

Supporting Information

for

Multi-state photochromism of bis-tetraarylethene luminogens modulated through oligosilane linkages

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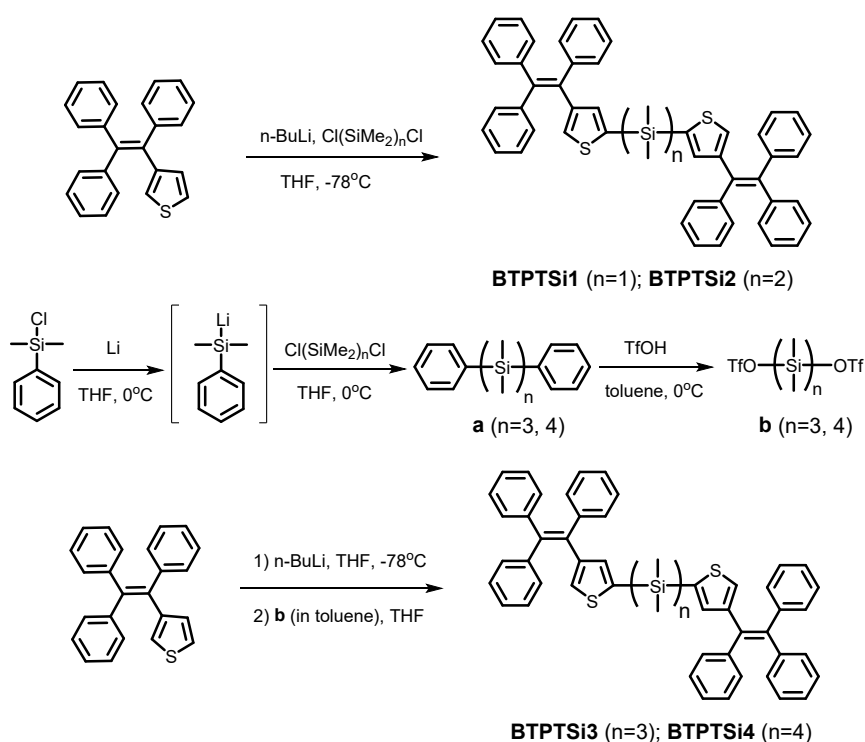
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1. Experimental Section

General, Measurement, and Materials.

Reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise indicated. All air and moisture-sensitive reactions were carried out under an argon atmosphere in glassware that was dried in an oven at 120 °C and cooled under a stream of inert gas before use. Tetrahydrofuran was refluxed with sodium and distilled out immediately before use. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX400 spectrometer and referenced to the residual proton signals of deuterated solvents (CDCl₃: 7.26 ppm; CD₂Cl₂: 5.32 ppm). HR-MS data were recorded on a Bruker Daltonics microTOF-Q II spectrometer. All solvents used for the spectroscopic measurements were of UV spectroscopic grade (Aldrich).

Synthetic and Characterization.

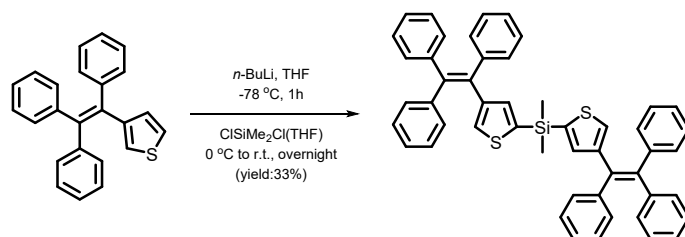


Scheme S1 The synthetic routes to **BTPTS₁**, **BTPTS₂**, **BTPTS₃** and **BTPTS₄**.

Synthesis of TPT

(1,2,2-triphenylvinyl)thiophene. A previously reported procedure was used to synthesize this compound as white solid in 68% yield. ¹H NMR (400 MHz, Chloroform-d) δ 7.19 (q, J = 2.8, 2.1 Hz, 3H), 7.16 – 7.04 (m, 10H), 7.00 (dt, J = 4.1, 2.8 Hz, 3H), 6.74 (s, 1H), 6.57 (s, 1H).

Synthesis of BTPTS₁.



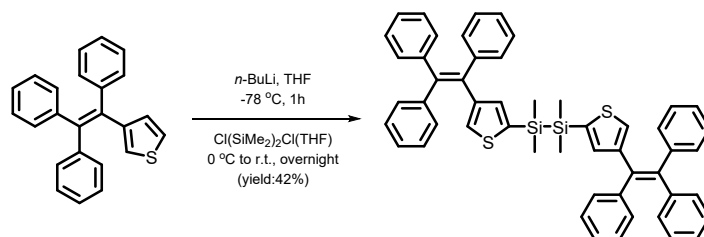
To a solution of 3-(1,2,2-triphenylvinyl)thiophene (1.69 g, 5.0 mmol) in THF (80 mL) was added *n*-butyllithium (7.5 mmol, 4.7 mL, 1.6 M solution in hexane) dropwise over 20 min at $-78\text{ }^{\circ}\text{C}$. Upon completion of addition, the reaction was stirred for 3 h. To the suspension in THF was added dichlorodimethylsilane (Cl-Si-Cl) (1.1 mL, 2.5 mmol, dilute to 1.25 mmol/L with THF) dropwise over 30 min at $-78\text{ }^{\circ}\text{C}$. Upon completion of addition, the reaction mixture was allowed to warm to room temperature and stirred for 6 h. The reaction mixture was evaporated, extracted by dichloromethane, and dried over Na_2SO_4 . The residue was subjected to silica gel column chromatography to obtain 0.63 g (33 % yield) of **BTPTS1** as white solids.

^1H NMR (400 MHz, CDCl_3) δ 7.13 (dd, $J = 12.9, 3.8$ Hz, 16H), 7.08 (d, $J = 6.9$ Hz, 10H), 7.03 – 6.98 (m, 4H), 6.97 (s, 2H), 6.59 (s, 2H), 0.25 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 145.49 (s), 143.83 (s), 143.28 (s), 143.22 (s), 140.24 (s), 138.32 (s), 135.18 (s), 135.14 (s), 131.90 (d, $J = 5.7$ Hz), 131.04 (s), 130.76 (s), 130.67 (d, $J = 3.7$ Hz), 127.75 (s), 127.45 (s), 127.41 (s), 126.57 (s), 126.39 (s), 126.11 (s), -0.88 (s).

HRMS-ESI: m/z : calcd. $[\text{C}_{50}\text{H}_{40}\text{S}_2\text{Si} + \text{Na}]^+$ 755.2239, found 755.2215.

Synthesis of BTPTS2.



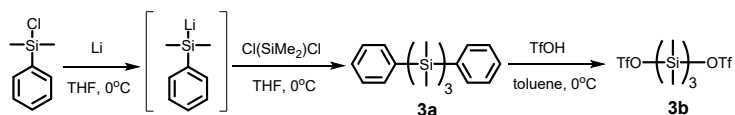
To a solution of 3-(1,2,2-triphenylvinyl)thiophene (0.67 g, 2 mmol) in THF (30 mL) was added *n*-butyllithium (2.2 mmol, 1.4 mL, 1.6 M solution in hexane) dropwise over 20 min at $-78\text{ }^{\circ}\text{C}$. Upon completion of addition, the reaction was stirred for 3 h. To a suspension in THF was added 1,2-dichloro-1,1,2,2-tetramethyldisilane (Cl-Si₂-Cl) (0.3 mL, 1 mmol, dilute to 0.3 mmol/L with THF) dropwise over 30 min at $-78\text{ }^{\circ}\text{C}$. Upon completion of addition, the reaction mixture was allowed to warm to room temperature and stirred for 6 h. The reaction mixture was evaporated by rotation, extracted by dichloromethane, and dried over Na_2SO_4 . The residue was subjected to silica gel column chromatography to obtain 0.33 g (42 % yield) of **BTPTS2** as white solids.

^1H NMR (400 MHz, CDCl_3) δ 7.11 (t, $J = 9.6$ Hz, 26H), 7.01-6.95 (m, 4H), 6.95 (s, 2H), 6.56 (s, 2H), 0.11 (s, 12H).

^{13}C NMR (101 MHz, CDCl_3) δ 145.88 (s), 144.25 (s), 143.67 (s), 140.49 (s), 137.66 (s), 136.20 (s), 135.58 (s), 131.78 (s), 131.35 (d, $J = 5.7$ Hz), 130.99 (s), 128.09 (s), 127.72 (d, $J = 3.7$ Hz), 126.85 (s), 126.64 (s), 126.39 (s), -2.88 (s).

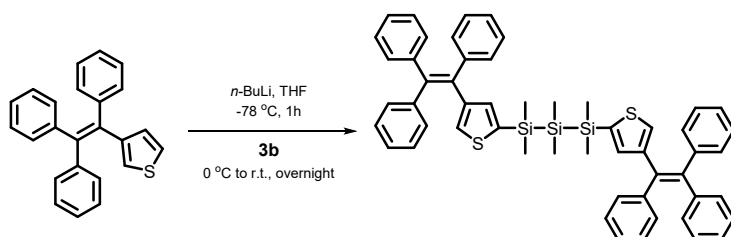
HRMS-ESI: m/z : calcd. $[\text{C}_{52}\text{H}_{46}\text{S}_2\text{Si}_2 + \text{Na}]^+$ 813.2477, found 813.2483.

Synthesis of 3b.



To a suspension of hexane-washed lithium shot (5.0 g, 714 mmol) in THF (100 mL) at 0 °C was added chlorodimethylphenylsilane (15 mL, 89 mmol) over 5 min and the mixture was stirred overnight at 0 °C. Dichlorodimethylsilane (4.3 mL, 44.5 mmol) was dissolved in THF (150 mL) in a flask fitted with a dropping funnel and cooled to 0 °C. The deep red phenyldimethylsilyllithium solution was syringed off from the excess lithium and transferred to the dropping funnel. The silyllithium solution was added dropwise to the dichlorodimethylsilane solution over 4 h at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. THF was removed in vacuum and diethyl ether (100 mL) was added. The precipitated lithium chloride was filtered off and the diethyl ether solution was concentrated in vacuum. Purification of the residue by column chromatography gave **3a** as a colorless oil (9.5 g, 64%). To a solution of **3a** (328 mg, 1 mmol) in toluene (5 mL) at 0 °C was added triflic acid (228 μL, 2.4 mmol). The solution was stirred for 20 min before being cooled to -78 °C. The resultant solution was used directly into the next step.

Synthesis of BTPTS₃.



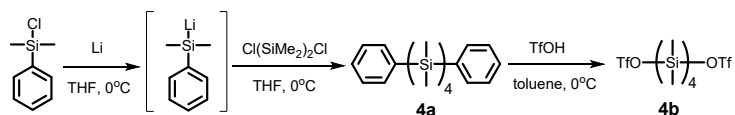
To a solution of 3-(1,2,2-triphenylvinyl)thiophene (0.67 g, 2 mmol) in THF (30 mL) at -78 °C under argon, was added n-BuLi (1.4 mL, 2.2 mmol, 1.6 M solution in n-hexane). The solution was stirred at the same temperature for an hour and then the temperature was raised to -60 °C and stirring continued for another 30 min. The abovementioned silyl triflate **3b** solution was added dropwise into the TPE-lithium reagent solution. After stirring at -78°C overnight, the reaction mixture was allowed to warm to room temperature and stirred for 6 h. Saturated NH₄Cl solution (10 mL) was added and the mixture was extracted by dichloromethane and the combined organic layers were dried over Na₂SO₄ and concentrated in vacuum. The residue was subjected to silica gel column chromatography to obtain 0.34 g (40 % yield) of **BTPTS₃** as white solids.

¹H NMR (400 MHz, CDCl₃) δ 7.16 (d, *J* = 5.8 Hz, 6H), 7.12 – 7.04 (m, 20H), 7.01 – 6.96 (m, 4H), 6.94 (s, 2H), 6.56 (s, 2H), 0.14 (s, 12H), -0.09 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 145.63 (s), 144.11 (s), 143.51 (d, *J* = 2.6 Hz), 140.28 (s), 137.15 (d, *J* = 6.9 Hz), 135.44 (s), 131.44 (s), 131.18 (d, *J* = 5.3 Hz), 130.81 (s), 127.95 (s), 127.55 (d, *J* = 3.8 Hz), 126.57 (d, *J* = 19.7 Hz), 126.21 (s), -2.08 (s), -6.81 (s).

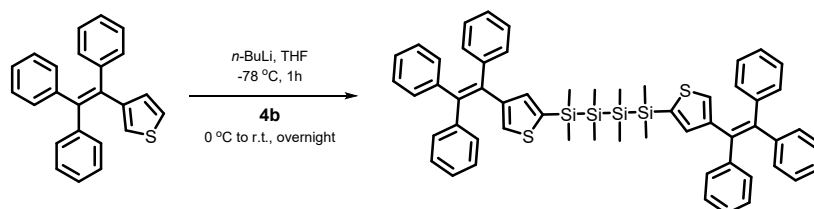
HRMS-ESI: *m/z*: calcd. [C₅₄H₅₂S₂Si₃ + Na]⁺ 871.2716, found 871.2725.

Synthesis of 4b.



To a suspension of hexane-washed lithium shot (5.0 g, 714 mmol) in THF (100 mL) at 0 °C was added chlorodimethylphenylsilane (15 mL, 89 mmol) over 5 min and the mixture was stirred overnight at 0 °C. Dichlorotetramethyldisilane (8.3 mL, 44.5 mmol) was dissolved in THF (150 mL) in a flask fitted with a dropping funnel and cooled to 0 °C. The deep red phenyldimethylsilyllithium solution was syringed off from the excess lithium and transferred to the dropping funnel. The silyllithium solution was added dropwise to the dichlorotetramethyldisilane solution over 4 h at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. THF was removed in vacuum and diethyl ether (100 mL) was added. The precipitated lithium chloride was filtered off and the diethyl ether solution concentrated in vacuum. Purification of the residue by column chromatography gave the product **4a** as a colorless oil (11.2 g, 65%). To a solution of **4a** (386 mg, 1 mmol) in toluene (5 mL) at 0 °C was added triflic acid (228 μ L, 2.4 mmol). The solution was stirred for 20 min before being cooled to -78 °C. The resultant solution was used directly into the next step.

Synthesis of BTPTSi4.



To a solution of 3-(1,2,2-triphenylvinyl)thiophene (0.67 g, 2 mmol) in THF (30 mL) at -78 °C under argon, was added n-BuLi (1.4 mL, 2.2 mmol, 1.6 M solution in n-hexane). The solution was stirred at the same temperature for an hour and then the temperature was raised to -60 °C and stirring continued for another 30 min. The abovementioned silyl triflate **4b** solution was added dropwise into the TPE-lithium reagent solution. After stirring at -78 °C overnight, the reaction mixture was allowed to warm to room temperature and stirred for 6 h. Saturated NH₄Cl solution (10 mL) was added and the mixture was extracted by dichloromethane and the combined organic layers were dried over Na₂SO₄ and concentrated in vacuum. The residue was subjected to silica gel column chromatography to obtain 0.46 g (51 % yield) of **BTPTSi4** as white solids.

¹H NMR (400 MHz, CDCl₃) δ 7.16 (t, J = 5.0 Hz, 6H), 7.12 – 7.05 (m, 20H), 6.99 (dd, J = 7.2, 2.4 Hz, 4H), 6.95 (s, 2H), 6.57 (s, 2H), 0.21 (s, 12H), -0.04 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 145.61 (s), 144.12 (s), 143.51 (d, J = 3.2 Hz), 140.26 (s), 137.23 (d, J = 11.6 Hz), 135.44 (s), 131.41 (s), 131.18 (d, J = 4.4 Hz), 130.80 (s), 127.95 (s), 127.54 (d, J = 3.5 Hz), 126.56 (d, J = 19.7 Hz), 126.20 (s), -1.87 (s), -5.79 (s).

HRMS-ESI: m/z : calcd. [C₅₆H₅₈S₂Si₄ + Na]⁺ 929.2955, found 929.2966.

2. Properties Analysis

Spectroscopic Measurements

UV-visible absorption spectra were recorded on a Shimadzu 1800 spectrophotometer. Fluorescence spectra and the fluorescence lifetimes of the samples were determined with a Horiba Jobin Yvon Fluorolog-3 spectrofluorimeter. The goodness of the fits of the single exponential decays were assessed by using chi-squared (χ^2) and autocorrelation function $C(j)$ values. Low

residuals ($\chi_R^2 < 1.2$) were consistently observed. For samples in solution, absorption and emission measurements were carried out in 1×1 cm quartz cuvettes. The absolute quantum yields (Φ_F) and emission spectra in the solid state were measured on Horiba Jobin Yvon Fluorolog-3 spectrofluorimeter with an integrating sphere. For all measurements, the temperature was kept constant at (298 ± 2) K.

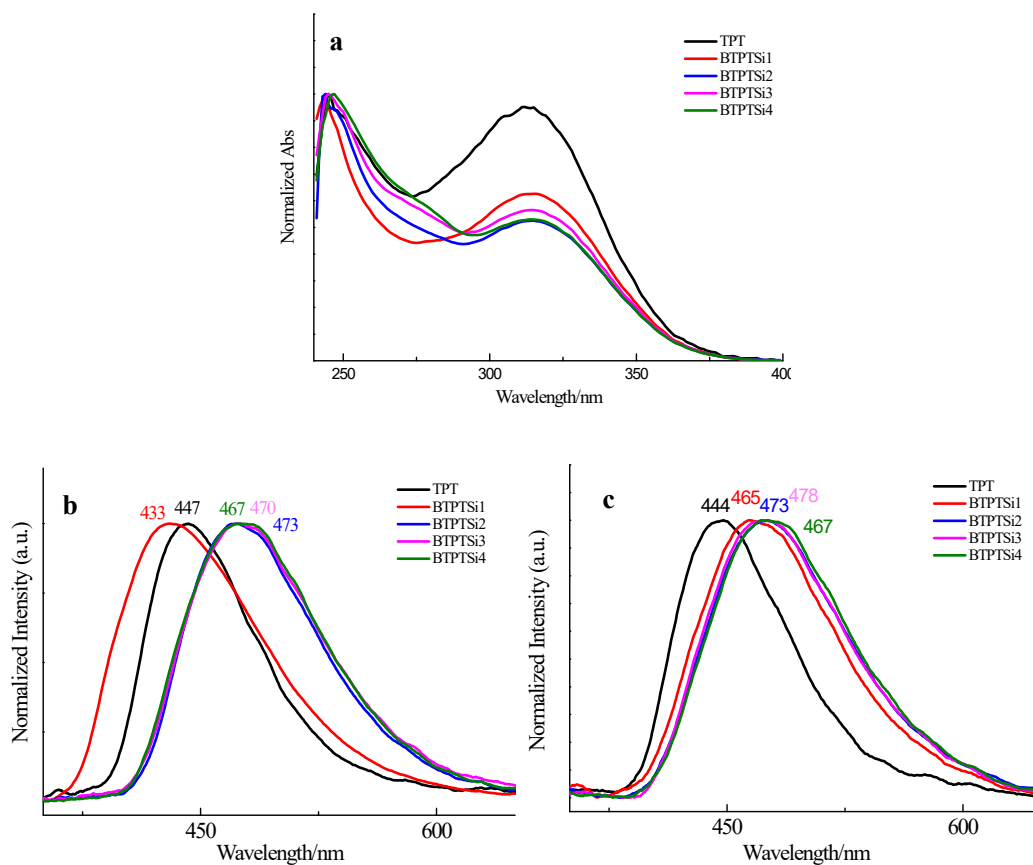


Figure S1. UV absorption spectra in THF (a). Emission spectra of drop-cast films (b) and compounds adsorbed on filter paper (c).

Table S1 Quantum yields of TPT, BTPTS1, BTPTS2, BTPTS3 and BTPTS4 and after UV 1min.

Conditions	TPT	BTPTS1	BTPTS2	BTPTS3	BTPTS4
Powder	6%	28%	61%	7%	1%
Powder-UV-1min	1%	18%	53%	2%	1%
Film	10%	11%	6%	5%	6%
Film-UV-1min	1%	9%	1%	1%	1%
Filter paper	10%	13%	17%	14%	15%
Filter paper -UV-1min	3%	12%	7%	6%	6%

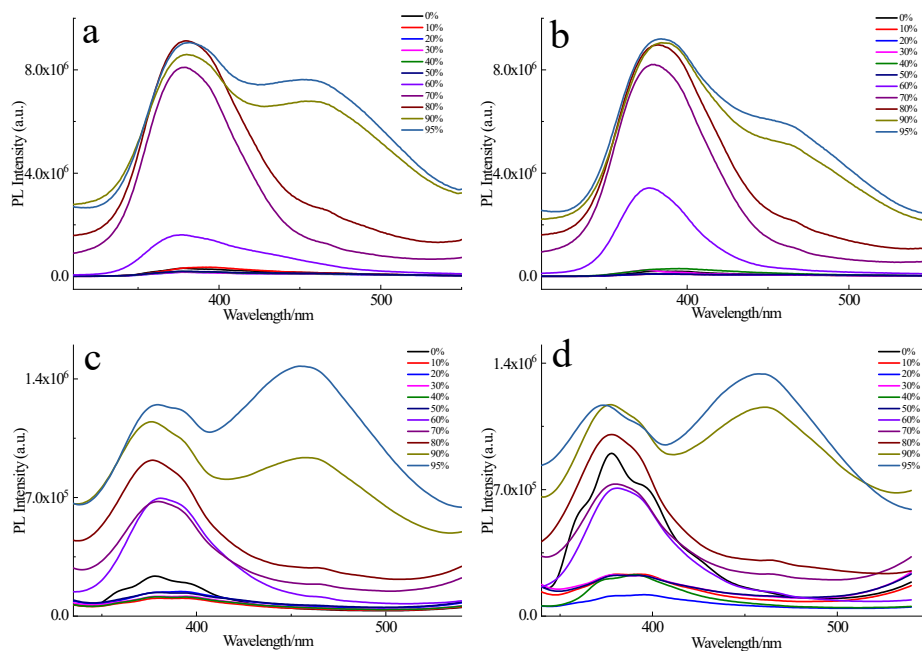


Figure S2 PL spectra of BTPTSi1 (a), BTPTSi2 (b), BTPTSi3 (c) and BTPTSi4 (d) in THF solution (1×10^{-4} M) with varying fractions of water.

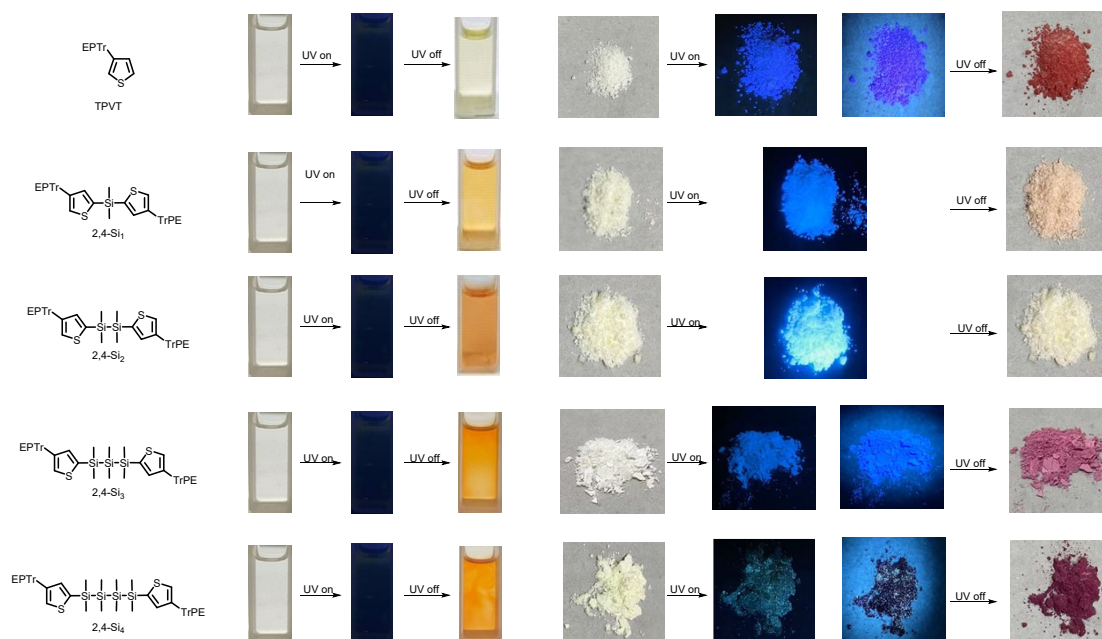


Figure S3 Photographs of distinct color changes of TPT and BTPTSin ($n = 1-4$) in solution and powder forms.

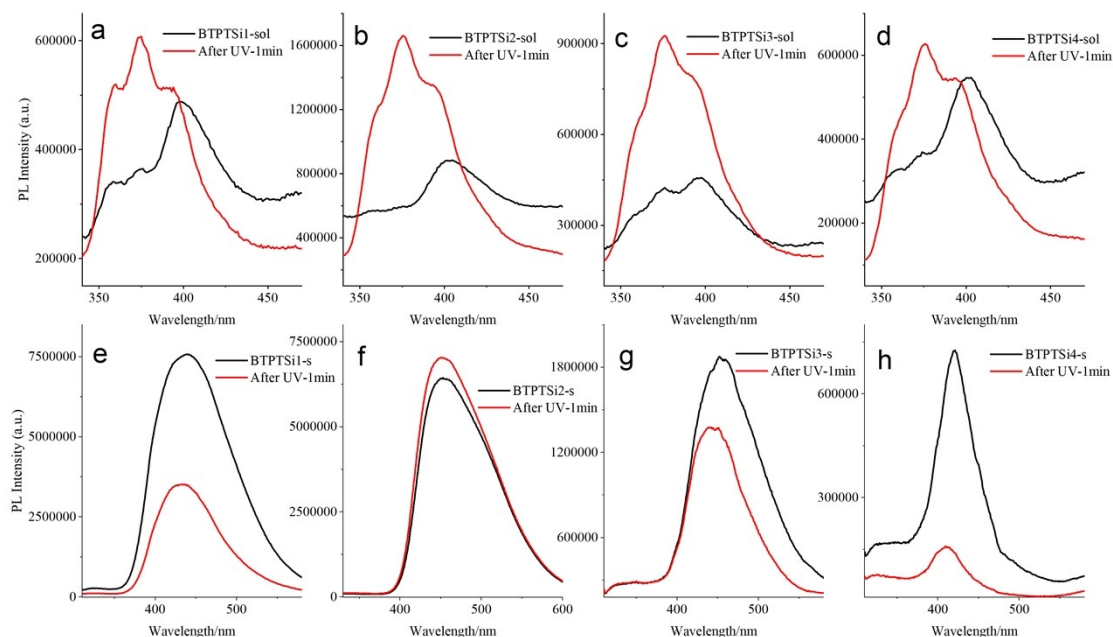


Figure S4 Photoluminescent spectra change before (black line) and after (red line) UV irradiation of (a) **BTPTSi1**, (b) **BTPTSi2**, (c) **BTPTSi3** and (d) **BTPTSi4** in THF (5×10^{-5} M), and photoluminescent spectra change before (black line) and after (red line) UV irradiation of (e) **BTPTSi1**, (f) **BTPTSi2**, (g) **BTPTSi3** and (h) **BTPTSi4** in solid state.

Note: Due to AIE nature of compounds **BTPTSi1-BTPTSi4**, their photoluminescence in THF solution are very weak, the above spectra a-d were recorded by employing large optical grating. As a result, the baselines are not steady and smooth.

Crystallographic Data

Diffraction data were collected on a Bruker Smart Apex II CCD diffractometer or Bruker AXS Apex II diffractometer with graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å). An empirical (multi-scan) or numerical absorption correction was applied with the program SADABS.^[S4] The structures were solved by the direct method and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXTL).^[S5] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions or found in the F_{map} . A summary of the crystallographic data and selected experimental information are given in Table S3 and Table S4. CCDC 2061563-2061564 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].

Table S2 Crystallographic data for **BTPTSi1**.

Empirical formula	$\text{C}_{50}\text{H}_{40}\text{S}_2\text{Si}$
Formula weight	733.03
Temperature / K	296.15
Crystal system	monoclinic
Space group	$C2/c$

a / Å	24.455(4)
b / Å	10.2558(18)
c / Å	17.933(3)
α / °	90
β / °	120.312(3)
γ / °	90
Volume / Å ³	3882.7(12)
Z	4
ρ_{calc} / cm ³	1.254
μ / mm ⁻¹	0.203
Crystal size / mm ³	0.15 × 0.15 × 0.1
Goodness-of-fit on F ²	1.030
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0488, wR ₂ = 0.1124
Final R indexes [all data]	R ₁ = 0.0924, wR ₂ = 0.1321

Table S3 Crystallographic data for **BTPTS₂**.

Empirical formula	C ₅₂ H ₄₆ S ₂ Si ₂
Formula weight	791.19
Temperature / K	296.15
Crystal system	triclinic
Space group	P-1
a / Å	9.971(3)
b / Å	10.036(3)
c / Å	12.357(3)
α / °	107.875(5)
β / °	109.985(5)
γ / °	90.207(5)
Volume / Å ³	1097.8(5)
Z	1
ρ_{calc} / cm ³	1.197
μ / mm ⁻¹	0.210
Crystal size / mm ³	0.2 × 0.15 × 0.15
Goodness-of-fit on F ²	1.054
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0469, wR ₂ = 0.1091
Final R indexes [all data]	R ₁ = 0.0827, wR ₂ = 0.1270

Table S4 Crystallographic data for **BTPTS₃**.

Empirical formula	C ₅₄ H ₅₂ S ₂ Si ₃
Formula weight	849.34

Temperature / K	296.15
Crystal system	triclinic
Space group	P-1
a / Å	10.977(4)
b / Å	13.320(5)
c / Å	18.025(7)
α / °	73.779(8)
β / °	74.749(9)
γ / °	79.285(10)
Volume / Å ³	2423.5(15)
Z	2
ρ_{calc} / cm ³	1.164
μ / mm ⁻¹	0.218
Crystal size / mm ³	0.15 × 0.12 × 0.12
Goodness-of-fit on F ²	0.965
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0594, wR ₂ = 0.1213
Final R indexes [all data]	R ₁ = 0.1701, wR ₂ = 0.1631

Table S5 Crystallographic data for **BTPTS₄**.

Empirical formula	C ₅₆ H ₅₈ S ₂ Si ₄
Formula weight	906.30
Temperature / K	296.15
Crystal system	triclinic
Space group	P-1
a / Å	8.1795(16)
b / Å	11.749(2)
c / Å	13.931(3)
α / °	100.658(5)
β / °	93.743(5)
γ / °	91.205(4)
Volume / Å ³	1312.1(5)
Z	2
ρ_{calc} / cm ³	1.148
μ / mm ⁻¹	0.227
Crystal size / mm ³	0.15 × 0.12 × 0.1
Goodness-of-fit on F ²	0.981
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0586, wR ₂ = 0.1261
Final R indexes [all data]	R ₁ = 0.1459, wR ₂ = 0.1617

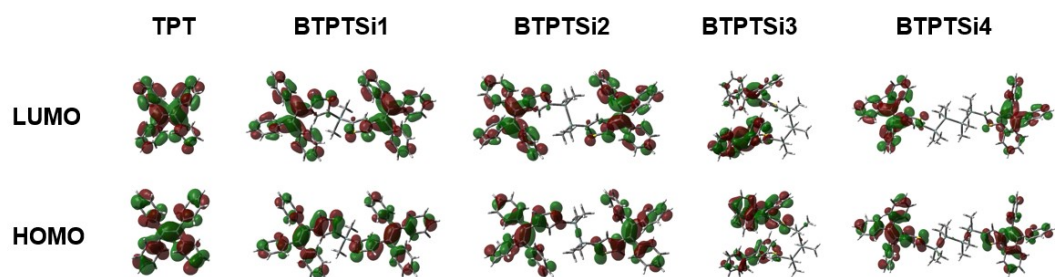


Figure S5 HOMOs and LUMOs of TPT, BTPTSi1, BTPTSi2, BTPTSi3 and BTPTSi4 calculated with B3LYP/6-31G(d) level.

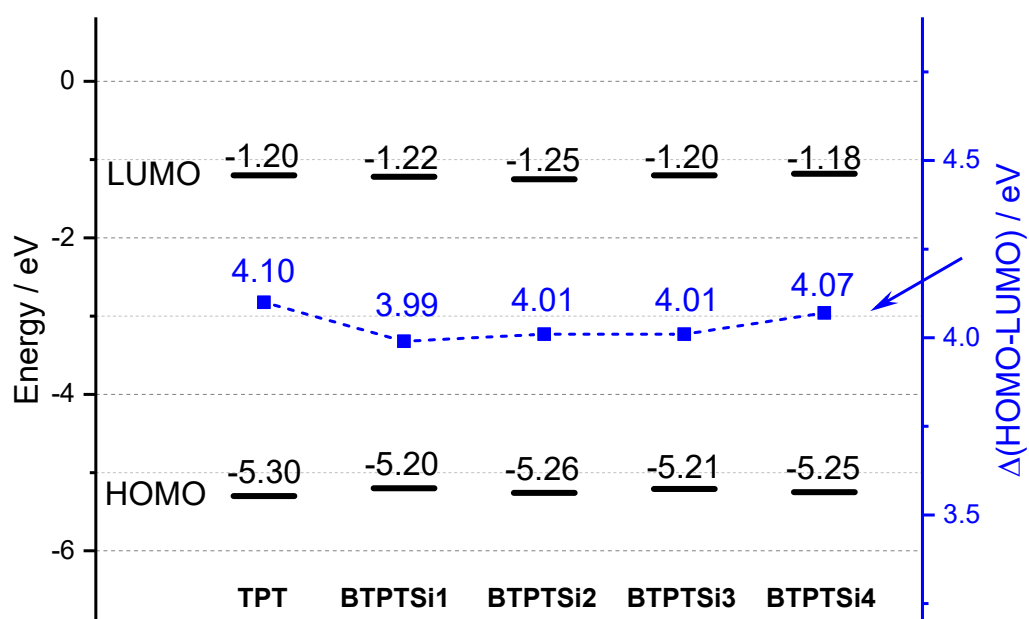


Figure S6 HOMOs and LUMOs energy levels and HOMO-LUMO gaps of TPT, BTPTSi1, BTPTSi2, BTPTSi3 and BTPTSi4 calculated with B3LYP/6-31G(d) level.

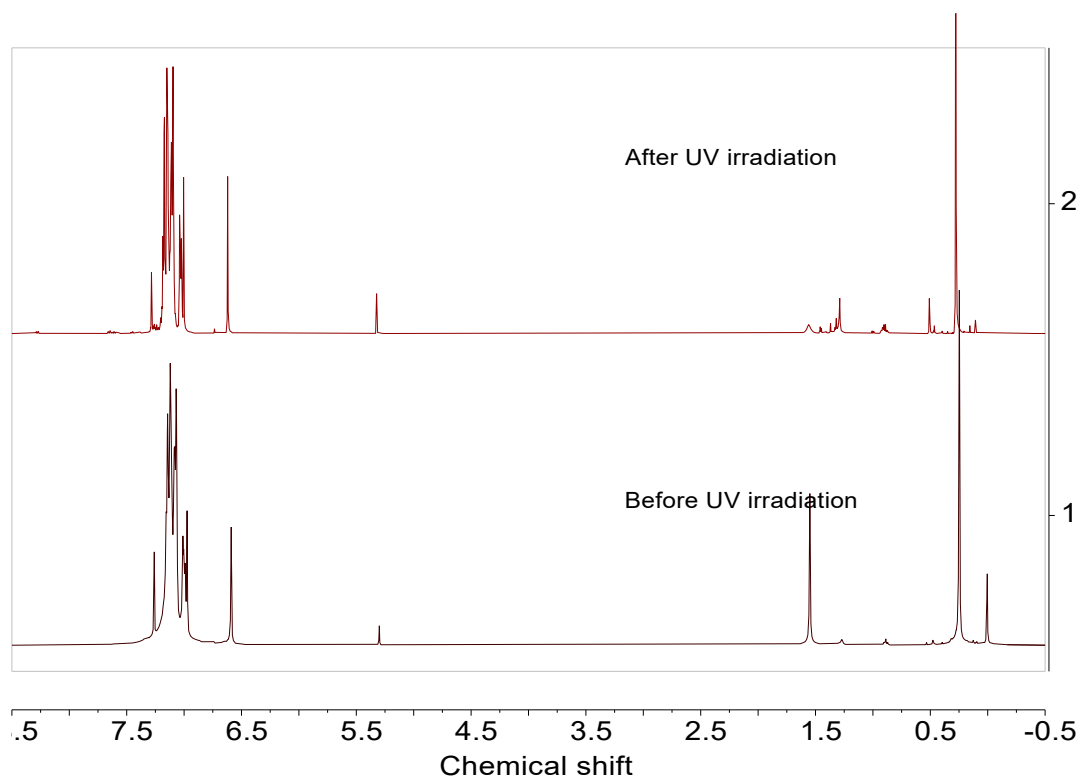


Figure S7 The ^1H NMR spectra (400 MHz, CDCl_3) of **BTPTS11** before and after UV irradiation for 10s.

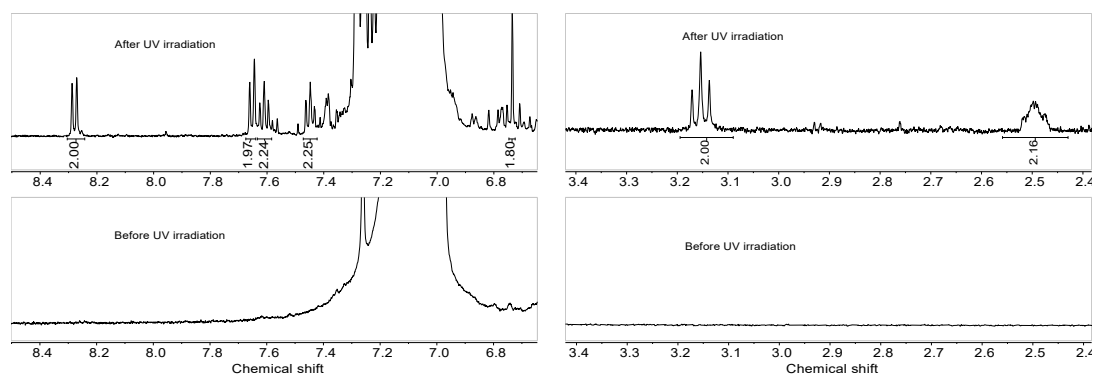


Figure S8 Partially magnified ^1H NMR spectra (400 MHz, CDCl_3) of **BTPTS11** before and after UV irradiation for 10s.

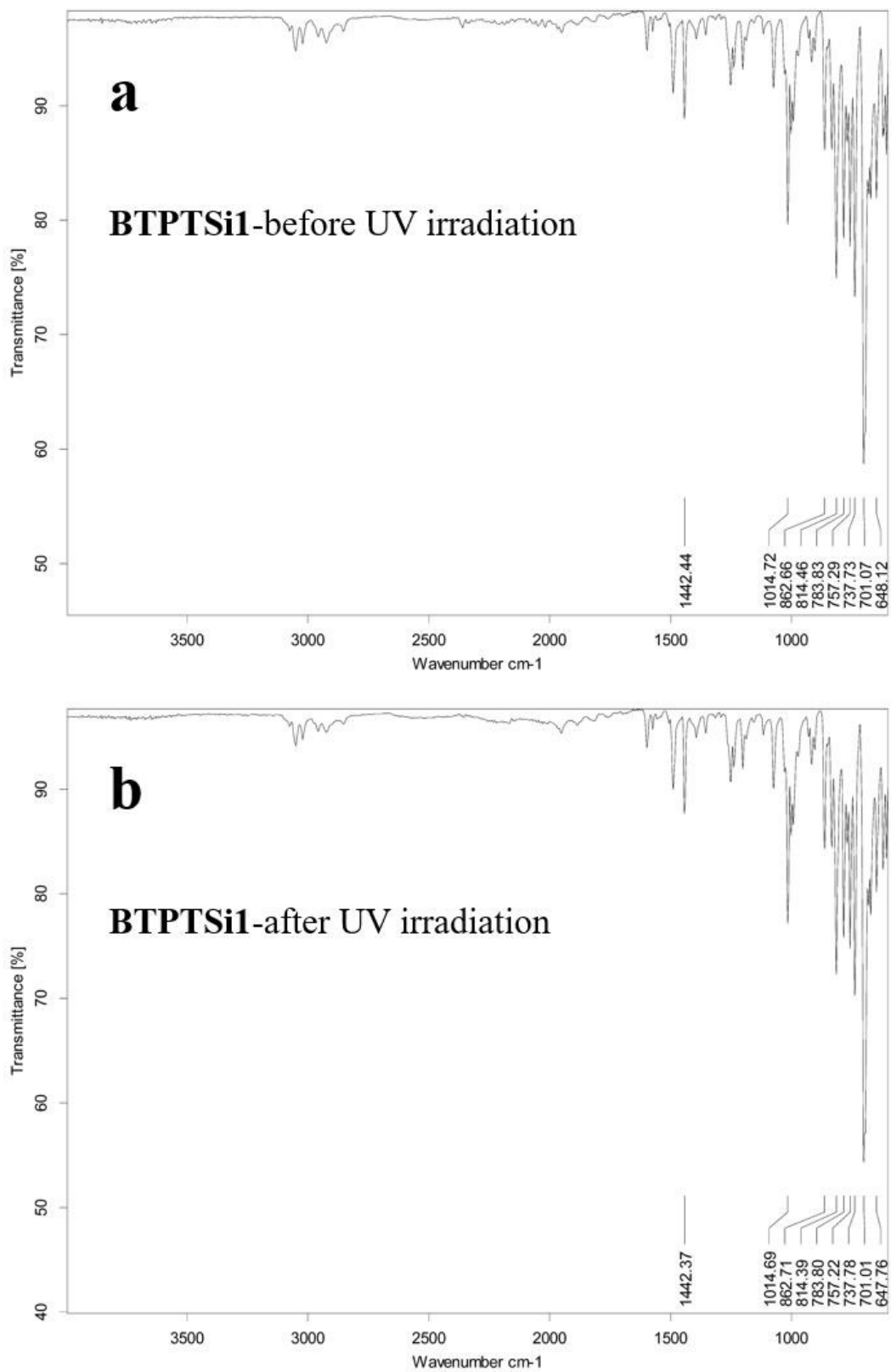


Figure S9 The IR spectra of BTPTSi1 before and after UV irradiation for 1 min.

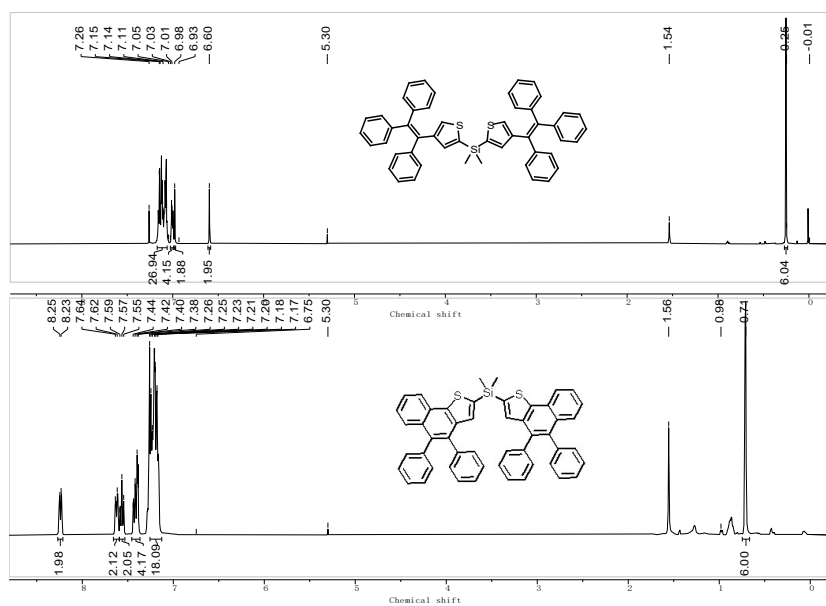


Figure S10 The ^1H NMR spectra (400 MHz, CDCl_3) of BTPTS11 in dark (top) and isolated product of after UV irradiation for 3h under air (bottom).

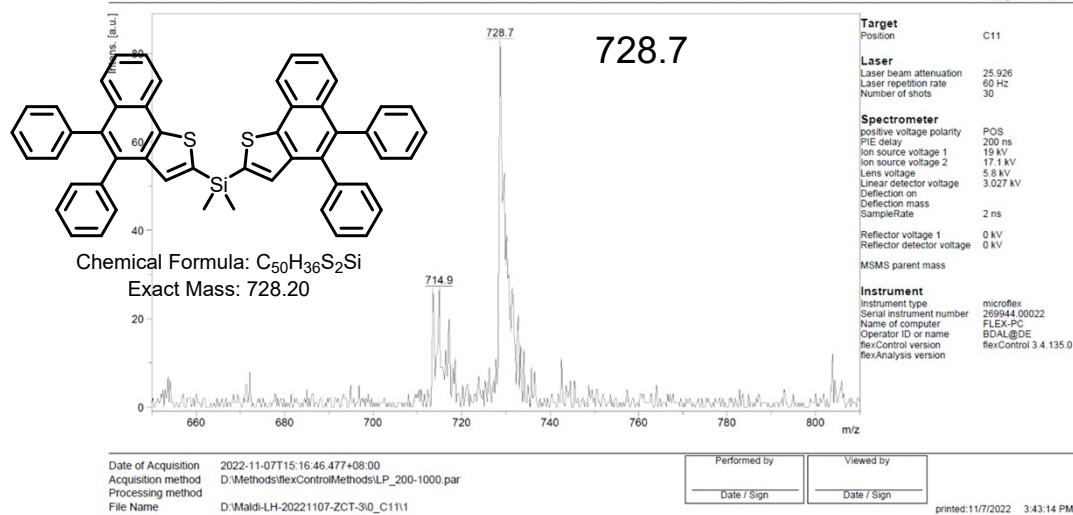
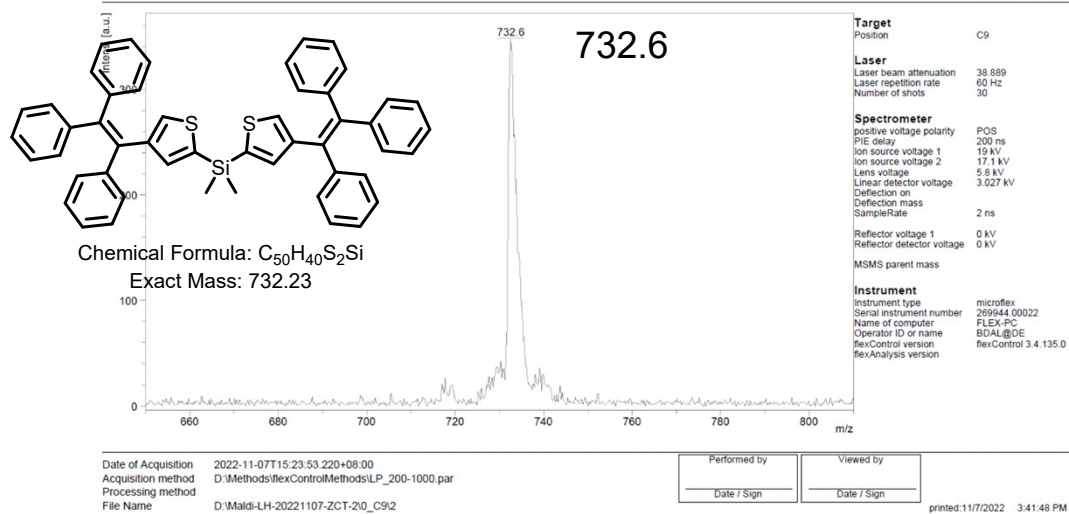
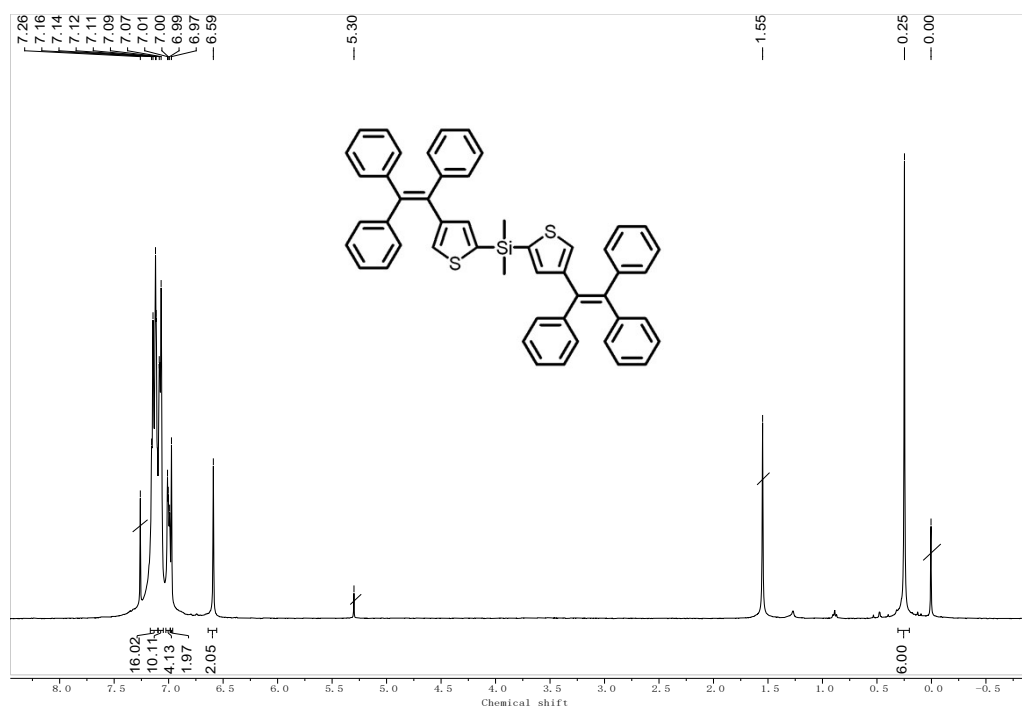
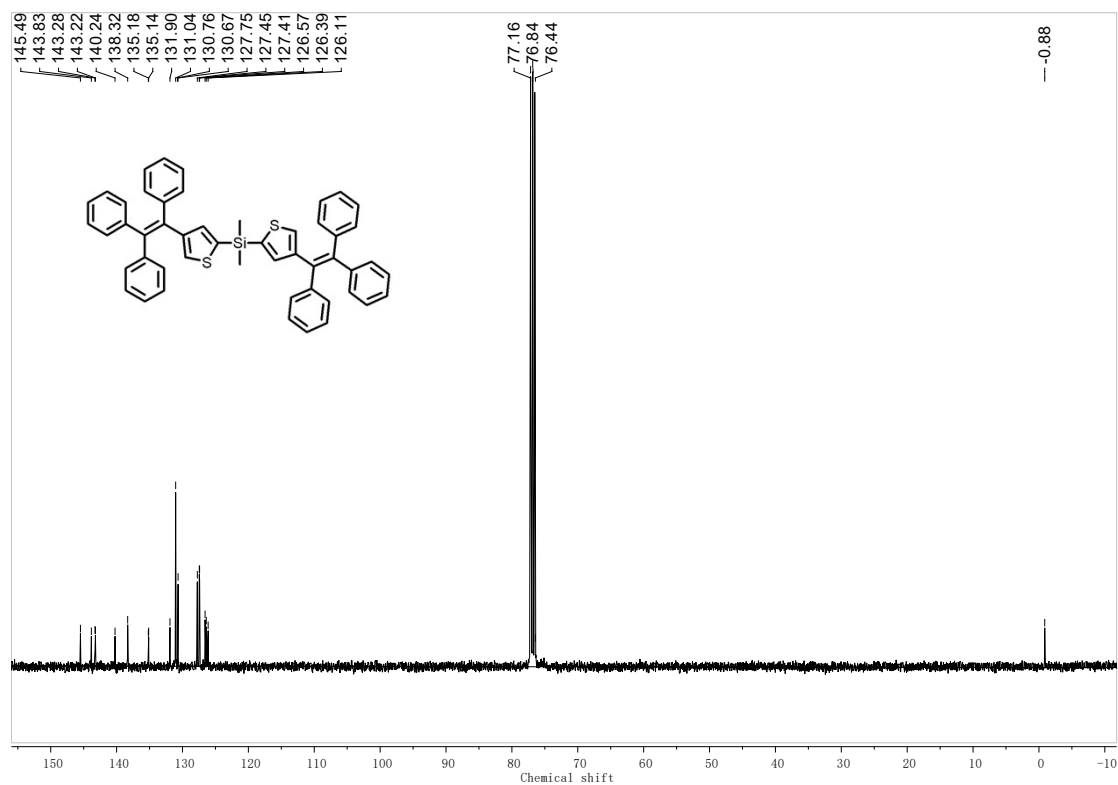


Figure S11 MALDI-TOF-MS spectra of **BTPTSiI** and the isolated photocyclization-dehydrogenation product.

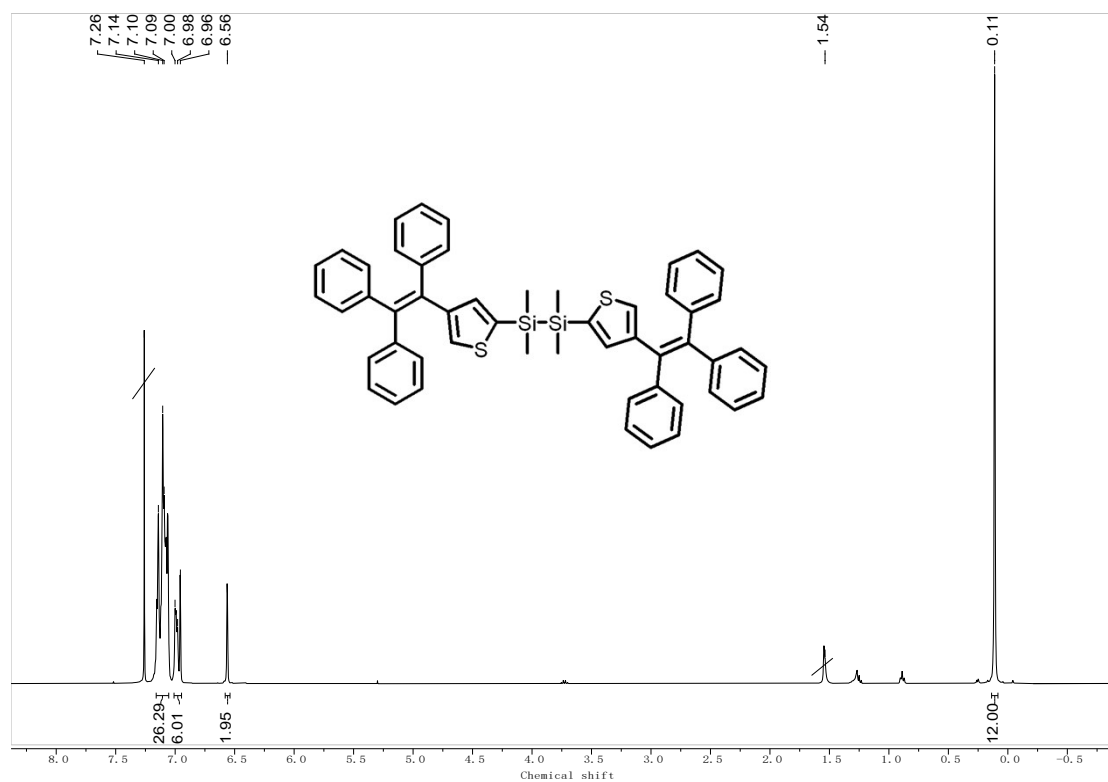
1H NMR and ^{13}C NMR spectra



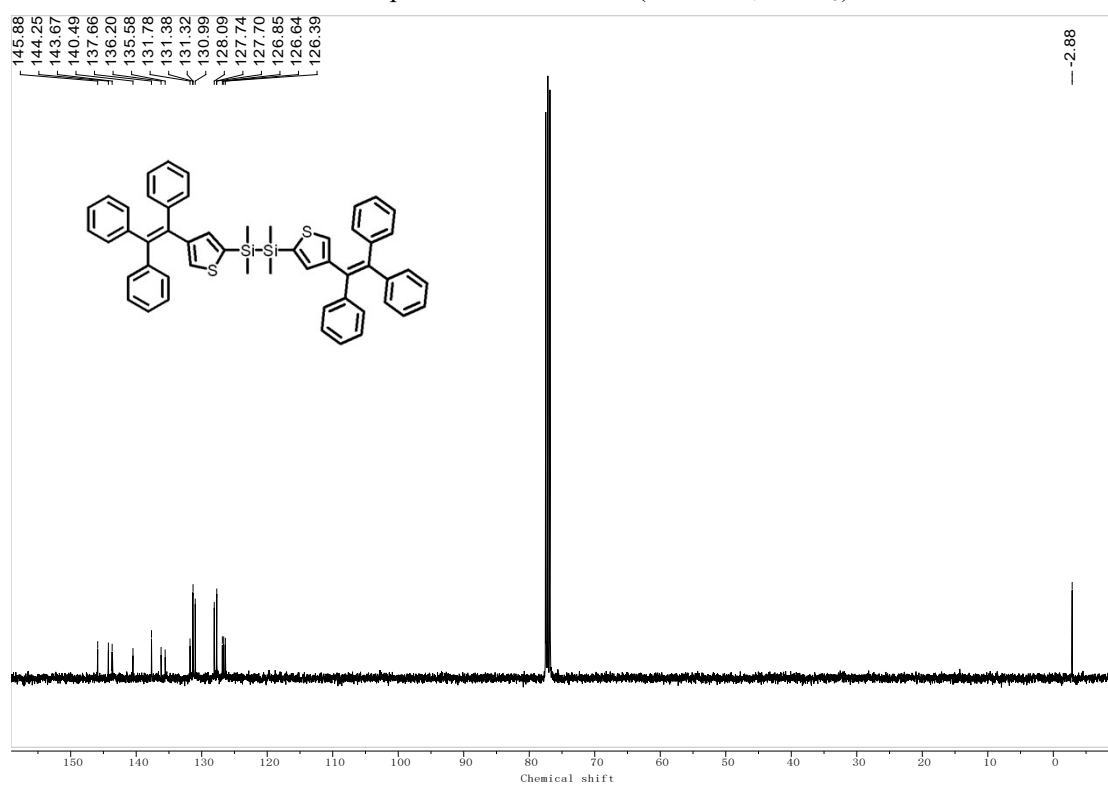
^1H NMR spectrum of **BTPTSil** (400 MHz, CDCl_3).



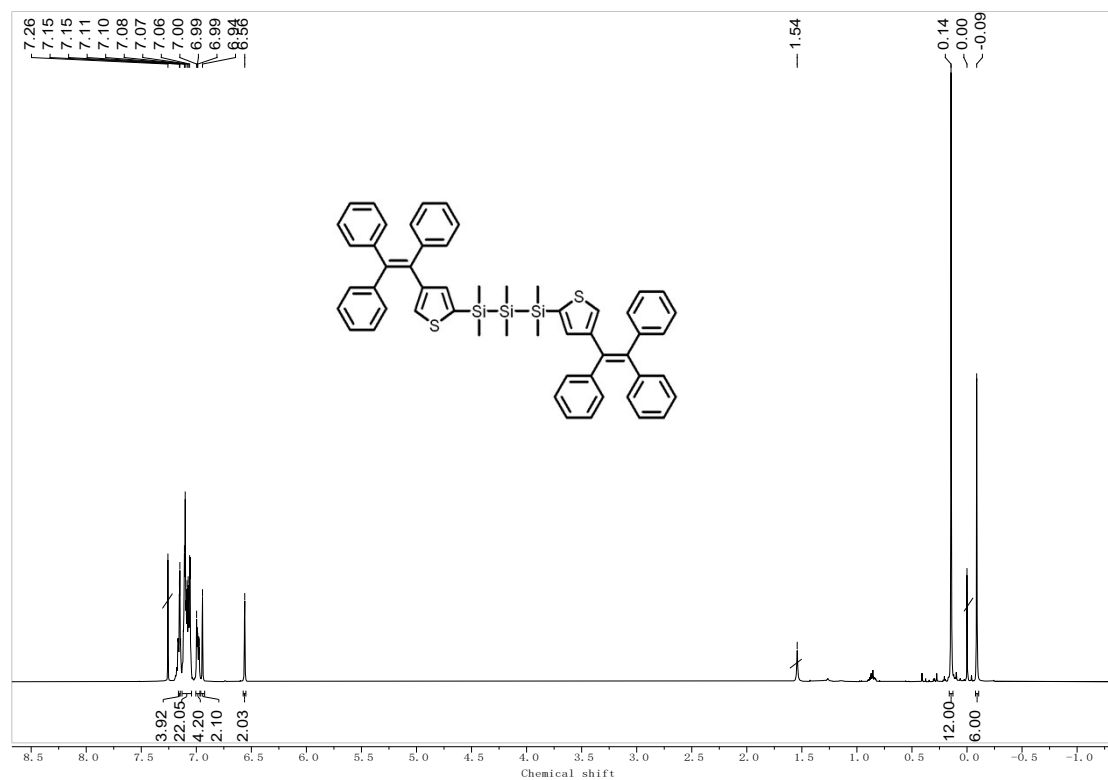
^{13}C NMR spectrum of **BTPTSil** (101 MHz, CDCl_3).



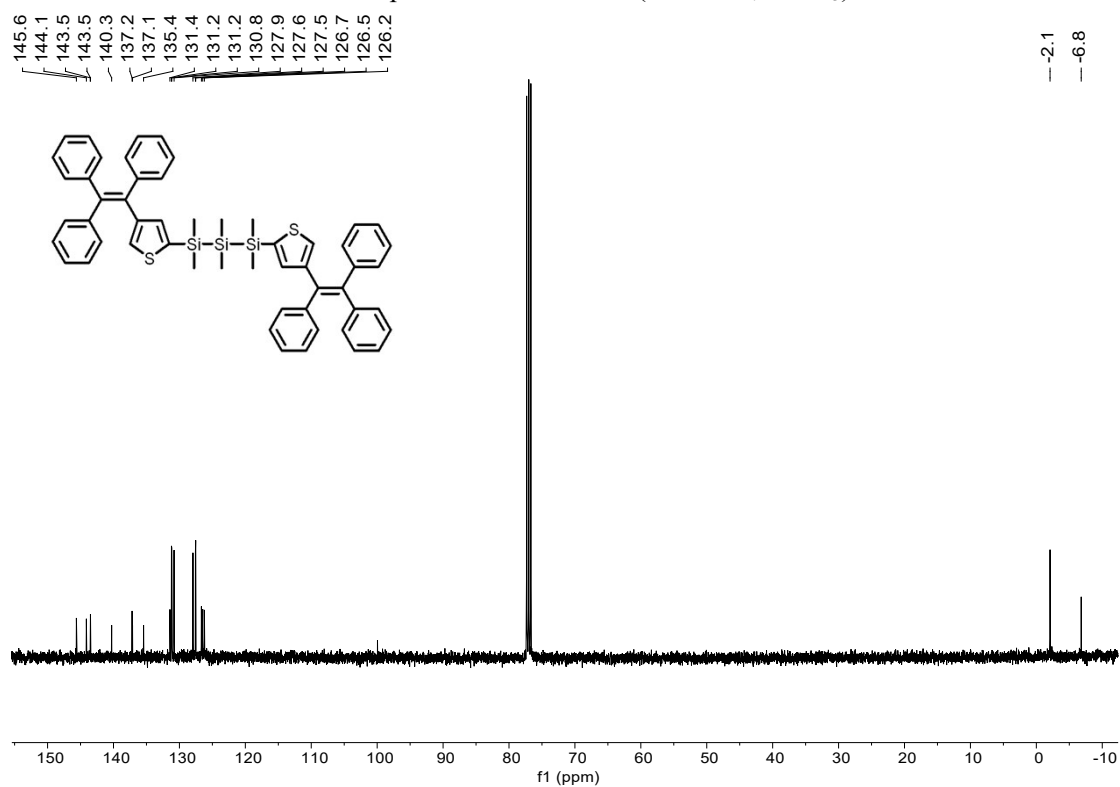
¹H NMR spectrum of BTPTSi2 (400 MHz, CDCl₃).



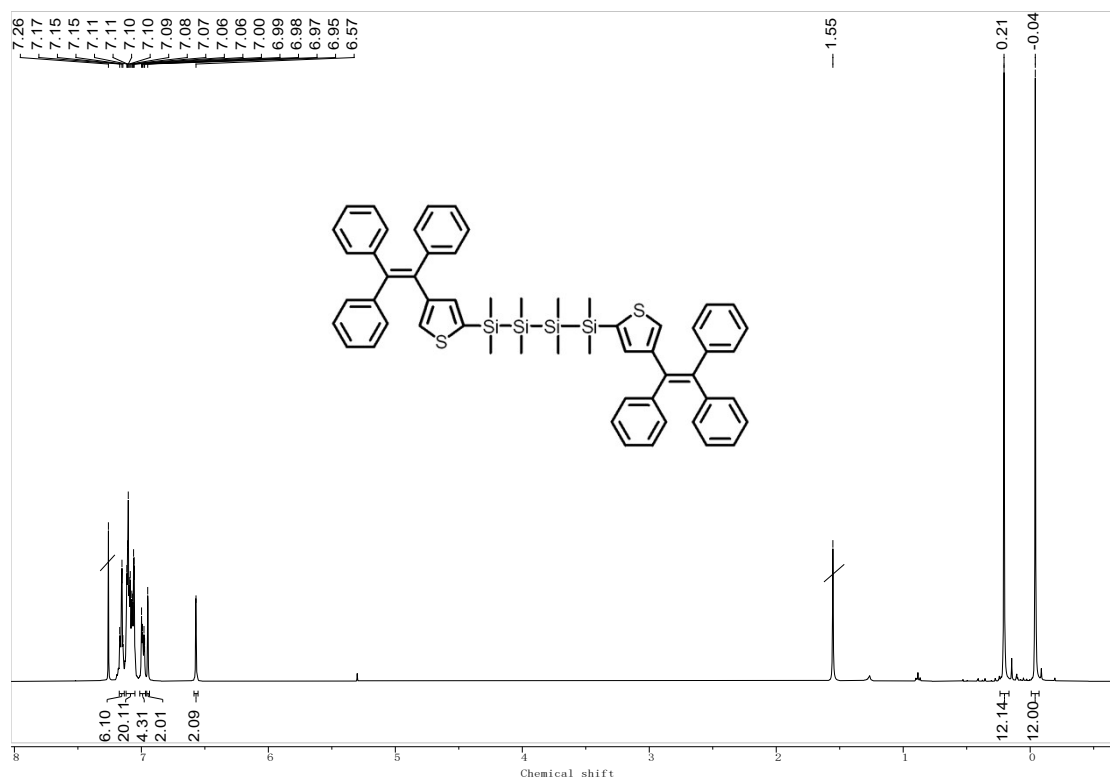
The ¹³C NMR spectrum of BTPTSi2 (101 MHz, CDCl₃).



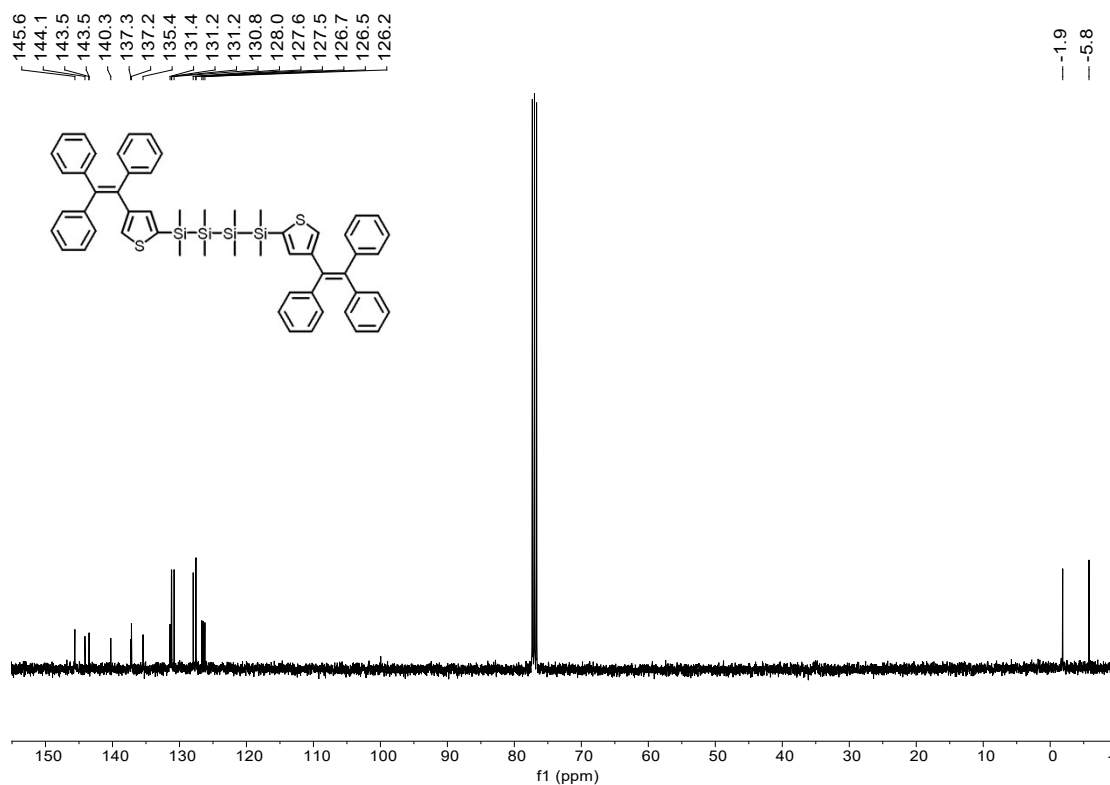
¹H NMR spectrum of BTPTSi3 (400 MHz, CDCl₃).



¹³C NMR spectrum of BTPTSi3 (101 MHz, CDCl₃).



The ^1H NMR spectrum of **BTPTS₄** (400 MHz, CDCl_3)



The ^{13}C NMR spectrum of **BTPTS₄** (101 MHz, CDCl_3).