Supporting Information

Direct comparison of dithienosilole and dithienogermole as π-conjugated linkers in photosensitizers for dye-sensitized solar cells

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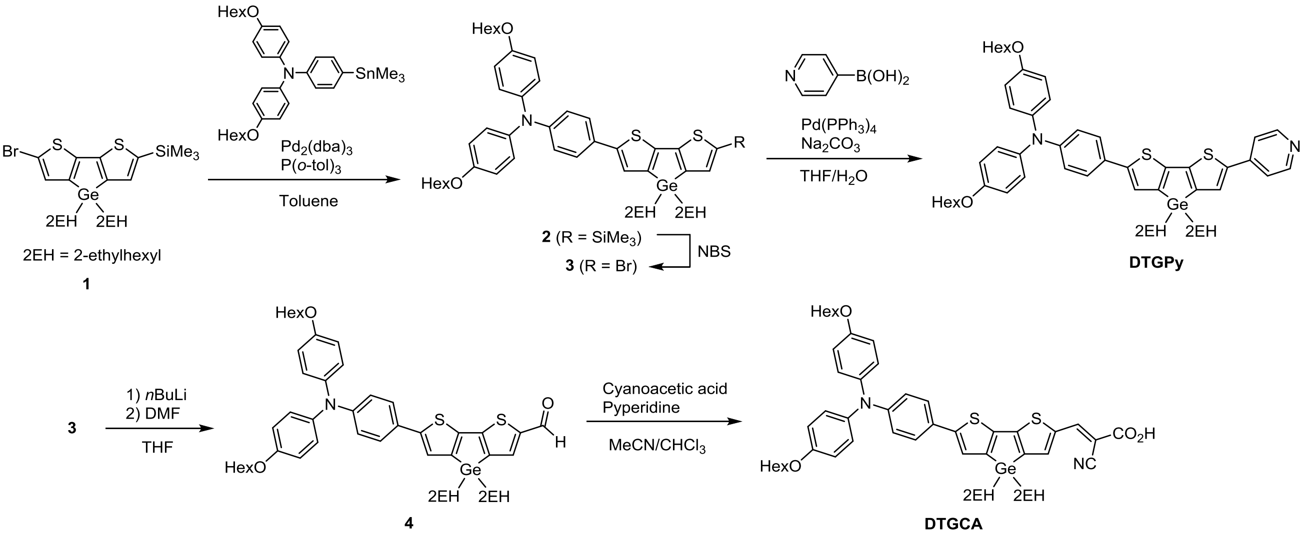
General

All reactions were carried out under dry argon. Toluene, acetonitrile, dichloromethane, THF, and diethyl ether were purchased from Kanto Chemical Co., Ltd. and were distilled from calcium hydride and stored over activated molecular sieves under argon until use, whereas chloroform was distilled from calcium hydride immediately before use. All other chemicals were purchased from Wako Pure Chemical Industries, Ltd. and TCI Co., Ltd. Starting materials **1**,[S1] **5**,[S2] and **8**[S3] were prepared according to the literature. NMR spectra were recorded on Varian System 500 and 400MR spectrometers. High-resolution mass spectra were obtained on a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer at N-BARD, Hiroshima University.

Usual workup mentioned below includes the following steps in that order: 1) hydrolysis of the reaction mixture with water and separation of the organic layer; 2) the aqueous layer was extracted with dichloromethane; 3) the organic layer and the extract were combined and washed with water then brine; 4) after drying over anhydrous magnesium sulfate, the solvent was evaporated.



Synthesis of 2.

A mixture of 198 mg (0.323 mmol) of **1**, 196 mg (0.322 mmol) of bis(*p*-hexyloxyphenyl)[*p*-(trimethylstannyl)phenyl]amine, 6.0 mg (6.6 μmol, 2 mol%) of $Pd_2(dba)_3$, 9.8 mg (32 μmol, 10 mol%) of P(*o*-tol)$_3$, and 10 mL of toluene was heated to 80 °C for 24 hours. After the usual workup, the residue was purified by silica gel chromatography with a mixed solvent of hexane/dichloromethane = 3/1 as the eluent to afford a diastereomeric mixture of compound **2** in 82% yield (257 mg, 0.263 mmol) as an orange viscous oil: ^{1}H NMR (in acetone-d_6, 500 MHz) δ: 0.33 (9H, s, CH_3-Si), 0.77-0.84 (12H, m, CH_3 in 2EH), 0.89-0.94 (6H, m, CH_3 in OHex), 1.11-1.41 (28H, m, CH_2 in OHex and 2EH), 1.45-1.58 (6H, m, CH_2 in OHex and CH), 1.74-1.81 (4H, m, CH_2 in OHex), 3.99 (4H, t, OCH_2, *J* = 6.5 Hz), 6.87 (2H, d, phenylene, *J* = 8.8 Hz), 6.92 (4H, d, phenylene, *J* = 8.9 Hz), 7.07 (4H, d, phenylene, *J* = 8.9 Hz), 7.31 (1H, s, DTG), 7.36-7.38 (1H, m, DTG), 7.46-7.50 (2H, d, phenylene, *J* = 8.8 Hz). ^{13}C NMR (in CD_2Cl_2, 125 MHz) δ: 0.1, 0.2, 11.0, 11.2, 14.2, 14.3, 14.4, 20.92, 20.95, 21.03, 21.04, 23.1, 23.4, 26.1, 29.2, 29.3, 29.4, 29.7, 32.0, 35.8, 35.9, 37.4, 37.5, 68.7, 115.6, 120.7, 125.1, 126.42, 126.44, 126.45, 127.1, 137.27, 137.29, 137.30, 140.67, 140.69, 140.71, 140.8, 144.5, 145.34, 145.37, 145.45, 145.47, 145.50, 146.4, 146.6, 146.7, 148.5, 152.3, 156.1. HR-MS (APCI) Calcd for $C_{57}H_{79}GeNO_4S_2Si$: $[M+H]^+$: 980.49190, Found: 980.49329.

Synthesis of 3.

To a solution of 157 mg (0.161 mmol) of **2** in 10 mL of CH_2Cl_2 was added 28.8 mg (0.162 mmol) of NBS in several portions at room temperature, and the reaction mixture was stirred for 2 hours at this temperature. After the usual workup, the residue was purified by silica gel chromatography with a mixed solvent of hexane/dichloromethane = 3/1 as the eluent to give a diastereomeric mixture of compound **3** in 96% yield (153 mg, 0.155 mmol) as an orange viscous oil: ^{1}H NMR (in acetone-d_6, 500 MHz) δ: 0.76-0.83 (12H, m, CH_3 in 2EH), 0.89-0.94 (6H, m, CH_3 in OHex), 1.10-1.41 (28H, m, CH_2 in OHex and 2EH), 1.44-1.56 (6H, m, CH_2 in OHex and CH), 1.74-1.81 (4H, m, CH_2 in OHex), 3.99 (4H, t, OCH_2, *J* = 6.5 Hz), 6.86 (2H, d, phenylene, *J* = 8.8 Hz), 6.93 (4H, d, phenylene, *J* = 8.9 Hz), 7.07 (4H, d, phenylene, *J* = 8.9 Hz), 7.22-7.24 (1H, m, DTG), 7.37-7.39 (1H, m, DTG), 7.47 (2H, d, phenylene, *J* = 8.8 Hz). ^{13}C NMR (in CD_2Cl_2, 125 MHz) δ: 11.2, 14.4, 14.5, 21.17, 21.20, 23.2, 23.52, 23.53, 26.3, 29.2, 29.3, 29.40, 29.43, 29.9, 32.1, 32.2, 35.9, 36.0, 37.5, 68.7, 110.5, 115.7, 115.8, 120.7, 120.8, 124.8, 124.9, 126.5, 126.6, 126.9, 127.2, 127.3, 133.0, 133.1, 140.8, 143.8, 143.9, 144.0, 145.0, 145.1, 145.3, 146.05, 146.07, 146.09, 147.7, 148.7, 156.3. HR-MS (APCI) Calcd for $C_{57}H_{70}BrGeNO_4S_2$: $[M+H]^+$: 986.36289, Found: 986.36443.

Synthesis of DTGPy.

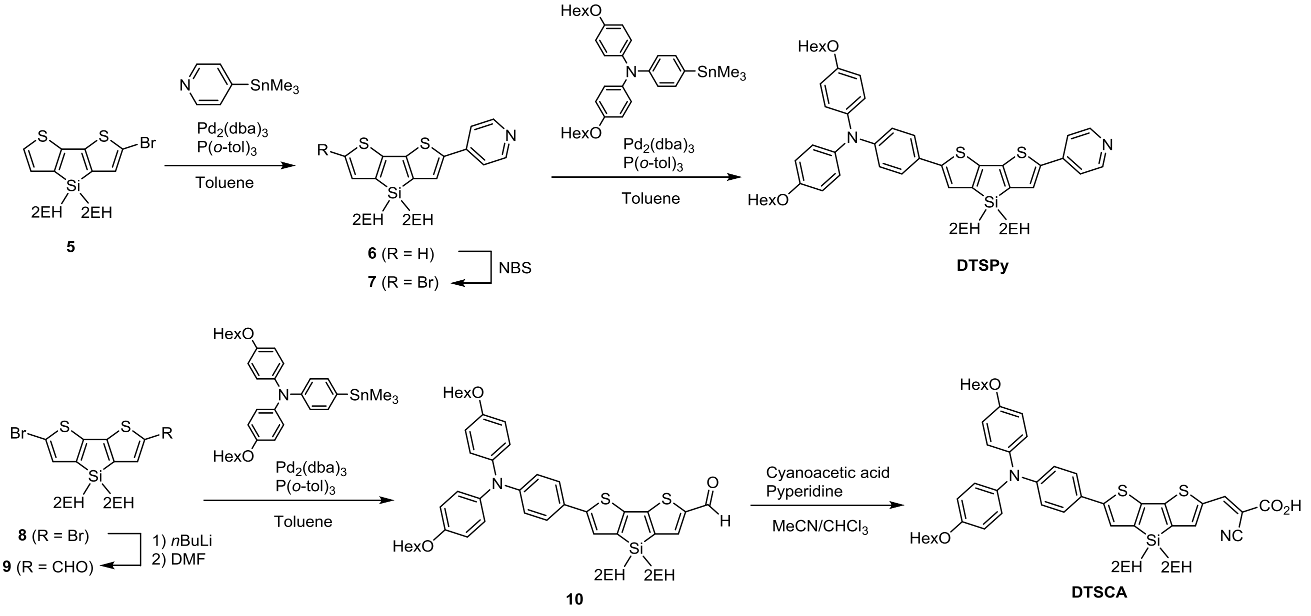
A mixture of 228 mg (0.231 mmol) of **3**, 31.5 mg (0.256 mmol) of 4-pyridylboronic acid, 8.8 mg (7.6 μmol, 3.3 mol%) of $Pd(PPh_3)_4$, 3.0 mL of 0.12 M aqueous solution of Na_2CO_3, and 7.5 mL of THF was heated to 80 °C overnight. After the usual workup, the residue was purified by silica gel chromatography with a mixed solvent of hexane/dichloromethane = 3/1 as the eluent to afford a diastereomeric mixture of **DTGPy** in 84% yield (190 mg, 0.193 mmol) as a reddish-brown viscous oil: ^{1}H NMR (in acetone-d_6, 500 MHz) δ: 0.75-0.83 (12H, m, CH_3 in 2EH), 0.89-0.94 (6H, m, CH_3 in OHex), 1.10-1.40 (28H, m, CH_2 in OHex and 2EH), 1.45-1.59 (6H, m, CH_2 in OHex and CH), 1.74-1.81 (4H, m, CH_2 in OHex), 3.99 (4H, t, OCH_2, J = 6.5 Hz), 6.87 (2H, d, phenylene, J = 8.7 Hz), 6.94 (4H, d, phenylene, J = 8.9 Hz), 7.09 (4H, d, phenylene, J = 8.9 Hz), 7.42-7.44 (1H, m, DTG), 7.51 (2H, d, phenylene, J = 8.7 Hz), 7.59 (2H, br d, pyridyl, J = 6.0 Hz), 7.83-7.85 (1H, m, DTG), 8.53-8.56 (2H, m, pyridyl). ^{13}C NMR (in CD_2Cl_2, 125 MHz) δ: 11.1, 14.3, 14.4, 21.1, 23.08, 23.11, 23.5, 26.18, 29.20, 29.35, 29.36, 29.8, 32.1, 35.9, 37.46, 37.49, 68.7, 115.7, 119.6, 120.5, 125.0, 126.6, 126.7, 127.2, 128.9, 140.7, 141.07, 141.09, 141.11, 142.0, 143.86, 143.89, 143.92, 145.4, 145.5, 145.6, 146.93, 146.95, 146.98, 147.2, 147.3, 147.4, 148.8, 150.7, 156.3. HR-MS (APCI) Calcd for $C_{57}H_{74}GeN_2O_4S_2$: $[M+H]^+$: 985.47893, Found: 985.48023.

Synthesis of 4.

To a solution of 185 mg (0.188 mmol) of **3** in 10 mL of THF was slowly added 0.367 mL (0.467 mmol) of 1.60 M *n*BuLi in hexane at −80 °C, and the mixture was stirred at this temperature for 20 min. To this was added 0.110 mL (1.42 mmol) of DMF at this temperature, and the mixture was stirred at room temperature overnight. After the usual workup, the residue was purified by silica gel chromatography with a mixed solvent of hexane/ethyl acetate = 15/1 as the eluent to afford a diastereomeric mixture of compound **4** in 55% yield (95.6 mg, 0.102 mmol) as a reddish-brown viscous oil: ^{1}H NMR (in acetone-d_6, 500 MHz) δ: 0.75-0.83 (12H, m, CH_3 in 2EH), 0.89-0.94 (6H, m, CH_3 in OHex), 1.10-1.40 (28H, m, CH_2 in OHex and 2EH), 1.45-1.57 (6H, m, CH_2 in OHex and CH), 1.74-1.81 (4H, m, CH_2 in OHex), 3.99 (4H, t, OCH_2, J = 6.5 Hz), 6.86 (2H, d, phenylene, J = 8.8 Hz), 6.93 (4H, d, phenylene, J = 8.9 Hz), 7.09 (4H, d, phenylene, J = 8.9 Hz), 7.48-7.49 (1H, m, DTG), 7.52 (2H, d, phenylene, J = 8.8 Hz) 8.00-8.02 (1H, m, DTG), 9.92 (1H, s, CHO). ^{13}C NMR (in CD_2Cl_2, 125 MHz) δ: 11.08, 11.10, 14.28, 14.34, 21.1, 21.2, 23.1, 23.41, 23.42, 26.2, 29.17, 29.20, 29.33, 29.34, 29.8, 30.2, 32.1, 35.89, 35.92, 37.4, 68.7, 115.7, 120.2, 125.2, 126.01, 126.02, 126.03, 126.84, 126.85, 126.86, 126.87, 127.4, 140.3, 140.5, 143.14, 143.16, 143.18, 144.21, 144.22, 144.23, 144.6, 144.7, 144.8, 149.3, 149.58, 149.61, 149.63, 151.3, 151.4, 151.5, 156.4, 156.63, 156.66, 156.69, 182.6. HR-MS (APCI) Calcd for $C_{55}H_{71}GeNO_5S_2$: M^+: 935.43947, Found: 935.44043.

Synthesis of DTGCA.

A mixture of 87.3 mg (93.4 μmol) of **4**, 18.4 mg (0.216 mmol) of cyanoacetic acid, 15 μL of piperidine, and 16 mL of a mixed solvent of acetonitrile/chloroform = 1/1 was heated to reflux for three days. The solvent was evaporated, and the residue was dissolved to dichloromethane. The organic layer was washed with water, 0.1 M HCl, then brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated. The residue was subjected to silica gel chromatography with ethyl acetate to elute unreacted aldehyde and byproducts. A diastereomeric mixture of **DTGCA** was then eluted with methanol to give 54.8 mg (54.7 μmol, 59%) as purple powder: ^{1}H NMR (in DMSO-d_6 with acetic acid-d_4, 500 MHz): δ = 0.70-0.76 (12H, m, CH_3 in 2EH), 0.82-0.90 (6H, m, CH_3 in OHex), 1.00-1.35 (28H, m, CH_2 in OHex and 2EH), 1.38-1.51 (6H, m, CH_2 in OHex and CH), 1.65-1.73 (4H, m, CH_2 in OHex), 3.93 (4H, t, OCH_2, *J* = 6.5 Hz), 6.75 (2H, d, phenylene, *J* = 8.7 Hz), 6.91 (4H, d, phenylene, *J* = 8.8 Hz), 7.04 (4H, d, phenylene, *J* = 8.8 Hz), 7.45-7.50 (2H, m, DTG and phenylene), 8.01-8.05 (1H, m, DTG), 8.49 (1H, br s, olefin). ^{13}C NMR spectrum was not obtained because of the low solubility of the product. HR-MS (APCI) Calcd for $C_{58}H_{72}GeN_2O_6S_2$: $[M+H]^+$: 1003.45310, Found: 1003.45477.



Synthesis of 6.

A mixture of 1.18 g (2.36 mmol) of **5**, 0.403 mL (2.37 mmol) of 4-trimethylstannylpyridine, 43.3 mg (47.3 μmol, 2 mol%) of $Pd_2(dba)_3$, 72.0 mg (0.237 mmol, 10 mol%) of P(*o*-tol)$_3$, and 30 mL of toluene was heated to 100 °C for 2 days. After the usual workup, the residue was purified by silica gel chromatography with a mixed solvent of hexane/ethyl acetate = 2/1 as the eluent to afford a diastereomeric mixture of **6** in 30% yield (363 mg, 0.733 mmol) as a brownish viscous oil: ^{1}H NMR (in $CDCl_3$, 400 MHz) δ: 0.73-0.84 (12H, m, CH_3), 0.95-1.01 (4H, m, CH_2), 1.09-1.31 (16H, m, CH_2), 1.35-1.47 (2H, m, CH), 7.08 (1H, d, DTS, J = 6.0 Hz), 7.28 (1H, d, DTS, J = 6.0 Hz), 7.44-7.48 (2H, m, pyridyl), 7.48-7.49 (1H, m, DTS), 8.53-8.58 (2H, m, pyridyl). ^{13}C NMR (in $CDCl_3$, 125 MHz) δ: 10.8, 14.2, 17.7 23.0, 29.0, 35.7, 36.0, 119.4, 119.5, 126.2, 126.4, 128.2, 128.3, 129.9, 130.1, 141.24, 141.26, 141.29, 141.8, 143.4, 143.5, 143.6, 144.2, 144.3, 144.4, 148.41, 148.43, 150.3, 150.4, 150.6. ^{29}Si NMR (in $CDCl_3$, 99 MHz) δ: -5.96. HR-MS (APCI) Calcd for $C_{29}H_{41}NS_2Si$: $[M+H]^+$: 496.25224, Found: 496.25256.

Synthesis of 7.

To a solution of 363 mg (0.733 mmol) of **7** in 20 mL of CH_2Cl_2 was added 130 mg (0.733 mmol) of NBS in several portions at room temperature, and the reaction mixture was stirred for 2 hours at this temperature. After the usual workup, the residue was purified by silica gel chromatography with a mixed solvent of hexane/ethyl acetate = 3/1 as the eluent, followed by preparative GPC with toluene as the eluent to give a diastereomeric mixture of compound **8** in 70% yield (293 mg, 0.510 mmol) as a brownish viscous oil: ^{1}H NMR (in $CDCl_3$, 500 MHz) δ: 0.75-0.86 (12H, m, CH_3), 0.92-1.01 (4H, m, CH_2), 1.10-1.33 (16H, m, CH_2), 1.36-1.45 (2H, m, CH), 7.02 (1H, s, DTS), 7.41-7.44 (2H, m, pyridyl), 7.45-7.46 (1H, m, DTS), 8.54-8.60 (2H, m, pyridyl). ^{13}C NMR (in $CDCl_3$, 125 MHz) δ: 10.6, 13.9, 17.3, 22.75, 22.78, 28.61, 28.63, 28.68, 28.71, 35.39, 35.40, 35.6, 112.32, 112.34, 112.37, 119.1, 119.2, 127.85, 127.91, 132.3, 132.4, 141.3, 141.47, 141.49, 141.52, 143.0, 143.1, 143.2, 143.5, 143.6, 143.7, 148.47, 148.50, 148.52, 149.44, 149.47, 149.49, 150.04, 150.09. ^{29}Si NMR (in $CDCl_3$, 99 MHz) δ: -4.73. HR-MS (APCI) Calcd for $C_{29}H_{40}BrNS_2Si$: $[M+H]^+$: 574.16276, Found: 574.16364.

Synthesis of DTSPy.

A mixture of 293 mg (0.509 mmol) of **7**, 403 mg (0.662 mmol) of bis(*p*-hexyloxyphenyl)-[*p*-(trimethylstannyl)phenyl]amine, 9.32 mg (10.2 μmol, 2 mol%) of $Pd_2(dba)_3$, 15.5 mg (50.9 μmol, 10 mol%) of P(*o*-tol)$_3$, and 20 mL of toluene was heated to 100 °C for 24 hours. After the usual workup, the residue was purified by preparative GPC with toluene as the eluent to afford a diastereomeric mixture of **DTSPy** in 29% yield (139 mg, 0.147 mmol) as a reddish-brown viscous oil: ^{1}H NMR (in acetone-d$_6$, 500 MHz) δ: 0.75-0.81 (12H, m, CH_3 in 2EH), 0.89-0.94 (6H, m, CH_3 in OHex), 1.04-1.39 (28H, m, CH_2 in OHex and 2EH), 1.44-1.53 (6H, m, CH_2 in OHex and CH), 1.74-1.81 (4H, m, CH_2 in OHex), 3.99 (4H, t, OCH_2, *J* = 6.5 Hz), 6.87 (2H, d, phenylene, *J* = 8.8 Hz), 6.93 (4H, d, phenylene, *J* = 9.0 Hz), 7.07 (4H, d, phenylene, *J* = 9.0 Hz), 7.42-7.44 (1H, m, DTS), 7.50 (2H, d, phenylene, *J* = 8.8 Hz), 7.57-7.60 (2H, m, pyridyl), 7.83-7.85 (1H, m, DTS), 8.53-8.56 (2H, m, pyridyl). ^{13}C NMR (in CD_2Cl_2, 500 MHz) δ: 11.0, 11.1, 14.3, 14.4, 18.0, 23.1, 23.4, 26.1, 26.2, 26.3, 29.30, 29.35, 29.36, 29.6, 29.8, 29.9, 32.1, 36.1, 36.3, 36.40, 36.44, 68.5, 68.7, 68.9, 115.6, 115.8, 119.6, 119.7, 120.4, 120.6, 124.9, 125.1, 126.6, 126.69, 126.71, 126.73, 127.1, 127.4, 128.8, 128.9, 140.69, 140.70, 141.32, 141.35, 141.38, 142.0, 144.0, 144.1, 144.2, 145.8, 145.9, 146.0, 146.38, 146.39, 146.42, 147.18, 147.22, 147.3, 148.8, 150.6, 150.8, 151.23, 151.24, 151.26, 156.27. ^{29}Si NMR (in acetone-d$_6$, 99 MHz) δ: -5.59. HR-MS (APCI) Calcd for $C_{58}H_{74}N_2O_4S_2Si$: $[M+H]^+$: 939.53467, Found:939.53503.

Synthesis of 9.

To a solution of 861 mg (1.49 mmol) of **8** in 30 mL of ether was added 1.0 mL (1.6 mmol) of 1.55 M *n*BuLi in hexane at −80 °C over a period of 5 min and the mixture was stirred at this temperature for 30 min. To this was added 0.5 mL (6.5 mmol) of DMF at this temperature. The mixture was warmed up to room temperature immediately, and stirred for 3 hours at this temperature. After the usual workup, the residue was purified by silica gel chromatography with a mixed solvent of hexane/dichloromethane = 1/1 as the eluent to afford a diastereomeric mixture of compound **9** in 51% yield (400 mg, 0.761 mmol) as a yellowish viscous oil: ^{1}H NMR (in $CDCl_3$, 400 MHz) δ: 0.74-0.86 (12H, m, CH_3), 0.94-0.99 (4H, m, CH_2), 1.16-1.30 (16H, m, CH_2), 1.33-1.43 (2H, m, CH), 7.07 (1H, s, DTS), 7.68 (1H, s, DTS), 9.87 (1H, s, CHO). ^{13}C NMR (in $CDCl_3$, 125 MHz) δ: 10.7, 14.0, 17.3, 22.83, 22.84, 28.71, 28.73, 28.77, 28.79, 35.5, 35.71, 35.73, 115.39, 115.41, 115.43, 132.77, 132.78, 132.80, 139.4, 142.3, 142.4, 142.5, 144.66, 144.67, 144.68, 147.4, 147.5, 147.6, 147.98, 148.00, 148.01, 157.10, 157.14, 157.17, 182.5. ^{29}Si NMR (in $CDCl_3$, 99 MHz) δ: -4.35. HR-MS (APCI) Calcd for $C_{25}H_{38}OS_2Si$: $[M+H]^+$: 525.13112, Found: 525.13190.

Synthesis of 10.

A mixture of 373 mg (0.709 mmol) of **9**, 805 mg (1.33 mmol) of bis(*p*-hexyloxyphenyl)-[*p*-(trimethylstannyl)phenyl]amine, 13.1 mg (14.3 µmol, 2 mol%) of $Pd_2(dba)_3$, 21.4 mg (70.3 µmol, 10 mol%) of P(*o*-tol)$_3$, and 30 mL of toluene was heated to reflux for overnight. After the usual workup, the residue was purified by preparative GPC with toluene as the eluent to afford a diastereomeric mixture of compound **10** in 71% yield (449 mg, 0.504 mmol) as a reddish-brown viscous oil: ^{1}H NMR (in acetone-d$_6$, 500 MHz) δ: 0.75-0.82 (12H, m, CH_3 in 2EH), 0.87-0.93 (6H, m, CH_3 in OHex), 1.06-1.37 (28H, m, CH_2 in OHex and 2EH), 1.43-1.53 (6H, m, CH_2 in OHex and CH), 1.72-1.79 (4H, m, CH_2 in OHex), 3.92 (4H, t, OCH_2, *J* = 6.5 Hz), 6.82-6.88 (6H, m, phenylene), 7.02 (4H, d, phenylene, *J* = 9.0 Hz), 7.41-7.46 (3H, m, phenylene and DTS), 7.94-7.98 (1H, m, DTS), 9.89 (1H, s, CHO). ^{13}C NMR (in acetone-d$_6$, 125 MHz) δ: 11.20, 11.21, 14.4, 14.48, 14.49, 18.00, 18.03, 23.28, 23.31, 23.59, 23.61, 26.5, 29.61, 29.64, 30.1, 32.3, 32.4, 36.36, 36.37, 36.62, 36.63, 68.7, 116.1, 120.4, 125.63, 125.67, 125.70, 126.2, 127.2, 127.8, 140.8, 141.0, 143.5, 143.6, 143.7, 145.34, 145.37, 145.39, 145.60, 145.62, 145.65, 149.7, 150.12, 150.16, 150.19, 156.8, 158.37, 158.41, 158.45, 182.9. ^{29}Si NMR (in $CDCl_3$, 99 MHz) δ: -5.87. HR-MS (APCI) Calcd for $C_{55}H_{76}NO_3S_2Si$: $[M+H]^+$: 890.50304, Found: 890.50342.

Synthesis of DTSCA.

A mixture of 199 mg (0.223 mmol) of **10**, 39.0 mg (0.458 mmol) of cyanoacetic acid, 11 µL of piperidine, and 30 mL of a mixed solvent of acetonitrile/chloroform = 1/1 was heated to reflux for 24 hours. The solvent was evaporated and the residue was dissolved to dichloromethane. The organic layer was washed with water, 0.1 M HCl, then brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated. The residue was subjected to silica gel chromatography with ethyl acetate to elute unreacted aldehyde and byproducts. A diastereomeric mixture of **DTGCA** was then eluted with methanol to give 126 mg (0.131 mmol, 59%) as purple powder: ^{1}H NMR (in DMSO-d$_6$ with TFA, 400 MHz): δ = 0.70-0.76 (12H, m, CH_3

in 2EH), 0.84-0.90 (6H, m, CH_3 in OHex), 0.98-1.24 (20H, m, CH_2 in OHex and 2EH), 1.25-1.47 (14H, m, CH and CH_2 in OHex and 2EH), 1.65-1.74 (4H, m, CH_2 in OHex), 3.94 (4H, t, OCH_2, J = 6.4 Hz), 6.76 (2H, d, phenylene, J = 8.8 Hz), 6.92 (4H, d, phenylene, J = 9.0 Hz), 7.05 (4H, d, phenylene, J = 9.0 Hz), 7.46-7.52 (3H, m, DTS and phenylene), 8.02-8.08 (1H, m, DTS), 8.49 (1H, br s, olefin). ^{13}C and ^{29}Si NMR spectra could not be obtained because of the low solubility of the product. HR-MS (APCI) Calcd for $C_{58}H_{77}N_2O_4S_2Si$: $[M+H]^+$: 957.50885, Found: 957.50842.

Photophysical measurements

UV–vis absorption spectra were measured with a HITACHI U-2910 spectrophotometer. Photoluminescence (PL) spectra were measured with a HORIBA FluoroMax-4 spectrophotometer. The absolute PL quantum yields were determined by using a HORIBA FluoroMax-4 spectrophotometer attached to an integration sphere.

Computational methods

DFT calculations were performed on a Gaussian 09 program at B3LYP/6-31G(d) level of theory.

Preparation of DSSCs

A TiO_2 paste (JGC Catalysts and Chemicals Ltd., PST-18NR) was deposited on a FTO substrate by doctor-blading. The deposited TiO_2 layer on the FTO substrate was sintered at 450 °C for 50 min (film thickness: approximately 9 μm). The TiO_2 electrode (0.5×0.5 cm^2 in photoactive area) was immersed into a solution at a concentration of 0.1 mM of dye with 0.1 mM CDCA as a co-adsorbent. As the immersing solvent, acetonitrile and acetone were used for pyridine dyes (**DTSPy** and **DTGPy**) and cyanoacrylic acid dyes (**DTSCA** and **DTGPy**), respectively. TiO_2 photoelectrodes were immersed in the dye-adsorption solvent for 15 h at room temperature. Photoelectrochemical measurements were performed in a two-electrode sandwich cell configuration composed of the dye-adsorbed TiO_2 photoelectrode, a platinum-sputtered glasses counter electrode, a spacer film, and an electrolyte solution 0.05 M I_2, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile. The photocurrent-voltage characteristics were measured using a potentiostat under a simulated solar light (AM1.5G, 100 mW

cm^{-2}). IPCE spectra were measured under monochromatic irradiation with a tungsten-halogen lamp and a monochromator. The amount of adsorbed dye on TiO_2 nanoparticles was determined by absorption spectral measurement of the concentration change of the dye solution before and after adsorption. Absorption spectra of the dyes adsorbed on TiO_2 film were measured on the dyes-adsorbed TiO_2 film (film thickness: approximately 2 μm).

EIS measurements

EIS measurements were performed on the DSSC with the highest PCE in the dark under a forward bias of 800 mV using an AMETEK Versa-STAT 4 potentiostat/galvanostat.

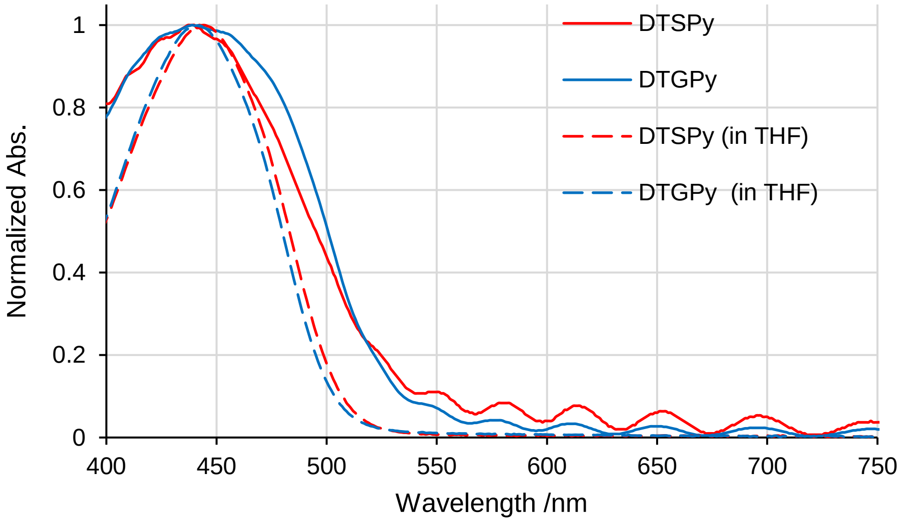


Fig. S1 Absorption spectra of **DTSPy** and **DTGPy** on TiO_2 films. Those in THF are also shown for comparison. The TiO_2 films were modified with 0.1 mM dye solution with 0.1 mM CDCA for 15 hours.

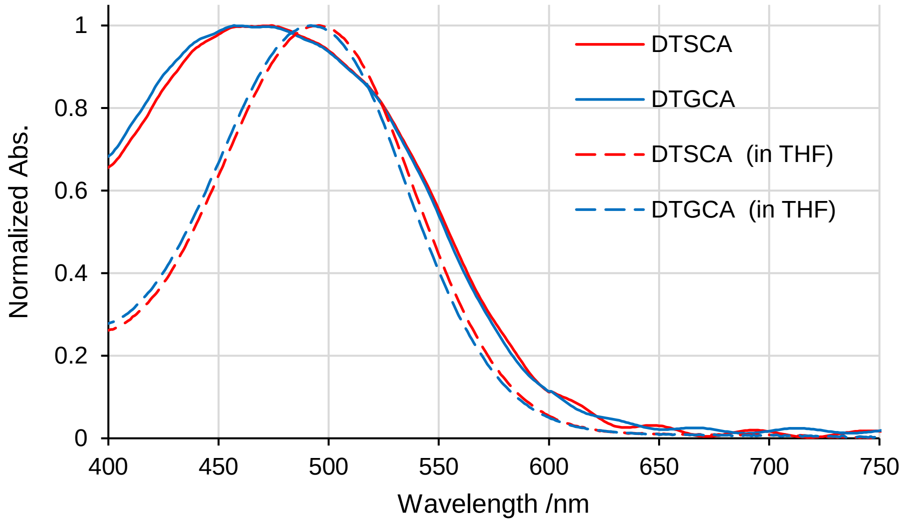


Fig. S2 Absorption spectra of **DTSCA** and **DTGCA** on TiO_2 films. Those in THF are also shown for comparison. The TiO_2 films were modified with 0.1 mM dye solution with 0.1 mM CDCA for 15 hours.

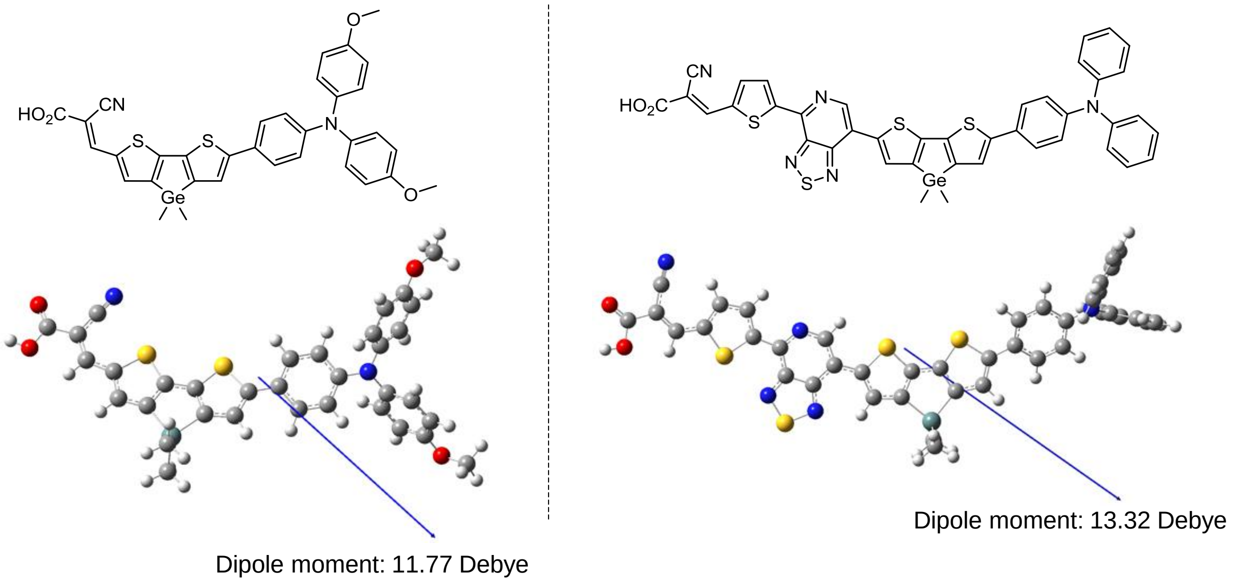


Fig. S3 DFT calculated dipole moment of **DTGCA** (left) and **DTGPTzCA2** (right) at B3LYP/6-31G(d,p) level. The alkyl chains were replaced with methyl groups.

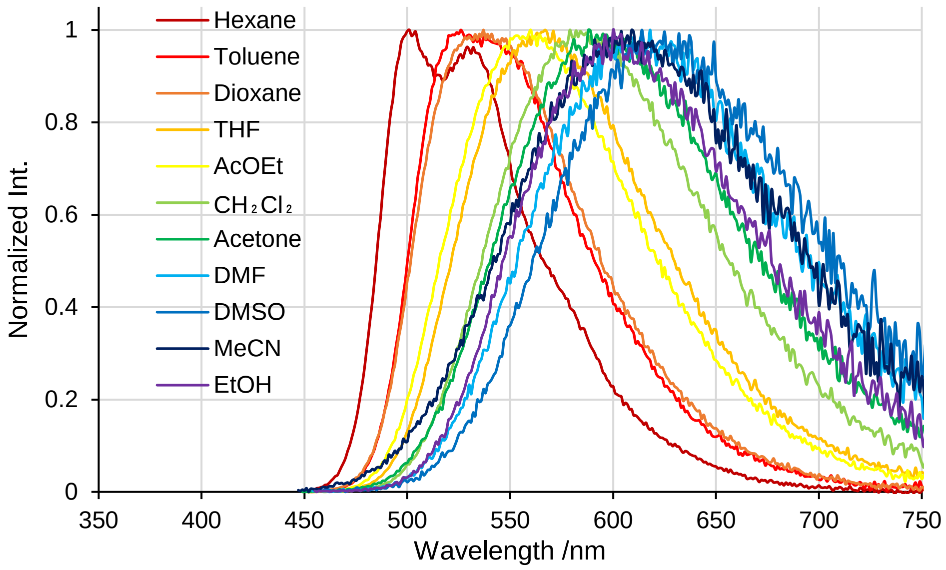


Fig. S4 Photoluminescence spectra of **DTSPy** in various solvents.

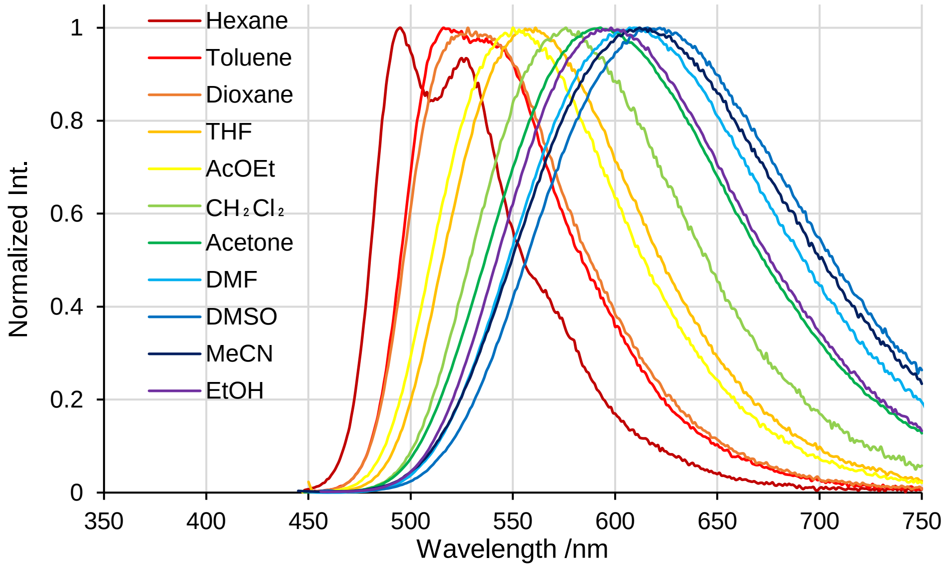
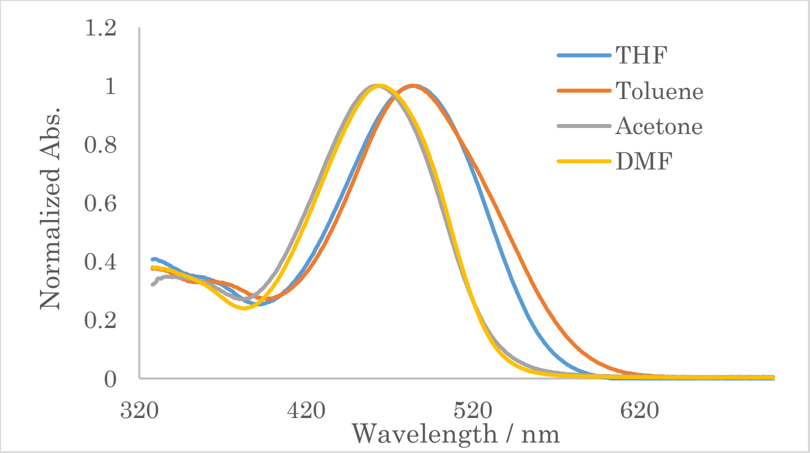


Fig. S5 Photoluminescence spectra of **DTGPy** in various solvents.

Table S1 Optical data of **DTSPy** and **DTGPy** in various solvents.

Solvent	**DTSPy**			**DTGPy**		
	λ_{max}^{abs} /nm	λ_{max}^{em} /nm	Φ_F /%	λ_{max}^{abs} /nm	λ_{max}^{em} /nm	Φ_F /%
Hexane	439	501, 529	72	438	495, 525	72
Toluene	443	526	78	443	516	79
1,4-Dioxane	443	537	81	440	528	79
THF	443	567	83	441	561	73
AcOEt	442	560	84	437	550	68
CH_2Cl_2	443	579	78	445	576	76
Acetone	439	588	22	438	593	42
DMF	444	618	22	440	607	20
DMSO	448	614	21	446	616	18
MeCN	437	609	10	435	612	7
EtOH	445	600	23	446	598	15



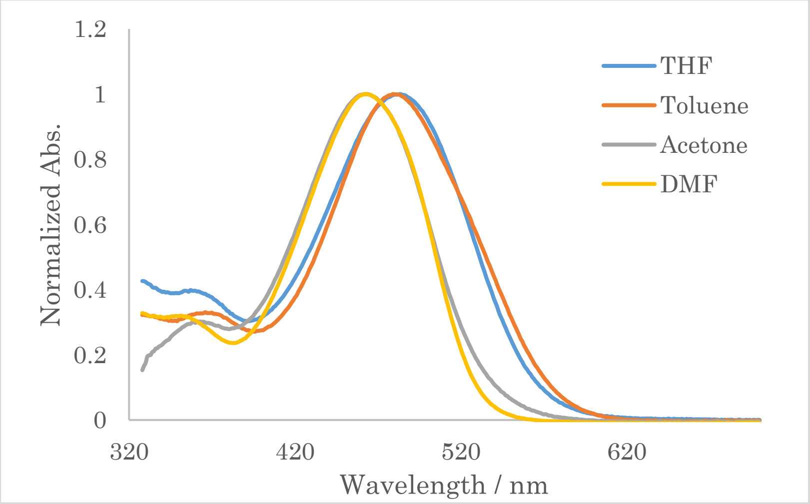
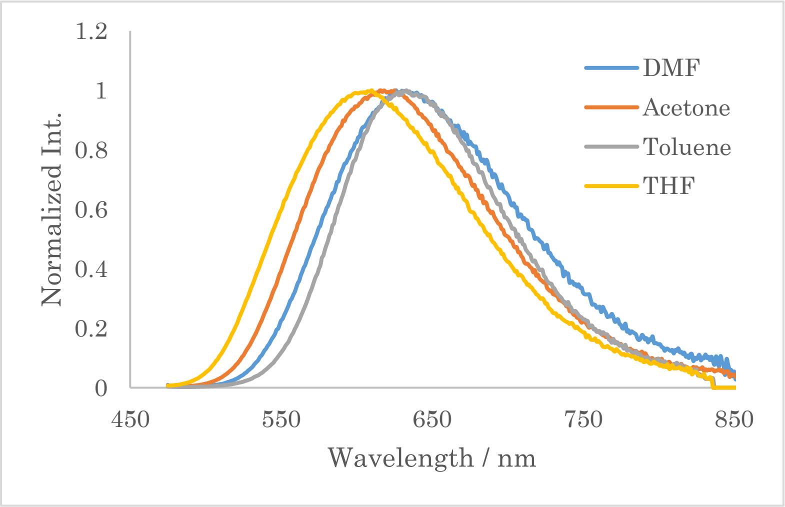


Fig. S6 Absorption spectra of **DTSCA** (top) and **DTGCA** (bottom) in various solvents.



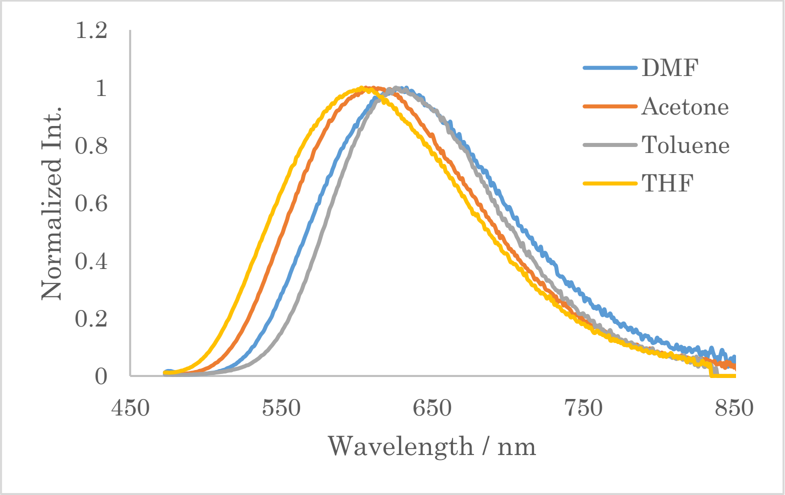


Fig. S7 Photoluminescence spectra of **DTSCA** (top) and **DTGCA** (bottom) in various solvents.

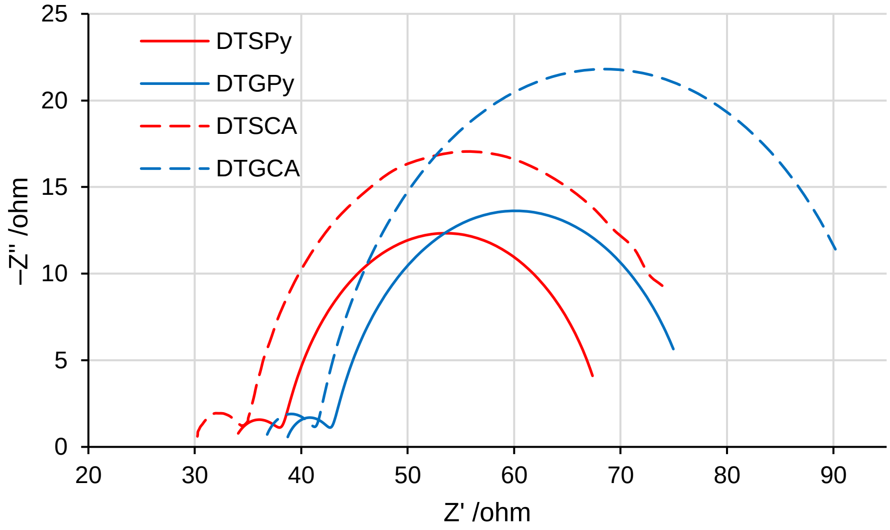


Fig. S8 EIS Nyquist plots of DSSCs based on DTS- and DTG-containing dyes.

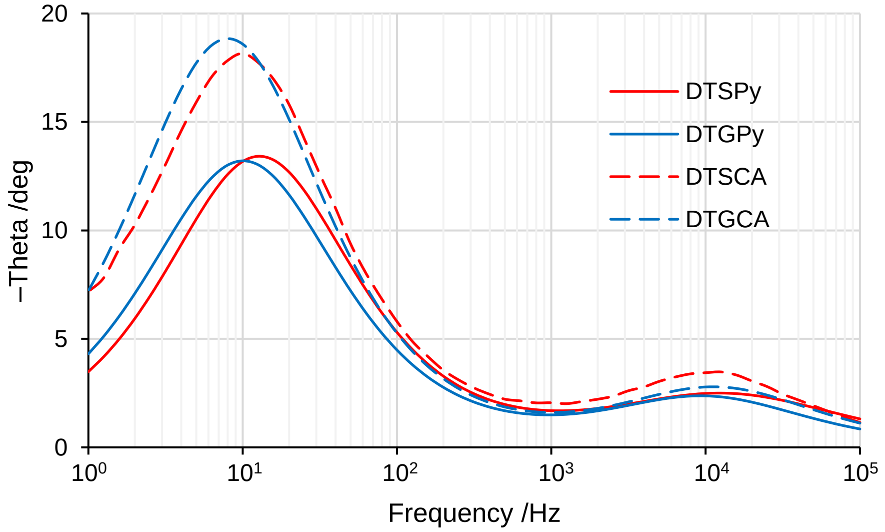
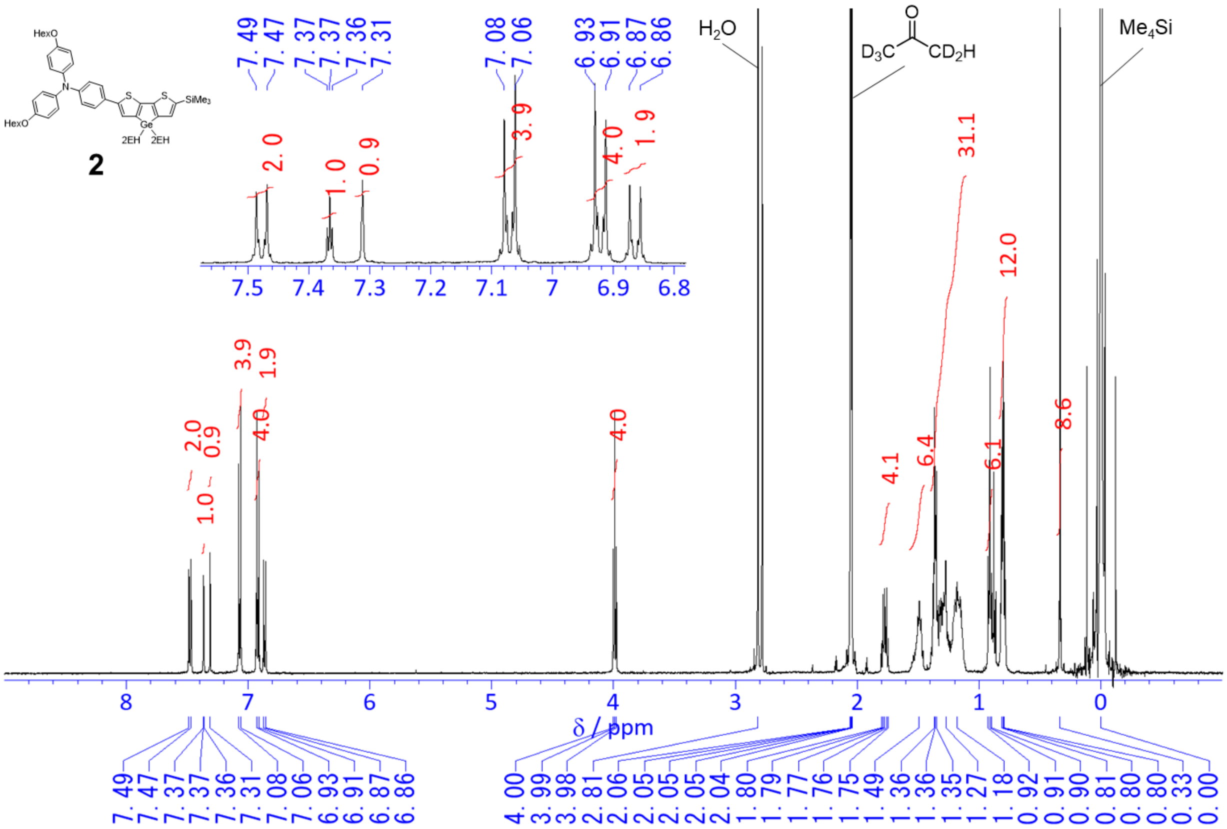
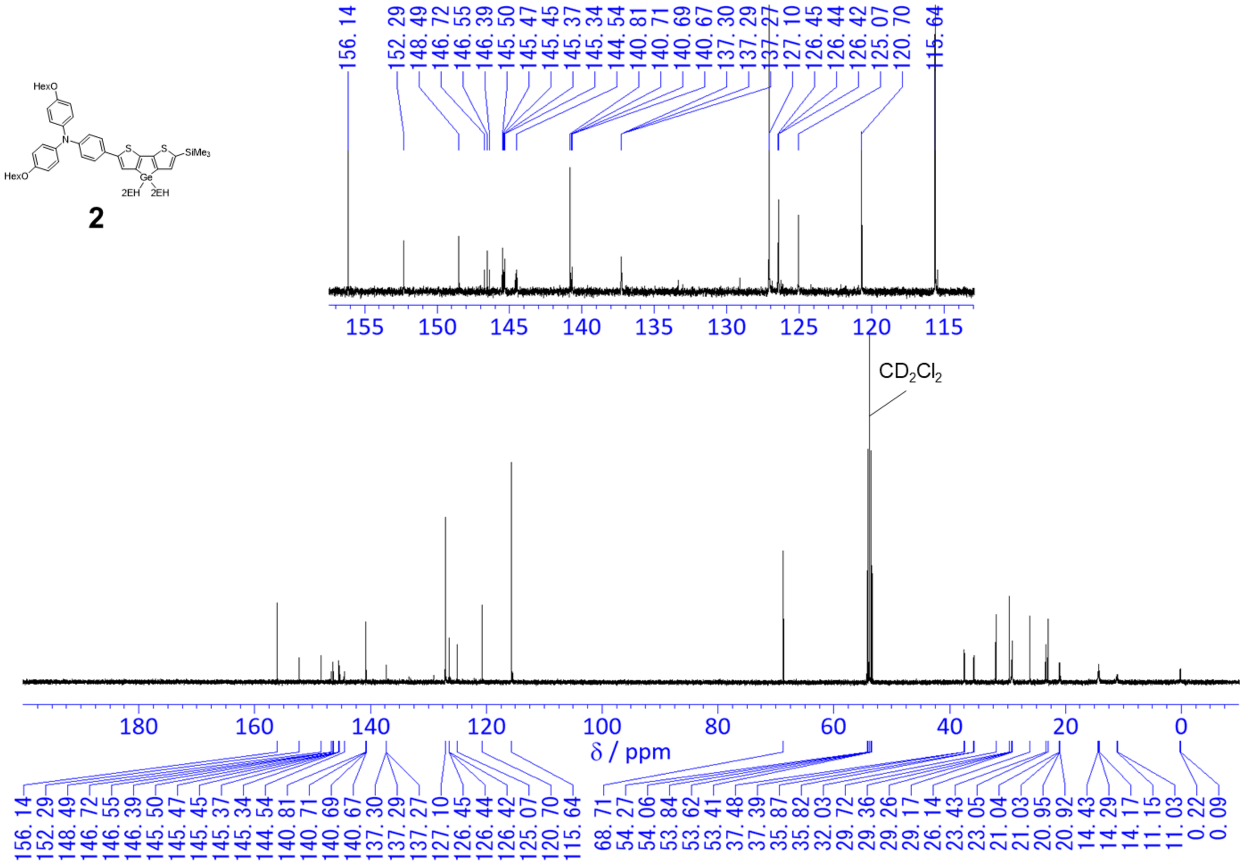


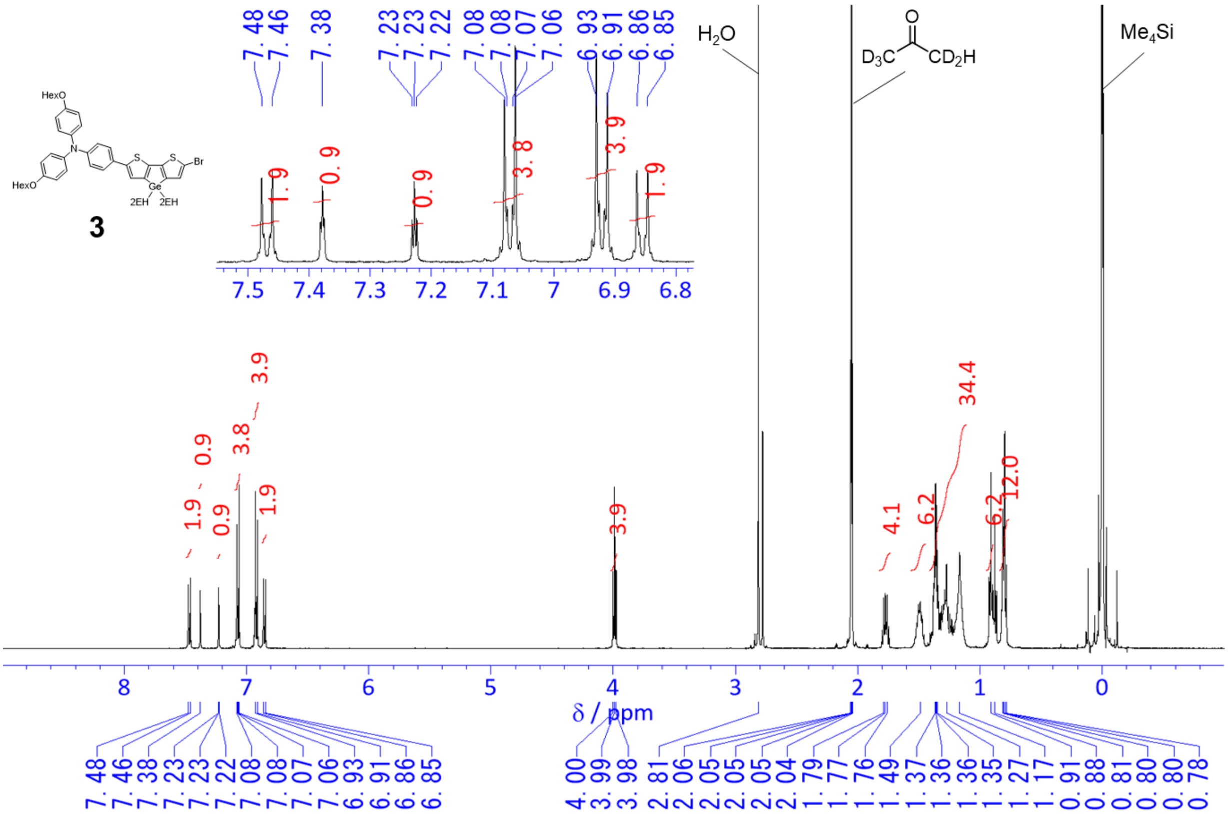
Fig. S9 EIS Bode plots of DSSCs based on DTS- and DTG-containing dyes.



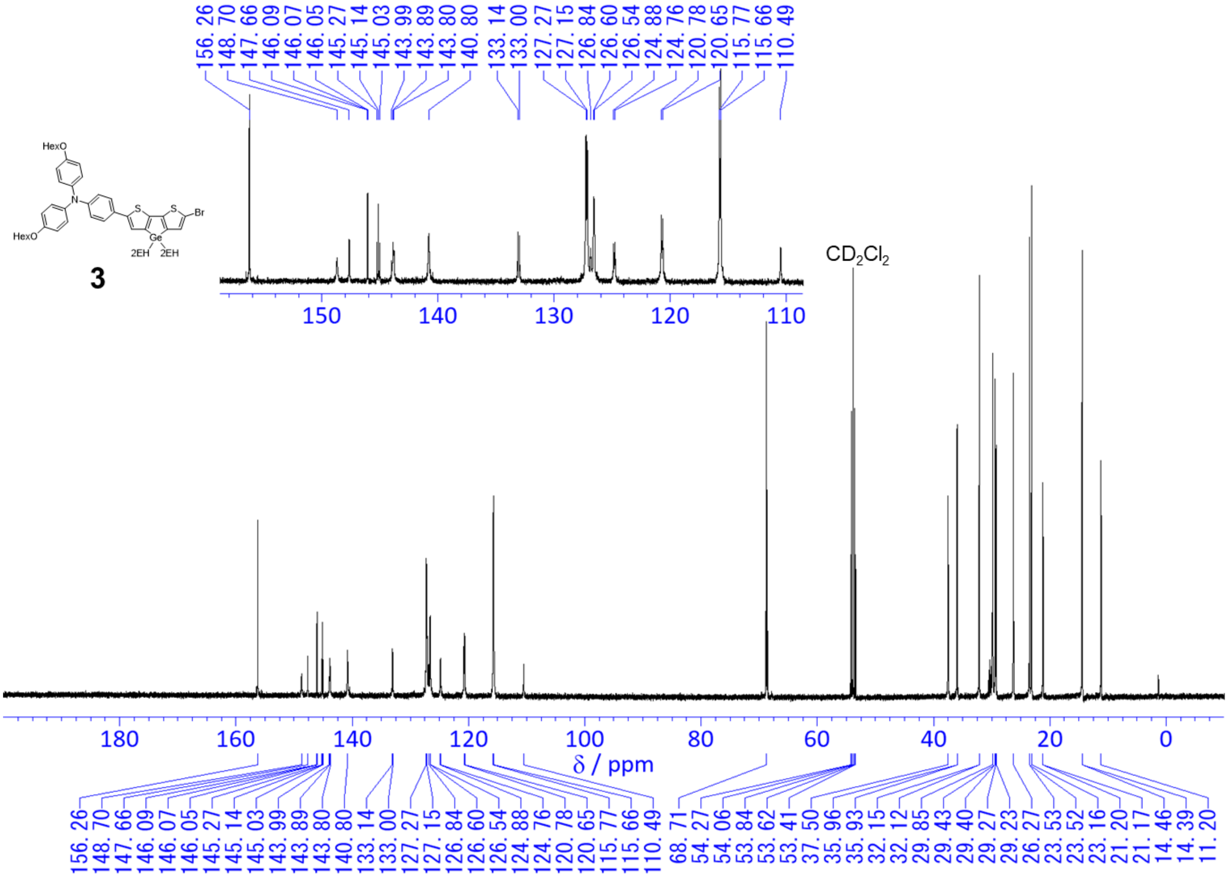
^{1}H NMR spectrum of **2** in acetone-d$_6$ at room temperature (500 MHz).



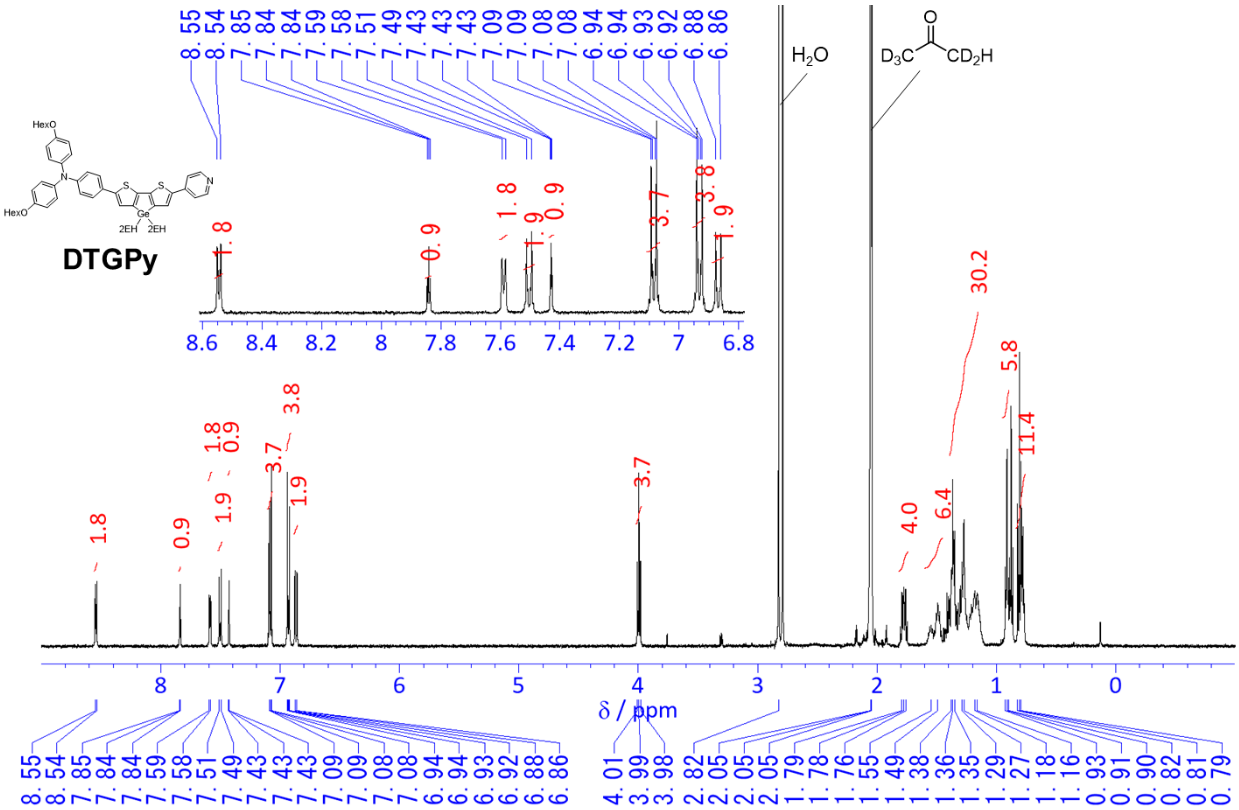
^{13}C NMR spectrum of **2** in CD_2Cl_2 at room temperature (125 MHz).



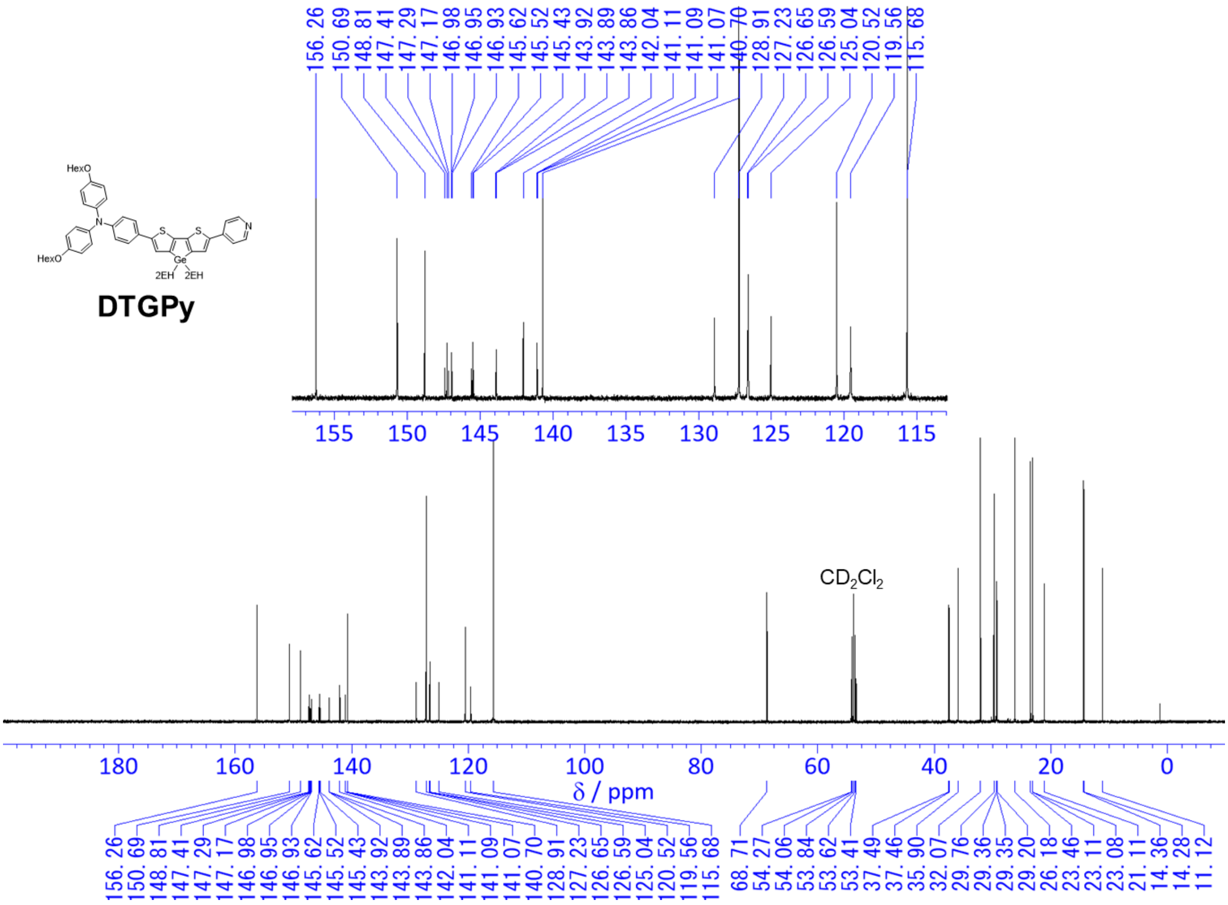
^{1}H NMR spectrum of **3** in acetone-d$_6$ at room temperature (500 MHz).



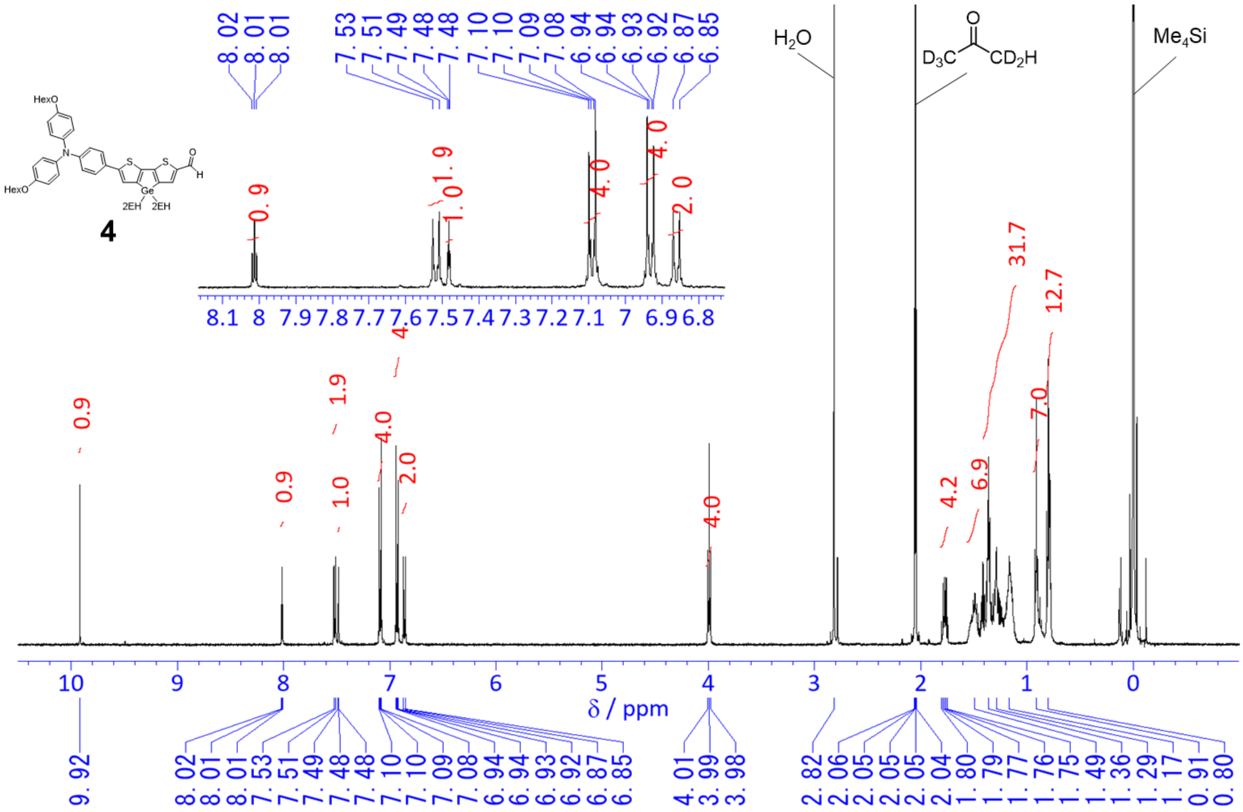
^{13}C NMR spectrum of **3** in CD$_2$Cl$_2$ at room temperature (125 MHz).



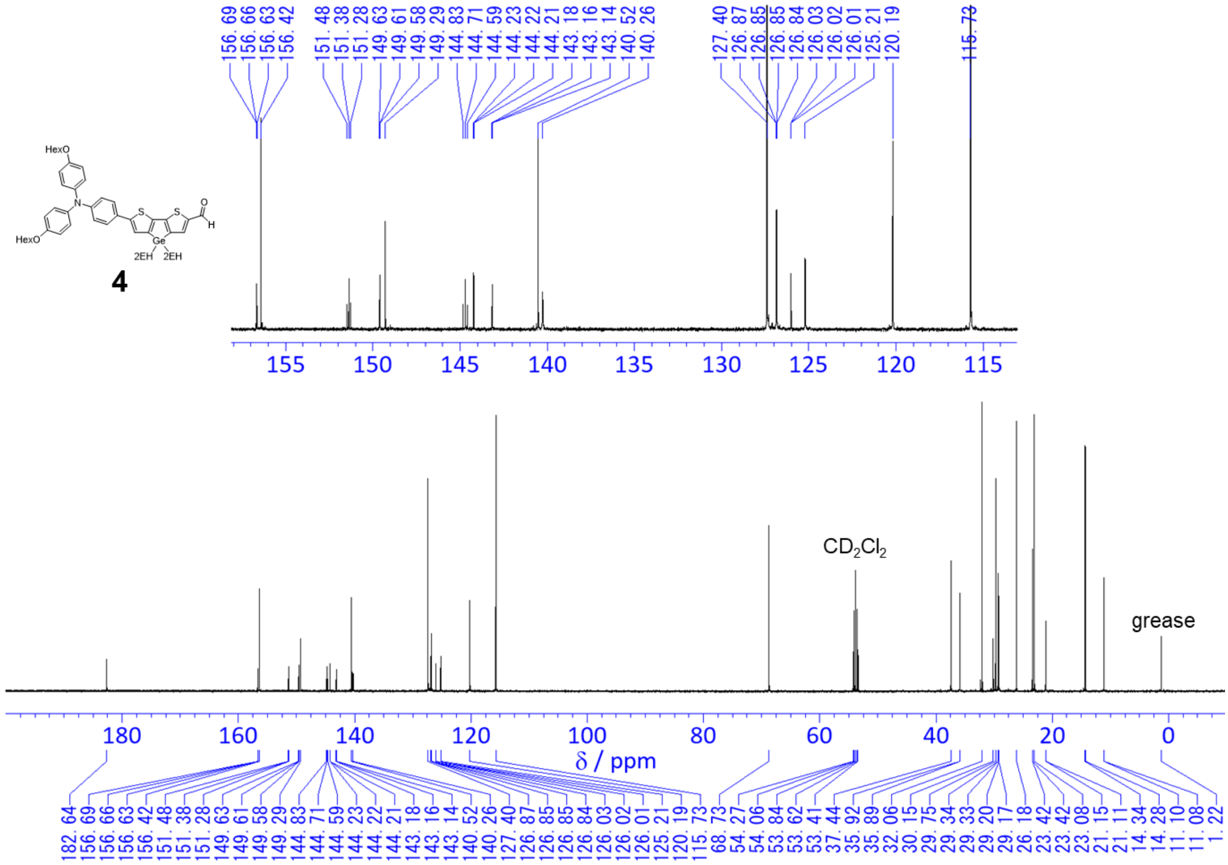
^{1}H NMR spectrum of **DTSPy** in acetone-d_6 at room temperature (500 MHz).



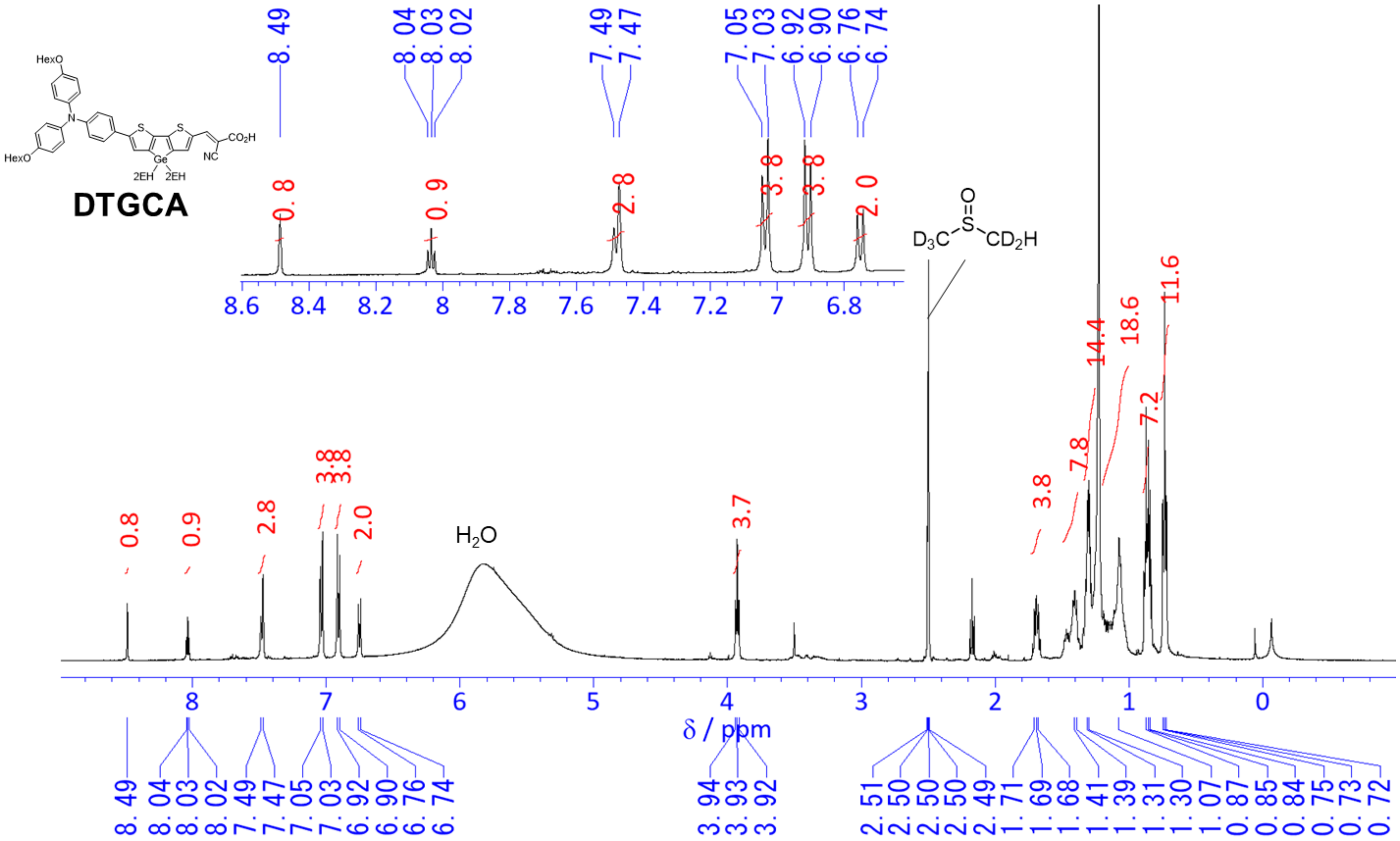
^{13}C NMR spectrum of **DTSPy** in CD_2Cl_2 at room temperature (125 MHz).



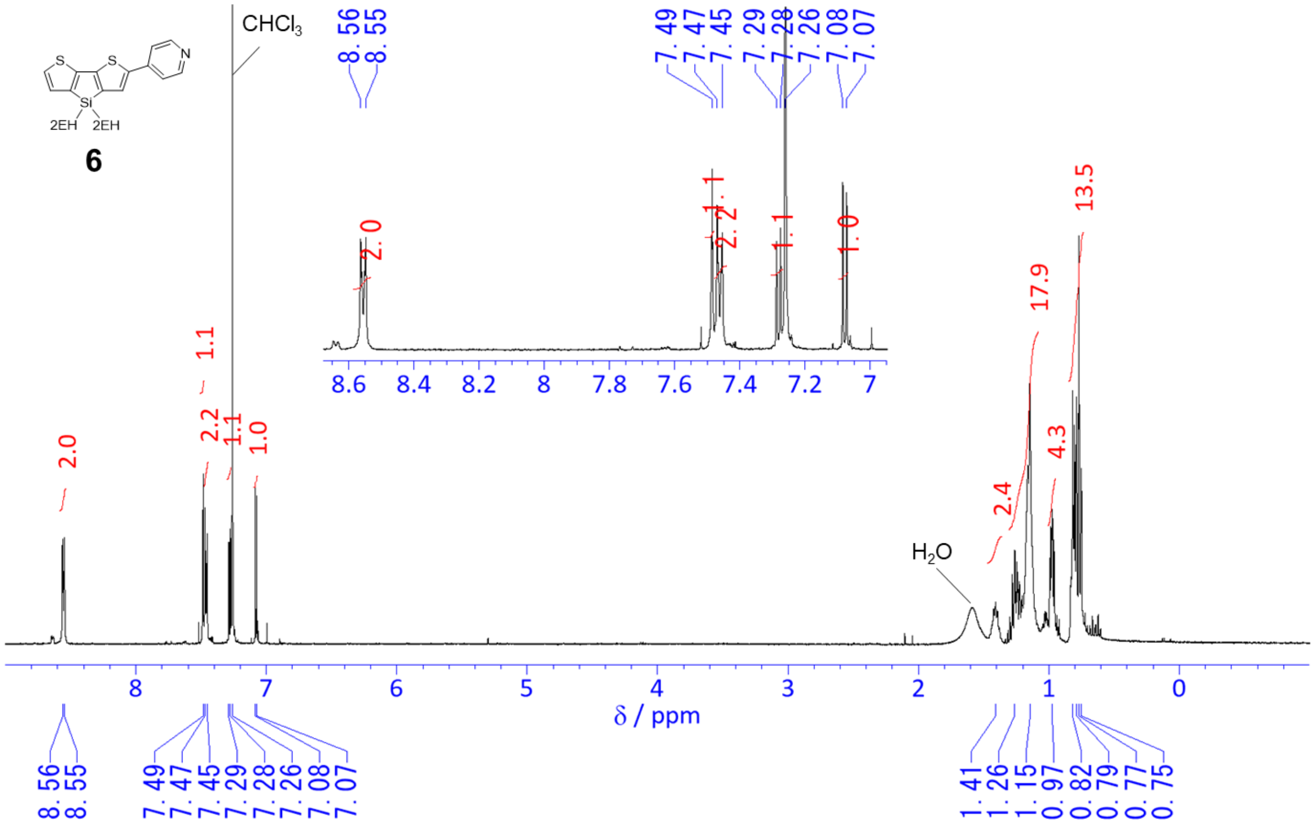
^{1}H NMR spectrum of **4** in acetone-d$_6$ at room temperature (500 MHz).



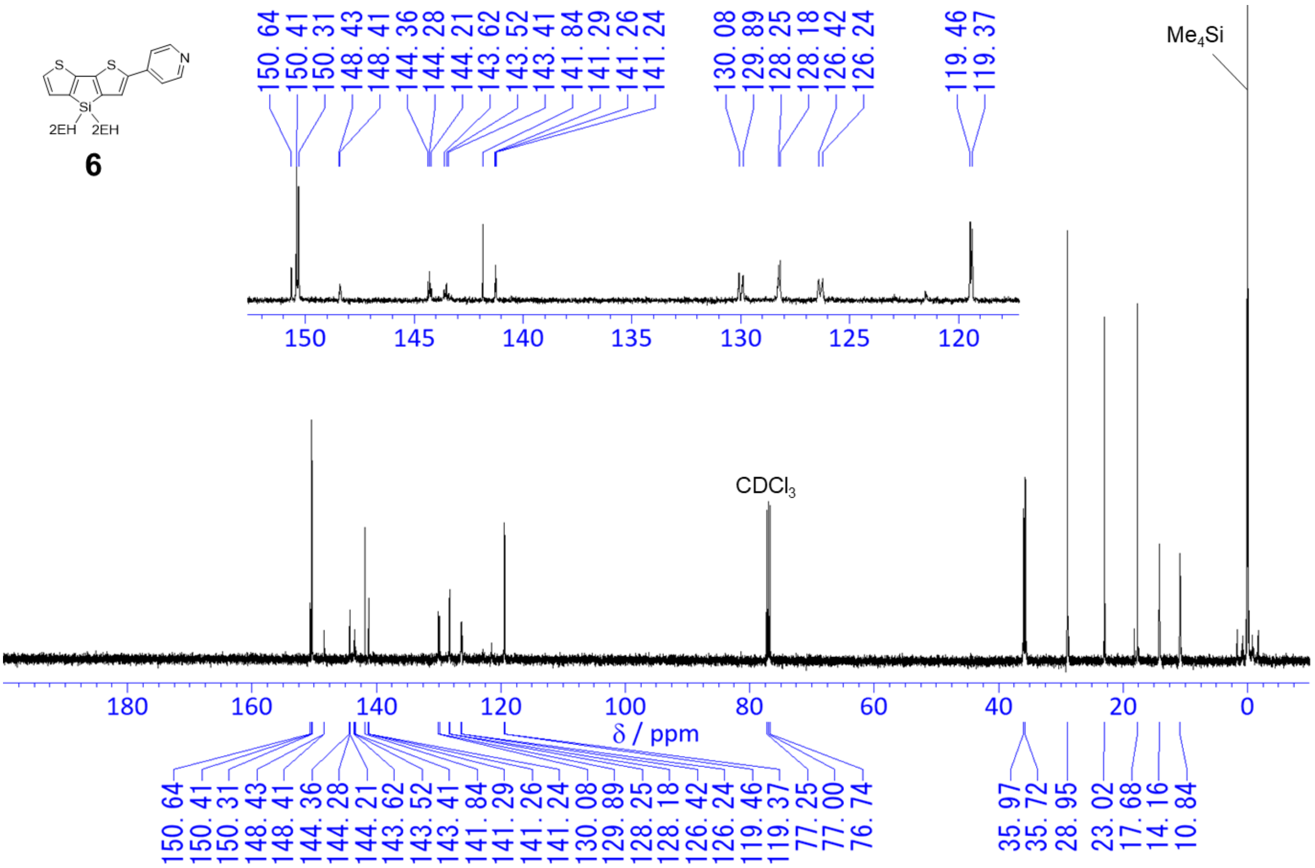
^{13}C NMR spectrum of **4** in CD$_2$Cl$_2$ at room temperature (125 MHz).



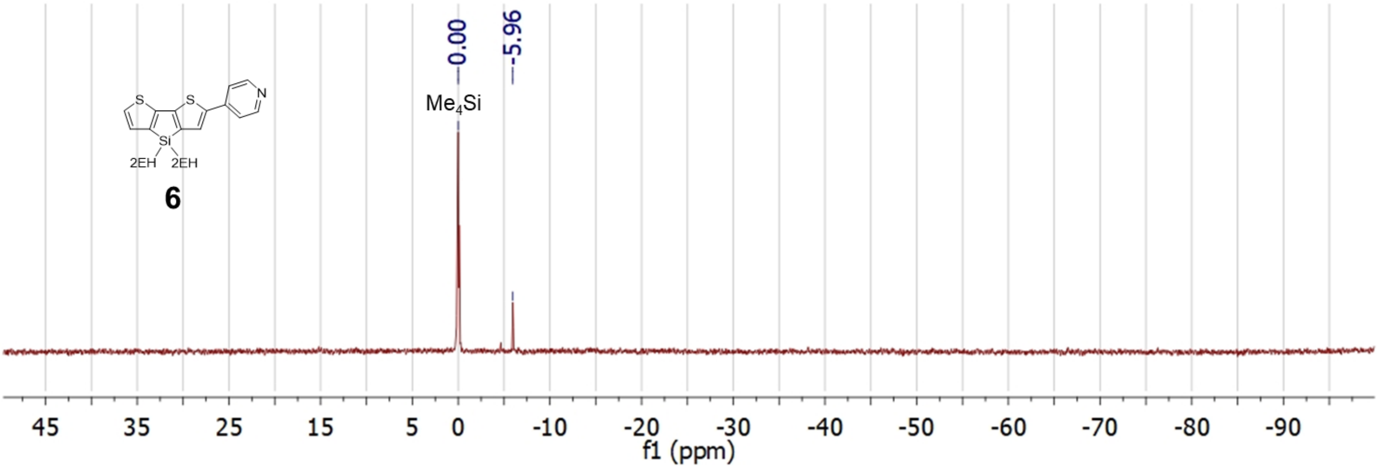
^{1}H NMR spectrum of **DTGCA** in DMSO-d_6 with a droplet of acetic acid-d_4 at room temperature (500 MHz).



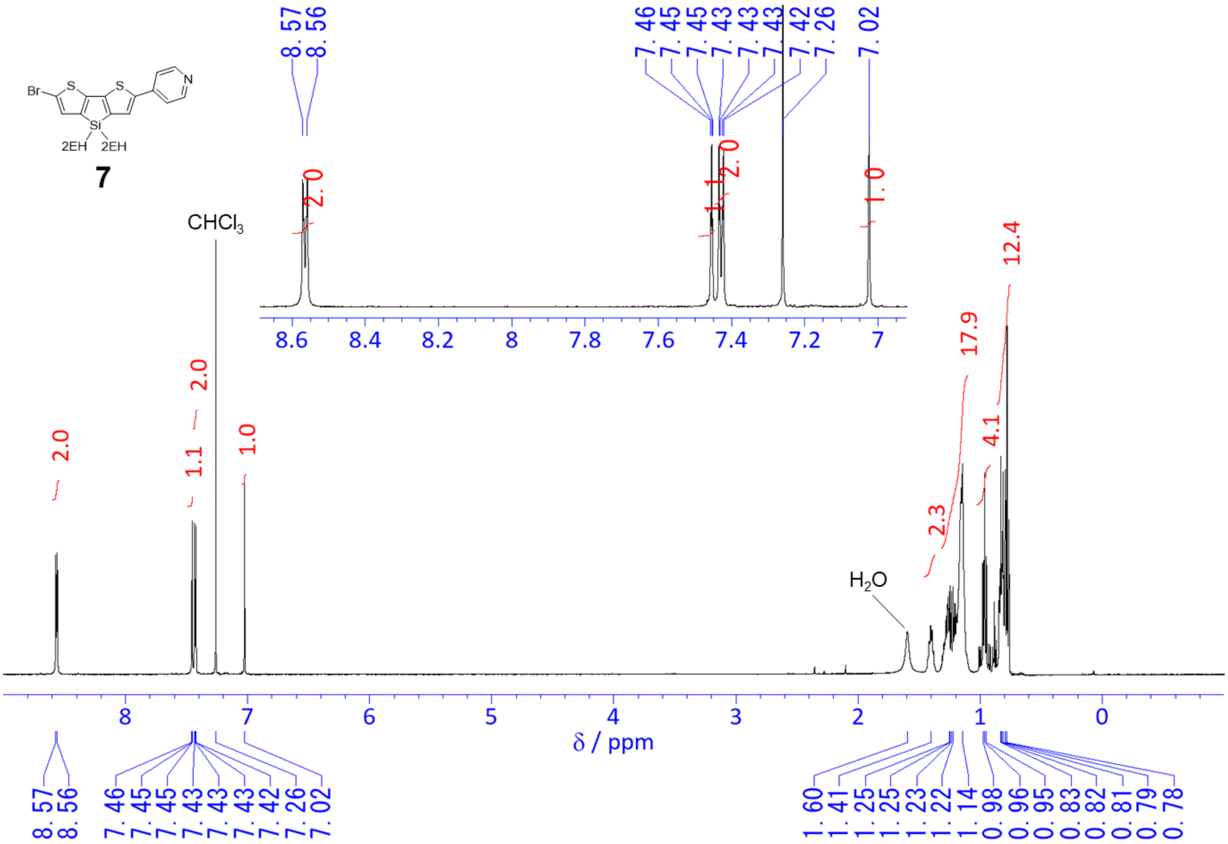
^{1}H NMR spectrum of **6** in $CDCl_3$ at room temperature (400 MHz).



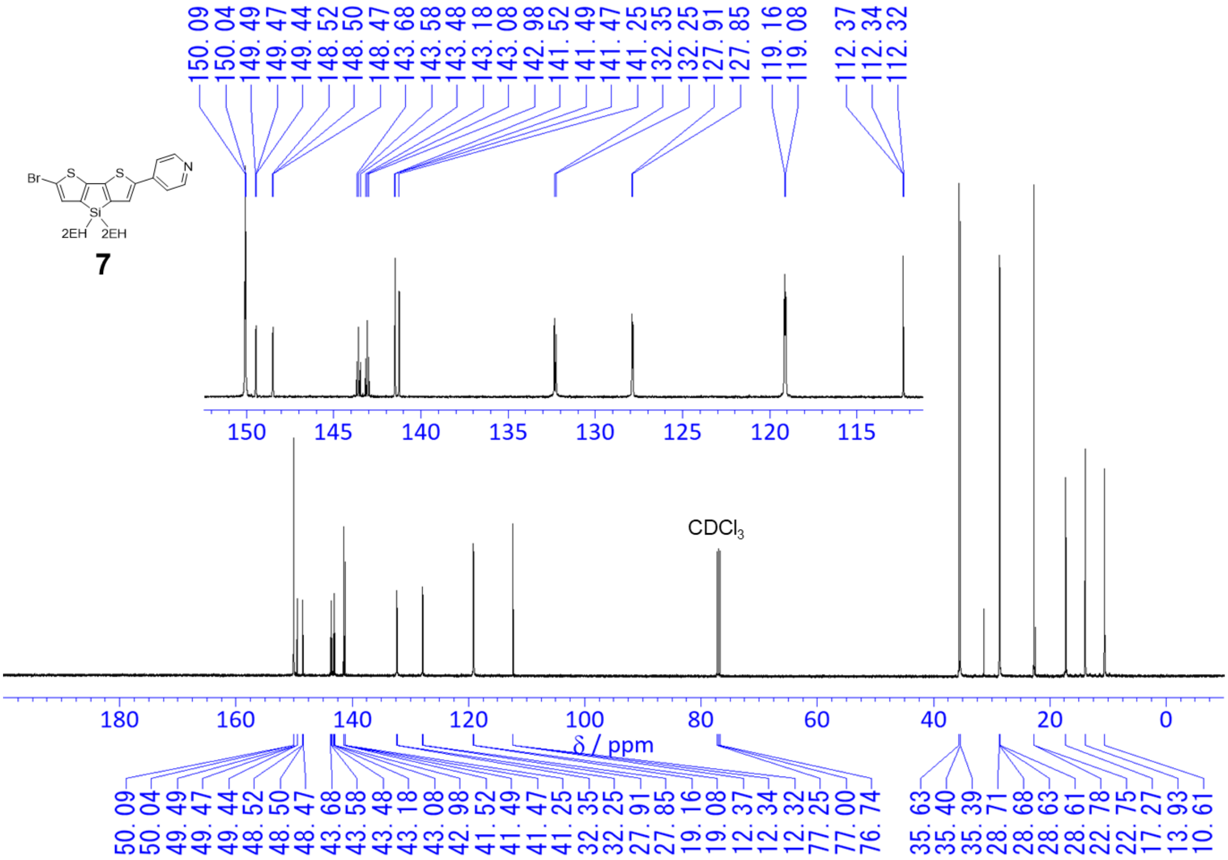
^{13}C NMR spectrum of **6** in CDCl$_3$ at room temperature (125 MHz).



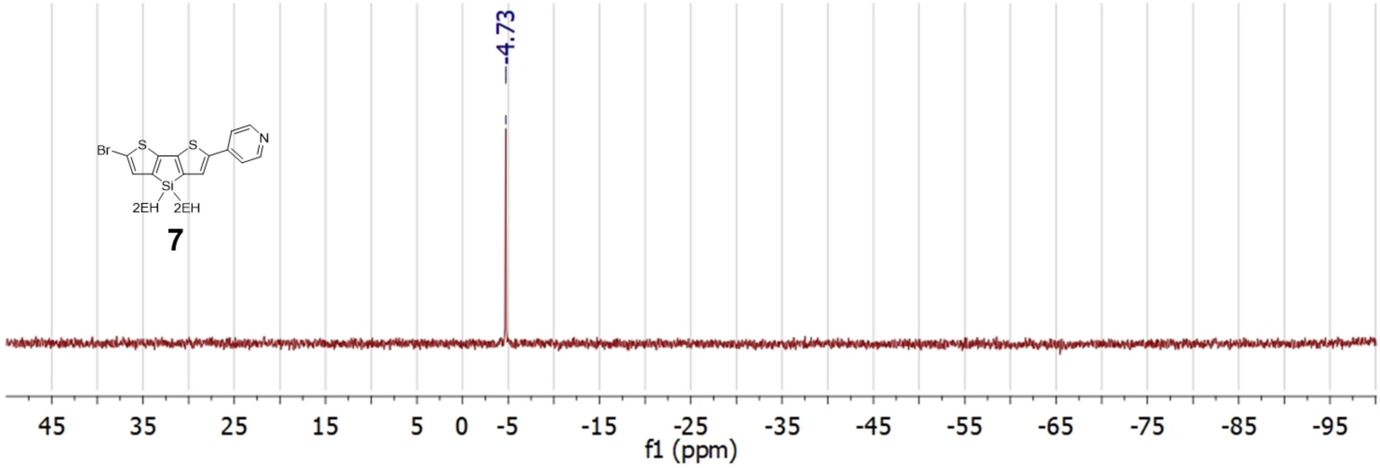
^{29}Si NMR spectrum of **6** in CDCl$_3$ at room temperature (99 MHz).



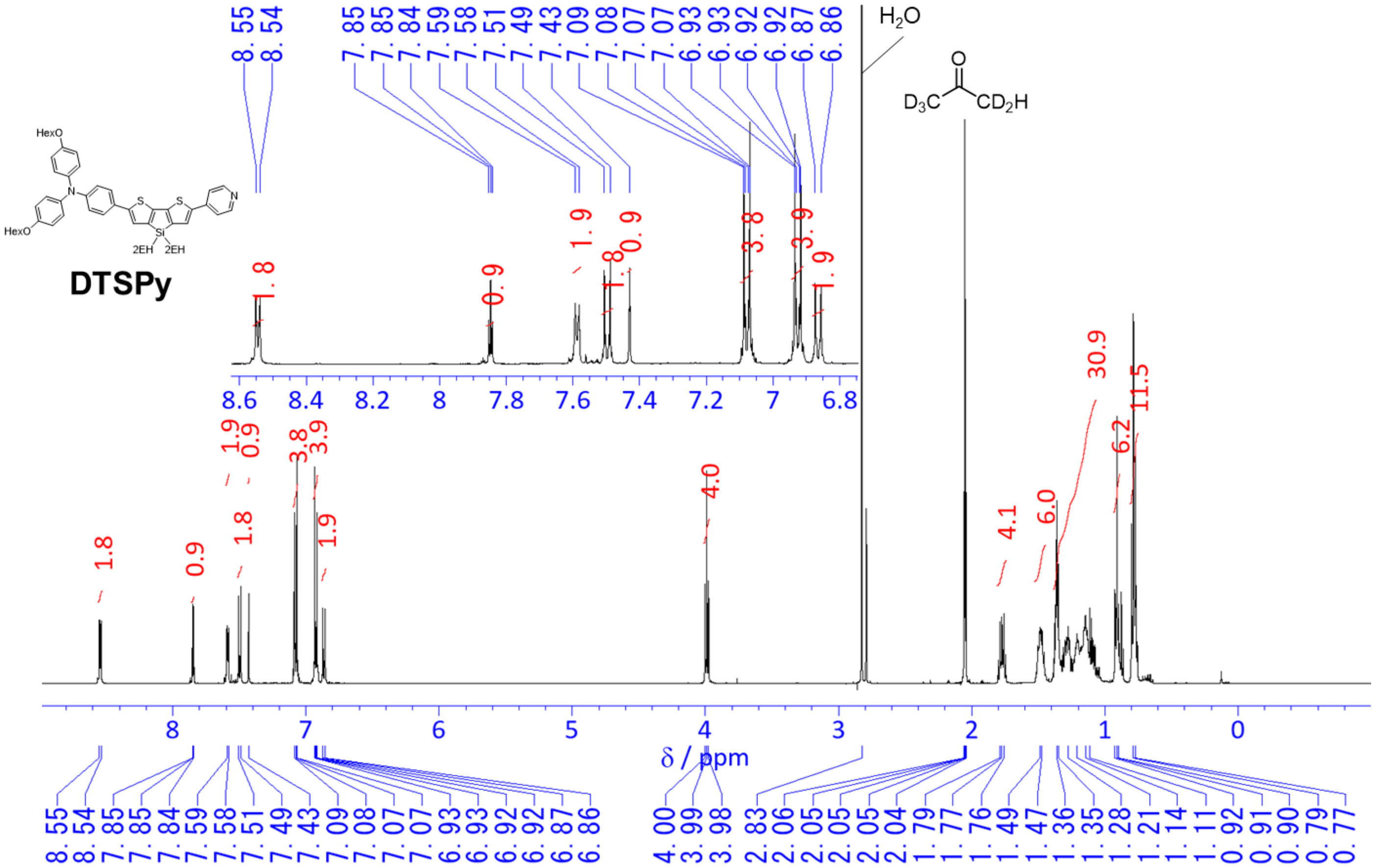
^{1}H NMR spectrum of **7** in CDCl$_3$ at room temperature (500 MHz).



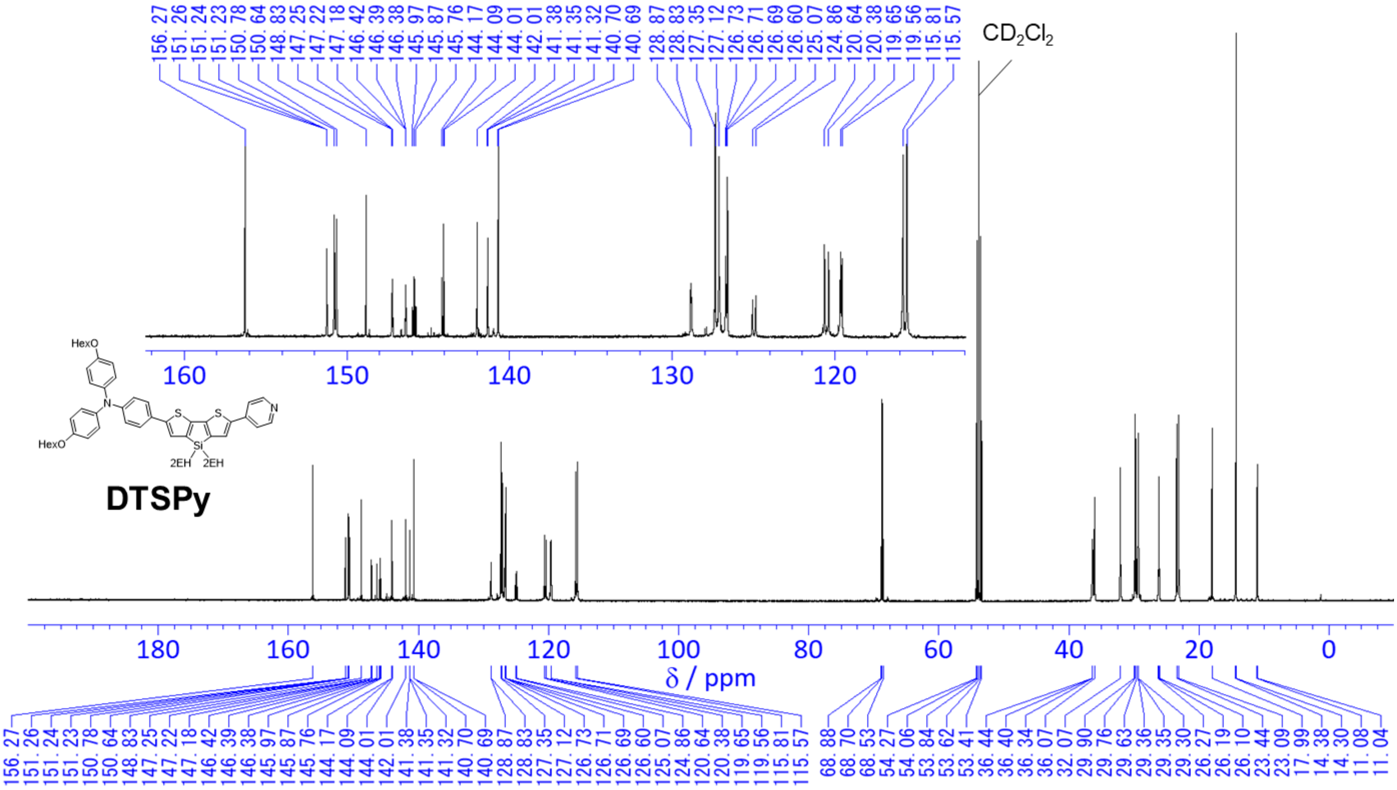
^{13}C NMR spectrum of **7** in CDCl$_3$ at room temperature (125 MHz).



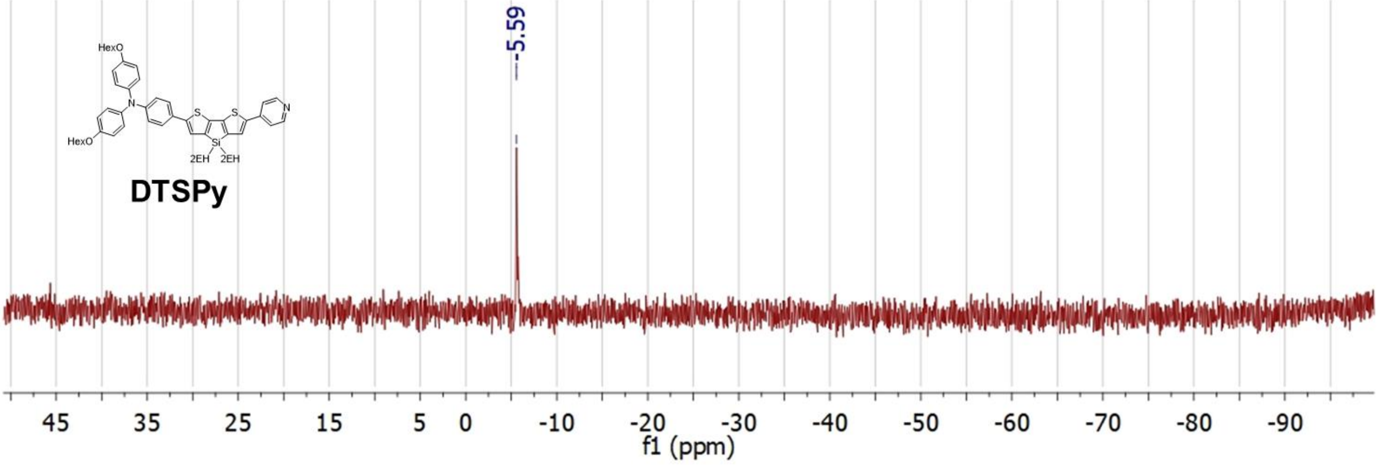
^{29}Si NMR spectrum of **7** in $CDCl_3$ at room temperature (99 MHz).



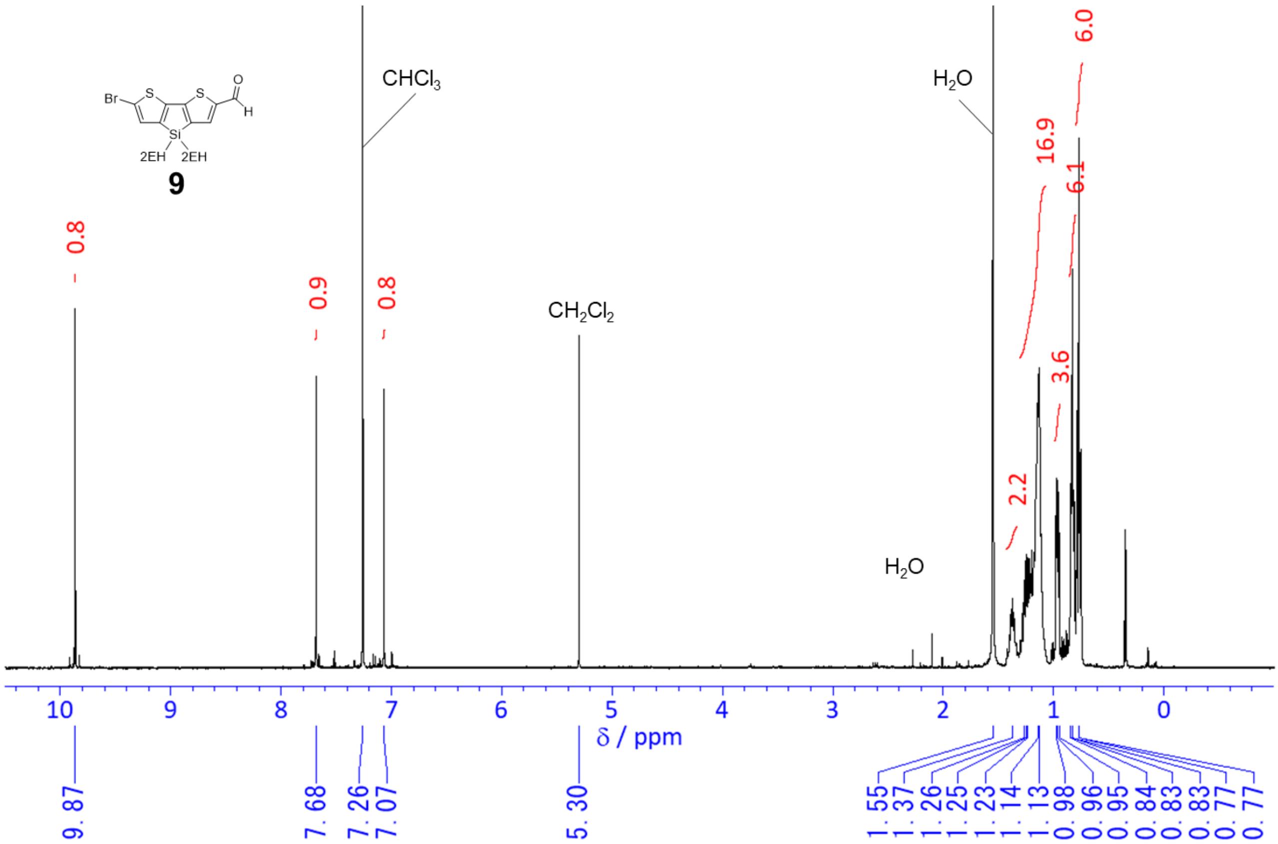
^{1}H NMR spectrum of **DTSPy** in acetone-d_6 at room temperature (500 MHz).



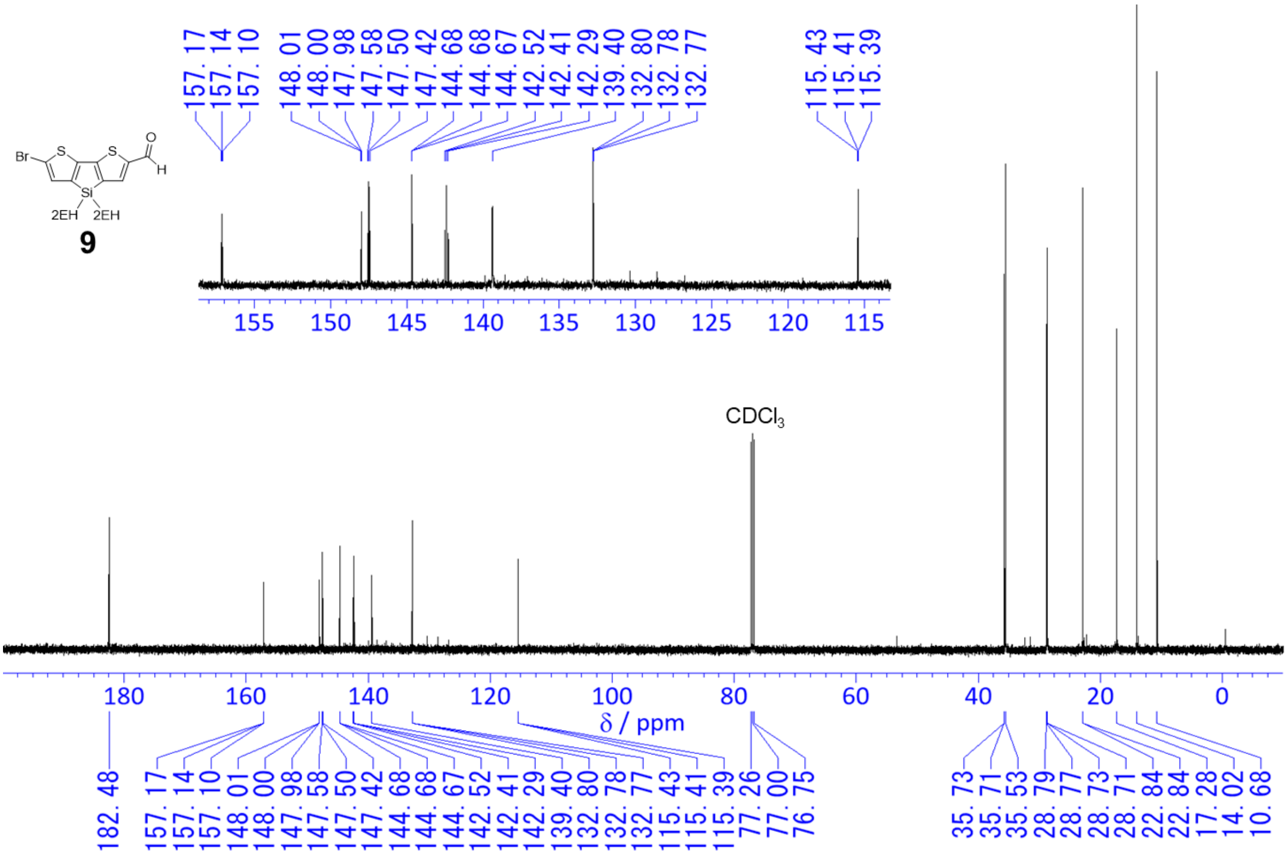
^{13}C NMR spectrum of **DTSPy** in CD_2Cl_2 at room temperature (125 MHz).



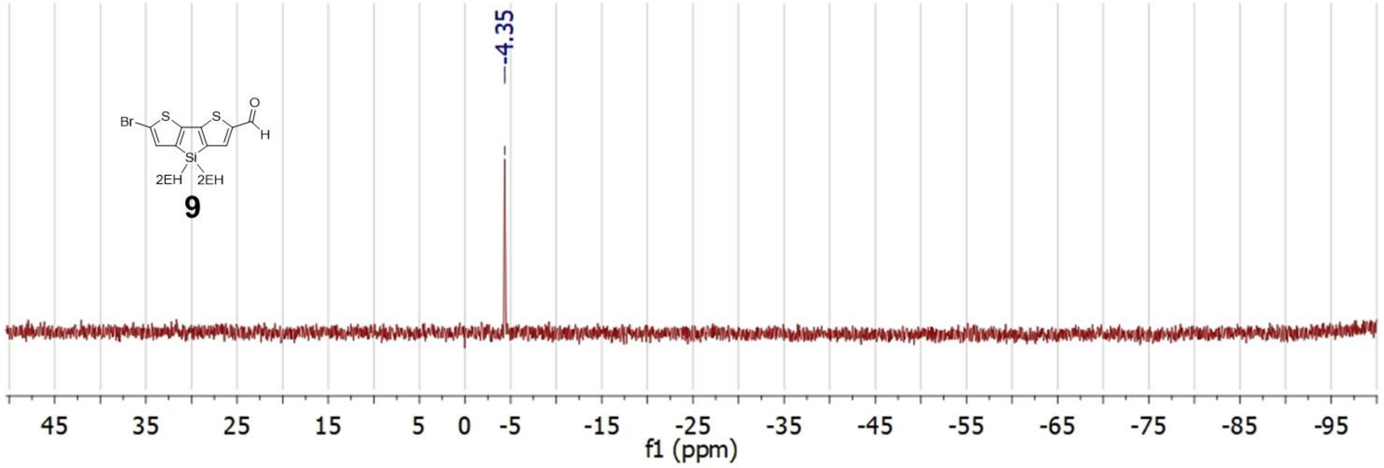
^{29}Si NMR spectrum of **DTSPy** in acetone-d_6 at room temperature (99 MHz).



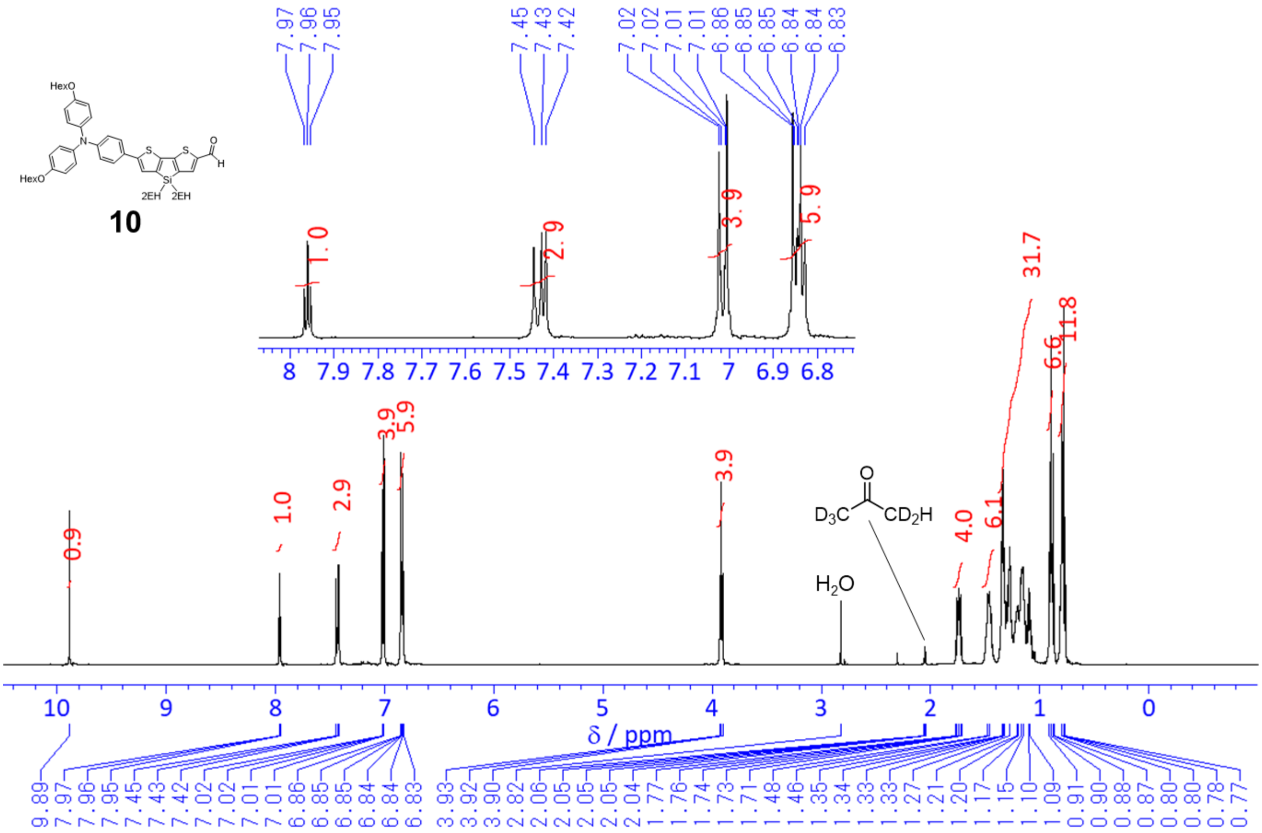
^{1}H NMR spectrum of **9** in $CDCl_3$ at room temperature (400 MHz).



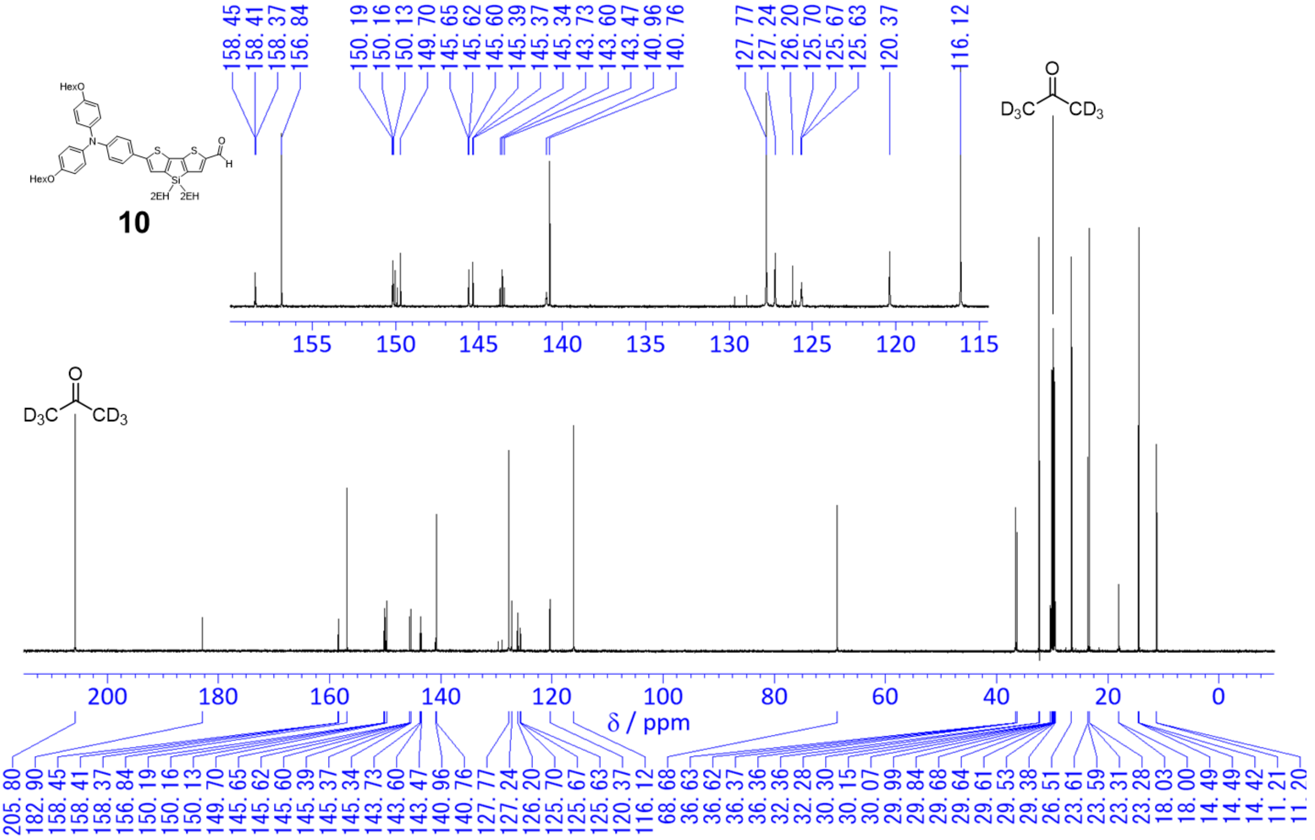
^{13}C NMR spectrum of **9** in $CDCl_3$ at room temperature (125 MHz).



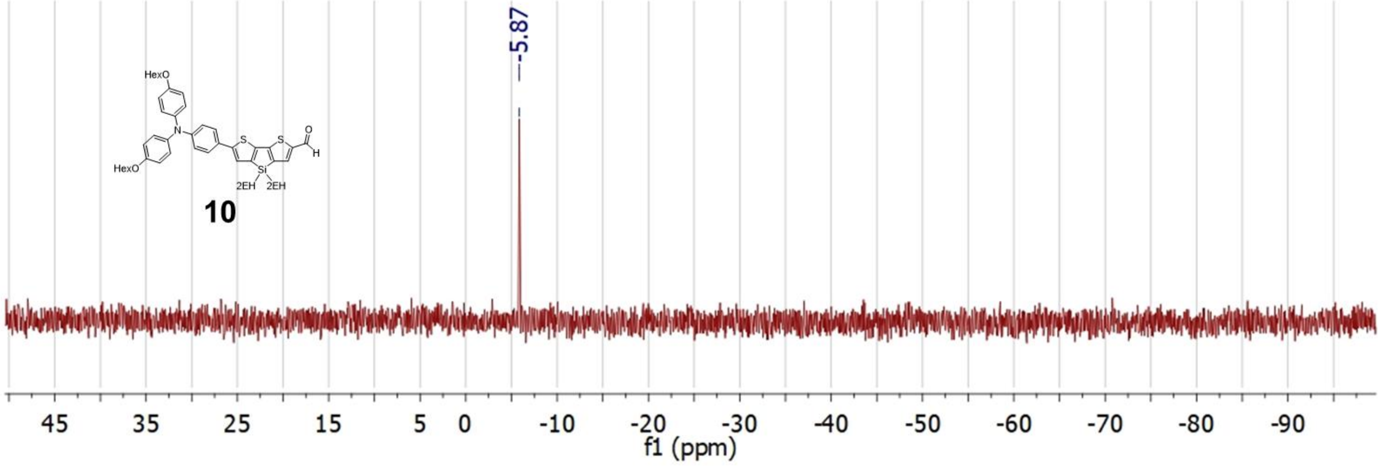
^{29}Si NMR spectrum of **9** in $CDCl_3$ at room temperature (99 MHz).



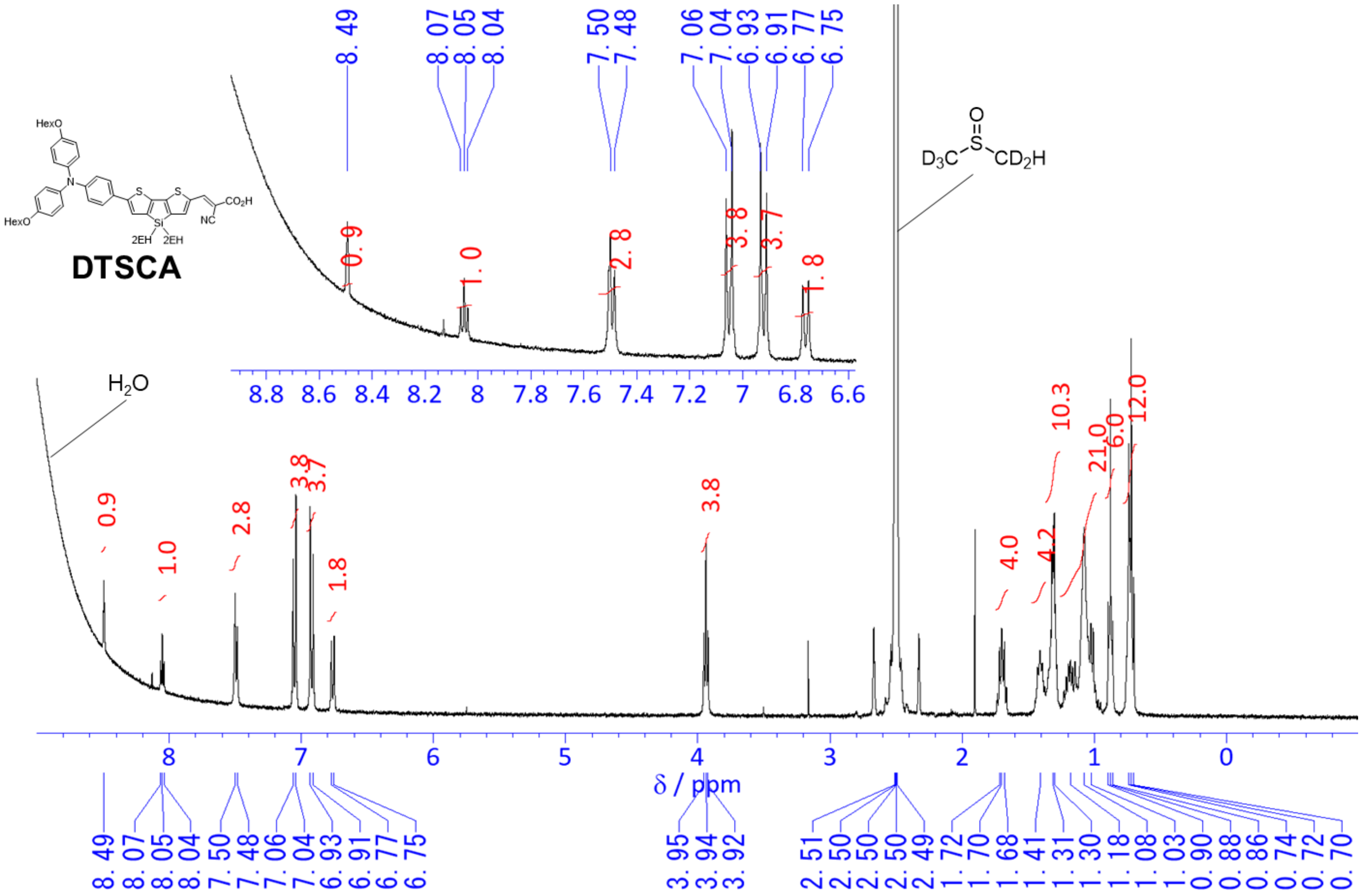
^{1}H NMR spectrum of **10** in acetone-d_6 at room temperature (500 MHz).



^{13}C NMR spectrum of **10** in acetone-d_6 at room temperature (125 MHz).



^{29}Si NMR spectrum of **10** in acetone-d_6 at room temperature (99 MHz).



^{1}H NMR spectrum of **DTGCA** in DMSO-d_6 with a droplet of trifluoroacetic acid at room temperature (400 MHz).

References

[S1] J. Ohshita, M. Miyazaki, D. Tanaka, Y. Morihara, Y. Fujita, Y. Kunugi, *Polym. Chem.*, 2013, **4**, 3116–3122.

[S2] B. Nketia-Yawson, A-R. Jung, Y. Noh, G.-S. Ryu, G. D. Tabi, K.-K. Lee, B. Kim, Y.-Y. Noh, *ACS Appl. Mater. Interfaces*, 2017, **9**, 7322–7330.

[S3] J. Hou, H.-Y. Chen, S. Zhang, G. Li, Y. Yang, *J. Am. Chem. Soc.*, 2008, **130**, 16144–16145.