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Electronic Supplementary Information

Development of light-emitting liquid-crystalline polymers with a pentafluorinated bistolane-based luminophore

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Contents

1. Experimental procedure

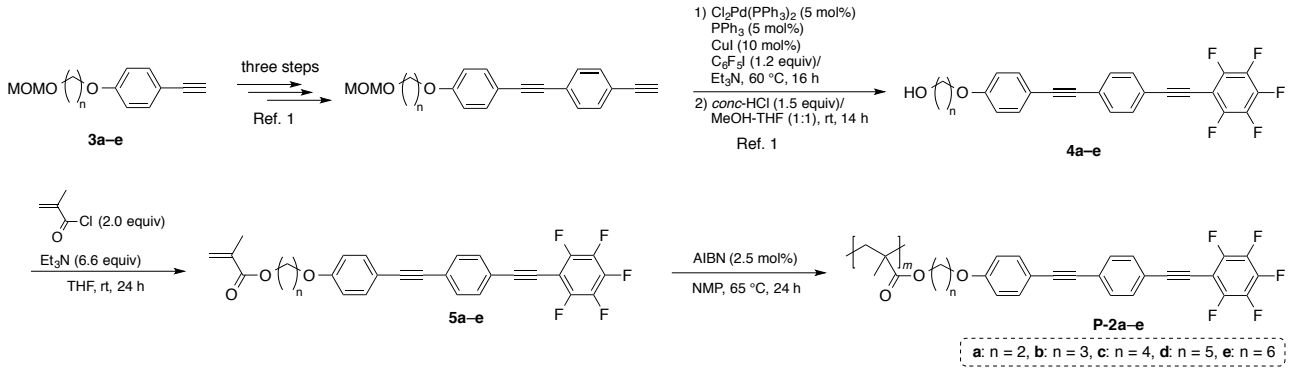
1-1. General

^{1}H and ^{13}C NMR spectra were obtained with a Bruker AVANCE III 400 NMR spectrometer (^{1}H: 400 MHz and ^{13}C: 100 MHz) in chloroform-*d* ($CDCl_3$) solution and the chemical shifts are reported in parts per million (ppm) using the residual proton in the NMR solvent. ^{19}F NMR (376 MHz) spectra were obtained with a Bruker AVANCE III 400 NMR spectrometer in $CDCl_3$ solution with $CFCl_3$ (δ_F = 0 ppm) as an internal standard. Infrared spectra (IR) were recorded in a KBr method with a JASCO FT/IR-4100 type A spectrometer; all spectra were reported in wavenumber (cm^{-1}). High resolution mass spectra (HRMS) were recorded on a JEOL JMS700MS spectrometer using fast atom bombardment (FAB) methods. All chemicals including solvent were of reagent grade and where necessary were purified in the usual manner prior to use. Column chromatography was carried out on silica gel (Wakogel® 60N, 38–100 μm) and thin-layer chromatography (TLC) analysis was performed on silica gel TLC plates (Merck, Silica gel $60F_{254}$). The number average molecular weight (M_n), weight average molecular weight (M_w), molecular weight distribution (M_w/M_n) were estimated by gel-permeation chromatography (GPC, TOSOH HLC-8320GPC system) using chloroform as an eluent with polystyrene standard.

Thermal properties: Thermal stability of the polymer materials was evaluated by thermogravimetric analysis (TGA; TA Instrument) at a heating rate of 10 °C min^{-1}. Phase transition behavior of the polymer material were determined using a differential scanning calorimeter (DSC, SHIMADZU DSC-60 PLUS) at the rate of heating/cooling process of 5.0 °C min^{-1}. The liquid-crystalline phase of the polymer materials was observed by using polarizing optical microscope (POM, Olympus BX53) equipped with a cooling and heating stage (Linkam Scientific Instruments, 10002L). The microphotographs were taken with a DP27 (Olympus) camera, adapted to the microscope.

Photophysical properties: UV-vis absorption spectra were recorded on a JASCO V-500 absorption spectrometer. Samples for the absorption measurements were prepared by dissolving the pristine powder solid sample of **P-2** in a common organic solvent to a concentration of $1.0x10^{-5}$ mol L^{-1}, and the solution was transferred into quartz cuvettes with an optical path length 1.0 cm. The steady-state PL spectra and quantum yields in solution, and pristine powder solid states were acquired using a JASCO FP-6600 fluorescence spectrometer and an absolute PL quantum yield measurement system (Hamamatsu Photonics, C11347-01). A solution-phase sample with a concentration of $1.0x10^{-6}$ mol L^{-1} was used for PL measurements using quartz cuvettes (1.0 cm path length). The excitation wavelength (λ_{ex}) corresponded to the maximum absorption wavelength. Pristine powder solid samples for PL measurements were prepared by re-precipitation from MeOH, and were used without further purification. The excitation or PL measurements were performed using powder sample placed between two quartz glass plates. The PL samples in N phase for photophysical measurements were prepared by quick freezing using liquid N_2 bath after thermal phase transition at 150 °C. For the quantum yields, the N-phase samples were also put a quartz Petri dish, and characterized using a calibrated integrating sphere.

Synthetic pathway for the polymer materials **P-2**–**e** bearing pentafluorinated bistolane-based luminophore used in this study.



Scheme S1. Synthetic pathway for polymer materials **P-2a**–**e** bearing pentafluorinated bistolane-based luminophore.

1-2. Typical procedure for the preparation of 2,3,4,5,6-pentafluoro-1-[2-[4-(2-(4-(6-hydroxyhexyloxy)phenyl)ethyn-1-yl)phenyl]ethyn-1-yl]benzene (4e)

In a 100 mL two-necked round-bottomed flask was placed 1-ethynyl-4-[2-[4-(6-(methoxymethoxy)hexyloxy)phenyl]ethyn-1-yl]benzene (1.7 g, 4.7 mmol), prepared in three steps starting from 4-[6-(methoxymethoxy)hexyloxy]phenylacetylene (**3e**), iodopentafluorobenzene (2.1 g, 7.0 mmol) $Cl_2Pd(PPh_3)_2$ (0.17 g, 0.24 mmol), PPh_3 (0.062 g, 0.24 mmol), CuI (89 mg, 0.47 mmol), and Et_3N (40 mL). The whole was heated at 60 °C for 16 h. After this time, the resulting precipitate was separated by atmospheric filtration and the filtrate was poured into a saturated aqueous NH_4Cl solution. The crude product was then extracted with AcOEt (three times), and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and the solvent was removed using a rotary evaporator. The resulting residue was passed through silica gel using a mixed solvent system (hexane/AcOEt = 10:1), followed by removing the solvent, being obtained the corresponding MOM-protected precursor (1.9 g, 3.6 mmol), which was used for the subsequent deprotection reaction without further purification. The precursor (1.9 g, 3.6 mmol) dissolved in MeOH (54 mL) and THF (54 mL) was cooled by dipping iced water. Into the ice-coold solution was added dropwise concentrated HCl solution (12 N, 9.4 mL, 4.1 mmol) and the whole was continuously stirred at room temperature overnight (22 h). The resultant was poured into saturated aqueous NH_4Cl solution. The crude product was then extracted with AcOEt (three times), and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and the solvent was removed in vacuo. The resulting residue was purified by silica-gel column chromatography using a mixed solvent system (hexane/AcOEt = 3:1) to obtain the desired product **4e** in 68% (1.6 g, 3.2 mmol, white solid). Spectral data for **4b** and **4e** are already reported in Ref. [1].

[1] S. Yamada, T. Tanaka, T. Ichikawa, T. Konno, *ACS Omega* **2019**, *4*, 3922–3932.

1-2-1. 2,3,4,5,6-pentafluoro-1-[2-[4-(2-(4-(2-hydroxyethoxy)phenyl)ethyn-1-yl)phenyl]ethyn-1-yl]benzene (4a)

Yield: 89% (white solid); M.p.: 166–167 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (t, J = 6.0 Hz, 1H), 3.95–4.03 (m, 2H), 4.12 (t, J = 4.0 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.51 (ABq, J = 8.4 Hz, 2H), 7.55 (ABq, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.4, 69.3, 74.6 (q, J = 3.6 Hz), 87.8, 92.0, 101.2 (d, J = 2.9 Hz), 114.7, 115.4, 120.8, 125.0, 131.5, 131.8, 133.2, 159.0, four carbons on the C_6F_5 moiety cannot be found due to the low solubility; ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.43 (dd, J = 21.8, 6.8 Hz, 2F), –152.92 (t, J = 20.3 Hz, 1F), –162.21 (ddd, J = 21.8, 20.3, 6.8 Hz, 2F); IR (KBr): ν 3350, 3068, 2937, 2869, 2205, 1597, 1498, 1242, 1058, 993, 834 cm^{-1}; HRMS (FAB+): *m/z* $[M]^+$ calcd for $C_{24}H_{13}F_5O_2$: 428.0836; found: 428.0842.

1-2-2. 2,3,4,5,6-pentafluoro-1-[2-[4-(2-(4-(4-hydroxybutoxy)phenyl)ethyn-1-yl)phenyl]ethyn-1-yl]benzene (4c)

Yield: 81% (white solid); M.p.: 153–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50–1.59 (m, 1H), 1.72–1.81 (m, 2H), 1.85–1.97 (m, 2H), 3.74 (t, J = 6.0 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.51 (ABq, J = 8.8 Hz, 2H), 7.55 (ABq, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.7, 29.4, 62.6, 67.8, 74.6 (q, J = 5.8 Hz), 87.6, 92.3, 101.2 (d, J = 2.1 Hz), 114.6, 114.8, 120.7, 125.1, 131.4, 131.8, 133.2, 159.3, four carbons on the C_6F_5 moiety cannot be found due to the low solubility; ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.44 (dd, J = 21.8, 6.8 Hz, 2F), –152.96 (t, J = 20.3 Hz, 1F), –162.23 (ddd, J = 21.8, 20.3, 6.8 Hz, 2F); IR (KBr): ν 3418, 3359, 2946, 2862, 2206, 1597, 1525, 1496, 1241, 1177, 1059, 993, 837 cm^{-1}; HRMS (FAB+): *m/z* $[M]^+$ calcd for $C_{26}H_{17}F_5O_2$: 456.1149; found: 456.1156.

1-2-3. 2,3,4,5,6-pentafluoro-1-[2-[4-(2-(4-(5-hydroxypentyloxy)phenyl)ethyn-1-yl)phenyl]ethyn-1-yl]benzene (4d)

Yield: 97% (white solid); M.p.: 149–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.2–1.4 (m, 1H), 1.52–1.61 (m, 2H), 1.62–1.71 (m, 2H), 1.84 (quint., J = 6.4 Hz, 2H), 3.70 (t, J = 6.4 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.51 (ABq, J = 8.8 Hz, 2H), 7.55 (ABq, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.3, 29.0, 32.4, 62.8, 68.0, 74.5 (q, J = 2.9 Hz), 87.5, 92.3, 100.2 (td, J = 17.6, 3.6 Hz), 101.2 (d, J = 3.7 Hz), 114.6, 114.7, 120.7, 125.1, 131.4, 131.8, 133.2, 136.2–139.0 (dm, J = 250.8), 140.0–143.0 (dm, J = 258.2 Hz), 145.6–148.5 (dm, J = 261.8 Hz), 159.4; ^{19}F NMR (100 MHz, $CDCl_3$): δ –136.44 (dd, J = 20.7, 6.8 Hz, 2F), –152.97 (t, J = 20.7 Hz, 1F), –162.23 (ddd, J = 20.7, 20.7, 6.8 Hz, 2F); IR (KBr): ν 3438, 2937, 2859, 2205, 1597, 1525, 1496, 1284, 1242, 1177, 1058, 993, 961, 834 cm^{-1}; HRMS (FAB+): *m/z* $[M]^+$ calcd for $C_{27}H_{19}F_5O_2$: 470.1305; found: 470.1303.

1-3. Typical **procedure for the preparation of 6-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]hexyl methacrylate (5e).**

In a two-necked round-bottomed flask, equipped with a reflux condenser, was placed **4e** (1.6 g, 3.2 mmol) in THF (60 mL). To the solution was added dropwise methacryloyl chloride (0.67 g, 6.4 mmol) and Et_3N

(0.9 mL) at 0 °C, followed by stirring at room temperature. After stirring at that temperature for 24 h, precipitate was separated by atmospheric filtration, followed by evaporation of the solvent. The crude product was extracted with CH_2Cl_2 (three times) and organic layer combined was washed with aqueous saturated $NaHCO_3$ solution (three times) and brine (once). Organic layer collected was dried over anhydrous Na_2SO_4, filtered, and evaporated in vacuo. The residue was purified by silica-gel column chromatography using hexane/CH_2Cl_2 (2/1) as an eluent to obtain the title compound **5e** in 90% yield (1.6 g, 2.9 mmol) as a white solid.

1-3-1. 2-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]ethyl methacrylate (5a)

Yield: 96% (white solid); M.p.: 157–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.96 (s, 3H), 4.25 (dd, J = 5.2, 4.4 Hz, 2H), 4.51 (dd, J = 5.2, 4.4 Hz, 2H), 5.60 (quint., J = 1.6 Hz, 1H), 6.15 (brs, 1H), 6.91 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.51 (ABq, J = 8.4 Hz, 2H), 7.55 (ABq, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 62.9, 66.0, 74.6 (d, J = 2.9 Hz), 87.8, 92.0, 100.2 (td, J = 17.5, 4.4 Hz), 101.2 (d, J = 3.7 Hz), 114.8, 115.4, 120.8, 125.0, 126.1, 131.4, 131.8, 133.2, 135.9, 136.4–139.0 (dm, J = 252.3 Hz), 140.0–142.8 (dm, J = 256.8 Hz), 145.6–148.4 (dm, J = 254.5 Hz), 158.9, 167.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.43 (dd, J = 21.8, 6.8 Hz, 2F), –152.94 (t, J = 20.3 Hz, 1F), –162.22 (ddd, J = 21.8, 20.3, 6.8 Hz, 2F); IR (KBr): ν 3044, 2964, 2880, 2203, 1714, 1638 (C=C), 1596, 1454, 1252, 1171, 1066, 986, 834 cm^{-1}; HRMS (FAB+): *m/z* [M]$^+$ calcd for $C_{28}H_{17}F_5O_3$: 496.1098; found: 496.1105.

1-3-2. 3-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]propyl methacrylate (5b)

Yield: 91% (white solid); M.p.: 147–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (s, 3H), 2.19 (quint., J = 6.4 Hz, 2H), 4.10 (t, J = 6.4 Hz, 2H), 4.36 (t, J = 6.4 Hz, 2H), 5.58 (quint., J = 1.6 Hz, 1H), 6.11 (brs, 1H), 6.88 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.51 (ABq, J = 8.4 Hz, 2H), 7.55 (ABq, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.3, 28.6, 61.4, 64.5, 74.5 (d, J = 3.6 Hz), 87.6, 92.2, 100.2 (td, J =18.3, 3.7 Hz), 101.2 (d, J = 2.9 Hz), 114.5, 115.0, 120.7, 125.0, 125.5, 131.4, 131.8, 133.2, 136.3, 136.4–139.2 (dm, J = 255.2 Hz), 140.1–142.8 (dm, J = 257.5 Hz), 145.6–148.4 (dm, J = 249.4 Hz), 159.1, 167.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.44 (dd, J = 21.8, 6.8 Hz, 2F), –152.95 (t, J = 20.3 Hz, 1F), –162.23 (ddd, J = 21.8, 20.3, 6.8 Hz, 2F); IR (KBr): ν 2977, 2900, 2206, 1709, 1633 (C=C), 1596, 1506, 1469, 1321, 1247, 1167, 1038, 982, 833 cm^{-1}; HRMS (FAB+): *m/z* [M]$^+$ calcd for $C_{29}H_{19}F_5O_3$: 510.1254; found: 510.1254.

1-3-3. 4-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]butyl methacrylate (5c)

Yield: 99% (white solid); M.p.: 126–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.88–1.93 (m, 4H), 1.95 (dd, J = 1.2, 0.8 Hz, 3H), 4.03 (t, J = 5.6 Hz, 2H), 4.24 (t, J = 6.0 Hz, 2H), 5.56 (quint., J = 1.6 Hz, 1H), 6.10–6.12 (m, 1H), 6.88 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.51 (ABq, J = 8.4 Hz, 2H), 7.55 (ABq, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.3, 25.4, 25.9, 64.2, 67.4, 74.5 (d, J = 2.9 Hz), 87.6, 92.2,

100.2 (td, *J* = 17.6, 3.7 Hz), 101.2 (d, *J* = 2.9 Hz), 114.5, 114.8, 120.7, 125.0, 125.3, 131.4, 131.8, 133.2, 136.4, 136.0–139.2 (m), 140.0–142.9 (dm *J* = 250.9 Hz), 145.5–148.4 (dm, *J* = 252.3 Hz), 159.3, 167.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.44 (dd, *J* = 20.7, 6.8 Hz, 2F), –152.96 (t, *J* = 20.3 Hz, 1F), –162.23 (ddd, *J* = 20.7, 20.3, 6.8 Hz, 2F); IR (KBr): ν 1959, 2894, 2206, 1712, 1637 (C=C), 1597, 1503, 1451, 1288, 1184, 1047, 968, 838 cm^{-1}; HRMS (FAB+): *m/z* [M]$^+$ calcd for $C_{30}H_{21}F_5O_3$: 524.1411; found: 524.1404.

1-3-4. 5-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]pentyl methacrylate (5d)

Yield: 92% (white solid); M.p.: 113–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53–1.64 (m, 2H), 1.77 (quint., *J* = 6.8 Hz, 2H), 1.85 (quint., *J* = 7.2 Hz, 2H), 1.95 (t, *J* = 0.8 Hz, 3H), 3.99 (t, *J* = 6.0 Hz, 2H), 4.19 (t, *J* = 6.8 Hz, 2H), 5.56 (quint., *J* = 1.6 Hz, 1H), 6.09–6.12 (m, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.51 (ABq, *J* = 8.4 Hz, 2H), 7.55 (ABq, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.3, 22.6, 28.4, 28.8, 64.4, 67.7, 74.5 (d, *J* = 2.9 Hz), 87.5, 92.3, 100.2 (td, *J* = 18.3, 2.9 Hz), 101.2 (d, *J* = 3.0 Hz), 114.5, 114.7, 120.7, 125.1, 125.2, 131.4, 131.7, 133.1, 136.4, 136.0–139.1 (m), 140.0–142.9 (dm, *J* = 256.8 Hz), 145.5–148.6 (dm, *J* = 254.4 Hz), 159.4, 167.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.44 (dd, *J* = 21.8, 6.8 Hz, 2F), –152.97 (t, *J* = 20.3 Hz, 1F), –162.23 (ddd, *J* = 21.8, 20.3, 6.8 Hz, 2F); IR (KBr): ν 3041, 2942, 2867, 2206, 1709, 1633 (C=C), 1597, 1525, 1498, 1247, 1172, 989, 959, 830 cm^{-1}; HRMS (FAB+): *m/z* [M]$^+$ calcd for $C_{31}H_{23}F_5O_3$: 538.1567; found: 538.1561.

1-3-5. 6-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]hexyl methacrylate (5e)

Yield: 90% (white solid); M.p.: 108–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42–1.60 (m, 4H), 1.72 (quint., *J* = 6.8 Hz, 2H), 1.82 (quint., *J* = 6.4 Hz, 2H), 1.95 (dd, *J* = 1.2, 1.2 Hz, 3H), 3.98 (t, *J* = 6.4 Hz, 2H), 4.16 (t, *J* = 6.4 Hz, 2H), 5.55 (quint., *J* = 2.0 Hz, 1H), 6.09–6.11 (m, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.51 (ABq, *J* = 8.4 Hz, 2H), 7.54 (ABq, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.3, 25.7, 25.8, 28.5, 29.1, 64.4, 67.8, 74.5 (d, *J* = 3.6 Hz), 87.5, 92.3, 100.2 (td, *J* = 16.9, 3.7 Hz), 101.2 (d, *J* = 2.9 Hz), 114.5, 114.7, 120.7, 125.1, 125.2, 131.4, 131.8, 133.1, 136.5, 136.3–138.9 (dm, *J* = 241.4 Hz), 140.0–142.8 (dm, *J* = 251.6 Hz), 147.5–148.5 (dm, *J* = 253.8 Hz), 159.4, 167.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.45 (dd, *J* = 20.3, 6.8 Hz, 2F), –152.98 (t, *J* = 20.3 Hz, 1F), –162.24 (ddd, *J* = 20.3, 20.3, 6.8 Hz, 2F); IR (KBr): ν 3034, 2949, 2897, 2208, 1704, 1634 (C=C), 1598, 1492, 1255, 1172, 1107, 1014, 965, 847 cm^{-1}; HRMS (FAB+): *m/z* [M]$^+$ calcd for $C_{32}H_{25}F_5O_3$: 552.1724; found: 552.1729.

1-4. Typical procedure for the preparation of Poly[6-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]hexyl methacrylate] (P-2e) (Condition A).

In a two-necked round-bottomed flask was added freshly prepared monomer **5e** (0.28 g, 0.5 mmol) and NMP (5.0 mL). To the solution was added *N,N'*-azobis(isobutyronitrile) (AIBN, 2 mg, 0.012 mmol) in one portion. The whole was degassed with a freeze-pump-thaw technique, followed by raising temperature to 65 °C (bath temp.). After vigorous stirring at that temperature for 24 h, followed by addition of excess

amount of MeOH, the precipitate formed was separated by vacuum filtration. The filter-cake obtained was washed with MeOH twice and the title polymer **P-2e** was finally obtained in 75% conversion (0.21 g) as a white solid.

1-4-1. Poly[2-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]ethyl methacrylate] (P-2a)

Conversion: 48% (Brown solid); M_n = 4820; M_w = 7230; M_w/M_n = 1.50; T_g: 85 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8–1.5 (m, 3H), 1.8–2.5 (m, 2H), 3.8–4.6 (m, 4H), 6.6–7.0 (m, 2H), 7.2–7.6 (m, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.3 to –136.9 (m, 2F), –152.8 to –153.1 (m, 1F), –162.0 to –162.7 (m, 2F); IR (KBr): ν 3043, 2938, 2212, 1730, 1590, 1525, 1505, 1244, 1178, 1056, 989, 834 cm^{-1}.

1-4-2. Poly[3-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]propyl methacrylate] (P-2b)

Conversion: 81% (White solid); M_n = 8330; M_w = 1320; M_w/M_n = 1.59; T_g: 79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.7–1.2 (m, 3H), 1.7–2.2 (m, 4H), 3.8–4.4 (m, 4H), 6.6–6.9 (m, 2H), 7.2–7.6 (m, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.3 to –136.8 (m, 2F), –152.5 to –153.1 (m, 1F), –162.0 to –162.5 (m, 2F); IR (KBr): ν 3043, 2955, 2897, 2212, 1730, 1598, 1525, 1499, 1248, 1174, 1049, 909, 837 cm^{-1}.

1-4-3. Poly[4-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]butyl methacrylate] (P-2c)

Conversion: 70% (White solid); M_n = 9490; M_w = 16400; M_w/M_n = 1.73; T_g: 73 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8–1.2 (m, 3H), 1.6–2.1 (m, 6H), 3.8–4.2 (m, 4H), 6.6–6.9 (m, 2H), 7.3–7.6 (m, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.3 to –136.9 (m, 2F), –152.8 to –153.1 (m, 1F), –162.0 to –162.6 (m, 2F); IR (KBr): ν 3039, 2952, 2873, 2212, 1727, 1598, 1525, 1498, 1248, 1174, 1140, 991, 833 cm^{-1}.

1-4-4. Poly[5-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]pentyl methacrylate] (P-2d)

Conversion: 89% (Brown solid); M_n = 9570; M_w = 16900; M_w/M_n = 1.77; T_g: 62 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8–1.2 (m, 3H), 1.6–2.2 (m, 8H), 3.8–4.2 (m, 4H), 6.6–6.9 (m, 2H), 7.3–7.6 (m, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.3 to –136.8 (m, 2F), –152.7 to –153.1 (m, 1F), –162.1 to –162.5 (m, 2F); IR (KBr): ν 3042, 2947, 2869, 2211, 1728, 1598, 1525, 1498, 1248, 1110, 989, 965, 834 cm^{-1}.

1-4-5. Poly[6-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]hexyl methacrylate] (P-2e)

Conversion: 75% (Yellow solid); M_n = 12500; M_w = 18900; M_w/M_n = 1.53; T_g: 47 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8–1.2 (m, 3H), 1.3–2.2 (m, 10H), 3.7–4.1 (m, 4H), 6.7–6.9 (m, 2H), 7.3–7.6 (m, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.4 to –136.8 (m, 2F), –152.8 to –153.1 (m, 1F), –162.1 to –162.5 (m, 2F); IR (KBr): ν 2939, 2865, 2211, 1727, 1598, 1525, 1499, 1247, 1174, 1140, 989, 965, 831 cm^{-1}.

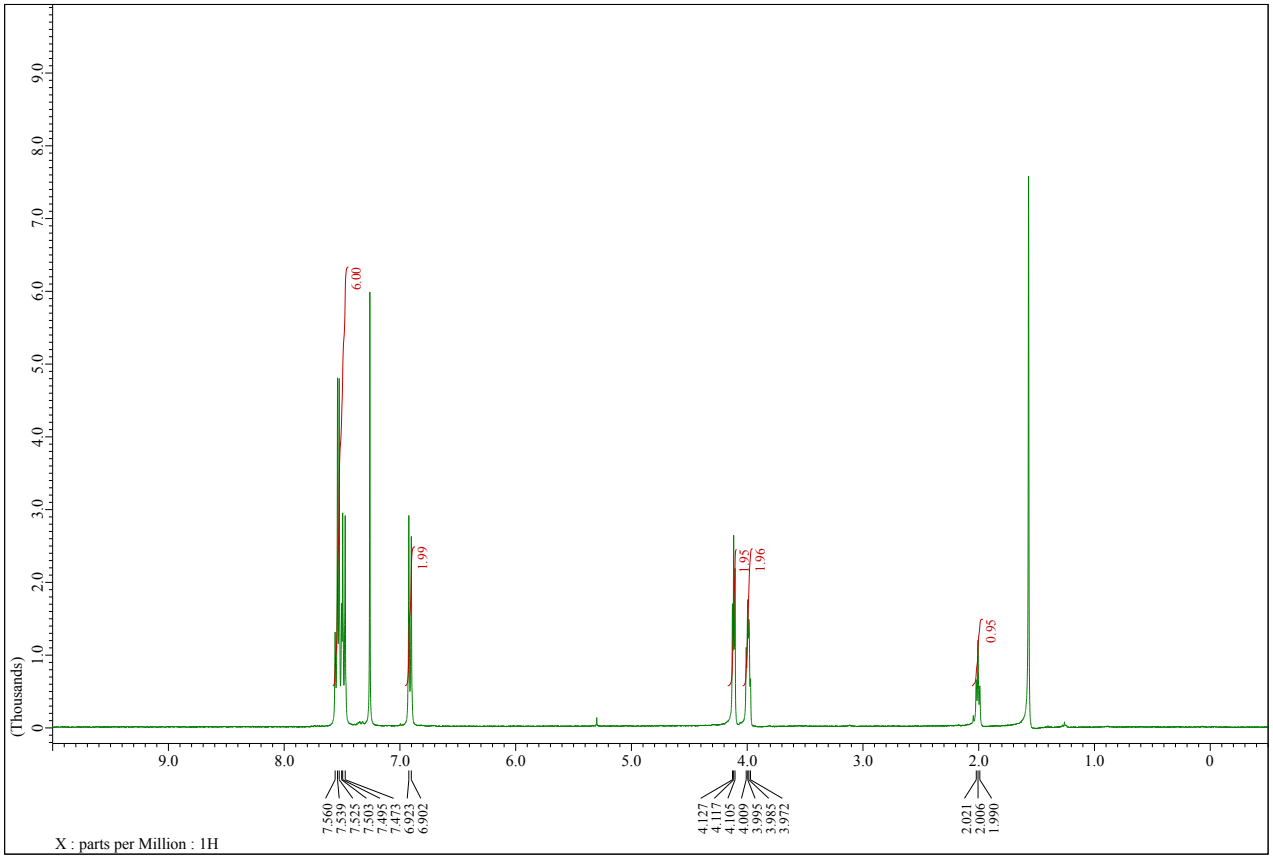
1-5. Typical procedure for the preparation of Poly[6-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]hexyl methacrylate] (P_B-2e) (Condition B).
In a two-necked round-bottomed flask was added freshly prepared monomer **5e** (0.11 g, 0.2 mmol) and NMP (3.6 mL). To the solution was added AIBN (0.8 mg, 4.8 μmol) in one portion. The whole was degassed with a freeze-pump-thaw technique, followed by raising temperature to 50 °C (bath temp.). After vigorous stirring at that temperature for 24 h, followed by addition of excess amount of MeOH, the precipitate formed was separated by vacuum filtration. The filter-cake obtained was washed with MeOH twice and the title polymer **P-2e** was finally obtained in 77% conversion (0.083 g) as a white solid.

1-6. Typical procedure for the preparation of Poly[6-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]hexyl methacrylate] (P_C-2e) (Condition C).
In a two-necked round-bottomed flask was added freshly prepared monomer **5e** (0.17 g, 0.3 mmol) and NMP (5.0 mL). To the solution was added bezoyl peroxide (BPO, 18 mg, 0.075 mmol) in one portion. The whole was degassed with a freeze-pump-thaw technique, followed by raising temperature to 78 °C (bath temp.). After vigorous stirring at that temperature for 24 h, followed by addition of excess amount of MeOH, the precipitate formed was separated by vacuum filtration. The filter-cake obtained was washed with MeOH twice and the title polymer **P-2e** was finally obtained in 80% conversion (0.13 g) as a white solid.

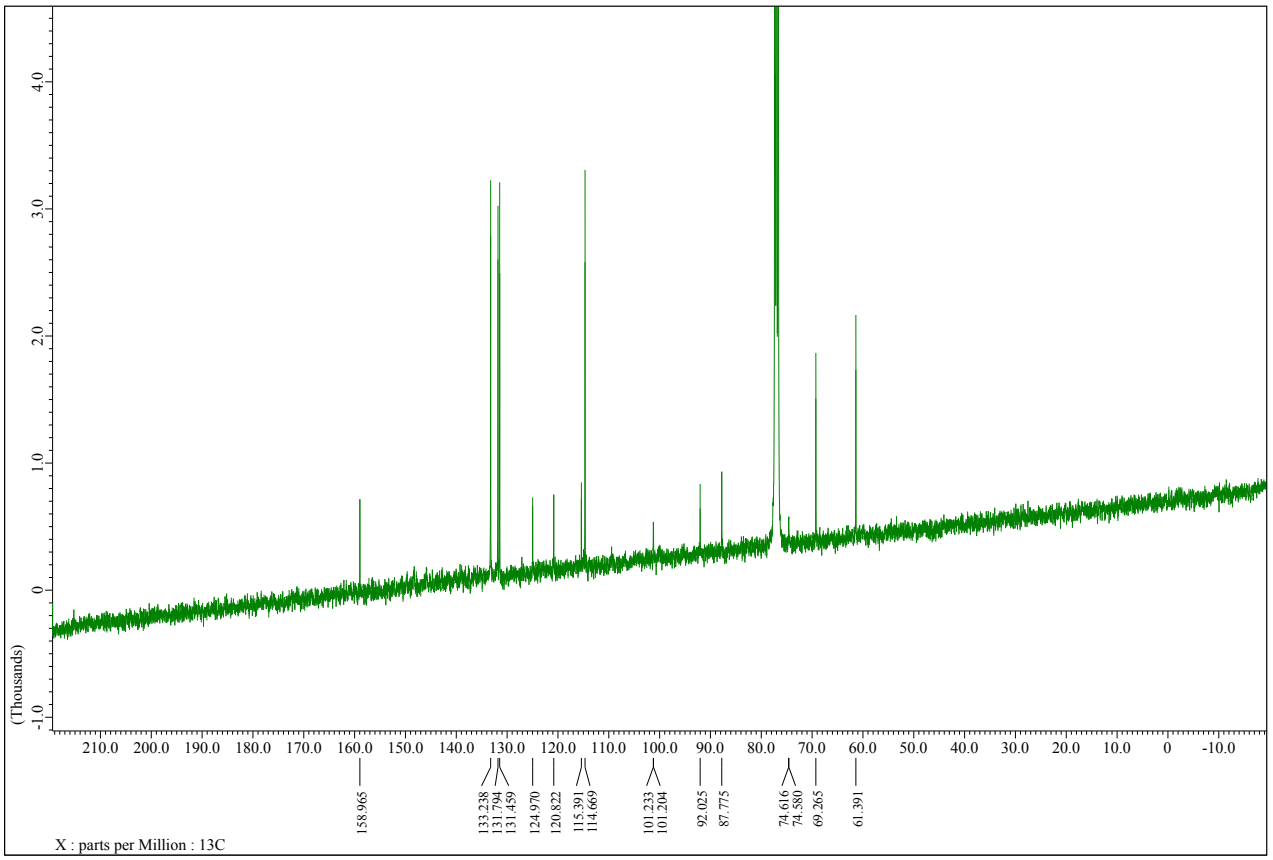
1-7. Typical procedure for the preparation of Poly[6-[4-[4-[(2,3,4,5,6-pentafluorophenyl)ethynyl]phenylethynyl]phenoxy]hexyl methacrylate] (P_D-2e) (Condition D).
In a two-necked round-bottomed flask, equipped with a reflux condenser, was added freshly prepared monomer **5e** (0.83 g, 1.5 mmol) and NMP (20 mL). To the solution was added AIBN (12 mg, 0.075 mmol) in one portion. The whole was degassed with a freeze-pump-thaw technique, followed by raising temperature to 60 °C (bath temp.). After vigorous stirring at that temperature for 24 h, followed by addition of excess amount of MeOH, the precipitate formed was separated by vacuum filtration. The filter-cake obtained was washed with MeOH twice and the title polymer **P-2e** was finally obtained in 82% conversion (0.68 g) as a white solid.

2. NMR spectra

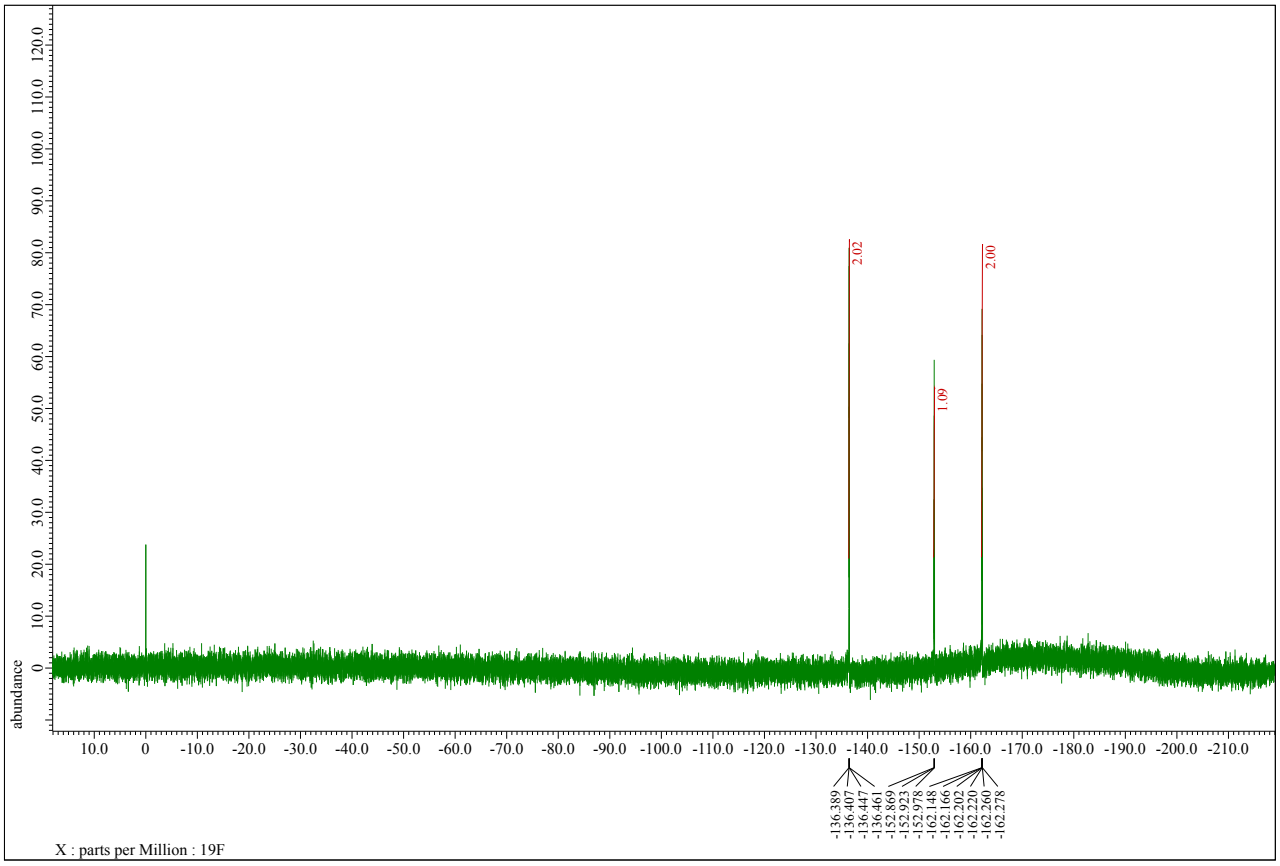
^{1}H NMR spectrum for **4a** (400 MHz, $CDCl_3$)



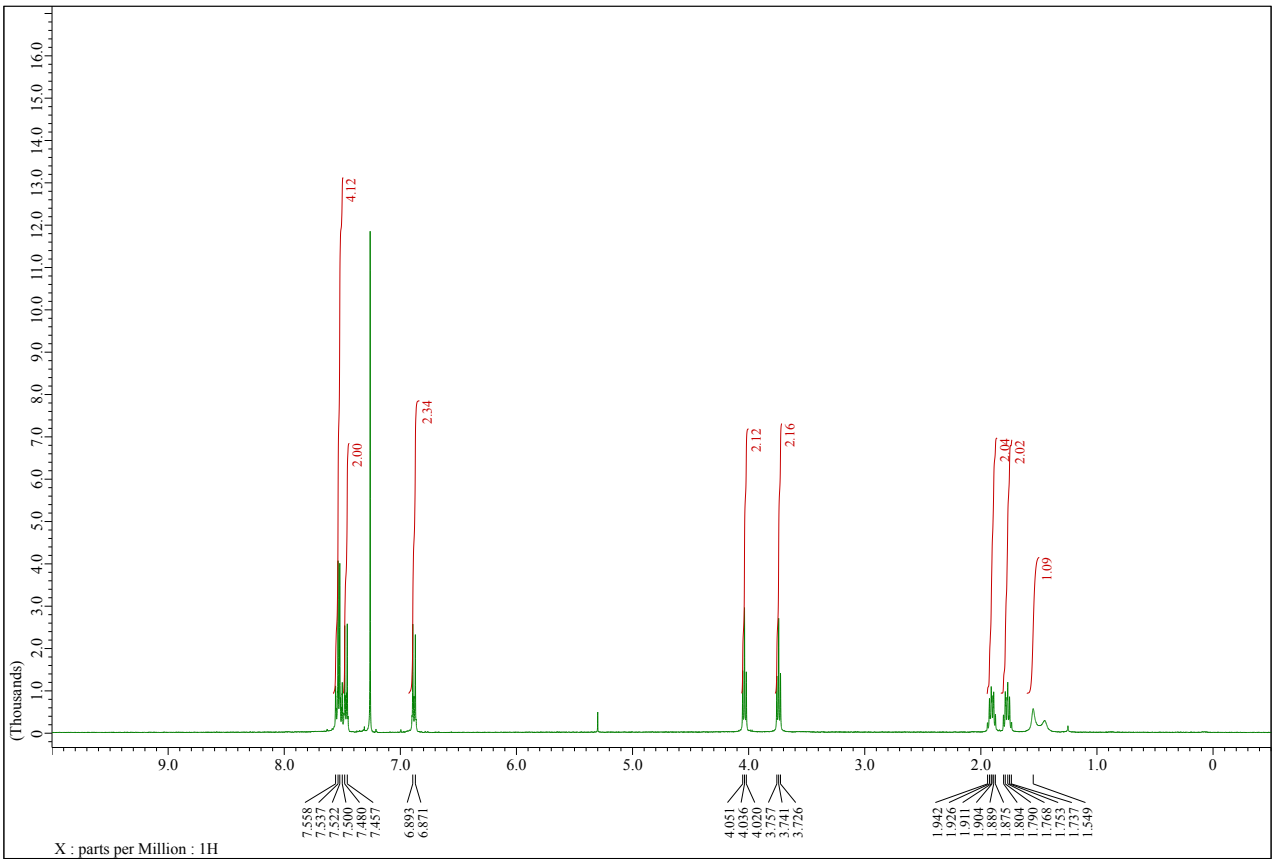
^{13}C NMR spectrum for **4a** (100 MHz, $CDCl_3$)



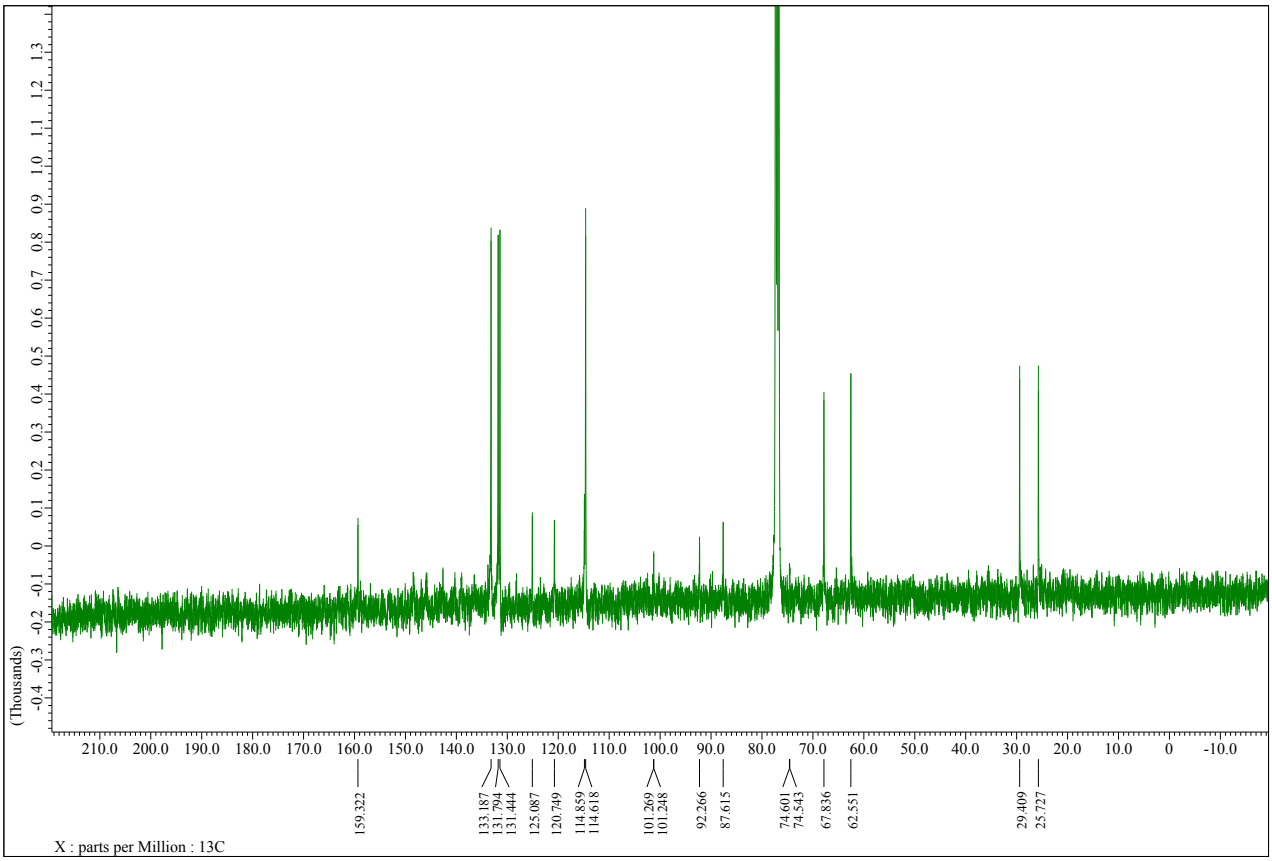
^{19}F NMR spectrum for **4a** (376 MHz, $CDCl_3$)



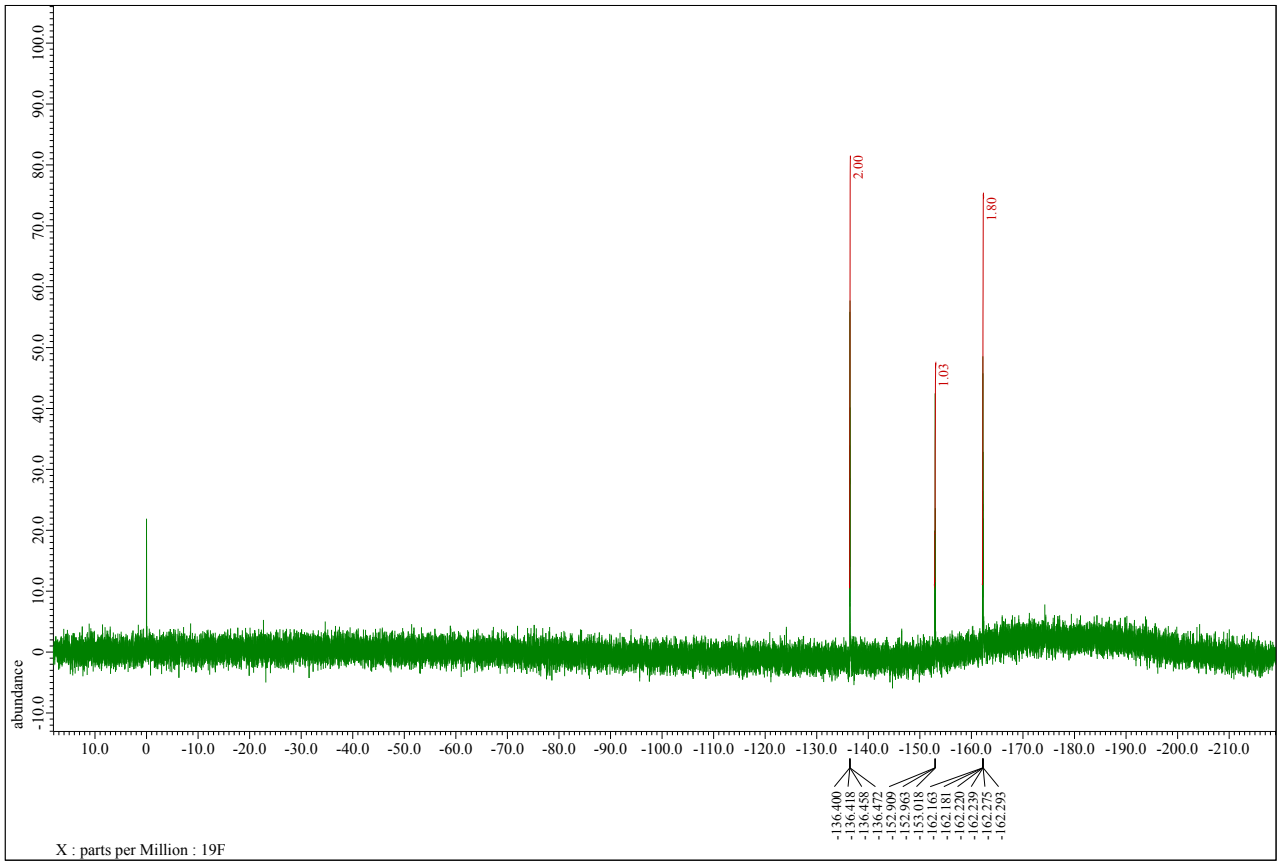
^{1}H NMR spectrum for **4c** (400 MHz, $CDCl_3$)



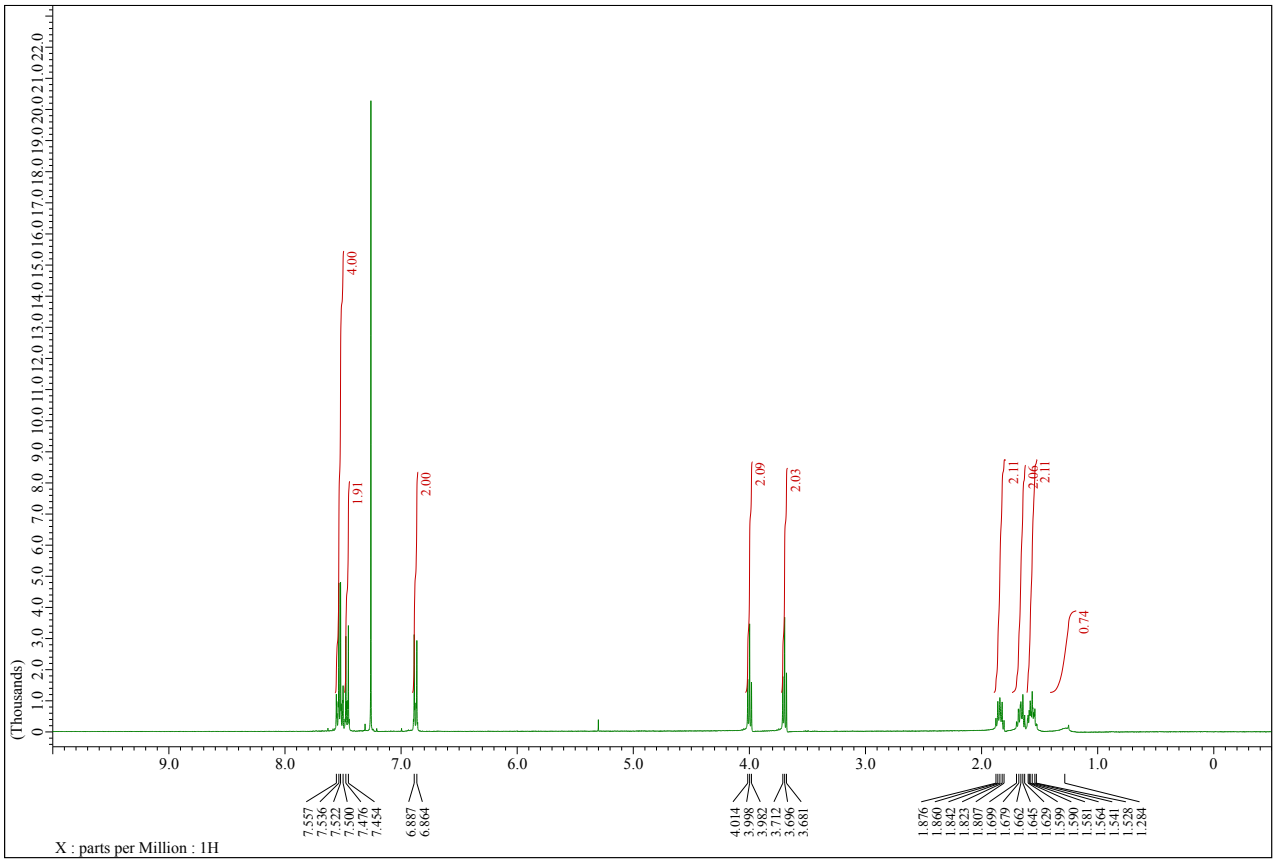
^{13}C NMR spectrum for **4c** (100 MHz, $CDCl_3$)



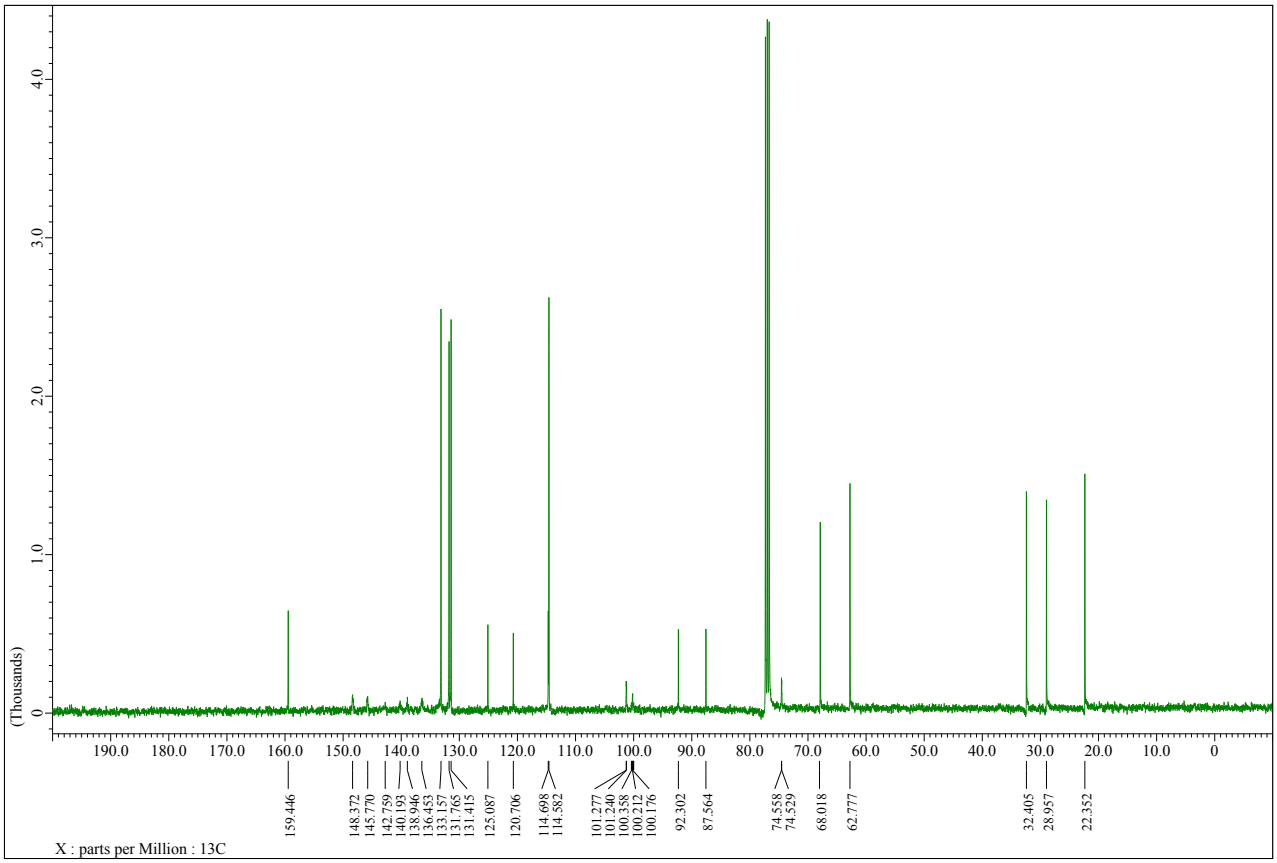
^{19}F NMR spectrum for **4c** (376 MHz, $CDCl_3$)



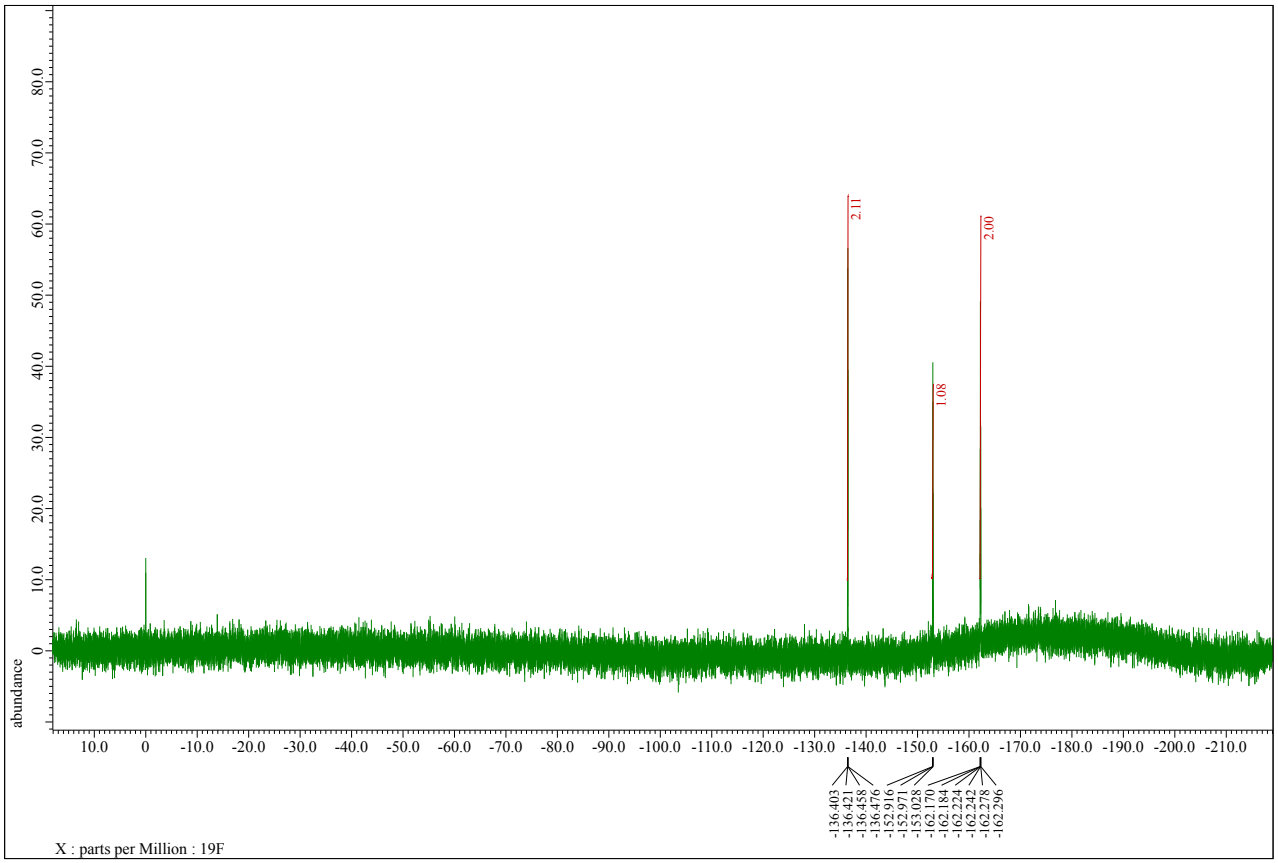
^{1}H NMR spectrum for **4d** (400 MHz, $CDCl_3$)



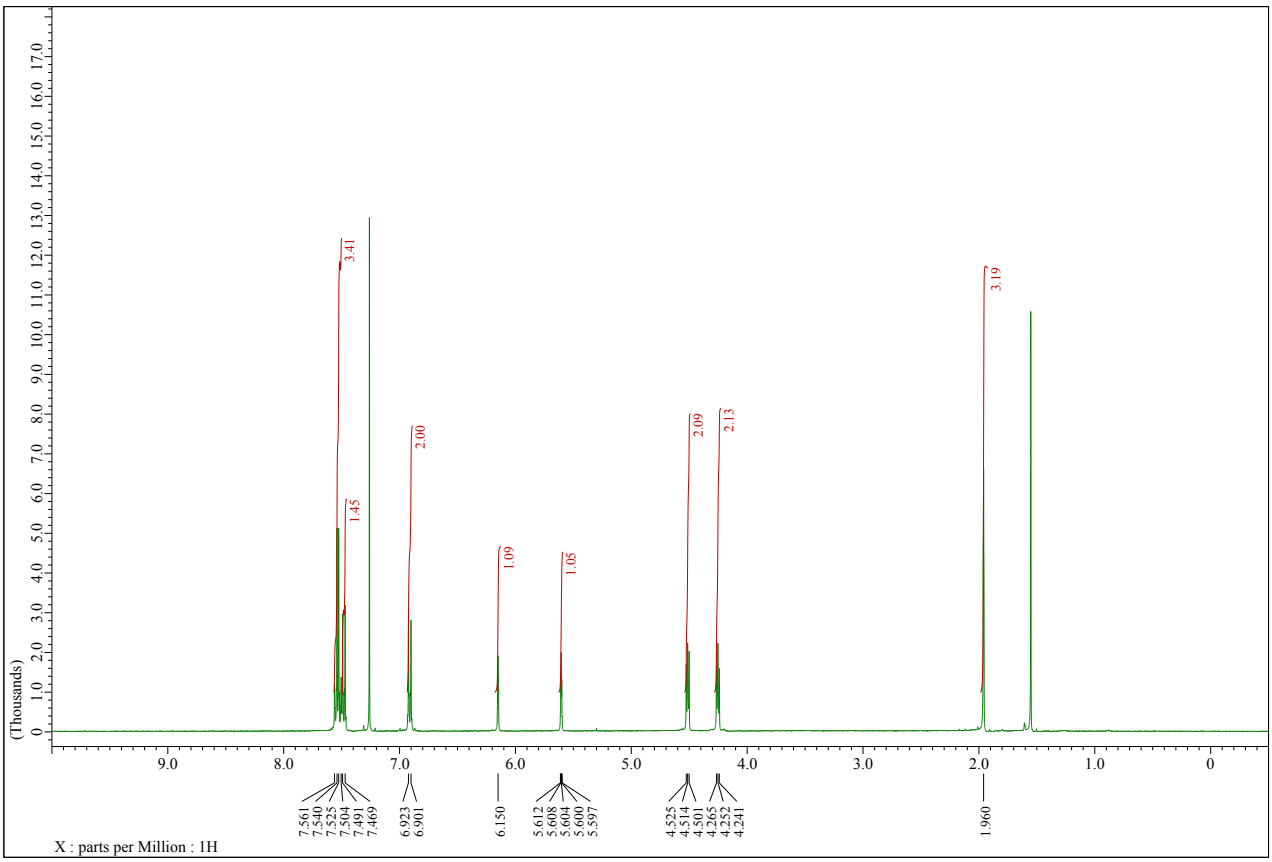
^{13}C NMR spectrum for **4d** (100 MHz, $CDCl_3$)



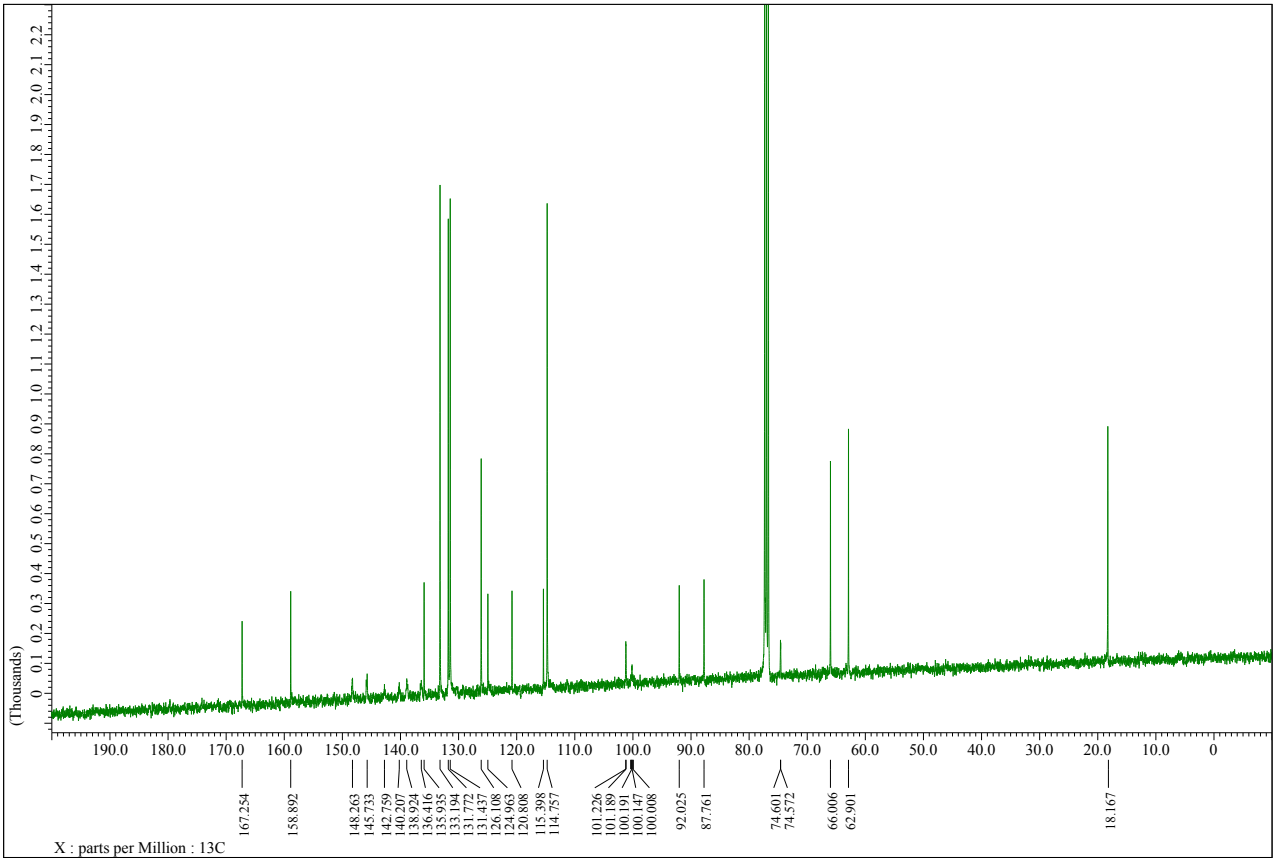
^{19}F NMR spectrum for **4d** (376 MHz, $CDCl_3$)



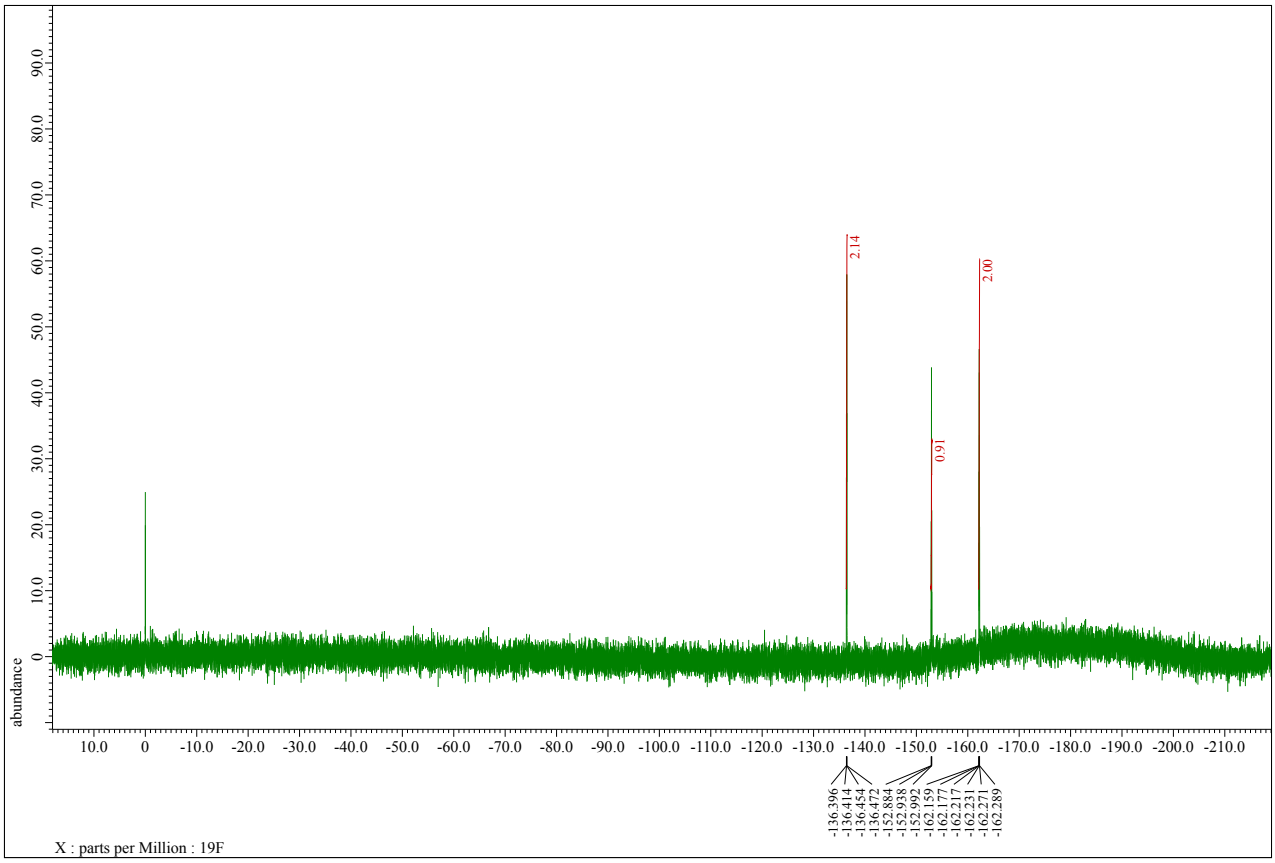
^{1}H NMR spectrum for **5a** (400 MHz, $CDCl_3$)



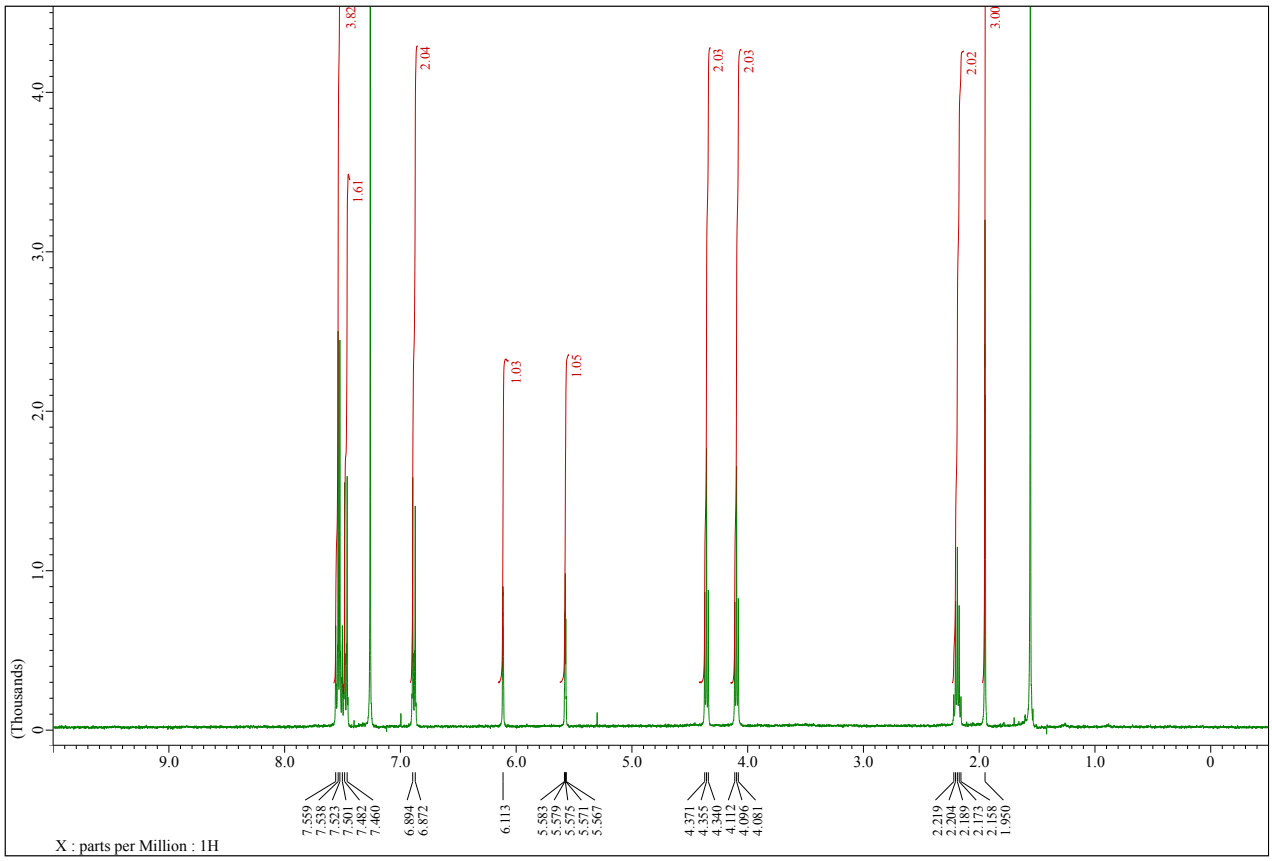
^{13}C NMR spectrum for **5a** (100 MHz, $CDCl_3$)



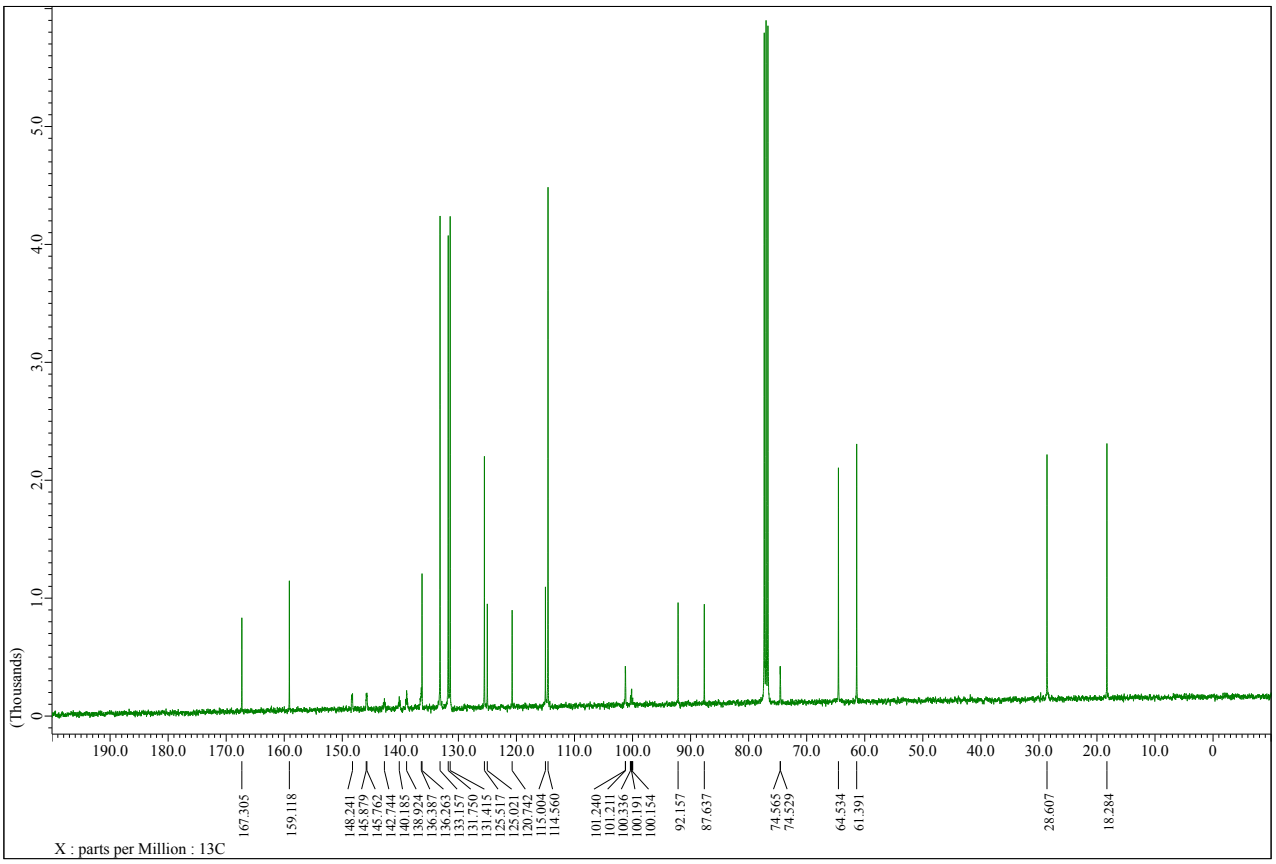
^{19}F NMR spectrum for **5a** (376 MHz, $CDCl_3$)



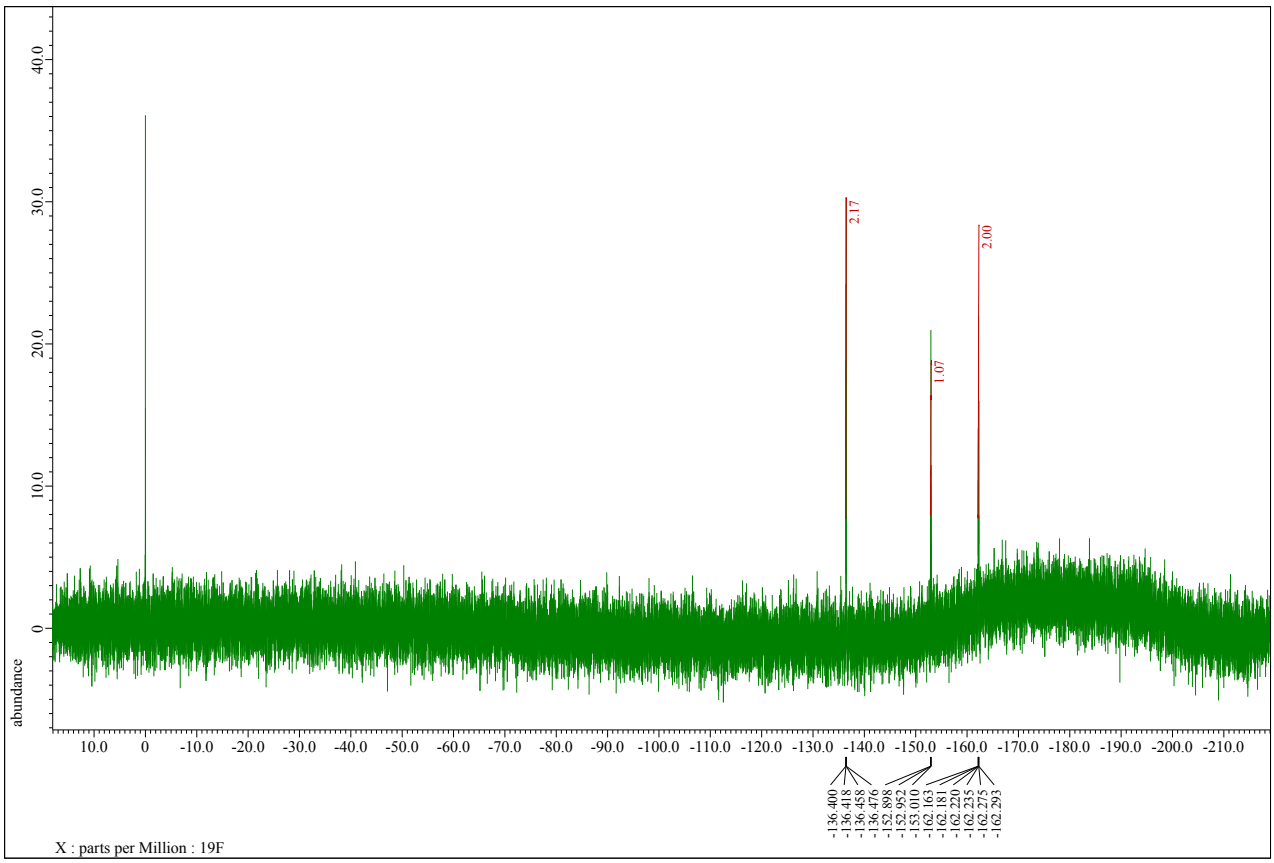
^{1}H NMR spectrum for **5b** (400 MHz, $CDCl_3$)



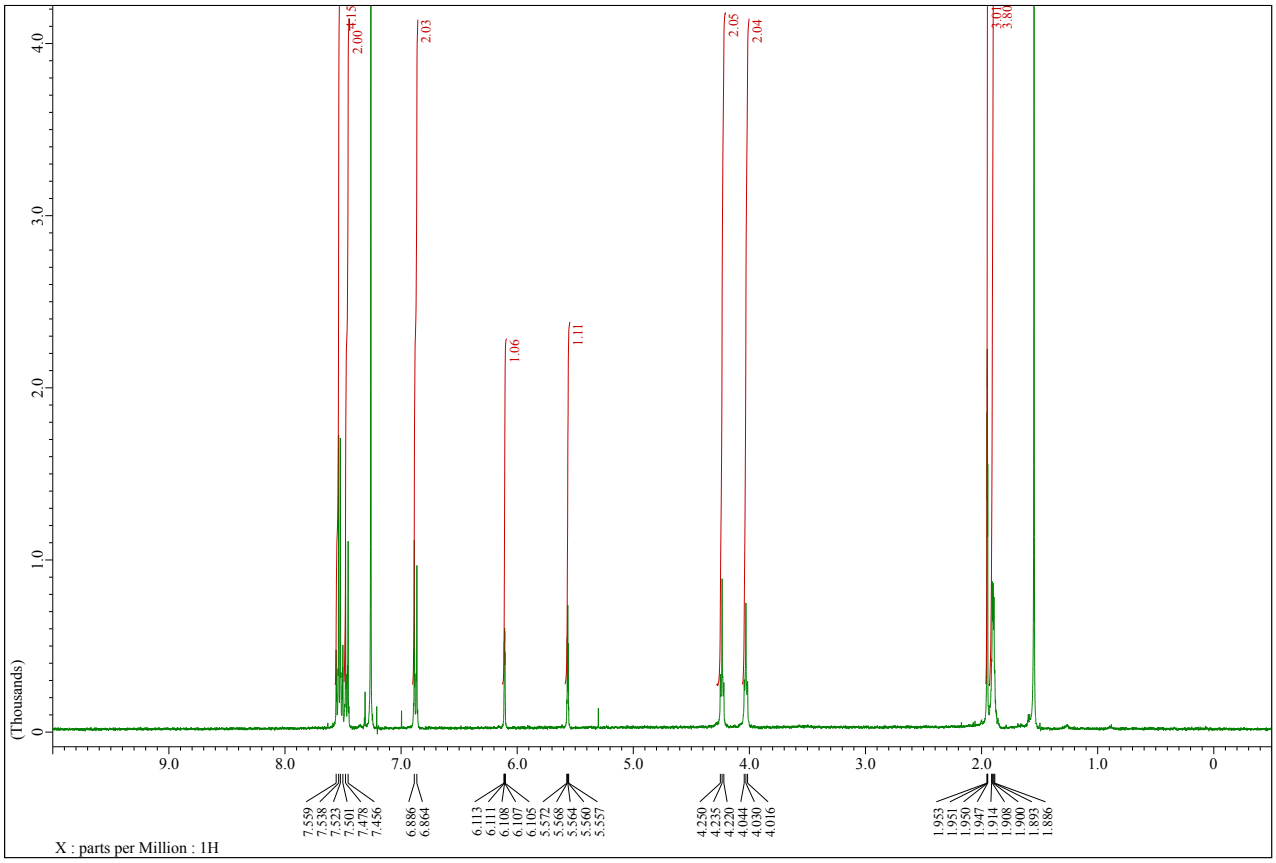
^{13}C NMR spectrum for **5b** (100 MHz, $CDCl_3$)



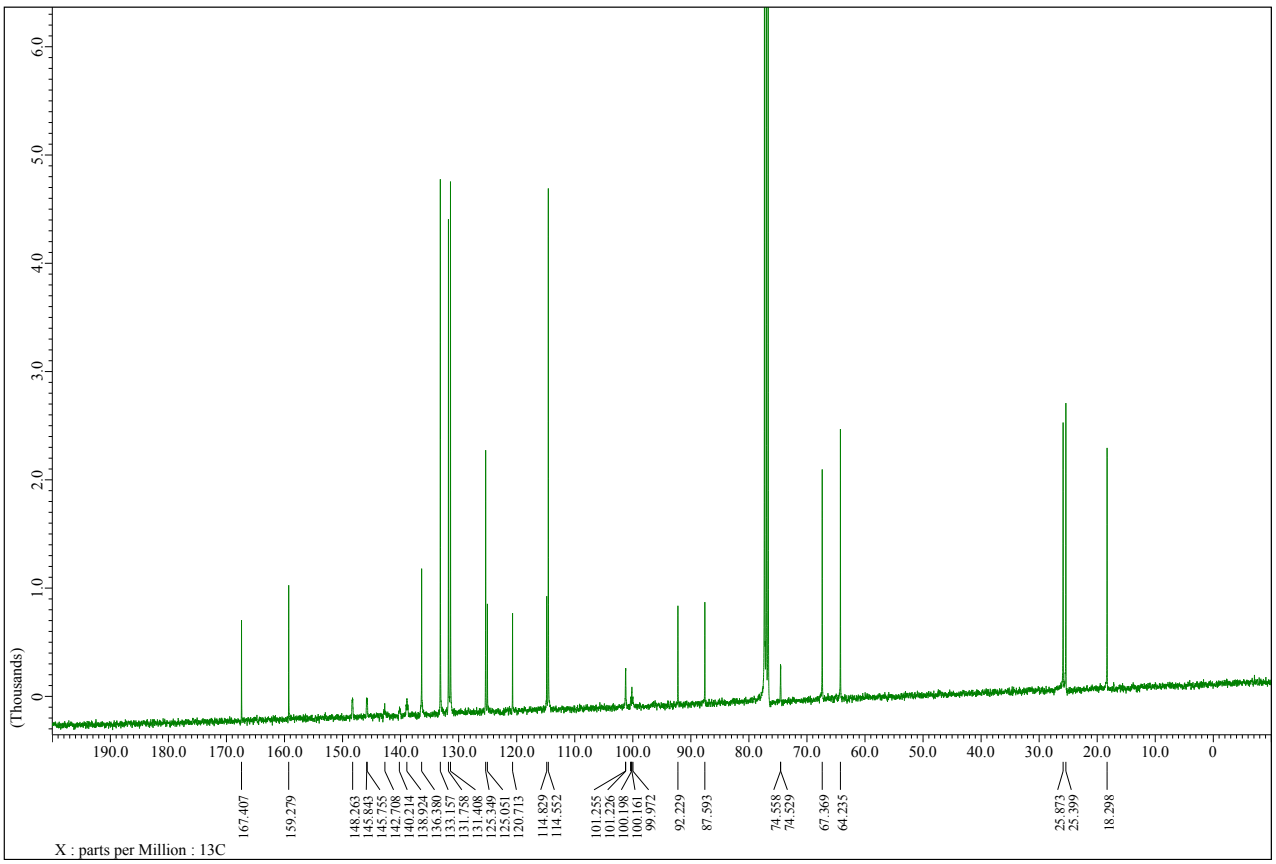
^{19}F NMR spectrum for **5b** (376 MHz, $CDCl_3$)



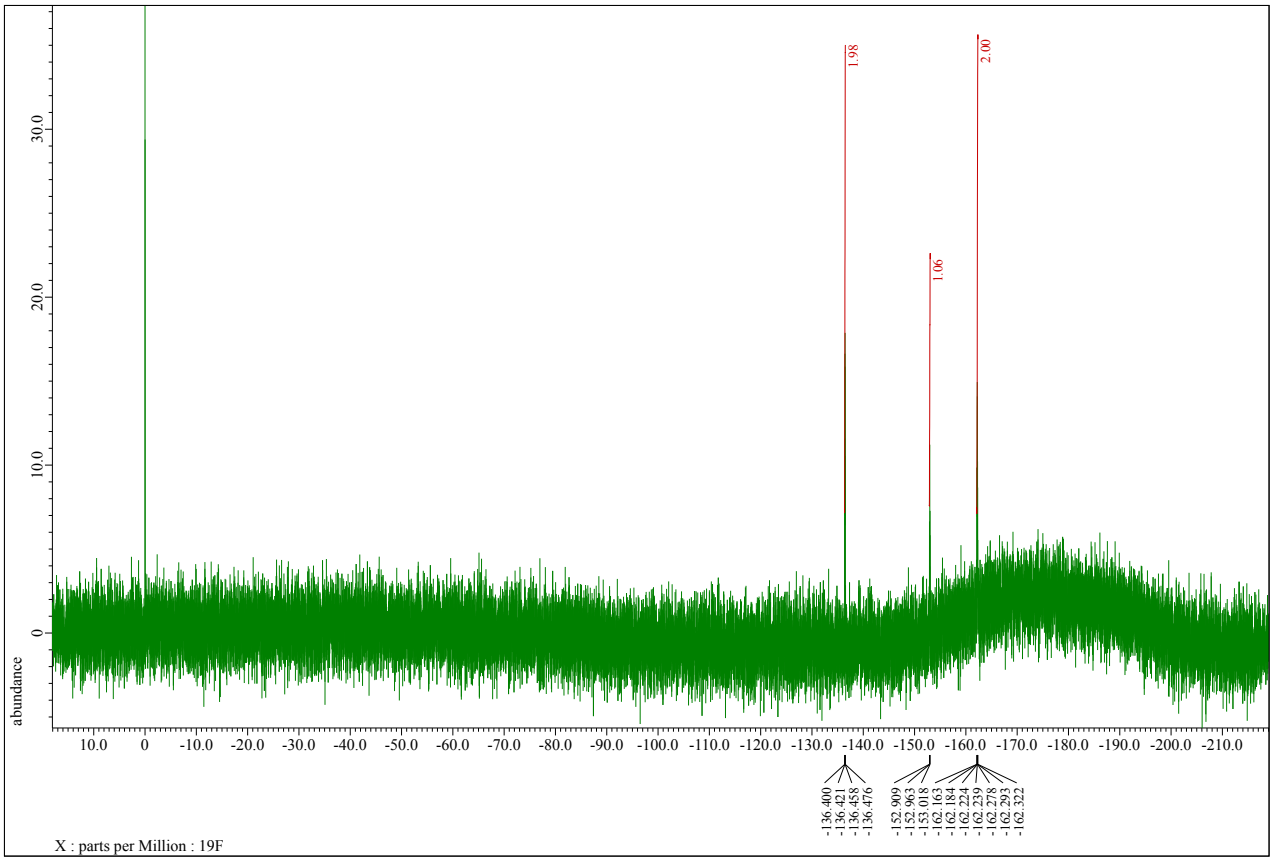
^{1}H NMR spectrum for **5c** (400 MHz, $CDCl_3$)



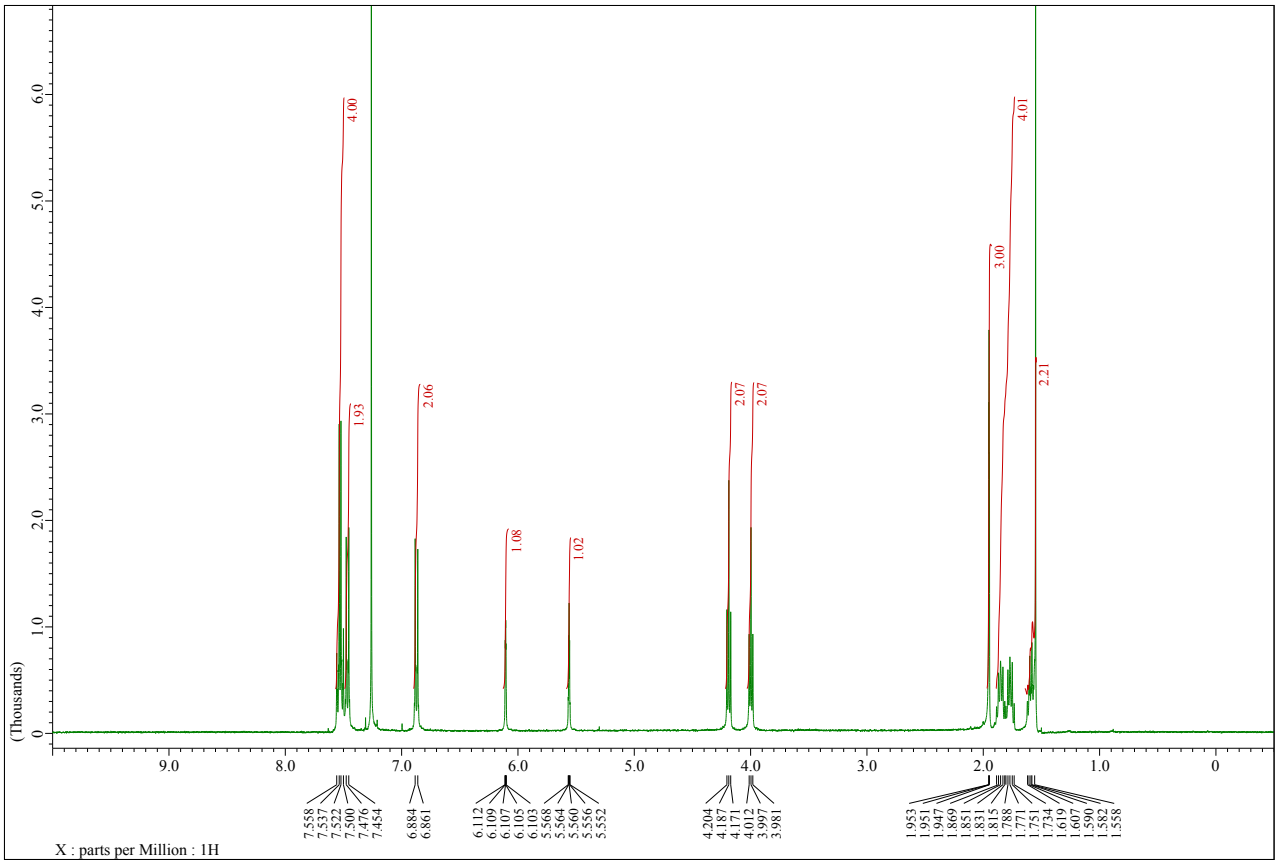
^{13}C NMR spectrum for **5c** (100 MHz, $CDCl_3$)



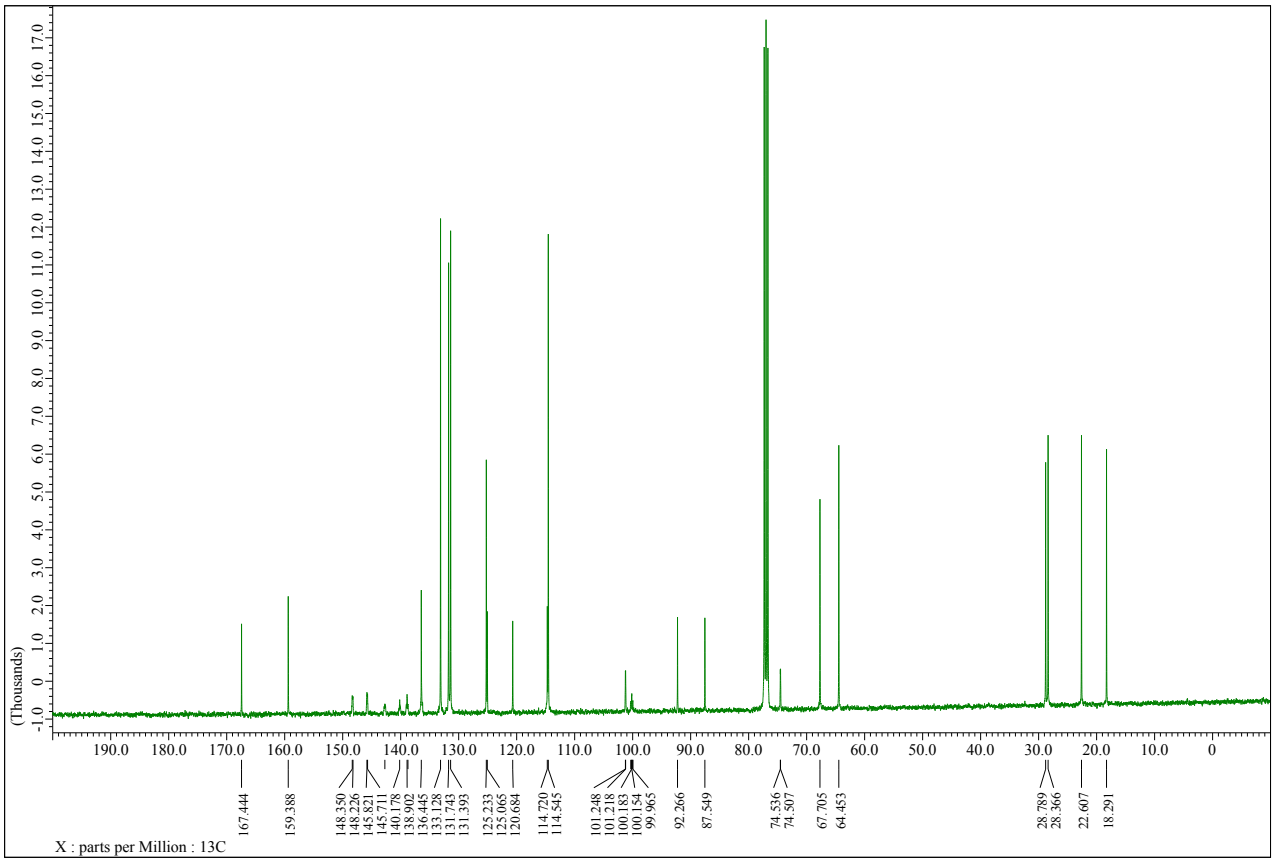
^{19}F NMR spectrum for **5c** (376 MHz, $CDCl_3$)



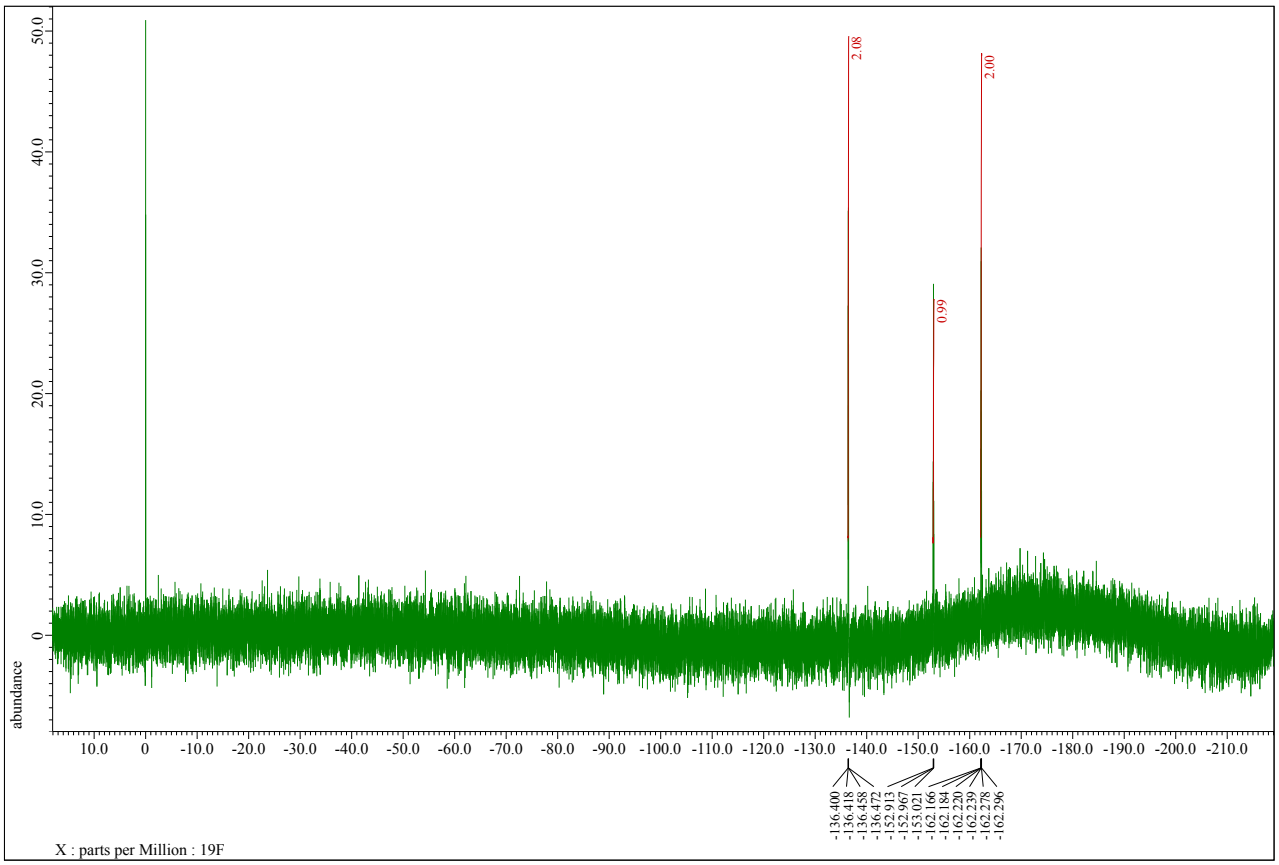
^{1}H NMR spectrum for **5d** (400 MHz, $CDCl_3$)



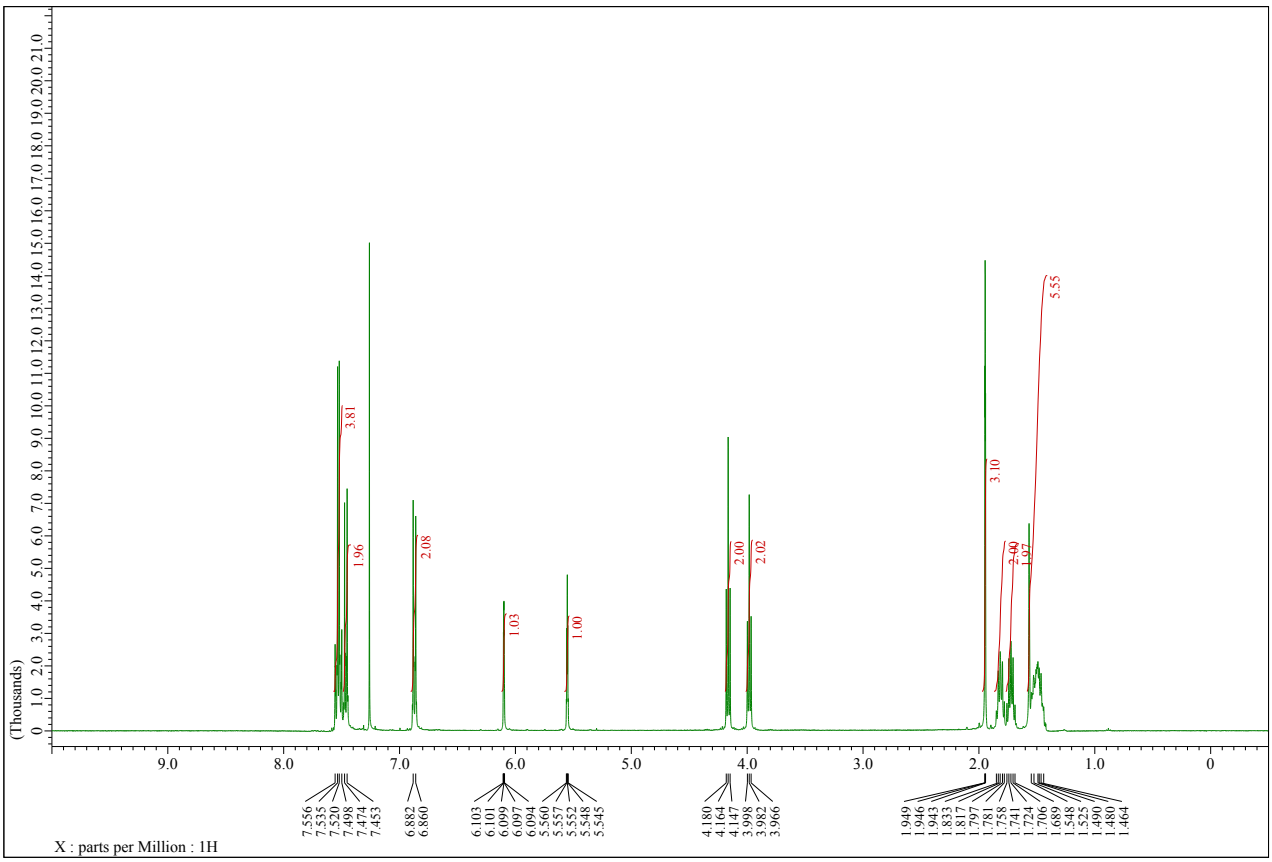
^{13}C NMR spectrum for **5d** (100 MHz, $CDCl_3$)



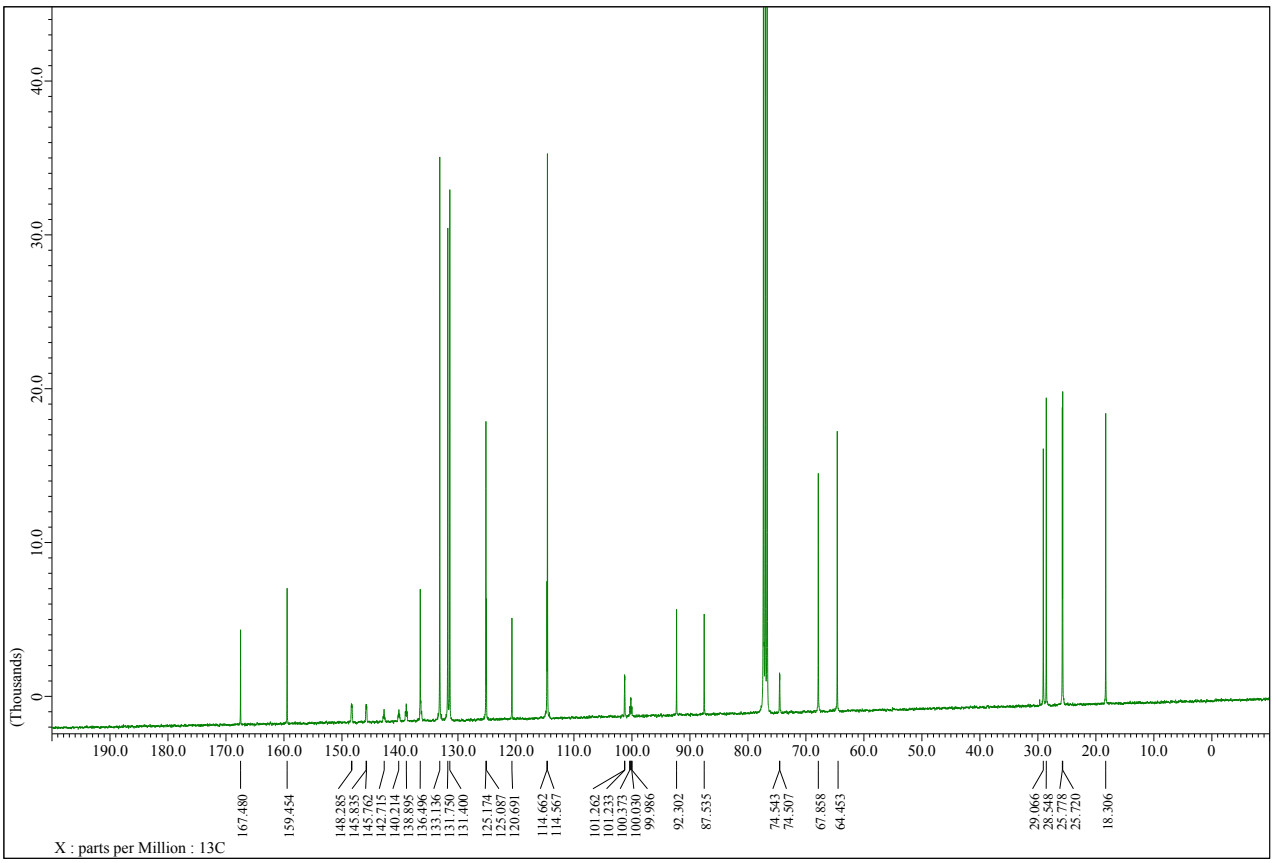
^{19}F NMR spectrum for **5d** (376 MHz, $CDCl_3$)



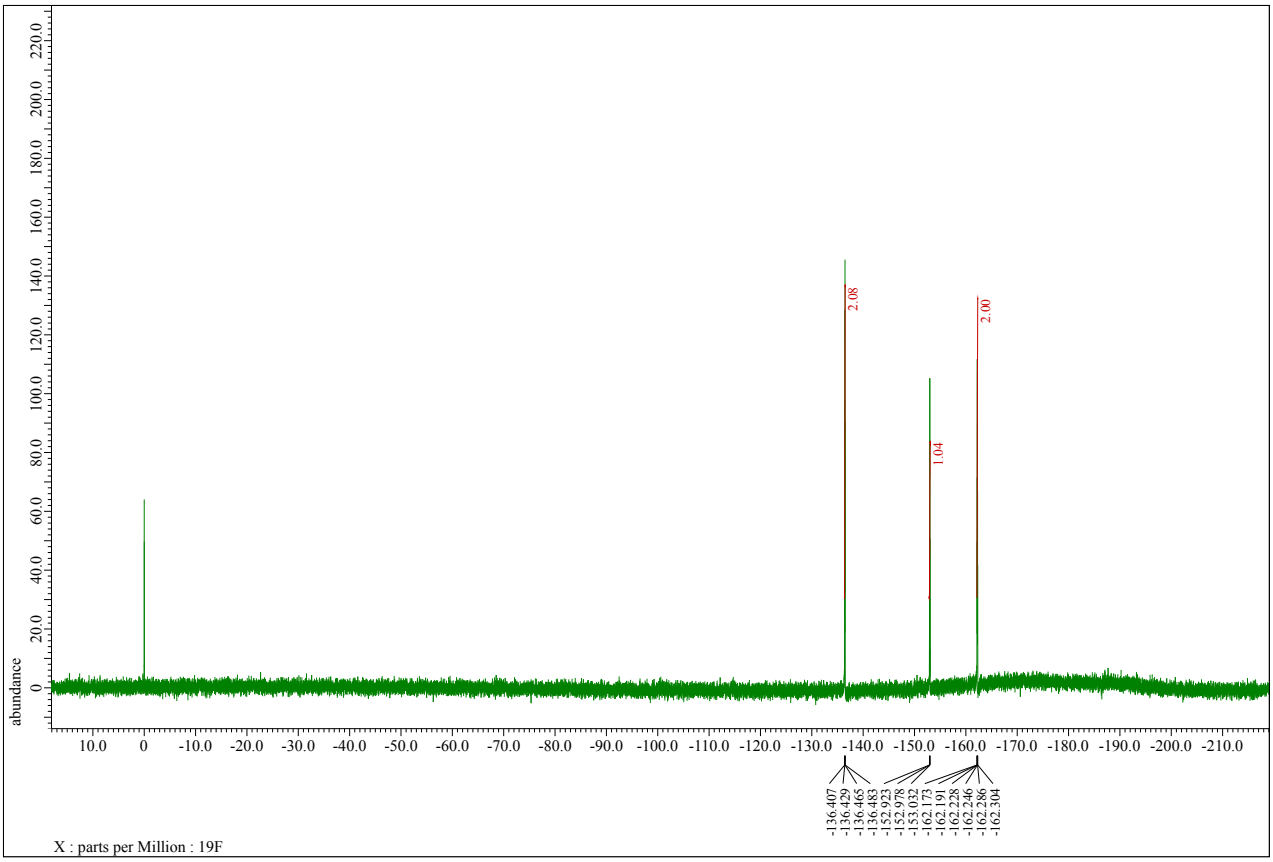
^{1}H NMR spectrum for **5e** (400 MHz, $CDCl_3$)



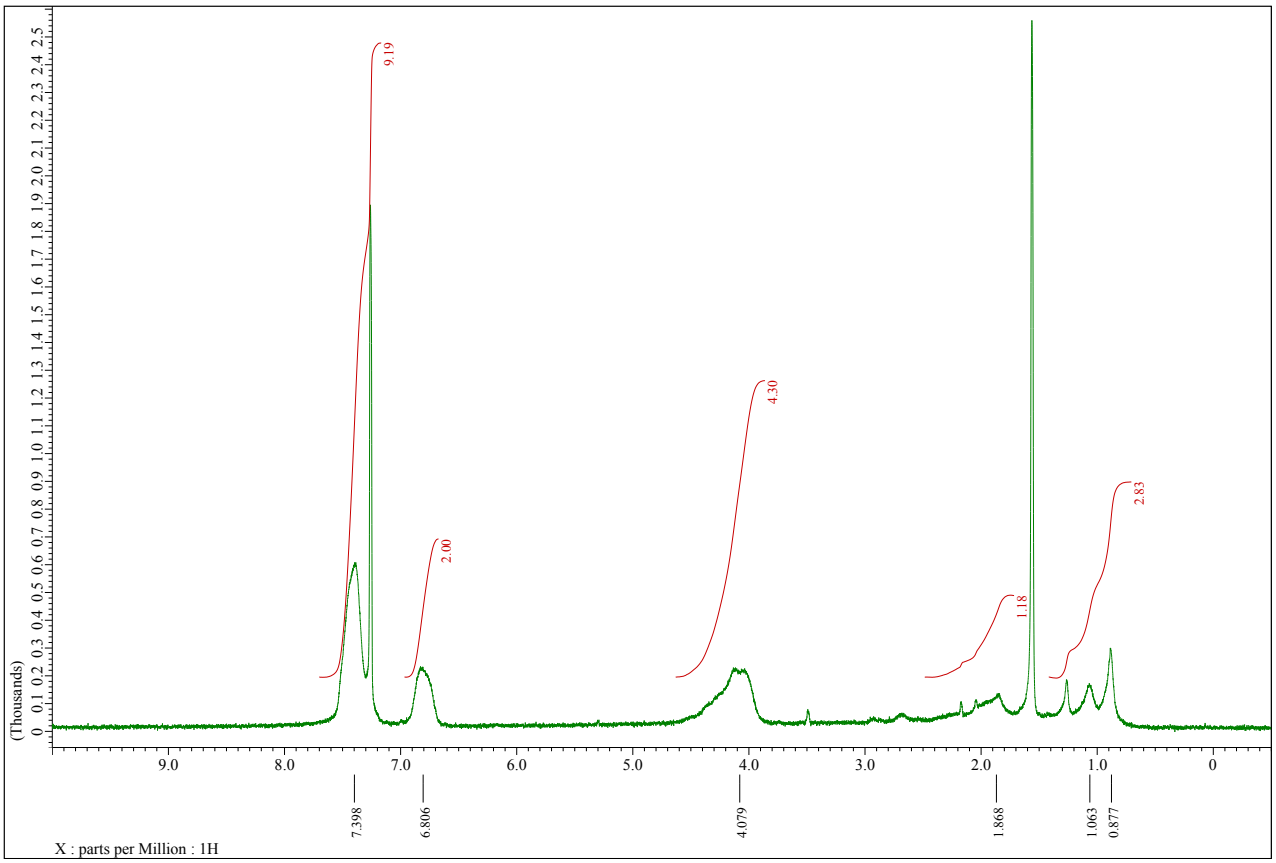
^{13}C NMR spectrum for **5e** (100 MHz, $CDCl_3$)



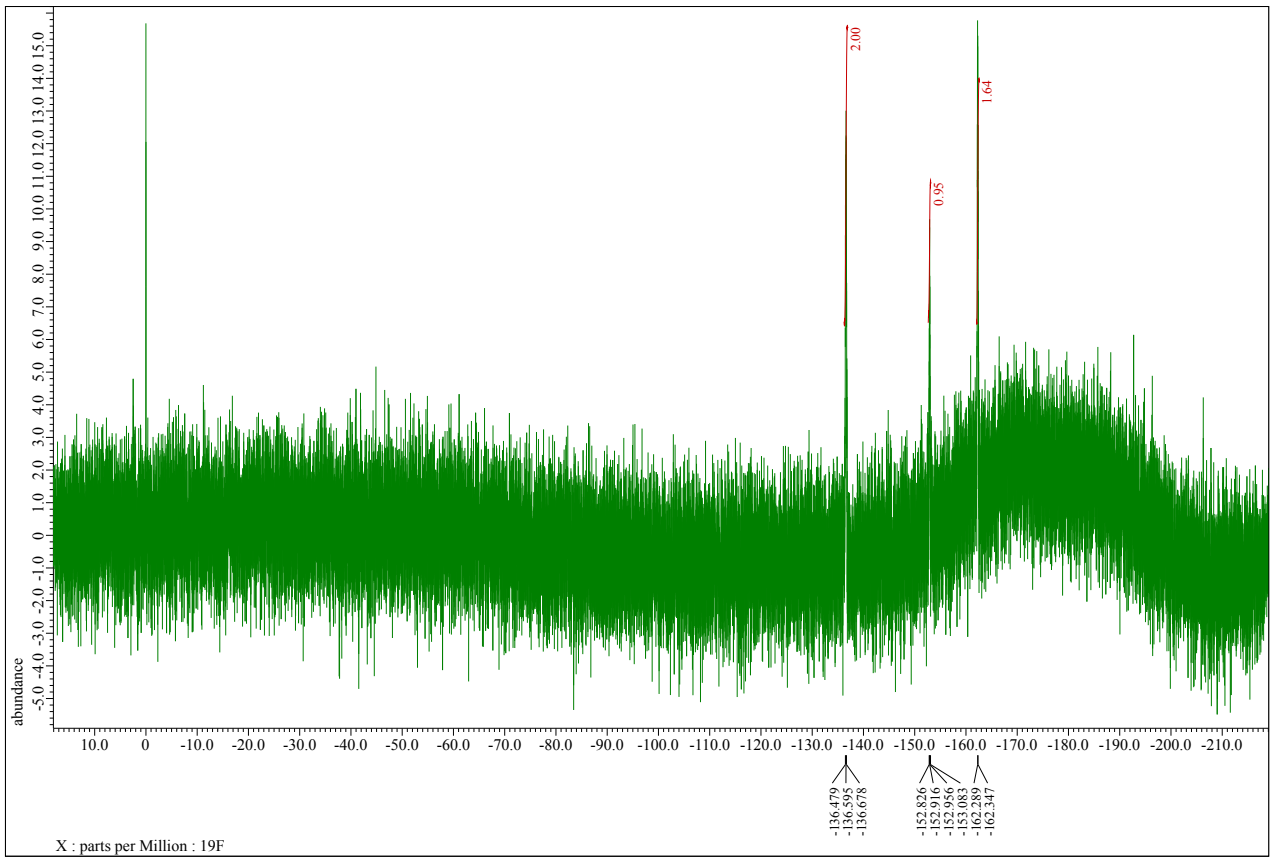
^{19}F NMR spectrum for **5e** (376 MHz, $CDCl_3$)



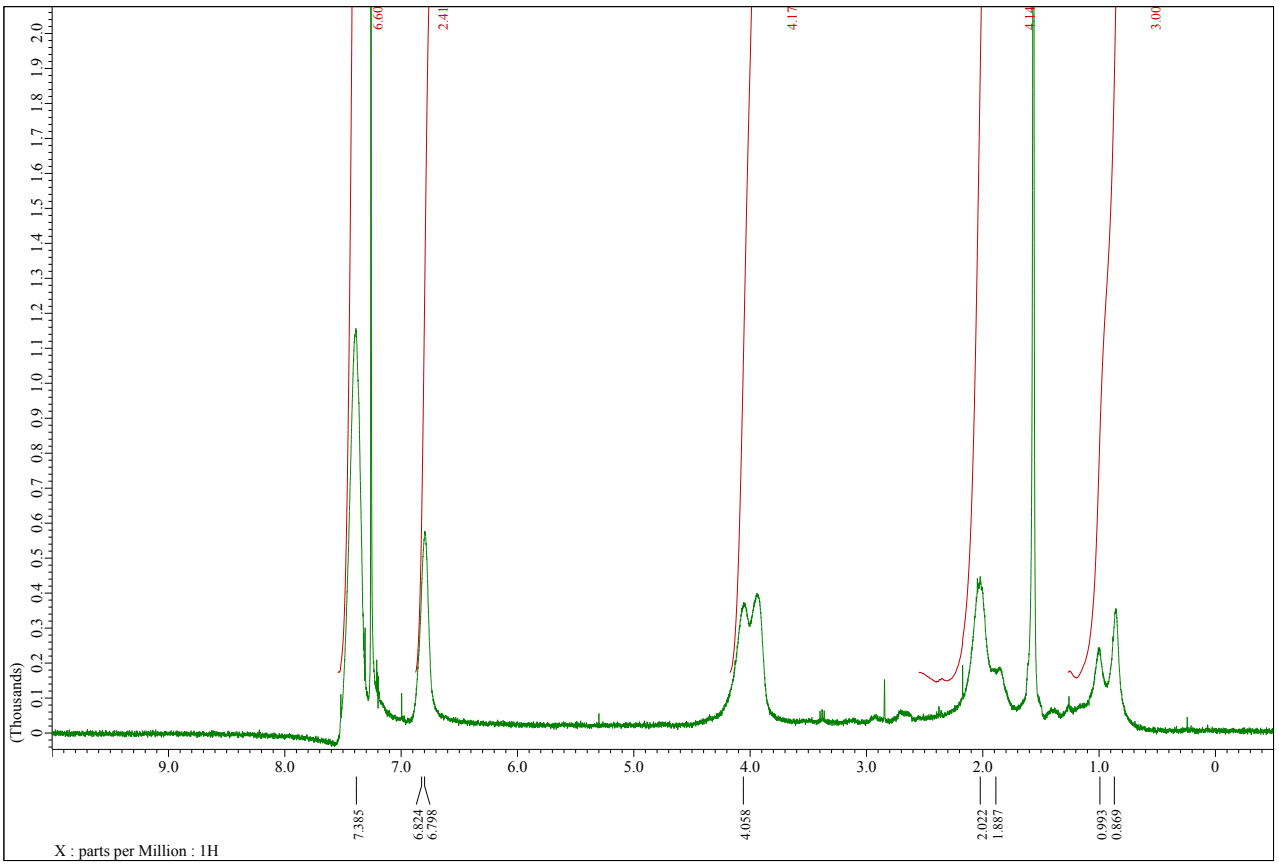
^{1}H NMR spectrum for **P-2a** (400 MHz, $CDCl_3$)



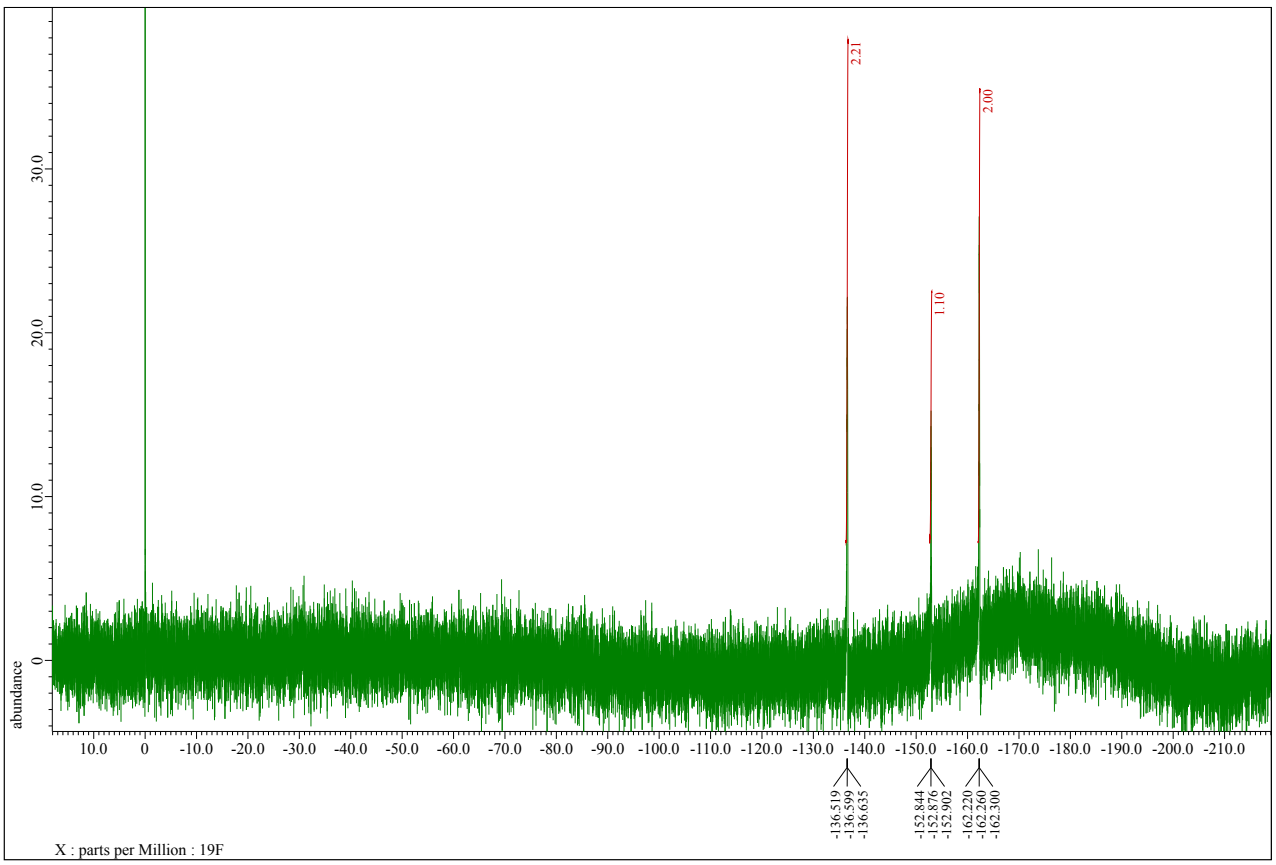
^{19}F NMR spectrum for **P-2a** (376 MHz, $CDCl_3$)



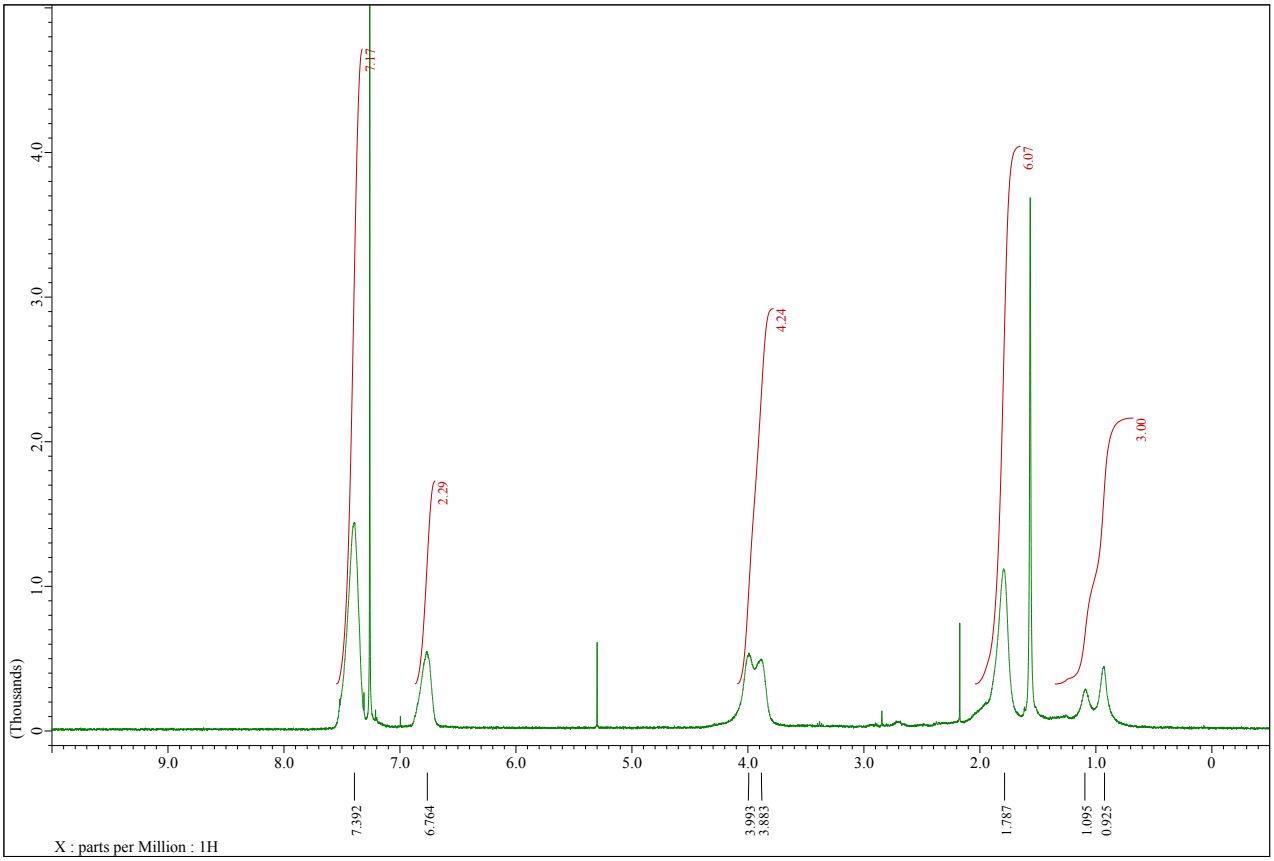
^{1}H NMR spectrum for **P-2b** (400 MHz, $CDCl_3$)



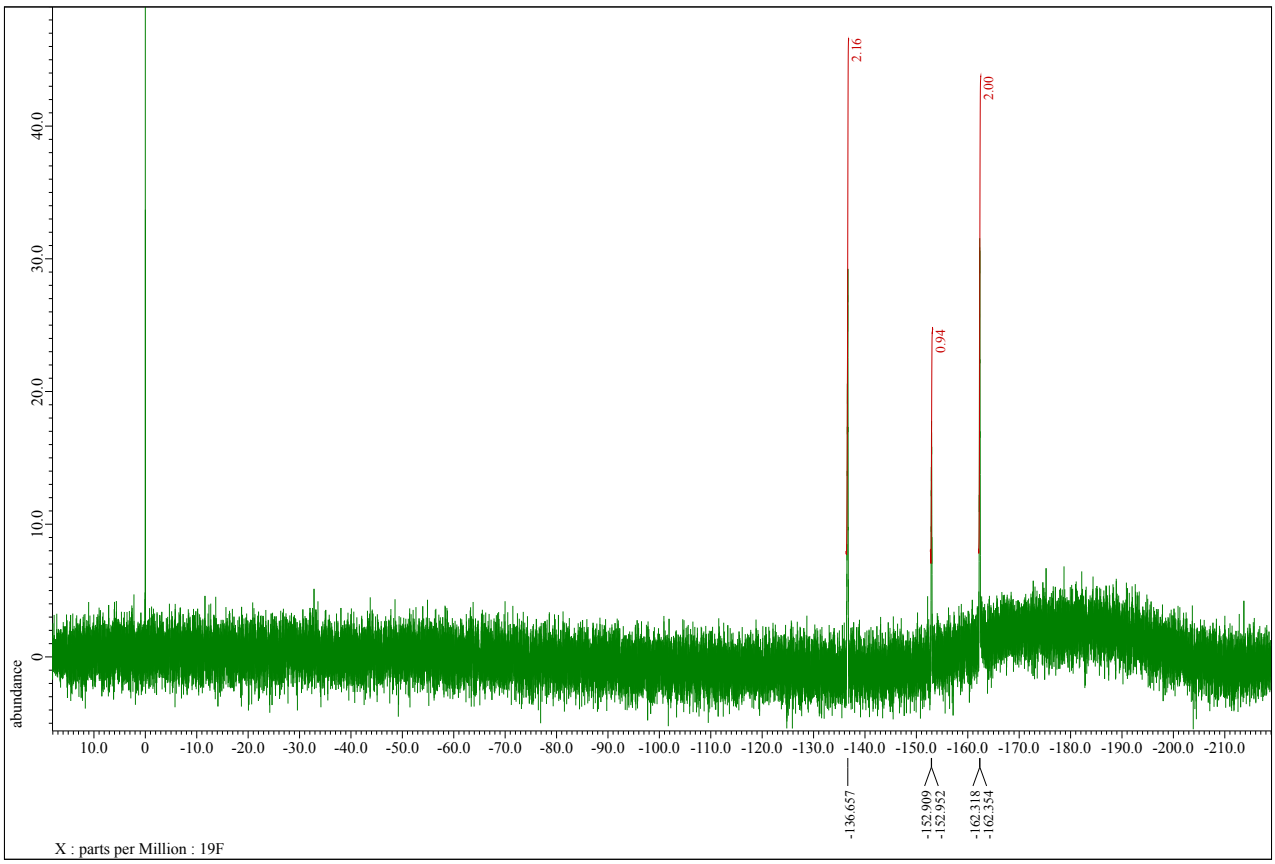
^{19}F NMR spectrum for **P-2b** (376 MHz, $CDCl_3$)



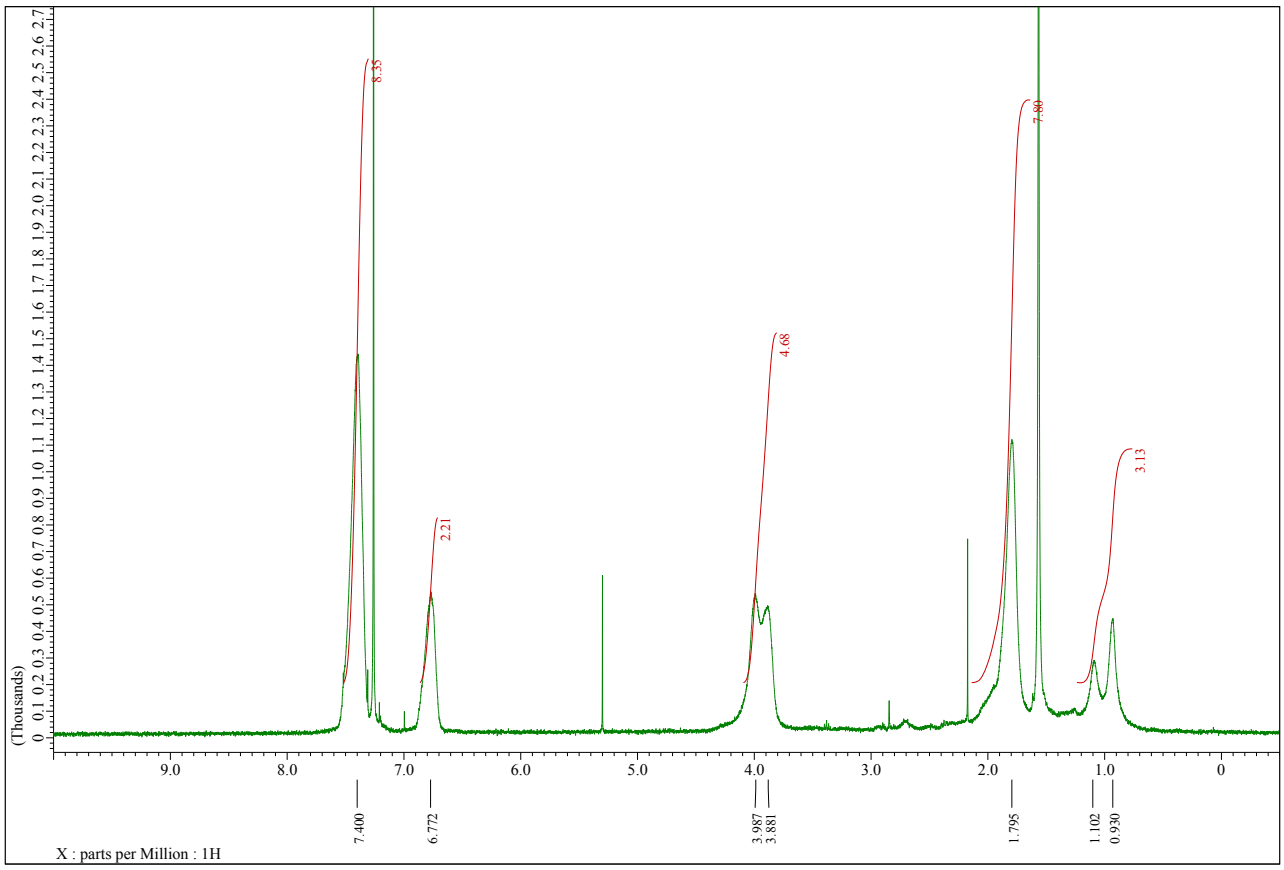
^{1}H NMR spectrum for **P-2c** (400 MHz, $CDCl_3$)



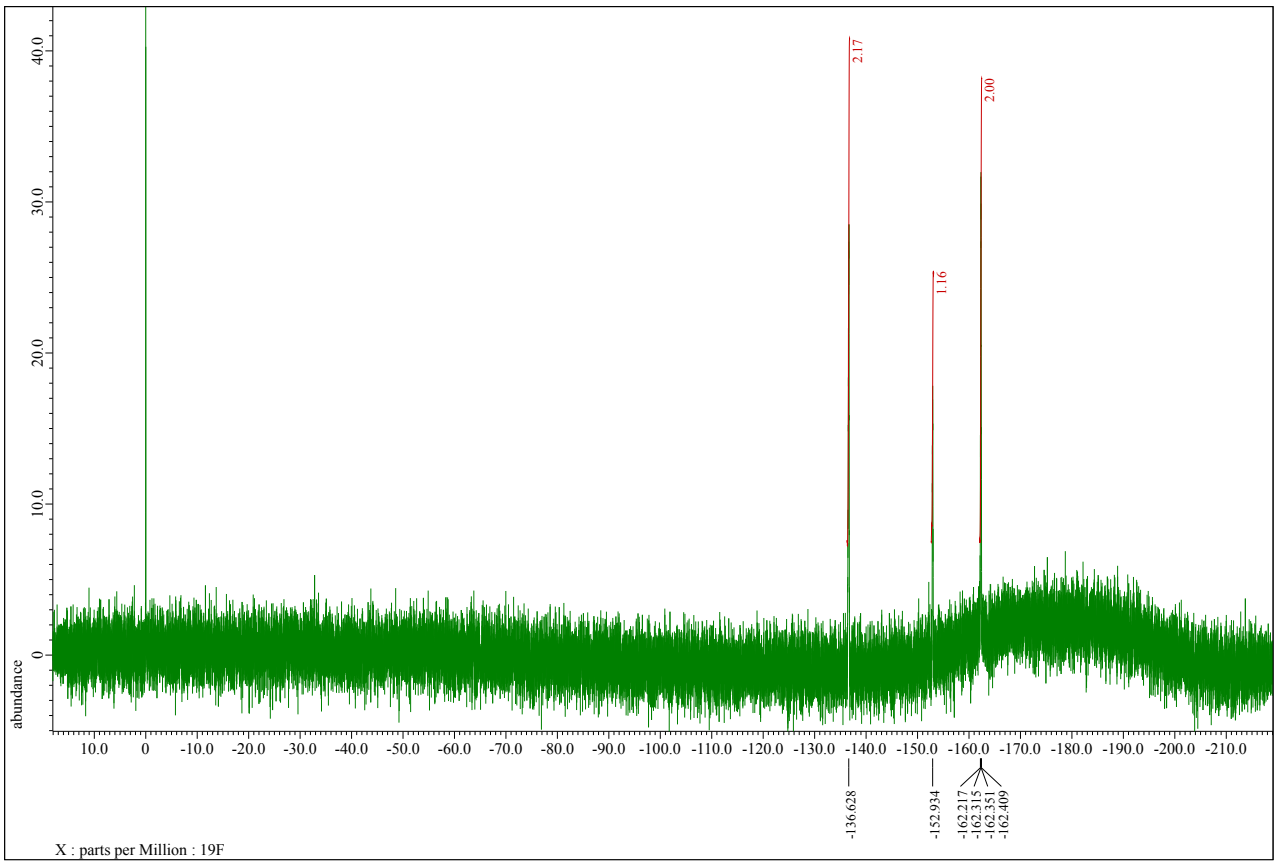
^{19}F NMR spectrum for **P-2c** (376 MHz, $CDCl_3$)



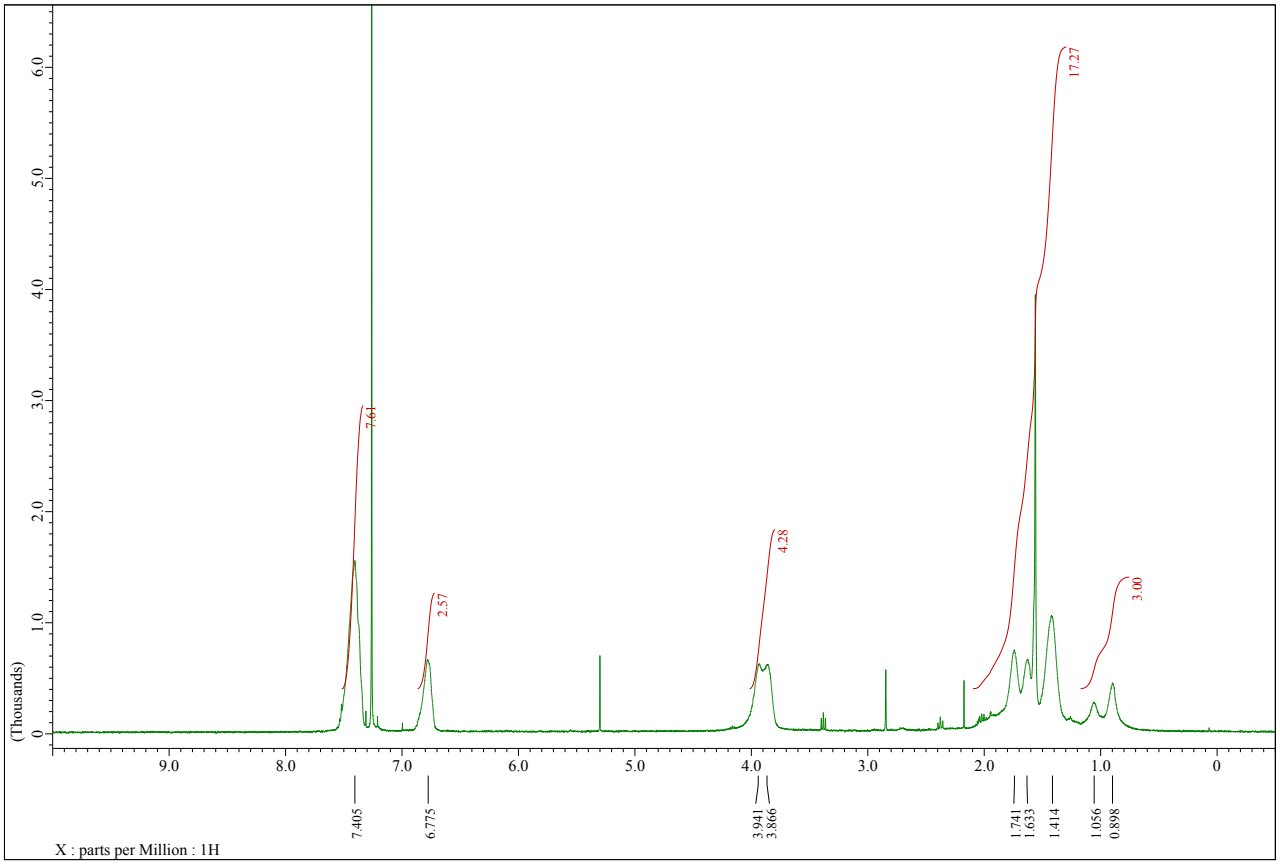
^{1}H NMR spectrum for **P-2d** (400 MHz, $CDCl_3$)



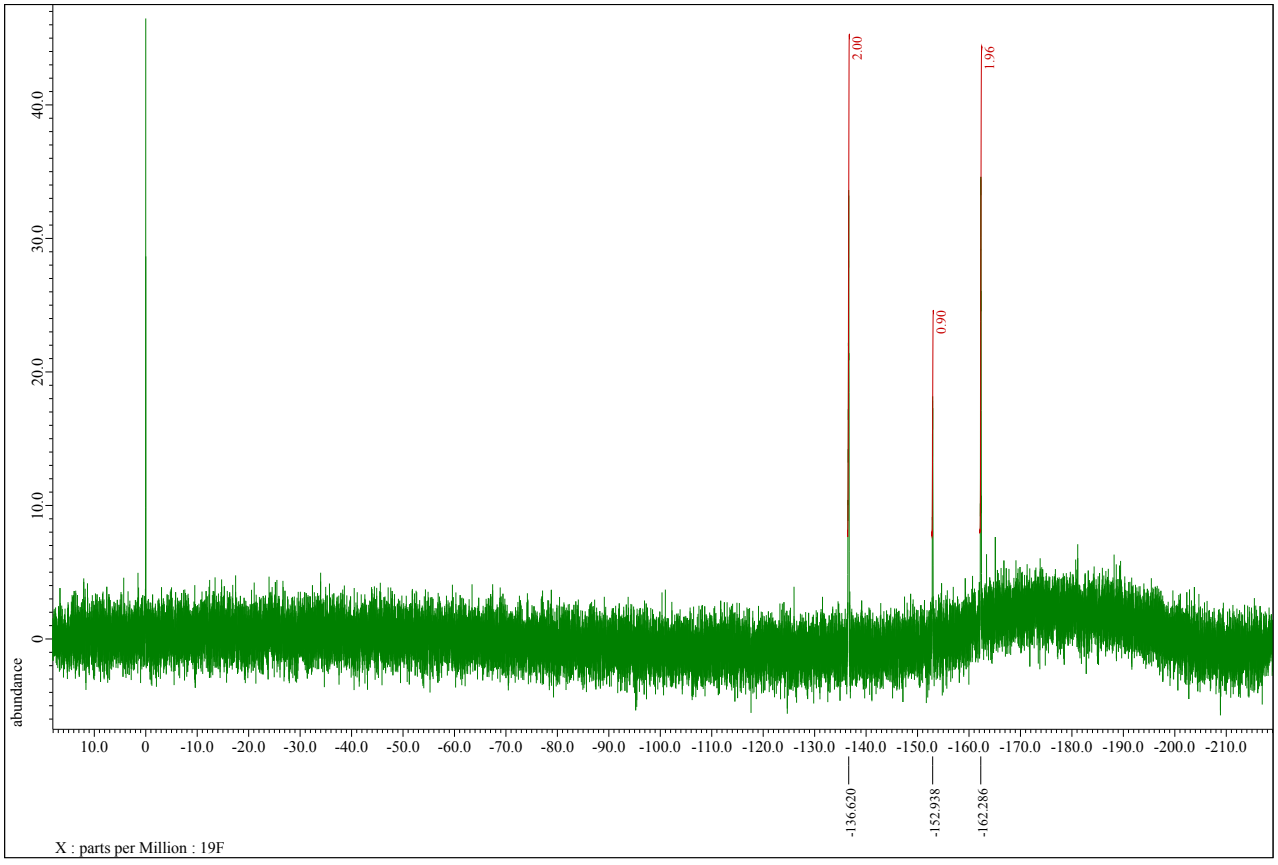
^{19}F NMR spectrum for **P-2d** (376 MHz, $CDCl_3$)



^{1}H NMR spectrum for **P-2e** (400 MHz, $CDCl_3$)



^{19}F NMR spectrum for **P-2e** (376 MHz, $CDCl_3$)



3. GPC analysis

Table S1. Polymer characterization

	P-2a	**P-2b**	**P-2c**	**P-2d**	**P-2e**
Retention time [min]	16.188	15.558	15.262	15.205	15.12
Peak area [mV•sec]	6193.277	5951.297	8355.121	4816.097	5374.071
Peak height [mV]	47.924	44.955	59.755	33.503	42.412
FWHM [sec]	121.505	124.073	128.993	132.429	120.952
M_n	4818	8330	9488	9566	12450
M_w	7215	13213	16397	16922	19104
M_w/M_n	1.497	1.586	1.728	1.769	1.534

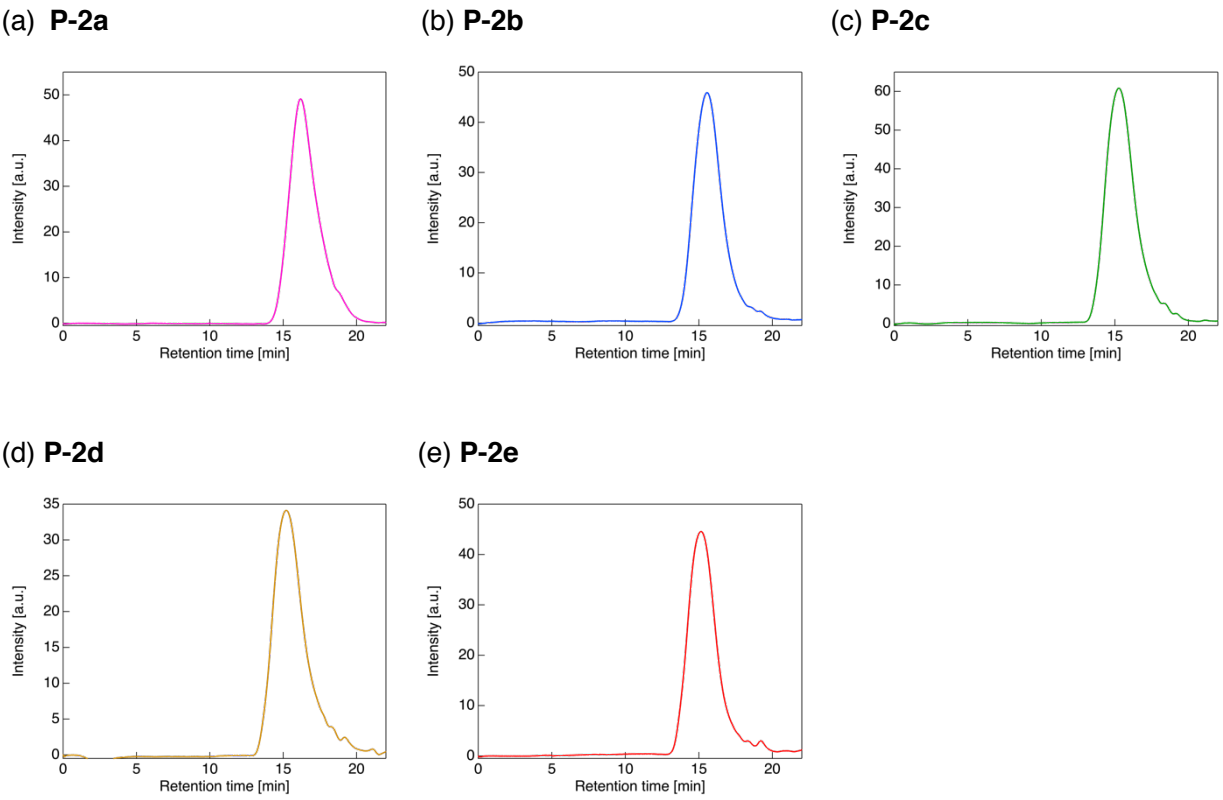
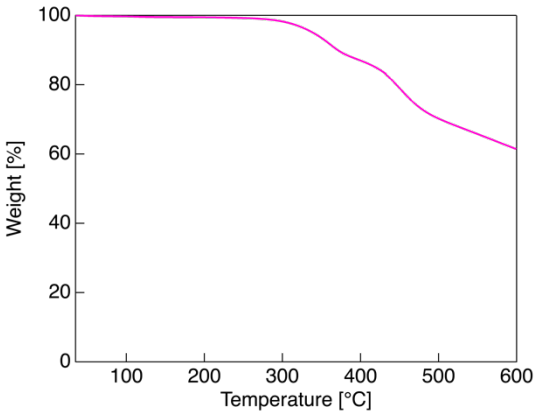


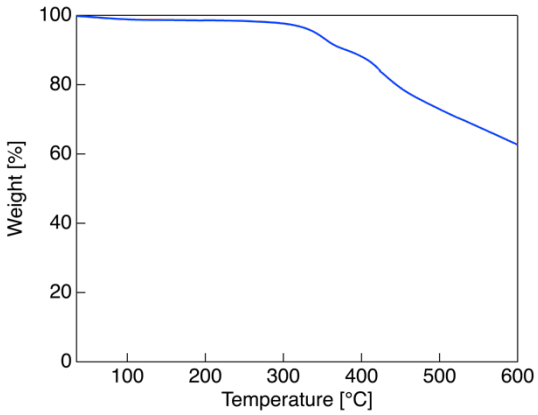
Figure S1. Elusion curve for **P-2a–e** obtained by GPC analysis (Eluent: $CHCl_3$, standard: polystyrene).

4. Thermogravimetric (TG) analysis

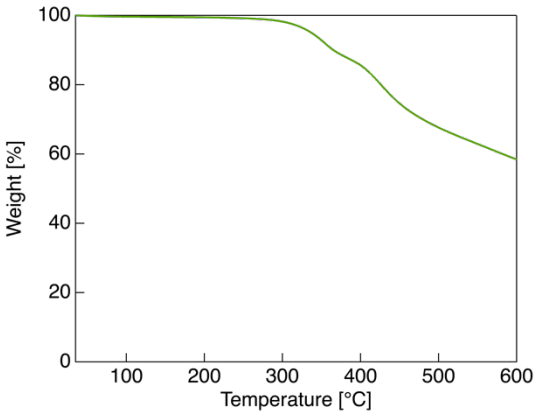
(a) **P-2a**



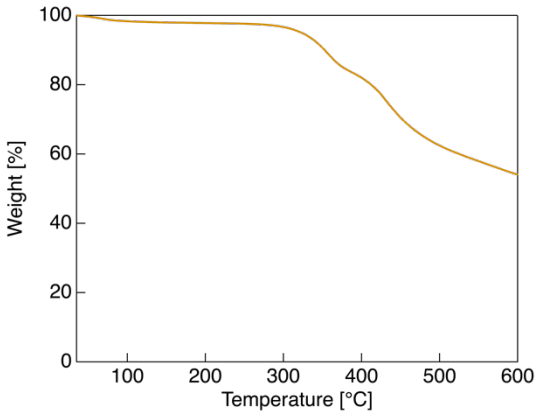
(b) **P-2b**



(c) **P-2c**



(d) **P-2d**



(e) **P-2e**

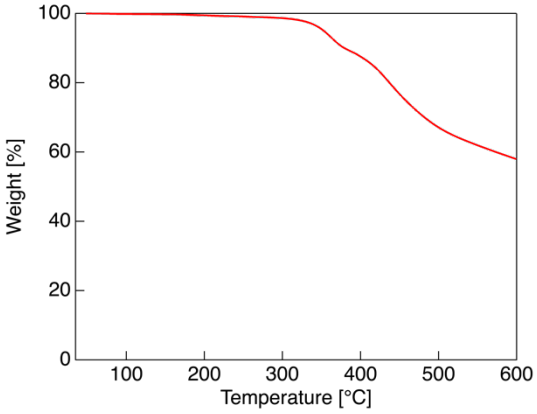
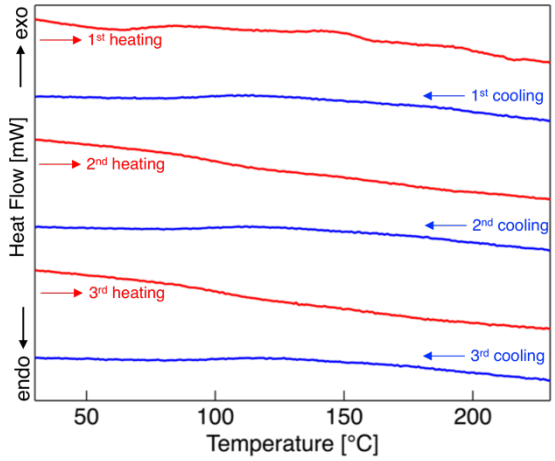


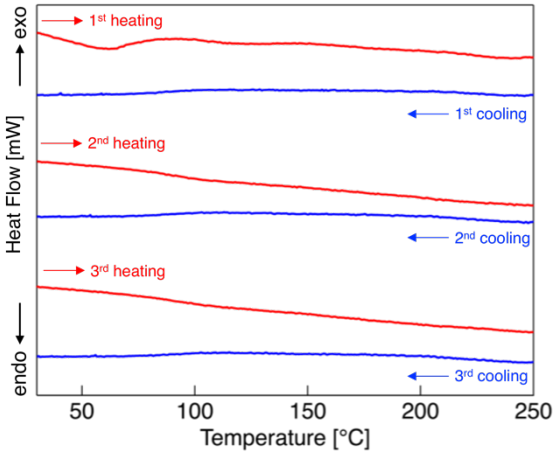
Figure S2. Thermograms of **P-2a–e** obtained by TG analysis (heating rate: 10 °C min^{-1}).

5. Differential scanning calorimetry (DSC) measurement

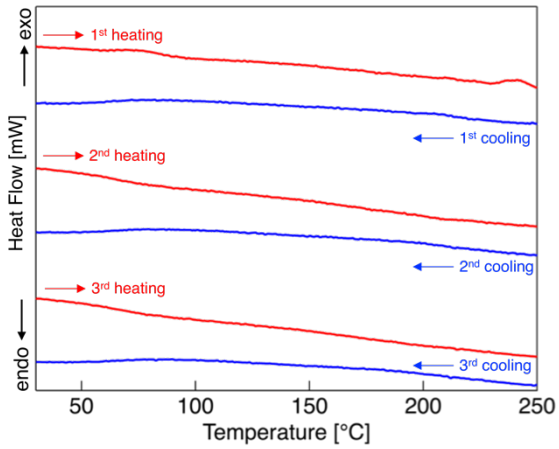
(a) **P-2a**



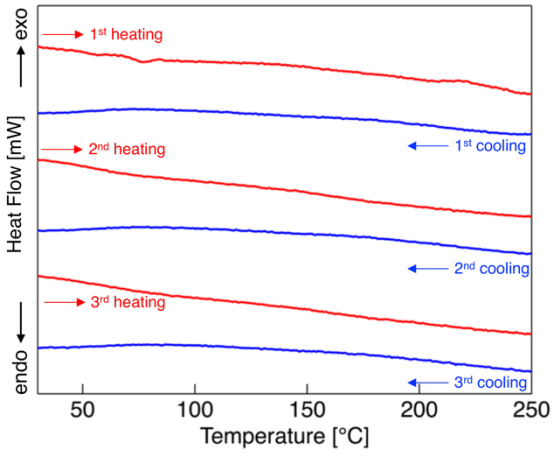
(b) **P-2b**



(c) **P-2c**



(d) **P-2d**



(e) **P-2e**

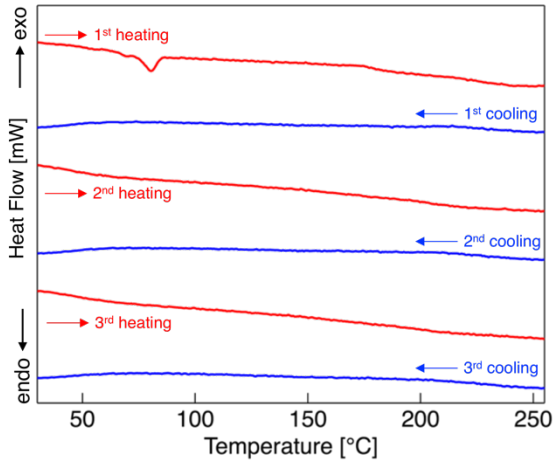


Figure S3. Thermograms of **P-2a**–**e** obtained by DSC (scan rate: 5.0 °C min^{-1}).

6. Polarizing optical microscopy (POM) measurement

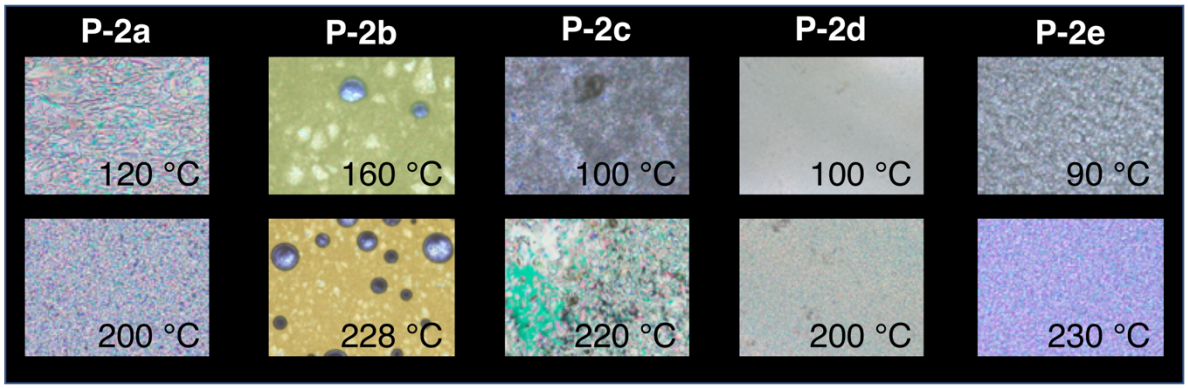
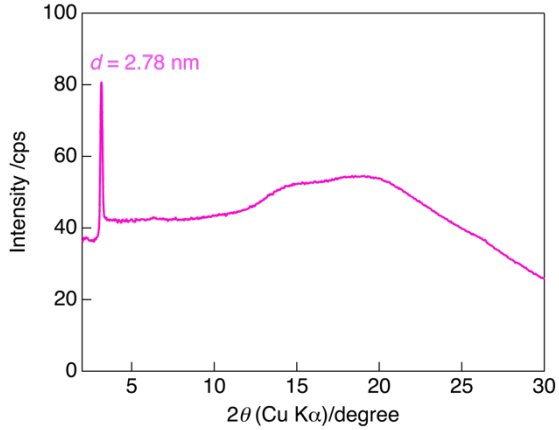


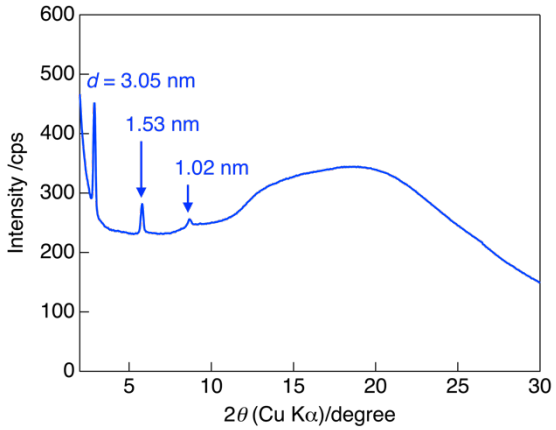
Figure S4. Microphotographs obtained by POM measurement

7. PXRD measurement for the LC phases (at 150 °C)

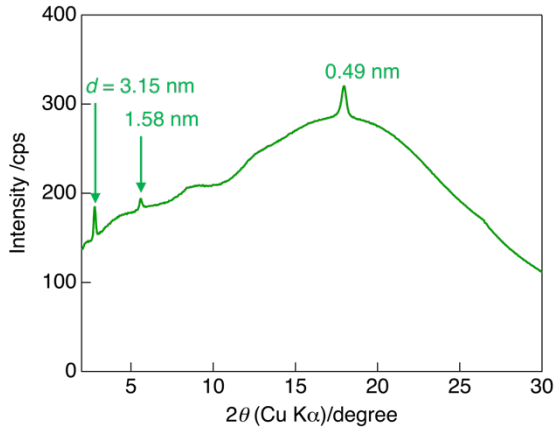
(a) **P-2a**



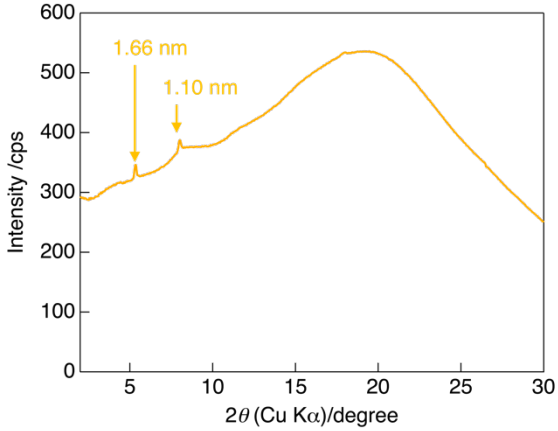
(b) **P-2b**



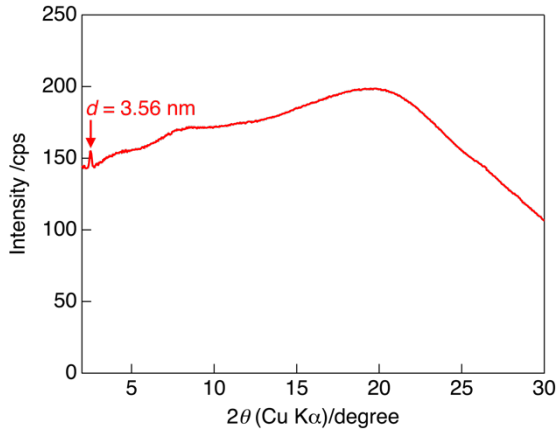
(c) **P-2c**



(d) **P-2d**



(e) **P-2e**



(f) number of alkylene linkage vs *d* spacing

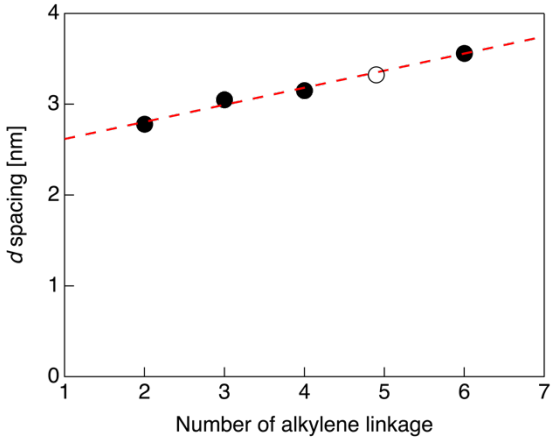
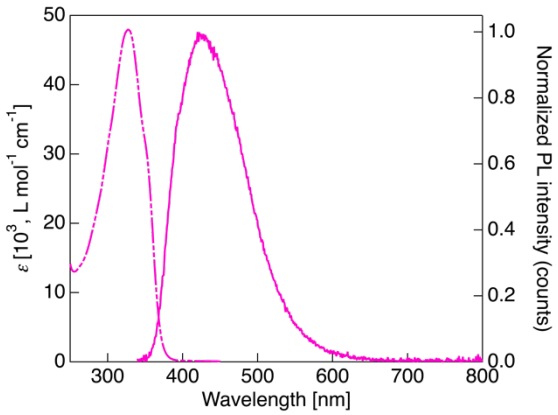


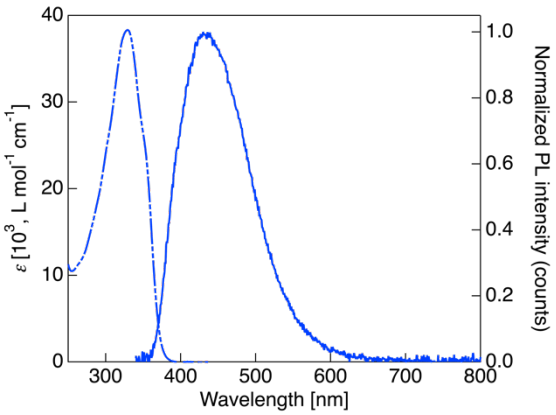
Figure S5. (a–e) PXRD pattern and (f) relationship between the number of alkylene linkage and interlayer *d* pacing of **P-2a**–**e** observed at 150 °C on the cooling process.

8. Photophysical properties in CH_2Cl_2 solution

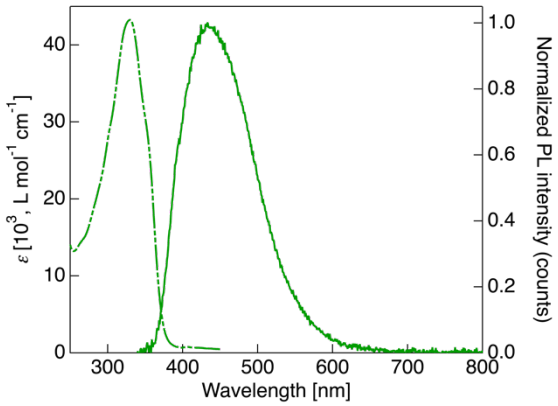
(a) **P-2a**



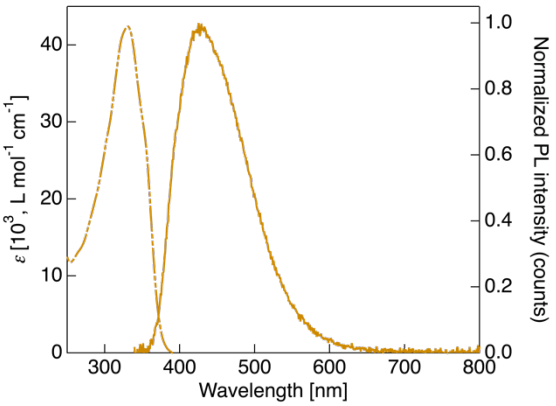
(b) **P-2b**



(c) **P-2c**



(d) **P-2d**



(e) **P-2e**

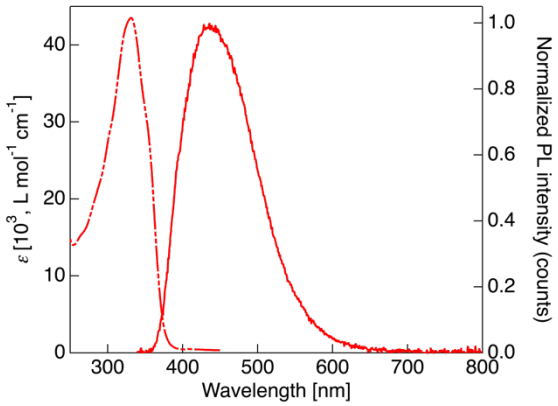
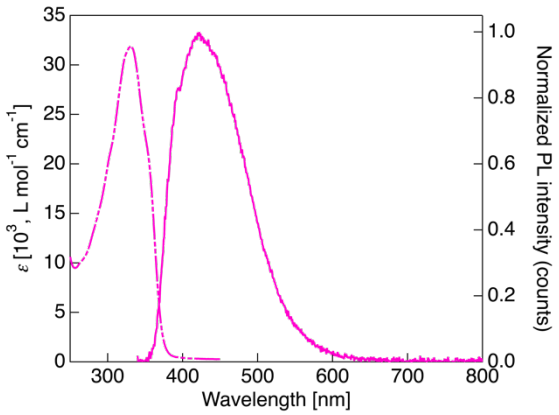


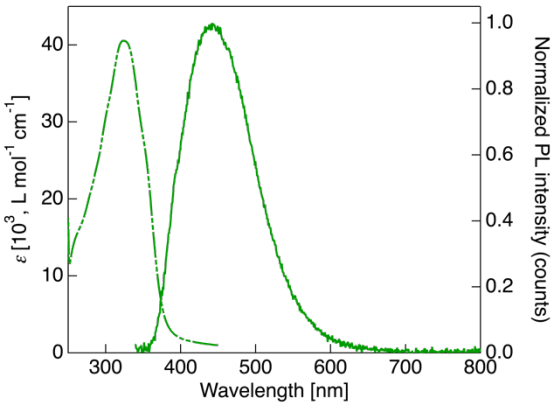
Figure S6. Absorption (dotted line) and PL spectra (solid line, λ_{ex} = 330 nm) for **P-2a–e** in CH_2Cl_2 solution (concentration: 1.0x10^{-5} mol L^{-1} for absorption; 1.0x10^{-6} mol L^{-1} for PL).

9. Photophysical properties of P-2e in various solvent

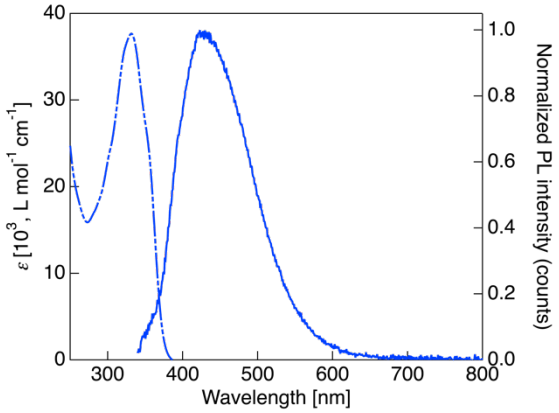
(a) in $CHCl_3$



(b) in AcOEt



(c) in THF



(d) in DMF

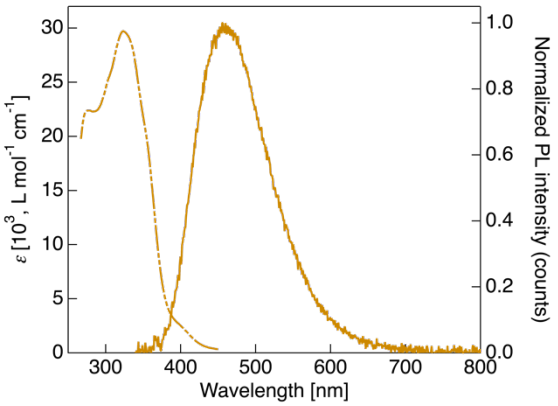
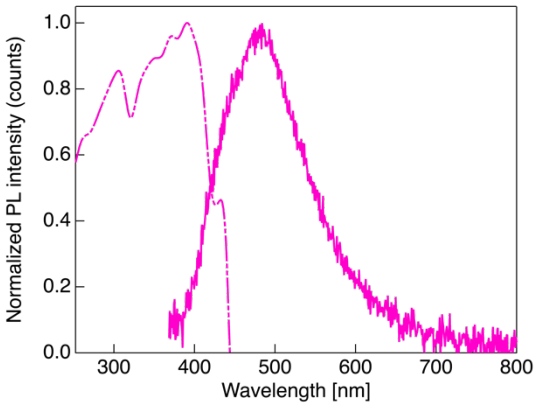


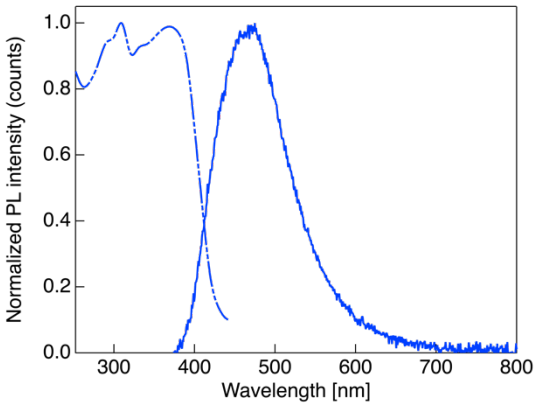
Figure S7. Absorption (dotted line) and PL spectra (solid line, λ_{ex} = 330 nm) for **P-2e** in (a) $CHCl_3$, (b) AcOEt, (c) THF, and (d) DMF solution (concentration: 1.0×10^{-5} mol L^{-1} for absorption; 1.0×10^{-6} mol L^{-1} for PL).

10. Photophysical properties in the pristine powder solid

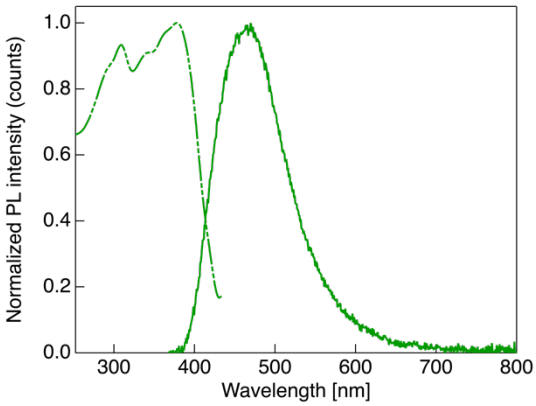
(a) **P-2a** (λ_{em} = 485 nm, λ_{ex} = 360 nm)



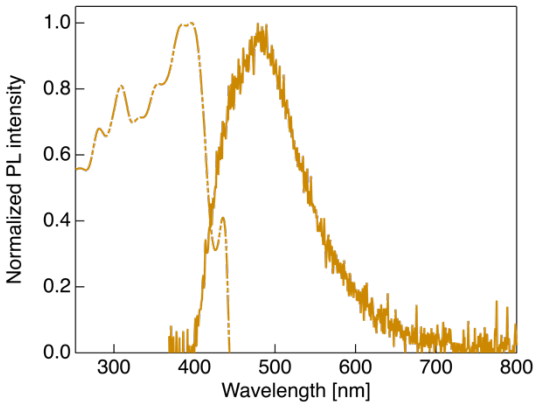
(b) **P-2b** (λ_{em} = 470 nm, λ_{ex} = 360 nm)



(c) **P-2c** (λ_{em} = 470 nm, λ_{ex} = 360 nm)



(d) **P-2d** (λ_{em} = 480 nm, λ_{ex} = 360 nm)



(e) **P-2e** (λ_{em} = 475 nm, λ_{ex} = 360 nm)

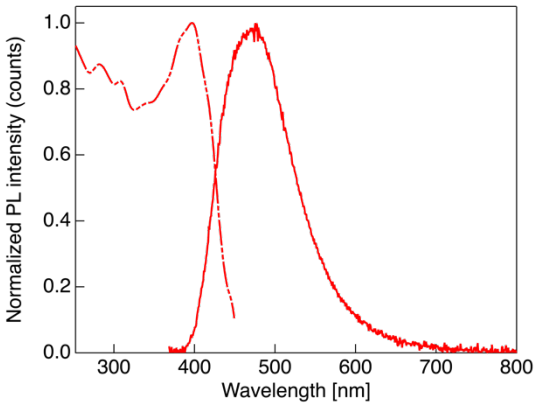
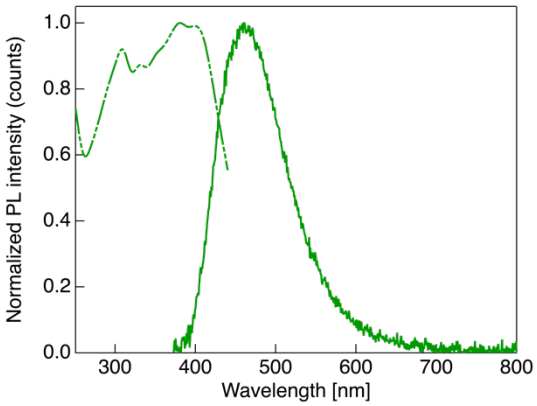


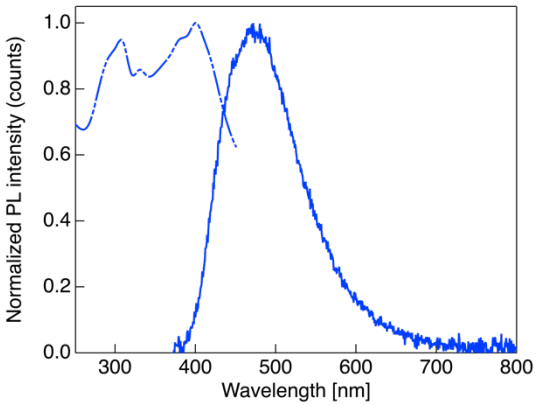
Figure S8. Excitation (dotted line) and PL spectra (solid line) for **P-2a**–**e** in the pristine powder solid.

11. Photophysical properties of $P_{B–D}$-2e with various M_n and PDI in the pristine powder solid

(a) **P_B-2e** (λ_{em} = 460 nm, λ_{ex} = 360 nm)



(b) **Pc-2e** (λ_{em} = 470 nm, λ_{ex} = 360 nm)



(c) **P_D-2e** (λ_{em} = 465 nm, λ_{ex} = 360 nm)

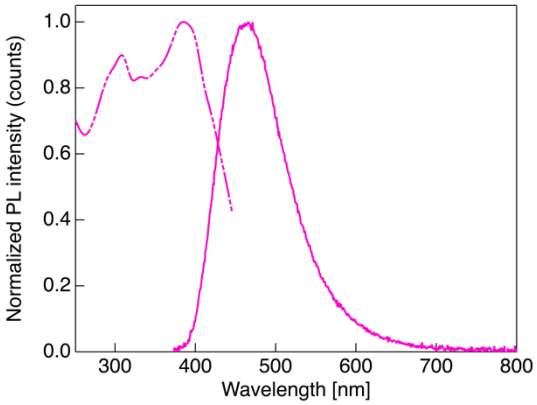
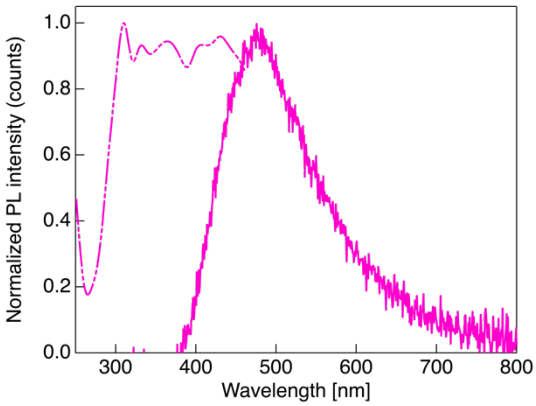


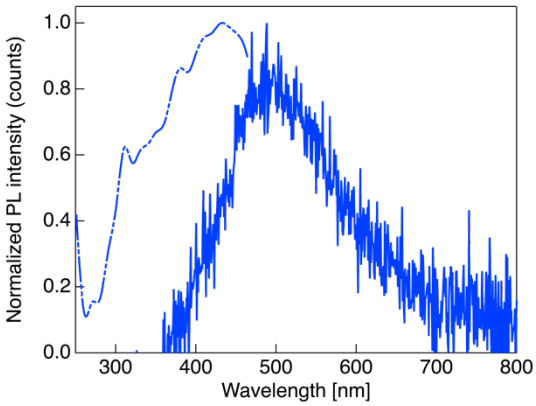
Figure S9. Excitation (dotted line) and PL spectra (solid line) for **P-2e** with various M_n and PDI in the pristine solid states.

12. Photophysical property of P-2a–e in the N phase

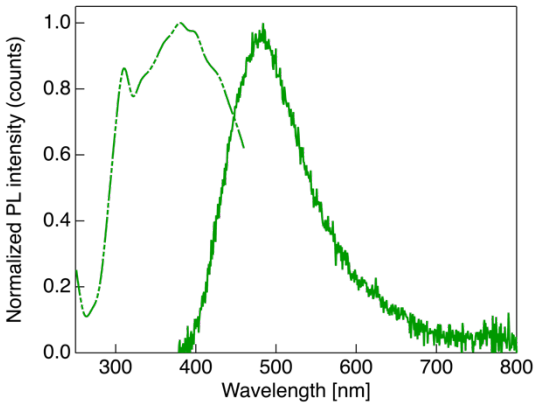
(a) **P-2a** (λ_{em} = 485 nm, λ_{ex} = 310 nm)



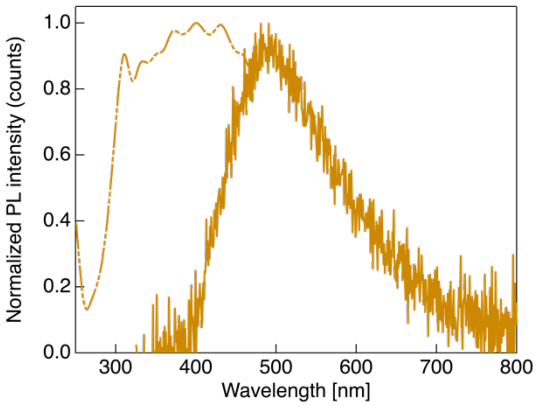
(b) **P-2b** (λ_{em} = 490 nm, λ_{ex} = 310 nm)



(c) **P-2c** (λ_{em} = 485 nm, λ_{ex} = 310 nm)



(d) **P-2d** (λ_{em} = 490 nm, λ_{ex} = 310 nm)



(e) **P-2e** (λ_{em} = 490 nm, λ_{ex} = 310 nm)

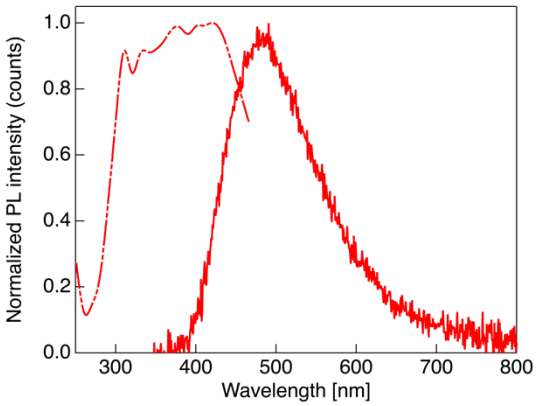
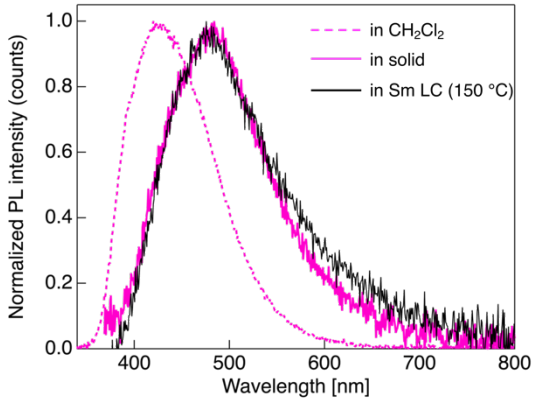


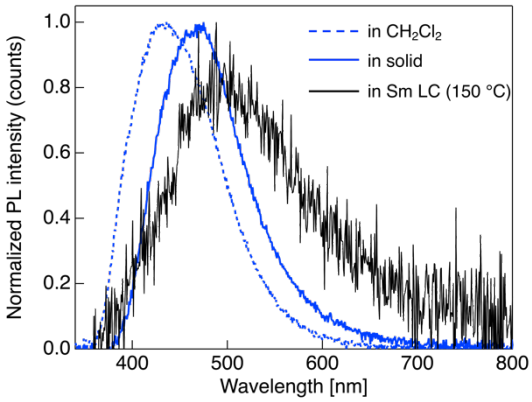
Figure S10. Excitation (dotted line) and PL spectra (solid line) for **P-2a–e** in the Sm phase (150 °C).

13. Comparison for photophysical properties of P-2 in CH_2Cl_2, solid, and Sm LC phases

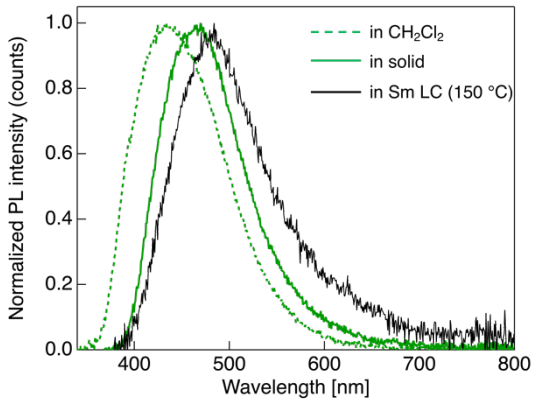
(a) **P-2a**



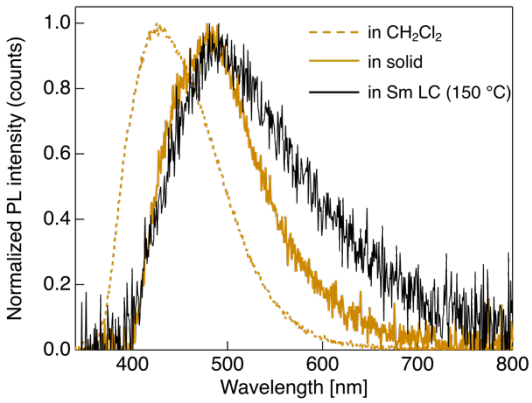
(b) **P-2b**



(c) **P-2c**



(d) **P-2d**



(e) **P-2e**

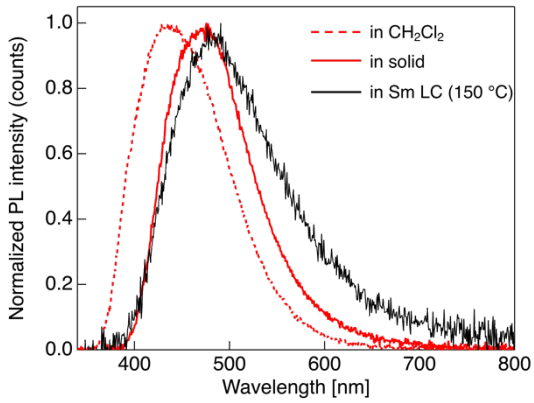


Figure S11. PL spectra in CH_2Cl_2 solution (dotted line, λ_{ex} = 330 nm), in pristine powder solid (solid line, λ_{ex} = 360 nm), and in Sm LC phase at 150 °C (black solid line, λ_{ex} = 310 nm) for **P-2a–e**.