Electronic Supplementary Information (ESI)

Donor-acceptor type silole compounds with aggregation-induced deep-red emission enhancement: synthesis and application for significant intensification of near-infrared photoluminescence

Xiaobo Du and Zhi Yuan Wang*

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences and Graduate School of Chinese Academy of Sciences, Changchun, 130022, China

Table of Contents

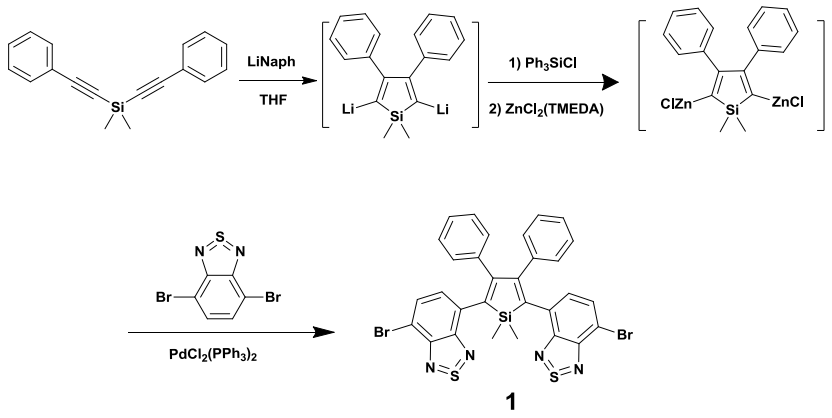
Materials and Measurement

All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to standard procedures. All the reactions were carried out under an argon atmosphere. Column chromatography was performed using 300-400 mesh silica gels. Dimethylbis(phenylethynyl)silane,[1] phenyltributylstannane (**4a**), 2-tributylstannyl-thiophene (**4b**),[2] tributyl[4-(N,N-bis(4-octyloxyphenyl)amino)phenyl]stannane (**4c**), tributyl[5-(9,9-dioctylfluoren-2-yl)thiophene-2-yl]stannane (**4d**),[3] 2-diphenylamino-5-tributylstannylthiophene (**4e**)[4] and 4,9-dibromo-6,7-diphenyl [1,2,5]thiadiazolo-[3,4-g]quinoxaline (**5**)[5] were prepared as described in the literature.

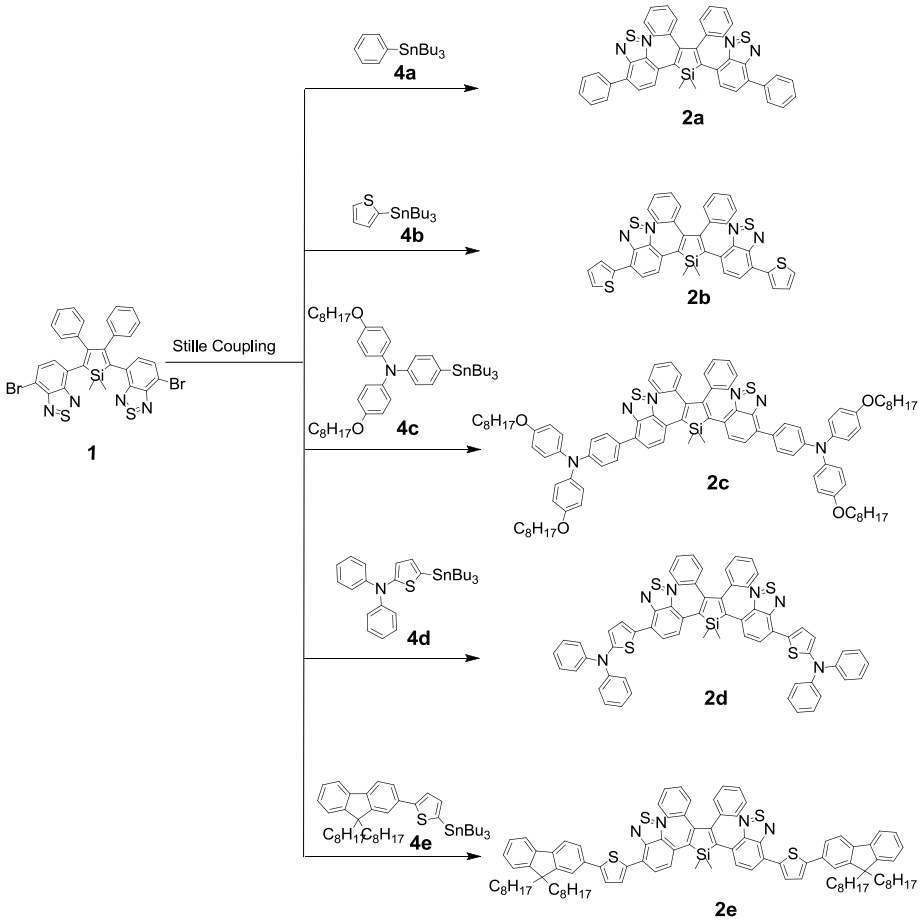
^{1}H NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer using deuterated chloroform as solvent. Tetramethylsilane (TMS) was used as internal reference for the NMR analyses. Elemental analysis was performed on a FlashEA1112 Elementar Analysis Instrument. The UV-vis-NIR absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. MALDI-TOF-MS was obtained from Bruker Daltonics Autoflex III TOF/TOF. Photoluminescence spectra in visible region were measured on a RF-5301 fluorescence spectrophotometer. Photoluminescence spectra in the near-infrared region were measured on a PTI fluorescence system. The $\Phi_{F,\,s}$ values in THF solution were estimated using Nile Red (Φ_F = 0.78 in acetonitrile) as a standard and the $\Phi_{F,\,f}$ values of the solid films were determined using an integrating sphere. The fluorescence quantum yield of **3** was determined in toluene, relative to IR-125 dye (Φ_F = 0.13, λ_{max}^{PL} = 835 in DMSO).

Synthetic Procedures

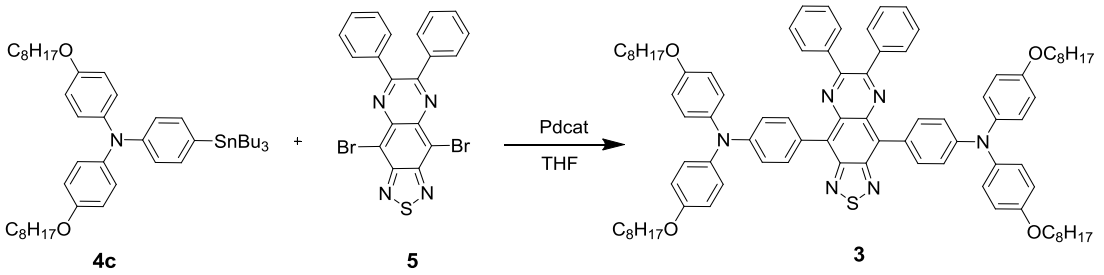
Silole derivatives **(2a-2e)** were synthesized in good yields (75-87%) from compound **1** and different donors by the Stille coupling reaction according to Schemes S1 and S2. Compound **3** was synthesized as shown in Scheme S3.



Scheme S1. Synthesis of compound **1** by the intramolecular reductive cyclization of diethynylsilanes.



Scheme S2. Synthesis of D-A type silole derivatives via stille coupling



Scheme S3. Synthesis of compound **3**

Synthesis of 1. A mixture of naphthalene (2.14 g, 16.8 mmol) and lithium (0.112g, 16 mmol) in dry THF (25 mL) was stirred at room temperature under an argon atmosphere for 6h to form a deep green solution of lithium naphthalenide. To the solution was added a THF (25 mL) solution of dimethylbis(phenylethynyl)silane (1.04 g, 4 mmol) dropwise over 10 min at room temperature. After stirring for 20 min, the mixture was cooled to -78 ℃, a solution of chlorotriphenylsilane (2.44 g, 8 mmol) in THF (30 mL) was added to the mixture. The mixture was stirred for 30 min and then $ZnCl_2$ (TMEDA) (2.24 g, 8.8 mmol) was added as a solid to the mixture at 0 ℃, followed by the dilution with THF (80 mL). After stirring for 1h at room temperature, 4,7-dibromo-2,1,3-benzothiadiazole (3.53 g, 12 mmol) and $PdCl_2(PPh_3)_2$ (150 mg) were added to the mixture. The mixture was reflux at 75 ℃ and stirred for 24 h. After being cooled to room temperature, the mixture was filtered to remove insoluble materials. Aqueous solution of NH_4Cl (150 mL) was added to the filtrate and the mixture was extracted with ethyl acetate twice. The combined extract was washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (PE/DCM=1:1) to gave 1.96 g (2.84 mmol) of **1** as a yellow solid in 71% yield. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.55 (d, 2H, J = 7.6Hz), 6.99-6.91 (m, 6H), 6.80-6.77(m, 6H), 0.46(s, 6H). Anal. Calcd for $C_{30}H_{20}Br_2N_4S_2Si$: C, 52.33; H, 2.93; N, 8.14. Found: C, 52.50; H, 3.08; N, 7.89. MALDI-TOF: *m*/*z* 688.9 (100%) $M+H^+$ (calcd 687.9).

General Procedure for Compounds 2a-2e. To a solution of **1** (0.172 g, 0.25 mmol) in anhydrous THF (20 mL) were added the corresponding tributyltin compound (0.6 mmol) and $PdCl_2(PPh_3)_2$ (15 mg). The mixture was stirred for 24 h at 75 ℃ under an argon atmosphere. After

being cooled to the room temperature, saturated aqueous solution of KF (50mL) was added and the mixture was extracted with ethyl acetate twice. The combined extract was washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (PE/DCM=1:1) to give the corresponding product (**2a-2e)**.

2a: Orange solid (unstable in the air, 53% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.92 (d, 4H, J = 7.2Hz), 7.53-7.40 (m, 8H), 7.00-6.94 (m, 8H), 6.89-6.86 (m, 4H), 0.55(s, 6H); Anal. Calcd for $C_{42}H_{30}N_4S_2Si$: C, 73.87; H, 4.43; N, 8.20, Found C, 74.07; H, 4.81; N, 7.63; MALDI-TOF: *m*/*z* 683.2(100%) $M+H^+$ (calcd 682.2).

2b. Red solid (79% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.04 (dd, 2H, J_1 = 1.0 Hz, J_2 = 3.7Hz), 7.58 (d, 2H, J= 7.5Hz), 7.40 (dd, 2H, J_1 = 1.0 Hz, J_2 = 5.1Hz), 7.17 (dd, 2H, J_1 = 3.7Hz, J_2 = 5.1Hz), 6.98-6.91 (m, 8H), 6.87-6.84 (m, 4H), 0.51(s, 6H); Anal. Calcd for $C_{38}H_{26}N_4S_4Si$: C, 65.67; H, 3.77; N, 8.06, Found C, 65.51; H, 3.76; N, 7.88; MALDI-TOF: *m*/*z* 694.0 (100%) M^+ (calcd 694.1).

2c. Red solid (81% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.76 (d, 4H, J = 8.8 Hz), 7.35 (d, 2H, J= 7.5 Hz), 7.12-7.06 (m, 8H), 7.04-6.91 (m, 12H), 6.88-6.80 (m, 12H), 3.94 (t, 8H, J = 6.5 Hz), 1.84-1.72 (m, 8H), 1.50-1.22 (b, 40H), 0.92-0.84 (m, 12H), 0.52(s, 6H); Anal. Calcd for $C_{98}H_{112}N_6O_4S_2Si$: C, 76.92; H, 7.38; N, 5.49, Found C, 76.63; H, 7.39; N, 5.24; MALDI-TOF: *m*/*z* 1528.8 (100%) $M-H^-$ (calcd 1529.8).

2d. Black solid (76% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.89 (d, 2H, J = 4.0 Hz), 7.39 (d, 2H, J= 7.6Hz), 7.34-7.26 (m, 6H), 7.25-7.16 (m, 10H), 7.09-7.02 (m, 4H), 6.99-6.90 (m, 6H), 6.86-6.80 (m, 6H), 6.70 (d, 2H, J = 4.0Hz), 0.48 (s, 6H); Anal. Calcd for $C_{62}H_{44}N_6S_4Si$: C, 72.34; H, 4.31; N, 8.16, Found C, 71.85; H, 4.32; N, 7.70; MALDI-TOF: *m*/*z* 1028.2 (100%) M^+ (calcd 1028.2).

2e. Red solid (84% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.06 (d, 2H, J = 3.9 Hz), 7.74-7.60 (m, 10H), 7.45 (d, 2H, J = 3.9 Hz), 7.38-7.29 (m, 6H), 7.06-6.85 (m, 12H), 2.06-1.95 (m, 8H), 1.25-0.97 (b, 40H), 0.79 (t, 12H, J = 6.9 Hz), 0.73-0.58 (m, 8H), 0.55(s, 6H); Anal. Calcd for $C_{96}H_{106}N_4S_4Si$: C, 78.32; H, 7.26; N, 3.81, Found C, 78.45; H, 7.51; N, 3.46; MALDI-TOF: *m*/*z* 1470.7 (100%) $M-H^+$ (calcd 1471.7).

Synthesis of 3. To a solution of **5** (0.25g, 0.5 mmol) in anhydrous THF (30 mL) were added **4c** (0.97g, 1.25 mmol) and $PdCl_2(PPh_3)_2$ (25 mg). The mixture was stirred for 24 h at 75 ℃ under an

argon atmosphere. After being cooled to the room temperature, an aqueous solution of KF was added and the mixture was extracted with ethyl acetate twice. The combined extract was washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by Al_2O_3 column chromatography (PE/DCM=1:1) to give **3** as a blue solid in 51% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.92 (d, 4H, J = 6.0 Hz), 7.65 (d, 4H, J = 6.6 Hz), 7.45-7.26 (m, 10H), 7.25-7.04 (m, 8H), 6.95-6.86 (m, 8H), 3.97 (s, 8H), 1.85-1.75 (m, 8H), 1.51-1.20 (b, 40H), 0.92-0.86 (m, 12H); Anal. Calcd for $C_{88}H_{102}O_4N_6S$: C, 78.88; H, 7.67; N, 6.27, Found C, 78.85; H, 7.72; N, 6.40; MALDI-TOF: *m*/*z* 1338.7 (100%) M^+ (calcd 1338.8).

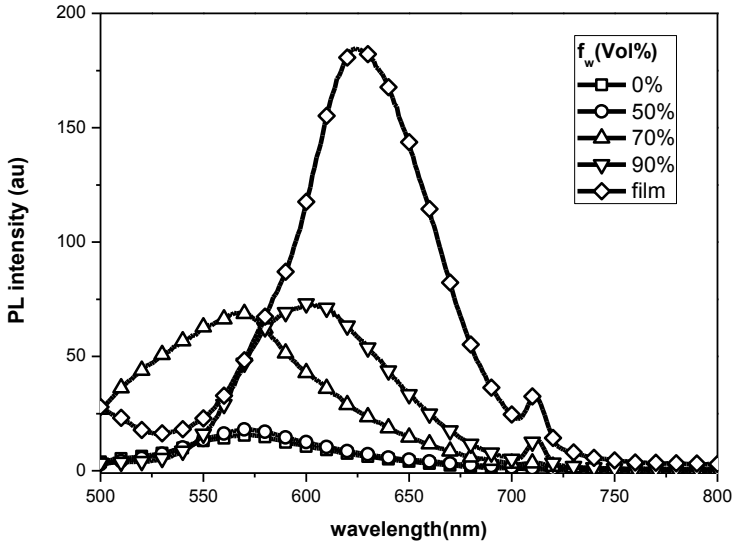


Figure S1. PL spectra of **2b** in the THF/hexane mixtures. Solution concentration: 20 μM. Excitation wavelength: 464 nm.

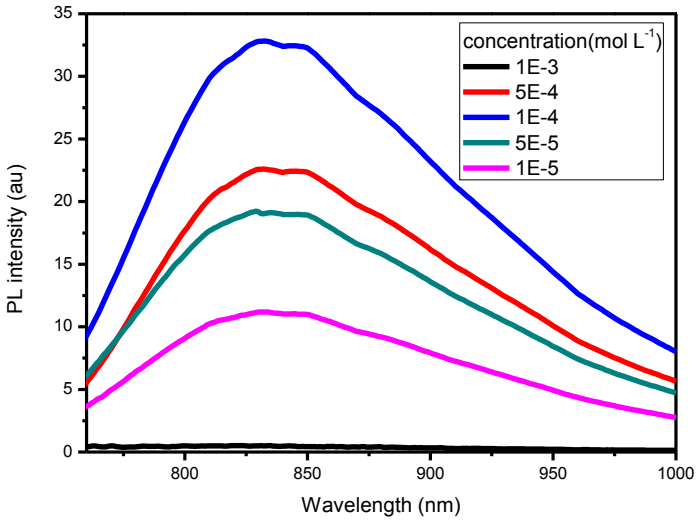


Figure S2. PL spectra of **3** in toluene dilute solution with different concentrations. Excitation wavelength: 650 nm.

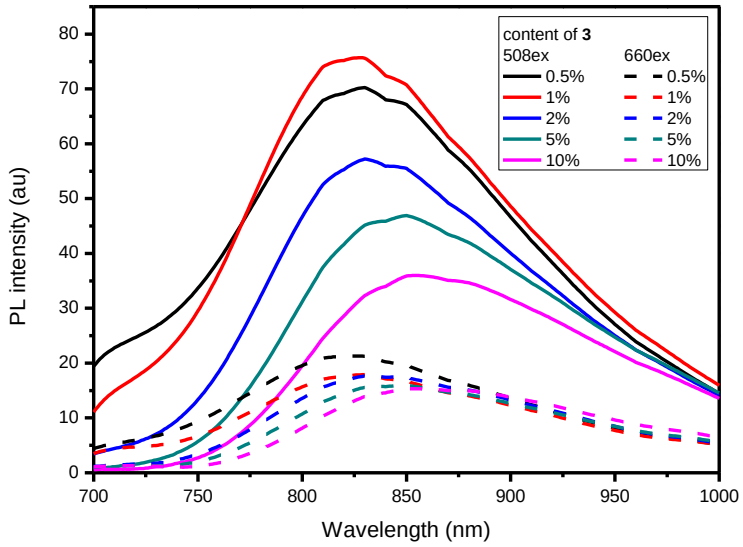


Figure S3. PL spectra in near-infrared region of **3** doped in the film of **2c** with different doping concentrations. Excitation at 508 nm and 660 nm.

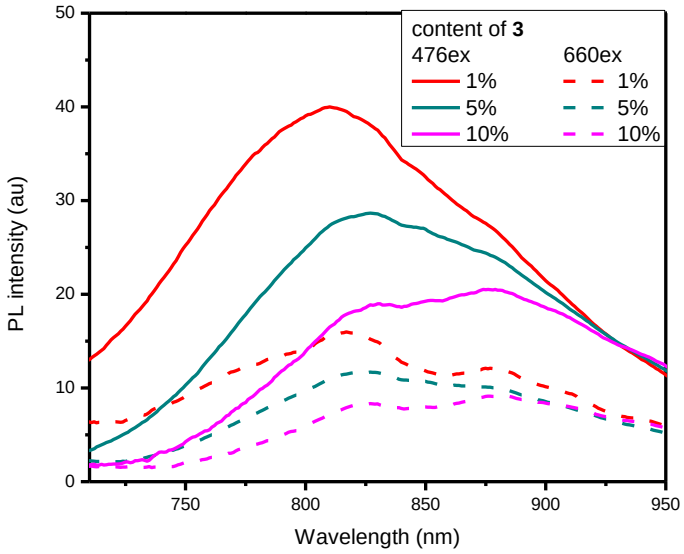


Figure S4. PL spectra in near-infrared region of **3** doped in the film of **2b** with different doping concentrations. Excitation at 476 nm and 660 nm.

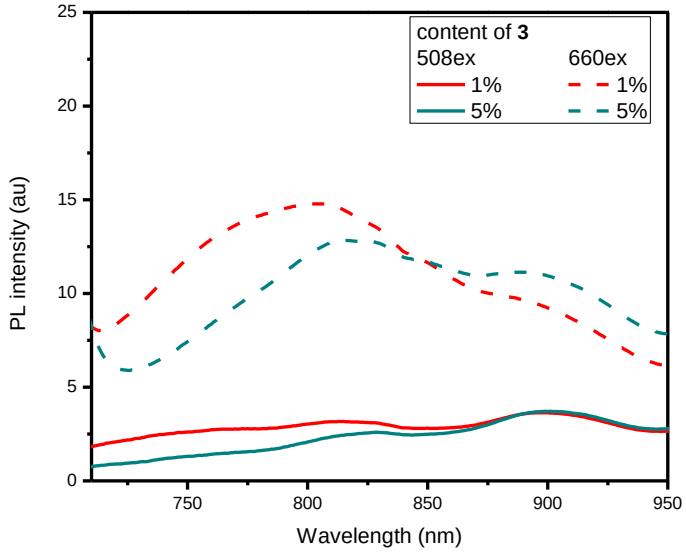


Figure S5. PL spectra in near-infrared region of **3** doped in PMMA with different doping concentrations. Excitation at 508 nm and 660 nm.

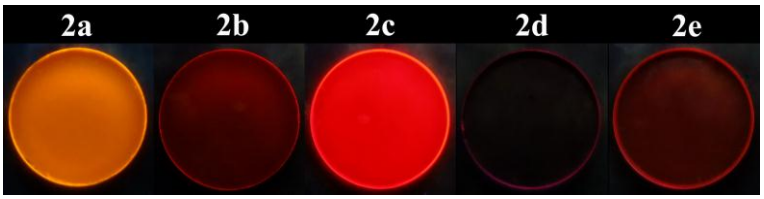


Figure S6. Photography of the thin films of **2a-e** under 365nm UV lamp.

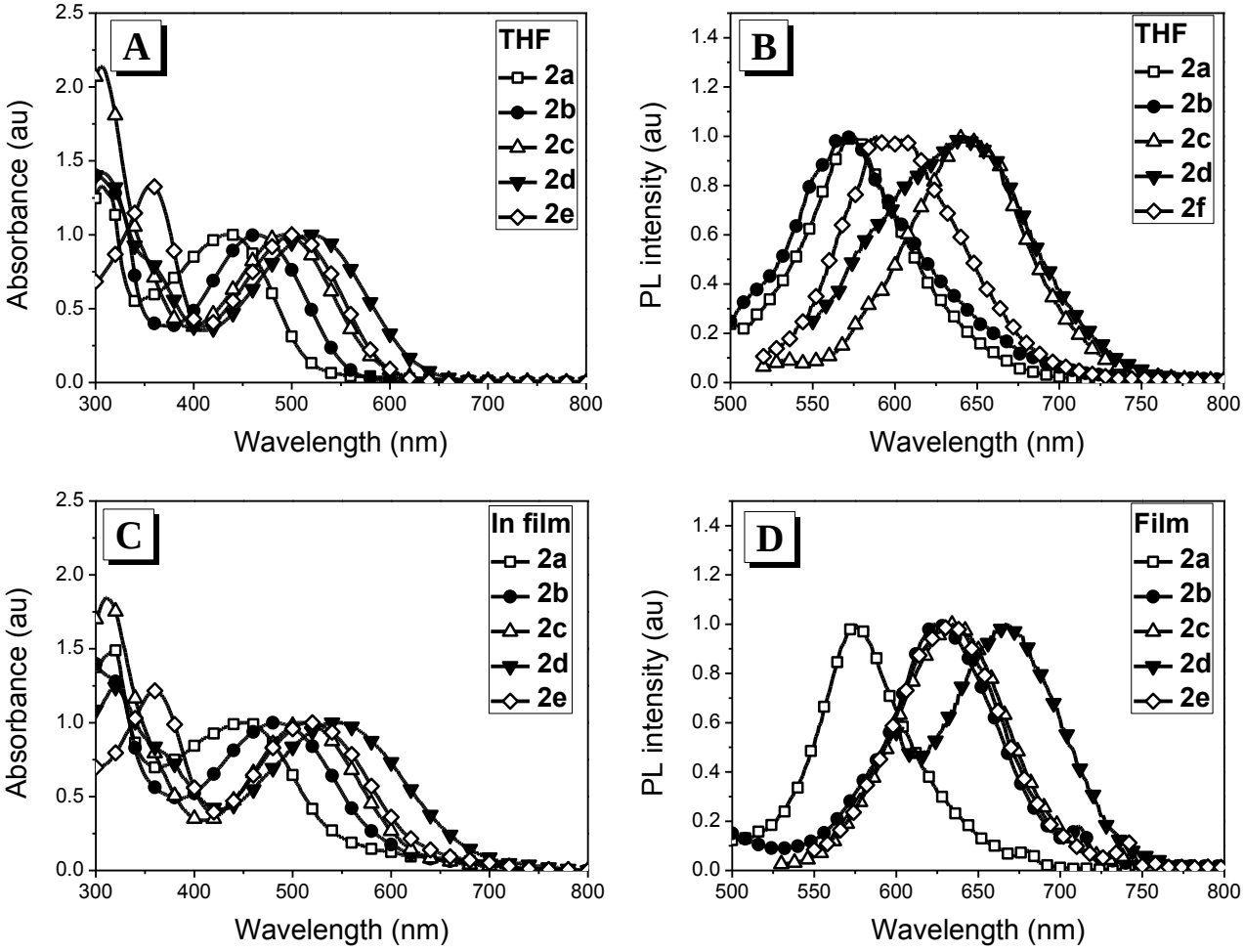


Figure S7. UV absorption and PL spectra for **2a-2e** in THF (A, B) and as films (C, D) at room temperature.

References

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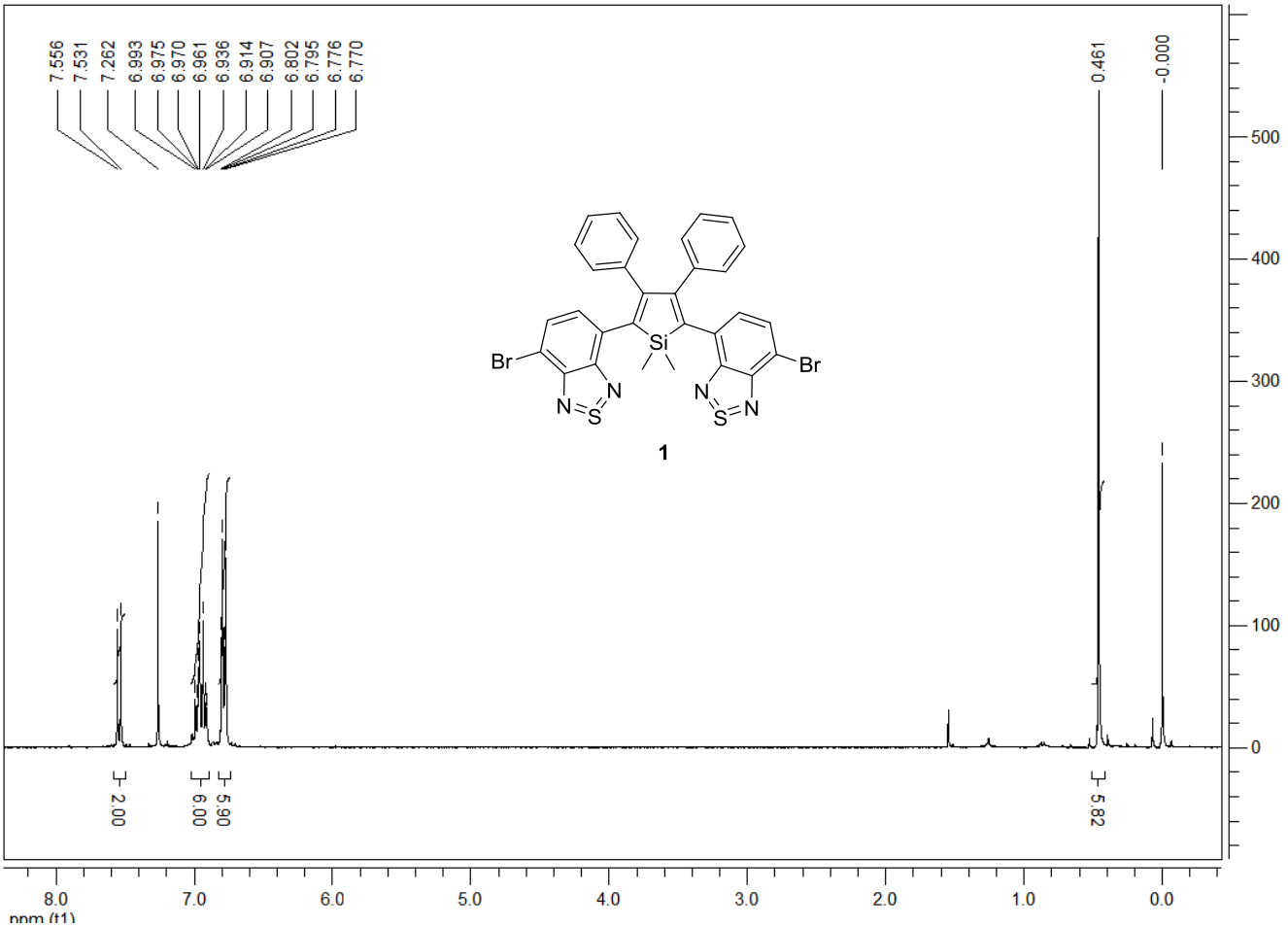
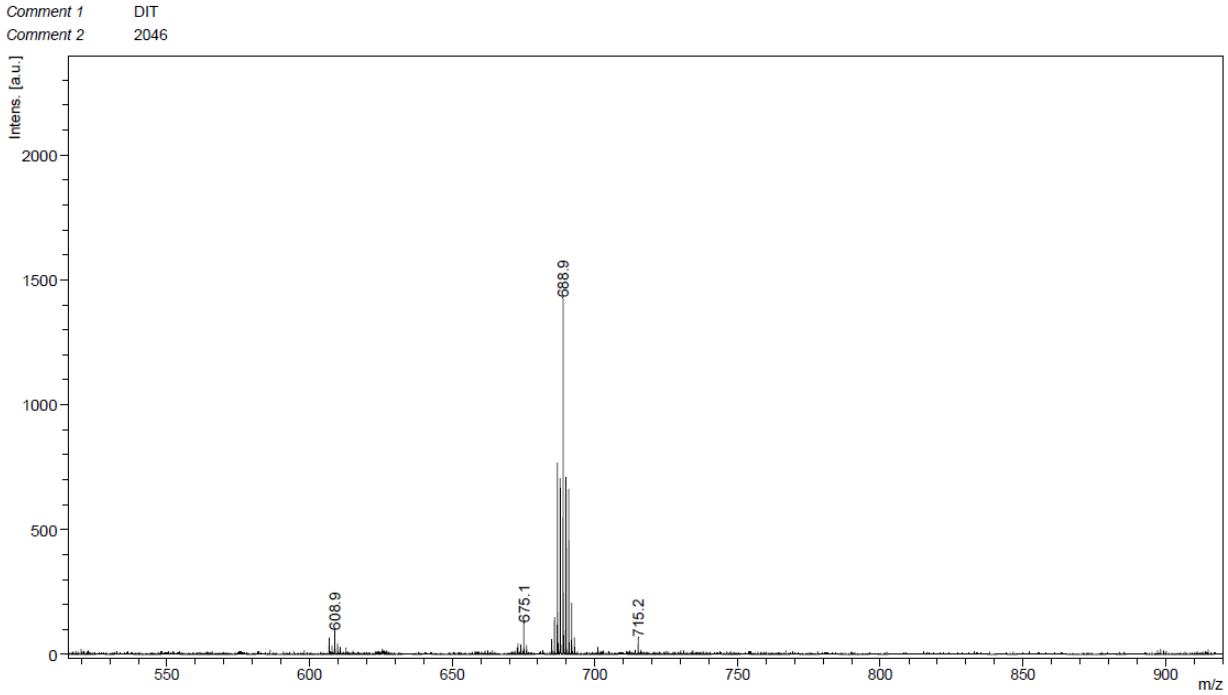
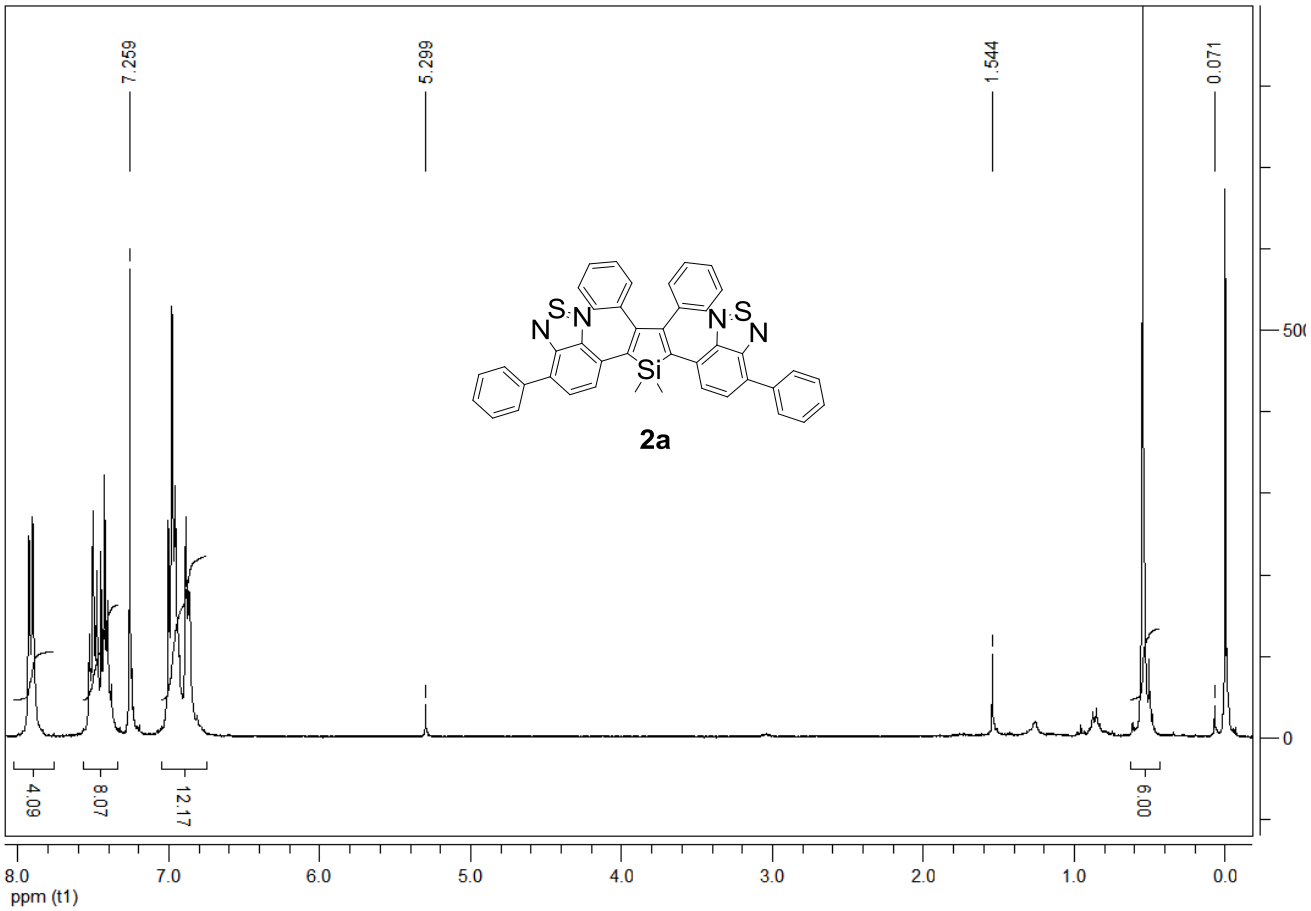


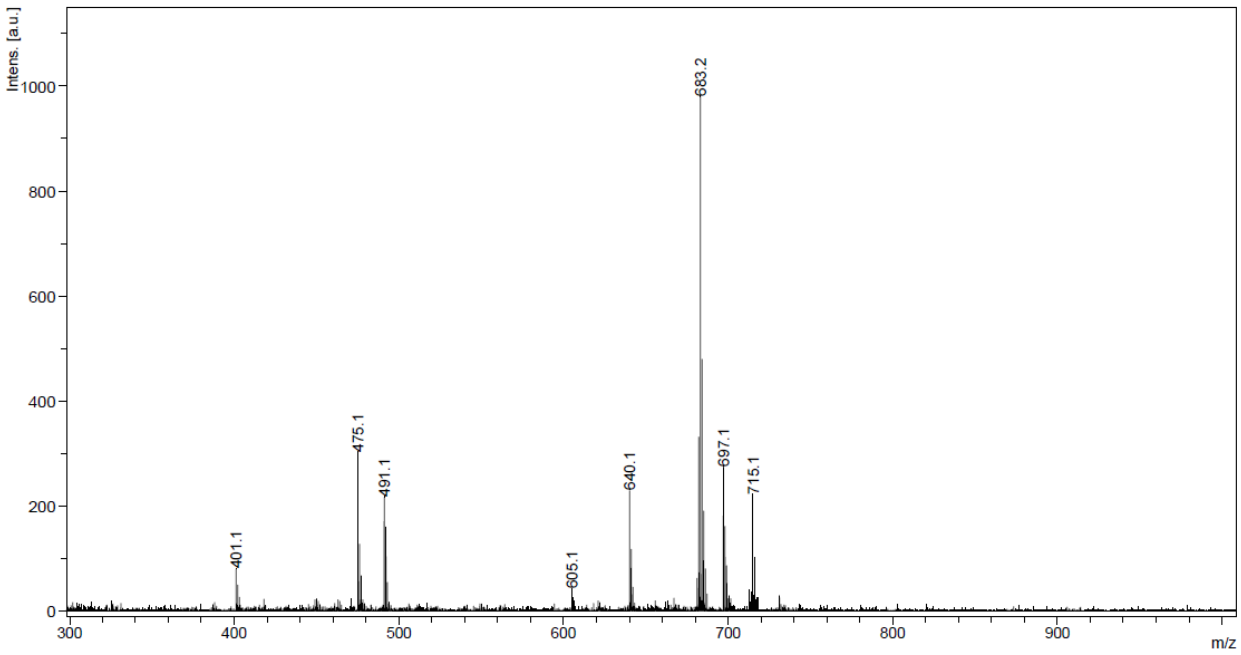
^{1}H NMR of **1** ($CDCl_3$, 300 MHz)



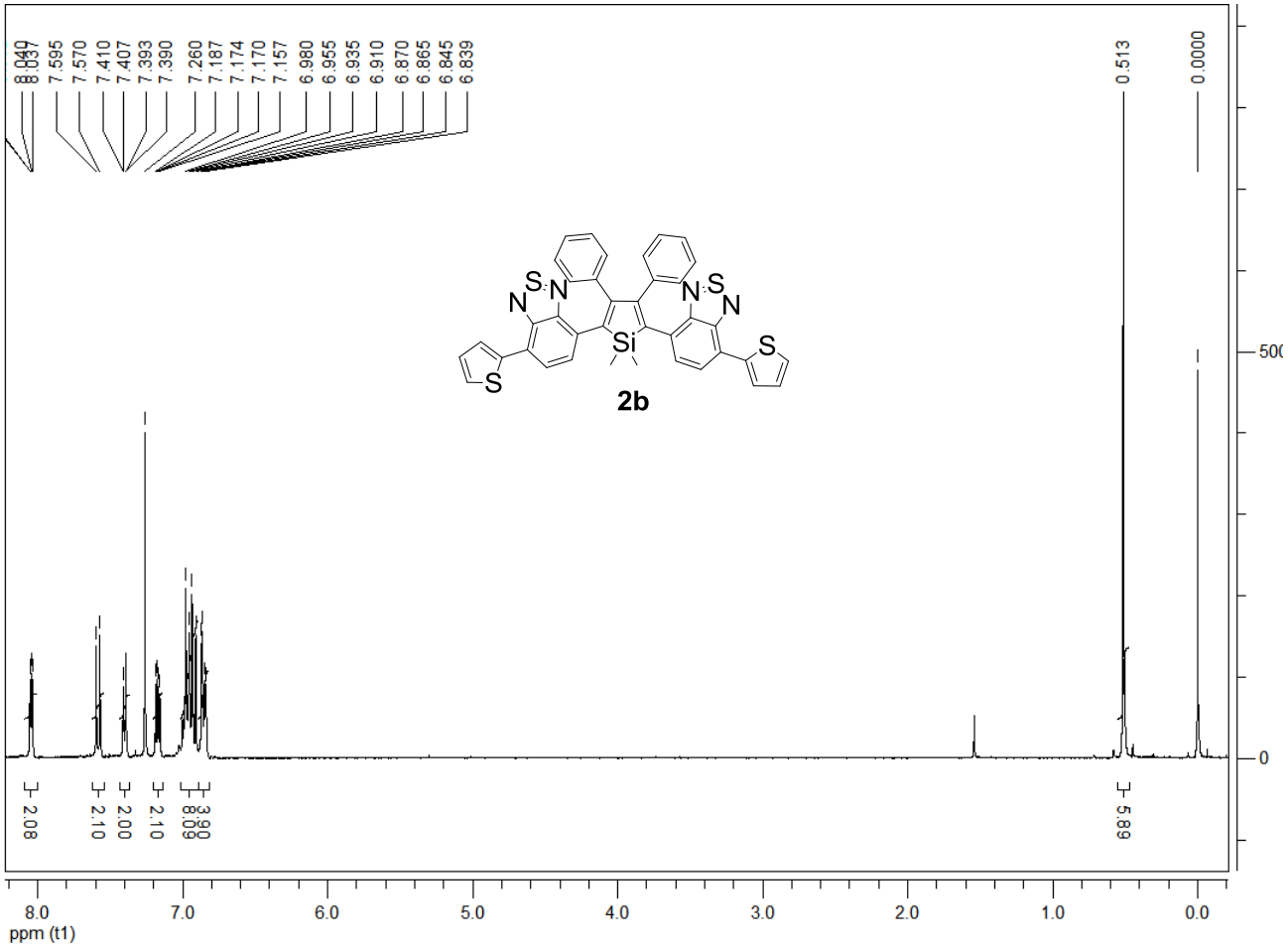
MALDI-TOF-MS of **1**



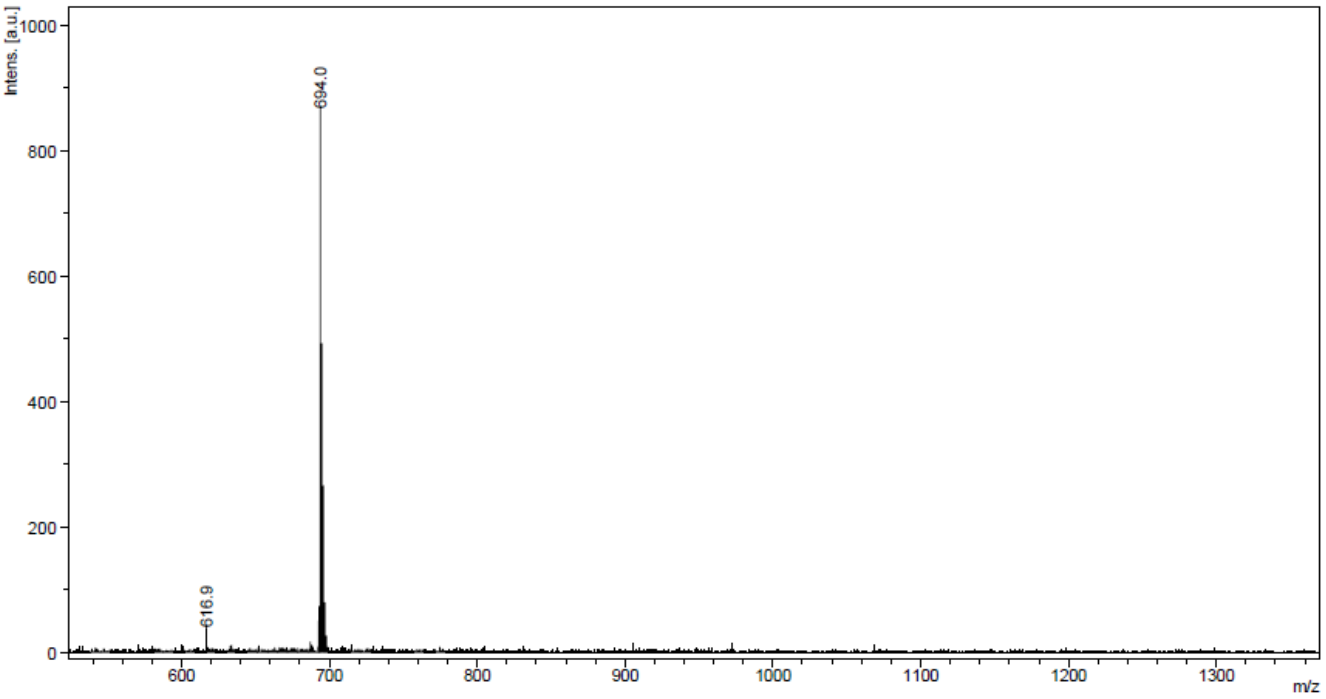
^{1}H NMR of **2a** ($CDCl_3$, 300 MHz)



MALDI-TOF-MS of **2a**



^{1}H NMR of **2b** ($CDCl_3$, 300 MHz)



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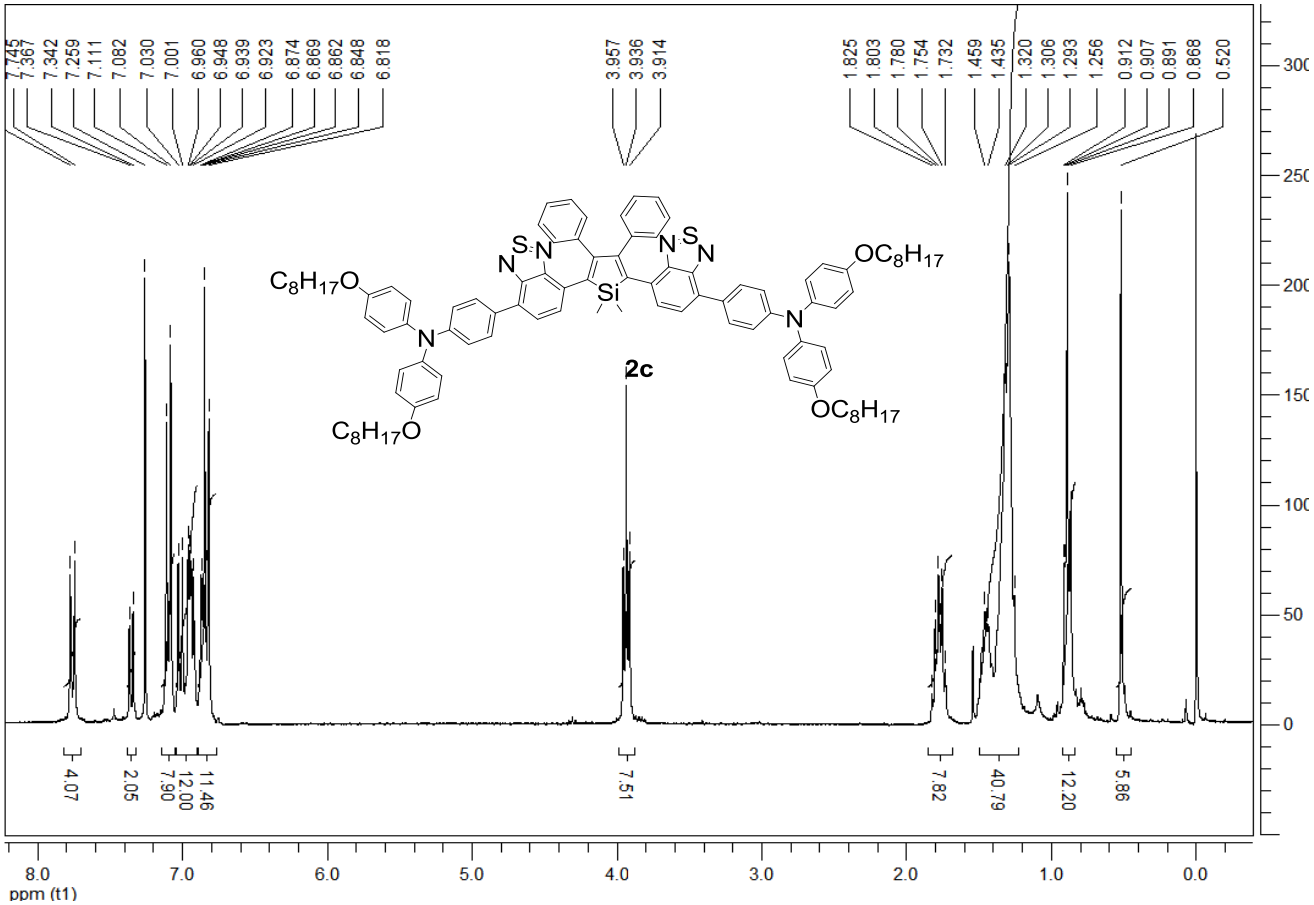
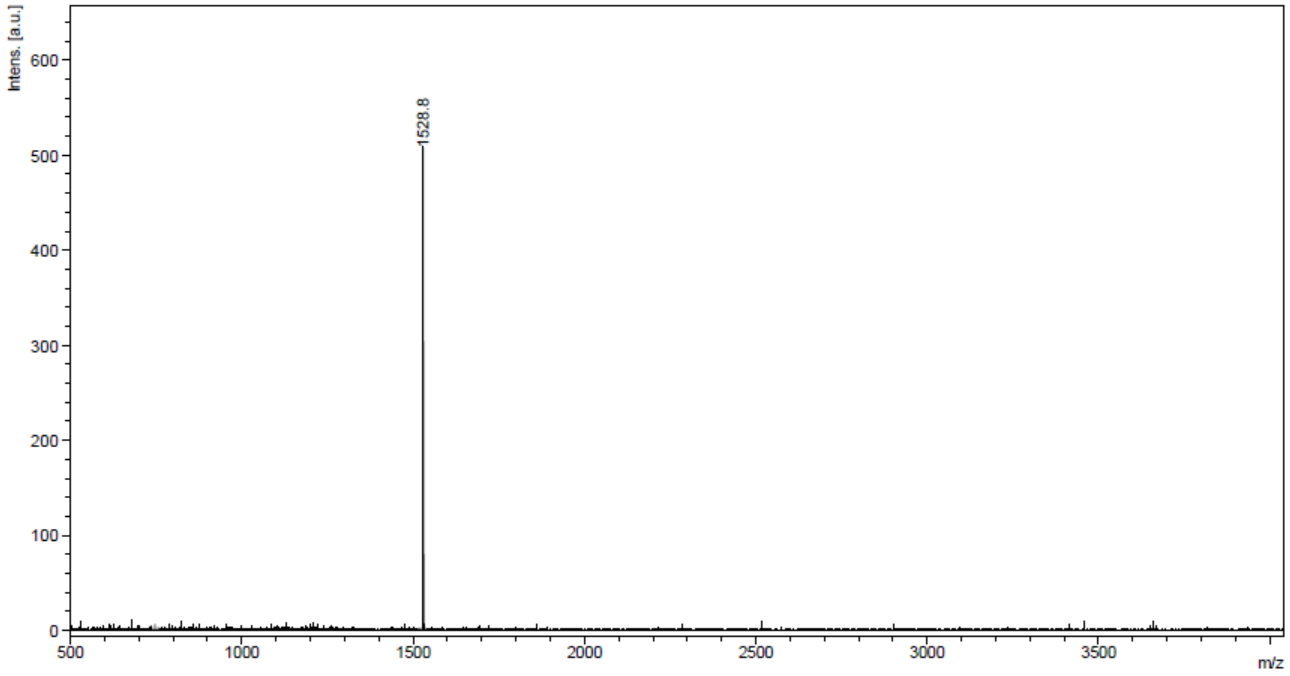
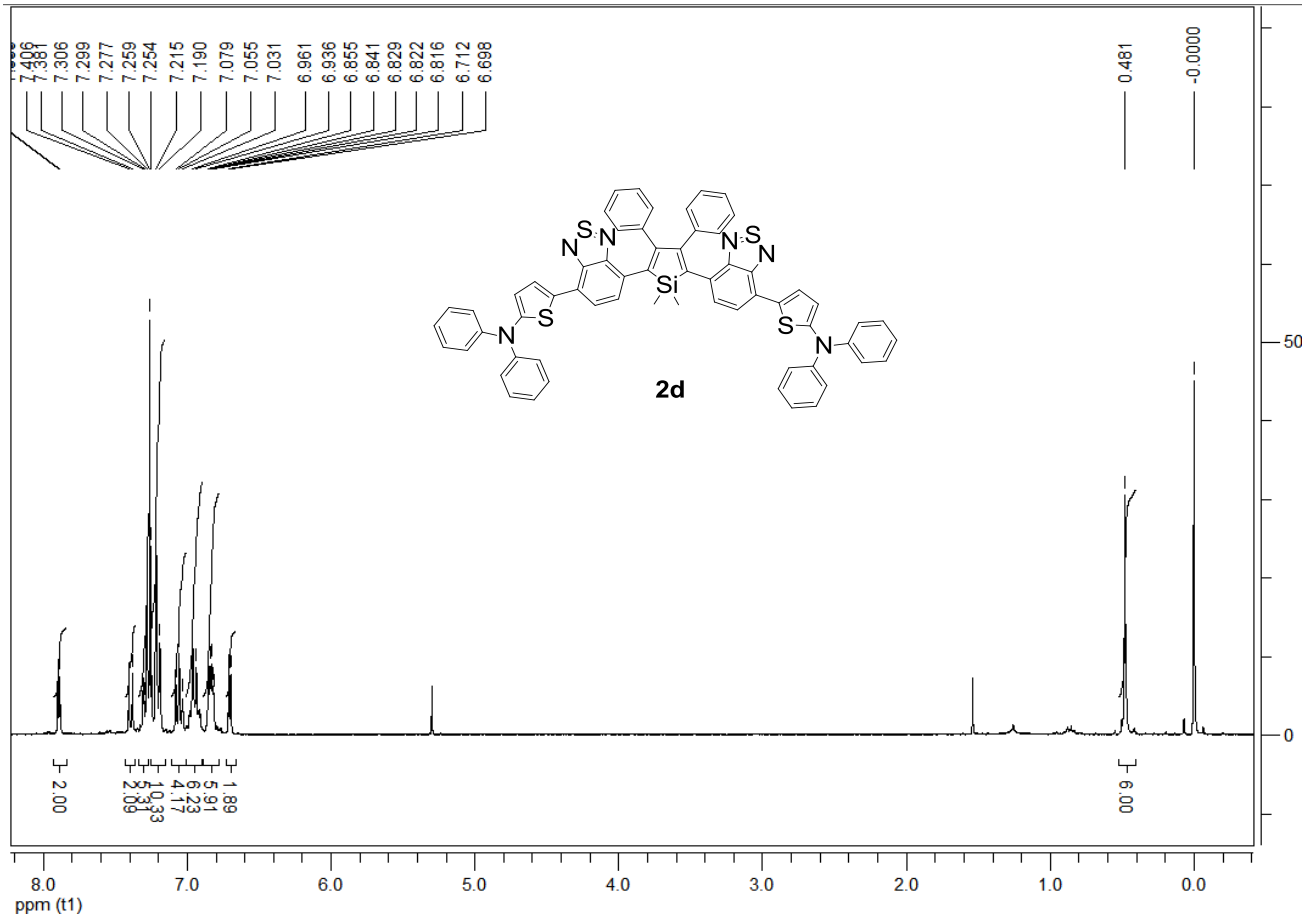


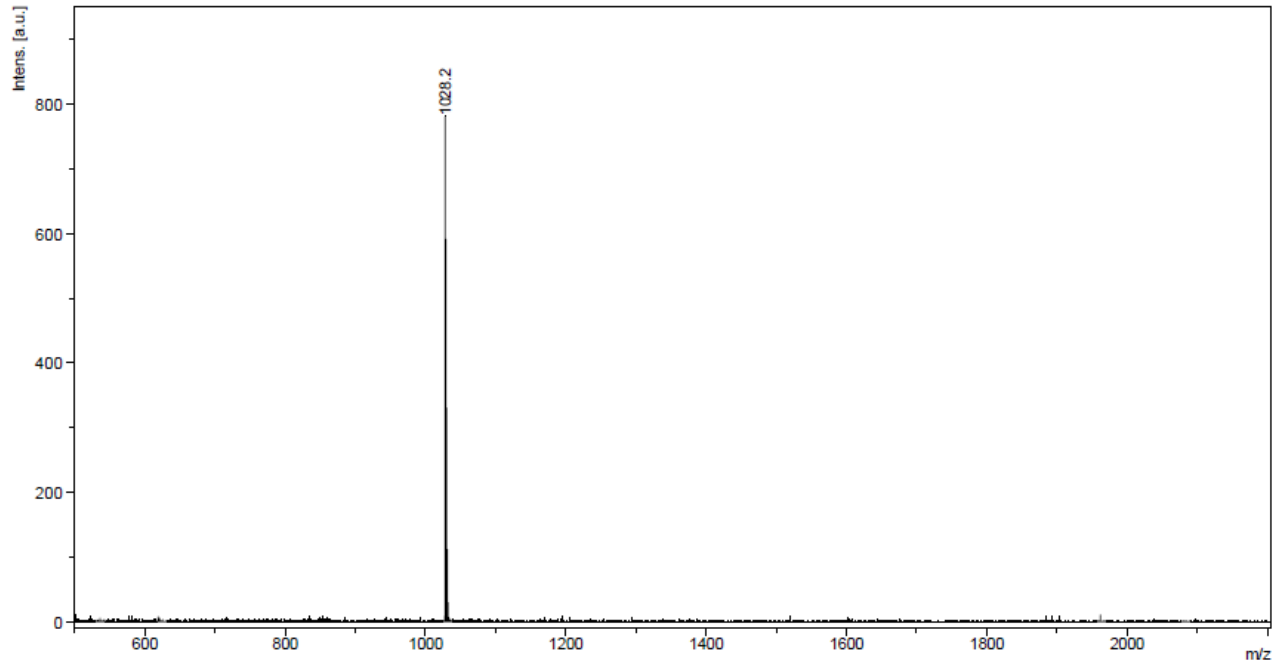
^{1}H NMR of **2c** ($CDCl_3$, 300 MHz)



MALDI-TOF-MS of **2c**



^{1}H NMR of **2d** ($CDCl_3$, 300 MHz)



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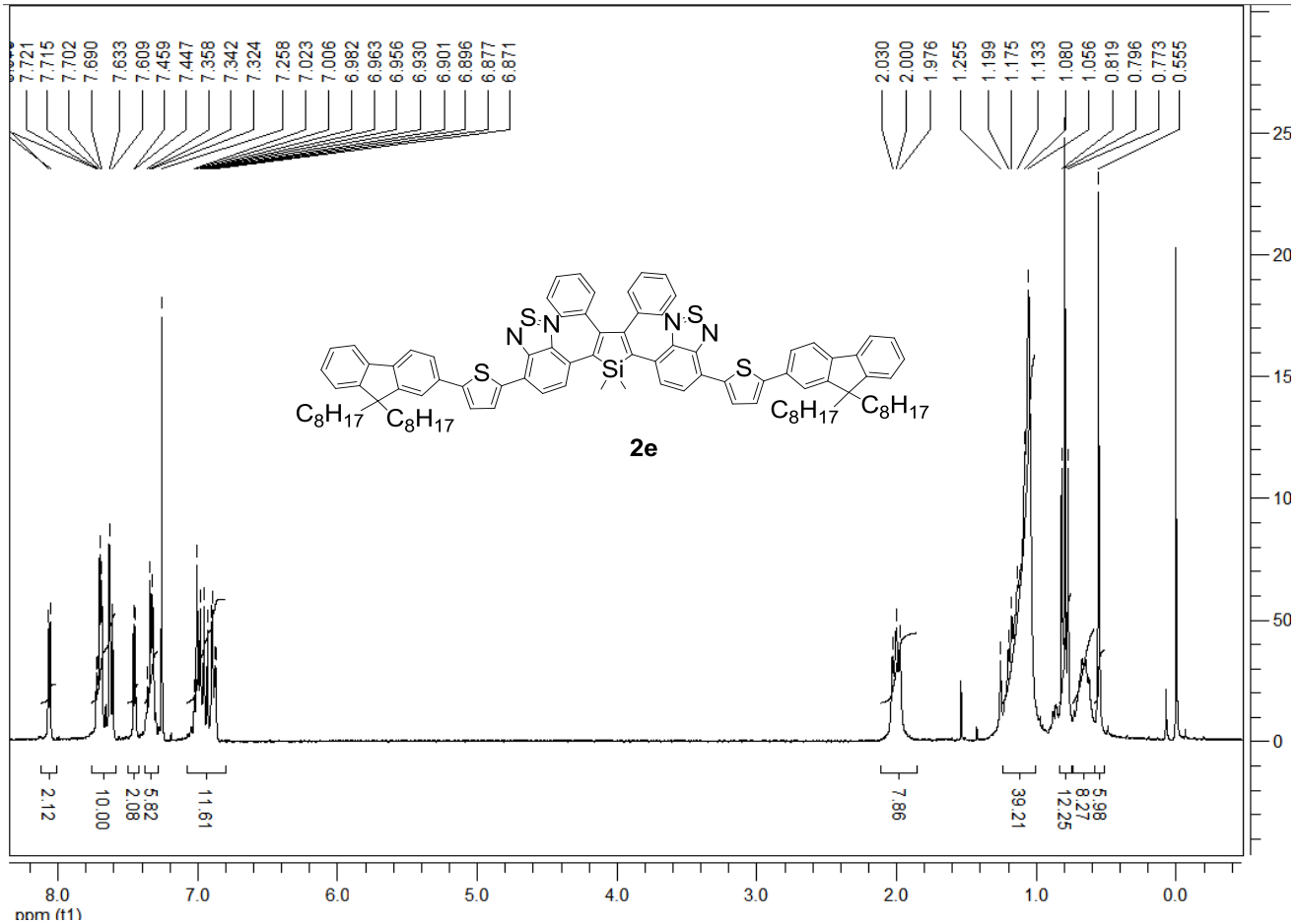
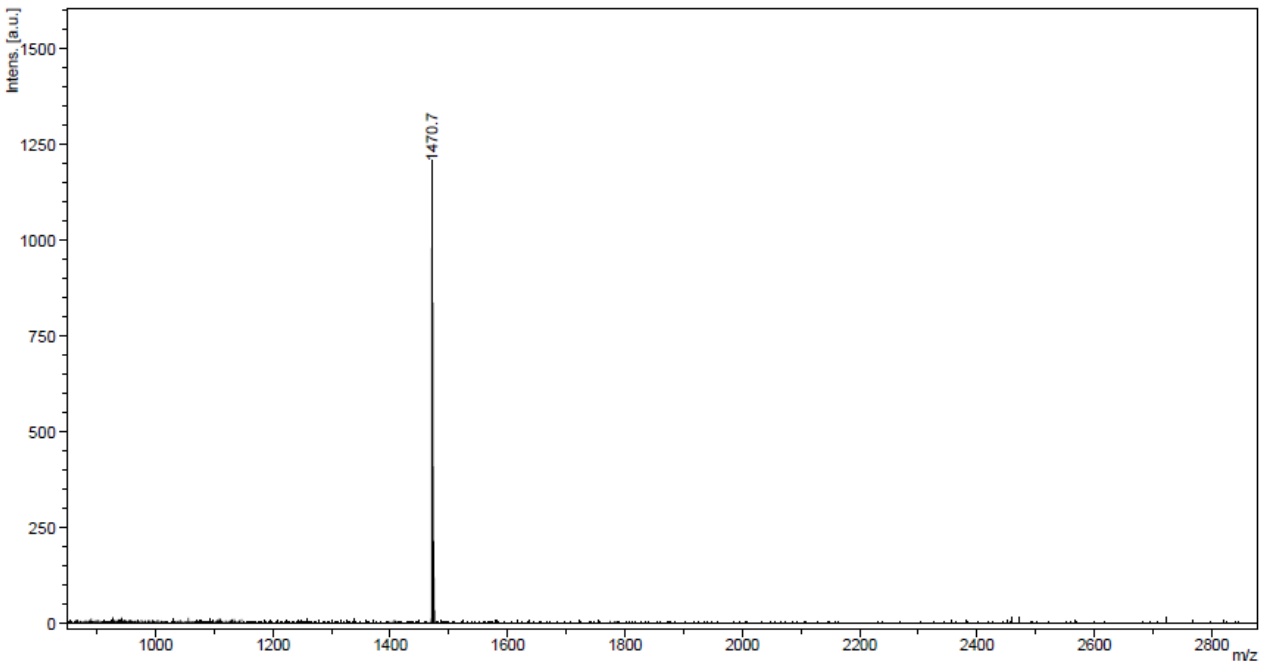


2e

^{1}H NMR of **2e** ($CDCl_3$, 300 MHz)



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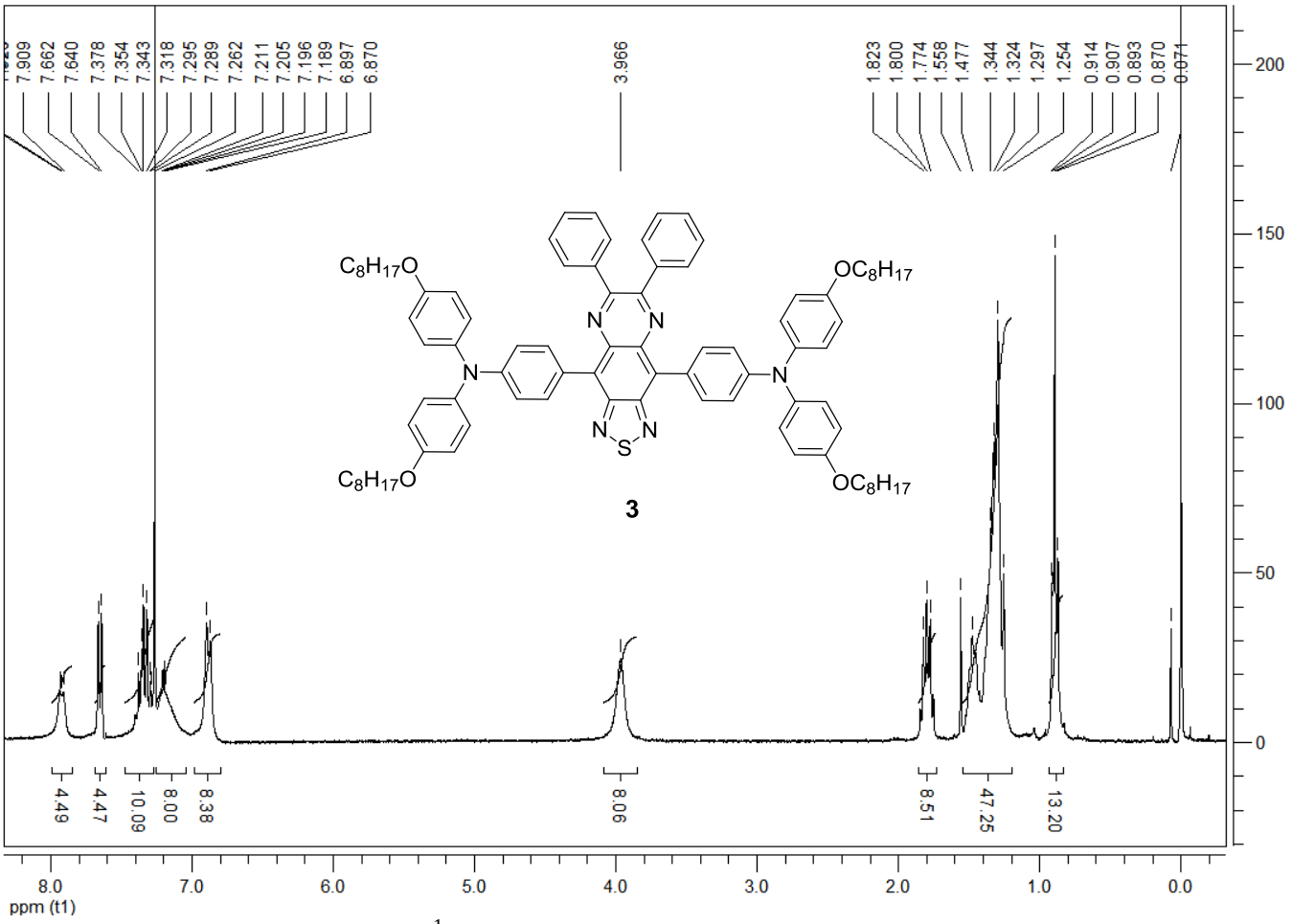
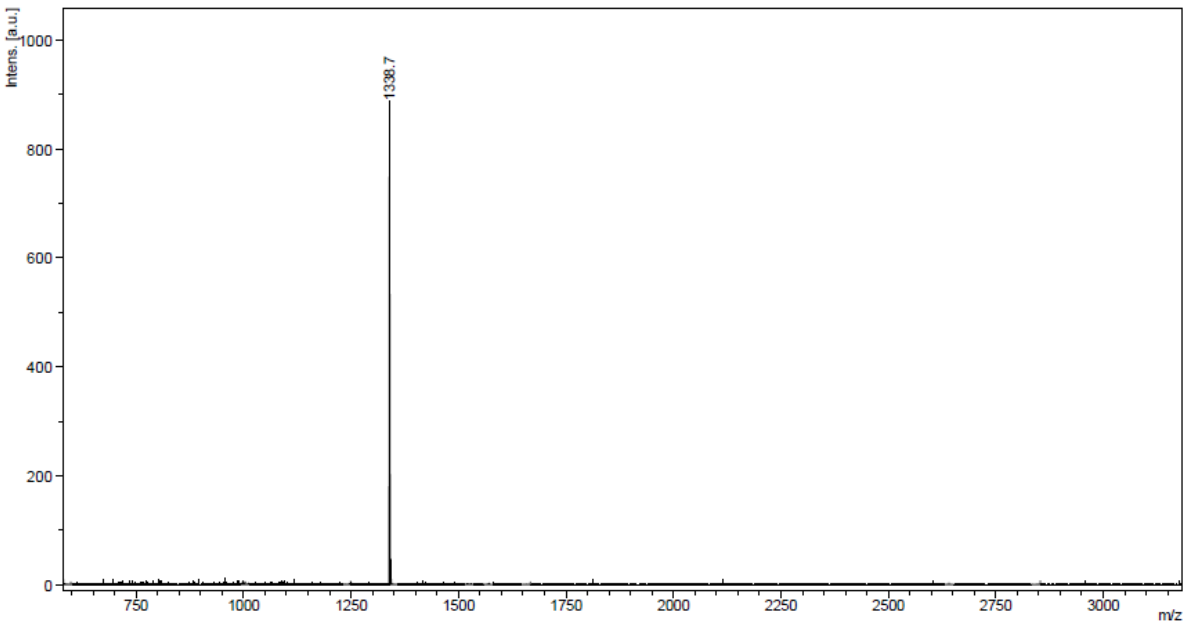


^{1}H NMR of **3** ($CDCl_3$, 300 MHz)



MALDI-TOF-MS of **3**