Electronic Supplementary Information *for*

Multicolor AIE-active Photoswitches with Improved Fatigue Resistance by Introducing Asymmetric Photoactive Units

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1. Experimental Section

Synthesis of (Z)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (DPDBE). A mixture of tetra (Triphenylphosphine) platinum ($Pt(PPh_3)_4$) (12.44 mg, 0.01 mmol), bis (pinacolato) diboron (5.08 g, 20 mmol) and 1,2-diphenylacetylene (1.78 g, 10 mmol) was added to DMF (40 mL) under the protection of N_2, and the mixture was heated at 110 ° C for 24 hours. After the reaction is completed, the mixture is poured into water and extracted three times with ethyl acetate, followed by drying the organic layer with $MgSO_4$. Remove the solvent under reduced pressure. The final crude product is recrystallized in ethanol to obtain a white solid with a yield of 68%. Molecular formula: $C_{26}H_{34}B_2O_4$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.02 (m, 6H), 6.96 – 6.94 (d, J = 8 Hz, 4H), 1.33 (s, 24H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.28, 129.32, 127.43, 125.79, 84.08, 24.89; HRMS (ESI) m/z: $[M+H]^+$, 433.2735 (calcd. for $C_{26}H_{34}B_2O_4$, 432.2643).

Synthesis of 3-bromo-2,5-dimethylthiophene. Add 2,5-dimethylthiophene (1.09 g, 9.71 mmol) and NBS (1.73 g, 9.72 mmol) into glacial acetic acid (20 mL) solution, stir overnight, then pour it into water and stir, adjust the PH to neutral with saturated Na_2CO_3 aqueous solution, add dichloromethane, separate the organic layer, wash it three times with water, dry it with $MgSO_4$, concentrate it under reduced pressure and purify it by silica gel Column chromatography to obtain a colorless and transparent oily liquid with a yield of 80%. Molecular formula: C_6H_7BrS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 2.42 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.88, 131.58, 127.59, 107.97, 15.31, 14.53; HRMS (ESI) m/z: $[M+H]^+$, 191.9 (calcd. for C_6H_7BrS, 189.9452)

Synthesis of (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DDTDE). A mixture of (Z)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (DPDBE) (4.32 g, 10 mmol), 3-bromo-2,5-dimethylthiophene (1.91 g, 10 mmol) and 2M cesium carbonate (10 mL), $Pd(PPh_3)_4$ (17.33 mg, 0.015 mmol) were added in 1,4-dioxane (30 mL) under the protection of N_2, and then the mixture was heated at 100 °C for 8 h. After the reaction was completed, the mixture was poured into water and extracted three times with

dichloromethane, and then the organic layer was dried by $MgSO_4$. The solvent was removed under reduced pressure and purified by silica gel column chromatography. The final crude product was recrystallized in ethanol to produce a white solid with a yield of 80%. Molecular formula: $C_{26}H_{29}BO_2S$. ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.13 (d, J = 8.0 Hz, 2H), 7.10 – 7.06 (m, 6H), 6.98 – 6.96 (m, 2H), 6.53 (s, 1H), 2.36 (s, 6H), 1.13 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.73, 141.14, 140.81, 140.72, 135.03, 134.20, 130.06, 129.31, 128.10, 127.82, 127.64, 126.78, 125.97, 83.56, 24.48, 15.12, 13.84; HRMS (ESI) m/z: $[M+H]^+$, 417.2046 (calcd. for $C_{26}H_{29}BO_2S$, 416.1981).

Synthesis of (Z)-3-(1,2-diphenyl-2-(thiophen-3-yl)vinyl)-2,5-dimethylthiophene (DPTDE). A mixture of (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.16 g, 10 mmol), 3-bromothiophene (2.44 g, 15 mmol) and 2M cesium carbonate (10 mL), $Pd(PPh_3)_4$ (17.33 mg, 0.015 mmol) were added in 1,4-dioxane (30 mL) under the protection of N_2, and then the mixture was heated at 100 °C for 8 h. After the reaction was completed, the mixture was poured into water and extracted three times with dichloromethane, and then the organic layer was dried by $MgSO_4$. The solvent was removed under reduced pressure and purified by silica gel column chromatography. The final crude product was recrystallized in ethanol to produce a white solid with a yield of 40.2%. Molecular formula: $C_{24}H_{20}S_2$. ^1H NMR (400 MHz, $CDCl_3$): δ 7.15 – 7.12 (m, 5H), 7.07 – 7.04 (m, 4H), 6.98 – 6.96 (d, J = 8 Hz, 2H), 6.78 – 6.77 (d, J = 4 Hz, 1H), 6.62 – 6.61 (d, J = 4 Hz, 1H), 6.30 (s, 1H), 2.34 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.52, 143.19, 142.49, 139.53, 136.67, 135.41, 134.78, 133.76, 131.35, 130.54, 129.29, 127.96, 127.71, 127.53, 126.66, 126.23, 125.59, 123.43, 15.30, 13.62; HRMS (ESI) m/z: $[M+H]^+$, 373.1068 (calcd. for $C_{24}H_{20}S_2$, 372.1006).

Synthesis of (Z)-1,2-bis(2,5-dimethylthiophen-3-yl)-1,2-diphenylethene (DPDPE). (Z)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (DPDBE) (4.32 g, 10 mmol), 3-bromo-2,5-dimethylthiophene (3.82 g, 20 mmol) and 2M cesium carbonate (10 mL), $Pd(PPh_3)_4$ (17.33 mg, 0.015 mmol) were added in 1,4-dioxane (30 mL) under the protection of N_2, and then the mixture was heated at 100 °C for 8 h. After the reaction was completed, the mixture was poured into

water and extracted three times with dichloromethane, and then the organic layer was dried by $MgSO_4$. The solvent was removed under reduced pressure and purified by silica gel column chromatography. The final crude product was recrystallized in ethanol to produce a white solid with a yield of 30.5%. Molecular formula: $C_{26}H_{24}S_2$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.07 (m, 6H), 7.01 – 6.99 (d, J = 4 Hz, 4H), 6.16 (s, 2H), 2.28 (s, 6H), 1.91 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.73, 139.61, 136.39, 134.14, 133.96, 130.91, 128.16, 127.59, 126.25, 15.17, 14.16; HRMS (ESI) m/z: $[M+H]^+$, 401.1388 (calcd. for $C_{26}H_{24}S_2$, 400.1319).

Synthesis of (Z)-3-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)benzo[b]thiophene (DPDBTE). A mixture of (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.16 g, 10 mmol), 3-bromobenzothiophene (3.20 g, 15 mmol) and 2M cesium carbonate (10 mL), $Pd(PPh_3)_4$ (17.33 mg, 0.015 mmol) were added in 1,4-dioxane (30 mL) under the protection of N_2, and then the mixture was heated at 100 °C for 8 h. After the reaction was completed, the mixture was poured into water and extracted three times with dichloromethane, and then the organic layer was dried by $MgSO_4$. The solvent was removed under reduced pressure and purified by silica gel column chromatography. The final crude product was recrystallized in ethanol to produce a white solid with a yield of 42.5%. Molecular formula: $C_{28}H_{22}S_2$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.76 (d, J = 8 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.15 – 7.08 (m, 12H), 6.21 (s, 1H), 2.21 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.28, 141.78, 139.79, 139.66, 138.48, 138.33, 137.58, 135.62, 134.73, 133.66, 130.83, 127.98, 127.82, 127.77, 126.92, 126.72, 126.58, 123.71, 123.63, 123.50, 122.48, 15.12, 14.12; HRMS (ESI) m/z: $[M+H]^+$, 423.1229 (calcd. for $C_{28}H_{22}S_2$, 422.1163).

Synthesis of (Z)-4-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)thiophene-2-carbaldehyde (DPDTCE). A mixture of (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.16 g, 10 mmol), 4-Bromothiophene-2 formaldehyde (2.86 g, 15 mmol) and 2M cesium carbonate (10 mL), $Pd(PPh_3)_4$ (17.33 mg, 0.015 mmol) were added in 1,4-dioxane (30 mL) under the protection of N_2, and then the mixture was heated at 100 °C

for 8 h. After the reaction was completed, the mixture was poured into water and extracted three times with dichloromethane, and then the organic layer was dried by $MgSO_4$. The solvent was removed under reduced pressure and purified by silica gel column chromatography. The final crude product was recrystallized in ethanol to produce a light green solid with a yield of 35.5%. Molecular formula: $C_{25}H_{20}OS_2$. ^1H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.25 (s, 1H), 7.21 (s, 1H), 7.18 – 7.16 (d, *J* = 8 Hz, 3H), 7.10 – 7.07 (m, 5H), 6.97 – 6.94 (d, *J* = 4 Hz, 2H), 6.31 (s, 1H), 2.35 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.31, 145.72, 142.23, 142.03, 141.66, 138.93, 138.85, 136.42, 136.40, 135.16, 134.85, 133.79, 131.11, 130.40, 128.12, 127.69, 127.38, 127.16, 126.73, 15.31, 13.67; HRMS (ESI) m/z: $[M+H]^+$, 401.1026 (calcd. for $C_{25}H_{20}OS_2$, 400.0956).

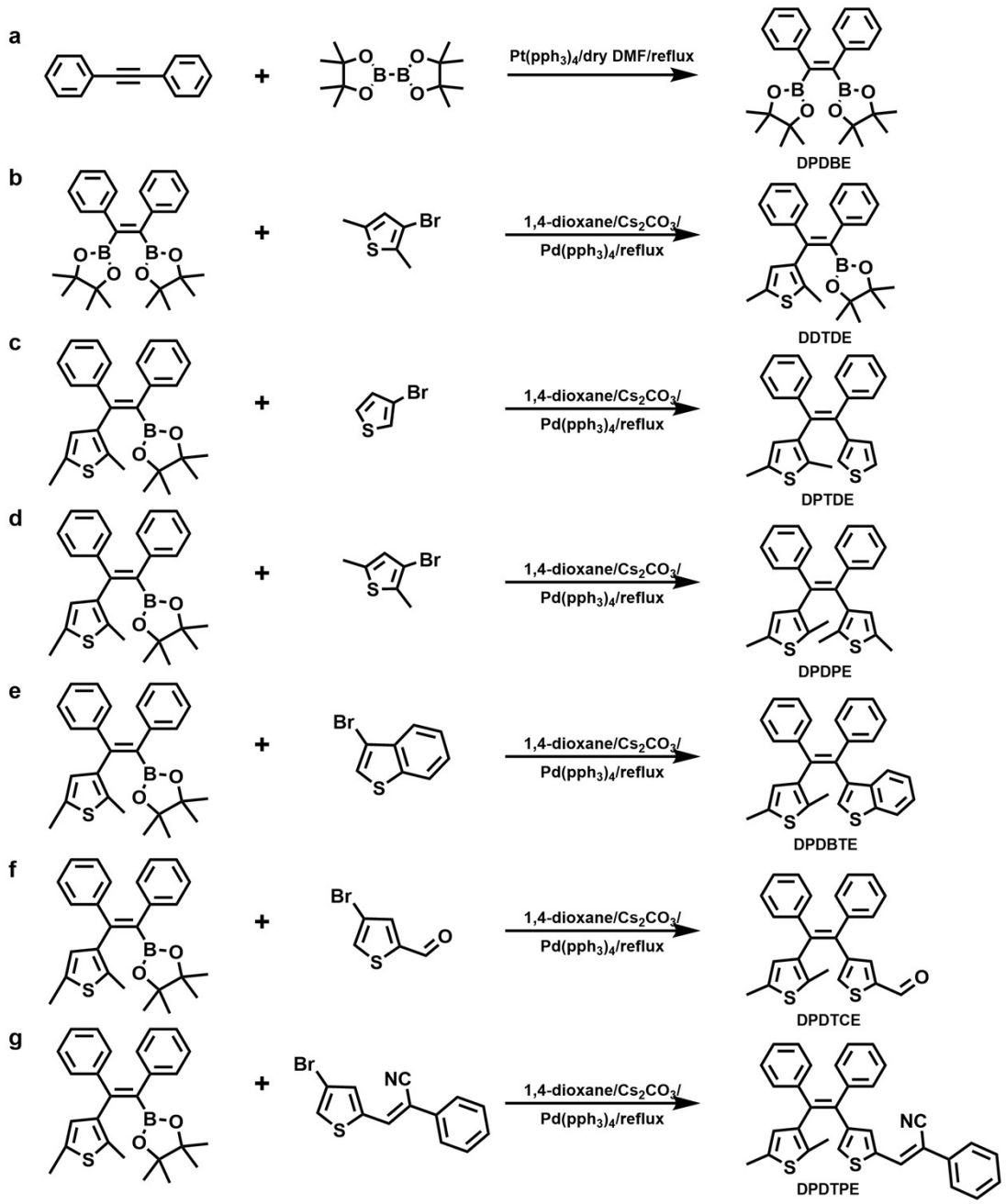
Synthesis of (Z)-3-(4-bromothiophen-2-yl)-2-phenylacrylonitrile. At room temperature, 4-bromothiophene-2-carboxaldehyde (0.191 g, 1.00 mmol), phenylacetonitrile (0.128 g, 1.1 mmol) and sodium methoxy (0.54 mg, 0.01 mmol) were added to the ethanol solution (10 ml), stirred for 4 to 6 h, then filtered, and the precipitate was washed with cold ethanol to obtain a yellow solid with a rate of 80%. Molecular formula: $C_{13}H_8BrNS$. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.63 (d, *J* = 4 Hz, 2H), 7.58 (s, 1H), 7.54 (s, 1H), 7.47 – 7.40 (d, *J* = 8 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.13, 133.72, 132.96, 132.47, 130.26, 129.22, 127.65, 125.84, 117.59, 111.31, 110.03; HRMS (ESI) m/z: $[M+H]^+$, 289.9598 (calcd. for $C_{13}H_8BrNS$, 289.9561).

Synthesis of (Z)-3-(4-((Z)-2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)thiophen-2-yl)-2-phenylacrylonitrile (DPDTPE). A mixture of (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.6655 g, 4 mmol), (Z)-3-(4-bromothiophen-2-yl)-2-phenylacrylonitrile (1.7411 g, 6 mmol) and 2M cesium carbonate (10 mL), $Pd(PPh_3)_4$ (17.33 mg, 0.015 mmol) were added in 1,4-dioxane (30 mL) under the protection of N_2, and then the mixture was heated at 100 °C for 8 h. After the reaction was completed, the mixture was poured into water and extracted three times with dichloromethane, and then the organic layer was dried by $MgSO_4$. The solvent was removed under reduced

pressure and purified by silica gel column chromatography. The final crude product was recrystallized in ethanol to produce a yellow solid with a yield of 25%. Molecular formula: $C_{33}H_{25}NS_2$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.58 (d, J = 4 Hz, 2H), 7.45 – 7.35 (m, 4H), 7.19 – 7.16 (m, 3H), 7.13 – 7.10 (m, 2H), 7.09 – 7.05 (m, 4H), 7.01 (s, 1H), 6.99 – 6.96 (m, 2H), 6.33 (s, 1H), 2.36 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.90, 142.36, 141.94, 139.11, 136.18, 136.14, 136.06, 135.50, 134.64, 134.02, 133.72, 131.20, 130.47, 130.28, 129.07, 128.85, 127.99, 127.64, 127.46, 127.00, 126.57, 125.66, 118.02, 107.54, 15.35, 13.75; HRMS (ESI) m/z: $[M+H]^+$, 500.1500 (calcd. for $C_{33}H_{25}NS_2$, 499.1428).

Characterization of UV-Visible and Fluorescence Properties of All Samples. UV-Visible absorption spectra were recorded using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. Steady PL spectra of all samples were performed on an Edinburgh Instruments model FLS980 fluorescence spectrophotometer equipped with a xenon arc lamp using a front face sample holder. Time-resolved fluorescence measurements were conducted with EPL-series lasers. The absolute PL quantum yields of all samples were determined `using an integrating sphere equipped with FLS980 spectrophotometer at least three times. The UV light source used in the experiments was an 8 W (type ZF-7A, 365 nm) portable UV lamp, and the visible light source powder used was 8 W with emission wavelengths of 440, 520 and 660 nm. The solid films were prepared as shown below. The compounds and sucrose octaacetate were mixed in a molar ratio of 1:50, then tetrahydrofuran was added dropwise until the mixture was completely dissolved, and finally the solid films were prepared by removing the tetrahydrofuran.

2. Supplementary Schemes, Figures and Tables



Scheme S1. Synthesis routes of DPDBE (a), DDTDE (b), DPTDE (c), DPDPE (d), DPDBTE (e), DPDTCE (f) and DPDTPE (g).

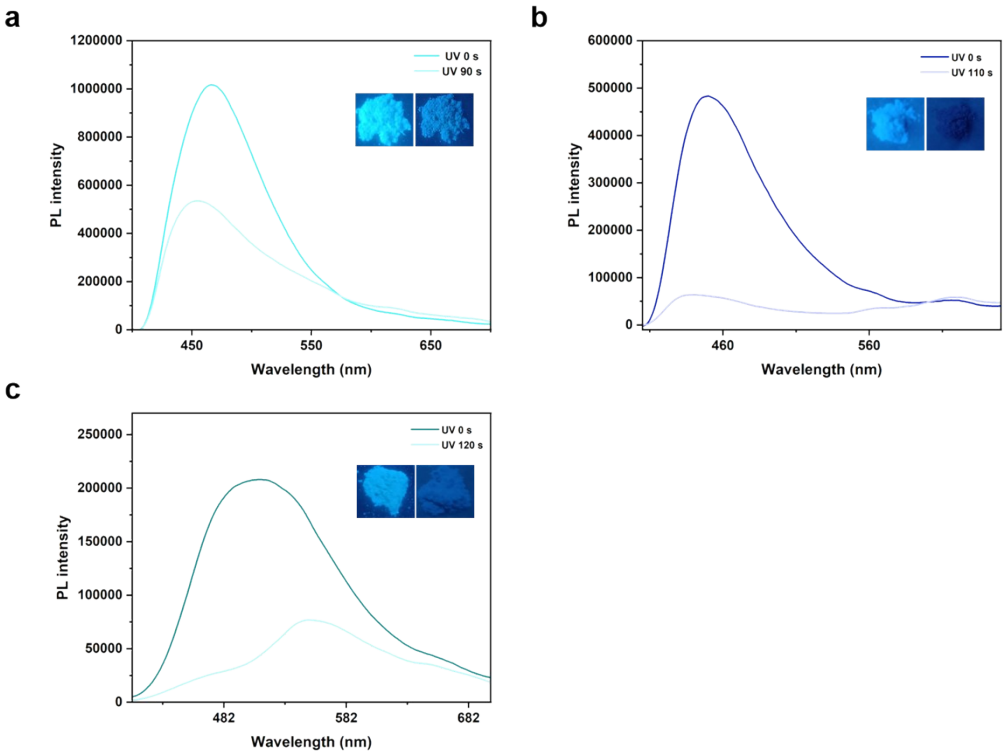


Figure S1. PL spectra and images of DPDTE (a), DPTDE (b) and DPDPE (c) in solid state before and after UV irradiation.

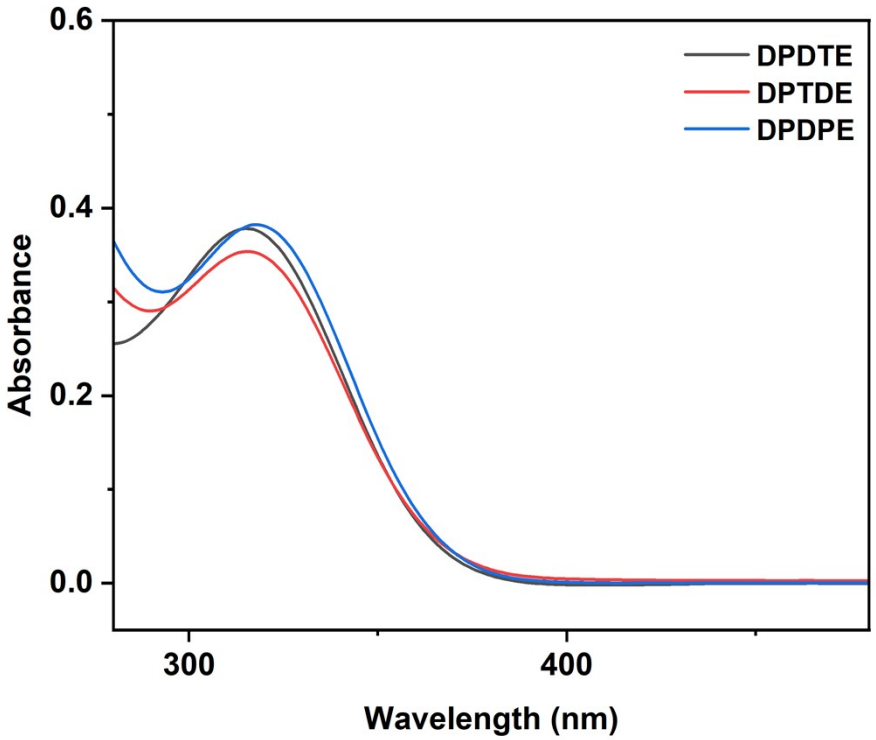


Figure S2. UV-visible spectra of DPDTE, DPTDE and DPDPE in THF at 25.0 μM.

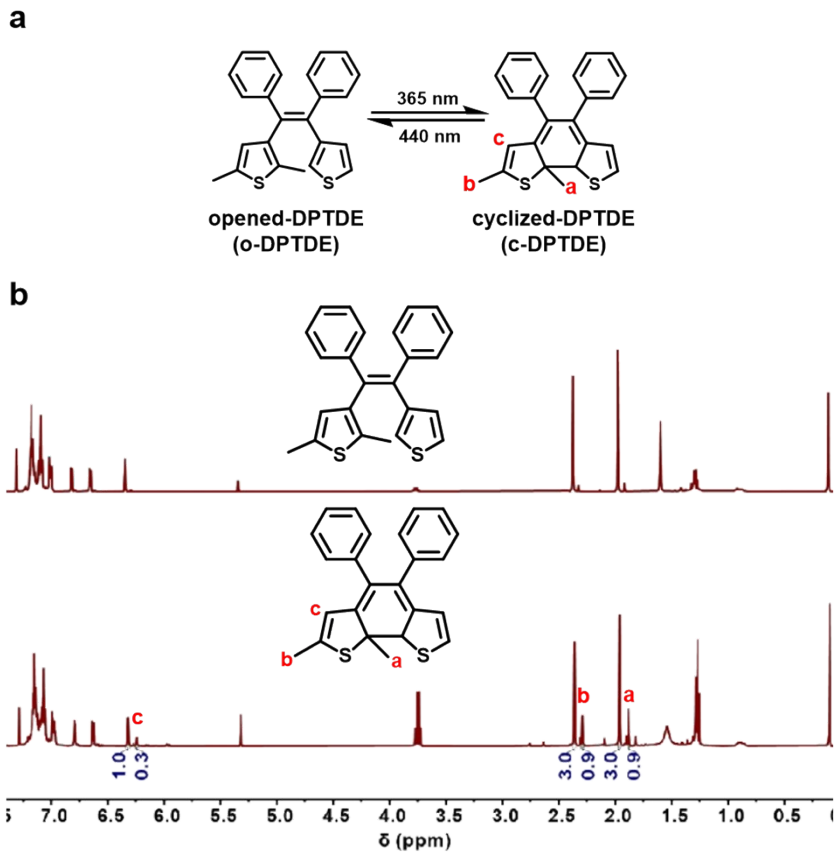


Figure S3. ^{1}H NMR spectra of DPTDE in $CDCl_3$ before and after UV irradiation.

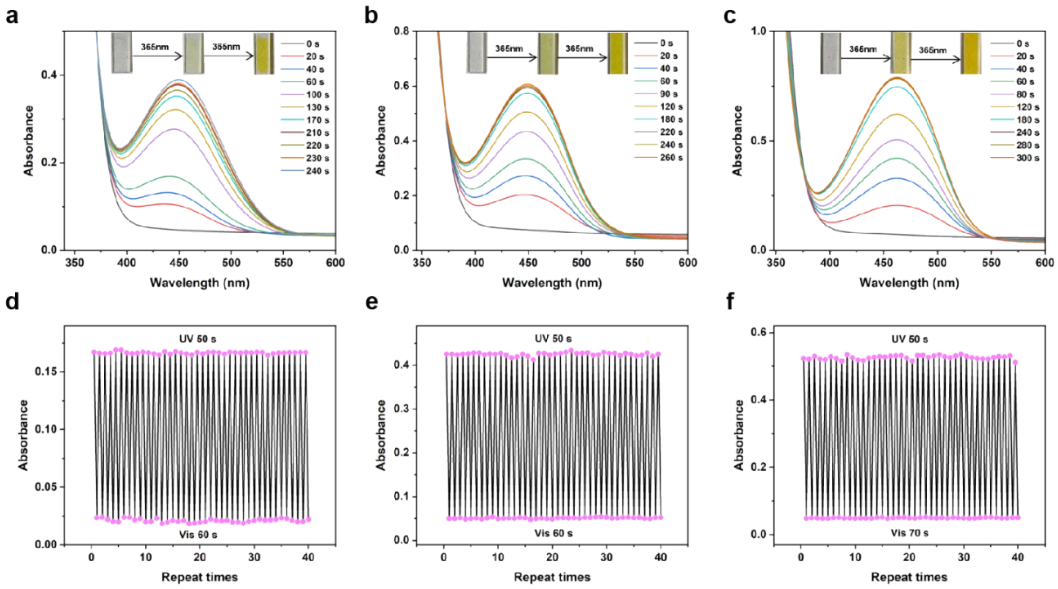


Figure S4. (a–c) Time-dependent UV-visible absorption spectra of DPDTE (a), DPTDE (b) and DPDPE (c) in sucrose octaacetate film (1:50 in mol ratio) with different periods of UV light irradiation. Insets: The images before and after the UV irradiation at 365 nm. (d–f) Photochromic recycles of DPDTE (d), DPTDE (e) and DPDPE (f) in the film as a function of exposure to UV light (365 nm) and visible light respectively.

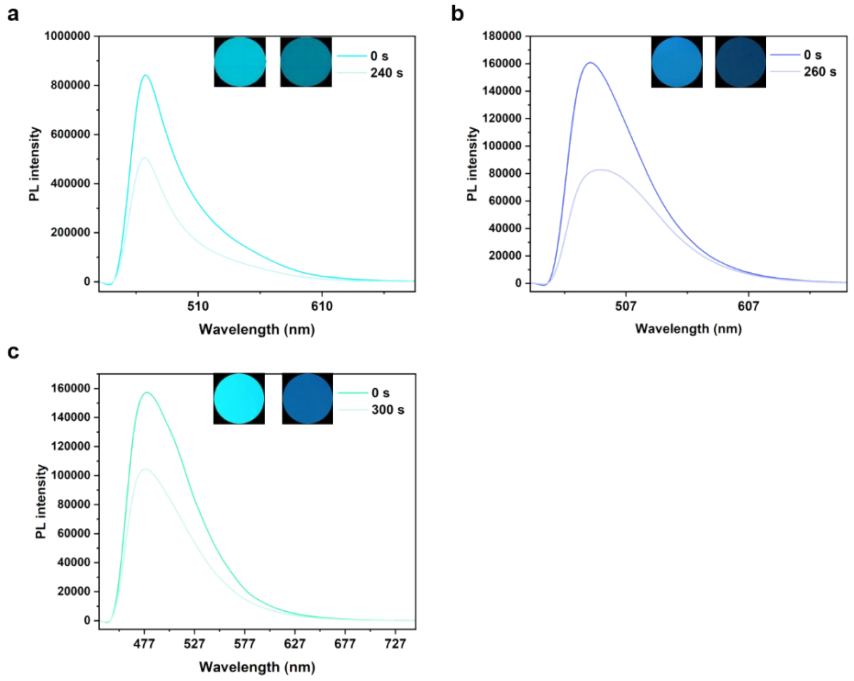


Figure S5. PL spectra and images of DPDTE (a), DPTDE (b) and DPDPE (c) in sucrose octaacetate film (1:50 in molar ratio) before and after UV irradiation.

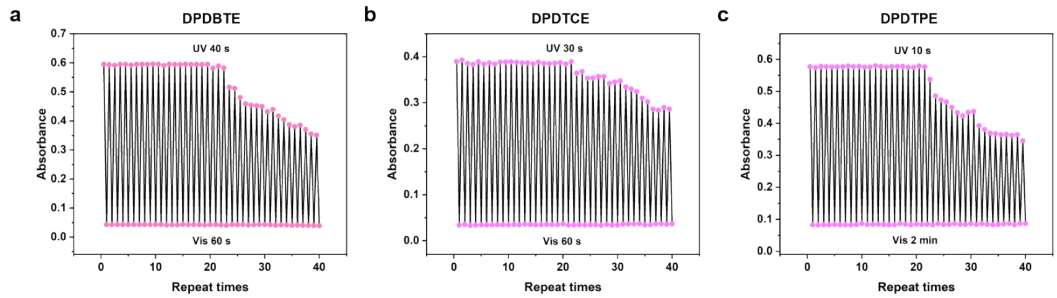


Figure S6. Photochromic recycling of DPDBTE (a), DPDTCE (b) and DPDTPE (c) in the THF as a function of exposure to UV light (365 nm) and visible light respectively.

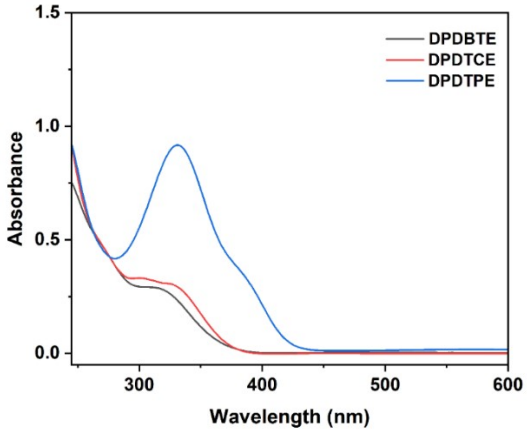


Figure S7. UV-visible spectra of DPDBTE, DPDTCE and DPDTPE in THF at 25.0 μM.

Table S1. Photocyclization quantum yields and photocyclic conversion quantum yield of all compounds in THF solution.

ring-opening isomer		closed-loop isomer	
Compounds	$\Phi_{o\rightarrow c}$	Compounds	$\Phi_{c\rightarrow o}$
o-DPDTE	0.0212	c-DPDTE	0.0113
o-DPTDE	0.0597	c-DPTDE	0.0345
o-DPDPE	0.0745	c-DPDPE	0.022
o-DPDBTE	0.1182	c-DPDBTE	0.0253
o-DPDTCE	0.1705	c-DPDTCE	0.0927
o-DPDTPE	0.2220	c-DPDTPE	0.0616

$\Phi_{o\rightarrow c}$ and $\Phi_{c\rightarrow o}$ are the photocyclization and photocycloreversion quantum yields.

3. NMR and HRMS Spectra of Compounds

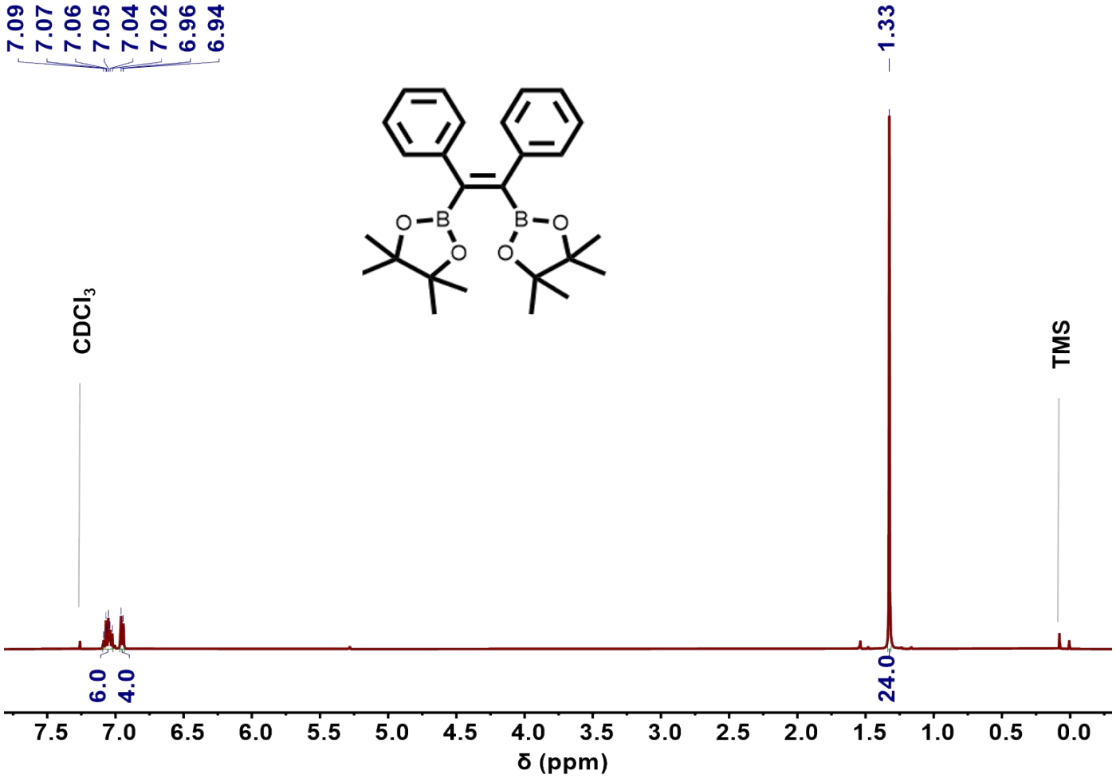


Figure S8. ^{1}H NMR spectrum of DPDBE in $CDCl_3$

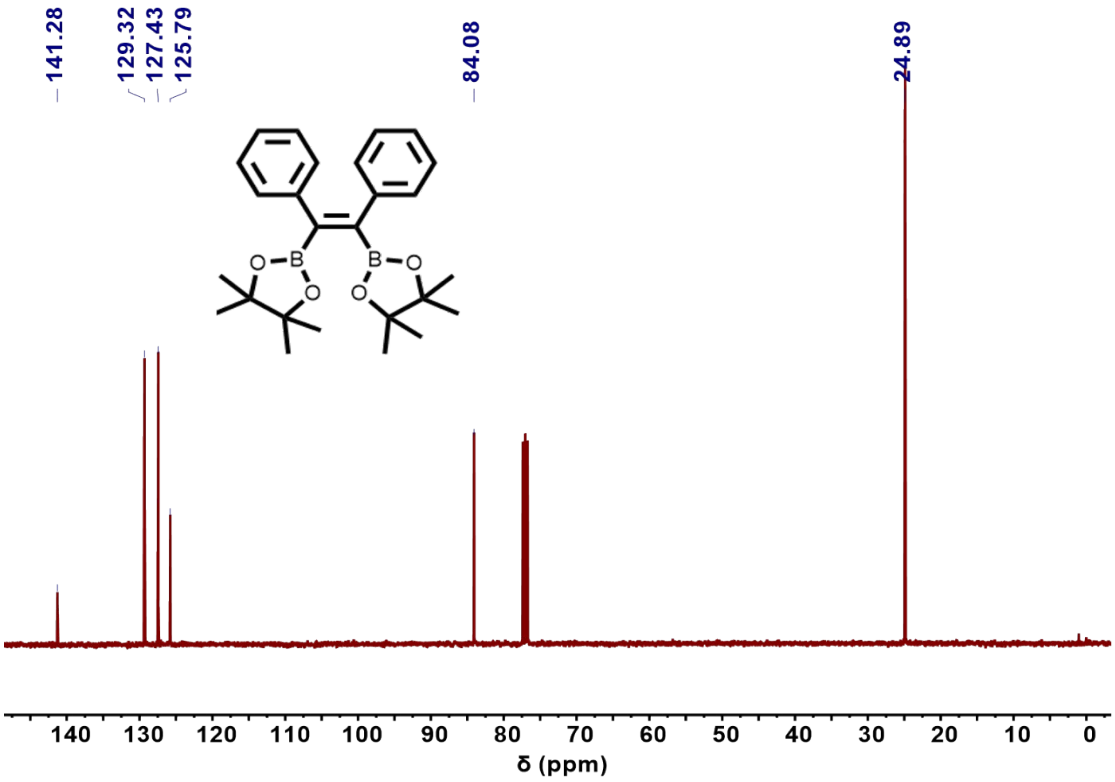


Figure S9. ^{13}C NMR spectrum of DPDBE in $CDCl_3$

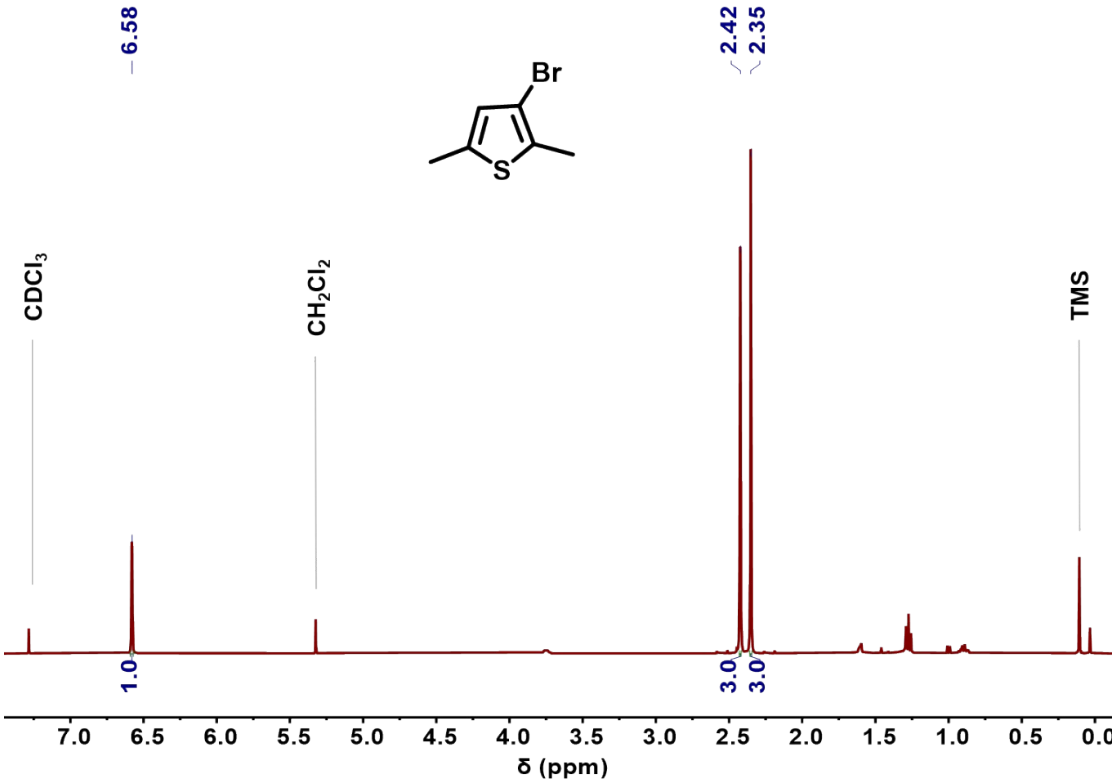


Figure S10. ^{1}H NMR spectrum of 3-bromo-2,5-dimethylthiophene in $CDCl_3$

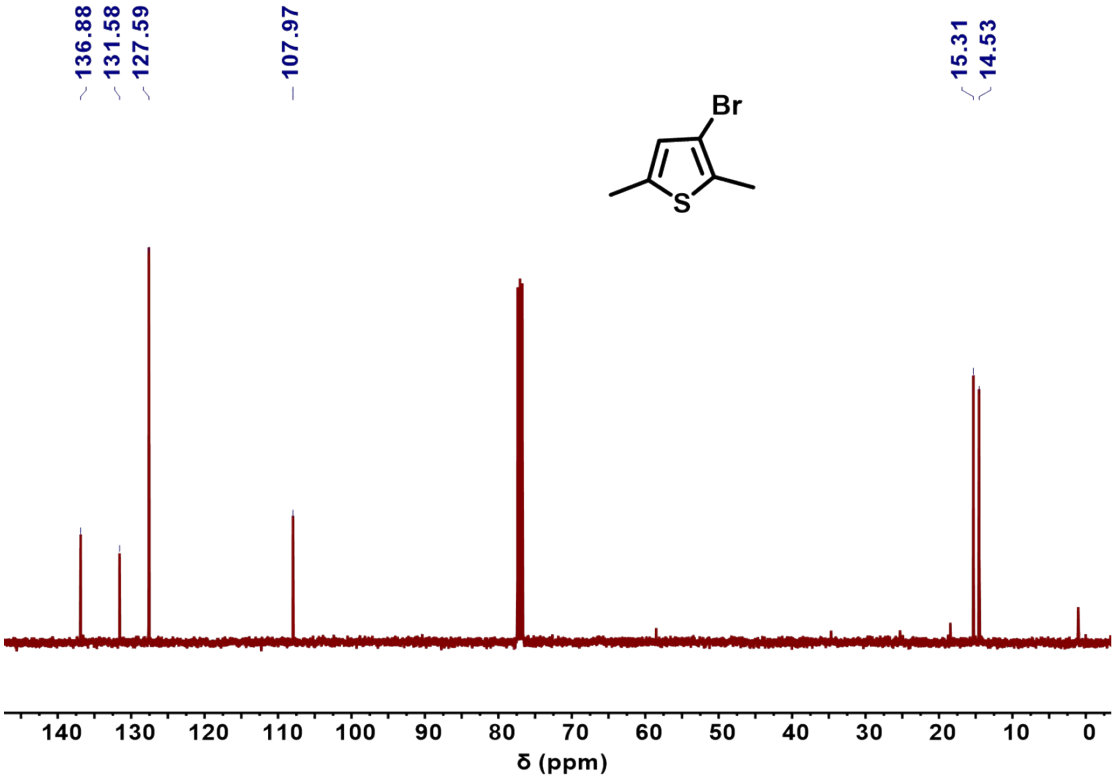


Figure S11. ^{13}C NMR spectrum of 3-bromo-2,5-dimethylthiophene in $CDCl_3$

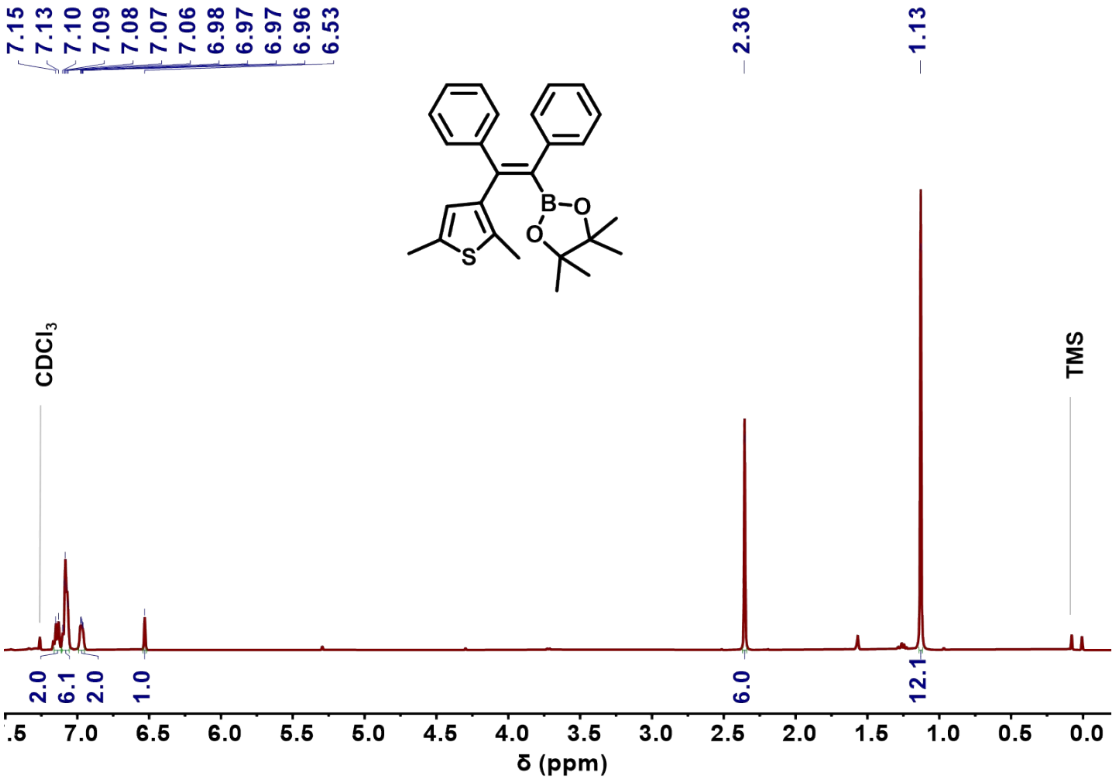


Figure S12. ^{1}H NMR spectrum of DDTDE in $CDCl_3$

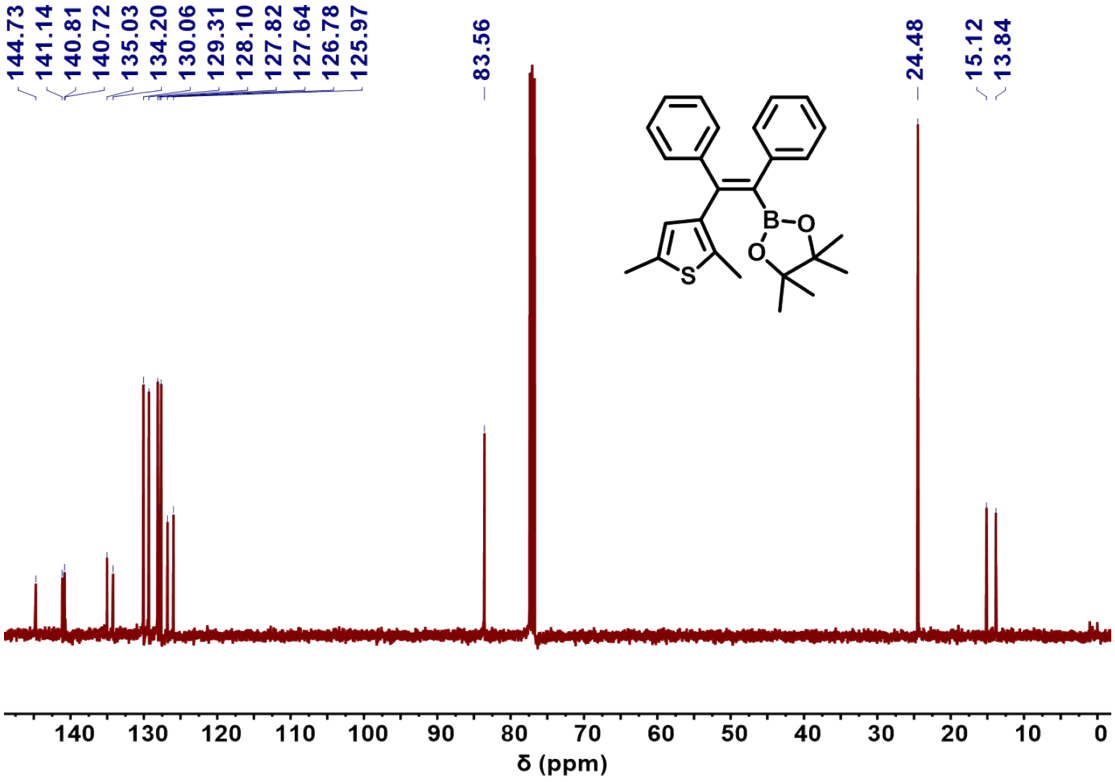


Figure S13. ^{13}C NMR spectrum of DDTDE in $CDCl_3$

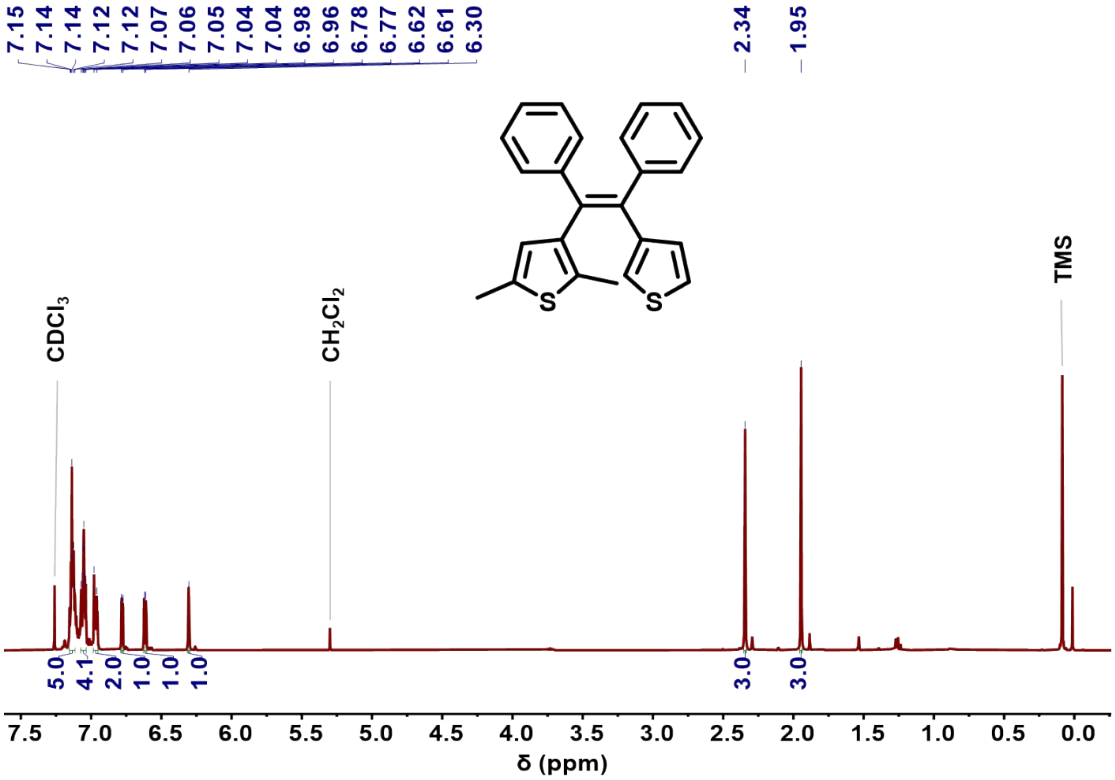


Figure S14. ^{1}H NMR spectrum of DPTDE in $CDCl_3$

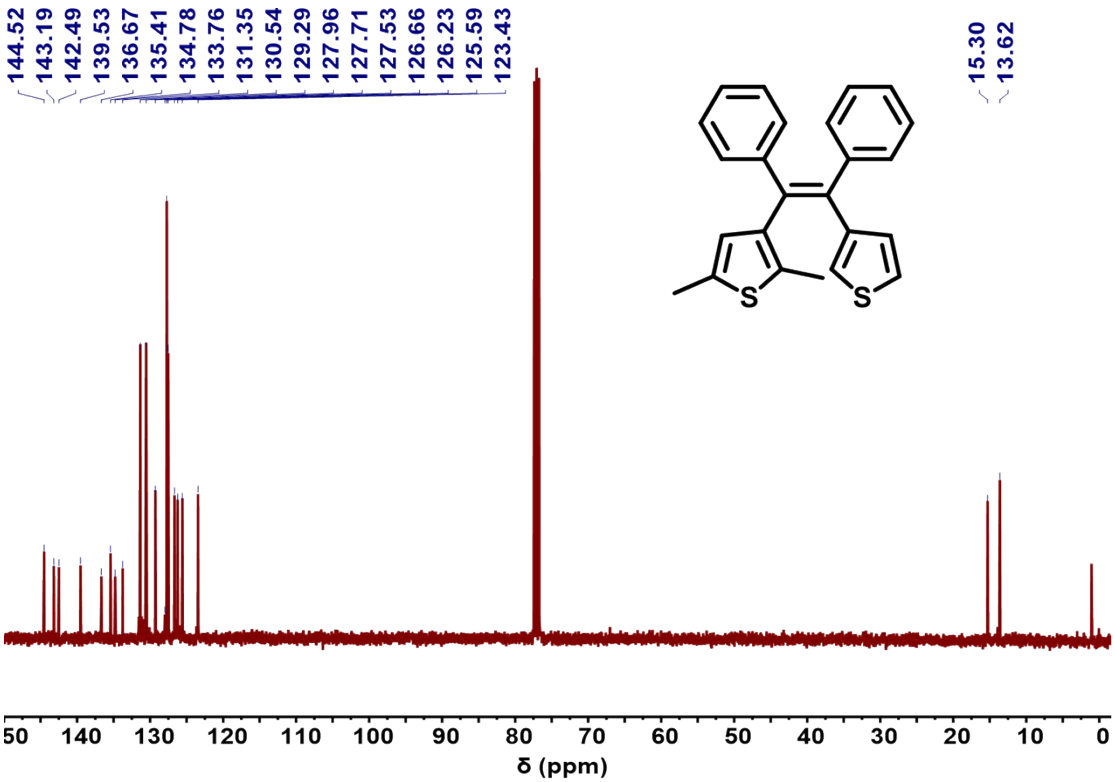


Figure S15. ^{13}C NMR spectrum of DPTDE in $CDCl_3$

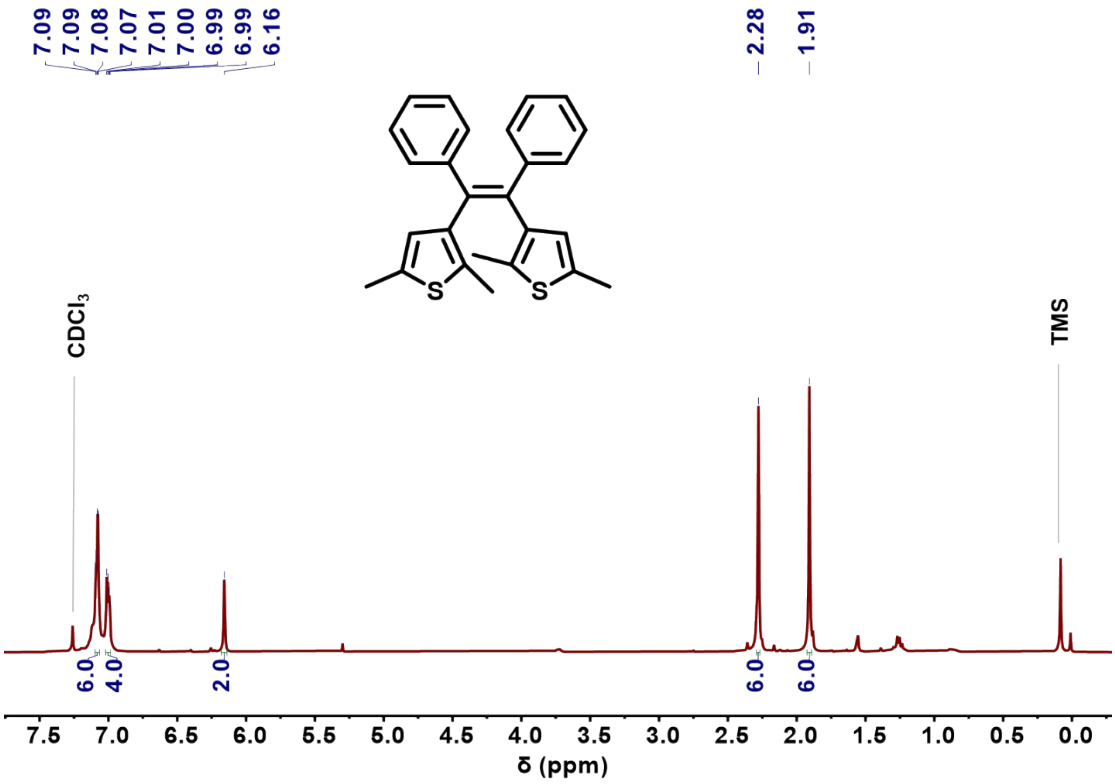


Figure S16. ^{1}H NMR spectrum of DPDPE in $CDCl_3$

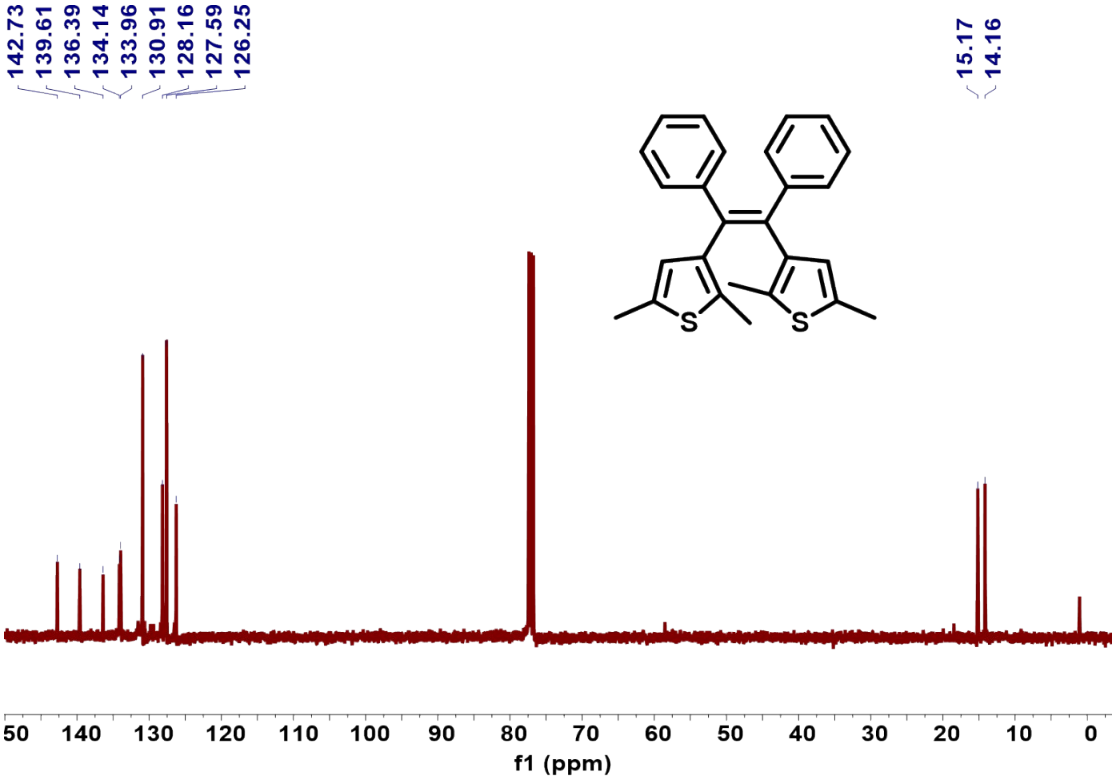


Figure S17. ^{13}C NMR spectrum of DPDPE in $CDCl_3$

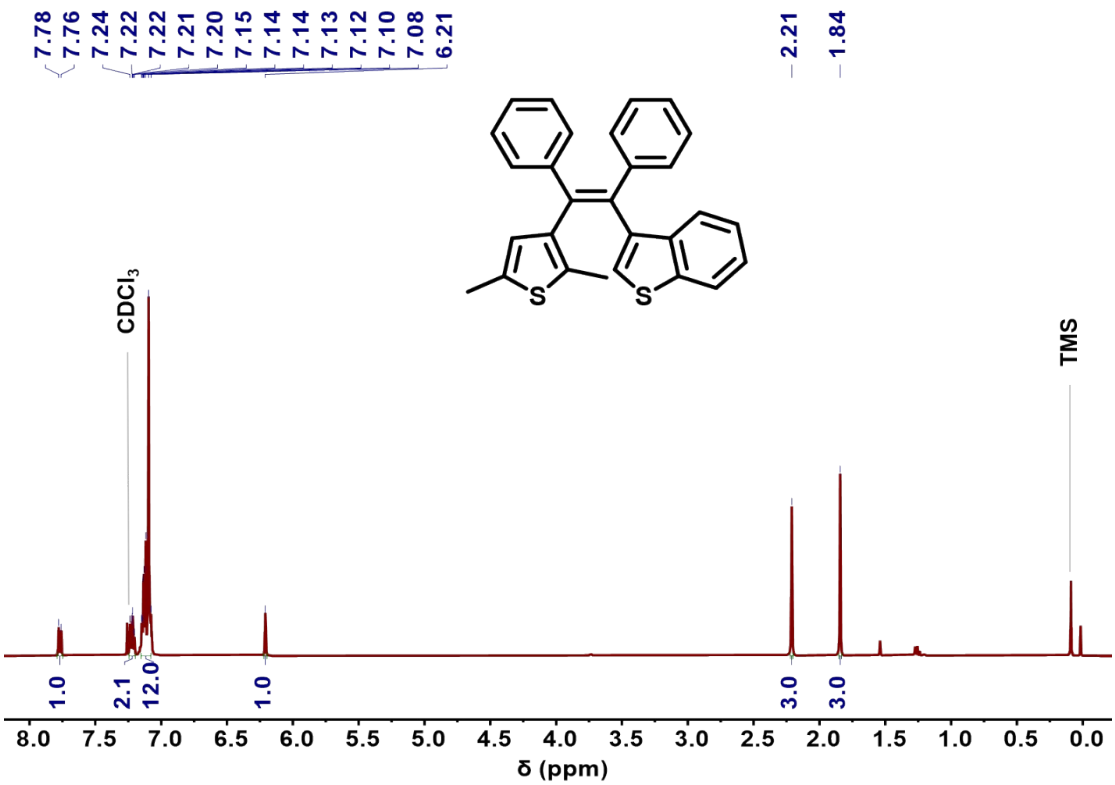


Figure S18. ^{1}H NMR spectrum of DPDBTE in $CDCl_3$

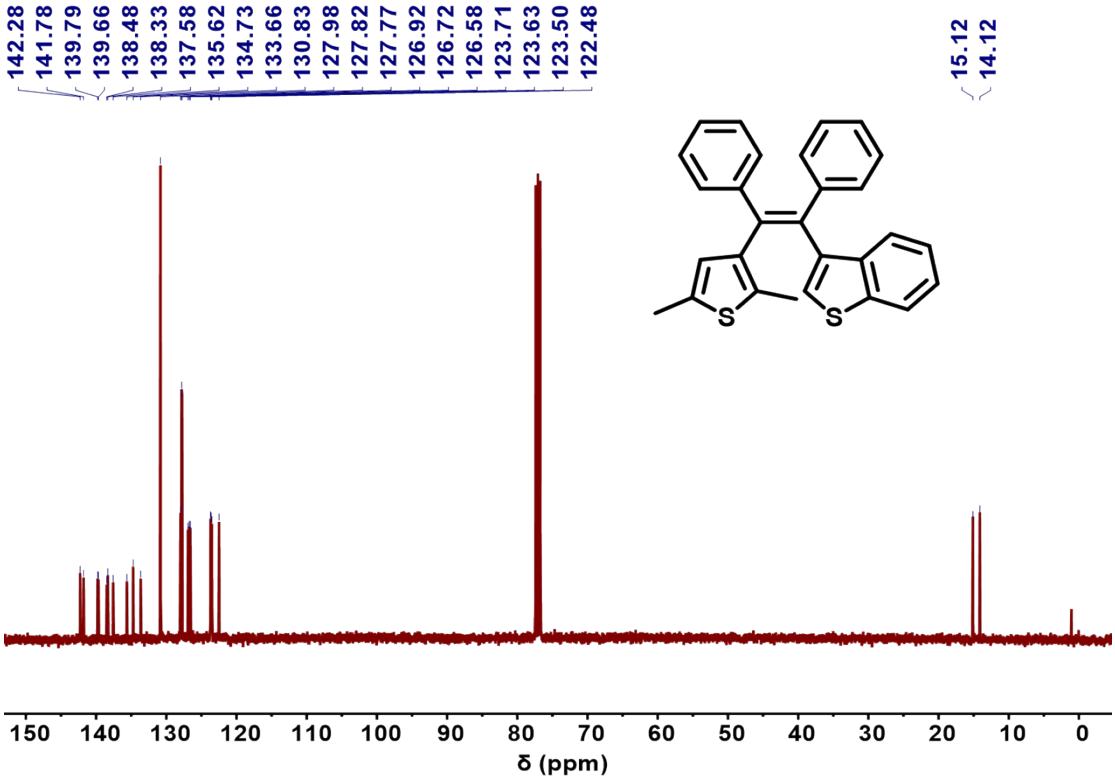


Figure S19. ^{13}C NMR spectrum of DPDBTE in $CDCl_3$

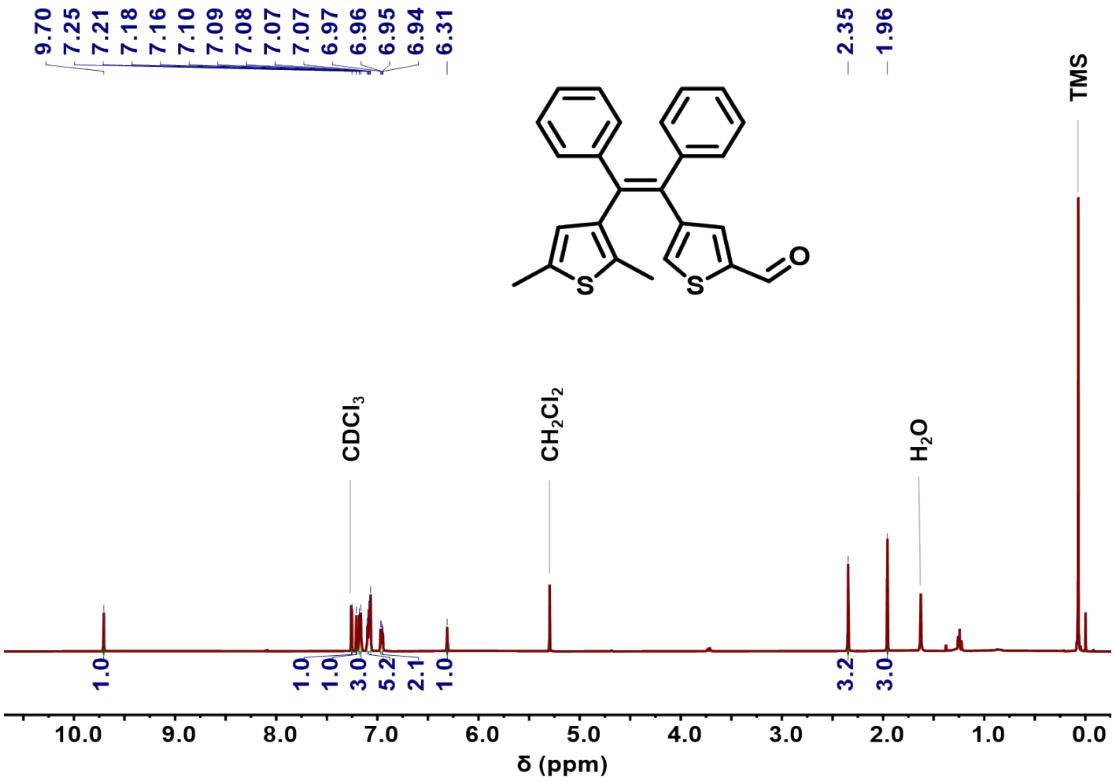


Figure S20. ^{1}H NMR spectrum of DPDTCE in $CDCl_3$

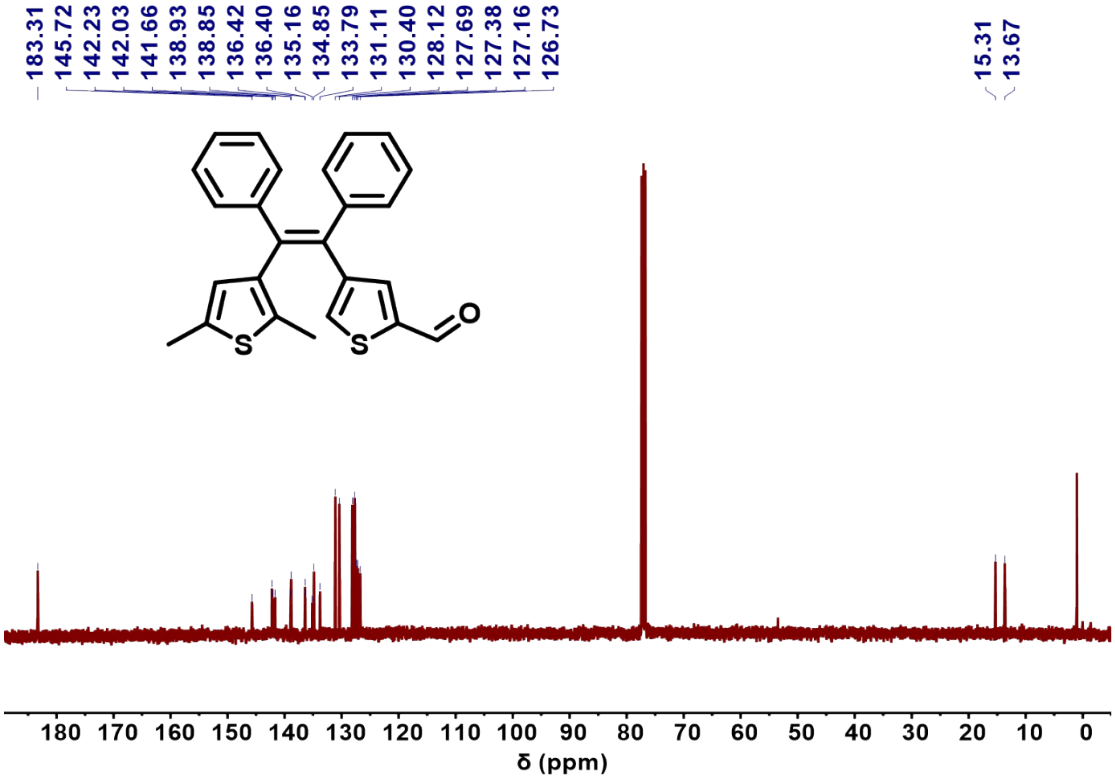


Figure S21. ^{13}C NMR spectrum of DPDTCE in $CDCl_3$

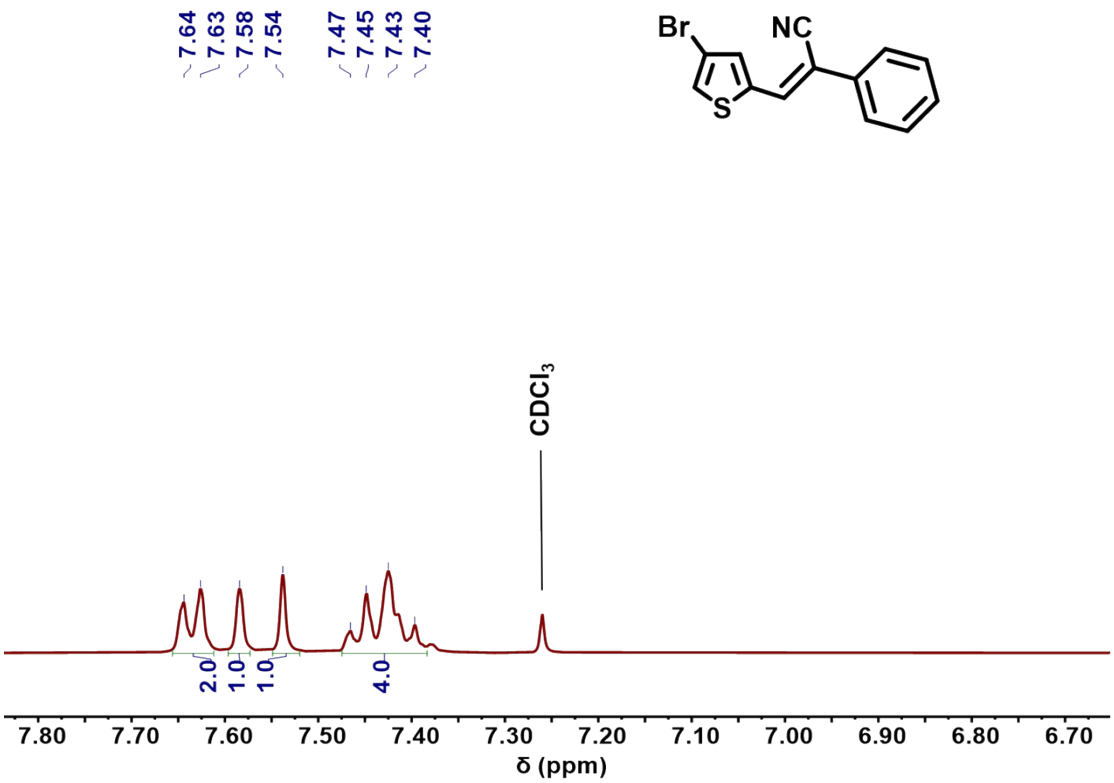


Figure S22. ^{1}H NMR spectrum of (Z)-3-(4-bromothiophen-2-yl)-2-phenylacrylonitrile in $CDCl_3$

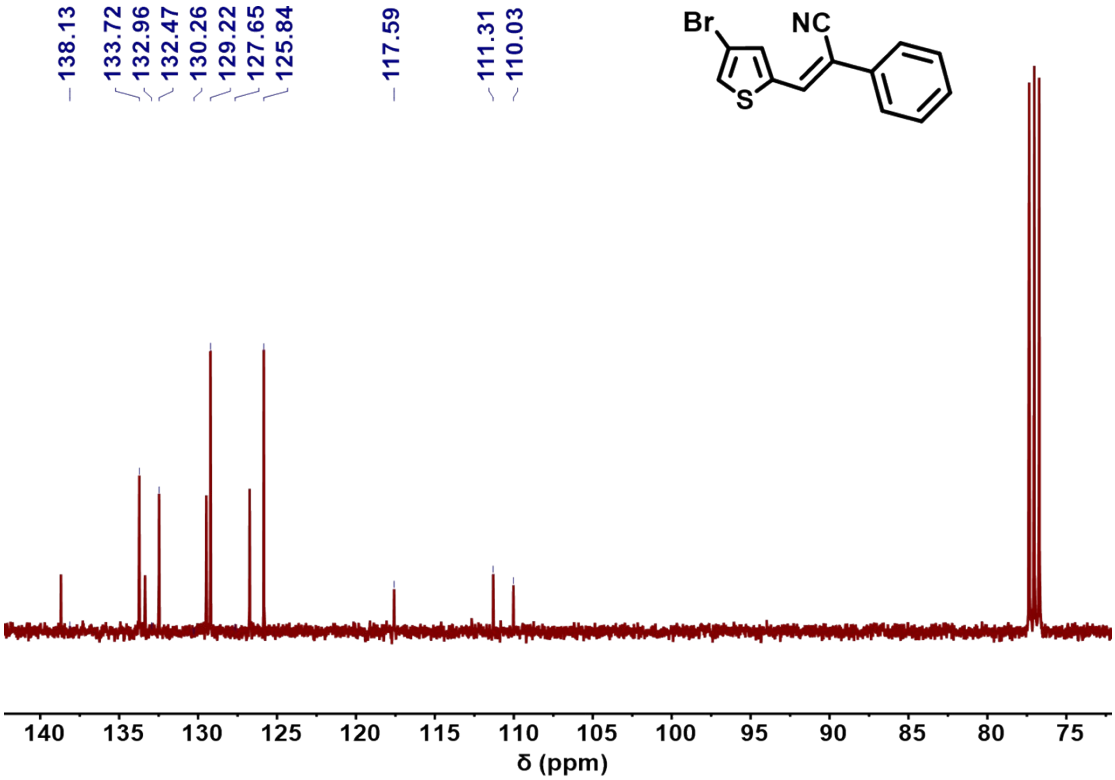


Figure S23. ^{13}C NMR spectrum of (Z)-3-(4-bromothiophen-2-yl)-2-phenylacrylonitrile in $CDCl_3$

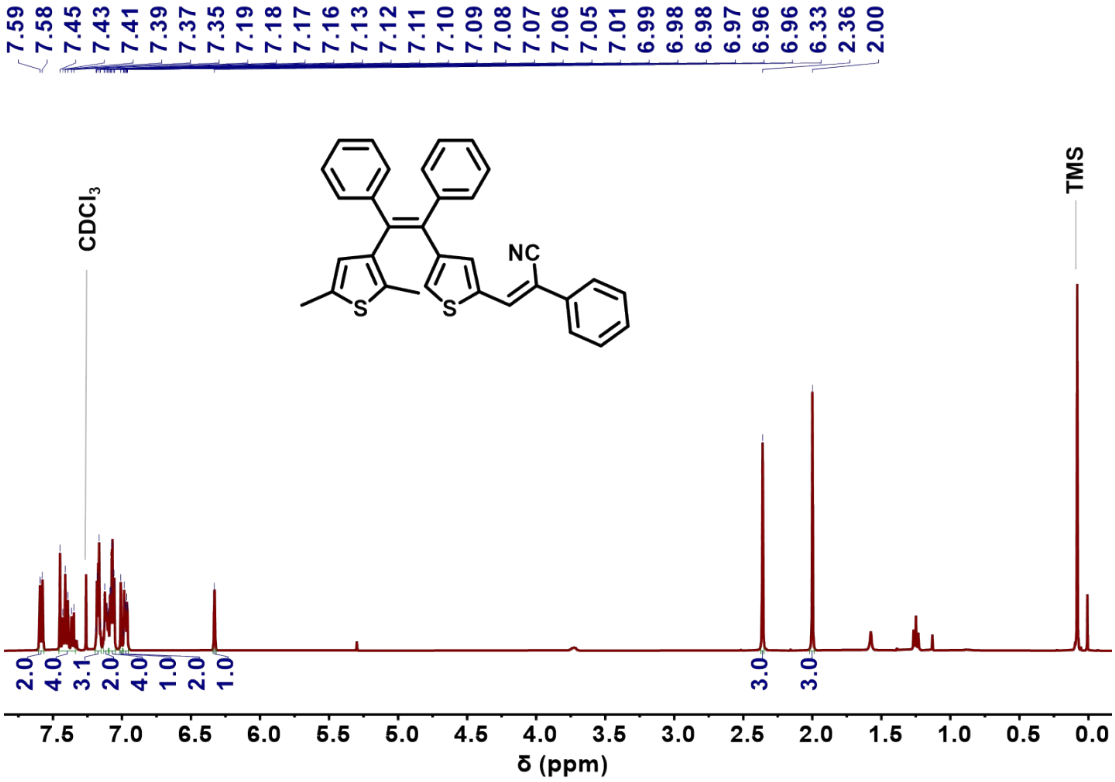


Figure S24. ^{1}H NMR spectrum of DPDTPE in $CDCl_3$

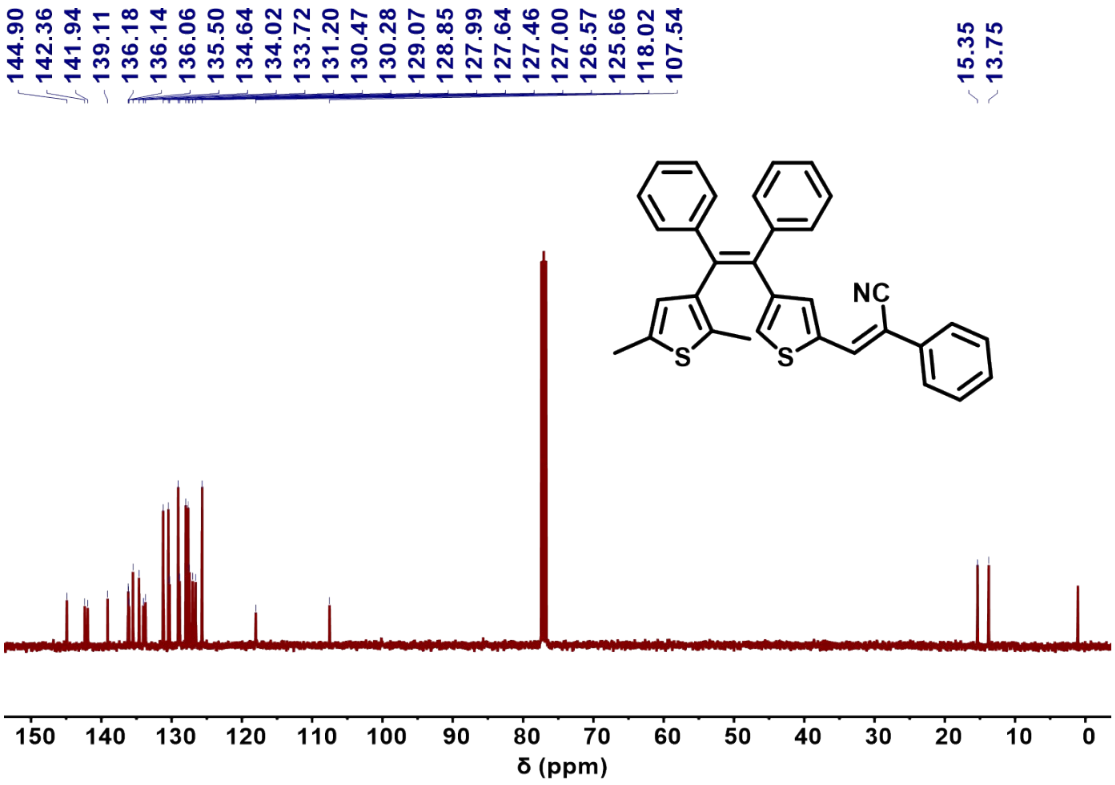


Figure S25. ^{13}C NMR spectrum of DPDTPE in $CDCl_3$

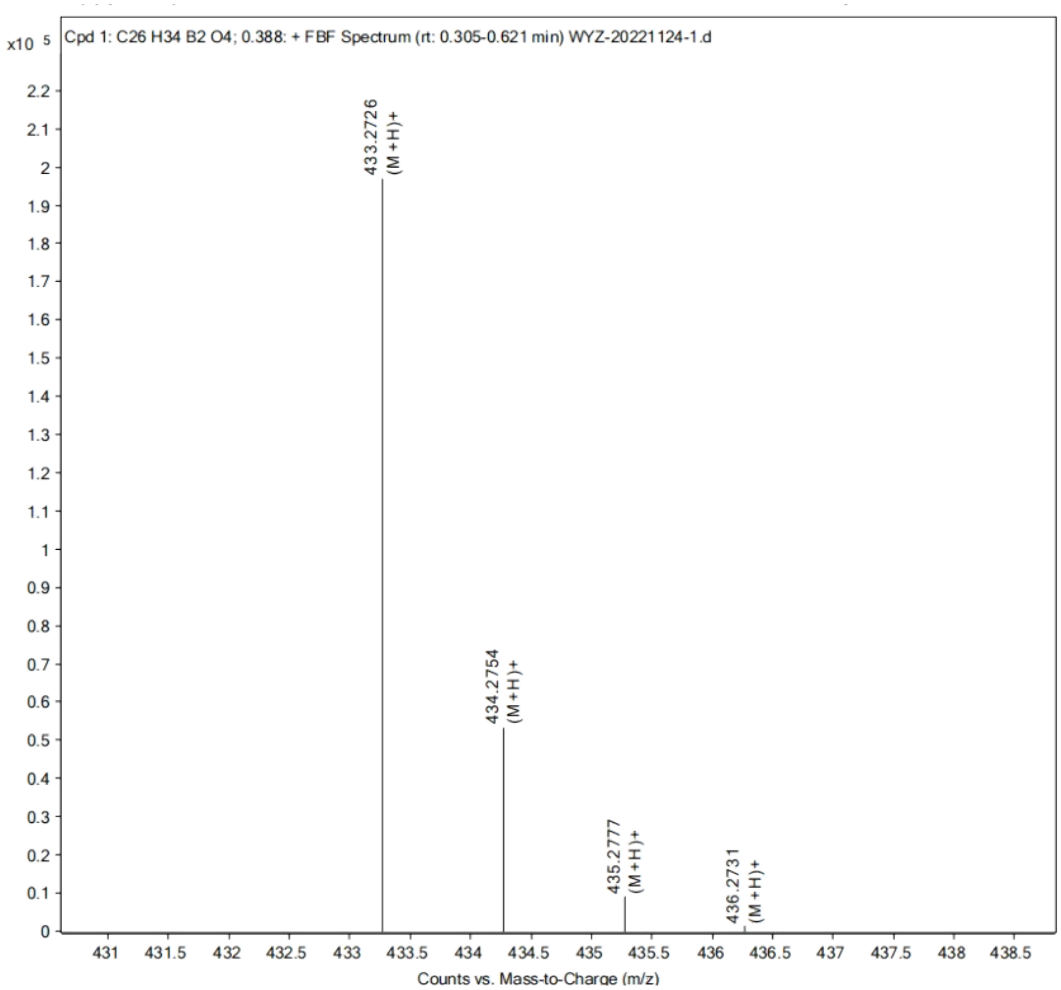


Figure S26. High-resolution mass spectrum of DPDBE.

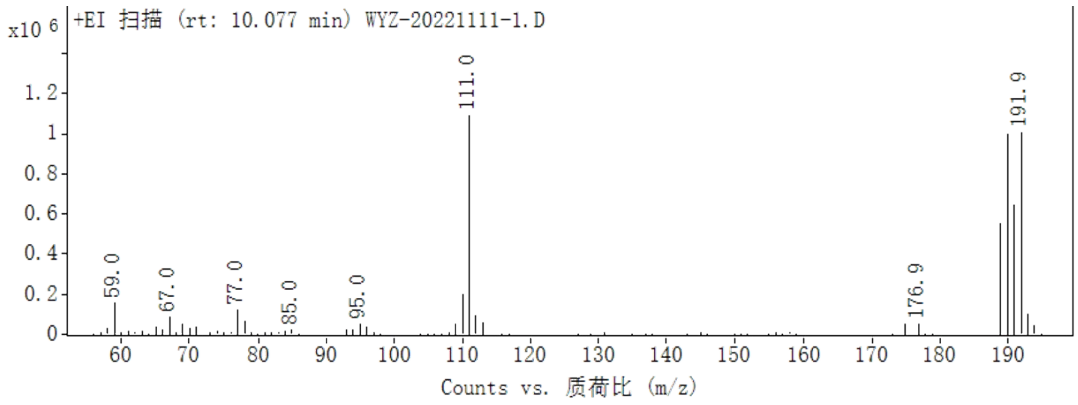


Figure S27. Mass spectrometry of 3- bromo-2,5-dimethylthiophene.

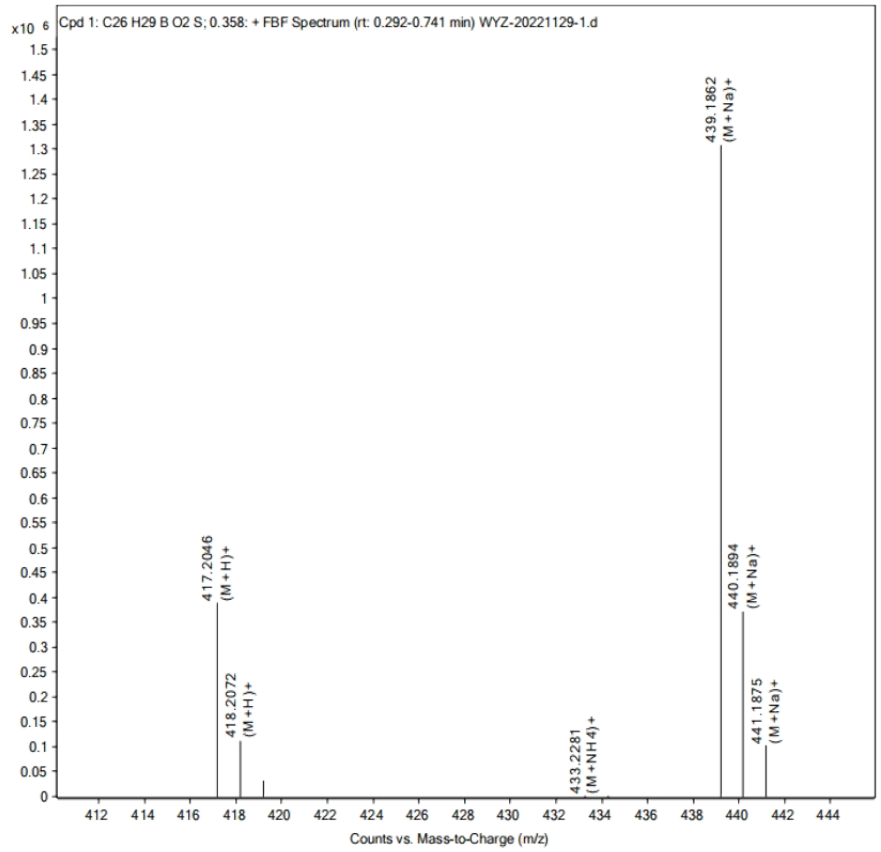


Figure S28. High-resolution mass spectrum of DDTDE.

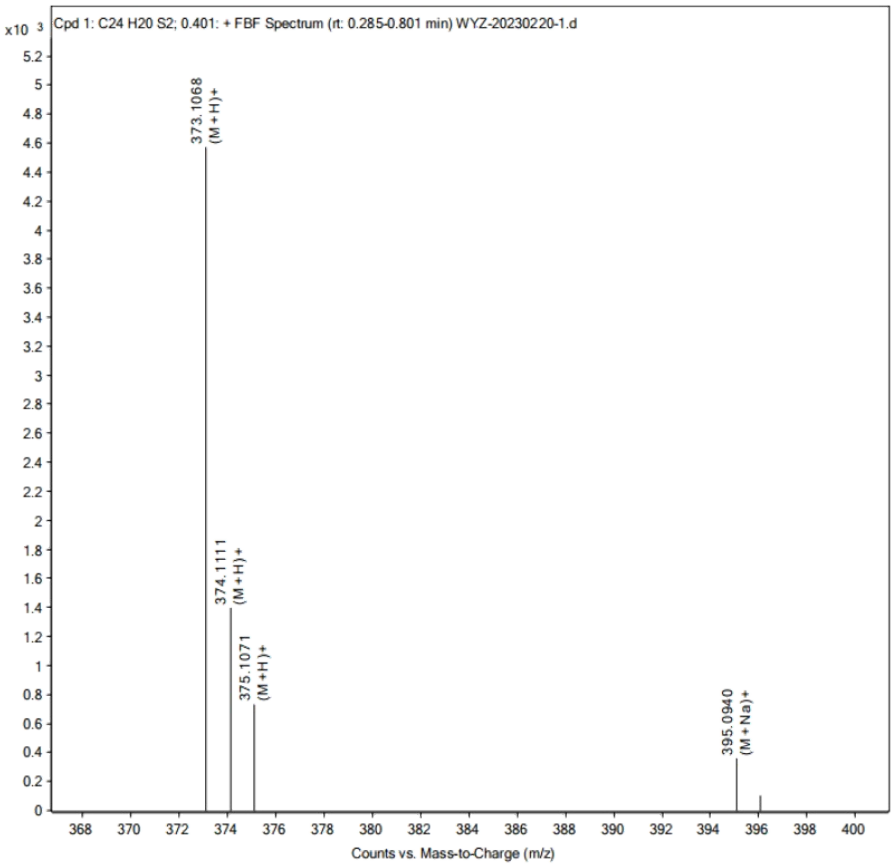


Figure S29. High-resolution mass spectrum of DPTDE.

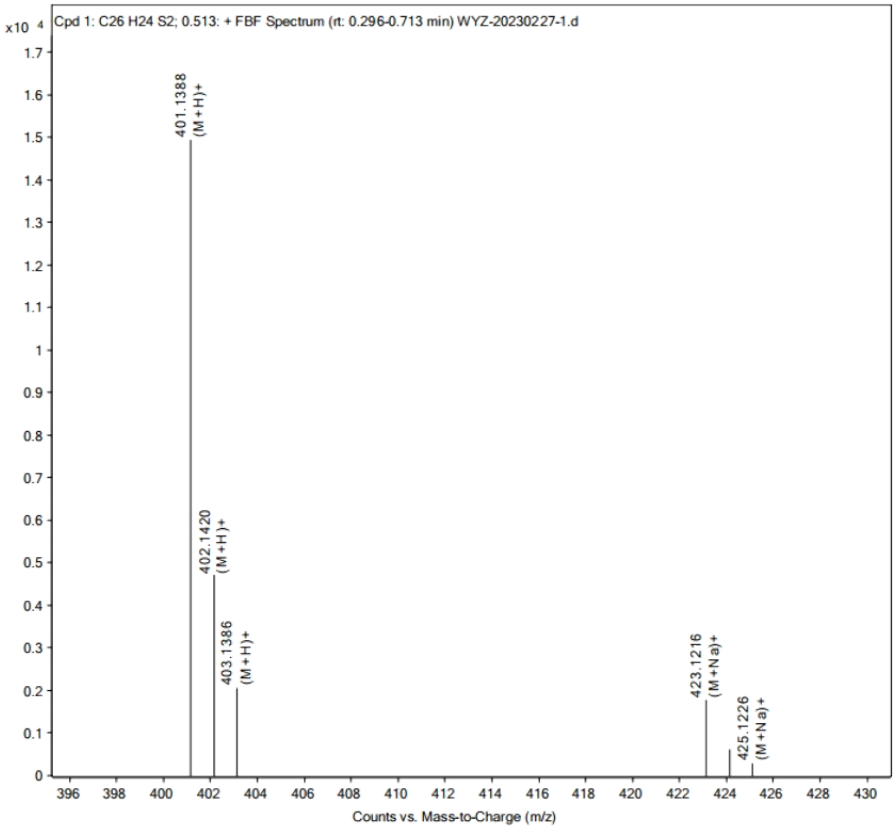


Figure S30. High-resolution mass spectrum of DPDPE.

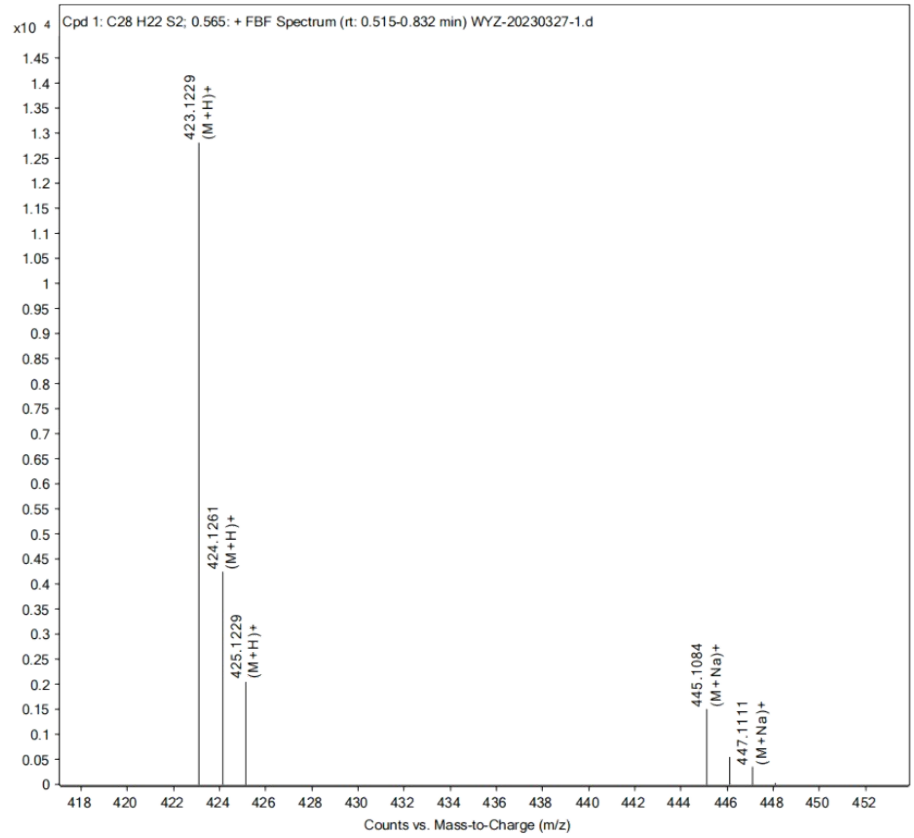


Figure S31. High-resolution mass spectrum of DPDBTE.

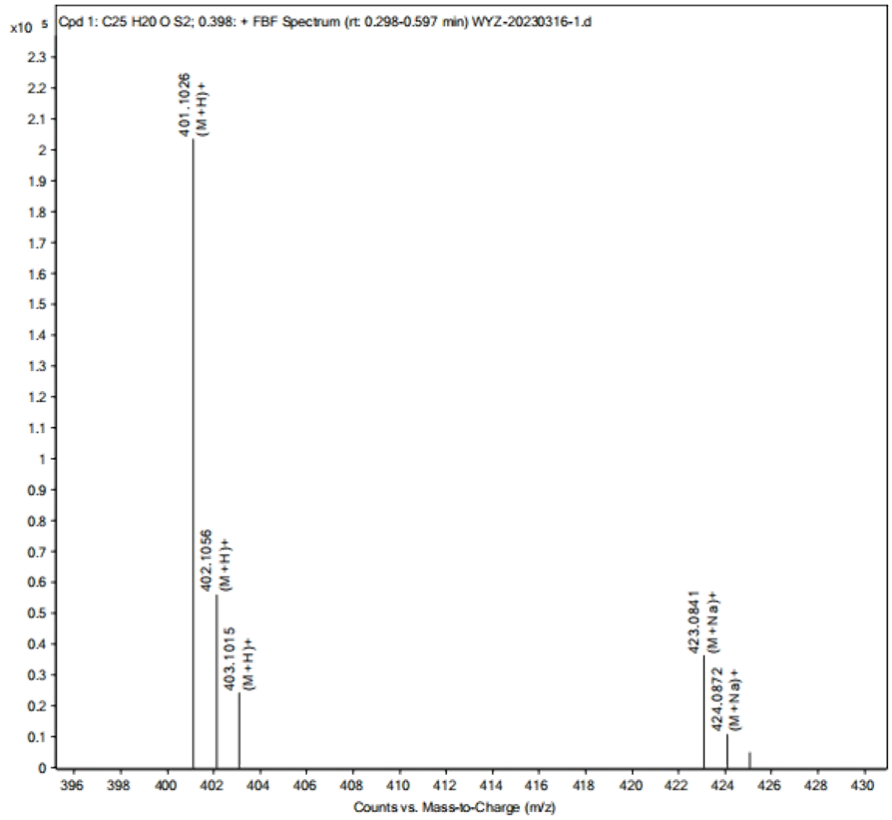


Figure S32. High-resolution mass spectrum of DPDTCE.

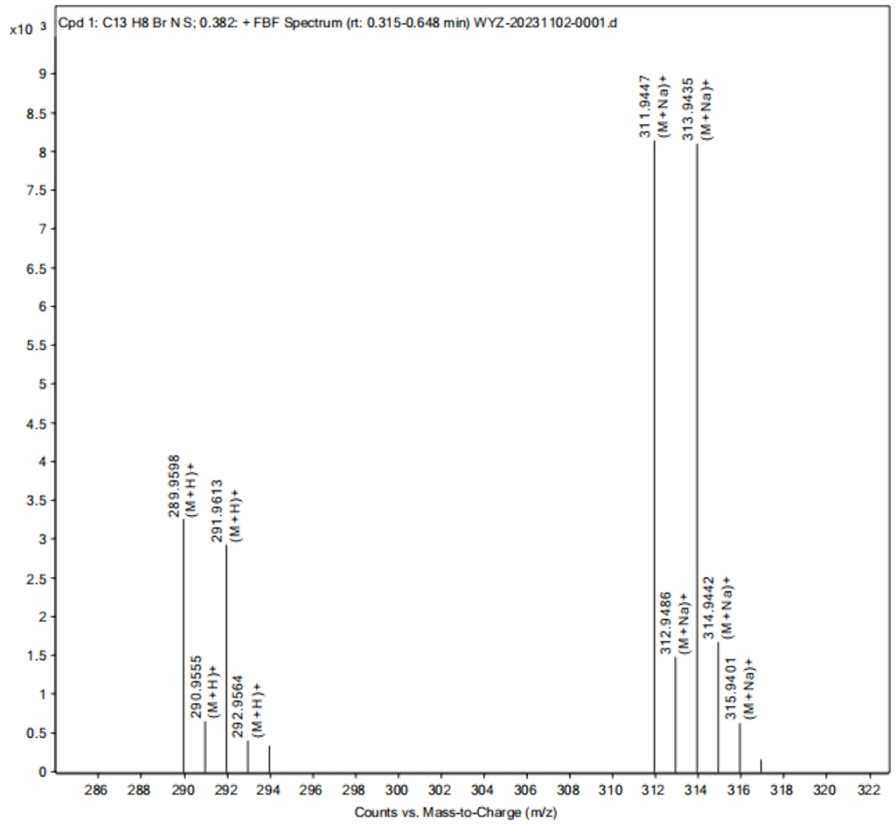


Figure S33. High-resolution mass spectrum of (Z)-3-(4-bromothiophen-2-yl)-2-phenylacrylonitrile.

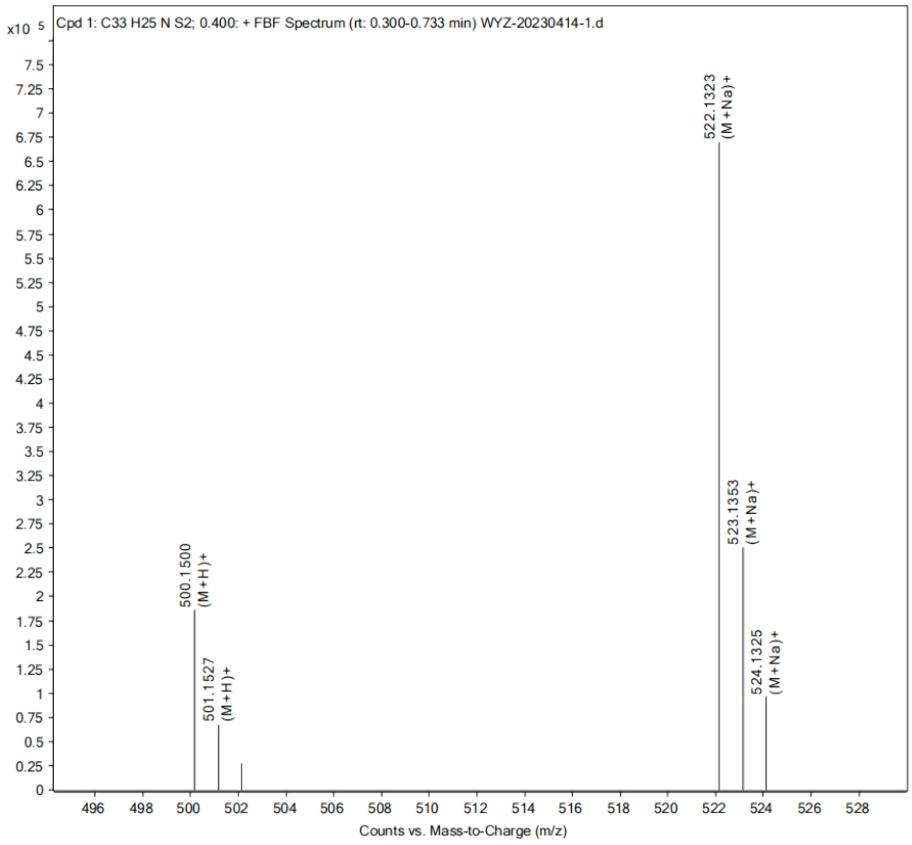


Figure S34. High-resolution mass spectrum of DPDTPE.