Electronic supplementary information (ESI) for

A fast controlled synthesis of poly(*p*-phenyleneethynylene)s under transition-metal-free conditions

Asahi Motoshige, Junko Kakinuma, Tomokazu Iyoda and Takanobu Sanji*
*E-mail for T.S.: sanji.t.aa@m.titech.ac.jp

Table of Contents

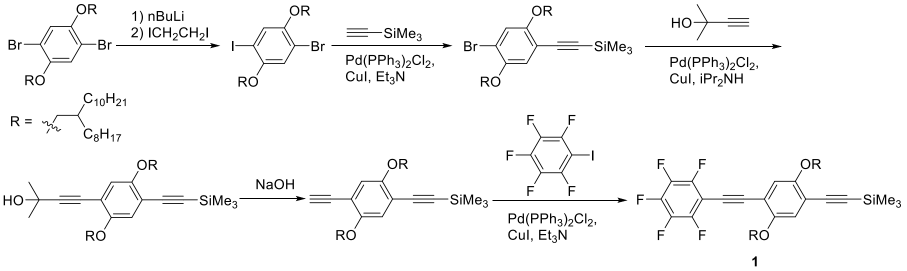
Experimental section

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. 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).

Synthesis of 2,5-bis(2-octyldodecyl)oxy)-1-pentafluorophenylethynyl-4-(trimethylsilylethynyl)benzene 1.

A synthetic route of **1** is shown in Scheme S1.



Scheme S1

1-Bromo-4-iodo-2,5-bis((2-octyldodecyl)oxy)benzene. To an ether solution (250 mL) of 1,4-dibromo-2,5-bis((2-octyldodecyl)oxy)benzene[S1] (73.0 g, 88.1 mmol) was added a hexane solution of *n*-butyllithium (1.6 M, 55.1 mL, 88.1 mmol) at −50 °C. After stirring the mixture at the temperature for 60 min, 1,2-diiodoethane (26.3 g, 93.4 mmol) was added to the mixture at one portion, and then the mixture was stirred at room temperature overnight. To the mixture was added a saturated aqueous solution of $NaHCO_3$ and the resulting mixture was extracted with ether. 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 compound (71.0 g, 81.1 mmol, 92%). Colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.97 (s, 2H), 3.81 (t, *J* = 2.7 Hz, 4H), 1.79 (m, 2H), 1.48-1.26 (m, 64H), 0.88 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 152.6, 150.6, 124.0, 116.8, 112.5, 108.3, 84.5, 73.1, 72.8, 38.0, 38.0, 36.1, 32.6, 31.9, 31.4, 31.3, 30.0, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 27.9, 26.8, 26.6, 22.7, 14.1; HRMS (FAB, matrix = 3-nitrobenzyl alcohol, NBA) calcd for $C_{46}H_{84}BrIO_2$ ($[M]^+$) *m/z*, 874.4699, found 874.4740.

1-Bromo-4-(trimethylsilylethynyl)-2,5-bis((2-octyldodecyl)oxy)benzene. To 1-bromo-4-iodo-2,5-bis((2-octyldodecyl)oxy)benzene (71.0 g, 81.1 mmol), $PdCl_2(PPh_3)_2$ (1.7 g, 2.4 mmol), and CuI (0.9 g, 4.7 mmol) in NEt_3 (180 mL) was added trimethylsilylacetylene (8.8 g, 89.2 mmol) at room temperature. The mixture was stirred at the room temperature overnight. 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/CH_2CH_2 = 10/1) to give the compound (54.3 g, 64.2 mmol, 79%). Colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.02 (s, 1H), 6.92 (s, 1H), 3.81 (d, *J* = 5.5 Hz, 4H), 1.79 (m, 2H), 1.47-1.26 (m, 64H), 0.25 (t, *J* = 3.5 Hz, 12H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 154.9, 149.3, 117.6, 117.4, 113.5, 112.1, 100.7, 99.0, 72.7, 72.1, 38.1, 378.0, 31.9, 31.9, 31.6, 31.3, 31.2, 30.1, 30.0, 29.7, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 26.9, 26.8, 22.7, 22.7, 14.1, 0.0; ^{29}Si NMR ($CDCl_3$, 99.4 MHz) δ -17.8; HRMS (FAB, matrix = 3-nitrobenzyl alcohol, NBA) calcd for $C_{51}H_{93}BrO_2Si$ ($[M]^+$) *m/z*, 844.6128, found 844.6104.

4-(2,5-Bis((2-octyldodecyl)oxy)-4-((trimethylsilyl)ethynyl)phenyl)-2-methylbut-3-yn-2-ol. To 1-bromo-4-(trimethylsilylethynyl)-2,5-bis((2-octyldodecyl)oxy)benzene (9.0 g, 10.6 mmol), $PdCl_2(PPh_3)_2$ (372.0 mg, 0.5 mmol), and CuI (201.9 mg, 1.1 mmol) in *i*Pr_2NH (50 mL) was added 2-methyl-3-butyn-2-ol (1.3 g, 15.9 mmol) at room temperature. The mixture was stirred at 60 °C overnight. 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/CH_2CH_2 = 1/1) to give the compound (7.2 g, 8.5 mmol, 80%), which was directly used in subsequent cross-coupling reactions. Pale yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.86 (d, *J* = 16.0 Hz, 2H), 3.81 (d, *J* = 5.4 Hz, 4H), 1.78 (m, 2H), 1.48-1.26 (m, 76H), 0.88 (t, *J* = 6.8 Hz, 9H), 0.25 (s, 6H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 154.2, 153.6, 116.5, 113.4, 101.1, 99.7, 99.0, 78.6, 71.8, 65.7, 38.2, 31.9, 31.6, 31.5, 31.3, 31.2, 30.1, 29.7, 29.3, 26.9, 22.7, 14.1, 0.0.

1-Ethynyl-4-(trimethylsilylethynyl)-2,5-bis((2-octyldodecyl)oxy)benzene. A mixture of 4-(2,5-bis((2-octyldodecyl)oxy)-4-((trimethylsilyl)ethynyl)phenyl)-2-methylbut-3-yn-2-ol (7.1 g, 8.4 mmol) and NaOH (1.7 g, 41.8 mmol) in toluene (100 mL) was heated at 130 °C for 4 h. After filtration, a saturated aqueous solution of NH_4Cl was added to the filtrate and 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/CH_2CH_2 = 10/1) to give the compound (6.6 g, 8.4 mmol, 99%). Pale yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.90 (d, *J* = 2.6 Hz, 2H), 3.82 (t, *J* = 4.6 Hz, 4H), 3.29 (s, 1H), 1.79 (m, 2H), 1.48-1.26 (m, 64H), 0.88 (t, *J* = 6.8 Hz, 12H), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 154.2, 117.1, 114.1, 112.8, 101.0, 99.9, 82.1, 80.0, 72.5, 71.9, 38.2, 37.9, 31.9, 31.6, 31.3, 31.2, 30.1, 30.0, 29.7, 29.7, 29.6, 29.6, 29.4, 26.9, 26.8, 22.7, 22.7, 14.1, 0.0; HRMS (FAB, matrix = 3-nitrobenzyl alcohol, NBA) calcd for $C_{53}H_{94}O_2Si$ ($[M]^+$) *m*/*z*, 790.7023, found 790.7012.

1-Pentafluorophenylethynyl-4-(trimethylsilylethynyl)-2,5-bis((2-octyldodecyl)oxy)benzene 1. A mixture of 1-ethynyl-4-(trimethylsilylethynyl)-2,5-bis((2-octyldodecyl)oxy)benzene (2.3 g, 2.8 mmol), pentafluoroiodobenzene (1.0 g, 3.3 mmol), $PdCl_2(PPh_3)_2$ (52.6 mg, 0.08 mmol), and CuI (28.6 mg, 0.15 mmol) in triethylamine (6 mL) was stirred at room temperature overnight. After filtration of the mixture and evaporation of the solvent, the residue was purified with chromatography (SiO_2, hexane/dichloromethane = 10/1) and GPC to give the compound (667 mg, 0.7 mmol, 24%). Pale yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.94 (s, 2H), 3.85 (d, *J* = 5.4 Hz, 4H), 1.80 (m, 2H), 1.50-1.26 (m, 64H), 0.87 (m, 12H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 154.2, 154.0, 148.0, 154.9, 116.6, 116.3, 115.2, 111.8, 100.8, 98.5, 76.9, 76.8, 72.1, 71.9, 38.2, 38.1, 31.9, 31.6, 31.3, 31.2, 30.1, 30.0, 29.7, 29.7, 29.6, 29.4, 29.4, 26.9, 26.9, 22.7, 14.1, 0.0; ^{19}F NMR ($CDCl_3$, 376.4 MHz) δ −136.1 (t, J_F = 6.8 Hz, 1F), −153.4 (t, J_F = 20.5 Hz, 2F), −162.3 (td, J_F = 20.5, 6.8 Hz, 2F); ^{29}Si NMR ($CDCl_3$, 99.4 MHz) δ −17.6; HRMS (FAB, matrix = 3-nitrobenzyl alcohol, NBA) calcd for $C_{59}H_{93}F_5O_2Si$ ($[M]^+$) *m*/*z*, 956.6865, found 956.6869.

Polymerization of 1.

A typical polymerization is as follows: in an argon filled glove box (MBRAUN Lab Master Sp), TBAF (1 M THF solution, 5 μL, 5×10^{-3} mmol, 5 mol %) was added to **1** (94 mg, 0.098 mmol) in THF (5 mL) at room temperature. After stirring for 90 s at room temperature, ethanol (0.2 mL) was added to the mixture. Then the mixture was poured into methanol (200 mL). The precipitate was collected by centrifugation. A second cycle of dissolving–precipitation followed by freeze-drying gave polymer **2** as a yellow powder (68 mg, 0.078 mmol for the monomer unit, 80%). A yellow powder: M_n = 6400, PDI = 1.46 (SEC relative to polystyrene standards); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.04-6.98, 3.92, 3.35, 1.86, 1.26, 0.87; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 154.11, 116.4, 114.42, 113.6, 99.9, 80.6, 72.6, 72.2, 38.1, 38.0, 32.1, 31.9, 31.6, 31.4, 31.2, 30.0, 29.7, 29.5, 29.4, 26.7, 22.7, 14.12; ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ −135.9, −137.2, −153.0, −162.2.

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

A stock solution of **1** (470 mg, 0.49 mmol), cryptand[2.2.2] (19 mg, 0.05 mmol), and fluorobenzene (160 μL as an internal standard) in THF (8 mL) was prepared. To a 1.0 mL of the solution was added 1 mL THF solution of 5 mol % of potassium *t*-butoxide. 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 **1** 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 **1**

Time/s	Conversion of **1**/%[a]	M_n[b]	PDI[b]
0	0	1280	1.01
0.2	10.2	2420	1.31
0.5	63.9	4990	1.6
1	69.8	5370	1.61
1.5	77.4	6400	1.65
3	84	6400	1.62
10	90.9	7280	1.61
20	94.3	8010	1.68

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

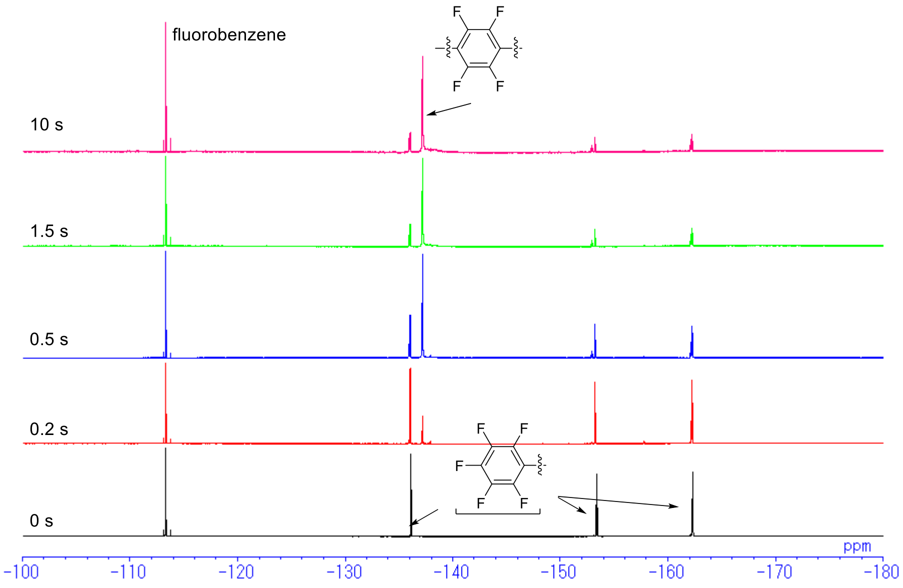


Fig. S1 ^{19}F NMR spectra of the polymerization of **1** in $CDCl_3$.

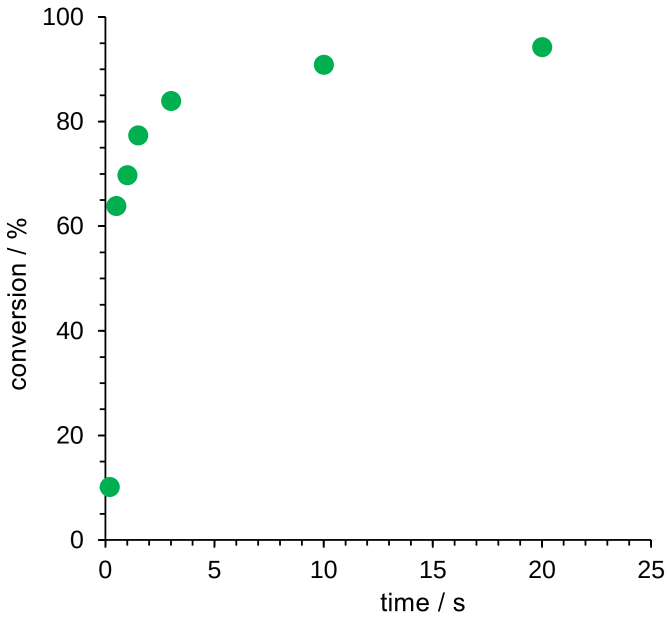


Fig. S2 Time vs monomer conversion % in the polymerization of **1** with 5 mol % potassium *t*-butoxide in the presence of 10 mol % cryptand[2.2.2] in THF.

In-situ monitoring of the polymerization of 1 with TBAF.

TBAF (1 M THF solution, 4 μL, 4 × 10^{-3} mmol) was added to **1** (39 mg, 0.041 mmol) in THF-*d*$_8$ (1.2 mL) at room temperature. After addition of TBAF, the mixture was subjected to a ^{1}H NMR analysis. A mixture of **1** and 10 mol% TBAF in THF-*d*$_8$, showed a signal of trimethylsilylfluoride at 0.14 ppm.[S2] The ^{19}F NMR spectrum of the mixture showed a signal of tetrafluorophenylene units of the polymer at −132 ppm and also three signals of monomer **1** at −132, −150, and −158 ppm. On the other hand, no ethynyl signal was found. This indicated the pentacoordinate silicate exists in a dynamic equilibrium with trimethylsilylethynyl group and trimethylsilylfluoride. After the NMR analysis, the mixture was poured into methanol (100 mL). The precipitate was collected by centrifugation. Freeze-drying gave polymer **2** (25 mg, 71%). M_n = 5700, PDI = 1.69 (SEC relative to polystyrene standards).

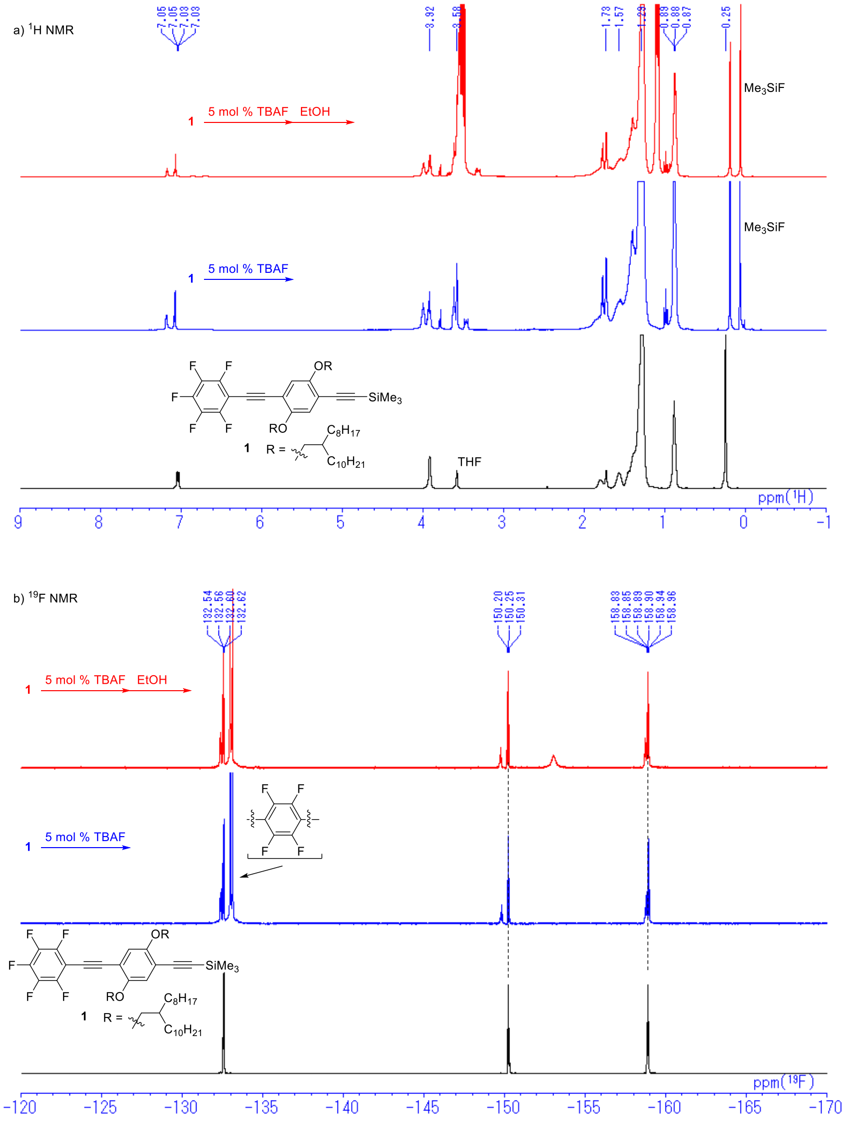
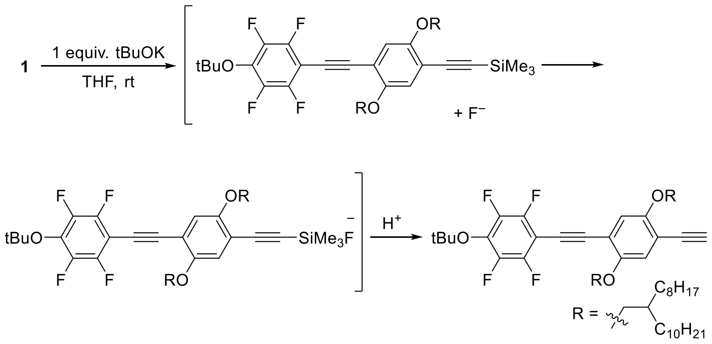


Fig. S3 (a) ^{1}H and (b) ^{19}F NMR monitoring of the polymerization of **1**; **1** (black line), a mixture of **1** and 10 mol% TBAF (blue line), and after quenching with ethanol (red line) in THF-*d*$_8$.

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

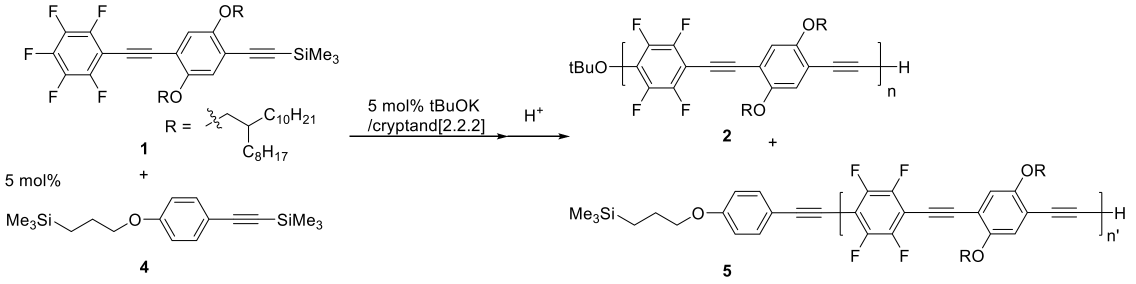


Scheme S2

3: 88% isolated yield

To **1** (305 mg, 0.319 mmol) in THF (8 mL) was added a THF solution (1.5 mL) of potassium *t*-butoxide (0.34 mL of 1 M THF solution, 0.34 mmol) at room temperature. After stirring for 90 s at the temperature, 0.2 mL of ethanol followed by a saturated aqueous solution of NH_4Cl aq. 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 = 20/1 to 10/1) to give 1-(4′-*t*-butoxytetrafluorophenyl)-4-ethynylbenzene **3** (263 mg, 0.280 mmol, 88%). A pale yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.00 (s, 2H), 6.98 (s, 2H), 3.88 (t, J = 4.0 Hz, 4H), 3.35 (s, 1H), 1.83 (m, 2H), 1.50-1.26 (m, 73H), 0.90-0.86 (m, 12H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 154.3, 153.9, 117.2, 116.8, 113.9, 112.9, 97.1, 85.8, 82.7, 79.9, 79.4, 72.6, 72.2, 38.1, 37.9, 31.9, 31.6, 31.4, 31.2, 30.0, 29.7, 29.7, 29.6, 29.4, 28.4, 26.9, 22.7, 14.1; ^{19}F NMR ($CDCl_3$, 376.4 MHz) δ −152.0 (dd, J_F = 22.4, 8.9 Hz, 2F), −138.3 (dd, J_F = 22.4, 8.9 Hz, 2F); HRMS (FAB, matrix = 2-nitrophenyl octyl ether, NPOE) calcd for $C_{60}H_{94}F_4O_3$ ([M]$^+$) *m*/*z*, 938.7139, found 938.7122.

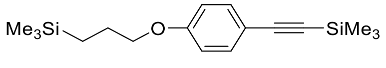
Competition reaction in the polymerization with 4.



Scheme S3

To investigate the reaction mechanism, the polymerization of **1** initiated by 5 mol % potassium *t*-butoxide/10 mol% cryptand[2.2.2] was examined in the presence of 5 mol % of 4-(3-trimethylsilylpropoxyphenyl)ethynyltrimethylsilane **4** used as an external ethynyltrimethylsilane (Scheme S3). When intermolecular fluoride anion transfers are occurred during the polymerization, a mixture of polymer **2** and **5** (initiated by a fluorosilicate originated from **4** and fluoride anion) could be found.

1-(trimethylsilyl)ethynyl-4-[(3'-trimethylsilyl)propoxy]benzene 4.



4

To a mixture of 4-[(3'-trimethylsilyl)propoxy]bromobenzene (2.0 g, 7.1 mmol), $PdCl_2(PPh_3)_2$ (26 mg, 0.37 mol), and CuI (80 mg, 0.95 mmol) in Et_3N (15 mL) was added trimethylsilylacetylene (2.20 g, 22.4 mmol) at room temperature. The mixture was stirred at 60 °C overnight. To the mixture was added a sat. NH_4Cl aq. and the resulting mixture was extracted with hexane. The organic layer was washed with a sat. NaCl aq. 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 (2.70 g, 3.44 mmol, 33%). A pale yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.06 (s, 9H), 0.28 (s, 9H), 0.61-0.65 (m, 2H), 1.79-1.83 (m, 2H), 3.93 (t, J = 6.8 Hz, 2H), 6.83 (d, J = 4.4 Hz, 2H), 7.42 (d, J = 4.4 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ −1.7, 0.1, 12.6, 23.8, 70.7, 92.3, 105.4, 114.4, 115.0, 133.5, 159.3; $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 79.5 MHz) δ −18.2, 1.9; HRMS (FAB, matrix = 3-nitrobenzyl alcohol) calcd for $C_{17}H_{28}OSi_2$ ($[M]^+$) *m*/*z* 304.1679, found 304.1680.

Polymerization in the presence of 5 mol % 4.

A mixture of **1** (110 mg, 0.115 mmol), **4** (1.8 mg, 5.9×10^{-3} mmol), cryptand[2.2.2] (6 mg, 0.016 mmol) in THF (10 mL) was prepared. 0.5 mL of the solution was sampled and analyzed by ^{1}H NMR. To the mixture was added potassium *t*-butoxide (1 M THF solution, 5.5 μL, 5.5×10^{-3} mmol, 5 mol %) at room temperature. After stirring for 90 s, ethanol (0.2 mL) was added to the mixture and 0.5 mL of the solution was sampled and analyzed by ^{1}H NMR to calculate for the conversion of **1** and consumption of **4** using the signal of cryptand[2.2.2] around 3.7 ppm as a reference. Then, the mixture was poured into methanol (200 mL). The precipitate was collected by centrifugation. A second cycle of dissolving–precipitation followed by freeze-drying gave polymer as a yellow powder (64 mg, 64%). A yellow powder: M_n = 4500, PDI = 1.40 (SEC relative to polystyrene standards).

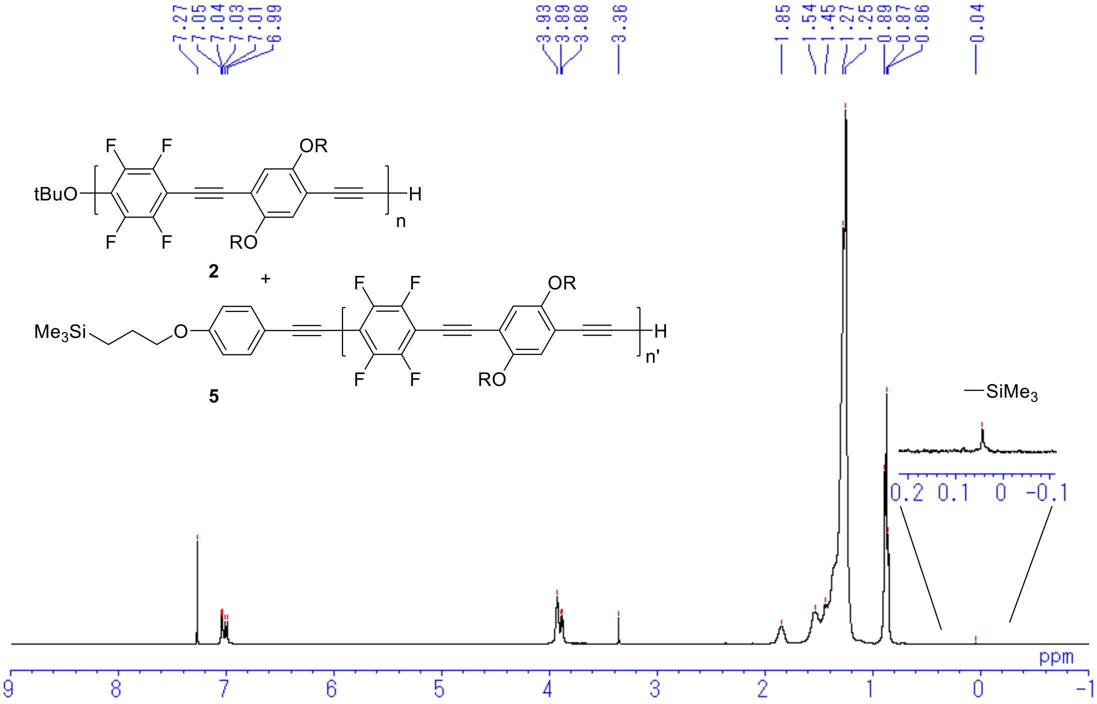


Fig. S4 ^{1}H NMR spectrum of the polymer obtained by the polymerization of **1** with 5 mol % *t*-BuOK/10 mol% cryptand[2.2.2] in the presence of 5 mol % **4** in THF at room temperature for 90 s.

After the polymerization, the NMR analysis of the mixture showed > 99% conversion of **1** and ≈ 10% consumption of **4**. In the ^{1}H NMR spectrum of the polymer, a signal of trimethylsilyl group originated from **4** was detected and the ratio of a trimethylsilyl-terminated polymer at the initiation end **5** was estimated to be < 1%.

In addition, the polymerization of **1** in the presence of 10 and 20 mol % **4** at room temperature and 5 mol% **4** at −20 and 50 °C were also examined. Table S2 summarizes the results.

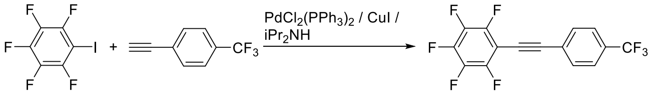
Table S2 Polymerization of **1** in the presence of **4**

entry	mol% of **4**	conditions	yield of polymer/%	M_n (PDI)[a]	introduction of **5**/%
1	5	rt, 90 s	64	4500 (1.40)	0.8
2	10	rt, 90 s	71	6400 (1.48)	3.4
3	20	rt, 90 s	34	7100 (1.55)	8.8
4	5	50 °C, 90 s	22	6800 (1.63)	4.7
5	5	−20 °C, 90 s	21	4600 (1.31)	0.8

[a] M_n and PDI were determined using size-exclusion chromatography with polystyrene standards.

End capping with 6.

Synthesis of 2,3,4,5,6-pentafluorophenyl-(4-(trifluoromethyl)phenyl)acetylene 6.



6

Scheme S4

A mixture of pentafluoroiodobenzene (2.62 g, 8.91 mmol), 4-(trifluoromethyl)phenyl)acetylene (1.10 g, 6.47 mmol), $PdCl_2(PPh_3)_2$ (210 mg, 0.30 mmol), and CuI (250 mg, 1.32 mmol) in *i*-Pr_2NH (30 mL) was stirred at room temperature for 10 min and then at 70 °C overnight. 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 (1.07 g, 3.2 mmol, 50%).

The spectrum were the same as that reported by Y. Wei, H. Zhao, J. Kan, W. Su, M. Hong, *J. Am. Chem. Soc.*, 2010, **132**, 2522.

End capping with 2,3,4,5,6-pentafluorophenyl-(4-(trifluoromethyl)phenyl)acetylene 6.

In an argon filled glove box, to a mixture of **1** (60.5 mg, 0.0627 mmol) and cryptand[2.2.2] (3.8 mg, 0.010 mmol) in THF (2 mL) was added potassium *t*-butoxide (1 M THF solution, 3.5 µL, 5 mol %) at room temperature. After stirring for 90 s at the temperature, 2,3,4,5,6-pentafluorophenyl-(4-(trifluoromethyl)phenyl)acetylene **6** (21.6 mg, 0.064 mmol) was added to the mixture. After stirring for 2 h, ethanol (0.2 mL) was added. Then the mixture was poured into methanol (200 mL) and the precipitate was collected by centrifugation. A second cycle of dissolving–precipitation with toluene/MeOH followed by freeze-drying gave **7** as a yellow powder (45 mg, 0.052 mmol for the monomer unit, 83%). A yellow powder: $M_n = 17400$, PDI = 1.56 (SEC relative to polystyrene standards); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.05 (b), 3.93 (b), 1.86 (b), 1.26 (bs), 0.87 (b); $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz) δ −63.3, −135.9, −137.0, −152.8, −162.1.

UV-Vis and fluorescence spectra of **2**.

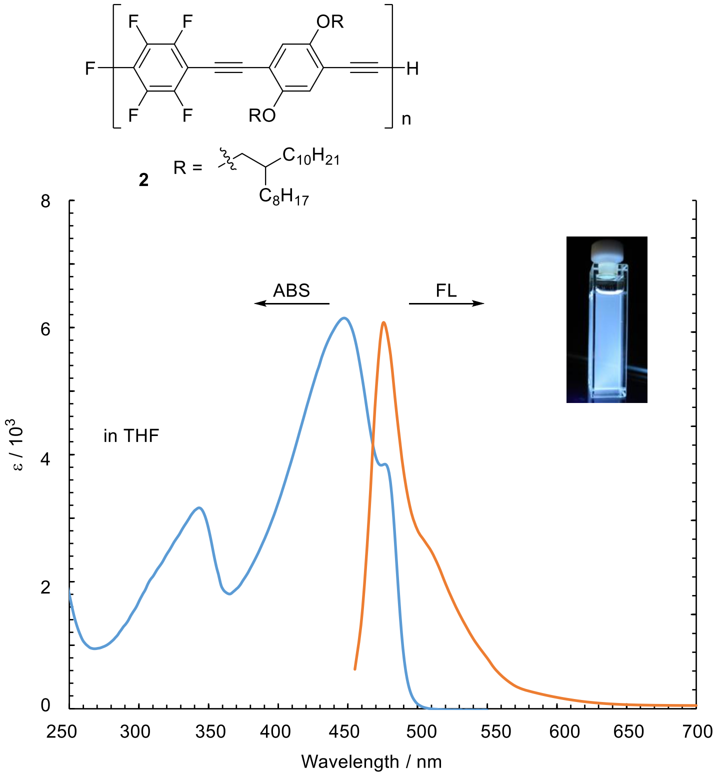


Fig. S5 UV-Vis and fluorescence spectra of **2** in THF (blue line: UV-vis; orange line: fluorescence excited at 445 nm). The inset shows a photograph of **2** in a THF solution under irradiation with UV light at a wavelength of 365 nm.

In dichloromethane, the polymer exhibited intense yellow emissions at wavelengths of 490 and 550 nm (not shoulder), probably because of aggregate formation rather than a charge transfer.

DFT calculation.

The geometry and electronic structure of the model molecule 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.[S3]

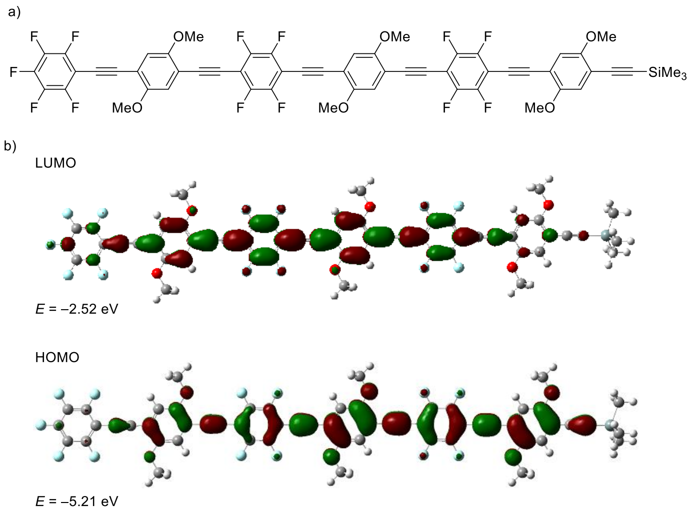


Fig. S6 (a) The chemical structure of the model compound for the calculation. (b) MO diagrams of the model compound based on the DFT calculations (B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p)).

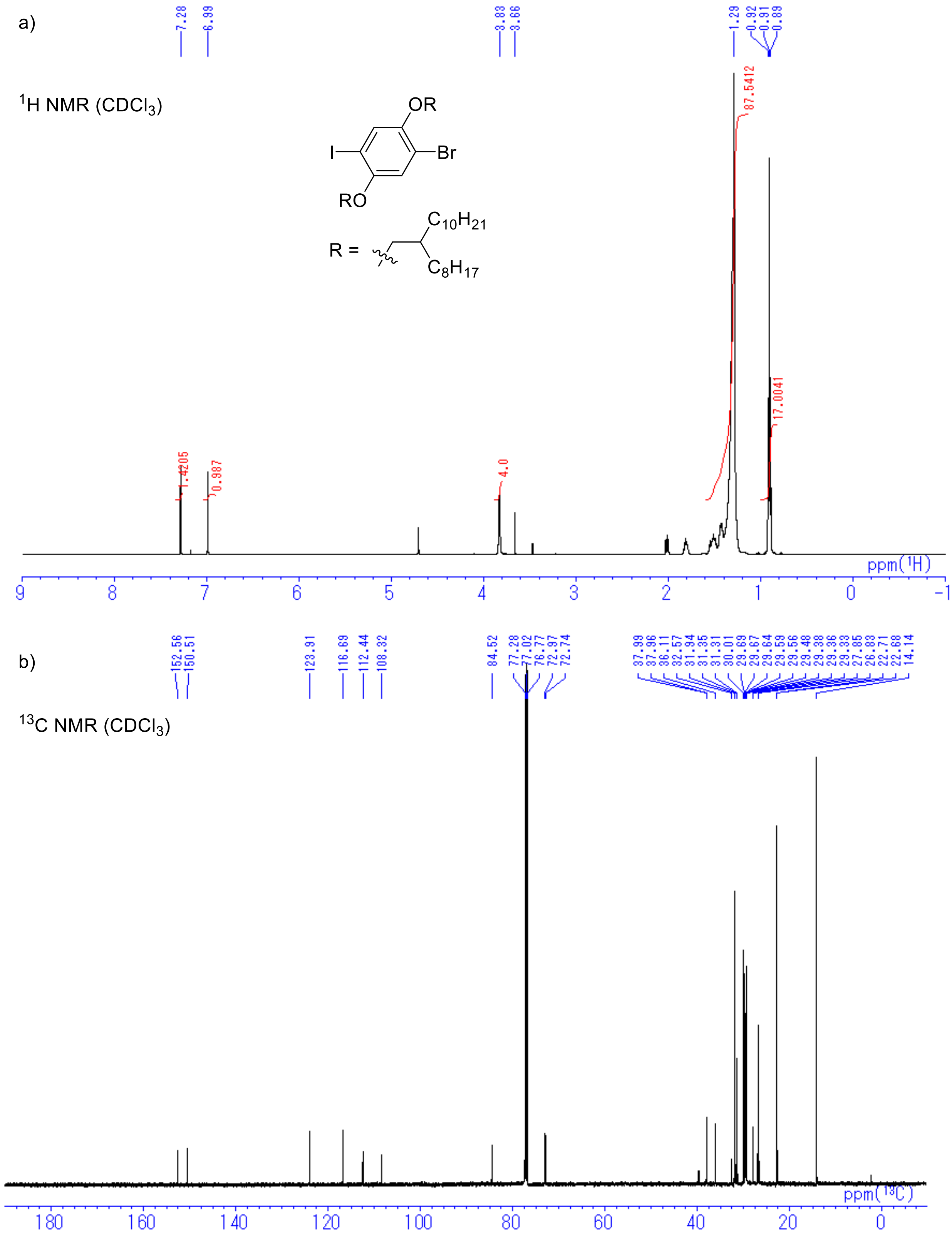
References

(S1) S. R. Bull, L. C. Palmer, N. J. Fry, M. A. Greenfield, B. W. Messmore, T. J. Meade and S. I. Stupp, *J. Am. Chem. Soc.*, 2008, **130**, 2742.

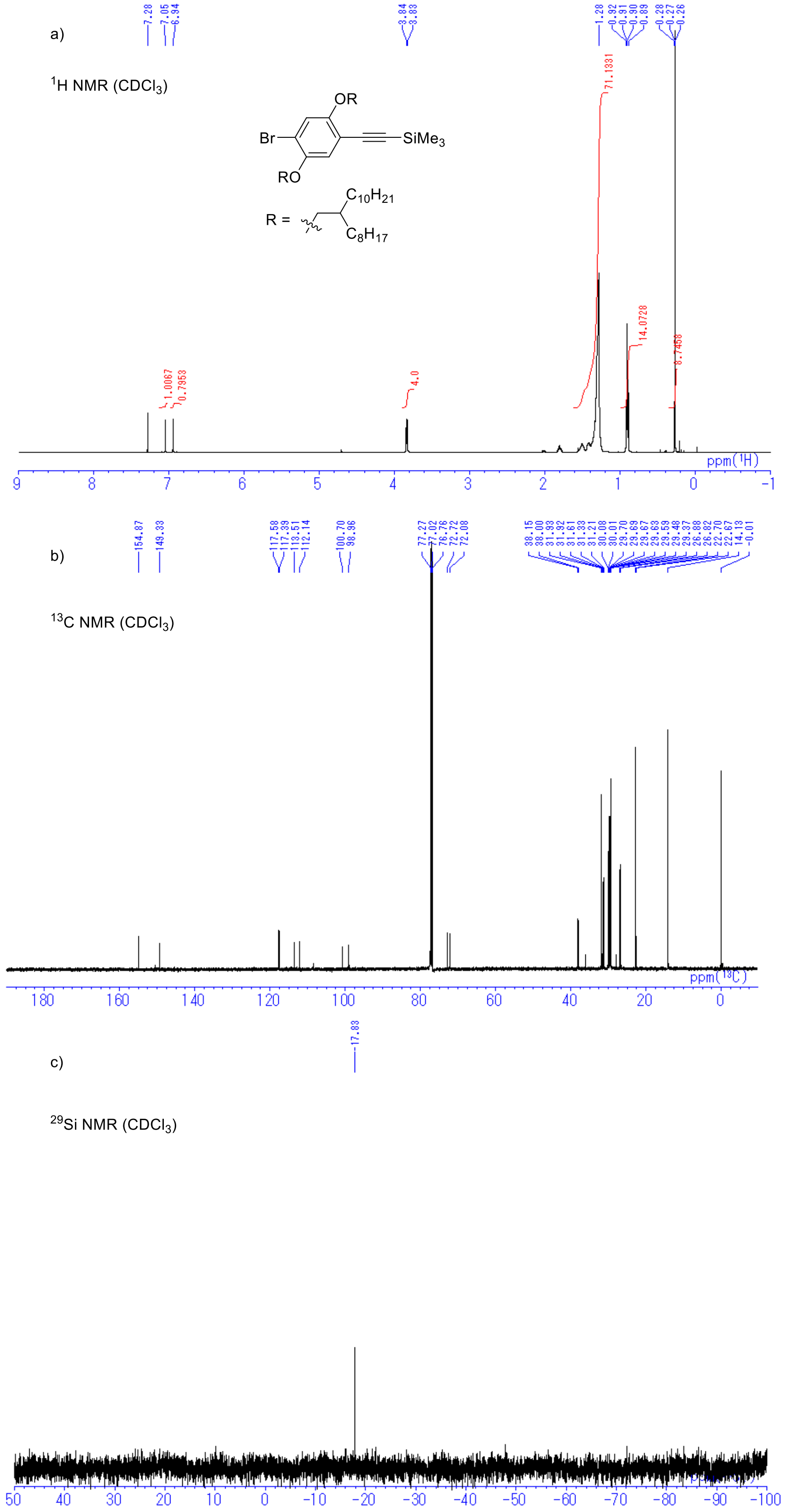
(S2) F. Ge, G. Kehr, C. G. Daniliuc and G. Erker, *Organometallics*, 2015, **34**, 229.

(S3) 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.

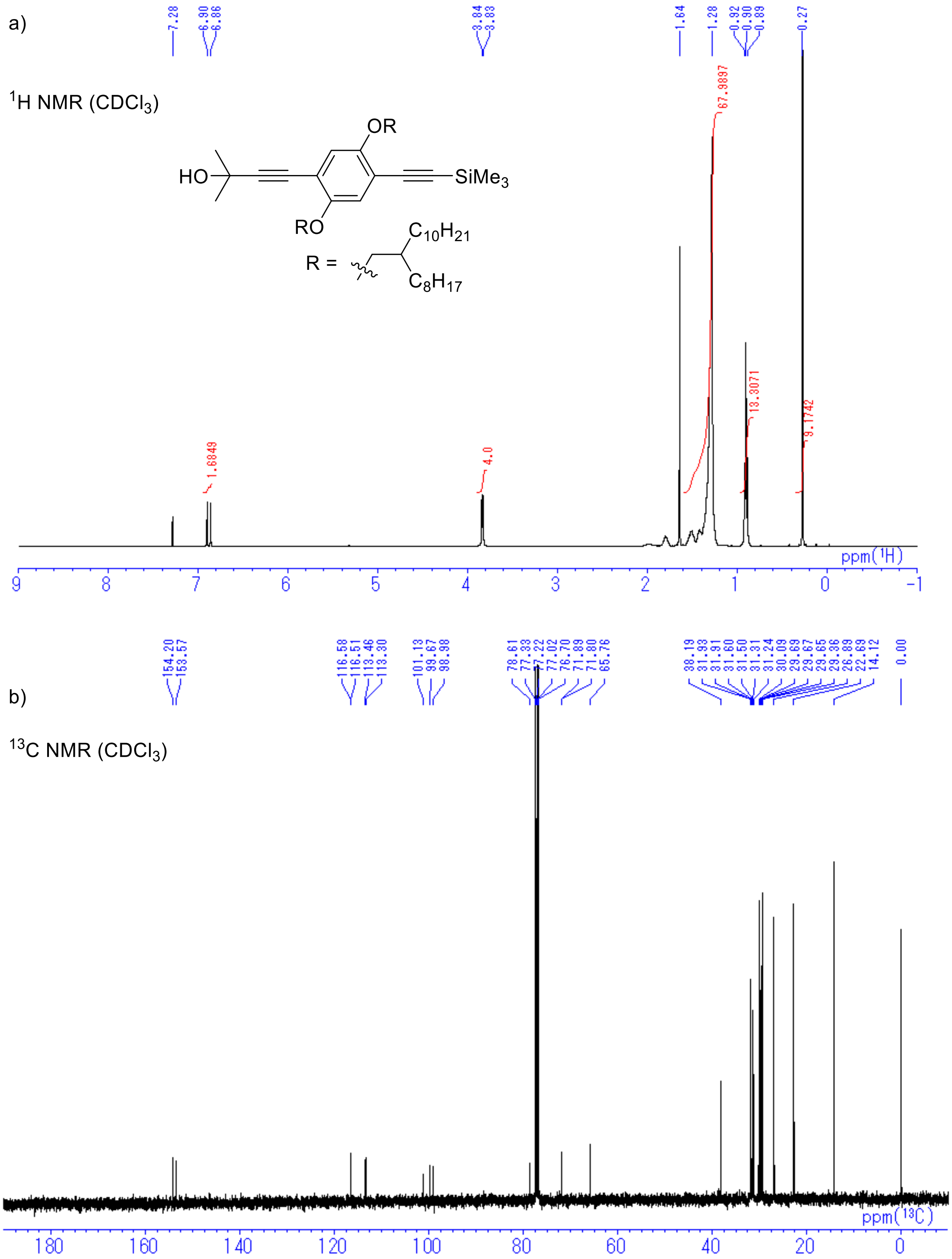
Appendix: NMR Spectra of new compounds



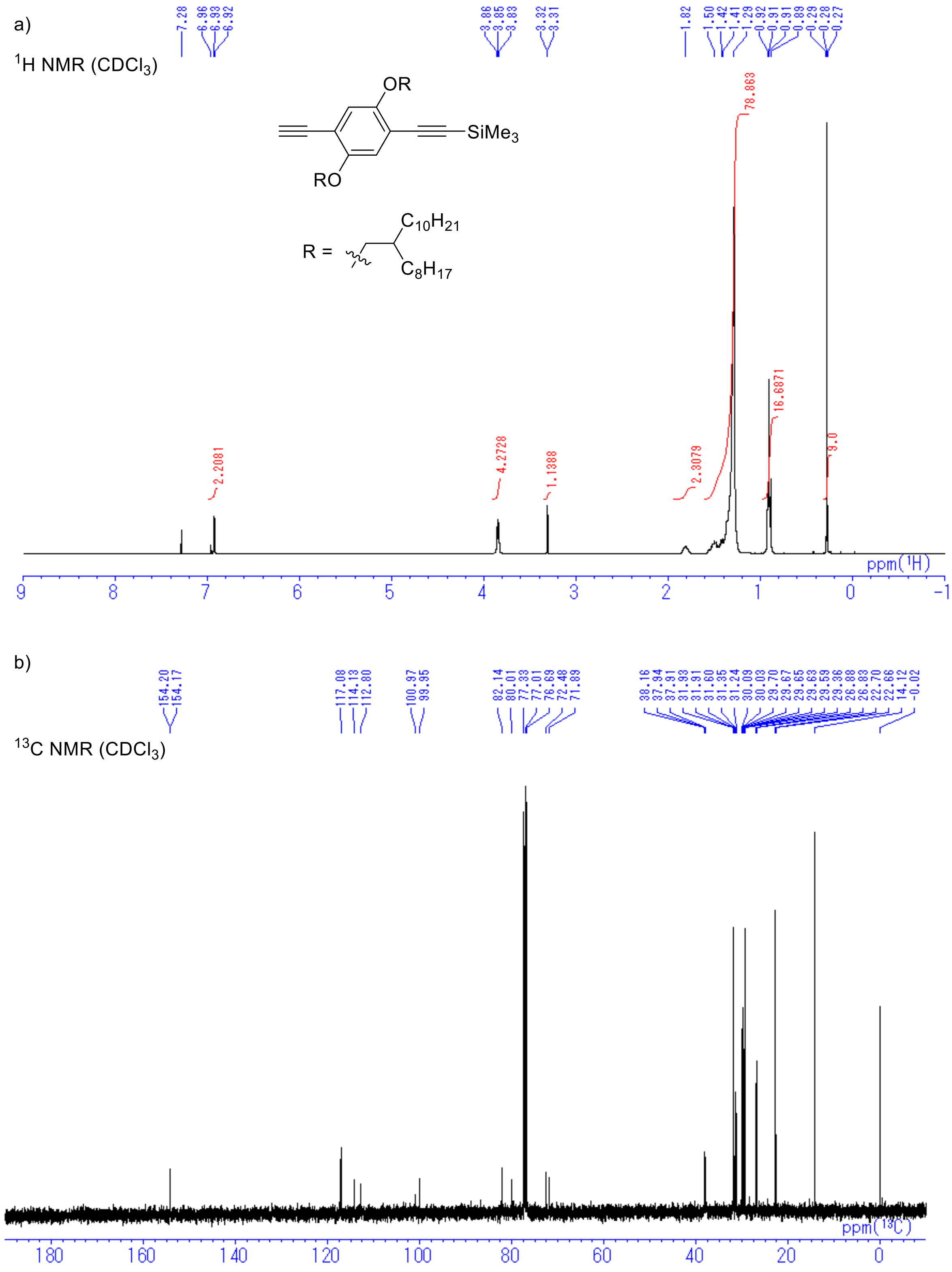
NMR spectra of 1-bromo-4-iodo-2,5-bis((2-octyldodecyl)oxy)benzene



NMR spectra of 1-bromo-4-(trimethylsilylethynyl)-2,5-bis((2-octyldodecyl)oxy)benzene

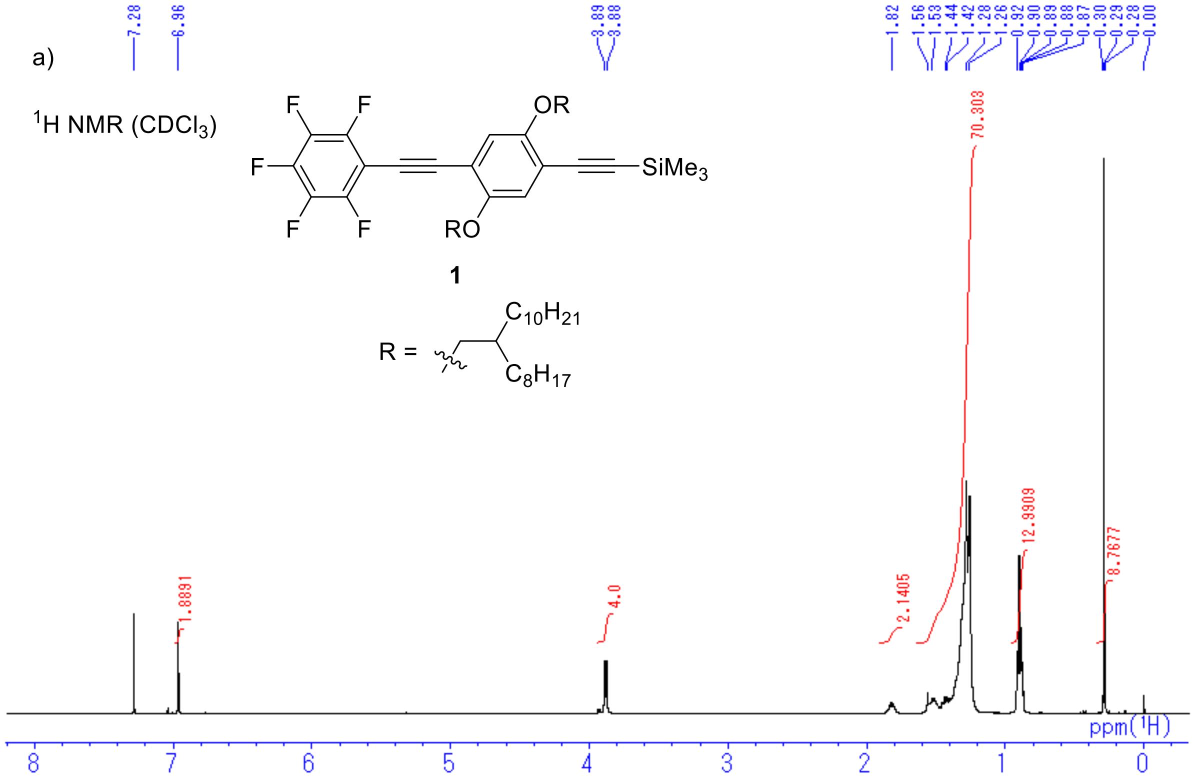


NMR spectra of 4-(2,5-bis((2-octyldodecyl)oxy)-4-((trimethylsilyl)ethynyl)phenyl)-2-methylbut-3-yn-2-ol



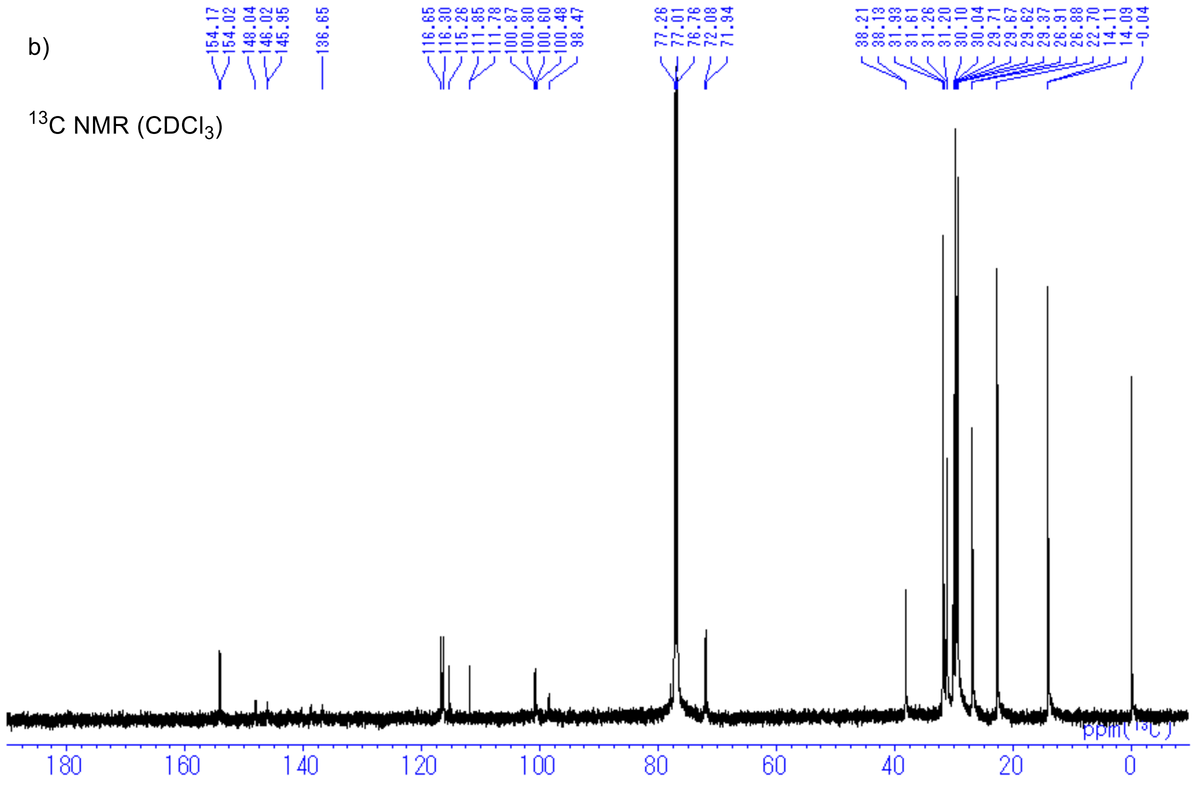
NMR spectra of 1-ethynyl-4-(trimethylsilylethynyl)-2,5-bis((2-octyldodecyl)oxy)benzene a)

^{1}H NMR (CDCl$_3$)

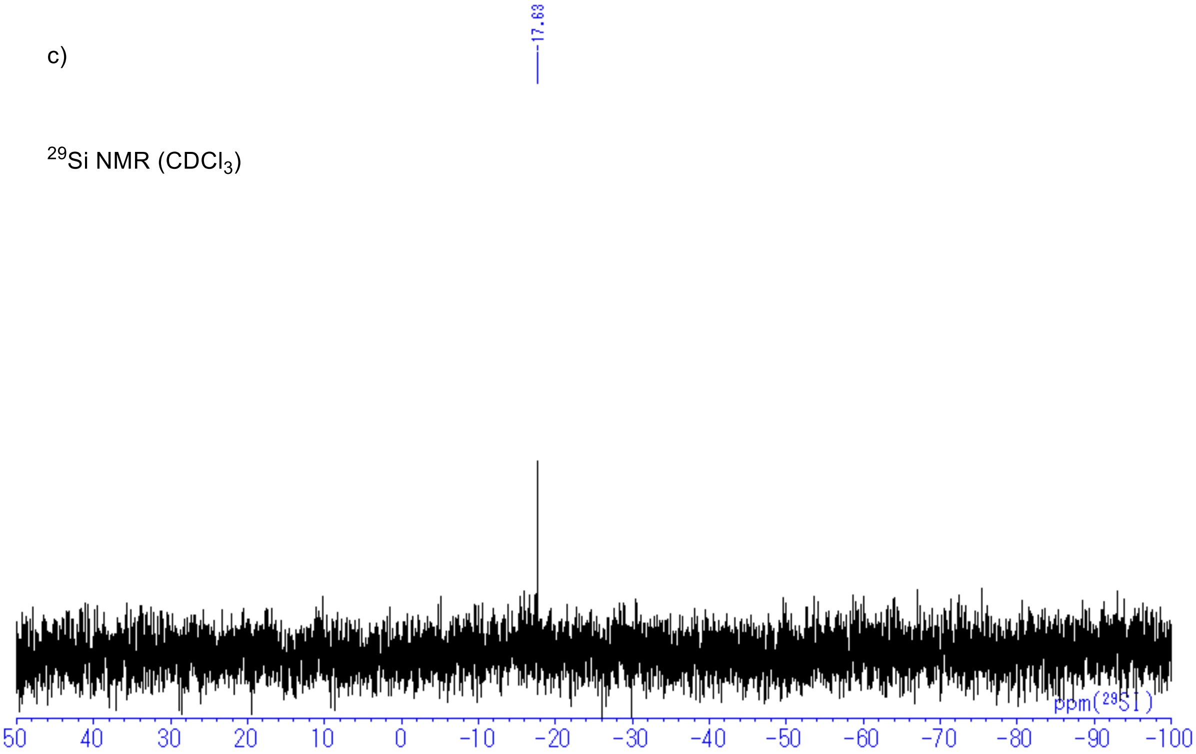


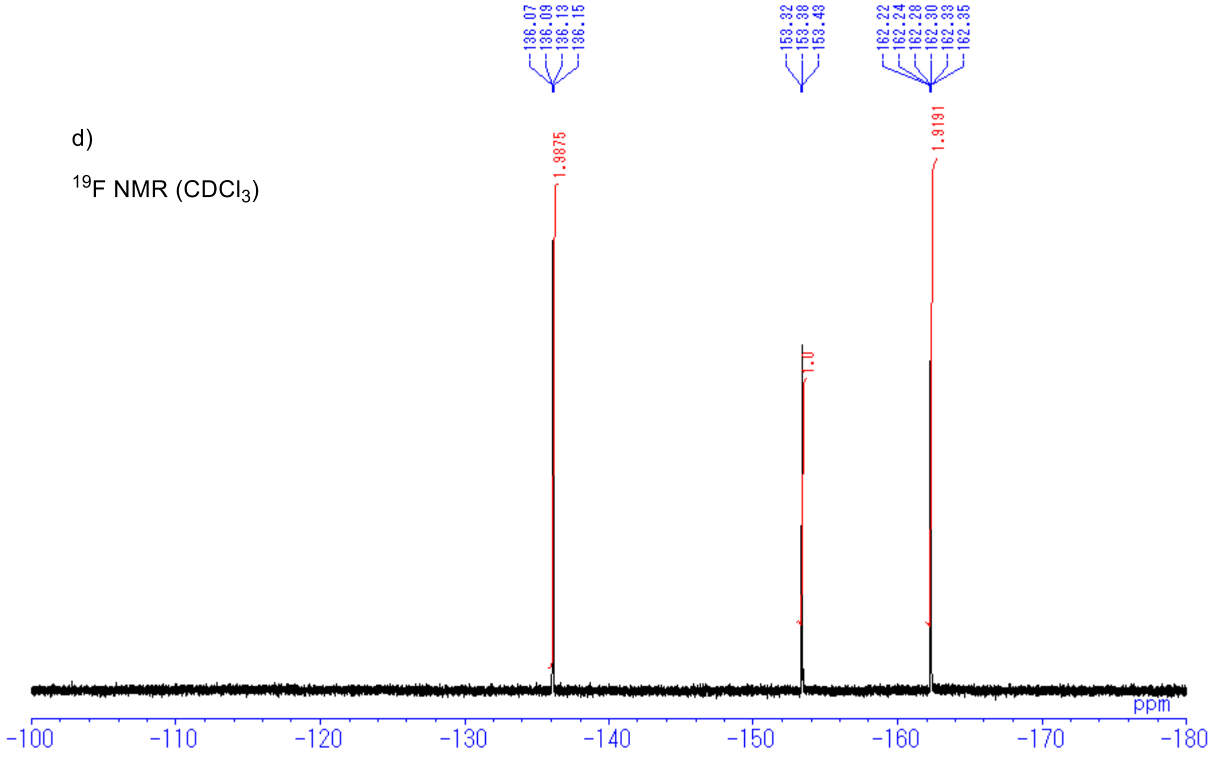
b)

^{13}C NMR (CDCl$_3$)

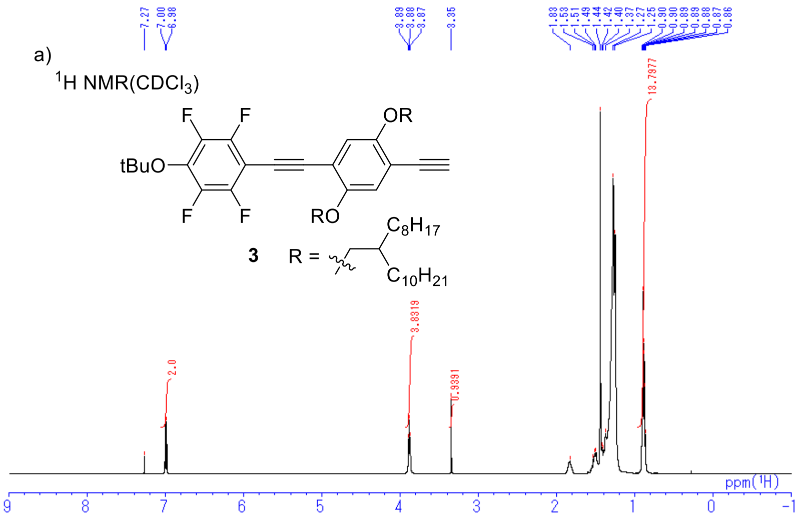


Continued…

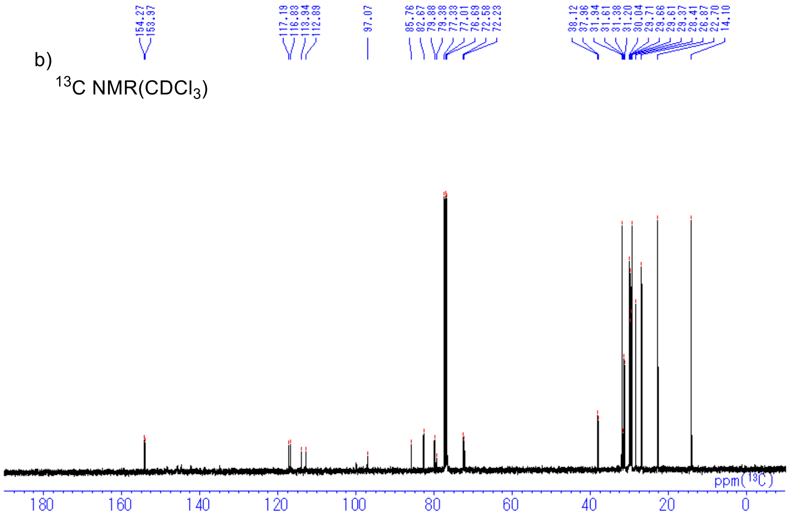




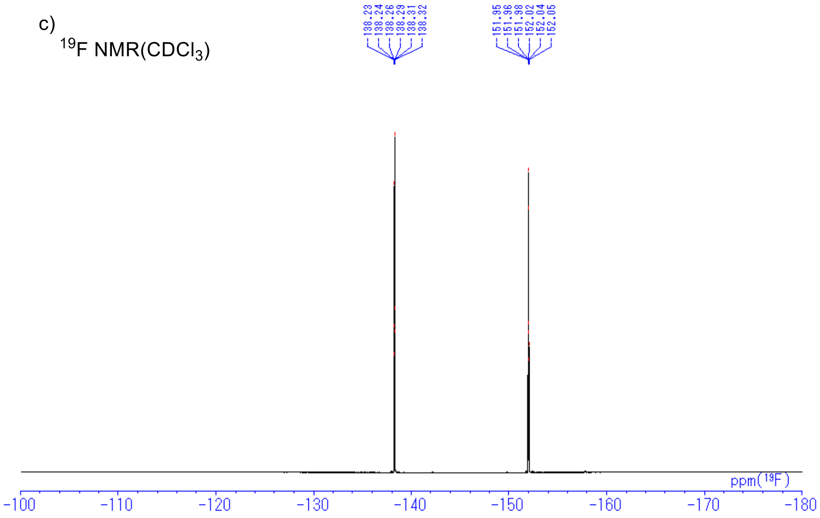
NMR spectra of 1-pentafluorophenylethynyl-4-(trimethylsilylethynyl)-2,5-bis((2-octyldodecyl)oxy)benzene **1**



a) ^1H NMR($CDCl_3$)



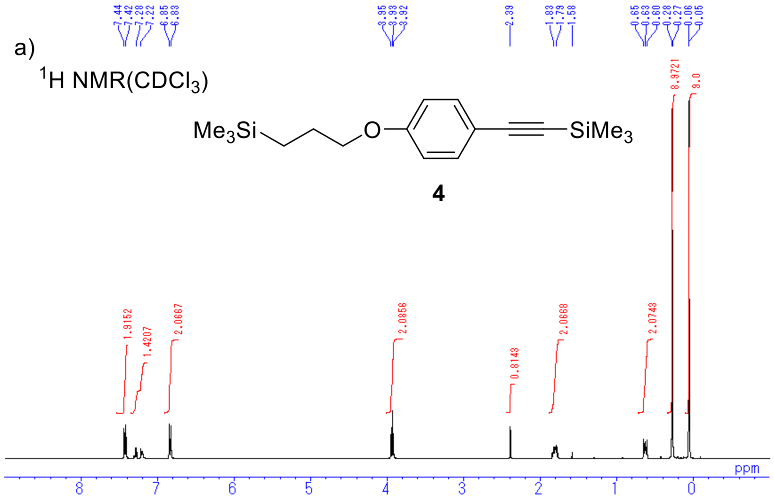
b) ^{13}C NMR($CDCl_3$)



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

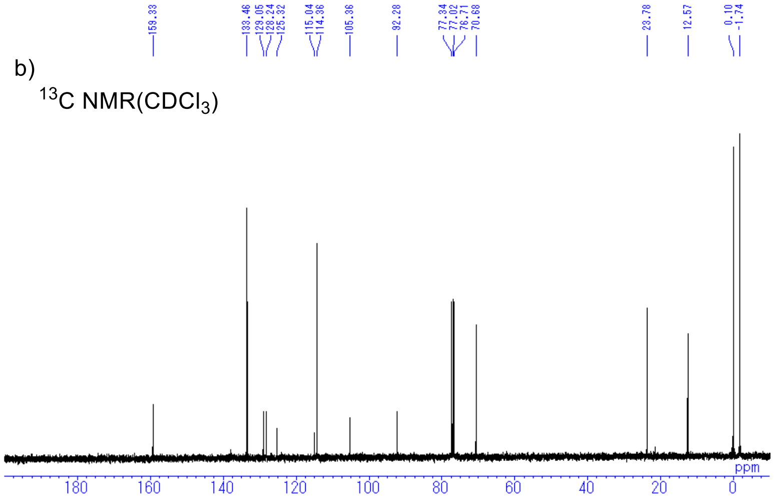
NMR spectra of 1-(4′-*t*-butoxytetrafluorophenyl)-4-ethynylbenzene **3** a)

^{1}H NMR($CDCl_3$)



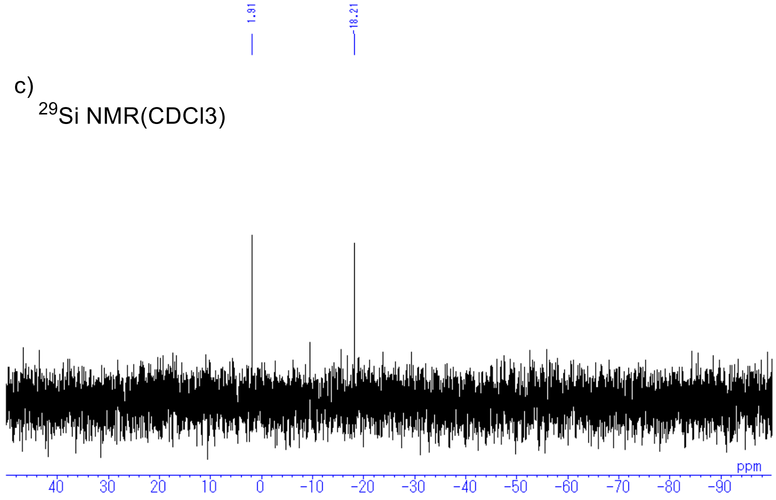
b)

^{13}C NMR($CDCl_3$)

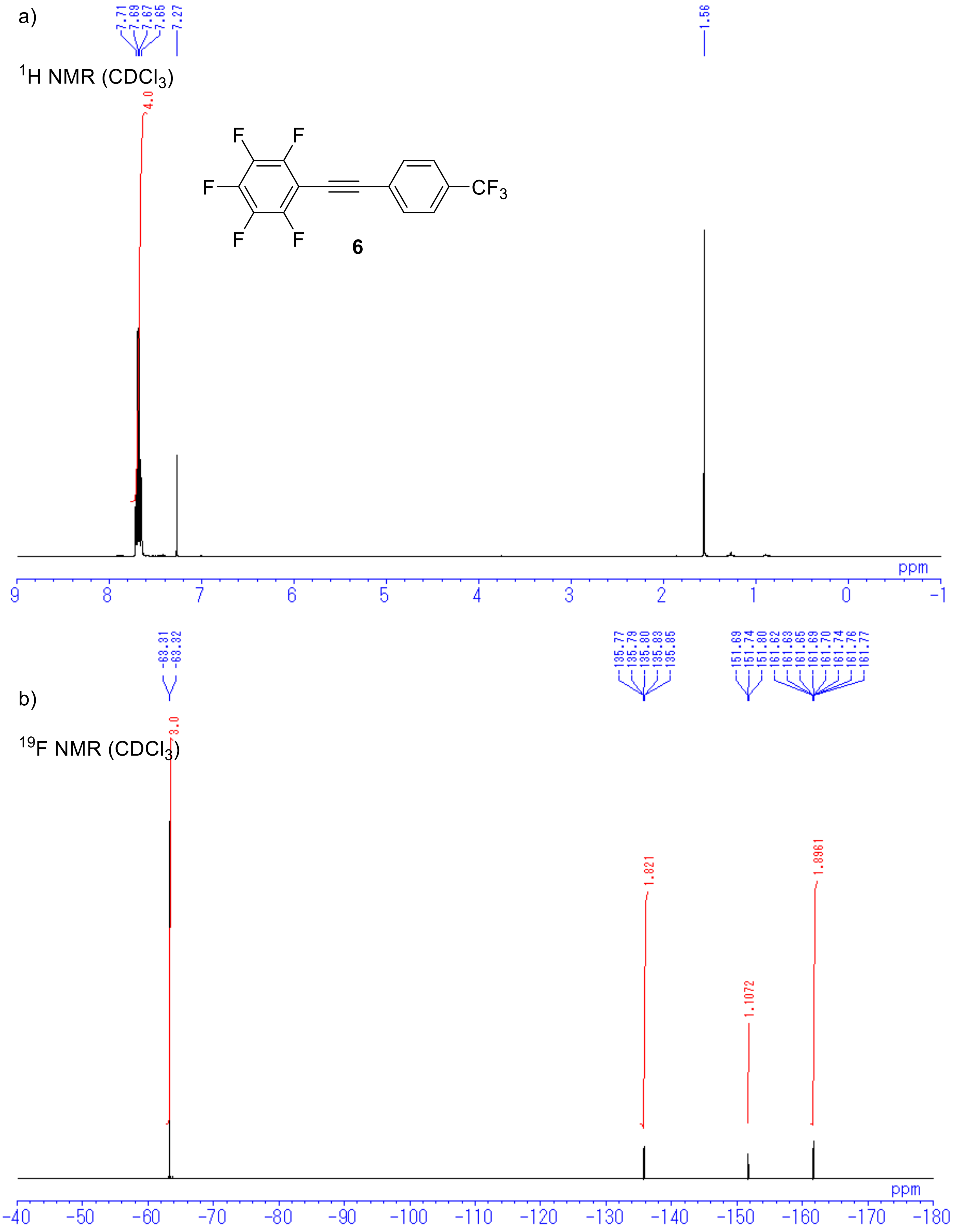


c)

^{29}Si NMR(CDCl3)



NMR spectra of 1-(trimethylsilyl)ethynyl-4-[(3’-trimethylsilyl)propoxy]benzene **4**



NMR spectra of 2,3,4,5,6-pentafluorophenyl-(4-(trifluoromethyl)phenyl)acetylene **6**