Supporting Information For:

Iron-Catalyzed Enyne Cross-Coupling Reaction

Takuji Hatakeyama, Yuya Yoshimoto, Toma Gabriel, and Masaharu Nakamura *

International Research Center for Elements Science,

Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611-0011, Japan

General. All of the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of argon or nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). TLC plates were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in an acidic staining solution of *p*-anisaldehyde followed by heating on a hot plate. Organic solutions were concentrated by a rotary evaporator at *ca.* 30 mmHg. Flash column chromatography was performed on Kanto silica gel 60 (spherical, neutral, 140–325 mesh) according to the procedure described by Still et al.[1] Reversed-phase chromatography was performed on YFLC-CARTRIDGE column (ODS-SM-50C-M, Yamazen Co.) with YFLC-Wprep preparative liquid chromatograph instrument (Yamazen Co.).

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on JEOL EX-270 (270 MHz) or VARIAN MercuryVX (300 MHz) NMR spectrometers. Proton chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the residual proton signal of $CDCl_3$ (δ 7.26). ^{13}C NMR spectra were recorded at 67.8 or 75 MHz: chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of $CDCl_3$ (δ 77.0). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), signal area integration in natural numbers, and assignment (*italic*). IR spectra were recorded on an ATR-FTIR spectrometer (FT/IR-Spectrum One, PerkinElmer). Characteristic IR absorptions are reported in cm^{-1}. High-resolution

(1) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

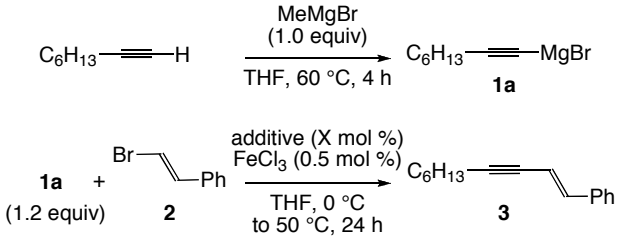
mass spectra (HRMS) were obtained using the electron impact (EI) method with JEOL JMS-700. NMR yield was determined for a crude product by ^{1}H NMR analyses by using dibromomethane as an internal standard and GC yield was determined upon calibration by using undecane as an internal standard. Purity of isolated compounds was determined by GC analysis on Shimadzu GC-17A instrument equipped with an FID detector and a capillary column, HR-1 (Shinwa, 25 m × 0.25 mm i.d., 0.25 μm film thickness) and/or ^{1}H NMR analyses.

Solvent. Anhydrous tetrahydrofuran (THF) was purchased from Wako Chemical Co. and distilled, immediately before use, from benzophenone ketyl under argon (atmospheric pressure). Water content of the solvent was determined with a Karl-Fischer moisture titrator (MKC-210, Kyoto Electronics Company) to be less than 30 ppm.

Materials. Materials were purchased from Wako Pure Chemical Industries, Ltd. (Wako), Tokyo Chemical Industry Co., Ltd., Aldrich Inc., and other commercial suppliers. Florisil® (100–200 mesh) was purchased from Nacalai Tesque, Inc. Anhydrous $FeCl_3$ (powder, 99.99%) was purchased from Aldrich Inc. and dissolved in THF at 0 °C prior to use. Lithium bromide (Aldrich, beads, 99.9%) and lithium chloride (Wako, 99.9%) were dried in vacuo at 120 °C for 2 h. Zinc chloride (beads, 99.999%) and magnesium bromide (98%) were purchased from Aldrich Inc. β-Bromostyrene (Wako, > 97%) was distilled in vacuo prior to use.

Screening of additives and metal salts (Table 1 and 2)

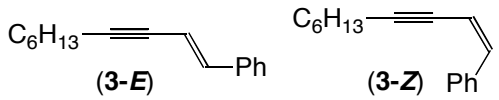
1-Octyne **1** (0.132 g, 1.20 mmol) was added to a THF solution of methylmagnesium bromide (1.14 mL, 1.05 M, 1.20 mmol) at 0 °C. After stirring at 60 °C for 4 h, a THF solution of additive (1.20 mmol) and a THF solution of $FeCl_3$ (0.050 mL, 0.10 M, 0.005 mmol) were added in turn at 0 °C. After stirring at the same temperature for 30 min, β-bromostyrene **2** (0.183 g, 1.00 mmol) was added at 0 °C and then stirred for 15 min. The reaction was carried out at 50 °C for 24 h. After cooling to 0 °C, aqueous ammonium chloride (saturated, 2.0 mL) was added. The aqueous layer was extracted five times with Et_2O. The combined organic extracts were filtered with a pad of Florisil®. The yield of dec-1-en-3-ynylbenzene **3** was determined by ^{1}H NMR analysis by using dibromomethane as an internal standard.



entry[a]	additive (X mol %)	yield of **3** (%)[b]	recovery of **2** (%)
1	none (–)	12	83
2	NMP (900)	2	69
3	HMTA/TMEDA (5/10)	15	76
4	SIPr·HCl (2)	11	76
5	PCy_3 (1)	17	75
6	TMEDA (120)	60	36
7	LiCl (120)	**82**	18
8	LiBr (120)	**85**	9
9	LiBr (60)	27	71
10	LiBr (20)	21	72
11	$MgBr_2$ (120)	28	65
12	$ZnCl_2$ (120)	1	93

[a] Reactions were carried out on a 1.0 mmol scale. [b] The yield was determined by ^{1}H NMR analysis by using dibromomethane as an internal standard.

A representative procedure for the reactions shown in Table 3; Synthesis of dec-1-en-3-ynylbenzene (3)

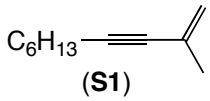


1-Octyne **1** (2.645 g, 24.0 mmol) was added to a THF solution of methylmagnesium bromide (24.5 mL, 0.98 M, 24 mmol) at 0 °C. After stirring at 60 °C for 4 h, a THF solution of lithium bromide (24.0 mL, 1.00 M, 24.0 mmol) and a THF solution of $FeCl_3$ (2.00 mL, 0.10 M, 0.200 mmol) was added at 0 °C. After stirring at same temperature for 30 min, β-bromostyrene **2** (3.662 g, 20.0 mmol, *E*:*Z* = 85:15) was added at 0 °C and then stirred for 15 min. The reaction was carried out at 60 °C for 24 h. After cooling to 0 °C, aqueous ammonium chloride (saturated, 40 mL) was added. The aqueous layer was extracted five times with Et_2O. The combined organic extracts were filtered with

a pad of Florisil®. After the solvent was removed in vacuo, the crude product was purified by chromatography on silica gel (pentane) to obtain the title compound **3** (3.924 g, 92% yield, *E*:*Z* = 88:12, 99% pure on GC analysis) as a pale yellow liquid. ^{1}H and ^{13}C NMR spectra have been attached. Analytical data for the title compound have been reported.[2] R_f = 0.30 (hexane); IR (neat) 2928, 2857, 1448, 951, 746, 689; ^{1}H NMR (270 MHz, $CDCl_3$) For **3-*E***: δ 0.90 (t, 3H, *J* = 6.7 Hz), 1.26–1.64 (m, 8H), 2.36 (td, 2H, *J* = 7.1 Hz, 2.1 Hz), 6.16 (dt, 1H, *J* = 16.2 Hz, 2.3 Hz), 6.87 (d, 1H, *J* = 16.2 Hz), 7.21–7.38 (m, 5H), for **3-*Z***: δ 0.90 (t, 3H, *J* = 6.7 Hz), 1.26–1.64 (m, 8H), 2.44 (td, 2H, *J* = 6.9 Hz, 2.5 Hz), 5.70 (dt, 1H, *J* = 11.9 Hz, 2.5 Hz), 6.54 (d, 1H, *J* = 11.9 Hz), 7.21–7.38 (m, 3H), 7.85–7.88 (m, 2H). Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.22; H, 9.76.

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using 1-octyne **1** (0.132 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.050 mL, 0.10 M, 0.005 mmol) and β-bromostyrene **2** (0.183 g, 1.00 mmol, *E*:*Z* = 85:15). Conditions: 60 °C, 24 h. The title compound **3** (0.202 g, 95% yield, *E*:*Z* = 88:12, 99% pure on GC analysis) was obtained as a pale yellow liquid after silica gel column chromatography (pentane).

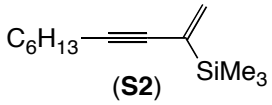
Synthesis of 2-methyldec-1-en-3-yne (S1)



(**S1**)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using 1-octyne **1** (0.132 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.10 mL, 0.10 M, 0.010 mmol) and 2-bromopropene (0.121 g, 1.00 mmol). Conditions: 60 °C, 24 h. The title compound **S1** (0.114 g, 76% yield, > 98% pure on GC analysis) was obtained as a pale yellow liquid after silica gel column chromatography (pentane). ^{1}H and ^{13}C NMR spectra have been attached. R_f = 0.45 (hexane); IR (neat) 2928, 2858, 1615, 1455, 888; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 6.8 Hz), 1.23–1.58 (m, 8H), 1.87 (t, 3H, *J* = 1.3 Hz), 2.29 (t, 2H, *J* = 7.0 Hz), 5.13 (dt, 1H, *J* = 1.6 Hz, 1.3 Hz), 5.19 (brs, 1H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 14.0, 19.3, 22.5, 23.9, 28.5, 28.7, 31.3, 81.8, 89.5, 120.2, 127.4.

Synthesis of dec-1-en-3-yn-2-yltrimethylsilane (S2)



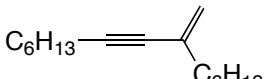
(**S2**)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using 1-octyne **1** (0.132 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.050 mL, 0.10 M, 0.005 mmol) and (1-bromovinyl)trimethylsilane (0.179 g, 1.00 mmol). Conditions: 60 °C, 12 h. The title compound **S2**

(2) Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972–980.

(0.211 g, > 99% yield, > 98% pure on GC analysis) was obtained as a pale yellow liquid after silica gel column chromatography (pentane). ^{1}H and ^{13}C NMR spectra have been attached. R_f = 0.45 (hexane); IR (neat) 2957, 2930, 2858, 1458, 1247, 919, 837; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.14 (s, 9H), 0.89 (t, 3H, J = 6.9 Hz), 1.29–1.56 (m, 8H), 2.35 (t, 2H, J = 6.9 Hz), 5.60 (d, 1H, J = 3.3 Hz), 5.99 (d, 1H, J = 3.3 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ –2.2 (3C), 14.0, 19.6, 22.6, 28.5, 29.0, 31.4, 81.7, 94.8, 132.3, 135.3. Anal. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 74.95; H, 11.71.

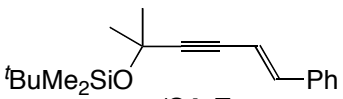
Synthesis of 9-methylenepentadec-7-yne (S3)



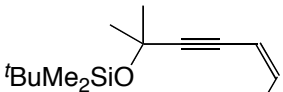
(**S3**)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using 1-octyne **1** (0.132 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.10 mL, 0.10 M, 0.010 mmol) and oct-1-en-2-yl trifluoromethanesulfonate (0.260 g, 1.00 mmol). Conditions: 60 °C, 24 h. The title compound **S3** (0.167 mg, 75% yield, 98% pure on GC analysis) was obtained as a pale yellow liquid after silica gel column chromatography (pentane). ^{1}H and ^{13}C NMR spectra have been attached. Analytical data for the title compound have been reported.[3] R_f = 0.50 (hexane); IR (neat) 2927, 2857, 1676, 1458, 1049, 891, 725; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 6.8 Hz), 0.89 (t, 3H, J = 6.8 Hz), 1.29–1.55 (m, 16H), 2.12 (t, 2H, J = 7.5 Hz), 2.30 (t, 2H, J = 7.0 Hz), 5.12 (d, 1H, J = 3.3 Hz), 5.19 (d, 1H, J = 3.3 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 14.0, 14.1, 19.3, 22.6 (2C), 28.1, 28.5, 28.6, 28.8, 31.4, 31.7, 37.6, 81.0, 90.1, 119.3, 132.5. Anal. Calcd for $C_{16}H_{28}$: C, 87.19; H, 12.81. Found: C, 86.99; H, 12.84.

Synthesis of *tert*-butyldimethyl(2-methyl-6-phenylhex-5-en-3-yn-2-yloxy)silane (S4)



(**S4-*E***)



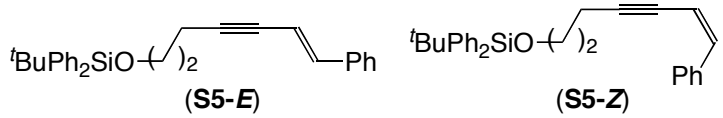
(**S4-*Z***)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using *tert*-butyldimethyl(2-methylbut-3-yn-2-yloxy)silane (0.238 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.10 mL, 0.10 M, 0.010 mmol) and β-bromostyrene **2** (0.183 g, 1.00 mmol, *E*:*Z* = 85:15). Conditions: 60 °C, 24 h. The title compound **S4** (0.246 g, 82% yield, *E*:*Z* = 92:8, > 99% pure on GC analysis) was obtained as a pale yellow liquid after silica gel column chromatography (hexane). ^{1}H and ^{13}C NMR spectra have been attached. R_f = 0.30 (hexane); IR (neat) 2929, 2856, 1462, 1359, 1244, 1157, 1032, 951, 827, 774, 688; ^{1}H NMR (270 MHz, $CDCl_3$) For **S4-*E***: δ 0.19 (s, 6H), 0.88 (s, 9H), 1.51 (s, 6H), 6.17 (d, 1H, J = 16.3 Hz), 6.89 (d, 1H, J = 16.3 Hz), 7.23–7.40 (m, 5H), for **S4-*Z***: δ 0.15 (s, 6H), 0.87 (s, 9H), 1.55 (s, 6H), 5.71 (d, 1H, J = 12.0 Hz), 6.61 (d, 1H, J = 12.0 Hz), 7.23–7.40 (m, 3H), 7.84–7.87 (m, 2H). ^{13}C NMR (67.5 MHz, $CDCl_3$) For **S4-*E***: δ –3.0 (2C), 18.0, 25.8

(3) Komeyama, K; Kawabata, T; Takehira, K; Takaki, K. *J. Org. Chem.* **2005**, *70*, 7260–7266.

(3C), 33.0 (2C), 66.7, 81.9, 97.1, 108.0, 126.2 (2C), 128.5, 128.7 (2C), 136.3, 140.7, for **S4-*Z***: δ –3.0 (2C), 18.0, 25.7 (3C), 32.7 (2C), 67.0, 81.2, 101.3, 107.2, 128.1, 128.4 (2C), 128.5 (2C), 136.5, 138.4. Anal. Calcd for $C_{19}H_{28}OSi$: C, 75.94; H, 9.39. Found: C, 75.83; H, 9.45.

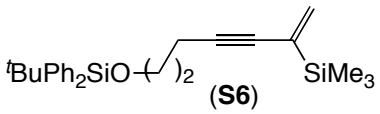
Synthesis of *tert*-butyldiphenyl(7-phenylhept-6-en-4-ynyloxy)silane (S5)



(**S5-*E***) (**S5-*Z***)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using *tert*-butyl(pent-4-ynyloxy)diphenylsilane (0.387 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.10 mL, 0.10 M, 0.010 mmol) and β-bromostyrene **2** (0.183 g, 1.00 mmol, *E*:*Z* = 85:15). Conditions: 60 °C, 24 h. The title compound **S5** (0.385 g, 91% yield, *E*:*Z* = 85:15, 99% pure on GC analysis) was obtained as a colorless liquid after ODS column chromatography (20, 10% H_2O in MeOH and MeOH). ^1H and ^{13}C NMR spectra have been attached. R_f = 0.08 (10% H_2O in MeOH); IR (neat) 3026, 2929, 2856, 1589, 1427, 1104, 951, 822, 741, 699; ^1H NMR (270 MHz, $CDCl_3$) For **S5-*E***: δ 1.06 (s, 9H), 1.82 (tt, 2H, *J* = 5.9 Hz, 7.1 Hz), 2.53 (td, 2H, *J* = 7.1 Hz, 2.3 Hz), 3.78 (t, 2H, *J* = 5.9 Hz), 6.12 (dt, 1H, *J* = 16.2 Hz, 2.3 Hz), 6.83 (d, 1H, *J* = 16.2), 7.22–7.46 (m, 11H), 7.63–7.71 (m, 4H), for **S5-*Z***: δ 1.05 (s, 9H), 1.85 (tt, 2H, *J* = 5.9 Hz, 6.9 Hz), 2.60 (td, 2H, *J* = 6.9 Hz, 2.5 Hz), 3.79 (t, 2H, *J* = 5.9 Hz), 5.67 (dt, 1H, *J* = 11.9 Hz, 2.5 Hz), 6.55 (d, 1H, *J* = 11.9 Hz), 7.22–7.46 (m, 9H), 7.63–7.71 (m, 4H), 7.82–7.86 (m, 2H). ^{13}C NMR (67.5 MHz, $CDCl_3$) For **S5-*E***: δ 16.2, 19.2, 26.8 (3C), 31.6, 62.4, 79.9, 92.4, 108.8, 126.0 (2C), 127.6 (4C), 128.2, 128.6 (2C), 129.6 (2C), 133.8 (2C), 135.6 (4C), 136.5, 140.0, for **S5-*Z***: δ 16.4, 19.2, 26.8 (3C), 31.5, 62.4, 79.3, 97.2, 108.1, 127.6 (4C), 128.1, 128.1 (2C), 128.4 (2C), 129.6 (2C), 133.7 (2C), 135.5 (4C), 136.5, 137.3. Anal. Calcd for $C_{29}H_{32}OSi$: C, 82.02; H, 7.60. Found: C, 81.85; H, 7.75.

Synthesis of *tert*-butyldiphenyl(6-(trimethylsilyl)hept-6-en-4-ynyloxy)silane (S6)

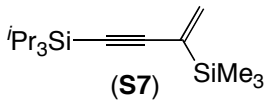


(**S6**)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using *tert*-butyl(pent-4-ynyloxy)diphenylsilane (0.387 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.10 mL, 0.10 M, 0.010 mmol) and (1-bromovinyl)trimethylsilane (0.179 g, 1.00 mmol). Conditions: 60 °C, 24 h. The title compound **S6** (0.371 g, 88% yield, 99% pure on GC analysis) was obtained as a colorless liquid after ODS column chromatography (20, 10% H_2O in MeOH and MeOH). ^1H and ^{13}C NMR spectra have been attached. R_f = 0.10 (10% H_2O in MeOH); IR (neat) 2955, 2857, 1472, 1427, 1247, 1105, 838, 699; ^1H NMR (270 MHz, $CDCl_3$) δ 0.12 (s, 9H), 1.05 (s, 9H), 1.79 (tt, 2H, *J* = 6.1 Hz, 7.1 Hz), 2.51 (t, 2H, *J* = 7.1 Hz), 3.76 (t, 2H, *J* = 6.1 Hz), 5.60 (d, 1H, *J* = 3.6 Hz), 5.99 (d, 1H, *J* = 3.6 Hz), 7.26–7.45 (m, 6H), 7.65–7.69 (m, 4H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ –2.2 (3C), 16.2,

19.2, 26.8 (3C), 32.0, 62.5, 81.8, 94.1, 127.6 (4C), 129.5 (2C), 132.6, 133.9 (2C), 135.2, 135.5 (4C). Anal. Calcd for $C_{26}H_{36}OSi_2$: C, 74.22; H, 8.62. Found: C, 74.50; H, 8.57.

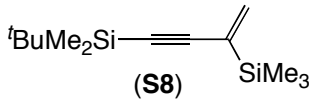
Synthesis of triisopropyl(3-(trimethylsilyl)but-3-en-1-ynyl)silane (S7)



(**S7**)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using ethynyltriisopropylsilane (0.219 mg, 1.20 mmol), a THF solution of $FeCl_3$ (0.050 mL, 0.10 M, 0.005 mmol) and (1-bromovinyl)trimethylsilane (0.179 g, 1.00 mmol). Conditions: 60 °C, 24 h. The title compound **S7** (0.233 g, 84% yield, 98% pure on GC analysis) was obtained as a colorless liquid after ODS column chromatography (7% H_2O in MeOH). ^1H and ^{13}C NMR spectra have been attached. R_f = 0.11 (10% H_2O in MeOH); IR (neat) 2942, 2865, 2121, 1462, 1248, 925, 822, 838, 755, 697, 673; ^1H NMR (270 MHz, $CDCl_3$) δ 0.17 (s, 9H), 1.08 (s, 18H), 1.08–1.09 (m, 3H), 5.70 (d, 1H, J = 3.5 Hz), 6.12 (d, 1H, J = 3.5 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ –2.2 (3C), 11.4 (3C), 18.7 (6C), 94.3, 108.3, 134.5, 135.2. Anal. Calcd for $C_{16}H_{32}Si_2$: C, 68.49; H, 11.49. Found: C, 68.69; H, 11.55.

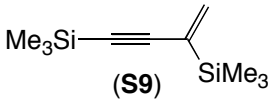
Synthesis of *tert*-butyldimethyl(3-(trimethylsilyl)but-3-en-1-ynyl)silane (S8)



(**S8**)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using *tert*-butyl(ethynyl)dimethylsilane (0.168 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.30 mL, 0.10 M, 0.030 mmol) and (1-bromovinyl)trimethylsilane (0.179 g, 1.00 mmol). Conditions: 60 °C, 24 h. The title compound **S8** (0.207 g, 87% yield, > 99% pure on GC analysis) was obtained as a colorless liquid after ODS column chromatography (20, 10% H_2O in MeOH and MeOH). ^1H and ^{13}C NMR spectra have been attached. R_f = 0.28 (10% H_2O in MeOH); IR (neat) 2955, 2929, 2857, 2123, 1471, 1249, 973, 927, 822, 808, 773; ^1H NMR (270 MHz, $CDCl_3$) δ 0.12 (s, 6H), 0.16 (s, 9H), 0.95 (s, 9H), 5.71 (d, 1H, J = 3.5 Hz), 6.13 (d, 1H, J = 3.5 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ –4.5 (2C), –2.2 (3C), 16.7, 26.1 (3C), 96.6, 107.1, 134.8, 134.9. HRMS (EI) m/z calcd for $C_{13}H_{26}Si_2$ (M^+) 238.1573, found 238.1572.

Synthesis of but-3-en-1-yne-1, 3-diylbis(trimethylsilane) (S9)

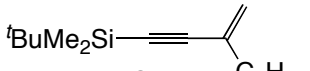


(**S9**)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using ethynyltrimethylsilane (0.118 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.30 mL, 0.10 M, 0.030 mmol) and (1-bromovinyl)trimethylsilane (0.179 g, 1.00 mmol). Conditions: 60 °C, 24 h. Yields of the title compound **S9** (39% yield, using dibromomethane as an internal standard) was determined by NMR analysis. The crude product was purified by silica gel column chromatography (hexane). ^1H NMR spectra have been attached. R_f = 0.59 (pentane); ^1H NMR (270 MHz, $CDCl_3$) δ 0.16 (s, 9H),

0.19 (s, 9H), 5.70 (d, 1H, J = 3.4 Hz), 6.12 (d, 1H, J = 3.4 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ –2.3 (3C), 0.1 (3C), 98.5, 106.5, 134.7, 134.8.

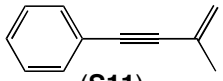
Synthesis of *tert*-butyldimethyl(3-methylenenon-1-ynyl)silane (S10)



(**S10**)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using *tert*-butyl(ethynyl)dimethylsilane (0.168 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.10 mL, 0.10 M, 0.010 mmol) and oct-1-en-2-yl trifluoromethanesulfonate (0.260 g, 1.00 mmol). Conditions: 60 °C, 12 h. The title compound **S10** (0.207 g, 83% yield, 96% pure on GC analysis) was obtained as a colorless liquid after ODS column chromatography (20, 10% H_2O in MeOH and MeOH). ^{1}H and ^{13}C NMR spectra have been attached. R_f = 0.15 (10% H_2O in MeOH); IR (neat) 2954, 2928, 2856, 2145, 1463, 1249, 898, 835, 823, 808, 774; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.12 (s, 6H), 0.89 (t, 3H, J = 6.9 Hz), 0.95 (s, 9H), 1.29–1.57 (m, 8H), 2.14 (t, 2H, J = 7.4 Hz), 5.23 (d, 1H, J = 1.5 Hz), 5.35 (d, 1H, J = 1.5 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ –4.6 (2C), 14.1, 16.7, 22.6, 26.1 (3C), 27.9, 28.5, 31.6, 37.1, 92.0, 106.4, 121.7, 132.0. Anal. Calcd for $C_{16}H_{30}Si$: C, 76.72; H, 12.07. Found: C, 76.44; H, 12.02.

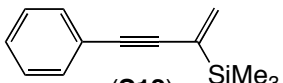
Synthesis of (3-methylbut-3-en-1-ynyl)benzene (S11)



(**S11**)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using ethynylbenzene (0.123 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.10 mL, 0.10 M, 0.010 mmol) and 2-bromopropene (0.121 g, 1.00 mmol). Conditions: 80 °C, 24 h. The title compound **S11** (0.082 g, 60% yield, 99% pure on GC analysis) was obtained as a colorless liquid after silica gel column chromatography (pentane). ^{1}H and ^{13}C NMR spectra have been attached. Analytical data for the title compound have been reported.[4] R_f = 0.53 (pentane); IR (neat) 2939, 2202, 1675, 1490, 1277, 1156, 1026, 689, 668; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.99 (s, 3H), 5.30 (s, 1H), 5.39 (s, 1H), 7.29–7.31 (m, 3H), 7.42–7.46 (m, 2H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 23.5, 88.4, 90.6, 121.9, 123.3, 126.9, 128.1, 128.3 (2C), 131.6 (2C).

Synthesis of trimethyl(4-phenylbut-1-en-3-yn-2-yl)silane (S12)



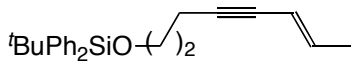
(**S12**)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using ethynylbenzene (0.123 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.05 mL, 0.10 M, 0.005 mmol) and oct-1-en-2-yl trifluoromethanesulfonate (0.260 g, 1.00 mmol). Conditions: 60 °C, 24 h. The title

(4) Feuerstein, M; Chahen, L; Doucet, H; Santelli, M. *Tetrahedron* **2006**, *62*, 112–120.

compound **S12** (0.183 g, 91% yield, > 99% pure on GC analysis) was obtained as a pale yellow liquid after ODS column chromatography (15, 10% H_2O in MeOH and MeOH). ^1H and ^{13}C NMR spectra have been attached. R_f = 0.35 (10% H_2O in MeOH); IR (neat) 2957, 2202, 1672, 1597, 1489, 1442, 1248, 836, 753, 688; ^1H NMR (270 MHz, $CDCl_3$) δ 0.22 (s, 9H), 5.75 (d, 1H, J = 3.4 Hz), 6.16 (d, 1H, J = 3.4 Hz), 7.28–7.34 (m, 3H), 7.41–7.44 (m, 2H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ –2.1 (3C), 90.7, 93.7, 124.0, 127.9, 128.3 (2C), 131.5 (2C), 133.7, 134.5. Anal. Calcd for $C_{13}H_{16}Si$: C, 77.93; H, 8.05. Found: C, 77.69; H, 8.01.

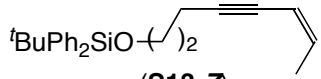
Synthesis of (*E*)-*tert*-butyl(oct-6-en-4-ynyloxy)diphenylsilane (S13-*E*)



(**S13-*E***)

The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using *tert*-butyl(pent-4-ynyloxy)diphenylsilane (0.387 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.10 mL, 0.10 M, 0.010 mmol) and (*E*)-1-bromopropene (0.121 g, 1.00 mmol, 99% pure). Conditions: 60 °C, 24 h. The title compound **S13** (0.336 g, 92% yield, *E*:*Z* = 93:7, 99% pure on GC analysis) was obtained as a pale yellow liquid after ODS column chromatography (30, 15% H_2O in MeOH and MeOH). ^1H and ^{13}C NMR spectra have been attached. R_f = 0.18 (10% H_2O in MeOH); IR (neat) 2930, 2856, 1472, 1427, 1104, 951, 821, 699, 613, 503; ^1H NMR of **S13-*E*** (270 MHz, $CDCl_3$) δ 0.14 (s, 9H), 1.75 (d, 3H, J = 6.8 Hz), 1.72–1.82 (m, 2H), 2.44 (td, 2H, J = 7.1 Hz, 1.6 Hz), 3.74 (t, 2H, J = 6.1 Hz), 5.44 (dq, 1H, J = 15.7 Hz, 1.6 Hz), 6.02 (dq, 1H, J = 15.7 Hz, 6.8 Hz), 7.34–7.46 (m, 6H), 7.65–7.70 (m, 4H). ^{13}C NMR of **S13-*E*** (67.5 MHz, $CDCl_3$) δ 15.8, 18.4, 19.2, 26.8 (3C), 31.7, 62.4, 79.3, 87.9, 111.1, 127.6 (4C), 129.5 (2C), 133.8 (2C), 135.5 (4C), 137.9. Anal. Calcd for $C_{24}H_{30}OSi$: C, 79.50; H, 8.34. Found: C, 79.22; H, 8.50.

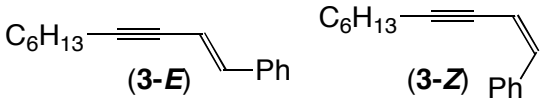
Synthesis of (*Z*)-*tert*-butyl(oct-6-en-4-ynyloxy)diphenylsilane (S13-*Z*)



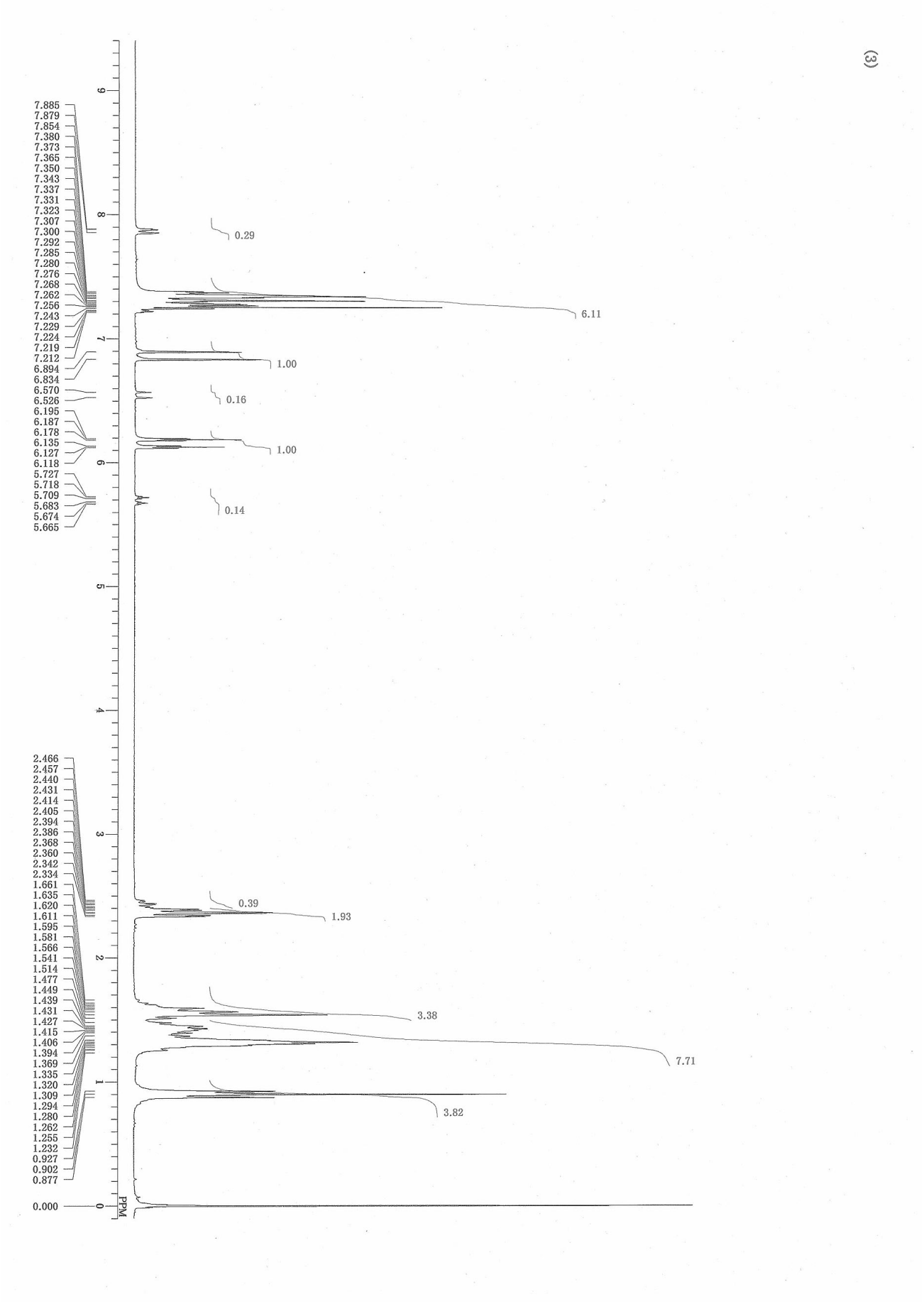
(**S13-*Z***)

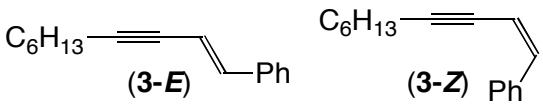
The reaction was carried out according to the representative procedure on a 1.0 mmol scale by using *tert*-butyl(pent-4-ynyloxy)diphenylsilane (0.387 g, 1.20 mmol), a THF solution of $FeCl_3$ (0.10 mL, 0.10 M, 0.010 mmol) and (*Z*)-1-bromopropene (0.121 g, 1.00 mmol, 99% pure). Conditions: 60 °C, 24 h. The crude product was obtained as a pale yellow liquid (0.442 g, 94% yield, *E*:*Z* = 35:65 determined by ^1H NMR analysis without further purification). ^1H NMR of **S13-*Z*** (270 MHz, $CDCl_3$) δ 0.15 (s, 9H), 1.81 (d, 3H, J = 6.8 Hz), 1.72–1.85 (m, 2H), 2.52 (td, 2H, J = 7.1 Hz, 1.8 Hz), 3.77 (t, 2H, J = 5.9 Hz), 5.41–5.49 (m, 1H), 5.88 (dq, 1H, J = 10.7 Hz, 6.8 Hz), 7.33–7.45 (m, 6H), 7.65–7.70 (m, 4H). ^{13}C NMR of **S13-*Z*** (67.5 MHz, $CDCl_3$) δ 15.7, 16.1, 19.2, 26.8 (3C), 31.8, 62.4, 77.3, 94.4, 110.4, 127.6 (4C), 129.5 (2C), 133.8 (2C), 135.5 (4C), 136.9.

^{1}H and ^{13}C NMR spectra for isolated compounds (3) and (S1)–(S13)

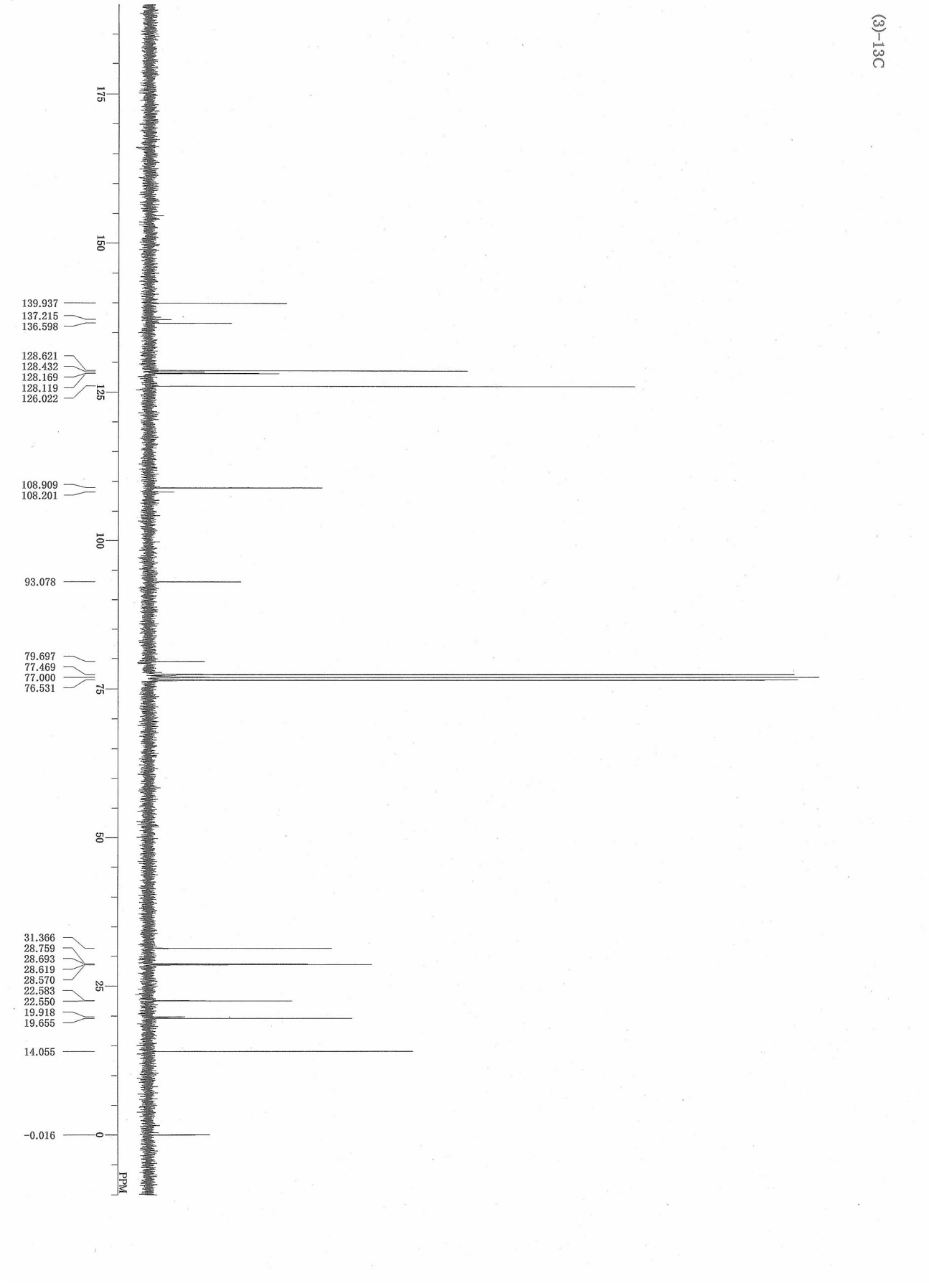


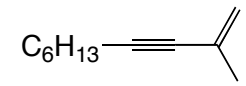
E:*Z* = 88:12




C6H13
(3-E)
Ph
C6H13
(3-Z)
Ph

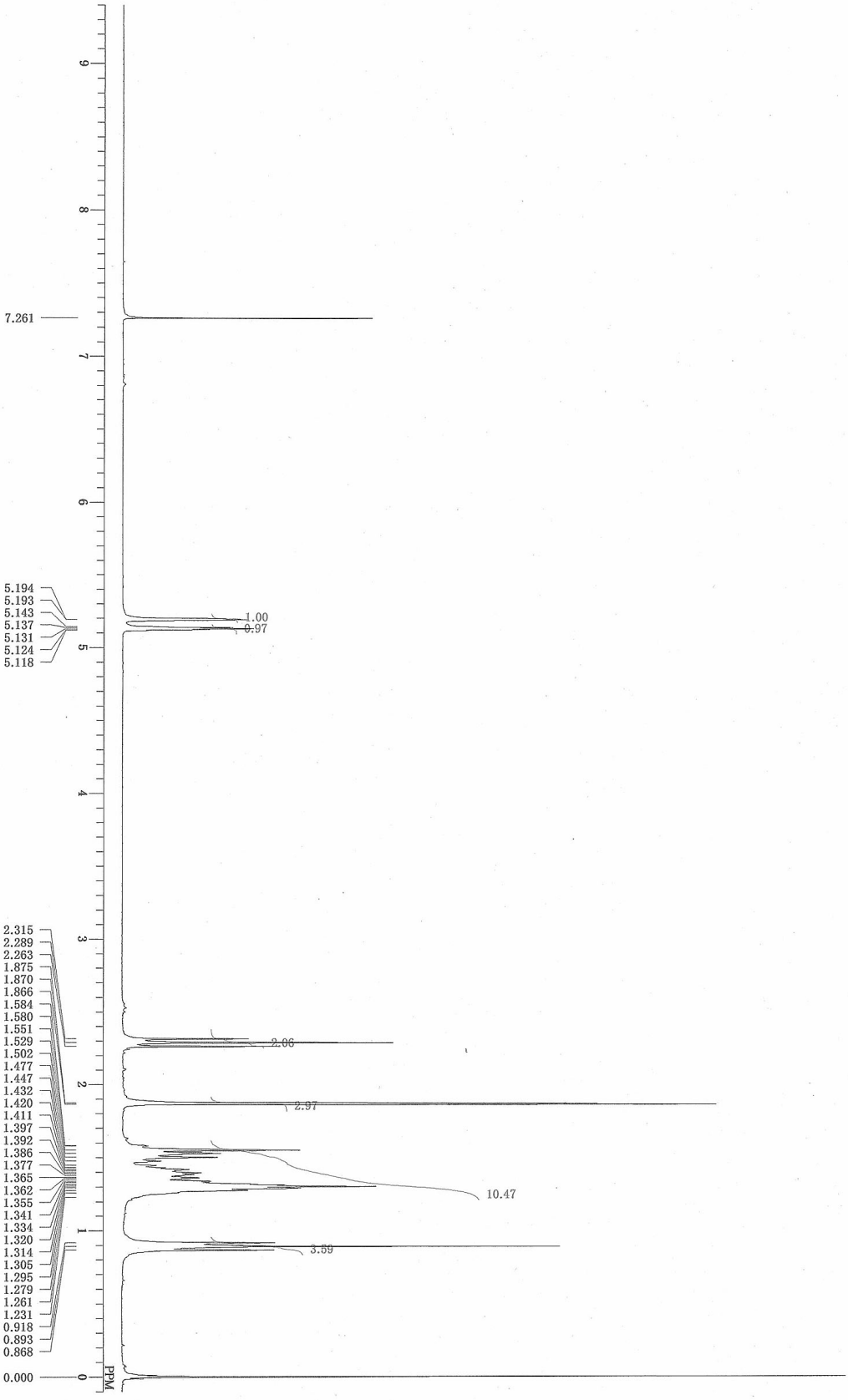
E:*Z* = 88:12

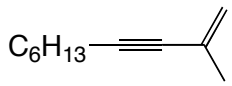

(3)-13C
175
150
125
100
75
50
25
0
PPM
139.937
137.215
136.598
128.621
128.432
128.169
128.119
126.022
108.909
108.201
93.078
79.697
77.469
77.000
76.531
31.366
28.759
28.693
28.619
28.570
22.583
22.550
19.918
19.655
14.055
-0.016



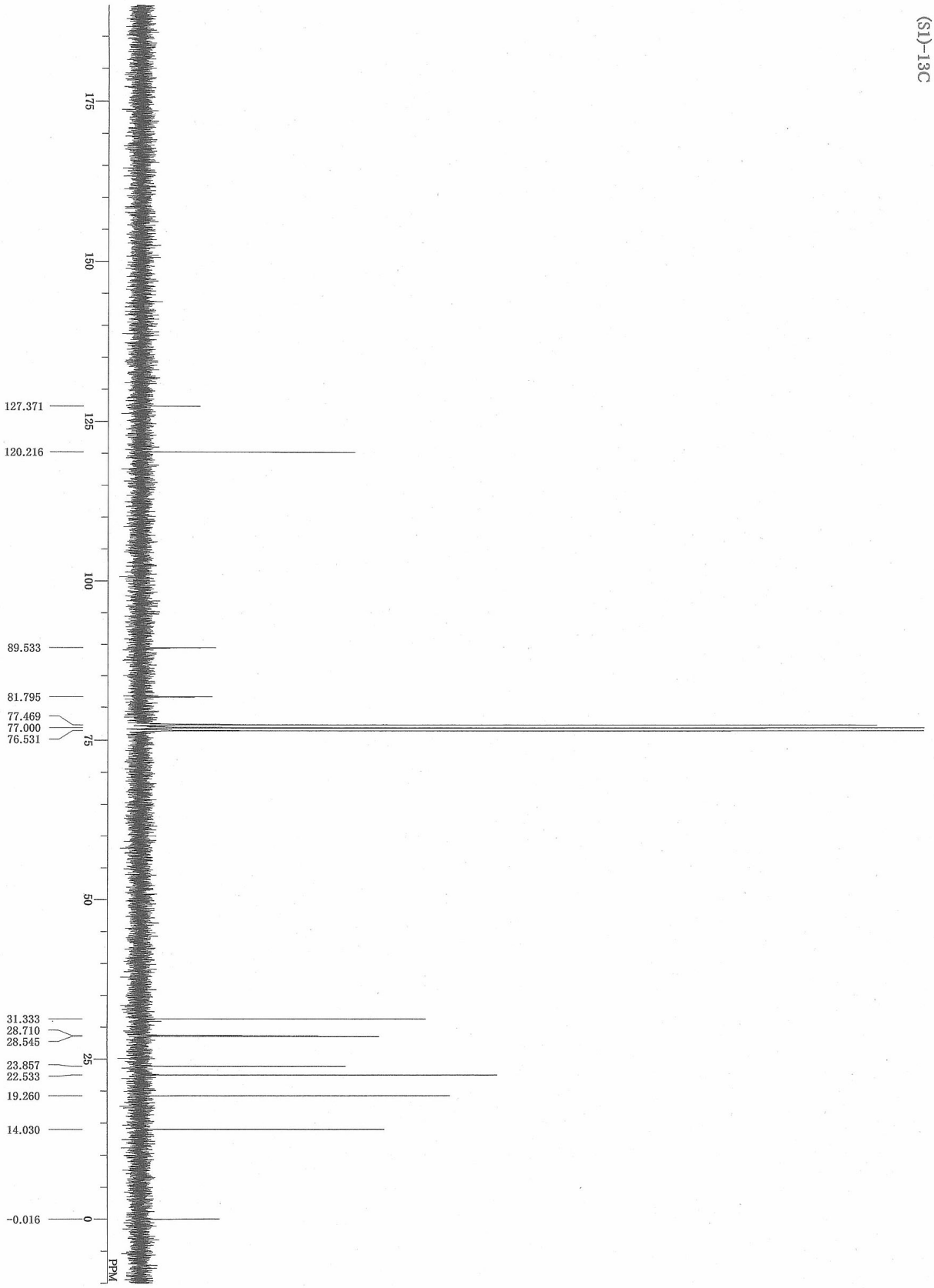
(S1)

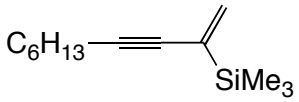
(S1)-1H


7.261
5.194
5.193
5.143
5.137
5.131
5.124
5.118
1.00
0.97
2.315
2.289
2.263
1.875
1.870
1.866
1.584
1.580
1.551
1.529
1.502
1.477
1.447
1.432
1.420
1.411
1.397
1.392
1.386
1.377
1.365
1.362
1.355
1.341
1.334
1.320
1.314
1.305
1.295
1.279
1.261
1.231
0.918
0.893
0.868
0.000
2.06
2.97
10.47
3.59
PPM

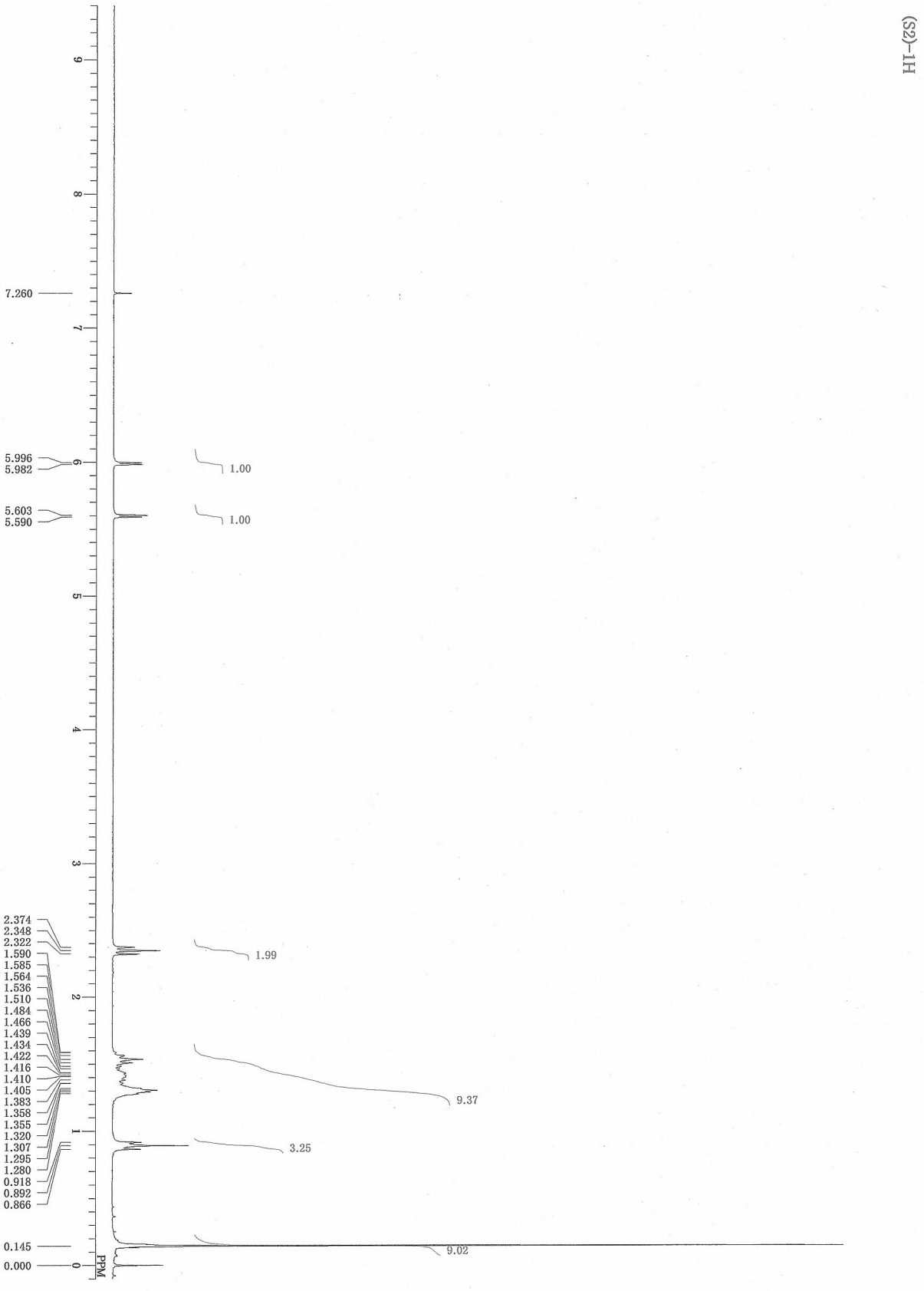

C6H13

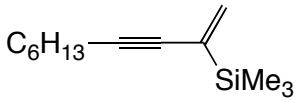
(S1)


(S1)-13C
175
150
125
100
75
50
25
0
PPM
127.371
120.216
89.533
81.795
77.469
77.000
76.531
31.333
28.710
28.545
23.857
22.533
19.260
14.030
-0.016

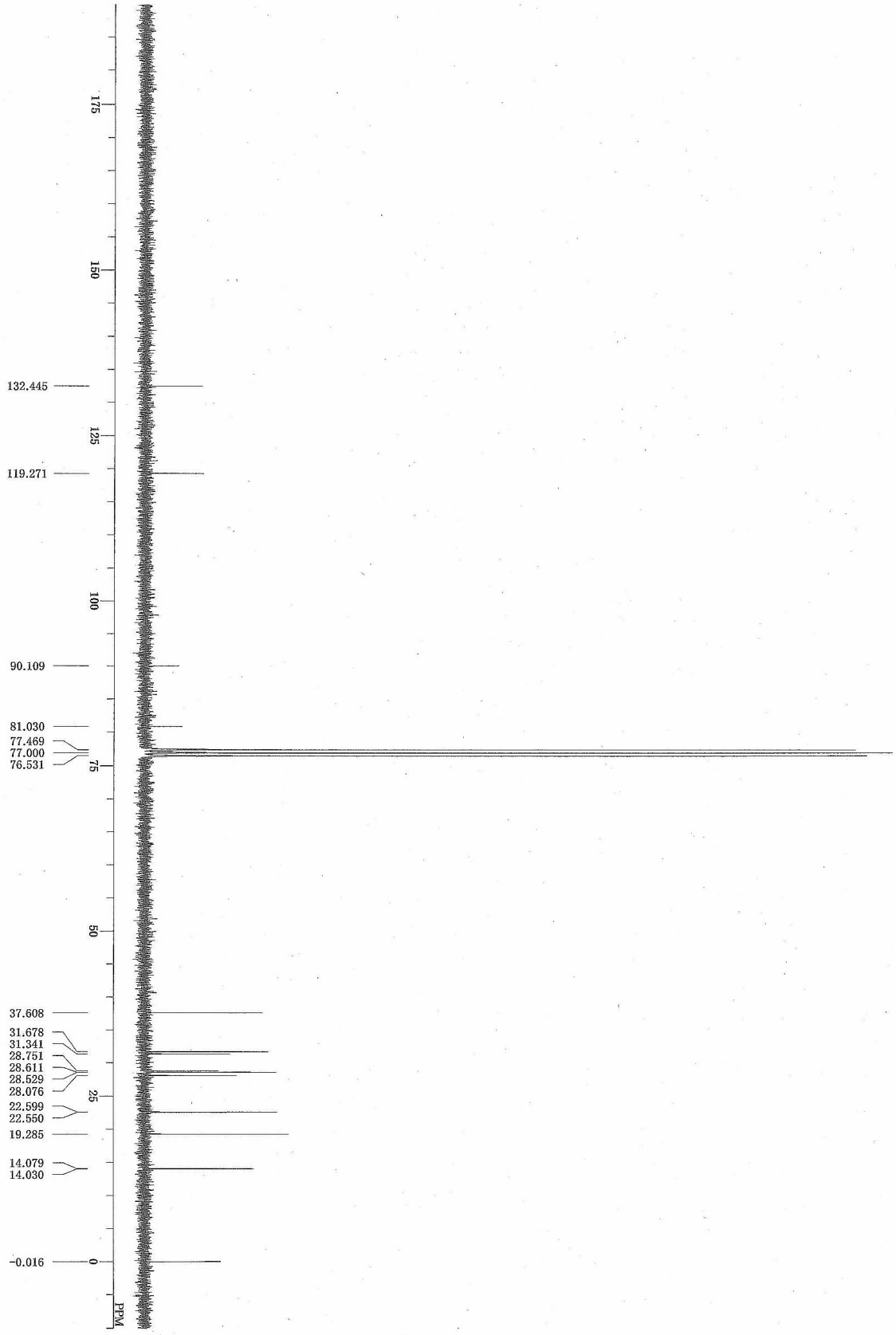

C6H13
SiMe3

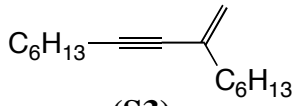
(S2)


(S2)-1H
7.260
5.996
5.982
5.603
5.590
2.374
2.348
2.322
1.590
1.585
1.564
1.536
1.510
1.484
1.466
1.439
1.434
1.422
1.416
1.410
1.405
1.383
1.358
1.355
1.320
1.307
1.295
1.280
0.918
0.892
0.866
0.145
0.000
1.00
1.00
1.99
9.37
3.25
9.02
PPM

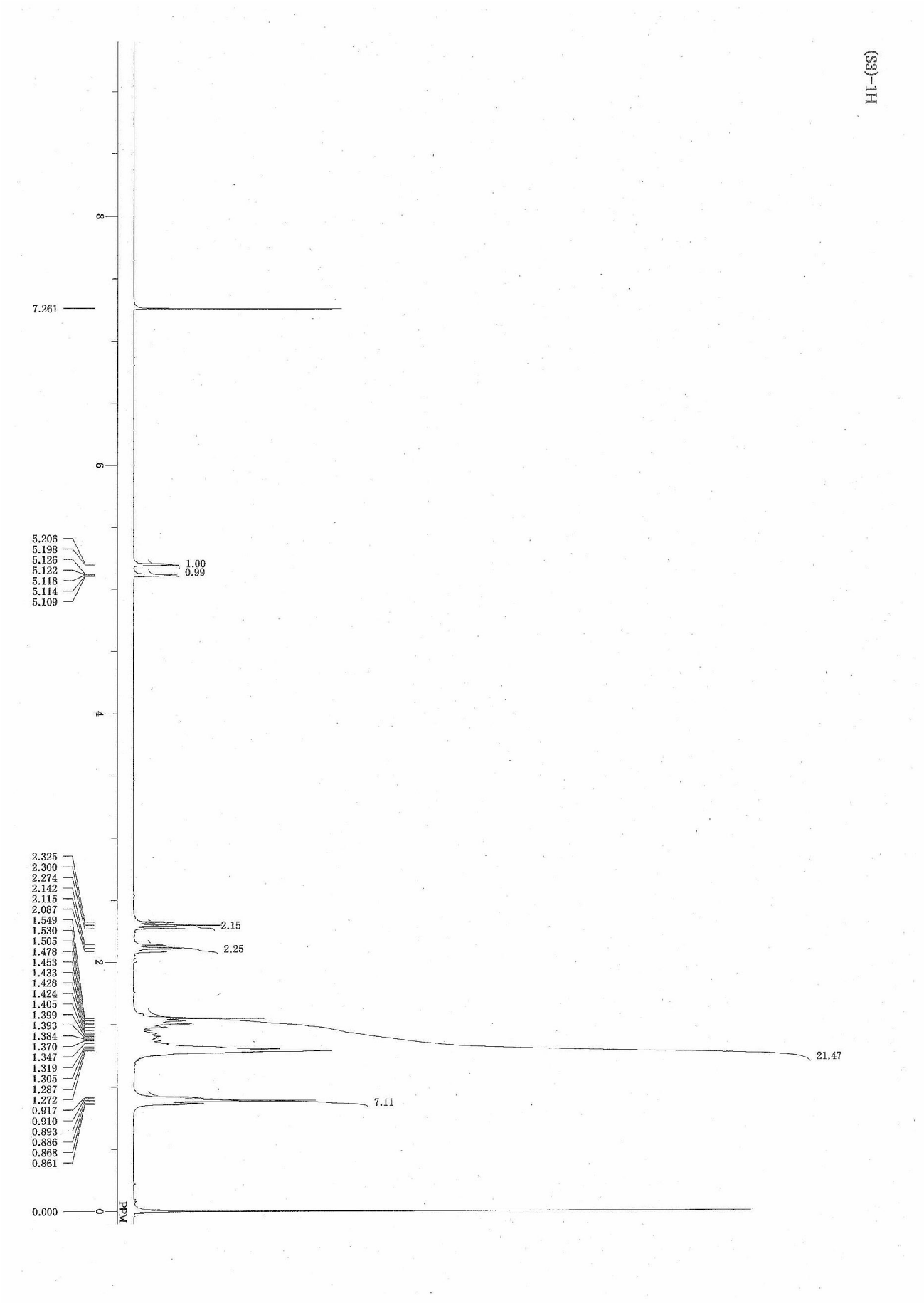

C6H13
SiMe3

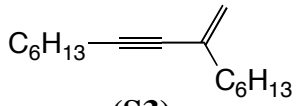
(S2)


(S2)-13C
175
150
125
100
75
50
25
0
PPM
132.445
119.271
90.109
81.030
77.469
77.000
76.531
37.608
31.678
31.341
28.751
28.611
28.529
28.076
22.599
22.550
19.285
14.079
14.030
-0.016

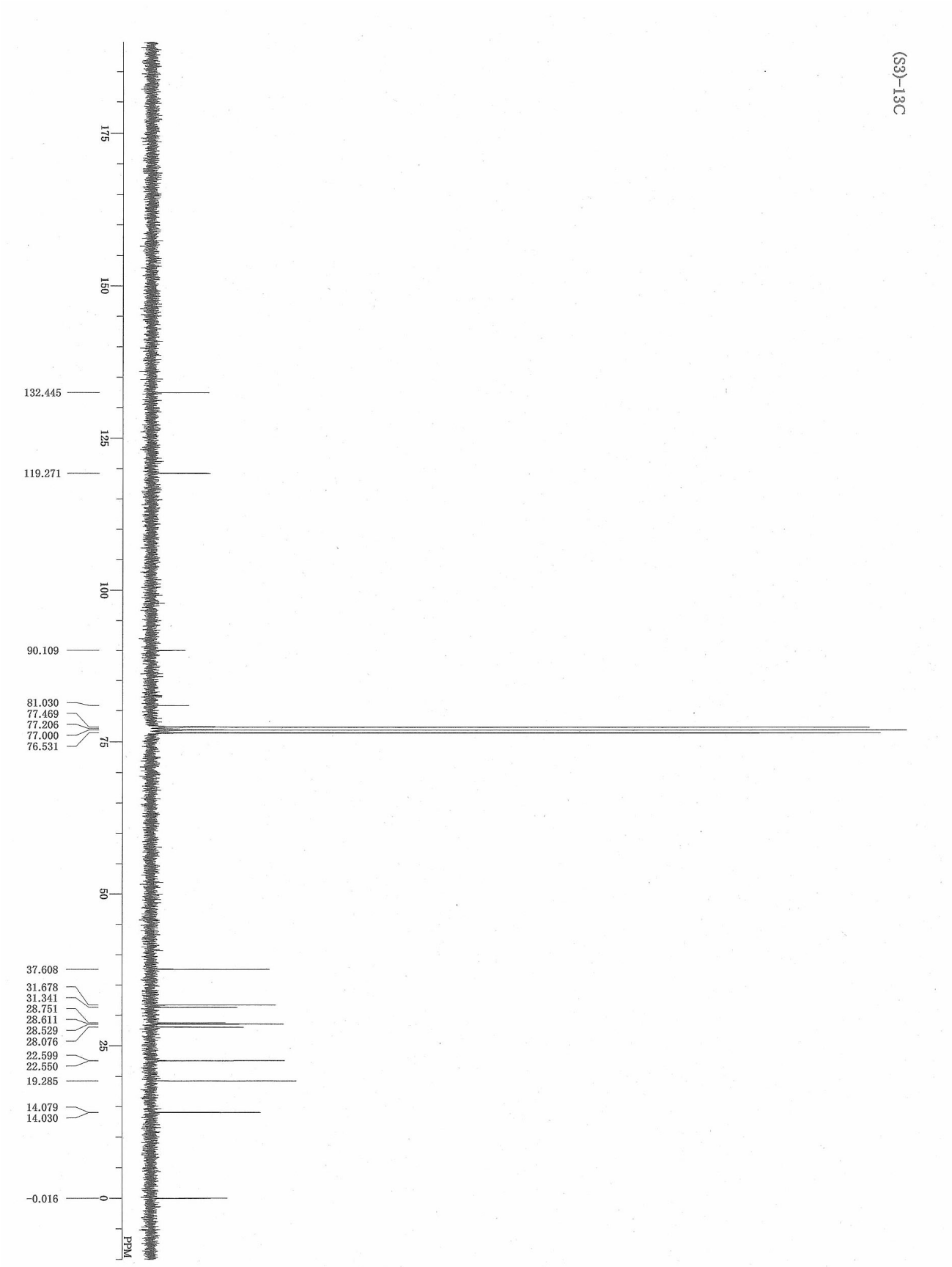

C6H13
C6H13

(S3)


(S3)-1H
7.261
5.206
5.198
5.126
5.122
5.118
5.114
5.109
1.00
0.99
2.325
2.300
2.274
2.142
2.115
2.087
1.549
1.530
1.505
1.478
1.453
1.433
1.428
1.424
1.405
1.399
1.393
1.384
1.370
1.347
1.319
1.305
1.287
1.272
0.917
0.910
0.893
0.886
0.868
0.861
2.15
2.25
21.47
7.11
0.000
PPM


C6H13
C6H13

(S3)


(S3)-13C
175
150
125
100
75
50
25
0
PPM
132.445
119.271
90.109
81.030
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77.206
77.000
76.531
37.608
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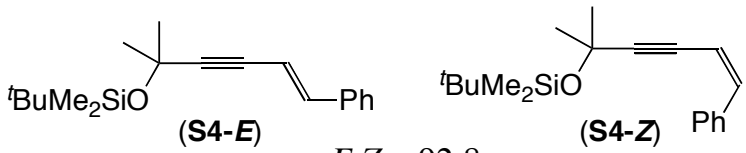
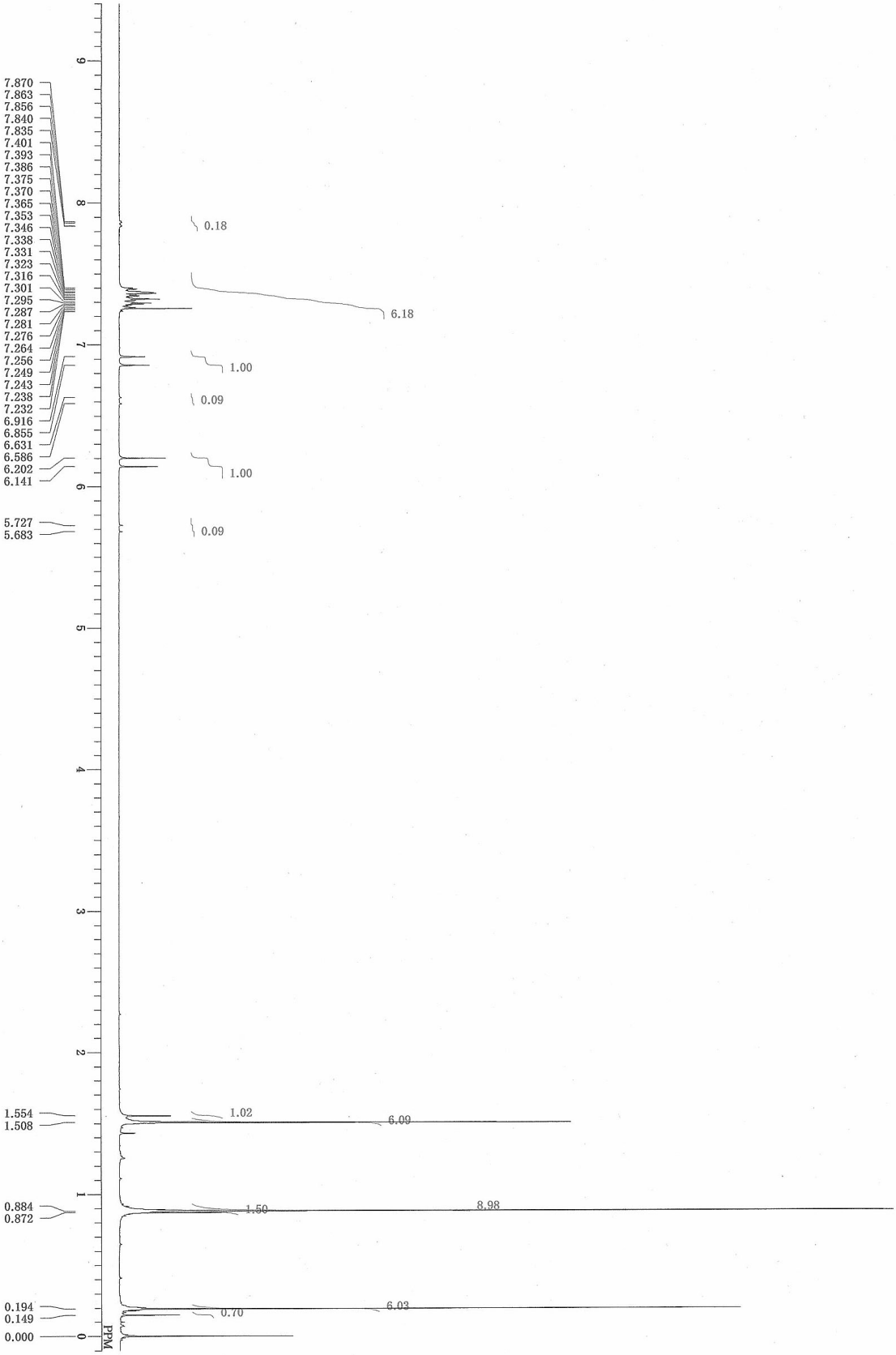
22.550
19.285
14.079
14.030
-0.016

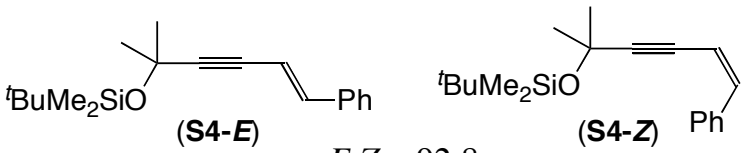


(**S4-*E***) (**S4-*Z***)

E:*Z* = 92:8

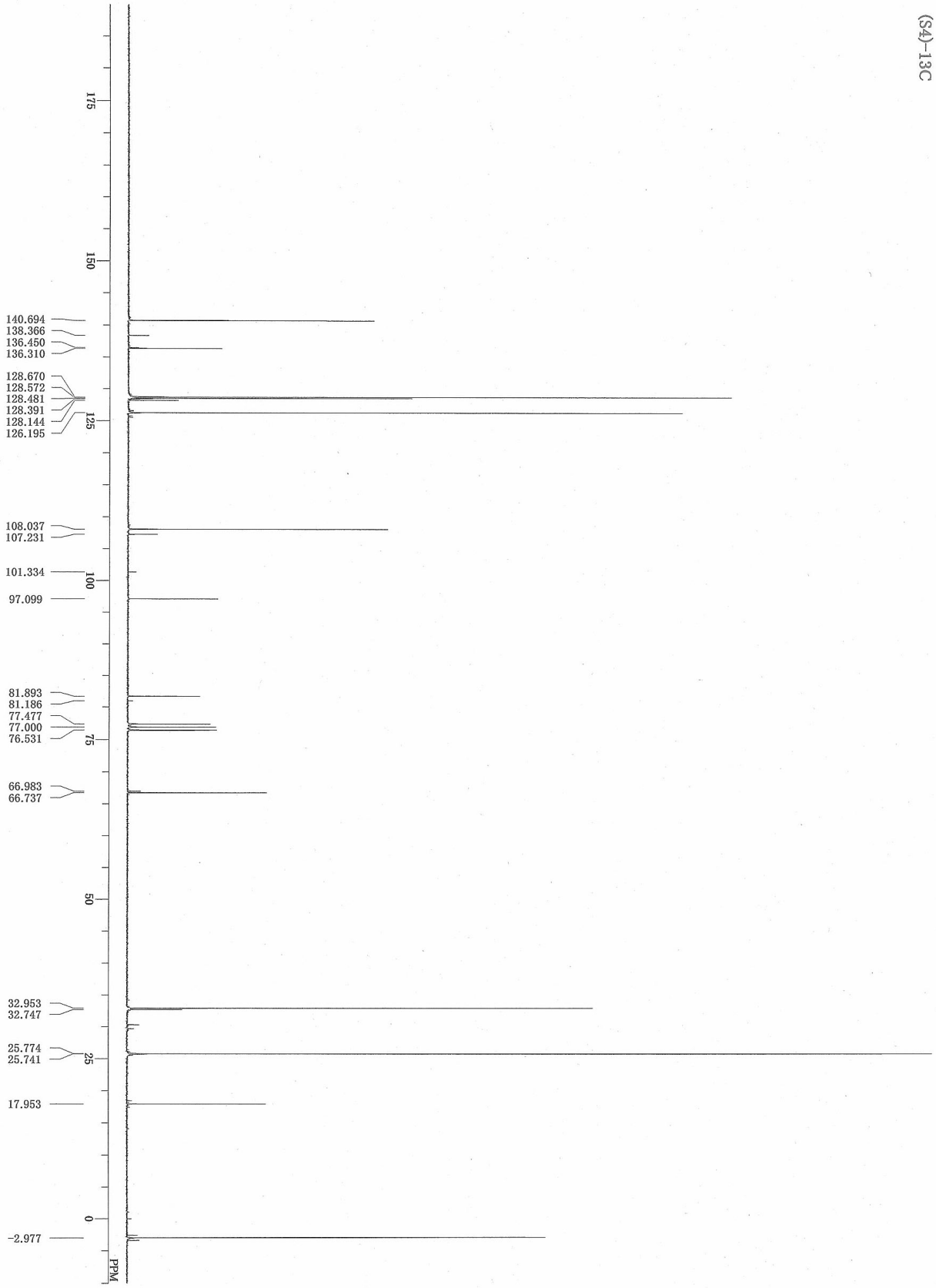
(S4)–1H

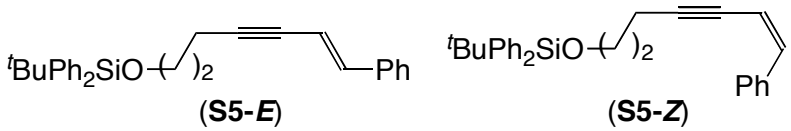




(**S4-*E***) (**S4-*Z***)

E:*Z* = 92:8

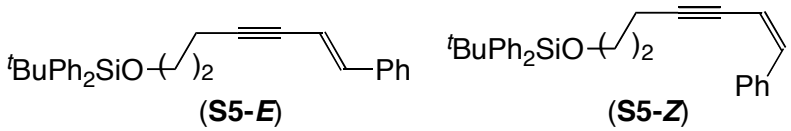




(**S5-*E***) (**S5-*Z***)

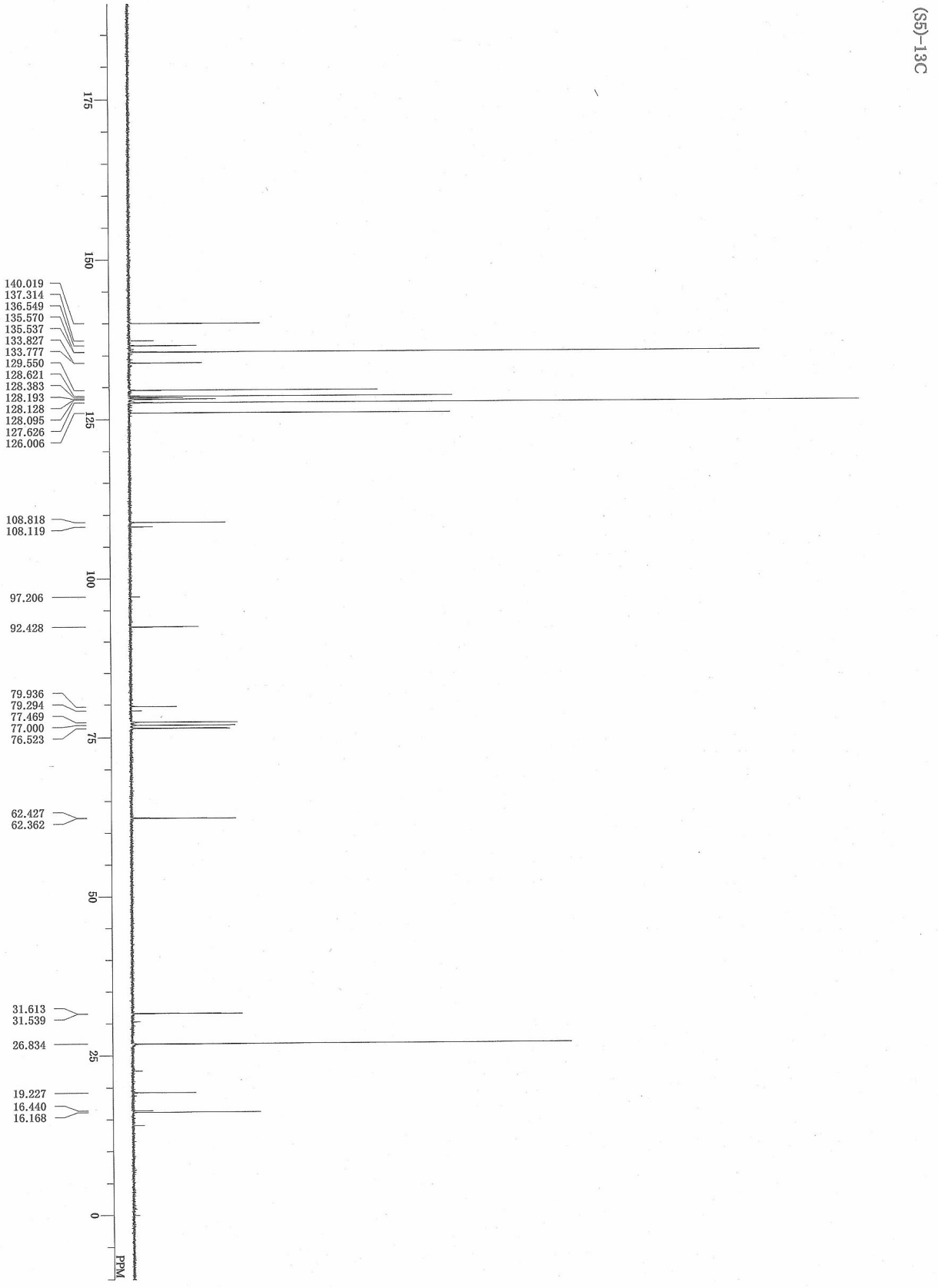
E:*Z* = 85:15

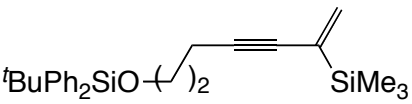
(S5)-1H



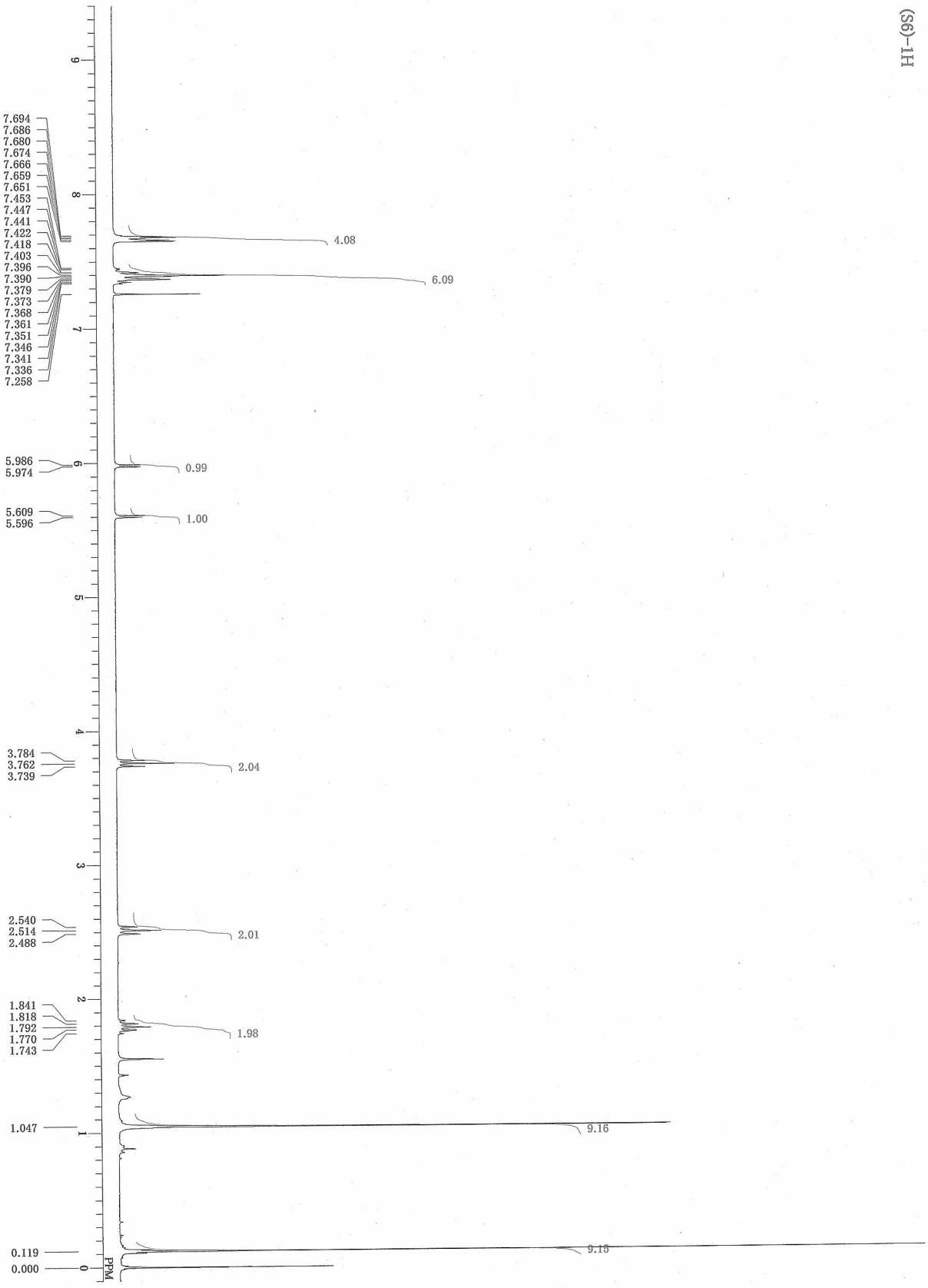
(**S5-*E***) (**S5-*Z***)

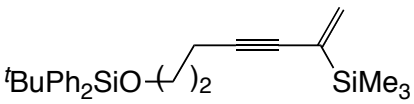
E:*Z* = 85:15



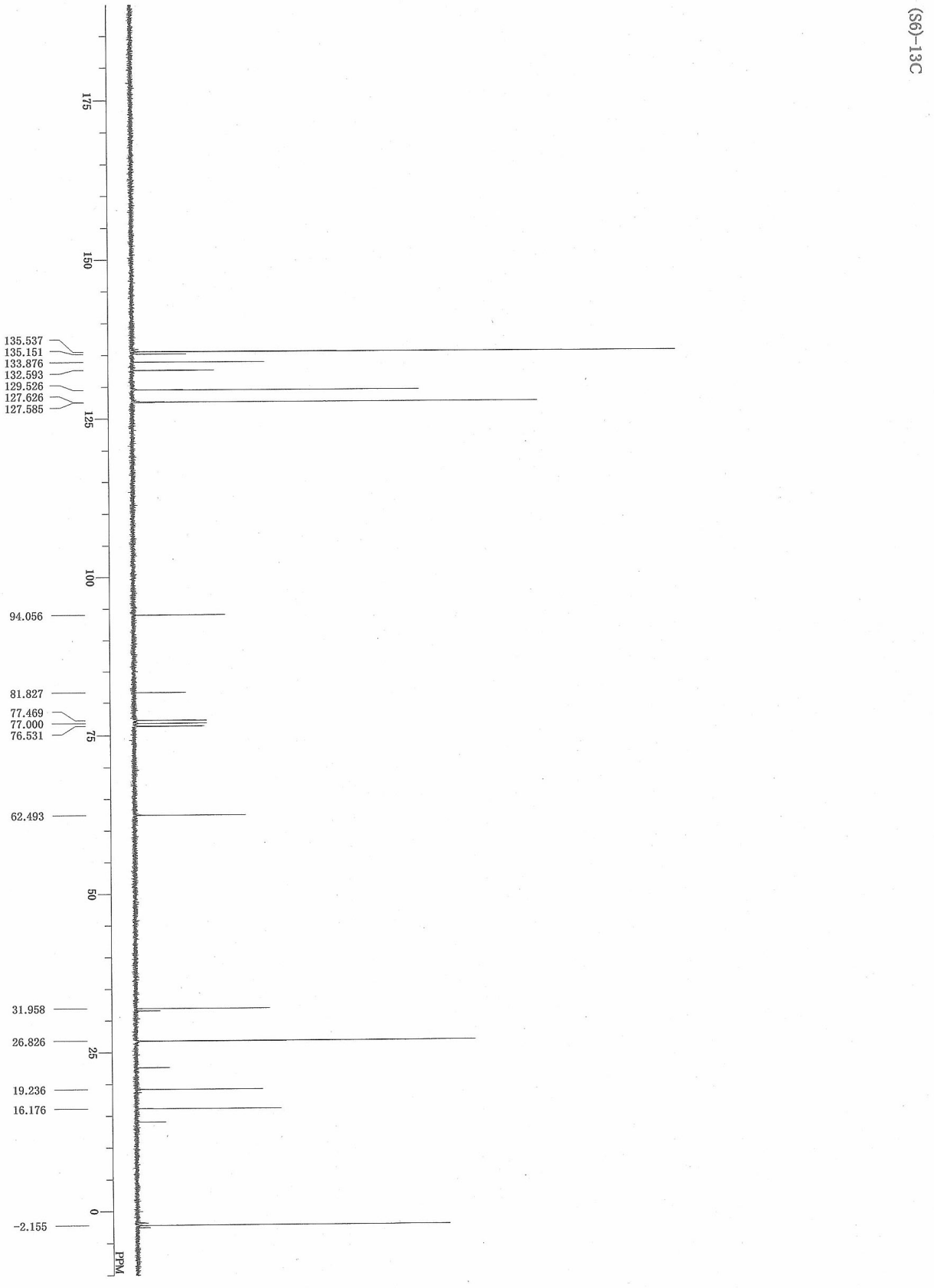

tBuPh2SiO
2
SiMe3

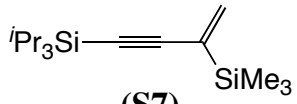
(S6)


(S6)-1H
7.694
7.686
7.680
7.674
7.666
7.659
7.651
7.453
7.447
7.441
7.422
7.418
7.403
7.396
7.390
7.379
7.373
7.368
7.361
7.351
7.346
7.341
7.336
7.258
4.08
6.09
5.986
5.974
0.99
5.609
5.596
1.00
3.784
3.762
3.739
2.04
2.540
2.514
2.488
2.01
1.841
1.818
1.792
1.770
1.743
1.98
1.047
9.16
0.119
0.000
9.15
PPM



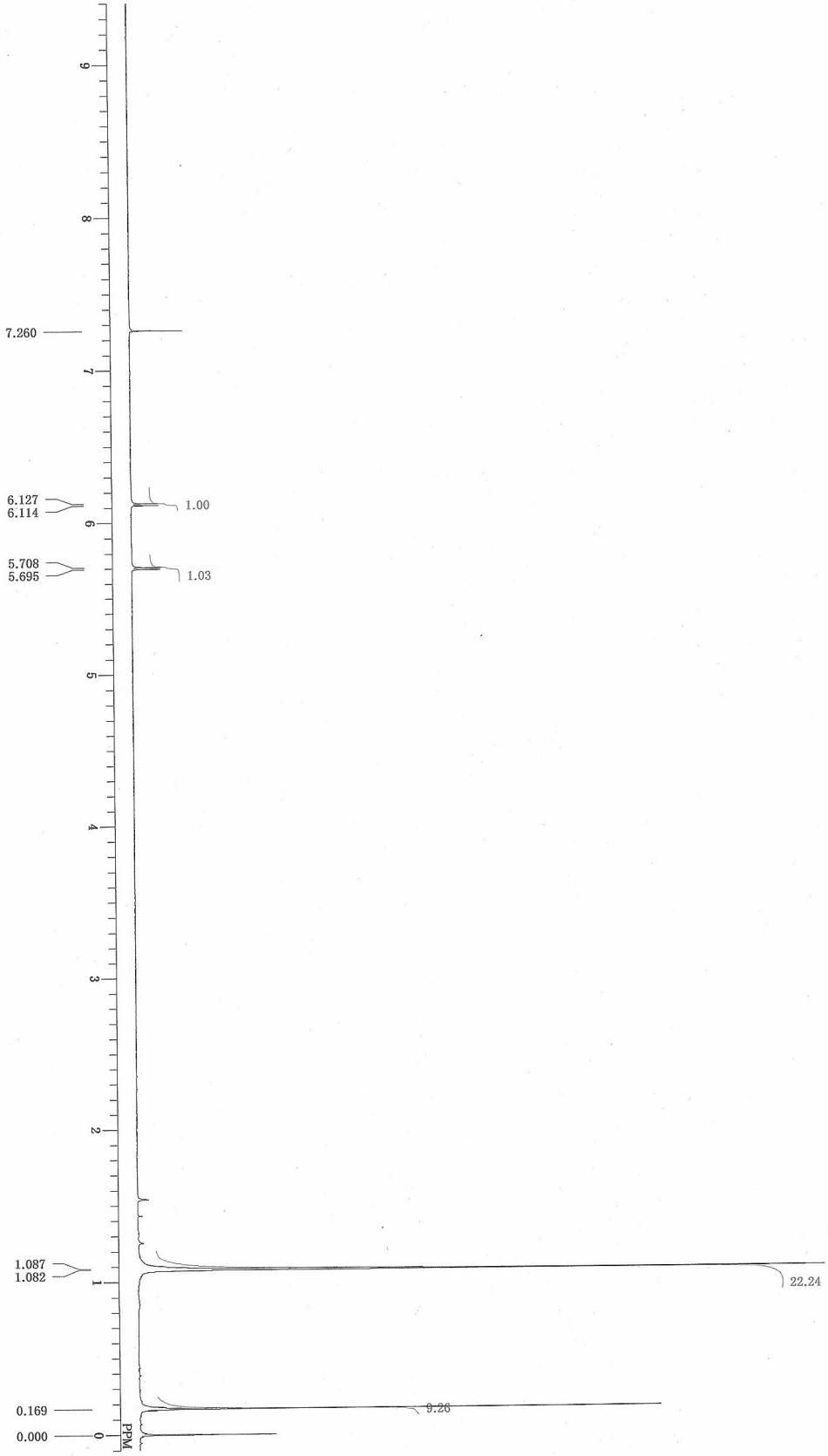
(S6)

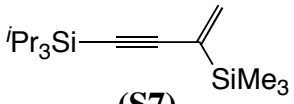

(S6)-13C
175
150
125
100
75
50
25
0
PPM
135.537
135.151
133.876
132.593
129.526
127.626
127.585
94.056
81.827
77.469
77.000
76.531
62.493
31.958
26.826
19.236
16.176
-2.155


$^{i}Pr_3Si$
SiMe3

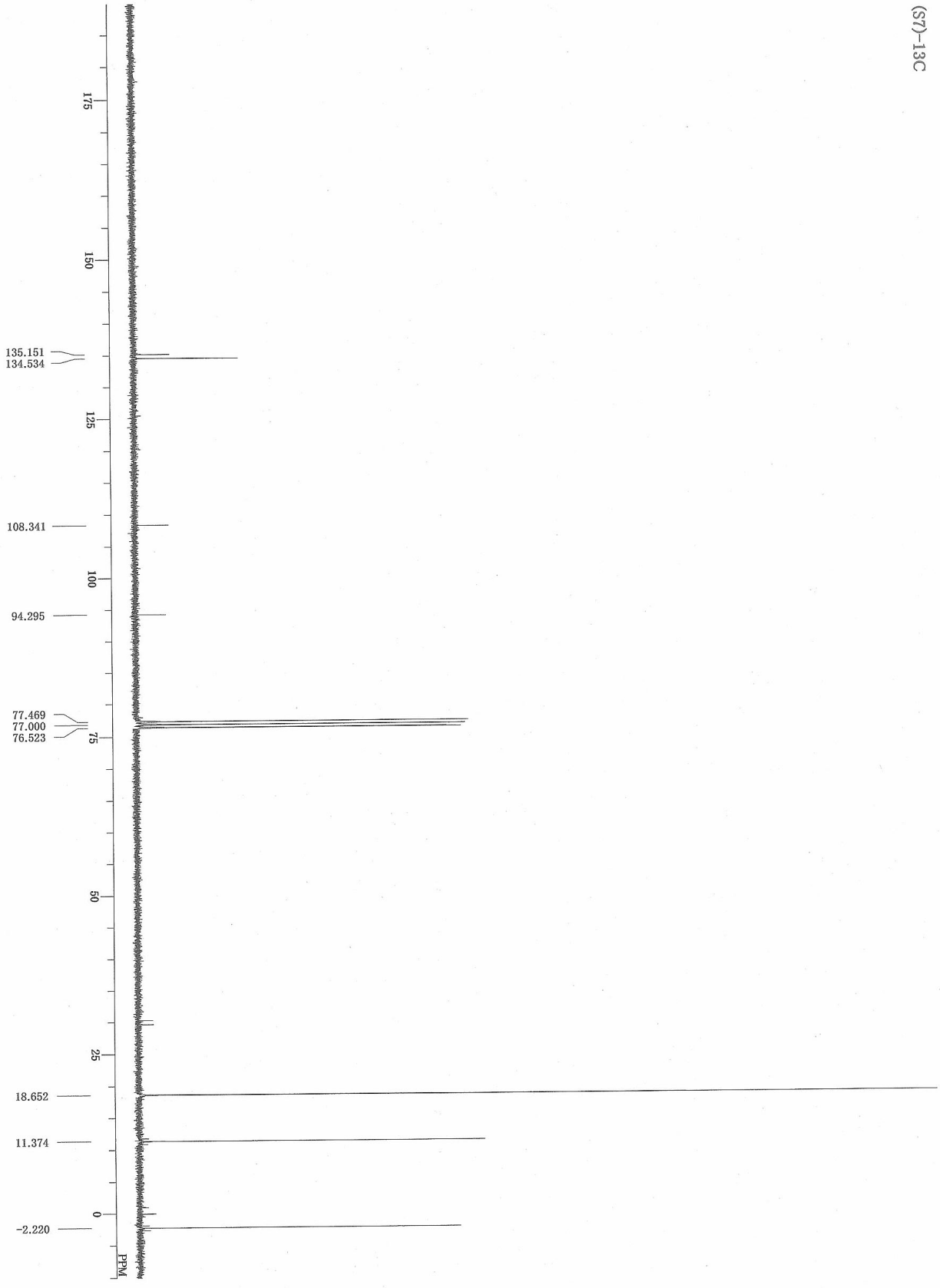
(S7)

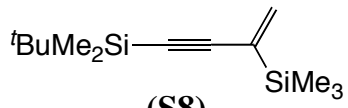
(S7)-1H


7.260
6.127
6.114
1.00
5.708
5.695
1.03
1.087
1.082
22.24
0.169
9.26
0.000
PPM


iPr3Si
SiMe3

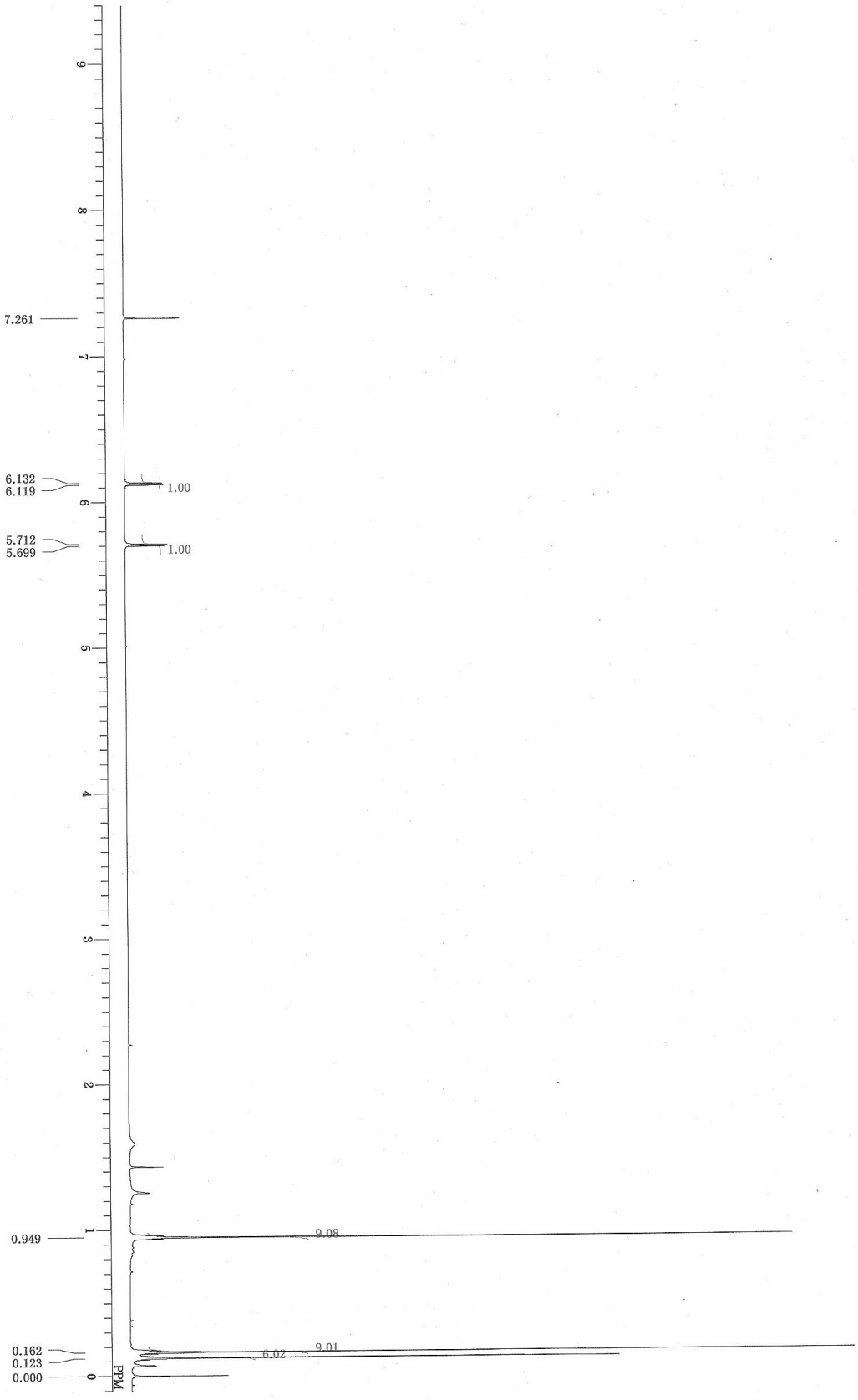
(S7)

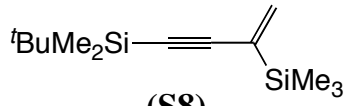

(S7)-13C
175
150
135.151
134.534
125
108.341
100
94.295
77.469
77.000
76.523
75
50
25
18.652
11.374
0
-2.220
PPM


tBuMe2Si
SiMe3

(S8)

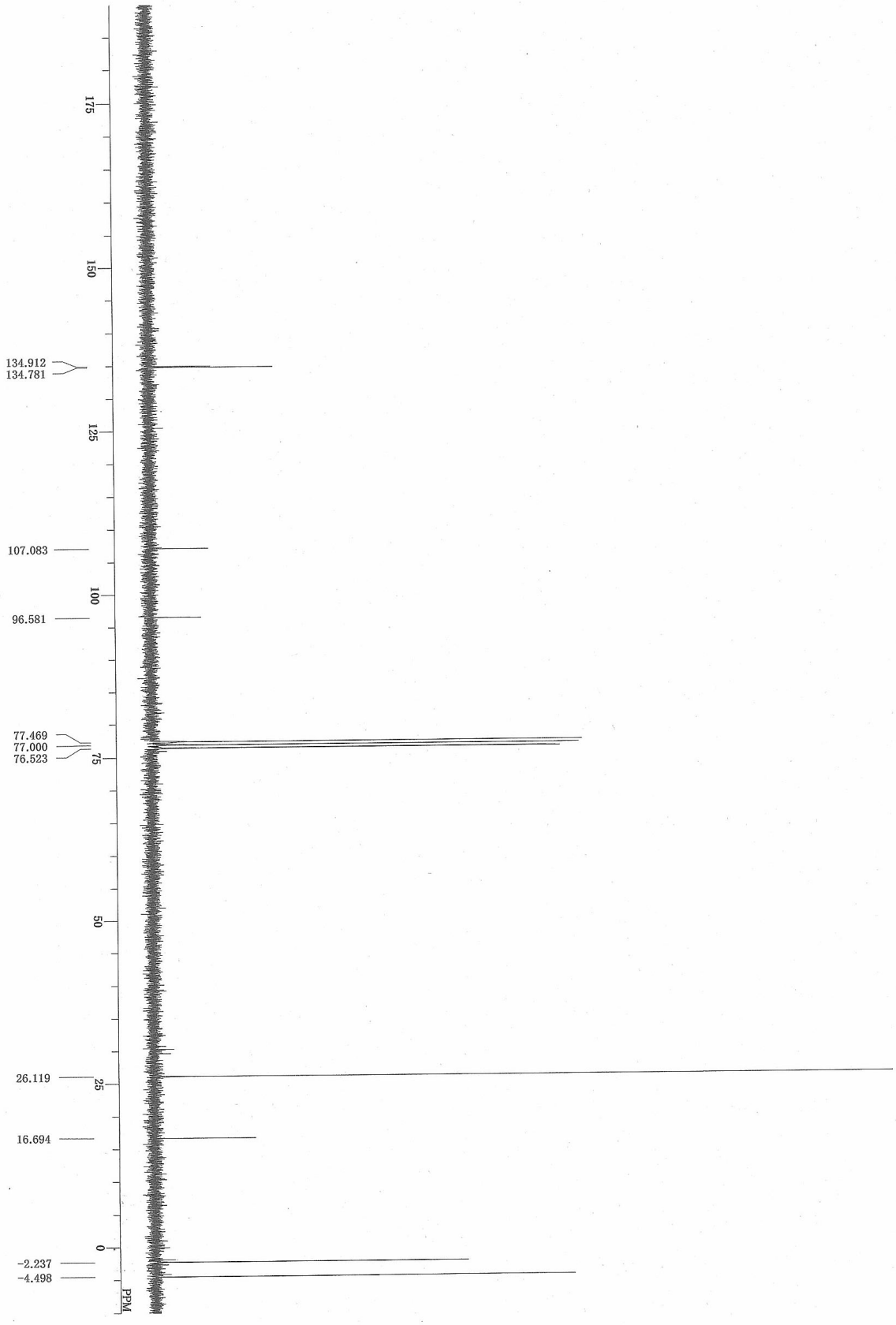
(S8)-1H

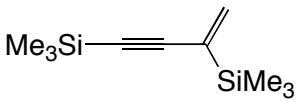

7.261
6.132
6.119
1.00
5.712
5.699
1.00
0.949
9.08
0.162
0.123
0.000
6.02
9.01
PPM


tBuMe2Si
SiMe3

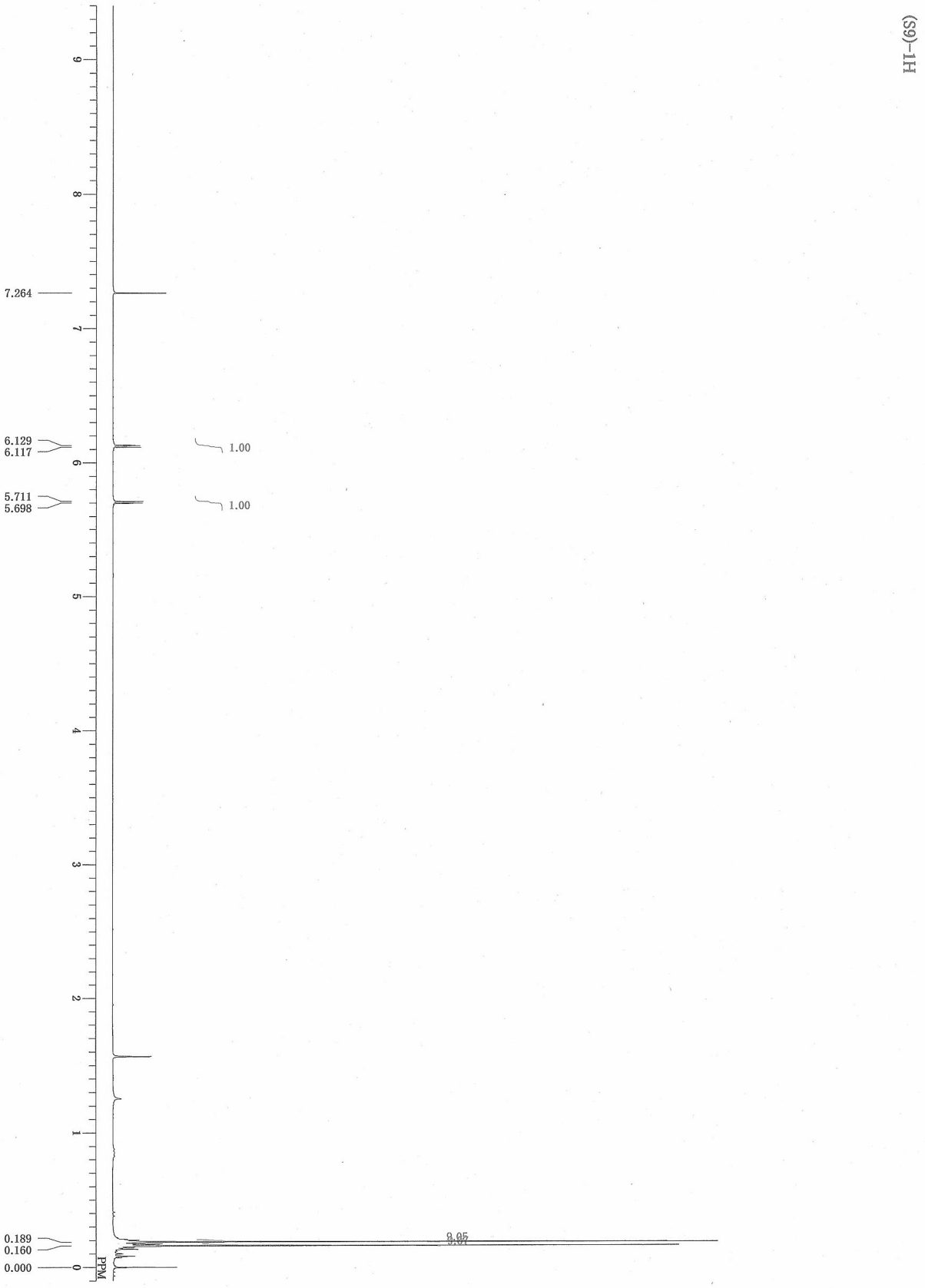
(S8)

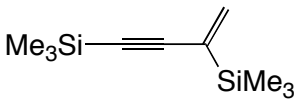
(S8)-13C


175
150
134.912
134.781
125
107.083
100
96.581
77.469
77.000
76.523
75
50
26.119
25
16.694
0
-2.237
-4.498
PPM

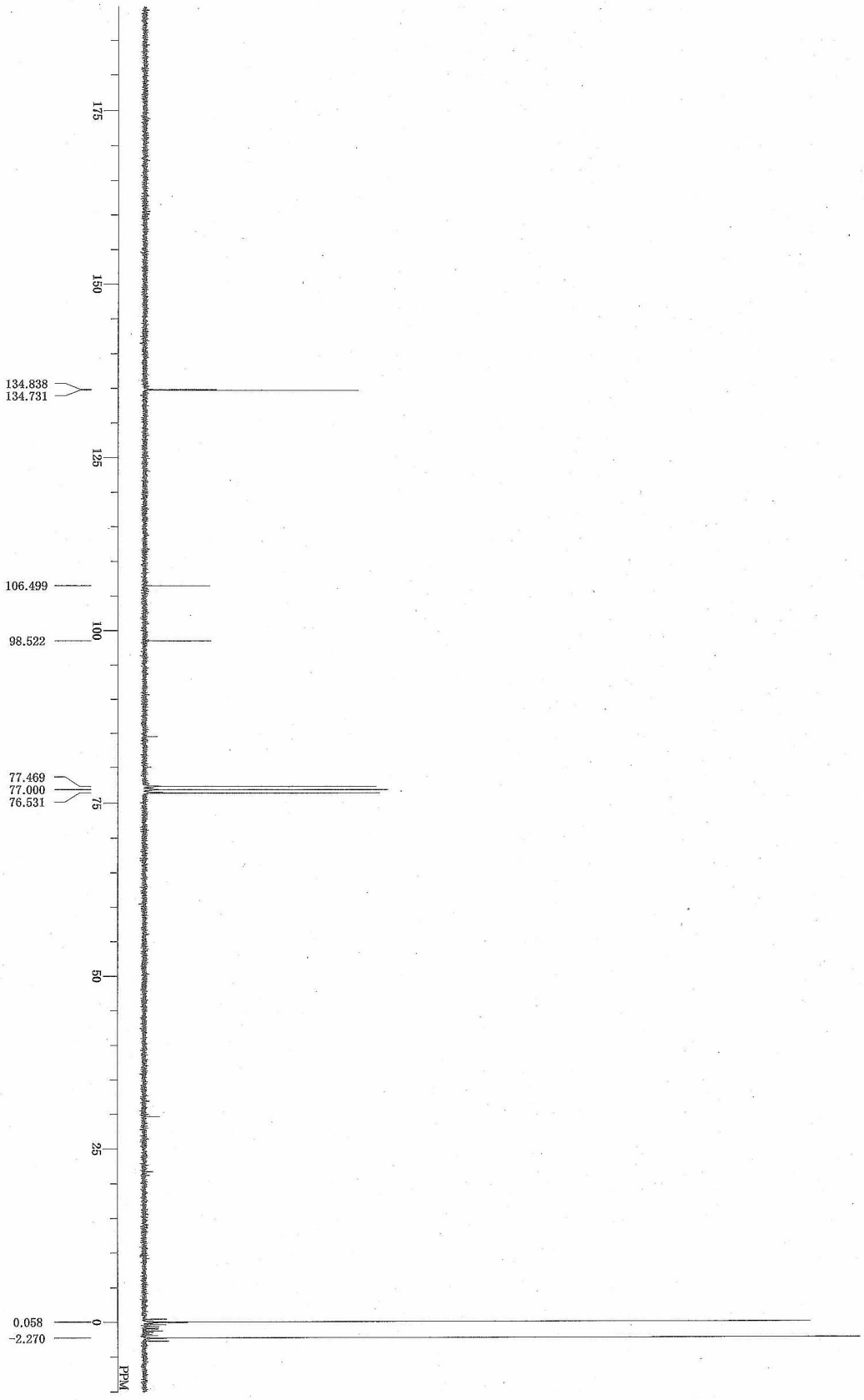

Me3Si
SiMe3

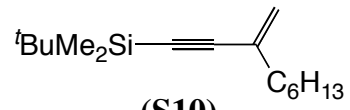
(S9)


(S9)-1H
7.264
6.129
6.117
1.00
5.711
5.698
1.00
0.189
0.160
0.000
9.05
PPM

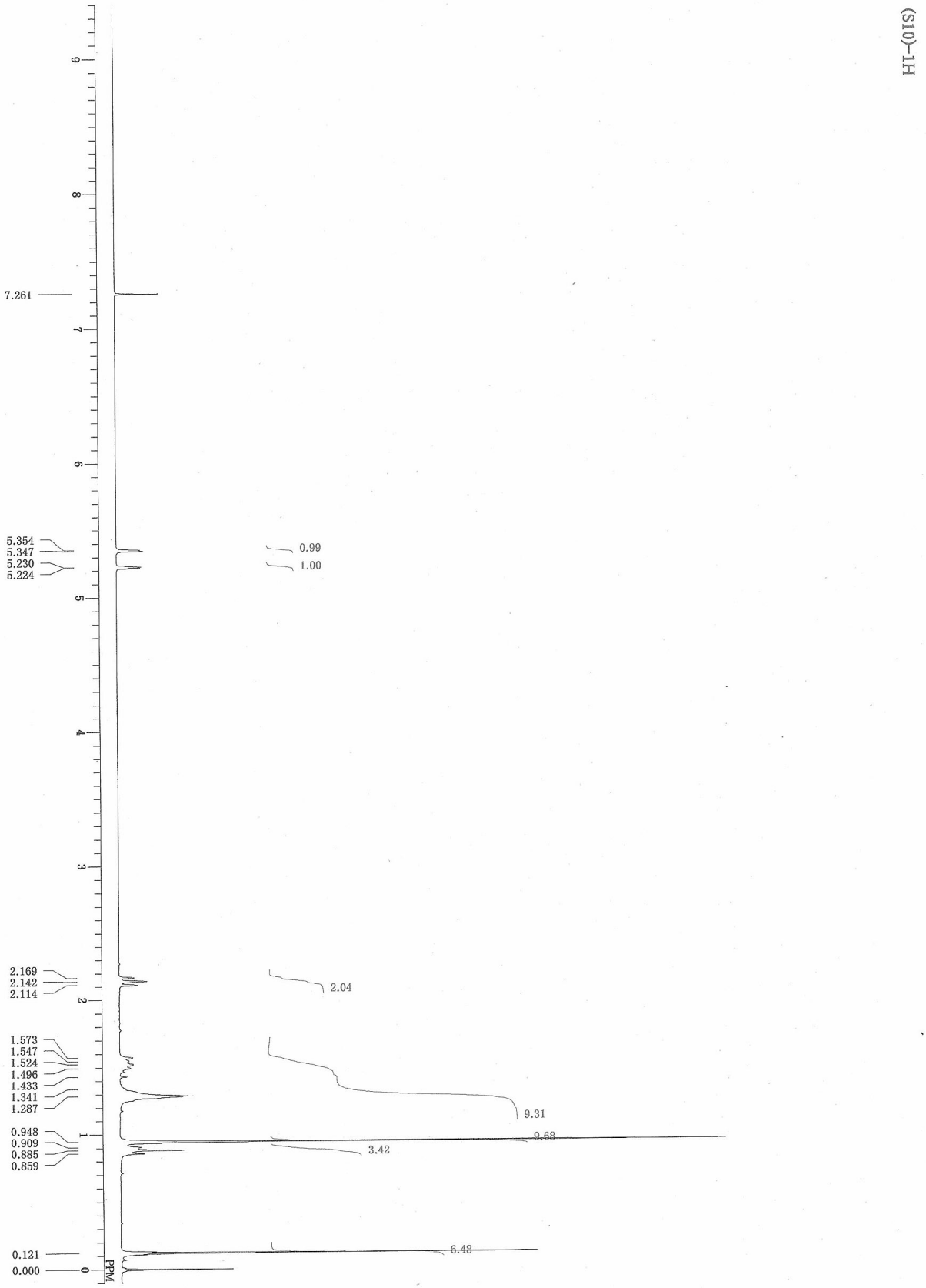

Me3Si
SiMe3

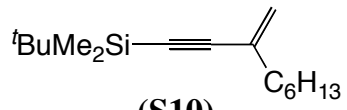
(S9)


(S9)-13C
175
150
134.838
134.731
125
106.499
100
98.522
77.469
77.000
76.531
75
50
25
0.058
0
-2.270
PPM

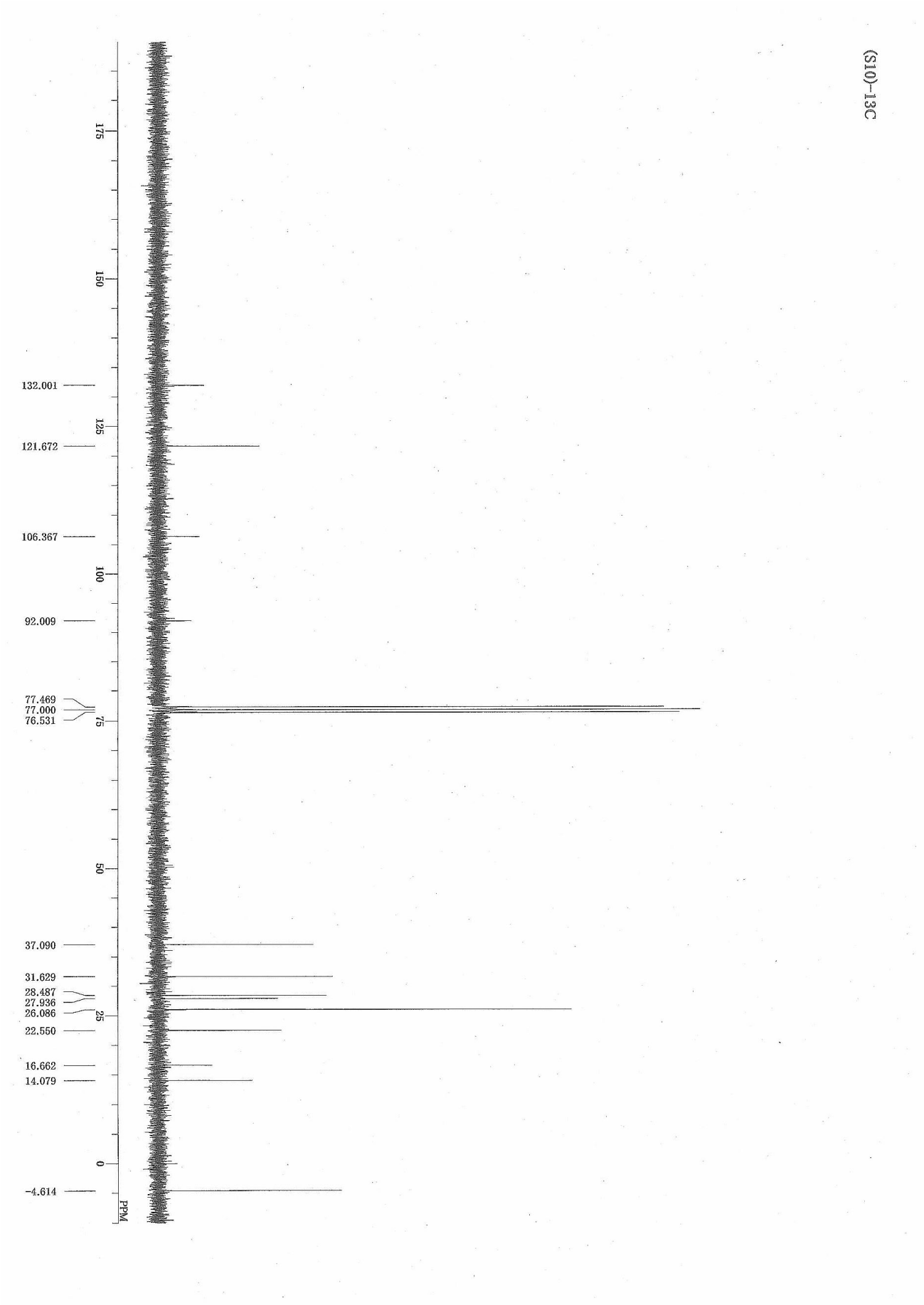

tBuMe2Si
C6H13

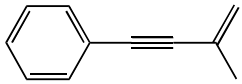
(S10)


(S10)-1H
7.261
5.354
5.347
5.230
5.224
0.99
1.00
2.169
2.142
2.114
2.04
1.573
1.547
1.524
1.496
1.433
1.341
1.287
9.31
0.948
0.909
0.885
0.859
9.68
3.42
0.121
0.000
6.48
PPM


tBuMe2Si
C6H13

(S10)

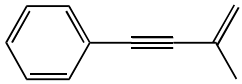

(S10)-13C
175
150
125
100
75
50
25
0
PPM
132.001
121.672
106.367
92.009
77.469
77.000
76.531
37.090
31.629
28.487
27.936
26.086
22.550
16.662
14.079
-4.614



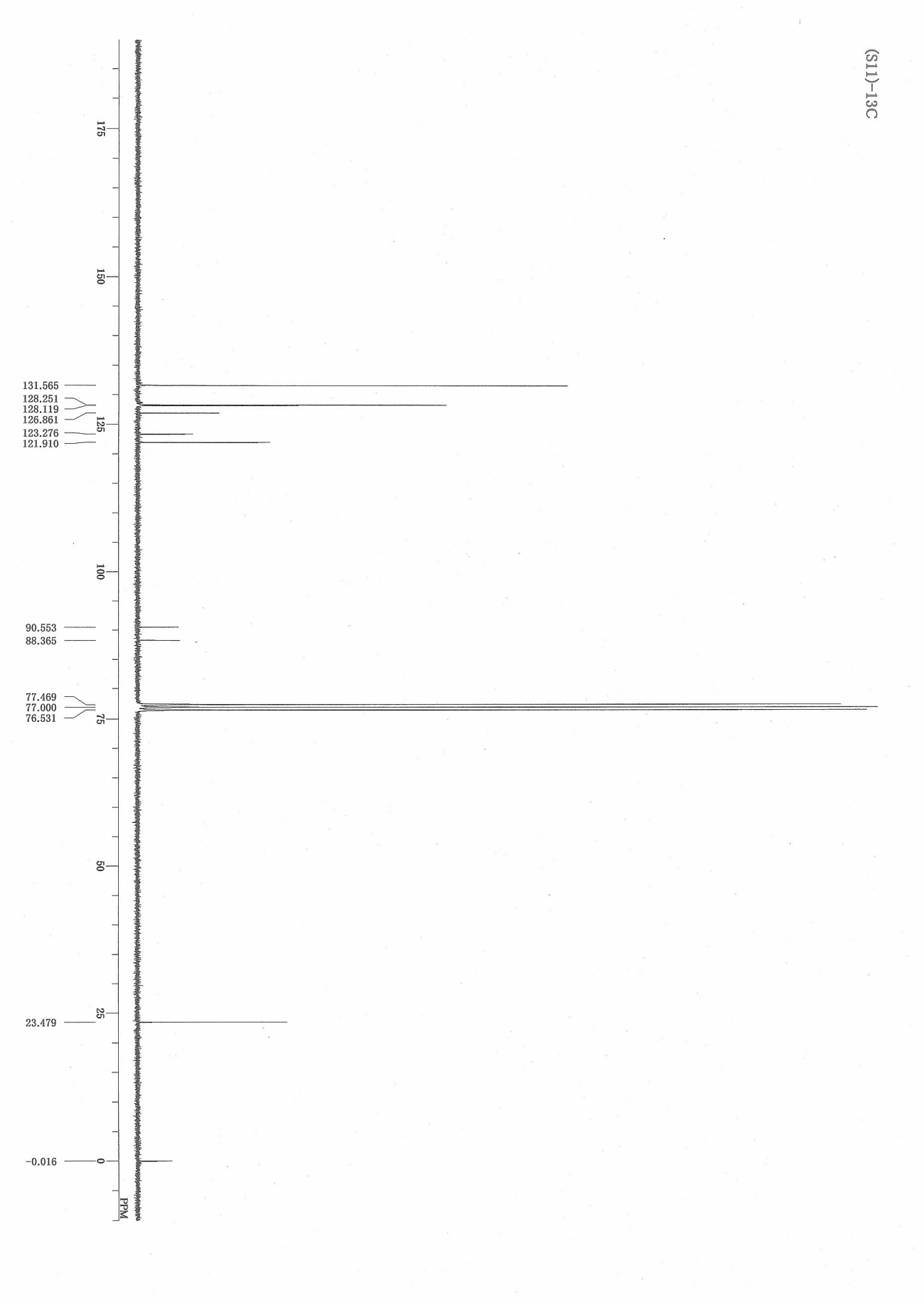
(S11)

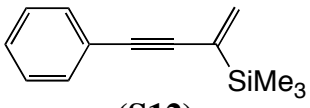
(S11)-1H

7.458
7.445
7.431
7.424
7.314
7.300
7.291
7.255
2.00
2.99
5.394
5.296
1.00
0.99
1.990
3.01
0.000
PPM

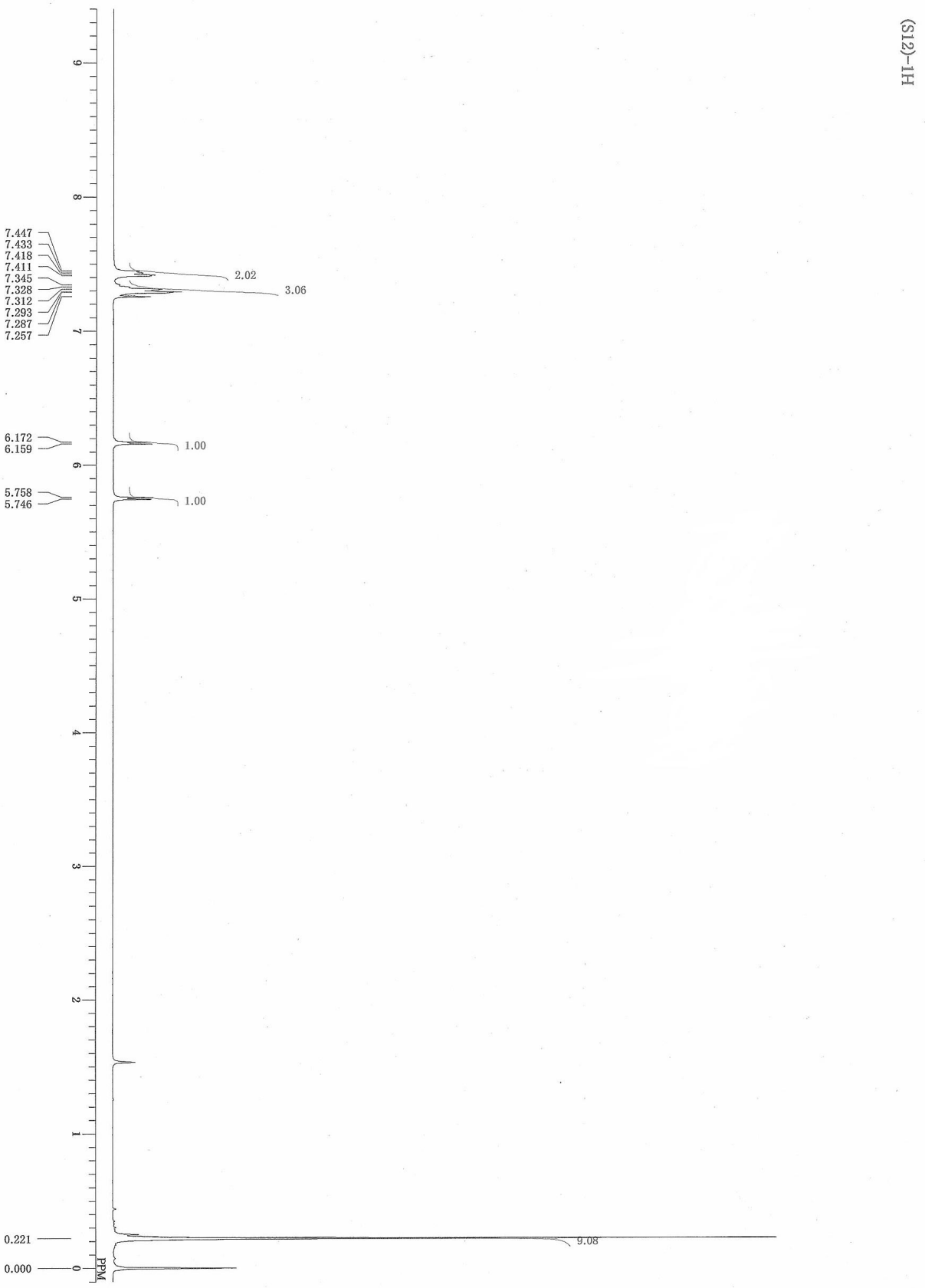


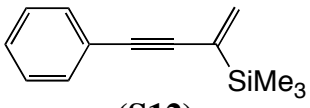
(S11)


(S11)-13C
175
150
131.565
128.251
128.119
126.861
125
123.276
121.910
100
90.553
88.365
77.469
77.000
76.531
75
50
25
23.479
-0.016
0
PPM

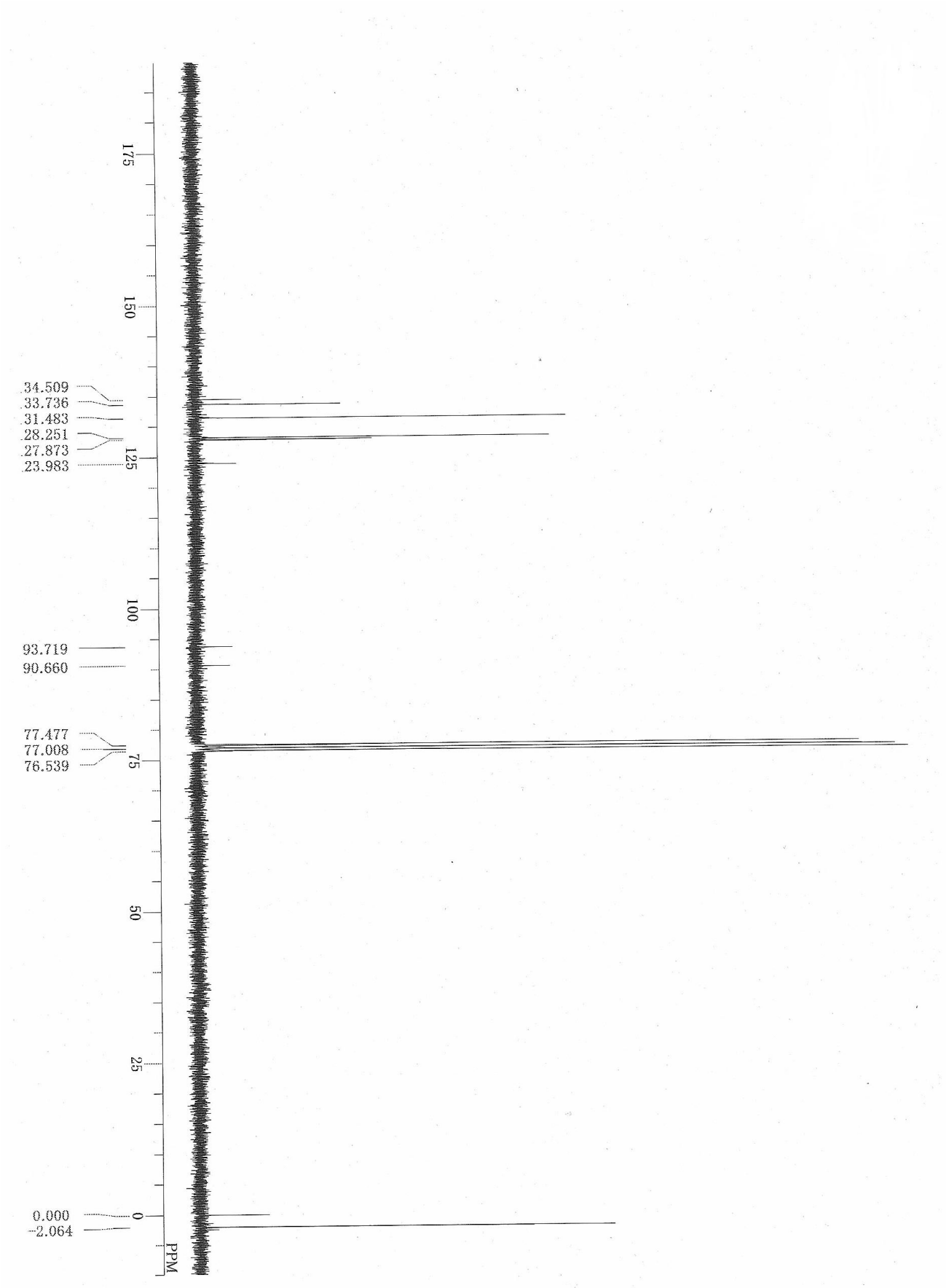

SiMe3

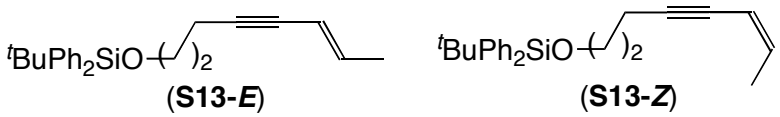
(S12)


(S12)-1H
7.447
7.433
7.418
7.411
7.345
7.328
7.312
7.293
7.287
7.257
2.02
3.06
6.172
6.159
1.00
5.758
5.746
1.00
0.221
9.08
0.000
PPM


SiMe3

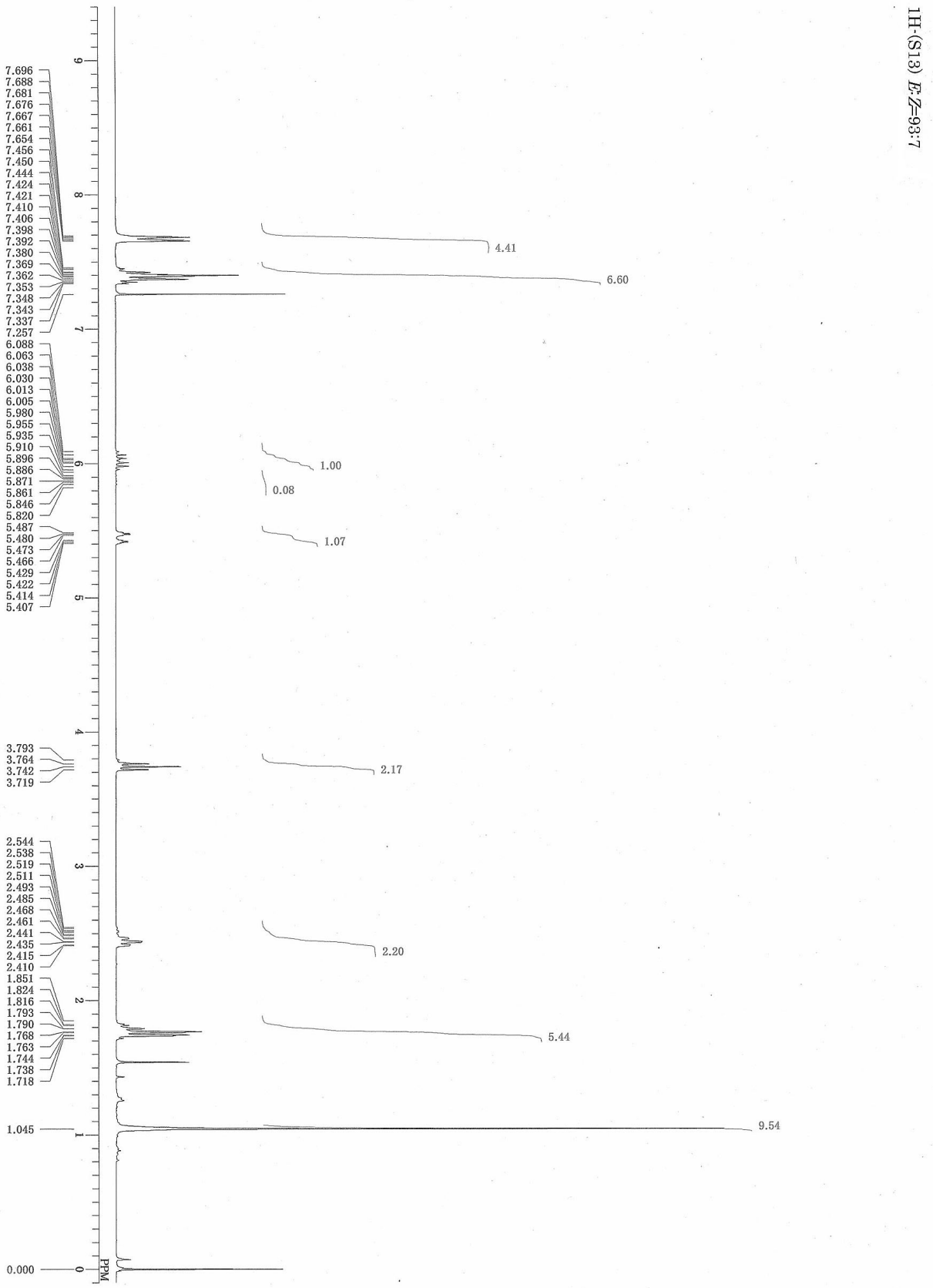
(S12)

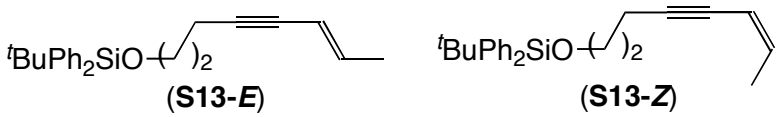

34.509
33.736
31.483
28.251
27.873
23.983
93.719
90.660
77.477
77.008
76.539
0.000
-2.064
175
150
125
100
75
50
25
0
PPM



(**S13-*E***) (**S13-*Z***)

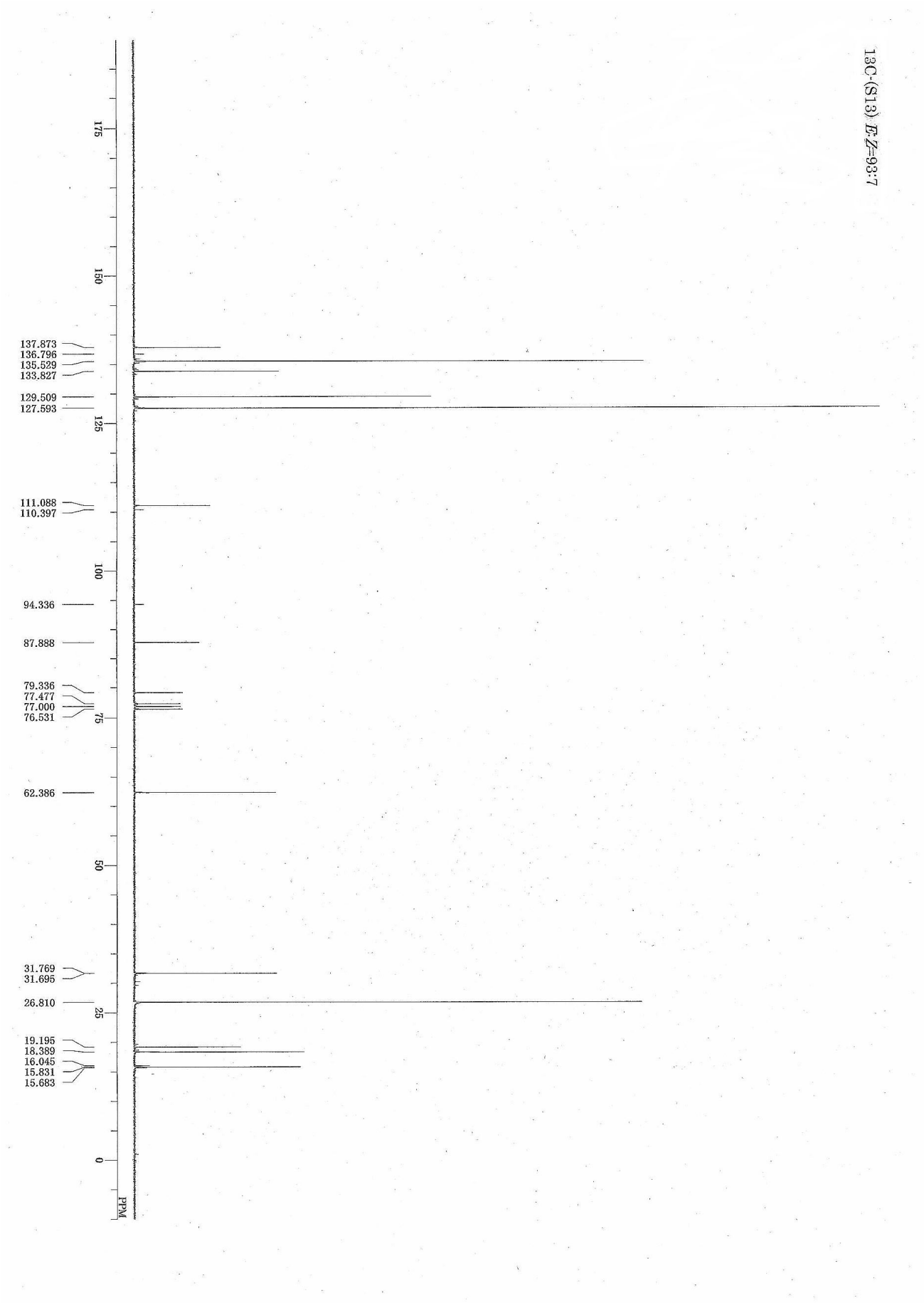
E:*Z* = 93:7

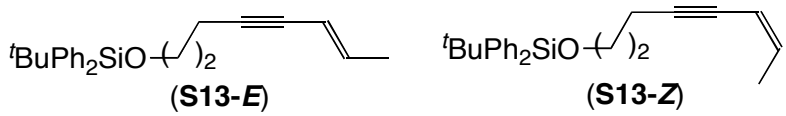




(**S13-*E***) (**S13-*Z***)

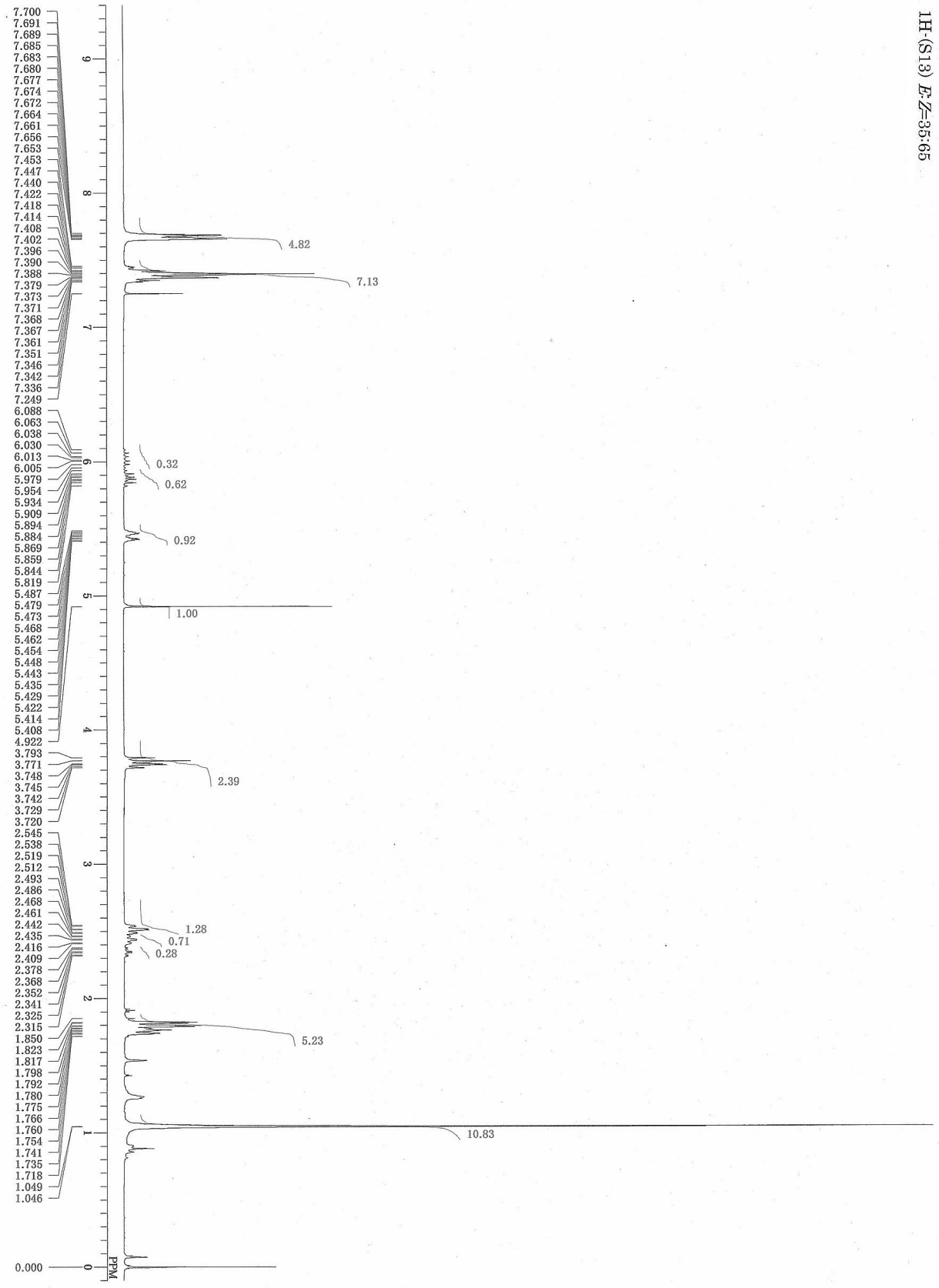
E:*Z* = 93:7

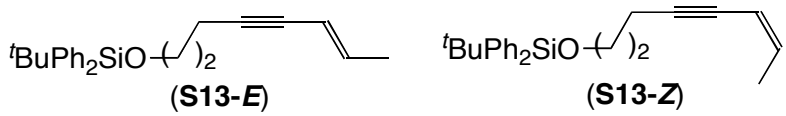




(**S13-*E***) (**S13-*Z***)

E:*Z* = 35:65





(**S13-*E***) (**S13-*Z***)

E:*Z* = 35:65