

Supporting Information

A Novel Cross-Coupling Polycondensation of Alkynylsilanes with Aryl Triflates Catalyzed by
 $\text{CuCl}/\text{Pd}(\text{PPh}_3)_4$

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General. All temperatures were uncorrected. All the reactions were carried out under an Ar atmosphere using standard Schlenk technique. Glassware was dried in an oven (120 °C) and heated under reduced pressure with a heat gun before use. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25mm). Silica gel column chromatography was carried out using Merck Kieselgel 60 (70-230 mesh) or Wakogel C-200 under an atmospheric or slightly positive pressure.

Measurements. Melting points were measured in Yanagimoto micro melting point apparatus. ¹H (300 MHz), ¹³C (75.5 MHz), and ²⁹Si (59.6 MHz) NMR spectra were measured on a Varian Mercury NMR spectrometer at an ambient temperature with the chemical shifts being expressed in parts per million downfield from tetramethylsilane ($\delta = 0$ ppm) or based on residual CHCl_3 as an internal standard. ¹⁹F (188 MHz) NMR spectra were measured on a Bruker AC-200 NMR spectrometer using fluorotrichloromethane (CFCl_3) as an internal standard. IR spectra were recorded on a Shimadzu FTIR-8000A spectrometer. GPC analyses were carried out with JASCO HPLC system equipped with a UV detector using THF as an eluent at a flow rate of 1.0 mL/min, with a Shodex KF-806L column. Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by polystyrene standards. Thermogravimetric analyses were performed with Seiko Instrument TG/DTA-220. UV absorption spectra were measured on Hewlett Packard HP8452A Diode Array Spectrophotometer using spectra grade chloroform as a solvent. Emission

and excitation spectra were recorded on a JASCO FP-77 scanning luminescence spectrometer (the slit bandwidth of 10 nm) under the concentration of 1.0×10^{-4} g/L in spectral grade chloroform as a solvent. Elemental analyses were carried out at Elemental Analysis Center of Tokyo Institute of Technology using Yanako MT2 CHN Corder and SX-Elements Micro Analyzer YS-10.¹

Materials. DMF was distilled from CaH_2 and stored over MS-4A. $\text{Pd}(\text{PPh}_3)_4$ was prepared according to the literature.² Copper(I) chloride was purified by the literature method.³ 1,2-Bis(trimethylsilylethynyl)benzene (**2b**),⁴ 1,4-bis[(trimethylsilyl)ethynyl]-2,5-dihexylbenzene (**2c**),⁵ 1,4-bis(trimethylsilyl)ethynyl-2,5-bis(nonyloxy)benzene (**2d**),⁶ 2,5-bis[2-(trimethylsilyl)ethynyl]-3-hexylthiophene (**2e**),⁷ 2,5-bis[(trimethylsilyl)ethynyl]pyridine (**2f**),⁸ and 1,8-bis[(trimethylsilyl)-1,7-octadiyne (**2g**)⁹ were prepared according to the literature procedure. Other chemicals were purchased and used as such.

2,2-Bis(4-trifluoromethanesulfonylphenyl)hexafluoropropane (1). To a suspension of 2,2-bis(4-hydroxyphenyl)hexafluoropropane (6.7 g, 20 mmol) and freshly distilled triethylamine (8.4 mL, 60 mmol) in a 100 mL of two necked flask equipped with a stirring bar and a rubber septum was added trifluoromethanesulfonic anhydride (8.1 mL, 48 mmol) through the septum by a syringe at 0 °C under an argon atmosphere. The reaction mixture was stirred at room temperature for 17 h. The mixture was quenched with 30 mL of 3 M hydrochloric acid and the organic layer was separated. The aqueous layer was extracted with diethyl ether (2 x 10 mL). The combined organic layers were successively washed with NaHCO_3 aq and brine and then dried over MgSO_4 . Filtration and evaporation yielded a pale yellow solid, which was subjected to column chromatography on silica gel with 5% of ethyl acetate in hexane to give 10.2 g (16.9 mmol, 85% yield) of **1** as a white solid. Mp: 98-99 °C. ^1H NMR (CDCl_3) δ 7.34 (d, J = 9.0 Hz, 4 H), 7.49 (d, J = 9.0 Hz, 4 H); ^{13}C NMR (CDCl_3) δ 118.69 (q, J = 320 Hz), 121.53, 123.60 (q, J = 285 Hz), 132.23, 133.11, 149.90; ^{19}F NMR (CDCl_3) δ -64.36, -73.30; IR (KBr): 3127, 1607, 1509, 1435, 1418, 1286, 1171, 1021, 972, 897, 843, 837, 783, 747, 720, 625, 577 cm^{-1} ; Anal. Calcd. for $\text{C}_{17}\text{H}_8\text{F}_{12}\text{O}_6\text{S}_2$: C, 34.01; H, 1.34; F, 37.97%. Found: C, 34.05; H, 1.40; F, 37.67%.

General procedure for the polycondensation. Polymerization of 1 with 2a Leading to 3a. To a monomer **1** (600 mg, 1.0 mmol) and bis(trimethylsilyl)acetylene (**2a**) (227 μL , 1.0

mmol) placed in a 20 mL of Schlenk tube equipped with a magnetic stirring bar and a rubber septum under an argon atmosphere were added dry DMF (1 mL), CuCl (10 mg, 0.1 mmol), and Pd(PPh₃)₄ (58 mg, 0.05 mmol). The reaction mixture was stirred at 80 °C. After 16 h the black solution was poured into a mixture of methanol (80 mL) and 3 M HCl (5 mL) to yield a black precipitate, which was collected by filtration, washed with methanol, and dried under vacuum overnight. The resulting gray residue was extracted with chloroform (30 mL) and extracts were concentrated. Reprecipitation was carried out by adding the chloroform solution dropwise into 80 mL of methanol to give gray precipitates. The solid was collected by filtration, rinsed with methanol, and then dried under vacuum. Isolated yield was 63%. ¹H NMR (CDCl₃) δ 7.39 (br d, *J* = 8.1 Hz, 4 H), 7.55 (br d, *J* = 8.1 Hz, 4 H); ¹³C NMR (CDCl₃) δ 89.80, 123.92 (q, *J* = 286 Hz), 129.93, 130.20, 131.47, 133.27; ¹⁹F NMR (CDCl₃) δ -64.10 (CF₃); IR (neat): 1613, 1520, 1325, 1256, 1208, 1175, 1138, 970, 959, 941, 928, 828, 750, 740, 717, 574 cm⁻¹; Anal. Calcd. for (C₁₇H₈F₆)_n: C, 62.59; H, 2.47; F, 34.94%. Found: C, 58.73; H, 2.26; F, 32.48; Ash, 11.50%.

Polymerization of 1 with 2b. Polymer 3b was isolated as a black solid in 52% yield. ¹H NMR (CDCl₃) δ 6.80-7.85 (m, 12 H); ¹³C NMR (CDCl₃) δ 64.46 (septet, *J* = 25 Hz), 89.85, 92.37, 123.90 (q, *J* = 285 Hz), 124.30, 125.39, 128.40, 130.15, 131.35, 132.00, 133.09; ¹⁹F NMR (CDCl₃) δ -64.18 (CF₃), -73.36 (OTf); IR (neat): 3060, 2218, 1609, 1514, 1480, 1437, 1431, 1323, 1252, 1208, 1175, 1140, 968, 941, 928, 828, 756, 740, 723, 706, 690, 574 cm⁻¹. Anal. Calcd. for (C₂₅H₁₂F₆)_n: C, 70.43; H, 2.84; F, 26.73%. Found: C, 65.39; H, 2.81; F, 26.25; Ash, 3.70%.

Polymerization of 1 with 2c. Polymer 3c was isolated as a gray solid in 80% yield. ¹H NMR (CDCl₃) δ 0.71-1.01 (m, 6 H), 1.08-1.52 (m, 12 H), 1.58-1.82 (m, 4 H), 2.65-2.96 (m, 4 H), 7.20-7.62 (m, 10 H); ¹³C NMR (CDCl₃) δ 14.09, 22.63, 29.23, 30.64, 31.74, 34.14, 64.50 (septet, *J* = 25 Hz), 90.10, 92.82, 122.44, 123.99 (q, *J* = 285 Hz), 124.55, 130.19, 131.21, 132.47, 132.93, 142.48; ¹⁹F NMR (CDCl₃) δ -64.09 (CF₃), -73.32 (OTf); IR (KBr): 3046, 2959, 2924, 2857, 2224, 1542, 1509, 1466, 1323, 1254, 1210, 1177, 1140, 1022, 970, 941, 928, 830, 741, 706 cm⁻¹. Anal. Calcd. For (C₃₇H₃₆F₆)_n: C, 74.73; H, 6.10; F, 19.17%. Found: C, 70.51; H, 5.96; F, 18.35; Ash, 4.15%.

Polymerization of 1 with 2d. Polymer 3d was isolated as a brown solid in 90% yield. ¹H

NMR (CDCl₃) δ 0.83-0.92 (m, 6 H), 1.25-1.37 (m, 18 H), 1.49-1.58 (m, 4 H), 1.80-1.87 (m, 4 H), 3.96-4.00 (m, 4 H), 7.02 (s, 2 H), 7.38 (d, J = 8.0 Hz, 4 H), 7.55 (d, J = 8.0 Hz, 4 H); ¹³C NMR (CDCl₃) δ 14.07, 22.64, 26.07, 29.26, 29.32, 29.41, 29.61, 31.87, 64.49 (septet, J = 25 Hz), 69.60, 87.70, 93.71, 113.86, 116.88, 123.97 (q, J = 285 Hz), 124.55, 130.10, 131.28, 132.90, 153.74; ¹⁹F NMR (CDCl₃) δ -64.10 (CF₃), -73.34 (OTf); IR (KBr): 2926, 2857, 2211, 2153, 1728, 1609, 1518, 1495, 1468, 1416, 1381, 1323, 1252, 1208, 1175, 1140, 968, 928, 830, 741, 704 cm⁻¹. Anal. Calcd. for (C₄₃H₄₈F₆O₂)_n: C, 72.66; H, 6.81; F, 14.04%. Found: C, 69.34; H, 6.51; F, 14.38; Ash, 2.20%.

Polymerization of 1 with 2e. Polymer 3e was isolated as a yellow solid in 58% yield. ¹H NMR (CDCl₃) δ 0.80-0.96 (m, 3 H), 1.20-1.44 (m, 6 H), 1.58-1.74 (m, 2 H), 2.56-2.76 (m, 2 H), 7.10 (s, 1 H), 7.30-7.42 (m, 4 H), 7.46-7.57 (m, 4 H); ¹³C NMR (CDCl₃) δ 14.08, 22.59, 28.88, 29.55, 30.08, 31.60, 64.50 (septet, J = 26 Hz), 83.71, 84.34, 92.74, 95.10, 119.98, 123.03, 123.82, 123.92 (q, J = 285 Hz), 124.05, 130.19, 131.09, 131.18, 133.07, 133.18, 133.40, 148.41; ¹⁹F NMR (188 MHz, CDCl₃) δ -64.09 (CF₃), -73.32 (OTf); IR (KBr): 2956, 2930, 2857, 2203, 1609, 1536, 1507, 1431, 1323, 1252, 1208, 1175, 1140, 970, 959, 928, 887, 830, 749, 729 cm⁻¹. Anal. Calcd. for (C₂₉H₂₂F₆S)_n: C, 67.43; H, 4.29; F, 22.07%. Found: C, 64.07; H, 3.95; F, 26.00; Ash, 3.31%.

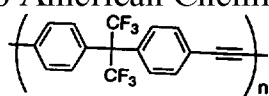
Polymerization of 1 with 2f. Polymer 3f was isolated as a brown solid in 43% yield. ¹H NMR (CDCl₃) δ 7.18-7.92 (m, 10 H), 8.78 (br s, 1 H); ¹³C NMR (CDCl₃) δ 64.52 (septet, J = 26 Hz), 87.50, 89.89, 89.95, 93.18, 119.29, 123.18, 123.47, 123.85 (q, J = 285 Hz), 126.65, 130.24, 131.50, 131.85, 132.31, 133.60, 133.82, 138.62, 141.81, 152.55; ¹⁹F NMR (CDCl₃) δ -64.05 (CF₃), -73.32 (OTf); IR (KBr): 2959, 2926, 2857, 2210, 1514, 1431, 1323, 1252, 1208, 1177, 1140, 968, 941, 928, 887, 830, 740, 704, 610, 550 cm⁻¹. Anal. Calcd. for (C₂₄H₁₁NF₆)_n: C, 67.45; H, 2.59; N, 3.28; F, 26.67%. Found: C, 62.61; H, 2.77; N, 2.90; F, 24.18; Ash, 0.90%.

Polymerization of 1 with 2g. Polymer 3g was isolated as a gray solid in 48% yield. ¹H NMR (CDCl₃) δ 1.78 (br s, 4 H), 2.48 (br s, 4 H), 7.27 (br d, J = 8.7 Hz, 4 H), 7.37 (br d, J = 8.7 Hz, 4 H); ¹³C NMR (CDCl₃) δ 19.00, 27.71, 64.32 (septet, J = 25 Hz), 79.97, 91.72, 123.97 (q, J = 285 Hz), 124.96, 129.97, 131.25, 132.28; ¹⁹F NMR (CDCl₃) δ -64.23 (CF₃), -73.34 (OTf); IR (neat):

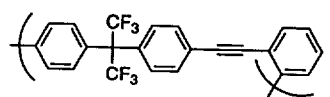
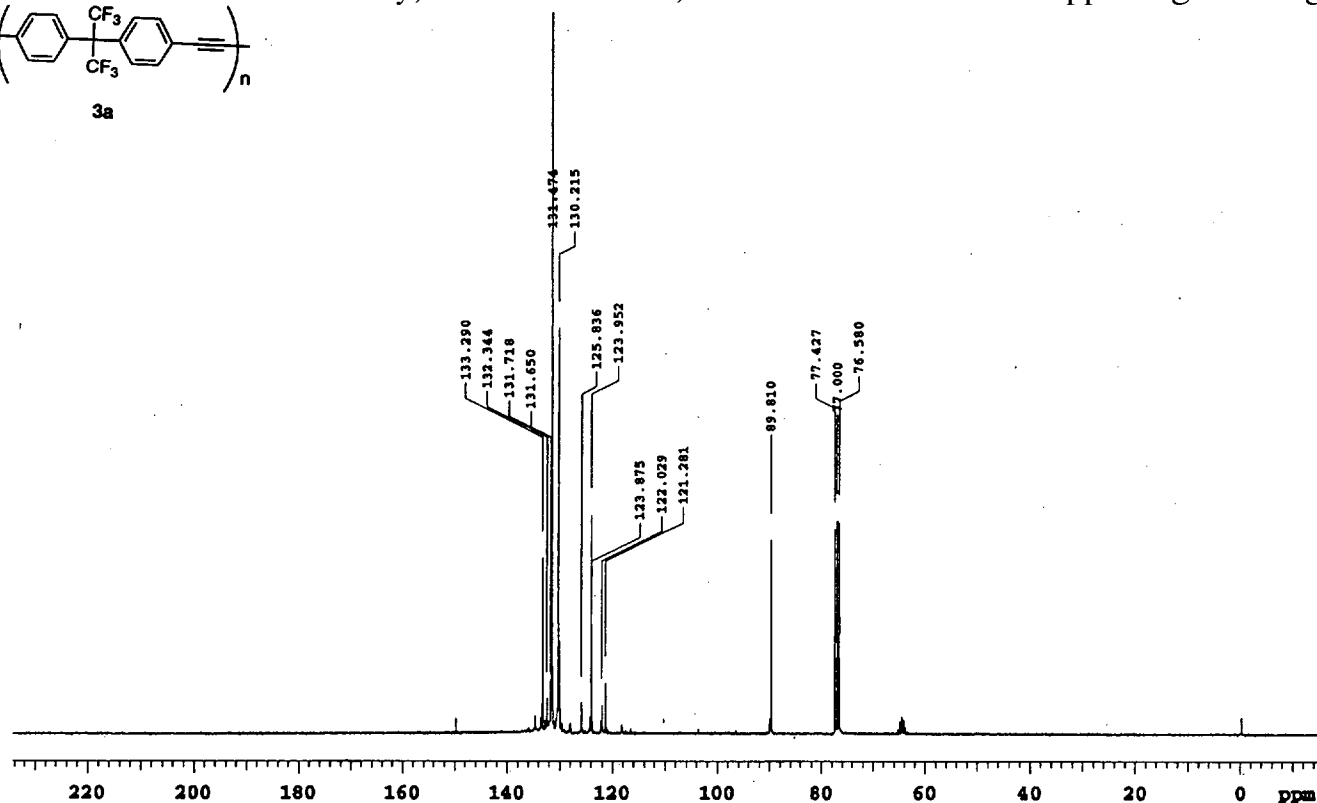
2926, 2863, 2232, 1609, 1512, 1460, 1431, 1323, 1254, 1208, 1175, 1138, 968, 928, 830, 741,
702, 550 cm^{-1} . Anal. Calcd. for $(\text{C}_{23}\text{H}_{16}\text{F}_6)_n$: C, 67.98; H, 3.97; F, 28.05%. Found: C, 64.03; H,
4.03; F, 22.93; Ash, 0.04%.

References

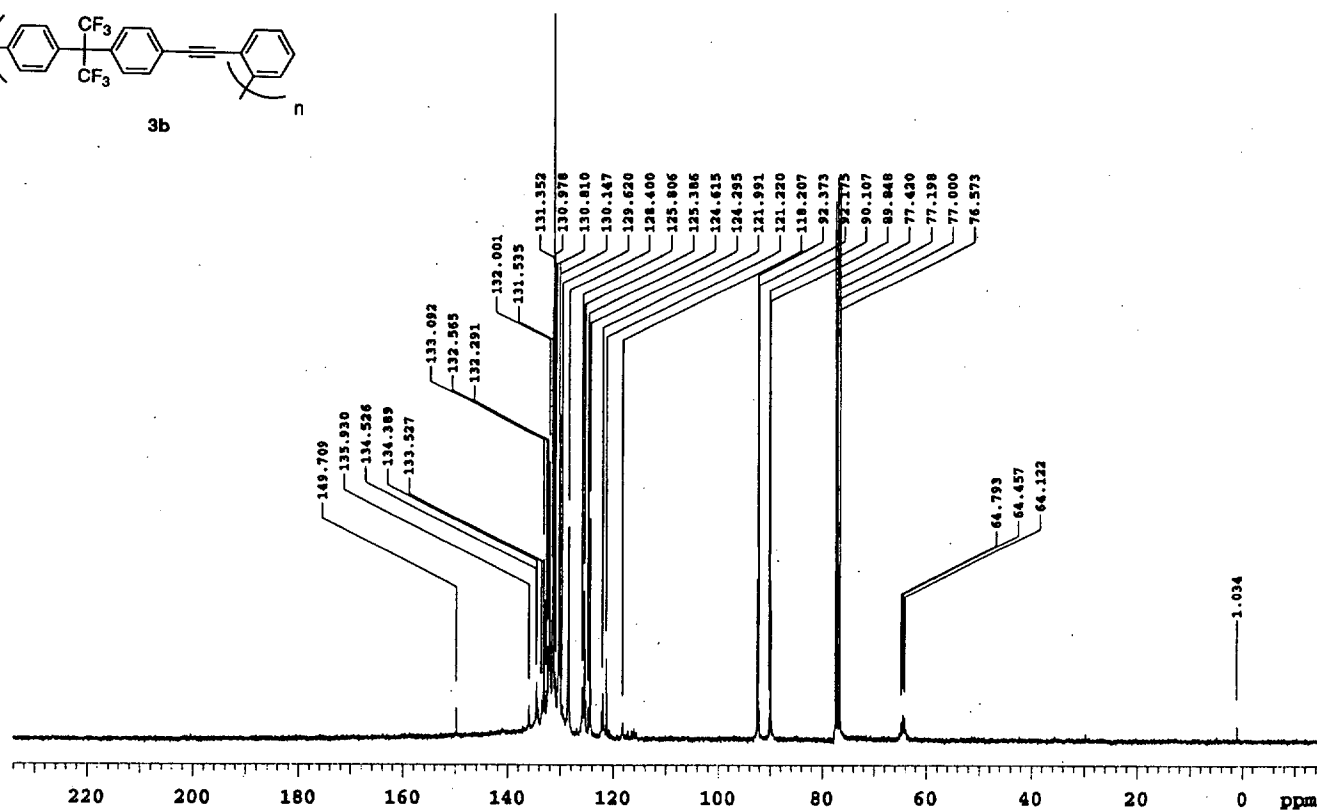
- (1) Incomplete combustion of the polymeric materials led to large deviations from the calculated value, especially for a fluorine atom. Thus, data of those elemental analyses were reported along with the percentage of ash residue.
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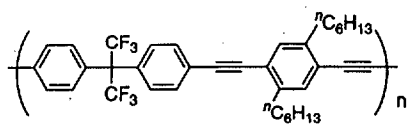


3a

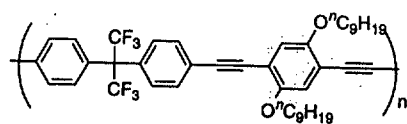
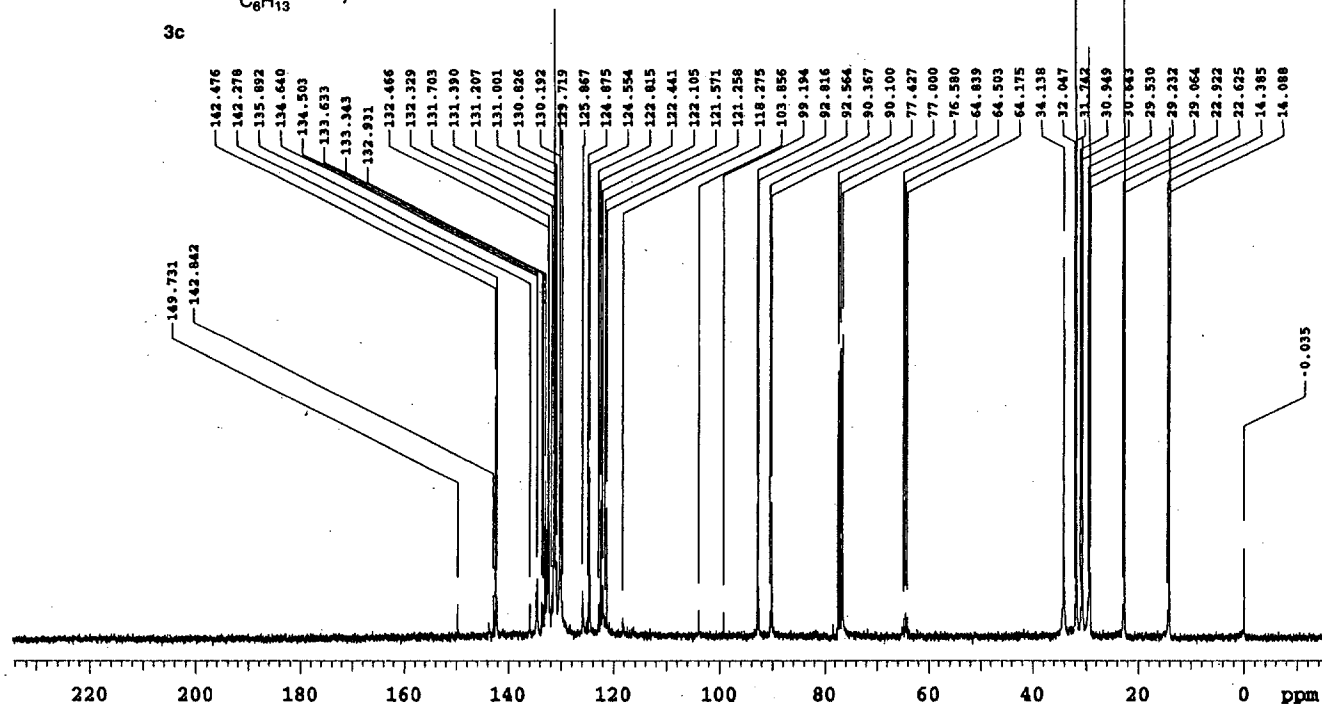


3b

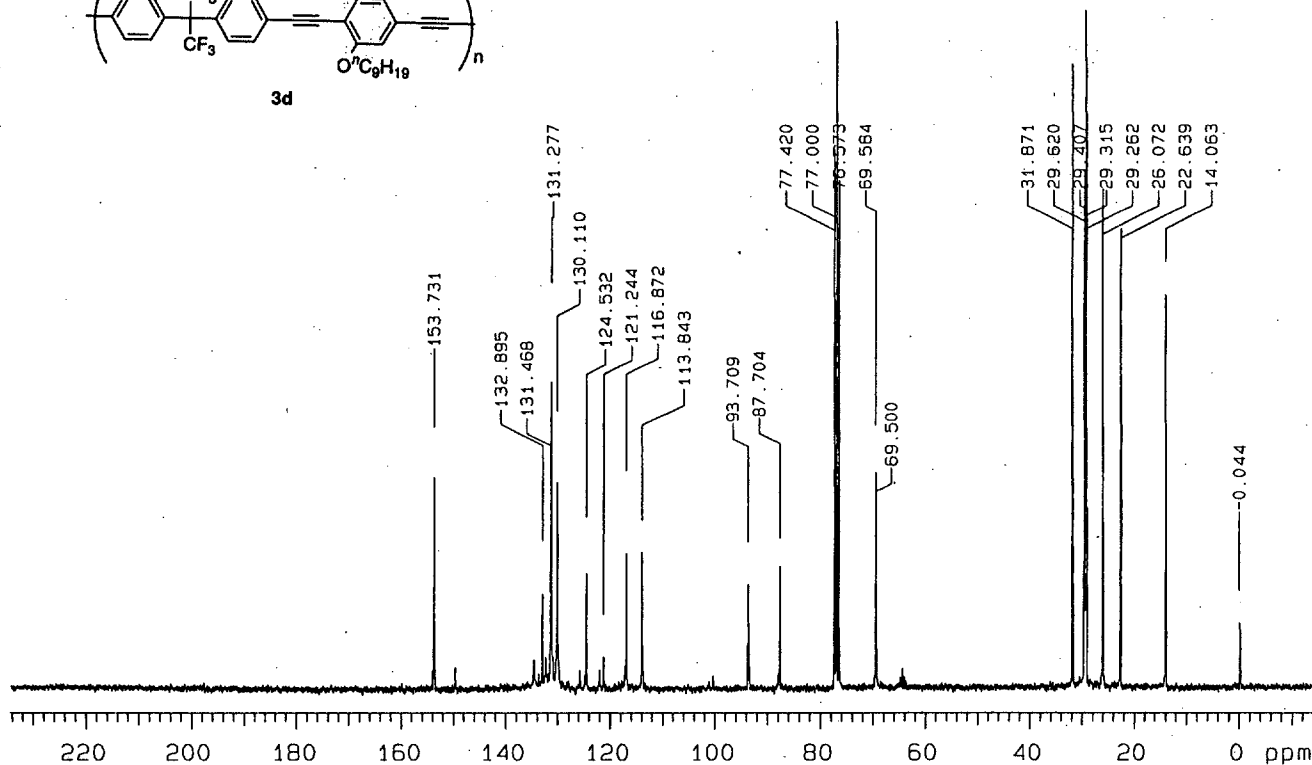


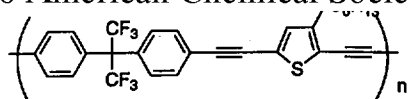


3c

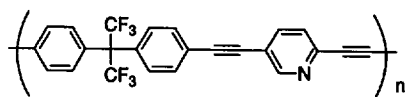
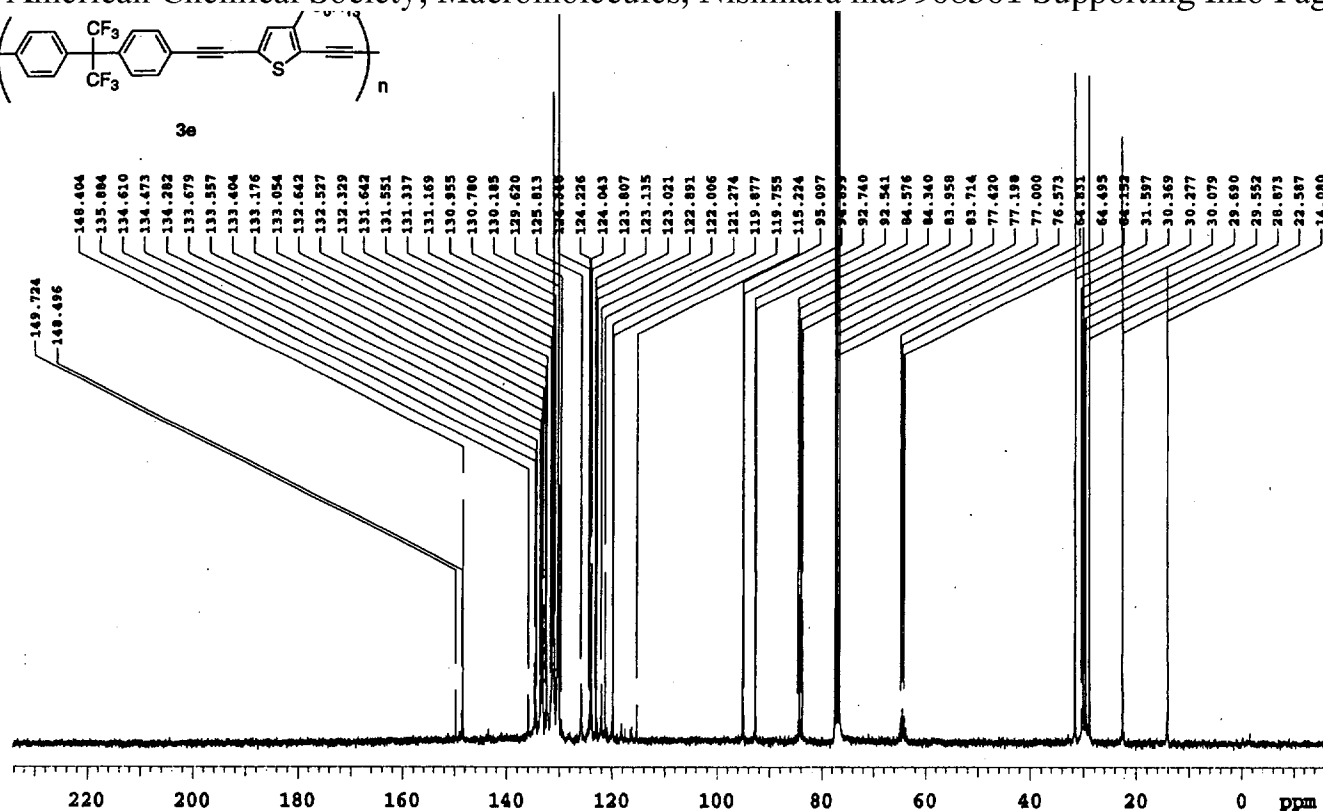


3d

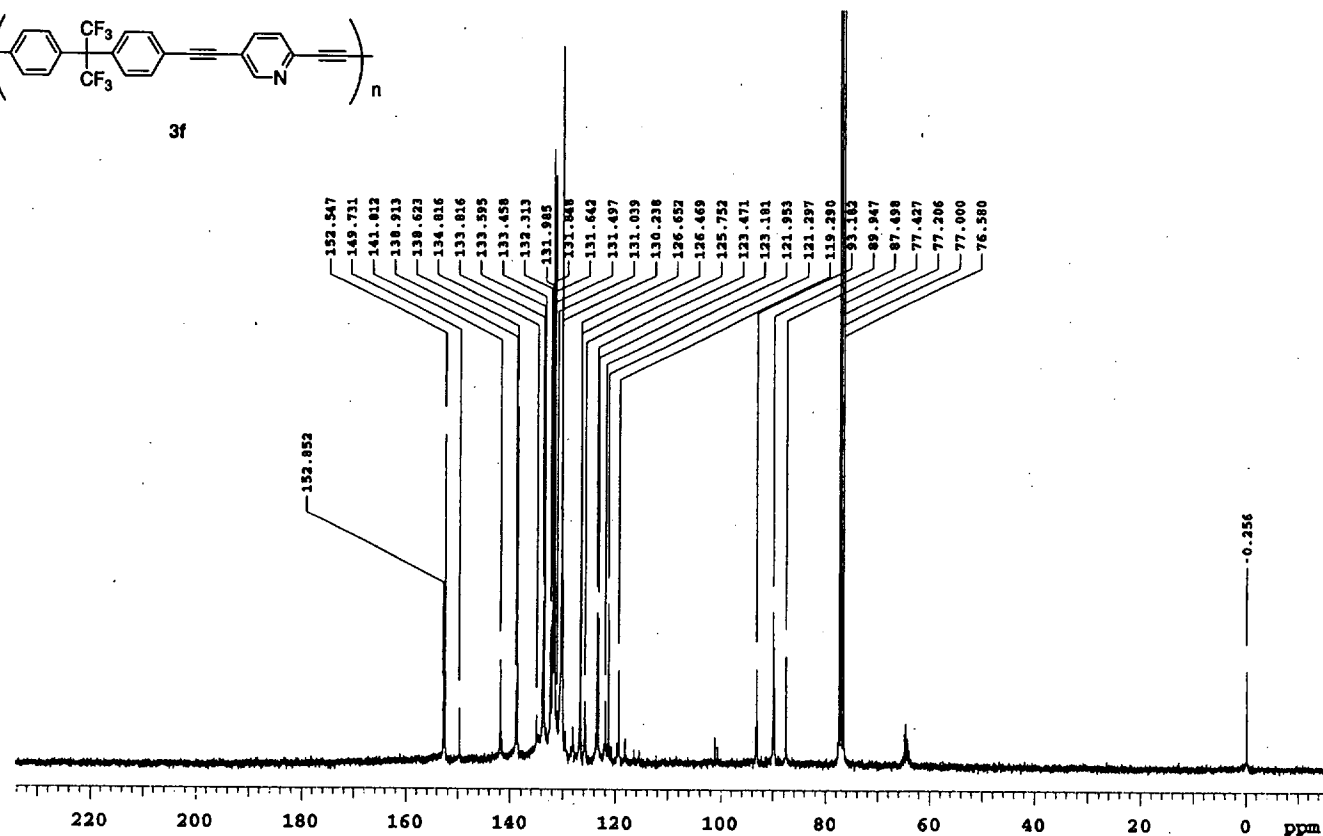


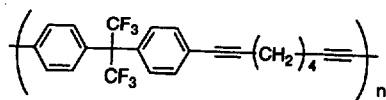


3e



3f





3g

