Supplementary Information for

Solvent-dependent fluorescence and circular dichroism properties of poly(quinoxaline-2,3-diyl)s bearing pyrene pendants

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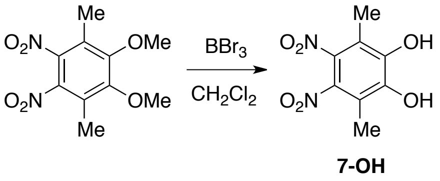
Contents

1 General

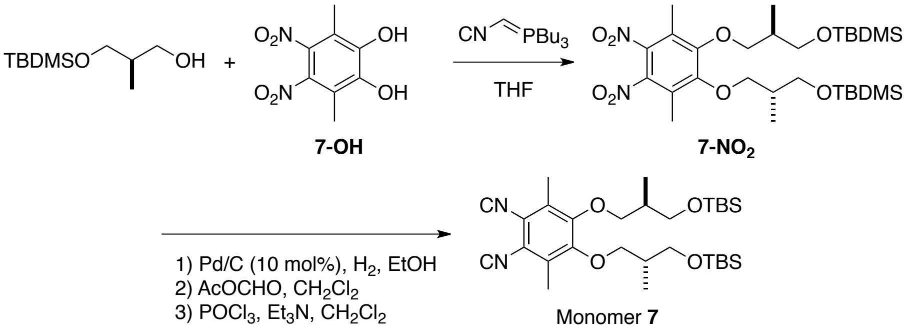
All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400-MR spectrometer at ambient temperature. ^{1}H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, m = multiplet and br = broad), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C NMR spectra were obtained with complete proton decoupling. IR spectra were obtained using a Shimadzu FTIR-8400 FT-IR spectrometer equipped with a PIKE MIRacle attenuated total reflectance (ATR) unit at room temperature. The GPC analysis was carried out with TSKgel GMH$_{XL}$ ($CHCl_3$, polystyrene standards). The microwave irradiation was performed on Biotage Initiator 2.5. The silica gel column chromatography was performed on Biotage Isolera One. Preparative GPC was performed on JAI LC-908 equipped with JAIGEL-1H and -2H columns in a series ($CHCl_3$). UV spectra were recorded on a JASCO V-500 spectrometer equipped with a JASCO type ETC-505T temperature/stirring controller at 20 °C. CD spectra were recorded on a JASCO J-750 spectrometer equipped with a JASCO type PTC-423L temperature/stirring controller at 20 °C. Fluorescence spectra were recorded on a JASCO FP-6300 spectrofluorometer. Absolute quantum yields were measured by a Hamamatsu absolute PL quantum yield spectrometer C11347. All solutions were deoxygenated by argon bubbling for 60 seconds just before measurements of fluorescent spectra and absolute quantum yields. Toluene and tetrahydrofurane (THF) were dried and deoxygenated using an alumina/catalyst column system (Glass Contour Co.).

(*R*)-3-((*tert*-butyldimethylsilyl)oxy)-2-methylpropan-1-ol,[1] 3,6-dimethylcatechol,[2] 1,2-dimethoxy-3,6-dimethyl-4,5-dinitrobenzene,[3] cyanomethylenetributylphosphorane,[4] acetic formic anhydride,[5] *o*-TolNiCl(PMe_3)$_2$,[6] monomer **Q**,[3] (*S*)-1-bromo-2--methylbutane,[7a] and 3-((*tert*-butyldimethylsilyl)oxy)propan-1-ol[8] were prepared according to the reported procedures. Triethylamine (Et_3N) and phosphoryl chloride ($POCl_3$) were distilled, degassed, and stored under nitrogen. Other chemical reagents were purchased from the commercial sources and were used without further purification.

2 Experimental Procedures and Special Data for New Compounds



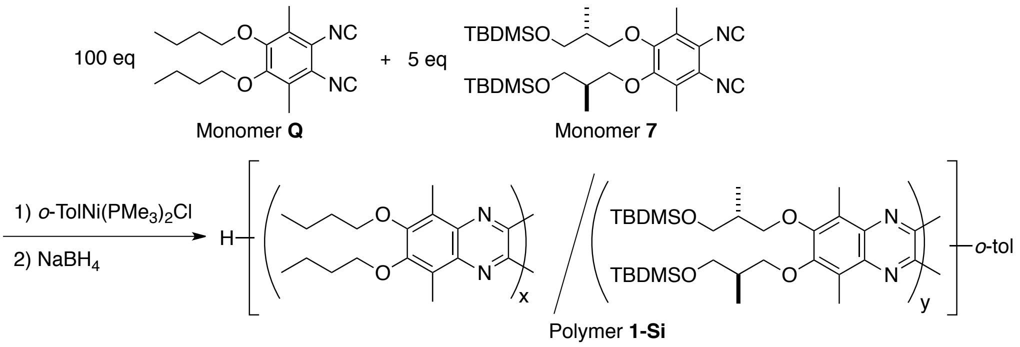
Synthesis of 7-OH: BBr_3 (1.0 mol/L in CH_2Cl_2, 33 mmol) was added to 1,2-dimethoxy--3,6-dimethyl-4,5-dinitrobenzene (2.85 g, 11.1 mmol) and stirred at 50 °C for 16 h. The reaction mixture was concentrated under reduced pressure and quenched with water (50 mL). Organic materials were extracted with Et_2O (50 mL × 2). The combined organic layer was washed with water (50 mL × 3) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was dissolved in Et_2O and reprecipitated by adding hexane. The product **7-OH** (2.33 g) was obtained as yellow powder in 92% yield. ^{1}H NMR ($CDCl_3$) δ 5.65 (2H, s), 2.32 (6H, s); ^{13}C NMR (dimethyl sulfoxide-*d*$_6$): δ 136.8, 127.3, 108.4, 1.98; IR (neat) 3539, 3405, 1532, 1367, 1282, 1242, 1191, 1080, 1021, 912, 759, 747 cm^{-1}; HRMS (ESI) m/z calcd for $C_8H_8N_2O_6^+$ (M^+): 228.0377, found: 228.0380.



Synthesis of 7-NO$_2$: To a solution of (*R*)-3-((*tert*-butyldimethylsilyl)oxy)-2-methylpropan-1-ol (0.694 g, 3.07 mmol) and **7-OH** (1.87 g, 9.20 mmol) in THF (3mL) was added a solution of cyanomethylenetributylphosphorane in THF (0.92 mol/L, 10 mL, 9.2 mmol). After stirring at 80 °C for 24 h under microwave irradiation, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt = 95/5) and preparative GPC to give the product **7-NO$_2$** (0.935 g) as pale yellow oil in 57% yield. ^{1}H NMR ($CDCl_3$) δ 4.00

(2H, dd, *J* = 6.0, 8.8 Hz), 3.84 (2H, dd, *J* = 6.0, 8.8 Hz), 3.66 (2H, dd, *J* = 5.2, 10.0 Hz), 3.59 (2H, dd, *J* = 6.0, 10.0 Hz), 2.29 (6H, s), 2.17–2.06 (2H, m), 1.05 (6H, d, *J* = 6.8 Hz), 0.88 (18H, s), 0.04 (12H, s); ^{13}C NMR ($CDCl_3$): δ 153.1, 140.4, 125.8, 75.8, 64.4, 36.9, 25.9, 18.2, 14.0, 11.7, −5.45, −5.50; IR (neat) 2928, 1541, 1356, 1250, 1092, 1040, 833, 773 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{56}N_3O_8Si_2$ ($M+NH_4^+$): 618.3600, found: 618.3592.

Synthesis of monomer 7: A suspension of **7-NO$_2$** (0.739 g, 1.23 mmol) and 10 wt% Pd/C (65.4 mg, 61.5 μmol) in EtOH (6.2 mL) was stirred for 66 h under H_2 atmosphere. The mixture was filtered through a pad of Celite and evaporated under vacuum to give a diamine compound as orange oil. Acetic formic anhydride (0.866 g, 9.83 mmol) was added to the diamine dissolved in CH_2Cl_2 (6.2 mL). After stirring for 14 h, removal of volatiles under reduced pressure gave a diformate compound as white solid. $POCl_3$ (1.09 mL, 1.80 g, 11.7 mmol) was added to a solution of diformate in Et_3N (5.4 mL) and CH_2Cl_2 (18.3 mL) at 0 °C. After stirring for 30 min at 0 °C, the reaction mixture was washed with saturated $NaHCO_3$ aq (30 mL × 2) and brine (30 mL × 2). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane to hexane/CH_2Cl_2 = 50/50) to give monomer **7** as pale yellow oil (0.194 g, 28%). ^{1}H NMR ($CDCl_3$) δ 3.93 (2H, dd, *J* = 6.0, 9.0 Hz), 3.78 (2H, dd, *J* = 6.4, 9.0 Hz), 3.65 (2H, dd, *J* = 5.4, 9.9 Hz), 3.60 (2H, dd, *J* = 6.0, 9.9 Hz), 2.33 (6H, s), 2.12–2.04 (2H, m), 1.04 (6H, d, *J* = 6.8 Hz), 0.88 (18H, s), 0.04 (12H, s); ^{13}C NMR ($CDCl_3$): δ 171.7, 151.7, 128.6, 119.9, 75.5, 64.5, 36.9, 25.8, 18.2, 14.0, 12.6, −5.48, −5.52; IR (neat) 2928, 2116, 1462, 1337, 1252, 1090, 1047, 986, 833, 773, 667 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{56}N_3O_4Si_2$ ($M+NH_4^+$): 578.3804, found: 578.3804; $[\alpha]_D^{28.3}$ +2. 4 (*c* 0.50, $CHCl_3$).



Synthesis of Polymer 1-Si: A solution of *o*-TolNiCl$(PMe_3)_2$ in THF (47.4 mmol/L, 44.2 µL, 2.1 µmol) was added to a solution of **8** (5.9 mg, 11 µmol) and **7** (62.9 mg, 209 µmol) in THF (5.4 mL). After stirring for 6 h, $NaBH_4$ (16.6 mg, 440 µmol) was added to the reaction mixture. After stirring for1 h, reaction mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (10 mL). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. After filtration and evaporation of solvents, the crude product was purified by preparative GPC, giving polymer **1-Si** as beige solid (60.9 mg, 89%). ^{1}H NMR ($CDCl_3$) δ 4.00 (H_e and H_i, (2x+4y)H, br s), 3.85 (H_b and H_i, (2x+4y)H, br s), 2.17 (H_a and H_h and H_m, (6x+6y+3)H, br s), 1.74 (H_d and H_j, (4x+2y)H, br s), 1.53–1.36 (H_k, 4xH, m), 1.20–0.89 (H_c and H_l, (6x+6y)H, br m), 0.86 (H_g, 18yH, s), 0.01 (H_f, 12yH, s), small peaks originated from end groups were observed in 7.84–7.12 ppm (H_n, 4H, m); GPC ($CHCl_3$, g/mol): $M_n = 2.23\times10^4$, $M_w/M_n = 1.42$.

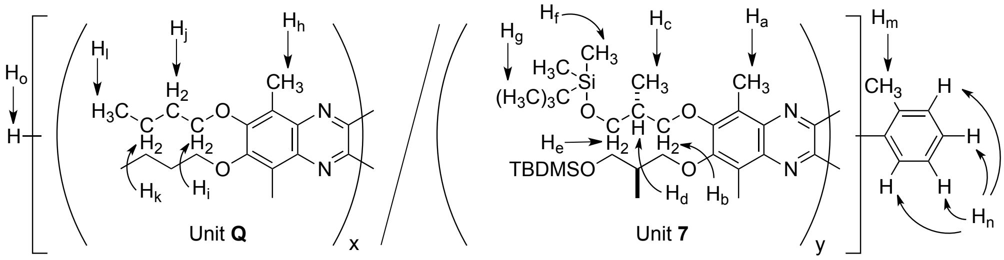
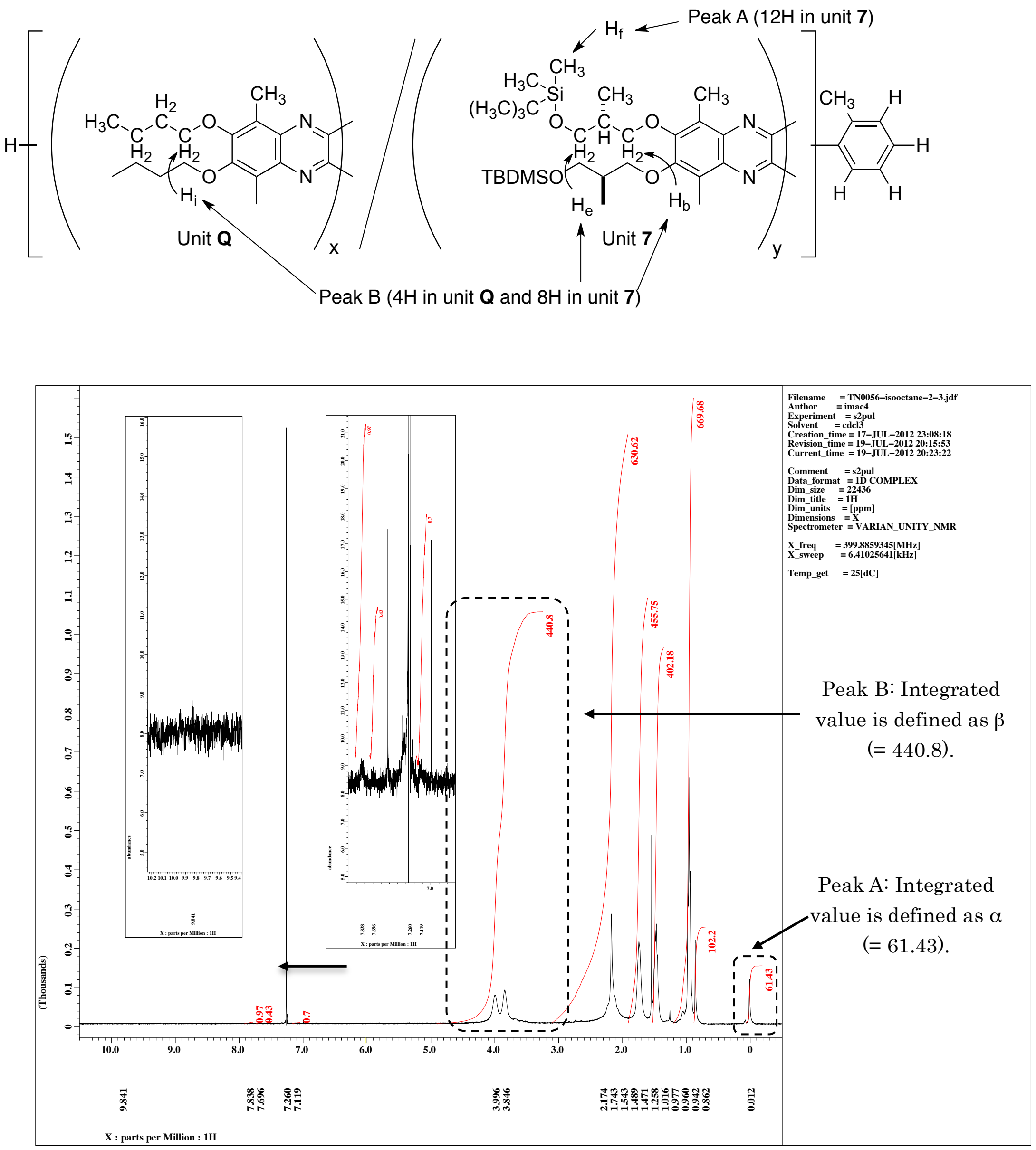


Figure S-1. Structure of polymer **1-Si** with ^{1}H NMR assignment.



Peak B: Integrated value is defined as β (= 440.8).

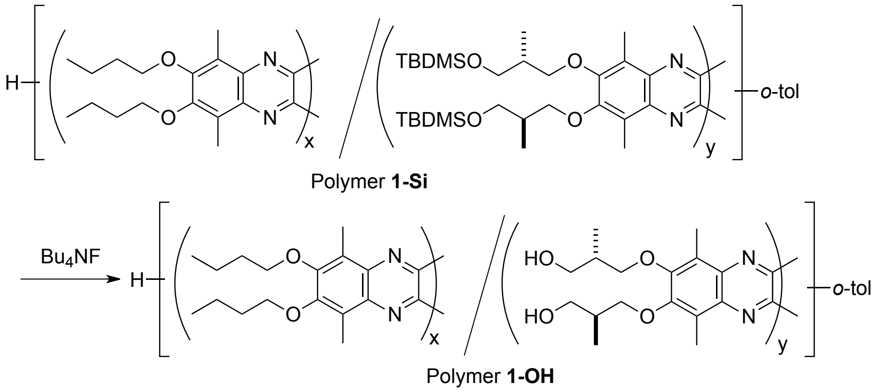
Peak A: Integrated value is defined as α (= 61.43).

Figure S-2. ^{1}H NMR spectrum of polymer **1-Si** in CDCl$_3$.

The ratio of unit **Q** and unit **7** (x/y) was calculated as follows. Integrated value of peak A, which is originated from unit **7** (H$_f$ in Figure X), was defined as α. Integrated value of peak B, which is originated from H$_b$ and H$_e$ in unit **Q** and H$_i$ in unit **7**, was defined as β. The ratio of units **Q** and **7** x/y can be expressed as

$$x/y = 3\beta/\alpha - 2 \qquad (1)$$

Here, the integrated values were measured as, $\alpha = 61.43$ and $\beta = 440.8$. Therefore, we could estimate the ratio as $x/y = 19.6$.



Synthesis of Polymer 1-OH: To a solution of polymer **1-Si** (21.3 mg) in THF (1.8 mL) was added a solution of tetrabutylammonium fluoride in THF (1.0 mol/L, 26 μL, 26 μmol). After stirring for 14 h, the reaction mixture was quenched with water (10 mL) and extracted with $CHCl_3$ (10 mL). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. After filtration and evaporation of solvents, the crude product was purified by preparative GPC, giving polymer **1-OH** as beige solid (14.9 mg, 73%). ^{1}H NMR ($CDCl_3$) δ 4.00 (H_e and H_g, (2x+4y)H, br s), 3.84 (H_b and H_g, (2x+4y)H, br s), 2.17 (H_a and H_f and H_k, (6x+6y+3)H, br s), 1.74 (H_d and H_h, (4x+2y)H, br s), 1.51–1.45 (H_i, 4xH, m), 1.20–0.22 (H_c and H_j, (6x+6y)H, br m), small peaks originated from end groups were observed in 9.95 ppm (H_m, 1H, s) and 7.83–7.12 ppm (H_l, 4H, m); GPC ($CHCl_3$, g/mol): $M_n = 2.03\times10^4$, $M_w/M_n = 1.38$.

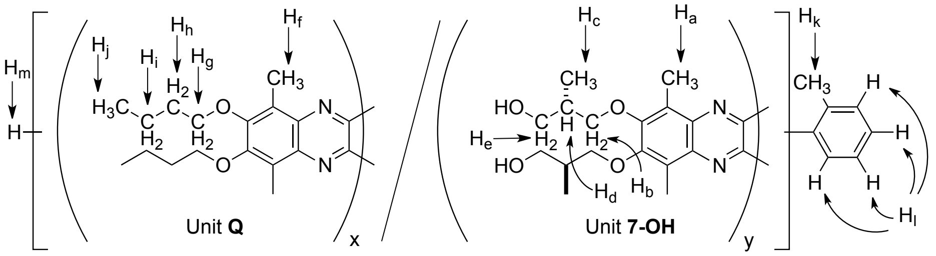
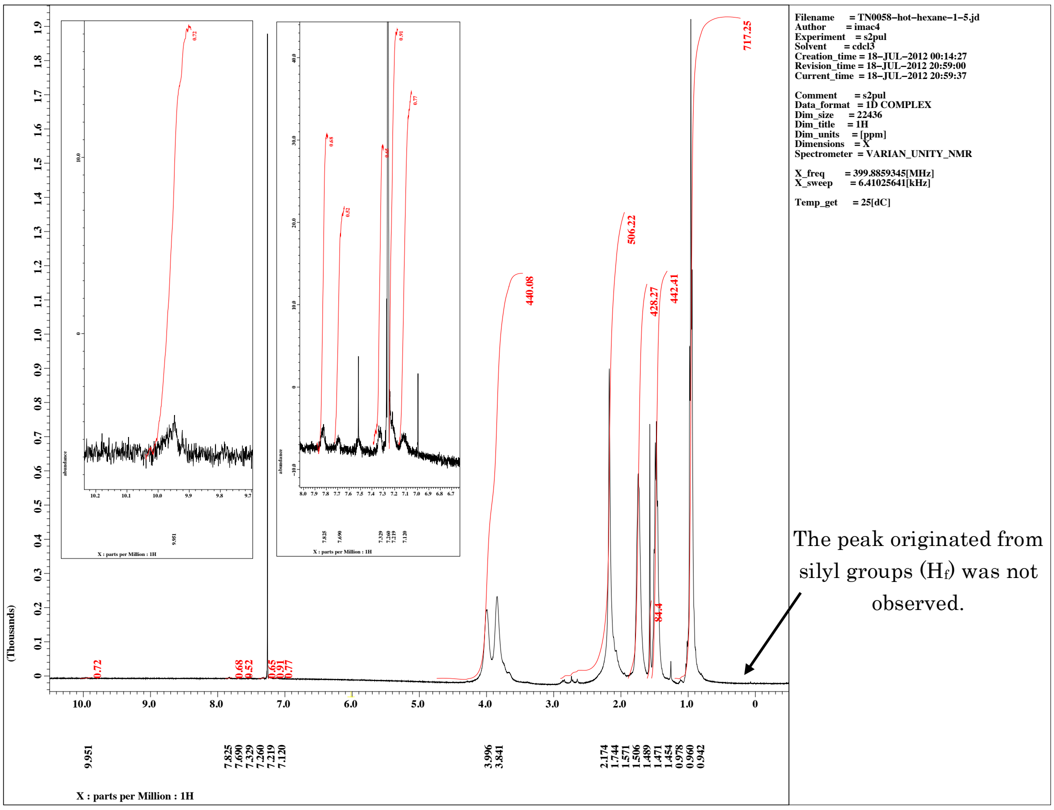


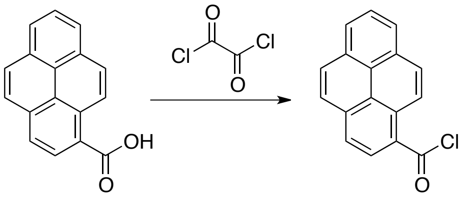
Figure S-3. Structure of polymer **1-OH** with ^{1}H NMR assignment.



The peak originated from silyl groups (H_f) was not observed.

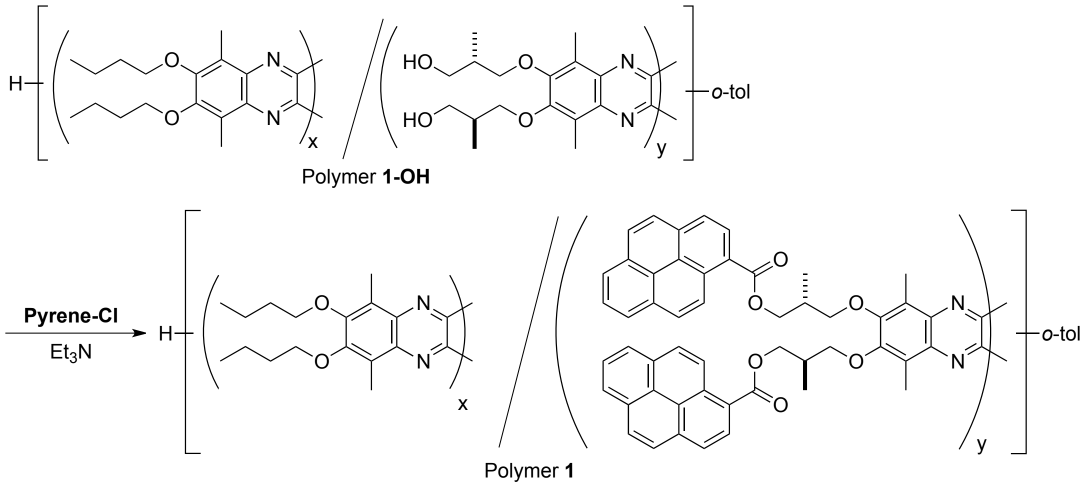
Figure S-4. ^{1}H NMR spectrum of polymer **1-OH** in $CDCl_3$.

The peaks originated from silyl group could not be observed. It indicated that the deprotection proceeded completely. Therefore, the ratio of the units, x/y should be identical to the ratio of polymer **1-Si** (x/y = 19.6).



Pyrene-Cl

The synthesis of Pyrene-Cl: To a solution of 1-pyrenecarboxylic acid (233 mg, 0.948 mmol) in toluene (1.9 mL) was added oxalyl chloride (163 μl, 1.90 mmol). After stirring at 120 °C for 3 h, the reaction mixture was concentrated under reduced pressure, giving **Pyrene-Cl** as yellow powder. The **Pyrene-Cl** was used for other reactions without further purification.



Synthesis of polymer 1: To a mixture of **1-OH** (14.9 mg), Et_3N (2.6 μL, 18.8 μmol), and CH_2Cl_2 (0.43 mL) was added a solution of **Pyrene-Cl** in CH_2Cl_2 (68.5 mmol/L, 275 μL, 18.8 μmol). After stirring for 12 h, the reaction mixture was quenched with water (10 mL) and extracted with $CHCl_3$ (10 mL). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. After filtration and evaporation of solvents, the crude product was purified by preparative GPC, giving polymer **1** as beige solid (13.4 mg, 86%). ^1H NMR (CD_2Cl_2) δ 9.33–8.79 (H_f, 2yH, br m), 8.78– 8.29 (H_g, 2yH, br m), 8.28–7.06 (H_h and H_o, (14y+4)H, br m), 4.52 (H_e, 2yH, br s), 4.47 (H_e, 2yH, br s), 3.85 (H_b and H_j, (4x+4y)H, br s), 2.16 (H_a and H_i and H_n, (6x+6y+3)H, br s), 1.86–1.53 (H_d and H_k, (4x+2y)H, br s), 1.52–1.32 (H_l, 4xH, br m), 1.32–1.06 (H_c, 6yH, br m), 0.93 (H_m, 6xH, t, J = 7.2 Hz), small peaks originated from end groups (H_p, 1H, s) was observed in 10.08 ppm. GPC ($CHCl_3$, g/mol): $M_n = 2.35\times10^4$, $M_w/M_n = 1.31$.

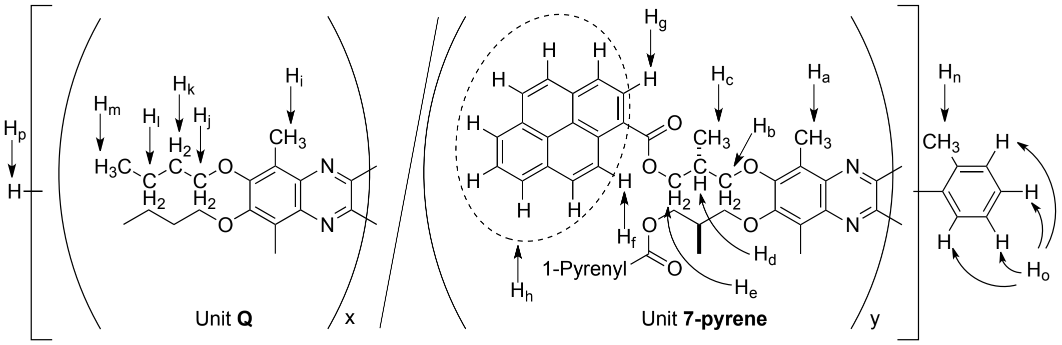


Figure S-5. Structure of polymer **1** with ^1H NMR assignment.

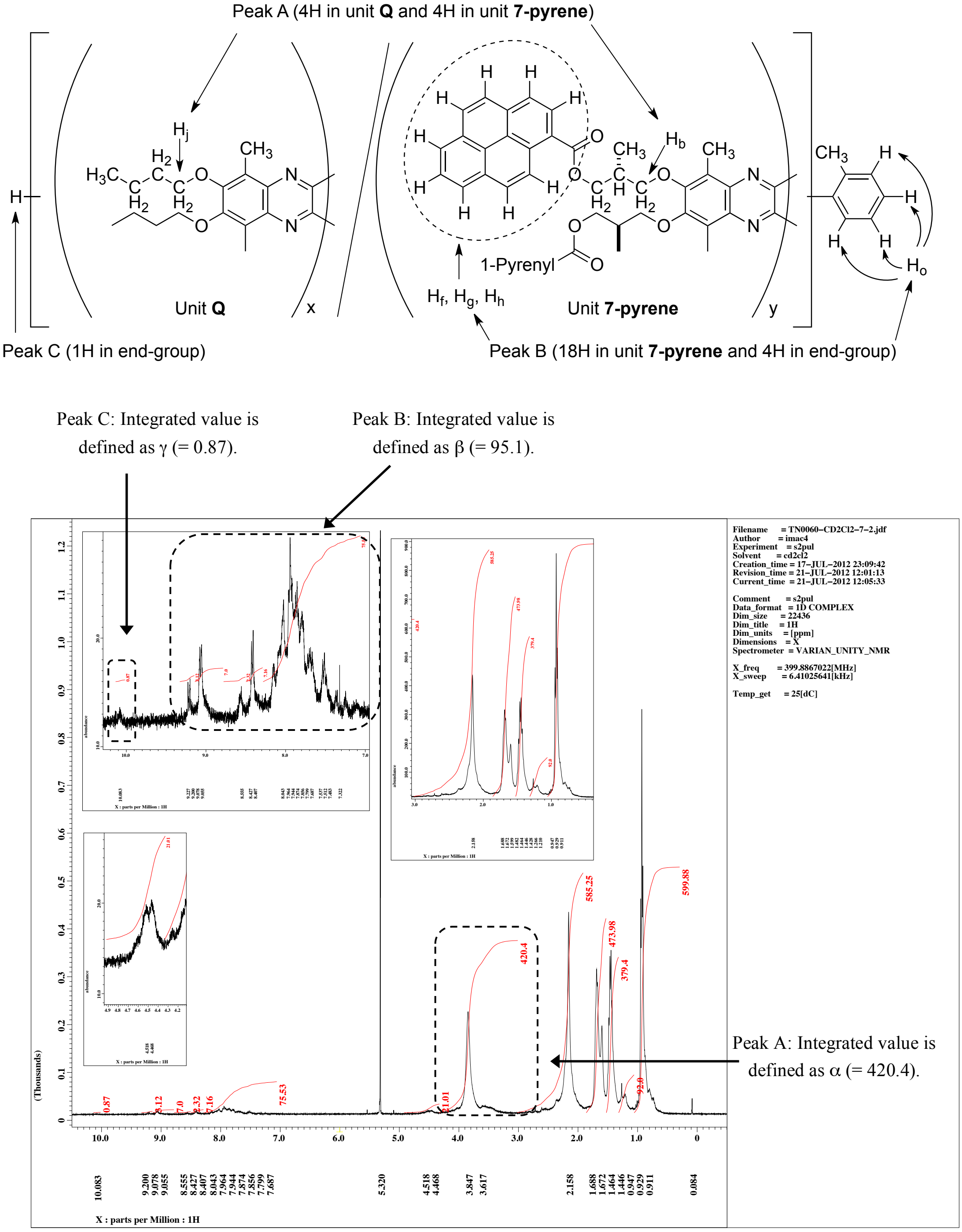


Figure S-6. ^{1}H NMR spectrum of polymer **1** in CD_2Cl_2.

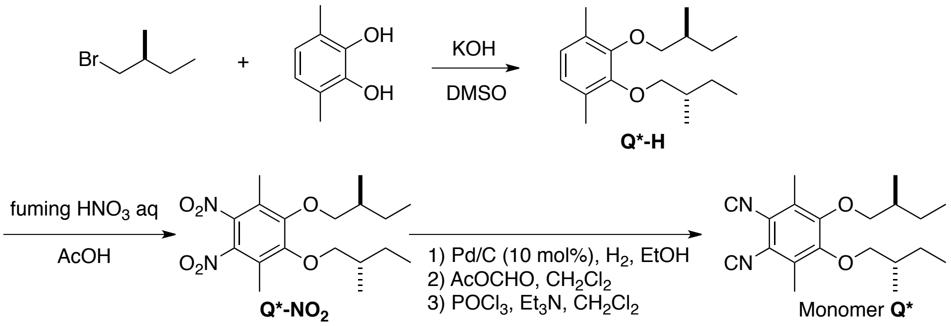
The ratio of pyrenyl group introduced to unit **7** was calculated as follows.

Integrated value of peak A, which originated from unit **7-pyrene** (H_b in Figure X) and unit **Q** (H_j in Figure X), was defined as α. Integrated value of peak B, which is originated from unit **7-pyrene** (H_f, H_g and H_h in Figure X) and end groups (H_n in

Figure X), was defined as β. Integrated value of peak C, which is originated from end groups (H_o in Figure X), was defined as γ. In the case that pyrenyl group is introduced quantitatively, β can be expressed as follows.

$$\beta = 4\gamma + 9\alpha/(2(x/y) + 2) \qquad (2)$$

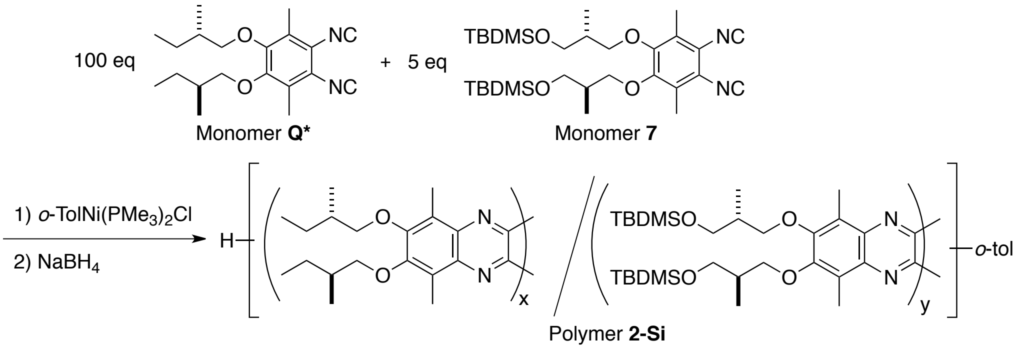
Here, the integrated values were measured as α = 420.4, γ = 0.87, x/y = 19.6. According to the equation (2), β is calculated to be 95.3. Since the calculated value showed good agreement with the observed β (= 95.1), it was confirmed that pyrenyl groups were introduced almost quantitatively (≈ 98%).



Synthesis of Q*-H: To a mixture of 3,6-dimethylcatechol (3.28 g, 23.8 mmol), a potassium hydroxide (10.8 g, 71.4 mmol), and (*S*)-1-bromo-2-methylbutane (10.8 g, 71.4 mmol) was added dimethyl sulfoxide (23.8 mL). After stirring for 7 h, the reaction mixture was quenched with water (100 mL) and extracted with Et_2O (50 mL × 3). The combined organic layer was washed with water (100 mL × 3) and brine (50 mL). The organic layer was dried over Na_2SO_4, filtered, and dried under reduced pressure to give **Q*-H** as colorless liquid, which required no further purification (6.59 g, 99% yield). ^{1}H NMR ($CDCl_3$) δ 6.78 (2H, s), 3.80 (2H, dd, *J* = 5.8, 8.9 Hz), 3.67 (2H, dd, *J* = 6.8, 8.9 Hz), 1.87–1.80 (2H, m), 1.64–1.58 (2H, m), 1.31–1.20 (2H, m), 1.05 (6H, d, *J* = 6.4 Hz), 0.95 (6H, t, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 150.8, 129.8, 125.2, 77.8, 35.9, 26.3, 16.7, 16.0, 11.5; IR (neat) 3018, 2961, 2925, 2876, 2730, 2358, 1582, 1558, 1491, 1463, 1425, 1382, 1280, 1218, 1162, 1107, 1077, 1027, 997, 935, 799, 689, 668 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{30}O_2$ (M^+): 278.2240, found: 278.2249.

Synthesis of Q*-NO$_2$: To fuming nitric acid (9.1 mL) was added dropwise an acetic acid (4.1 mL) solution of **Q*-H** (6.59 g, 29.0 mmol) at 0 °C. After stirring for 1 h, the reaction mixture was quenched with water (200 mL) and extracted with Et_2O (100 mL × 2). The combined organic layer was washed with NaOH aq (5 mol/L, 150 mL × 3), water (150 mL × 3), and brine (150 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was subjected to silica gel column chromatography (hexane/AcOEt = 95/5), giving **Q*-NO$_2$** (4.56 g, 52% yield) as yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.86 (2H, dd, J = 6.0, 9.0 Hz), 3.73 (2H, dd, J = 6.8, 9.0 Hz), 2.29 (6H, s), 1.93–1.81 (2H, m), 1.63–1.53 (2H, m), 1.34–1.23 (2H, m), 1.06 (6H, d, J = 6.8 Hz), 0.96 (6H, t, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 153.1, 140.3, 125.7, 78.8, 35.7, 26.0, 16.5, 11.8, 11.3; IR (neat) 2959, 2938, 2877, 1539, 1468, 1356, 1284, 1247, 1093, 1059, 1017, 939, 831, 788, 757 cm^{-1}. HRMS (EI) m/z calcd for $C_{18}H_{28}N_2O_6$ (M^+): 368.1942, found: 368.1947.

Synthesis of Q*: A mixture of **Q*-NO$_2$** (4.56 g, 12.4 mmol) and 10 wt% Pd/C (0.658 g, 0.619 mmol) in EtOH (62 mL) and THF (12 mL) was stirred for 26 h under H_2 atmosphere. The mixture was filtered through a pad of Celite and dried under vacuum. The residue was purified by silica gel column chromatography (hexane/AcOEt = 50/50) to give a diamine compound as yellow oil. Then, acetic formic anhydride (5.9 g, 67 mmol) was added to the diamine dissolved in CH_2Cl_2 (88 mL). After stirring for 7 h, removal of volatiles under reduced pressure gave a diformate compound as white powder (2.97 g). $POCl_3$ (2.28 mL, 3.75 g, 24.4 mmol) was added to a suspension of the diformate (2.97 g, 8.15 mmol) in Et_3N (11.3 mL) and CH_2Cl_2 (120 mL) at 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was washed with saturated $NaHCO_3$ aq (100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane to hexane/CH_2Cl_2 = 50/50) to give **Q*** as white solid (1.80 g, 67%). ^{1}H NMR ($CDCl_3$) δ 3.80 (2H, dd, J = 6.0, 9.0 Hz), 3.67 (2H, dd, J = 6.8, 9.0 Hz), 2.33 (6H, s), 1.90–1.78 (2H, m), 1.62-1.52 (2H, m), 1.32-1.21 (2H, m), 1.04 (6H, d, J = 6.8 Hz), 0.95 (6H, t, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 171.6, 151.8, 128.6, 35.8, 26.1, 16.5, 12.7, 11.4; IR (neat) 2961, 2114, 1454, 1383, 1337, 1270, 1092, 968, 779 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{28}N_2O_2$ (M^+): 328.2145, found: 328.2151; $[\alpha]_D^{25.7}$ +10.8 (*c* 0.52, $CHCl_3$).



Synthesis of Polymer 2-Si: A solution of *o*-TolNiCl$(PMe_3)_2$ in THF (48.8 mmol/L, 43 μL, 2.1 μmol) was added to a solution of monomer **7** (5.8 mg, 10 μmol) and monomer **Q*** (68.3 mg, 207.8 μmol) in THF (6.0 mL). After stirring for 3 h, $NaBH_4$ (16.5 mg, 436.4 μmol) was added to the reaction mixture and stirred for 1 h. The reaction mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (10 mL). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. After filtration and evaporation of solvents, the crude product was purified by preparative GPC, giving polymer **2-Si** as beige solid (67.9 mg, 92%). ^{1}H NMR ($CDCl_3$) δ 3.84 (H_e and H_i, (2x+4y)H, br s), 3.59 (H_b and H_i, (2x+4y)H, br s), 2.17 (H_a and H_h and H_n, (6x+6y+3)H, br s), 1.84 (H_d and H_j, (4x+2y)H, br s), 1.55 (H_l, 2xH, br s), 1.22 (H_l, 2xH, br s), 1.02 (H_c and H_k, (6x+6y)H, br s), 0.92 (H_m, 6xH, br s), 0.86 (H_g, 18yH, s), 0.00 (H_f, 12yH, s), small peaks originated from end groups were observed in 9.92 ppm (H_p, 1H, s) and 7.83–7.11 ppm (H_o, 4H, m); GPC ($CHCl_3$, g/mol): $M_n = 2.68 \times 10^4$, $M_w/M_n = 1.48$.

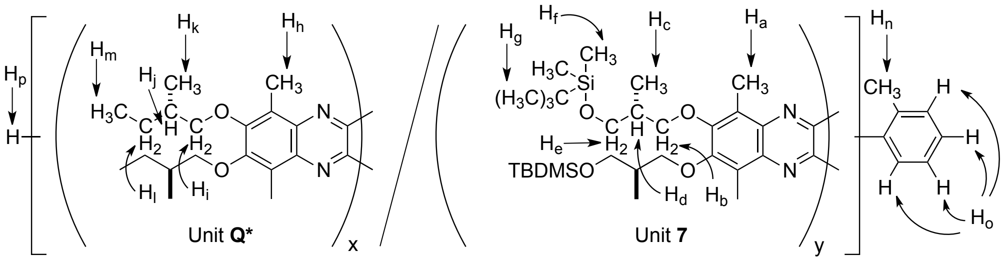
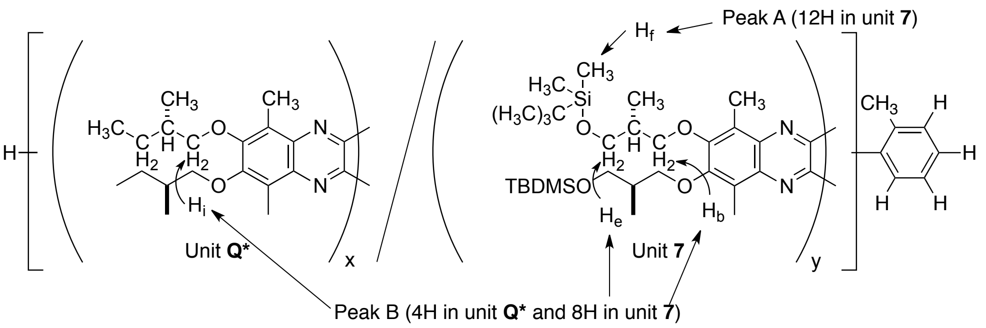


Figure S-7. Structure of polymer **2-Si** with ^{1}H NMR assignment.



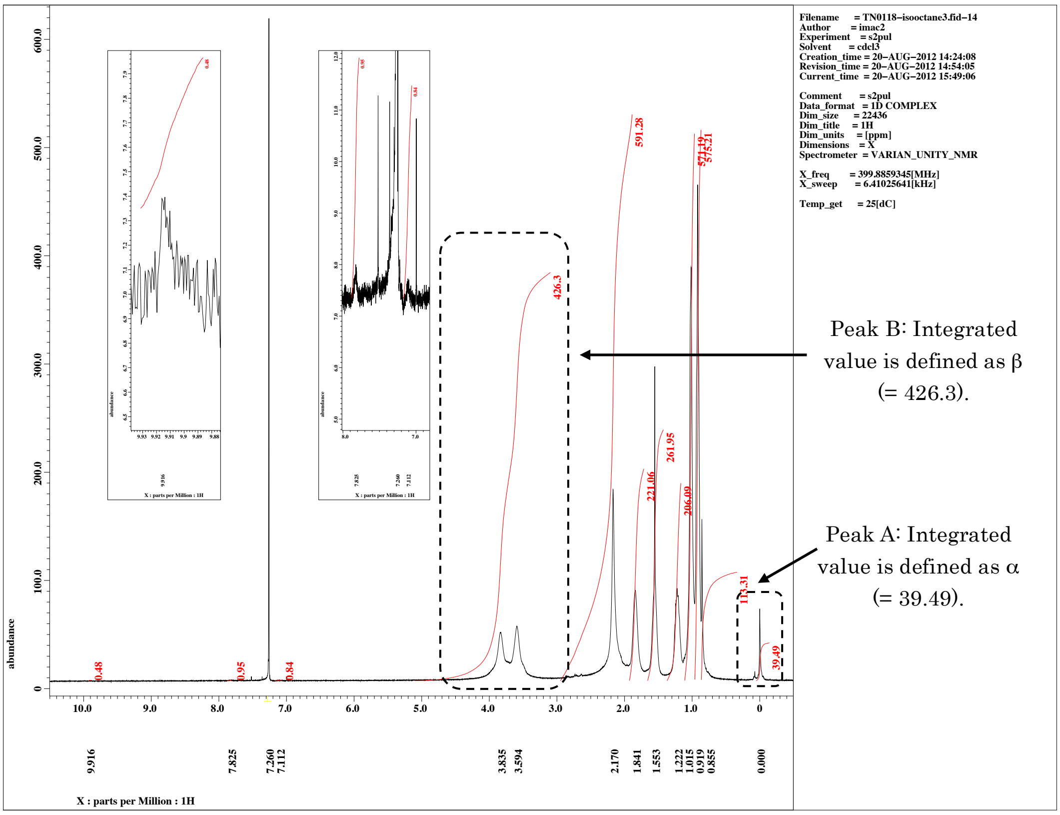
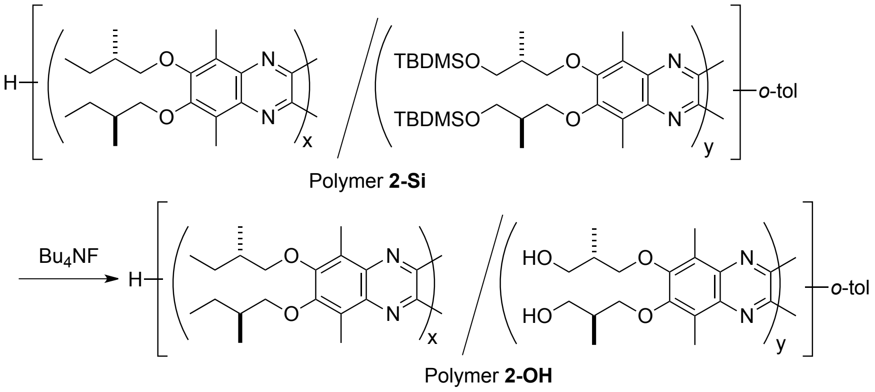


Figure S-8. ^{1}H NMR spectrum of polymer **2-Si** in $CDCl_3$.

The ratio of unit **Q*** and unit **7** (x/y) was calculated as follows. Integrated value of peak A, which is originated from unit **7** (H_f in Figure X), was defined as α. Integrated value of peak B, which is originated from H_b and H_e in unit **Q** and H_i in unit **7**, was defined as β. The ratio of units **Q*** and **7** x/y can be expressed as

$$x/y = 3\beta/\alpha - 2 \qquad (3)$$

Here, the integrated values were measured as, α = 39.49 and β = 426.3. Therefore, we could estimate the ratio as x/y = 30.4.



Synthesis of 2-OH: To a solution of **2-Si** (51.1 mg) in THF (4.4 mL) was added a solution of tetrabutylammonium fluoride in THF (1.0 mol/L, 57 μL, 57 μmol). After stirring for 14 h, the reaction mixture was quenched with water (10 mL) and extracted with $CHCl_3$ (10 mL). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. After filtration and evaporation of solvents, the crude product was purified by preparative GPC, giving polymer **2-OH** as beige solid (47.6 mg, 96%). ^{1}H NMR ($CDCl_3$) δ 3.84 (H_e and H_g, (2x+4y)H, br s), 3.59 (H_b and H_g, (2x+4y)H, br s), 2.17 (H_a and H_f and H_l, (6x+6y+3)H, br s), 1.84 (H_d and H_h, (4x+2y)H, br s), 1.56 (H_j, 4xH, br s), 1.23 (H_c and H_k, (6x+6y)H, br s), 1.02 (H_i, 6xH, br s), 0.92 (H_k, 6xH, br s), small peaks originated from end groups were observed in 10.1 ppm (H_n, 1H, s) and 7.82–7.12 ppm (H_l, 4H, m); GPC ($CHCl_3$, g/mol): $M_n = 2.63 \times 10^4$, $M_w/M_n = 1.33$.

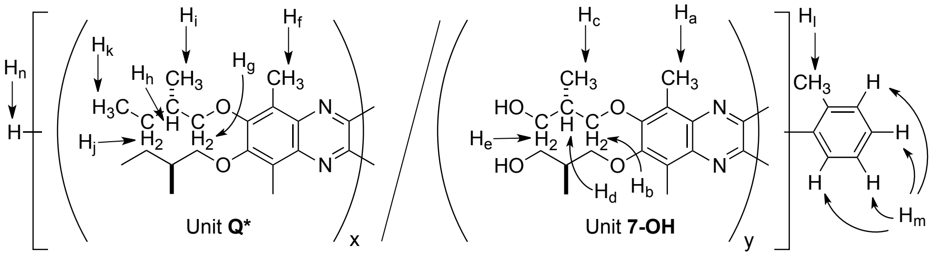
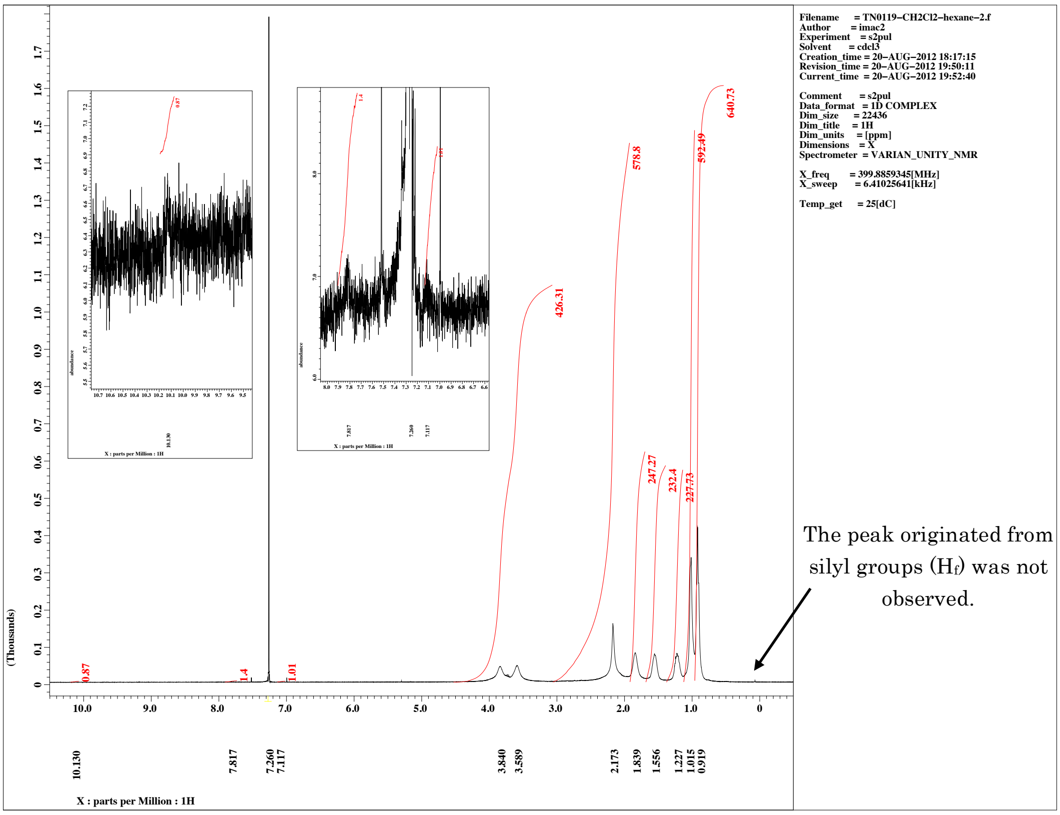


Figure S-9. Structure of polymer **2-OH** with ^{1}H NMR assignment.



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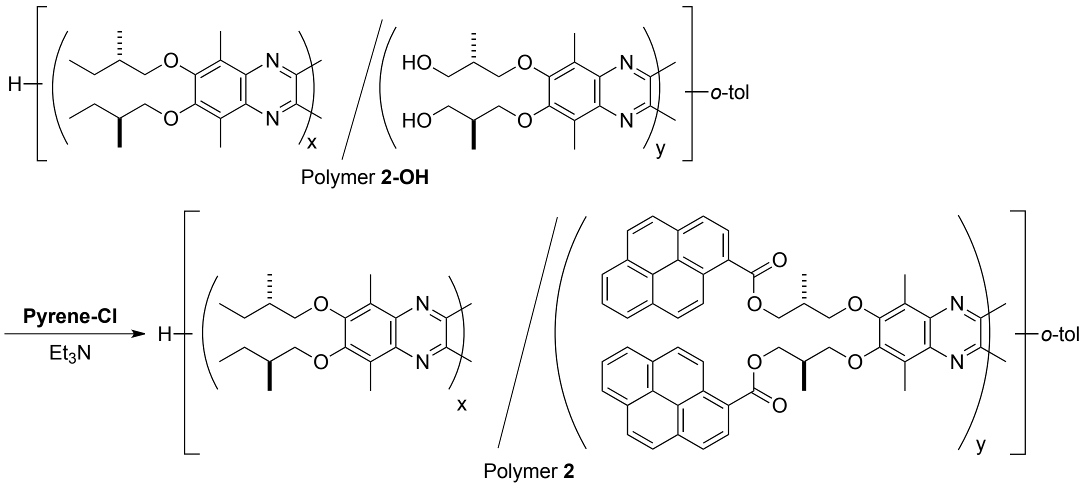
The peak originated from silyl groups (H_f) was not observed.

Figure S-10. ^{1}H NMR spectrum of polymer **2-OH** in $CDCl_3$.

The peaks originated from silyl group could not be observed. It indicated that the deprotection proceeded completely. Therefore, the ratio of the units, x/y should be identical to the ratio of polymer **2-Si** (x/y = 30.4).



Synthesis of Polymer 2: To a mixture of **2-OH** (45.6 mg), Et_3N (7.4 µL, 52.9 µmol) and CH_2Cl_2 (1.2 mL) was added a solution of **Pyrene-Cl** in CH_2Cl_2 (68.5 mmol/L, 772 µL, 52.9 µmol). After stirring for 16 h, the reaction mixture was quenched with water (10 mL) and extracted with $CHCl_3$ (10 mL). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. After filtration and evaporation of solvents, the crude product was purified by preparative GPC, giving polymer **Polymer 2** as beige solid (42.6 mg, 88%). ^{1}H NMR (CD_2Cl_2) δ 9.44–8.78 (H_f, 2yH, br m), 8.63–8.31 (H_g, 2yH, br m), 8.26–6.90 (H_h and H_p, (14y+4)H, br m), 4.50 (H_e, 2yH, br s), 4.46 (H_e, 2yH, br s), 3.77 (H_j, 2xH, br s), 3.64 (H_b, 4yH, br s), 3.46 (H_j, 2xH, br s), 2.15 (H_a and H_i and H_o, (6x+6y+3)H, br s), 1.79 (H_d and H_k, (4x+2y)H, br s), 1.55 (H_m, 2xH, br s), 1.39–1.11 (H_m, 2xH, br m), 0.99 (H_l, 6xH, d, J = 6.0 Hz), 0.90 (H_n, 6xH, t, J = 7.0 Hz), 0.74 (H_c, 6yH, br s), small peaks originated from end groups (H_q, 1H, s) was observed in 10.0 ppm. GPC ($CHCl_3$, g/mol): $M_n = 2.88 \times 10^4$, $M_w/M_n = 1.31$.

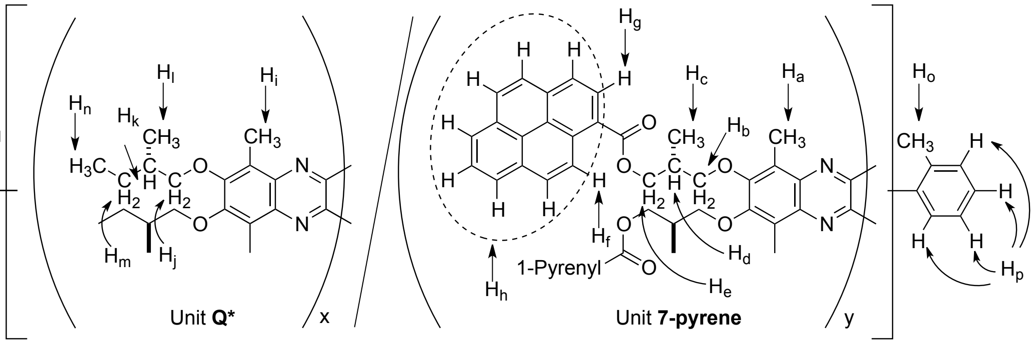
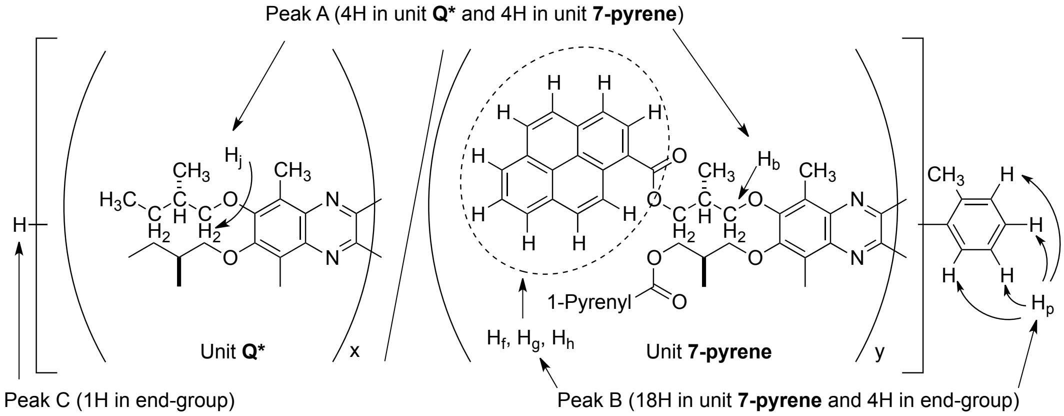


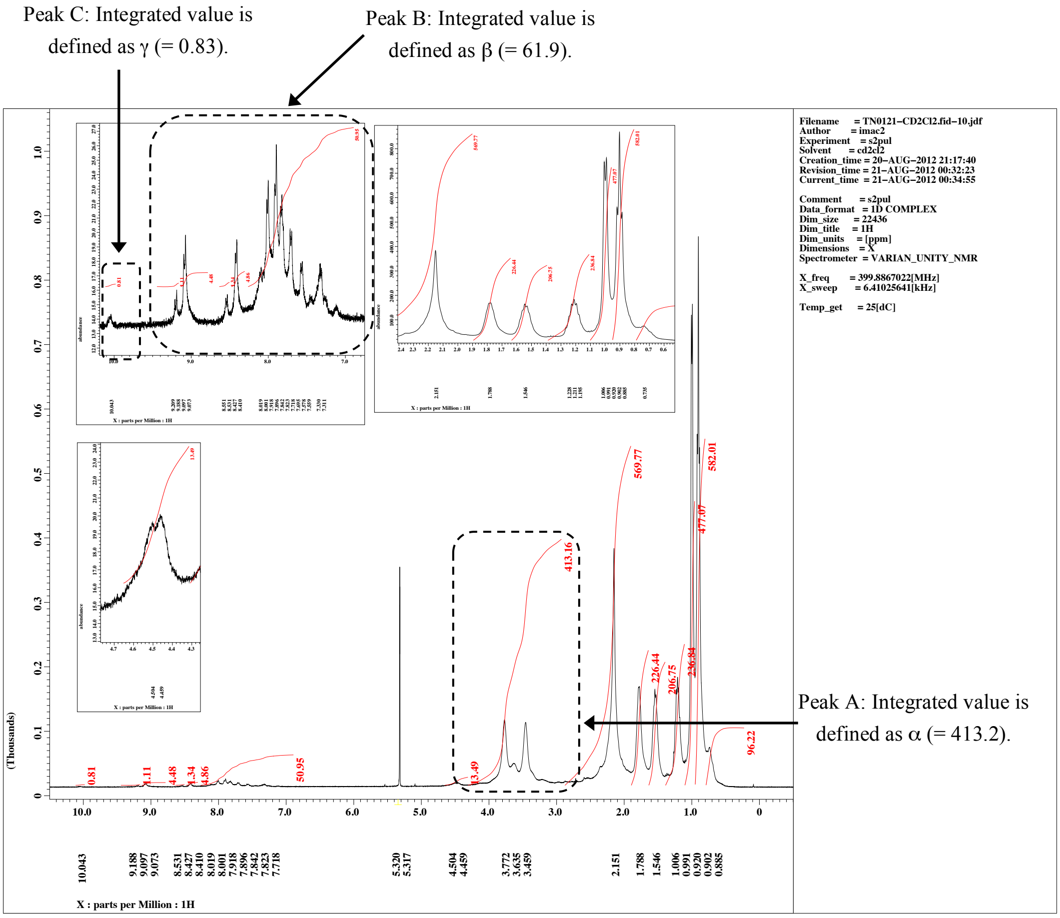
Figure S-11. Structure of polymer **2** with ^{1}H NMR assignment.



Peak A (4H in unit **Q*** and 4H in unit **7-pyrene**)

Peak C (1H in end-group)

Peak B (18H in unit **7-pyrene** and 4H in end-group)



Peak C: Integrated value is defined as γ (= 0.83).

Peak B: Integrated value is defined as β (= 61.9).

Peak A: Integrated value is defined as α (= 413.2).

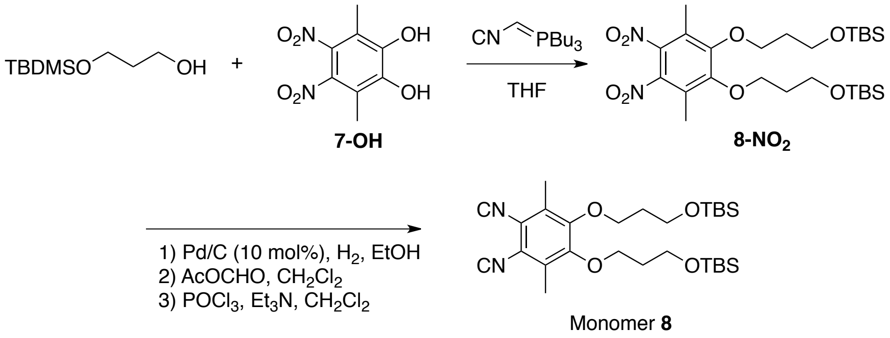
Figure S-12. ^{1}H NMR spectrum of polymer **2** in CD_2Cl_2.

The ratio of pyrenyl group introduced to unit **7** was calculated as follows.

Integrated value of peak A, which originated from unit **7-pyrene** (H_b in Figure X) and unit **Q*** (H_j in Figure X), was defined as α. Integrated value of peak B, which is originated from unit **7-pyrene** (H_f, H_g and H_h in Figure X) and end groups (H_p in Figure X), was defined as β. Integrated value of peak C, which is originated from end groups (H_q in Figure X), was defined as γ. In the case that pyrenyl group is introduced quantitatively, β can be expressed as follows.

$$\beta = 4\gamma + 9\alpha/(2(x/y) + 2) \qquad (4)$$

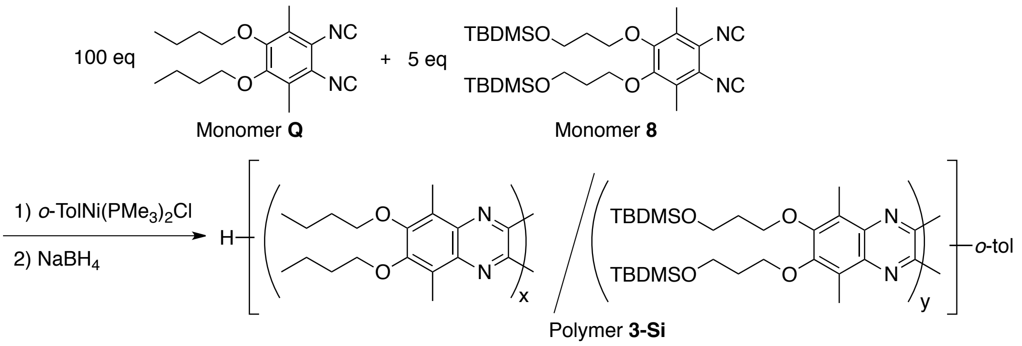
Here, the integrated values were measured as $\alpha = 413.2$, $\gamma = 0.81$, $x/y = 30.4$. According to the equation (2), β is calculated to be 62.5. Since the calculated value showed good agreement with the observed β (= 62.7), it was confirmed that pyrenyl groups were introduced quantitatively (≈ 100%).



The synthesis of 8-NO$_2$: To a mixture of (3-((*tert*-butyldimethylsilyl)oxy)propan-1-ol (2.00 g, 10.5 mmol) and **7-OH** (0.799 g, 3.50 mmol) was added a solution of cyanomethylenetributylphosphorane in THF (0.92 mol/L, 11 mL, 10.5 mmol). After stirring at 80 °C for 24 h under microwave irradiation, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt = 95/5) and preparative GPC to give the product **8-NO$_2$** (0.80 g) as pale yellowish green oil in 40% yield. ^{1}H NMR ($CDCl_3$) δ 4.11 (4H, t, *J* = 6.2 Hz), 3.80 (4H, t, *J* = 6.2 Hz), 2.29 (6H, s), 1.97 (4H, tt, *J* = 6.2, 6.2 Hz), 0.89 (18H, s), 0.05 (12H, s); ^{13}C NMR ($CDCl_3$): δ 152.9, 140.3, 125.8, 70.7, 59.1, 33.3, 25.8, 18.2, 11.7, −5.4; IR (neat) 2856, 1541, 1350, 1250, 1074, 833, 775 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{49}N_2O_8Si_2$ ($M+H^+$): 573.3022, found: 573.3020.

The synthesis of monomer 8: A suspension of **8-NO$_2$** (0.799 g, 1.39 mmol) and 10 wt% Pd/C (74.2 mg, 69.7 μmol) in EtOH (7.0 mL) was stirred for 62 h under H_2

atmosphere. The mixture was filtered through a pad of Celite. The filtrate was evaporated under vacuum and purified by silica gel column chromatography (hexane/AcOEt = 60/40), giving a diamine compound as yellow oil. To a solution of the diamine in CH_2Cl_2 (2.6 mL) was added acetic formic anhydride (0.31 mL, 4.2 mmol). After stirring for 14 h, removal of volatiles under reduced pressure gave a diformate compound as white solid. $POCl_3$ (0.34 mL, 3.7 mmol) was added to a solution of the diformate and Et_3N (1.7 mL) in CH_2Cl_2 (18.3 mL) at 0 °C. After stirring for 20 min at 0 °C, the reaction mixture was washed with saturated $NaHCO_3$ aq (10 mL ×3). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane to hexane/CH_2Cl_2 = 50/50) to give monomer **8** (0.278 g) as green oil in 15% yield. ^1H NMR ($CDCl_3$) δ 4.04 (4H, t, J = 6.2 Hz), 3.79 (4H, t, J = 6.2 Hz), 2.33 (6H, s), 1.94 (4H, tt, J = 6.2, 6.2 Hz), 0.88 (18H, s), 0.05 (12H, s); ^{13}C NMR ($CDCl_3$): δ 171.6, 151.5, 128.7, 119.9, 70.4, 59.2, 33.3, 25.8, 18.2, 12.6, −5.4; IR (neat) 2928, 2116, 1462, 1337, 1254, 1090, 833, 773 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{52}N_3O_4Si_2$ ($M+NH_4^+$): 550.3491, found: 550.3485.



Synthesis of 3-Si: A solution of o-TolNiCl(PMe_3)$_2$ in THF (48.8 mmol/L, 42.6 µL, 2.08 µmol) was added to a solution of monomer **8** (5.8 mg, 10 µmol) and monomer **Q** (68.3mg, 208 µmol) in THF (6.0 mL). After stirring for 13 h, $NaBH_4$ (16.5 mg, 436 µmol) was added to the reaction mixture and stirred for 1 h. The reaction mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (10 mL). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. After filtration and evaporation of solvents, the crude product was purified by preparative GPC, giving polymer **3-Si** as beige solid (67.9 mg, 92%). ^1H NMR ($CDCl_3$) δ 4.01 (H_b and H_h, (2x+4y)H, br s), 3.84

(H$_d$ and H$_h$, (2x+4y)H, br s), 2.18 (H$_a$ and H$_g$ and H$_m$, (6x+6y+3)H, br s), 1.75 (H$_c$ and H$_i$, (4x+4y)H, br s), 1.48 (H$_j$, 4xH, br s), 0.97 (H$_k$ and H$_l$, (6x+6y)H, br m), 0.87 (H$_f$, 18yH, s), 0.03 (H$_e$, 12yH, s), small peaks originated from end groups were observed in 9.95 ppm (H$_n$, 1H, s) and 7.83–7.12 ppm (H$_m$, 4H, m); GPC (CHCl$_3$, g/mol): $M_n = 3.65 \times 10^4$, $M_w/M_n = 1.24$.

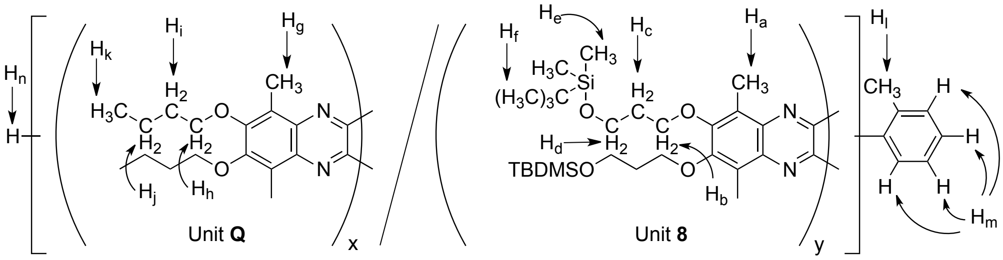


Figure S-13. Structure of polymer **3-Si** with ^{1}H NMR assignment.

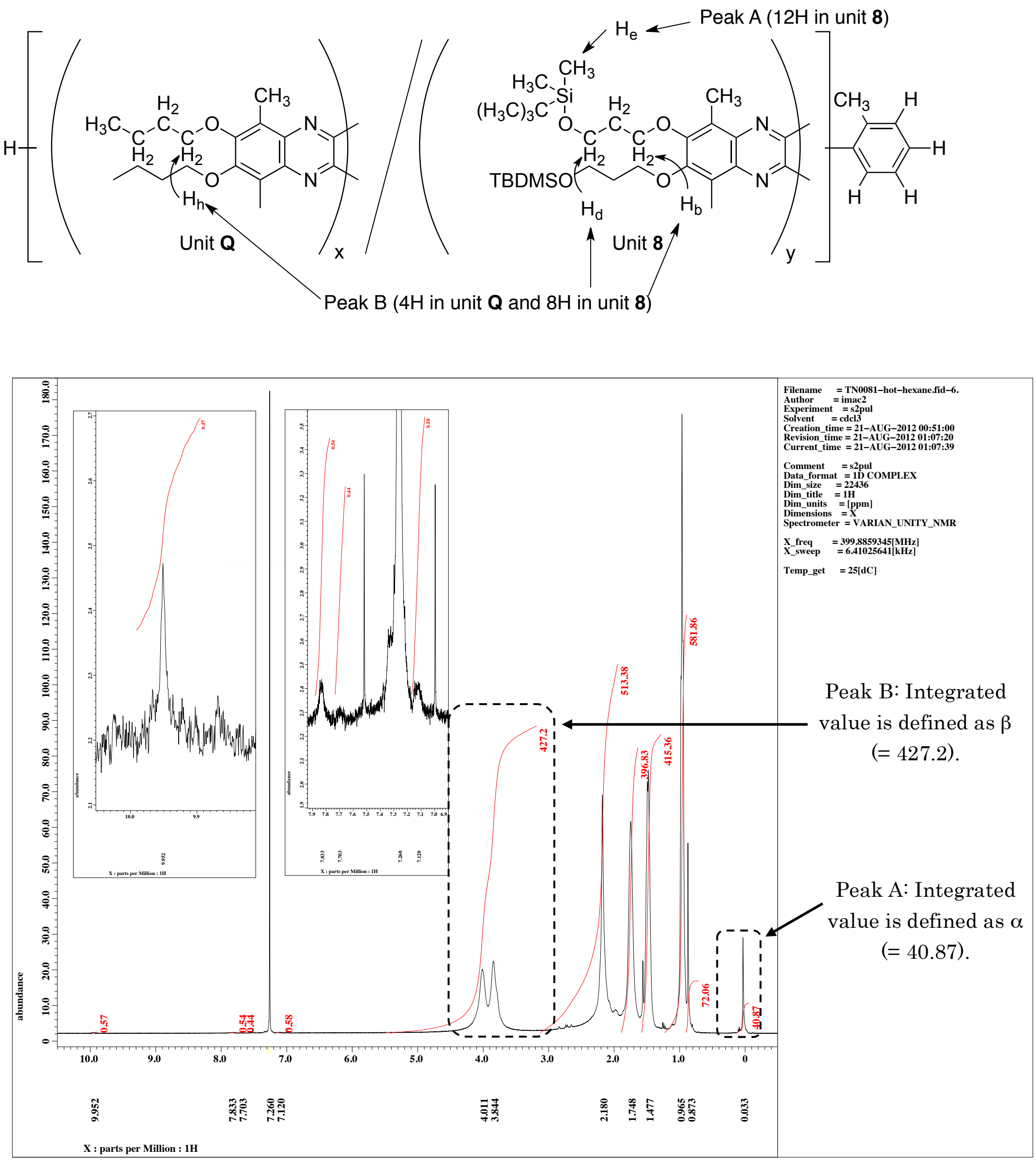
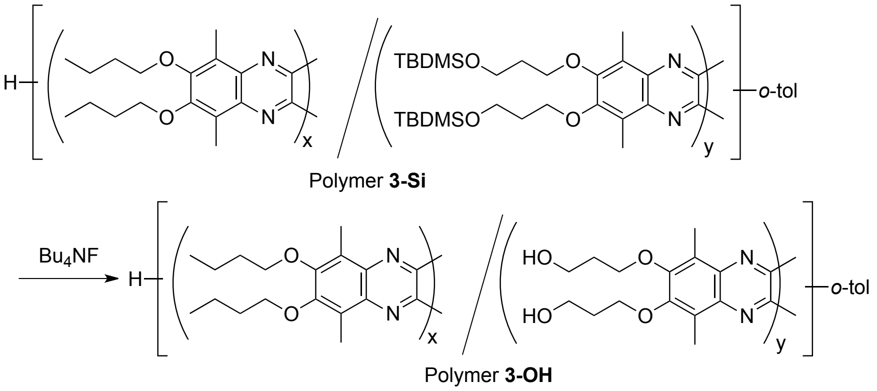


Figure S-14. ^{1}H NMR spectrum of polymer **3-Si** in $CDCl_3$.

The ratio of unit **Q** and unit **8** (x/y) was calculated as follows. Integrated value of peak A, which is originated from unit **8** (H_e in Figure X), was defined as α. Integrated value of peak B, which is originated from H_b and H_d in unit **Q** and H_h in unit **7**, was defined as β. The ratio of units **Q** and **8** x/y can be expressed as

$$x/y = 3\beta/\alpha - 2 \tag{3}$$

Here, the integrated values were measured as, a = 40.87 and b = 427.2. Therefore, we could estimate the ratio as x/y = 29.4.



Synthesis of 3-OH: To a solution of **3-Si** (47.1 mg) in THF (4.1 mL) was added a solution of tetrabutylammonium fluoride in THF (1.0 mol/L, 53 μL, 53 μmol). After stirring for 14 h, the reaction mixture was quenched with water (10 mL) and extracted with $CHCl_3$ (10 mL). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. After filtration and evaporation of solvents, the crude product was purified by preparative GPC, giving polymer **3-OH** as beige solid (39.4 mg, 86%). ^{1}H NMR ($CDCl_3$) δ 4.02 (H_b and H_f, (2x+4y)H, br s), 3.85 (H_d and H_f, (2x+4y)H, br s), 2.18 (H_a and H_e and H_j, (6x+6y+3)H, br s), 1.75 (H_c and H_g, (4x+4y)H, br s), 1.59–1.20 (H_h, 4xH, br m), 0.97 (H_i, 6xH, t, J = 6.4 Hz), small peaks originated from end groups were observed in 9.95 ppm (H_l, 1H, s) and 7.83–7.13 ppm (H_k, 4H, m); GPC ($CHCl_3$, g/mol): $M_n = 3.10 \times 10^4$, $M_w/M_n = 1.18$.

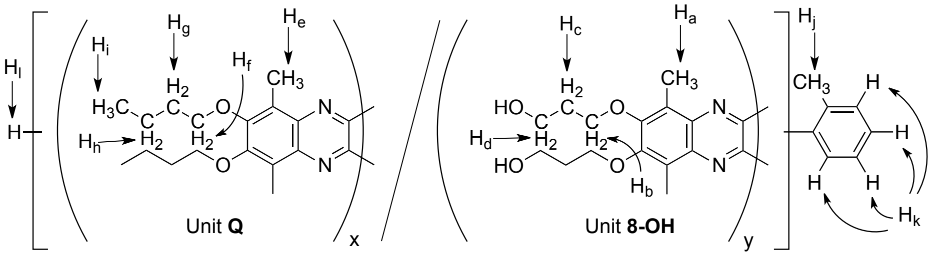
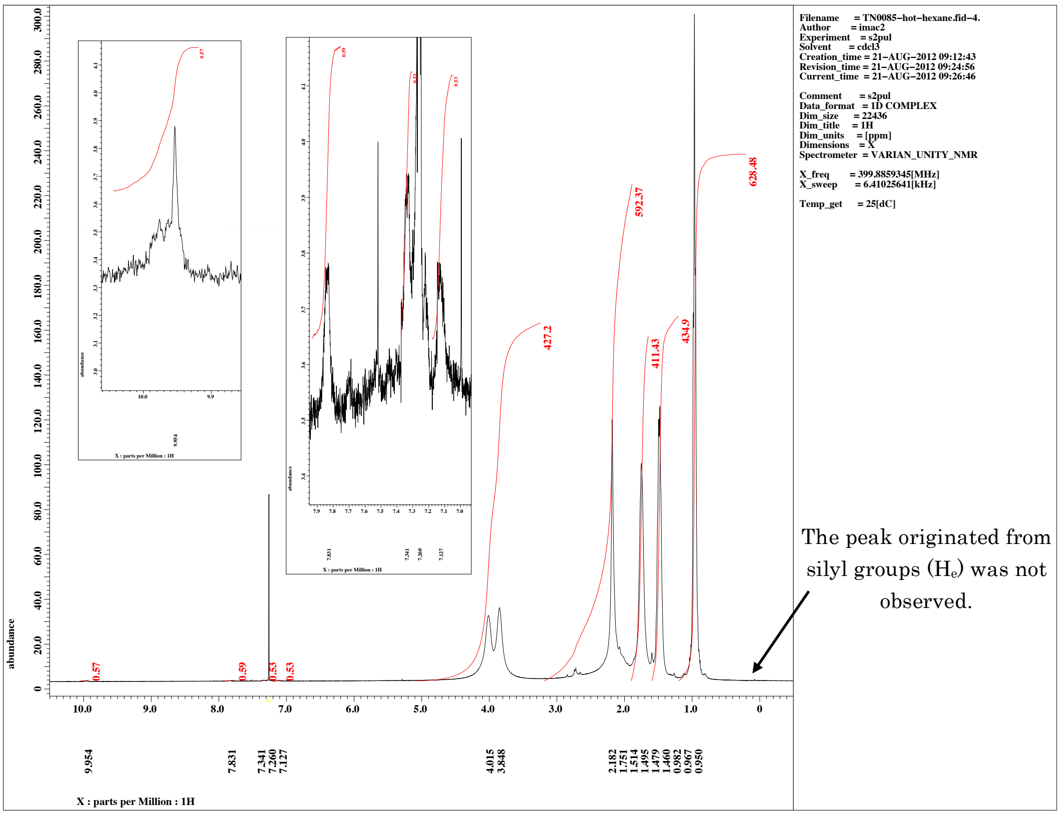


Figure S-15. Structure of polymer **3-OH** with ^{1}H NMR assignment.



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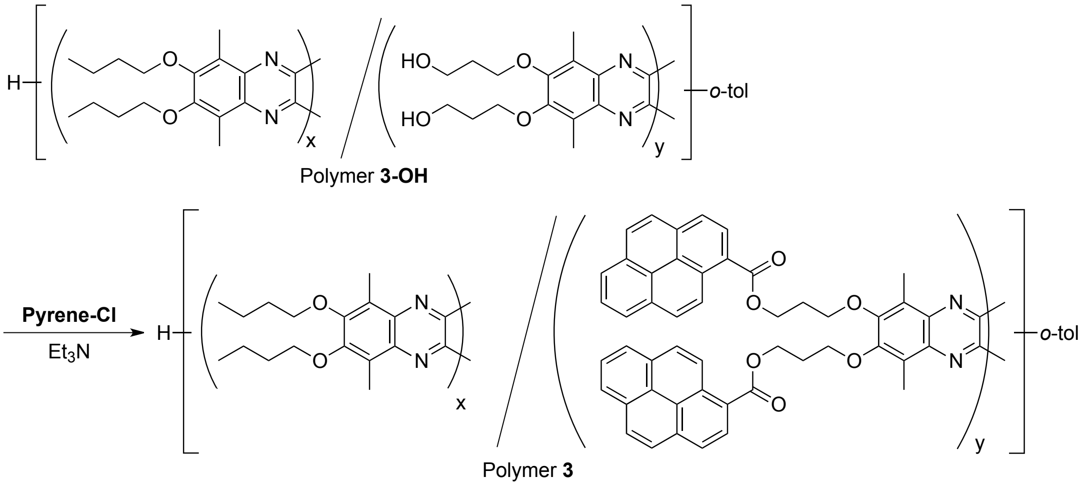
The peak originated from silyl groups (H_e) was not observed.

Figure S-16. ^{1}H NMR spectrum of polymer **2-OH** in $CDCl_3$.

The peaks originated from silyl group could not be observed. It indicated that the deprotection proceeded completely. Therefore, the ratio of the units, x/y should be identical to the ratio of polymer **3-Si** (x/y = 29.4).



Synthesis of Polymer 3: To a mixture of **3-OH** (39.3 mg), Et_3N (6.4 µL, 45.8 µmol) and CH_2Cl_2 (1.1 mL) was added a solution of **Pyrene-Cl** in CH_2Cl_2 (68.5 mmol/L, 669 µmol, 45.8 µmol). After stirring for 12 h, the reaction mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (10 mL). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. After filtration and evaporation of solvents, the crude product was purified by preparative GPC, giving polymer **Polymer 3** as beige solid (36.6 mg, 87%). ^{1}H NMR (CD_2Cl_2) δ 9.42–8.98 (H_e, 2yH, br m), 8.61–8.27 (H_f, 2yH, br m), 8.25–6.95 (H_g and H_n, (14y+4)H, br m), 4.65 (H_d, 4yH, br s), 3.85 (H_b and H_i, (4x+4y)H, br s), 2.16 (H_a and H_h and H_m, (6x+6y+3)H, br s), 1.69 (H_j, 4xH, br s), 1.54–1.33 (H_k, 4xH, br m), 1.21 (H_c, 6yH, br s), 0.93 (H_l, 6xH, t, J = 7.2 Hz), small peaks originated from end groups (H_o, 1H, s) was observed in 10.04 ppm. GPC ($CHCl_3$, g/mol): $M_n = 3.55\times10^4$, $M_w/M_n = 1.14$.

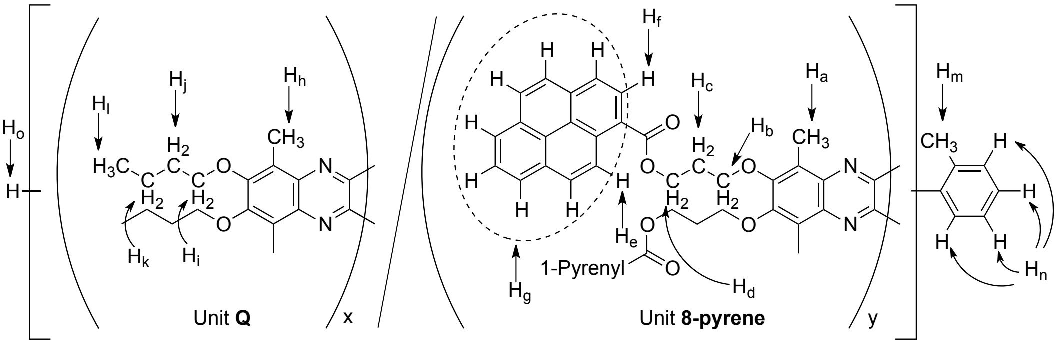


Figure S-17. Structure of polymer **3** with ^{1}H NMR assignment.

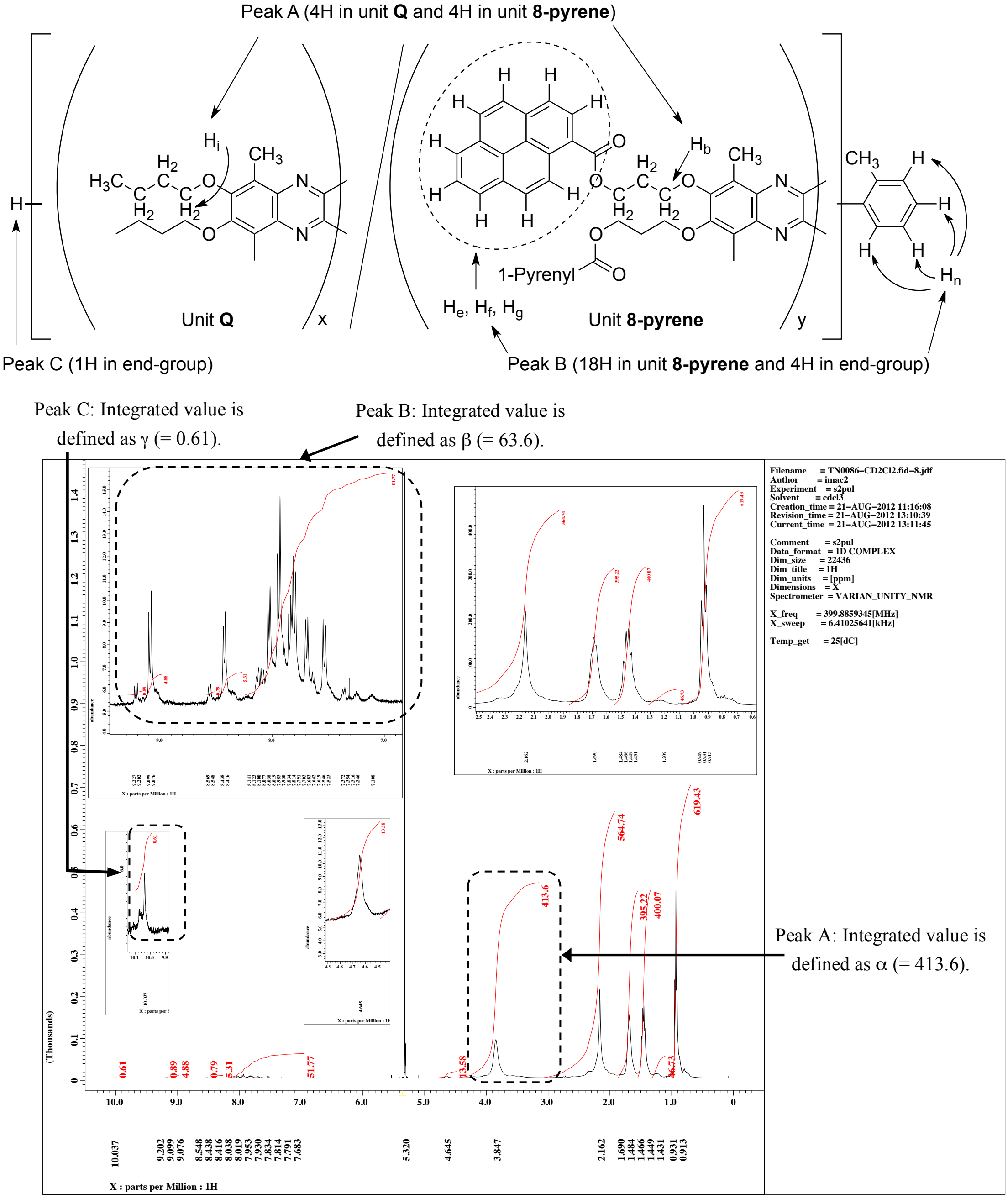


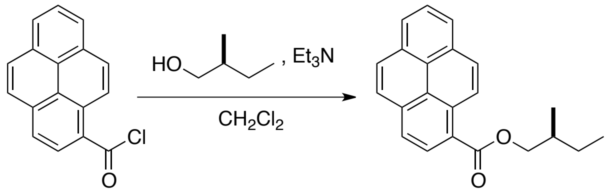
Figure S-18. ^{1}H NMR spectrum of polymer **3** in CD_2Cl_2.

The ratio of pyrenyl group introduced to unit **7** was calculated as follows.

Integrated value of peak A, which originated from unit **8-pyrene** (H_b in Figure X) and unit **Q** (H_i in Figure X), was defined as α. Integrated value of peak B, which is originated from unit **8-pyrene** (H_e, H_f and H_g in Figure X) and end groups (H_n in Figure X), was defined as β. Integrated value of peak C, which is originated from end groups (H_o in Figure X), was defined as γ. In the case that pyrenyl group is introduced quantitatively, β can be expressed as follows.

$$\beta = 4\gamma + 9\alpha/(2(x/y) + 2) \tag{2}$$

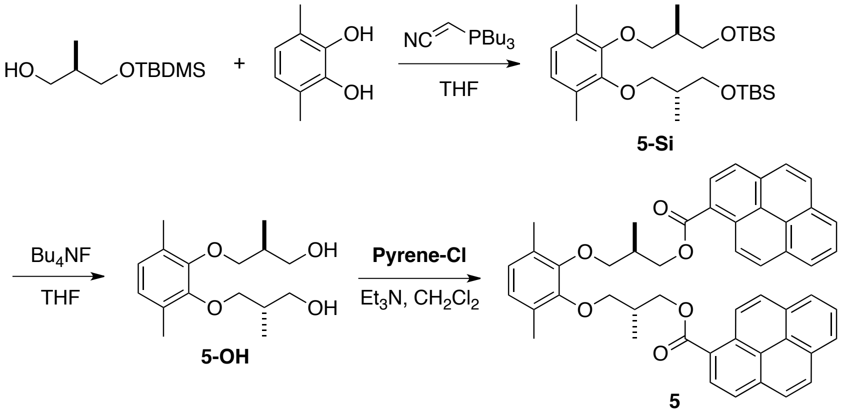
Here, the integrated values were measured as $\alpha = 413.6$, $\gamma = 0.61$, $x/y = 29.4$. According to the equation (2), β is calculated to be 63.7. Since the calculated value showed good agreement with the observed β (= 63.6), it was confirmed that pyrenyl groups were introduced quantitatively (≈ 100%).



Pyrene-Cl

4

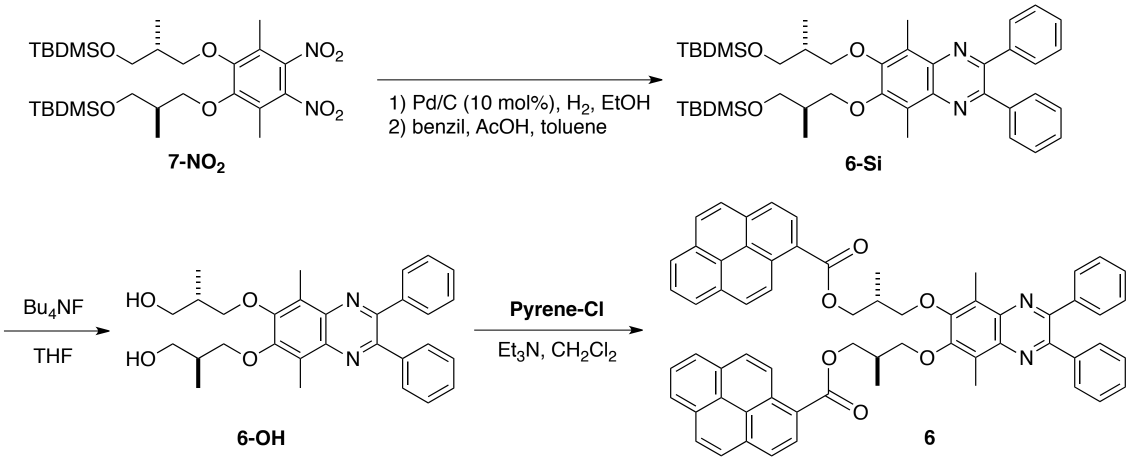
Synthesis of model 4: To a solution of **Pyrene-Cl** in CH_2Cl_2 (0.20 mol/L, 4.7 mL, 950 μmol) were added Et_3N (529 μl, 3.79 mmol) and (*S*)-2-methylbutanol (103 μl, 0.948 mmol). After stirring for 18 h, the reaction mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with water (10 mL × 2) and brine (10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt = 90/10) to give **4** (288 mg) as yellowish green oil in the yield of 96%. ^{1}H NMR ($CDCl_3$) δ 9.29 (1H, d, *J* = 9.6 Hz), 8.64 (1H, d, *J* = 7.6 Hz), 8.28 (1H, d, *J* = 7.0 Hz), 8.26 (1H, d, *J* = 7.0 Hz), 8.25 (1H, d, *J* = 9.6 Hz), 8.19 (1H, d, *J* = 9.2 Hz), 8.19 (1H, d, *J* = 7.6 Hz), 8.10 (1H, d, *J* = 9.2 Hz), 8.07 (1H, t, *J* = 7.0 Hz), 4.41 (1H, dd, *J* = 6.0, 10.8 Hz) 4.32 (1H, dd, *J* = 6.8, 10.8 Hz), 2.06–1.95 (1H, m), 1.70–1.62 (1H, m), 1.45–1.34 (1H, m), 1.13 (3H, d, *J* = 6.8 Hz), 1.03 (3H, t, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$): δ167.7, 133.8, 130.8, 130.5, 129.9, 129.1, 128.9, 127.9, 126.6 , 125.80, 125.78 , 125.7, 124.6, 124.3, 123.7, 123.3, 69.6, 34.3, 26.2, 16.6, 11.2; IR (neat) 2961, 1705, 1248, 1229, 1132, 1086, 1045, 976, 837, 708 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{20}O_2$ (M^+): 316.1458, found: 316.1469; $[\alpha]_D^{26.5}$ +1.4 (*c* 1.0, $CHCl_3$).



Synthesis of 5-Si: To a mixture of (*R*)-3-((*tert*-butyldimethylsilyl)oxy)-2-methylpropan-1-ol (139 mg, 0.680 mmol), 3,6-dimethylcatechol (31.3 mg, 0.227 mmol) was added a solution of cyanomethylenetributylphosphorane in THF (0.92 mol/L, 740 μL, 0.68 mmol). After stirring at 80 °C for 24 h under microwave irradiation, the reaction mixture was concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography (PTLC, hexane/AcOEt = 90/10) and preparative GPC to give **5-Si** (53.8 mg) as colorless oil in 47% yield. ^{1}H NMR ($CDCl_3$) δ 6.77 (2H, s), 3.88 (2H, dd, $J = 6.4, 9.0$ Hz), 3.77 (2H, dd, $J = 6.0, 9.0$ Hz), 3.70 (2H, dd, $J = 5.6, 10.0$ Hz), 3.62 (2H, dd, $J = 6.0, 10.0$ Hz), 2.21 (6H, s), 2.14–2.06 (2H, m), 1.05 (6H, d, $J = 6.8$ Hz), 0.89 (18H, s), 0.04 (12H, s); ^{13}C NMR ($CDCl_3$): δ 150.7, 129.8, 125.2, 74.8, 65.2, 37.2, 25.9, 18.3, 15.9, 14.2, −5.40, −5.42; IR (neat) 2928, 1462, 1250, 1074, 1028, 1005, 833, 773 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{55}O_4Si_2$ (M+H$^+$): 511.3633, found: 511.3634.

Synthesis of 5-OH: To a solution of **5-Si** (52.7 mg, 0.103 mmol) in THF (3 mL) was added a solution of tetrabutylammonium fluoride in THF (1.0 mol/L in THF, 0.41 mL, 0.41 mmol). After stirring for 16 h, the reaction mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (15 mL). The organic layer was washed with water (15 mL × 2) and brine (15 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by PTLC (hexane/AcOEt = 65/35) to give **5-OH** (21.9 mg) as colorless oil in 75% yield. ^{1}H NMR ($CDCl_3$) δ 6.82 (2H, s), 3.92 (2H, dd, $J = 7.4, 9.1$ Hz), 3.84 (2H, dd, $J = 4.8, 9.1$ Hz), 3.79 (2H, dd, $J = 4.2, 10.9$ Hz), 3.73 (2H, dd, $J = 6.8, 10.9$ Hz), 2.87 (2H, s), 2.29–2.17 (2H, m), 2.24 (6H, s), 1.02 (6H, d, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$): δ 150.3, 129.8, 125.9, 76.7, 66.2, 36.5, 15.9, 13.6; IR (neat) 3331, 2924, 1462, 1279, 1217, 1073, 1028, 1003, 800 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{27}O_4$ (M+H$^+$): 283.1904, found: 283.1899.

Synthesis of model 5: To a mixture of **Pyrene-Cl** (82.1 mg, 77.6 mmol), Et_3N (43.2 μL, 0.310 mmol), and CH_2Cl_2 (4.5 mL) was added **5-OH** (21.9 mg, 77.6 μmol). After stirring for 19 h, the reaction mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (10 mL). The organic layer was washed with water (10 mL × 2) and brine (10 mL). The organic layer was dried over Na_2SO_4, filtered, and dried under reduced pressure. The residue was purified by PTLC (hexane/AcOEt = 90/10) to give **5** (17.8 mg) as green oil in 31% yield. ^{1}H NMR ($CDCl_3$) δ 9.18 (2H, d, *J* = 9.4 Hz), 8.50 (2H, d, *J* = 7.8 Hz), 8.16 (2H, d, *J* = 7.6 Hz), 8.13 (2H, d, *J* = 7.6 Hz), 8.09 (2H, d, *J* = 9.4 Hz), 8.01 (2H, d, *J* = 8.8 Hz), 7.99 (2H, d, *J* = 7.8 Hz), 7.98 (2H, t, *J* = 7.6 Hz), 7.90 (2H, d, *J* = 8.8 Hz), 4.63 (1H, dd, *J* = 6.2, 10.8 Hz), 4.55 (1H, dd, *J* = 6.2, 10.8 Hz), 4.12 (1H, dd, *J* = 6.4, 9.3 Hz), 4.04 (1H, dd, *J* = 5.8, 9.3 Hz), 2.65–2.54 (2H, m), 2.28 (6H, s), 1.26 (6H, d, *J* = 6.8 Hz); ^{13}C NMR (CDC13): δ 167.8, 150.5, 134.1, 131.1, 130.8, 130.2, 129.9, 129.4, 129.3, 128.2, 127.0, 126.1, 126.0, 125.7, 124.8, 124.6, 124.0, 123.9, 123.3, 74.6, 67.0, 34.4, 16.0, 14.5; IR (neat) 1705, 1595, 1387, 1248, 1229, 1132, 1074, 1045, 837, 750, 708 cm^{-1}; HRMS (ESI) m/z calcd for $C_{50}H_{42}O_6Na$ (M+Na$^+$): 761.2874, found: 761.2852. ; $[\alpha]_D^{23.8}$ -2.5 (*c* 0.84, $CHCl_3$).



Synthesis of 6-Si: A suspension of **7-NO₂** (0.959 g, 1.60 mmol) and 10 wt% Pd/C (84.9

mg, 79.8 μmol) in EtOH (8.0 mL) was stirred for 27 h under H_2 atmosphere. The mixture was filtered through a pad of Celite and evaporated under vacuum to give a diamine compound as orange oil. To a solution of the diamine (99.3 mg, 0.184 mmol) and acetic acid (2.0 μL, 18 μmol) in toluene was added benzil (42.5 mg, 0.202 mmol). After stirring at 120 °C for 17 h, the reaction mixture was concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane/AcOEt = 90/10) to give **6-Si** (116 mg) as yellow oil in 88% yield. ^{1}H NMR ($CDCl_3$) δ 7.59–7.56 (4H, m), 7.37–7.30 (6H, m), 4.05 (2H, dd, *J* = 6.0, 8.8 Hz), 3.93 (2H, dd, *J* = 6.4, 8.8 Hz), 3.75 (2H, dd, *J* = 5.6, 9.8 Hz), 3.71 (2H, dd, *J* = 5.2, 9.8 Hz), 2.73 (6H, s), 2.27−1.13 (2H, m), 1.13 (6H, d, *J* = 6.8 Hz), 0.91 (18H, s), 0.07 (6H, s), 0.07 (6H, s); ^{13}C NMR (CDCl3): δ 153.0, 150.0, 139.8, 138.6, 130.1, 128.3, 128.0, 126.1, 75.7, 65.1, 37.2, 25.9, 18.3, 14.2, 10.0, −5.4; IR (neat) 2928, 1352, 1252, 1200, 1134, 1078, 835, 754, 698, 667 cm^{-1}; HRMS (ESI) m/z calcd for $C_{42}H_{63}N_2O_4Si_2$ (M+H$^+$): 715.4321, found: 715.4306.

Synthesis of 6-OH: To a solution of **6-Si** (100 mg, 0.103 mmol) in THF (3 mL) was added a solution of tetrabutylammonium fluoride in THF(1.0 mol/L, 1.1 mL, 1.1 mmol). After stirring for 16 h, the reaction mixture was concentrated under reduced pressure and quenched with water (10 mL). Organic materials were extracted with AcOEt (10 mL × 2) and washed with water (10 mL × 2) and brine (10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane/AcOEt = 25/75) to give **6-OH** as white solid (68.6 mg, quant). ^{1}H NMR ($CDCl_3$) δ 7.59–7.55 (4H, m), 7.38–7.31 (6H, m), 4.10 (2H, dd, *J* = 7.2, 9.0 Hz), 3.96 (2H, dd, *J* = 5.2, 9.0 Hz), 3.87 (2H, dd, *J* = 4.4, 10.9 Hz), 3.80 (2H, dd, *J* = 7.0, 10.9 Hz), 2.74 (6H, s), 2.58 (2H, s), 2.40–2.28 (2H, m), 1.10 (6H, d, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 152.4, 150.4, 139.5, 138.6, 130.0, 128.5, 128.1, 126.3, 66.0, 36.6 , 13.7, 10.1; IR (neat) 3238, 2874, 1348, 1197, 1132, 1040, 984, 773, 702 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{35}N_2O_4$ (M+H$^+$): 487.2591, found: 487.2578.

Synthesis of model 6: To a solution of **Pyrene-Cl** (68.0 mg, 257 μmol) and Et_3N (36 μL, 0.257 mmol) in CH_2Cl_2 (1.8 mL) was added **6-OH** (21.9 mg, 77.6 μmol). After stirring for 11 h, the reaction mixture was quenched with water (10 mL). Organic materials were extracted with CH_2Cl_2 (10 mL). The organic layer was washed with water (10 mL × 2) and brine (10 mL). The organic layer was dried over Na_2SO_4, filtered, and dried under reduced pressure. The residue was purified with silica gel column chromatography (hexane/AcOEt = 75/25) to give **6** (56.2 mg) as green oil in 51% yield. ^{1}H NMR ($CDCl_3$) δ 9.19 (2H, d, *J* = 9.6 Hz), 8.52 (2H, d, *J* = 8.0 Hz), 8.15 (2H, d, *J* = 8.0 Hz), 8.13 (2H, d, *J* = 8.0 Hz), 8.09 (2H, d, *J* = 9.6 Hz), 8.00 (2H, d, *J* = 9.0 Hz), 7.98 (2H, d, *J* = 8.0 Hz), 7.97 (2H, t, *J* = 8.0 Hz), 7.89 (2H, d, *J* = 9.0 Hz), 7.55 (4H, dd, *J* = 1.6, 7.6 Hz), 7.36–7.29 (6H, m), 4.69 (2H, dd, *J* = 6.2, 11.0 Hz), 4.62 (2H, dd, *J* = 5.8, 11.0 Hz), 4.27 (2H, dd, *J* = 6.4, 9.2 Hz), 4.18 (2H, dd, *J* = 6.0, 9.2 Hz), 2.78 (6H, s), 2.74–2.66 (2H, m), 1.33 (6H, d, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 167.7, 152.6, 150.3, 139.6, 138.6, 134.1, 131.0, 130.8, 130.1, 130.0, 129.4, 129.3, 128.4, 128.2, 128.0, 126.9, 126.3, 126.1, 126.0, 124.7, 124.5, 123.9, 123.0, 75.5, 66.9, 34.4, 14.6, 10.1; IR (neat) 1568, 1464, 1236, 1207, 1026, 750 cm^{-1}; HRMS (MALDI) m/z calcd for $C_{64}H_{51}N_2O_6$ ($M+H^+$): 943.37416, found: 943.37308; $[\alpha]_D^{19.4}$ +20.1 (*c* 0.93, $CHCl_3$).

3 UV-vis and CD and fluorescent spectra of New Compounds

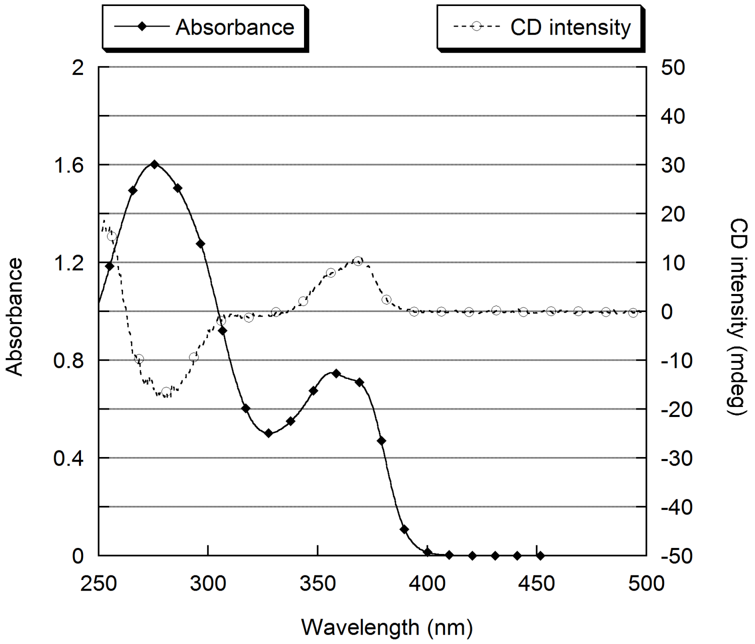


Figure S-19. UV-vis and CD spectra of polymer **1-Si** in $CHCl_3$ (25.3 mg/L).

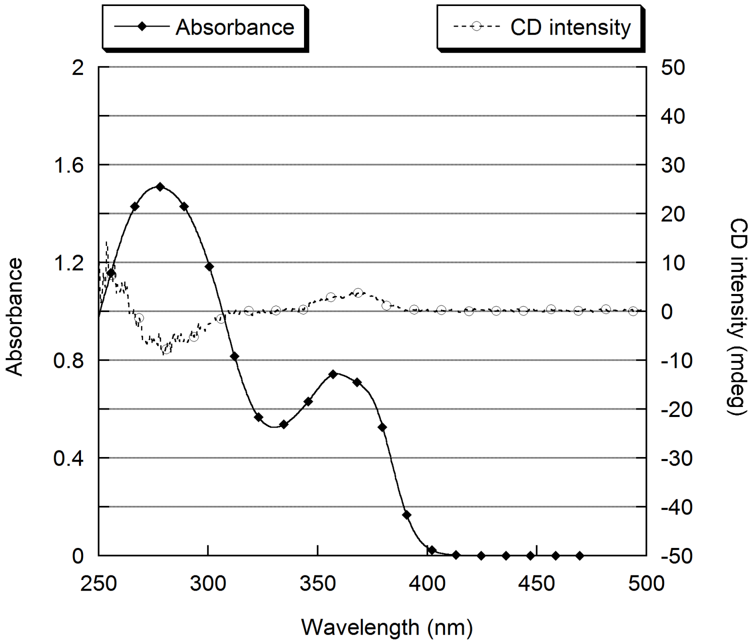


Figure S-20. UV-vis and CD spectra of polymer **1-Si** in 1,1,1-TCE (25.3 mg/L).

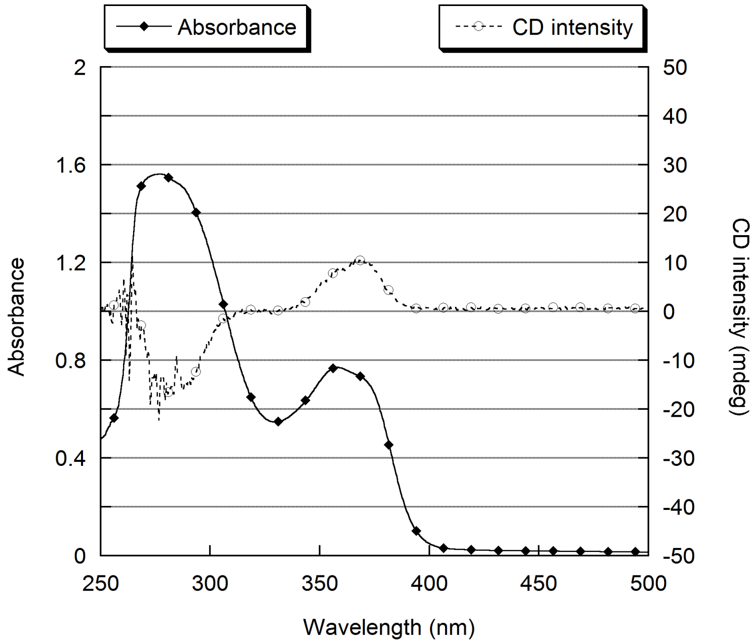


Figure S-21. UV-vis and CD spectra of polymer **1-Si** in 1,1,2-TCE (25.3 mg/L).

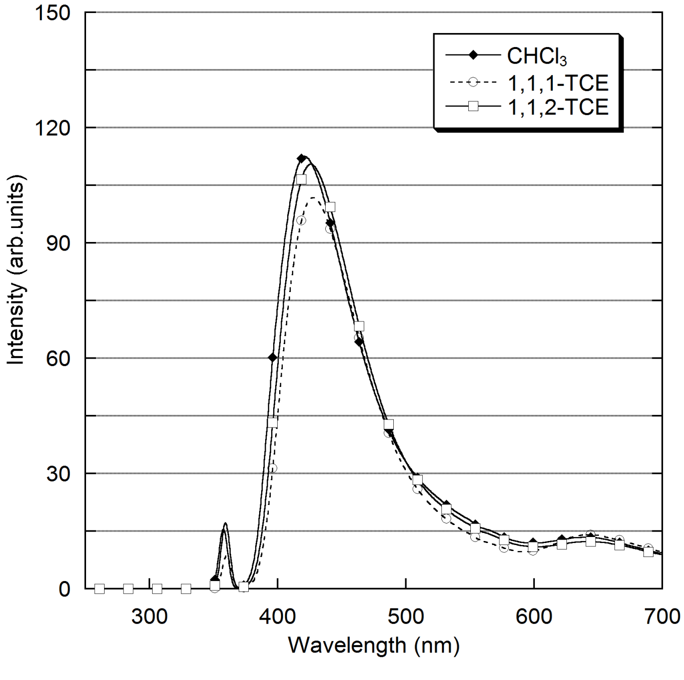


Figure S-22. Fluorescent spectra of **1-Si** in $CHCl_3$ and 1,1,1-TCE and 1,1,2-TCE (25.3 mg/L, excitation wavelengths were set to 356.5 nm in $CHCl_3$, 359.0 nm in 1,1,1-TCE, and 358.0 nm in 1,1,2-TCE.)

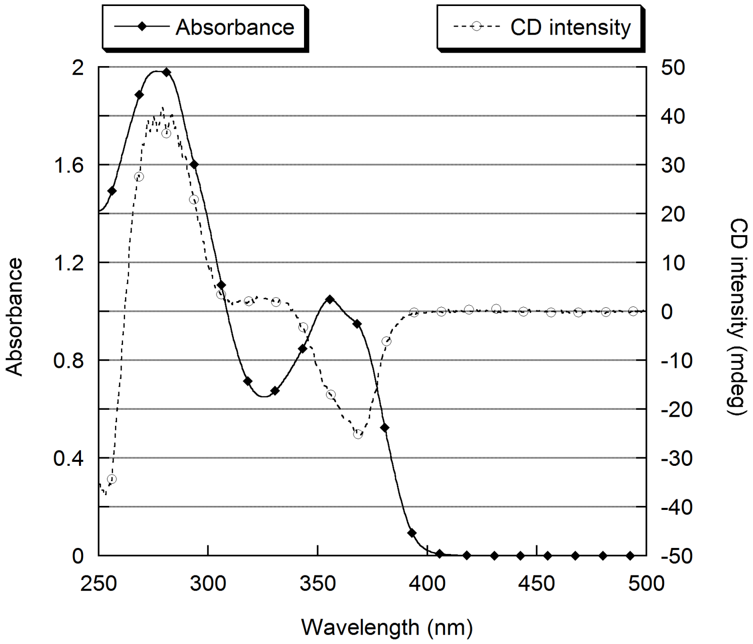


Figure S-23. UV-vis and CD spectra of polymer **1** in $CHCl_3$ (31.1 mg/L).

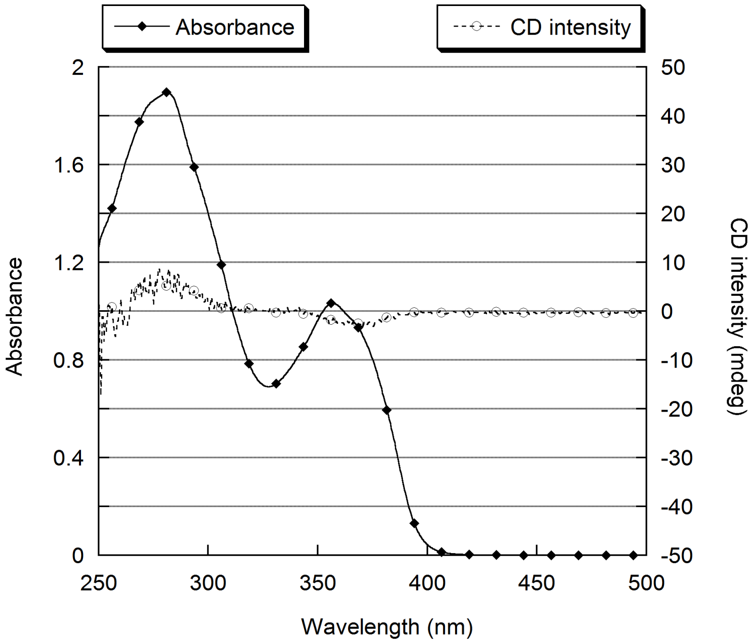


Figure S-24. UV-vis and CD spectra of polymer **1** in 1,1,1-TCE (31.1 mg/L).

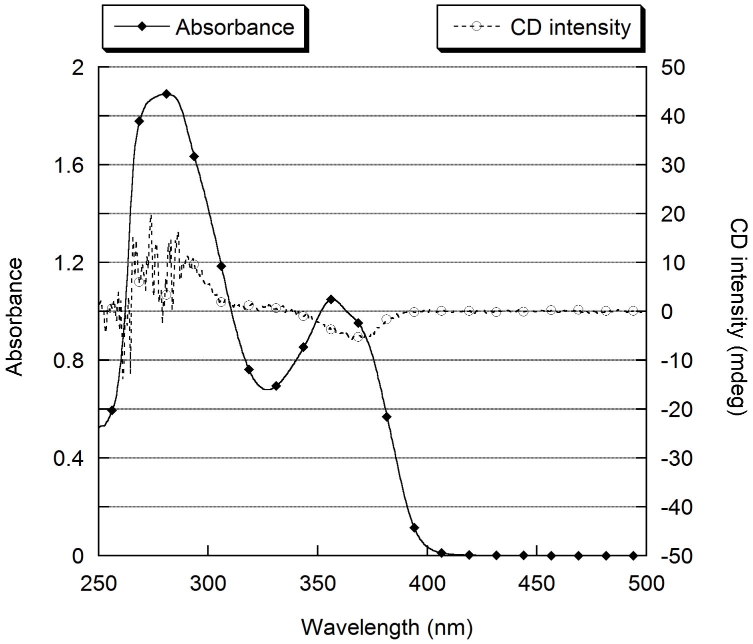


Figure S-25. UV-vis and CD spectra of polymer **1** in 1,1,2-TCE (31.1 mg/L).

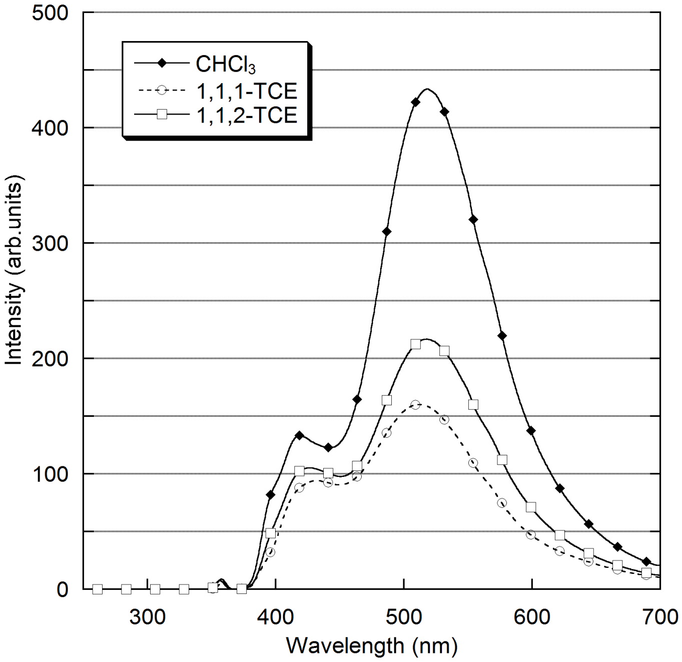


Figure S-26. Fluorescent spectra of **1** in $CHCl_3$ and 1,1,1-TCE and 1,1,2-TCE (31.1 mg/L, excitation wavelengths were set to 355.5 nm in $CHCl_3$, 357.0 nm in 1,1,1-TCE, and 356.5 nm in 1,1,2-TCE.)

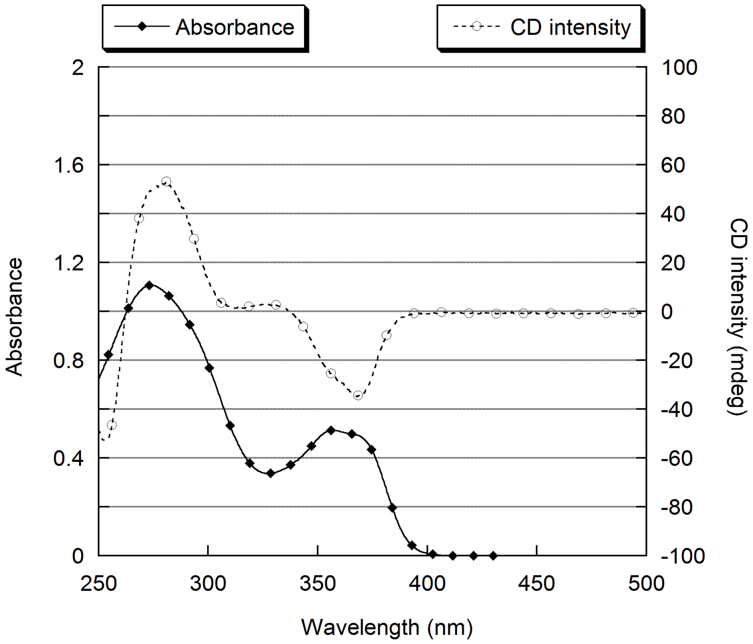


Figure S-27. UV-vis and CD spectra of polymer **2-Si** in $CHCl_3$ (20.5 mg/L).

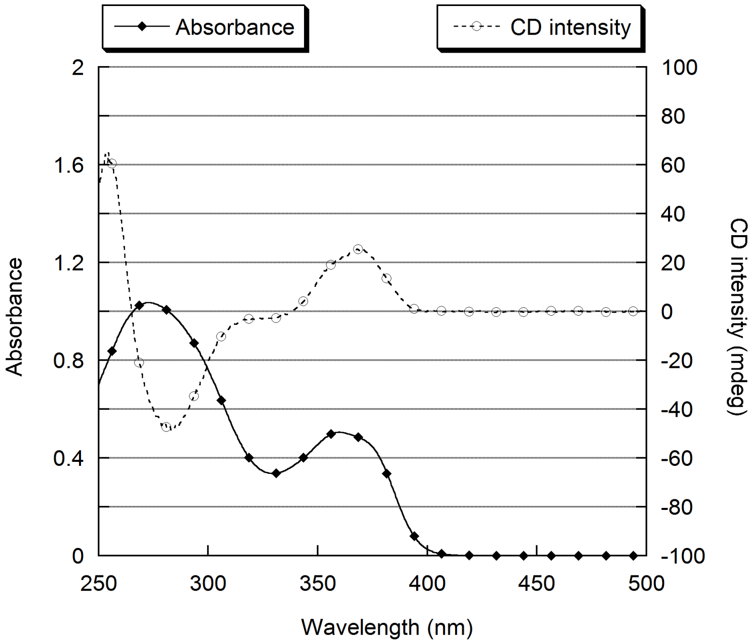


Figure S-28. UV-vis and CD spectra of polymer **2-Si** in 1,1,1-TCE (20.5 mg/L).

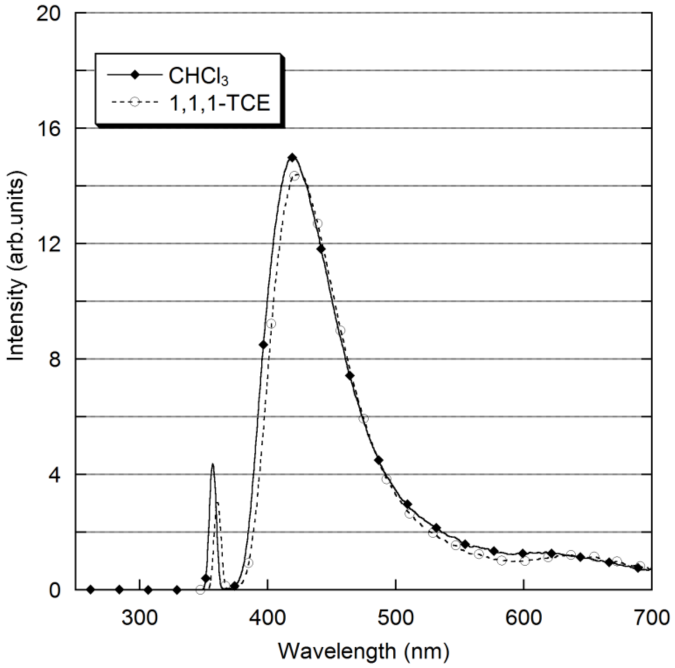


Figure S-29. Fluorescent spectra of **2-Si** in $CHCl_3$ and 1,1,1-TCE (20.5 mg/L, excitation wavelength is 356.5 nm in $CHCl_3$, 360 nm in 1,1,1-TCE.)

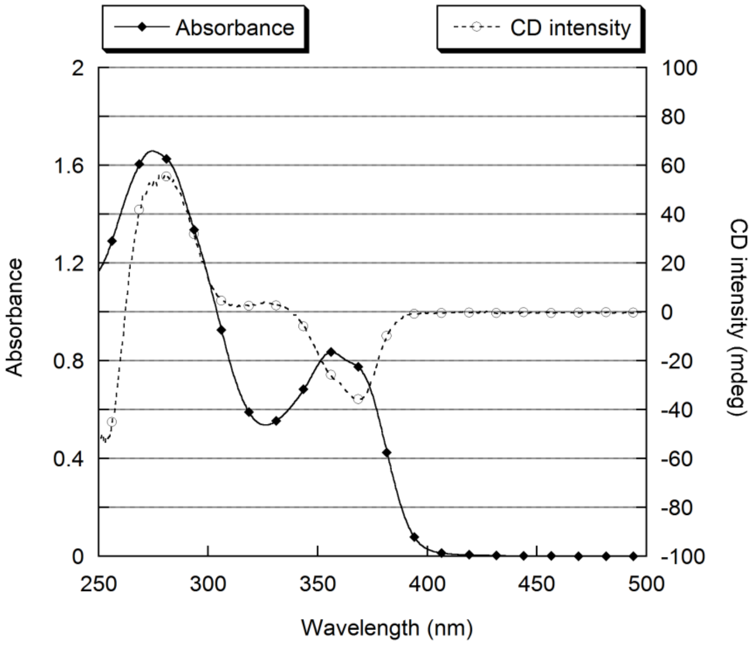


Figure S-30. UV-vis and CD spectra of polymer **2** in $CHCl_3$ (30.1 mg/L).

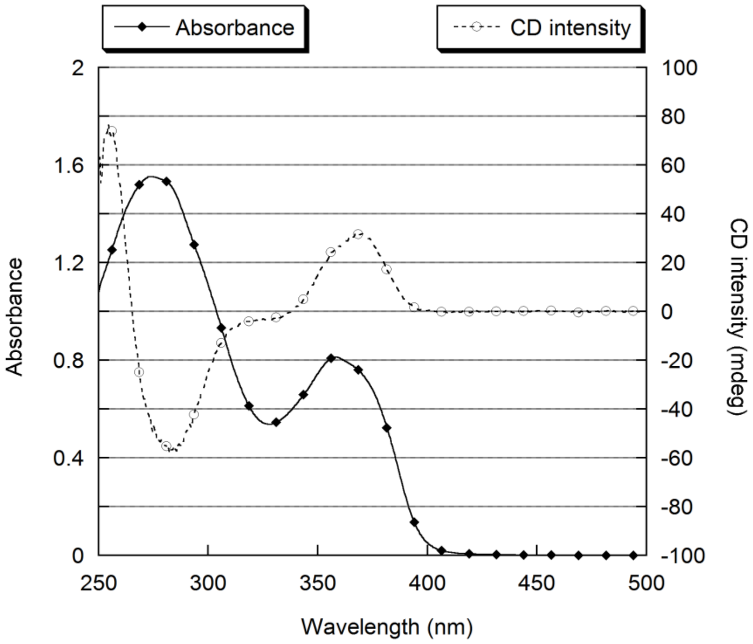


Figure S-31. UV-vis and CD spectra of polymer **2** in 1,1,1-TCE (31.0 mg/L).

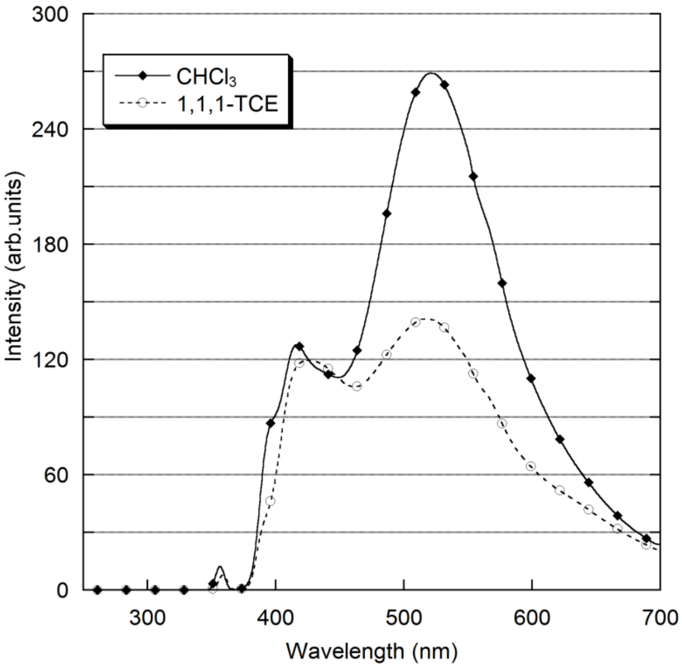


Figure S-32. Fluorescent spectra of **2** in $CHCl_3$ and 1,1,1-TCE (31.0 mg/L, excitation wavelengths were set to 356.5 nm in $CHCl_3$ and 358 nm in 1,1,1-TCE.)

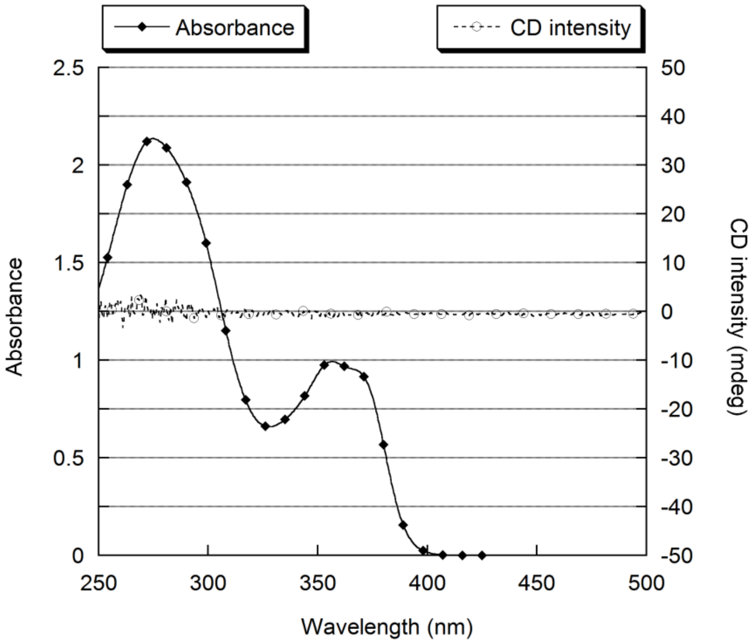


Figure S-33. UV-vis and CD spectra of polymer **3-Si** in $CHCl_3$ (32.2 mg/L).

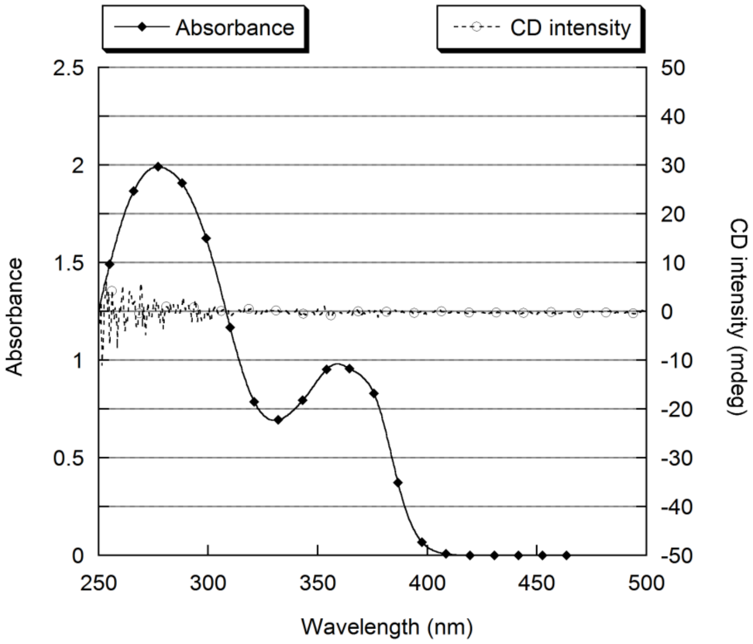


Figure S-34. UV-vis and CD spectra of polymer **3-Si** in 1,1,1-TCE (32.2 mg/L).

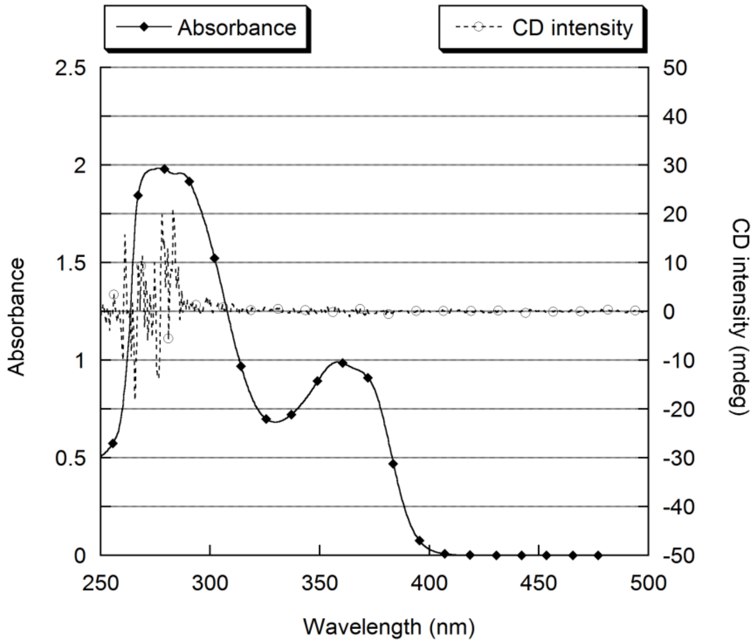


Figure S-35. UV-vis and CD spectra of polymer **3-Si** in 1,1,2-TCE (32.2 mg/L).

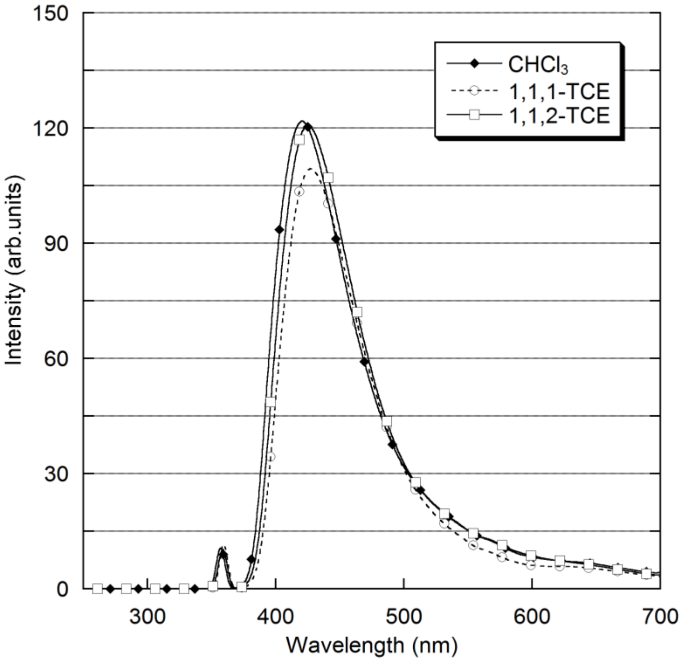


Figure S-36. Fluorescent spectra of **3-Si** in $CHCl_3$ and 1,1,1-TCE and 1,1,2-TCE (32.2 mg/L, excitation wavelengths were set to 356.5 nm in $CHCl_3$, 359 nm in 1,1,1-TCE, and 358.0 nm in 1,1,2-TCE.)

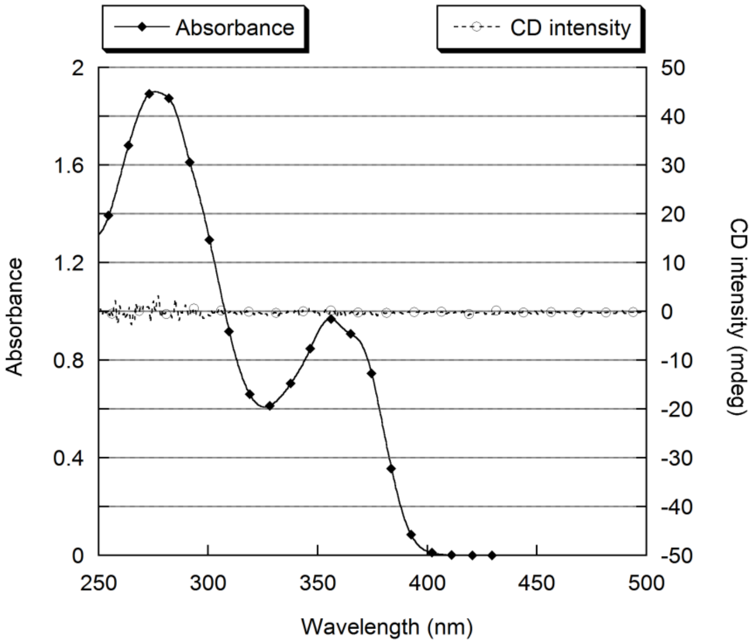


Figure S-37. UV-vis and CD spectra of polymer **3** in $CHCl_3$ (28.5 mg/L).

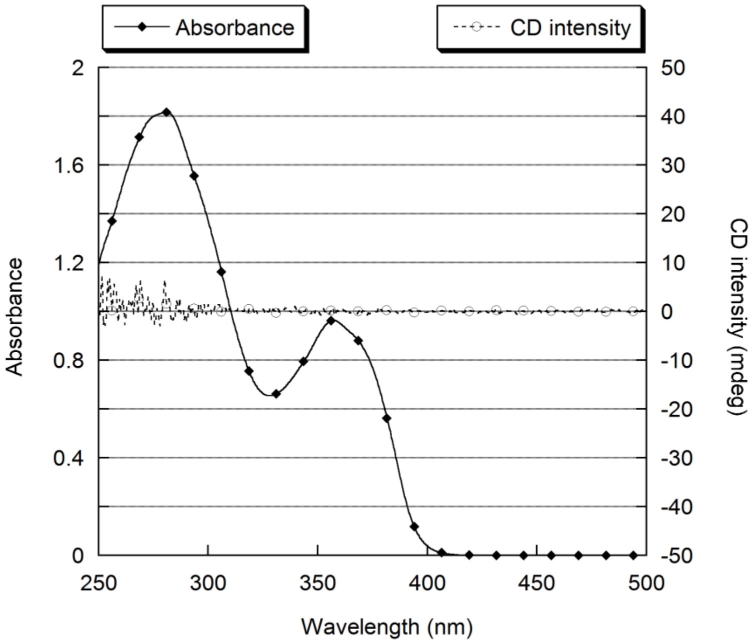


Figure S-38. UV-vis and CD spectra of polymer **3** in 1,1,1-TCE (28.5 mg/L).

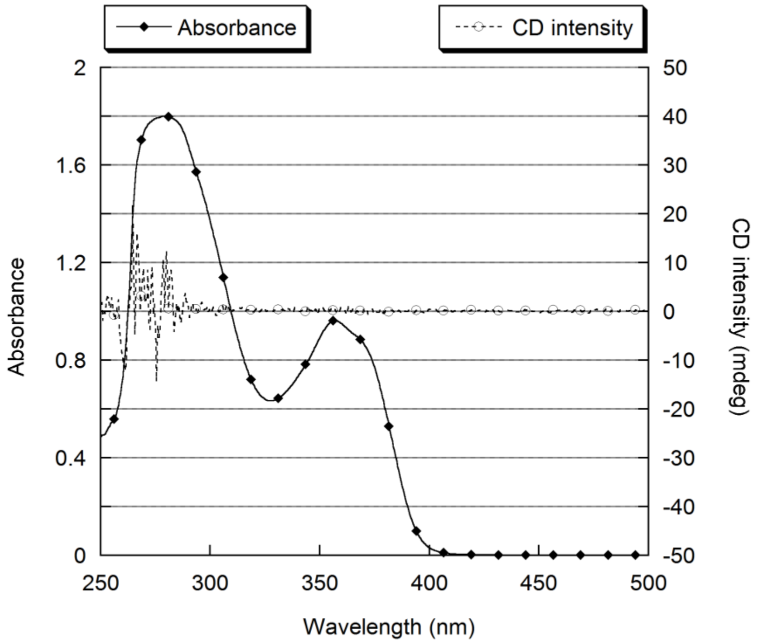


Figure S-39. UV-vis and CD spectra of polymer **3** in 1,1,2-TCE (28.5 mg/L).

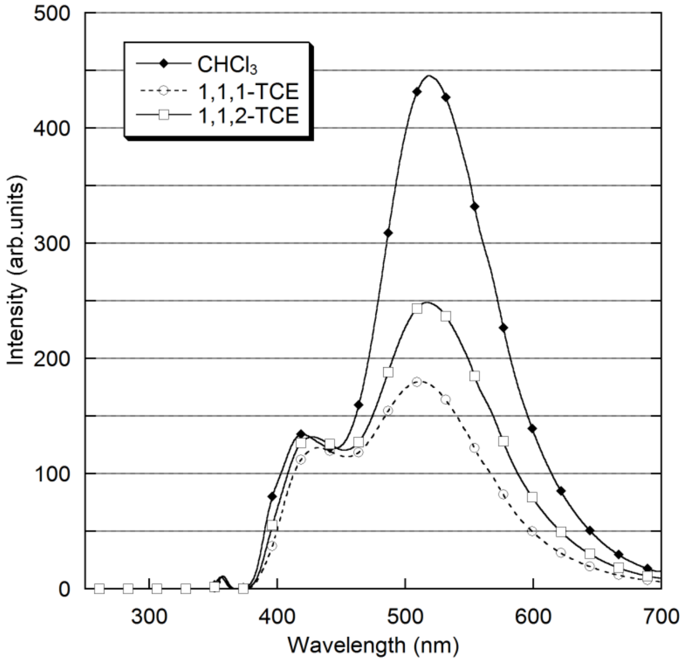


Figure S-40. Fluorescent spectra of **3** in $CHCl_3$, 1,1,1-TCE, and 1,1,2-TCE. (28.5 mg/L, excitation wavelengths were set to 355.5 nm in $CHCl_3$, 357.0 nm in 1,1,1-TCE, and 357.0 nm in 1,1,2-TCE.)

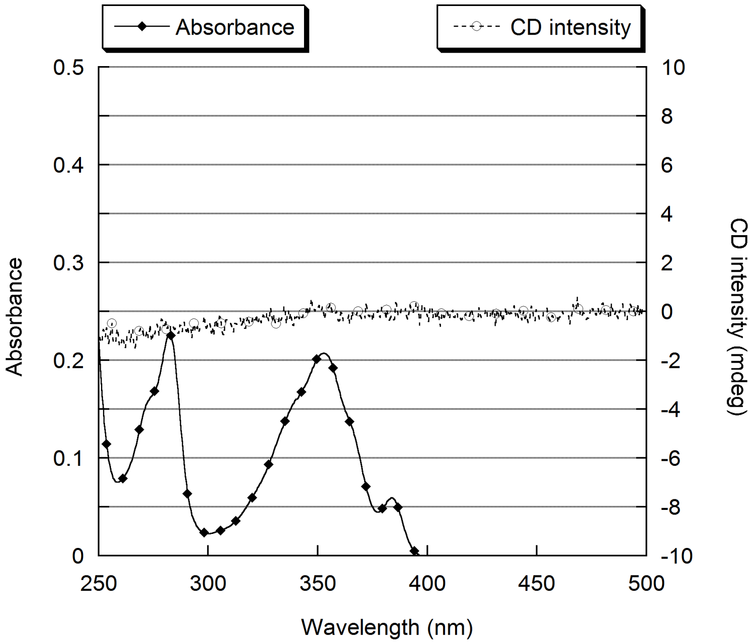


Figure S-41. UV-vis and CD spectra of **4** in $CHCl_3$ (28.4 mg/L).

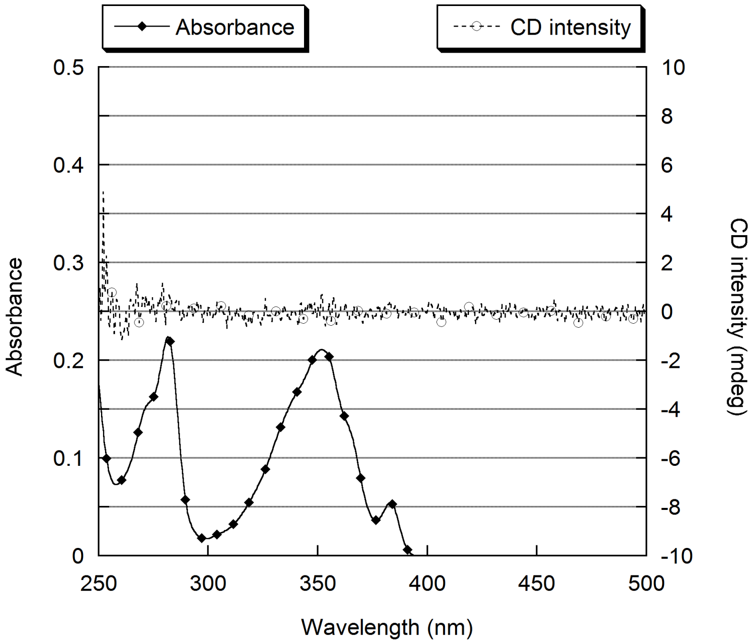


Figure S-42. UV-vis and CD spectra of **4** in 1,1,2-TCE (28.4 mg/L).

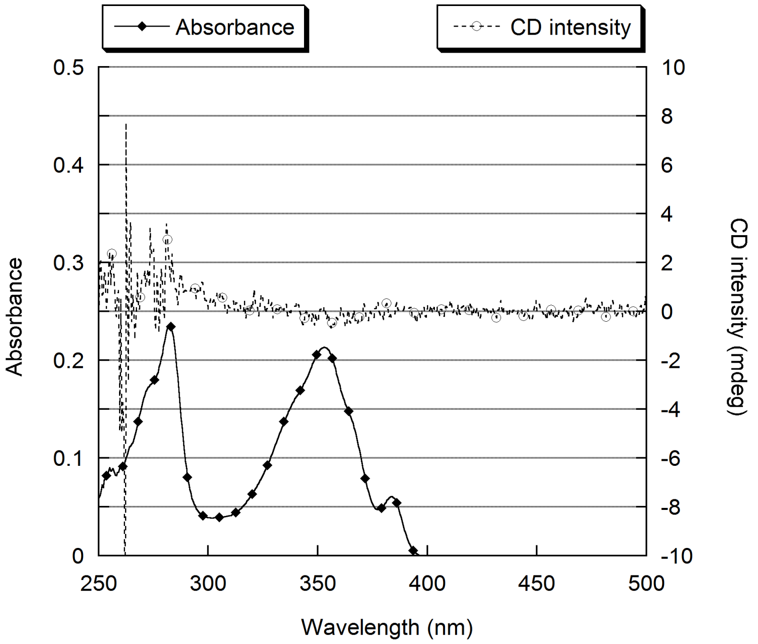


Figure S-43. UV-vis and CD spectra of **4** in 1,1,1-TCE (28.4 mg/L).

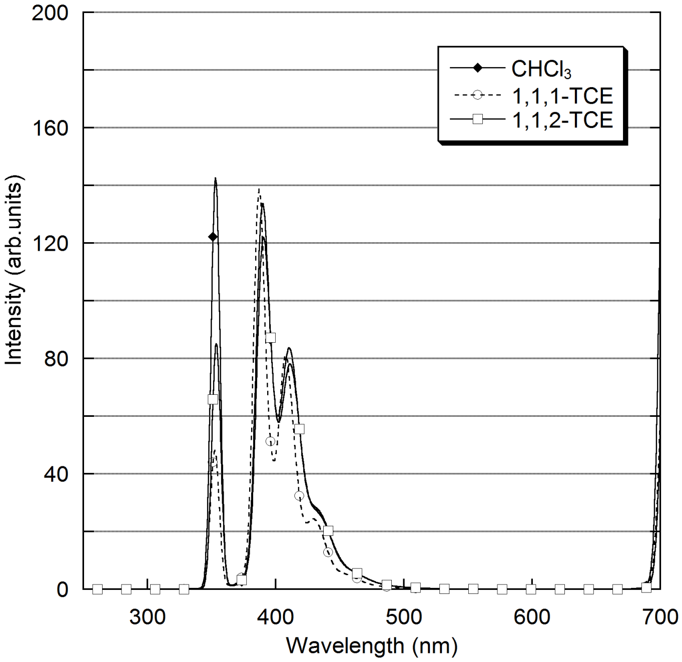


Figure S-44. Fluorescent spectra of **4** in $CHCl_3$ and 1,1,1-TCE and 1,1,2-TCE. (28.4 mg/L , excitation wavelengths were set to 353 nm in $CHCl_3$, 352.0 nm in 1,1,1-TCE, and 353.5 nm in 1,1,2-TCE.)

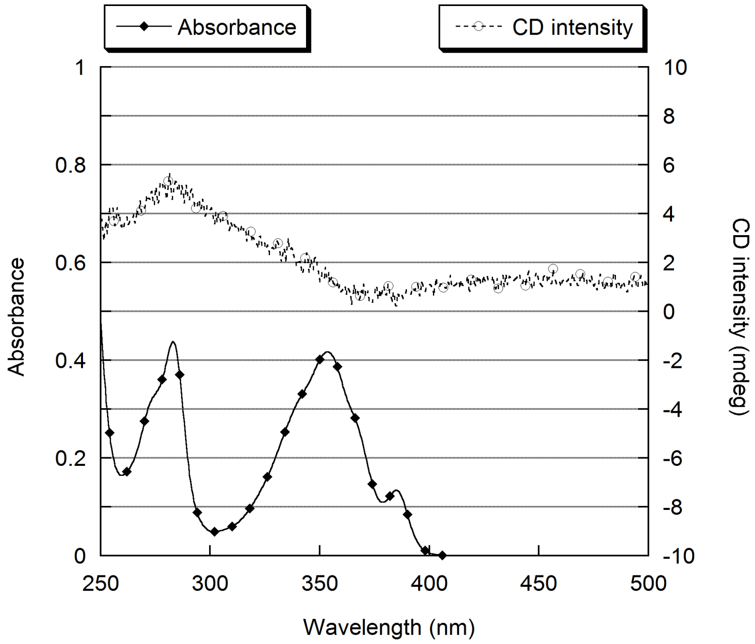


Figure S-45. UV-vis and CD spectra of **5** in $CHCl_3$ (71.2 mg/L).

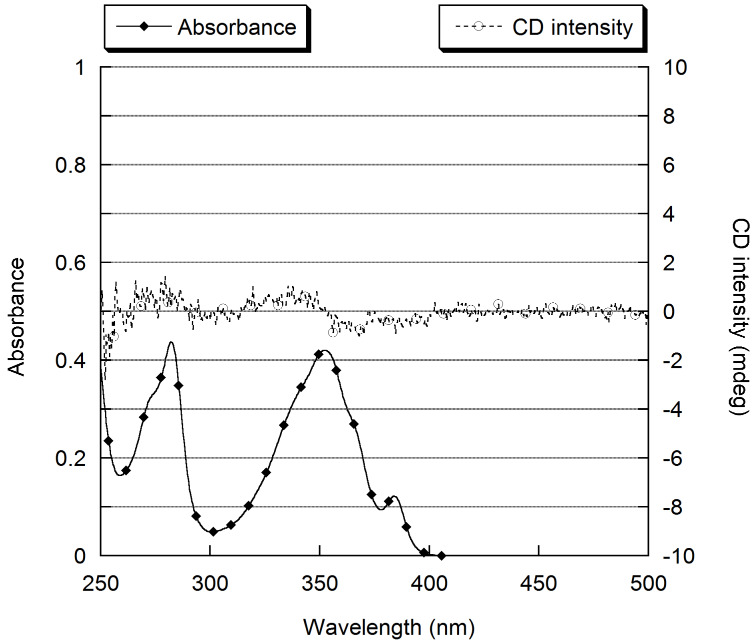


Figure S-46. UV-vis and CD spectra of **5** in 1,1,1-TCE (71.2 mg/L).

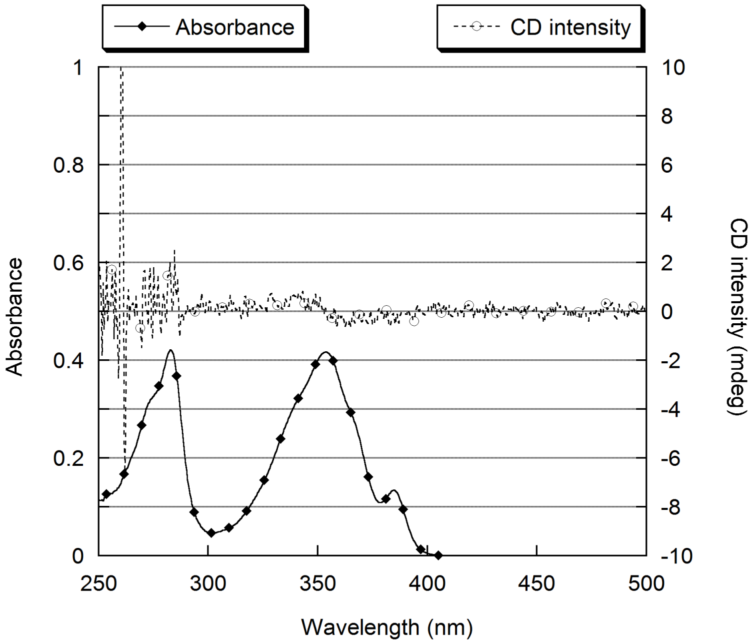


Figure S-47. UV-vis and CD spectra of **5** in 1,1,2-TCE (71.2 mg/L).

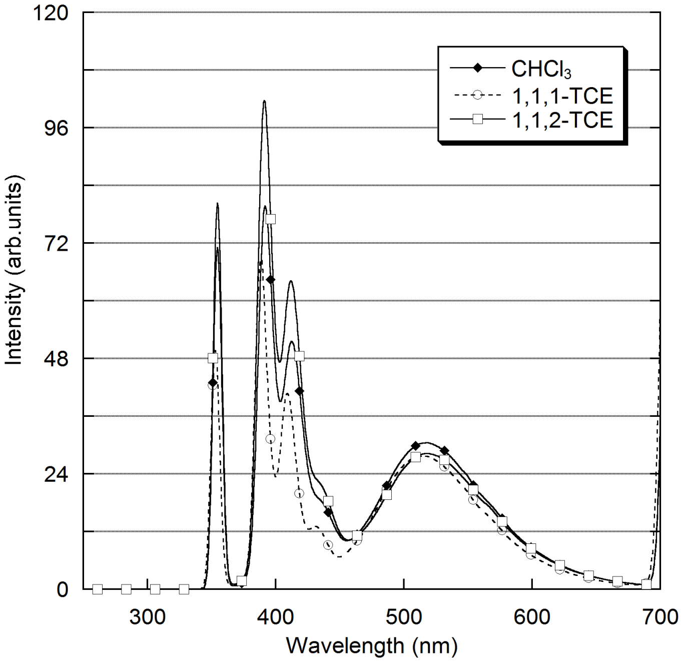


Figure S-48. Fluorescent spectra of **5** in $CHCl_3$ and 1,1,1-TCE and 1,1,2-TCE (71.2 mg/L, excitation wavelengths were set to 353.0 nm in $CHCl_3$, 352.0 nm in 1,1,1-TCE, and 353.5 nm in 1,1,2-TCE.)

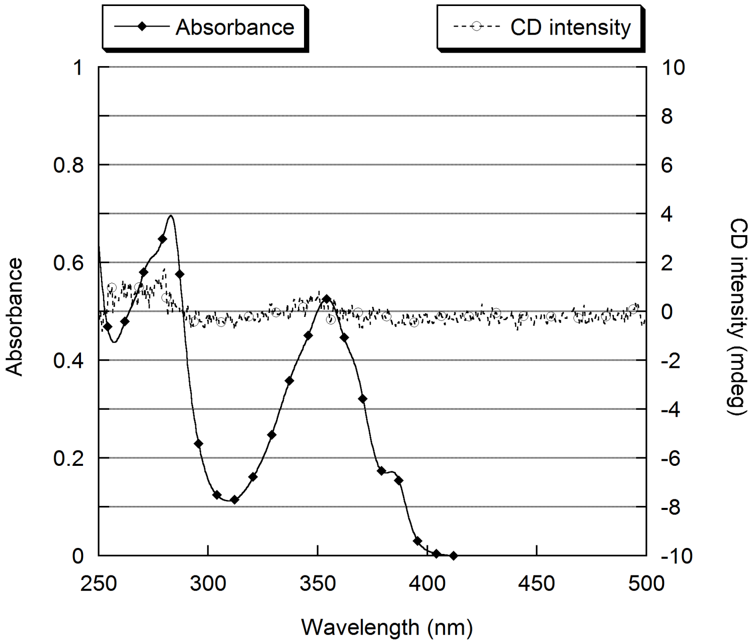


Figure S-49. UV-vis and CD spectra of **6** in $CHCl_3$ (87.3 mg/L).

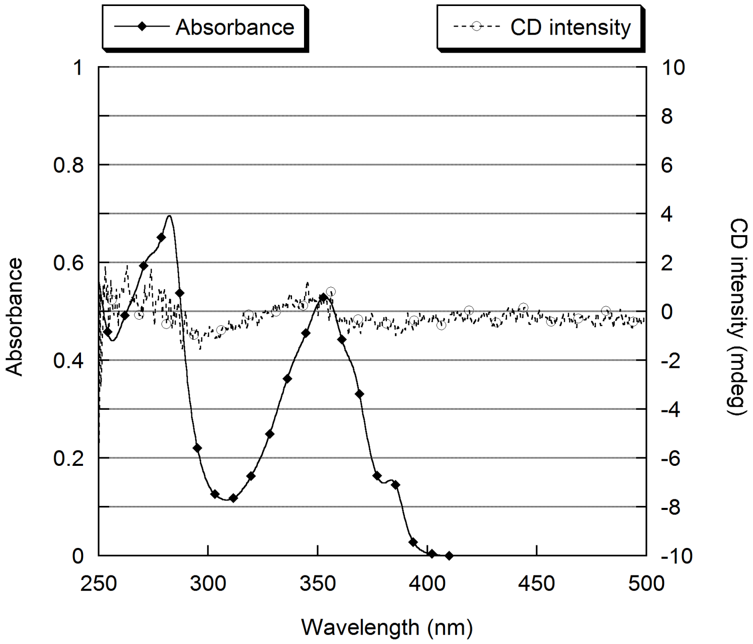


Figure S-50. UV-vis and CD spectra of **5** in 1,1,1-TCE (87.3 mg/L).

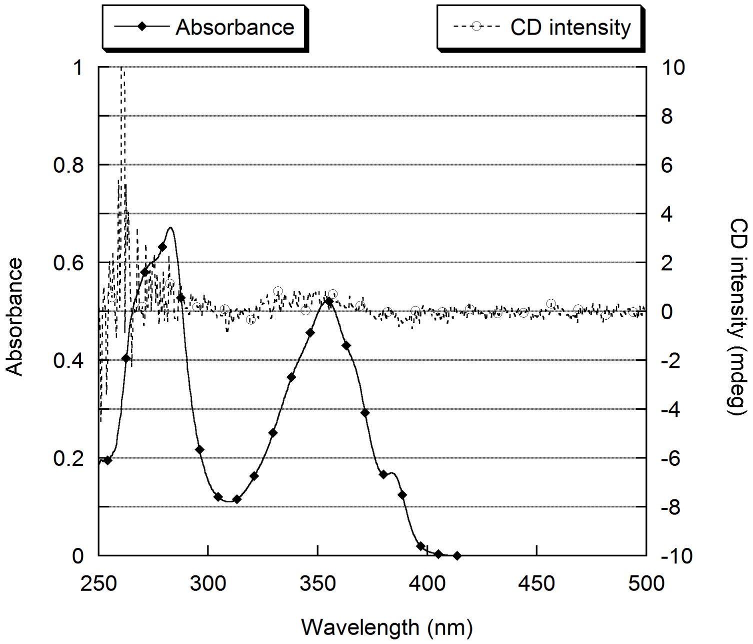


Figure S-51. UV-vis and CD spectra of **6** in 1,1,2-TCE (87.3 mg/L).

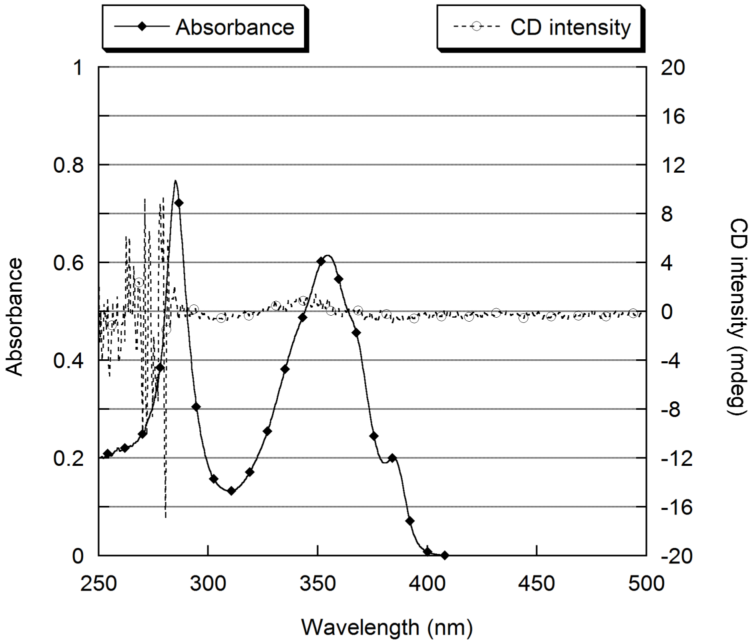


Figure S-52. UV-vis and CD spectra of **5** in toluene (120 mg/L).

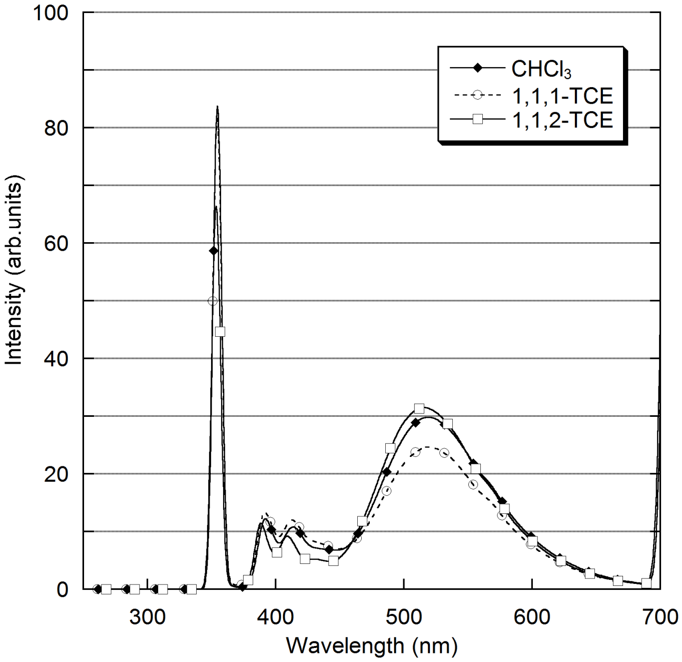


Figure S-53. Fluorescent spectra of **6** in $CHCl_3$ and 1,1,1-TCE and 1,1,2-TCE (87.3 mg/L, excitation wavelengths were set to 354 nm in $CHCl_3$, 353nm in 1,1,1-TCE, and 354 nm in 1,1,2-TCE.)

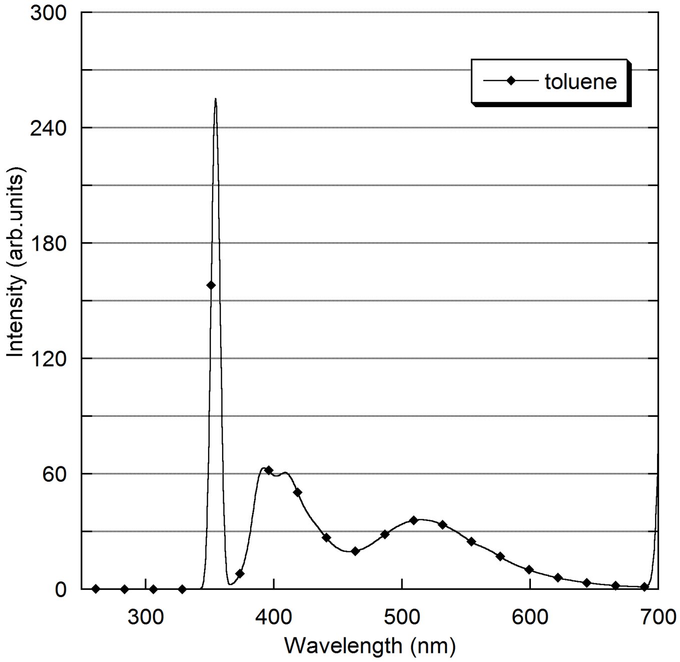


Figure S-54. Fluorescent spectra of **6** in toluene (120 mg/L, excited at 354.5 nm).

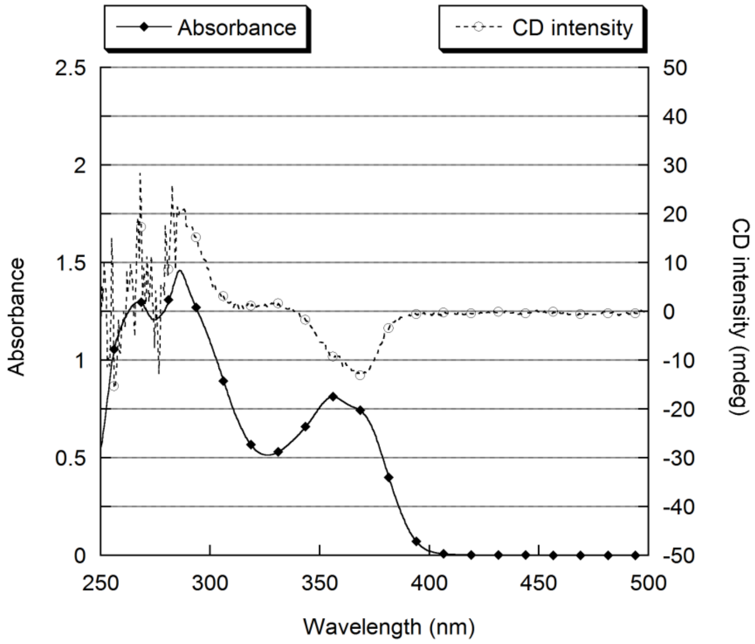


Figure S-55. UV-vis and CD spectra of polymer **1** in 1,1,2,2-tetrachloroethane. (30 mg/L.)

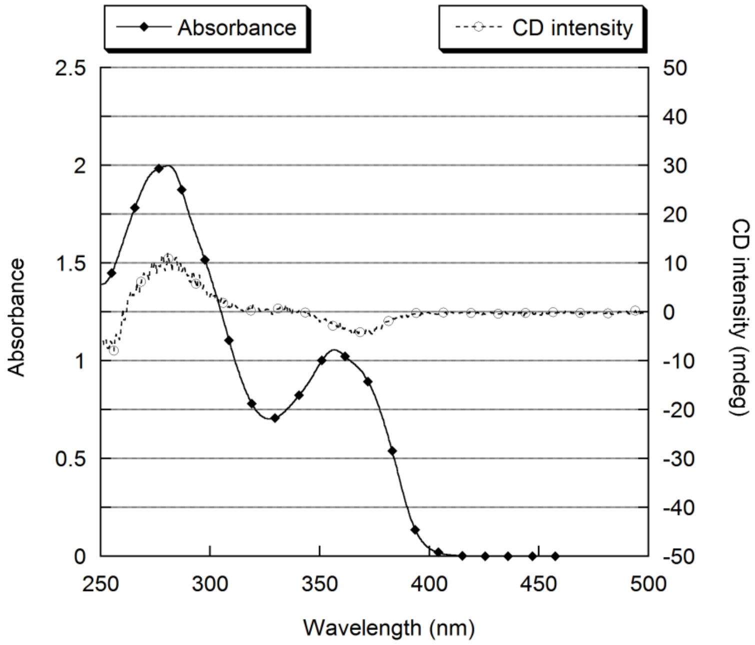


Figure S-56. UV-vis and CD spectra of polymer **1** in CH_2Cl_2. (30 mg/L.)

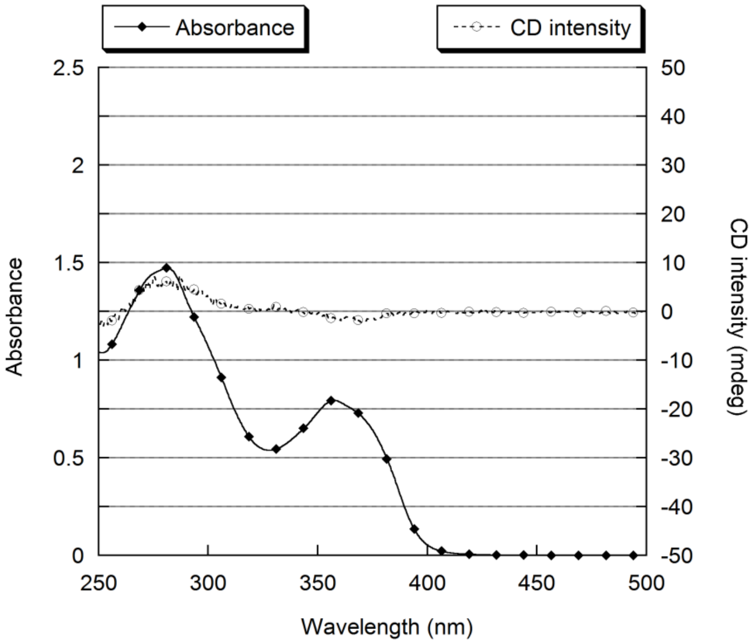


Figure S-57. UV-vis and CD spectra of polymer **1** in 1,2-dichloroethane. (30 mg/L.)

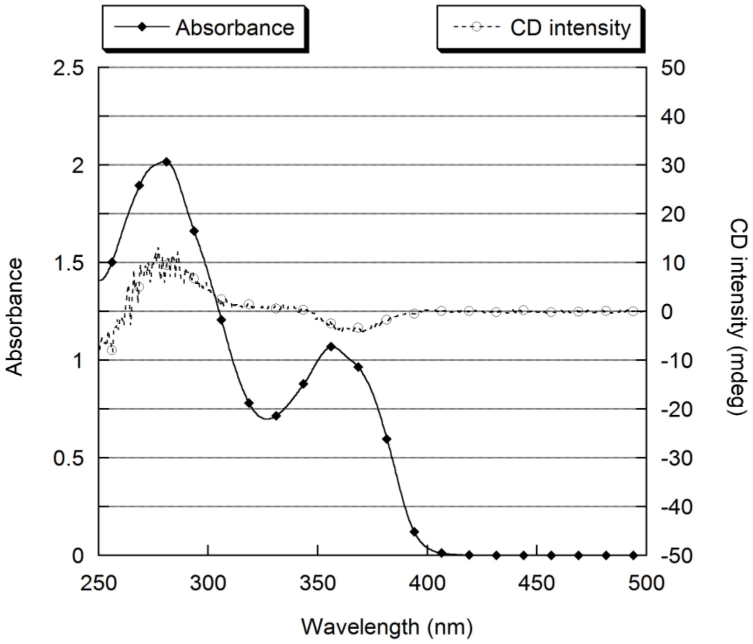


Figure S-58. UV-vis and CD spectra of polymer **1** in 1,1-dichloroethane. (30 mg/L.)

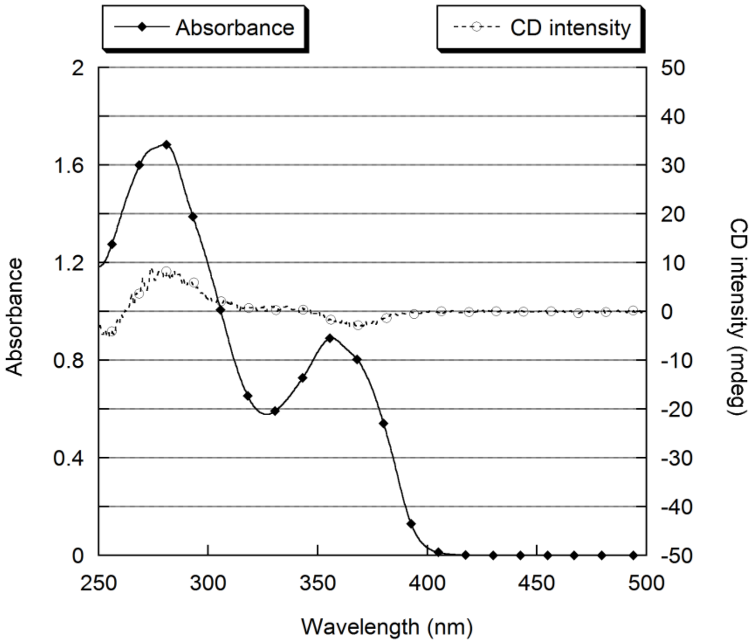


Figure S-59. UV-vis and CD spectra of polymer **1** in *n*-BuCl. (30 mg/L.)

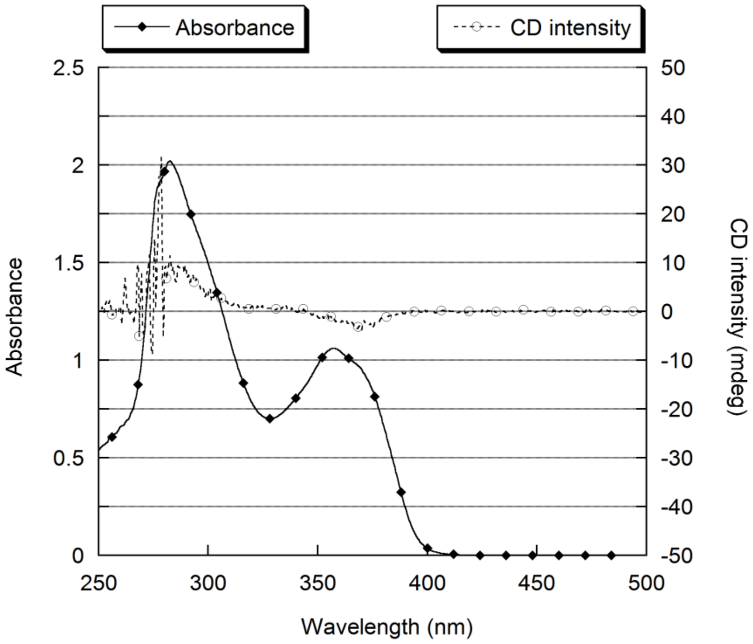


Figure S-60. UV-vis and CD spectra of polymer **1** in trichloroethylene. (30 mg/L.)

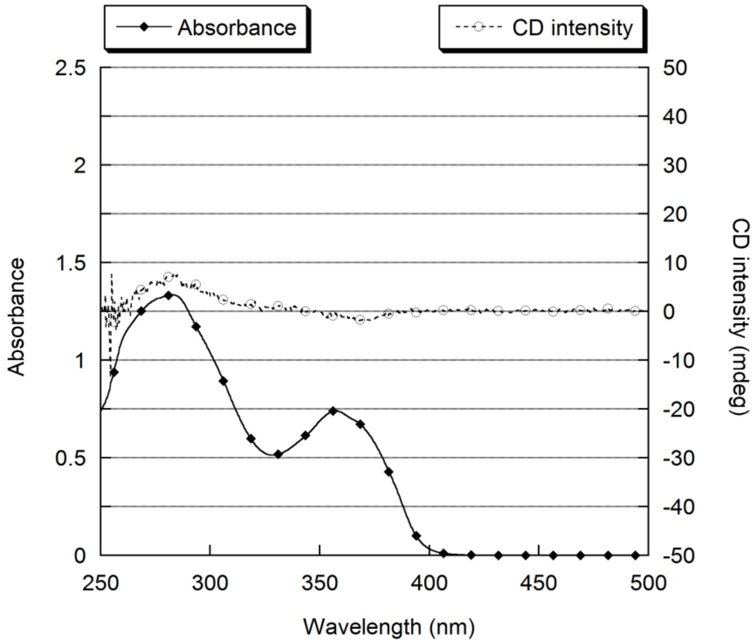


Figure S-61. UV-vis and CD spectra of polymer **1** in CCl_4. (30 mg/L.)

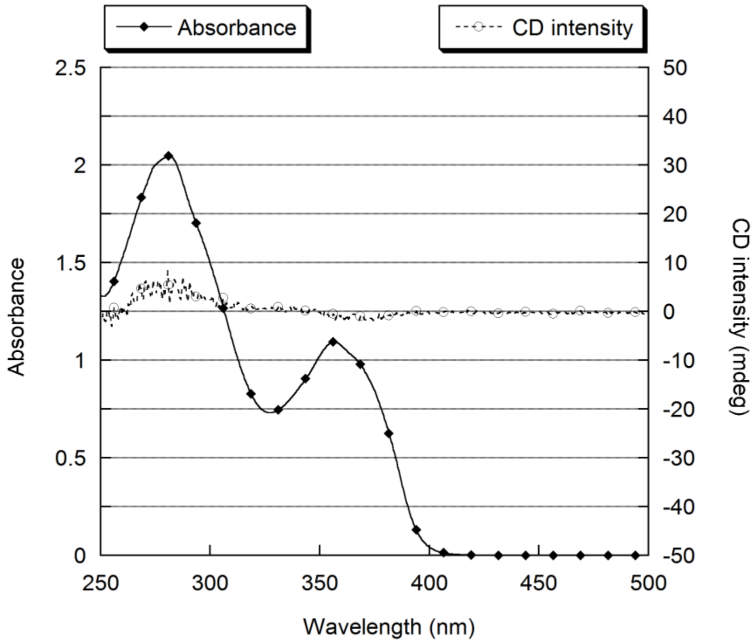


Figure S-62. UV-vis and CD spectra of polymer **1** in THF. (30 mg/L.)

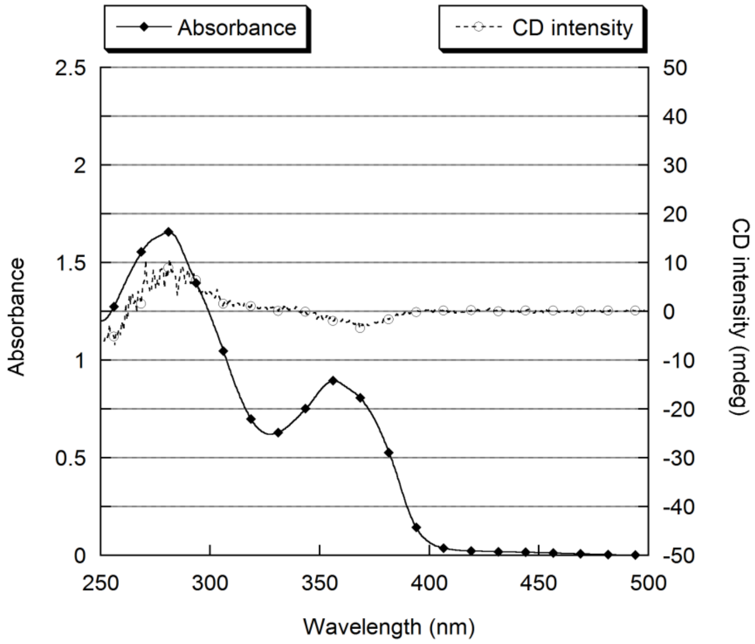


Figure S-63. UV-vis and CD spectra of polymer **1** in *t*-BuCl. (30 mg/L.)

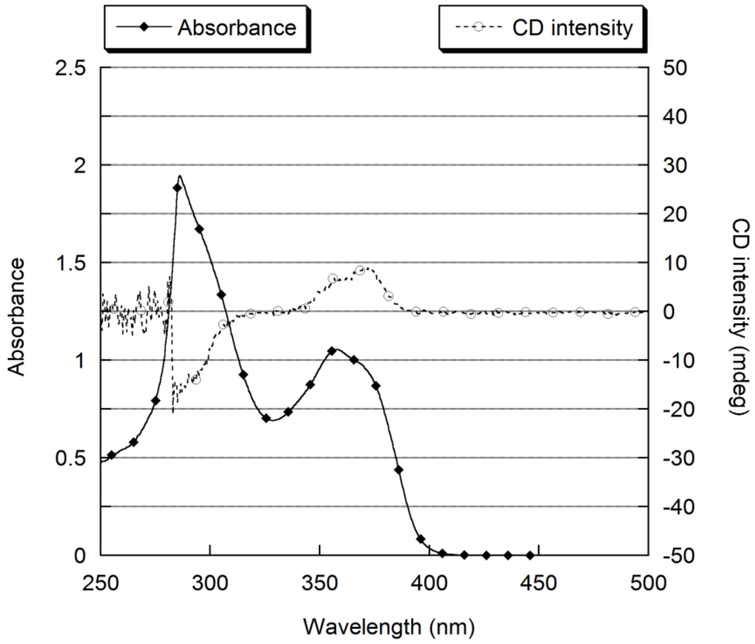


Figure S-64. UV-vis and CD spectra of polymer **1** in toluene. (30 mg/L.)

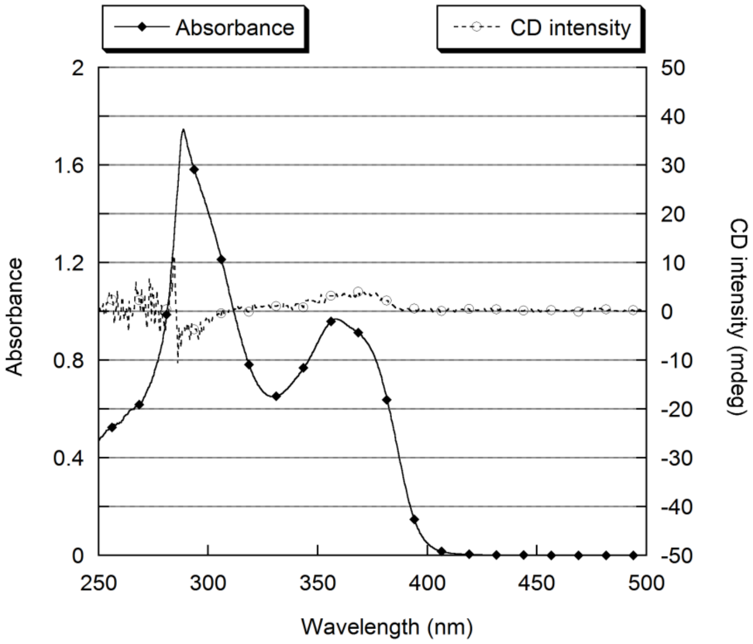


Figure S-65. UV-vis and CD spectra of polymer **1** in chlorobenzene. (30 mg/L.)

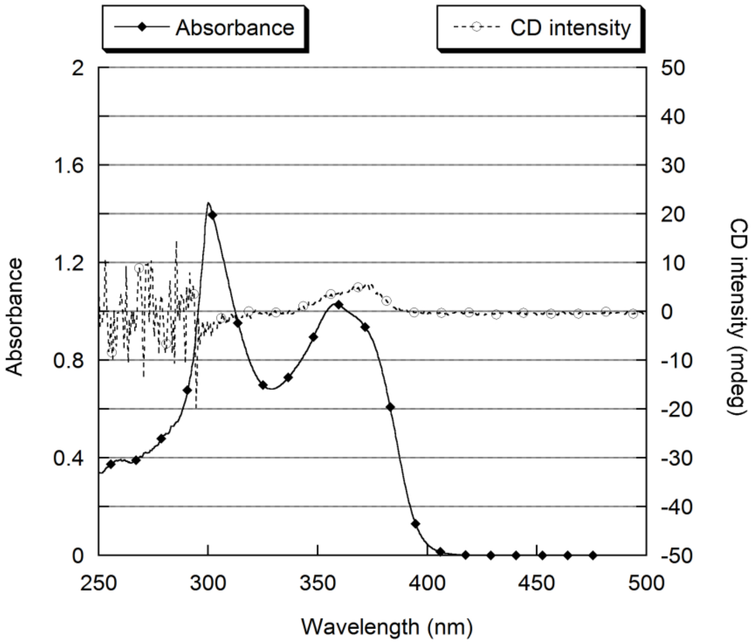


Figure S-66. UV-vis and CD spectra of polymer **1** in anisole. (30 mg/L.)

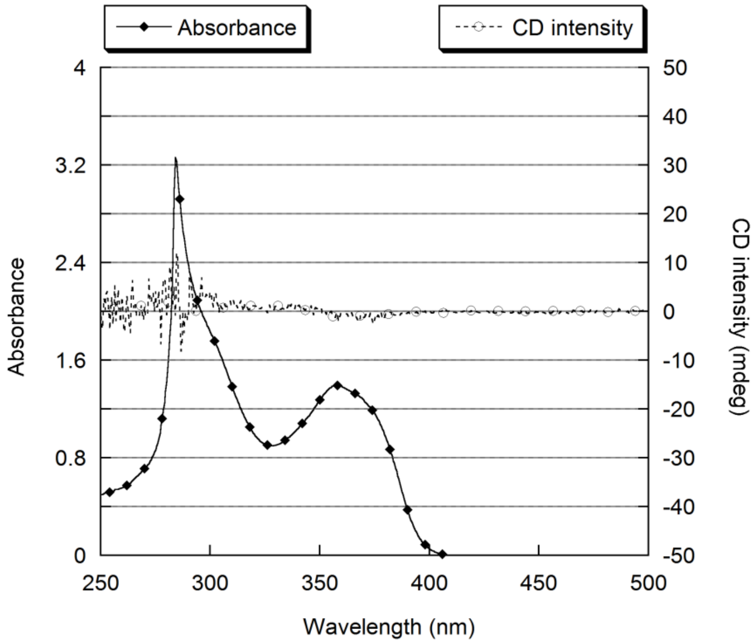


Figure S-67. UV-vis and CD spectra of polymer **1** in α,α,α-trifluorotoluene ($PhCF_3$) (30 mg/L.).

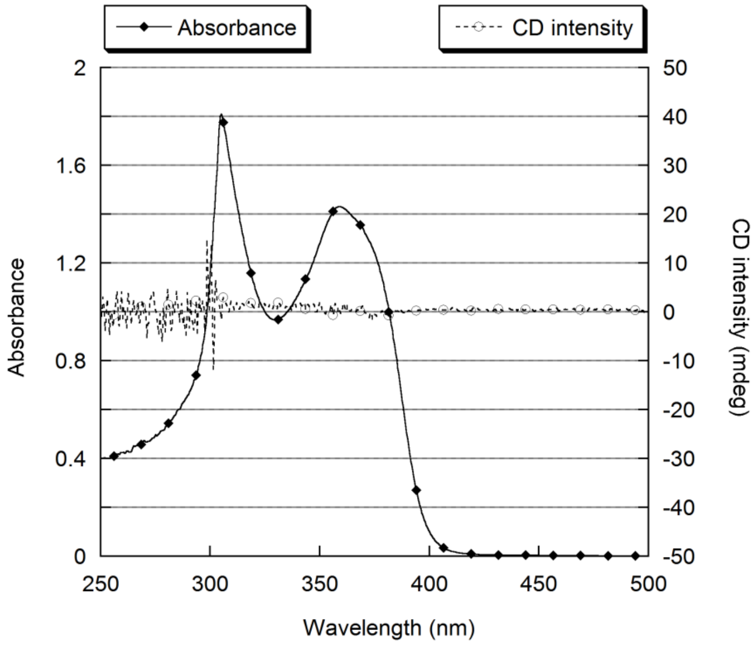


Figure S-68. UV-vis and CD spectra of polymer **1** in pyridine. (30 mg/L.)

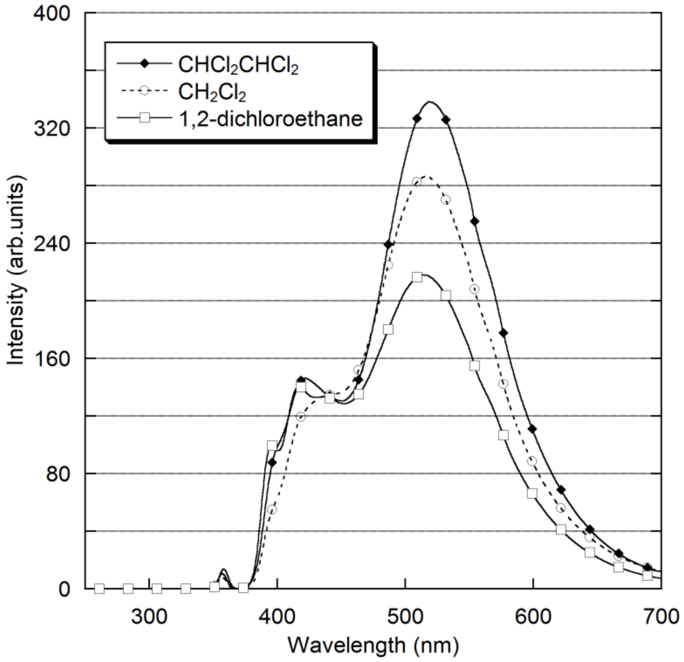


Figure S-69. Fluorescent spectra of **1** in 1,1,2,2-tetrachloroethane and in CH_2Cl_2 and 1,2-dichloroethane. (30 mg/L, excitation wavelengths were set to 356.5 nm in 1,1,2,2-tetrachloroethane, 356.5 nm in CH_2Cl_2, and 357.5 nm in 1,2-dichloroethane.)

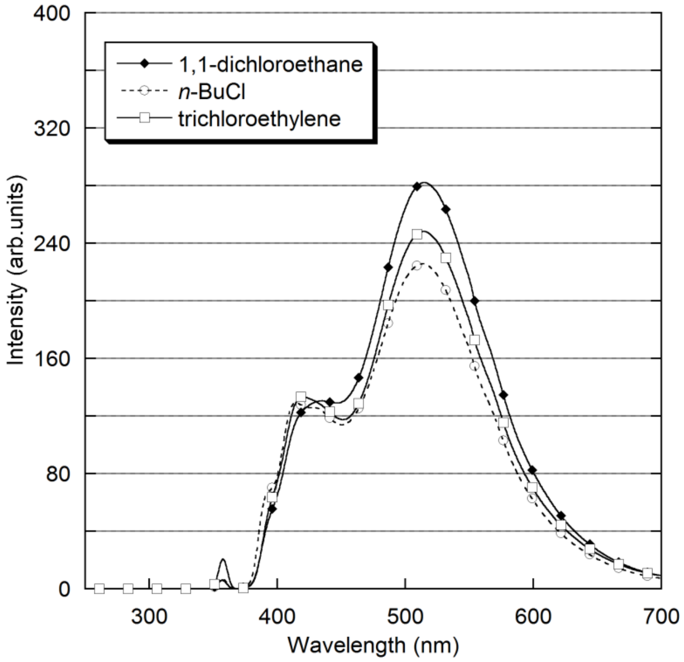


Figure S-70. Fluorescent spectra of **1** in 1,1-dichloroethane and *n*-BuCl and trichloroethylene. (30 mg/L, excitation wavelengths were set to 356.5 nm in 1,1-dichloroethane, 356.5 nm in *n*-BuCl, and 357.0 nm in trichloroethylene.)

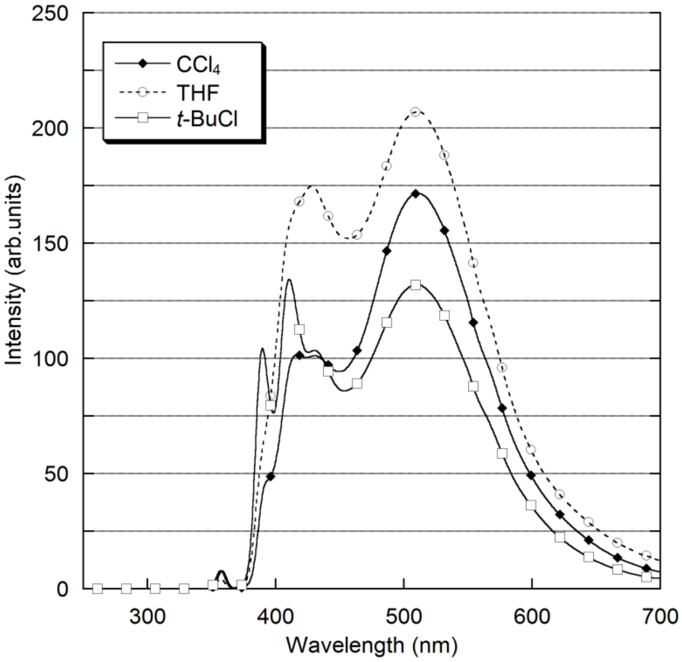


Figure S-71. Fluorescent spectra of **1** in CCl_4 and THF and *t*-BuCl. (30 mg/L, excitation wavelength is 357.5 nm in CCl_4, 356.5 nm in THF, 356.5 nm in *t*-BuCl.)

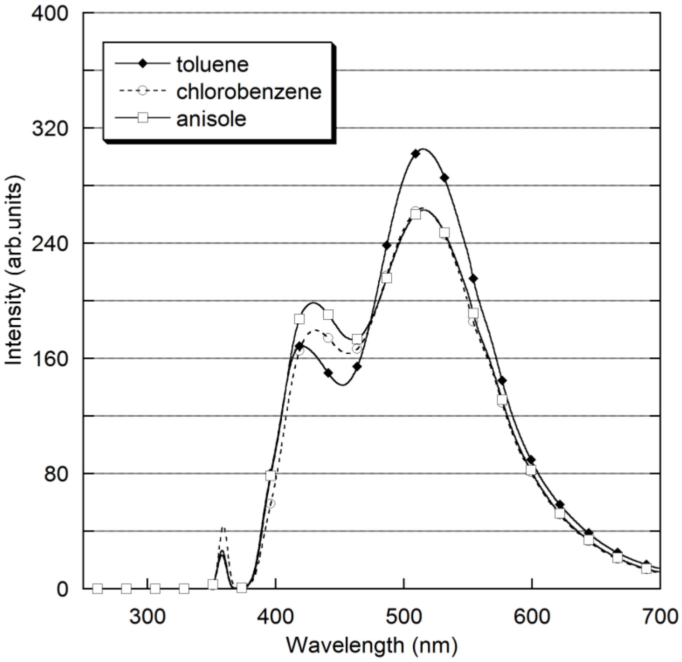


Figure S-72. Fluorescent spectra of **1** in toluene and chlorobenzene and anisole. (30 mg/L, excitation wavelength were set to 357.5 nm in 1,1,2,2-tetrachloroethane, 358.5 nm in CH_2Cl_2, and 357.5 nm in 1,2-dichloroethane.)

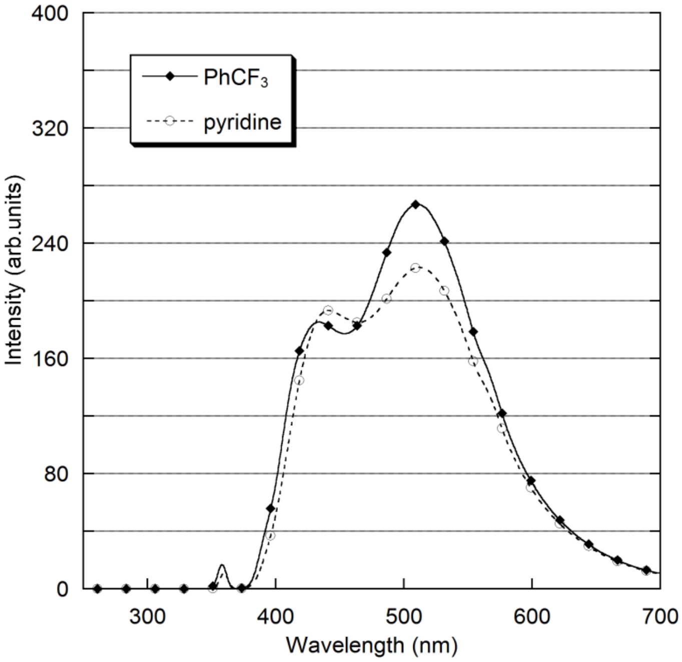


Figure S-73. Fluorescent spectra of **1** in $PhCF_3$ and pyridine. (30 mg/L, excitation wavelength were set to 357.5 nm in $PhCF_3$ and 359.0 nm in pyridine.)

4 Absolute quantum yields of new compounds

Table S-1. Absolute quantum yields of compounds in CHCl3, 1,1,1-TCE, and 1,1,2-TCE

compound	quantum yield in $CHCl_3$ (excitation wavelength)	quantum yield in 1,1,1-TCE (excitation wavelength)	quantum yield in 1,1,2-TCE (excitation wavelength)
1-Si	1.0% (356.5 nm)	0.8% (359.0 nm)	0.9% (358.0 nm)
1	4.8% (355.5 nm)	2.4% (357.0 nm)	3.2% (356.5 nm)
2-Si	0.6% (356.5 nm)	0.6% (360.0 nm)	-[a]
2	3.5% (356.5 nm)	2.0% (358.0 nm)	-[a]
3-Si	0.6% (356.5 nm)	0.4% (359.0 nm)	0.7% (358.0 nm)
3	4.5% (355.5 nm)	2.7% (357.0 nm)	2.0% (357.0 nm)
4	53.4% (353.0 nm)	37.4% (352.0 nm)	51.9% (353.5 nm)
5	48.1% (353.0 nm)	47.3% (352.0 nm)	47.8% (353.5 nm)
6	20.3% (354.0 nm)	18.5% (353.0 nm)	17.4% (354.0 nm)

[a] Absolute quantum yield was not determined due to their low solubility.

5 NMR spectra of New Compounds

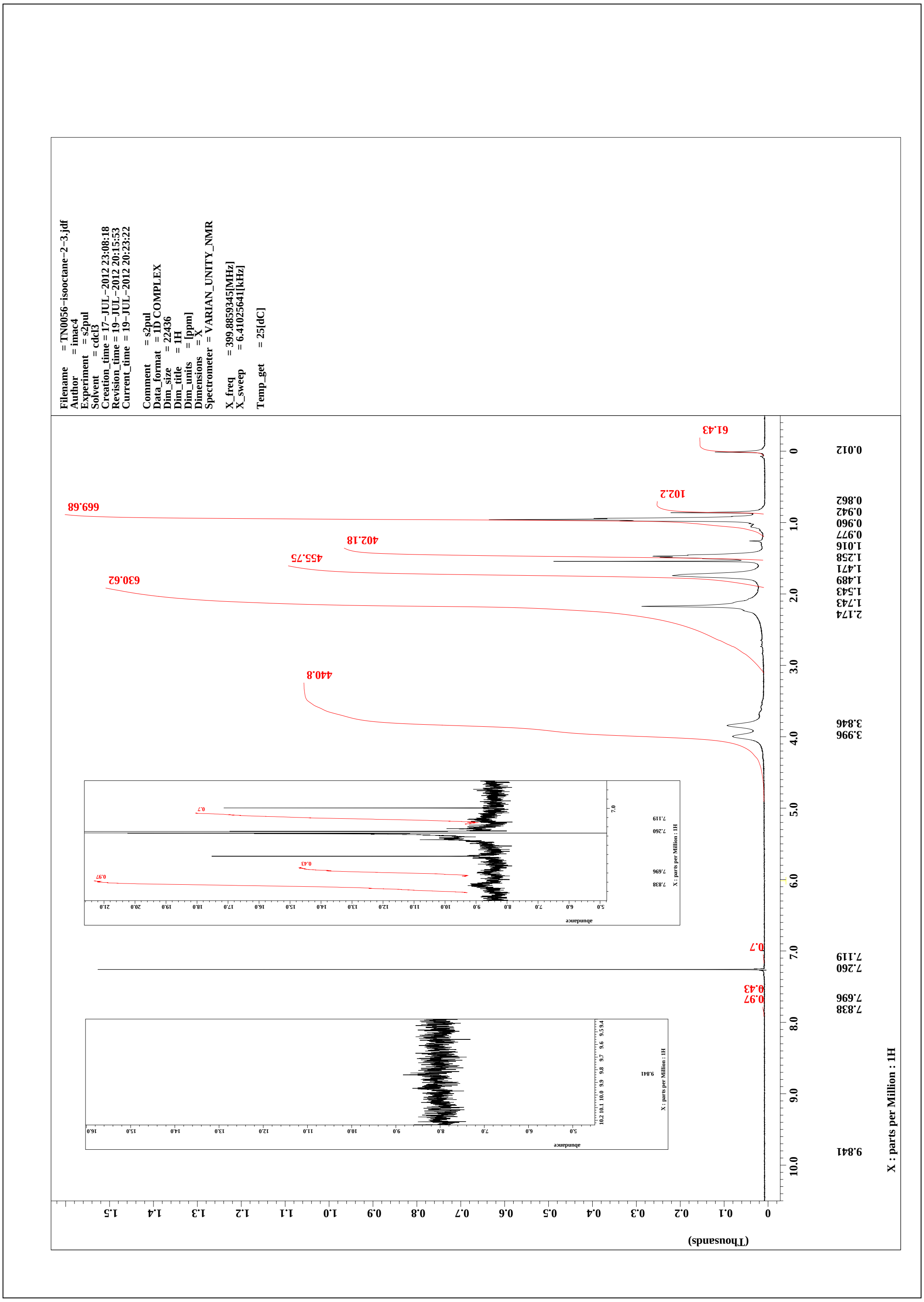


Figure S-74. ^{1}H NMR spectrum of **1-Si** in $CDCl_3$.

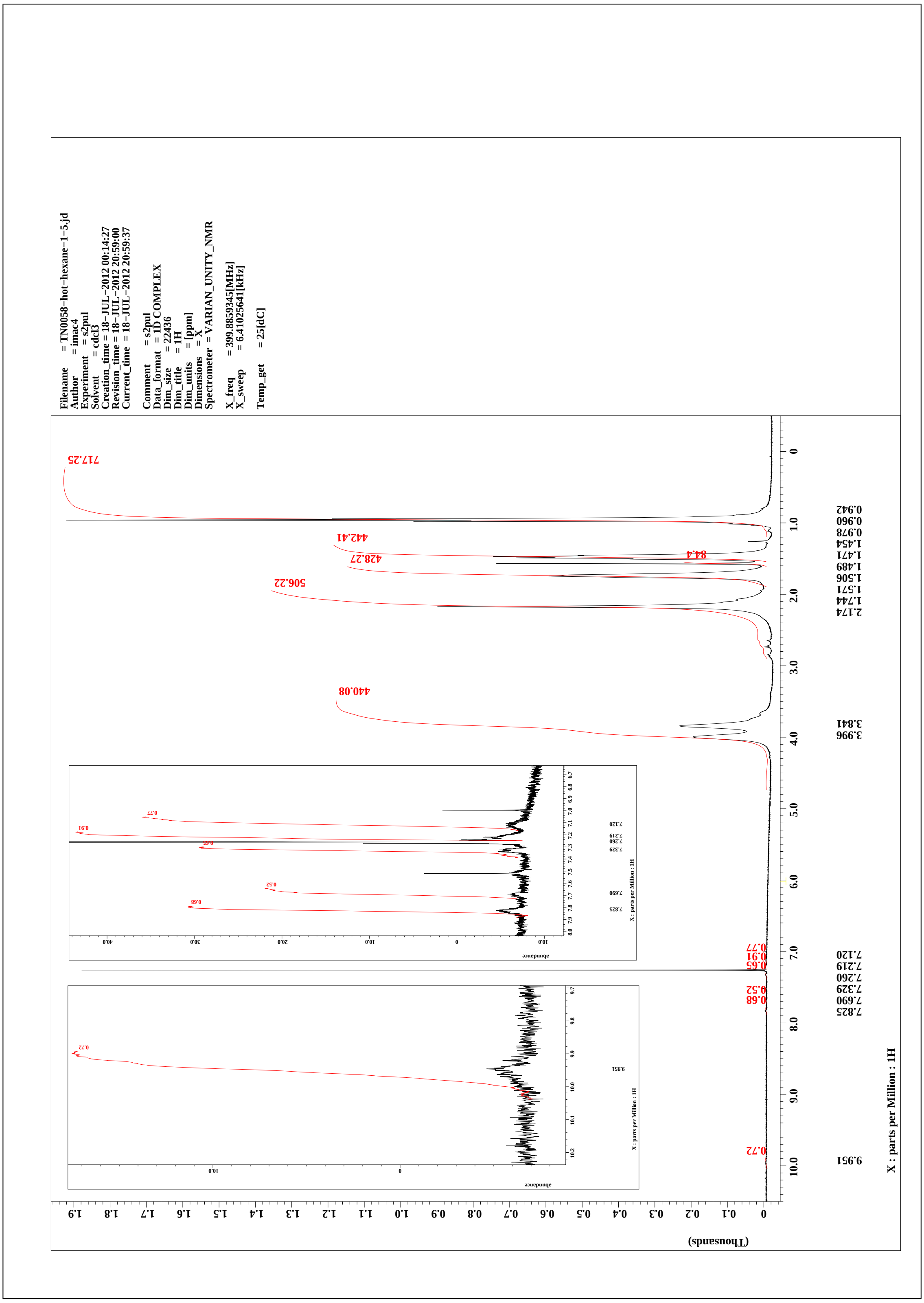


Figure S-75. ^{1}H NMR spectrum of **1-OH** in $CDCl_3$.

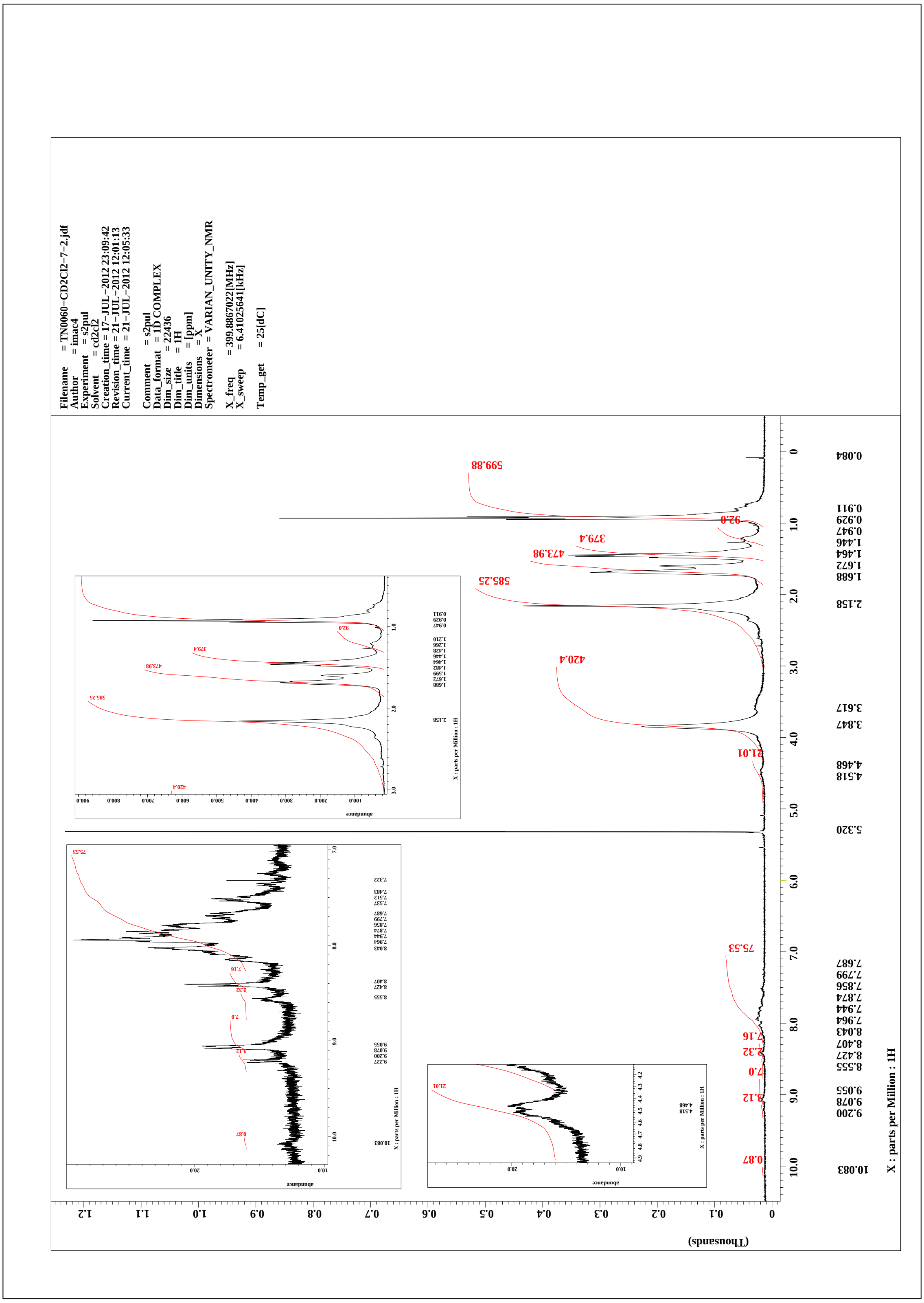


Figure S-76. ^{1}H NMR spectrum of **1** in CD_2Cl_2.

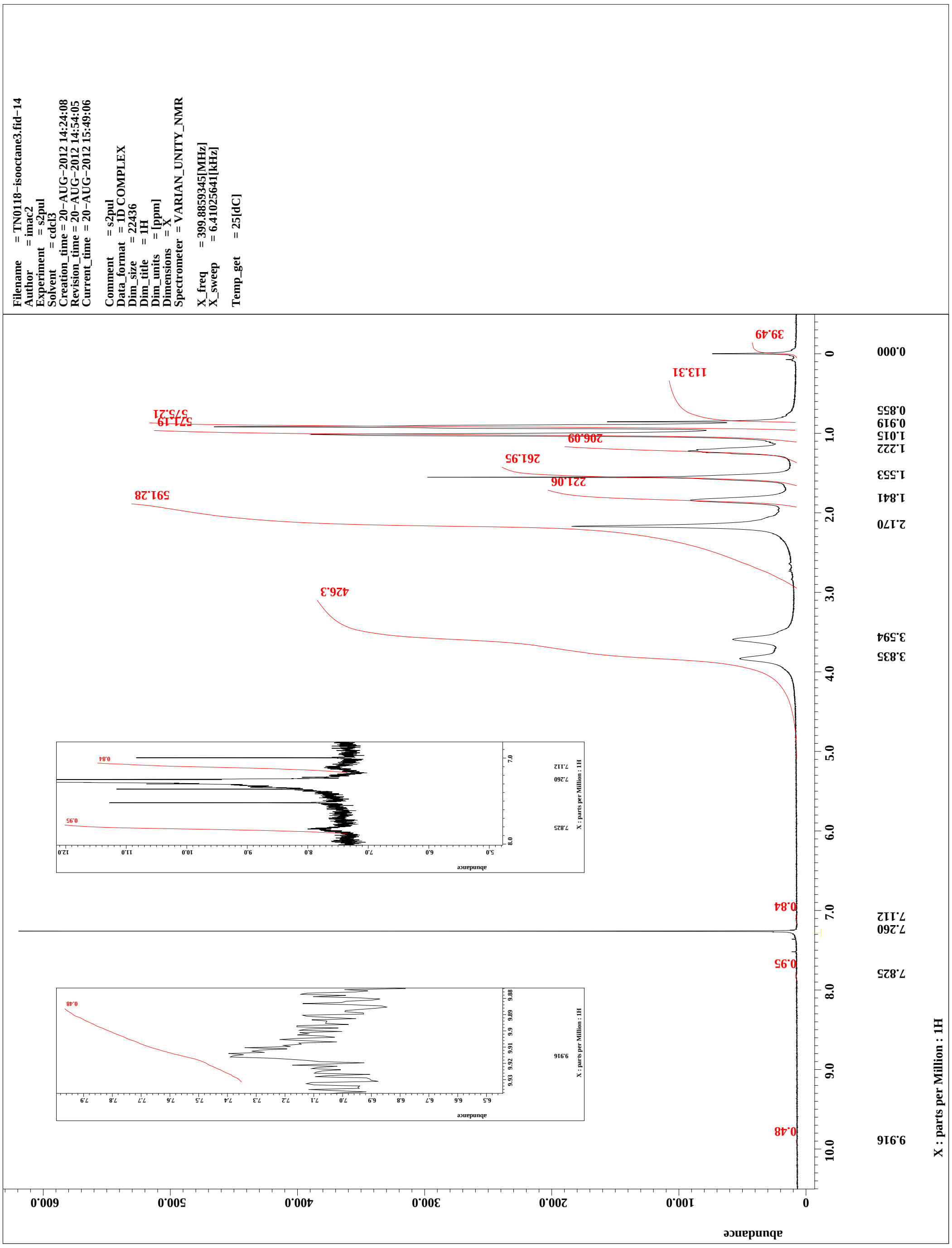


Figure S-77. ^{1}H NMR spectrum of **2-Si** in $CDCl_3$.

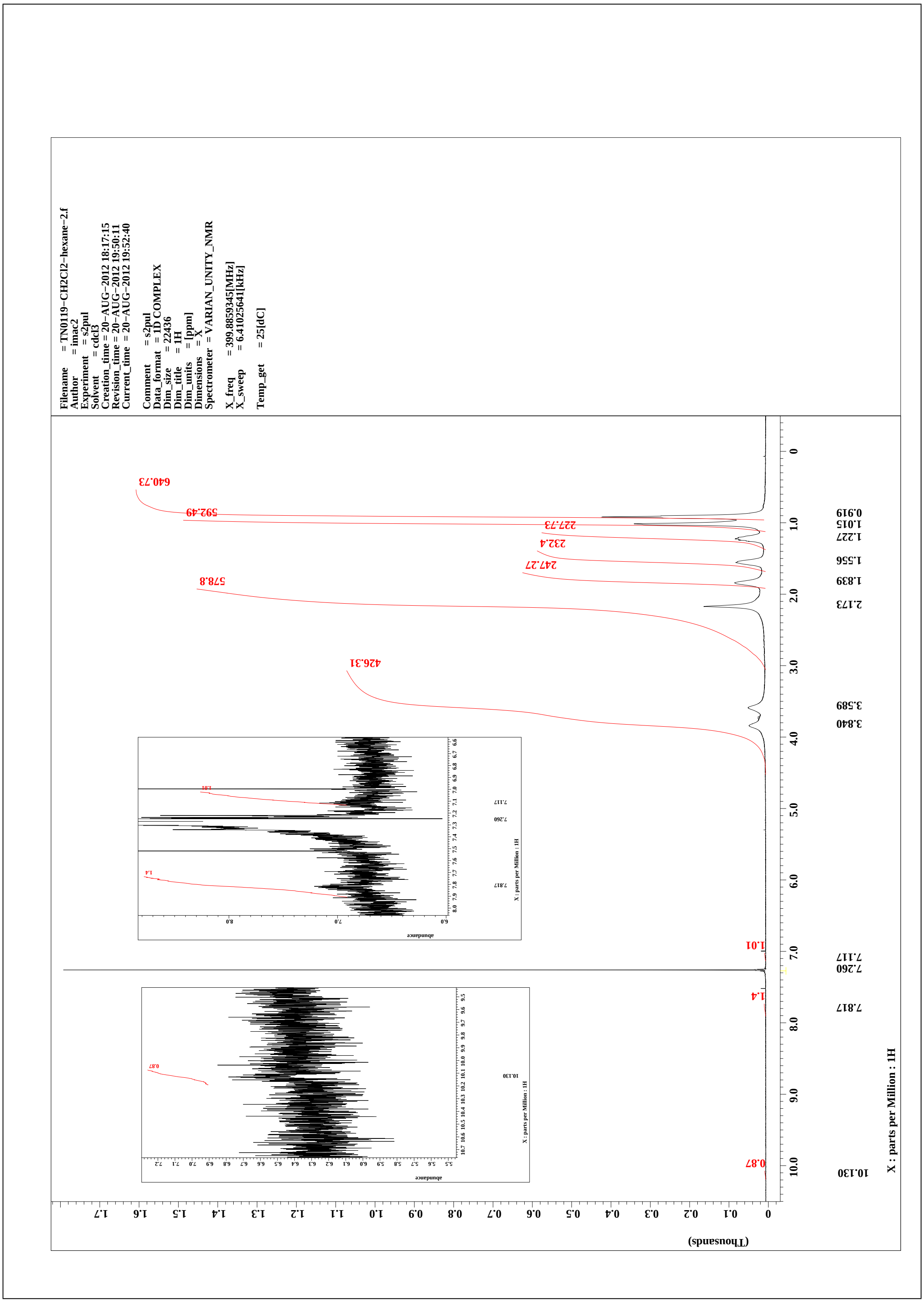


Figure S-78. ^{1}H NMR spectrum of **2-OH** in $CDCl_3$.

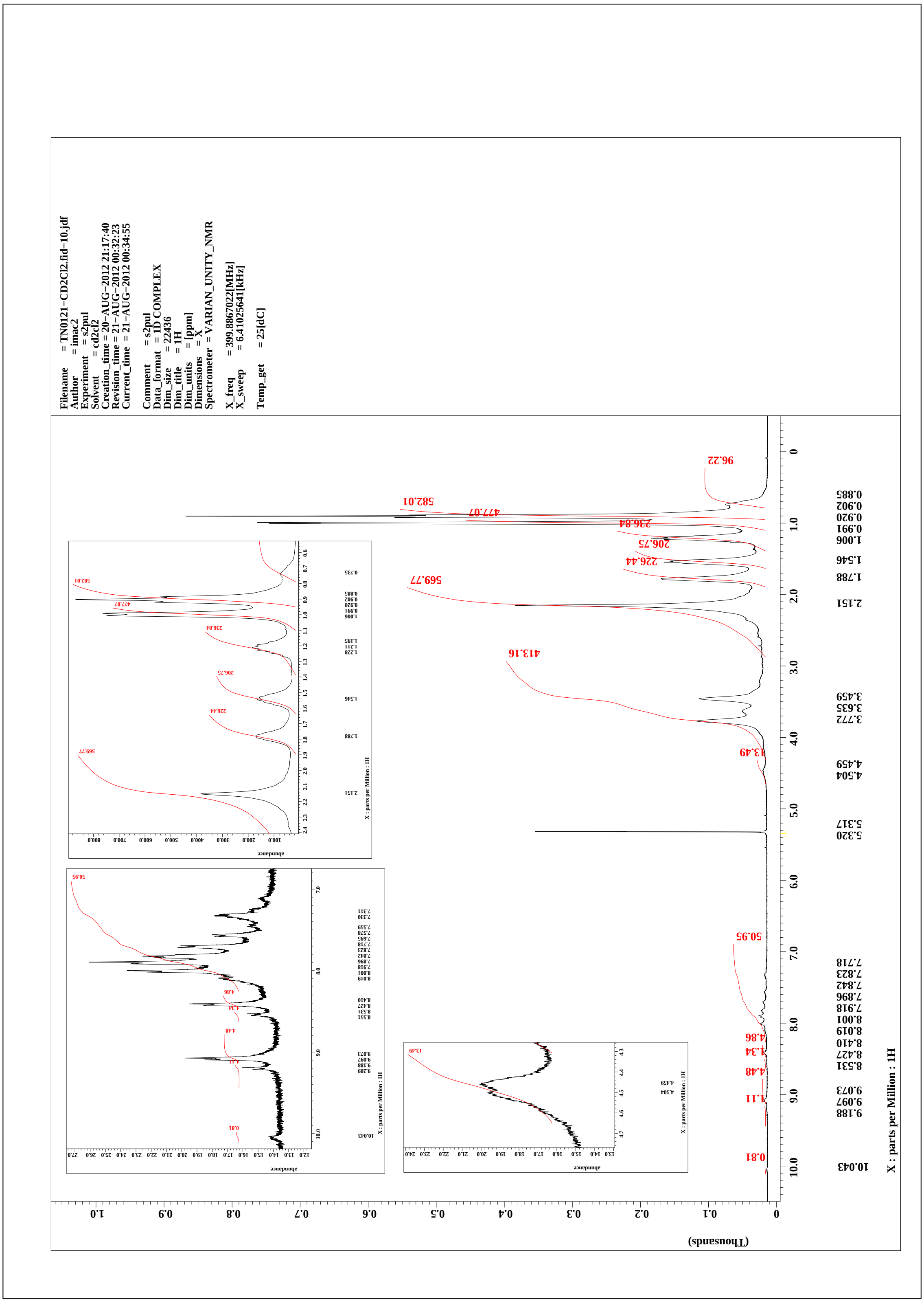


Figure S-79. ^{1}H NMR spectrum of **2** in CD_2Cl_2.

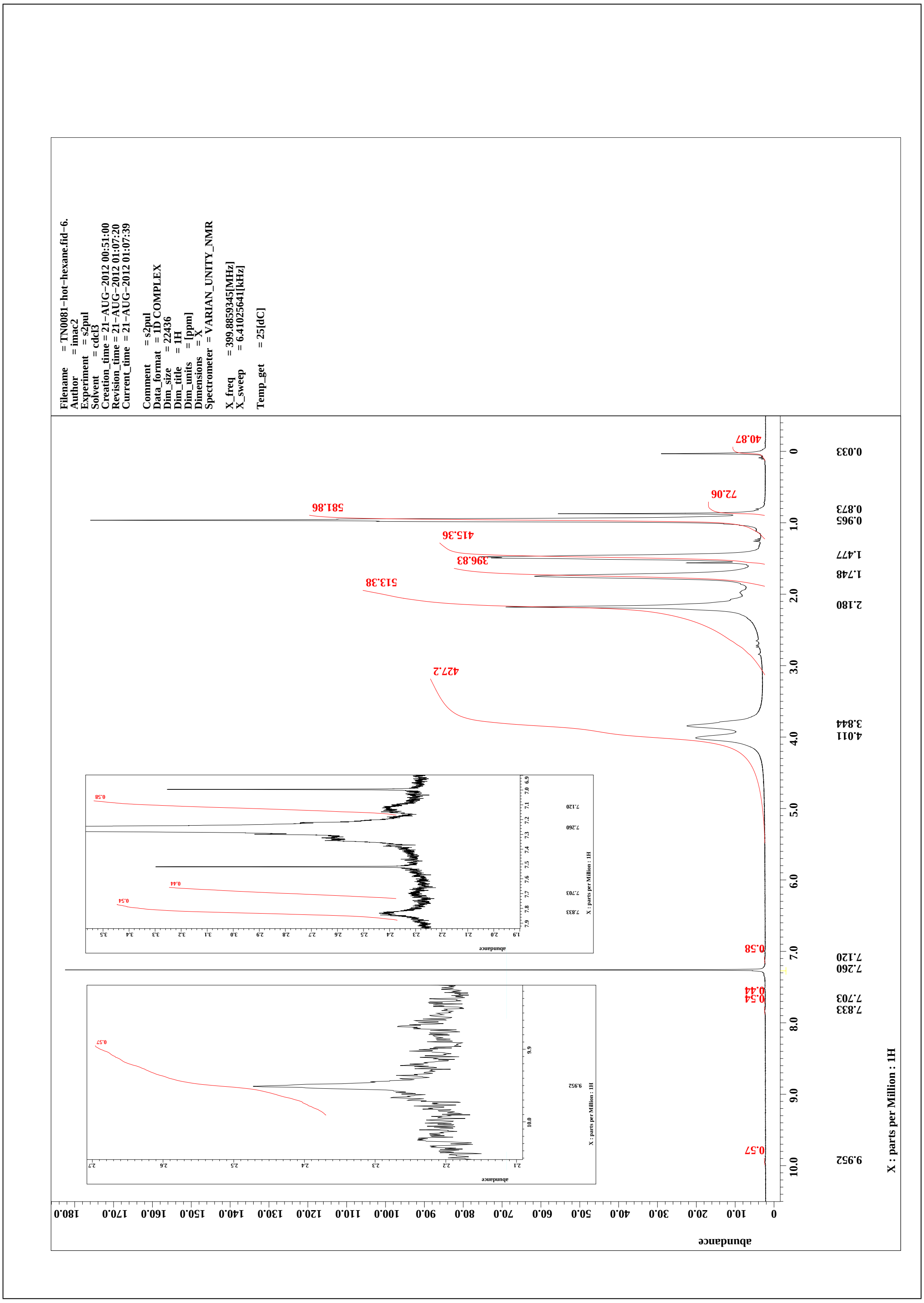


Figure S-80. ^{1}H NMR spectrum of **3-Si** in $CDCl_3$.

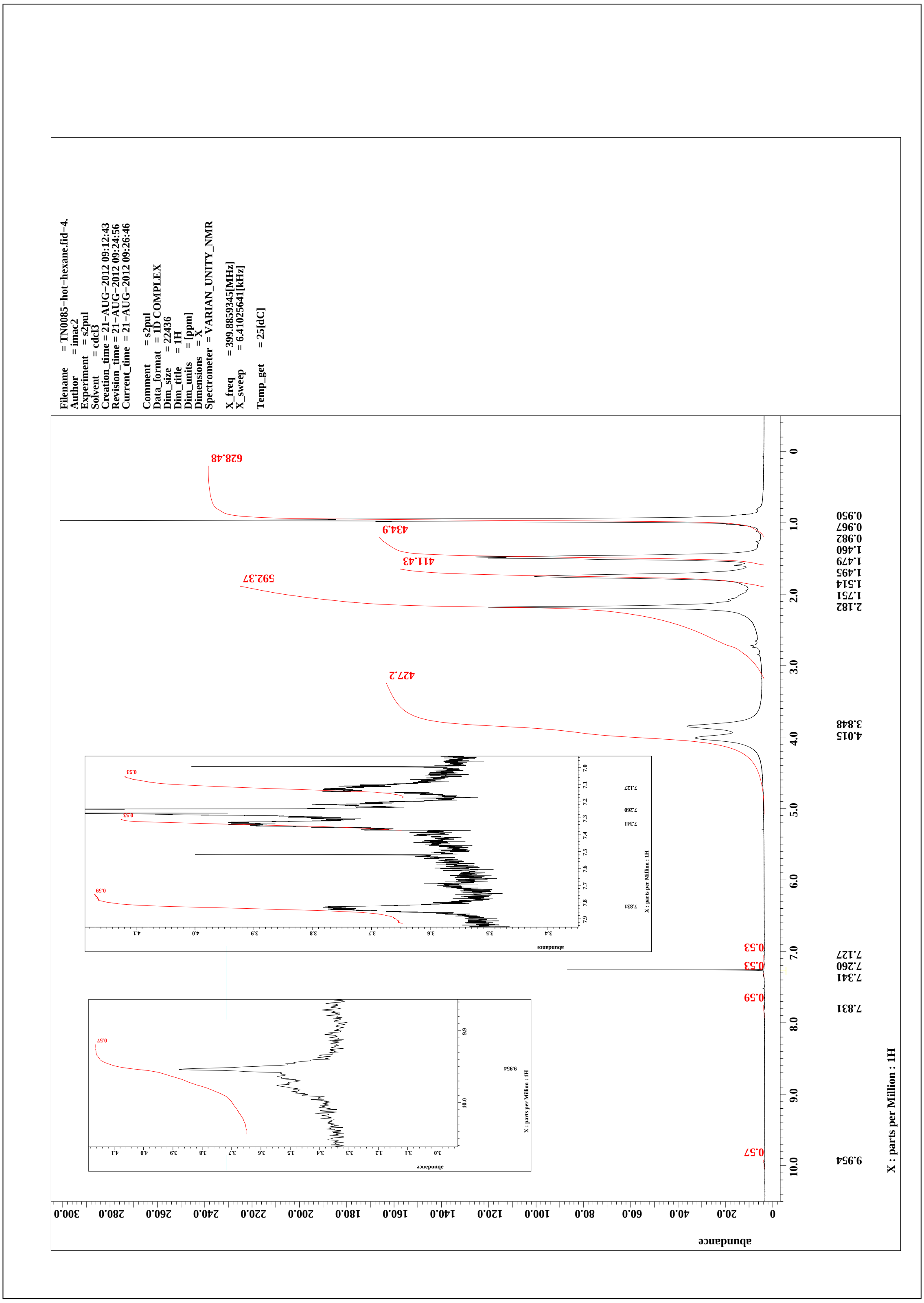


Figure S-81. ^{1}H NMR spectrum of **3-OH** in $CDCl_3$.

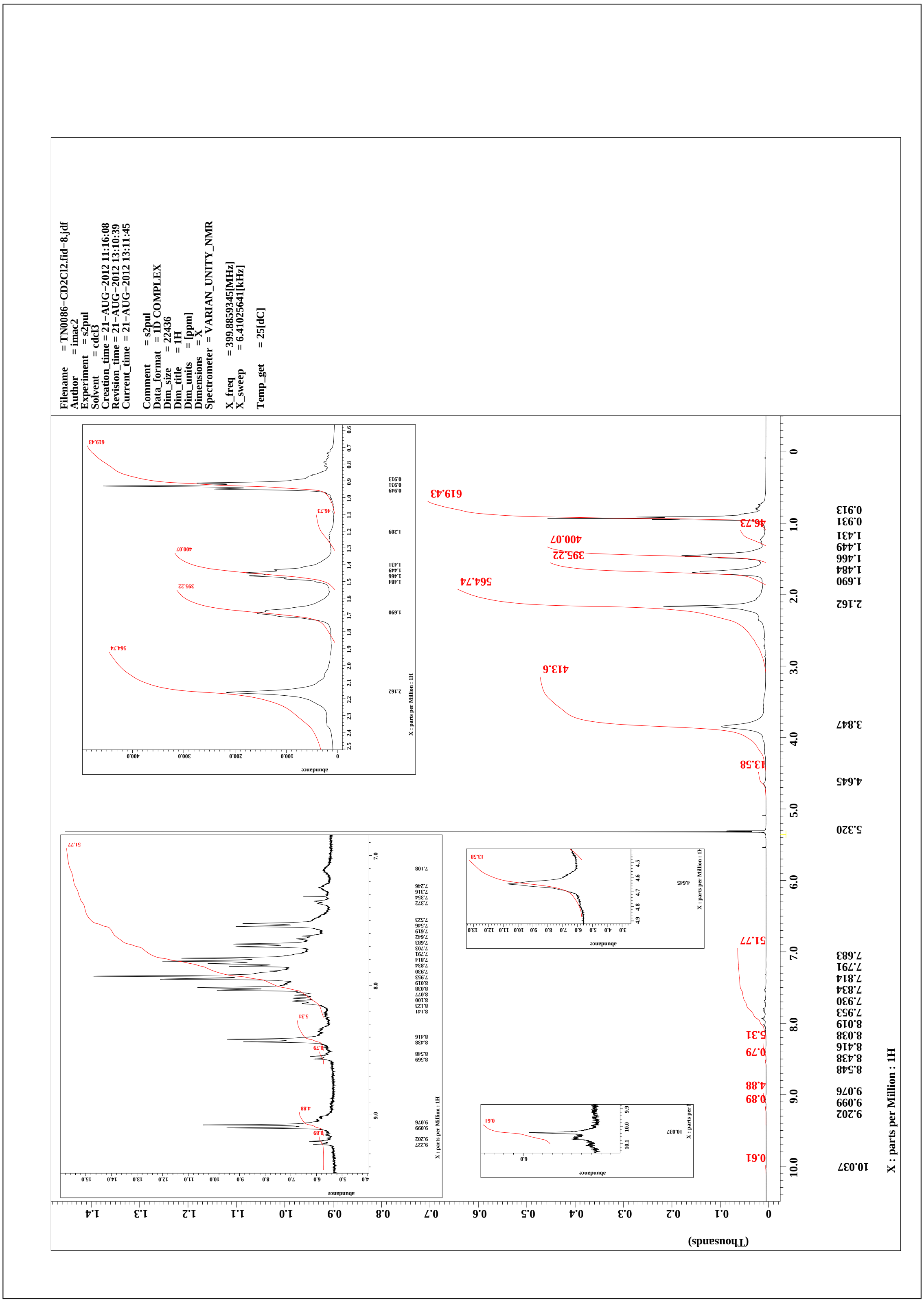


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Figure S-82. ^{1}H NMR spectrum of **3** in CD_2Cl_2.

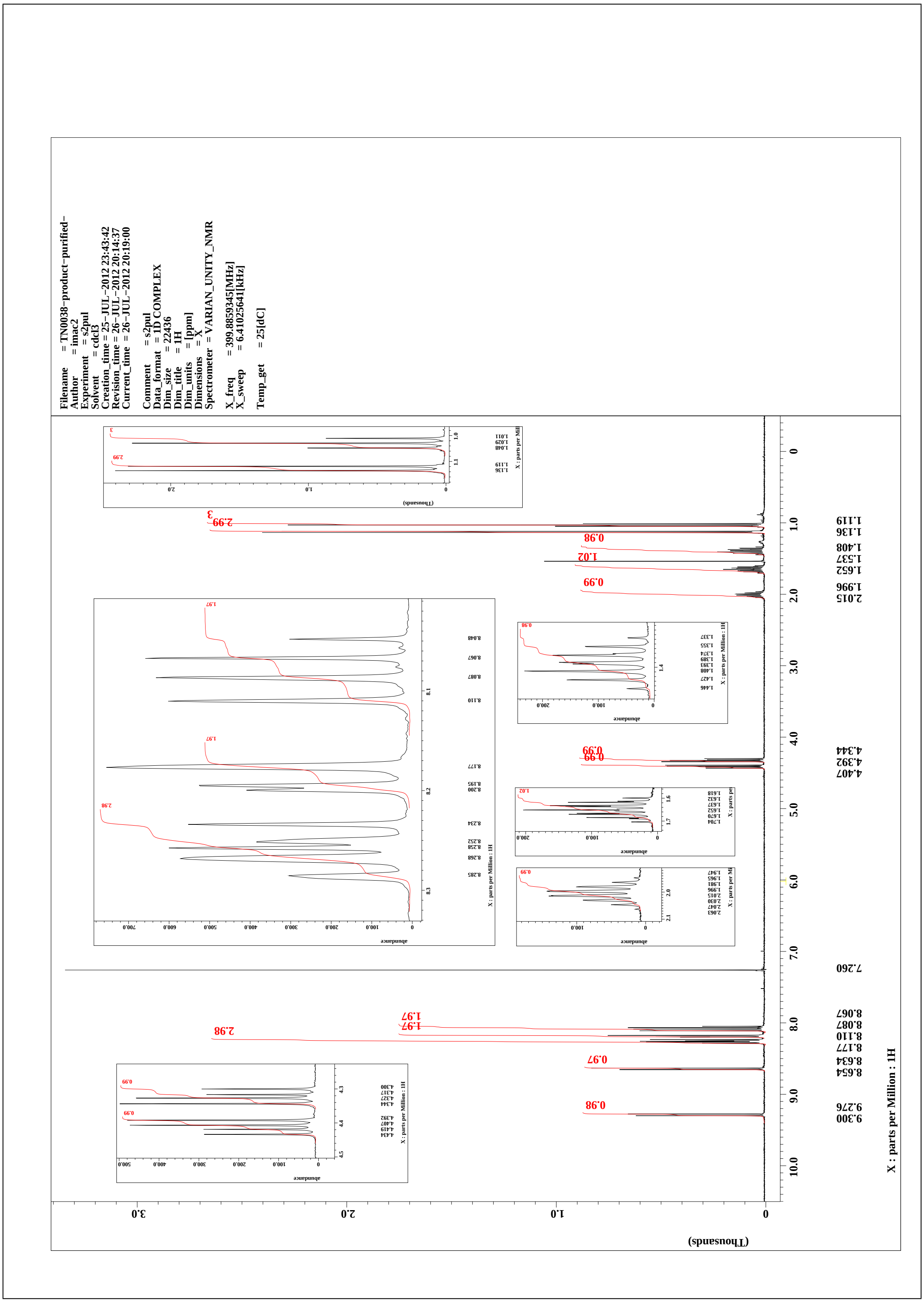

Figure S-83. ^{1}H NMR spectrum of **4** in $CDCl_3$.

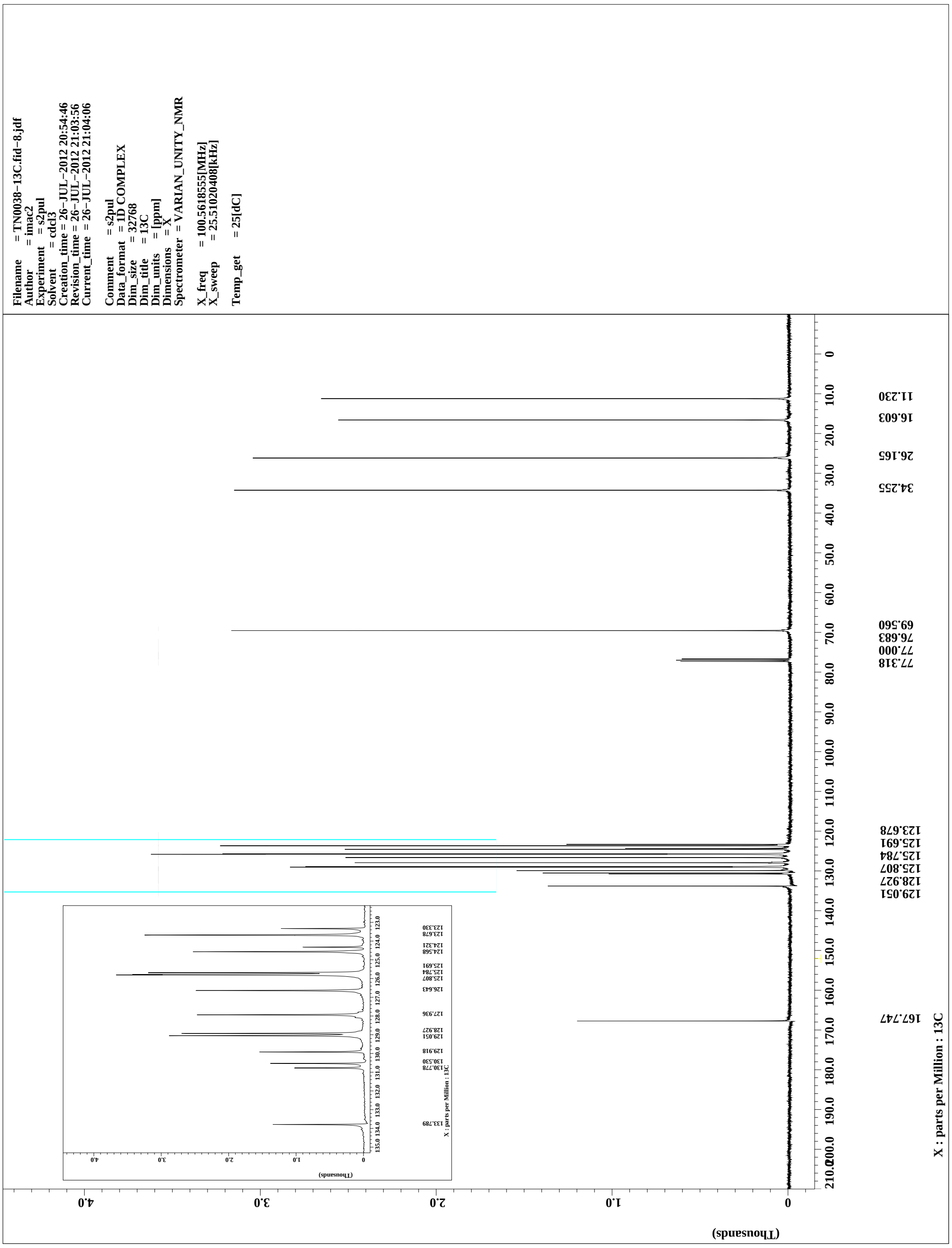

Figure S-84. ^{13}C NMR spectrum of **4** in $CDCl_3$.

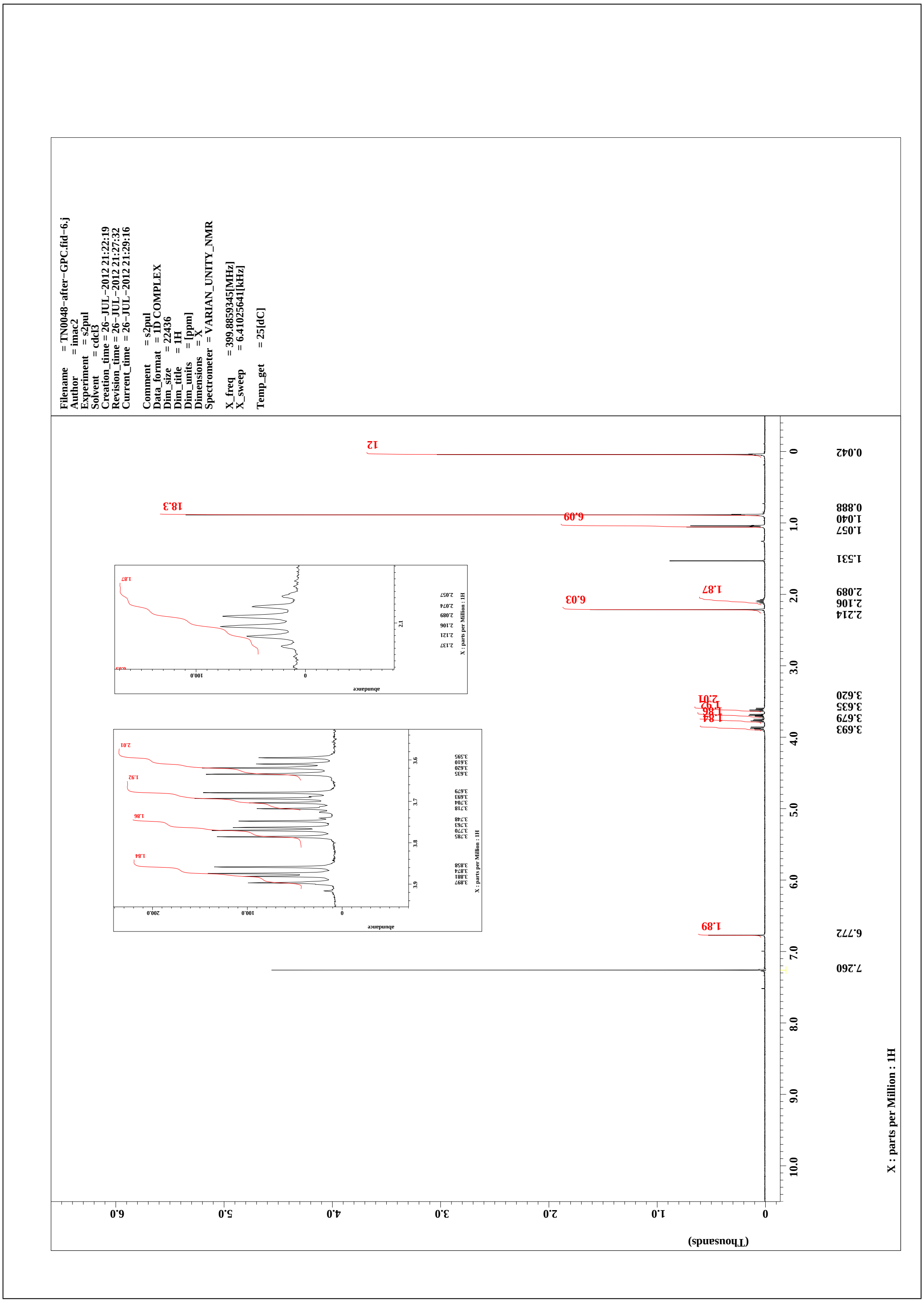

Figure S-85. ^{1}H NMR spectrum of **5-Si** in $CDCl_3$.

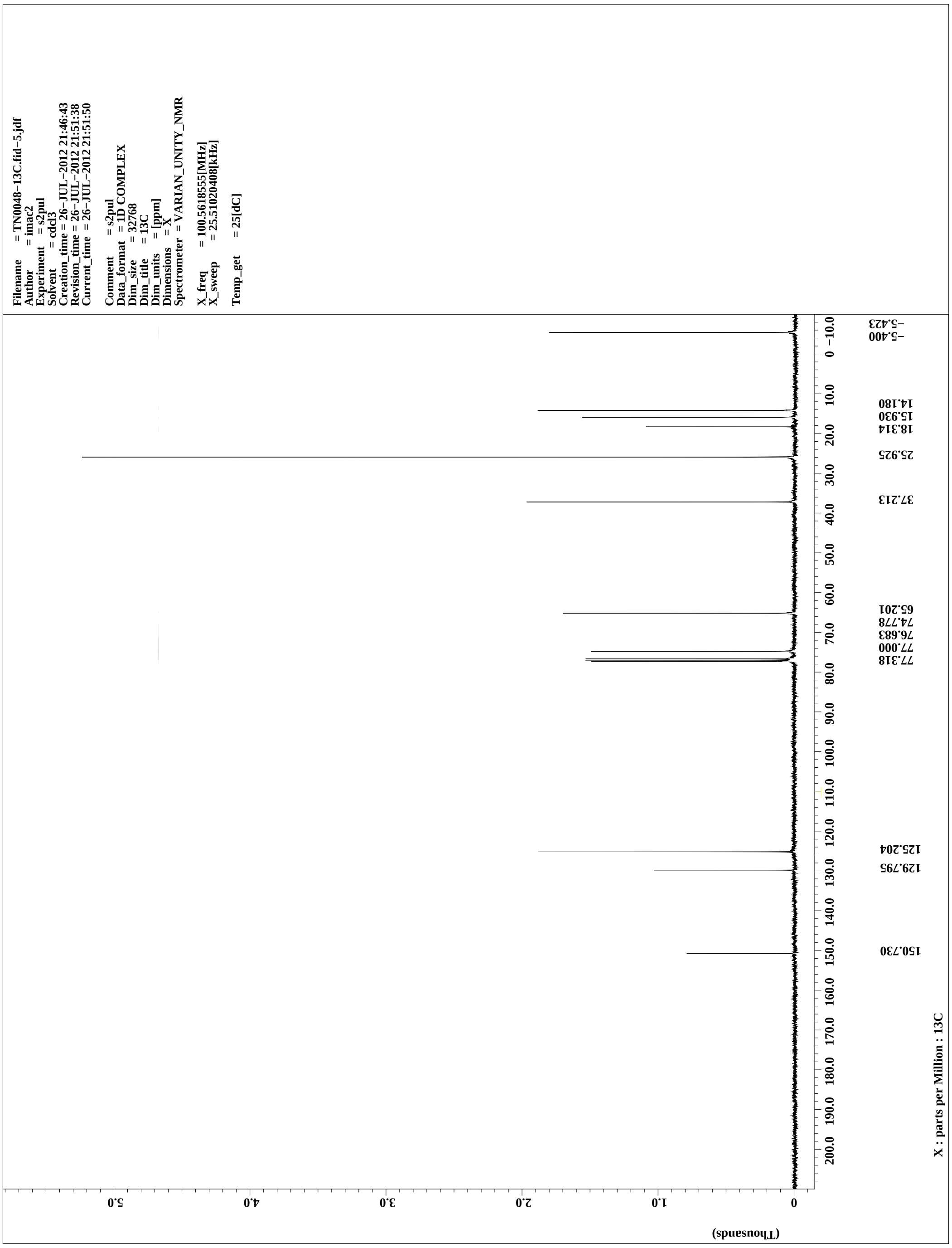

Figure S-86. ^{13}C NMR spectrum of **5-Si** in $CDCl_3$.

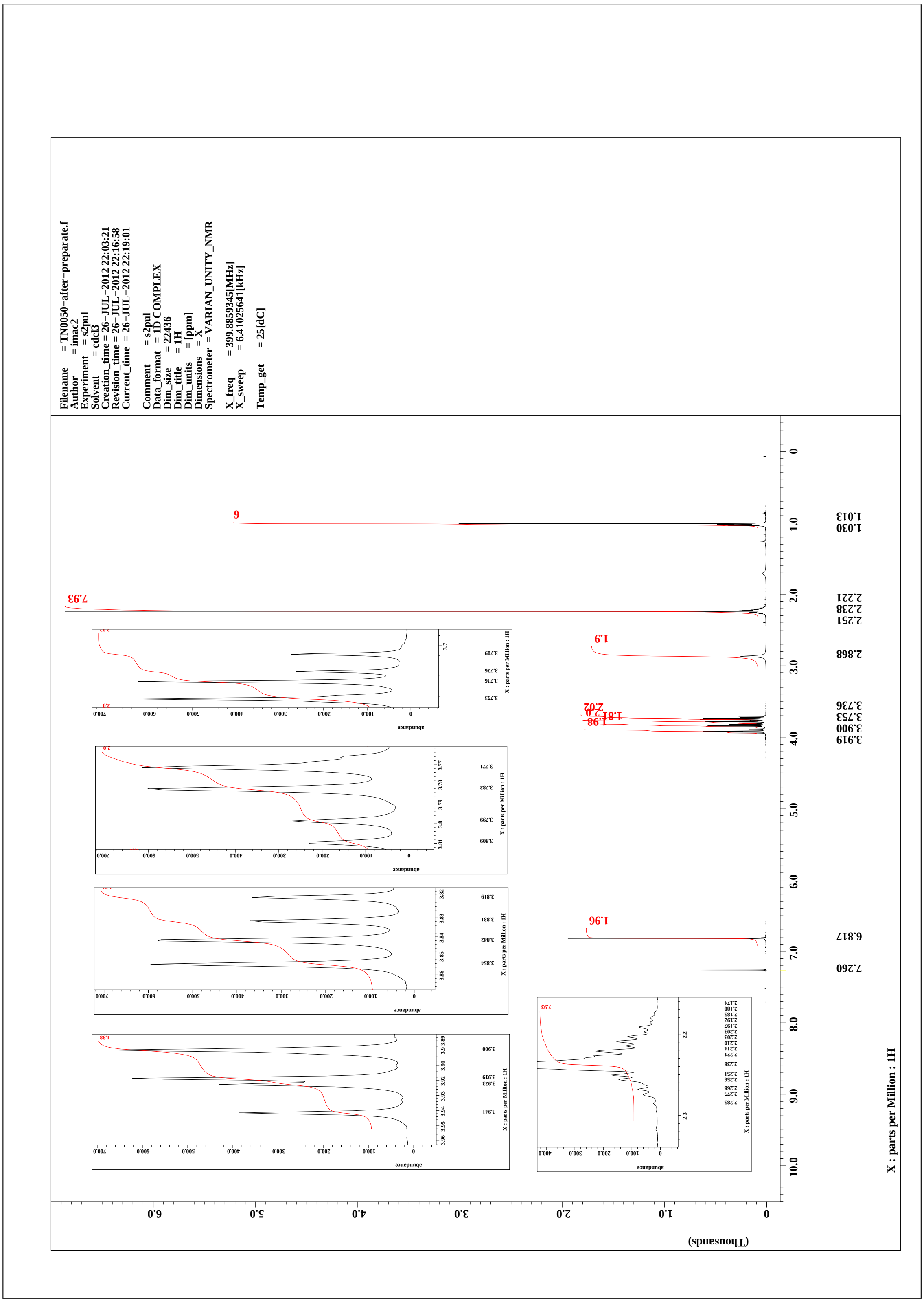

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Figure S-87. ^{1}H NMR spectrum of **5-OH** in $CDCl_3$.

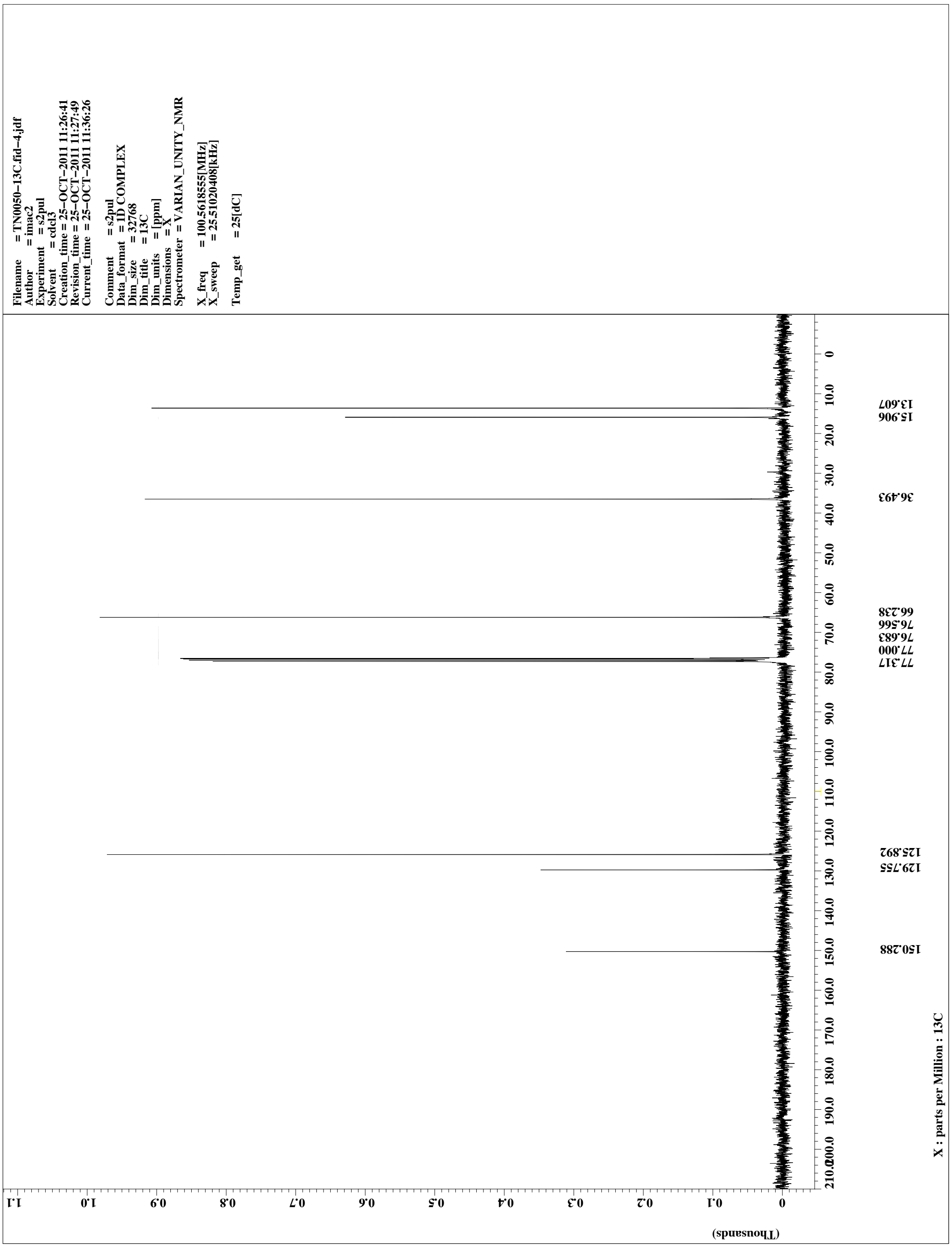

Figure S-88. ^{13}C NMR spectrum of **5-OH** in $CDCl_3$.

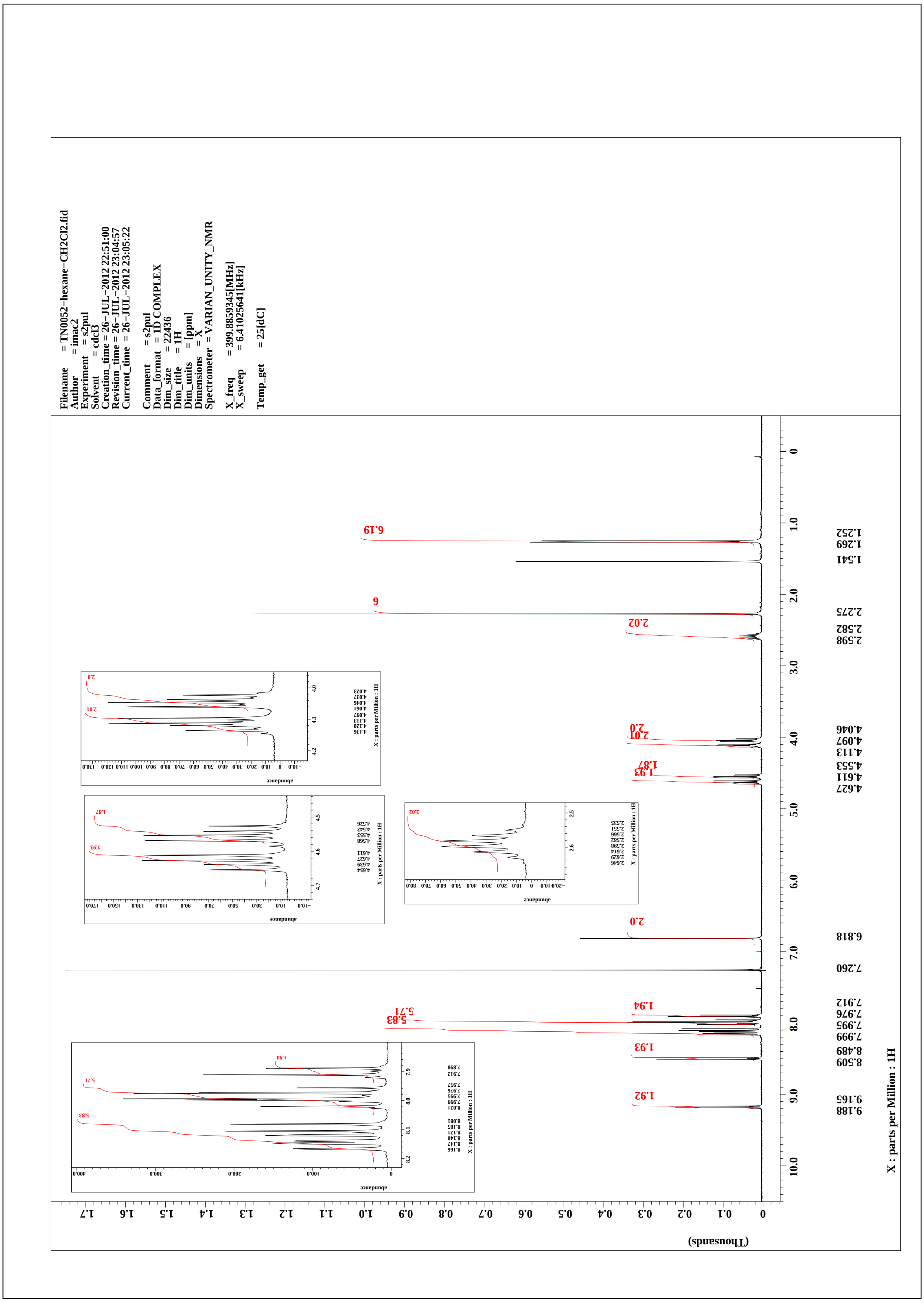

Figure S-89. ^{1}H NMR spectrum of **5** in $CDCl_3$.

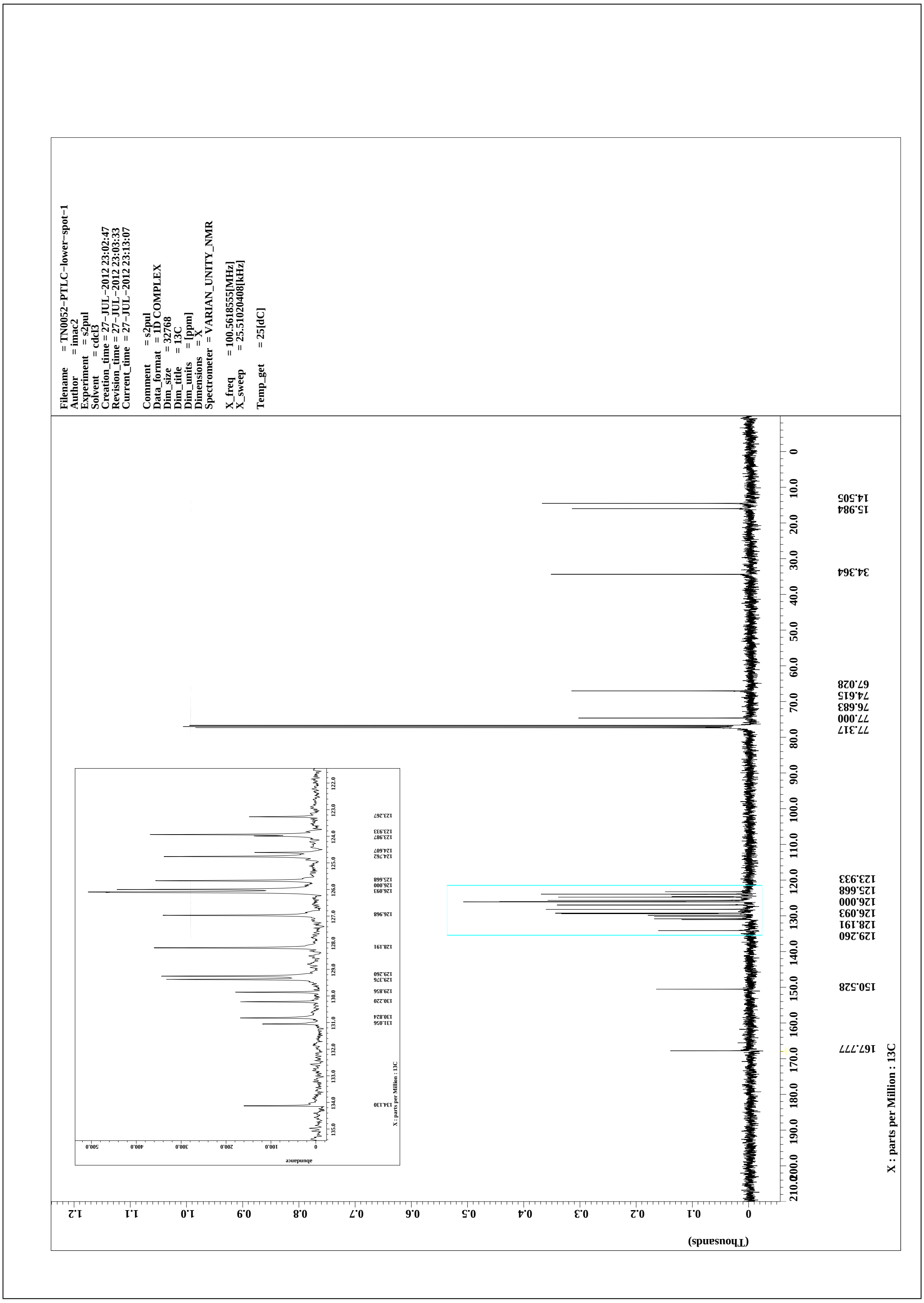

Figure S-90. ^{13}C NMR spectrum of **5** in $CDCl_3$.

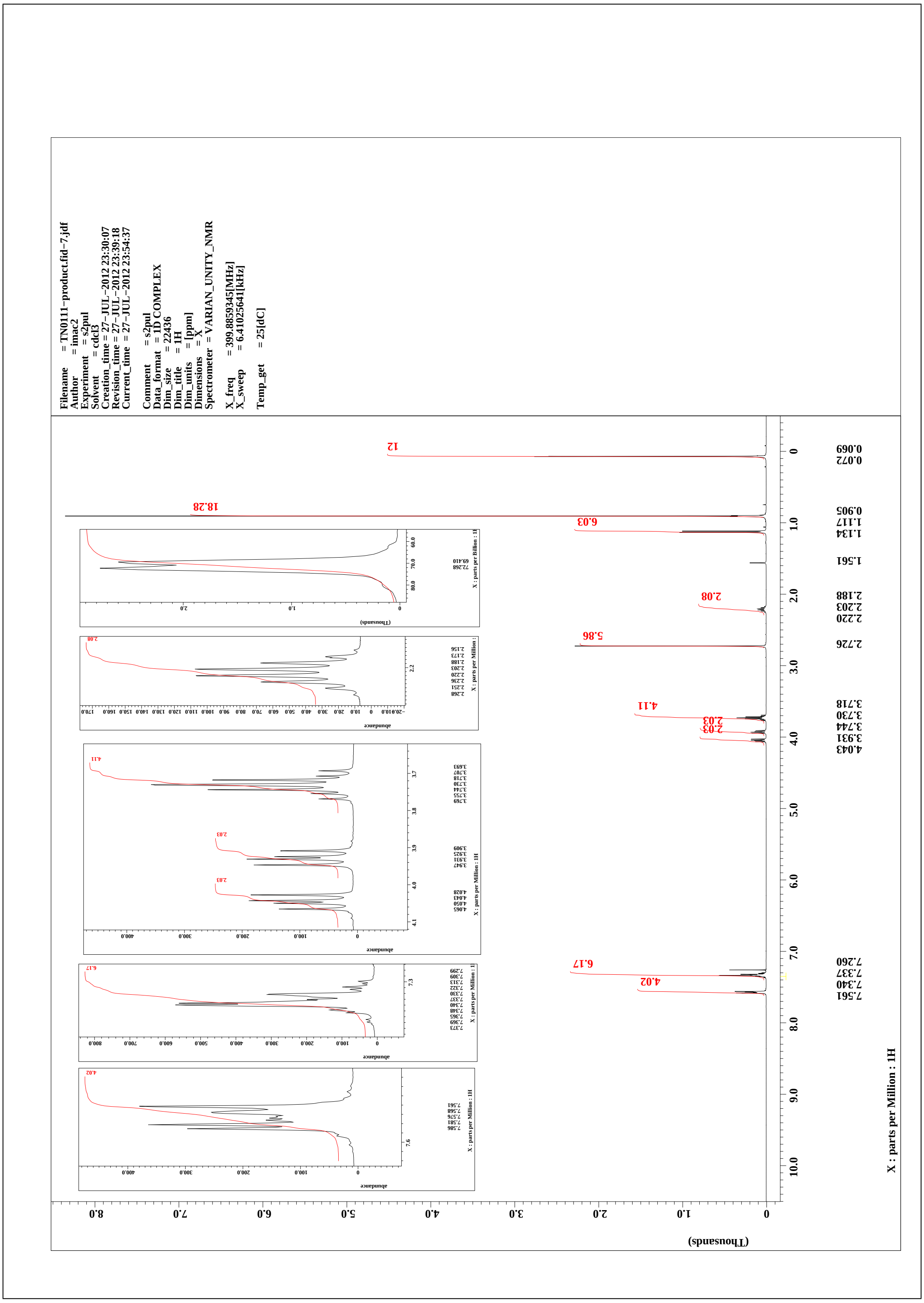

Figure S-91. ^{1}H NMR spectrum of **6-Si** in $CDCl_3$.

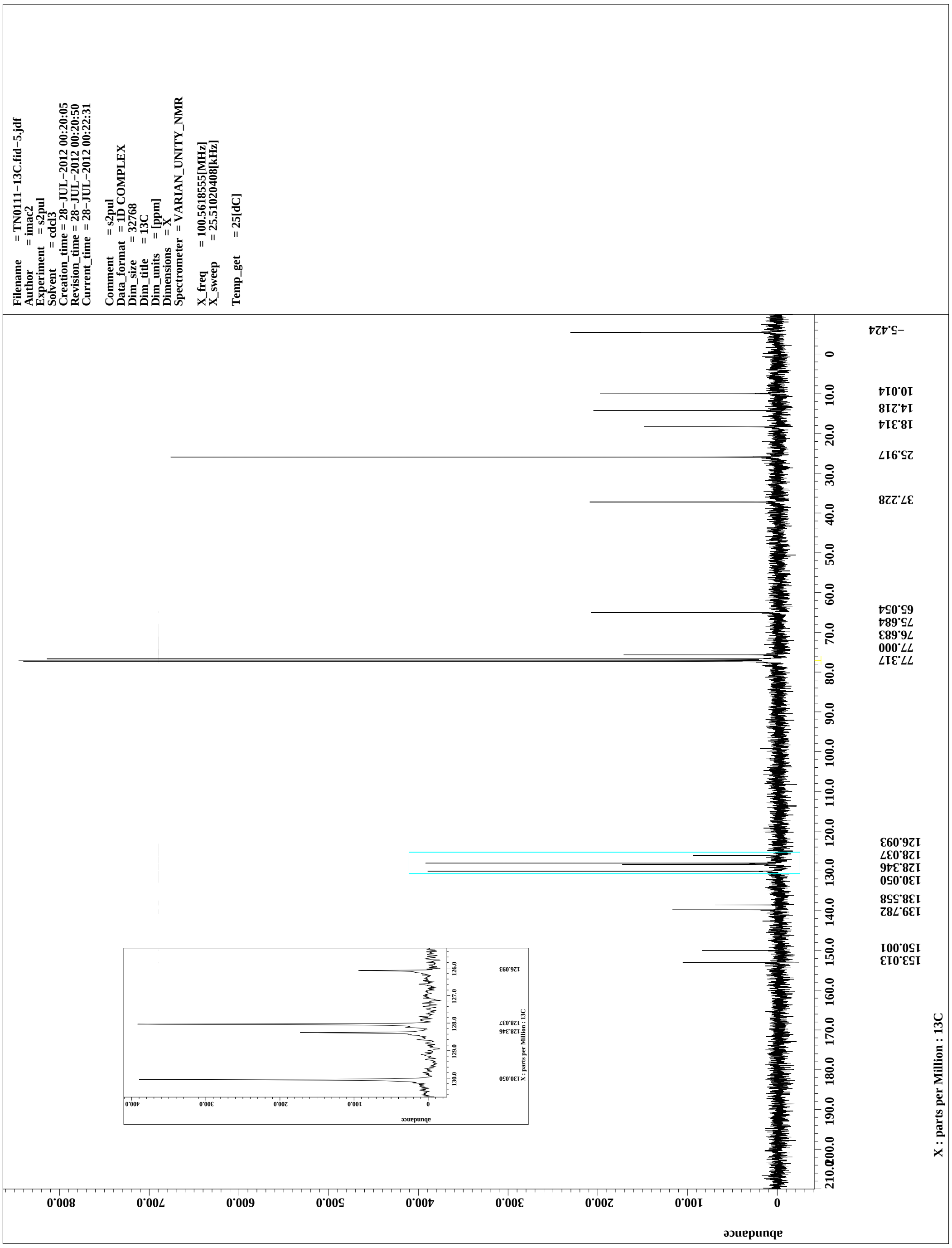

Figure S-92. ^{13}C NMR spectrum of **6-Si** in $CDCl_3$.

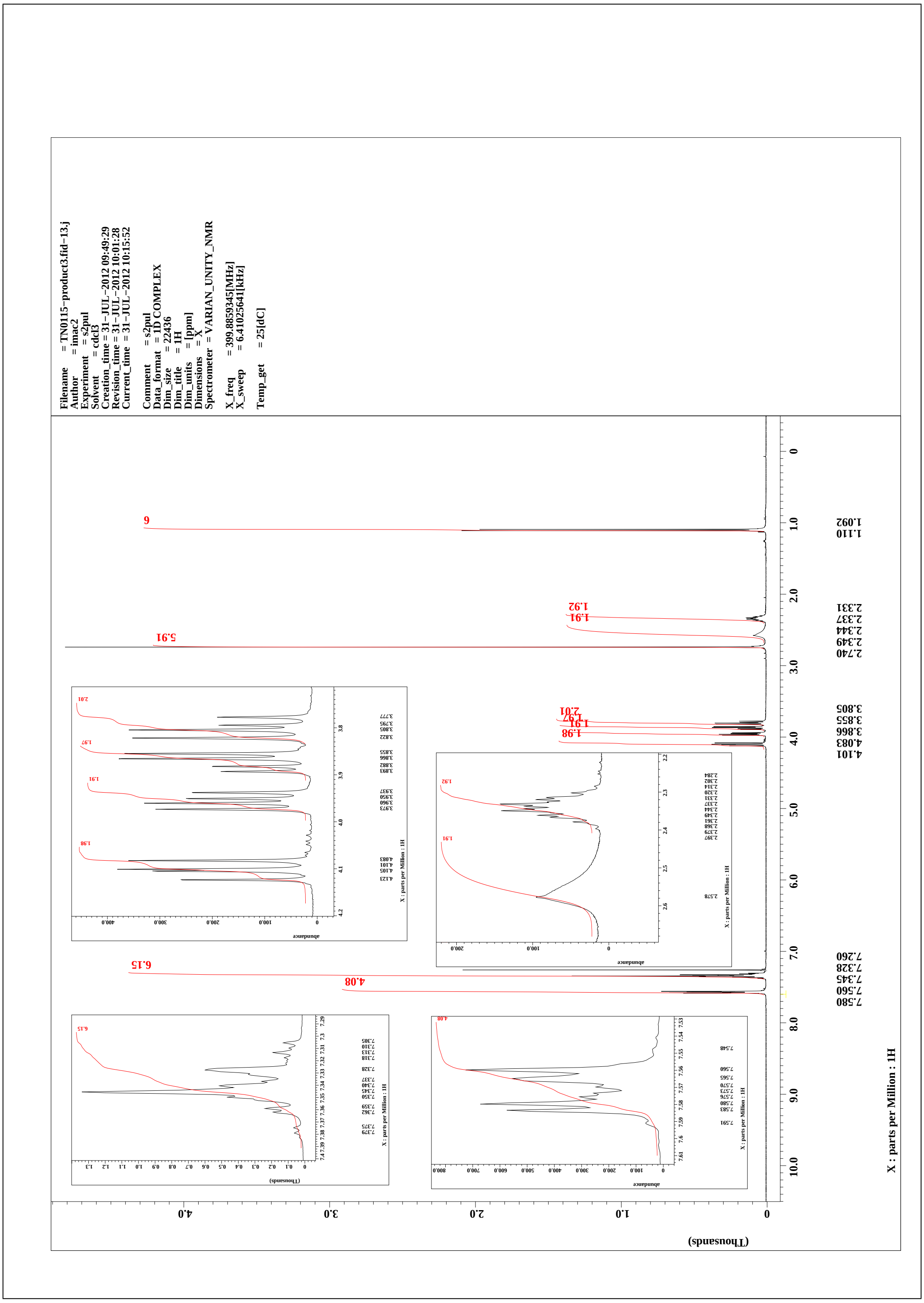

Figure S-93. ^{1}H NMR spectrum of **6-OH** in $CDCl_3$.

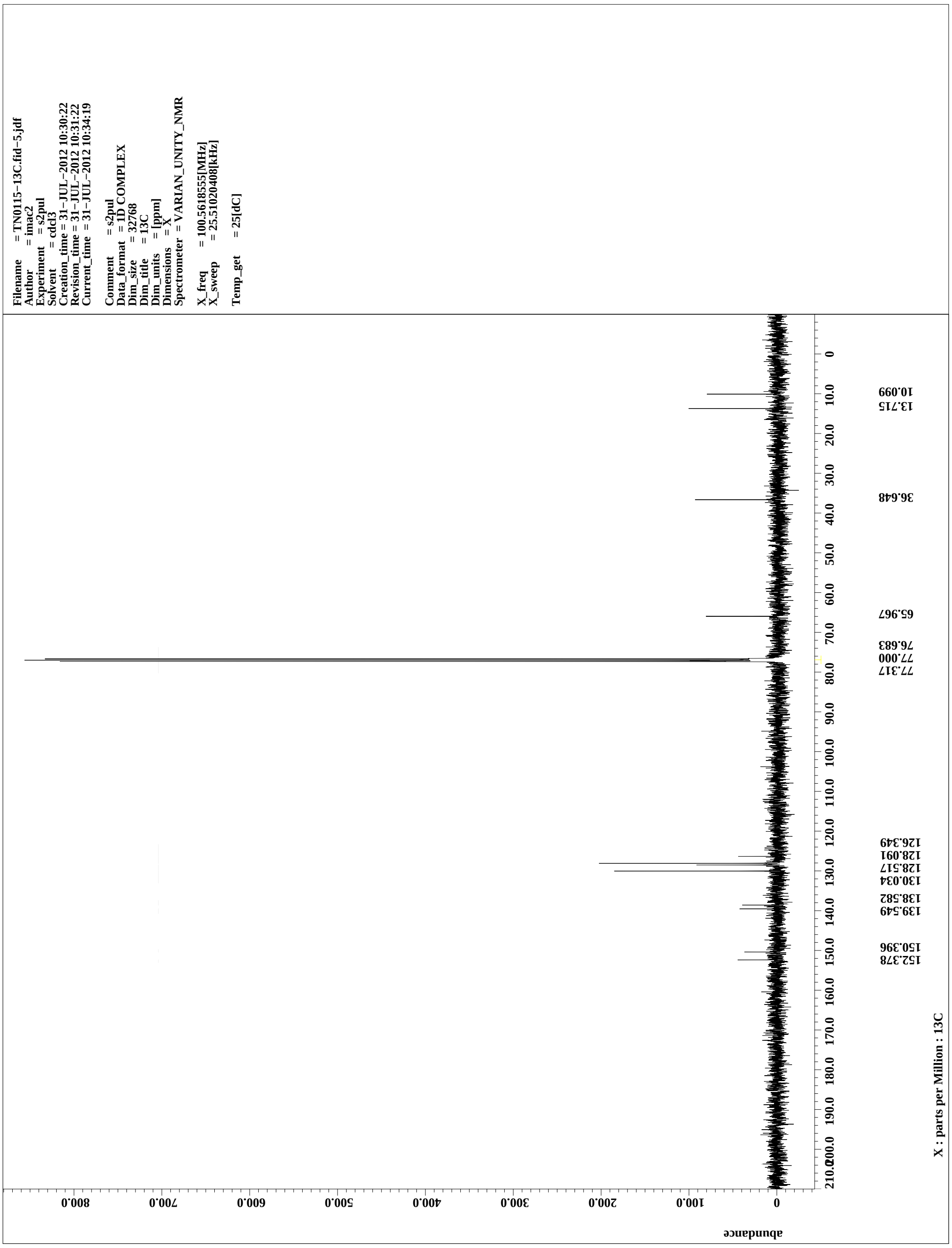

Figure S-94. ^{13}C NMR spectrum of **6-OH** in $CDCl_3$.

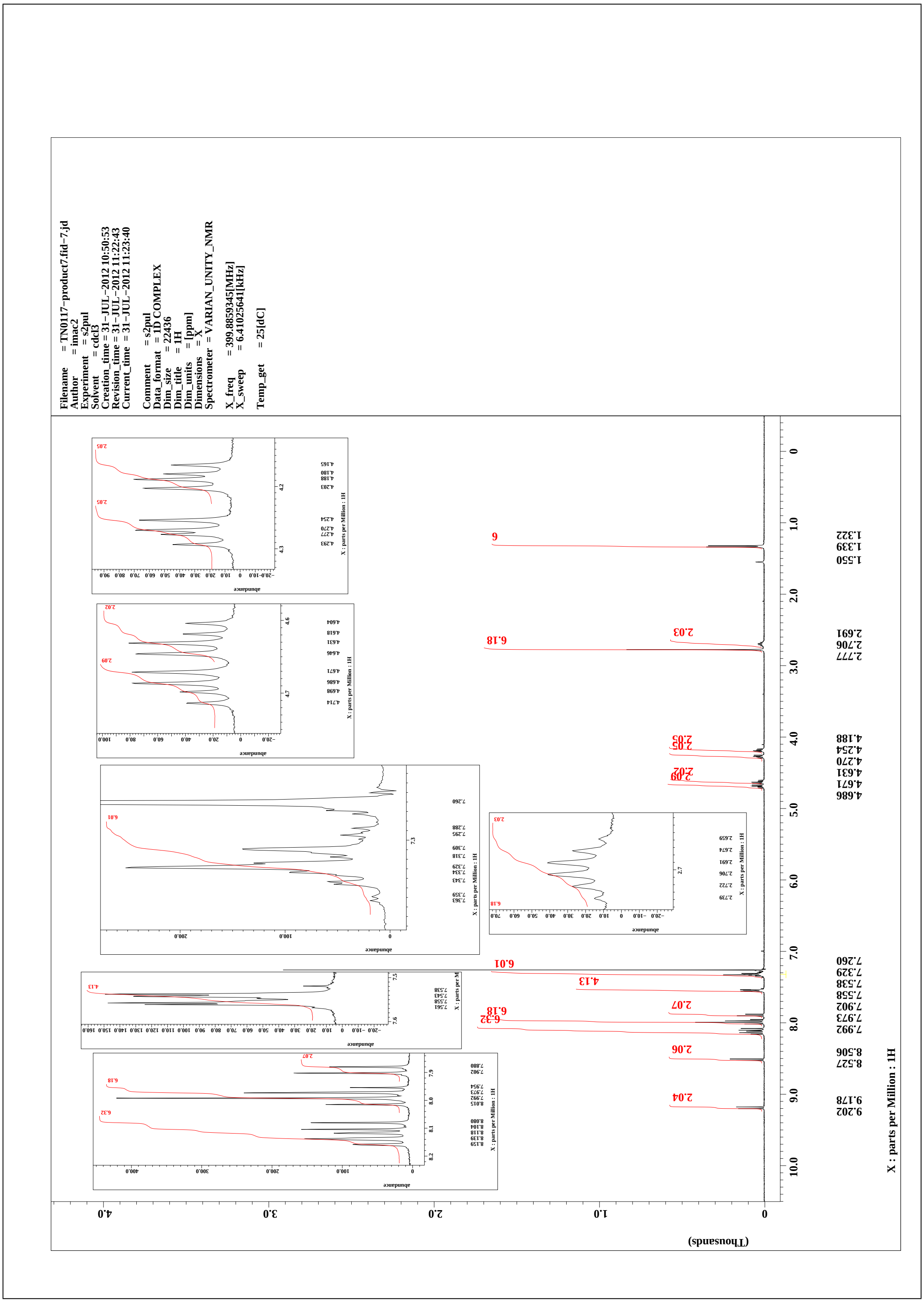

Figure S-95. ^{1}H NMR spectrum of **6** in $CDCl_3$.

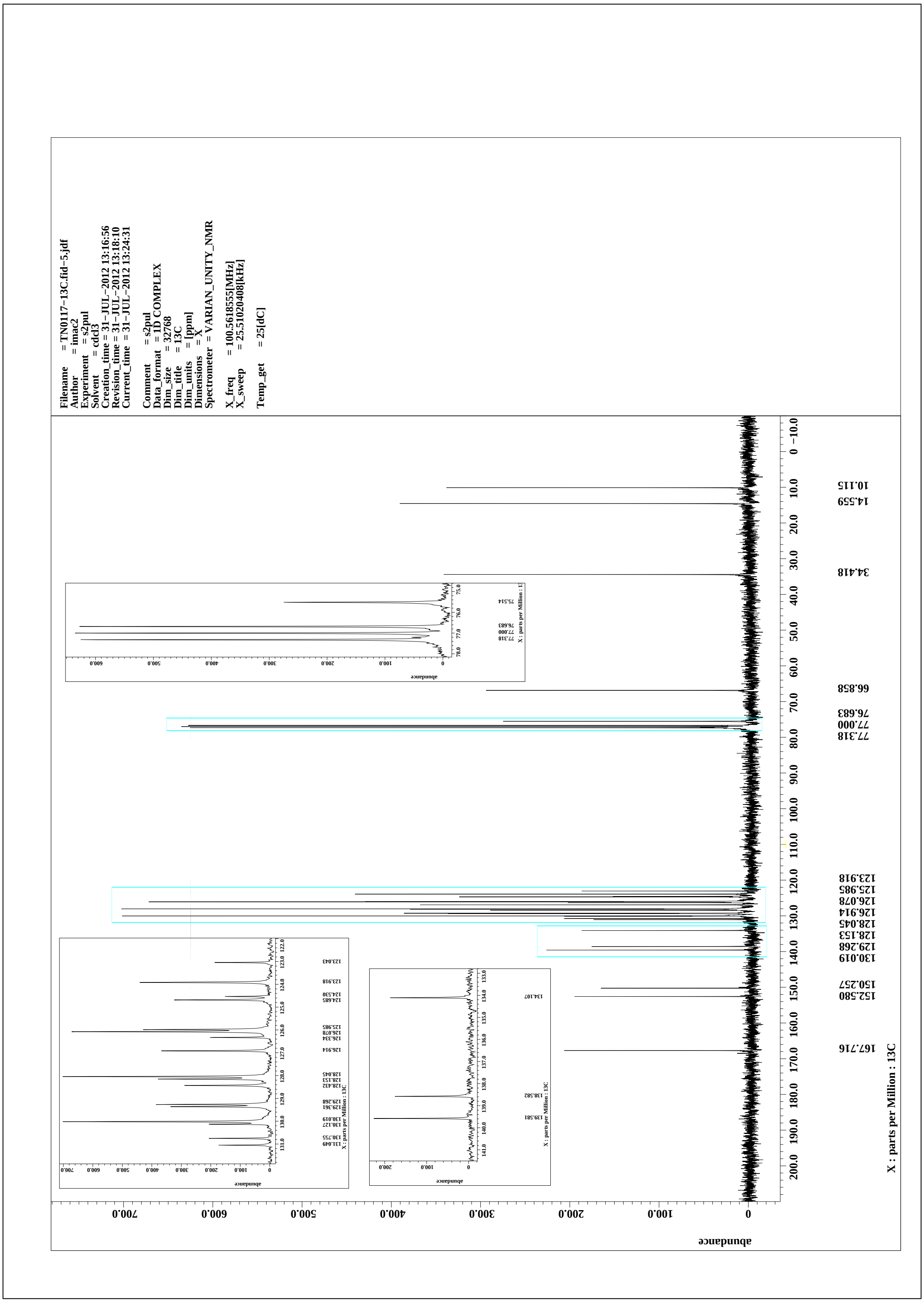

Figure S-96. ^{13}C NMR spectrum of **6** in CDCl$_3$.

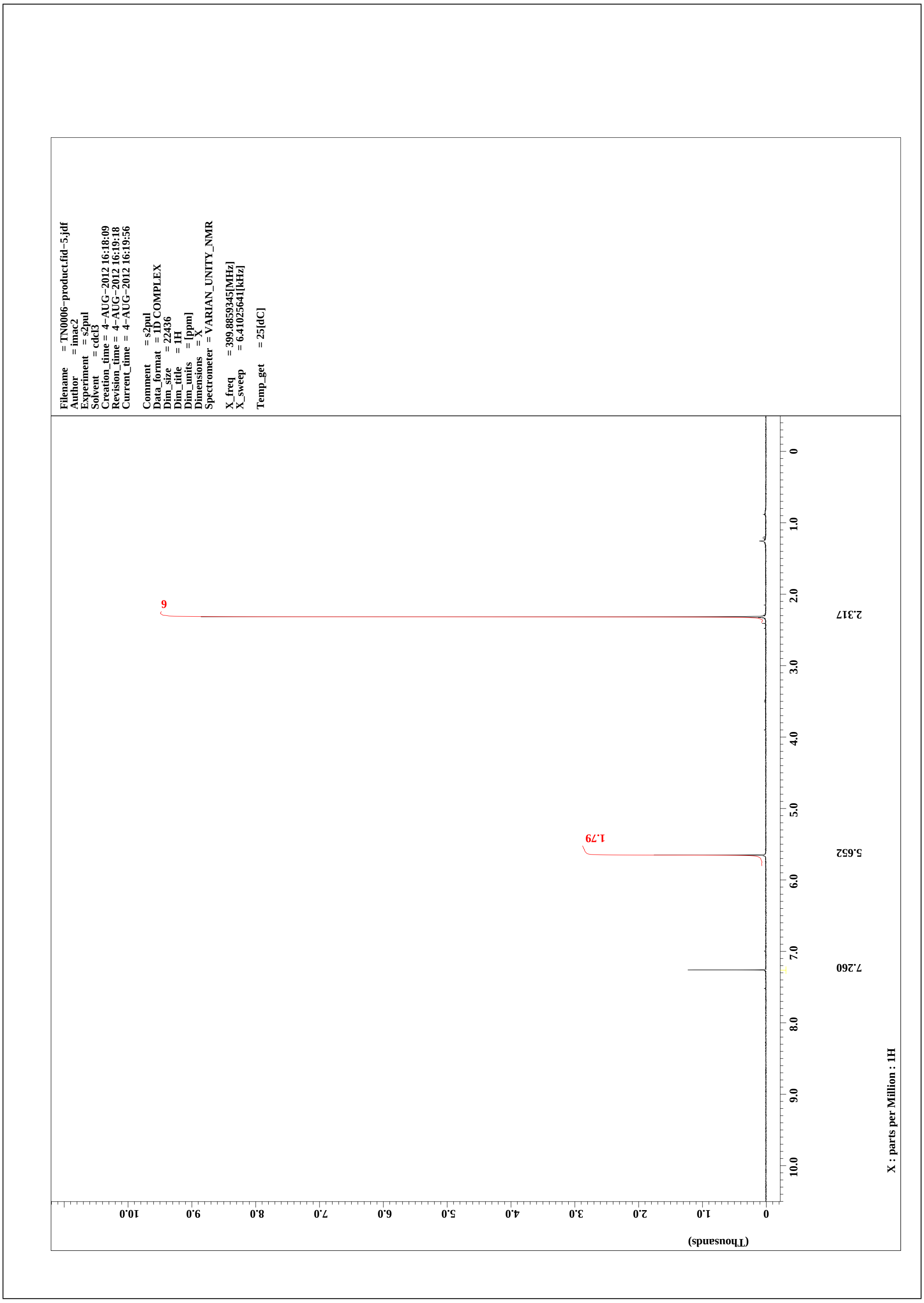

Figure S-97. ^{1}H NMR spectrum of **7-OH** in $CDCl_3$.

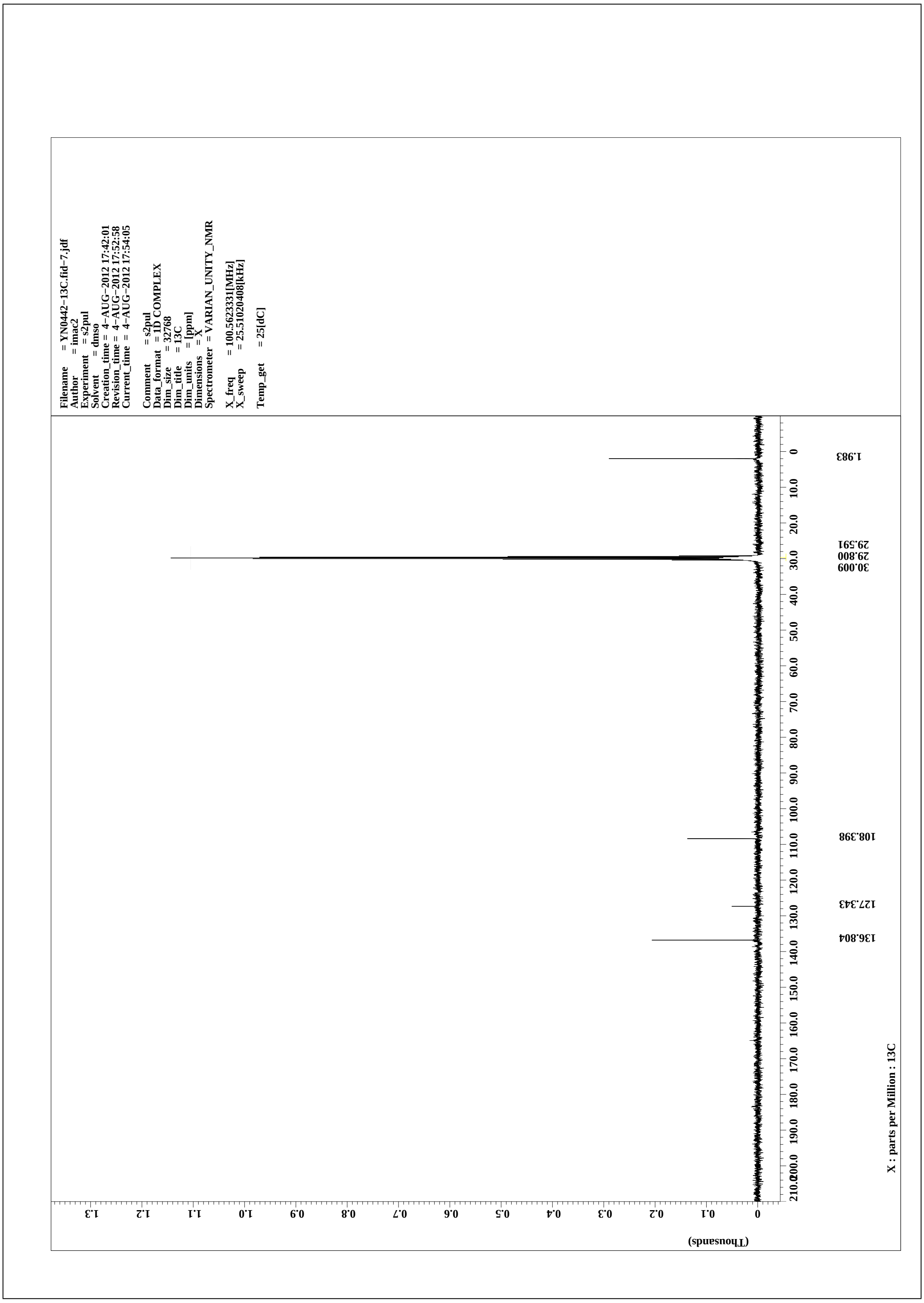

Figure S-98. ^{13}C NMR spectrum of **7-OH** in dimethyl sulfoxide-d_6.

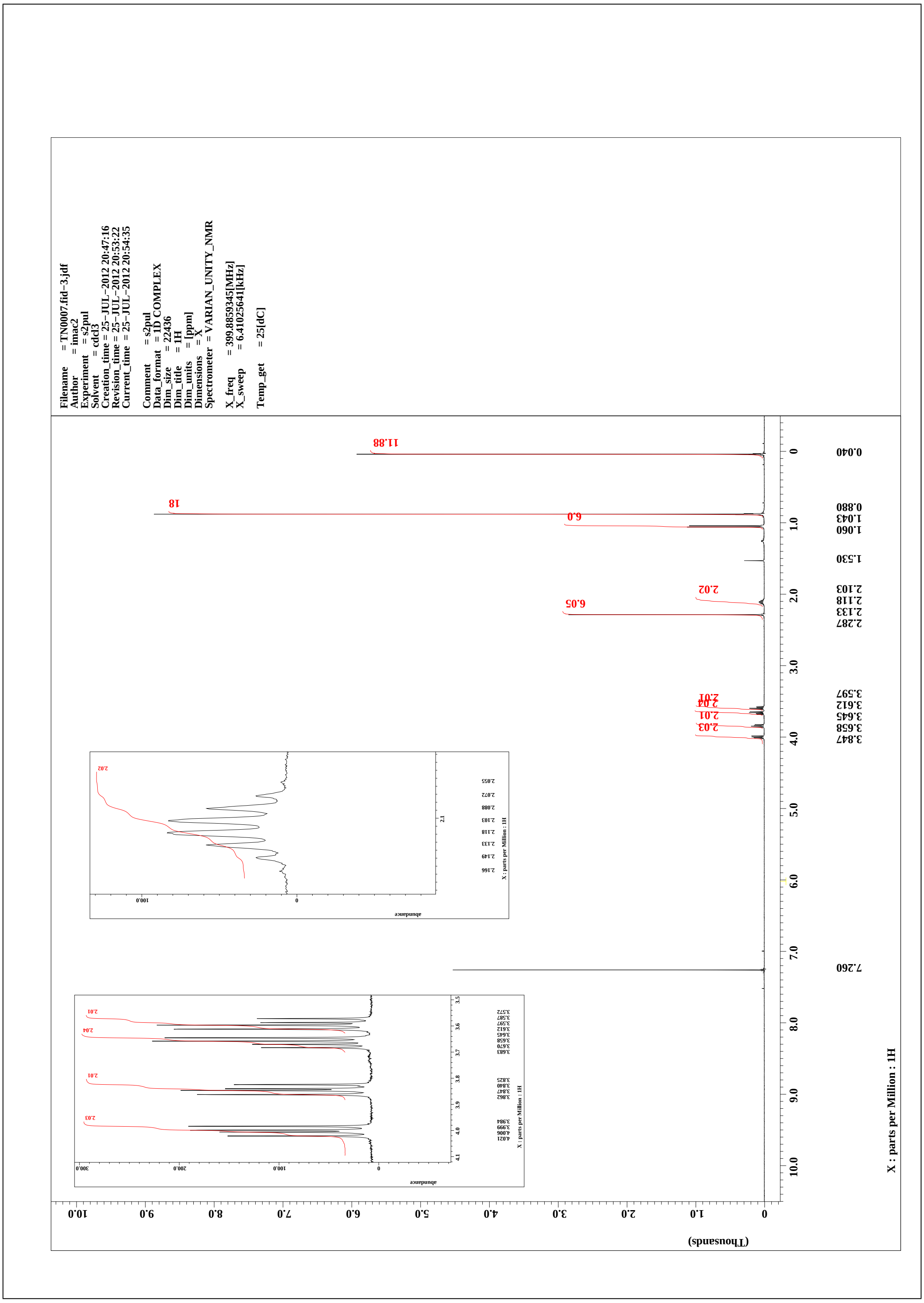

Figure S-99. ^{1}H NMR spectrum of **7-NO$_2$** in CDCl$_3$.

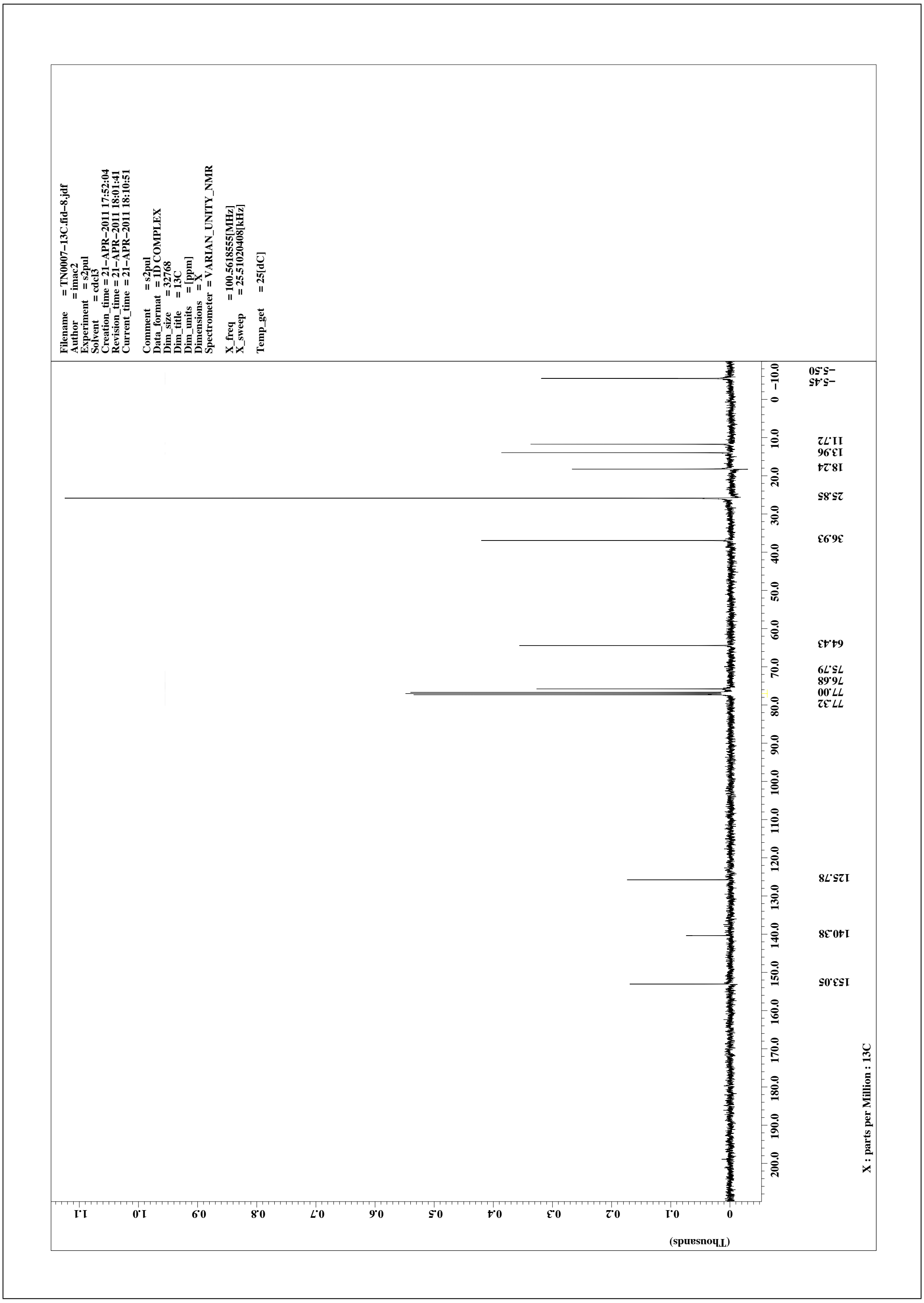

Figure S-100. ^{13}C NMR spectrum of **7-NO$_2$** in CDCl$_3$.

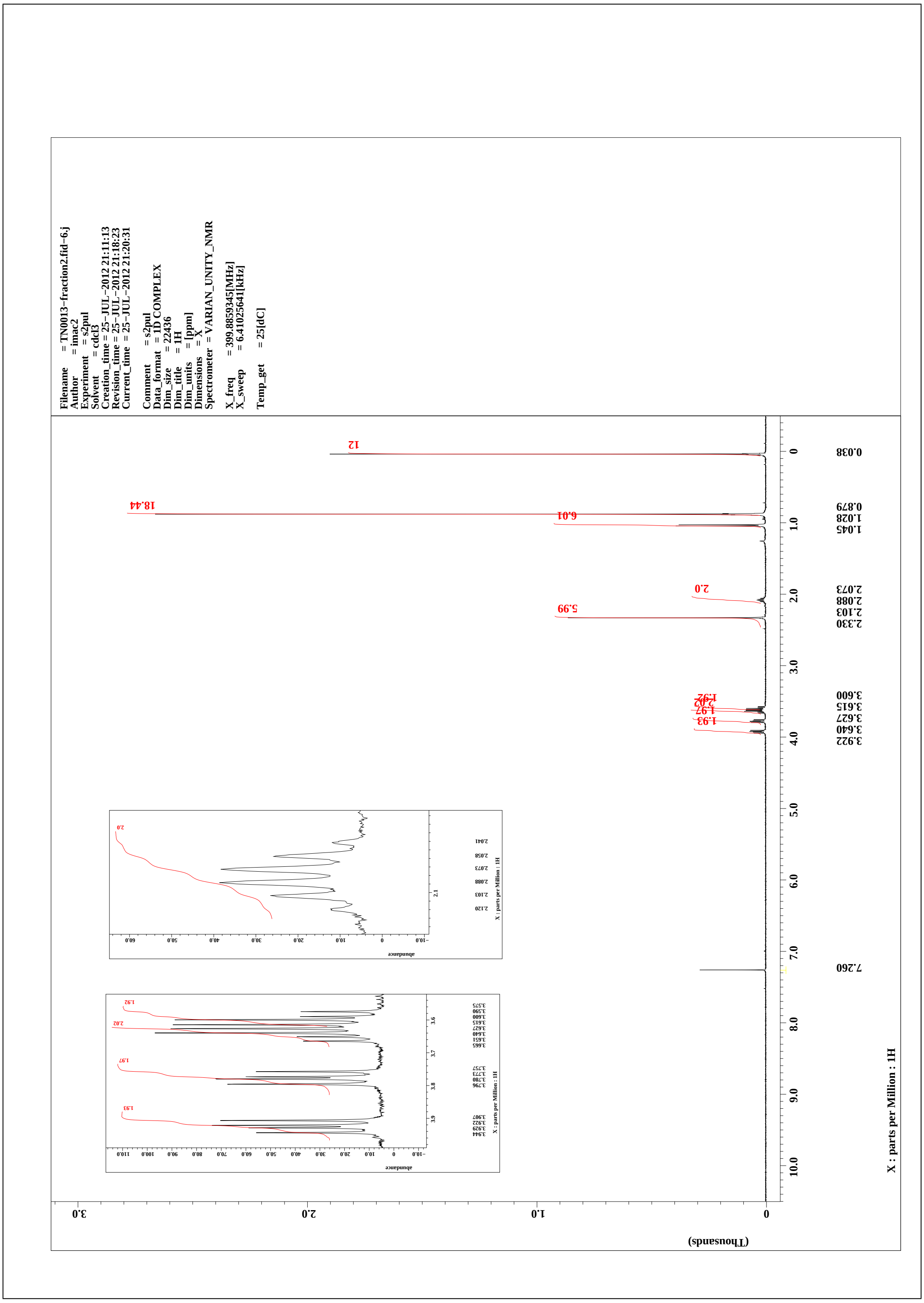

Figure S-101. ^{1}H NMR spectrum of monomer **7** in $CDCl_3$.

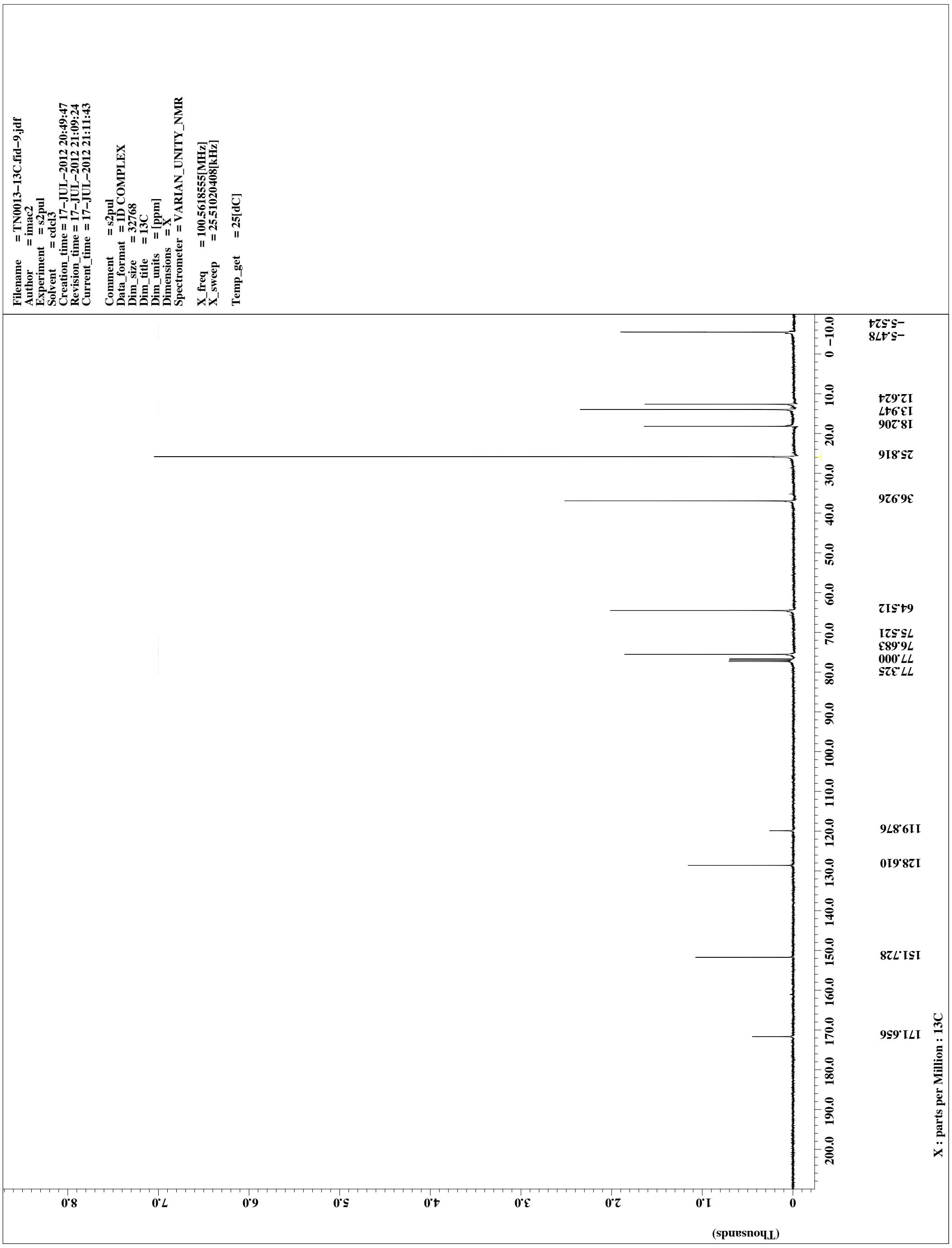

Figure S-102. ^{13}C NMR spectrum of monomer **7** in CDCl$_3$.

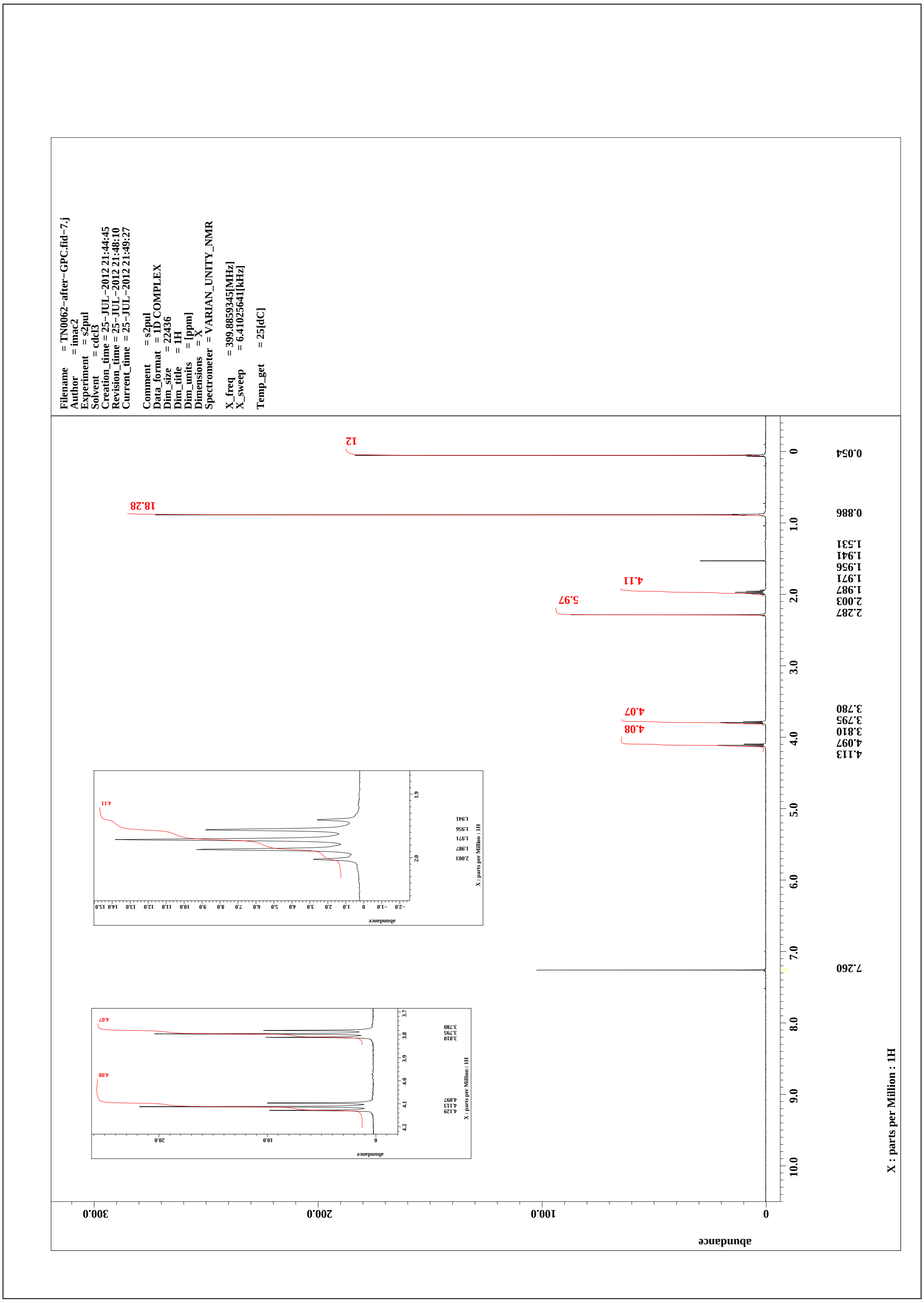

Figure S-103. ^1H NMR spectrum of **8-NO$_2$** in CDCl$_3$.

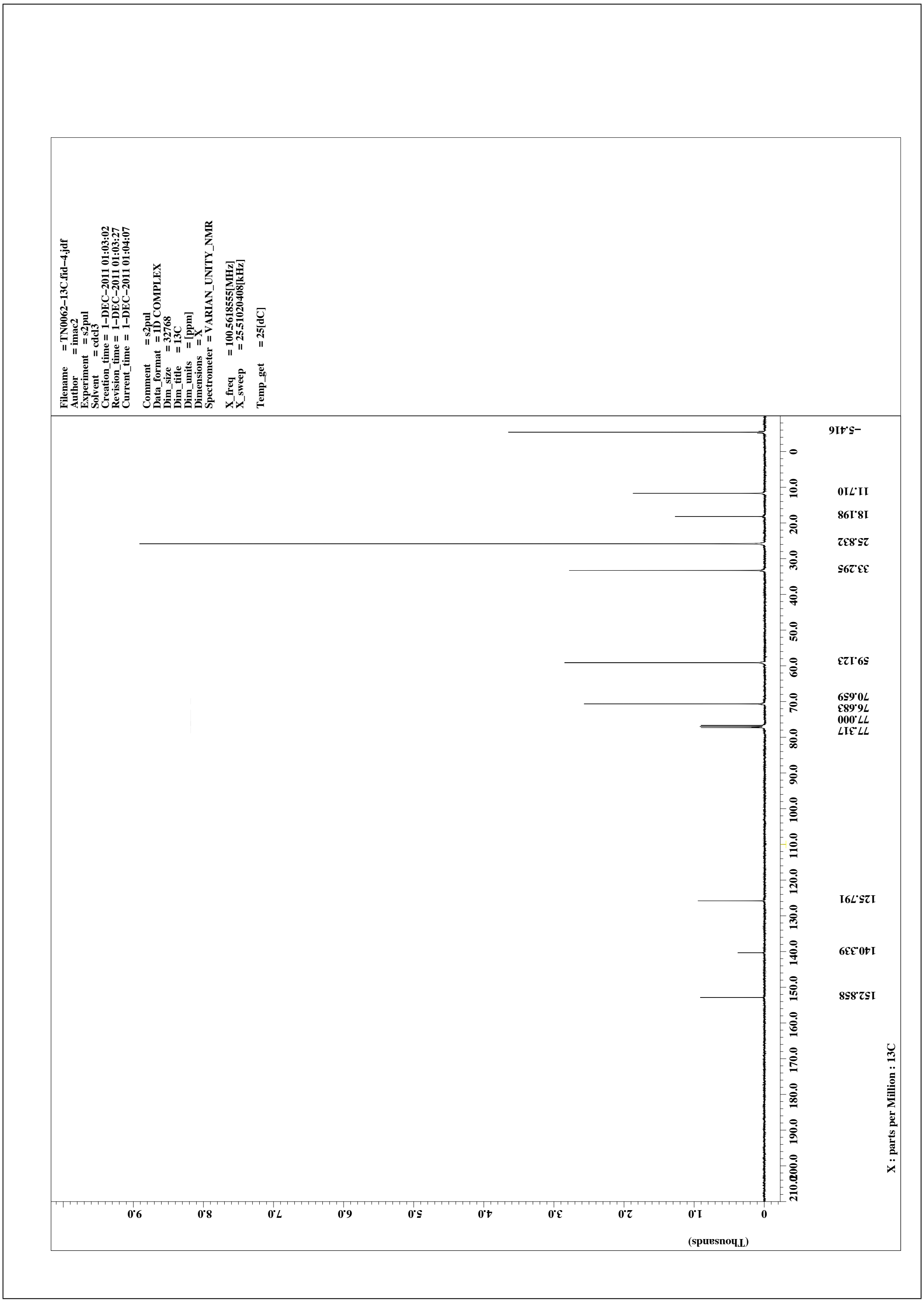

Figure S-104. ^{13}C NMR spectrum of **8-NO$_2$** in CDCl$_3$.

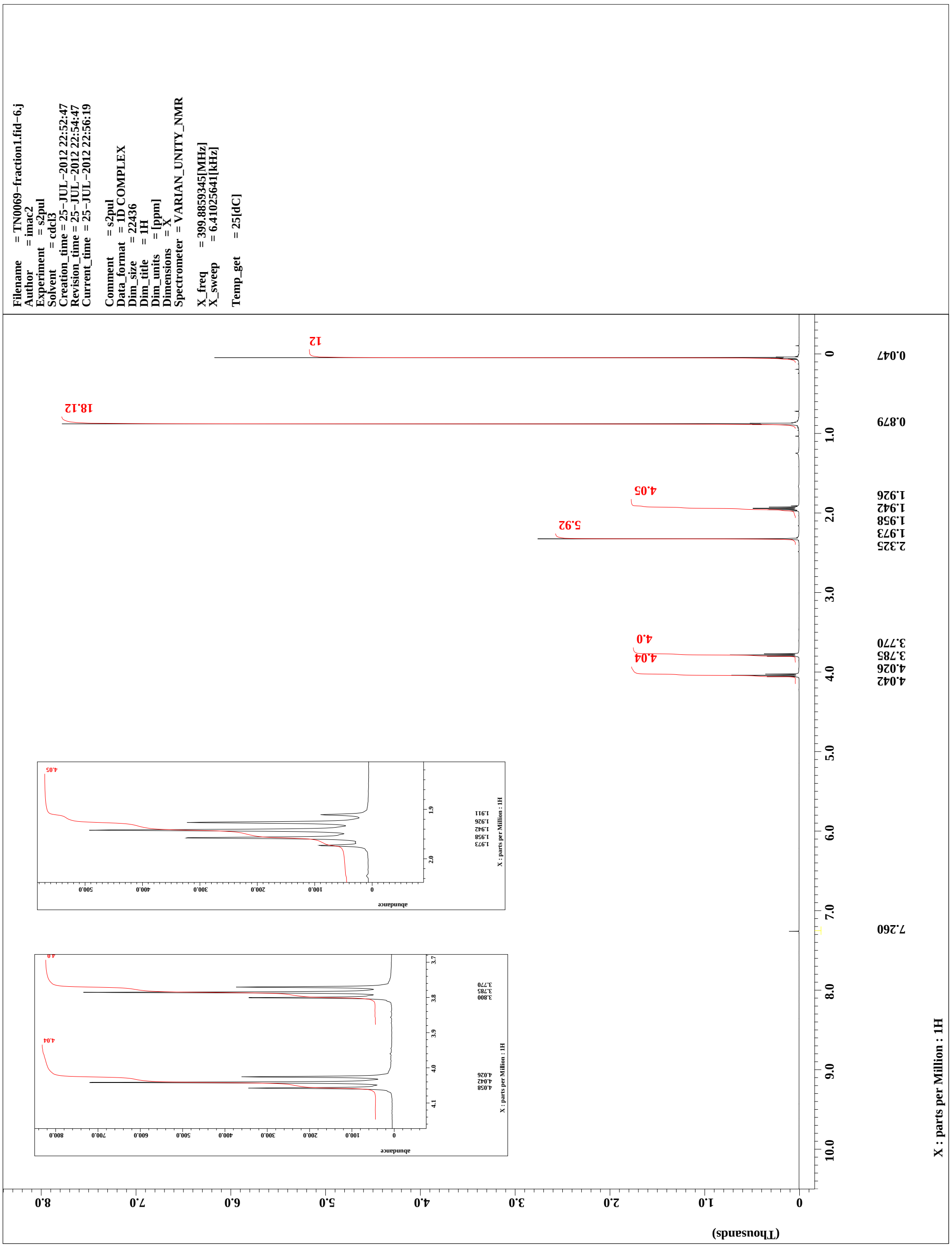

Figure S-105. ^{1}H NMR spectrum of monomer **8** in $CDCl_3$.

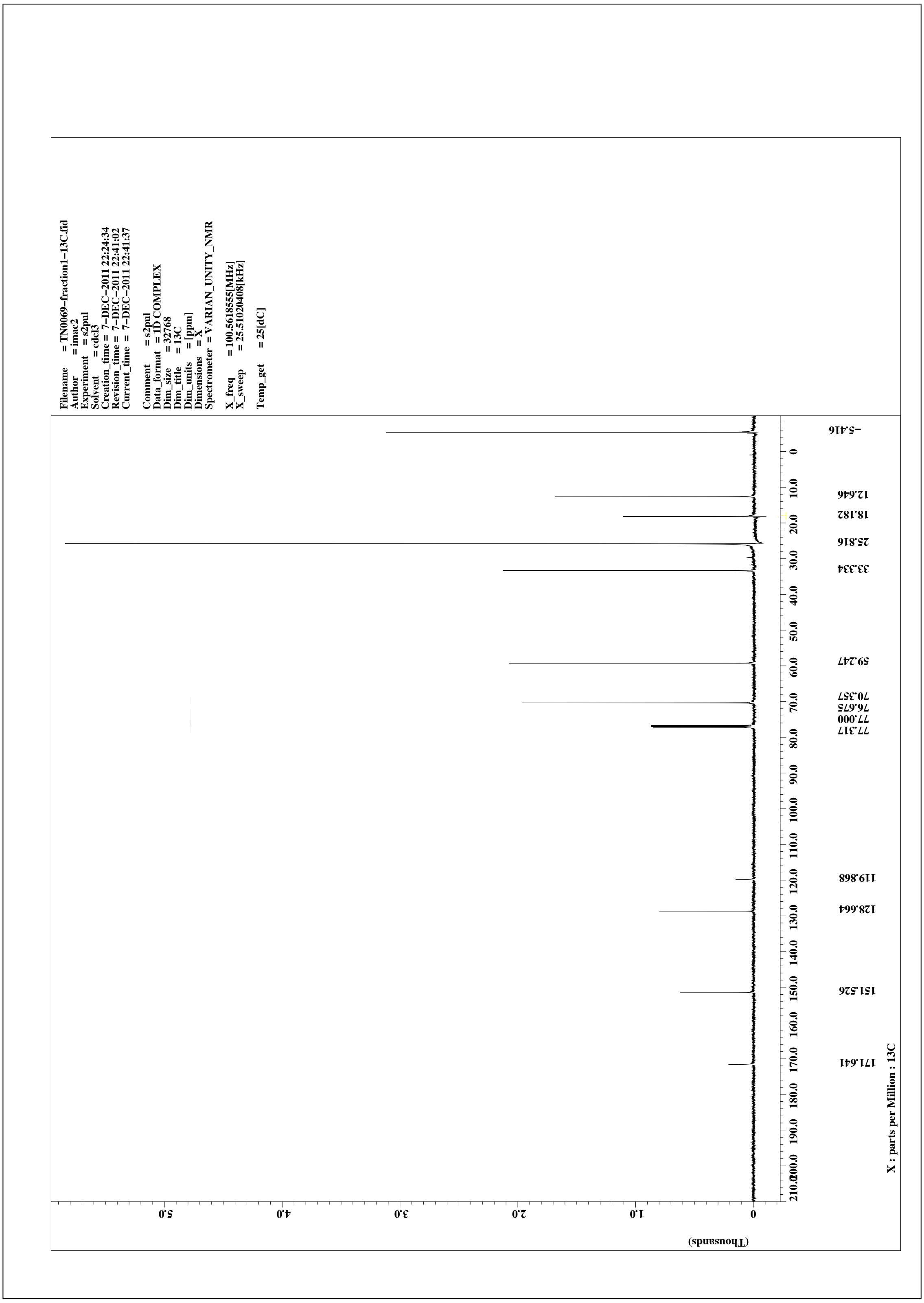

Figure S-106. ^{13}C NMR spectrum of monomer **8** in $CDCl_3$.

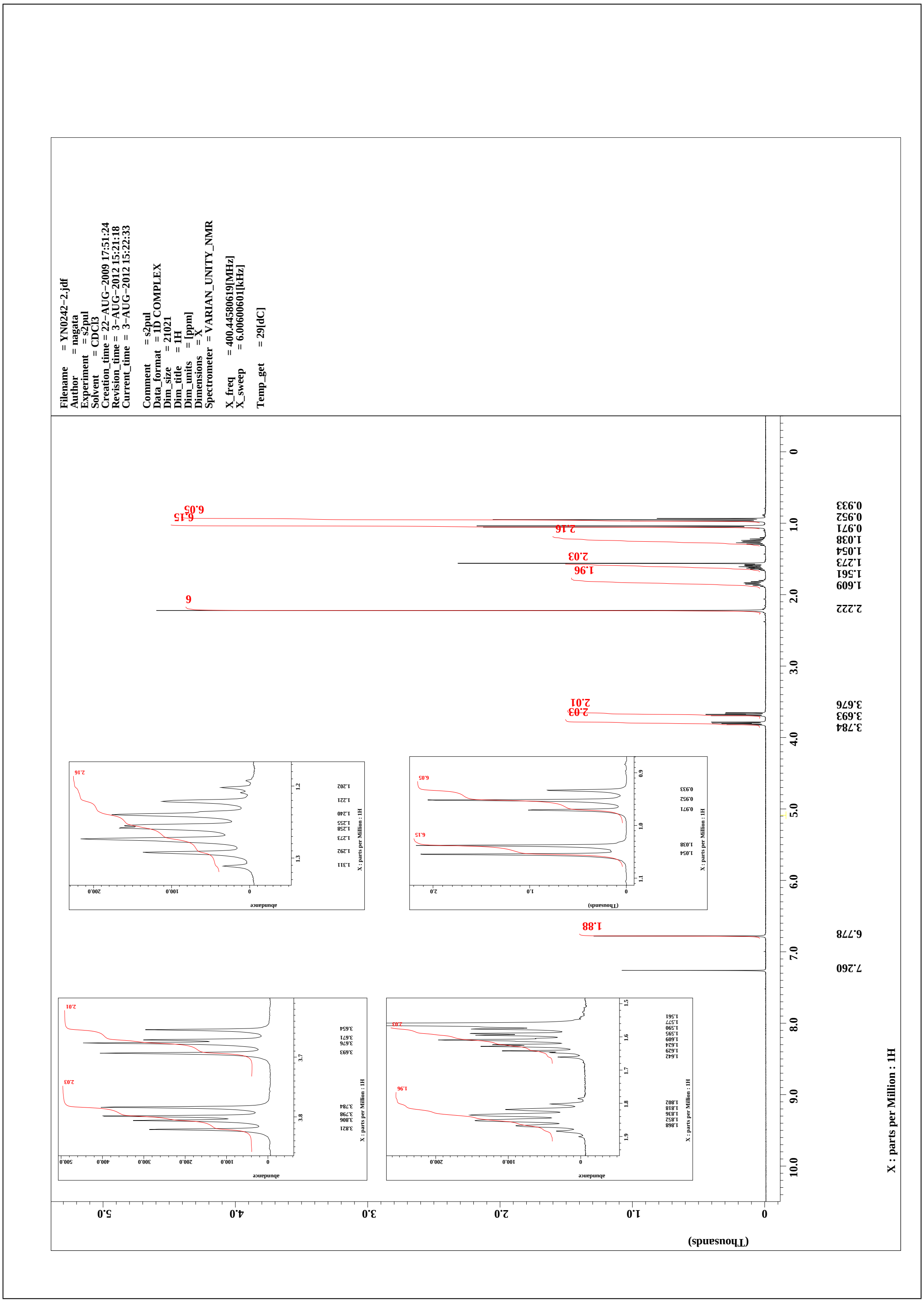

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Figure S-107. ^{1}H NMR spectrum of **Q*-H** in CDCl$_3$.

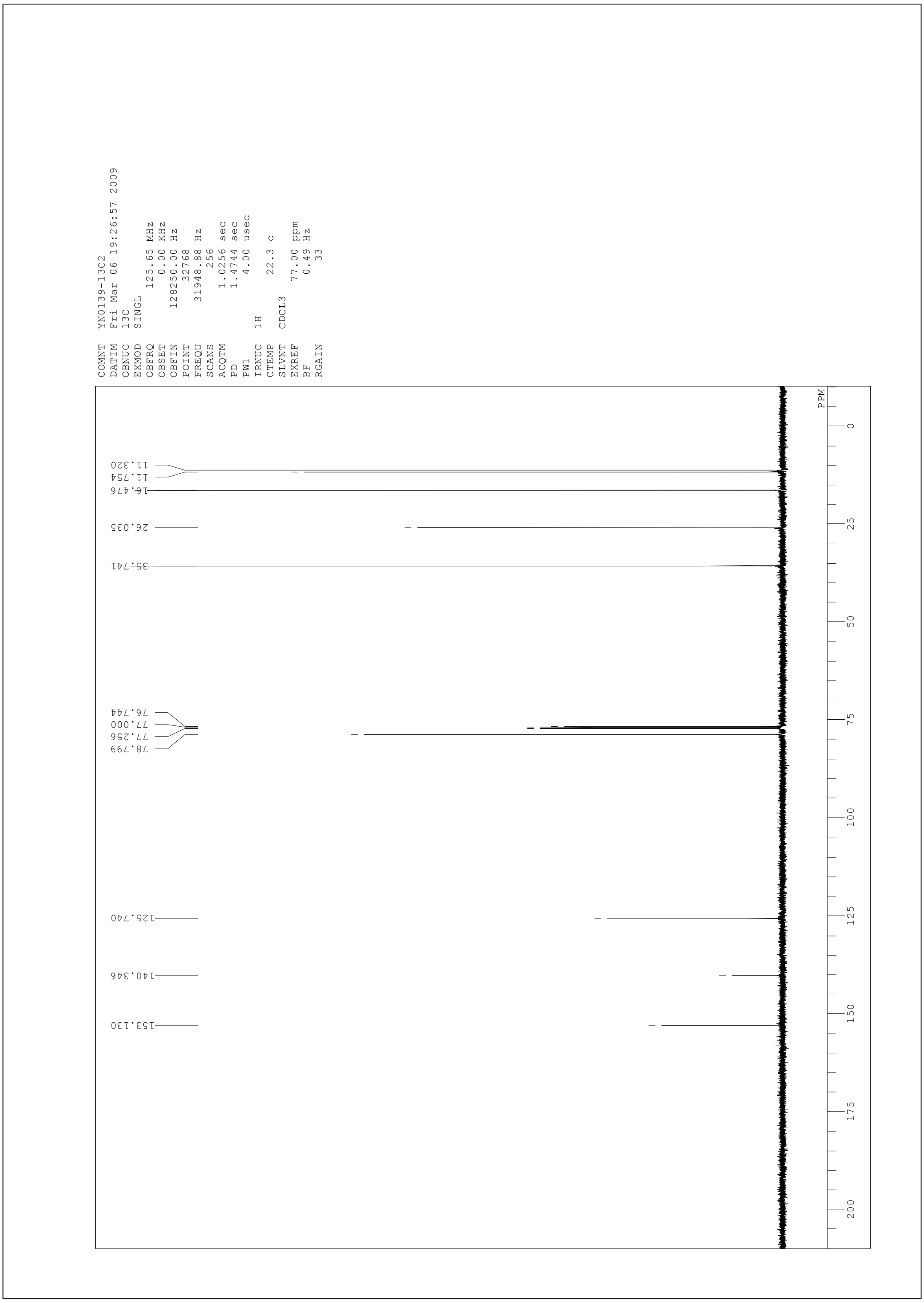

Figure S-108. ^{13}C NMR spectrum of **Q*-H** in $CDCl_3$.

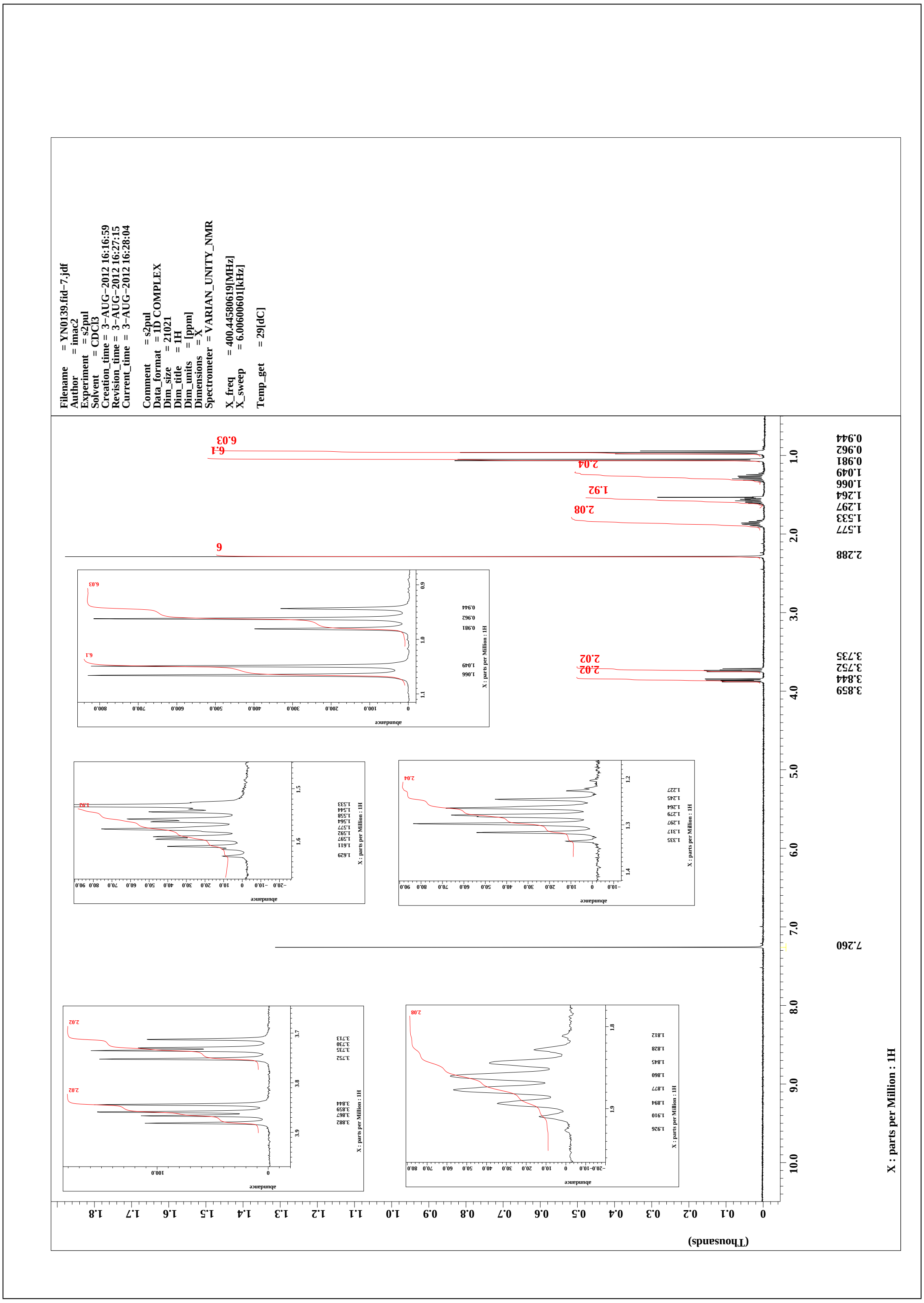

Figure S-109. ^{1}H NMR spectrum of **Q*-NO$_2$** in CDCl$_3$.

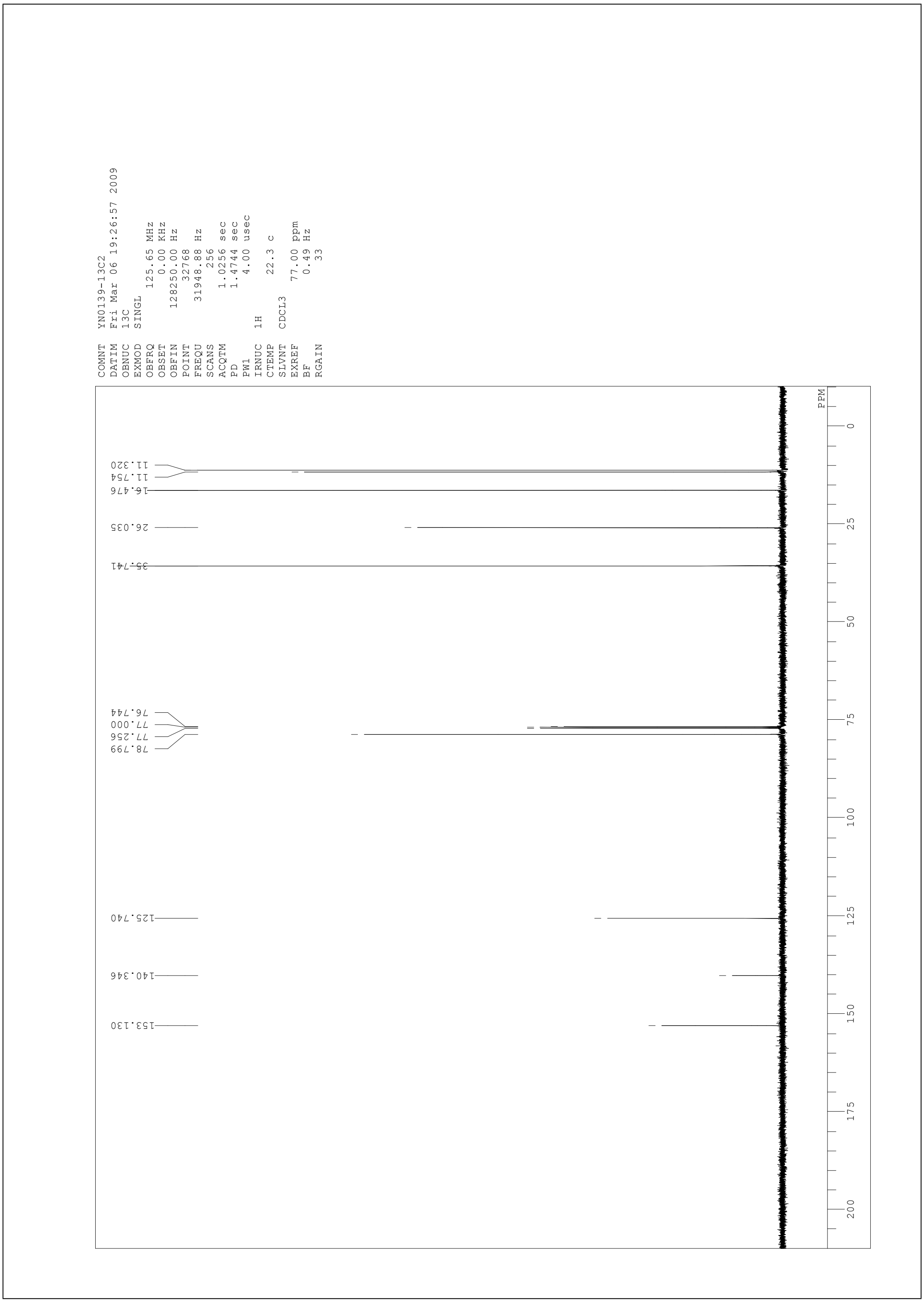

Figure S-110. ^{13}C NMR spectrum of **Q*-NO$_2$** in CDCl$_3$.

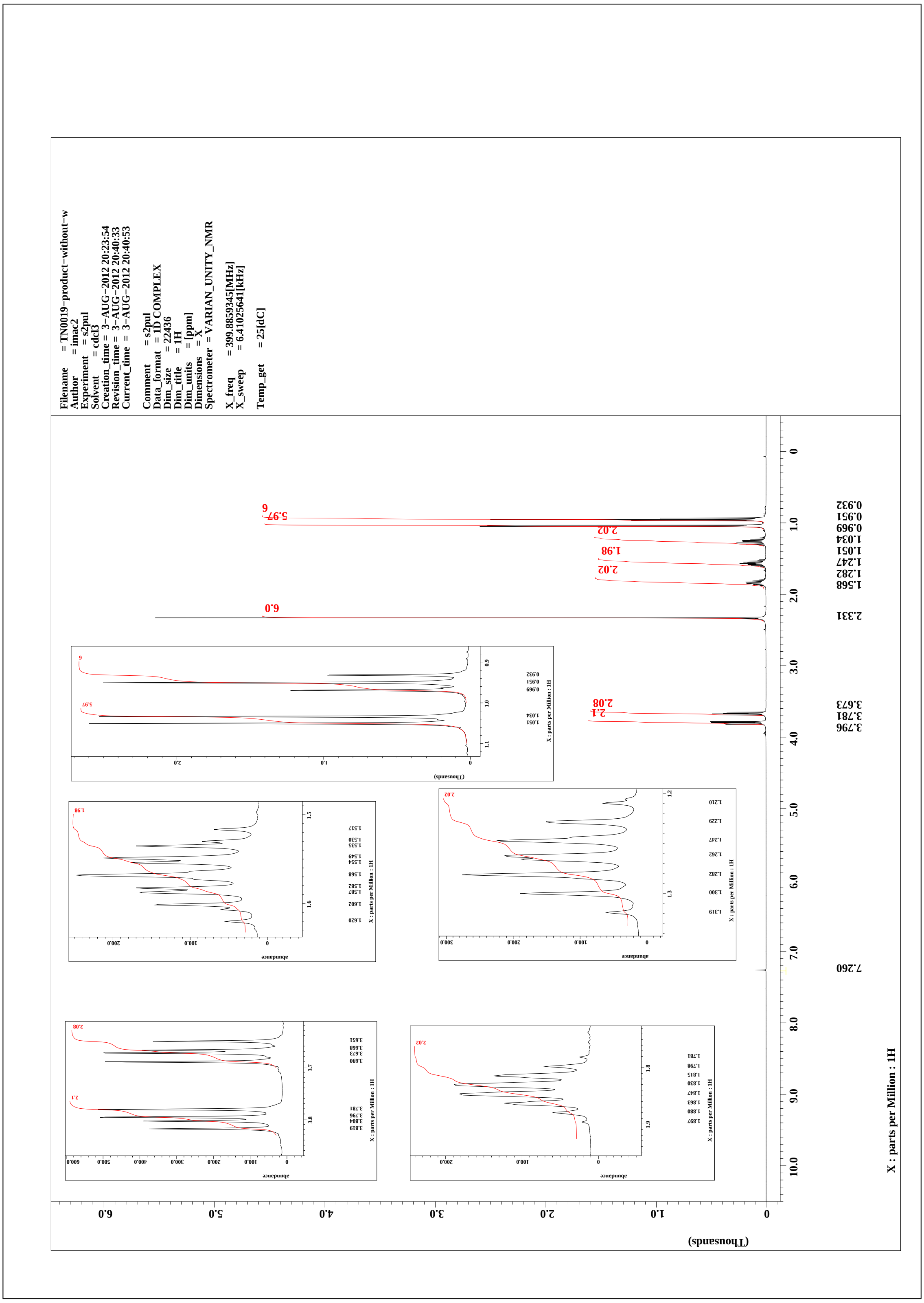

Figure S-111. ^{1}H NMR spectrum of monomer **Q*** in $CDCl_3$.

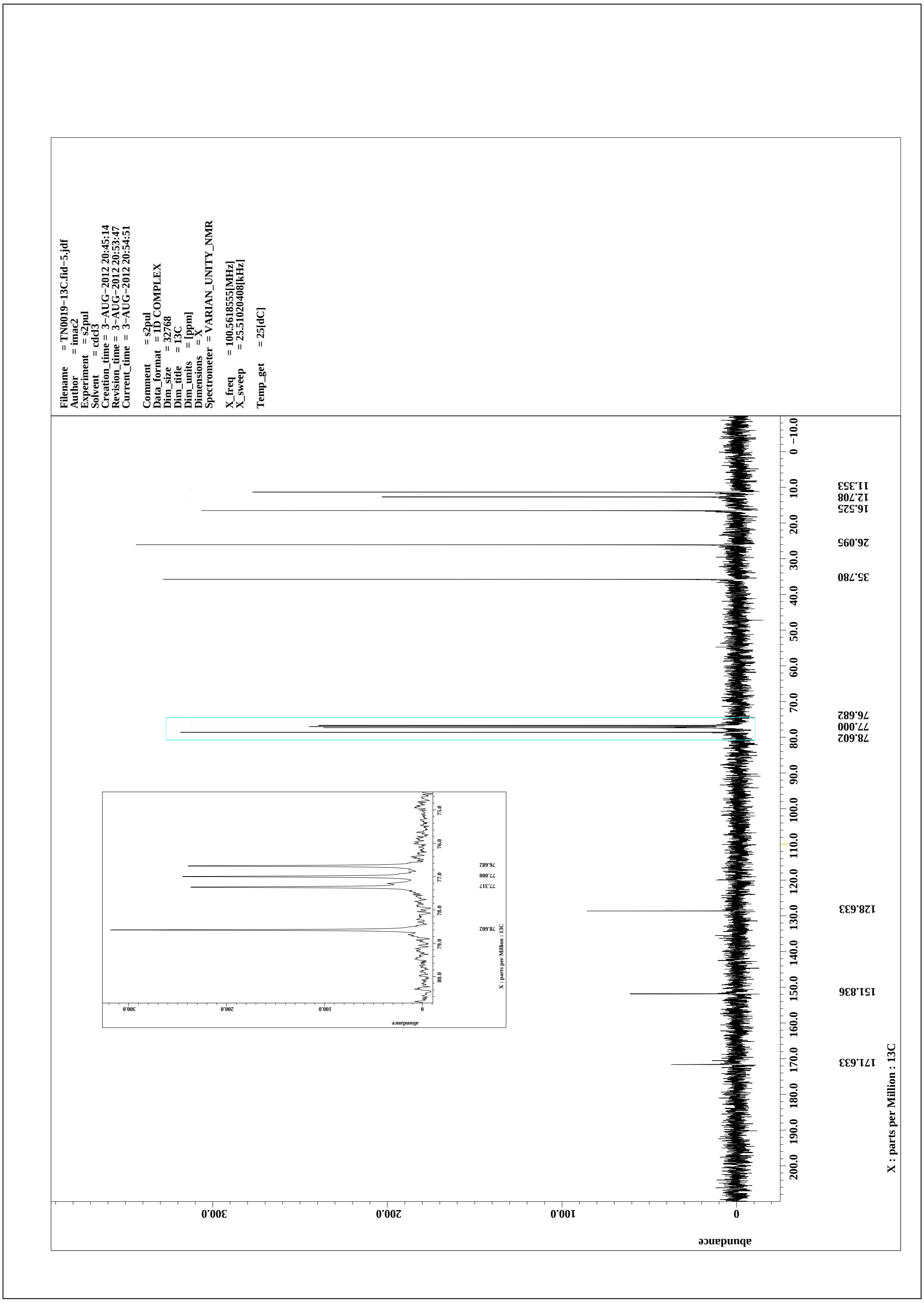

Figure S-112. ^{13}C NMR spectrum of monomer **Q*** in $CDCl_3$.

6 Reference

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