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*Electronic Supporting Information for*

# On the transition-metal-free controlled polymerization of 2-polyfluorophenyl-5-trimethylsilylthiophenes: Substituent impact of fluorine

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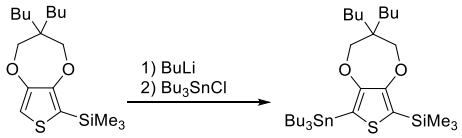
**Experimental section**

**Measurements**. $^{1}H$, $^{13}C$, $^{19}F$, and $^{29}Si$ NMR spectra were recorded using a Bruker Biospin AVANCE 400 (or 500) FT-NMR spectrometer at 400 (or 500), 100 (or 125.8), 376, and 79.5 (or 99.4) MHz, respectively. $^{1}H$ and $^{13}C$ chemical shifts were referenced to solvent residues. $^{19}F$, and $^{29}Si$ chemical shifts were referenced to trichlorofluoromethane ($CFCl_3$) and tetramethylsilane, respectively. Mass and FAB mass spectra were obtained with a JEOL JMS-700 mass spectrometer. Size-exclusion chromatography (SEC) was performed on a JASCO HPLC LC-2000Plus equipped with SHODEX LF804 (× 2) columns with THF as an eluent. MW and PDI were determined by SEC with polystyrene standards. UV/Vis spectra were recorded by using a Shimadzu UV-3100S spectrometer. Fluorescence spectra were recorded by using a JASCO FP-6300 spectrometer. Fluorescence quantum yields were obtained with a Quantaurus-QY C11347. Fluorescence life time were measured on a Quantaurus-Tau C11367.

**Materials**. All manipulations involving air and moisture-sensitive compounds were carried out under atmosphere of dry argon. All solvents and reagents were of reagent quality, purchased from commercial sources and used without further purification. Silica gel for column chromatography was purchased from WAKO Chemicals (Wakogel, C-300HG or Wakosil, HC-N). TLC plates were purchased from Merck (Silica Gel60F254 TLC plate).

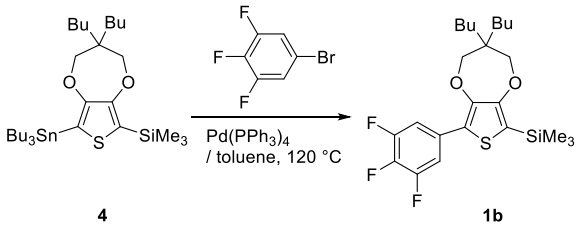
**3,4-(2′,2′-dibutylpropylene)dioxy-2-tributylstanyl-5-trimethylsilylthiophene 4**




**3** **4** (S1)

To 3,4-(2′,2′-dibutylpropylene)dioxy-2-trimethylsilylthiophene **3**[1] (11.1 g, 32.6 mmol) in THF (70 mL) was added a hexane solution of n-butyllithium (1.60 M, 24 mL, 38.4 mmol) at −78 °C for 10 min. The mixture was stirred at the temperature for 30 min and then 30 min at 0 °C. Chlorotributylstannane (12.1 g, 36.3 mmol) was added to the mixture at 0 °C at once and then the mixture was stirred at room temperature overnight. A saturated aqueous solution of $NH_4Cl$ was added to the mixture and the resulting mixture was extracted with hexane. The organic layer was washed with a saturated aqueous solution of NaCl and dried over anhydrous $MgSO_4$. After filtration and removal of the solvent, the title compound was obtained (19.1 g, 30.3 mmol, 93%), which was directly used in subsequent Stille cross-coupling reactions. A pale yellow oil; $^{1}H$ NMR ($CDCl_3$, 400 MHz) δ 0.27 (s, 9H), 0.89-1.58 (m, 45H), 3.73 (s, 2H), 3.78 (s, 2H).

**3,4-(2′,2′-dibutylpropylene)dioxy-2-(3,4,5-trifluorophenyl)-5-trimethylsilylthiophene 1b**

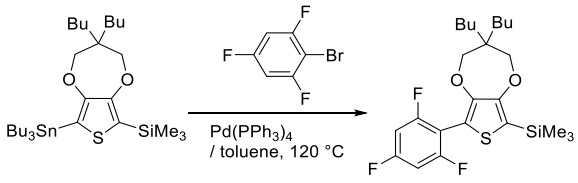



**4** **1b** (S2)

A mixture of 3,4-(2′,2′-dibutylpropylene)dioxy-2-tributylstanyl-5-trimethylsilylthiophene **4** (1.92 g, 3.05 mmol), 3,4,5-trifluorobromobenzene (1.01 g, 4.80 mmol), and $Pd(PPh_3)_4$ (0.35 g, 0.30 mmol)

in toluene 20 mL was stirred at 120 °C for 3 days. To the mixture was added a saturated aqueous solution of $NH_4Cl$ and the resulting mixture was extracted with hexane. The organic layer was washed with a saturated aqueous solution of NaCl and dried over anhydrous $MgSO_4$. After filtration and removal of the solvent, the residue was purified with chromatography ($SiO_2$, hexane) to give the title compound (0.65 g, 13.9 mmol, 45%). A colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) δ 0.34 (s, 9H), 0.94-0.99 (m, 6H), 1.30-1.49 (m, 12H), 3.89 (s, 2H), 3.99 (s, 2H), 7.35-7.39 (m, 2H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz) δ 0.80, 14.0, 14.1, 22.7, 23.6, 25.1, 31.6, 31.8, 43.7, 77.4, 77.5, 109.9, 110.0. 110.1, 110.2, 115.7, 122.7, 129.7 (bs), 139.6 (bs), 147.8, 149.9 (bs), 152.4 (bs), 156.1; $^{19}$F{$^1$H} NMR ($CDCl_3$, 376 MHz) δ −163.3 (t, *J* = 20 Hz, 1F), −135.2 (d, *J* = 20 Hz, 2F); $^{29}$Si{$^1$H} NMR ($CDCl_3$, 79.5 MHz) δ −6.8; HRMS calcd for $C_{24}H_{34}F_3O_2SSi$ ($[M]^+$) *m*/*z* 470.1923, found 470.1927.

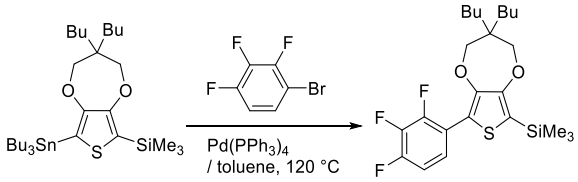
**3,4-(2′,2′-dibutylpropylene)dioxy-2-(2,4,6-trifluorophenyl)-5-trimethylsilylthiophene 1c**




(S3)

A mixture of 3,4-(2′,2′-dibutylpropylene)dioxy-2-tributylstanyl-5-trimethylsilylthiophene **4** (1.92 g, 3.05 mmol), 2,4,6-trifluorobromobenzene (0.73 g, 3.46 mmol), and $Pd(PPh_3)_4$ (0.11 g, 0.10 mmol) in toluene 20 mL was stirred at 120 °C for 3 days. To the mixture was added a saturated aqueous solution of $NH_4Cl$ and the resulting mixture was extracted with hexane. The organic layer was washed with a saturated aqueous solution of NaCl and dried over anhydrous $MgSO_4$. After filtration and removal of the solvent, the residue was purified with chromatography ($SiO_2$, hexane/toluene = 10/1) to give the title compound (0.62 g, 13.2 mmol, 41%). A colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) δ 0.33 (s, 9H), 0.95 (t, *J* = 7.1 Hz, 6H), 1.25-1.45 (m, 12H), 3.85 (s, 2H), 3.88 (s, 2H), 6.72-6.76 (m, 2H); $^{19}$F{$^1$H} NMR ($CDCl_3$, 376 MHz) δ −108.6 (t, *J* = 6.8 Hz, 1F), −107.4 (d, *J* = 6.8 Hz, 2F); HRMS calcd for $C_{24}H_{34}F_3O_2SSi$ ($[M]^+$) *m*/*z* 470.1923, found 470.1923.

**3,4-(2′,2′-dibutylpropylene)dioxy-2-(2,3,4-trifluorophenyl)-5-trimethylsilylthiophene 1d**

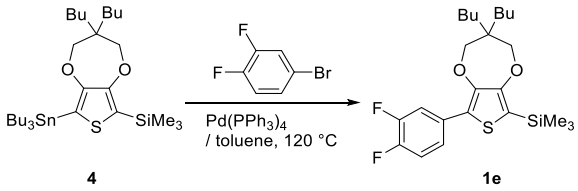



(S4)

A mixture of 3,4-(2′,2′-dibutylpropylene)dioxy-2-tributylstanyl-5-trimethylsilylthiophene **4** (6.3 g, 9.9 mmol), 2,3,4-trifluorobromobenzene (2.32 g, 11 mmol), and $Pd(PPh_3)_4$ (0.58 g, 0.50 mmol) in toluene 50 mL was stirred at 110 °C overnight. After removal of volatile under vacuum, hexane was added to the residue and filtered with Celite. After removal of the solvent, the residue was purified with chromatography ($SiO_2$, hexane/dichloromethane = 4/1) to give the title compound (1.25 g, 2.66 mmol, 27%). A colorless oil; $^1$H NMR ($CD_2Cl_2$, 400 MHz) δ 0.35 (s, 9H), 0.97 (t, *J* = 7.1 Hz, 6H), 1.30-1.45 (m, 12H), 3.89 (s, 2H), 3.93 (s, 2H), 7.01-7.09 (m, 1H), 7.35, 7.41 (m, 1); $^{13}$C{$^1$H} NMR

($CD_2Cl_2$, 100 MHz) δ -1.1, 13.8, 22.6, 23.6, 25.0, 31.5, 43.7, 77.8, 111.8, 111.8, 112.0, 117.4, 124.2, 148.5, 155.7; $^{19}F\{^1H\}$ NMR ($CD_2Cl_2$, 376 MHz) δ −161.6 (t, *J* = 22 Hz, 1F), −136.9 (dd, *J* = 8, 22 Hz, 2F), −134.5 (dd, *J* = 8, 22 Hz, 2F); HRMS calcd for $C_{24}H_{34}F_3O_2SSi$ ($[M]^+$) *m*/*z* 470.1923, found 470.1927.

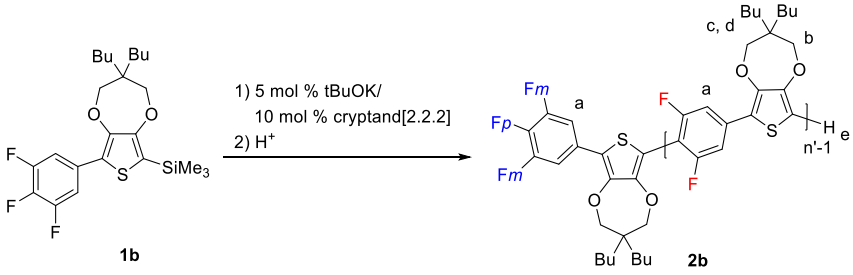
**3,4-(2′,2′-dibutylpropylene)dioxy-2-(3,4-difluorophenyl)-5-trimethylsilylthiophene 1e**




(S5)

A mixture of 3,4-(2′,2′-dibutylpropylene)dioxy-2-tributylstanyl-5-trimethylsilylthiophene **4** (2.02 g, 3.21 mmol), 3,4-difluorobromobenzene (0.88 g, 4.56 mmol), and $Pd(PPh_3)_4$ (86 mg, 0.075 mmol) in toluene 20 mL was stirred at 120 °C for 3 days. To the mixture was added a saturated aqueous solution of $NH_4Cl$ and the resulting mixture was extracted with hexane. The organic layer was washed with a saturated aqueous solution of NaCl and dried over anhydrous $MgSO_4$. After filtration and removal of the solvent, the residue was purified with chromatography ($SiO_2$, hexane) to give the title compound (0.74 g, 16.4 mmol, 63%). A colorless oil; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 0.37 (s, 9H), 1.00 (t, *J* = 7.1 Hz, 6H), 1.32-1.51 (m, 12H), 3.91 (s, 2H), 3.99 (s, 2H), 7.12-7.30 (m, 2H), 7.62-7.67 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ −0.7, 14.0, 23.6, 25.1, 31.8, 43.7, 77.3(8), 77.5, 114.8, 115.2, 115.4, 122.3 (bs), 130.8 (bs), 147.2, 147.9, 149.0, 150.0, 150.4, 151.5, 156.2; $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz) δ −140.1 (d, *J* = 22 Hz, 1F), −137.8 (d, *J* = 22 Hz, 1F); HRMS calcd for $C_{18}H_{32}O_2SSi$ ($[M]^+$) *m*/*z* 452.2107, found 452.2105.

**Polymerization of 1b with *t*-BuOK in the presence of cryptand[2.2.2] in THF**




(S6)

In an argon filled glove box, to a mixture of 1b (153 mg, 0.325 mmol) and cryptand[2.2.2] (14.5 mg, 0.039 mmol) in THF (5 mL) was added a 16 μL of a 1 M THF solution of potassium *tert*-butoxide ($1.6 \times 10^{-3}$ mmol) at room temperature. After stirring for 18 h at 80 °C, 0.2 mL of ethanol was added to the mixture at the room temperature. The mixture was poured into methanol (200 mL) and then the precipitate was collected by centrifugation. A second cycle of dissolving–precipitation with toluene/methanol followed by freeze-drying gave a polymer (95 mg, 0.27 mmol for the monomer unit, 83%). A pale yellow powder: $M_n$ = 7800, $M_w/M_n$ = 1.53 (SEC relative to polystyrene standards); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 0.94 (bt, *J* = 6.8 Hz, Hd), 1.27-1.55 (bm, Hc), 4.04 (bs, 4H, Hb), 6.48 (s, Ha), 6.72 (s, He); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ −0.8, 14.0, 22.7, 23.5, 25.0, 25.1, 29.7, 31.6, 31.8, 43.7, 43.9, 77.7, 77.9, 107.1, 107.3, 107.6, 109.2, 109.4, 110.3, 110.5, 119.7, 135.2, 147.3, 148.3, 148.6, 148.6, 156.1, 159.3, 159.4, 161.3, 161.4; $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376

MHz) δ−139.1 (bs, F), −137.9 (m, $F_m$), −162.7 (m, $F_p$).

**Studies on $M_n$ and PDI as a function of monomer conversion in the polymerization of 1b.**

A stock solution of **1b** (400 mg, 0.85 mmol), cryptand[2.2.2] (41 mg, 0.108 mmol), and fluorobenzene (40 μL as an internal standard) in THF (16 mL) was prepared. To a 2 mL of the solution was added 1 mL THF solution of 5 mol % of potassium *t*-butoxide. The mixture was stirred at 80 °C. The reaction was terminated by addition of 0.2 mL of ethanol. To the reaction mixture was added 1 mL of $CDCl_3$. The conversion of **1b** was estimated by $^{19}F$ NMR analysis using fluorobenzene as an internal standard. The $M_n$ and PDI were estimated by SEC analysis with polystyrene standards. The results are shown in Table S1.

**Table S1** *M*n and PDI as a function of monomer conversion in the polymerization of **1b** with 5 mol % / 10 mol % cryptand[2.2.2] in THF at 80 °C.

| time/min | conv/%[a] | $M_n$[b] | PDI[b] |
|---|---|---|---|
| 0 | 0 | - | - |
| 2 | 30 | 2600 | 1.26 |
| 5 | 62 | 3600 | 1.30 |
| 10 | 66 | 4500 | 1.50 |
| 20 | 76 | 5800 | 1.39 |
| 40 | 86 | 6000 | 1.56 |

[a] Determined by the integral ratio in the $^{19}F$ NMR with fluorobenzene as an internal standard. [b] Determined using SEC with polystyrene standards.

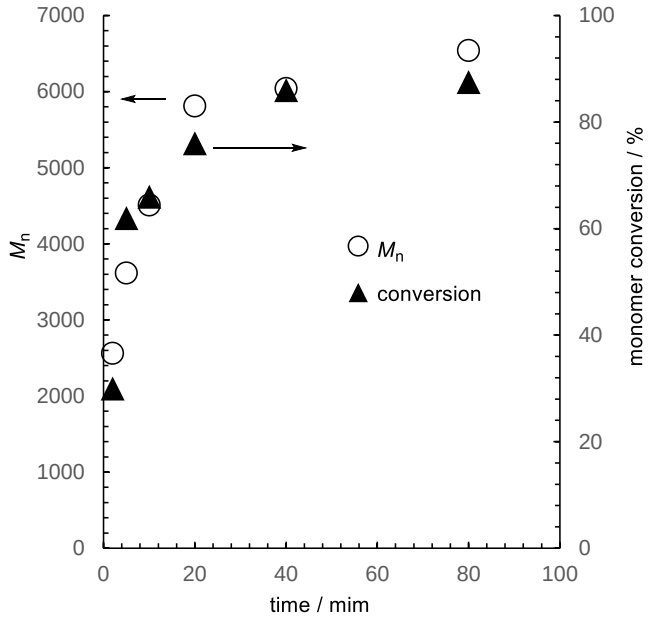
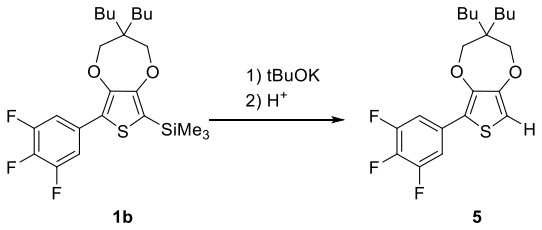



**Fig. S1** Plots of time vs $M_n$ and monomer conversion in the polymerization of **1b**.

**Reaction of 1b with a 1 equiv of potassium *t*-butoxide.**




**1b** **5** (S7)

To **1b** (87.4 mg, 0.186 mmol) in THF (4 mL) was added a THF solution of potassium *t*-butoxide (200 μL of 1 M THF solution, 0.2 mmol) at room temperature. After stirring for 3 days at room temperature, a buffer solution was added to the mixture. The organic layer was washed with a saturated aqueous solution of NaCl and dried over anhydrous $MgSO_4$. After filtration and removal of the solvent, the residue was purified with chromatography ($SiO_2$, hexane/dichloromethane = 1/1) to the title compound (55.1 mg, 0.139 mmol, 75%). A pale yellow oil: $^1$H NMR ($CDCl_3$, 400 MHz) δ 7.34 (dd, $J$ = 8, 8 Hz, 2H), 6.45 (s, 1H), 4.00 (s, 1H), 3.93 (s, 1H), 1.47-1.30 (m, 14H), 0.96 (t, $J$ = 8 Hz, 6H); $^{19}$F NMR ($CDCl_3$, 376.4 MHz) δ −135.0 (d, $J_F$ = 22 Hz, 2F), −163.1 (t, $J_F$ = 22 Hz, 2F); HRMS (FAB, matrix = NBA) calcd for $C_{21}H_{25}F_3O_2S$ ($[M]^+$) $m/z$, 398.1527, found 398.1525.

**NMR monitoring the reaction of 1b with a 1 equiv of potassium *t*-butoxide.**

To a mixture of **1b** (90 mg, 0.19 mmol) and cryptand[2.2.2] (90 mg, 0.23 mmol) in THF-$d_8$ (0.6 mL) was added potassium *t*-butoxide (22 mg, 0.19 mmol) at room temperature. After stirring for 2 h, the mixture was subjected to NMR analyses. The $^1$H, $^{13}$C, $^{19}$F, and $^{29}$Si NMR spectra are shown in Fig. S2.

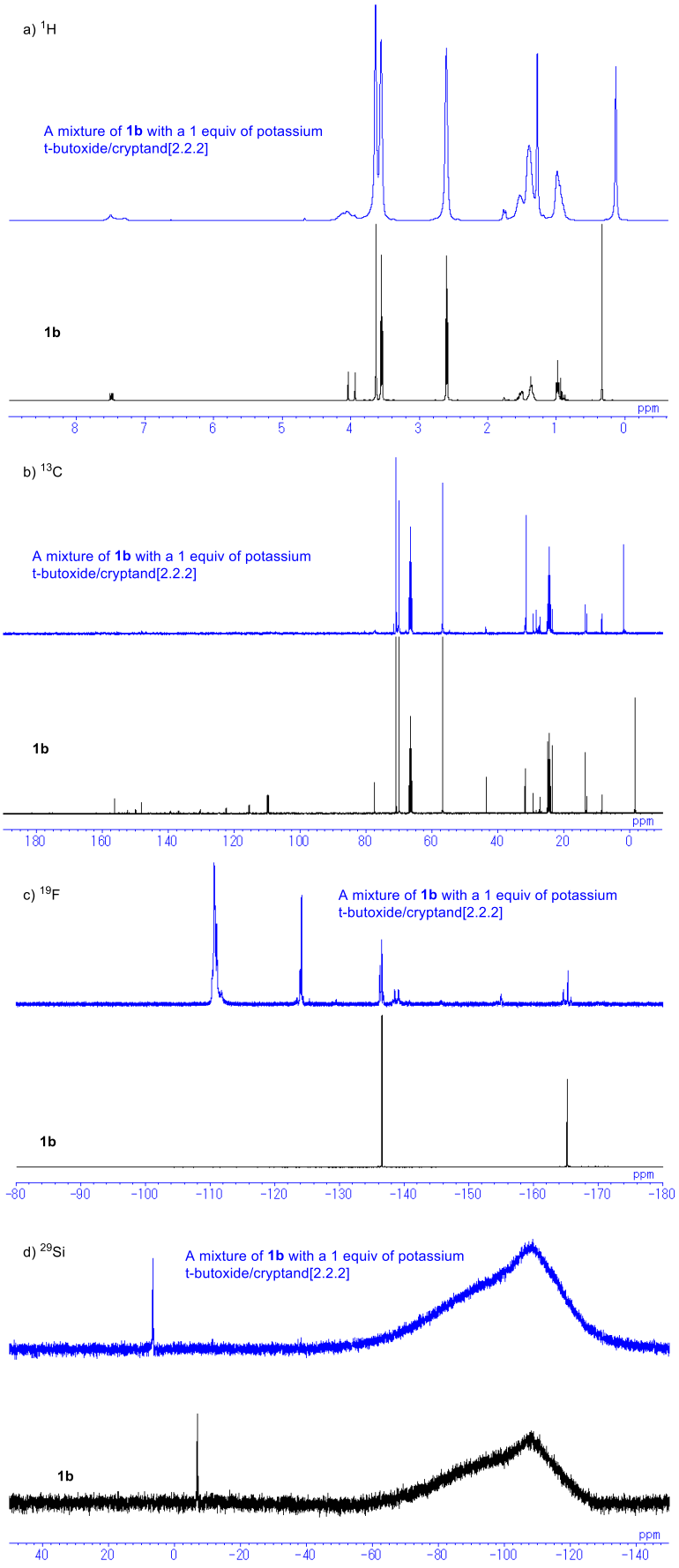
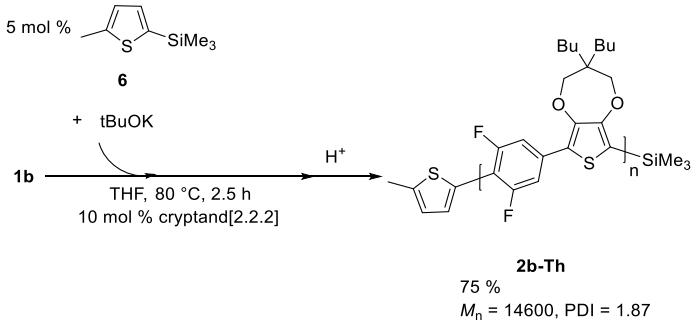



**Fig. S2** (a) H, (b) $^{13}$C, (c) $^{19}$F, and (d) $^{29}$Si NMR spectra of the reaction mixture of **1b** with a 1 equiv of potassium *t*-butoxide (black line: **1b**, blue line: the reaction mixture).

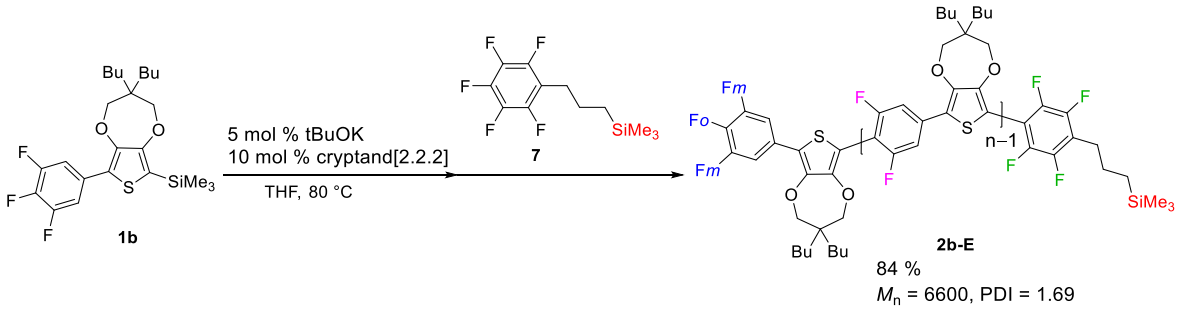
**Polymerization of 1b with pentacoordinated thienylsilicate**




(S8)

To a mixture of trimethyl(5-methylthienyl)silane **6**[2] (2.4 mg, 0.014 mmol) and cryptand[2.2.2] (11.4 mg, 0.030 mmol) in THF (1 mL) was added 1 M THF solution of potassium *t*-butoxide (14 μL, 0.014 mmol) at room temperature. After stirring for 30 min at room temperature, a THF solution (3 mL) of **1b** (133 mg, 0.281 mmol) was added to the mixture at room temperature. After the mixture was stirred at 80 °C for 2.5 h, the reaction was terminated at 0 °C by addition of 0.2 mL of ethanol. The mixture was poured into methanol (200 mL) and then the precipitate was collected by centrifugation. A second cycle of dissolving–precipitation with toluene/methanol followed by freeze-drying gave the polymer (80 mg, 75%) as a pale yellow powder. $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 7.42 (bs), 4.02 (s), 2.55 (s, Me-Th), 1.55-1.30 (m), 0.03 (s); $^{19}$F NMR ($CDCl_3$, 376.4 MHz) δ −110.1, −134.9, −162.7.

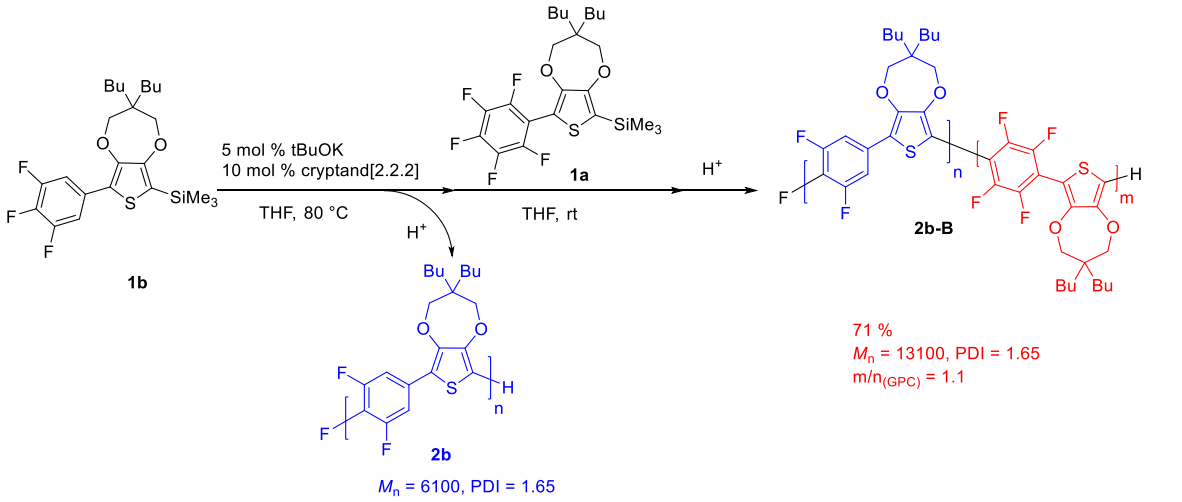
**End capping reaction with 3-(pentafluorophenyl)propyltrimethylsilane 7**




(S9)

In an argon filled glove box, to a mixture of **1b** (127 mg, 0.27 mmol) and cryptand[2.2.2] (10 mg, 0.026 mmol) in THF solution (5 mL) of was added a 1 M THF solution of potassium *tert*-butoxide (13 μL. $1.3 \times 10^{-3}$ mmol) at room temperature. After the mixture was stirred at 80 °C for 3.5 h, **7**[1] (0.1 mL, 0.5 mmol) was added to the mixture. After stirring for 2 h at room temperature, the mixture was poured into methanol (200 mL) and then the precipitate was collected by centrifugation. A second cycle of dissolving–precipitation with toluene/MeOH followed by freeze-drying gave the polymer as a pale yellow powder (98 mg, 0.26 mmol for the monomer unit, 84%). *M*n = 6600, PDI = 1.69 (SEC relative to polystyrene standards). $^1$H NMR ($CDCl_3$, 400 MHz) δ 7.41 (bs), 4.01 (s), 1.55-1.30 (m), 0.02 (s); $^{19}$F NMR ($CDCl_3$, 376.4 MHz) δ −110.1 (F), −134.9 ($F_o$), −140.4 (F), −145.2 (F), −162.7 ($F_m$).

**Block Copolymerization**




(S10)

In an argon filled glove box, to a mixture of **1b** (102 mg, 0.217 mmol) and cryptand[2.2.2] (7.5 mg, 0.020 mmol) in THF (2 mL) was added a 10 μL of a 1 M THF solution of potassium *tert*-butoxide ($1.0 \times 10^{-3}$ mmol) at room temperature. After stirring for 2.5 h at 80 °C, the mixture was allowed to room temperature. An aliquot of 0.2 mL was quenched with ethanol and subjected to SEC analysis (**2b**: $M_n$ = 6100, PDI = 1.65).

For the second polymerization of **1a**, [1] to the residue was added a 2 mL solution of **1a** (94 mg, 0.186 mmol) at room temperature. After stirring at room temperature for additional 2 h, 0.2 mL of ethanol was added. After purification in a similar manner as mentioned above, block copolymer **2b-B** was obtained as a white powder (105 mg, for the monomer unit, 71%). A pale yellow powder: $M_n$ =

13100, PDI = 1.65, $m/n_{(GPC)}$ = 1.1, $m/n_{(NMR)}$ = 1.5; $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 7.40 (bs), 6.72 (s), 3.98 (bs), 1.55-0.88 (bm); $^{19}$F NMR ($CDCl_3$, 376.4 MHz) δ −110.2 (F), −139.1 (F).

**DFT calculation**.

The geometries and electronic structures of the model molecules were calculated at the density functional theory (DFT) level using the B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) as the basis set of the Gaussian program.[3]

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(1) T. Sanji and T. Iyoda, *J. Am. Chem. Soc.*, 2014, **136**, 10238.

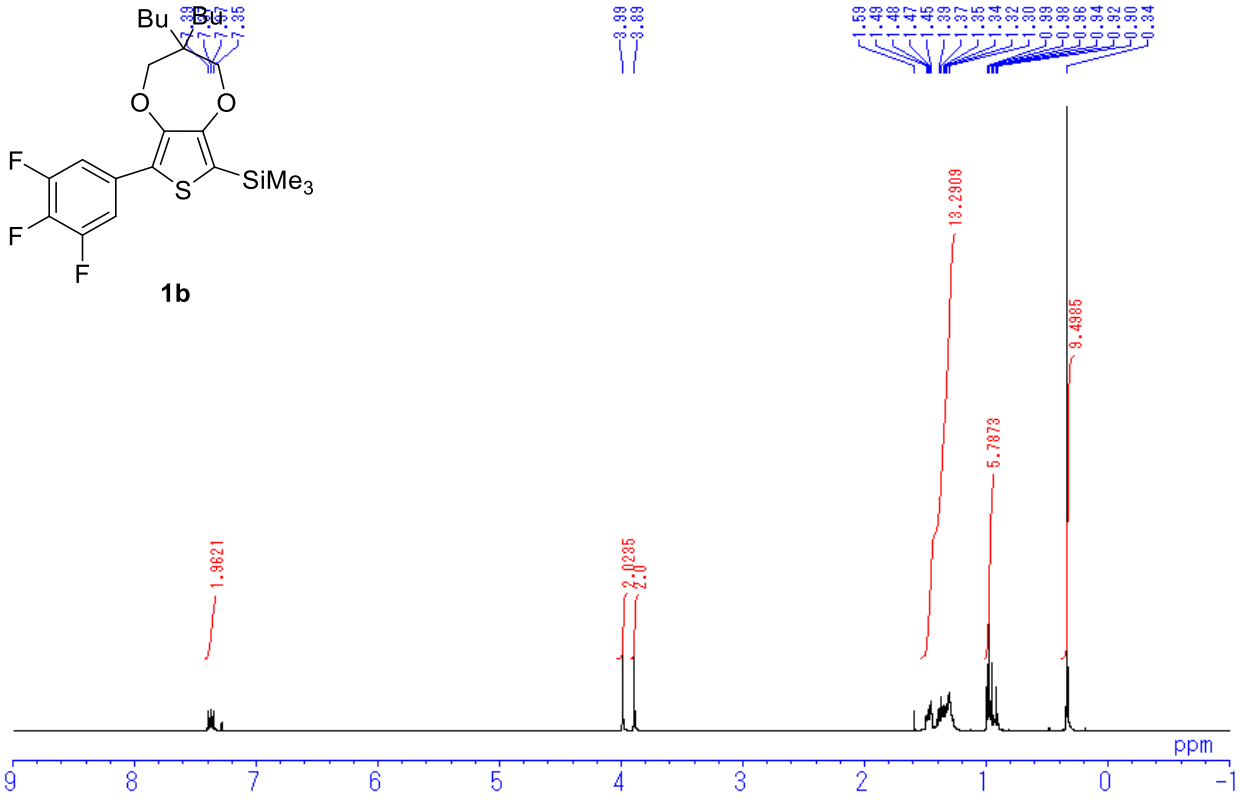
(2) G. Seconi, C. Eaborn and J. G. Stamper, *J. Organomet. Chem.*, 1981, **204**, 153.

(3) Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

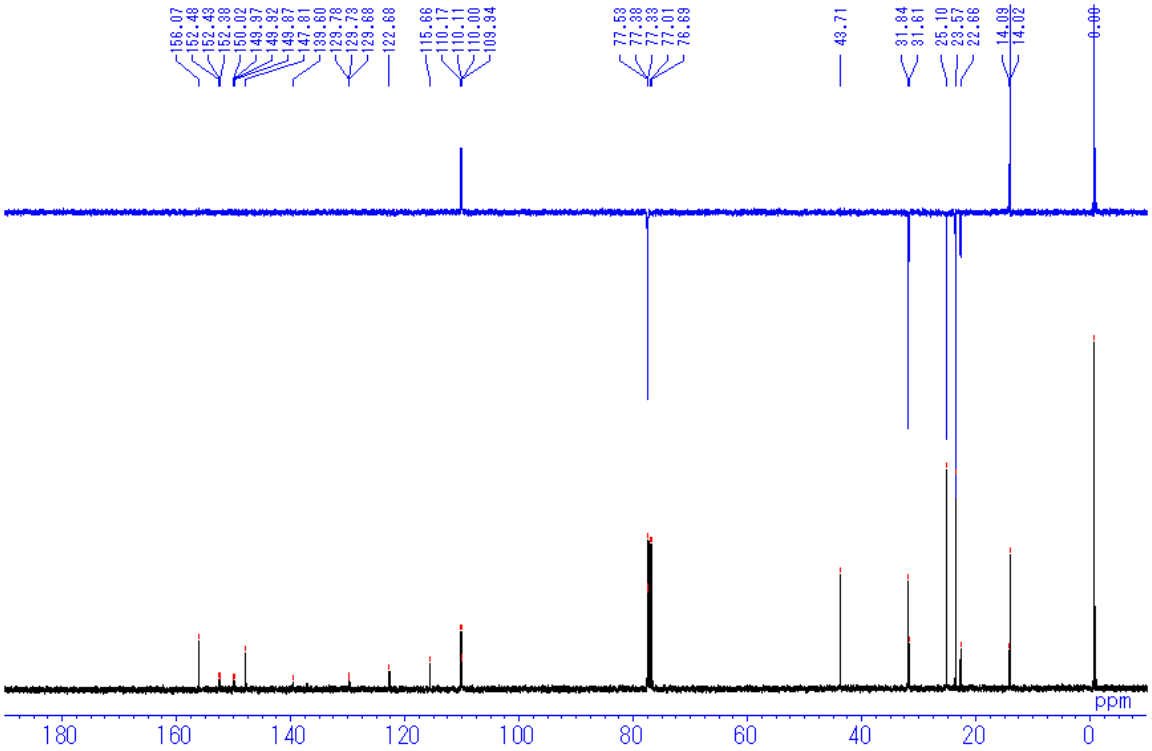
**Appendix:**

NMR spectra of new compounds

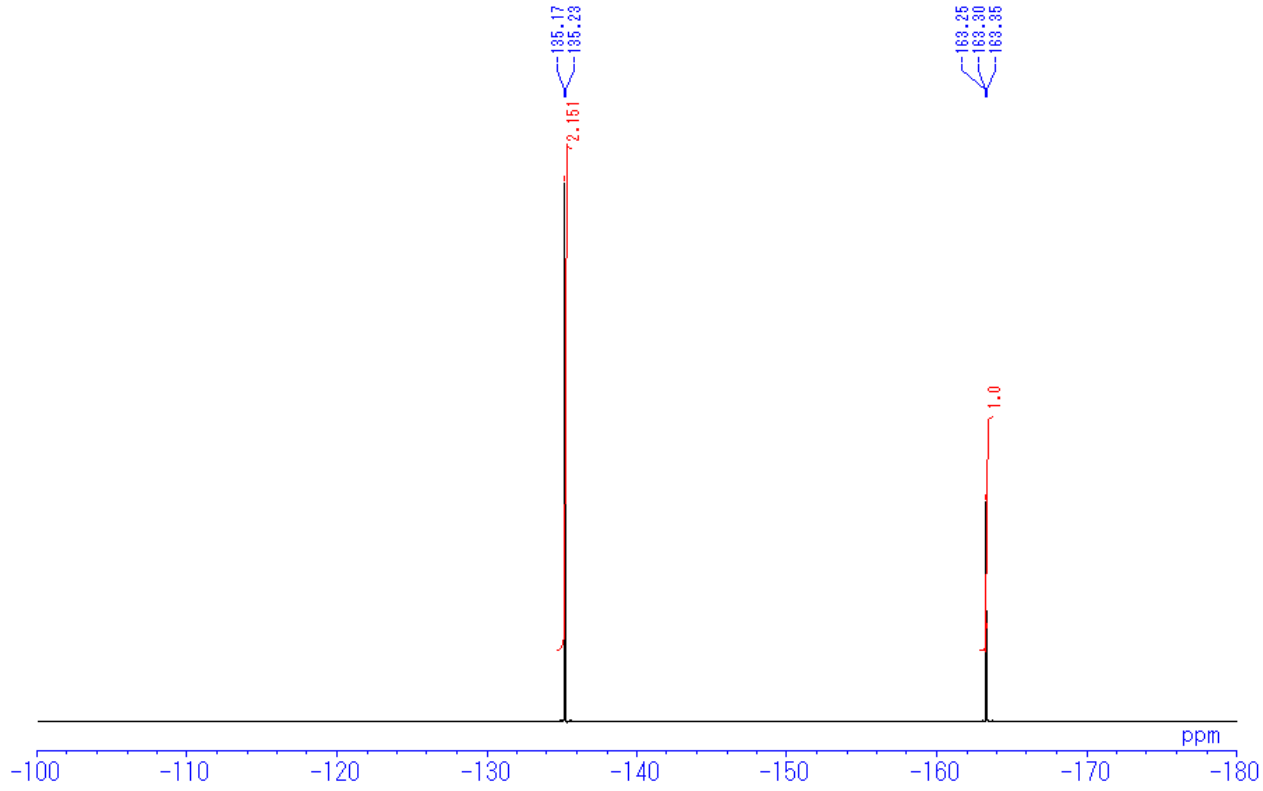
$^{1}H$ ($CDCl_3$)



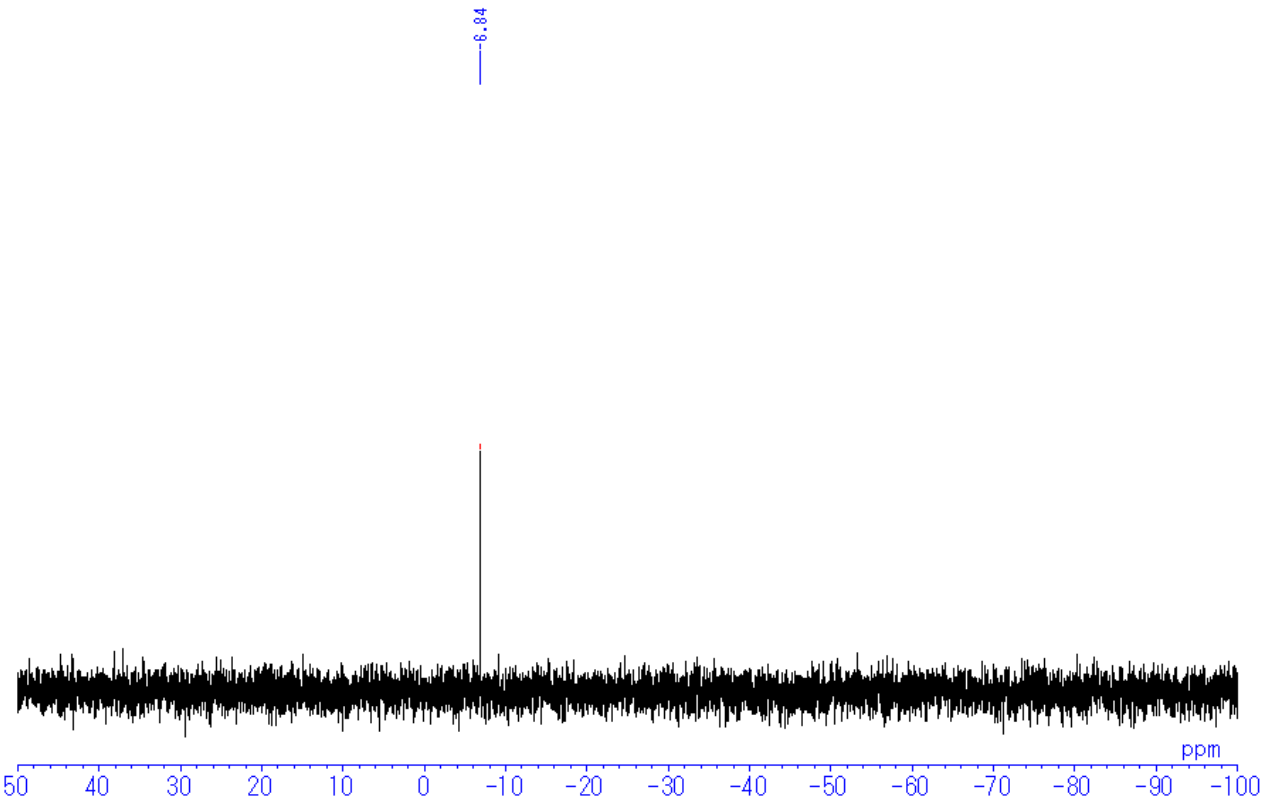

$^{13}C$ ($CDCl_3$)



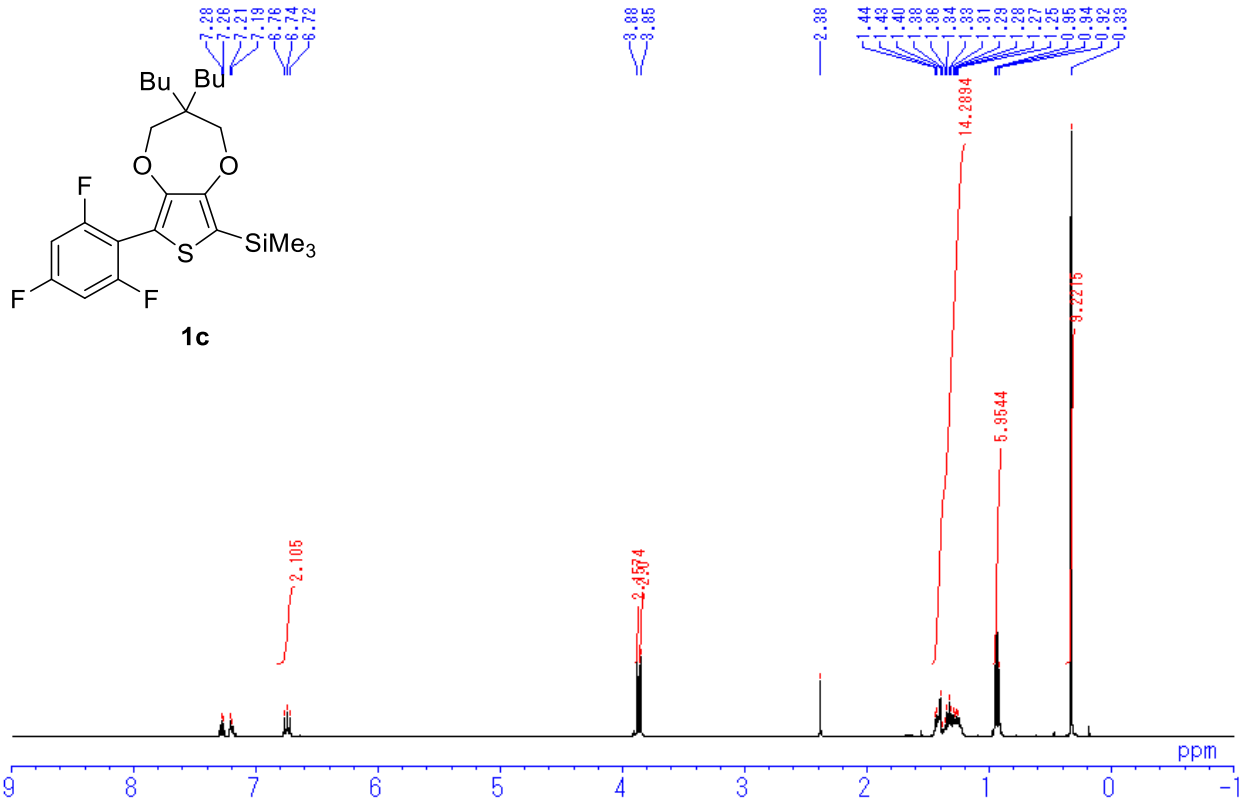
$^{19}F$ ($CDCl_3$)



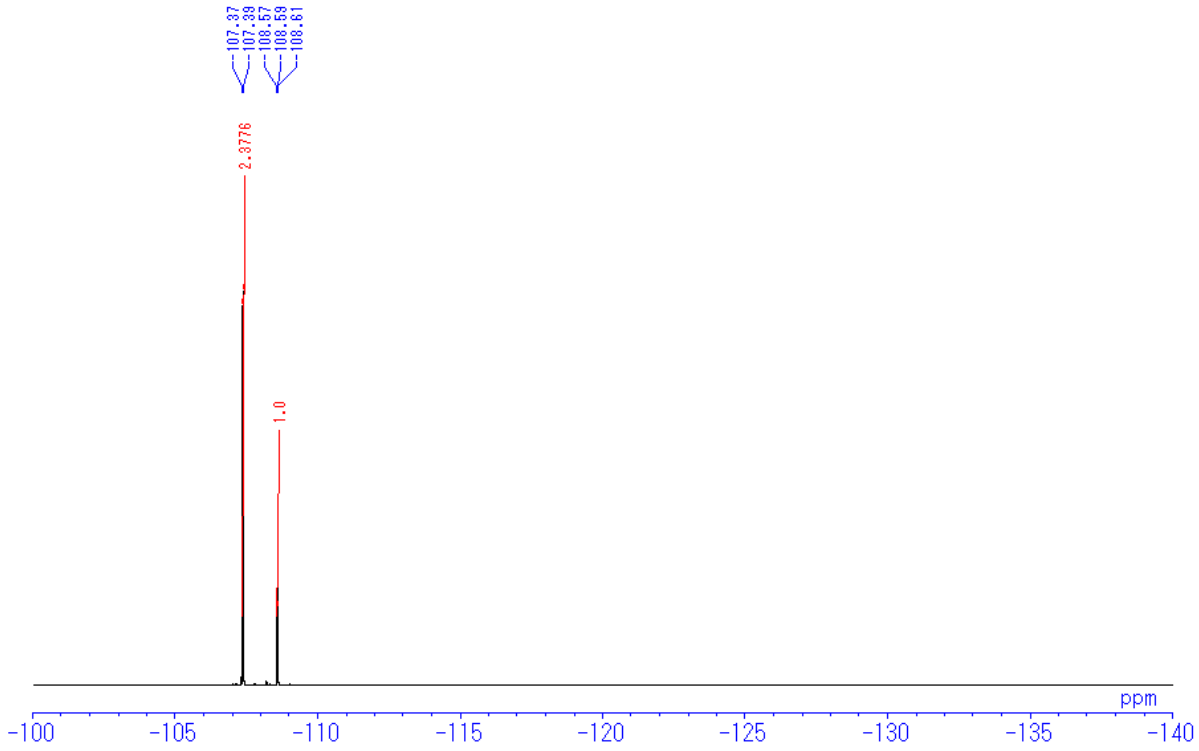

$^{29}Si$ ($CDCl_3$)



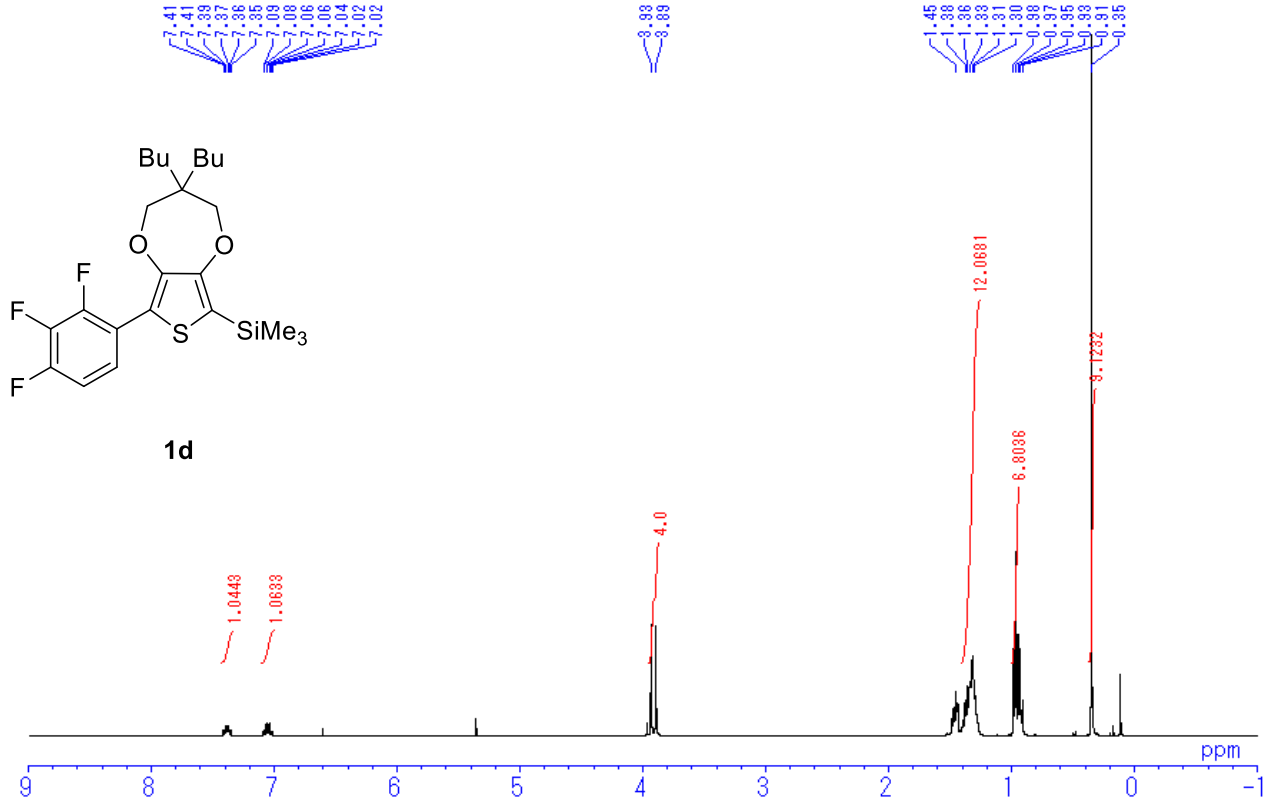
$^{1}H$ ($CDCl_3$)



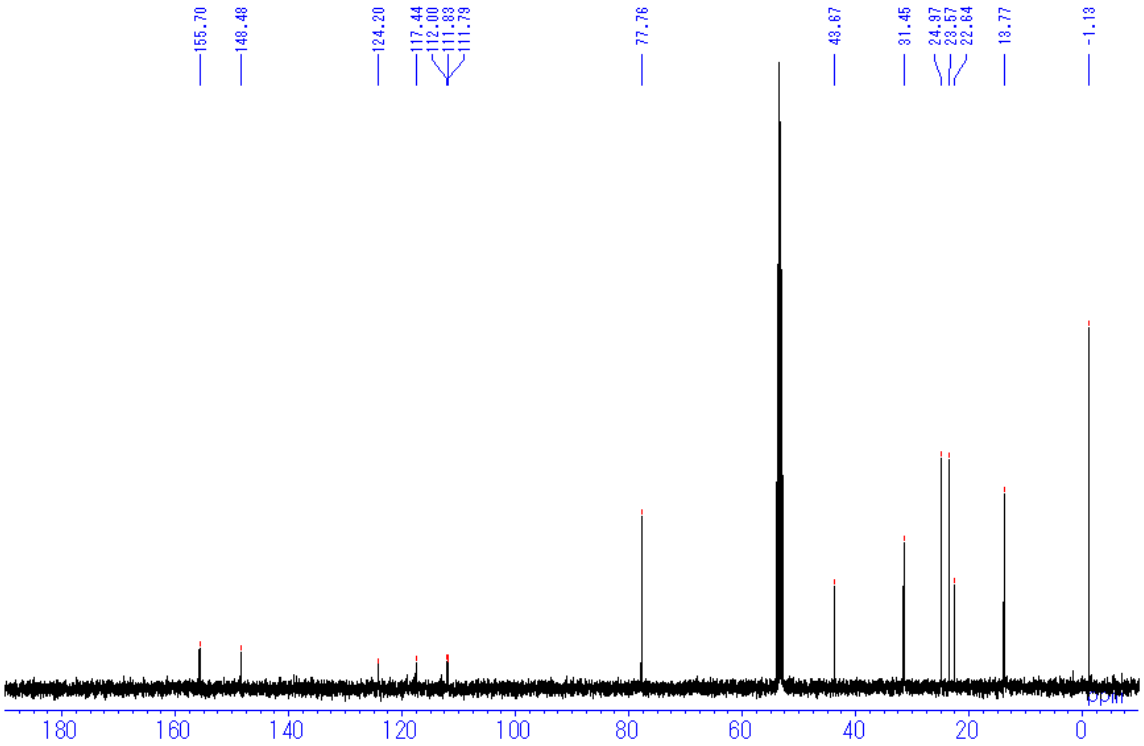

$^{19}F$ ($CDCl_3$)



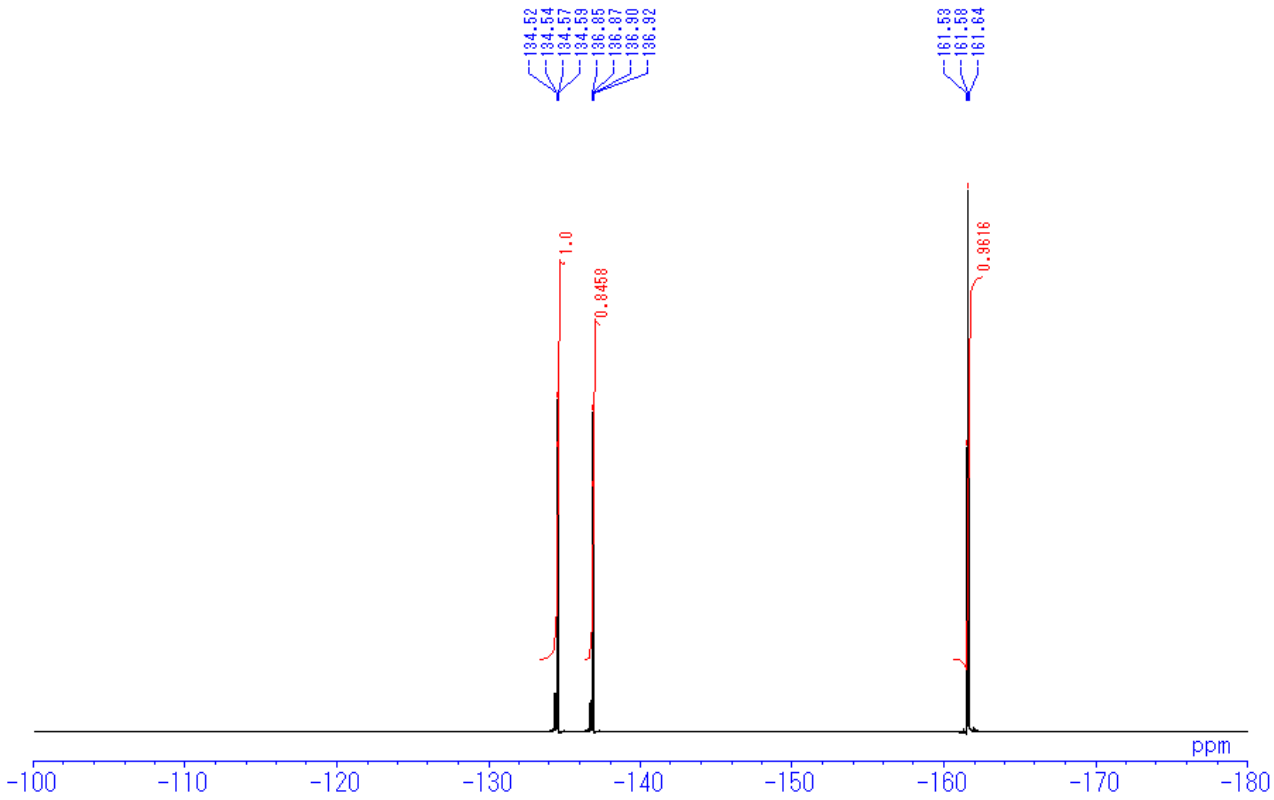
$^{1}H$ ($CD_2Cl_2$)



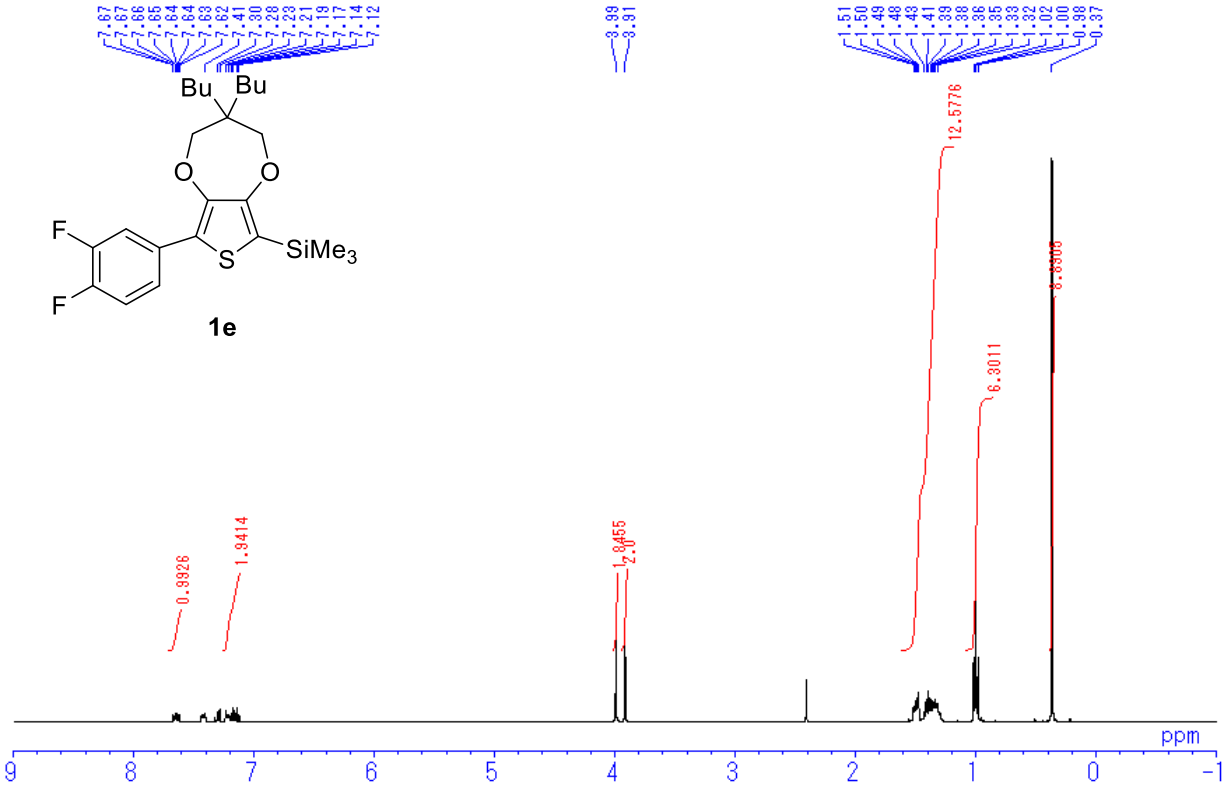

$^{13}C$ ($CD_2Cl_2$)



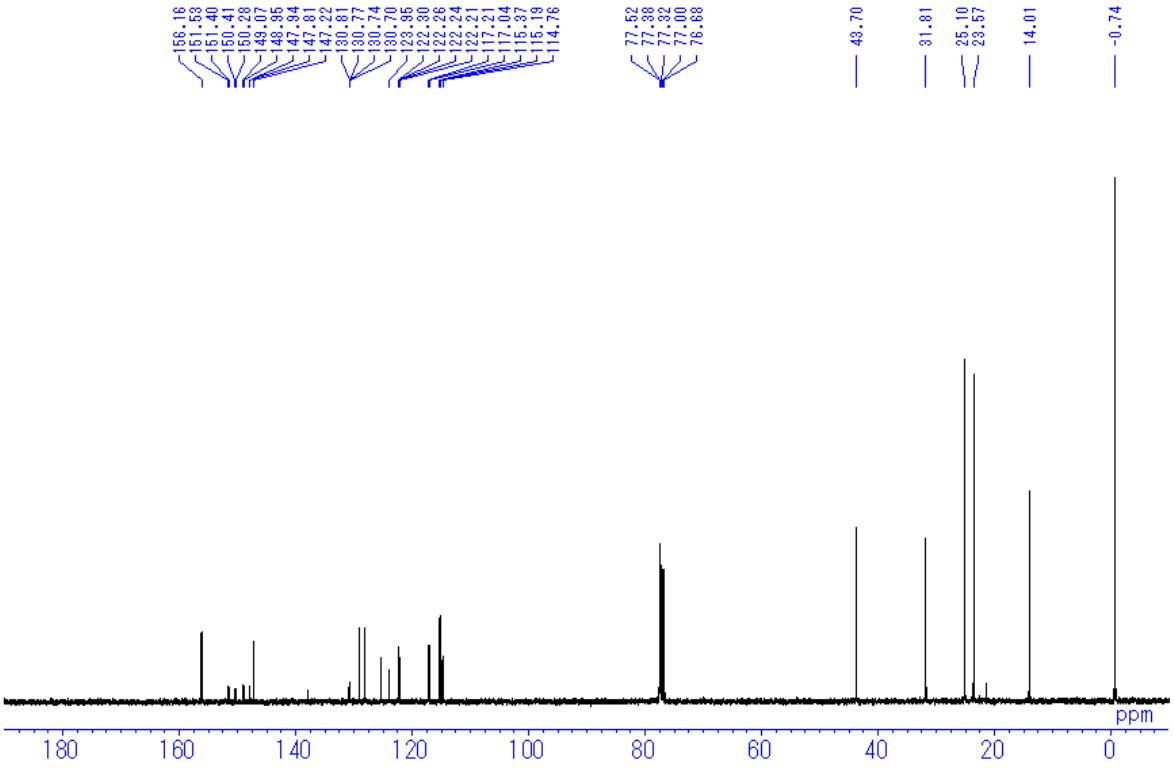
$^{19}F$ ($CD_2Cl_2$)


134.52
134.54
134.57
134.59
136.85
136.87
136.90
136.92
161.53
161.58
161.64
1.0
0.8458
0.9616
ppm
-100
-110
-120
-130
-140
-150
-160
-170
-180

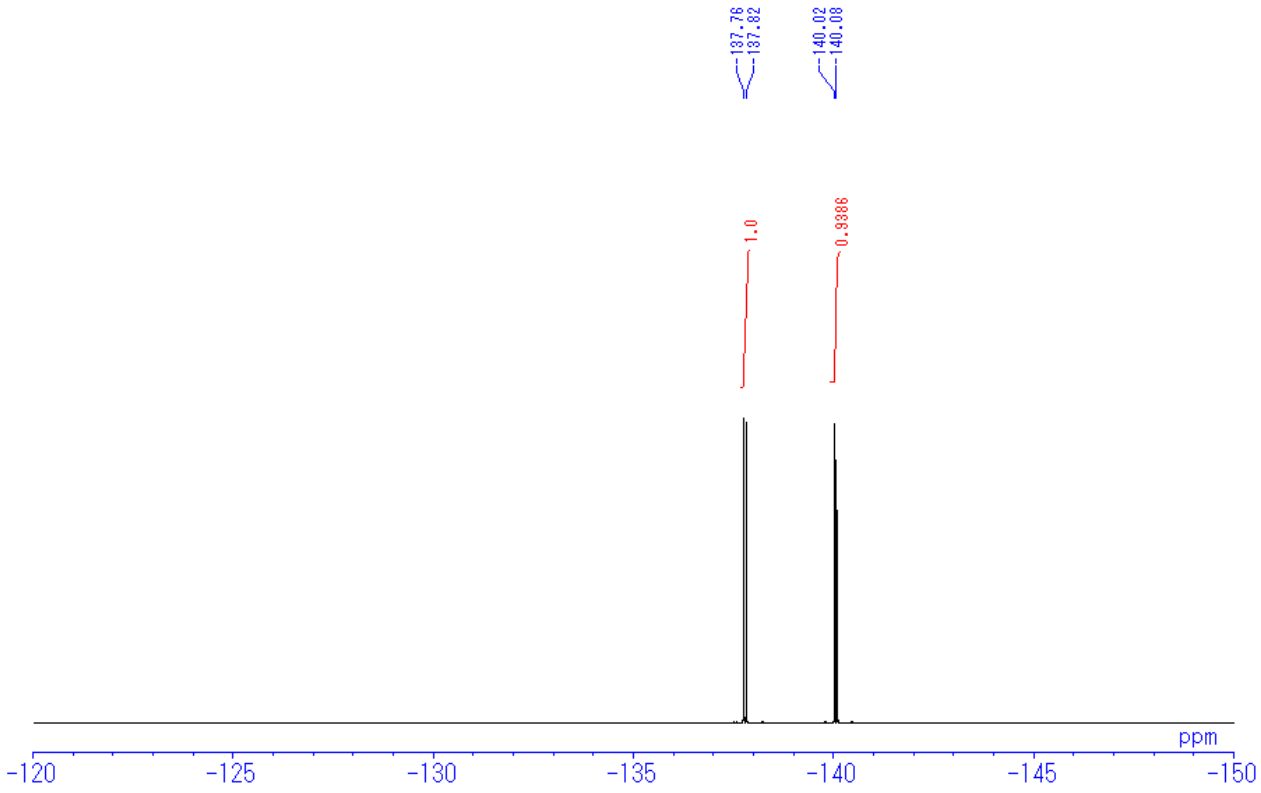
$^{1}H$ ($CDCl_3$)




$^{13}C$ ($CDCl_3$)



$^{19}F$ ($CDCl_3$)


-137.76
-137.82
-140.02
-140.08
1.0
0.9886
ppm
-120
-125
-130
-135
-140
-145
-150