

## Supporting information

### Novel and Asymmetric S, N -Heterocyclics with Fused Six-membered Rings for Organic Field Effect Transistors Application

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## 1. TGA of compounds

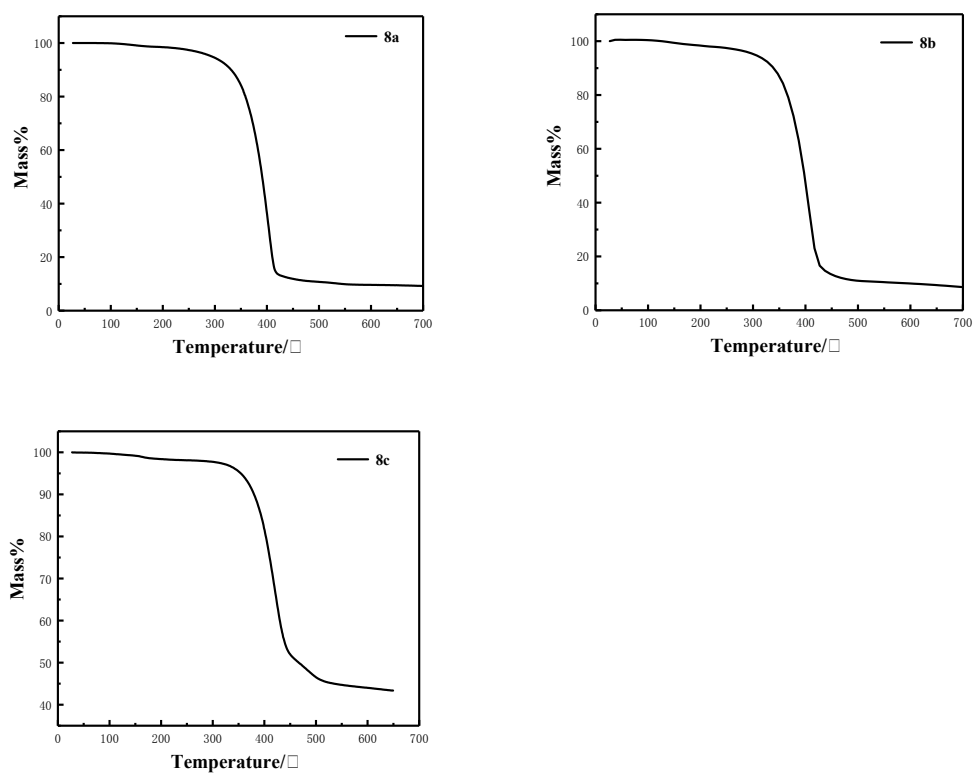
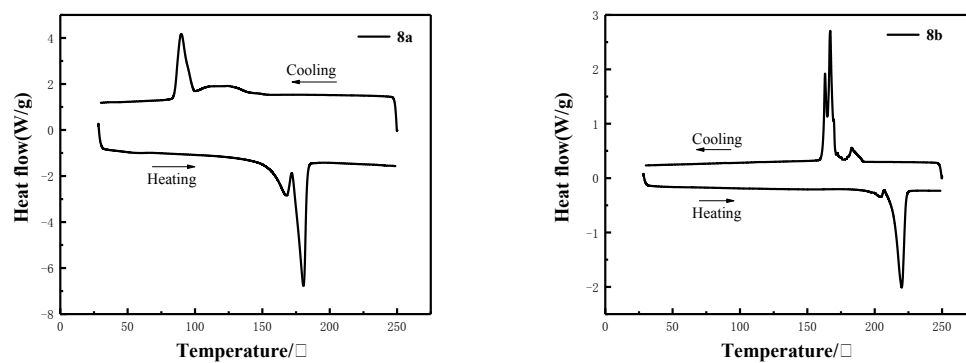


Figure S1: Thermal gravimetric analysis of **8a**, **8b** and **8c**, which were recorded at 10°C/min in a nitrogen atmosphere.

## 2. DSC of compounds



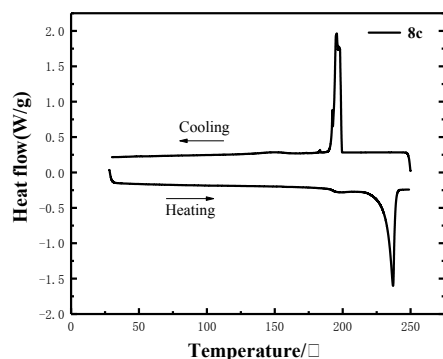


Figure S2: The second heating/cooling DSC traces of **8a**, **8b** and **8c** recorded at 10°C /min in a nitrogen atmosphere.

### 3. Single crystal of **8a**, **8b** and **8c**.

X-Ray structure analysis of **8a** (CCDC-2017379)

Bond precision: C-C = 0.0204 Å Wavelength=1.54184  
 Cell: a=19.5389(9) b=5.9354(4) c=38.670(3)  
 alpha=90 beta=98.166(5) gamma=90

Temperature: 150 K

	Calculated	Reported
Volume	4439.1(5)	4439.1(5)
Space group	I 2	I 1 2 1
Hall group	I 2y	I 2y
Moiety formula	C <sub>26</sub> H <sub>25</sub> N <sub>3</sub> S <sub>2</sub>	C <sub>26</sub> H <sub>25</sub> N <sub>3</sub> S <sub>2</sub>
Sum formula	C <sub>26</sub> H <sub>25</sub> N <sub>3</sub> S <sub>2</sub>	C <sub>26</sub> H <sub>25</sub> N <sub>3</sub> S <sub>2</sub>
Mr	443.61	443.61
Dx, g cm <sup>-3</sup>	1.327	1.328
Z	8	8
Mu (mm <sup>-1</sup> )	2.309	2.309
F000	1872.0	1872.0
F000'	1881.57	
h, k, lmax	23, 7, 46	23, 7, 46
Nref	7933[ 4387]	7243
Tmin, Tmax	0.847, 0.912	0.722, 1.000
Tmin'	0.776	

Correction method= # Reported T Limits: Tmin=0.722 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.65/0.91

Theta(max)= 67.071

R(reflections)= 0.1532( 5400)

wR2(reflections)= 0.3911( 7243)

S = 1.145

Npar= 629

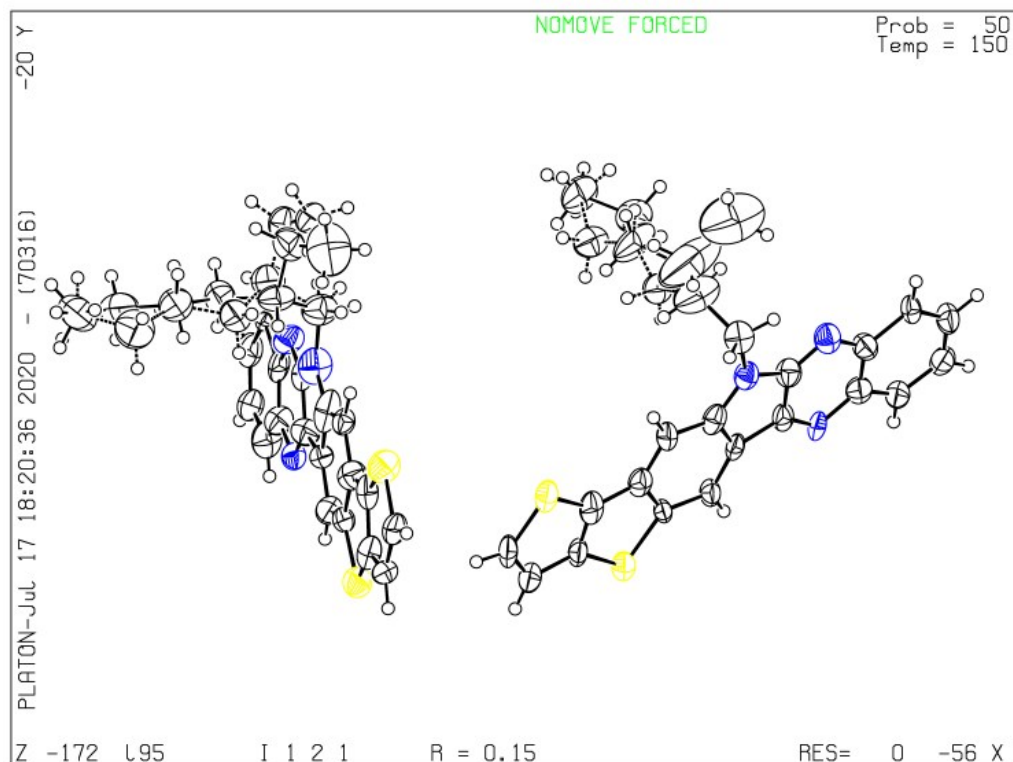


Figure S3: Structure of **8a** (CCDC-2017379).

X-Ray structure analysis of **8b** (CCDC-2009483)

Bond precision:	C-C = 0.0074 Å	Wavelength=1.54184
Cell:	a=15.1256(9)      b=10.6235(4)      c=13.7968(7)	
	alpha=90          beta=103.141(6)      gamma=90	
Temperature:	150 K	
	Calculated	Reported
Volume	2158.91(19)	2158.92(19)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C26 H25 N3 S2	C26 H25 N3 S2
Sum formula	C26 H25 N3 S2	C26 H25 N3 S2
Mr	443.61	443.61
Dx, g cm <sup>-3</sup>	1.365	1.365
Z	4	4
Mu (mm <sup>-1</sup> )	2.374	2.374
F000	936.0	936.0
F000'	940.78	
h, k, lmax	19, 13, 17	18, 13, 17
Nref	4526	4340
Tmin, Tmax	0.735, 0.931	0.044, 1.000
Tmin'	0.667	
Correction method=	# Reported T Limits: Tmin=0.044 Tmax=1.000	
AbsCorr =	MULTI-SCAN	
Data completeness=	0.959	Theta(max)= 76.228
R(reflections)=	0.1151( 2975)	wR2(reflections)= 0.3334( 4340)
S =	1.143	Npar= 281

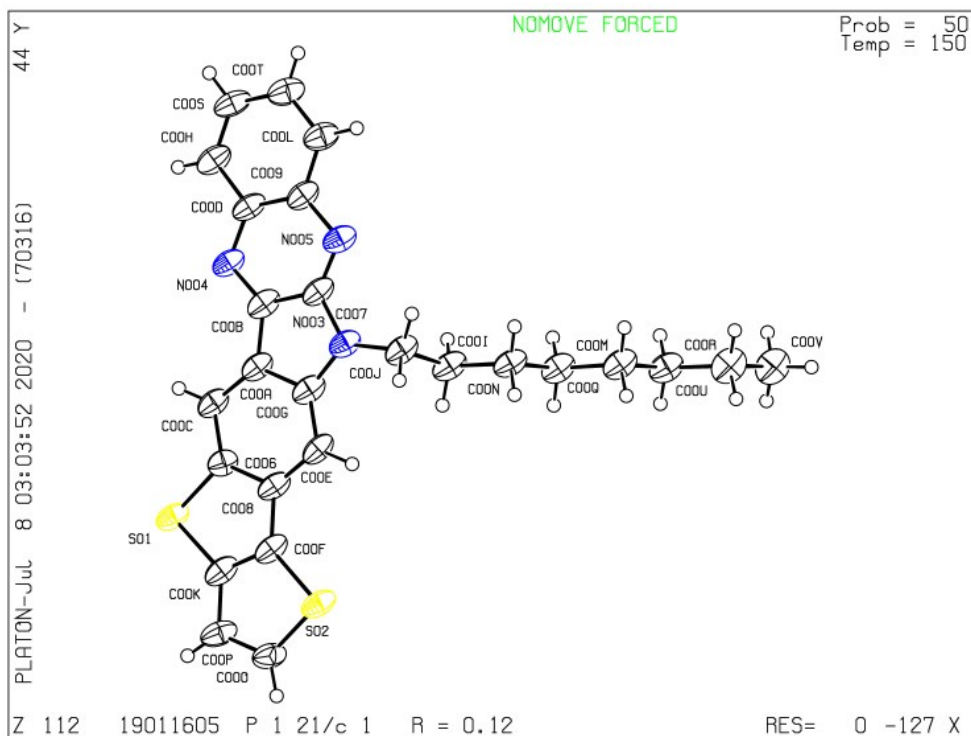


Figure S4: Structure of **8b** (CCDC-2009483).

### X-Ray structure analysis of **8c** (CCDC-2014175)

Bond precision:	C-C = 0.0133 Å	Wavelength=1.54184
Cell:	a=4.8755(2)      b=17.2179(7)      c=28.2672(13)	
	alpha=90      beta=90.483(4)      gamma=90	
Temperature: 149 K		
	Calculated	Reported
Volume	2372.83(18)	2372.83(18)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C26 H23 Cl2 N3 S2	C26 H23 Cl2 N3 S2
Sum formula	C26 H23 Cl2 N3 S2	C26 H23 Cl2 N3 S2
Mr	512.49	512.49
Dx, g cm <sup>-3</sup>	1.435	1.435
Z	4	4
Mu (mm <sup>-1</sup> )	4.264	4.264
F(000)	1064.0	1064.0
F(000')	1071.74	
h, k, lmax	6, 21, 35	6, 21, 34
Nref	4846	4698
Tmin, Tmax	0.836, 0.861	0.836, 0.861
Tmin'	0.278	
Correction method= # Reported T Limits: Tmin=0.836 Tmax=0.861 AbsCorr = MULTI-SCAN		
Data completeness= 0.969	Theta(max)= 74.609	
R(reflections)= 0.1334( 4019)	wR2(reflections)= 0.3522( 4698)	
S = 1.180	Npar= 299	

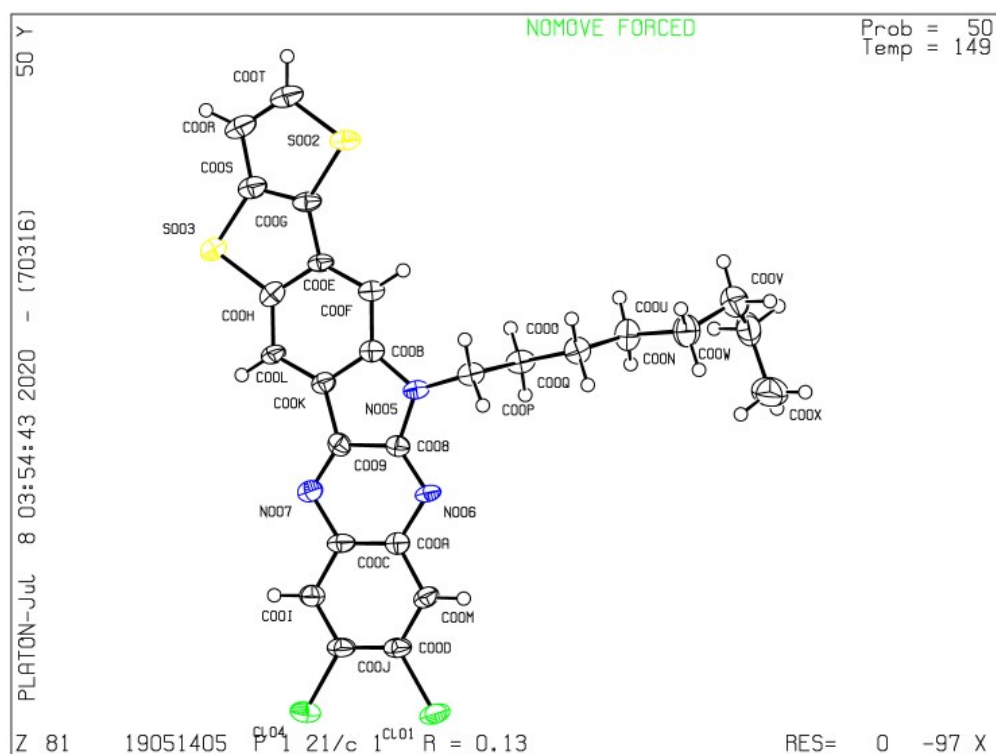


Figure S5: Structure of Structure of **8c** (CCDC-2014175).

#### 4. CVs of compounds

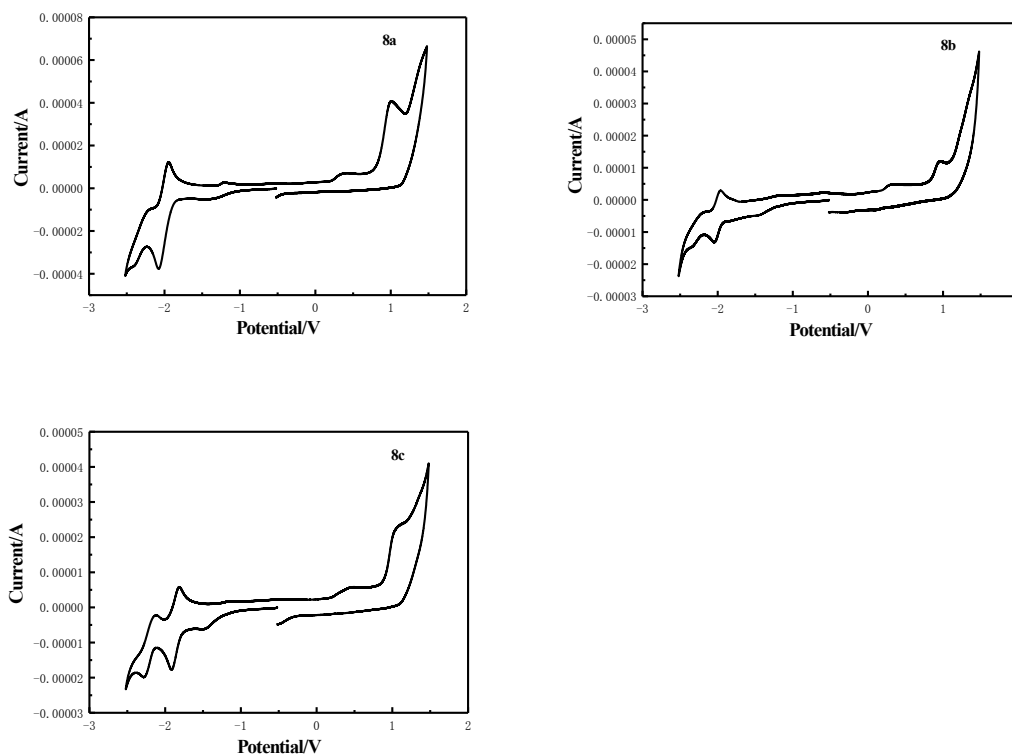


Figure S6: The CV of **8a**, **8b** and **8c** scanning in dichloromethane using an Ag/AgCl reference electrode with the rate of 100 mVs<sup>-1</sup> (the potential is referenced to the Fc/ Fc<sup>+</sup>).

## 5. Computational details

Geometry optimization of **8b** and **8c** molecules were carried out at B3PW91/6-31G(d,p) level of theory. Long alkyl side-chains were replaced with methyl groups to reduce computational cost. The electronic and optical properties of these molecules were evaluated using OT(PCM)- $\omega$ B97X/6-31G(d,p) level of theory using geometries obtained at B3PW91/6-31G(d,p) level of theory. The long-range parameter ( $\omega$ ) was tuned using IP-tuning method in the presence of polarizable continuum model.<sup>[s1]</sup> The optimal  $\omega$  values for **8b** and **8c** molecules considered as 0.019 and 0.018 bohr<sup>-1</sup>, respectively. The excited state energies were calculated using TD-DFT method using OT(PCM)- $\omega$ B97X/6-31G(d,p) level of theory. The nature of excited states is characterized using natural Transitional Orbital (NTO) analysis. Furthermore, the reorganization energies used structures optimized at B3PW91/6-31G(d,p) level of theory for the neutral and cationic molecules. The reorganization energy calculated as the sum of difference in energy between the cation in the neutral geometry and neutral molecule and the difference in energy between the neutral molecule in the cation geometry and the cation. All these calculations were carried out using Gaussian 16.<sup>[s2]</sup> The charge transfer integrals were calculated at B3LYP/6-31g\*\* level of theory.

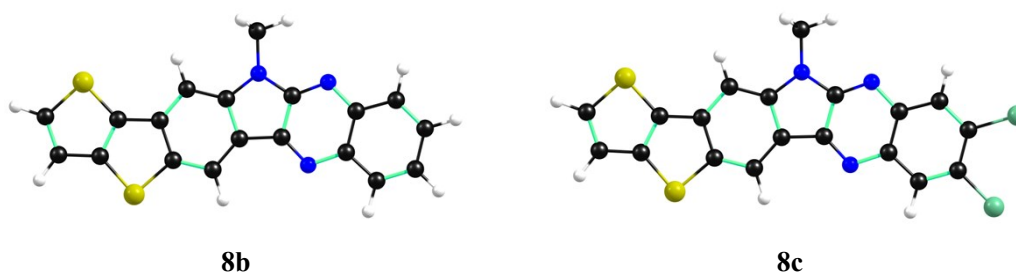


Figure S7: optimized geometries of **8b** and **8c** molecules as obtained at B3PW91/6-31G(d,p) level of theory.

Table S1: Calculated electronic and geometric properties of **8b** and **8c** molecules as obtained at OT- $\omega$ B97X-D/6-31G(d,p) level of theory.

	HOMO (eV)	LUMO (eV)	E(S <sub>1</sub> )/nm	E(S <sub>2</sub> )/nm	E(S <sub>5</sub> )/nm	E(S <sub>6</sub> )/nm
<b>8b</b>	-5.74	-1.73	423	376	300	-
<b>8c</b>	-5.87	-2.00	440	393	-	300

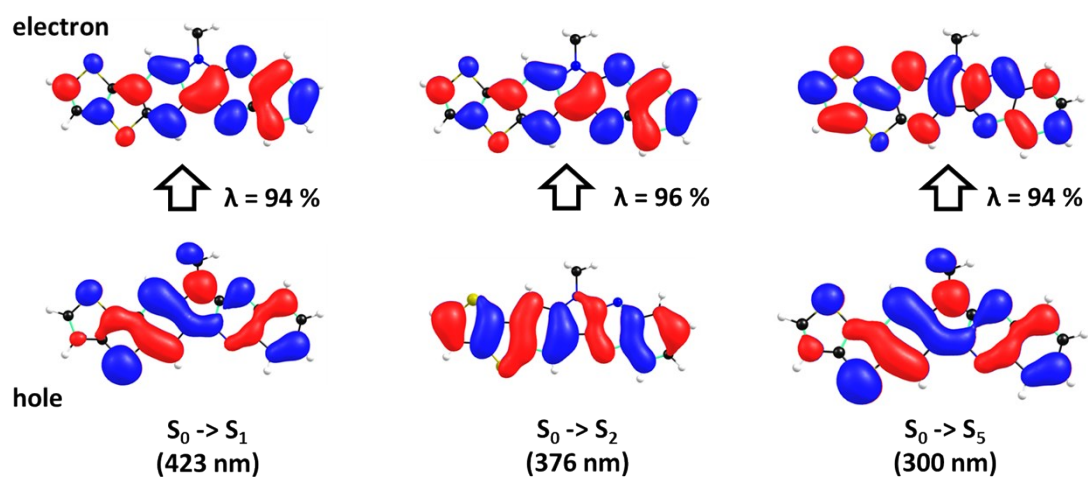
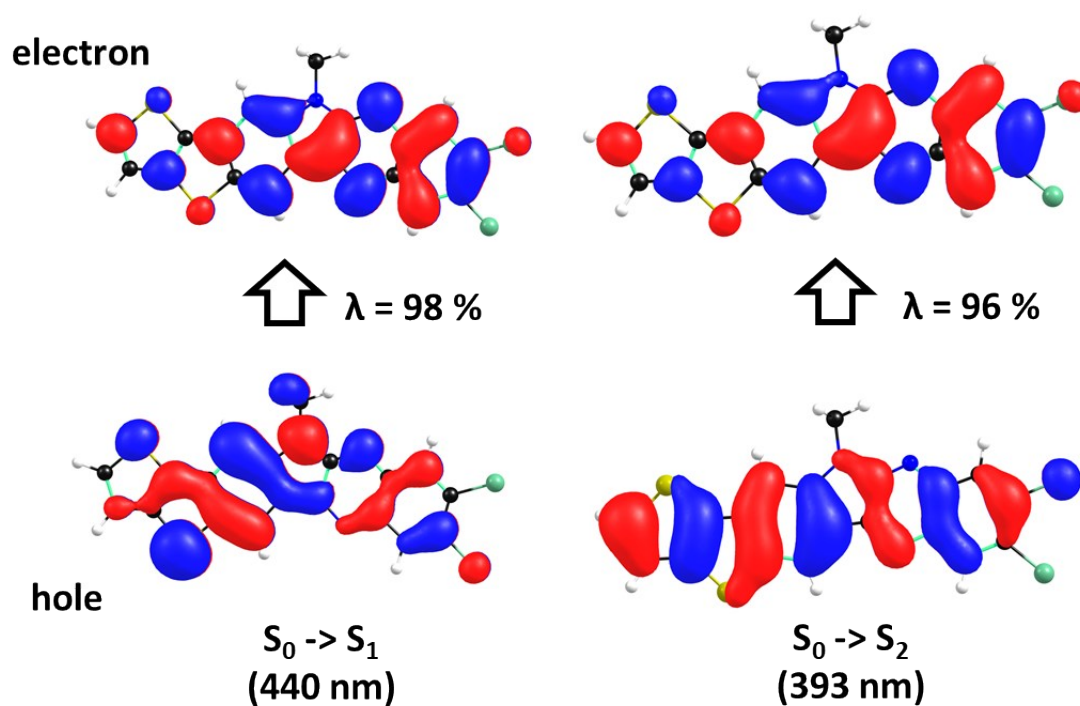


Figure S8: Pictorial representation of the NTOs for the  $S_0$  to  $S_n$  vertical excitation in the 8b molecule, calculated at the TD-OT- $\omega$ B97X-D/6-31G(d,p) level of theory. The weights of hole and electron contribution ( $\lambda$ ) to the excitation are also given.





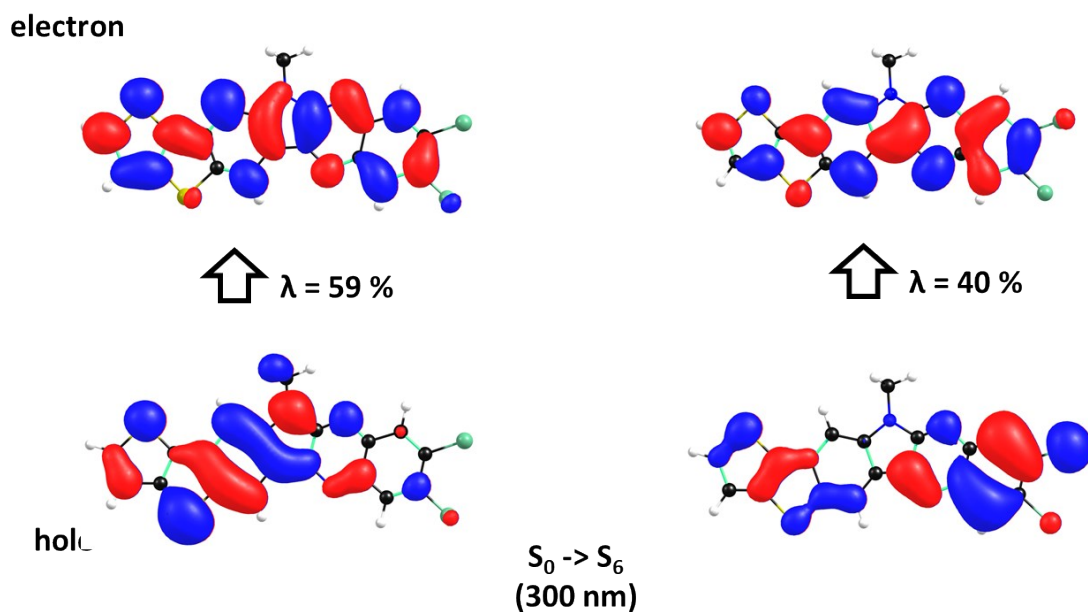


Figure S9: Pictorial representation of the NTOs for the  $S_0$  to  $S_n$  vertical excitation in the 8c molecule, calculated at the TD-OT- $\omega$ B97X-D/6-31G(d,p) level of theory. The weights of hole and electron contribution ( $\lambda$ ) to the excitation are also given.

## 6. Organic field effect transistor characteristics

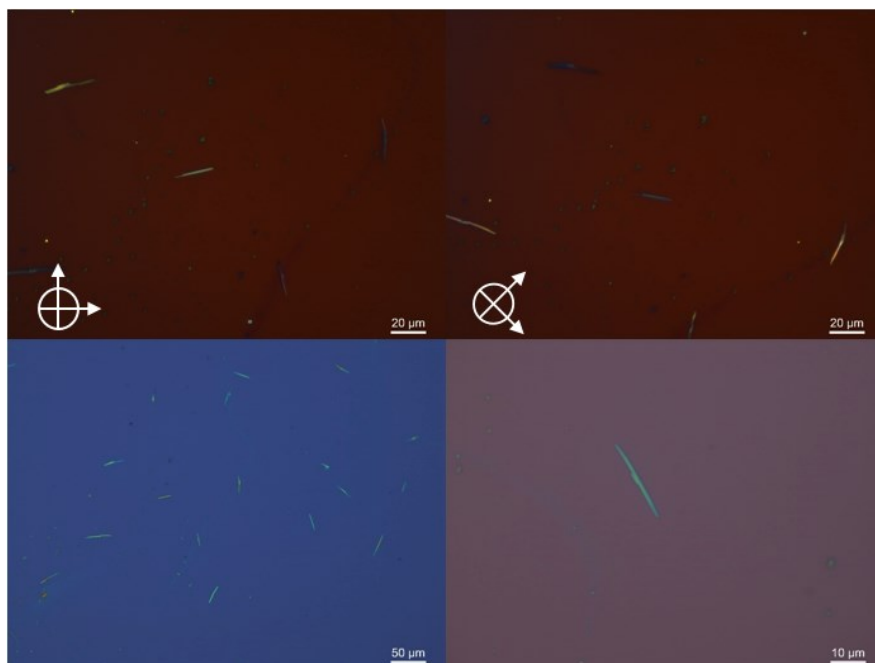


Figure S10: Optical images of **8a** single-crystalline micro-belts.

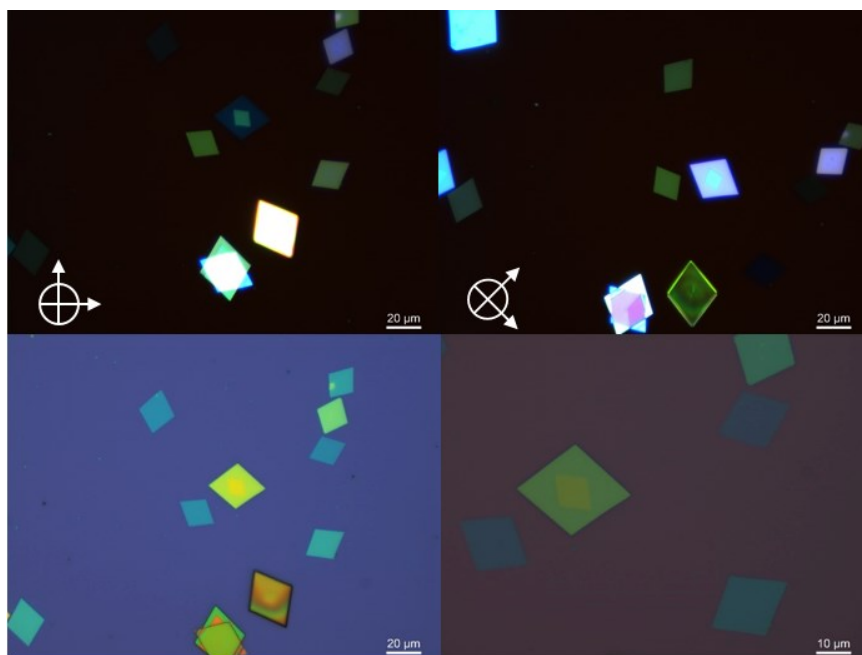
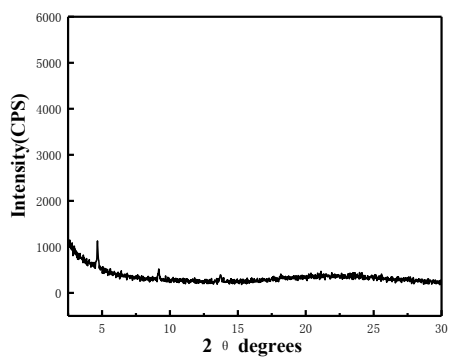


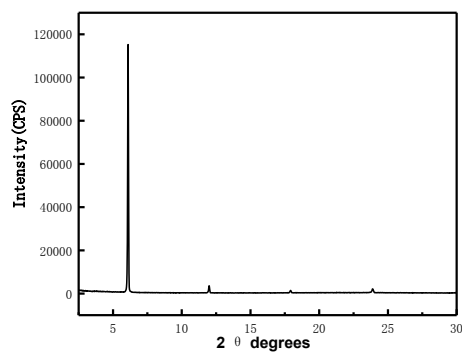
Figure S11: Optical images of **8b** single-crystalline micro-belts.



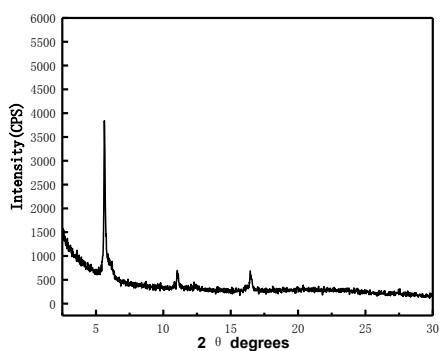
Figure S12: Optical images of **8c** single-crystalline micro-belts.



8a

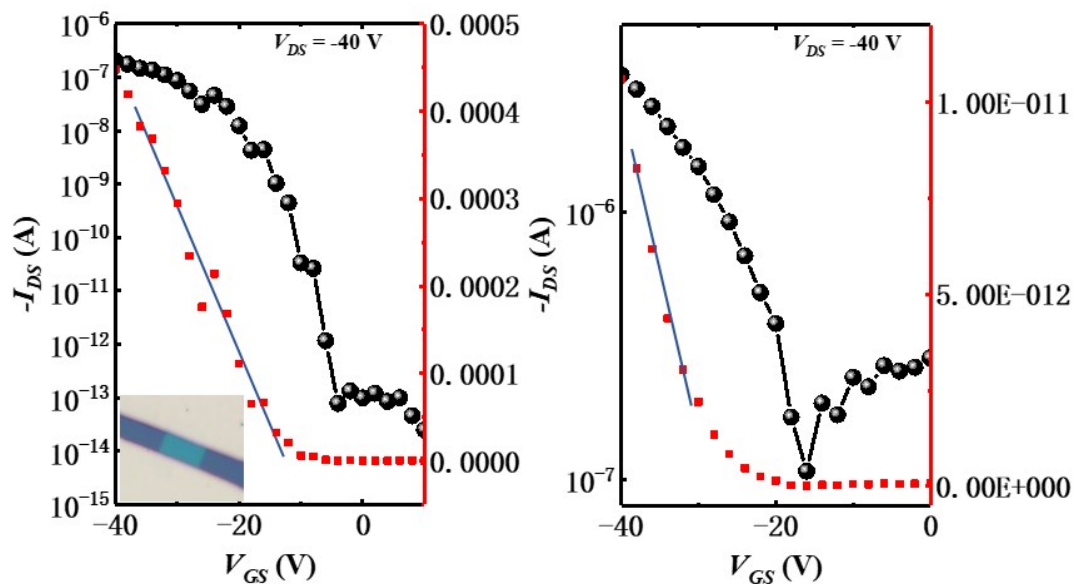


8b



8c

Figure S13: The XRD of **8a**, **8b** and **8c** micrometer-sized single-crystalline micro-belts.

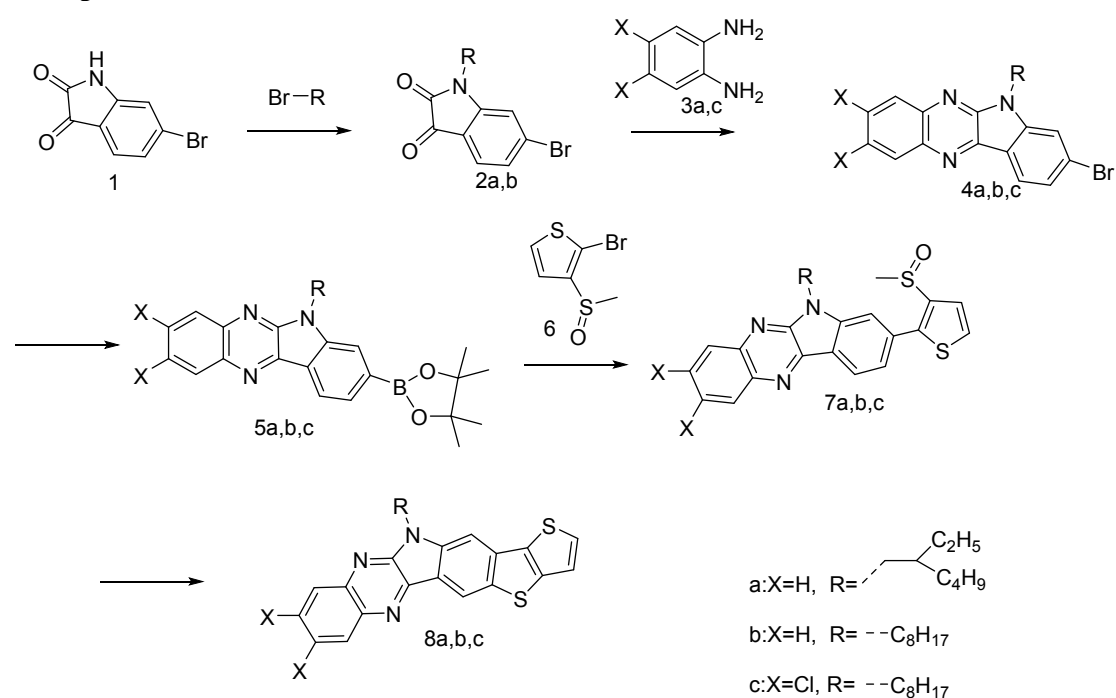


8b

8c

Figure S14. Transfer curves of optimal device of single crystal of compound **8b** and **8c**.

## 7. Experimental details



Scheme S1: Synthesis route of **8a**, **8b** and **8c**

**Compound 1** and **Compound 3a**, **3c** was purchased from Chemical reagent company.

**Compound 6** was obtained according to the literature. <sup>[S4]</sup>

### Compound 2a

In an oven dried Schlenk flask, compound **1** (2.0 g, 8.8 mmol) and dried  $\text{K}_2\text{CO}_3$  (2.5 g, 18 mmol) were dissolved in 15 ml dry DMF under nitrogen. After the reaction mixture heated to 60 °C and stirred for 10 minutes, then the 1-Bromo-iso-octane (2.0 g, 10 mmol) was injected into the reaction. The reaction was heated to 88 °C and stirred overnight. The reaction was poured into water and acidified to PH =7 with aqueous 1M HCl. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ , dried over  $\text{MgSO}_4$  and the solvent was removed by evaporator. The crude product was purified by column chromatography on silica gel (eluent: 1:1 = DCM: hexane) and concentrated in vacuo to yield an orange viscous liquid (2.7 g, 90 % yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 300 K),  $\delta$  (ppm): 7.46 (d,  $J$  = 8.0 Hz, 1H), 7.27 (d,  $J$  = 8.0 Hz, 1H), 7.03 (s, 1H), 3.57-3.61 (m, 2H), 1.76-1.84 (m, 1H), 1.25-1.43 (m, 12H), 0.86-0.98 (m, 7H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 300 K),  $\delta$  (ppm): 182.39, 158.31, 152.25, 133.51, 126.81, 126.34, 116.26, 114.00, 44.55, 37.23, 30.46, 28.45, 23.88, 23.01, 14.04, 10.48. MS (MALDI-TOF,  $\text{CHCl}_3$ ): Calculated for  $\text{C}_{16}\text{H}_{20}\text{BrNO}_2$ : 337.1, found  $[\text{M}+\text{H}]^+$ : 338.3.

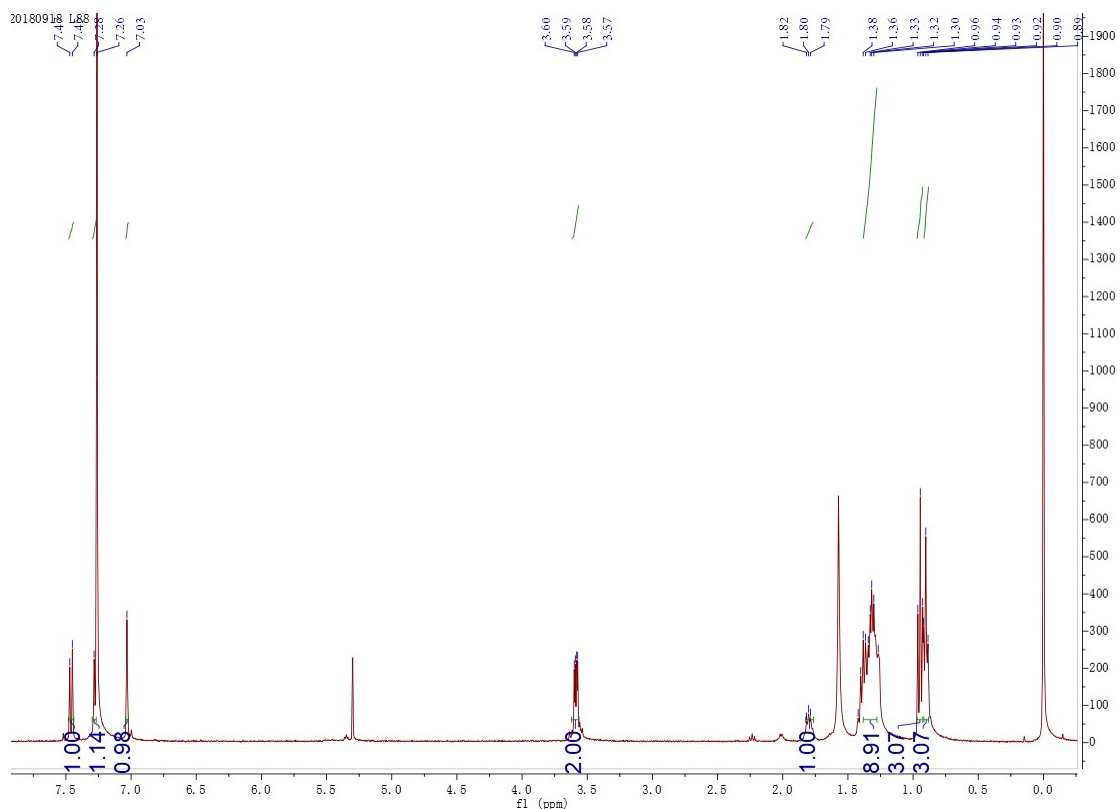


Figure S15:  $^1\text{H}$  NMR of **2a** in  $\text{CDCl}_3$  at 300K.

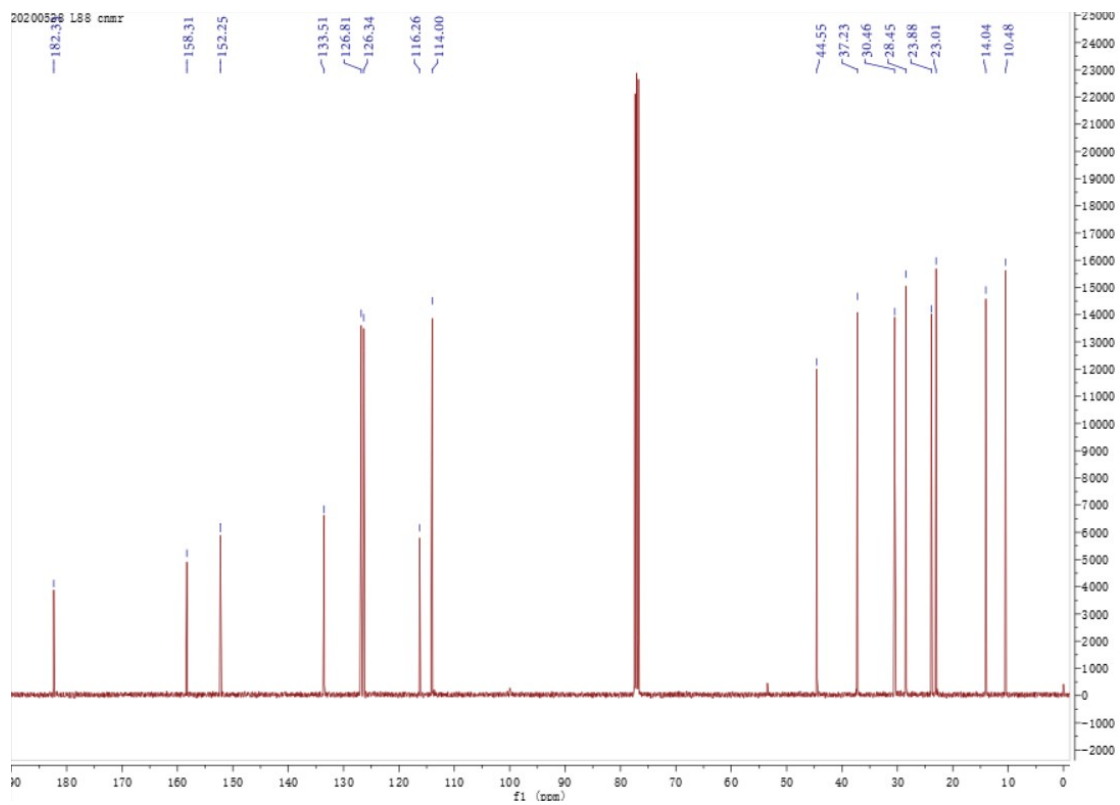


Figure S16:  $^{13}\text{C}$  NMR of **2a** in  $\text{CDCl}_3$  at 300K.

## Compound 2b

In an oven dried Schlenk flask, compound **1** (2.0 g, 8.8 mmol) and dried  $K_2CO_3$  (2.5 g, 18 mmol) were dissolved in 15 ml dry DMF under nitrogen. After the reaction mixture heated to 60 °C and stirred for 10 minutes, then the 1-octyl bromide (2.0 g, 10 mmol) was injected into the reaction. The reaction was heated to 88 °C and stirred overnight. The reaction was poured into water and acidified to PH = 7 with aqueous 1M HCl. The aqueous layer was extracted with  $CH_2Cl_2$ , dried over  $MgSO_4$  and the solvent was removed by evaporator. The crude product was purified by column chromatography on silica gel (eluent: 1:1 = DCM: hexane) and concentrated in vacuo to yield an orange solid (2.7 g, 90 % yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 300 K),  $\delta$  (ppm): 7.48 (d,  $J = 8.0$  Hz, 1H), 7.29 (d,  $J = 8.0$  Hz, 1H), 7.08 (s, 1H), 3.71 (t, 2H), 1.66-1.76 (m, 2H), 1.25-1.43 (m, 12H), 0.88-0.93 (m, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 300 K),  $\delta$  (ppm): 182.40, 157.98, 151.87, 133.56, 126.83, 126.41, 116.27, 113.78, 40.49, 31.73, 29.13, 27.19, 26.85, 22.62, 14.09. MS (MALDI-TOF,  $CHCl_3$ ): Calculated for  $C_{16}H_{20}BrNO_2$ : 337.1, found  $[M+H]^+$ :338.3.

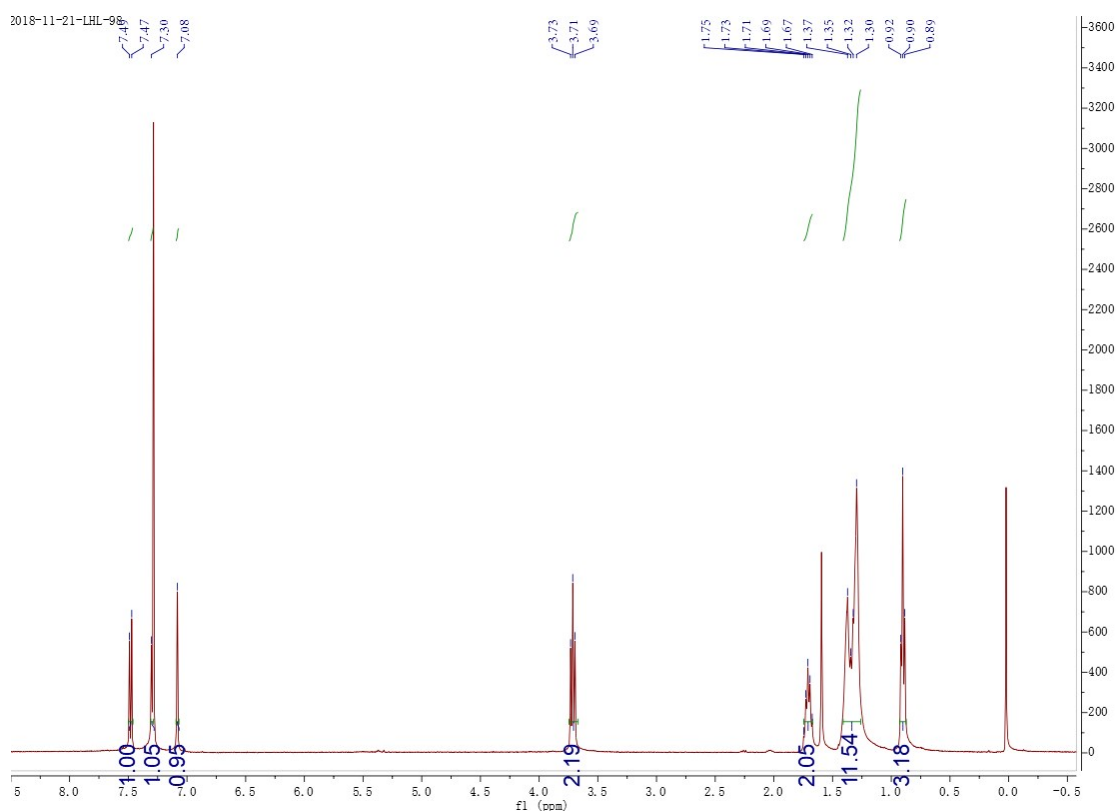


Figure S17:  $^1H$  NMR of **2b** in  $CDCl_3$  at 300K.

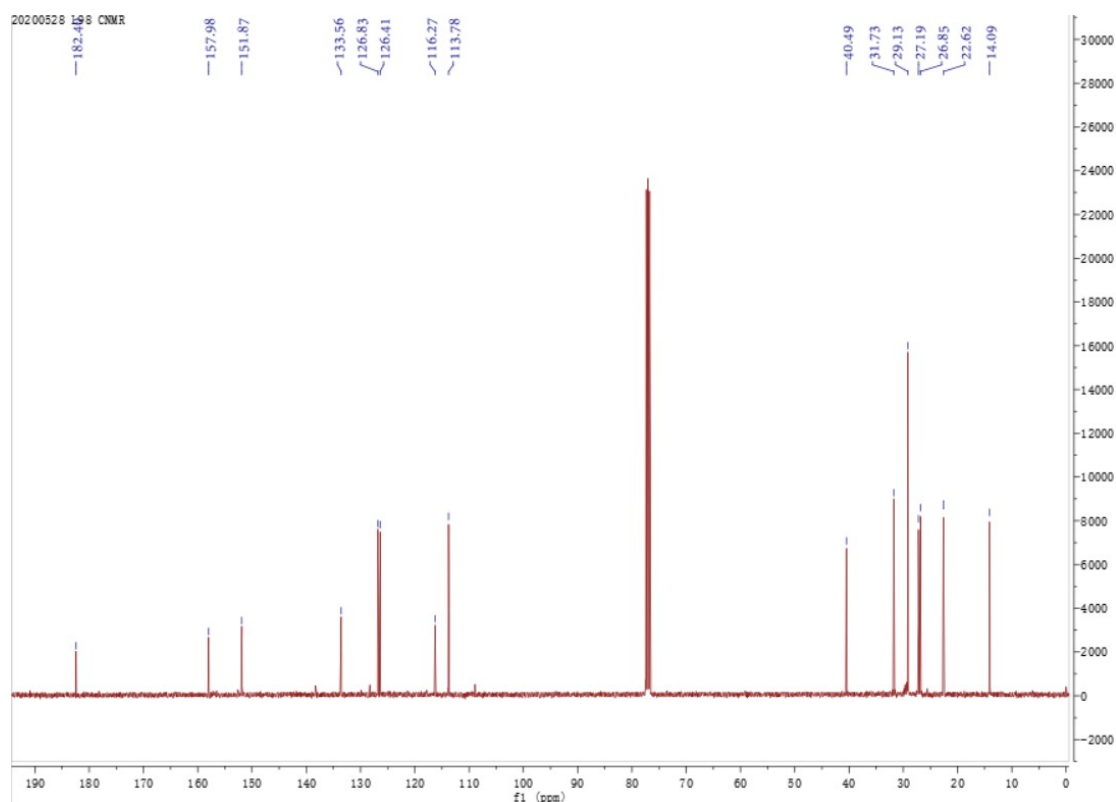


Figure S18:  $^{13}\text{C}$  NMR of **2b** in  $\text{CDCl}_3$  at 300K.

#### Compound 4a

Compound **2a** (1. g, 2.9 mmol) and 1,2-diaminobenzene (**3a**) (383 mg, 3.54 mmol) were added to a 20mL oven-dried microwave vial under nitrogen, the tube was sealed, then 8 mL acetic acid was added and heated to 120 °C for 12 hours. After being cooled down to room temperature, the acetic acid was removed by the reduced pressure. The crude product was purified by chromatography (eluent: DCM) and concentrated in vacuo to yield a bright yellow solid (813 mg, 67 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 300 K),  $\delta$  (ppm): 8.60 (d,  $J = 8.0$  Hz, 1H), 8.49 (d,  $J = 8.0$  Hz, 1H), 8.21 (d,  $J = 8.0$  Hz, 1H), 7.86 (t, 1H), 7.78 (t, 1H), 7.67 (s, 1H), 7.57 (d,  $J = 8.0$  Hz, 1H), 4.41 (d,  $J = 4.0$  Hz, 2H), 1.25-1.45 (m, 14H), 0.96-1.02 (t, 3H), 0.86-0.92 (t, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 300 K),  $\delta$  (ppm): 146.10, 145.41, 140.75, 139.45, 139.04, 129.27, 128.93, 128.05, 126.29, 125.05, 124.03, 123.71, 118.38, 113.04, 45.66, 38.43, 30.59, 28.42, 24.10, 23.03, 14.05, 10.67. MS (MALDI-TOF,  $\text{CHCl}_3$ ): Calculated for  $\text{C}_{22}\text{H}_{24}\text{BrN}_3$ : 409.1154; found  $[\text{M}+\text{H}]^+$ : 410, 1224.

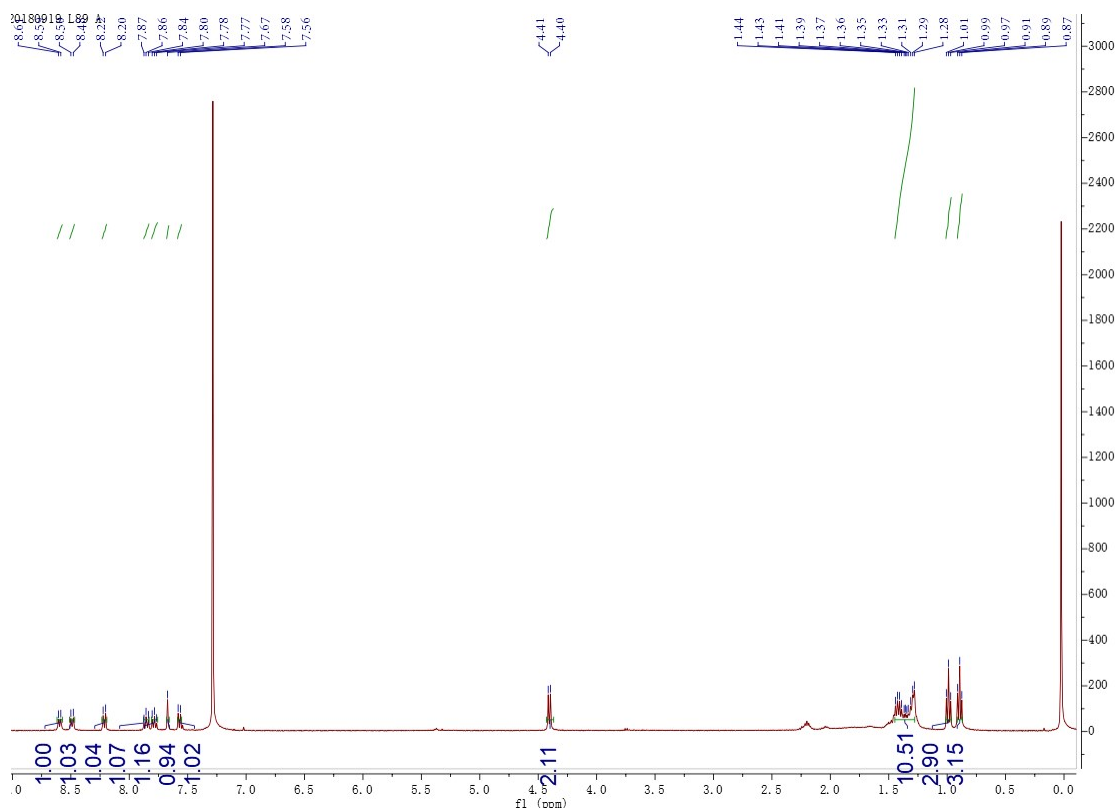


Figure S19:  $^1\text{H}$  NMR of **4a** in  $\text{CDCl}_3$  at 300K.

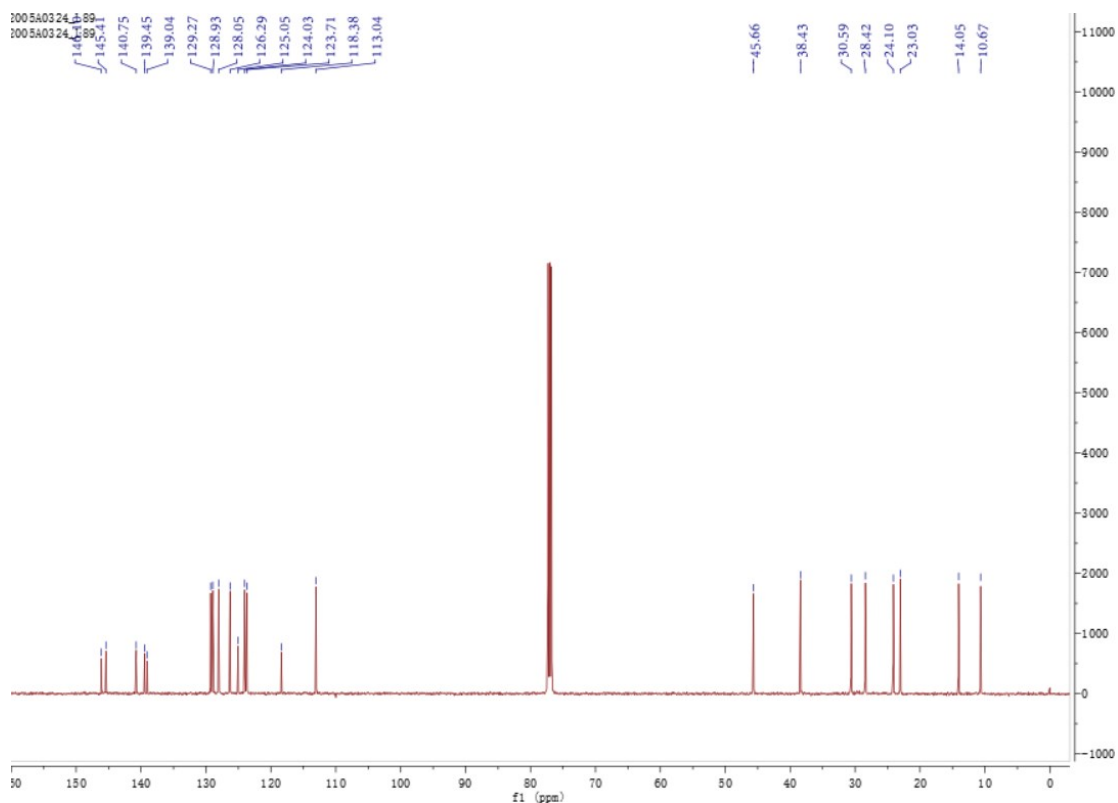


Figure S20:  $^{13}\text{C}$  NMR of **4a** in  $\text{CDCl}_3$  at 300K.



+MS, 0.13-0.19min

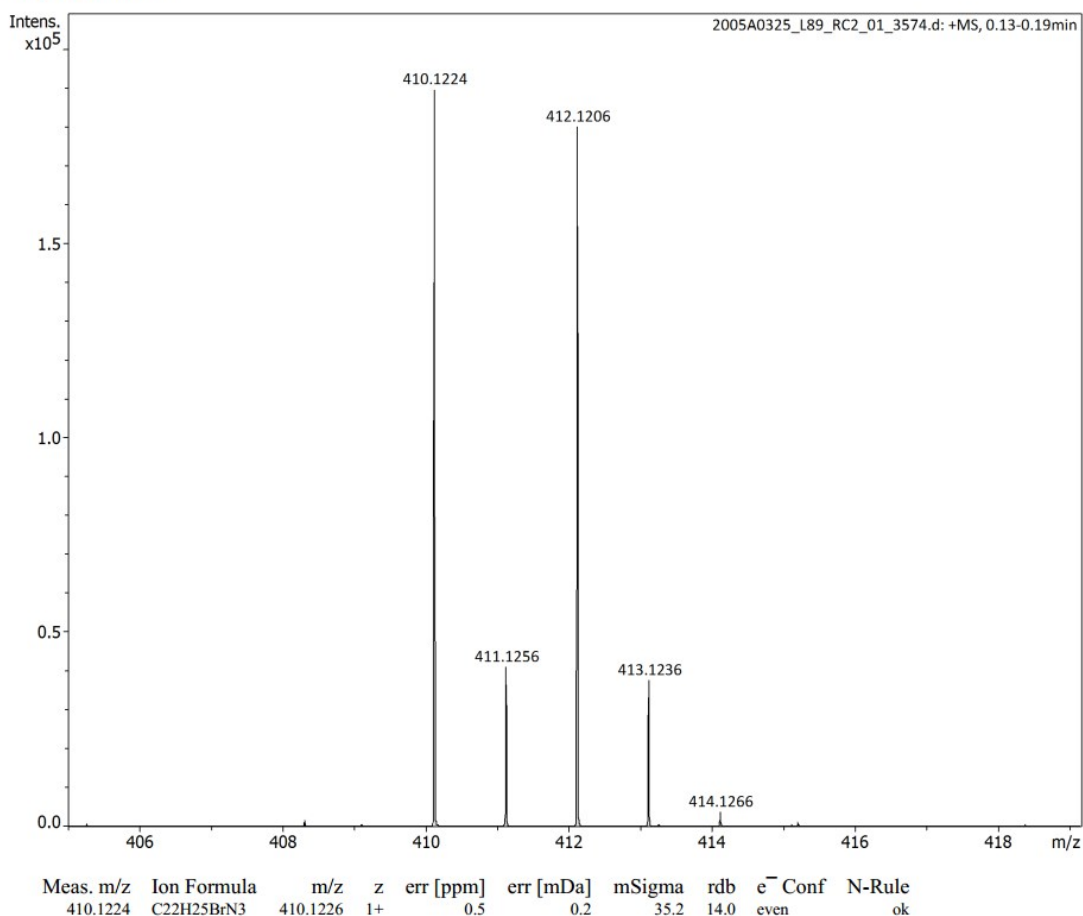


Figure S21: MALDI-TOF of **4a**.

### Compound **4b**

Compound **2b** (1.0 g, 2.9 mmol) and 1,2-diaminobenzene **3a** (383 mg, 3.54 mmol) were added to a 20 mL oven-dried microwave vial under nitrogen, the tube was sealed, then 8 mL acetic acid was added and heated to 120 °C for 12 hours. After being cooled down to room temperature, the acetic acid was removed by the reduced pressure. The crude product was purified by chromatography (eluent: DCM) and concentrated in vacuo to yield a bright yellow solid (970 mg, 81 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 300 K), δ (ppm): 8.42 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.16 (dd, *J* = 8.0 Hz, 1H), 7.77-7.83 (m, 1H), 7.70-7.75 (m, 1H), 7.65 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 4.47 (t, 2H), 1.90-2.00 (m, 2H), 1.20-1.45 (m, 13H), 0.83-0.89 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 300 K), δ (ppm): 145.64, 145.07, 140.71, 139.47, 139.21, 129.32, 128.97, 127.94, 126.28, 125.10, 124.04, 123.76, 118.38, 112.80, 41.62, 31.80, 29.22, 29.17, 28.38, 27.00, 22.62, 14.08. MS (MALDI-TOF, CHCl<sub>3</sub>): Calculated for C<sub>22</sub>H<sub>24</sub>BrN<sub>3</sub>: 409.1154, found [M+H]<sup>+</sup>:410,1227.

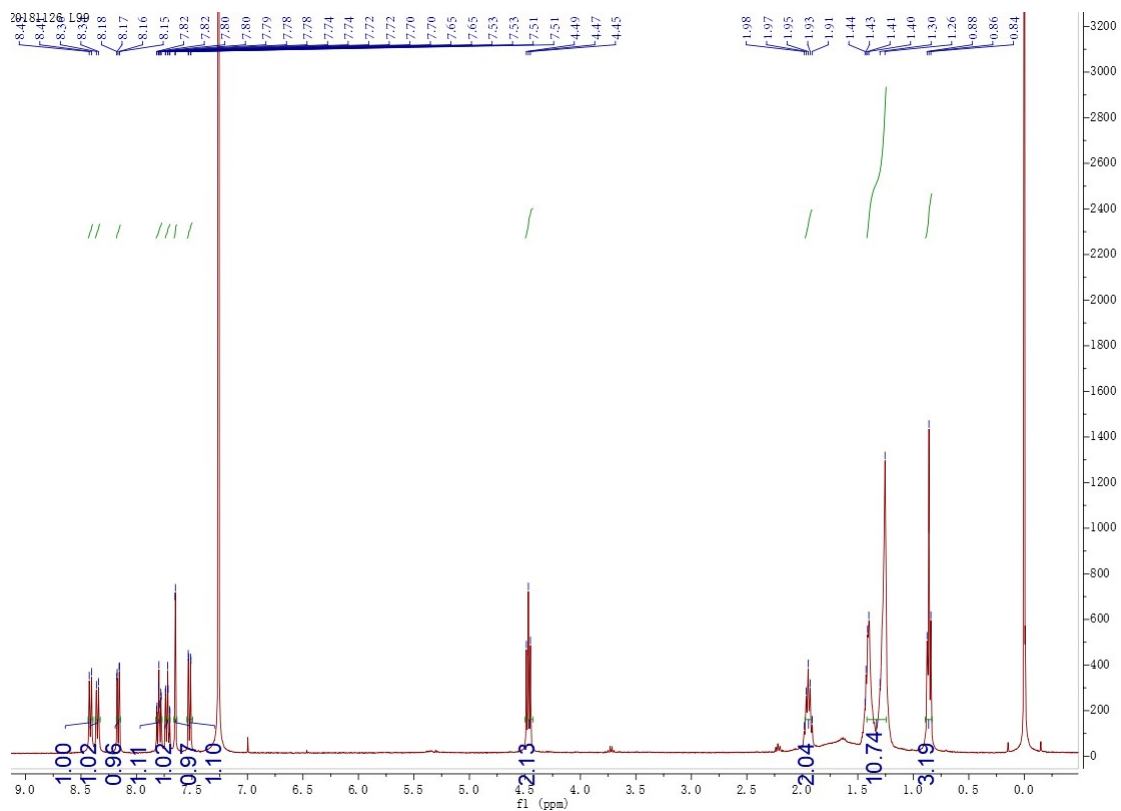


Figure S22:  $^1\text{H}$  NMR of **4b** in  $\text{CDCl}_3$  at 300K.

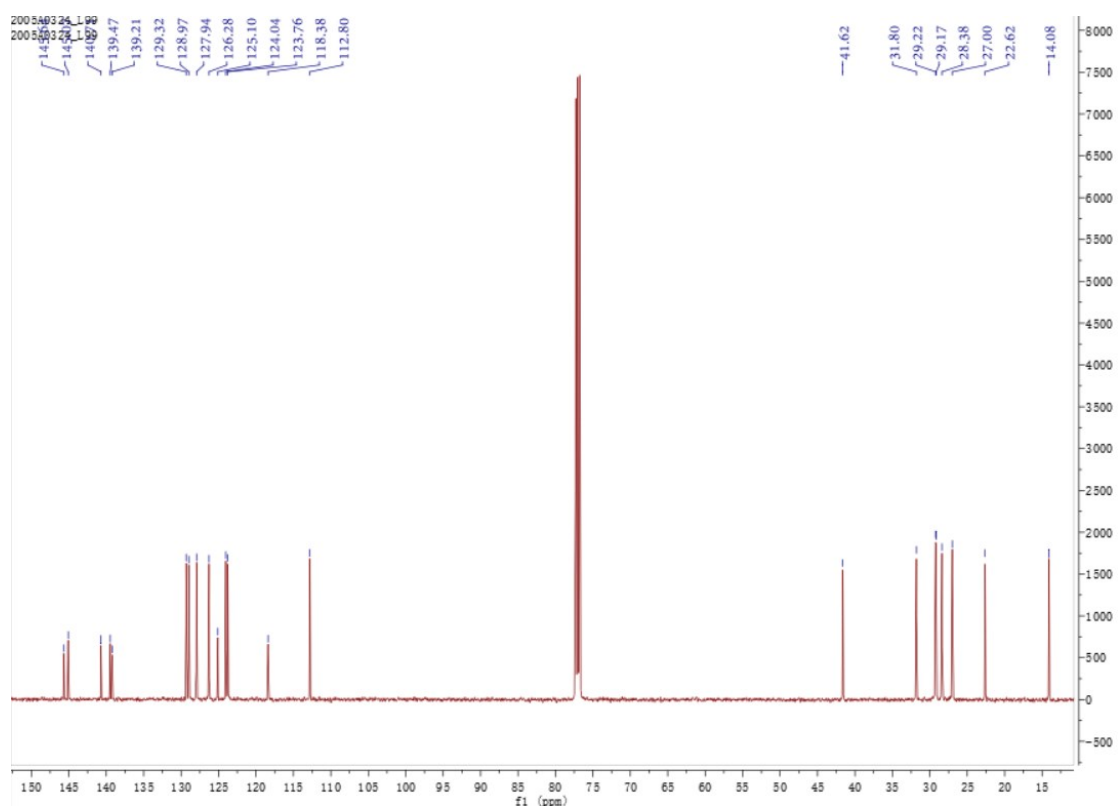
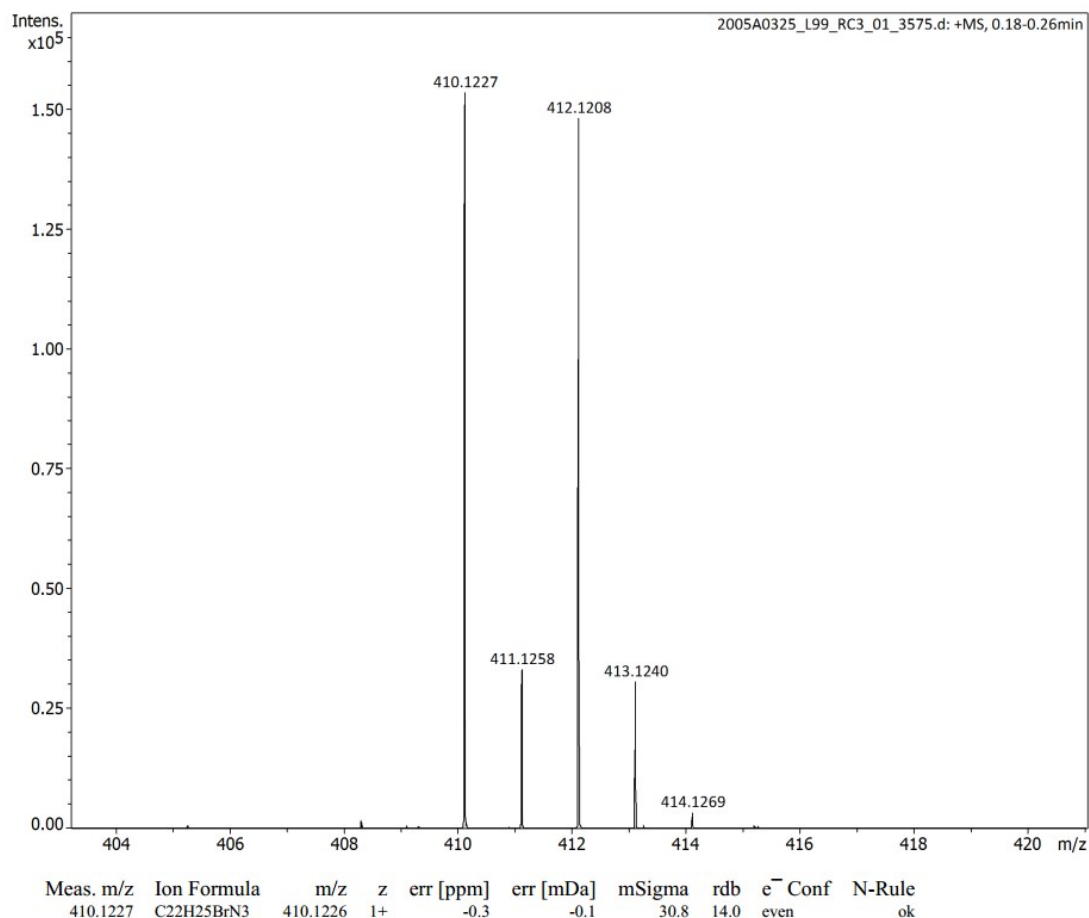


Figure S23:  $^{13}\text{C}$  NMR of **4b** in  $\text{CDCl}_3$  at 300K.

**+MS, 0.18-0.26min**Figure S24: MALDI-TOF of **4b**.**Compound 4c**

Compound **2b** (1.0 g, 2.9 mmol) and 4,5-dichloro-1,2-benzenediamine (**3c**) (523 mg, 3.54 mmol) were added to a 20mL oven-dried microwave vial under nitrogen, the tube was sealed, then 8 mL acetic acid was added and heated to 120 °C for 12 hours. After being cooled down to room temperature, the acetic acid was removed by the reduced pressure. The crude product was purified by chromatography (eluent: DCM) and concentrated in vacuo to yield a bright yellow solid (923 mg, 65 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 300 K), δ (ppm): 8.47 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.27 (s, 1H), 7.65 (s, 1H), 7.54 (dd, *J* = 8.0 Hz, 1H), 4.43 (t, 2H), 1.85-1.97 (m, 2H), 1.20-1.45 (m, 13H), 0.84-0.89 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 300 K), δ (ppm): 145.76, 145.29, 140.02, 139.37, 138.04, 133.10, 130.16, 129.66, 128.42, 125.92, 124.56, 123.99, 117.95, 113.01, 41.72, 31.79, 29.18, 29.16, 28.32, 26.99, 22.62, 14.08. MS (MALDI-TOF, CHCl<sub>3</sub>): Calculated for C<sub>22</sub>H<sub>22</sub>BrCl<sub>2</sub>N<sub>3</sub>: 477.0374; found [M+H]<sup>+</sup>:478,0443.

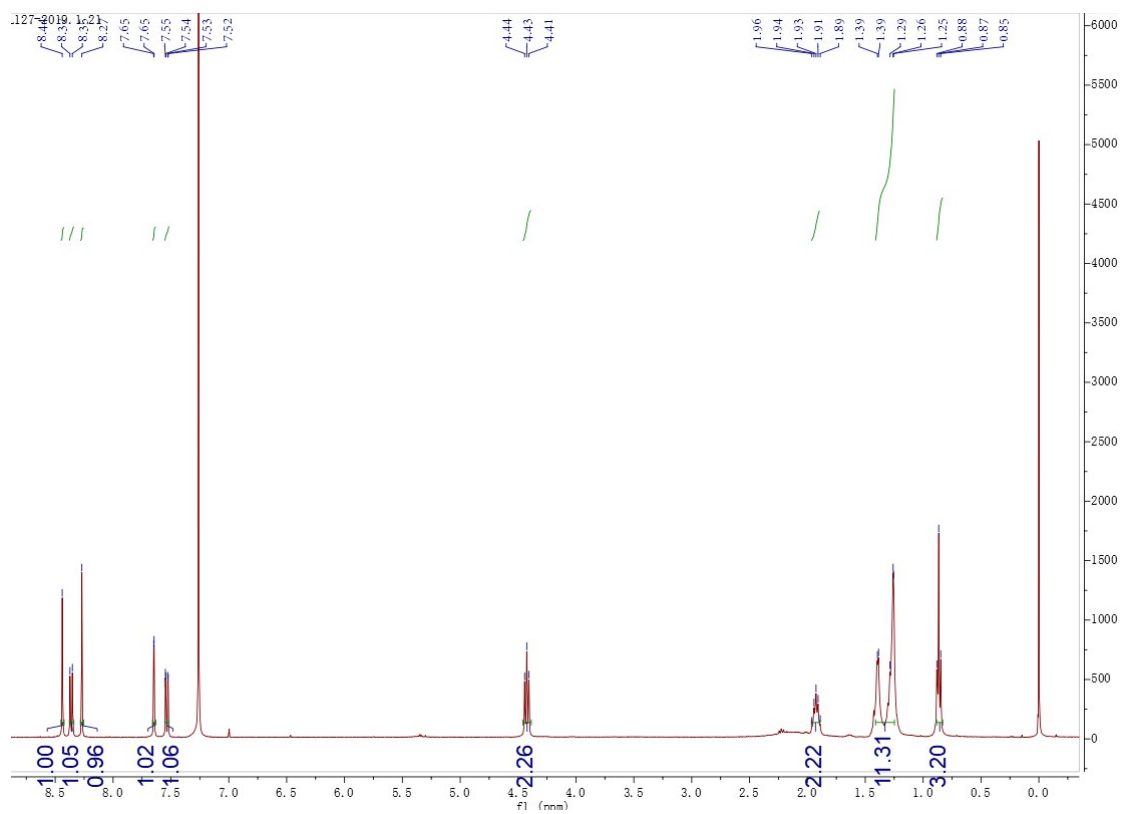


Figure S25:  $^1\text{H}$  NMR of **4c** in  $\text{CDCl}_3$  at 300K.

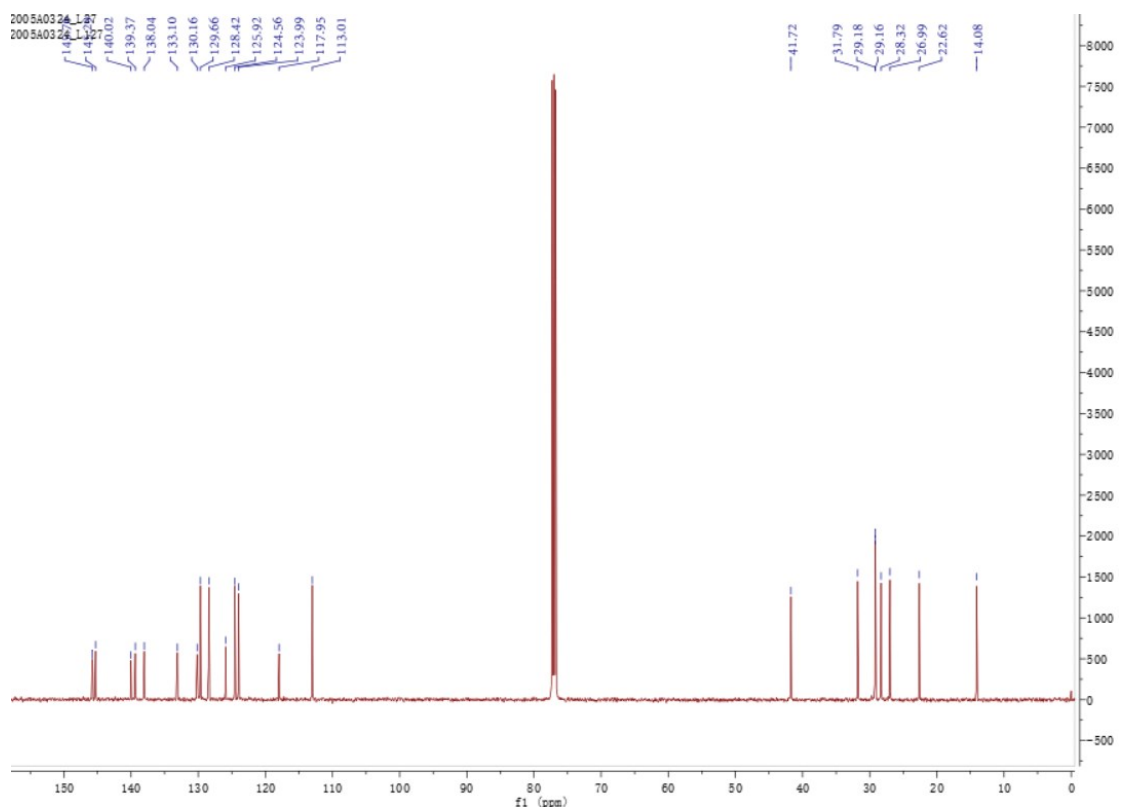


Figure S26:  $^{13}\text{C}$  NMR of **4c** in  $\text{CDCl}_3$  at 300K.

+MS, 0.07-0.13min

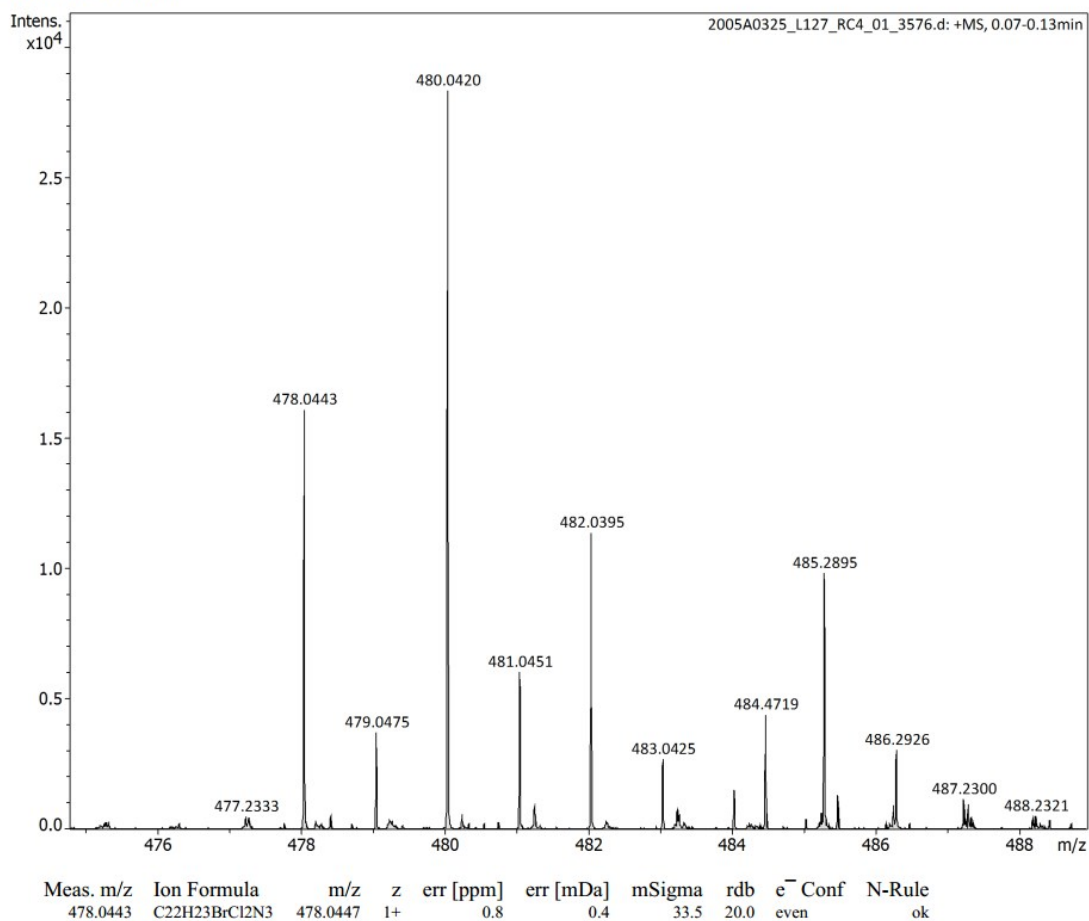


Figure S27: MALDI-TOF of **4c**.

### Compound **5a**

Compound **4a** (500 mg, 1.21 mmol) and bis(pinacolato)diboron (370 mg, 1.54 mmol) were added to a single-port flask under nitrogen. Then potassium phosphate (258 mg, 1.21 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (10.66 mg, 0.014 mmol) were added as catalyst, and 6mL of super dry dioxane was added as solvent. The reaction was conducted at 90°C for 12h. After the reaction was completed, removed the solvent and purified rapidly by chromatography column, methylene chloride as eluent, and concentrated in vacuo to yield a crude yellow solid (540 mg, 98 %).

### Compound **5b**

Compound **4b** (500 mg, 1.21 mmol) and bis(pinacolato)diboron (370 mg, 1.54 mmol) were added to a single-port flask under nitrogen. Then potassium phosphate (258 mg, 1.21 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (10.66 mg, 0.014 mmol) were added as catalyst, and 6mL of super dry dioxane was added as solvent. The reaction was conducted at 90°C for 12h. After the reaction was completed, removed the solvent and purified rapidly by chromatography column, methylene chloride as eluent, and concentrated in vacuo to yield a crude yellow solid (546 mg, 98 %).

### Compound 5c

Compound **4c** (500 mg, 1.04 mmol) and bis(pinacolato)diboron (318 mg, 1.25 mmol) were added to a single-port flask under nitrogen. Then potassium phosphate (221 mg, 1.21 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (9.16 mg, 0.012 mmol) were added as catalyst, and 6mL of super dry dioxane was added as solvent. The reaction was conducted at 90°C for 12h. After the reaction was completed, removed the solvent and purified rapidly by chromatography column, methylene chloride as eluent, and concentrated in vacuo to yield a crude yellow solid (538 mg, 98 %)

### Compound 7a

To an oven-dried 20 mL microwave vial, compound **5a** (400 mg, 0.875 mmol), Tetrakis(triphenylphosphine)palladium (10 mg, 0.008 mmol), bromo-3-methylsulfanylthiophene **6** (200 mg, 0.88 mmol), the tube was sealed under nitrogen, then dry toluene (5 mL) with 2 drops of aliquat and degassed under Argon for half an hour, then 2M aq.  $K_3PO_4$  (2.5 mL) was added. The reaction was conducted at 90 °C for 12h. After cooling to room temperature, the reaction mixture was extracted with EA, and the organic phase was collected and dried with magnesium sulfate, solvent was removed by the reduced pressure, purified by column chromatography (eluent: DCM: EA=10:1) to afford a yellow viscous compound. (200 mg, 48 %).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 300 K),  $\delta$  (ppm): 8.50 (d,  $J = 8.0$  Hz, 1H), 8.29 (d,  $J = 8.0$  Hz, 1H), 8.13 (d,  $J = 8.0$  Hz, 1H), 7.76 (t, 1H), 7.64-7.70 (m, 2H), 7.59 (s, 1H), 7.55 (d,  $J = 8.0$  Hz, 1H), 7.45-7.47 (m, 1H), 4.35-4.41 (m, 2H), 2.83 (s, 3H), 2.17-2.23 (m, 1H), 1.25-1.50 (m, 10H), 0.94-1.00 (m, 3H), 0.82-0.88 (m, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 300 K),  $\delta$  (ppm): 146.12, 144.44, 144.22, 140.86, 139.54, 139.19, 133.86, 129.39, 129.15, 127.96, 127.33, 126.31, 125.11, 123.18, 122.00, 119.89, 110.30, 42.00, 41.66, 31.79, 29.29, 29.19, 28.52, 27.10, 22.61, 14.07. MS (MALDI-TOF,  $CHCl_3$ ): Calculated for  $C_{27}H_{29}N_3OS_2$ : 475.1752, found  $[M+H]^+$ :476,1822.

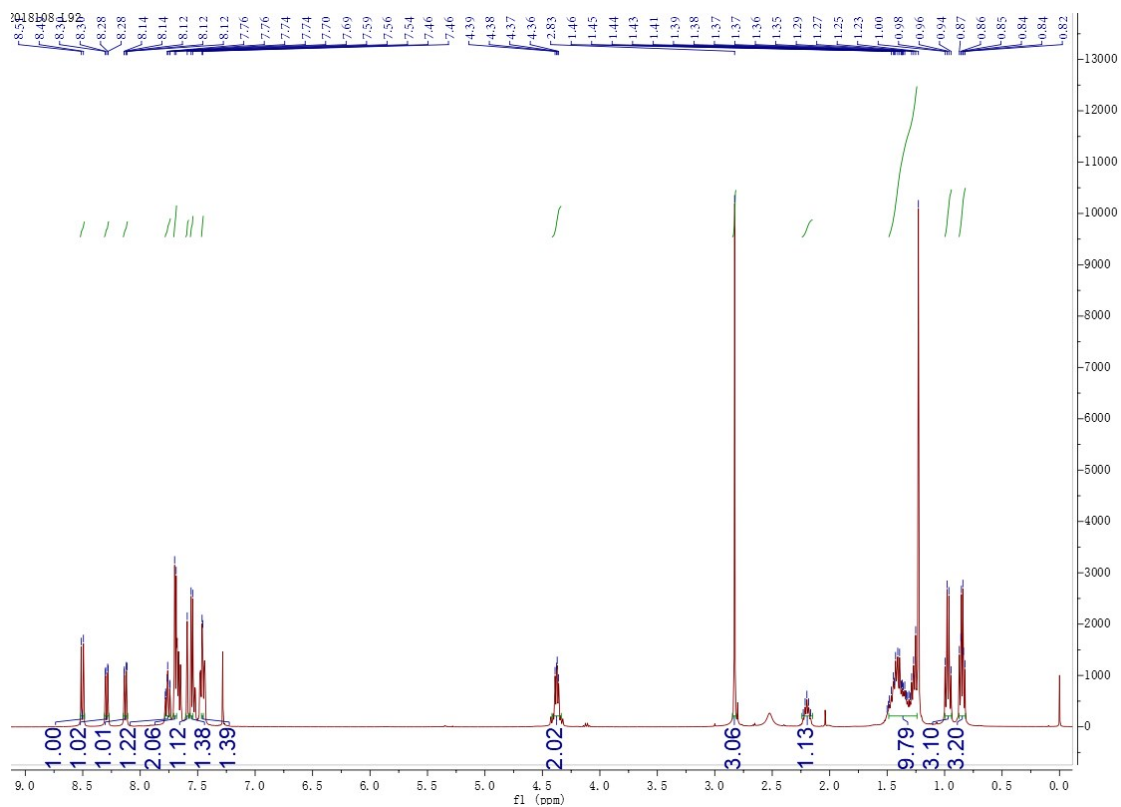


Figure S28:  $^1\text{H}$  NMR of **7a** in  $\text{CDCl}_3$  at 300K.

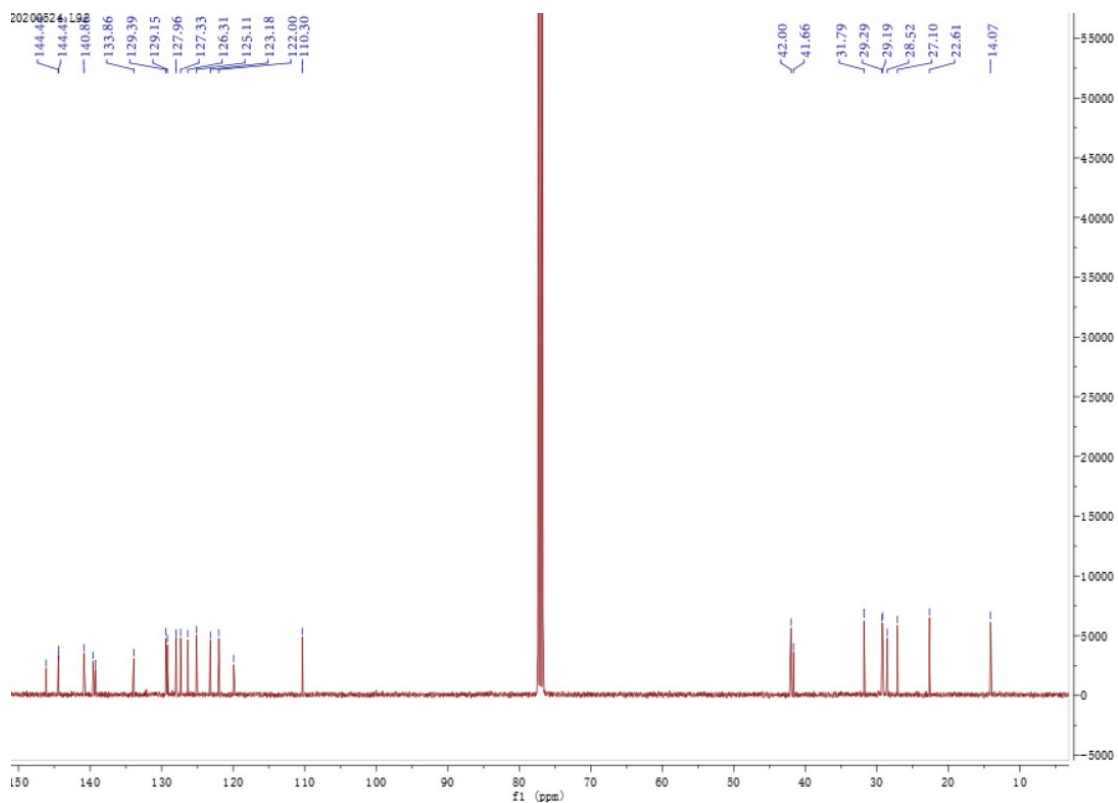


Figure S29:  $^{13}\text{C}$  NMR of **7a** in  $\text{CDCl}_3$  at 300K.

**+MS, 0.1min, Background Subtracted (51)**

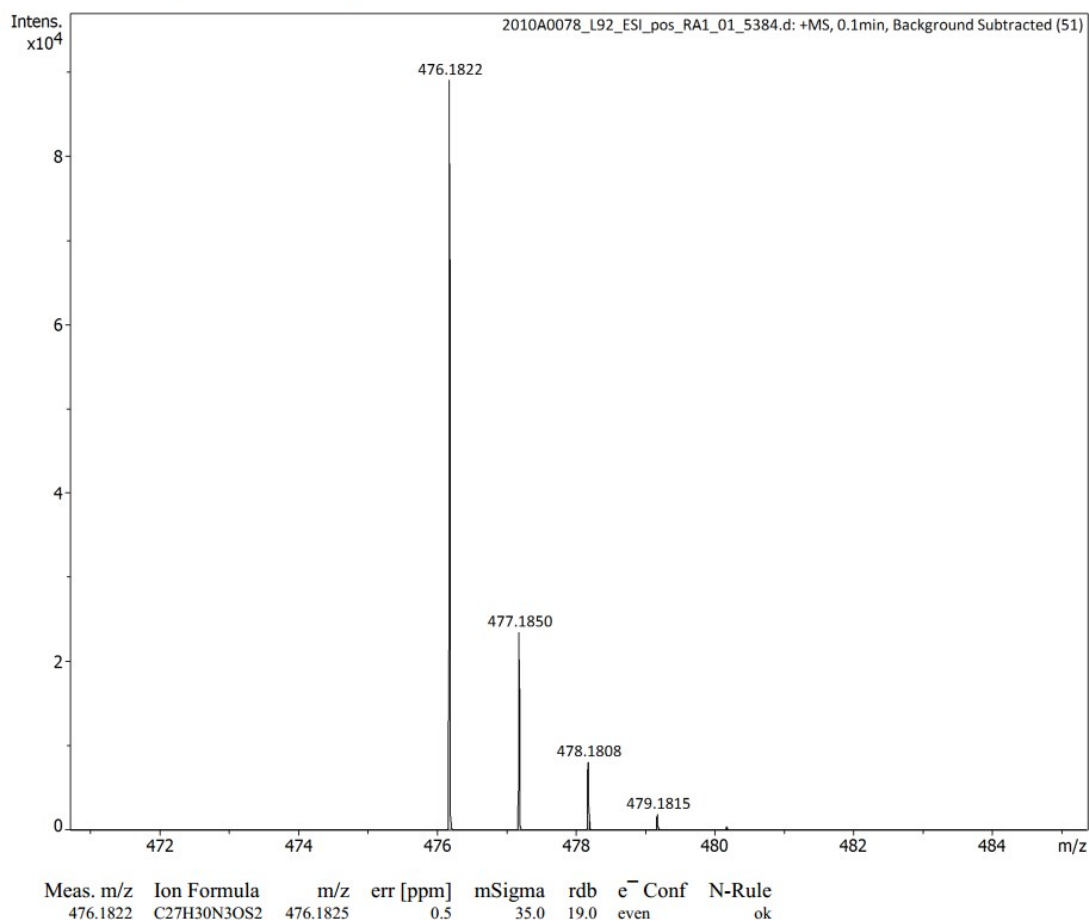


Figure S30: MALDI-TOF of **7a**.

**Compound 7b**

To an oven-dried 20 mL microwave vial, compound **5b** (400 mg, 0.875 mmol), Tetrakis(triphenylphosphine)palladium (10 mg, 0.008 mmol), bromo-3-methylsulfinylthiophene **6** (200 mg, 0.88 mmol), the tube was sealed under nitrogen, then dry toluene (5 mL) with 2 drops of aliquat and degassed under Argon for half an hour 2M K<sub>3</sub>PO<sub>4</sub> (2.5 mL) was added. The reaction was conducted at 90 °C for 12h. After cooling to room temperature, the reaction mixture was extracted with EA, and the organic phase was collected and dried with magnesium sulfate, solvent was removed by the reduced pressure, purified by column chromatography (eluent: DCM: EA= 10:1) to afford a yellow solid. (166 mg, 40 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 300 K), δ (ppm): 8.70 (d, *J* = 4.0 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.84 (t, 1H), 7.76 (t, 1H), 7.70 (d, *J* = 4.0 Hz, 1H), 7.69 (s, 1H), 7.57 (d, *J* = 4.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 4.56 (t, 2H), 2.83 (s, 3H), 1.96-2.02 (m, 2H), 1.20-1.47 (m, 15H), 0.84 (t, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 300 K), δ (ppm): 146.13, 144.44, 140.88, 139.56, 139.20, 133.88, 129.40, 129.16, 127.98, 127.34, 126.33, 125.13, 123.20, 122.01, 119.91, 110.31, 42.03, 41.67, 31.80, 29.30, 29.21, 28.53, 27.11, 22.62, 14.09. MS (MALDI-TOF, CHCl<sub>3</sub>): Calculated for C<sub>27</sub>H<sub>29</sub>N<sub>3</sub>OS<sub>2</sub>: 475.1752, found [M+H]<sup>+</sup>:476,1823.



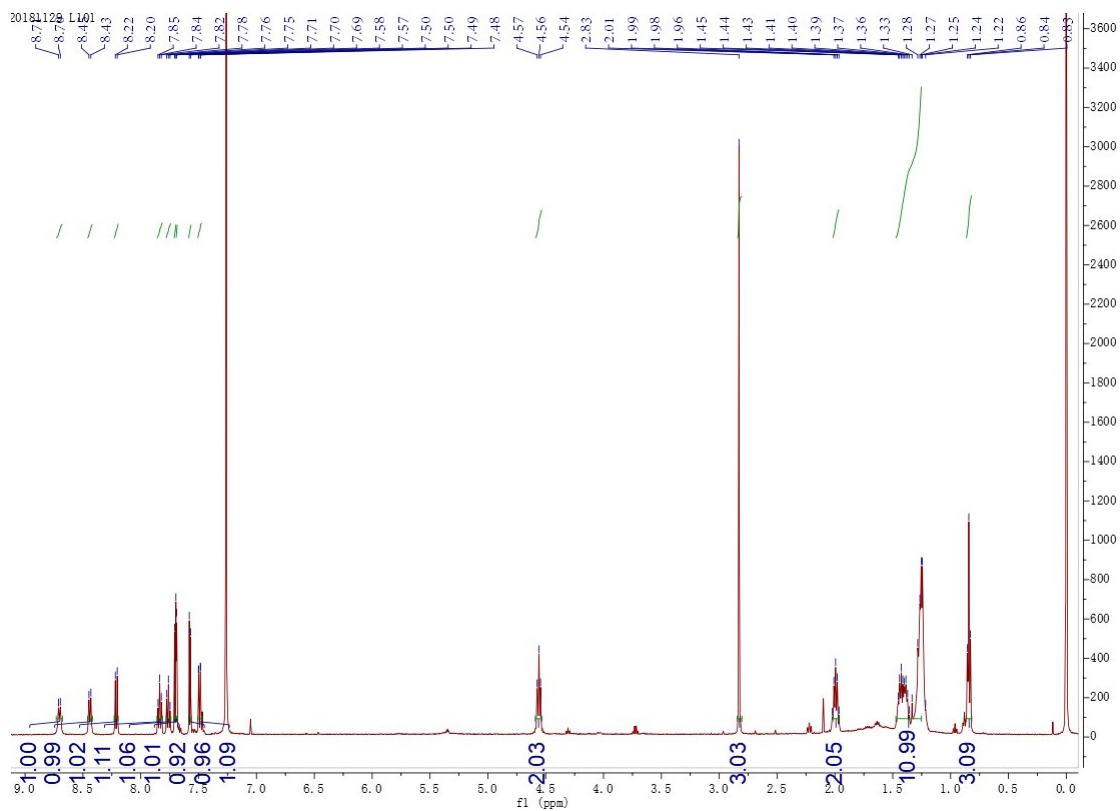


Figure S31:  $^1\text{H}$  NMR of **7b** in  $\text{CDCl}_3$  at 300K.

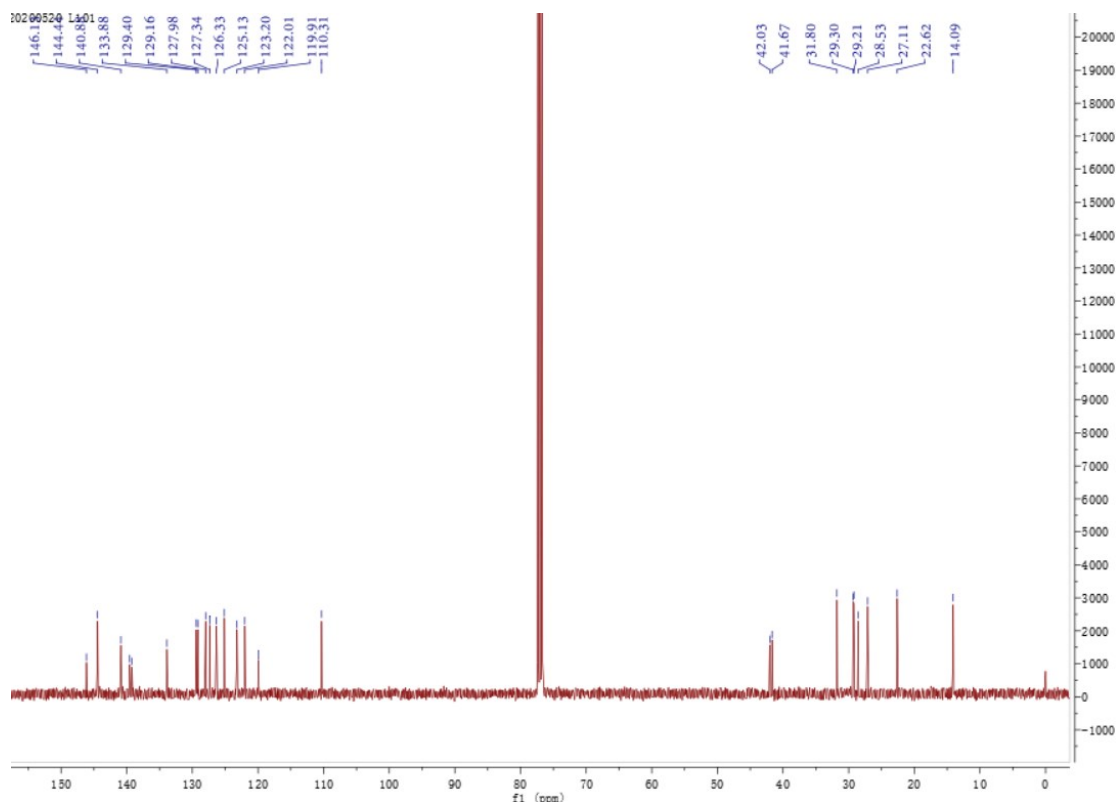
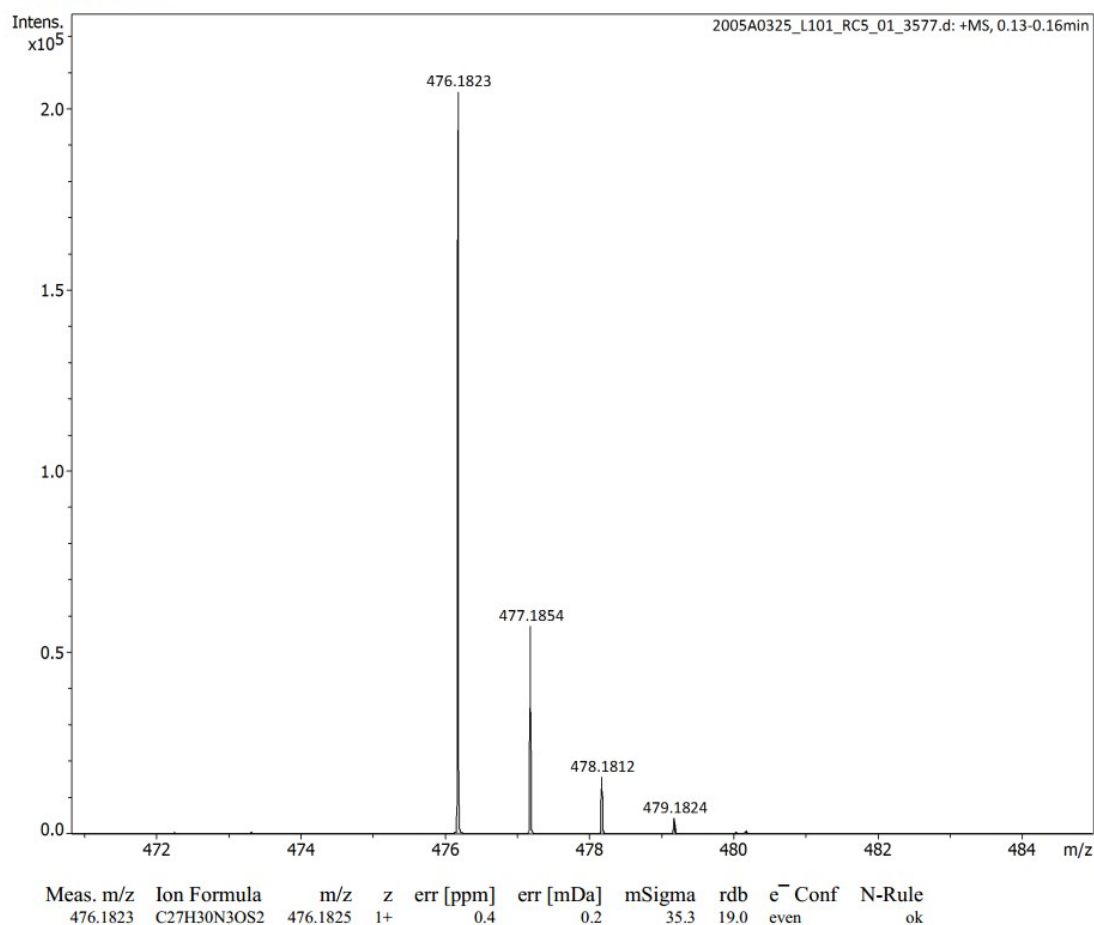


Figure S32:  $^{13}\text{C}$  NMR of **7b** in  $\text{CDCl}_3$  at 300K.

**+MS, 0.13-0.16min**Figure S33: MALDI-TOF of **7b**.**Compound 7c**

To an oven-dried 20 mL microwave vial, compound **5c** (400 mg, 0.76 mmol), Tetrakis(triphenylphosphine)palladium (10 mg, 0.008 mmol), bromo-3-methylsulfinylthiophene (compound **6**) (171 mg, 0.76 mmol), the tube was sealed under nitrogen, then dry toluene (5 mL) with 2 drops of aliquat and degassed under Argon for half an hour, and then 2M aq. K<sub>3</sub>PO<sub>4</sub> (2.5 mL) was added. The reaction was conducted at 90°C for 12h. After cooling to room temperature, the reaction mixture was extracted with EA, and the organic phase was collected and dried with magnesium sulfate, solvent was removed by the reduced pressure, purified by column chromatography (eluent: DCM: EA=10:1) to afford a yellow solid. (206 mg, 50 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 300 K),  $\delta$  (ppm): 8.47 (d,  $J$  = 8.0 Hz, 1H), 8.37 (s, 1H), 8.23 (s, 1H), 7.68 (d,  $J$  = 4.0 Hz, 1H), 7.64 (s, 1H), 7.56 (d,  $J$  = 8.0 Hz, 1H), 7.47 (d,  $J$  = 8.0 Hz, 1H), 4.47 (t, 2H), 2.81 (s, 3H), 1.92-1.99 (m, 2H), 1.25-1.45 (m, 13H), 0.84 (t, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, 300 K),  $\delta$  (ppm): 147.67, 146.14, 145.52, 142.55, 141.32, 140.93, 139.39, 136.04, 134.66, 133.53, 133.43, 133.31, 131.60, 131.04, 129.93, 129.83, 128.86, 126.60, 124.92, 123.84, 120.79, 111.89, 43.33, 43.17, 33.13, 30.59, 30.52, 29.80, 28.44, 26.23, 23.95, 15.39. MS (MALDI-TOF, CHCl<sub>3</sub>): Calculated for C<sub>27</sub>H<sub>27</sub>Cl<sub>2</sub>N<sub>3</sub>OS<sub>2</sub>: 543.0973, found [M+H]<sup>+</sup>: 544.1063.

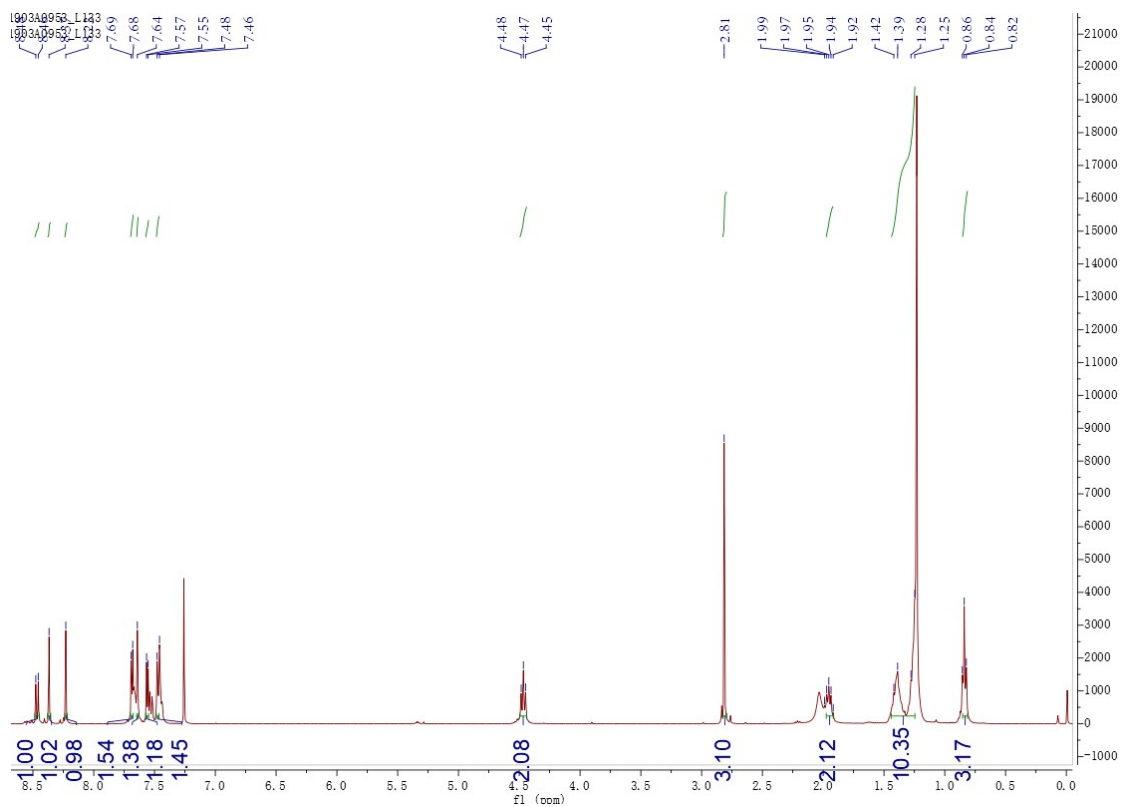


Figure S34:  $^1\text{H}$  NMR of **7c** in  $\text{CDCl}_3$  at 300K.

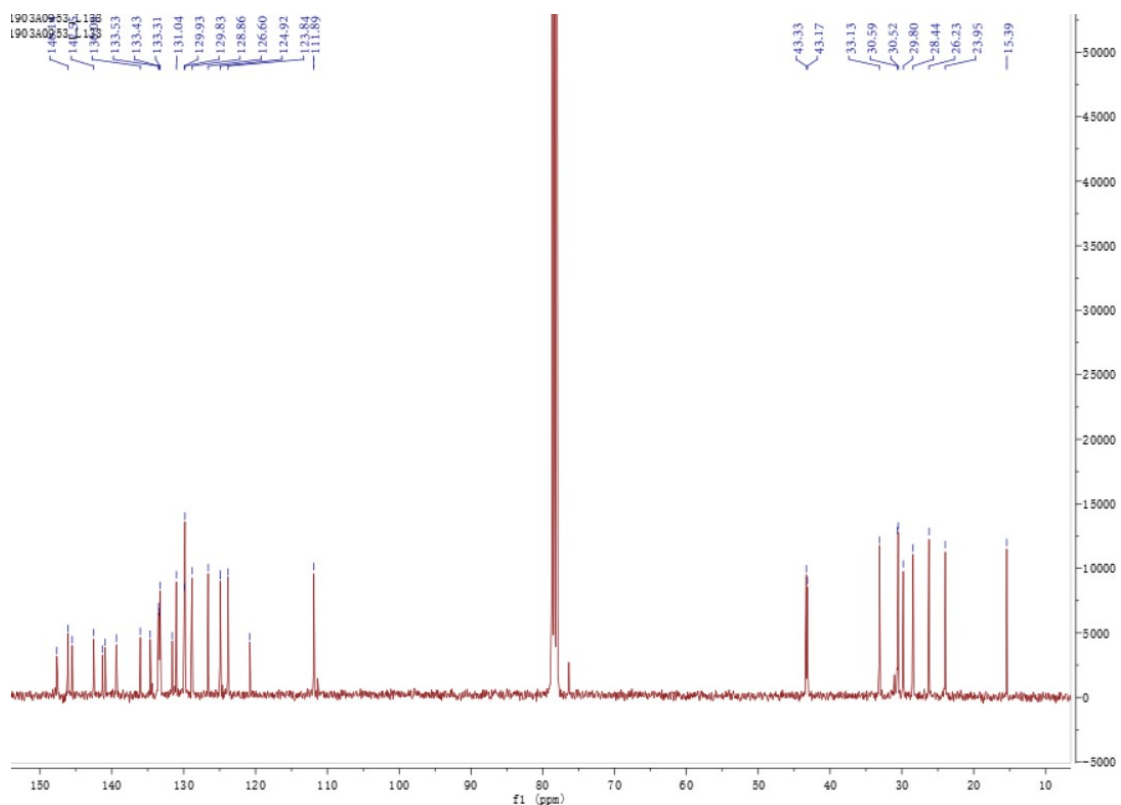


Figure S35:  $^{13}\text{C}$  NMR of **7c** in  $\text{CDCl}_3$  at 300K.

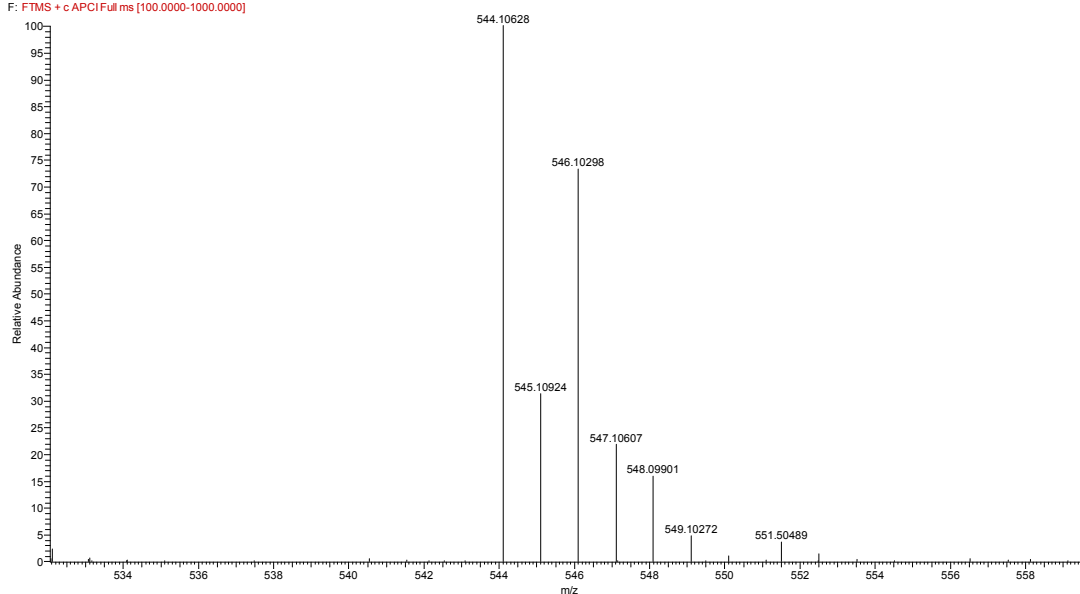


Figure S36: MALDI-TOF of **7c**.

### Compound **8a**

Compound **7a** (200 mg, 0.42 mmol) was stirred with  $P_2O_5$  (24 mg, 0.17 mmol) and trifluoromethanesulfonic acid (5 ml) at room temperature in the dark for 3 days. The mixture was poured into ice-water, extracted with chloroform and the organic phase was dried with  $MgSO_4$ , the solvent was removed by reduced pressure and the crude product was dried in vacuum, which was followed to be redissolved in pyridine (5 mL) and then the mixture was refluxed overnight. After the mixture was cooled to room temperature, extracted with chloroform and diluted hydrochloride acid, the separated organic phase was dried over  $MgSO_4$ , and solvent was removed by reduced pressure. The crude was purified by column chromatography on silica gel (eluent: DCM) to afford a yellow solid. (112 mg, 60 %).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 300 K),  $\delta$  (ppm): 8.84 (s, 1H), 8.25 (d,  $J = 8.0$  Hz, 1H), 8.08 (d,  $J = 8.0$  Hz, 1H), 7.69-7.73 (m, 1H), 7.61-7.65 (m, 1H), 7.63 (s, 1H), 7.56 (d,  $J = 4.0$  Hz, 1H), 7.32 (d,  $J = 8.0$  Hz, 1H), 4.34 (d,  $J = 8.0$  Hz, 2H), 2.20-2.28 (m, H), 1.23-1.52 (m, 11H), 0.97 (t, 3H), 0.88 (t, H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , 300 K),  $\delta$  (ppm): 148.46, 144.15, 142.22, 142.04, 140.78, 140.34, 136.93, 129.97, 129.17, 127.15, 122.09, 119.62, 119.29, 101.98, 47.01, 39.57, 32.07, 29.89, 25.61, 24.40, 15.44, 12.11, 2.39. MS (MALDI-TOF,  $CHCl_3$ ): Calculated for  $C_{26}H_{25}N_3S_2$ : 443.14899, found  $[M+H]^+$ : 444.15789.

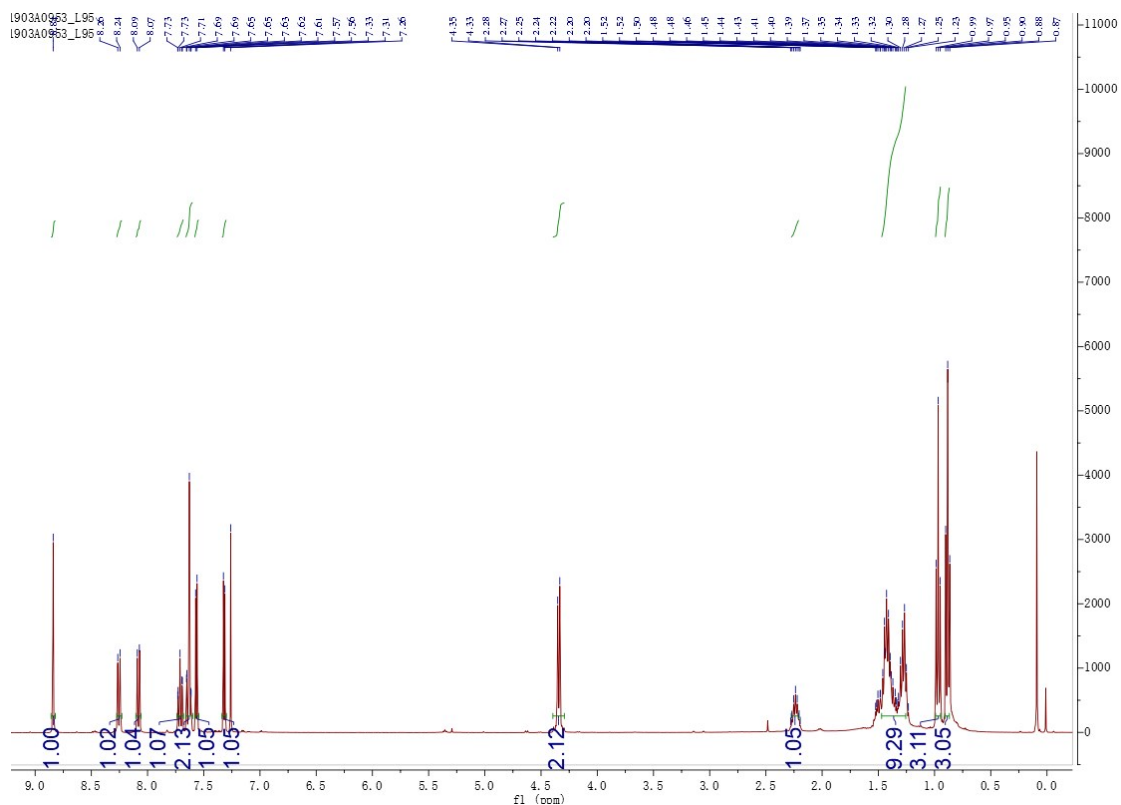


Figure S37:  $^1\text{H}$  NMR of **8a** in  $\text{CDCl}_3$  at 300K.

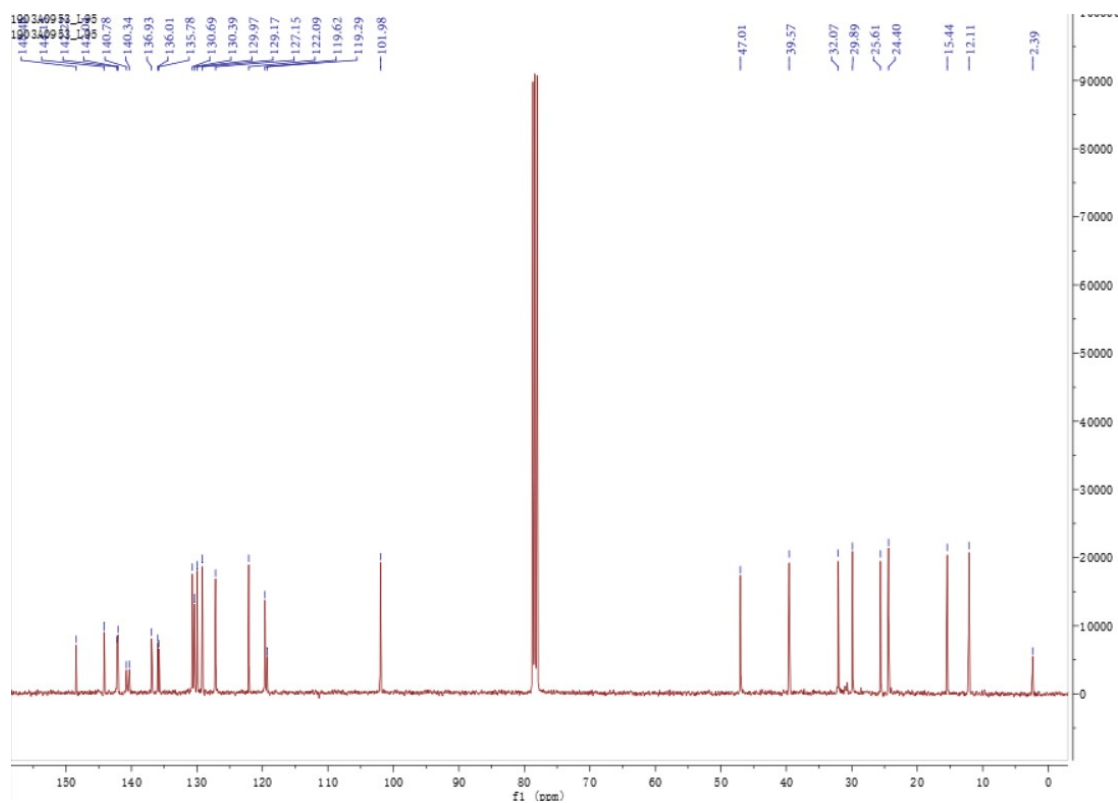


Figure S38:  $^{13}\text{C}$  NMR of **8a** in  $\text{CDCl}_3$  at 300K.

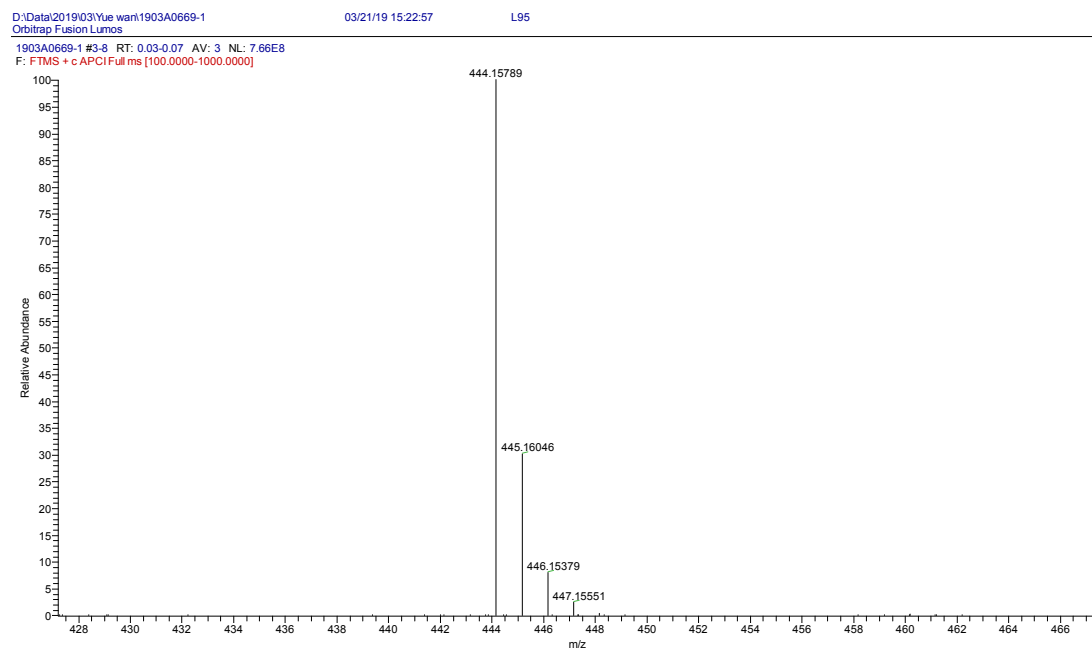


Figure S39: MALDI-TOF of **8a**.

### Compound **8b**

Compound **7b** (166 mg, 0.34 mmol) was Eaton's reagent (3 mL) at room temperature in the dark for 3 days. The mixture was poured into ice-water, extracted with chloroform and the organic phase was dried with MgSO<sub>4</sub>, the solvent was removed by reduced pressure and the crude product was dried in vacuum, which was followed to be redissolved in pyridine (5 mL) and then the mixture was refluxed overnight. After the mixture was cooled to room temperature, extracted with chloroform and diluted hydrochloride acid, the separated organic phase was dried over MgSO<sub>4</sub>, and solvent was removed by reduced pressure. The crude was purified by column chromatography on silica gel (eluent: DCM) to afford a yellow solid. (93 mg, 60 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 300 K), δ (ppm): 9.50 (s, 1H), 8.70 (d, *J* = 8.0 Hz, 1H), 7.88 (t, 1H), 7.80-7.83 (m, 1H), 7.82 (s, 1H), 7.71 (d, *J* = 4.0 Hz, 1H), 7.40 (d, *J* = 4.0 Hz, 1H), 4.64 (t, 2H), 2.00-2.06 (m, 2H), 1.40-1.45 (m, 4H), 1.23-1.50 (m, 18H), 0.85 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 300 K), δ (ppm): 148.20, 144.10, 141.96, 135.79, 131.16, 130.34, 129.08, 127.65, 122.21, 102.00, 43.12, 33.17, 30.63, 30.54, 29.55, 28.42, 23.97, 15.40. MS (MALDI-TOF, CHCl<sub>3</sub>): Calculated for C<sub>26</sub>H<sub>25</sub>N<sub>3</sub>S<sub>2</sub>: 443.14899, found [M+H]<sup>+</sup>: 444.15668.

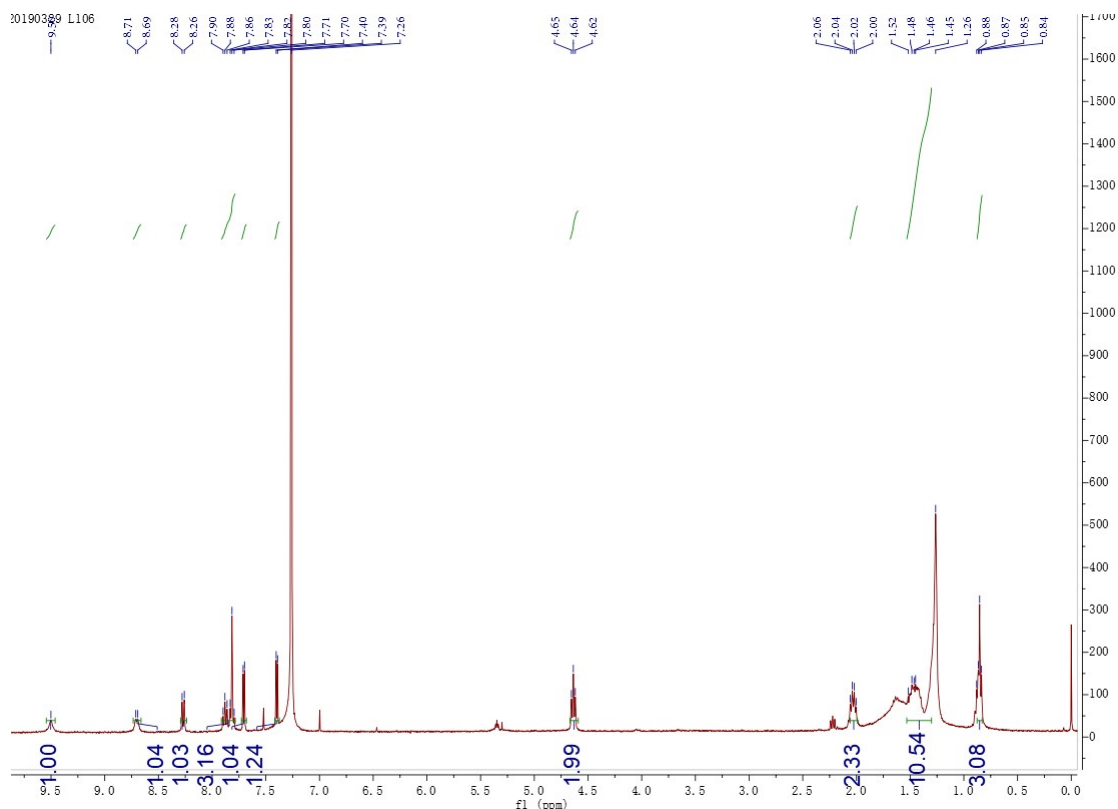


Figure S40:  $^1\text{H}$  NMR of **8b** in  $\text{CDCl}_3$  at 300K.

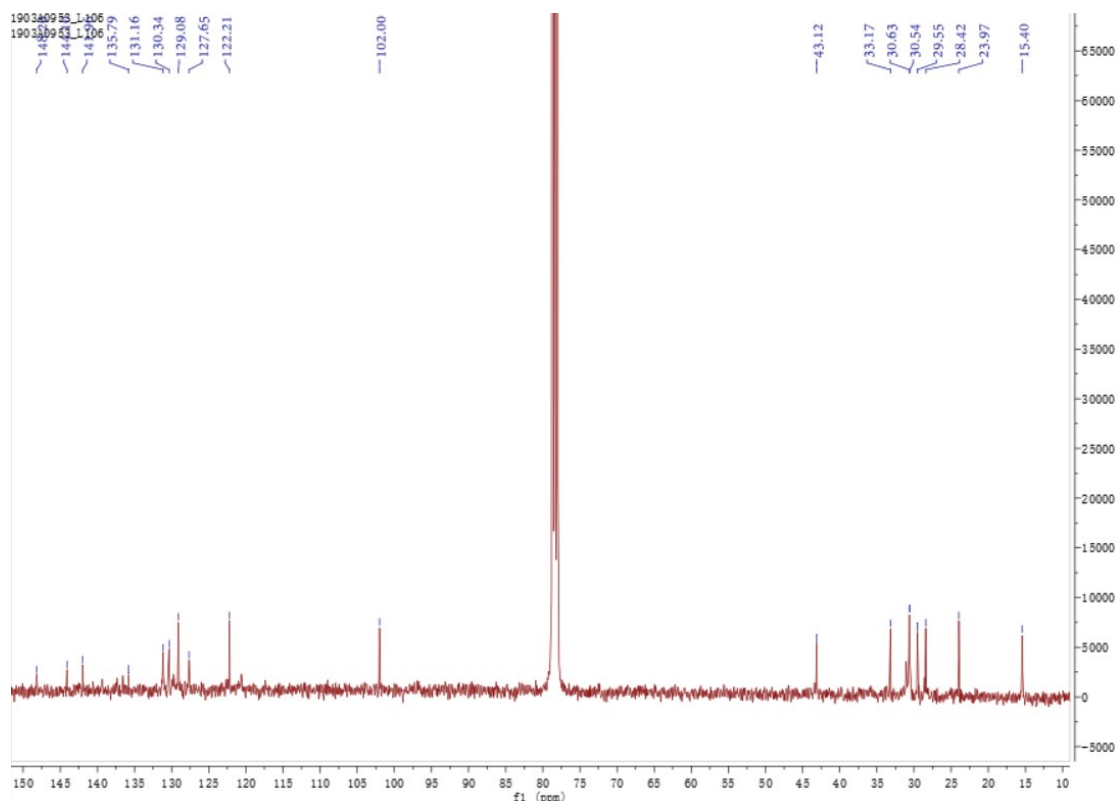


Figure S41:  $^{13}\text{C}$  NMR of **8b** in  $\text{CDCl}_3$  at 300K.

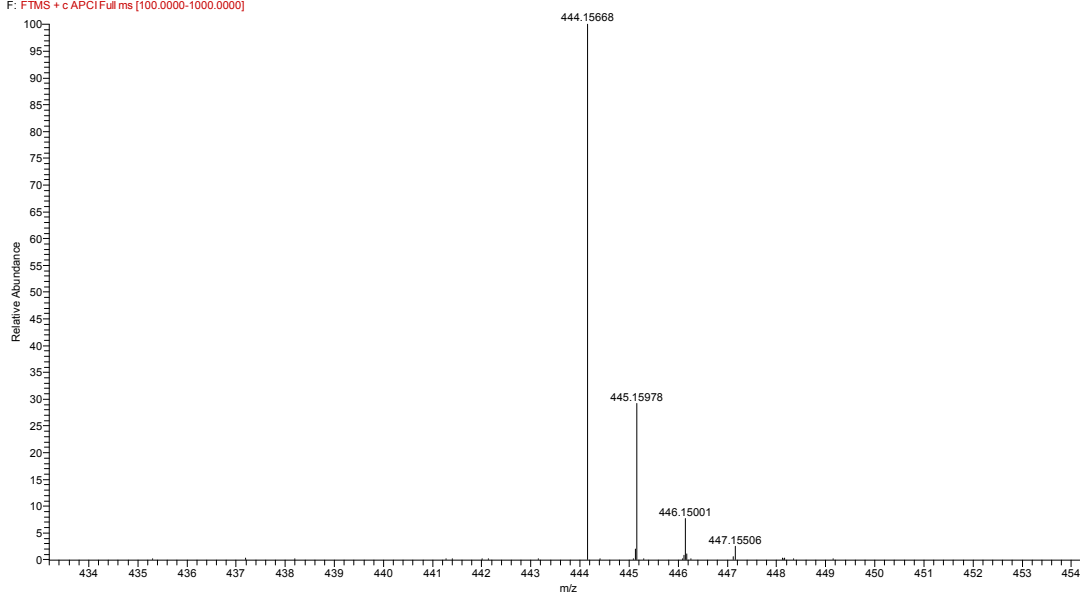


Figure S42: MALDI-TOF of **8b**.

### Compound **8c**

Compound **7c** (200 mg, 0.36 mmol) was stirred with Eaton's reagent (3 mL) at room temperature in the dark for 3 days. The mixture was poured into ice-water, extracted with chloroform and the organic phase was dried with MgSO<sub>4</sub>, the solvent was removed by reduced pressure and the crude product was dried in vacuum, which was followed to be redissolved in pyridine (5 mL) and then the mixture was refluxed overnight. After the mixture was cooled to room temperature, extracted with chloroform and diluted hydrochloride acid, the separated organic phase was dried over MgSO<sub>4</sub>, and solvent was removed by reduced pressure. The crude was purified by column chromatography on silica gel (eluent: DCM) to afford a yellow solid. (110 mg, 58 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 300 K),  $\delta$  (ppm): 9.11 (s, 1H), 8.56 (s, 1H), 8.26 (s, 1H), 7.76 (s, 1H), 7.70 (d,  $J$  = 4.0 Hz, 1H), 7.38 (d,  $J$  = 8.0 Hz, 1H), 4.57 (t, 2H), 1.97-2.02 (m, 4H), 1.25-1.48 (m, 17H), 1.20-1.30 (m, 37H), 0.84-0.90 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 300 K),  $\delta$  (ppm): 148.26, 144.14, 143.08, 140.65, 137.56, 136.84, 135.69, 134.34, 131.58, 130.11, 129.57, 122.14, 120.61, 118.06, 102.11, 43.20, 33.16, 30.60, 30.53, 29.51, 28.41, 23.97, 15.40. MS (MALDI-TOF, CHCl<sub>3</sub>): Calculated for C<sub>26</sub>H<sub>25</sub>Cl<sub>2</sub>N<sub>3</sub>S<sub>2</sub>: 511.07104, found [M+H]<sup>+</sup>: 512.07843.



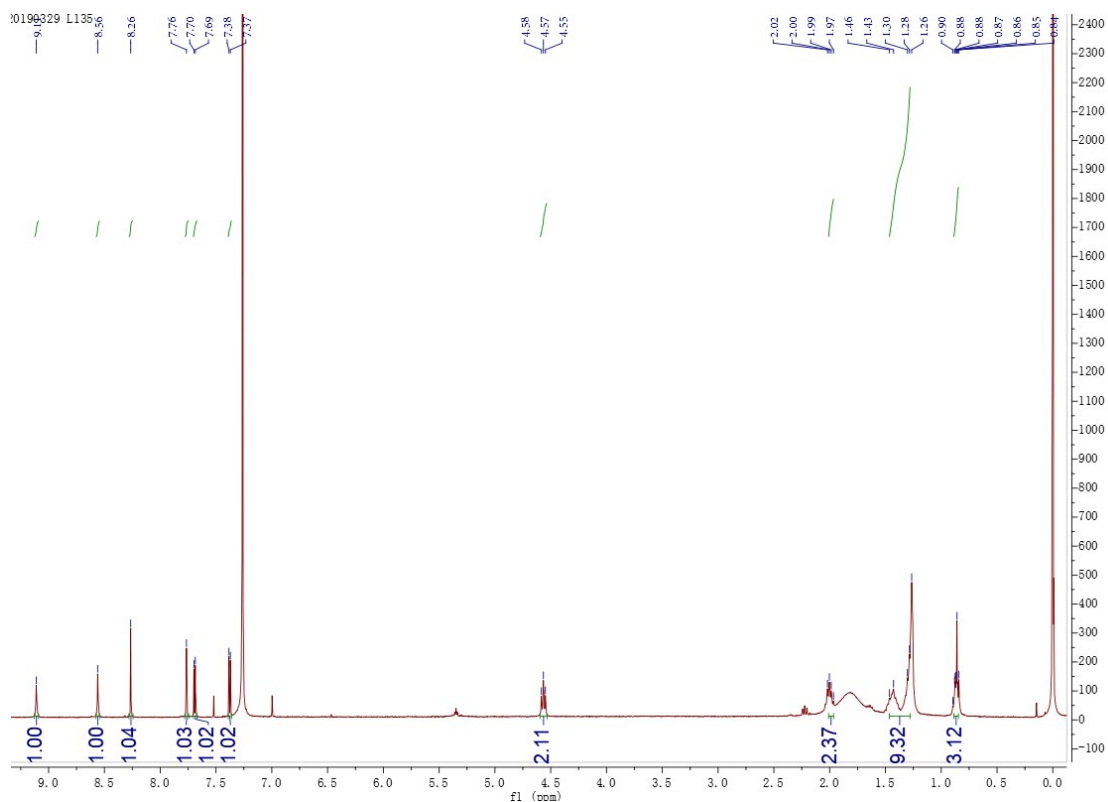


Figure S43:  $^1\text{H}$  NMR of **8c** in  $\text{CDCl}_3$  at 300K.

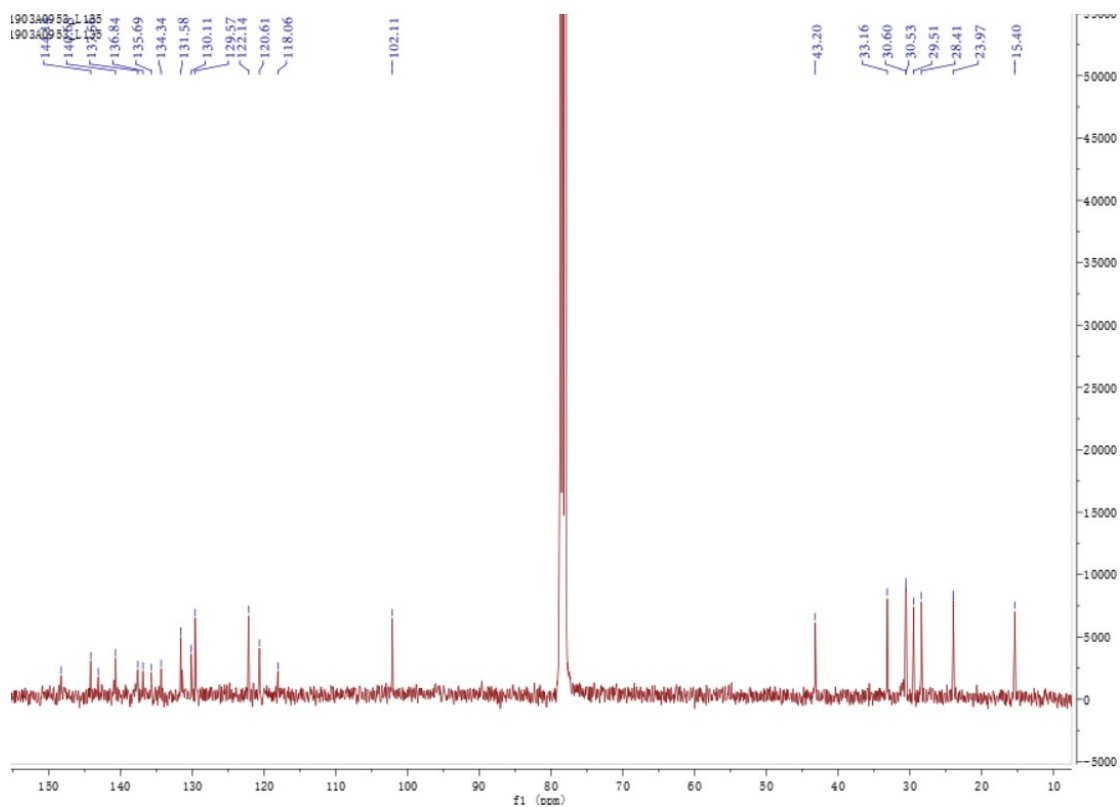


Figure S44:  $^{13}\text{C}$  NMR of **8c** in  $\text{CDCl}_3$  at 300K.

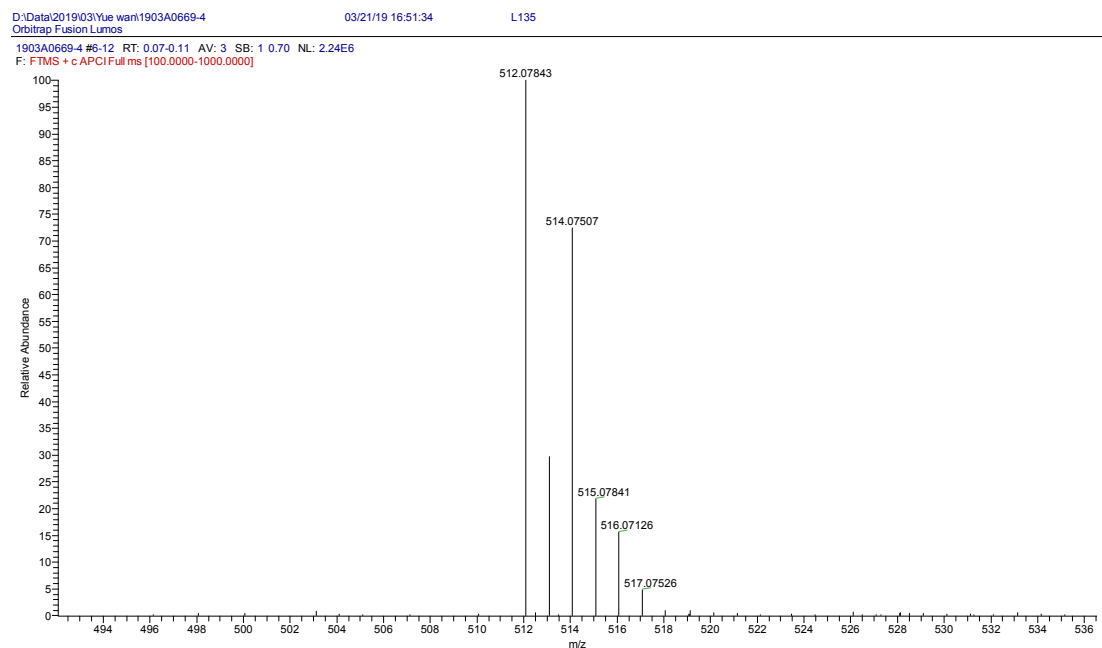


Figure S45: MALDI-TOF of **8c**.

## 8. References

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- [S2] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.