Supplementary information

A Heterogeneous Mercury Salt Catalyst Stabilized by *m*-Carbaborane

Hirofumi Yamamoto,* Naoto Yamasaki, Hiroshi Hamauchi, Shinya Shiomi, Ikuo Sasaki, Koichiro Seyama, Yasuko Mima, Mayo Nakano, Takashige Kawakami, Hideki Miyataka, Yusuke Kasai, and Hiroshi Imagawa.

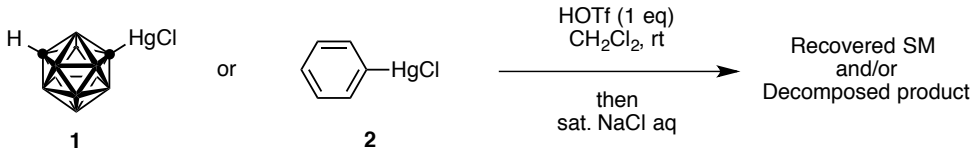
Faculty of Pharmaceutical Science, Tokushima Bunri University, Yamashiro-cho, Tokushima 770-8514, Japan.

1. General information

Reactions were performed under argon unless otherwise stated. Commercially available chemicals were used as purchased. Specialty grade and dehydrated solvents were purchased from Kanto Chemical Co., Inc. Progress of the reactions was monitored

using thin layer chromatography (TLC) with precoated silica gel 60 F254 plates (Merck). Spots were visualized under 254 nm UV light after immersion in 2% *p*-anisaldehyde and 5% H_2SO_4 in EtOH, followed by heating on a hot plate. Solvents were removed under reduced pressure using standard rotary evaporators. Flash column chromatography was performed using 63-210 mesh silica gel 60 (Kanto Chemical Co., Inc.). Filtration was performed using ADVANTEC 5C filter paper (Toyo Roshi Co., Ltd.). For all polymer catalyst reactions, a mechanical shaker (KS-130 control, IKA® laboratory technology) was used to stir the reaction mixture. FT-IR spectra were measured on a JASCO FT/IR-410 infrared spectrophotometer and the location of significant peaks reported in wavenumbers (cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury plus-300-4N spectrometer, a Varian 400-MR spectrometer or a Varian 500-MR spectrometer. The ^1H chemical shifts are reported in parts per million (ppm) from an internal standard of TMS (0.00 ppm), residual $CHCl_3$ (7.26 ppm), or C_6D_6 (7.17 ppm), and the ^{13}C chemical shifts are reported using an internal standard of $CDCl_3$ (77.03 ppm, central peak). The ^1H NMR spectra are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin. = quintet and br = broad), relative integral, coupling constants *J* (Hz). High-resolution mass spectra (HRMS) were recorded on a JEOL Mstation JMS-700. HPLC and inductively coupled plasma mass spectra (HPLC-ICP-MS) were recorded on an Agilent Technologies *7700x* series ICP-MS (ZORBAX SB-AQ 600 Bar (4.6 x 50 mm, 1.8 μm) column and 1260 Infinity Bio-Inert Quaternary LC System). The particle size of the polymer catalyst was determined using image analysis software (Image-Pro PLAS, Media Cybernetics, Inc.). Residual mercury was detected as Hg(0) via atomic absorption spectrometry with a Mercury Analyzer RA-3 (Nippon Instruments Co., Ltd.). Scanning Electron Microscope (SEM) analysis was performed on a JSM-6480LA and a JSM-6510 (JEOL Ltd.). Energy Dispersive X-ray Spectroscopy (EDX) analysis was carried out with a JED-2300 (JEOL Ltd.). Female Slc:ICR mice and the lab food were purchased from Japan SLC. Inc. and Oriental Yeast Co Ltd., respectively. Excel statistics 2012 was used for the statistical analysis of the *in vivo* study with *m*-carbaboranylmercury chloride (**1**).

2. Kinetic study on the decomposition of 1 and 2 (Figure 1A)



To a solution of *m*-carbaboranyl HgCl (**1**)[1] (38.0 mg, 0.1 mmol) and phenylmercury chloride (**2**) (31.4 mg, 0.1 mmol) in CH_2Cl_2 (3 mL), HOTf (9.7 μL, 0.11 mmol) was added dropwise at room temperature, and the reaction mixture was then stirred for various lengths of time (1 min, 5 min, 10 min, 30 min, 1 h, 3 h, 6 h, 24 h, 48 h and 120 h). Subsequently, the reaction mixture was diluted with CH_2Cl_2 (2 mL) and saturated NaCl solution (5 mL). After the organic phase was separated, the aqueous phase was extracted three times with 5 mL of CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, and concentrated *in vacuo*. The recovery yield (%) of **1** and **2** were determined by ^{1}H-NMR analysis using $CHBr_3$ solution (0.1 mL, 1 mol/L in $CDCl_3$) as the internal standard. The reaction of **1** (38.0 mg, 0.1 mmol) with 10 equivalents of HOTf (88 μL, 1.0 mmol) was also carried out in the same manner.

ICP-MS analysis (Figure 1D)

The analysis conditions used followed Sannac's method,[2] with gradient conditions (Figure S1). Details are below.

HPLC conditions

Mobile phase (A+B)

A = L-Cystein (500 mg/mL)
L-Cystein·HCl·H_2O (500 mg/mL)
pH = 2.3 with HCl aq. (The solution was prepared with 18 MΩ·cm water.)

B = Methanol

Injection volume = 50 μL (0.1-0.5 mg/mL)

ICP-MS Conditions

PF power ……..1600 W
Carrier gas flow rate ……...0.54 L/min
Make-up gas flow rate ...….0.1 L/min
Option gas (20% O_2 in Ar) ……...9%
Spray chamber temperature…. –5 °C
Sampling depth …… 8.0 mm

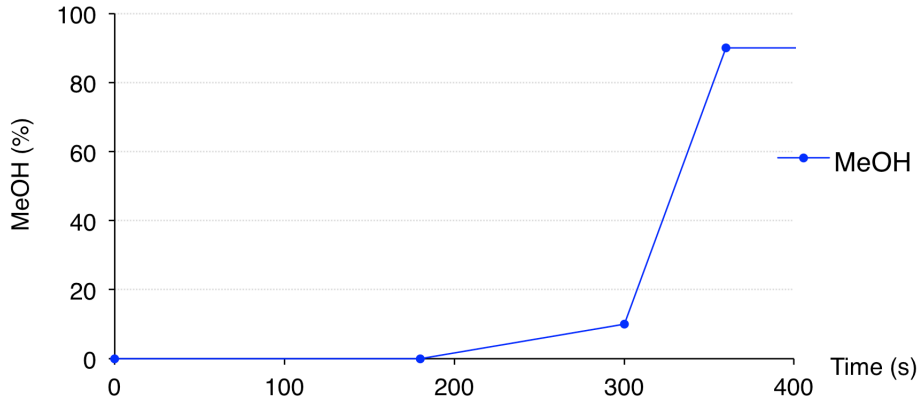


Figure S1. Gradient conditions

3. *In vivo* study with *m*-carbaboranylmercury chloride (1)

Animals: Female Slc:ICR mice at 7 weeks of age were purchased and allowed to acclimate to their surroundings for 7 days before experimental procedures. The animals were maintained in a controlled environment with a temperature of 22 ± 1.5 °C, humidity of 45 ± 5%, and 12/12 h light/dark cycle, and they were given lab food (type MF) and tap water *ad libitum*. The animal experiments were approved by the Animal Ethics Committee of Tokushima Bunri University.

a) Treatment of *m*-carbaboranylmercury chloride (**1**)

Initially, compound **1** was dissolved in DMSO, and the solution was then diluted with sesame oil so that the intended dose of **1** would be delivered in a dose volume of 10 mL/kg. A single dose of 50, 100, 150 and 300 mg/kg body weight or an equivalent volume of 2% DMSO and 98% sesame oil solution (control) were orally administered to female ICR mice. (A single dose of >300 mg/kg body weight was unable to administered because the mice vomited it.) The animals were observed twice daily and body weights were recorded every day for 14 days to investigate the effects of **1**.

b) Statistical analysis

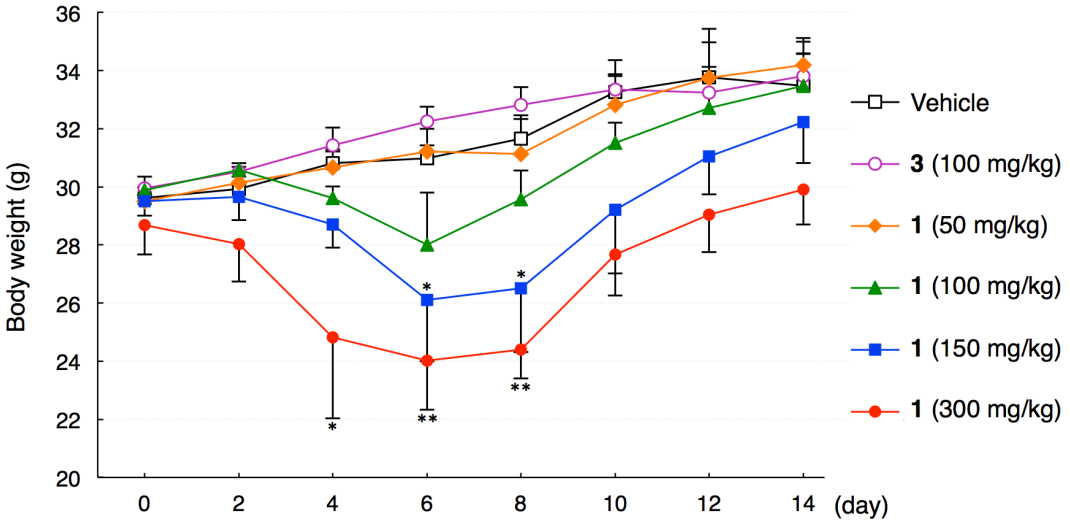
Results are presented as mean ± SEM (n = 4-5). Data for comparison of studies were analyzed by one-way ANOVA followed by Tukey's multiple comparison as a *post hoc* test ($^{*}p < 0.05$). Differences were considered statistically significant when the p value was less than 0.05.

Table S1. Number of surviving mice (n = 5)

	Day 0	Day 2	Day 4	Day 6	Day 8	Day 10	Day 12	Day 14
Vehicle	5	5	5	5	5	5	5	5
50 mg/kg	5	5	5	5	5	5	5	5
100 mg/kg	5	5	5	5	5	5	5	5
150 mg/kg	5	5	4	4	4	4	4	4
300 mg/kg	5	5	3	3	3	3	3	3

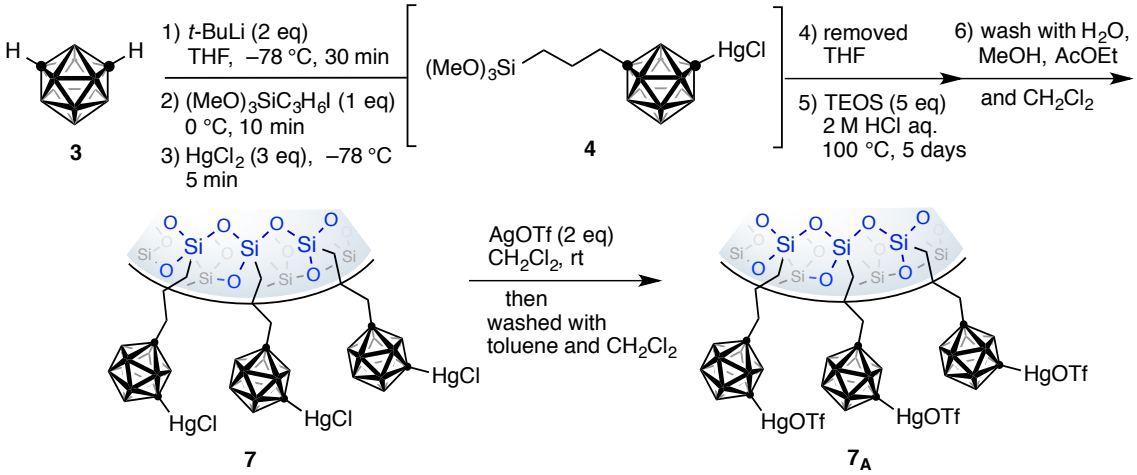
Note that the median lethal oral dose of compound **1** was more than 300 mg/kg body weight for female ICR mice.

Table S2. Body weight change



A transient inhibition of body weight gain was seen in ICR mice treated with 150 and 300 mg/kg of compound **1** compared with *m*-carborane-treated mice, but they gradually recovered thereafter. Statistical significance relative to *m*-carborane group: $^{*}p < 0.05$, $^{**}p < 0.01$.

4. Synthesis and characterization of SiCB-Hg catalysts. (Scheme 1)



a) Synthesis of polysiloxane-linked *m*-carbaboranylmercury chloride (**7**)

m-Carbaborane (**3**) (576 mg, 4 mmol) was dissolved in THF (14 mL), which was cooled to –78 °C. Next, *t*-BuLi (1.6 M in pentane solution, 5 mL, 8 mmol) was added dropwise to the solution at –78 °C. After the mixture was stirred for 30 min at –78 °C, (3-iodopropyl)trimethoxysilane (0.78 mL, 4 mmol) was added to the mixture, and stirred for 10 min at 0 °C. The mixture was cooled to –78 °C once more, and a 1.0 M solution of $HgCl_2$ (12 mL in THF) was added to the solution. It was stirred for 5 min at 0 °C, and the reaction solvent was removed *in vacuo*. Subsequently, the residue was dissolved in EtOH (40 mL), and tetraethyl orthosilicate (TEOS) (4.4 mL, 20 mmol) and 2 M HCl (440 mL) was added to the mixture at room temperature. The polymerization was carried out for 5 days at 400 rpm just under 100 °C. The suspension generated was cooled to room temperature, and filtered using commercially available filter paper to obtain **7** (2.65 g) as white solid particles. **7** was washed sequentially with H_2O (400 mL), MeOH (400 mL), AcOEt (400 mL), and CH_2Cl_2 (400 mL), and then dried *in vacuo*. The Hg-loading of **7** was determined to be 2.22 mmol/g by measuring the mercury content of the via atomic absorption spectrometry. The mean particle size (3.27 μm) of **7** was determined using image analysis software (Figure 2A). The surface of **7** (Figure 2C) was analyzed via energy dispersive X-ray spectroscopy (EDX).

b) Activation of polysiloxane-linked *m*-carbaboranylmercury chloride (**7**) with AgOTf.

To a suspension of **7** (100 mg, 0.22 mmol) in CH_2Cl_2 (6 mL) was added AgOTf (114 mg, 0.44 mmol) at room temperature, and the mixture was stirred for 20 min. Activated

7 (**7A**) was filtered using commercially available filter paper, and then washed with toluene (10 mL × 2) and CH_2Cl_2 (10 mL × 2) to remove excess AgOTf. The mean particle size (3.11 μm) of $\mathbf{7_A}$ was determined using image analysis software (Figure 2A). The surface of $\mathbf{7_A}$ (Figure 2D) was analyzed via energy dispersive X-ray spectroscopy (EDX).

Preliminary experiments for the polymerization of 4

Using TfOH as a condensing agent, undesirable aggregation of **4** occurred, generating sticky precipitates (Figure S2-A). Identical or similar aggregations occurred using AcOH and TFA. Figure S2-B is polysiloxane-linked *m*-carbaboranylmercury chloride (**5**) which was prepared with 2M HCl in the same manner as **7**. SiCB-Hg salts **6** (TEOS 3 eq), **8** (TEOS 10 eq) and **9** (TEOS 20 eq) were also prepared in the same manner as **7** with 2M HCl (Table S3).

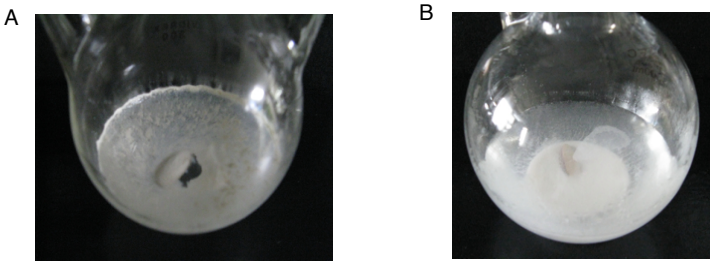
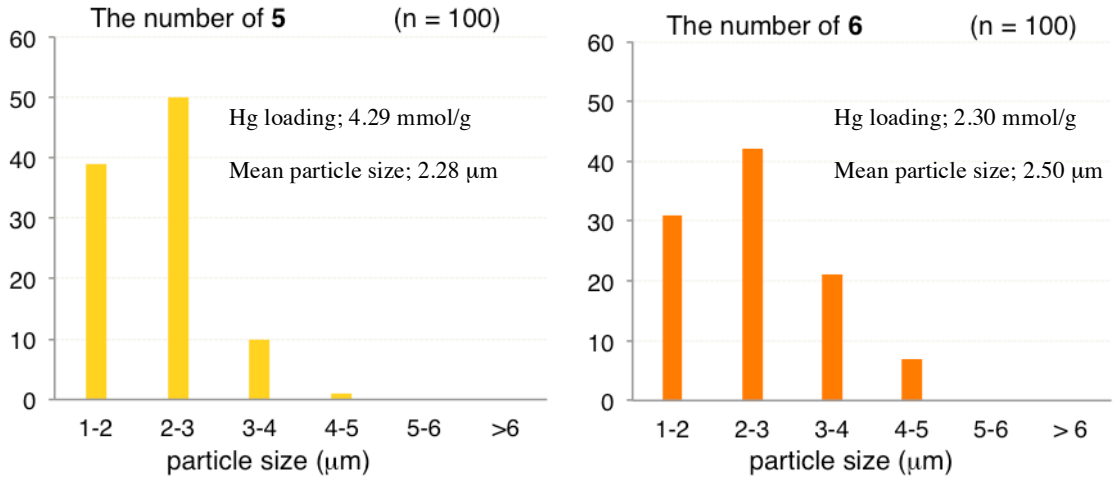
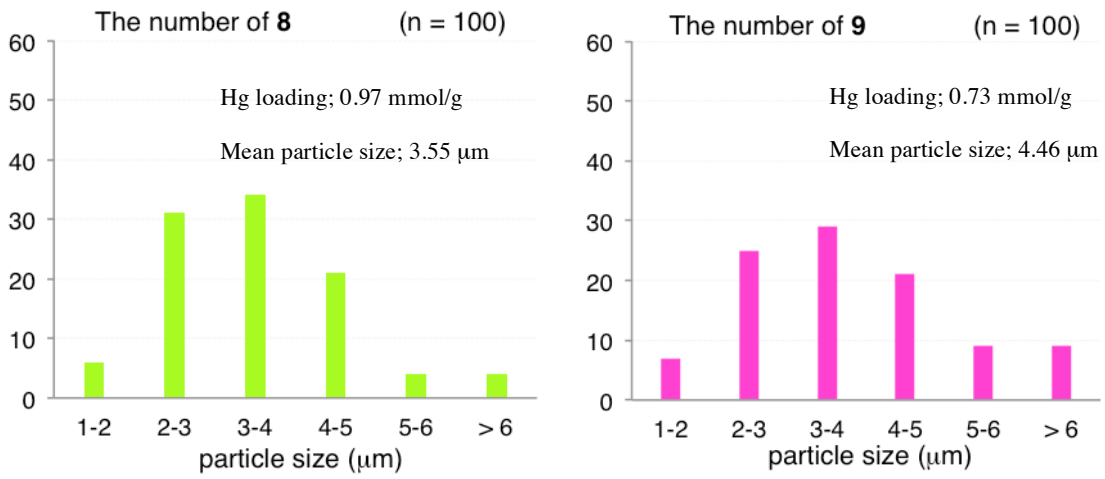


Figure S2. Polymerization of **4** with TfOH (A) and 2M HCl (B).

Table S3. Physical properties of **5**, **6**, **8** and **9**.

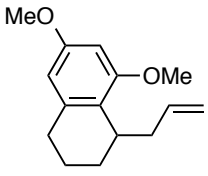




5. Cyclizations with SiCB-Hg catalyst 7A. (Tables 1-3, and Scheme 2B)

General procedure: To a stirred the solution of substrate (1 eq, 0.3-0.6 mmol) in CH_2Cl_2 (0.15 M) was added **7A** (20 mol%) at room temperature under an argon atmosphere. The mixture was stirred at 280 rpm using a mechanical shaker. The end point of the reaction was judged by TLC analysis, and the catalyst was removed by filtration. The filtrate was evaporated *in vacuo*, and the residue was purified by silica gel chromatography to give the cyclization product.

1-Allyl-6,8-dimethoxy-1,2,3,4-tetrahydronaphthalene (11a)



11a

The reaction of **10a**[3] (93.2 mg, 0.401 mmol) using **7A** (36.0 mg, 0.08 mmol, corresponding to 16.04 mg of Hg) in CH_2Cl_2 (6 mL) was carried out for 12 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. **11a** (87.4 mg, 0.376 mmol) was obtained in 94% yield with complete regioselectivity. ^1H and ^{13}C NMR spectra correspond with literature data for **11a** and **12a** (93:7).[1]

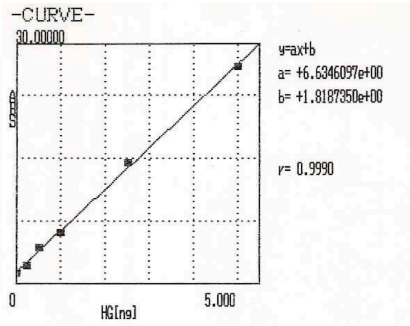
The reaction was performed again with **10a** and **7A** to measure residual **7A** and mercury leakage in the filtrate. The filtrate obtained was initially evaporated *in vacuo*, and the residue was diluted with a 3:1 solution (2 mL) of 64% sulfuric acid and 61% nitric acid. The mixture was heated at 115 °C for 0.5 h and then at 140 °C for 0.5 h. The

resulting mixture (20 μL) was diluted to 5 mL with distilled water, and reduced using 10% $SnCl_2$ solution in order to determine the mercury content of the solution (5 mL) via atomic absorption spectrometry. As shown in Table S4, a mercury content of 0.079-0.237 ng as Hg(0), corresponding to 0.016-0.047 ppb, was detected (nearly the quantitative limit). Consequently, the residue of **7A** (or mercury leakage) in the filtrate was proven to be <0.001%.

Table S4

-STD TABLE-

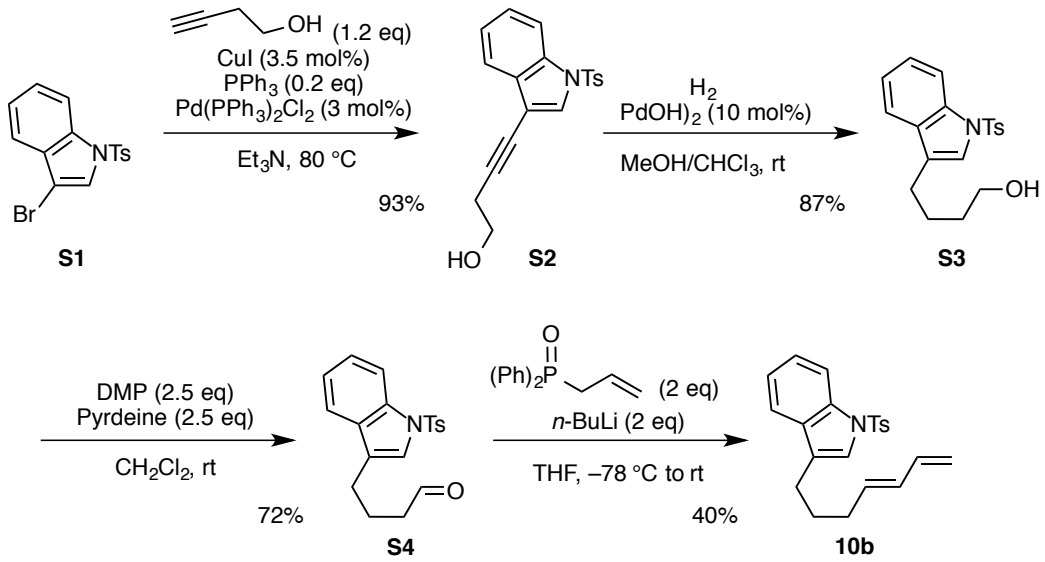
No.	STD ng	ABS(INTE)	HG ng	DEV %
1	0.000	1.73695	-0.012	0.00
2	0.250	2.84115	0.154	38.4
3	0.500	5.68730	0.583	16.6
4	1.000	8.18444	0.959	4.10
5	2.500	19.21566	2.622	4.88
6	5.000	34.61705	4.944	1.12



- SAMPLE TABLE-

No.	NAME	ABS(INTE)	HG ng	CONC ppb	S.VOL ml	C.VOL ml	D.VOL ml
1		3.39204	0.237	0.047	5.0000	5	5
2		2.64990	0.125	0.025	5.0000	5	5
3		2.45451	0.096	0.019	5.0000	5	5
4		2.34045	0.079	0.016	5.0000	5	5

Preparation of (*E*)-3-(hepta-4,6-dien-1-yl)-1-tosyl-1*H*-indole (10b)



To a suspension of 3-bromo-1-tosylindole[4] (**S1**) (8.5 g, 24.3 mmol) in triethylamine (34 mL, 243 mmol) was added CuI (162 mg, 0.85 mmol), triphenylphosphine (1.3 g,

4.9 mmol), and $Pd(PPh_3)_2Cl_2$ (511 mg, 0.73 mmol) at room temperature in a 2-neck flask. The mixture was warmed to 80 °C, and 3-butyn-1-ol (2.0 γ, 29.2 mmol) was added to the mixture. After the reaction mixture was stirred for 12 h, it was cooled to room temperature and then diluted with CH_2Cl_2 and NH_4Cl aq. The aqueous phase was extracted three times with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography (hexane:AcOEt:CH_2Cl_2 = 4:1:1 to 2:2:1) to give **S2** (7.64 g, 93%) as a pale yellow powder. **S2**; FT IR (neat) 3567, 3384, 3140, 3088, 3064, 2949, 2886, 2245, 1596 cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ 7.96 (1H, dt, *J* = 0.6 Hz, 8.4 Hz), 7.76 (2H, d, *J* = 8.1 Hz), 7.69 (1H, s), 7.60 (1H, m), 7.34 (1H, dt, *J* = 1.2 Hz, 8.4 Hz), 7.27 (1H, dt, *J* = 1.2 Hz, 8.4 Hz), 7.20 (2H, br d, *J* = 8.1 Hz), 3.84 (2H, br s), 2.75 (2H, t, *J* = 6.3 Hz), 2.32 (3H, s), 1.96 (OH, br s); ^{13}C NMR (75 MHz in $CDCl_3$) δ 145.2, 134.6, 134, 130.9, 129,8 128.5, 126.7, 125.3, 123.6, 120.4, 113.4, 105.3, 91.0, 72.9, 61.0, 23.9, 21.4; MS (Cl) *m/z* 339 $[M]^+$; HRMS (CI^+) *m/z* calcd for $C_{19}H_{17}NO_3S$; 339.0913, found for 339.0921.

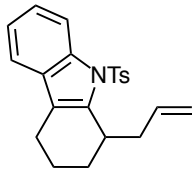
Next, the alkyne **S2** (7.64 g, 22.5 mmol) was dissolved in MeOH/$CHCl_3$ (2:1) (75 mL). $Pd(OH)_2$ (315 mg, 2.25 mmol) was added to the mixture, which was stirred for 6 h under an H_2 atmosphere (1 atm). $Pd(OH)_2$ was removed by simple filtration through filter paper, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel chromatography (hexane:AcOEt:CH_2Cl_2 = 2:1:1) to give the alkane product **S3** (6.7 g, 87%) as a pale yellow syrup. **S3**; FT IR (neat) 3567, 3383, 3110, 3052, 2938, 2862, 1596 cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ 7.97 (1H, d, *J* = 8.1 Hz), 7.73 (2H, d, *J* = 8.4 Hz), 7.47 (1H, d, *J* = 7.8 Hz), 7.31 (1H, s), 7.30 (1H, dt, *J* = 1.2 Hz, 8.1 Hz), 7.21 (1H, dt, *J* = 0.9 Hz, 7.8 Hz), 7.19 (2H, d, *J* = 8.4 Hz), 3.68 (2H, br s), 2.69 (2H, dt, *J* = 0.9 Hz, 7.5 Hz), 2.33 (3H, s), 1.72-1.82 (2H, m), 1.61-1.67 (2H, m), 1.25 (OH, br s); ^{13}C NMR (75 MHz in $CDCl_3$) δ 144.6, 135.1, 134.9, 130.9, 129.6, 126.4, 124.4, 123.2, 122.8, 122.4, 119.3, 113.5, 62.2, 32.2, 24.9, 24.4, 21.2; MS (Cl) *m/z* 343 $[M]^+$; HRMS (CI^+) *m/z* calcd for $C_{19}H_{21}NO_3S$; 343.1242, found for 343.1234.

The alkane product **S3** (1.0 g, 2.9 mmol) was dissolved in CH_2Cl_2 (10 mL), and then pyridine (0.59 mL, 7.25 mmol) and Dess-Martin periodinane (DMP, 3.1 g, 7.25 mmol) were added to the solution at 0 °C. After the mixture was stirred for 10 h at room temperature, the reaction was quenched with saturated $NaHCO_3$. The organic phase was

separated and washed with $Na_2S_2O_3$ aq (x 2) and then brine. The organic phase was dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography (hexane:AcOEt = 10:1) to give **S4** as a white powder (720 mg, 72%). **S4**; FT IR (neat) 3108, 3050, 2932, 2889, 2857, 2829, 2722, 1722, 1597 cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ 9.76 (1H, t, *J* = 1.5 Hz), 7.98 (1H, dt, *J* = 0.9 Hz, 8.1 Hz), 7.74 (2H, d, *J* = 8.4 Hz), 7.47 (1H, dt, *J* = 0.9 Hz, 8.1 Hz), 7.36 (1H, s), 7.31 (1H, dt, *J* = 0.9 Hz, 8.1 Hz), 7.23 (1H, dt, 0.9 Hz, 7.2 Hz), 7.20 (2H, d, 8.4 Hz), 2.71 (2H, dt, *J* = 0.9 Hz, 7.2Hz), 2.49 (2H, dt, *J* = 1.5 Hz, 7.5 Hz), 2.33 (3H, s), 2.01 (2H, quin., *J* = 7.5 Hz); ^{13}C NMR (75 MHz in $CDCl_3$) δ 201.9, 144.8 135.3, 135.1, 130.7, 129.8, 126.8, 124.7, 123, 122.8, 122.1, 119.4, 113.7, 43.2, 24.1, 21.5, 21.3; MS (Cl) *m/z* 341 $[M]^+$; HRMS (CI^+) *m/z* calcd for $C_{19}H_{19}NO_3S$; 341.1086, found for 341.1061.

Allyldiphenylphosphine oxide[5] (1.0 g 4.2 mmol) was dissolved in THF (7 mL, 0.3 M), and then *n*-BuLi (2.6 mL in 1.6 M hexane, 4.2 mmol) was added to the solution at -78 °C. The mixture was stirred for 30 min at –78 °C, and a solution of aldehyde **S4** (720 mg, 2.1 mmol) in THF was added to the mixture at –78 °C. After stirring for 8 h at room temperature, the reaction was quenched with saturated NH_4Cl. The organic phase was separated and washed with NH_4Cl aq (× 2) and brine. It was then dried over $MgSO_4$, and concentrated *in vacuo*, and the residue was purified by silica gel chromatography (hexane:AcOEt = 10:1) to give **10b** as a white powder (307 mg, 40%). **10b**; FT IR (neat) 3019, 3083, 3063, 3034, 3006, 2928, 2856, 2535, 1914, 1798, 1738, 1599 cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ 7.98 (1H, d, *J* = 8.1 Hz), 7.71 (2H, d, *J* = 8.4 Hz), 7.44 (1H, d, *J* = 7.2 Hz), 7.30 (1H, s), 7.28 (1H, br t, *J* = 7.2 Hz), 7.14 (2H, br d, *J* = 8.4 Hz), 6.30 (1H, dt, *J* = 8.4 Hz, 16.8 Hz), 6.04 (1H, br dd, *J* = 10.5 Hz, 15,3 Hz), 5.89 (1H, dt, *J* = 7.2Hz, 15.3 Hz), 5.09 (1H, d, *J* = 17.4 Hz), 4.96 (1H, d, *J* = 9.8 Hz), 2.64 (2H, t, *J* = 7.2 Hz), 2.27 (3H, s), 2.62 (2H, q, *J* = 7.2 Hz), 1.76 (2H, quin. *J* = 7.2 Hz) ^{13}C NMR (75 MHz in $CDCl_3$) δ 144.6, 137.1, 135.3, 135.2, 134.3, 131.5, 131.0, 129.7, 126.6, 124.5, 123.1, 122.9, 122.6, 122.6, 119.4, 115.1, 113.8, 32.0, 28.2, 24.3, 21.4; MS (Cl) *m/z* 365 $[M]^+$; HRMS (CI^+) *m/z* calcd for $C_{22}H_{23}NO_2S$; 365.1450, found for 365.1451.

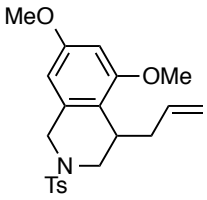
1-Allyl-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazole (11b)



11b

The cyclization of **10b** (110 mg, 0.3 mmol) using **7A** (27.1 mg, 0.06 mmol) in CH_2Cl_2 (4.5 mL) was carried out for 15 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. **11b** (101 mg, 0.276 mmol) was obtained as a white powder in 92% yield with complete regioselectivity. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **11b**; FT IR (neat) 3071, 3032, 3000, 2933, 2855, 1911, 1731, 1683, 1638, 1598 cm^{-1}; ^1H NMR (500 MHz in $CDCl_3$) δ 8.14 (1H, d, *J* = 8.0 Hz), 7.52 (1H, d, *J* = 8.0 Hz), 7.30 (1H, dd, *J* = 1.0 Hz, 7.5 Hz), 7.26 (1H, dt, *J* = 1.5 Hz, 7.5 Hz), 7.21 (1H, dt, *J* = 1.0 Hz, 7.5 Hz), 7.11 (2H, d, *J* = 8.0 Hz), 5.94 (1H, m), 5.09 (2H, br t, *J* = 10 Hz, 18 Hz), 3.44 (1H, dt, *J* = 2.5 Hz, 8.0 Hz), 2.90 (1H, m), 2.67 (1H, dt, *J* = 3.5 Hz, 12 Hz), 2.46 (1H, m), 2.29 (3H, s), 2.18 (1H, m), 2.03 (1H, m), 1.67-1.82 (3H, m); ^{13}C NMR (125 MHz in $CDCl_3$) δ 144.3, 139.4, 137.3, 136.1, 135.5, 130.8, 129.6, 126.2, 124.2, 123.6, 119.9, 118.2, 116.4, 115.4, 39.2, 33.6, 26.0, 21.5, 21.1, 17.1; MS (Cl) *m/z* 366 $[M+H]^+$; HRMS (CI^+) *m/z* calcd for $C_{22}H_{24}NO_2S$; 366.1528, found for 366.1530.

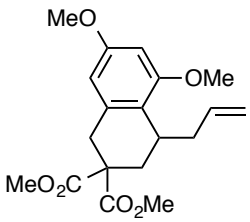
4-Allyl-5,7-dimethoxy-2-tosyl-1,2,3,4-tetrahydroisoquinoline (11c)



11c

The cyclization of **10c**[1] (155 mg, 0.4 mmol) using **7A** (36.0 mg, 0.08 mmol) in CH_2Cl_2 (6.0 mL) was carried out for 14 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **11c** (133 mg, 0.343 mmol) was obtained in 86% yield with complete regioselectivity. The ^1H and ^{13}C NMR spectra correspond with literature data for **11c**.[1]

Dimethyl 4-allyl-5,7-dimethoxy-3,4-dihydronaphthalene-2,2(1*H*)-dicarboxylate (11d)

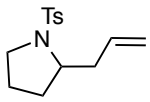


11d

The cyclization of **10d**[1] (140 mg, 0.4 mmol) using **7A** (36.0 mg, 0.08 mmol) in CH_2Cl_2 (6.0 mL) was carried out for 24 h at room temperature according to the general procedure for cyclization

with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be ≦0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **11d** (123 mg, 0.351 mmol) was obtained in 88% yield with complete regioselectivity. The ^{1}H and ^{13}C NMR spectra correspond with literature data for **11d**.[1]

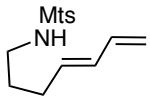
2-Allyl-1-tosylpyrrolidine (11e)



11e

The cyclization of **10e**[3] (106 mg, 0.4 mmol) using **7A** (36.0 mg, 0.08 mmol) in CH_2Cl_2 (6.0 mL) was carried out for 24 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **11e** (98.6 mg, 0.372 mmol) was obtained in 93% yield with complete regioselectivity. The ^{1}H and ^{13}C NMR spectra correspond with literature data for **11e**.[1]

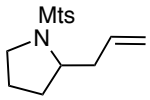
Preparation of 2-allyl-1-(mesitylsulfonyl)pyrrolidine (10f)



10f

To a solution of (*E*)-hepta-4,6-dien-1-amine[6] (500 mg, 4.0 mmol) in CH_2Cl_2 (14 mL) was added triethylamine (2.7 mL, 20 mmol), 4,4-dimethylaminopyridine (244 mg, 2.0 mmol), and 2,4,6-trimethylbenzenesulfonyl chloride (MtsCl) (0.62 mL, 8.0 mmol) at 0 °C. After stirring for 1.5 h at 0 °C, the reaction was quenched with NH_4Cl aq. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 three times. The combined organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (hexane:AcOEt = 5:1) to give **10f** as a white powder (1.17 g, 99%). **10f**; FT IR (neat) 3313, 3084, 3028, 2972, 2937, 2858, 1604, 1565 cm^{-1}; ^{1}H NMR (300 MHz in $CDCl_3$) δ 6.94 (2H, s), 6.22 (1H, dt, *J* = 10.3 Hz, 16.8 Hz), 5.93 (1H, br dd, *J* = 10.3 Hz, 16,8 Hz), 5.52 (1H, dt, *J* = 7.2 Hz, 15 Hz), 5.01 (1H, d, *J* = 16,8 Hz), 4.94 (1H, d, *J* = 10.3 Hz), 4.47 (NH, br t, 6.0 Hz), 2.88 (2H, q, *J* = 6.6 Hz), 2.61 (6H, s), 2.28, (3H, s), 2.03 (2H, q, *J* = 7.2 Hz), 1.53 (2H, m) ^{13}C NMR (75 MHz in $CDCl_3$) δ 142.2, 139.1, 136.8, 133.6, 133.2, 132.0, 115.6, 42.0, 29.5, 29.0, 23.0, 21.0; MS (Cl) *m/z* 294 $[M+H]^+$; HRMS (CI^+) *m/z* calcd for $C_{16}H_{24}NO_2S$; 294.1528, found for 294.1528.

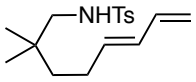
2-Allyl-1-(mesitylsulfonyl)pyrrolidine (11f)



11f

The cyclization of **10f** (160 mg, 0.545 mmol) using **7A** (49.2 mg, 0.18 mmol) in CH_2Cl_2 (9 mL) was carried out for 18 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **11f** (144 mg, 0.491 mmol) was obtained as a white powder in 90% yield with complete regioselectivity. **11f**; FT IR (neat) 2974, 2939, 2873, 1639, 1604, 1565 cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ 6.94 (2H, s), 5.59 (1H, m), 4.96 (1H, d, *J* = 9.3 Hz), 4.95 (1H, d, *J* = 6.4 Hz), 3.87 (1H, m), 3.36 (1H, dt, *J* = 7.2, 12.8 Hz), 3.10 (1H, dt, 6.0Hz, 9.9 Hz), 2.63 (6H, s), 2.28, (3H, s), 2.21 (2H, m), 1.69-2.05 (5H, m), ^{13}C NMR (75 MHz in $CDCl_3$) δ 142.5, 140.1, 134.6, 133.3, 131.9, 117.5, 58.5, 47.8, 39.5, 30.5, 24.2, 22.9, 21.0; MS (Cl) *m/z* 294 $[M+H]^+$; HRMS (CI^+) *m/z* calcd for $C_{16}H_{24}NO_2S$; 294.1528 found for 294.1520.

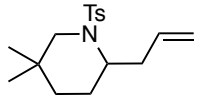
Preparation of *N*-(2,2-dimethyloct-7-en-1-yl)-4-methylbenzenesulfonamide (10g)



10g

To a solution of (*E*)-2,2-dimethylocta-5,7-dien-1-amine[7] (460 mg, 3.0 mmol) in CH_2Cl_2 (10 mL) was added triethylamine (0.84 mL, 6.0 mmol), 4,4-dimethylaminopyridine (183 mg, 1.5 mmol), and 4-methylbenzenesulfonyl chloride (1.14 g, 6.0 mmol) at 0 °C. After stirring for 1 h at 0 °C, the reaction was quenched with saturated NH_4Cl. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 three times. The combined organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (hexane:AcOEt = 4:1) to give **10g** as a white powder (913 mg, 99%). **10g**; FT IR (neat) 3283, 2916, 2870, 1650, 1598 cm^{-1}; ^1H NMR (500 MHz in $CDCl_3$) δ 7.74 (2H, d, *J* = 8.0 Hz), 7.31 (2H, d, *J* = 8.0 Hz), 6.28 (1H, dt, *J* = 10.5 Hz, 17 Hz), 6.01 (1H, dd, *J* = 10.5 Hz, 15 Hz), 5.62 (1H, dt, *J* = 6.5 Hz, 15 Hz), 5.08 (1H, d, *J* = 17 Hz), 4.96 (1H, *J* = 10 Hz), 4.42 (NH, br t, 6.0 Hz), 2.69 (2H, d, *J* = 7.0 Hz), 2.43 (3H, s), 1.96 (2H, dt, *J* = 7.0 Hz, 8.5 Hz), 1.28 (2H, t, *J* = 8.5 Hz), 0.85 (6H, s), ^{13}C NMR (75 MHz in $CDCl_3$) δ 143.4, 137.1, 136.9, 135.0, 131.0, 129.7, 127.1, 115.0, 52.7, 38.7, 33.8, 26.9, 24.8, 21.5; MS (Cl) *m/z* 307 $[M]^+$; HRMS (CI^+) *m/z* calcd for $C_{17}H_{25}NO_2S$; 307.1606, found for 307.1608.

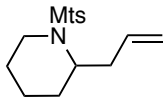
2-Allyl-5,5-dimethyl-1-tosylpiperidine (11g)



11g

The cyclization of **10g** (123 mg, 0.4 mmol) using **7A** (36.0 mg, 0.08 mmol) in CH_2Cl_2 (6.0 mL) was carried out for 29 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **11g** (104 mg, 0.338 mmol) was obtained as a white powder in 85% yield with complete regioselectivity. **11g**; FT IR (neat) 3076, 2951, 2863, 1640, 1599 cm^{-1}; ^1H NMR (500 MHz in $CDCl_3$) δ 7.68 (2H, d, *J* = 8.5 Hz), 7.27 (2H, d, *J* = 8.0 Hz), 5.58 (1H, m), 4.95 (2H, d, *J* = 12.5 Hz), 4.05 (1H, quin., *J* = 5.0 Hz), 3.31 (1H, dd, *J* = 1.5 Hz, 13 Hz), 2.67 (1H, d, *J* = 13 Hz), 2.41 (3H, s), 2.28 (1H, dt, *J* = 9.0 Hz, 13.5 Hz), 1.95 (1H, dt, *J* = 5.0 Hz, 13.5 Hz), 1.76 (1H, m), 1.52 (1H, dt, *J* = 4.5 Hz, 14 Hz), 1.31 (1H, dt, *J* = 3.5 Hz, 14 Hz), 1.22 (1H, dt, *J* = 4.5 Hz, 14 Hz), 0.90 (3H, s), 0.88 (3H, s) ^{13}C NMR (125 MHz in $CDCl_3$) δ 142.8, 138.6, 134.9, 129.5, 127.0, 117.3, 51.9, 51.2, 32.6, 31.6, 30.4, 29.0, 23.5, 23.0, 21.5; MS (Cl) *m/z* 308 $[M+H]^+$; HRMS (CI^+) *m/z* calcd for $C_{17}H_{26}NO_2S$; 308.1684, found for 308.1666.

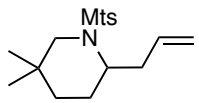
2-Allyl-1-(mesitylsulfonyl)piperidine (11h)



11h

The cyclization of **10h**[1] (123 mg, 0.4 mmol) using **7A** (36.0 mg, 0.08 mmol) in CH_2Cl_2 (6.0 mL) was carried out for 19 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **11h** (113 mg, 0.367 mmol) was obtained in 92% yield with complete regioselectivity. The ^1H and ^{13}C NMR spectra correspond with literature data for **11h**.[1]

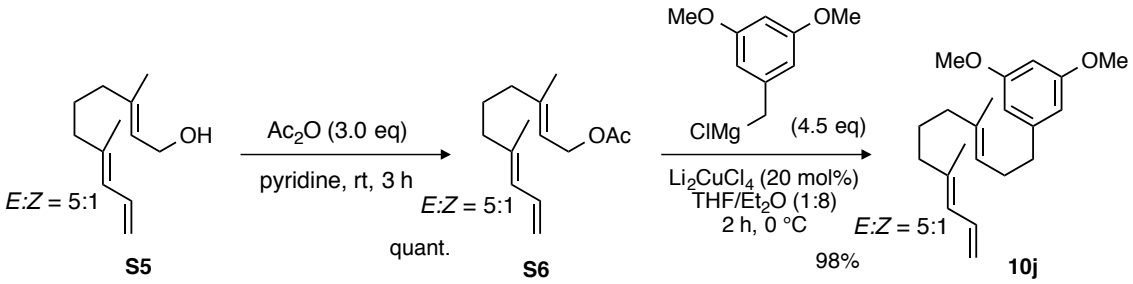
2-Allyl-1-(mesitylsulfonyl)-5,5-dimethylpiperidine (11i)



11i

The cyclization of **10i**[1] (101 mg, 0.3 mmol) using **7A** (27.0 mg, 0.06 mmol) in CH_2Cl_2 (5.0 mL) was carried out for 24 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **11i** (96.9 mg, 0.288 mmol) was obtained in 96% yield with complete regioselectivity. The ^1H and ^{13}C NMR spectra correspond with literature data for **11i**.[1]

Preparation of 1-[(3*E*,8*E*)-4,8-dimethylundeca-3,8,10-trien-1-yl]-3,5-dimethoxybenzene (10j)



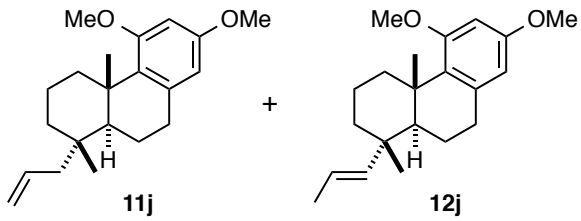
The allyl alcohol substrate **S5**[8] (500 mg, 2.77 mmol) was dissolved in pyridine (9.2 mL), and Ac_2O (0.78 mL, 8.31 mmol) was added to the solution at 0 °C. After the mixture was stirred for 3 h at room temperature, it was diluted with Et_2O and quenched with saturated $NaHCO_3$. The organic phase was separated and washed with 1 M HCl aq (× 2), H_2O (× 2) and brine. It was then dried over $MgSO_4$, and concentrated *in vacuo*, and the residue was purified by silica gel chromatography (hexane:AcOEt = 5:1) to give **S6** as a colorless oil (616 mg, quant.). **S6**; FT IR (neat) 2936, 2862, 1738, 1648 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) δ 6.57 (1H, dt, *J* = 10.8 Hz, 16.8 Hz), 5.85 (1H, d, *J* = 10.8 Hz), 5.09 (1H, dd, *J* = 2.0 Hz, 16.8 Hz), 4.99 (1H, dd, *J* = 2.0 Hz, 10.8 Hz), 2.06 (3H, s), 2.02 (4H, m), 1.75 (3H, s), 1.69 (3H, s), 1.57 (2H, m) ^{13}C NMR (100 MHz in $CDCl_3$) δ 171.1, 142.2, 139.3, 133.3, 125.7, 118.4, 114.7, 61.4, 39.3, 39.1, 25.6, 21.7, 16.6, 16.4; MS (Cl) *m/z* 222 $[M]^+$; HRMS (CI^+) *m/z* calcd for $C_{14}H_{22}O_2$; 222.1620, found for 222.1608.

Compound **S6** (476 mg 2.14 mmol) was dissolved in THF (2.2 mL), and 0.1 M THF solution of dilithium tetrachlorocuprate (II) (0.43 mmol, 4.3 mL) was added to the solution of **S6** at 0 °C. The mixture was stirred for 15 min at 0 °C, and the prepared 0.2 M Et_2O solution of (3,5-dimethoxybenzyl)magnesium chloride (9.53 mmol, 48.2 mL) was added to the mixture at 0 °C. After stirring for 2 h at 0 °C, the reaction was quenched with 1 M HCl aq. The organic phase was separated and washed with 1 M HCl aq (× 2), H_2O (× 2) and brine. It was then dried over $MgSO_4$, and concentrated *in vacuo*, and the residue was purified by silica gel chromatography (hexane:AcOEt = 40:1) to give **10j** as a colorless oil (659 mg, 98%). **10j**; FT IR (neat) 2999, 2931, 2854, 2835, 1593 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) δ 6.58 (1H, dt, *J* = 10.4 Hz, 16.8 Hz), 6.36 (2H, d, *J* = 2.4 Hz), 6.30 (1H, t, *J* = 2.4 Hz), 5.83 (1H, d, *J* = 10.4 Hz), 5.17 (1H, m),

5.09 (1H, dd, *J* = 1.4 Hz, 16.8 Hz), 4.97 (1H, dd, *J* = 1.4 Hz, 10.4 Hz), 3.76 (6H, s), 2.58 (2H, t, *J* = 7.6 Hz), 2.30 (2H, q, *J* = 7.6 Hz), 1.97 (4H, m), 1.75 (3H, s), 1.57 (3H, s), 1.51 (2H, m) ^{13}C NMR (100 MHz in $CDCl_3$) δ 160.7, 144.8, 139.8, 135.7, 133.5, 125.4, 123.8, 114.5, 106.5, 97.7, 55.3, 39.4, 39.3, 36.4, 29.7, 26.1, 16.6, 15.9; MS (Cl) *m/z* 315 $[M+H]^+$; HRMS (CI^+) *m/z* calcd for $C_{21}H_{31}O_2$; 315.2324, found for 315.2326.

(±)-(1*S*,4a*S*,10a*S*)-1-allyl-5,7-dimethoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (11j)

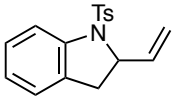
(±)-(1*S*,4a*S*,10a*S*)-5,7-dimethoxy-1,4a-dimethyl-1-((*E*)-prop-1-en-1-yl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (12j)



The reaction of **10j** (100 mg, 0.318 mmol) using **7A** (28.6 mg, 0.095 mmol, corresponding to 19.1 mg of Hg) in CH_3NO_2 (4.8 mL) was carried out for 38 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **11j** (67.2 mg, 0.213 mmol) and **12j** (11.4 mg, 0.036 mmol) were obtained in 67% and 11% yields, respectively. **11j**; colorless syrup; FT IR (neat) 3071, 2944, 2924, 2856, 1636 cm^{-1}; ^{1}H NMR (500 MHz in $CDCl_3$) δ 6.27 (1H, d, *J* = 2.5 Hz), 6.18 (1H, d, *J* = 2.5 Hz), 5.82 (1H, m), 5.01 (2H, m), 3.75 (6H, s), 3.05 (1H, dt, *J* = 3.5 Hz, 13.0 Hz), 2.74-2.87 (2H, m), 2.15 (1H, dd, *J* = 8.0 Hz, 13.5 Hz), 1.94 (1H, dd, *J* = 7.0 Hz, 13.5 Hz), 1.78-1.66 (3H, m), 1.59-1.46 (1H, m), 1.31-1.24 (3H, m), 1.29 (3H, s), 1.11 (1H, dt, *J* = 3.0 Hz, 13.0 Hz), 0.93 (3H, s) ^{13}C NMR (150 MHz in $CDCl_3$) δ 159.6, 157.8, 138.8, 135.5, 130.4, 116.9, 104.8, 97.6, 55.1, 55.0, 49.9, 48.9, 39.2, 37.0, 36.9, 36.5, 33.0, 21.6, 20.4, 19.1, 18.5; MS (Cl) *m/z* 314 $[M]^+$; HRMS (CI^+) *m/z* calcd for $C_{21}H_{30}O_2$; 314.2246, found for 314.2231. **12j**; colorless syrup; FT IR (neat) 3155, 2953, 2929, 2857, 1793 cm^{-1}; ^{1}H NMR (600 MHz in $CDCl_3$) δ 6.27 (1H, d, *J* = 2.4 Hz), 6.19 (1H, d, *J* = 2.4 Hz), 5.56 (1H, m), 5.38 (1H, m), 3.75 (3H, s), 3.75 (3H, s), 3.05 (1H, dt, *J* = 2.4 Hz, 13.2 Hz), 2.84 (2H, m), 1.91 (1H, dd, *J* = 1.8 Hz, 12.6 Hz), 1.86 (1H, dd, *J* = 6.0 Hz, 12.6 Hz), 1.79-1.70 (1H, m), 1.68 (3H, dd, *J* = 1.8 Hz, 12.0 Hz), 1.59 (1H, m), 1.45 (2H, m), 1.34 (1H, m), 1.20 (3H, s), 1.18 (1H, m), 0.99 (3H, s)

^{13}C NMR (150 MHz in $CDCl_3$) δ 159.8, 157.7, 138.7, 136.9, 129.9, 119.5, 104.9, 97.6, 55.1, 55.0, 54.7, 39.3, 38.8, 38.0, 36.9, 33.7, 32.3, 19.2, 19.1, 18.8, 18.5; MS (Cl) *m/z* 314 $[M]^+$; HRMS (CI^+) *m/z* calcd for $C_{21}H_{30}O_2$; 314.2246, found for 314.2240.

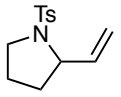
1-Tosyl-2-vinylindoline (14a)



14a

The cyclization of **13a**[9] (95.0 mg, 0.3 mmol) using **7A** (27.0 mg, 0.06 mmol) in CH_2Cl_2 (5.0 mL) was carried out for 8 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **14a** (89.7 mg, 0.3 mmol) was obtained quantitatively. The ^{1}H and ^{13}C NMR spectra correspond with literature data for **14a**.[9]

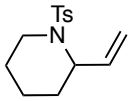
1-Tosyl-2-vinylpyrrolidine (14b)



14b

The cyclization of **13b**[10] (105 mg, 0.356 mmol) using **7A** (32.0 mg, 0.072 mmol) in CH_2Cl_2 (6.0 mL) was carried out for 10 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **14b** (83.4 mg, 0.332 mmol) was obtained in 93% yield. The ^{1}H and ^{13}C NMR spectra correspond with literature data for **14b**.[10]

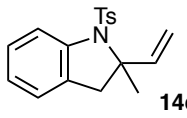
1-Tosyl-2-vinylpiperidine (14c)



14c

The cyclization of **13c**[11] (101 mg, 0.356 mmol) using **7A** (32.0 mg, 0.072 mmol) in CH_2Cl_2 (6.0 mL) was carried out for 24 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be ≦0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **14c** (77.0 mg, 0.252 mmol) was obtained in 71% yield. The ^{1}H and ^{13}C NMR spectra correspond with literature data for **14c**.[11]

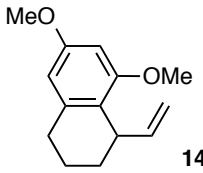
2-Methyl-1-tosyl-2-vinylindoline (14d)



14d

The cyclization of **13d**[12] (118 mg, 0.356 mmol) using **7A** (32.0 mg, 0.072 mmol) in CH_2Cl_2 (6.0 mL) was carried out for 16 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **14d** (92.8 mg, 0.296 mmol) was obtained as a white powder in 83% yield. **14d**; FT IR (neat) 3068, 3030, 2973, 2924, 2853, 2256, 1916, 1644, 1599 cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ 7.79 (2H, d, *J* = 8.4 Hz), 7.51 (1H, d, *J* = 8.1 Hz), 7.23 (2H, d, *J* = 8.1 Hz), 7.15 (1H, dt, *J* = 0.6 Hz, 7.5 Hz), 7.09 (1H, dd, *J* = 0,9 Hz, 7.5 Hz), 6.94 (1H, dt, *J* = 0.9 Hz, 7.2 Hz), 6.10 (1H, dd, *J* = 10.5 Hz, 17.1 Hz), 5.31 (1H, d, *J* = 17.1 Hz), 5.15 (1H, d, *J* = 10.5 Hz), 3.13 (1H, d, *J* = 16.2 Hz), 2.96 (1H, d, *J* = 16.2 Hz), 2.38 (3H, s), 1.78 (3H, s), ^{13}C NMR (75 MHz in $CDCl_3$) δ 143.5, 141.8, 141.3, 138.7, 129.5, 128.6, 127.7, 127.0, 124.9, 122.8, 114.0, 113.8, 72.0, 44.8, 25.2, 21.5; MS (Cl) *m/z* 313 $[M]^+$; HRMS (CI^+) *m/z* calcd for $C_{18}H_{19}NO_2S$; 313.1136 found for 313.1129.

6,8-Dimethoxy-1-vinyl-1,2,3,4-tetrahydronaphthalene (14e)

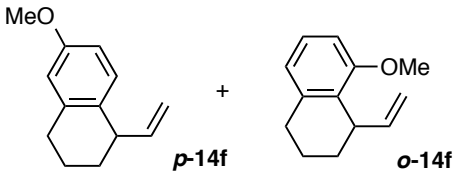


14e

The cyclization of **13e**[13] (84 mg, 0.356 mmol) using **7A** (32.0 mg, 0.072 mmol) in CH_2Cl_2 (6.0 mL) was carried out for 6 h at reflux according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **14e** (69.0 mg, 0.316 mmol) was obtained in 89% yield. The ^1H and ^{13}C NMR spectra correspond with literature data for **14e**.[13]

6-Methoxy-1-vinyl-1,2,3,4-tetrahydronaphthalene (*p*-14f)

8-Methoxy-1-vinyl-1,2,3,4-tetrahydronaphthalene (*o*-14f)

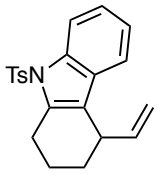


***p*-14f** ***o*-14f**

The cyclization of **13f**[13] (73.4 mg, 0.356 mmol) using **7A** (32.0 mg, 0.072 mmol) in CH_2Cl_2 (6.0 mL) was carried out for 12 h at reflux according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be ≦0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. The *p*-cyclization product ***p*-14f** (41.6 mg, 0.221 mmol) and *o*-cyclization product ***o*-14f** (5.4

mg, 0.029 mmol) were obtained in 62% and 8% yield, respectively. The ^{1}H and ^{13}C NMR spectra correspond with literature data for ***p*-14f** and ***o*-14f**.[13]

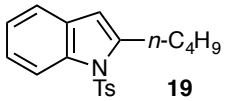
9-Tosyl-4-vinyl-2,3,4,9-tetrahydro-1*H*-carbazole (14g)



14g

The cyclization of **13g**[13] (127 mg, 0.356 mmol) using **7A** (32.0 mg, 0.072 mmol) in CH_2Cl_2 (6.0 mL) was carried out for 18 h at reflux according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** (and mercury leakage) in the filtrate was proven to be 0.001-0.002% by measuring the mercury content of the filtrate in the same manner as for **11a**. **14g** (110 mg, 0.313 mmol) was obtained in 88% yield. The ^{1}H and ^{13}C NMR spectra correspond with literature data for **14g**.[13]

2-Butyl-1-tosyl-1*H*-indole (19)



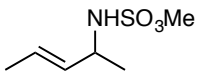
19

The cycloisomerization of **18**[14] (163.8 mg, 0.5 mmol) using **7A** (45.1 mg, 0.1 mmol) in CH_2Cl_2 (8.0 mL) was carried out for 1 h at room temperature according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **19** (163.7 mg, 0.5 mmol) was obtained quantitatively. The ^{1}H and ^{13}C NMR spectra correspond with literature data for **19**.[14]

6. Intermolecular aminations with SiCB-Hg catalyst 7A. (Scheme 2A)

General procedure: To a solution of allyl alcohol substrate (1 eq, 0.3-0.5 mmol) and methylsulfamate (**16a**)[15] (1.5 eq) or 4-methylbenzenesulfonamide (**16b**) (1.5 eq) in CH_2Cl_2 (0.1 M) was added $\mathbf{7_A}$ (20 mol%) at room temperature under an argon atmosphere. The reaction mixture was stirred at 280 rpm using a mechanical shaker. The end point of the reaction was judged by TLC analysis, and the catalyst was removed by filtration. The filtrate was evaporated *in vacuo*, and the residue was purified by silica gel chromatography to give the allylamine product.

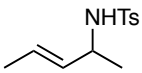
Methyl (*E*)-pent-3-en-2-ylsulfamate (17aa)



17aa

The reaction of (*E*)-pent-3-en-2-ol (**15a**) (43.0 mg, 0.5 mmol) with **16a** (83.5 mg, 0.75 mmol) using **7A** (45.1 mg, 0.1 mmol) in CH_2Cl_2 (8.0 mL) was carried out for 5 h at room temperature according to the general procedure for intermolecular amination with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **17aa** (78.0 mg, 0.435 mmol) was obtained as a colorless oil in 87% yield. **17aa**; FT IR (neat) 3298, 2980, 2958 2935, 2016, 2884 cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ 5.71 (1H, qd, *J* = 1.2 Hz, 6.3 Hz, 15.3 Hz), 5.44 (1H, m), 4.26 (NH, br s), 4.00 (1H, m), 3.82 (3H, s), 1.70 (3H, dq, *J* = 0.9 Hz, 6.6 Hz), 1.31 (3H, d, *J* = 6.9 Hz) ^{13}C NMR (75 MHz in $CDCl_3$) δ 131.5, 127.4, 56.2, 52.2, 21.5, 17.6; MS (Cl) *m/z* 179 $[M]^+$; HRMS (CI^+) *m/z* calcd for $C_6H_{13}NO_3S$; 179.0616 found for 179.0613.

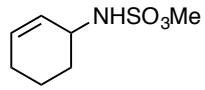
(*E*)-4-Methyl-*N*-(pent-3-en-2-yl)benzenesulfonamide (17ab)



17ab

The reaction of (*E*)-pent-3-en-2-ol (**15a**) (43.0 mg, 0.501 mmol) with **16b** (128.4 mg, 0.75 mmol) using **7A** (45.1 mg, 0.1 mmol) in CH_2Cl_2 (8.0 mL) was carried out for 6 h at room temperature according to the general procedure for intermolecular amination with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **17ab** (110 mg, 0.460 mmol) was obtained in 92% yield. The ^1H and ^{13}C NMR spectra correspond with literature data for **17ab**.[15]

Methyl cyclohex-2-en-1-ylsulfamate (17ba)

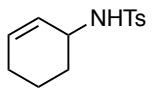


17ba

The reaction of cyclohex-2-en-1-ol (**15b**) (49.0 mg, 0.5 mmol) with **16** (83.5 mg, 0.75 mmol) using **7A** (45.1 mg, 0.1 mmol) was carried out for 16 h at room temperature according to the general procedure for intermolecular amination with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **17ba** (88.0 mg, 0.46 mmol) was obtained in 92% yield. The ^1H and ^{13}C NMR spectra correspond with literature data for **17ba**.[15]

***N*-(cyclohex-2-en-1-yl)-4-methylbenzenesulfonamide (17bb)**

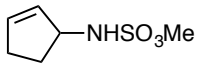
The reaction of cyclohex-2-en-1-ol (**15b**) (49.0 mg, 0.5 mmol) with **16** (128.4 mg, 0.75 mmol) using **7A** (45.1 mg, 0.1 mmol) was carried out for 26 h at room temperature



17bb

according to the general procedure for intermolecular amination with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **17bb** (122 mg, 0.485 mmol) was obtained in 97% yield. The ^{1}H and ^{13}C NMR spectra correspond with literature data for **17bb**.[15]

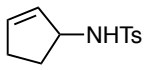
Methyl cyclopent-2-en-1-ylsulfamate (17ca)



17ca

The reaction of cyclopent-2-en-1-ol (**15c**) (42.0 mg, 0.5 mmol) with **16** (128.4 mg, 0.749 mmol) using **7A** (45.1 mg, 0.1 mmol) was carried out for 0.5 h at room temperature according to the general procedure for intermolecular amination with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **17ca** (61.9 mg, 0.349 mmol) was obtained in 70% yield. The ^{1}H and ^{13}C NMR spectra correspond with literature data for **17ca**.[15]

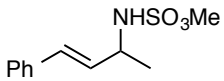
***N*-(cyclopent-2-en-1-yl)-4-methylbenzenesulfonamide (17cb)**



17cb

The reaction of cyclopent-2-en-1-ol (**15c**) (42.0 mg, 0.5 mmol) with **16** (128.2 mg, 0.749 mmol) using **7A** (45.1 mg, 0.1 mmol) was carried out for 3 h at room temperature according to the general procedure for intermolecular amination with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **17cb** (92.4 mg, 0.389 mmol) was obtained in 78% yield. The ^{1}H and ^{13}C NMR spectra correspond with literature data for **17cb**.[15]

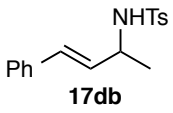
Methyl (*E*)-(4-phenylbut-3-en-2-yl)sulfamate (17da)



17da

The reaction of **15d** (44.5 mg, 0.3 mmol) with **16** (50.0 mg, 0.45 mmol) using **7A** (27.1 mg, 0.06 mmol) was carried out for 6 h at room temperature according to the general procedure for intermolecular amination with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **17da** (57.2 mg, 0.237 mmol) was obtained in 79% yield. The ^{1}H and ^{13}C NMR spectra correspond with literature data for **17da**.[15]

(*E*)-4-Methyl-*N*-(4-phenylbut-3-en-2-yl)benzenesulfonamide (17db)



17db

The reaction of **15d** (44.5 mg, 0.3 mmol) with **16** (77.0 mg, 0.45 mmol) using **7A** (27.1 mg, 0.06 mmol) was carried out for 7 h at room temperature according to the general procedure for intermolecular amination with SiCB-Hg catalyst **7A**. The residue of **7A** in the filtrate was proven to be <0.001% by measuring the mercury content of the filtrate in the same manner as for **11a**. **17db** (81.7 mg, 0.271 mmol) was obtained in 90% yield. The ^{1}H and ^{13}C NMR spectra correspond with literature data for **17db**.[16]

7. Reuse of SiCB-Hg catalyst 7A for the synthesis of 14a (Table 4)

The reaction of **13a** (63.5 mg, 0.2 mmol) using **7A** (45 mg, 0.1 mmol) was repeated 20 times according to the general procedure for cyclization with SiCB-Hg catalyst **7A**. Further reactions (21st – 23rd runs) were performed with 0.1 mmol of **13a** using 50 mol% of reactivated **7A**.

Wash and reactivation of **7A**: To a 2M HCl solution (3 mL) was added the reused catalyst **7A** (22.0 mg) at room temperature. The mixture was stirred at 280 rpm using a mechanical shaker for 1 day at room temperature, and the catalyst particles were separated by filtration. The particles collected were washed with H_2O (6 mL × 2), MeOH (5 mL), Et_2O (5 mL) and CH_2Cl_2 (5 mL) in succession, and dried over P_2O_5 overnight *in vacuo*. EDX analysis of the washed **7A** are shown in Figure S3 of the manuscript. Reactivation of the washed **7A** with AgOTf was conducted in the same manner as in the activation of polysiloxane-linked *m*-carbaboranylmercury chloride (**7**).

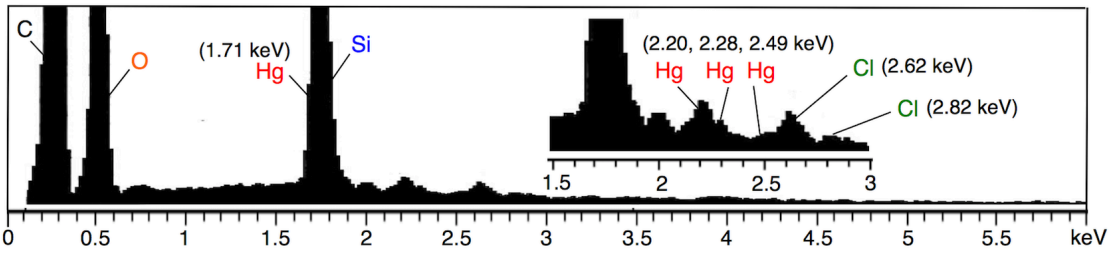
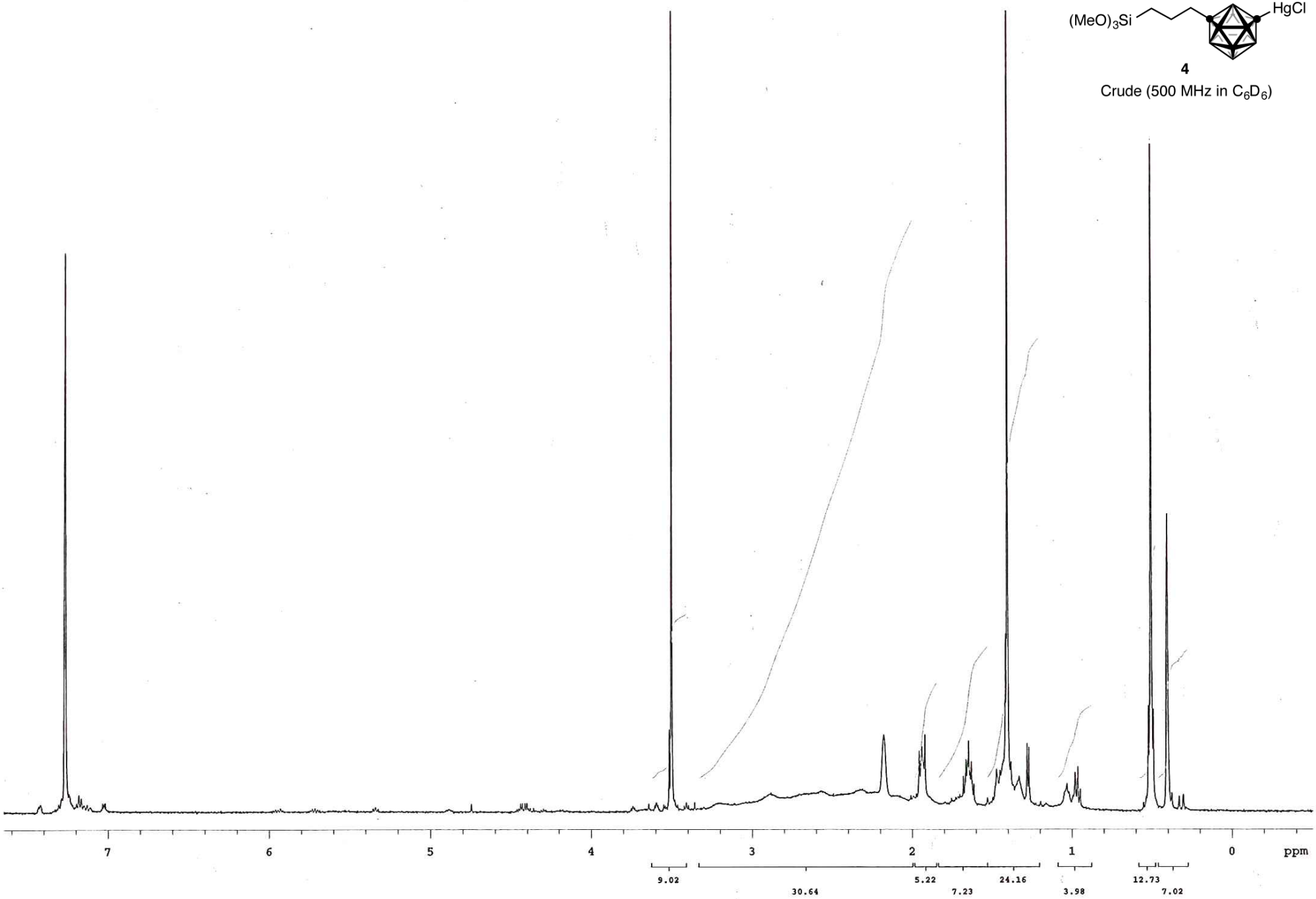


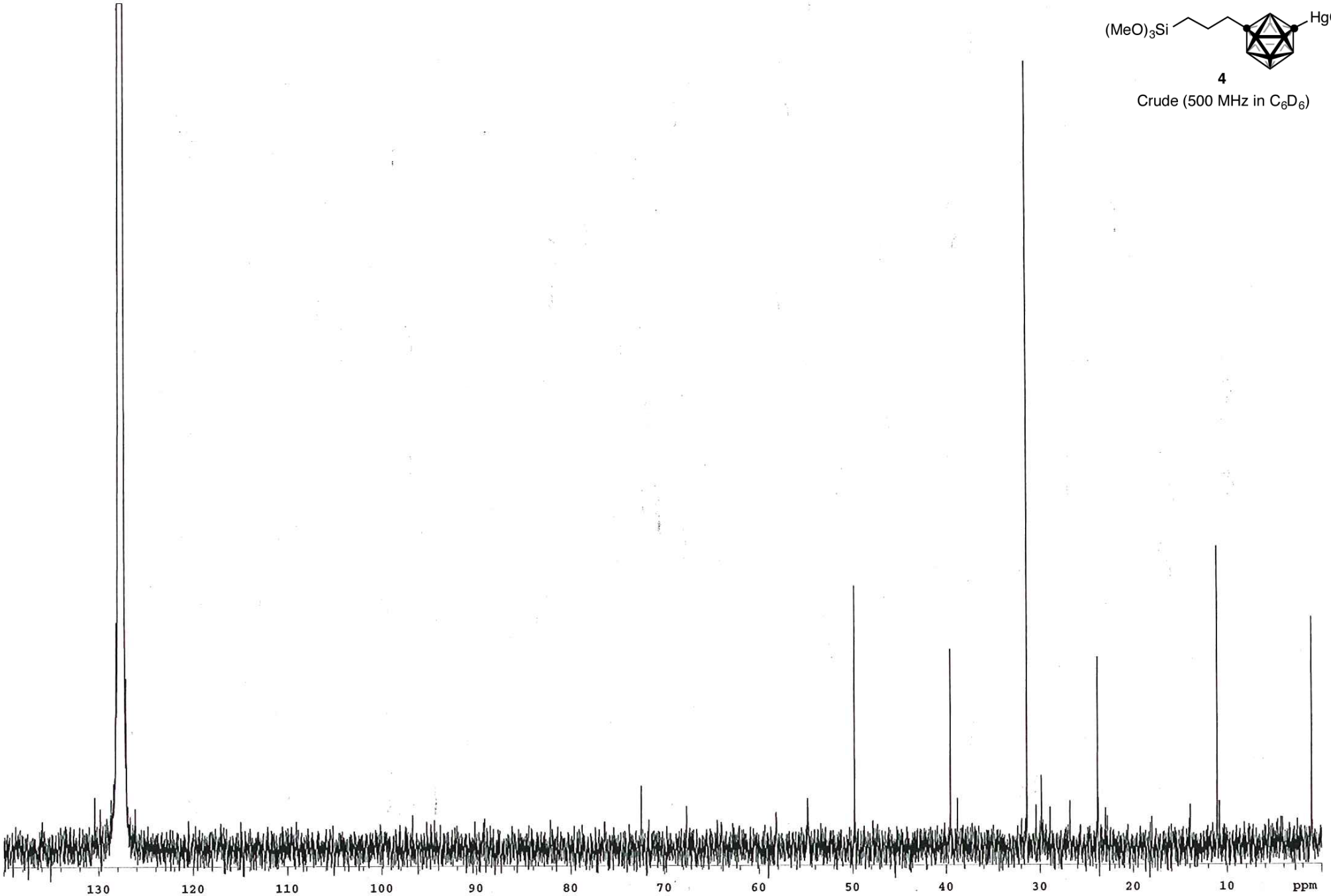
Figure S3. EDX analysis of washed **7A**.

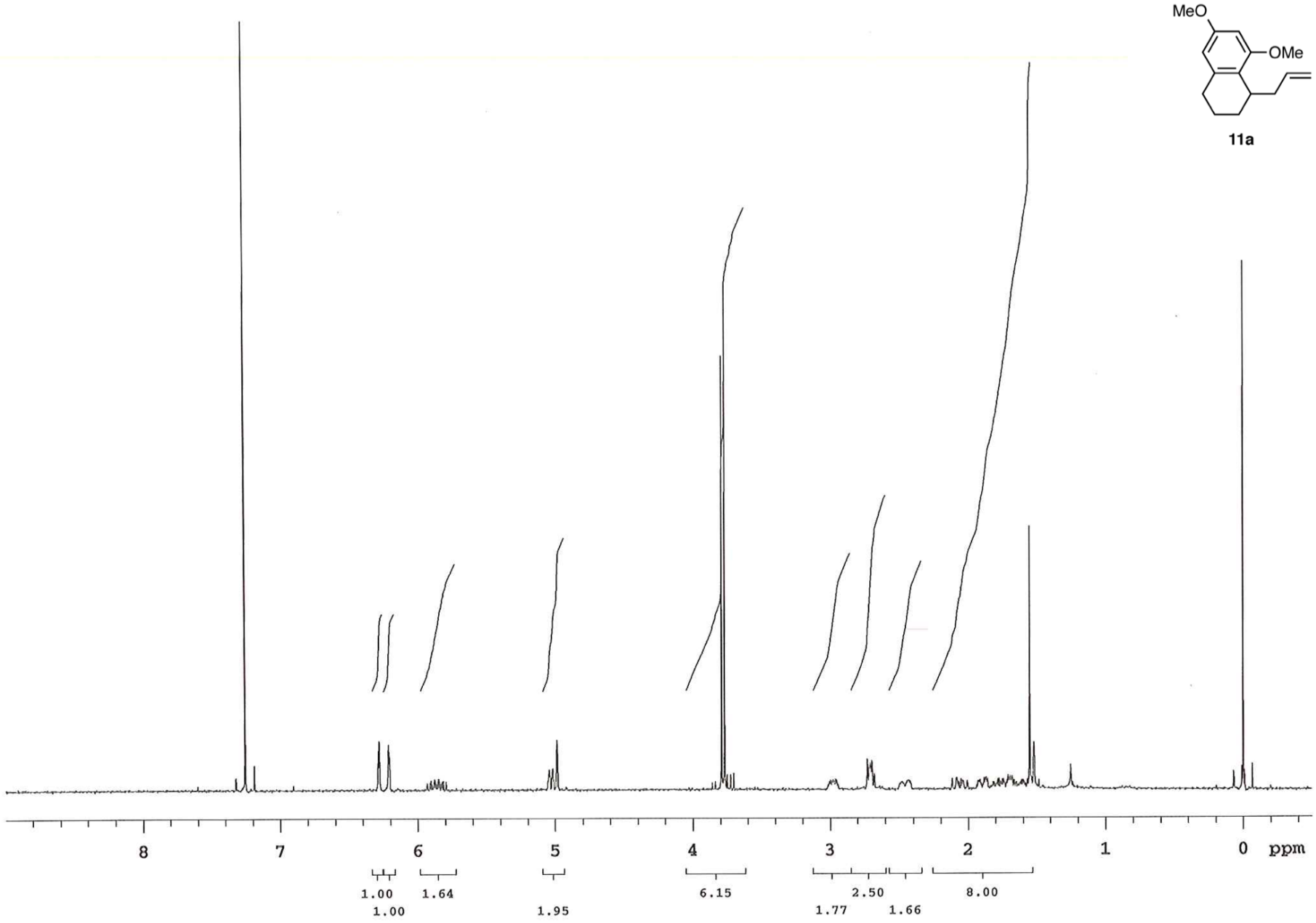
8. References

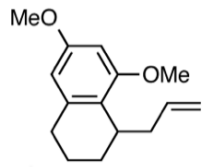
1) H. Yamamoto, I. Sasaki, S. Shiomi, N. Yamasaki, H. Imagawa, *Org. Lett.* 2012, **14**, 2266.

2) Handbook of hyphenated ICP-MS applications (2nd Edition), (Eds.: S. Sannac, Y. Chen, R. Wahlen, E. McCurdy) pp. 23-24.
3) H. Yamamoto, S. Shiomi, D. Odate, I. Sasaki, K. Namba, H. Imagawa, M. Nishizawa, *Chem. Lett.* 2010, **39**, 830.
4) T. An, Y. Wang, X. Hu, *Eur. J. Org. Chem.* 2014, **17**, 3715.
5) Y. Ikeda, J. Ukai, N. Ikeda, H. Yamamoto, *Tetrahedron* 1987, **43**, 723.
6) P. A. Grieco, P. Galatsis, R. F. Spohn, *Tetrahedron* 1986, **42**. 2847.
7) S. Hong, A. M. Kawaoka, T. J. Marks, *J. Am. Chem. Soc.* 2003, **125**, 15878.
8) J. Huang, J. R. Yang. J. Zhang, J. Yang, *J. Am. Chem. Soc.* **2012**, *134*, 8806.
9) H. Yamamoto, E. Ho, K. Namba, H. Imagawa, M. Nishizawa, *Chem. Eur. J.* 2010, **16**, 11271.
10) K. Miyata, H. Kutsuna, S. Kawakami, M. Kitamura, *Angew. Chem. Int. Ed.* 2011, **50**, 4649.
11) A. Guerinot, A. Serra-Muns, C. Gnamm, C. Bensoussan, S. Reymond, J. Cossy, *Org. Lett.* 2010, **12**, 1808.
12) K. Namba, Y. Nakagawa, H. Yamamoto, H. Imagawa, M. Nishizawa, *Synlett* 2008, **11**, 1719.
13) K. Namba, H. Yamamoto, I. Sasaki, K. Mori, H. Imagawa, M. Nishizawa, *Org. Lett.* 2008, **10**, 1767.
14) T. Kurisaki, T. Naniwa, H. Yamamoto, H. Imagawa, M. Nishizawa, *Tetrahedron Lett.* 2007, **48**, 1871.
15) H. Yamamoto, E. Ho, I. Sasaki, M. Mitsutake, Y. Takagi, H. Imagawa, M. Nishizawa, *Eur. J. Org. Chem.* 2011, **13**, 2417.
16) P. Trillo, A. Baeza, A. Nájera, *J. Org. Chem.*, 2012, **77**, 7344.

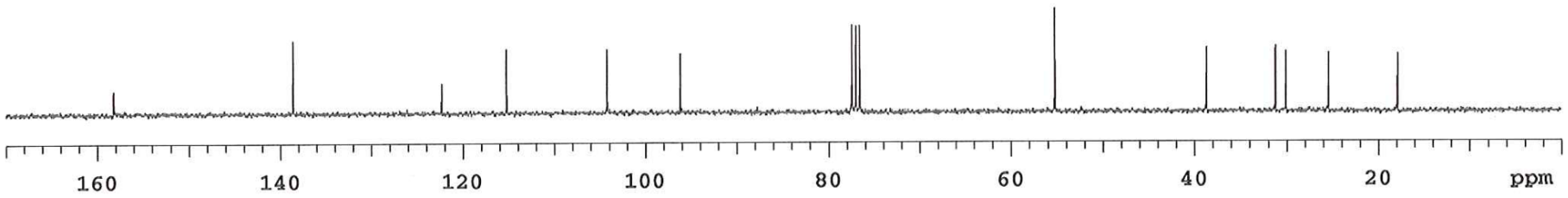

(MeO)3Si
HgCl
4
Crude (500 MHz in C6D6)
7
6
5
4
3
2
1
0
ppm
9.02
30.64
5.22
7.23
24.16
3.98
12.73
7.02

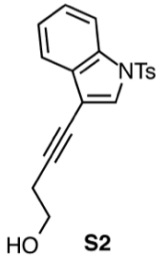

(MeO)3Si
HgCl
4
Crude (500 MHz in C6D6)
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


MeO
OMe
11a
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.64
1.95
6.15
1.77
2.50
1.66
8.00

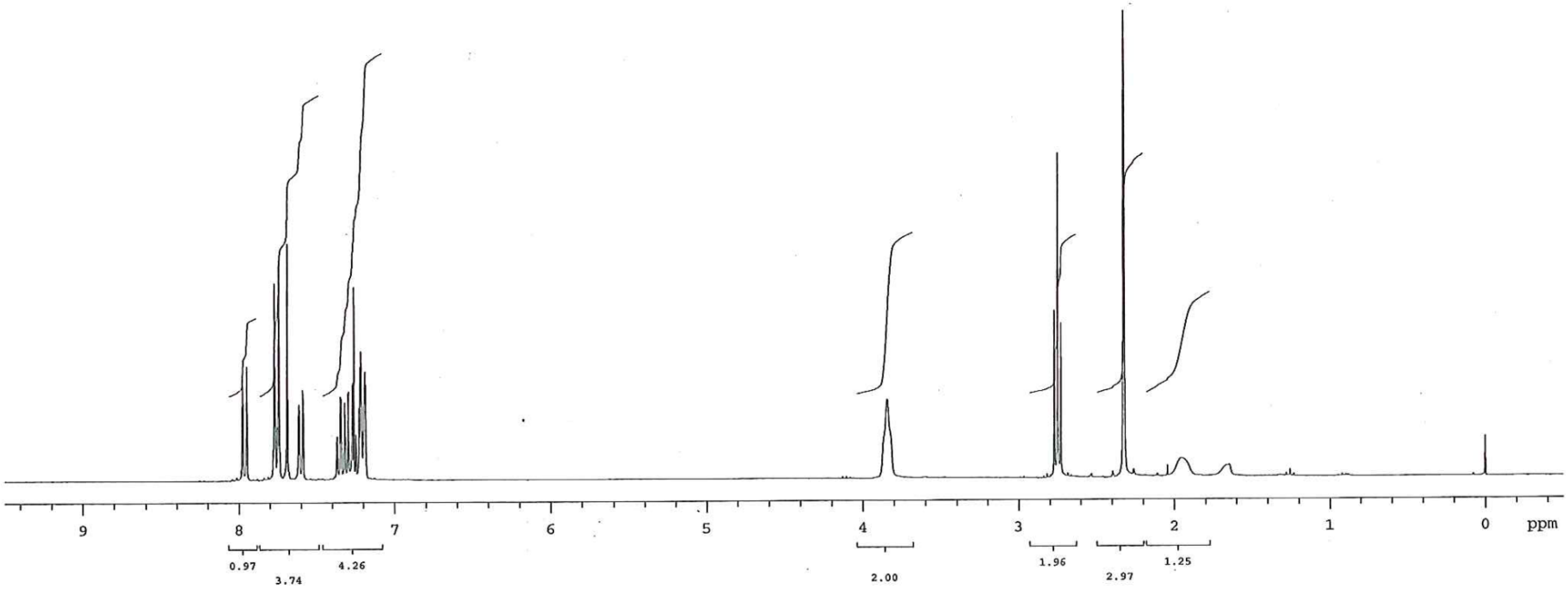


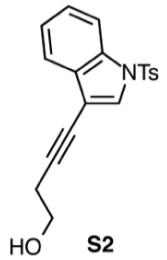
11a



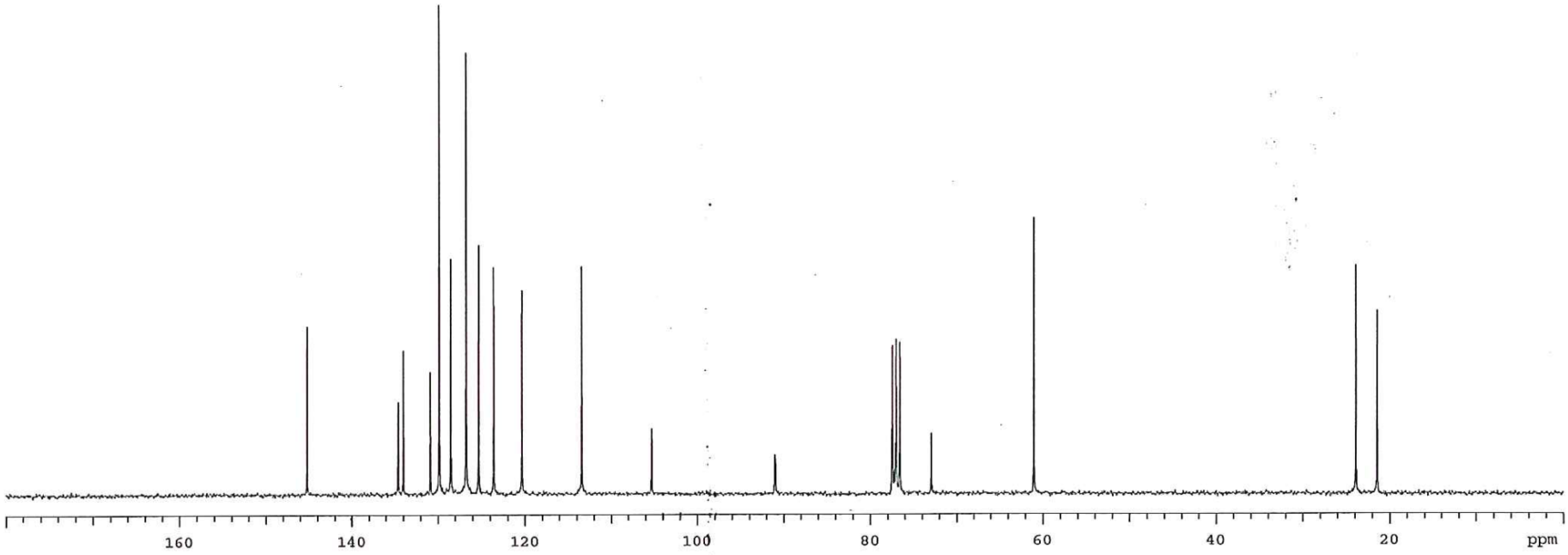


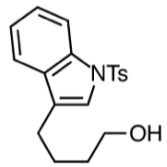
S2



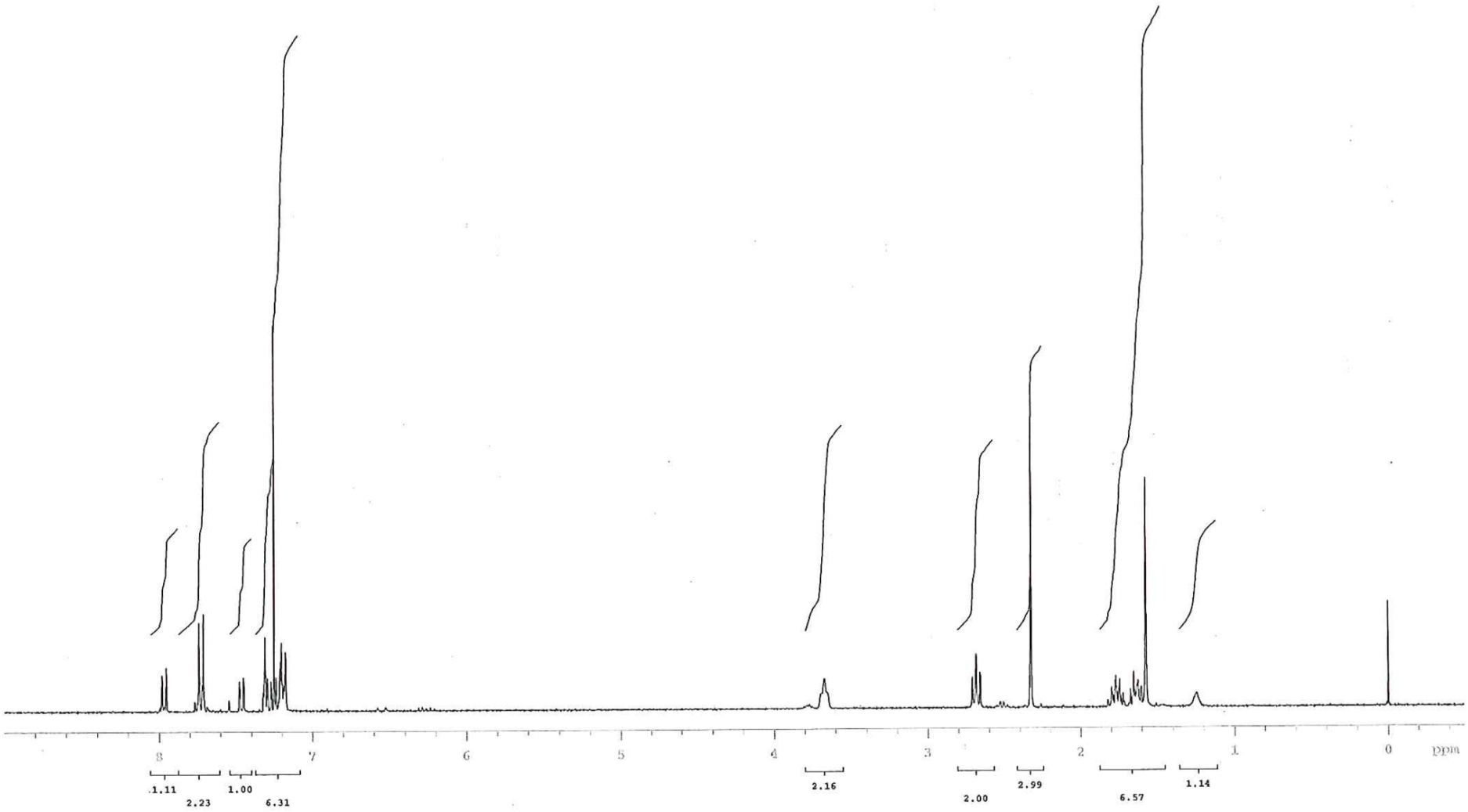


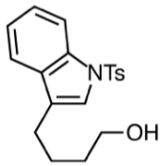
S2



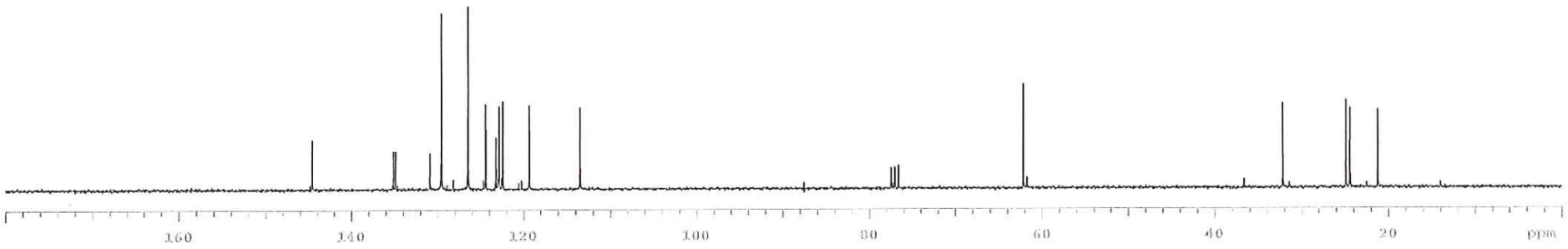


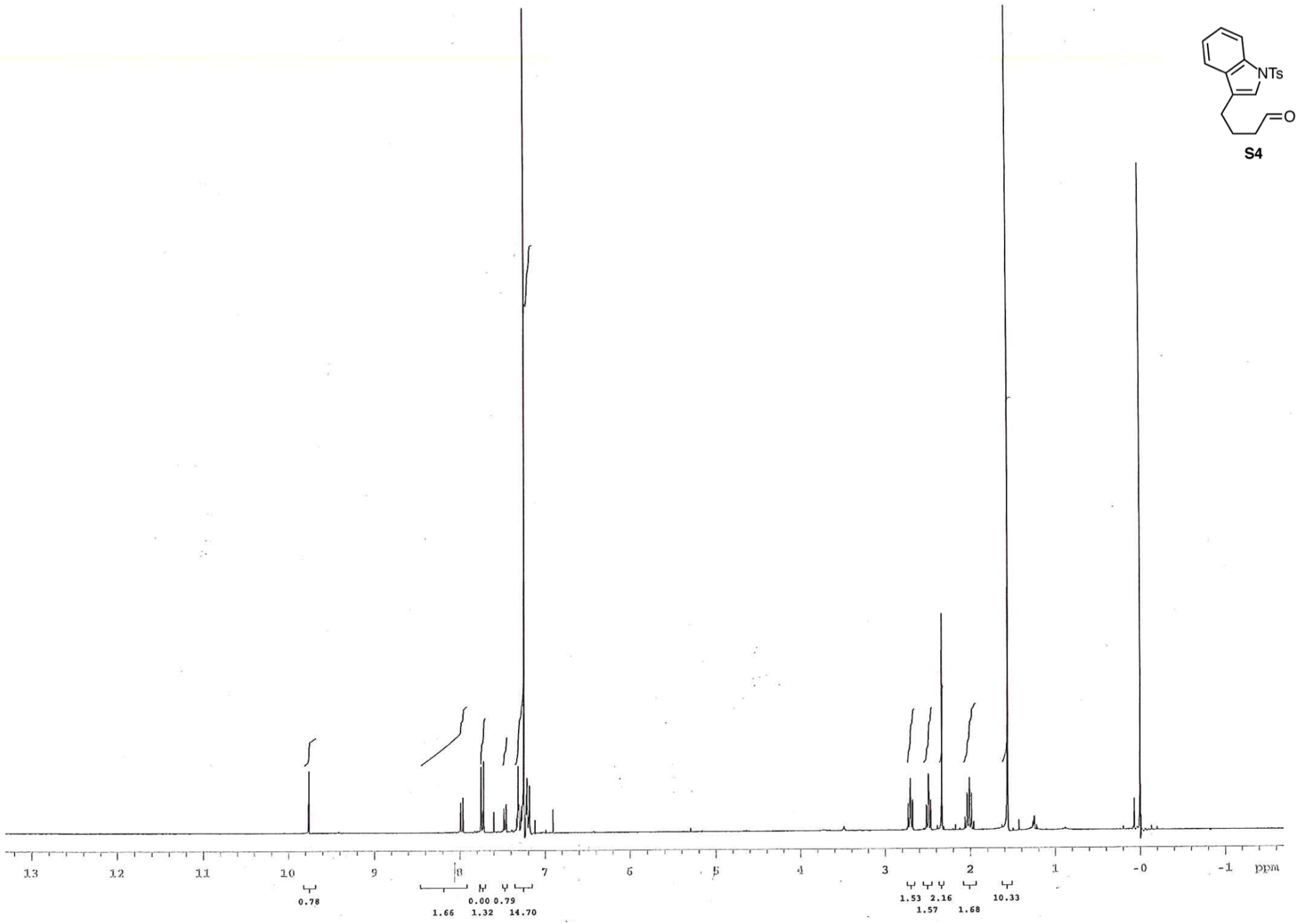
S3

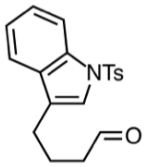




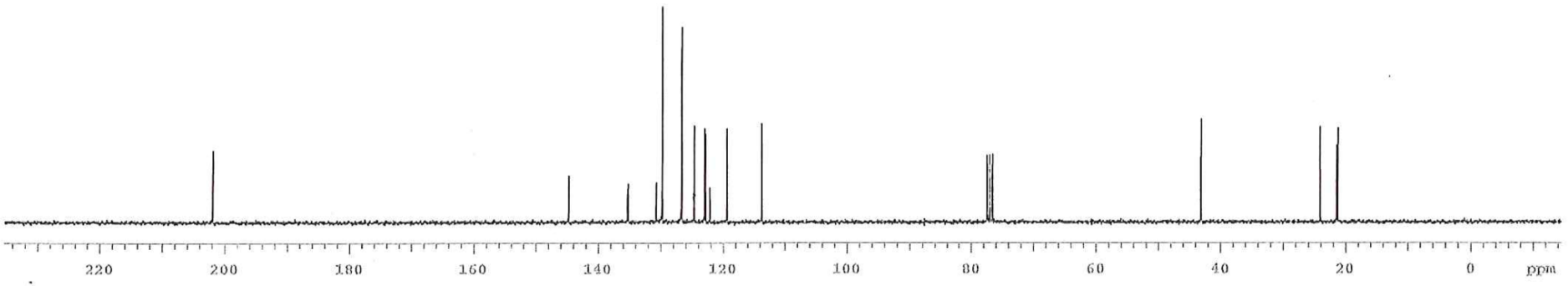
S3

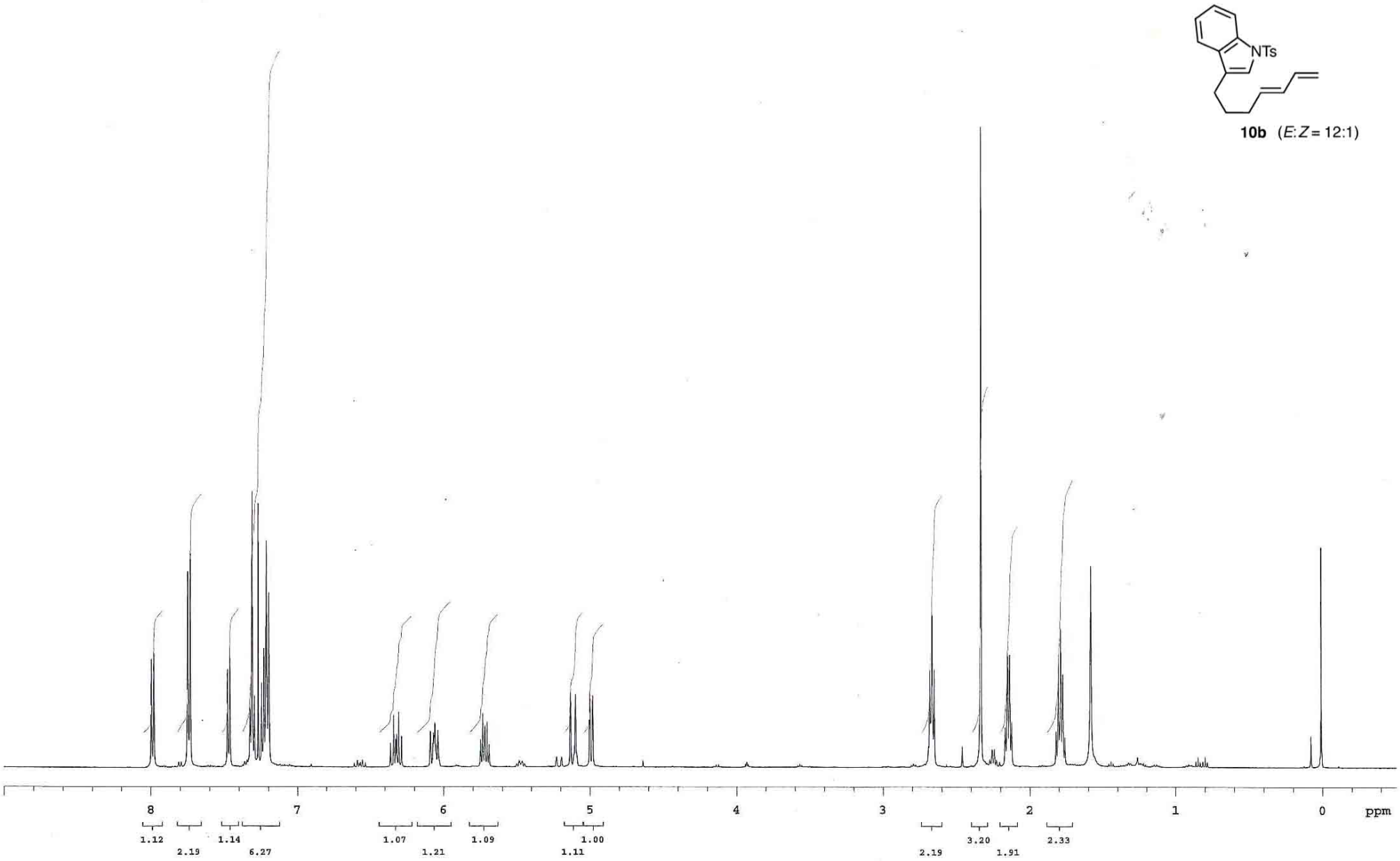



NTs
O
S4
13
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
0.78
1.66
0.00
1.32
0.79
14.70
1.53
1.57
2.16
1.68
10.33

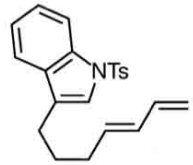


S4

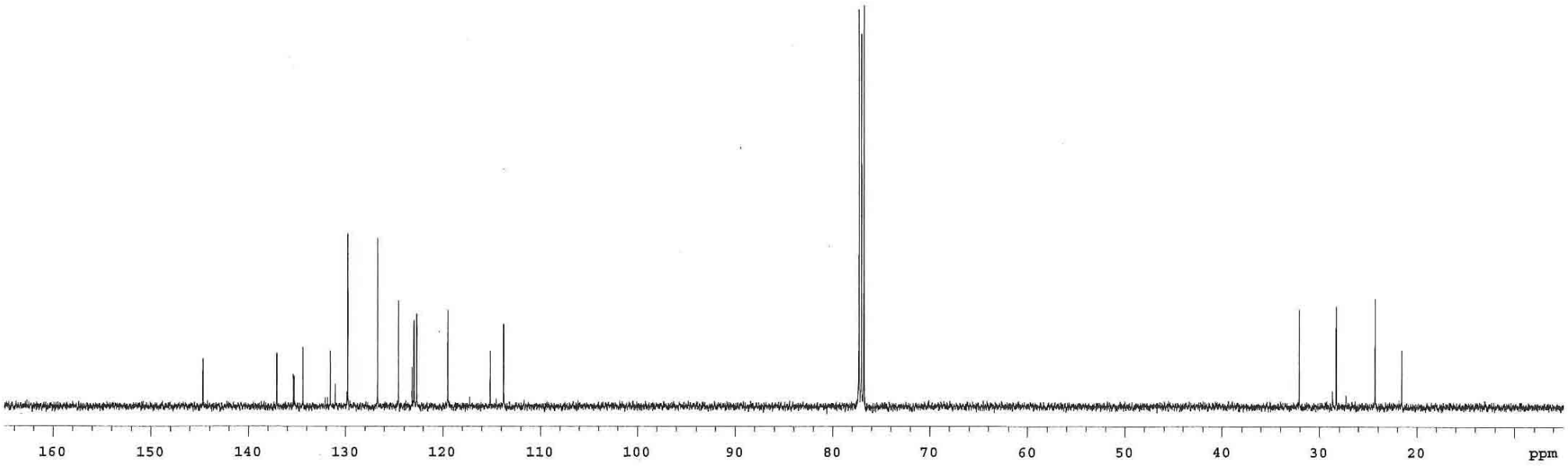


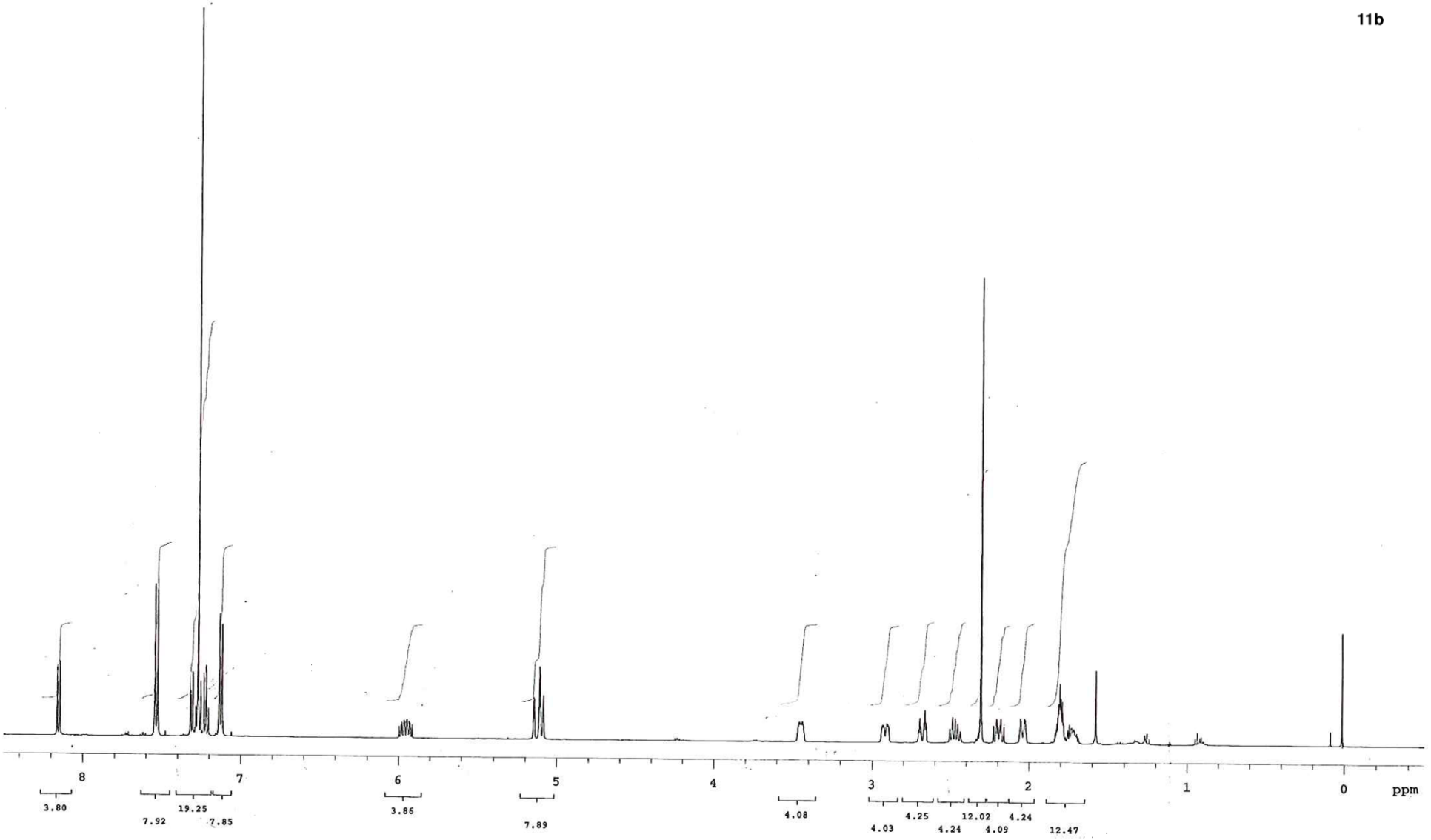

NTs
8
7
6
5
4
3
2
1
0
ppm
1.12
2.19
1.14
6.27
1.07
1.21
1.09
1.11
1.00
2.19
3.20
1.91
2.33

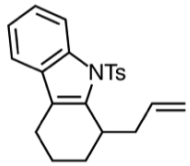
10b (*E*:*Z* = 12:1)



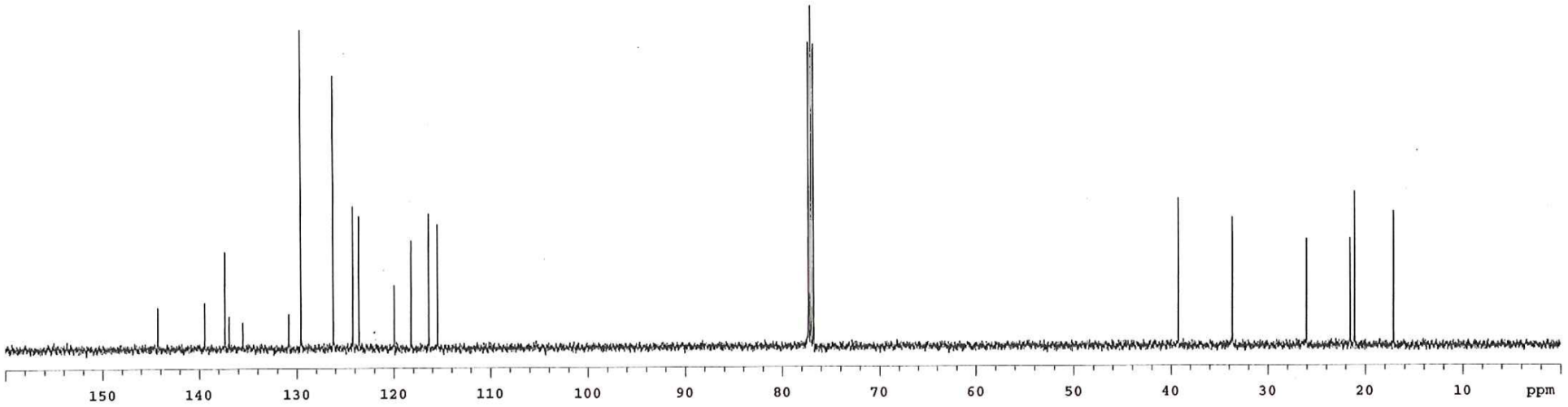
10b (*E*:*Z* = 12:1)

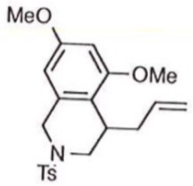



NTs
11b
8
7
6
5
4
3
2
1
0
ppm
3.80
7.92
19.25
7.85
3.86
7.89
4.08
4.03
4.25
4.24
12.02
4.09
4.24
12.47

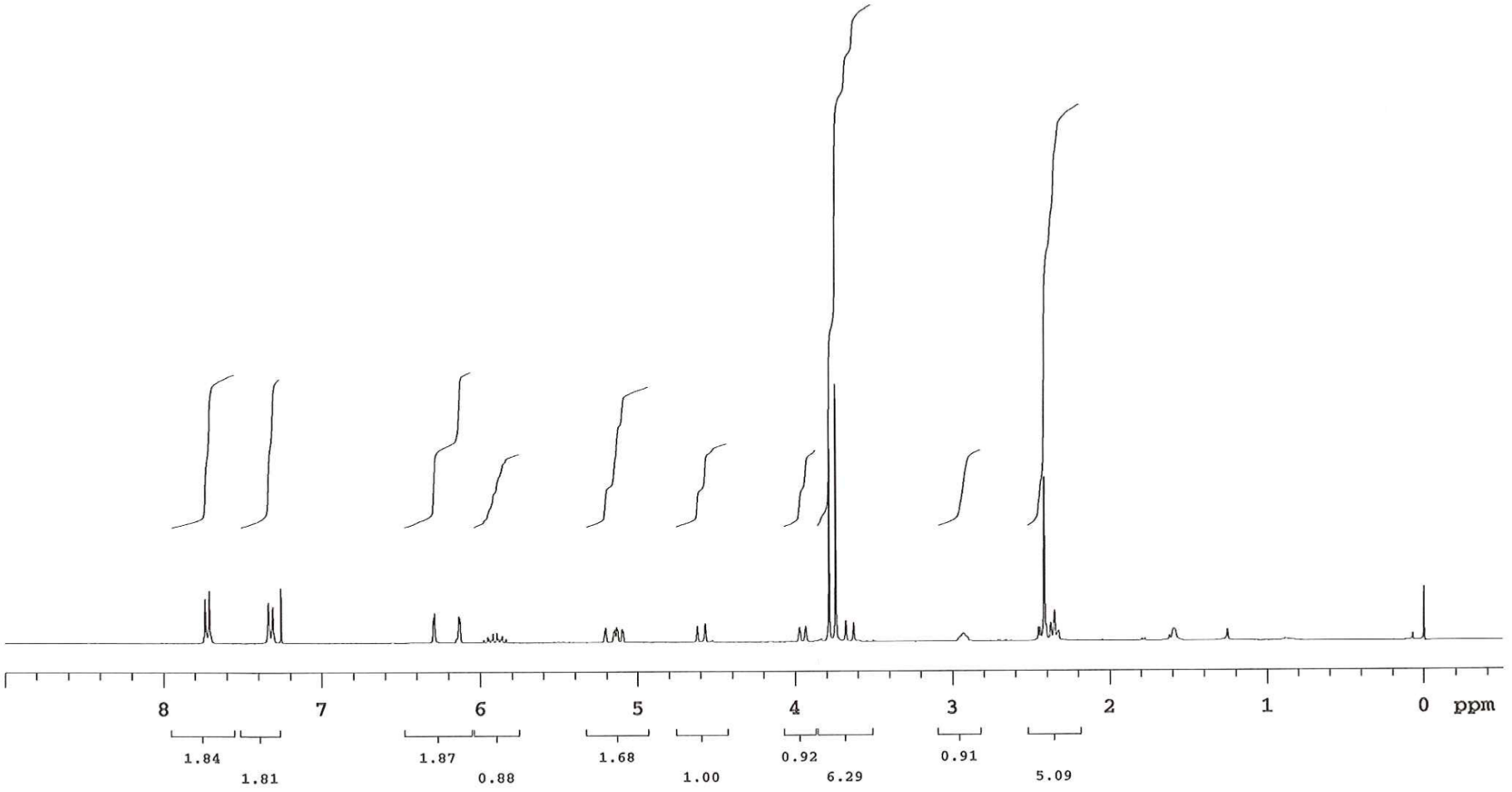


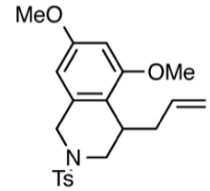
11b



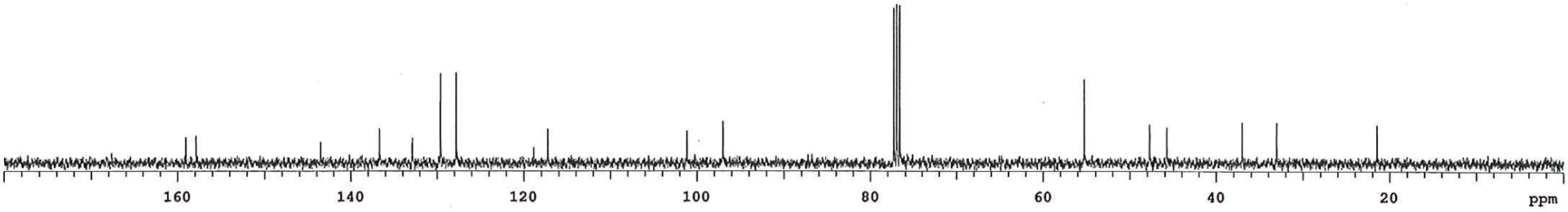

MeO
OMe
N
Ts

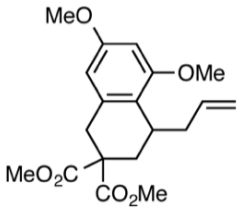
11c


8
7
6
5
4
3
2
1
0
ppm
1.84
1.81
1.87
0.88
1.68
1.00
0.92
6.29
0.91
5.09

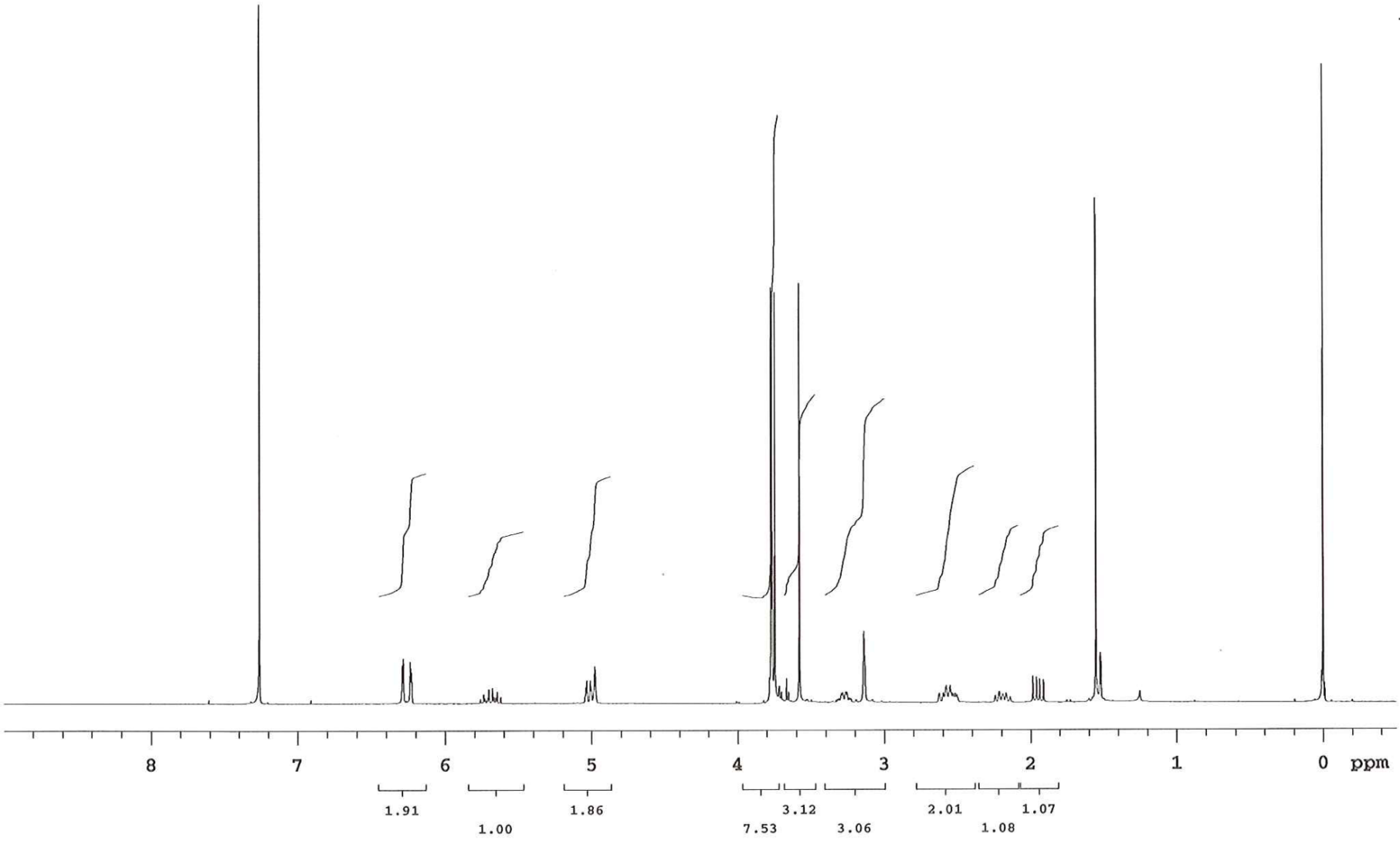


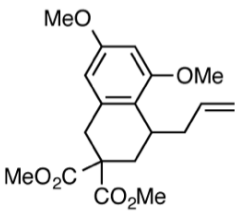
11c



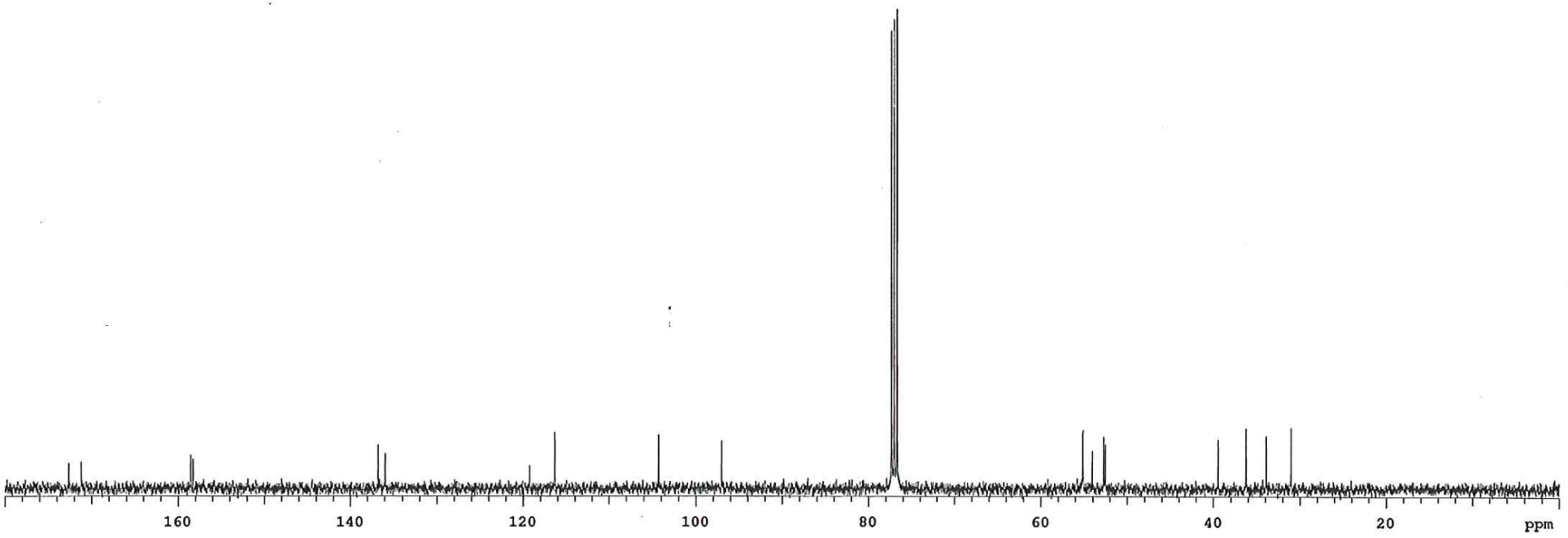

MeO
OMe
MeO2C
CO2Me

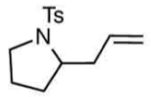
11d


8
7
6
5
4
3
2
1
0
ppm
1.91
1.00
1.86
7.53
3.12
3.06
2.01
1.08
1.07

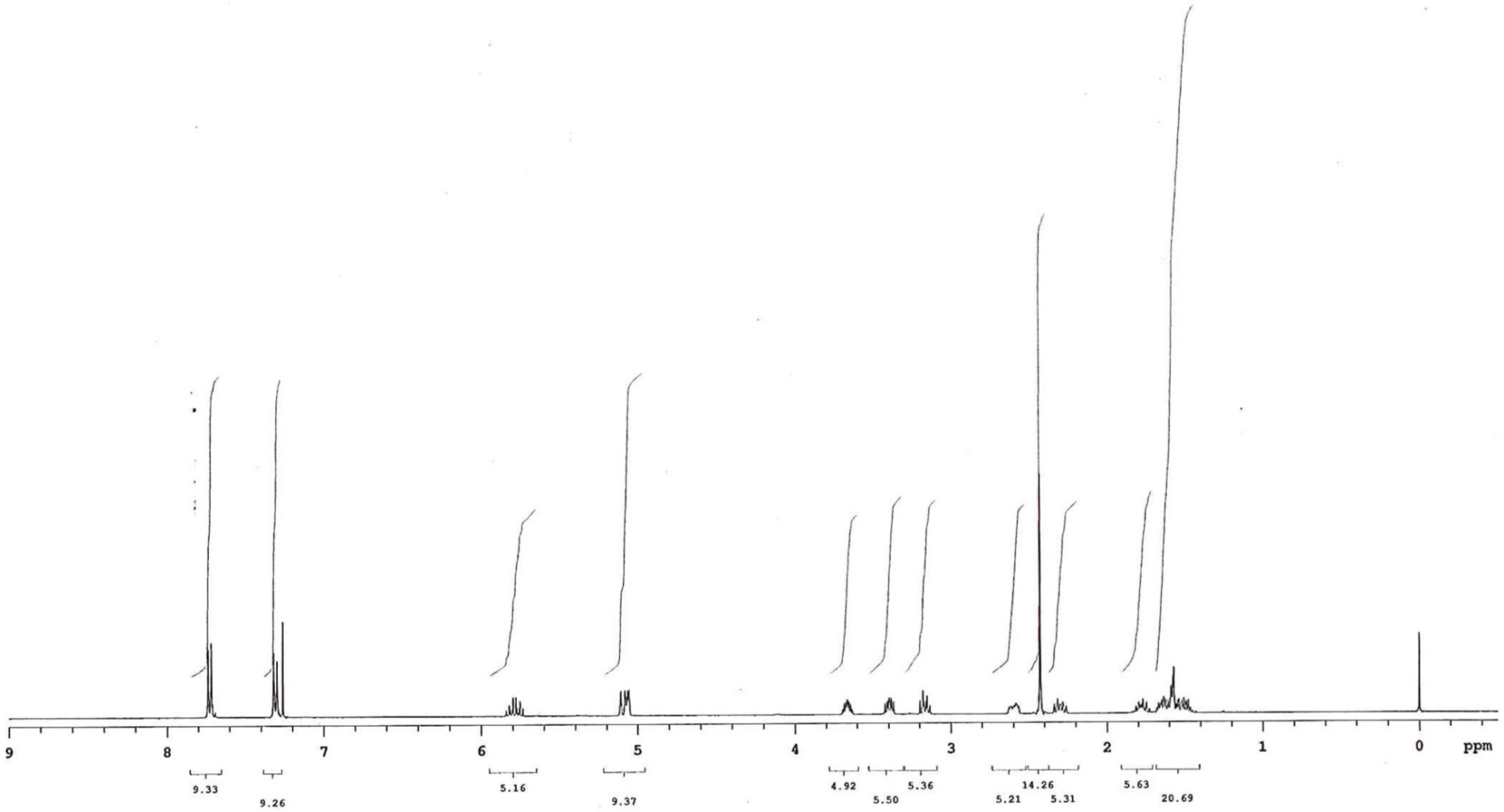


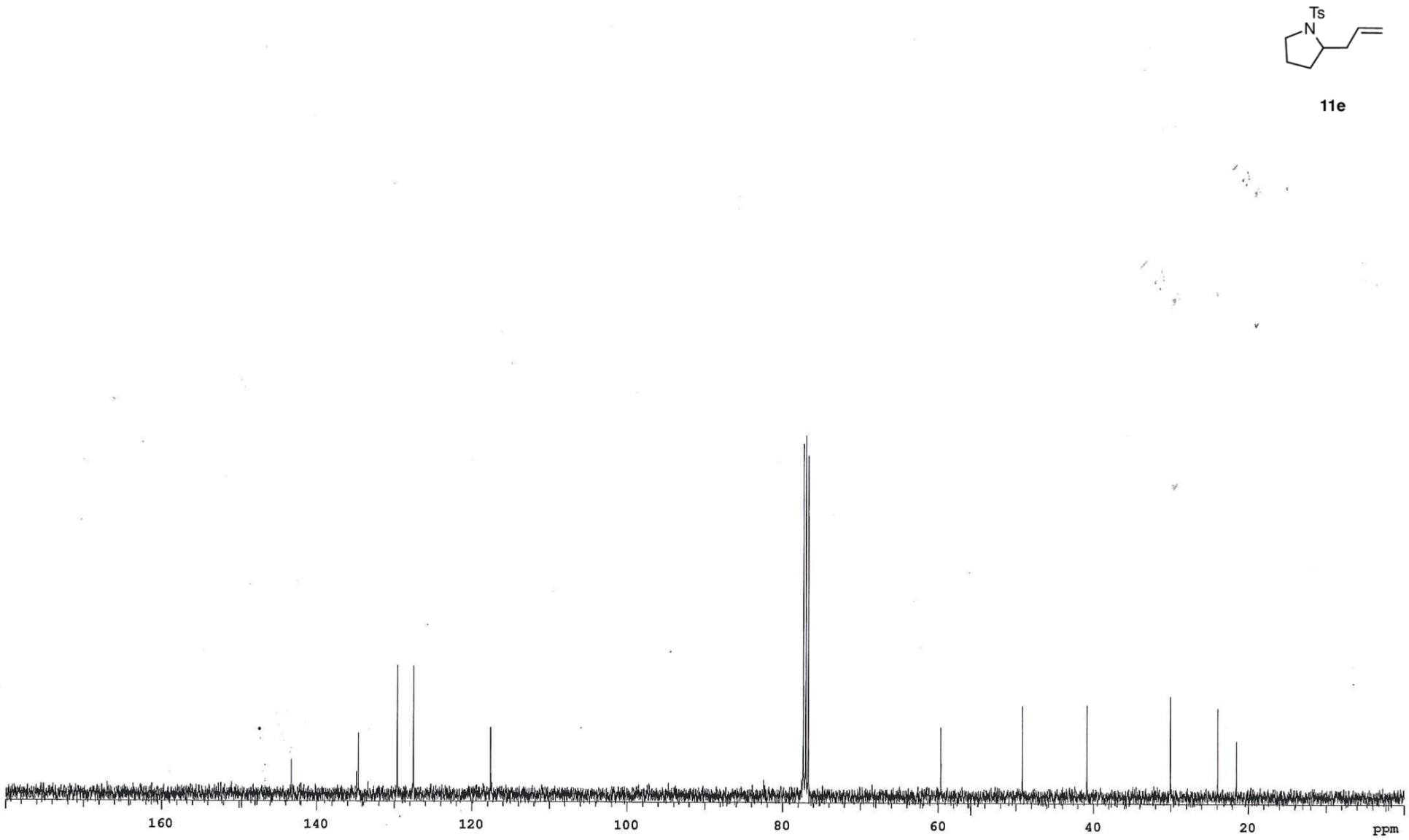
11d

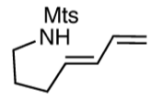



Ts
N

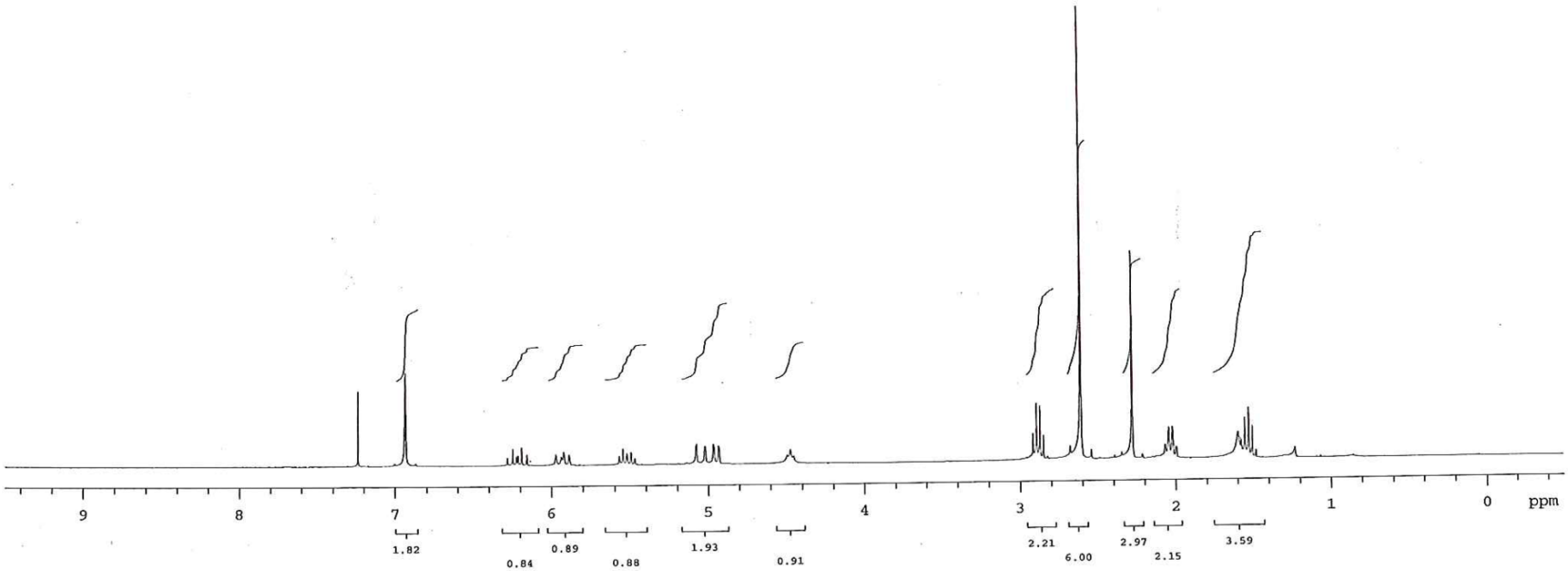
11e

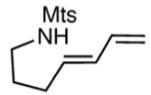

9
8
7
6
5
4
3
2
1
0
ppm
9.33
9.26
5.16
9.37
4.92
5.50
5.36
5.21
14.26
5.31
5.63
20.69


Ts
N
11e
160
140
120
100
80
60
40
20
ppm

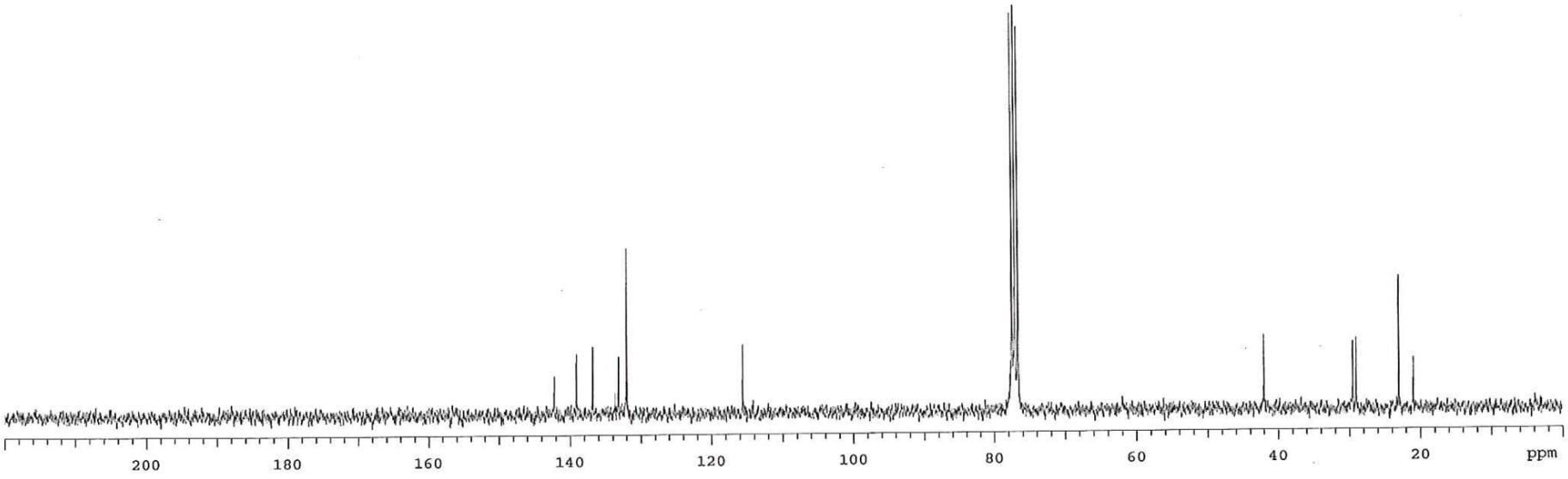

Mts
NH

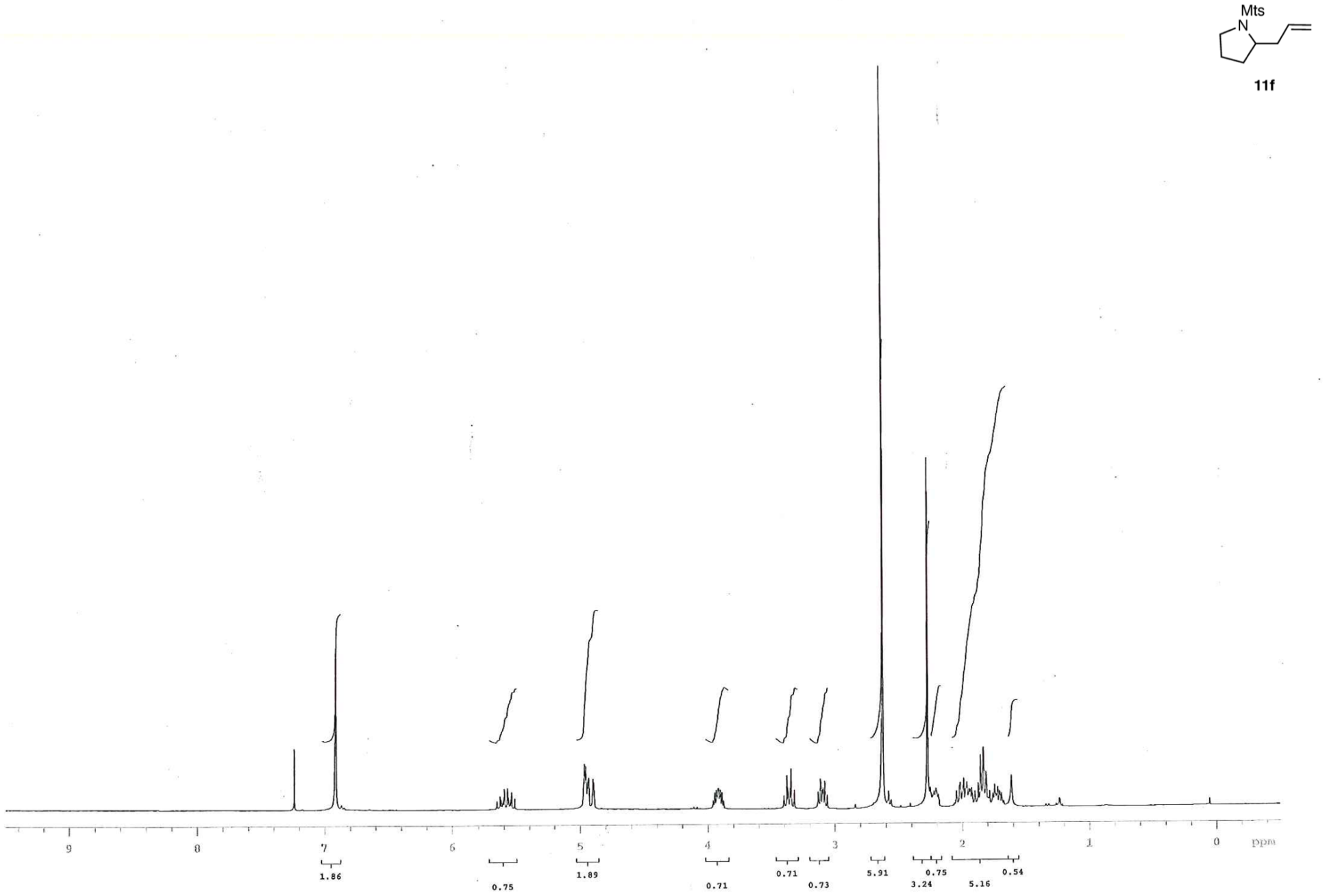
10f

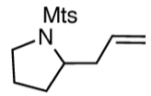

9
8
7
6
5
4
3
2
1
0
ppm
1.82
0.84
0.89
0.88
1.93
0.91
2.21
6.00
2.97
2.15
3.59



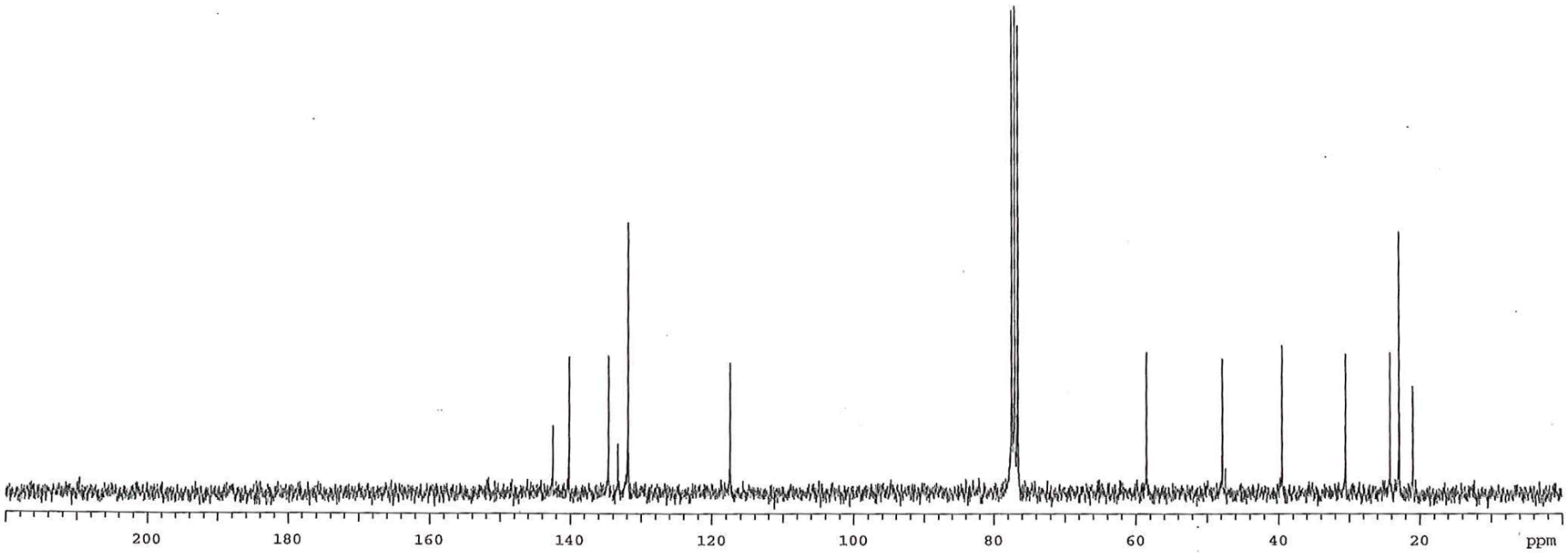
10f

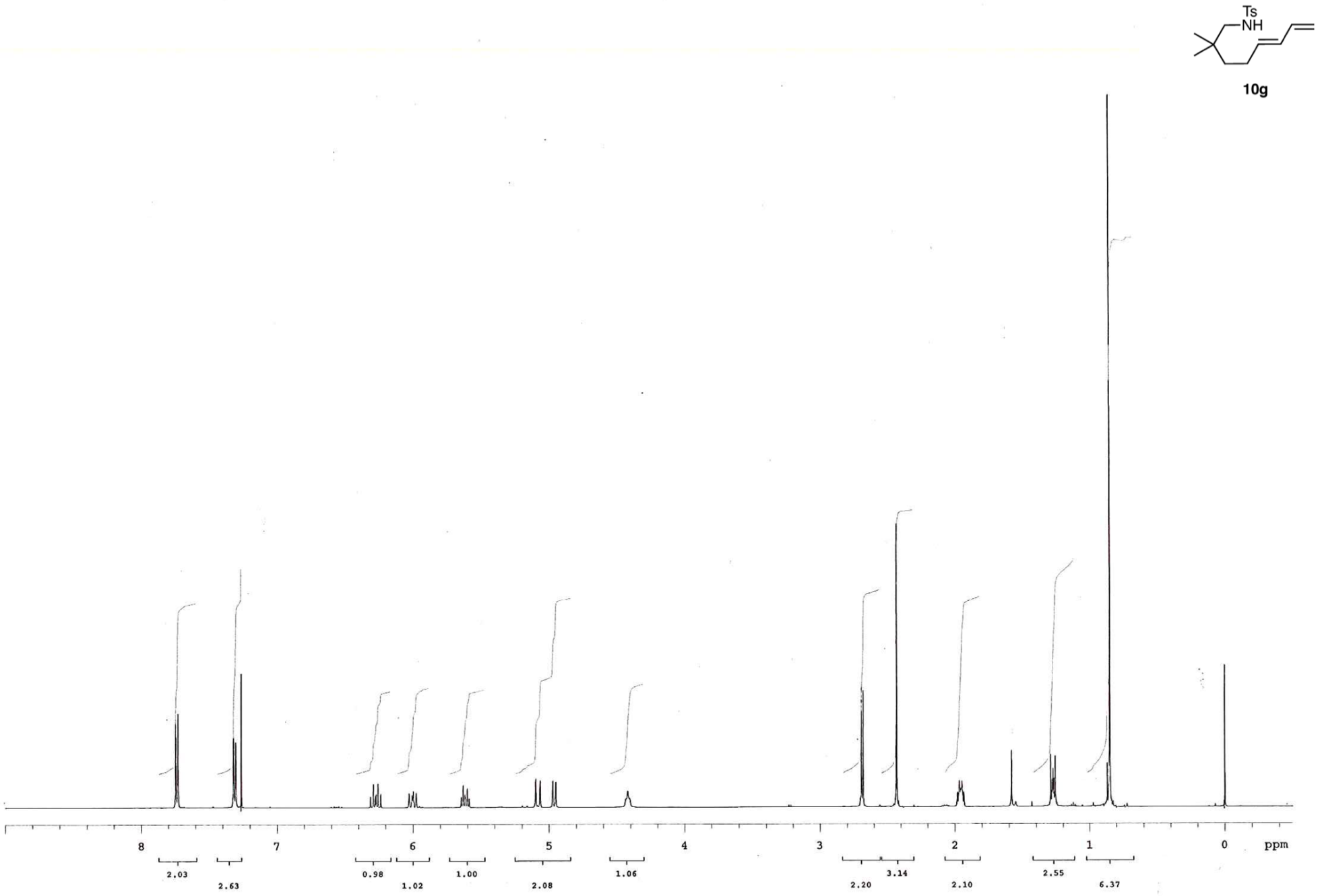


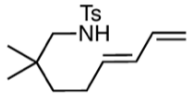

Mts
N
11f
9
8
7
6
5
4
3
2
1
0
ppm
1.86
0.75
1.89
0.71
0.71
0.73
5.91
3.24
0.75
5.16
0.54



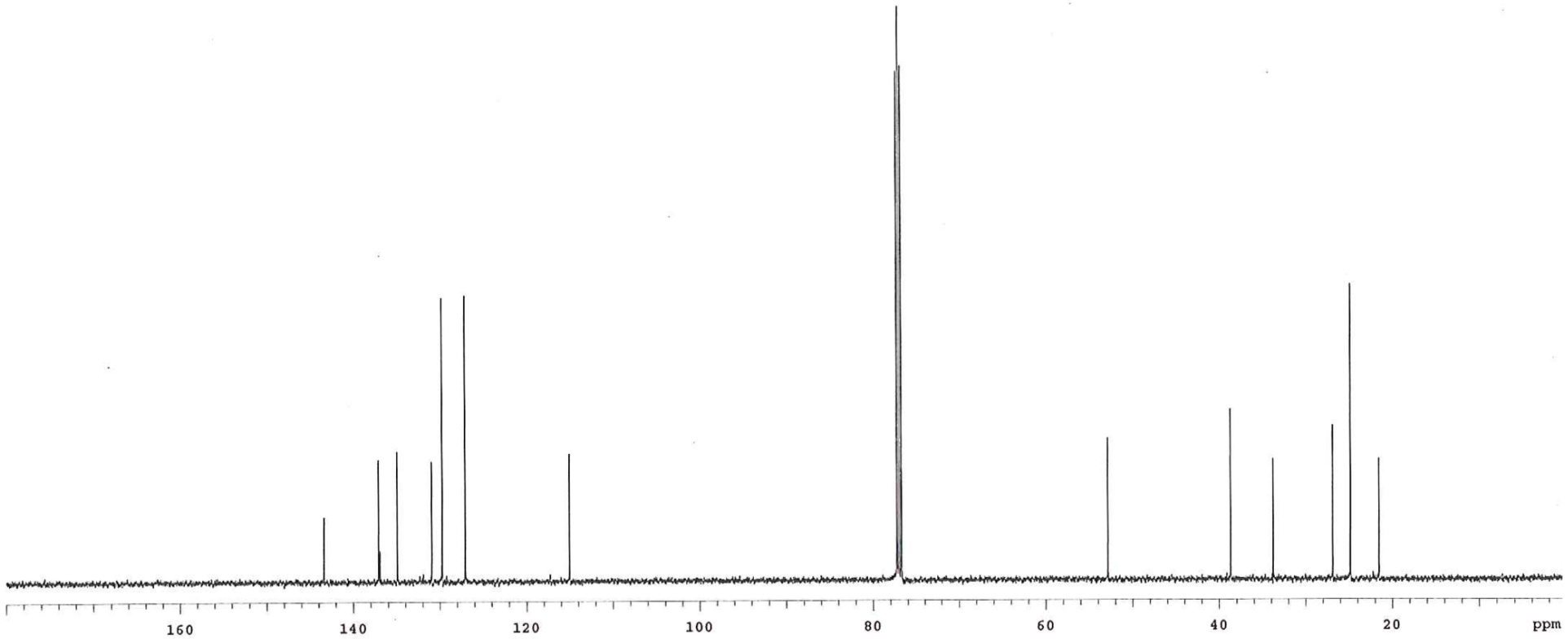
11f

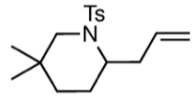



Ts
NH
10g
8
7
6
5
4
3
2
1
0
ppm
2.03
2.63
0.98
1.02
1.00
2.08
1.06
2.20
3.14
2.10
2.55
6.37

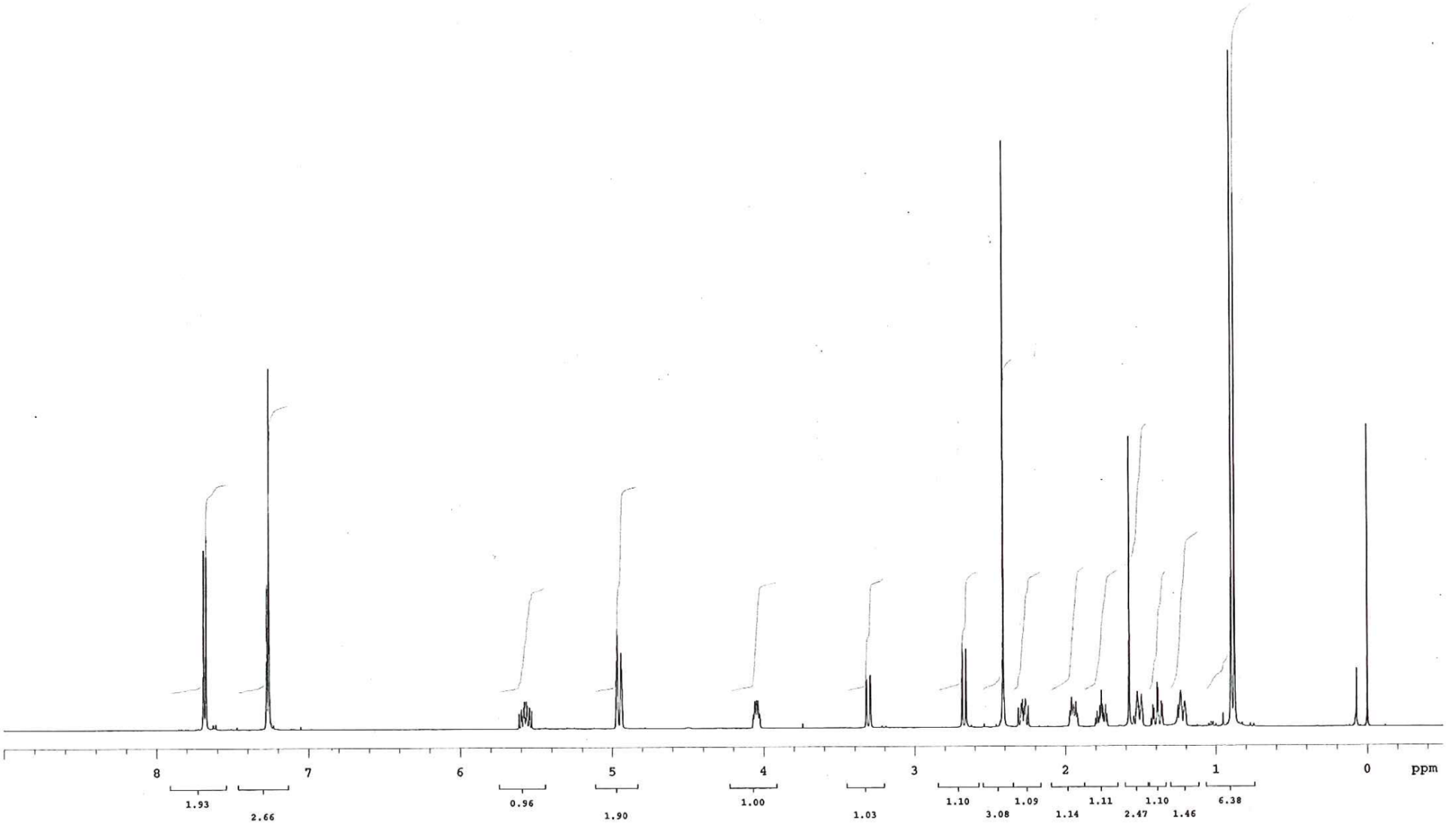


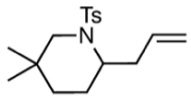
10g



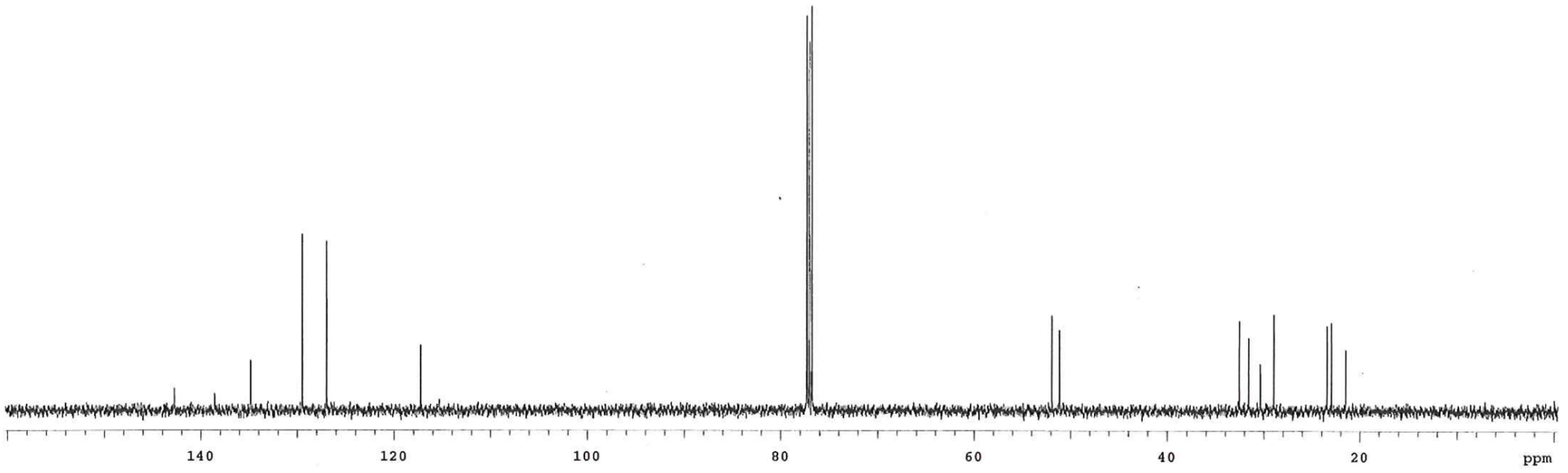

Ts
N

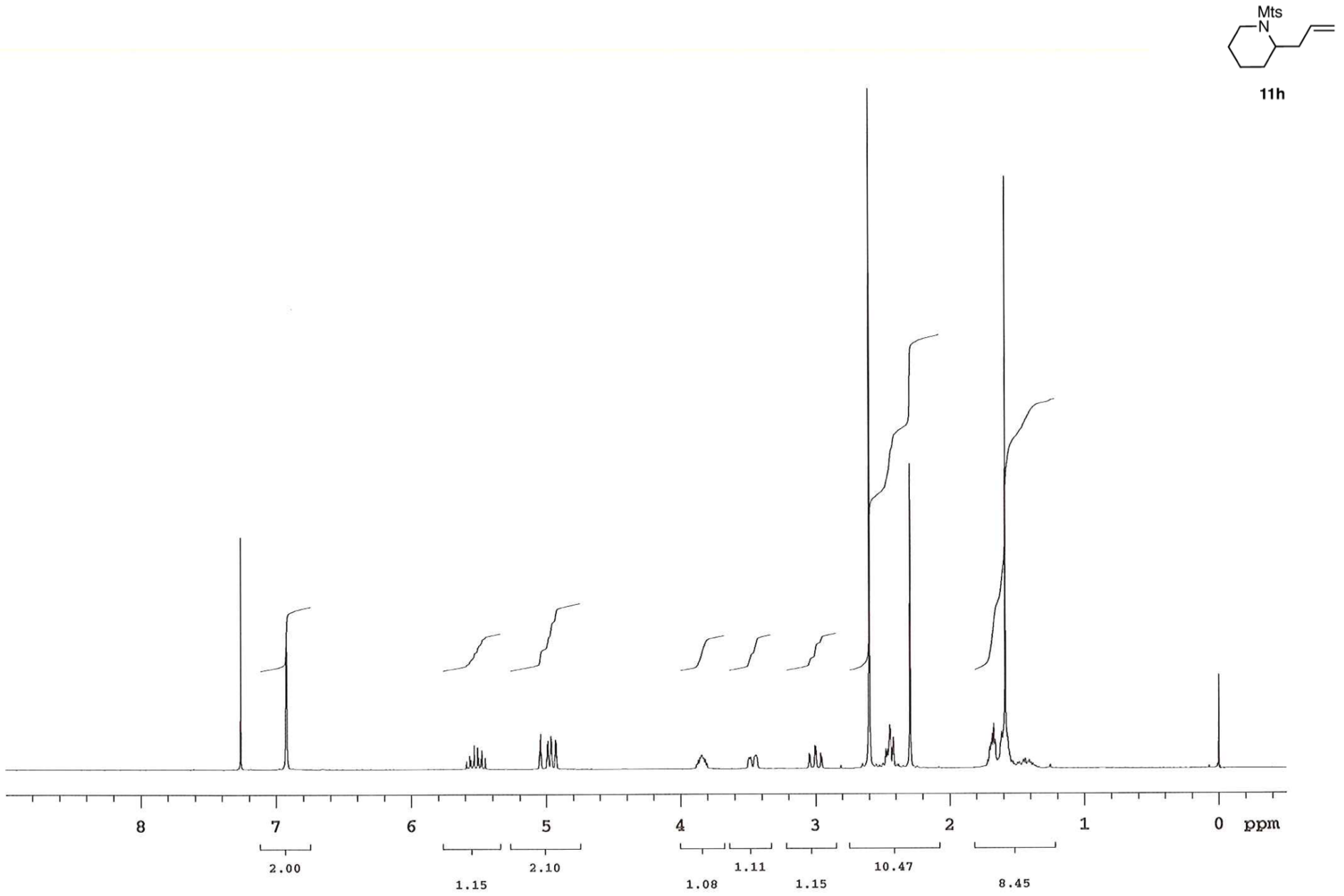
11g

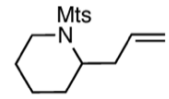

8
7
6
5
4
3
2
1
0
ppm
1.93
2.66
0.96
1.90
1.00
1.03
1.10
3.08
1.09
1.14
1.11
2.47
1.10
1.46
6.38



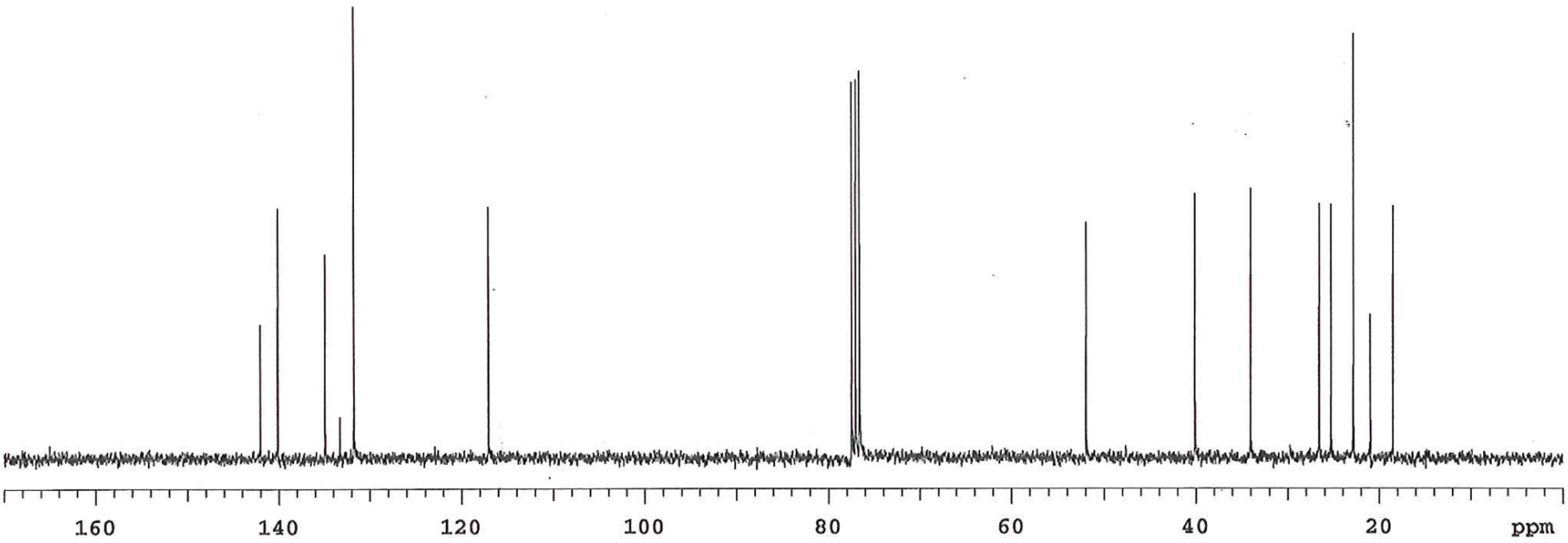
11g

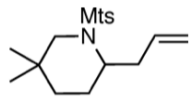



Mts
N
11h
8
7
6
5
4
3
2
1
0
ppm
2.00
1.15
2.10
1.08
1.11
1.15
10.47
8.45

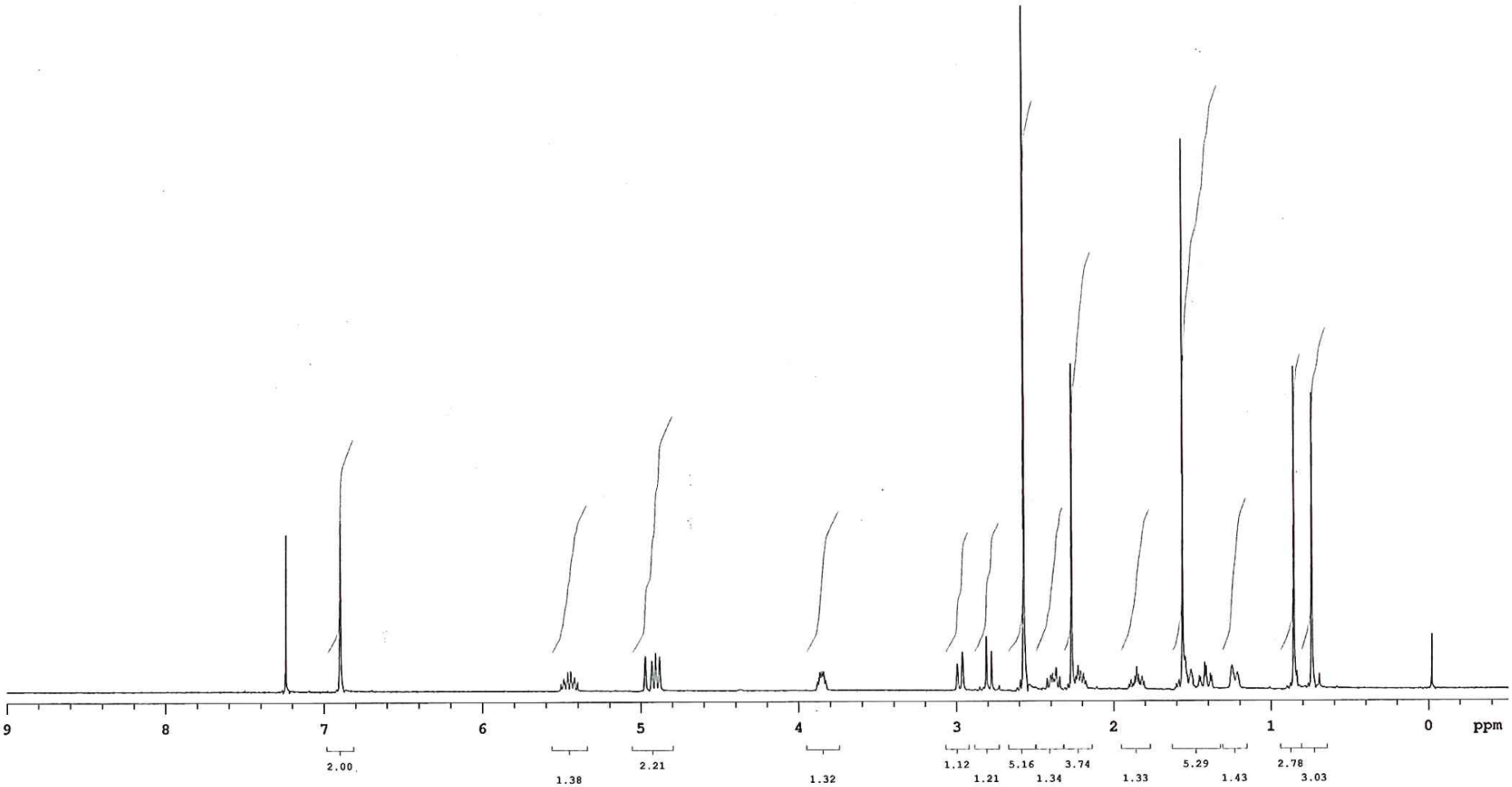


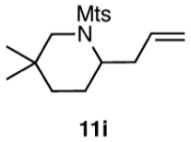
11h



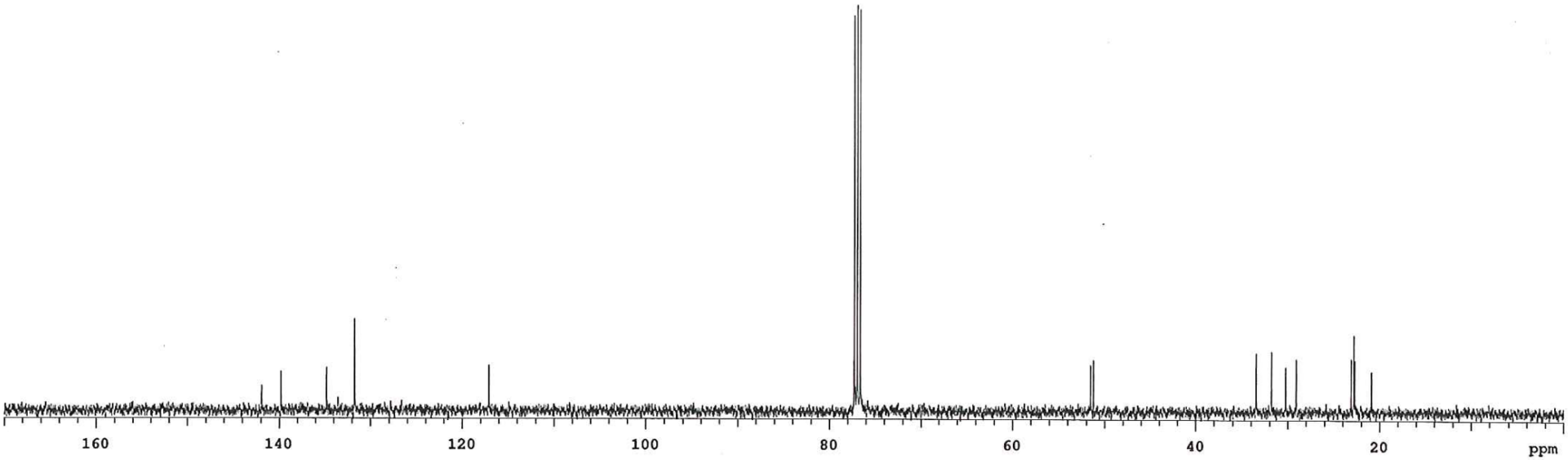

Mts
N

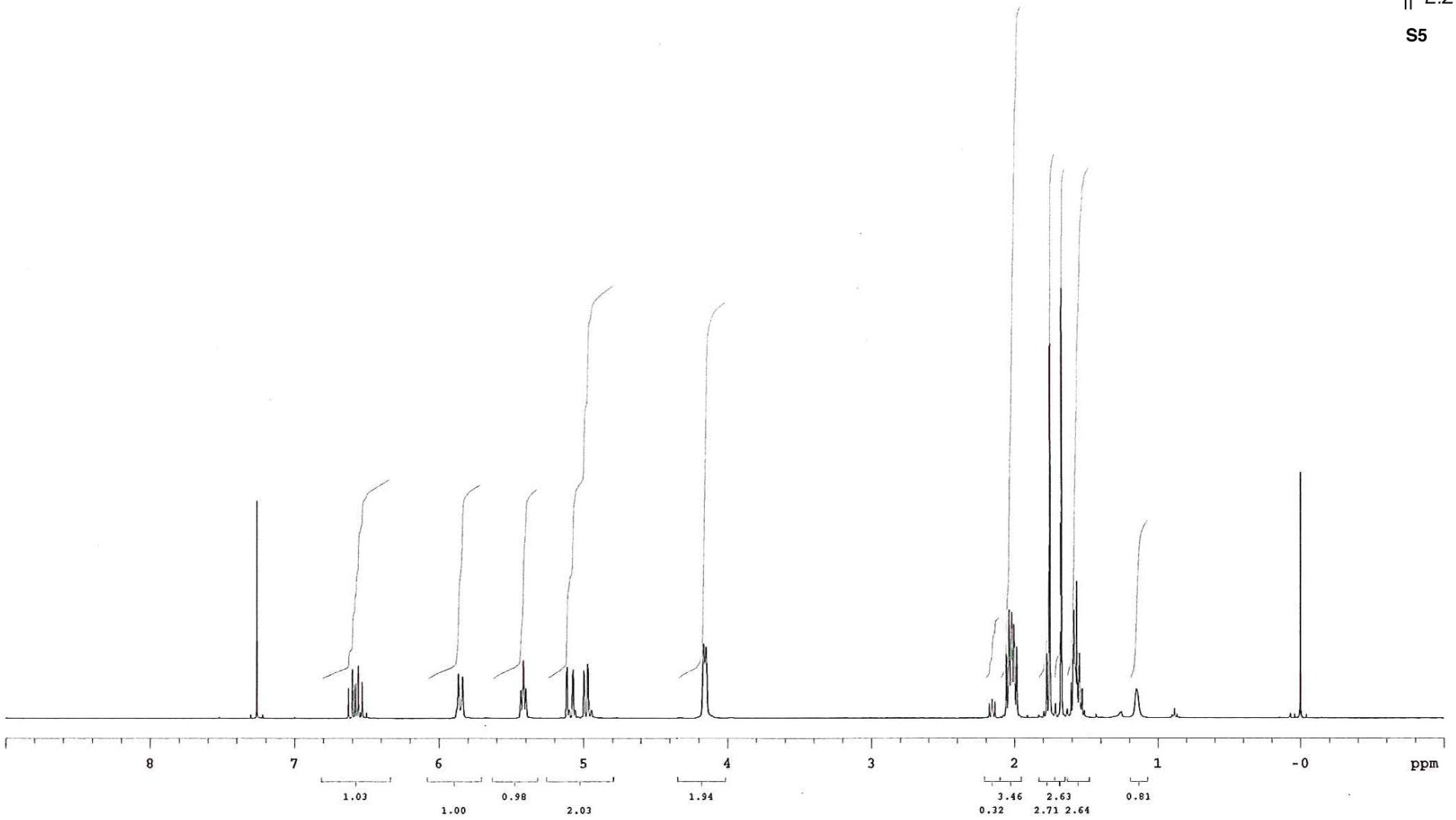
11i

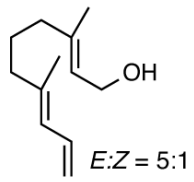

9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.38
2.21
1.32
1.12
1.21
5.16
1.34
3.74
1.33
5.29
1.43
2.78
3.03



11i

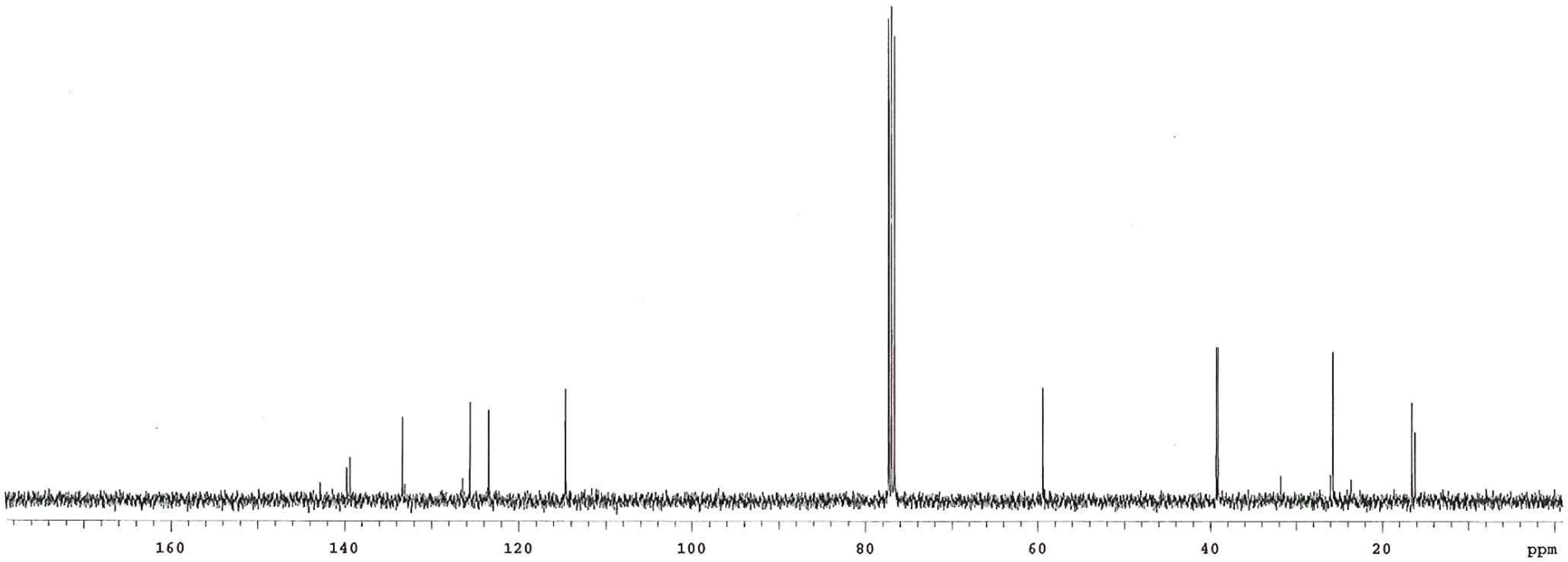


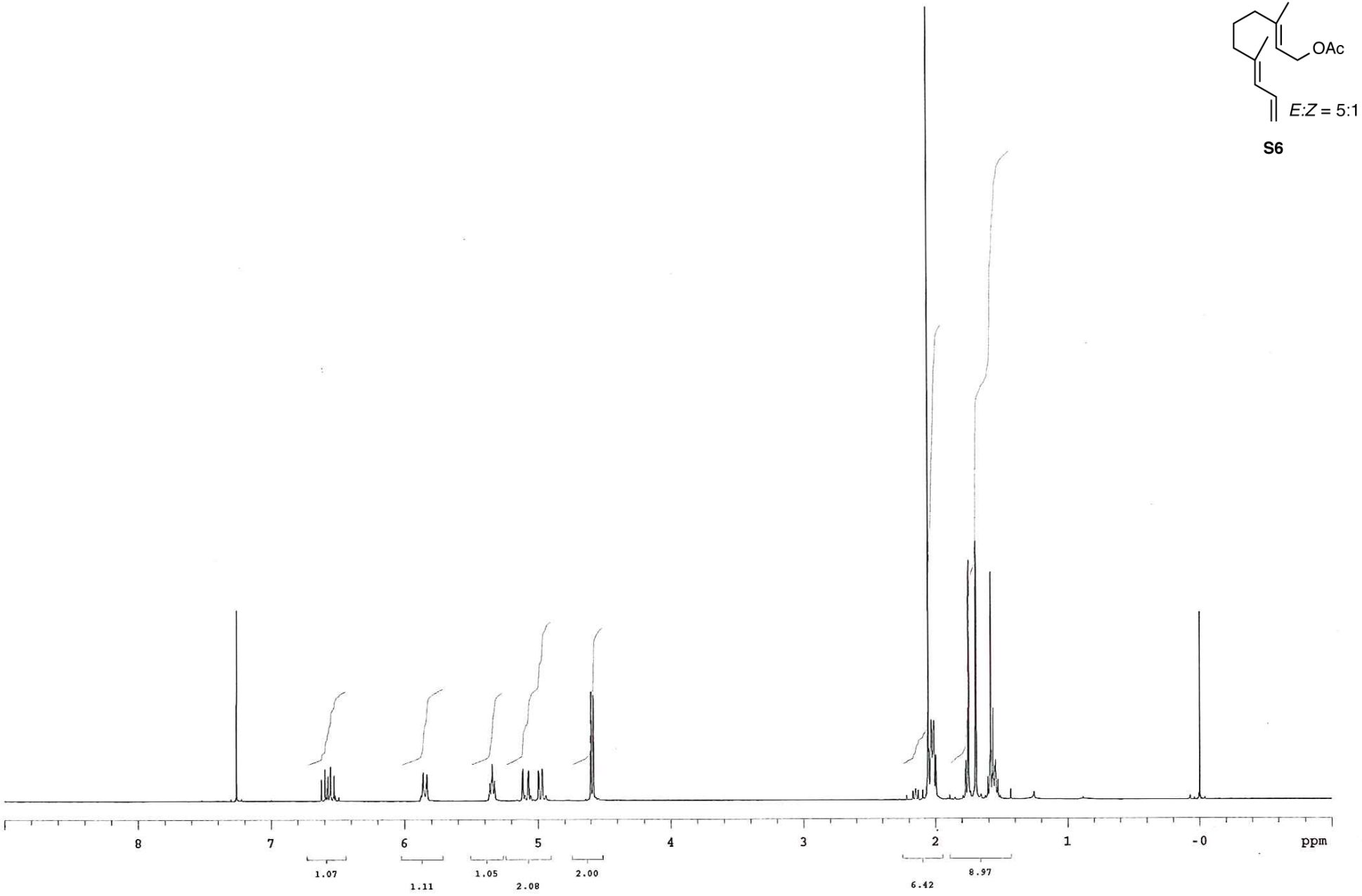

OH
E:Z = 5:1
S5
8
7
6
5
4
3
2
1
-0
ppm
1.03
1.00
0.98
2.03
1.94
0.32
3.46
2.71
2.63
2.64
0.81

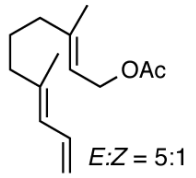


E:*Z* = 5:1

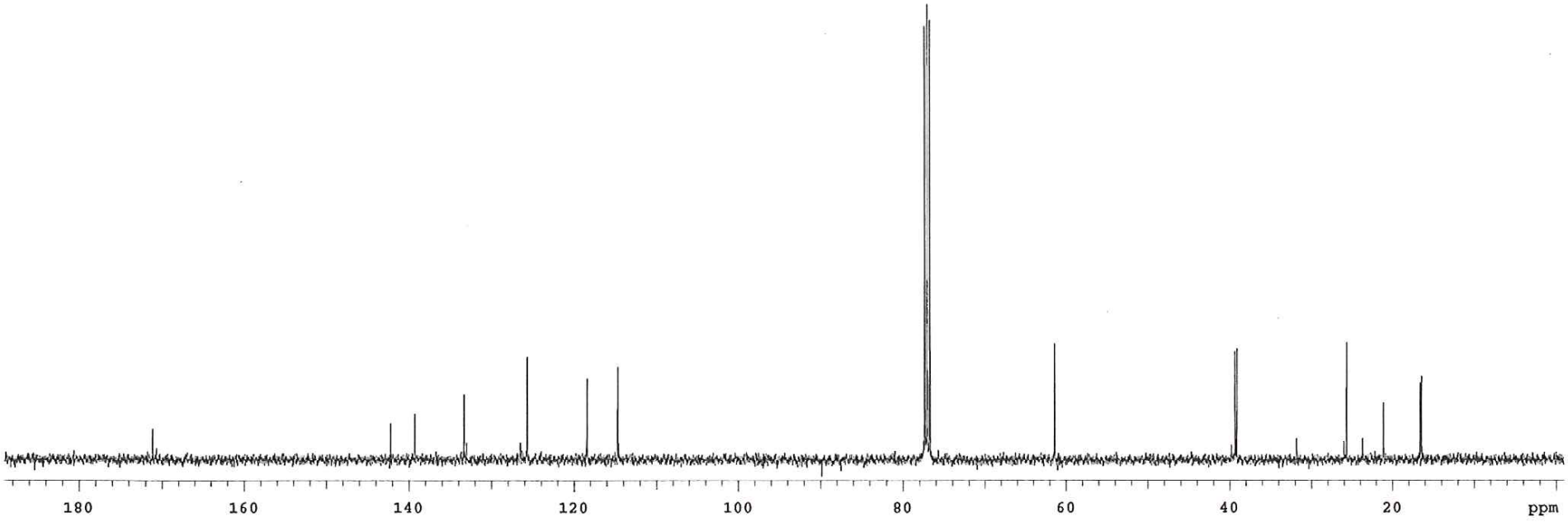
S5

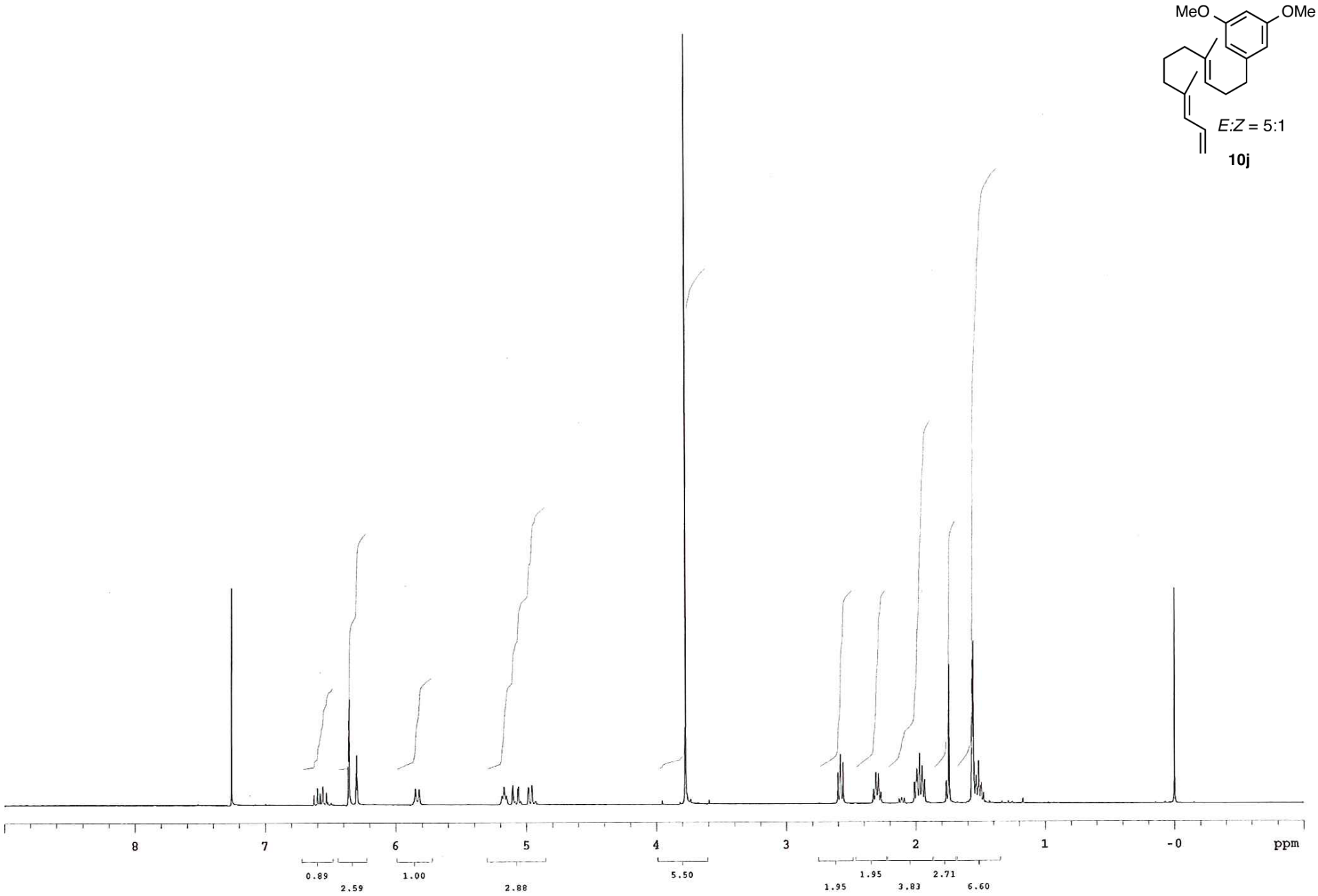


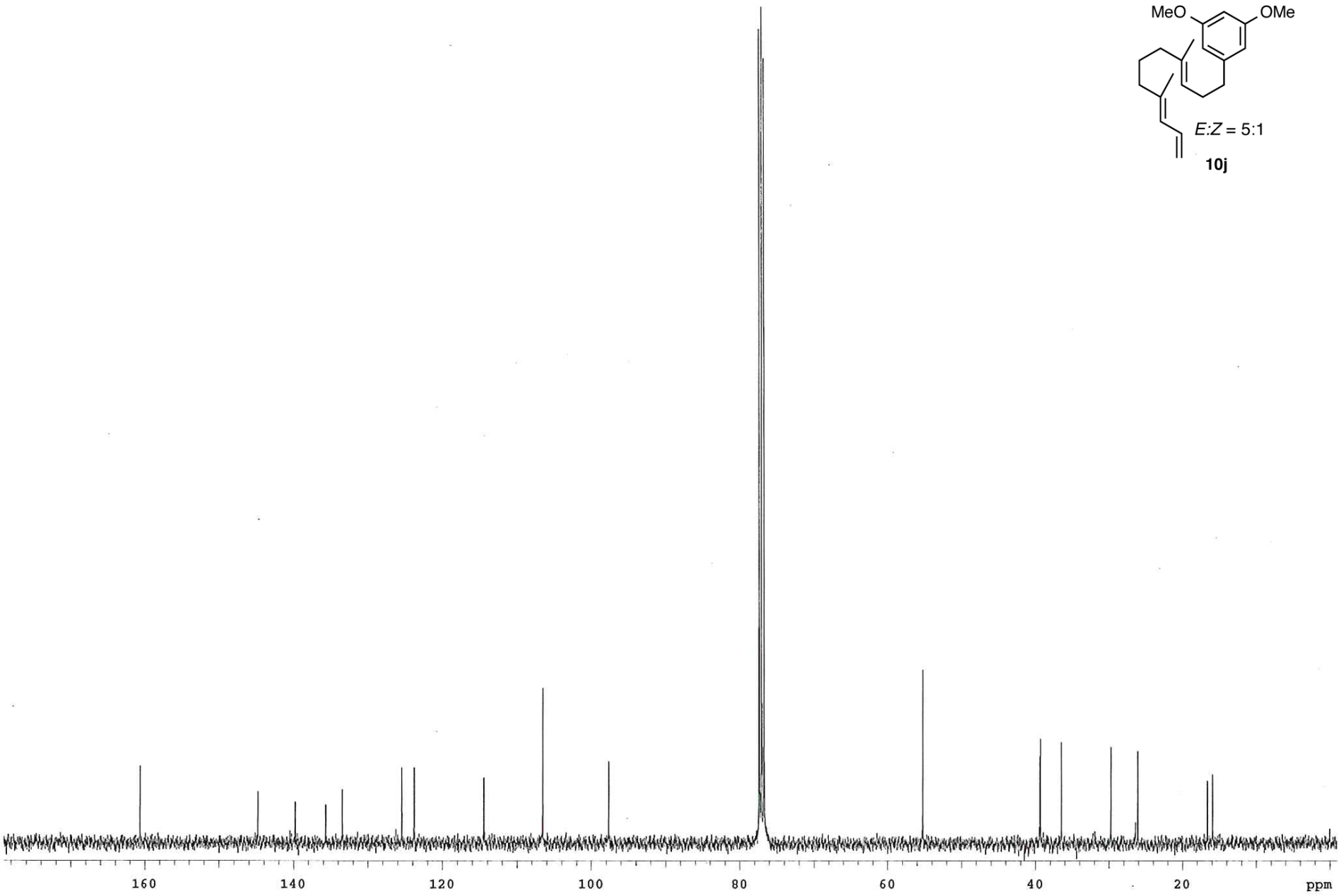

OAc
E:Z = 5:1
S6
8
7
6
5
4
3
2
1
-0
ppm
1.07
1.11
1.05
2.08
2.00
6.42
8.97

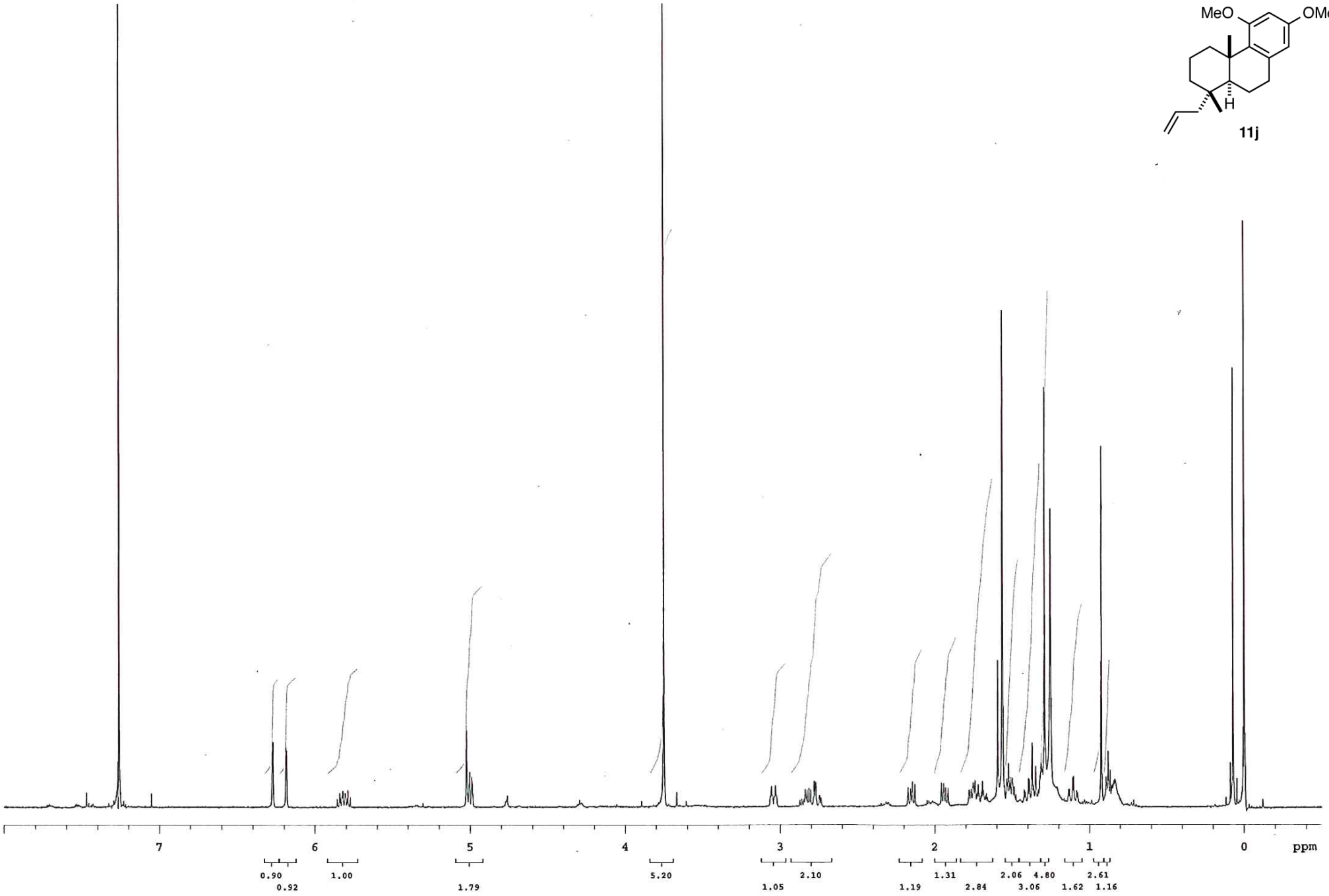


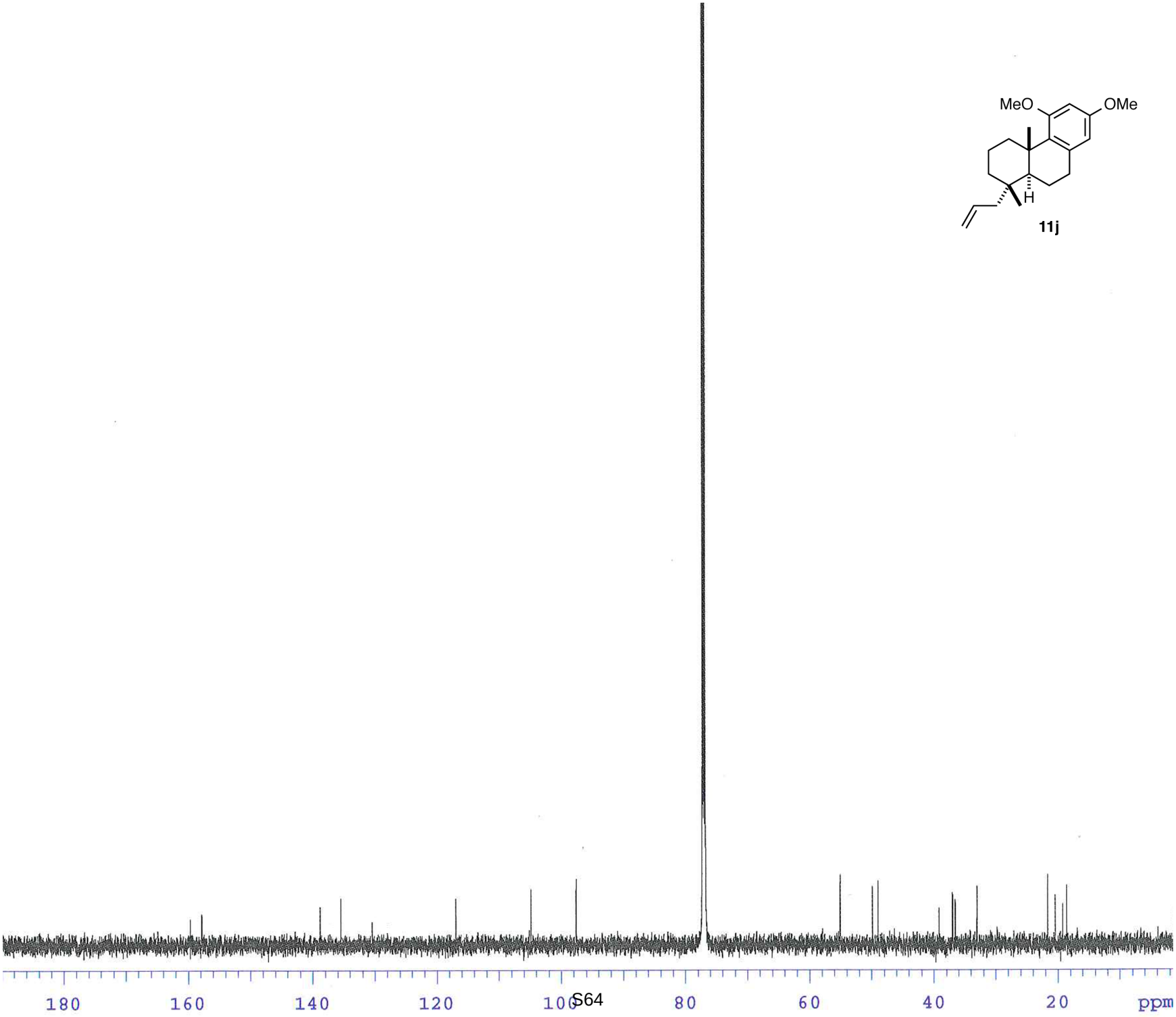
S6



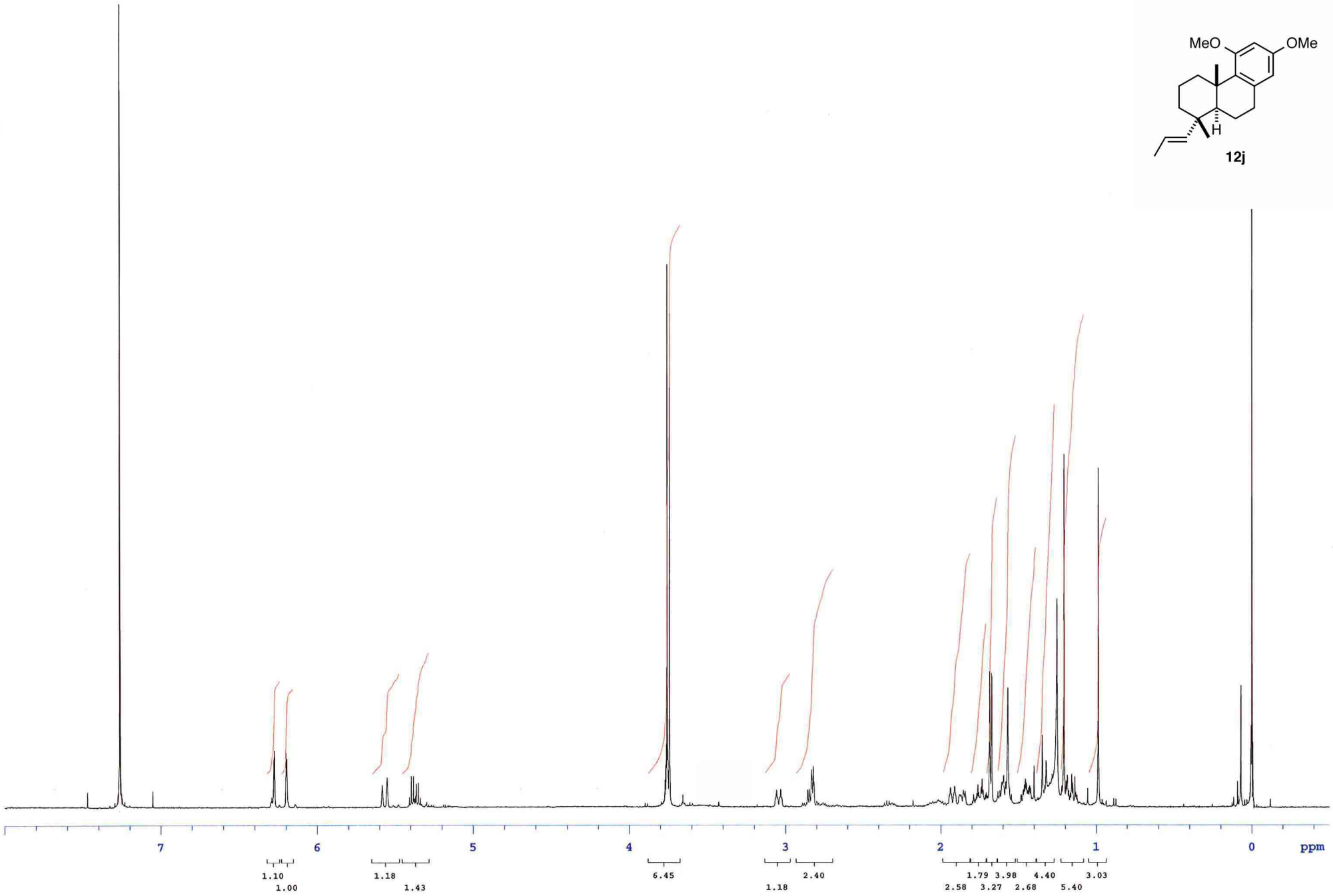

MeO
OMe
E:Z = 5:1
10j
8
7
6
5
4
3
2
1
-0
ppm
0.89
2.59
1.00
2.88
5.50
1.95
1.95
3.83
2.71
6.60

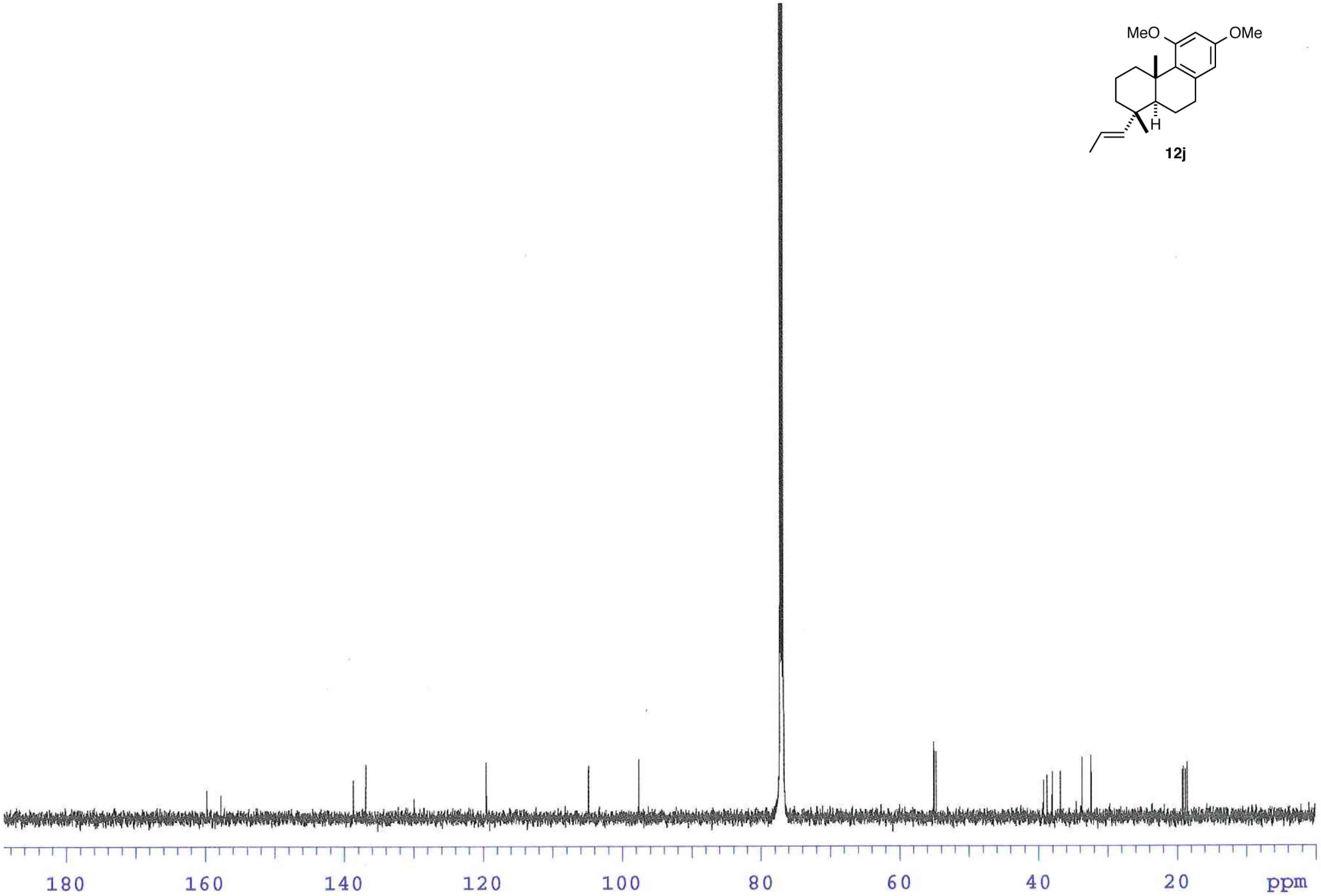

MeO
OMe
E:Z = 5:1
10j
160
140
120
100
80
60
40
20
ppm

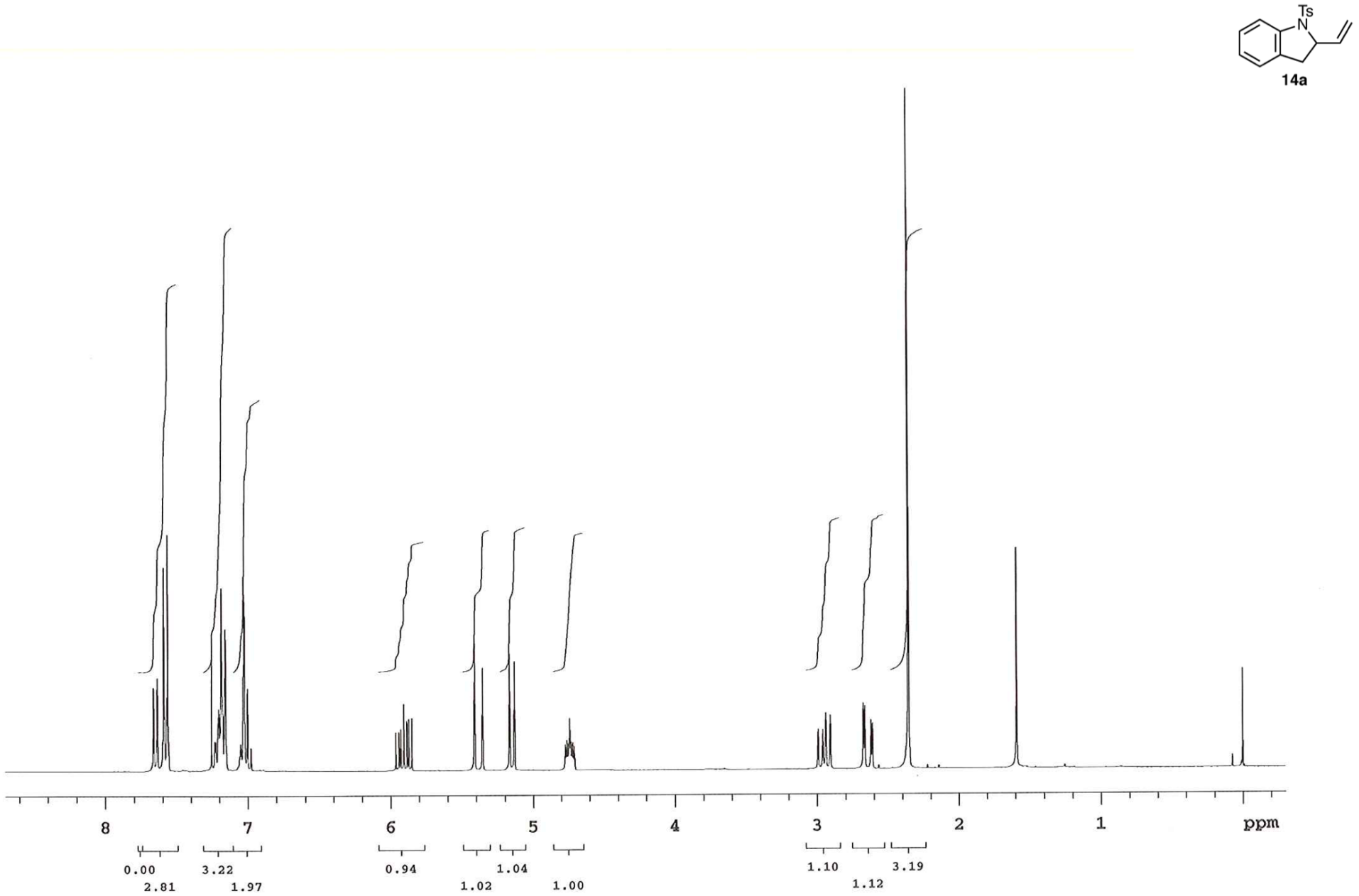

MeO
OMe
H
11j
7
6
5
4
3
2
1
0
ppm
0.90
0.92
1.00
1.79
5.20
1.05
2.10
1.19
1.31
2.84
2.06
4.80
3.06
1.62
2.61
1.16

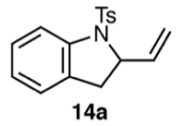


11j

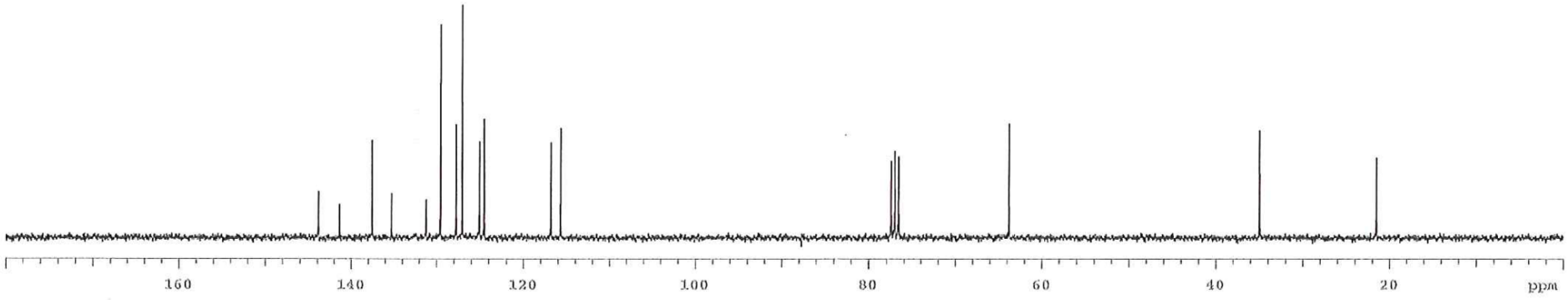

MeO
OMe
H
12j
7
6
5
4
3
2
1
0
ppm
1.10
1.00
1.18
1.43
6.45
1.18
2.40
1.79
3.98
4.40
3.03
2.58
3.27
2.68
5.40

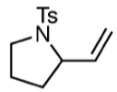

MeO
OMe
H
12j
180
160
140
120
100
80
60
40
20
ppm


Ts
N
14a
8
7
6
5
4
3
2
1
ppm
0.00
2.81
3.22
1.97
0.94
1.02
1.04
1.00
1.10
1.12
3.19

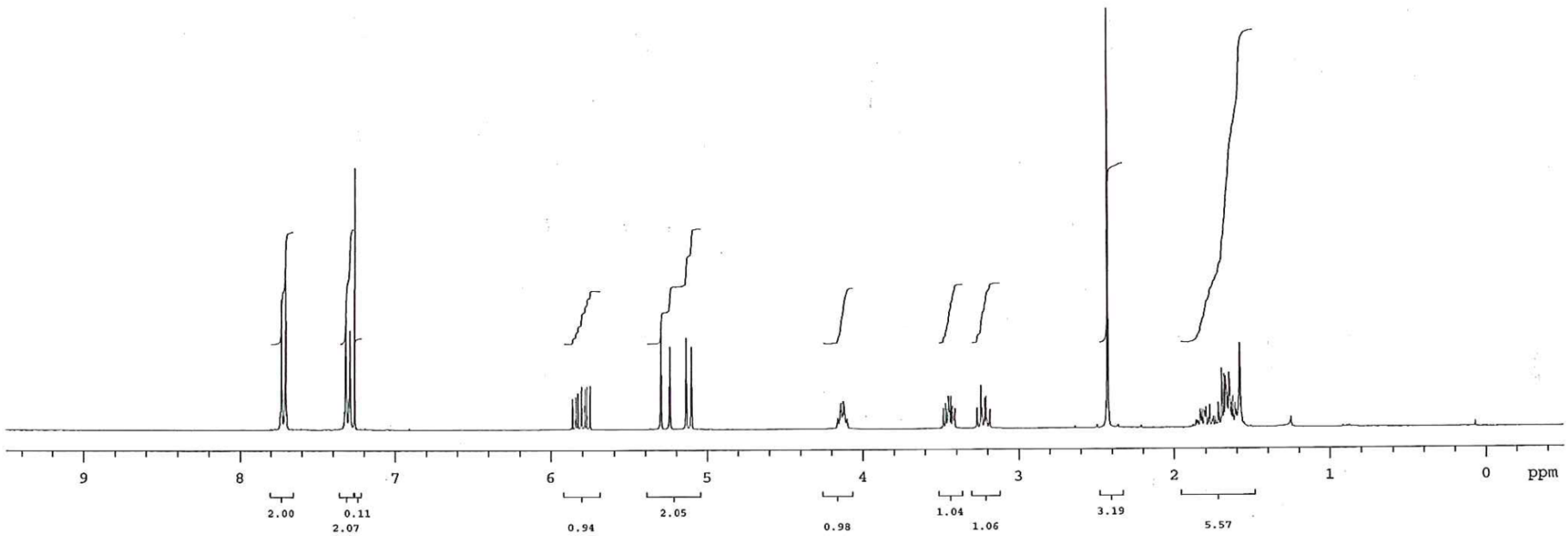


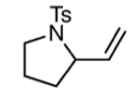
14a



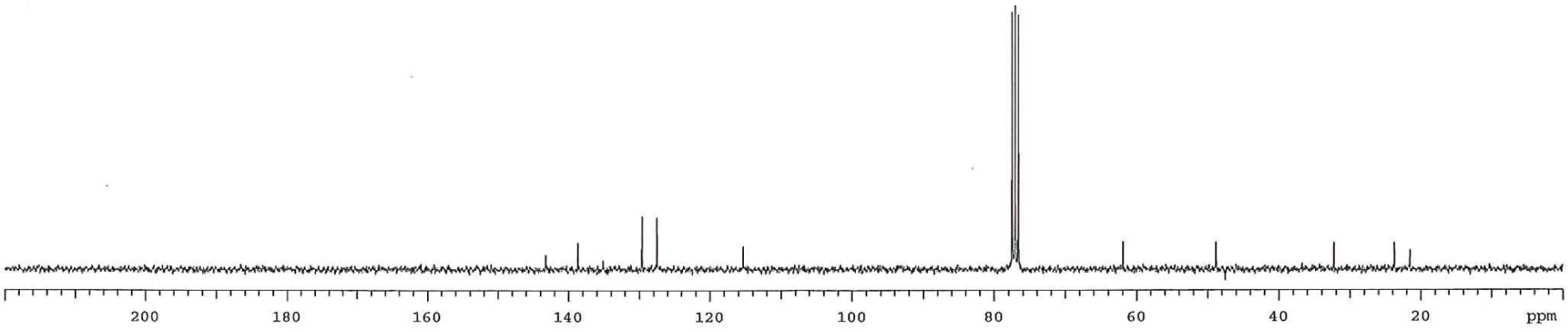


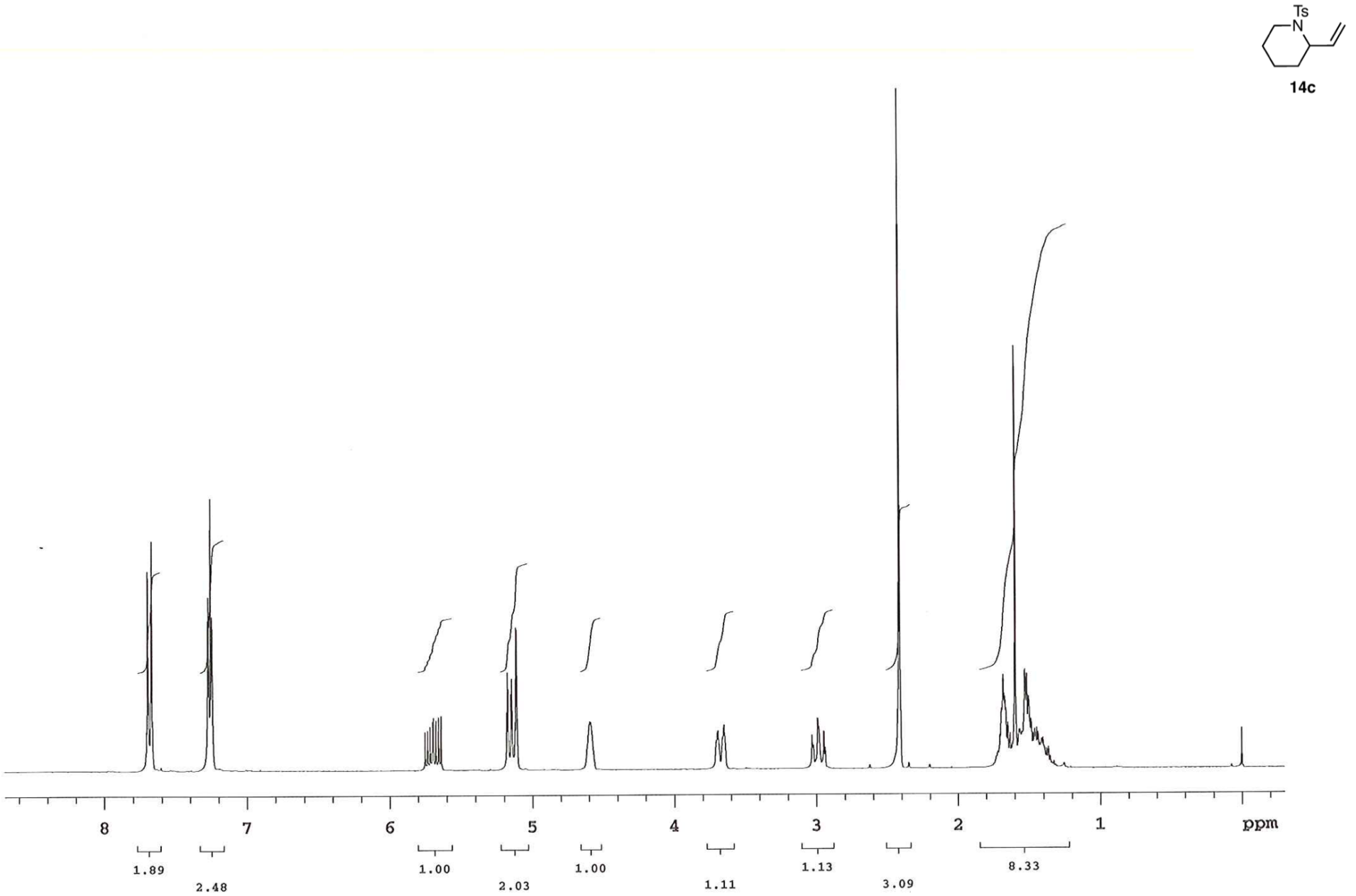
14b

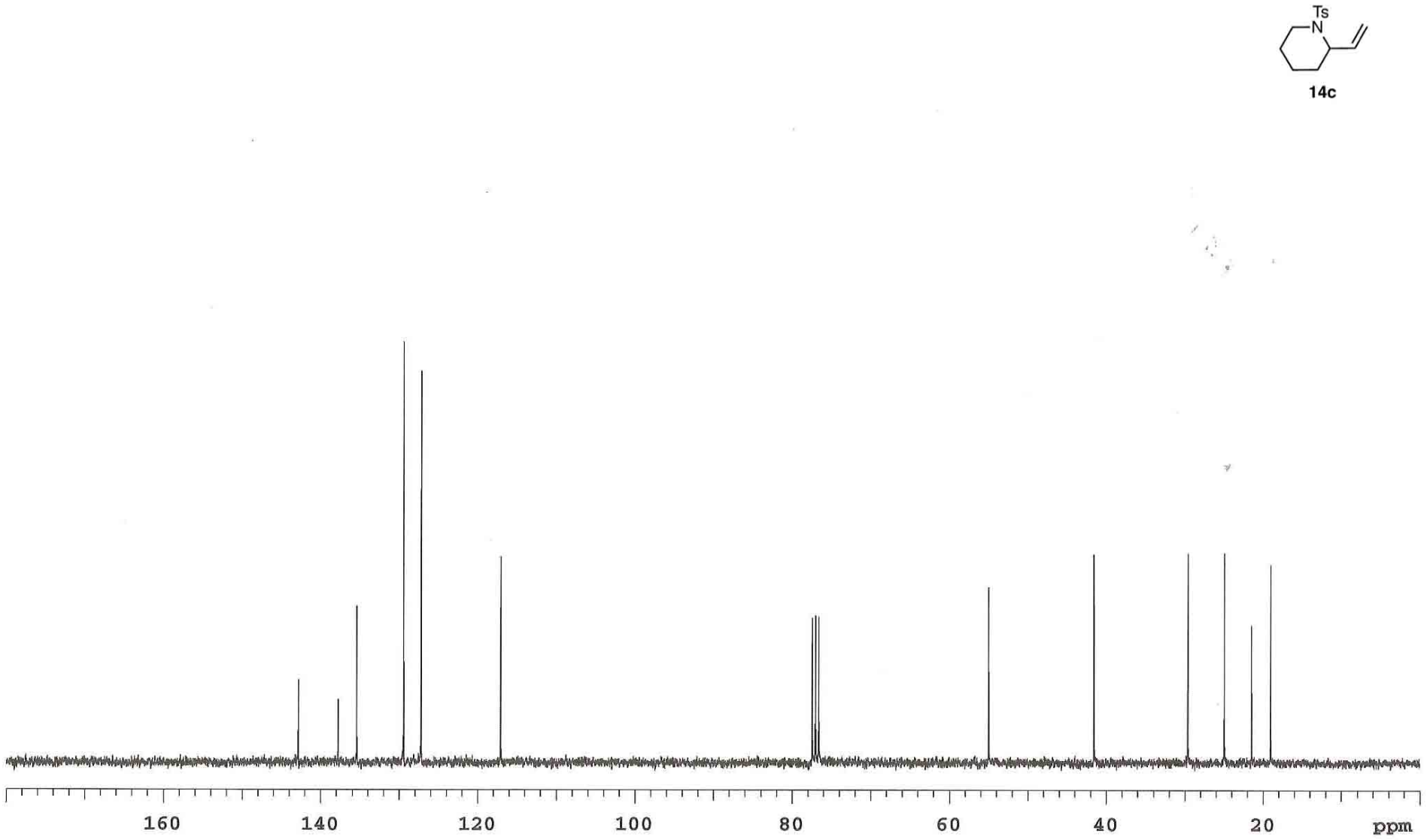


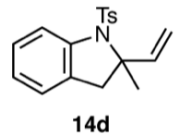


14b

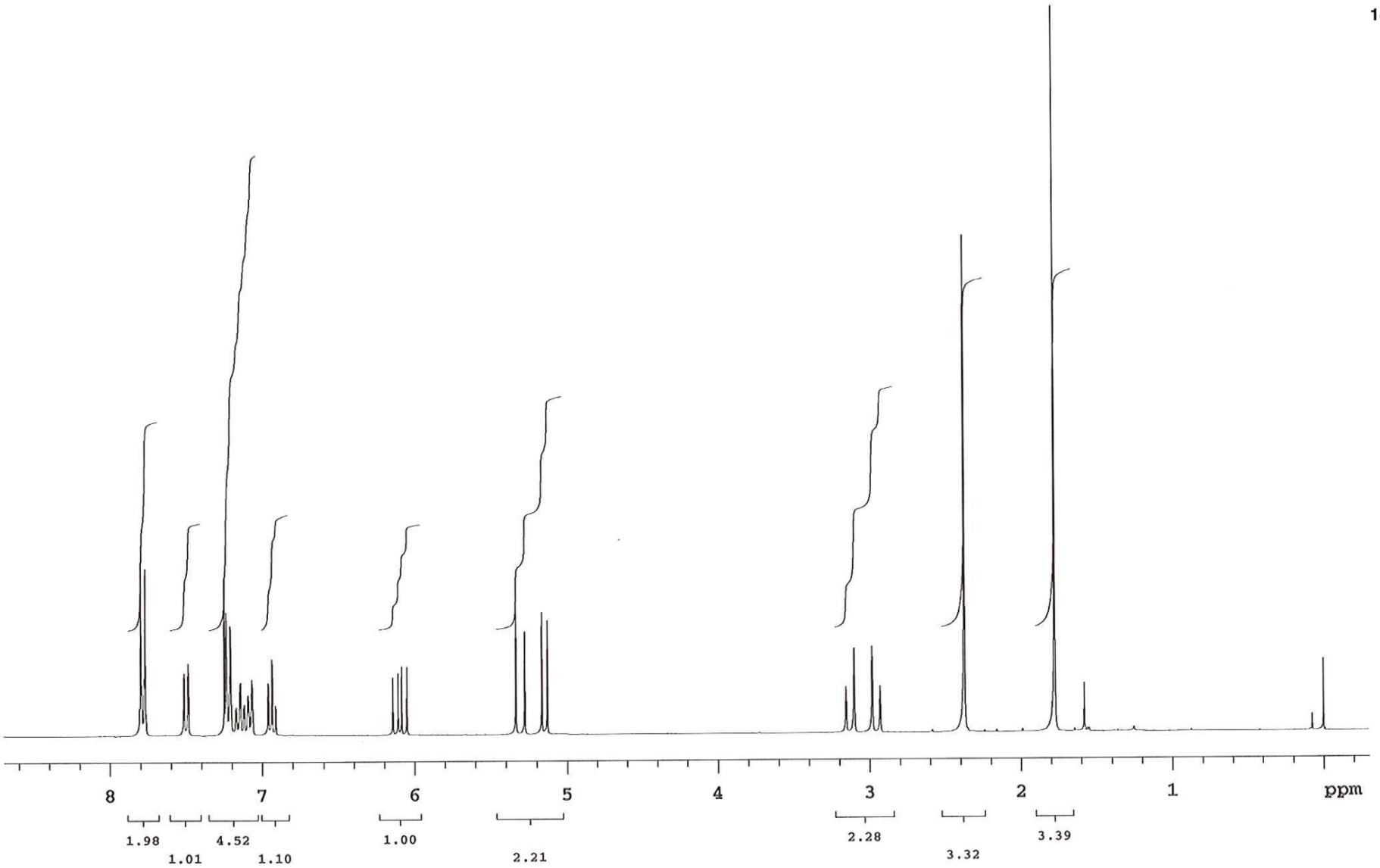


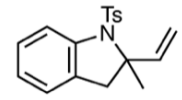

Ts
N
14c
8
7
6
5
4
3
2
1
ppm
1.89
2.48
1.00
2.03
1.00
1.11
1.13
3.09
8.33


Ts
N
14c
160
140
120
100
80
60
40
20
ppm

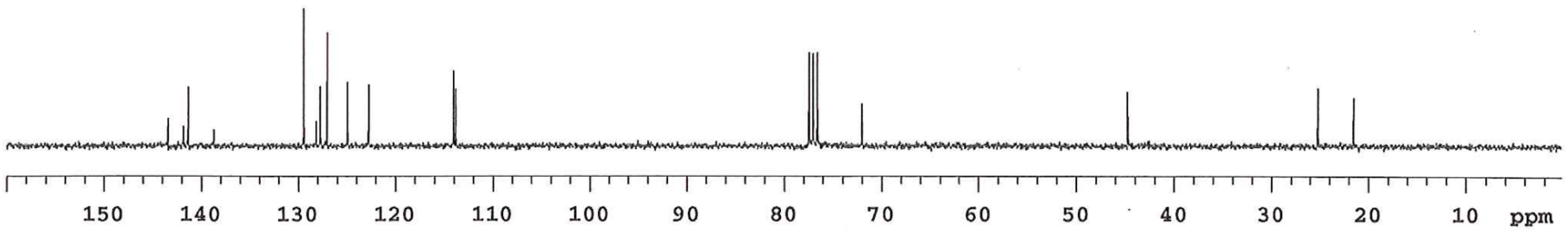


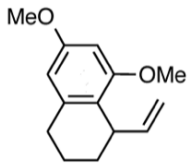
14d



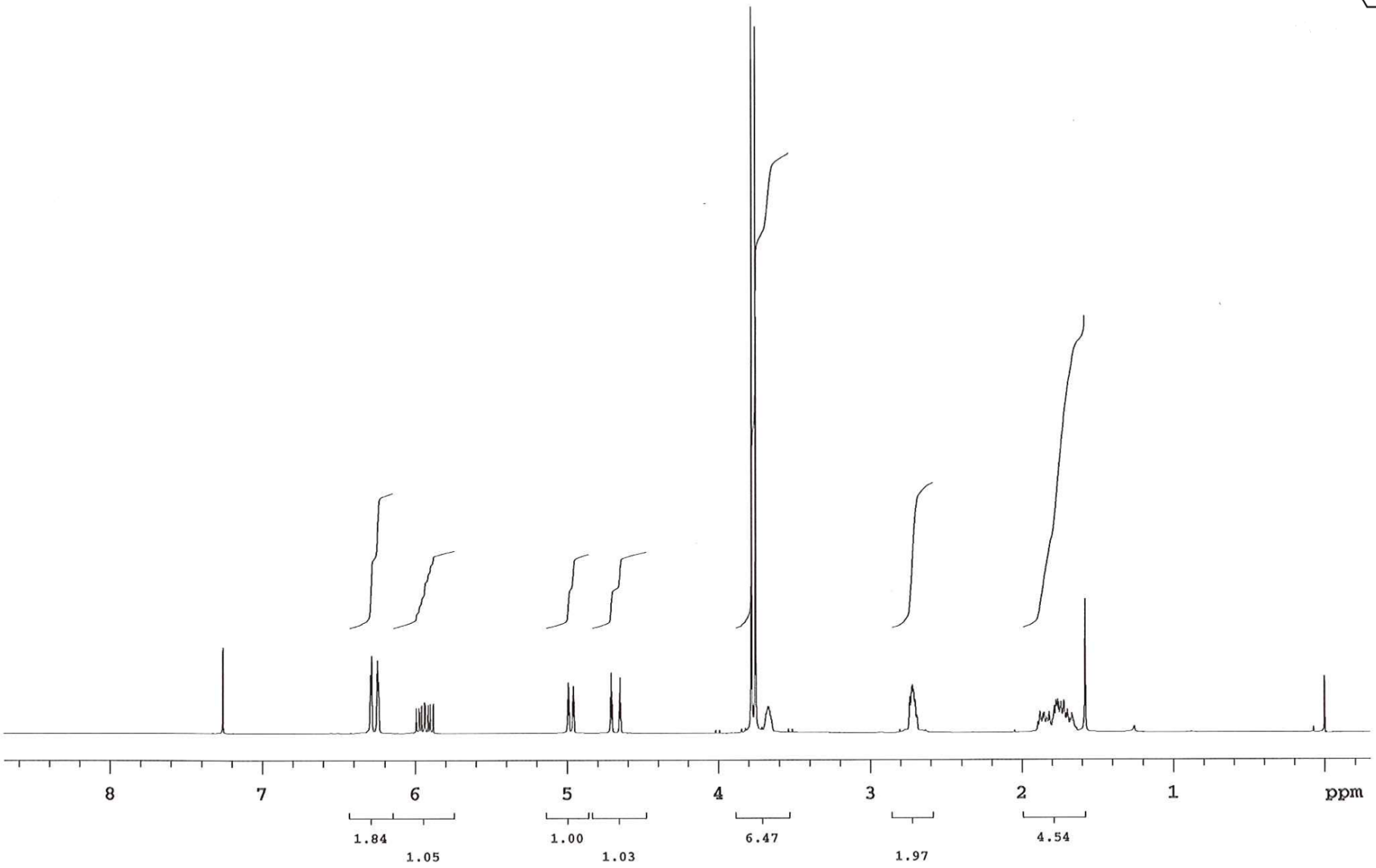


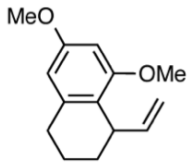
14d



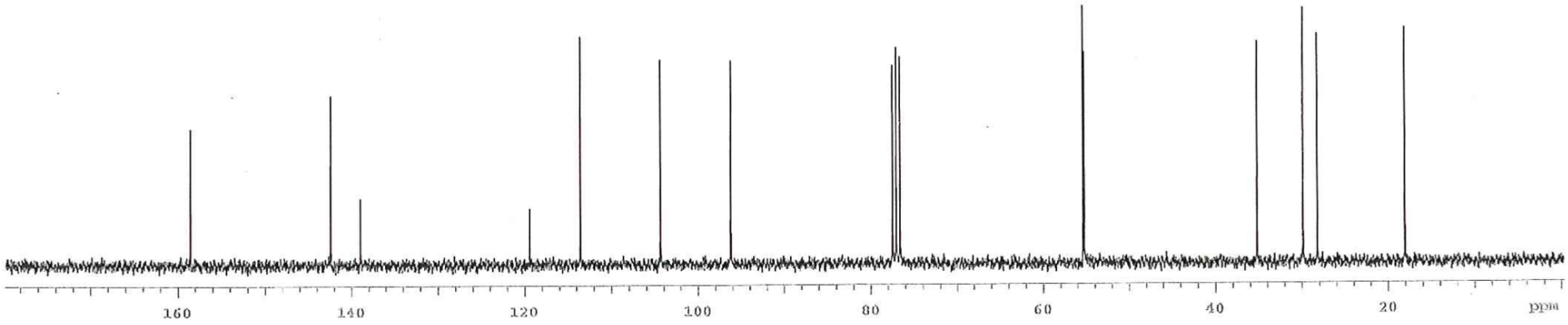


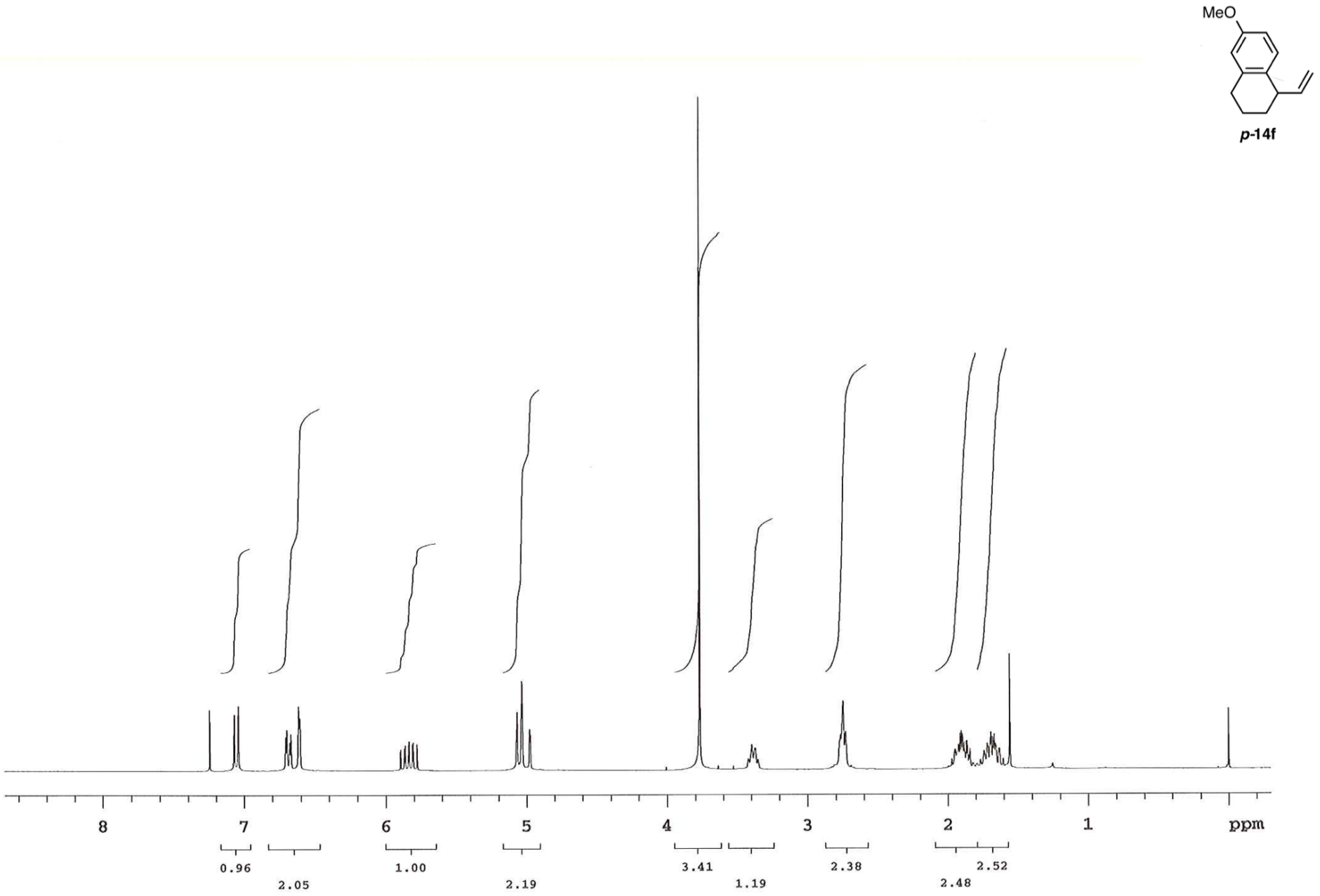
14e

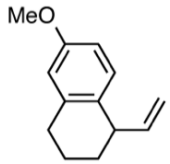




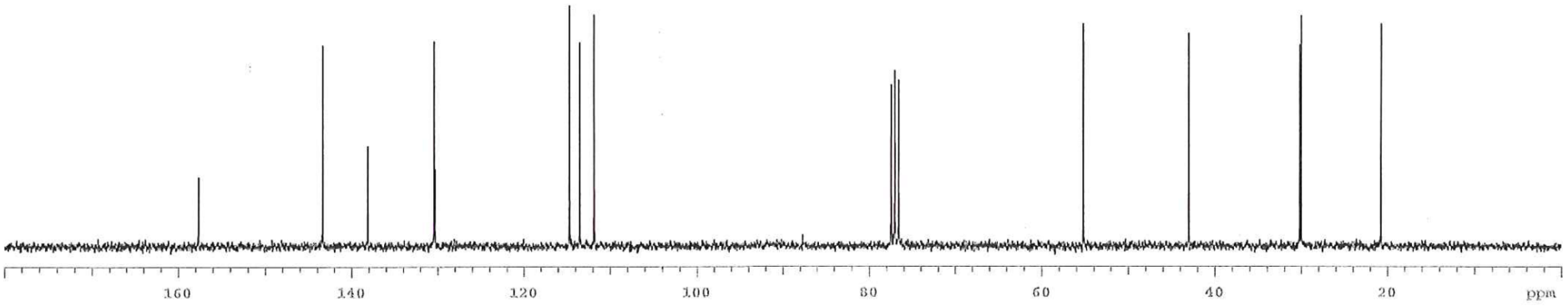
14e

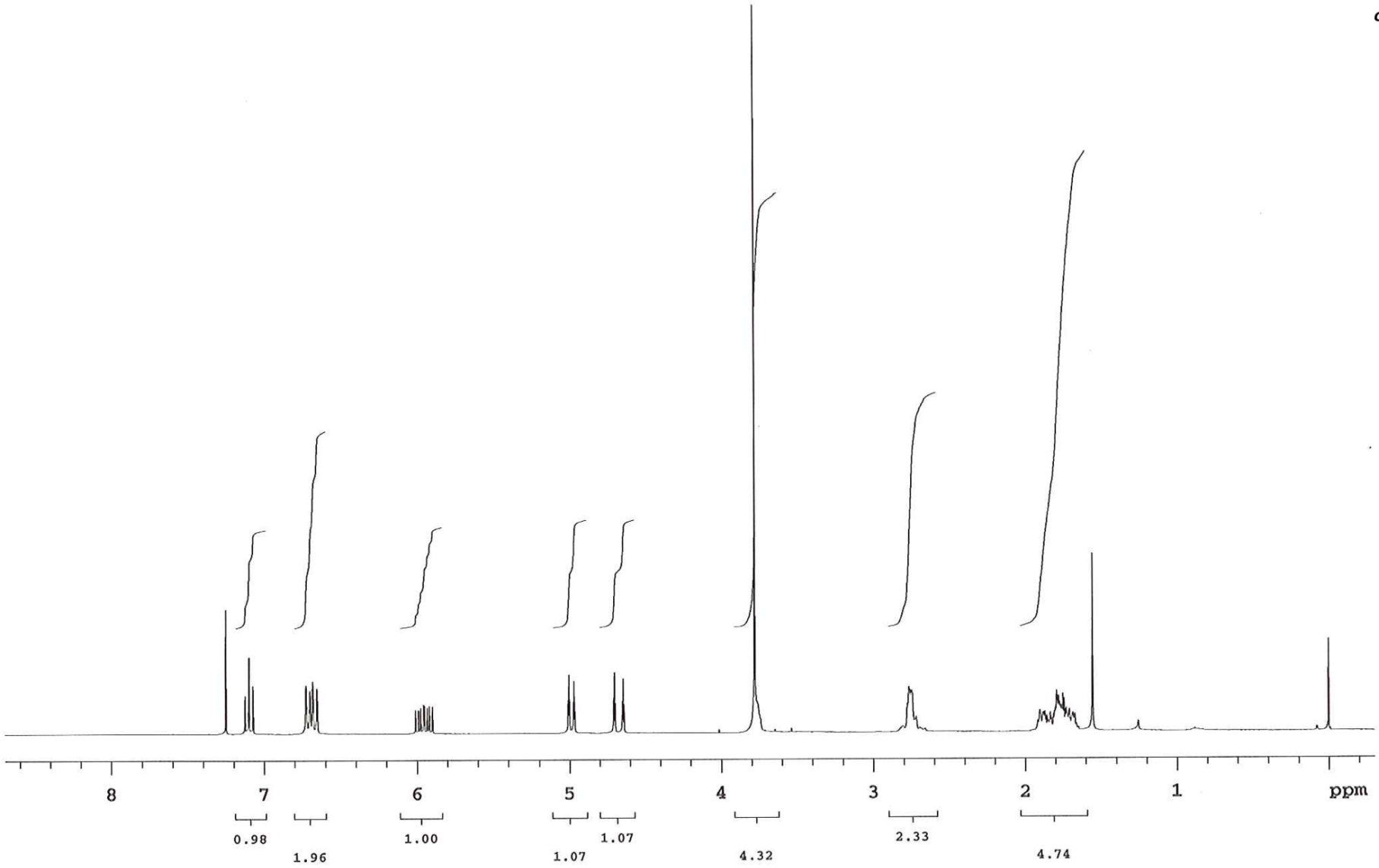



MeO
p-14f
8
7
6
5
4
3
2
1
ppm
0.96
2.05
1.00
2.19
3.41
1.19
2.38
2.48
2.52

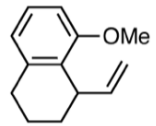


***p*-14f**

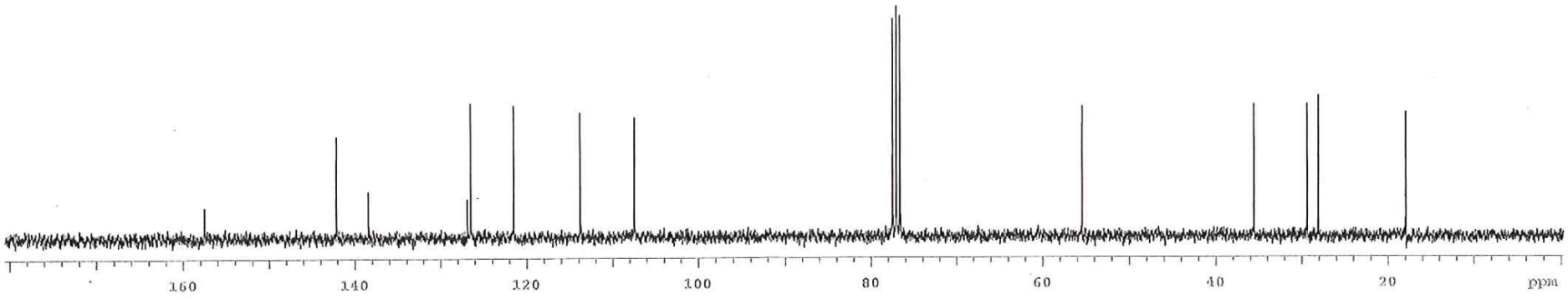


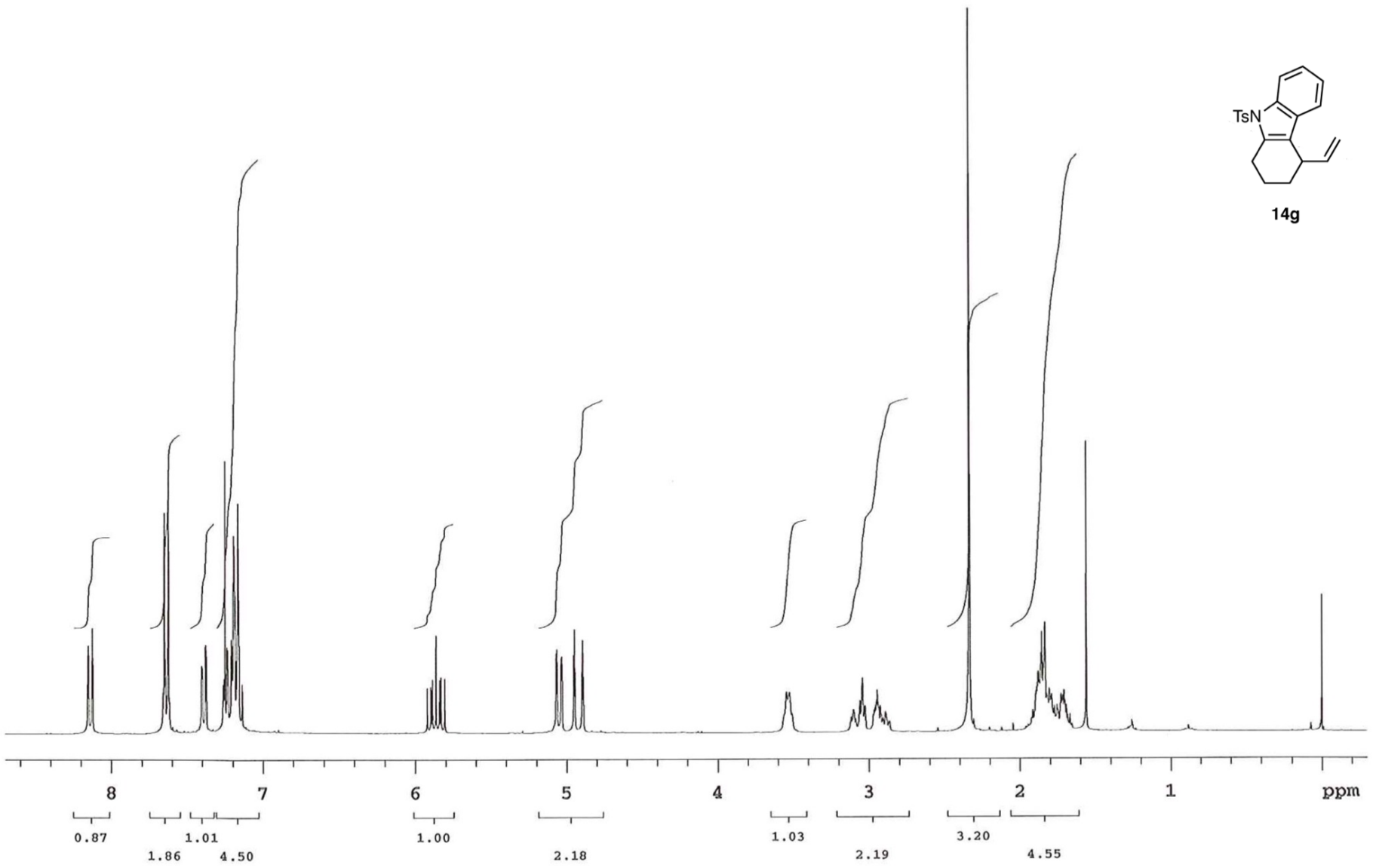


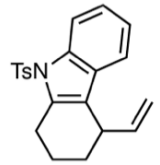
***o*-14f**



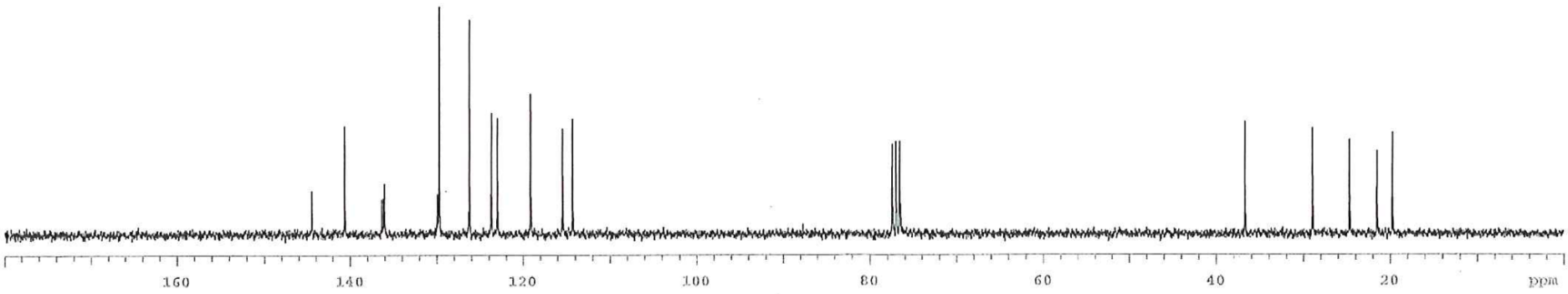
***o*-14f**

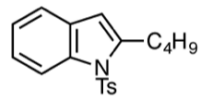



TsN
14g
8
7
6
5
4
3
2
1
ppm
0.87
1.86
1.01
4.50
1.00
2.18
1.03
2.19
3.20
4.55

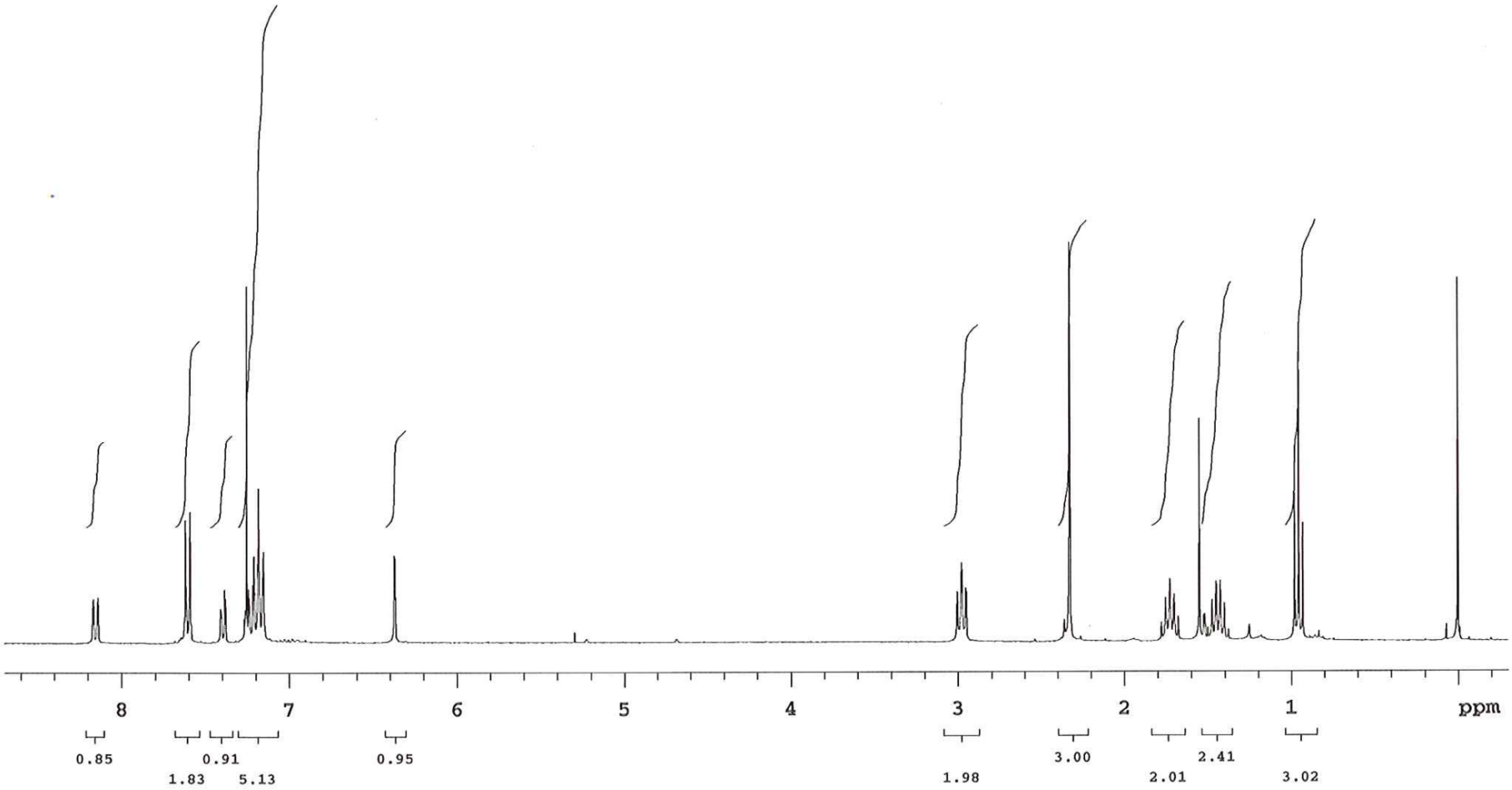


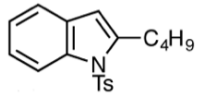
14g



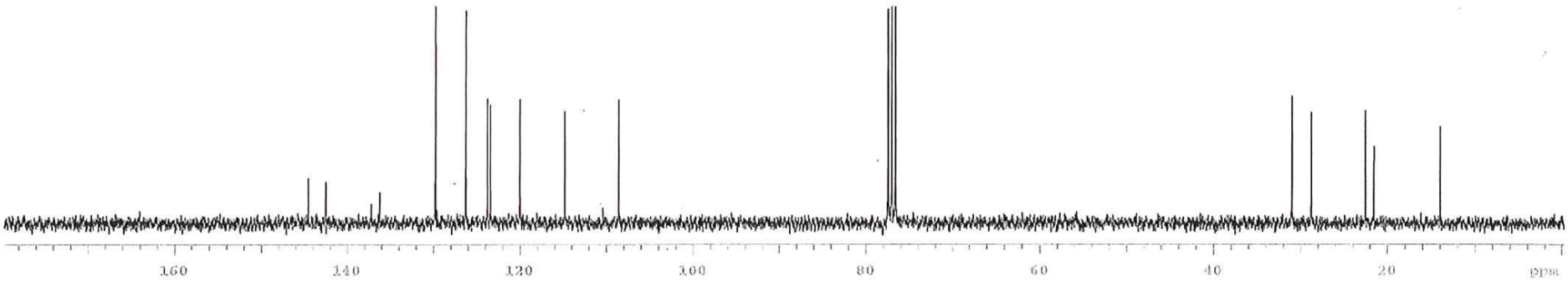


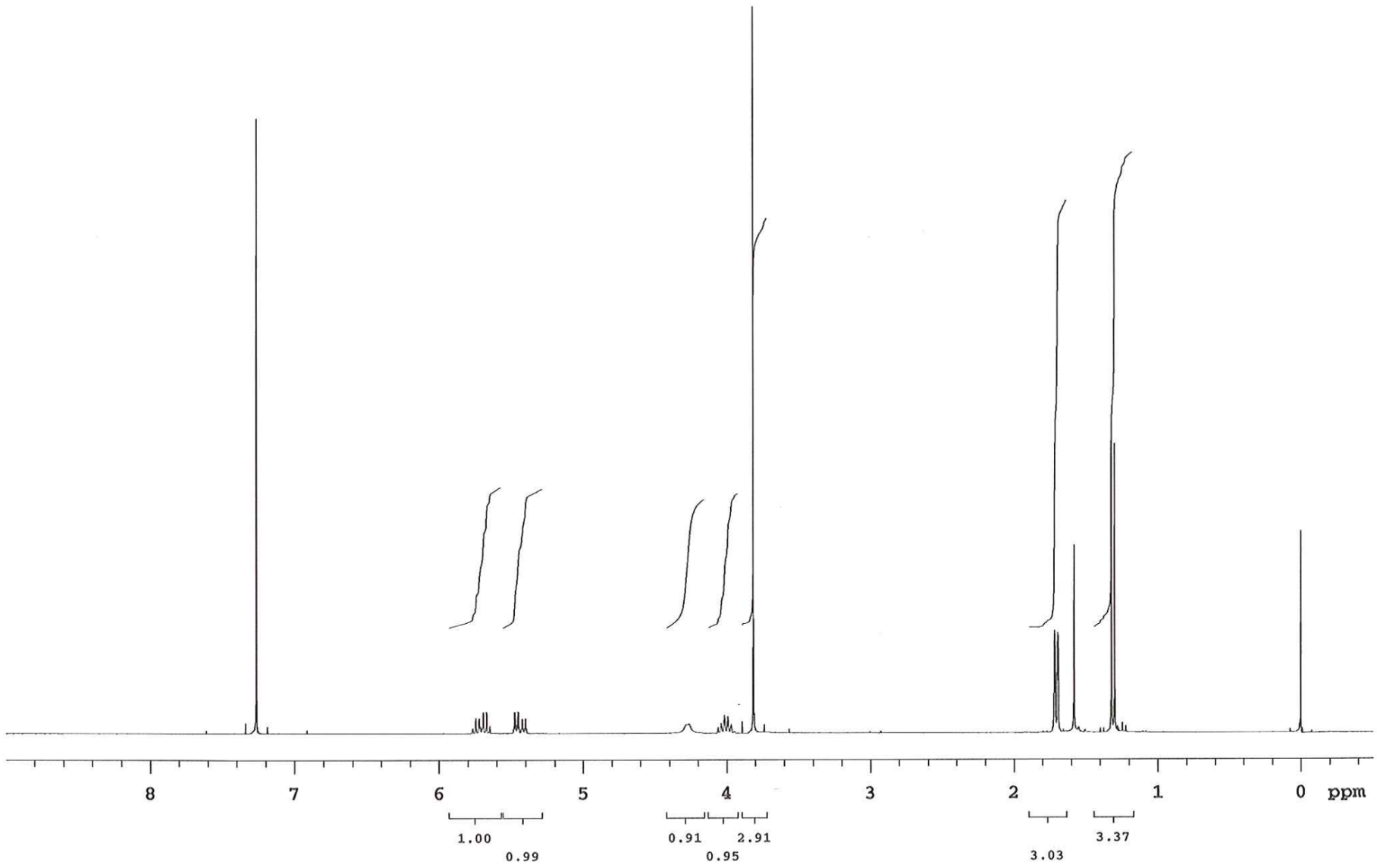
19

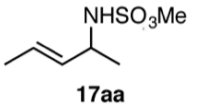




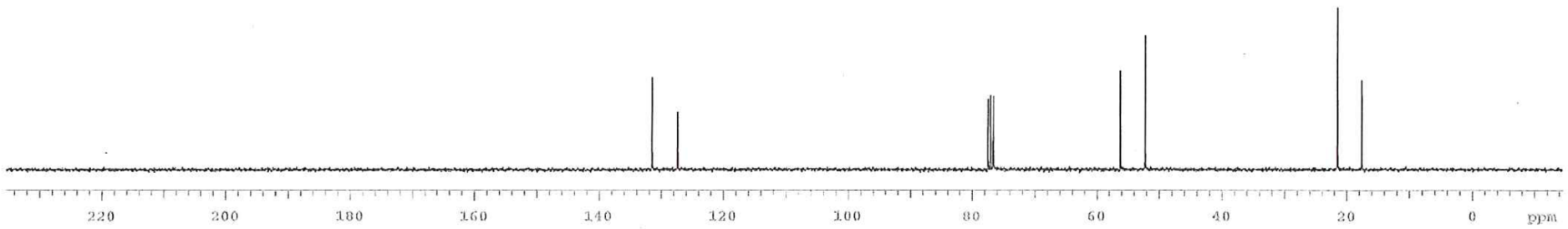
19

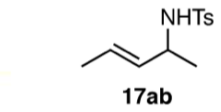



NHSO3Me
17aa
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
0.91
2.91
0.95
3.03
3.37

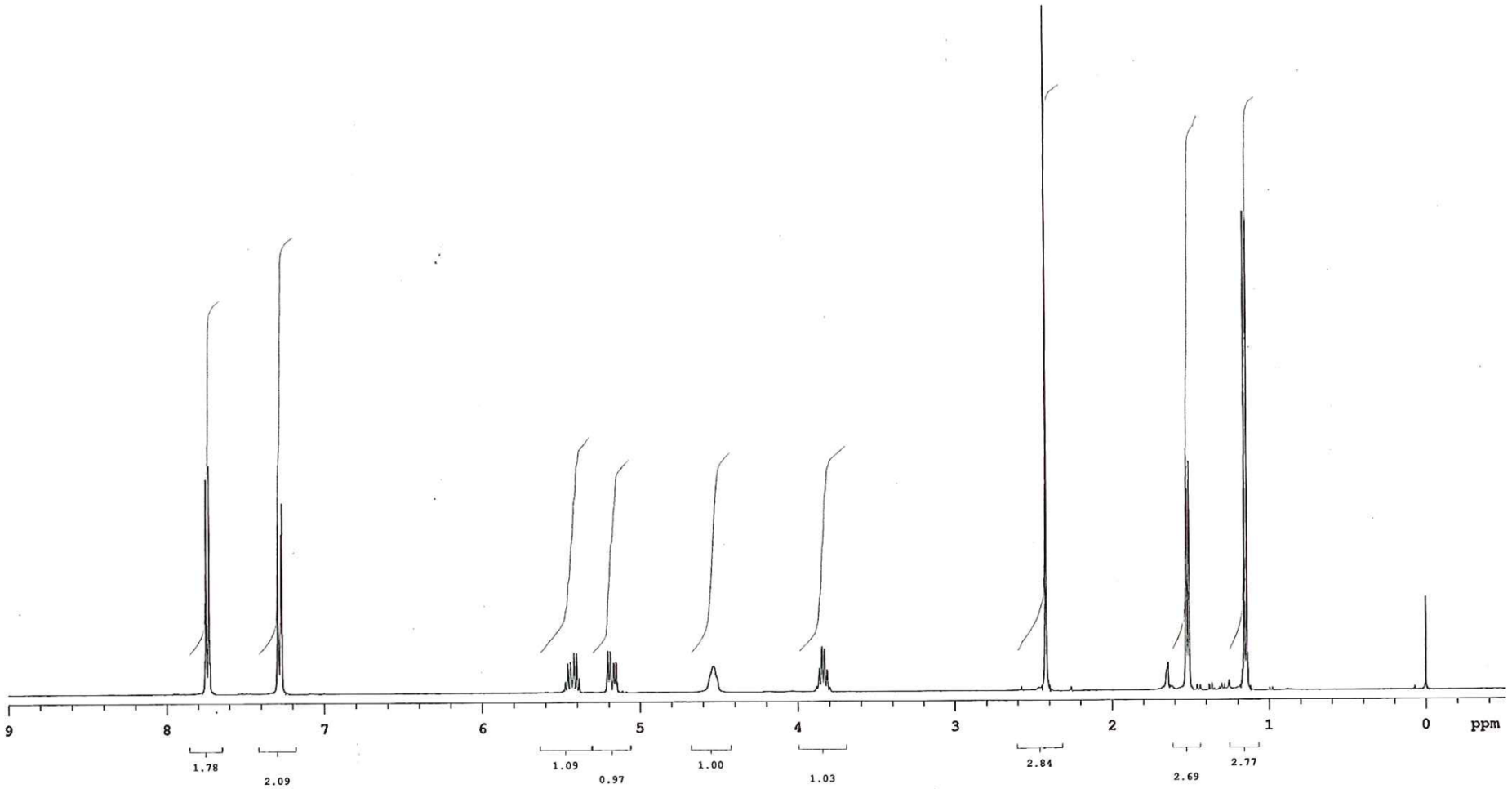


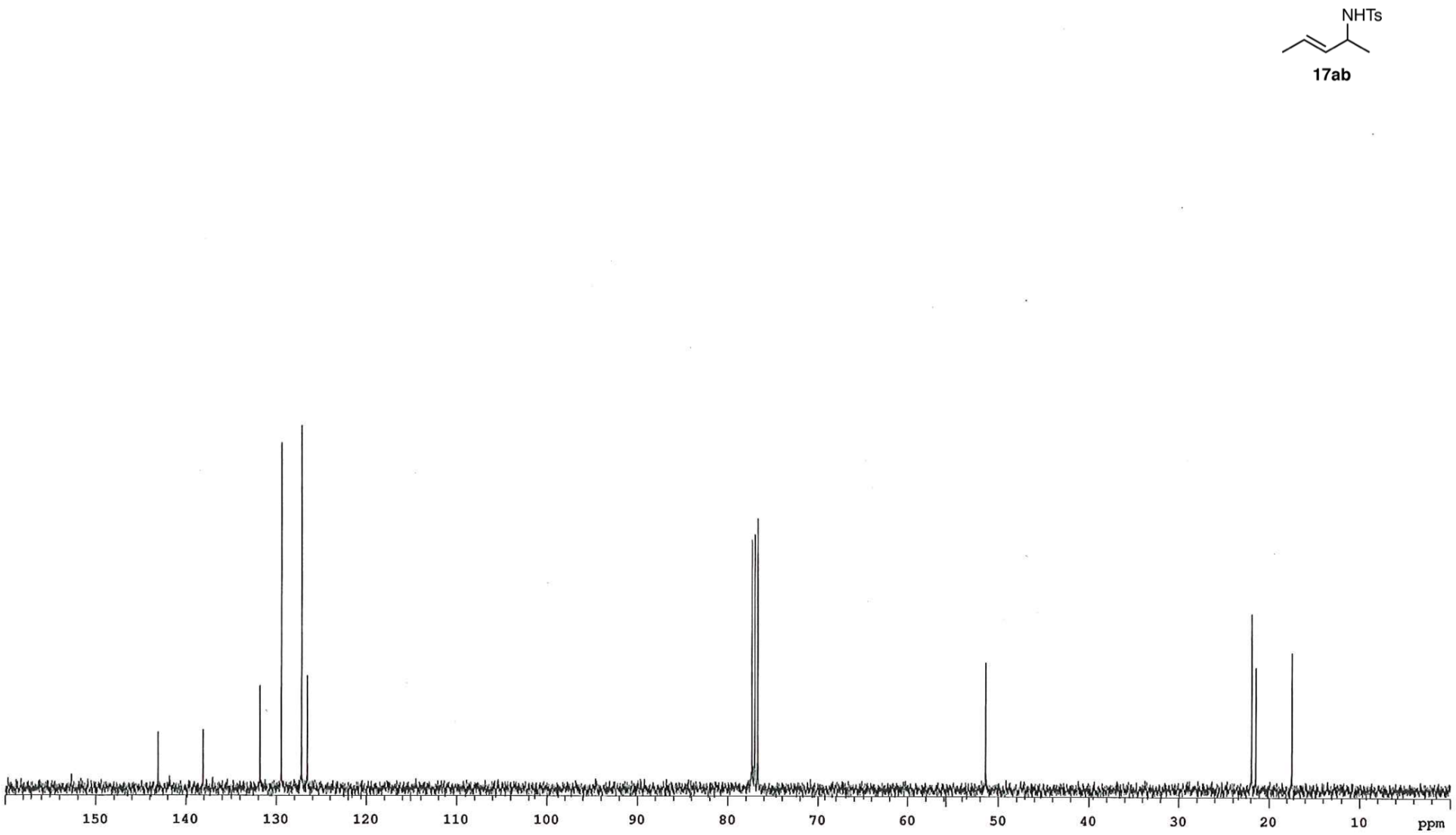
17aa

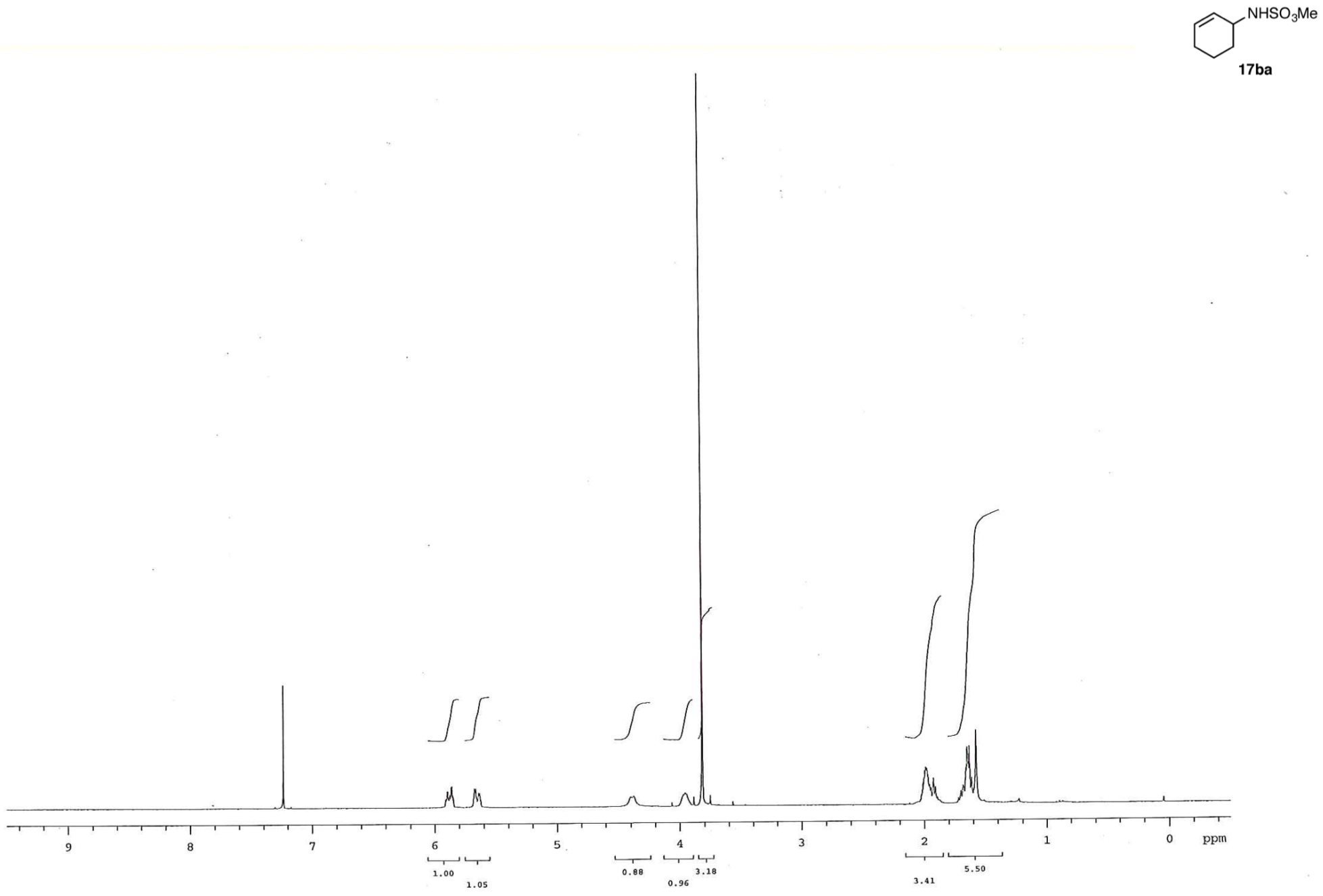


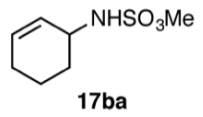


17ab

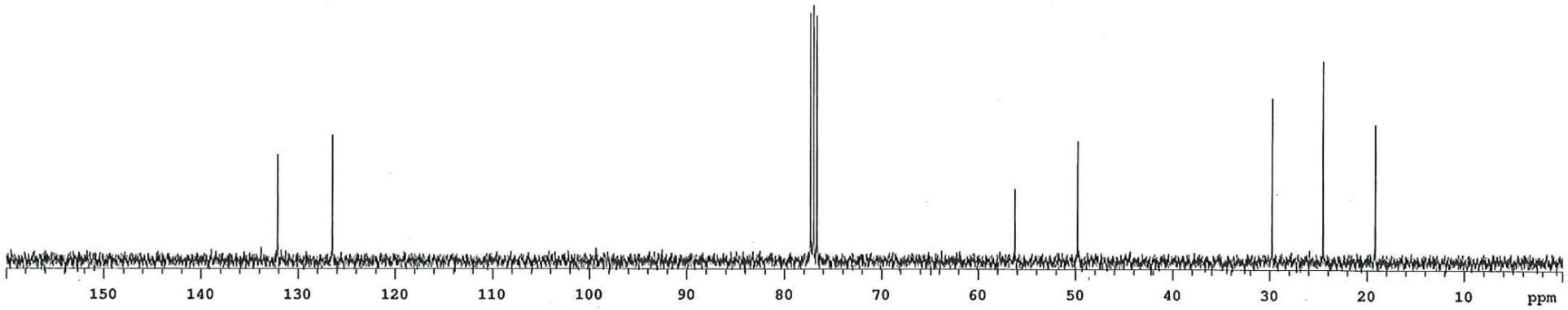


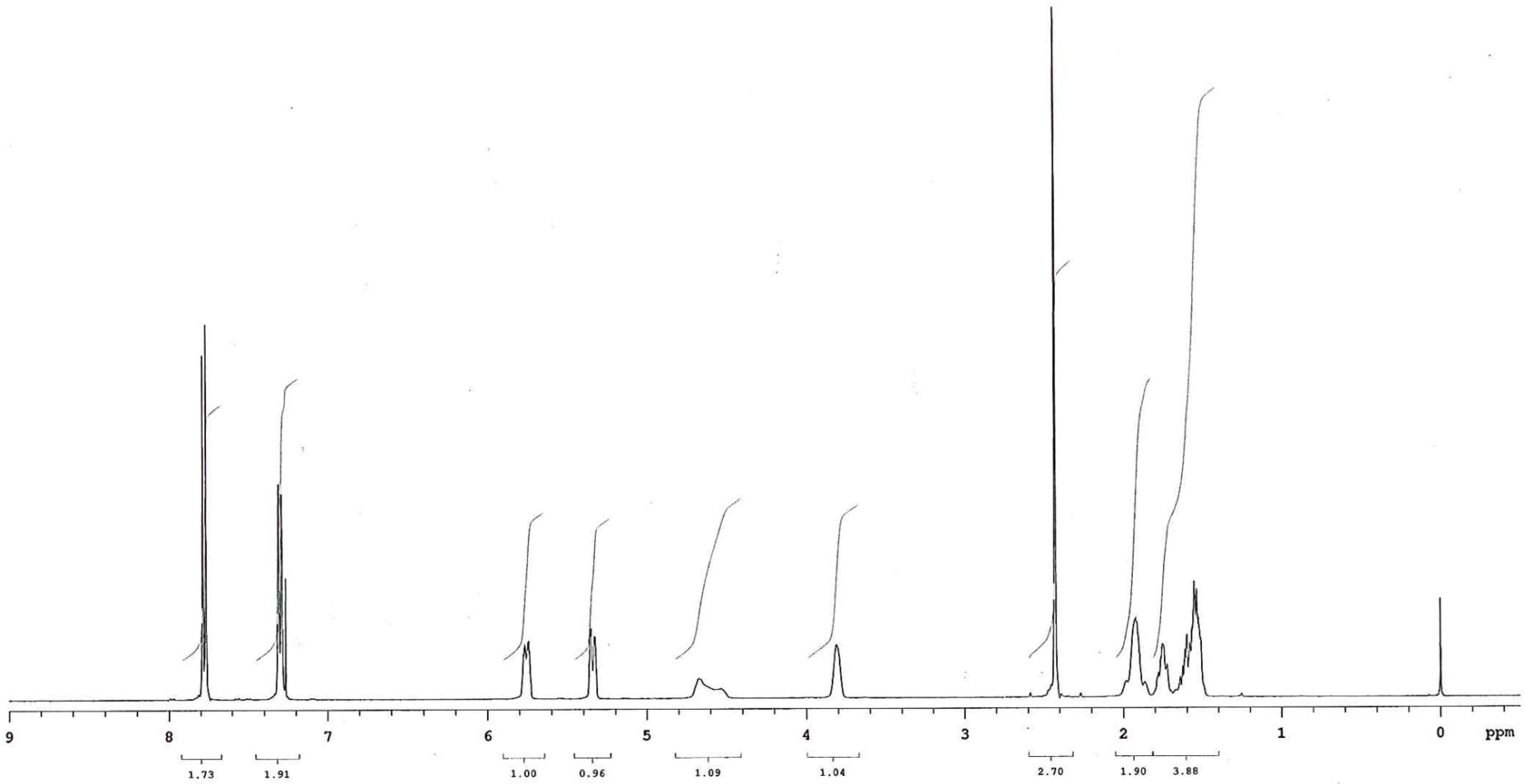

NHTs
17ab
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

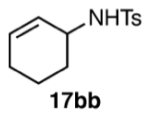

NHSO3Me
17ba
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
0.88
0.96
3.18
3.41
5.50



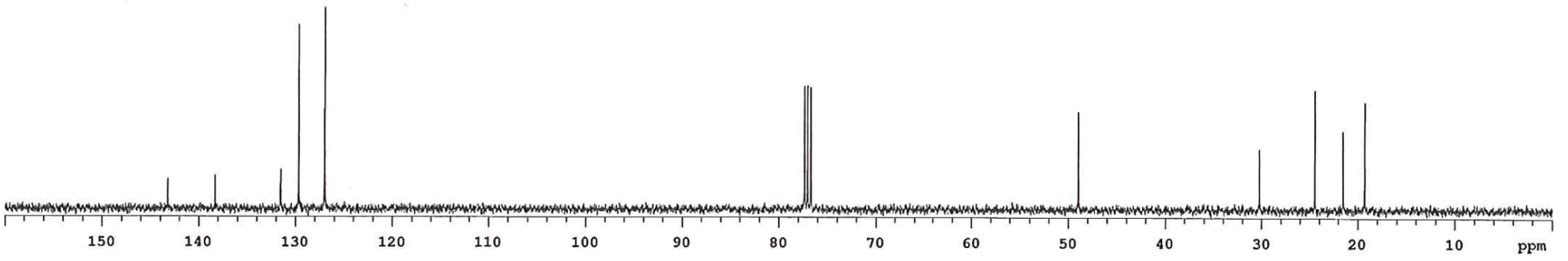
17ba

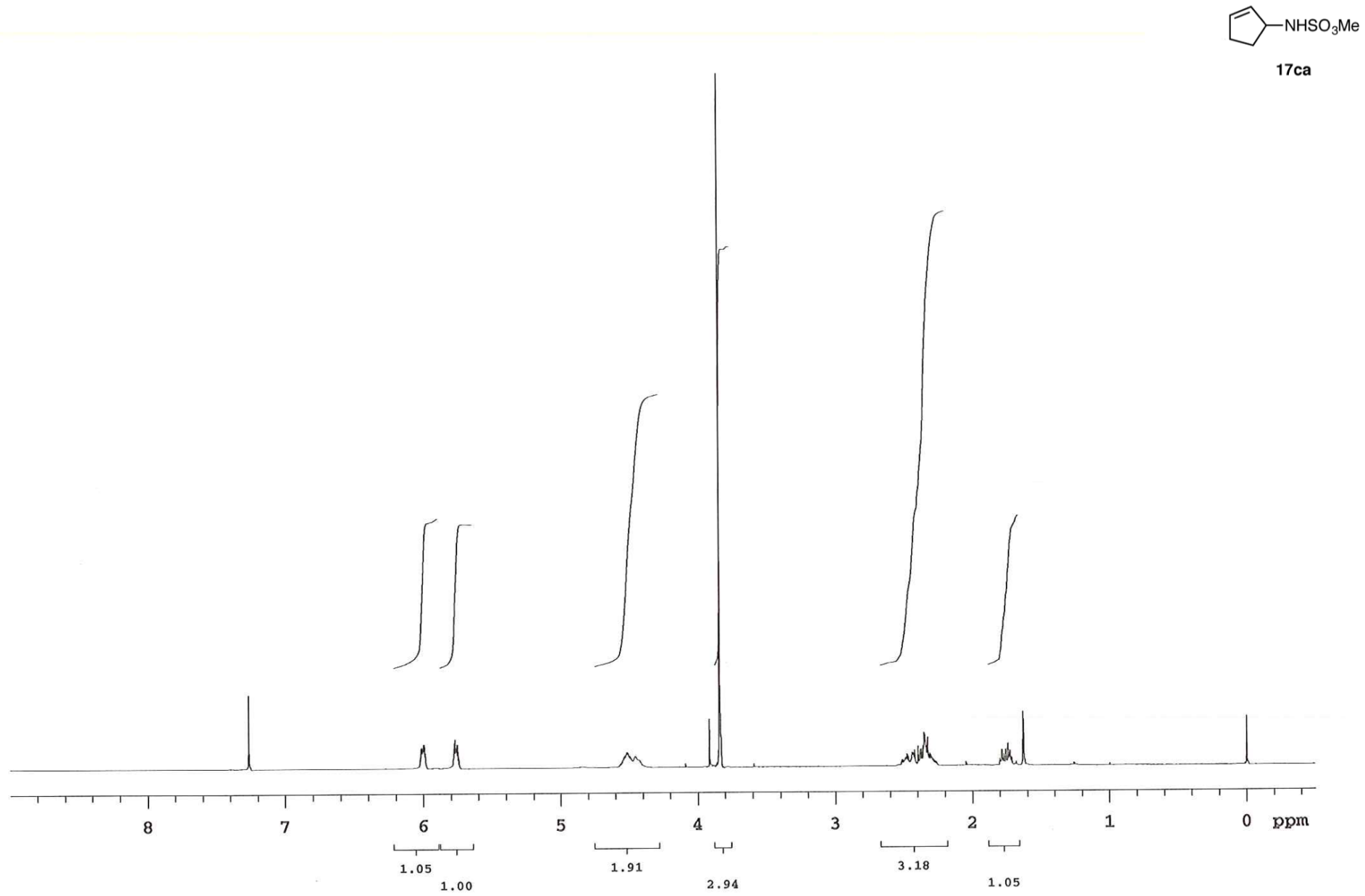


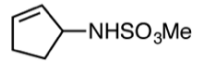

NHTs
17bb
9
8
7
6
5
4
3
2
1
0
ppm
1.73
1.91
1.00
0.96
1.09
1.04
2.70
1.90
3.88



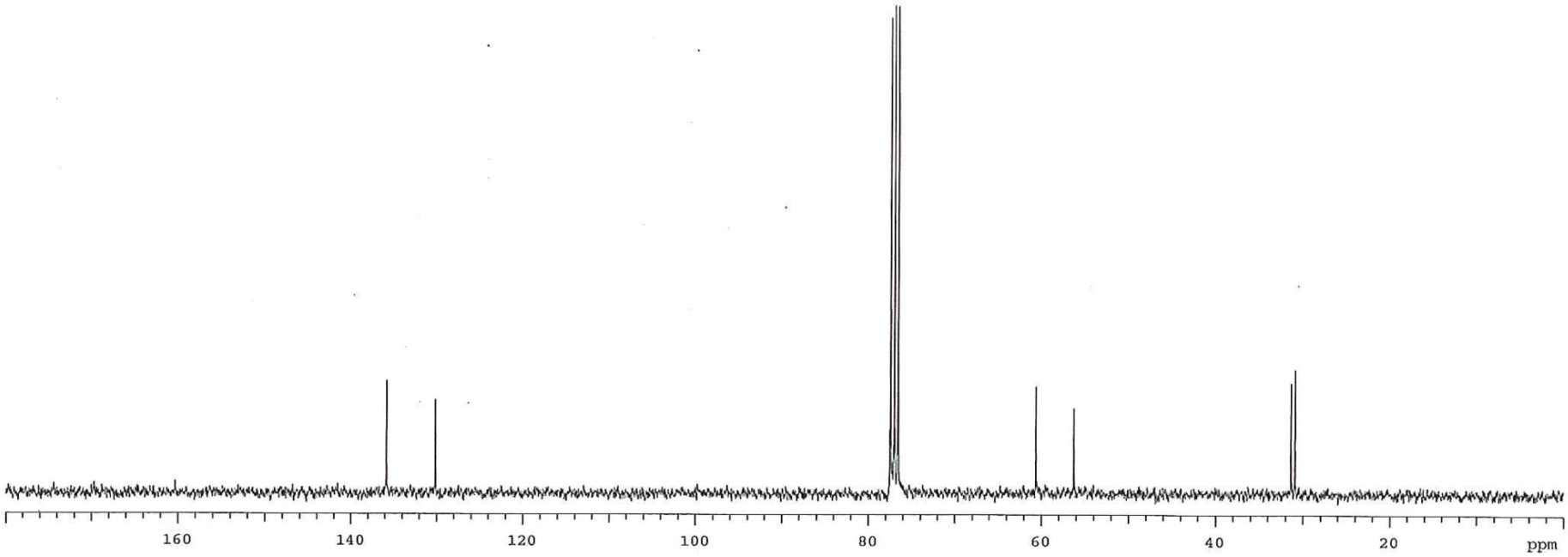
17bb

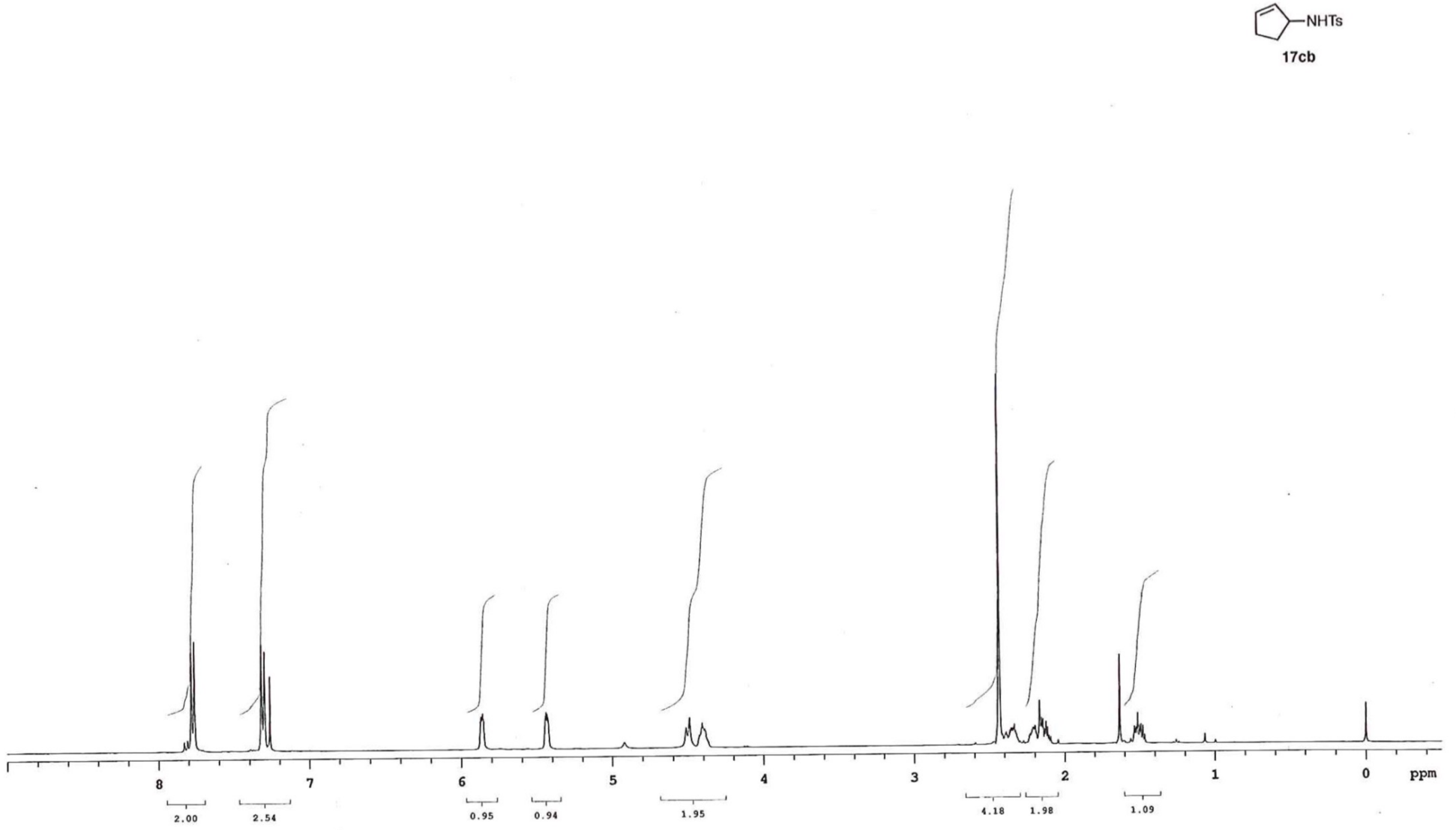


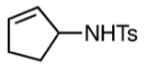

NHSO3Me
17ca
8
7
6
5
4
3
2
1
0
ppm
1.05
1.00
1.91
2.94
3.18
1.05



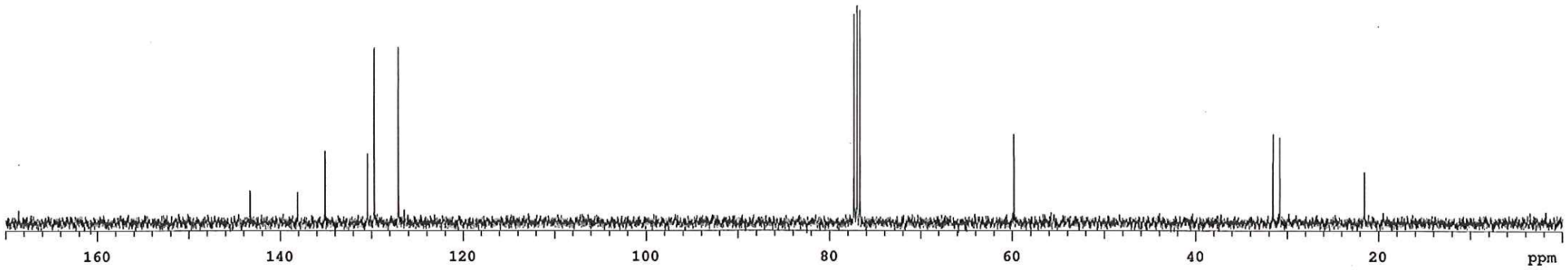
17ca

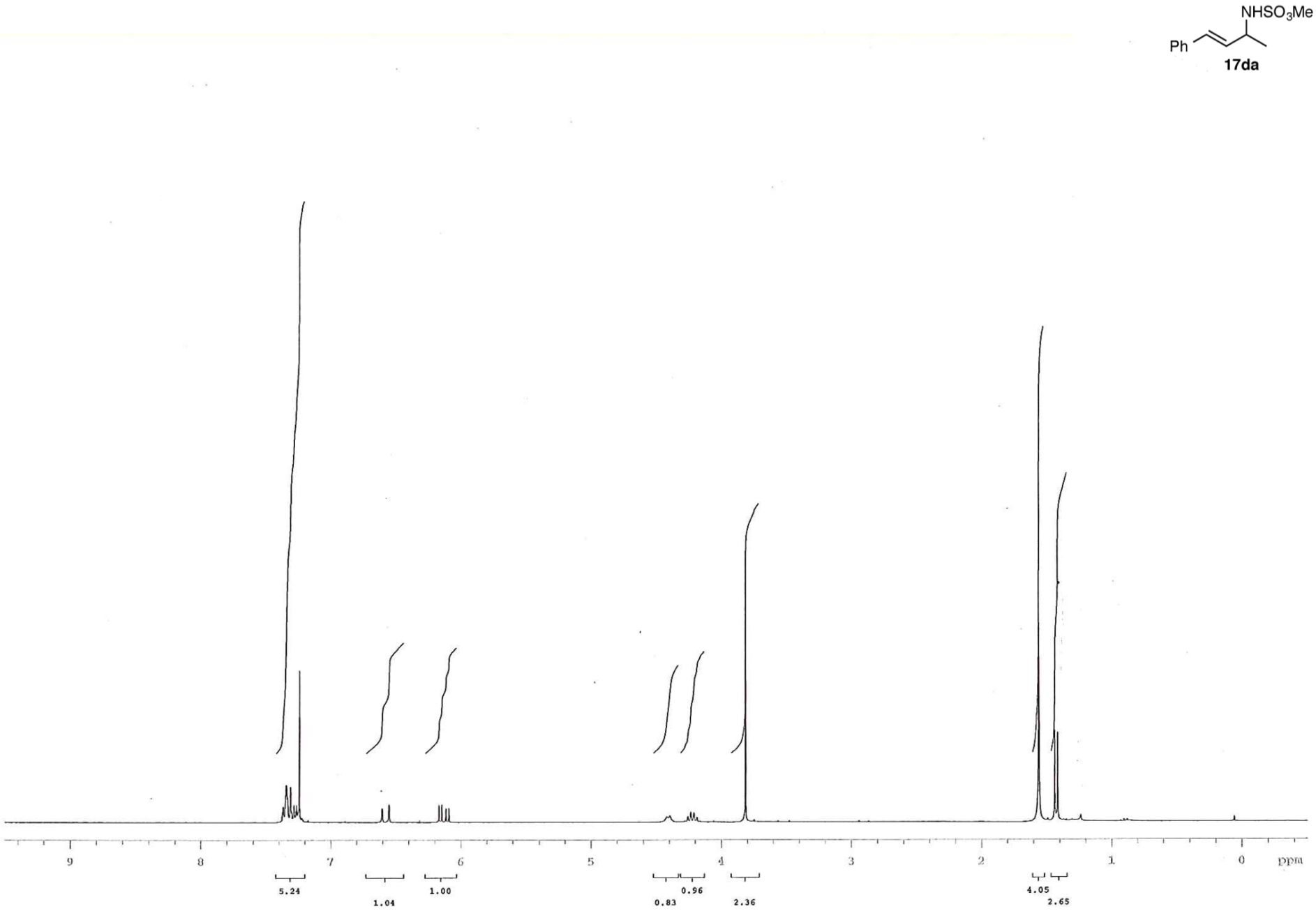


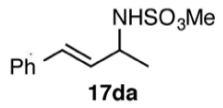

NHTs
17cb
8
7
6
5
4
3
2
1
0
ppm
2.00
2.54
0.95
0.94
1.95
4.18
1.98
1.09



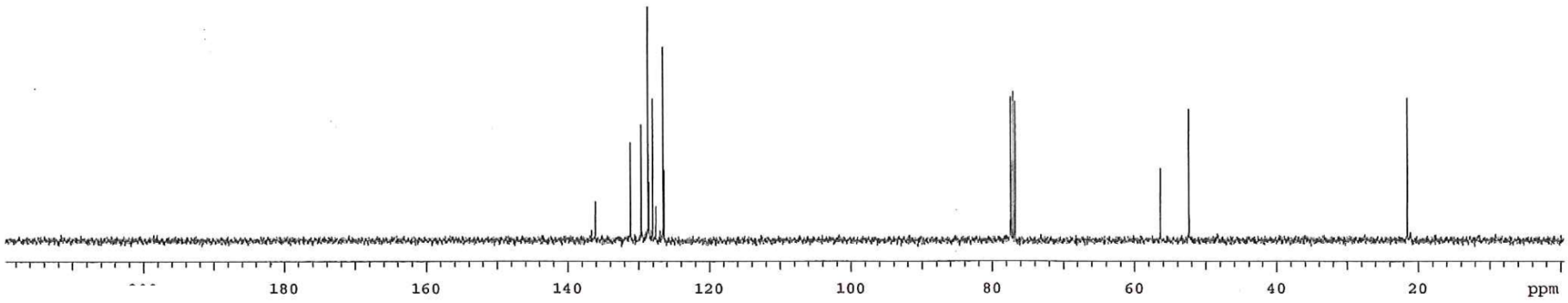
17cb

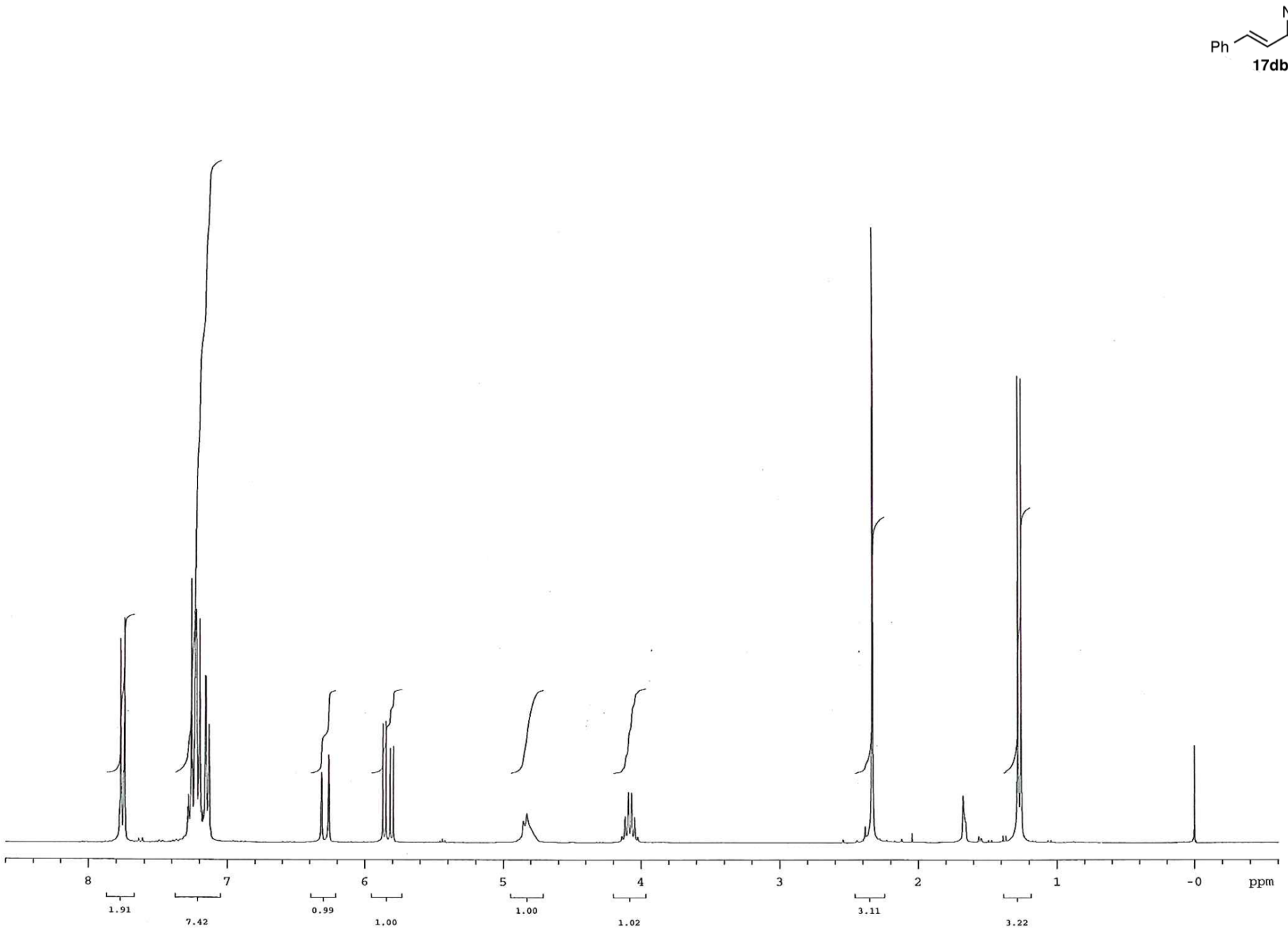


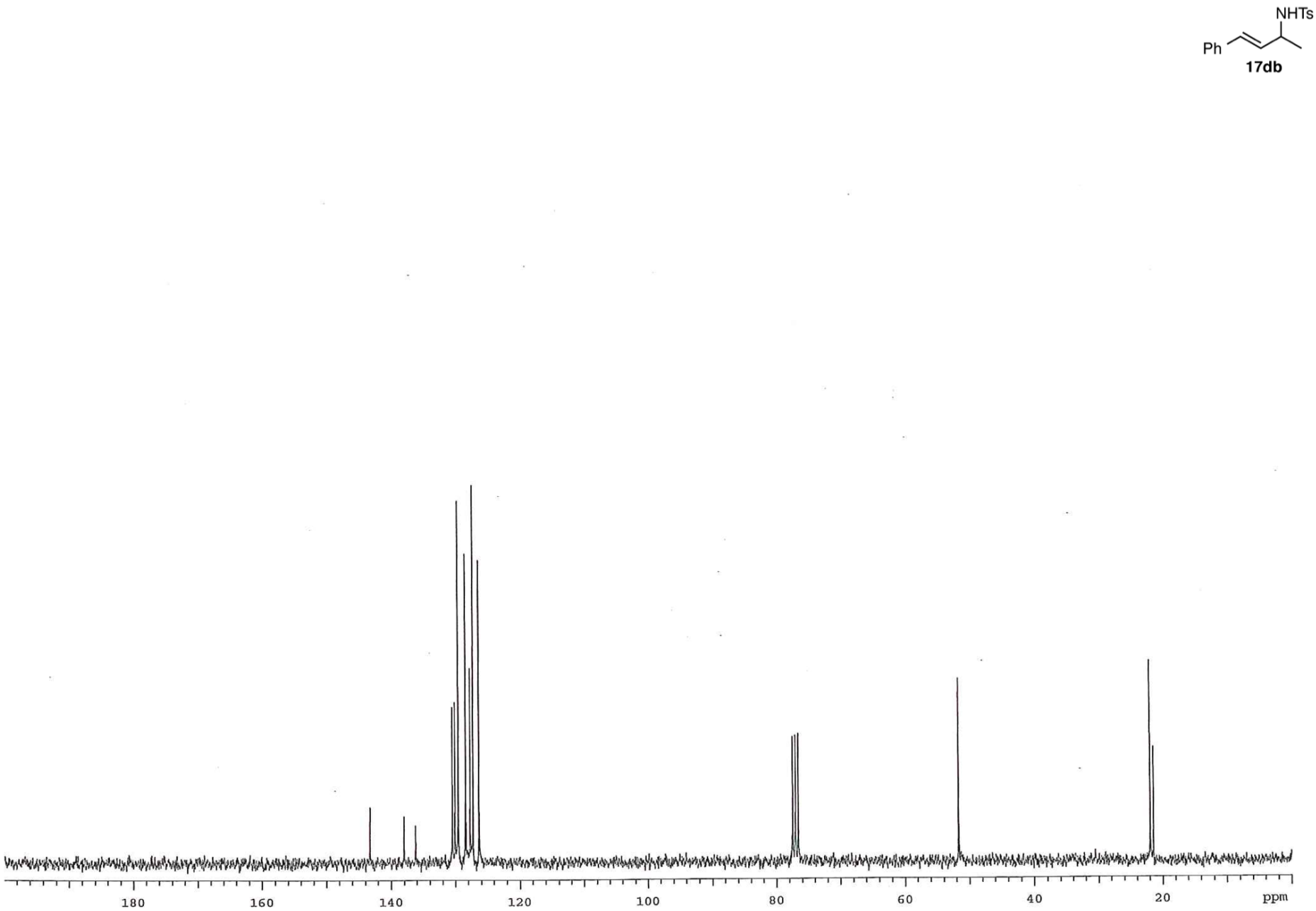

NHSO3Me
Ph
17da
9
8
7
6
5
4
3
2
1
0
ppm
5.24
1.04
1.00
0.83
0.96
2.36
4.05
2.65



17da




NHTs
Ph
17db
8
7
6
5
4
3
2
1
-0
ppm
1.91
7.42
0.99
1.00
1.00
1.02
3.11
3.22


NHTs
Ph
17db
180
160
140
120
100
80
60
40
20
ppm