity.

Single crystal X-ray diffraction structure analysis

Intensity data were collected on a Rigaku Saturn 724+ with MicroMax-007HF CCD diffractometer with Varimax Mo optics using graphite-monochromated MoK α radiation. The structures were solved and refined by full-matrix least-squares procedures based on F^2 (SHELXL-2018/3).^[10]

Table S2. Crystallographic data of TAmH (CCDC 2380540)

Empirical formula	C ₂₅ H ₁₇ Br ₂ NO ₂ Sn
Formula weight	641.9340
Temperature (K)	143(2)
Wavelength (Å)	0.71075
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions (Å)	$a = 12.231(4)$ $b = 10.352(4)$ $c = 18.077(7)$
Unit cell dimensions (°)	$\alpha = 90$ $\beta = 105.841(6)$ $\gamma = 90$
Volume (Å ³)	2201.9 (14)
Z, calculated density (g cm ⁻³)	4, 1.936
Absorption coefficient	4.813
F(000)	1240.0
Crystal size (mm)	0.160×0.150×0.030
θ range for data collection (°)	3.058–27.469
Limiting indices	$-15 \leq h \leq 13$, $-13 \leq k \leq 13$, $-23 \leq l \leq 20$
Reflections collected (unique)	17357/5058 [R(int) = 0.0493]
Completeness to theta	0.978
Max. and min. transmission	1.000 and 0.698
Goodness-of-fit on F^2	1.059
Final R indices [$I > 2\sigma(I)$] ^[a]	$R_1 = 0.0425$ $wR_2 = 0.0785$
R indices (all data)	$R_1 = 0.0567$ $wR_2 = 0.0838$

^[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

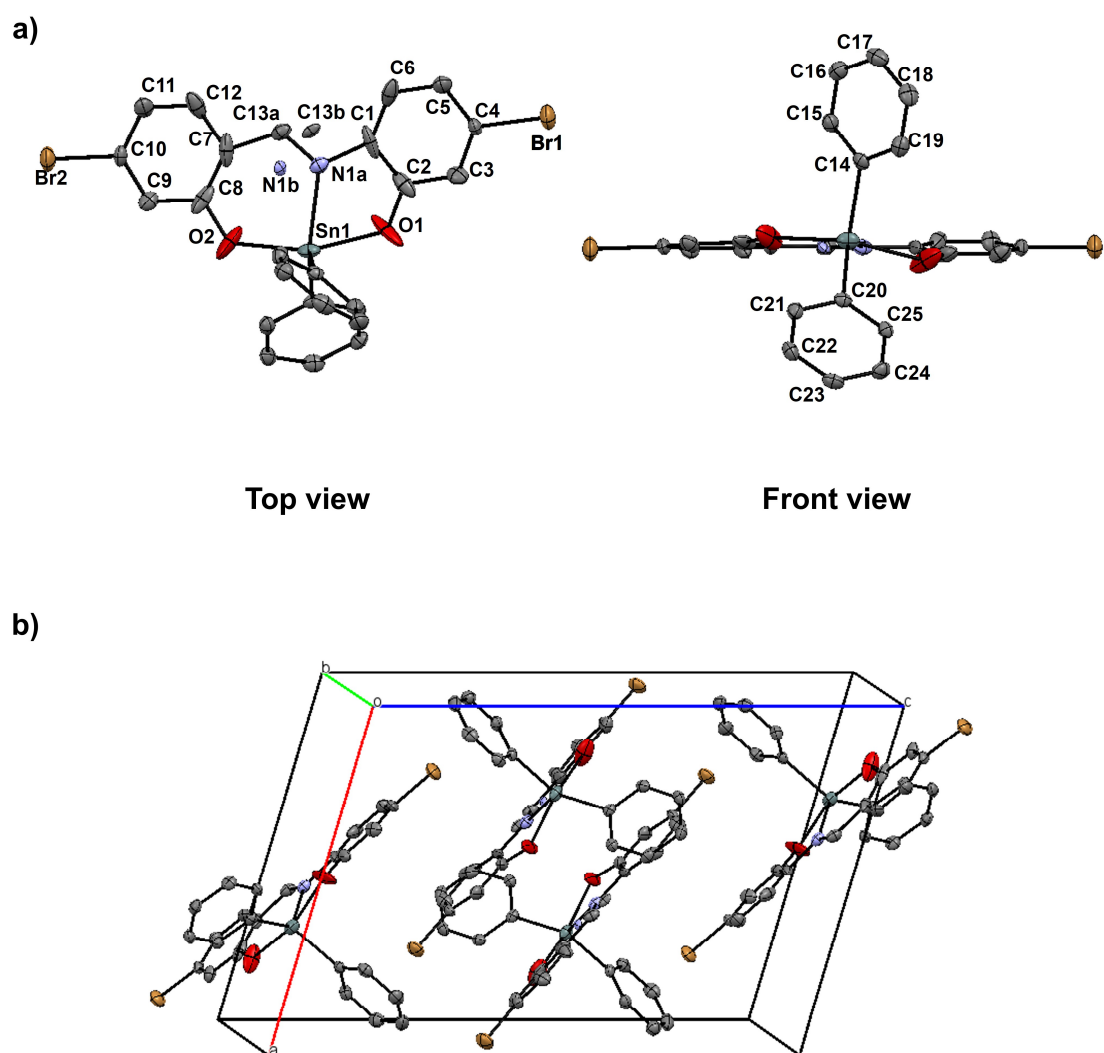


Figure S2. a) ORTEP drawings and b) a packing structure of **TAmH**. Hydrogen atoms are omitted for clarity.

Table S3. Crystallographic data of TAmMe (CCDC 2380541)

Empirical formula	C ₂₆ H ₁₉ Br ₂ NO ₂ Sn
Formula weight	655.9610
Temperature (K)	143(2)
Wavelength (Å)	0.71075
Crystal system, space group	Monoclinic, Cc
Unit cell dimensions (Å)	$a = 13.306(4)$ $b = 16.480(4)$ $c = 11.821(3)$
Unit cell dimensions (°)	$\alpha = 90$ $\beta = 118.481(3)$ $\gamma = 90$
Volume (Å ³)	2278.4 (11)
Z, calculated density (g cm ⁻³)	4, 1.912
Absorption coefficient	4.653
F(000)	1272.0
Crystal size (mm)	0.160×0.070×0.020
θ range for data collection (°)	3.155–27.483
Limiting indices	$-17 \leq h \leq 17, -14 \leq k \leq 21, -15 \leq l \leq 13$
Reflections collected (unique)	9033/3731 [R(int) = 0.0308]
Completeness to theta	1.65/0.83
Max. and min. transmission	1.000 and 0.769
Goodness-of-fit on F^2	1.047
Final R indices [$I > 2\sigma(I)$] ^[a]	$R_1 = 0.0338$ $wR_2 = 0.0669$
R indices (all data)	$R_1 = 0.0382$ $wR_2 = 0.0691$

^[a] $R_1 = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|$. $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma w(F_0^2)^2]^{1/2}$. $w = 1 / [\sigma^2(F_0^2) + (ap)^2 + bp]$, where $p = [\max(F_0^2, 0) + 2F_c^2] / 3$.

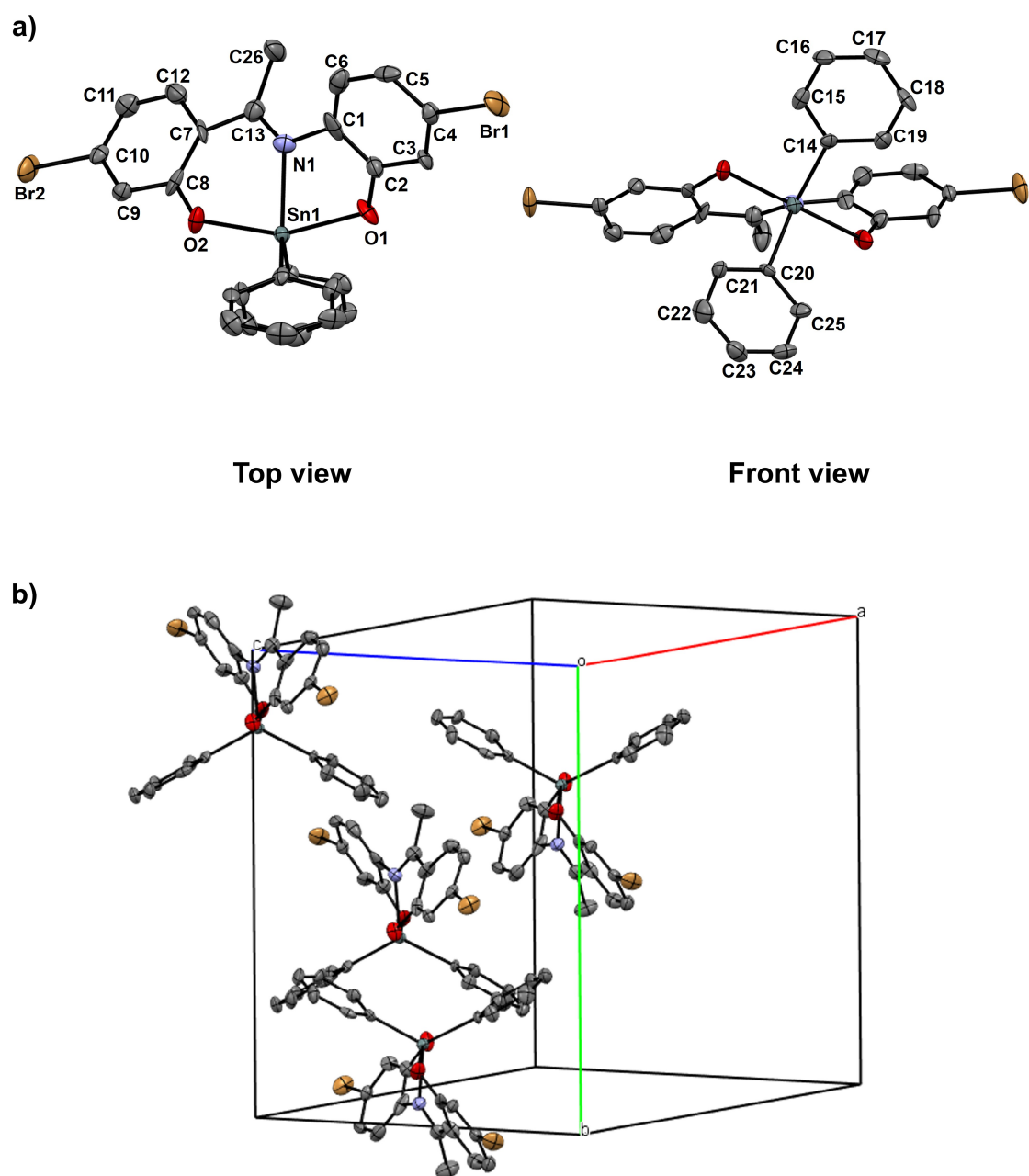


Figure S3. a) ORTEP drawings and b) a packing drawing of **TAmMe**. Hydrogen atoms are omitted for clarity.

Table S4. Crystallographic data of TAmPh (CCDC 2380542)

Empirical formula	C ₃₁ H ₂₁ Br ₂ NO ₂ Sn
Formula weight	718.0320
Temperature (K)	143(2)
Wavelength (Å)	0.71075
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ /n
Unit cell dimensions (Å)	<i>a</i> = 11.929(4) <i>b</i> = 16.987(6) <i>c</i> = 13.147(4)
Unit cell dimensions (°)	<i>α</i> = 90 <i>β</i> = 94.583(5) <i>γ</i> = 90
Volume (Å ³)	2655.6 (15)
Z, calculated density (g cm ⁻³)	4, 1.796
Absorption coefficient	4.001
F(000)	1400
Crystal size (mm)	0.170×0.040×0.020
<i>θ</i> range for data collection (°)	3.109–27.490
Limiting indices	−15 ≤ <i>h</i> ≤ 15, −15 ≤ <i>k</i> ≤ 22, −17 ≤ <i>l</i> ≤ 14
Reflections collected (unique)	21323/75148 [R(int) = 0.0643]
Completeness to theta	0.998
Max. and min. transmission	1.000 and 0.615
Goodness-of-fit on <i>F</i> ²	1.030
Final R indices [<i>I</i> > 2σ(<i>I</i>)] ^[a]	<i>R</i> ₁ = 0.0445 <i>wR</i> ₂ = 0.0974
R indices (all data)	<i>R</i> ₁ = 0.0600 <i>wR</i> ₂ = 0.1047

^[a] $R_1 = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|$. $wR_2 = [\Sigma w(F^2_0 - F^2_c)^2 / \Sigma w(F^2_0)^2]^{1/2}$. $w = 1 / [\sigma^2(F^2_0) + (ap)^2 + bp]$, where $p = [\max(F^2_0, 0) + 2F^2_c] / 3$.

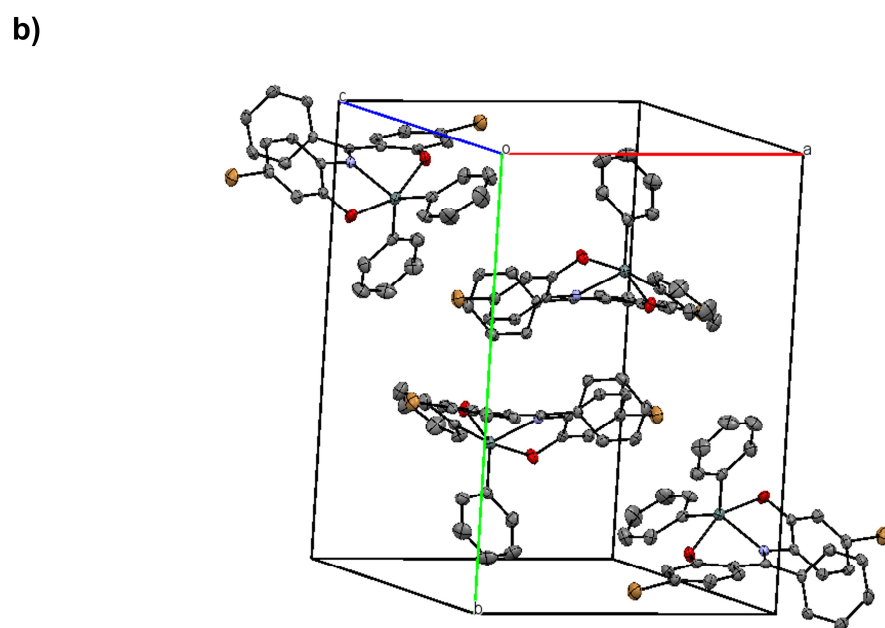
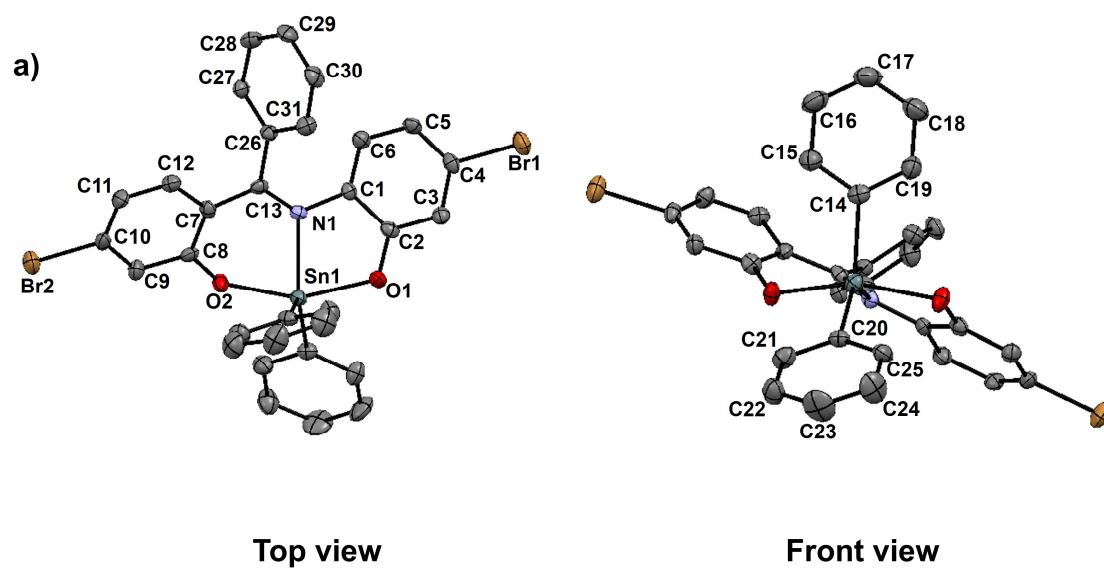


Figure S4. a) ORTEP drawings and b) a packing drawing of **TAmPh**. Hydrogen atoms are omitted for clarity.

UV-vis absorption and PL spectra of 1 wt% PS films

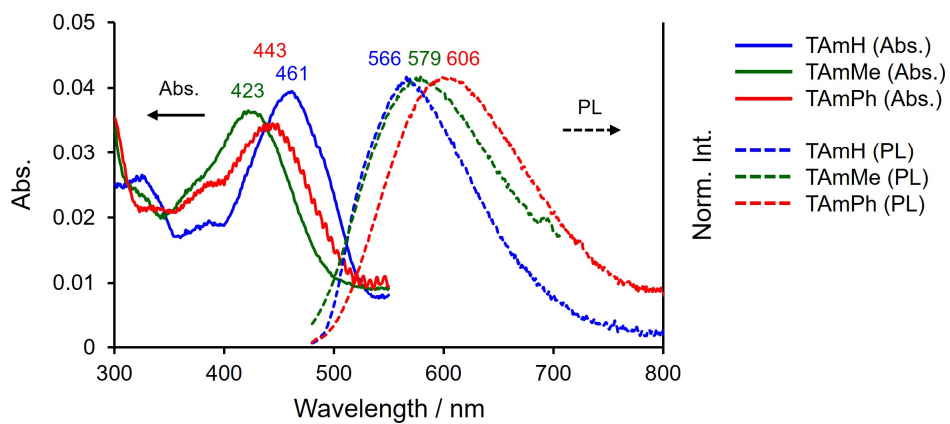


Figure S5. UV-vis absorption and PL spectra of the PS films doped 1 wt% TAM derivatives (**TAMH**, **TAMMe**, and **TAMPh**), excited at the absorption maximum wavelength. The doped films were prepared by a spin-coating method (1000 rpm, 30 s) on a quartz substrate (0.9 cm × 2.5 cm). The numbers of the maximum PL wavelengths were shown on the spectra. PS: polystyrene ($M_n = 81,400$, $M_w = 215,000$, $M_w/M_n = 2.64$), used after reprecipitation in MeOH from CHCl_3 solution.

Table S5. The optical parameters for radiative and nonradiative constants (k_r and k_{nr}) of **TAmH**, **TAmMe**, and **TAmPh**

		$\Phi_{PL}^a / \%$	$\tau^b / \text{ns} (\alpha)$	$k_r^c / 10^8 \text{ s}^{-1}$	$k_{nr}^c / 10^8 \text{ s}^{-1}$
TAmH	CHCl_3 ($1.0 \times 10^{-5} \text{ M}$)	34.5	0.10 (1%)	1.1	2.1
			3.1 (99%)		
	Solid	8.3	0.56 (12%)	0.58	6.4
			1.6 (88%)		
	1 wt% PS Film	44.3	0.37 (2%)	1.3	1.6
			3.6 (98%)		
TAmMe	CHCl_3 ($1.0 \times 10^{-5} \text{ M}$)	<1	— ^d	— ^d	— ^d
			—		
	Solid	20.3	0.41 (3%)	1.0	4.1
			2.0 (97%)		
	1 wt% PS Film	3.7	0.16 (12%)	0.24	6.3
			0.84 (34%)		
TAmPh	CHCl_3 ($1.0 \times 10^{-5} \text{ M}$)	<1	— ^d	— ^d	— ^d
			—		
	Solid	21.1	0.75 (7%)	1.0	3.9
			2.1 (93%)		
	1 wt% PS Film	16.7	0.75 (10%)	0.71	3.5
			2.5 (90%)		

^a Absolute FL quantum yield from Table 1; ^b PL lifetime, excited at the 375 nm LED laser, monitored at λ_{PL} ; ^c $k_r = \Phi_{PL} / \tau_{av}$, $k_{nr} = (1 - \Phi_{PL}) / \tau_{av}$, $\tau_{av} = \sum \alpha_i \tau_i$, α : relative amplitude; ^d Not detected.

PL lifetime measurement of TAmH, TAmMe, and TAmPh

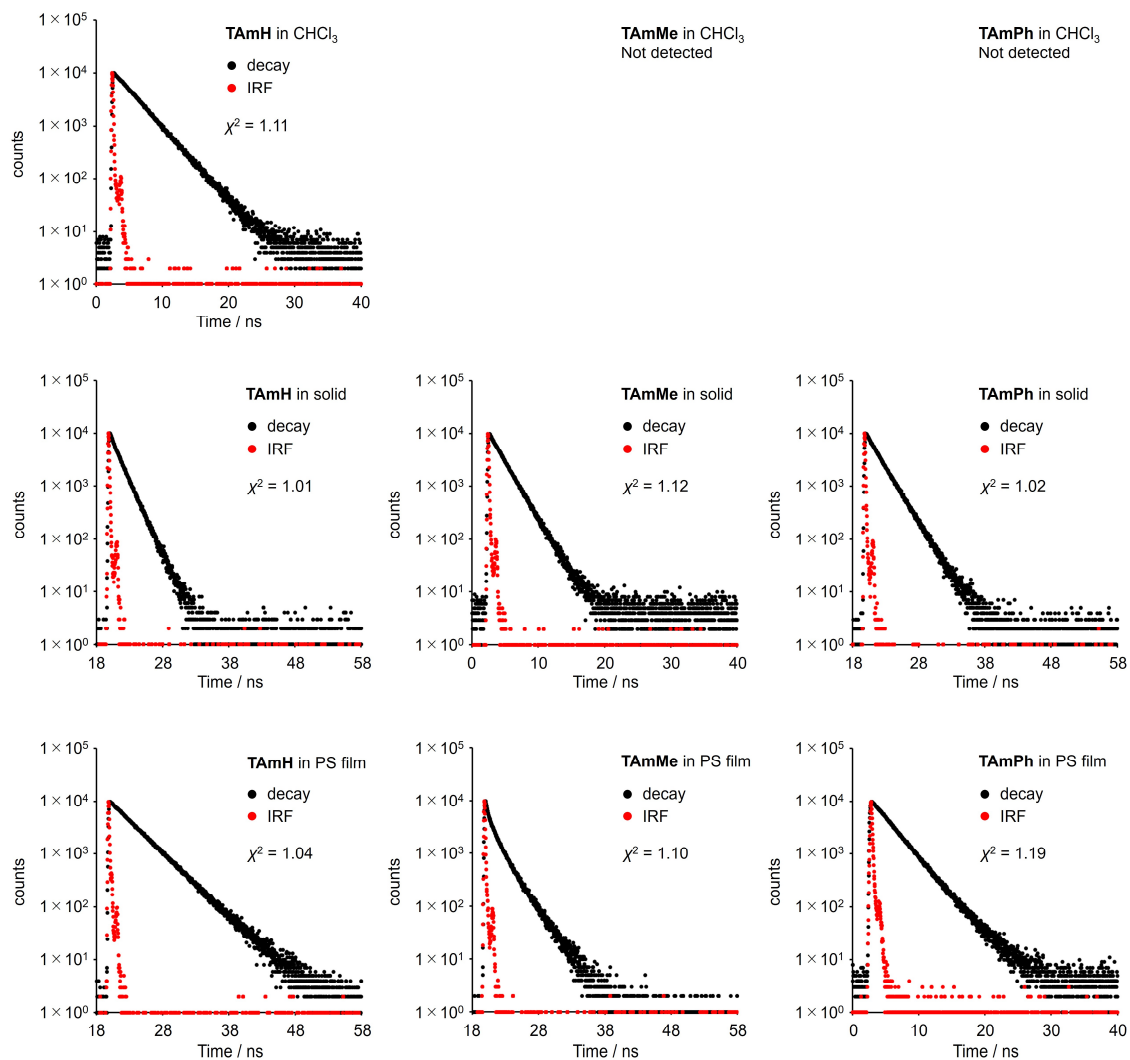


Figure S6. PL lifetime decay curves of **TAmH**, **TAmMe**, and **TAmPh** in each condition, excited at 375 nm LED laser at room temperature. Their emissions at the PL peak tops (λ_{PL}) were monitored.

UV-vis absorption and PL spectra of TAmHCF3 and TAmMeCF3

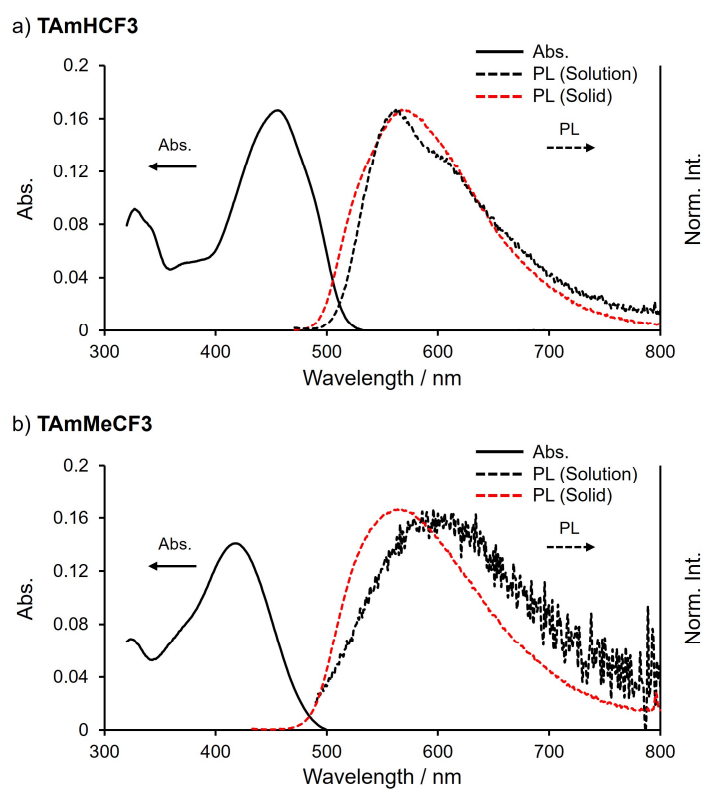


Figure S7. UV-vis absorption and PL spectra of a) **TAmHCF3** and b) **TAmMeCF3** in CHCl_3 (1.0×10^{-5} M) and solid, excited at absorption maximum wavelength in CHCl_3 .

Table S6. The optical parameters for radiative and nonradiative constants (k_r and k_{nr}) of monomers and polymers

		$\Phi_{PL}^a / \%$	$\tau^b / \text{ns} (\alpha)$	$k_r^c / 10^8 \text{ s}^{-1}$	$k_{nr}^c / 10^8 \text{ s}^{-1}$
TAmHCF3	CHCl ₃ (1.0×10^{-5} M)	31.7	0.11 (1%)	1.3	2.7
			1.2 (0.3%)		
			2.6 (98%)		
	Solid	8.1	0.37 (58%)	2.1	24
			0.77 (17%)		
			1.7 (25%)		
TAmMeCF3	CHCl ₃ (1.0×10^{-5} M)	<1	— ^d	— ^d	— ^d
	Solid	11.6	0.30 (9%)	1.4	11
			0.86 (91%)		
P-TAmHCF3	CHCl ₃ (1.0×10^{-5} M)	49.1	0.47 (8%)	2.9	3.0
			1.8 (92%)		
	Film	4.7	0.024 (27%)	2.2	44
			0.19 (52%)		
			0.53 (21%)		
P-TAmMeCF3	CHCl ₃ (1.0×10^{-5} M)	1	— ^d	— ^d	— ^d
	Film	4.7	0.014 (32%)	2.6	52
			0.16 (48%)		
			0.51 (20%)		

^a Absolute FL quantum yield from Table 1; ^b PL lifetime, excited at the 375 nm LED laser, monitored at λ_{PL} ; ^c $k_r = \Phi_{PL} / \tau_{av}$, $k_{nr} = (1 - \Phi_{PL}) / \tau_{av}$, $\tau_{av} = \sum \alpha_i \tau_i$, α : relative amplitude; ^d Not detected

PL lifetime measurement of monomers and polymers

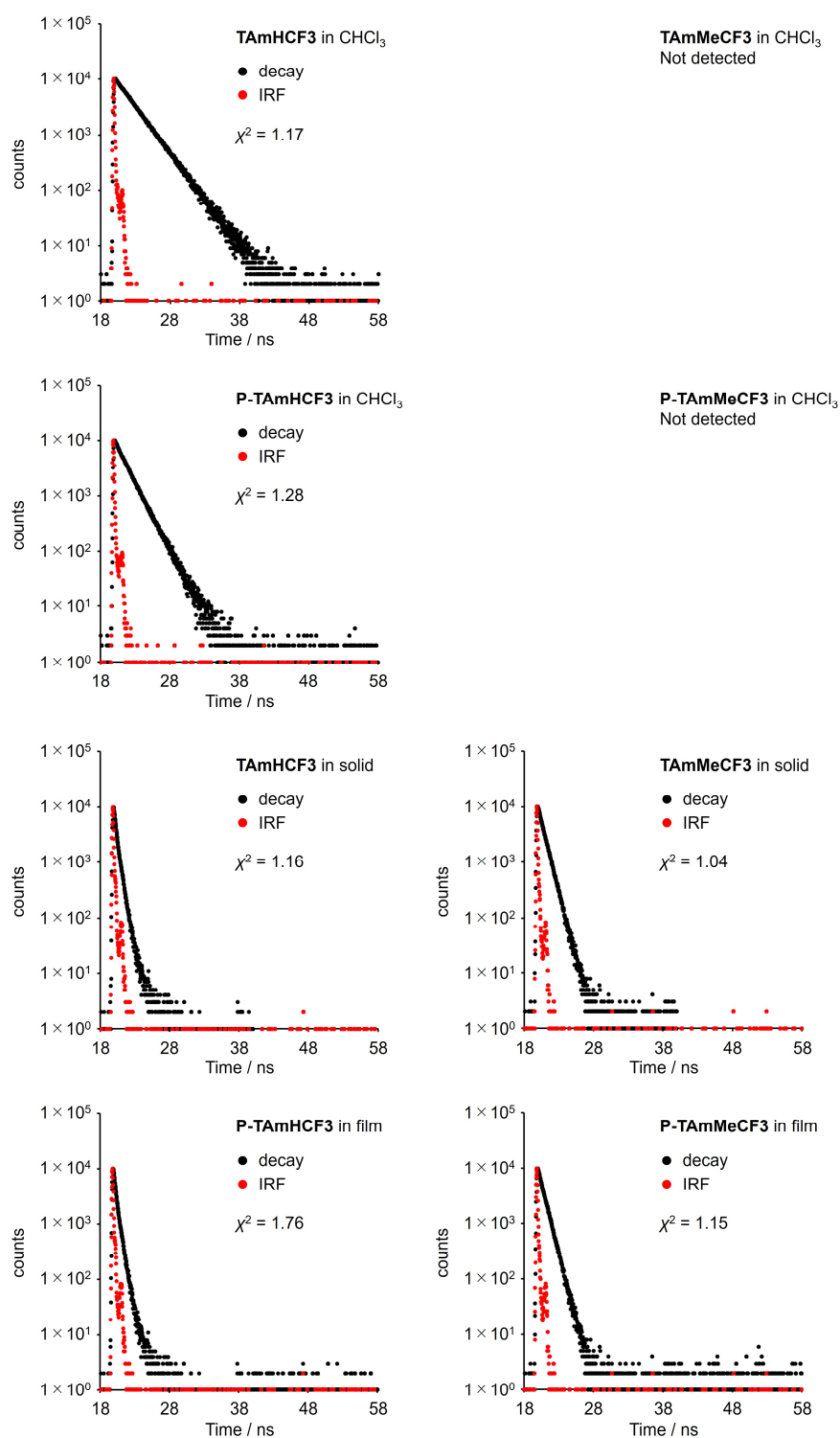
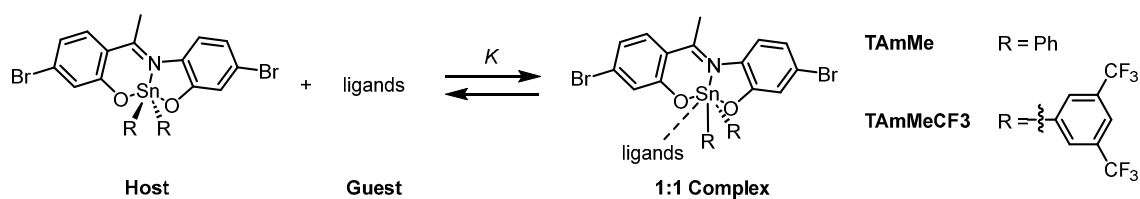


Figure S8. PL lifetime decay curves of TAmH, TAmMe, and TAmPh in each condition, excited at 375 nm LED laser at room temperature. Their emissions at the PL peak tops (λ_{PL}) were monitored.

Determination of binding constant

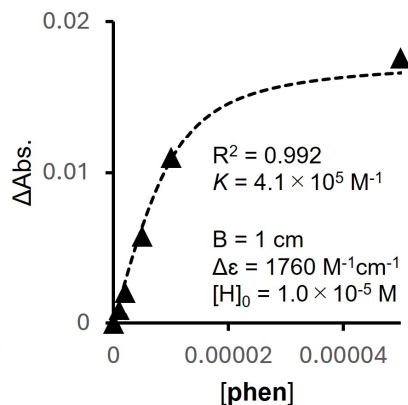
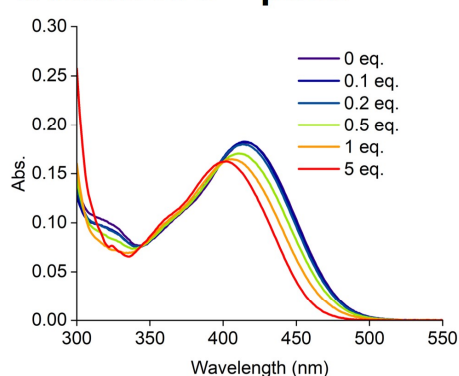
Determination of binding constants for **TAmMe** and **TAmMeCF3** was carried out by means of an absorption titration technique in toluene at room temperature (25 °C) (Figure S9) according to our previous research.^[11] We assumed equilibrium 1:1 binding of tin compounds and ligands (Scheme S1). The concentration of **TAmMe** or **TAmMeCF3**, $[H]_0$ was kept constant and the concentration of guest (ligands), $[G]$ was varied in non-coordinating solvent, toluene. The mixed solutions of tin compounds and guests were prepared, and UV–vis absorption spectra were recorded. The host-guest complexation immediately reach equilibrium after preparation of the mixed solutions. The binding constants were determined by a non-linear curve fitting analysis of hypsochromic shifts and reduction of absorption spectra by increasing guest concentration. The y-axis is ΔA and the x-axis is $[G]$. The binding constants K_{guest} were calculated from eq(1) using non-linear curve fitting (A : absorbance, b : optical path length, ϵ : molar extinction coefficient, $\Delta\epsilon = \epsilon(H) - \epsilon(HG)$). $\epsilon(H)$ and $\epsilon(HG)$ means a value of a molar extinction coefficient of tin compounds (H) and 1:1 complex (HG), respectively.

$$\Delta A = (b\Delta\epsilon/2K_{\text{guest}})[1 + K_{\text{a, guest}}[G] + K_{\text{guest}}[H_0] - \{(1 + K_{\text{guest}}[H_0] + K_{\text{guest}}[G])^2 - 4K_{\text{guest}}^2[G][H_0]\}^{1/2}] \quad (1)$$



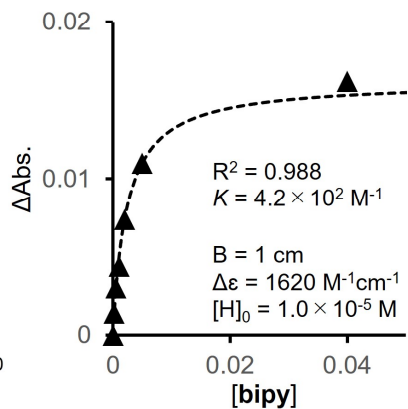
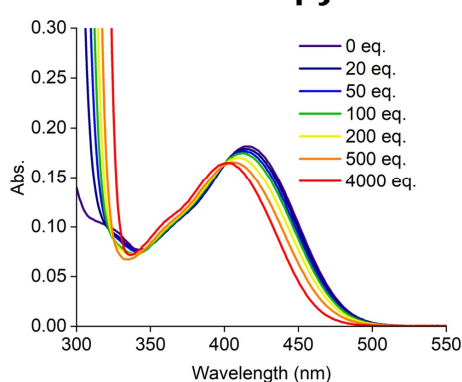
Scheme S1. Equilibrium reaction between host **TAmMe** and **TAmMeCF3** and guest ligands.

TAmMeCF3 + phen



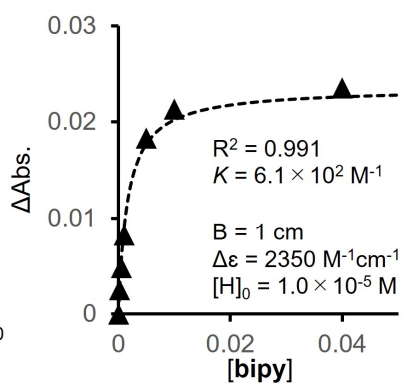
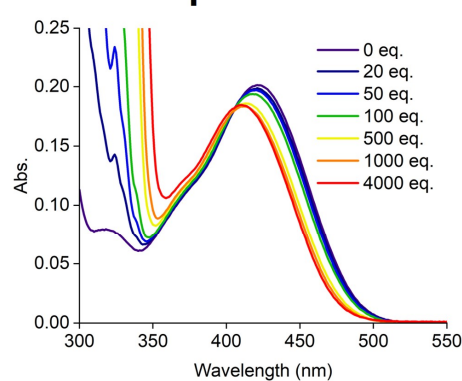
[phen]	ΔAbs.
0	0
0.000001	0.0009
0.000002	0.0021
0.000005	0.0058
0.00001	0.011
0.00005	0.0176

TAmMeCF3 + bipy



[bipy]	ΔAbs.
0	0
0.0002	0.0014
0.0005	0.003
0.001	0.0044
0.002	0.0074
0.005	0.011
0.04	0.0162

TAmMe + phen



[phen]	ΔAbs.
0	0
0.0002	0.0025
0.0005	0.0048
0.001	0.0082
0.005	0.0183
0.01	0.0213
0.04	0.0235

Figure S9. Absorption titration spectra, non-linear curve fitting graphs, and parameters of TAmMe and TAmMeCF3 with ligands in toluene at room temperature.

^{119}Sn NMR spectra of **TAmMeCF3** with ligands

^{119}Sn NMR spectra of **TAmMeCF3** (−327.4 ppm) were measured with nucleophiles under the same conditions as the film preparation. The mixture of **TAmMeCF3** and **phen** (8 eq.) at room temperature (r.t.), the mixture of **TAmMeCF3** and **bipy** (10 eq.) at 225 K and room temperature were measured.

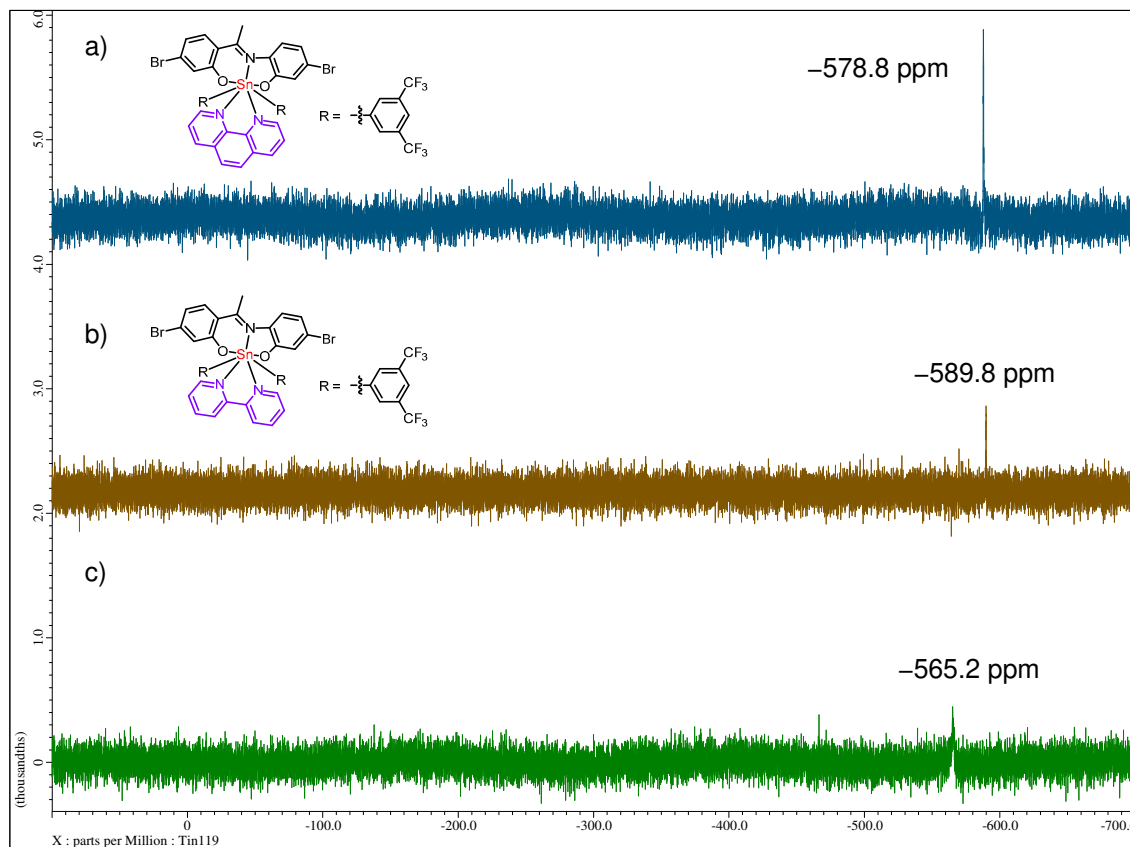


Figure S10. ^{119}Sn NMR spectrum of the mixture of a) **TAmMeCF3** and **phen** in CDCl_3 (r.t.), b) **TAmMeCF3** and **bipy** in CD_2Cl_2 (225 K), and c) **TAmMeCF3** and **bipy** in CD_2Cl_2 (r.t.) at 149 MHz.

Film preparation methods for VT-PL spectra

The film containing **P-TAmMeCF3** and **phen**:

The polymer thin film was prepared by a spin-coating method (1000 rpm, 30 s) on the quartz substrate (0.9 cm × 4 cm) from a mixed solution (80 μ L) of **P-TAmMeCF3** and **phen** (8.0 eq. (1.14 mg) per repeating unit of the polymer) (concentration; **P-TAmMeCF3** (1.0 mg) in CHCl_3 (300 μ L)).

The film containing **P-TAmMeCF3** and **bipy**:

We placed a mixed solution (100 μ L) of **P-TAmMeCF3** and **bipy** (10 eq. (1.23 mg) per repeating unit of the polymer) (concentration; **P-TAmMeCF3** (1.0 mg) in CH_2Cl_2 (200 μ L)) in the quartz cell in the measurement vessel, and prepared the film in a vacuum ($< 10^{-3}$ hPa, 15 min) at 225 K.

The film containing pure **P-TAmMeCF3**:

Spin-coating method: The polymer thin film was prepared by a spin-coating method (1000 rpm, 30 s) on the quartz substrate (0.9 cm × 4 cm) from a solution (80 μ L) of **P-TAmMeCF3** (concentration; **P-TAmMeCF3** (1.0 mg) in CHCl_3 (300 μ L)).

Vacuum in the measurement vessel: We placed a solution (100 μ L) of **P-TAmMeCF3** (concentration; **P-TAmMeCF3** (1.0 mg) in CH_2Cl_2 (200 μ L)) in the quartz cell in the measurement vessel, and prepared the film in a vacuum ($< 10^{-3}$ hPa, 15 min) at 225 K.

The film containing **P-TAmMeCF3** and **DPA**:

We placed a mixed solution (100 μ L) of **P-TAmMeCF3** and **DPA** (10 eq. (1.33 mg) per repeating unit of the polymer) (concentration; **P-TAmMeCF3** (1.0 mg) in CH_2Cl_2 (200 μ L)) in the quartz cell in the measurement vessel, and prepared the film in a vacuum ($< 10^{-3}$ hPa, 15 min) at 225 K.

VT-PL spectra of the polymer films

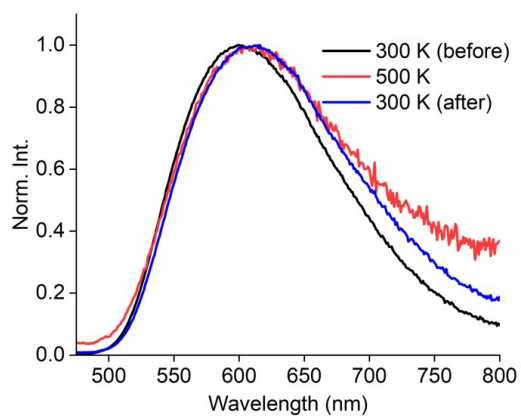


Figure S11. PL spectra of the film containing **P-TAmMeCF3** and **phen** at 300 K before heating (black line), 500 K (red line), and 300 K after cooling (blue line), excited at 465 nm.

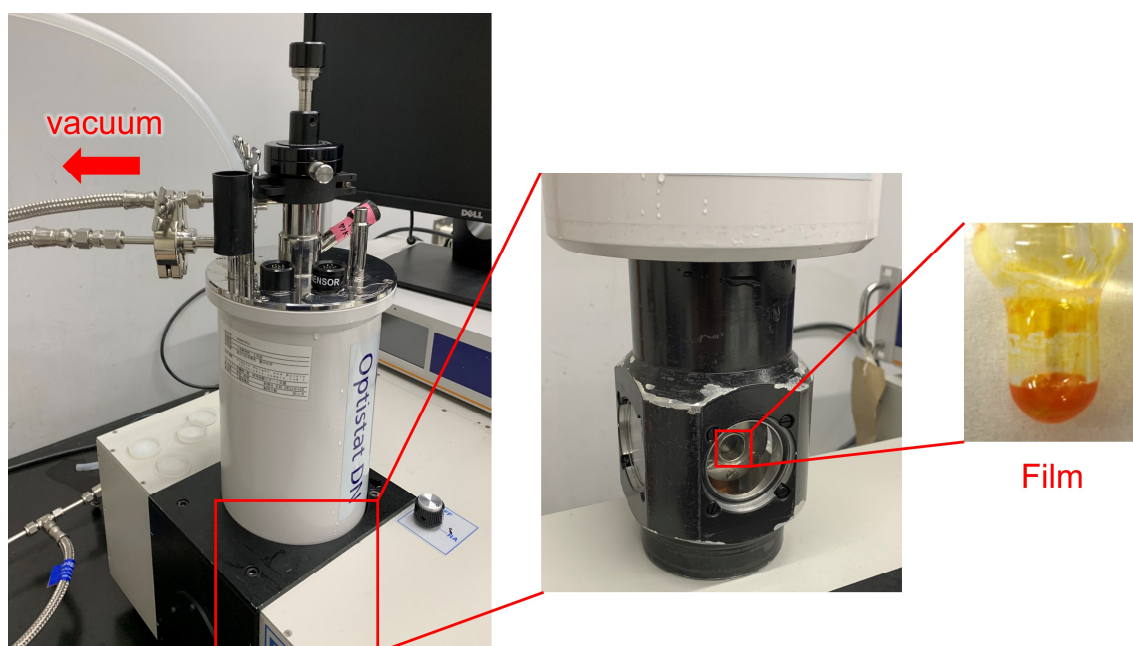


Figure S12. The setup of equipment for the preparation of the film containing **P-TAmMeCF3** and **bipy** (10 eq. per repeating unit of the polymer) at 225 K in the measurement vessel.

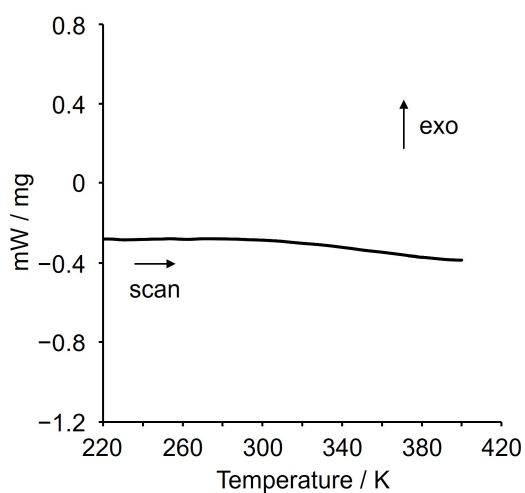


Figure S13. The first scan of the differential scanning calorimetry (DSC) curve of **P-TAmMeCF3** in film (scan rate, 5 °C min⁻¹) under N₂. The films were prepared by a drop-casting method from CH₂Cl₂ solution on the hot plate at 100 °C, and dried in vacuo for 4 h at room temperature.

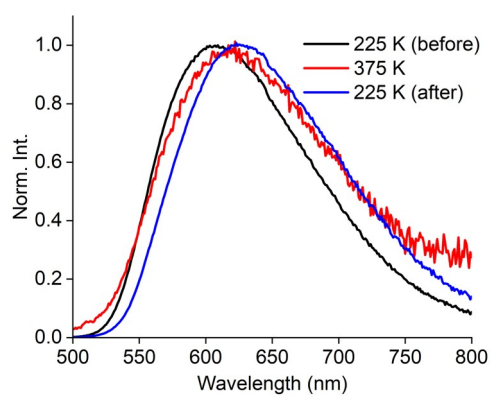


Figure S14. PL spectra of the film containing **P-TAmMeCF3** and **bipy** at 225 K before heating (black line), 375 K (red line), and 225 K after cooling (blue line), excited at 465 nm.

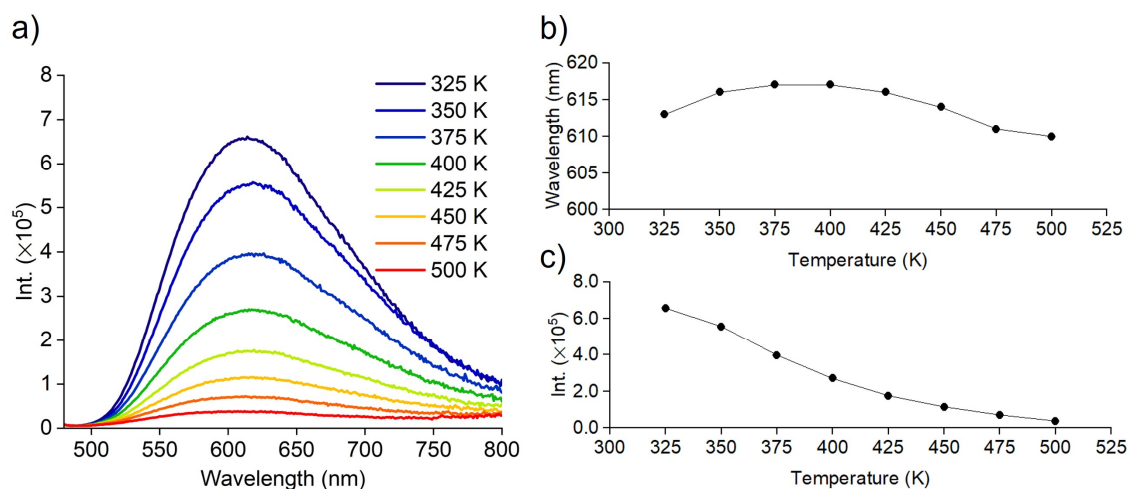


Figure S15. a) VT-PL spectrum of **P-TAmMeCF3** film prepared by a spin-coating method from 325 to 500 K, excited at 465 nm. b) Relationship of temperature and the peak wavelength. c) Relationship of temperature and PL intensity.

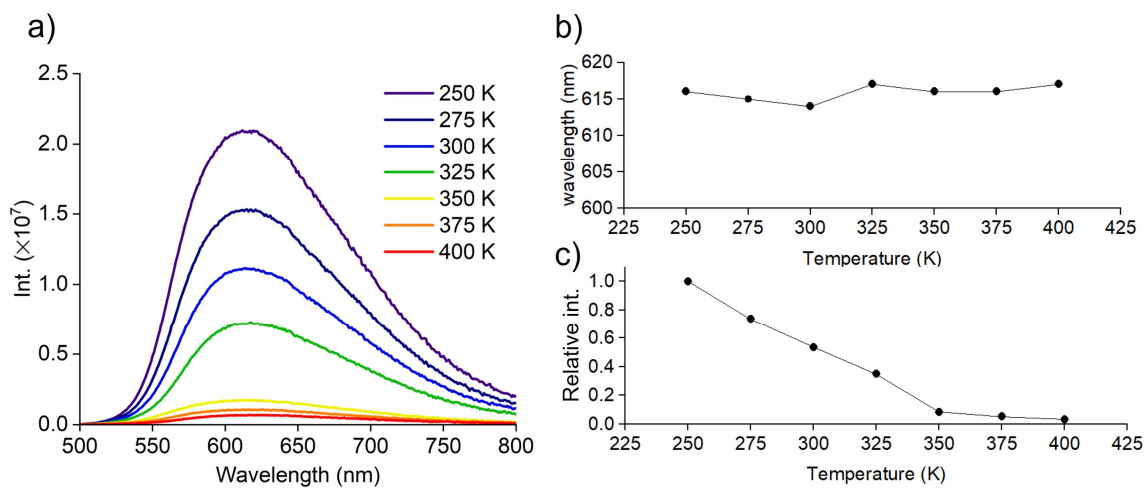


Figure S16. a) VT-PL spectra of **P-TAmMeCF3** film prepared by vacuum in the measurement vessel from 225 to 400 K, excited at 465 nm. b) Relationship of temperature and the peak wavelength. c) Relationship of temperature and PL intensity.

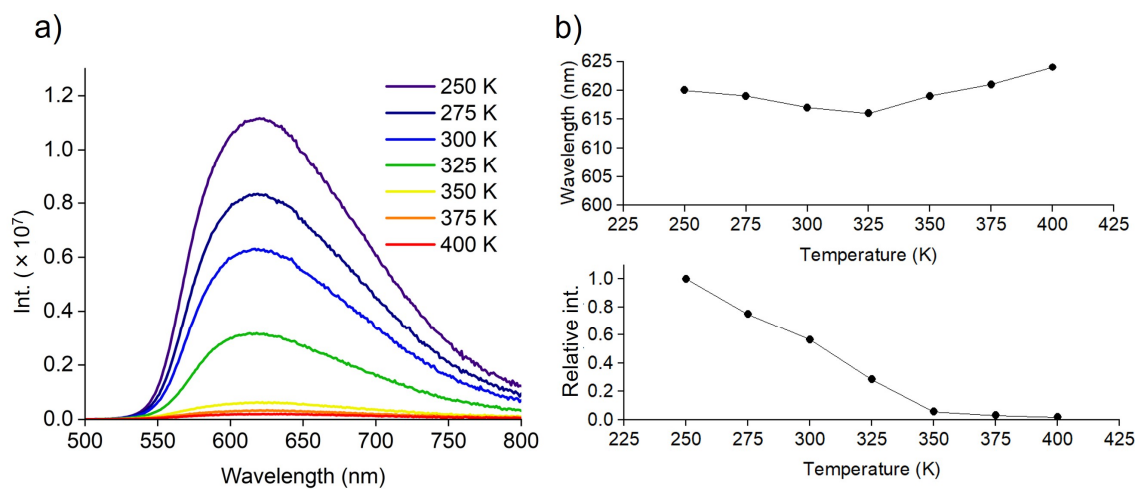


Figure S17. a) VT-PL spectra of the film containing **P-TAmMeCF3** and **DPA** prepared by vacuum in the measurement vessel from 250 K to 400 K, excited at 465 nm. b) Relationship of temperature and the peak wavelength. c) Relationship of temperature and PL intensity.

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Cartesian coordinates for the optimized geometries

TAmH (S₀)

C	-1.83981	-1.88894	-0.13451
C	-2.48715	-0.62273	-0.30343
O	-1.8286	0.505823	-0.3977
Sn	0.113144	1.076387	0.083277
N	0.490492	-1.10165	-0.09854
C	-0.41947	-2.04409	-0.07525
O	2.144333	0.901365	0.45184
C	2.700698	-0.27589	0.208512
C	1.876137	-1.39351	-0.09488
C	4.098526	-0.44786	0.25046
C	4.632701	-1.69885	-0.01743
C	3.838114	-2.8024	-0.34479
C	2.455278	-2.63525	-0.38681
C	-2.63332	-3.0621	-0.05149
C	-4.01253	-3.02497	-0.12967
C	-4.62211	-1.76963	-0.30275
C	-3.90182	-0.59438	-0.3915
Br	-6.57157	-1.69265	-0.42176
Br	6.577942	-1.92777	0.043352
C	0.318204	2.26491	-1.66604
C	1.561232	2.842943	-1.97935
C	1.707619	3.645548	-3.11567
C	0.613564	3.880884	-3.95324
C	-0.62715	3.310786	-3.65266
C	-0.7742	2.508123	-2.51667
H	-0.06948	-3.07557	-0.00126
H	4.723221	0.404431	0.491881
H	4.285097	-3.76209	-0.57684
H	1.839702	-3.48317	-0.67287
H	-2.13436	-4.02061	0.075703
H	-4.60592	-3.92917	-0.06369
H	-4.38711	0.365509	-0.52671
H	2.419523	2.662221	-1.33799

H	2.675435	4.084538	-3.34618
H	0.727217	4.504825	-4.83652
H	-1.48082	3.489385	-4.30231
H	-1.74157	2.067263	-2.2941
C	-0.37748	1.767905	2.033407
C	0.638924	2.025838	2.970472
C	0.325403	2.496655	4.249904
C	-1.00737	2.717873	4.609222
C	-2.02692	2.466471	3.686323
C	-1.71349	1.994653	2.407445
H	-2.51596	1.801704	1.700663
H	1.677762	1.856946	2.700747
H	1.121921	2.690265	4.964522
H	-1.25052	3.084568	5.603596
H	-3.06532	2.636685	3.96075

TAmH (S_I)

C	-1.82868	-1.84694	-0.19402
C	-2.51034	-0.58639	-0.40927
O	-1.85786	0.564723	-0.51815
Sn	0.034457	1.047939	0.070067
N	0.487772	-0.97563	-0.28689
C	-0.43377	-1.98144	-0.15033
O	2.204703	0.858178	0.515464
C	2.735378	-0.29178	0.230349
C	1.861738	-1.32393	-0.27775
C	4.128682	-0.52691	0.348719
C	4.651578	-1.73729	-0.10532
C	3.829637	-2.71192	-0.65215
C	2.420694	-2.48136	-0.75865
C	-2.63951	-3.01972	-0.03776
C	-4.01519	-2.98543	-0.13192
C	-4.63736	-1.7472	-0.37526
C	-3.91232	-0.5692	-0.50671
Br	-6.587	-1.68332	-0.51689
Br	6.571055	-2.0721	0.054023

C	0.411217	2.420198	-1.50628
C	1.614308	3.144918	-1.57681
C	1.836632	4.06092	-2.6102
C	0.858407	4.265502	-3.58758
C	-0.34275	3.552949	-3.52774
C	-0.5663	2.637835	-2.49366
H	-0.03575	-2.97552	0.049915
H	4.752057	0.250699	0.775161
H	4.239992	-3.65848	-0.98638
H	1.804044	-3.24346	-1.22534
H	-2.14168	-3.96936	0.146029
H	-4.60425	-3.88905	-0.02171
H	-4.40123	0.383479	-0.67793
H	2.387587	2.994159	-0.82841
H	2.77235	4.613533	-2.65074
H	1.030792	4.977642	-4.39099
H	-1.10751	3.708947	-4.28494
H	-1.5053	2.092904	-2.45424
C	-0.4199	1.623037	2.070059
C	0.588697	1.926289	3.002019
C	0.262436	2.319769	4.303976
C	-1.07679	2.415434	4.693521
C	-2.08888	2.116782	3.777179
C	-1.76262	1.724585	2.474591
H	-2.56129	1.497345	1.77365
H	1.634401	1.854329	2.716081
H	1.054257	2.550495	5.012851
H	-1.33001	2.720915	5.705852
H	-3.13255	2.188014	4.073956

TAmMe (S₀)

C	-1.87882	-1.80929	0.11356
C	-2.39609	-0.59362	-0.44986
O	-1.66376	0.463683	-0.71597
Sn	0.108652	1.069101	0.13545
N	0.4582	-1.12737	0.084309

C	-0.45793	-2.04326	0.352934
O	2.024605	0.840318	0.895829
C	2.639615	-0.26915	0.50412
C	1.855071	-1.37187	0.069103
C	4.042849	-0.37572	0.495858
C	4.626055	-1.54145	0.019623
C	3.8747	-2.60792	-0.48085
C	2.483439	-2.50818	-0.45868
C	-2.80672	-2.8598	0.353613
C	-4.15462	-2.76245	0.059962
C	-4.61995	-1.56569	-0.50467
C	-3.77816	-0.50568	-0.76052
Br	-6.5202	-1.40323	-0.93382
Br	6.581583	-1.68304	0.013042
C	0.66967	2.221426	-1.55776
C	1.929977	2.843536	-1.59822
C	2.304272	3.626483	-2.69523
C	1.422872	3.797702	-3.76653
C	0.167129	3.183593	-3.73853
C	-0.20783	2.401333	-2.64132
H	4.635069	0.460287	0.850072
H	4.357899	-3.48791	-0.88942
H	1.891198	-3.31302	-0.88199
H	-2.45945	-3.79831	0.767438
H	-4.82771	-3.58949	0.253346
H	-4.13666	0.421363	-1.19312
H	2.625915	2.71245	-0.77383
H	3.283178	4.099676	-2.71308
H	1.713413	4.405956	-4.61979
H	-0.52104	3.312274	-4.57077
H	-1.18446	1.926161	-2.63067
C	-0.72685	1.816089	1.941948
C	0.086765	2.025159	3.069996
C	-0.45469	2.537361	4.253833
C	-1.81537	2.850557	4.325509

C	-2.63463	2.649669	3.210706
C	-2.09319	2.135966	2.027753
H	-2.74391	1.984335	1.170319
H	1.145744	1.786222	3.023625
H	0.186515	2.69275	5.118367
H	-2.23536	3.250134	5.245474
H	-3.69358	2.891777	3.260856
C	-0.0517	-3.37289	0.958954
H	-0.13049	-4.20112	0.244777
H	0.972001	-3.33818	1.329713
H	-0.70852	-3.60264	1.802605

TAmMe (S₁)

C	-1.89022	-1.73801	0.214264
C	-2.46092	-0.57039	-0.43397
O	-1.76026	0.526038	-0.71693
Sn	0.027382	1.071725	0.059512
N	0.43825	-0.9924	0.033712
C	-0.50448	-1.91227	0.474868
O	2.154604	0.899061	0.769157
C	2.689543	-0.24107	0.469529
C	1.81964	-1.2867	-0.02351
C	4.096274	-0.44829	0.530826
C	4.626632	-1.61621	-0.00303
C	3.804931	-2.58567	-0.57274
C	2.391573	-2.39137	-0.60677
C	-2.81812	-2.76911	0.588652
C	-4.16324	-2.72621	0.271669
C	-4.65299	-1.61009	-0.42018
C	-3.82873	-0.54577	-0.75763
Br	-6.55237	-1.53423	-0.88741
Br	6.55792	-1.91259	0.056428
C	0.666984	2.203042	-1.62002
C	1.843807	2.972357	-1.58836
C	2.23007	3.733304	-2.69647
C	1.444243	3.73592	-3.85263

C	0.270545	2.977898	-3.8963
C	-0.11765	2.218946	-2.7872
H	4.716813	0.329503	0.961076
H	4.227377	-3.50556	-0.96201
H	1.76573	-3.1545	-1.05948
H	-2.45361	-3.64457	1.112749
H	-4.8218	-3.54152	0.550135
H	-4.21392	0.338955	-1.25223
H	2.469402	2.977782	-0.6998
H	3.142681	4.323301	-2.65573
H	1.744166	4.327292	-4.71442
H	-0.3456	2.978102	-4.79237
H	-1.03578	1.639758	-2.8287
C	-0.62568	1.920383	1.89668
C	0.277643	2.292212	2.908255
C	-0.18106	2.867468	4.097803
C	-1.54917	3.079734	4.292789
C	-2.45757	2.715013	3.295247
C	-1.99878	2.140369	2.105185
H	-2.71829	1.861967	1.339503
H	1.343745	2.131607	2.772755
H	0.529961	3.149221	4.87099
H	-1.90526	3.526974	5.217704
H	-3.52296	2.875761	3.441542
C	-0.05712	-3.06582	1.346307
H	-0.26555	-4.0395	0.882282
H	1.009807	-3.022	1.564347
H	-0.58955	-3.05192	2.307053

TAmPh (S₀)

C	1.861602	1.38468	-0.27922
C	2.398549	0.116304	-0.6832
O	1.662274	-0.95837	-0.86493
Sn	-0.01782	-1.47694	0.214868
N	-0.46732	0.668702	-0.16003
C	0.428804	1.639813	-0.16179

O	-1.8952	-1.19464	1.039341
C	-2.5827	-0.20618	0.476203
C	-1.87956	0.839402	-0.18478
C	-3.98957	-0.17978	0.51386
C	-4.65924	0.847269	-0.13356
C	-3.99044	1.847663	-0.84341
C	-2.59657	1.83276	-0.86631
C	2.78207	2.439928	-0.03517
C	4.146055	2.304584	-0.2218
C	4.627048	1.072564	-0.68894
C	3.791397	0.000473	-0.92124
Br	6.547591	0.867217	-0.99544
Br	-6.61948	0.881271	-0.07648
C	-0.6237	-2.91186	-1.22993
C	-1.8519	-3.58027	-1.0831
C	-2.25327	-4.54733	-2.01061
C	-1.43178	-4.85815	-3.09797
C	-0.20873	-4.19929	-3.25573
C	0.193684	-3.2332	-2.32771
H	-4.51456	-0.97068	1.037202
H	-4.53929	2.618849	-1.37151
H	-2.07643	2.598456	-1.42826
H	2.408218	3.392847	0.319693
H	4.820432	3.128076	-0.01788
H	4.167073	-0.95765	-1.26203
H	-2.50178	-3.34183	-0.24535
H	-3.20691	-5.0545	-1.88465
H	-1.74353	-5.60937	-3.81974
H	0.43268	-4.43621	-4.10148
H	1.144039	-2.72468	-2.46088
C	0.955918	-1.88564	2.059582
C	0.222833	-1.89542	3.259926
C	0.850014	-2.18868	4.475509
C	2.217042	-2.47995	4.507717
C	2.956446	-2.47761	3.321305

C	2.329176	-2.18267	2.106464
H	2.919519	-2.18463	1.193762
H	-0.84115	-1.67495	3.24432
H	0.270367	-2.19186	5.395697
H	2.703762	-2.70932	5.452635
H	4.019774	-2.70431	3.340276
C	-0.00299	3.069029	-0.00796
C	0.213504	4.007002	-1.02882
C	-0.61254	3.480184	1.186753
C	-0.19407	5.332891	-0.86474
H	0.69376	3.696192	-1.95311
C	-1.00087	4.810406	1.356123
H	-0.78142	2.758686	1.98154
C	-0.8001	5.737761	0.328813
H	-0.03278	6.048937	-1.66622
H	-1.46563	5.12011	2.288235
H	-1.1111	6.770861	0.458895

TAmPh (Si)

C	1.905736	1.394242	-0.32683
C	2.486289	0.11892	-0.70428
O	1.808574	-1.02454	-0.733
Sn	0.093321	-1.43102	0.281675
N	-0.39418	0.541529	-0.22992
C	0.50211	1.598703	-0.12946
O	-2.01503	-1.14315	0.989672
C	-2.60989	-0.17903	0.358918
C	-1.78541	0.730969	-0.40907
C	-4.02648	-0.05311	0.336372
C	-4.59716	0.861144	-0.53423
C	-3.81111	1.665493	-1.36507
C	-2.39741	1.571593	-1.31408
C	2.833473	2.465526	-0.11204
C	4.179628	2.372182	-0.40773
C	4.671392	1.155595	-0.90369
C	3.855828	0.04443	-1.03029

Br	6.568477	1.009323	-1.36007
Br	-6.54276	1.038114	-0.6081
C	-0.54072	-2.98657	-1.01851
C	-1.68489	-3.75595	-0.74196
C	-2.06787	-4.79821	-1.59233
C	-1.31153	-5.08602	-2.73221
C	-0.1704	-4.33073	-3.01731
C	0.214664	-3.29012	-2.16542
H	-4.61772	-0.70994	0.964118
H	-4.27609	2.391011	-2.02346
H	-1.80059	2.216081	-1.95081
H	2.469695	3.396548	0.304057
H	4.840523	3.216334	-0.24533
H	4.244774	-0.91662	-1.34786
H	-2.28796	-3.54163	0.136309
H	-2.95534	-5.38383	-1.36422
H	-1.60915	-5.89594	-3.39388
H	0.422441	-4.5513	-3.9019
H	1.106821	-2.71353	-2.39248
C	0.859186	-1.75007	2.237011
C	0.011705	-1.84249	3.355382
C	0.53734	-2.07396	4.630687
C	1.917034	-2.21746	4.805553
C	2.770166	-2.12864	3.702102
C	2.244482	-1.89797	2.426515
H	2.922483	-1.83063	1.5794
H	-1.06288	-1.73217	3.23575
H	-0.13064	-2.14217	5.486163
H	2.325127	-2.39719	5.797203
H	3.844189	-2.23732	3.832043
C	-0.04778	2.893208	0.311671
C	-0.94967	2.936884	1.400835
C	0.215779	4.099936	-0.37702
C	-1.54922	4.13505	1.790017
H	-1.14641	2.028949	1.963466

C	-0.39708	5.290013	0.005769
H	0.870393	4.088132	-1.24374
C	-1.28146	5.317027	1.094561
H	-2.2265	4.144123	2.640369
H	-0.19464	6.200298	-0.55313
H	-1.75407	6.248898	1.3929