Supporting Information
for
Rhodium-Catalyzed Stitching Polymerization of Alkynylsilylacetylenes

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I. General

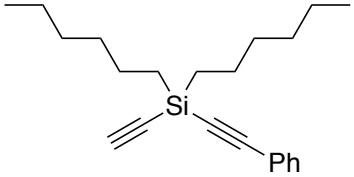
All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen. Preparative GPC was performed with JAI LC-9201 or LaboACE LC-5060 equipped with JAIGEL-2HR columns using $CHCl_3$ as an eluent. NMR spectra were recorded on JEOL JNM-ECS400, Agilent Unity-Inova500, or BRUKER AVANCE Ⅲ 700 spectrometer. Size-exclusion chromatography analyses were performed with JASCO-GPC900 equipped with PLgel MIXED-C columns using THF as an eluent and the molecular weights were calibrated against standard polystyrene samples. Absolute molecular weight analyses were performed on Wyatt Technology DAWN HELEOS II multi-angle light scattering instrument. High resolution mass spectra were recorded on JEOL JMS700 spectrometer. Thermogravimetric analyses were performed with SII Exstar TG/DTA6200 under nitrogen atmosphere. UV-vis spectra were recorded on HITACHI U-2900 and JASCO V-770 spectrophotometers. Elemental analysis was performed on YANACO CHN CORDER MT-6. Electrical resistance was measured using two-terminal or four-terminal sensing with Keithley 6430 sourcemeter. Film thickness was measured with OLYMPUS OLS4100 laser microscope. Computations were performed using workstation at Research Center for Computational Science, National Institutes of Natural Sciences, Okazaki, Japan.

THF (Kanto Chemical; dehydrated), CH_2Cl_2 (Kanto Chemical; dehydrated), and MeCN (Wako Chemicals; dehydrated) were degassed by purging nitrogen prior to use. CCl_4 (Wako Chemicals) was dried over $MgSO_4$ and degassed by purging nitrogen prior to use. Diisopropylamine (Wako Chemicals) and triethylamine (Wako Chemicals) were distilled over KOH under vacuum. 1-Bromohexane (Wako Chemicals), iodobenzene (Wako Chemicals), 4-bromobenzyl bromide (TCI), phenylacetylene (Kanto Chemical), 1,5-hexadiyne (TCI), tetradecafluorohexane (Aldrich), dimethylcarbamoyl chloride (Nacalai Tesque), dichlorodiethylsilane (TCI), trichlorosilane (TCI), tetrachlorosilane (TCI), di-*sec*-butylamine (TCI), trichloroisocyanuric acid (TCI), tetrabutylammonium fluoride (Wako Chemicals; trihydrate), *n*BuLi (Kanto Chemical; 1.55–1.59 M solution in hexane), ethynylmagnesium bromide (Aldrich; 0.5 M solution in THF), ethylmagnesium bromide (Kanto Chemical; 0.97 M solution in THF), Mg turnings (Wako Chemicals), iodine (Wako Chemicals), K_2CO_3 (Wako Chemicals), KI (Wako Chemicals), D_2O (ISOTEC), $PdCl_2$ (Tanaka Kikinzoku), and CuI (Kanto Chemical) were used as received. 4-(2-Methoxyethoxy)phenylacetylene,[1–4] (1,2,2-triphenylvinyl)lithium,[5] $[Rh(OH)(cod)]_2$,[6] $Rh(cod)[(\eta^6\text{-}C_6H_5)BPh_3]$,[7] $[RhCl(cod)]_2$,[8] $[RhCl(tfb)]_2$,[9] and $Pd(PPh_3)_4$,[10] were synthesized following the literature procedures.

II. Synthesis of Monomers

Representative Procedures:

Dihexyl(phenylethynyl)silylacetylene (1a)



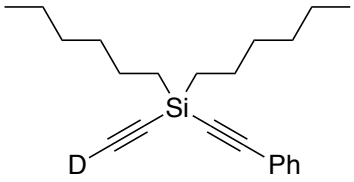
A solution of 1-bromohexane (7.92 g, 48.0 mmol) in THF (20 mL) was added dropwise over 30 min to a suspension of Mg turnings (1.02 g, 42.0 mmol) in THF (20 mL), and the mixture was stirred for 1 h at room temperature. The resulting solution was added slowly over 15 min to trichlorosilane (2.01 mL, 20 mmol) at –78 ºC, and the mixture was stirred for 21 h at –78 ºC. A solution of phenylethynyllithium [generated from phenylacetylene (2.04 g, 20 mmol) and *n*BuLi (13.2 mL, 21 mmol; 1.59 M solution in hexane) in THF (30 mL) at –78 °C] was then added to it, and the mixture was stirred for 12 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane and dried under vacuumed at 40 ºC to afford dihexyl(phenylethynyl)silane as a colorless oil (5.36 g, 17.8 mmol; 89% yield).

^{1}H NMR ($CDCl_3$): δ 7.52-7.43 (m, 2H), 7.37-7.27 (m, 3H), 4.11 (quint, $^3J_{HH}$ = 3.3 Hz, 1H), 1.57-1.23 (m, 16H), 0.89 (t, $^3J_{HH}$ = 6.9 Hz, 6H), 0.83-0.72 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 132.2, 128.8, 128.4, 123.2, 107.3, 90.0, 32.8, 31.7, 24.5, 22.7, 14.3, 12.3.

Dihexyl(phenylethynyl)silane (1.50 g, 4.99 mmol) was added to a suspension of $PdCl_2$ (8.8 mg, 50 μmol) in CCl_4 (10 mL) at room temperature, and the mixture was stirred for 4 h at 40 ºC. The precipitates were filtered off through Celite with THF (3 mL) and the volatiles were removed under vacuum. The residue was dissolved in THF (3 mL) and the volatiles were removed under vacuum. This was repeated again to afford chlorodihexyl(phenylethynyl)silane as a pale yellow oil. Ethynylmagnesium bromide (10.0 mL, 5.00 mmol; 0.5 M solution in THF) was added to it and the mixture was stirred for 2 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford compound **1a** as a yellow oil (974 mg, 3.00 mmol; 60% yield).

^{1}H NMR ($CDCl_3$): δ 7.54-7.43 (m, 2H), 7.38-7.27 (m, 3H), 2.48 (s, 1H), 1.61-1.21 (m, 16H), 0.89 (t, $^3J_{HH}$ = 6.6 Hz, 6H), 0.85-0.75 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 132.3, 129.0, 128.4, 122.9, 107.0, 94.8, 89.0, 85.9, 32.8, 31.6, 23.7, 22.7, 14.7, 14.3. HRMS (EI) calcd for $C_{22}H_{32}Si$ (M^+) 324.2268, found 324.2268.

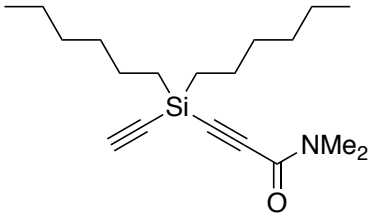
Dihexyl(phenylethynyl)silylacetylene (1a-*d*)



A solution of lithium diisopropylamide [generated from diisopropylamine (310 μL, 2.21 mmol) and *n*BuLi (1.40 mL, 2.23 mmol; 1.59 M solution in hexane) in THF (2.5 mL) at –78 °C] was added to a solution of compound **1a** (651 mg, 2.01 mmol) in THF (2.5 mL) at –78 °C, and the resulting solution was stirred for 30 min at –78 °C. D_2O (2 mL) was added to this solution, and the resulting mixture was warmed to room temperature and stirred for 30 min. This was extracted with Et_2O, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford compound **1a-*d*** as a colorless oil (343 mg, 1.05 mmol; 53% yield, 98% D).

^{1}H NMR ($CDCl_3$): δ 7.51-7.46 (m, 2H), 7.38-7.27 (m, 3H), 2.48 (s, 0.02H), 1.58-1.45 (m, 4H), 1,45-1.36 (m, 4H), 1.36-1.25 (m, 8H), 0.89 (t, $^3J_{HH}$ = 7.1 Hz, 6H), 0.85-0.77 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 132.3, 129.0, 128.3, 122.8, 107.0, 94.6 (t, $^1J_{CD}$ = 35.0 Hz), 88.9, 85.3 (t, $^2J_{CD}$ = 5.8 Hz), 32.8, 31.6, 23.7, 22.7, 14.7, 14.3. HRMS (EI) calcd for $C_{22}H_{31}DSi$ (M^+) 325.2331, found 325.2331.

3-(Dihexylethynylsilyl)-*N*,*N*-dimethylpropiolamide (1d)



A solution of 1-bromohexane (7.92 g, 48.0 mmol) in THF (10 mL) was added dropwise over 30 min to a suspension of Mg turnings (1.02 g, 42.0 mmol) in THF (30 mL), and the mixture was stirred for 3 h at room temperature. The resulting solution was added slowly over 15 min to trichlorosilane (2.01 mL, 20.0 mmol) at –78 ºC, and the mixture was stirred for 1 h at –78 ºC. Ethynylmagnesium bromide (40.0 mL, 20.0 mmol; 0.5 M solution in THF) was then added to it, and the mixture was stirred for 21 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane and dried under vacuum at 40 ºC to afford dihexylethynylsilane as a colorless oil (4.12 g, 18.4 mmol; 92% yield).

^{1}H NMR ($CDCl_3$): δ 3.98 (quint, $^3J_{HH}$ = 3.2 Hz, 1H), 2.40 (s, 1H), 1.48-1.19 (m, 16H), 0.89 (t, $^3J_{HH}$ = 6.6 Hz, 6H), 0.78-0.63 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 95.3, 86.0, 32.7, 31.7, 24.3, 22.7, 14.2, 12.0.

Dihexylethynylsilane (1.79 g, 7.97 mmol) was added over 3 min to a suspension of trichloroisocyanuric acid (639 mg, 2.75 mmol) in CH_2Cl_2 (24 mL) at room temperature, and the mixture was stirred for 2 days. The precipitates were filtered off through Celite with THF (5 mL) and

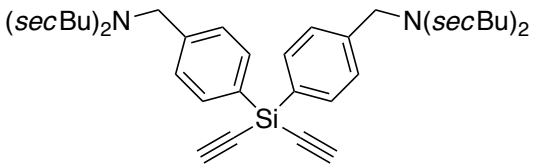
the volatile were removed under vacuum. The residue was dissolved in THF (3 mL) and the volatiles were removed again. This was repeated again to afford chlorodihexylethynylsilane as a colorless oil. Ethylnylmagnesium bromide (15.0 mL, 7.50 mmol; 0.5 M solution in THF) was added to it slowly over 5 min and the mixture was stirred for 15 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford dihexyl(diethynyl)silane as a white solid (1.77 g, 7.12 mmol; 89% yield).

^{1}H NMR ($CDCl_3$): δ 2.46 (s, 2H), 1.53-1.22 (m, 16H), 0.89 (t, $^3J_{HH}$ = 6.9 Hz, 6H), 0.80-0.71 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 95.1, 85.2, 32.8, 31.6, 23.5, 22.7, 14.3, 14.2.

Ethylmagnesium bromide (3.20 mL, 3.10 mmol; 0.97 M solution in THF) was added over 10 min to a solution of dihexyl(diethynyl)silane (745 mg, 3.00 mmol) in THF (6 mL) at room temperature, and this was stirred for 1 h at room temperature. The resulting solution was added to a solution of dimethylcarbamoyl chloride (339 mg, 3.15 mmol) in THF (10 mL) at –78 ºC with the aid of THF (2 mL), and the mixture was warmed to room temperature and stirred for 5 h. The reaction was quenched with saturated NH_4Claq and this was extracted with EtOAc. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 3/1 and further purified by GPC with $CHCl_3$ to afford compound **1d** as a yellow oil. (178 mg, 0.56 mmol; 19% yield).

^{1}H NMR ($CDCl_3$): δ 3.23 (s, 3H), 2.97 (s, 3H), 2.47 (s, 1H), 1.51-1.22 (m, 16H), 0.89 (t, $^3J_{HH}$ = 6.8 Hz, 6H), 0.84-0.74 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.7, 97.5, 95.8, 92.0, 84.3, 38.4, 34.2, 32.7, 31.5, 23.5, 22.6, 14.2, 14.0. HRMS (FAB) calcd for $C_{19}H_{34}NOSi$ ($M+H^+$) 320.2404, found 320.2409.

Bis(4-(di-*sec*-butylaminomethyl)phenyl)diethynylsilane (1g)



A mixture of 4-bromobenzyl bromide (13.1 g, 52.4 mmol), K_2CO_3 (14.5 g, 105 mmol), KI (434 mg, 2.61 mmol), and di-*sec*-butylamine (9.10 mL, 52.8 mmol) in MeCN (48 mL) was stirred for 23 h at room temperature. The mixture was filtered through a pad of Celite and the solvent was removed under vacuum. The residue was chromatographed on silica gel with hexane to afford 1-bromo-4-(di-*sec*-butylaminomethyl)benzene as a colorless oil (13.1 g, 43.9 mmol; 84% yield).

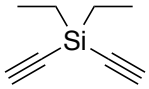
^{1}H NMR ($CDCl_3$): δ 7.39 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.23 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 3.66 (d, $^2J_{HH}$ = 14.7 Hz, 0.5H), 3.60 (s, 1H), 3.48 (d, $^2J_{HH}$ = 14.7 Hz, 0.5H), 2.65-2.52 (m, 2H), 1.64-1.40 (m, 2H), 1.34-1.12 (m, 2H), 1.00 (d, $^3J_{HH}$ = 6.4 Hz, 3H), 0.99 (d, $^3J_{HH}$ = 6.4 Hz, 3H), 0.85 (t, $^3J_{HH}$ = 7.6 Hz, 3H), 0.84 (t, $^3J_{HH}$ = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.1, 141.8, 131.1, 130.3, 130.1, 120.0, 54.3, 53.8,

49.0, 48.7, 29.2, 27.8, 18.1, 16.9, 12.2, 12.1.

A solution of 1-bromo-4-(di-*sec*-butylaminomethyl)benzene (3.58 g, 12.0 mmol) in THF (12 mL) was added dropwise over 1 h to a suspension of Mg turnings (292 mg, 12.0 mmol) in THF (12 mL) at 60 ºC, and the mixture was stirred for 3.5 h at 60 ºC. The resulting solution was added slowly over 10 min to tetrachlorosilane (460 μL, 4.01 mmol) at –78 ºC, and the mixture was stirred for 2.5 h at –78 ºC. This was warmed to room temperature and ethynylmagnesium bromide (24.0 mL, 12.0 mmol; 0.5 M solution in THF) was added to it, and the mixture was stirred for 4 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by GPC with $CHCl_3$ to afford compound **1g** as a yellow oil (1.21 g, 2.35 mmol; 59% yield).

^{1}H NMR ($CDCl_3$): δ 7.681 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.675 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.41 (d, $^3J_{HH}$ = 7.8 Hz, 4H), 3.75 (d, $^2J_{HH}$ = 15.1 Hz, 1H), 3.68 (s, 2H), 3.57 (d, $^2J_{HH}$ = 15.1 Hz, 1H), 2.72 (s, 2H), 2.69-2.57 (m, 4H), 1.63-1.43 (m, 4H), 1.33-1.33 (m, 4H), 1.01 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 0.99 (d, $^3J_{HH}$ = 6.4 Hz, 6H), 0.86 (t, $^3J_{HH}$ = 7.3 Hz, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.0, 145.7, 134.68, 134.66, 129.0, 128.9, 128.4, 128.2, 97.0, 84.2, 54.2, 53.8, 49.5, 49.2, 29.2, 27.8, 18.2, 16.9, 12.2, 12.1. HRMS (FAB) calcd for $C_{34}H_{50}N_2Si$ (M^+) 514.3738, found 514.3727.

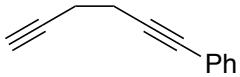
Diethyldiethynylsilane (1i) (CAS 18292-19-8)



Ethynylmagnesium bromide (42.0 mL, 21.0 mmol; 0.5 M solution in THF) was added to dichlorodiethylsilane (1.57 g, 9.99 mmol) in THF (10 mL) and the mixture was stirred for 4 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and the solvent was distilled off. The residue was chromatographed on silica gel with pentane to afford compound **1i** as a colorless oil (2.29 g, 8.23 mmol; 82% yield, 49 wt% in THF).

^{1}H NMR ($CDCl_3$): δ 2.46 (s, 2H), 1.08 (t, $^3J_{HH}$ = 8.0 Hz, 6H), 0.76 (q, $^3J_{HH}$ = 8.1 Hz, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 95.2, 84.5, 7.0, 6.0.

1-Phenyl-1,5-hexadiyne (3) (CAS 37124-88-2)

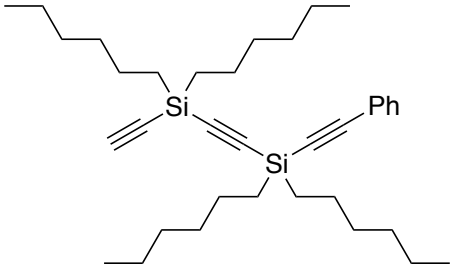


Triethylamine (2.78 mL, 20.0 mmol), 1,5-hexadiyne (1.25 g, 16.0 mmol), and THF (8.0 mL) were successively added to a mixture of $Pd(PPh_3)_4$ (231 mg, 0.200 mmol), CuI (76.2 mg, 0.400 mmol), and iodobenzene (1.63 g, 8.00 mmol) in THF (4.0 mL) at room temperature, and the resulting mixture was stirred for 46 h at room temperature. The precipitates were filtered off through a pad of silica gel with Et_2O and the solvents were removed 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 pale yellow (450 mg, 2.68 mmol; 33% yield).

^{1}H NMR (CDCl3): δ 7.44-7.37 (m, 2H), 7.32-7.26 (m, 3H), 2.69-2.60 (m, 2H), 2.54-2.46 (m, 2H), 2.05 (t, $^4J_{HH}$ = 2.8 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 131.7, 128.3, 128.0, 123.7, 88.1, 82.8, 81.7, 69.5, 19.7, 19.0.

Dihexyl(dihexyl(phenylethynyl)silylethynyl)silylacetylene (**4a**)



A solution of lithium diisopropylamide [generated from diisopropylamine (1.11 mL, 7.87 mmol) and *n*BuLi (5.00 mL, 7.75 mmol; 1.55 M solution in hexane) in THF (8 mL) at –78 °C] was added to a solution of dihexylethynylsilane (1.79 g, 7.97 mmol) in THF (2 mL) at –78 °C, and the resulting mixture was stirred for 1.5 h at –78 °C to afford a solution of dihexylsilylethynyllithium. Separately, dihexyl(phenyethynyl)silane (2.36 g, 7.85 mmol) was added to a suspension of $PdCl_2$ (13.3 mg, 75.0 μmol) in CCl_4 (15 mL) at room temperature, and the mixture was stirred for 2 h at room temperature. The precipitates were filtered off through Celite with CCl_4 (5 mL) and the volatiles were removed under vacuum. The residue was dissolved in THF (2 mL) and the volatiles were removed under vacuum. This was repeated again and the residue was dissolved THF (10 mL) and cooled to –78 °C. The solution of dihexylsilylethynyllithium generated above was added to it at –78 °C, and the resulting mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford dihexyl(dihexyl(phenylethynyl)silylethynyl)silane as a yellow oil (2.81 g, 5.37 mmol; 68% yield).

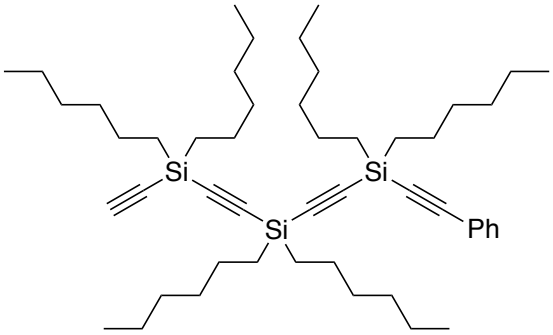
^{1}H NMR ($CDCl_3$): δ 7.55-7.43 (m, 2H), 7.37-7.27 (m, 3H), 3.98 (quint, $^3J_{HH}$ = 3.4 Hz, 1H), 1.58-1.22 (m, 32H), 0.95-0.84 (m, 12H), 0.83-0.76 (m, 4H), 0.75-0.67 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 132.3, 128.9, 128.3, 123.1, 111.8, 111.7, 106.7, 89.5, 32.8, 32.7, 31.7, 24.5, 23.8, 22.74, 22.73, 14.9, 14.3, 12.1.

Dihexyl(dihexyl(phenylethynyl)silylethynyl)silane (2.64 g, 5.05 mmol) was added to a suspension of $PdCl_2$ (8.8 mg, 50 μmol) in CCl_4 (10 mL) at room temperature, and the mixture was stirred for 10 h at 60 ºC. Additional $PdCl_2$ (8.8 mg, 50 μmol) was added to it and the mixture was further stirred for 12 h at 60 ºC. The precipitates were filtered off through Celite with CCl_4 (3 mL) and the volatiles were removed under vacuum. The residue was dissolved in THF (2 mL) and the volatiles were removed under vacuum. This was repeated again to afford chlorodihexyl(dihexyl(phenylethynyl)silylethynyl)-

silane as a yellow oil. Ethynylmagnesium bromide (10.5 mL, 5.25 mmol; 0.5 M solution in THF) was added to it at room temperature and the mixture was stirred for 5 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, 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 **4a** as a yellow oil (1.56 g, 2.85 mmol; 56% yield).

^{1}H NMR ($CDCl_3$): δ 7.54-7.45 (m, 2H), 7.37-7.27 (m, 3H), 2.44 (s, 1H), 1.61-1.22 (m, 32H), 0.98-0.85 (m, 12H), 0.85-0.71 (m, 8H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 132.3, 128.9, 128.3, 123.1, 111.6, 110.3, 106.8, 94.8, 89.3, 85.5, 32.8, 31.69, 31.65, 23.8, 23.6, 22.74, 22.72, 14.8, 14.5, 14.3, 14.2. HRMS (EI) calcd for $C_{36}H_{58}Si_2$ (M^+) 546.4072, found 546.4067.

Dihexyl(dihexyl(dihexyl(phenylethynyl)silylethynyl)silylethynyl)silylacetylene (5a)



A solution of lithium diisopropylamide [generated from diisopropylamine (740 μL, 5.24 mmol) and *n*BuLi (3.30 mL, 5.25 mmol; 1.59 M solution in hexane) in THF (5 mL) at –78 °C] was added to a solution of dihexylethynylsilane (1.19 g, 5.30 mmol) in THF (5 mL) at –78 °C, and the resulting solution was stirred for 20 min at –78 °C to afford a solution of dihexylsilylethynyllithium. Separately, dihexylethynylsilane (1.19 g, 5.30 mmol) was added to a suspension of trichloroisocyanuric acid (425 mg, 1.83 mmol) in CH_2Cl_2 (20 mL) at room temperature, and the mixture was stirred for 2 h at room temperature. The precipitates were filtered off through Celite with THF (5 mL) and the volatiles were removed under vacuum. The residue was dissolved in THF (2 mL) and the volatiles were removed under vacuum. This was repeated again and the residue was dissolved in THF (5 mL) and cooled to –78 °C. The solution of dihexylsilylethynyllithium generated above was added to it at –78 °C, and the resulting mixture was warmed to room temperature and stirred for 13 h. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford dihexyl(dihexyl(ethynyl)silylethynyl)silane as a colorless oil (1.64 g, 3.67 mmol; 69% yield).

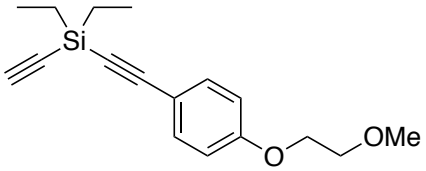
^{1}H NMR ($CDCl_3$): δ 3.97 (quint, $^3J_{HH}$ = 3.4 Hz, 1H), 2.43 (s, 1H), 1.55-1.20 (m, 32H), 0.89 (t, $^3J_{HH}$ = 6.6 Hz, 12H), 0.79-0.62 (m, 8H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 112.2, 110.8, 94.7, 85.5, 32.8, 32.7, 31.70, 31.65, 24.4, 23.6, 22.7, 14.5, 14.2, 12.0.

A solution of lithium diisopropylamide [generated from diisopropylamine (220 μL, 1.56 mmol) and *n*BuLi (980 μL, 1.56 mmol; 1.59 M solution in hexane) in THF (1.5 mL) at –78 °C] was added to a solution of dihexyl(phenylethynyl)silylacetylene (488 mg, 1.50 mmol) in THF (1.5 mL) at –78 °C, and the resulting solution was stirred for 20 min at –78 °C to afford a solution of dihexyl(phenylethynyl)silylethynyllithium. Separately, dihexyl(dihexyl(ethynyl)silylethynyl)silane (670 mg, 1.50 mmol) was added to a suspension of trichloroisocyanuric acid (137 mg, 0.589 mmol) in CH_2Cl_2 (6 mL) at room temperature, and the mixture was stirred for 13 h at room temperature. The precipitates were filtered off through Celite with THF (3 mL) and the volatiles were removed under vacuum. The residue was dissolved in THF (1 mL) and the volatiles were removed under vacuum. This was repeated again and the residue was dissolved in THF (3 mL) and cooled to –78 °C. The solution of dihexyl(phenylethynyl)silylethynyllithium generated above was added to it at –78 °C, and the resulting mixture was stirred for 15 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, 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 to compound **5a** as a yellow oil (657 mg, 0.854 mmol; 57% yield).

^{1}H NMR ($CDCl_3$): δ 7.51-7.45 (m, 2H), 7.36-7.26 (m, 3H), 2.42 (s, 1H), 1.57-1.21 (m, 48H), 0.95-0.83 (m, 18H), 0.83-0.70 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 132.3, 128.9, 128.3, 123.1, 111.30, 111.28, 110.6, 110.3, 106.7, 94.8, 89.4, 85.5, 32.83, 32.79, 31.7, 31.6, 23.8, 23.7, 23.6, 22.8, 22.7, 14.8, 14.6, 14.4, 14.3. HRMS (EI) calcd for $C_{50}H_{84}Si_3$ (M^+) 768.5875, found 768.5880.

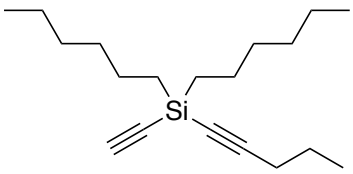
Analytical Data for Other Monomers:

Diethyl(4-(2-methoxy)ethoxyphenylethynyl)silylacetylene (1b)



^{1}H NMR ($CDCl_3$): δ 7.42 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.85 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 4.12 (t, $^3J_{HH}$ = 4.8 Hz, 2H), 3.75 (t, $^3J_{HH}$ = 4.8 Hz, 2H), 3.45 (s, 3H), 2.47 (s, 1H), 1.12 (t, $^3J_{HH}$ = 7.8 Hz, 6H), 0.80 (q, $^3J_{HH}$ = 7.8 Hz, 4H).$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.4, 133.9, 115.1, 114.6, 107.2, 94.7, 86.7, 85.4, 71.0, 67.5, 59.4, 7.3, 6.5. HRMS (FAB) calcd for $C_{17}H_{22}O_2Si$ (M^+) 286.1384, found 286.1384.

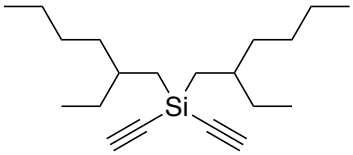
Dihexyl(1-pentynyl)silylacetylene (1c)



^{1}H NMR ($CDCl_3$): δ2.42 (s, 1H), 2.23 (t, $^3J_{HH}$ = 7.1 Hz, 2H), 1.55 (sext, $^3J_{HH}$ = 7.1 Hz, 2H), 1.51-

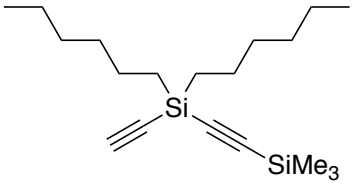
1.22 (m, 16H), 0.99 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.89 (t, $^3J_{HH}$ = 6.9 Hz, 6H), 0.78-0.64 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 109.9, 94.2, 86.4, 79.4, 32.8, 31.6, 23.7, 22.7, 22.1, 22.0, 14.8, 14.2, 13.5. HRMS (EI) calcd for $C_{19}H_{34}Si$ (M^+) 290.2424, found 290.2427.

Di(2-ethylhexyl)diethynylsilane (**1e**)



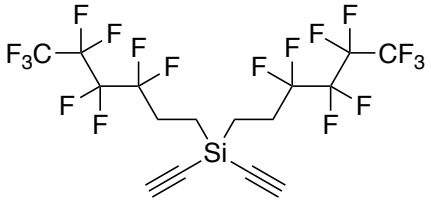
^1H NMR ($CDCl_3$): δ 2.48 (s, 2H), 1.65 (sept, $^3J_{HH}$ = 6.2 Hz, 2H), 1.47-1.20 (m, 16H), 0.90 (t, $^3J_{HH}$ = 6.4 Hz, 6H), 0.86 (t, $^3J_{HH}$ = 7.3 Hz, 6H), 0.77 (d, $^3J_{HH}$ = 6.9 Hz, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 95.2, 86.2, 35.5, 35.4, 28.8, 28.6, 23.1, 19.8, 14.3, 10.8. HRMS (EI) calcd for $C_{20}H_{36}Si$ (M^+) 304.2581, found 304.2582.

Dihexyl(trimethylsilylethynyl)silylacetylene (**1f**)



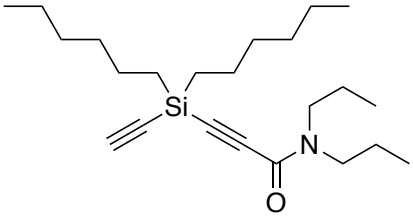
^1H NMR ($CDCl_3$): δ 2.43 (s, 1H), 1.51-1.22 (m, 16H), 0.89 (t, $^3J_{HH}$ = 6.9 Hz, 6H), 0.77-0.68 (m, 4H), 0.18 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 116.7, 108.1, 94.7, 85.8, 32.7, 31.6, 23.6, 22.7, 14.5, 14.2, –0.10. HRMS (EI) calcd for $C_{19}H_{36}Si_2$ (M^+) 320.2350, found 320.2359.

Diethynyldi(3,3,4,4,5,5,6,6,6-nonafluorohexyl)silane (**1h**)



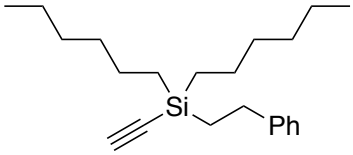
^1H NMR ($CDCl_3$): δ 2.62 (s, 2H), 2.36-2.16 (m, 4H), 1.14-0.99 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 98.1, 81.4, 25.5 (t, $^2J_{CF}$ = 23.5 Hz), 4.3. Carbons having fluorine atoms were not observed under our measurement conditions. Anal. Calcd for $C_{16}H_{10}F_{18}Si$: C, 33.58; H,1.76. Found: C, 33.53, H, 1.61.

3-(Dihexylethynylsilyl)-*N*,*N*-dipropylpropiolamide (1j)



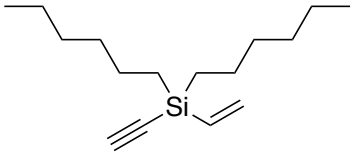
^{1}H NMR ($CDCl_3$): δ 3.50 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 3.37-3.26 (m, 2H), 2.46 (s, 1H), 1.71-1.53 (m, 4H), 1.53-1.21 (m, 16H), 1.00-0.84 (m, 12H), 0.83-0.73 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 153.5, 98.0, 95.6, 90.8, 84.2, 50.9, 46.5, 32.7, 31.5, 23.5, 22.6, 22.2, 20.7, 14.1, 14.0, 11.4, 11.2. HRMS (EI) calcd for $C_{23}H_{41}NOSi$ (M^+) 375.2952, found 375.2954.

Dihexyl(2-phenylethyl)silylacetylene (2a)



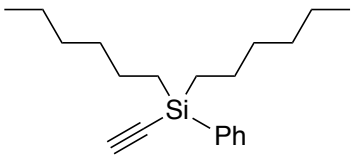
^{1}H NMR ($CDCl_3$): δ 7.28 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 7.21 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 7.17 (t, $^3J_{HH}$ = 7.1 Hz, 1H), 2.76-2.68 (m, 2H), 2.41 (s, 1H), 1.43-1.21 (m, 16H), 1.04-0.96 (m, 2H), 0.89 (t, $^3J_{HH}$ = 7.1 Hz, 6H), 0.68-0.60 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.0, 128.5, 128.0, 125.8, 94.7, 87.9, 33.2, 31.6, 30.1, 23.9, 22.7, 15.4, 14.3, 13.2. HRMS (EI) calcd for $C_{22}H_{36}Si$ (M^+) 328.2581, found 328.2583.

Dihexylvinylsilylacetylene (2b)



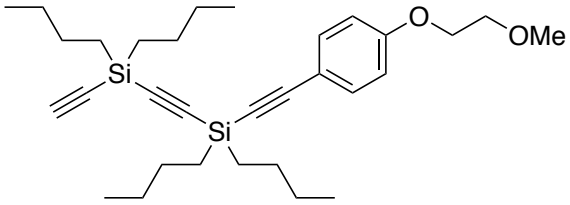
^{1}H NMR ($CDCl_3$): δ 6.13-6.01 (m, 2H), 5.97-5.86 (m, 1H), 2.43 (s, 1H), 1.46-1.20 (m, 16H), 0.88 (t, $^3J_{HH}$ = 6.9 Hz, 6H), 0.75-0.64 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 134.4, 134.2, 95.0, 86.9, 33.1, 31.7, 23.7, 22.7, 14.2, 13.5. HRMS (EI) calcd for $C_{16}H_{30}Si$ (M^+) 250.2111, found 250.2114.

Dihexylphenylsilylacetylene (2c)



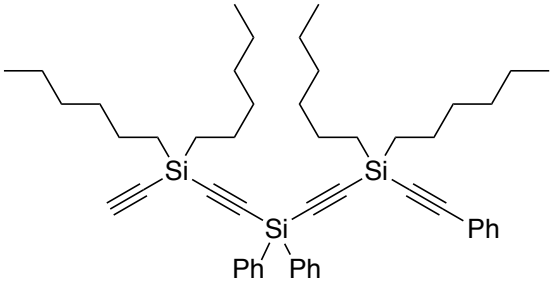
^{1}H NMR ($CDCl_3$): δ 7.65-7.59 (m, 2H), 7.42-7.33 (m, 3H), 2.53 (s, 1H), 1.48-1.19 (m, 16H), 0.93-0.81 (m, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 135.0, 134.4, 129.6, 128.0, 95.7, 87.0, 33.1, 31.6, 23.8, 22.7, 14.2, 14.0. HRMS (EI) calcd for $C_{20}H_{32}Si$ (M^+) 300.2268, found 300.2269.

Dibutyl(dibutyl(4-(2-methoxy)ethoxyphenylethynyl)silylethynyl)silylacetylene (4b)



^{1}H NMR ($CDCl_3$): δ 7.41 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 6.85 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 4.12 (t, $^{3}J_{HH}$ = 4.6 Hz, 2H), 3.75 (t, $^{3}J_{HH}$ = 4.6 Hz, 2H), 3.45 (s, 3H), 2.44 (s, 1H), 1.55-1.35 (m, 16H), 0.97-0.87 (m, 12H), 0.83-0.72 (m, 8H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.3, 133.8, 115.4, 114.6, 111.9, 110.0, 106.9, 94.8, 87.6, 85.5, 71.0, 67.5, 59.4, 26.12, 26.08, 26.0, 25.9, 14.6, 14.2, 13.9, 13.8. HRMS (EI) calcd for $C_{31}H_{48}O_2Si_2$ (M^+) 508.3193, found 508.3194.

Dihexyl(diphenyl(dihexyl(phenylethynyl)silylethynyl)silylethynyl)silylacetylene (5b)



^{1}H NMR ($CDCl_3$): δ 7.76 (d, $^{3}J_{HH}$ = 6.4 Hz, 2H), 7.52-7.46 (m, 2H), 7.45-7.28 (m, 9H), 2.45 (s, 1H), 1.62-1.18 (m, 32H), 0.98-0.75 (m, 20H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 135.0, 132.5, 132.3, 130.4, 129.0, 128.4, 128.1, 123.0, 114.4, 113.3, 108.7, 108.1, 107.1, 95.2, 89.0, 85.1, 32.8, 32.7, 31.7, 31.6, 23.8, 23.6, 22.72, 22.68, 14.7, 14.4, 14.29, 14.26. HRMS (EI) calcd for $C_{50}H_{68}Si_3$ (M^+) 752.4623, found 752.4627.

III. Polymerization and Post-derivatization Reactions

General Procedure for Table 2, Table 3 (Entries 1 and 3), Table 4, Table 5 (Entries 1 and 2), and Equations 1–3.

Triethylamine (10.4 μL, 74.6 μmol) and THF (0.3 mL) were added to a solution of $[RhCl(tfb)]_2$ (2.7 mg, 7.5 μmol Rh) in THF (0.2 mL). This was stirred for 5 min at –10 ºC and monomer **1**, **3**, **4**, or **5** (0.250 mmol) was added with the aid of THF (0.5 mL). The mixture was stirred for 22 h at –10 ºC and warmed to room temperature. This was added dropwise to stirring MeOH (50 mL) with the aid of CH_2Cl_2 (5.0 mL), and the precipitates that formed were collected by filtration and the solid thus obtained was dried under vacuum to afford **poly-1**, **poly-3**, **poly-4**, or **poly-5**.

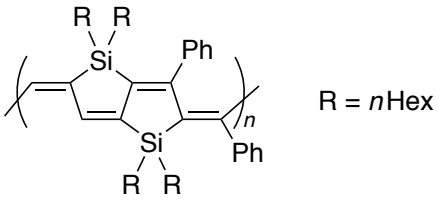
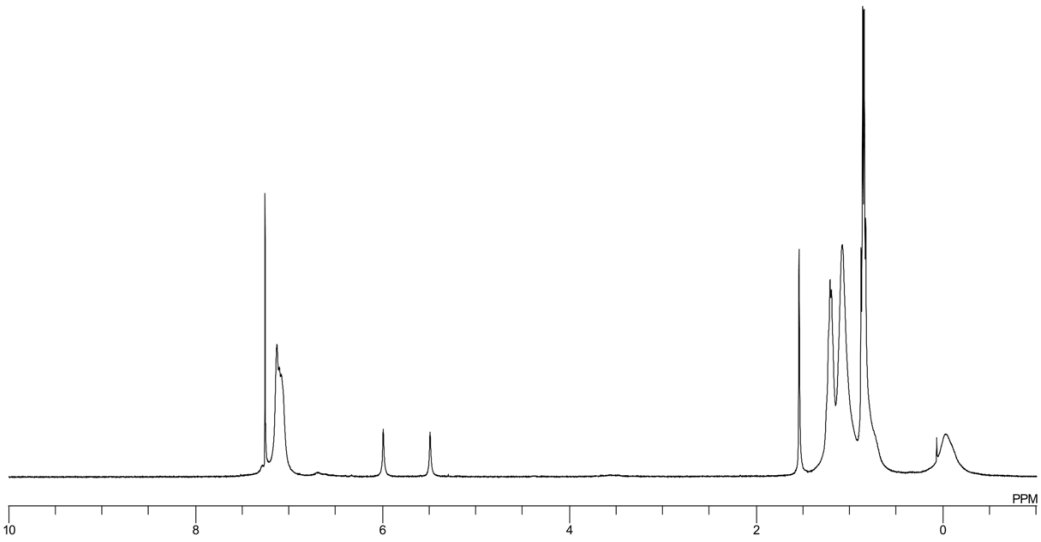
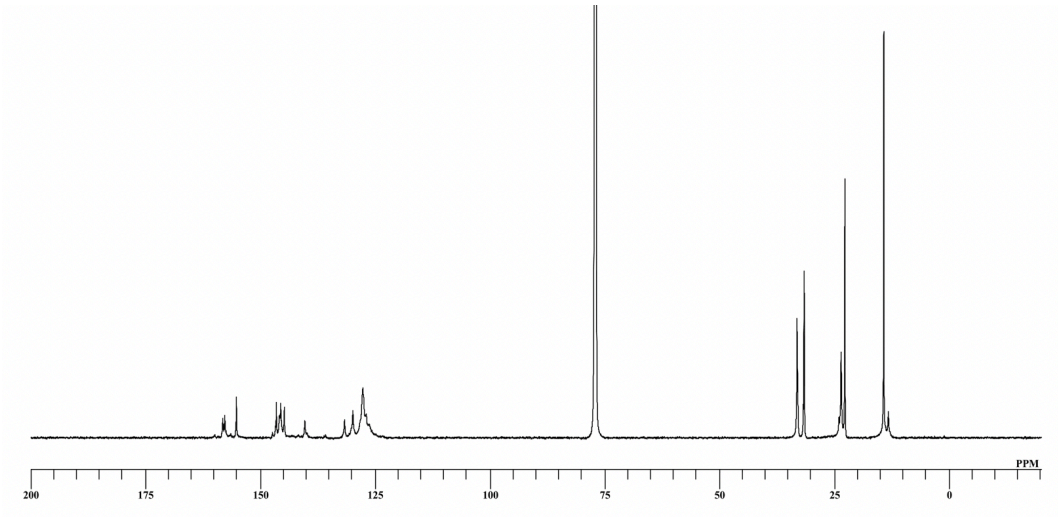


Table 2, Entry 1. Purple solid. 96% yield (77.7 mg). The same polymerization was conducted using 1.00 mmol of monomer **1a** and the reaction progress (by ^{1}H NMR against an internal standard (1,4-dimethoxybenzene)) and the molecular weight of the polymer component (by SEC against a polystyrene standard) were checked to confirm the chain-growth nature of this stitching polymerization: M_n = 25000, PDI = 1.7 at 16% conversion; M_n = 32000, PDI = 1.7 at 31% conversion; M_n = 66000, PDI = 1.8 at 59% conversion.

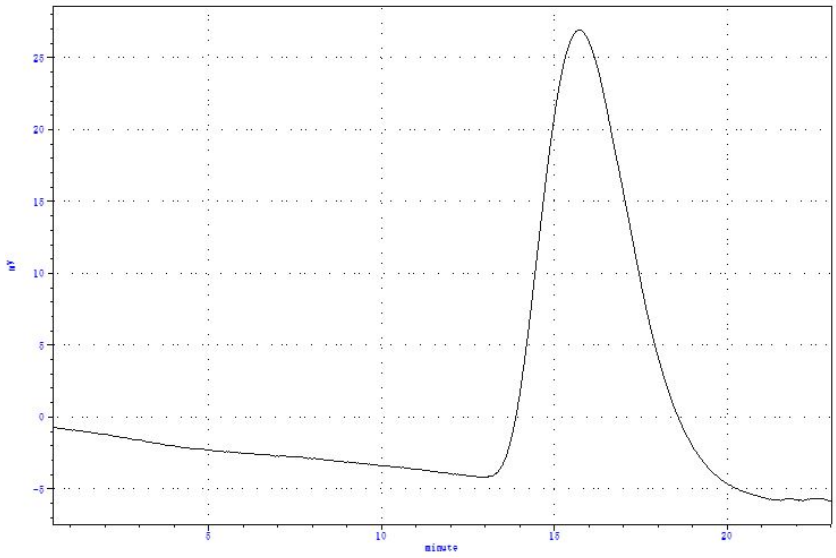
^{1}H NMR (400 MHz in $CDCl_3$)



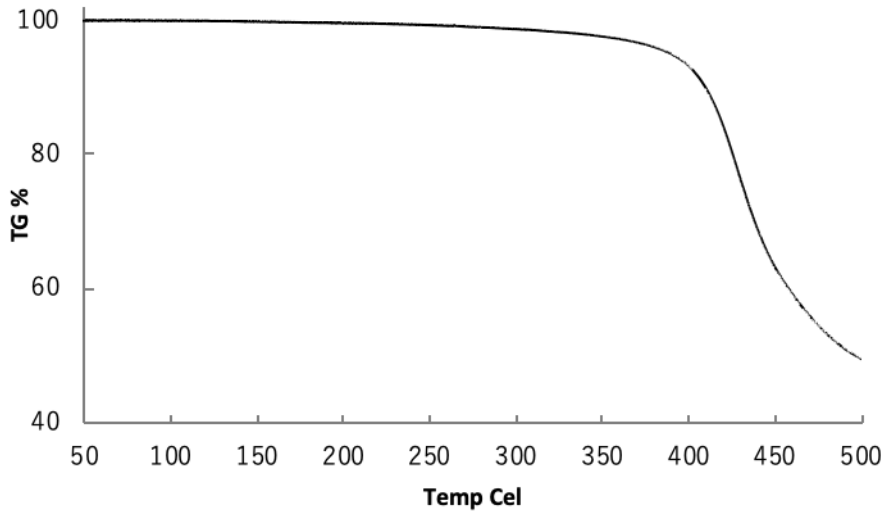
Inverse gated $^{13}C\{^{1}H\}$ NMR (176 MHz in $CDCl_3$)



GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)



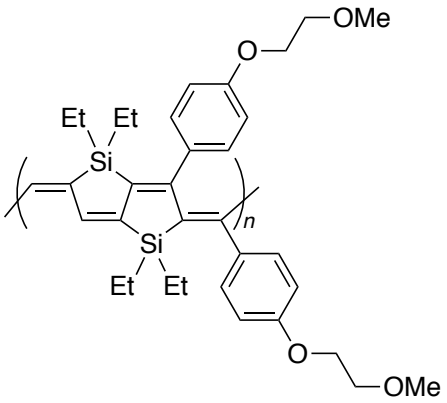
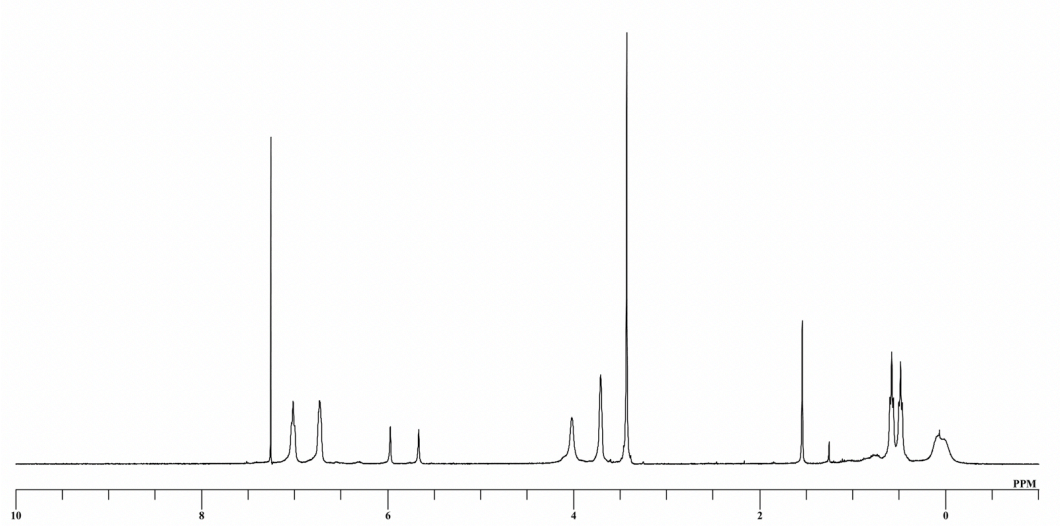
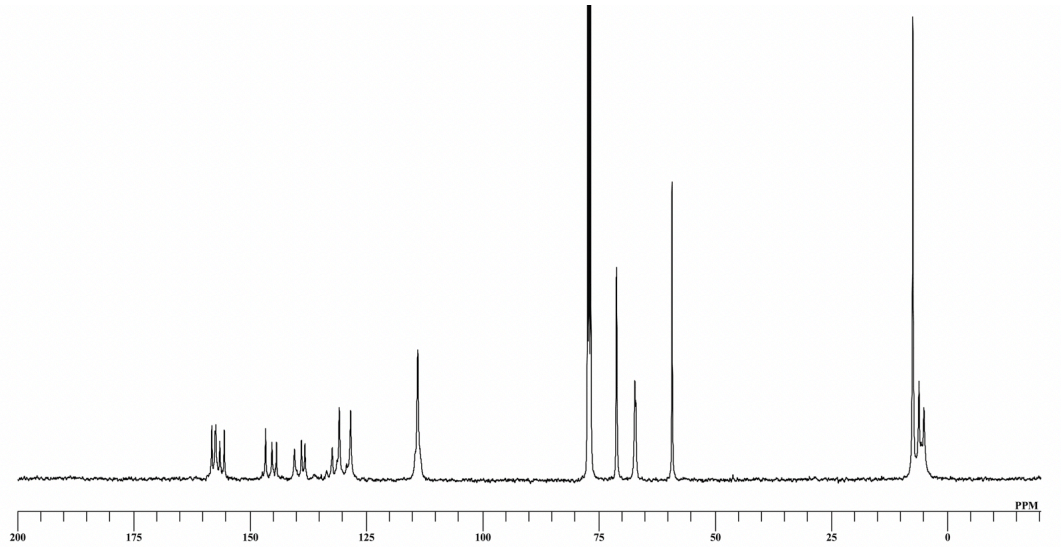


Table 2, Entry 2. Purple solid. 88% yield (505 mg). The polymerization was conducted on a 2.00 mmol scale.

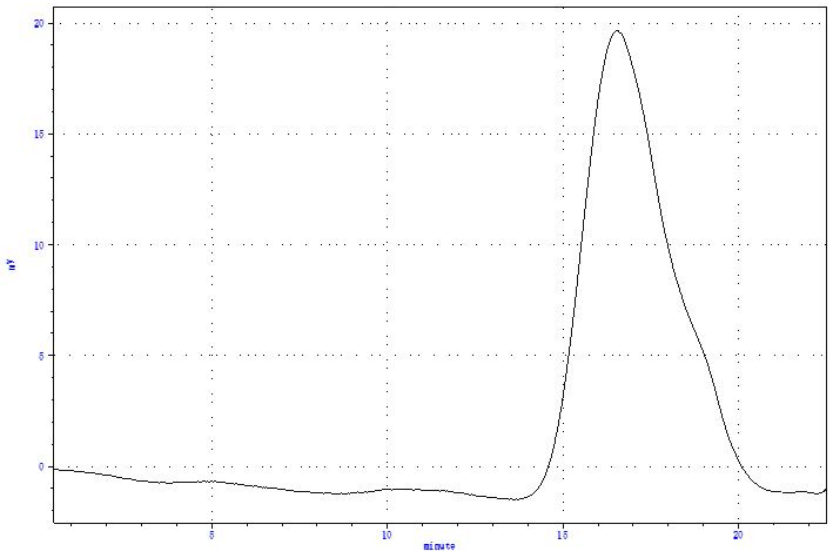
^{1}H NMR (400 MHz in $CDCl_3$)



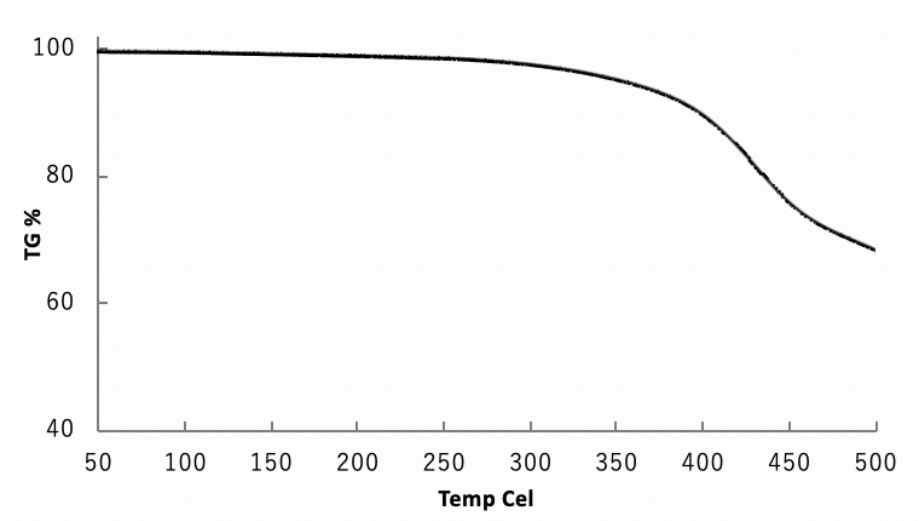
$^{13}C\{^{1}H\}$ NMR (101 MHz in $CDCl_3$)



GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)



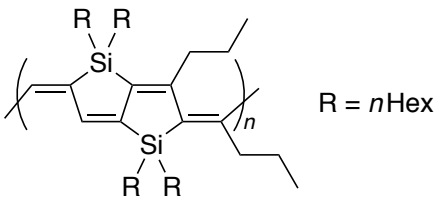
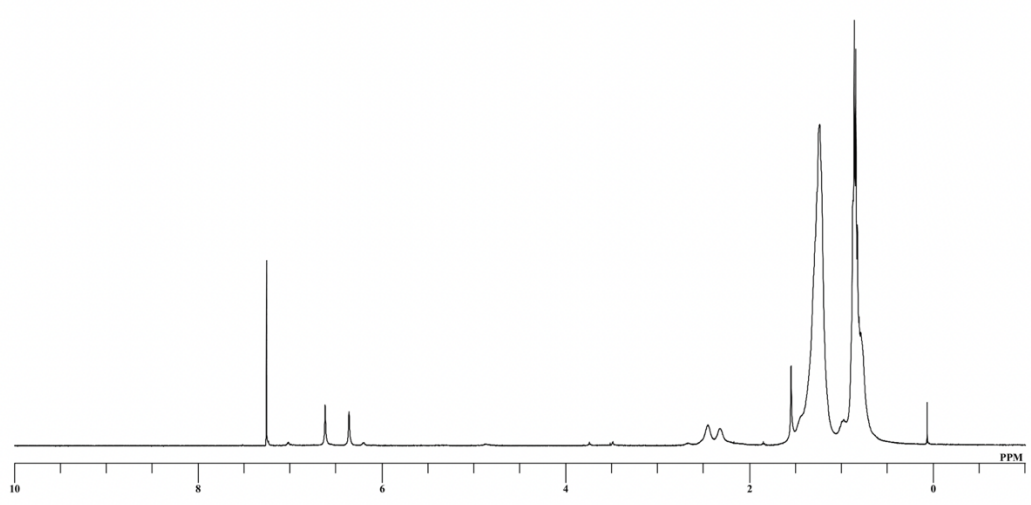
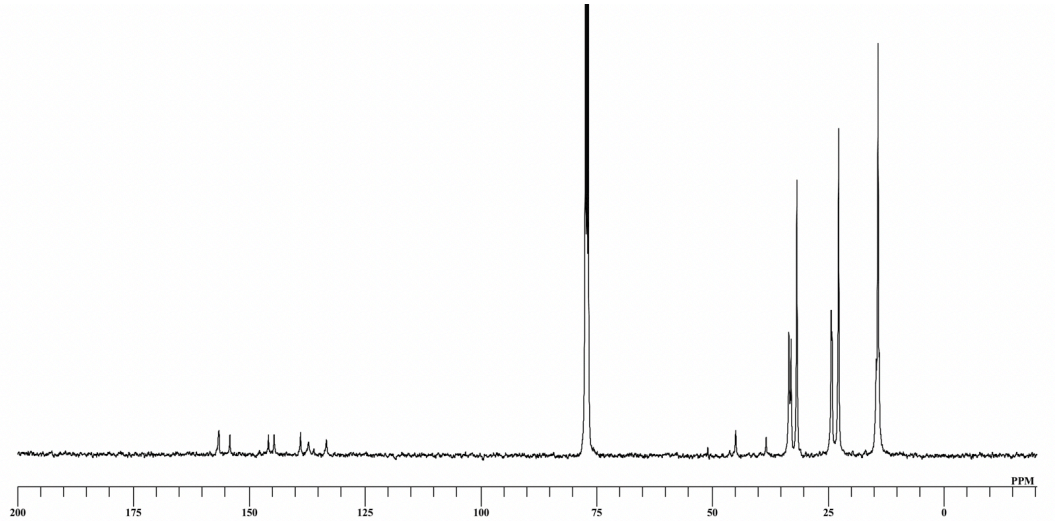


Table 2, Entry 3. Red solid. 92% yield (67.1 mg). 6 mol% Rh of $[RhCl(tfb)]_2$ and 60 mol% of triethylamine were used.

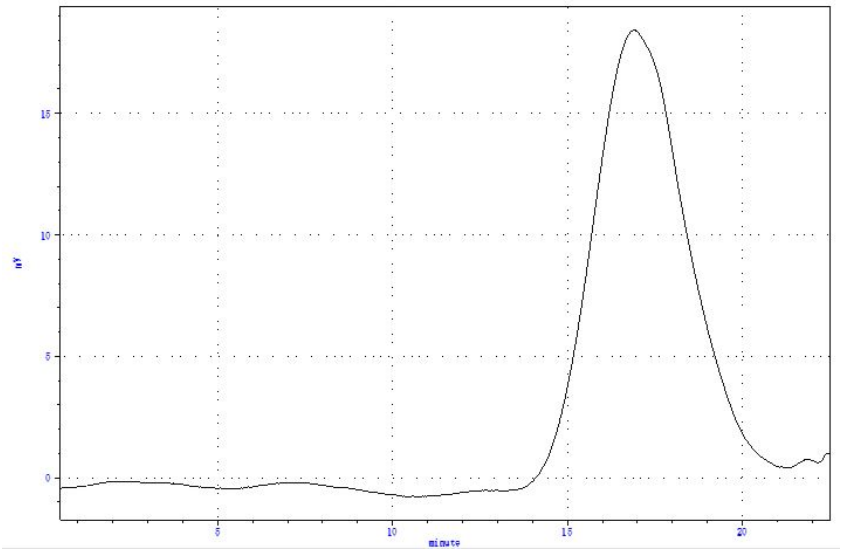
^{1}H NMR (400 MHz in $CDCl_3$)



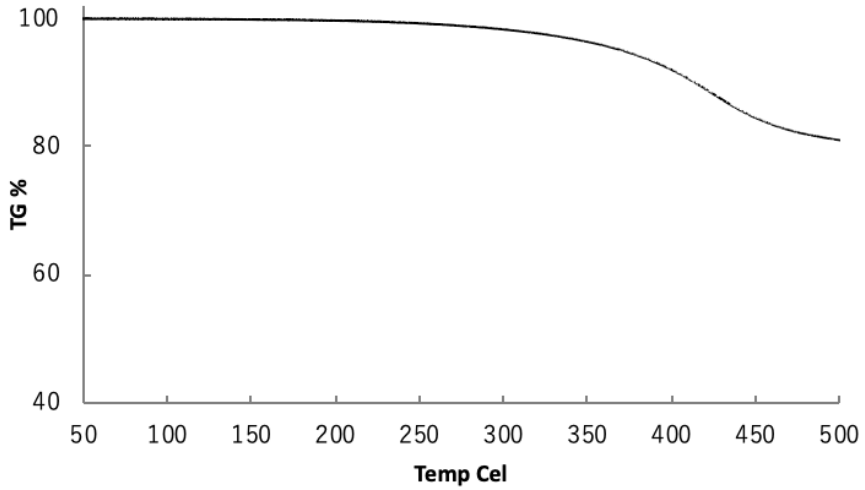
$^{13}C\{^{1}H\}$ NMR (101 MHz in $CDCl_3$)



GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)



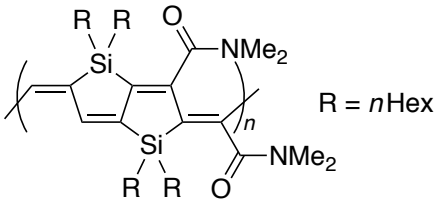
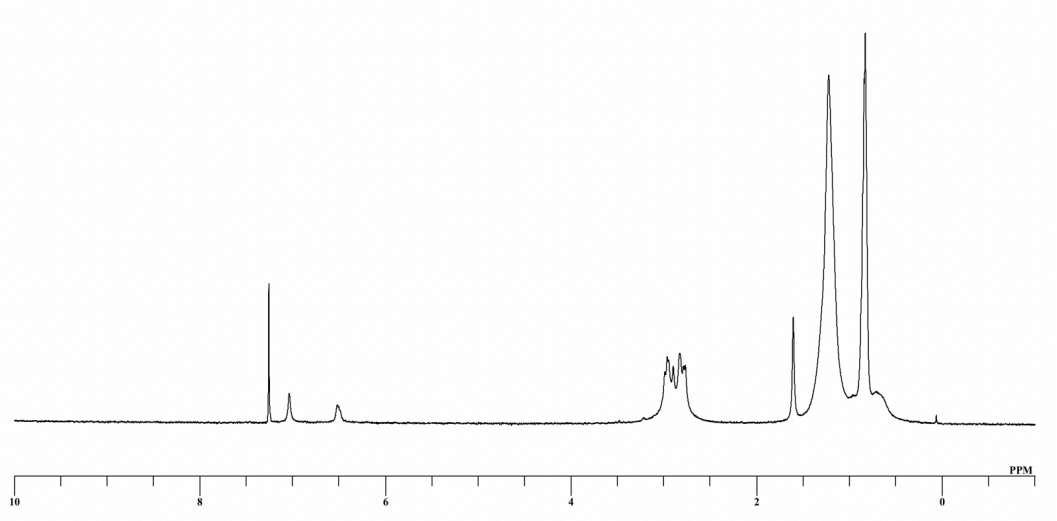
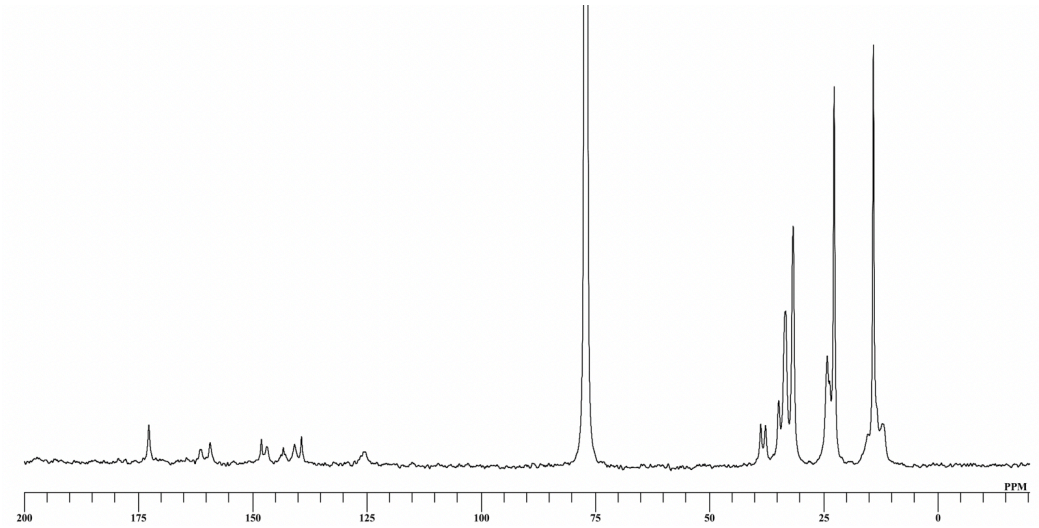


Table 2, Entry 4. Purple solid. 82% yield (65.6 mg). 6 mol% Rh of $[RhCl(tfb)]_2$ and 60 mol% of triethylamine were used.

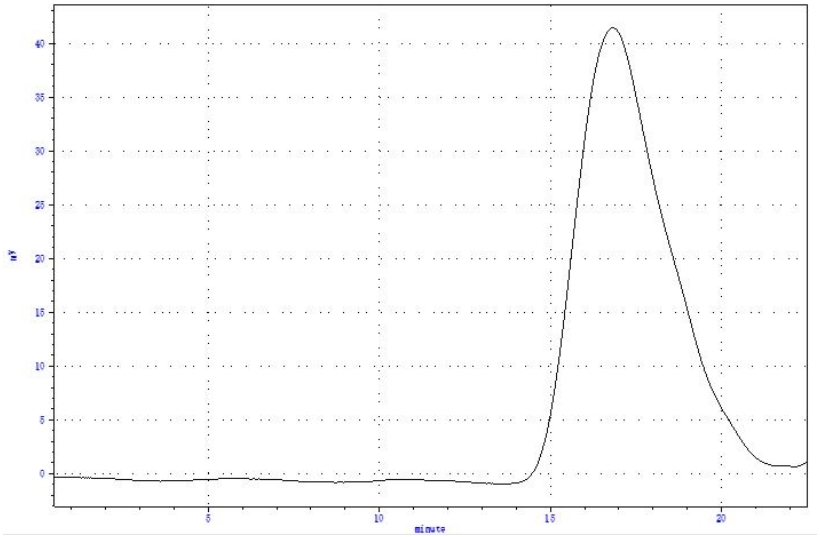
^1H NMR (498 MHz in $CDCl_3$)



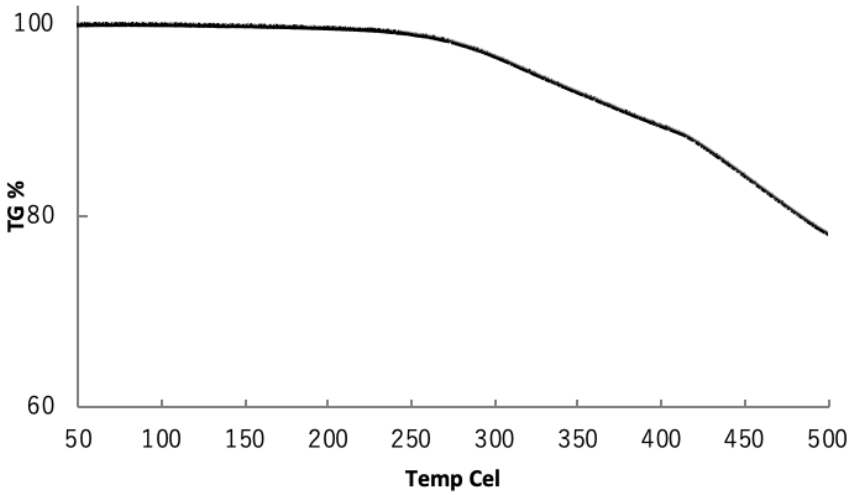
$^{13}C\{^{1}H\}$ NMR (101 MHz in $CDCl_3$)

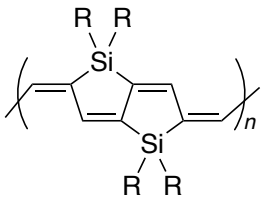


GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)

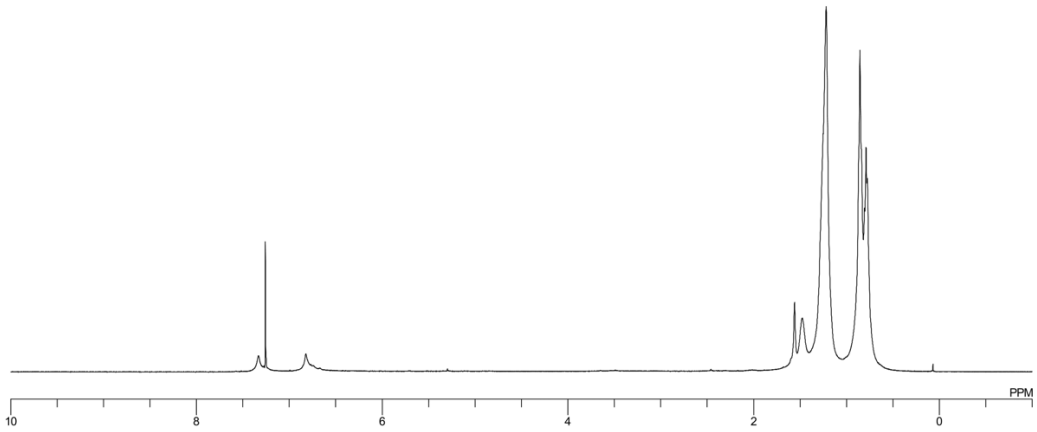




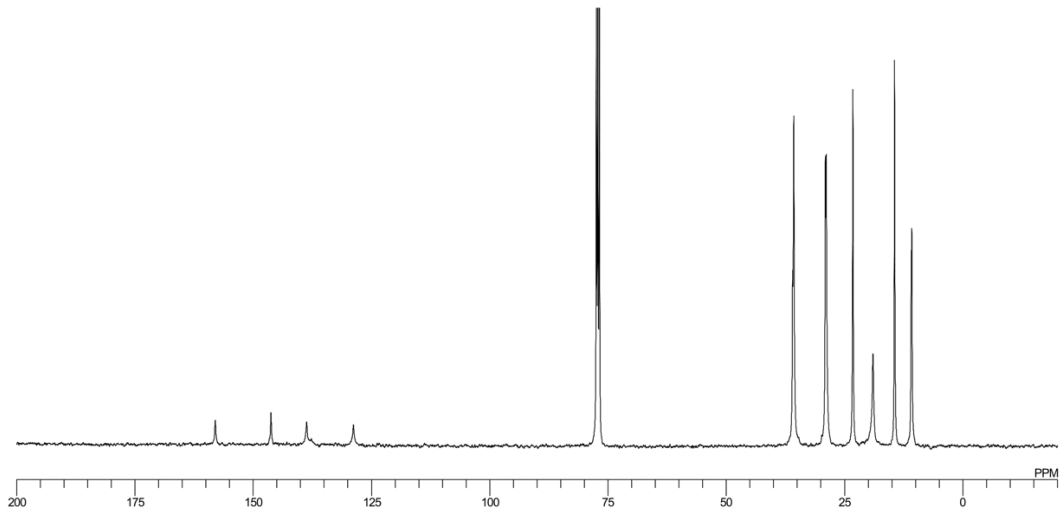
R = 2-ethylhexyl

Table 2, Entry 5. Purple solid. 95% yield (72.4 mg). 6 mol% Rh of $[RhCl(tfb)]_2$ and 60 mol% of triethylamine were used at 20 °C.

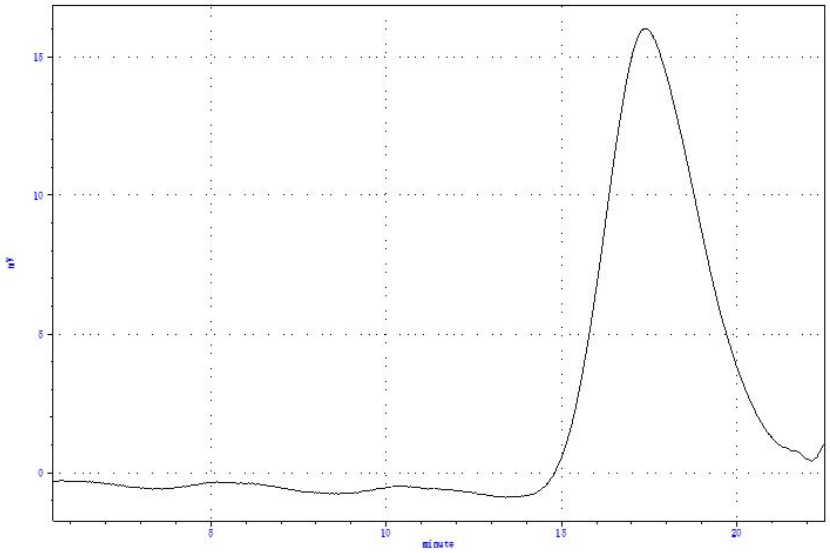
^1H NMR (400 MHz in $CDCl_3$)



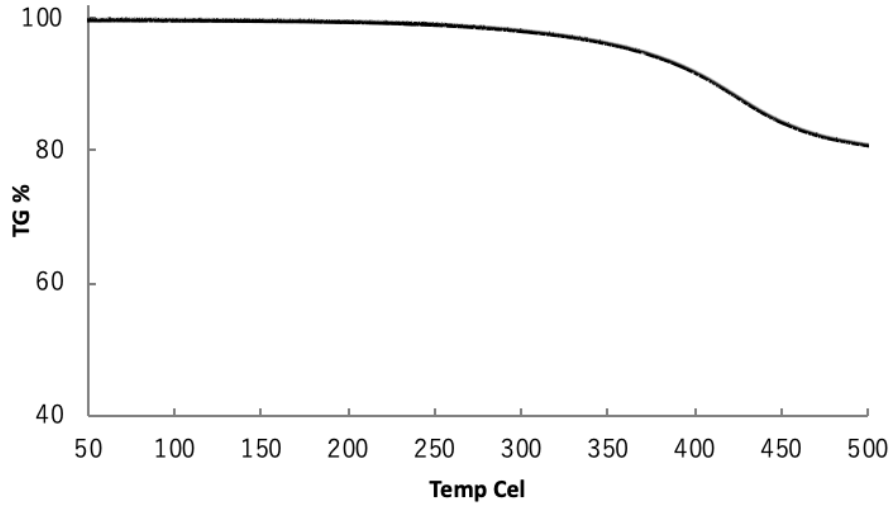
$^{13}C\{^1H\}$ NMR (101 MHz in $CDCl_3$)



GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)



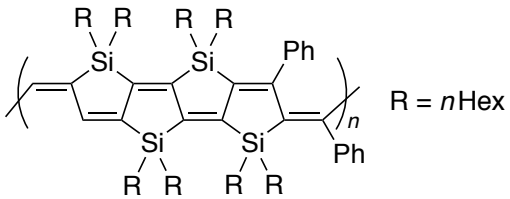
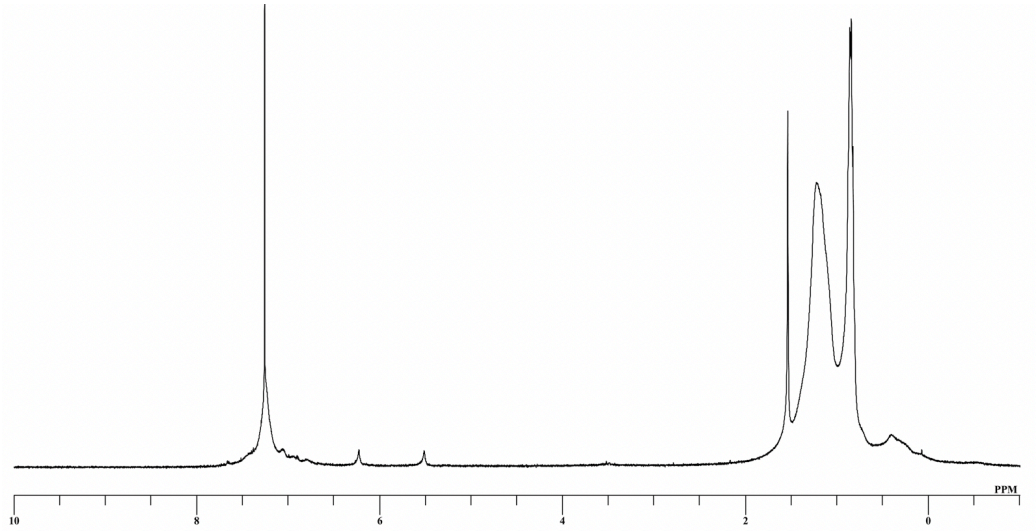
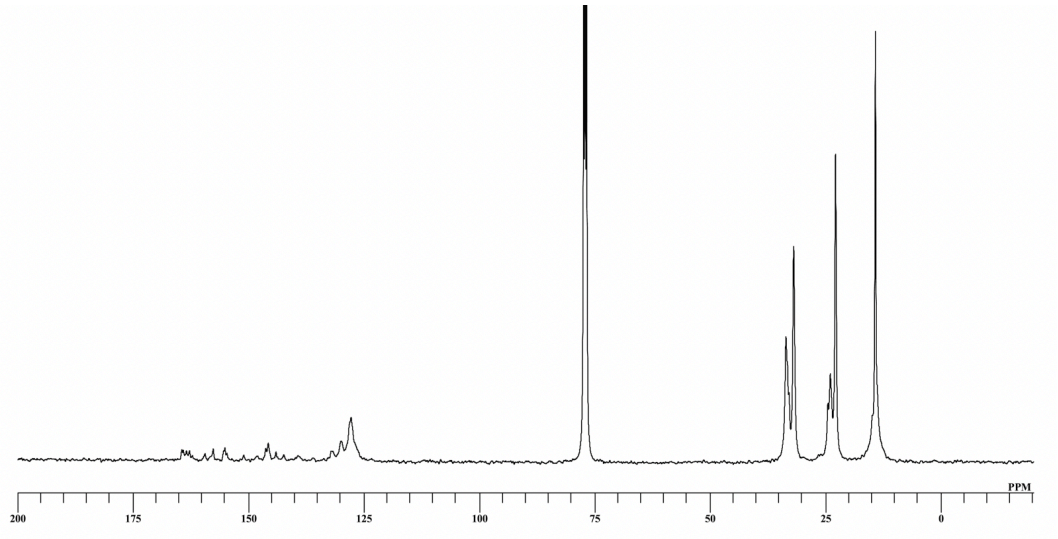


Table 3, Entry 1. Purple solid. 78% yield (105 mg). 6 mol% Rh of $[RhCl(tfb)]_2$ and 60 mol% of triethylamine were used.

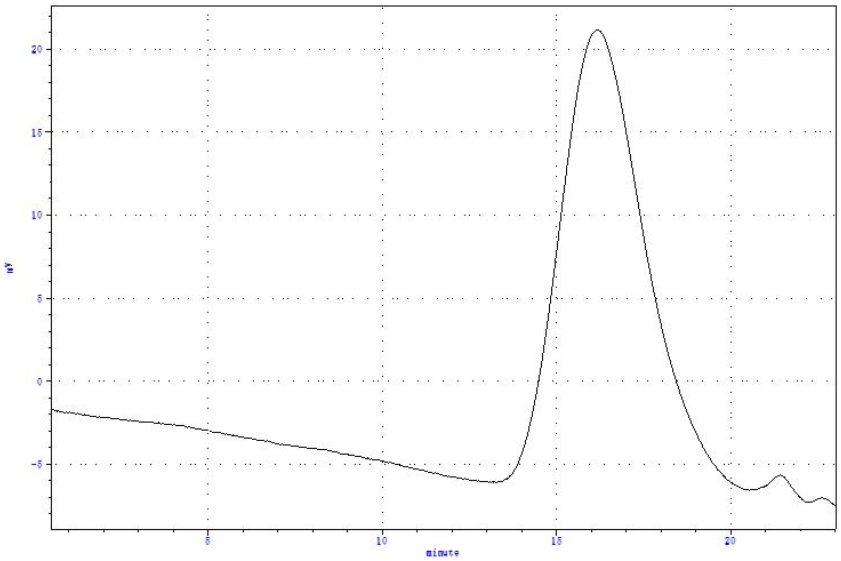
^{1}H NMR (400 MHz in $CDCl_3$)



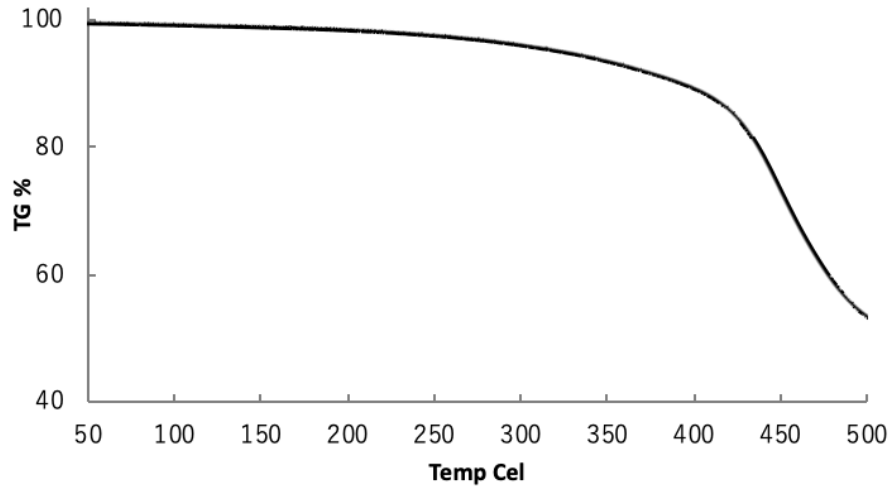
Inverse gated $^{13}C\{^{1}H\}$ NMR (176 MHz in $CDCl_3$)



GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)



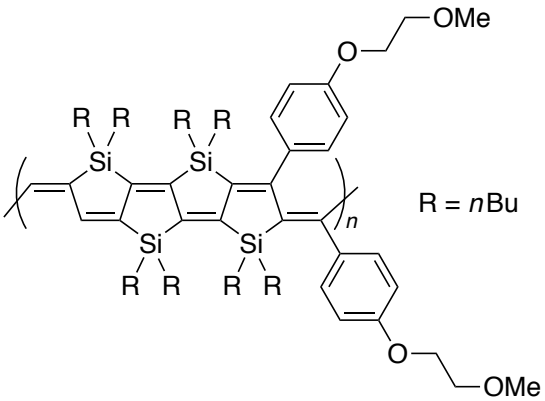
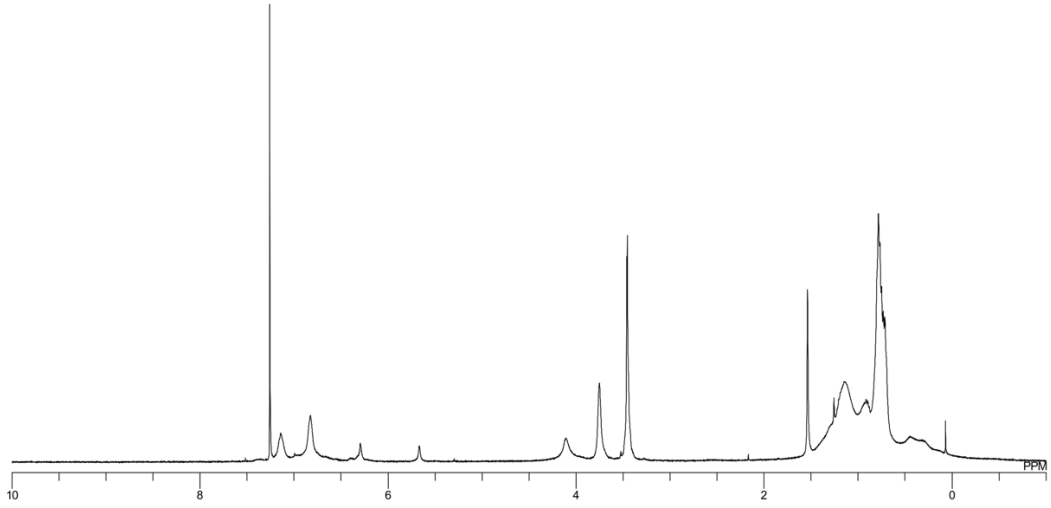
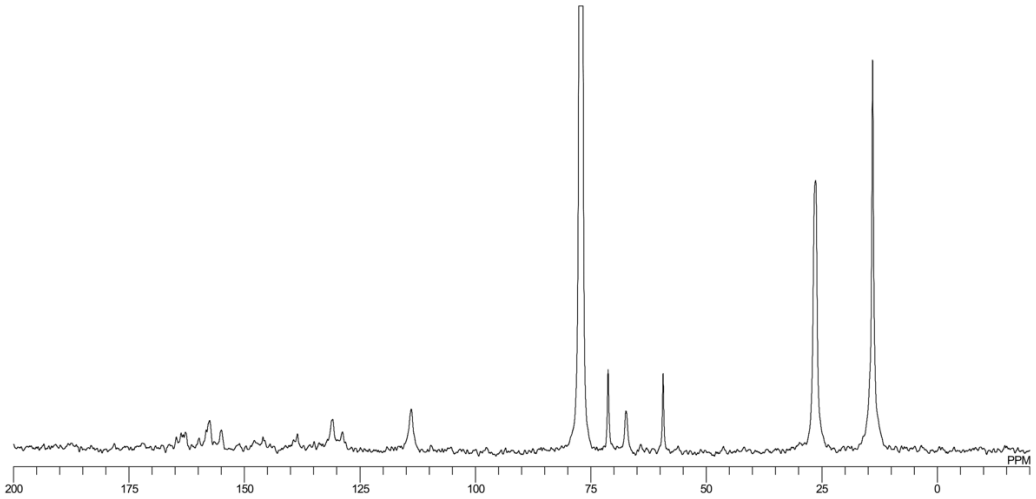


Table 3, Entry 3. Purple solid. 93% yield (485 mg). The polymerization was conducted on a 1.00 mmol scale and 6 mol% Rh of $[RhCl(tfb)]_2$ and 60 mol% of triethylamine were used.

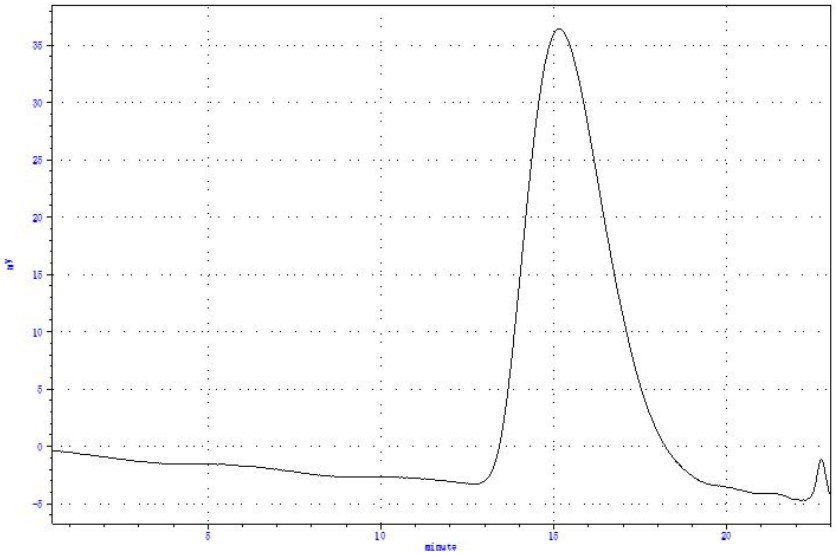
^1H NMR (400 MHz in $CDCl_3$)



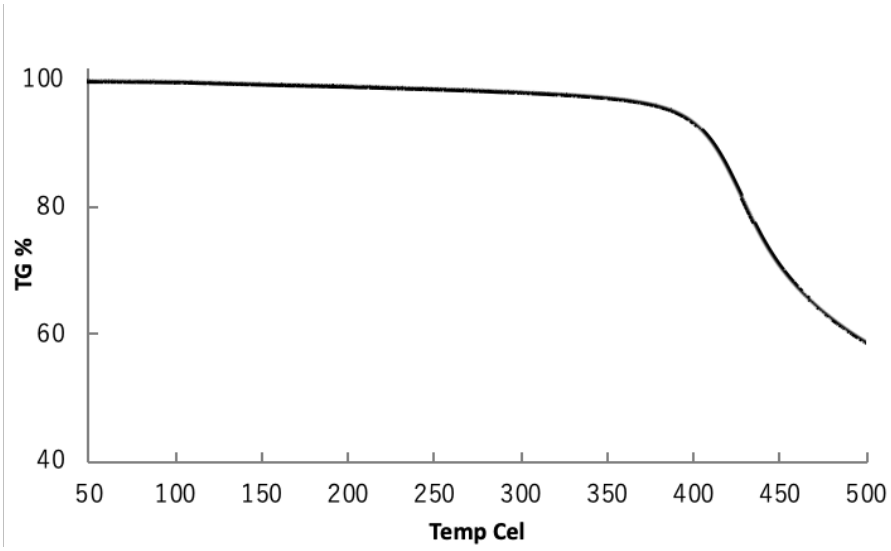
$^{13}C\{^{1}H\}$ NMR (101 MHz in $CDCl_3$)



GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)



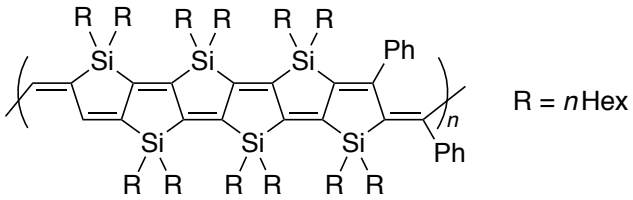
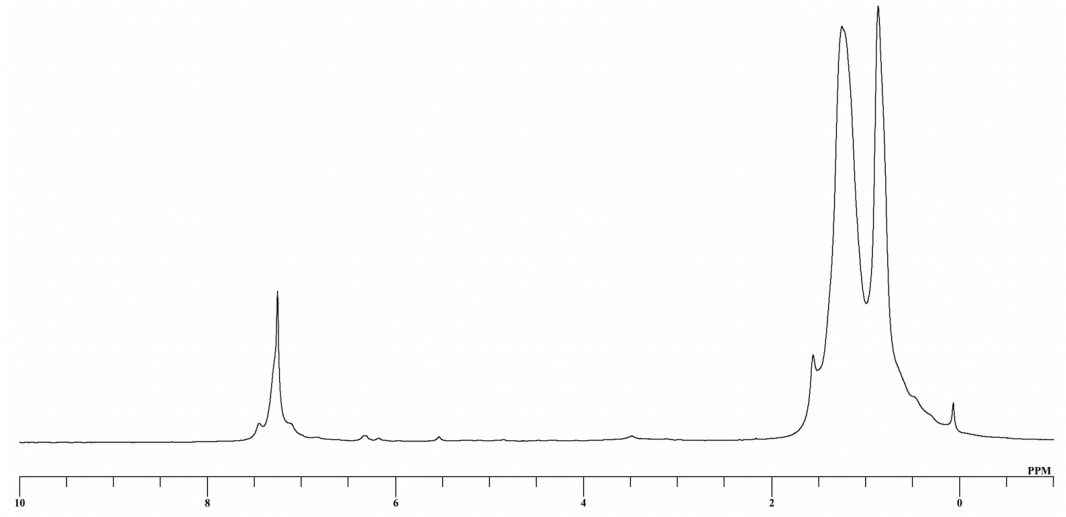
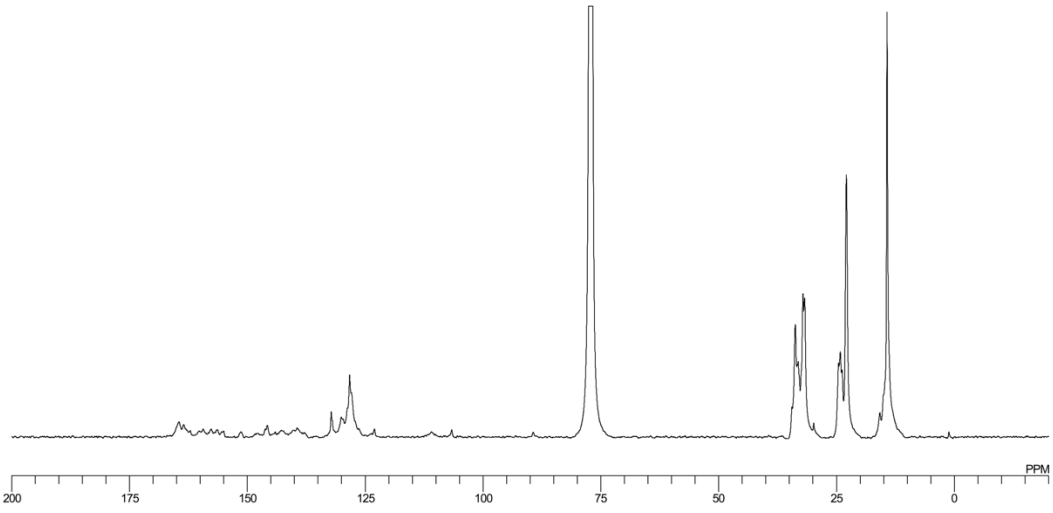


Table 4, Entry 1. Purple solid. 79% yield (76.3 mg). The polymerization was conducted on a 0.125 mmol scale and 20 mol% Rh of $[RhCl(tfb)]_2$ and 200 mol% of triethylamine were used. Incorporation efficiency of internal alkynes (83%) was estimated by the area ratio of sp^2 carbon peaks, sp carbon peaks, and sp^3 carbon peaks of the quantitative ^{13}C NMR spectrum.

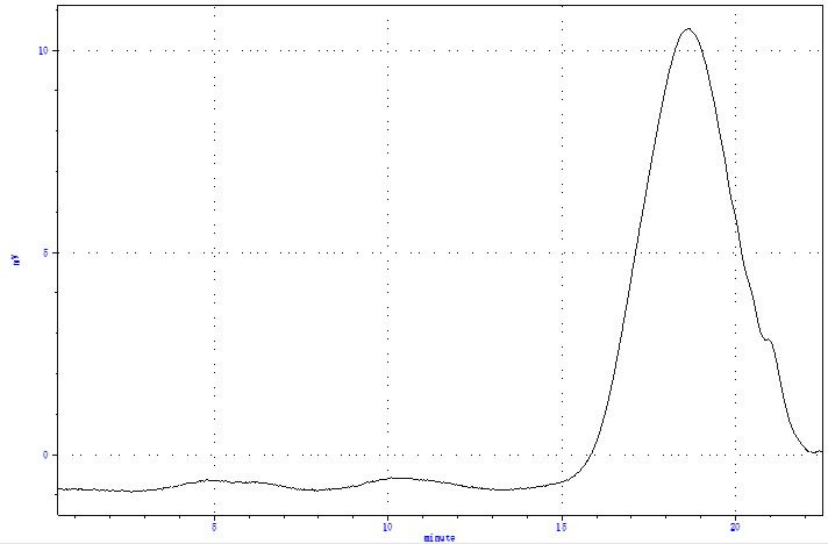
^1H NMR (400 MHz in $CDCl_3$)



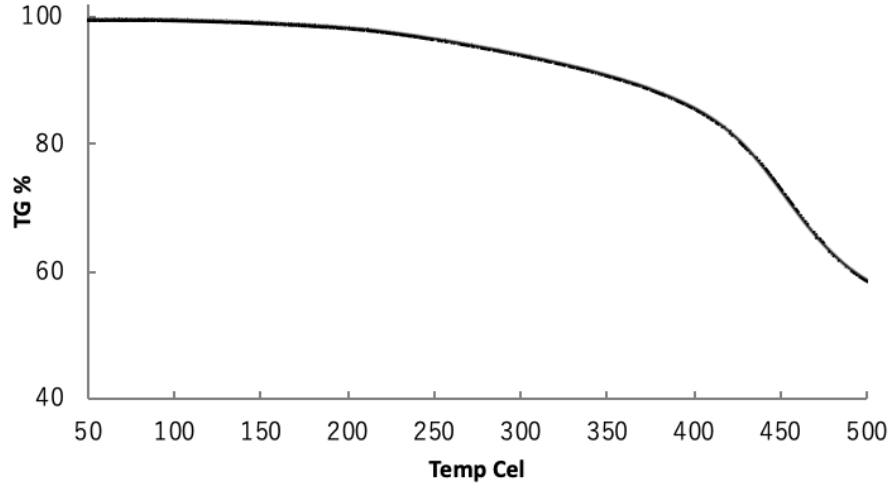
Inverse gated $^{13}C\{^1H\}$ NMR (176 MHz in $CDCl_3$)

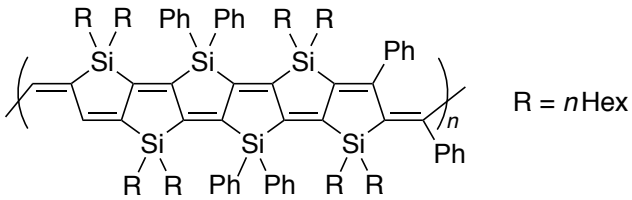


GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)

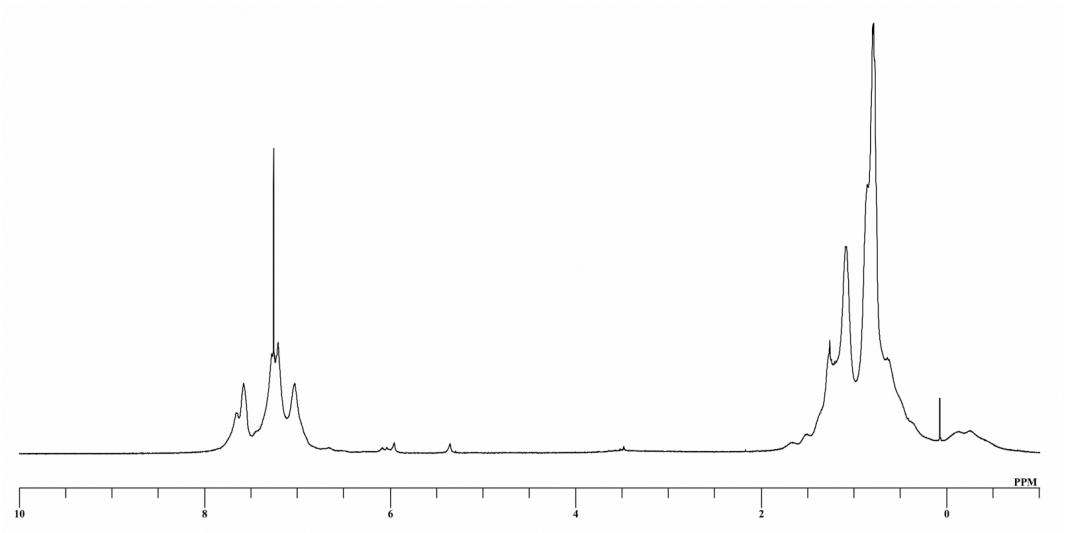




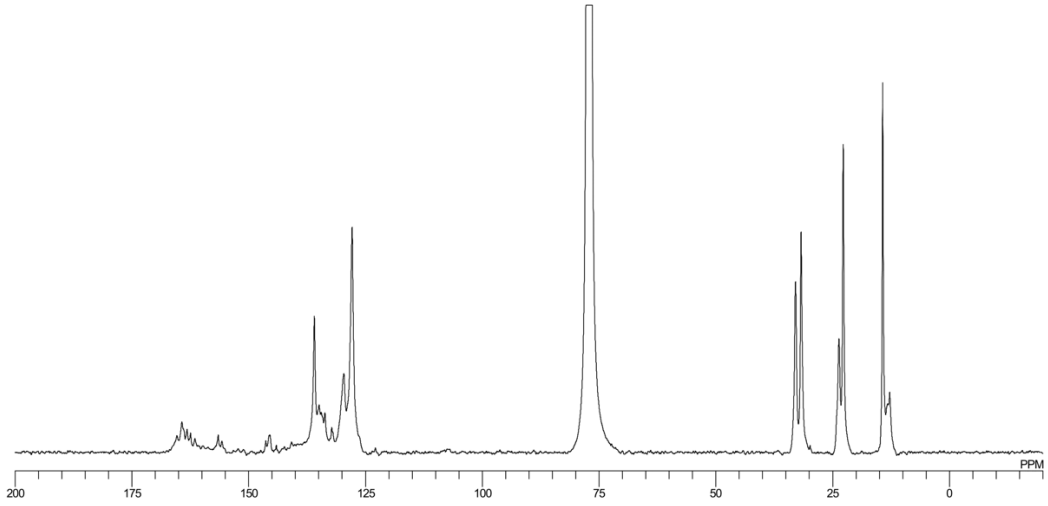
R = *n*Hex

Table 4, Entry 2. Purple solid. 89% yield (84.2 mg). The polymerization was conducted on a 0.125 mmol scale and 20 mol% Rh of $[RhCl(tfb)]_2$ and 200 mol% of triethylamine were used. Incorporation efficiency of internal alkynes (97%) was estimated by the area ratio of sp^2 carbon peaks, sp carbon peaks, and sp^3 carbon peaks of the quantitative ^{13}C NMR spectrum.

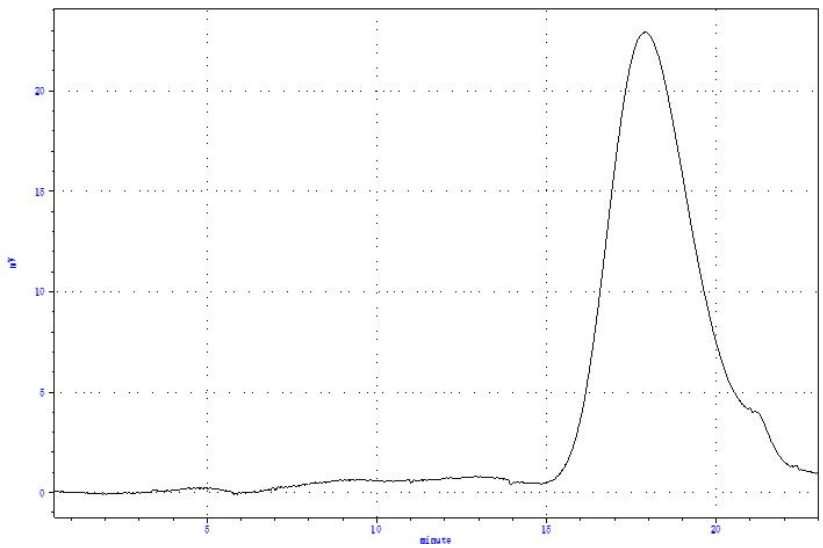
^{1}H NMR (400 MHz in $CDCl_3$)



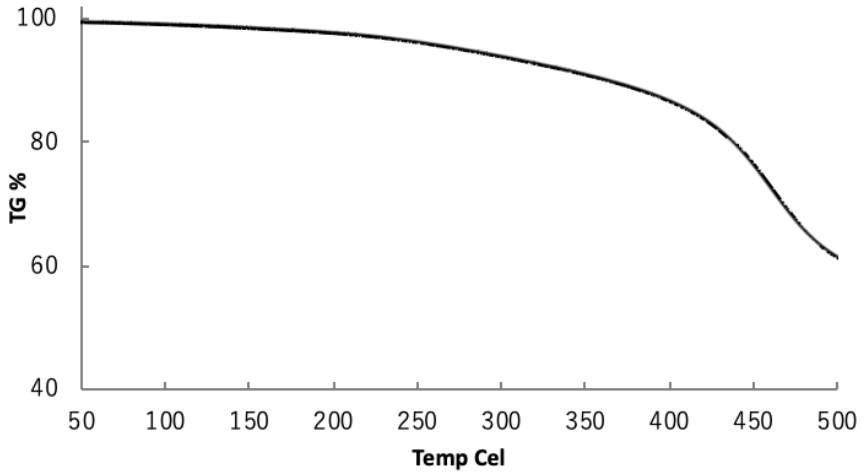
Inverse gated $^{13}C\{^{1}H\}$ NMR (176 MHz in $CDCl_3$)

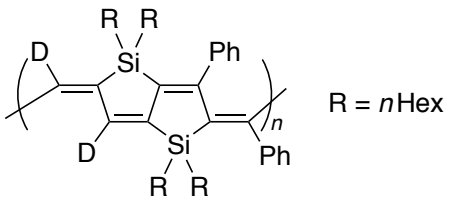


GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)

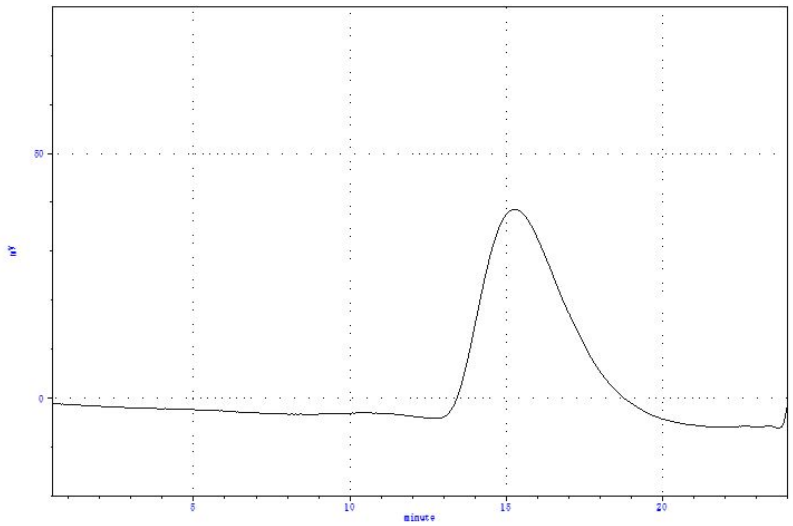


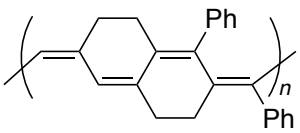


R = *n*Hex

Table 5, Entry 2. Purple solid. 90% yield (73.3 mg).

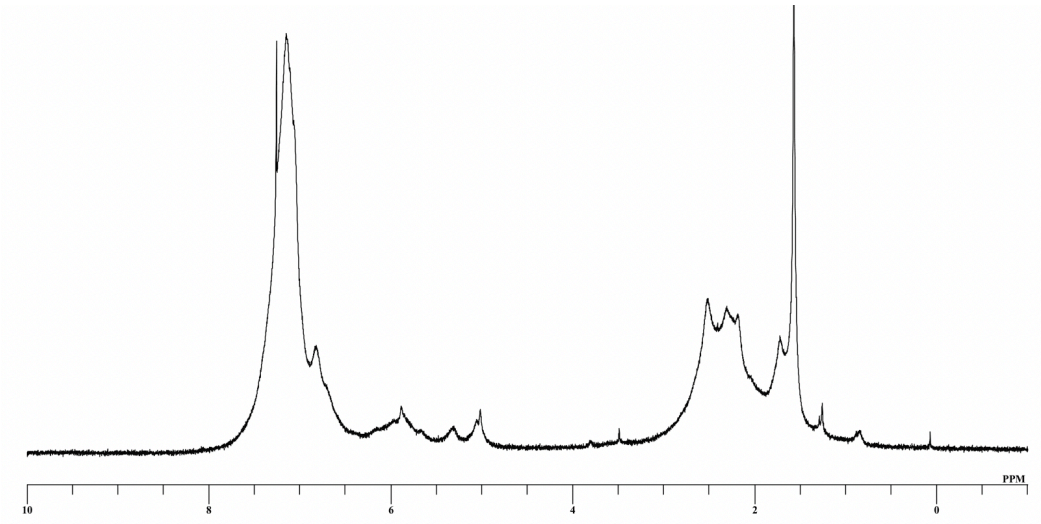
GPC (THF; 1.0 mL/min flow)



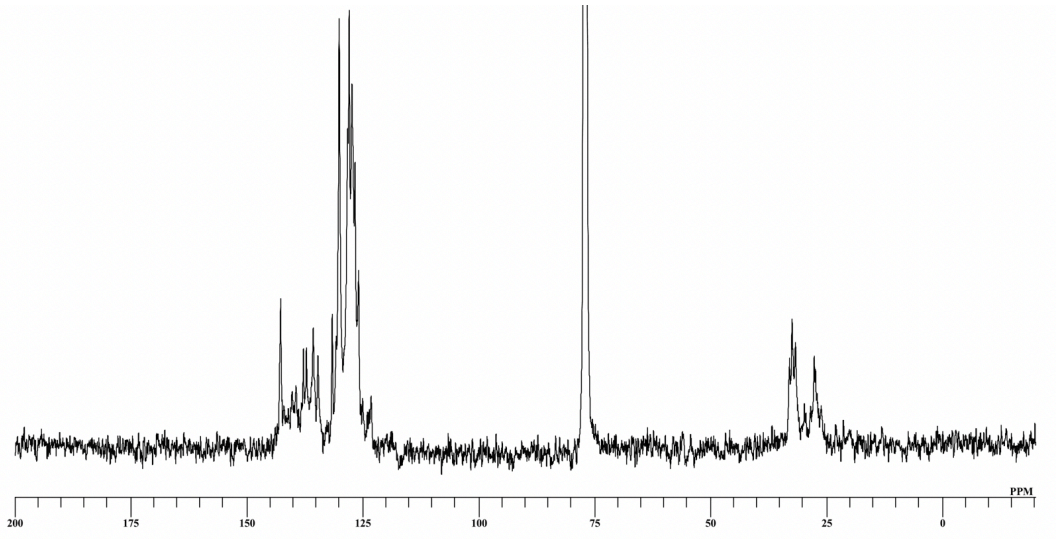


Equation 1. Red solid, 98% yield (75.2 mg). The polymerization was conducted on a 0.500 mmol scale.

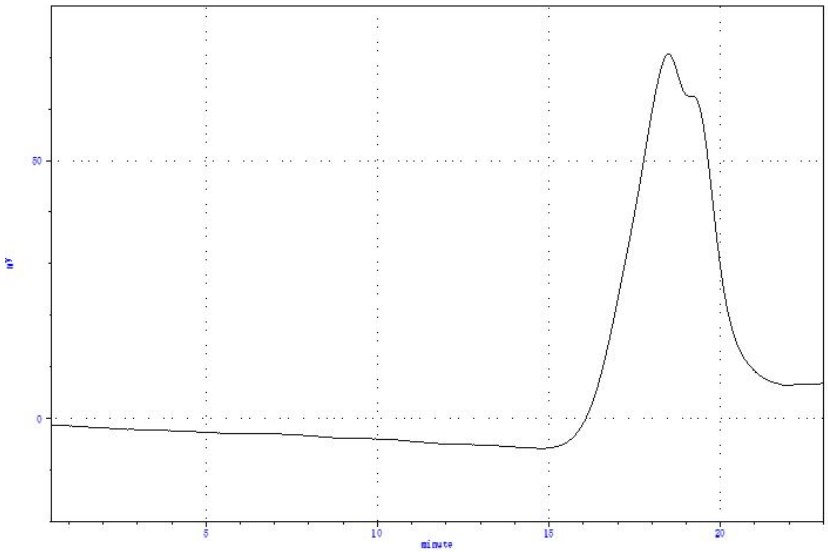
^{1}H NMR (400 MHz in $CDCl_3$)



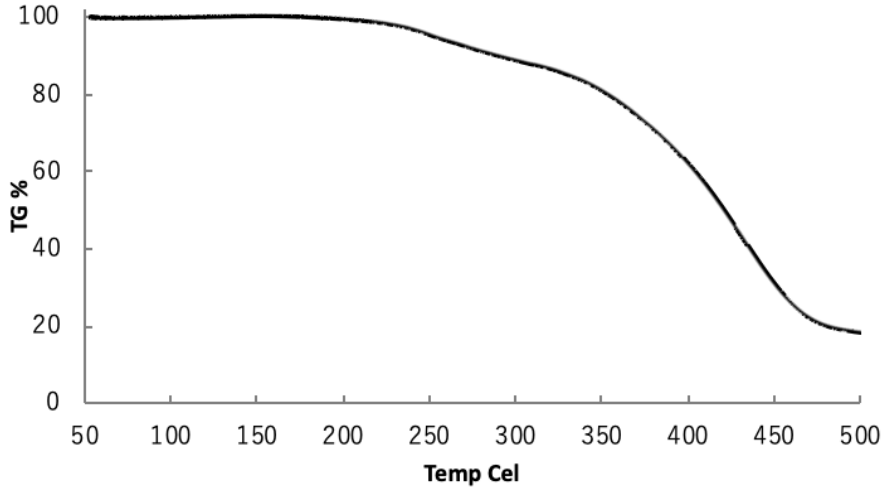
$^{13}C\{^{1}H\}$ NMR (101 MHz in $CDCl_3$)

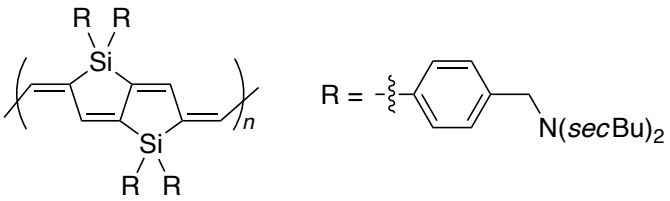


GPC (THF; 1.0 mL/min flow)



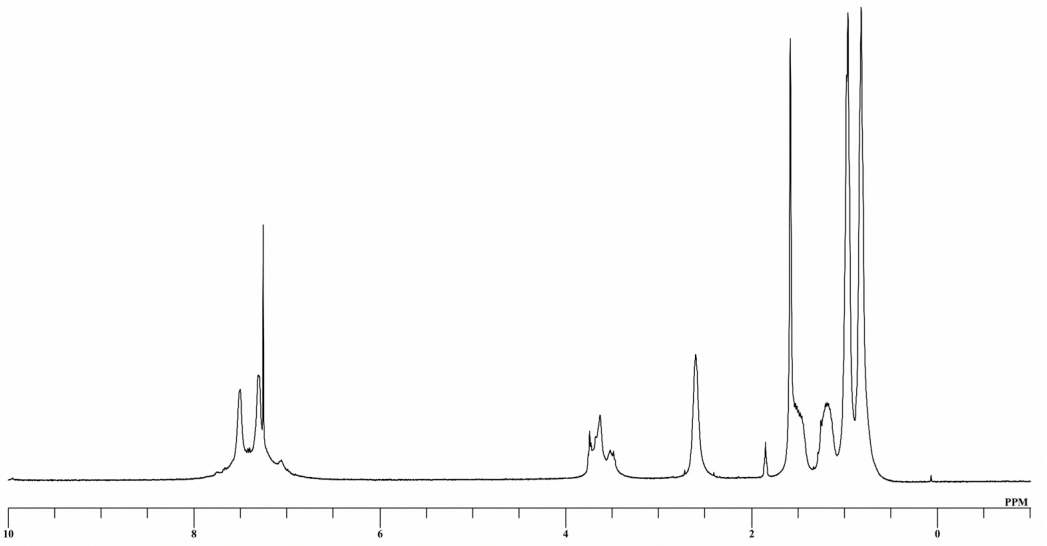
TG (+10 ºC/min from 50 ºC to 500 ºC)



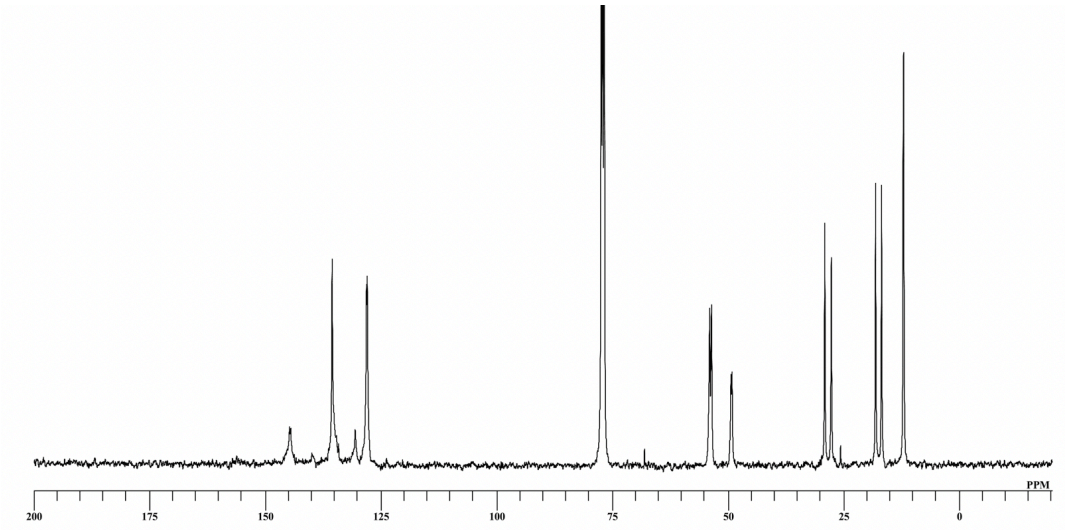


Equation 2. Purple solid. 70% yield (89.6 mg). 6 mol% Rh of $[RhCl(tfb)]_2$ and 60 mol% of triethylamine were used at 20 °C.

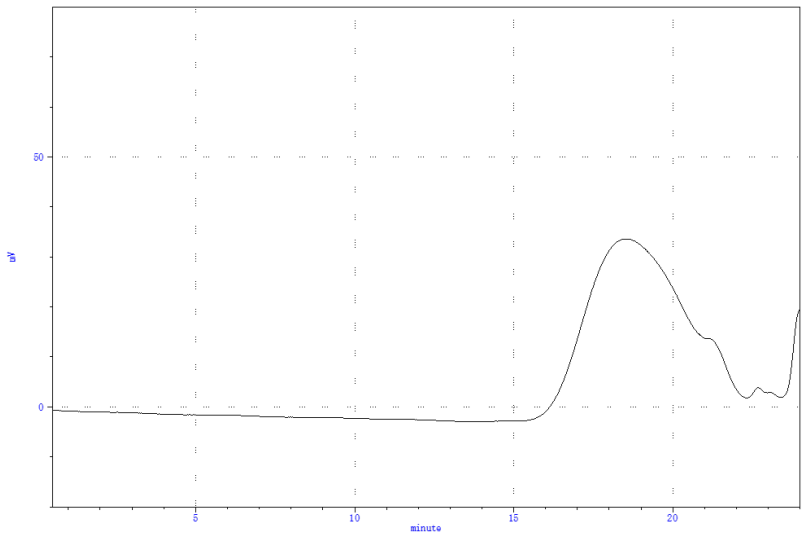
^{1}H NMR (400 MHz in $CDCl_3$)



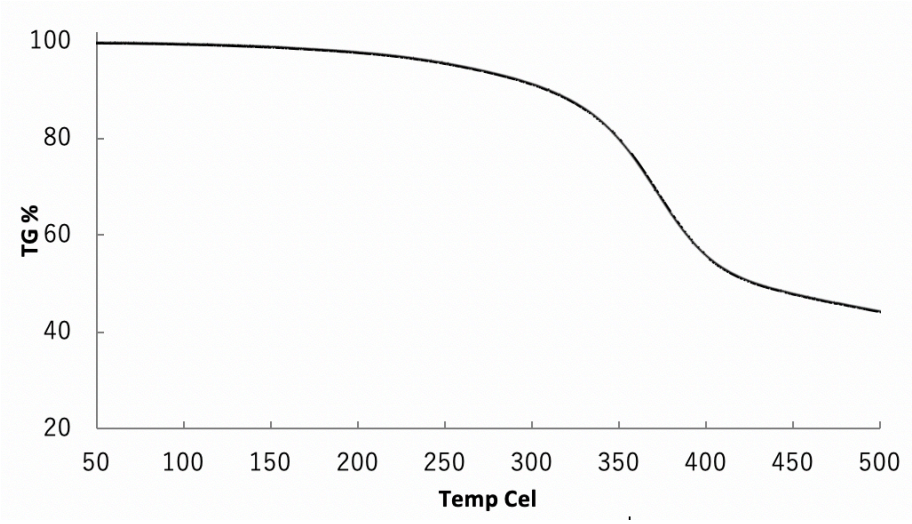
$^{13}C\{^{1}H\}$ NMR (101 MHz in $CDCl_3$)

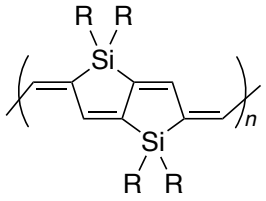


GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)

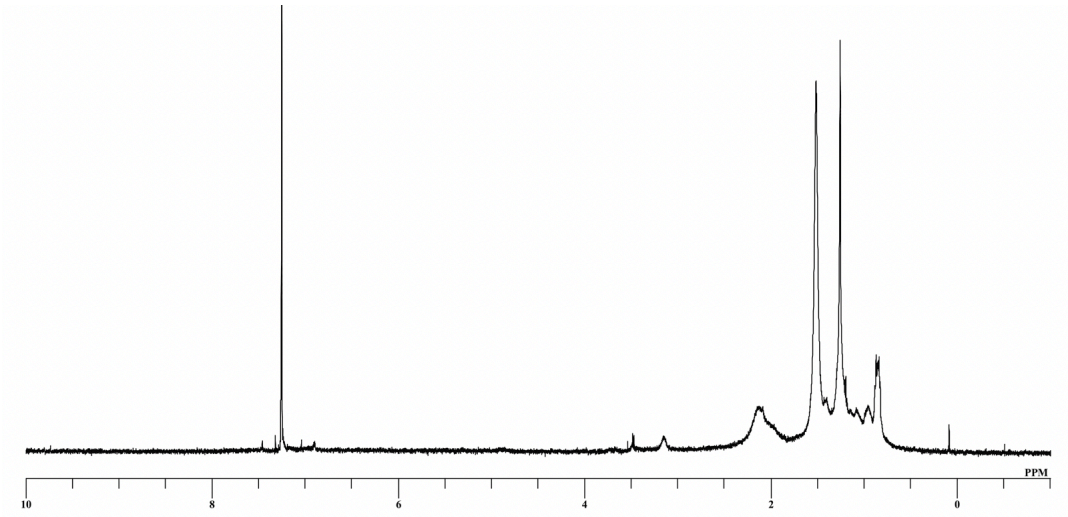




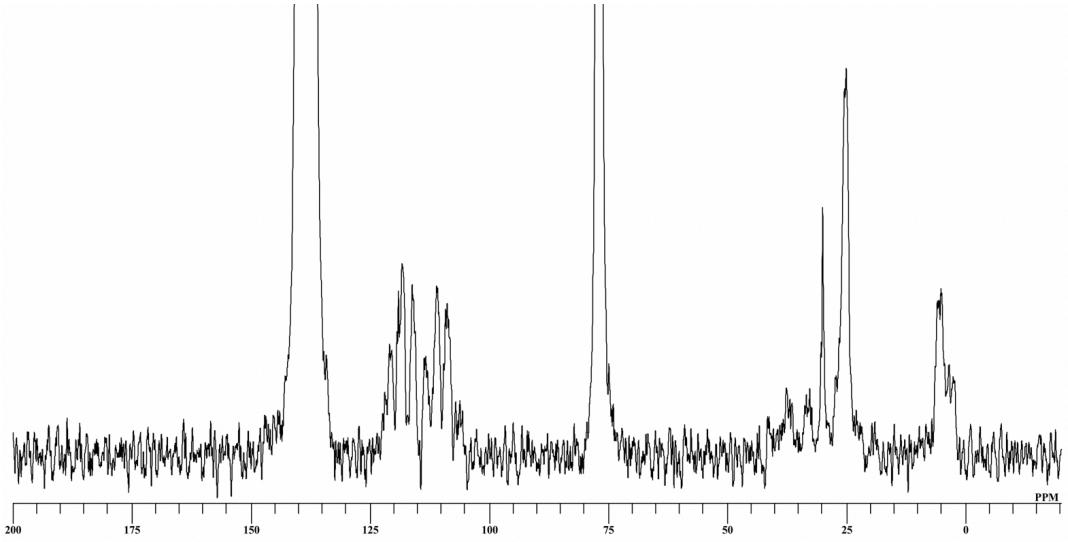
R = $(CH_2)_2(CF_2)_3CF_3$

Equation 3. Purple-red solid. 98% yield (140 mg). 12 mol% Rh of $[RhCl(tfb)]_2$ and 120 mol% of triethylamine were used at 60 °C. Molecular weights were not determined due to the poor solubility in THF.

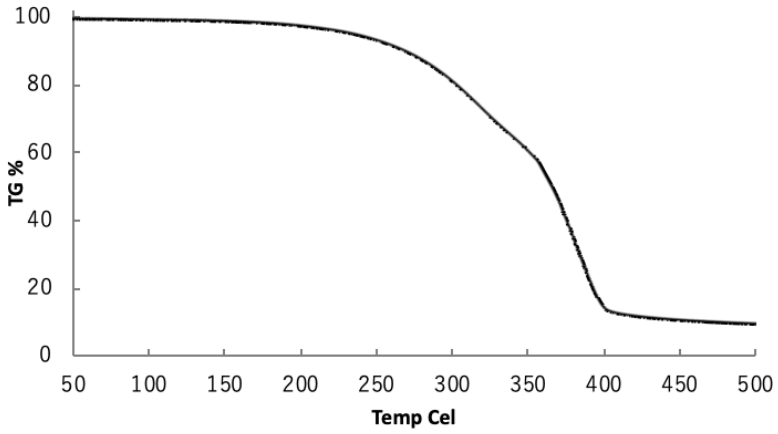
^1H NMR (498 MHz in $CDCl_3$)



$^{13}C\{^1H\}$ NMR (101 MHz in $CDCl_3/C_6F_6$)

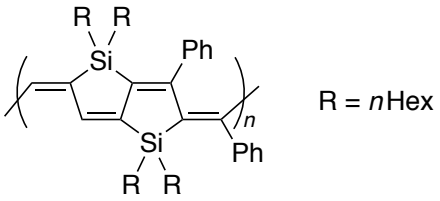


TG (+10 ºC/min from 50 ºC to 500 ºC)



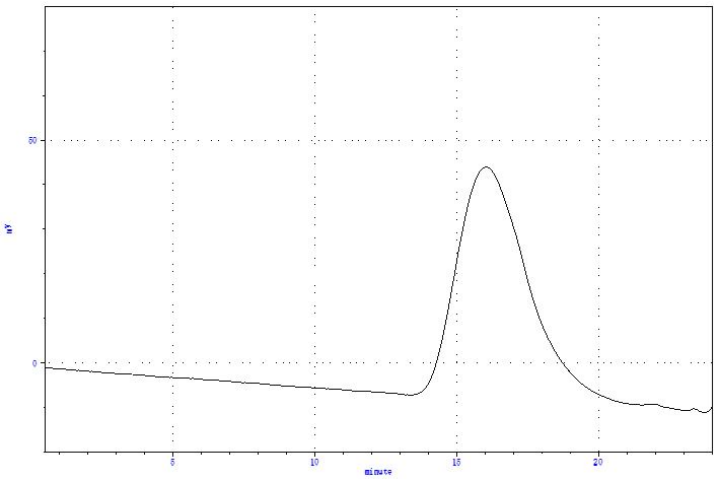
Procedure for Table 5 (Entries 3 and 4).

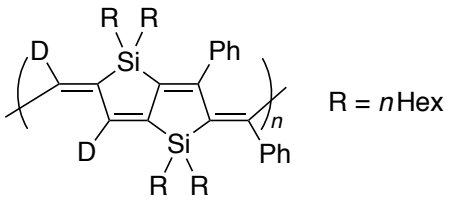
(1,2,2-Triphenylvinyl)lithium (112 µL, 11.2 µmol; 0.10 M solution in toluene) and THF (0.3 mL) were added to a solution of $[RhCl(tfb)]_2$ (2.7 mg, 7.5 µmol Rh) in THF (0.2 mL). This was stirred for 5 min at –10 ºC and monomer **1a** or **1a-*d*** (0.250 mmol) was added with the aid of THF (0.5 mL). The mixture was stirred for 22 h at –10 ºC and warmed to room temperature. This was added dropwise to stirring MeOH (50 mL) with the aid of CH_2Cl_2 (5.0 mL), and the precipitates that formed were collected by filtration and the solid thus obtained was dried under vacuum to afford **poly-1a** or **poly-1a-*d***.



Entry 3. Purple solid. 82% yield (66.8 mg).

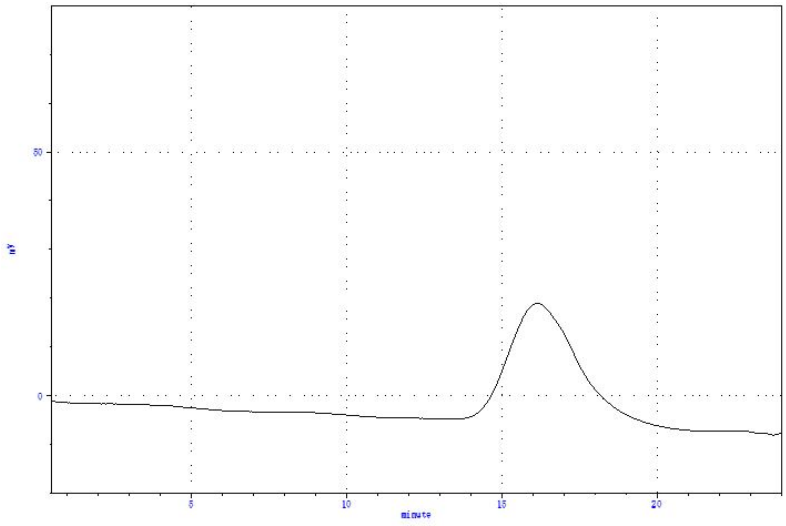
GPC (THF; 1.0 mL/min flow)



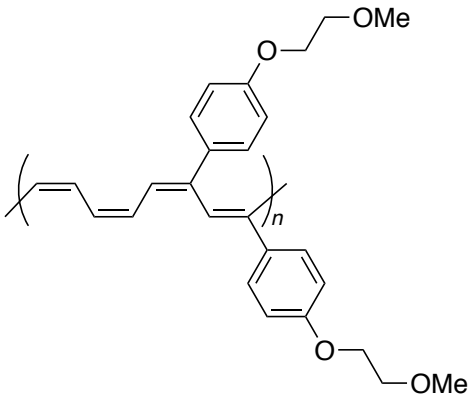


Entry 4. Purple solid. 90% yield (73.8 mg).

GPC (THF; 1.0 mL/min flow)

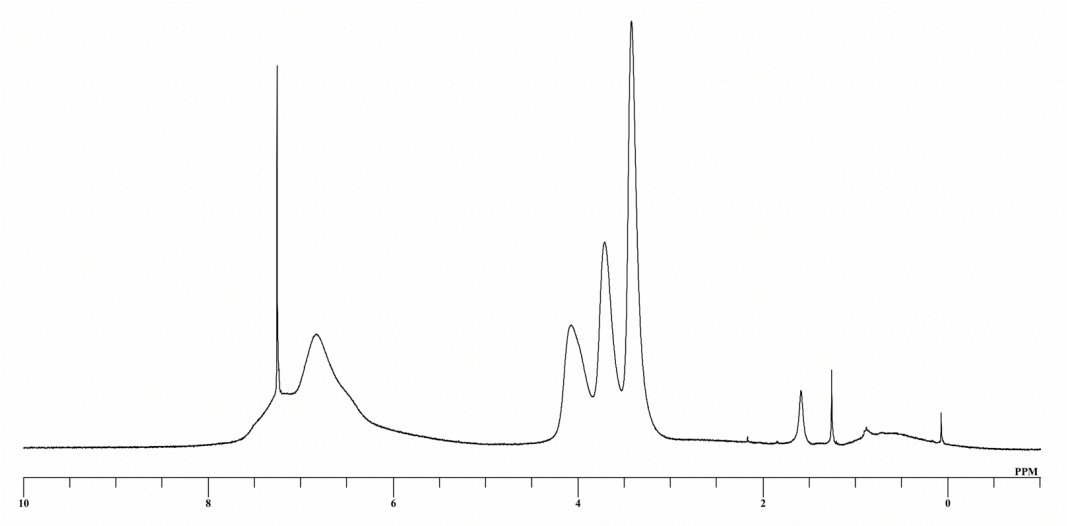


Procedure for Equation 4.

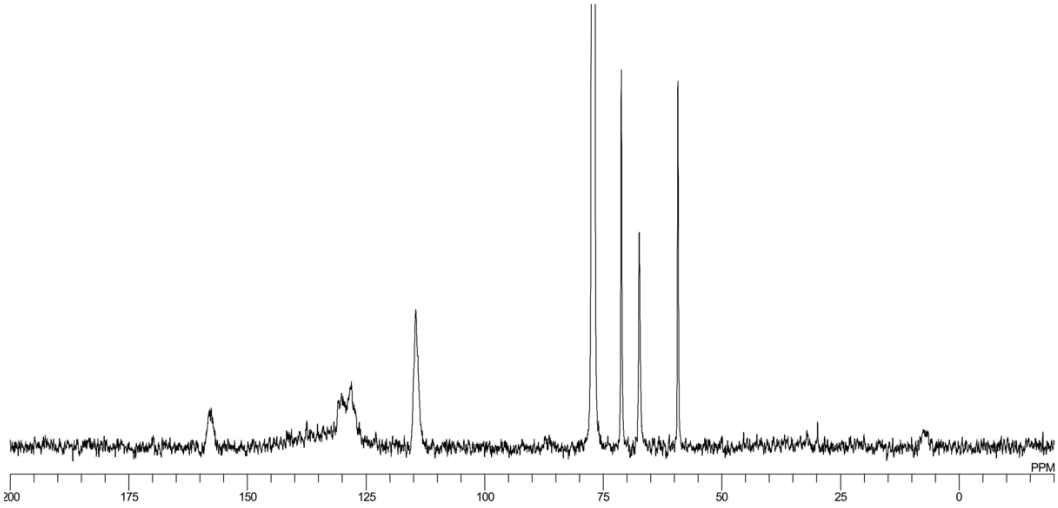


A solution of tetrabutylammonium fluoride (394 mg, 1.25 mmol; trihydrate) in THF (10 mL) was added to a solution of **poly-1b** (143 mg) in THF (10 mL), and the mixture was stirred for 22 h at 60 ºC. After cooled to room temperature, this was washed with H_2O and extracted with toluene. The organic layer was concentrated and this was added dropwise to stirring MeOH (50 mL) with the aid of CH_2Cl_2 (5 mL), and the precipitates that formed were collected by filtration. The resulting solid was dissolved in CH_2Cl_2 (5 mL) and this was added dropwise to stirring hexane (50 mL) with the aid of CH_2Cl_2 (5 mL). The precipitates that formed were collected by filtration and the solid thus obtained was dried under vacuum to afford **poly-6b** as a red solid (85.3 mg; 84% yield). The desilylation efficiency (95%) was estimated by the ^{1}H NMR spectrum.

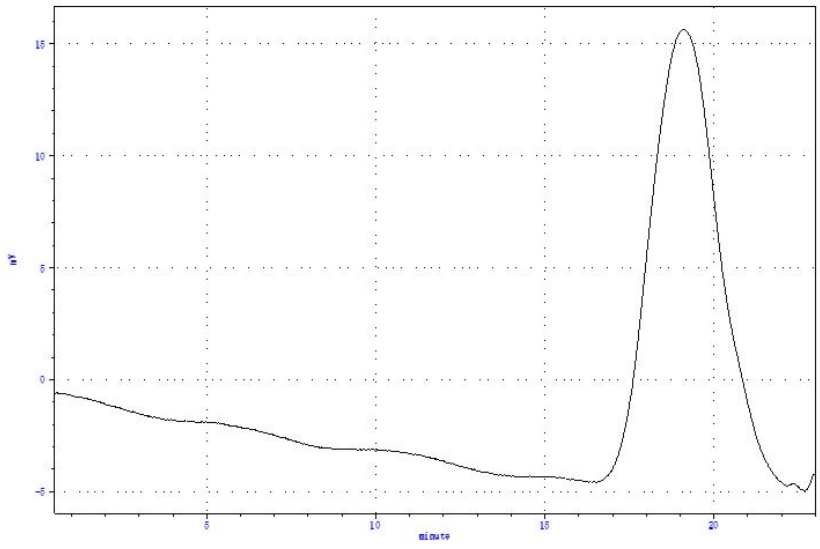
^{1}H NMR (400 MHz in $CDCl_3$)



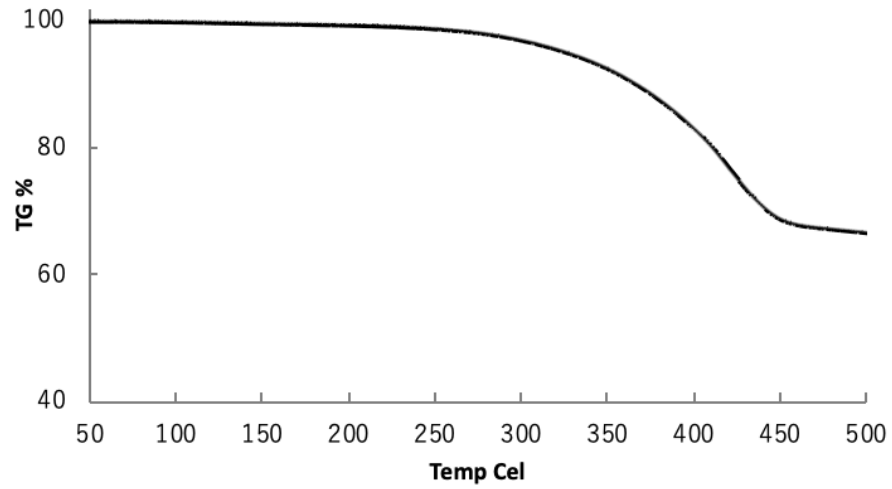
$^{13}C\{^{1}H\}$ NMR (101 MHz in $CDCl_3$)



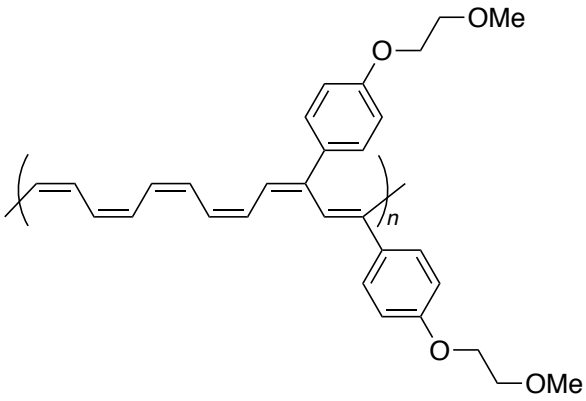
GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)

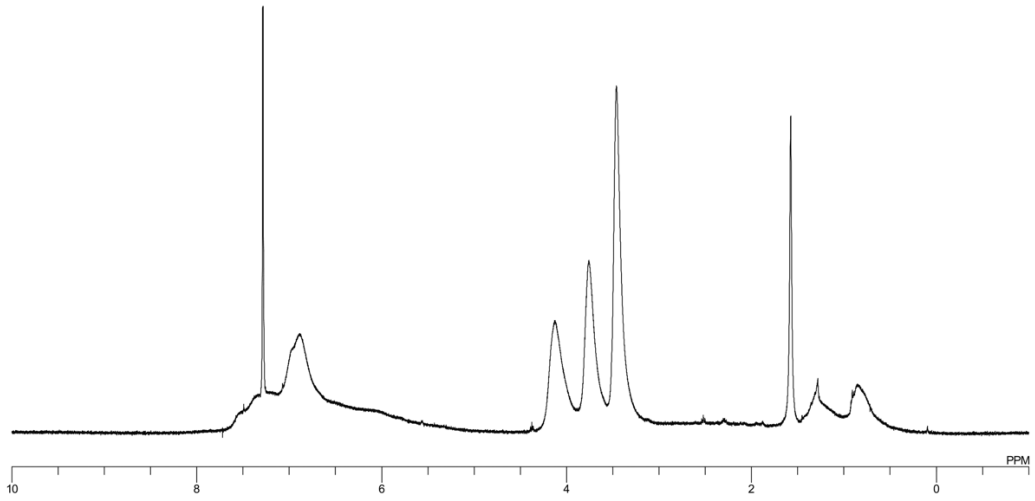


Procedure for Equation 5.

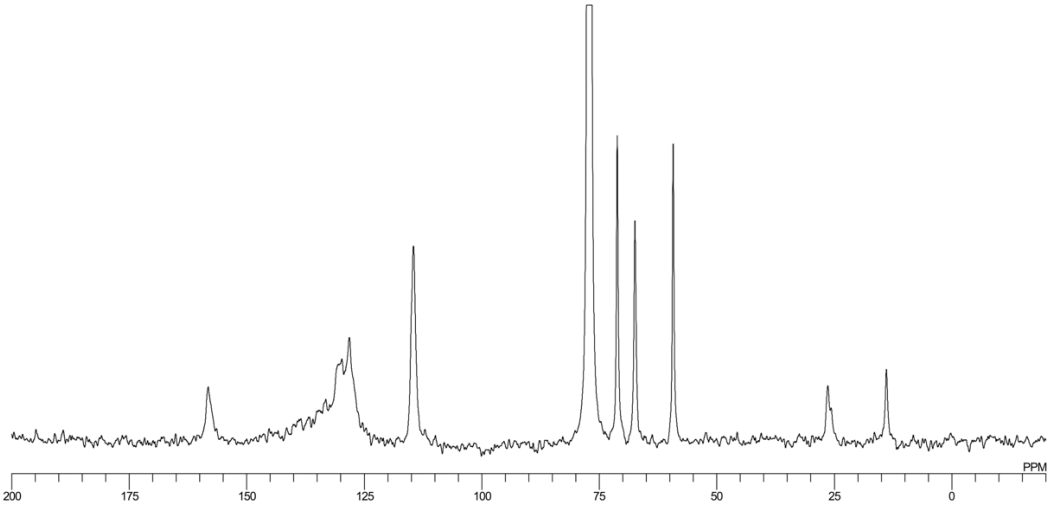


A solution of tetrabutylammonium fluoride (789 mg, 1.25 mmol; trihydrate) in THF (10 mL) was added to a solution of **poly-4b** (262 mg) in THF (10 mL), and the mixture was stirred for 22 h at 60 ºC. After cooled to room temperature, this was washed with H_2O and extracted with toluene. The organic layer was concentrated and this was added dropwise to stirring MeOH (50 mL) with the aid of CH_2Cl_2 (5 mL), and the precipitates that formed were collected by filtration. The resulting solid was dissolved in CH_2Cl_2 (5 mL) and this was added dropwise to stirring hexane (50 mL) with the aid of CH_2Cl_2 (5 mL). The precipitates that formed were collected by filtration and the solid thus obtained was dried under vacuum to afford **poly-7b** as a dark red solid (109 mg; 95% yield). The desilylation efficiency (94%) was estimated by the ^{1}H NMR spectrum.

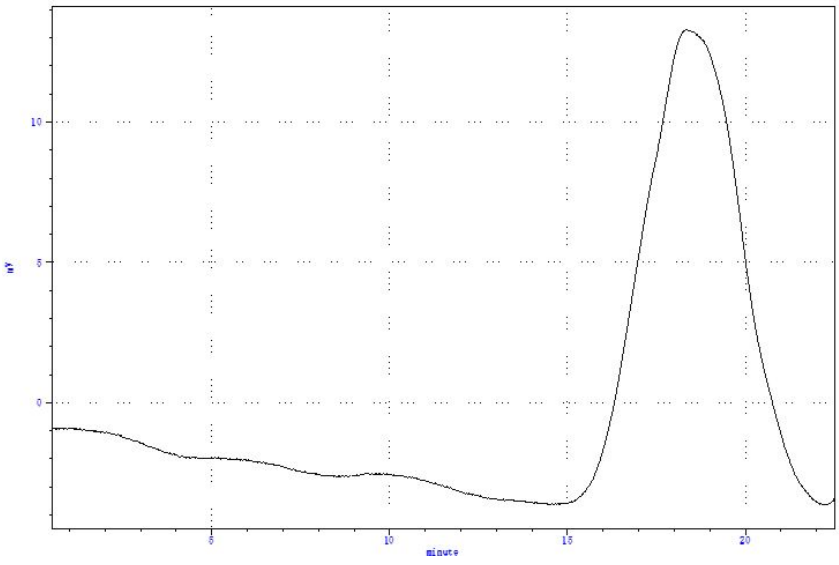
^{1}H NMR (498 MHz in $CDCl_3$)



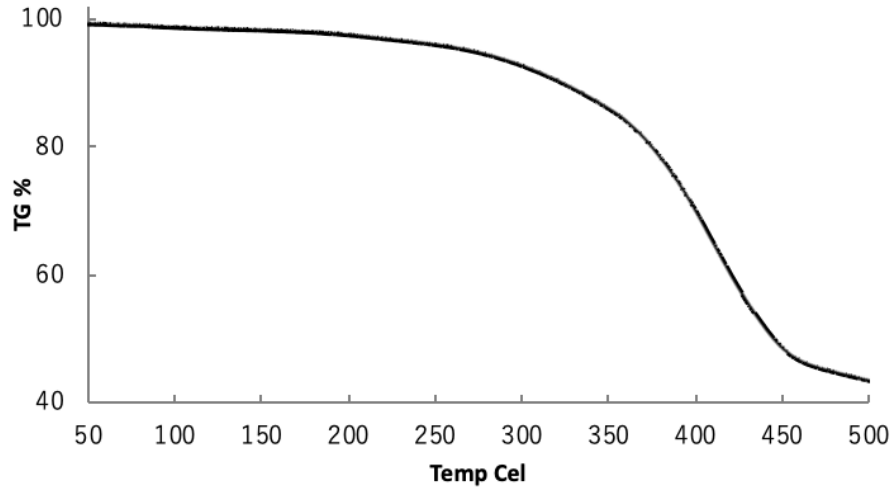
$^{13}C\{^{1}H\}$ NMR (101 MHz in $CDCl_3$)



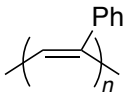
GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)

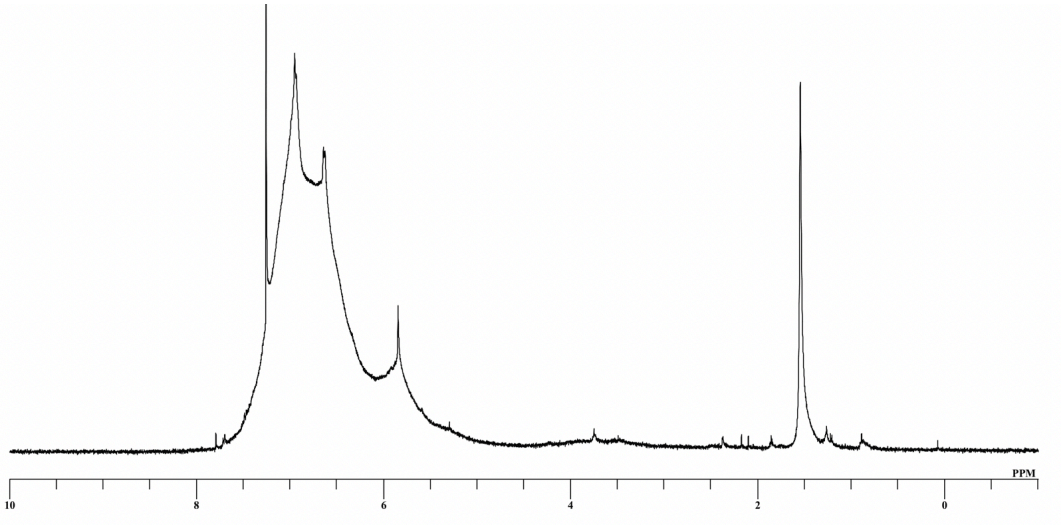


Procedure for Polyphenylacetylene.

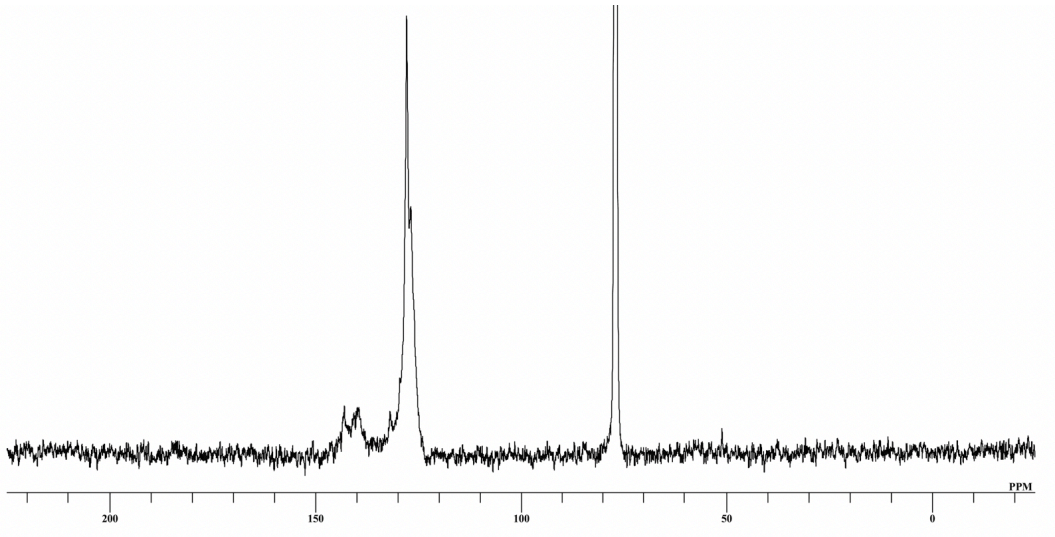


Phenylacetylene (102 mg, 1.00 mmol) and THF (2.0 mL) were added to a solution of $[Rh(OH)(cod)]_2$ (3.4 mg, 15 μmol Rh) in THF (2.0 mL), and the mixture was stirred for 22 h at 60 ºC. This was added dropwise to stirring MeOH (50 mL) with the aid of CH_2Cl_2 (5.0 mL), and the precipitates that formed were collected by filtration and the solid thus obtained was dried under vacuum to afford polyphenylacetylene as a yellow solid (81.4 mg; 80% yield, M_n = 24000, M_w/M_n = 1.8).

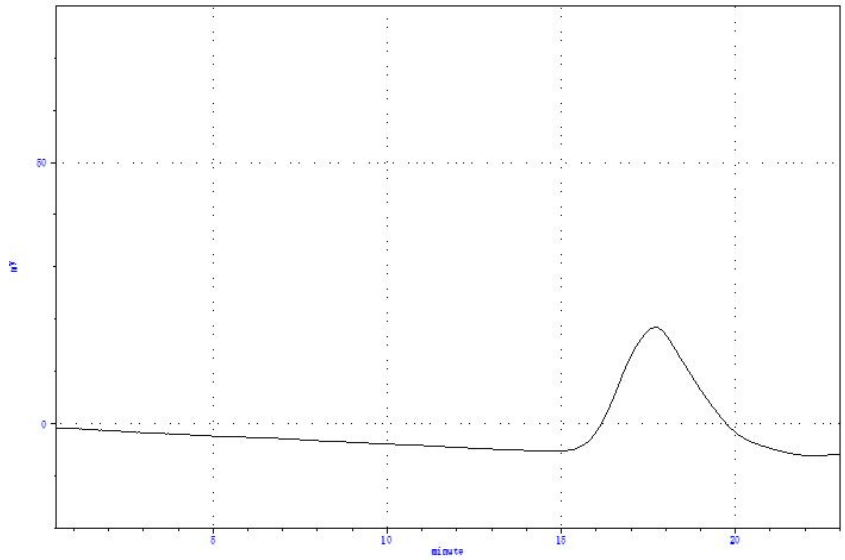
^{1}H NMR (400 MHz in $CDCl_3$)



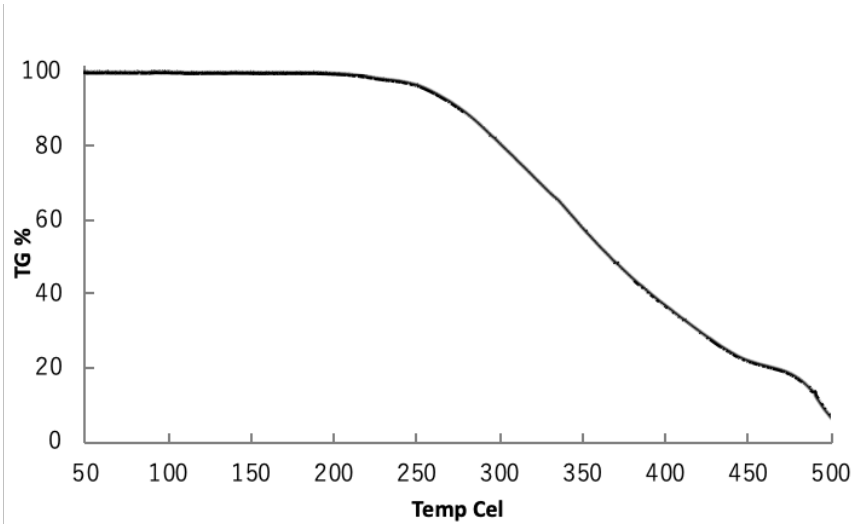
$^{13}C\{^{1}H\}$ NMR (101 MHz in $CDCl_3$)



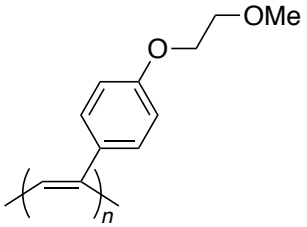
GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)

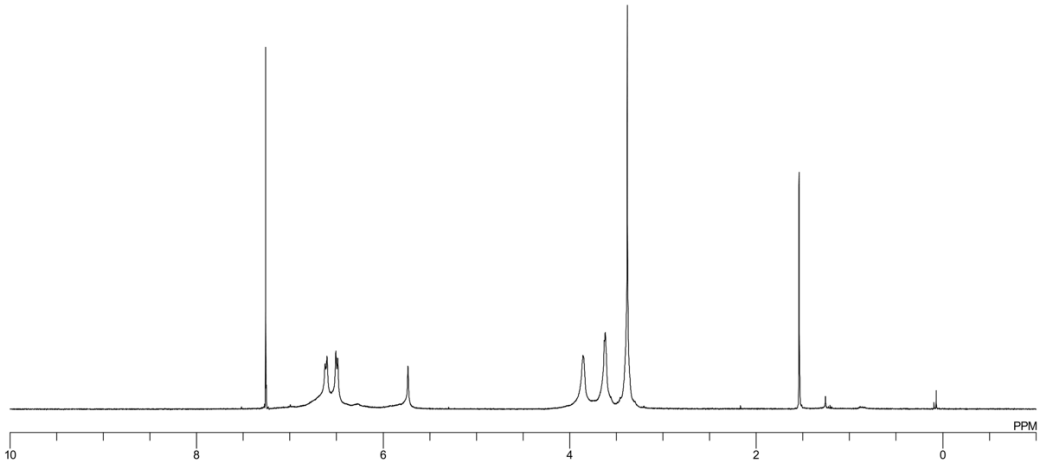


Procedure for Poly(4-(2-methoxyethoxy)phenyl)acetylene.

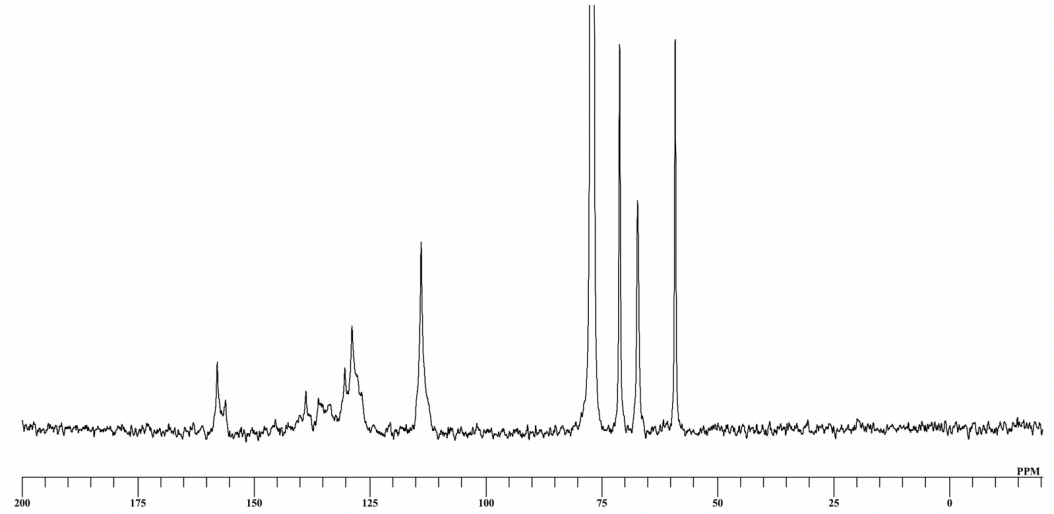


4-(2-Methoxyethoxy)phenylacetylene (88.0 mg, 0.500 mmol) and THF (1.0 mL) were added to a solution of $[Rh(OH)(cod)]_2$ (3.4 mg, 15 mmol Rh) in THF (1.0 mL), and the mixture was stirred for 2 days at room temperature. This was added dropwise to stirring MeOH (50 mL) with the aid of CH_2Cl_2 (5.0 mL), and the precipitates that formed were collected by filtration and the solid thus obtained was dried under vacuum to afford poly(4-(2-methoxyethoxy)phenyl)acetylene as a yellow solid (73.5 mg; 84% yield, M_n = 44000, M_w/M_n = 2.0).

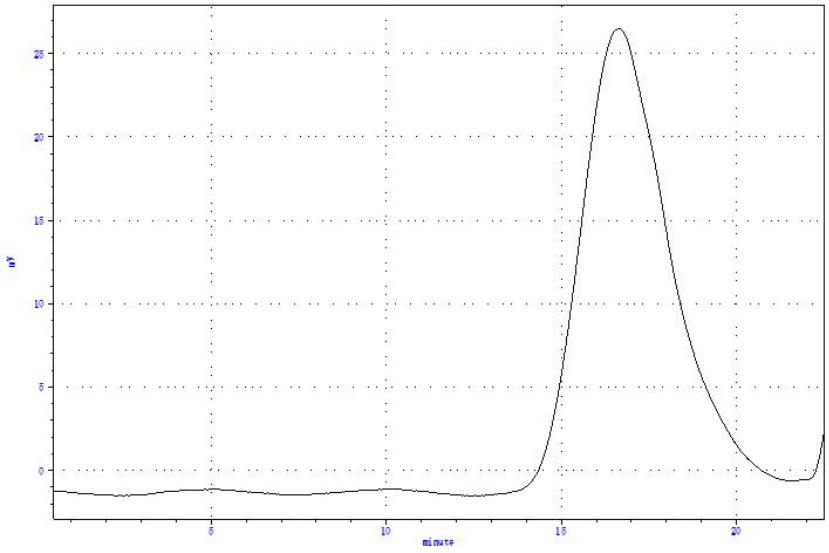
^{1}H NMR (400 MHz in $CDCl_3$)



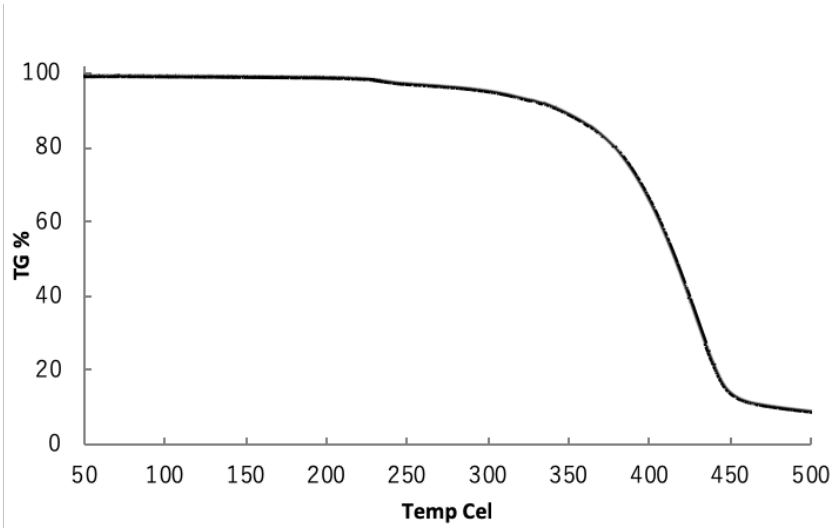
$^{13}C\{^1H\}$ NMR (101 MHz in $CDCl_3$)



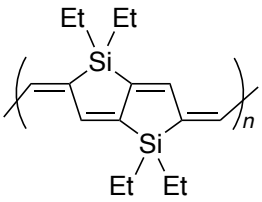
GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)



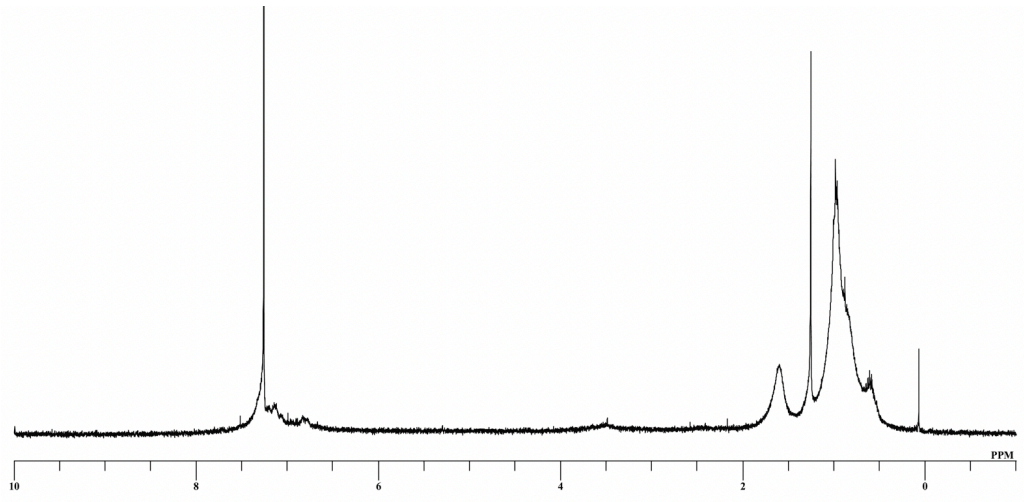
Procedure for Poly-1i.



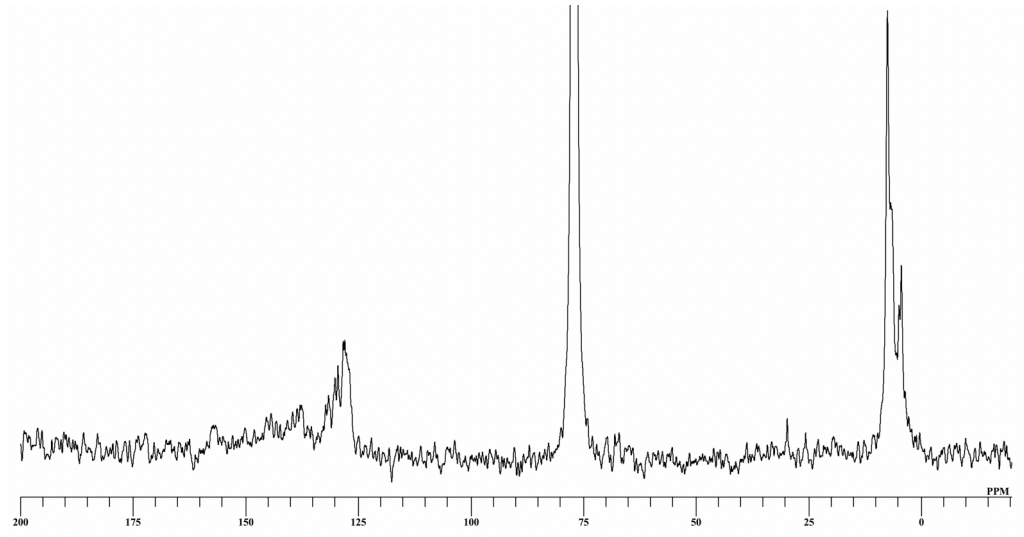
(1,2,2-Triphenylvinyl)lithium (600 µL, 60.0 µmol; 0.10 M solution in toluene) and THF (0.3 mL) were added to a solution of $[RhCl(tfb)]_2$ (10.9 mg, 30.0 µmol Rh) in THF (0.2 mL). This was stirred for 5 min at room temperature and monomer **1i** (34.0 mg, 0.250 mmol) was added with the aid of THF (0.5 mL). The mixture was stirred for 22 h at room temperature, and this was added dropwise to stirring MeOH (50 mL) with the aid of CH_2Cl_2 (5.0 mL). The precipitates that formed were collected by filtration and the solid thus obtained was dried under vacuum to afford **poly-1i** as a purple solid (32.0

mg; 94% yield, M_n = 3300, M_w/M_n = 2.5).

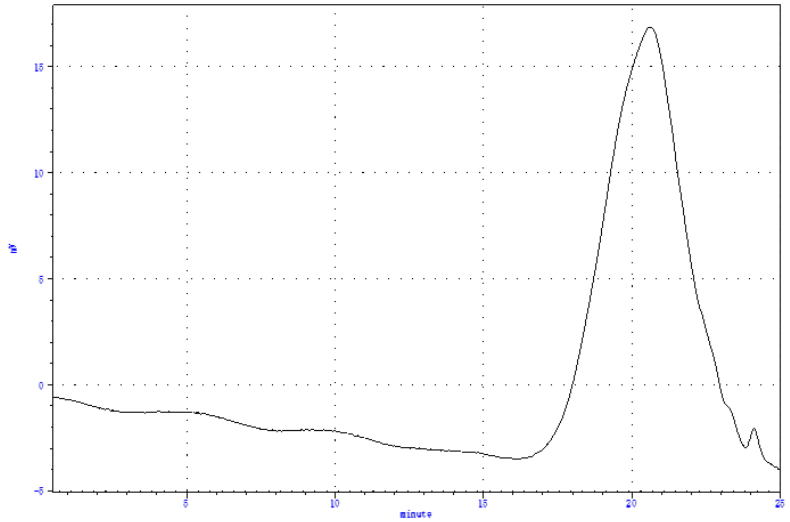
^{1}H NMR (400 MHz in $CDCl_3$)



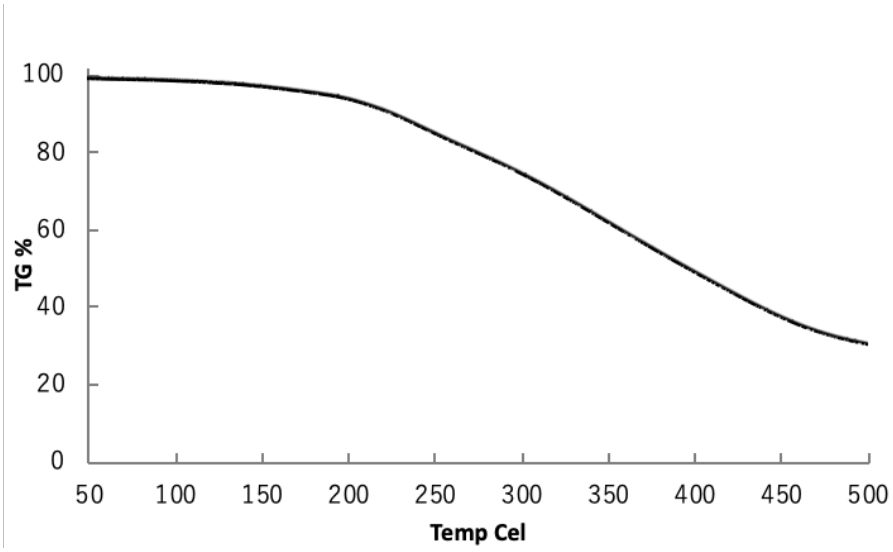
$^{13}C\{^1H\}$ NMR (101 MHz in $CDCl_3$)



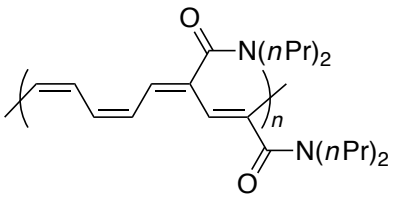
GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)



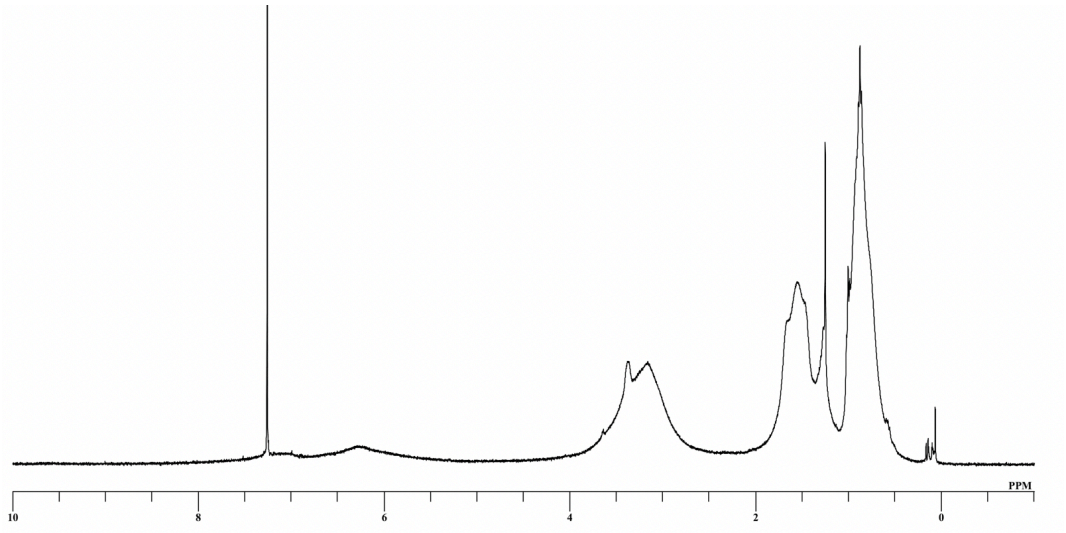
Procedure for Poly-6j.



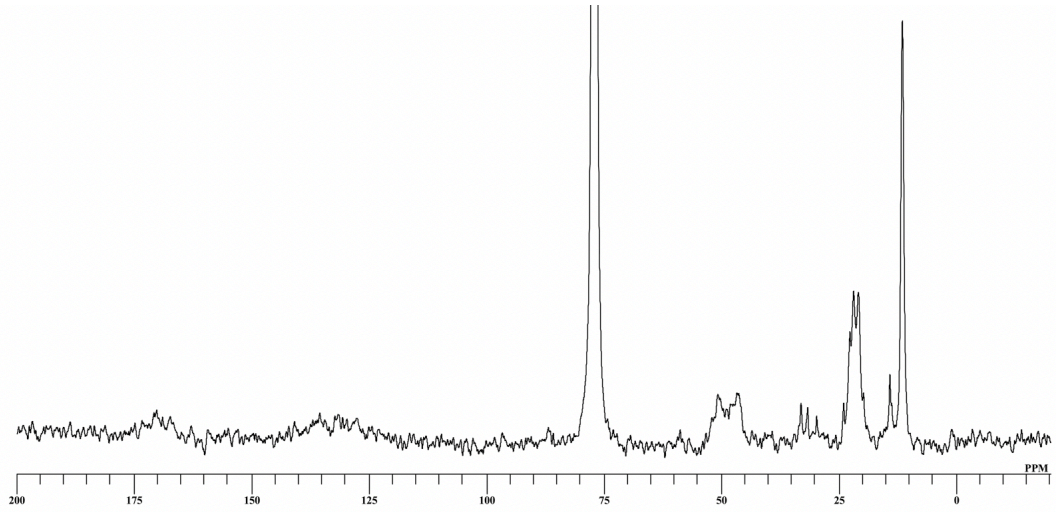
Triethylamine (41.8 μL, 300 μmol) and THF (1.2 mL) were added to a solution of $[RhCl(tfb)]_2$ (10.9 mg, 30.0 μmol Rh) in THF (0.8 mL). This was stirred for 5 min at 20 ºC and monomer **1j** (376 mg, 1.00 mmol) was added with the aid of THF (2.0 mL). The mixture was stirred for 22 h at 20 ºC and this was added dropwise to stirring MeOH (50 mL) with the aid of CH_2Cl_2 (5.0 mL). The precipitates that formed were collected by filtration and the solid thus obtained was dried under vacuum to afford **poly-1j** as a purple solid (291 mg; 78% yield, M_n = 33000, M_w/M_n = 1.9).

A solution of tetrabutylammonium fluoride (197 mg, 0.625 mmol; trihydrate) in THF (5 mL) was added to a solution of **poly-1j** (93.9 mg) in THF (5 mL), and the mixture was stirred for 22 h at 60 ºC. After cooled to room temperature, this was washed with H_2O and extracted with toluene. The organic layer was concentrated and this was added dropwise to stirring hexane (50 mL) with the aid of CH_2Cl_2 (5 mL). The precipitates that formed were collected on Celite with hexane, and this was dissolved in CH_2Cl_2 and concentrated under vacuum to afford **poly-6j** as a dark red solid (40.1 mg; 83% yield, M_n = 6000, M_w/M_n = 2.4).

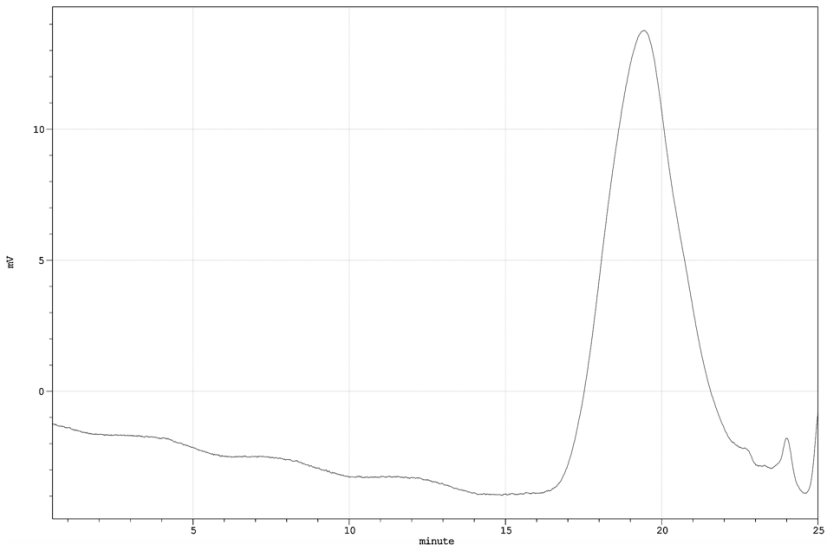
^{1}H NMR (400 MHz in $CDCl_3$)



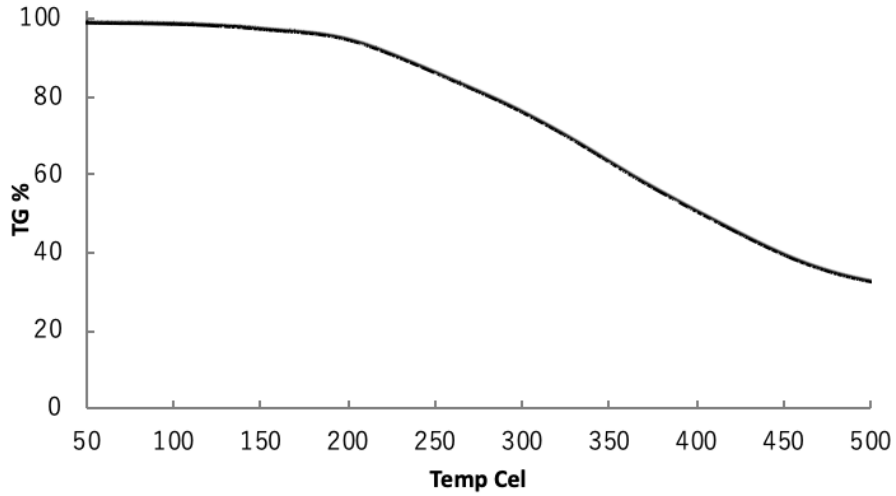
$^{13}C\{^{1}H\}$ NMR (101 MHz in $CDCl_3$)



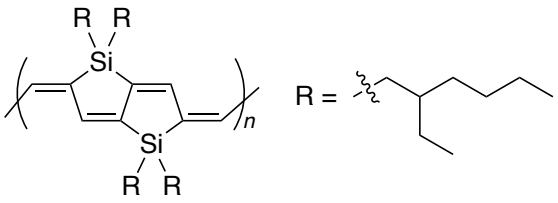
GPC (THF; 1.0 mL/min flow)



TG (+10 ºC/min from 50 ºC to 500 ºC)



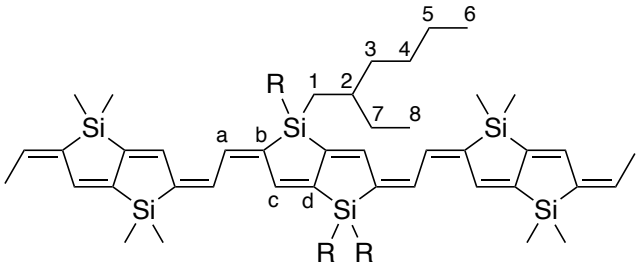
IV. Structural Consideration



poly-1e

The structures of polymer repeating units were analyzed by using the ^{1}H and ^{13}C NMR data of **poly-1e** coupled with the DFT calculations of model compound **S1** in Table S1. For the ^{1}H NMR spectrum shown in Figure S1, two broad singlets at 7.34 ppm and 6.82 ppm were assigned as alkenyl protons $\mathbf{H^{c}}$ and $\mathbf{H^{a}}$ on the main chain, respectively, and the alkyl protons were also consistent with the 2-ethylhexyl signals as indicated by black, blue, and red marks. For the ^{13}C NMR spectrum shown in Figure S2, sp^{2}-carbon signals at 158, 146, 139, and 129 ppm were assigned as alkenyl carbons **d**, **b**, **c**, and **a**, respectively, and the alkyl carbons were also consistent with the 2-ethylhexyl signals. In overall, the polymer repeating units can be concluded as drawn through the expected stitching polymerization.

Table S1. Calculated ^{1}H and ^{13}C NMR chemical shifts of compound **S1** (in ppm, calculated at the B3LYP/6-31G(d) level of theory).



S1 (R = 2-ethylhexyl)

	a	**b**	**c**	**d**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
^{1}H	6.92	—	7.22	—	0.90	1.67	1.45	1.50	1.33	0.95	1.43	1.01
^{13}C	123.9	139.5	133.6	152.7	23.2	37.8	38.0	32.7	26.2	16.4	35.0	14.7

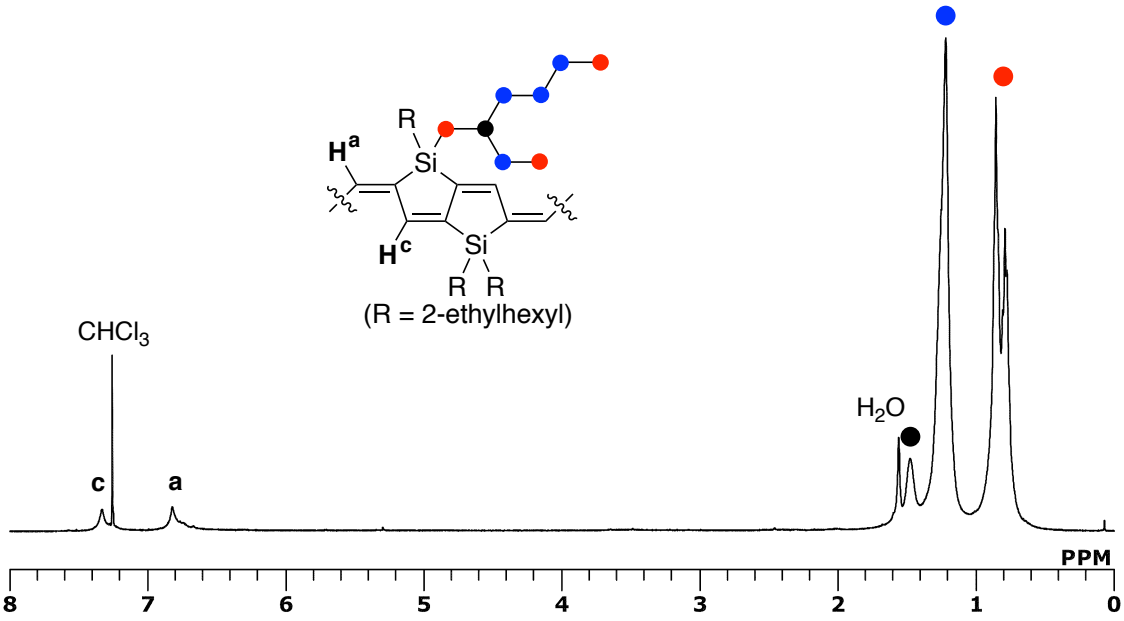


Figure S1. [1]H NMR signal assignment for **poly-1e**.

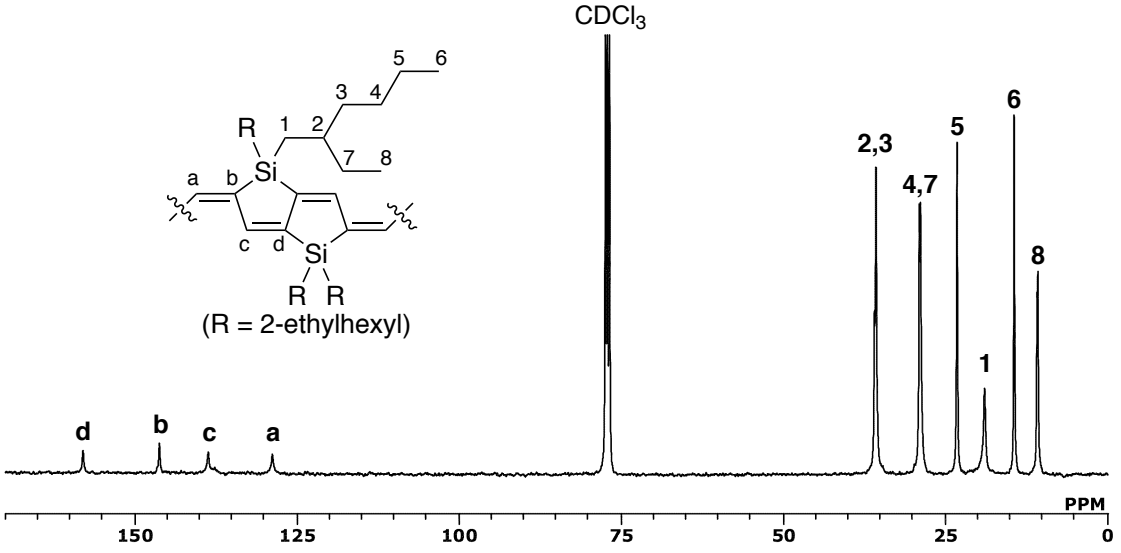
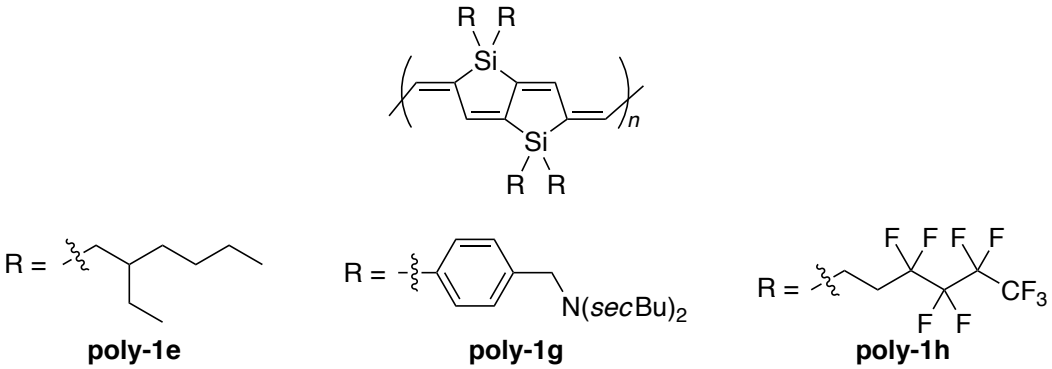


Figure S2. [13]C NMR signal assignment for **poly-1e**.

V. Solubility Control



Solubility of **poly-1** can be controlled by the substituents on the silicon atoms. While **poly-1e** having 2-ethylhexyl groups is soluble in typical organic solvents such as hexane and CH_2Cl_2 (1.0 g/L) and insoluble in aqueous phase, **poly-1g** having amino groups is soluble in diluted aqueous hydrochloric acid (1.0 g/L in 0.05 M HClaq). On the other hand, **poly-1h** having polyfluoroalkyl groups is soluble in perfluorohexane (4.0 g/L) over CH_2Cl_2.

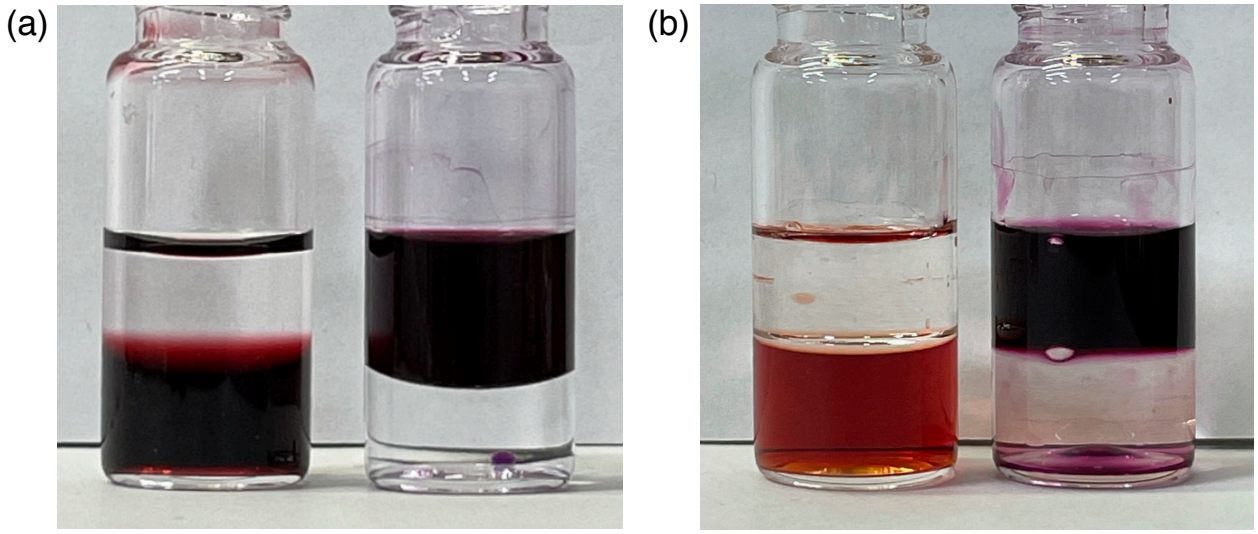
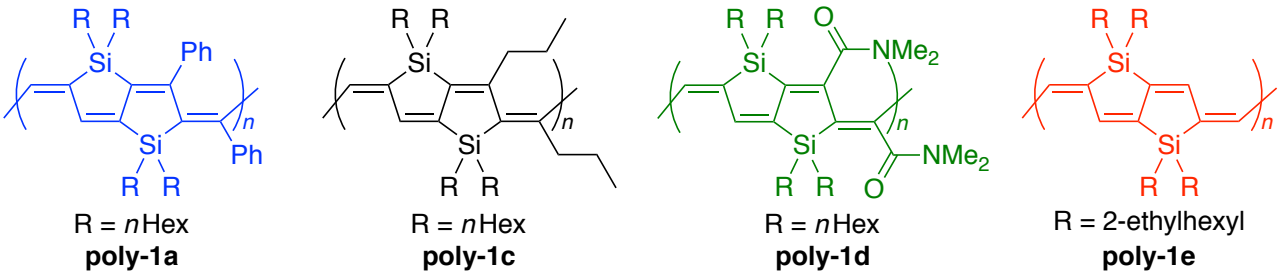


Figure S3. Photographs of solutions: (a) left **poly-1g** in 0.05 M HClaq (bottom phase) with hexane (top phase); right **poly-1e** in hexane (top phase) with 0.05 M HClaq (bottom phase). (b) left **poly-1h** in perfluorohexane (bottom phase, d = 1.67) with CH_2Cl_2 (top phase, d = 1.33); right **poly-1e** in CH_2Cl_2 (top phase) with perfluorohexane (bottom phase).

VI. Additional UV-vis Absorption Spectra



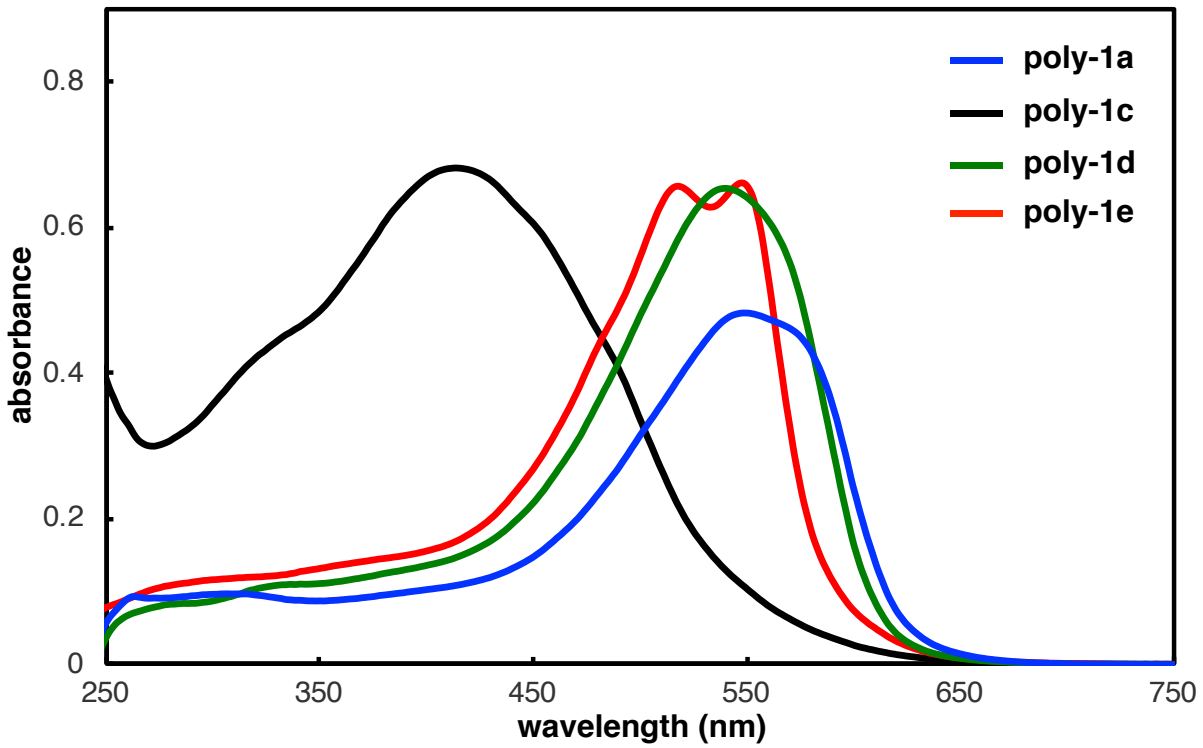
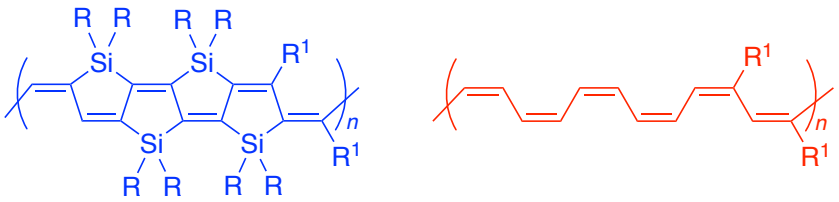


Figure S4. UV-vis spectra of **poly-1a** (blue; at 1.6 x 10^{-2} g/L), **poly-1c** (black; at 2.9 x 10^{-2} g/L), and **poly-1d** (green; at 1.2 x 10^{-2} g/L), and **poly-1e** (red; at 1.3 x 10^{-2} g/L) in THF at 25 °C.

VII. Cyclic Voltammograms



poly-4b **poly-7b**

(R^1 = 4-MeO$(CH_2)_2OC_6H_4$, R = *n*Bu)

Electrochemical analysis was conducted by cyclic voltammetry for silicon-bridged **poly-4b** and protodesilylated **poly-7b**. As shown in Figure S5, the oxidation potential of **poly-4b** (E_{ox}^{onset} = 0.75 V) is lower than that of **poly-7b** (E_{ox}^{onset} = 1.25 V), and the reduction potential of **poly-4b** (E_{red}^{onset} = –2.20 V) is higher than that of **poly-7b** (E_{red}^{onset} = –2.35 V). These results indicate that the HOMO–LUMO energy gap is narrower for **poly-4b** compared with **poly-7b**, which is consistent with the UV-vis absorption spectra in Figure 3 in the manuscript.

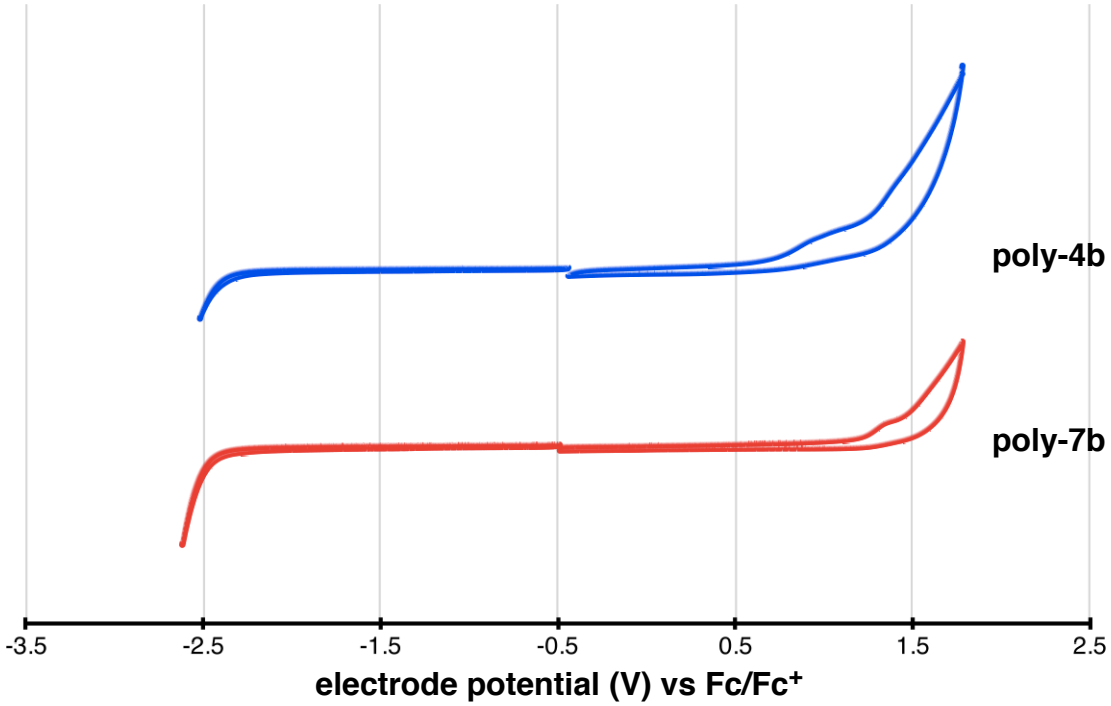
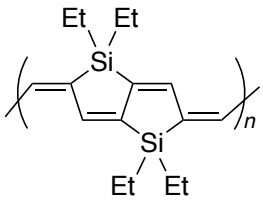


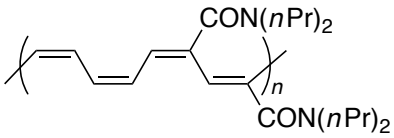
Figure S5. Cyclic voltammograms of **poly-4b** (blue) and **poly-7b** (red) containing 0.1 M $(n\text{Bu})_4NBF_4$ as the supporting electrolyte, Ag/Ag^+ as the reference electrode, glassy carbon as the working electrode, Pt plate as the counter electrode, and a scan rate of 100 mV/s. The oxidation potential and the reduction potential were measured at room temperature under nitrogen in CH_2Cl_2. The potential was externally calibrated against the ferrocene/ferrocenium couple.

VIII. Electrical Conductivity



poly-1i

σ = 1.0 x 10^{-8} S/cm (I_2 doping)



poly-6j

σ = 1.3 x 10^{-6} S/cm (I_2 doping)

Electrical conductivity of **poly-1i** and **poly-6j** was determined by measuring the electrical resistance and the film thickness of the polymer thin films. Polymer thin films were prepared by dropping the polymer solution (10 mg/mL in CH_2Cl_2) on the electrode and the films were exposed to iodine vapor for 1 day. For the resistance measurement, two-terminal sensing was used for **poly-1i** and four-terminal sensing was used for **poly-6j** under floating conditions.

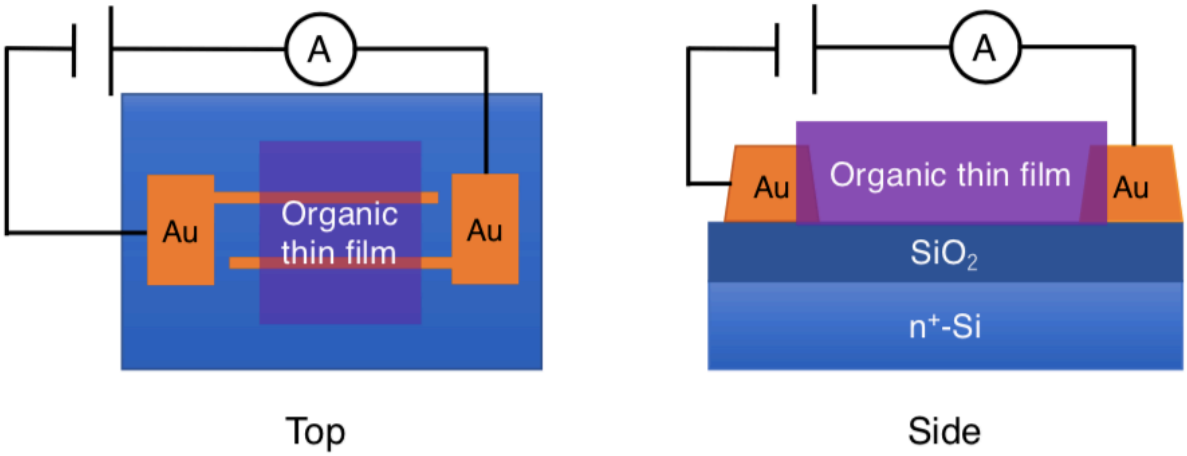
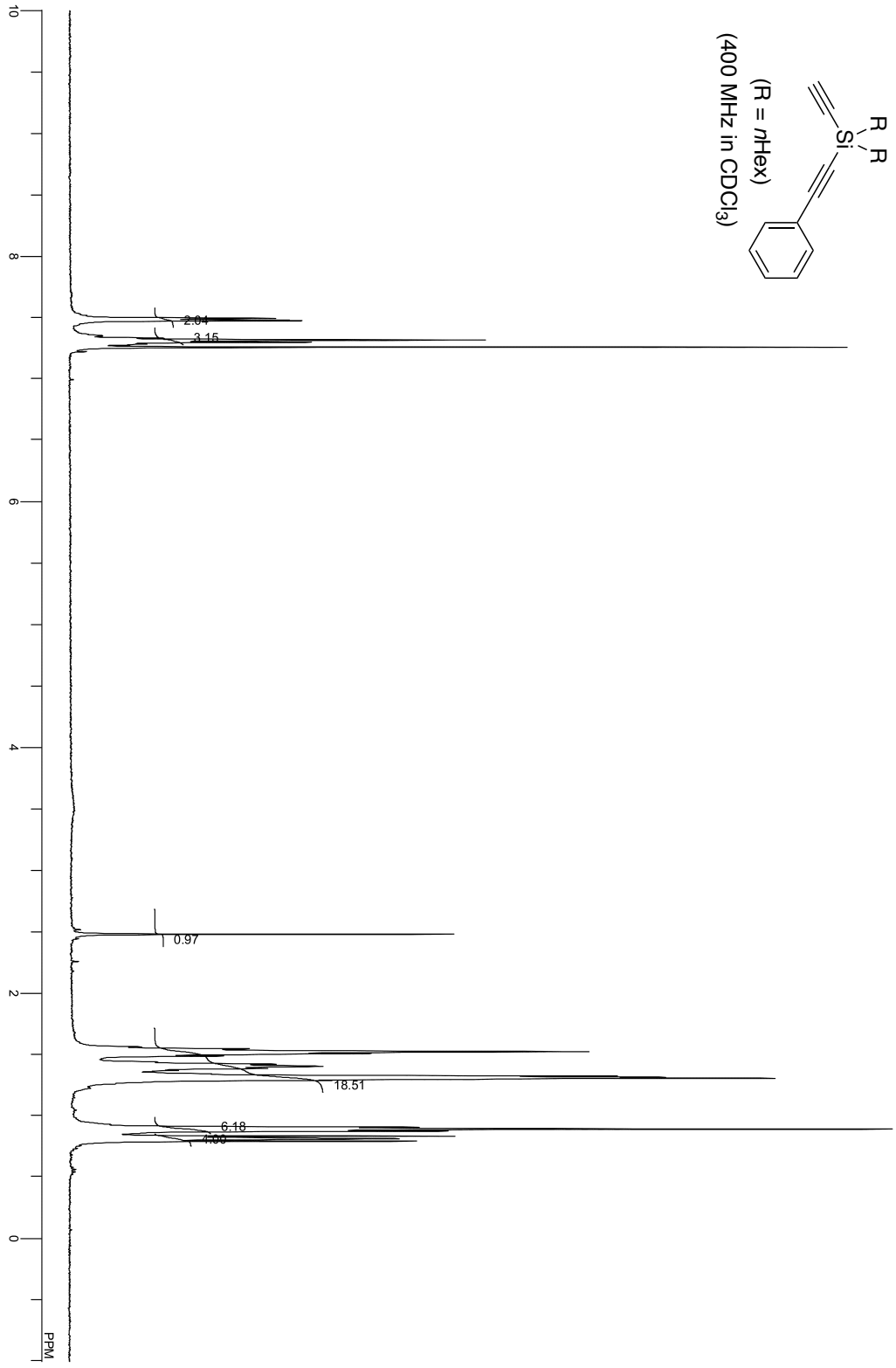


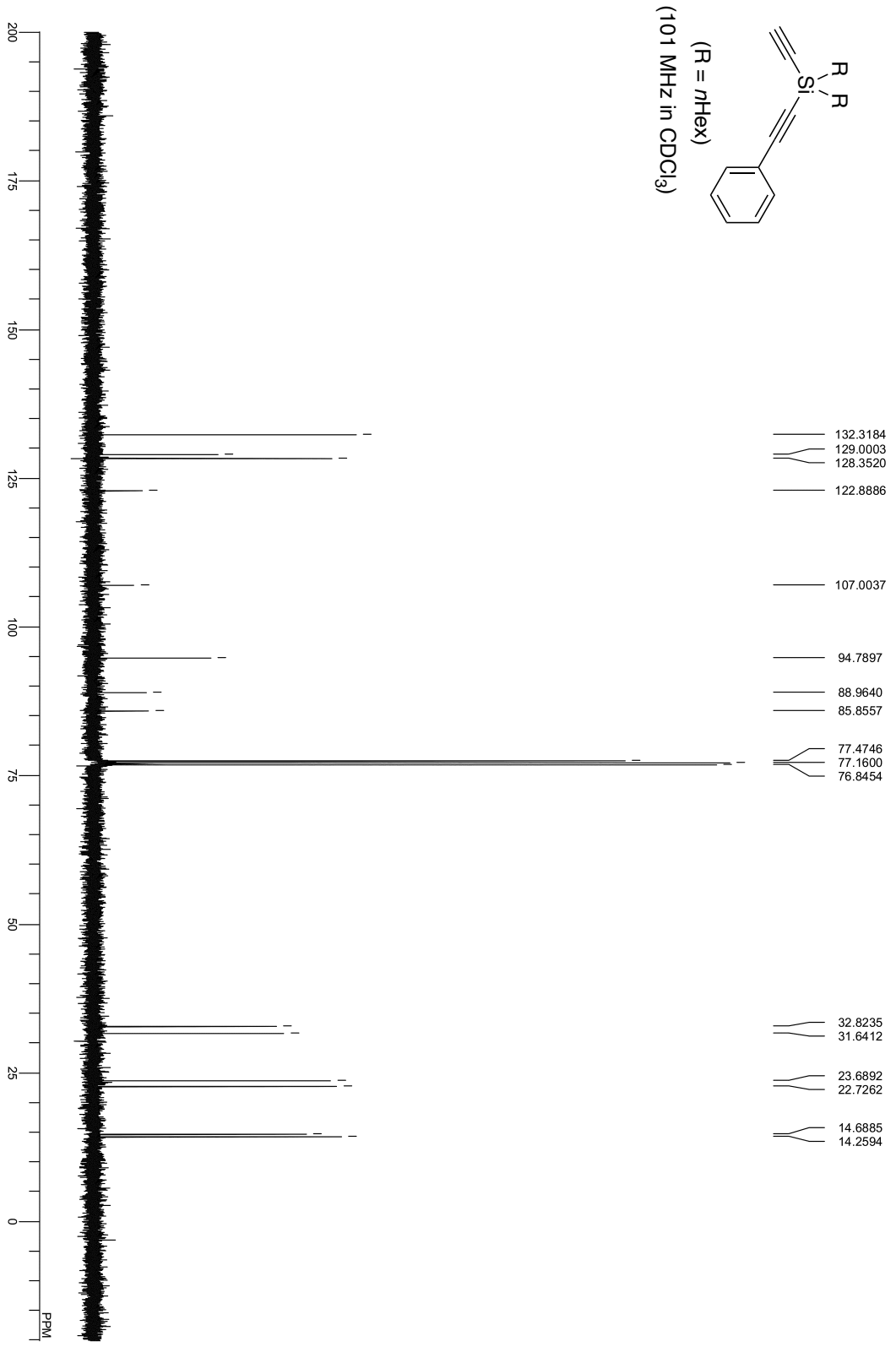
Figure S6. Illustrations of the set-up for the resistance measurement (left: top view, right: side view).

IX. ^{1}H and ^{13}C NMR Spectra of Monomers

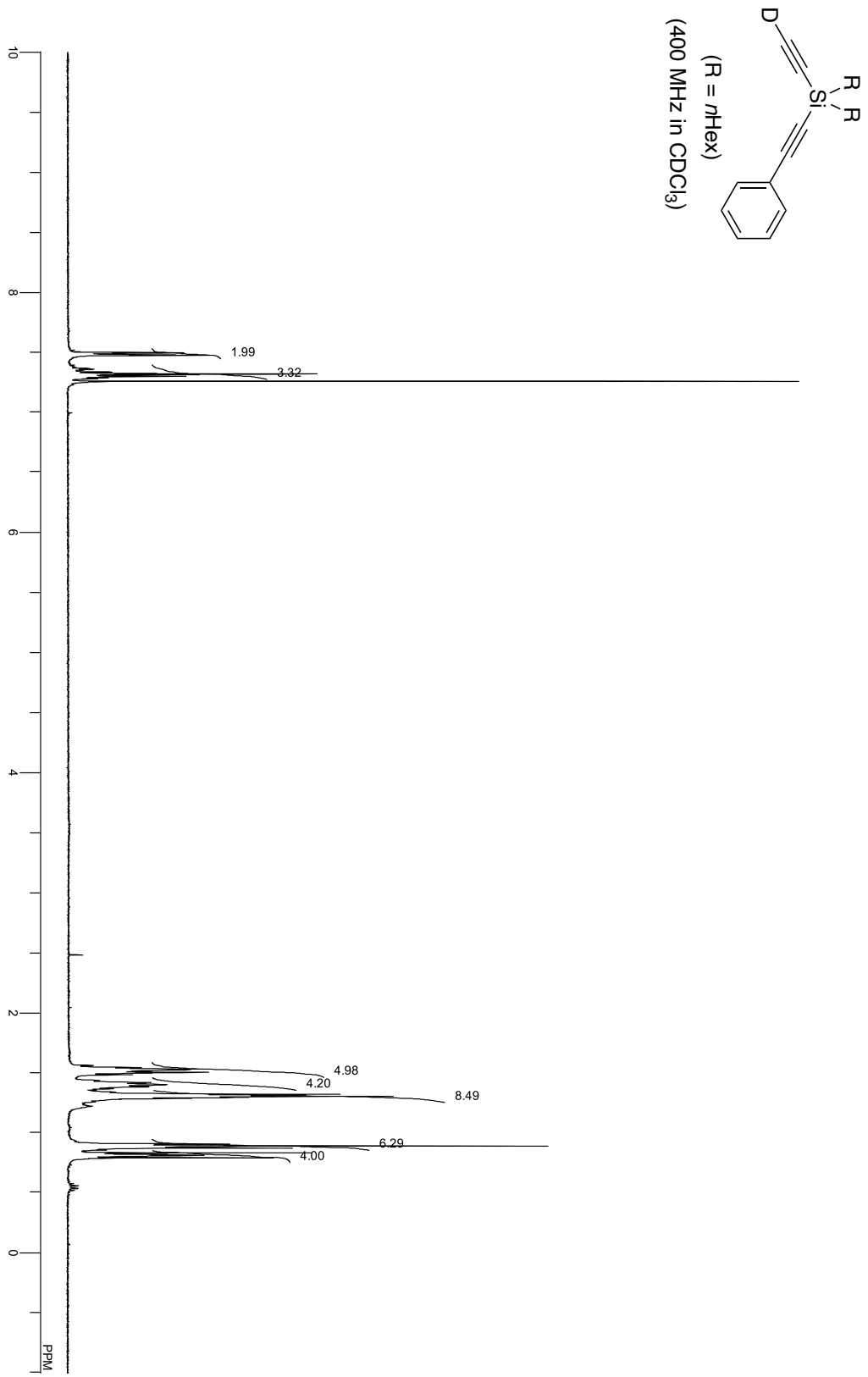
compound **1a**



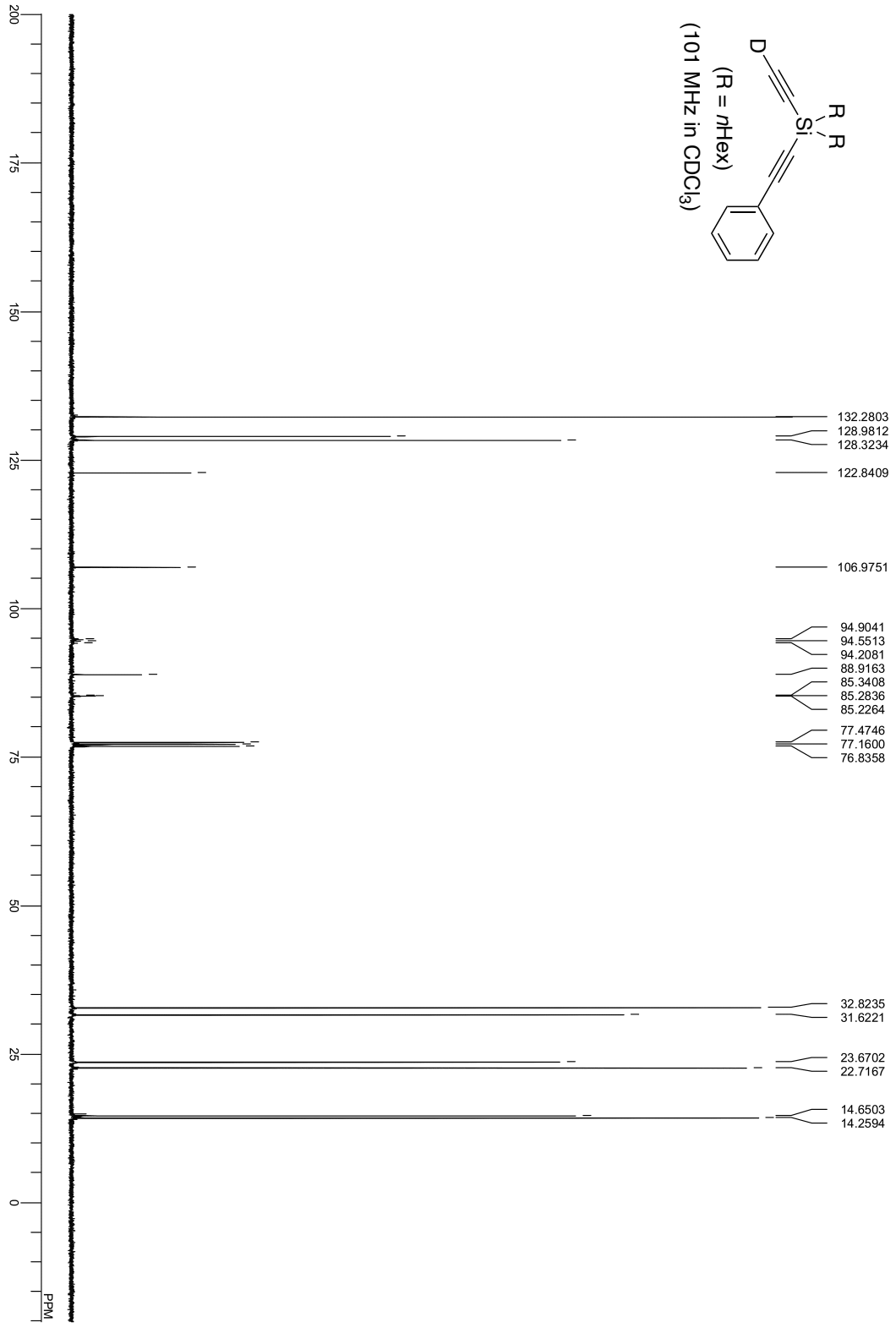
compound **1a**


(R = nHex)
(101 MHz in CDCl3)
Si
R R
132.3184
129.0003
128.3520
122.8886
107.0037
94.7897
88.9640
85.8557
77.4746
77.1600
76.8454
32.8235
31.6412
23.6892
22.7262
14.6885
14.2594
200
175
150
125
100
75
50
25
0
PPM

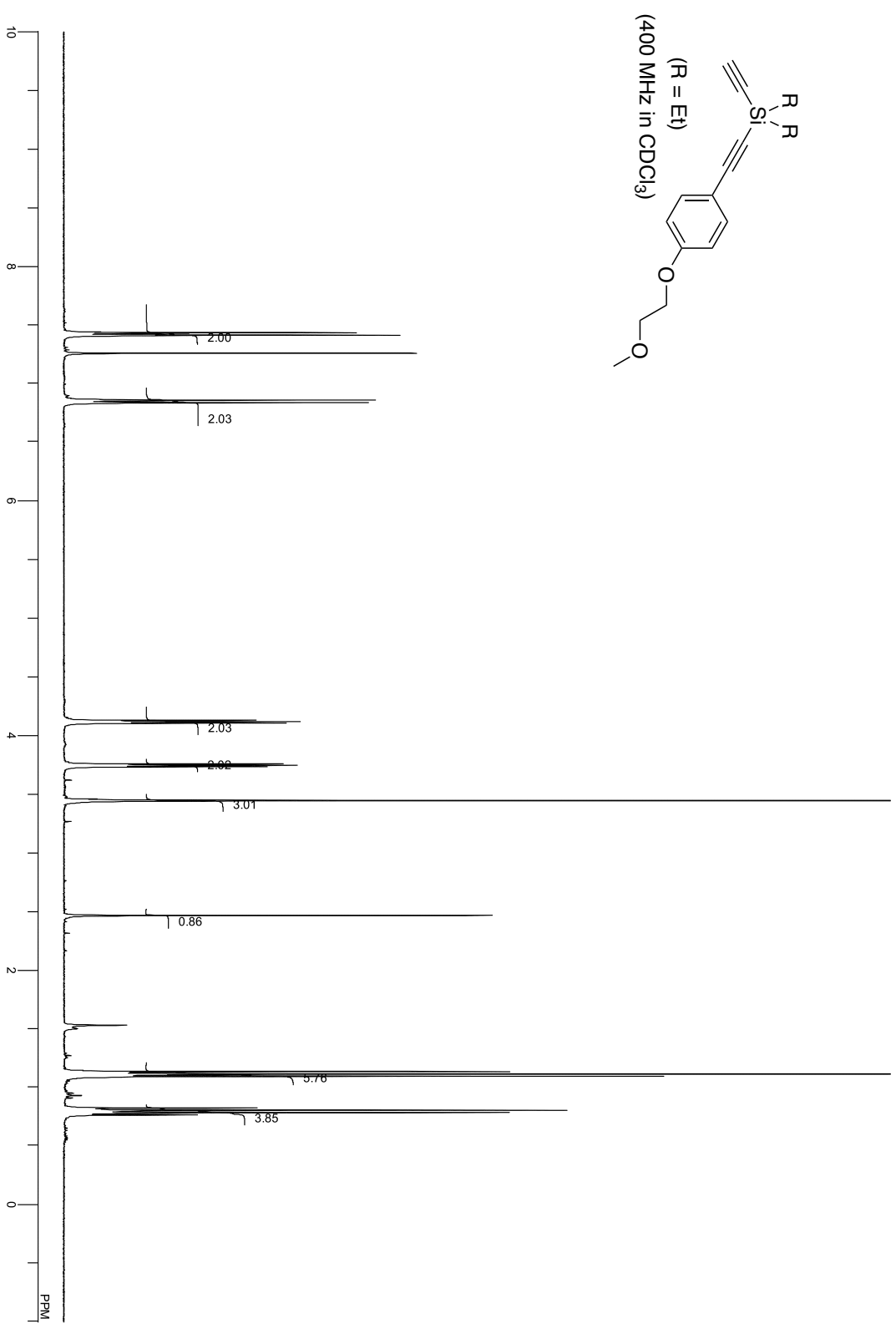
compound **1a-*d***



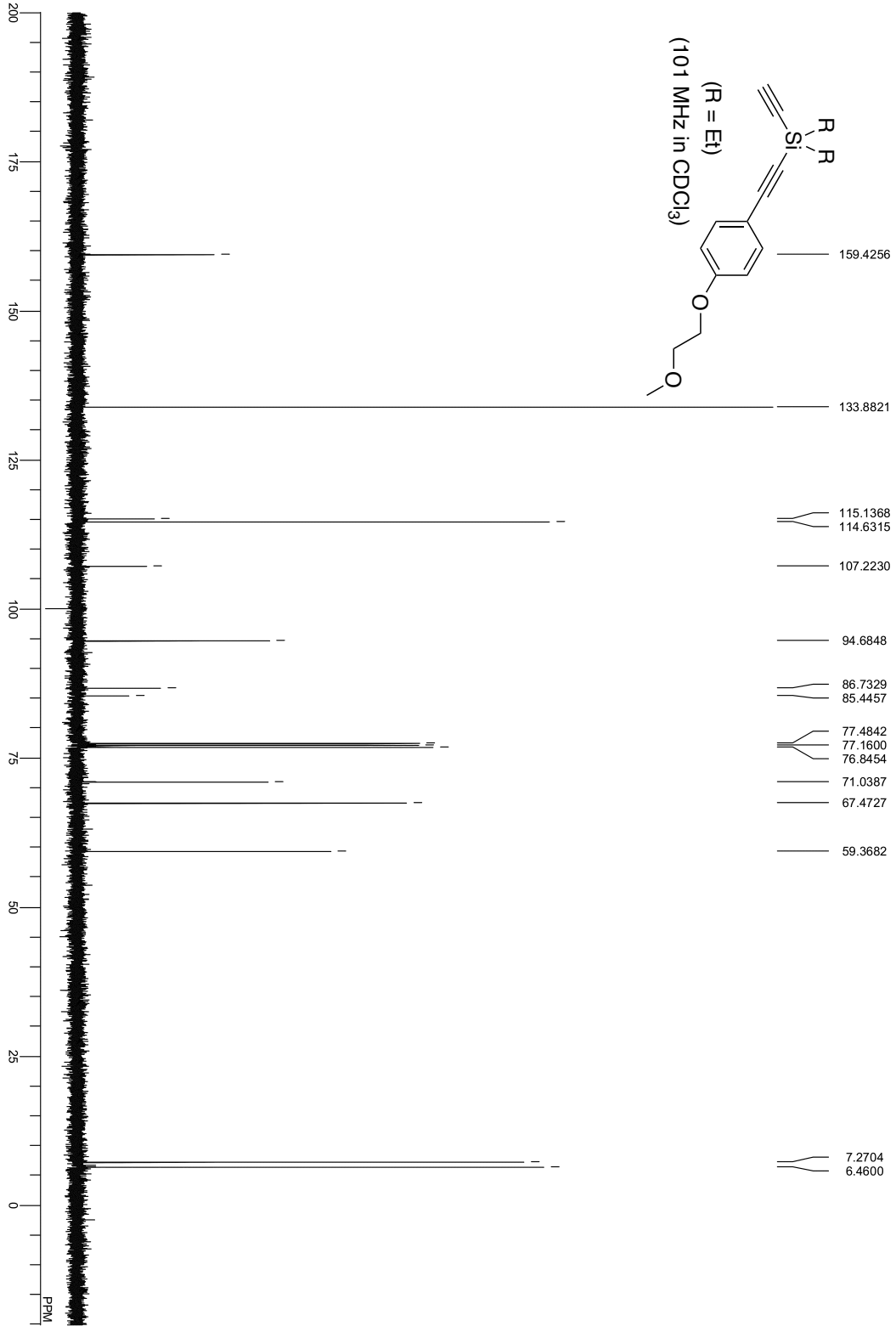
compound **1a-*d***



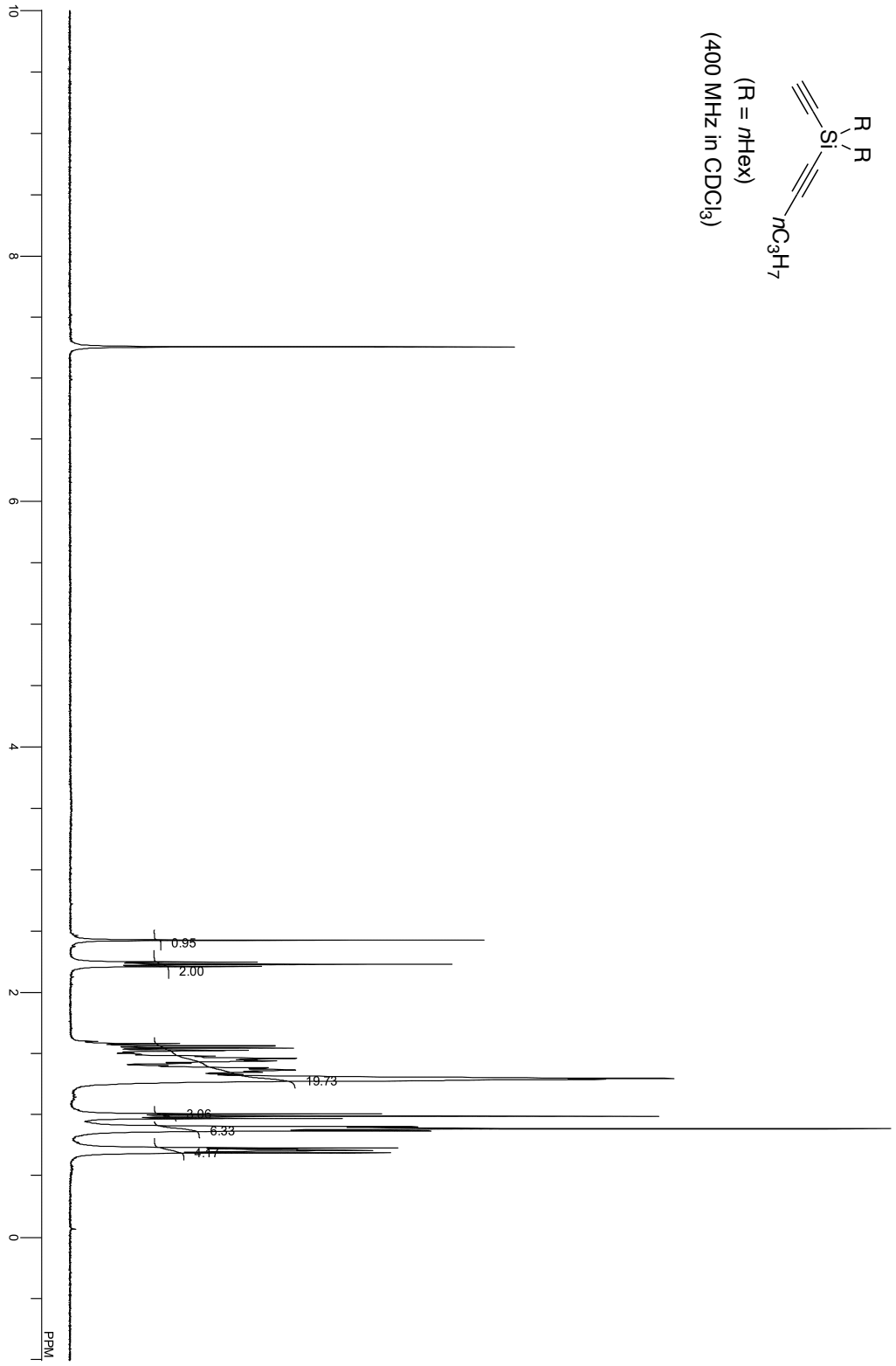
compound **1b**


(400 MHz in CDCl3)
(R = Et)
R R
Si
O
O
10
8
6
4
2
0
PPM
2.00
2.03
2.03
2.02
3.01
0.86
5.76
3.85

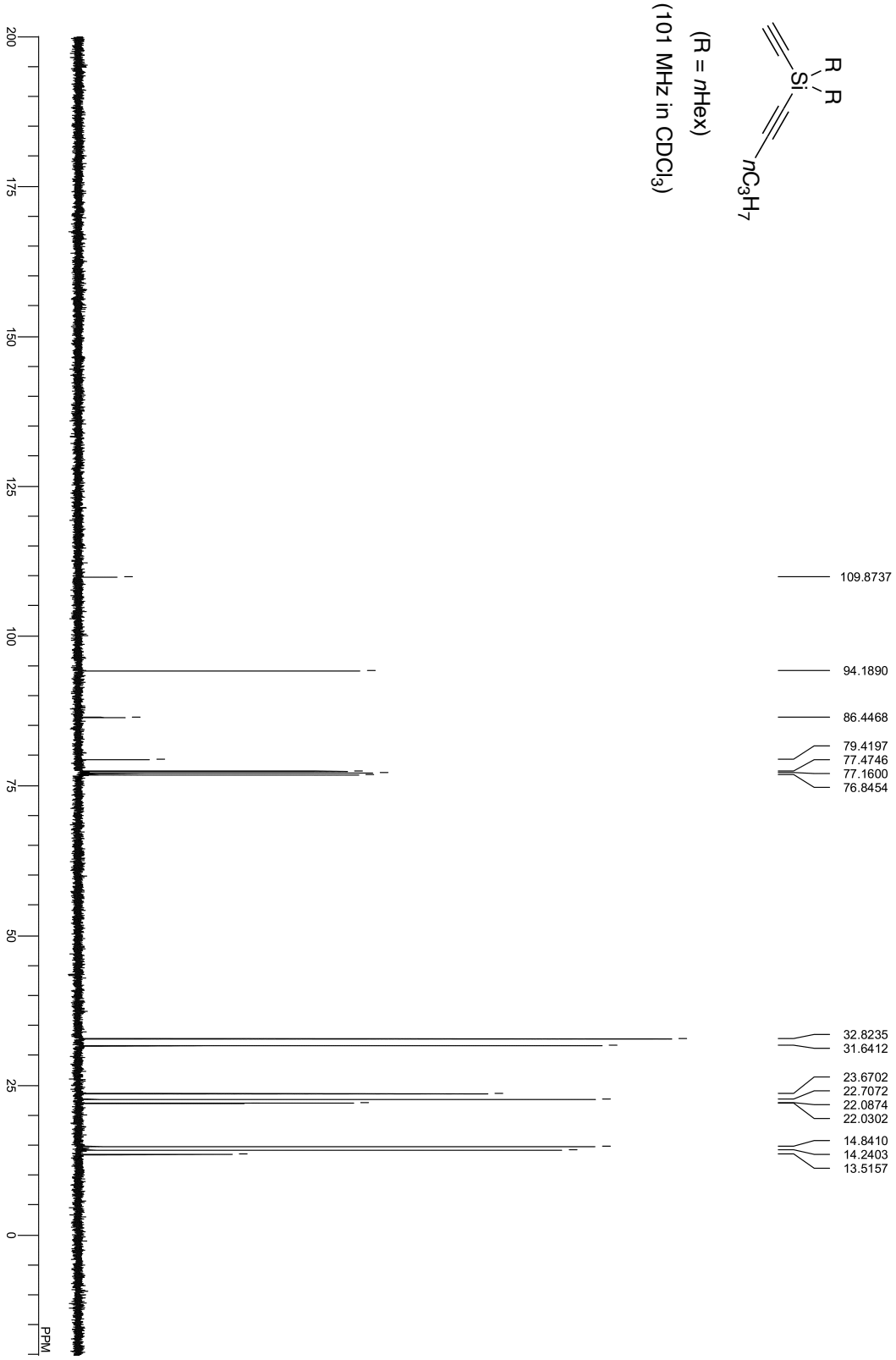
compound **1b**


(101 MHz in CDCl3)
(R = Et)
R R
Si
O
O
159.4256
133.8821
115.1368
114.6315
107.2230
94.6848
86.7329
85.4457
77.4842
77.1600
76.8454
71.0387
67.4727
59.3682
7.2704
6.4600
200
175
150
125
100
75
50
25
0
PPM

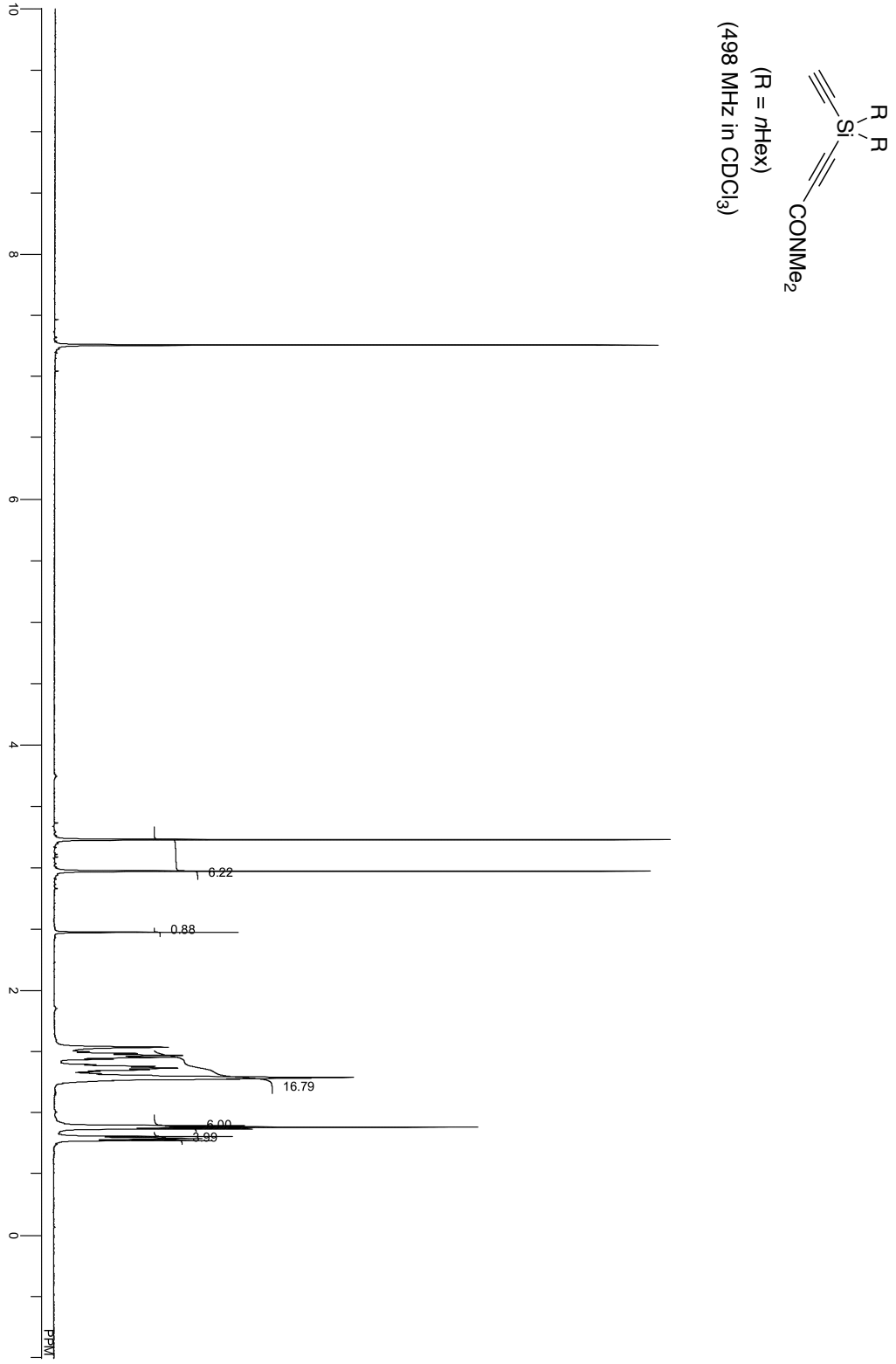
compound **1c**


R R
Si
nC3H7
(R = nHex)
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
0.95
2.00
19.73
3.06
6.33
4.17

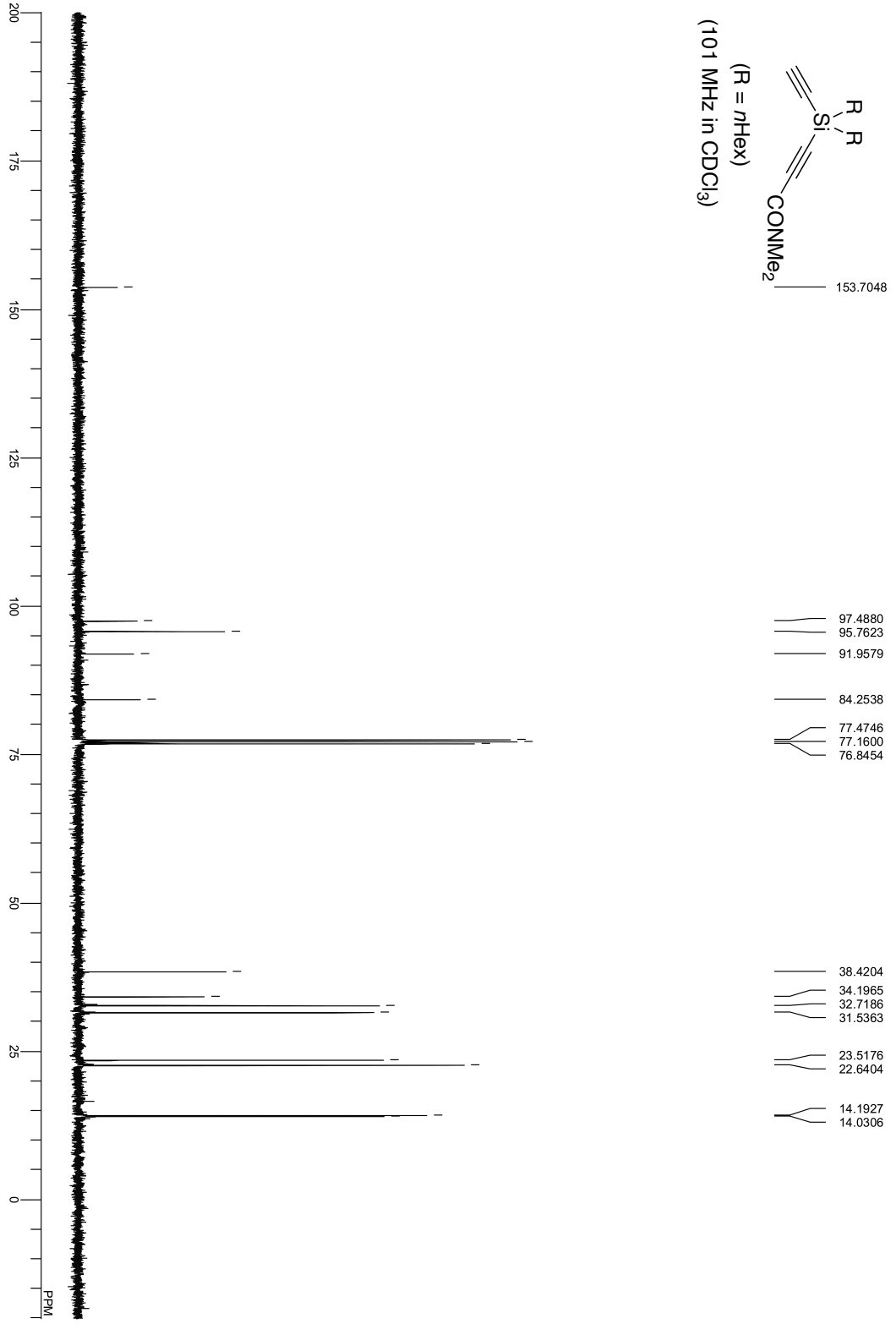
compound **1c**


(101 MHz in CDCl3)
(R = nHex)
R R
Si
nC3H7
200
175
150
125
100
75
50
25
0
PPM
109.8737
94.1890
86.4468
79.4197
77.4746
77.1600
76.8454
32.8235
31.6412
23.6702
22.7072
22.0874
22.0302
14.8410
14.2403
13.5157

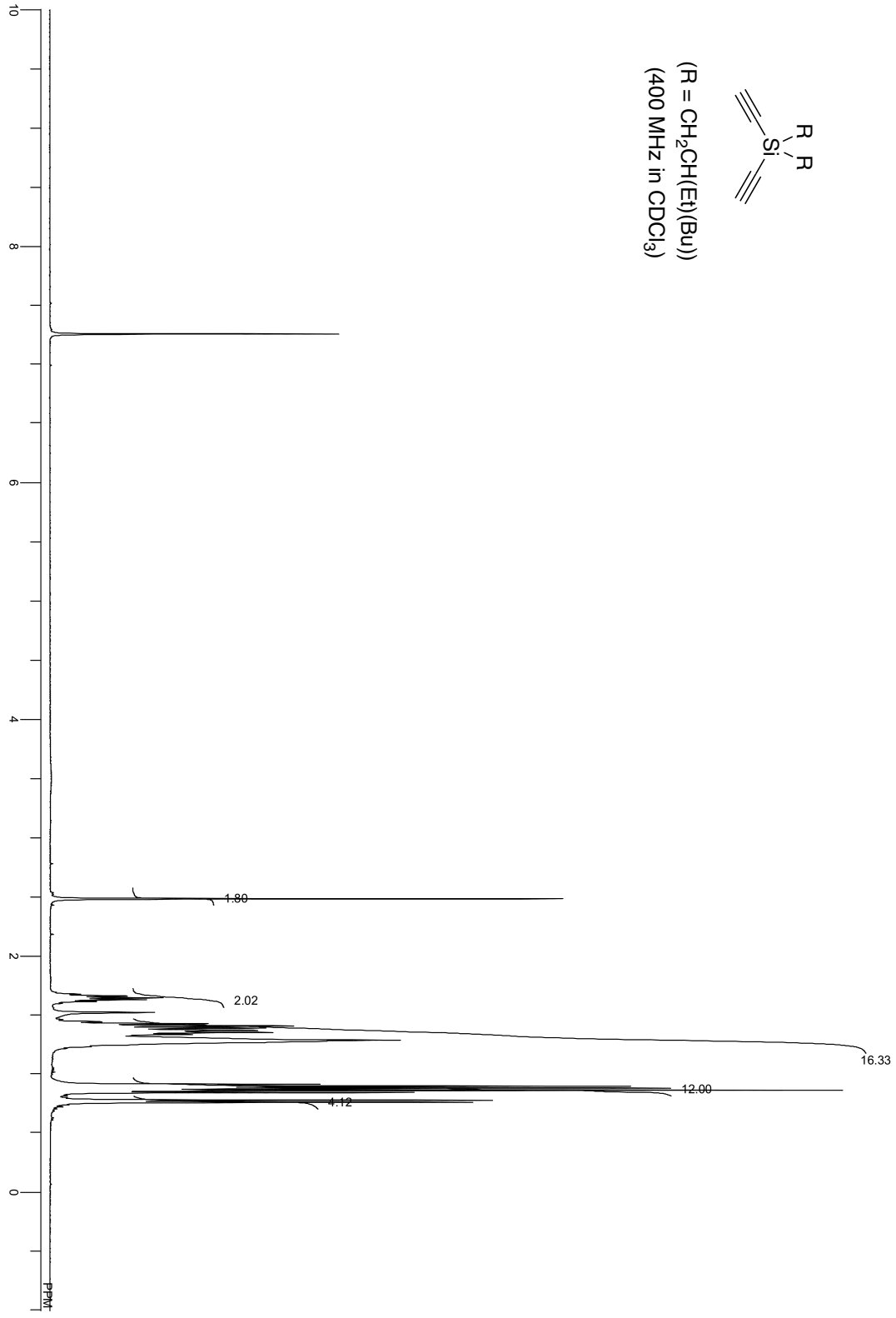
compound **1d**


R R
Si
CONMe2
(R = nHex)
(498 MHz in CDCl3)
10
8
6
4
2
0
PPM
6.22
0.88
16.79
6.00
3.99

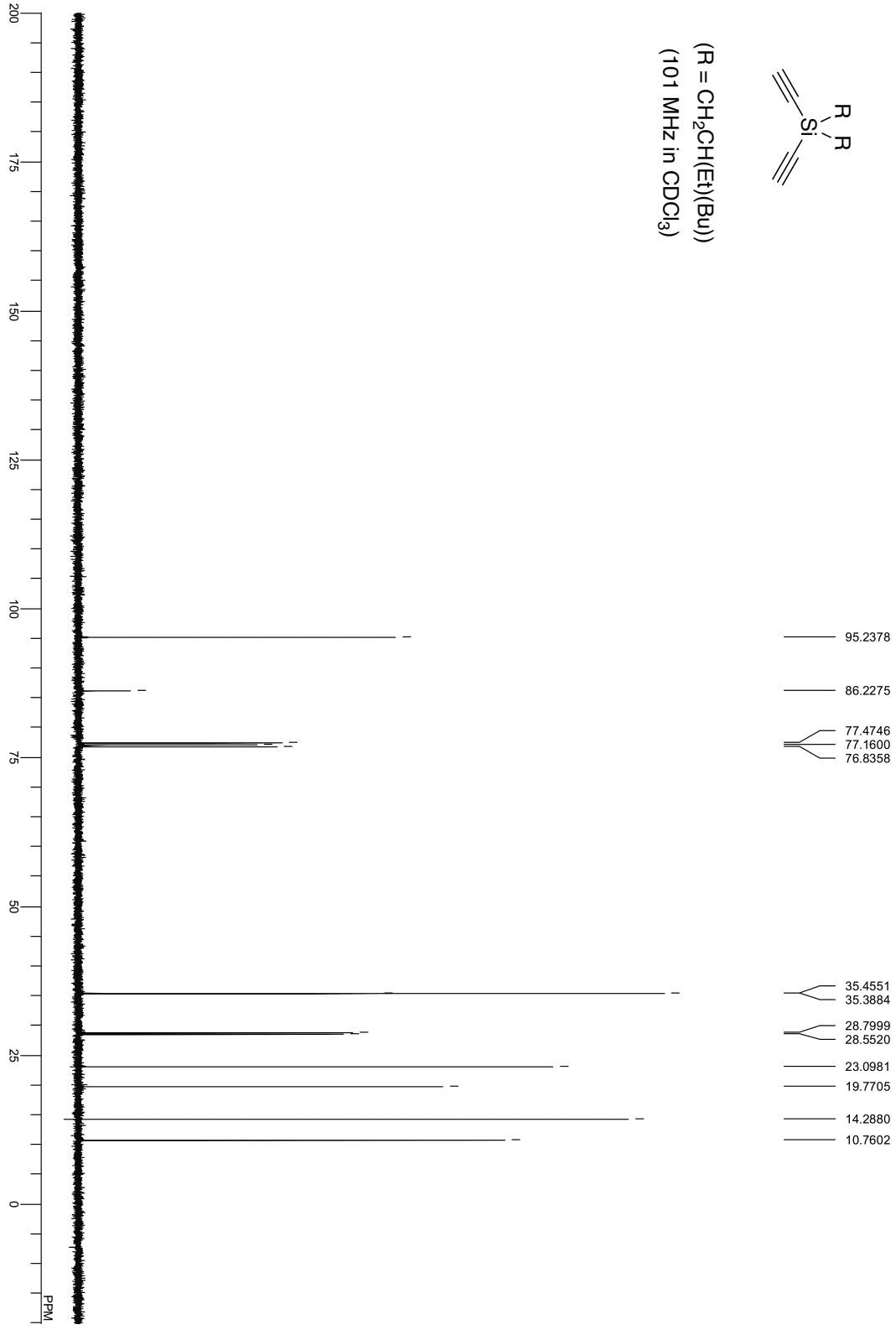
compound **1d**


(R = nHex)
(101 MHz in CDCl3)
Si
R R
CONMe2
153.7048
97.4880
95.7623
91.9579
84.2538
77.4746
77.1600
76.8454
38.4204
34.1965
32.7186
31.5363
23.5176
22.6404
14.1927
14.0306
200
175
150
125
100
75
50
25
0
PPM

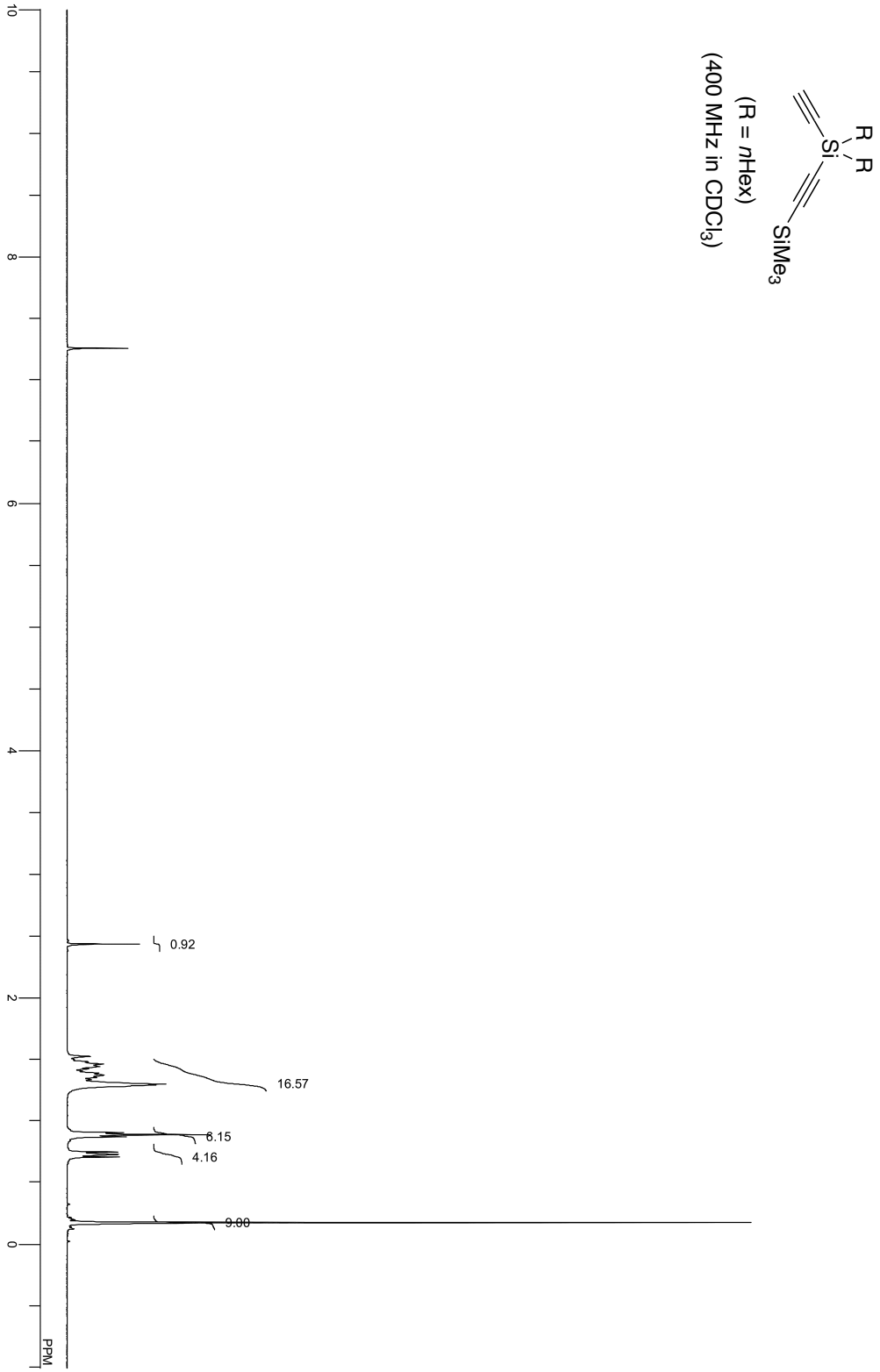
compound **1e**


(R = CH2CH(Et)(Bu))
(400 MHz in CDCl3)
R R
Si
10
8
6
4
2
0
PPM
1.80
2.02
16.33
12.00
4.12

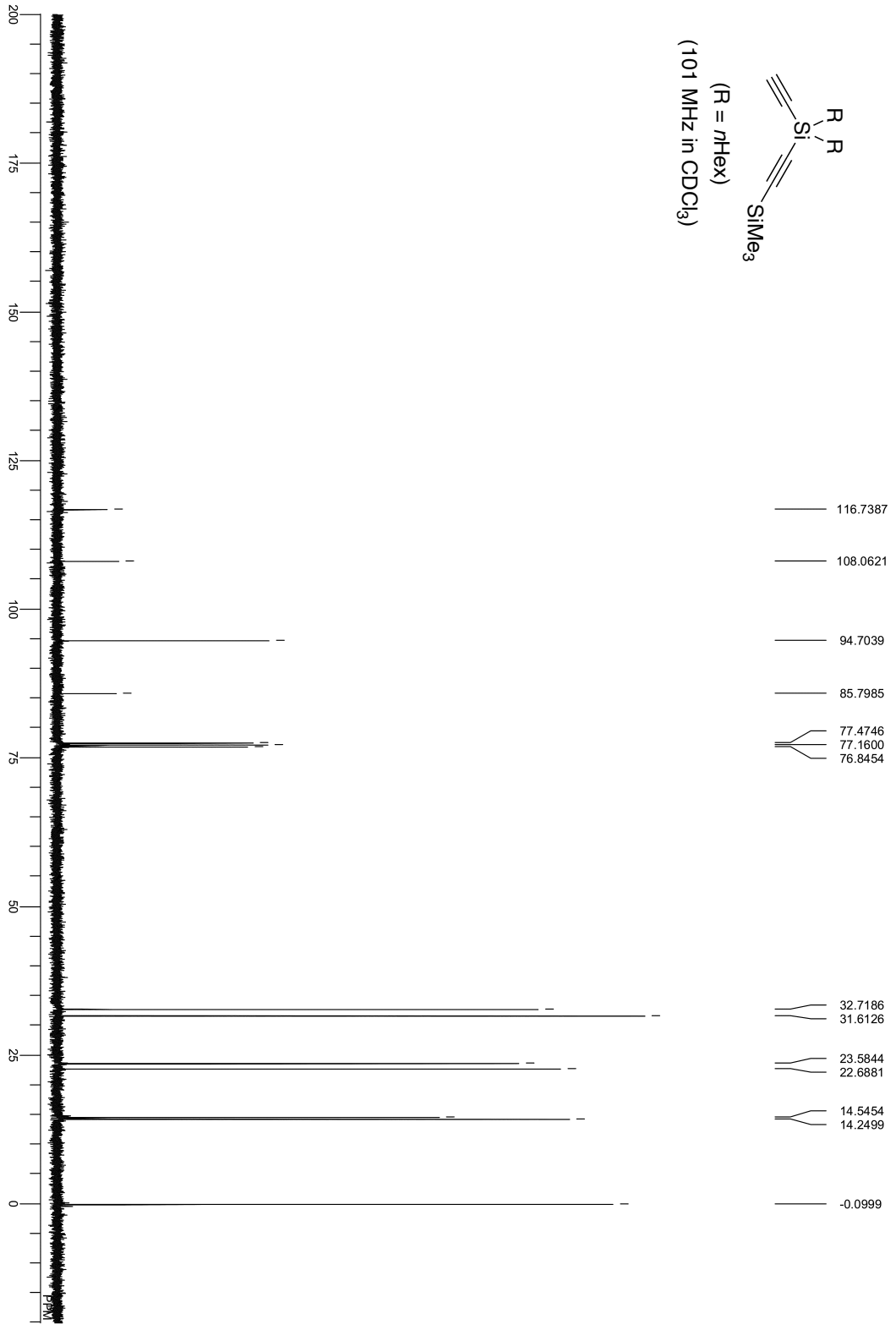
compound **1e**


(R = CH2CH(Et)(Bu))
(101 MHz in CDCl3)
R R
Si
95.2378
86.2275
77.4746
77.1600
76.8358
35.4551
35.3884
28.7999
28.5520
23.0981
19.7705
14.2880
10.7602
200
175
150
125
100
75
50
25
0
PPM

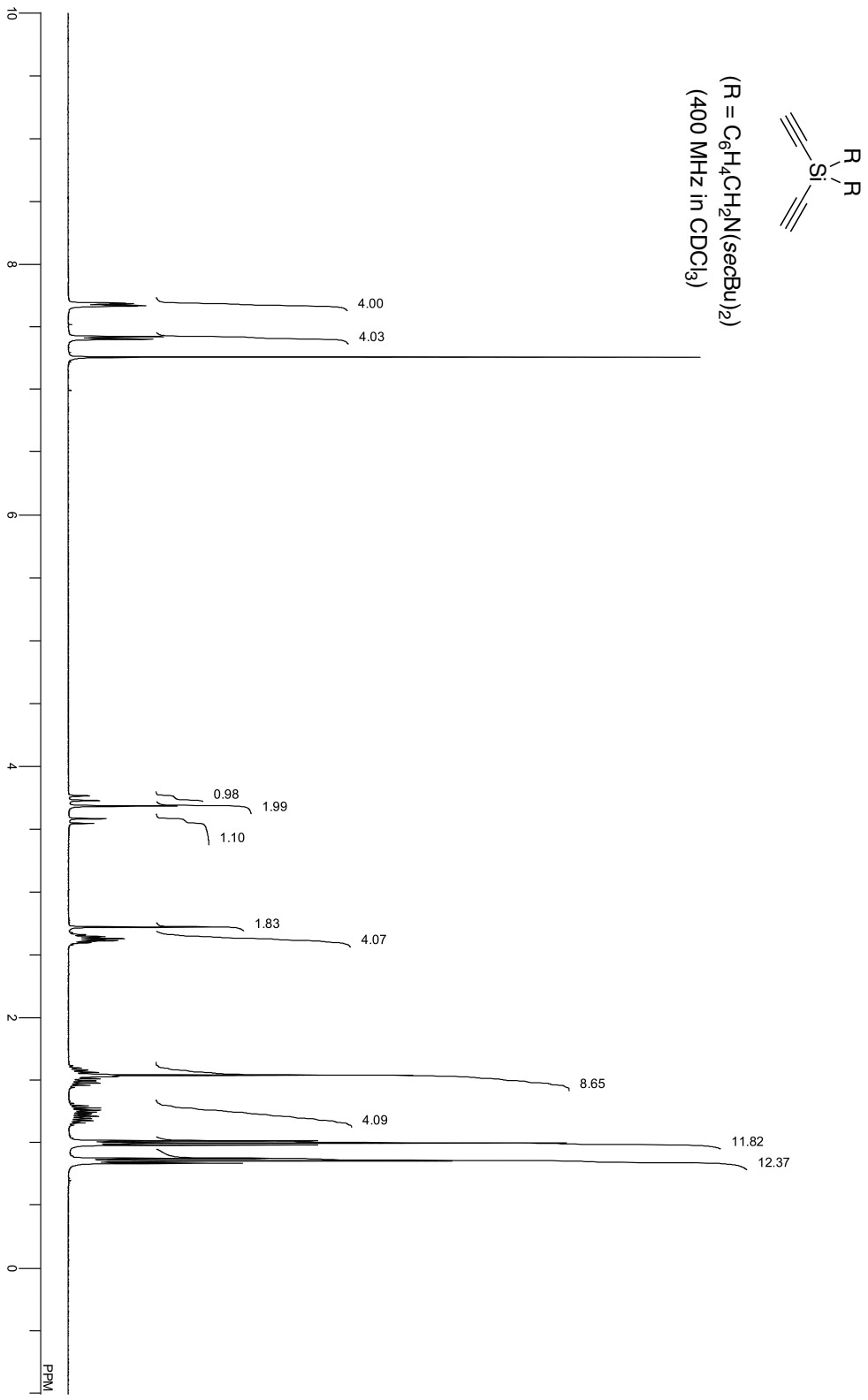
compound **1f**


R R
Si
SiMe3
(R = nHex)
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
0.92
16.57
6.15
4.16
9.00

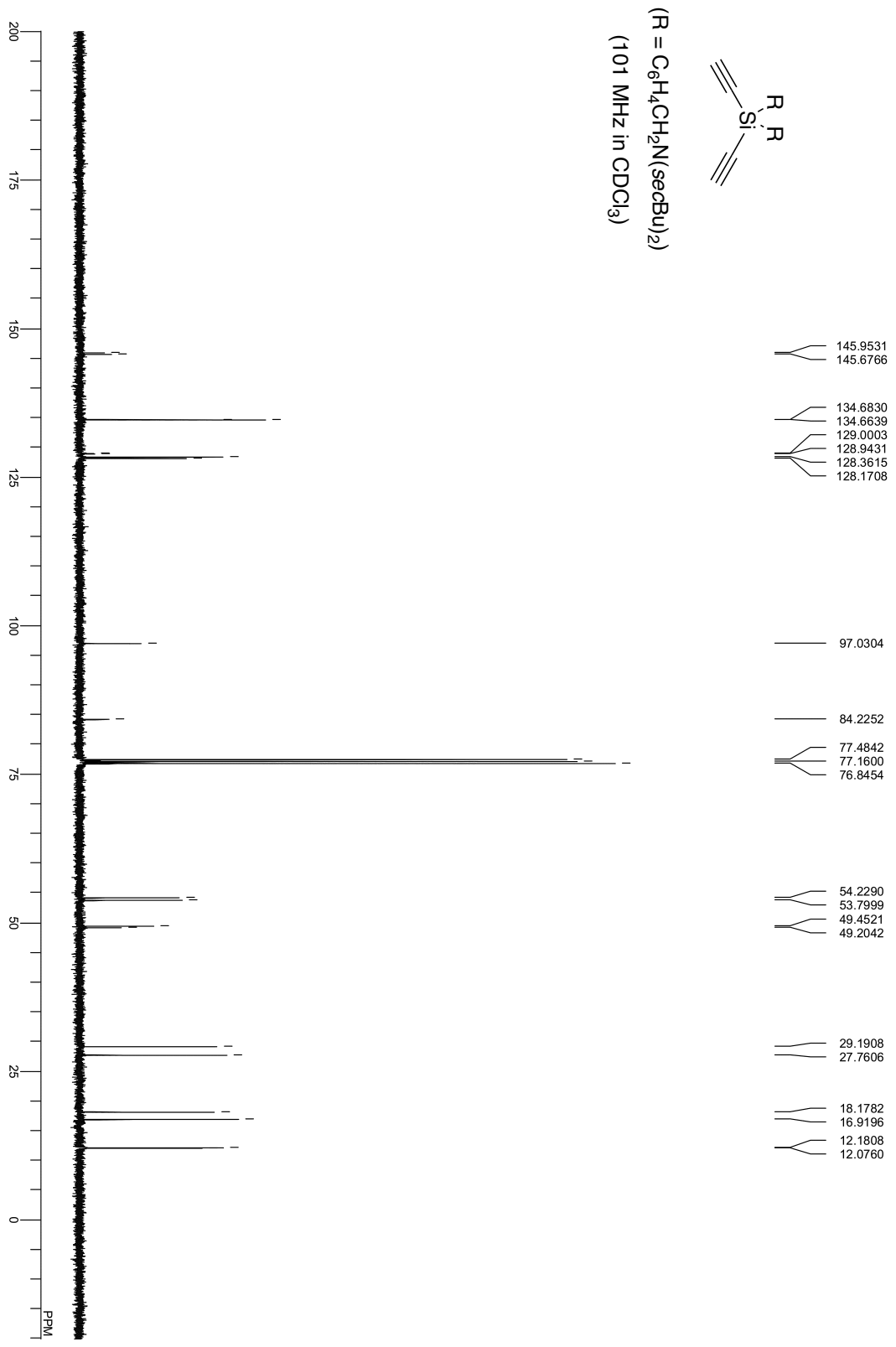
compound **1f**


(R = nHex)
(101 MHz in CDCl3)
R R
Si
SiMe3
116.7387
108.0621
94.7039
85.7985
77.4746
77.1600
76.8454
32.7186
31.6126
23.5844
22.6881
14.5454
14.2499
-0.0999
200
175
150
125
100
75
50
25
0
PPM

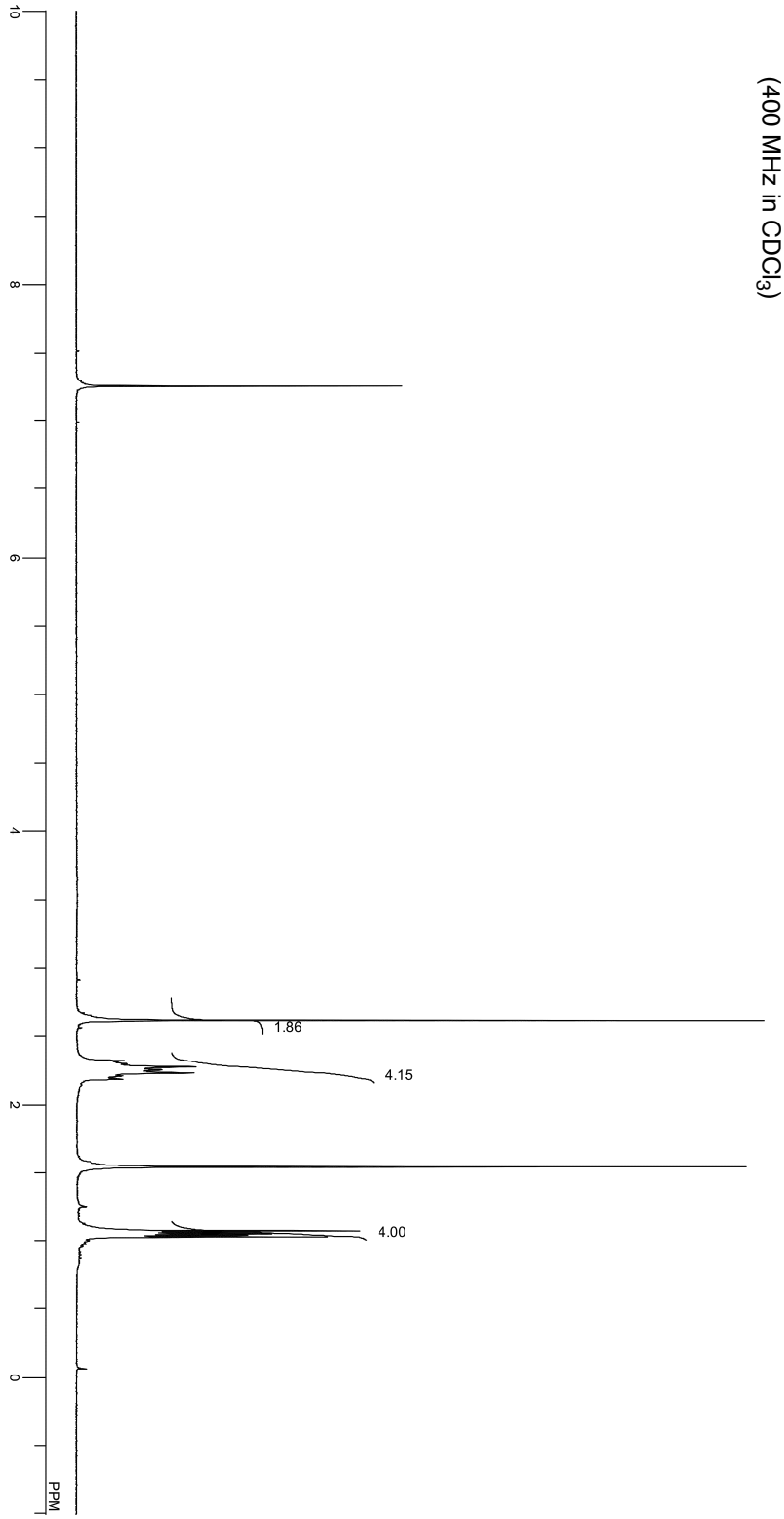
compound **1g**


(R = C6H4CH2N(secBu)2)
(400 MHz in CDCl3)
R R
Si
4.00
4.03
0.98
1.99
1.10
1.83
4.07
8.65
4.09
11.82
12.37
PPM

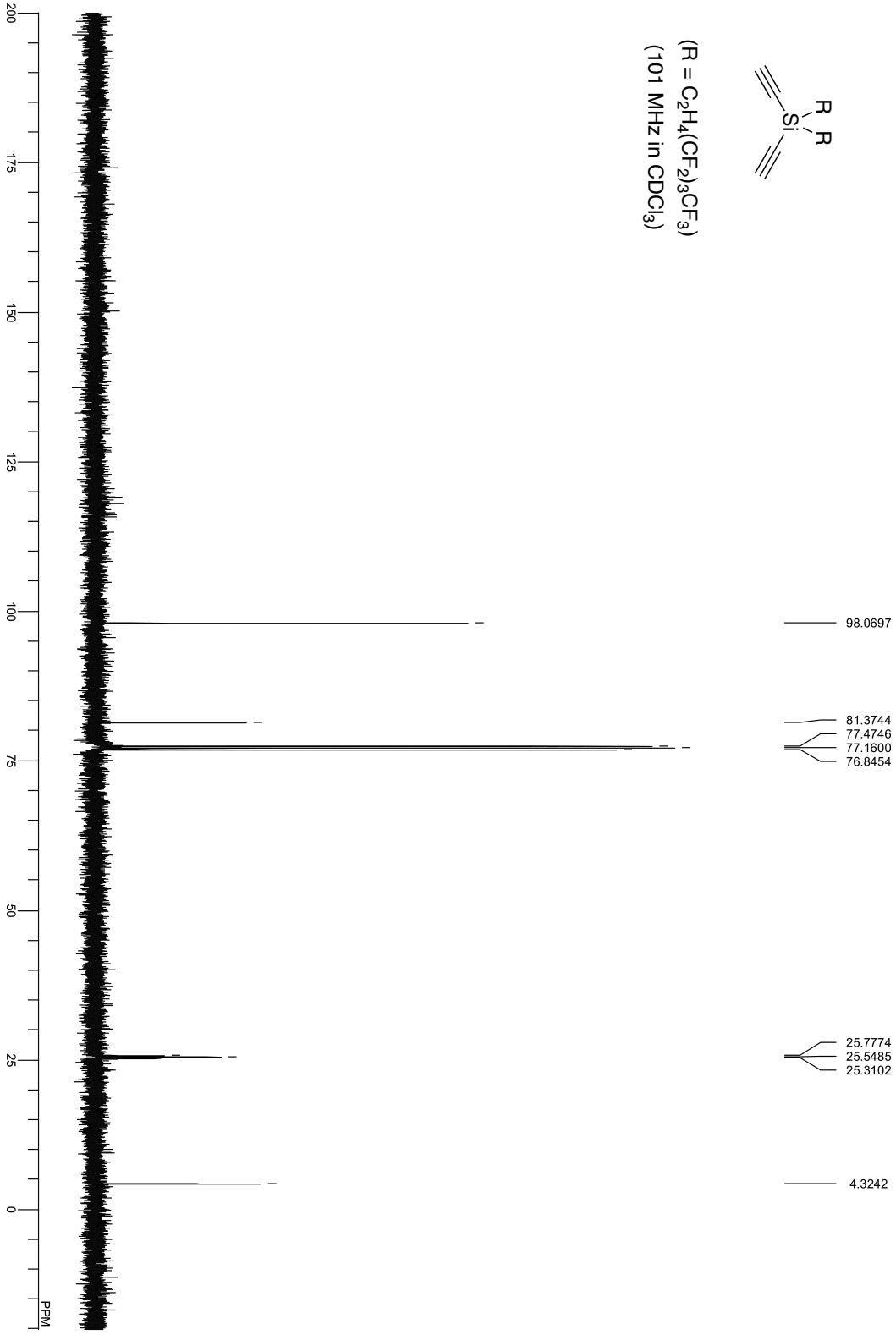
compound **1g**


(R = C6H4CH2N(secBu)2)
(101 MHz in CDCl3)
R R
Si
145.9531
145.6766
134.6830
134.6639
129.0003
128.9431
128.3615
128.1708
97.0304
84.2252
77.4842
77.1600
76.8454
54.2290
53.7999
49.4521
49.2042
29.1908
27.7606
18.1782
16.9196
12.1808
12.0760
200
175
150
125
100
75
50
25
0
PPM

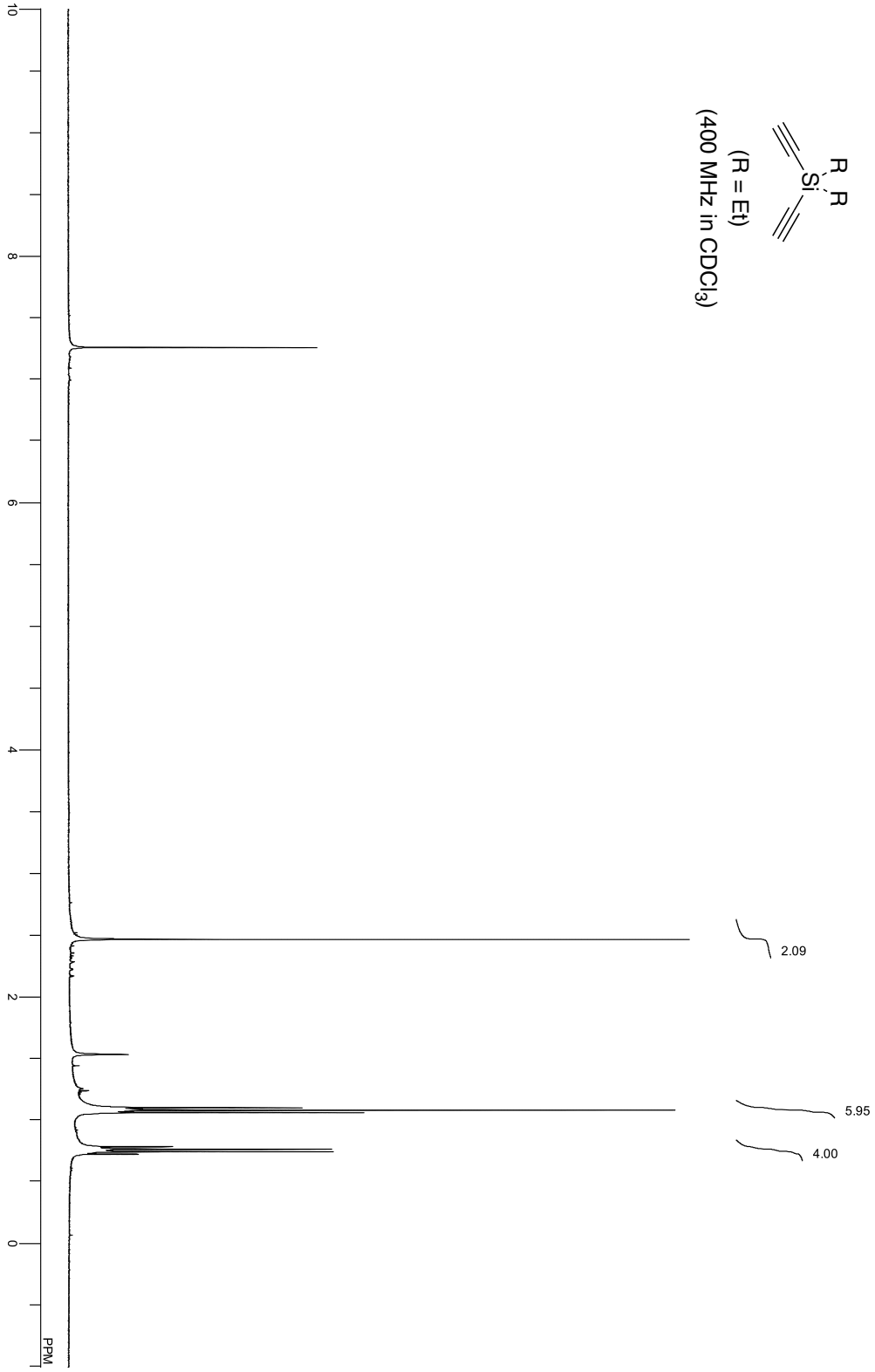
compound **1h**



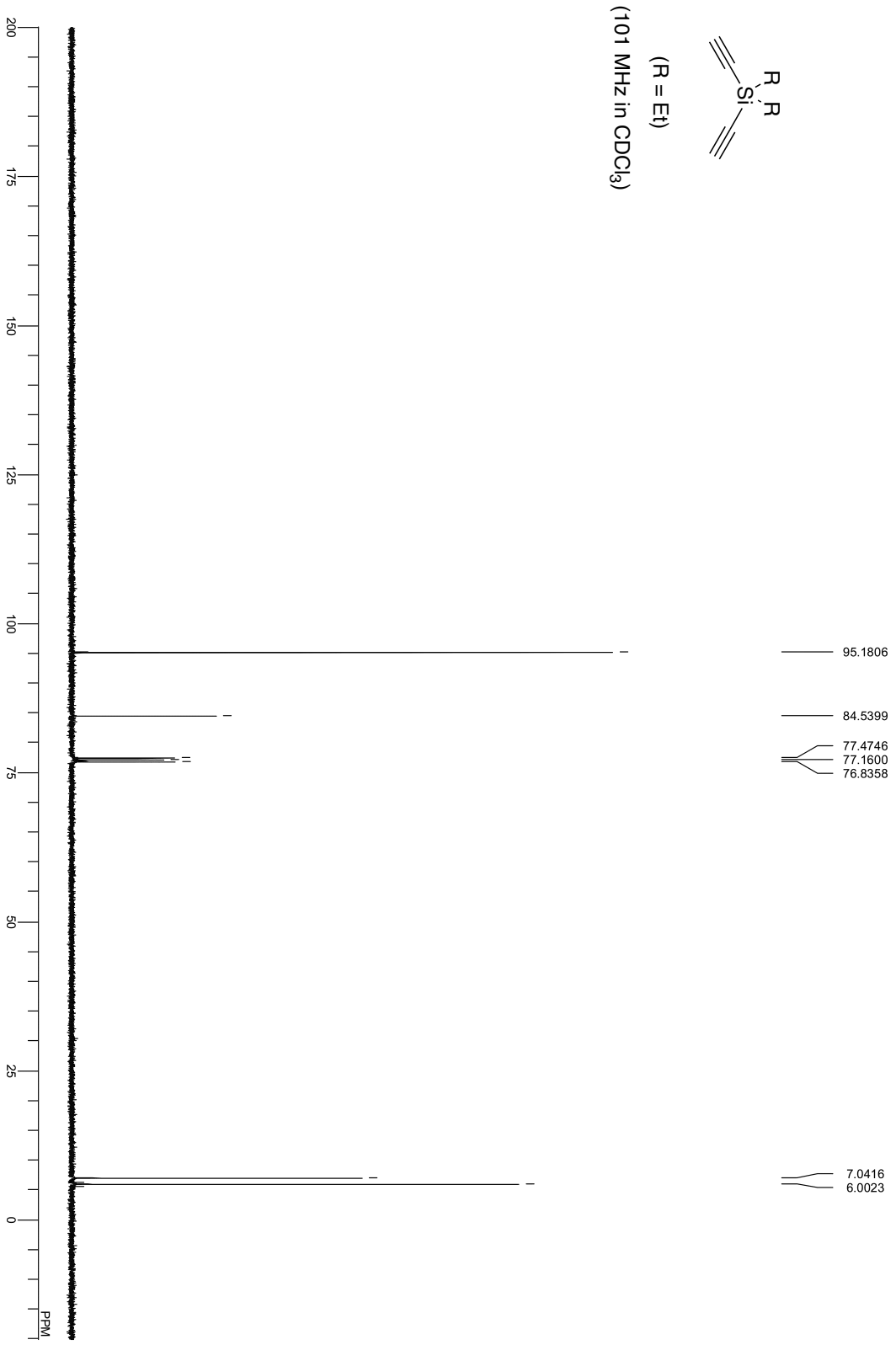
compound **1h**


(R = C2H4(CF2)3CF3)
(101 MHz in CDCl3)
R R
Si
98.0697
81.3744
77.4746
77.1600
76.8454
25.7774
25.5485
25.3102
4.3242
200
175
150
125
100
75
50
25
0
PPM

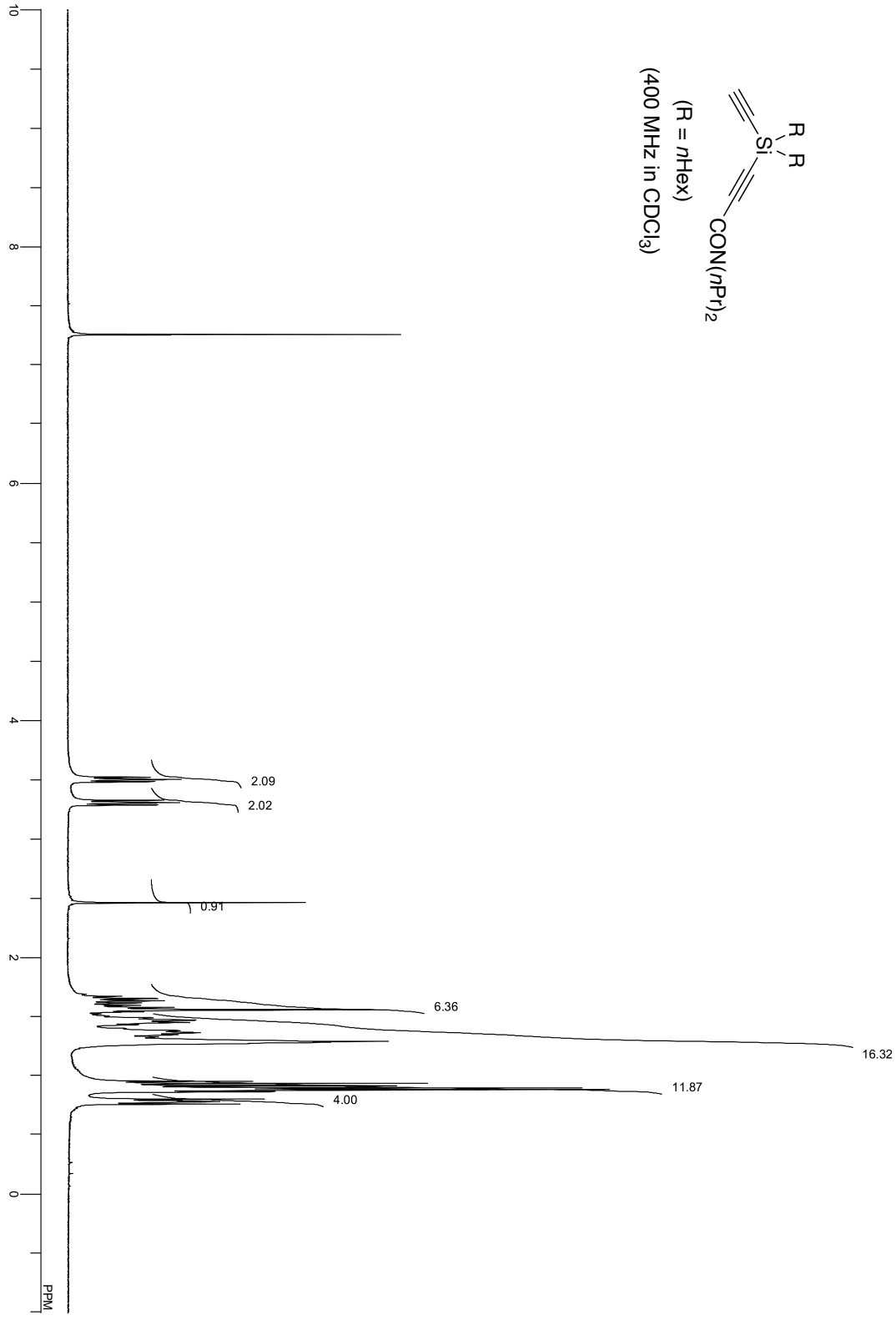
compound **1i**



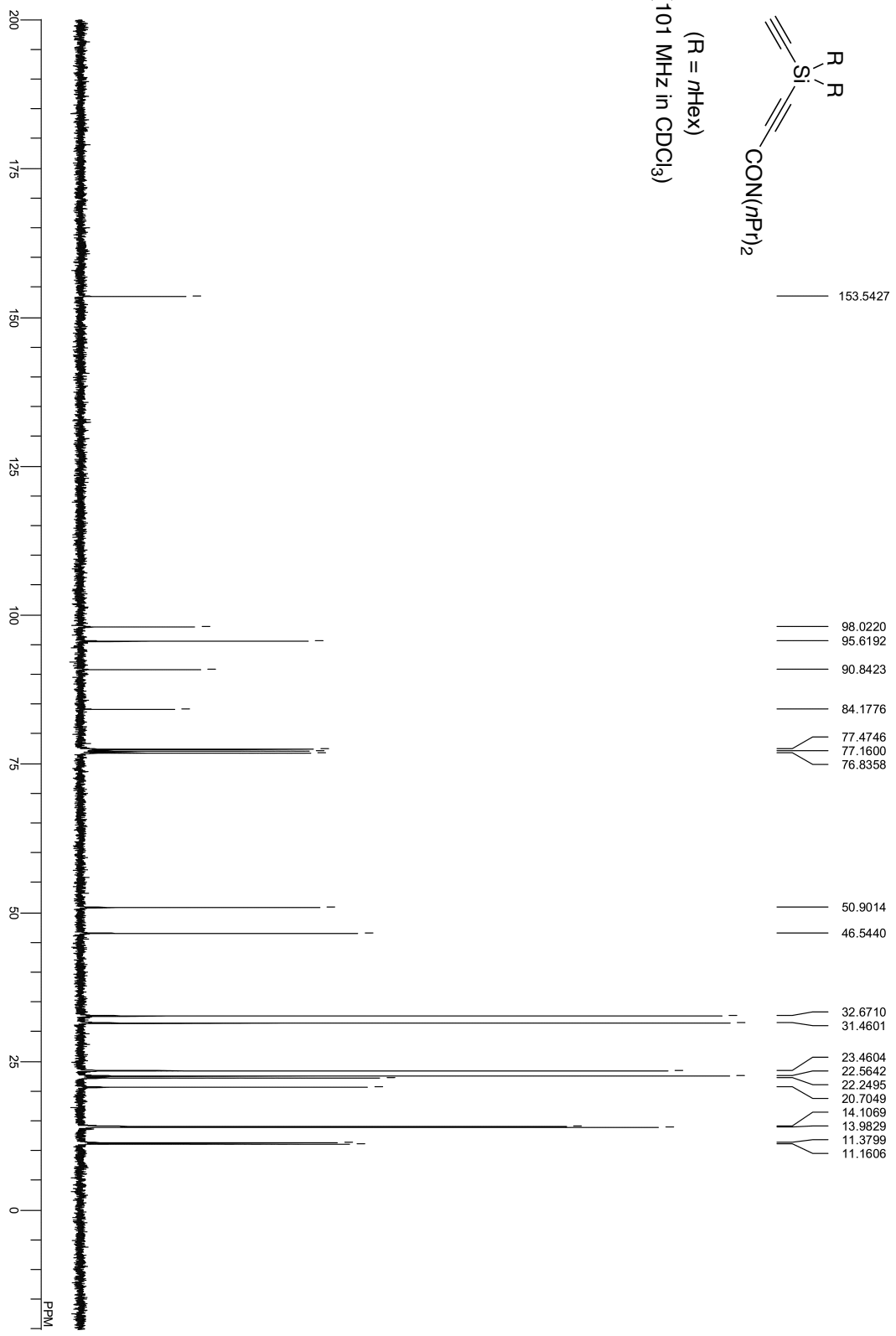
compound **1i**


R R
Si
(R = Et)
(101 MHz in CDCl3)
200
175
150
125
100
75
50
25
0
PPM
95.1806
84.5399
77.4746
77.1600
76.8358
7.0416
6.0023

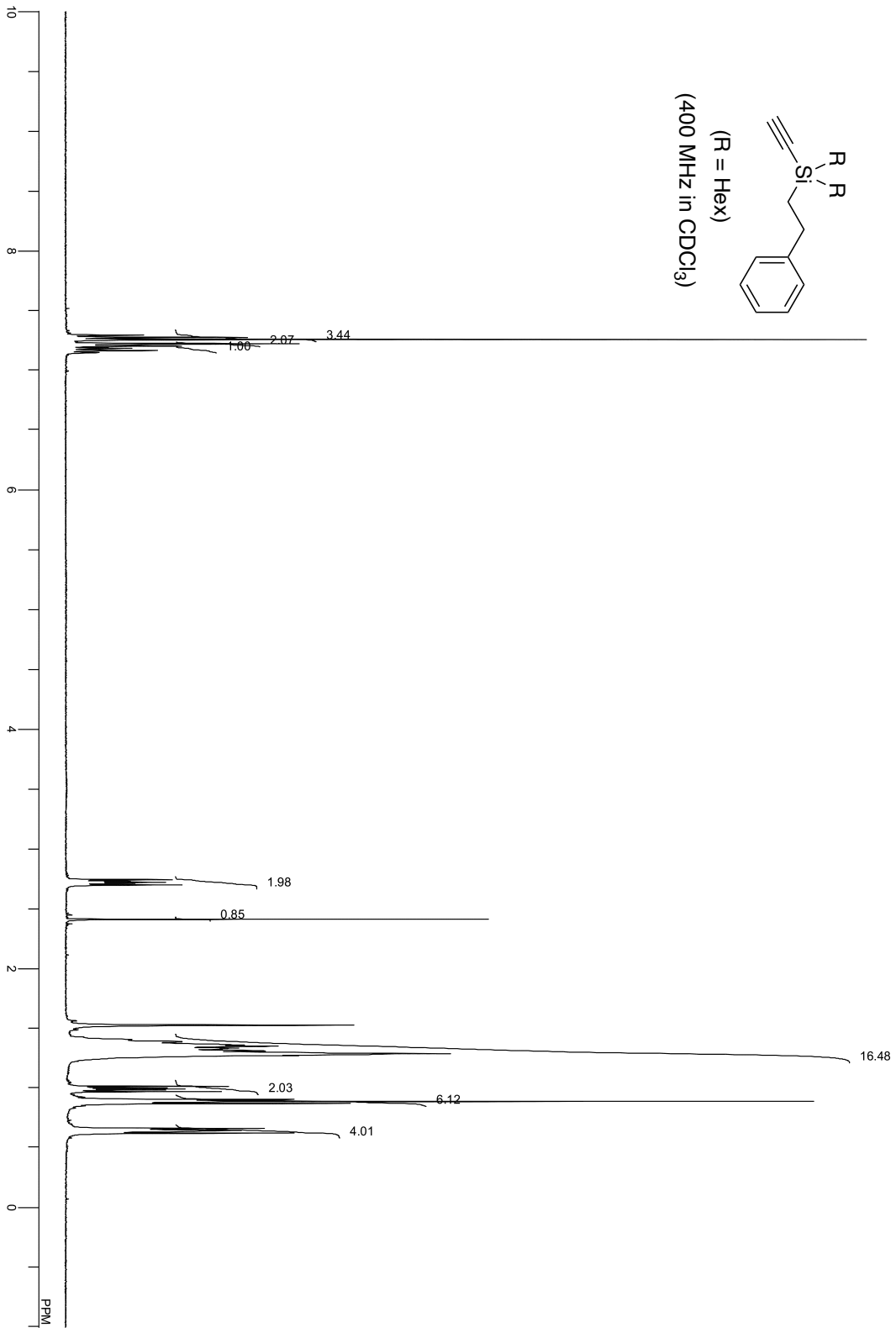
compound **1j**


R R
Si
CON(nPr)2
(R = nHex)
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
2.09
2.02
0.91
6.36
16.32
11.87
4.00

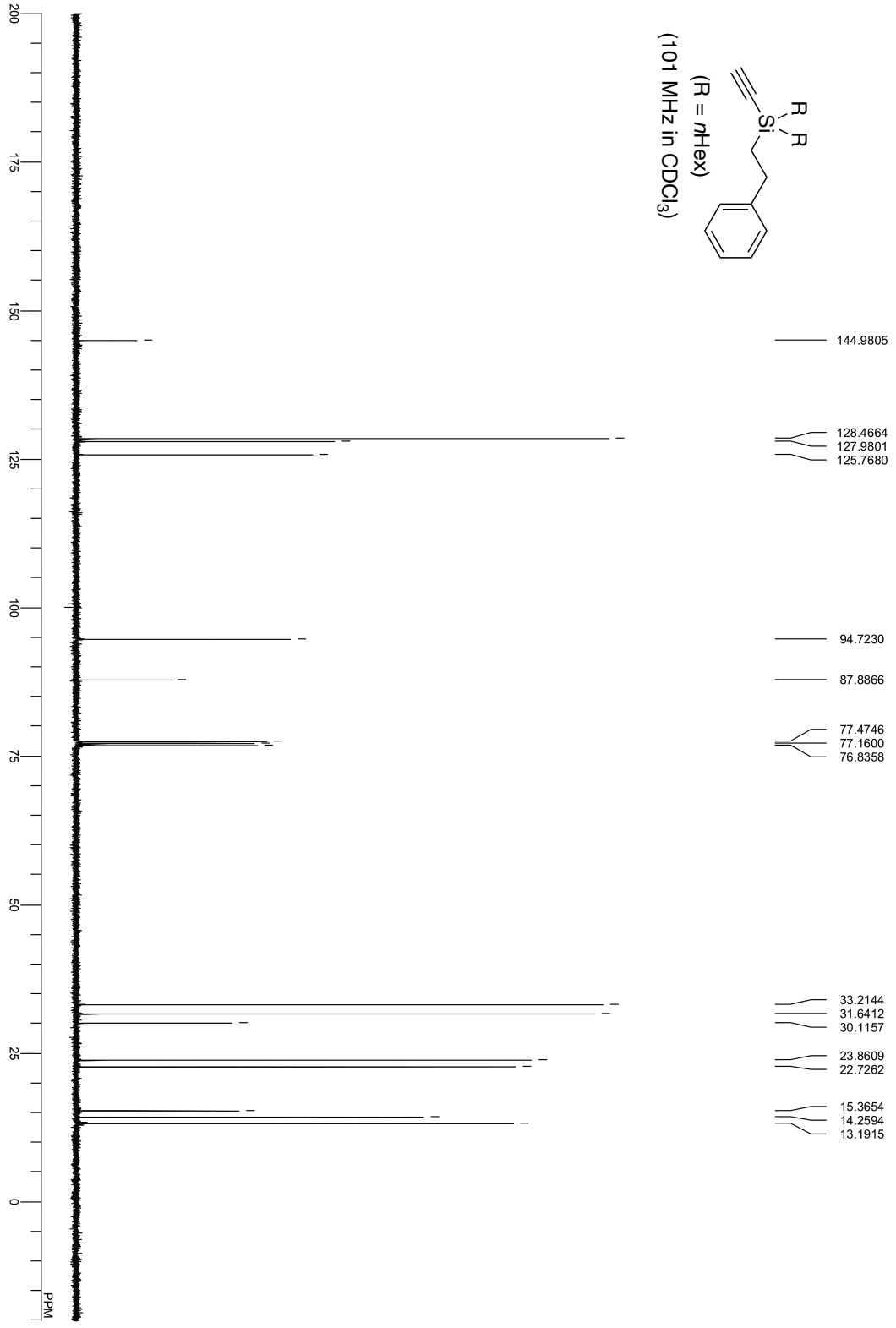
compound **1j**


(R = nHex)
(101 MHz in CDCl3)
R R
Si
CON(nPr)2
153.5427
98.0220
95.6192
90.8423
84.1776
77.4746
77.1600
76.8358
50.9014
46.5440
32.6710
31.4601
23.4604
22.5642
22.2495
20.7049
14.1069
13.9829
11.3799
11.1606
200
175
150
125
100
75
50
25
0
PPM

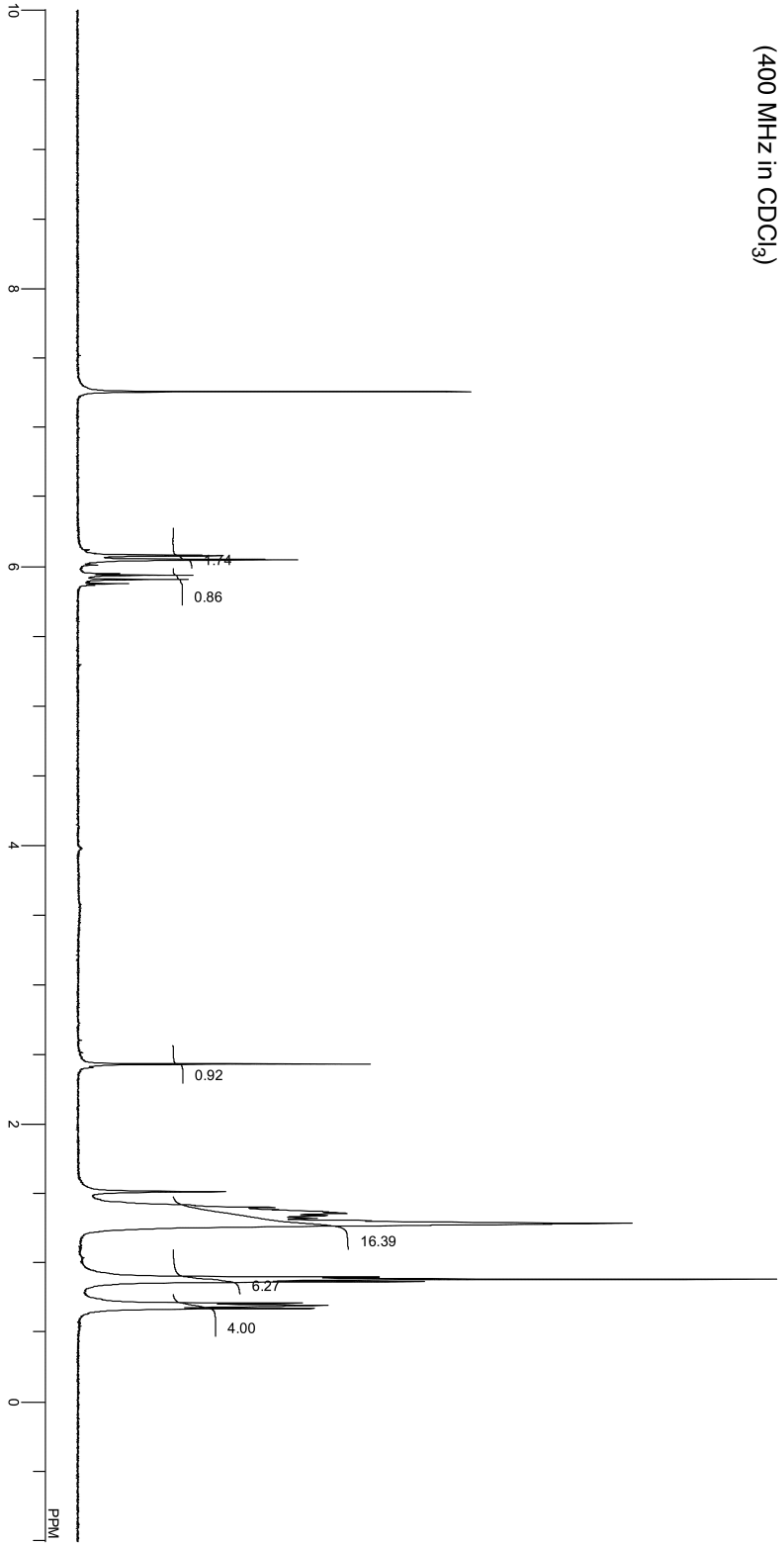
compound **2a**


(400 MHz in CDCl3)
(R = Hex)
R R
Si
10
8
6
4
2
0
PPM
3.44
2.07
1.00
1.98
0.85
16.48
2.03
6.12
4.01

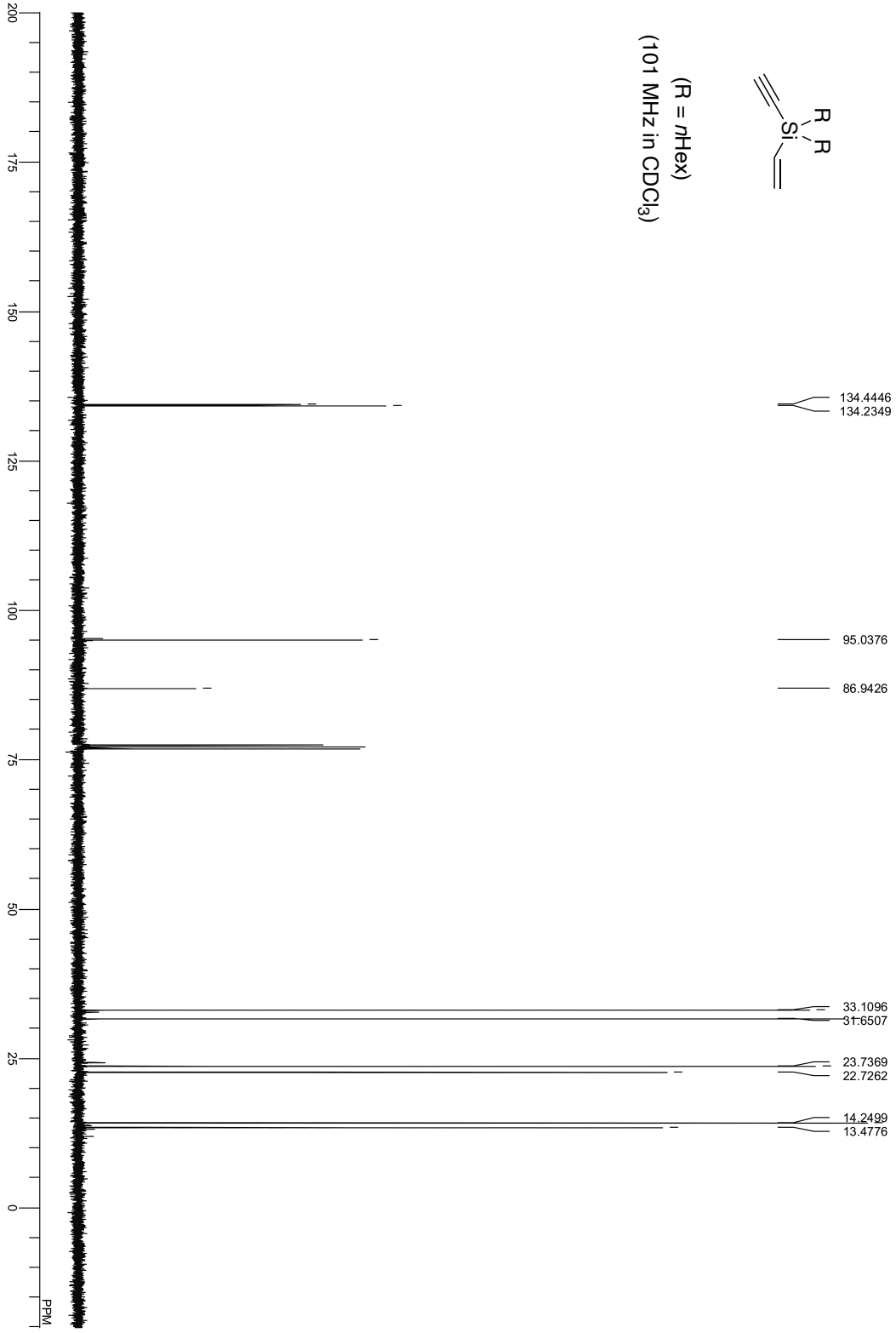
compound **2a**


(R = nHex)
(101 MHz in CDCl3)
R R
Si
144.9805
128.4664
127.9801
125.7680
94.7230
87.8866
77.4746
77.1600
76.8358
33.2144
31.6412
30.1157
23.8609
22.7262
15.3654
14.2594
13.1915
PPM

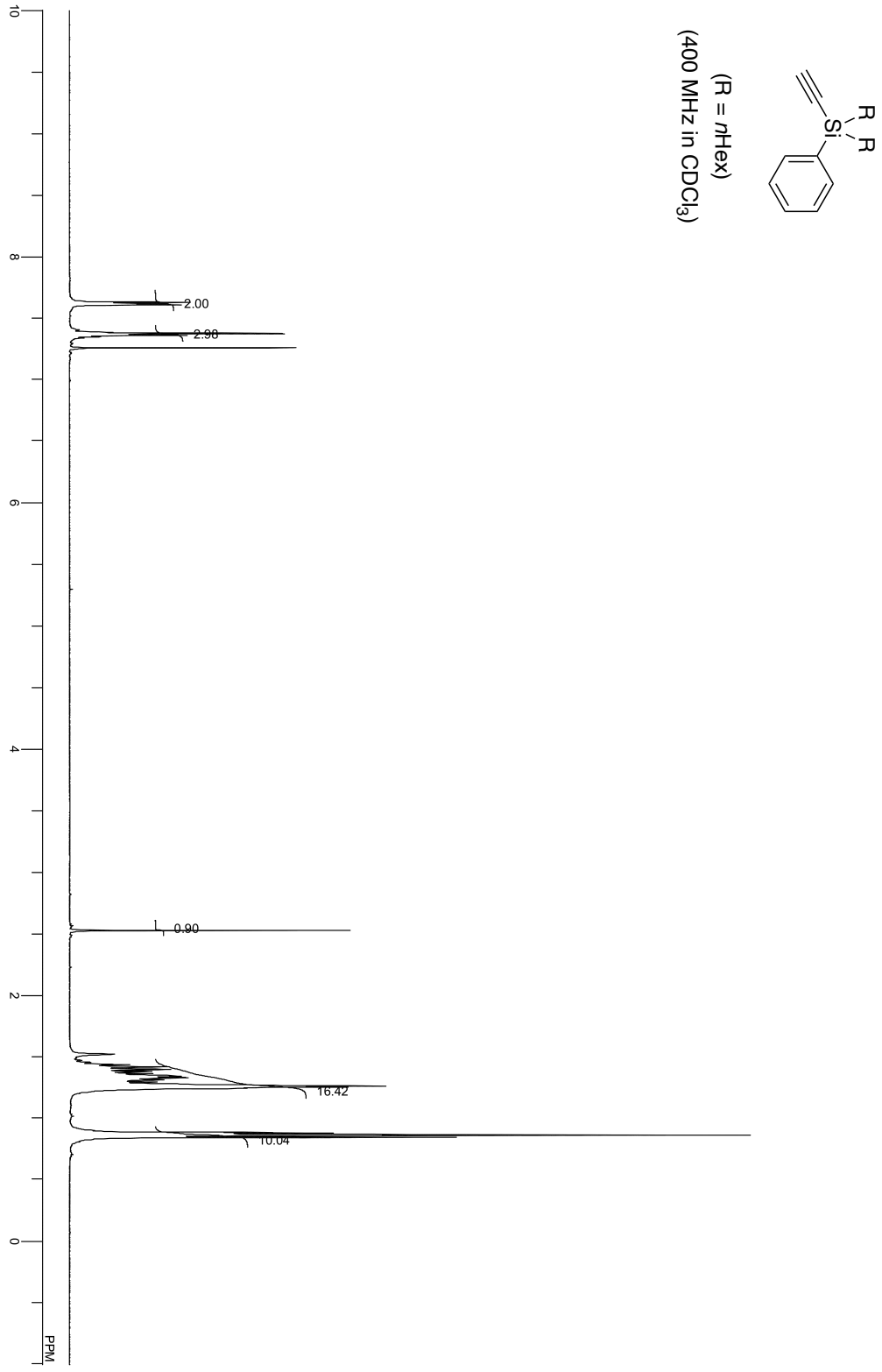
compound **2b**


(R = nHex)
(400 MHz in CDCl3)
R R
Si
10
8
6
4
2
0
PPM
1.74
0.86
0.92
16.39
6.27
4.00

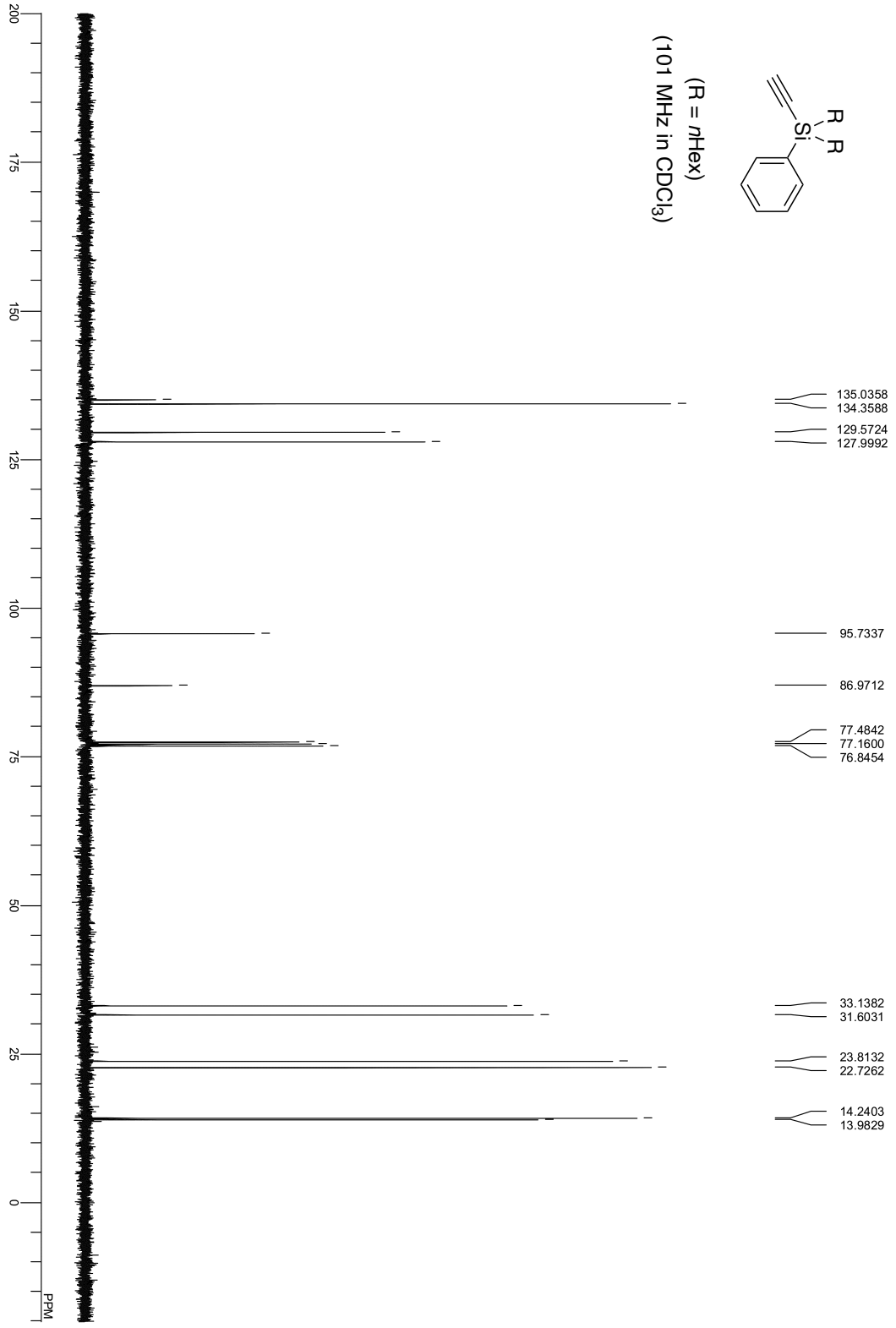
compound **2b**


(R = nHex)
(101 MHz in CDCl3)
R R
Si
134.4446
134.2349
95.0376
86.9426
33.1096
31.6507
23.7369
22.7262
14.2499
13.4776
200
175
150
125
100
75
50
25
0
PPM

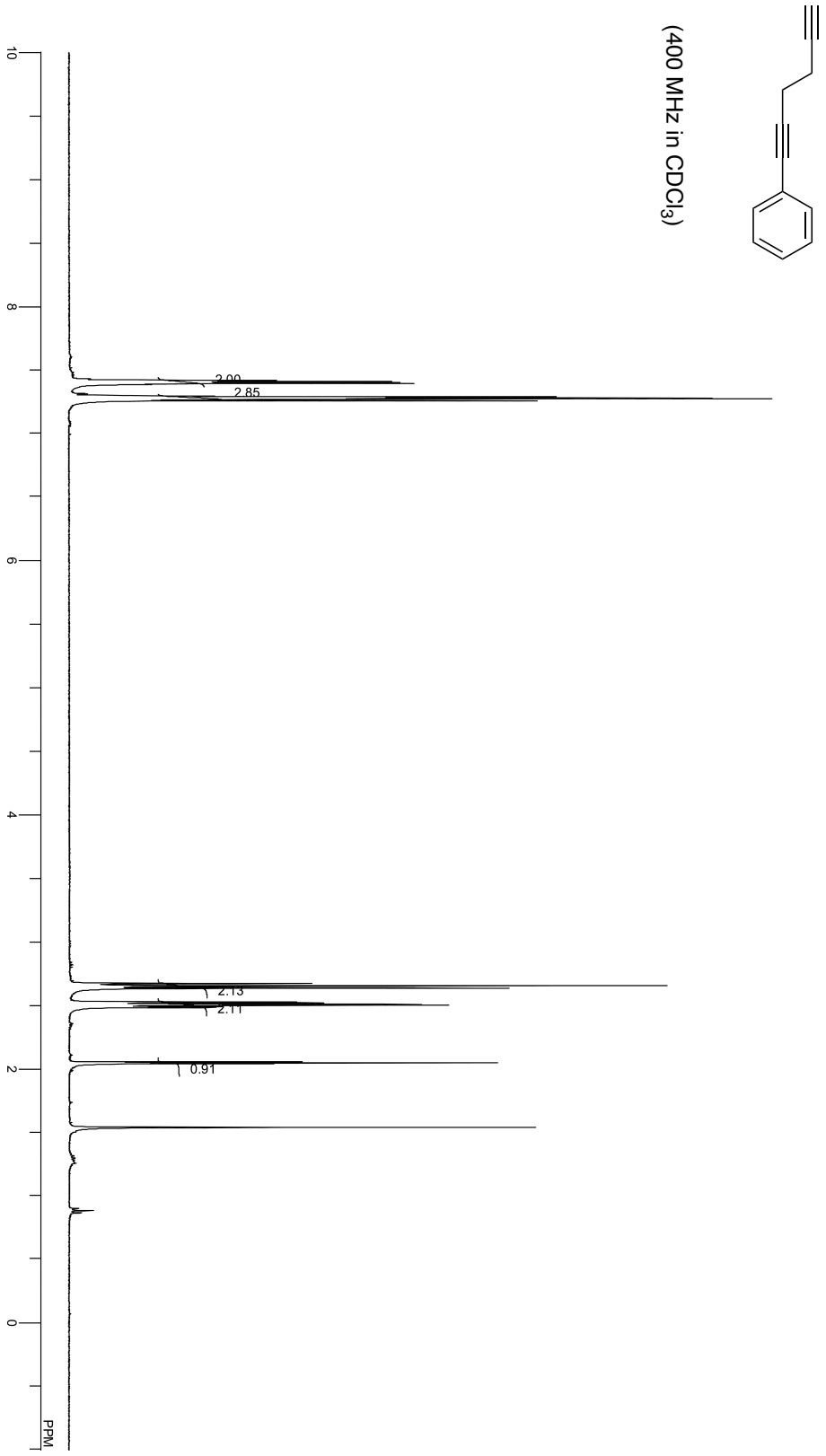
compound **2c**



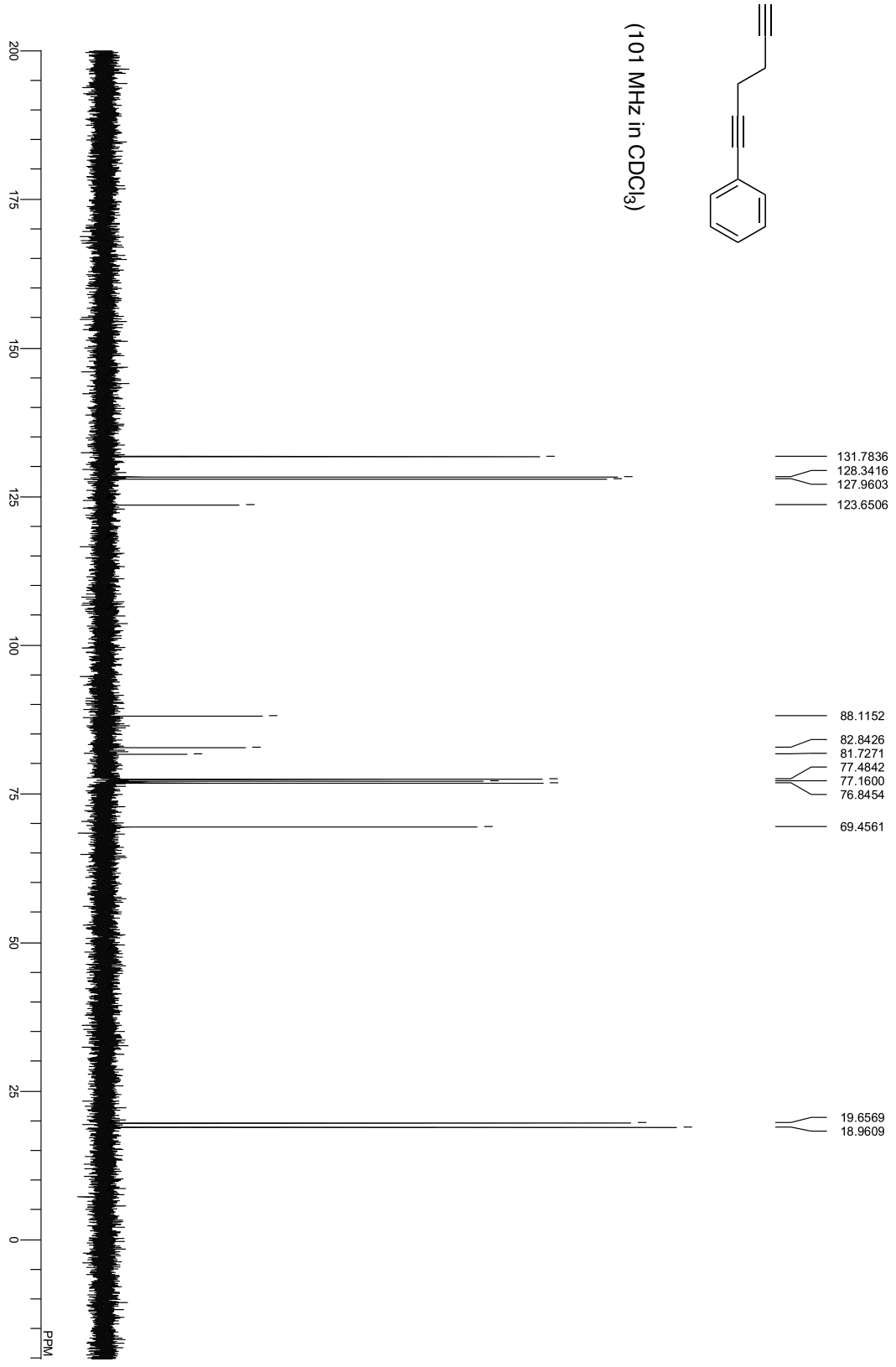
compound **2c**


(R = nHex)
(101 MHz in CDCl3)
Si
R R
135.0358
134.3588
129.5724
127.9992
95.7337
86.9712
77.4842
77.1600
76.8454
33.1382
31.6031
23.8132
22.7262
14.2403
13.9829
200
175
150
125
100
75
50
25
0
PPM

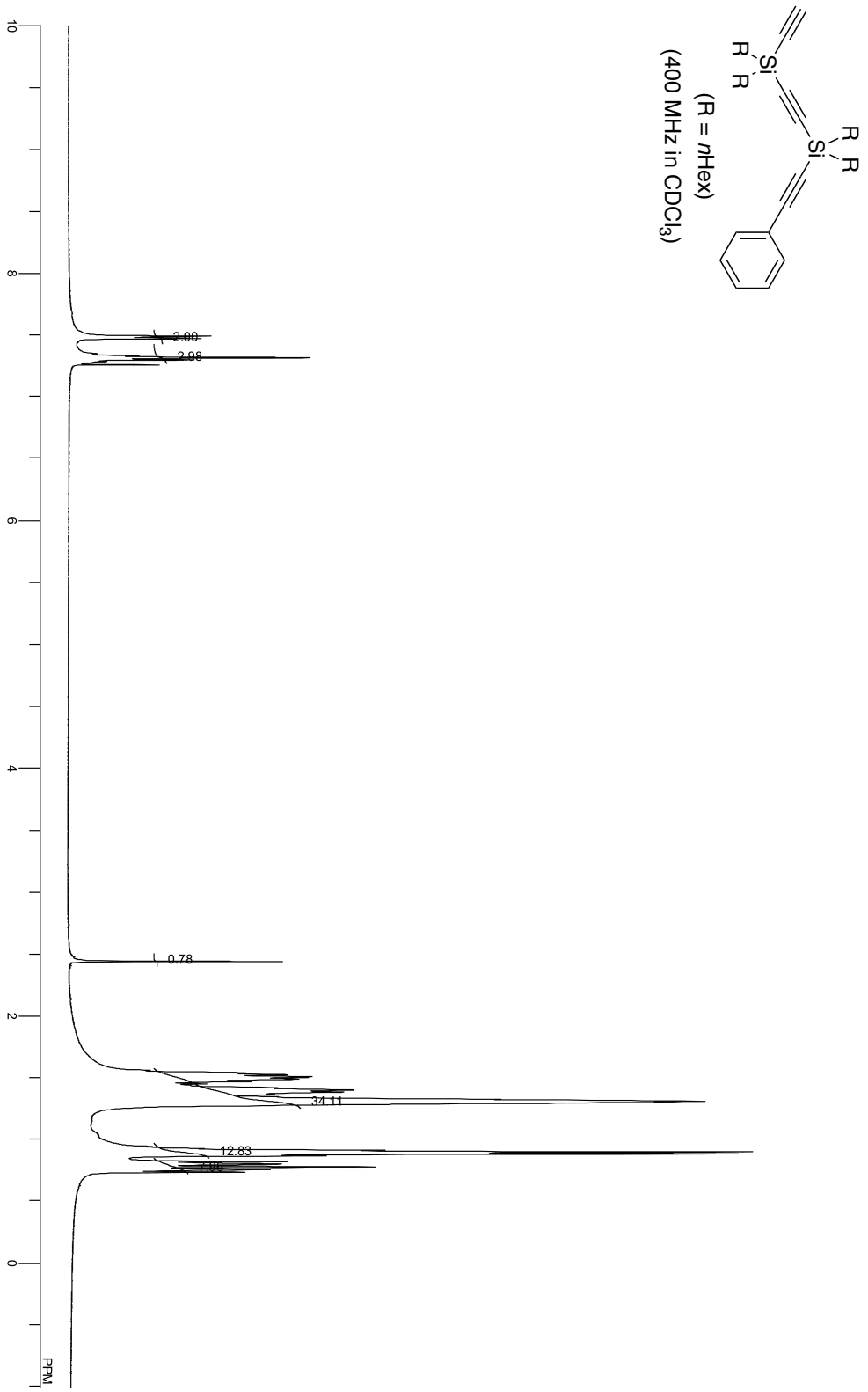
compound **3**



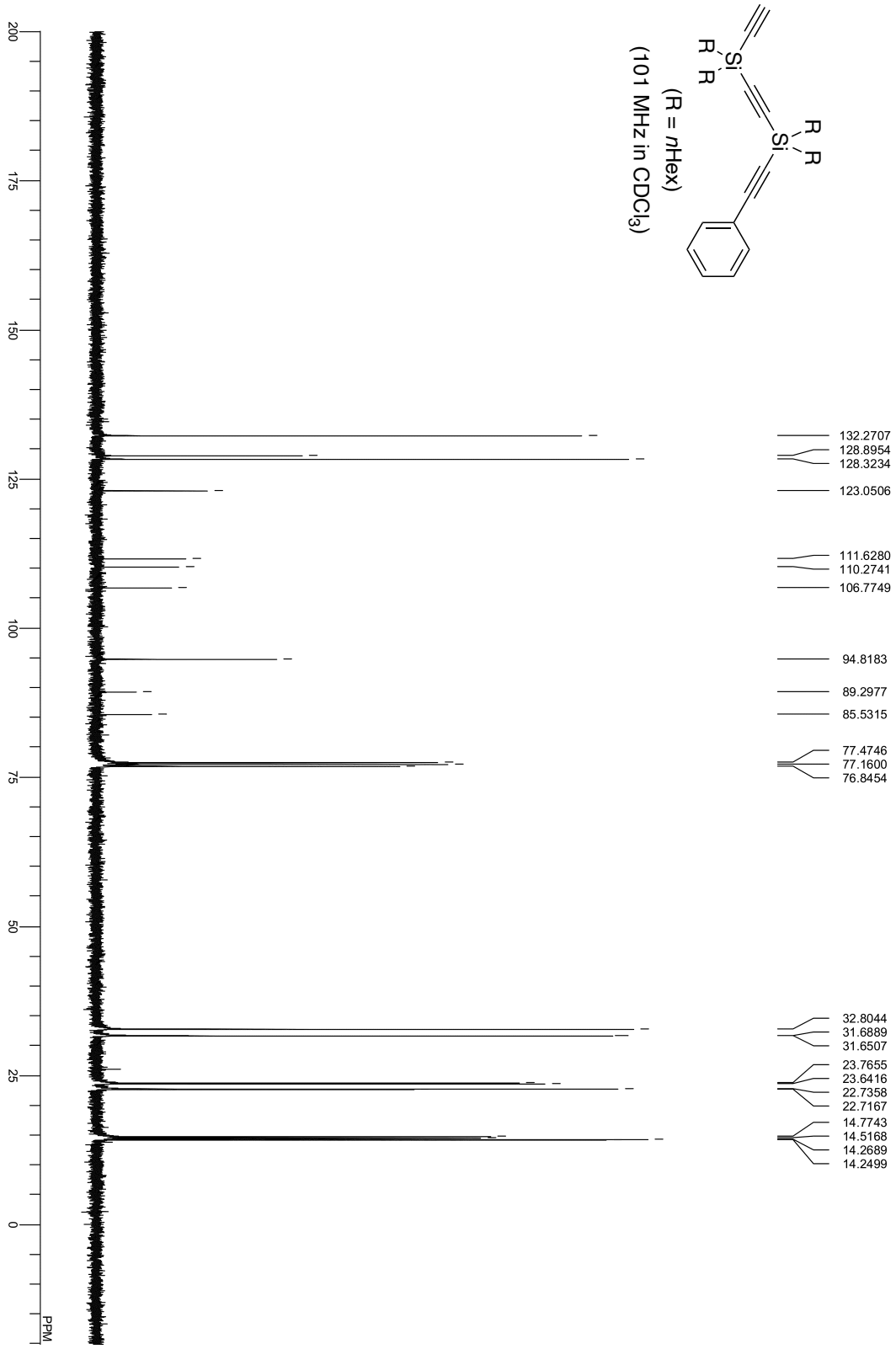
compound **3**


(101 MHz in CDCl3)
131.7836
128.3416
127.9603
123.6506
88.1152
82.8426
81.7271
77.4842
77.1600
76.8454
69.4561
19.6569
18.9609
PPM

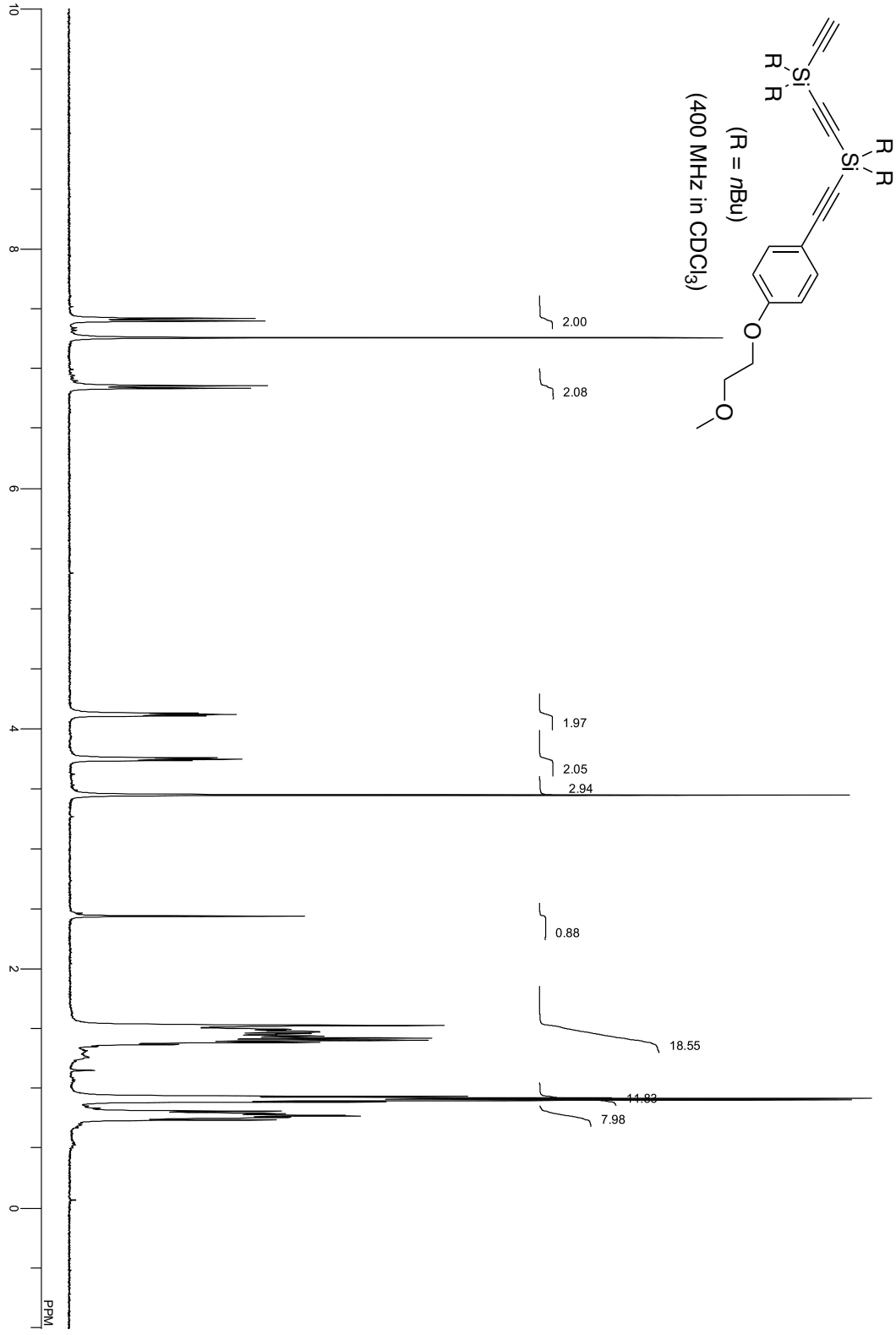
compound **4a**



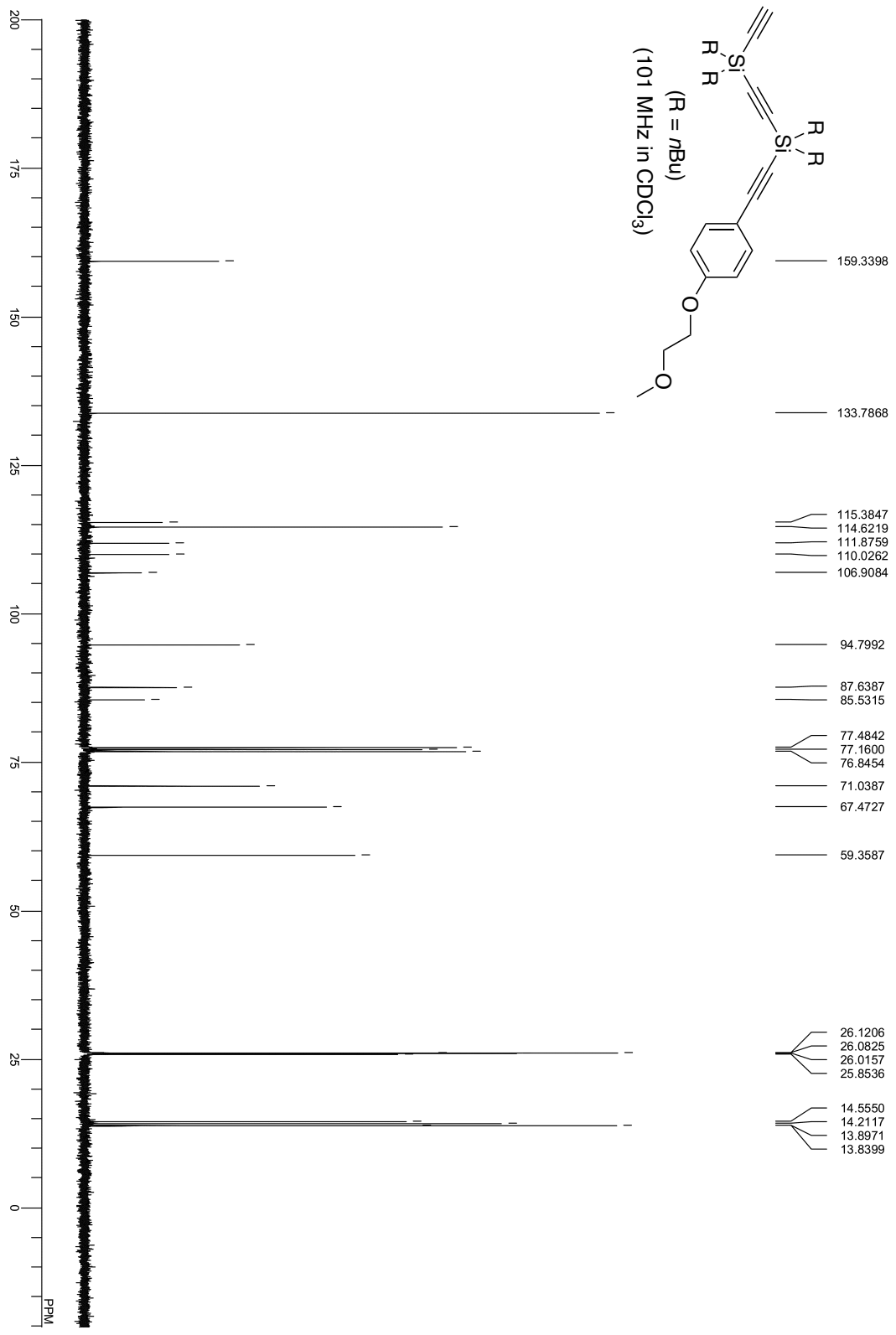
compound **4a**


(R = nHex)
(101 MHz in CDCl3)
132.2707
128.8954
128.3234
123.0506
111.6280
110.2741
106.7749
94.8183
89.2977
85.5315
77.4746
77.1600
76.8454
32.8044
31.6889
31.6507
23.7655
23.6416
22.7358
22.7167
14.7743
14.5168
14.2689
14.2499
PPM

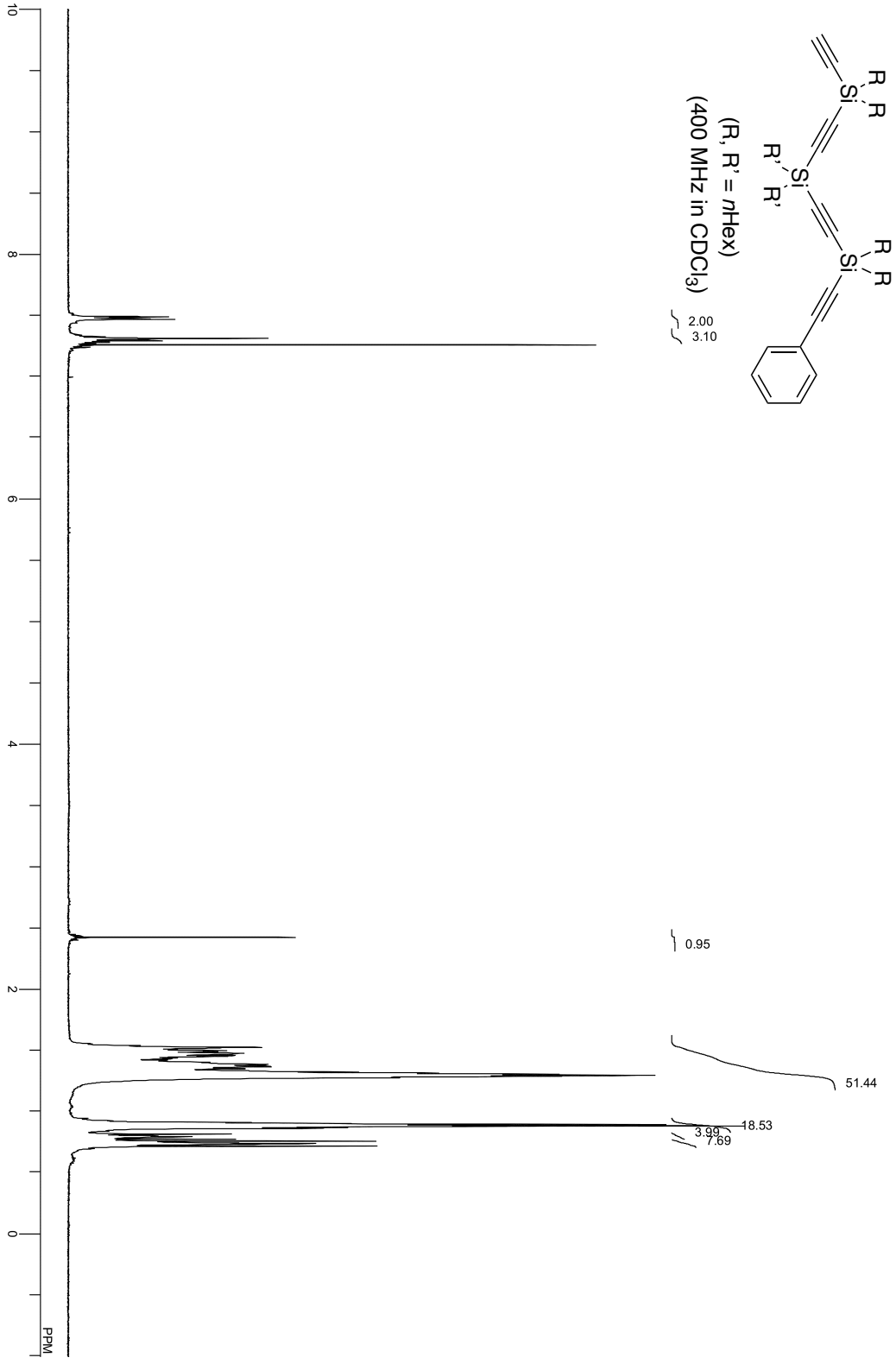
compound **4b**



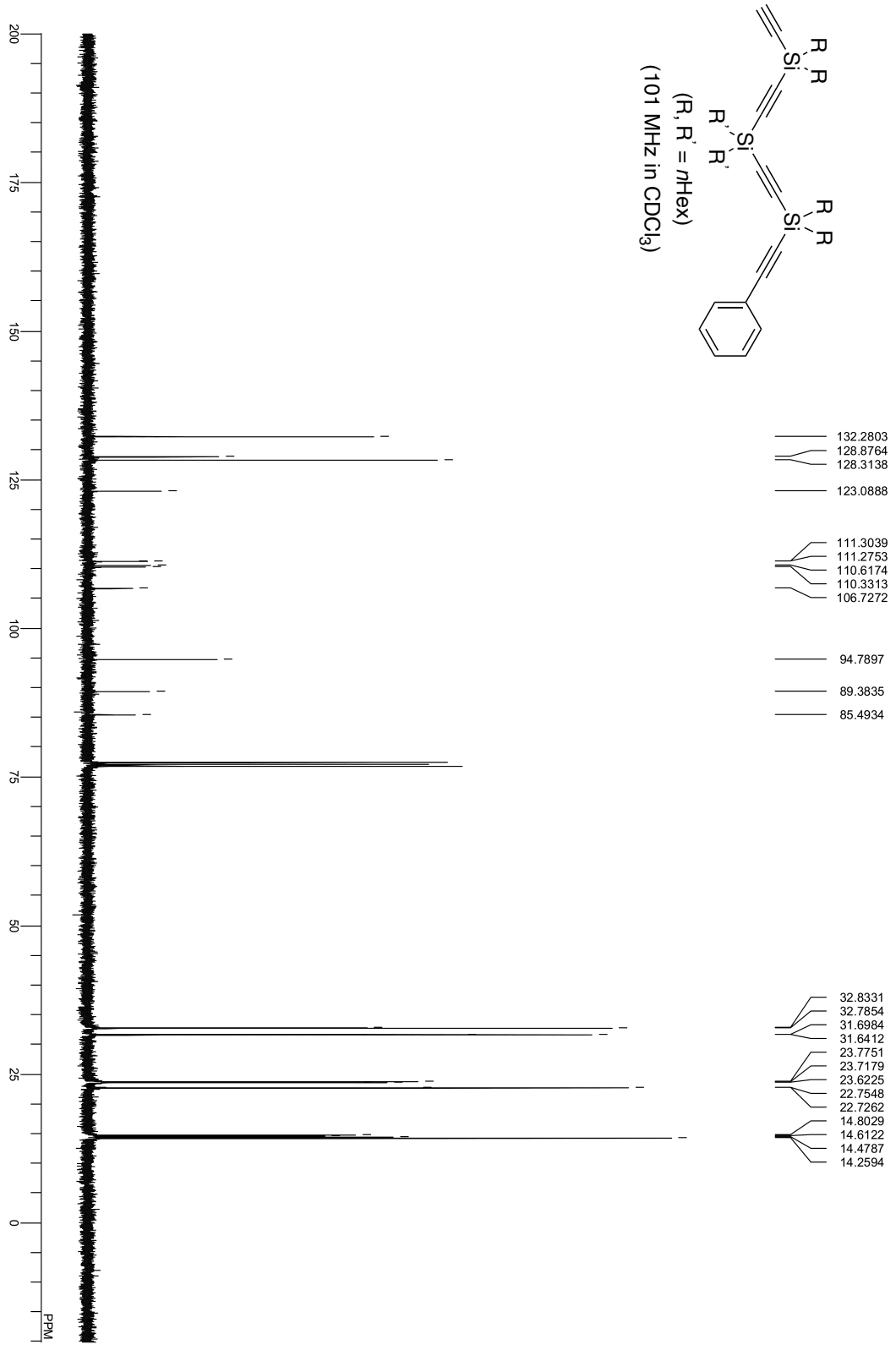
compound **4b**


(R = nBu)
(101 MHz in CDCl3)
159.3398
133.7868
115.3847
114.6219
111.8759
110.0262
106.9084
94.7992
87.6387
85.5315
77.4842
77.1600
76.8454
71.0387
67.4727
59.3587
26.1206
26.0825
26.0157
25.8536
14.5550
14.2117
13.8971
13.8399
PPM

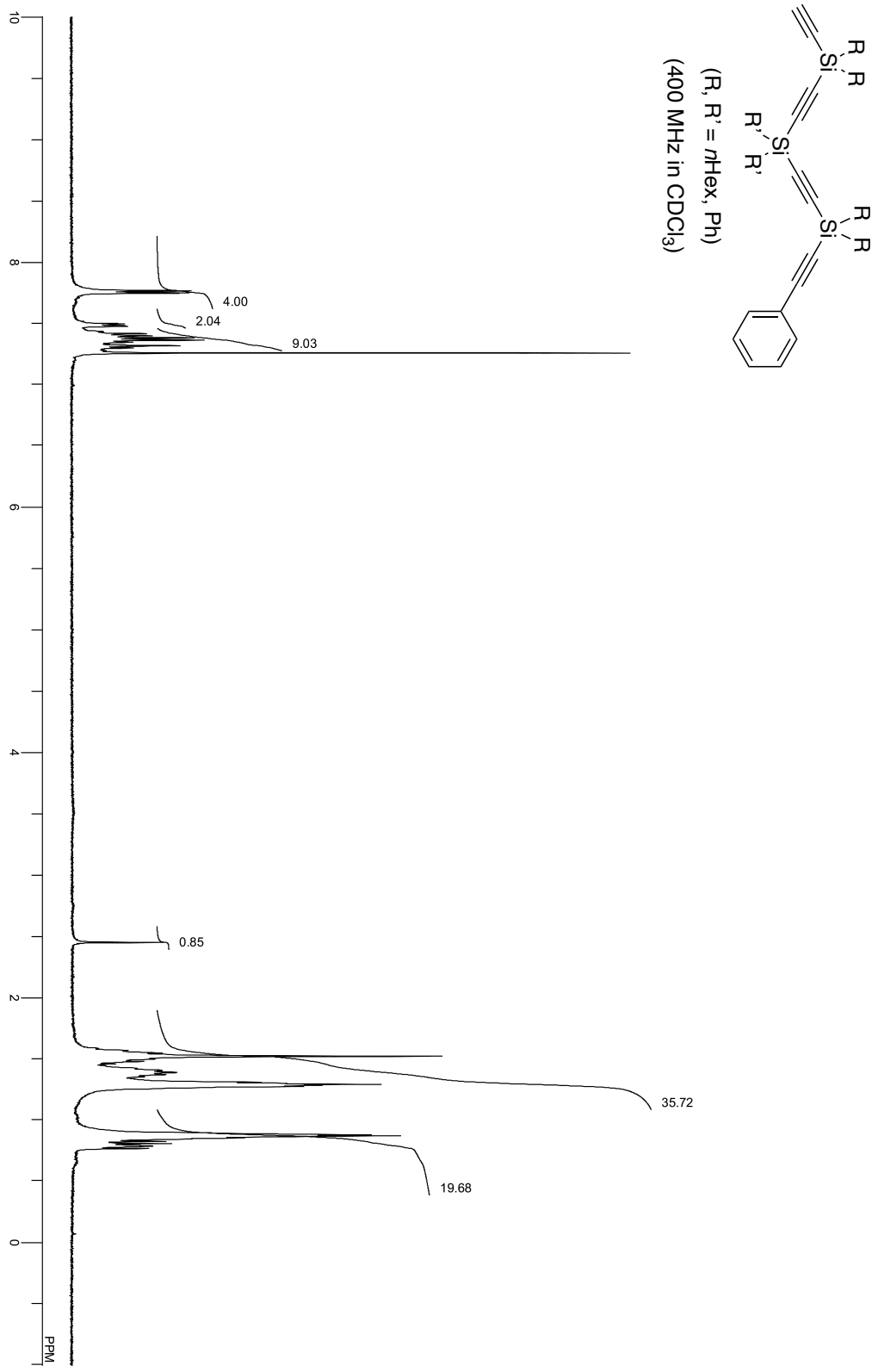
compound **5a**



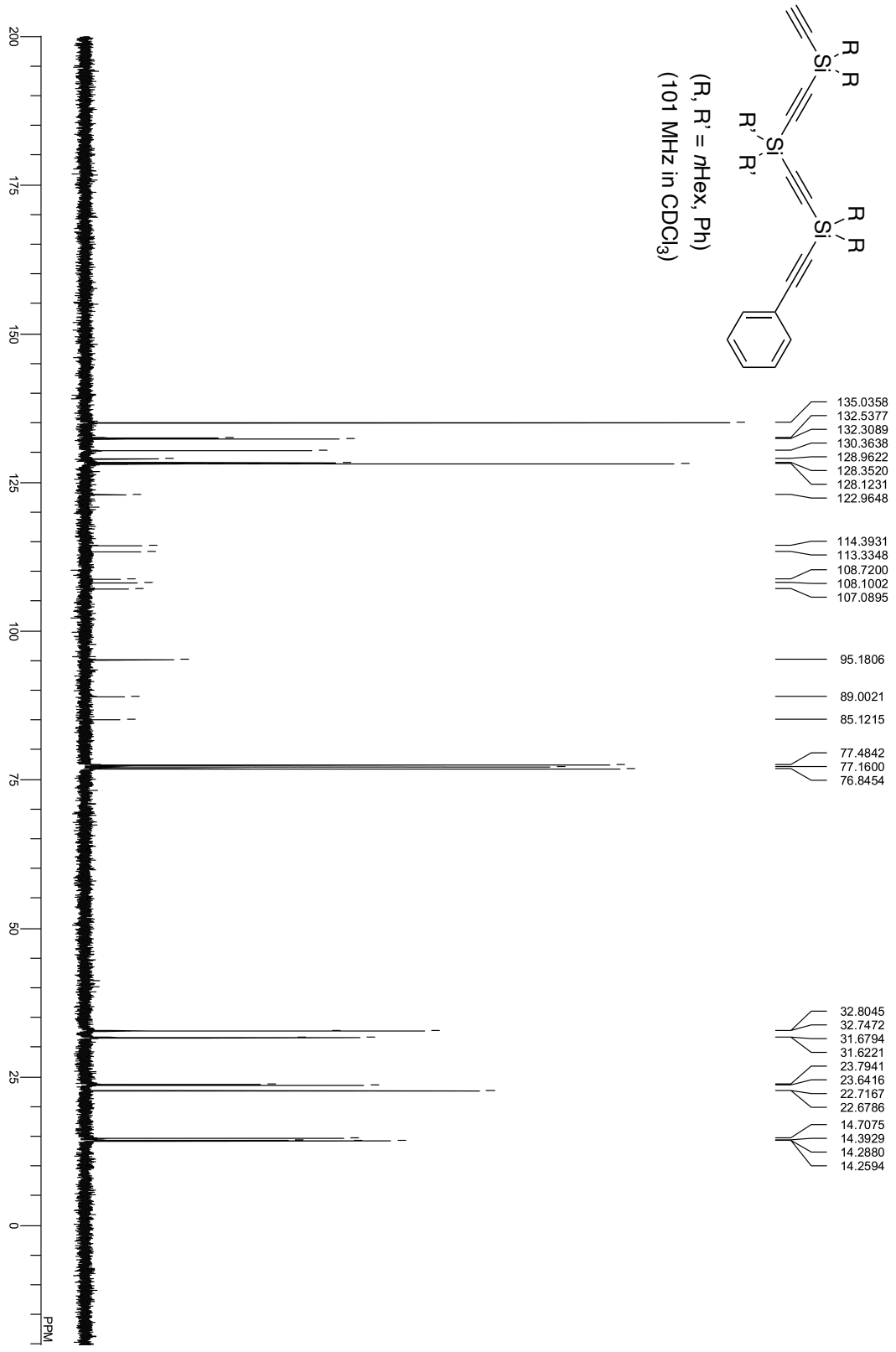
compound **5a**


(R, R' = nHex)
(101 MHz in CDCl3)
132.2803
128.8764
128.3138
123.0888
111.3039
111.2753
110.6174
110.3313
106.7272
94.7897
89.3835
85.4934
32.8331
32.7854
31.6984
31.6412
23.7751
23.7179
23.6225
22.7548
22.7262
14.8029
14.6122
14.4787
14.2594
PPM

compound **5b**



compound **5b**


(R, R' = nHex, Ph)
(101 MHz in CDCl3)
Si
R
R'
135.0358
132.5377
132.3089
130.3638
128.9622
128.3520
128.1231
122.9648
114.3931
113.3348
108.7200
108.1002
107.0895
95.1806
89.0021
85.1215
77.4842
77.1600
76.8454
32.8045
32.7472
31.6794
31.6221
23.7941
23.6416
22.7167
22.6786
14.7075
14.3929
14.2880
14.2594
200
175
150
125
100
75
50
25
0
PPM

X. References

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