

# Supporting Information

## Chromium(0)-promoted $[6\pi+2\pi]$ cycloadditions of allenes with cycloheptatriene

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### Table of Contents

1. General -----	S2
2. Experimental procedures for allenes <b>2c</b> , <b>4a</b> , ( <i>S</i> )- <b>4a</b> and <b>4b-c</b> , and characterization data -	S2
3. General procedures for cycloadditions between ( $\eta^6$ -cycloheptatriene)tricarbonyl-chromium(0) (CHT-Cr) complex <b>1</b> and allenes, and characterization data -----	S7
4. Cycloaddition between <b>1</b> and ( <i>S</i> )- <b>4a</b> , and determination of ee -----	S23
5. Some examples of stereochemical rationales -----	S24
5.1. Indirect stereochemical assignment for <b>3c</b> via its alcohol derivative <b>17</b> -----	S24
5.2. Representative $^1\text{H}$ NMR NOE data for ( <i>E</i> )- <b>5a</b> , ( <i>Z</i> )- <b>8e</b> , and <b>9h-i</b> -----	S25
6. Derivatization of <b>5a</b> into <i>p</i> -nitrobenzoate ester <b>18</b> , and X-Ray structure of <b>18</b> -----	S25
7. Deprotection of TBS-protecting groups in <b>11</b> , and X-Ray structure of the corresponding diol <b>19</b> -----	S27
8. Copies of the $^1\text{H}$ and $^{13}\text{C}$ NMR spectra for new compounds -----	S29

## 1. General

All reactions were carried out under nitrogen using standard syringe, cannula and septa techniques. Reagents and solvents that were commercially available were used as received, except tetrahydrofuran: distilled over sodium-benzophenone ketyl; dichloromethane: distilled over calcium hydride. Thin-layer chromatography (TLC) was performed with 0.25 mm precoated glass silica gel plates (EMD, Silica Gel 60F<sub>254</sub>). Detection was done by UV (254 nm) followed by using visualizing reagents such as *p*-anisaldehyde or phosphomolybdic acid. Flash chromatography was performed with Whatman silica gel (Purasil 60Å, 230-400 Mesh) and refers to the method of Still *et al.*<sup>1</sup> IR spectra were recorded on a Perkin Elmer Spectrum RX-1 FT-IR system. Positions of absorption bands are reported in cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded respectively at 400 or 300 and 100 or 75 MHz on a Varian Mercury 400 NMR spectrometer or Varian Unity 300 NMR. Chemical shifts are reported in ppm relative to the residual solvent signal (<sup>1</sup>H NMR:  $\delta$  7.26; <sup>13</sup>C: 77.0 for CDCl<sub>3</sub>, <sup>1</sup>H NMR:  $\delta$  7.12; <sup>13</sup>C: 128.0 for C<sub>6</sub>D<sub>6</sub>). Multiplicities are described as s (singlet), d (doublet), dd, ddd, etc. (doublet of doublets, doublet of doublets of doublets, etc.), t (triplet), q (quartet), quint (quintuplet), m (multiplet), and further qualified as br (broad), c (complex); coupling constants (*J*) are reported in Hz. The protons were assigned with the aid of COSY, and the carbons with the aid of Dept and HMQC experiments. Low resolution mass spectra were recorded on a Micromass QuattroLC triple quadrupole spectrometer in the ElectroSpray Ionisation (ESI) mode. High resolution mass spectra were performed with a Micromass GCT using a solid state probe in the Electron Impact (EI, ionization potential of 70eV) mode. GC-MS was carried out using a Agilent Technologies 6890N GC system instrument coupled with a mass detector (EI mode at an ionization potential of 70eV). Melting points (Mp) were obtained on a Thomas-Hoover Unimelt apparatus in open capillary tubes and are not corrected. Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter using a sodium lamp (D line, 589.25 nm) in a quartz cell (cell length = 1 dm). Elemental analyses were performed by Atlantic Microlab, Inc. in Georgia.

## 2. Experimental procedures for allenes **2c**, **4a**, (*S*)-**4a** and **4b-c**, and characterization data

Allene **7e** was commercially available and used as supplied.

Allenes **2a**<sup>2</sup>, **2b**<sup>3</sup>, **7a**<sup>4</sup>, **7b-d**<sup>5,6</sup>, **7f-g**,<sup>7</sup> **7h**<sup>8</sup>, **7i**<sup>9</sup> have been prepared as described in the literature.

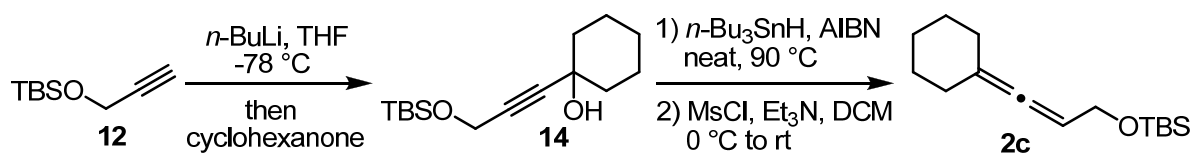
<sup>1</sup> Still, W. C.; Khan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

<sup>2</sup> Vermeer, P.; Meijer, J.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 112-114.

<sup>3</sup> Bailey, W. J.; Pfeifer, C. R. *J. Org. Chem.* **1955**, *20*, 95-101.

<sup>4</sup> Moreau, J. L.; Gaudemard, M. *J. Organomet. Chem.* **1976**, *108*, 159-154.

***tert*-Butyl(3-cyclohexylideneallyloxy)dimethylsilane (2c).**



To a solution of *tert*-butyldimethyl(prop-2-ynyloxy)silane **12**<sup>10</sup> (2.04 g, 12 mmols) in THF (12 mL) was introduced at -78 °C *n*-BuLi (2.5 M in hexanes, 4.8 mL, 12 mmols) over 5 min, and the resulting mixture was stirred for 2 h at the same temperature. Then, cyclohexanone (1.24 mL, 12 mmols) was added and the mixture was stirred at -78 °C for two more hours. The temperature was allowed to warm to rt and sat. aq. NH<sub>4</sub>Cl was added. The mixture was extracted with EtOAc (3 times); the organic extracts were combined, washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated. The crude residue was purified by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 98:2) to afford **14**<sup>11</sup> (2.04 g, 64%) as a clear liquid which solidifies at rt: **R<sub>f</sub>** 0.13 (pentane/EtOAc, 96:4); **IR** (thin film): 3272 (broad, OH), 2358 (C≡C), 1101, 1071 cm<sup>-1</sup>(C-O-Si); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ = 4.32 (s, 2H, CH<sub>2</sub>OTBS), 2.27 (br s, 1H, OH), 1.87-1.83 (m, 2H, CH<sub>2</sub>), 1.66-1.61 (m, 2H, CH<sub>2</sub>), 1.54-1.20 (m, 6H, CH<sub>2</sub>), 0.87 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.09 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 88.4, 82.6 (C≡C), 68.4 (C-OH), 51.7 (CH<sub>2</sub>OTBS), 39.7 (CH<sub>2</sub> of cyclohexane), 25.7 (C(CH<sub>3</sub>)<sub>3</sub>), 25.1, 23.1 (CH<sub>2</sub> of cyclohexane), 18.2 (C(CH<sub>3</sub>)<sub>3</sub>), -5.1 (Si(CH<sub>3</sub>)<sub>2</sub>); **MS** (ESI): *m/z* = 291 (M+Na<sup>+</sup>); **HRMS** (EI): *m/z* calcd for C<sub>15</sub>H<sub>26</sub>OSi (M<sup>+</sup> - H<sub>2</sub>O): 250.1753; found: 250.1747.

Then, according to a literature procedure,<sup>12</sup> a mixture of **14** (2.04 g, 7.6 mmols) and *n*-Bu<sub>3</sub>SnH (3.06 mL, 11.4 mmols) was heated (oil-bath temperature 90 °C) for 2h in the presence of a catalytic amount of AIBN (62 mg, 5 mol %). The mixture was then cooled to rt and 10 mL of DCM was added. Et<sub>3</sub>N (2.12 mL, 15.2 mmols) and MsCl (0.89 mL, 11.4 mmols) were introduced at 0 °C, and the reaction mixture was warmed to rt and stirred for 30 min. The mixture was poured into aq. 1N HCl and extracted with DCM. The combined organic extracts were washed with sat. aq. NaHCO<sub>3</sub>, dried (MgSO<sub>4</sub>), filtered and concentrated. The crude residue was purified by flash chromatography on SiO<sub>2</sub> (100%

<sup>5</sup> Lee, K.; Seomoon, D.; Lee, P. H. *Angew. Chem. Int. Ed.* **2002**, *41*, 3901-3903.

<sup>6</sup> (a) Nakamura, H.; Kamakura, T.; Ishikura, M.; Biellmann, J.-F. *J. Am. Chem. Soc.* **2004**, *126*, 5958-5959. (b) Nakamura, H.; Kamakura, T.; Onagi, S. *Org. Lett.* **2006**, *8*, 2095-2098.

<sup>7</sup> (a) Crabbé, P.; Nassim, B.; Robert-Lopes, M.-T. *Org. Synth.* **1984**, *63*, 203-205. (b) Searles, S.; Li, Y.; Nassim, B.; Robert-Lopes, M.-T.; Tran, P. T.; Crabbé, P. *J. Chem. Soc. Perkin Trans. I* **1984**, 747-751.

<sup>8</sup> Weiberth, F. J.; Hall, S. S. *J. Org. Chem.* **1985**, *50*, 5308-5314.

<sup>9</sup> Stergiades, I. A.; Tius, M. A. *J. Org. Chem.* **1999**, *64*, 7547-7551.

<sup>10</sup> You, Z.-W.; Jiang, Z.-X.; Wang, B.-L.; Qing, F.-L. *J. Org. Chem.* **2006**, *71*, 7261-7267.

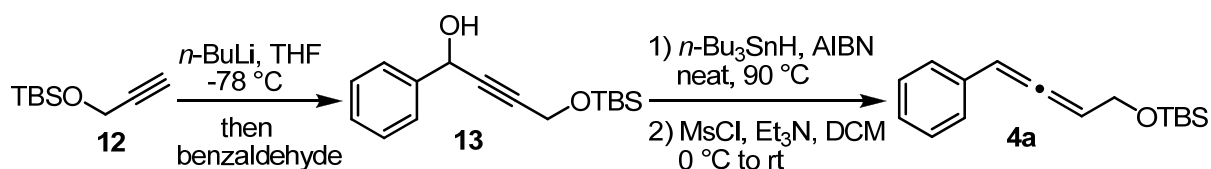
<sup>11</sup> Synthesis of compound **14** was mentioned in the literature: Shibata, T.; Takami, K.; Arai, Y.; Tsuchikama, K.; Maekawa, S. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1937-1938; but no spectroscopic data were reported.

<sup>12</sup> Konoike, T.; Araki, Y. *Tetrahedron Lett.* **1992**, *33*, 5093-5096.

pentane) to afford **2c** (168mg, 9%) as a clear liquid\*: **R<sub>f</sub>** 0.13 (100% pentane); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.11-5.05 (m, 1H, =CHCH<sub>2</sub>OTBS), 4.14 (d, *J* = 6.3 Hz, 2H, CH<sub>2</sub>OTBS), 1.70-1.50 (m, 10H, CH<sub>2</sub> of cyclohexane), 0.90 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.08 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); **GC-MS** (EI): relative t<sub>R</sub>: t<sub>R</sub> = 9.09 min (*m/z* = 252 (M<sup>+</sup>)).

\* **2c** was contaminated by 35 mg of (*Z, E*)-*tert*-butyl(3-cyclohexenylallyloxy)-dimethylsilane.

***tert*-Butyldimethyl(4-phenylbuta-2,3-dienyloxy)silane (4a).**

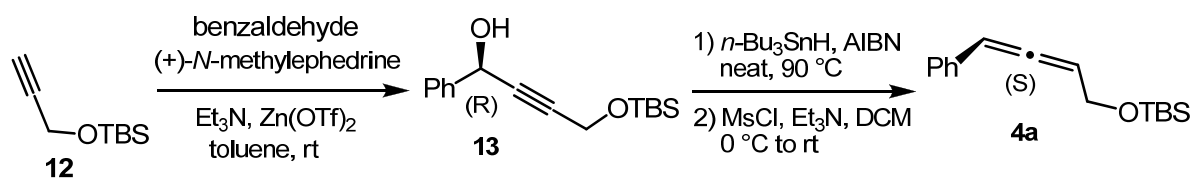


Synthesis of compound **4a** was mentioned in the literature,<sup>12</sup> but no spectroscopic data were reported. Following the procedure described above for synthesis of **14**, addition of **12** (1.7 g, 10 mmols) to benzaldehyde (1 mL, 10 mmols) furnished, after purification by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 100:0 to 90:10), alcohol **13**<sup>13</sup> (2.51 g, 91%) as a yellow liquid: **R<sub>f</sub>** 0.20 (pentane/EtOAc, 95:5); **IR** (thin film): 3382 (broad, OH), 2360, 2338 (C≡C), 1127, 1082, 1004 cm<sup>-1</sup> (C-O-Si); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.54-7.32 (m, 5H, H<sub>arom</sub>), 5.50 (br s, 1H, CHOH), 4.40 (br d, *J* = 1.6 Hz, 2H, CH<sub>2</sub>), 2.12 (br s, 1H, OH), 0.91 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.11 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.8 (*i*-C<sub>arom</sub>), 128.8 (*m*-CH<sub>arom</sub>), 128.5 (*p*-CH<sub>arom</sub>), 126.9 (*o*-CH<sub>arom</sub>), 85.5, 84.8 (C≡C), 64.8 (CHOH), 52.0 (CH<sub>2</sub>), 26.0 (C(CH<sub>3</sub>)<sub>3</sub>), 18.5 (C(CH<sub>3</sub>)<sub>3</sub>), -4.9 (Si(CH<sub>3</sub>)<sub>2</sub>); **MS** (ESI): *m/z* = 277 (M+H<sup>+</sup>), 299 (M+Na<sup>+</sup>); **HRMS** (EI): *m/z* calcd for C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>Si (M<sup>+</sup>): 276.1546; found: 276.1546.

Then, compound **13** (2.21 g, 8 mmols) was engaged in the procedure described above for synthesis of **2c**. Purification by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 100:0 to 98:2) gave **4a** (1.02 g, 49%) as a yellow liquid: **R<sub>f</sub>** 0.29 (pentane/EtOAc, 98:2); **IR** (thin film): 1951 (=C=), 1132, 1084 cm<sup>-1</sup> (C-O-Si); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.30-7.18 (m, 5H, H<sub>arom</sub>), 6.24 (dt, *J* = 6.6, 2.4 Hz, 1H, PhCH=C=), 5.69 (br q, *J* = 6.4 Hz, 1H, =C=CHCH<sub>2</sub>), 4.33-4.30 (m, 2H, CH<sub>2</sub>), 0.91 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.10, 0.09 (2\*s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 204.9 (=C=), 134.5 (*i*-C<sub>arom</sub>), 128.8, 127.2, 127.1 (*o, m, p*-CH<sub>arom</sub>), 96.3, 96.1 (HC=C=CH), 61.6 (CH<sub>2</sub>), 26.2 (C(CH<sub>3</sub>)<sub>3</sub>), 18.6 (C(CH<sub>3</sub>)<sub>3</sub>), -4.81, -4.85 (Si(CH<sub>3</sub>)<sub>2</sub>); **HRMS** (EI): *m/z* calcd for C<sub>16</sub>H<sub>24</sub>OSi (M<sup>+</sup>): 260.1596; found: 260.1589.

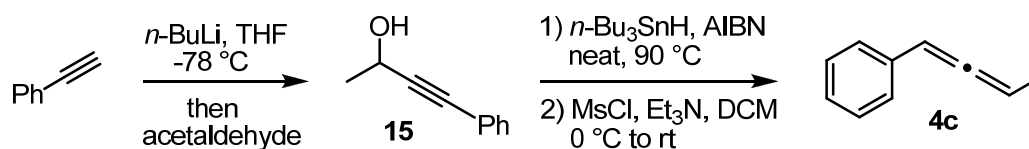
<sup>13</sup> Synthesis of compound **13** was mentioned in the literature: Jiang, B.; Feng, Y. *Tetrahedron Lett.* **2002**, *43*, 2975-2978; but no spectroscopic data were reported.

### Preparation of enantioenriched (S)-4a.



According to a literature procedure,<sup>14</sup> Zn(OTf)<sub>2</sub> (2 g, 5.5 mmols) and (+)-*N*-methylephedrine (1.07 g, 6 mmols) were mixed together and purged with argon for 15 min. Then, toluene (15 mL) and freshly distilled triethylamine (0.84 mL, 6 mmols) were added, and the resulting mixture was stirred at rt for 2 hours. *tert*-Butyldimethyl(prop-2-ynyloxy)silane **12** (1.02 g, 6 mmols) was introduced, followed after 30 min of stirring by benzaldehyde (0.51 mL, 5 mmols), and the reaction mixture was stirred at rt for 20 h. The mixture was quenched with sat. aq. NH<sub>4</sub>Cl and extracted with EtOAc (3 times). The combined organic extracts were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated. The crude residue was purified by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 100:0 to 90:10) to give (*R*)-**13** (436 mg, 31%) in 88% ee ( $[\alpha]_{\text{D}}^{23} = +12.7^\circ$  (*c* = 1.02, CHCl<sub>3</sub>)). The ee was determined by <sup>1</sup>H-NMR analysis after derivatization into the corresponding Mosher ester<sup>15</sup> ((*R*)-(-)-MTPA chloride, Et<sub>3</sub>N, DMAP, CDCl<sub>3</sub>, rt, 1h). Then, compound (*R*)-**13** (436 mg, 1.58 mmols) was engaged in the procedure described above for synthesis of **2c** to afford, after flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 100:0 to 98:2), (*S*)-**4a** (135 mg, 33%) in 60% ee as measured by <sup>1</sup>H-NMR analysis with chiral shift reagents (+)-Yb(tfc)<sub>3</sub> and Ag(fod).<sup>16</sup>  $[\alpha]_{\text{D}}^{23} = +177^\circ$  (*c* = 1.04, acetone).

### 1-(Buta-1,2-dienyl)benzene (4c).



Synthesis of compound **4c** was already mentioned in the literature; however **4c** was here prepared in a manner analogous to that for allene **2c**. Following the procedure described above for synthesis of **14**, addition of phenylacetylene (2.72 mL, 24 mmols) to acetaldehyde (1.35 mL, 24 mmols) gave, after purification by flash chromatography on SiO<sub>2</sub>

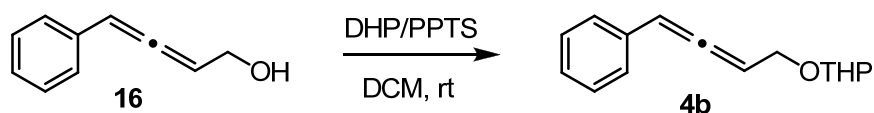
<sup>14</sup> a) Frantz, D. E.; Fässler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 1806-1807. (b) Anand, N. K.; Carreira, E. M. *J. Am. Chem. Soc.* **2001**, *123*, 9687-9688. (c) Boyall, D.; Frantz, D. E.; Carreira, E. M. *Org. Lett.* **2002**, *4*, 2605-2606.

<sup>15</sup> Ward, D. E.; Rhee, C. K. *Tetrahedron Lett.* **1991**, *32*, 7165-7166.

<sup>16</sup> Mannschreck, A.; Munninger, W.; Burgemeister, T.; Gore, J.; Cazes, B. *Tetrahedron* **1986**, *42*, 399-408.

(pentane/EtOAc, 96:4), alcohol **15**<sup>17</sup> (595 mg, 17%) as a slightly yellow liquid: **R<sub>f</sub>** 0.28 (pentane/EtOAc, 96:4); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.42-7.30 (m, 5H, H<sub>arom</sub>), 4.76 (q, *J* = 6.6 Hz, 1H, CHOH), 1.85 (br s, 1H, OH), 1.55 (d, *J* = 6.6 Hz, 3H, CH<sub>3</sub>). Then, compound **15** (837 mg, 5.73 mmols) was engaged in the procedure described above for synthesis of **2c** to afford, after flash chromatography on SiO<sub>2</sub> (100% pentane), **4c** (535 mg, 72%) as a slightly yellow liquid: **R<sub>f</sub>** 0.69 (100% pentane); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.40-7.10 (m, 5H, H<sub>arom</sub>), 6.12-6.07 (m, 1H, =CHPh), 5.54 (br quint, *J* = 7.2 Hz, 1H, =CHCH<sub>3</sub>), 1.78 (dd, *J* = 7.2, 3.0 Hz, 3H, CH<sub>3</sub>); GC-MS (EI): *m/z* = 130 (M<sup>+</sup>). The <sup>1</sup>H NMR data were in full agreement with those reported in the literature.<sup>18</sup>

## 2-(4-Phenylbuta-2,3-dienyloxy)tetrahydro-2H-pyran (**4b**).



The title compound was prepared from 4-phenylbuta-2,3-dien-1-ol **16** by simple protection.<sup>19</sup> To a solution of **16** (424 mg, 2.9 mmols) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added successively dihydropyran (530 μL, 5.8 mmols) and PPTS (a pinch), and the resulting solution was stirred at rt for 2.5 h. The mixture was diluted with water. The water layer was separated and extracted with DCM. The organic layers were combined, washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated. Purification of the residue by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 98:2) furnished **4b** (496 mg, 74%) as a slightly yellow liquid: **R<sub>f</sub>** 0.25 (pentane/EtOAc, 98:2); IR (thin film): 1951 (=C=), 1124, 1069, 1027 cm<sup>-1</sup> (C-O); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.32-7.15 (m, 5H, H<sub>arom</sub>), 6.27-6.23 (m, 1H, PhCH=C=), 5.71 (br q, *J* = 6.4 Hz, 1H, =CHCH<sub>2</sub>OTHP), 4.76-4.72 (m, 1H, O-CH-O), 4.38-4.32 (m, 1H, CHHOTHP), 4.21-4.15 (m, 1H, CHHOTHP), 3.92-3.86 (m, 1H, CHHO of THP), 3.55-3.48 (m, 1H, CHHO of THP), 1.90-1.50 (m, 6H, CH<sub>2</sub> of THP); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 205.9, 205.8 (=C=), 133.9\*<sup>20</sup> (*i*-C<sub>arom</sub>), 128.5, 127.0, 126.8\* (*o*, *m*, *p*-CH<sub>arom</sub>), 97.7\* (O-CH-O), 95.6, 95.5, 92.7, 92.6 (HC=C=CH), 64.6\*, 62.2 (CH<sub>2</sub>-O), 30.5\*, 25.4, 19.4\* (CH<sub>2</sub> of THP); GC-MS (EI): *m/z* = 230 (M<sup>+</sup>); HRMS (ESI-TOF): *m/z* calcd for C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>Na (M+Na<sup>+</sup>): 253.1204; found: 253.1209.

<sup>17</sup> Tanaka, K.; Shoji, T. *Org. Lett.* **2005**, *7*, 3561-3563.

<sup>18</sup> Riveiros, R.; Rodríguez, D.; Pérez Sestelo, J.; Sarandeses, L. A. *Org. Lett.* **2006**, *8*, 1403-1406.

<sup>19</sup> Synthesis of 4-phenylbuta-2,3-dien-1-ol **16** is well-described in the literature: Vinson, N. A.; Day, C. S.; Welker, M. E. *Organometallics* **2000**, *19*, 4356-4368. However, synthesis of **4b** has never been reported so far.

<sup>20</sup> The \* at <sup>13</sup>C NMR data points indicates a doublet due to the presence of the diastereomers of **4b** associated with the stereocenter of THP group.

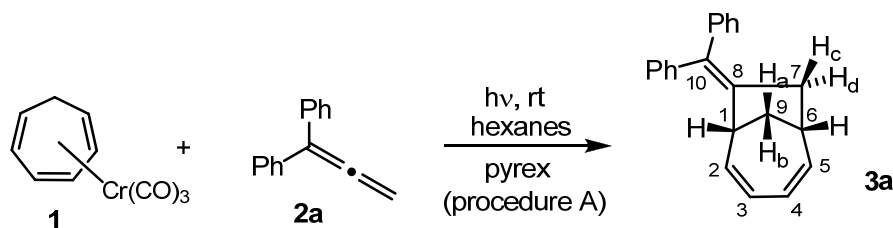
### 3. General procedures for cycloadditions between ( $\eta^6$ -cycloheptatriene)tricarbonylchromium(0) (CHT-Cr) complex **1** and allenes, and characterization data

**Procedure A:** In a dried pyrex tube, CHT-Cr **1**<sup>21</sup> (1 equiv) and allene (2 equiv) were diluted in hexanes ( $c = 2 \times 10^{-3}$  M in **1**). The tube was placed 14 cm from a water-cooled pyrex immersion well containing a Canrad-Hanovia 450W medium-pressure mercury vapor lamp. The resulting red solution was irradiated with a concomitant moderate N<sub>2</sub> bubbling for periods of 4-6 h. After irradiation, the solution usually turned yellow\* (disappearance of all CHT-Cr) with a precipitate in the bottom of the tube. The reaction mixture was filtered over a pad of celite and the cake washed with hexanes. The filtrate was concentrated and the resultant crude residue was purified by flash chromatography on SiO<sub>2</sub>.

\* In some cases (when using some allenes or when working with higher concentrated solutions ( $c = 4 \times 10^{-3}$  M in **1**)), the color of the reaction mixture was still orange-red after irradiation, indicating that all CHT-Cr was not consumed. Consequently, in order to simplify purification, after filtration, the filtrate was reduced in volume to 10 mL and stirred with P(OMe)<sub>3</sub> (2-3 mL) at rt until the solution turned yellow to colorless (16-20h) (decomplexation of CHT-Cr). Concentration was followed by flash chromatography on SiO<sub>2</sub>.

**Procedure B:** In a dried pyrex tube placed 14 cm from a water-cooled pyrex immersion well containing the medium-pressure mercury vapor lamp, CHT-Cr **1** (1 equiv) was diluted with hexanes ( $c = 2 \times 10^{-3}$  M). To the resultant red solution was introduced slowly a solution of allene (2 equiv) in hexanes using a syringe pump (10 mL/h), under irradiation and with moderate N<sub>2</sub> bubbling. After addition, irradiation was kept for an additional time (4-6 h). The mixture was then filtered over celite and the cake washed with hexanes. The filtrate was concentrated and the resultant crude residue was purified by flash chromatography on SiO<sub>2</sub>. When an orange-red solution was obtained after irradiation, treatment with P(OMe)<sub>3</sub> was performed as described above in the procedure A.

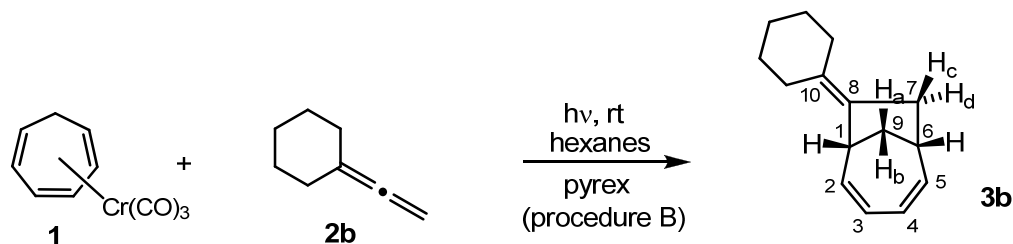
#### 7-(Diphenylmethylene)bicyclo[4.2.1]nona-2,4-diene (**3a**) (Table 1, entry 1).



<sup>21</sup> Complex **1** was prepared by a literature procedure: Rigby, J. H.; Fales, K. R. *Org. Synth.* **2000**, 77, 121-134.

Following the Procedure A, a solution of CHT-Cr **1** (50 mg, 0.22 mmols) and allene **2a** (84 mg, 0.44 mmols) in hexanes (100 mL) was irradiated for 5 h. Work-up and purification by flash chromatography on SiO<sub>2</sub> (100% pentane) provided **3a** (31 mg, 50%) as a colorless oil: **R<sub>f</sub>** 0.53 (100% pentane); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.32-7.13 (m, 10H, H<sub>arom</sub>), 6.02 (dd,  $J$  = 9.6, 8.0 Hz, 1H, 2-H), 5.70-5.57 (m, 3H, 3,4,5-H), 3.43 (br t,  $J$  = 6.4 Hz, 1H, 1-H), 2.76 (d,  $J$  = 17.2 Hz, 1H, 7-H<sub>d</sub>), 2.78-2.72 (m (q overlapping with d at 2.76 ppm), 1H, 6-H), 2.64 (dd,  $J$  = 17.2, 8.0 Hz, 1H, 7-H<sub>c</sub>), 2.29-2.23 (m, 1H, 9-H<sub>a</sub>), 1.91 (br d,  $J$  = 12 Hz, 1H, 9-H<sub>b</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.6 (C-8), 144.3, 142.7 (*i*-C<sub>arom</sub>), 138.8, 137.2 (C-2, C-5), 133.1 (C-10), 129.3, 129.2, 128.3, 128.2, 126.6, 126.4, 123.8 (*o*, *m*, *p*-CH<sub>arom</sub>, C-3, C-4), 44.9 (C-7), 44.2 (C-1), 38.7 (C-6), 32.6 (C-9); **HRMS** (EI):  $m/z$  calcd for C<sub>22</sub>H<sub>20</sub> (M<sup>+</sup>): 284.1559; found: 284.1574.

### 7-Cyclohexylidenebicyclo[4.2.1]nona-2,4-diene (**3b**) (Table 1, entry 2).

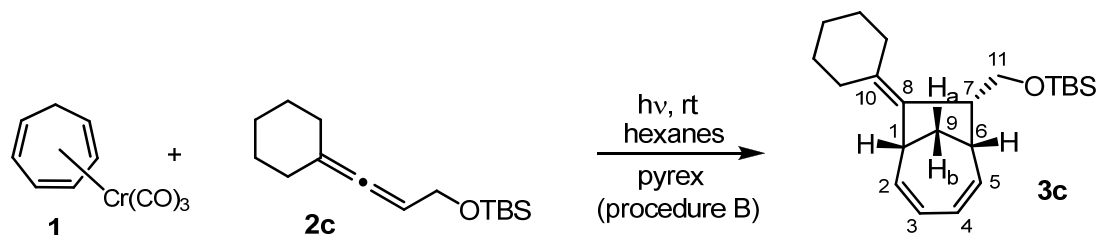


According to the procedure B, a solution of vinylidenecyclohexane (**2b**) (86 mg, 0.8 mmols) in hexanes (20 mL) was added over 2 h to a solution of CHT-Cr **1** (91 mg, 0.4 mmols) in hexanes (180 mL), under irradiation. After addition, irradiation was kept 4 more hours. Work-up and purification by flash chromatography on SiO<sub>2</sub> (100% cyclohexane) furnished product **3b** (41 mg, 51%) as a colorless oil: **R<sub>f</sub>** 0.80 (100% cyclohexane); **IR** (thin film): 3015, 2923, 2849, 1598, 1444 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.06-5.93 (m, 2H, H<sub>ethylenic</sub>), 5.66-5.53 (m, 2H, H<sub>ethylenic</sub>), 3.42 (br t,  $J$  = 8.1 Hz, 1H, 1-H), 2.74-2.67 (m, 1H, 6-H), 2.60 (d,  $J$  = 15.9 Hz, 1H, 7-H<sub>d</sub>), 2.46 (dd,  $J$  = 15.9, 7.7 Hz, 1H, 7-H<sub>c</sub>), 2.26-2.01 (m, 7H, 9-H<sub>a</sub>, H of cyclohexane), 1.93 (dd,  $J$  = 11.7, 1.8 Hz, 1H, 9-H<sub>b</sub>), 1.60-1.40 (m, 4H, H of cyclohexane); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.7 (C-8 or C-10), 138.4, 137.2 (C-2, C-5), 129.2 (C-8 or C-10), 123.3, 122.9 (C-3, C-4), 44.1 (C-7), 42.1 (C-1), 39.1 (C-6), 33.5, 32.7, 31.2, 27.6, 27.5, 26.7 (C-9, CH<sub>2</sub> of cyclohexane); **HRMS** (EI):  $m/z$  calcd for C<sub>15</sub>H<sub>20</sub> (M<sup>+</sup>): 200.1565; found: 200.1570.

(The product was contaminated by a small amount (4%, based on GC) of isomer 7-cyclohexenylbicyclo[4.2.1]nona-2,4-diene).

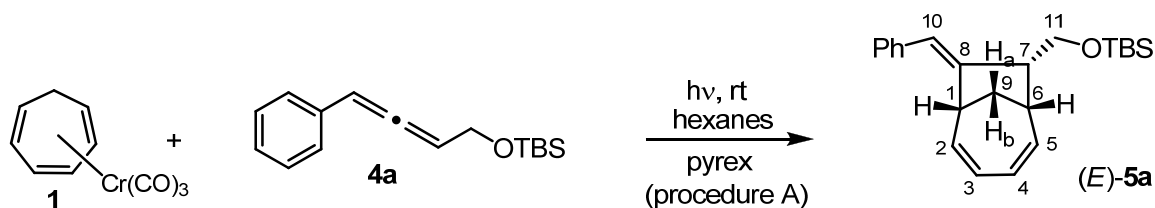


***tert*-Butyl((8-cyclohexylidenebicyclo[4.2.1]nona-2,4-dien-7-yl)methoxy)dimethylsilane (3c) (Table 1, entry 3).**



According to the procedure B, a solution of **2c** (168 mg, 0.67 mmols) in hexanes (16 mL) was added over 1.5 h to a solution of CHT-Cr **1** (75 mg, 0.33 mmols) in hexanes (150 mL), under irradiation. After addition, irradiation was kept 6 more hours. Work-up and purification by flash chromatography on SiO<sub>2</sub> (100% cyclohexane) furnished product **3c** (39 mg, 35%) as a colorless oil: *R<sub>f</sub>* 0.45 (100% cyclohexane); **IR** (thin film): 3017 (CH<sub>ethylene</sub>), 1106, 1085, 1056 cm<sup>-1</sup> (broad, C-O-Si); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.98 (dd, *J* = 11.7, 7.8 Hz, 1H, 5-H), 5.83-5.71 (m, 2H, 4-H, 2-H), 5.56 (dd, *J* = 11.7, 7.8 Hz, 1H, 3-H), 3.75 (dd, *J* = 9.6, 4.2 Hz, 1H, 11-H), 3.44 (dd, *J* = 10.8, 9.6 Hz, 1H, 11-H'), 3.30 (br t, *J* = 7.8 Hz, 1H, 1-H), 3.11-2.94 (m, 2H, 6-H, 7-H), 2.20-1.94 (m, 7H, 9-H<sub>a</sub>, H of cyclohexane), 1.98 (br d, *J* = 12.4 Hz, 1H, 9-H<sub>b</sub>), 1.60-1.43 (m, 4H, H of cyclohexane), 0.89 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.03, 0.02 (2\*s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.0 (C-8 or C-10), 137.0, 135.1 (C-2, C-5), 130.0 (C-8 or C-10), 125.0, 123.3 (C-3, C-4), 64.0 (C-11), 54.5 (C-7), 44.1 (C-1), 40.7 (C-6), 33.7 (CH<sub>2</sub> of cyclohexane), 31.9 (C-9), 30.3, 28.2, 28.0, 26.6 (CH<sub>2</sub> of cyclohexane), 26.0 (C(CH<sub>3</sub>)<sub>3</sub>), 18.2 (C(CH<sub>3</sub>)<sub>3</sub>), -5.2, -5.3 (Si(CH<sub>3</sub>)<sub>2</sub>); **HRMS** (EI): *m/z* calcd for C<sub>22</sub>H<sub>36</sub>OSi (M<sup>+</sup>): 344.2535; found: 344.2539. The relative *endo* stereochemistry at C-7 of **3c** was determined by <sup>1</sup>H NMR NOE studies performed on its alcohol derivative **17** (See page S24).

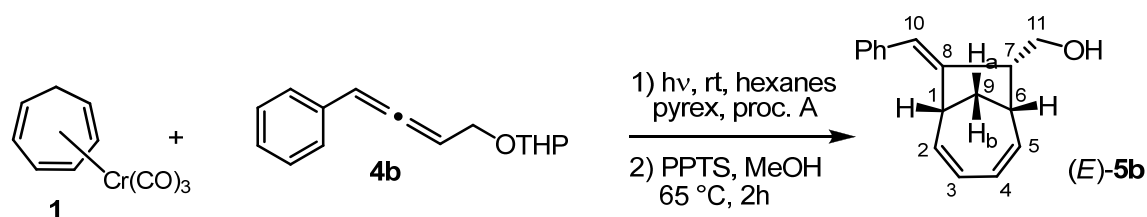
**(*E*)-((8-Benzylidenebicyclo[4.2.1]nona-2,4-dien-7-yl)methoxy)(*tert*-butyl)dimethylsilane (5a) (Table 2, entry 1).**



Following Procedure A, a solution of CHT-Cr **1** (91 mg, 0.4 mmols) and allene **4a** (208 mg, 0.8 mmols) in hexanes (200 mL) was irradiated for 6 h. Work-up and purification by flash chromatography on SiO<sub>2</sub> (cyclohexane/DCM, 96:4) provided unique (*E*)-**5a** (83 mg, 59%) as a colorless oil: *R<sub>f</sub>* 0.17 (cyclohexane/DCM, 96:4); **IR** (thin film): 3023 (CH<sub>arom</sub>), 1086 cm<sup>-1</sup>

(broad, C-O-Si); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.35-7.18 (m, 5H, H<sub>arom</sub>), 6.14 (br s, 1H, 10-H), 6.11 (dd,  $J$  = 11.6, 7.4 Hz, 1H, 2-H), 5.93 (dd,  $J$  = 11.6, 7.2 Hz, 1H, 5-H), 5.80 (dd,  $J$  = 11.6, 7.6 Hz, 1H, 4-H), 5.59 (dd,  $J$  = 11.6, 7.6 Hz, 1H, 3-H), 3.90 (dd,  $J$  = 9.6, 5.6 Hz, 1H, 11-H), 3.80 (br t,  $J$  = 10.0, 9.6 Hz, 1H, 11-H'), 3.70 (br t,  $J$  = 7.4 Hz, 1H, 1-H), 3.20-3.14 (m, 1H, 7-H), 2.96 (br q,  $J$  = 6.4 Hz, 1H, 6-H), 2.32-2.25 (m, 1H, 9-H<sub>a</sub>), 2.02 (br d,  $J$  = 12.4 Hz, 1H, 9-H<sub>b</sub>), 0.94 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.10 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 152.3 (C-8), 138.3 (*i*-C<sub>arom</sub>), 135.4, 135.0 (C-2, C-5), 128.2, 127.7, 126.2 (*o*, *m*, *p*-CH<sub>arom</sub>), 125.7 (C-4), 124.1 (C-3), 121.4 (C-10), 63.7 (C-11), 61.0 (C-7), 43.0 (C-1), 40.7 (C-6), 31.9 (C-9), 25.9 (C(CH<sub>3</sub>)<sub>3</sub>), 18.2 (C(CH<sub>3</sub>)<sub>3</sub>), -5.30, -5.35 (Si(CH<sub>3</sub>)<sub>2</sub>); **MS** (ESI):  $m/z$  = 353 (M+H<sup>+</sup>), 375 (M+Na<sup>+</sup>); **HRMS** (EI):  $m/z$  calcd for C<sub>23</sub>H<sub>32</sub>OSi (M<sup>+</sup>): 352.2222; found: 352.2222. The relative *endo* stereochemistry at C-7 and the *E* geometry of **5a** were established by <sup>1</sup>H NMR NOE studies (See Figure 1, page S25) and confirmed by X-ray crystallographic analysis performed on its *p*-nitrobenzoate ester derivative **18** (See pages S25-S26). (Traces (ca <1%) of the *Z* isomer could be detected by GC on the crude residue before chromatography).

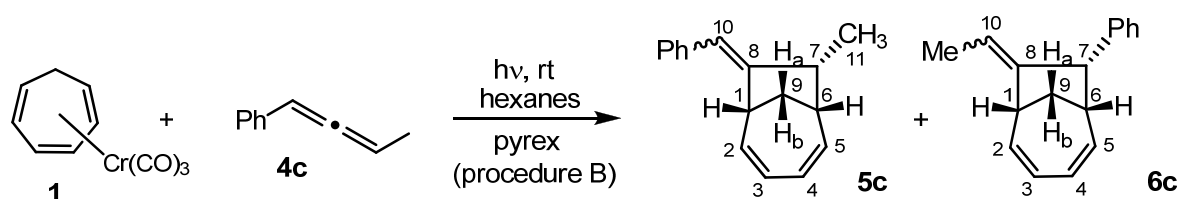
**(*E*)-(8-Benzylidenebicyclo[4.2.1]nona-2,4-dien-7-yl)methanol (**5b**) (Table 2, entry 3).**



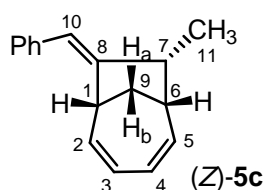
Following the Procedure A, a solution of CHT-Cr **1** (520 mg, 2.28 mmols) and allene **4b** (1.3 g, 5.6 mmols) in hexanes (300 mL) was irradiated for 4 h. After filtration over celite and concentration, the residue was dissolved in methanol (15 mL), and the resulting solution was refluxed for 2 h in the presence of a catalytic amount of PPTS. Then, the solvent was removed and the residue diluted in EtOAc. The solution was washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated. The crude residue was purified by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 80:20) to give (*E*)-**5b** (304 mg, 56%) as a slightly yellow oil: **R<sub>f</sub>** 0.22 (pentane/EtOAc, 80:20); **IR** (thin film): 3358 (broad, OH), 3022 cm<sup>-1</sup> (CH<sub>arom</sub>); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.35-7.18 (m, 5H, H<sub>arom</sub>), 6.15 (br s, 1H, 10-H), 6.13 (dd,  $J$  = 11.6, 7.4 Hz, 1H, 2-H), 5.98 (dd,  $J$  = 11.6, 8.0 Hz, 1H, 5-H), 5.86 (dd,  $J$  = 11.6, 7.2 Hz, 1H, 4-H), 5.62 (dd,  $J$  = 11.6, 7.2 Hz, 1H, 3-H), 3.95 (dd,  $J$  = 10.4, 5.6 Hz, 1H, 11-H), 3.88 (br t,  $J$  = 10.4, 9.6 Hz, 1H, 11-H'), 3.69 (br t,  $J$  = 7.4 Hz, 1H, 1-H), 3.23-3.16 (m, 1H, 7-H), 3.03-2.97 (m, 1H, 6-H), 2.34-2.28 (m, 1H, 9-H<sub>a</sub>), 2.04 (br d,  $J$  = 12.4 Hz, 1H, 9-H<sub>b</sub>), 1.52 (br s, 1H, OH); **<sup>13</sup>C**

**NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.9 (C-8), 138.3 (*i*-C<sub>arom</sub>), 135.5, 134.7 (C-2, C-5), 128.5, 127.9 (*o*, *m*-CH<sub>arom</sub>), 126.8, 126.7, 124.4, (*p*-CH<sub>arom</sub>, C-3, C-4), 121.9 (C-10), 64.0 (C-11), 60.6 (C-7), 43.2 (C-1), 40.5 (C-6), 32.3 (C-9); **MS** (ESI):  $m/z$  = 239 (M+H<sup>+</sup>), 261 (M+Na<sup>+</sup>); **HRMS** (EI):  $m/z$  calcd for C<sub>17</sub>H<sub>18</sub>O (M<sup>+</sup>): 238.1358; found: 238.1368. The relative *endo* stereochemistry at C-7 and the *E* geometry of **5b** were confirmed by comparing the <sup>1</sup>H and <sup>13</sup>C NMR data of **5b** with those obtained from material obtained after removal of the TBS protecting group in (*E*)-**5a**, and both were found to be exactly the same.

**7-Benzylidene-8-methylbicyclo[4.2.1]nona-2,4-diene (5c) and 7-ethylidene-8-phenylbicyclo[4.2.1]nona-2,4-diene (6c) (Table 2, entry 4).**



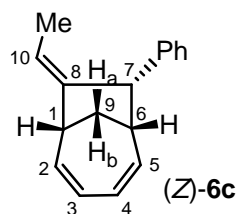
According to the procedure B, a solution of **4c** (156 mg, 1.2 mmols) in hexanes (20 mL) was added over 2 h to a solution of CHT-Cr **1** (137 mg, 0.6 mmols) in hexanes (220 mL), under irradiation. After addition, irradiation was kept 6 more hours. Work-up and purification by flash chromatography on SiO<sub>2</sub> (100% cyclohexane) furnished **6c** (11 mg, 8%) as an inseparable 23:77 mixture of *E* and *Z* isomers (ratio determined by GC on the crude product before chromatography) and **5c** (74 mg, 56%) as a separable 90:10 mixture of *Z* and *E* isomers (ratio determined by GC on the crude product before chromatography). Ratio **5c**/**6c** was determined by GC on the crude residue before chromatography.



*Z* isomer of **5c** could be isolated with a purity of 93% (by GC): *R<sub>f</sub>* 0.35 (100% cyclohexane); **IR** (thin film): 3052, 3019, 2958, 2923, 2859 cm<sup>-1</sup> (CH<sub>arom</sub>, CH<sub>ethylenic</sub>); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.40-7.18 (m, 5H, H<sub>arom</sub>), 6.17 (dd, *J* = 10.4, 8.8 Hz, 1H, 2-H), 6.10 (br s, 1H, 10-H), 5.86-5.76 (m, 2H, 5-H, 4-H), 5.52 (dd, *J* = 10.8, 7.6 Hz, 1H, 3-H), 3.83 (br t, *J* = 7.6 Hz, 1H, 1-H), 3.02-2.94 (m, 1H, 7-H), 2.72 (br q, *J* = 6.2 Hz, 1H, 6-H), 2.34-2.27 (m, 1H, 9-H<sub>a</sub>), 2.00 (br d, *J* = 12.0 Hz, 1H, 9-H<sub>b</sub>), 1.26 (d, *J* = 7.2 Hz, 3H, CH<sub>3</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 155.5 (C-8), 138.7 (*i*-C<sub>arom</sub>), 135.9 (C-2), 135.1 (C-5), 128.2, 127.8 (*o*, *m*-CH<sub>arom</sub>), 126.0, 125.7 (*p*-CH<sub>arom</sub>, C-4), 123.9 (C-3), 120.3 (C-10), 54.5 (C-7), 43.8 (C-6), 42.0

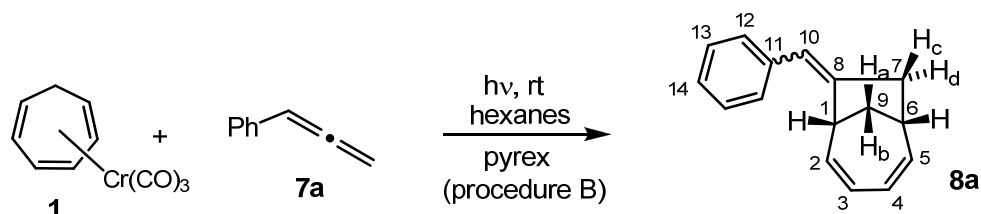
(C-1), 32.1 (C-9), 13.7 (C-11); **HRMS** (EI):  $m/z$  calcd for  $C_{17}H_{18}$  ( $M^+$ ): 222.1409; found: 222.1412. The relative *endo* stereochemistry at C-7 and the *Z* geometry of the major isomer of **5c** was confirmed by  $^1H$  NMR NOE studies.

The *E* isomer (7% by GC) could be seen in the  $^1H$  NMR spectrum at  $\delta$  3.52 ppm (1-H) and  $^{13}C$  spectrum, but it could not be isolated in a pure state.



*Z* isomer of **6c**, major (contaminated by 23% of *E* isomer):  $R_f$  0.42 (100% cyclohexane);  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.40-7.18 (m, 5H,  $H_{arom}$ ), 6.00 (br t,  $J$  = 9.4 Hz, 1H, 2-H), 5.62 (dd,  $J$  = 11.2, 7.2 Hz, 1H, 3-H), 5.49 (dd,  $J$  = 11.2, 7.2 Hz, 1H, 4-H), 5.40-5.32 (m, 1H, 10-H), 5.22 (dd,  $J$  = 10.4, 9.2 Hz, 1H, 5-H), 4.20 (br d,  $J$  = 8 Hz, 1H, 7-H), 3.31 (br t,  $J$  = 7.0 Hz, 1H, 1-H), 3.11 (br q,  $J$  = 7.2 Hz, 1H, 6-H), 2.44-2.37 (m, 1H, 9- $H_a$ ), 2.16 (br d,  $J$  = 12.0 Hz, 1H, 9- $H_b$ ), 1.12 (d,  $J$  = 6.8 Hz, 3H,  $CH_3$ ); **MS** (EI):  $m/z$  = 222 ( $M^+$ ). The relative *endo* stereochemistry at C-7 and the *Z* geometry of the major isomer of **6c** was confirmed by  $^1H$  NMR NOE studies.

**(*Z,E*)-7-Benzylidenebicyclo[4.2.1]nona-2,4-diene (8a) (Table 3, entry 1).**

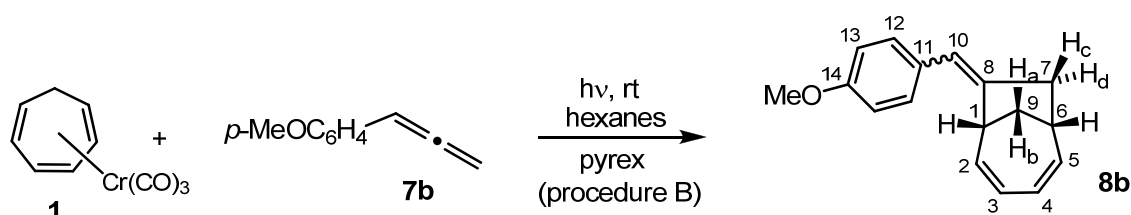


According to the procedure B, a solution of **7a** (150 mg, 1.2 mmols) in hexanes (20 mL) was added over 2 h to a solution of CHT-Cr **1** (137 mg, 0.6 mmols) in hexanes (200 mL), under irradiation. After addition, irradiation was kept 6 more hours. Work-up and purification by flash chromatography on  $SiO_2$  (pentane/EtOAc, 99:1) afforded product **8a** (63 mg, 50%) as an inseparable 45:55 mixture of *Z* and *E* isomers (ratio based on  $^1H$  NMR on the purified mixture): **IR** (thin film) (*Z* + *E*): 3052, 2923 ( $CH_{arom}$ ,  $CH_{ethylenic}$ );  $^1H$  NMR (500 MHz,  $CDCl_3$ ) (*Z* + *E*):  $\delta$  = 7.36-7.14 (m, 10H,  $H_{arom}$  (*Z* + *E*)), 6.22 (br s, 2H, 10-H (*Z* + *E*)), 6.21-6.03 (m, 4H,  $H_{ethylenic}$  (*Z* + *E*)), 5.71-5.62 (m, 4H,  $H_{ethylenic}$  (*Z* + *E*)), 3.75 (br t,  $J$  = 7.5 Hz, 1H, 1-H (*Z*)), 3.48 (br t,  $J$  = 7.8 Hz, 1H, 1-H (*E*)), 2.97 (d,  $J$  = 16.4 Hz, 1H, 7- $H_d$  (*Z* or *E*)), 2.87-2.74 (m, 5H, 6-H, 7-H (*Z* + *E*)), 2.31-2.26 (m, 2H, 9- $H_a$  (*Z* + *E*)), 2.01 (br d,  $J$  = 12.0 Hz, 1H,

9-H<sub>b</sub> (*Z* or *E*)), 1.98 (br d, *J* = 12.0 Hz, 1H, 9-H<sub>b</sub> (*Z* or *E*)); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) (*Z* + *E*): δ = 154.3, 152.2 (C-8, *Z* + *E*), 138.8, 138.3, 137.1, 134.8 (C-2, C-5, *Z* + *E*), 138.4 (C-11), 128.2, 128.13, 128.10, 127.6 (C-12, C-13, *Z* + *E*), 126.1, 125.8, 124.4, 123.8, 123.7, 123.6, 120.8, 120.7 (C-14, C-10, C-3, C-4, *Z* + *E*), 49.0 (C-7, *Z*), 47.8 (C-1, *E*), 43.9 (C-7, *E*), 42.0 (C-1, *Z*), 39.2, 37.4 (C-6, *Z* + *E*), 33.4, 31.2 (C-9, *Z* + *E*); **HRMS** (EI): *m/z* calcd for C<sub>16</sub>H<sub>16</sub> (M<sup>+</sup>): 208.1257; found: 208.1252.

Traces (ca 3%) of isomer 7-methylene-8-phenylbicyclo[4.2.1]nona-2,4-diene could also be detected by GC on the crude residue before chromatography.

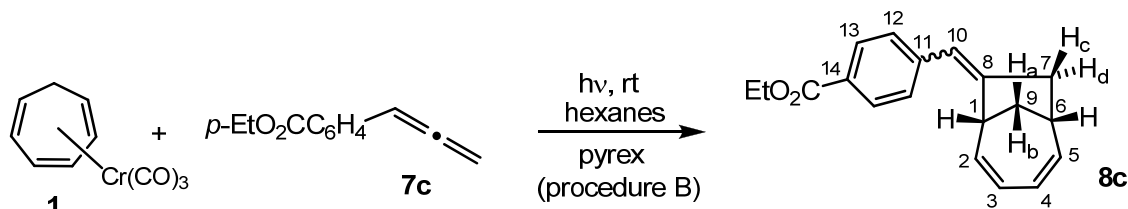
**(*Z,E*)-7-(4-Methoxybenzylidene)bicyclo[4.2.1]nona-2,4-diene (8b) (Table 3, entry 2).**



According to the procedure B, a solution of **7b** (88 mg, 0.60 mmols) in hexanes (15 mL) was added over 1.5 h to a solution of CHT-Cr **1** (68 mg, 0.30 mmols) in hexanes (140 mL), under irradiation. After addition, irradiation was kept 6 more hours. Work-up and purification by flash chromatography on SiO<sub>2</sub> (100% cyclohexane) furnished **8b** (30 mg, 42%) as an inseparable 48:52 mixture of *Z* and *E* isomers (ratio based on <sup>1</sup>H NMR on the purified mixture): **R<sub>f</sub>** 0.18 (100% cyclohexane); **IR** (thin film) (*Z* + *E*): 3017, 2926, 2834 (CH<sub>arom</sub>, CH<sub>ethylenic</sub>), 1298, 1248, 1177 cm<sup>-1</sup> (C-O-C); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) (*Z* + *E*): δ = 7.29 (d, *J* = 8.4 Hz, 2H, 12-H<sub>arom</sub> (*Z*)), 7.20 (d, *J* = 8.4 Hz, 2H, 12-H<sub>arom</sub> (*E*)), 6.88-6.84 (m, 4H, 13-H<sub>arom</sub> (*Z* + *E*)), 6.22-6.16 (m, 3H, 10-H (*Z* + *E*), H<sub>ethylenic</sub> (*Z*)), 6.10-6.02 (m, 3H, H<sub>ethylenic</sub> (*Z* + *E*)), 5.74-5.60 (m, 4H, H<sub>ethylenic</sub> (*Z* + *E*)), 3.81 (s, 3H, OCH<sub>3</sub> (*Z* or *E*)), 3.80 (s, 3H, OCH<sub>3</sub> (*Z* or *E*)), 3.71 (br t, *J* = 7.8 Hz, 1H, 1-H (*Z*)), 3.45 (br t, *J* = 7.2 Hz, 1H, 1-H (*E*)), 2.93 (d, *J* = 17.2 Hz, 1H, 7-H<sub>d</sub> (*Z* or *E*)), 2.88-2.72 (m, 5H, 6-H, 7-H (*Z* + *E*)), 2.32-2.23 (m, 2H, 9-H<sub>a</sub> (*Z* + *E*)), 2.00 (br d, *J* = 12.0 Hz, 1H, 9-H<sub>b</sub> (*Z* or *E*)), 1.97 (br d, *J* = 12.0 Hz, 1H, 9-H<sub>b</sub> (*Z* or *E*)); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) (*Z* + *E*): δ = 158.2, 157.9 (C-14, *Z* + *E*), 152.5, 150.4 (C-8, *Z* + *E*), 139.1, 138.6, 137.5, 135.2 (C-2, C-5, *Z* + *E*), 131.6, 131.4 (C-11, *Z* + *E*), 129.5, 128.9 (C-12, *Z* + *E*), 124.6, 123.93, 123.90, 120.40, 120.33 (C-10, C-3, C-4, *Z* + *E*), 113.95, 113.86 (C-13, *Z* + *E*), 55.5 (OCH<sub>3</sub>, *Z* + *E*), 49.3 (C-7, *Z* or *E*), 48.0 (C-1, *E*), 44.0 (C-7, *Z* or *E*), 42.1 (C-1, *Z*), 39.5, 37.8 (C-6, *Z* + *E*), 33.8, 31.5 (C-9, *Z* + *E*); **GC-MS** (EI): relative t<sub>R</sub>: t<sub>R</sub> = 12.65 min (*Z* isomer, *m/z* = 238 (M<sup>+</sup>)), t<sub>R</sub> = 13.05 min (*E* isomer, *m/z* = 238 (M<sup>+</sup>)); **HRMS** (EI): *m/z* calcd for C<sub>17</sub>H<sub>18</sub>O (M<sup>+</sup>): 238.1358; found: 238.1361.

Traces (ca 3%) of isomer 7-(4-methoxyphenyl)-8-methylenebicyclo[4.2.1]nona-2,4-diene could also be detected by GC on the crude residue before chromatography.

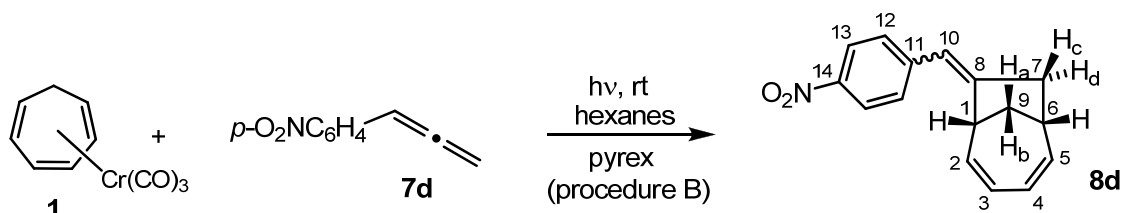
**(Z,E)-Ethyl 4-(bicyclo[4.2.1]nona-2,4-dien-7-ylidenemethyl)benzoate (8c) (Table 3, entry 3).**



According to the procedure B, a solution of **7c** (104 mg, 0.55 mmols) in hexanes (15 mL) was added over 1.5 h to a solution of CHT-Cr **1** (64 mg, 0.28 mmols) in hexanes (140 mL), under irradiation. After addition, irradiation was kept 6 more hours. Work-up and purification by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 99:1) afforded **8c** (18 mg, 23%) as an inseparable 48:52 mixture of *Z* and *E* isomers (ratio based on <sup>1</sup>H NMR on the purified mixture): **R<sub>f</sub>** 0.24 (pentane/EtOAc, 99:1); **IR** (thin film) (*Z* + *E*): 3018, 2975, 2930 (CH<sub>arom</sub>, CH<sub>ethylenic</sub>), 1713 (C=O), 1275, 1178, 1106 cm<sup>-1</sup> (C-O-C); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) (*Z* + *E*): δ = 8.00-7.94 (m, 4H, 13-H<sub>arom</sub> (*Z* + *E*)), 7.39 (d, *J* = 8.0 Hz, 2H, 12-H<sub>arom</sub> (*Z* or *E*)), 7.29 (d, *J* = 8.4 Hz, 2H, 12-H<sub>arom</sub> (*Z* or *E*)), 6.25 (br s, 2H, 10-H (*Z* + *E*)), 6.18-6.00 (m, 4H, H<sub>ethylenic</sub> (*Z* + *E*)), 5.73-5.62 (m, 4H, H<sub>ethylenic</sub> (*Z* + *E*)), 4.39-4.33 (m, 4H, OCH<sub>2</sub>CH<sub>3</sub> (*Z* + *E*)), 3.76 (br t, *J* = 7.8 Hz, 1H, 1-H (*Z*)), 3.49 (br t, *J* = 7.8 Hz, 1H, 1-H (*E*)), 2.98 (d, *J* = 16.0 Hz, 1H, 7-H<sub>d</sub> (*Z* or *E*)), 2.88-2.72 (m, 5H, 6-H, 7-H (*Z* + *E*)), 2.32-2.24 (m, 2H, 9-H<sub>a</sub> (*Z* + *E*)), 2.01 (br d, *J* = 12.0 Hz, 1H, 9-H<sub>b</sub> (*Z* or *E*)), 1.98 (br d, *J* = 12.0 Hz, 1H, 9-H<sub>b</sub> (*Z* or *E*)), 1.39, 1.38 (2\*s\*t, 6H, CH<sub>3</sub> (*Z* + *E*)); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) (*Z* + *E*): δ = 166.8 (C=O, *Z* + *E*), 157.3, 155.0 (C-8, *Z* + *E*), 143.14, 143.08 (C-11, *Z* + *E*), 138.9, 138.4, 136.8, 134.5 (C-2, C-5, *Z* + *E*), 129.8, 129.7 (C-13, *Z* + *E*), 128.1, 127.6 (C-12, *Z* + *E*), 127.8 (C-14, *Z* + *E*), 125.0, 124.4, 123.95, 123.91, 120.55, 120.46 (C-10, C-3, C-4, *Z* + *E*), 61.0 (OCH<sub>2</sub>CH<sub>3</sub>, *Z* + *E*), 49.8 (C-7, *Z* or *E*), 48.2 (C-1, *E*), 44.4 (C-7, *Z* or *E*), 42.3 (C-1, *Z*), 39.4, 37.7 (C-6, *Z* + *E*), 33.7, 31.3 (C-9, *Z* + *E*), 14.6 (CH<sub>3</sub>, *Z* + *E*); **GC-MS** (EI): relative t<sub>R</sub>: t<sub>R</sub> = 17.06 min (*Z* isomer, *m/z* = 280 (M<sup>+</sup>)), t<sub>R</sub> = 18.01 min (*E* isomer, *m/z* = 280 (M<sup>+</sup>)); **HRMS** (EI): *m/z* calcd for C<sub>19</sub>H<sub>20</sub>O<sub>2</sub> (M<sup>+</sup>): 280.1463; found: 280.1466.

Traces (ca 3%) of isomer ethyl 4-(8-methylenebicyclo[4.2.1]nona-2,4-dien-7-yl)benzoate could also be detected by GC on the crude residue before chromatography.

**(*Z,E*)-7-(4-Nitrobenzylidene)bicyclo[4.2.1]nona-2,4-diene (8d) (Table 3, entry 4).**

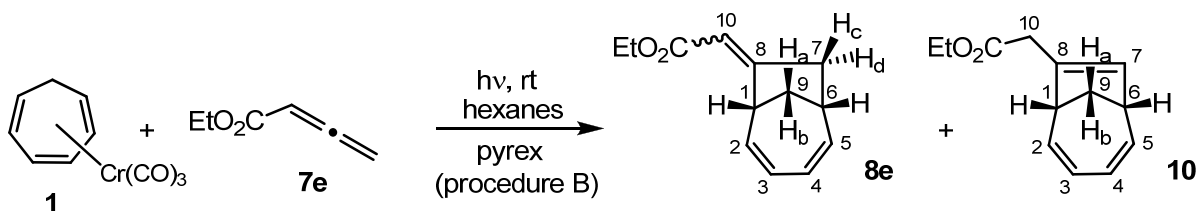


According to the procedure B, a solution of **7d** (43 mg, 0.267 mmols) (contaminated by 171 mg of 1-iodo-4-nitrobenzene) in hexanes (8 mL + 3 mL of DCM in order to dissolve all the nitroallene) was added over 1 h to a solution of CHT-Cr **1** (31 mg, 0.134 mmols) in hexanes (60 mL), under irradiation. After addition, irradiation was kept 6 more hours. Work-up and purification by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 99:1) gave an inseparable mixture of **8d** (19 mg, 56%, inseparable 40:60 mixture of *Z* and *E* isomers, ratio based on GC), starting allene **7d** (28 mg) and contaminant 1-iodo-4-nitrobenzene (126 mg). Masses were determined from molar ratios of each compound determined by <sup>1</sup>H NMR on the purified mixture.

**8d**: *R<sub>f</sub>* 0.30 (pentane/EtOAc, 99:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (*Z* + *E*): δ = 8.20-8.10 (m, 4H, 13-H<sub>arom</sub> (*Z* + *E*)), 7.45 (d, *J* = 8.0 Hz, 2H, 12-H<sub>arom</sub> (*Z*)), 7.35 (d, *J* = 8.4 Hz, 2H, 12-H<sub>arom</sub> (*E*)), 6.28 (br s, 2H, 10-H (*Z* + *E*)), 6.16-6.00 (m, 4H, H<sub>ethylenic</sub> (*Z* + *E*)), 5.74-5.63 (m, 4H, H<sub>ethylenic</sub> (*Z* + *E*)), 3.76 (br t, *J* = 7.2 Hz, 1H, 1-H (*Z*)), 3.52 (br t, *J* = 7.2 Hz, 1H, 1-H (*E*)), 2.98 (d, *J* = 16.8 Hz, 1H, 7-H<sub>d</sub> (*Z* or *E*)), 2.92-2.76 (m, 5H, 6-H, 7-H (*Z* + *E*)), 2.36-2.26 (m, 2H, 9-H<sub>a</sub> (*Z* + *E*)), 2.02 (br d, *J* = 12.0 Hz, 1H, 9-H<sub>b</sub> (*Z* or *E*)), 2.00 (br d, *J* = 12.0 Hz, 1H, 9-H<sub>b</sub> (*Z* or *E*)); **GC-MS** (EI): relative *t<sub>R</sub>*: *t<sub>R</sub>* = 16.05 min (minor *Z* isomer, *m/z* = 253 (*M*<sup>+</sup>)), *t<sub>R</sub>* = 16.77 min (major *E* isomer, *m/z* = 253 (*M*<sup>+</sup>)); **HRMS** (EI): *m/z* calcd for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub> (*M*<sup>+</sup>): 253.1103; found: 253.1101.

Traces (ca 3%) of isomer 7-methylene-8-(4-nitrophenyl)bicyclo[4.2.1]nona-2,4-diene could also be detected by GC on the crude residue before chromatography.

**(*Z,E*)-Ethyl 2-(bicyclo[4.2.1]nona-2,4-dien-7-ylidene)acetate (8e) and ethyl 2-(bicyclo[4.2.1]nona-2,4,7-trien-7-yl)acetate (10) (Table 3, entry 6).**



Following the procedure B, a solution of **7e** (450 mg, 4 mmols) in hexanes (20 mL) was added over 2 h to a solution of CHT-Cr **1** (182 mg, 0.8 mmols) in hexanes (220 mL), under irradiation. After addition, irradiation was kept 4 more hours. Work-up and purification by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 96:4) afforded pure (*Z*)-**8e** (65 mg, 40%) and an inseparable mixture of (*E*)-**8e** (27 mg, 16%) and isomer **10** (6 mg, 4%) (ratio (*E*)-**8e**/**10** determined by GC on the purified mixture). Ratio (*Z*)-**8e**/*(E)*-**8e** of the cycloaddition was determined by GC on the crude residue before chromatography.

(*Z*)-**8e**: colorless liquid; **R<sub>f</sub>** 0.72 (pentane/EtOAc, 96:4); **IR** (thin film): 3021, 2933, 2820 (CH<sub>ethylene</sub>), 1710 (C=O), 1288, 1199, 1147, 1110 cm<sup>-1</sup> (C-O-C); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.34 (br t, *J* = 10.0 Hz, 1H, 2-H), 6.00-5.95 (m, 1H, 5-H), 5.70-5.62 (m, 2H, 4-H, 3-H), 5.63 (br s, 1H, 10-H), 4.18-4.11 (m, 3H, 1-H, OCH<sub>2</sub>CH<sub>3</sub>), 2.77-2.69 (m, 3H, 7-H, 6-H), 2.24-2.17 (m, 1H, 9-H<sub>a</sub>), 1.98 (br d, *J* = 12.0 Hz, 1H, 9-H<sub>b</sub>), 1.26 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>); **<sup>1</sup>H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 6.70 (br t, *J* = 9.6 Hz, 1H, 2-H), 5.77-5.72 (m, 1H, 5-H), 5.67 (br s, 1H, 10-H), 5.64-5.57 (m, 2H, 4-H, 3-H), 4.36 (br t, *J* = 7.8 Hz, 1H, 1-H), 4.07-3.99 (m, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.47 (br d, *J* = 15.8 Hz, 1H, 7-H<sub>d</sub>), 2.29-2.20 (m, 2H, 7-H<sub>c</sub>, 6-H), 1.90 (br d, *J* = 12.0 Hz, 1H, 9-H<sub>b</sub>), 1.86-1.80 (m, 1H, 9-H<sub>a</sub>), 0.98 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 170.9 (C=O), 166.5 (C-8), 137.0 (C-5), 134.9 (C-2), 123.9, 123.8 (C-4, C-3), 110.7 (C-10), 59.6 (OCH<sub>2</sub>CH<sub>3</sub>), 48.7 (C-7), 43.5 (C-1), 37.4 (C-6), 32.5 (C-9), 14.3 (CH<sub>3</sub>); **GC-MS** (EI): relative t<sub>R</sub>: t<sub>R</sub> = 9.23 min (*m/z* = 204 (M<sup>+</sup>)); **HRMS** (EI): *m/z* calcd for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub> (M<sup>+</sup>): 204.1150; found: 204.1157. The *Z* geometry was established by <sup>1</sup>H NMR NOE studies (See Figure 1, page S25).

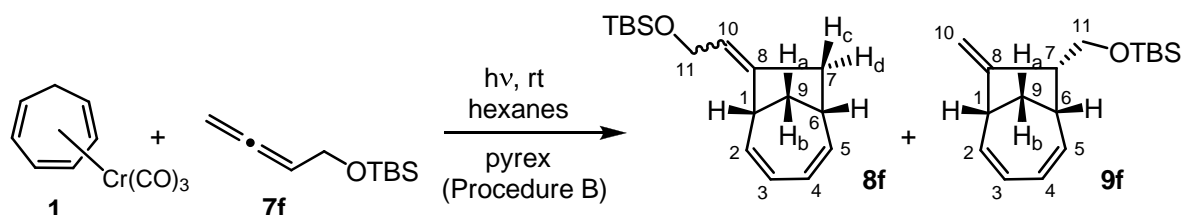
(*E*)-**8e**: **R<sub>f</sub>** 0.61 (pentane/EtOAc, 96:4); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.02 (dd, *J* = 10.4, 7.2 Hz, 1H, 5-H), 5.90 (br t, *J* = 10.0 Hz, 1H, 2-H), 5.68-5.58 (m, 3H, 4-H, 3-H, 10-H) 4.10 (q, *J* = 7.2 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 3.43 (br t, *J* = 7.6 Hz, 1H, 1-H), 3.29 (d, *J* = 19.2 Hz, 1H, 7-H<sub>d</sub>), 2.86 (ddd, *J* = 19.2, 8.0, 2.4 Hz, 1H, 7-H<sub>c</sub>), 2.79 (br q, *J* = 7.8 Hz, 1H, 6-H), 2.24-2.17 (m, 1H, 9-H<sub>a</sub>), 1.96 (br d, *J* = 12.4 Hz, 1H, 9-H<sub>b</sub>), 1.23 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 173.0 (C=O), 166.9 (C-8), 138.8 (C-5), 134.8 (C-2), 125.0, 123.2 (C-4, C-3), 111.5 (C-10), 59.5 (OCH<sub>2</sub>CH<sub>3</sub>), 46.9 (C-1), 45.7 (C-7), 38.6 (C-6), 30.9 (C-9), 14.3 (CH<sub>3</sub>); **GC-MS** (EI): relative t<sub>R</sub>: t<sub>R</sub> = 9.42 min (*m/z* = 204 (M<sup>+</sup>)).

**10**: **R<sub>f</sub>** 0.61 (pentane/EtOAc, 96:4); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.17-6.06 (m, 2H, H<sub>ethylene</sub>), 5.85-5.77 (m, 2H, H<sub>ethylene</sub>), 5.18 (br s, 1H, 7-H), 4.14-4.10 (hidden q, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 3.17 (d, *J* = 15.6 Hz, 1H, 10-H), 3.05 (d, *J* = 15.6 Hz, 1H, 10-H'), 3.01 (br t, *J* = 7.2 Hz, 1H, 1-H), 1.48 (br d, *J* = 12.4 Hz, 1H, 9-H<sub>b</sub>), 1.25-1.22 (hidden t, 3H, CH<sub>3</sub>) (6-H and 9-H<sub>a</sub> were hidden and not found); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 171.3 (C=O), 138.6,



138.2 (C-5, C-2), 131.5 (C-8), 125.1, 123.8, 123.0 (C-4, C-3, C-7), 60.6 (OCH<sub>2</sub>CH<sub>3</sub>), 45.5, 43.1 (C-1, C-6), 34.3 (C-10), 31.0 (C-9), 14.1 (CH<sub>3</sub>); **GC-MS** (EI): relative  $t_R$ :  $t_R$  = 8.73 min ( $m/z$  = 204 ( $M^+$ )).

**(*Z,E*)-(2-(Bicyclo[4.2.1]nona-2,4-dien-7-ylidene)ethoxy)(*tert*-butyl)dimethylsilane (8f) and *tert*-butyldimethyl((8-methylenebicyclo[4.2.1]nona-2,4-dien-7-yl)methoxy)silane (9f) (Table 3, entry 7).**



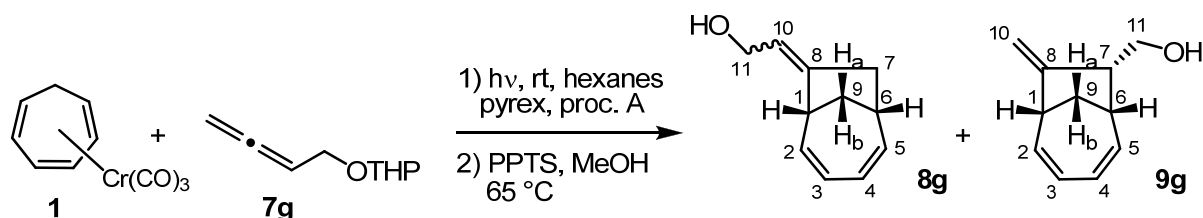
Following the procedure B, a solution of **7f** (294 mg, 1.6 mmols) in hexanes (20 mL) was added over 2 h to a solution of CHT-Cr **1** (182 mg, 0.8 mmols) in hexanes (220 mL), under irradiation. After addition, irradiation was kept 4 more hours. Work-up and purification by flash chromatography on SiO<sub>2</sub> (cyclohexane/EtOAc, 100:0 to 98:2) afforded **9f** (57 mg, 26%) and **8f** (26 mg, 12%, inseparable 15:85 mixture of *Z* and *E* isomers, ratio determined by <sup>1</sup>H NMR on the purified mixture). Ratio **8f/9f** of the reaction was determined by GC on the crude product before chromatography.

**9f**: colorless liquid; **R<sub>f</sub>** 0.44 (cyclohexane/EtOAc, 98:2); **IR** (thin film): 3070, 3021, 2929, 2858 (CH<sub>ethylene</sub>), 1075 cm<sup>-1</sup> (broad, C-O-Si); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.05 (br t,  $J$  = 10.0 Hz, 1H, 2-H), 5.88 (dd,  $J$  = 11.6, 7.4 Hz, 1H, 5-H), 5.75 (dd,  $J$  = 11.6, 7.4 Hz, 1H, 4-H), 5.55 (dd,  $J$  = 10.8, 7.4 Hz, 1H, 3-H), 4.82 (br t,  $J$  = 2.1 Hz, 1H, one of 10-H), 4.78 (br t,  $J$  = 2.1 Hz, 1H, one of 10-H), 3.83 (dd,  $J$  = 9.6, 5.7 Hz, 1H, 11-H), 3.76 (dd,  $J$  = 9.6, 9.3 Hz, 1H, 11-H'), 3.36 (br t,  $J$  = 8.1 Hz, 1H, 1-H), 3.00-2.85 (m, 2H, 7-H, 6-H), 2.31-2.23 (m, 1H, 9-H<sub>a</sub>), 1.98 (br d,  $J$  = 12.0 Hz, 1H, 9-H<sub>b</sub>), 0.91 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.06 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 160.5 (C-8), 138.0 (C-2), 135.5 (C-5), 125.8 (C-4), 123.7 (C-3), 106.1 (C-10), 62.9 (C-11), 59.7 (C-7), 45.2 (C-1), 41.9 (C-6), 31.1 (C-9), 25.9 (C(CH<sub>3</sub>)<sub>3</sub>), 18.2 (C(CH<sub>3</sub>)<sub>3</sub>), -5.38, -5.42 (Si(CH<sub>3</sub>)<sub>2</sub>); **GC-MS** (EI): relative  $t_R$ :  $t_R$  = 9.83 min ( $m/z$  = 276 ( $M^+$ )); **HRMS** (EI):  $m/z$  calcd for C<sub>17</sub>H<sub>28</sub>OSi ( $M^+$ ): 276.1909; found: 276.1919.

**8f**: colorless liquid; **R<sub>f</sub>** 0.28 (cyclohexane/EtOAc, 98:2); **IR** (thin film) (*Z* + *E*): 3019, 2928, 2857 (CH<sub>ethylene</sub>), 1099, 1065 cm<sup>-1</sup> (broad, C-O-Si); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) (*Z* + *E*): *E* isomer, major:  $\delta$  = 6.00-5.92 (m, 2H, 2-H, 5-H), 5.62-5.57 (m, 2H, 4-H, 3-H), 5.28 (br t,  $J$  = 6.0 Hz, 1H, 10-H), 4.11-4.09 (m, 2H, 11-H), 3.30 (br t,  $J$  = 7.6 Hz, 1H, 1-H), 2.76-2.71 (m (br q), 1H, 6-H), 2.57 (br d,  $J$  = 17.2 Hz, 1H, 7-H<sub>d</sub>), 2.48 (br dd,  $J$  = 17.2, 8.4 Hz, 1H, 7-H<sub>c</sub>),

2.23-2.16 (m, 1H, 9-H<sub>a</sub>), 1.92 (br d,  $J = 12.0$  Hz, 1H, 9-H<sub>b</sub>), 0.88 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.04 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); *Z* isomer, minor:  $\delta$  (residual) = 3.42 (br t,  $J = 7.6$  Hz, 1H, 1-H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (*Z* + *E*): *E* isomer, major:  $\delta = 152.3$  (C-8), 138.5, 137.3 (C-2, C-5), 123.56, 123.54 (C-4, C-3), 120.3 (C-10), 61.5 (C-11), 45.5 (C-1), 42.1 (C-7), 38.6 (C-6), 31.7 (C-9), 26.0 (C(CH<sub>3</sub>)<sub>3</sub>), 18.4 (C(CH<sub>3</sub>)<sub>3</sub>), -5.03, -5.11 (Si(CH<sub>3</sub>)<sub>2</sub>); *Z* isomer, minor:  $\delta = 152.0$  (C-8), 138.1, 135.8 (C-2, C-5), 123.9, 123.8 (C-4, C-3), 120.0 (C-10), 62.9 (C-11), 47.6 (C-7), 41.4 (C-1), 38.9 (C-6), 32.8 (C-9), 26.0 (C(CH<sub>3</sub>)<sub>3</sub>), 18.4 (C(CH<sub>3</sub>)<sub>3</sub>), -5.03, -5.11 (Si(CH<sub>3</sub>)<sub>2</sub>); **GC-MS** (EI): 1 peak at  $t_R = 10.31$  min ( $m/z = 276$  (M<sup>+</sup>)); **HRMS** (EI):  $m/z$  calcd for C<sub>17</sub>H<sub>28</sub>OSi (M<sup>+</sup>): 276.1909; found: 276.1904. The *E* geometry for the major isomer of **8f** was established by <sup>1</sup>H NMR NOE studies.

**(*Z,E*)-2-(Bicyclo[4.2.1]nona-2,4-dien-7-ylidene)ethanol (8g) and (8-methylenebicyclo[4.2.1]nona-2,4-dien-7-yl)methanol (9g) (Table 3, entry 8).**



Following the Procedure A, a solution of CHT-Cr **1** (137 mg, 0.6 mmols) and **7g** (185 mg, 1.2 mmols) in hexanes (200 mL) was irradiated for 4 h. After filtration over celite and concentration, the residue was dissolved in methanol (4 mL), and the resulting solution was refluxed for 2 h in the presence of a catalytic amount of PPTS. Then, the solvent was removed and the obtained residue diluted in EtOAc. The solution was washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated. The crude residue was purified by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 80:20) to give **9g** (23 mg, 24%) and **8g** (17 mg, 17%, inseparable 35:65 mixture of *Z* and *E* isomers, ratio based on <sup>1</sup>H NMR on the purified mixture).

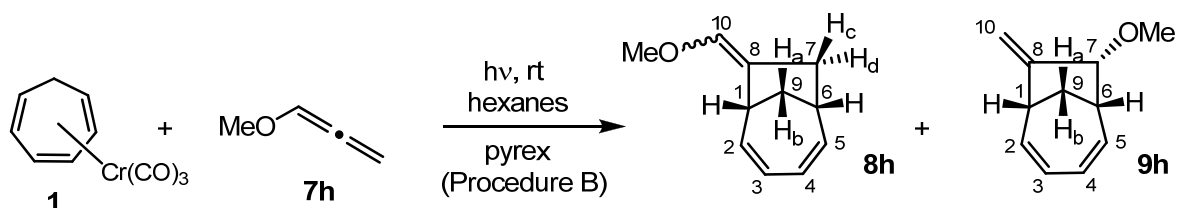
**9g**: colorless oil;  $R_f$  0.41 (pentane/EtOAc, 80:20); **IR** (thin film): 3348 (broad, OH), 3071, 3021, 2928, 2874 cm<sup>-1</sup> (CH<sub>ethylene</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 6.04$  (br t,  $J = 10.0$  Hz, 1H, 2-H), 5.91 (dd,  $J = 12.0, 7.6$  Hz, 1H, 5-H), 5.79 (dd,  $J = 12.0, 7.2$  Hz, 1H, 4-H), 5.56 (dd,  $J = 10.4, 7.2$  Hz, 1H, 3-H), 4.84 (br s, 1H, one of 10-H), 4.78 (br s, 1H, one of 10-H), 3.90 (dd,  $J = 10.4, 5.6$  Hz, 1H, 11-H), 3.84 (dd,  $J = 10.4, 9.2$  Hz, 1H, 11-H'), 3.36 (br t,  $J = 7.6$  Hz, 1H, 1-H), 3.02-2.94 (m, 1H, 7-H), 2.93-2.88 (m (br q), 1H, 6-H), 2.32-2.26 (m, 1H, 9-H<sub>a</sub>), 2.00 (br d,  $J = 12.0$  Hz, 1H, 9-H<sub>b</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 159.8$  (C-8), 138.1 (C-2), 134.5 (C-5), 126.5 (C-4), 123.6 (C-3), 106.2 (C-10), 62.9 (C-11), 59.1 (C-7), 45.2 (C-1), 41.5 (C-6), 31.1 (C-9). **MS** (ESI):  $m/z = 163$  (M+H<sup>+</sup>), 185 (M+Na<sup>+</sup>); **HRMS** (EI):  $m/z$  calcd

for  $C_{11}H_{14}O$  ( $M^+$ ): 162.1045; found: 162.1047. The relative *endo* stereochemistry at C-7 of **9g** was determined by  $^1H$  NMR NOE studies performed on its *p*-nitrobenzoate ester derivative.

**8g**: colorless oil;  $R_f$  0.30 (pentane/EtOAc, 80:20); **IR** (thin film) (*Z* + *E*): 3334 (broad, OH), 3016, 2923, 2876  $cm^{-1}$  ( $CH_{ethylene}$ );  $^1H$  NMR (300 MHz,  $CDCl_3$ ) (*Z* + *E*):  $\delta$  = 6.10-5.93 (m, 4H,  $H_{ethylene}$  (*Z* + *E*)), 5.70-5.57 (m, 4H,  $H_{ethylene}$  (*Z* + *E*)), 5.46-5.35 (m, 2H, 10-H (*Z* + *E*)), 4.14-4.02 (m, 4H, 11-H (*Z* + *E*)), 3.49 (br t,  $J$  = 7.8 Hz, 1H, 1-H (*Z*)), 3.32 (br t,  $J$  = 7.8 Hz, 1H, 1-H (*E*)), 2.79-2.45 (m, 6H, 6-H, 7-H (*Z* + *E*)), 2.27-2.16 (m, 2H, 9- $H_a$  (*Z* + *E*)), 1.94 (br d,  $J$  = 12.3 Hz, 1H, 9- $H_b$  (*E*)), 1.92 (br d,  $J$  = 12.0 Hz, 1H, 9- $H_b$  (*Z*));  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ) (*Z* + *E*): *E* isomer, major:  $\delta$  = 154.7 (C-8), 138.5, 137.2 (C-2, C-5), 123.7, 123.5 (C-4, C-3), 119.5 (C-10), 60.6 (C-11), 45.4 (C-1), 42.0 (C-7), 38.5 (C-6), 31.7 (C-9); *Z* isomer, minor:  $\delta$  = 153.8 (C-8), 138.1, 136.4 (C-2, C-5), 124.2, 123.6 (C-4, C-3), 119.3 (C-10), 62.3 (C-11), 47.8 (C-7), 41.0, 38.9 (C-1, C-6), 32.7 (C-9).

**Obtention of pure isomer (Z)-8g.** To a suspension of LAH (11 mg, 0.27 mmols) in diethyl ether (1 mL) at -78 °C was introduced slowly a solution of pure ester (*Z*)-**8e** (69 mg, 0.338 mmols) in  $Et_2O$  (1 mL). The resulting mixture was stirred for 1 h by warming up the mixture to rt. Water was added and the resulting mixture was filtered through a short pad of celite, and the cake was washed with  $Et_2O$ . The organic layer was separated from the aqueous layer, dried ( $MgSO_4$ ), filtered and concentrated. The residue was purified by flash chromatography on  $SiO_2$  (pentane/EtOAc, 80:20) to yield alcohol **Z-8g** (33 mg, 53%) as a colorless oil:  $R_f$  0.30 (pentane/EtOAc, 80:20); **IR** (thin film): 3331 (broad, OH), 3016, 2926, 2879  $cm^{-1}$  ( $CH_{ethylene}$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 6.06 (br t,  $J$  = 9.8 Hz, 1H, 2-H), 5.98 (dd,  $J$  = 10.8, 7.2 Hz, 1H, 5-H), 5.68-5.59 (m, 2H, 4-H, 3-H), 5.44-5.40 (m (ct), 1H, 10-H), 4.13-4.02 (m, 2H, 11-H), 3.48 (br t,  $J$  = 7.8 Hz, 1H, 1-H), 2.70-2.65 (m, 1H, 6-H), 2.63-2.55 (m, 2H, 7-H), 2.25-2.19 (m, 1H, 9- $H_a$ ), 1.91 (dd,  $J$  = 12.0, 1.6 Hz, 1H, 9- $H_b$ );  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 153.8 (C-8), 138.1 (C-5), 136.3 (C-2), 124.2, 123.6 (C-4, C-3), 119.3 (C-10), 62.2 (C-11), 47.8 (C-7), 41.0 (C-1), 38.9 (C-6), 32.7 (C-9); **HRMS** (EI):  $m/z$  calcd for  $C_{11}H_{14}O$  ( $M^+$ ): 162.1045; found: 162.1043. The *Z* geometry was confirmed by  $^1H$  NMR NOE studies.

**(*Z,E*)-7-(Methoxymethylene)bicyclo[4.2.1]nona-2,4-diene (8h) and 7-methoxy-8-methylenebicyclo[4.2.1]nona-2,4-diene (9h) (Table 3, entry 9).**



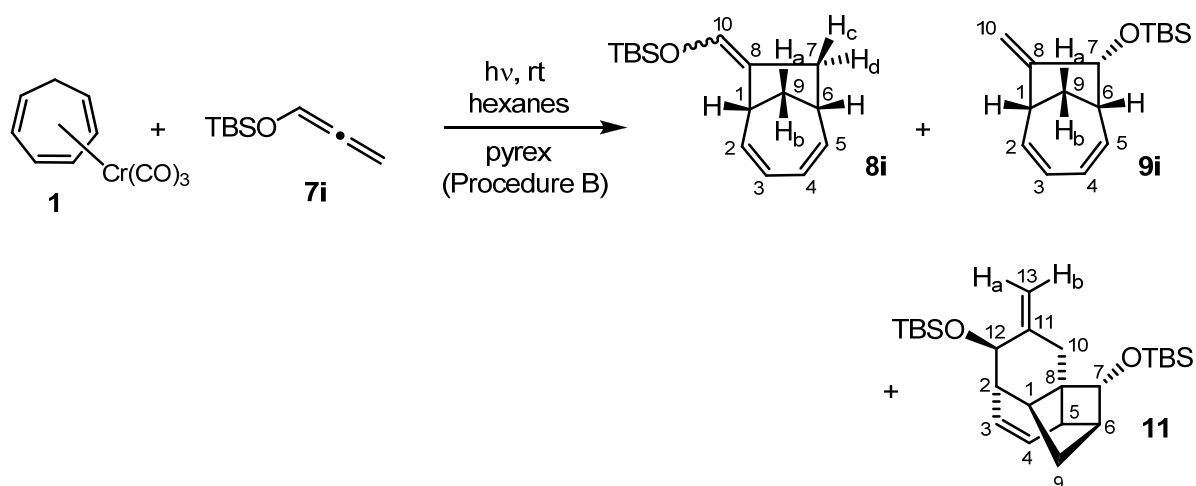
Following the procedure B, a solution of **7h** (56 mg, 0.8 mmols) in hexanes (20 mL) was added over 2 h to a solution of CHT-Cr **1** (91 mg, 0.4 mmols) in hexanes (200 mL), under irradiation. After addition, irradiation was kept 4 more hours. Treatment with P(OMe)<sub>3</sub> after irradiation, followed by purification by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 96:4) gave **8h** (8 mg, 12%, inseparable 35:65 mixture of *Z* and *E* isomers, ratio determined by GC on the purified mixture) and **9h** (25 mg, 39%). Ratios **8h/9h** and (*Z*)-**8h**/(*E*)-**8h** of the reaction were determined by GC on the crude product before chromatography.

**8h**: colorless liquid; *R<sub>f</sub>* 0.54 (pentane/EtOAc, 96:4); **IR** (thin film) (*Z* + *E*): 3015, 2924, 2833 (CH<sub>ethylene</sub>), 1688 (O-C=C), 1221, 1176, 1117 cm<sup>-1</sup> (C-O-C); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) (*Z* + *E*):  $\delta$  = 6.22-5.54 (m, 10H, H<sub>ethylene</sub> (*Z* + *E*)), 3.54 (s, 3H, OCH<sub>3</sub> (*E*, major)), 3.52 (s, 3H, OCH<sub>3</sub> (*Z*, minor)), 3.44 (br t, *J* = 7.6 Hz, 1H, 1-H (*Z*)), 3.22 (br t, *J* = 7.2 Hz, 1H, 1-H (*E*)), 2.75-2.45 (m, 6H, 6-H, 7-H (*Z* + *E*)), 2.23-2.13 (m, 2H, 9-H<sub>a</sub> (*Z* + *E*)), 1.97 (br d, *J* = 12.0 Hz, 1H, 9-H<sub>b</sub> (*E*)), 1.88 (br d, *J* = 12.4 Hz, 1H, 9-H<sub>b</sub> (*Z*)); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) (*Z* + *E*): *E* isomer, major:  $\delta$  = 139.6, 139.0, 138.2 (C-5, C-2, C-10), 130.1 (C-8), 123.4, 123.3 (C-3, C-4), 59.4 (OCH<sub>3</sub>), 41.2 (C-1), 40.5 (C-7), 38.7 (C-6), 32.8 (C-9); *Z* isomer, minor:  $\delta$  = 139.3, 137.8, 137.0 (C-5, C-2, C-10), 127.8 (C-8), 124.0, 123.1 (C-3, C-4), 59.4 (OCH<sub>3</sub>), 43.0 (C-7), 39.69, 39.66 (C-1, C-6), 32.9 (C-9); **GC-MS** (EI): relative *t<sub>R</sub>*: *t<sub>R</sub>* = 7.18 min (minor *Z* isomer, *m/z* = 162 (M<sup>+</sup>)), *t<sub>R</sub>* = 7.34 min (major *E* isomer, *m/z* = 162 (M<sup>+</sup>)); **HRMS** (EI): *m/z* calcd for C<sub>11</sub>H<sub>14</sub>O (M<sup>+</sup>): 162.1045; found: 162.1048. The *E* geometry for the major isomer of **8h** was determined by <sup>1</sup>H NMR NOE studies.

**9h**: colorless liquid; *R<sub>f</sub>* 0.43 (pentane/EtOAc, 96:4); **IR** (thin film): 3079, 3019, 2925, 2820 (CH<sub>ethylene</sub>), 1220, 1196, 1118 cm<sup>-1</sup> (C-O-C); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.19 (br t, *J* = 9.6 Hz, 1H, 2-H), 5.90-5.80 (m, 2H, 5-H, 4-H), 5.59 (dd, *J* = 11.4, 6.6 Hz, 1H, 3-H), 5.18 (br s, 1H, one of 10-H), 4.96 (br s, 1H, one of 10-H), 4.20 (dt, *J* = 6.4, 2.4 Hz, 1H, 7-H), 3.48 (s, 3H, OCH<sub>3</sub>), 3.34 (br t, *J* = 7.6 Hz, 1H, 1-H), 2.99 (br q, *J* = 5.6 Hz, 1H, 6-H), 2.20-2.14 (m, 1H, 9-H<sub>a</sub>), 1.89 (br d, *J* = 12.4 Hz, 1H, 9-H<sub>b</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 156.6 (C-8), 138.8 (C-2), 132.4 (C-5), 126.8 (C-4), 123.9 (C-3), 109.1 (C-10), 94.1 (C-7), 58.3 (OCH<sub>3</sub>),

41.4 (C-6), 40.6 (C-1), 27.4 (C-9); **GC-MS** (EI): relative  $t_R$ :  $t_R = 7.08$  min ( $m/z = 162$  ( $M^+$ )); **HRMS** (EI):  $m/z$  calcd for  $C_{11}H_{14}O$  ( $M^+$ ): 162.1045; found: 162.1049. The relative *endo* stereochemistry at C-7 of **9h** was determined by  $^1H$  NMR NOE studies (See Figure 1, page S25).

**(Z,E)-(Bicyclo[4.2.1]nona-2,4-dien-7-ylidenemethoxy)(tert-butyl)dimethylsilane (8i), tert-butyl(dimethyl(8-methylenebicyclo[4.2.1]nona-2,4-dien-7-yloxy)silane (9i) and tetracycle 11 (Table 3, entry 13).**



Following the procedure B, a solution of **7i** (136 mg, 0.8 mmols) in hexanes (20 mL) was added over 2 h to a solution at 0 °C of CHT-Cr **1** (91 mg, 0.4 mmols) in hexanes (200 mL), under irradiation. After addition, irradiation was kept 1 more hour. Treatment with  $P(OMe)_3$  after irradiation, followed by purification by flash chromatography on  $SiO_2$  (cyclohexane/DCM, 96:4) furnished **8i** (38 mg, 36%, separable 40:60 mixture of *Z* and *E* isomers, ratio determined by GC on the purified mixture), **9i** (29 mg, 28%), and tetracycle **11** (8 mg, 5%, one unique stereomer). Ratios **8i/9i** and (*Z*)-**8i**/(*E*)-**8i** of the reaction were determined by GC on the crude product before chromatography.

Pure (*Z*)-**8i**: colorless liquid;  $R_f$  0.43 (cyclohexane/EtOAc, 96:4); **IR** (thin film): 3018, 2929, 2858 ( $CH_{\text{ethylenic}}$ ), 1680 ( $O-C=C$ ), 1253, 1154, 1120  $cm^{-1}$  ( $C-O-Si$ );  $^1H$  **NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  = 6.18 (dd,  $J = 10.4, 8.8$  Hz, 1H, 2-H), 6.11 (br d,  $J = 1.6$  Hz, 1H, 10-H), 5.91 (dd,  $J = 11.4, 7.4$  Hz, 1H, 5-H), 5.66 (dd,  $J = 11.4, 7.4$  Hz, 1H, 4-H), 5.55 (dd,  $J = 10.4, 7.6$  Hz, 1H, 3-H), 3.47 (br t,  $J = 7.8$  Hz, 1H, 1-H), 2.69-2.53 (br q,  $J = 6.8$  Hz, 1H, 6-H), 2.53-2.42 (m, 2H, 7-H), 2.19-2.13 (m, 1H, 9- $H_a$ ), 1.88 (dd,  $J = 11.6, 1.6$  Hz, 1H, 9- $H_b$ ), 0.92 (s, 9H,  $C(CH_3)_3$ ), 0.09, 0.08 (2\*s, 6H,  $Si(CH_3)_2$ );  $^{13}C$  **NMR** (100 MHz,  $CDCl_3$ ):  $\delta$  = 137.9 (C-2), 136.9 (C-5), 131.6 (C-10), 131.0 (C-8), 124.0 (C-4), 122.9 (C-3), 42.5 (C-7), 39.82, 39.76 (C-1, C-6), 32.7 (C-9), 25.6 ( $C(CH_3)_3$ ), 18.1 ( $C(CH_3)_3$ ), -5.20, -5.30 ( $Si(CH_3)_2$ ); **GC-MS** (EI):

relative  $t_R$ :  $t_R = 9.54$  min ( $m/z = 262$  ( $M^+$ )); **HRMS** (EI):  $m/z$  calcd for  $C_{16}H_{26}OSi$  ( $M^+$ ): 262.1753; found: 262.1750. The *Z* geometry was established by  $^1H$  NMR NOE studies.

(*E*)-**8i** (purity 93% by GC): colorless liquid; **R<sub>f</sub>** 0.34 (cyclohexane/EtOAc, 96:4); **IR** (thin film): 3018, 2930, 2857 ( $CH_{\text{ethylenic}}$ ), 1678 (O-C=C), 1254, 1175, 1129  $cm^{-1}$  (C-O-Si);  **$^1H$  NMR** (400 MHz,  $CDCl_3$ ):  $\delta = 6.07$  (br s, 1H, 10-H), 6.00-5.96 (m, 1H, 5-H), 5.91 (br t,  $J = 10.0$  Hz, 1H, 2-H), 5.61-5.52 (m, 2H, 4-H, 3-H), 3.22 (br t,  $J = 7.8$  Hz, 1H, 1-H), 2.73-2.68 (br q (overlapping with d at 2.67 ppm),  $J = 8.0$  Hz, 1H, 6-H), 2.67 (d,  $J = 16.8$  Hz, 1H, 7- $H_d$ ), 2.49 (ddd,  $J = 16.8, 8.0, 2.4$  Hz, 1H, 7- $H_c$ ), 2.23-2.17 (m, 1H, 9- $H_a$ ), 1.96 (dd,  $J = 12.0, 1.6$  Hz, 1H, 9- $H_b$ ), 0.89 (s, 9H,  $C(CH_3)_3$ ), 0.09, 0.08 (2\*s, 6H,  $Si(CH_3)_2$ );  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ ):  $\delta = 138.9$  (C-5), 138.3 (C-2), 134.3 (C-8), 132.1 (C-10), 123.4, 123.1 (C-3, C-4), 41.0 (C-1), 40.6 (C-7), 38.4 (C-6), 32.9 (C-9), 25.6 ( $C(CH_3)_3$ ), 18.2 ( $C(CH_3)_3$ ), -5.26, -5.30 ( $Si(CH_3)_2$ ); **GC-MS** (EI): relative  $t_R$ :  $t_R = 9.58$  min ( $m/z = 262$  ( $M^+$ )); **HRMS** (EI):  $m/z$  calcd for  $C_{16}H_{26}OSi$  ( $M^+$ ): 262.1753; found: 262.1759. The *E* geometry was established by  $^1H$  NMR NOE studies.

**9i**: yellowish liquid; **R<sub>f</sub>** 0.26 (cyclohexane/DCM, 96:4); **IR** (thin film): 3079, 3023, 2929, 2856 ( $CH_{\text{ethylenic}}$ ), 1130  $cm^{-1}$  (C-O-Si);  **$^1H$  NMR** (400 MHz,  $CDCl_3$ ):  $\delta = 6.22$  (br t,  $J = 10.0$  Hz, 1H, 2-H), 5.88-5.81 (m, 2H, 5-H, 4-H), 5.64-5.59 (m, 1H, 3-H), 5.12 (m, 1H, one of 10-H), 4.92 (m, 1H, one of 10-H), 4.59 (dt,  $J = 5.6, 2.4$  Hz, 1H, 7-H), 3.34 (br t,  $J = 7.6$  Hz, 1H, 1-H), 2.76-2.71 (m, 1H, 6-H), 2.17 (ddd,  $J = 12.0, 8.2, 5.0$  Hz, 1H, 9- $H_a$ ), 1.81 (br d,  $J = 12.8$  Hz, 1H, 9- $H_b$ ), 0.94 (s, 9H,  $C(CH_3)_3$ ), 0.11 (s, 6H,  $Si(CH_3)_2$ );  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ ):  $\delta = 158.7$  (C-8), 139.1 (C-2), 134.6 (C-5), 126.1 (C-4), 124.2 (C-3), 108.1 (C-10), 86.4 (C-7), 45.0 (C-6), 39.8 (C-1), 27.4 (C-9), 25.9 ( $C(CH_3)_3$ ), 18.4 ( $C(CH_3)_3$ ), -4.9 ( $Si(CH_3)_2$ ); **GC-MS** (EI): relative  $t_R$ :  $t_R = 9.31$  min ( $m/z = 262$  ( $M^+$ )); **HRMS** (EI):  $m/z$  calcd for  $C_{16}H_{26}OSi$  ( $M^+$ ): 262.1753; found: 262.1761. The relative *endo* stereochemistry at C-7 of **9i** was determined by  $^1H$  NMR NOE studies (See Figure 1, page S25).

**11**: white oil which solidifies at rt; **R<sub>f</sub>** 0.63 (cyclohexane/EtOAc, 96:4); **Mp** = 57-58 °C; **IR** (thin film): 3070, 3024, 2952, 2935, 2886, 2862 ( $CH_{\text{ethylenic}}$ ), 1151, 1104, 1065, 1010 (C-O-Si), 863, 842  $cm^{-1}$  (C-Si);  **$^1H$  NMR** (400 MHz,  $CDCl_3$ ):  $\delta = 5.65$  (br dd,  $J = 9.6, 5.6$  Hz, 1H, 4-H), 5.46-5.41 (m, 1H, 3-H), 4.82 (br s, 1H, 13- $H_b$ ), 4.63 (br s, 1H, 13- $H_a$ ), 4.01 (br d,  $J = 2.4$  Hz, 1H, 12-H), 3.63 (br s, 1H, 7-H), 2.81 (br m, 1H, 5-H), 2.34-2.22 (m, 5H, 1-H, 2-H, 6-H, 10-H), 1.64-1.59 (m, 1H, 9-H), 1.44 (br d,  $J = 10.8$  Hz, 1H, 9- $H'$ ), 0.90 (s, 9H,  $C(CH_3)_3$  of one TBS), 0.88 (s, 9H,  $C(CH_3)_3$  of one TBS), 0.06, 0.04, 0.03, 0.01 (4\*s, 12H,  $Si(CH_3)_2$  of two TBS);  **$^1H$  NMR** (400 MHz,  $C_6D_6$ ):  $\delta = 5.72$  (br dd,  $J = 9.6, 5.6$  Hz, 1H, 4-H), 5.44 (br ddd,  $J = 9.6, 5.6, 1.6$  Hz, 1H, 3-H), 4.86 (br t,  $J = 2$  Hz, 1H, 13- $H_b$ ), 4.69 (br t,  $J = 2$  Hz, 1H,

13-H<sub>a</sub>), 4.10 (br d,  $J = 3.6$  Hz, 1H, 12-H), 3.69 (br s, 1H, 7-H), 3.08 (br m, 1H, 5-H), 2.69 (br d,  $J = 13.6$  Hz, 1H, 10-H), 2.62 (br d,  $J = 13.6$  Hz, 1H, 10-H'), 2.58-2.52 (m, 1H, 1-H), 2.43-2.40 (m, 1H, 2-H), 2.31 (br s, 1H, 6-H), 1.66-1.58 (m, 2H, 9-H), 0.99 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> of one TBS), 0.97 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> of one TBS), 0.09, 0.08 (2\*s, 6H, Si(CH<sub>3</sub>)<sub>2</sub> of one TBS), 0.02 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub> of one TBS); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 146.4$  (C-11), 129.2 (C-4), 128.0 (C-3), 112.7 (C-13), 81.0 (C-7), 76.3 (C-12), 50.6 (C-8), 49.2 (C-6), 45.0 (C-2), 42.9 (C-5), 32.2 (C-10), 31.6 (C-1), 26.5 (C-9), 25.9, 25.8 (C(CH<sub>3</sub>)<sub>3</sub>), 18.2, 18.1 (C(CH<sub>3</sub>)<sub>3</sub>), -4.6, -4.7, -4.9, -5.1 (Si(CH<sub>2</sub>)<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 146.2$  (C-11), 129.6 (C-4), 128.1 (C-3), 113.5 (C-13), 81.5 (C-7), 76.9 (C-12), 51.1 (C-8), 49.7 (C-6), 45.5 (C-2), 43.5 (C-5), 32.9 (C-10), 32.2 (C-1), 26.9 (C-9), 26.0 (C(CH<sub>3</sub>)<sub>3</sub>), 18.4 (C(CH<sub>3</sub>)<sub>3</sub>), -4.5, -4.6, -4.8, -4.9 (Si(CH<sub>2</sub>)<sub>3</sub>); **GC-MS** (EI): relative  $t_R$ :  $t_R = 13.42$  ( $m/z = 432$  (M<sup>+</sup>)); **HRMS** (EI):  $m/z$  calcd for C<sub>25</sub>H<sub>44</sub>O<sub>2</sub>Si<sub>2</sub> (M<sup>+</sup>): 432.2880; found: 432.2890. **Elemental analysis** (%) calcd for C<sub>25</sub>H<sub>44</sub>O<sub>2</sub>Si<sub>2</sub>: C, 69.38; H, 10.25; found: C, 69.19; H, 10.42. The structural and stereochemical assignment of **11** was confirmed by X-ray crystallographic analysis performed on its diol derivative **19** (See pages S27-S28).

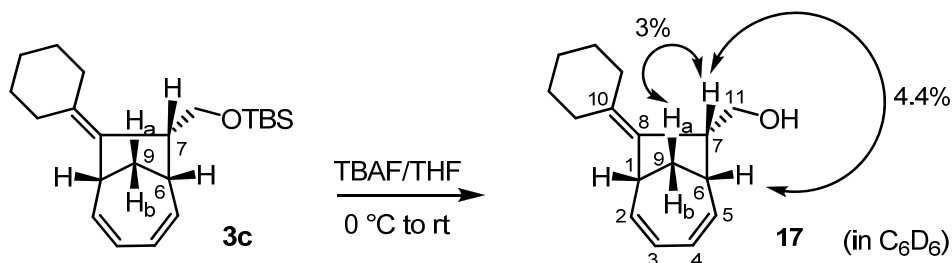
#### 4. Cycloaddition between **1** and (*S*)-**4a**, and determination of ee

Following the Procedure A, a solution of CHT-Cr **1** (74 mg, 0.32 mmols) and allene (*S*)-**4a** (126 mg, 0.48 mmols, 60% ee) in hexanes (100 mL) was irradiated for 6 h. Treatment with P(OMe)<sub>3</sub> after irradiation, followed by purification by flash chromatography (cyclohexane/DCM, 96:4) provided (*E*)-**5a** (50 mg, 45%). Then, cycloadduct **5a** was diluted in THF (2 mL), and TBAF (1M in THF, 185  $\mu$ L, 0.185 mmols) was introduced slowly at 0 °C. The resulting mixture was held at 0 °C for 5 min and then stirred at rt for 3 h. The mixture was quenched with water and extracted with EtOAc. The organic extracts were combined, washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated. The residue was purified by flash chromatography (pentane/EtOAc, 90:10 to 80:20) to give **5b** (22 mg, 65%) in 54% ee ( $[\alpha]_D^{23} = -350.3^\circ$  ( $c = 0.90$  in CHCl<sub>3</sub>)). The ee was determined by <sup>1</sup>H NMR analysis after derivatization into the corresponding Mosher ester<sup>15</sup>: to a solution of **5b** (9.5 mg, 0.4 mmols) in CDCl<sub>3</sub> (500  $\mu$ L) at rt was added successively pyridine (3 equiv), DMAP and (R)-(-)-MTPA chloride (1.5 equiv). After 1.5 h of stirring, the mixture was filtered through cotton and the resultant solution was directly analysed by <sup>1</sup>H NMR. The signal at 3.95 ppm (one proton 11-H) appears split as two dd at 4.69 and 4.58 ppm. The ee was measured by integration. See copies of <sup>1</sup>H NMR spectra (racemic + enantioenriched) attached (See pages S95-S96).

## 5. Some examples of stereochemical rationales

### 5.1. Indirect stereochemical assignment for **3c** via its alcohol derivative **17**

NOE studies could not be done directly on **3c** because the protons 7-H and 6-H were not split enough. It could be however performed on its alcohol derivative **17** obtained after removal of the TBS protecting group in **3c** as described after:



To a solution of **3c** (39 mg, 0.113 mmols) in THF (2 mL) at 0 °C was introduced slowly TBAF (1M in THF, 423  $\mu$ L, 0.423 mmols). The mixture was held at 0 °C for 5 min and then stirred at rt for 4 h. The mixture was quenched with water and extracted with EtOAc. The organic extracts were combined, washed with brine, dried over  $\text{MgSO}_4$ , filtered and concentrated. The residue was purified by flash chromatography on  $\text{SiO}_2$  (pentane/EtOAc, 90:10) to give alcohol **17** (17 mg, 65%) as a colorless oil:  $R_f$  0.25 (pentane/EtOAc, 90:10); **IR** (thin film): 3347 (broad, OH), 3016  $\text{cm}^{-1}$  ( $\text{CH}_{\text{ethylenic}}$ );  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.01 (dd,  $J$  = 11.2, 8.0 Hz, 1H, 5-H), 5.88-5.81 (m, 2H, 4-H, 2-H), 5.59 (dd,  $J$  = 11.2, 7.2 Hz, 1H, 3-H), 3.76 (dd,  $J$  = 10.4, 4.0 Hz, 1H, 11-H), 3.52 (br t,  $J$  = 11.2, 10.4 Hz, 1H, 11-H'), 3.33 (br t,  $J$  = 6.6 Hz, 1H, 1-H), 3.17-3.11 (m, 1H, 7-H), 3.05-2.99 (br q,  $J$  = 7.2 Hz, 1H, 6-H), 2.22-1.96 (m, 7H, 9- $\text{H}_a$ , H of cyclohexane), 1.98 (br d,  $J$  = 12.0 Hz, 1H, 9- $\text{H}_b$ ), 1.60-1.40 (m, 4H, H of cyclohexane);  **$^1\text{H}$  NMR** (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 5.92 (dd,  $J$  = 11.2, 8.0 Hz, 1H, 5-H), 5.77-5.69 (m, 2H, 4-H, 2-H), 5.54 (br dd,  $J$  = 12.0, 6.6 Hz, 1H, 3-H), 3.74 (dd,  $J$  = 10.8, 4.8 Hz, 1H, 11-H), 3.56 (br t,  $J$  = 10.8 Hz, 1H, 11-H'), 3.15 (m, 1H, 1-H), 3.08-2.99 (m, 1H, 7-H), 2.92-2.83 (m, 1H, 6-H), 2.00-1.80 (m, 8H, 9-H, H of cyclohexane), 1.45-1.30 (m, 4H, H of cyclohexane);  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 140.2 (C-8 or C-10), 136.1, 134.6 (C-2, C-5), 130.2 (C-8 or C-10), 126.9 (C-4), 123.1 (C-3), 64.2 (C-11), 53.9 (C-7), 44.1 (C-1), 40.0 (C-6), 33.5 ( $\text{CH}_2$  of cyclohexane), 31.9 (C-9), 30.2, 28.2, 27.9, 26.6 ( $\text{CH}_2$  of cyclohexane); **MS** (ESI):  $m/z$  = 231 ( $\text{M}+\text{H}^+$ ), 253 ( $\text{M}+\text{Na}^+$ ); **HRMS** (EI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{22}\text{O}$  ( $\text{M}^+$ ): 230.1671; found: 230.1678. NOE correlations were seen between 7-H and 6-H, as well as between 7-H and 9- $\text{H}_a$ , which is consistent with the *endo* stereochemistry assignment.



## 5.2. Representative $^1\text{H}$ NMR NOE data for (*E*)-**5a**, (*Z*)-**8e**, and **9h-i**

In compounds (*E*)-**5a** and (*Z*)-**8e**, no NOE was seen between 1-H and 10-H, which does suggest that 10-H is *syn* to C-7 (Figure 1). NOE correlations were seen between 10-H and 7-H, and between 10-H and 11-H in **5a**.

In compounds **5a**, **9h** and **9i**, NOE correlations were seen between 7-H and 6-H, as well as between 7-H and 9-H<sub>a</sub>, suggestive of the *endo* stereochemistry at C-7. Moreover, in compounds **9h** and **9i**, 7-H and 6-H display a coupling constant with a *J* value of 6.4 Hz (in **9h**) and 5.6 Hz (in **9i**), which also confirms the stereochemical assignment. In the case of the *exo* isomer, this constant would be close to zero because of an angle H<sub>endo</sub>-(C-7)-(C-6)-H around 90° (from molecular models).

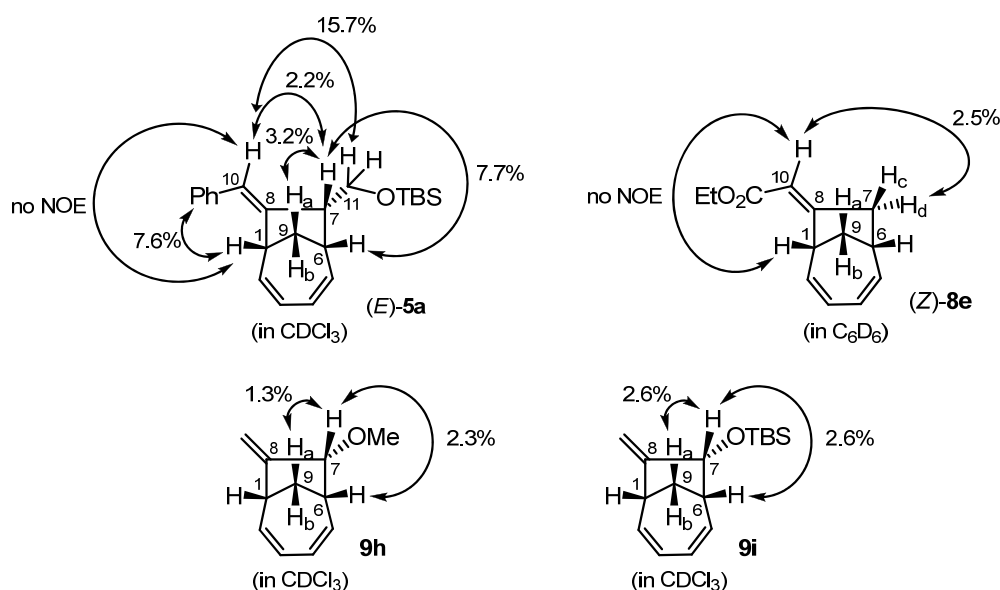
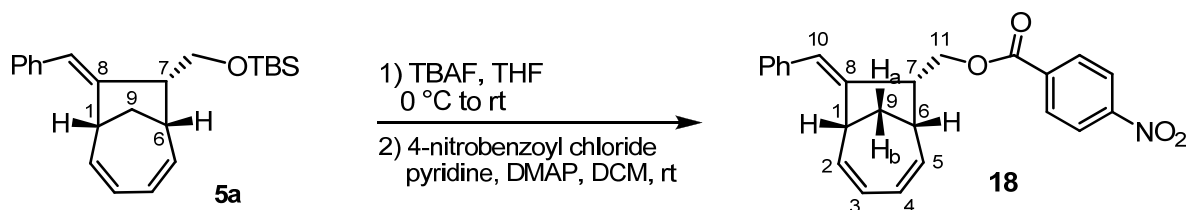


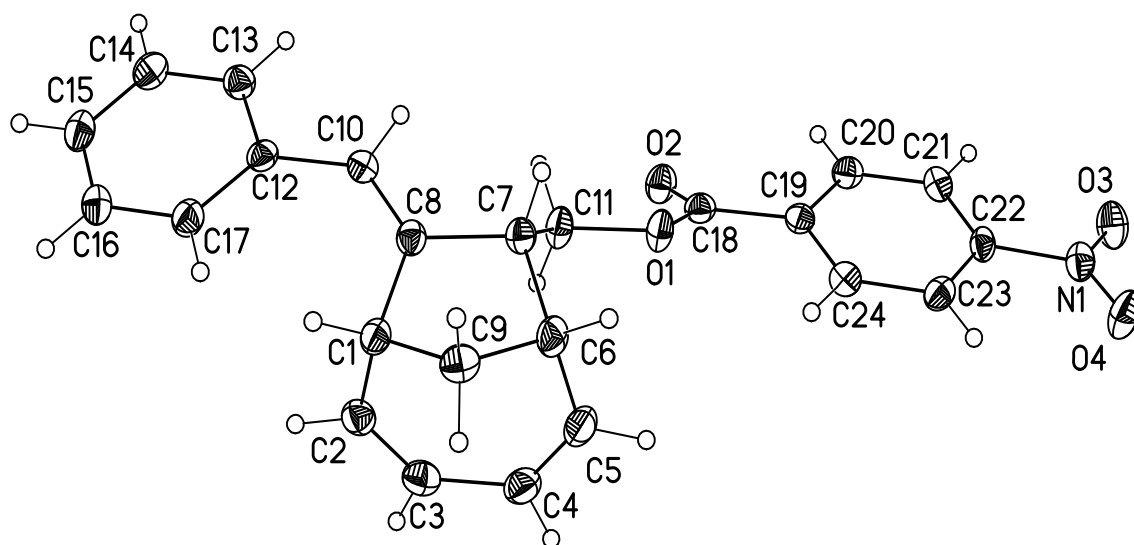
Figure 1.

## 6. Derivatization of **5a** into *p*-nitrobenzoate ester **18**, and X-Ray structure of **18**



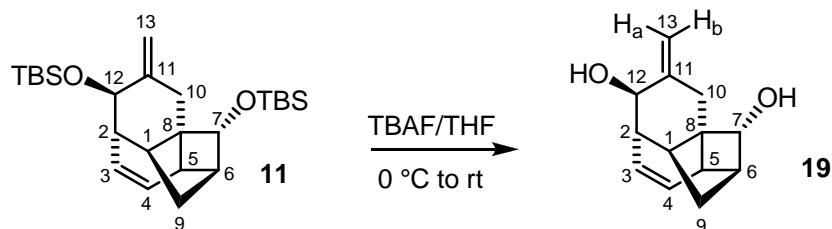
To a solution of (*E*)-**5a** (55 mg, 0.156 mmols) in THF (2 mL) at 0 °C was introduced slowly TBAF (1M in THF, 172  $\mu\text{L}$ , 0.172 mmols). The mixture was held at 0 °C for 5 min and then stirred at rt for 3 h. The mixture was quenched with water and extracted with EtOAc. The combined organic extracts were washed with brine, dried over  $\text{MgSO}_4$ , filtered and concentrated. The residue was purified by flash chromatography (pentane/EtOAc, 80:20) to give alcohol (*E*)-**5b** (27 mg, 73%) as a colorless oil. The IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra as well

as the mass data were in complete accord with those obtained from material prepared above by cycloaddition with allene **4b** (Table 2, entry 3). Then, to a solution of the obtained alcohol **5b** (21 mg, 0.09 mmols) in DCM (2 mL) at rt was added successively DMAP (1 mg, 0.009 mmols), pyridine (23  $\mu$ L, 0.28 mmols) and 4-nitrobenzoyl chloride (33 mg, 0.18 mmols). The mixture was stirred at rt for 41 h. Water was added, and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated. The residue was purified by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 100:0 to 90:10) to afford ester **18** (21 mg, 60%) as a yellow solid: **R<sub>f</sub>** 0.60 (100% pentane); **Mp** = 105 °C; **IR** (KBr): 1724 cm<sup>-1</sup> (C=O); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.31 (d, *J* = 8.8 Hz, 2H, H<sub>arom</sub> of nitro benzyl), 8.24 (d, *J* = 8.8 Hz, 2H, H<sub>arom</sub> of nitro benzyl), 7.35-7.21 (m, 5H, H<sub>arom</sub> of phenyl), 6.24 (br s, 1H, 10-H), 6.17-6.12 (m, 1H, 2-H), 5.92-5.84 (m, 2H, 4-H, 5-H), 5.67-5.62 (m, 1H, 3-H), 4.78 (dd, *J* = 10.4, 5.6 Hz, 1H, 11-H), 4.50 (t, *J* = 10.4 Hz, 1H, 11-H'), 3.76 (br t, *J* = 7.2 Hz, 1H, 1-H), 3.48-3.42 (m, 1H, 7-H), 3.06-3.01 (m, 1H, 6-H), 2.39-2.32 (m, 1H, 9-H<sub>a</sub>), 2.10 (br d, *J* = 12.4 Hz, 1H, 9-H<sub>b</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 164.5 (C=O of ester), 150.6 (2 lines, C-8 and O<sub>2</sub>N-C<sub>arom</sub>), 137.8 (*i*-C<sub>arom</sub> of phenyl), 135.7 (RO<sub>2</sub>C-C<sub>arom</sub>), 135.3, 133.3 (C-2, C-5), 130.7, 128.4, 127.7, 126.9, 126.7, 124.2, 123.6, 122.5 (CH<sub>arom</sub> of phenyl and nitrobenzyl, C-3, C-4, C-10), 66.8 (C-11), 56.3 (C-7), 42.6 (C-1), 40.5 (C-6), 32.0 (C-9); **HRMS** (EI): *m/z* calcd for C<sub>24</sub>H<sub>21</sub>NO<sub>4</sub> (M<sup>+</sup>): 387.1471; found: 387.1477. **Elemental analysis** (%) calcd for C<sub>24</sub>H<sub>21</sub>NO<sub>4</sub>: C, 74.40; H, 5.46; N, 3.62; found: C, 74.14; H, 5.45; N, 3.57. The solid was dissolved with a minimum of diethyl ether, and hexanes was added. Solvents were evaporated very slowly to give yellow crystals which were dried and further analyzed by X-ray analysis (See Figure 2).

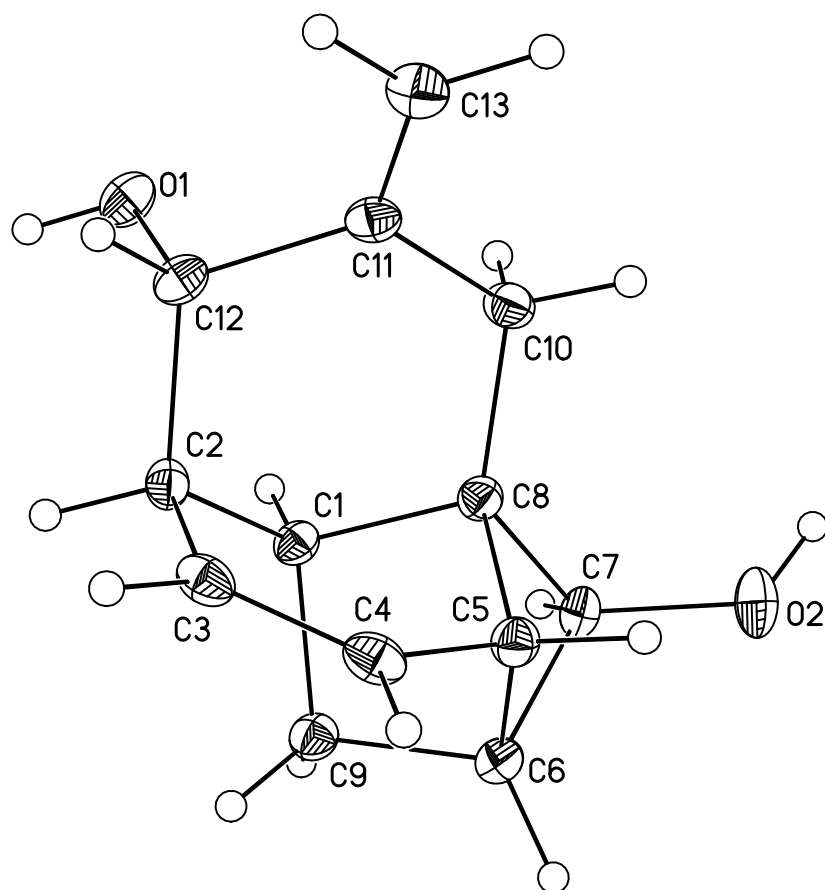


**Figure 2. X-Ray structure of 18**

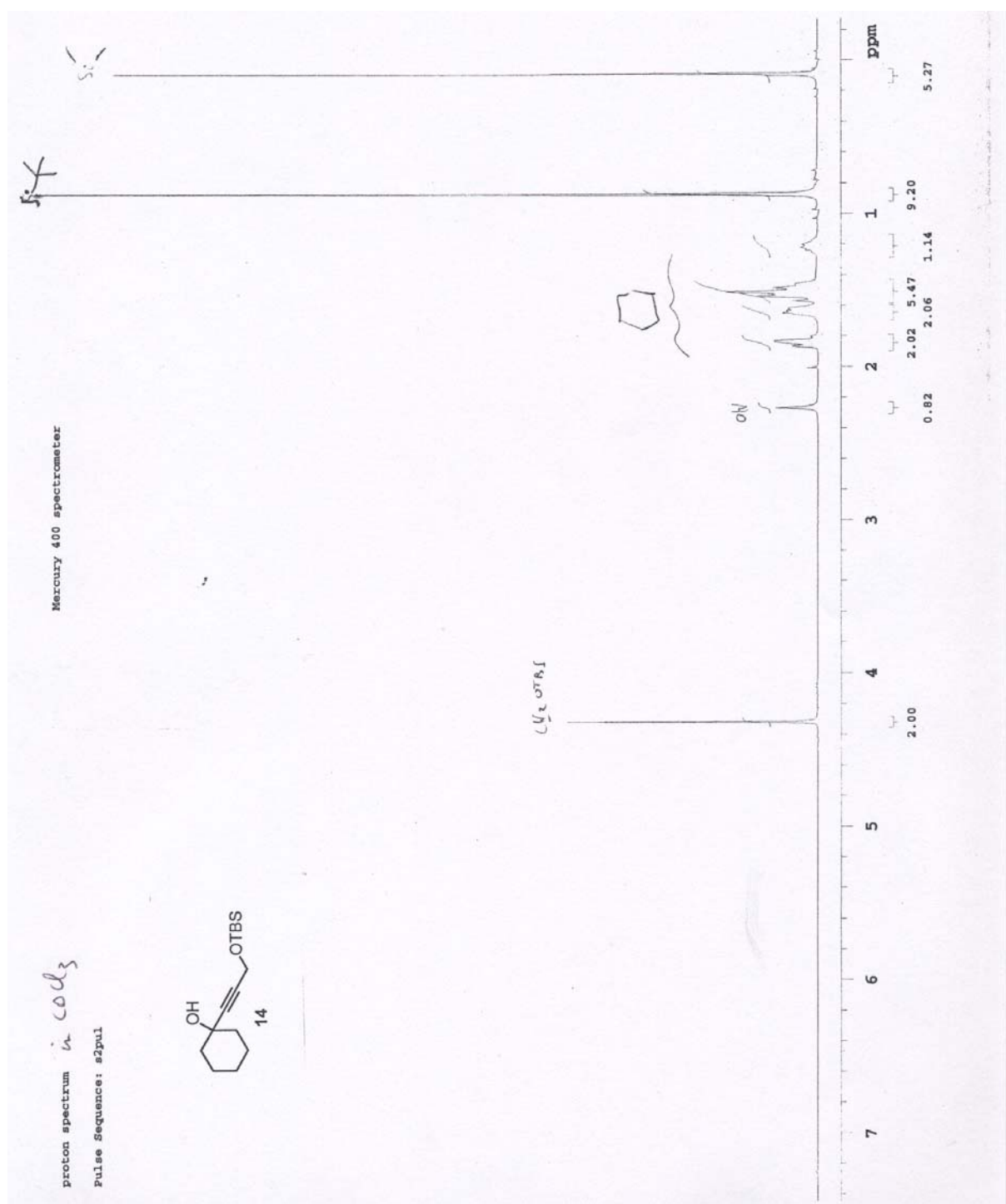
## 7. Deprotection of TBS-protecting groups in **11**, and X-Ray structure of the corresponding diol **19**



To a solution of **11** (59 mg, 0.136 mmols) in THF (2 mL) at 0 °C was introduced slowly TBAF (1M in THF, 1.36 mL, 1.36 mmols). The mixture was held at 0 °C for 5 min and then stirred at rt for 3 days. The mixture was quenched with water and extracted with EtOAc. The combined organic extracts were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated. The residue was purified by flash chromatography on SiO<sub>2</sub> (pentane/EtOAc, 30:70) to give diol **19** (18 mg, 64%) as a yellow visqueous oil. The oil was triturated in diethyl ether, and the resultant solid residue was filtered, washed with cold Et<sub>2</sub>O and dried to give a white solid: **R<sub>f</sub>** 0.37 (pentane/EtOAc, 30:70); **Mp** (Et<sub>2</sub>O) = 157-158 °C; **IR** (thin film): 3362, 3281 cm<sup>-1</sup> (broad, OH); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.68 (dd,  $J$  = 9.6, 5.6 Hz, 1H, 4-H), 5.50 (br ddd,  $J$  = 9.6, 5.6, 1.6 Hz, 1H, 3-H), 4.92 (br t,  $J$  = 2 Hz, 1H, 13-H<sub>b</sub>), 4.81 (br t,  $J$  = 2 Hz, 1H, 13-H<sub>a</sub>), 4.12 (br d,  $J$  = 3.2 Hz, 1H, 12-H), 3.77 (br s, 1H, 7-H), 2.88 (m, 1H, 5-H), 2.52 (br dt,  $J$  = 14.8, 2.4 Hz, 1H, one of 10-H), 2.46-2.31 (m, 4H, 1-H, 2-H, 6-H, one of 10-H), 1.71-1.68 (m, 1H, 9-H), 1.52 (br dt,  $J$  = 11.6, 2.8 Hz, 1H, 9-H'); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 145.4 (C-11), 128.9, 128.0 (C-4, C-3), 114.8 (C-13), 80.9 (C-7), 75.8 (C-12), 49.9 (C-8), 48.9 (C-6), 43.0, 42.9 (C-2, C-5), 31.8 (C-1), 31.5 (C-10), 26.5 (C-9); **HRMS** (EI):  $m/z$  calcd for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub> (M<sup>+</sup>): 204.1150; found: 204.1150. **Elemental analysis** (%) calcd for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub>: C, 76.44; H, 7.90; found: C, 76.19; H, 7.99. The solid was dissolved in diethyl ether by heating, and the resulting solution was evaporated very slowly to furnish yellow crystals which were dried and further analyzed by X-ray analysis (See Figure 3, page S28).



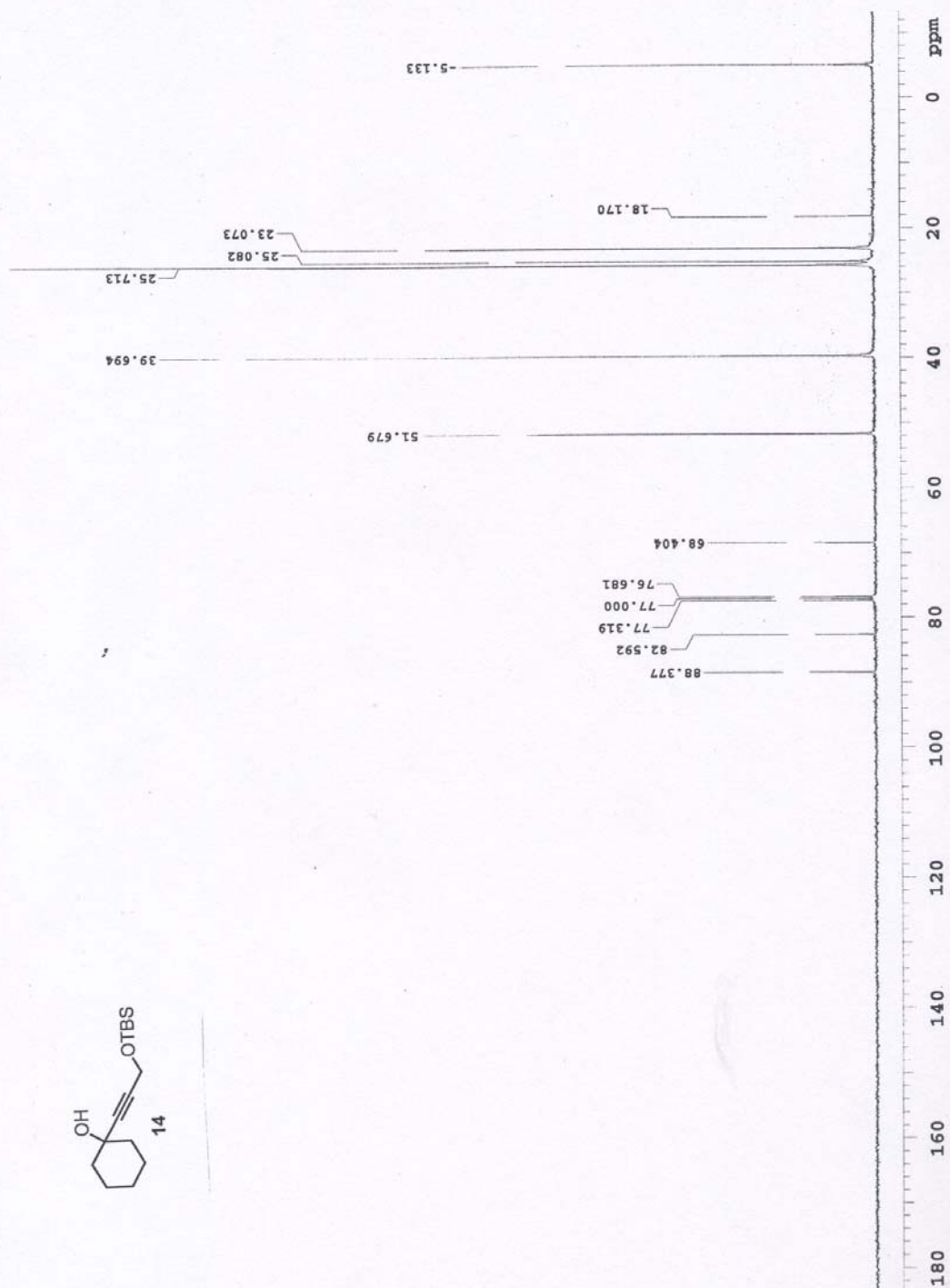
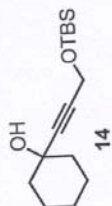
**Figure 3. X-Ray structure of diol 19 (one enantiomer represented)**

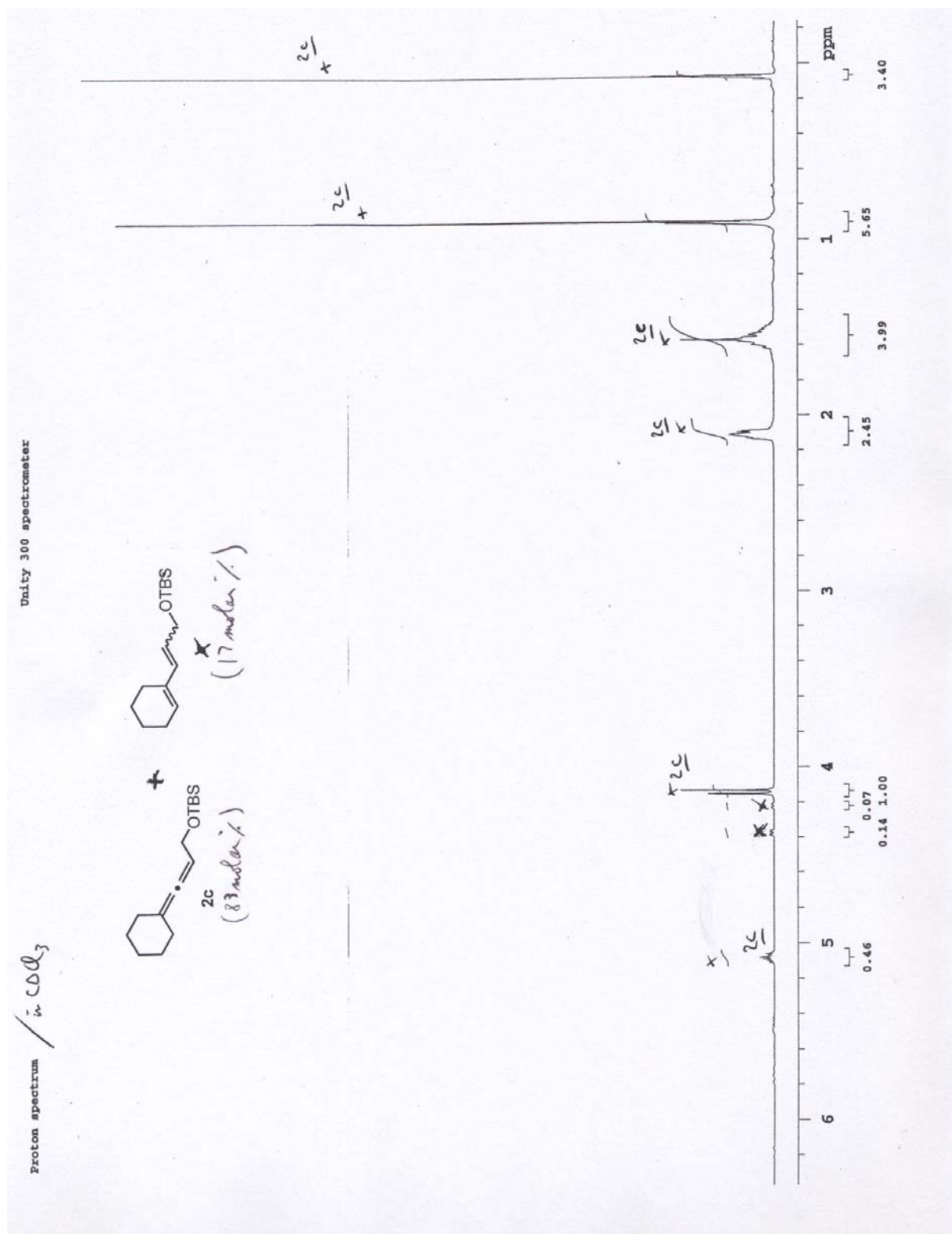


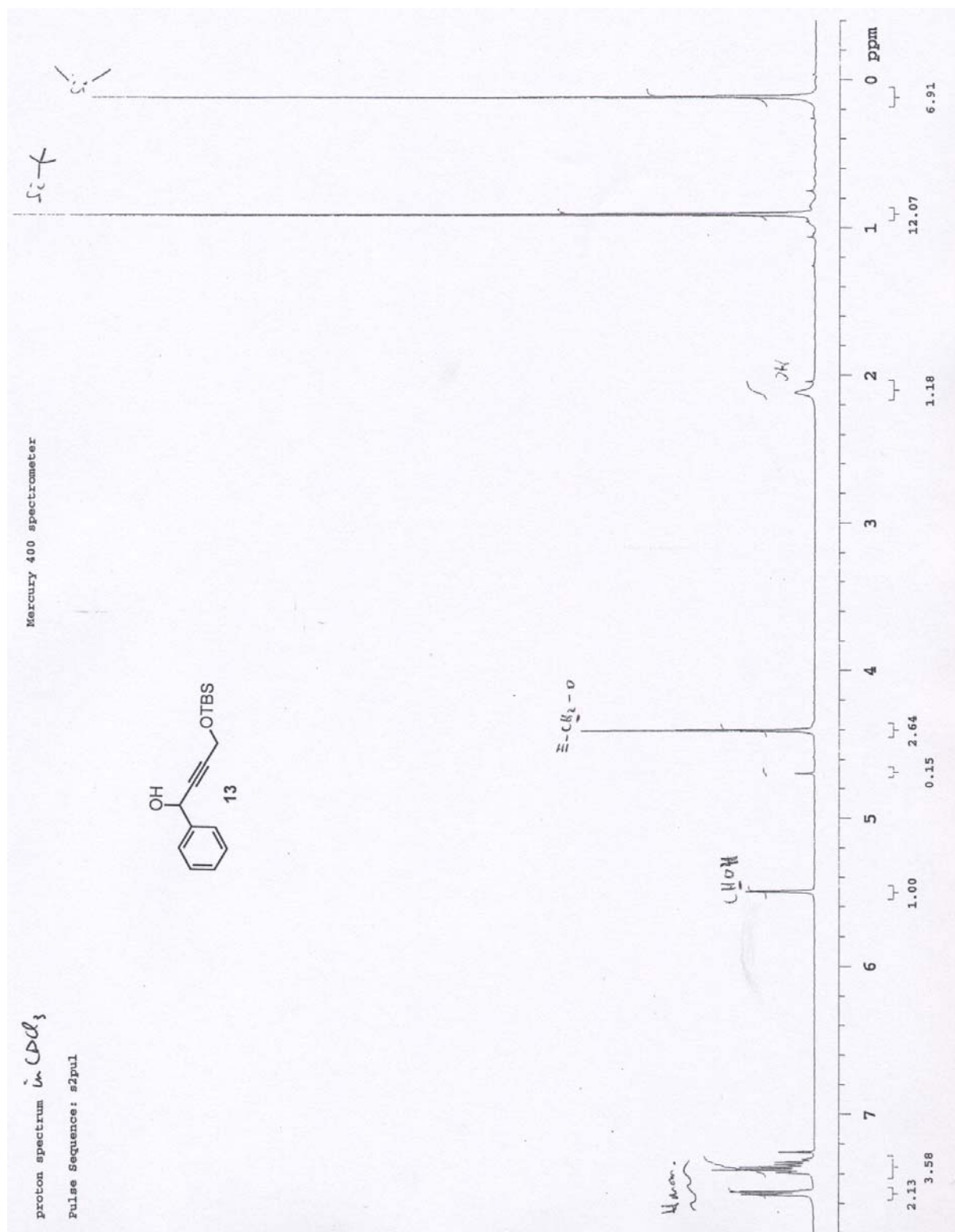
Mercury 400 spectrometer

Carbon spectrum in  $CDCl_3$

Pulse Sequence: s2pul





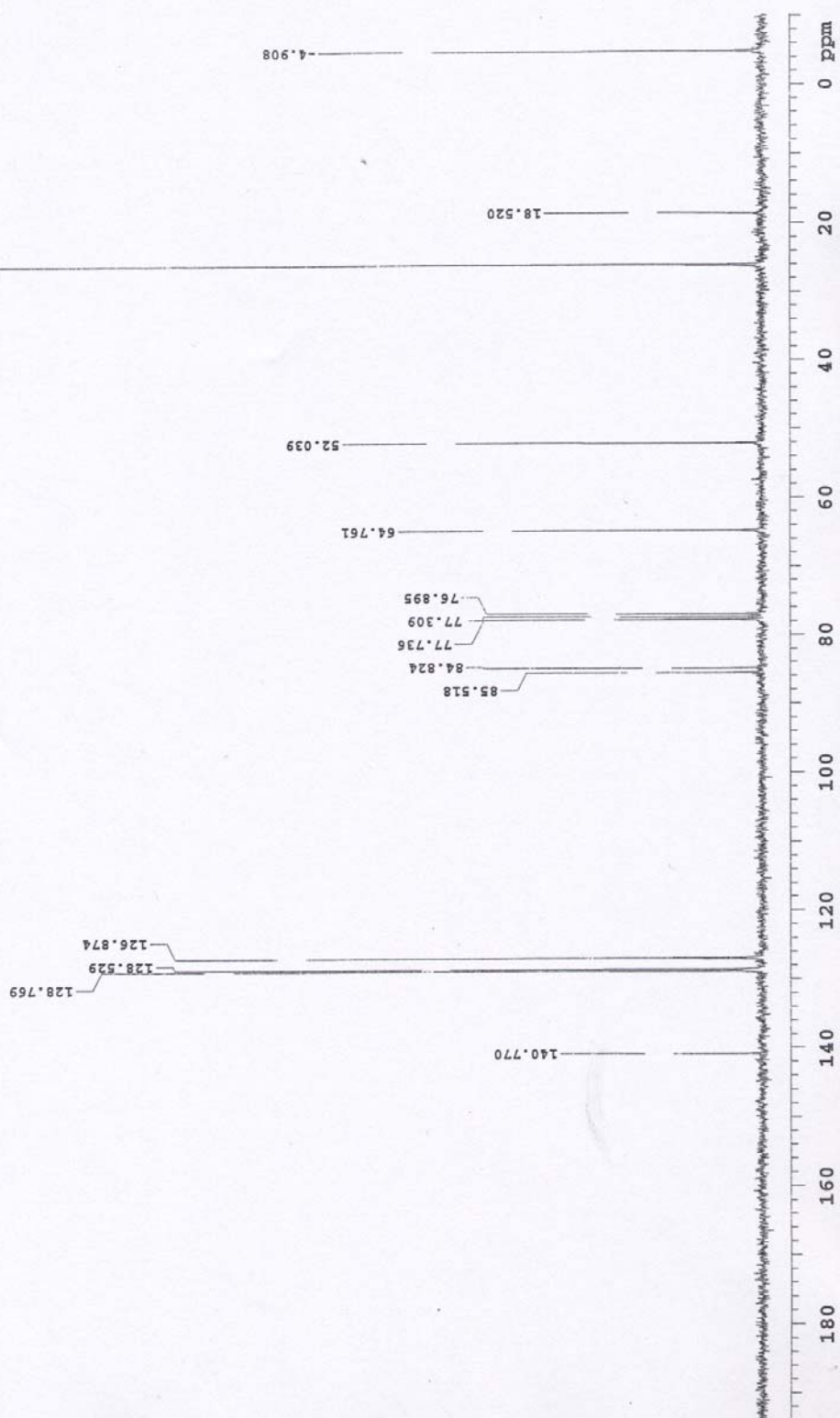
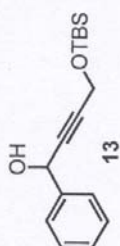


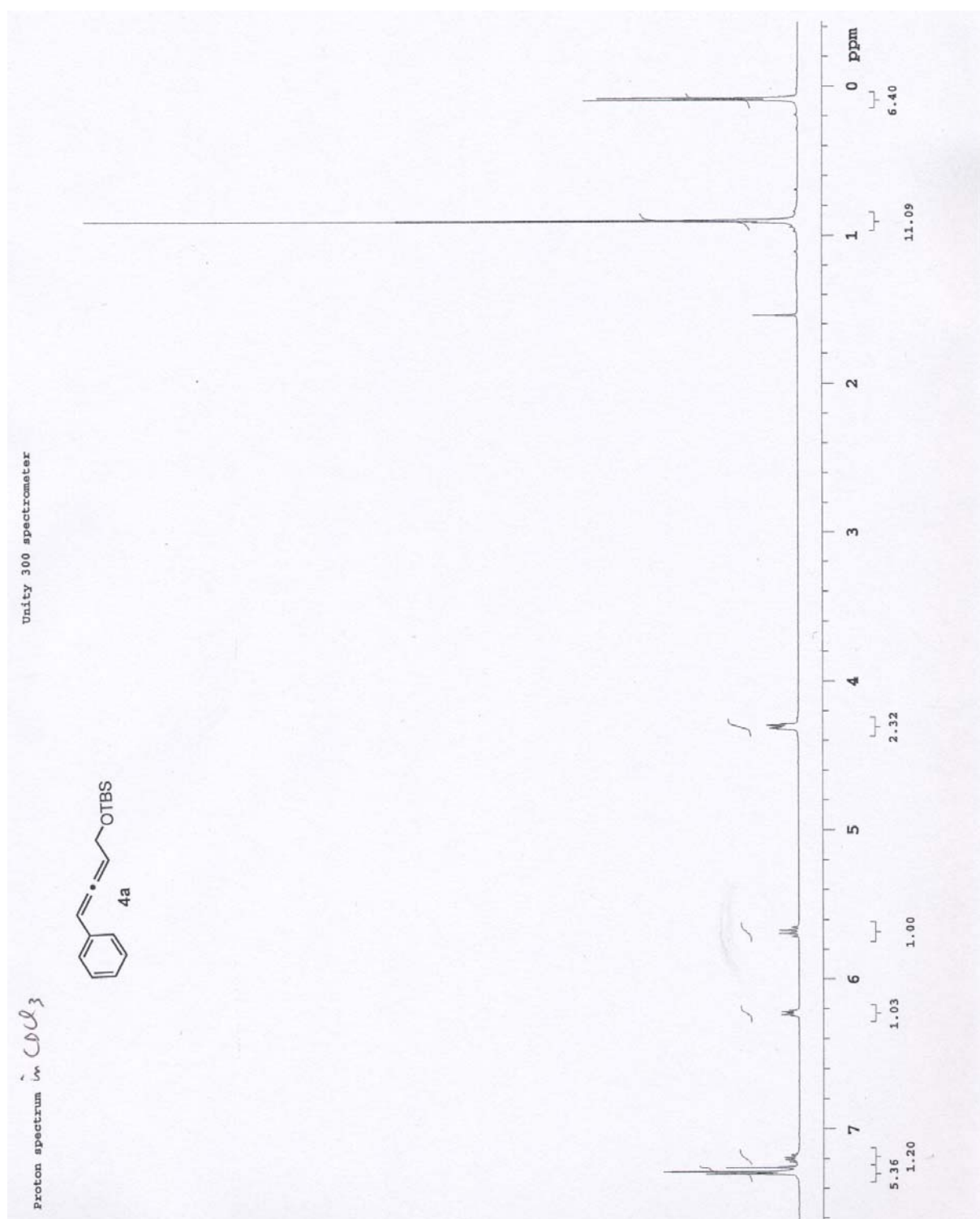


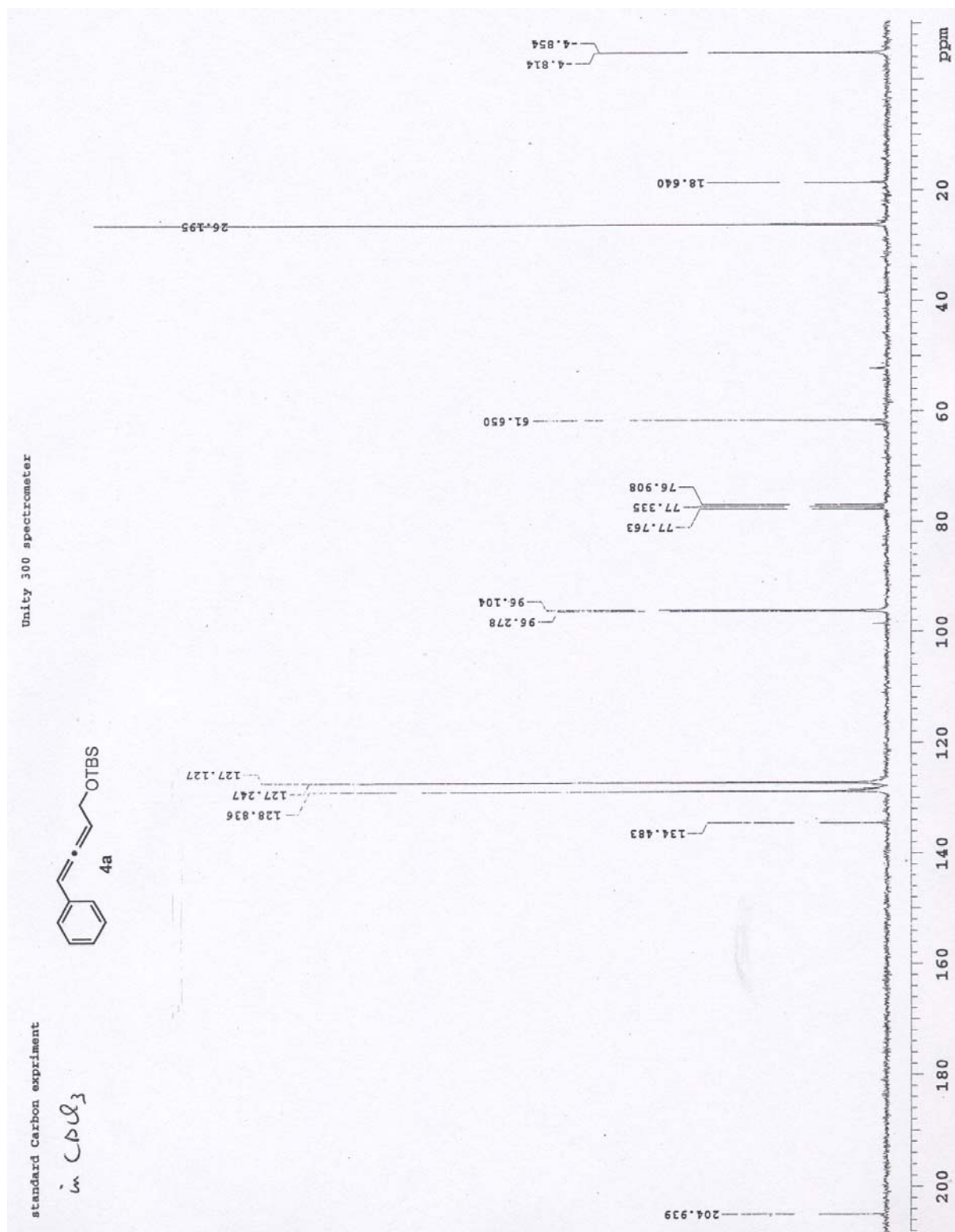
Unity 300 spectrometer

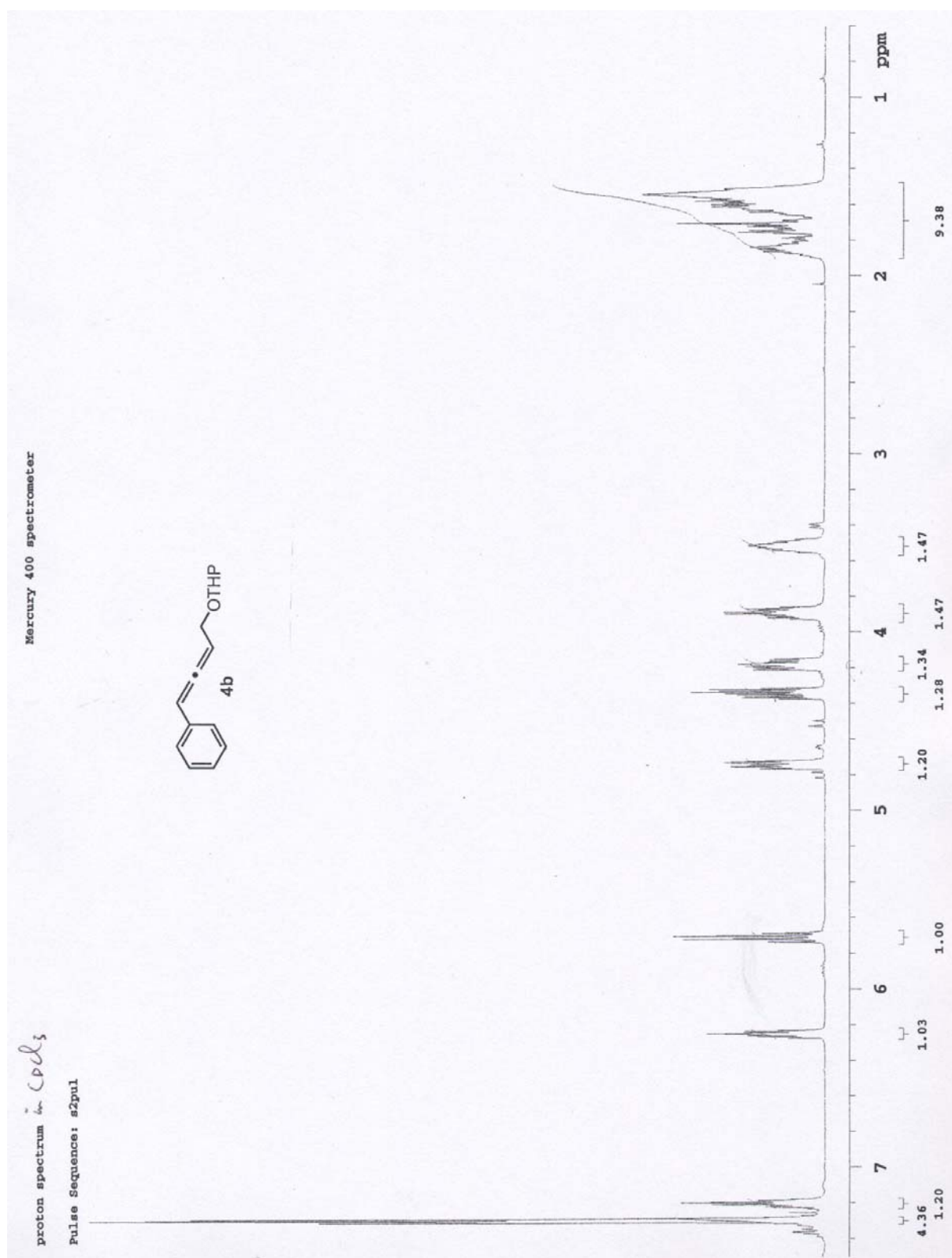
standard Carbon experiment

in CDCl<sub>3</sub>





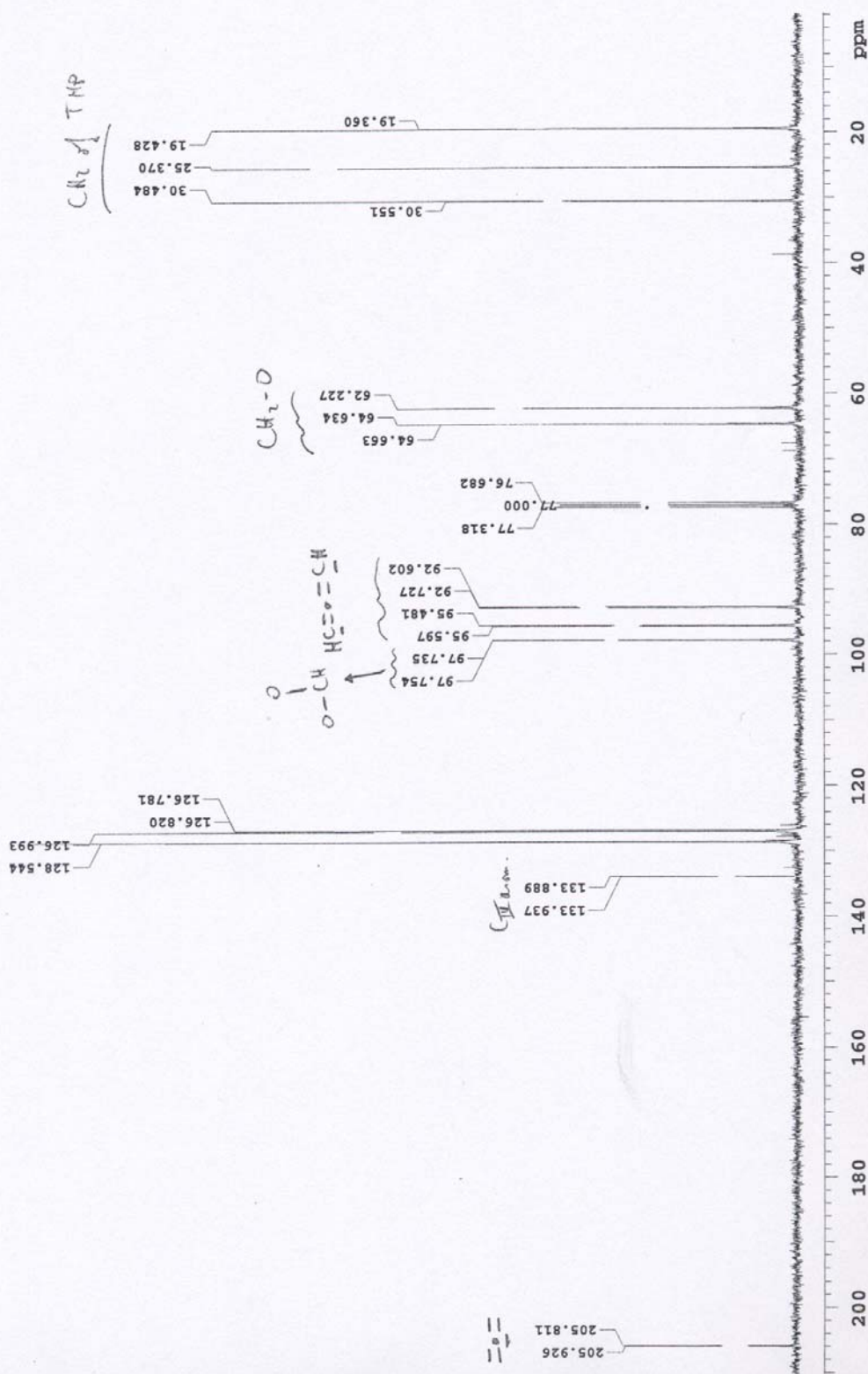
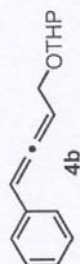




Mercury 400 spectrometer

Carbon spectrum in CDCl<sub>3</sub>

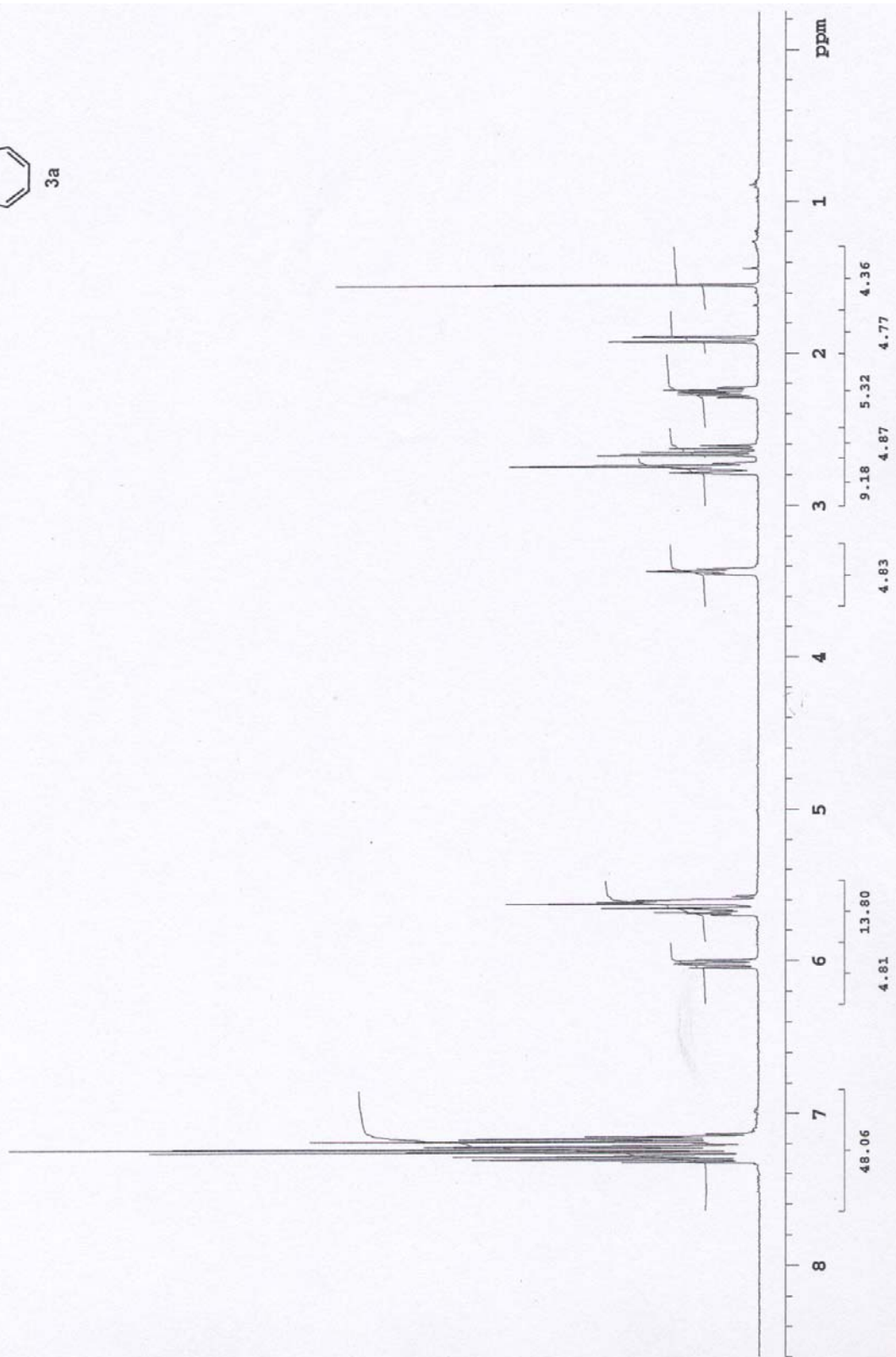
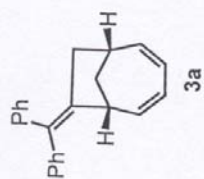
Pulse Sequence: s2pul

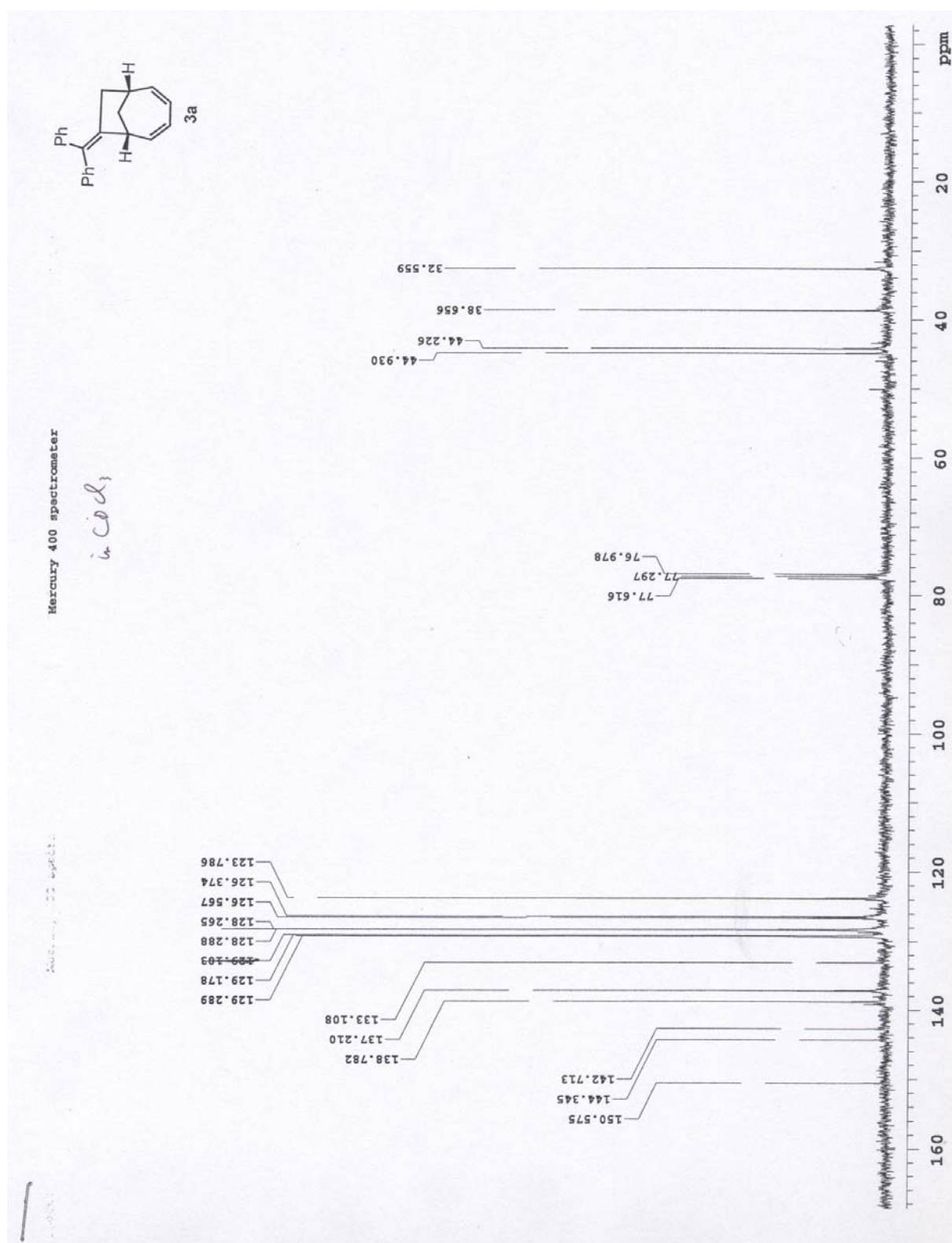




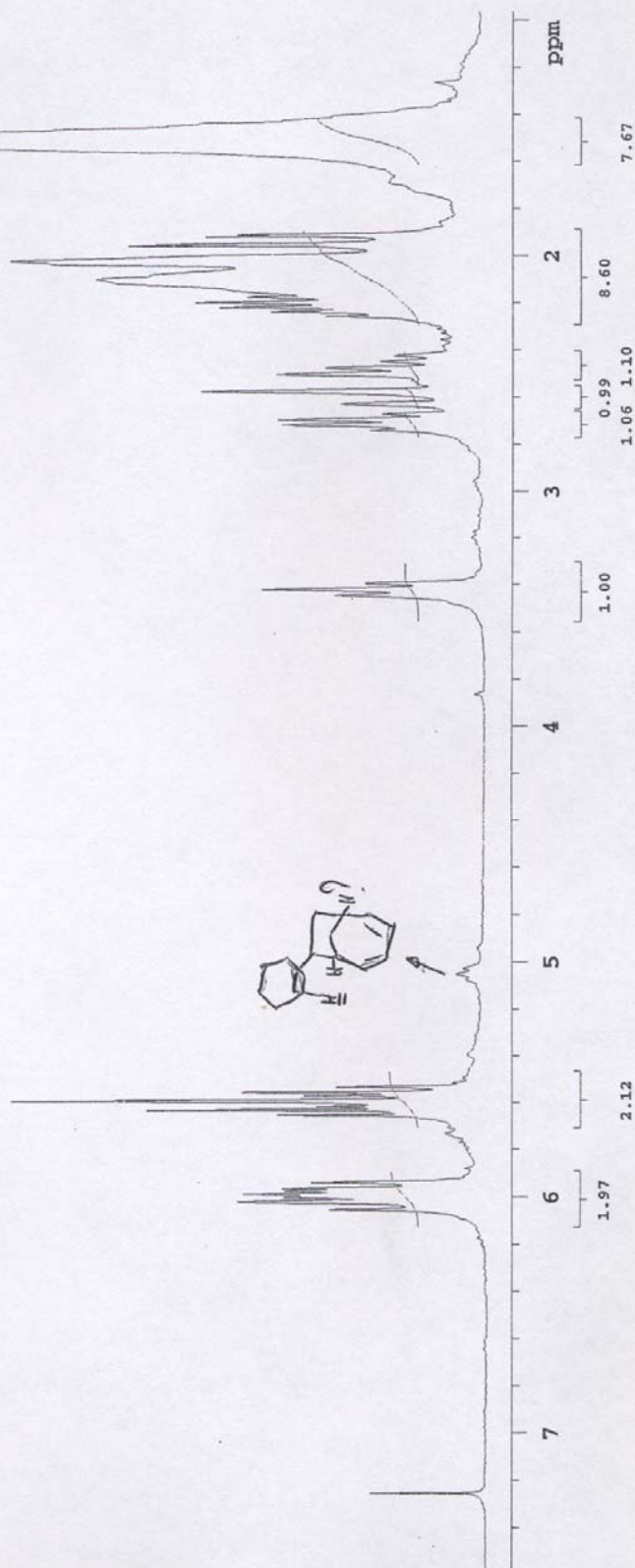
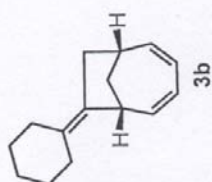
Mercury 400 spectrometer

*in CDCl<sub>3</sub>*

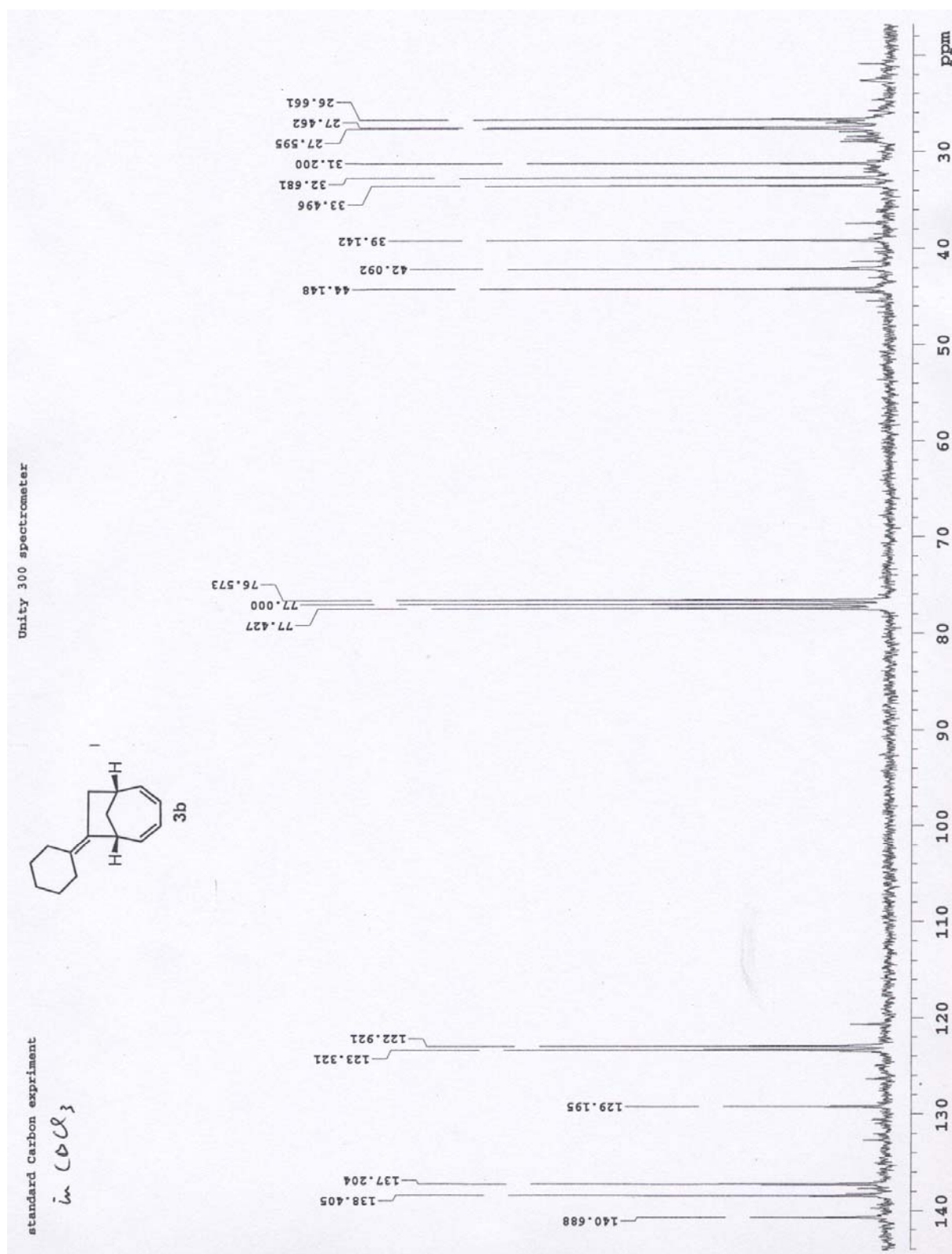


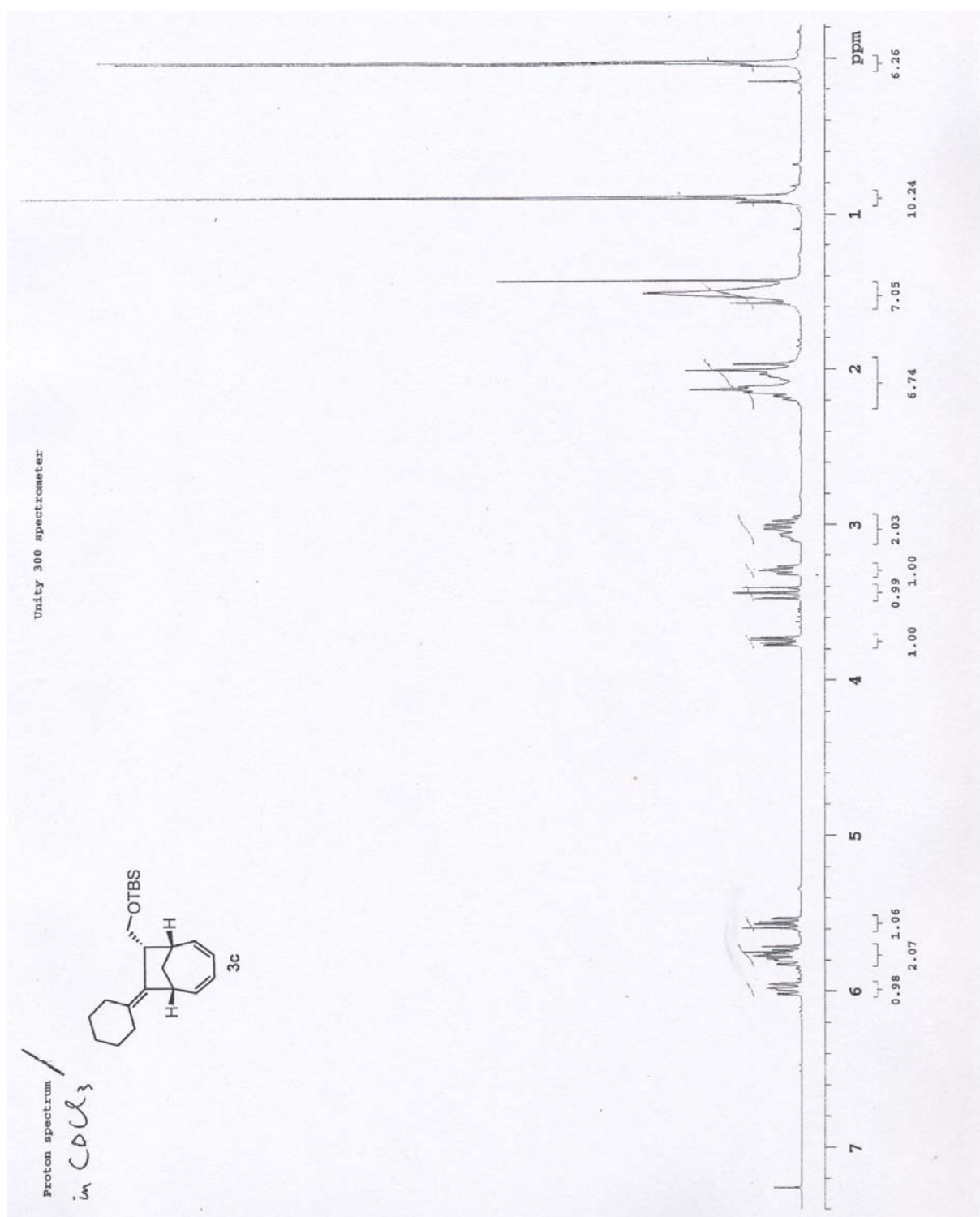


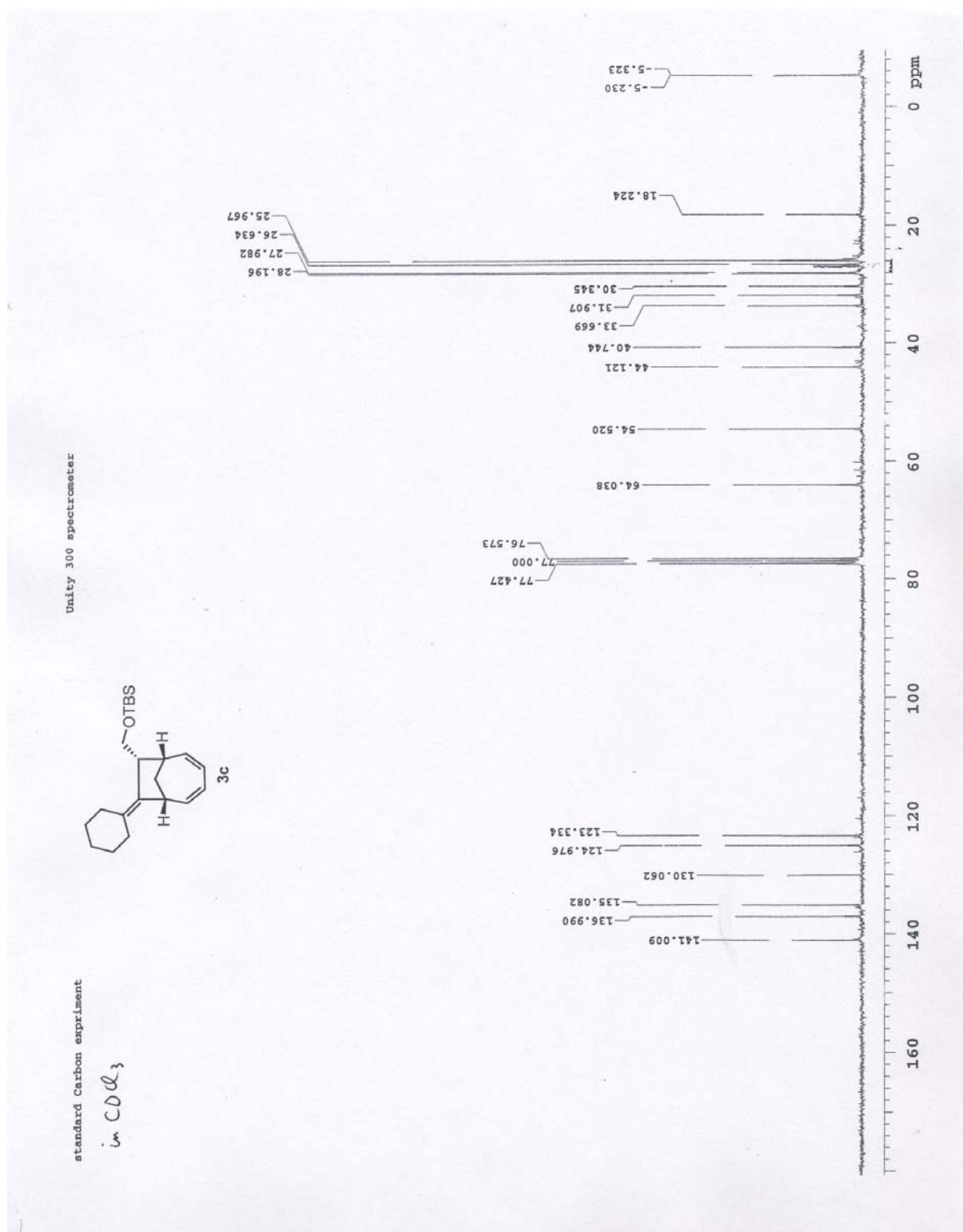
Proton spectrum

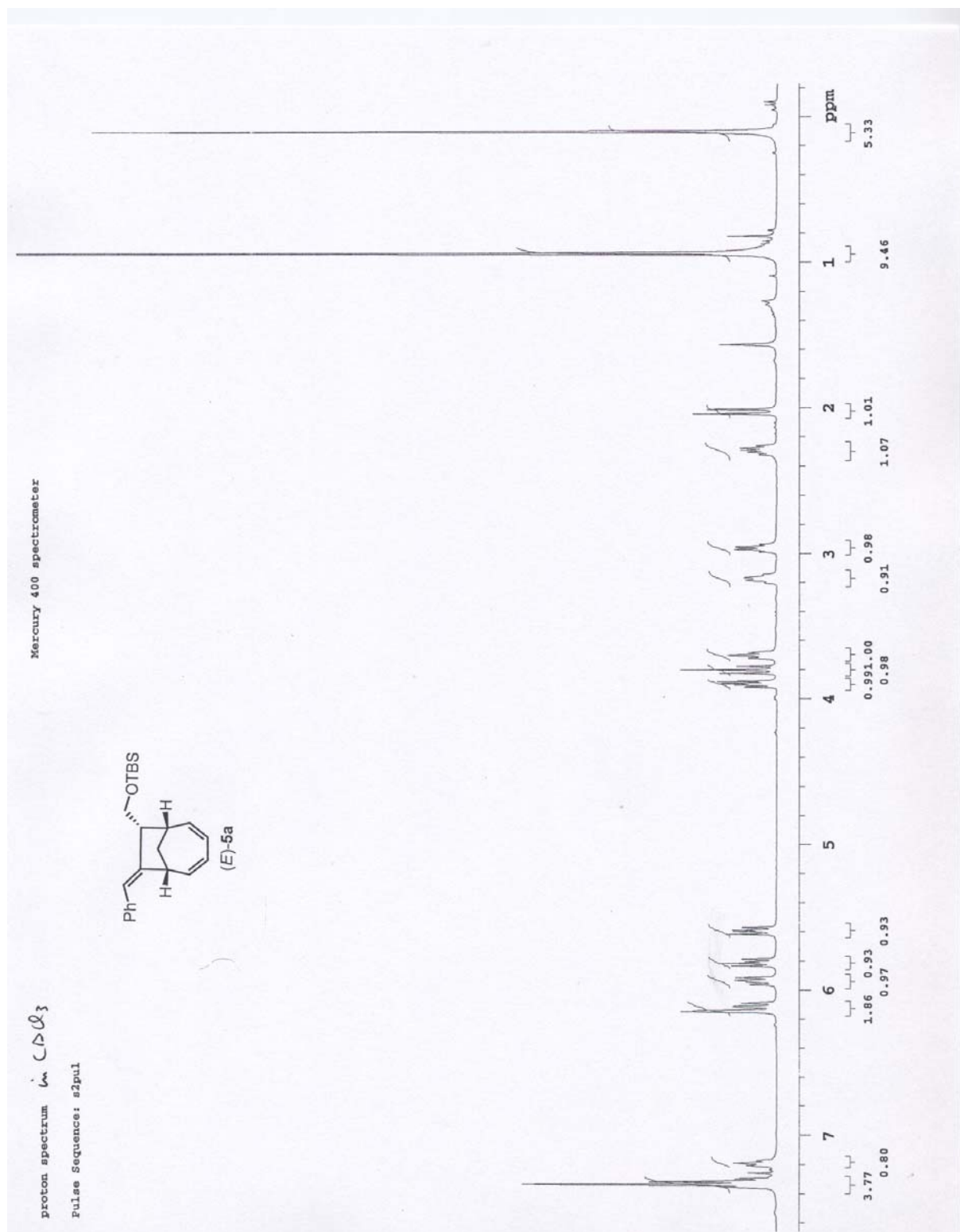
 $\in \mathcal{CD}_3$ 

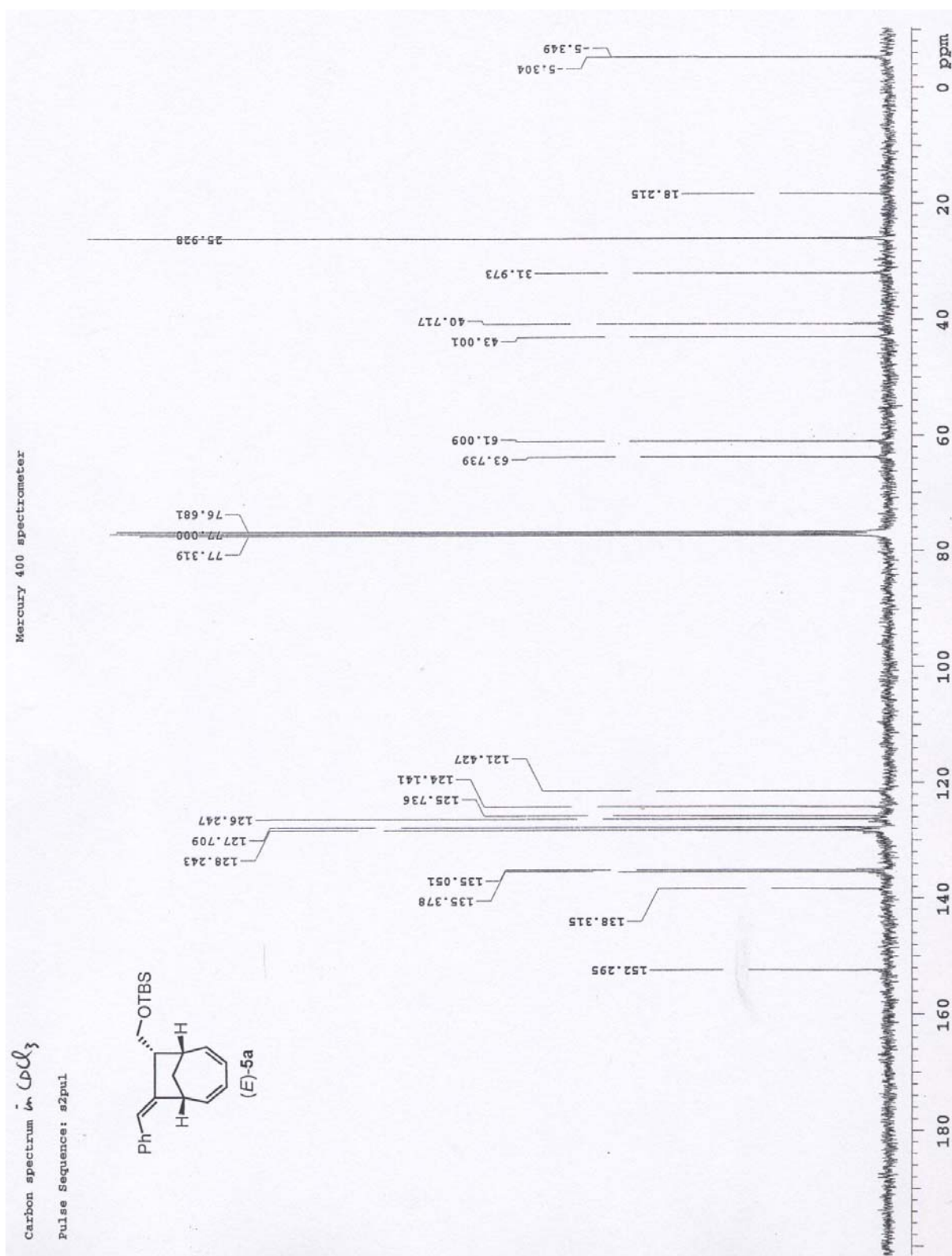




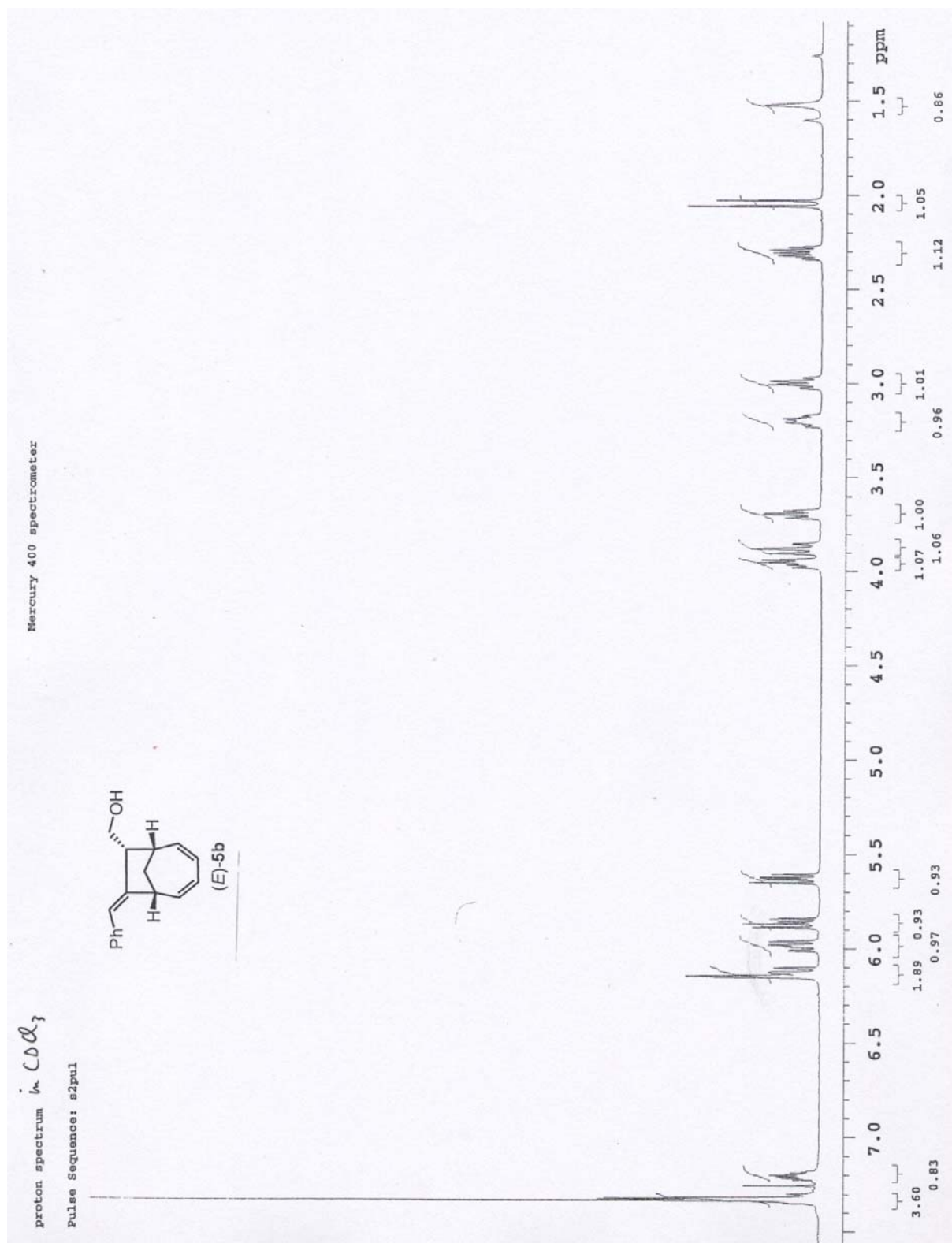




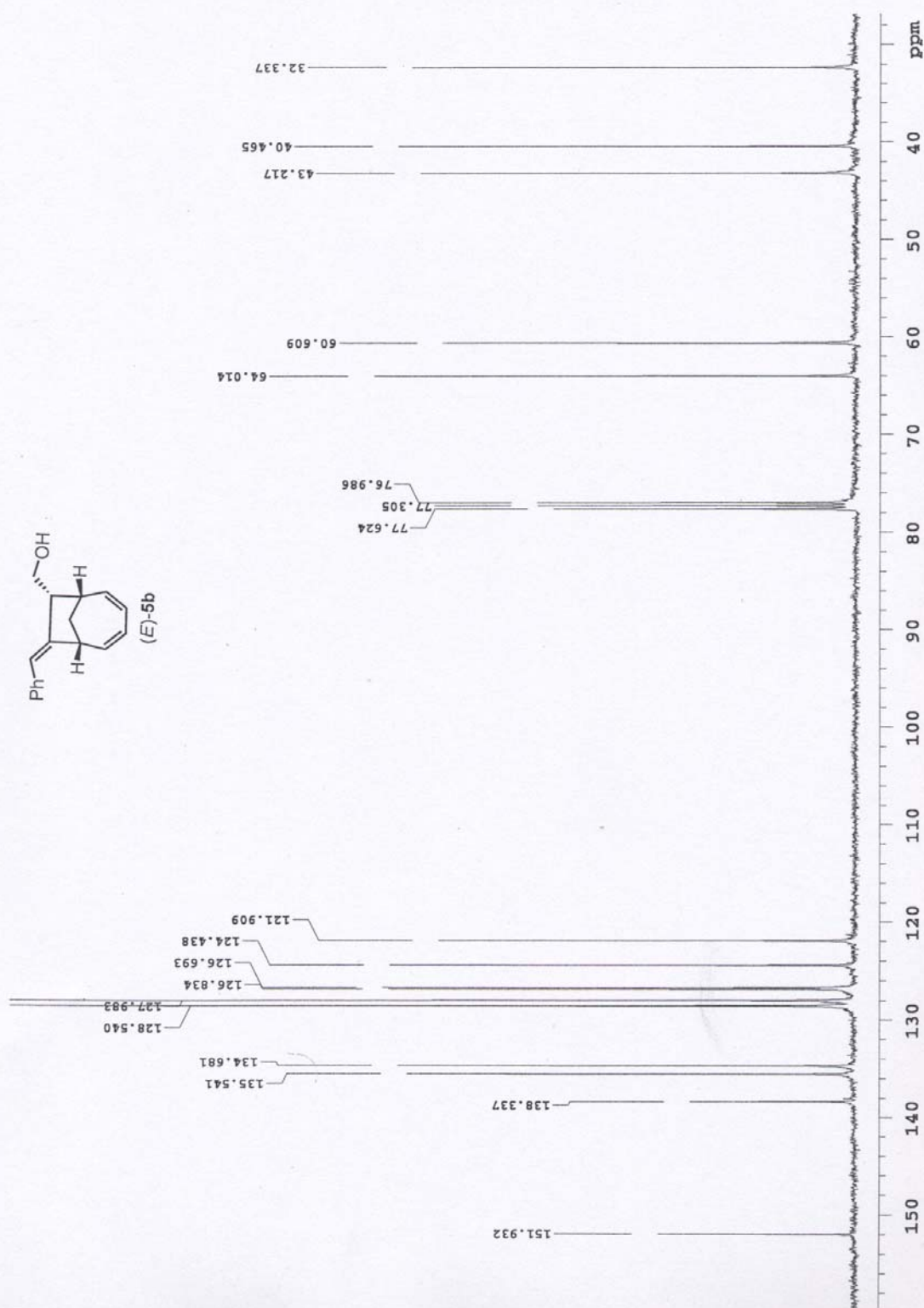
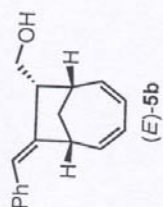








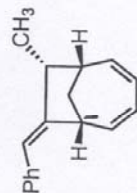
Carbon spectrum in Col3  
Pulse Sequence: s2pul



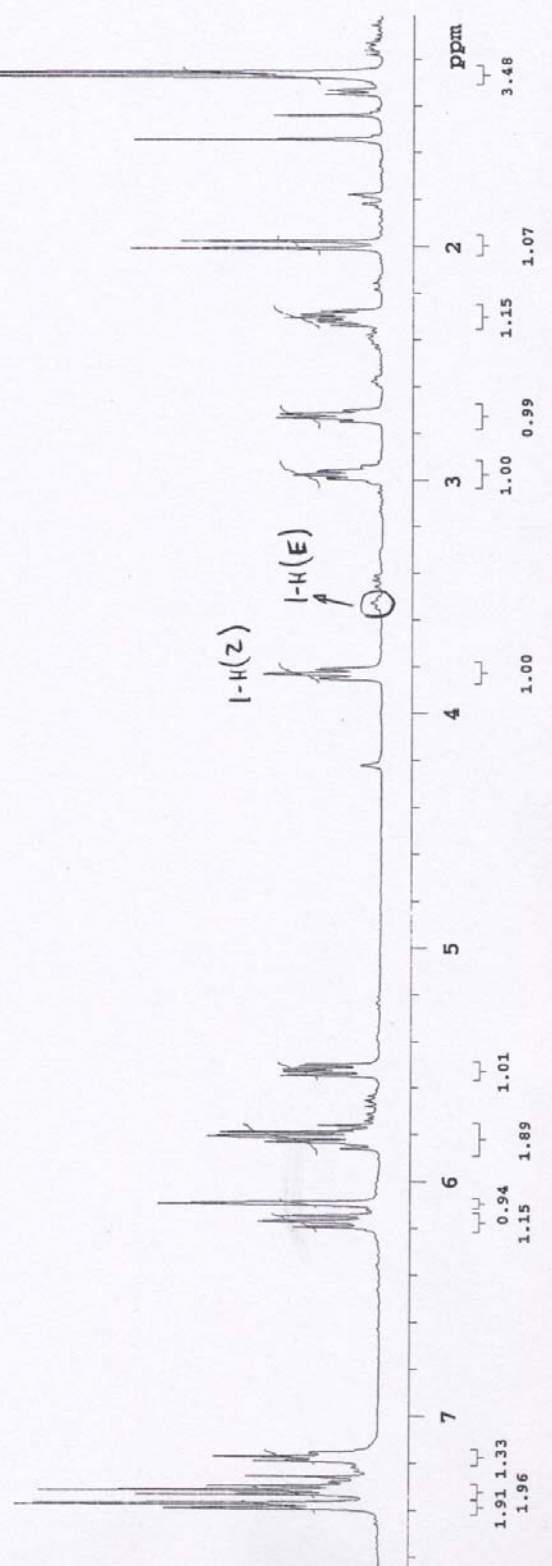
proton spectrum in  $CDCl_3$

Pulse Sequence: a2pul

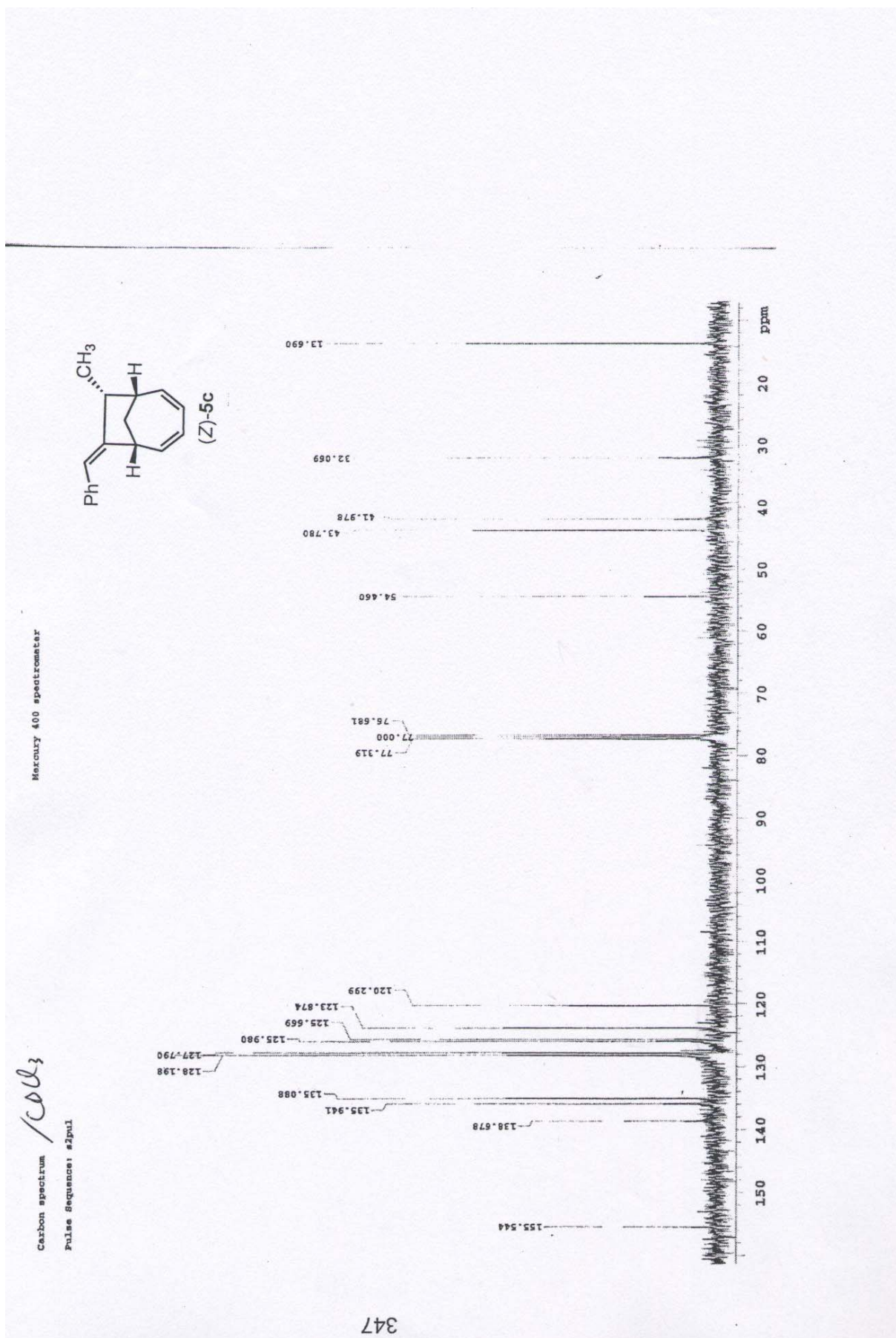
Mercury 400 spectrometer



(Z)-5c  
(contaminated by 7% of isomer E)



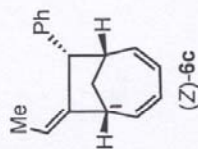




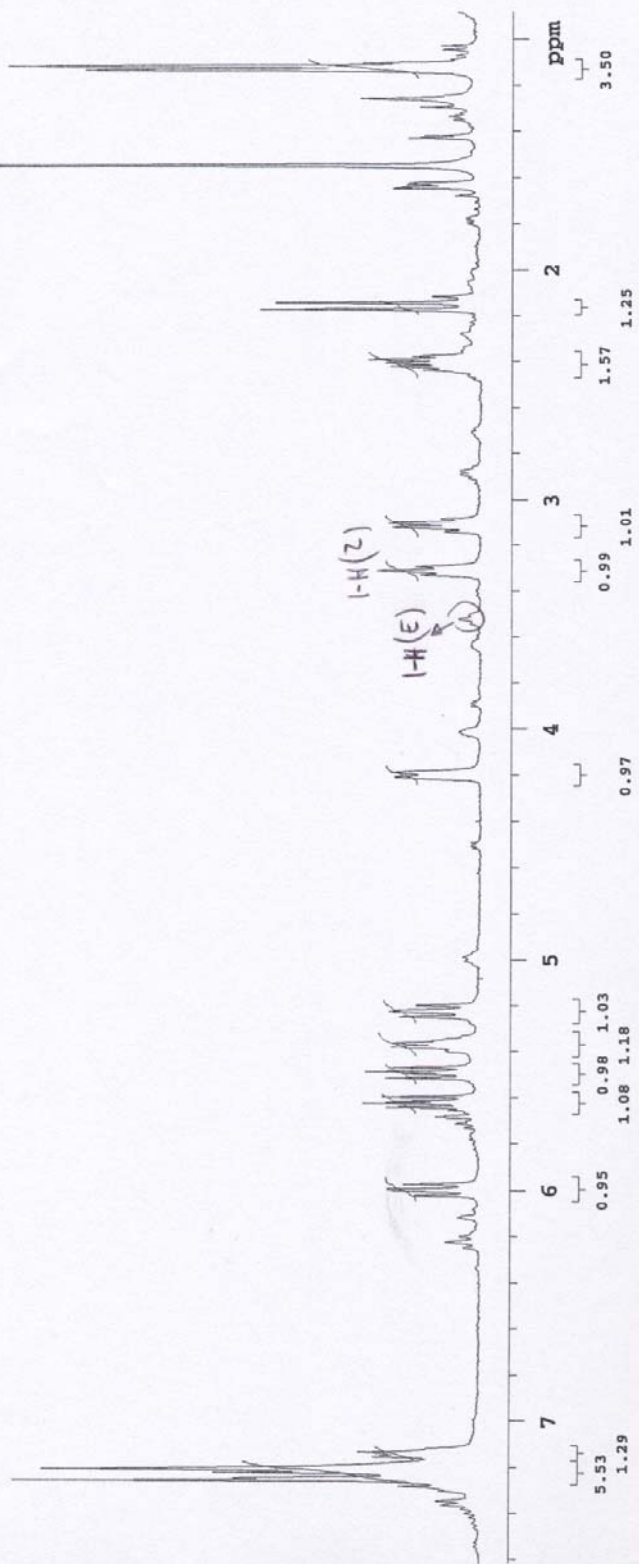
proton spectrum in  $CDCl_3$

Pulse Sequence: s2pul

Mercury 400 spectrometer



(contaminated by 23% of isomer E)



Unity 500 spectrometer

std menthol  
res=0.7Hz  
sw probe  
April 1 99  
lock freq=1.470  
new.shima

Pulse Sequence: #2pm  
Solvent: CDCl3  
Ambient temperature

UNITY-500 "0500"

PULSE SEQUENCE

Relax. delay 2.500 sec

Pulse 10.1 degrees

Acq. time 1.928 sec

Width 8297.0 Hz

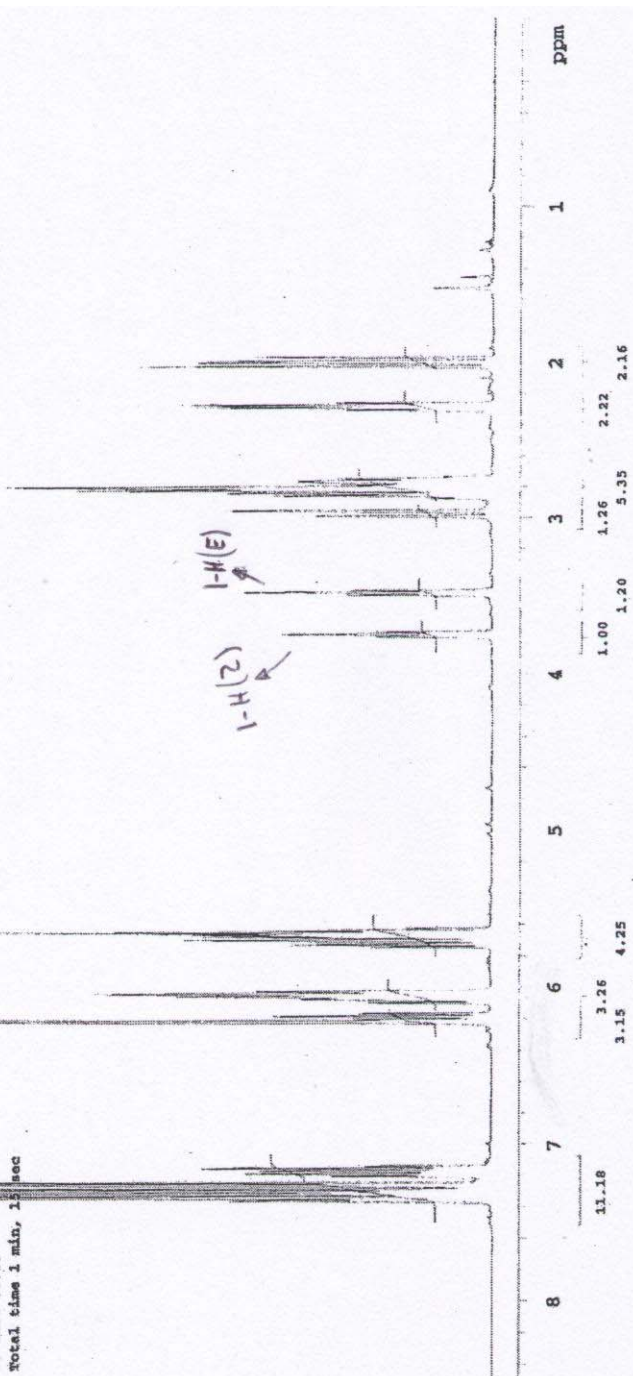
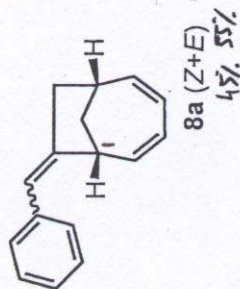
16 repetitions

OBSERVE H1, 499.616459 MHz

DATA PROCESSING

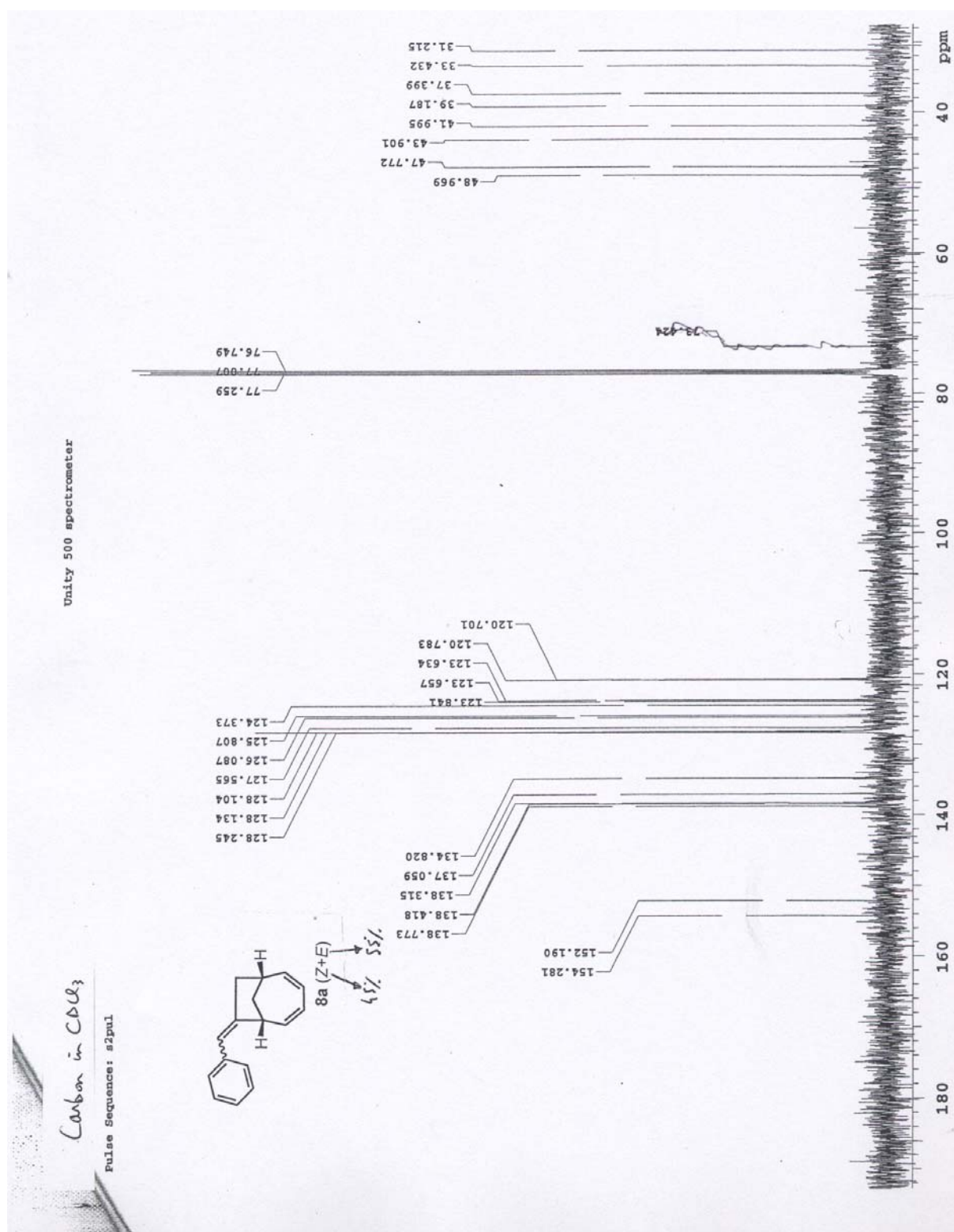
FT size 32768

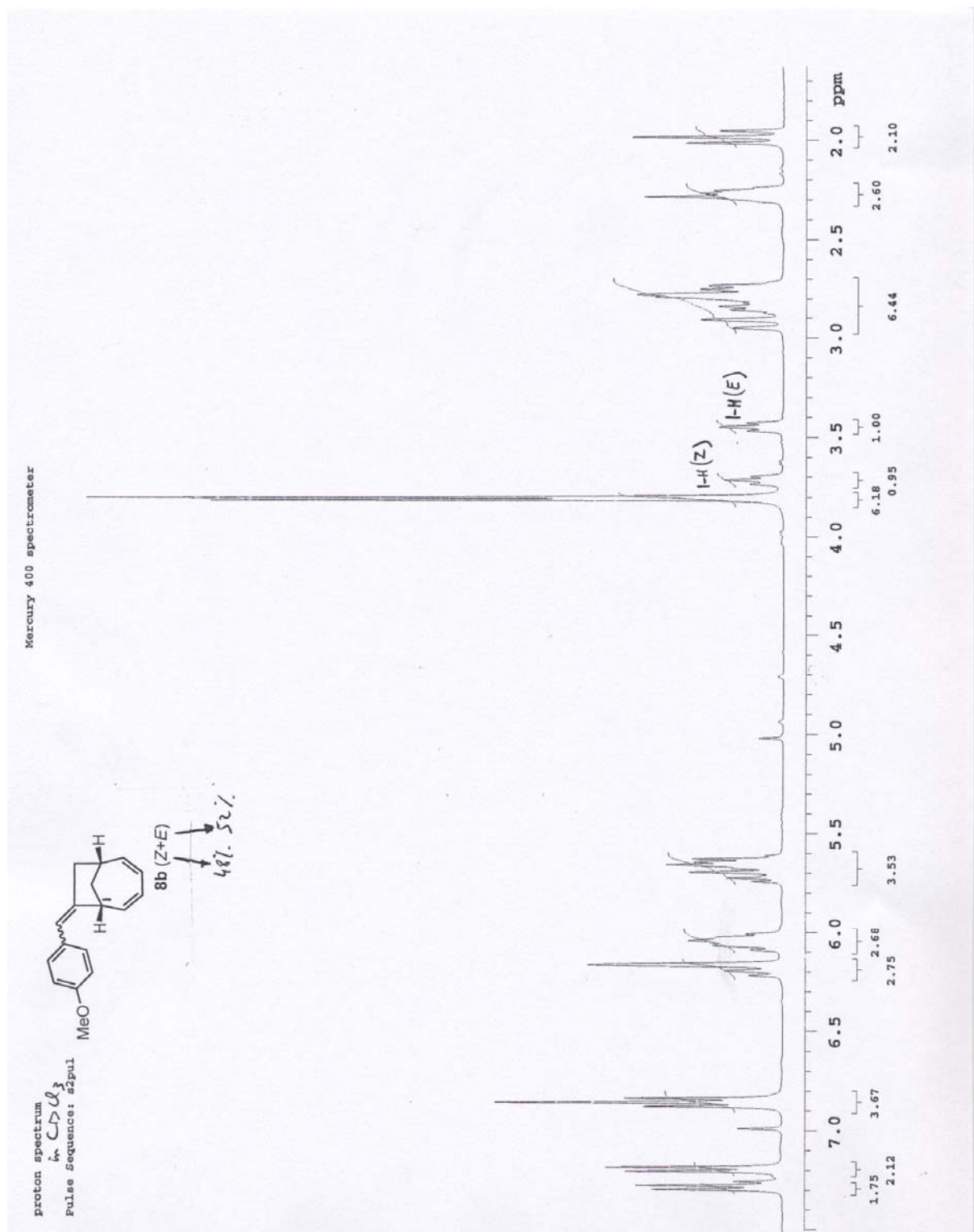
Total time 1 min, 13 sec

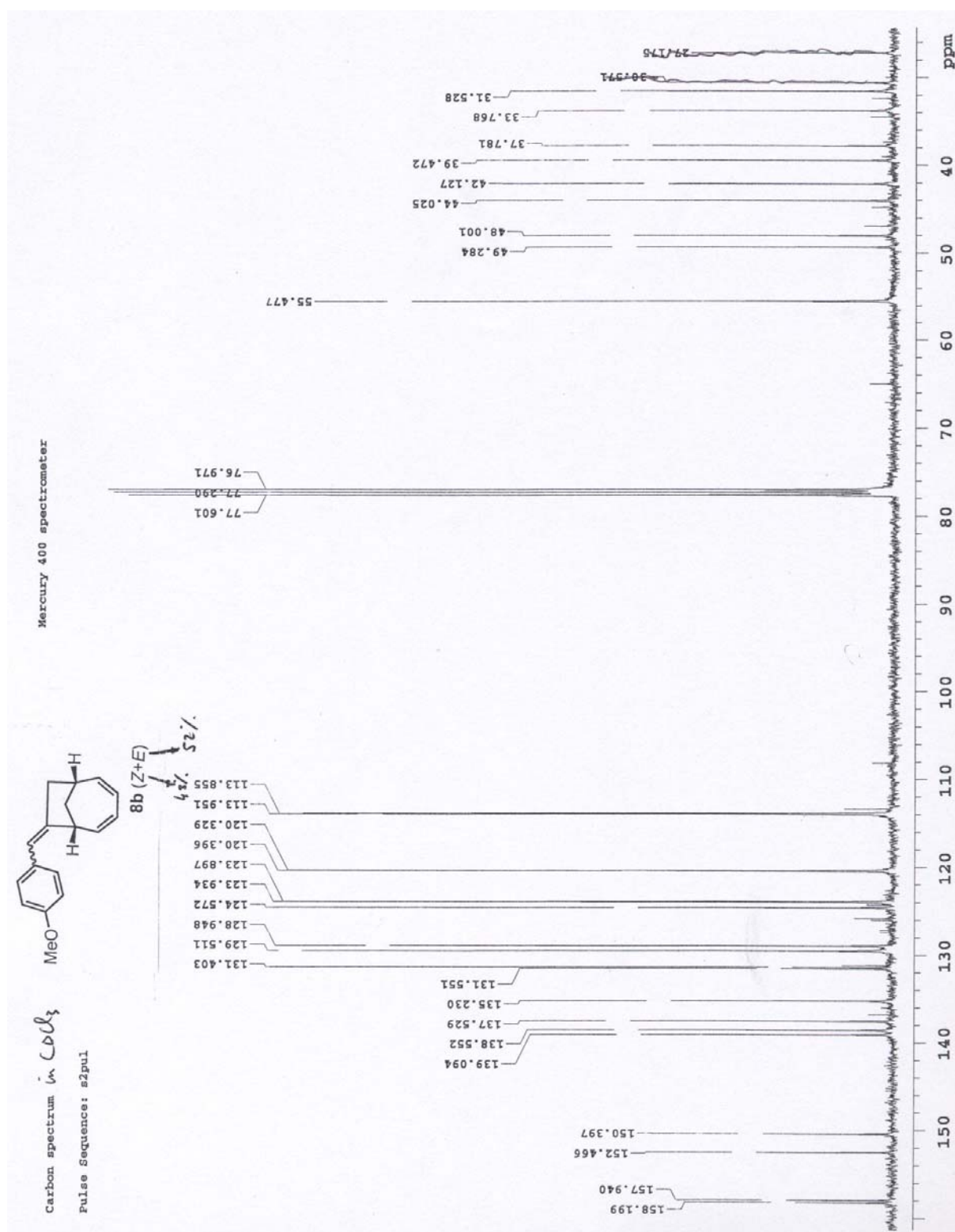


337





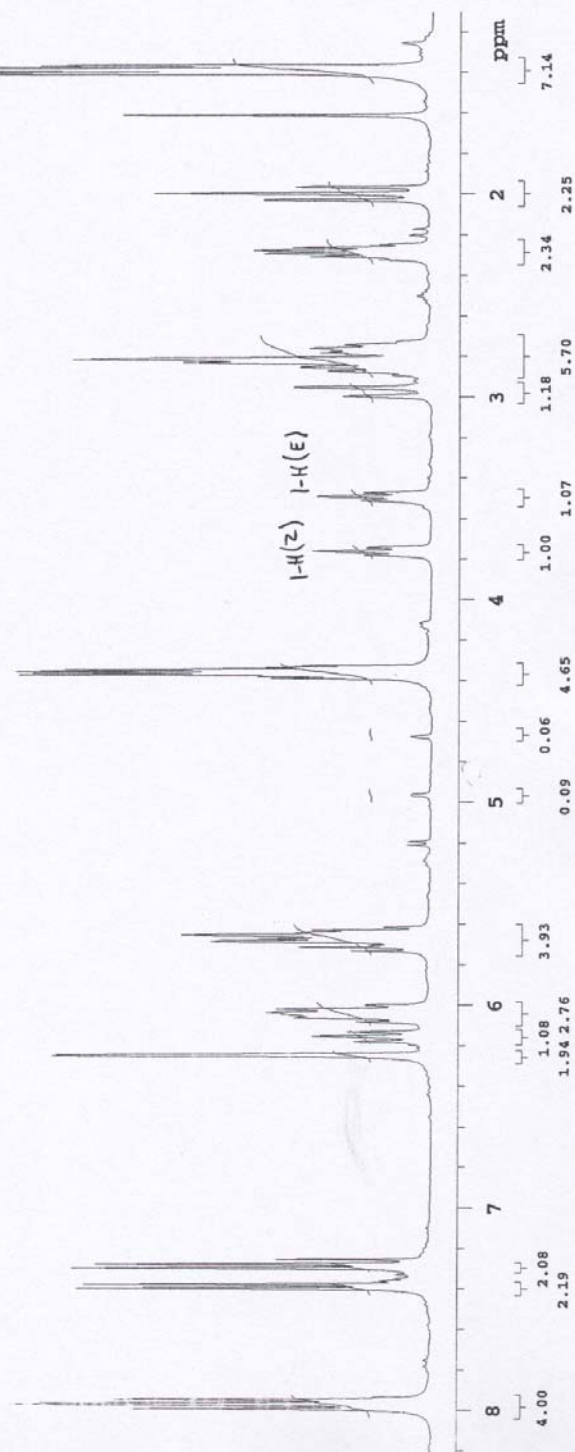
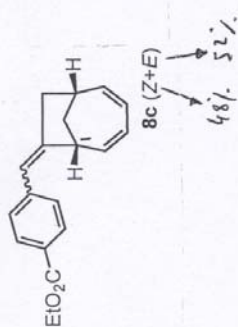


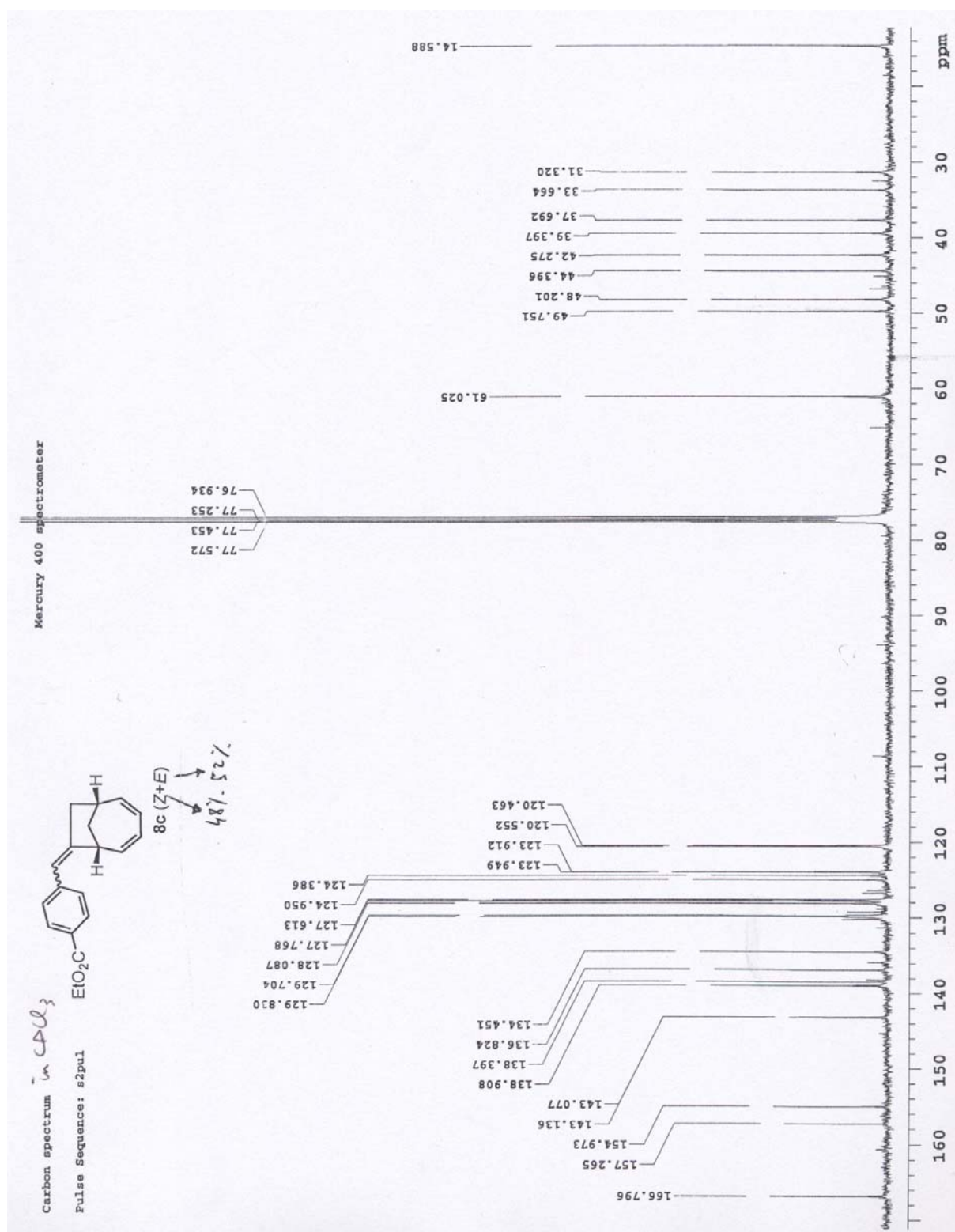


proton spectrum in CDCl<sub>3</sub>

Pulse Sequence: s2pul

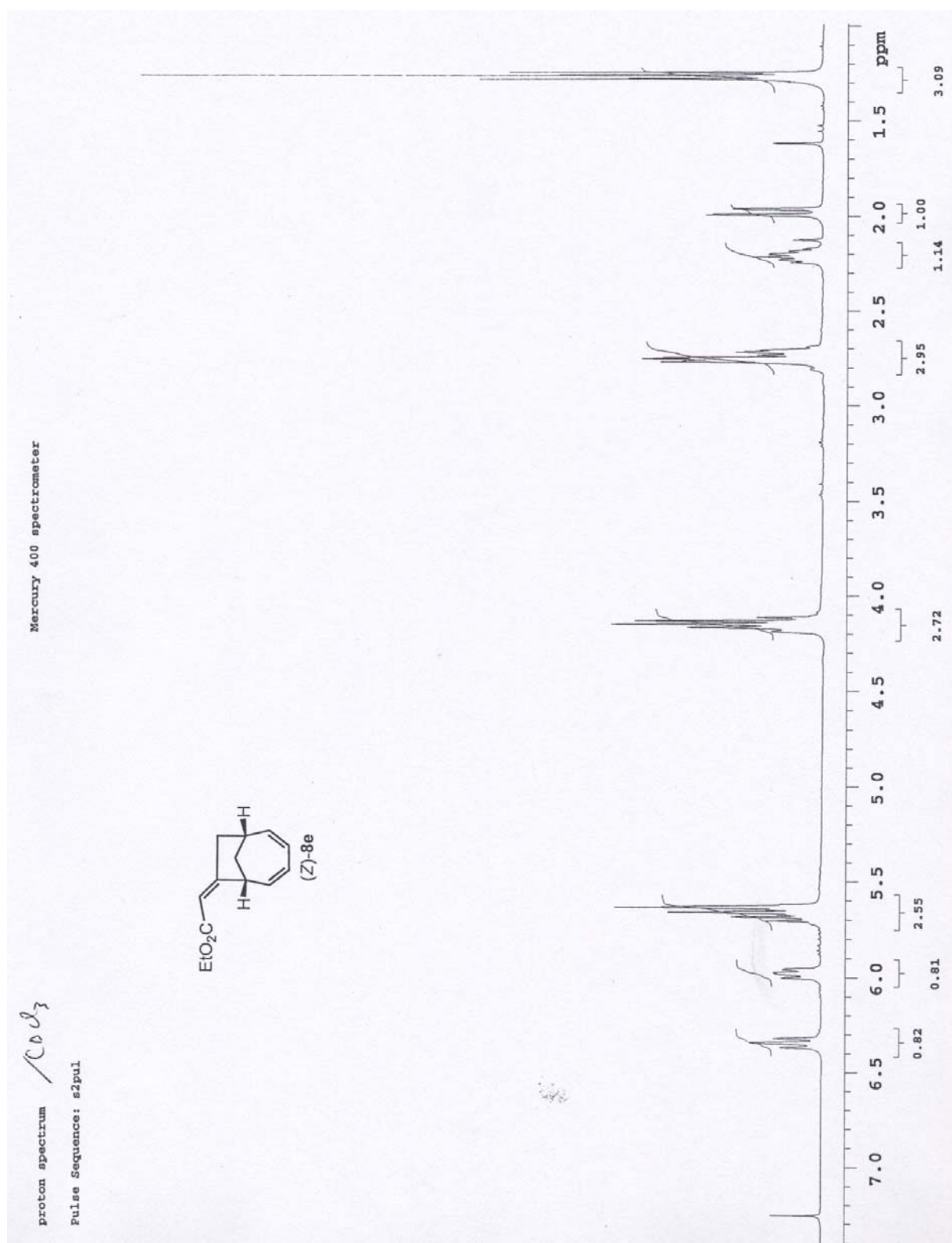
Mercury 400 spectrometer

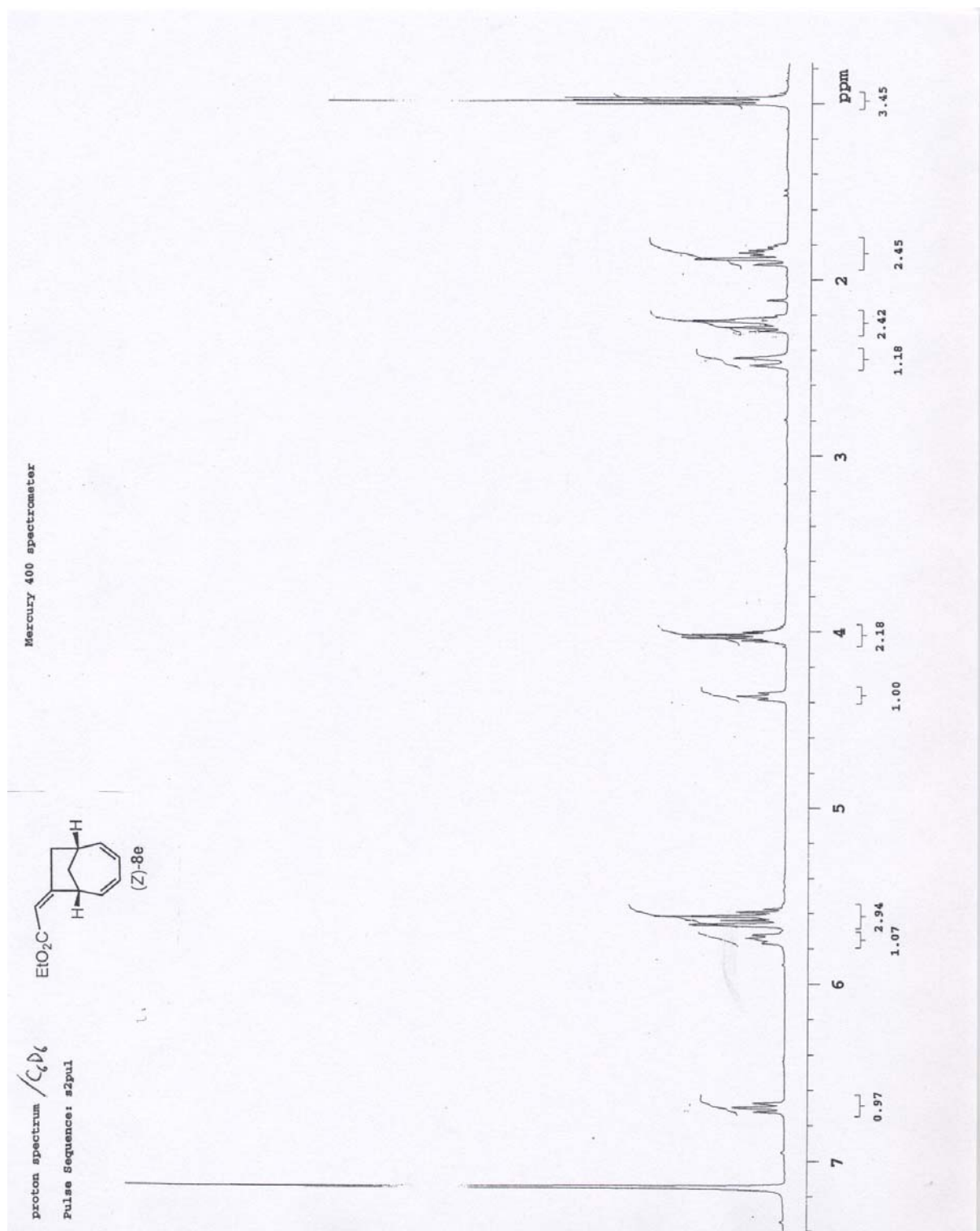


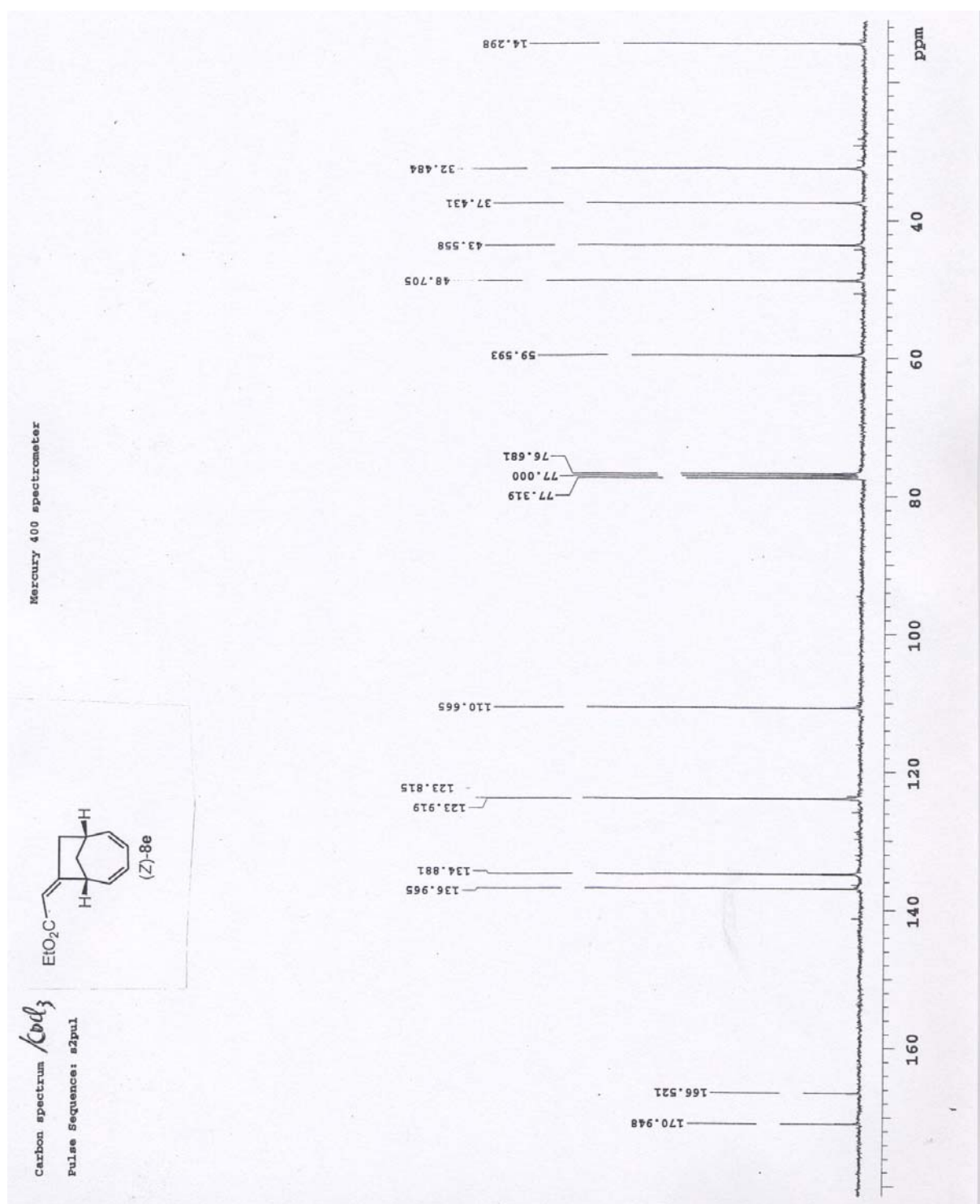








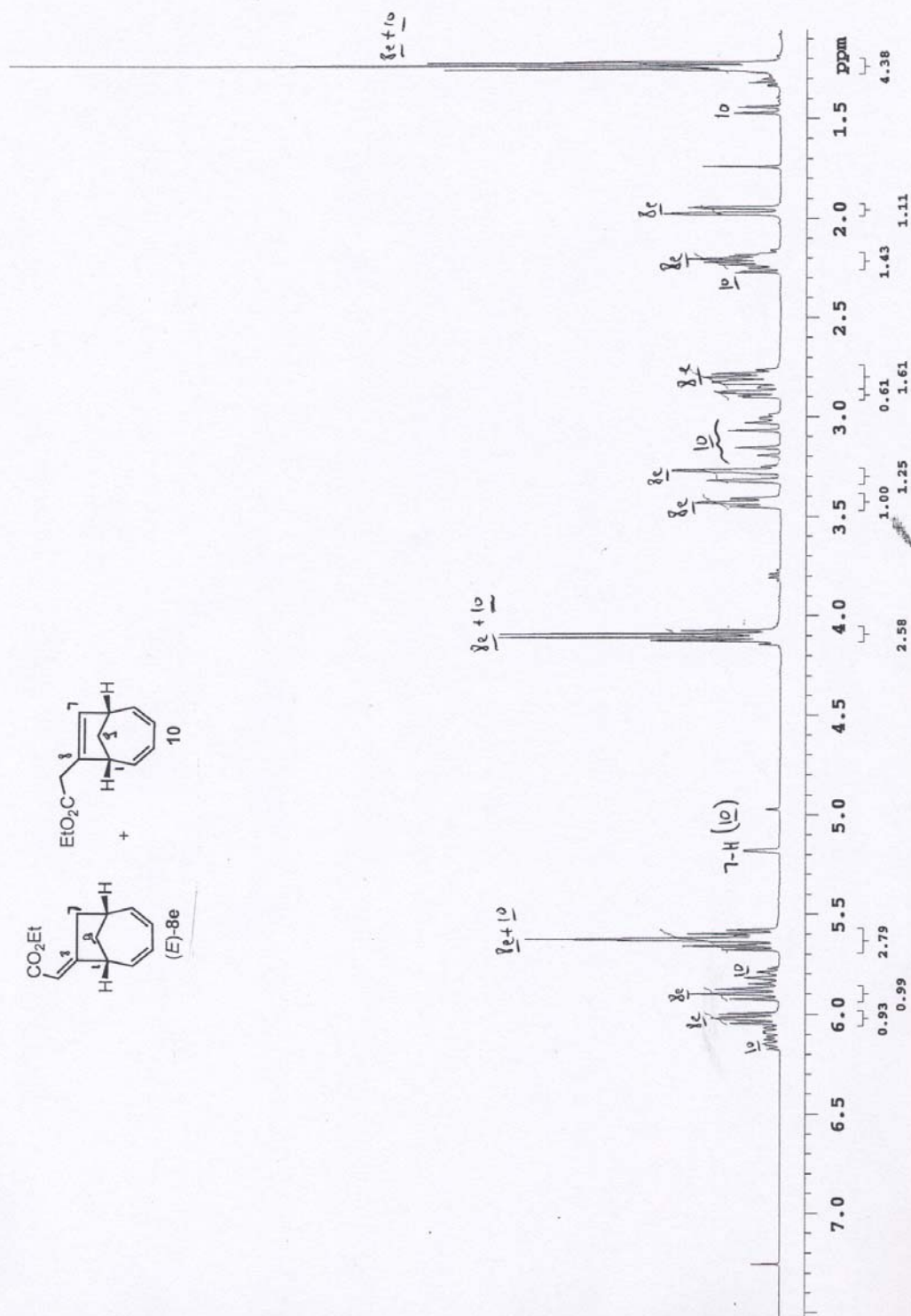
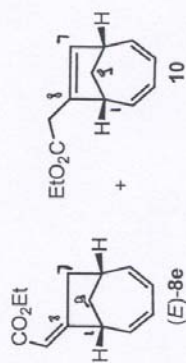




proton spectrum  $\delta$  C 100

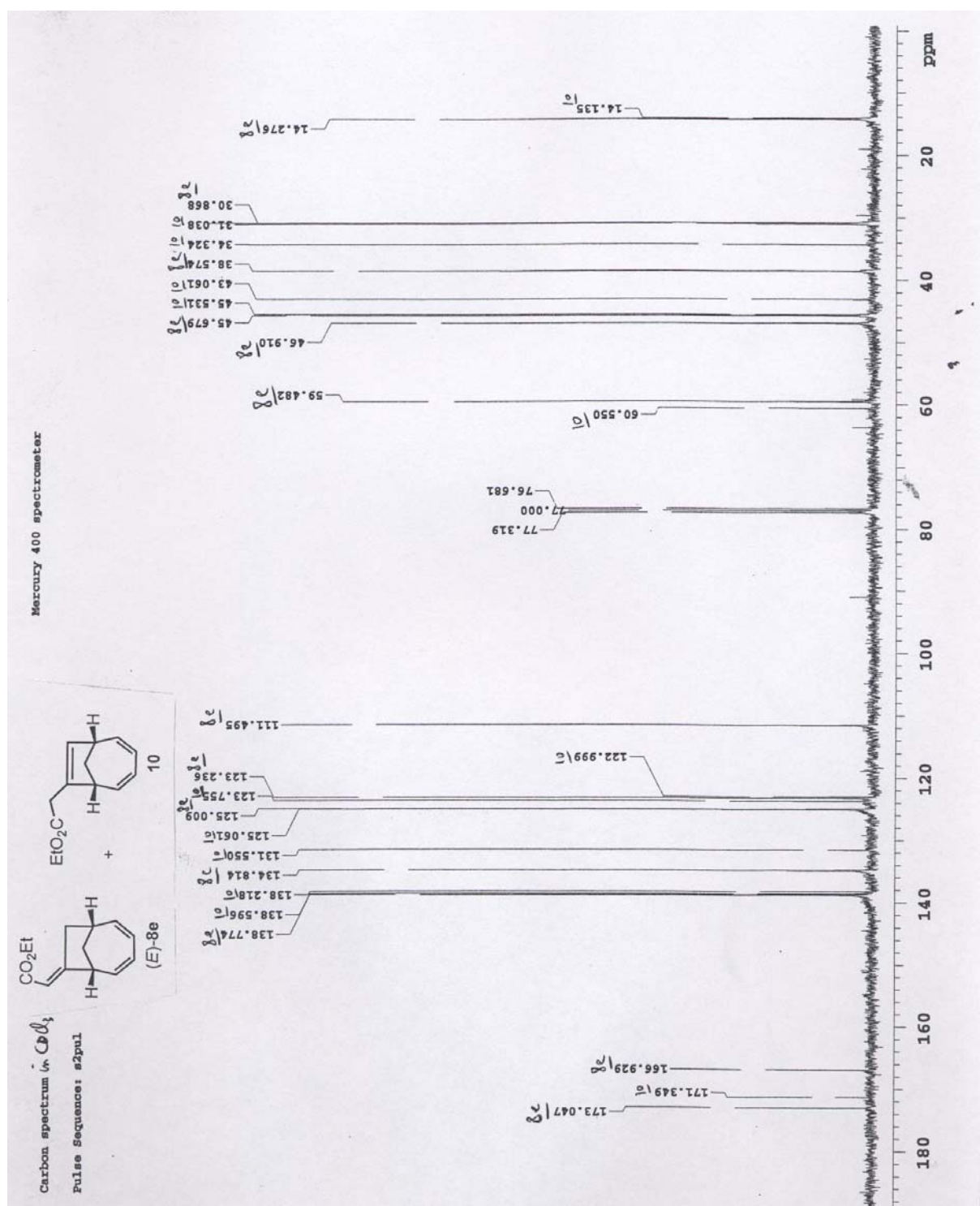
Pulse Sequence: s2pul

Mercury 400 spectrometer



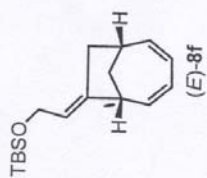




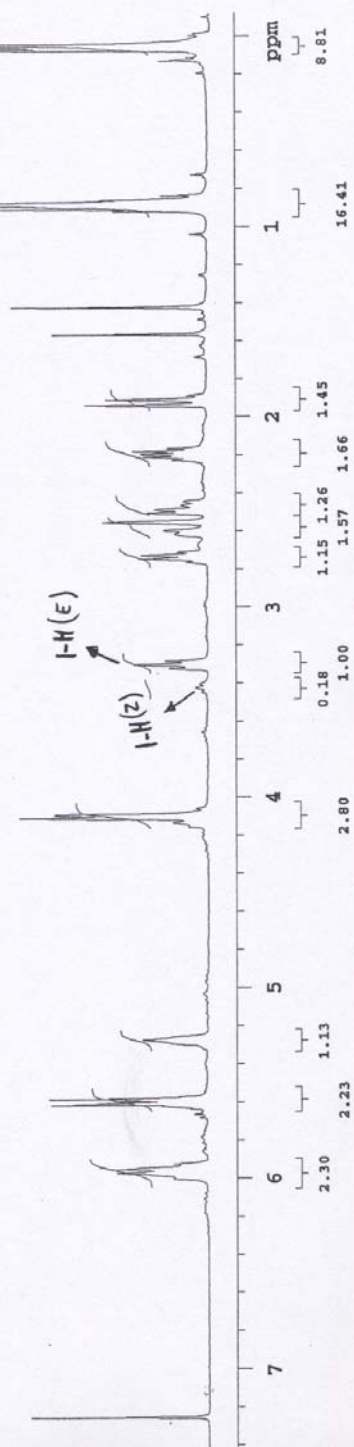


proton spectrum /  $CDCl_3$   
Pulse Sequence: s2pul

Mercury 400 spectrometer



(contaminated by 15% of isomer Z)

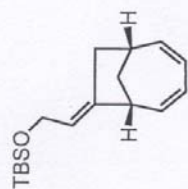




Carbon spectrum / CD3  
Pulse Sequence: s2pul

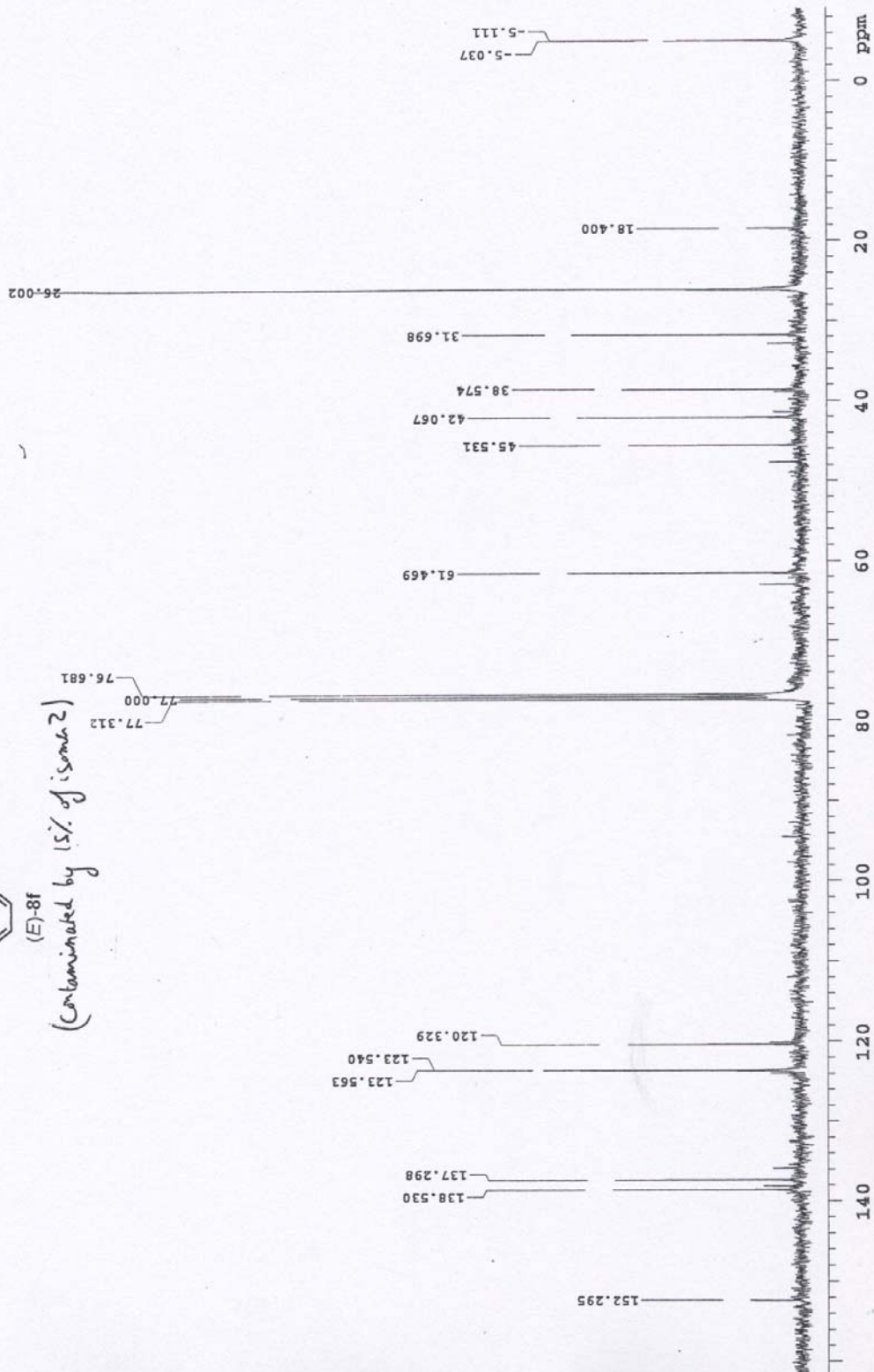
Carbon spectrum / CD3  
Pulse Sequence: s2pul

Pulse Sequence: s2pul



(E)-8f  
(contaminated by 15% of isomer 2)

(Contaminated by 15% of isomer 2)



138.530  
137.298

137.298

—123.563

—123.540

120.329

77.312  
77.000  
76.681

000-77

189.94

—61.469

—45.531

-42.067

—38.574

—31.698

18.400

—5.037  
-5.111

III-5-111

26-002

0  
wāḍā

20

40

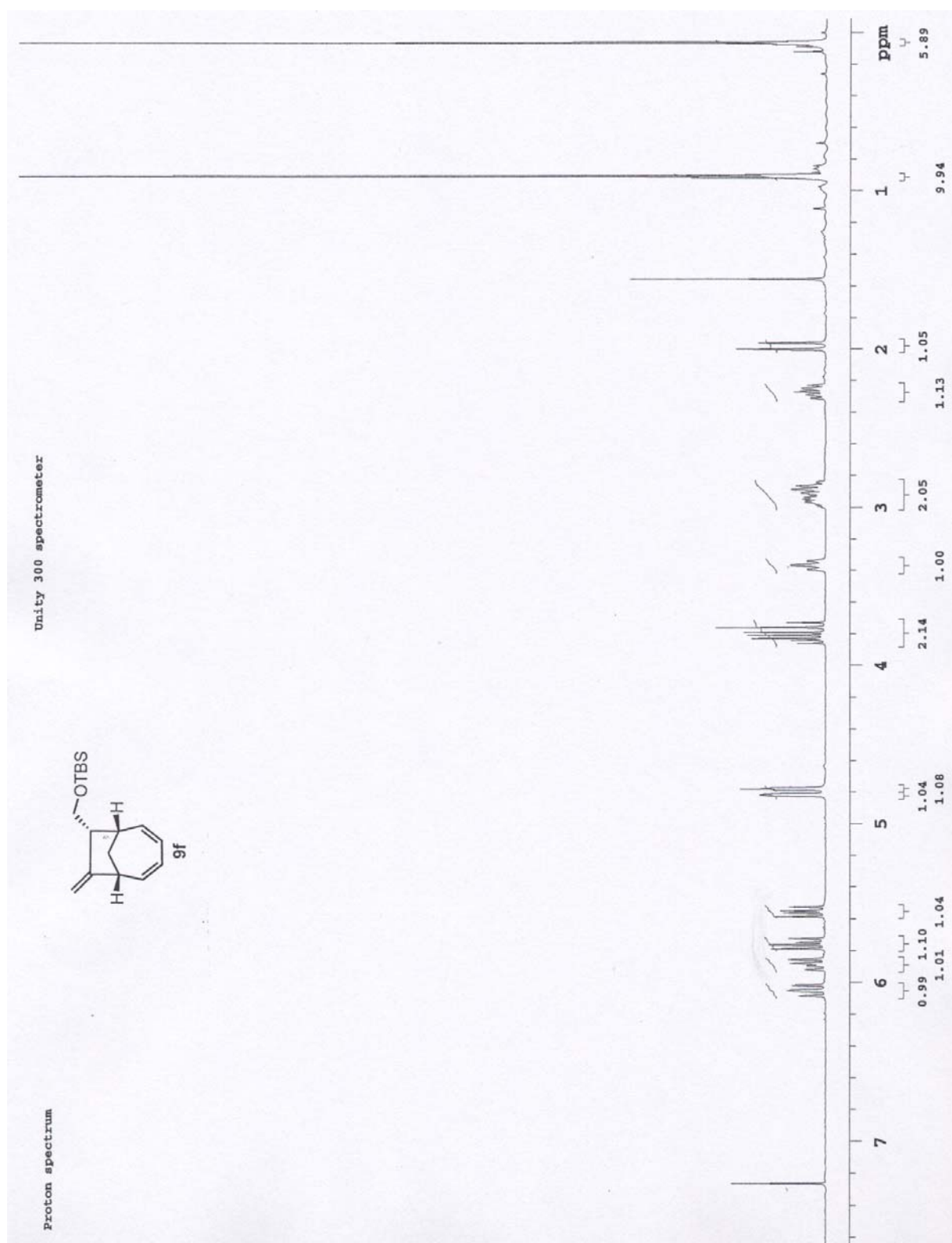
50

80

10

20

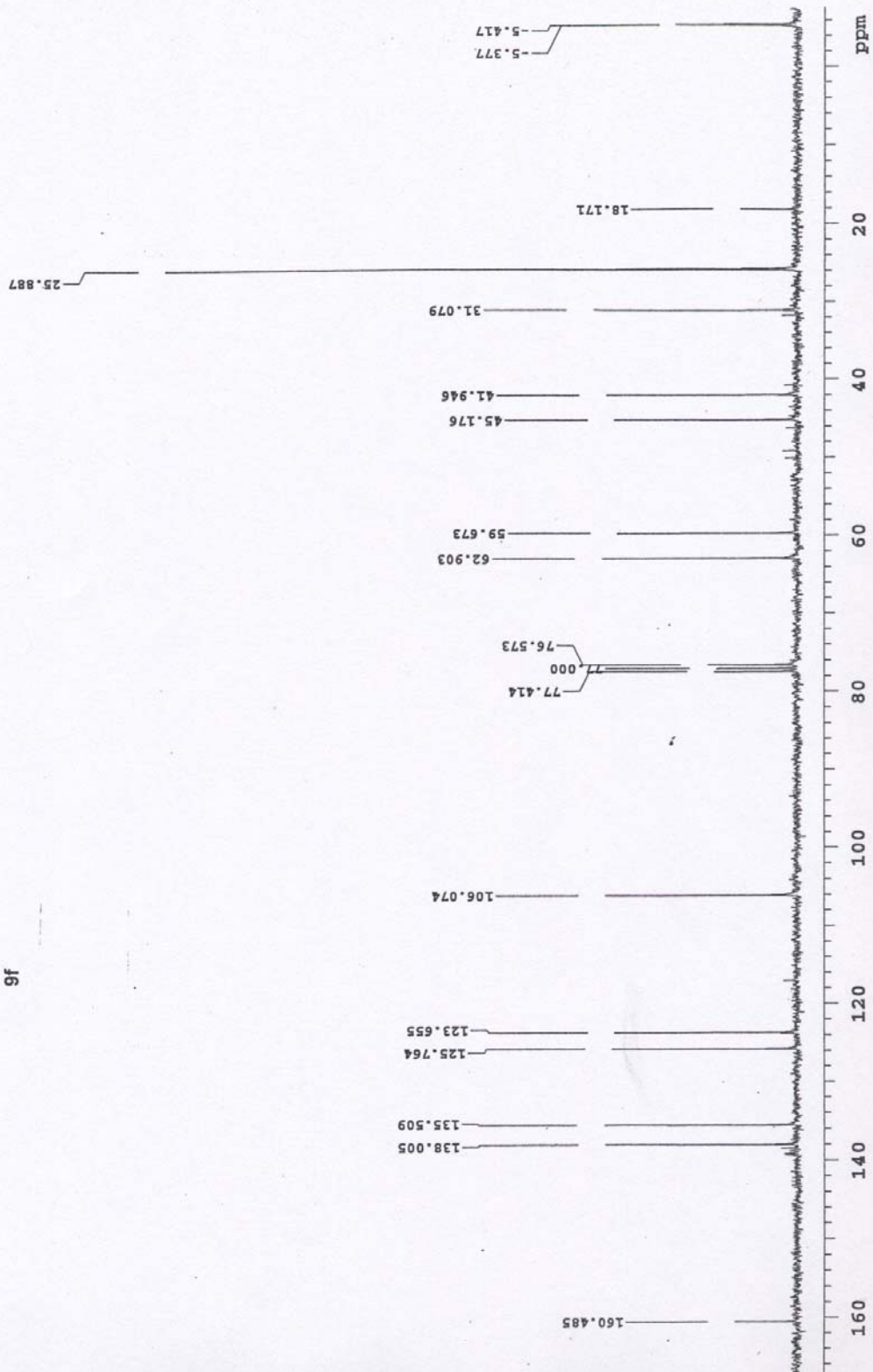
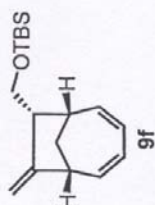
L40

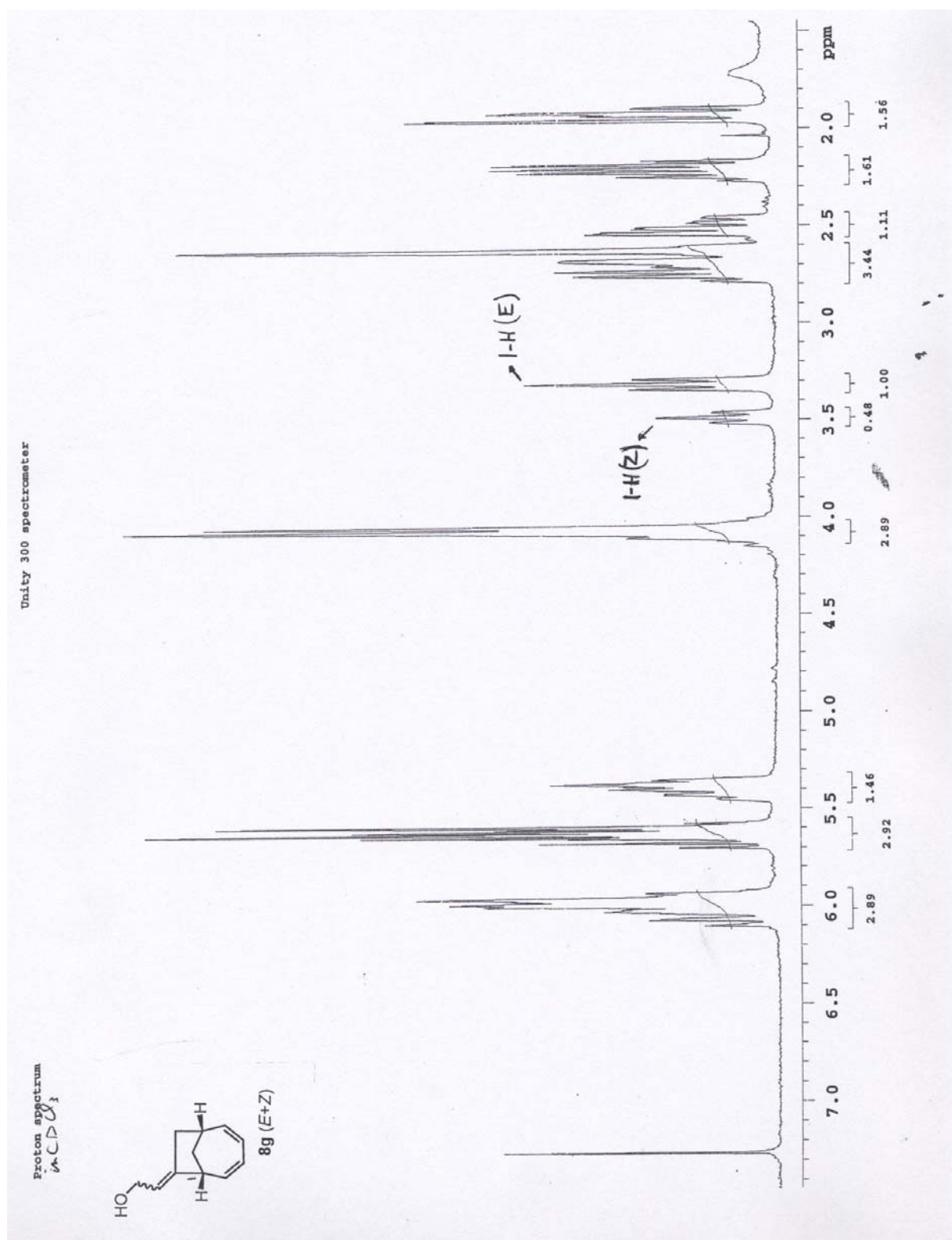


Unity 300 spectrometer

standard Carbon experiment

in CDCl<sub>3</sub>

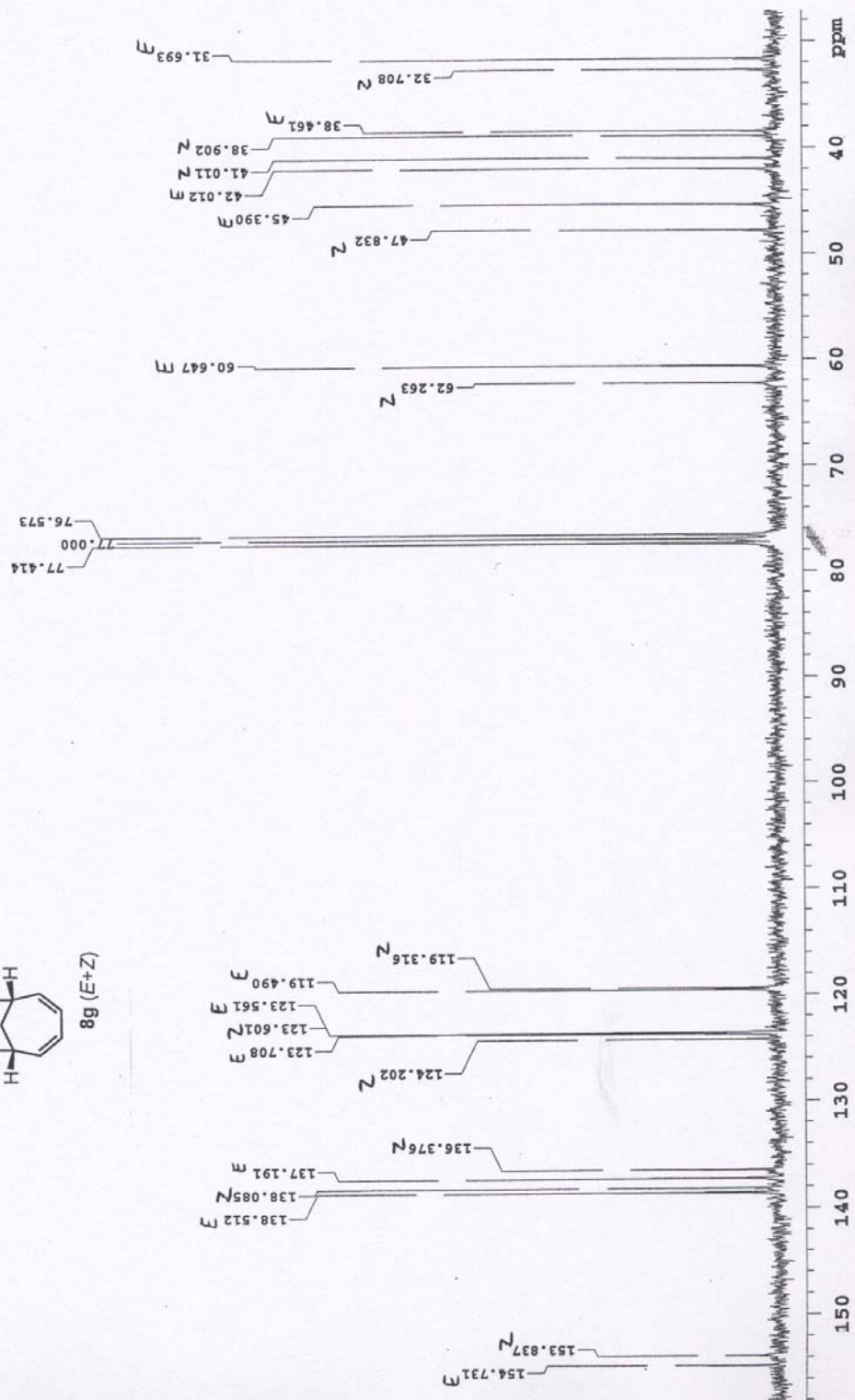
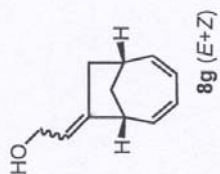




Unity 300 spectrometer

standard Carbon experiment

in CDCl<sub>3</sub>

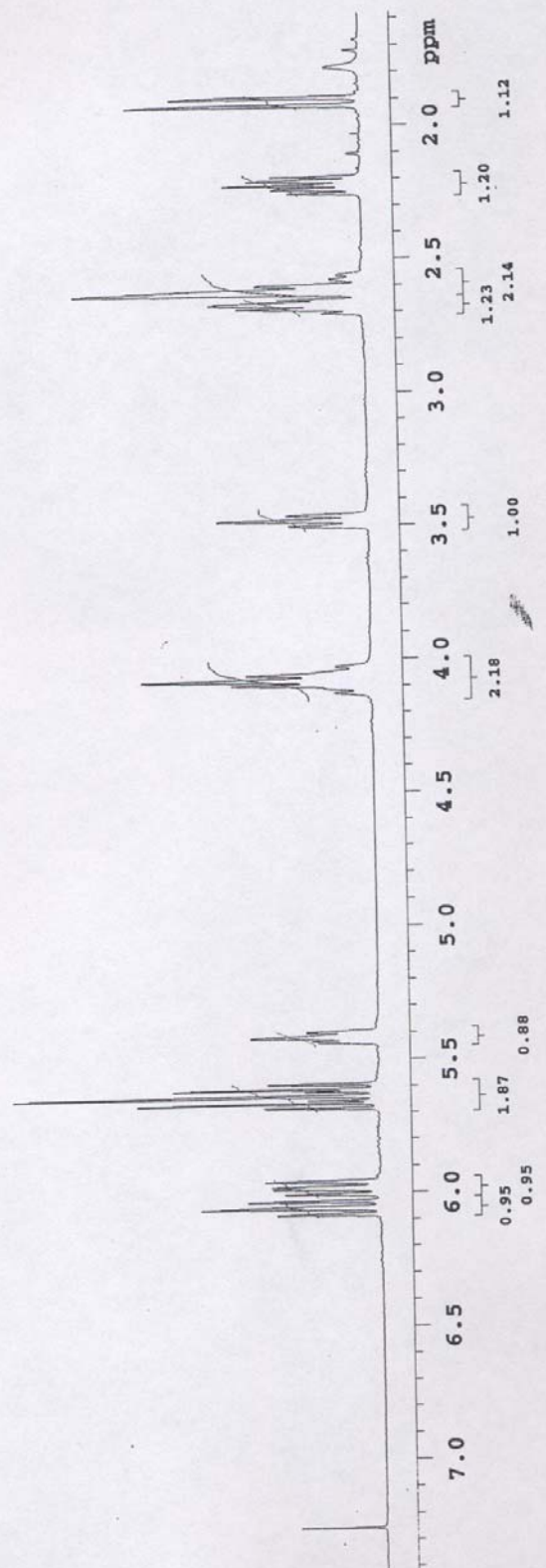
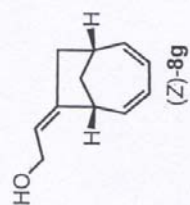




Mercury 400 spectrometer

proton spectrum in  $CDCl_3$

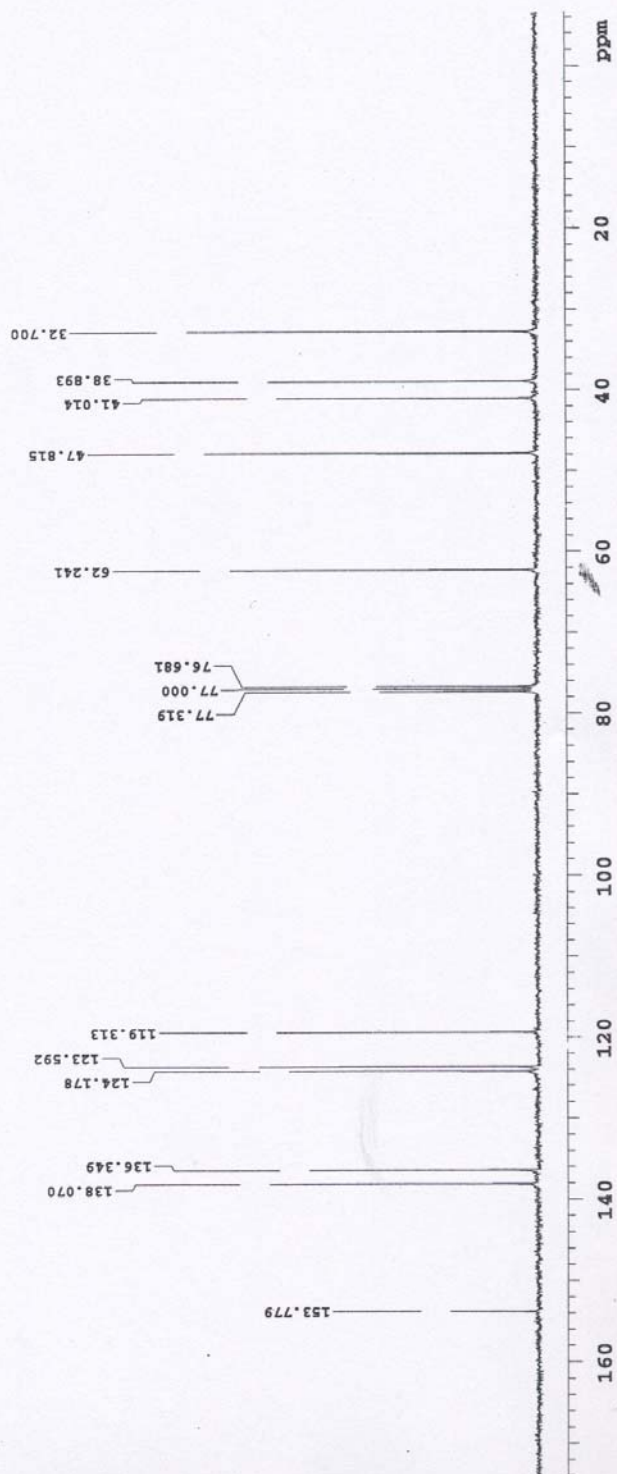
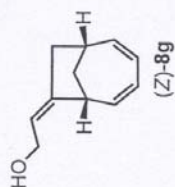
Pulse Sequence: s2pul



Carbon spectrum in  $CDCl_3$

Pulse Sequence: zgpg30

Mercury 400 spectrometer

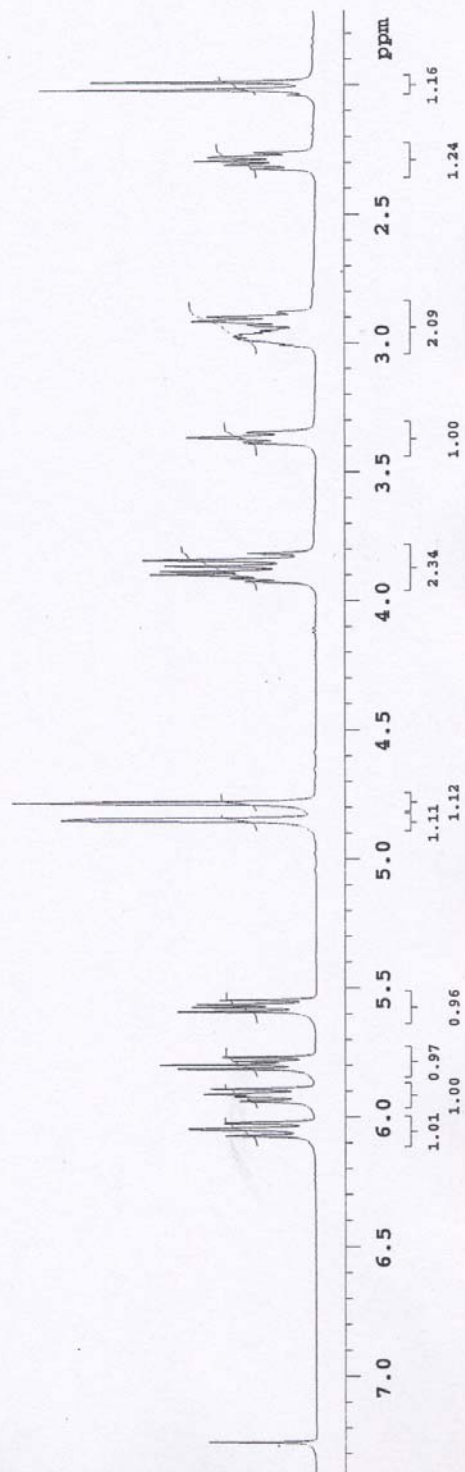
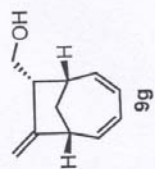


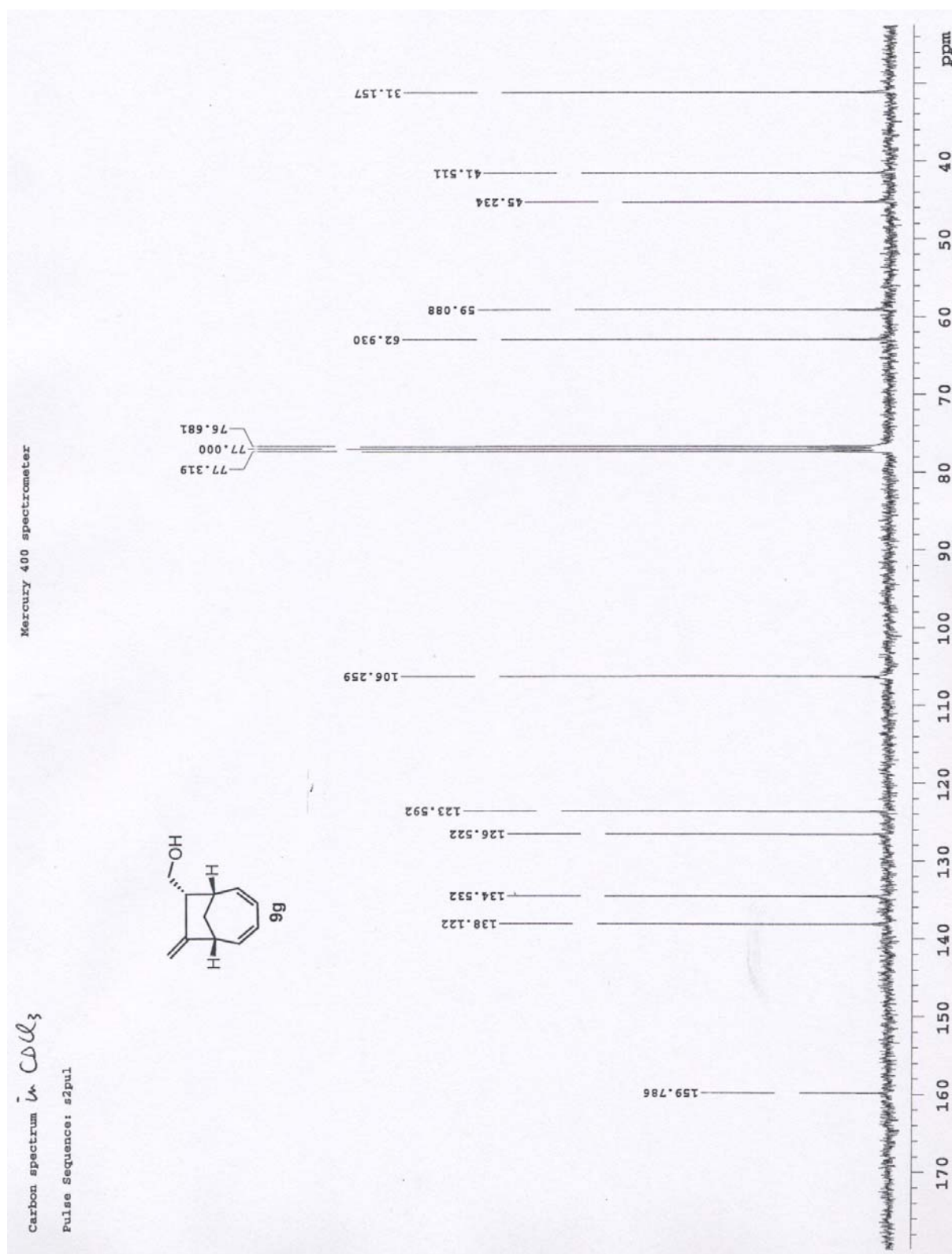


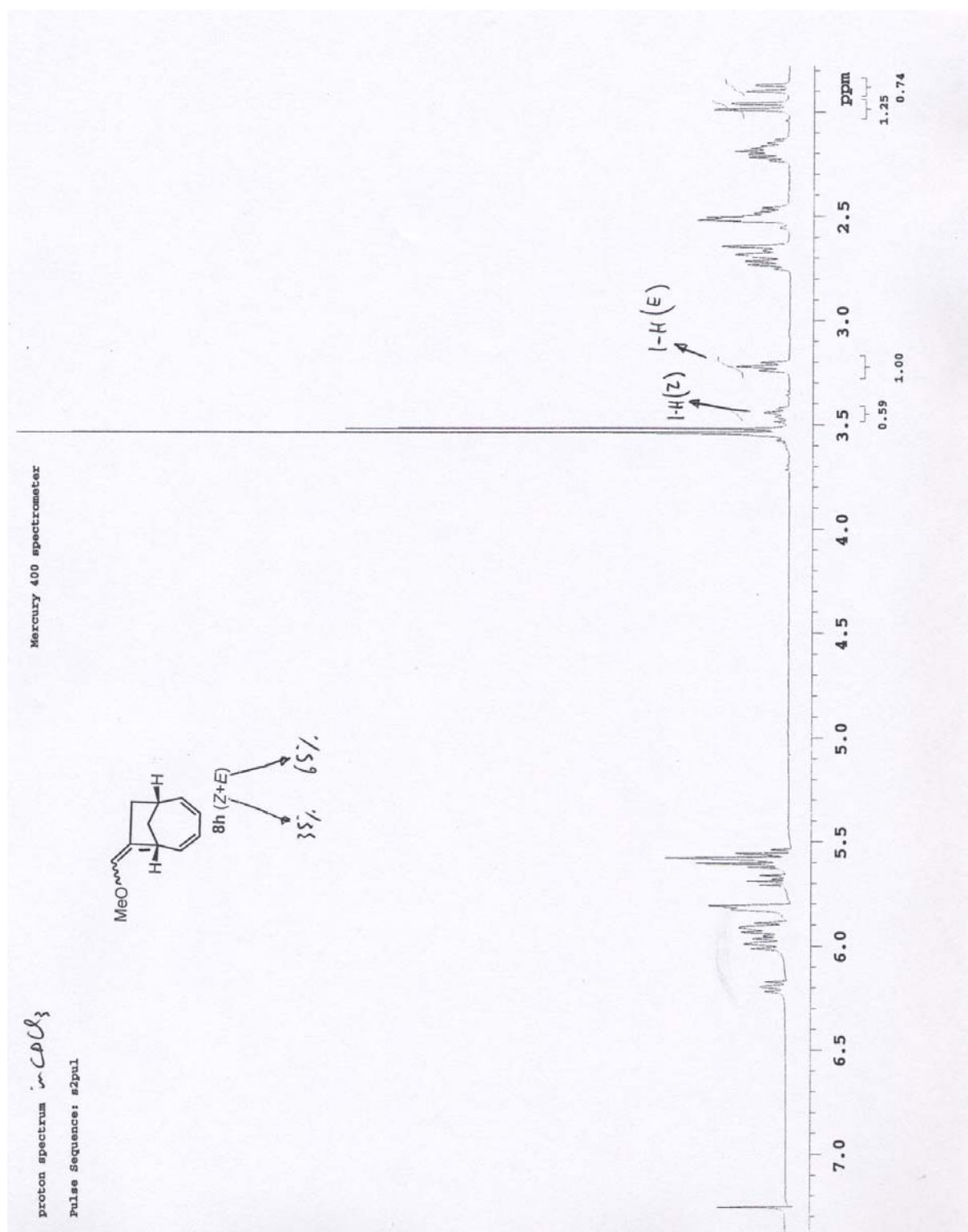
proton spectrum in *cdcl*<sub>3</sub>

Pulse Sequence: s2pul

Mercury 400 spectrometer



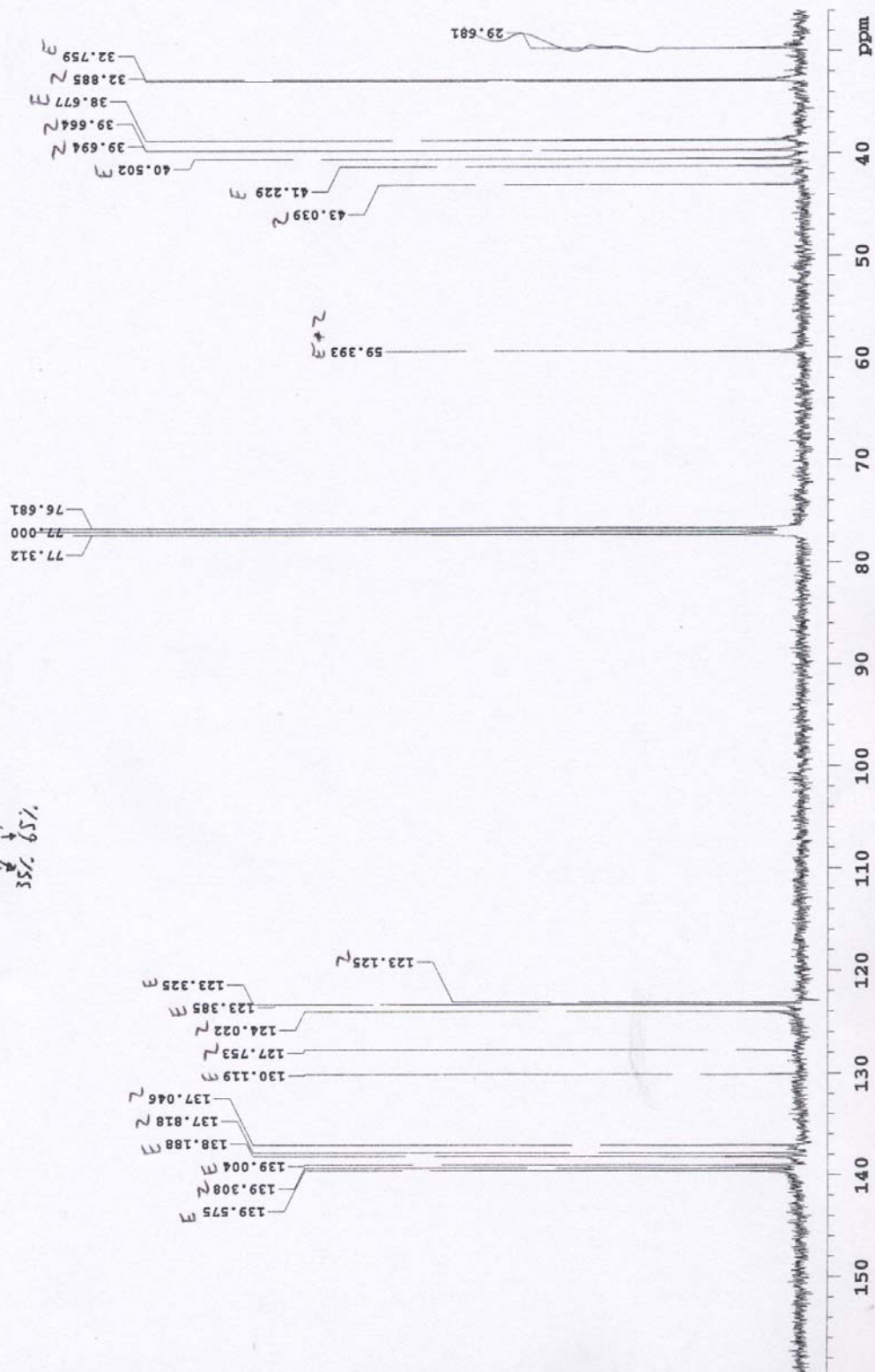
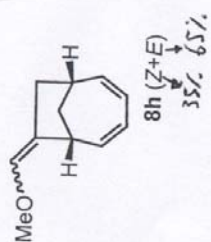


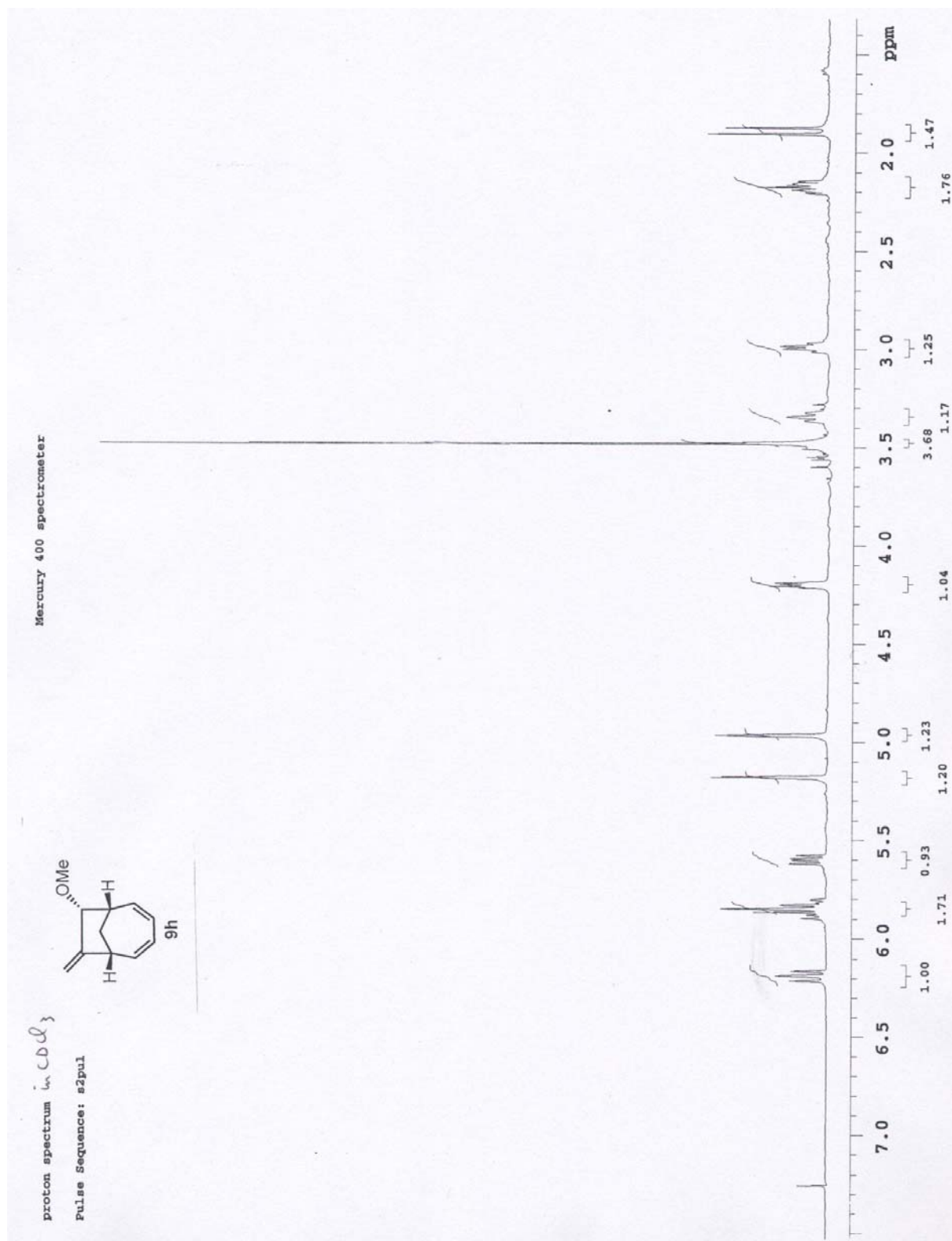


Carbon spectrum in CDCl<sub>3</sub>

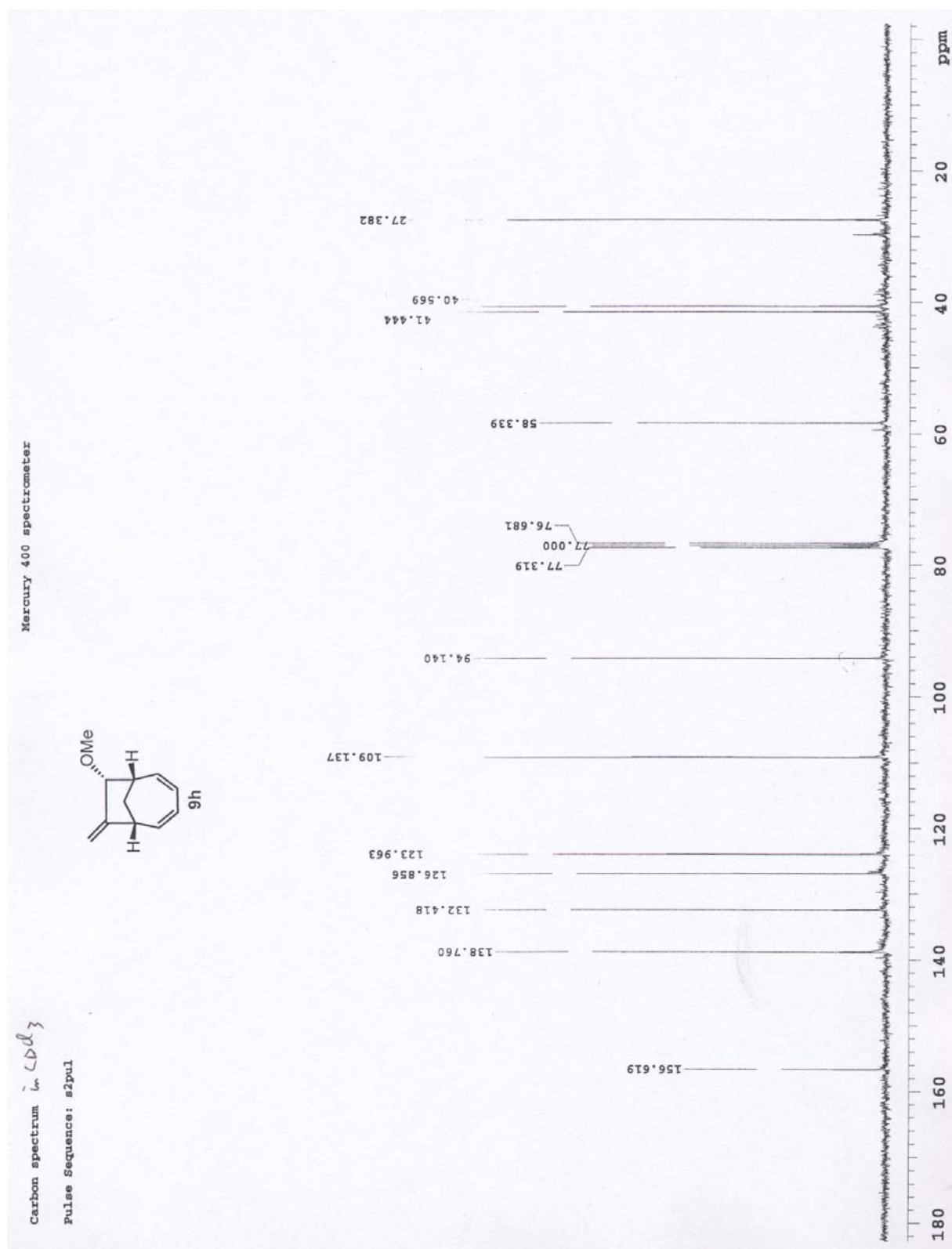
Pulse Sequence: s2pul

Mercury 400 spectrometer





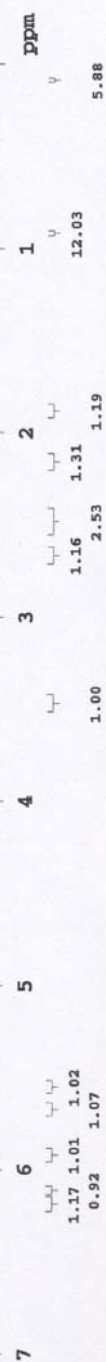
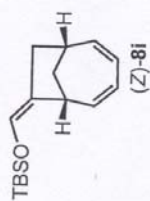




proton spectrum in CDCl<sub>3</sub>

Pulse Sequence: s2pul

Mercury 400 spectrometer

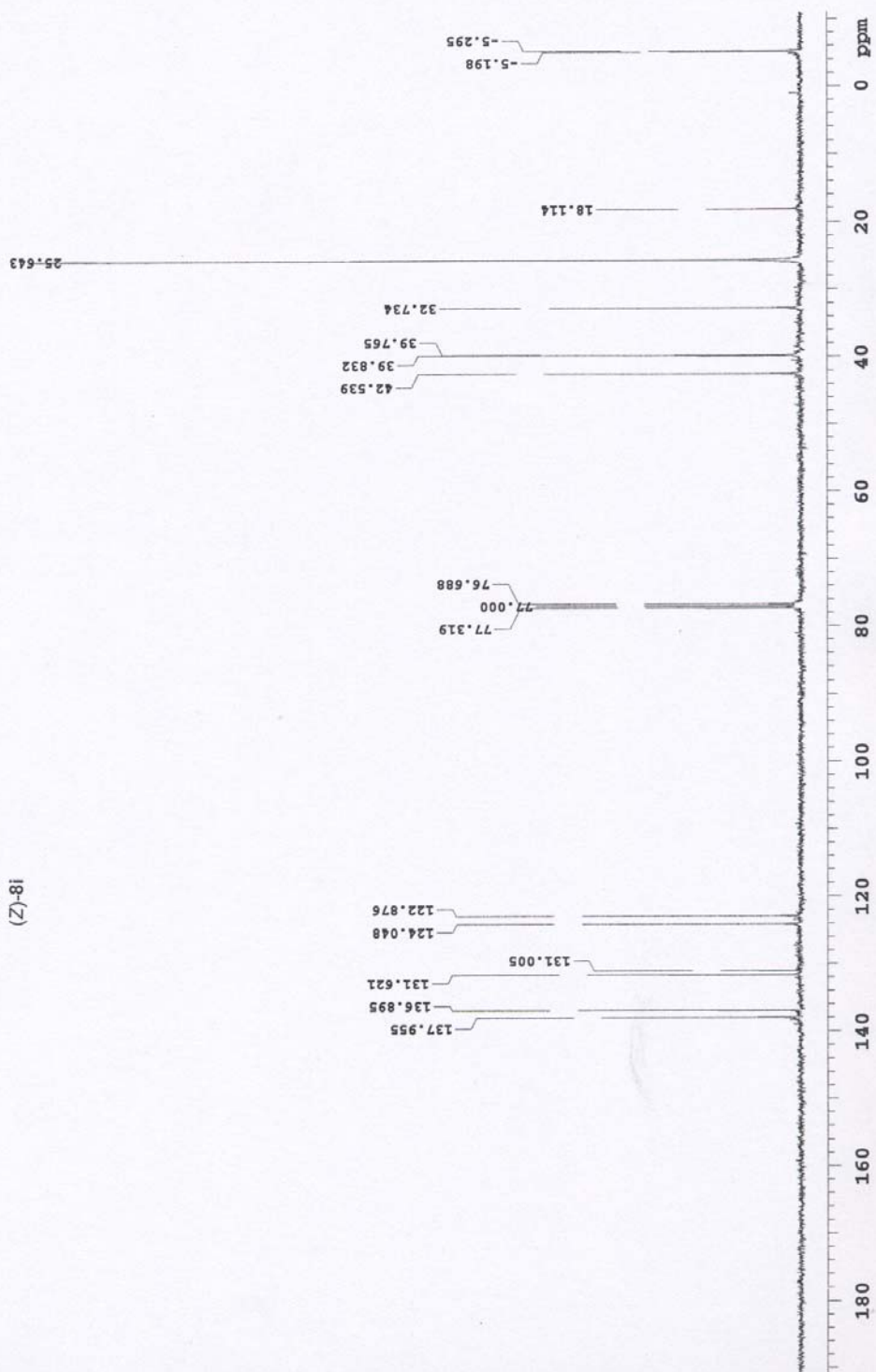
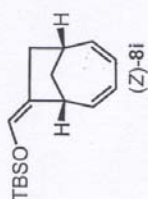




Carbon spectrum in CDCl<sub>3</sub>

Pulse sequence: s2pul

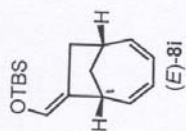
Mercury 400 spectrometer



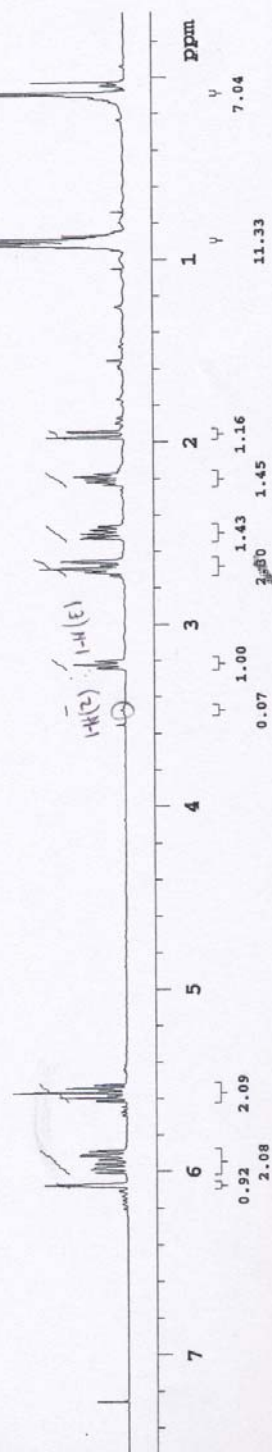
proton spectrum in  $CDCl_3$

Pulse Sequence: s2pul

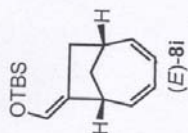
Mercury 400 spectrometer



(contaminated by 7% of isomer Z)

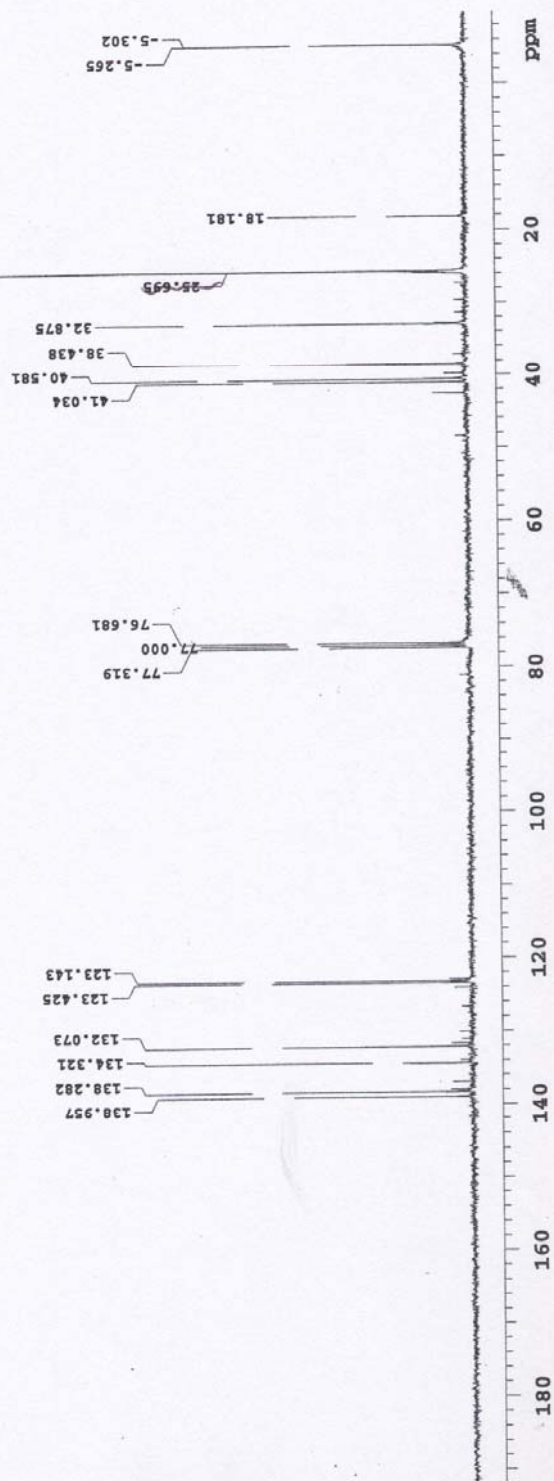


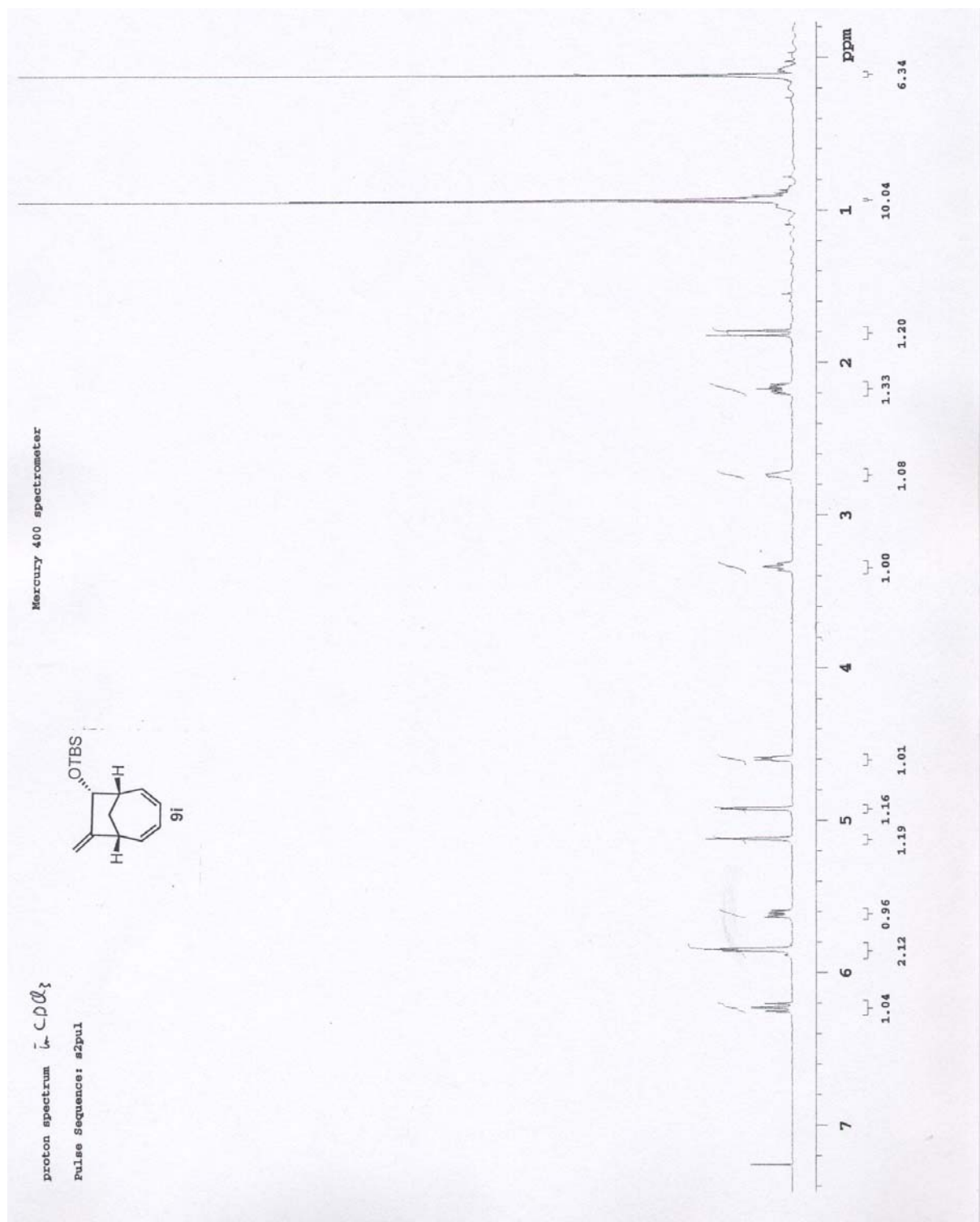
Mercury 400 spectrometer



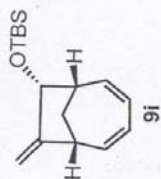
(contaminated by 7% of isomer Z)

Carbon spectrum  
in CDCl<sub>3</sub>  
Pulse Sequence: s2pul

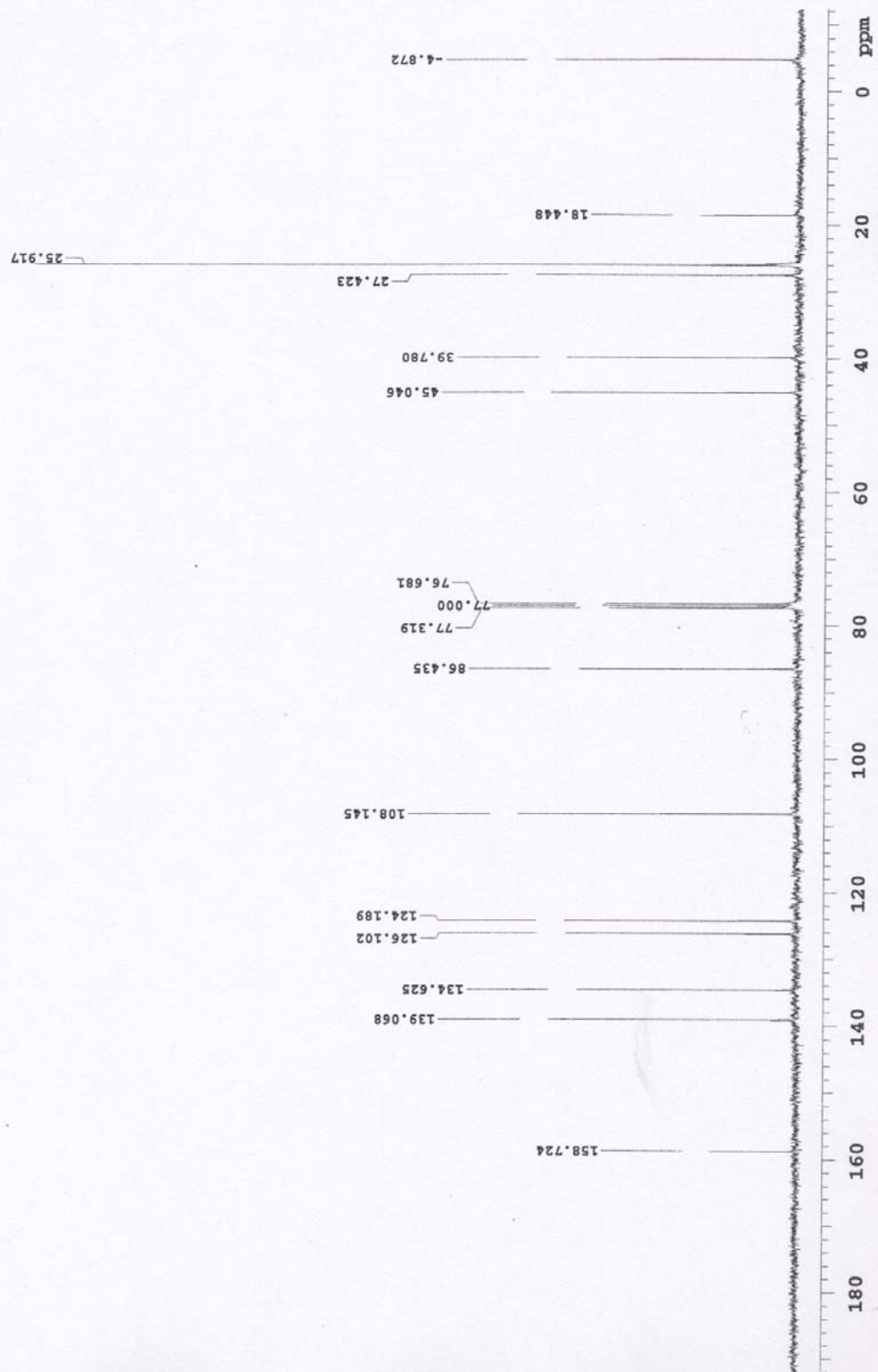




Carbon spectrum in CDCl<sub>3</sub>  
Pulse Sequence: s2pul



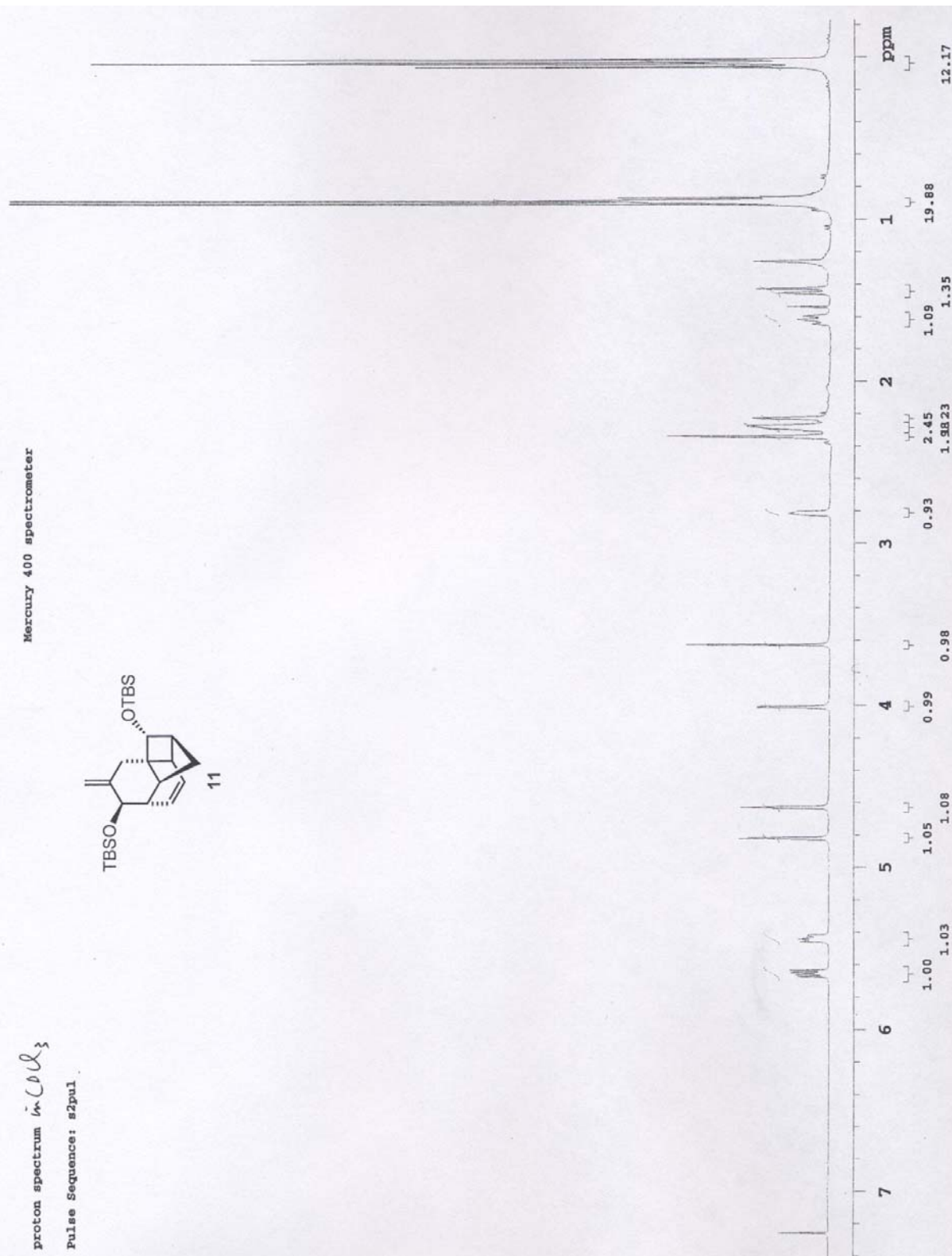
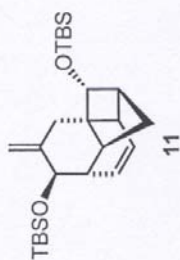
Mercury 400 spectrometer



proton spectrum in  $CDCl_3$

Pulse Sequence: s2pul

Mercury 400 spectrometer

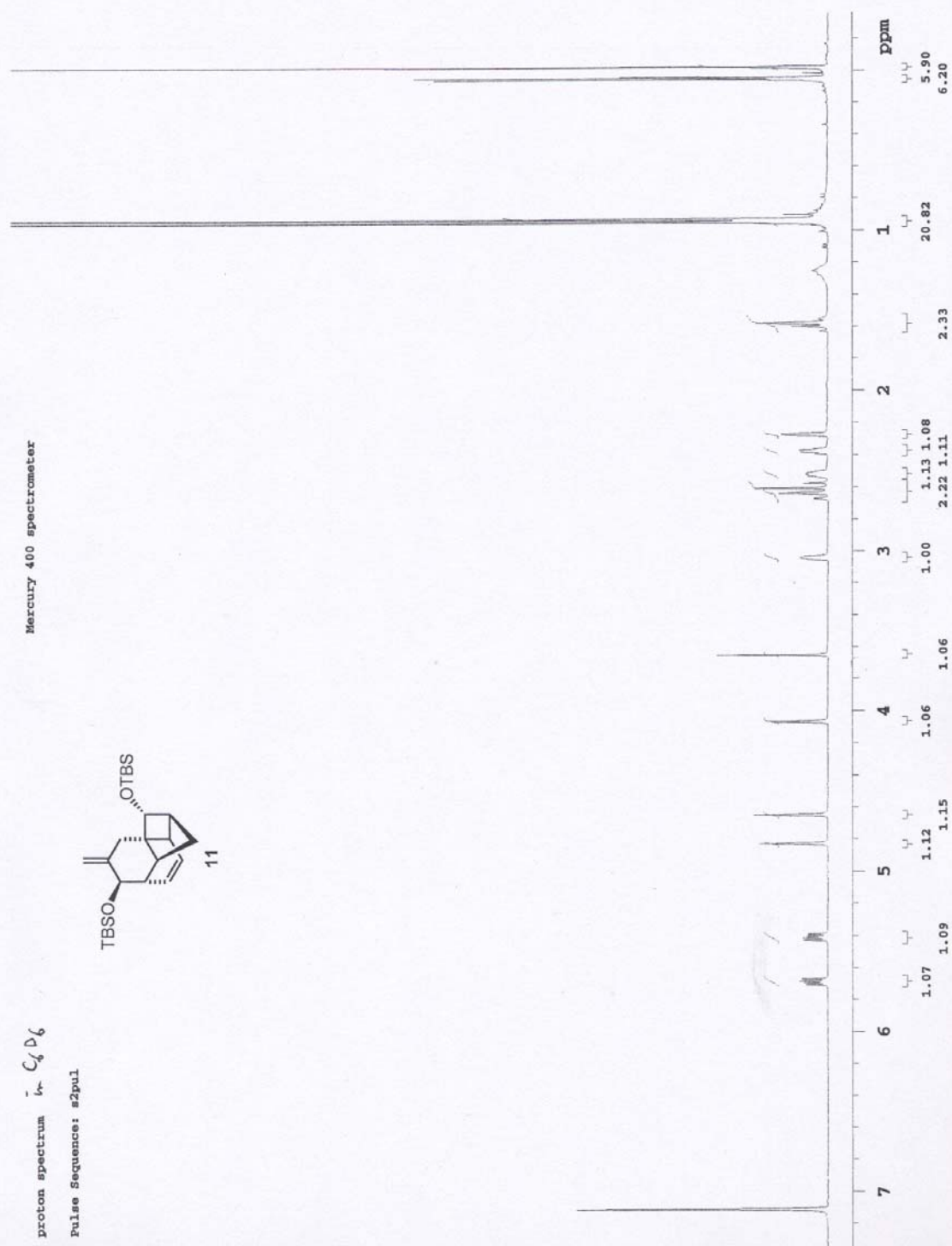
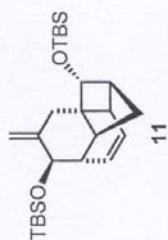




proton spectrum in C<sub>6</sub>D<sub>6</sub>

Pulse Sequence: s2pul

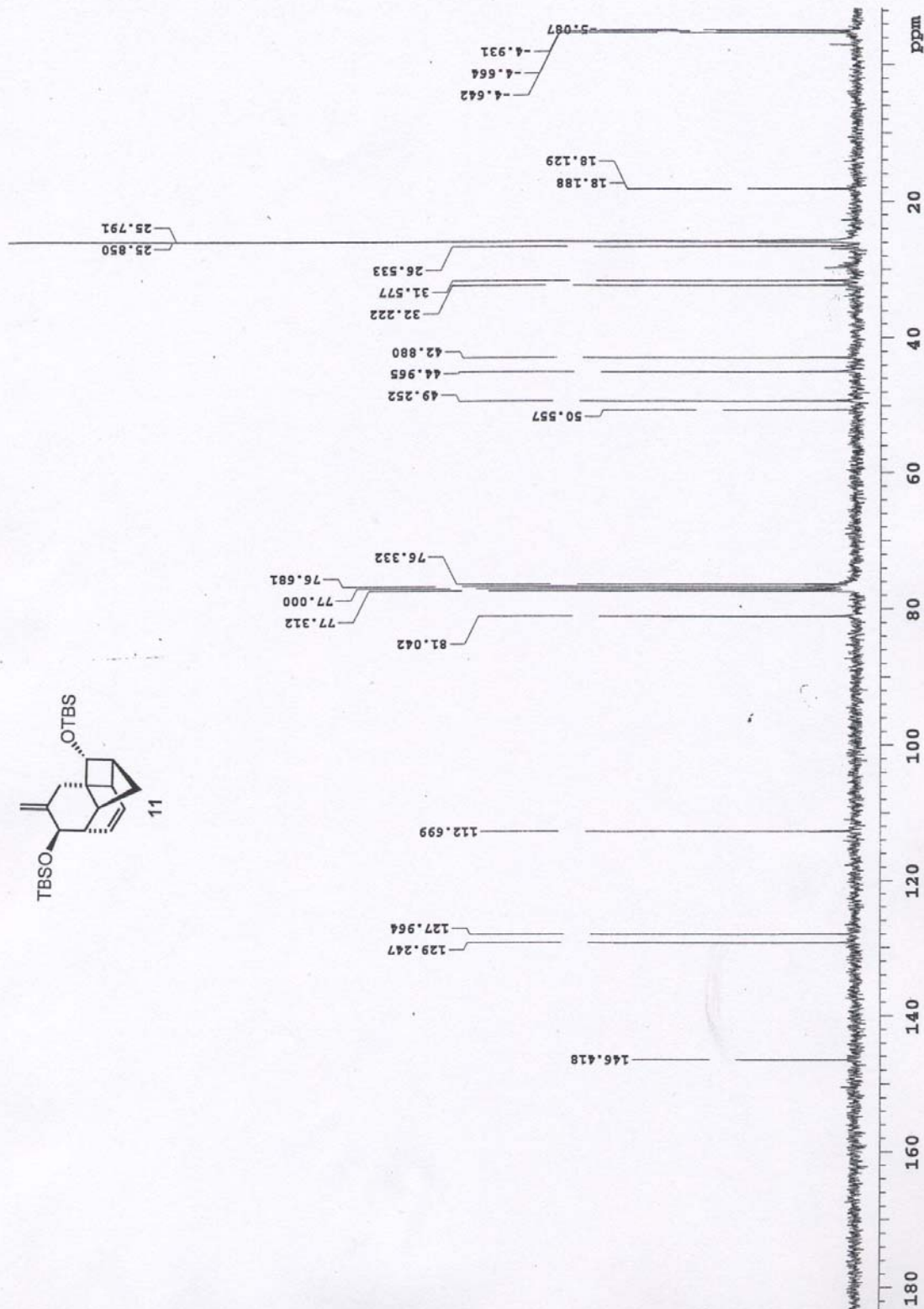
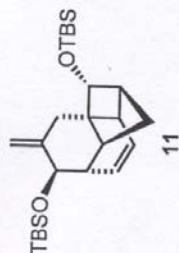
Mercury 400 spectrometer

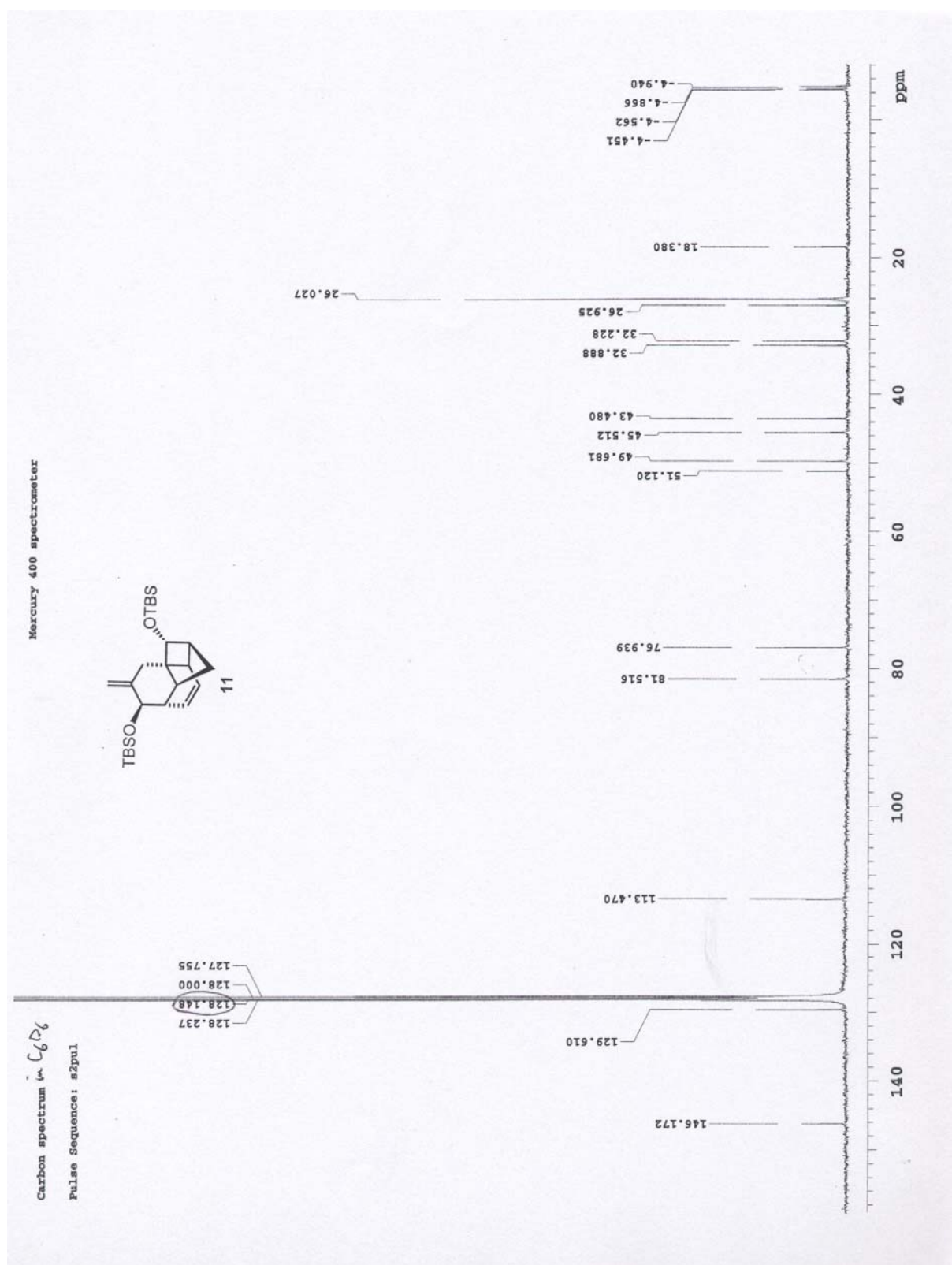




Carbon spectrum  
in  $CaCl_2$

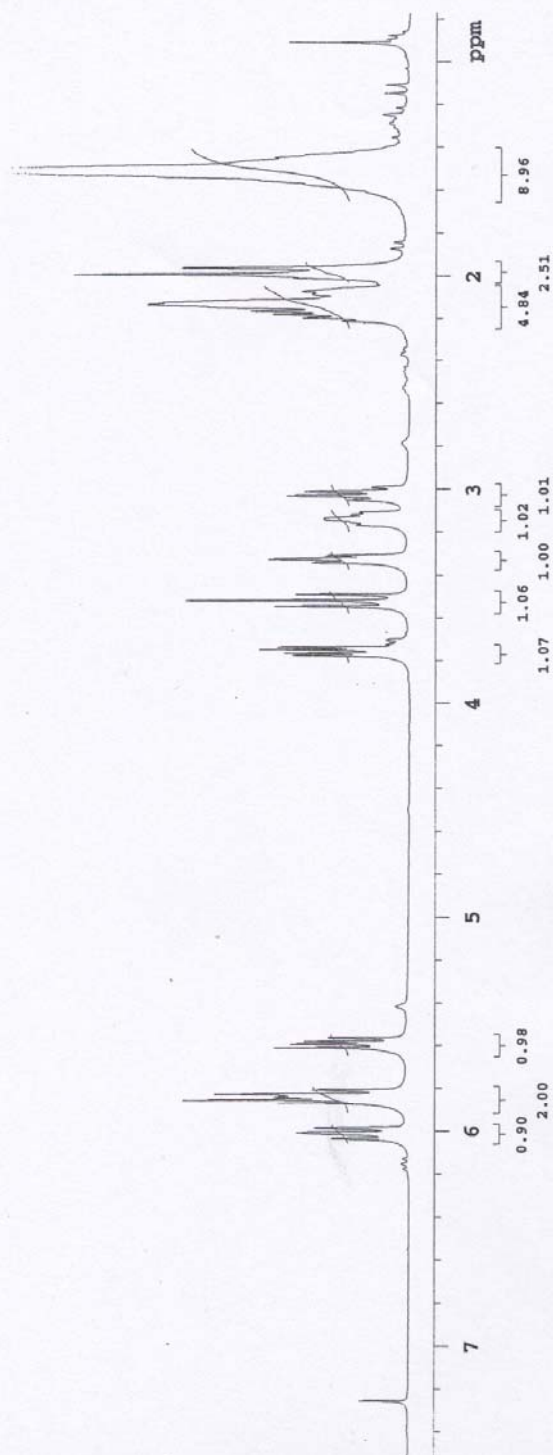
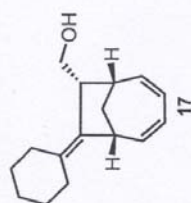
Pulse Sequence: s2pul





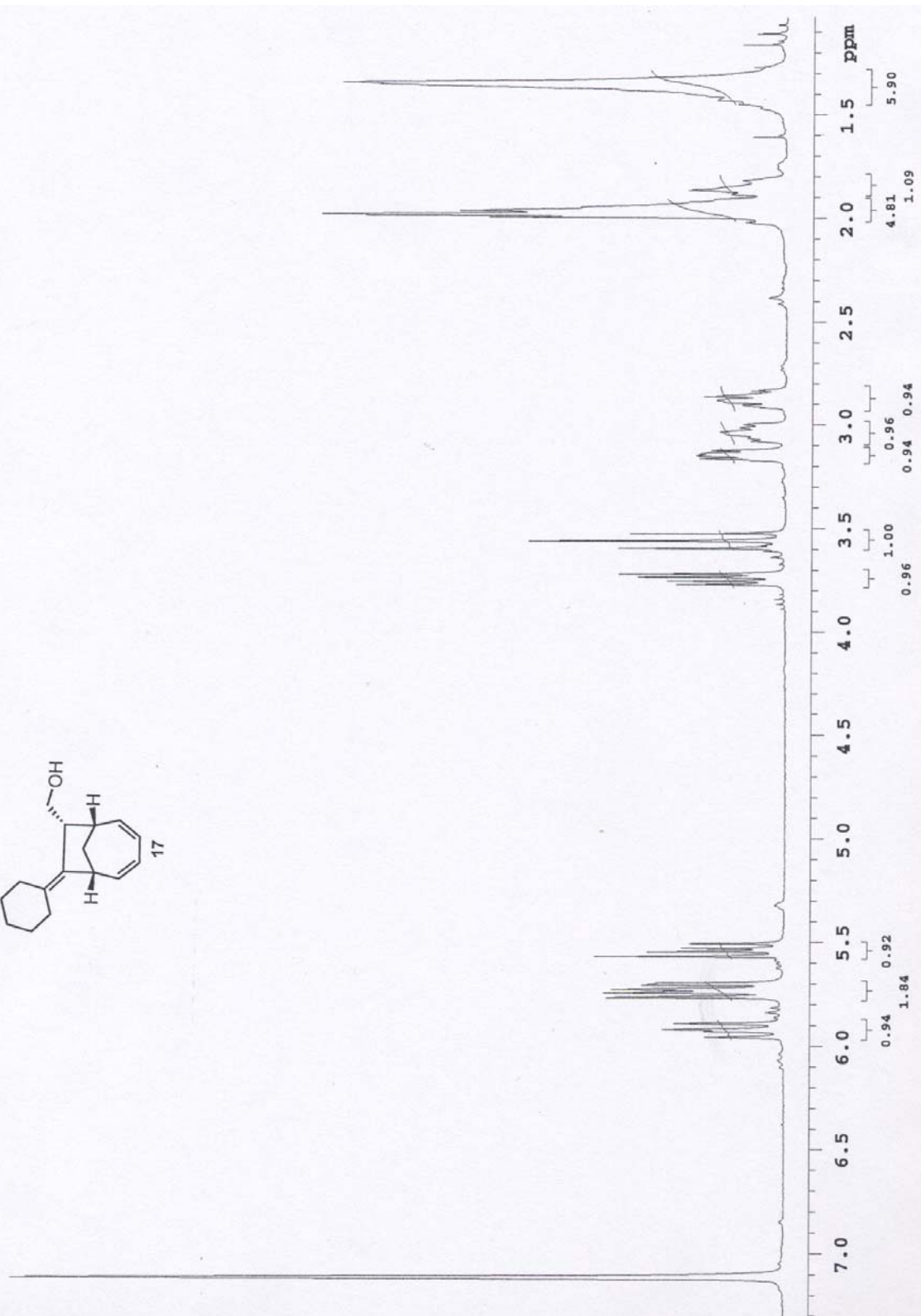
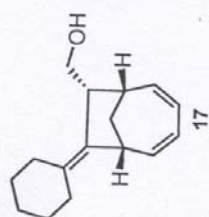
proton spectrum in  $CDCl_3$   
Pulse Sequence: s2pul

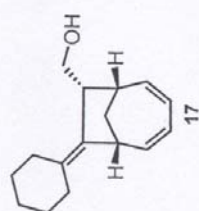
Mercury 400 spectrometer



Proton spectrum in  $C_6D_6$

Unity 300 spectrometer

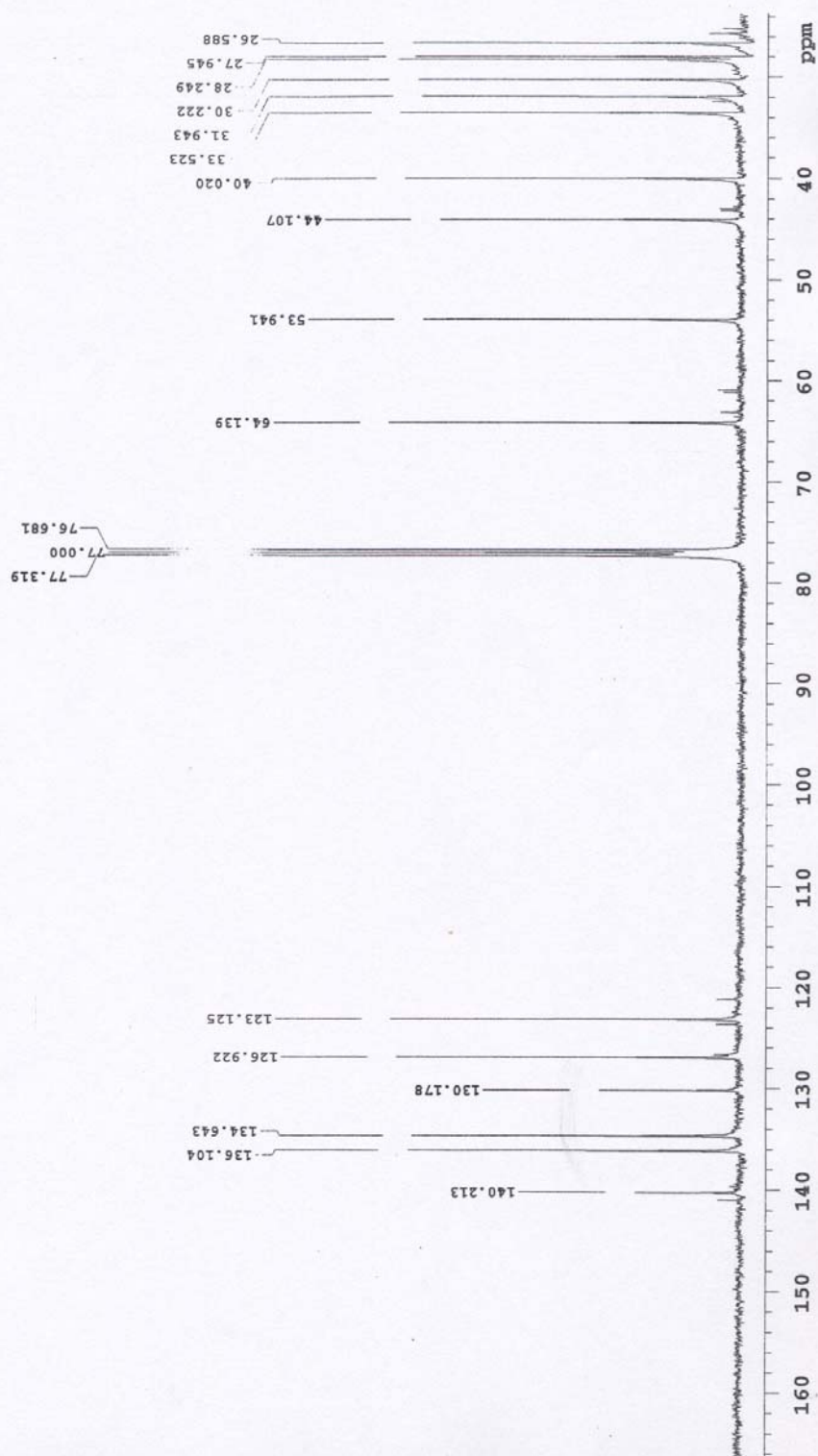




Carbon spectrum in CDCl<sub>3</sub>

Pulse Sequence: s2pul

Mercury 400 spectrometer

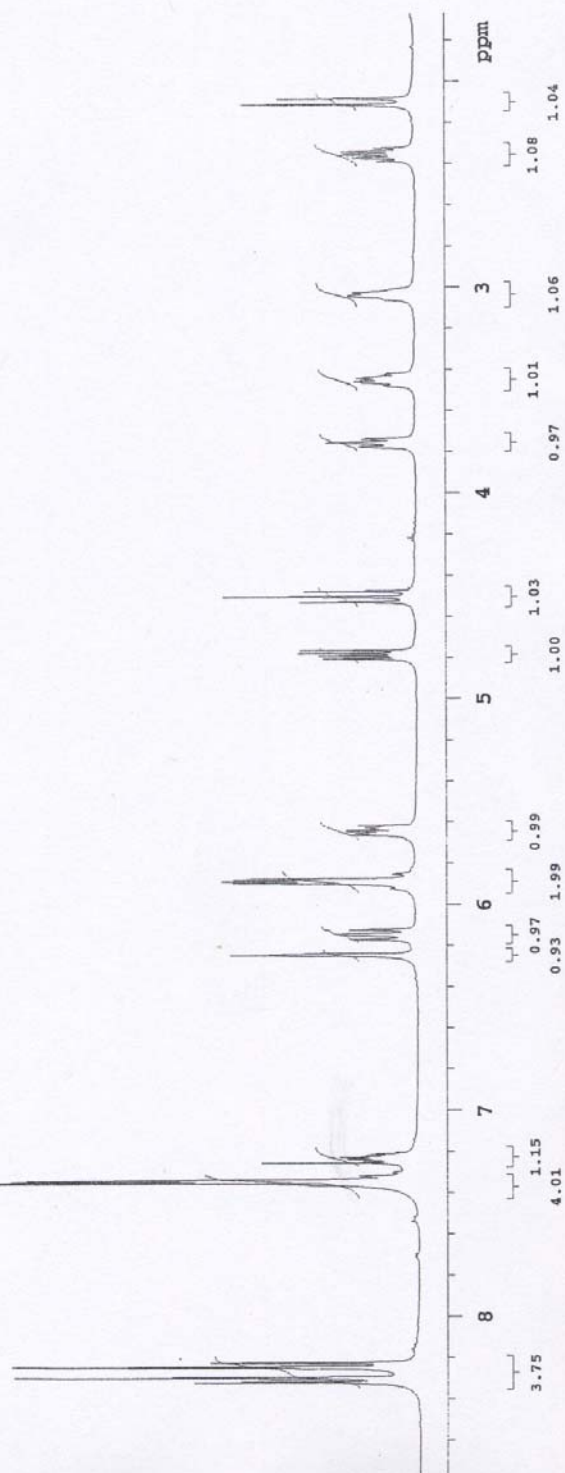
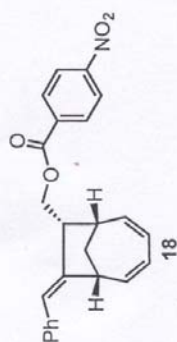


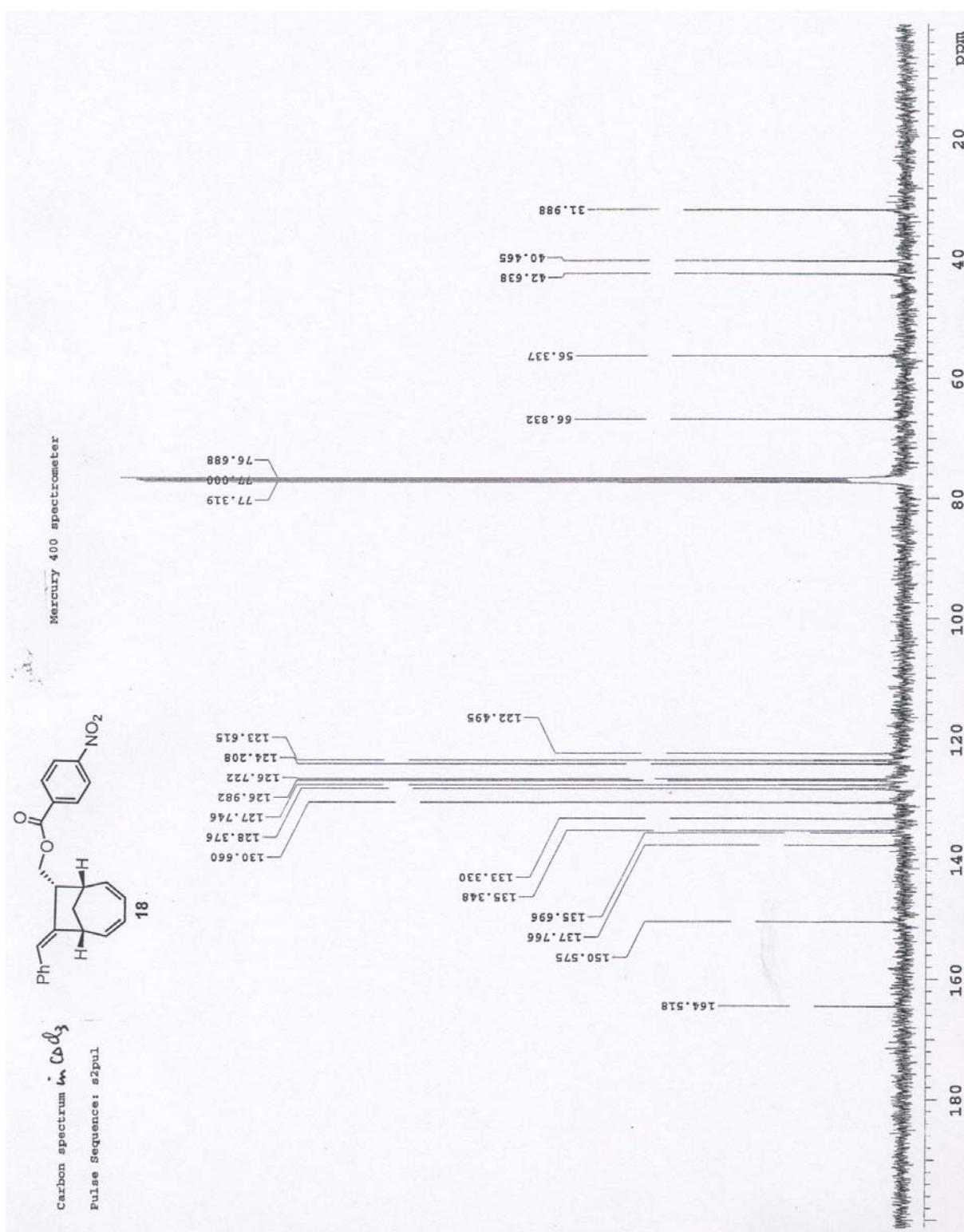


proton spectrum in  $CDCl_3$

Pulse Sequence: s2pul

Mercury 400 spectrometer



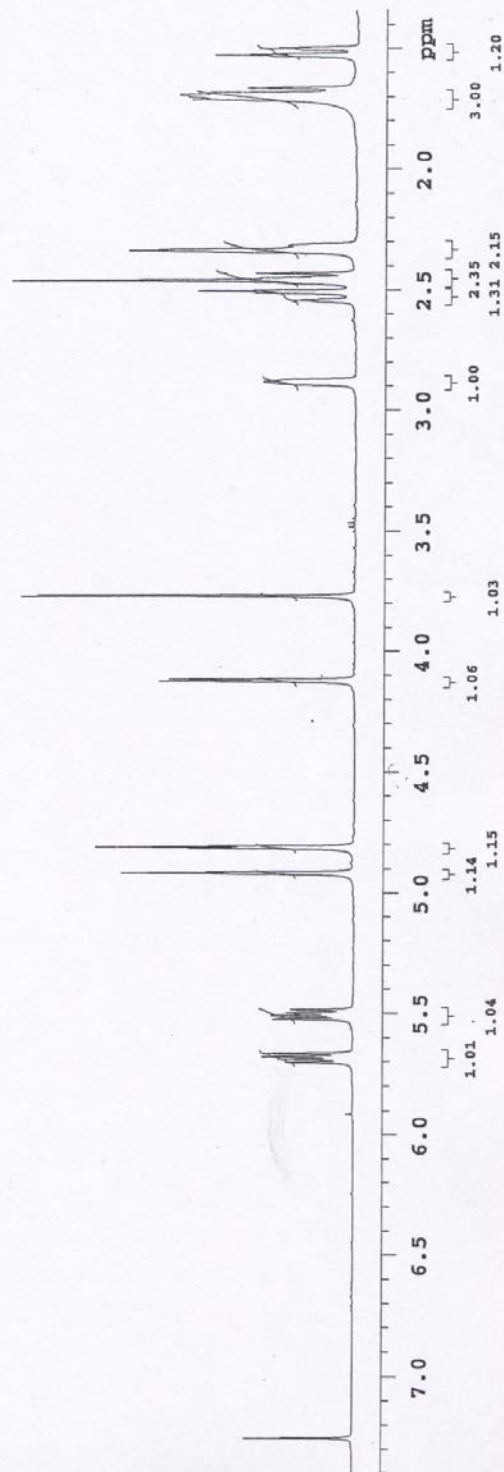
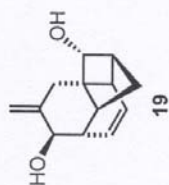


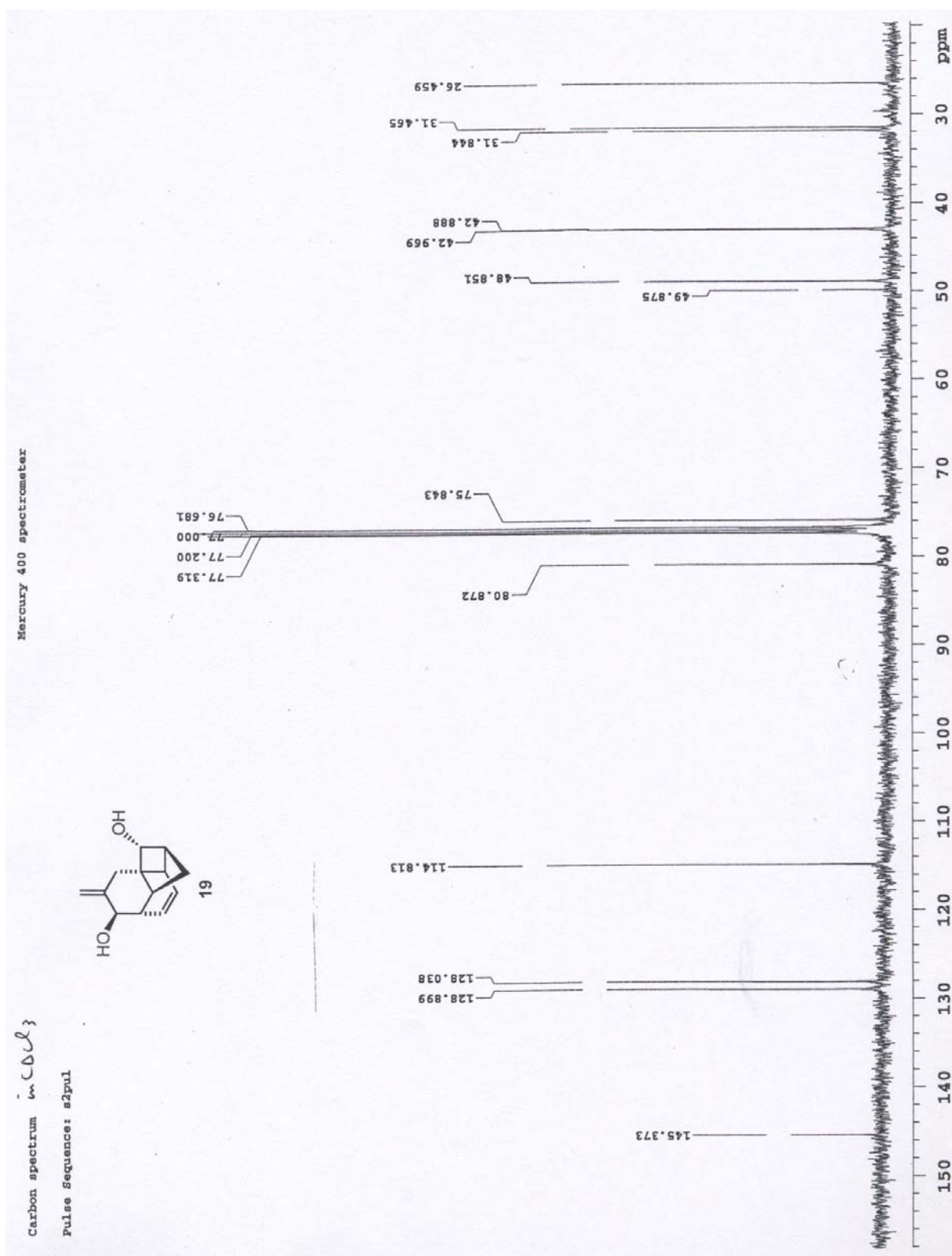


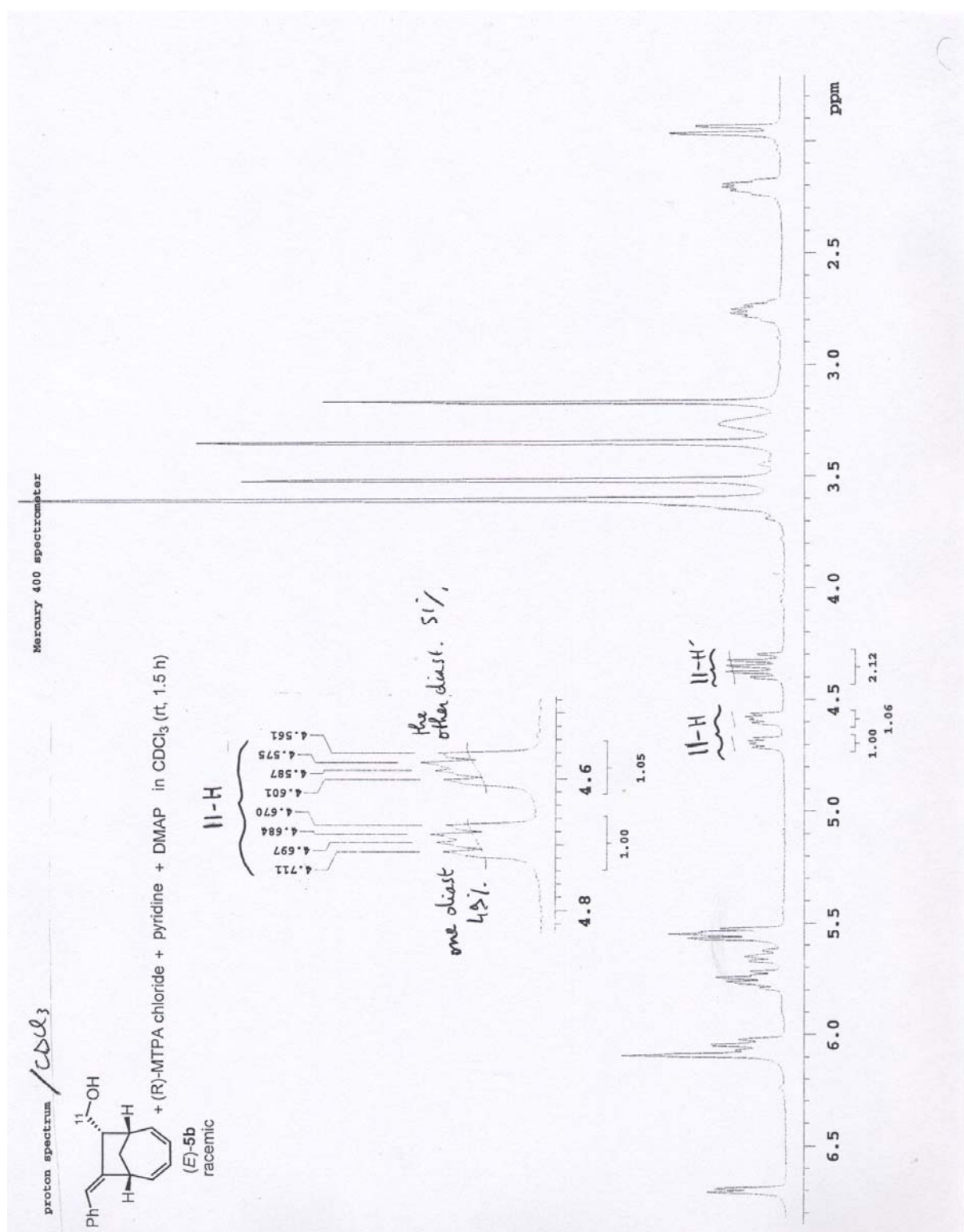
proton spectrum in CDCl<sub>3</sub>

Pulse Sequence: zgpg30

Mercury 400 spectrometer







Mercury 400 spectrometer

proton spectrum /  $CDCl_3$

