Electronic Supplementary Information *for*

Fluorescent Photoswitches with Improved Emission Efficiency Based on Aggregation-Induced Emission Luminogens by Eliminating the Heavy-Atom Effect

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1. Experimental Section

Synthesis of ((*Z*)-(1,2-diphenyl-)-(*Z*)-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))ethene (DPDBE). A certain amount of $Pt(PPh_3)_4$ (0.35 g, 1 mol%) was added to a degassed solution of diphenylacetylene (5.00 g, 28.0 mmol) and bis(pinacolato)diboron (14.25 g, 56.0 mmol) in DMF (150 ml), and then the mixture was heated at 90°C for 24 h. After cooling to room temperature, the reaction mixture was extracted three times with ethyl acetate. The crude product of DPDBE was obtained after removal of the solvent under reduced pressure. DPDBE (10.00 g) was obtained by washing several times with ethanol as a white solid in a yield of 82%. Molecular formula: $C_{26}H_{34}B_2O_4$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.14 (m, 2H), 7.12 – 7.08 (m, 6H), 6.99 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.55 (s, 1H), 2.37 (s, 6H), 1.15 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.27, 129.31, 127.42, 125.78, 84.07, 24.89. HRMS (m/z): calcd. for $[M+H]^+$ 433.2643, found 433.2725.

Synthesis of 3-bromo-2,5-dimethylthiophene (3-BDMT). A certain amount of N-bromosuccinimide (1.58 g, 8.9 mmol) was added to a solution of 2,5-dimethylthiophene (1.00 g, 8.9 mmol) in acetic acid, and then mixture was stirred at room temperature overnight. After the reaction was completed, the mixture was poured into water and extracted 3 times with dichloromethane. The organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether) to obtain a colorless liquid (1.55 g, 91.3%). Molecular formula: C_6H_7BrS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (s, 1H), 2.40 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.88, 131.58, 127.58, 107.97, 15.31, 14.53. MS (m/z): calcd. for $[M]^+$ 191.9, found 191.9.

Synthesis of 3-(1,2,2-triphenylvinyl)thiophene (1a). 3-Thienylboronic acid (1.02 g, 9.0 mmol), 1-bromo-1,2,2-triphenylethylene (2.01 g, 6.0 mmol), and potassium carbonate (1.24 g, 9.0 mmol) were dissolved in a mixed solution of toluene (60 mL) and tetrahydrofuran (30 mL). The reaction solution was stirred at room temperature under nitrogen for 30 min, and then Pd $(PPh_3)_4$ (50 mg, 0.043 mmol) was added. The resulting solution was heated at 80 °C for 18 h. After the reaction was completed, the mixture was poured into water and extracted 3 times with dichloromethane. The organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether) to obtain a white solid powder (1.43 g, 70.5%). Molecular formula: $C_{24}H_{18}S$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.19 (m, 3H), 7.12–7.16 (m, 5H), 7.12 – 7.08 (m, 5H), 7.04 – 7.00 (m, 3H), 6.76 (d, *J* = 5.0 Hz, 1H), 6.59 (d, *J* = 5.0 Hz,

1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.09, 143.44, 140.62, 135.48, 131.20, 130.85, 130.08, 127.96, 127.64, 126.67, 126.33, 126.01, 123.67. HRMS (m/z): calcd. for $[M+H]^+$ 339.1163, found 339.1198.

Synthesis of 3-(1,2,2-triphenylvinyl)thiophene 1,1-dioxide (2a). A solution of m-chloroperbenzoic acid (m-CPBA) (2.03 g, 11.8 mmol) in 60 mL of CH_2Cl_2 was added over a period of 1 h to a stirred solution of 2-(1,2,2-triphenylvinyl)thiophene (1.00 g, 3.0 mmol) in 60 mL of CH_2Cl_2. After the addition, the mixture was stirred at room temperature for 24 h. After the reaction was completed, the mixture washed with aqueous $NaHSO_3$, $NaHCO_3$, and water, and then the organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether) to obtain a yellow solid (0.94 g, 86.4%). Molecular formula: $C_{24}H_{18}O_2S$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 3H), 7.23 – 7.18 (m, 5H), 7.14 – 7.08 (m, 5H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.28 (d, *J* = 6.8 Hz, 1H), 6.08 (s, 1H), 6.04 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.37, 145.70, 141.96, 141.59, 140.79, 132.81, 132.09, 131.24, 130.94, 129.41, 128.83, 128.51, 127.85. HRMS (m/z): calcd. for $[M+H]^+$ 371.1061, found 371.1100.

Synthesis of (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DPVBT). ((Z)-(1,2-diphenyl-)-(Z)-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))ethene (2.00 g, 4.6 mmol), 3-bromo-2,5-dimethylthiophene (2.01 g, 6.9 mmol), and potassium carbonate (1.32 g, 9.0 mmol) were dissolved in a mixed solution of 1,4-dioxane (60 mL). The reaction solution was stirred at room temperature under nitrogen for 30 min, and then Pd $(PPh_3)_4$ (265 mg, 0.23 mmol) was added. The resulting solution was heated at 80 °C for 16 h. After the reaction was completed, the mixture was poured into water and extracted 3 times with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether) to obtain a white solid (1.49 g, 78.3%). Molecular formula: $C_{26}H_{29}BO_2S$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.12 (m, 2H), 7.07 (m, 6H), 6.98 – 6.95 (m, 2H), 6.52 (s, 1H), 2.35 (s, 6H), 1.12 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.72, 141.13, 140.75, 135.04, 134.21, 130.05, 129.31, 128.10, 127.72, 126.78, 125.97, 83.56, 24.48, 15.12, 13.84. HRMS (m/z): calcd. for $[M+H]^+$ 417.2015, found 417.2063.

Synthesis of 2,5-dimethyl-3-(1,2,2-triphenylvinyl)thiophene (3a). (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.00 g, 4.8 mmol), bromobenzene (0.98 g, 6.2 mmol), and potassium carbonate (1.32 g, 9.6 mmol) were dissolved in a mixed solution of 1,4-dioxane (60 mL). The reaction

solution was stirred at room temperature under nitrogen for 30 min, and then Pd (PPh3)4 (277 mg, 0.24 mmol) was added. The resulting solution was heated at 80 °C for 16 h. After the reaction was completed, the mixture was poured into water and extracted 3 times with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether) to obtain a white solid (1.53g, 86.9%). Molecular formula: $C_{26}H_{22}S$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 9H), 7.06 (d, *J* = 4.0 Hz, 4H), 7.01 (d, *J* = 7.0 Hz, 2H), 6.27 (s, 1H), 2.31 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.93, 143.40, 142.79, 142.06, 139.41, 135.43, 134.92, 133.37, 131.54, 130.60, 128.22, 127.69, 127.59, 127,48, 126.49, 126.41, 126.32, 15.23, 13.92. HRMS (m/z): calcd. for $[M+H]^+$ 367.1476, found 367.1506.

Synthesis of 2,5-dimethyl-3-(1,2,2-triphenylvinyl)thiophene 1,1-dioxide (4a). A solution of m-chloroperbenzoic acid (m-CPBA) (1.86 g, 10.8 mmol) in 60 mL of CH_2Cl_2 was added over a period of 1 h to a stirred solution of 2,5-dimethyl-3-(1,2,2-triphenylvinyl)thiophene (1.00 g, 2.7 mmol) in 60 mL of CH_2Cl_2. After the addition, the mixture was stirred at room temperature for 24 h. After the reaction was completed, the mixture washed with aqueous $NaHSO_3$, $NaHCO_3$, and water, and then the organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether) to obtain a white solid (0.91 g, 84.2%). Molecular formula: $C_{26}H_{12}O_2S$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.18 (dd, *J* = 3.6, 2.8 Hz, 5H), 7.16 (s, 1H), 7.14 – 7.12 (m, 2H), 7.05 – 7.01 (m, 4H), 5.97 (s, 1H), 2.04 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.78, 142.11, 141.62, 138.65, 137.84, 136.44, 133.47, 131.77, 131.45, 130.65, 130.10, 128.47, 128.43, 128.37, 127.91, 127.66, 127.63, 127.01, 9.09, 8.09. HRMS (m/z): calcd. for $[M+H]^+$ 399.1374, found 399.1413.

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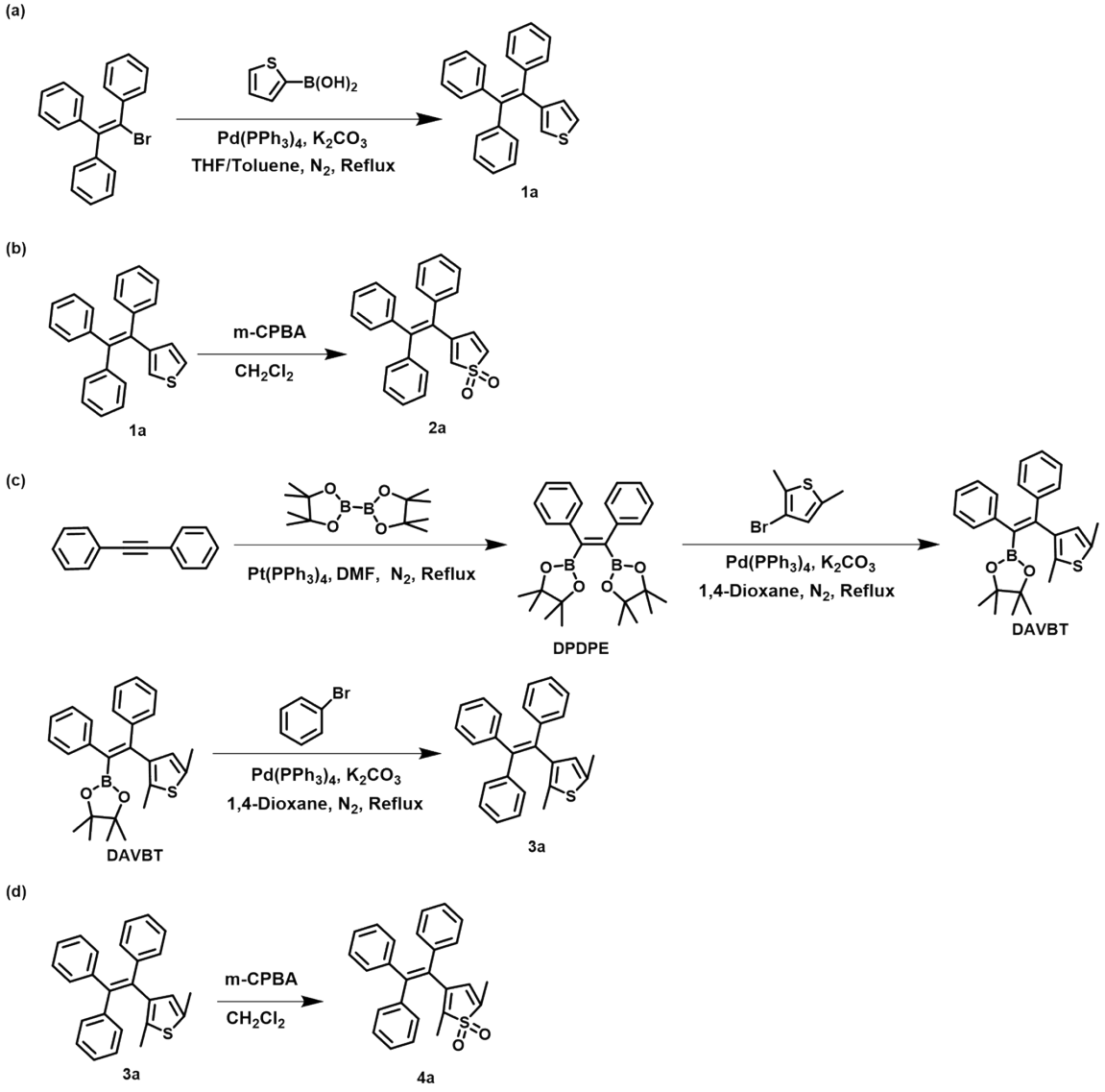
2. Computational Details

All the calculations were performed with density functional theory (DFT) and time-dependent density functional theory (TDDFT) implemented in Gaussian 09 program package.[1] The ground state equilibrium geometries and the normal modes of vibration of the single-molecules of 1a, 2a, 3a and 4a were computed using density functional theory (DFT) with the hybrid M062X functional at 6-311+G(d,p) level.[2] NBO analysis of all the four compounds and their photocyclized products were performed with the same basis set to the optimization.

3. Supplementary Schemes and Figures



Scheme S1. Synthesis routes of 1a, 2a, 3a and 4a.

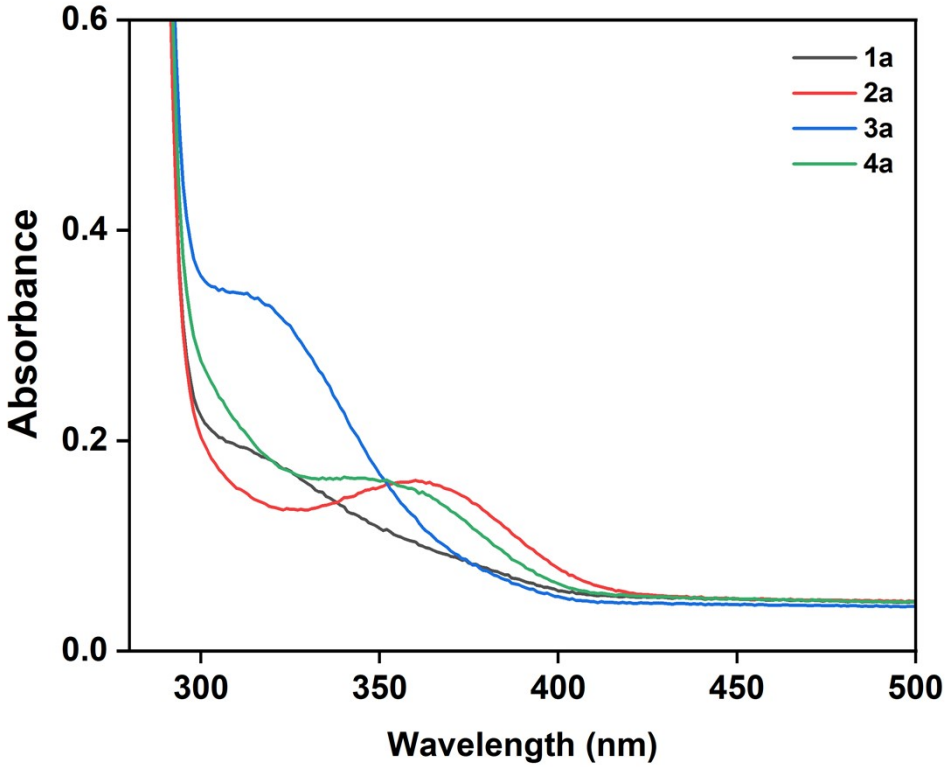


Figure S1. UV-visible spectra of 1a, 2a ,3a and 4a in THF at 25.0 μM.

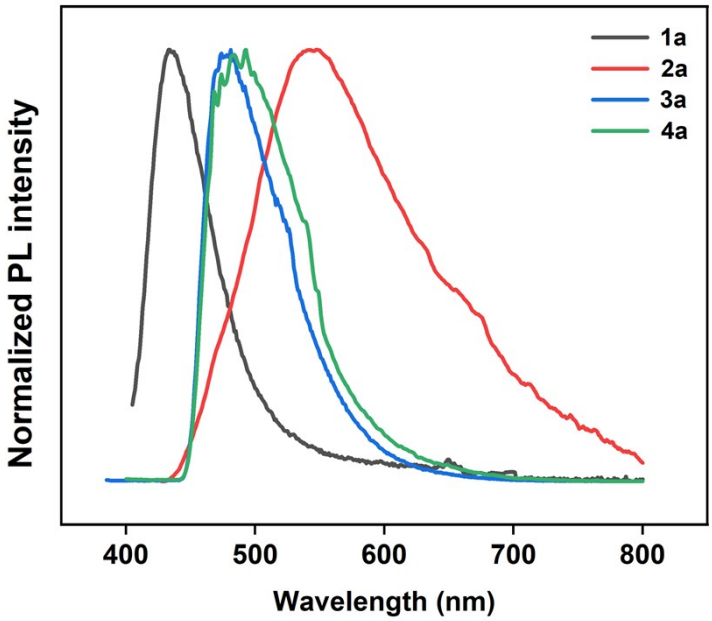


Figure S2. Normalized PL spectra 1a, 2a, 3a and 4a in solid under transient UV irradiation.

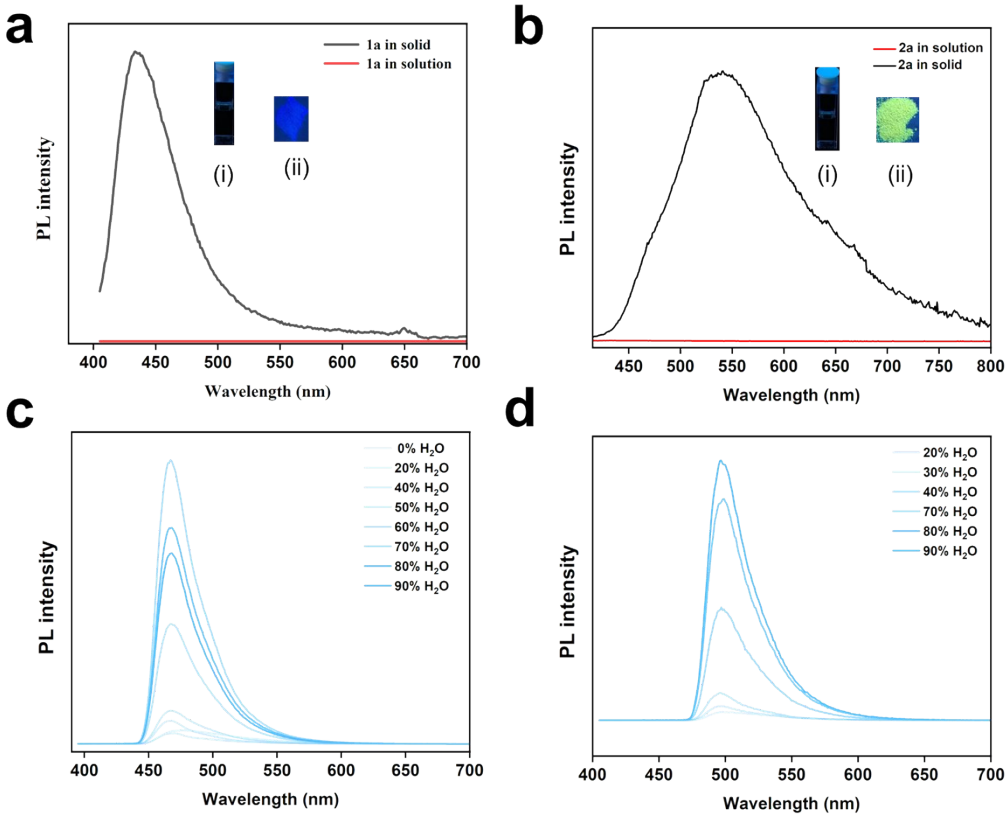


Figure S3. (a-b) PL spectra and images of 1a (a) and 2a (b) in solution and in solid state. (c-d) PL spectra of 1a and 2a in THF (50.0 mM) within creasing amounts of water from 0% to 90%.

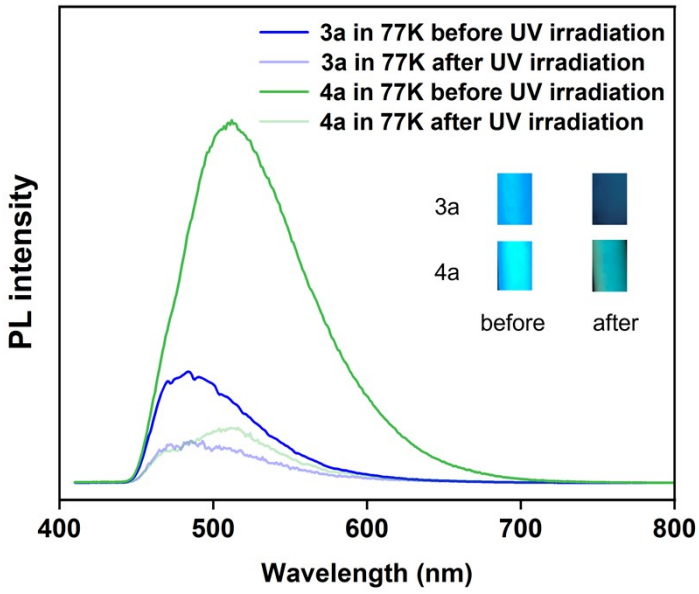


Figure S4. PL spectra of 3a and 4a in THF(50 μM) at 77 K before and after irradiation.

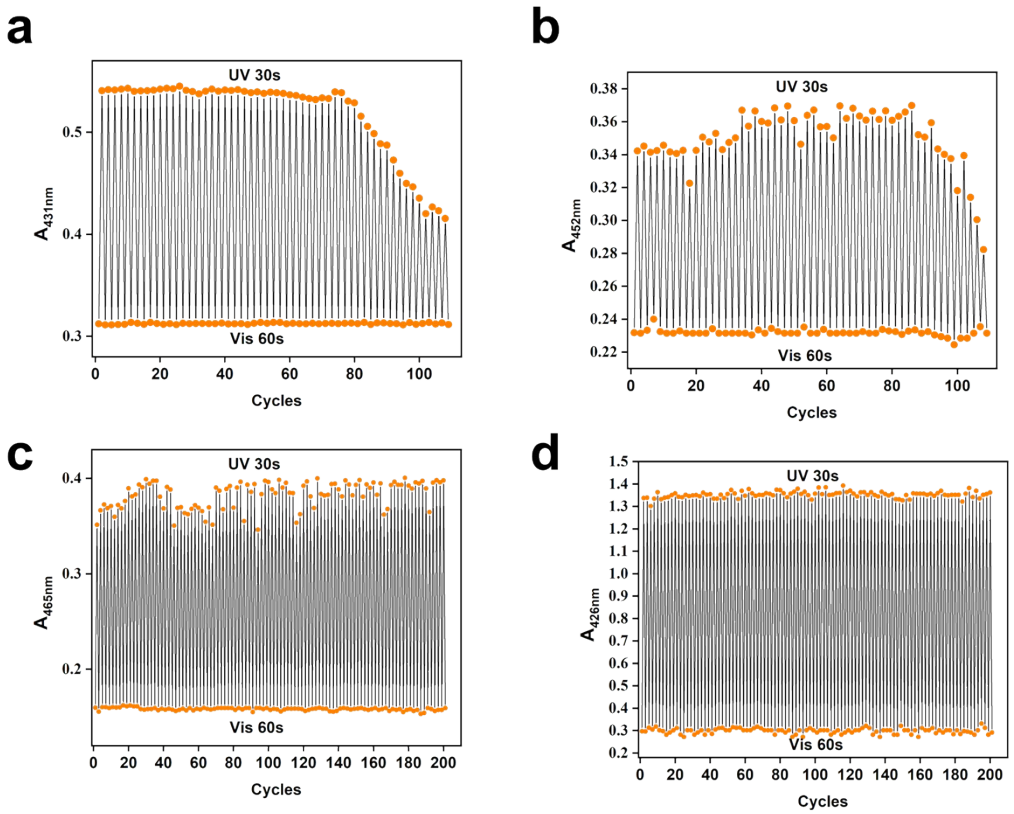


Figure S5. Photochromic recycles of 1a (a), 2a (b), 3a (c) and 4a (d) in film as a function of exposure to UV-light (365 nm) and visible-light (440 nm) respectively.

4. Supplementary Tables

Table S1. Optical properties of the four compounds in solution, film and solid.

	solution				film		solid				
	λ_{ab}[a] (nm)	λ_{ab}[b] (nm)	$\Phi_{o\text{-}c}$	$\Phi_{c\text{-}o}$	λ_{ab}[a] (nm)	λ_{ab}[b] (nm)	λ_{ab}[a] (nm)	λ_{ab}[b] (nm)	λ_{fl}[a] (nm)	λ_{fl}[b] (nm)	Φ(%)
1a	311	462	0.0372	0.0141	372	452	384	506	435	424	3.7
2a	362	448	0.0753	0.0284	387	454	430	488	549	541	11.4
3a	325	469	0.0380	0.0203	362	465	366	501			
4a	365	454	0.4506	0.2759	392	458	366	482			

λ_{ab} and λ_{fl} represents absorption maximum and fluorescence maximum respectively.

[a] The open form. [b] The closed form.

Table S2. Compositions of natural transition orbitals of cyclized forms 1a, 2a, 3a and 4a for $S_0 \rightarrow S_1$ state.

Compounds	NTOs	Contribution (%)
1a	HOMO→LUMO	100
2a	HOMO→LUMO	100
3a	HOMO→LUMO	100
4a	HOMO→LUMO	100

Table S3. Contribution ratios of different groups to natural transition orbitals of 1a，2a, 3a and 4a.

Compounds	Group	Contribution to HOMO (%)	Contribution to LUMO (%)
1a	ethene	18.09	16.24
	phenyl	37.07	48.35
	thiophene	39.27	30.70
	S	12.88	2.52
2a	ethene	19.32	18.49
	phenyl	50.13	42.21
	thiophene dioxide	23.33	35.20
	S	0.15	0.65
3a	ethene	15.90	13.11
	phenyl	48.98	49.79
	2,5-dimethylthiophene	35.11	37.11
	S	12.23	6.64
4a	ethene	15.97	13.97
	phenyl	55.12	54.19
	2,5-dimethylthiophene dioxide	18.93	26.57
	S	0.23	0.56

5. NMR and MS Spectra of Compounds

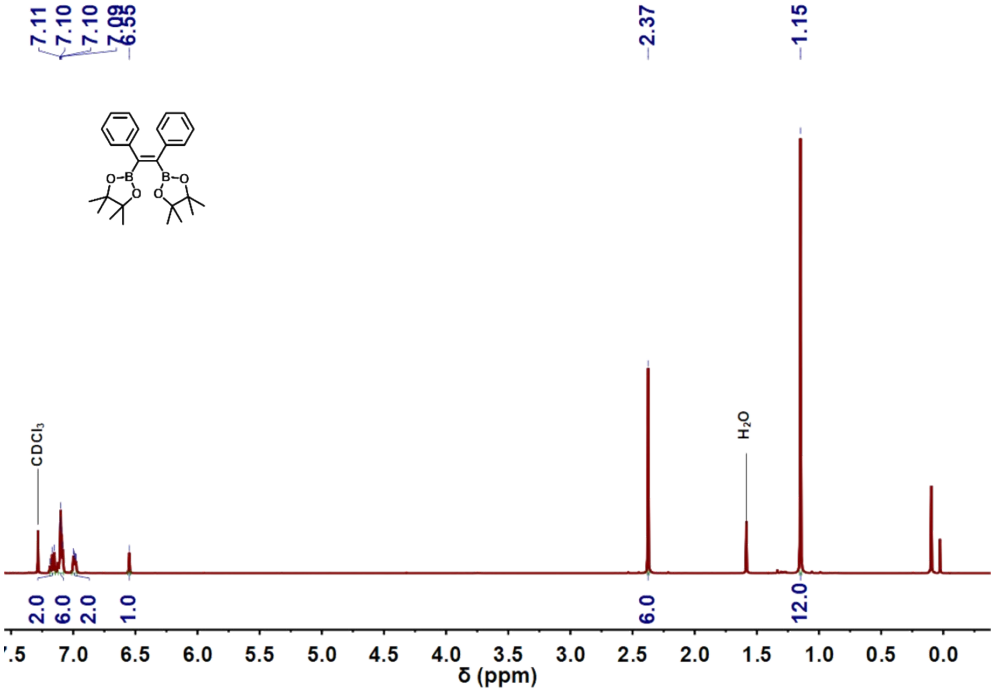


Figure S6. ^{1}H NMR spectra of ((Z)-(1,2-diphenyl-)-(Z)-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))ethene (DPDBE) in $CDCl_3$

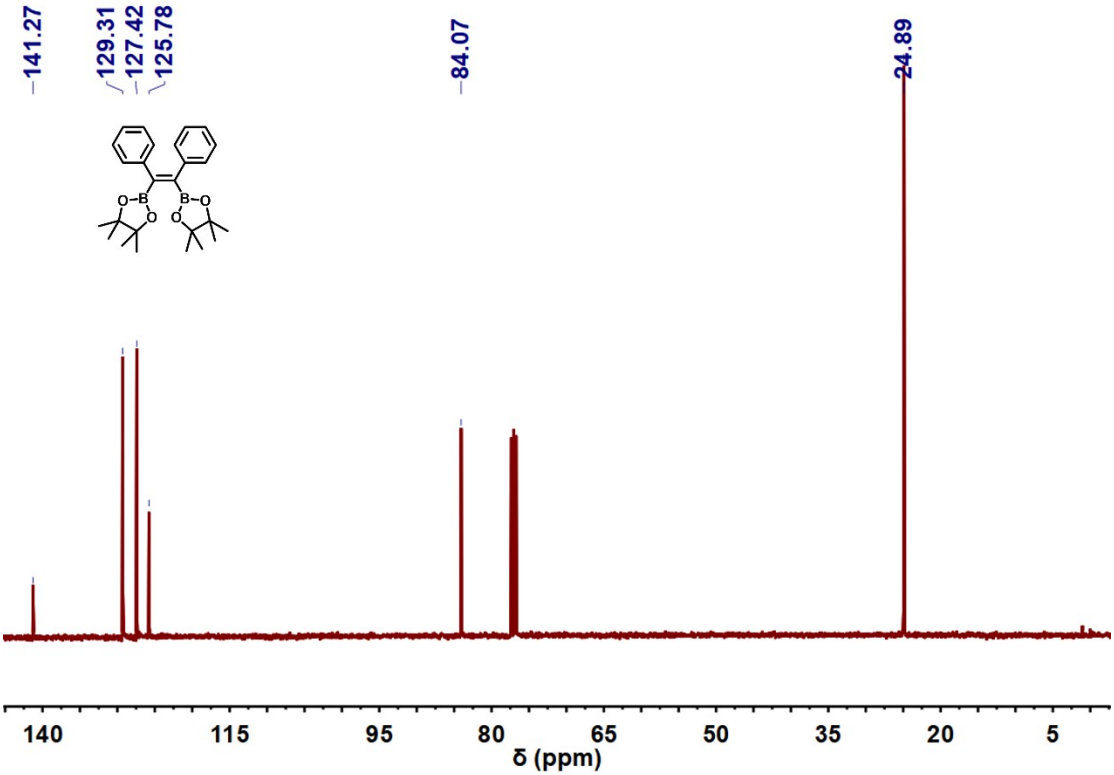


Figure S7. ^{13}C NMR spectra of ((Z)-(1,2-diphenyl-)-(Z)-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))ethene (DPDBE) in $CDCl_3$

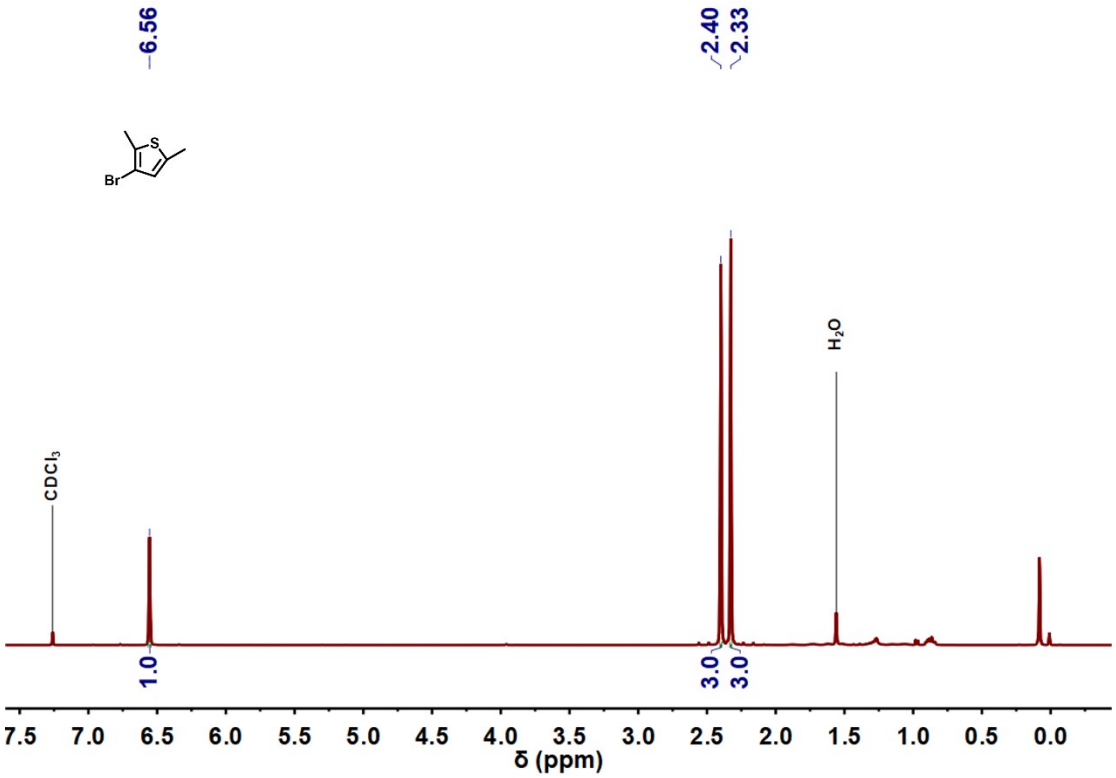


Figure S8. ^{1}H NMR spectra of 3-bromo-2,5-dimethylthiophene (3-BDMT) in CDCl3

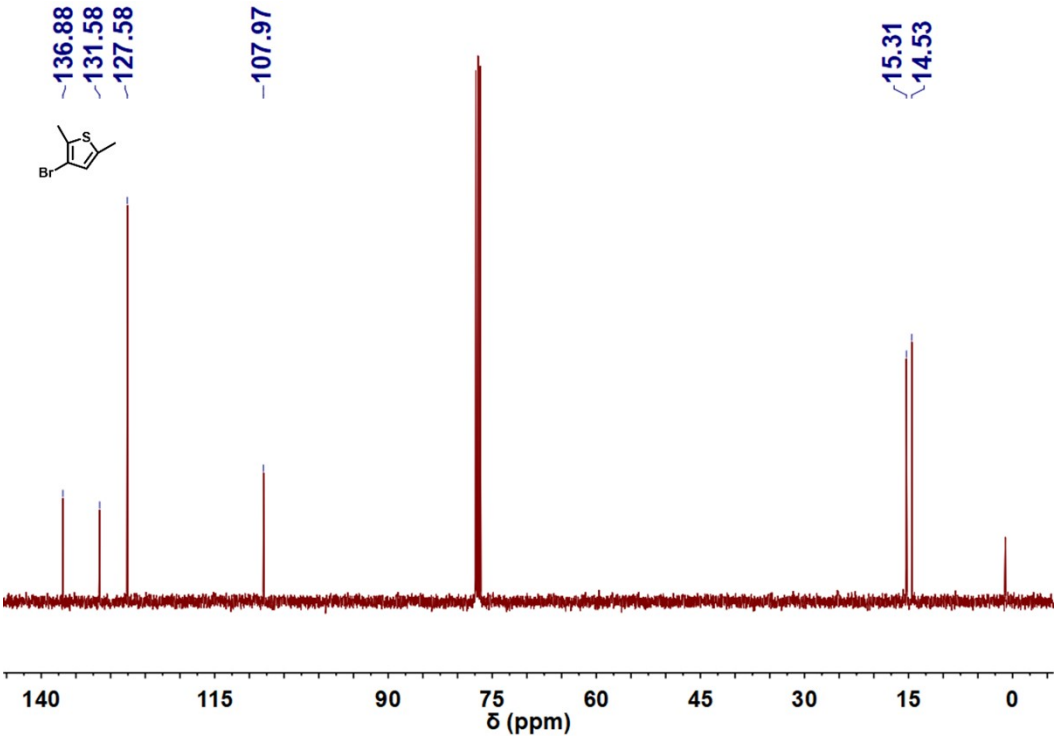


Figure S9. ^{13}C NMR spectra of 3-bromo-2,5-dimethylthiophene (3-BDMT) in $CDCl_3$

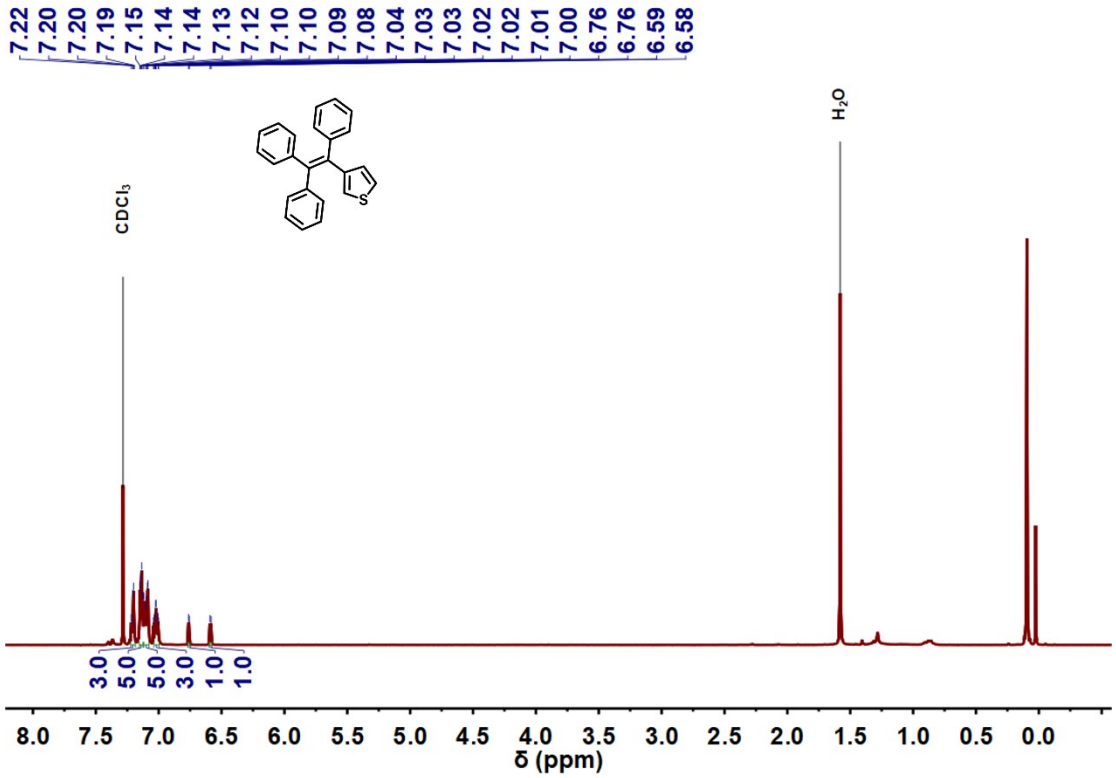


Figure S10. ^{1}H NMR spectra of 3-(1,2,2-TriPhenylVinyl)Thiophene (3-TPVT) in $CDCl_3$

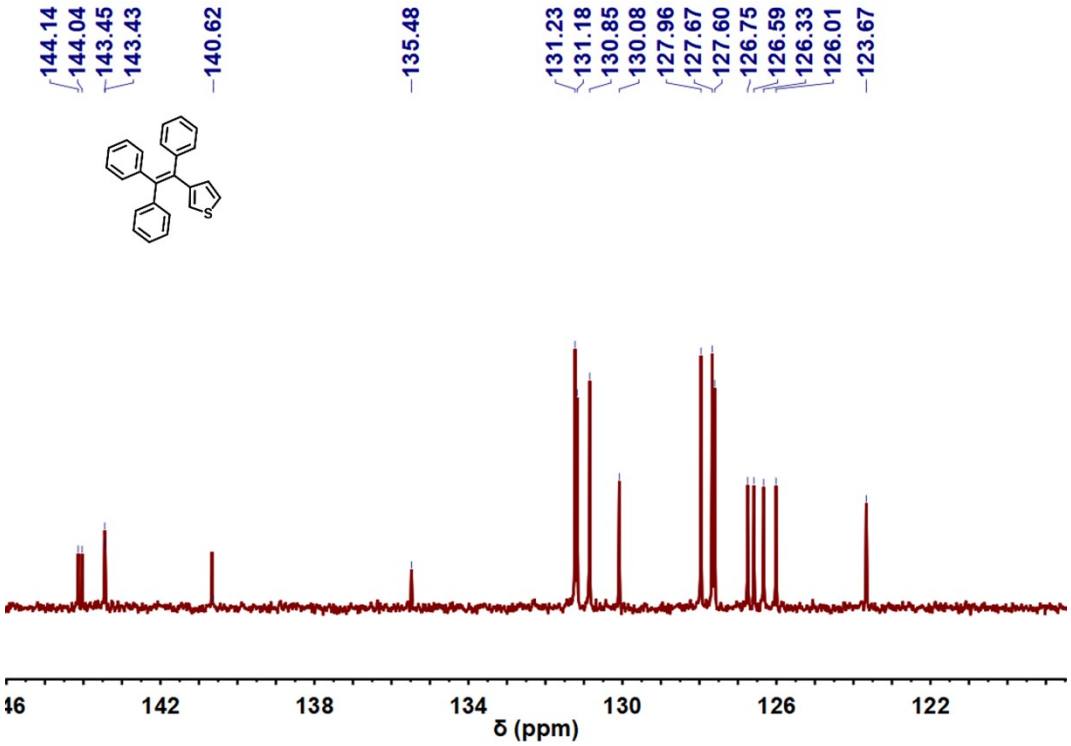


Figure S11. ^{13}C NMR spectra of 3-(1,2,2-TriPhenylVinyl)Thiophene (3-TPVT) in $CDCl_3$

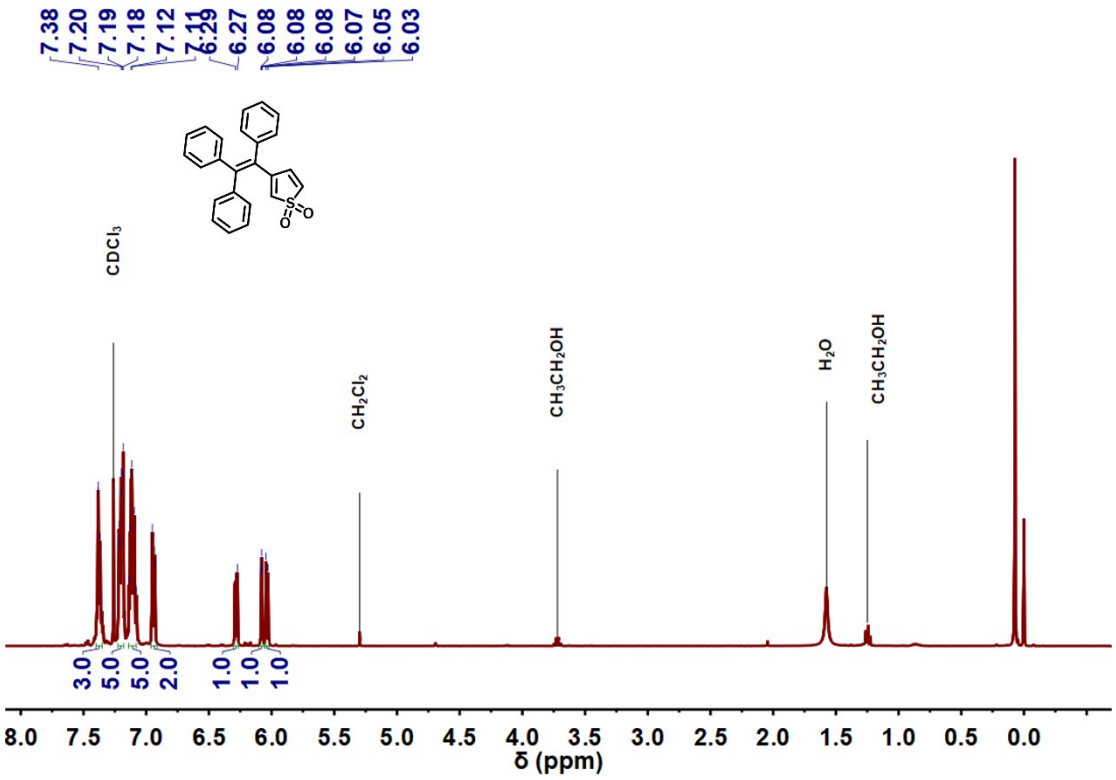


Figure S12. ^{1}H NMR spectra of 3-(1,2,2-triphenylvinyl)thiophene 1,1-dioxide (3-TPVTO) in $CDCl_3$

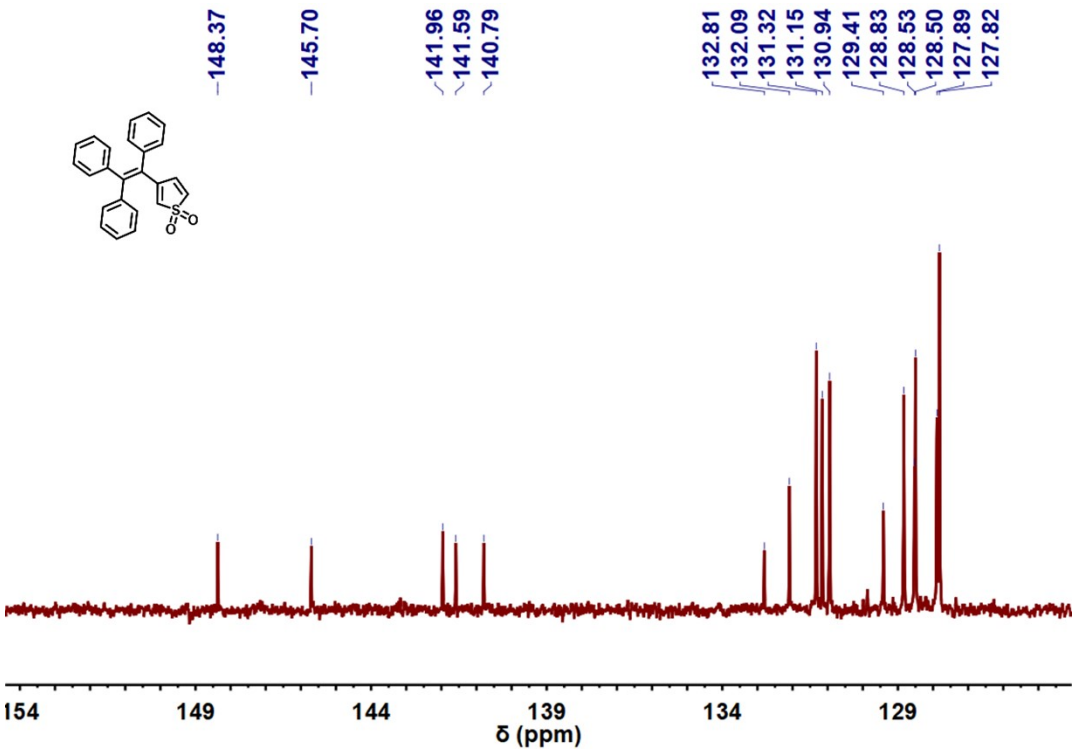


Figure S13. ^{13}C NMR spectra of 3-(1,2,2-triphenylvinyl)thiophene 1,1-dioxide (3-TPVTO) in $CDCl_3$

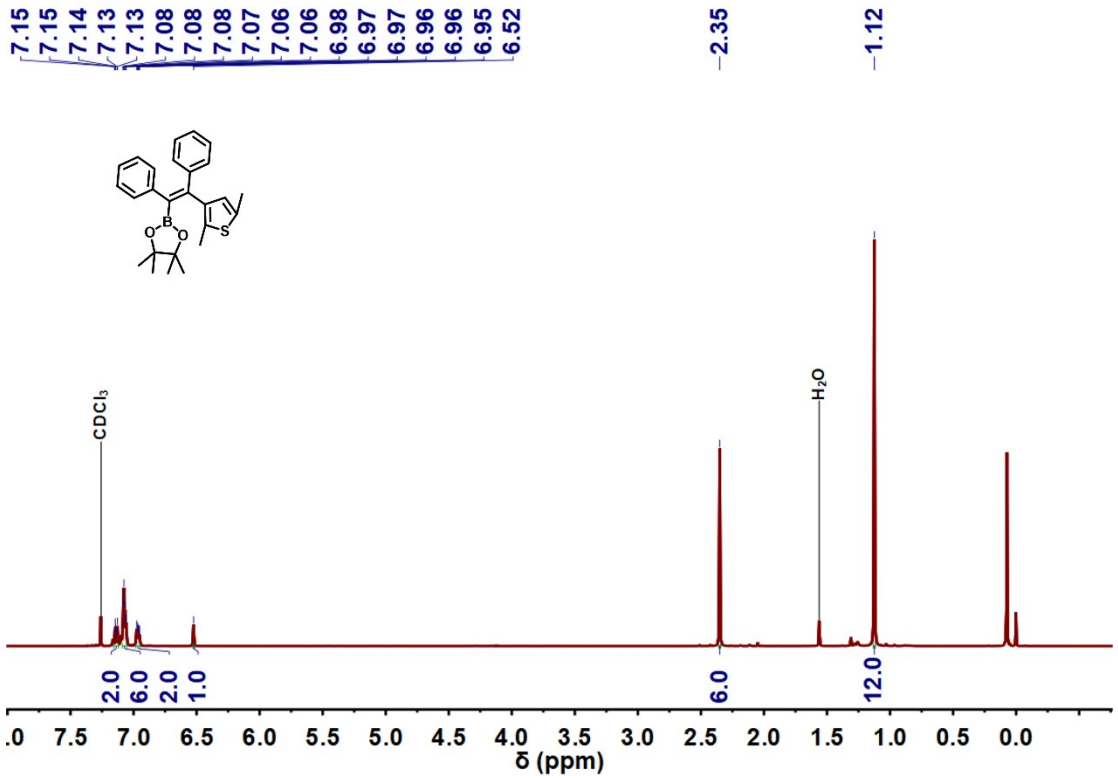


Figure S14. ^{1}H NMR spectra of (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DPVBT) in $CDCl_3$

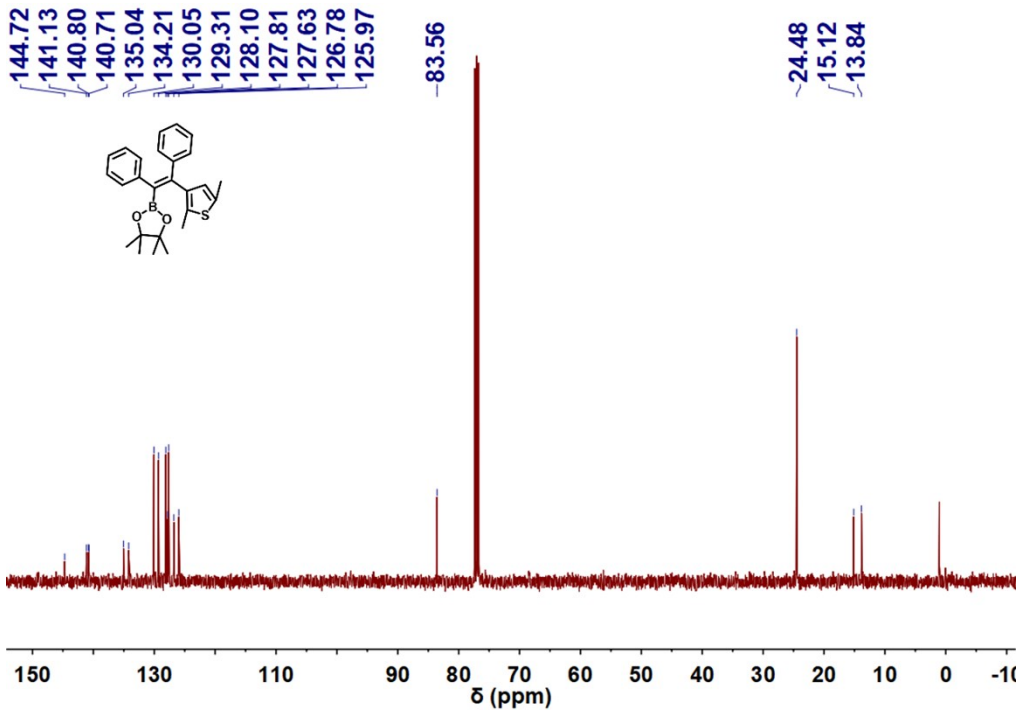


Figure S15. ^{13}C NMR spectra of (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DPVBT) in

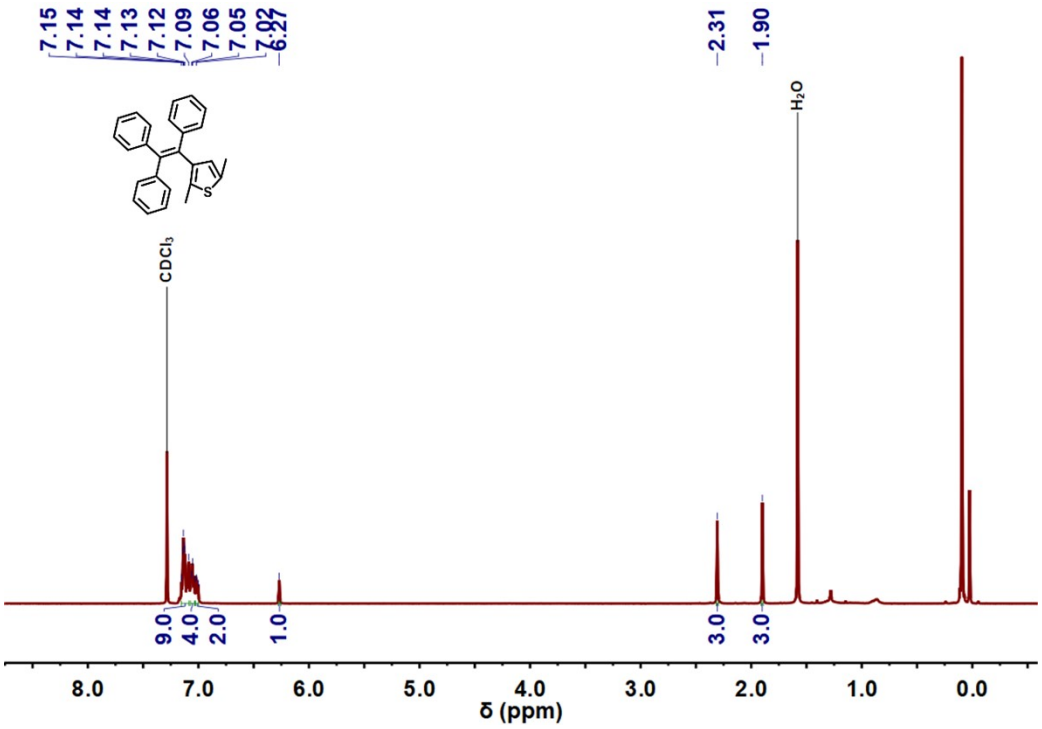


Figure S16. ^{1}H NMR spectra of 2,5-dimethyl-3-(1,2,2-triphenylvinyl)thiophene (3-TPVMT) in $CDCl_3$

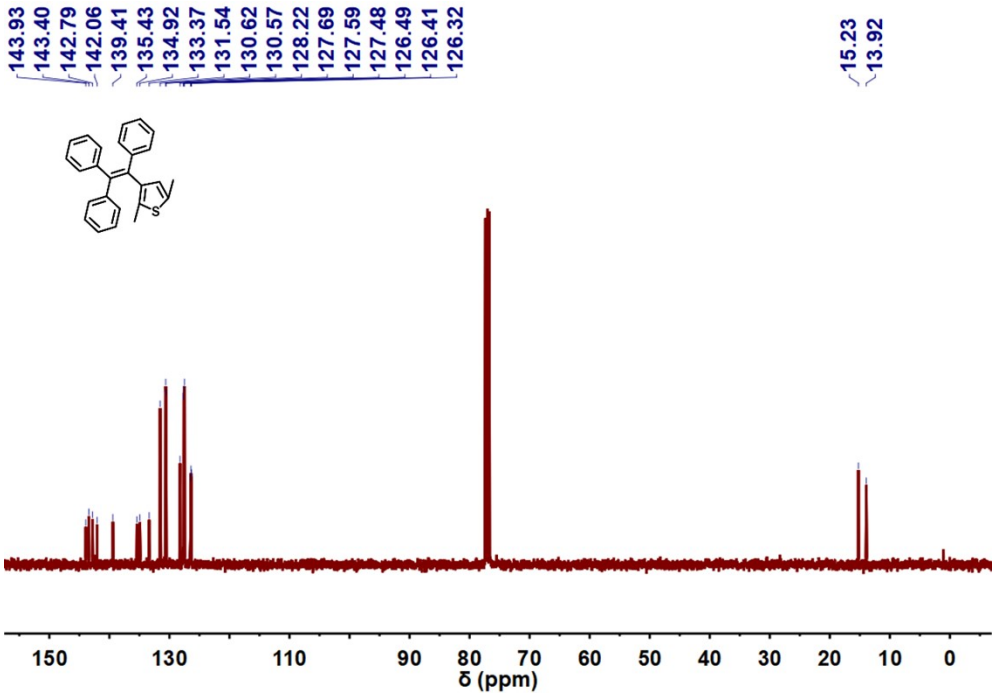


Figure S17. ^{13}C NMR spectra of 2,5-dimethyl-3-(1,2,2-triphenylvinyl)thiophene (3-TPVMT) in $CDCl_3$

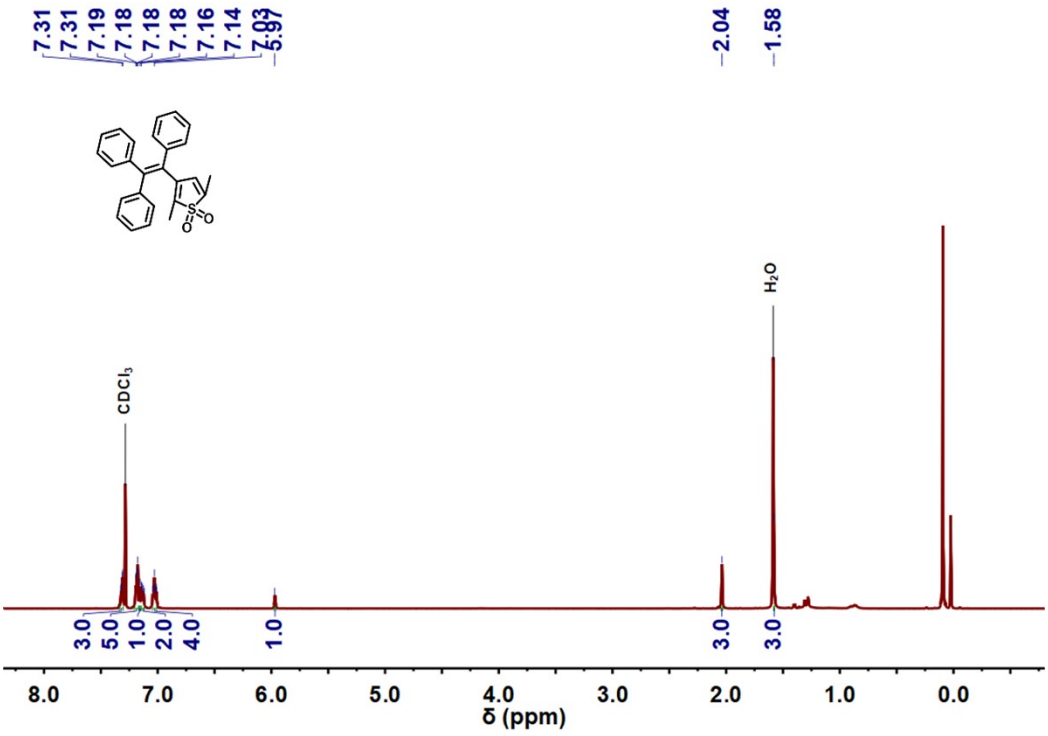


Figure S18. ^{1}H NMR spectra of 2,5-dimethyl-3-(1,2,2-triphenylvinyl)thiophene 1,1-dioxide (3-TPVMTO) in CDCl2,5-dimethyl-3-(1,2,2-triphenylvinyl)thiophene 1,1-dioxide (3-TPVMTO) in CDCl3

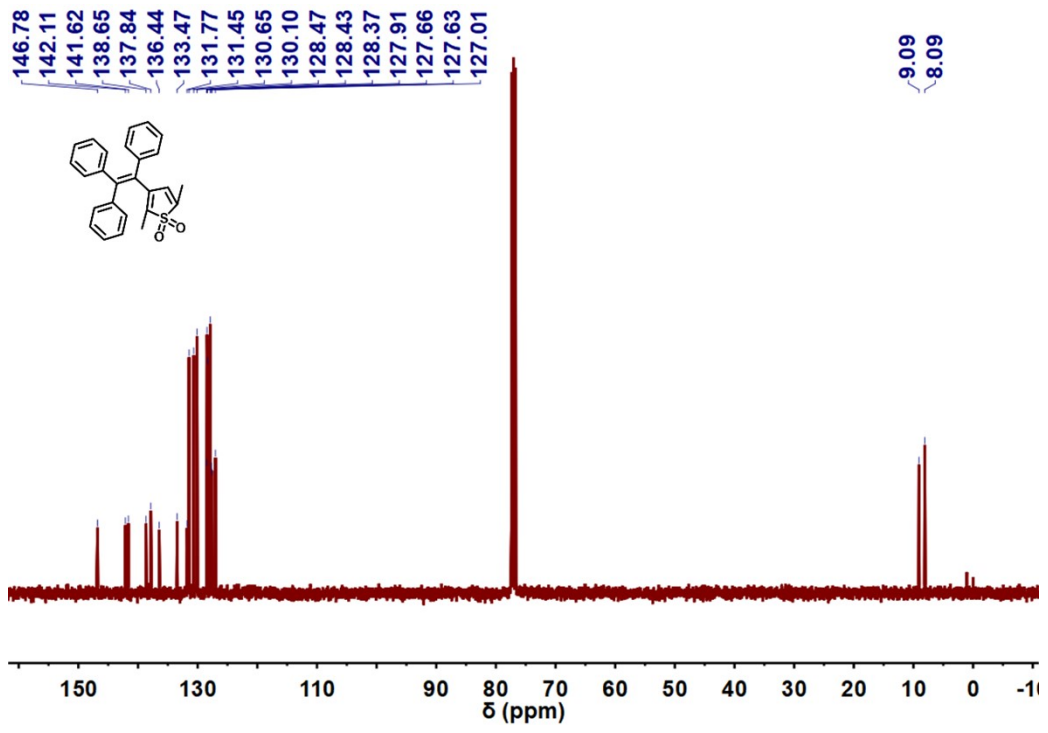


Figure S19. ^{13}C NMR spectra of 2,5-dimethyl-3-(1,2,2-triphenylvinyl)thiophene 1,1-dioxide (3-TPVMTO) in $CDCl_3$

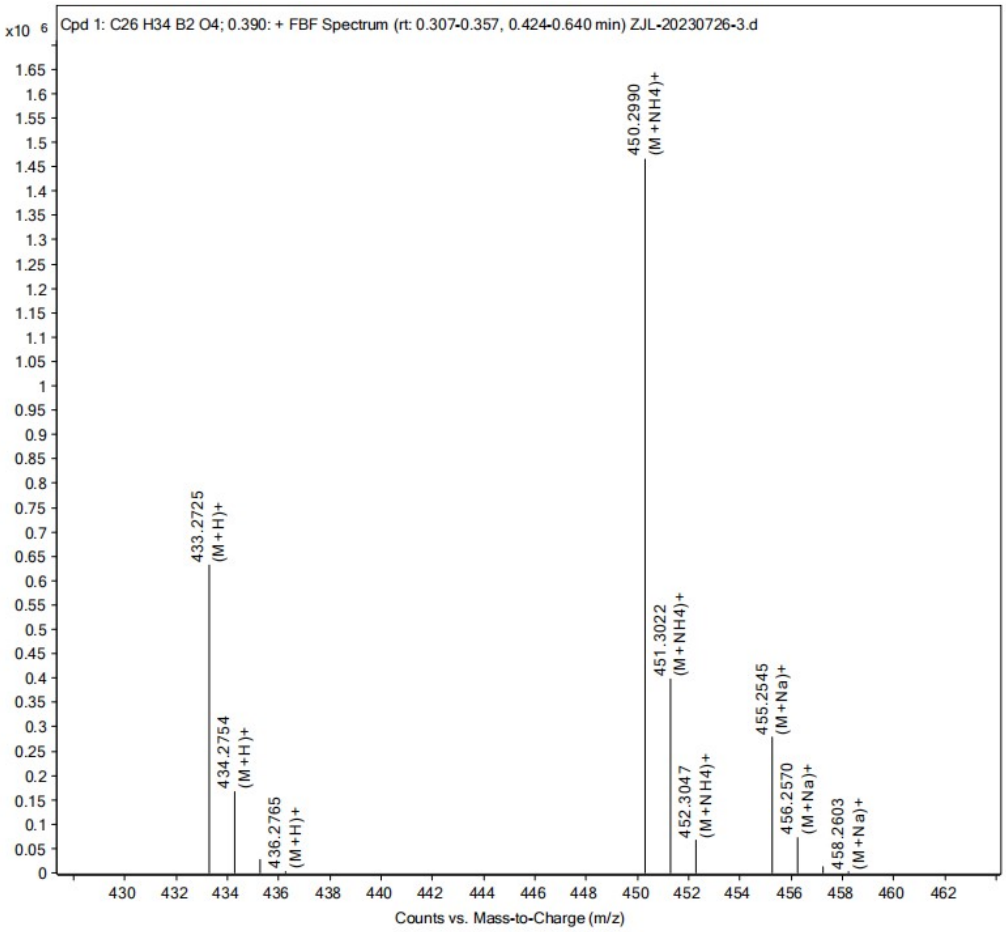


Figure S20. ^{1}H NMR spectra of ((Z)-(1,2-diphenyl-)-(Z)-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))ethene (DPDBE)

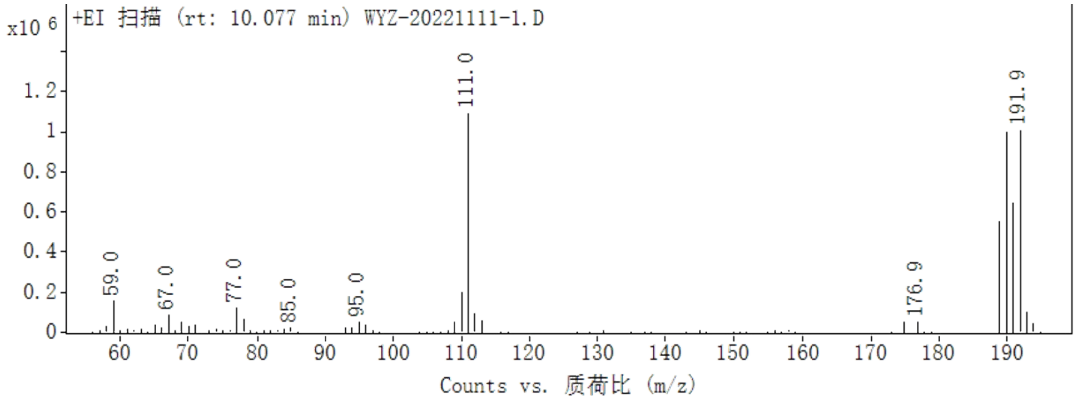


Figure S21. ^{13}C NMR spectra of 3-bromo-2,5-dimethylthiophene (3-BDMT)

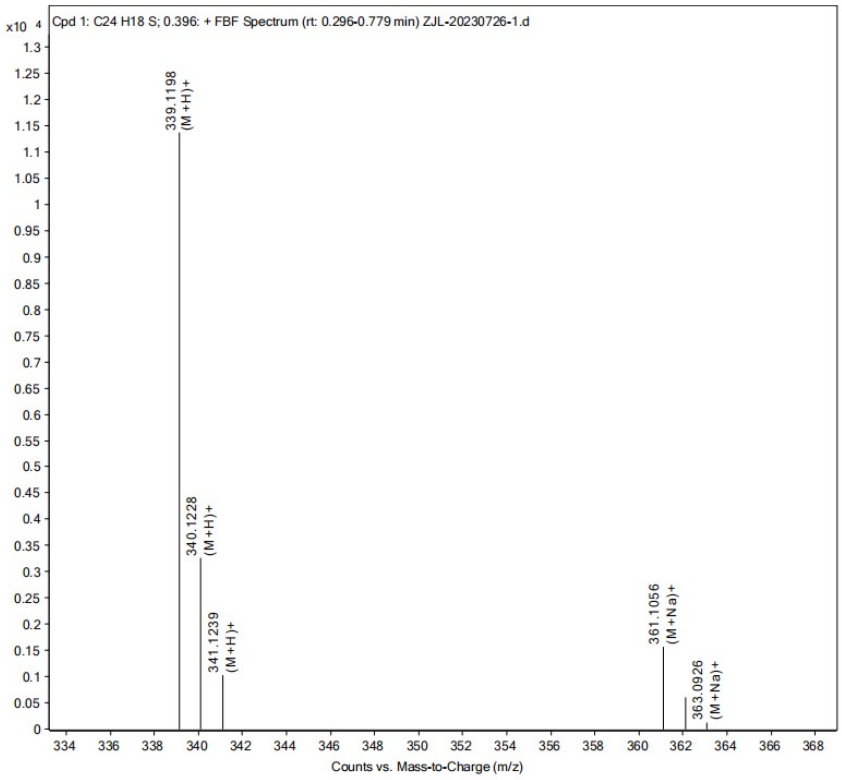


Figure S22. ^{1}H NMR spectra of 3-(1,2,2-TriPhenylVinyl)Thiophene (3-TPVT)

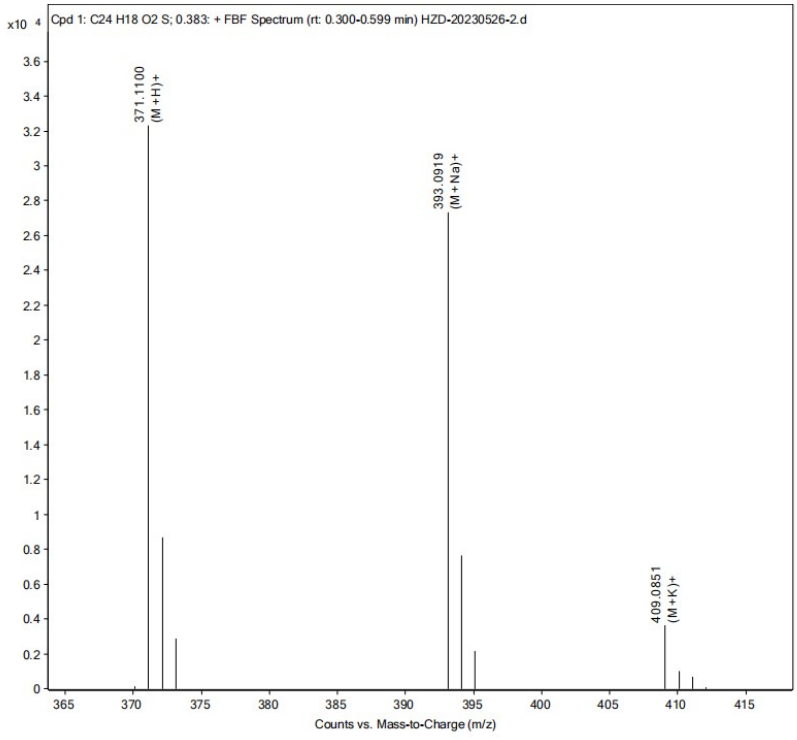


Figure S23. ^{13}C NMR spectra of 3-(1,2,2-triphenylvinyl)thiophene 1,1-dioxide (3-TPVTO)

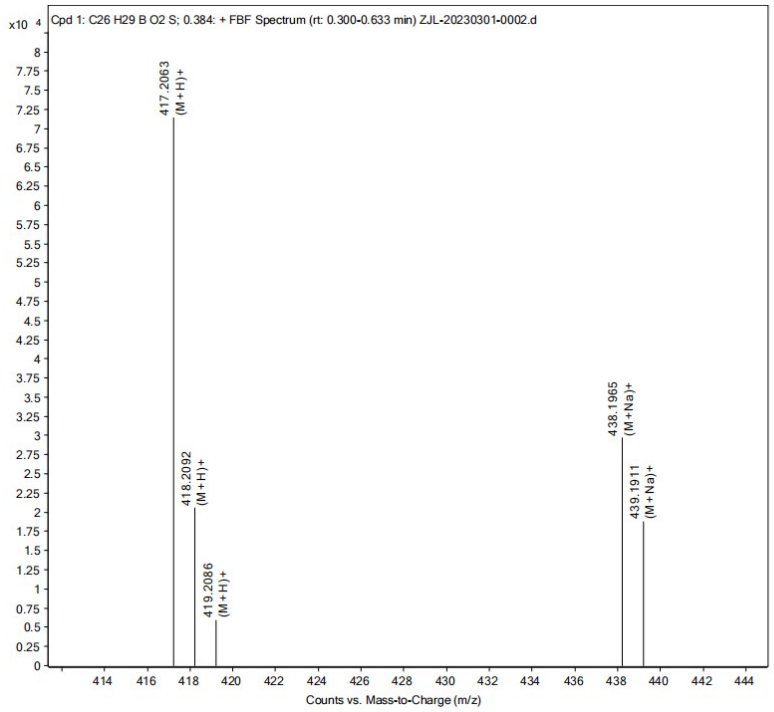


Figure S24. ^{1}H NMR spectra of (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DPVBT)

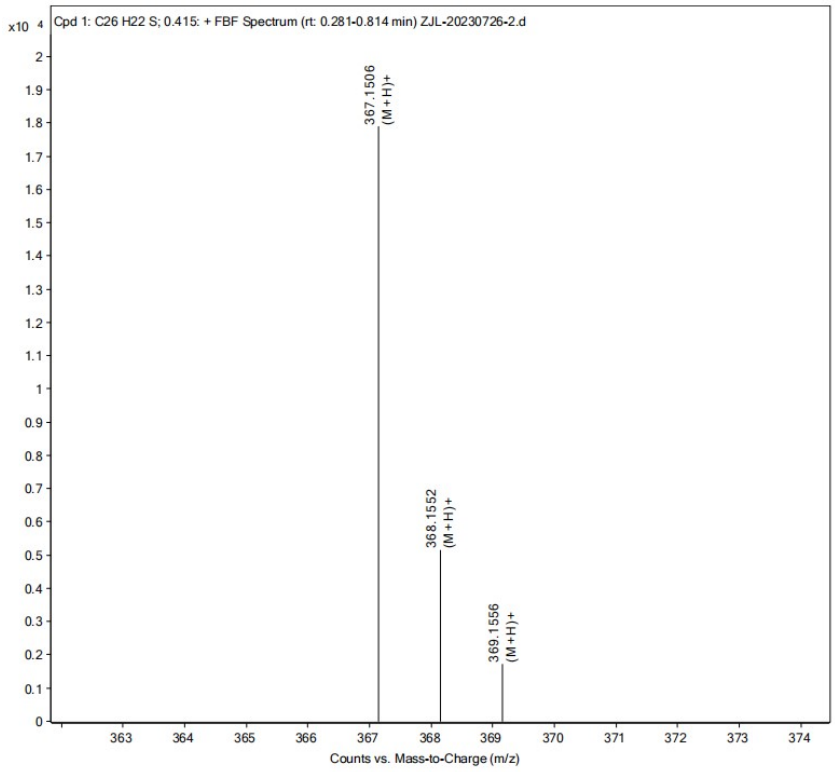


Figure S25. ^{13}C NMR spectra of 2,5-dimethyl-3-(1,2,2-triphenylvinyl)thiophene (3-TPVMT)

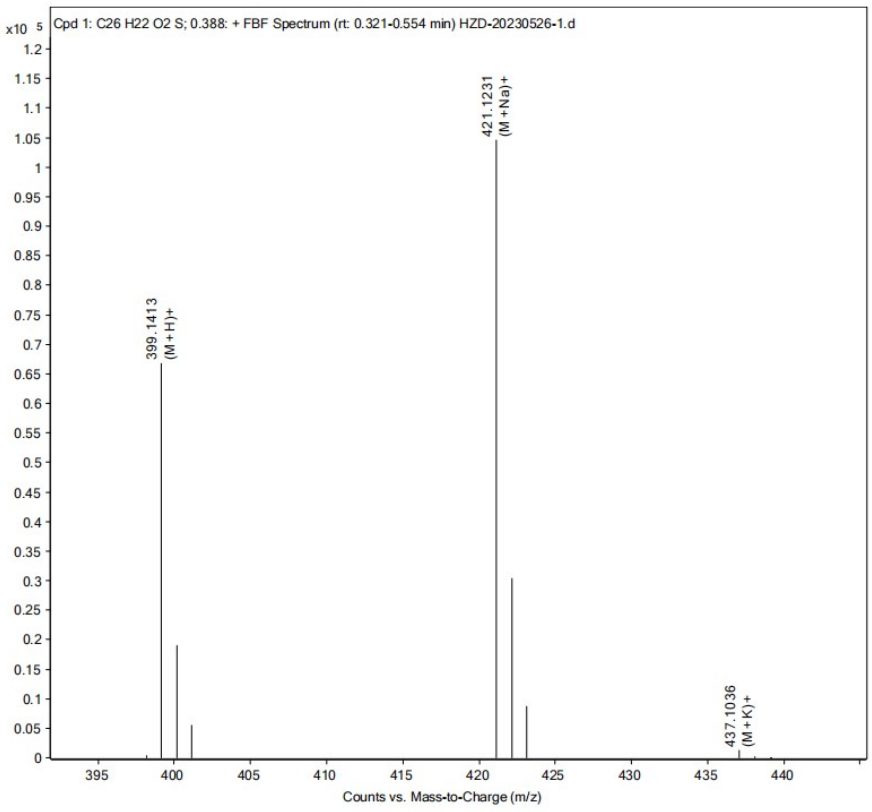


Figure S26 Mass spectrum of 2,5-dimethyl-3-(1,2,2-triphenylvinyl)thiophene 1,1-dioxide (3-TPVMTO)