Electronic Supplementary Information *for*

Dual-Mode Molecular Photoswitches with Multiple-Stimuli Response by Eliminating the Heavy Atom Effect and Introducing Multifunctionality

Zhengdong Han,† Jiale Zhan,† Xin Peng, Penglei Wu, Tian Li, Weidong Liu,* Zhaosheng Qian and Hui Feng*

*Corresponding authors. E-mails: fenghui@zjnu.cn; liuwd@zjnu.cn.

† These authors contributed to this work equally.

Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Materials Science, Zhejiang Normal University, Jinhua 321004, People's Republic of China.

Table of Contents

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 DPDPE was obtained after removal of the solvent under reduced pressure. DPDPE (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. 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 (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DPTB). ((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 (Z)-4-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-N,N-diphenylaniline (1a). (E)-2-(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), 4-bromotriphenylamine (2.33 g, 7.2 mmol), and potassium carbon (1.32 g, 9.6 mmol) were dissolved in a mixture of toluene (60 ml) and tetrahydrofuran (30 ml) in a mixed solution. The reaction solution was stirred at room temperature under nitrogen for 30 min, then tetrakis(triphenylphosphine)palladium (277 mg, 0.24 mmol) was added. After completion of the reaction, the mixture was poured into water and extracted three times with dichloromethane. The organic layer was dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether) to give a white solid powder (2.09 g, 85.3%). Molecular formula: $C_{38}H_{31}NS$. ^{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 $[M+H]^+$ 534.2211, found 534.2243.

Synthesis of (Z)-3-(2-(4-(diphenylamino)phenyl)-1,2-diphenylvinyl)-2,5-dimethylthiophene 1,1-dioxide (2a). (Z)-4-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylethenyl)-N,N-diphenylphenylaniline (DPTPS) (1.00 g, 1.8 mmol) was stirred in 60 mL of dichloromethane solution for 1 h. m-Chloroperbenzoic acid (m-CPBA) (1.242 g, 7.2 mmol) was added slowly. Upon completion of the reaction, the mixture was washed with sodium bisulfite, sodium bicarbonate, and aqueous solution, and the organic layer was dried with anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether) to give a yellow solid (0.91 g, 89.4%).Molecular formula: $C_{38}H_{31}NO_2S$. ^{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 $[M+H]^+$ 566.2109, found 566.2144.

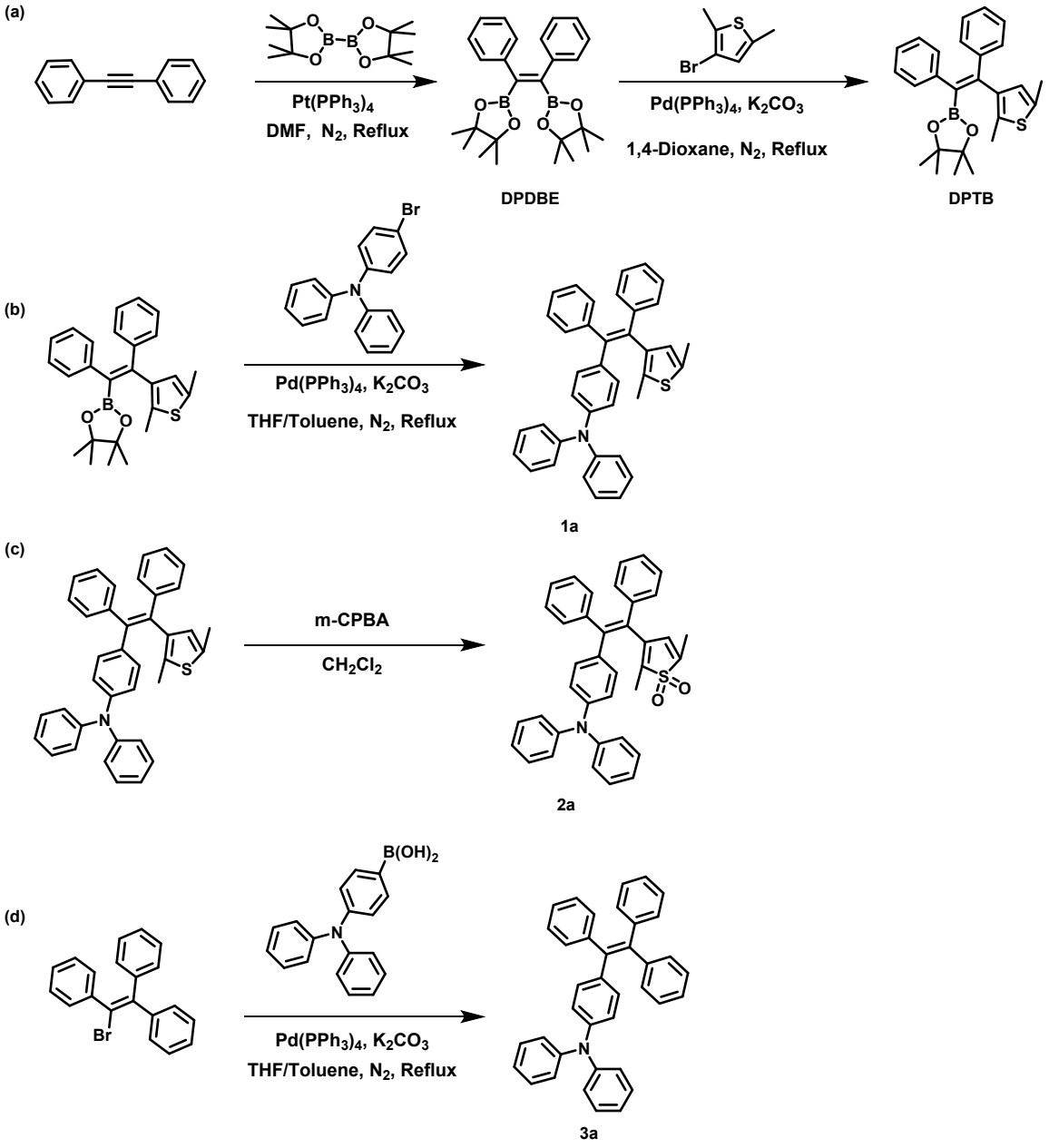
Synthesis of N,N-diphenyl-4-(1,2,2-triphenylvinyl)aniline (3a). 4-(Diphenylamino)benzeneboronic acid (2.60 g, 9.0 mmol), 1-bromo-1,2,2-triphenylethylene (2.01 g, 6.0 mmol) and potassium carbonate (1.24 g, 9.0 mmol) were

dissolved in a mixture of toluene (60 ml) and tetrahydrofuran (30 ml). The reaction solution was stirred at room temperature under nitrogen for 30 min, then tetrakis(triphenylphosphine)palladium (50 mg, 0.043 mmol) was added. After completion of the reaction, the mixture was poured into water and extracted three times with dichloromethane. The organic layer was dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether) to give a white solid powder (2.44 g, 81.4%). Molecular formula: $C_{38}H_{29}N$. ^{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 $[M+H]^+$ 500.2334, found 500.2360.

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 and 2a were computed using density functional theory (DFT) with the hybrid M06-2X 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** and **3a**.

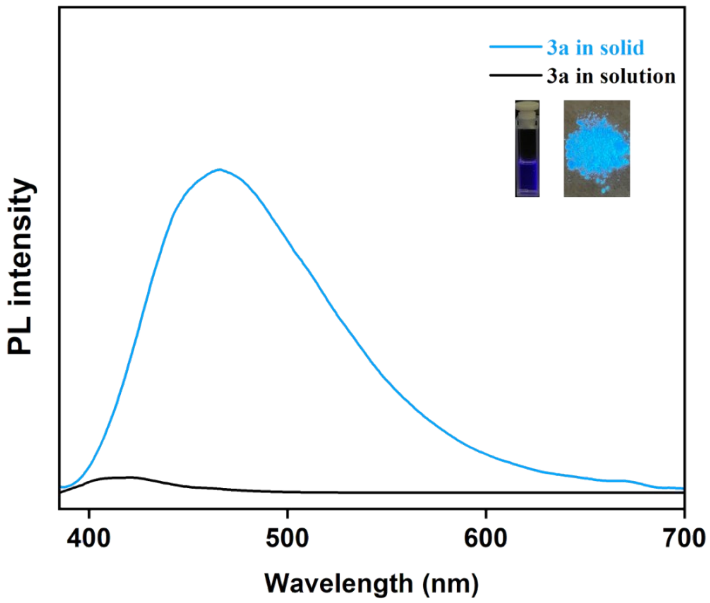


Figure S1. PL spectra of compounds **3a** in solution (10.0 μM) and in the solid state. Insets: Fluorescence images under UV light.

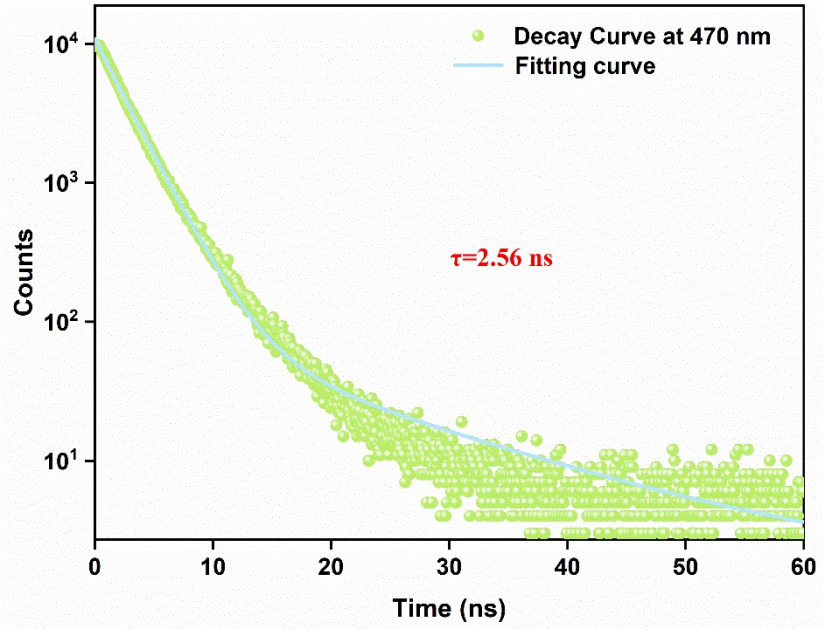


Figure S2. Time-resolved PL decay curve of compounds **3a** in the solid state.

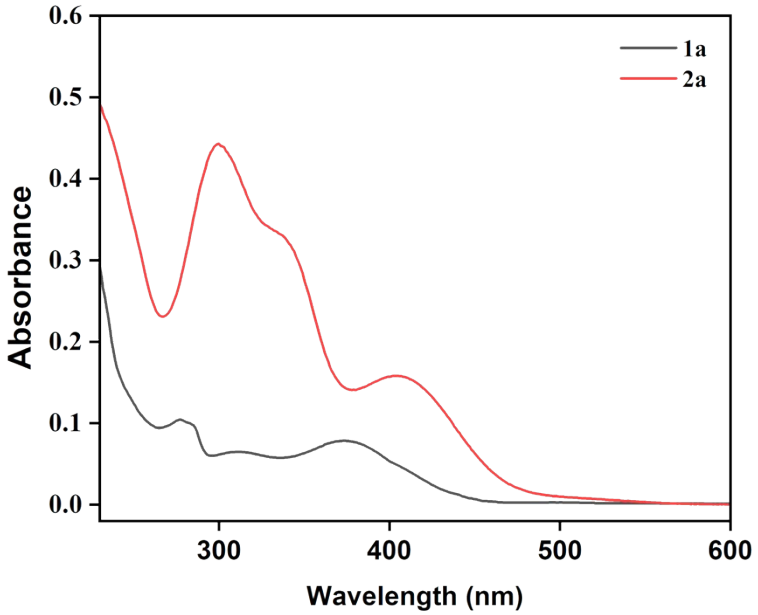


Figure S3. UV-visible absorption spectra of compounds **1a** and **2a** in THF solution (25.0 μM).

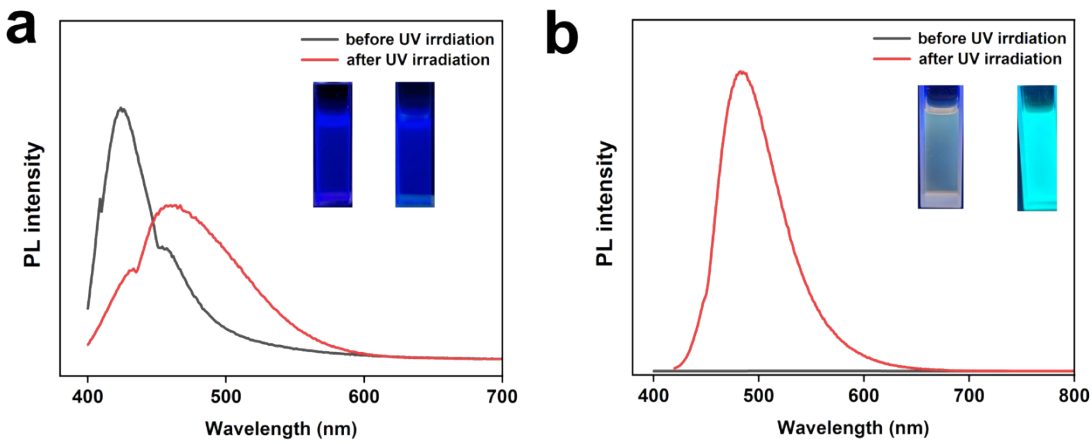


Figure S4. PL spectra of compounds **1a** and **2a** in THF solution (25.0 μM) before and after UV irradiation. Insets: fluorescent images under UV light.

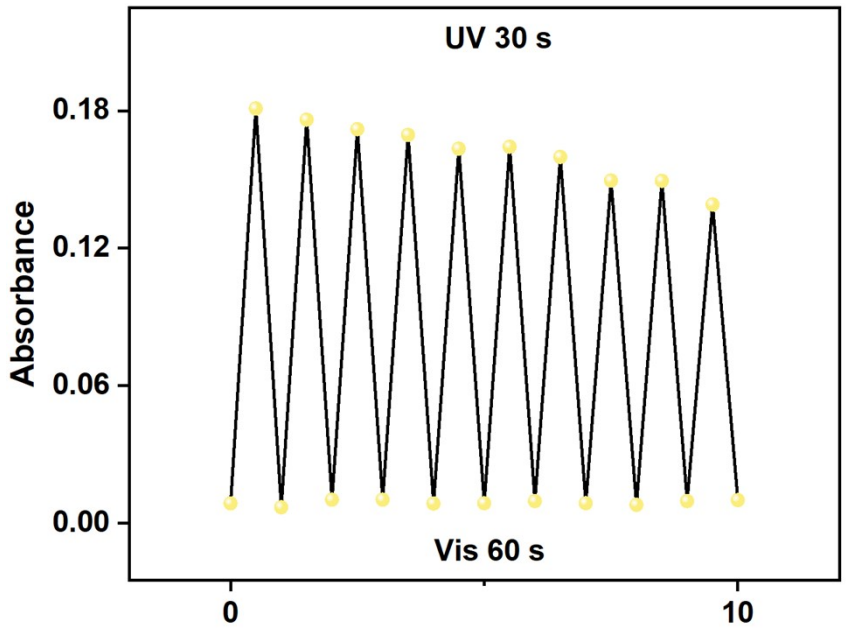


Figure S5. Time-dependent UV-vis absorption spectra of **2a** in THF with a concentration of 50 μM.

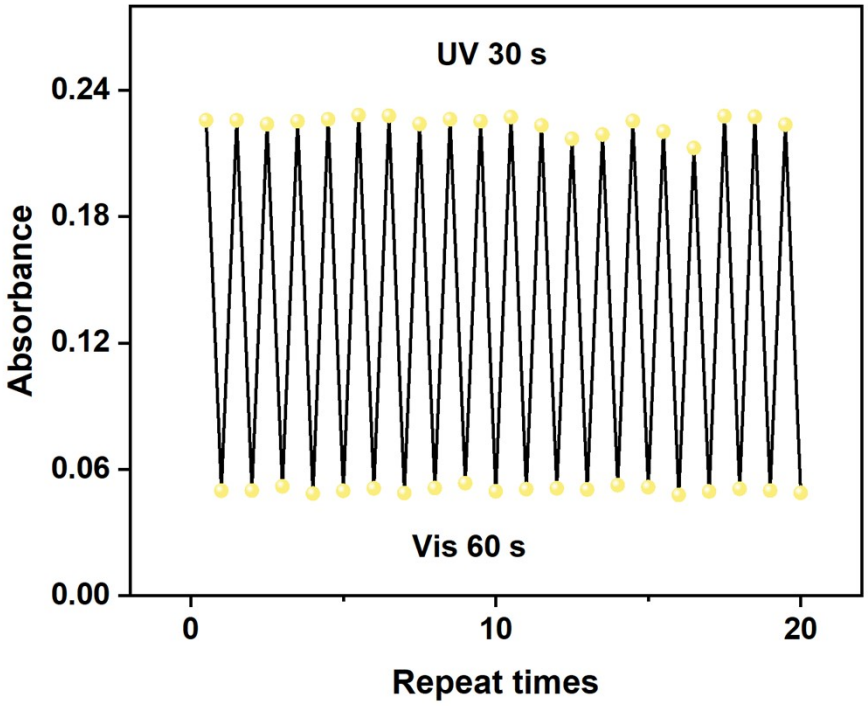


Figure S6. Photochromic recycles of **2a** in film as a function of exposure to UV-light (365 nm) and visible-light respectively.

4. Supplementary Tables

Table S1. Optical properties of the compounds **1a** and **2a** in solution in response to light stimulation and in response to acid stimulation.

	solution							
	λ_{fl}^{a} (nm)	λ_{fl}^{b} (nm)	λ_{fl}^{c} (nm)	λ_{fl}^{d} (nm)	Φ_{fl}^{a} (%)	Φ_{fl}^{b} (%)	Φ_{fl}^{c} (%)	Φ_{fl}^{d} (%)
1a	424	458			7.0	5.8		
1b	547	484	573	547	8.7	93.4		92.5

[a] The open form. [b] The closed form. [c] add TFA. [d] than add TEA

Table S2. Contribution ratios of different groups to natural transition orbitals of **1a** and **2a**.

Compounds	Group	Contribution to HOMO (%)	Contribution to LUMO (%)
1a	ethene	16.02	16.19
	triphenylamine	45.64	49.50
	2,5-dimethylthiophene	33.80	29.21
	S	9.68	2.03
1b	ethene	6.44	5.15
	triphenylamine	84.26	42.62
	2,5-dimethylthiophene dioxide	7.48	34.12
	S	0.00	0.01

5. NMR and MS Spectra of Compounds

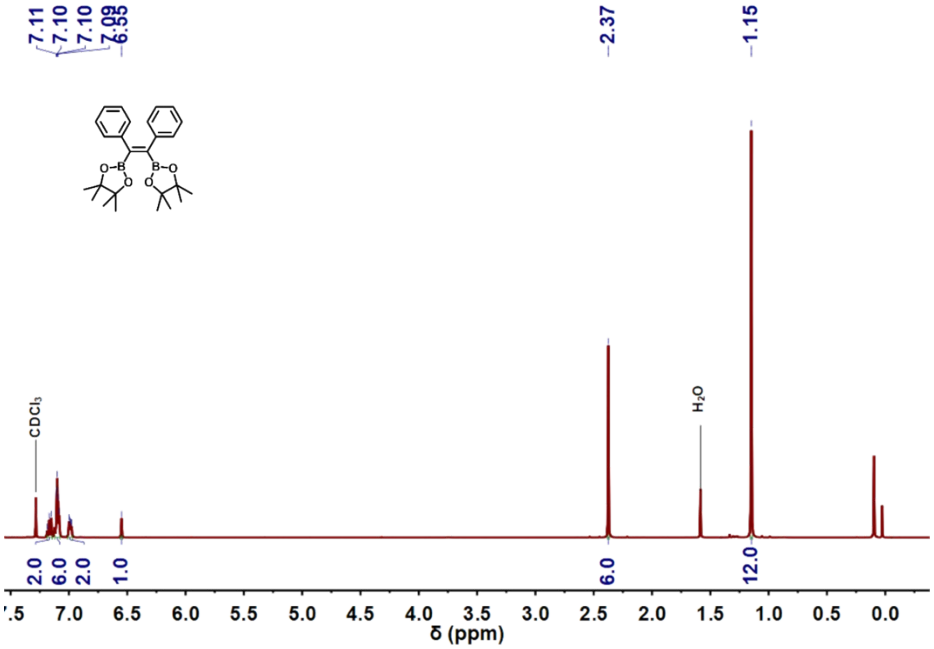


Figure S7. ^{1}H NMR spectrum of ((Z)-(1,2-diphenyl-)-(Z)-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))ethene (DPDBE) in $CDCl_3$.

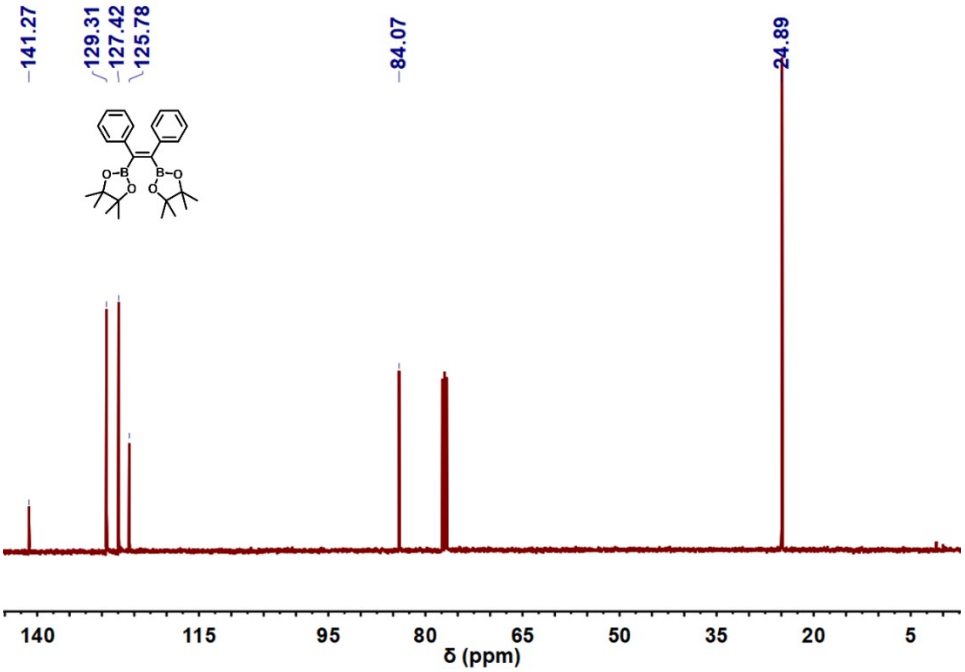


Figure S8. ^{13}C NMR spectrum of ((Z)-(1,2-diphenyl-)-(Z)-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))ethene (DPDBE) in $CDCl_3$.

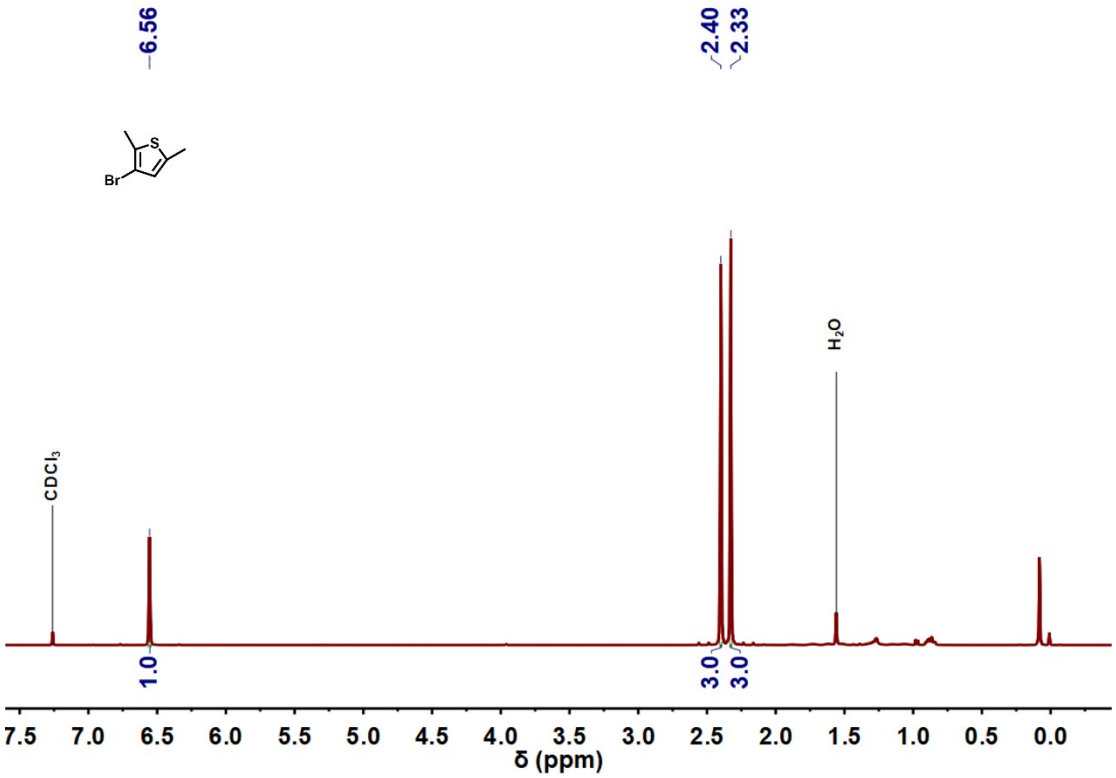


Figure S9. ^{1}H NMR spectrum of 3-bromo-2,5-dimethylthiophene in $CDCl_3$.

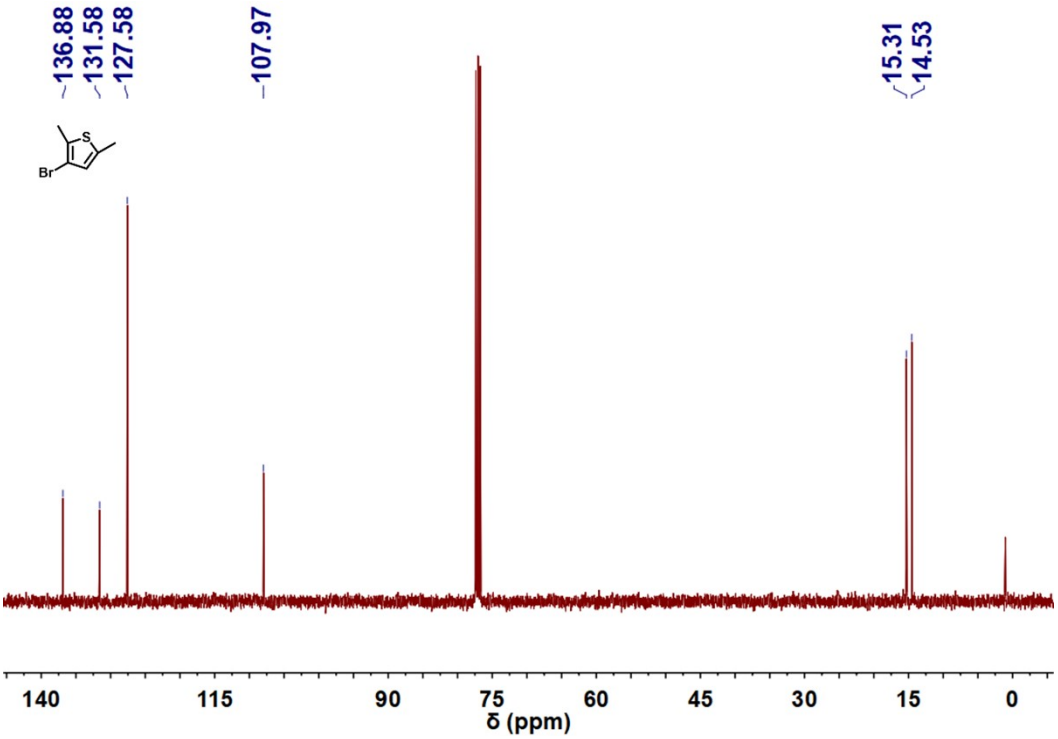


Figure S10. ^{13}C NMR spectrum of 3-bromo-2,5-dimethylthiophene in $CDCl_3$.

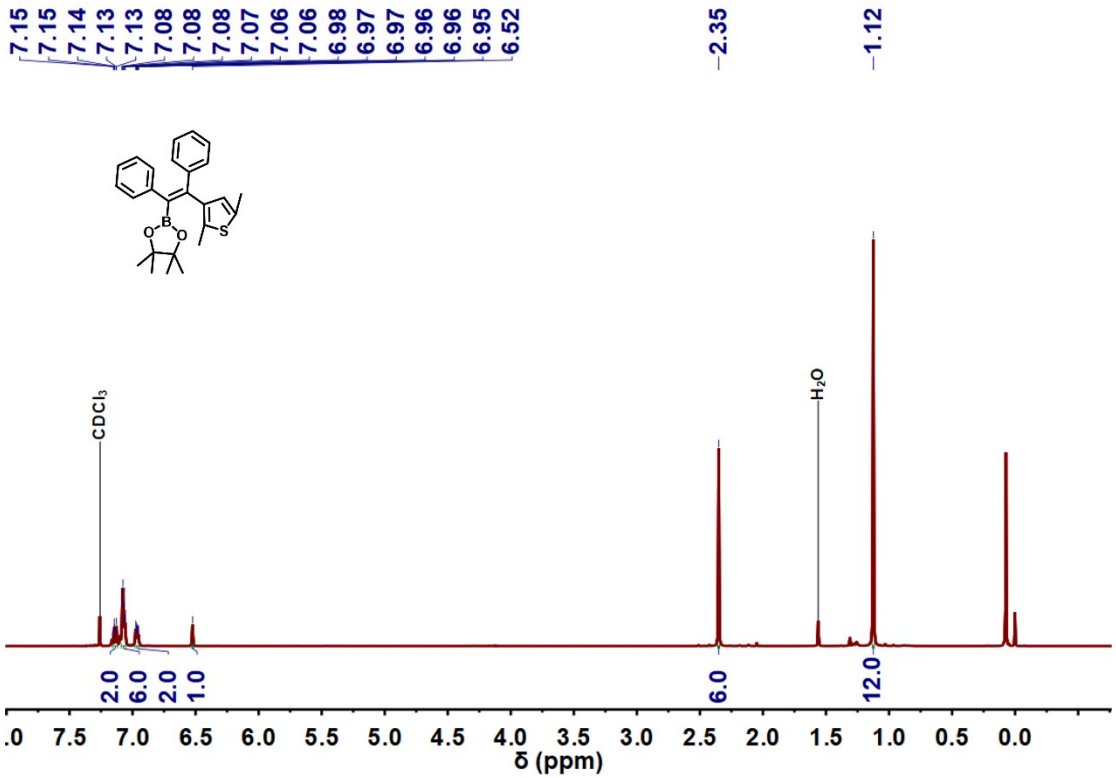


Figure S11. ^{1}H NMR spectrum of (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DPTB) in $CDCl_3$.

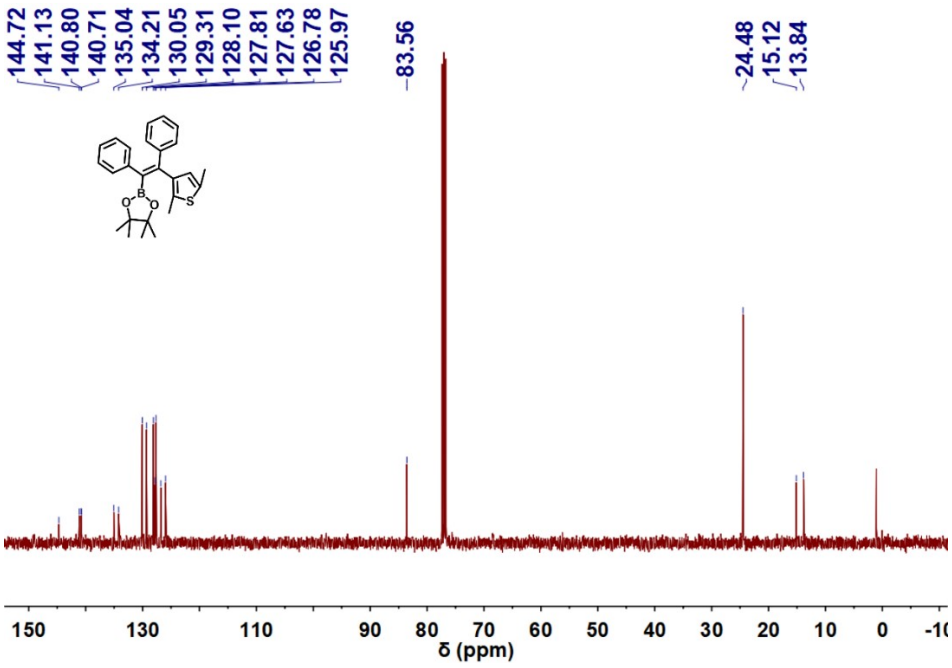


Figure S12. ^{13}C NMR spectrum of (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DPTB) in $CDCl_3$.

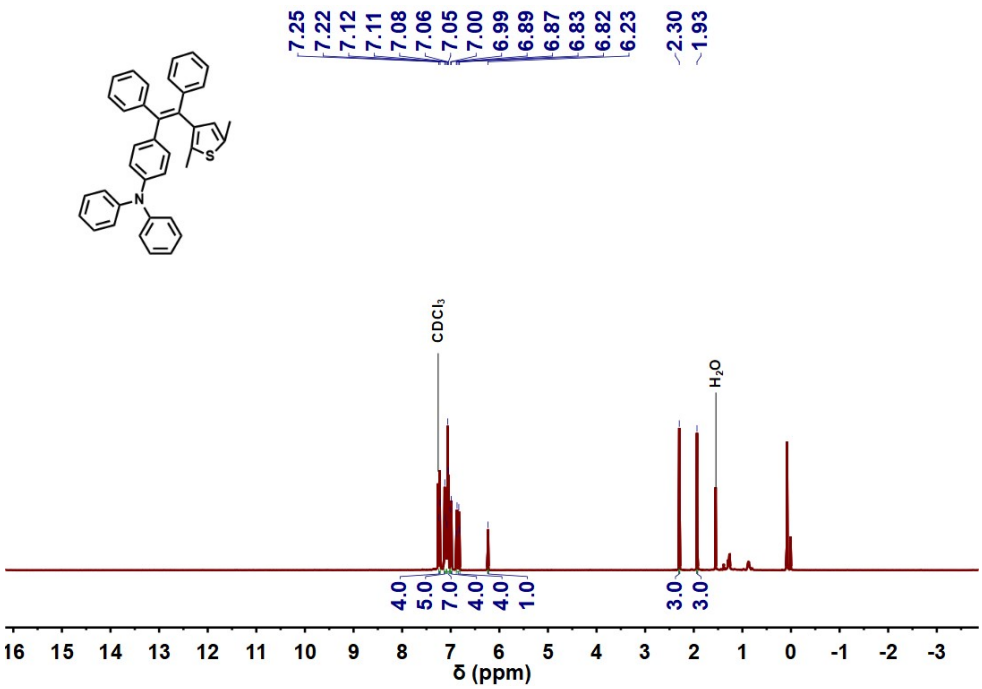


Figure S13. ^{1}H NMR spectrum of (Z)-4-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-N,N-diphenylaniline (**1a**) in $CDCl_3$.

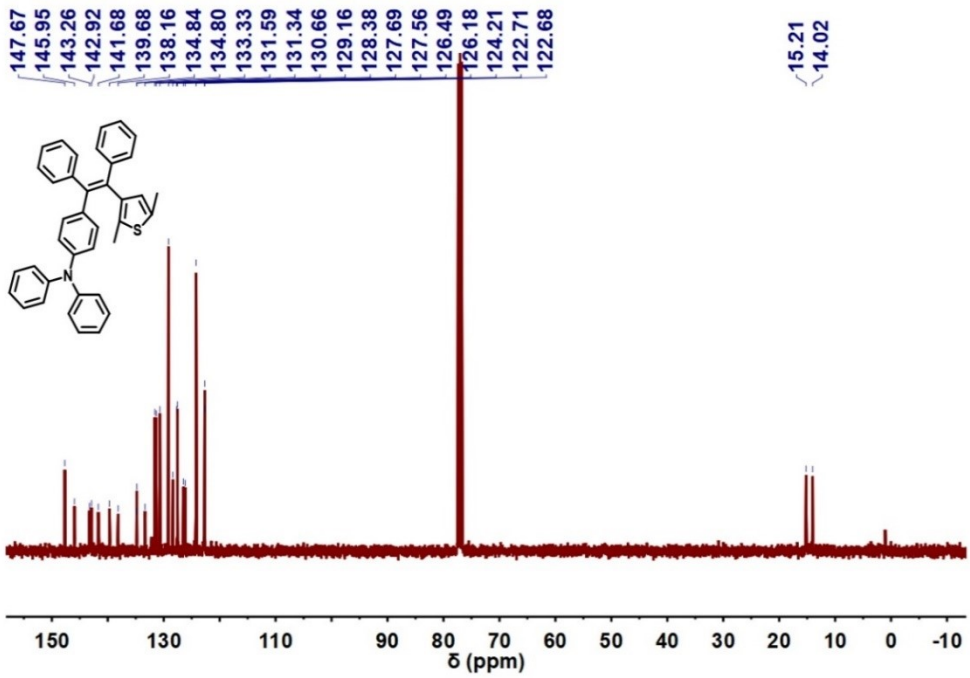


Figure S14. ^{13}C NMR spectrum of (Z)-4-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-N,N-diphenylaniline (**1a**) in $CDCl_3$.

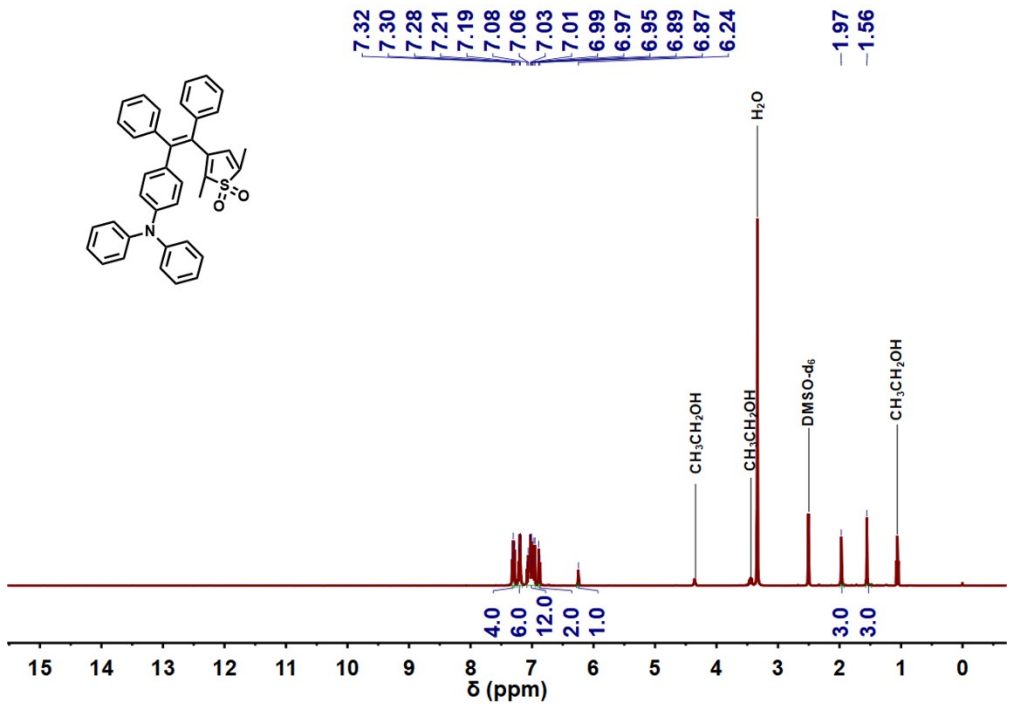


Figure S15. ^{1}H NMR spectrum of (Z)-3-(2-(4-(diphenylamino)phenyl)-1,2-diphenylvinyl)-2,5-dimethylthiophene 1,1-dioxide (**2a**) in $CDCl_3$.

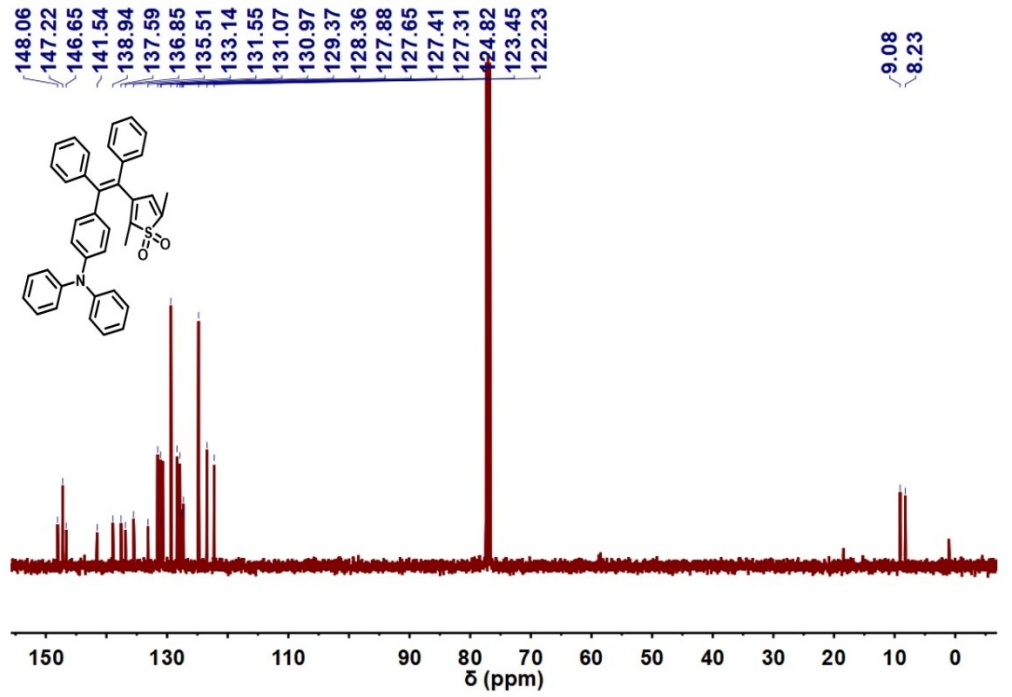


Figure S16. ^{13}C NMR spectrum of (Z)-3-(2-(4-(diphenylamino)phenyl)-1,2-diphenylvinyl)-2,5-dimethylthiophene 1,1-dioxide (**2a**) in $CDCl_3$.

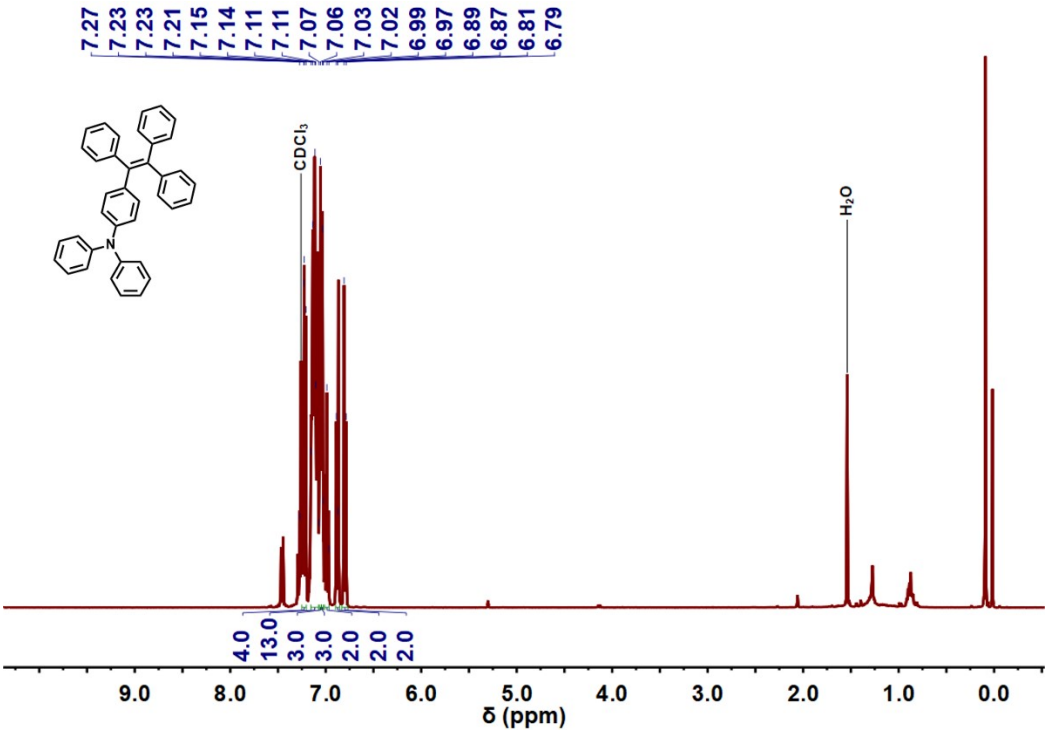


Figure S17. ^{1}H NMR spectrum of N,N-diphenyl-4-(1,2,2-triphenylvinyl)aniline (**3a**) in $CDCl_3$.

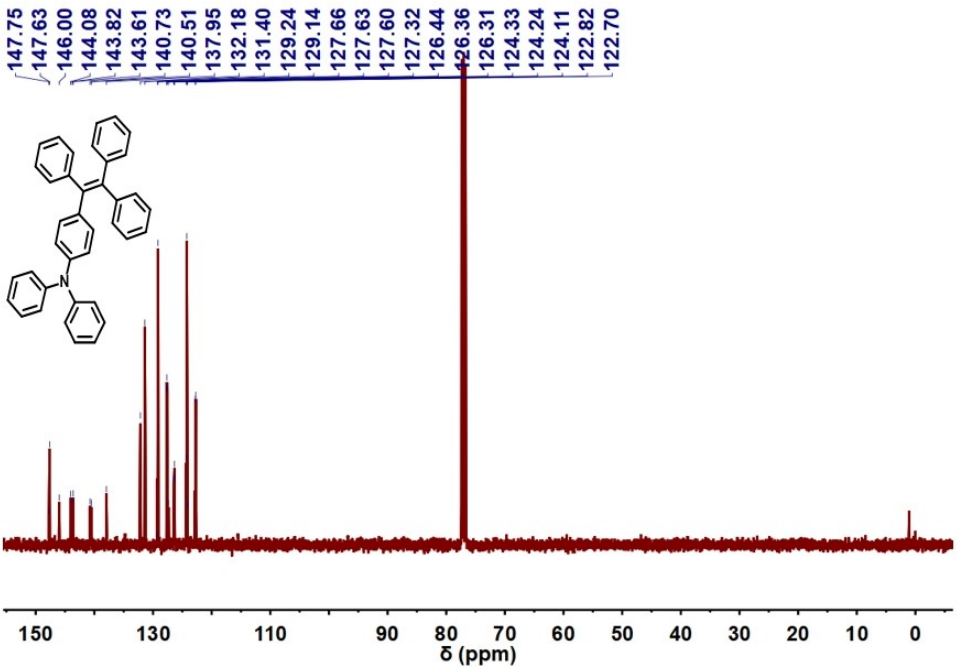


Figure S18. ^{13}C NMR spectrum of N,N-diphenyl-4-(1,2,2-triphenylvinyl)aniline (**3a**) in $CDCl_3$.

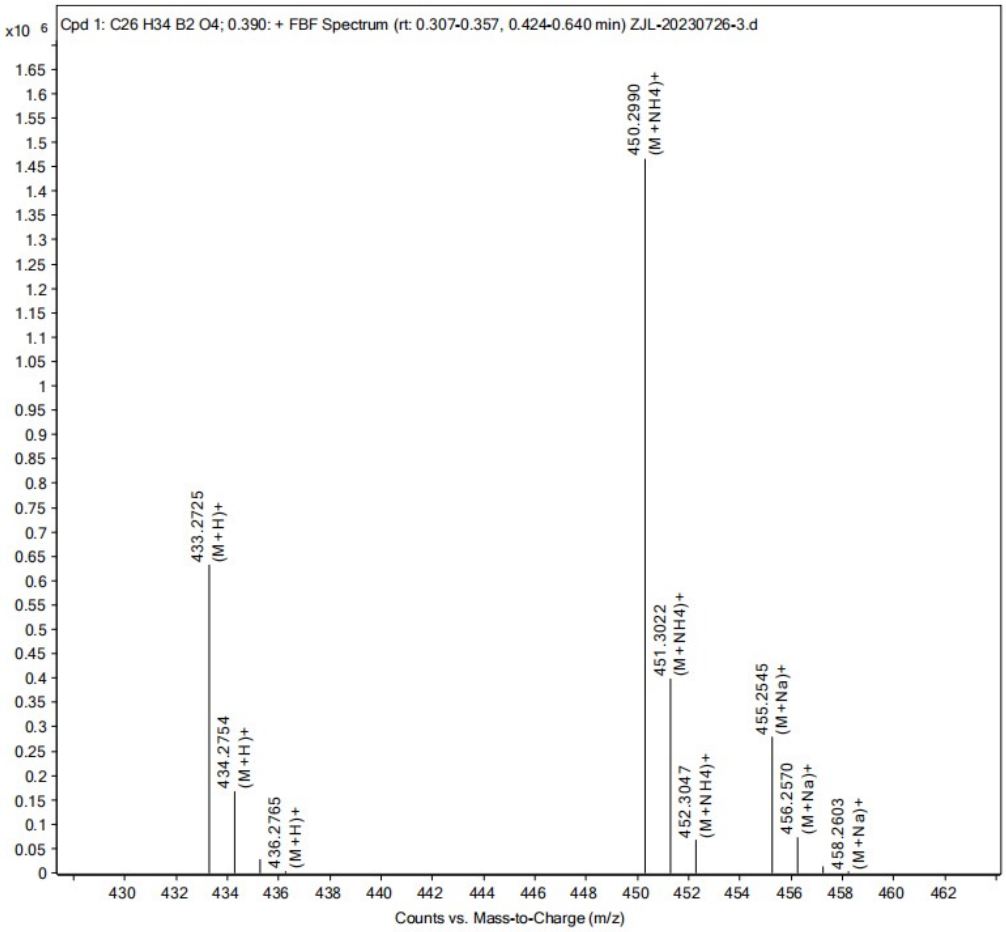


Figure S19. Mass spectrum of ((Z)-(1,2-diphenyl-)-(Z)-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))ethene (DPDBE).

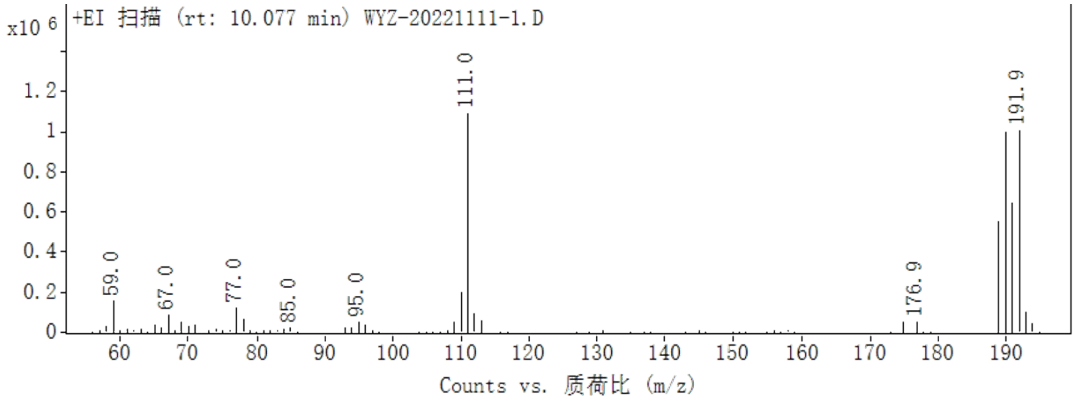


Figure S20. Mass spectrum of 3-bromo-2,5-dimethylthiophene.

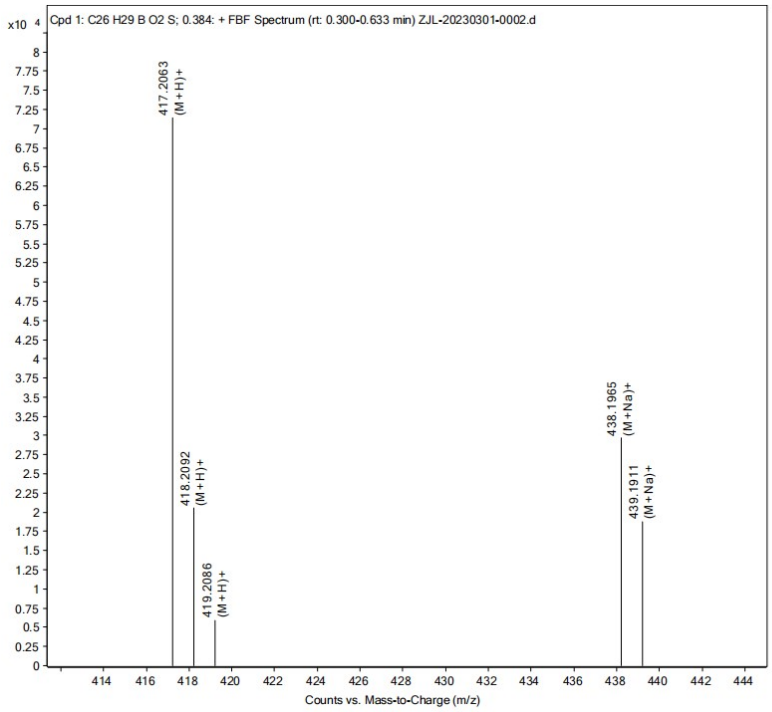


Figure S21. Mass spectrum of (E)-2-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (DPTB).

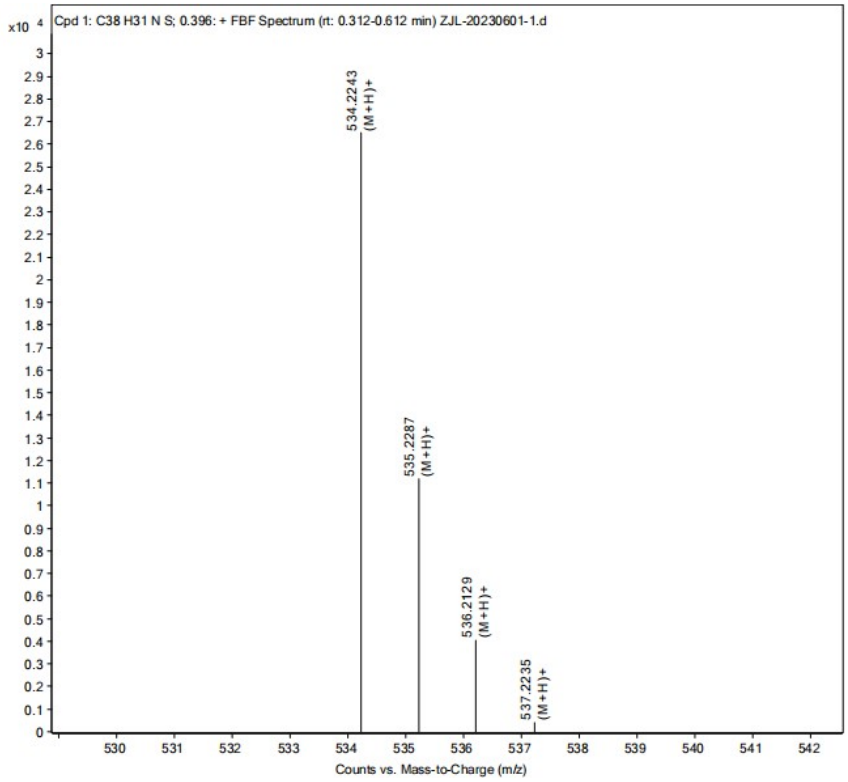


Figure S22. Mass spectrum of (Z)-4-(2-(2,5-dimethylthiophen-3-yl)-1,2-diphenylvinyl)-N,N-diphenylaniline (**1a**).

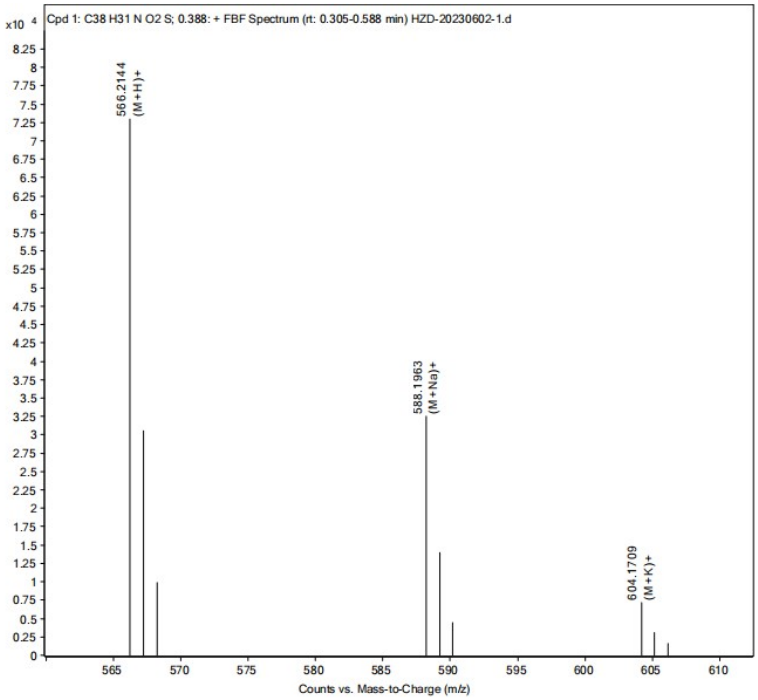


Figure S23. Mass spectrum of (Z)-3-(2-(4-(diphenylamino)phenyl)-1,2-diphenylvinyl)-2,5-dimethylthiophene 1,1-dioxide (**2a**).

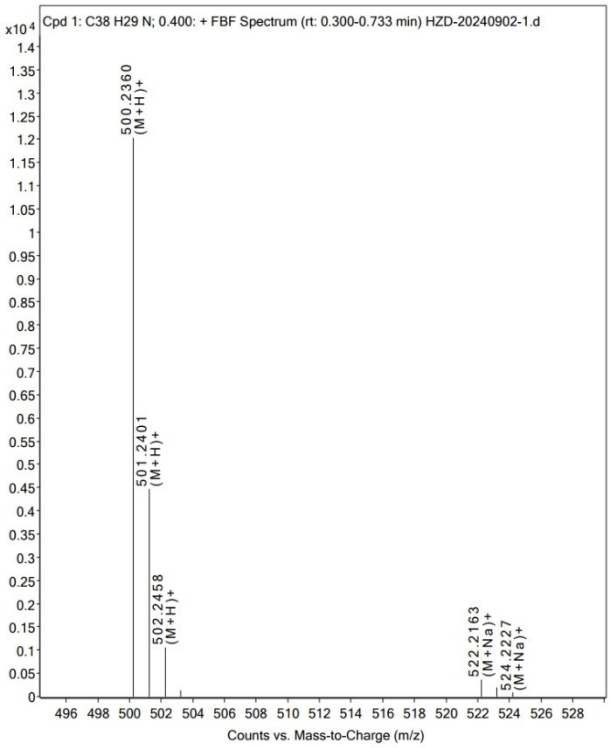


Figure S24. Mass spectrum of N,N-diphenyl-4-(1,2,2-triphenylvinyl)aniline (**3a**).

6. Cartesian Coordinates

Cartesian coordinate of **1a**

C	-1.58960000	-1.62930000	1.26900000
C	-2.91950000	-1.35370000	1.16580000
C	-0.70010000	-0.84910000	0.59920000
C	-1.18810000	-2.67740000	2.03790000
C	-3.33850000	-0.06480000	1.12570000
C	-3.81290000	-2.37260000	1.04440000
C	-1.92830000	-3.10500000	3.08460000
C	-1.55900000	-4.14230000	3.85240000
C	-0.42350000	-4.80300000	3.59120000
C	0.32750000	-4.41230000	2.55310000
C	-0.05480000	-3.37130000	1.79650000
C	-3.45720000	-3.57630000	0.54370000
C	-4.32510000	-4.59370000	0.42650000
C	-5.59720000	-4.44260000	0.81730000
C	-5.98100000	-3.26430000	1.32560000
C	-5.10100000	-2.25620000	1.43370000
C	0.57570000	-0.66710000	0.98940000
C	1.42890000	0.13610000	0.33330000
C	1.10500000	0.84470000	-0.77140000
C	-0.17500000	0.64100000	-1.15490000
C	-1.03470000	-0.16330000	-0.51030000
C	-2.78340000	1.03120000	1.68580000
S	-3.51470000	2.27490000	1.38640000
C	-4.57120000	1.68810000	0.55970000
C	-4.42100000	0.36310000	0.45440000
C	-1.63730000	1.08130000	2.67180000
C	-5.66150000	2.48860000	-0.10020000
N	1.92600000	1.63220000	-1.39350000
C	1.46280000	2.64190000	-2.06420000

C	3.20340000	1.41140000	-1.33930000
C	2.10050000	3.18490000	-3.12930000
C	1.63080000	4.22780000	-3.83280000
C	0.46970000	4.80120000	-3.49580000
C	-0.19910000	4.30480000	-2.44860000
C	0.29280000	3.25830000	-1.76620000
C	4.13470000	2.38660000	-1.47350000
C	5.45910000	2.17250000	-1.41720000
C	5.93510000	0.93730000	-1.22230000
C	5.05700000	-0.06280000	-1.08480000
C	3.73800000	0.18190000	-1.14140000
H	-2.85750000	-2.59050000	3.38270000
H	-2.18550000	-4.44980000	4.70690000
H	-0.11670000	-5.65890000	4.21470000
H	1.25200000	-4.96350000	2.31090000
H	0.58320000	-3.14990000	0.92450000
H	-2.43890000	-3.76770000	0.16590000
H	-3.99620000	-5.55620000	-0.00100000
H	-6.31420000	-5.27520000	0.72770000
H	-7.02020000	-3.13240000	1.67230000
H	-5.47860000	-1.33840000	1.91480000
H	0.94690000	-1.10590000	1.93150000
H	2.40830000	0.26260000	0.82730000
H	-0.57030000	1.07480000	-2.09040000
H	-2.03040000	-0.28060000	-0.97140000
H	-5.09190000	-0.25440000	-0.15950000
H	-1.41540000	0.09240000	3.12710000
H	-0.71380000	1.47880000	2.19280000
H	-1.86710000	1.74100000	3.54010000
H	-6.34920000	1.83560000	-0.68350000
H	-6.27830000	3.02530000	0.65670000
H	-5.23690000	3.23750000	-0.80760000

H	3.02590000	2.74550000	-3.53980000
H	2.18840000	4.60580000	-4.70690000
H	0.07530000	5.65890000	-4.06480000
H	-1.14740000	4.77590000	-2.13750000
H	-0.30410000	2.98200000	-0.87950000
H	3.85580000	3.45070000	-1.56250000
H	6.16390000	3.01670000	-1.50960000
H	7.02020000	0.74900000	-1.17580000
H	5.42650000	-1.09330000	-0.94580000
H	3.11130000	-0.72500000	-1.08940000

Cartesian coordinate of **2a**.

C	-0.33110000	0.73990000	-1.91330000
C	-0.15160000	-0.07590000	-2.98990000
C	0.15140000	0.36030000	-0.69970000
C	-0.98900000	1.91930000	-2.08030000
C	0.99760000	-0.78570000	-3.12220000
C	-1.15400000	-0.22180000	-3.89890000
C	-0.98500000	2.56520000	-3.26740000
C	-1.63400000	3.72440000	-3.45960000
C	-2.32700000	4.28220000	-2.45820000
C	-2.36120000	3.66170000	-1.27150000
C	-1.70440000	2.50420000	-1.09520000
C	-2.45000000	-0.02240000	-3.57270000
C	-3.44600000	-0.15300000	-4.46340000
C	-3.17590000	-0.48750000	-5.73190000
C	-1.90060000	-0.68580000	-6.09040000
C	-0.91660000	-0.55330000	-5.18690000
C	0.49280000	1.22980000	0.27040000
C	0.99620000	0.84130000	1.45320000
C	1.22230000	-0.44710000	1.79320000
C	0.86980000	-1.30630000	0.81100000

C	0.35770000	-0.92920000	-0.37130000
C	2.23410000	-0.43950000	-2.70540000
S	3.55740000	-1.63650000	-2.94760000
C	2.23550000	-2.59630000	-3.69460000
C	1.03450000	-2.00900000	-3.68010000
C	2.66740000	0.91070000	-2.18610000
C	2.49840000	-3.97390000	-4.23450000
O	3.95540000	-2.22670000	-1.67730000
O	4.49240000	-1.18390000	-3.96810000
N	1.72300000	-0.81830000	2.93030000
C	2.39520000	-1.92570000	3.00290000
C	1.55470000	-0.08230000	3.98550000
C	2.50100000	-2.66420000	4.13380000
C	3.19310000	-3.81200000	4.21670000
C	3.83720000	-4.29140000	3.14610000
C	3.76820000	-3.59740000	2.00420000
C	3.06520000	-2.45480000	1.95050000
C	2.41420000	-0.07310000	5.03300000
C	2.25300000	0.68510000	6.12950000
C	1.19260000	1.49350000	6.24090000
C	0.31200000	1.52120000	5.23390000
C	0.50140000	0.75490000	4.14770000
H	-0.40830000	2.18620000	-4.12820000
H	-1.59240000	4.22660000	-4.44100000
H	-2.86640000	5.23150000	-2.61030000
H	-2.94880000	4.09680000	-0.44530000
H	-1.83100000	2.02350000	-0.11050000
H	-2.75630000	0.21770000	-2.54080000
H	-4.49240000	0.00540000	-4.15160000
H	-3.98870000	-0.59290000	-6.46930000
H	-1.66160000	-0.94120000	-7.13680000
H	0.11010000	-0.67800000	-5.57090000

H	0.45520000	2.31850000	0.09360000
H	1.31720000	1.67010000	2.10850000
H	0.90870000	-2.39940000	0.96370000
H	0.05690000	-1.74360000	-1.05210000
H	0.15430000	-2.55040000	-4.05710000
H	1.94100000	1.72430000	-2.39490000
H	2.87730000	0.86250000	-1.09420000
H	3.60890000	1.23280000	-2.68560000
H	1.58030000	-4.44420000	-4.65190000
H	3.25750000	-3.92790000	-5.04780000
H	2.88450000	-4.63600000	-3.42670000
H	1.95030000	-2.40210000	5.05360000
H	3.21810000	-4.37920000	5.16300000
H	4.40980000	-5.23150000	3.20350000
H	4.31100000	-3.95910000	1.11390000
H	3.13910000	-1.92730000	0.98430000
H	3.35960000	-0.64210000	5.01650000
H	3.00500000	0.66320000	6.93700000
H	1.04880000	2.11930000	7.13680000
H	-0.58200000	2.16340000	5.31320000
H	-0.32320000	0.80360000	3.41580000