

Electronic Supplementary Information
for
Anionic stitching polymerization of styryl(vinyl)silanes
for the synthesis of sila-cyclic olefin polymers

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I. General

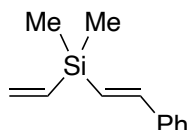
All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen. Preparative GPC was performed with JAI LC-9201 or LaboACE LC-5060 equipped with JAIGEL-2HR columns using CHCl_3 as an eluent. NMR spectra were recorded on JEOL JNM-ECS400 or Agilent Unity-Inova500 spectrometers. Size-exclusion chromatography analyses were performed with JASCO-RI4030 (refractive index detector), JASCO-PU4180 (RHPLC pump), and CO-4060 (column oven) equipped with Shodex GPC LF-804 columns using THF as an eluent, and the molecular weights were calibrated against standard polystyrene samples. High resolution mass spectra were recorded on JEOL JMS700 spectrometer. Thermogravimetric analyses were performed with SII Exstar TG/DTA6200 under nitrogen atmosphere. The glass-transition temperatures were monitored with SII Exstar DSC6200 under nitrogen atmosphere. UV-vis absorption and transmittance spectra were recorded on HITACHI U-2900 spectrophotometer. Film thickness was measured with surfcoorder ET200.

THF (Kanto Chemical; dehydrated), toluene (Kanto Chemical; dehydrated), and CH_2Cl_2 (Kanto Chemical; dehydrated) were degassed by purging nitrogen prior to use. Styrene (TCI) and trimethyl(vinyl)silane (Wako Chemicals) were distilled over CaH_2 under vacuum prior to polymerization. **1**, **6**, and dimethyldivinylsilane (TCI) were dried over microwave-activated molecular sieves 4A 1/16 (Wako Chemicals) prior to polymerization. β -Bromostyrene (TCI), chlorodimethyl(vinyl)silane (TCI), chlorodimethylsilane (TCI), dichlorodimethylsilane (TCI), vinylmagnesium bromide (Aldrich; 1.0 M solution in THF), ethynylmagnesium bromide (Aldrich; 0.5 M solution in THF), *n*BuLi (Kanto Chemical; 1.57 M solution in hexane), *sec*BuLi (Kanto Chemical; 1.23 M solution in cyclohexane/hexane), platinum(0)-1,3-divinyltetramethyldisiloxane complex (TCI; 19.0–21.5% Pt in 1,3-divinyltetramethylsiloxane), and Mg turnings (Nacalai Tesque), were used as received. 1-Ethynyl-naphthalene was synthesized following the literature procedure.¹

II. Synthesis of Monomers

Representative Procedures:

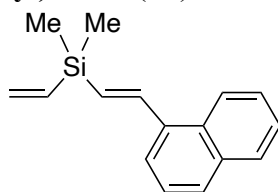
(*E*)-Dimethyl(styryl)(vinyl)silane (**1a**)



A solution of β -bromostyrene (4.96 g, 27.1 mmol) in THF (10 mL) was added dropwise over 30 min to a suspension of Mg turnings (481 mg, 19.8 mmol) in THF (10 mL), and the mixture was stirred for 2 h at room temperature. The resulting solution was added over 2 min to a solution of chlorodimethyl(vinyl)silane (1.30 mL, 9.59 mmol) in THF (10 mL) and the mixture was stirred for 3 h at room temperature. The reaction was quenched with saturated NH_4Cl aq and this was extracted with Et_2O . The organic layer was washed with saturated NaCl aq, dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane and further purified by GPC with CHCl_3 to afford compound **1a** as a colorless oil (1.53 g, 8.12 mmol; 85% yield).

^1H NMR (CDCl_3): δ 7.44 (d, $^3J_{\text{HH}} = 7.8$ Hz, 2H), 7.33 (t, $^3J_{\text{HH}} = 7.6$ Hz, 2H), 7.28-7.21 (m, 1H), 6.91 (d, $^3J_{\text{HH}} = 19.2$ Hz, 1H), 6.46 (d, $^3J_{\text{HH}} = 19.3$ Hz, 1H), 6.23 (dd, $^3J_{\text{HH}} = 20.1$ and 14.7 Hz, 1H), 6.02 (dd, $^3J_{\text{HH}} = 14.6$ Hz and $^2J_{\text{HH}} = 3.6$ Hz, 1H), 5.76 (dd, $^3J_{\text{HH}} = 20.1$ Hz and $^2J_{\text{HH}} = 4.1$ Hz, 1H), 0.24 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 145.0, 138.4, 132.5, 128.7, 128.2, 127.4, 126.6, -2.8. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): -13.14. HRMS (EI) calcd for $\text{C}_{12}\text{H}_{16}\text{Si}$ (M^+) 188.1016, found 188.1017.

(*E*)-Dimethyl(2-(1-naphthyl)vinyl)(vinyl)silane (**1d**)

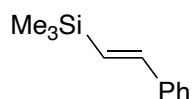


Platinum(0)-1,3-divinyltetramethyldisiloxane complex (25.0 mg, ca. 26 μmol ; 19.0–21.5% Pt in 1,3-divinyltetramethylsiloxane) was added to a solution of chlorodimethylsilane (544 μL , 5.00 mmol) and 1-ethynynaphthalene (761 mg, 5.00 mmol) in toluene (5 mL), and the mixture was stirred for 2 h at room temperature. Vinylmagnesium bromide (5.00 mL, 5.00 mmol; 1.0 M solution in THF) was added to the resulting solution, and the mixture was stirred for 2 h at room temperature. The reaction was quenched with saturated NH_4Cl aq and this was extracted with Et_2O . The organic layer was washed with saturated NaCl aq, dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane and further purified by GPC with CHCl_3 to afford compound **1d** as a colorless oil (699 mg, 2.93 mmol; 59% yield).

^1H NMR (CDCl_3): δ 8.16 (d, $^3J_{\text{HH}} = 8.5$ Hz, 1H), 7.85 (d, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 7.79 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1H), 7.71 (d, $^3J_{\text{HH}} = 19.0$ Hz, 1H), 7.68 (d, $^3J_{\text{HH}} = 7.0$ Hz, 1H), 7.55-7.43 (m, 3H), 6.54 (d, $^3J_{\text{HH}} = 18.9$ Hz, 1H), 6.29 (dd, $^3J_{\text{HH}} = 20.2$ and 14.5 Hz, 1H), 6.07 (dd, $^3J_{\text{HH}} = 14.6$ Hz and $^2J_{\text{HH}} = 3.9$ Hz, 1H),

5.83 (dd, $^3J_{\text{HH}} = 20.4$ Hz and $^2J_{\text{HH}} = 3.9$ Hz, 1H), 0.31 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 142.4, 138.5, 136.8, 134.0, 132.6, 131.8, 131.3, 128.7, 128.4, 126.2, 125.9, 125.8, 123.9, 123.8, -2.6 . $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): -13.16 . HRMS (EI) calcd for $\text{C}_{16}\text{H}_{18}\text{Si}$ (M^+) 238.1172, found 238.1178.

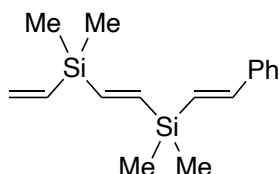
(E)-Trimethyl(styryl)silane (3) (CAS 19372-00-0)



A solution of β -bromostyrene (3.66 g, 20.0 mmol) in THF (10 mL) was added dropwise over 15 min to a suspension of Mg turnings (486 mg, 20.0 mmol) in THF (10 mL), and the mixture was stirred for 1 h at room temperature. The resulting solution was added over 5 min to chlorotrimethylsilane (1.27 mL, 10.0 mmol) and the mixture was stirred for 1 h at room temperature. The reaction was quenched with saturated NH_4Cl and this was extracted with Et_2O . The organic layer was washed with saturated NaCl , dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane and further purified by GPC with CHCl_3 to afford compound **3** as a colorless oil (1.00 g, 5.67 mmol; 57% yield).

^1H NMR (CDCl_3): δ 7.44 (d, $^3J_{\text{HH}} = 7.4$ Hz, 2H), 7.33 (t, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 7.28-7.22 (m, 1H), 6.88 (d, $^3J_{\text{HH}} = 19.2$ Hz, 1H), 6.48 (d, $^3J_{\text{HH}} = 19.3$ Hz, 1H), 0.16 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 143.7, 138.5, 129.7, 128.7, 128.1, 126.5, -1.1 .

((E)-2-(Dimethyl((E)-styryl)silyl)vinyl)dimethyl(vinyl)silane (6)



A solution of β -bromostyrene (4.03 g, 22.0 mmol) in THF (10 mL) was added dropwise over 5 min to a suspension of Mg turnings (534 mg, 22.0 mmol) in THF (10 mL), and the mixture was stirred for 1 h at room temperature. The resulting solution was added over 5 min to dichlorodimethylsilane (1.20 mL, 10.0 mmol), and the mixture was stirred for 1 h at room temperature. Ethynylmagnesium bromide (20.0 mL, 10.0 mmol; 0.5 M in THF) was then added to the resulting solution, and the mixture was stirred for 1 h at room temperature. The reaction was quenched with saturated NH_4Cl and this was extracted with Et_2O . The organic layer was washed with saturated NaCl , dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane and further purified by GPC with CHCl_3 to afford (*E*)-ethynyldimethyl(styryl)silane as a colorless oil (849 mg, 4.56 mmol; 46% yield).

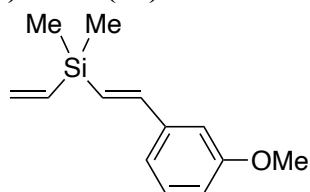
^1H NMR (CDCl_3): δ 7.46 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 7.34 (t, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 7.27 (t, $^3J_{\text{HH}} = 6.9$ Hz, 1H), 7.06 (d, $^3J_{\text{HH}} = 19.2$ Hz, 1H), 6.40 (d, $^3J_{\text{HH}} = 18.7$ Hz, 1H), 2.49 (s, 1H), 0.35 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 146.2, 138.0, 128.7, 128.6, 126.8, 124.8, 94.4, 88.5, -1.1 .

Platinum(0)-1,3-divinyltetramethyldisiloxane complex (34.4 mg, ca. 35 μmol ; 19.0–21.5% Pt in 1,3-divinyltetramethylsiloxane) was added to a solution of chlorodimethylsilane (370 μL , 3.40 mmol) and (*E*)-ethynyldimethyl(styryl)silane (641 mg, 3.44 mmol) in toluene (3 mL), and the mixture was stirred for 17.5 h at room temperature. Vinylmagnesium bromide (3.40 mL, 3.40 mmol; 1.0 M solution in THF) was added to the resulting solution, and the mixture was stirred for 2 h at room temperature. The reaction was quenched with saturated NH_4Cl and this was extracted with Et_2O . The organic layer was washed with saturated NaCl , dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane and further purified by GPC with CHCl_3 to afford compound **6** as a colorless oil (637 mg, 2.34 mmol; 69% yield).

^1H NMR (CDCl_3): δ 7.44 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 7.33 (t, $^3J_{\text{HH}} = 7.6$ Hz, 2H), 7.30-7.22 (m, 1H), 6.89 (d, $^3J_{\text{HH}} = 19.2$ Hz, 1H), 6.73-6.63 (m, 2H), 6.46 (d, $^3J_{\text{HH}} = 19.2$ Hz, 1H), 6.17 (dd, $^3J_{\text{HH}} = 20.1$ and 14.7 Hz, 1H), 5.99 (dd, $^3J_{\text{HH}} = 14.7$ Hz and $^2J_{\text{HH}} = 4.2$ Hz, 1H), 5.70 (dd, $^3J_{\text{HH}} = 20.1$ Hz and $^2J_{\text{HH}} = 4.1$ Hz, 1H), 0.23 (s, 6H), 0.16 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 150.3, 150.2, 144.8, 138.4, 132.3, 128.7, 128.2, 127.6, 126.6, -2.8, -3.2. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): -13.93, -14.45. HRMS (EI) calcd for $\text{C}_{16}\text{H}_{24}\text{Si}_2$ (M^+) 272.1411, found 272.1417.

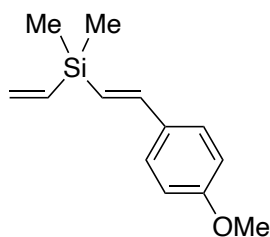
Analytical Data for Other Monomers:

(*E*)-(3-Methoxystyryl)dimethyl(vinyl)silane (1b)



^1H NMR (CDCl_3): δ 7.24 (t, $^3J_{\text{HH}} = 7.9$ Hz, 1H), 7.03 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 6.98 (dd, $^4J_{\text{HH}} = 2.6$ and 1.5 Hz, 1H), 6.88 (d, $^3J_{\text{HH}} = 19.0$ Hz, 1H), 6.82 (ddd, $^3J_{\text{HH}} = 8.3$ Hz and $^4J_{\text{HH}} = 2.7$ and 1.0 Hz, 1H), 6.45 (d, $^3J_{\text{HH}} = 19.2$ Hz, 1H), 6.22 (dd, $^3J_{\text{HH}} = 20.2$ and 14.6 Hz, 1H), 6.02 (dd, $^3J_{\text{HH}} = 14.6$ Hz and $^2J_{\text{HH}} = 3.7$ Hz, 1H), 5.76 (dd, $^3J_{\text{HH}} = 20.4$ Hz and $^2J_{\text{HH}} = 3.9$ Hz, 1H), 3.83 (s, 3H), 0.24 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 160.0, 144.8, 139.9, 138.3, 132.6, 129.6, 127.8, 119.4, 114.2, 111.5, 55.4, -2.8. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): -13.14. HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{18}\text{OSi}$ (M^+) 218.1121, found 218.1119.

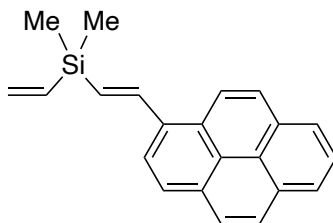
(*E*)-(4-Methoxystyryl)dimethyl(vinyl)silane (1c)



^1H NMR (CDCl_3): δ 7.38 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H), 6.86 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 6.85 (d, $^3J_{\text{HH}} = 19.0$ Hz, 1H), 6.28 (d, $^3J_{\text{HH}} = 19.2$ Hz, 1H), 6.22 (dd, $^3J_{\text{HH}} = 20.4$ and 14.6 Hz, 1H), 6.01 (dd, $^3J_{\text{HH}} = 14.6$

Hz and $^2J_{\text{HH}} = 3.9$ Hz, 1H), 5.75 (dd, $^3J_{\text{HH}} = 20.4$ Hz and $^2J_{\text{HH}} = 3.9$ Hz, 1H), 3.81 (s, 3H), 0.22 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 159.8, 144.4, 138.7, 132.3, 131.4, 127.8, 124.5, 114.0, 55.4, -2.7 . $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): -13.35 . HRMS (EI) calcd for $\text{C}_{13}\text{H}_{18}\text{OSi}$ (M^+) 218.1121, found 218.1123.

(E)-Dimethyl(2-(1-pyrenyl)vinyl)(vinyl)silane (1e)



^1H NMR (CDCl_3): δ 8.44 (d, $^3J_{\text{HH}} = 9.2$ Hz, 1H), 8.26 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H), 8.20-8.08 (m, 4H), 8.07-7.96 (m, 4H), 6.75 (d, $^3J_{\text{HH}} = 18.8$ Hz, 1H), 6.35 (dd, $^3J_{\text{HH}} = 20.6$ and 14.7 Hz, 1H), 6.11 (dd, $^3J_{\text{HH}} = 14.7$ Hz and $^2J_{\text{HH}} = 3.7$ Hz, 1H), 5.88 (dd, $^3J_{\text{HH}} = 20.1$ Hz and $^2J_{\text{HH}} = 3.7$ Hz, 1H), 0.37 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 141.9, 138.4, 133.2, 132.8, 131.8, 131.6, 131.2, 131.0, 128.1, 127.7, 127.6, 127.5, 126.1, 125.4, 125.2, 125.12, 125.08, 123.9, 123.0, -2.6 . $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): -12.89 . HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{20}\text{Si}$ (M^+) 312.1329, found 312.1327.

III. Stoichiometric Reactions and Polymerization Reactions

Procedure for Equation 1.

*n*BuLi (200 μ L, 0.314 mmol; 1.57 M solution in hexane) was added to a solution of compound **1a** (59.1 mg, 0.314 mmol) in THF (0.5 mL) at -78 $^{\circ}$ C. The mixture was warmed to -50 $^{\circ}$ C and stirred for 3 h at -50 $^{\circ}$ C. The reaction was quenched with MeOH (0.5 mL) and the mixture was concentrated under vacuum to give crude hexyldimethyl(styryl)silane (**2**) (CAS 96816-06-7). The yield was determined to be 68% by 1 H NMR against an internal standard (CH_3NO_2). For analytical purpose, this was purified by GPC with CHCl_3 .

1 H NMR (CDCl_3): δ 7.46-7.42 (m, 2H), 7.33 (t, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 7.27-7.22 (m, 1H), 6.87 (d, $^3J_{\text{HH}} = 19.2$ Hz, 1H), 6.46 (d, $^3J_{\text{HH}} = 19.2$ Hz, 1H), 1.40-1.23 (m, 8H), 0.88 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H), 0.67-0.60 (m, 2H), 0.14 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 144.0, 138.6, 128.9, 128.6, 128.0, 126.5, 33.4, 31.8, 24.0, 22.8, 15.9, 14.3, -2.9 . HRMS (EI) calcd for $\text{C}_{16}\text{H}_{26}\text{Si}$ (M^+) 246.1798, found 246.1802.

Procedure for Equation 2.

*n*BuLi (200 μ L, 0.314 mmol; 1.57 M solution in hexane) was added to a solution of (*E*)-trimethyl(styryl)silane (**3**) (47.6 mg, 0.270 mmol) in THF (0.5 mL) at -78 $^{\circ}$ C. The mixture was warmed to -50 $^{\circ}$ C and stirred for 22 h at -50 $^{\circ}$ C. The reaction was quenched with MeOH (0.5 mL) and the mixture was concentrated under vacuum to give crude trimethyl(1-phenyl-2-hexyl)silane (**4**). The yield was determined to be 65% by 1 H NMR against an internal standard (CH_3NO_2). For analytical purpose, this was purified by GPC with CHCl_3 .

1 H NMR (CDCl_3): δ 7.29-7.22 (m, 2H), 7.19-7.13 (m, 3H), 2.73 (dd, $^2J_{\text{HH}} = 14.2$ Hz and $^3J_{\text{HH}} = 5.5$ Hz, 1H), 2.51 (dd, $^2J_{\text{HH}} = 13.8$ Hz and $^3J_{\text{HH}} = 9.6$ Hz, 1H), 1.43-1.13 (m, 6H), 1.01-0.92 (m, 1H), 0.82 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H), -0.03 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 143.3, 129.0, 128.2, 125.6, 36.2, 31.2, 29.3, 28.0, 23.2, 14.1, -2.0 . HRMS (EI) calcd for $\text{C}_{15}\text{H}_{26}\text{Si}$ (M^+) 234.1798, found 234.1802.

General Procedure for Table 1 and Equation 3.

*sec*BuLi (40.7 μ L, 50.0 μ mol; 1.23 M solution in cyclohexane/hexane) was added to a solution of monomer **1** or **6** (0.500 mmol) in toluene (0.25 mL) and the mixture was stirred for 22 h at 30 $^{\circ}$ C. The reaction was quenched with MeOH (0.5 mL) and this was dissolved in CH_2Cl_2 (2.0 mL). The resulting solution was added dropwise into stirring MeOH (50 mL) with the aid of CH_2Cl_2 (2.0 mL), and the precipitates that formed were collected by filtration with MeOH. The solid thus obtained was dried under vacuum to afford **poly-1** or **poly-6**.

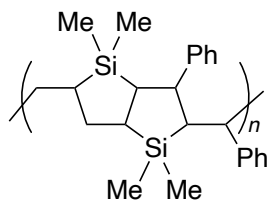
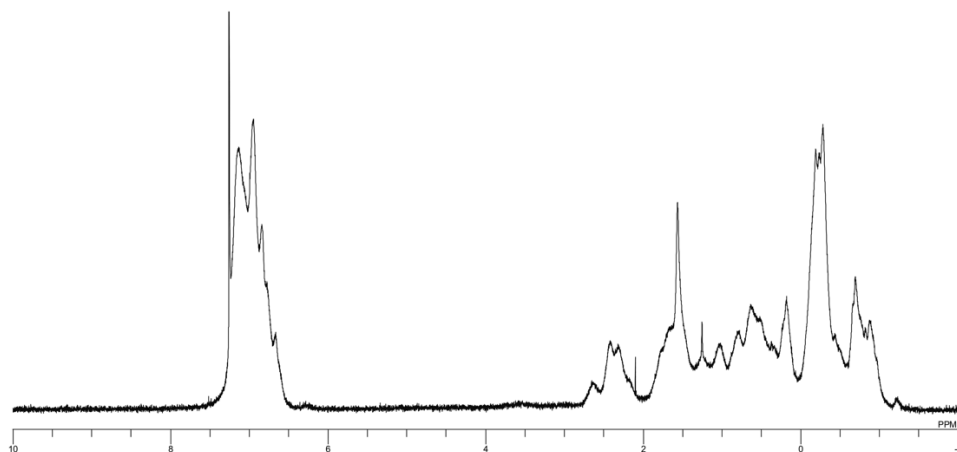
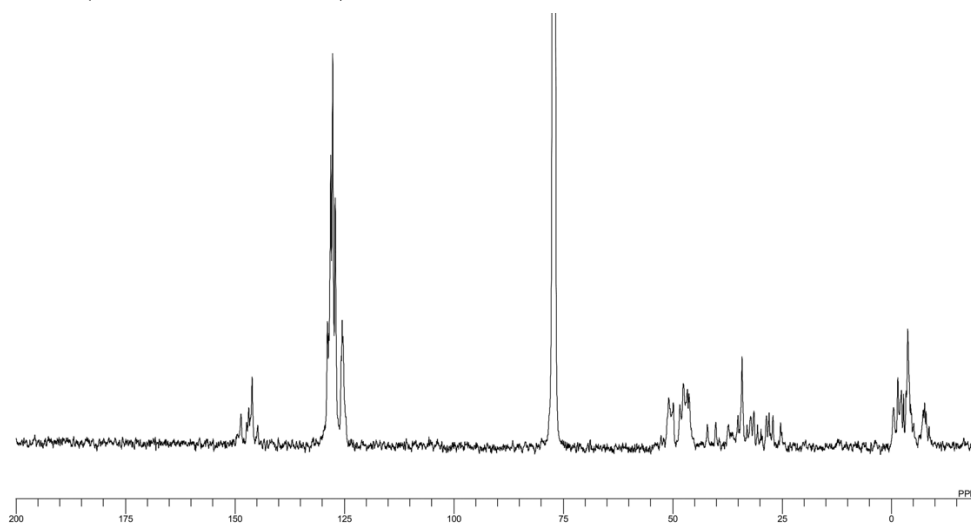


Table 1, entry 3 (poly-1a). 5 mol% of *sec*BuLi was used. White solid. 79% yield (74.1 mg). $T_d = 323\text{ }^\circ\text{C}$, $T_g = 173\text{ }^\circ\text{C}$.

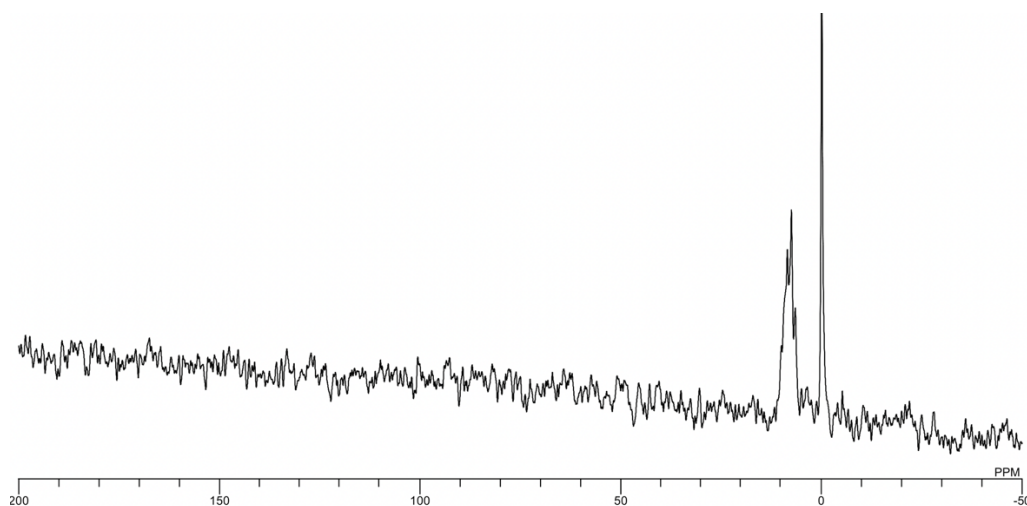
^1H NMR (400 MHz in CDCl_3)



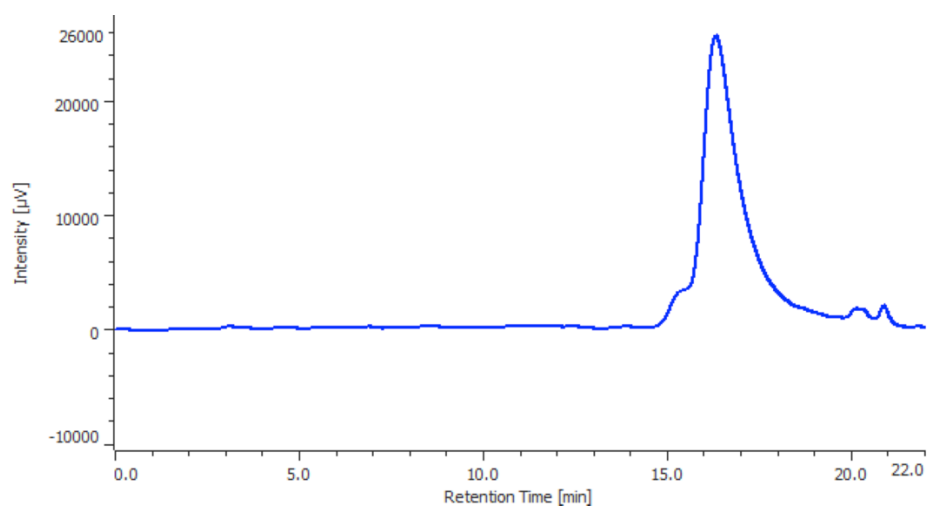
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz in CDCl_3)



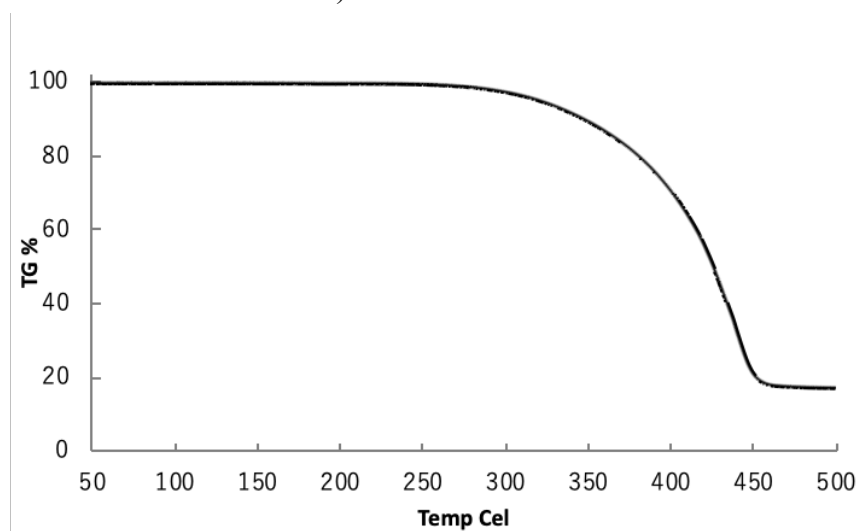
$^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz in CDCl_3)



GPC (THF; 1.0 mL/min flow)



TG (+10 $^\circ\text{C}/\text{min}$ from 50 $^\circ\text{C}$ to 500 $^\circ\text{C}$)



DSC (+10 °C/min from 20 °C to 250 °C, second heating)

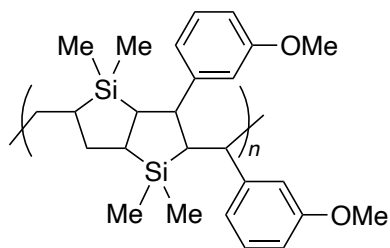
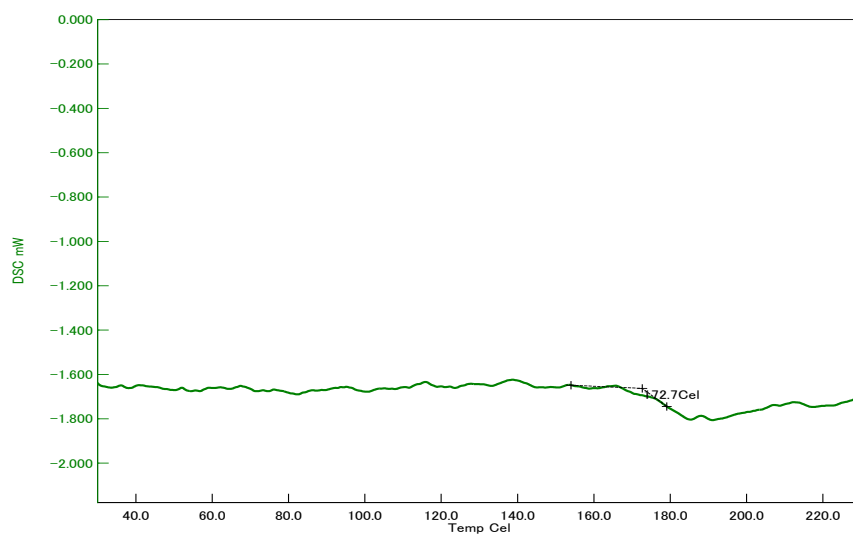
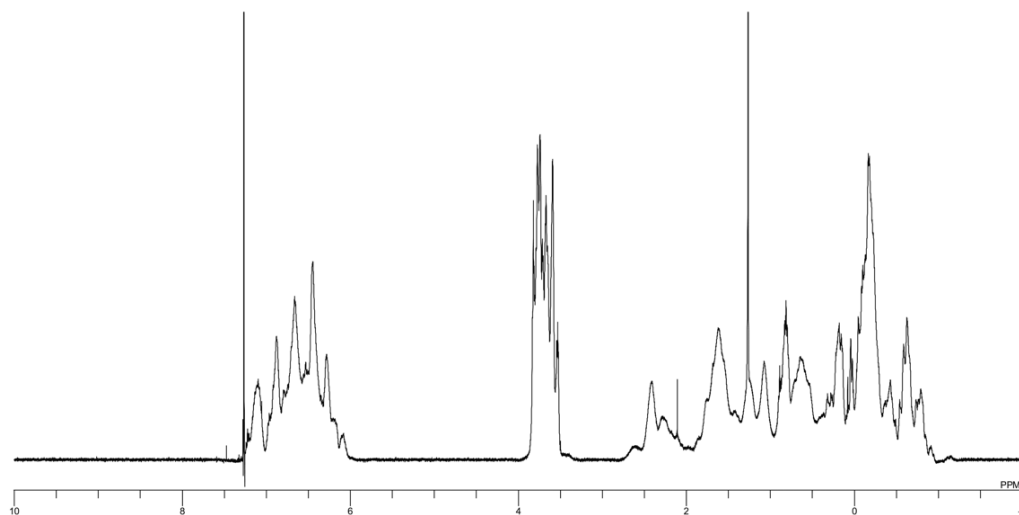
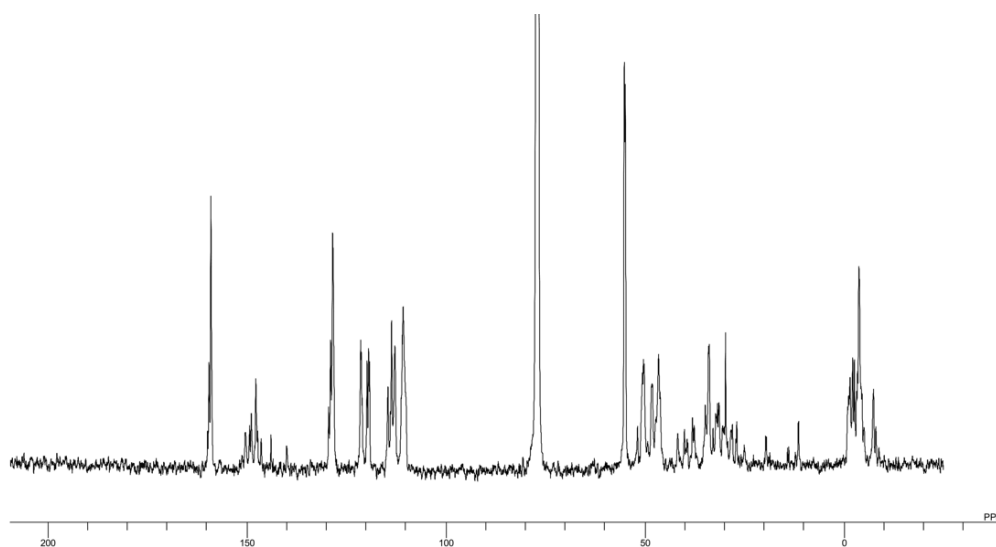


Table 1, Entry 4 (poly-1b). White solid. 67% yield (73.3 mg). $T_d = 341$ °C, $T_g = 96$ °C.

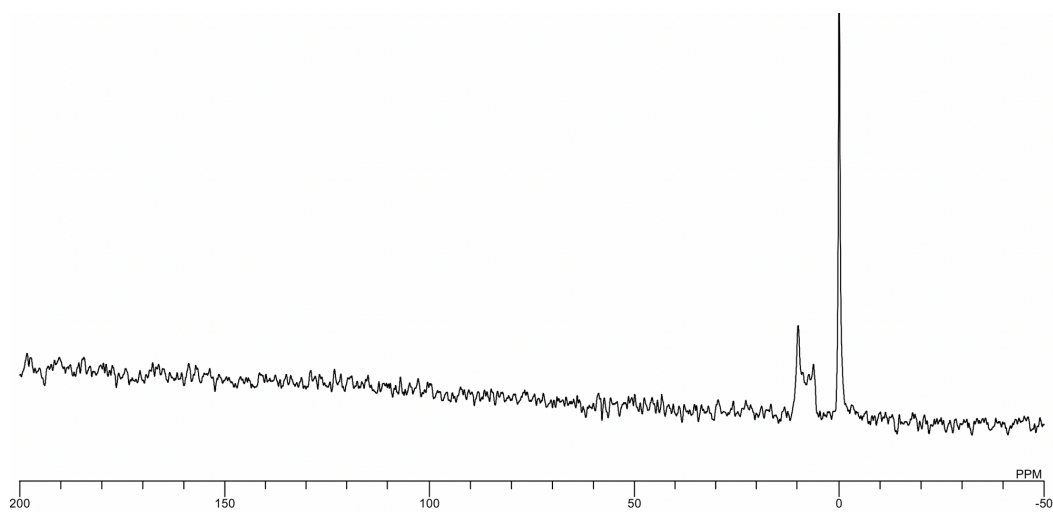
^1H NMR (498 MHz in CDCl_3)



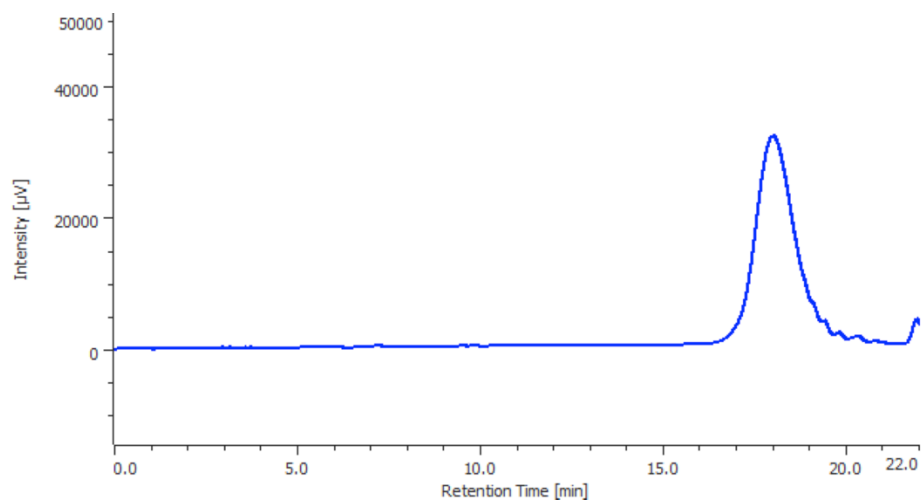
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz in CDCl_3)



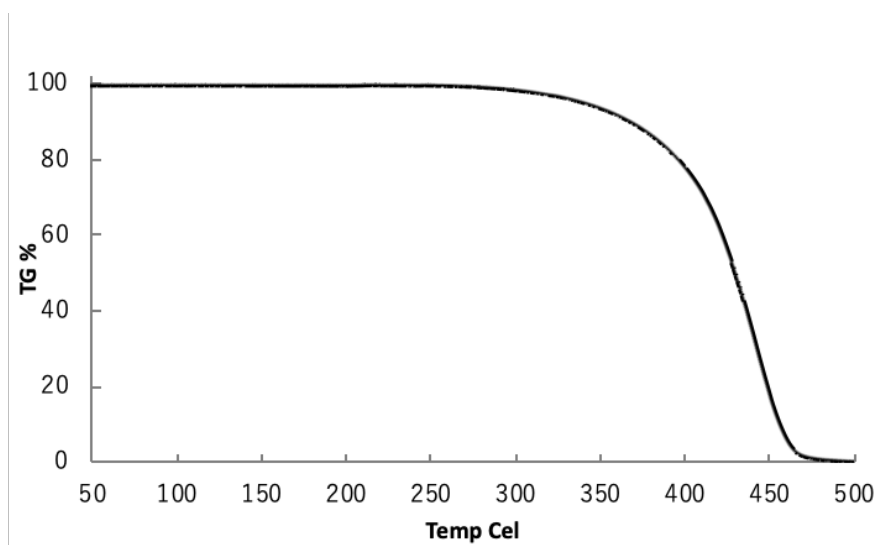
$^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz in CDCl_3)



GPC (THF; 1.0 mL/min flow)



TG (+10 °C/min from 50 °C to 500 °C)



DSC (+10 °C/min from 20 °C to 250 °C, second heating)

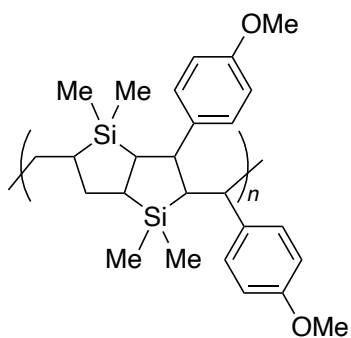
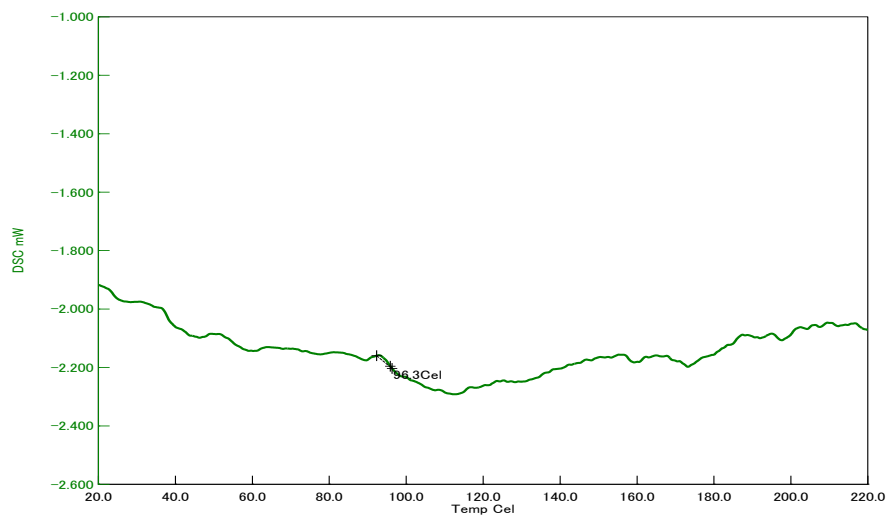
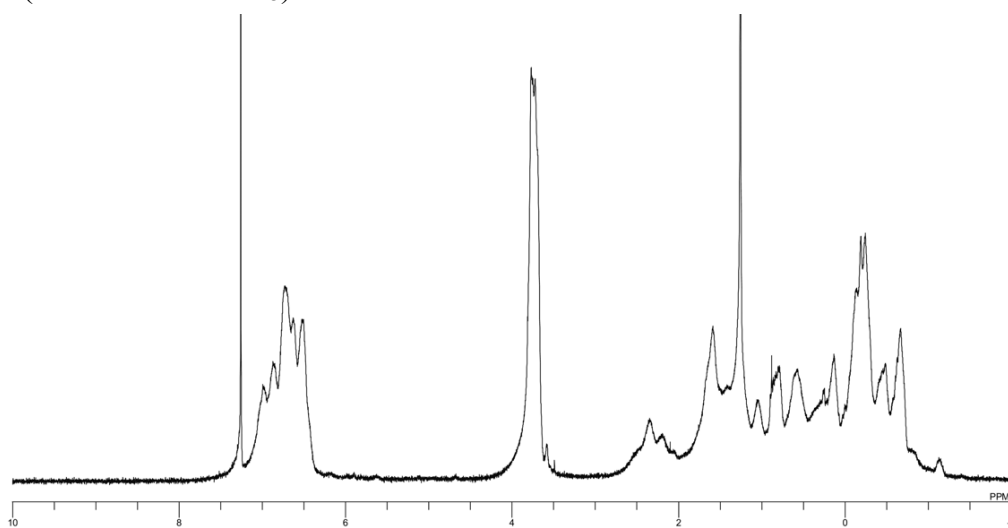
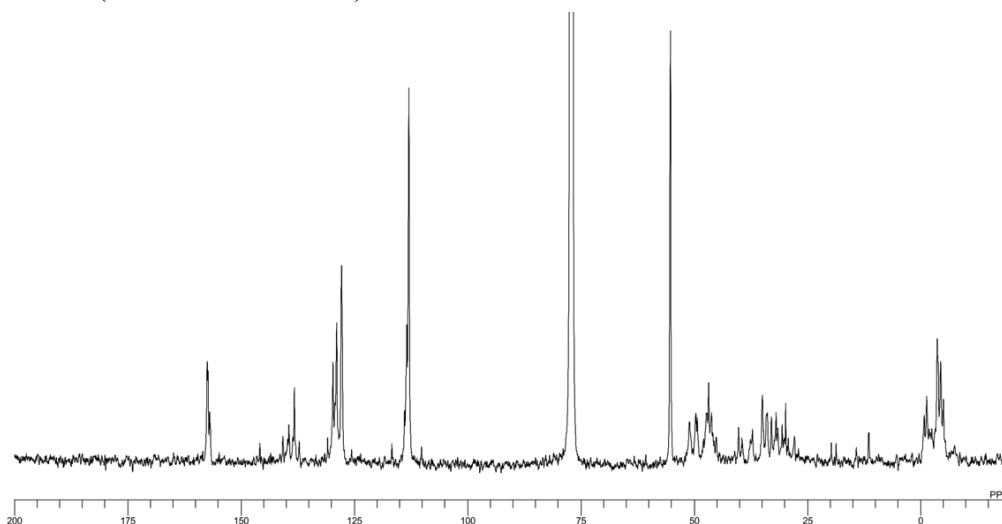


Table 1, Entry 5 (poly-1c). White solid. 69% yield (65.0 mg). $T_d = 378$ °C, $T_g = 112$ °C.

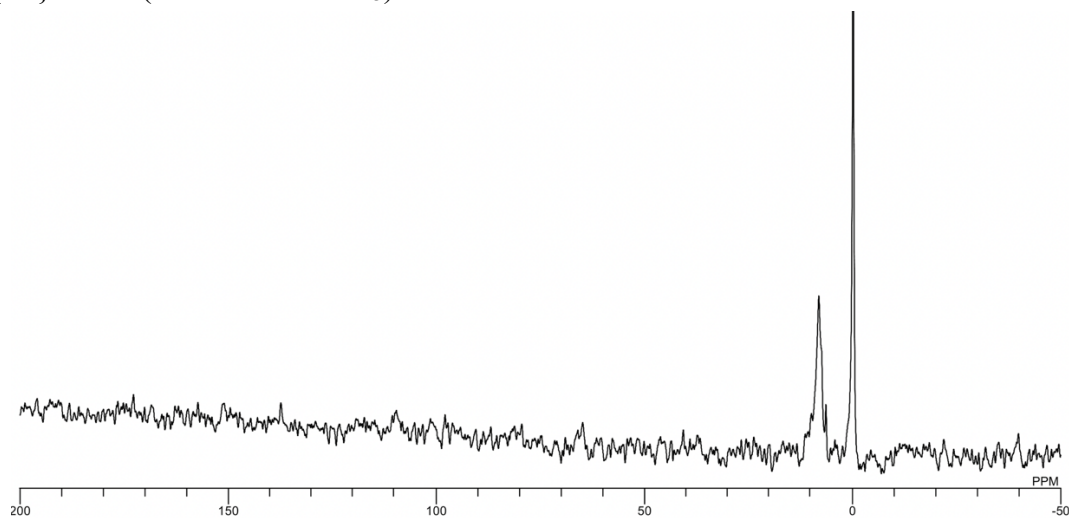
^1H NMR (400 MHz in CDCl_3)



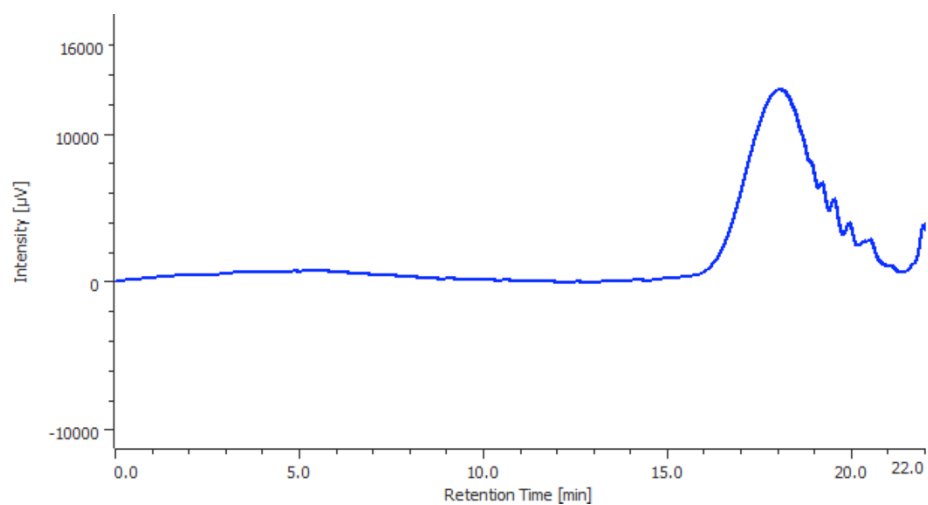
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz in CDCl_3)



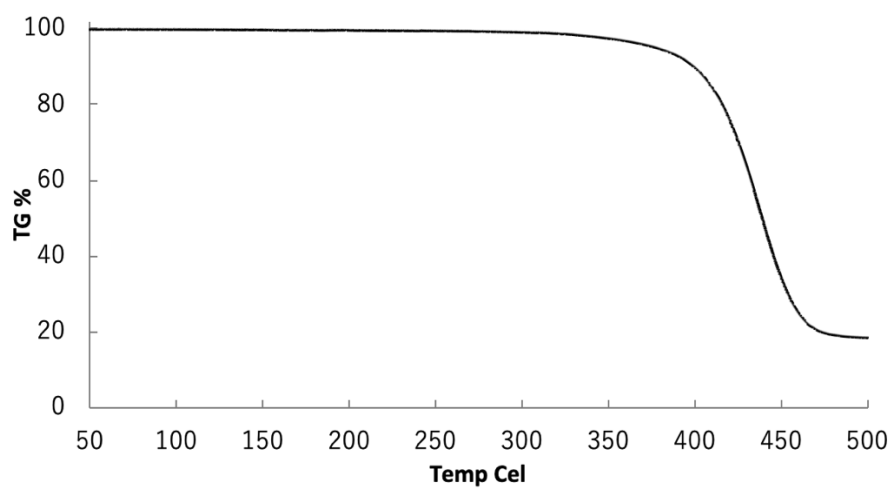
$^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz in CDCl_3)



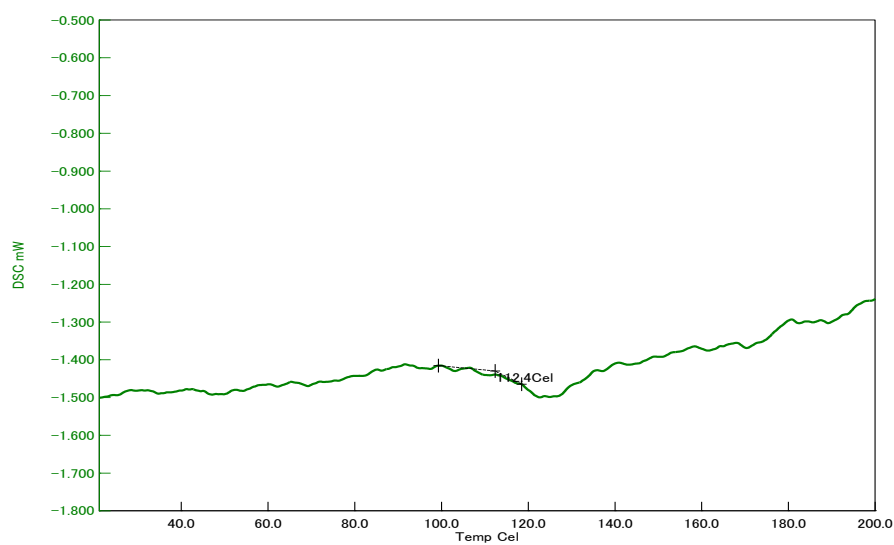
GPC (THF; 1.0 mL/min flow)



TG (+10 °C/min from 50 °C to 500 °C)



DSC (+10 °C/min from 20 °C to 250 °C, second heating)



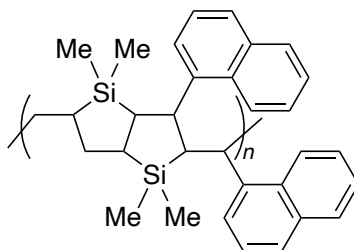
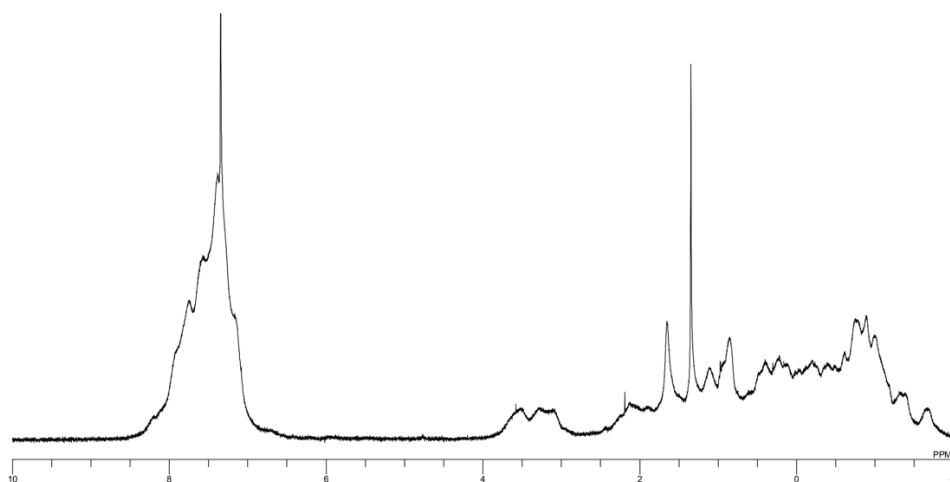
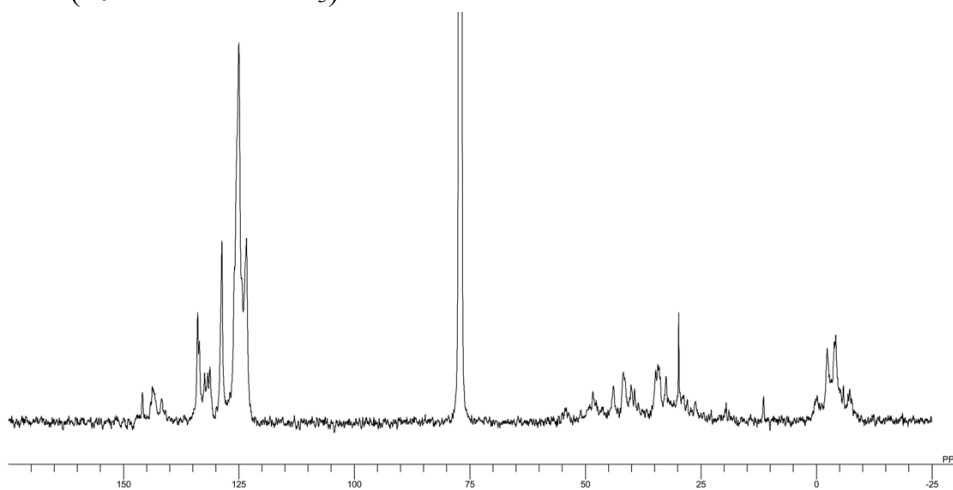


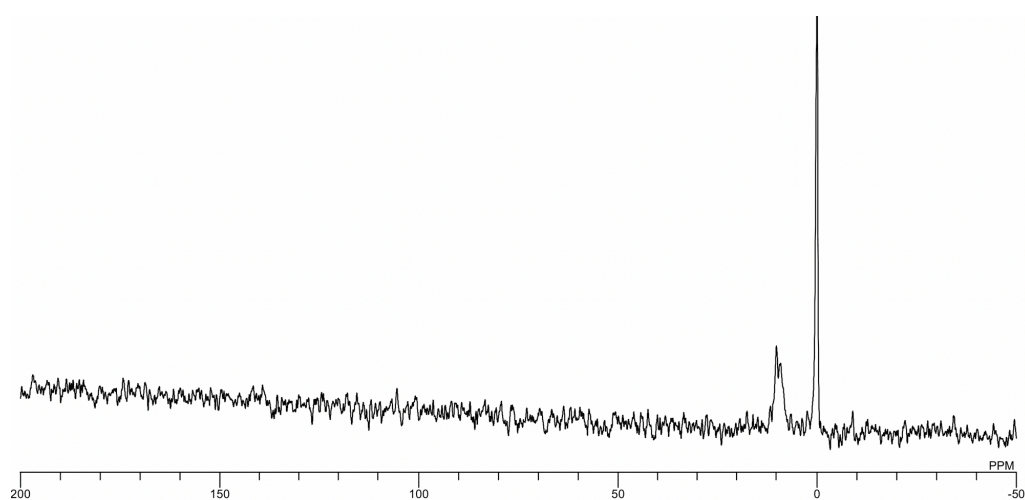
Table 1, Entry 6 (poly-1d). White solid. 89% yield (106 mg). $T_d = 361\text{ }^\circ\text{C}$, $T_g = 187\text{ }^\circ\text{C}$.
 ^1H NMR (400 MHz in CDCl_3)



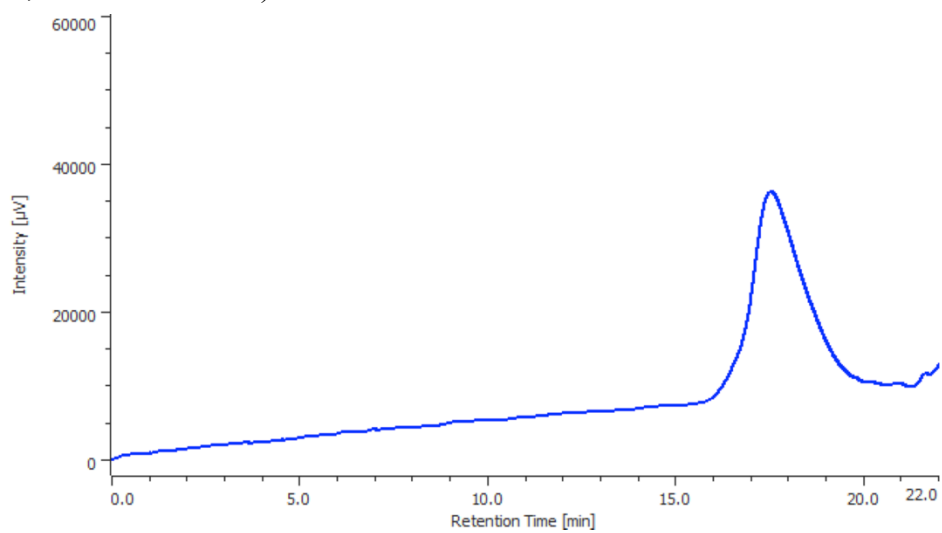
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz in CDCl_3)



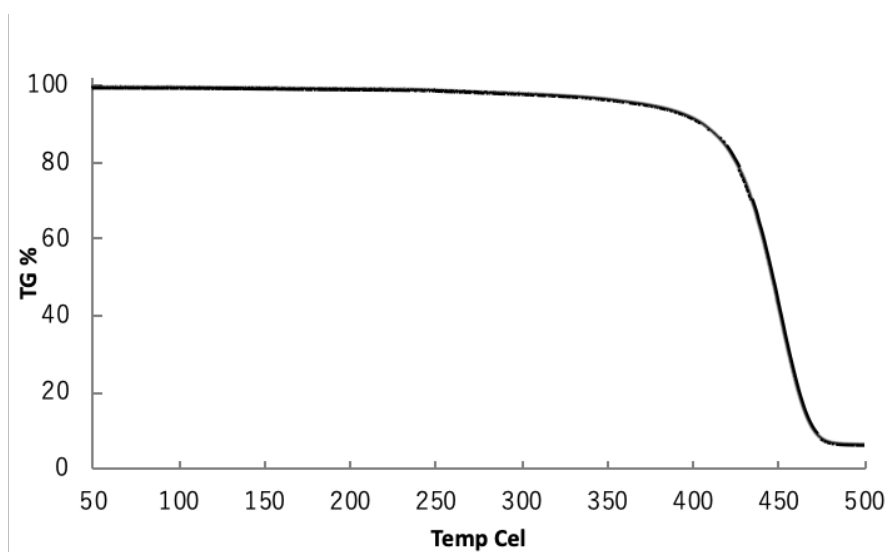
$^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz in CDCl_3)



GPC (THF; 1.0 mL/min flow)



TG (+10 $^\circ\text{C}/\text{min}$ from 50 $^\circ\text{C}$ to 500 $^\circ\text{C}$)



DSC (+10 °C/min from 20 °C to 250 °C, second heating)

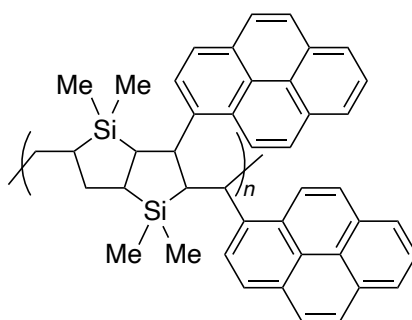
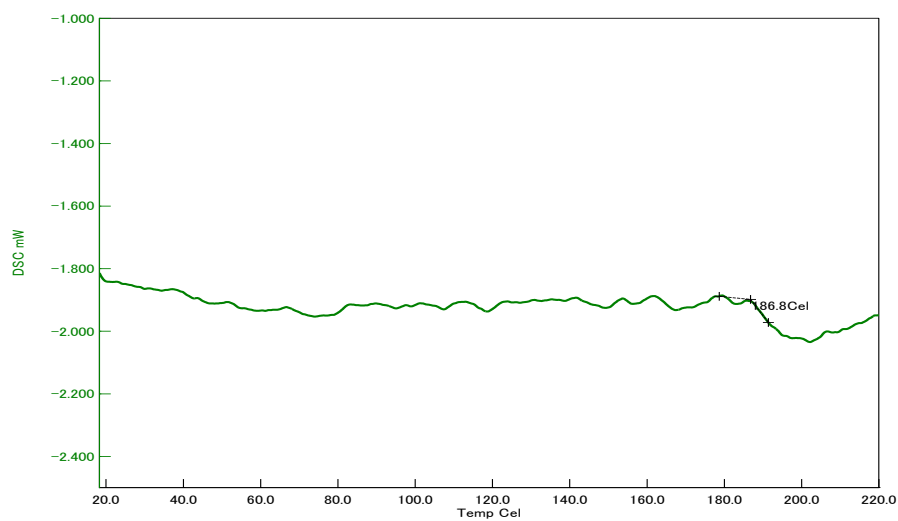
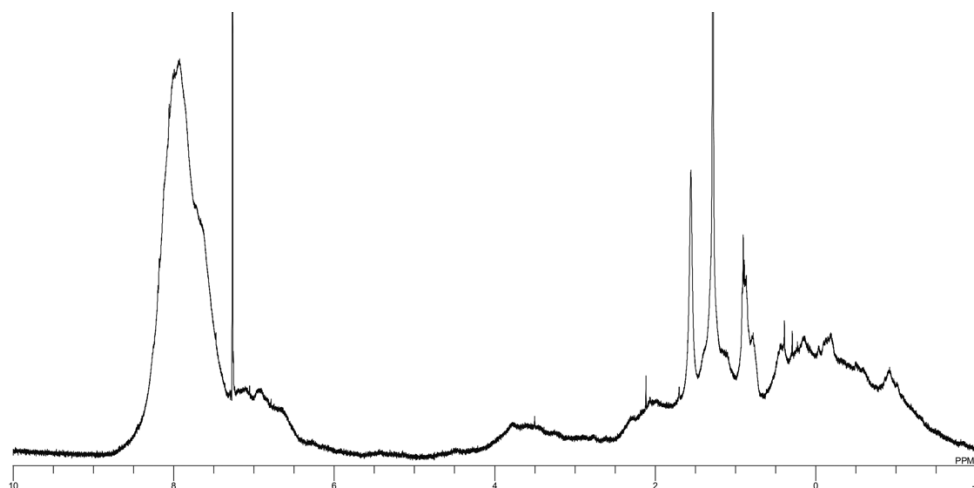
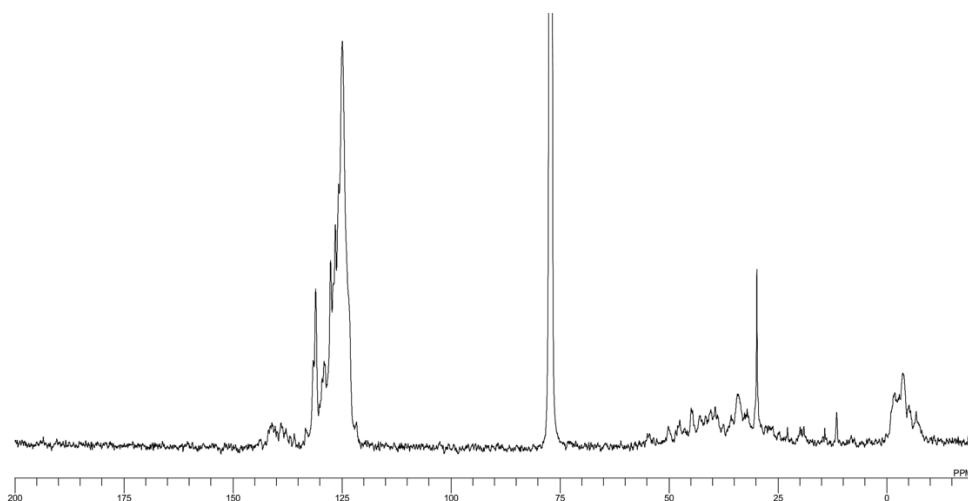


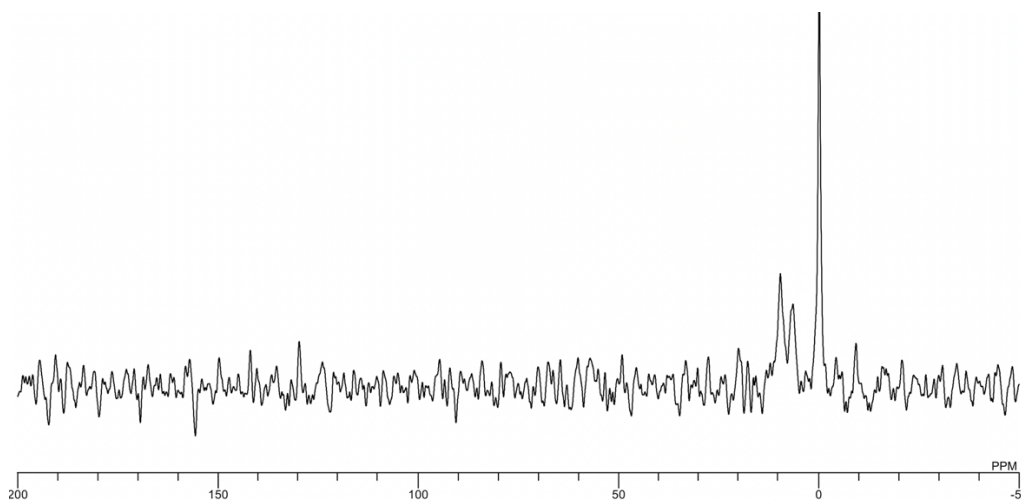
Table 1, Entry 7 (poly-1e). Yellow solid. 89% yield (139 mg). $T_d = 396\text{ °C}$, T_g : not observed.
 $^1\text{H NMR}$ (498 MHz in CDCl_3)



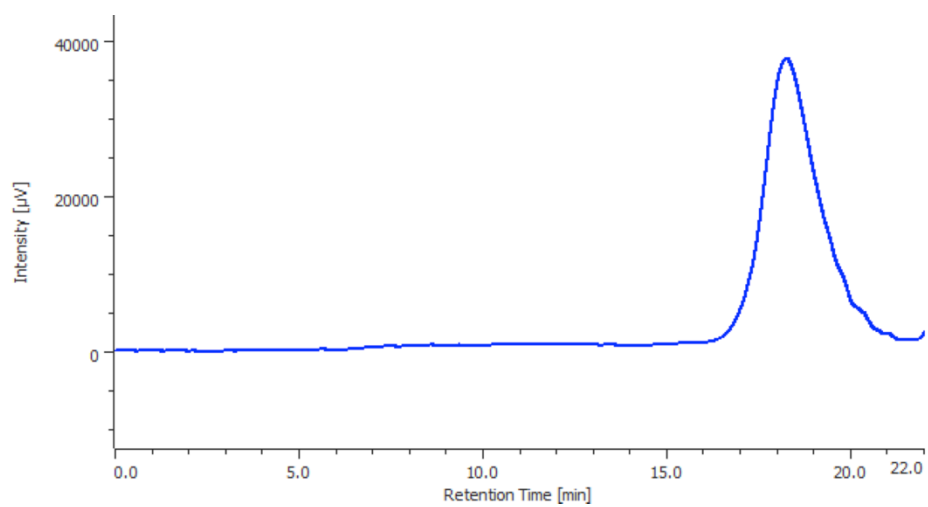
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz in CDCl_3)



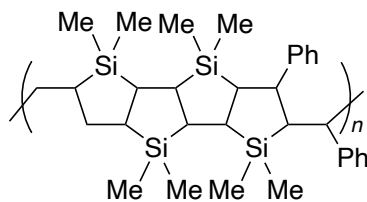
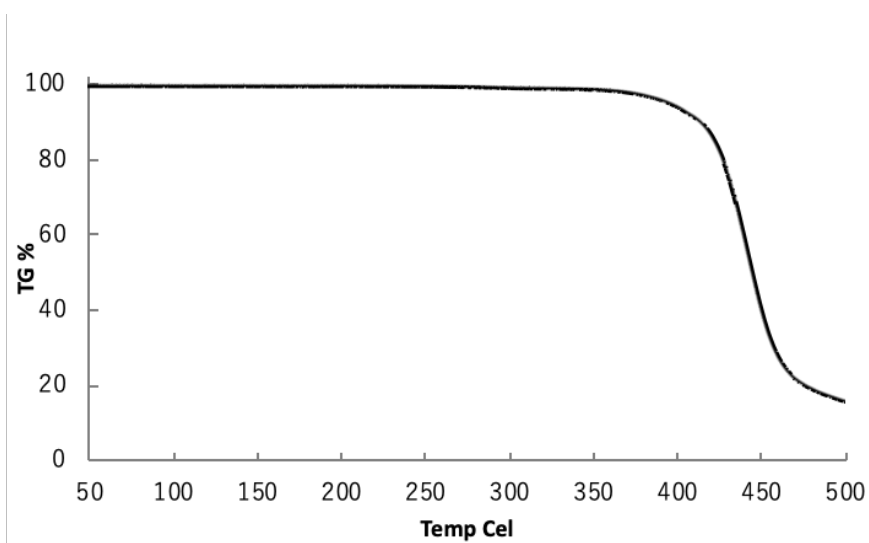
$^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz in CDCl_3)



GPC (THF; 1.0 mL/min flow)

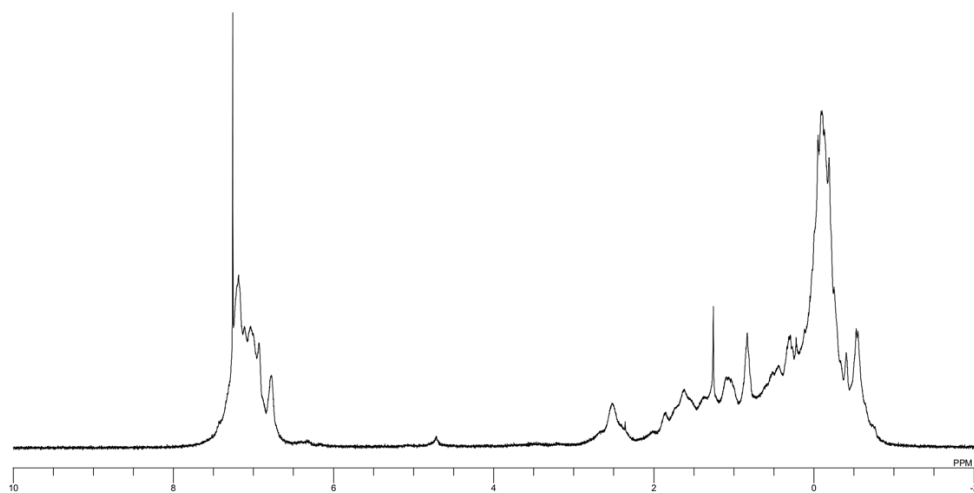


TG (+10 °C/min from 50 °C to 500 °C)

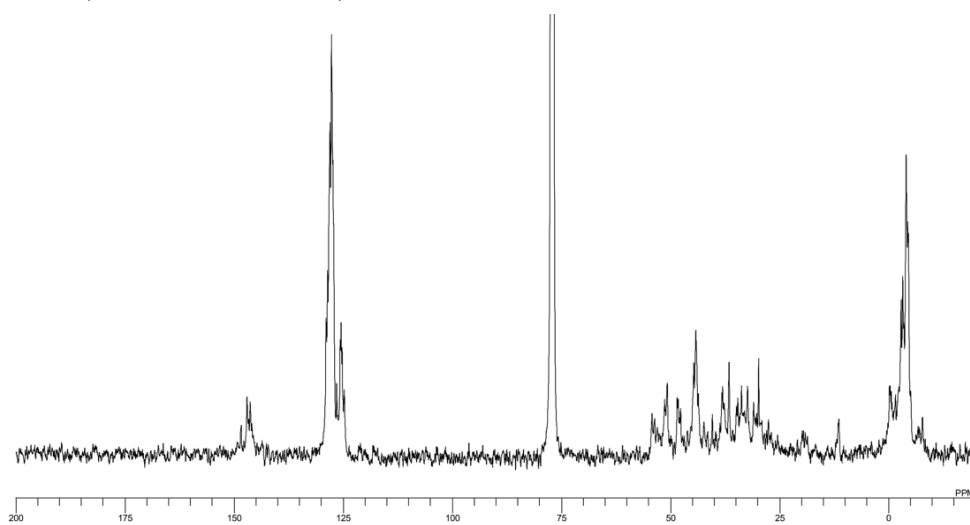


Equation 3 (poly-6). White solid. 89% yield (121 mg). $T_d = 374\text{ }^\circ\text{C}$, $T_g = 158\text{ }^\circ\text{C}$.

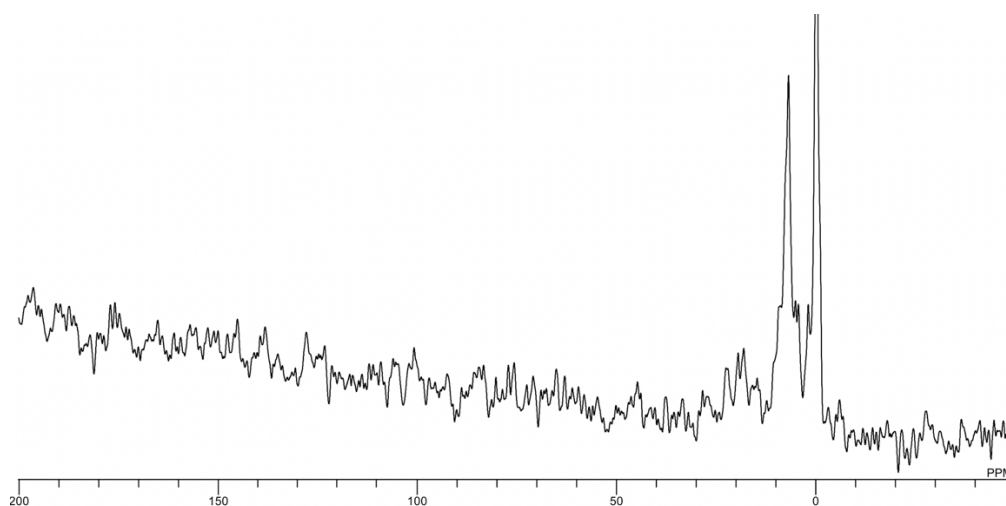
$^1\text{H NMR}$ (400 MHz in CDCl_3)



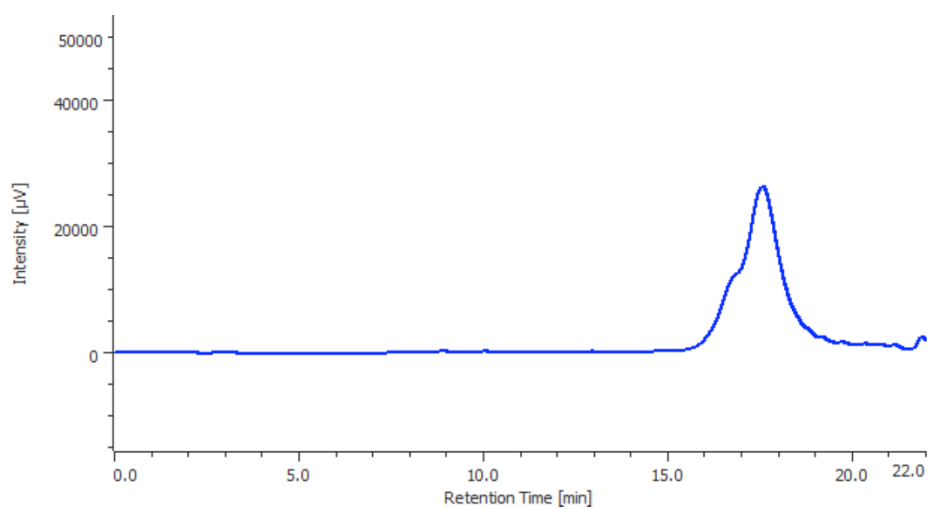
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz in CDCl_3)



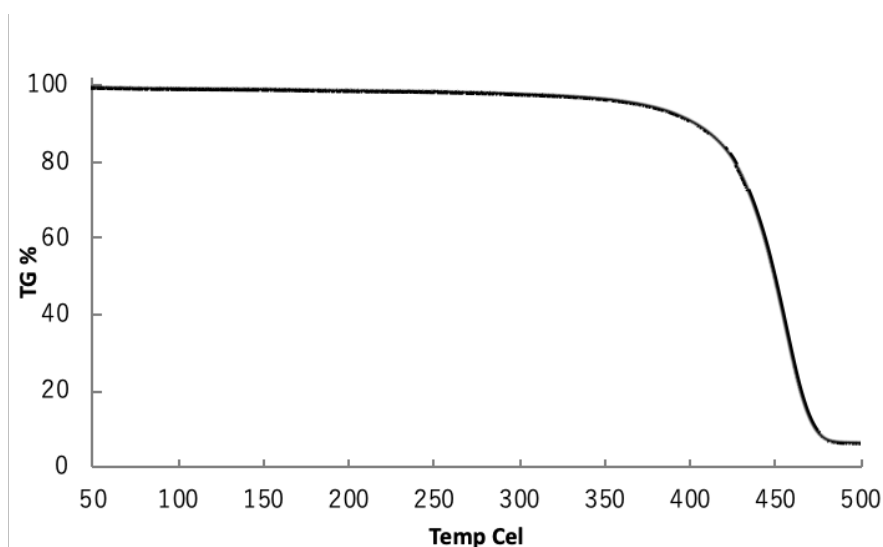
$^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz in CDCl_3)



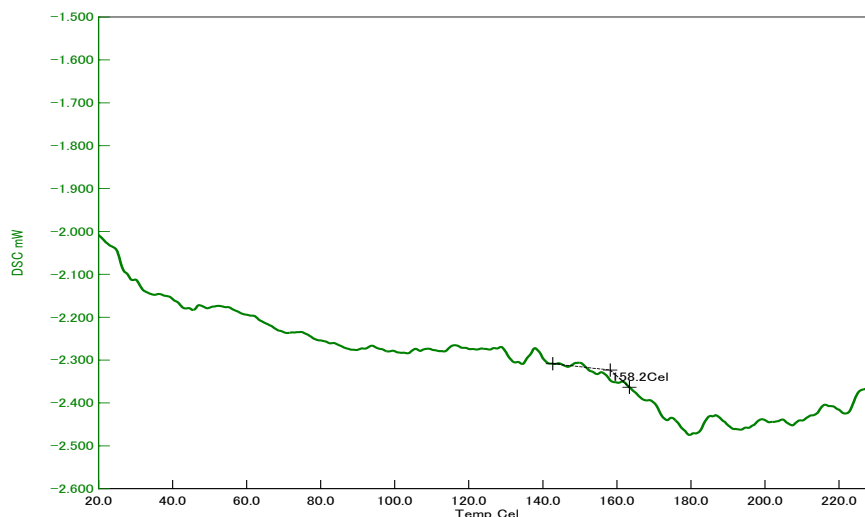
GPC (THF; 1.0 mL/min flow)



TG (+10 °C/min from 50 °C to 500 °C)

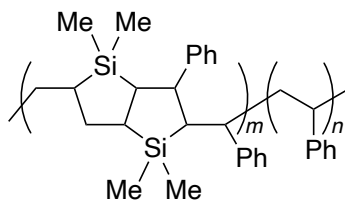


DSC (+10 °C/min from 20 °C to 250 °C, second heating)



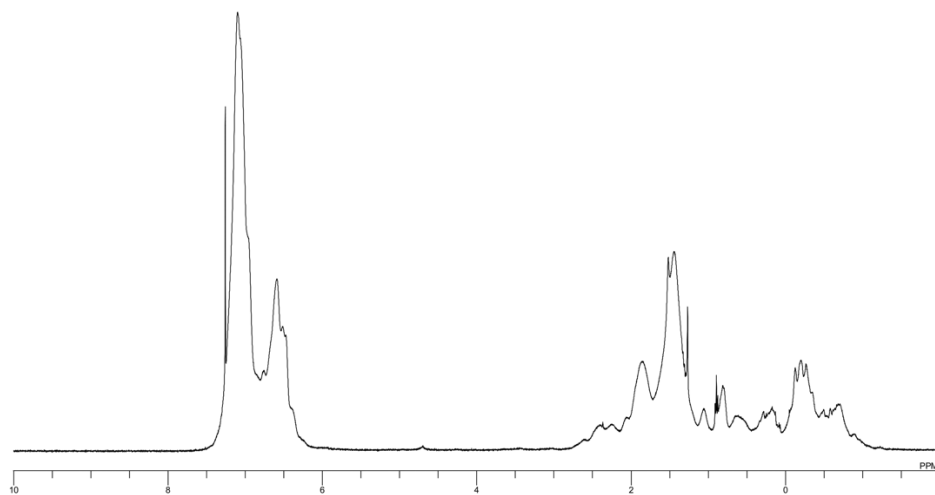
Procedure for Equations 4 and 5.

*sec*BuLi (40.7 μ L, 50.0 μ mol; 1.23 M solution in cyclohexane/hexane) was added to a solution of monomer **1a** (94.2 mg, 0.500 mmol) in toluene (0.5 mL). The mixture was stirred for 6 h at 30 °C, and an aliquot (5.0 μ L) was taken for molecular weight analysis. Styrene or trimethyl(vinyl)silane (1.00 mmol) was then added to the reaction mixture and this was stirred for 22 h at 30 °C. The reaction was quenched with MeOH (0.5 mL) and this was dissolved in CH₂Cl₂ (2.0 mL). The resulting solution was added dropwise into stirring MeOH (50 mL) with the aid of CH₂Cl₂ (2.0 mL), and the precipitates that formed were collected by filtration with MeOH. The solid thus obtained was dried under vacuum to afford **poly-1a-b-PS** or **poly-1a-b-PTMVS**.

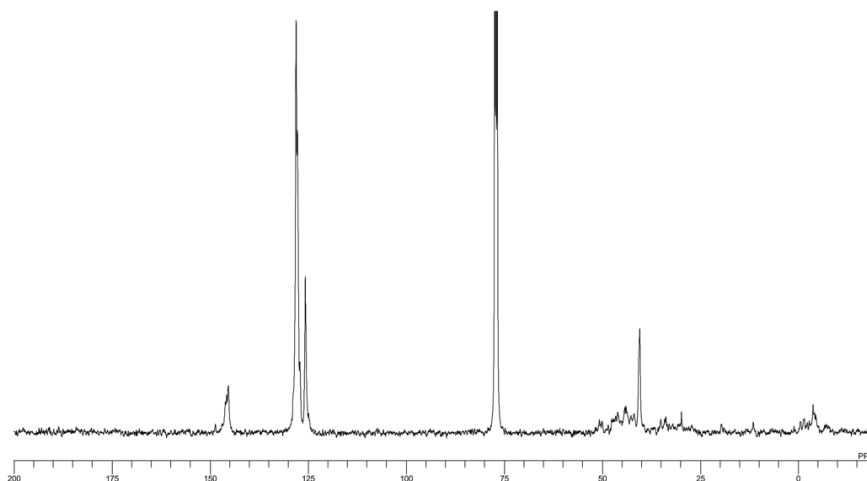


Equation 4 (poly-1a-b-PS). White solid. 96% yield (190 mg). $T_d = 358\text{ }^\circ\text{C}$, $T_g = 84\text{ }^\circ\text{C}$.

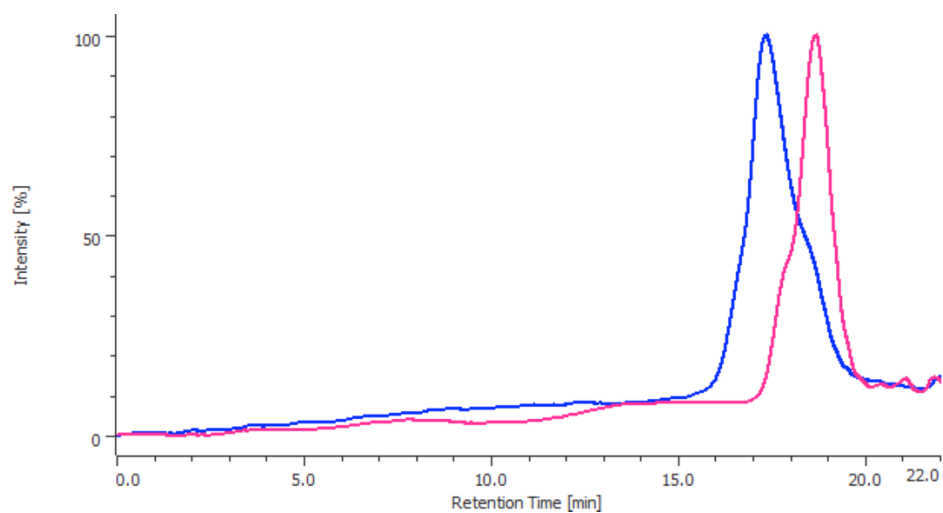
^1H NMR (400 MHz in CDCl_3)



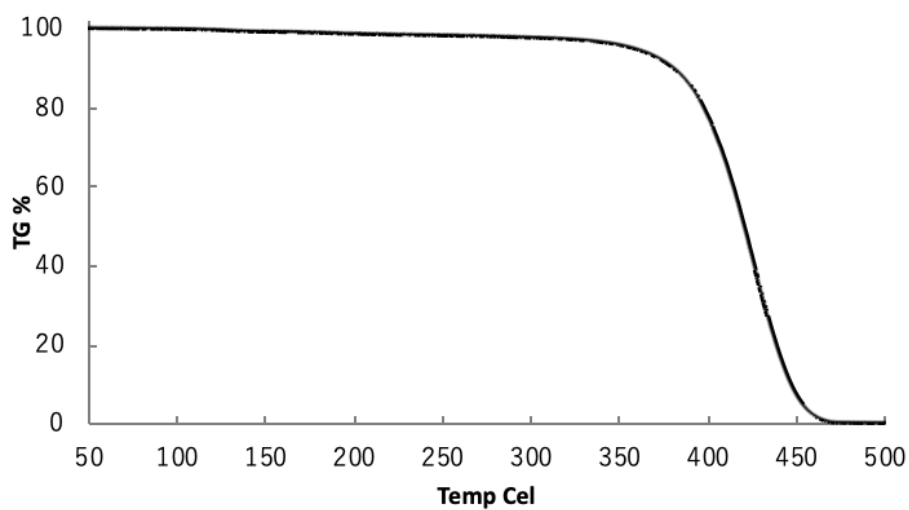
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz in CDCl_3)



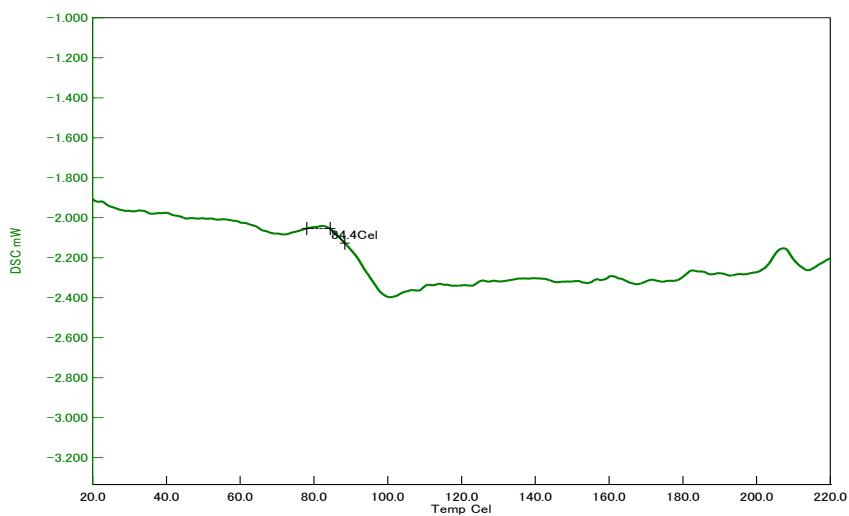
GPC (THF; 1.0 mL/min flow; pink: after stitching polymerization, blue: after block copolymerization)

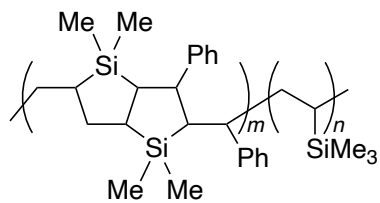


TG (+10 °C/min from 50 °C to 500 °C)



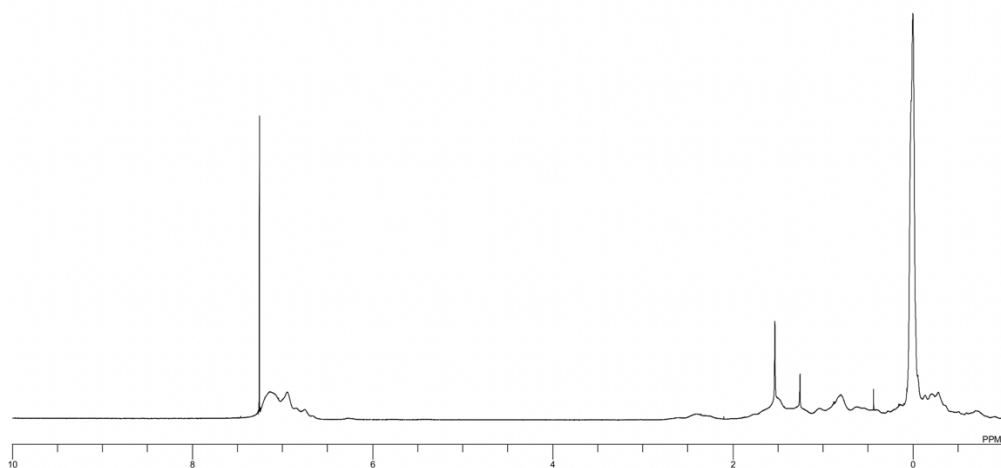
DSC (+10 °C/min from 20 °C to 250 °C, second heating)



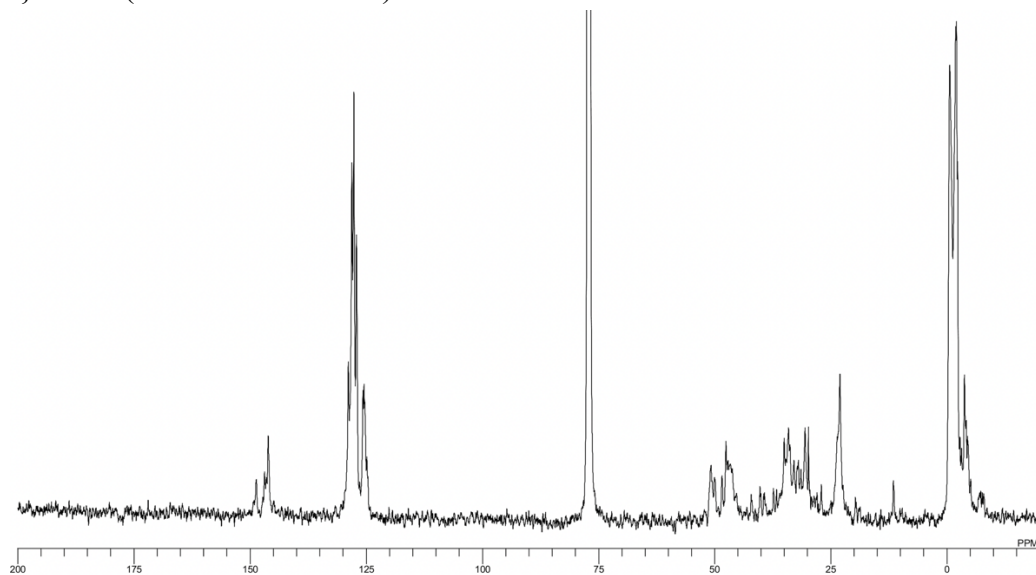


Equation 5 (poly-1a-b-PTMVS). White solid. 81% yield (157 mg). $T_d = 296\text{ }^\circ\text{C}$, $T_g = 142\text{ }^\circ\text{C}$.

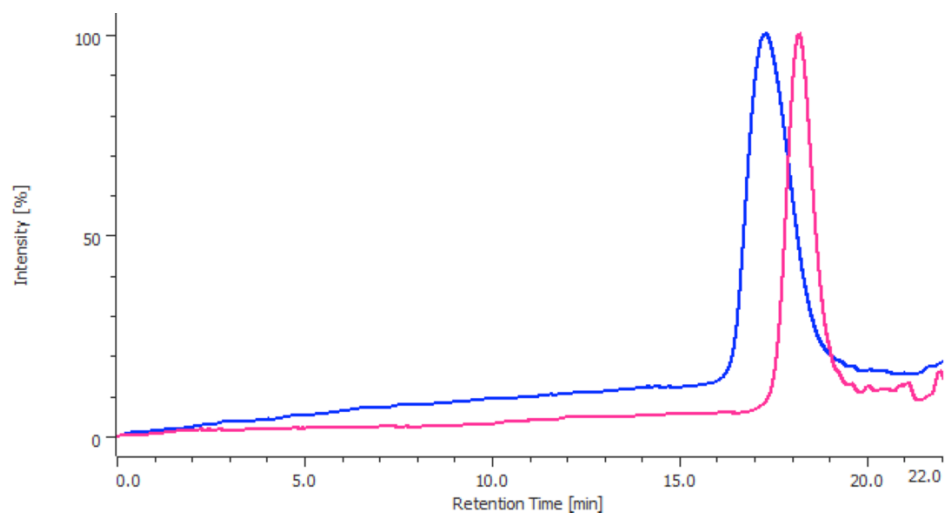
^1H NMR (498 MHz in CDCl_3)



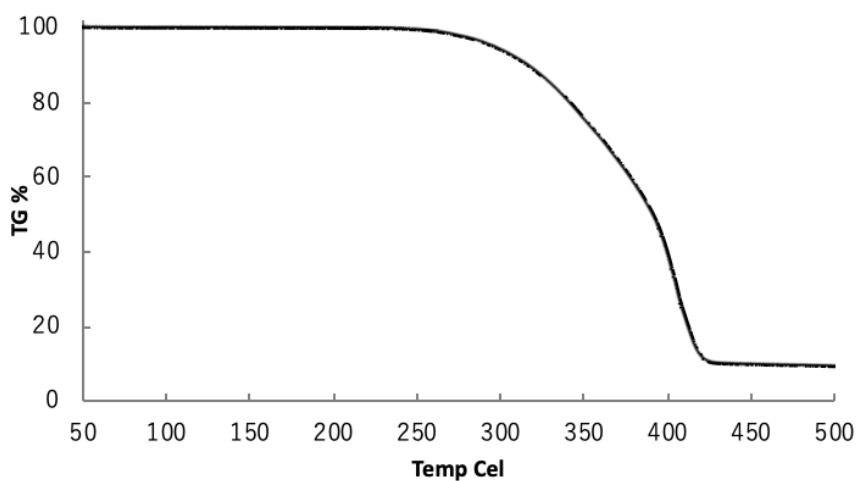
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz in CDCl_3)



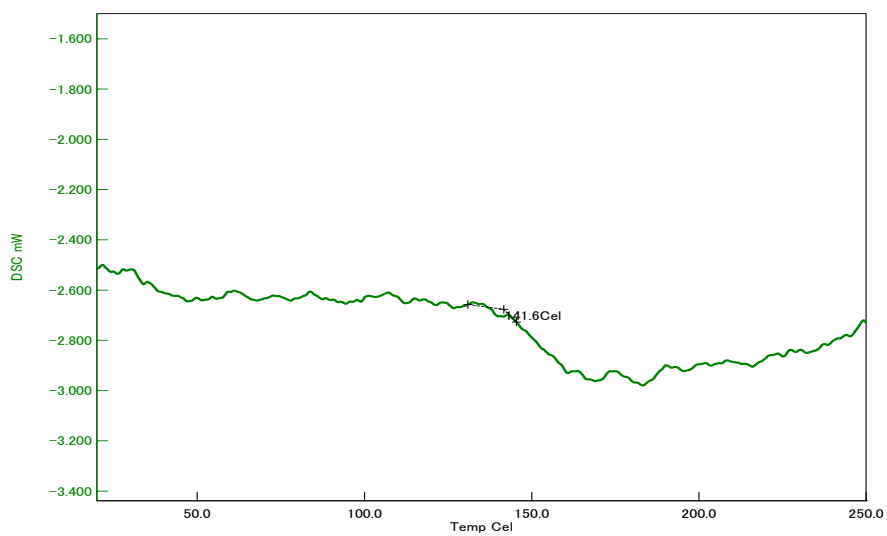
GPC (THF; 1.0 mL/min flow; pink: after stitching polymerization, blue: after block copolymerization)



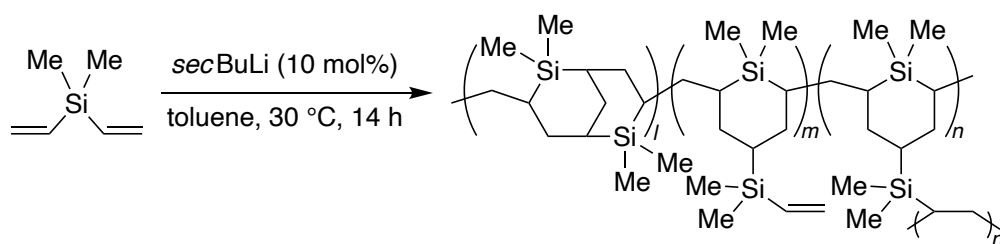
TG (+10 °C/min from 50 °C to 500 °C)



DSC (+10 °C/min from 20 °C to 250 °C, second heating)

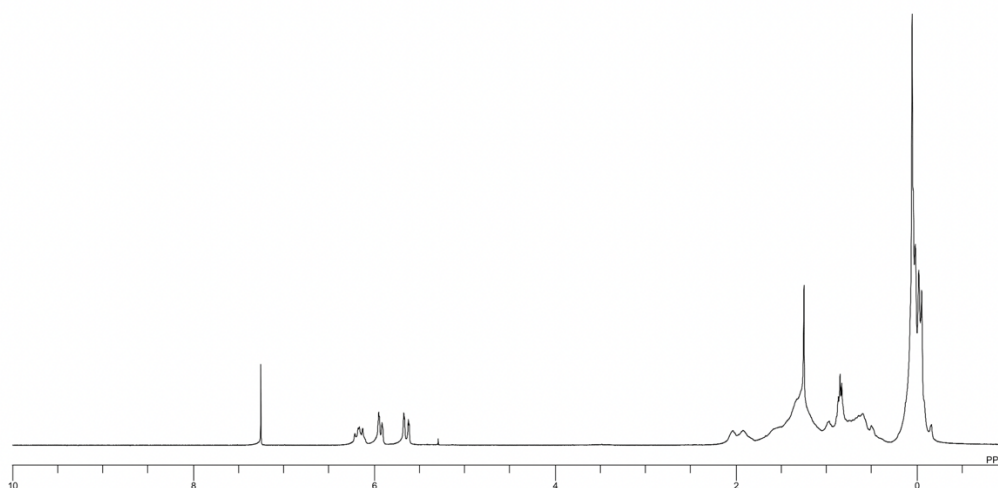


Procedure for the Polymerization of Dimethyldivinylsilane.

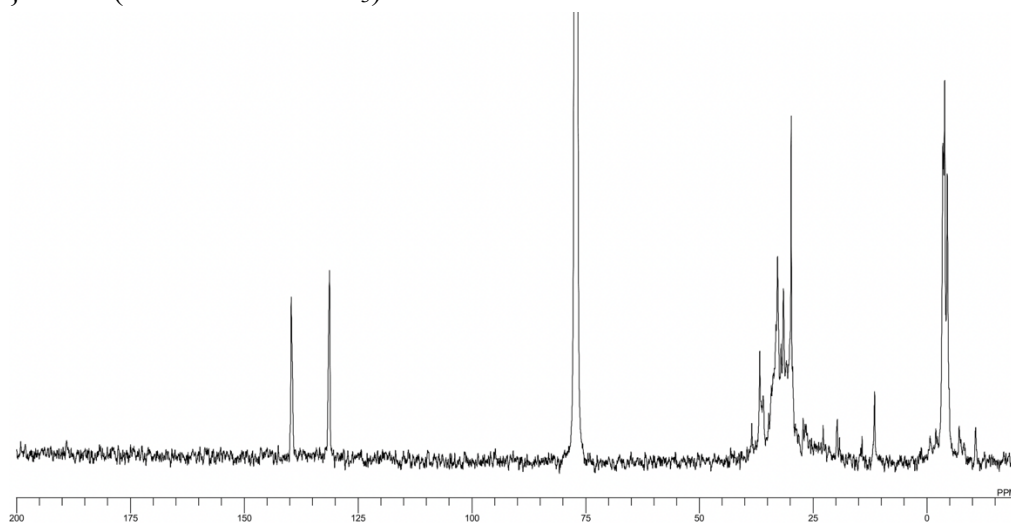


To compare the present stitching polymerization of styryl(vinyl)silanes **1** with the reported anionic polymerization of divinylsilanes,² we conducted a polymerization of dimethyldivinylsilane as follows: *sec*BuLi (81.2 μ L, 100 μ mol; 1.23 M solution in cyclohexane/hexane) was added to a solution of dimethyldivinylsilane (112 mg, 1.00 mmol) in toluene (1.0 mL) and the mixture was stirred for 14 h at 30 °C. The reaction was quenched with MeOH (0.5 mL) and this was dissolved in CH₂Cl₂ (2.0 mL). The resulting solution was added dropwise into stirring MeOH (50 mL) with the aid of CH₂Cl₂ (2.0 mL), and the precipitates that formed were collected by filtration with MeOH. The solid thus obtained was dried under vacuum to afford polydimethyldivinylsilane as a white solid. 73% yield (81.8 mg). $M_n = 9300$, $M_w/M_n = 13.2$. The structure was deduced based on the literature and ca. 15% of vinyl group remained unreacted. Prolonged reaction time resulted in the formation of an insoluble gel, presumably due to the cross-linking between the uncyclized vinyl groups.

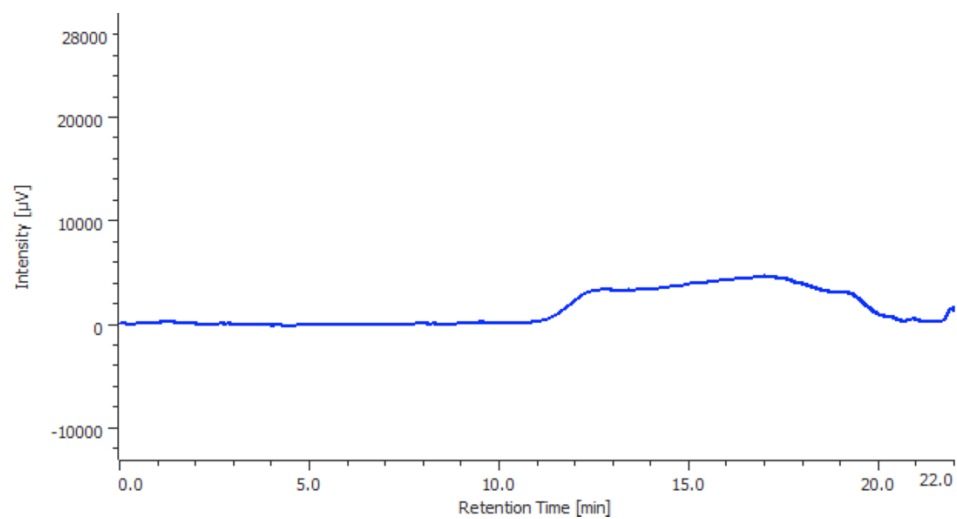
¹H NMR (400 MHz in CDCl₃)



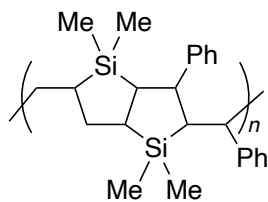
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz in CDCl_3)



GPC (THF; 1.0 mL/min flow)



IV. UV-vis Absorption and Transmittance Spectra



The UV-vis absorption spectrum of **poly-1a** ($M_n = 3400$, PDI = 1.17) in THF and the transmittance spectrum of its thin film (thickness: 3 μm) was measured to examine the transparency of this polymer, and the results are shown in Figures S1 and S2, respectively.

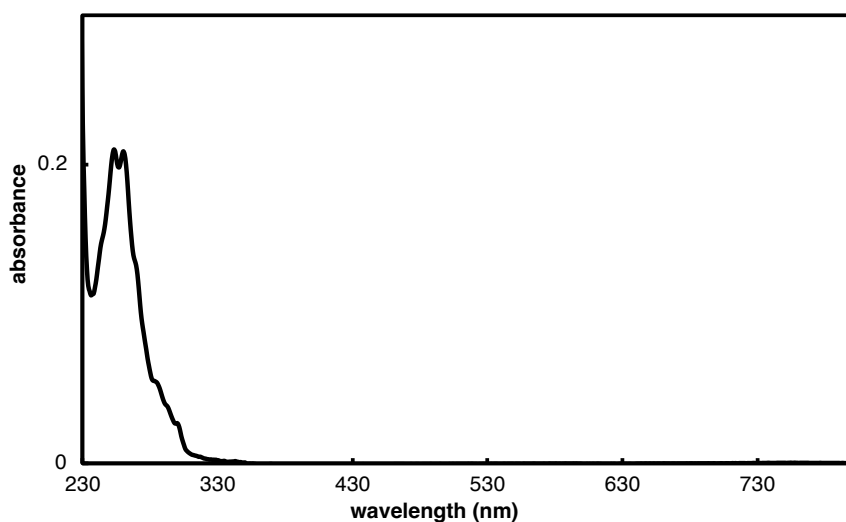


Figure S1. UV-vis absorption spectrum of **poly-1a** (3.0×10^{-2} g/L) in THF at 25 °C.

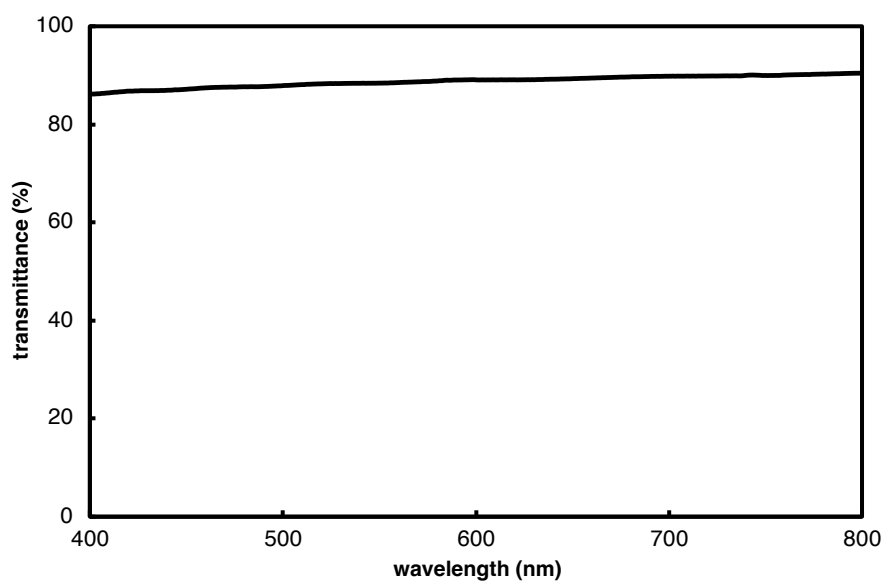
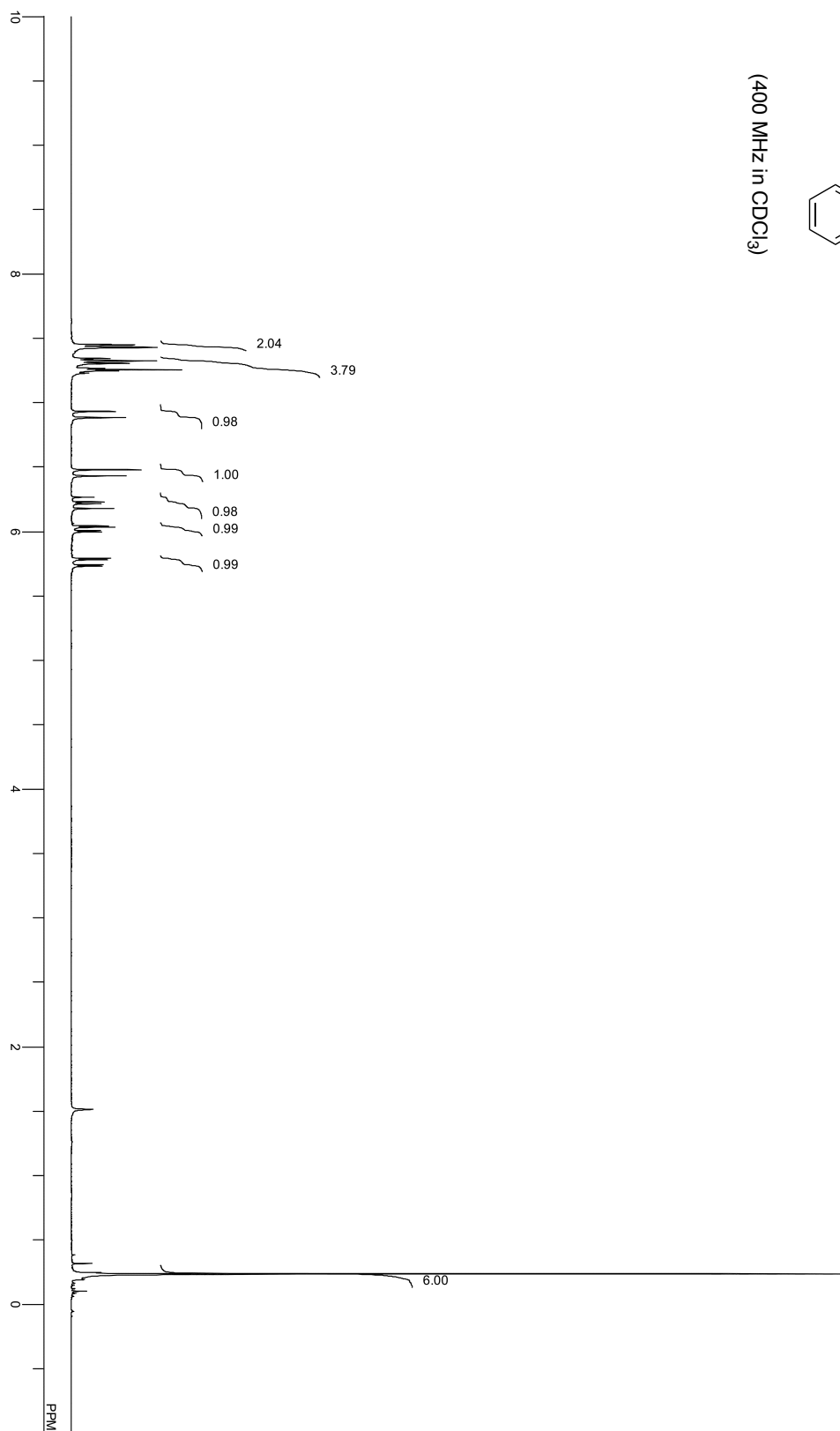


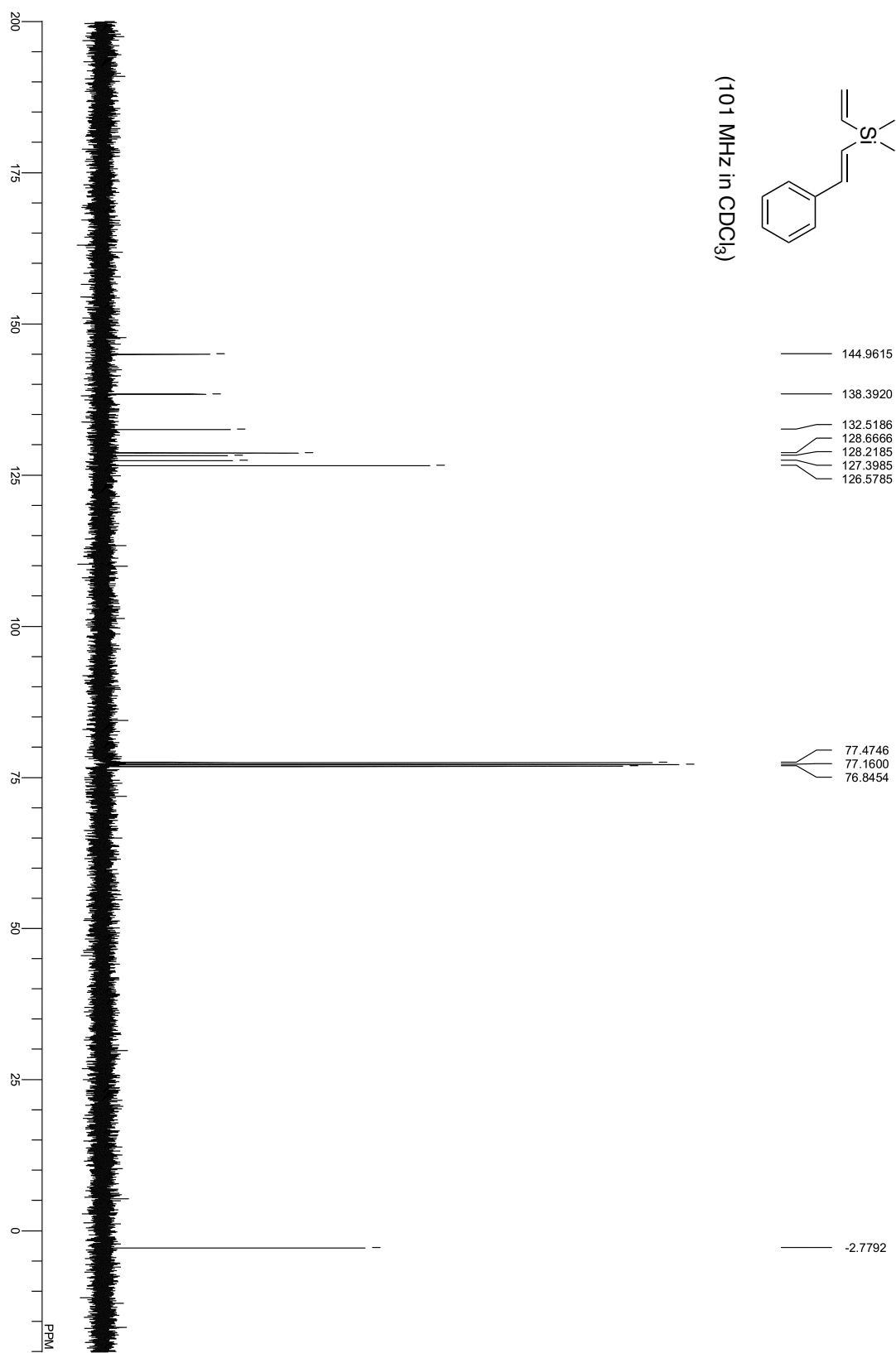
Figure S2. Transmittance spectrum of **poly-1a** (3 μm thin film).

V. ^1H and ^{13}C NMR Spectra

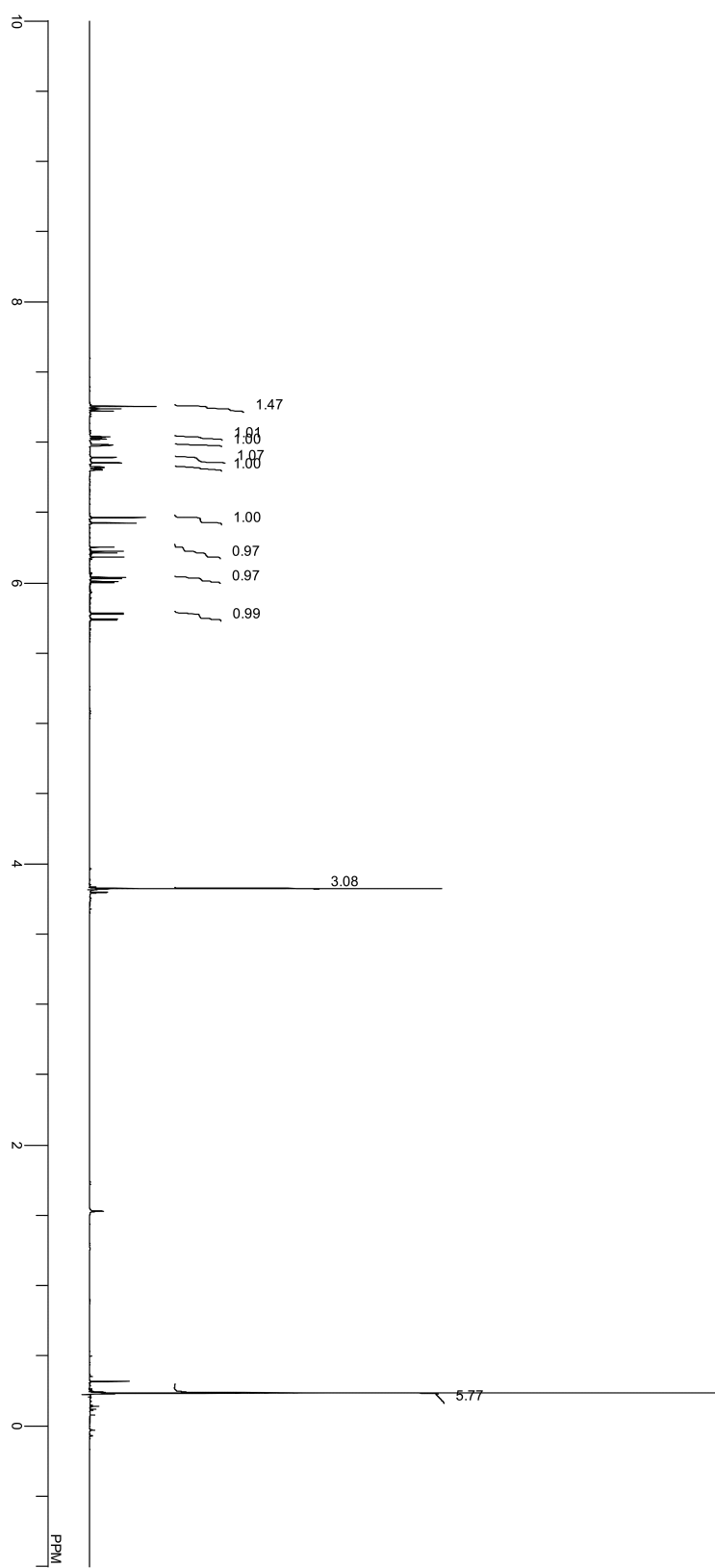
compound **1a**



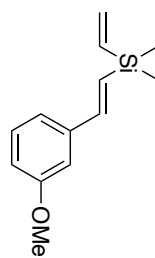
compound 1a



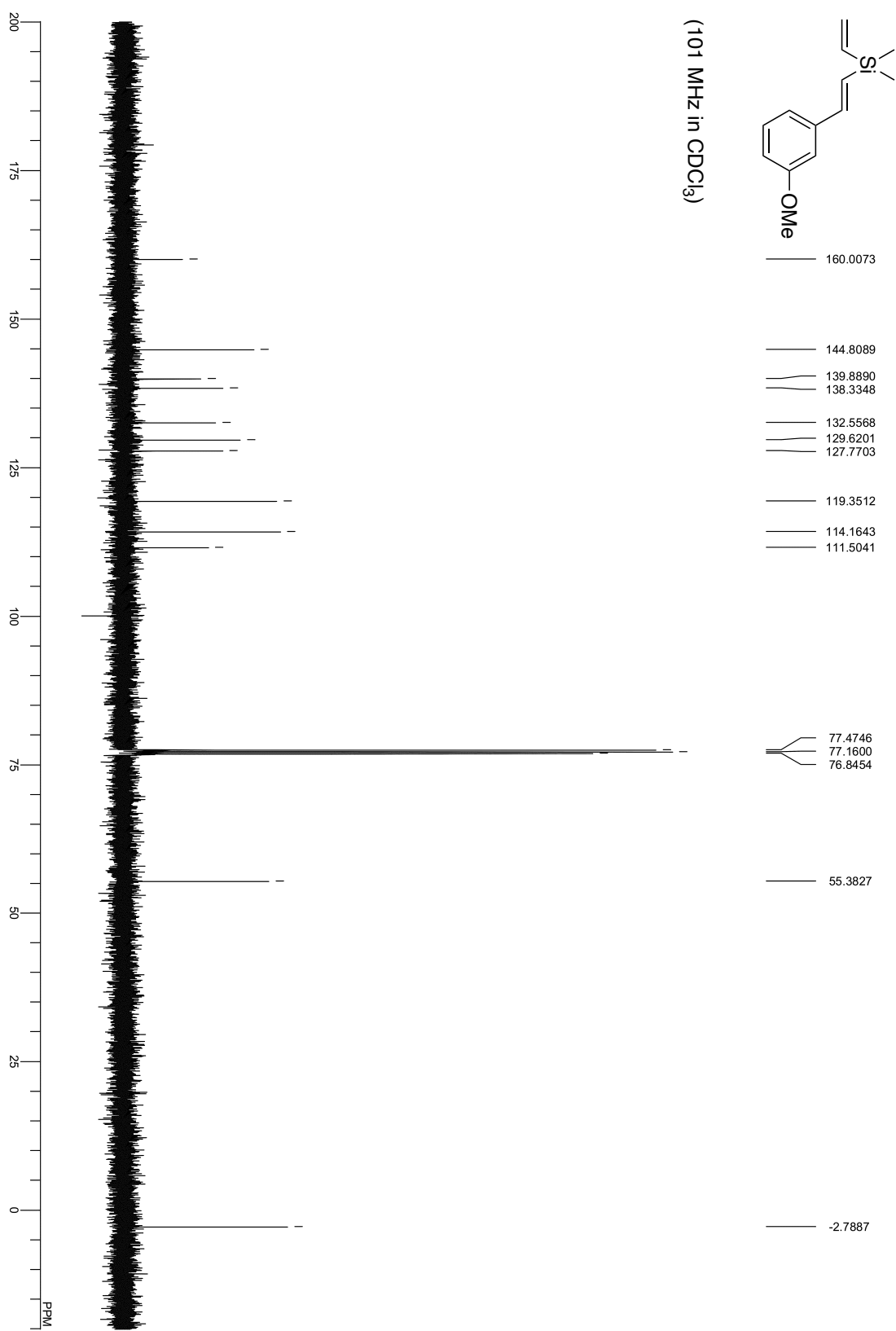
compound **1b**



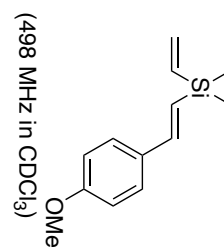
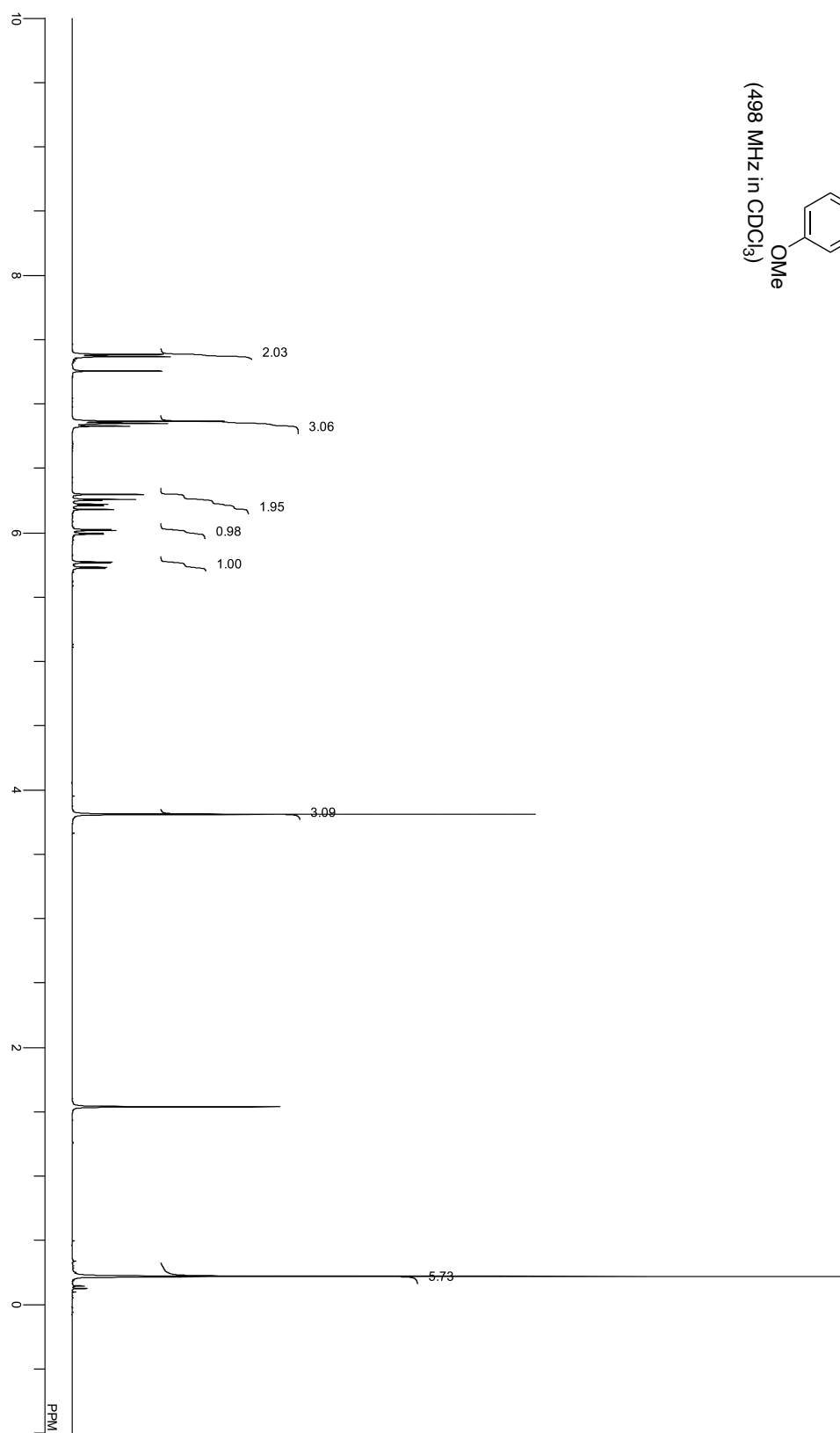
(498 MHz in CDCl₃)



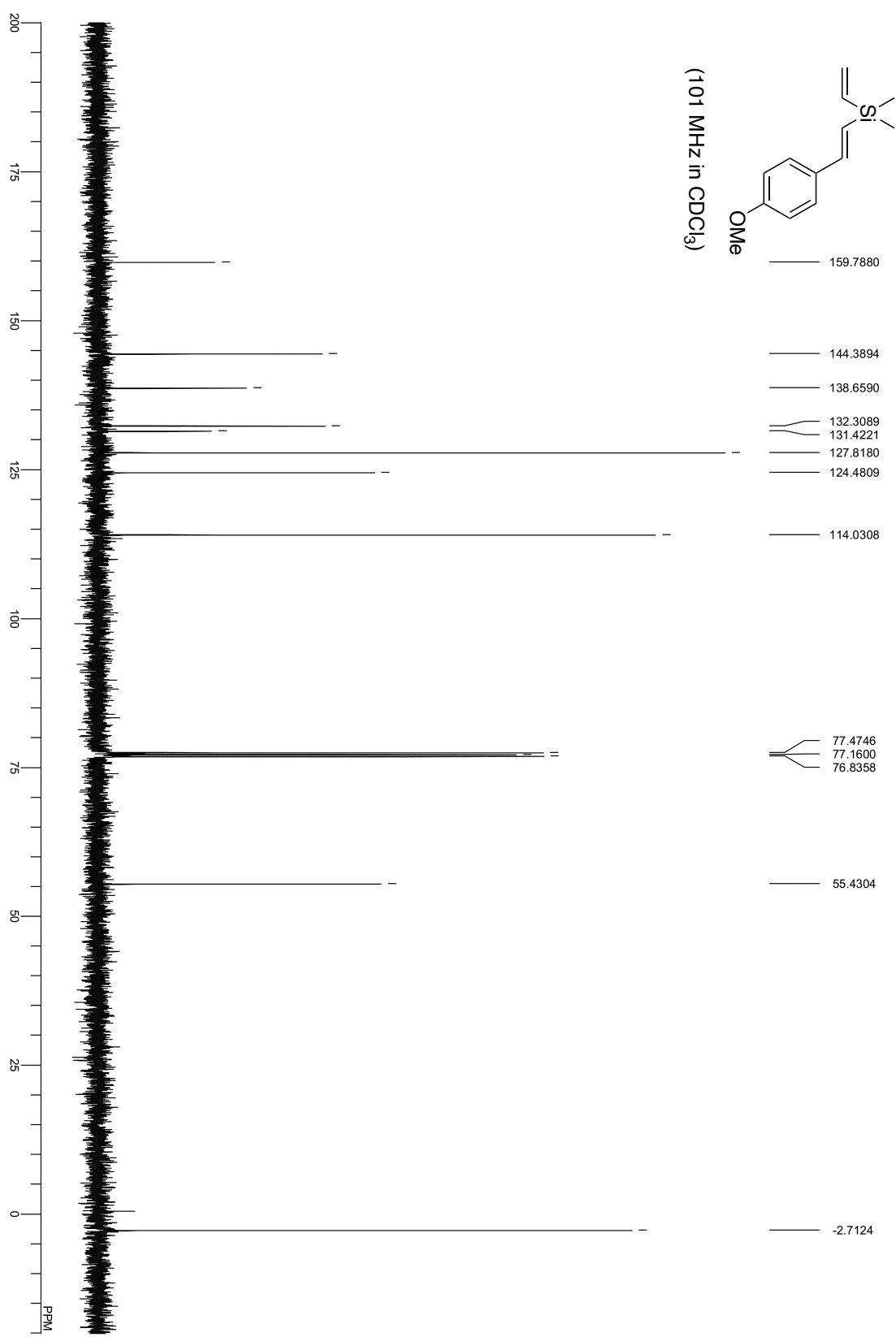
compound **1b**



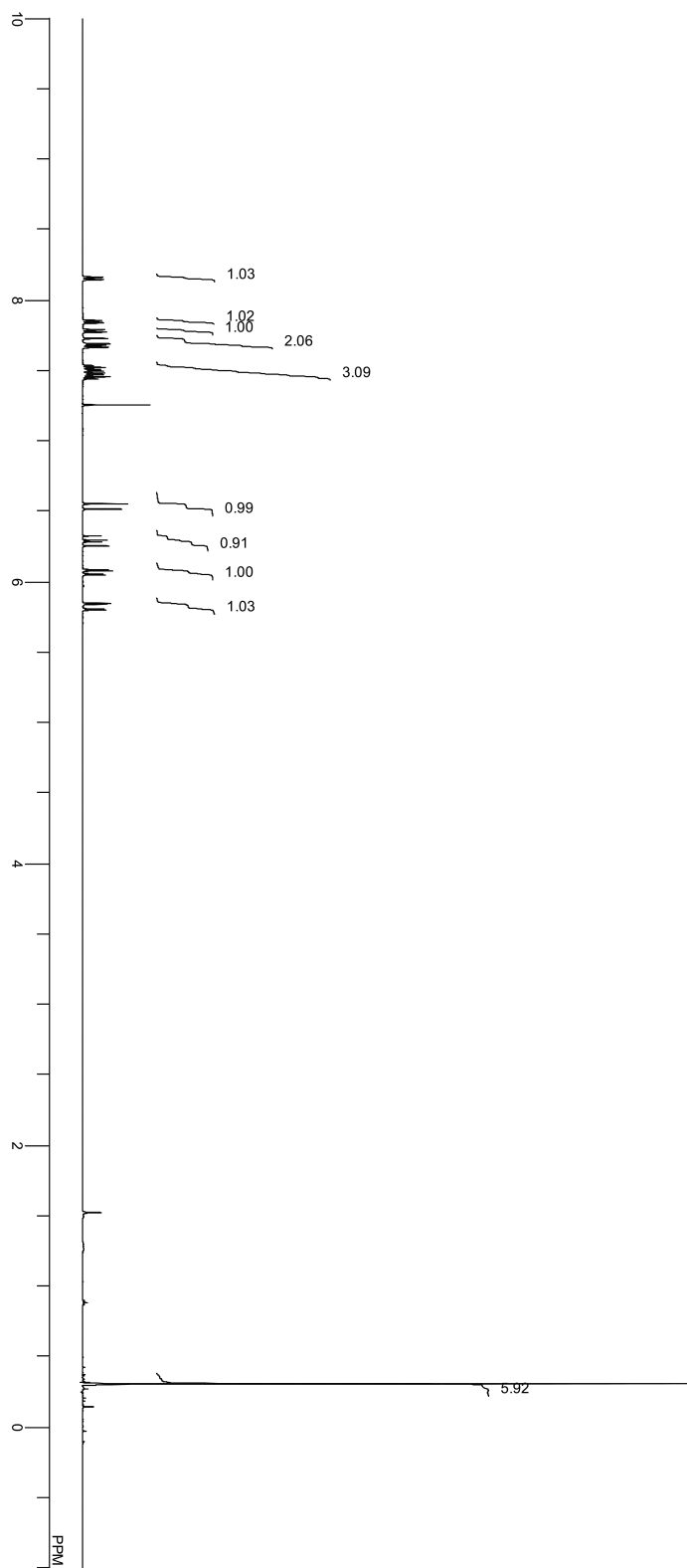
compound **1c**



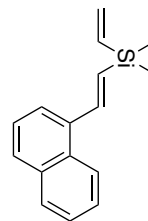
compound 1c



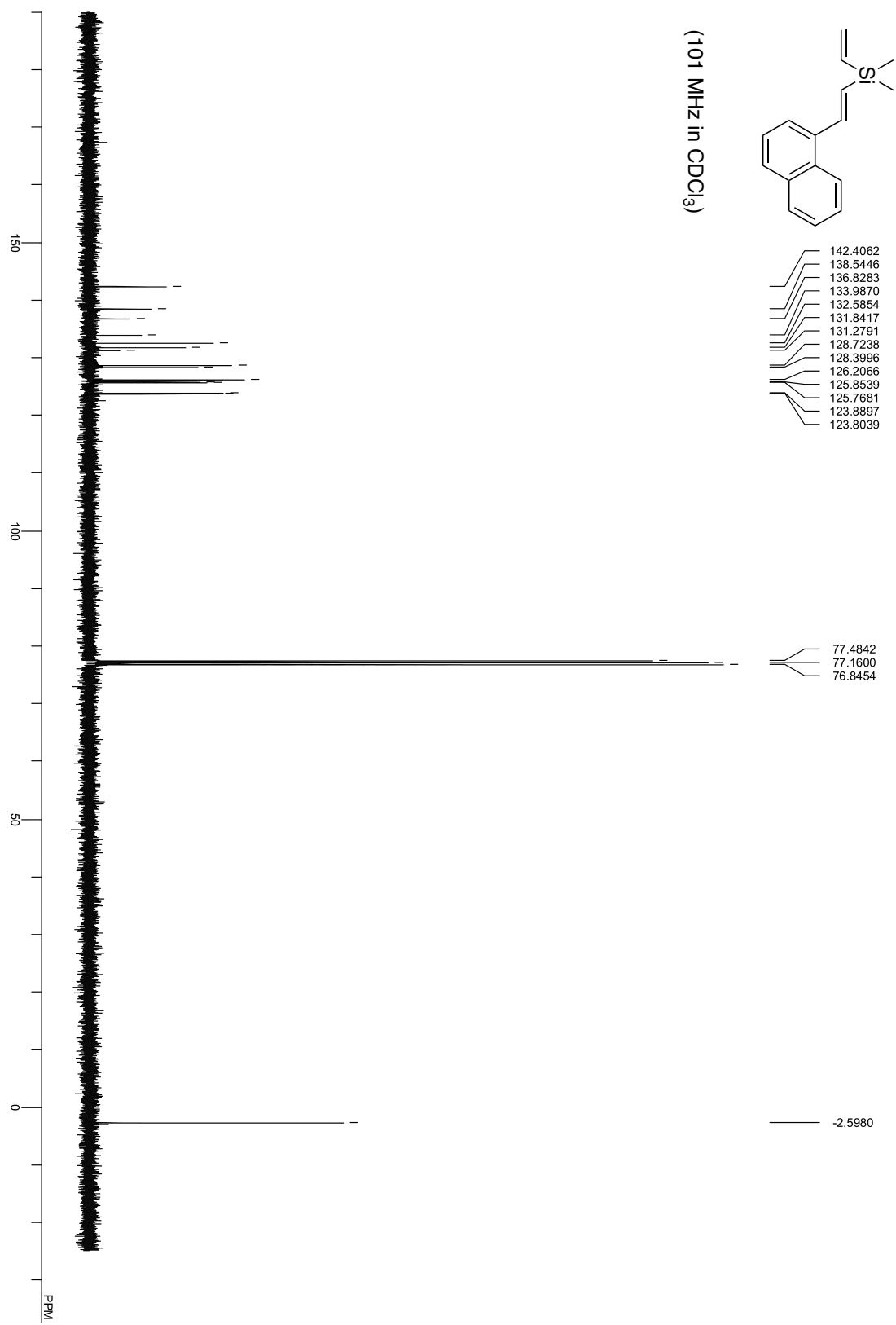
compound **1d**



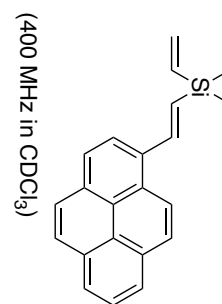
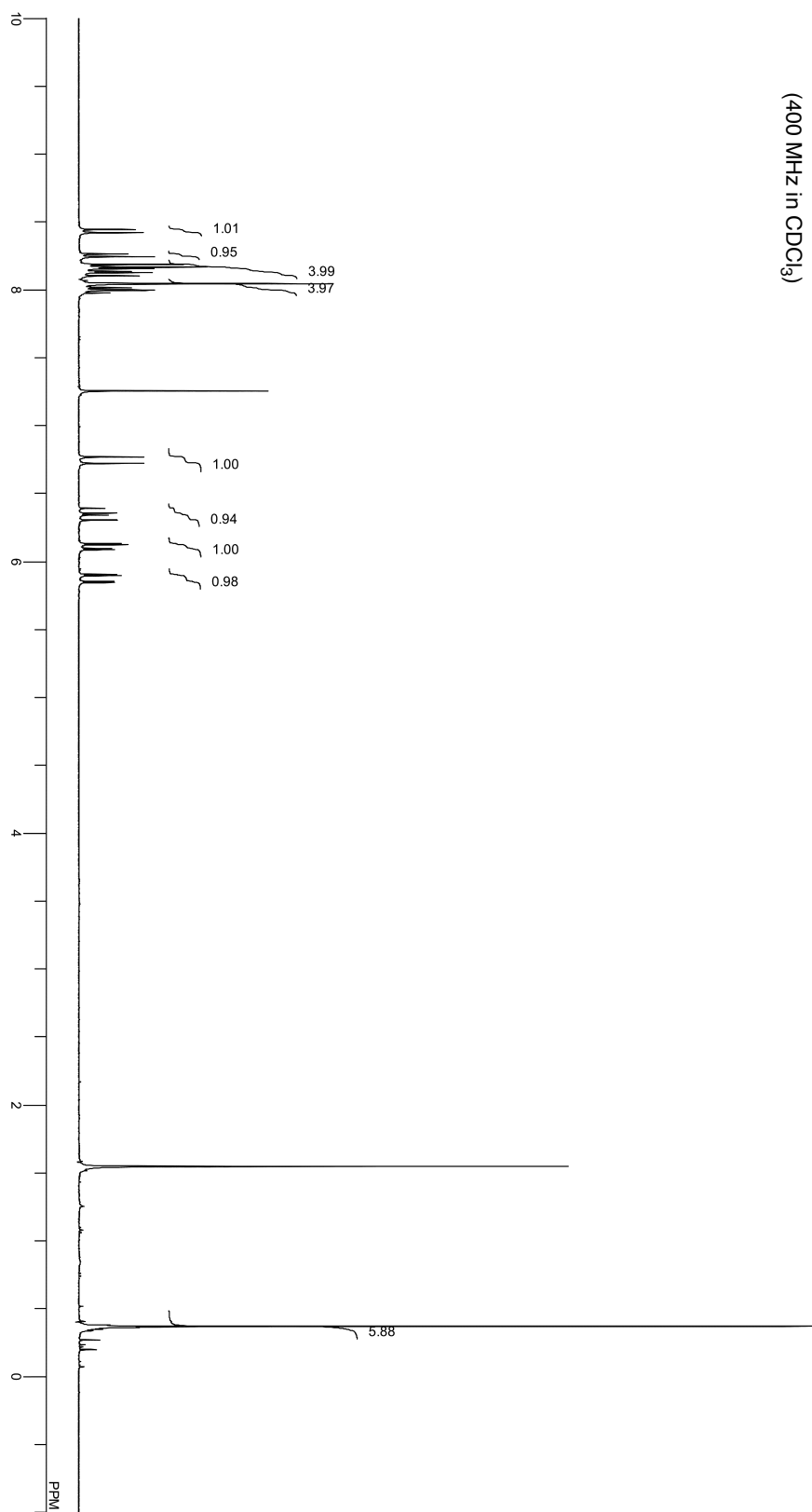
(498 MHz in CDCl₃)



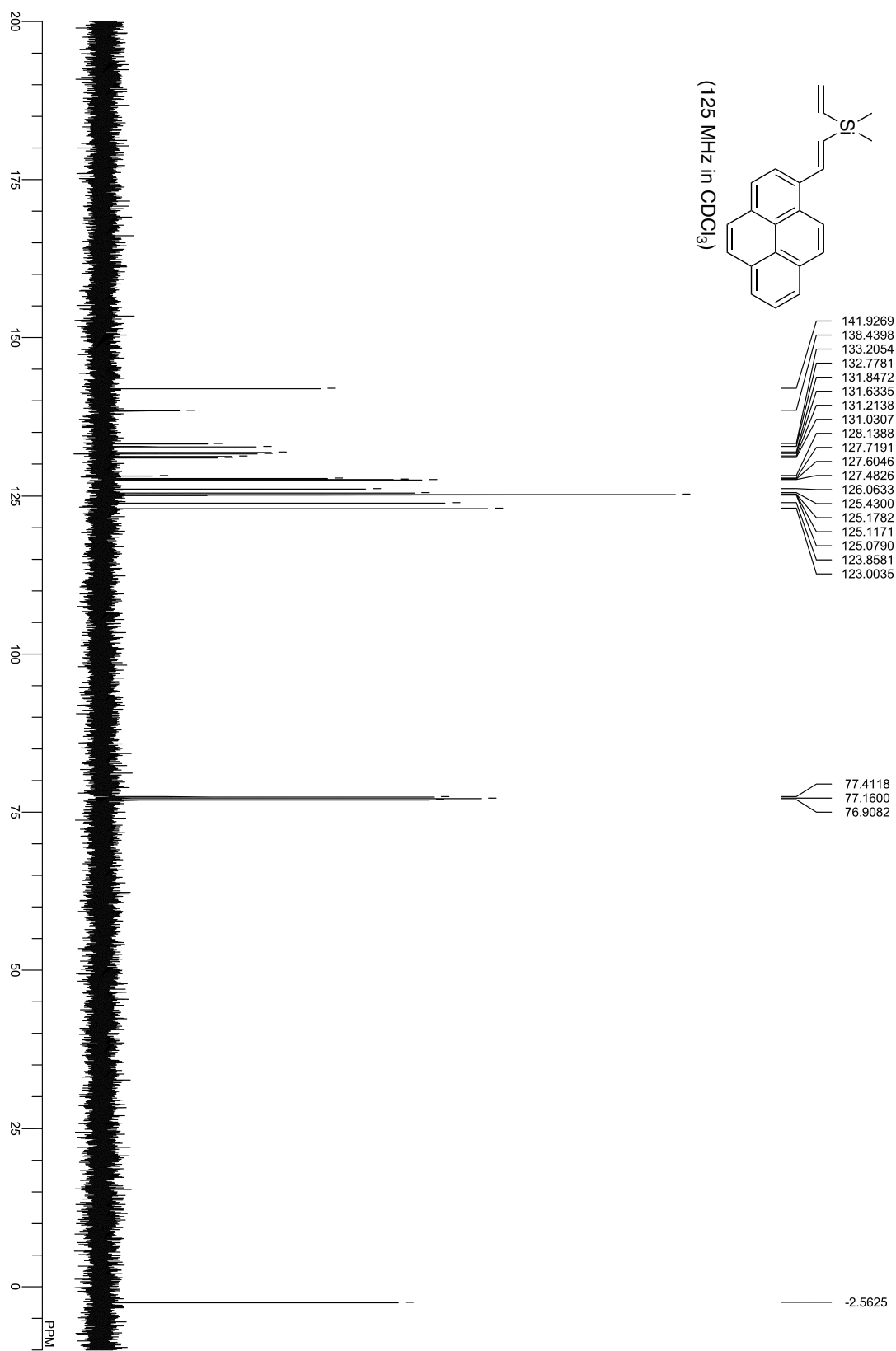
compound **1d**



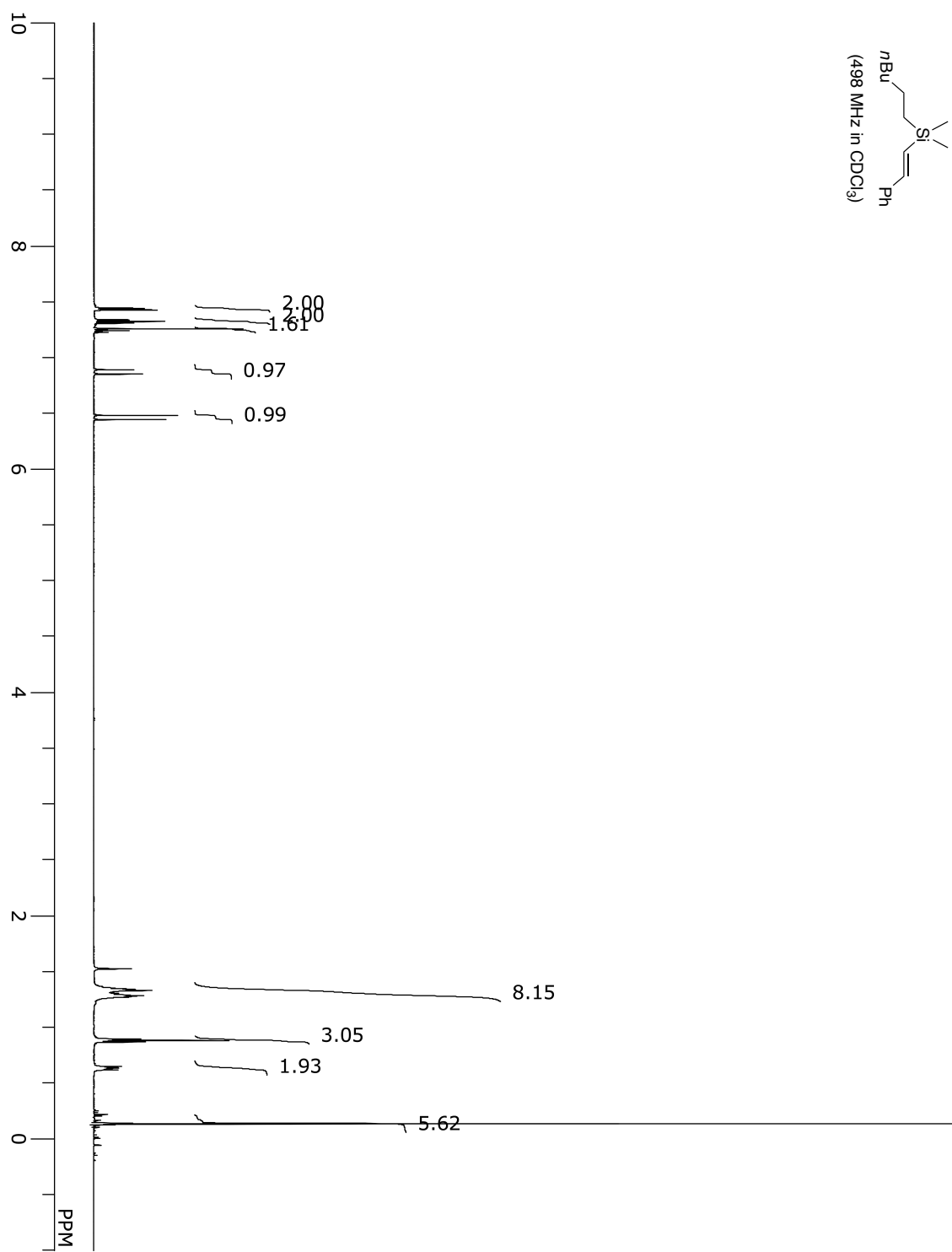
compound **1e**



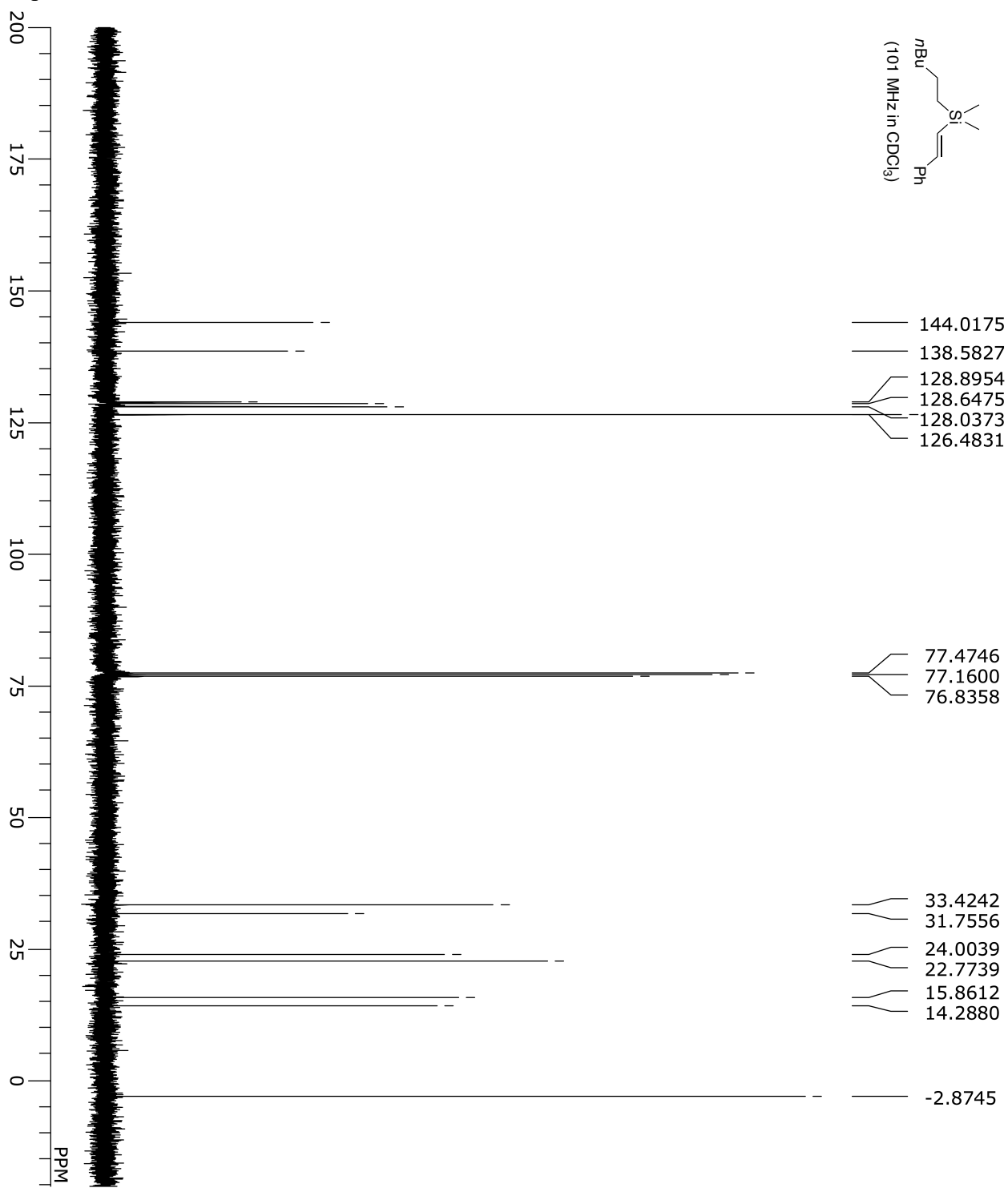
compound 1e



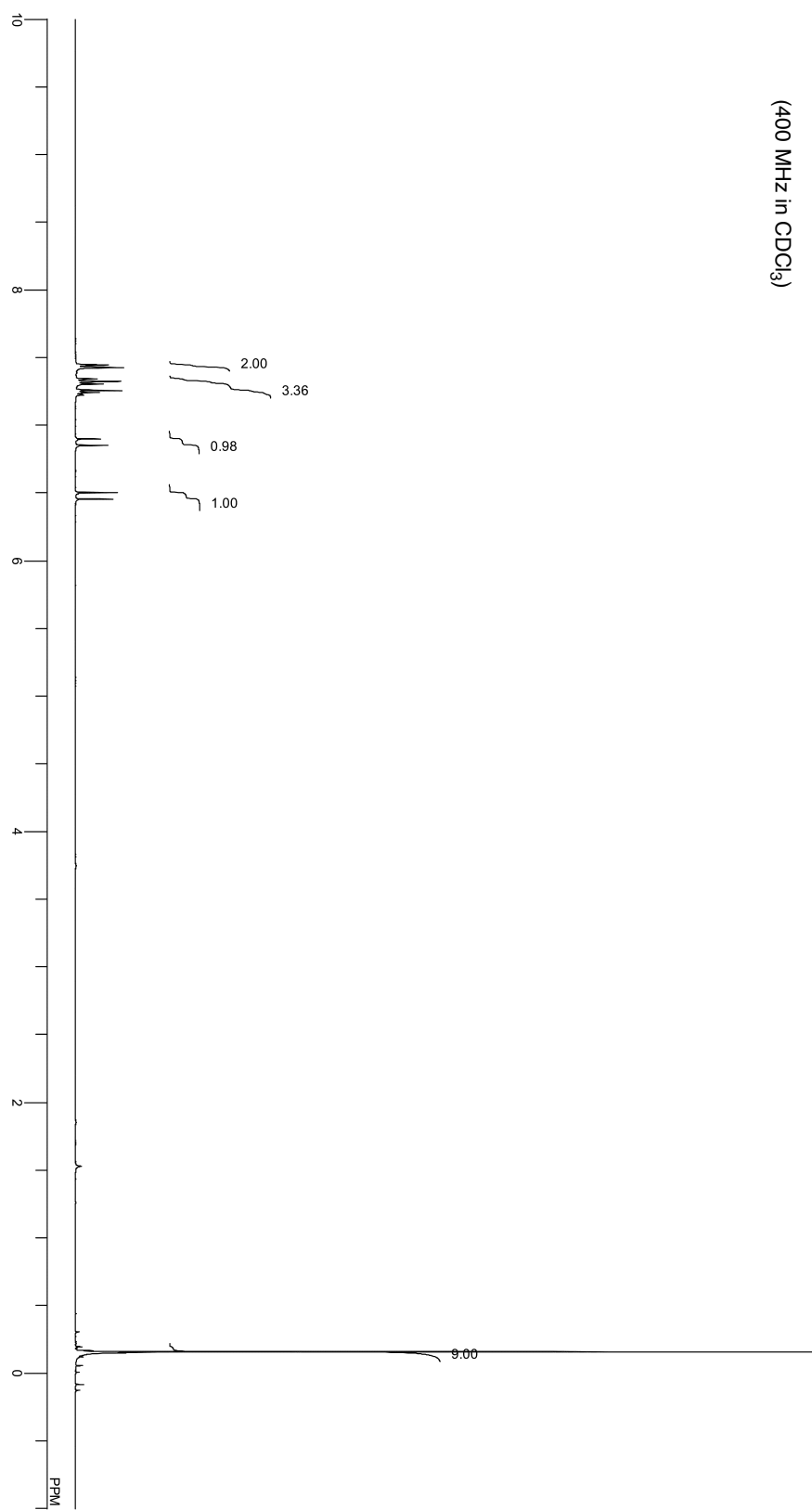
compound 2



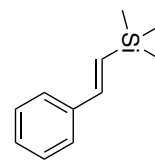
compound 2



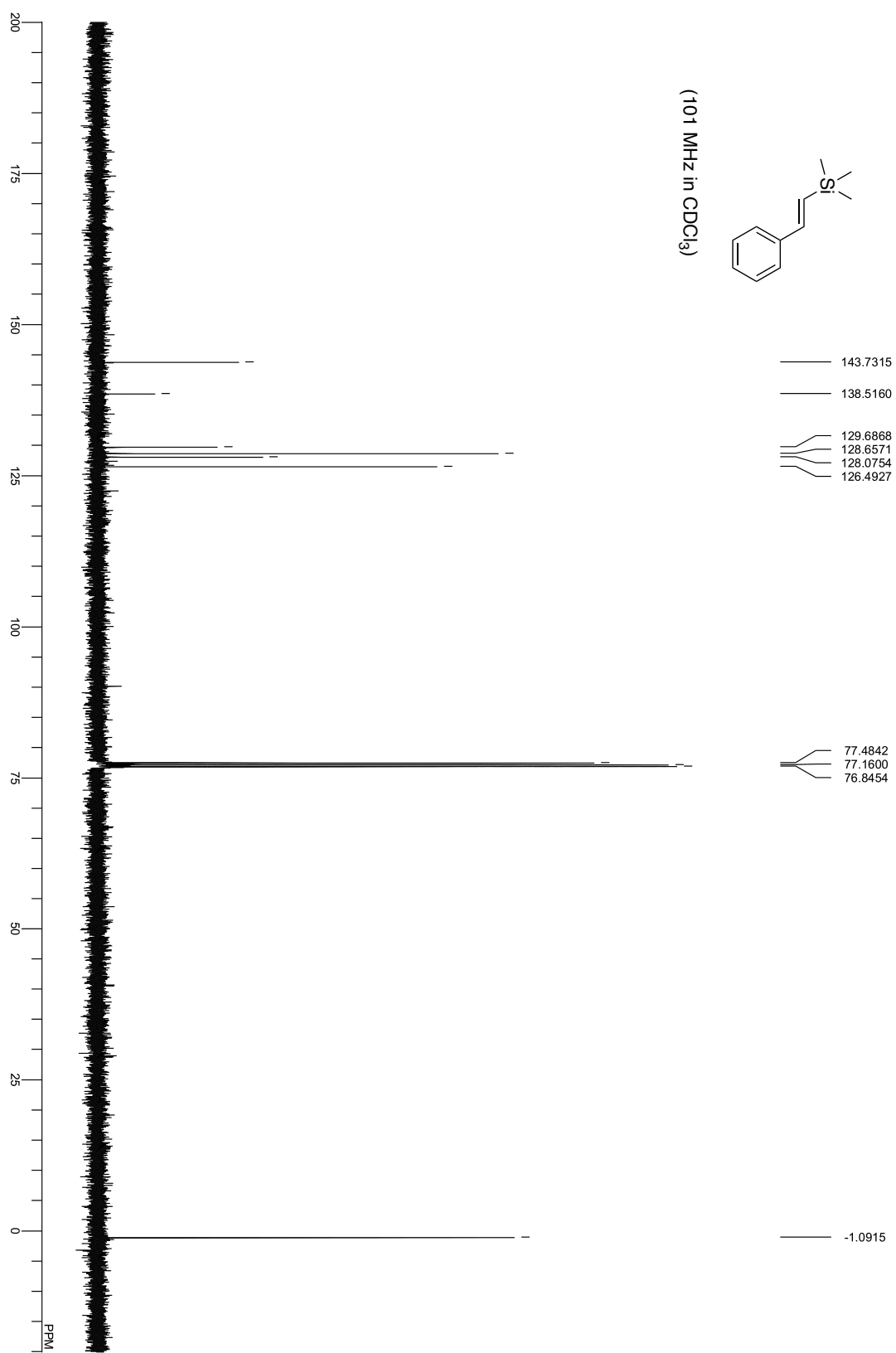
compound 3



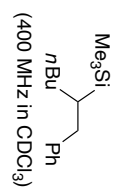
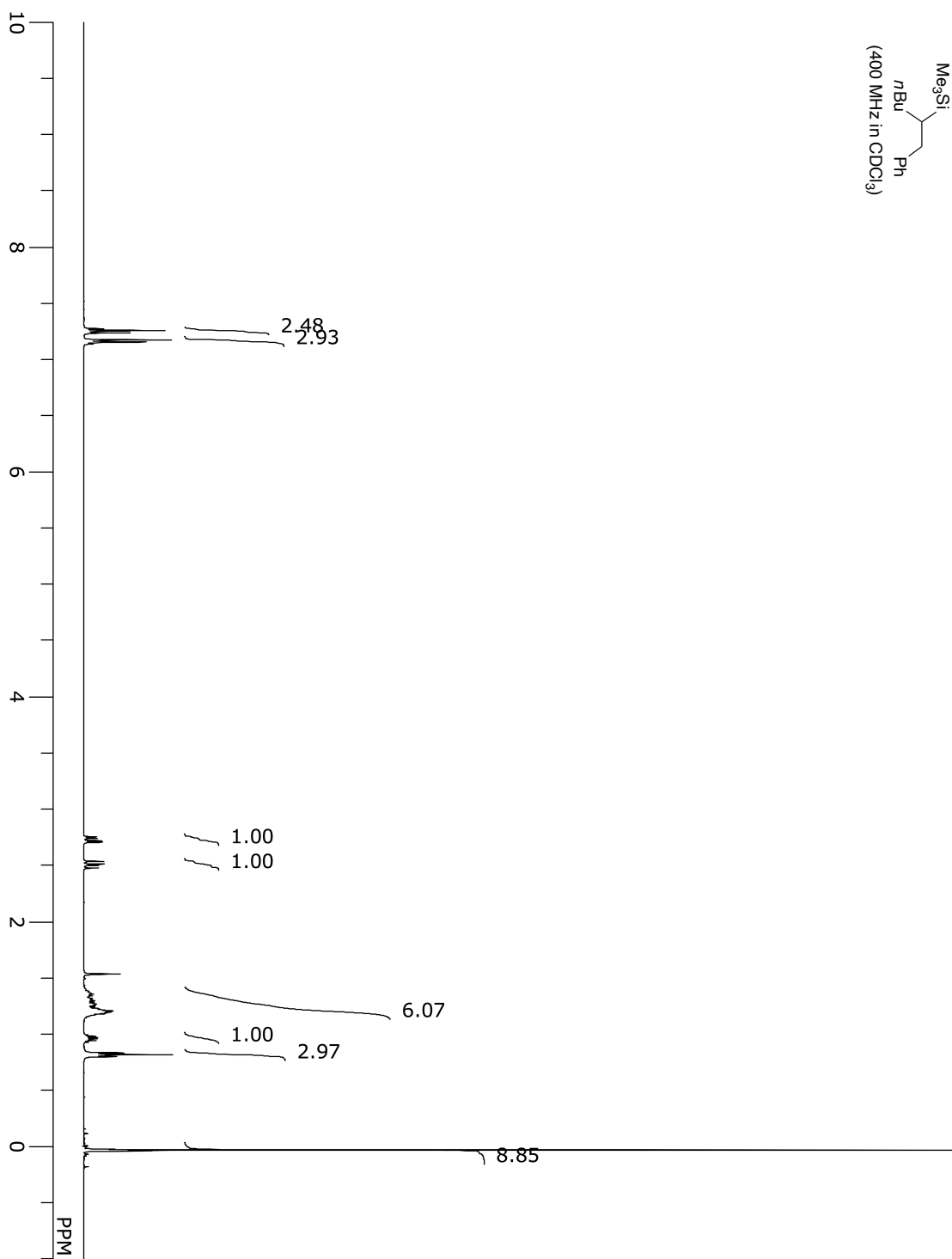
(400 MHz in CDCl₃)



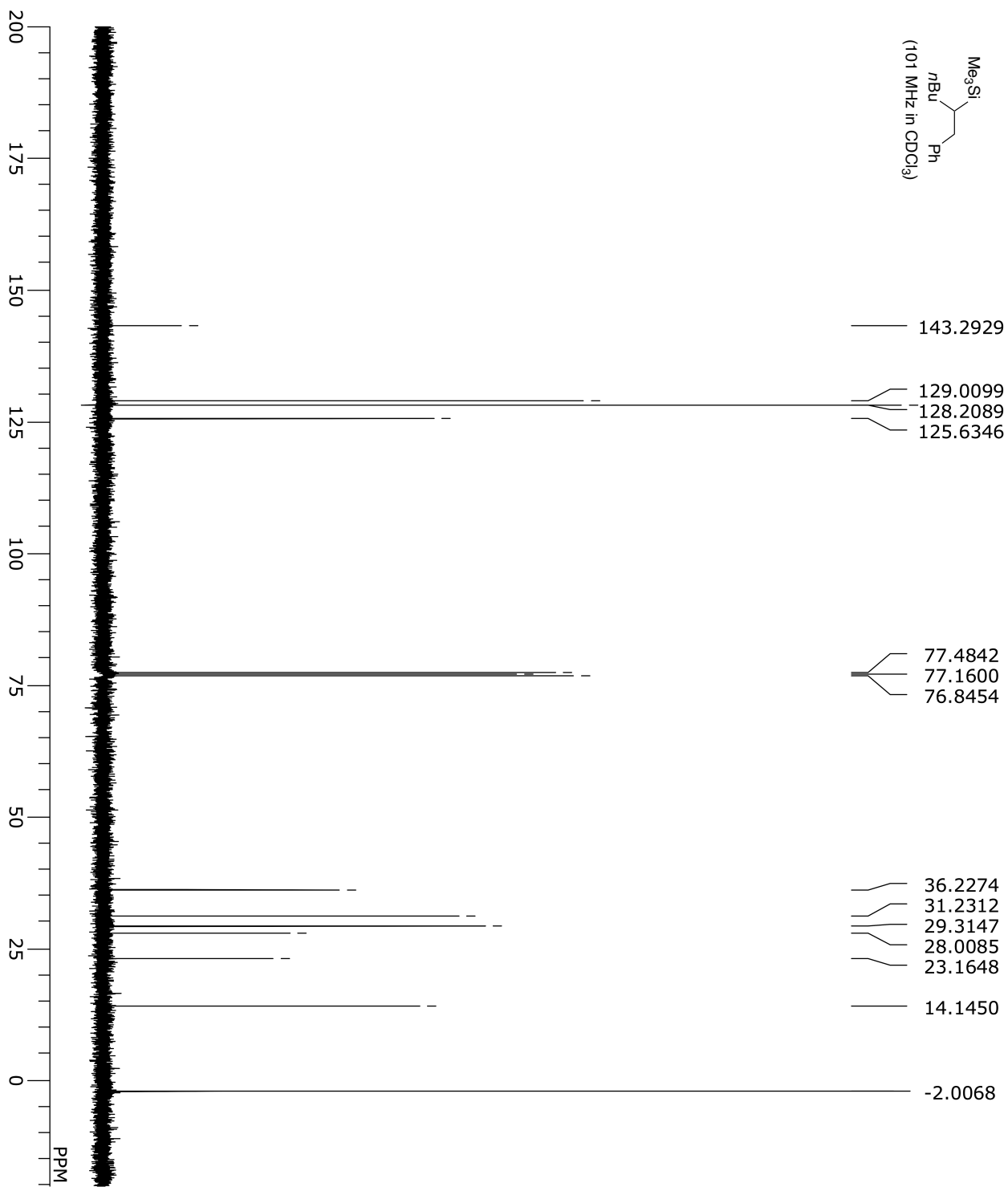
compound 3



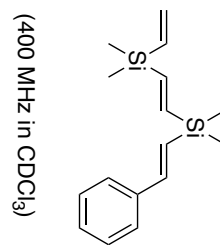
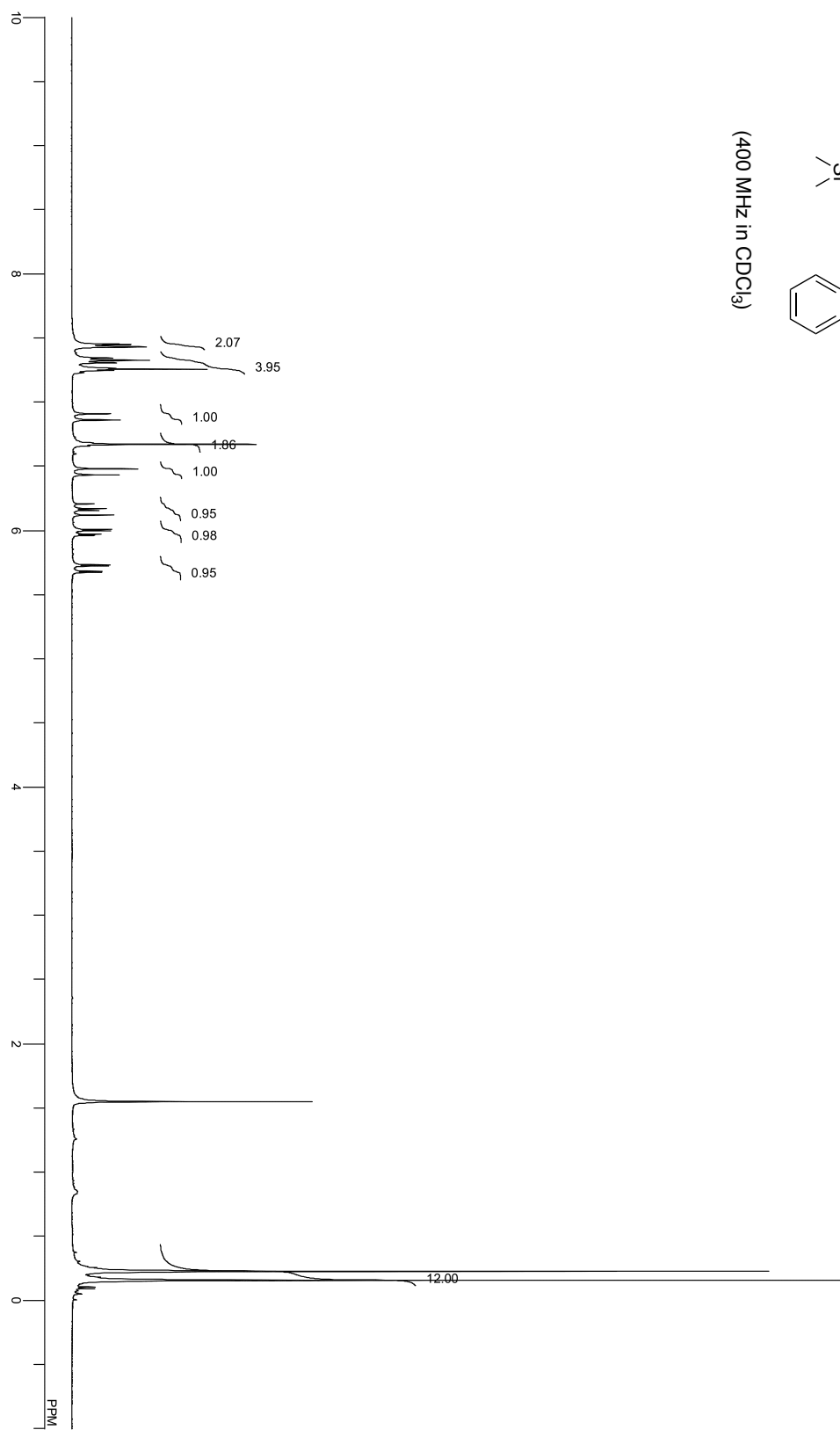
compound 4



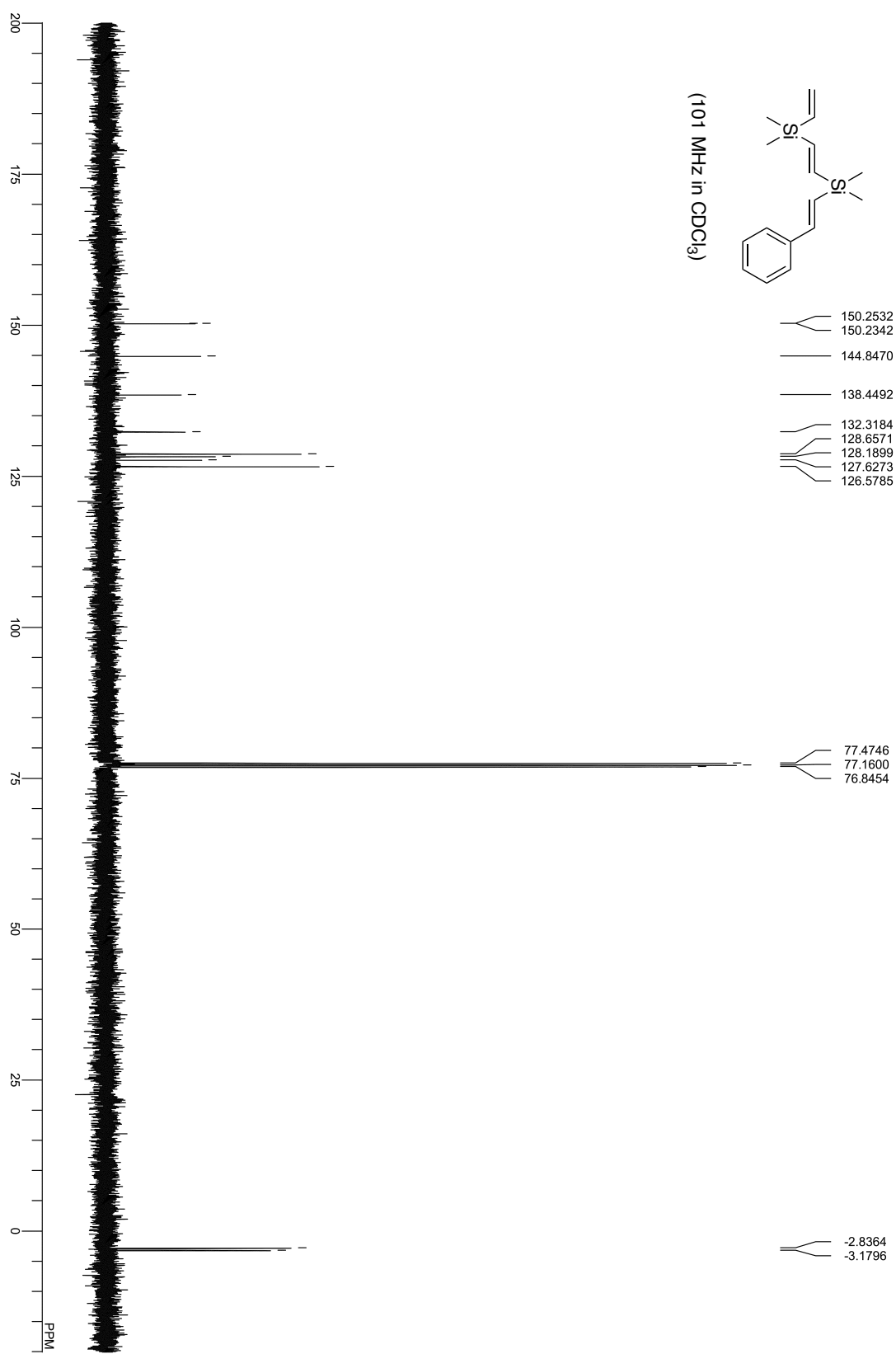
compound 4



compound 6



compound 6



VI. References

1. A. Ikeda, M. Omote, K. Kusumoto, A. Tarui, K. Sato and A. Ando, *Org. Biomol. Chem.*, 2015, **13**, 8886.
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