Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Thioarylmaleimides: Accessible, tunable, and strongly emissive building blocks

Jayden Price, Emily Albright, Andreas Decken, and Sara Eisler*

Supporting Information

Table of Contents:

Experimental Details	**S2**
Tables S1 and S2	**S3**
Figures S1-S10	**S4 – S9**
Synthesis and characterization of TAMs 3-11	**S10 – S16**
^{1}H & ^{13}C NMR spectra	**S17 – S34**
Computational details	**S35**
Spectral Scans of TAMs 3-11	**S38**
Crystal data and refinement for TAM 8	**S48**

Experimental Section

Materials: All commercially available reagents were used as received and without further purification. 2,3-Dibromomaleimide, benzo[b]thiophene-2-boronic acid, benzo[b]thiophene-3-boronic acid, 1-thianthrenylboronic acid, and dibenzothiophen-4-boronic acid were purchased from Sigma Aldrich. Thieno[2,3-b]thiophene-2-boronic acid was purchased from Combi Building Blocks. Dithieno[3,2-*b*:2',3'-*d*]thiophene-2-boronic acid was purchased from TCI Chemicals. Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) was prepared according to a literature procedure[1] using $PdCl_2$ and triphenylphosphine purchased from Sigma Aldrich. All reactions were run under nitrogen unless otherwise specified. TLC analysis was performed on glass-backed plates (60Å), and flash chromatography was performed on ultra-pure flash silica (230-400 mesh size) or activated alumina (X-Y mesh size).

Nuclear magnetic resonance (NMR): NMR spectra were recorded using a Varian Inova 300 MHz (^{1}H: 299.838 MHz, ^{13}C: 75.402 MHz) or Varian Unity 400 MHz spectrometer (^{1}H: 399.945 MHz, ^{13}C: 100.577 MHz) with $CDCl_3$ referenced at 7.26 ppm (^{1}H) and 77.16 ppm (^{13}C) or DMSO-d6 referenced at 2.50 ppm (^{1}H) and 39.52 (^{13}C).

High-resolution mass spectrometry (HRMS): HRMS spectra were recorded on a Bruker Daltonics spectrometer using Positive Electrospray Ionization (ESI^+).

UV-visible (UV-vis) & fluorescence spectroscopy: UV-visible spectra were recorded at room temperature in chloroform (10^{-5} $molL^{-1}$) on an Agilent 8453 spectrophotometer. Emission spectra were acquired in chloroform (10^{-5} $molL^{-1}$) on an Agilent Cary Eclipse Fluorescence Spectrophotometer. Solid-state emission spectra were recorded at 298 K using Edinburgh Instruments FS5 Fluorescence Spectrometer. An SC-10 Front Face Sample Holder was used along with a solid-state cuvette.

Photoluminescent quantum yields (ϕ_f): Acquired via direct measurement at 298 K using an Edinburg Instruments FS5 Spectrofluorimeter equipped with an integration sphere. Resulting data was processed using Fluoracle software.

Fourier-Transform Infrared spectroscopy (IR): Samples were prepared as a film by drop casting onto a KBr disc. Spectra were recorded using on a Nicolet iS10 spectrometer.

Melting points (mp ˚C): Determined using a DigiMelt melting point apparatus.

Computational: All DFT calculations were carried out with the Gaussian 09 program package. Structures were modelled using WebMO's free World Wide Web-based interface (https://www.webmo.net/). Pre-minimization of the structures were performed using Molecular Mechanics (MM). The molecular structure optimizations were conducted in gas-phase and in chloroform using a Self-Consistent Reaction Field (SCRF) at Becke, three parameter, Lee-Yang-Pang (B3LYP), 6-31G (d,p) level of theory. Excited state calculations were conducted in chloroform using TD-DFT. Additionally, vibrational frequency calculations were performed to verify the acquired ground-state minima. Population analyses were performed to assess Highest Occupied and Lowest Unoccupied Molecular Orbitals (HOMO and LUMO, respectively). Molecular orbitals were visualized using Avogadro's free molecular editing software (https://avogadro.cc/).

[1] D.R. Coulson, L. C. Satek, S. O. Grim. Tetrakis(Triphenylphosphine)Palladium(0). *Inorganic Syntheses*., 2007, 28, 107-109.

Table S1. Kohn-Sham orbitals illustrating the electron density distribution within the frontier molecular orbitals of compounds **3 - 11** in chloroform calculated using B3LYP/6-31G(d,p).

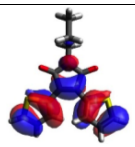
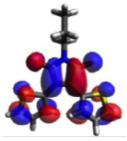
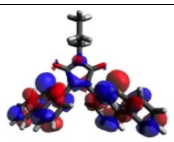
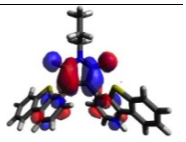
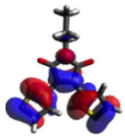
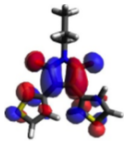
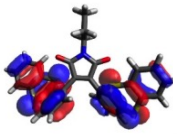
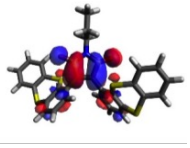
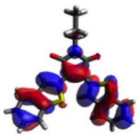
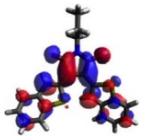
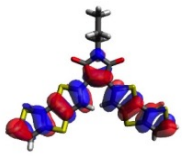
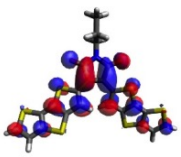
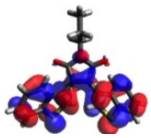
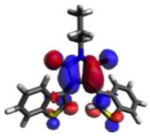
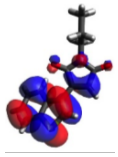
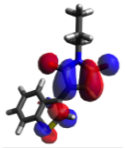
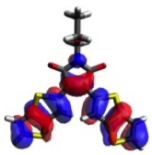
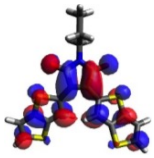
	HOMO	LUMO		HOMO	LUMO
3	 **(-) 5.712 eV**	 **(-) 2.861 eV**	**8**	 **(-) 5.925 eV**	 **(-) 2.721 eV**
4	 **(-) 6.004 eV**	 **(-) 2.644 eV**	**9**	 **(-) 5.946 eV**	 **(-) 2.583 eV**
5	 **(-) 5.754 eV**	 **(-) 2.967 eV**	**10**	 **(-) 5.267 eV**	 **(-) 3.022 eV**
6	 **(-) 5.795 eV**	 **(-) 2.695 eV**	**11**	 **(-) 6.050 eV**	 **(-) 2.655 eV**
7	 **(-) 5.448 eV**	 **(-) 2.974 eV**			

Table S2. Tabulated frontier molecular orbital data acquired at B3LYP/6-31G(d,p) level of theory in $CHCl_3$.

Compound	HOMO (eV)	LUMO (eV)	H-L (eV)
3	-5.712	-2.861	2.851
4	-6.004	-2.644	3.360
5	-5.754	-2.967	2.787
6	-5.795	-2.695	3.100
7	-5.448	-2.974	2.474
8	-5.925	-2.721	3.204
9	-5.946	-2.583	3.363
10	-5.267	-3.022	2.245
11	-6.050	-2.655	3.395

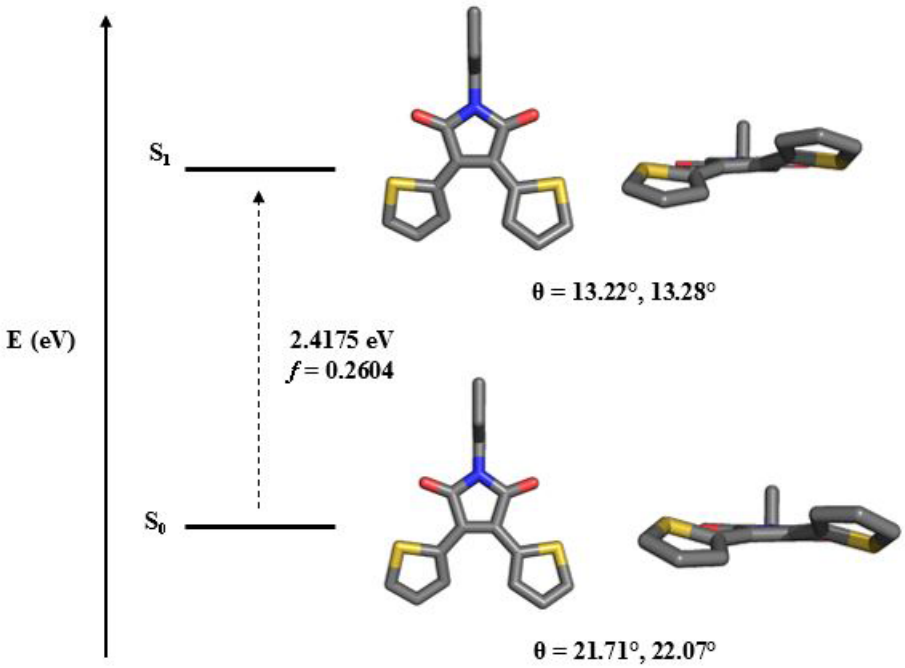


Figure S1. Compound **3** ground to excited state ($S_0 \rightarrow S_1$) transition, oscillator strength (***f***) and geometries in chloroform calculated using TD-DFT.

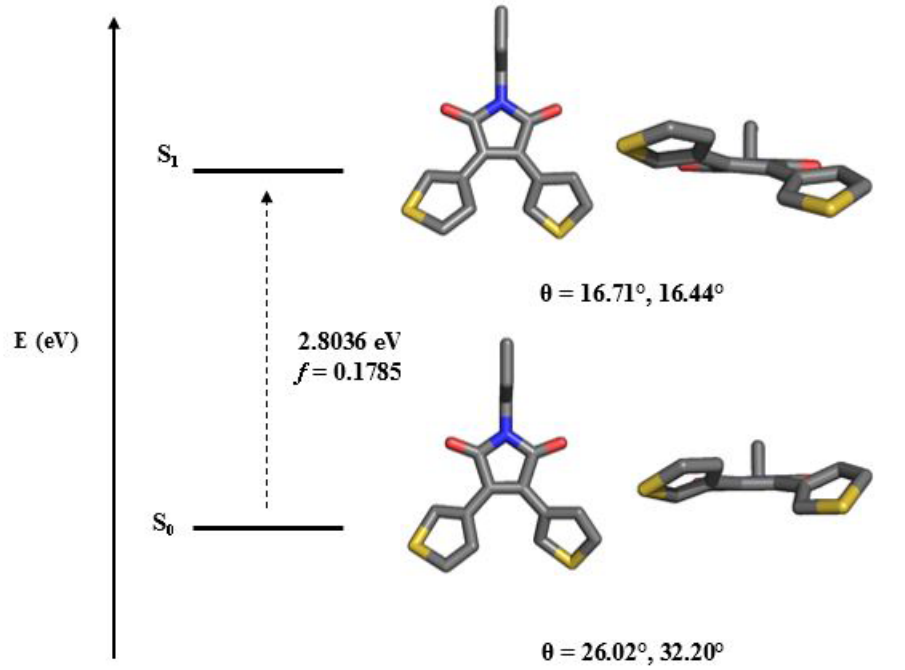


Figure S2. Compound **4** ground to excited state ($S_0 \rightarrow S_1$) transition, oscillator strength (***f***) and geometries in chloroform calculated using TD-DFT.

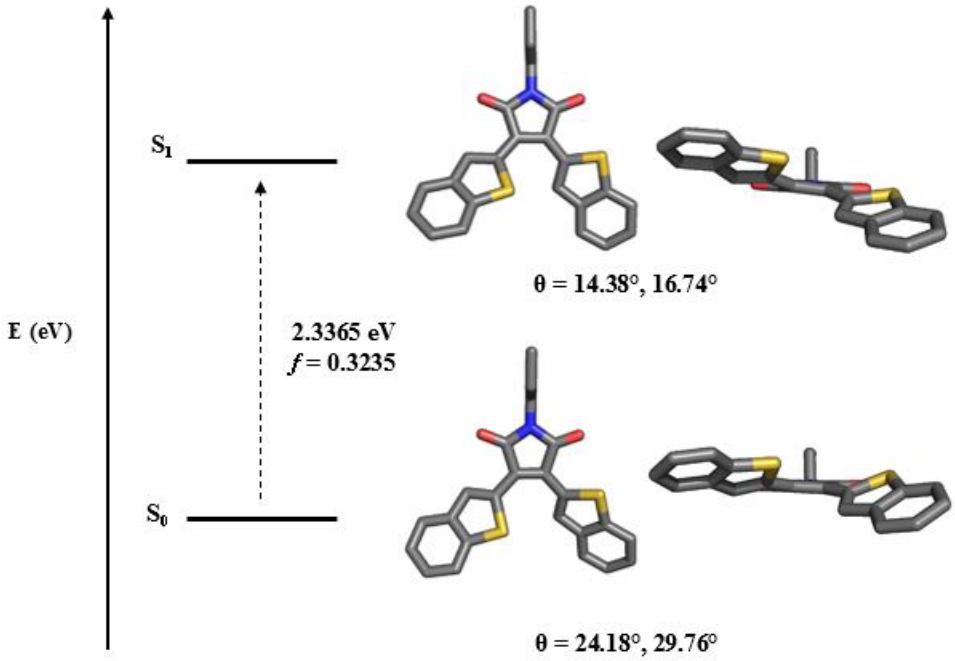


Figure S3. Compound **5** ground to excited state ($S_0 \rightarrow S_1$) transition, oscillator strength (***f***) and geometries in chloroform calculated using TD-DFT.

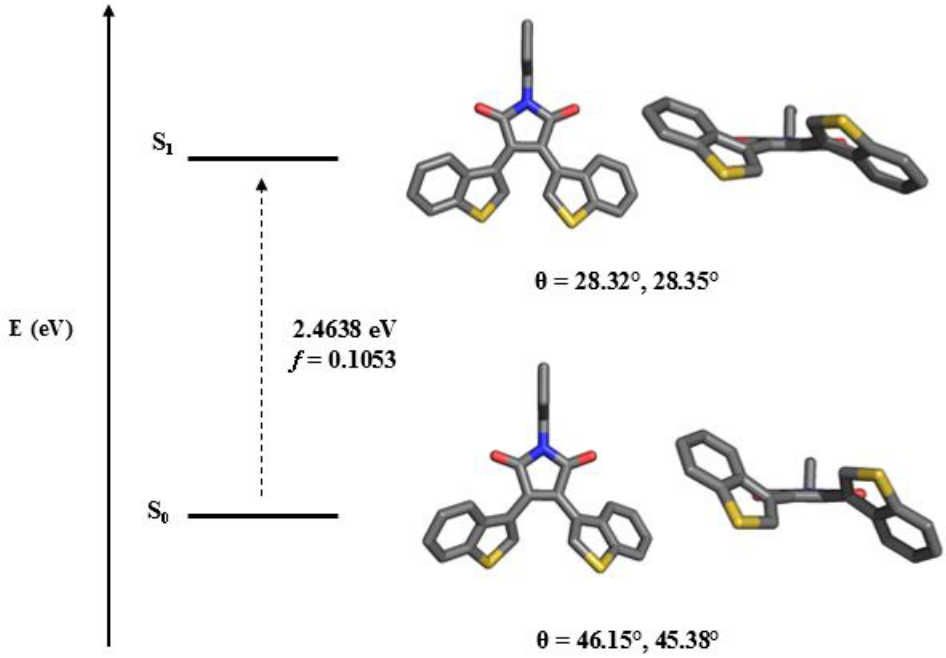


Figure S4. Compound **6** ground to excited state ($S_0 \rightarrow S_1$) transition, oscillator strength (***f***) and geometries in chloroform calculated using TD-DFT.

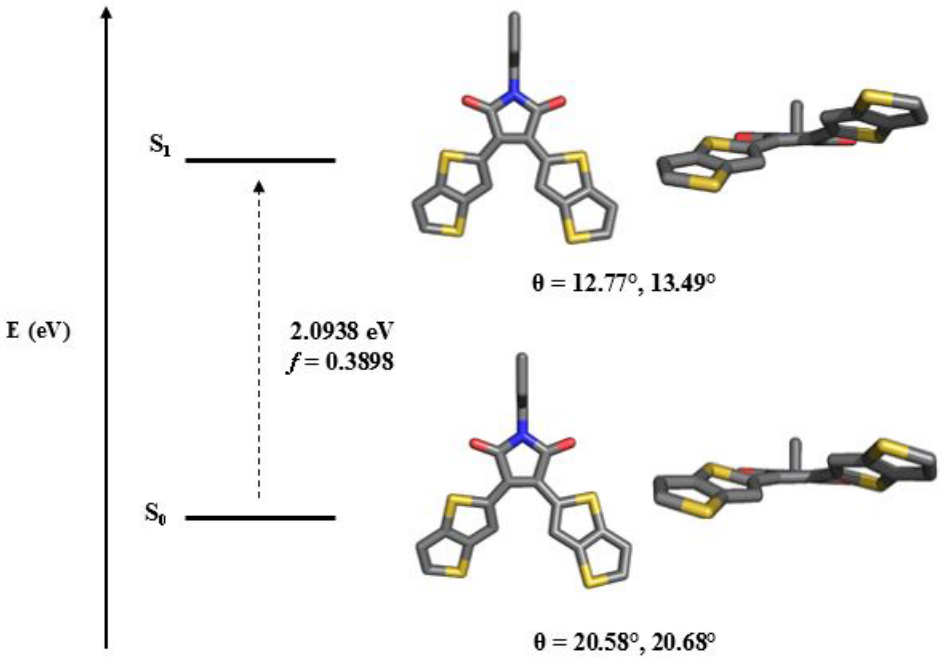


Figure S5. Compound **7** ground to excited state ($S_0 \rightarrow S_1$) transition, oscillator strength (***f***) and geometries in chloroform calculated using TD-DFT.

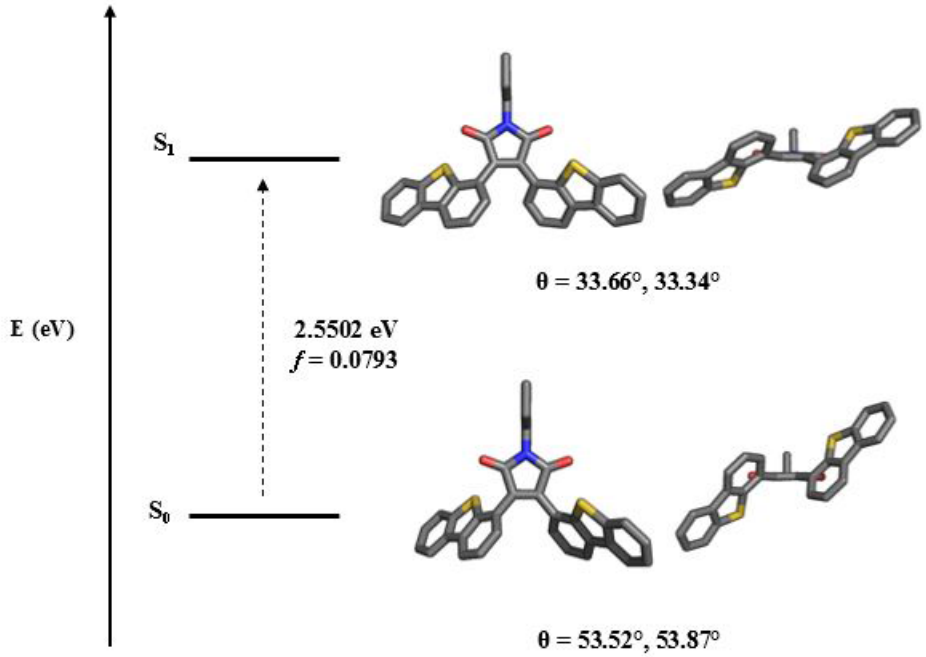


Figure S6. Compound **8** ground to excited state ($S_0 \rightarrow S_1$) transition, oscillator strength (***f***) and geometries in chloroform calculated using TD-DFT.

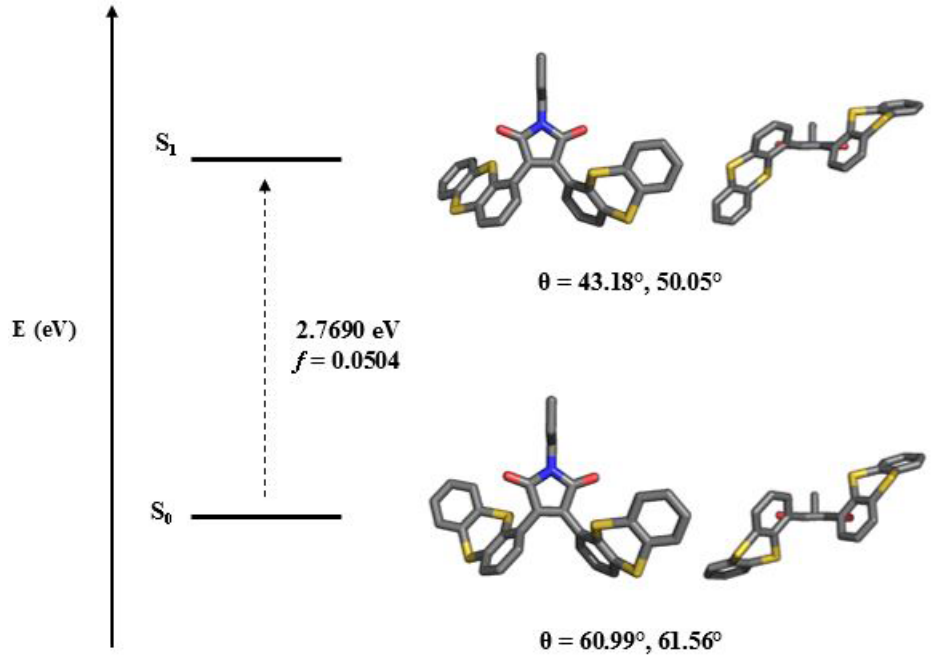


Figure S7. Compound **9** ground to excited state ($S_0 \rightarrow S_1$) transition, oscillator strength (***f***) and geometries in chloroform calculated using TD-DFT.

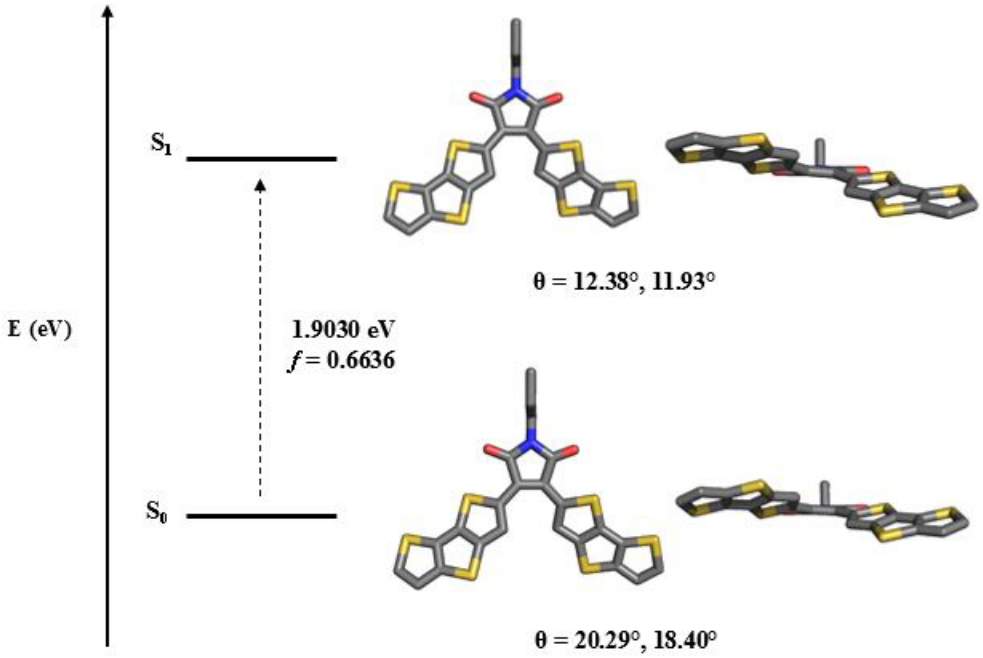


Figure S8. Compound **10** ground to excited state ($S_0 \rightarrow S_1$) transition, oscillator strength (***f***) and geometries in chloroform calculated using TD-DFT.

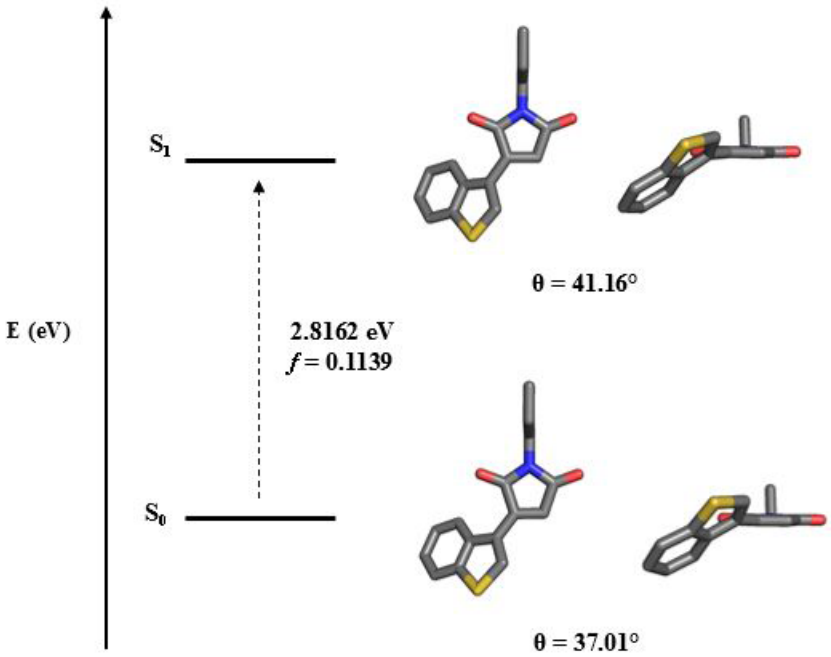


Figure S9. Compound **11** ground to excited state ($S_0 \rightarrow S_1$) transition, oscillator strength (*f*) and geometries in chloroform calculated using TD-DFT.

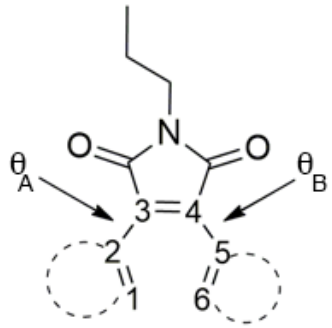
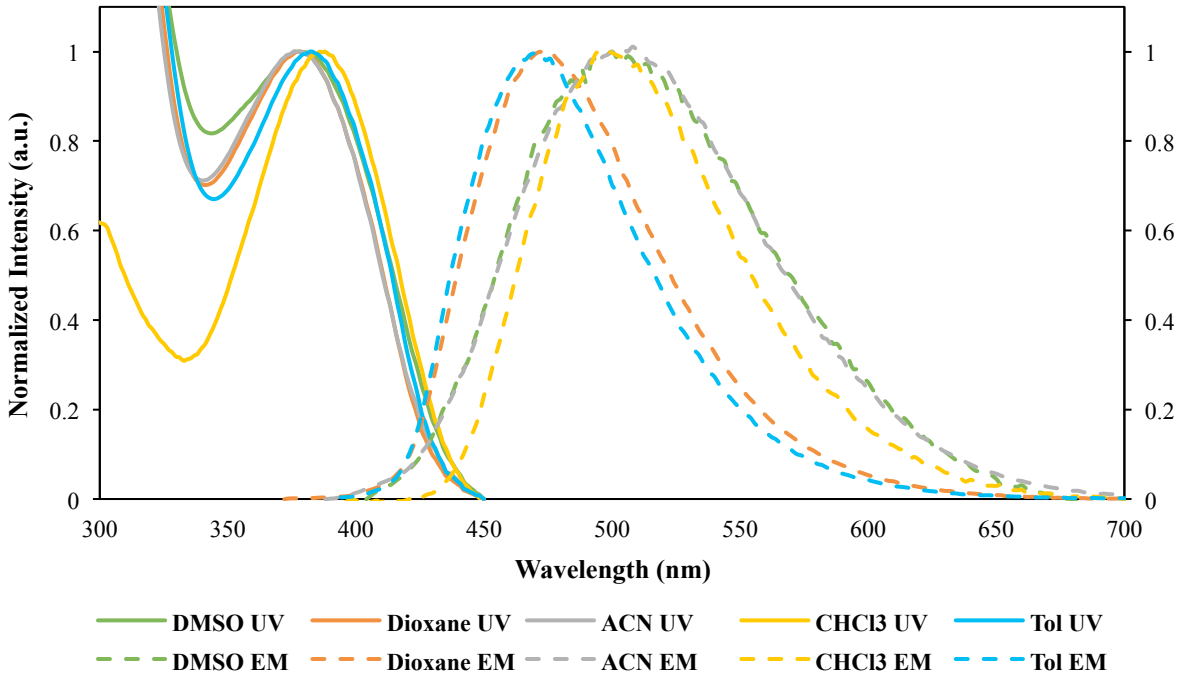


Table S3. Calculated electronic transition ($S_0 \rightarrow S_1$), oscillator strength (*f*), and torsion angles (θ_A and θ_B in degrees) of TAMs **3-11** in their S_0 and S_1 TD-DFT optimized geometries. θ_A and θ_B are defined as dihedral angles centered about C1-C2-C3-C4 and C3-C4-C5-C6, respectively.

Compound	S_0-S_1 (eV)	*f*	Ground State (S_0)			Excited State (S_1)		
			θ_A	θ_B	Avg θ	θ_A	θ_B	Avg θ
3	2.4175	0.2604	21.71	22.07	21.9	13.22	13.28	13.3
4	2.8036	0.1785	26.02	32.2	29.1	16.71	16.44	16.6
5	2.3365	0.3235	24.18	29.76	27.0	14.38	16.74	15.6
6	2.4638	0.1053	46.15	45.38	45.8	28.32	28.35	28.3
7	2.0938	0.3898	20.58	20.68	20.6	12.77	13.49	13.1
8	2.5502	0.0793	53.52	53.87	53.7	33.66	33.34	33.5
9	2.769	0.0504	60.99	61.56	61.3	43.18	50.05	46.6
10	1.903	0.6636	20.29	18.4	19.4	12.38	11.93	12.2
11	2.8162	0.1139	37.01	-	37.0	41.16	-	41.2



Photophysical properties of TAM **11** in various solvents.

		TAM 11			
Solvent	**Dipole**	λ_{max}	λ_{emm}	$\Delta\nu$	ϕ_f
DMSO	3.96	377	500	123	18
ACN	3.92	378	506	128	35
CHCl3	1.15	388	498	110	48
Dioxane	0.45	378	476	98	72
Toluene	0.31	382	472	90	79

Synthesis and Characterization

General Procedure for Bromination of N-propylmaleimide [2]

In a 3-neck RBF equipped with a magnetic stir bar was added *N*-propylmaleimide (1 equiv.) followed by the addition of chloroform (50 v/m equiv.) and cooled in an ice-bath. A solution of bromine (1.1 equiv.) in chloroform (100 v/v equiv.) was prepared and added dropwise via addition funnel over 10 minutes. The reaction was left stirring in an ice-bath until TLC showed completion (R_f 0.50, 1:9 v/v EtOAc: Hexanes). The reaction was washed with a saturated $NaHCO_3$ (3x) solution and $NaCl_{(aq)}$ (1x). The organic layer was isolated, dried over $MgSO_4$, and then vacuum filtered. The filtrate was concentrated down to dryness. The solid was purified via flash chromatography using a stationary silica phase and hexanes: EtOAc mobile gradient (9:1 to 1:1 v/v).

General Procedure for Alkylation of 2,3-dibromomaleimide [3]

In a 3-neck RBF equipped with a magnetic stir bar was added 2,3-dibromomaleimide (1 equiv.), THF (50 v/m equiv.), and *N*-methylmorpholine (1.2 equiv.). After 15 minutes of equilibration, chloro-methylformate (1.2 equiv) was added. The reaction was left stirring at room temperature until TLC (1:2 v/v EtOAc: Hexanes) showed completion (approx. 30 min). The reaction was vacuum filtered, and the filtrate was isolated. The filtrate was diluted with DCM then the solution was washed with H_2O (3x) and $NaCl_{(aq)}$ (1x). The organic layer was isolated, dried over $MgSO_4$, and then vacuum filtered. The filtrate was concentrated down to dryness. The resulting solid was transferred into a clean 3-neck RBF equipped with a magnetic stir bar and dissolved in DCM (50 v/m equiv.). The solution cooled in an ice-bath. After 15 minutes of equilibration, n-propylamine (1.1 equiv.) was added dropwise over 5 minutes. The reaction was left stirring in an ice-bath until TLC showed completion (Rf 0.56, 1:9 v/v EtOAc: Hexanes). The reaction was transferred into a separatory funnel and washed with H_2O (3x) and $NaCl_{(aq)}$ (1x). The organic layer was isolated, dried over $MgSO_4$, and then vacuum filtered. The filtrate was concentrated down to dryness. The solid was purified via flash chromatography using a stationary silica phase and hexanes: DCM mobile gradient (9:1 to 1:1 v/v).

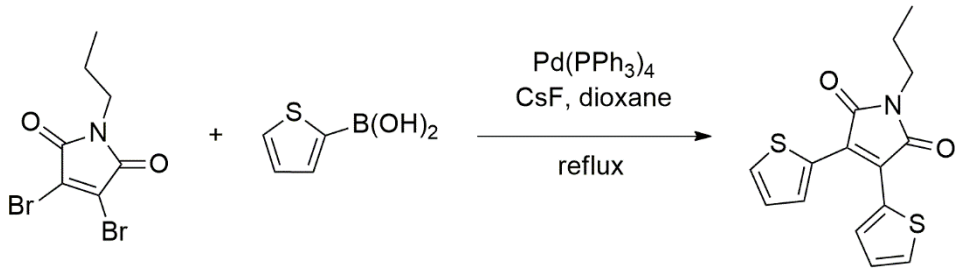
[2] A. R. Katritzky, W. Q. Fan, Q. L. Li & S. Bayyuk. Novel chromophoric heterocycles based on maleimide and naphthoquinone. *Journal of Heterocyclic Chemistry.*, 1989, 26(4), 885–892.

[3] L. Castañeda, Z. Wright, C. Marculescu, T. Tran, V. Chudasama, A. Maruani, E. Hull, J. Nunes, R. Fitzmaurice, M. Smith, L. Jones, S. Caddick and J. Baker. A mild synthesis of N-functionalized bromomaleimides, thiomaleimides and bromopyridazinediones. *Tetrahedron Lett.,* 2013, 54, 3493-3495.

General procedure for Suzuki-Miyaura Coupling [4]

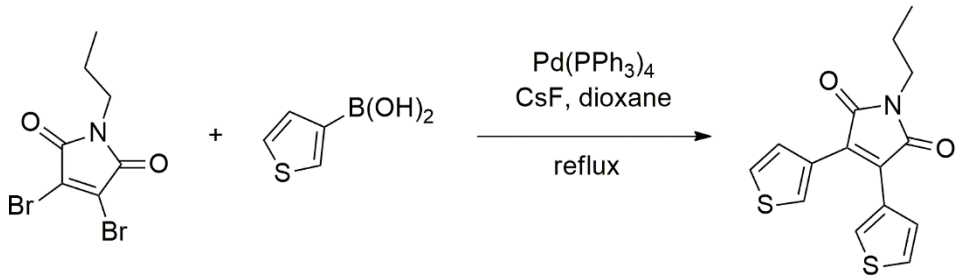
A flame-dried 3-neck RBF, fitted with a condenser, and a magnetic stir-bar was backfilled with nitrogen and charged with 2,3-dibromo-N-propylmaleimide (1 equiv.), boronic acid (2.2 equiv.), cesium fluoride (3 equiv. w.r.t. boronic acid), and $Pd(PPh_3)_4$ (0.05 equiv.). The flask was backfilled with nitrogen followed by the addition of dioxane (~ 60 v/m equiv.) via syringe through a rubber septum. Reflux is initiated and held until TLC showed completion (approx. 5 – 6 h). The crude mixture was filtered through celite, rinsed with dichloromethane, and then washed with H_2O (3x) and $NaCl_{(aq)}$ (1x). The organic layer was isolated, dried over Na_2SO_4, and then vacuum filtered. The filtrate was concentrated down to dryness. The resulting crude product was dry-loaded onto celite and purified via flash chromatography using an alumina or silica stationary phase and hexanes: DCM mobile gradient (9:1 to 1:1 v/v).

[4] M. Weimar and M. Fuchter. Synthesis of sterically encumbered C10-arylated benzo[*h*]quinolines using *ortho*-substituted aryl boronic acids. *Org. Biomol. Chem.,* 2013, 11, 31-34.



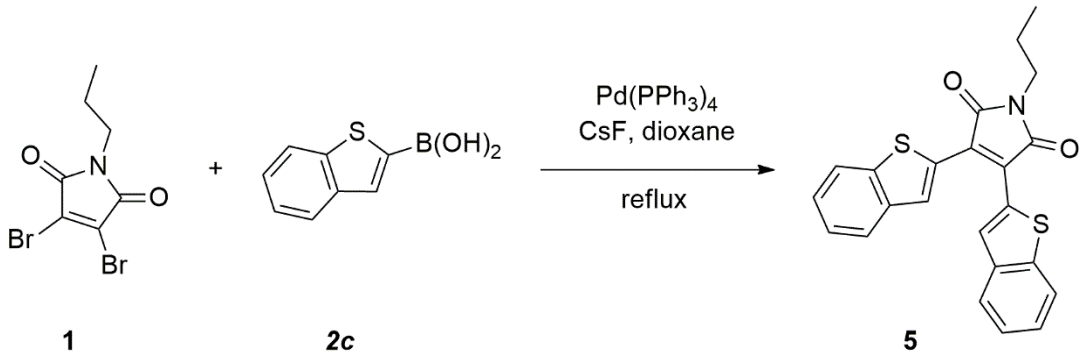
1 **2a** **3**

1-propyl-3,4-di(thiophen-2-yl)-1H-pyrrole-2,5-dione (**3**)*:* Prepared via general Suzuki-Coupling procedure using *N*-propyl-3,4-dibromomaleimide (**1**) (0.205 g, 0.690 mmol), thiophene-2-boronic acid (**2a**) (0.182 g, 1.42 mmol), cesium fluoride (0.313 g, 2.06 mmol), and $Pd(PPh_3)_4$ (0.040 g, 0.035 mmol). Purified by flash chromatography on silica gel using 9:1 Hexanes: DCM to afford thioarylmaleimide **3** as an orange solid (0.172 g, 82%). mp 124-125 ˚C; R_f 0.40 (9:1 Hex: EtOAc); IR (film, KBr) vmax/cm^{-1}: 3108 (CH), 2954 (CH), 2923 (CH), 2870 (CH), 1763 (CO), 1697 (CO), 1416 (CC), 1384 (CC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 0.8, 4.0 Hz, 2H), 7.57 (dd, *J* = 0.8, 5.2 Hz, 2H), 7.13 (dd, *J* = 4.0, 5.2 Hz, 2H), 3.60 (t, *J* = 7.2 Hz, 2H) , 1.70 (sext, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 131.4, 131.0, 129.9, 127.7, 127.6, 40.4, 22.0, 11.5; HRMS (ESI$^+$) for $C_{15}H_{14}NO_2S_2$ $[M+H]^+$: calcd. 304.0460, found 304.0449.



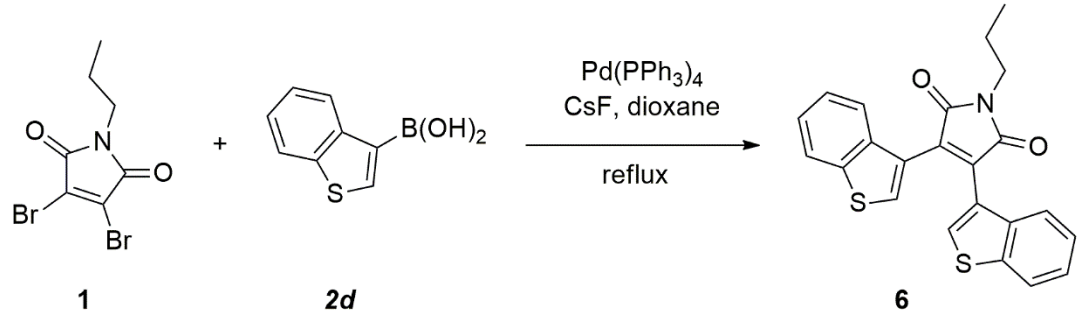
1 **2b** **4**

1-propyl-3,4-di(thiophen-3-yl)-1H-pyrrole-2,5-dione (**4**): Prepared via general Suzuki-Coupling procedure using *N*-propyl-3,4-dibromomaleimide (**1**) (0.211 g, 0.711 mmol), thiophene-3-boronic acid (**2b**) (0.200 g, 1.56 mmol) cesium fluoride (0.456 g, 3.00 mmol), and $Pd(PPh_3)_4$ (0.041 g, 0.036 mmol). Purified by flash chromatography on silica gel using 9:1 Hexanes: DCM to afford the thioarylmaleimide **4** as a yellow solid (0.181 g, 84%). mp 134-136 ˚C; R_f 0.48 (9:1 Hex: EtOAc); IR (film, KBr) vmax/cm^{-1}: 3098 (CH), 2952 (CH), 2872 (CH), 1760 (CO), 1698 (CC), 1409 (CC); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.04 (dd, *J* = 1.2, 2.8 Hz, 2H), 7.65 (dd, *J* = 2.8, 5.2 Hz, 2H), 7.14 (dd, *J* = 1.2, 5.2 Hz, 2H), 3.48 (t, *J* = 7.2 Hz, 2H), 1.59 (sext, *J* = 7.2 Hz, 2H), 0.88 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 129.5, 129.2, 129.1, 127.3, 126.8, 39.4, 21.3, 11.2; HRMS (ESI$^+$) for $C_{15}H_{14}NO_2S_2$ $[M+H]^+$: calcd. 304.0460, found 304.0447.



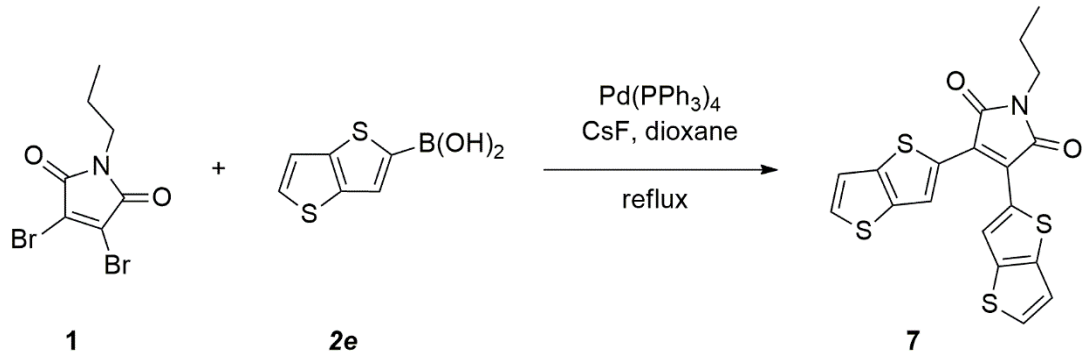
1 **2c** **5**

3,4-bis(benzo[b]thiophen-2-yl)-1-propyl-1H-pyrrole-2,5-dione (**5**): Prepared via general Suzuki-Coupling procedure using *N*-propyl-3,4-dibromomaleimide (**1**) (0.100 g, 0.337 mmol), benzo[b]thiophen-3-ylboronic acid (**2c**) (0.150 g, 0.842 mmol), cesium fluoride (0.256 g, 1.69 mmol), and $Pd(PPh_3)_4$ (0.019 g, 0.016 mmol). Purified by flash chromatography on silica gel using 3:1 DCM: Hexanes to afford the desired thioarylmaleimide **5** as an orange solid (0.068 g, 50%). mp 171-172 ˚C; R_f 0.64 (5:1 Hexanes: EtOAc). IR (film, KBr) vmax/cm^{-1}: 2920 (CH), 2851 (CH), 1704 (CO), 1401 (CC); ^{1}H NMR (400 MHz, $CDCl_3$): 8.14 (s, 2H), 7.81-7.86 (m, 4H), 7.37-7.42 (m, 4H), 3.66 (t, *J* = 7.2 Hz, 2H), 1.74 (sext, *J* = 7.2 Hz, 2H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 141.9, 139.2, 129.9, 129.8, 129.7, 126.5, 125.0, 124.9, 122.4, 40.6, 22.0, 11.5; HRMS (ESI$^+$) for $C_{23}H_{17}NO_2S_2Na$ $[M+Na]^+$: calcd. 426.0593, found 426.0578.



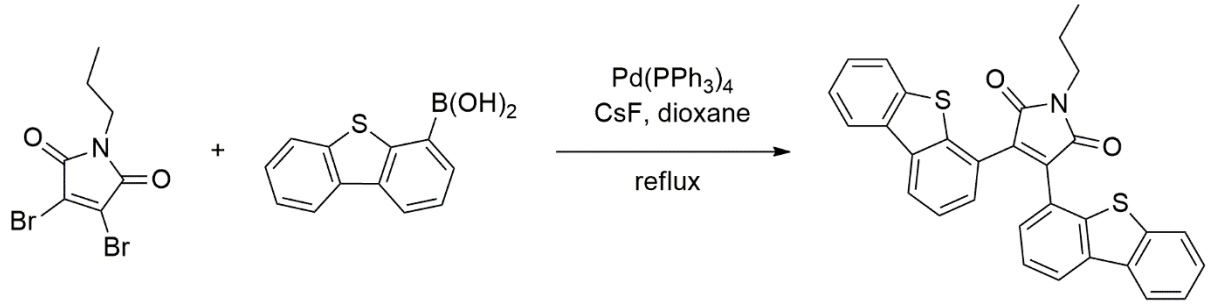
1 **2d** **6**

3,4-bis(benzo[b]thiophen-3-yl)-1-propyl-1H-pyrrole-2,5-dione (**6**): Prepared via general Suzuki-Coupling procedure using *N*-propyl-3,4-dibromomaleimide (**1**) (0.200 g, 0.674 mmol), benzo[b]thiophen-3-ylboronic acid (**2d**) (0.300 g, 1.69 mmol), cesium fluoride (0.765 g, 5.04 mmol), and $Pd(PPh_3)_4$ (0.040 g, 0.035 mmol). Purified by flash chromatography on silica gel using 5:1 Hexanes: EtOAc to afford the desired thioarylmaleimide **6** as a yellow solid (0.242 g, 89%). mp 141-143 ˚C; R_f 0.54 (5:1 Hexanes: EtOAc); IR (film, KBr) vmax/cm^{-1}: 3107 (CH), 2965 (CH), 2875 (CH), 1703 (CO), 1403 (CC), 1244 (CH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.12-7.18 (m, 4H), 6.92-6.96 (m, 2H), 3.71 (t, *J* = 7.2 Hz, 2H), 1.79 (sext, *J* = 7.2 Hz, 2H), 1.02 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 139.5, 136.7, 131.7, 130.5, 125.7, 124.7, 124.3, 123.1, 122.6, 40.5, 22.2, 11.6; HRMS (ESI$^+$) for $C_{23}H_{17}NO_2S_2Na$ $[M+Na]^+$: calcd. 426.0593, found 426.0585.



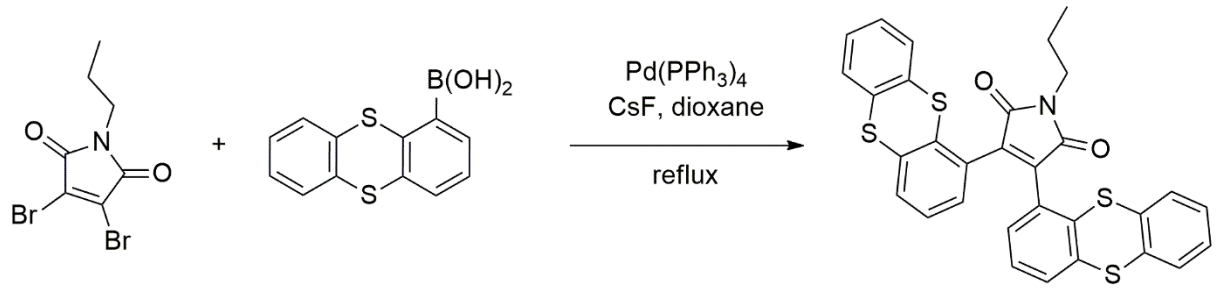
1 **2e** **7**

1-propyl-3,4-bis(thieno[3,2-b]thiophen-2-yl)-1H-pyrrole-2,5-dione (**7**)**:** Prepared via general Suzuki-Coupling procedure using *N*-propyl-3,4-dibromomaleimide (**1**) (0.115 g, 0.387 mmol), thieno[2,3-b]thiophene-2-boronic acid (**2e**) (0.150 g, 0.815 mmol), cesium fluoride (0.371 g, 2.44 mmol), and $Pd(PPh_3)_4$ (0.023 g, 0.0199 mmol). Purified by flash chromatography on silica gel using 9:1 Hexanes: DCM to afford thioarylmaleimide **7** as a red solid (0.144 g, 89%). mp 209-210 ˚C; R_f 0.30 (9:1 Hex: EtOAc); IR (film, KBr) vmax/cm^{-1}: 3120 (CH), 3071 (CH), 2936 (CH), 2873 (CH), 1753 (CO), 1693 (CO), 1384 (CC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 0.8 Hz, 2H), 7.52 (d, *J* = 5.2 Hz, 2H), 7.27 (dd, *J* = 0.4, 5.2 Hz, 2H), 3.62 (t, *J* = 7.2 Hz, 2H), 1.72 (sext, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 143.6, 139.8, 131.8, 130.9, 127.8, 124.2, 119.8, 40.5, 22.0, 11.5; HRMS (ESI$^+$) for $C_{19}H_{13}NO_2S_4Na$ [M+Na]$^+$: calcd. 437.9721, found 437.9706.



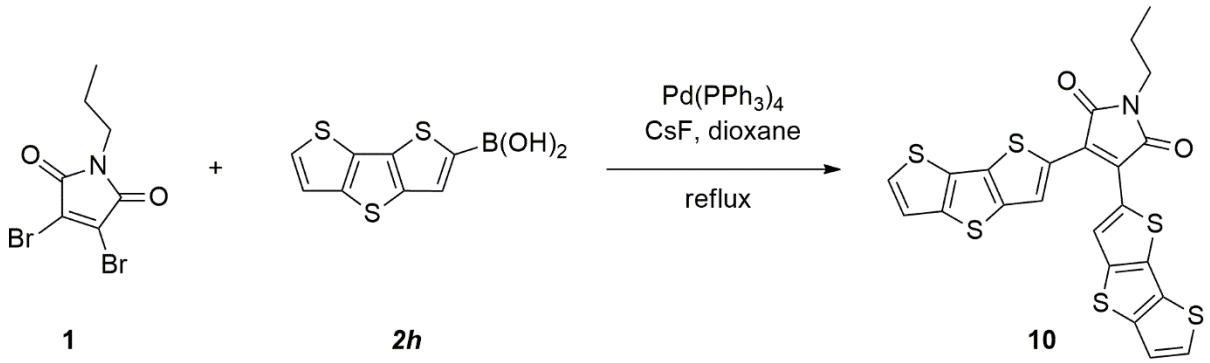
1 **2f** **8**

3,4-bis(dibenzo[b,d]thiophen-4-yl)-1-propyl-1H-pyrrole-2,5-dione (**8**)**:** Prepared via general Suzuki-Coupling procedure using *N*-propyl-3,4-dibromomaleimide (**1**) (0.267 g, 0.900 mmol), dibenzothiophene-4-boronic acid (**2f**) (0.500 g, 2.19 mmol), cesium fluoride (1.000 g, 6.58 mmol), and $Pd(PPh_3)_4$ (0.052 g, 0.045 mmol). Purified by flash chromatography on silica gel using 3:1 DCM: Hexanes to afford the desired thioarylmaleimide **8** as a yellow solid (0.380 g, 84%). mp 184–187 ˚C; R_f 0.80 (3:1 DCM: Hexanes); IR (film, KBr) vmax/cm^{-1}: 3060 (CH), 2961 (CH), 2926 (CH), 2870 (CH), 2844 (CH), 1771 (CO), 1705 (CO), 1442 (CC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, *J* = 1.2, 8.0 Hz, 2H), 8.02-8.05 (m, 2H), 7.73 (dd, *J* = 0.8, 7.6 Hz, 2H), 7.54-7.62 (m, 4H), 7.31-7.37 (m, 4H), 3.74 (t, *J* = 7.6 Hz, 2H), 1.81 (sext, *J* = 7.6 Hz, 2H), 1.04 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 139.3, 136.8, 136.4, 134.9, 129.4, 126.9, 124.6, 124.4, 124.3, 123.4, 122.5, 121.6, 40.7, 22.1, 11.6; HRMS (ESI$^+$) for $C_{31}H_{21}NO_2S_2Na$ [M+Na]$^+$: calcd. 526.0906, found 526.0903.



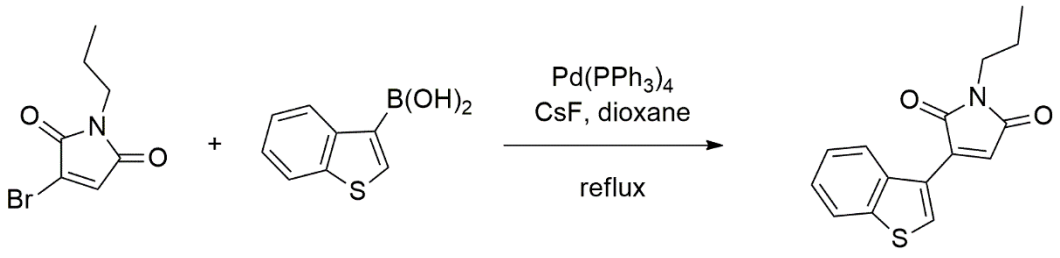
1 **2g** **9**

1-propyl-3,4-di(thianthren-1-yl)-1H-pyrrole-2,5-dione (**9**)**:** Prepared via general Suzuki-Coupling procedure using *N*-propyl-3,4-dibromomaleimide (**1**) (0.203 g, 0.684 mmol), 1-thianthrenylboronic acid (**2g**) (0.417 g, 1.60 mmol), cesium fluoride (0.780 g, 5.13 mmol), and $Pd(PPh_3)_4$ (0.040 g, 0.035 mmol). Purified by flash chromatography on silica gel using 9:1 Hexanes: DCM to afford thioarylmaleimide **9** as a yellow-orange solid (0.238 g, 61%). mp > 260 ˚C; R_f 0.13 (9:1 Hex: EtOAc); IR (film, KBr) vmax/cm^{-1}: 3054 (CH), 2964 (CH), 1768 (CO), 1705 (CO), 1399 (CC); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.55-7.61 (m, 4H), 7.23-7.36 (m, 10H), 3.63 (t, *J* = 8.0 Hz, 2H), 1.73 (sext, *J* = 7.2 Hz, 2H), 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.8, 139.2, 136.7, 135.4, 135.3, 134.5, 130.6, 130.4, 129.5, 129.4, 129.1, 129.0, 128.6, 128.2, (resonance under DMSO), 22.0, 11.7; HRMS (ESI$^+$) for $C_{31}H_{22}NO_2S_4$ $[M+H]^+$: calcd. 568.0528, found 568.0516.



1 **2h** **10**

3,4-bis(dithieno[3,2-b:2',3'-d]thiophen-2-yl)-1-propyl-1H-pyrrole-2,5-dione (**10**): Prepared via general Suzuki-Coupling procedure using *N*-propyl-3,4-dibromomaleimide (**1**) (0.0560 g, 0.189 mmol), dithieno[3,2-*b*:2',3'-*d*]thiophene-2-boronic acid (**2h**) (0.100 g, 0.416 mmol), cesium fluoride (0.190 g, 1.25 mmol), and $Pd(PPh_3)_4$ (0.011 g, 0.0095 mmol). Purified by flash chromatography on silica gel using 9:1 Hexanes: DCM to afford thioarylmaleimide **10** as a red-purple solid. (0.042 g, 42%). mp > 260 ˚C; R_f 0.28 (9:1 Hex: EtOAc); IR (film, KBr) vmax/cm^{-1}: 3060 (CH), 2923 (CH), 1757 (CO), 1696 (CO), 1638, 1384 (CC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 2H), 7.47 (d, *J* = 5.2 Hz, 2H), 7.32 (d, *J* = 5.2 Hz, 2H), 3.64 (t, *J* = 7.2 Hz, 2H), 1.73 (sext, *J* = 7.2 Hz, 2H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 153.5, 144.2, 142.1, 131.0, 130.4, 128.4, 126.9, 125.4, 121.0, 40.5, 22.0, 11.5; HRMS (ESI$^+$) for $C_{23}H_{14}NO_2S_6$ $[M+H]^+$: calcd. 527.9343, found 527.9339.



2d **11**

3-(benzo[b]thiophen-3-yl)-1-propyl-1H-pyrrole-2,5-dione (**11**): Prepared via general Suzuki-Coupling procedure using 3-bromo-*N*-propylmaleimide [5] (0.076 g, 0.35 mmol), benzo[b]thiophen-3-ylboronic acid (**2d**) (0.071 g, 0.40 mmol), cesium fluoride (0.186 g, 1.22 mmol), and $Pd(PPh_3)_4$ (0.021 g, 0.018 mmol). Purified by flash chromatography on silica gel using 9:1 Hexanes: DCM to afford thioarylmaleimide **11** as a yellow solid (0.071 g, 74.5%). mp 99.0–101.5 ˚C; R_f 0.48 (9:1 Hex: EtOAc); IR (film, KBr) vmax/cm^{-1}: 2965 (CH), 2933 (CH), 1701 (CO), 1603 (CO), 1403 (CC), 1384 (CC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.44-7.50 (m, 2H), 6.85 (s, 1H), 3.59 (t, *J* = 7.2 Hz, 2H), 1.69 (sext, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 171.3, 140.1, 137.7, 137.1, 134.4, 125.6, 125.4, 124.6, 123.5, 122.6, 121.1, 39.9, 22.1, 11.5; HRMS (ESI^+) for $C_{15}H_{14}NO_2S$ $[M+H]^+$: calcd. 272.0740, found 272.0740.

[5] M. Weimar and M. Fuchter. Synthesis of sterically encumbered C10-arylated benzo[*h*]quinolines using *ortho*-substituted aryl boronic acids. *Org. Biomol. Chem.,* 2013, **11**, 31-34.

^{1}H & ^{13}C NMR Spectra

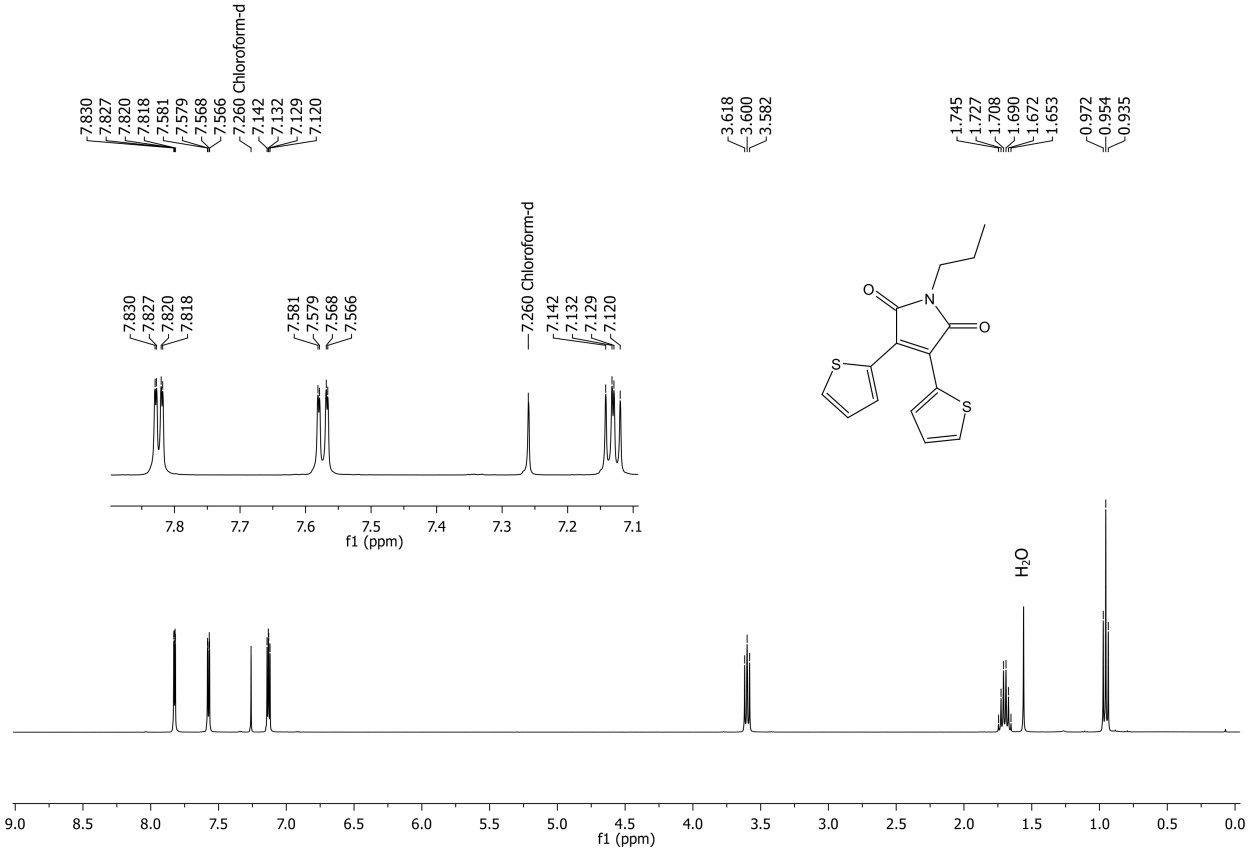


Figure S11. (400 MHz, 298 K, $CDCl_3$) ^{1}H-NMR spectra of thioarylmaleimide **3**.

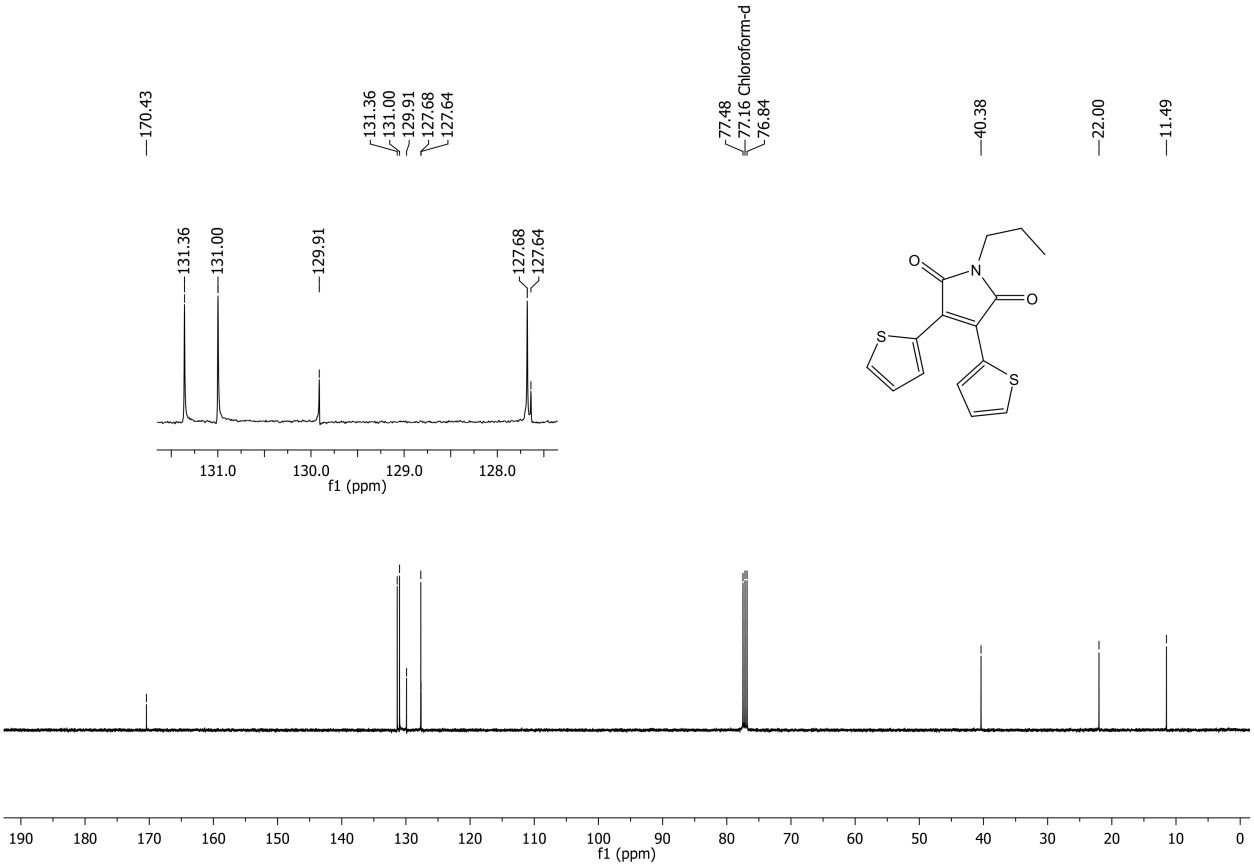


Figure S12. (100 MHz, 298 K, $CDCl_3$) ^{13}C-NMR spectra of thioarylmaleimide **3**.

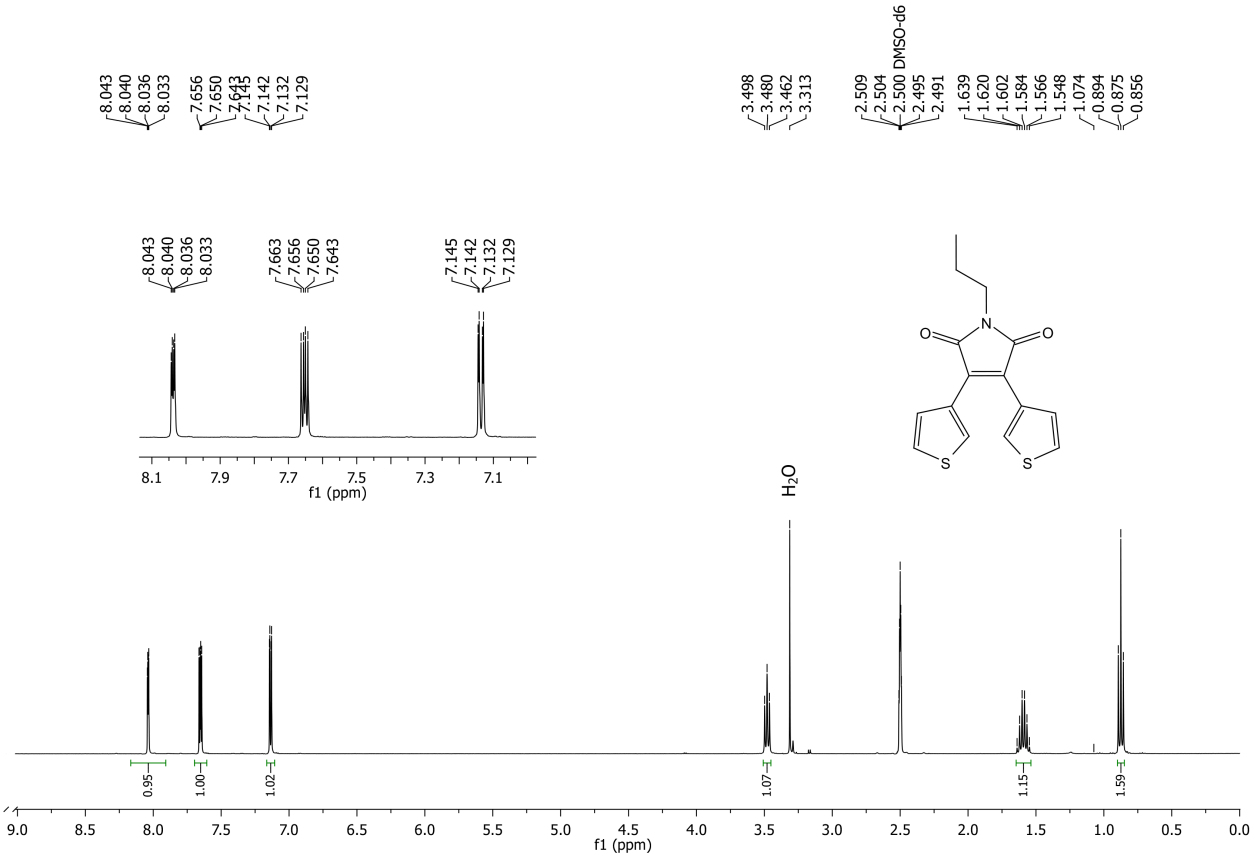


Figure S13. (400 MHz, 298 K, DMSO-d_6) ^{1}H-NMR spectra of thioarylmaleimide **4**.

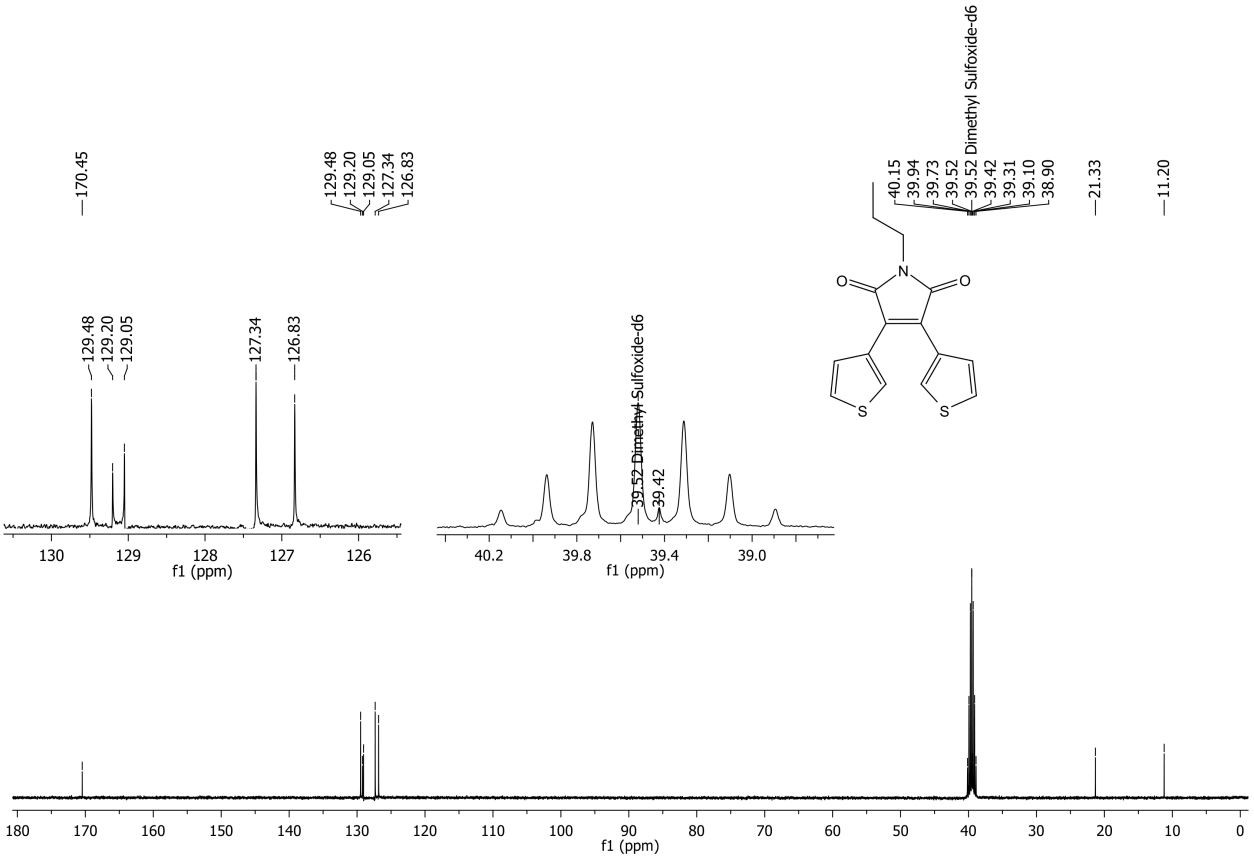


Figure S14. (100 MHz, 298 K, DMSO-d_6) ^{13}C-NMR spectra of thioarylmaleimide **4**.

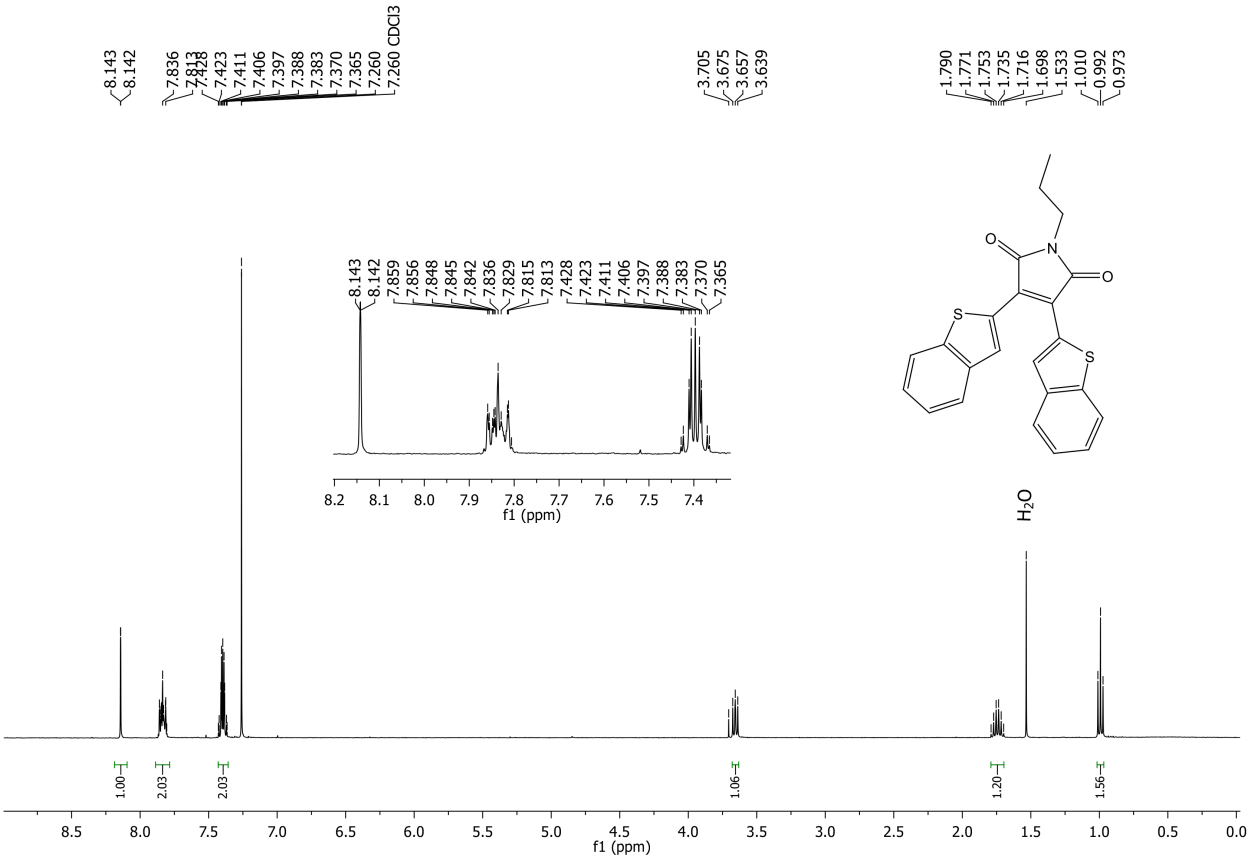


Figure S15. (400 MHz, 298 K, $CDCl_3$) ^{1}H-NMR spectra of thioarylmaleimide **5**.

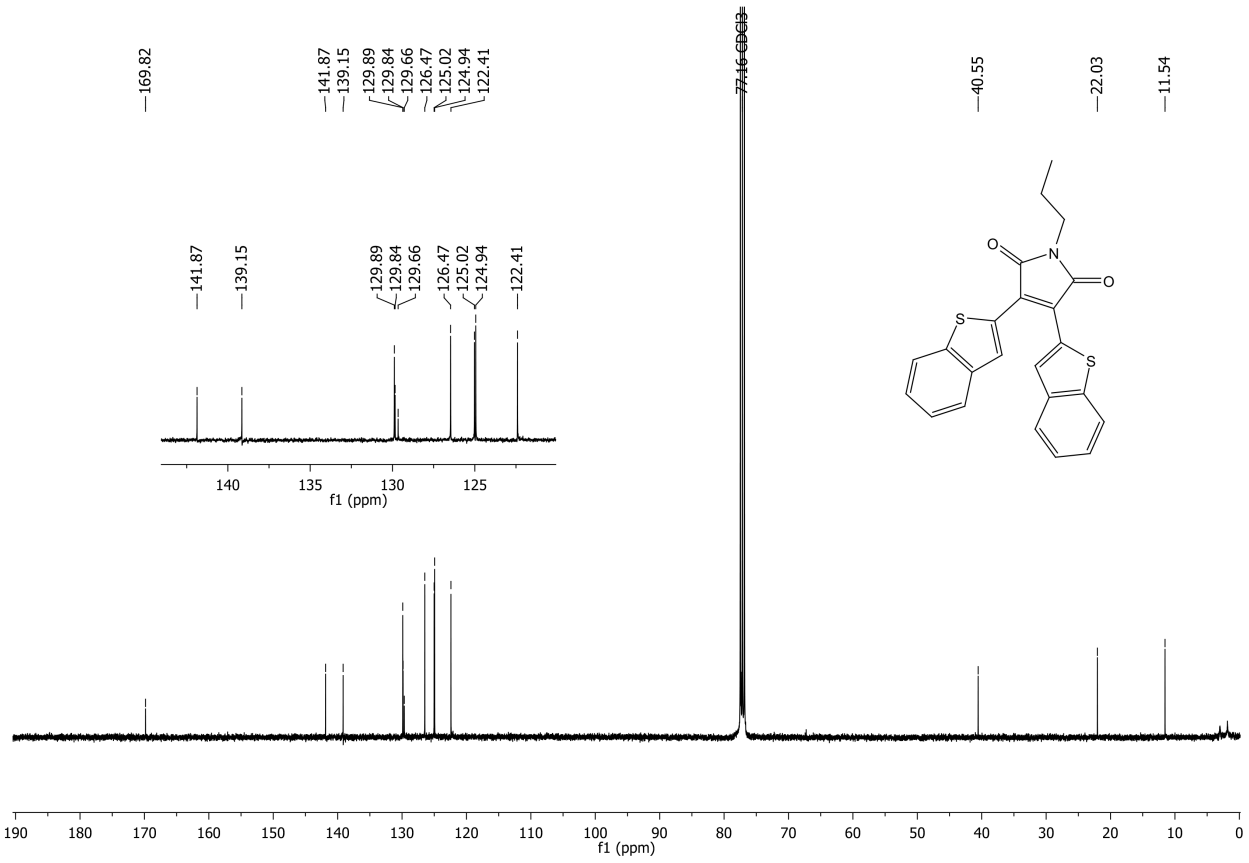


Figure S16. (100 MHz, 298 K, $CDCl_3$) ^{13}C-NMR spectra of thioarylmaleimide **5**.

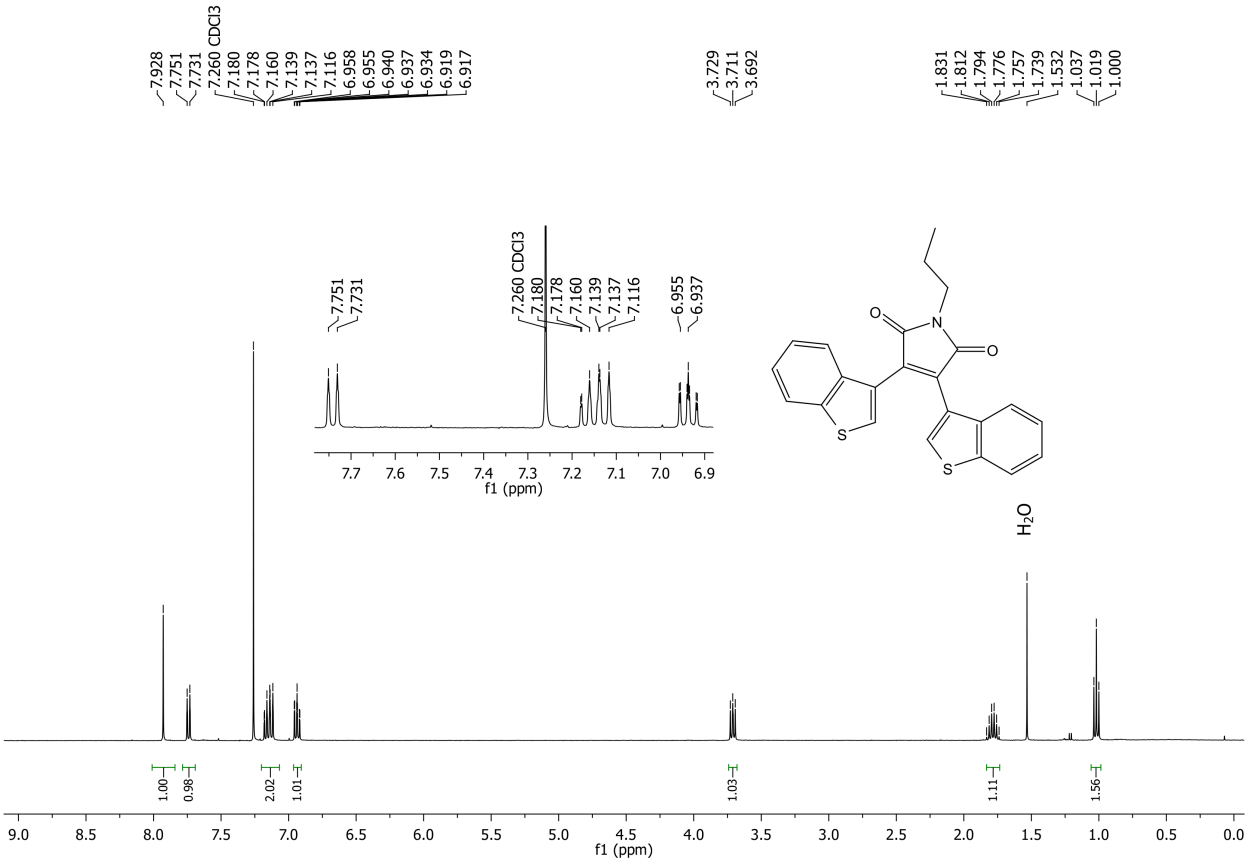


Figure S17. (400 MHz, 298 K, $CDCl_3$) ^{1}H-NMR spectra of thioarylmaleimide **6**.

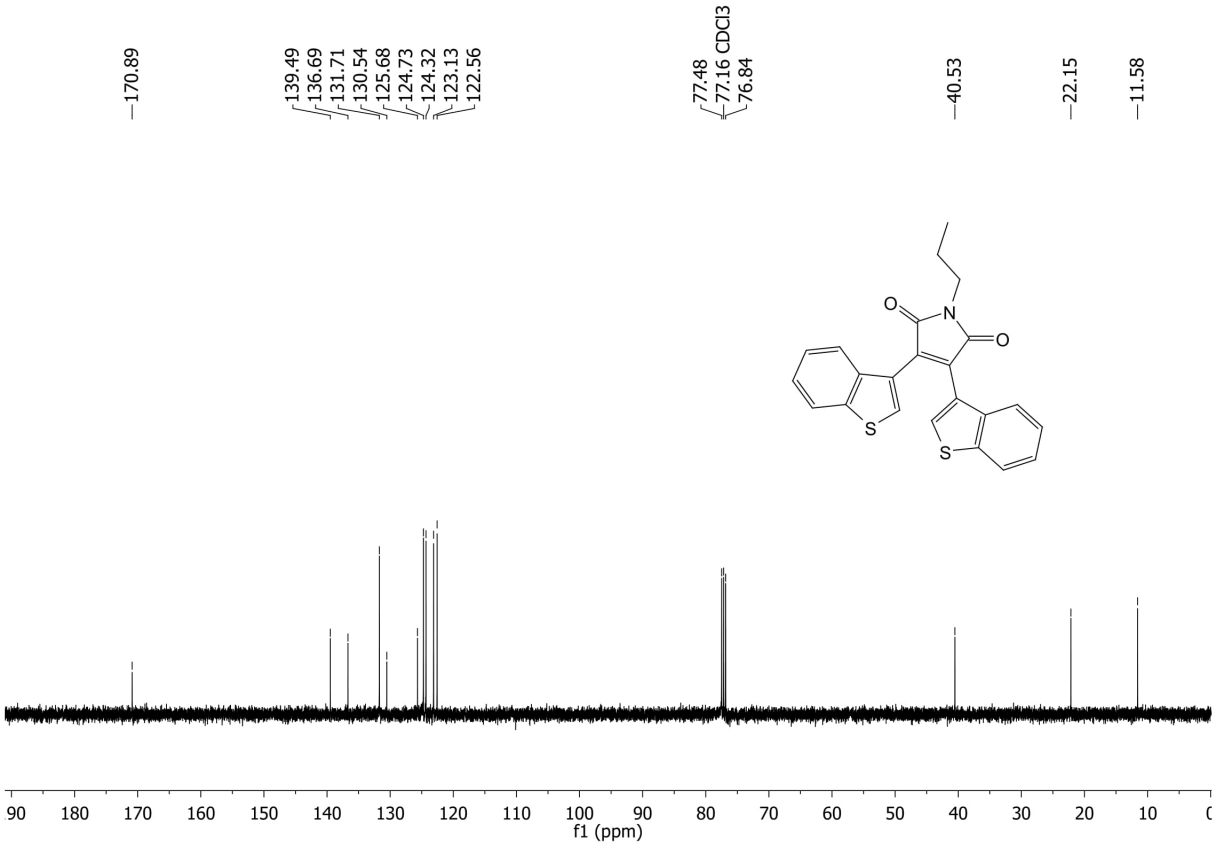


Figure S18. (100 MHz, 298 K, $CDCl_3$) ^{13}C-NMR spectra of thioarylmaleimide **6**.

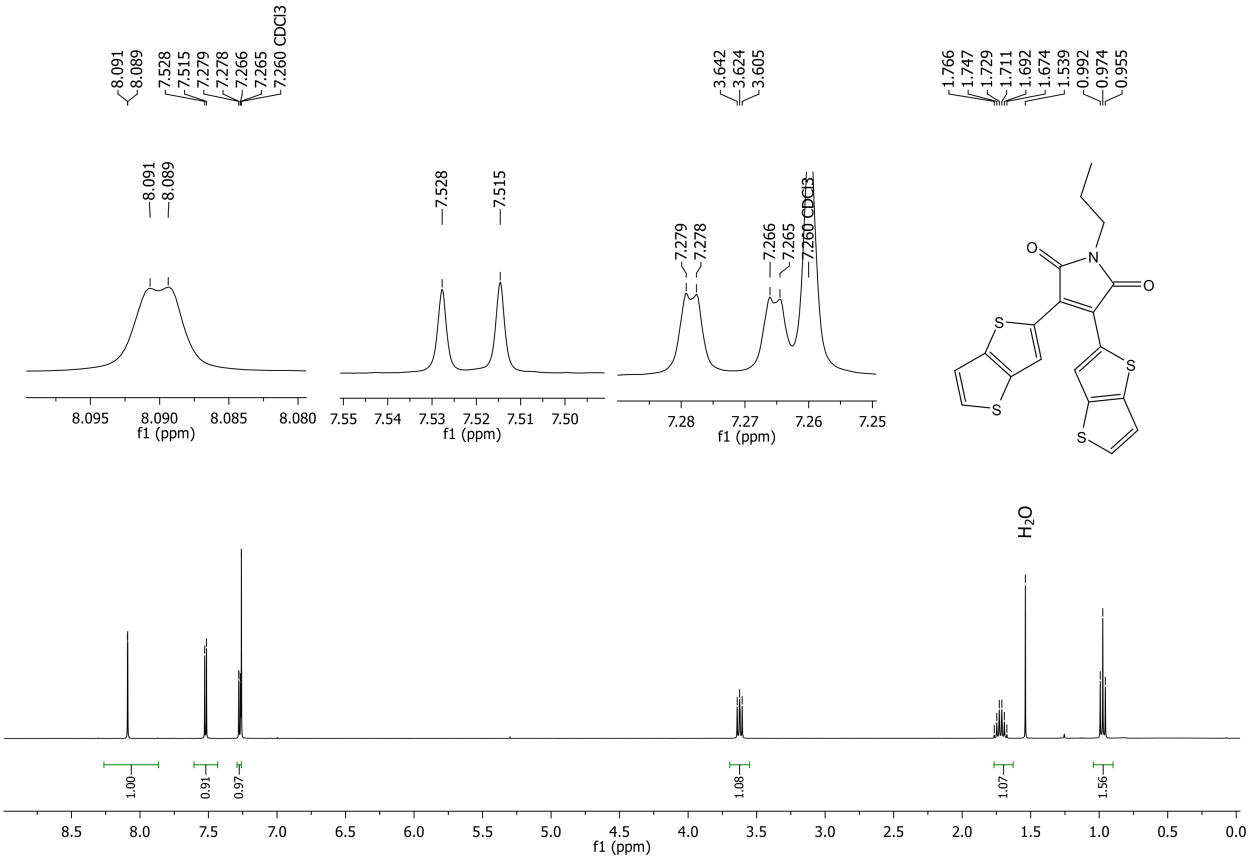


Figure S19. (400 MHz, 298 K, $CDCl_3$) ^{1}H-NMR spectra of thioarylmaleimide **7**.

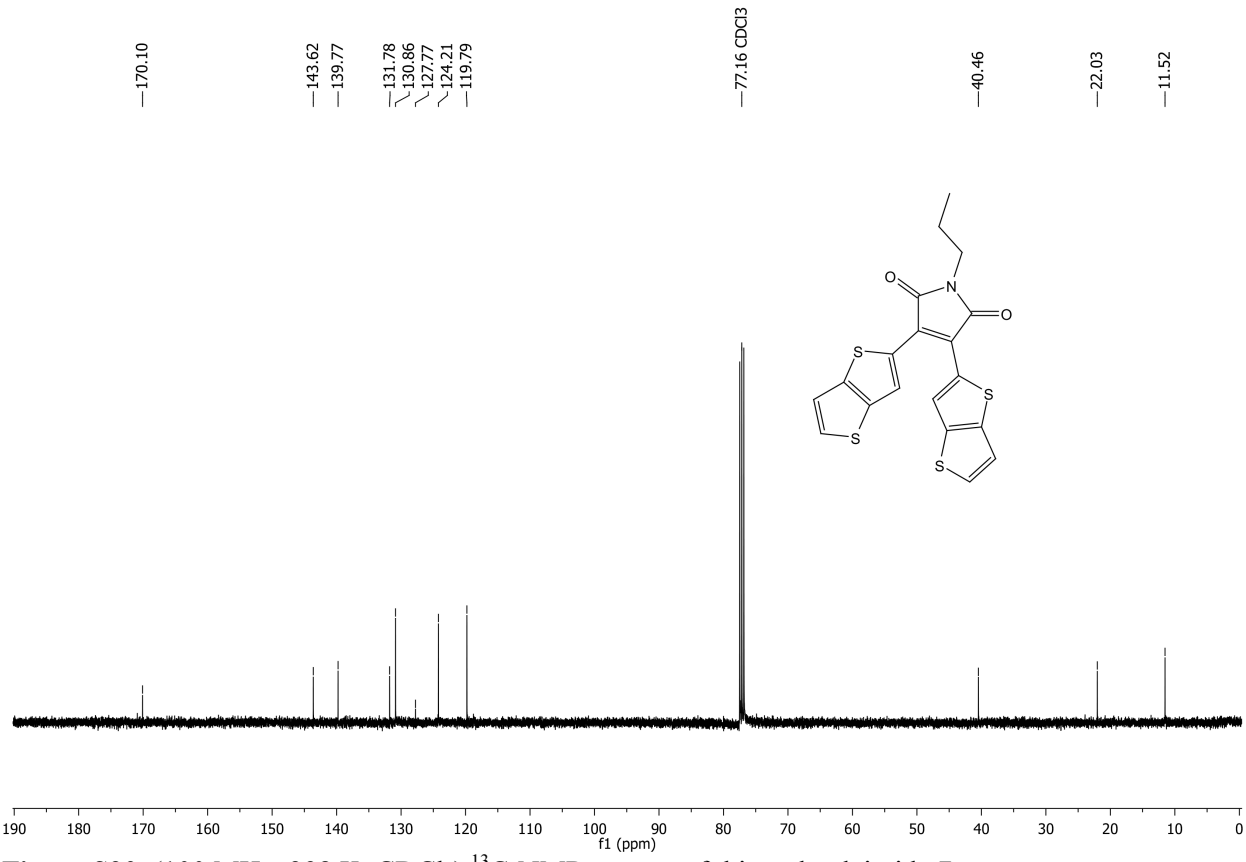


Figure S20. (100 MHz, 298 K, $CDCl_3$) ^{13}C-NMR spectra of thioarylmaleimide **7**.

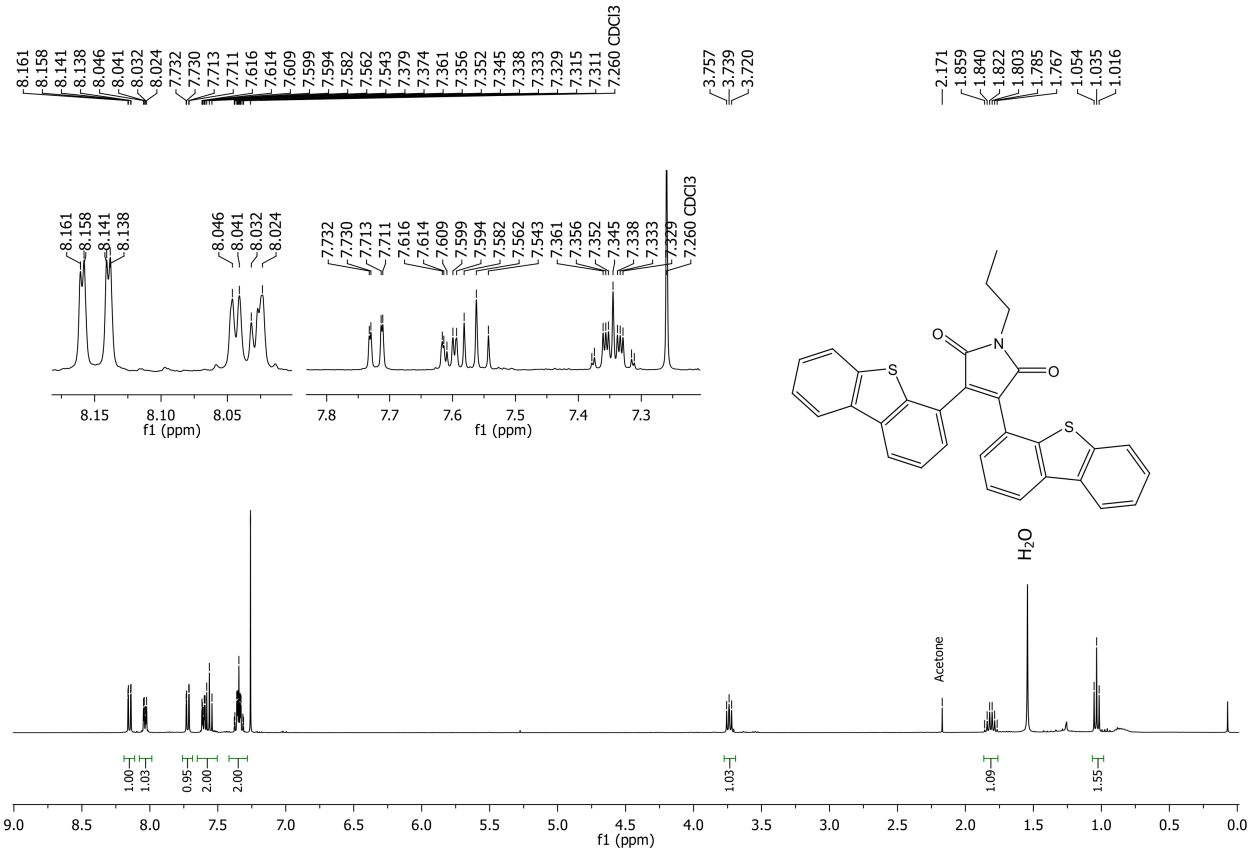


Figure S21. (400 MHz, 298 K, $CDCl_3$) ^{1}H-NMR spectra of thioarylmaleimide **8**.

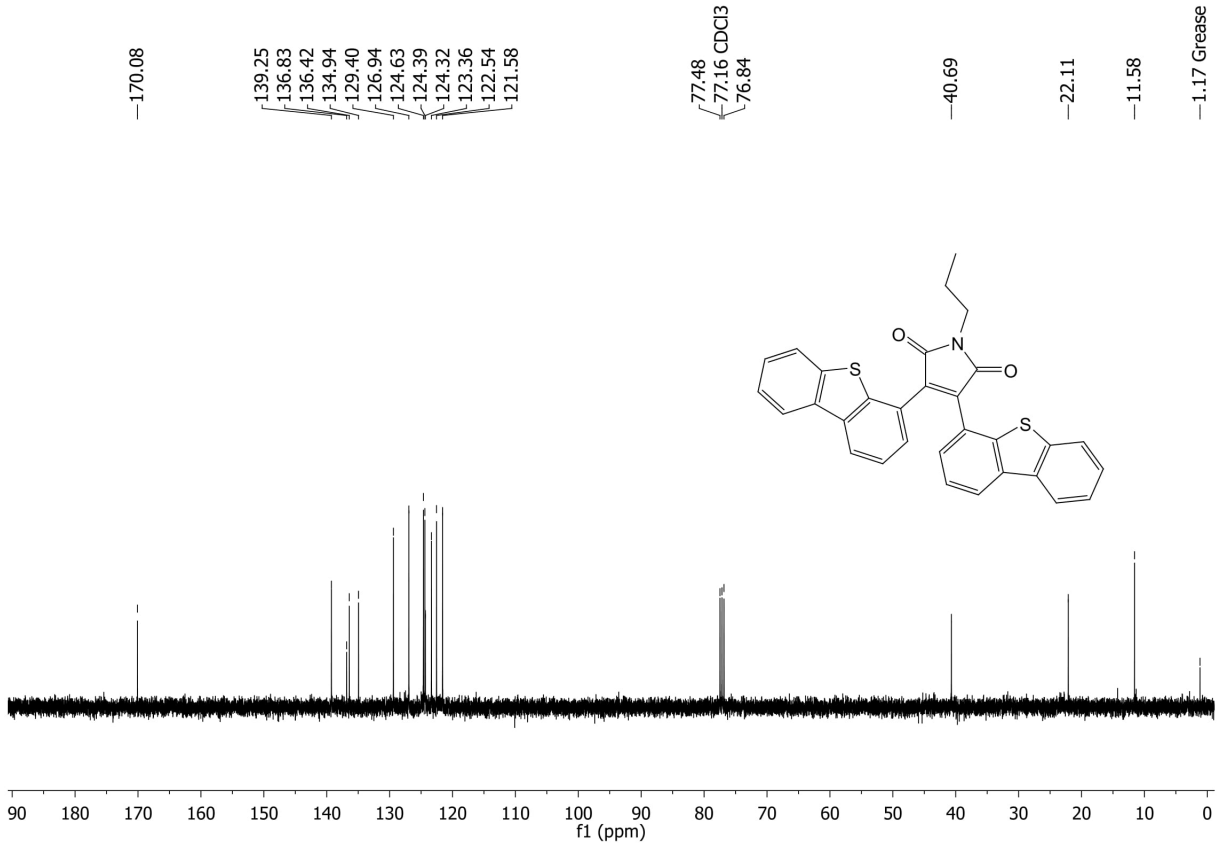


Figure S22. (100 MHz, 298 K, $CDCl_3$) ^{13}C-NMR spectra of thioarylmaleimide **8**.

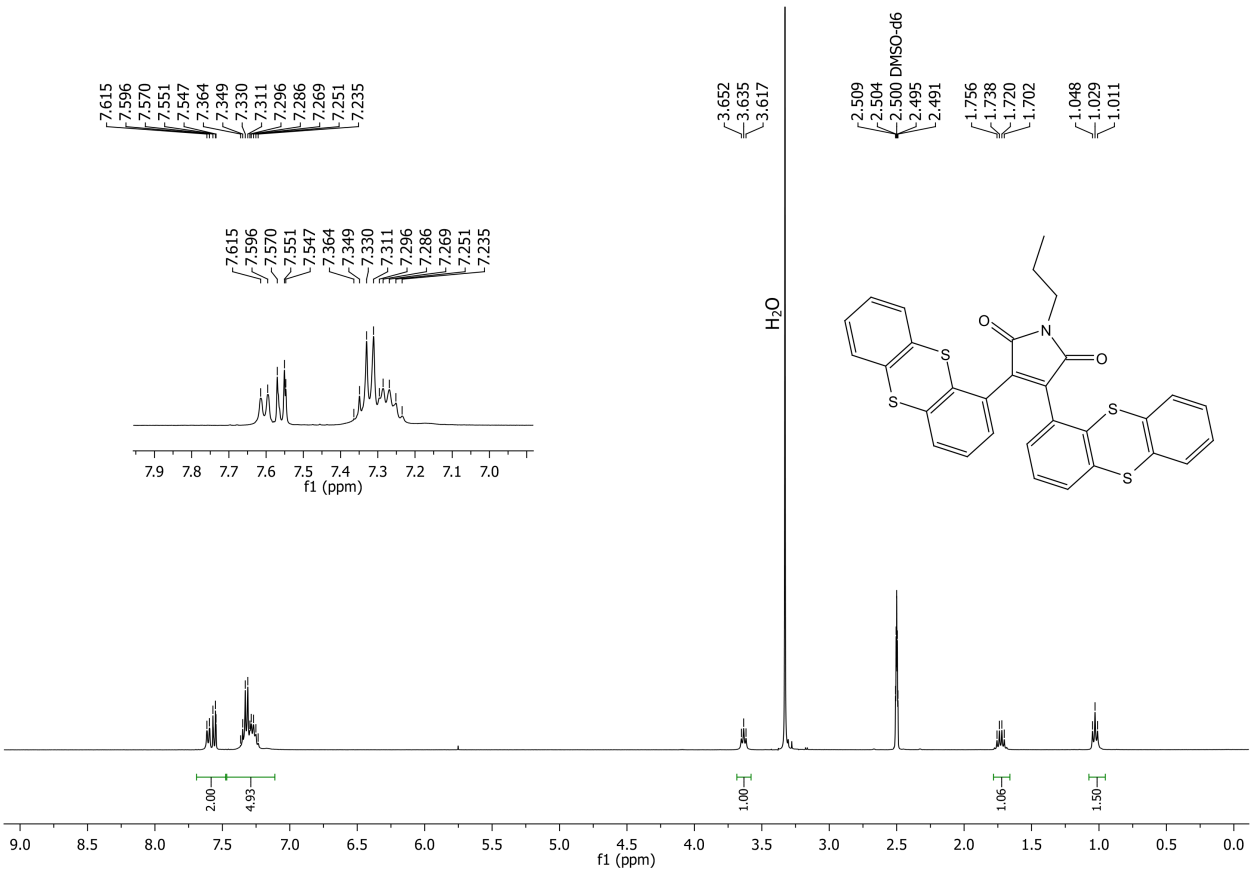


Figure S23. (400 MHz, 298 K, DMSO-d_6) ^{1}H-NMR spectra of thioarylmaleimide **9**.

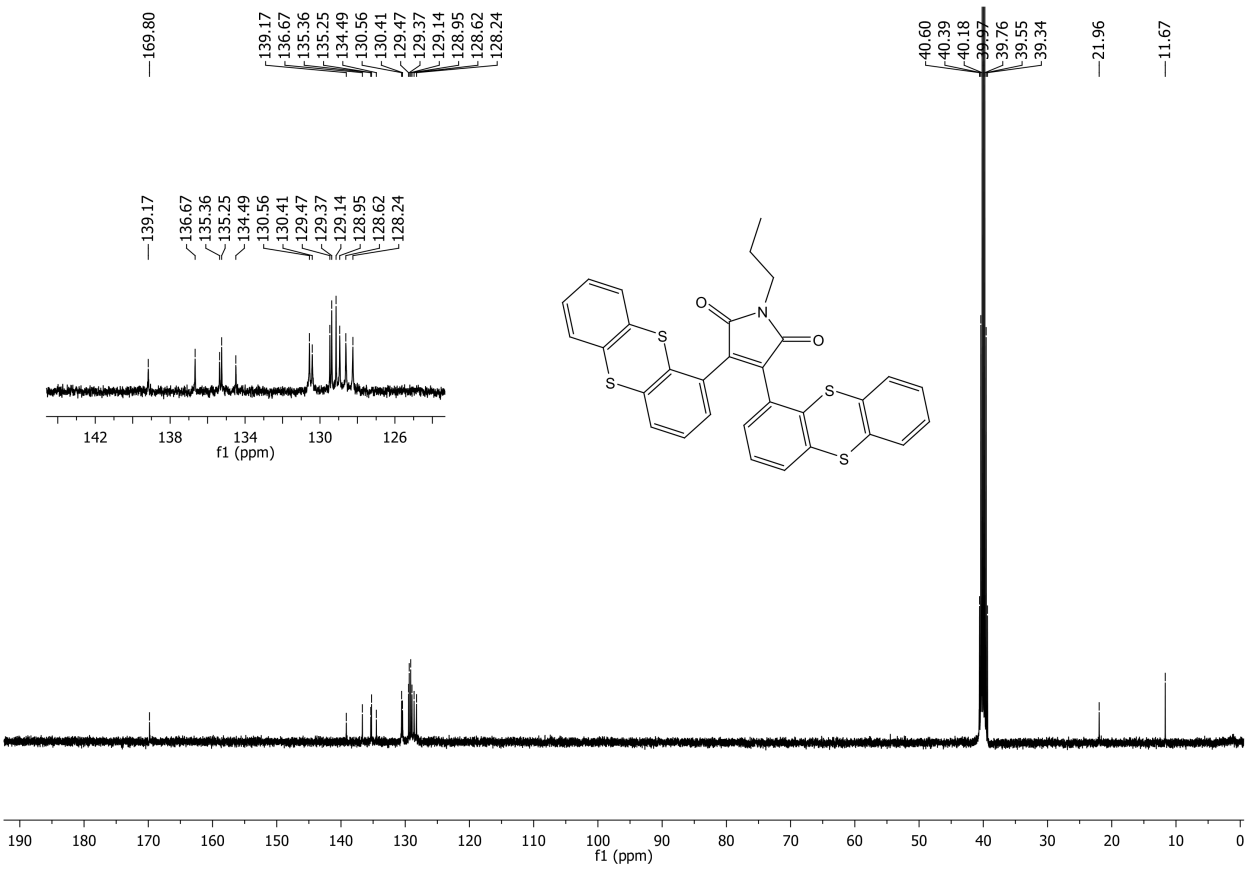


Figure S24. (100 MHz, 298 K, DMSO-d_6) ^{13}C-NMR spectra of thioarylmaleimide **9**.

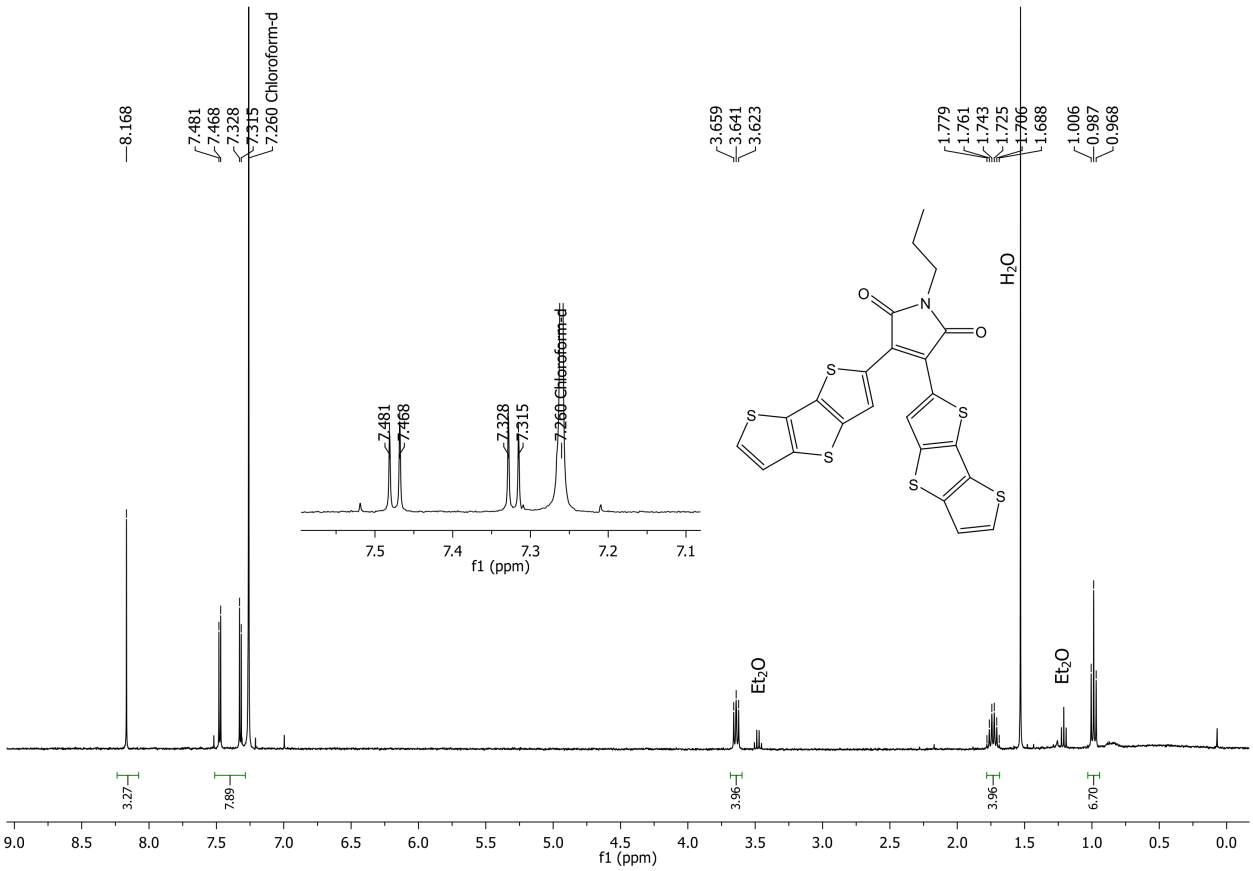


Figure S25. (400 MHz, 298 K, $CDCl_3$) ^{1}H-NMR spectra of thioarylmaleimide **10**.

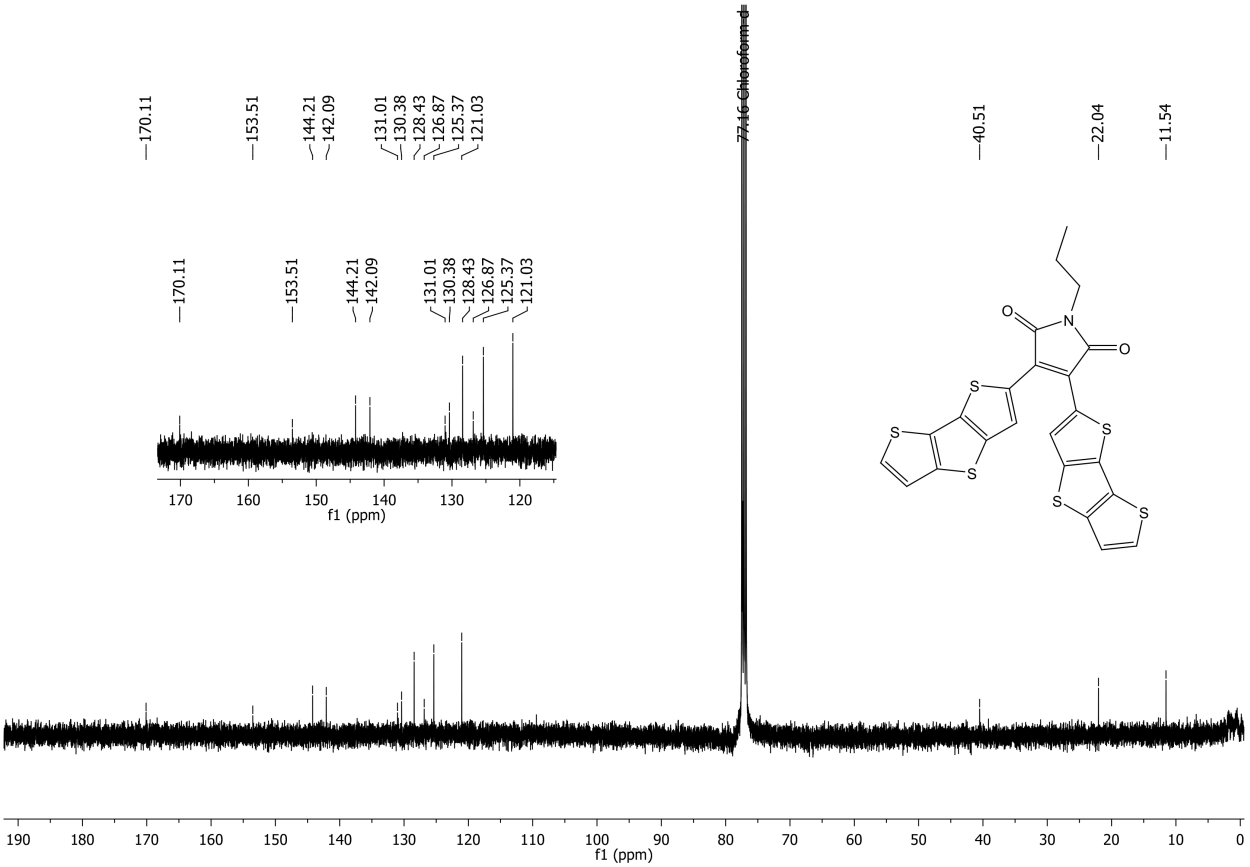


Figure S26. (100 MHz, 298 K, $CDCl_3$) ^{13}C-NMR spectra of thioarylmaleimide **10**.

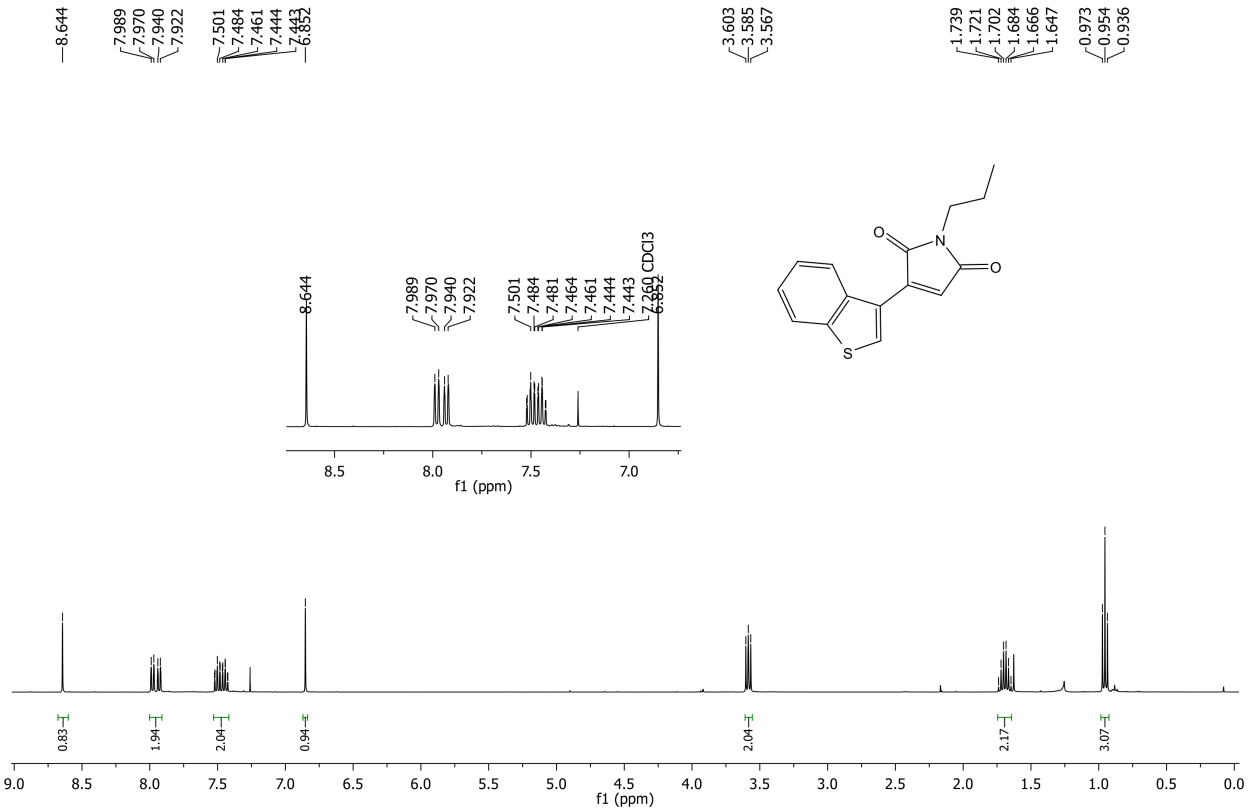


Figure S27. (400 MHz, 298 K, $CDCl_3$) ^{1}H-NMR spectra of thioarylmaleimide **11**.

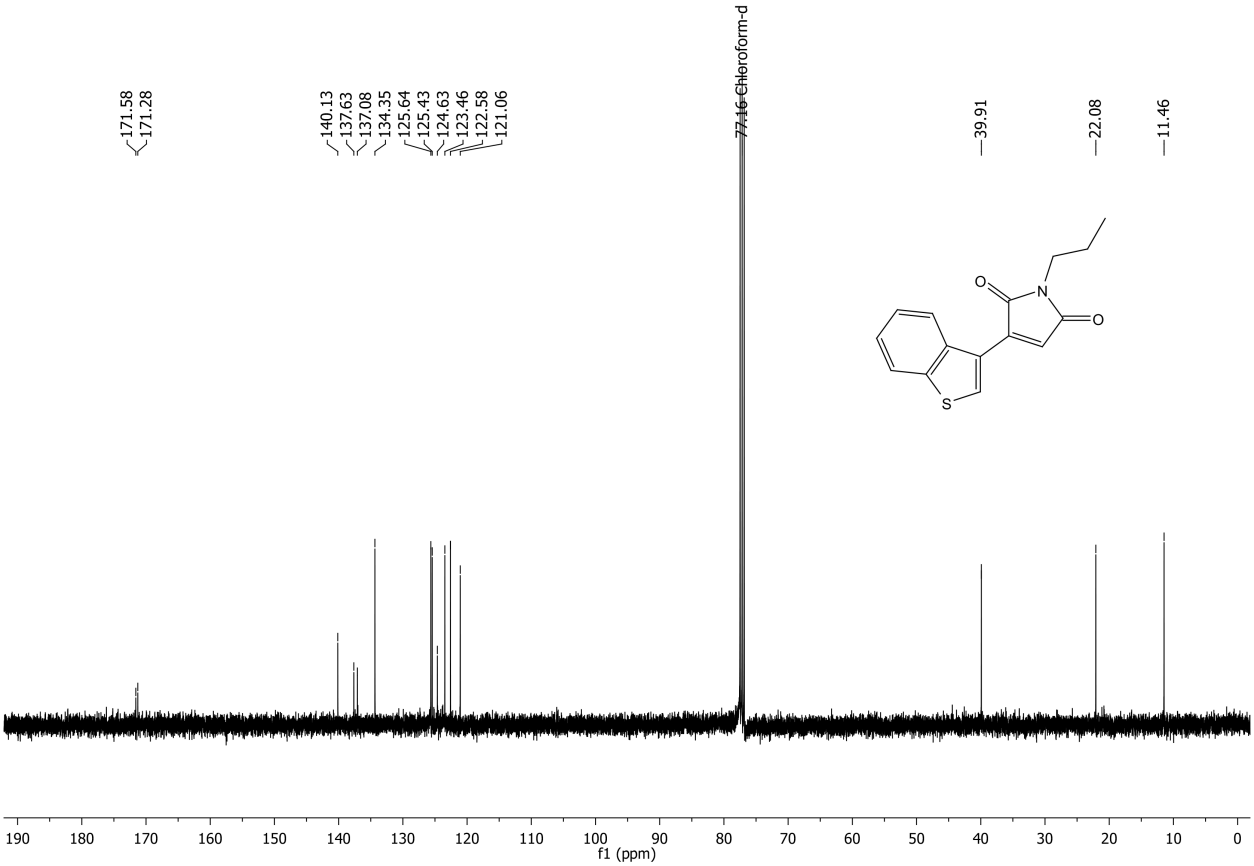


Figure S28. (100 MHz, 298 K, $CDCl_3$) ^{13}C-NMR spectra of thioarylmaleimide **11**.

Cartesian coordinates for ground-state optimized geometries

Compound 3

(ground state in $CHCl_3$, B3LYP/6-31G(d,p))

0 1

N	-2.03164	-0.02449	-0.40317
C	-1.23561	-1.15282	-0.26475
C	-1.24991	1.12111	-0.34306
O	-1.65085	-2.29901	-0.25689
O	-1.67457	2.25843	-0.45410
C	0.17780	0.68636	-0.12667
C	0.19374	-0.68807	-0.13805
C	2.65599	-3.72911	0.06874
C	2.55593	3.77784	0.24986
S	1.02198	3.34665	-0.41308
C	1.21031	1.67142	0.10698
C	3.37944	-2.65369	-0.38202
C	2.59767	-1.47667	-0.48330
C	2.41201	1.52410	0.78072
C	3.17113	2.71719	0.86597
C	-3.48323	-0.03931	-0.55869
H	-3.73634	-0.93842	-1.12714
H	-3.74686	0.83446	-1.16063
C	-4.23121	-0.01923	0.77937
H	-3.91832	-0.88622	1.37255
H	-3.93412	0.87594	1.33804
C	-5.74924	-0.03689	0.58249
H	-6.07014	-0.93590	0.04478
H	-6.08631	0.83374	0.00917
H	-6.26762	-0.02231	1.54560
S	0.99882	-3.33220	0.34160
C	1.27227	-1.65106	-0.11876
H	3.00052	-4.73962	0.24182
H	2.91150	4.79536	0.16051
H	2.72525	0.58513	1.21770
H	2.98819	-0.52953	-0.83163
H	4.43241	-2.70066	-0.63314
H	4.13137	2.78580	1.36323

Compound 4

(ground state in $CHCl_3$, B3LYP/6-31G(d,p))

0 1

N	2.25130	-0.07891	-0.40209
C	1.47681	1.07425	-0.35390
C	1.45185	-1.20539	-0.23822
O	1.91313	2.20601	-0.47386
O	1.86349	-2.35250	-0.23478
C	0.02938	-0.72312	-0.09163
C	0.04528	0.64040	-0.13140
C	-0.95590	2.90805	-0.45716
C	-2.31362	-1.49420	-0.57923
S	-3.34579	-2.85726	-0.35211
C	-2.10413	-3.71561	0.51068
C	-1.01111	1.62777	0.05828
C	-2.20835	1.42331	0.83735
C	-0.95828	-2.98373	0.60047
C	-1.06715	-1.68566	-0.01838
C	3.69948	-0.10391	-0.58008
H	3.95929	0.75788	-1.20084
H	3.93891	-1.01440	-1.13644
C	4.47026	-0.06503	0.74459
H	4.18744	0.84142	1.29238
H	4.16248	-0.91972	1.35808
C	5.98473	-0.09523	0.52327
H	6.31715	0.76302	-0.07109
H	6.29153	-1.00544	-0.00378
H	6.51948	-0.06667	1.47710
S	-2.33810	3.84578	-0.02499
C	-3.01012	2.52269	0.88433
H	-0.16764	3.33751	-1.05549
H	-2.66719	-0.63425	-1.12891
H	-2.29907	-4.70692	0.89460
H	-0.05731	-3.33471	1.08439
H	-3.95022	2.64378	1.40372
H	-2.43948	0.49887	1.34972

Compound 5

(ground state in $CHCl_3$, B3LYP/6-31G(d,p))

0 1

N	-0.93638	3.03746	-0.46573
C	-1.78198	1.93523	-0.50671
C	0.37756	2.63628	-0.26728
O	-2.98885	2.00015	-0.65654
O	1.32850	3.38946	-0.15184
C	0.38330	1.13028	-0.22957
C	-0.91639	0.70354	-0.32328
C	-1.53863	-0.59503	-0.18841
C	1.62970	0.39689	-0.17716
S	3.05695	1.07190	0.63994
C	3.99730	-0.35285	0.24590
C	-2.78728	-0.94290	-0.64741
C	-3.19562	-2.26472	-0.28276
C	3.24199	-1.27955	-0.51841
C	1.90561	-0.82427	-0.74262
H	1.18075	-1.37891	-1.32449
C	3.85481	-2.47537	-0.94740
H	3.28785	-3.19184	-1.53437
C	5.33222	-0.60241	0.58414
H	5.90341	0.11278	1.16728
C	5.91018	-1.79117	0.15283
H	6.94419	-2.00356	0.40665
C	5.17596	-2.72222	-0.60921
H	5.65352	-3.64161	-0.93333
C	-1.37990	4.42650	-0.54879
H	-2.22232	4.45276	-1.24529
H	-0.55511	4.99750	-0.98315
C	-1.78481	5.01018	0.80986
H	-2.58835	4.39665	1.23308
H	-0.93145	4.93889	1.49414
C	-2.24226	6.46606	0.68880
H	-3.10965	6.55663	0.02563
H	-1.44557	7.10093	0.28565
H	-2.52649	6.86835	1.66544
H	-3.40172	-0.25973	-1.21751
S	-0.80356	-1.91734	0.74860
C	-2.21621	-2.92868	0.49805
C	-4.39649	-2.93609	-0.58960
H	-5.15575	-2.43827	-1.18531
C	-2.41416	-4.22907	0.97067
H	-1.65834	-4.72902	1.56770
C	-4.59424	-4.22640	-0.12090
H	-5.51687	-4.74939	-0.35216
C	-3.60933	-4.86839	0.65421
H	-3.78263	-5.87906	1.01086

Compound 6

(ground state in $CHCl_3$, B3LYP/6-31G(d,p))

0 1

N	-0.13492	2.70642	-0.42307
C	-1.18925	1.82096	-0.62649
C	1.01114	2.01756	-0.03813
O	-2.30847	2.13795	-0.98568
O	2.08146	2.53558	0.22367
C	0.65106	0.55044	-0.00279
C	-0.65890	0.43480	-0.34416
C	-1.03547	-1.83388	-1.27603

C	1.26846	-1.40756	1.38951
S	2.55593	-2.51017	1.77393
C	3.61664	-1.72274	0.61280
C	-1.47537	-0.76671	-0.54218
C	-2.81541	-0.98390	-0.01581
C	2.96740	-0.63732	-0.02448
C	1.59821	-0.47533	0.44414
C	3.67532	0.08307	-1.00535
H	3.20755	0.92174	-1.50720
C	4.93241	-2.08509	0.30624
H	5.41079	-2.91978	0.80855
C	5.60874	-1.35164	-0.66128
H	6.63081	-1.61434	-0.91594
C	4.98021	-0.27543	-1.31327
H	5.52450	0.28435	-2.06758
C	-0.22484	4.15673	-0.56577
H	-0.97836	4.35470	-1.33280
H	0.74356	4.50434	-0.93606
C	-0.58693	4.86776	0.74329
H	-1.54486	4.47649	1.10561
H	0.16708	4.62126	1.49958
C	-0.67425	6.38530	0.56186
H	-1.43602	6.65392	-0.17833
H	0.28135	6.80116	0.22401
H	-0.93671	6.87664	1.50326
S	-2.18178	-3.13600	-1.38633
C	-3.32963	-2.24875	-0.39202
C	-3.60476	-0.15821	0.80741
H	-3.24034	0.81690	1.10857
C	-4.59257	-2.68853	0.01784
H	-4.96771	-3.66142	-0.28321
C	-4.85755	-0.59271	1.21716
H	-5.46532	0.04753	1.84902
C	-5.35213	-1.84953	0.82446
H	-6.33531	-2.16980	1.15502
H	-0.08340	-1.92305	-1.78066
H	0.32135	-1.50084	1.90262

Compound 7

(ground state in $CHCl_3$, B3LYP/6-31G(d,p))

0 1

N	-3.17704	-0.50834	-0.37759
C	-2.23366	-1.50138	-0.15614
C	-2.55624	0.73013	-0.46030
O	-2.49189	-2.68471	-0.01335
O	-3.13291	1.78337	-0.67317
C	-1.08005	0.51457	-0.24838
C	-0.87765	-0.84471	-0.13519
C	1.95601	-3.52979	0.23068
C	0.82782	3.94003	-0.23010
S	-0.66356	3.24089	-0.78349
C	-0.19284	1.64701	-0.13651
C	2.50919	-2.37900	-0.33358
C	1.59331	-1.32067	-0.50558
C	1.04077	1.70760	0.49473
C	1.60728	2.99800	0.44337
C	-4.61674	-0.73072	-0.47662
H	-4.76036	-1.70227	-0.95738
H	-5.01147	0.04343	-1.13986
C	-5.32493	-0.69188	0.88241
H	-4.88056	-1.45303	1.53388
H	-5.13847	0.28111	1.35179
C	-6.83101	-0.92958	0.74553
H	-7.04078	-1.90858	0.30071
H	-7.29775	-0.16751	0.11167
H	-7.32168	-0.89606	1.72258
S	0.25480	-3.33054	0.52351
C	0.31620	-1.65289	-0.07887
H	1.49342	0.85801	0.98734
H	1.83744	-0.36196	-0.94201
C	1.40818	5.23951	-0.28573
H	0.96057	6.10303	-0.76161
S	3.08916	3.72077	1.02545
C	2.62108	5.26604	0.34627
H	3.28596	6.11130	0.46003
S	4.21305	-2.60310	-0.65594
C	4.13459	-4.23414	-0.02225
H	5.03368	-4.83486	-0.00858
C	2.88691	-4.59292	0.40886
H	2.65328	-5.56332	0.82864

Compound 8

(ground state in $CHCl_3$, B3LYP/6-31G(d,p))

0 1

C	0.08382	4.45595	-0.52097
C	0.76310	5.14779	0.66644
C	0.79214	6.66900	0.49676
H	1.27890	7.14819	1.35113
H	1.34209	6.95796	-0.40569
H	-0.22057	7.07929	0.41658
H	1.78370	4.76036	0.76587
H	0.22742	4.88105	1.58478
N	0.03744	3.00240	-0.38648
C	-0.98591	2.29600	0.23833
C	-0.62398	0.82966	0.14692
C	0.57950	0.73486	-0.46545
C	1.02196	2.13120	-0.84363
O	2.02283	2.45726	-1.45312
O	-1.96370	2.79312	0.76411
H	-0.94812	4.80122	-0.62775
H	0.61750	4.67315	-1.45025
C	1.34135	-0.46697	-0.84812
C	-1.44700	-0.23173	0.75349
C	-2.79495	-0.44562	0.40790
C	-0.88251	-1.07831	1.71858
H	0.15313	-0.92590	2.00364
C	-1.63022	-2.09093	2.32834
H	-1.16406	-2.72050	3.07921
C	-2.96020	-2.29444	1.97838
H	-3.53477	-3.08610	2.44930
C	-3.55535	-1.47771	1.00656
C	0.73176	-1.45249	-1.63790
H	-0.29506	-1.30471	-1.95561
C	1.42523	-2.59997	-2.03640
H	0.92587	-3.33727	-2.65649
C	2.67694	-0.67933	-0.45717
C	2.74381	-2.80002	-1.64381
H	3.27585	-3.69508	-1.95103
C	3.38225	-1.84398	-0.84129
S	-3.71565	0.43028	-0.82168
C	-5.13488	-0.58117	-0.53009
C	-4.90719	-1.54868	0.47259
S	3.64369	0.36863	0.58863
C	5.00877	-0.75053	0.50732
C	4.72982	-1.87953	-0.29324
C	-6.36586	-0.47524	-1.18192
H	-6.52758	0.27446	-1.94974
C	-5.94801	-2.42508	0.81784
H	-5.79523	-3.17664	1.58662
C	-7.17546	-2.32520	0.17218
H	-7.98081	-3.00209	0.43955
C	-7.38306	-1.35585	-0.82222
H	-8.34670	-1.28923	-1.31781
C	6.24439	-0.58455	1.13740
H	6.44541	0.28927	1.74880
C	5.72372	-2.85749	-0.45572
H	5.53189	-3.73359	-1.06800
C	7.21423	-1.56859	0.96192
H	8.18061	-1.45756	1.44404
C	6.95549	-2.69848	0.16958
H	7.72455	-3.45407	0.04346

Compound 9

(ground state in $CHCl_3$, B3LYP/6-31G(d,p))

0 1

C	0.03239	4.00701	-0.47118
C	0.70168	4.69765	0.72270
C	0.71774	6.22018	0.56378
H	1.19703	6.69799	1.42318
H	1.26793	6.52058	-0.33482
H	-0.29838	6.62184	0.48301
H	1.72524	4.31808	0.82322
H	0.16540	4.41972	1.63728
N	0.00019	2.55272	-0.34542
C	-1.00888	1.83632	0.29252
C	-0.63395	0.37335	0.18344
C	0.57019	0.29419	-0.42236
C	0.99011	1.69399	-0.81777
O	1.96822	2.03026	-1.45634
O	-1.97429	2.32367	0.84776
H	-1.00213	4.34450	-0.57863
H	0.56667	4.23431	-1.39768
C	5.56871	1.35772	0.68100
C	-5.60662	1.36359	-1.08978
C	-5.04069	0.13492	-0.73228
C	-6.95434	1.61230	-0.83068
H	-7.39140	2.56097	-1.12557
C	-7.73046	0.65248	-0.17797
H	-8.77589	0.84901	0.03781
C	-7.16054	-0.55714	0.21863
H	-7.75317	-1.29618	0.74834
C	-5.81923	-0.82865	-0.07401
C	6.92596	1.50327	0.39455
H	7.39451	2.47693	0.49651
C	7.67160	0.40547	-0.03973
H	8.72456	0.51924	-0.27724
C	4.96186	0.10162	0.57267
C	7.06164	-0.83976	-0.19039
H	7.63067	-1.69037	-0.55184
C	5.70980	-1.00092	0.13344
S	-3.34163	-0.20426	-1.17008
C	-2.74575	-0.99283	0.31878
S	3.24907	-0.08502	1.04738
C	2.63473	-1.13739	-0.25997
C	-1.45195	-0.69473	0.79305
C	-3.00621	-2.65322	2.07267
H	-3.62134	-3.38974	2.57933
C	-1.70738	-2.39693	2.50799
H	-1.30334	-2.94225	3.35457
C	-0.93621	-1.42620	1.87342
H	0.06398	-1.20559	2.23073
C	1.35516	-0.89825	-0.80110
C	2.84885	-3.12253	-1.64307
H	3.44099	-3.96563	-1.98384
C	0.82183	-1.81265	-1.72164
H	-0.16771	-1.63507	-2.12896
C	1.56334	-2.91507	-2.13959
H	1.14690	-3.60449	-2.86665
S	4.97291	-2.62535	0.02581
C	3.37726	-2.24962	-0.68650
S	-5.13663	-2.42339	0.35472
C	-3.51875	-1.97044	0.96482
H	4.97815	2.21233	0.99471
H	-4.99216	2.11517	-1.57466

Compound 10

(ground state in $CHCl_3$, B3LYP/6-31G(d,p))

0 1

N	-0.01851	3.82014	-0.37170
C	-1.14581	3.01155	-0.41313
C	1.11880	3.04402	-0.20312
O	-2.28503	3.41691	-0.57526
O	2.25200	3.48446	-0.10158
C	0.68741	1.60160	-0.17797
C	-0.69315	1.58798	-0.22969
C	-3.77780	-0.81706	-0.06773
C	3.81312	-0.74794	-0.01137
S	3.36332	0.89879	0.29380
C	1.67624	0.55524	-0.17884
C	-2.69490	-1.45370	0.54758
C	-1.50820	-0.69694	0.54032
C	1.53003	-0.76786	-0.57604
C	2.73052	-1.49637	-0.48496
C	-0.03377	5.27816	-0.44860
H	-0.85339	5.55369	-1.11767
H	0.90783	5.58389	-0.91219
C	-0.20458	5.94838	0.91982
H	-1.13861	5.59608	1.37242
H	0.61197	5.62560	1.57600
C	-0.21702	7.47511	0.80732
H	-1.04250	7.82094	0.17545
H	0.71630	7.84905	0.37213
H	-0.33454	7.93805	1.79137
S	-3.34590	0.76491	-0.63323
C	-1.66600	0.53745	-0.07602
H	0.59605	-1.17305	-0.94037
H	-0.57753	-1.01568	0.98930
C	5.00262	-1.51488	0.07225
S	3.16628	-3.16774	-0.83634
C	4.82102	-2.83752	-0.33453
S	-3.11251	-3.04936	1.16860
C	-4.75968	-2.84159	0.58362
C	-4.95280	-1.61110	-0.04583
S	-6.59496	-1.45304	-0.60721
S	6.65248	-1.23581	0.55761
C	5.99960	-3.63115	-0.25895
H	6.06377	-4.67760	-0.52969
C	7.06020	-2.90066	0.20371
H	8.07560	-3.23634	0.36219
C	-5.92281	-3.66053	0.61953
H	-5.97639	-4.64674	1.06339
C	-6.98382	-3.04123	0.01702
H	-7.98940	-3.41959	-0.10342

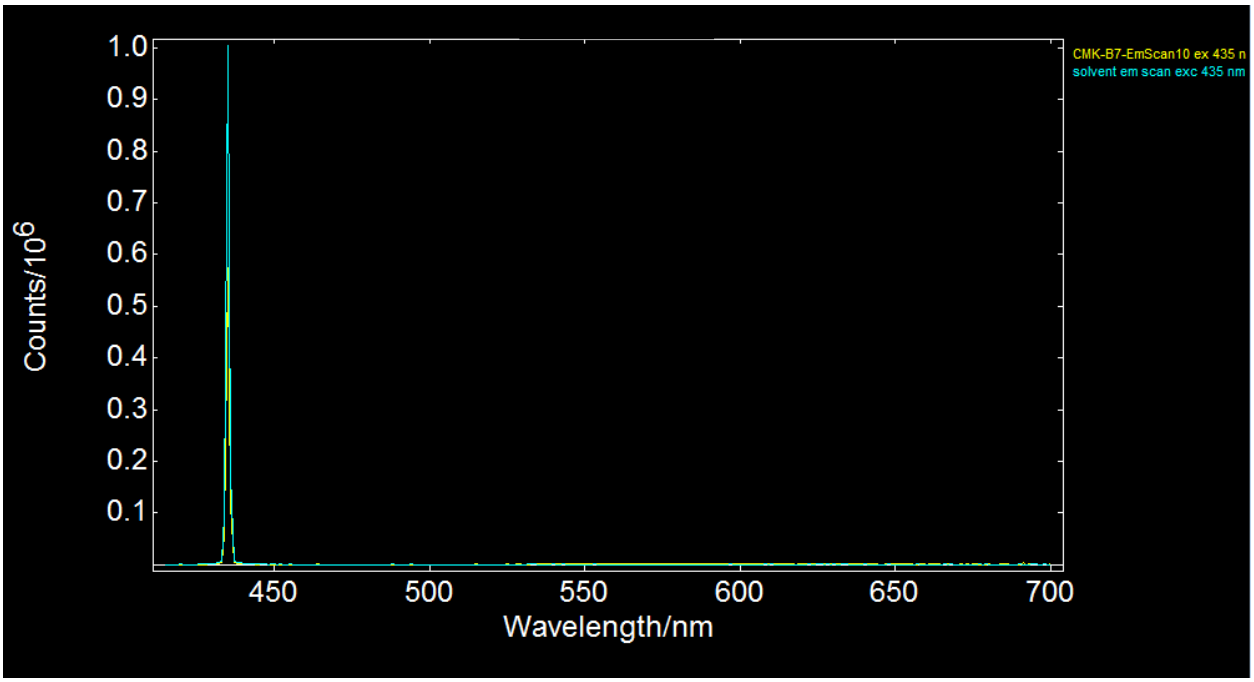


Figure S29. Spectral scans of the excitation scatter and the emission of TAM **3** and chloroform.

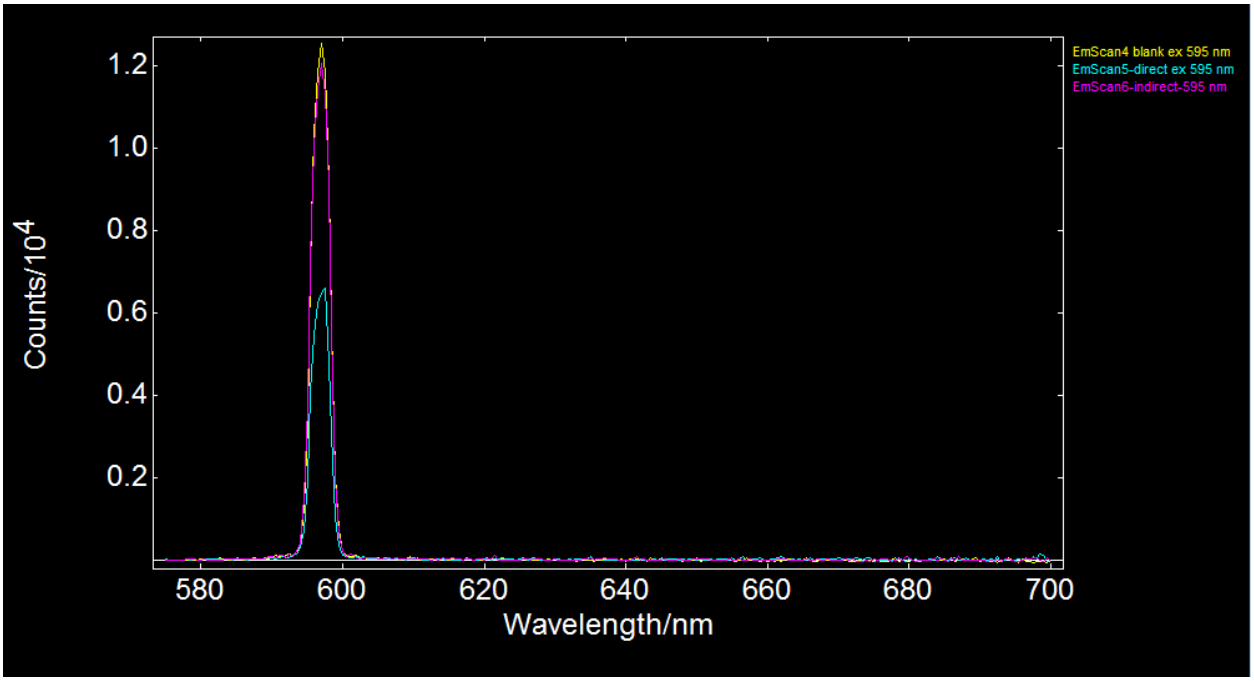


Figure S30. Spectral scans of the excitation scatter and the emission of TAM **3** powder and blank.

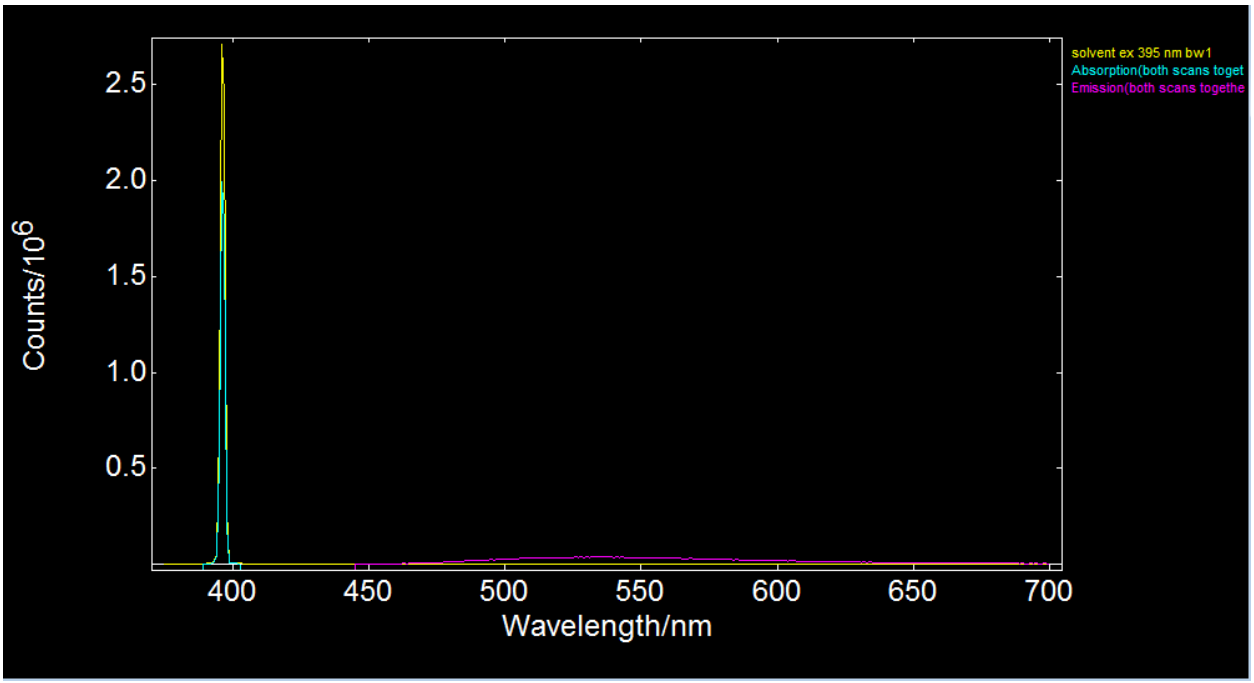


Figure S31. Spectral scans of the excitation scatter and the emission of TAM **4** and chloroform.

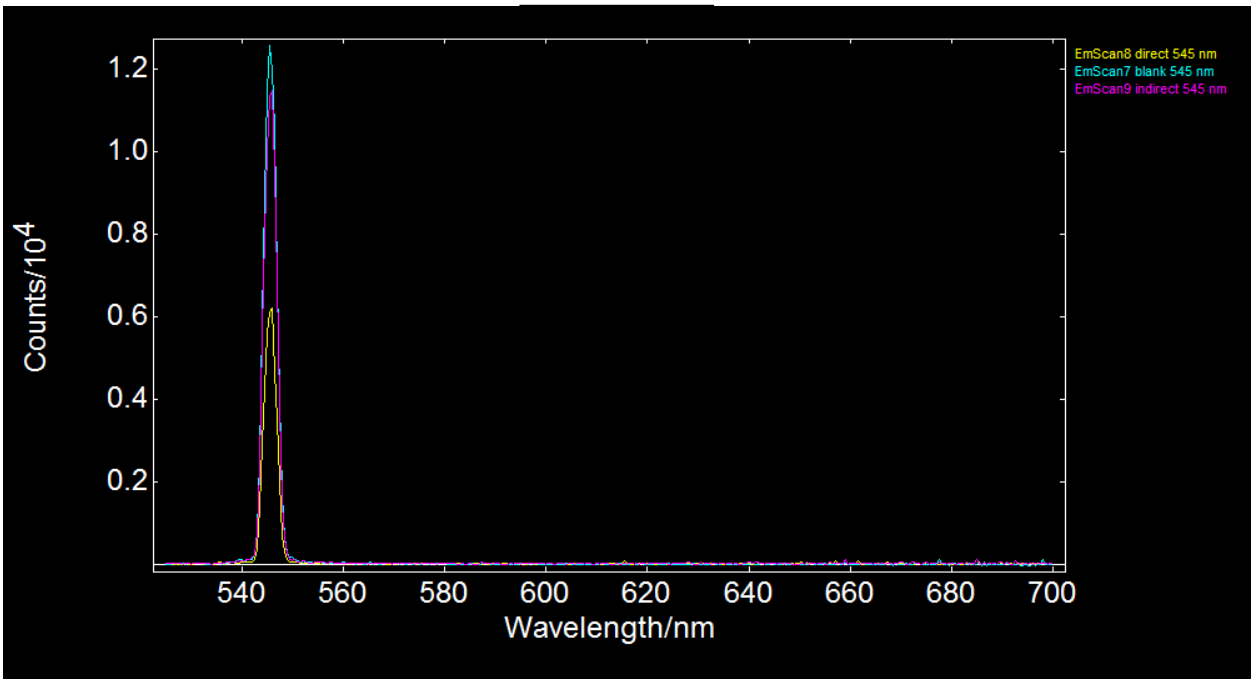


Figure S32. Spectral scans of the excitation scatter and the emission of TAM **4** powder and blank.

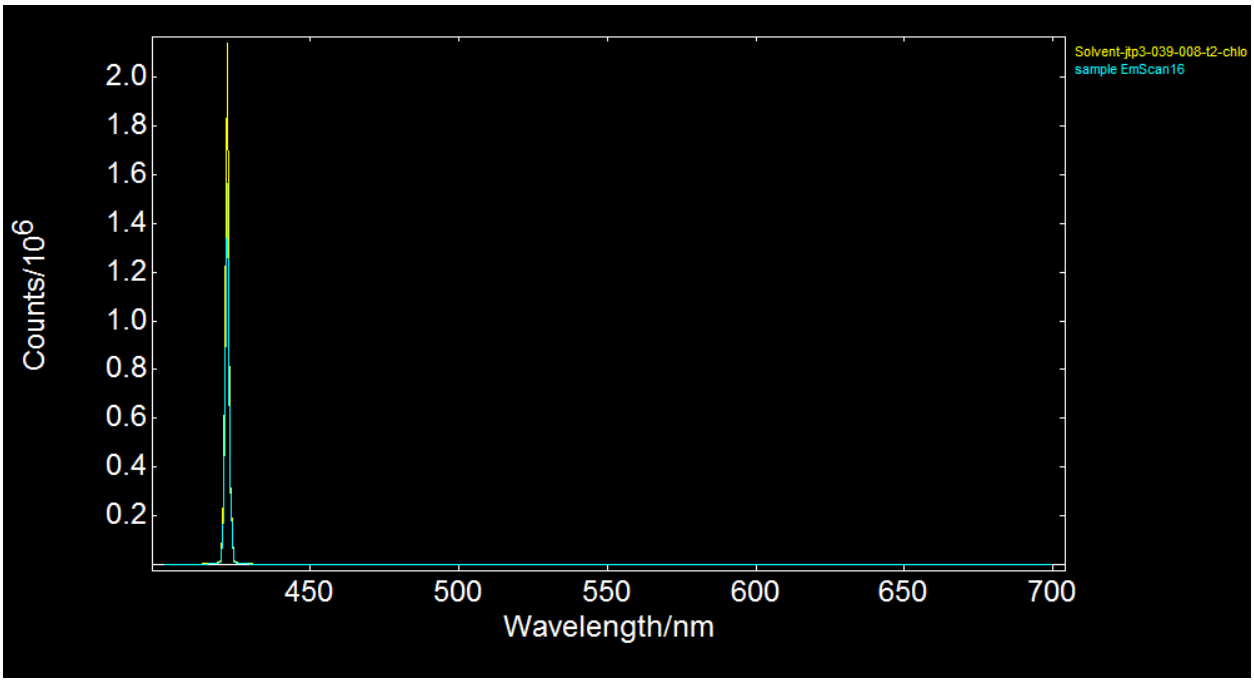


Figure S33. Spectral scans of the excitation scatter and the emission of TAM **5** and chloroform.

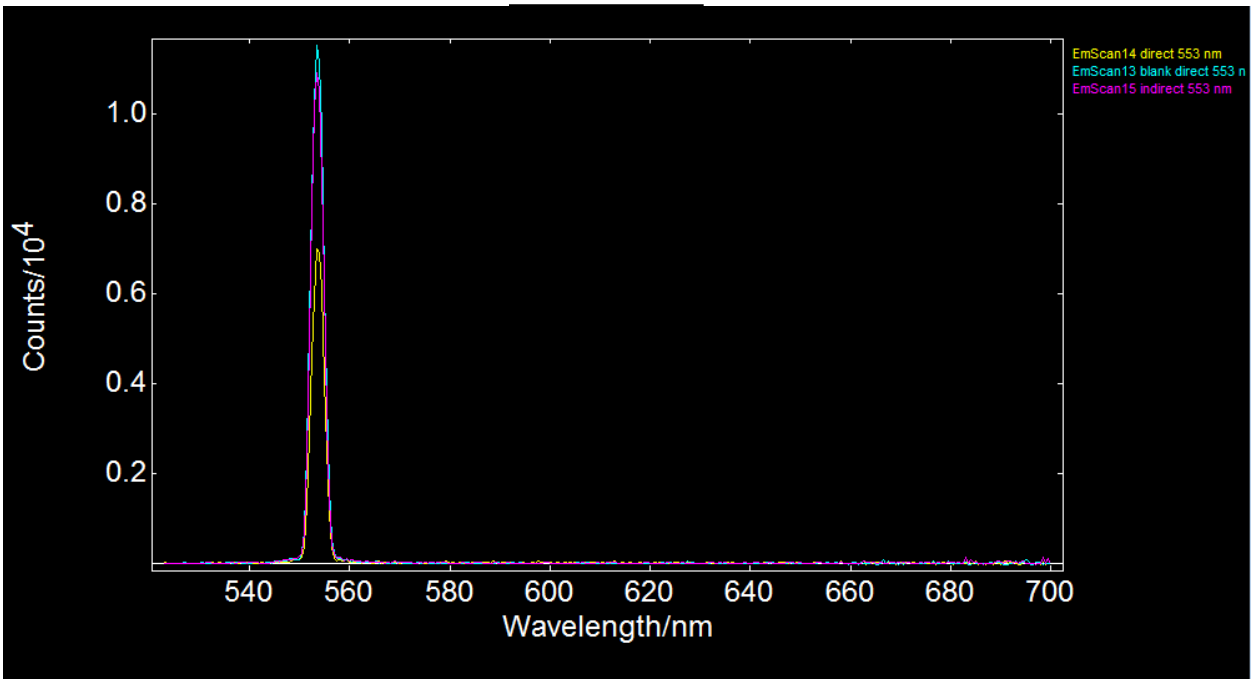


Figure S34. Spectral scans of the excitation scatter and the emission of TAM **5** powder and blank.

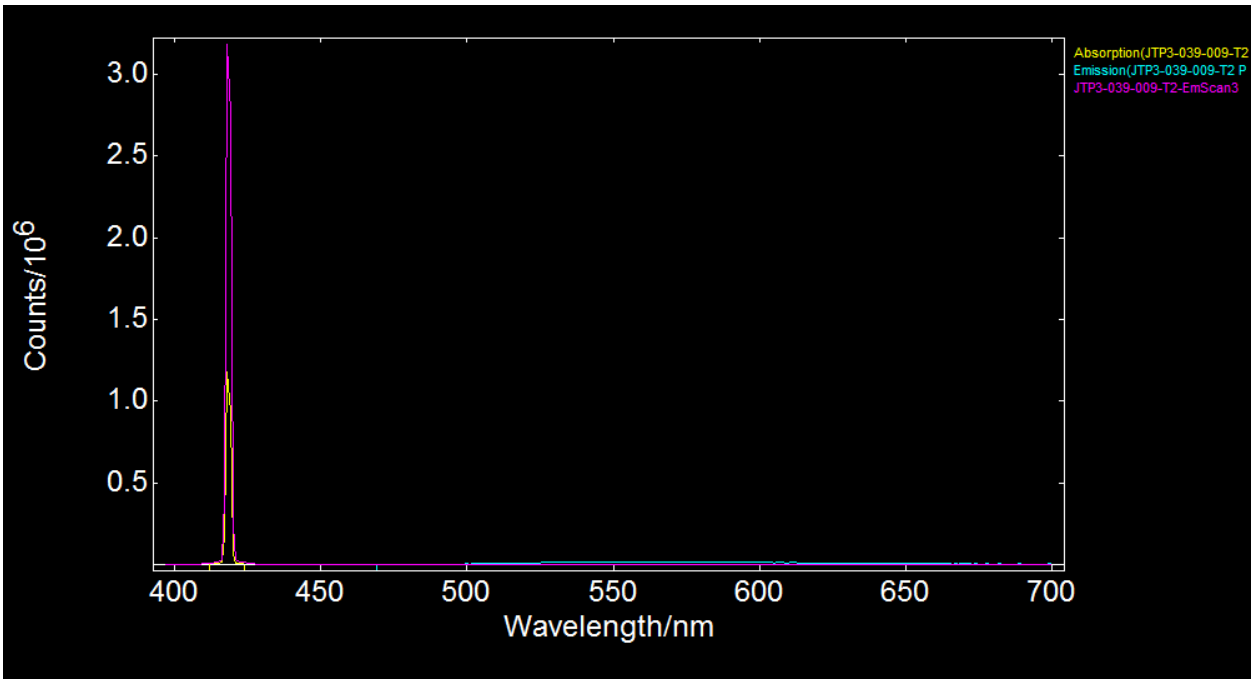


Figure S35. Spectral scans of the excitation scatter and the emission of TAM **6** and chloroform.

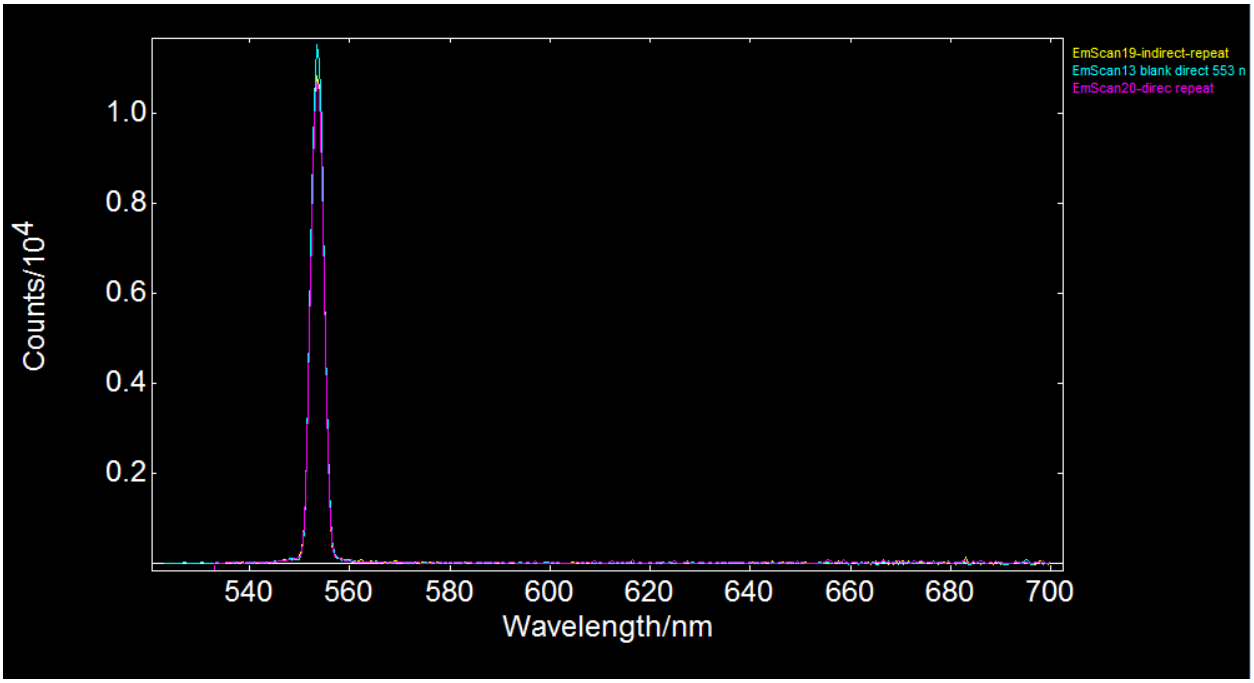


Figure S36. Spectral scans of the excitation scatter and the emission of TAM **6** powder and blank.

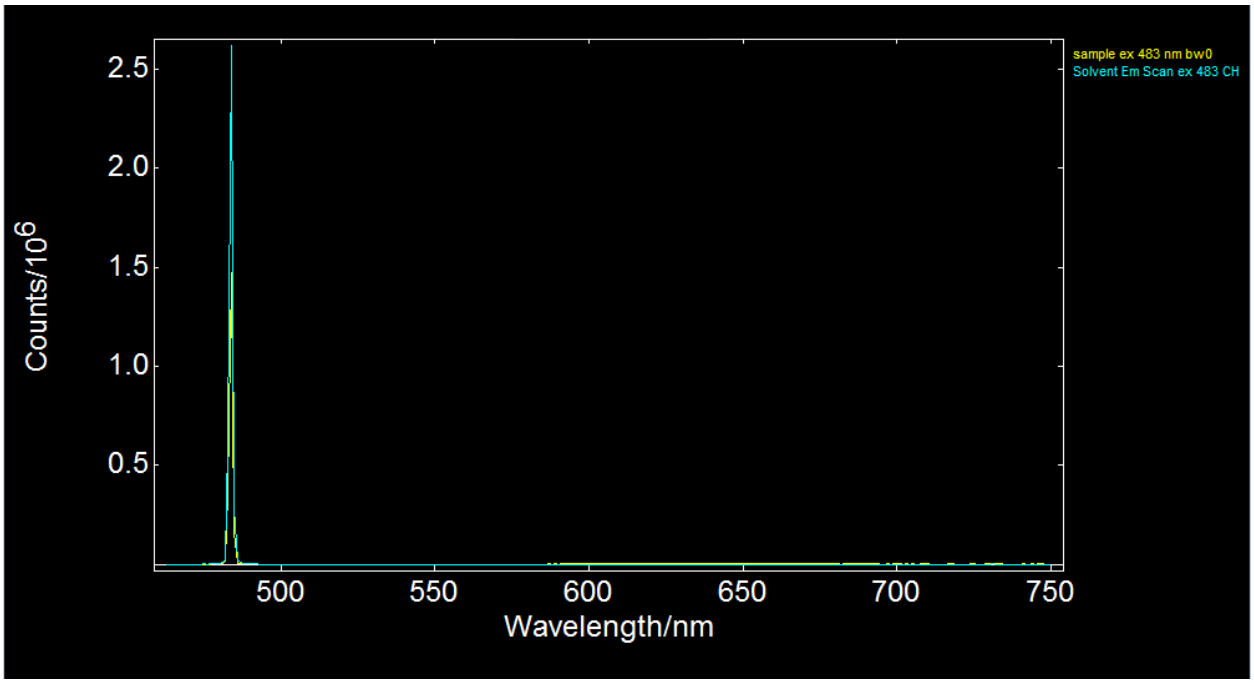


Figure S37. Spectral scans of the excitation scatter and the emission of TAM **7** and chloroform.

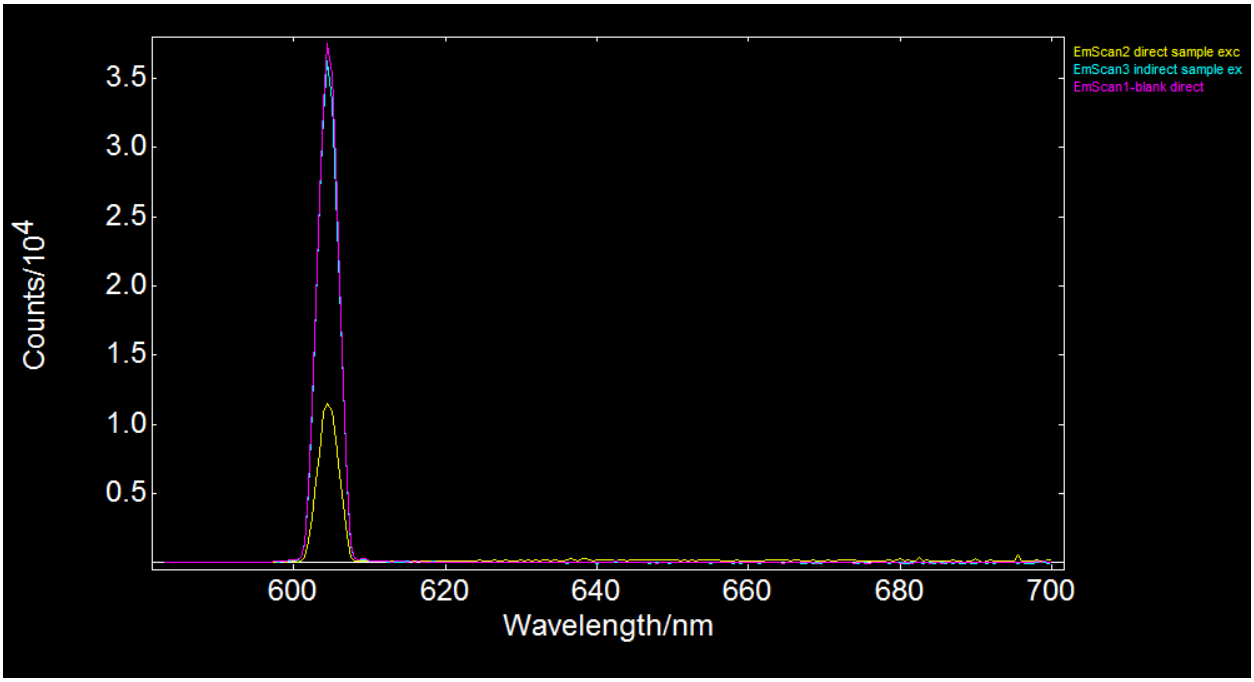


Figure S38. Spectral scans of the excitation scatter and the emission of TAM **7** powder and blank.

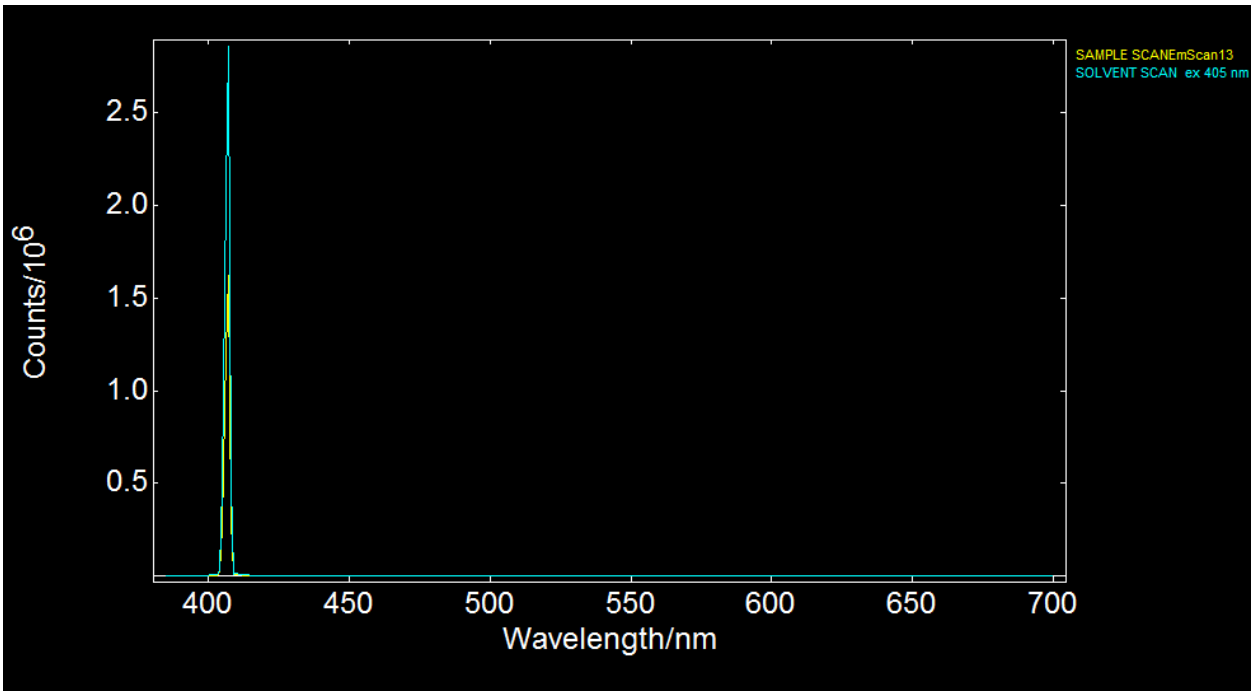


Figure S39. Spectral scans of the excitation scatter and the emission of TAM **8** and chloroform.

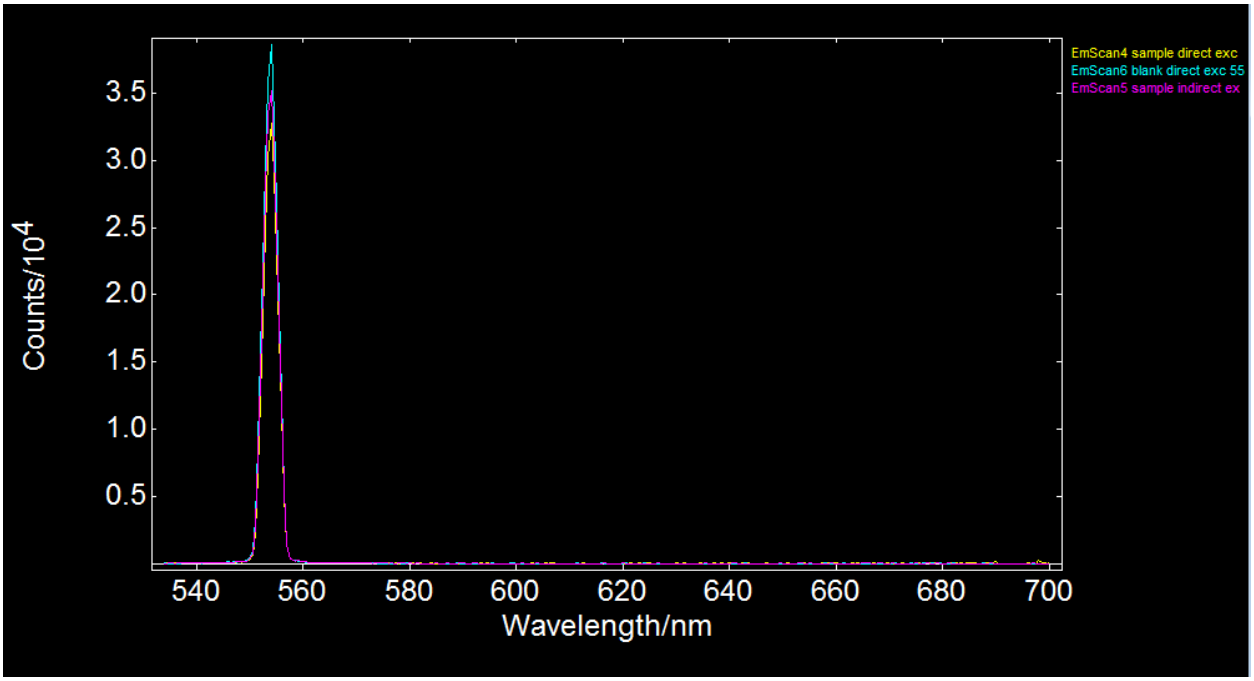


Figure S40. Spectral scans of the excitation scatter and the emission of TAM **8** powder and blank.

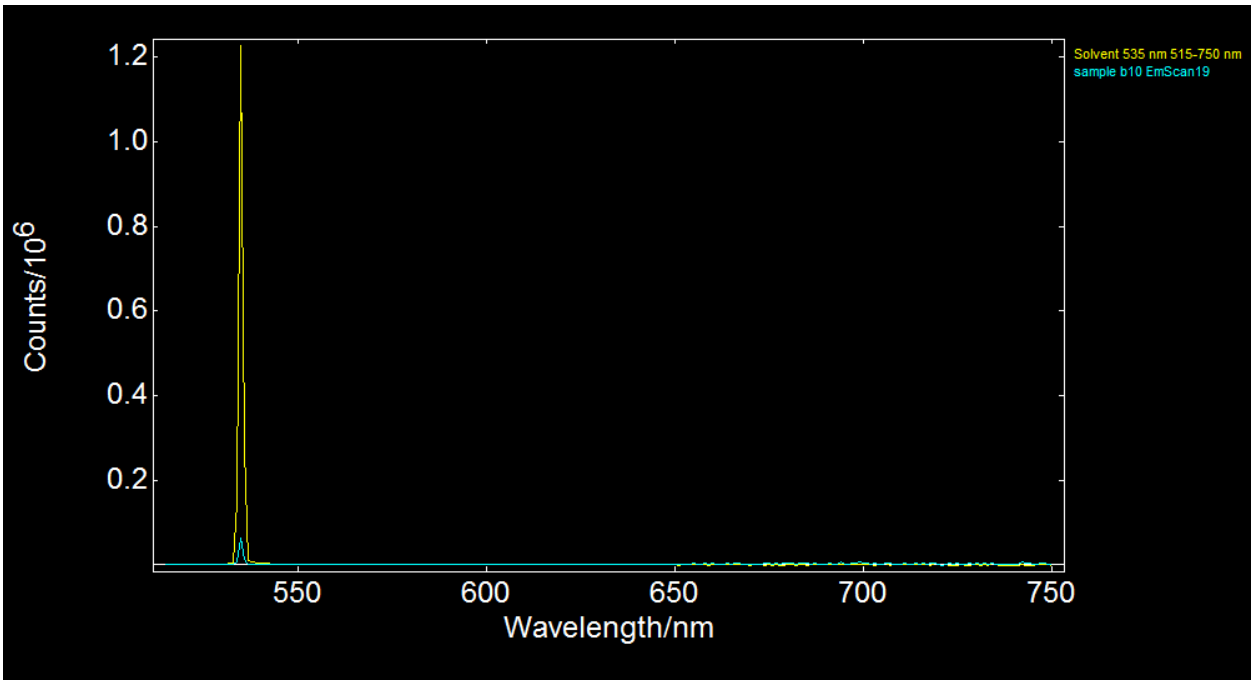


Figure S41. Spectral scans of the excitation scatter and the emission of TAM **10** and chloroform.

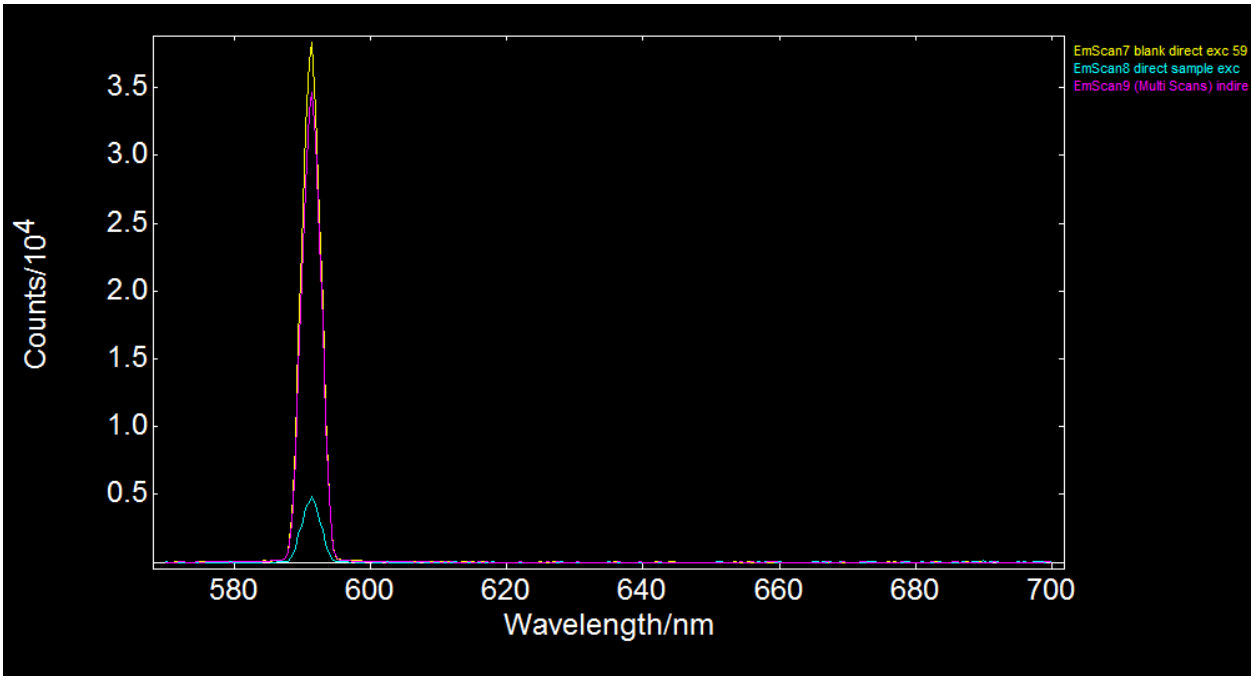


Figure S42. Spectral scans of the excitation scatter and the emission of TAM **10** powder and blank.

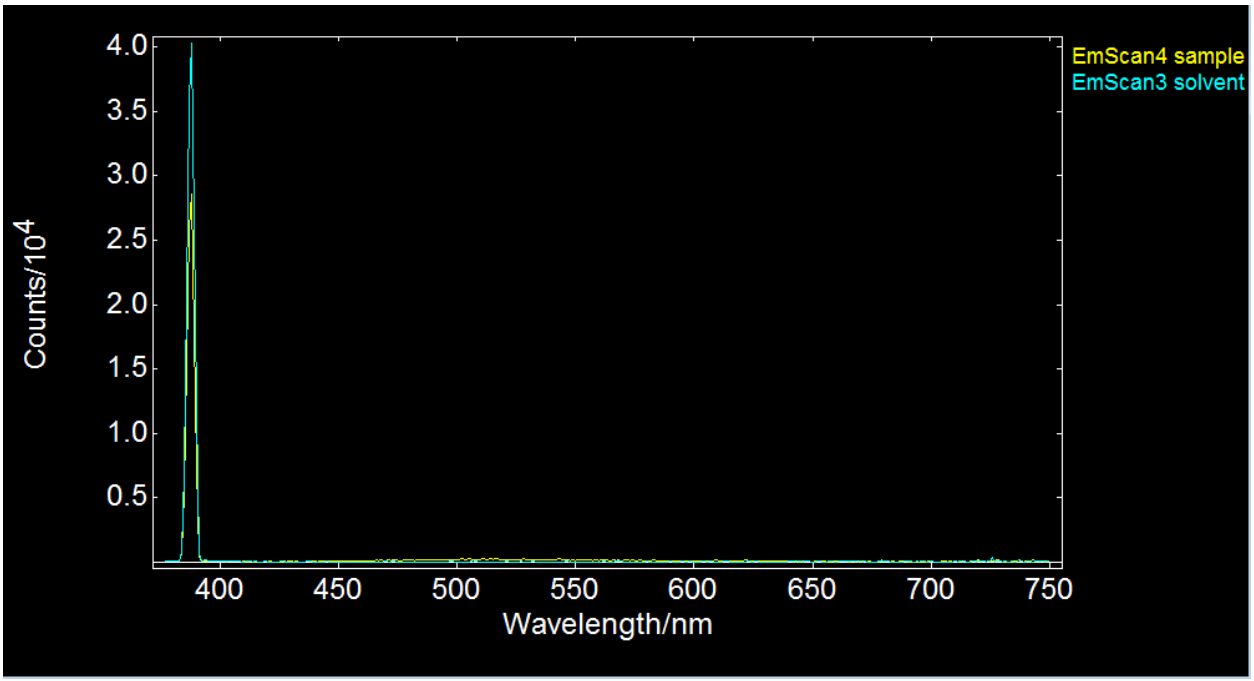


Figure S43. Spectral scans of the excitation scatter and the emission of TAM **11** and chloroform.

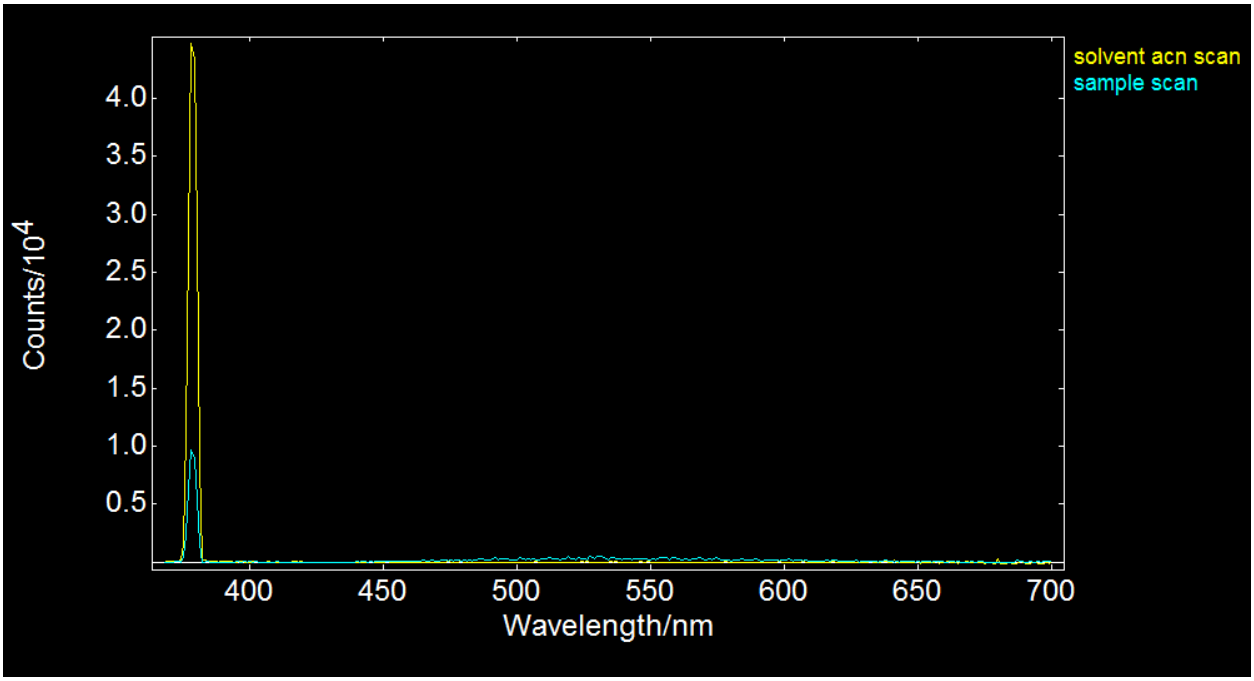


Figure S44. Spectral scans of the excitation scatter and the emission of TAM **11** and acetonitrile.

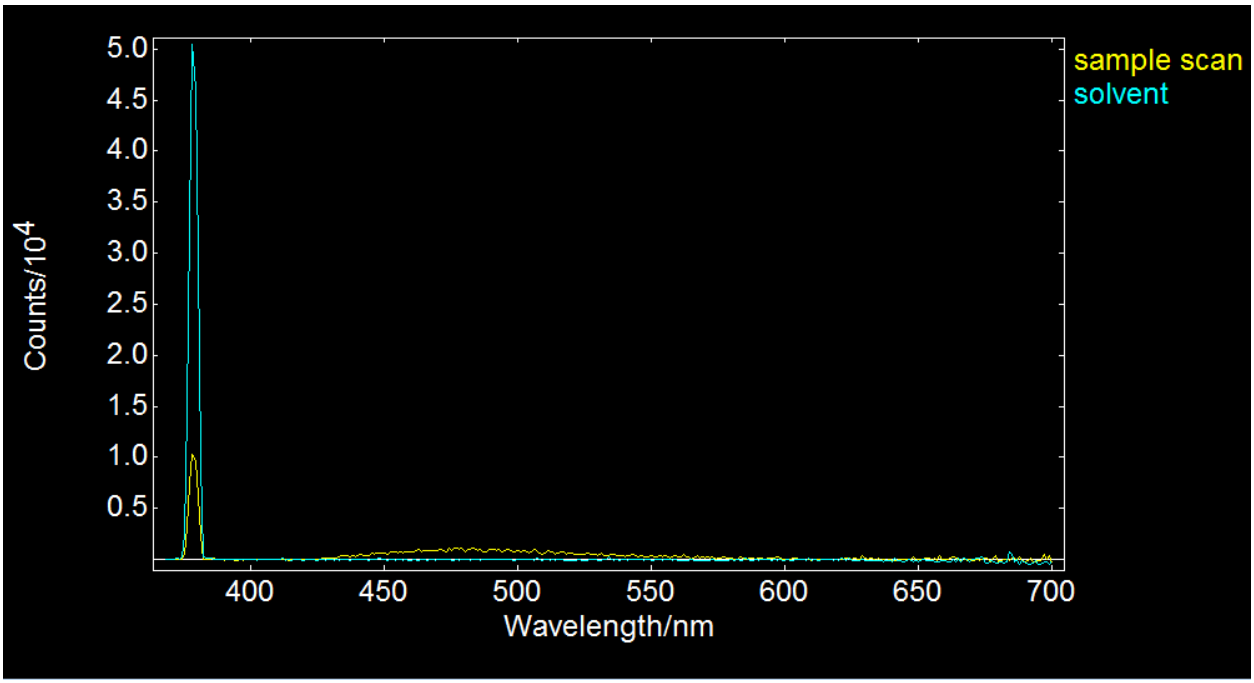


Figure S45. Spectral scans of the excitation scatter and the emission of TAM **11** and dioxane.

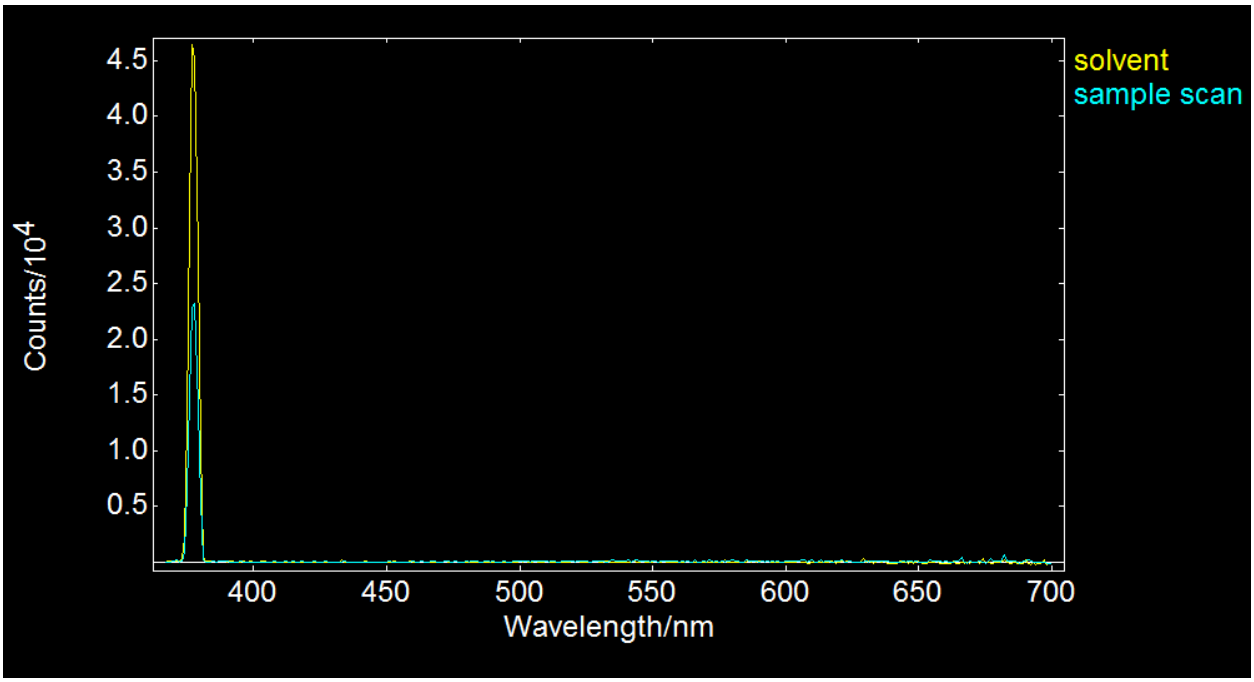


Figure S46. Spectral scans of the excitation scatter and the emission of TAM **11** and dimethylsulfoxide.

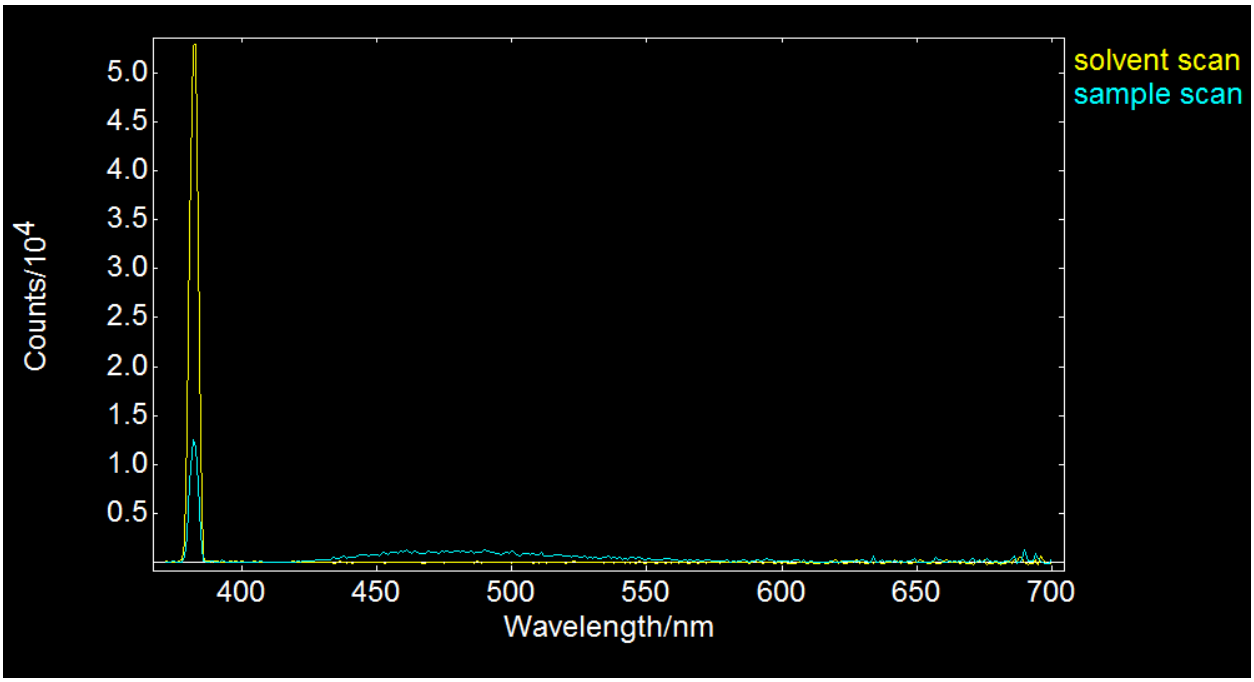


Figure S47. Spectral scans of the excitation scatter and the emission of TAM **11** and toluene.

Table S4. Crystal data and structure refinement for TAM **8**.

Identification code	SE190540	
Empirical formula	C31 H21 N O2 S2	
Formula weight	503.61	
Temperature	173(1) K	
Wavelength	0.71073 Å	
Diffractometer used	Bruker AXS P4/SMART 1000	
Detector distance	5 cm	
Monochromator used	Graphite	
Crystal size	0.60 x 0.50 x 0.25 mm^3	
Colour and habit	Yellow, parallelpiped	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 32.295(4) Å	$\alpha = 90°$
	b = 10.4015(11) Å	$\beta = 102.706(3)°$
	c = 30.021(4) Å	$\gamma = 90°$
Volume	9838(2) $Å^3$	
Z	16	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	0.247 mm^{-1}	
F(000)	4192	
Theta range for data collection	1.68 to 27.50°	
Completeness to theta = 25.00°	99.9 %	
Scan type	ω and ϕ	
Scan range	0.3°	
Exposure time	10s	
Index ranges	$-39 \le h \le 41$, $-13 \le k \le 13$, $-34 \le l \le 39$	
Standard reflections	50 frames at beginning and end of data collection	
Crystal stability	no decay	
Reflections collected	32999	
Independent reflections	11006 [R(int) = 0.0256]	
Solution	Direct methods	
Hydrogen atoms	Calculated positions, riding model	
Absorption correction	SADABS	
Max. and min. transmission	0.9408 and 0.8660	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11006 / 0 / 651	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0877	
R indices (all data)	R1 = 0.0450, wR2 = 0.0937	
Largest/mean shift/esd	0.001/0.000	
Largest diff. peak and hole	0.344 and -0.220 $e.Å^{-3}$	

$wR2 = (\sum[w(F_o^2-F_c^2)^2]/\sum[wF_o^4])^{1/2}$

$R1 = \sum \big| |F_o| - |F_c| \big| / \sum |F_o|$

$Weight = 1 / [\sigma^2(F_o^2) + (0.0447 * P)^2 + (7.5071 * P)]$

where $P = (\max(F_o^2, 0) + 2 * F_c^2)/3$

Table S5. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 x\ 10^3$) for TAM **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	2924(1)	2689(1)	4465(1)	33(1)
O(1)	2286(1)	3403(1)	4602(1)	38(1)
O(2)	3425(1)	1424(1)	4235(1)	41(1)
S(1)	2135(1)	-1548(1)	4419(1)	33(1)
S(2)	2007(1)	672(1)	3101(1)	30(1)
C(1)	2491(1)	2618(2)	4443(1)	30(1)
C(2)	2337(1)	1393(2)	4189(1)	28(1)
C(3)	2672(1)	832(2)	4065(1)	27(1)
C(4)	3061(1)	1630(2)	4257(1)	31(1)
C(5)	1893(1)	984(2)	4132(1)	28(1)
C(6)	1564(1)	1877(2)	4012(1)	35(1)
C(7)	1142(1)	1512(2)	3961(1)	42(1)
C(8)	1036(1)	248(2)	4025(1)	42(1)
C(9)	1355(1)	-678(2)	4151(1)	34(1)
C(10)	1316(1)	-2022(2)	4265(1)	36(1)
C(11)	948(1)	-2765(2)	4240(1)	50(1)
C(12)	987(1)	-4029(2)	4385(1)	60(1)
C(13)	1384(1)	-4575(2)	4557(1)	56(1)
C(14)	1752(1)	-3874(2)	4581(1)	44(1)
C(15)	1713(1)	-2597(2)	4432(1)	35(1)
C(16)	1783(1)	-292(2)	4208(1)	29(1)
C(17)	2694(1)	-282(2)	3769(1)	27(1)
C(18)	3008(1)	-1218(2)	3890(1)	32(1)
C(19)	3027(1)	-2275(2)	3610(1)	35(1)
C(20)	2740(1)	-2410(2)	3197(1)	32(1)
C(21)	2430(1)	-1468(1)	3055(1)	27(1)
C(22)	2123(1)	-1367(1)	2624(1)	27(1)
C(23)	2057(1)	-2194(2)	2246(1)	32(1)
C(24)	1753(1)	-1880(2)	1860(1)	36(1)
C(25)	1512(1)	-766(2)	1843(1)	36(1)
C(26)	1570(1)	70(2)	2210(1)	33(1)
C(27)	1879(1)	-243(2)	2599(1)	28(1)
C(28)	2407(1)	-420(1)	3345(1)	26(1)
C(29)	3197(1)	3720(2)	4697(1)	38(1)
C(30)	3317(1)	4682(2)	4376(1)	44(1)
C(31)	3569(1)	5788(2)	4627(1)	40(1)
N(2)	610(1)	6914(1)	516(1)	30(1)
O(3)	585(1)	4821(1)	261(1)	40(1)
O(4)	665(1)	8667(1)	995(1)	39(1)
S(3)	-55(1)	4802(1)	1695(1)	33(1)
S(4)	1367(1)	4970(1)	2025(1)	28(1)
C(41)	605(1)	5587(2)	565(1)	29(1)
C(42)	618(1)	5327(1)	1066(1)	26(1)
C(43)	652(1)	6467(1)	1283(1)	26(1)
C(44)	644(1)	7514(1)	933(1)	29(1)

C(45)	567(1)	4014(1)	1223(1)	25(1)
C(46)	787(1)	2994(1)	1080(1)	29(1)
C(47)	726(1)	1730(2)	1204(1)	31(1)
C(48)	430(1)	1441(1)	1461(1)	29(1)
C(49)	195(1)	2429(1)	1602(1)	25(1)
C(50)	-150(1)	2334(1)	1842(1)	26(1)
C(51)	-336(1)	1244(2)	1988(1)	30(1)
C(52)	-677(1)	1377(2)	2194(1)	35(1)
C(53)	-833(1)	2596(2)	2263(1)	41(1)
C(54)	-652(1)	3687(2)	2126(1)	40(1)
C(55)	-316(1)	3549(1)	1910(1)	30(1)
C(56)	272(1)	3712(1)	1492(1)	25(1)
C(57)	715(1)	6805(1)	1769(1)	26(1)
C(58)	476(1)	7791(1)	1904(1)	32(1)
C(59)	545(1)	8181(2)	2359(1)	35(1)
C(60)	864(1)	7641(2)	2686(1)	33(1)
C(61)	1113(1)	6655(1)	2563(1)	27(1)
C(62)	1466(1)	5969(2)	2848(1)	28(1)
C(63)	1649(1)	6123(2)	3313(1)	36(1)
C(64)	1984(1)	5350(2)	3518(1)	42(1)
C(65)	2141(1)	4405(2)	3268(1)	41(1)
C(66)	1965(1)	4230(2)	2808(1)	34(1)
C(67)	1631(1)	5024(1)	2601(1)	27(1)
C(68)	1027(1)	6218(1)	2107(1)	25(1)
C(69)	600(1)	7583(2)	86(1)	36(1)
C(70)	154(1)	7655(2)	-214(1)	43(1)
C(71)	-168(1)	8199(2)	33(1)	61(1)

Table S6. Bond lengths [Å] and angles [°] for TAM **8**.

N(1)-C(1)	1.386(2)	C(23)-H(23)	0.9500
N(1)-C(4)	1.386(2)	C(24)-C(25)	1.391(3)
N(1)-C(29)	1.464(2)	C(24)-H(24)	0.9500
O(1)-C(1)	1.2137(19)	C(25)-C(26)	1.385(2)
O(2)-C(4)	1.2118(19)	C(25)-H(25)	0.9500
S(1)-C(15)	1.7528(17)	C(26)-C(27)	1.398(2)
S(1)-C(16)	1.7546(16)	C(26)-H(26)	0.9500
S(2)-C(27)	1.7517(15)	C(29)-C(30)	1.500(2)
S(2)-C(28)	1.7531(15)	C(29)-H(29A)	0.9900
C(1)-C(2)	1.512(2)	C(29)-H(29B)	0.9900
C(2)-C(3)	1.353(2)	C(30)-C(31)	1.513(2)
C(2)-C(5)	1.469(2)	C(30)-H(30A)	0.9900
C(3)-C(17)	1.471(2)	C(30)-H(30B)	0.9900
C(3)-C(4)	1.510(2)	C(31)-H(31A)	0.9800
C(5)-C(6)	1.397(2)	C(31)-H(31B)	0.9800
C(5)-C(16)	1.405(2)	C(31)-H(31C)	0.9800
C(6)-C(7)	1.391(2)	N(2)-C(44)	1.381(2)
C(6)-H(6)	0.9500	N(2)-C(41)	1.3891(19)
C(7)-C(8)	1.382(3)	N(2)-C(69)	1.4599(19)
C(7)-H(7)	0.9500	O(3)-C(41)	1.2029(18)
C(8)-C(9)	1.400(2)	O(4)-C(44)	1.2134(18)
C(8)-H(8)	0.9500	S(3)-C(55)	1.7488(16)
C(9)-C(16)	1.413(2)	S(3)-C(56)	1.7496(14)
C(9)-C(10)	1.452(3)	S(4)-C(67)	1.7522(15)
C(10)-C(15)	1.403(2)	S(4)-C(68)	1.7524(14)
C(10)-C(11)	1.405(2)	C(41)-C(42)	1.517(2)
C(11)-C(12)	1.382(3)	C(42)-C(43)	1.346(2)
C(11)-H(11)	0.9500	C(42)-C(45)	1.467(2)
C(12)-C(13)	1.393(3)	C(43)-C(57)	1.469(2)
C(12)-H(12)	0.9500	C(43)-C(44)	1.511(2)
C(13)-C(14)	1.383(3)	C(45)-C(46)	1.397(2)
C(13)-H(13)	0.9500	C(45)-C(56)	1.412(2)
C(14)-C(15)	1.399(3)	C(46)-C(47)	1.392(2)
C(14)-H(14)	0.9500	C(46)-H(46)	0.9500
C(17)-C(18)	1.397(2)	C(47)-C(48)	1.387(2)
C(17)-C(28)	1.407(2)	C(47)-H(47)	0.9500
C(18)-C(19)	1.394(2)	C(48)-C(49)	1.395(2)
C(18)-H(18)	0.9500	C(48)-H(48)	0.9500
C(19)-C(20)	1.381(2)	C(49)-C(56)	1.410(2)
C(19)-H(19)	0.9500	C(49)-C(50)	1.458(2)
C(20)-C(21)	1.398(2)	C(50)-C(51)	1.397(2)
C(20)-H(20)	0.9500	C(50)-C(55)	1.404(2)
C(21)-C(28)	1.408(2)	C(51)-C(52)	1.385(2)
C(21)-C(22)	1.453(2)	C(51)-H(51)	0.9500
C(22)-C(23)	1.402(2)	C(52)-C(53)	1.396(2)
C(22)-C(27)	1.402(2)	C(52)-H(52)	0.9500
C(23)-C(24)	1.384(2)	C(53)-C(54)	1.380(2)
		C(53)-H(53)	0.9500

C(54)-C(55)	1.391(2)	C(7)-C(6)-C(5)	121.17(17)
C(54)-H(54)	0.9500	C(7)-C(6)-H(6)	119.4
C(57)-C(58)	1.398(2)	C(5)-C(6)-H(6)	119.4
C(57)-C(68)	1.404(2)	C(8)-C(7)-C(6)	120.71(16)
C(58)-C(59)	1.393(2)	C(8)-C(7)-H(7)	119.6
C(58)-H(58)	0.9500	C(6)-C(7)-H(7)	119.6
C(59)-C(60)	1.377(2)	C(7)-C(8)-C(9)	120.13(16)
C(59)-H(59)	0.9500	C(7)-C(8)-H(8)	119.9
C(60)-C(61)	1.401(2)	C(9)-C(8)-H(8)	119.9
C(60)-H(60)	0.9500	C(8)-C(9)-C(16)	118.68(16)
C(61)-C(68)	1.411(2)	C(8)-C(9)-C(10)	129.01(15)
C(61)-C(62)	1.454(2)	C(16)-C(9)-C(10)	112.17(15)
C(62)-C(63)	1.400(2)	C(15)-C(10)-C(11)	118.61(17)
C(62)-C(67)	1.404(2)	C(15)-C(10)-C(9)	112.04(14)
C(63)-C(64)	1.379(2)	C(11)-C(10)-C(9)	129.33(17)
C(63)-H(63)	0.9500	C(12)-C(11)-C(10)	119.3(2)
C(64)-C(65)	1.396(3)	C(12)-C(11)-H(11)	120.3
C(64)-H(64)	0.9500	C(10)-C(11)-H(11)	120.3
C(65)-C(66)	1.387(2)	C(11)-C(12)-C(13)	121.14(19)
C(65)-H(65)	0.9500	C(11)-C(12)-H(12)	119.4
C(66)-C(67)	1.392(2)	C(13)-C(12)-H(12)	119.4
C(66)-H(66)	0.9500	C(14)-C(13)-C(12)	120.9(2)
C(69)-C(70)	1.521(2)	C(14)-C(13)-H(13)	119.5
C(69)-H(69A)	0.9900	C(12)-C(13)-H(13)	119.5
C(69)-H(69B)	0.9900	C(13)-C(14)-C(15)	117.98(19)
C(70)-C(71)	1.514(3)	C(13)-C(14)-H(14)	121.0
C(70)-H(70A)	0.9900	C(15)-C(14)-H(14)	121.0
C(70)-H(70B)	0.9900	C(14)-C(15)-C(10)	121.99(16)
C(71)-H(71A)	0.9800	C(14)-C(15)-S(1)	125.67(14)
C(71)-H(71B)	0.9800	C(10)-C(15)-S(1)	112.33(13)
C(71)-H(71C)	0.9800	C(5)-C(16)-C(9)	121.51(15)
C(1)-N(1)-C(4)	110.81(13)	C(5)-C(16)-S(1)	126.53(12)
C(1)-N(1)-C(29)	123.85(14)	C(9)-C(16)-S(1)	111.81(12)
C(4)-N(1)-C(29)	125.27(14)	C(18)-C(17)-C(28)	117.50(14)
C(15)-S(1)-C(16)	91.53(8)	C(18)-C(17)-C(3)	121.32(13)
C(27)-S(2)-C(28)	91.21(7)	C(28)-C(17)-C(3)	121.15(13)
O(1)-C(1)-N(1)	125.18(15)	C(19)-C(18)-C(17)	121.18(14)
O(1)-C(1)-C(2)	128.15(15)	C(19)-C(18)-H(18)	119.4
N(1)-C(1)-C(2)	106.67(13)	C(17)-C(18)-H(18)	119.4
C(3)-C(2)-C(5)	131.55(14)	C(20)-C(19)-C(18)	120.84(15)
C(3)-C(2)-C(1)	107.83(13)	C(20)-C(19)-H(19)	119.6
C(5)-C(2)-C(1)	120.56(13)	C(18)-C(19)-H(19)	119.6
C(2)-C(3)-C(17)	130.76(14)	C(19)-C(20)-C(21)	119.70(14)
C(2)-C(3)-C(4)	107.89(13)	C(19)-C(20)-H(20)	120.2
C(17)-C(3)-C(4)	121.16(13)	C(21)-C(20)-H(20)	120.2
O(2)-C(4)-N(1)	125.22(15)	C(20)-C(21)-C(28)	119.17(14)
O(2)-C(4)-C(3)	128.10(15)	C(20)-C(21)-C(22)	128.71(14)
N(1)-C(4)-C(3)	106.67(13)	C(28)-C(21)-C(22)	112.06(13)
C(6)-C(5)-C(16)	117.76(14)	C(23)-C(22)-C(27)	119.10(14)
C(6)-C(5)-C(2)	120.25(15)	C(23)-C(22)-C(21)	128.97(14)
C(16)-C(5)-C(2)	121.96(14)	C(27)-C(22)-C(21)	111.88(13)

C(24)-C(23)-C(22)	119.08(15)	O(4)-C(44)-C(43)	127.84(14)
C(24)-C(23)-H(23)	120.5	N(2)-C(44)-C(43)	106.94(12)
C(22)-C(23)-H(23)	120.5	C(46)-C(45)-C(56)	117.37(13)
C(23)-C(24)-C(25)	121.05(15)	C(46)-C(45)-C(42)	120.45(13)
C(23)-C(24)-H(24)	119.5	C(56)-C(45)-C(42)	122.01(13)
C(25)-C(24)-H(24)	119.5	C(47)-C(46)-C(45)	121.48(14)
C(26)-C(25)-C(24)	121.21(15)	C(47)-C(46)-H(46)	119.3
C(26)-C(25)-H(25)	119.4	C(45)-C(46)-H(46)	119.3
C(24)-C(25)-H(25)	119.4	C(48)-C(47)-C(46)	120.68(14)
C(25)-C(26)-C(27)	117.74(15)	C(48)-C(47)-H(47)	119.7
C(25)-C(26)-H(26)	121.1	C(46)-C(47)-H(47)	119.7
C(27)-C(26)-H(26)	121.1	C(47)-C(48)-C(49)	119.67(14)
C(26)-C(27)-C(22)	121.82(14)	C(47)-C(48)-H(48)	120.2
C(26)-C(27)-S(2)	125.58(12)	C(49)-C(48)-H(48)	120.2
C(22)-C(27)-S(2)	112.60(11)	C(48)-C(49)-C(56)	119.34(13)
C(17)-C(28)-C(21)	121.54(13)	C(48)-C(49)-C(50)	128.69(13)
C(17)-C(28)-S(2)	126.18(11)	C(56)-C(49)-C(50)	111.91(12)
C(21)-C(28)-S(2)	112.21(11)	C(51)-C(50)-C(55)	118.82(13)
N(1)-C(29)-C(30)	113.30(13)	C(51)-C(50)-C(49)	129.53(13)
N(1)-C(29)-H(29A)	108.9	C(55)-C(50)-C(49)	111.60(13)
C(30)-C(29)-H(29A)	108.9	C(52)-C(51)-C(50)	119.82(14)
N(1)-C(29)-H(29B)	108.9	C(52)-C(51)-H(51)	120.1
C(30)-C(29)-H(29B)	108.9	C(50)-C(51)-H(51)	120.1
H(29A)-C(29)-H(29B)	107.7	C(51)-C(52)-C(53)	120.38(15)
C(29)-C(30)-C(31)	111.92(14)	C(51)-C(52)-H(52)	119.8
C(29)-C(30)-H(30A)	109.2	C(53)-C(52)-H(52)	119.8
C(31)-C(30)-H(30A)	109.2	C(54)-C(53)-C(52)	120.86(15)
C(29)-C(30)-H(30B)	109.2	C(54)-C(53)-H(53)	119.6
C(31)-C(30)-H(30B)	109.2	C(52)-C(53)-H(53)	119.6
H(30A)-C(30)-H(30B)	107.9	C(53)-C(54)-C(55)	118.62(15)
C(30)-C(31)-H(31A)	109.5	C(53)-C(54)-H(54)	120.7
C(30)-C(31)-H(31B)	109.5	C(55)-C(54)-H(54)	120.7
H(31A)-C(31)-H(31B)	109.5	C(54)-C(55)-C(50)	121.47(14)
C(30)-C(31)-H(31C)	109.5	C(54)-C(55)-S(3)	125.71(12)
H(31A)-C(31)-H(31C)	109.5	C(50)-C(55)-S(3)	112.82(11)
H(31B)-C(31)-H(31C)	109.5	C(49)-C(56)-C(45)	121.37(13)
C(44)-N(2)-C(41)	110.64(12)	C(49)-C(56)-S(3)	112.32(11)
C(44)-N(2)-C(69)	124.58(13)	C(45)-C(56)-S(3)	126.19(11)
C(41)-N(2)-C(69)	124.73(13)	C(58)-C(57)-C(68)	117.60(14)
C(55)-S(3)-C(56)	91.28(7)	C(58)-C(57)-C(43)	120.05(14)
C(67)-S(4)-C(68)	91.23(7)	C(68)-C(57)-C(43)	122.25(13)
O(3)-C(41)-N(2)	125.21(14)	C(59)-C(58)-C(57)	121.27(15)
O(3)-C(41)-C(42)	128.26(14)	C(59)-C(58)-H(58)	119.4
N(2)-C(41)-C(42)	106.52(12)	C(57)-C(58)-H(58)	119.4
C(43)-C(42)-C(45)	131.81(13)	C(60)-C(59)-C(58)	120.84(14)
C(43)-C(42)-C(41)	107.80(13)	C(60)-C(59)-H(59)	119.6
C(45)-C(42)-C(41)	120.23(12)	C(58)-C(59)-H(59)	119.6
C(42)-C(43)-C(57)	132.12(13)	C(59)-C(60)-C(61)	119.63(14)
C(42)-C(43)-C(44)	108.02(13)	C(59)-C(60)-H(60)	120.2
C(57)-C(43)-C(44)	119.76(12)	C(61)-C(60)-H(60)	120.2
O(4)-C(44)-N(2)	125.21(14)	C(60)-C(61)-C(68)	119.26(14)

C(60)-C(61)-C(62)	128.75(14)
C(68)-C(61)-C(62)	111.99(13)
C(63)-C(62)-C(67)	118.79(14)
C(63)-C(62)-C(61)	129.37(14)
C(67)-C(62)-C(61)	111.83(13)
C(64)-C(63)-C(62)	119.63(15)
C(64)-C(63)-H(63)	120.2
C(62)-C(63)-H(63)	120.2
C(63)-C(64)-C(65)	120.85(15)
C(63)-C(64)-H(64)	119.6
C(65)-C(64)-H(64)	119.6
C(66)-C(65)-C(64)	120.70(16)
C(66)-C(65)-H(65)	119.7
C(64)-C(65)-H(65)	119.7
C(65)-C(66)-C(67)	118.25(15)
C(65)-C(66)-H(66)	120.9
C(67)-C(66)-H(66)	120.9
C(66)-C(67)-C(62)	121.76(14)
C(66)-C(67)-S(4)	125.57(12)
C(62)-C(67)-S(4)	112.66(11)
C(57)-C(68)-C(61)	121.25(13)
C(57)-C(68)-S(4)	126.40(11)
C(61)-C(68)-S(4)	112.27(11)
N(2)-C(69)-C(70)	112.49(13)
N(2)-C(69)-H(69A)	109.1
C(70)-C(69)-H(69A)	109.1
N(2)-C(69)-H(69B)	109.1
C(70)-C(69)-H(69B)	109.1
H(69A)-C(69)-H(69B)	107.8
C(71)-C(70)-C(69)	112.93(15)
C(71)-C(70)-H(70A)	109.0
C(69)-C(70)-H(70A)	109.0
C(71)-C(70)-H(70B)	109.0
C(69)-C(70)-H(70B)	109.0
H(70A)-C(70)-H(70B)	107.8
C(70)-C(71)-H(71A)	109.5
C(70)-C(71)-H(71B)	109.5
H(71A)-C(71)-H(71B)	109.5
C(70)-C(71)-H(71C)	109.5
H(71A)-C(71)-H(71C)	109.5
H(71B)-C(71)-H(71C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for TAM **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	36(1)	34(1)	30(1)	-5(1)	7(1)	-6(1)
O(1)	45(1)	34(1)	33(1)	-5(1)	6(1)	5(1)
O(2)	29(1)	48(1)	44(1)	-3(1)	6(1)	-4(1)
S(1)	31(1)	32(1)	37(1)	-1(1)	10(1)	1(1)
S(2)	32(1)	31(1)	26(1)	-3(1)	3(1)	6(1)
C(1)	37(1)	32(1)	22(1)	2(1)	4(1)	0(1)
C(2)	31(1)	30(1)	21(1)	1(1)	3(1)	2(1)
C(3)	28(1)	31(1)	22(1)	1(1)	3(1)	0(1)
C(4)	32(1)	36(1)	24(1)	3(1)	3(1)	-3(1)
C(5)	28(1)	36(1)	22(1)	-3(1)	5(1)	2(1)
C(6)	37(1)	40(1)	27(1)	0(1)	5(1)	6(1)
C(7)	32(1)	54(1)	38(1)	3(1)	3(1)	11(1)
C(8)	26(1)	64(1)	34(1)	1(1)	4(1)	0(1)
C(9)	30(1)	48(1)	23(1)	-4(1)	7(1)	-4(1)
C(10)	37(1)	48(1)	26(1)	-6(1)	12(1)	-8(1)
C(11)	43(1)	65(1)	45(1)	-4(1)	16(1)	-15(1)
C(12)	62(1)	66(1)	57(1)	-3(1)	24(1)	-31(1)
C(13)	74(2)	46(1)	53(1)	0(1)	25(1)	-15(1)
C(14)	56(1)	40(1)	39(1)	-4(1)	20(1)	-5(1)
C(15)	42(1)	38(1)	28(1)	-7(1)	15(1)	-6(1)
C(16)	28(1)	37(1)	22(1)	-4(1)	6(1)	2(1)
C(17)	26(1)	32(1)	25(1)	0(1)	7(1)	0(1)
C(18)	27(1)	39(1)	31(1)	2(1)	5(1)	3(1)
C(19)	32(1)	33(1)	40(1)	4(1)	10(1)	8(1)
C(20)	34(1)	29(1)	36(1)	-2(1)	13(1)	2(1)
C(21)	26(1)	28(1)	29(1)	-1(1)	10(1)	-3(1)
C(22)	26(1)	30(1)	27(1)	-2(1)	10(1)	-5(1)
C(23)	32(1)	32(1)	34(1)	-6(1)	13(1)	-7(1)
C(24)	37(1)	44(1)	28(1)	-8(1)	10(1)	-15(1)
C(25)	32(1)	50(1)	25(1)	1(1)	3(1)	-10(1)
C(26)	28(1)	39(1)	30(1)	2(1)	5(1)	0(1)
C(27)	28(1)	31(1)	24(1)	-2(1)	8(1)	-4(1)
C(28)	24(1)	27(1)	26(1)	1(1)	8(1)	1(1)
C(29)	44(1)	38(1)	28(1)	-3(1)	2(1)	-11(1)
C(30)	60(1)	46(1)	26(1)	-3(1)	8(1)	-16(1)
C(31)	48(1)	40(1)	34(1)	-3(1)	12(1)	-11(1)
N(2)	32(1)	24(1)	30(1)	3(1)	3(1)	-3(1)
O(3)	57(1)	32(1)	33(1)	-4(1)	14(1)	-3(1)
O(4)	49(1)	21(1)	41(1)	2(1)	-2(1)	-5(1)
S(3)	35(1)	19(1)	51(1)	-2(1)	19(1)	1(1)
S(4)	32(1)	25(1)	26(1)	-3(1)	6(1)	5(1)
C(41)	27(1)	26(1)	34(1)	0(1)	7(1)	-2(1)
C(42)	25(1)	23(1)	30(1)	0(1)	6(1)	0(1)
C(43)	24(1)	21(1)	32(1)	1(1)	3(1)	0(1)
C(44)	25(1)	25(1)	34(1)	2(1)	-1(1)	-3(1)

C(45)	26(1)	21(1)	27(1)	-2(1)	3(1)	0(1)
C(46)	29(1)	26(1)	32(1)	-1(1)	9(1)	1(1)
C(47)	35(1)	24(1)	35(1)	-2(1)	10(1)	6(1)
C(48)	35(1)	20(1)	32(1)	2(1)	7(1)	3(1)
C(49)	26(1)	22(1)	24(1)	1(1)	2(1)	0(1)
C(50)	26(1)	24(1)	26(1)	0(1)	3(1)	1(1)
C(51)	31(1)	24(1)	32(1)	2(1)	5(1)	1(1)
C(52)	35(1)	32(1)	40(1)	6(1)	12(1)	-3(1)
C(53)	37(1)	40(1)	53(1)	2(1)	22(1)	1(1)
C(54)	40(1)	30(1)	57(1)	-3(1)	22(1)	2(1)
C(55)	30(1)	24(1)	38(1)	0(1)	9(1)	-1(1)
C(56)	26(1)	20(1)	28(1)	-3(1)	4(1)	2(1)
C(57)	28(1)	18(1)	33(1)	-2(1)	6(1)	-3(1)
C(58)	28(1)	22(1)	43(1)	-2(1)	4(1)	0(1)
C(59)	33(1)	26(1)	47(1)	-10(1)	12(1)	2(1)
C(60)	34(1)	31(1)	35(1)	-9(1)	11(1)	-2(1)
C(61)	28(1)	24(1)	30(1)	-3(1)	10(1)	-3(1)
C(62)	29(1)	28(1)	27(1)	-2(1)	10(1)	-3(1)
C(63)	38(1)	42(1)	29(1)	-5(1)	10(1)	0(1)
C(64)	44(1)	56(1)	26(1)	-2(1)	5(1)	3(1)
C(65)	37(1)	51(1)	32(1)	5(1)	5(1)	9(1)
C(66)	35(1)	36(1)	31(1)	1(1)	10(1)	6(1)
C(67)	29(1)	28(1)	25(1)	0(1)	8(1)	-2(1)
C(68)	27(1)	19(1)	30(1)	-2(1)	9(1)	-1(1)
C(69)	38(1)	35(1)	34(1)	8(1)	6(1)	-7(1)
C(70)	44(1)	47(1)	34(1)	7(1)	-2(1)	-1(1)
C(71)	44(1)	78(2)	56(1)	0(1)	-2(1)	14(1)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for TAM **8**.

	x	y	z	U(eq)
H(6)	1630	2749	3964	42
H(7)	924	2138	3881	50
H(8)	746	8	3984	51
H(11)	676	-2403	4125	60
H(12)	739	-4534	4367	72
H(13)	1402	-5442	4660	67
H(14)	2022	-4248	4696	53
H(18)	3213	-1133	4169	39
H(19)	3240	-2910	3703	42
H(20)	2753	-3140	3010	39
H(23)	2220	-2959	2255	38
H(24)	1708	-2435	1602	43
H(25)	1305	-574	1574	43
H(26)	1404	829	2199	39
H(29A)	3458	3336	4884	45
H(29B)	3048	4170	4907	45
H(30A)	3056	5020	4172	53
H(30B)	3487	4249	4183	53
H(31A)	3388	6294	4783	60
H(31B)	3672	6336	4409	60
H(31C)	3812	5451	4853	60
H(46)	984	3166	894	34
H(47)	888	1059	1112	37
H(48)	387	575	1541	35
H(51)	-227	414	1946	35
H(52)	-806	635	2289	42
H(53)	-1066	2674	2407	50
H(54)	-756	4516	2179	48
H(58)	262	8204	1683	38
H(59)	370	8828	2444	42
H(60)	915	7934	2993	40
H(63)	1543	6757	3487	43
H(64)	2110	5461	3833	51
H(65)	2371	3878	3416	49
H(66)	2070	3584	2637	40
H(69A)	788	7130	-82	43
H(69B)	711	8465	152	43
H(70A)	161	8200	-483	52
H(70B)	64	6782	-326	52
H(71A)	-212	7587	266	91
H(71B)	-437	8347	-186	91
H(71C)	-62	9014	179	91