## Supporting Information

# Dithienonaphthobisthiadiazole Synthesized by Thienannulation of Electron-Deficient Ring: Building Unit for High-Performance π-Conjugated Polymers

*Tsubasa Mikie,[1,2]* Tomokazu Morioku,[1] Shota Suruga,[1] Momoka Hada,[2] Yuki Sato,[3] Hideo Ohkita,[3] and Itaru Osaka[1,2]**

[1] Applied Chemistry Program, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

[2] School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

[3] Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

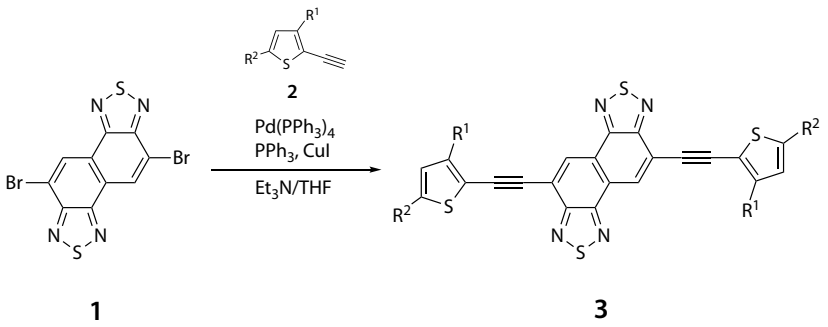
E-mail: mikie@hiroshima-u.ac.jp, iosaka@hiroshima-u.ac.jp

## 1. Materials and synthesis.

### 1-1. Materials

All chemicals and solvents were used as received unless otherwise indicated. Super dehydrated tetrahydrofuran (THF) and toluene was purchased from Wako Pure Chemical Industries Ltd. (4,8-Bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis-(trimethylstannane) (**7**) and 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**11**) were purchased from Ossila Ltd. and Tokyo Chemical Industry Co., Ltd., respectively. 5,10-Dibromonaphtho[1,2-*c*:5,6-*c'*]bis[1,2,5]thiadiazole (**1**),[S1] 2-bromo-3-(2-decyltetradecyl)thiophene (**8**: $R^1$ = DT, $R^2$ = H),[S2] 2-bromo-3-(2-hexyldecyl)thiophene (**8**: $R^1$ = HD, $R^2$ = H),[S3] 2-bromo-3-(2-butyloctyl)thiophene (**8**: $R^1$ = BO, $R^2$ = H),[S3] 2-bromo-3-dodecylthiophene (**8**: $R^1$ = C12, $R^2$ = H),[S3] 5,10-bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)naphtho[1,2-*c*:5,6-*c'*]bis([1,2,5]thiadiazole) (**14**),[S1] **PNTz4T**[S1] and **PNTz1-F**[S4] were synthesized according to the reported procedure. Nuclear magnetic resonance (NMR) spectra of all the compounds were taken on a Varian-500 or a Varian-400 spectrometer, using $CDCl_3$ calibrated with chloroform (CF) at 7.26 ppm for $^1$H-NMR spectra and at 77.16 ppm for $^{13}$C-NMR spectra, respectively. $^1$H-NMR spectrum for the polymer was taken on a JNM-ECA500 spectrometer, using deuterated *o*-dichlorobenzene (DCB-$d_4$) calibrated with *o*-dichlorobenzene (DCB) at 7.15 and 6.87 ppm. High-resolution mass spectrum (HRMS) was measured using LTQ Orbitrap XL (Thermo Fisher Scientific, Inc.). Polymerization was carried out using a microwave reactor (Biotage Initiator). Molecular weights were determined by gel permeation chromatography (GPC) by calibrating with polystyrene standards using a TOSOH at 180 °C with 1,2,4-trichlorobenzene (TCB) as a solvent, which was calibrated with polystyrene standards.

## 1-2. Synthesis and characterization of TNT-based polymers




*5,10-Bis((3-(2-decyltetradecyl)thiophen-2-yl)ethynyl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**3 (R¹ = DT, R² = H)**]*

Under argon atmosphere, **1** (3.2 g, 8.0 mmol), **2 (R¹ = DT, R² = H)** (8.9 g, 20 mmol), CuI (30 mg, 0.16 mmol), $Pd(PPh_3)_4$ (185 mg, 0.16 mmol), $PPh_3$ (50 mg, 0.19 mmol), triethylamine (100 mL), and THF (100 mL) were placed to a three-necked round-bottom flask equipped with condenser. The solution was degassed by argon bubbling and then stirred at 90 ℃ for 12 h. After cooling to room temperature, water was added, and the resulting mixture was extracted with CF. The organic layer was washed with water and brine, and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was purified by silica-gel column chromatography using hexane/CF (gradually changing the ratio from 10/1 to 3/1) as eluent ($R_f$ = 0.4 for the ratio of 3/1) and then reprecipitated from methanol to obtain **3 (R¹ = DT, R² = H)** (8.5 g, 7.5 mmol) in the 94% yield as orange solid.

$^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.01 (s, 2H), 7.31 (d, *J* = 5.1 Hz, 2H), 6.94 (d, *J* = 5.1 Hz, 2H), 2.89 (d, *J* = 7.0 Hz, 4H), 1.87–1.80 (m, 2H), 1.34–1.16 (m, 80H), 0.87–0.83 (m, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 154.30, 152.54, 149.38, 129.34, 129.20, 127.58, 125.61, 118.28, 117.32, 91.68, 91.50, 39.53, 34.58, 33.65, 32.07, 32.05, 30.27, 29.87, 29.85, 29.83, 29.79, 29.50, 29.48, 26.79, 22.84, 22.81, 14.26, 14.25; HRMS (APCI): Calcd. for $C_{70}H_{104}N_4S_4$ $[M+H]^+$: 1129.7217, Found 1129.72327.

*5,10-Bis((5-(tert-butyldimethylsilyl)-3-(2-decyltetradecyl)thiophen-2-yl)ethynyl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**3 ($R^1$ = DT, $R^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using **1** (3.0 g, 7.5 mmol), **2 ($R^1$ = DT, $R^2$ = TBS)** (14 g, 24 mmol), CuI (46 mg, 0.25 mmol), $Pd(PPh_3)_4$ (277 mg, 0.25 mmol), $PPh_3$ (105 mg, 0.40 mmol), triethylamine (80 mL), and THF (80 mL). **3 ($R^1$ = DT, $R^2$ = TBS)** (9.1 g, 6.7 mmol) was obtained in 89% yield as orange solid. $R_f$ value of the product was 0.2 using hexane as eluent.

$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.99 (s, 2H), 7.03 (s, 2H), 2.88 (d, $J$ = 7.0 Hz, 4H), 1.92–1.75 (m, 2H), 1.36–1.16 (m, 80H), 0.95 (s, 18H), 0.89–0.81 (m, 12H), 0.33 (s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 154.25, 152.50, 149.94, 141.00, 137.20, 129.00, 125.53, 123.32, 117.33, 92.70, 91.61, 39.52, 34.32, 33.76, 32.08, 32.06, 30.31, 29.89, 29.85, 29.81, 29.52, 29.50, 26.83, 26.47, 22.85, 22.83, 17.10, 14.28, 14.27, −4.93; HRMS (APCI): Calcd. for $C_{82}H_{132}N_4S_4Si_2$ $[M+H]^+$: 1357.8946, Found 1358.89783.

*5,10-Bis((5-(tert-butyldimethylsilyl)-3-(2-hexyldecyl)thiophen-2-yl)ethynyl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**3 ($R^1$ = HD, $R^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using **1** (1.33 g, 3.3 mmol), **2 ($R^1$ = HD, $R^2$ = TBS)** (4.4 g, 8.2 mmol), CuI (31 mg, 0.17 mmol), $Pd(PPh_3)_4$ (191 mg, 0.17 mmol), $PPh_3$ (52 mg, 0.20 mmol), triethylamine (80 mL), and THF (80 mL). **3 ($R^1$ = HD, $R^2$ = TBS)** (3.36 g, 2.96 mmol) was obtained in 90% yield as orange solid. $R_f$ value of the product was 0.3 using hexane/CF for 10/1 (v/v) as eluent.

$^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.99 (s, 2H), 7.03 (s, 2H), 2.88 (d, $J$ = 7.1 Hz, 4H), 1.89–1.81 (m, 2H), 1.42–1.10 (m, 48H), 0.95 (s, 18H), 0.84–0.77 (m, 12H), 0.33 (s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 154.33, 152.57, 149.99, 141.09, 137.27, 129.09, 125.61, 123.27, 117.38, 92.66, 91.62, 39.56, 34.35, 33.76, 32.05, 30.30, 29.94, 29.81, 29.53, 26.81, 26.47, 26.45,

22.83, 22.79, 17.10, 14.23, −4.90, −4.97; HRMS (ESI): Calcd. for $C_{66}H_{100}N_4S_4Si_2$ $[M+H]^+$: 1133.63909, Found 1133.64172.

*5,10-Bis((5-(tert-butyldimethylsilyl)-3-(2-butyloctyl)thiophen-2-yl)ethynyl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**3 ($R^1$ = BO, $R^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using **1** (2.7 g, 6.6 mmol), **2 ($R^1$ = BO, $R^2$ = TBS)** (6.4 g, 16 mmol), CuI (68 mg, 0.36 mmol), $Pd(PPh_3)_4$ (277 mg, 0.25 mmol), $PPh_3$ (111 mg, 0.42 mmol), triethylamine (66 mL), and THF (66 mL). **3 ($R^1$ = BO, $R^2$ = TBS)** (4.7 g, 4.6 mmol) was obtained in 70% yield as orange solid. $R_f$ value of the product was 0.25 using hexane/CF for 10/1 (v/v) as eluent.

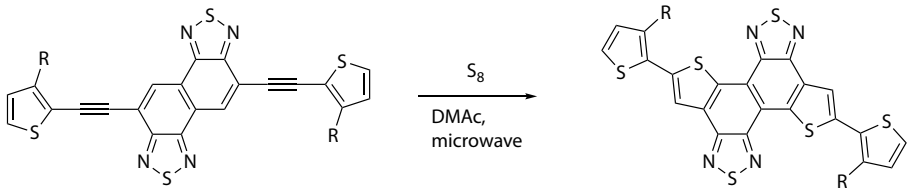
$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.00 (s, 2H), 7.03 (s, 2H), 2.88 (d, $J$ = 7.2 Hz, 4H), 1.89–1.81 (m, 2H), 1.36–1.19 (m, 32H), 0.95 (s, 18H), 0.84–0.77 (m, 12H), 0.33 (s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 154.30, 152.55, 149.97, 141.09, 137.20, 129.09, 125.59, 123.26, 117.35, 92.67, 91.59, 39.48, 34.38, 33.74, 33.44, 32.06, 29.95, 29.04, 26.77, 26.45, 23.26, 22.83, 17.10, 14.27, 14.22, −4.94; HRMS (APCI): Calcd. for $C_{58}H_{84}N_4S_4Si_2$ $[M+H]^+$: 1020.51119, Found: 1020.51190.

*5,10-Bis((5-(tert-butyldimethylsilyl)-3-dodecylthiophen-2-yl)ethynyl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**3 ($R^1$ = C12, $R^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using **1** (0.80 g, 2.0 mmol), **2 ($R^1$ = C12, $R^2$ = TBS)** (2.2 g, 5.6 mmol), CuI (21 mg, 0.11 mmol), $Pd(PPh_3)_4$ (277 mg, 0.25 mmol), $PPh_3$ (35 mg, 0.13 mmol), triethylamine (10 mL), and THF (10 mL). **3 ($R^1$ = C12, $R^2$ = TBS)** (1.2 g, 1.2 mmol) was obtained in 60% yield as orange solid.

$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.98 (s, 2H), 7.07 (s, 2H), 2.94 (t, 4H), 1.77 (q, $J$ = 7.5 Hz, 4H), 1.51–1.07 (m, 36H), 0.95 (s, 18H), 0.85 (t, $J$ = 6.9 Hz, 6H), 0.33 (s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 154.29, 152.51, 150.86, 141.43, 136.52, 129.04, 125.55, 122.77, 117.31, 92.71, 91.38, 32.05, 30.66, 29.86, 29.80, 29.61, 29.50, 26.47, 22.82, 17.08, 14.25,

−4.89; HRMS (APCI): Calcd. for $C_{58}H_{84}N_4S_4Si_2$ $[M+H]^+$: 1021.5190, Found 1021.5199.

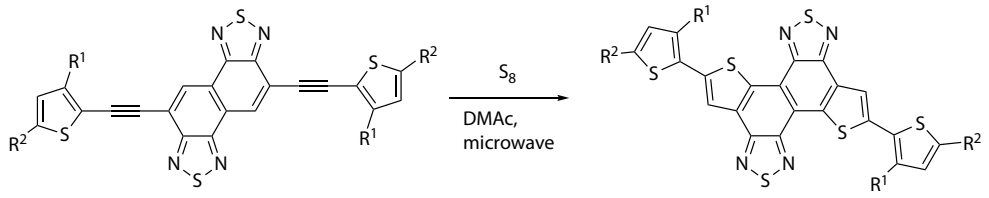



**3** **5**

*5,11-Bis(3-(2-decyltetradecyl)thiophen-2-yl)dithieno[3',2':3,4;3'',2'':7,8]naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**5a (R = DT)**]*

**3 (R[1] = DT)** (282 mg, 0.25 mmol), $S_8$ (257 mg, 1.0 mmol), and *N*,*N*-dimethylacetamide (DMAc) (10 mL) were placed into a reaction vessel. The vessel was purged with argon and sealed. The vessel was inserted into the microwave reactor and heated at 200 ℃ for 45 min. After cooling to room temperature, the mixture was poured into water, and was then extracted with dichloromethane (DCM). The organic layer was washed with brine, and then dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was purified by silica-gel column chromatography using hexane/DCM (gradually changing the ratio from 10/0 to 10/1) as eluent ($R_f$ = 0.3 for the ratio of 10/1) to obtain **5a (R[1] = DT)** (76 mg, 0.063 mmol) in the 25% yield as red solid.

$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81 (s, 2H), 7.32 (d, *J* = 5.2 Hz, 2H), 6.99 (d, *J* = 5.2 Hz, 2H), 2.87 (d, *J* = 7.0 Hz, 4H), 1.85–1.74 (m, 2H), 1.41–0.95 (m, 80H), 0.89–0.80 (m, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 150.43, 150.40, 142.12, 140.59, 136.81, 131.32, 130.80, 130.35, 125.07, 120.81, 118.50, 39.20, 34.33, 33.73, 32.07, 32.05, 30.31, 29.89, 29.86, 29.84, 29.80, 29.50, 26.73, 22.83, 14.25; HRMS (ESI): Calcd. for $C_{70}H_{104}N_4S_6$ $[M+H]^+$: 1193.6658, Found 1193.66418.




**3** **4**

*5,11-Bis(5-(tert-butyldimethylsilyl)-3-(2-decyltetradecyl)thiophen-2-yl)dithieno[3',2':3,4;3'',2'':7,8]naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**4** (**$R^1$ = DT, $R^2$ = TBS**)]*

The title compound was synthesized by the same procedure as above using **3** (**$R^1$ = DT, $R^2$ = TBS**) (1.5 g, 1.1 mmol), $S_8$ (1.1 g, 4.4 mmol), and DMAc (20 mL). **4** (**$R^1$ = DT, $R^2$ = TBS**) (0.92 g, 0.65 mmol) was obtained in the 59% yield as red solid. $R_f$ value of the product was 0.2 using hexane/DCM for 10/1 (v/v) as eluent.

$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.22 (s, 2H), 7.12 (s, 2H), 2.96 (d, $J$ = 7.3 Hz, 4H), 1.84–1.78 (m, 2H), 1.38–1.09 (m, 80H), 0.99 (s, 18H), 0.89–0.80 (m, 12H), 0.36 (s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 150.16, 150.13, 142.01, 141.27, 139.73, 136.89, 136.40, 136.17, 130.22, 120.09, 118.19, 38.95, 34.31, 33.85, 32.10, 30.41, 29.94, 29.89, 29.84, 29.55, 26.75, 26.65, 22.86, 17.23, 14.29, –4.77; HRMS (ESI): Calcd. for $C_{82}H_{132}N_4S_6Si_2$ $[M+H]^+$: 1421.8388, Found 1422.84363.

*5,11-Bis(5-(tert-butyldimethylsilyl)-3-(2-hexyldecyl)thiophen-2-yl)dithieno[3',2':3,4;3'',2'':7,8]naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**4** (**$R^1$ = HD, $R^2$ = TBS**)]*

The title compound was synthesized by the same procedure as above using **3** (**$R^1$ = HD, $R^2$ = TBS**) (3.42 g, 3.0 mmol), $S_8$ (3.08 g, 12.0 mmol), and DMAc (14 mL). **4** (**$R^1$ = HD, $R^2$ = TBS**) (1.65 g, 1.4 mmol) was obtained in the 46% yield as red solid. $R_f$ value of the product was 0.2 using hexane/CF for the ratio of 10/1 as eluent.

$^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.20 (s, 2H), 7.12 (s, 2H), 2.96 (d, $J$ = 7.2 Hz, 4H), 1.87–

1.77 (m, 2H), 1.37–1.11 (m, 48H), 1.00 (s, 18H), 0.84–0.75 (m, 12H), 0.36 (s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 150.21, 150.18, 142.04, 141.31, 139.73, 136.98, 136.46, 136.11, 130.26, 120.16, 118.26, 38.98, 34.31, 33.88, 33.83, 32.09, 32.06, 30.37, 30.04, 29.85, 29.56, 26.72, 26.63, 22.87, 22.82, 17.22, 14.27, −4.78; HRMS (ESI): Calcd. for $C_{66}H_{100}N_4S_6Si_2$ $[M+H]^+$: 1197.58780, Found 1197.58618.

*5,11-Bis(5-(tert-butyldimethylsilyl)-3-(2-butyloctyl)thiophen-2-yl)dithieno[3',2':3,4;3'',2'':7,8]naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**4 (R$^1$ = BO, R$^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using **3 (R$^1$ = BO, R$^2$ = TBS)** (1.0 g, 1.0 mmol), $S_8$ (1.0 g, 4.0 mmol), and DMAc (15 mL). **4 (R$^1$ = BO, R$^2$ = TBS)** (0.54 g, 0.50 mmol) was obtained in the 50% yield as red solid. $R_f$ value of the product was 0.2 using hexane/DCM for 10/1 (v/v) as eluent.

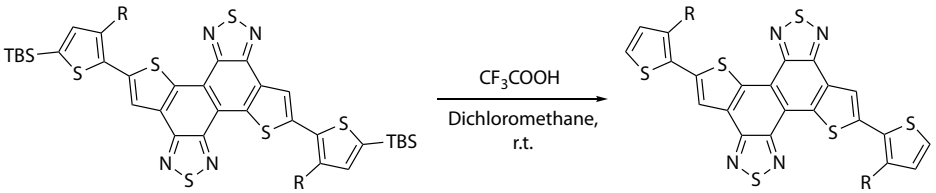
$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.11 (s, 2H), 7.12 (s, 2H), 2.95 (d, $J$ = 7.2 Hz, 4H), 1.88–1.78 (m, 2H), 1.32–1.20 (m, 32H), 1.02 (s, 18H), 0.83–0.79 (m, 12H), 0.38 (s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$) : δ (ppm) 151.00, 150.97, 142.51, 141.62, 139.63, 137.57, 137.30, 136.04, 130.89, 120.93, 119.19, 39.25, 34.40, 33.98, 33.72, 32.07, 29.97, 29.86, 29.09, 26.79, 26.60, 23.29, 22.82, 17.18, 14.23, 14.18, −4.78; HRMS (APCI): Calcd. for $C_{58}H_{84}N_4S_6Si_2$ $[M+H]^+$: 1084.45533, Found: 1084.45642.

*5,11-Bis(5-(tert-butyldimethylsilyl)-3-dodecylthiophen-2-yl)dithieno[3',2':3,4;3'',2'':7,8]naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**4 (R$^1$ = C12, R$^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using **3 (R$^1$ = C12, R$^2$ = TBS)** (0.10 g, 0.10 mmol), $S_8$ (0.10 g, 0.40 mmol), and DMAc (4 mL). **4 (R$^1$ = C12, R$^2$ = TBS)** (61 mg, 0.056 mmol) was obtained in the 56% yield as red solid. $R_f$ value of the product

was 0.2 using hexane/DCM for 10/1 (v/v) as eluent.

$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.00 (s, 2H), 7.17 (s, 2H), 3.02 (t, 4H), 1.85–1.76 (m, 4H), 1.52–1.18 (m, 36H), 1.03 (s, 18H), 0.84 (t, 6H), 0.39 (s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 150.47, 150.42, 142.23, 142.19, 138.76, 137.71, 136.66, 135.68, 130.53, 120.10, 118.54, 32.07, 30.79, 29.88, 29.82, 29.75, 29.70, 29.51, 26.63, 22.82, 17.18, 14.24, –4.72; HRMS (ESI): Calcd. for $C_{58}H_{84}N_4S_6Si_2$ $[M+H]^+$: 1085.4632, Found 1085.46411.




**4** **5**

*5,11-Bis(3-(2-decyltetradecyl)thiophen-2-yl)dithieno[3',2':3,4;3'',2'':7,8]naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**5a (R = DT)**]*

To a solution of **4a (R = DT)** (2.6 g, 1.8 mmol) in DCM (5 mL), trifluoroacetic acid (15 mL) in DCM (40 mL) was added dropwise. The solution was then stirred for 2.5 h at room temperature. The reaction was quenched by adding saturated aqueous solution of sodium bicarbonate, and the resulting mixture was extracted with CF. The organic layer was washed with water and brine, and then dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was purified by silica-gel column chromatography using hexane/CF (gradually changing the ratio from 10/1 to 1/1) as eluent ($R_f$ = 0.5 for the ratio of 3/1 (v/v)) and recrystallized from DCM/hexane to obtain **5a (R = DT)** (2.2 g, 1.8 mmol) in the 98% yield as purple solid.

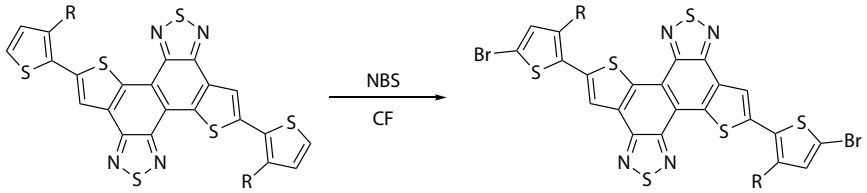
$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81 (s, 2H), 7.32 (d, $J$ = 5.2 Hz, 2H), 6.99 (d, $J$ = 5.2 Hz, 2H), 2.87 (d, $J$ = 7.0 Hz, 4H), 1.85–1.74 (m, 2H), 1.41–0.95 (m, 80H), 0.89–0.80 (m, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 150.43, 150.40, 142.12, 140.59, 136.81, 131.32, 130.80, 130.35, 125.07, 120.81, 118.50, 39.20, 34.33, 33.73, 32.07, 32.05, 30.31, 29.89, 29.86, 29.84,

29.80, 29.50, 26.73, 22.83, 14.25; HRMS (ESI): Calcd. for $C_{70}H_{104}N_4S_6$ $[M+H]^+$: 1193.6658, Found 1193.66418.

*5,11-Bis(3-(2-hexyldecyl)thiophen-2-yl)dithieno[3',2':3,4;3'',2'':7,8]naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**5b (R = HD)**]*

The title compound was synthesized by the same procedure as above using **4b (R = HD)** (1.32 g, 1.1 mmol) in DCM (11 mL) and trifluoroacetic acid (16 mL) in DCM (33 mL), and then purified by silica-gel column chromatography using hexane/CF (gradually changing the ratio from 10/1 to 1/1) as eluent ($R_f$ = 0.35 for the ratio of 10/1) and recrystallized from DCM/hexane to obtain **5b (R = HD)** (1.04 g, 1.08 mmol) in the 98% yield as purple solid. $R_f$ value of the product was 0.5 using hexane/DCM for 3/1 (v/v) as eluent.

$^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.07 (s, 2H), 7.35 (d, $J$ = 5.2 Hz, 2H), 7.02 (d, $J$ = 5.2 Hz, 2H), 2.93 (d, $J$ = 7.2 Hz, 4H), 1.84–1.72 (m, 2H), 1.35–1.10 (m, 48H), 0.84–0.75 (m, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 150.76, 150.72, 142.22, 140.75, 137.19, 131.42, 131.19, 130.62, 125.36, 121.28, 118.93, 39.34, 39.23, 34.19, 33.71, 33.64, 32.07, 32.04, 30.29, 29.95, 29.83, 29.50, 26.68, 22.81, 22.80, 14.23; HRMS (ESI): Calcd. for $C_{54}H_{72}N_4S_6$ $[M+H]^+$: 969.41053, Found 969.41315.




**5** **6**

*5,11-Bis(5-bromo-3-(2-decyltetradecyl)thiophen-2-yl)dithieno[3',2':3,4;3'',2'':7,8]naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**6a (R = DT)**]*

**5a (R = DT)** (2.9 g, 2.4 mmol) and CF (50 mL) were placed in a three-necked round-bottom flask. *N*-Bromosuccinimide (NBS) (0.87 g, 4.9 mmol) was added in several portions at

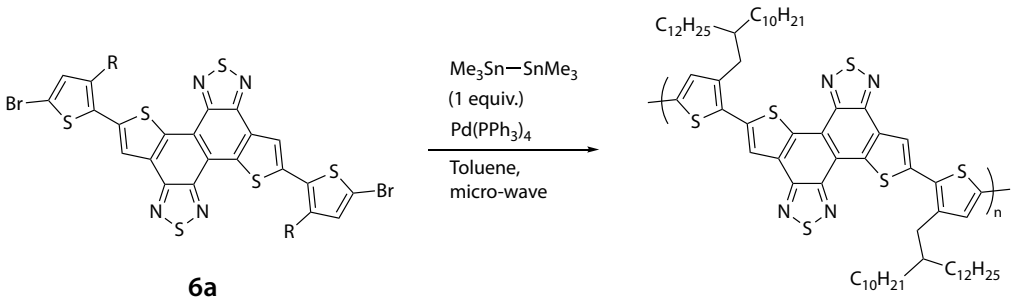
0 °C. The reaction mixture was gradually warmed to room temperature and then further stirred for 2 h. The reaction was quenched by adding saturated aqueous solution of sodium bicarbonate, and the resulting mixture was extracted with CF. The organic layer was washed with water and brine, and then dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was purified by silica-gel column chromatography using hexane/CF (gradually changing the solvent ratio from 10/1 to 5/1) as eluent ($R_f$ = 0.5 for the ratio of 10/1), and recrystallized from CF/ethyl acetate to give **6a (R = DT)** (2.9 g, 2.1 mmol) in the 88% yield as purple solid.

$^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.97 (s, 2H), 6.97 (s, 2H), 2.85 (d, *J* = 7.1 Hz, 4H), 1.78–1.72 (m, 2H), 1.32–1.11 (m, 80H), 0.89–0.80 (m, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 150.37, 150.34, 141.32, 140.89, 137.01, 133.87, 132.25, 130.33, 121.23, 118.56, 112.35, 39.23, 34.29, 33.62, 32.07, 32.05, 30.25, 29.88, 29.84, 29.80, 29.51, 29.48, 26.68, 22.84, 22.82, 14.25; HRMS (APCI): Calcd. for $C_{70}H_{102}N_4Br_2S_6$ $[M+H]^+$: 1349.4868, Found: 1351.48669.

*5,11-Bis(5-bromo-3-(2-hexyldecyl)thiophen-2-yl)dithieno[3',2':3,4;3'',2'':7,8]naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) [**6b (R = HD)**]*

The title compound was synthesized by the same procedure as above using **5b (R = HD)** (0.94 g, 0.97 mmol) in CF (40 mL), NBS (0.35 g, 1.9 mmol), hexane/CF (gradually changing the solvent ratio from 4/1 to 1/1) as eluent ($R_f$ = 0.5 for the ratio of 10/1) for silica-gel column chromatography, and CF/ethanol for recrystallization. **6b (R = HD)** (1.0 g, 0.90 mmol) was obtained in the 93% yield as purple solid.

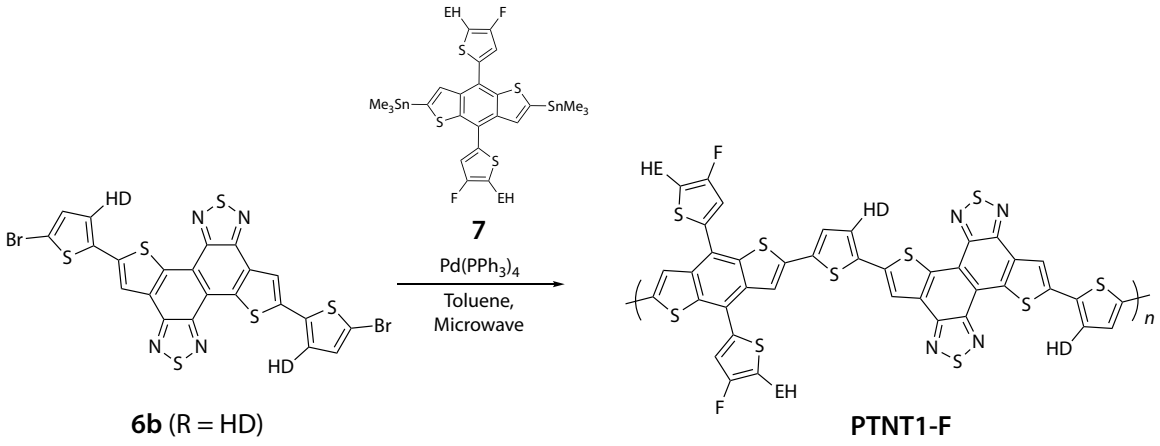
$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.08 (s, 2H), 6.98 (s, 2H), 2.87 (d, *J* = 7.1 Hz, 4H), 1.87–1.80 (m, 2H), 1.35–1.05 (m, 48H), 0.84–0.74 (m, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 150.51, 150.47, 141.38, 140.87, 137.17, 133.84, 132.15, 130.44, 121.43, 118.74, 112.37, 39.25, 34.21, 33.62, 33.54, 32.07, 32.04, 30.24, 29.91, 29.82, 29.49, 26.65, 26.63, 22.82, 22.80, 14.25, 14.24; HRMS (ESI): Calcd. for $C_{54}H_{70}N_4Br_2S_6$ $[M+H]^+$: 1126.22700, Found: 1126.22913.




**6a** **PTNT2T**

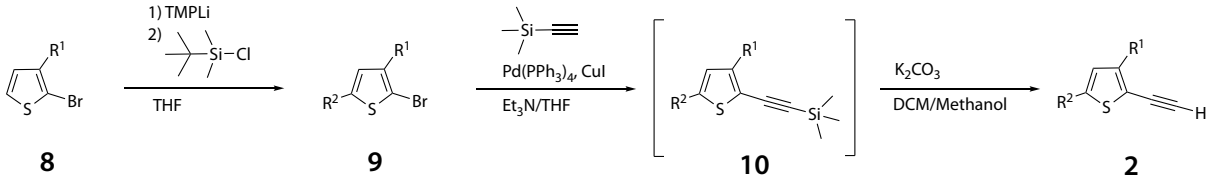
***PTNT2T***

**6a** (67.6 mg, 0.05 mmol), hexamethylditin (16.4 mg, 0.05 mmol), $Pd(PPh_3)_4$, (1.16 mg, 0.0005 mmol), and 2 mL of toluene were placed in a reaction vessel. The vessel was purged with argon and sealed. The vessel was inserted into the microwave reactor and heated at 200 ℃ for 2 h. After cooling to room temperature, the reaction mixture was poured into 50 mL of methanol (HCl 5 vol%), and then vigorously stirred for 2 h at room temperature. The precipitate was collected by filtration and subjected to sequential Soxhlet extraction with methanol, hexane, DCM, the mixing solvent with DCM: CF (1:3) to remove low molecular weight fractions. The residue was extracted with CF and the fraction was reprecipitated in methanol. The precipitate was filtered and dried in vacuo to obtain **PTNT2T** (60 mg) in 93% yield as green-black solid. $^1$H-NMR (500 MHz, DCB-$d_4$): $\delta$ (ppm) 8.34–6.65, 4.97, 3.42–2.69, 2.36–0.41.




***PTNT1-F***

**6b** (56.4 mg, 0.05 mmol), **7** (47.0 mg, 0.05 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.53 mg, 0.0005 mmol), P(*o*-tol)$_3$ (1.22 mg, 0.002 mmol), and 2 mL of toluene were placed in a reaction vessel. The vessel was purged with argon and sealed. The vessel was inserted into the microwave reactor and heated at 140 ℃ for 1 h. After cooling to room temperature, the reaction mixture was poured into 50 mL of methanol (HCl 5 vol%), and then vigorously stirred for 2 h at room temperature. The precipitate was collected by filtration and subjected to sequential Soxhlet extraction with methanol, hexane, and DCM to remove low molecular weight fractions. The residue was extracted with CF and then CB. Both fractions were individually reprecipitated in methanol. The precipitate was filtered and dried in vacuo to obtain **PTNT1-F** (70.7 mg for CF fraction, 0.046 mmol) in 92% yield as lustrous blue-black solid. $^1$H-NMR (500 MHz, DCB-$d_4$): δ (ppm) 8.40–6.50, 3.40–2.70, 2.18–0.63.




Scheme S1. Synthetic route to **2**

*tert-Butyl(4-(2-decyltetradecyl)-5-ethynylthiophen-2-yl)dimethylsilane [**2** (**R**$^1$ = **DT, R**$^2$ = **H**)]*

Under argon atmosphere, **8** (**R**$^1$ = **DT**) (47 g, 95 mmol), CuI (0.90 g, 4.7 mmol), $Pd(PPh_3)_4$ (5.5 g, 4.7 mmol), $PPh_3$ (1.5 mg, 0.54 mmol), trimethylsilylacethylene (19.7 mL, 142 mmol, $d$ = 0.71 g mL$^{-1}$), and $Et_3N$/THF (150 mL/150 mL) were placed into a 500 mL of three-necked round-bottom flask equipped with condenser. The reaction mixture was degassed by babbling argon gas, was then stirred at 90 ℃ overnight. After cooling to room temperature, the mixture was extracted with DCM, and the organic layer was washed with water and brine and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was roughly purified by flash silica-gel column chromatography using hexane as eluent ($R_f$ = 0.8) to obtain **10** (**R**$^1$ = **DT, R**$^2$ = **H**) as orange oil. The next desilylation was carried out without further purification.

In a 100 mL round-bottom flask, **10** (**R**$^1$ = **DT, R**$^2$ = **H**), $K_2CO_3$ (20 g, 142 mmol), and DCM/methanol (50/50 mL v/v) were placed, and the mixture was stirred for 12 h at room temperature. Water was added and the resulting mixture was extracted with hexane, and the organic layer was washed with water and brine, and then dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by silica-gel column chromatography using hexane as eluent ($R_f$ = 0.7) to obtain **2** (**R**$^1$ = **DT, R**$^2$ = **H**) (28 g, 65 mmol) in the 68% yield in 2 steps as orange oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.14 (d, $J$ = 5.1 Hz, 1H), 6.81 (d, $J$ = 5.2 Hz, 1H), 3.41 (s, 1H), 2.63 (d, $J$ = 7.1 Hz, 2H), 1.71–1.62 (m, 1H), 1.35–1.14 (m, 40H), 0.90–0.85 (m, 6H);

$^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 148.36, 128.74, 126.04, 117.80, 83.19, 83.19, 39.16, 34.21, 33.61, 32.11, 30.16, 29.88, 29.85, 29.84, 29.83, 29.54, 29.53, 26.72, 22.86, 14.27; HRMS (APCI): Calcd. for $C_{30}H_{52}S$ $[M+H]^+$: 445.3863, Found 445.38638.

*(5-Bromo-4-(2-hexyldecyl)thiophen-2-yl)(tert-butyl)dimethylsilane [**9 (R$^1$ = HD, R$^2$ = TBS)**]*

Under argon atmosphere, *n*-BuLi (1.6 M in hexane, 30 mL, 48 mmol) was added dropwise to a solution of 2,2,6,6-tetramethylpiperidine (8.7 mL, 51 mmol) in THF (25 mL) at 0 ℃ to form lithium tetramethylpiperidine (TMPLi). After stirring at 0 ℃ for 30 min, a solution of **9 (R$^1$ = HD)** (17 g, 44 mmol) in THF (30 mL) was then added slowly, and then the resulting solution was stirred at 0 ℃ for 30 min. *tert*-Butyldimethylchlorosilane (15 g, 102 mmol) was then added in several portions. The reaction mixture was then warmed to room temperature and further stirred for 16 h. The reaction was quenched by adding water, and the resulting mixture was extracted with hexane. The organic layer was washed with water and brine, and then dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was purified by silica-gel column chromatography using hexane as eluent ($R_f$ = 0.8) to obtain **9 (R$^1$ = HD, R$^2$ = TBS)** (23 g, 42.3 mmol) in the 96 % yield as orange oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.86 (s, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.69–1.62 (m, 1H), 1.33–1.13 (m, 24H), 0.95–0.80 (m, 15H), 0.25 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 142.36, 137.40, 136.99, 114.50, 38.66, 34.09, 33.69, 32.14, 32.08, 30.22, 29.89, 29.82, 29.58, 26.76, 26.72, 26.45, 22.90, 17.01, 14.33, −5.03; HRMS (ESI): Calcd. for $C_{26}H_{50}BrSSi$ $[M+H]^+$: 501.25804, Found: 501.25714.

*(5-Bromo-4-(2-decyltetradecyl)thiophen-2-yl)(tert-butyl)dimethylsilane [**9 (R$^1$ = DT, R$^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using *n*-BuLi (1.6 M in hexane, 30 mL, 48 mmol), 2,2,6,6-tetramethylpiperidine (11 mL, 52 mmol) in THF (80 mL),

**8 ($R^1$ = DT)** (20 g, 40 mmol) in THF (80 mL), and *tert*-butyldimethylchlorosilane (12 g, 80 mmol). **9 ($R^1$ = DT, $R^2$ = TBS)** (32 g, 39 mmol) was obtained in the 98% yield as orange oil. $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.86 (s, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.71–1.60 (m, 1H), 1.27–1.23 (m, 40H), 0.91–0.88 (m, 15H), 0.25 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 148.79, 138.77, 136.89, 101.63, 39.28, 34.16, 33.76, 32.10, 30.26, 30.17, 29.87, 29.82, 29.52, 26.80, 26.76, 26.44, 22.85, 17.02, 14.26, 0.16, –4.96; HRMS (ESI): Calcd. for $C_{34}H_{65}BrSSi$ $[M+H]^+$: 613.3833, Found: 615.38123.

*(5-Bromo-4-(2-butyloctyl)thiophen-2-yl)(tert-butyl)dimethylsilane [**9 ($R^1$ = BO, $R^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using *n*-BuLi (1.6 M in hexane, 20 mL, 21 mmol), 2,2,6,6-tetramethylpiperidine (5.7 mL, 24 mmol) in THF (30 mL), **8 ($R^1$ = BO)** (8.6 g, 26 mmol) in THF (10 mL), and *tert*-butyldimethylchlorosilane (7.9 g, 52 mmol). **9 ($R^1$ = BO, $R^2$ = TBS)** (10 g, 23 mmol) was obtained in the 88% yield as orange oil. $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.86 (s, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.70–1.62 (m, 1H), 1.27–1.22 (m, 16H), 0.91–0.84 (m, 15H), 0.25 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 142.38, 137.47, 137.00, 114.44, 38.63, 37.90, 34.08, 33.64, 33.35, 32.04, 29.85, 28.97, 26.69, 26.42, 22.86, 17.00, 14.28, –5.04; HRMS (APCI): Calcd. for $C_{22}H_{41}BrSSi$ $[M+H]^+$: 445.19544, Found: 445.19498.

*(5-Bromo-4-dodecylthiophen-2-yl)(tert-butyl)dimethylsilane [**9 ($R^1$ = C12, $R^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using *n*-BuLi (1.6 M in hexane, 6.1 mL, 9.7 mmol), 2,2,6,6-tetramethylpiperidine (1.8 mL, 11 mmol) in THF (20 mL), **8 ($R^1$ = C12)** (2.0 g, 6.0 mmol) in THF (10 mL), and *tert*-butyldimethylchlorosilane (2.4 g, 16 mmol). **9 ($R^1$ = C12, $R^2$ = TBS)** (3.1 g, 6.0 mmol) was obtained in the 99% yield as orange oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.90 (s, 1H), 2.55 (t, 2H), 1.64–1.49 (m, 2H), 1.34–1.28

(m, 18H), 0.93–0.86 (m, 12H), 0.25 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 143.20, 137.80, 136.33, 113.91, 32.14, 30.00, 29.85, 29.79, 29.57, 29.50, 26.46, 22.90, 16.98, 14.31, –4.96.; HRMS (ESI): Calcd. for $C_{22}H_{41}BrSSi$ $[M+H]^+$: 445.19544, Found: 445.19611.

*tert-Butyl(4-(2-hexyldecyl)-5-((trimethylsilyl)ethynyl)thiophen-2-yl)dimethylsilane* ***[10 ($R^1$ = HD, $R^2$ = TBS)]***

Under argon atmosphere, **9 ($R^1$ = HD, $R^2$ = TBS)** (6.7 g, 12 mmol), CuI (69 mg, 0.36 mmol), $Pd(PPh_3)_4$ (416 mg, 0.36 mmol), $PPh_3$ (142 mg, 0.54 mmol), trimethylsilylacethylene (3.1 mL, 22 mmol, $d$ = 0.71 g $mL^{-1}$), and $Et_3N$/THF (9 mL/9 mL) were placed into a 50 mL of three-necked round-bottom flask equipped with condenser. The reaction mixture was degassed by babbling argon gas, was then stirred at 95 ℃ for 18 h. After cooling to room temperature, the mixture was extracted with DCM, and the organic layer was washed with water and brine and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was roughly purified by flash silica-gel column chromatography using hexane as eluent to obtain **10 ($R^1$ = HD, $R^2$ = TBS)** as orange oil. The next desilylation was carried out without further purification.

*tert-Butyl(4-(2-decyltetradecyl)-5-((trimethylsilyl)ethynyl)thiophen-2-yl)dimethylsilane* ***[10 ($R^1$ = DT, $R^2$ = TBS)]***

The title compound was synthesized by the same procedure as above using **9 ($R^1$ = DT, $R^2$ = TBS)** (29 g, 44 mmol), CuI (0.17 g, 0.88 mmol), $Pd(PPh_3)_4$ (1.0 g, 0.88 mmol), $PPh_3$ (0.35g, 1.3 mmol), trimethylsilylacethylene (9.1 mL, 66 mmol, $d$ = 0.71 g $mL^{-1}$), $Et_3N$/THF (40 mL/40 mL). **10 ($R^1$ = DT, $R^2$ = TBS)** was obtained as orange oil.

*tert-Butyl(4-(2-butyloctyl)-5-((trimethylsilyl)ethynyl)thiophen-2-yl)dimethylsilane [**10 ($R^1$ = BO, $R^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using **9 ($R^1$ = BO, $R^2$ = TBS)** (10 g, 23 mmol), CuI (0.23 g, 1.2 mmol), $Pd(PPh_3)_4$ (1.4 g, 1.2 mmol), $PPh_3$ (0.38 g, 1.4 mmol), trimethylsilylacethylene (4.8 mL, 35 mmol, $d$ = 0.71 g $mL^{-1}$), $Et_3N$/THF (30 mL/30 mL). **10 ($R^1$ = BO, $R^2$ = TBS)** was obtained as orange oil.

*tert-Butyl(4-dodecyl-5-((trimethylsilyl)ethynyl)thiophen-2-yl)dimethylsilane [**10 ($R^1$ = C12, $R^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using **9 ($R^1$ = C12, $R^2$ = TBS)** (3.1 g, 7.0 mmol), CuI (78 mg, 0.41 mmol), $Pd(PPh_3)_4$ (0.47 g, 0.41 mmol), $PPh_3$ (128 mg, 0.49 mmol), trimethylsilylacethylene (1.7 mL, 12 mmol, $d$ = 0.71 g $mL^{-1}$), $Et_3N$/THF (20 mL/20 mL). **10 ($R^1$ = C12, $R^2$ = TBS)** was obtained as orange oil.

*tert-Butyl(4-(2-hexyldecyl)-5-ethynylthiophen-2-yl)dimethylsilane [**2 ($R^1$ = HD, $R^2$ = TBS)**]*

In a 100 mL round-bottom flask, **10 ($R^1$ = HD, $R^2$ = TBS)**, $K_2CO_3$ (1.8 g, 13 mmol), and DCM/methanol (12 mL/12 mL v/v) were placed, and the mixture was stirred for 15 h at room temperature. Water was added and the resulting mixture was extracted with hexane, and the organic layer was washed with water and brine, and then dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by silica-gel column chromatography using hexane as eluent ($R_f$ = 0.7) to obtain **2 ($R^1$ = HD, $R^2$ = TBS)** (4.4 g, 8.2 mmol) in the 70% yield in 2 steps as orange oil.

$^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.91 (s, 1H), 3.47 (s, 1H), 2.63 (d, $J$ = 7.1 Hz, 2H), 1.73–1.64 (m, 1H), 1.33–1.19 (m, 24H), 0.93–0.84 (m, 15H), 0.27 (s, 6H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ (ppm) 149.09, 139.16, 136.77, 122.87, 84.11, 84.05, 39.12, 33.98, 33.69, 32.09, 32.05, 30.18, 29.84, 29.78, 29.53, 26.73, 26.69, 26.42, 22.86, 17.00, 14.29, −4.95, −5.00; Calcd.

for $C_{28}H_{50}SSi$ $[M+H]^+$: 446.33970, Found: 446.34003.

*tert-Butyl(4-(2-decyltetradecyl)-5-ethynylthiophen-2-yl)dimethylsilane [**2 (R$^1$ = DT, R$^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using **10 (R$^1$ = DT, R$^2$ = TBS)**, $K_2CO_3$ (7.2 g, 52 mmol), DCM/methanol (50 mL/50 mL). **2 (R$^1$ = DT, R$^2$ = TBS)** (19 g, 34 mmol) was obtained in the 73% yield in 2 steps as orange oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.91 (s, 1H), 3.47 (s, 1H), 2.63 (d, *J* = 7.1 Hz, 2H), 1.73–1.64 (m, 1H), 1.35–1.22 (m, 40H), 0.94–0.84 (m, 15H), 0.28 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 149.04, 139.09, 136.72, 123.01, 84.08, 39.16, 34.02, 33.75, 32.16, 30.23, 29.93, 29.90, 29.88, 29.60, 26.46, 22.91, 17.02, 14.32, −4.95; HRMS (APCI): Calcd. for $C_{36}H_{66}SSi$ $[M+H]^+$: 559.4727, Found: 559.47260.

*tert-Butyl(4-(2-butyloctyl)-5-ethynylthiophen-2-yl)dimethylsilane [**2 (R$^1$ = BO, R$^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using **10 (R$^1$ = BO, R$^2$ = TBS)**, $K_2CO_3$ (3.1 g, 23 mmol), DCM/methanol (25 mL/25 mL). **2 (R$^1$ = BO, R$^2$ = TBS)** (6.8 g, 22 mmol) was obtained in the 85% yield in 2 steps as orange oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.93 (s, 1H), 3.48 (s, 1H), 2.64 (d, *J* = 7.1 Hz, 2H), 1.73–1.64 (m, 1H), 1.32–1.20 (m, 16H), 0.97–0.82 (m, 15H), 0.28 (s, 6H) ; $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 148.78, 136.89, 101.60, 97.96, 39.21, 37.86, 34.05, 33.67, 33.33, 32.02, 29.90, 28.93, 26.40, 22.86, 17.01, 14.27, –5.00; HRMS (APCI): Calcd. for $C_{24}H_{42}SSi$ $[M+H]^+$: 391.28045, Found: 391.28452.

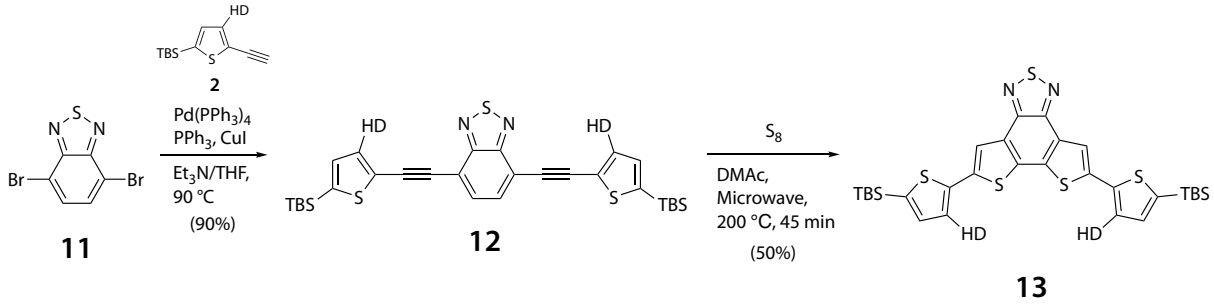
*tert-Butyl(4- dodecyl-5-ethynylthiophen-2-yl)dimethylsilane [**2 (R$^1$ = C12, R$^2$ = TBS)**]*

The title compound was synthesized by the same procedure as above using **10 (R$^1$ = C12, R$^2$ = TBS)**, $K_2CO_3$ (1.2 g, 8.9 mmol), and DCM/methanol (15 mL/15 mL). **2 (R$^1$ = C12, R$^2$ =**

**TBS)** (2.2 g, 5.6 mmol) was obtained in the 93% yield in 2 steps as orange oil.

$^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.96 (s, 1H), 3.49 (s, 1H), 2.70 (t, *J* = 7.1 Hz, 2H), 1.67–1.58 (q, 2H), 1.33–1.27 (m, 18H), 0.96–0.84 (m, 12H), 0.28 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 149.95, 139.56, 136.10, 122.32, 84.17, 84.09, 32.09, 30.44, 29.82, 29.75, 29.55, 29.52, 29.38, 26.43, 22.85, 16.98, 14.28, –4.92; HRMS: Calcd. for $C_{24}H_{42}SSi$ $[M+H]^+$: 391.285, HRMS data for the title compound were not found in either ESI or APCI measurements.

## 1-3. Synthesis and characterization of DTBT derivatives




Scheme S2. Synthetic route to **13**

*4,7-Bis((5-(tert-butyldimethylsilyl)-3-(2-hexyldecyl)thiophen-2-yl)ethynyl)benzo[c][1,2,5]thiadiazole* (***12***)

Under argon atmosphere, **11** (0.74 g, 2.5 mmol), **2 ($R^1$ = HD, $R^2$ = TBS)** (2.82 g, 6.3 mmol), CuI (29 mg, 0.15 mmol), $Pd(PPh_3)_4$ (173 mg, 0.15 mmol), $PPh_3$ (47 mg, 0.18 mmol), triethylamine (30 mL), and THF (30 mL) were placed to a three-necked round-bottom flask equipped with condenser. The solution was degassed by argon bubbling and then stirred at 90 °C for 2 h. After cooling to room temperature, water was added, and the resulting mixture was extracted with CF. The organic layer was washed with water and brine, and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was purified by silica-gel column chromatography using hexane/CF (gradually changing the ratio of 20/1) as eluent ($R_f$ = 0.3 for the ratio of 20/1) and then reprecipitated from methanol to obtain **12** (2.3 g, 2.25 mmol) in the 90% yield as orange solid.

$^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.68 (s, 2H), 7.00 (d, 2H), 2.82 (d, $J$ = 7.0 Hz, 4H), 1.84–1.76 (m, 2H), 1.34–1.16 (m, 48H), 0.95 (s, 18H), 0.84–0.77 (m, 12H), 0.33 (s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 154.21, 149.41, 140.47, 136.99, 131.31, 123.25, 117.02, 92.49, 91.24, 39.27, 34.15, 33.56, 31.89, 30.10, 29.75, 29.63, 29.34, 26.60, 26.56, 26.28, 22.65, 16.19, 14.10, 14.07; HRMS (APCI): Calcd. for $C_{62}H_{100}N_2S_3Si_2$ $[M+H]^+$: 1024.65817, Found 1024.66052.

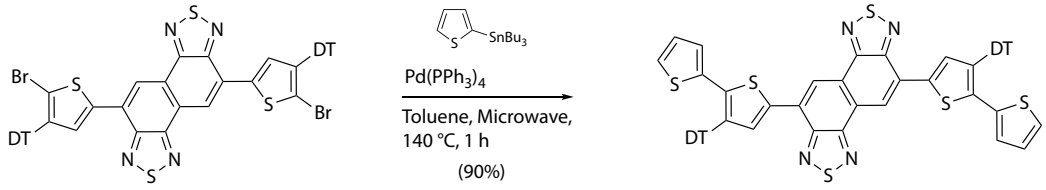
*5,8-Bis(5-(tert-butyldimethylsilyl)-3-(2-hexyldecyl)thiophen-2-yl)dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]thiadiazole* (***13***)

**12** (2.0 g, 1.97 mmol), $S_8$ (2.0 g, 7.8 mmol), and DMAc (20 mL) were placed into a reaction vessel. The vessel was purged with argon and sealed. The vessel was inserted into the microwave reactor and heated at 200 ℃ for 45 min. After cooling to room temperature, the mixture was poured into water, and was then extracted with hexane. The organic layer was washed with brine, and then dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was purified by silica-gel column chromatography using hexane/DCM (gradually changing the ratio of 20/1) as eluent ($R_f$ = 0.3 for the ratio of 20/1) to obtain **13** (1.07 g, 0.98 mmol) in the 50% yield as orange solid.

$^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.04 (s, 2H), 7.07 (d, 2H), 2.85 (d, $J$ = 7.0 Hz, 4H), 1.78–1.70 (m, 2H), 1.34–1.16 (m, 48H), 0.97 (s, 18H), 0.84–0.77 (m, 12H), 0.33 (s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 150.45, 141.27, 139.18, 139.04, 137.25, 136.75, 135.34, 129.17, 122.04, 39.04, 38.99, 33.69, 31.88, 30.05, 29.71, 29.32, 26.59, 26.37, 26.33, 22.65, 16.94, 14.09; HRMS (APCI): Calcd. for $C_{62}H_{100}N_2S_5Si_2$ $[M+H]^+$: 1088.60231, Found 1088.60352.

## 1-4. Synthesis and characterization of NTz4T

*5,10-bis(3-(2-decyltetradecyl)-[2,2'-bithiophen]-5-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole)* (***NTz4T***)

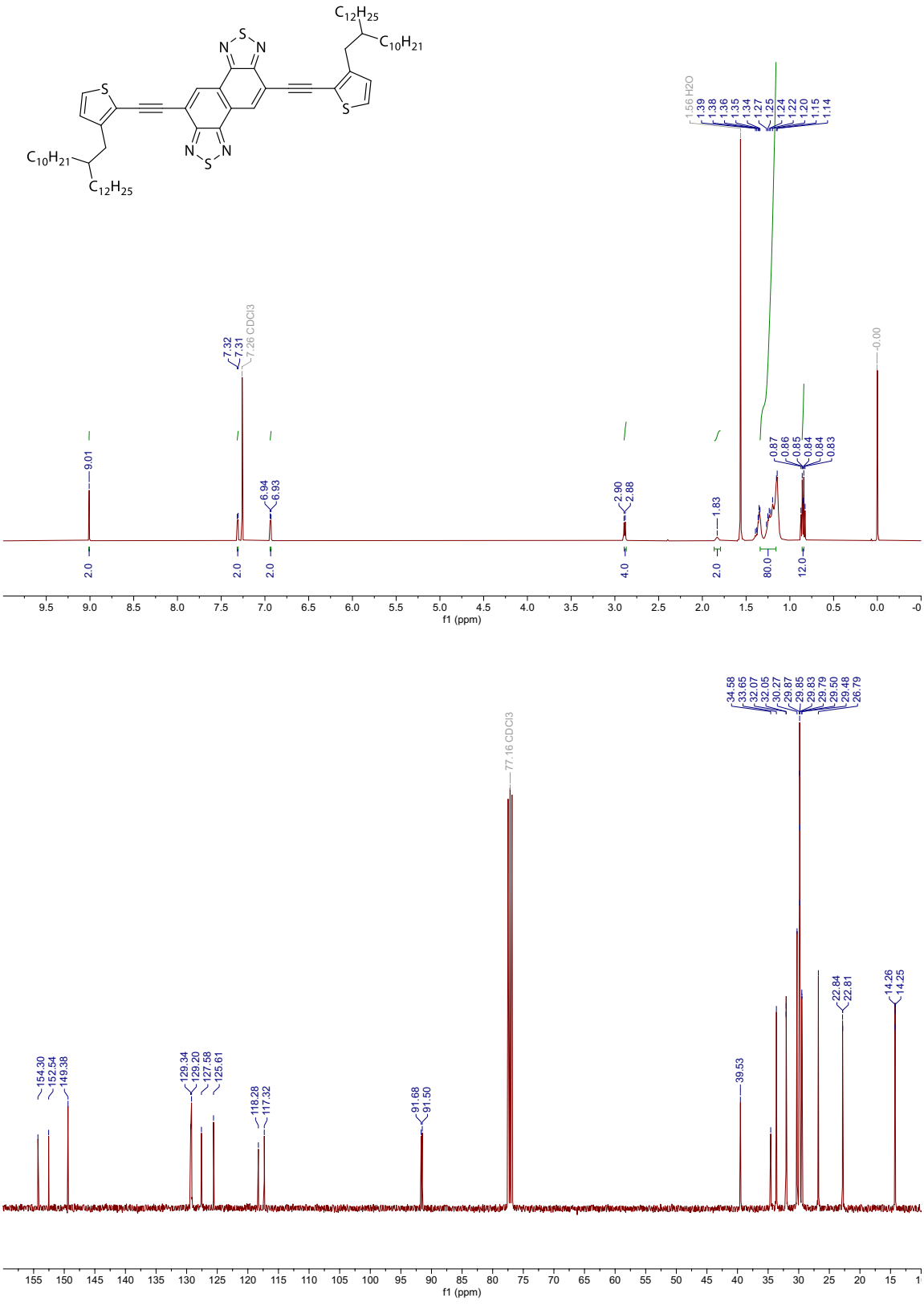



**14** **NTz4T**

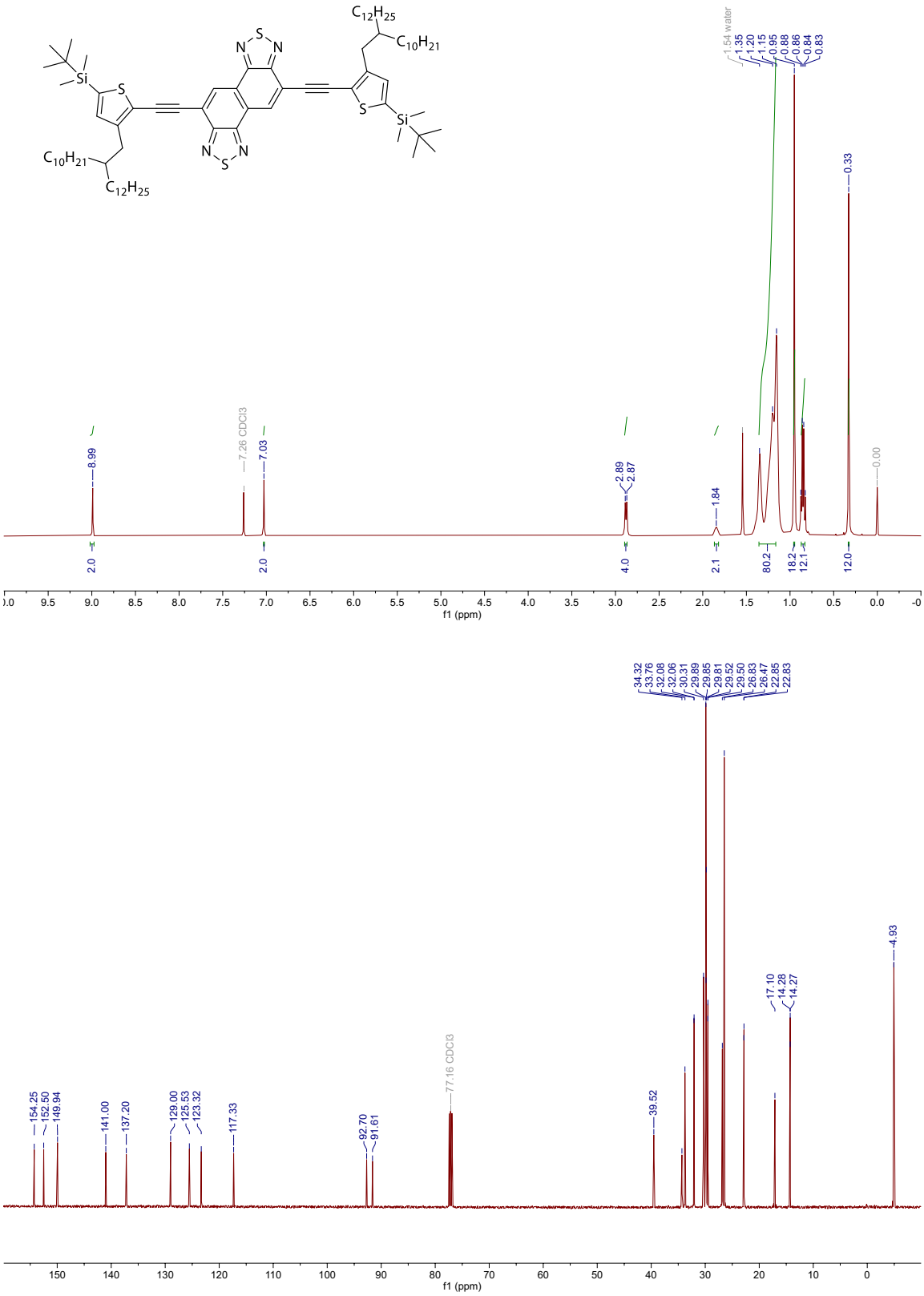
**14** (30 mg, 0.024 mmol), 2-tributylstannylthiophene (22.6 mg, 0.061 mmol), $Pd(PPh_3)_4$ (1.15 mg, 0.001 mmol), and toluene (2 mL) were added in a 2 mL reaction vessel. The vessel was purged with argon and sealed. The vessel was put into a microwave reactor and heated at 140 ºC for 1 h. After cooling to room temperature, the solvent was removed and the crude

product was purified by silica-gel column chromatography using Hexane/CF (1/1) as the eluent to obtain **NTz4T** (27 mg, 0.022 mmol) in 90% yield as dark purple solid. $^{1}$H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.04 (s, 2H), 7.07 (d, 2H), 2.85 (dd, 4H), 1.78–1.70 (m, 2H), 1.34–1.16 (m, 48H), 0.97 (s, 18H), 0.84–0.77 (m, 12H), 0.33 (s, 12H); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 2H), 8.11 (s, 2H), 7.37 (dd, 2H), 7.27 (dd, 2H), 7.12 (dd, 2H), 2.81(d, *J* = 7.0 Hz, 4H), 1.86–1.81 (m, 2H), 1.37–1.21 (m, 80H), 0.90–0.82 (m, 12H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 153.47, 152.39, 139.85, 136.39, 135.95, 133.78, 132.06, 127.45, 126.52, 126.16, 125.79, 124.72, 121.93, 77.25, 76.99, 76.74, 38.80, 34.00, 33.45, 31.91, 30.08, 29.72, 29.70, 29.67, 29.65, 29.35, 26.46, 22.67, 14.10; HRMS (APCI): Calcd. for $C_{74}H_{108}N_4S_6$ $[M+H]^+$: 1244.68928, Found 1244.69128.

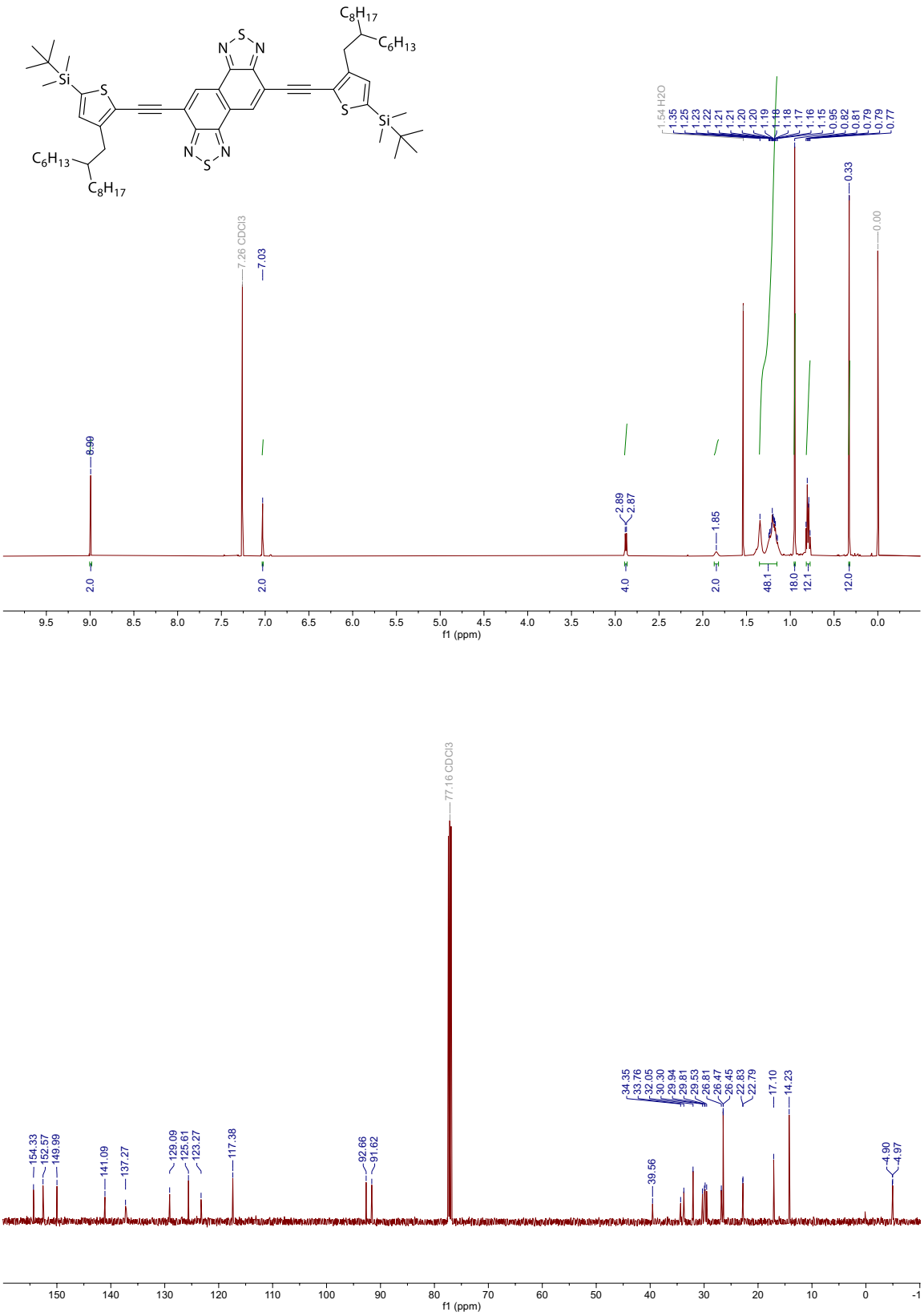
## 1-5. NMR charts.



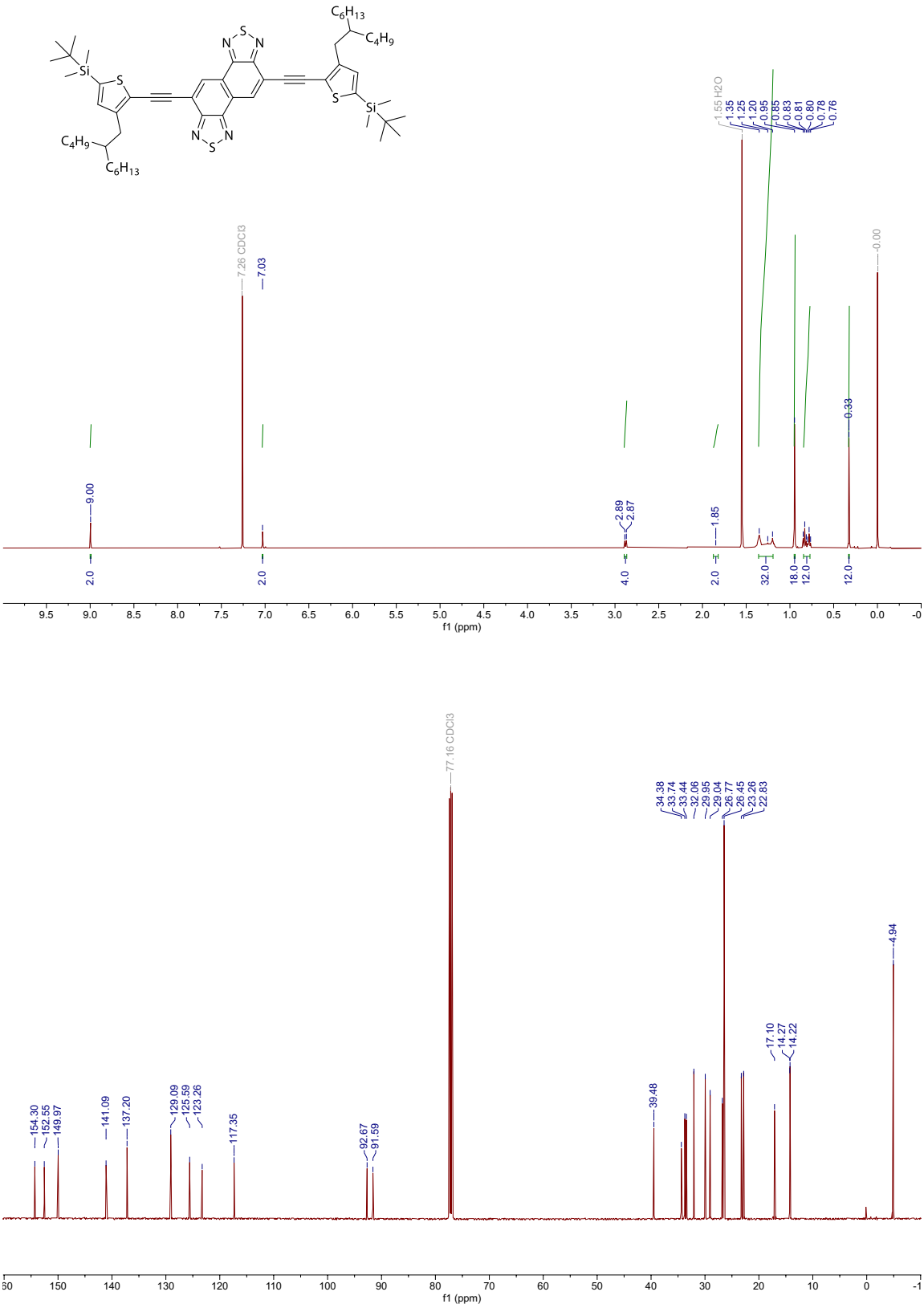

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **3 ($R^1$ = DT, $R^2$ = H)**.



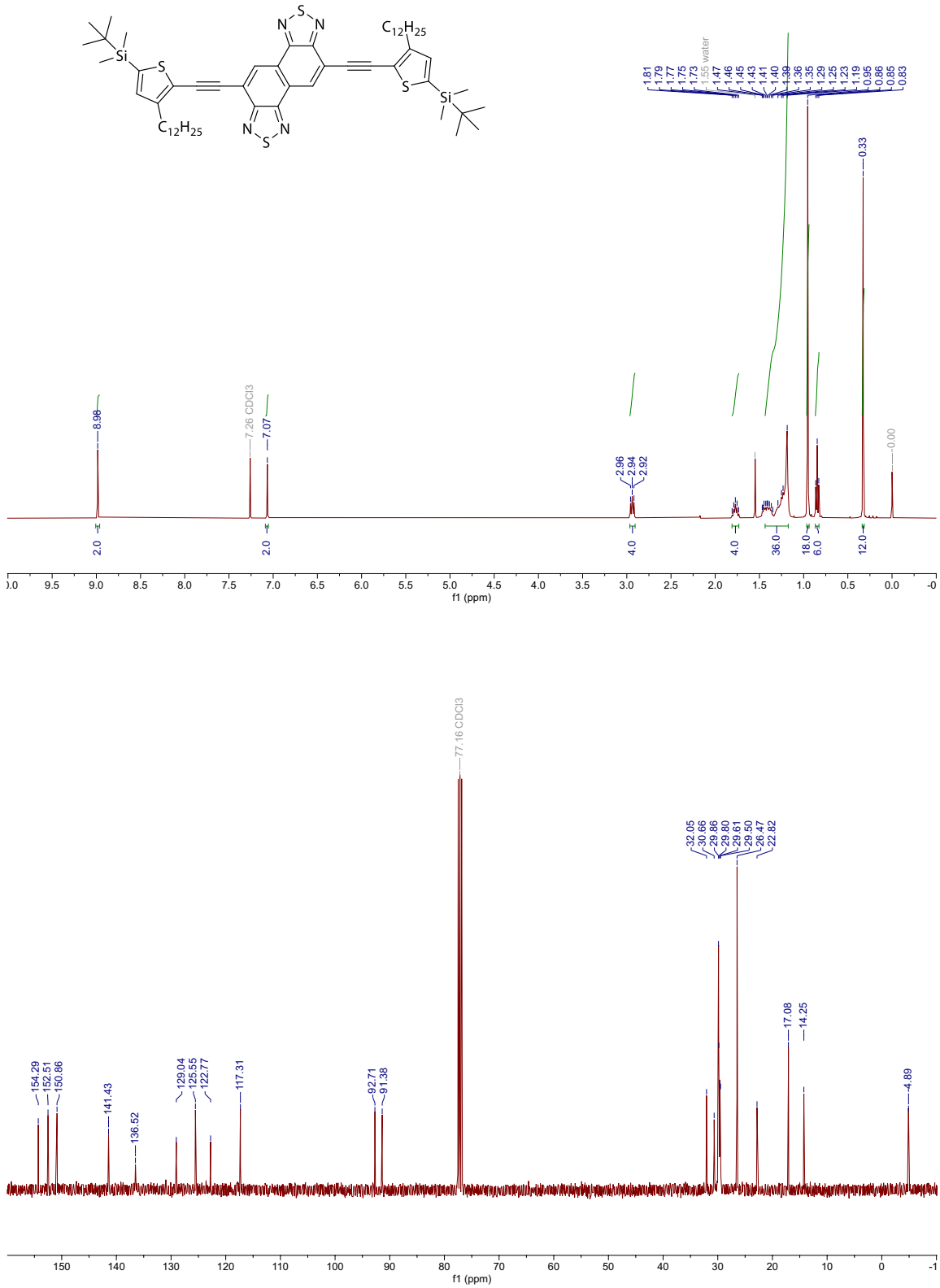

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **3 ($R^1$ = DT, $R^2$ = TBS)**.



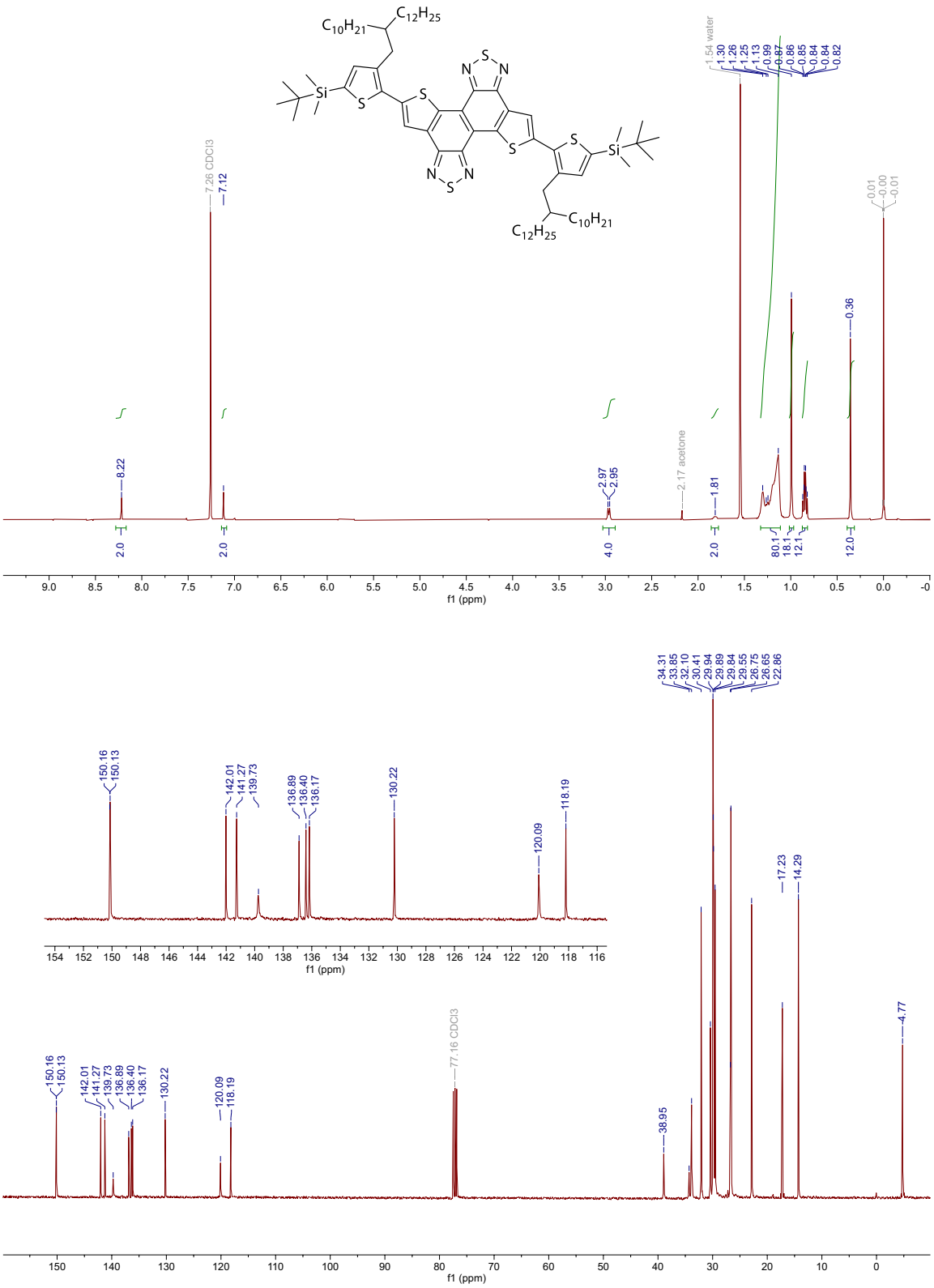

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **3 ($R^1$ = HD, $R^2$ = TBS)**.



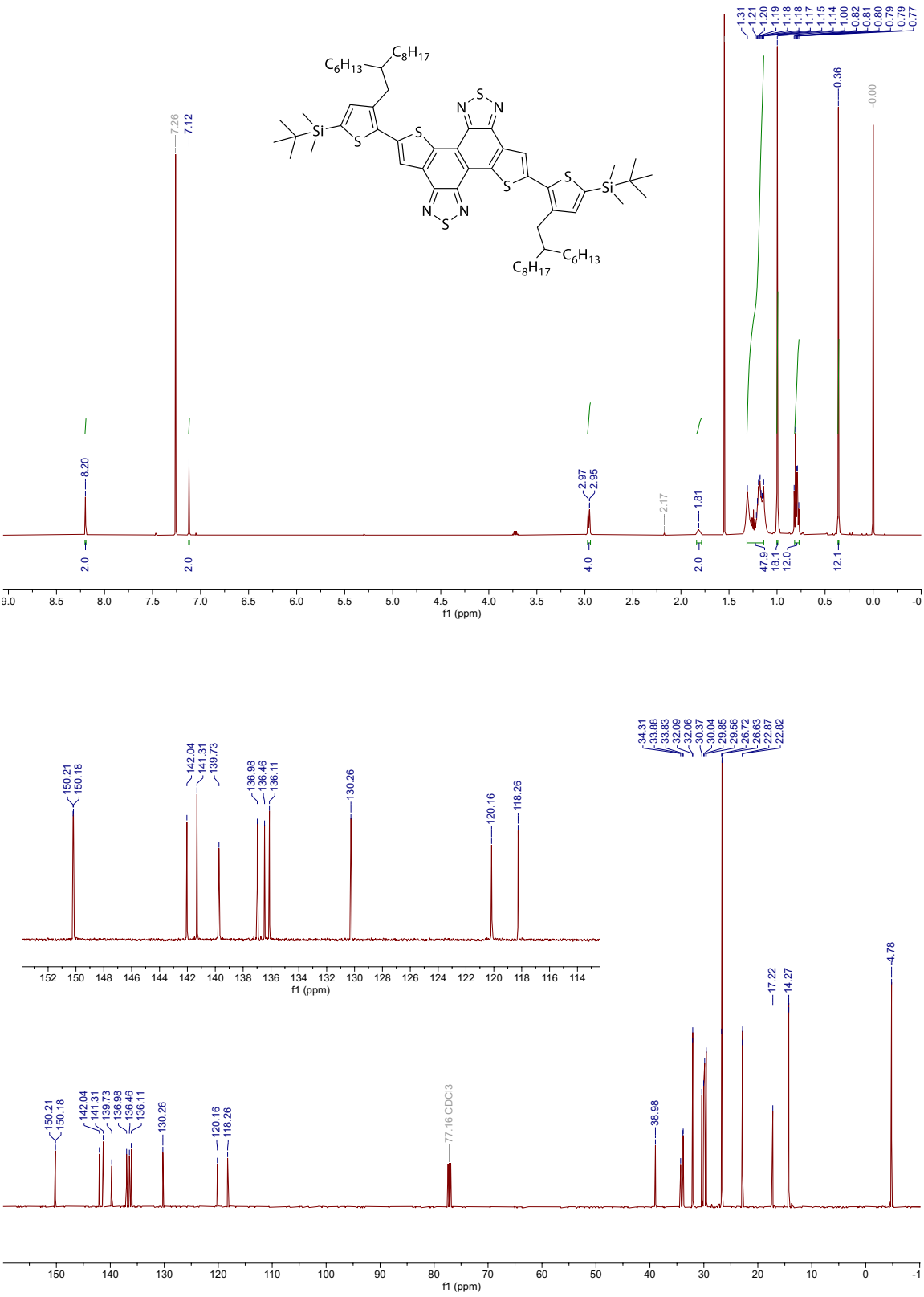

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **3 ($R^1$ = BO, $R^2$ = TBS)**.



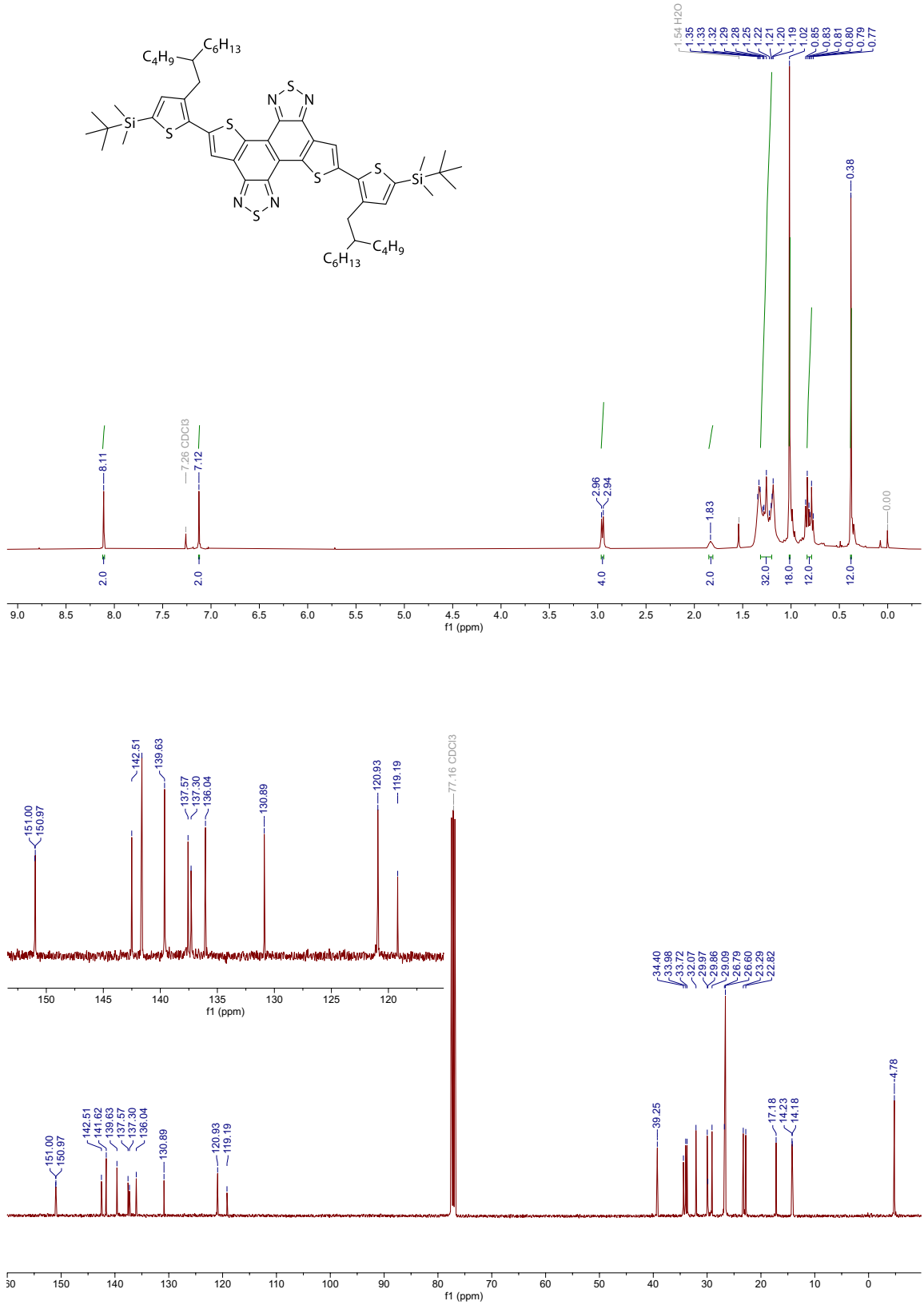

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **3 ($R^1$ = C12, $R^2$ = TBS)**.



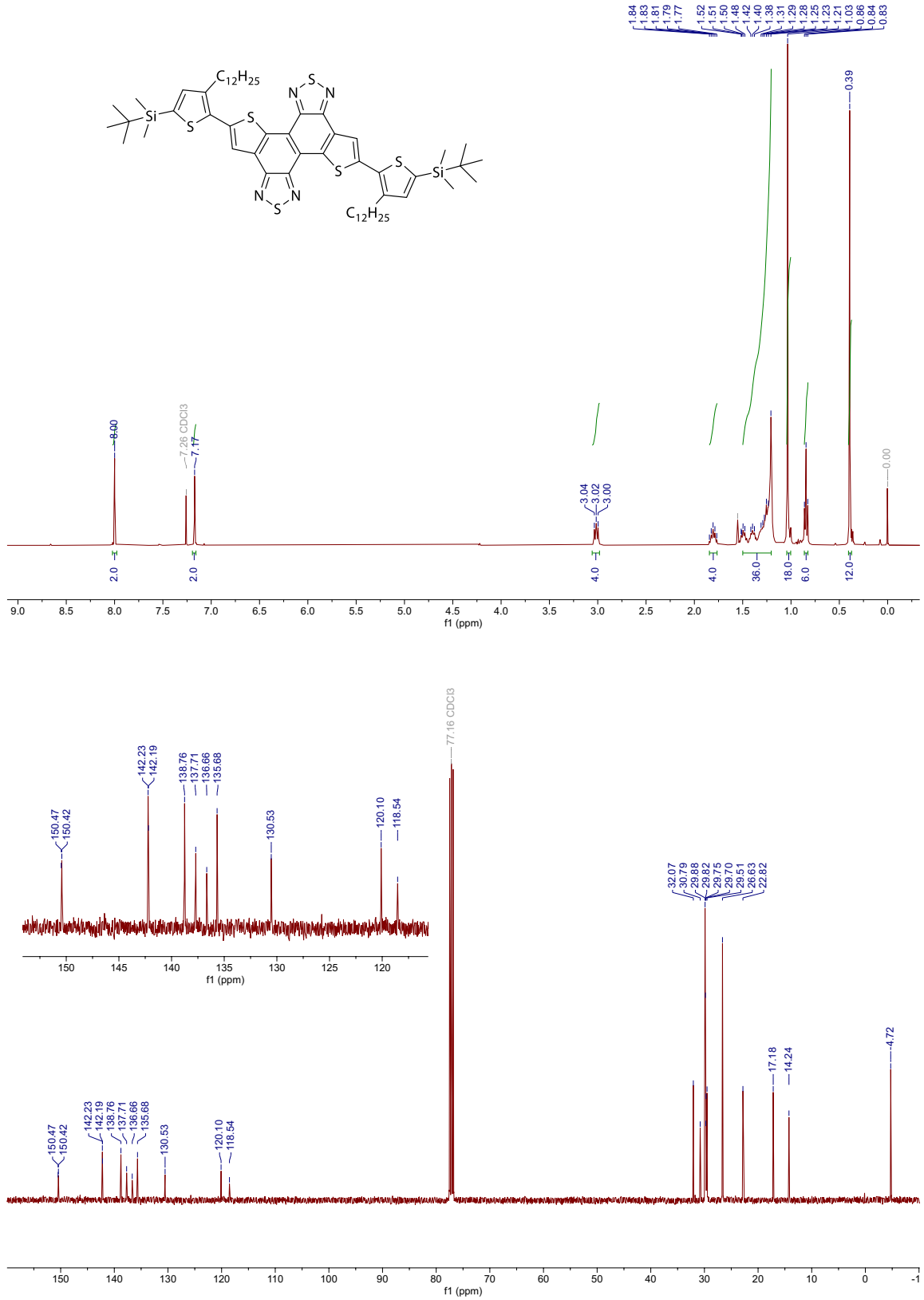

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **4 ($R^1$ = DT, $R^2$ = TBS)**.



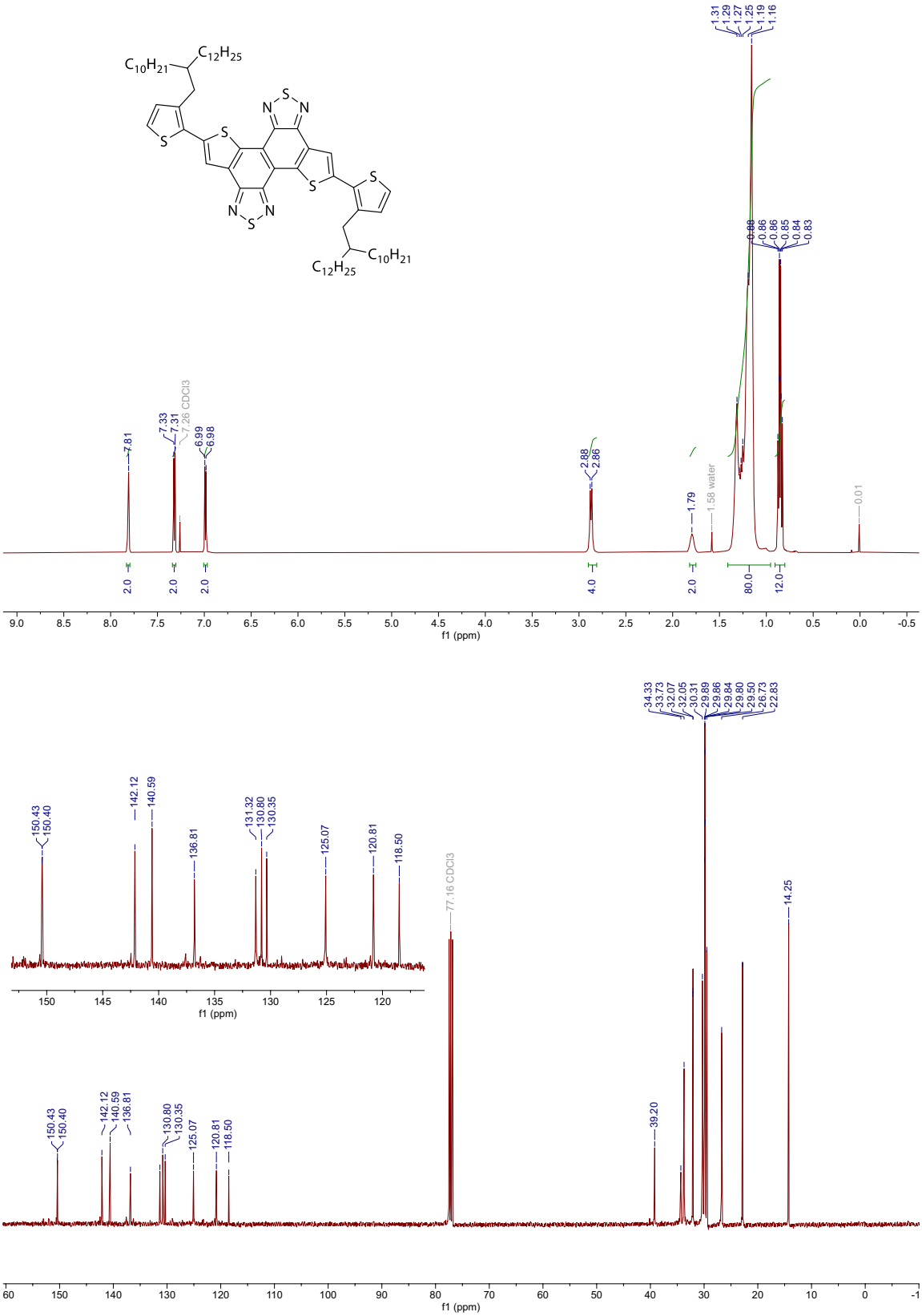

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **4 ($R^1$ = HD, $R^2$ = TBS)**.



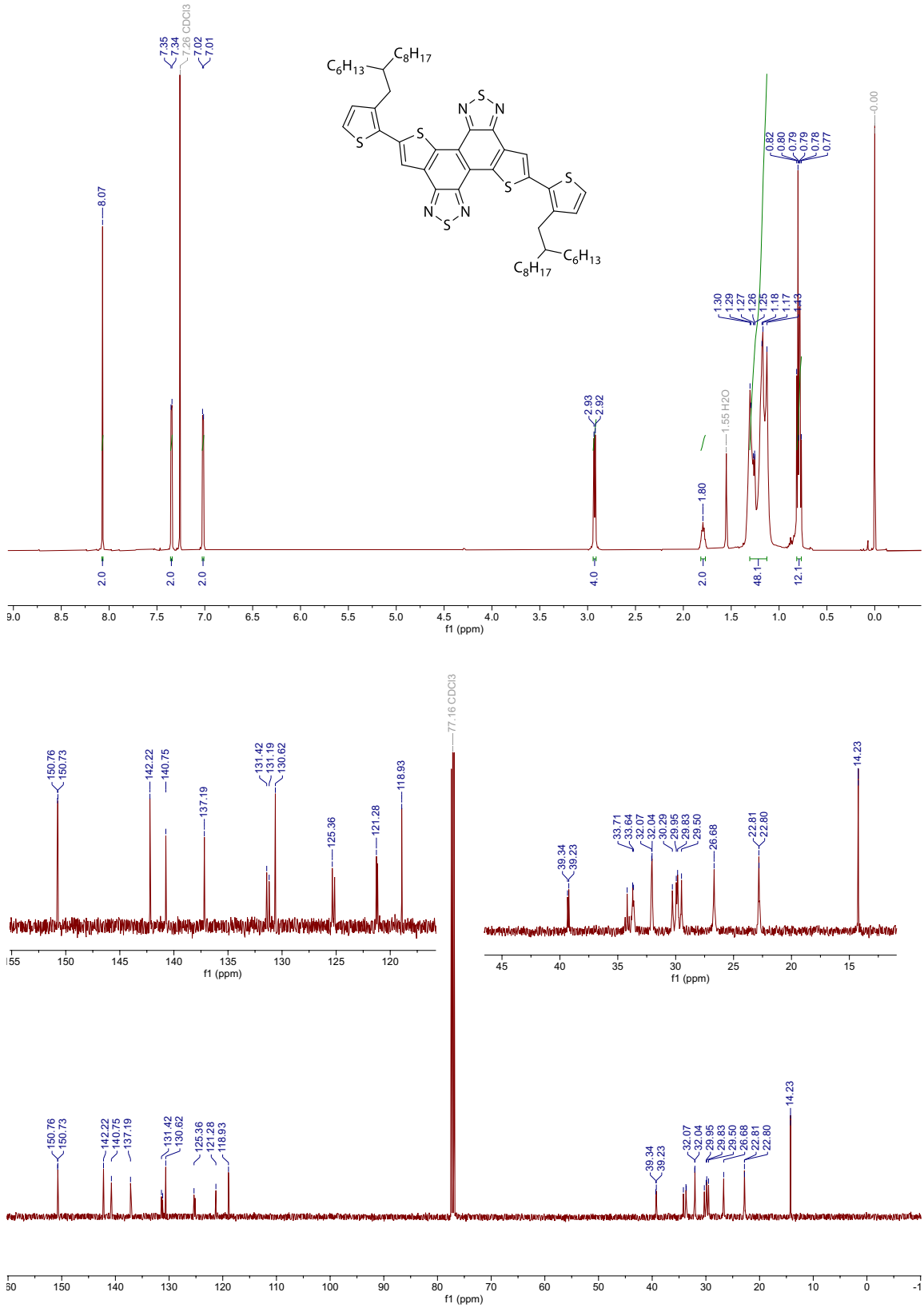

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **4 ($R^1$ = BO, $R^2$ = TBS)**.



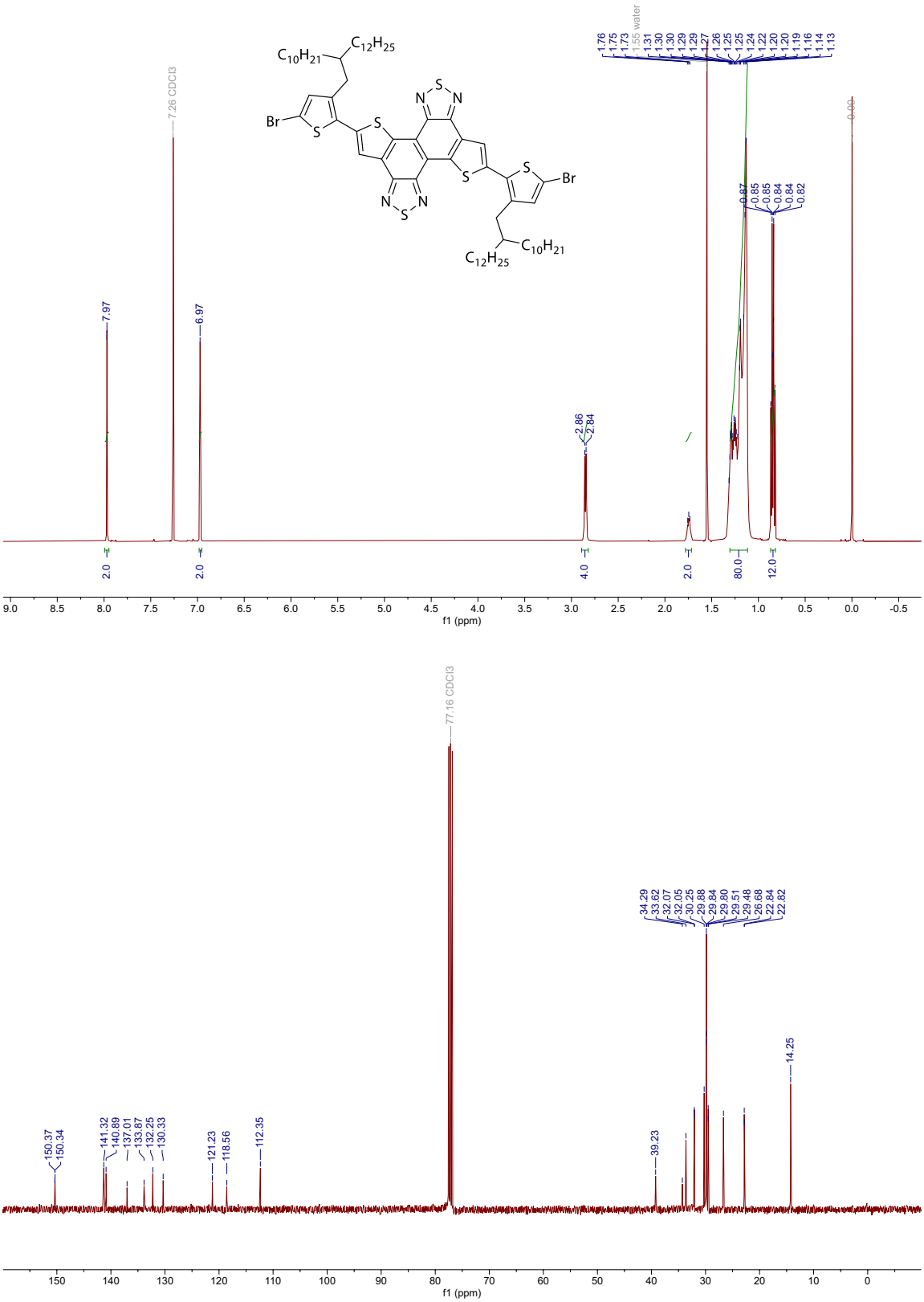

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **4 ($R^1$ = C12, $R^2$ = TBS)**.



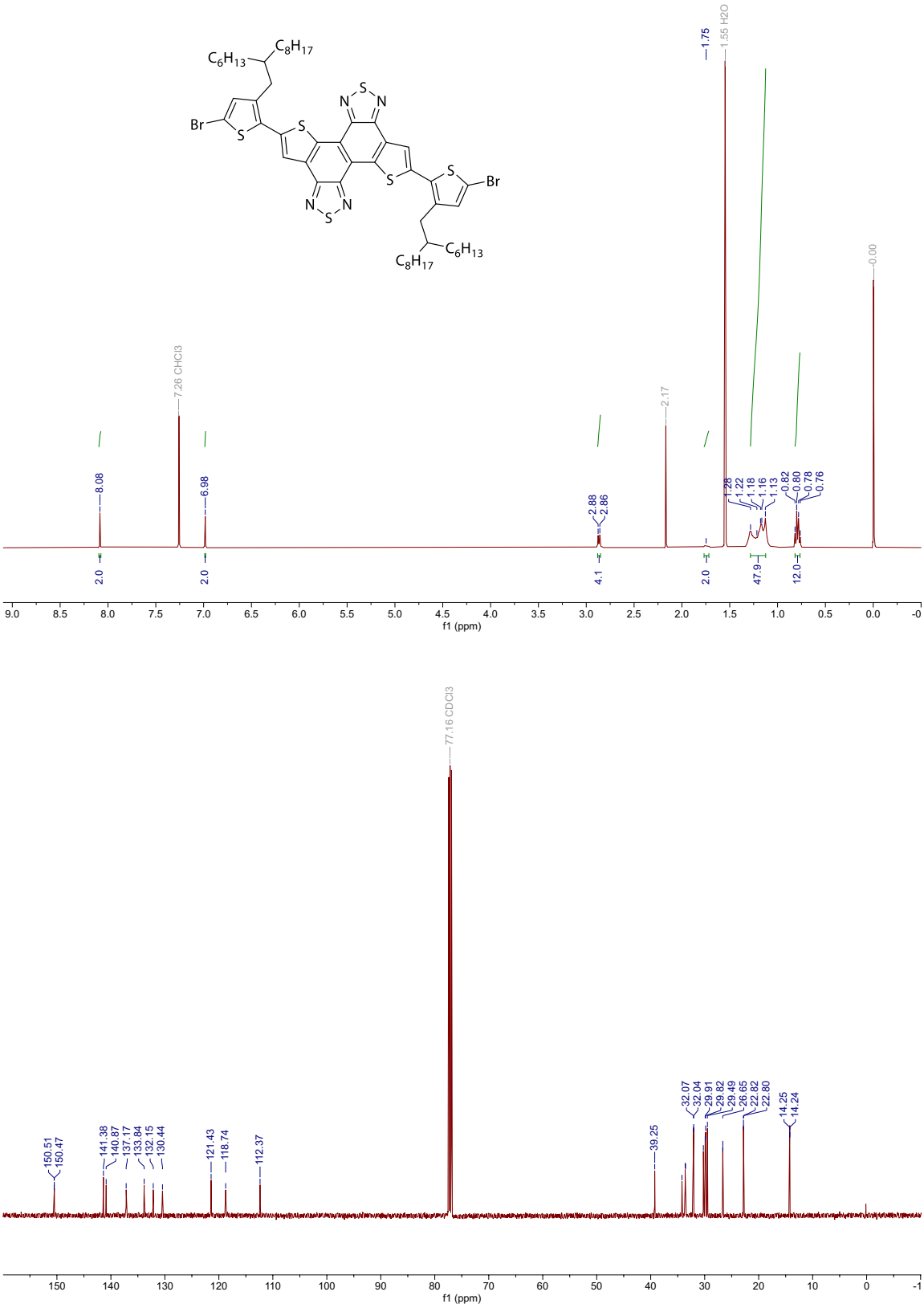

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **5a ($R^1$ = DT, $R^2$ = H)**.



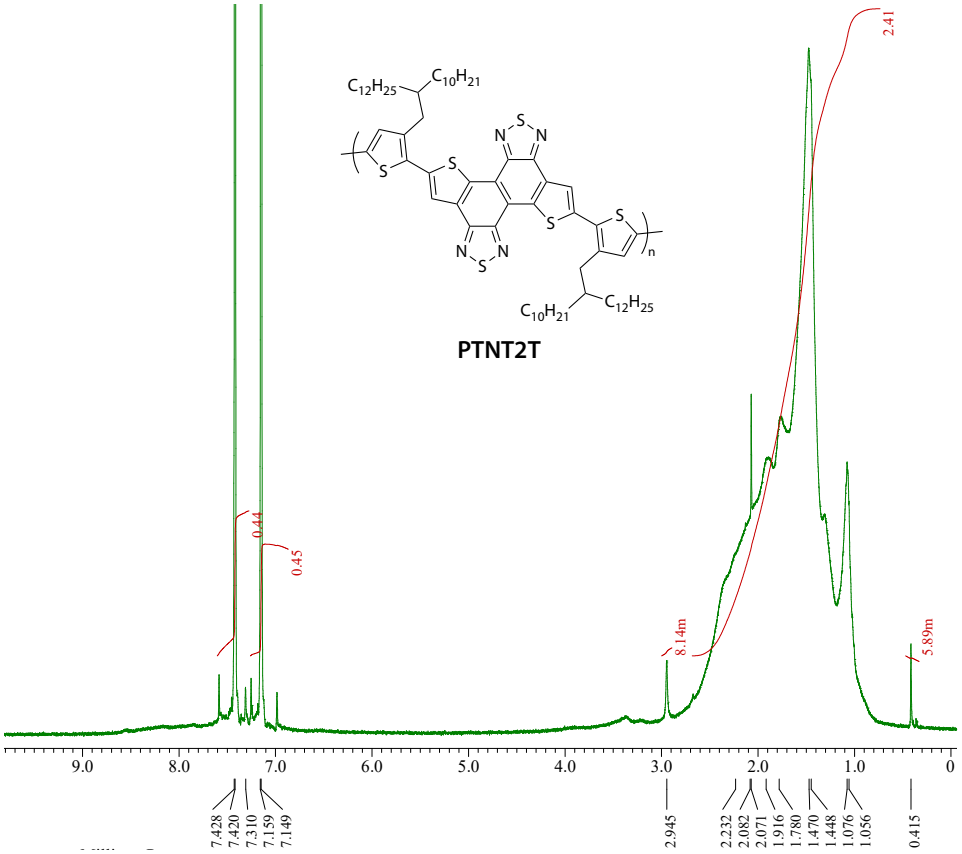

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **5b (R = HD)**.



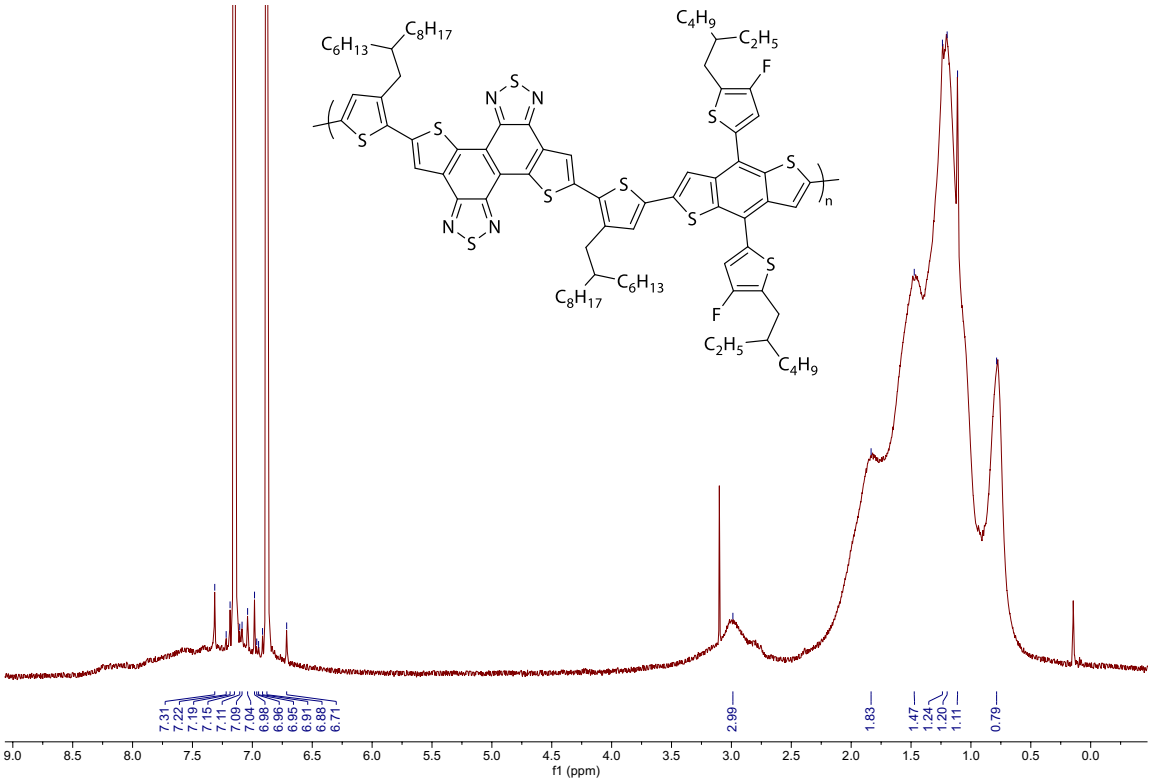

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **6a (R = DT)**.



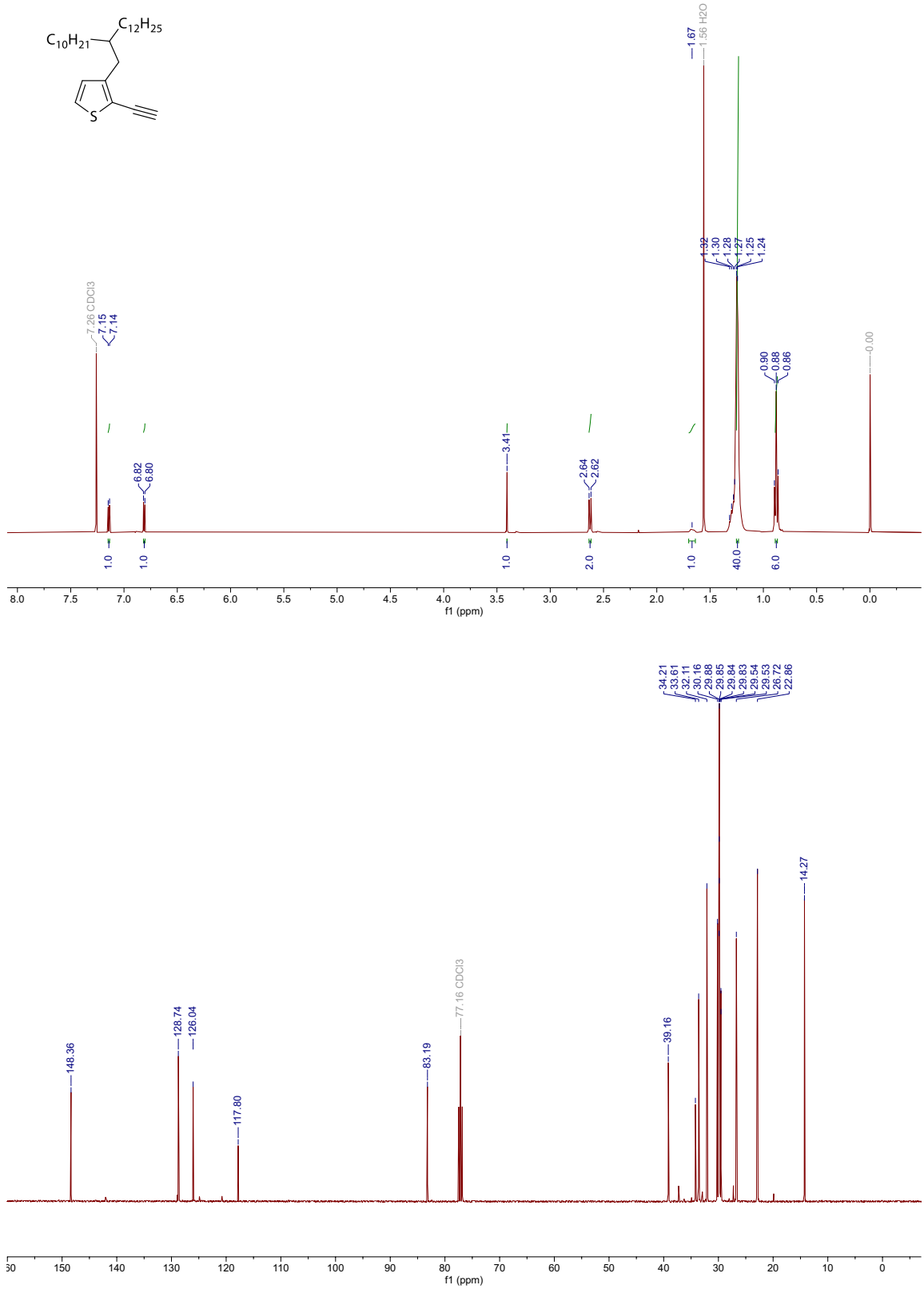

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **6b (R = HD)**.



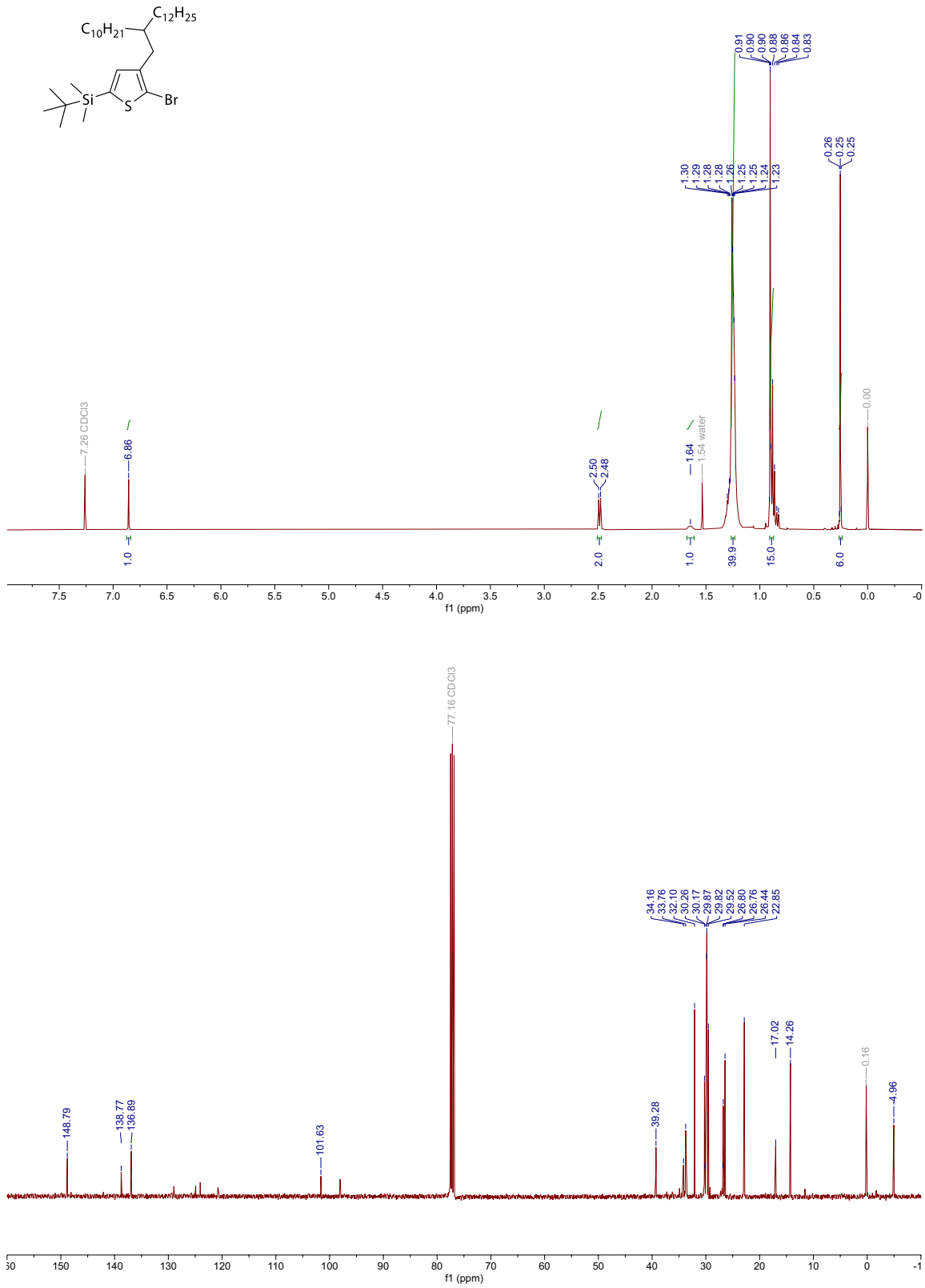

$^{1}$H-NMR spectra of **PTNT2T**.



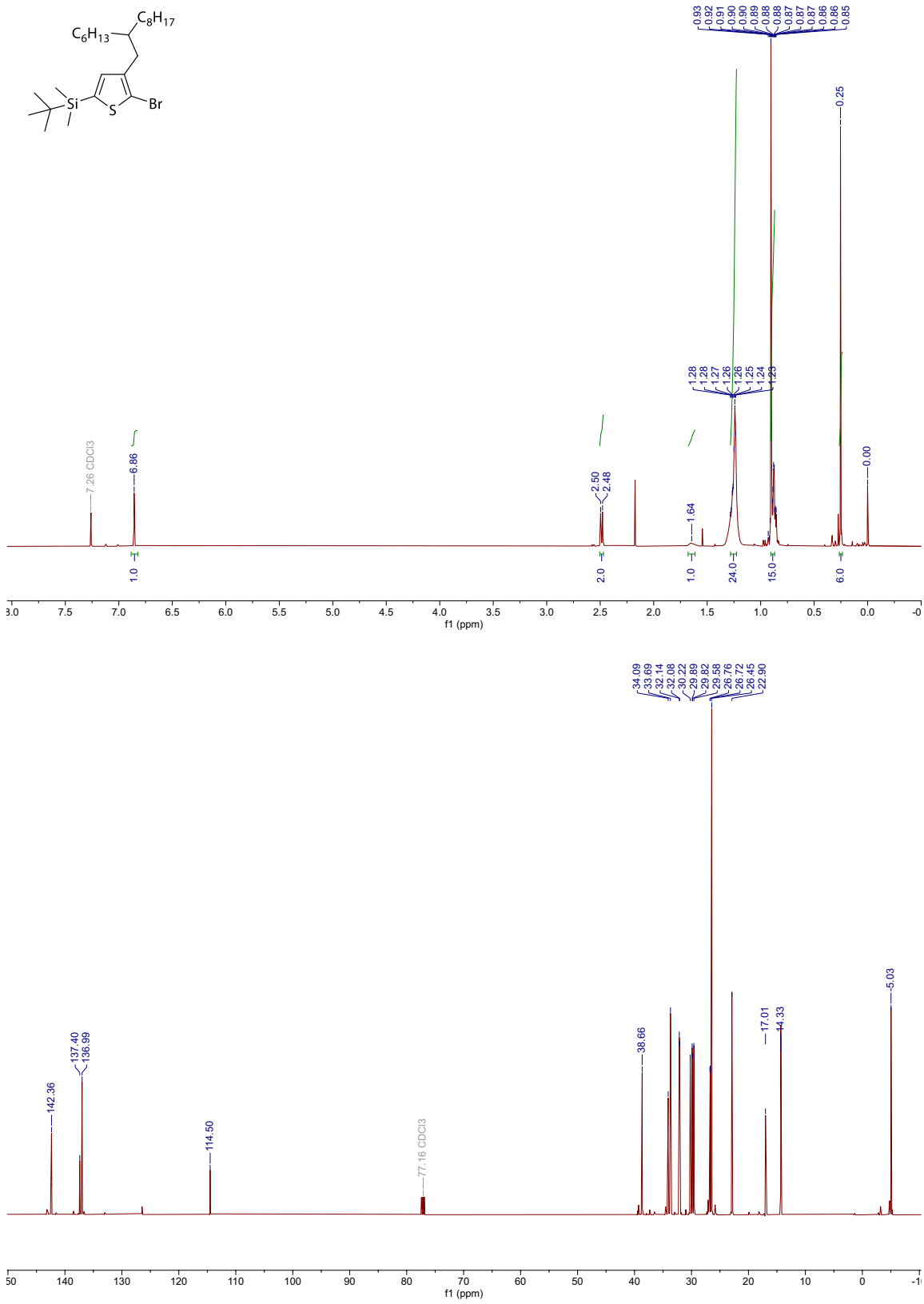

$^{1}$H-NMR spectrum of **PTNT1-F**.



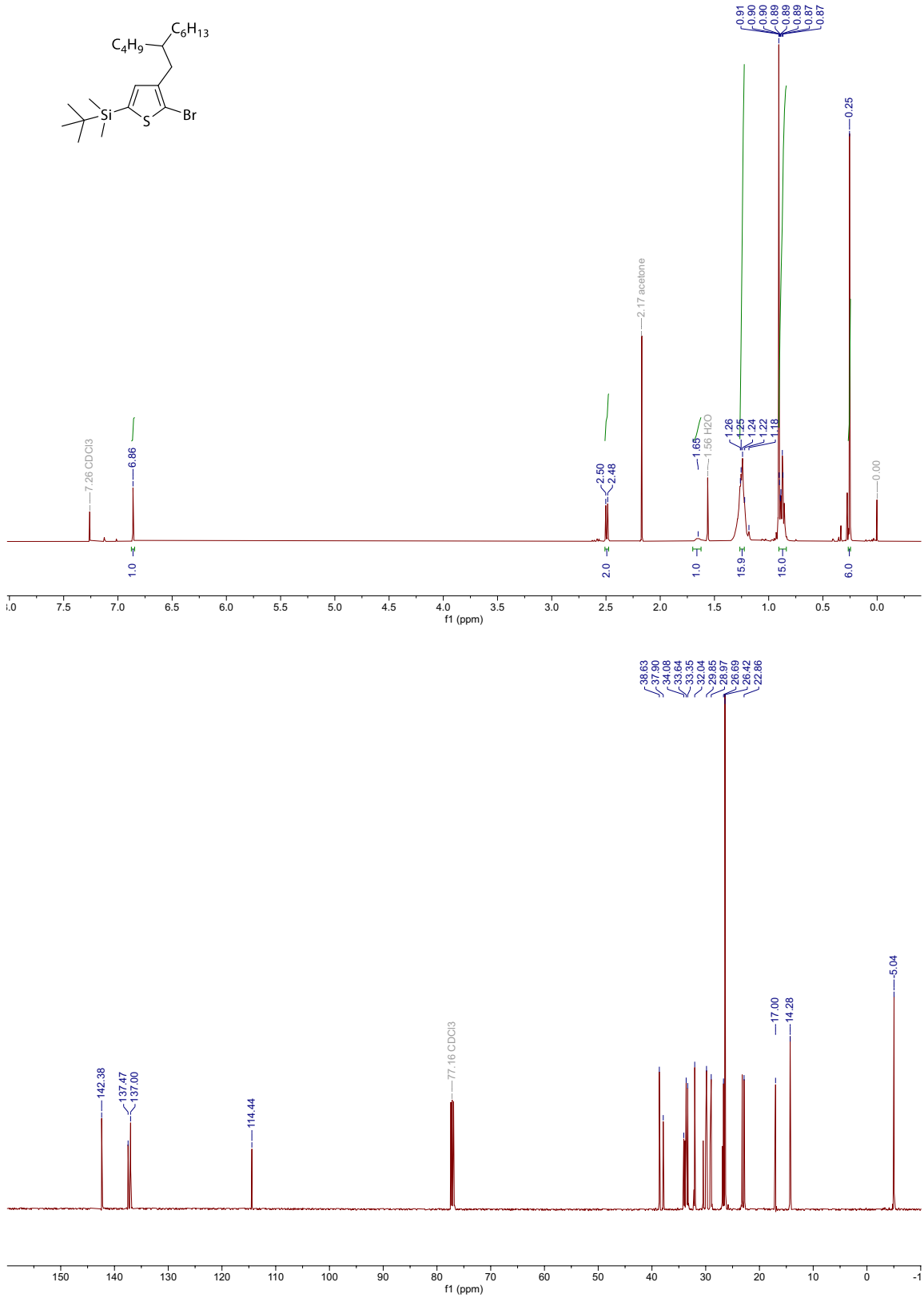

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **2 (R = DT)**.



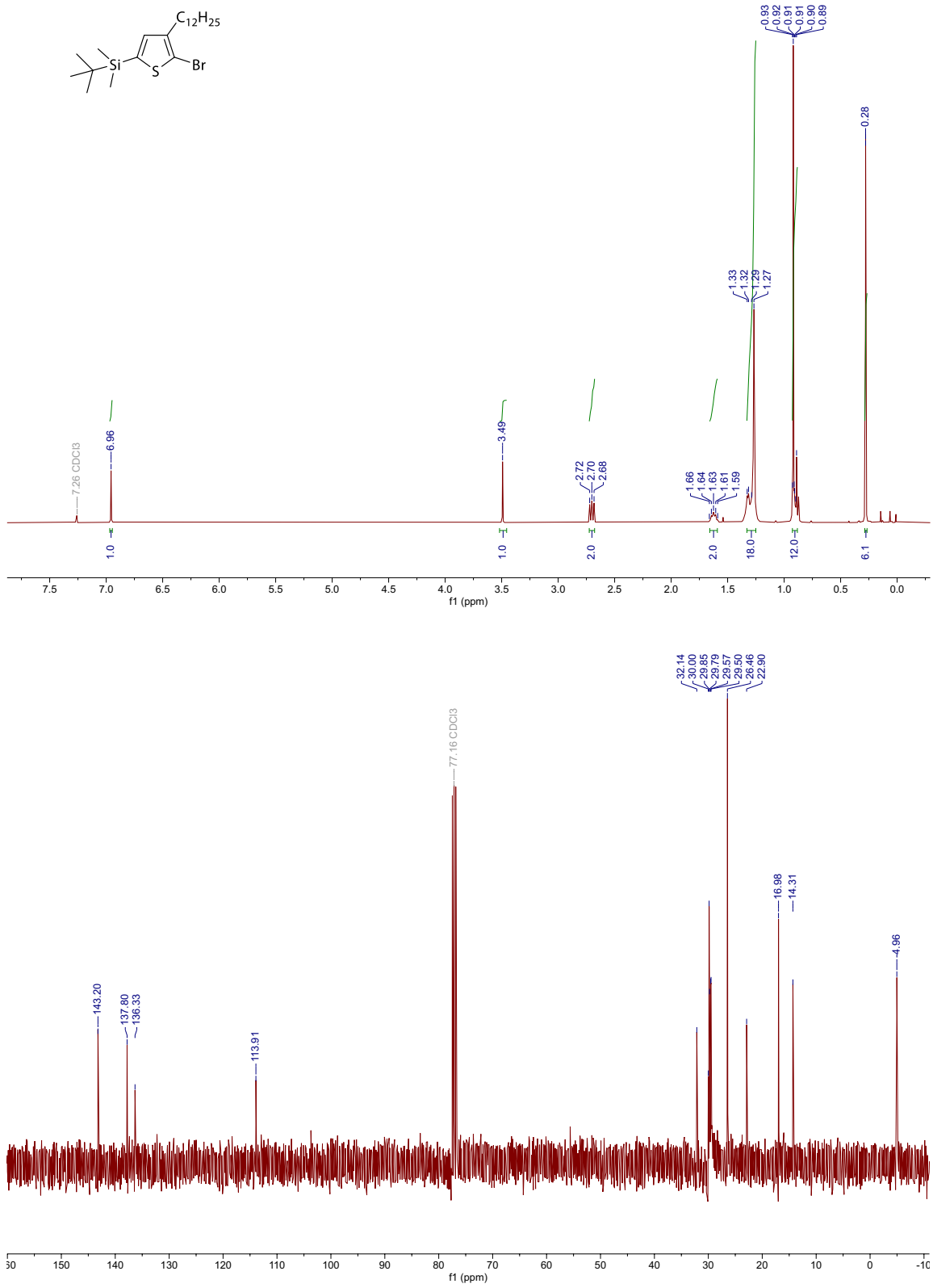

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **10 ($R^1$ = DT, $R^2$ = TBS)**.



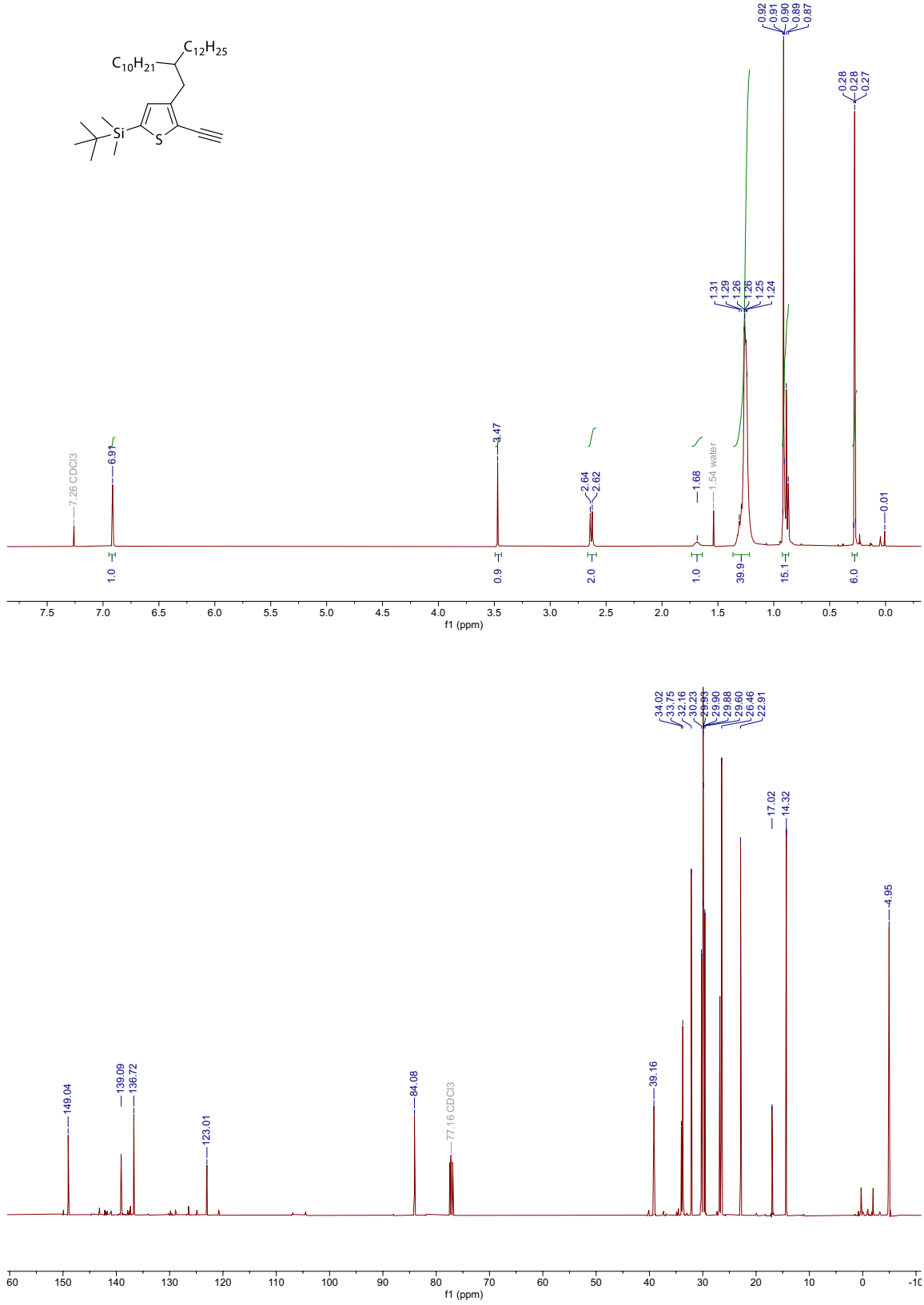

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **10 ($R^1$ = HD, $R^2$ = TBS)**.



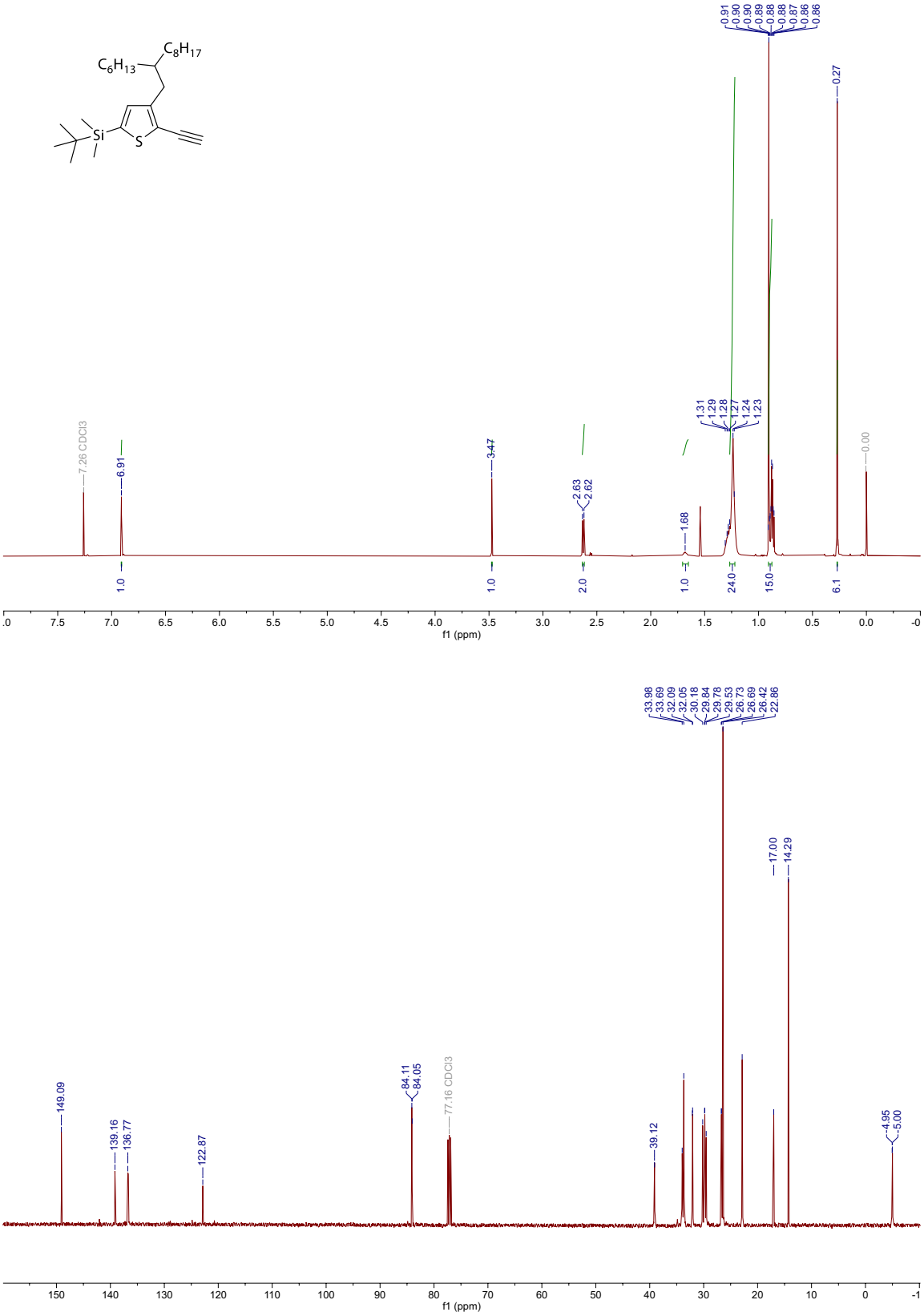

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **10 ($R^1$ = BO, $R^2$ = TBS)**.



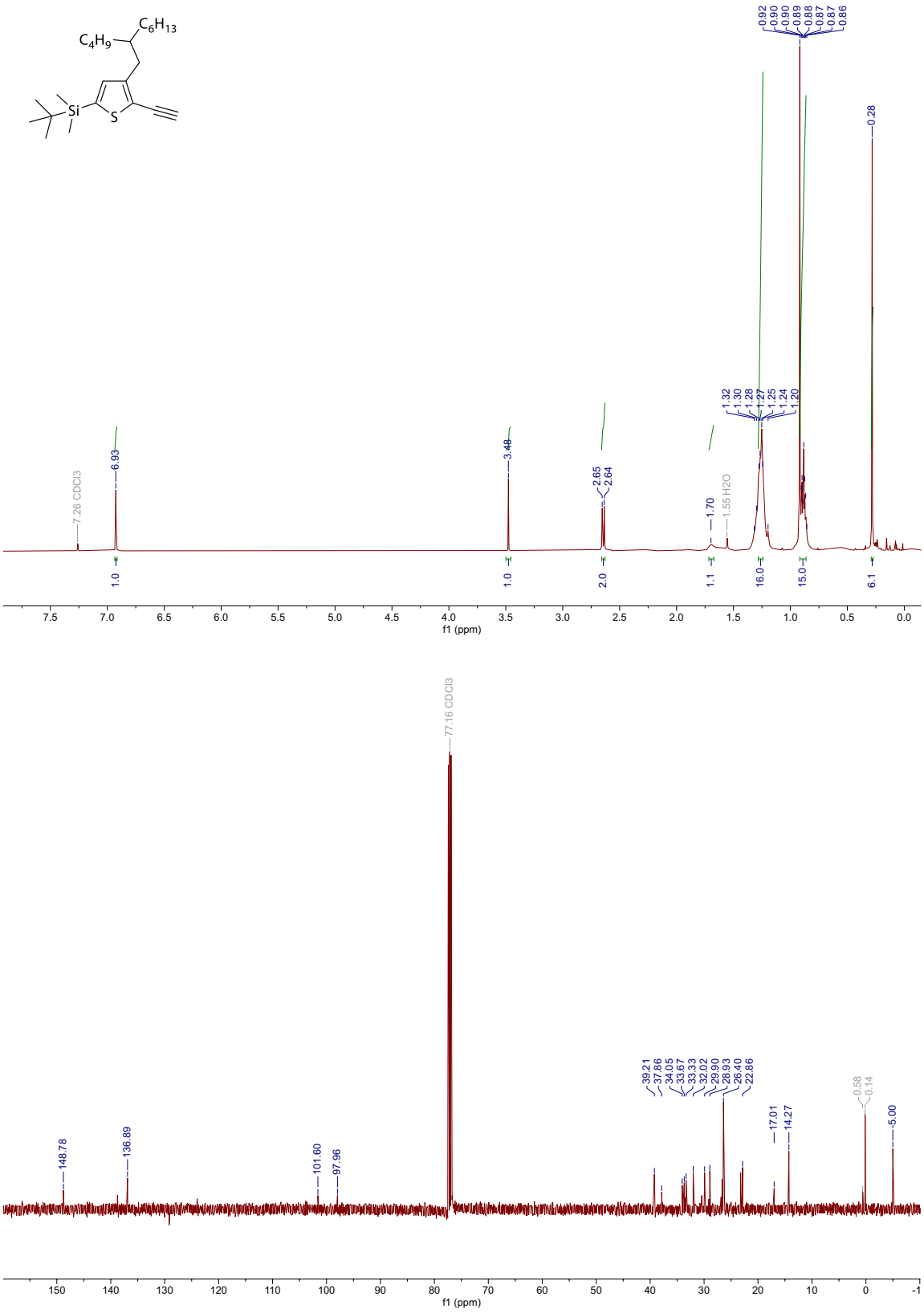

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **10 ($R^1$ = C12, $R^2$ = TBS)**.



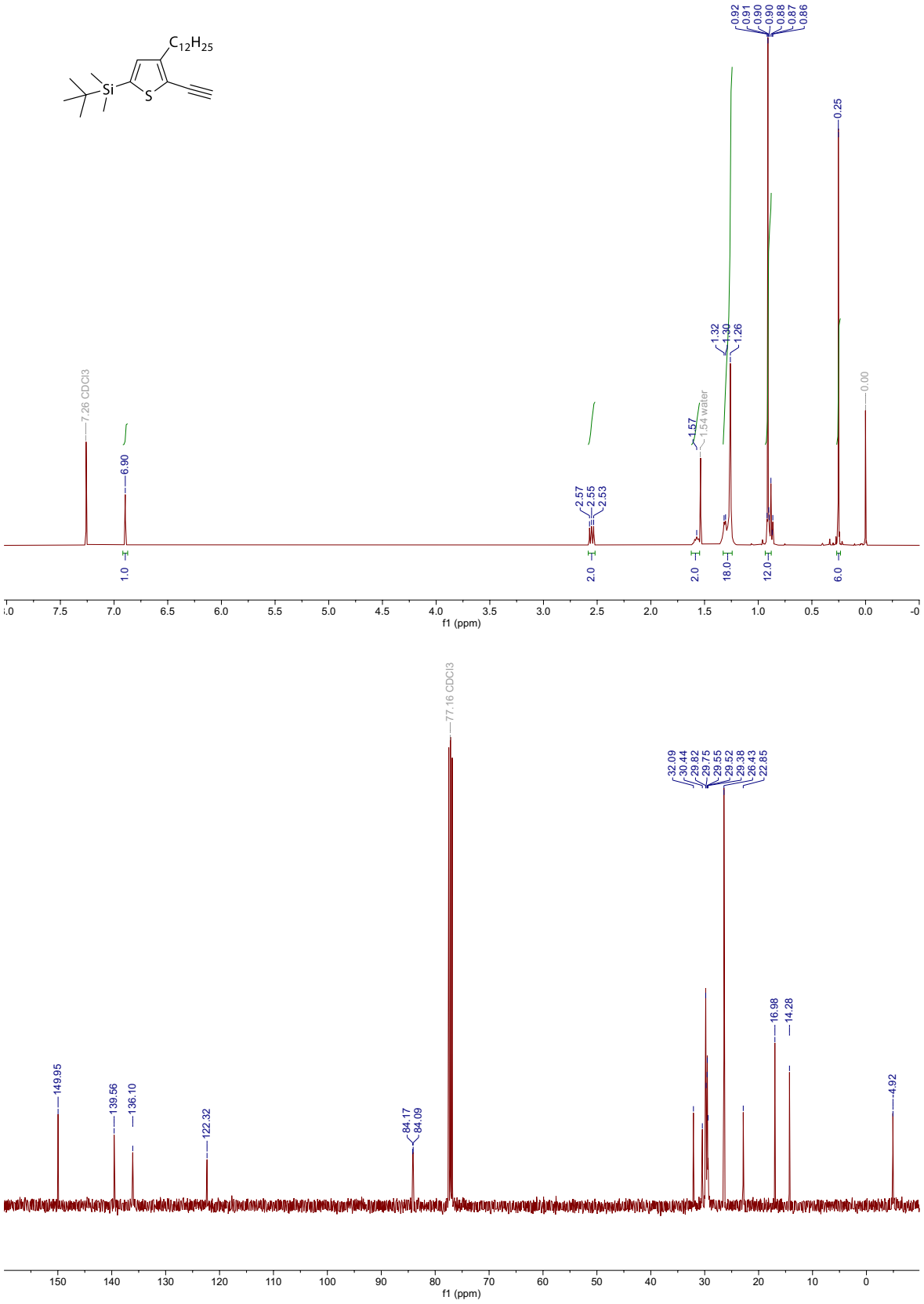

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **2 ($R^1$ = DT, $R^2$ = TBS)**.



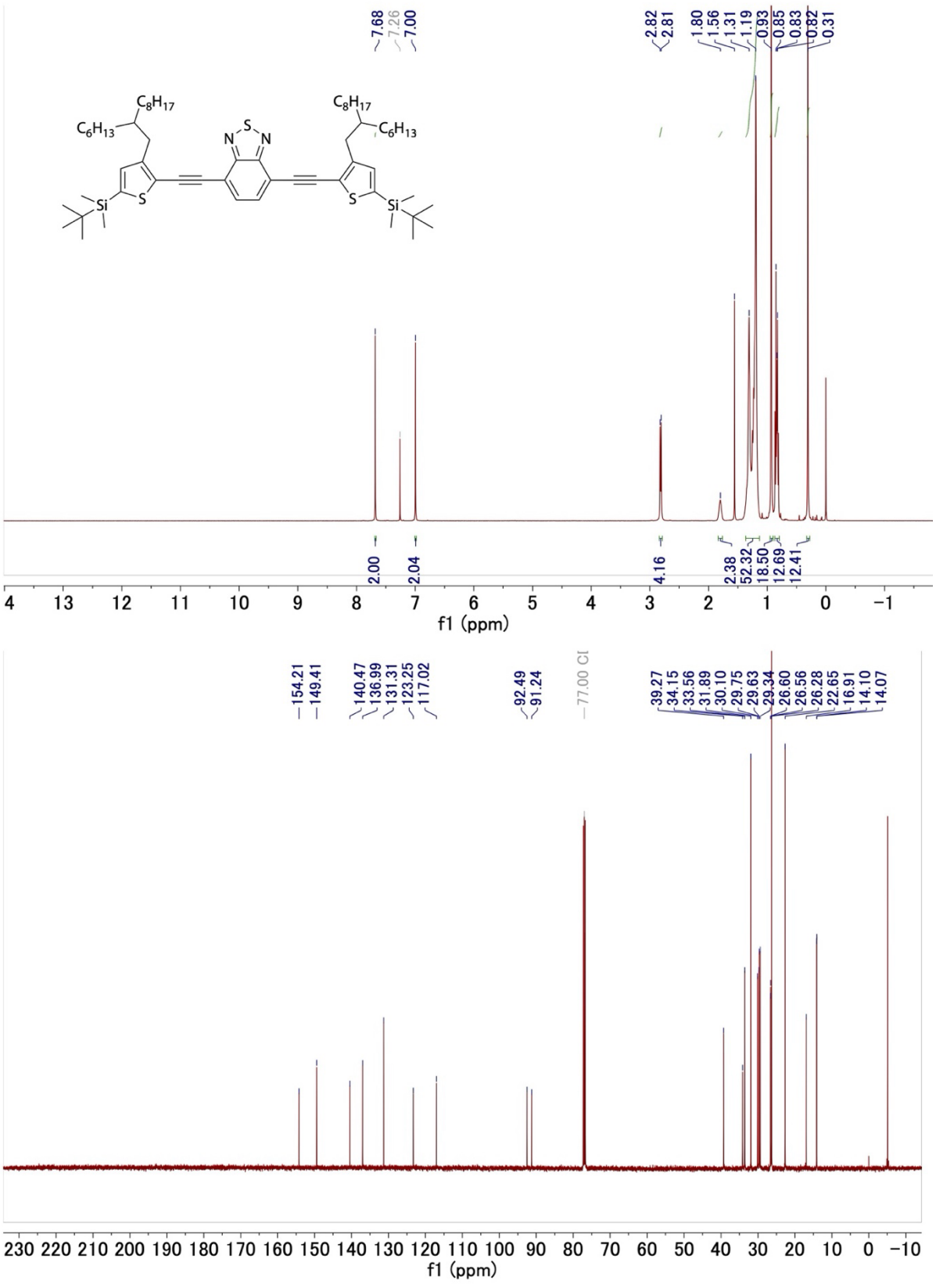

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **2 ($R^1$ = HD, $R^2$ = TBS)**.



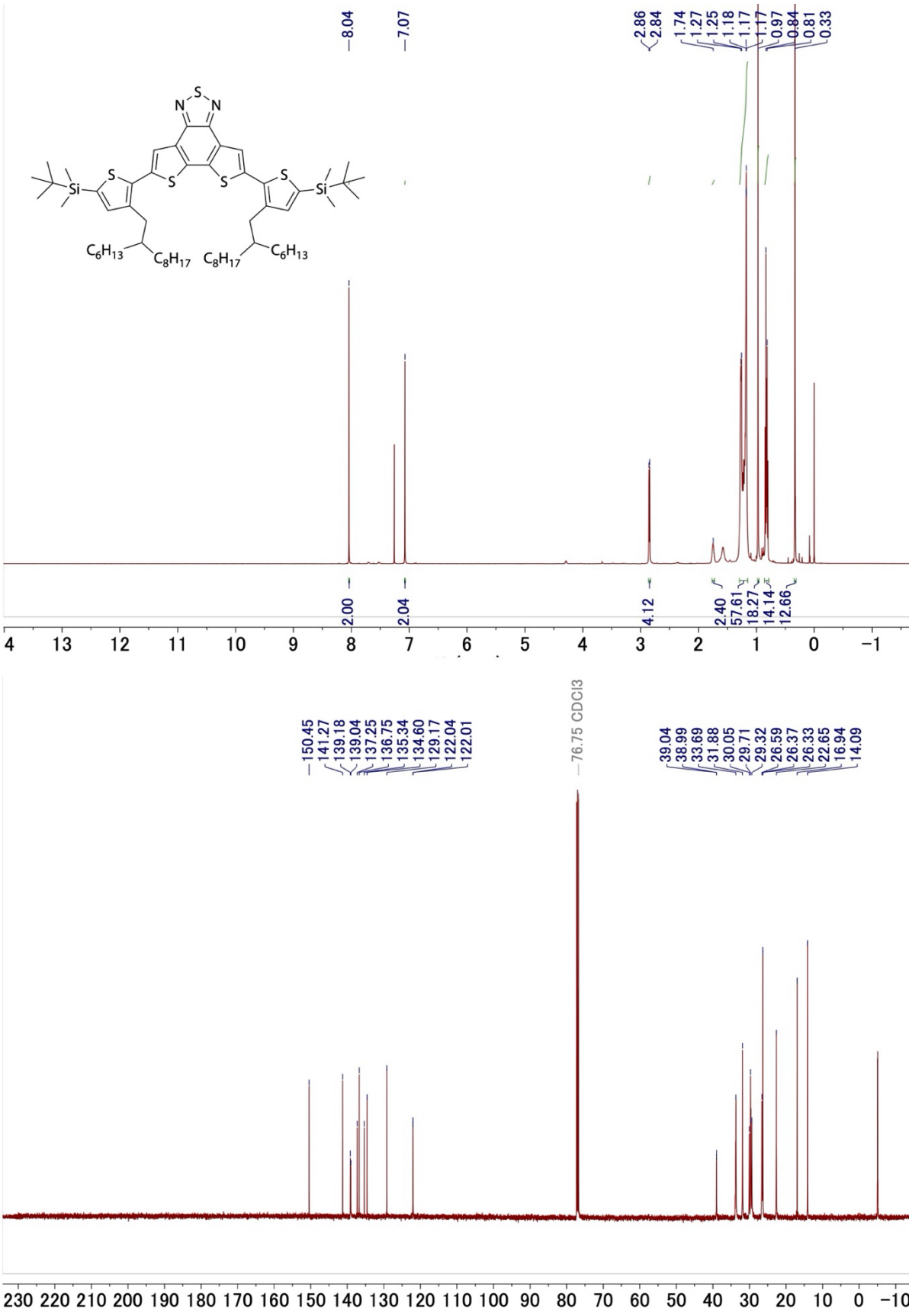

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **2 ($R^1$ = BO, $R^2$ = TBS)**.



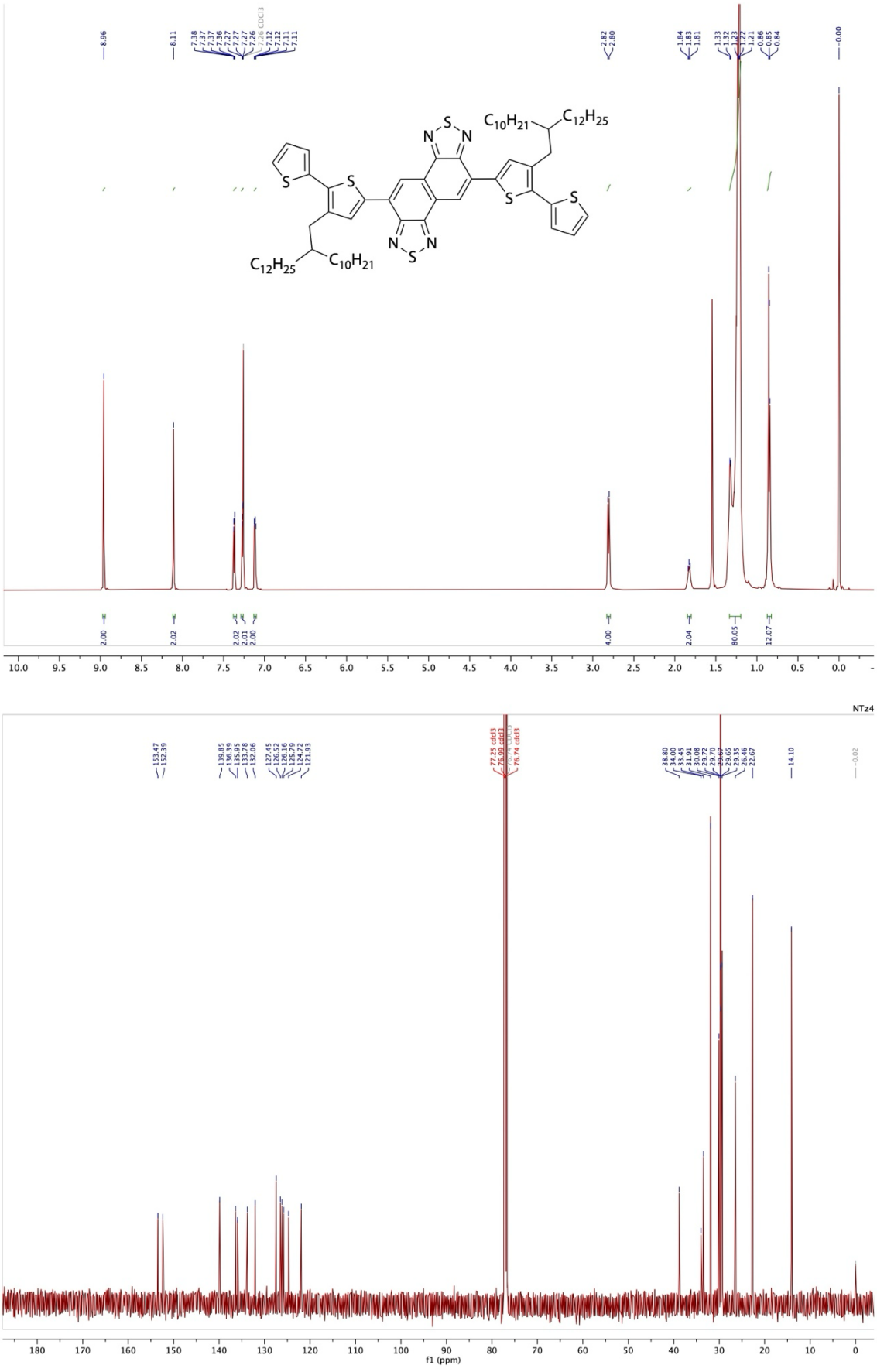

$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **2 ($R^1$ = C12, $R^2$ = TBS)**.




$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **12**.




$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **13**.




$^{1}$H-(upper) and $^{13}$C-NMR spectra (lower) of **NTz4T**.

## 2. Instrumentation.

Density functional theory (DFT) calculations of the model compounds for **PNTz4T**, **PTNT2T**, **PNTz1-F** and **PTNT1-F** were carried out based on the B3LYP/6-31G(d) basis set implemented in the Gaussian 16 Revision C.01 suite programs with default thresholds and algorithms, where the model of the polymer with methyl groups instead of long branched alkyl groups were employed for the calculation. Thermogravimetric analysis (TGA) was carried out on an SII TG/DTA-6200 analyzer under gentle nitrogen flow (100 mL $min^{-1}$) at a heating rate of 10 °C $min^{-1}$. Differential scanning calorimetry (DSC) analysis was carried out with an Exstar DSC6200 thermal analyzer (Seiko Instruments) at a cooling and heating rate of 10 °C $min^{-1}$.

Cyclic voltammograms were recorded on an ALS Electrochemical Analyzer Model 612D with the three electrodes system consisting of a platinum disc working electrode ($\varphi$ = 3 mm), a platinum wire counter electrode, and an $Ag/Ag^+$ reference electrode in acetonitrile containing tetrabutylammonium hexafluorophosphate (0.1 M) at a scan rate of 100 mV $s^{-1}$. The thin films of the materials were cast from CB solution directly on the working electrode. All the potentials were calibrated with the half-wave potential of the ferrocene/ferrocenium redox couple ($Fc/Fc^+$) measured under identical condition; $Fc/Fc^+$ (vs $Ag/Ag^+$) was 0.21 and 0.26 V for **NTz2T** and **TNT2T**, respectively, 0.14 V for **PNTz4T** and **PTNT2T**, and 0.17 V for **PNTz1-F** and **PTNT1-F**. HOMO and LUMO energy levels ($E_{HOMO}$ and $E_{LUMO}$) were estimated by the following equations, $E_{HOMO}$: $-4.80 - E_{ox}^{onset}$, $E_{LUMO}$: $-4.80 - E_{red}^{onset}$, where $E_{ox}^{onset}$ and $E_{red}^{onset}$ are onset potentials for the oxidation and reduction peaks. UV–vis absorption spectroscopy was performed with Shimadzu UV-3600 Plus spectrometer. As for the samples for the UV–vis measurements, the polymer solutions ($5 \times 10^{-6}$ M) were prepared using CB as the solvent and the polymer thin films were prepared by spin-coating from the CF solution. Photoluminescence (PL) spectra were measured with a fluorescence spectrometer (Horiba Jobin Yvon, NanoLog) equipped with a photomultiplier tube (Hamamatsu, R928P) and a liquid-nitrogen-cooled InGaAs near-infrared array detector (Horiba Jobin Yvon, Symphony II) under ambient

atmosphere.

GIXD experiments were conducted at the SPring-8 on the beamline BL46XU. The sample was irradiated with the X-ray energy of 12.39 keV ($\lambda$ = 1 Å) at a fixed incident angle on the order of 0.12 ° through a Huber diffractometer. The two-dimensional (2D) GIXD patterns were recorded with a 2D image detector (Pilatus 300 K). Samples for the X-ray measurements were prepared in the same manner as that for solar cell fabrication. Tapping mode atomic force microscopy was carried out on an SPM-9700HT scanning probe microscope.

**3. OFET fabrication and measurements.**

Top-gate-bottom-contact (TGBC) devices were fabricated on an alkaline-free glass substrate patterned with Cr/Au source and drain electrode, deposited via photolithography. The glass substrates were ultrasonicated with isopropanol for 10 min, and rinsed in boiled isopropanol for 10 min, and then were subjected to UV-ozone treatment for 30 min. The cleaned substrates were treated by 1-octanethiol (OT) to modify the Au source and drain electrodes. Polymer thin films were spin-coated from of the CB solution (5 g $L^{-1}$ for **PNTz4T** and **PTNT2T** and 7 g $L^{-1}$ for **PNTz1-F** and **PTNT1-F**, respectively), and then were annealed at 200 °C for 30 min. The CYTOP dielectric layer ($C_i$ = 4.13 nF $cm^{-2}$) with ca. 450 nm thickness was spin-coated on top of the polymer layer and then was dried at room temperature for 12 h. Finally, 100 nm Ag was evaporated on top as the gate electrode through a shadow mask.

Current–voltage characteristics were measured at room temperature under vacuum with a KEYSIGHT B2902A and a semiconductor parameter analysis software (SYSTEMHOUSE SUNRISE). Threshold voltages were estimated from the transfer plots by extrapolating the square root of the drain current to the horizontal axis. Hole and electron field-effect mobilities were extracted from the square root of the drain current in the saturation regime by using the following equation,

$$\mu = \frac{2L}{WC_i}\left(\frac{d\sqrt{|I_d|}}{dV_g}\right)^2$$

where, $L$ (25 μm) and $W$ (10000 μm) are channel length and width, respectively, and $C_i$ is capacitance of the gate insulator. The average hole and electron mobilities and threshold voltages were obtained over more than five devices.

**4. OPV fabrication and measurements.**

ITO/glass substrates were pre-cleaned sequentially by sonicating in a detergent bath, then with deionized water, acetone, and isopropanol at room temperature and in a boiled isopropanol bath, each for 10 min, and then baked at 120 ℃ for 3 min in air. They were then subjected to a UV/ozone treatment at room temperature for 20 min. The pre-cleaned ITO/glass substrates were coated with PEDOT:PSS (Clevios P VP Al 4083) by spin-coating at 4000 rpm for 30 s. The photoactive layer was deposited by spin-coating a polymer:acceptor solution in a glove box (KIYON, KK-011AS-EXTRA) as follows. For the **PNTz4T** and **PTNT2T**, 5 g $L^{-1}$ of the polymer:Y6 (eFlexPV, Ltd.) (1/1.2 w/w) solution in CF, where the concentration was based on the polymer weight, was stirred at 80 ℃ for 10 min, during which time the materials were completely dissolved. After cooling to room temperature, the solution was then spun at 1000 rpm for 20 s. Then, the photoactive layer was immediately baked at 90 ℃ for 5 min. For the **PNTz1-F** and **PTNT1-F**, 6 g $L^{-1}$ of the polymer:Y6 (1/1.2 w/w) solution in CF containing 0.5 vol% of 1-chloronaphthalene as the solvent additive, where the concentration was based on the polymer weight, was stirred at 60 ℃ for 0.5 h, during which time the materials were completely dissolved. The solution was then spun at 2500 rpm for 10 s. Then, the photoactive layer was immediately baked at 120 ℃ for 5 min. PNDIT-F3N-Br (Luminescence Technology Corp.) was subsequently deposited by spin-coating from 1 g $L^{-1}$ of the methanol solution onto the photoactive layer at 2000 rpm for 10 s in the glove box. The thin films were transferred into a vacuum evaporator (ALS Technology, E-100J) connected to the glove box. Ag layer (150 nm) was deposited by thermal evaporation through a shadow mask under ~$10^{-5}$ Pa, where the photoactive area was 0.04 $cm^2$.

The *J*−*V* characteristics of the cells were measured using a Keithley 2400 source–measure unit under 1 sun (AM1.5G) conditions using a solar simulator (SAN-EI Electric, XES-40S1) in the glove box. The light intensity for the *J*−*V* measurements was calibrated with a reference PV cell (Bunkoukeiki, BS520BK). $EQE_{PV}$ spectra were measured with a spectral response measuring system (SOMA OPTICS, S-9241). More than 10 different substrates (four photoactive areas each) were prepared for the optimized cells, and their photovoltaic properties were measured. Photoactive layer thickness was measured with an ET4000 (Kosaka Laboratory, Ltd.), where the optimal photoactive layer thickness was around 100 nm.

**5. Hole-only device fabrication and measurements.**[S4]

The pre-cleaned ITO substrates were coated with PEDOT:PSS by spin-coating (5000 rpm for 30 s, thickness of ~30 nm). The blend films were then spin-coated as described above. The thin films were transferred into a vacuum evaporator connected to the glove box, and $MoO_x$ (7.5 nm) and Ag (100 nm) were deposited sequentially through a shadow mask. The *J*–*V* characteristics were measured in the range of −0.2–7 V using a Keithley 2400 source measure unit under nitrogen in the dark. The mobility was calculated by fitting the *J*–*V* curves to a space charge limited current (SCLC) model according to the Mott–Gurney equation described by

$$J = (9/8)\, \varepsilon_r\, \varepsilon_0\, \mu^{SCLC}\, (V^2/L^3)$$

where $\varepsilon_r$ is the relative dielectric constant of the polymer, $\varepsilon_0$ is the permittivity of free space, $\mu^{SCLC}$ is the mobility, $V = V_{appl} - V_{bi}$, where $V_{appl}$ is the applied voltage to the device and $V_{bi}$ is the built-in voltage due to the difference in work function of the two electrodes (determined to be 0 V for the hole-only device), and $L$ is the polymer thickness. The relative dielectric constant $\varepsilon_r$ is assumed to be 3, which is a typical value for semiconducting polymers. The $\mu^{SCLC}$ was calculated by converting the equation as follows,

$$\mu^{SCLC} = (8\, L^3/9\, \varepsilon_r\, \varepsilon_0) \times (J^{0.5}/V)^2$$

where, $J^{0.5}/V$ corresponds to the slope of the $J^{0.5}$–*V* plot.

## 6. Supporting references

[S1] I. Osaka, M. Shimawaki, H. Mori, I. Doi, E. Miyazaki, T. Koganezawa, K. Takimiya, *J. Am. Chem. Soc.,* 2012, **134**, 3498–3507.

[S2] B. M. Kobilka, A. V. Dubrovskiy, M. D. Ewan, A. L. Tomlinson, R. C. Larock, S. Chaudhary, M. Jeffries-EL, *Chem. Commun.,* 2012, **48**, 8919–8921.

[S3] L.-H. Chou, T. Mikie, M. Saito, C.-L. Liu, I. Osaka, *ACS Appl. Mater. Interfaces,* 2022, **14**, 14400–14409.

[S4] C. Li, J. Zhou, J. Song, J. Xu, H. Zhang, X. Zhang, J. Guo, L. Zhu, D. Wei, G. Han, J. Min, Y. Zhang, Z. Xie, Y. Yi, H. Yan, F. Gao, F. Liu, Y. Sun, *Nat. Energy,* 2021, **6**, 605–613.

## 7. Supporting figures and tables.

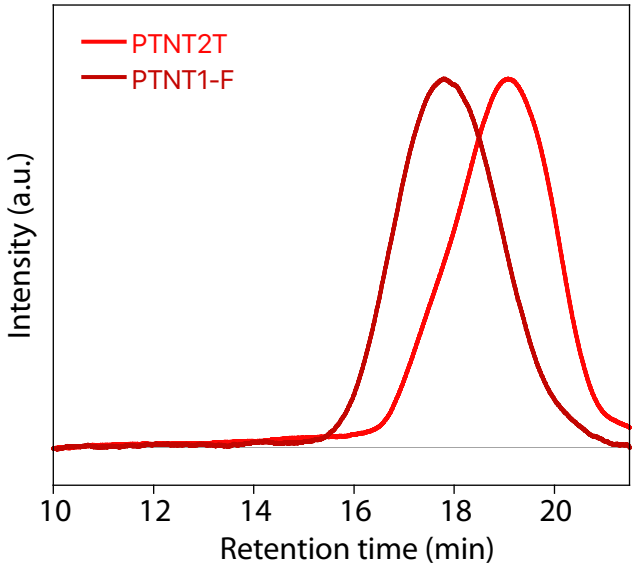



**Figure S1.** GPC chart for **PTNT2T** and **PTNT1-F**.

**Table S1.** Polymerization results of **PTNT2T** and **PTNT1-F**.

| Polymer | $M_n$[a] | $M_w$[a] | $Đ$[b] |
|---|---|---|---|
| **PTNT2T** | 20,000 | 40,000 | 2.0 |
| **PTNT1-F** | 41,000 | 88,000 | 2.1 |

[a]Determined by high-temperature GPC using polystyrene standard and TCB as the eluent at 180 °C. [b]Dispersity index ($M_w/M_n$).

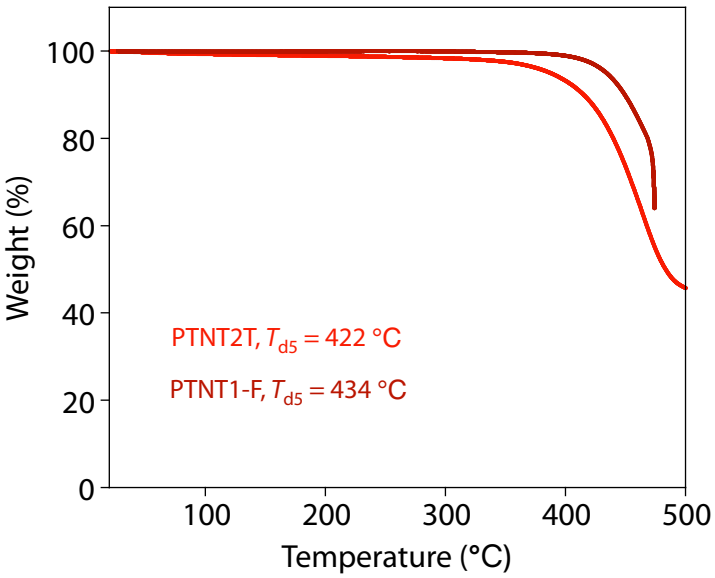



**Figure S2.** TGA curves of TNT-based polymers. The value is the temperatures of 5% weight loss ($T_{d5}$).

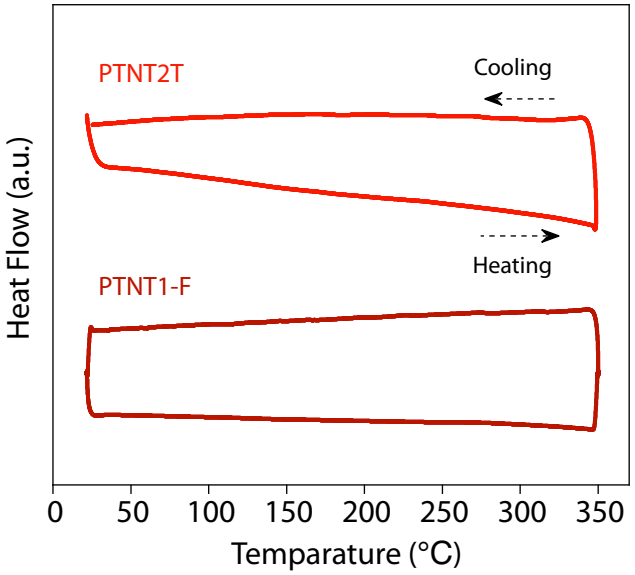



**Figure S3.** DSC curves of TNT-based polymers.

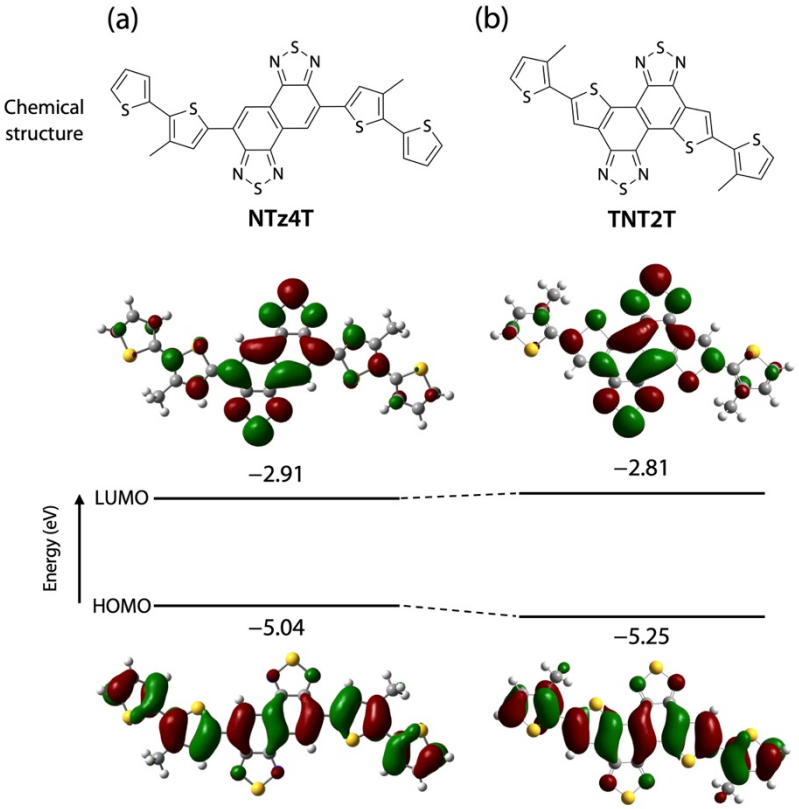



**Figure S4.** Optimized structures and geometries of HOMO and LUMO for (a) **NTz4T** and (b) **TNT2T** (**5a**) calculated by the DFT method at the B3LYP/6-31g(d) level. The branched alkyl groups were replaced by the methyl groups to simplify the calculation.

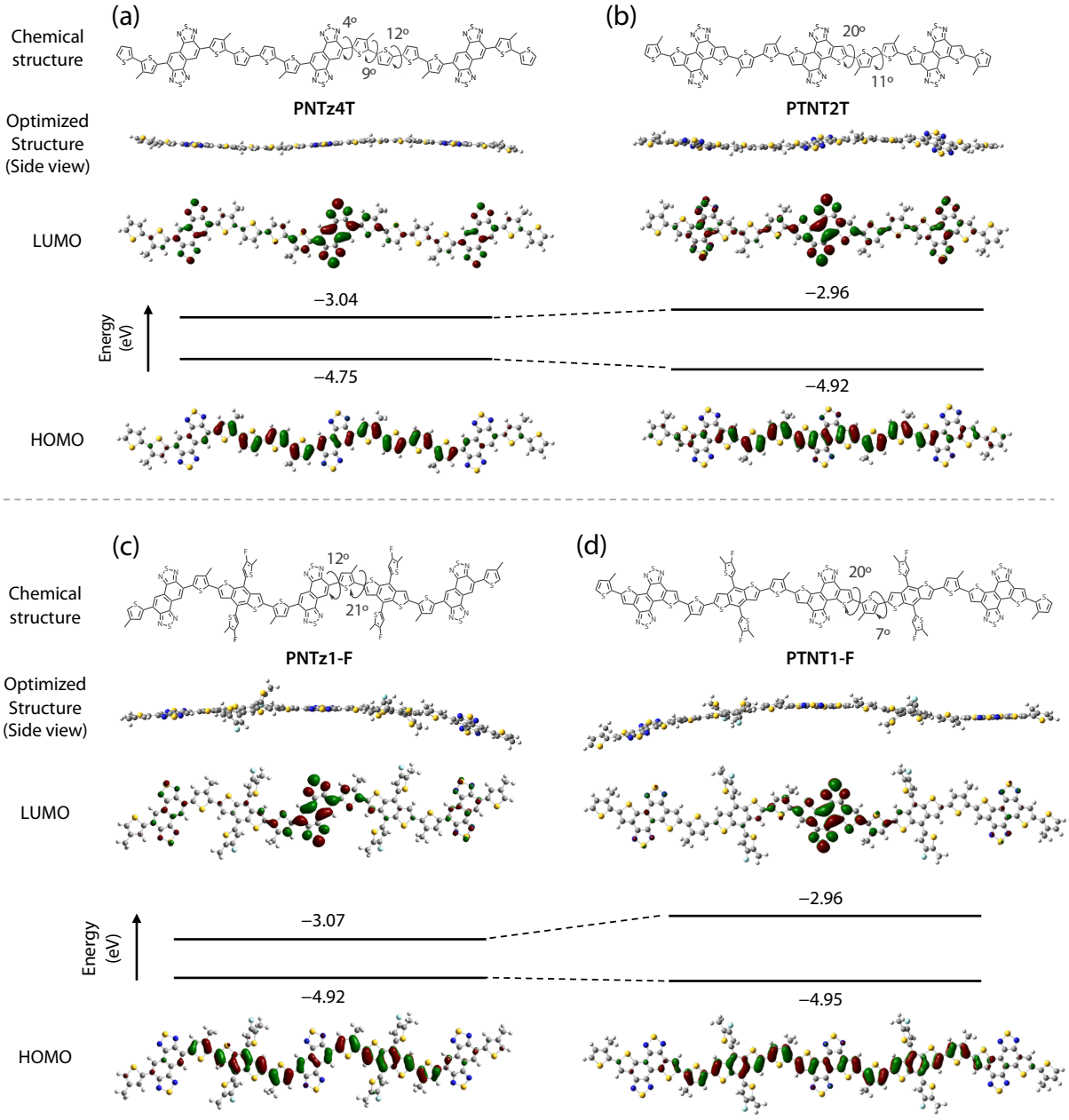
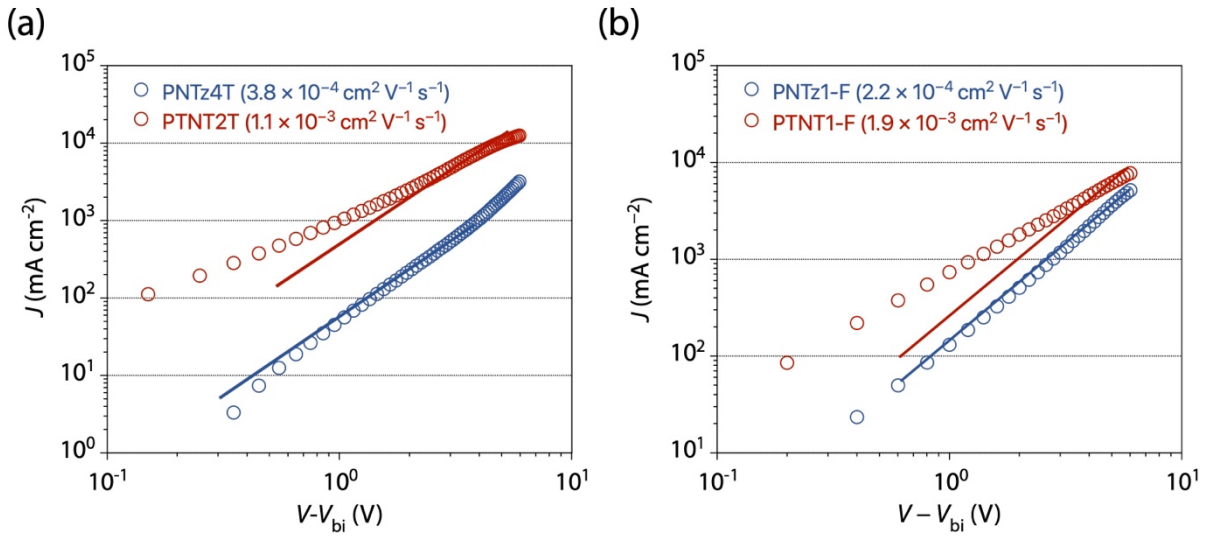



**Figure S5.** Optimized structures and geometries of HOMO and LUMO for the model of (a) **PNTz4T**, (b) **PTNT2T**, (c) **PNTz1-F** and (d) **PTNT1-F** calculated by the DFT method at the B3LYP/6-31g(d) level. To better reflect the electronic structure in the polymer system, we carried out the calculation by using the model trimers. The branched alkyl groups were replaced by the methyl groups to simplify the calculation.




~~**Figure S5.** *J–V* curves of the cells based on (a) **PNTz4T** and **PTNT2T**, and (b) **PNTz1-F** and **PTNT1-F**. Film thicknesses were 110, 110, 120, 90 nm for the **PNTz4T**, **PTNT2T**, **PNTz1-F**, and **PTNT1-F** cells, respectively.~~

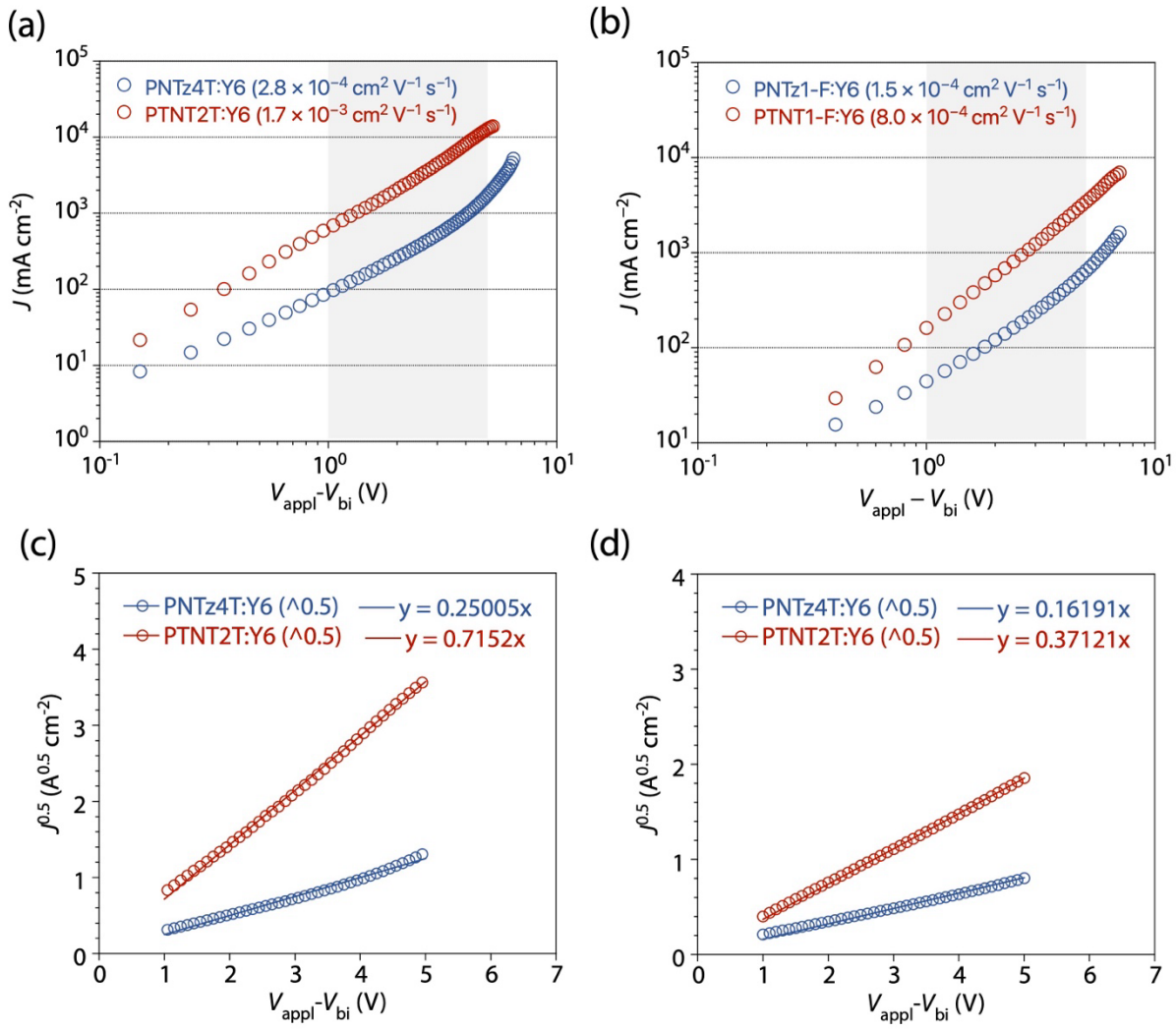



**Figure S6.** (a, b) *J*–*V* logarithm plots for the cells based on (a) **PNTz4T**:Y6 and **PTNT2T**:Y6, and (b) **PNTz1-F**:Y6 and **PTNT1-F**:Y6. Film thicknesses were 100, 110, 120, 120 nm for the **PNTz4T**:Y6, **PTNT2T**:Y6, **PNTz1-F**:Y6, and **PTNT1-F**:Y6 cells, respectively. (c, d) $J^{0.5}$–*V* plots for the cells based on (c) **PNTz4T**:Y6 and **PTNT2T**:Y6, and (d) **PNTz1-F**:Y6 and **PTNT1-F**:Y6. The plots were fitted according to the Mott–Gurney equation for mobility calculation.

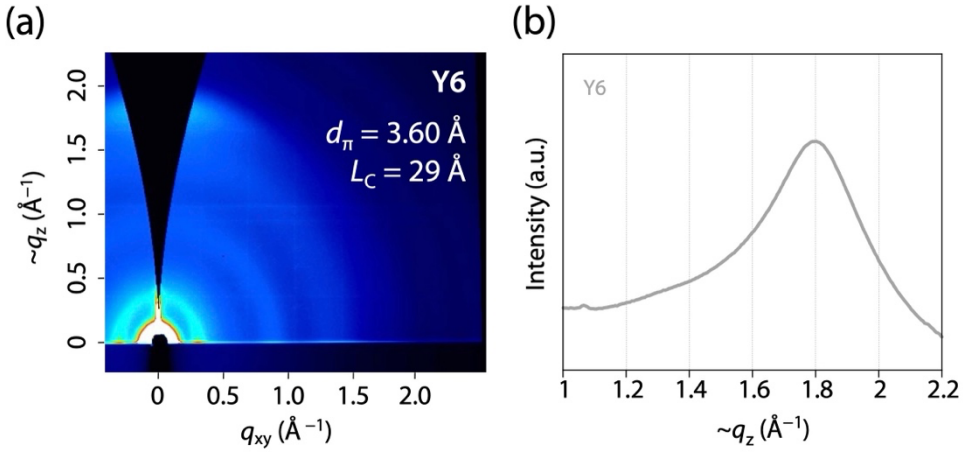



**Figure S7.** 2D GIXD of the (a) Y6 and fabricated using CF as the solvent. (b) Cross-sectional diffraction profiles cut from the 2D GIXD patterns along the ~$q_z$ for the film.

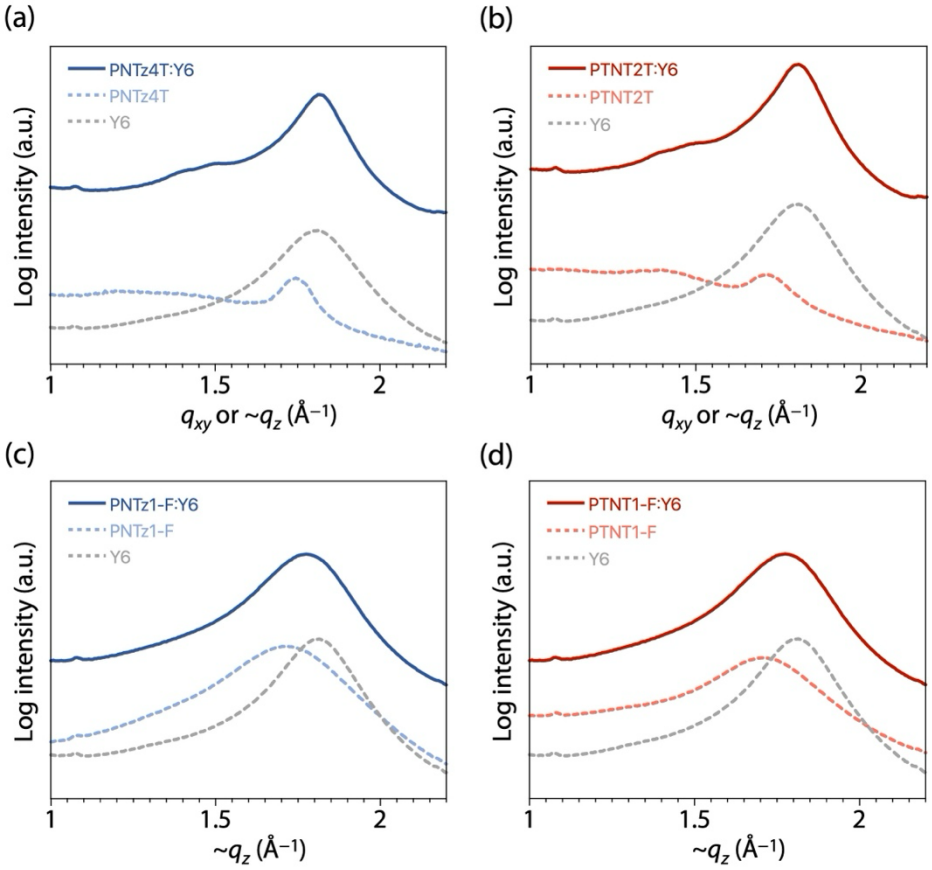



**Figure S8.** Cross-sectional diffraction profiles cut from the 2D GIXD patterns of (a) **PNTz4T**:Y6 blend film along with PNTz4T and Y6 neat films, (b) **PTNT2T**:Y6 blend film along with PTNT2T and Y6 neat films, (c) **PNTz1-F**:Y6 blend film along with **PNTz1-F** and Y6 neat films and (d) **PTNT1-F**:Y6 blend film along with **PTNT1-F** and Y6 neat films along the ~$q_z$ axis.

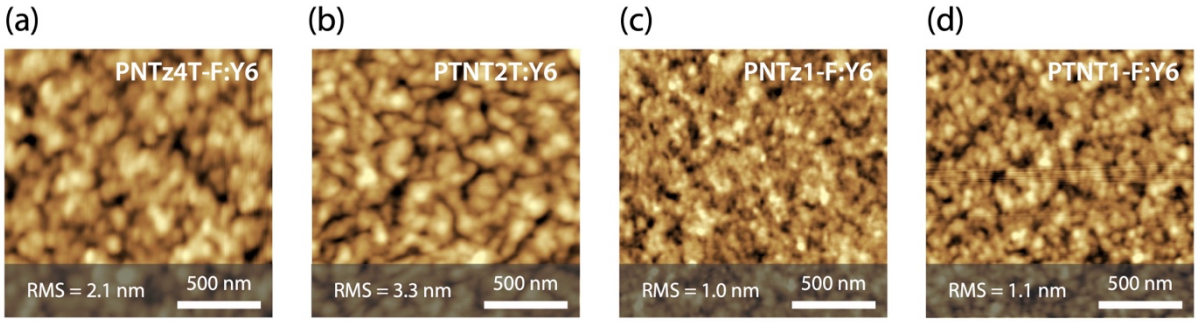



**Figure S9.** AFM images of the (a) **PNTz4T**:Y6, (b) **PTNT2T**:Y6, (c) **PNTz1-F**:Y6, (d) **PTNT1-F**:Y6. RMS = root-mean-square value.