

**Synthesis of Vinylcycloheptadienes by the Nickel-Catalyzed Three-Component [3+2+2] Cocyclization.
Application to the Synthesis of Polycyclic Compounds**

Shinsuke Komagawa,[†] Kouhei Takeuchi,[†] Ikuo Sotome,[†] Isao Azumaya,[‡] Hyuma Masu,[‡] Ryu Yamasaki,[†] and Shinichi Saito^{*,†}

Department of Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka, Shinjuku, Tokyo 162-8601, Japan, and Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, Kagawa 769-2193, Japan

ssaito@rs.kagu.tus.ac.jp

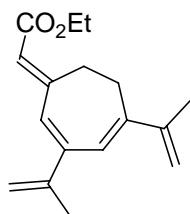
Table of contents

Experimental details.	S2-11
Figure S1, S2 and S3.	S12
¹ H and ¹³ C NMR spectra of 3a-3e , 4g , 6a-6c , 6g , 8 , 10 , 12a-12d , 13b , 14c , 15b , 16d .	S13-56
NOESY Spectrum of <i>endo</i> - 12a .	S57

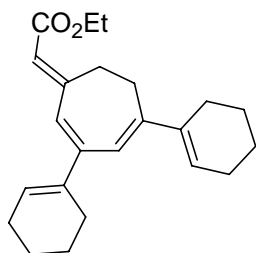
General Information

Reagents were commercially available and used without further purification unless otherwise noted. Ethyl cyclopropylideneacetate (**1**),¹ 2-benzyl-1-buten-3-yne (**2c**),²⁻⁵ 3-decen-1-yne (**2d**),^{6,7} 8-hexyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-(7*E*)-buten-9-yne (**2e**),^{8,9} 1-decen-3-yne (**2f**),¹⁰ and diisopropoxytitanium(IV) dichloride¹¹ were prepared as reported. Chemical shifts were reported in delta units (δ) relative to chloroform (7.24 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR) or dimethyl sulfoxide (2.49 ppm for ^1H NMR and 39.7 ppm for ^{13}C NMR). Multiplicity is indicated by s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). Coupling constants, *J*, are reported in Hz. The crystal structure was solved by direct methods SIR92 (Altomare et al., 1994). For refining the structures, performing a structure analysis, and producing crystallographic illustrations, the program TEXSAN (Rigaku/MS, 1998) was used. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included as their calculated positions.

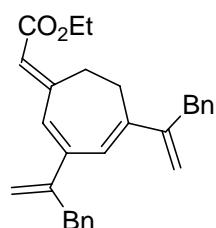
Nickel(0)-Catalyzed Cycloaddition of Ethyl Cyclopropylideneacetate (1**) and Conjugated Enynes (Table 1). A Representative Procedure.** To a dark red mixture of $\text{Ni}(\text{cod})_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in dry toluene (0.5 mL) was added dropwise a solution of **1** (126 mg, 1 mmol) and **2** (3 mmol) in dry toluene (0.5 mL) at room temperature over 3 h under Ar. The progress of the reaction was monitored by TLC and GC-MS, and the mixture was stirred until the starting material **1** disappeared. The mixture was passed through a short silica gel column (ether). Evaporation of the solvent gave an oil, which was further purified by silica gel column chromatography to give **3**.



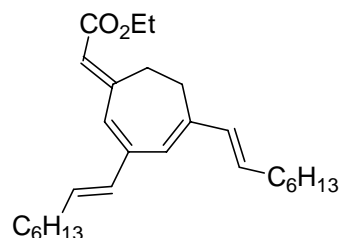
(*E*)-1-Ethoxycarbonylmethylene-3,5-(di-1-methylethenyl)-2,4-cycloheptadiene (3a**):** purified by silica gel column chromatography (hexane/AcOEt 30:1 and hexane/ CH_2Cl_2 3:1); yellow oil; ^1H NMR (300 MHz, CDCl_3) 6.39 (s, 1H), 6.19 (s, 1H), 5.71 (s, 1H), 5.23 (s, 1H), 5.14 (s, 1H), 5.05 (s, 2H), 4.13 (q, $J = 7.2$ Hz, 2H), 3.16-3.11 (m, 2H), 2.54-2.50 (m, 2H), 1.97 (s, 3H), 1.96 (s, 3H), 1.25 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 166.8, 158.3, 147.3, 146.0, 143.9, 143.0, 131.0, 122.7, 117.4, 115.1, 114.1, 59.6, 31.8, 26.1, 21.8, 21.1, 14.3; IR (neat) 2976, 1706, 1585, 1444, 1374, 1264, 1213, 1154, 1040, 891 cm^{-1} . HR-MS (EI) Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_2$: 258.1620. Found: 258.1611.



(E)-1-Ethoxycarbonylmethylene-3,5-(di-1-cyclohexenyl)-2,4-cycloheptadiene (3b): purified by silica gel column chromatography (hexane/AcOEt 30:1 and hexane/CH₂Cl₂ 3:1); yellow oil; ¹H NMR (300 MHz, CDCl₃) 6.27 (s, 1H), 6.04 (t, *J* = 4 Hz, 1H), 6.02 (s, 1H), 5.91 (t, *J* = 4 Hz, 1H), 5.64 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.13-3.09 (m, 2H), 2.49-2.45 (m, 2H), 2.22-2.11 (m, 8H), 1.69-1.54 (m, 8H), 1.25 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) 167.1, 159.4, 148.4, 145.8, 139.9, 136.6, 128.2, 127.1, 125.9, 120.2, 115.7, 59.4, 32.3, 27.2, 26.3, 26.2, 26.0, 25.9, 23.0, 23.0, 22.1, 22.0, 14.4; IR (neat) 2928, 1704, 1582, 1236, 1150, 1039, 756 cm⁻¹. HR-MS (ESI) Calcd for (C₂₃H₃₀O₂)[M+Na]⁺: 361.2138. Found: 361.2138.

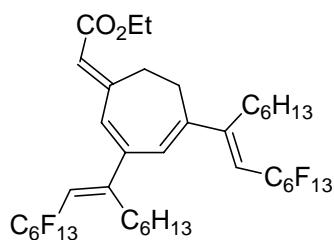


(E)-1-Ethoxycarbonylmethylene-3,5-(di-1-benzylethenyl)-2,4-cycloheptadiene (3c): purified by silica gel column chromatography (hexane/AcOEt 20:1); yellow oil; ¹H NMR (300 MHz, CDCl₃) 7.29-6.99 (m, 10H), 6.27 (s, 1H), 6.08 (s, 1H), 5.55 (s, 1H), 5.40 (s, 1H), 5.06 (s, 1H), 4.94 (s, 1H), 4.85 (s, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.65 (s, 2H), 3.41 (s, 2H), 3.07-3.04 (m, 2H), 2.45-2.41 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) 166.7, 157.9, 150.2, 146.6, 146.5, 143.6, 139.8, 139.2, 131.9, 128.7, 128.5, 128.4, 128.3, 126.1, 126.1, 124.4, 117.2, 116.0, 59.6, 41.4, 40.8, 31.6, 26.7, 14.3; IR (neat) 3027, 2979, 1704, 1585, 1495, 1453, 1400, 1266, 1215, 1154, 1039, 895, 735, 699 cm⁻¹. HR-MS (ESI) Calcd for (C₂₉H₃₀O₂)[M+Na]⁺: 433.2138. Found: 433.2139.

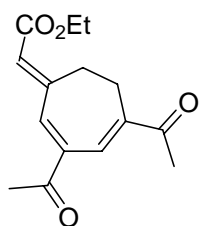


(E)-1-Ethoxycarbonylmethylene-3,5-(di-1-octenyl)-2,4-cycloheptadiene (3d): purified by silica gel column chromatography (hexane/ether 30:1); yellow oil; ¹H NMR (300 MHz, CDCl₃) 6.16-5.83 (m, 6H), 5.64 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.14-3.11 (m, 2H), 2.46-2.43 (m, 2H), 2.13 (quint, *J* = 6.8 Hz, 4H), 1.40-1.23 (m, 19H), 0.89-0.85 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) 167.0, 158.4, 146.8, 140.4, 134.4, 133.1, 133.0, 132.7, 132.2, 122.9, 116.4, 59.6, 33.2, 33.1, 31.7, 29.5, 29.4, 29.3, 28.9, 25.1, 22.6, 14.4, 14.1; IR (neat) 2926, 2854, 1705, 1579, 1465, 1402, 1279, 1230, 1148, 1040, 961, 890 cm⁻¹. HR-MS (ESI) Calcd

for (C₂₇H₄₂O₂)[M+Na]⁺: 421.3077. Found: 421.3079.



(E)-1-Ethoxycarbonylmethylene-3,5-[di-1-hexyl-(2E)-perfluorohexyletenyl]-2,4-cycloheptadiene (3e): purified by silica gel column chromatography (hexane/AcOEt 30:1); yellow oil; ¹H NMR (300 MHz, CDCl₃) 6.31 (s, 1H), 5.88 (s, 1H), 5.77 (s, 1H), 5.48 (t, *J* = 15.6 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.19-3.16 (m, 2H), 2.45-2.42 (m, 6H), 1.40-1.15 (m, 16H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.87-0.82 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) 166.4, 159.5 (t, ³*J*_{CF} = 5 Hz), 155.4 (t, ³*J*_{CF} = 5 Hz), 150.1, 143.1, 134.4, 124.6, 119.9, 114.3 (t, ²*J*_{CF} = 23 Hz), 112.8 (t, ²*J*_{CF} = 23 Hz), 119-108 (m), 60.1, 31.5, 31.5, 30.8, 30.1, 29.3, 29.2, 29.0, 28.1, 22.5, 14.2, 13.8; IR (neat) 2933, 2862, 1712, 1240, 1202, 1165, 1146 cm⁻¹. Anal. Calcd for C₃₉H₄₀F₂₆O₂: C, 45.27; H, 3.90. Found: C, 45.08; H, 3.89.

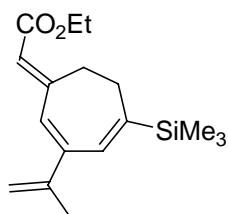


(E)-1-Ethoxycarbonylmethylene-3,5-(di-1-oxoethyl)-2,4-cycloheptadiene (4g): purified by silica gel column chromatography (hexane/AcOEt 3:1); yellow oil; ¹H NMR (300 MHz, CDCl₃) 7.57 (s, 1H), 7.31 (s, 1H), 6.03 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.09-3.05 (m, 2H), 2.64-2.61 (m, 2H), 2.47 (s, 3H), 2.42 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) 198.4, 198.3, 165.5, 154.0, 146.3, 145.5, 138.6, 131.0, 125.5, 60.6, 28.5, 26.3, 25.7, 22.8, 14.2; IR (neat) 2981, 1711, 1668, 1597, 1435, 1356, 1250, 1166, 1034, 899 cm⁻¹. HR-MS (ESI) Calcd for (C₁₅H₁₈O₄)[M+Na]⁺: 285.1097. Found: 285.1056.

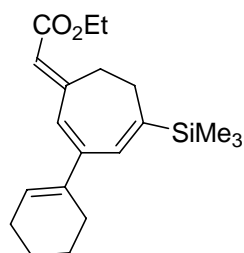
Nickel(0)-Catalyzed Three-Component Cycloaddition of Ethyl Cyclopropylideneacetate (1), Conjugated Enynes and (Trimethylsilyl)acetylene (5) (Table 2). A Representative Procedure. To a dark red mixture of Ni(cod)₂ (27.5 mg, 0.1 mmol) and PPh₃ (52.5 mg, 0.2 mmol) in dry toluene (0.5 mL) was added dropwise a solution of **1** (126 mg, 1 mmol), **2** (1 mmol), and (trimethylsilyl)acetylene **5** (4 mmol) in dry toluene (0.5 mL) at room temperature over 3 h under Ar. The progress of the reaction was monitored by TLC and GC-MS, and the mixture was stirred until the starting material **1** disappeared. The mixture was passed through a short silica gel column (ether). Evaporation of the solvent gave an oil, which was further purified by silica gel column chromatography to give **6**.

Reaction Condition for the Ni(PPh₃)₂Br₂-Zn-PPh₃ System (entry 2, Table 2). A mixture of Ni(PPh₃)₂Br₂ (372 mg, 0.5 mmol), PPh₃ (262 mg, 1 mmol), and Zn dust (654 mg, 10 mmol) in dry toluene

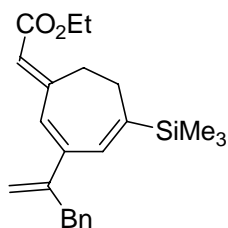
(2.5 mL) was stirred at room temperature over 1 h and changed color from green to dark red. To this mixture was added dropwise a solution of **1a** (630 mg, 5 mmol), **2a** (0.48 mL, 5 mmol), and **5** (2.1 mL, 15 mmol) in dry toluene (2.5 mL) at room temperature for 5 h under Ar. The mixture was stirred for 14 h and passed through a short silica gel column (ether). Evaporation of the solvent gave an oil, which was further purified by silica gel column chromatography (hexane/ether 30:1) to give **6a** (905 mg, 62%).



(E)-1-Ethoxycarbonylmethylene-3-(1-methylethenyl)-5-trimethylsilyl-2,4-cycloheptadiene (6a): purified by silica gel column chromatography (hexane/CH₂Cl₂ 3:1); pale yellow oil; ¹H NMR (300 MHz, CDCl₃) 6.38 (s, 1H), 6.36 (s, 1H), 5.71 (s, 1H), 5.13 (s, 1H), 5.05 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.07-3.04 (m, 2H), 2.33-2.29 (m, 2H), 1.95 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.10 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) 166.8, 158.5, 151.7, 145.6, 143.5, 133.7, 131.6, 117.4, 115.1, 59.6, 32.3, 27.6, 21.7, 14.3, -2.2; IR (neat) 2954, 1709, 1586, 1444, 1403, 1376, 1249, 1214, 1155, 1088, 1067, 1039, 892, 838, 752 cm⁻¹. HR-MS (ESI) Calcd for (C₁₇H₂₆O₂Si)[M+Na]⁺: 313.1594. Found: 313.1594.

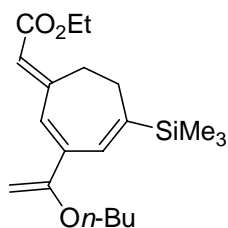


(E)-1-Ethoxycarbonylmethylene-3-(1-cyclohexenyl)-5-trimethylsilyl-2,4-cycloheptadiene (6b): purified by silica gel column chromatography (hexane/AcOEt 30:1); pale yellow oil; ¹H NMR (300 MHz, CDCl₃) 6.30 (s, 1H), 5.91 (t, *J* = 4.0 Hz, 1H), 5.67 (s, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.07-3.03 (m, 2H), 2.31-2.27 (m, 2H), 2.18-2.14 (m, 4H), 1.70-1.64 (m, 2H), 1.62-1.56 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.10 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) 167.0, 159.2, 151.4, 144.6, 139.0, 134.1, 129.6, 127.3, 116.4, 59.5, 32.8, 27.6, 26.9, 26.0, 22.9, 21.9, 14.3, -2.2; IR (neat) 2930, 1707, 1585, 1248, 1217, 1152, 1087, 1039, 838, 752 cm⁻¹. HR-MS (ESI) Calcd for (C₂₀H₃₀O₂Si)[M+Na]⁺: 353.1907. Found: 353.1907.



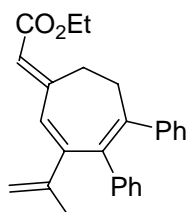
(E)-1-Ethoxycarbonylmethylene-3-(1-benzylethenyl)-5-trimethylsilyl-2,4-cycloheptadiene (6c): purified

by silica gel column chromatography (hexane/AcOEt 25:1 and hexane/CH₂Cl₂ 3:1); pale yellow oil; ¹H NMR (300 MHz, CDCl₃) 7.28-7.13 (m, 5H), 6.34 (s, 1H), 6.26 (s, 1H), 5.58 (s, 1H), 5.23 (d, *J* = 1.3 Hz, 1H), 4.98 (d, *J* = 1.3 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.59 (s, 2H), 3.02-2.98 (m, 2H), 2.25-2.22 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.08 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) 166.8, 158.4, 152.2, 149.8, 143.3, 139.3, 134.1, 132.6, 128.8, 128.3, 126.1, 117.1, 116.0, 59.6, 41.5, 32.3, 27.6, 14.3, -2.3; IR (neat) 2954, 1708, 1586, 1453, 1401, 1249, 1214, 1154, 1086, 1039, 895, 838, 751, 699 cm⁻¹. HR-MS (ESI) Calcd for (C₂₂H₂₀O)[M+Na]⁺: 389.1907. Found: 389.1907.

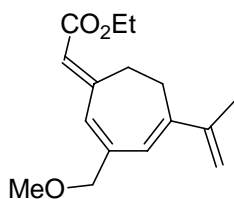


(*E*)-1-Ethoxycarbonylmethylene-3-(1-butoxyethenyl)-5-trimethylsilyl-2,4-cycloheptadiene (6g):

purified by silica gel column chromatography (hexane/AcOEt 30:1 and hexane/ether 30:1); pale yellow oil; ¹H NMR (300 MHz, C₆D₆) 7.09 (s, 1H), 6.62 (s, 1H), 5.97 (s, 1H), 4.51 (d, *J* = 2.3 Hz, 1H), 4.13 (d, *J* = 2.3 Hz, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.50 (t, *J* = 6.3 Hz, 1H), 3.39-3.35 (m, 2H), 2.29-2.25 (m, 2H), 1.52 (tt, *J* = 7.3 Hz, 6.3 Hz, 2H), 1.31 (qt, *J* = 7.3 Hz, 7.3 Hz, 2H), 0.99 (t, *J* = 7.2 Hz, 3H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.02 (s, 9H); ¹³C NMR (125 MHz, C₆D₆) 166.4, 162.2, 158.0, 152.2, 138.6, 133.3, 132.8, 119.1, 85.1, 67.6, 59.6, 32.0, 31.3, 28.1, 19.7, 14.4, 13.9, -2.4; IR (neat) 2957, 1710, 1594, 1266, 1249, 1214, 1154, 1081, 838 cm⁻¹. HR-MS (ESI) Calcd for (C₂₀H₃₂O₃Si)[M+Na]⁺: 371.2013. Found: 371.2013.



(*E*)-1-Ethoxycarbonylmethylene-3-(1-methylethenyl)-4,5-diphenyl-2,4-cycloheptadiene (8): purified by silica gel column chromatography (hexane/CH₂Cl₂ 2:1); pale yellow solid; mp 86-87 °C; ¹H NMR (300 MHz, CDCl₃) 7.13-6.79 (m, 10H), 6.68 (s, 1H), 5.84 (d, *J* = 1.2 Hz, 1H), 4.89 (s, 1H), 4.80 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.26-3.21 (m, 2H), 2.78-2.74 (m, 2H), 1.67 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) 166.6, 157.9, 148.7, 145.6, 145.0, 142.3, 140.2, 135.2, 131.3, 130.6, 129.6, 127.7, 127.1, 126.3, 125.9, 117.2, 116.5, 59.6, 37.1, 34.0, 21.6, 14.3; IR (KBr) 2966, 1700, 1587, 1488, 1443, 1396, 1252, 1208, 1149, 1031, 899, 752, 697 cm⁻¹. Anal. Calcd for C₂₆H₂₆O₂: C, 84.29; H, 7.07. Found: C, 84.15; H, 7.13.

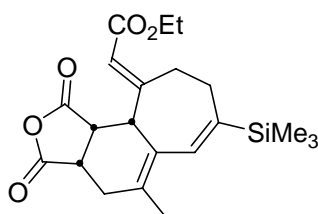


(*E*)-1-Ethoxycarbonylmethylene-3-methoxymethyl-5-(1-methylethenyl)-2,4-cycloheptadiene (10): purified by silica gel column chromatography (hexane/AcOEt 10:1); pale yellow oil; ^1H NMR (300 MHz, CDCl_3) 6.29 (s, 1H), 6.00 (s, 1H), 5.66 (s, 1H), 5.23 (s, 1H), 5.06 (s, 1H), 4.13 (q, $J = 7.2$ Hz, 2H), 3.97 (s, 2H), 3.32 (s, 3H), 3.14-3.11 (m, 2H), 2.56-2.52 (m, 2H), 1.95 (s, 3H), 1.25 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 166.9, 157.3, 148.9, 143.3, 140.6, 132.1, 122.4, 117.0, 114.5, 78.4, 59.7, 57.9, 29.3, 26.6, 21.1, 14.3; IR (KBr) 2980, 1705, 1592, 1445, 1402, 1269, 1158, 1905, 1042, 879 cm^{-1} . HR-MS (ESI) Calcd for $(\text{C}_{16}\text{H}_{22}\text{O}_3)[\text{M}+\text{Na}]^+$: 285.1461. Found: 285.1460.

Diels-Alder Reaction of 6a and 11 (Table 3). A Representative Procedure. A mixture of **6a** (145 mg, 0.5 mmol) and **11** (0.75 mmol) in toluene (2 mL) was stirred at the designated temperature. After the reaction completed, the mixture was purified by silica gel column chromatography to give **12**.

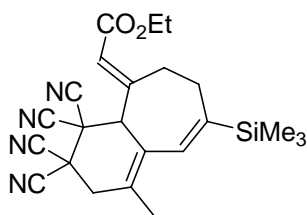
Diels-Alder Reaction of 5a and 6 in the presence of $\text{TiCl}_2(\text{O}i\text{-Pr})_2$. A Representative Procedure. To a mixture of **6a** (145 mg, 0.5 mmol) and **11** (0.75 mmol) in toluene (2 mL) was added a solution of $\text{TiCl}_2(\text{O}i\text{-Pr})_2$ (1.2 mL, 0.5 M in toluene, 0.6 mmol) at rt. After the reaction completed, the mixture was purified by silica gel column chromatography to give **12** or **16**.

Four-Component One-Pot [3+2+2]/[4+2] Cycloaddition of 1, 2, 5, and 11b (eq 9). To a dark red mixture of $\text{Ni}(\text{cod})_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in dry toluene (0.5 mL) was added dropwise a solution of **1** (127 mg, 1 mmol), **2a** (0.095 mL, 1 mmol), and **5** (0.57 mL, 4 mmol) in dry toluene (0.5 mL) at rt over 3 h under Ar. After 16 h, toluene (1 mL) and **11b** (128 mg, 1 mmol) was added and the mixture was stirred at rt for 23 h. The crude product was passed through a short silica gel column (ether) and further purified by silica gel column chromatography (hexane/AcOEt 8:1) to give **12b** (227.9 mg, 54%).

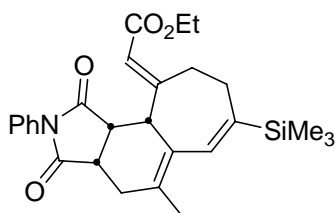


endo-12a: purified by silica gel column chromatography (hexane/AcOEt 3:1); white solid; mp 67-68 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) 6.39 (s, 1H), 5.92 (s, 1H), 4.16 (q, $J = 7.2$ Hz, 2H), 3.61 (dd, $J = 9.8, 5.8$ Hz, 1H), 3.44 (ddd, $J = 9.8, 6.7, 2.4$ Hz, 1H), 3.32 (m, 1H), 3.04-2.99 (m, 1H), 2.83-2.78 (m, 1H), 2.68 (dd, $J = 15.5, 2.3$ Hz, 1H), 2.49-2.41 (m, 3H), 1.89 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) 173.3, 170.5, 165.9, 159.1, 144.6, 134.7, 130.8, 130.4, 116.7, 59.9, 50.2, 44.8, 41.3, 31.8, 31.6, 31.2,

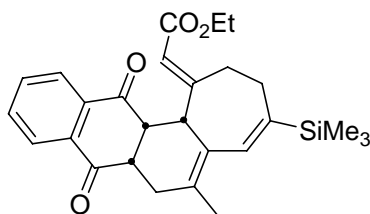
20.4, 14.2, -1.9; IR (KBr) 2955, 1844, 1779, 1704, 1650, 1248, 1179, 992, 937, 837 cm^{-1} . HR-MS (EI) Calcd for $\text{C}_{21}\text{H}_{28}\text{O}_5\text{Si}$: 388.1706. Found: 388.1714.



12b: purified by silica gel column chromatography (hexane/AcOEt 8:1); colorless solid; mp 156-158 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) 6.17 (s, 2H), 4.21 (qd, $J = 7.2, 3.4$ Hz, 2H), 3.89 (s, 1H), 3.59 (dt, $J = 11.5, 4.1$ Hz, 1H), 3.20 (d, $J = 18.4$ Hz, 1H), 3.00 (d, $J = 18.4$ Hz, 1H), 2.62-2.56 (m, 2H), 2.52-2.43 (m, 1H), 1.82 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H), 0.06 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) 164.5, 152.7, 150.1, 130.2, 125.7, 125.4, 124.2, 110.8, 110.7, 110.5, 109.0, 60.6, 53.4, 44.2, 38.7, 37.0, 34.1, 27.7, 19.7, 14.1, -2.1; IR (KBr) 2954, 1715, 1658, 1446, 1381, 1248, 1209, 1189, 1154, 1041, 837, 751 cm^{-1} . Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{N}_4\text{O}_2\text{Si}$: C, 66.00; H, 6.26; N, 13.39. Found: C, 65.97; H, 6.26; N, 13.19.

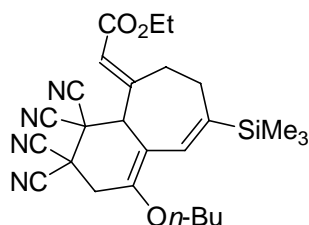


endo-12c: purified by silica gel column chromatography (CH_2Cl_2 /ether 20:1); white amorphous; mp 59-61 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) 7.45-7.16 (m, 5H), 6.47 (s, 1H), 5.97 (s, 1H), 4.13 (qd, $J = 7.2, 1.3$ Hz, 2H), 3.54-3.49 (m, 2H), 3.33-3.27 (m, 1H), 3.05-2.99 (m, 1H), 2.93-2.85 (m, 1H), 2.71 (dd, $J = 15.8, 3.8$ Hz, 1H), 2.52-2.44 (m, 3H), 1.88 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 3H), 0.05 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) 178.0, 175.9, 166.2, 160.4, 144.0, 134.6, 131.9, 131.3, 130.4, 129.1, 128.6, 126.3, 119.8, 115.5, 59.7, 50.0, 43.6, 40.6, 31.7, 31.3, 20.3, 14.3, -1.8; IR (KBr) 2954, 1712, 1499, 1383, 1249, 1177, 1044, 839, 754, 692 cm^{-1} . Anal. Calcd for $\text{C}_{27}\text{H}_{33}\text{NO}_4\text{Si}$: C, 69.94; H, 7.17; N, 3.02. Found: C, 69.71; H, 7.27; N, 3.06.

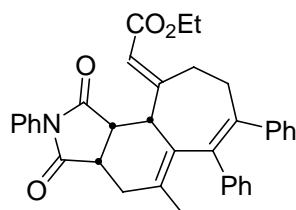


endo-12d: purified by silica gel column chromatography (hexane/AcOEt 10:1); white solid; mp 141-142 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) 8.01-7.99 (m, 1H), 7.89-7.88 (m, 1H), 7.70-7.68 (m, 2H), 6.34 (s, 1H), 5.58 (s, 1H), 4.06 (q, $J = 7.2$ Hz, 2H), 3.80 (t, $J = 5.2$ Hz, 1H), 3.58-3.49 (m, 2H), 3.30 (tt, $J = 5.2, 4.9$ Hz, 1H), 2.92 (td, $J = 11.9, 3.1$ Hz, 1H), 2.58 (d, $J = 18.5$ Hz, 1H), 2.41-2.21 (m, 3H), 1.70 (s, 3H), 1.20 (t, $J = 7.2$ Hz, 3H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) 198.0, 196.3, 167.2, 166.0, 144.9, 136.0, 134.5, 134.1, 134.0,

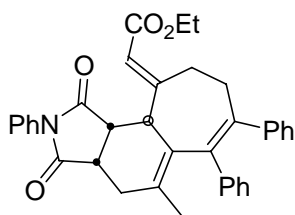
132.9, 130.5, 127.5, 126.8, 126.6, 116.3, 59.4, 55.0, 49.9, 48.5, 34.1, 32.3, 30.6, 20.2, 14.3, -1.8; IR (KBr) 2952, 1713, 1692, 1631, 1594, 1449, 1376, 1285, 1251, 1205, 1165, 1047, 967, 836 cm^{-1} . Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{O}_4\text{Si}$: C, 72.28; H, 7.19. Found: C, 72.05; H, 7.17.



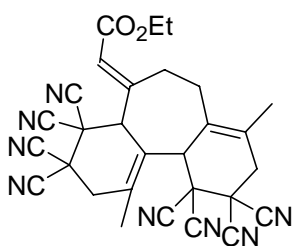
13b: purified by silica gel column chromatography (hexane/AcOEt 10:1); colorless solid; mp 133-134 °C; ^1H NMR (300 MHz, CDCl_3) 6.34 (s, 1H), 6.17 (s, 1H), 4.21 (qd, $J = 7.2, 3.2$ Hz, 2H), 3.97 (s, 1H), 3.82 (m, 2H), 3.64-3.59 (m, 1H), 3.26 (d, $J = 18.0$ Hz, 1H), 3.17 (d, $J = 18.0$ Hz, 1H), 2.67-2.46 (m, 3H), 1.62 (tt, $J = 7.3, 6.6$ Hz, 2H), 1.40 (qt, $J = 7.3, 7.3$ Hz, 2H), 1.30 (t, $J = 7.2$ Hz, 3H), 0.92 (t, $J = 7.3$ Hz, 3H), 0.06 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) 164.6, 152.8, 148.4, 144.0, 127.8, 124.1, 113.6, 110.5, 110.4, 110.1, 108.7, 70.8, 60.7, 52.7, 44.1, 39.0, 34.5, 33.3, 31.7, 27.8, 19.0, 14.1, 13.7, -2.1; IR (KBr) 2960, 1718, 1650, 1443, 1379, 1249, 1178, 1039, 835, 748 cm^{-1} . Anal. Calcd for $\text{C}_{26}\text{H}_{32}\text{N}_4\text{O}_3\text{Si}$: C, 65.52; H, 6.77; N, 11.75. Found: C, 65.64; H, 6.79; N, 11.52.



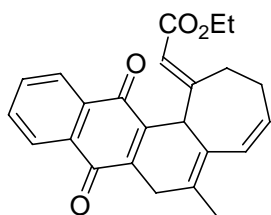
endo-14c: purified by silica gel column chromatography (hexane/AcOEt 2:1); white solid; mp 181-182 °C; ^1H NMR (300 MHz, CDCl_3 at 50 °C) 7.47-6.83 (m, 15H), 6.33 (bs, 1H), 4.13 (q, $J = 7.2$ Hz, 2H), 3.68-3.62 (m, 1H), 3.64 (dd, $J = 9.4, 6.3$ Hz, 1H), 3.38-3.31 (m, 2H), 2.87-2.52 (m, 5H), 1.49 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 at 50 °C) 177.9, 176.6, 166.2, 142.5, 141.7, 141.3, 137.4, 133.8, 132.4, 130.0, 129.5, 129.0, 128.6, 127.9, 127.6, 126.7, 126.4, 125.9, 59.7, 49.2, 44.4, 40.6, 34.7, 30.0, 21.3, 14.2; ^1H NMR (300 MHz, DMSO-d_6 at 90 °C) 7.52-6.87 (m, 15H), 6.46 (bs, 1H), 4.08 (q, $J = 7.2$ Hz, 2H), 3.80-3.71 (m, 1H), 3.77 (d, $J = 6.0$ Hz, 1H), 3.55-3.47 (m, 1H), 3.23-3.11 (m, 1H), 2.80-2.92 (1H, overlap), 2.67-2.53 (m, 4H), 1.43 (s, 3H), 1.18 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6 at 90 °C) 177.5, 176.3, 165.3, 141.8, 141.1, 139.8, 136.4, 132.5, 132.2, 129.1, 128.5, 128.2, 127.6, 127.1, 126.6, 126.1, 125.6, 125.1, 119.2, 58.6, 47.7, 43.8, 33.3, 30.1, 28.6, 20.2, 13.4; IR (KBr) 2933, 1707, 1498, 1378, 1234, 1165, 702, 691 cm^{-1} . Anal. Calcd for $\text{C}_{36}\text{H}_{33}\text{NO}_4$: C, 79.53; H, 6.12; N, 2.58. Found: C, 79.48; H, 6.18; N, 2.54.



exo-14c: purified by silica gel column chromatography (hexane/AcOEt 2:1); white solid; mp 245 °C; ^1H NMR (300 MHz, CDCl_3) 7.53-6.72 (m, 15H), 5.68(s, 1H), 4.21-4.16 (m, 1H), 4.17 (q, $J = 7.2$ Hz, 2H), 3.64 (dd, $J = 9.4, 2.1$ Hz, 1H), 3.42-3.33 (m, 2H), 3.19-3.11 (m, 1H), 2.86-2.67 (m, 2H), 2.56-2.54 (m, 2H), 1.34 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) 190.7, 178.6, 166.2, 160.8, 143.3, 142.1, 141.7, 139.6, 134.5, 133.3, 131.9, 129.8, 129.6, 129.2, 128.8, 127.8, 127.6, 126.4, 126.3, 125.9, 112.7, 60.1, 48.8, 41.7, 38.7, 36.3, 30.7, 29.0, 21.5, 14.3; IR (KBr) 2903, 1711, 1637, 1497, 1283, 1195, 1165, 1138, 1043, 745, 700 cm^{-1} . Anal. Calcd for $\text{C}_{36}\text{H}_{33}\text{NO}_4$: C, 79.53; H, 6.12; N, 2.58. Found: C, 79.63; H, 6.15; N, 2.58.



15b: purified by silica gel column chromatography (hexane/AcOEt 1:1); white solid; mp 247 °C (decomp.); ^1H NMR (300 MHz, CDCl_3) 6.30 (s, 2H), 4.63 (s, 1H), 4.39 (s, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 4.08-3.97 (m, 1H), 3.45-3.20 (m, 3H), 2.97-2.84 (m, 2H), 2.65-2.57 (m, 1H), 2.21 (s, 3H), 2.21-2.06 (m, 1H), 1.82 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) 164.5, 145.7, 137.9, 130.4, 125.9, 124.8, 121.9, 110.4, 110.3, 110.2, 110.2, 109.9, 109.8, 109.4, 109.4, 61.2, 51.5, 47.8, 44.3, 42.1, 39.4, 38.5, 38.2, 37.2, 25.4, 23.4, 21.5, 18.8, 14.1; IR (KBr) 2964, 1718, 1647, 1438, 1384, 1257, 1227, 1189, 1032 cm^{-1} . Anal. Calcd for $\text{C}_{29}\text{H}_{22}\text{N}_8\text{O}_2$: C, 67.69; H, 4.31; N, 21.78. Found: C, 67.61; H, 4.44; N, 21.71. The coupling product (**15b**) was isolated as a single isomer, but the stereochemistry has not been determined.



16d: purified by silica gel column chromatography (hexane/AcOEt 10:1); red solid; mp 162-163 °C; ^1H NMR (300 MHz, CDCl_3) 8.13-8.11 (m, 1H), 8.05-8.01 (m, 1H), 7.75-7.68 (m, 2H), 6.38 (d, $J = 11.5$ Hz, 1H), 5.88 (dt, $J = 11.5, 3.9$ Hz, 1H), 5.26 (s, 1H), 4.94 (s, 1H), 4.02 (q, $J = 7.2$ Hz, 2H), 3.46-3.09 (m, 4H), 3.05-2.88 (m, 1H), 2.41-2.29 (m, 1H), 1.85 (s, 3H), 1.16 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) 184.0, 183.1, 166.4, 164.4, 143.5, 142.9, 133.8, 133.7, 132.1, 132.0, 130.7, 128.1, 127.3, 126.7, 126.5, 126.4, 113.4, 59.7, 43.2, 33.3, 31.2, 25.2, 18.7, 14.2; IR (KBr) 3444, 1705, 1659, 1631, 1591, 1331, 1294, 1216, 1175, 1142 cm^{-1} . HR-MS (EI) Calcd for $\text{C}_{24}\text{H}_{22}\text{O}_4$: 374.1518. Found: 374.1518.

References

- (1) Kortmann, I.; Westermann, B. *Synthesis*. **1995**, 931-933.
- (2) Gevorgyan, V.; Takeda, A.; Homma, M.; Sadayori, N.; Radhakrishnan, U.; Yamamoto, Y. *J. Am. Chem. Soc.* **1999**, *121*, 6391-6402.
- (3) Iso, Y.; Grajkowska, E.; Wroblewski, J. T.; Davis, J.; Goeders, N. E.; Johnson, K. M.; Sanker, S.; Roth, B. L.; Tueckmantel, W.; Kozikowski, A. P. *J. Med. Chem.* **2006**, *49*, 1080-1100.
- (4) Schwab, J. M.; Lin, D. C. T. *J. Am. Chem. Soc.* **1985**, *107*, 6046-6052.
- (5) Ager, D. J. *Synthesis*, **1984**, 384-398.
- (6) Ren, H.; Krasovskiy, A.; Knochel, P. *Org. Lett.* **2004**, *6*, 4215-4217.
- (7) Negishi, E.; Kitora, M.; Xu, C. *J. Org. Chem.* **1997**, *62*, 8957-8960.
- (8) Saito, S.; Kawasaki, T.; Tsuboya, N.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 796-802.
- (9) Ishihara, T.; Kuroboshi, M.; Okada, Y. *Chem. Lett.* **1986**, 1895-1896.
- (10) Miller, K. M.; Luanphaisarnnant, T.; Molinaro, C.; Jamison, T. F. *J. Am. Chem. Soc.* **2004**, *126*, 4130-4131.
- (11) Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1990**, *112*, 3949-3954.

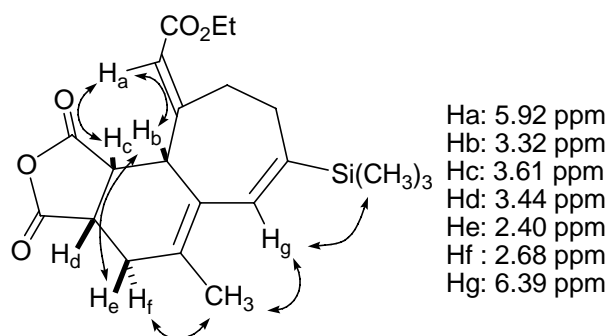


Figure S1. A NOESY experiment of **12a**.

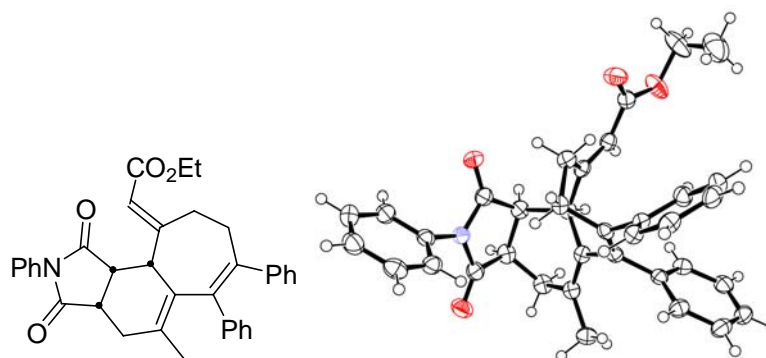


Figure S2. An ORTEP view of *endo*-**14c**. Crystal data for *endo*-**14c**: $C_{36}H_{33}NO_4$; $M = 543.63 \text{ g mol}^{-1}$, monoclinic, $P2_1/c$, colorless prism measuring $0.40 \times 0.30 \times 0.30 \text{ mm}$, $T = 150 \text{ K}$, $a = 11.818 (1)$, $b = 8.5654(7)$, $c = 28.864(3) \text{ \AA}$, $\beta = 101.646(1)^\circ$, $V = 2861.5 (4) \text{ \AA}^3$, $Z = 4$, $D_c = 1.262 \text{ Mg m}^{-3}$, $\mu(\text{CuK}\alpha) = 0.082 \text{ mm}^{-1}$, $T_{\text{max}} = 0.9759$, $T_{\text{min}} = 0.9681$, $GOF \text{ on } F^2 = 1.080$, $R_1 = 0.0469$, $wR_2 = 0.1213 [I > 2\sigma(I)]$, $R_1 = 0.0641$, and $wR_2 = 0.1324$ (all data).

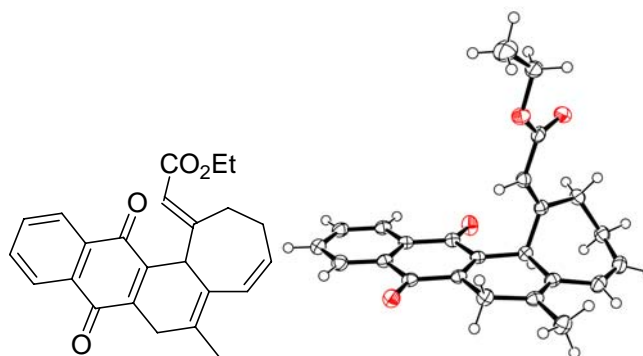
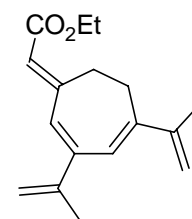


Figure S3. An ORTEP view of **16d**. Crystal data for **16d**: $C_{24}H_{22}O_4$; $M = 374.42 \text{ g mol}^{-1}$, monoclinic, $P2_1/n$, colorless prism measuring $0.30 \times 0.10 \times 0.10 \text{ mm}$, $T = 120 \text{ K}$, $a = 8.319(3)$, $b = 15.649(5)$, $c = 14.325(4) \text{ \AA}$, $\beta = 93.669(2)^\circ$, $V = 1861(1) \text{ \AA}^3$, $Z = 4$, $D_c = 1.336 \text{ Mg m}^{-3}$, $\mu(\text{CuK}\alpha) = 0.090 \text{ mm}^{-1}$, $T_{\text{max}} = 0.9910$, $T_{\text{min}} = 0.9734$, $GOF \text{ on } F^2 = 0.821$, $R_1 = 0.0419$, $wR_2 = 0.1197 [I > 2\sigma(I)]$, $R_1 = 0.0603$, and $wR_2 = 0.1382$ (all data).

¹H NMR spectrum of 3a



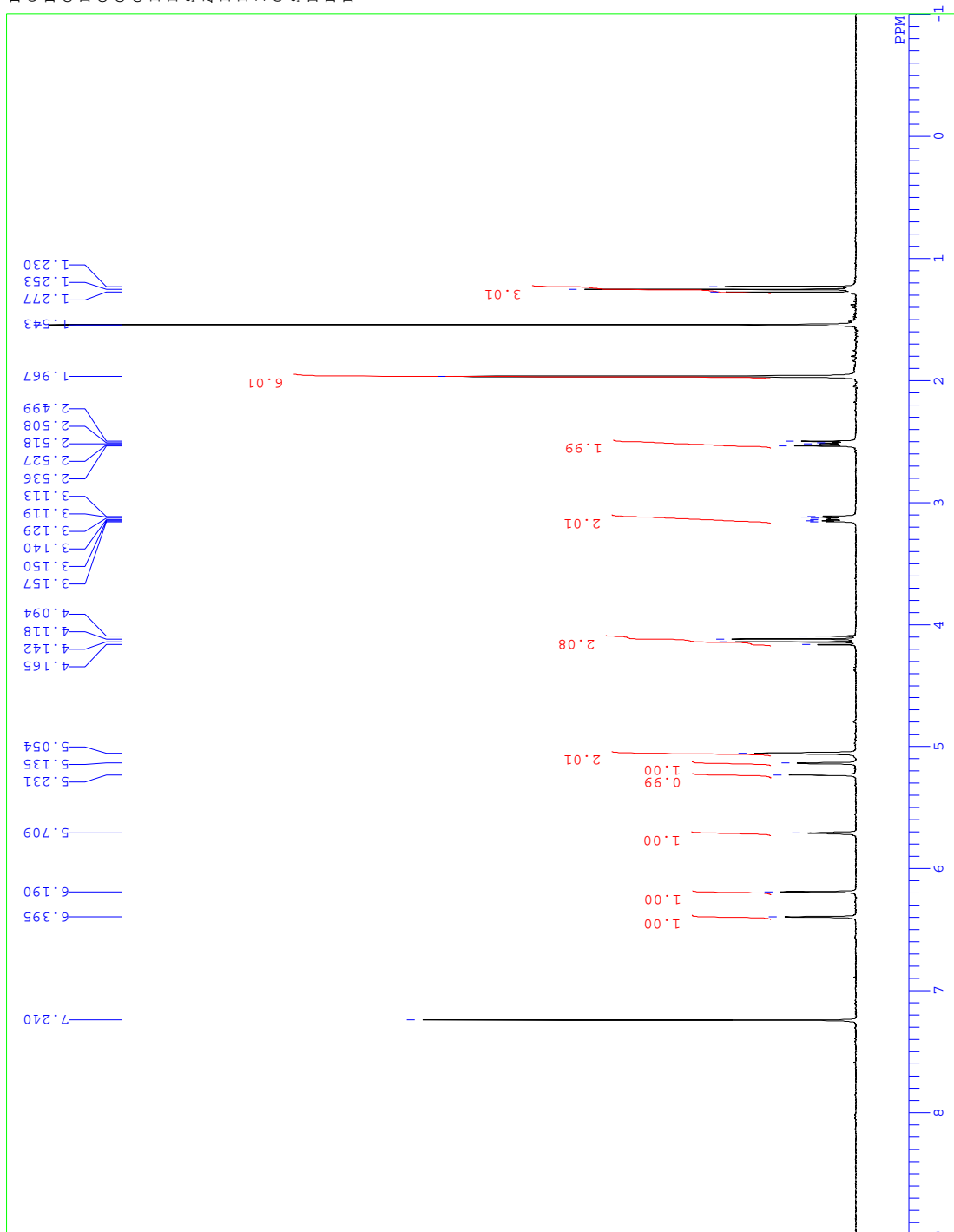
Z:\koma\nmrdata\SK14-01-4.als

Z:\koma\nmrdata\SK14-01-4.als

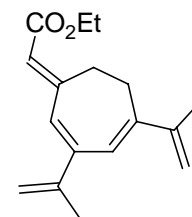
DFILE
COMNT
DATIM
OENUC
EXMOD
OBFRO
OBSER
OBFIN
POINT
FREQU
SCANS
AQUTM
PD
PWL
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

1H

300.01 MHz
1.85 KHz
2.7 Hz
32768
6172.8 Hz
8
0.000 sec
0.000 sec
10.0 us
0.0 C
7.24 ppm
1.20 Hz
0

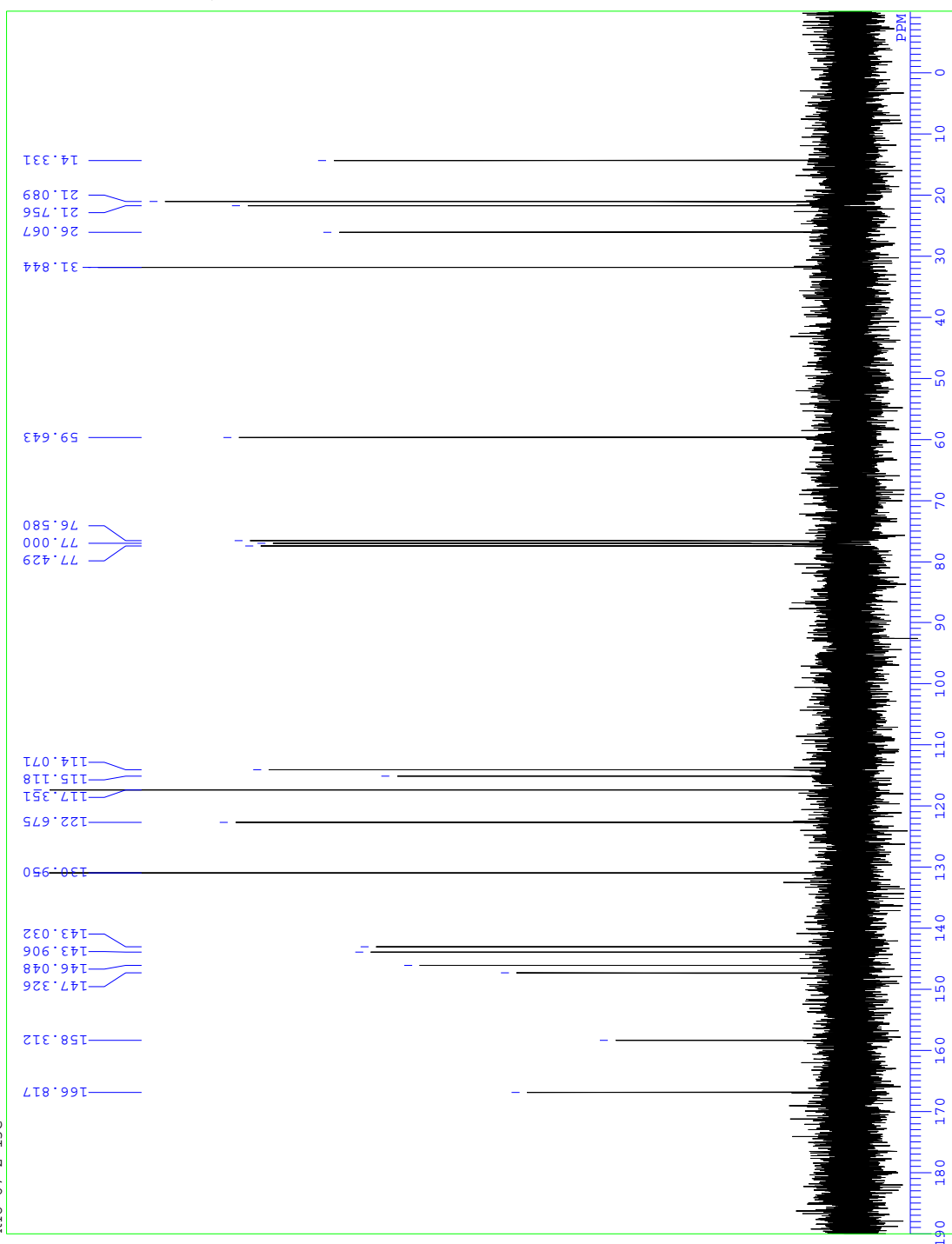


¹³C NMR spectrum of 3a

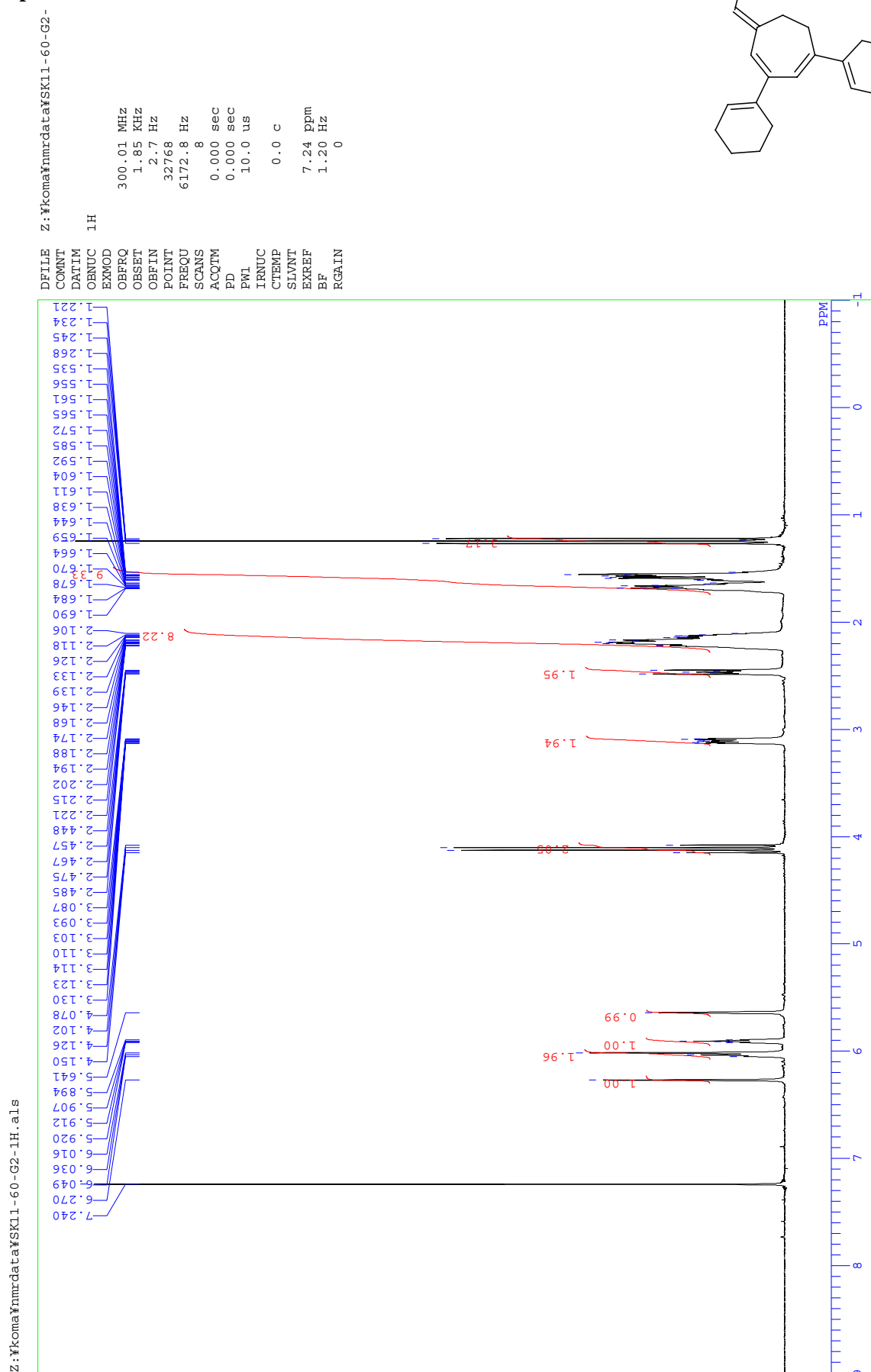
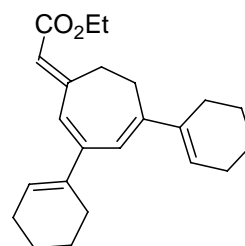


Z:\koma\nmrdata\KT8-67-2 13C.als
KT8-67-2 13C

DFILE Z:\koma\nmrdata\KT8-67-2 13
 COMNT KT8-67-2 13C
 DATIM Wed Feb 01 18:17:51 2006
 OBNUC 13C
 EXMOD BCM
 OBFREQ 75.45 MHz
 OBSSET 124.00 KHz
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 150
 ACQTM 1.606 sec
 PD 1.394 sec
 PWL 4.1 us
 IRNUC 1H
 CTEMP 19.9 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 22

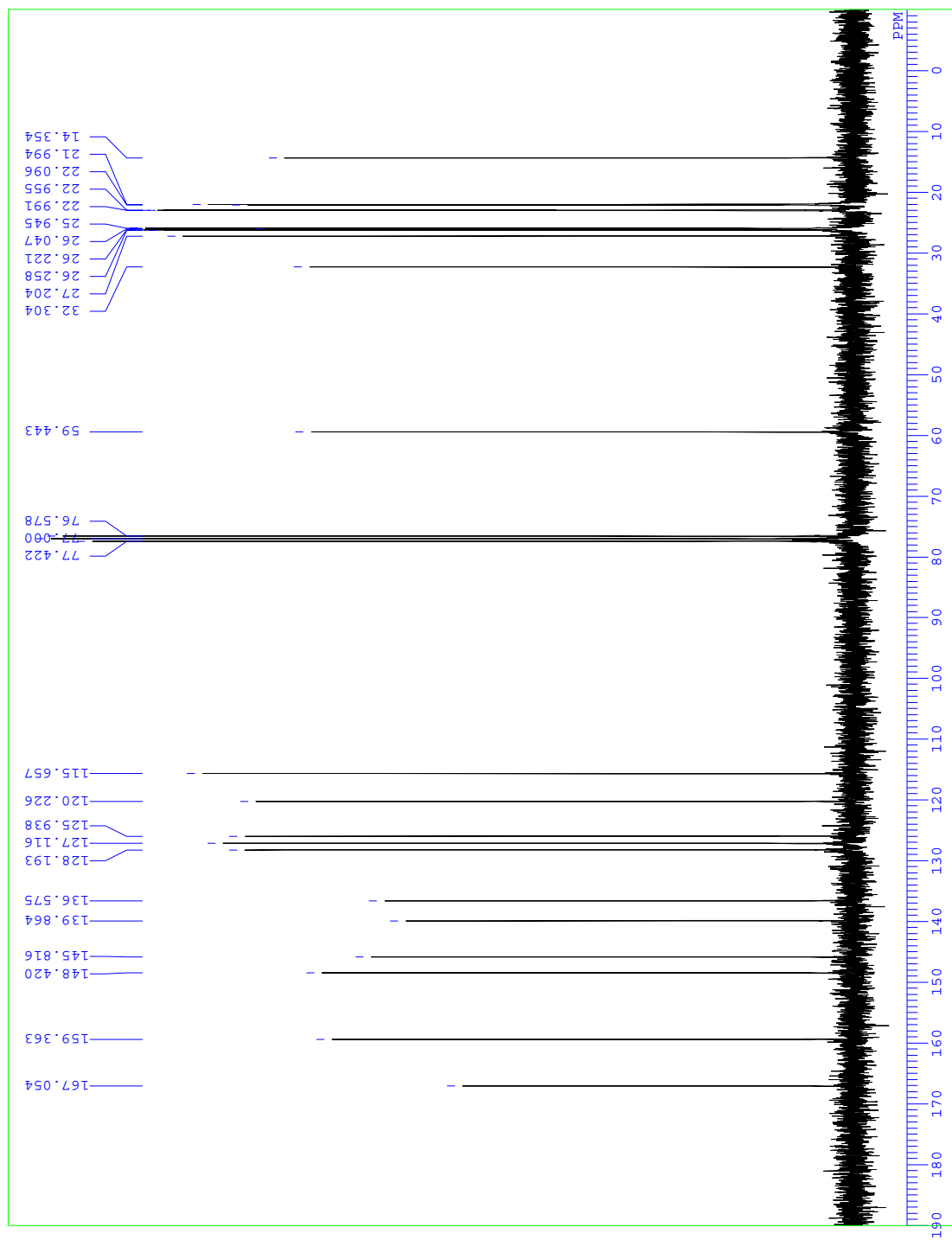


¹H NMR spectrum of 3b



¹³C NMR spectrum of 3b

Z:\koma\nmrdata\SK11-60-3-13C.als

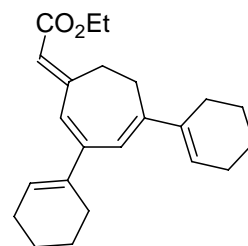


Z:\koma\nmrdata\SK11-60-3-1

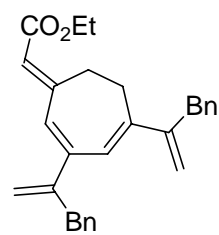
COMET
DATIM
OENUC
EXMOD
OEFRO
OBSER
OBFIN
POINT
FREQU
SCANS
AQTM
PD
PWL
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

13C

75.44 MHz
5.11 KHz
8.3 Hz
32768
17985.6 Hz
8
0.000 sec
0.000 sec
10.0 us
0.0 C
77.00 ppm
1.20 Hz
0



¹H NMR spectrum of 3c

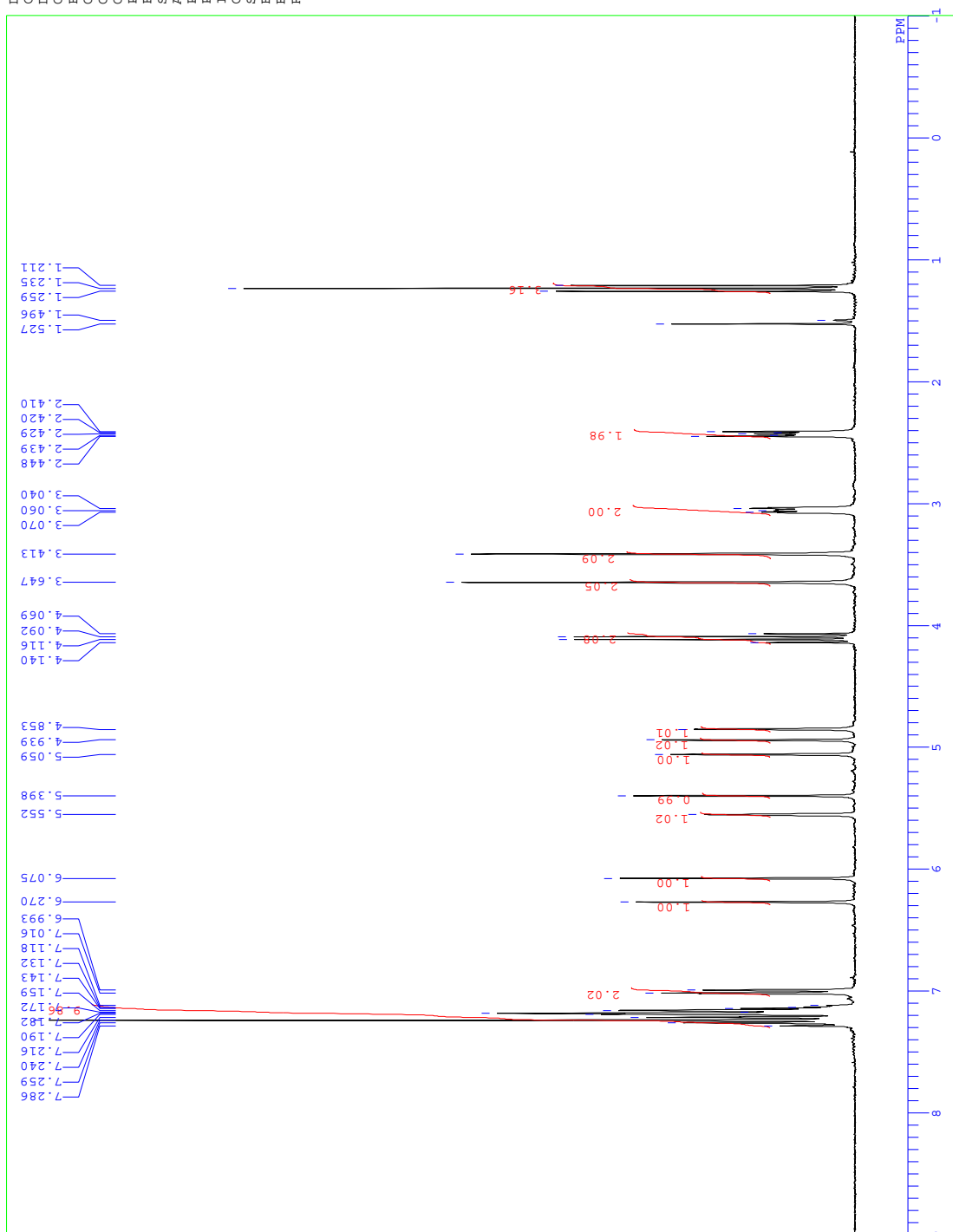


L:\Koma\nmrdata\SK13-47-4-1H.a:

DEFILE
COMNT
DATIM
ORNUC
EXMOD
OEFRO
OBSFI
OEFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

1H
300.01 MHz
1.85 KHz
2.7 Hz
32768
6172.8 Hz
8
0.000 sec
0.000 sec
10.0 us
0.0 C
7.24 ppm
0.12 Hz
0

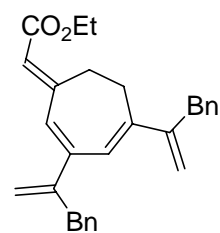
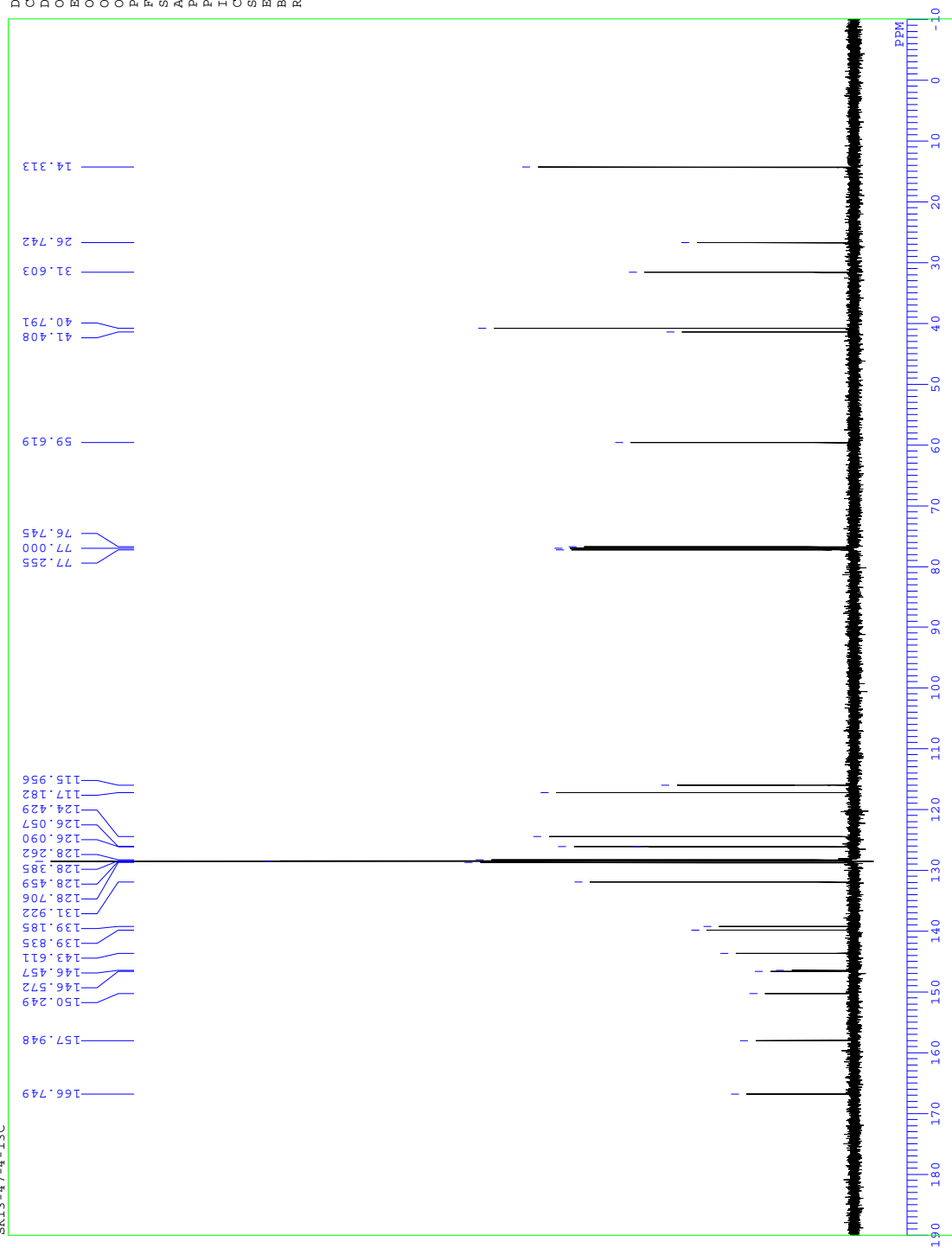
L:\Koma\nmrdata\SK13-47-4-1H.als



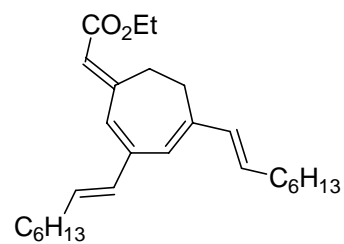
¹³C NMR spectrum of 3c

E:\SK13-47-4-13C.ALS
SK13-47-4-13C

DFILE E:\SK13-47-4-13C.ALS
COMNT SK13-47-4-13C
DATIM Mon Apr 07 16:07:12 2008
ORNUC 13C
EXMOD bcm
OBFRO 125.65 MHz
OBSEI 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 542
ACQTM 0.967 sec
PD 2.033 sec
PW1 5.1 us
IRNUC 1H
CTEMP 26.3 C
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 31

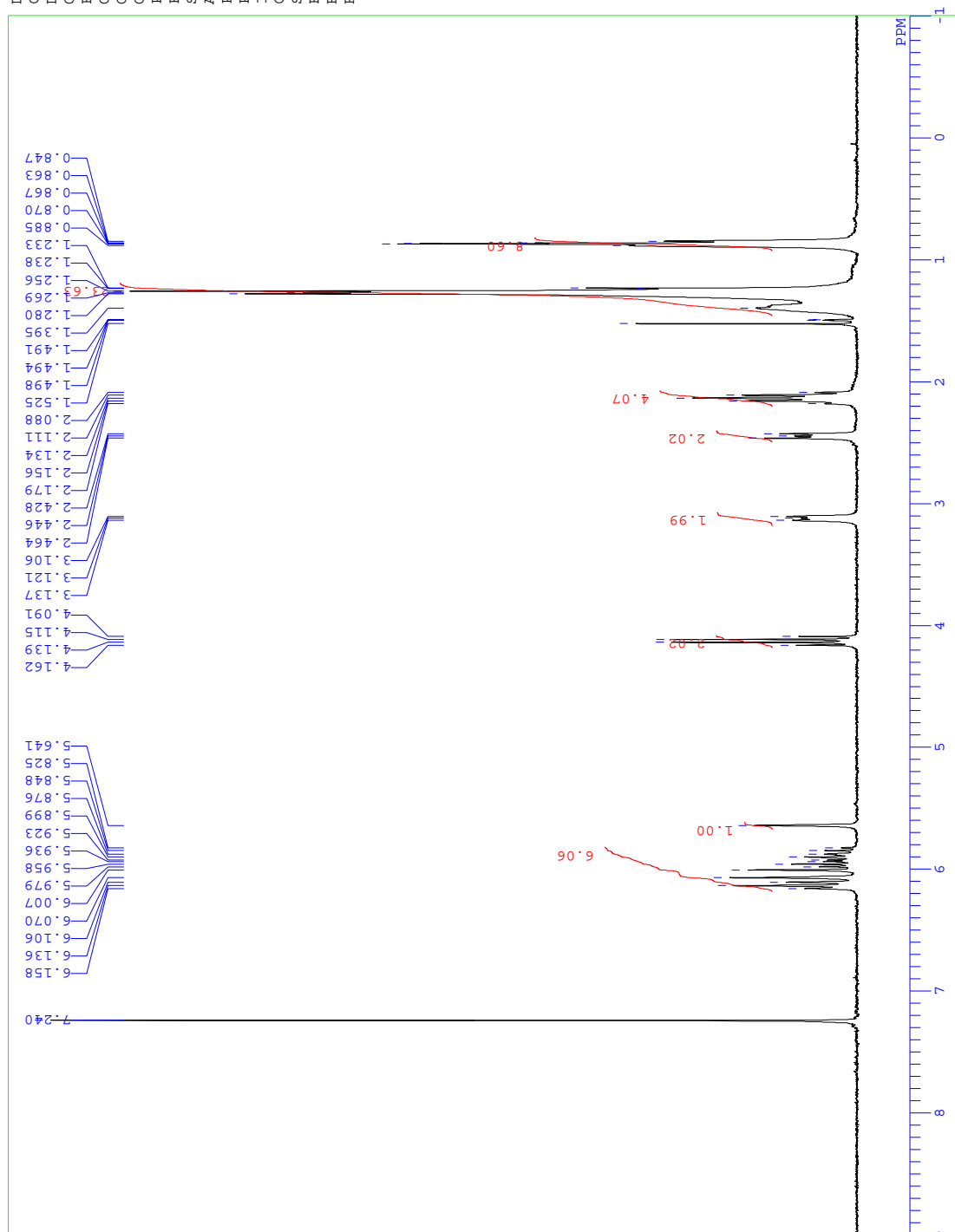


¹H NMR spectrum of 3d



DFILE L:\koma\nmrdata\SK13-37-2-1
 COMNT 1H
 DATIM
 OENUC 300.01 MHz
 EXMOD 1.85 KHz
 OBFREQ 2.7 Hz
 OBFIN 32768
 POINT 6172.8 Hz
 FREQU 8
 SCANS 0.000 sec
 ACQTM 0.000 sec
 PD 10.0 us
 PULP 0.0 c
 IRNUC 7.24 ppm
 CTEMP 1.20 Hz
 SLVNT
 EXREF
 BF 0
 RGAIN

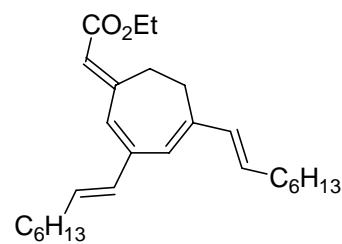
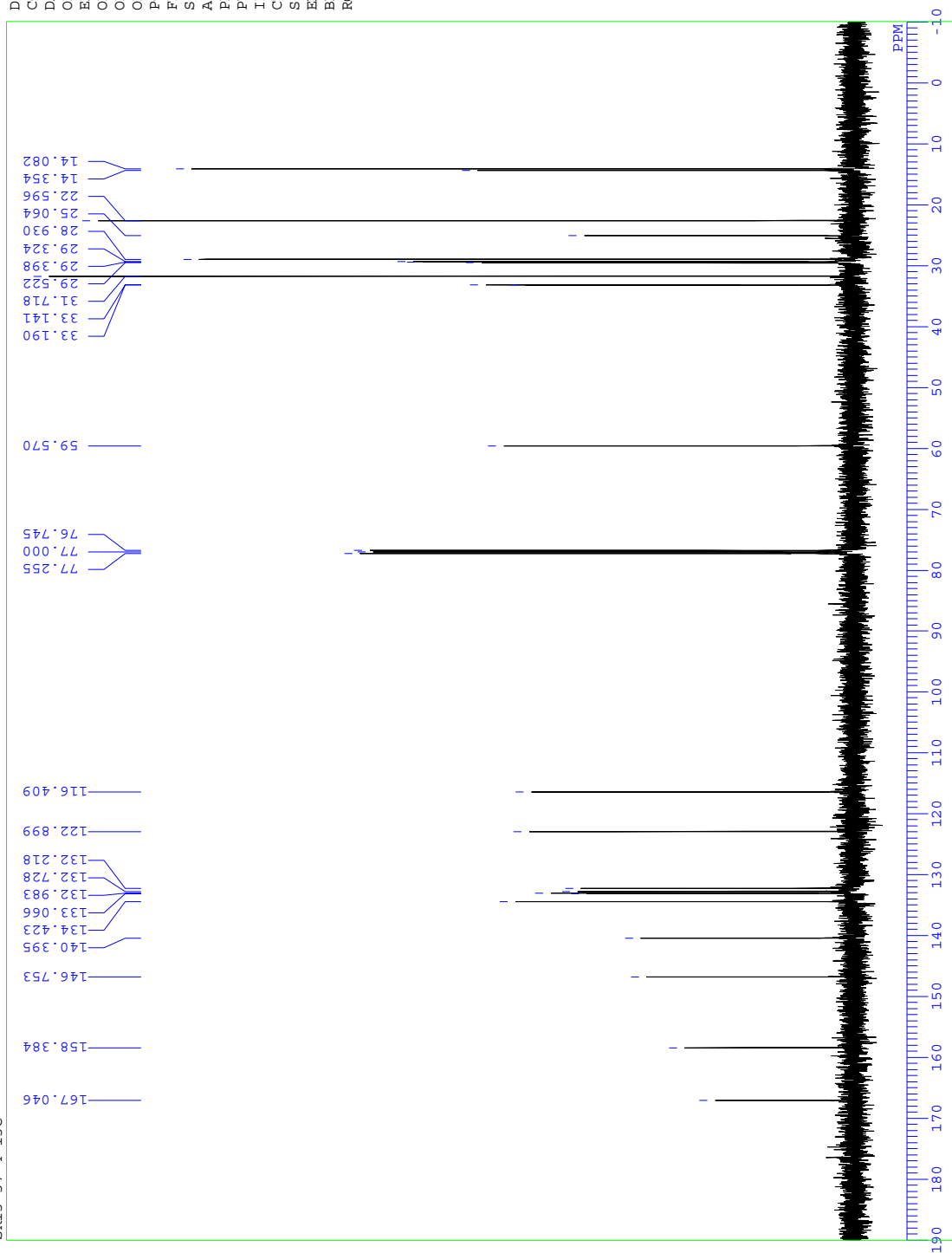
L:\koma\nmrdata\SK13-37-2-1H.als



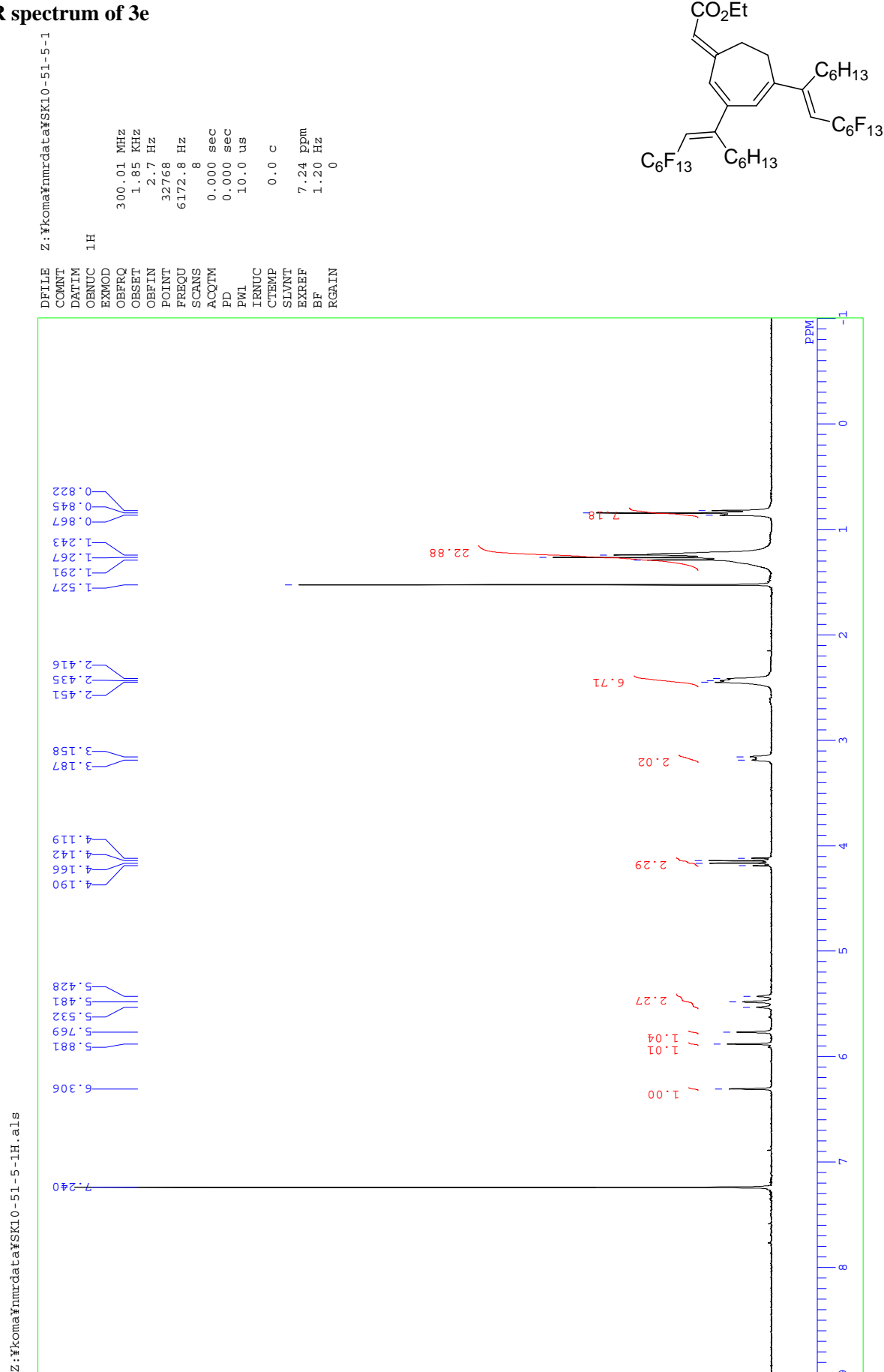
¹³C NMR spectrum of 3d

E:\SK13-37-4-13C.ALS
SK13-37-4-13C

DFILE E:\SK13-37-4-13C.ALS
COMNT SK13-37-4-13C
DATIM Fri Mar 07 14:48:49 2008
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 349
AQTM 0.967 sec
PD 2.033 sec
PWL 5.1 us
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 31



¹H NMR spectrum of 3e

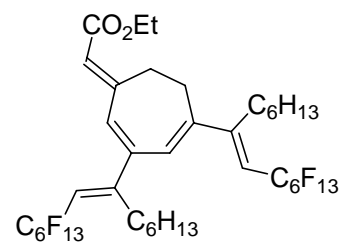
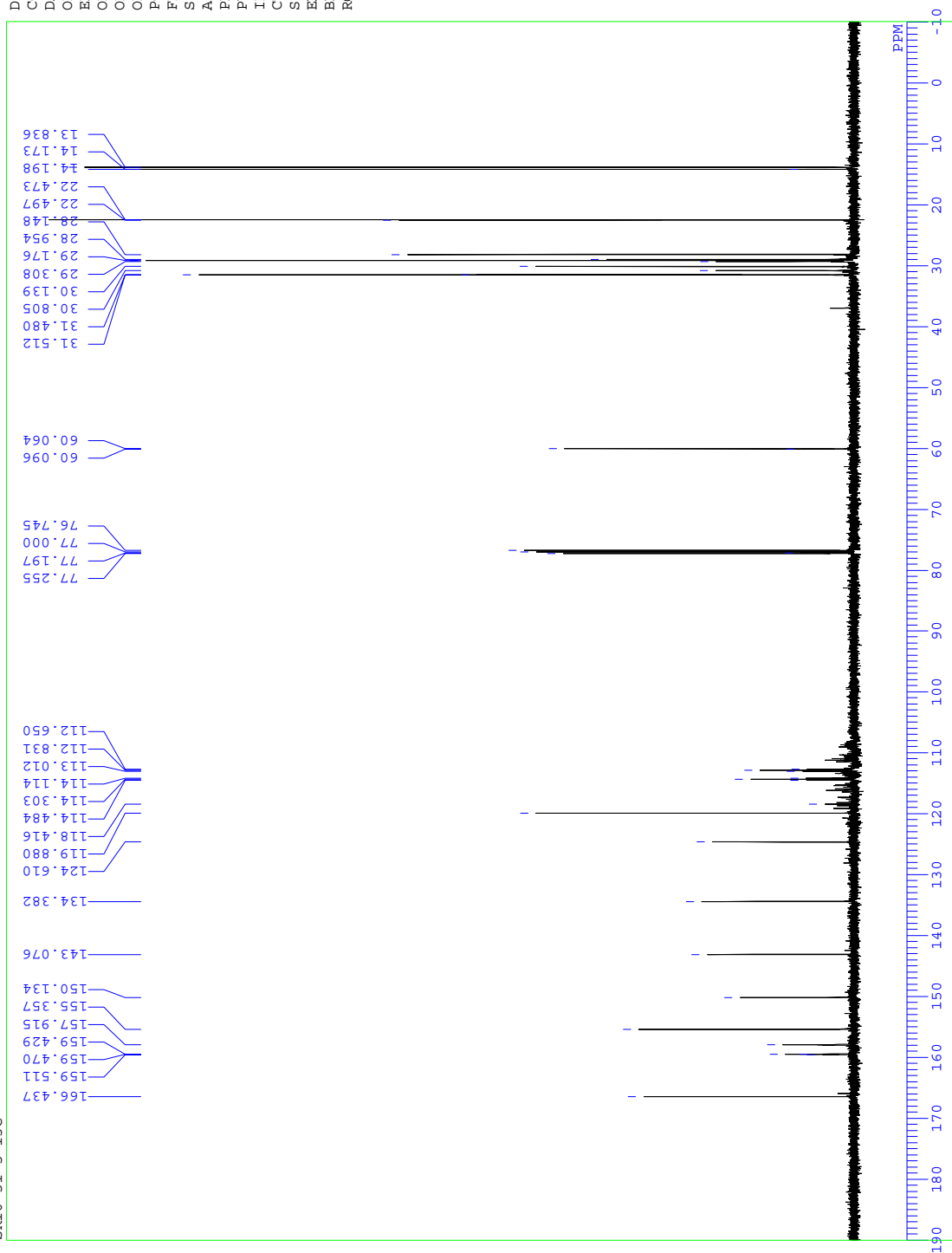


¹³C NMR spectrum of 3e

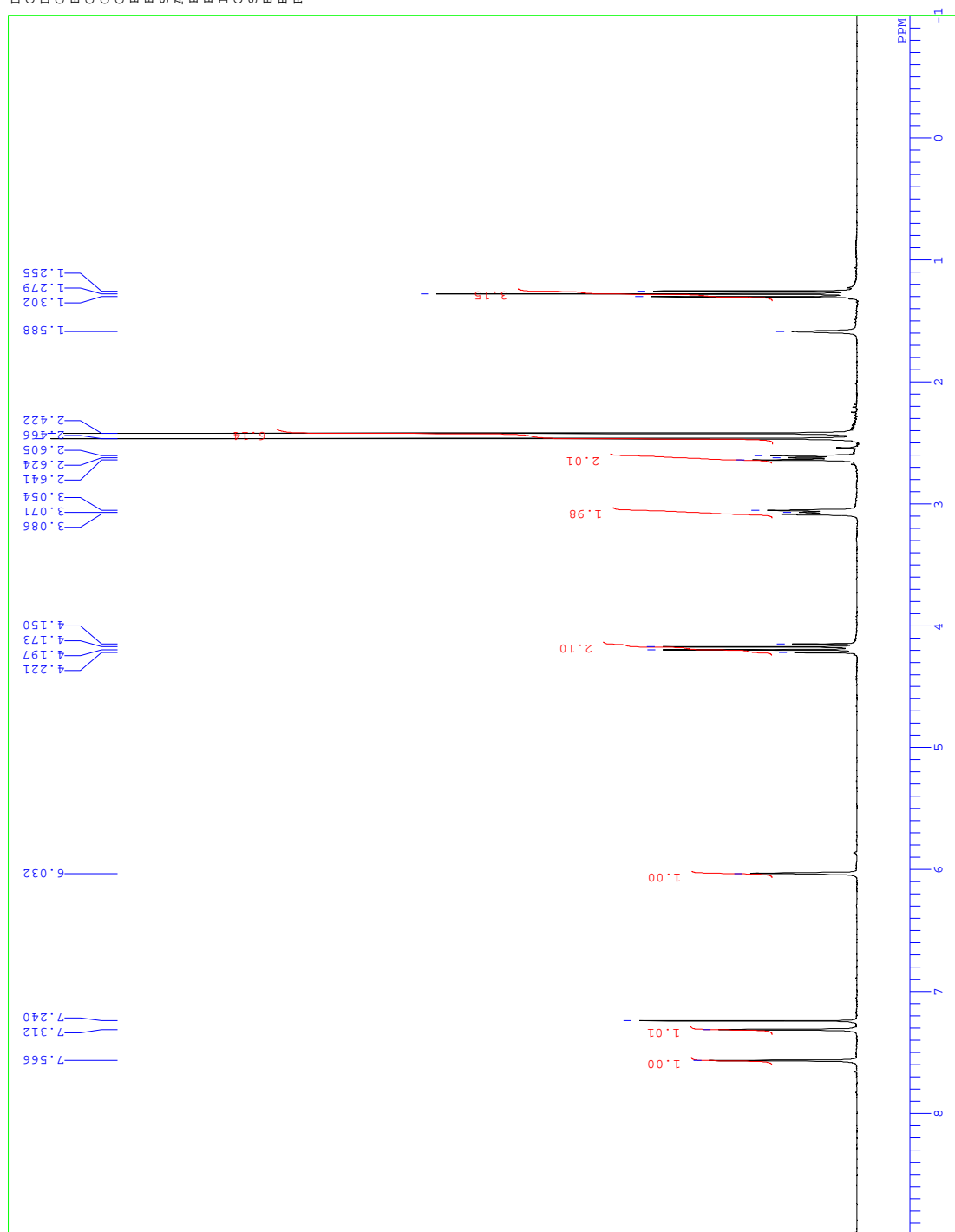
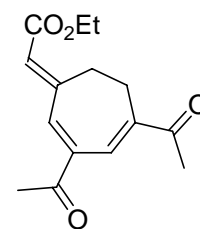
Z:\koma\nmrdata\SK10-51-5-13C.als
SK10-51-5-13C

DFILE
COMNT
DATIM
ORNUC
EXMOD
OBFRO
OBFIN
POINT
FREQU
SCANS
AQUTM
PD
PWL
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

2:\koma\nmrdata\SK10-51-5-1
SK10-51-5-13C
Thu Jan 18 16:44:48 2007
13C
bcm
125.65 MHz
0.00 KHz
127958.0 Hz
32768
33898.3 Hz
812
0.967 sec
2.033 sec
5.1 us
1H
24.7 c
CDCL3
77.00 ppm
1.20 Hz
28



¹H NMR spectrum of 4g

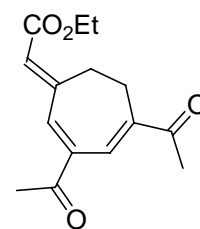


C:\Documents and Settings\admin\My Documents\koma\NMR\SK14-13-7-1H.dx

C:\Documents and Settings\admin\My Documents\koma\NMR\SK14-13-7-1H.dx
 1H

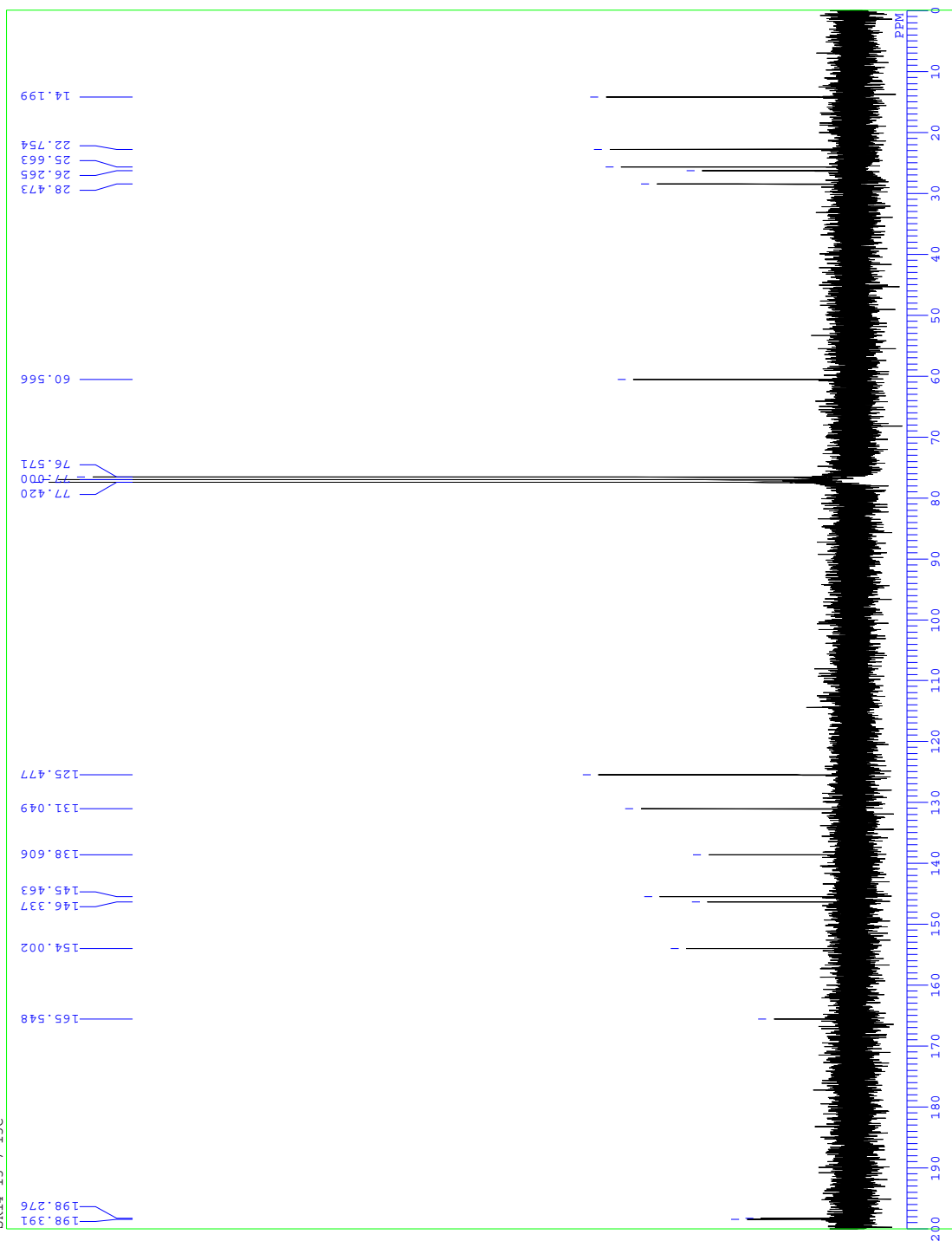
300.01 MHz
 1.85 KHz
 32768
 6172.8 Hz
 8
 0.000 sec
 0.000 sec
 10.0 us
 0.0 C
 7.24 ppm
 0.12 Hz
 0

¹³C NMR spectrum of 4g

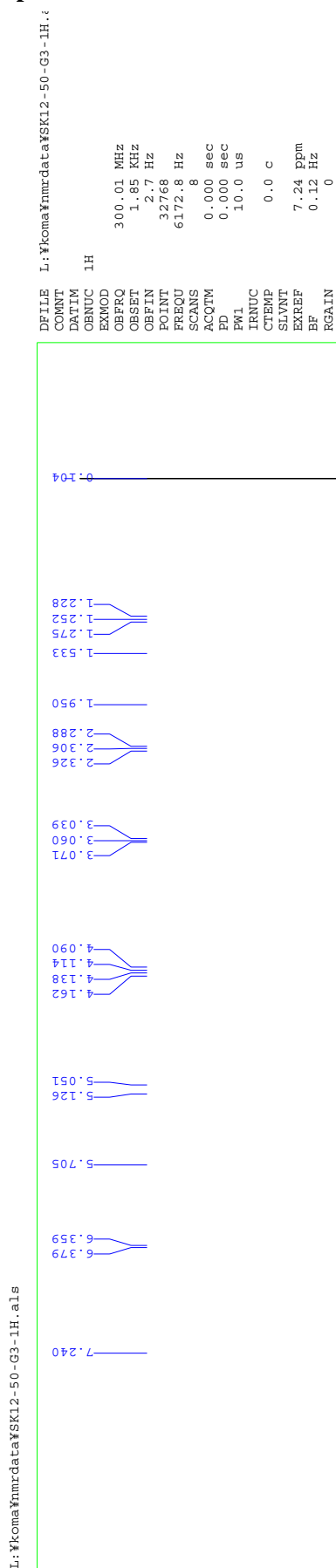
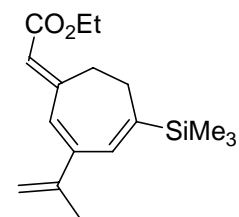


Z:\koma\nmrdata\SK14-13-7-13C.als
SK14-13-7-13C

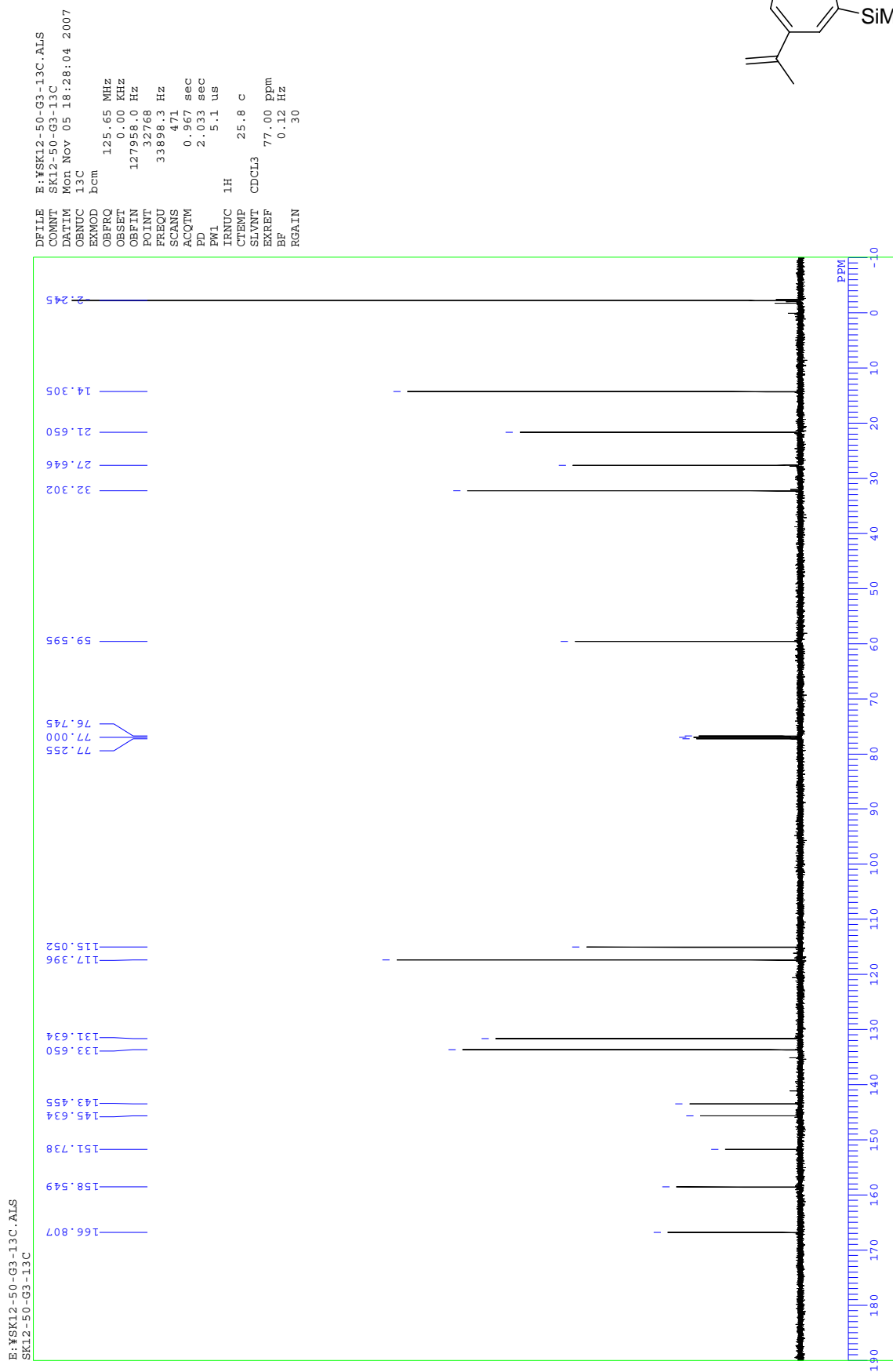
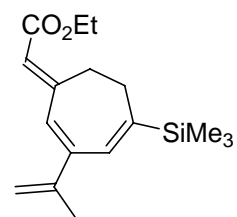
DFILE Z:\koma\nmrdata\SK14-13-7-13C.als
COMNT SK14-13-7-13C
DATIM Sat Aug 02 11:27:58 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 506
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.1 us
IRNUC 1H
CTEMP 22.3 C
SILNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 22



¹H NMR spectrum of 6a



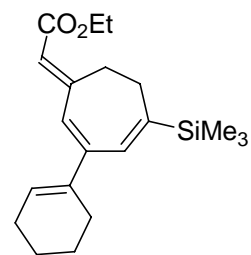
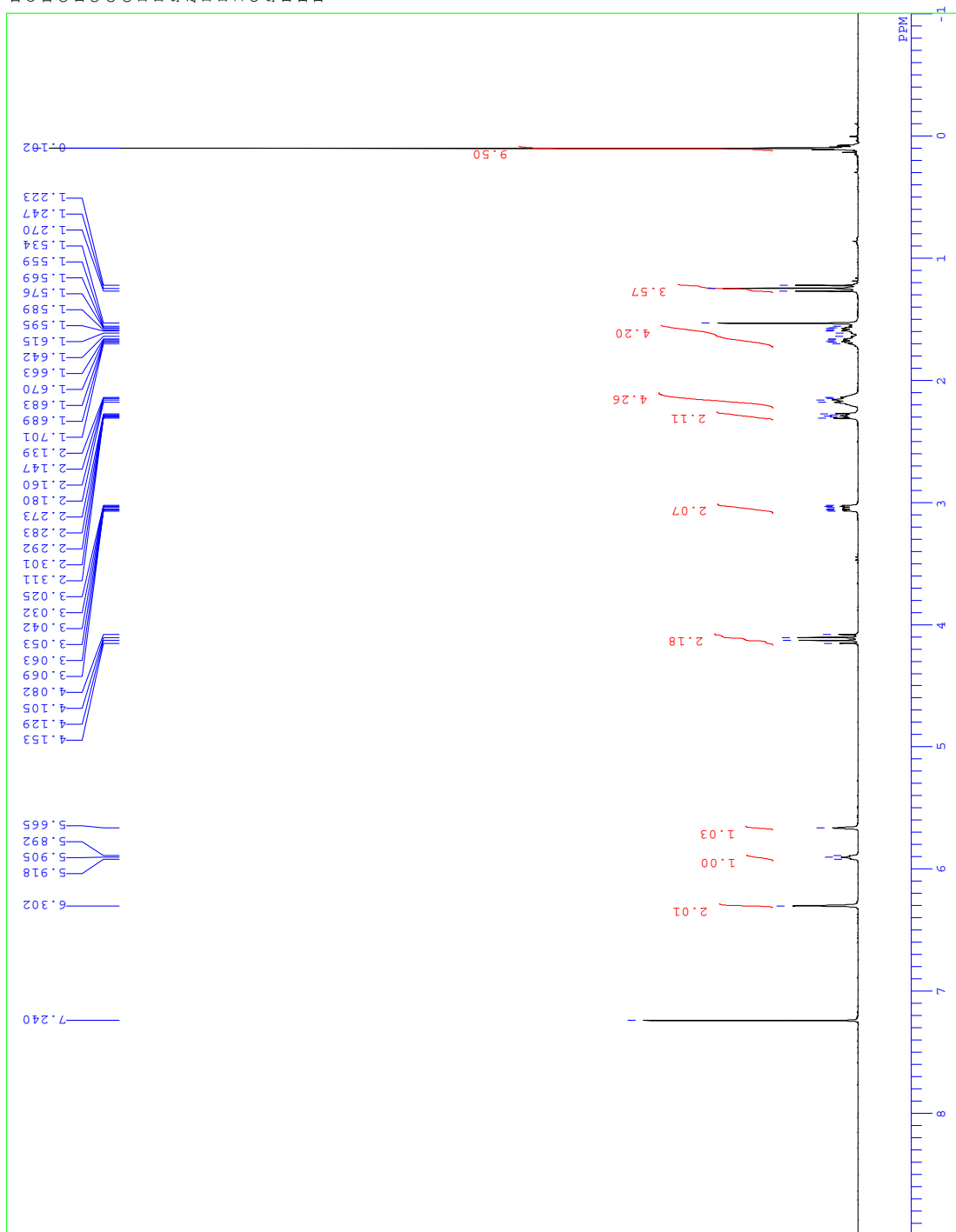
¹³C NMR spectrum of 6a



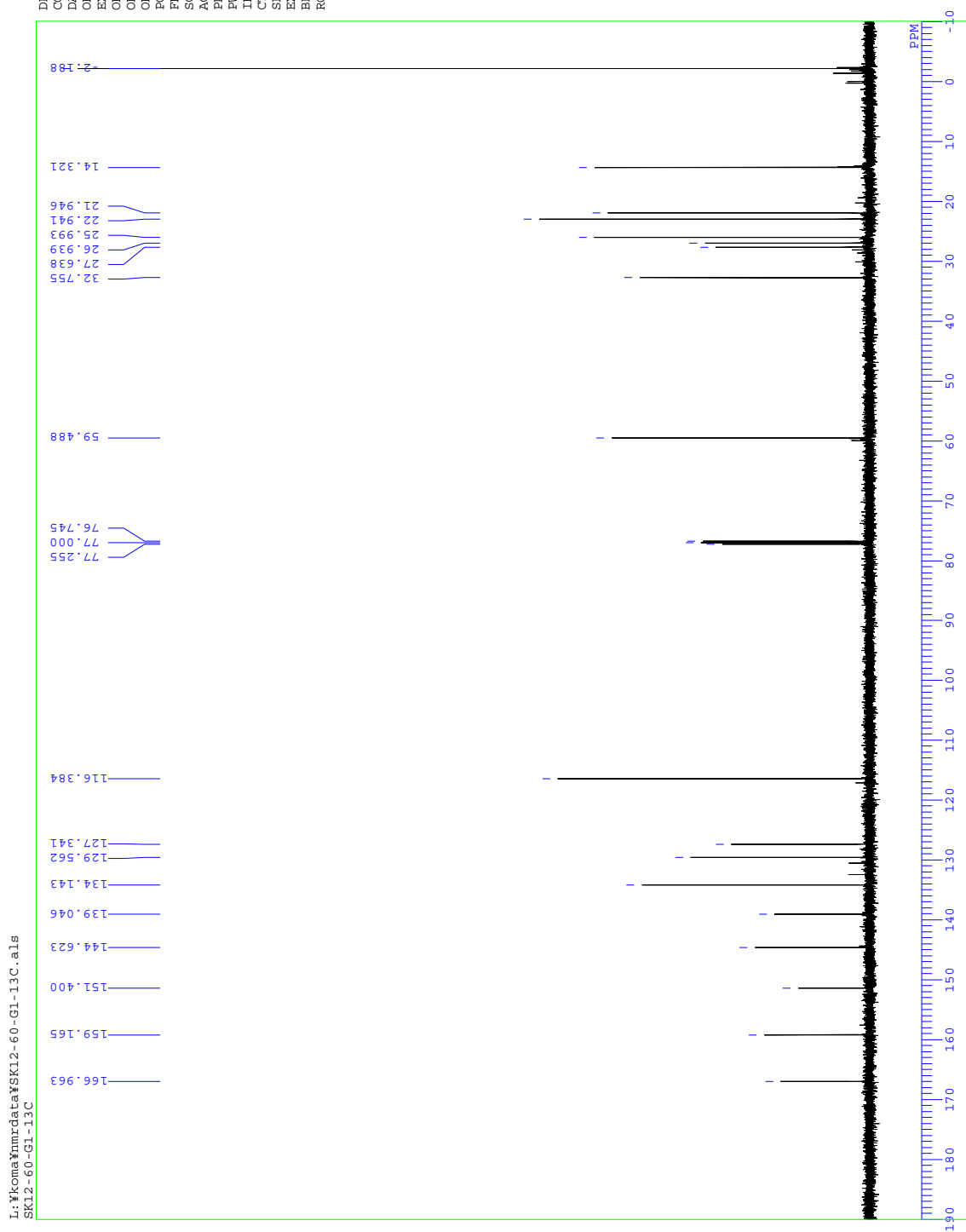
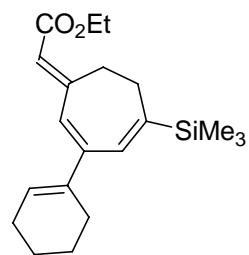
¹H NMR spectrum of 6b

E:\MSK12-60-G1.dxp

DFILE E:\MSK12-60-G1.dxp
 COMNT
 DATIM
 OBNUC 1H
 EXMOD 300.01 MHz
 OBFRQ 1.85 KHz
 OBSET 2.7 Hz
 OFBIN 32768
 POINT 6172.8 Hz
 FREQU 8
 ACQTM 0.000 sec
 PD 0.000 sec
 PW1 10.0 us
 IRNUC 0.0 C
 CTEMP 7.24 ppm
 SLVNT EXREF 0.12 Hz
 BF 0
 RGAIN 0



^{13}C NMR spectrum of 6b



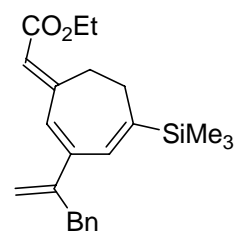
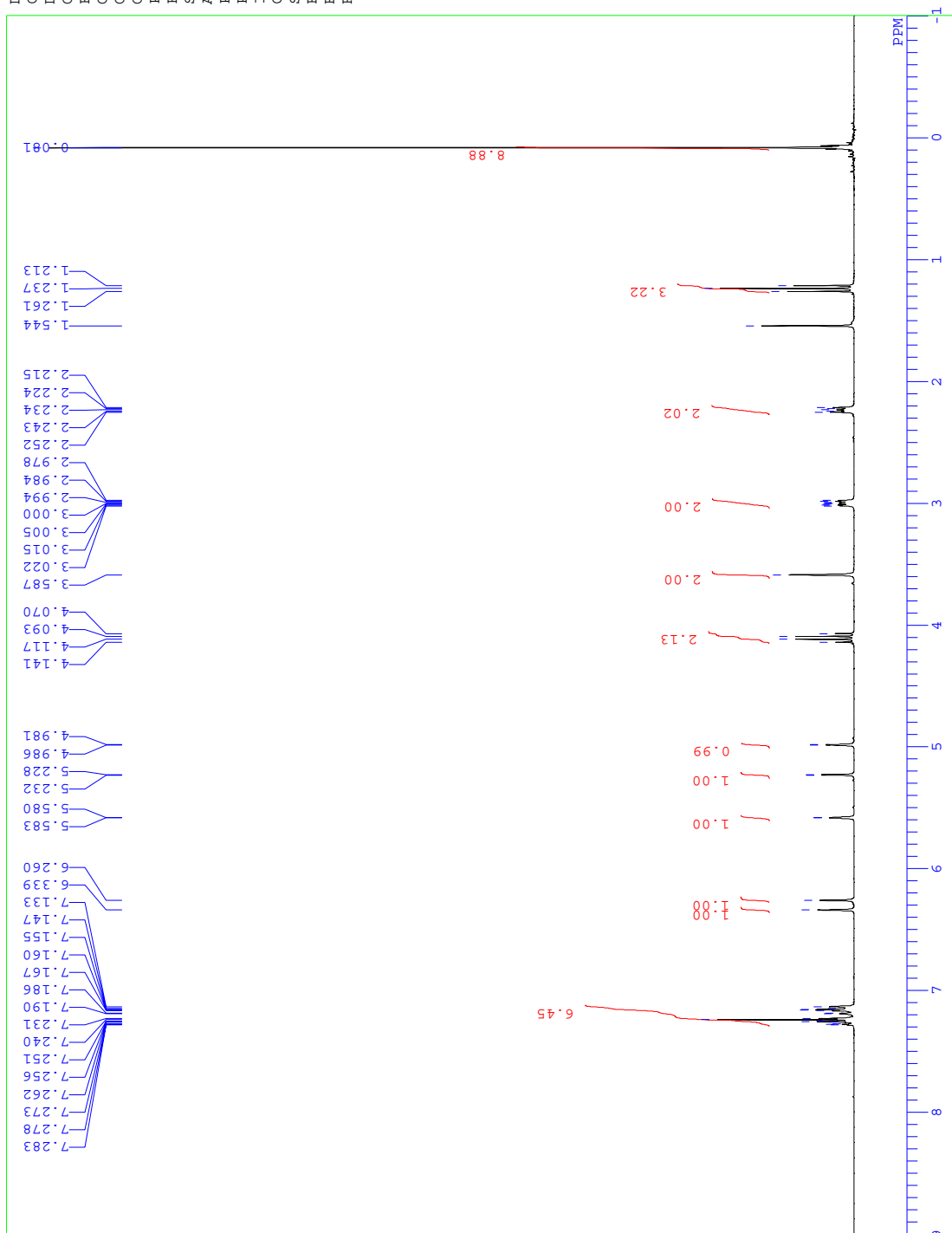
¹H NMR spectrum of 6c

Z:\koma\nmrdata\SK11-47-G1-1H.als

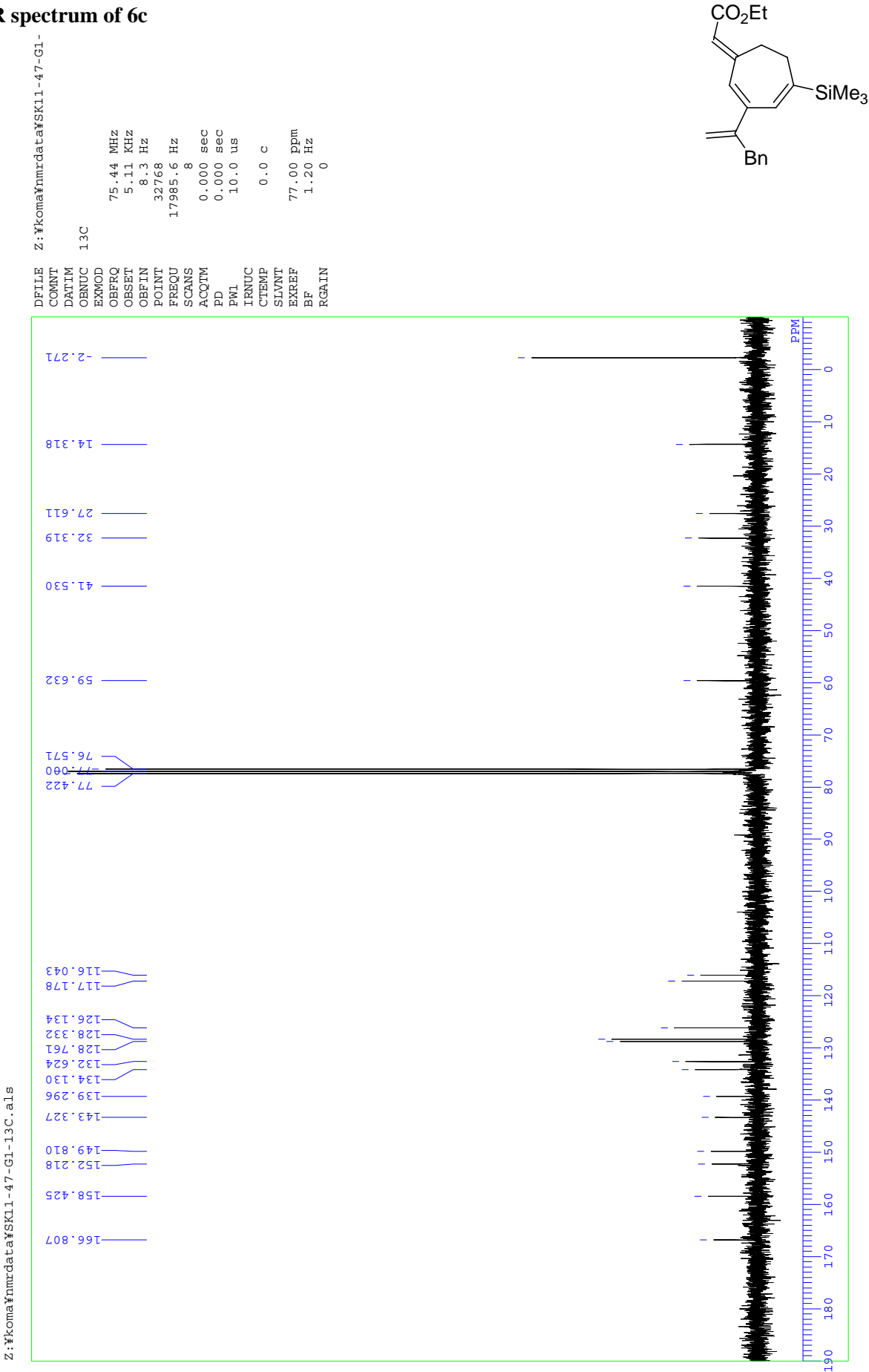
DFILE Z:\koma\nmrdata\SK11-47-G1-
 COMNT
 DATIM
 OENUC
 EXMOD
 OBFREQ
 OBSFET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PWL
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN

1H

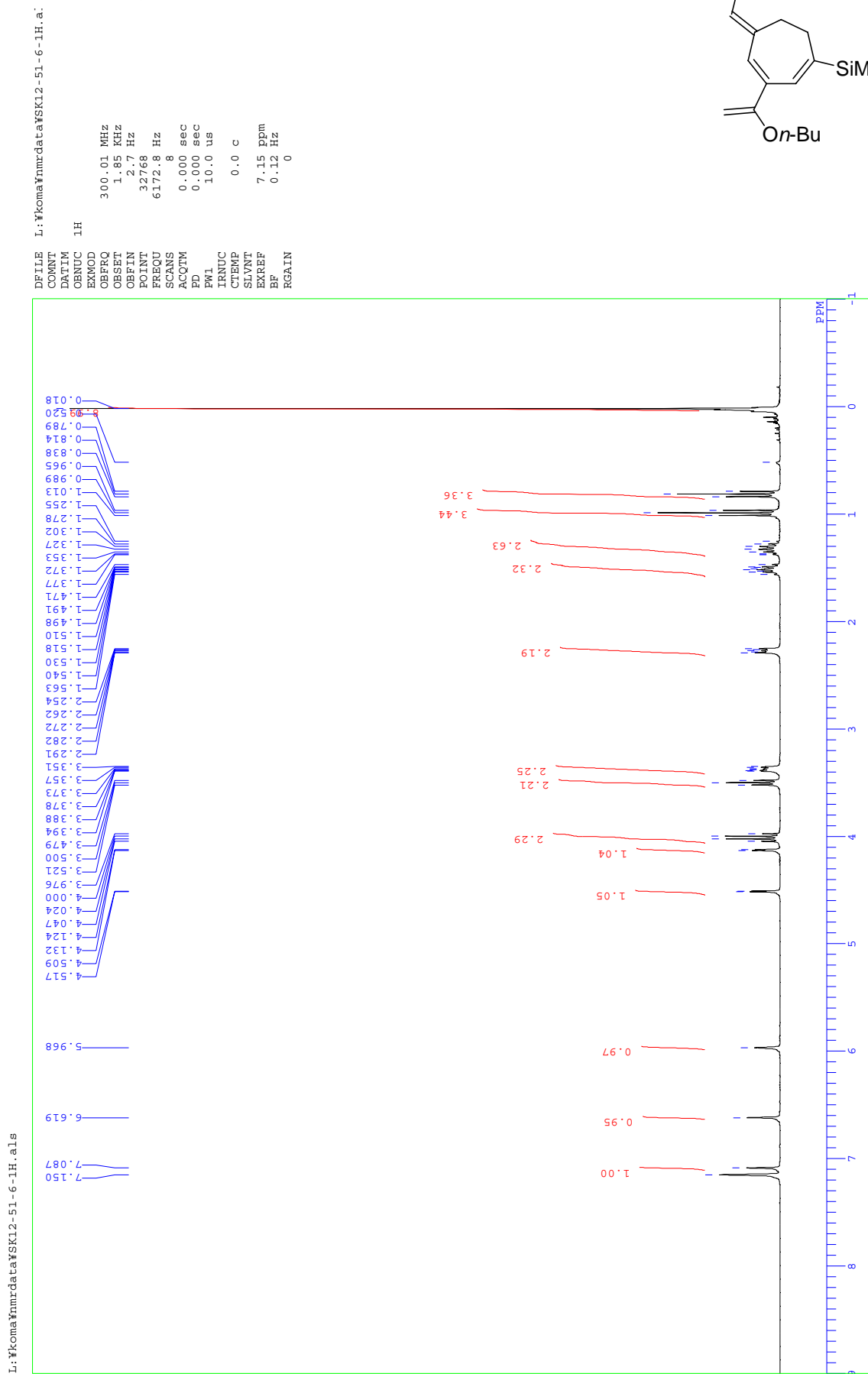
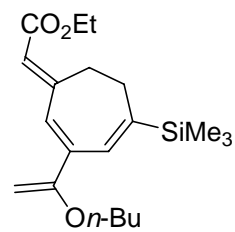
300.01 MHz
 1.85 KHz
 2.7 Hz
 32768
 6172.8 Hz
 8
 0.000 sec
 0.000 sec
 10.0 us
 0.0 C
 7.24 ppm
 1.20 Hz
 0



¹³C NMR spectrum of 6c



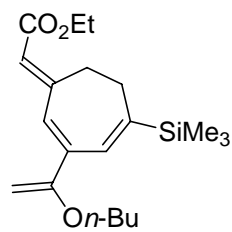
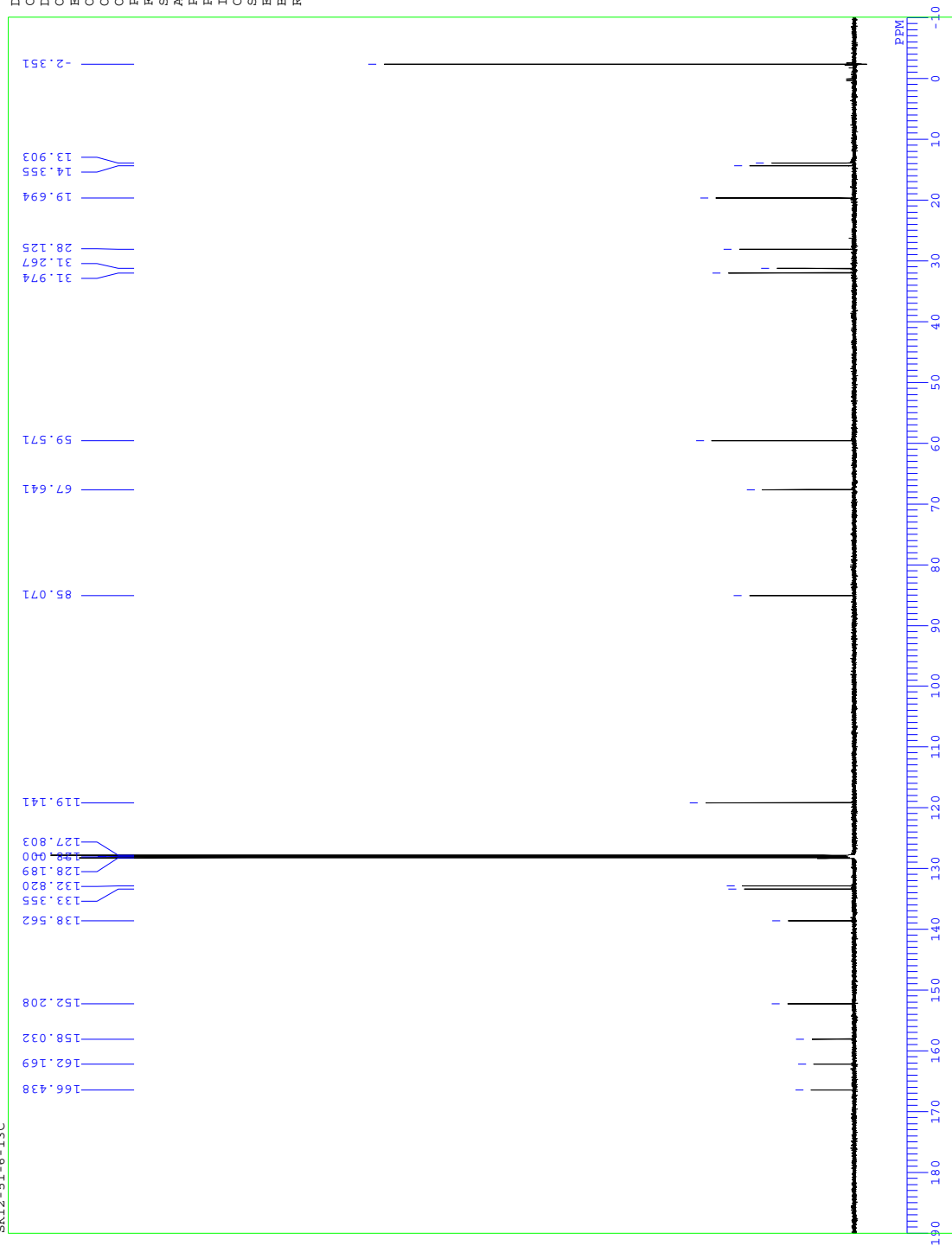
¹H NMR spectrum of 6g



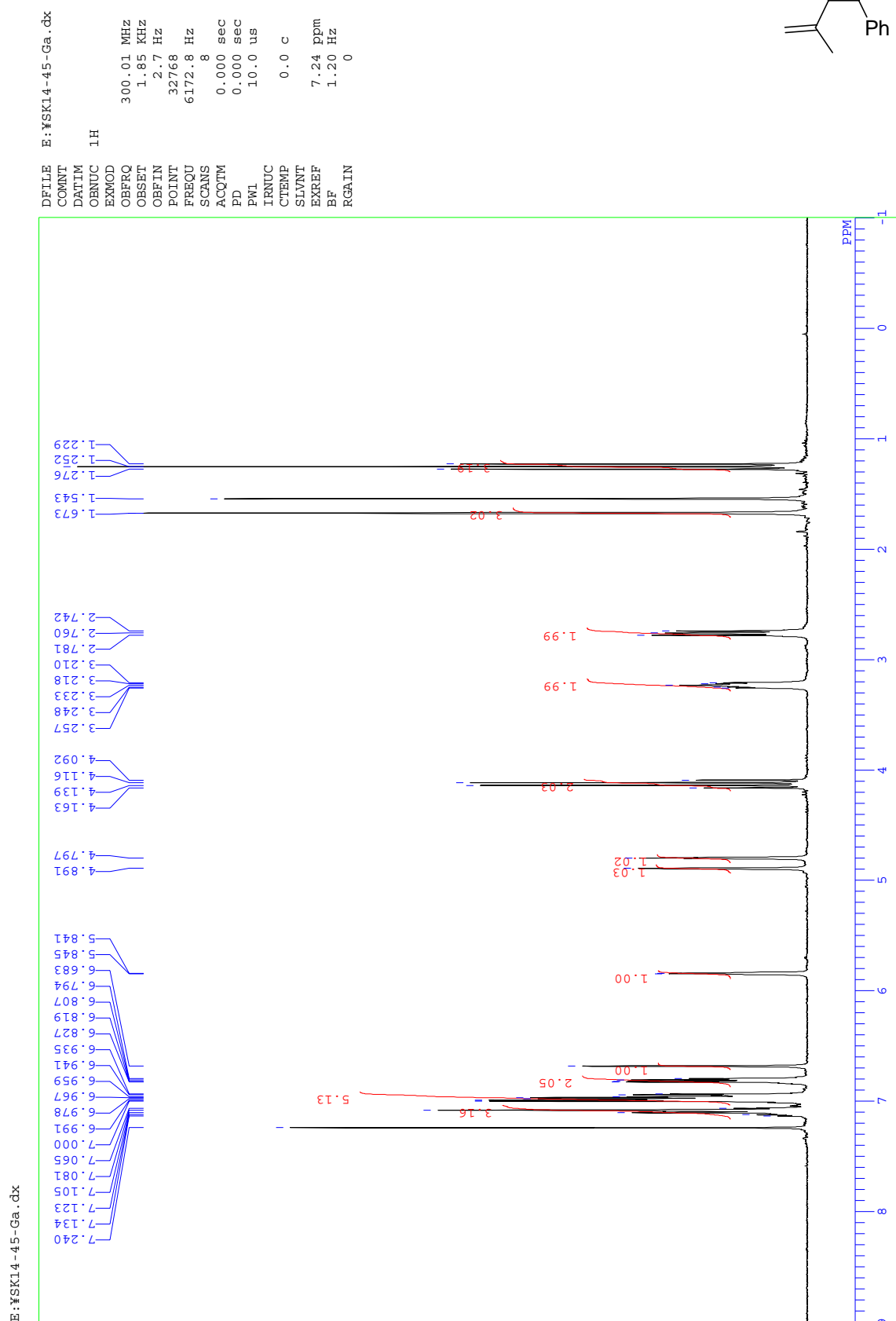
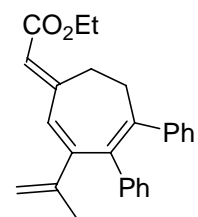
¹³C NMR spectrum of 6g

L:\Koma\Nmrdata\SK12-51-6-13C.als
SK12-51-6-13C

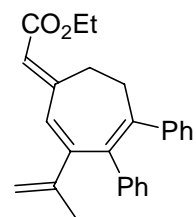
DFILE L:\Koma\Nmrdata\SK12-51-6-13C.als
COMNT SK12-51-6-13C
DATIM Wed Nov 07 15:47:35 2007
PROB 13C
PULPROG zgpg30
EXMOD bcm
OBSFREQ 125.65 MHz
OBSF1 0.00 KHz
OBSF2 127958.0 Hz
POINT 32768
FREQ 33898.3 Hz
SCANS 634
ACQTM 0.967 sec
PD 2.033 sec
PW1 5.1 us
IRNUC 1H
CTEMP 25.6 c
SLVNT C6D6
EXREF 128.00 ppm
BF 0.12 Hz
RGAIN 26



¹H NMR spectrum of 8

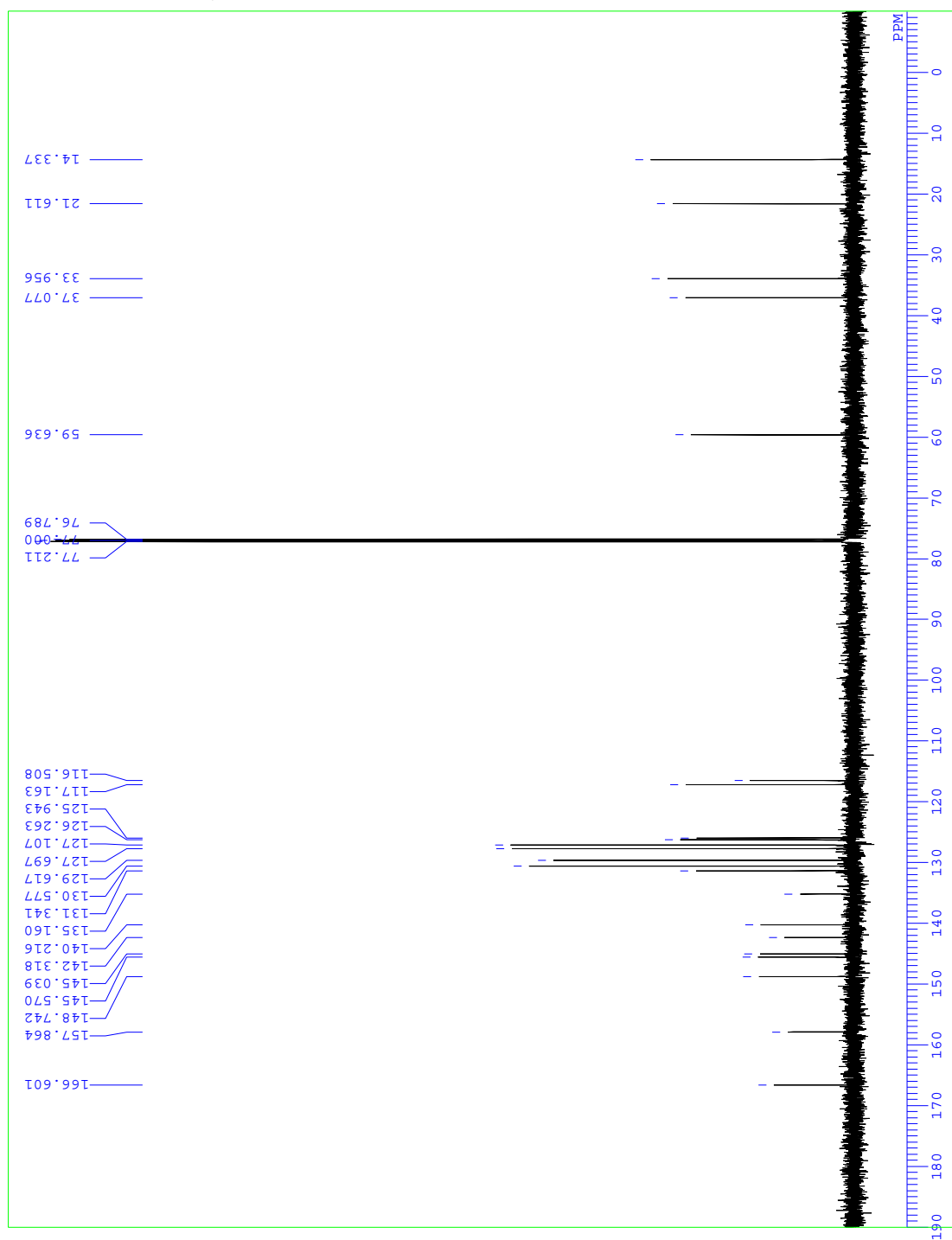


¹³C NMR spectrum of 8

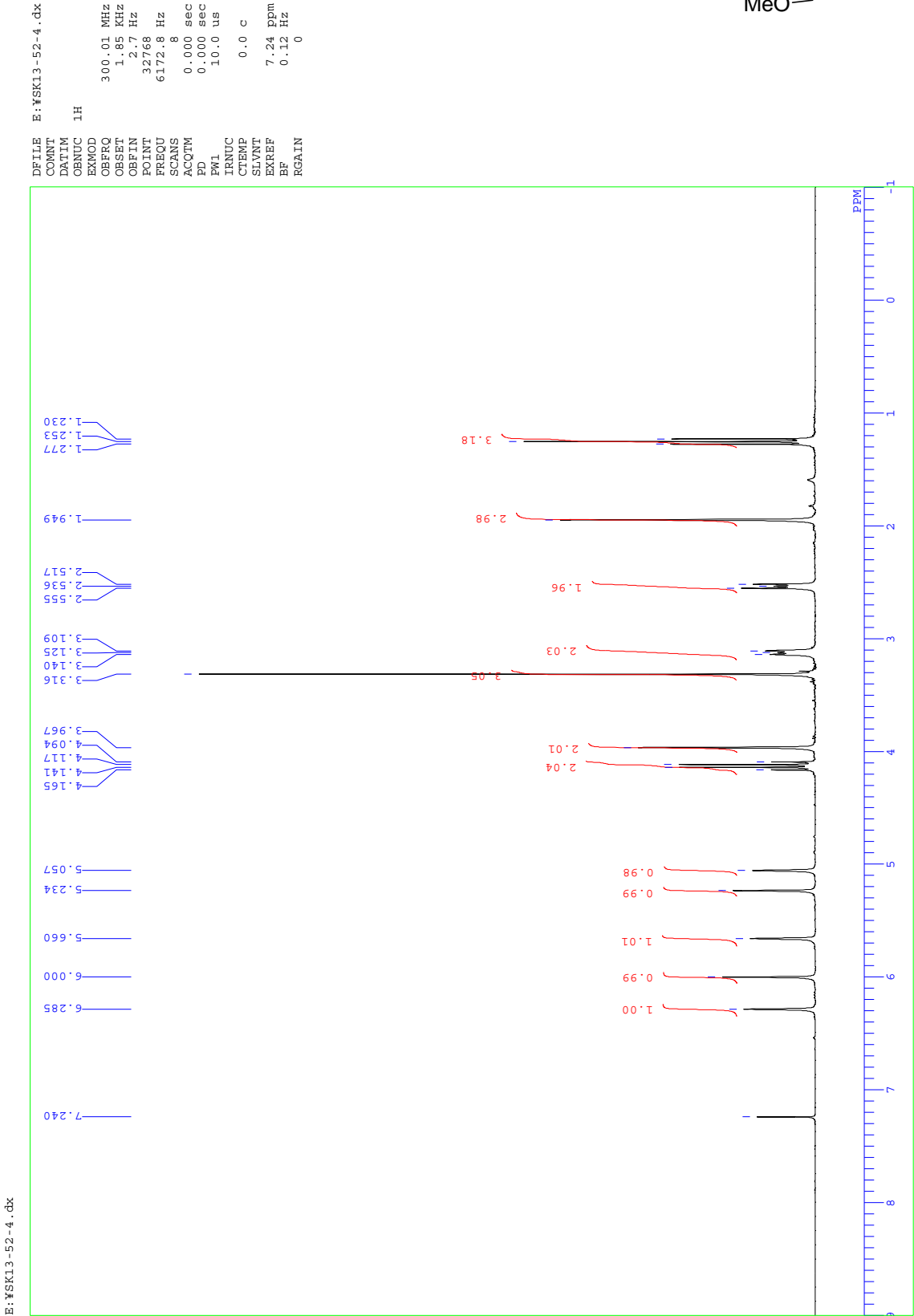
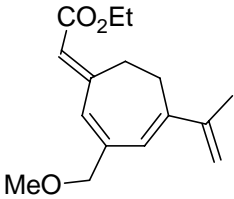


C:\Documents and Settings\ya
 DFILE
 COMNT
 DATIM
 OBNUC 13C
 EXMOD
 OFFRQ 150.91 MHz
 OBSET 7.89 KHz
 OFBIN 8.8 Hz
 POINT 32768
 FREQU 35971.2 Hz
 SCANS 8
 ACQTM 0.000 sec
 PD 0.000 sec
 PWL 10.0 us
 IRNUC 0.0 c
 CTEMP
 SLVNT
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 0

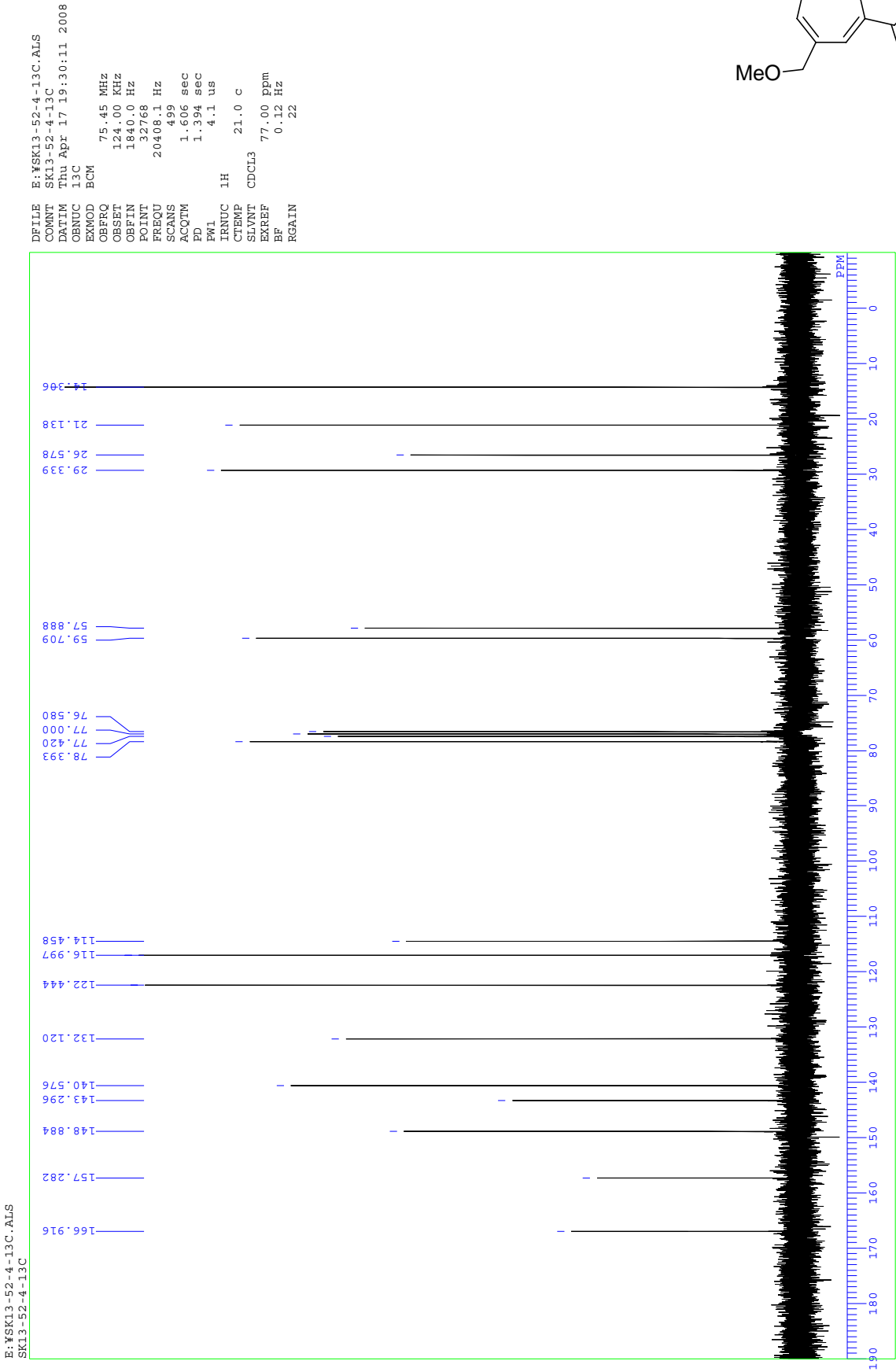
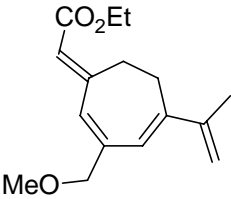
C:\Documents and Settings\admin\My Documents\koma\NMR\ysk14-01-3-13C.dx



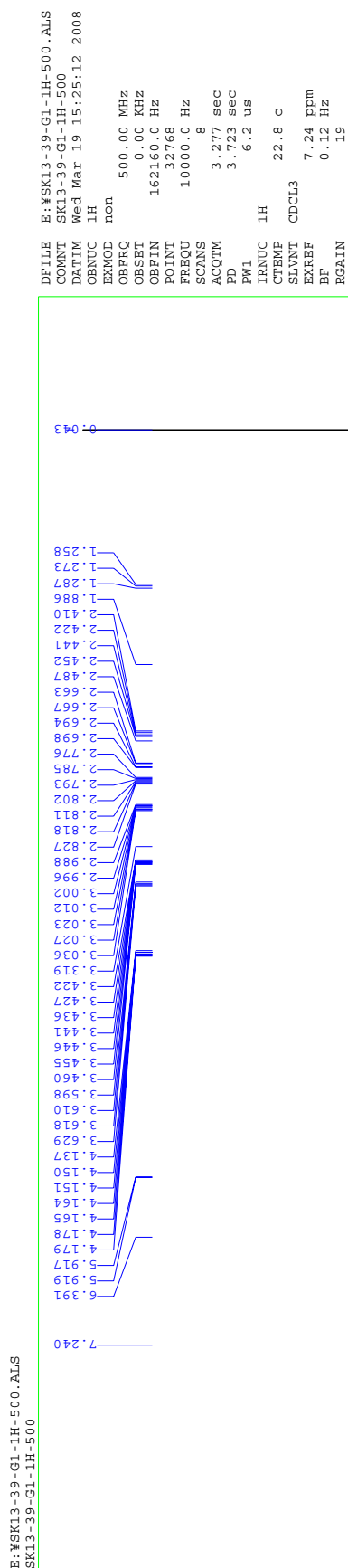
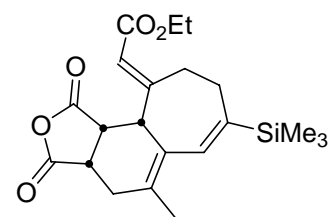
¹H NMR spectrum of 10



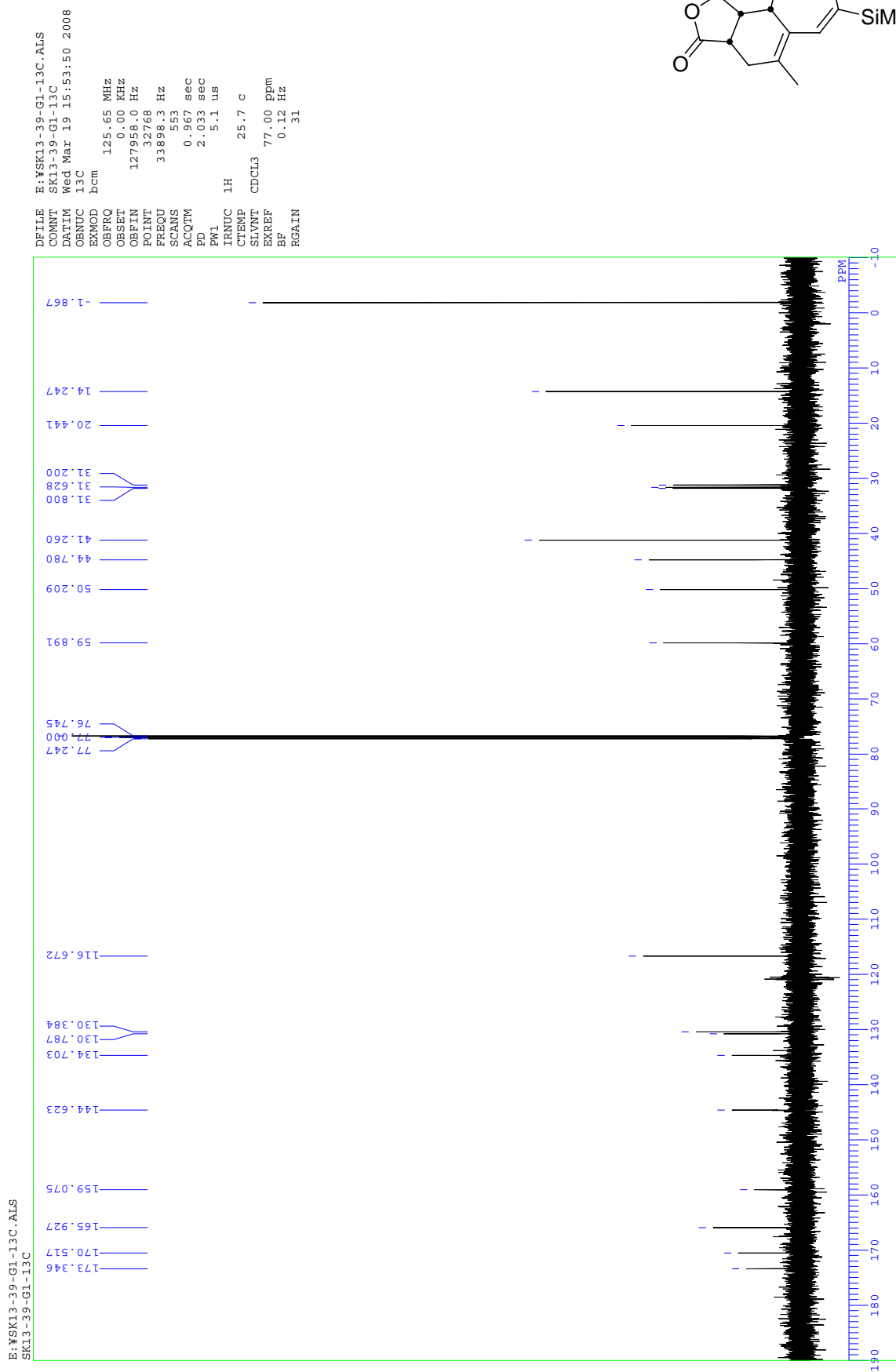
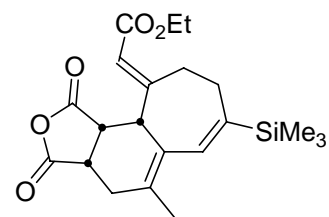
¹³C NMR spectrum of 10



¹H NMR spectrum of *endo*-12a

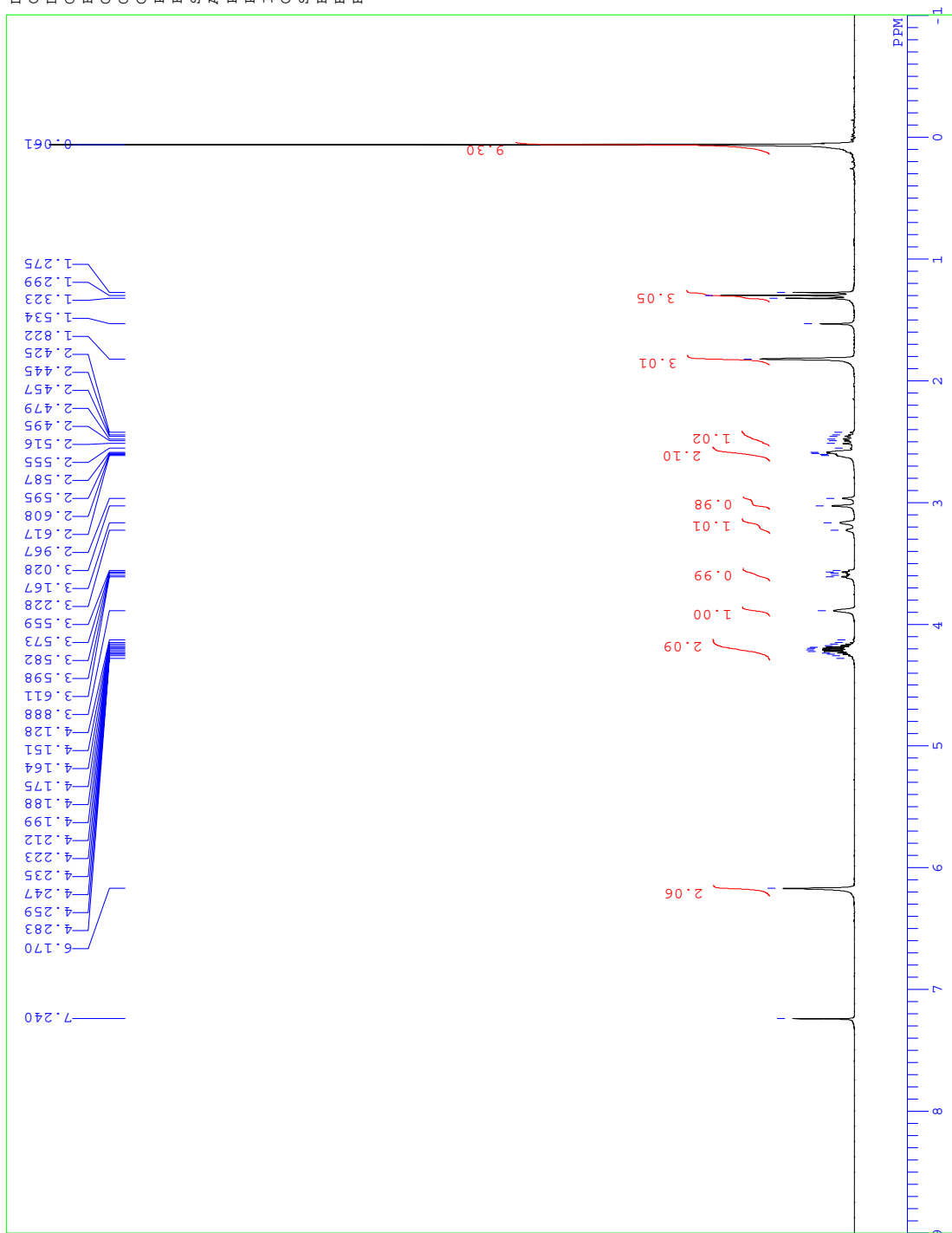


¹³C NMR spectrum of *endo*-12a



¹H NMR spectrum of 12b

L:\Ykoma\Nmrdata\YSK12-65-4-1H.als

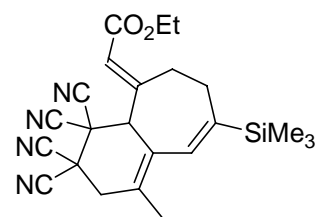


DFTL L:\Ykoma\Nmrdata\YSK12-65-4

1H

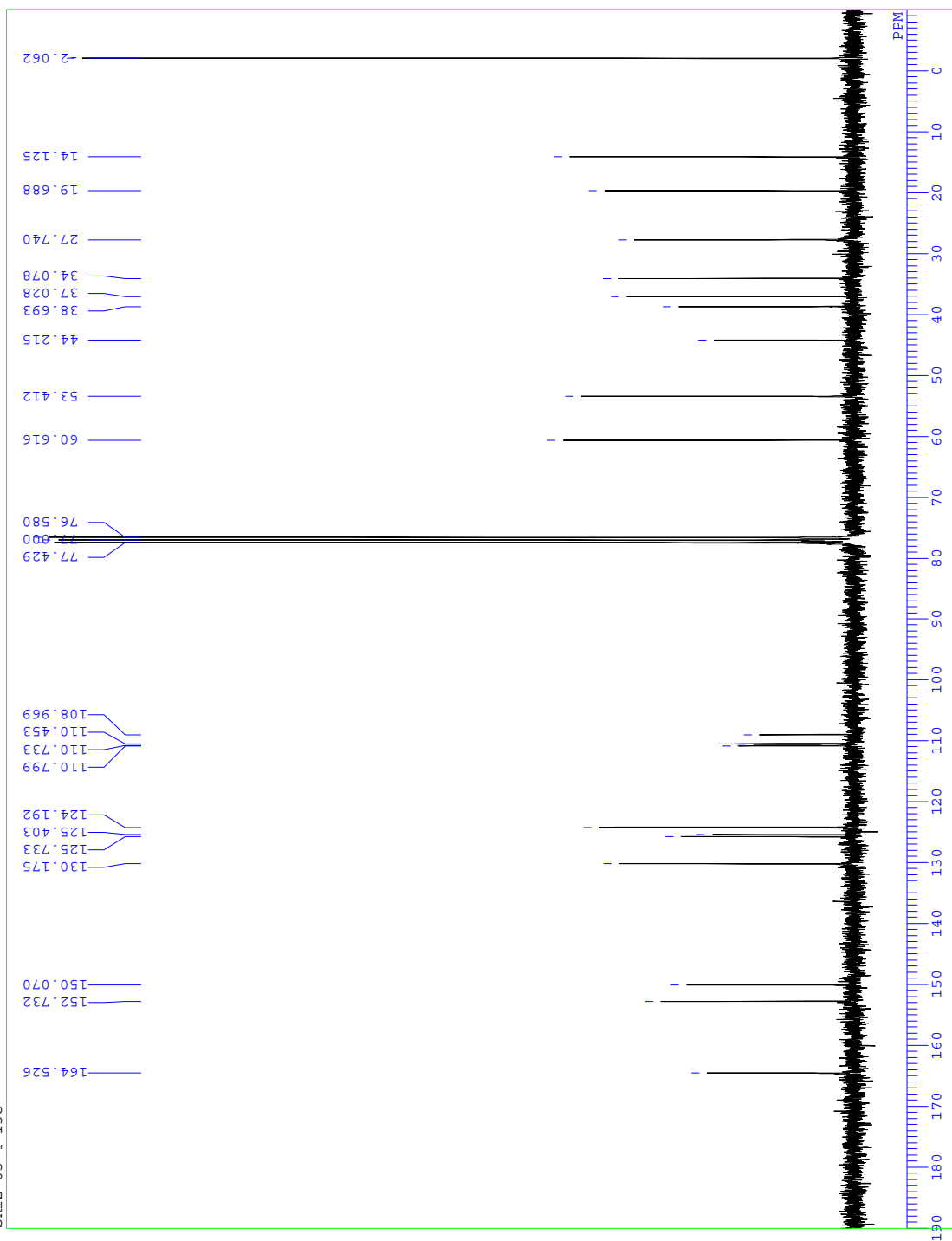
COMNT
DATIM
OBNUC
EXMOD
OBFRO
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

300.01 MHz
1.85 KHz
2.7 Hz
32768
6172.8 Hz
8
0.000 sec
0.000 sec
10.0 us
0.0 c
7.24 ppm
1.20 Hz
0

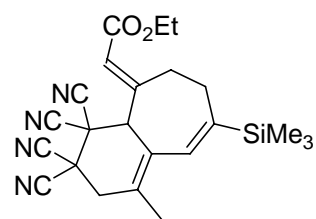


¹³C NMR spectrum of 12b

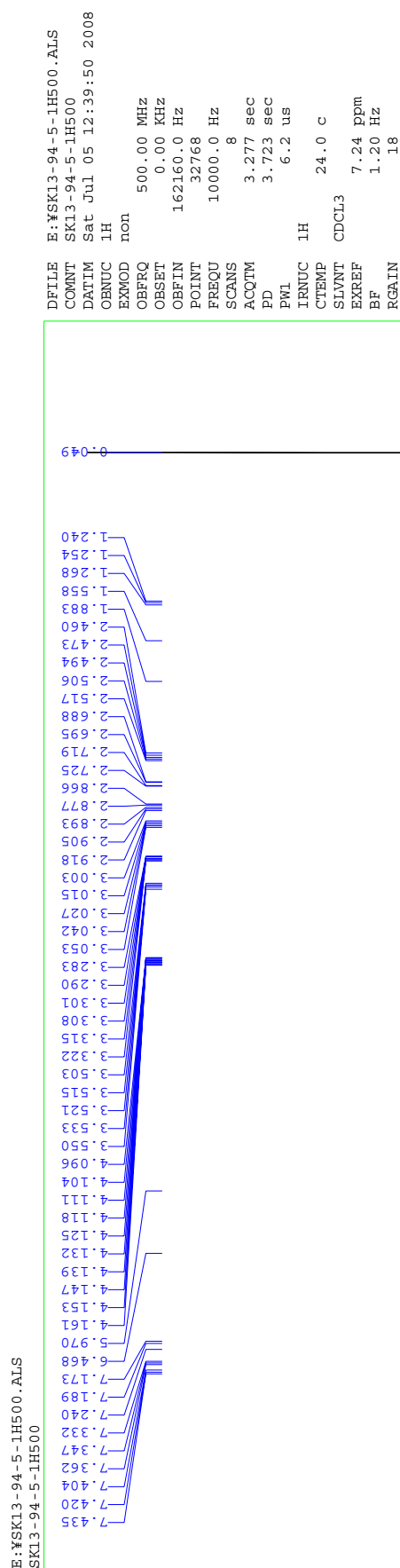
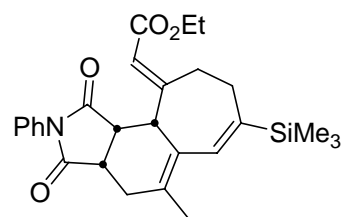
E:\MSK12-65-4-13C.ALS
SK12-65-4-13C



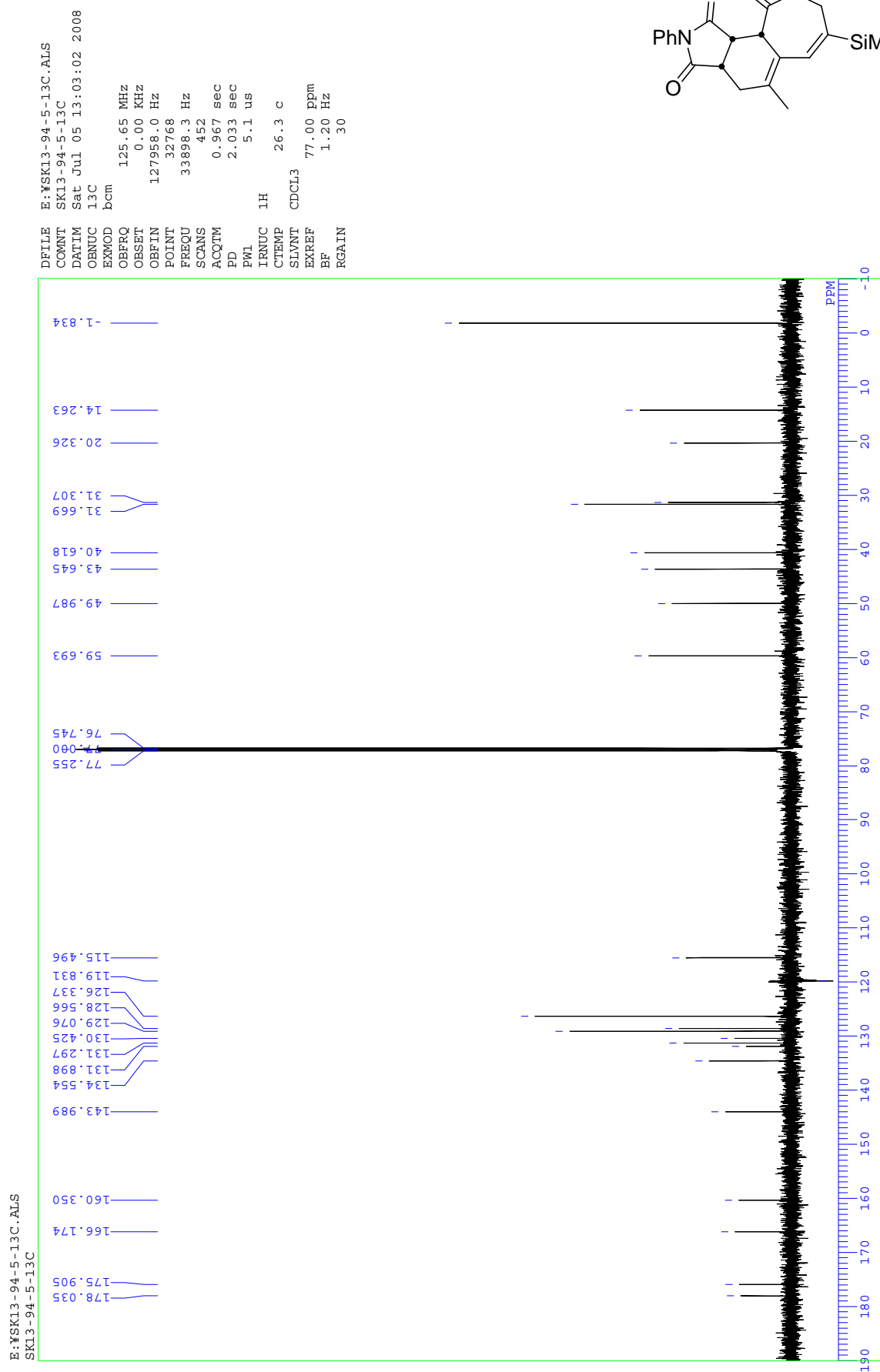
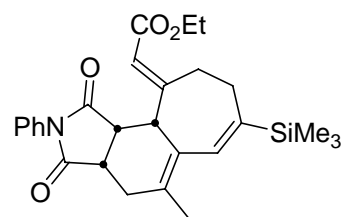
DFILE E:\MSK12-65-4-13C.ALS
COMNT SK12-65-4-13C
DATIM Fri Nov 30 12:53:19 2007
OBNUC 13C
EXMOD BCM
OBFREQ 75.45 MHz
OBSSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 502
AQUTM 1.606 sec
PD 1.394 sec
PWL 4.1 us
IRNUC 1H
CTEMP 21.0 C
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 22



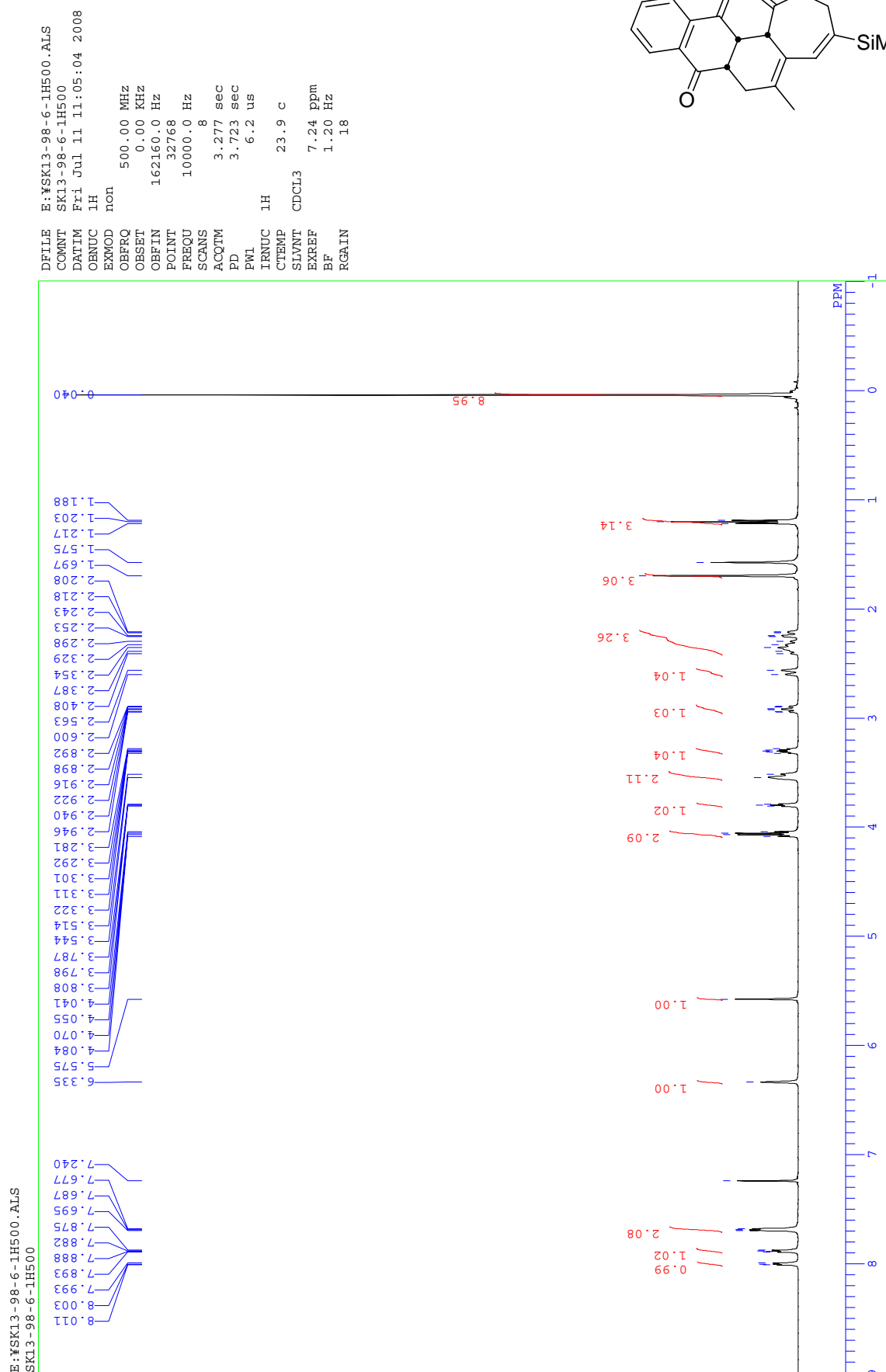
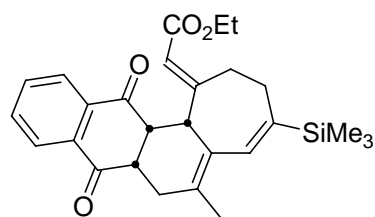
¹H NMR spectrum of *endo*-12c



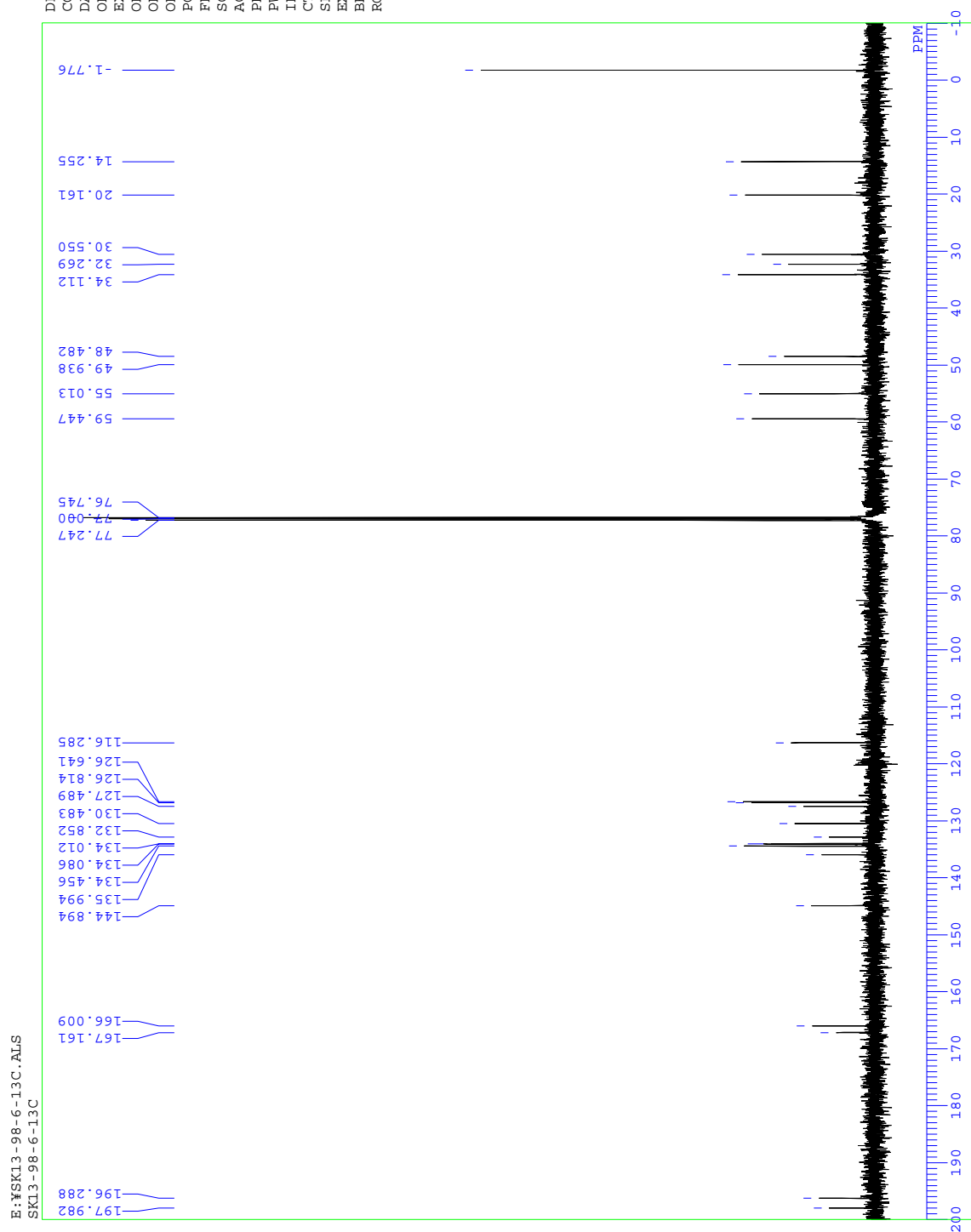
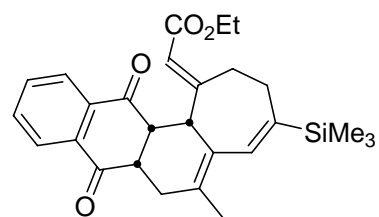
¹³C NMR spectrum of *endo*-12c



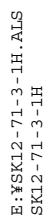
¹H NMR spectrum of *endo*-12d



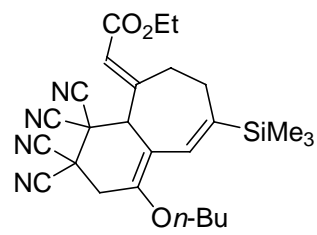
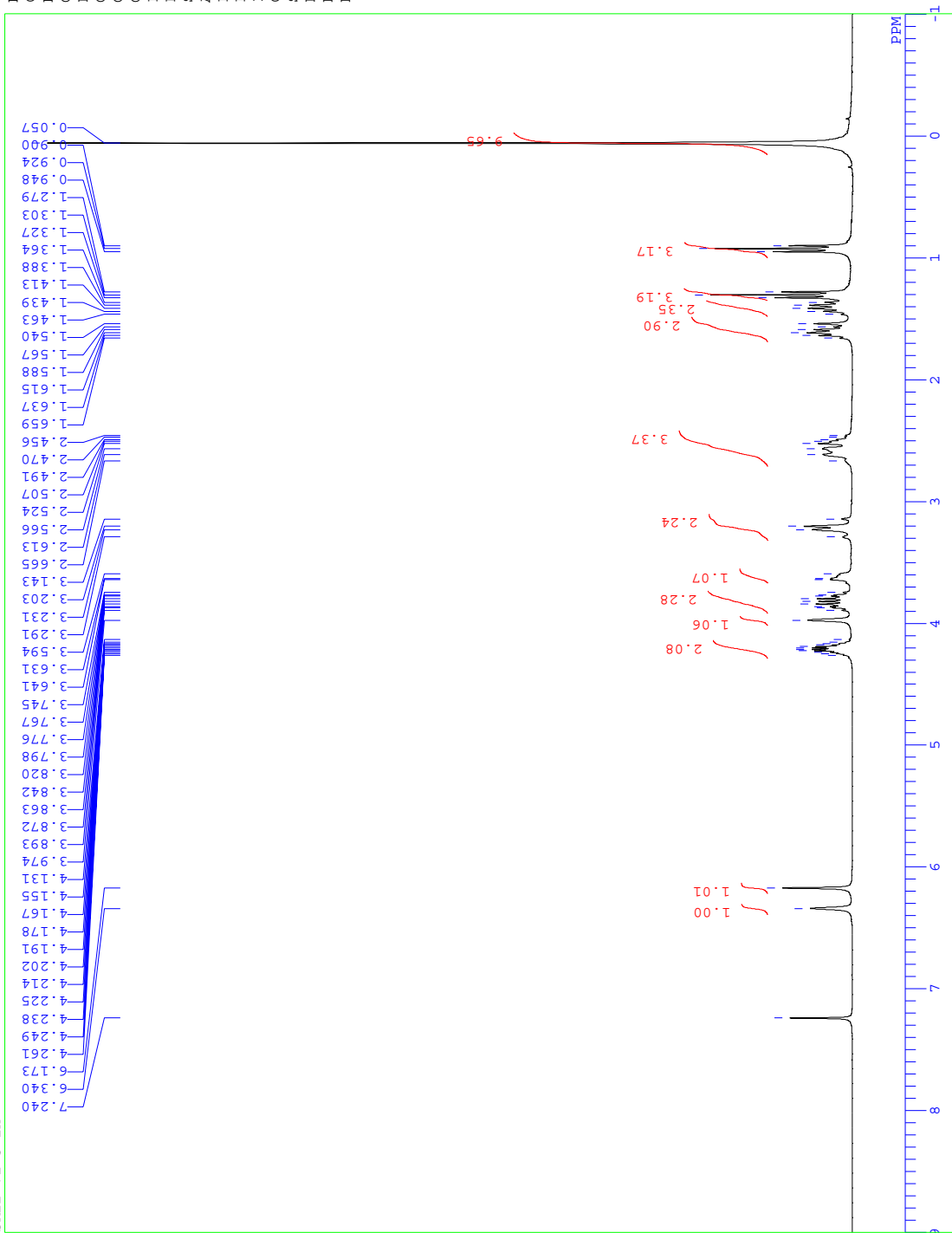
¹³C NMR spectrum of *endo*-12d



¹H NMR spectrum of 13b

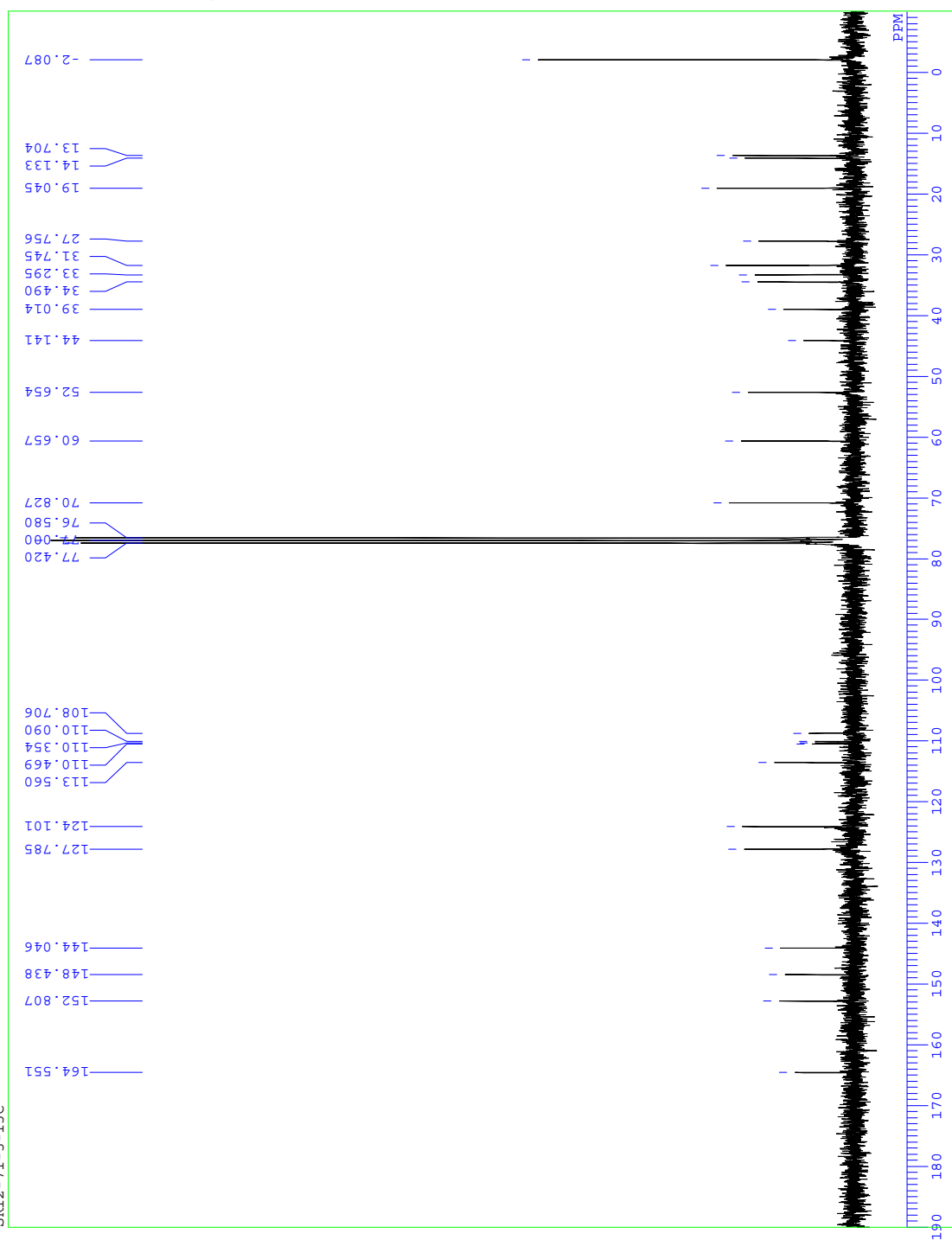


DFILE	E:\\$K12-71-3-1H.ALS
COMMT	SK12-71-3-1H
DATIM	Mon Dec 03 17:04:08 2007
ONUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.0 Hz
POINT	32768
FREQU	6013.2 Hz
SCANS	8
ACQTM	5.449 sec
PD	1.551 sec
PW1	5.4 us
IRNUC	1H
CTEMP	20.6 c
SOLNT	CDCL3
EXREF	7.24 ppm
BF	1.20 Hz
RGAIN	17

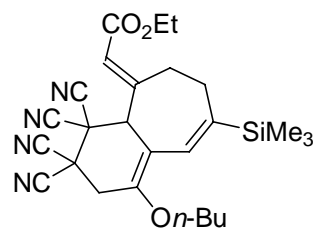


¹³C NMR spectrum of 13b

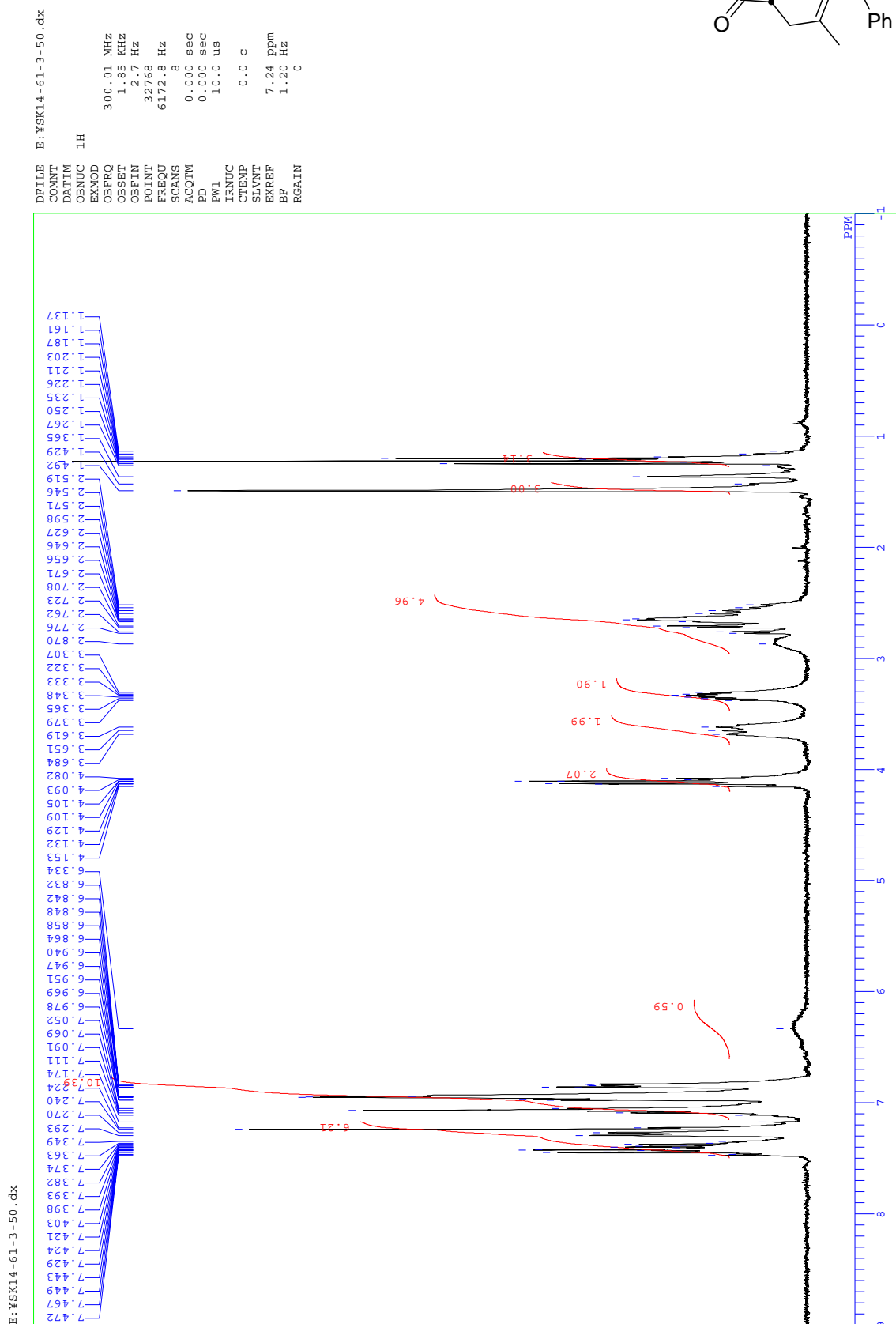
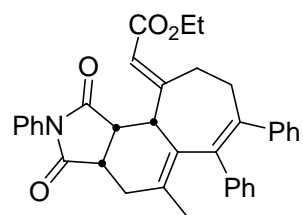
E:\SK12-71-3-13C.ALS
SK12-71-3-13C



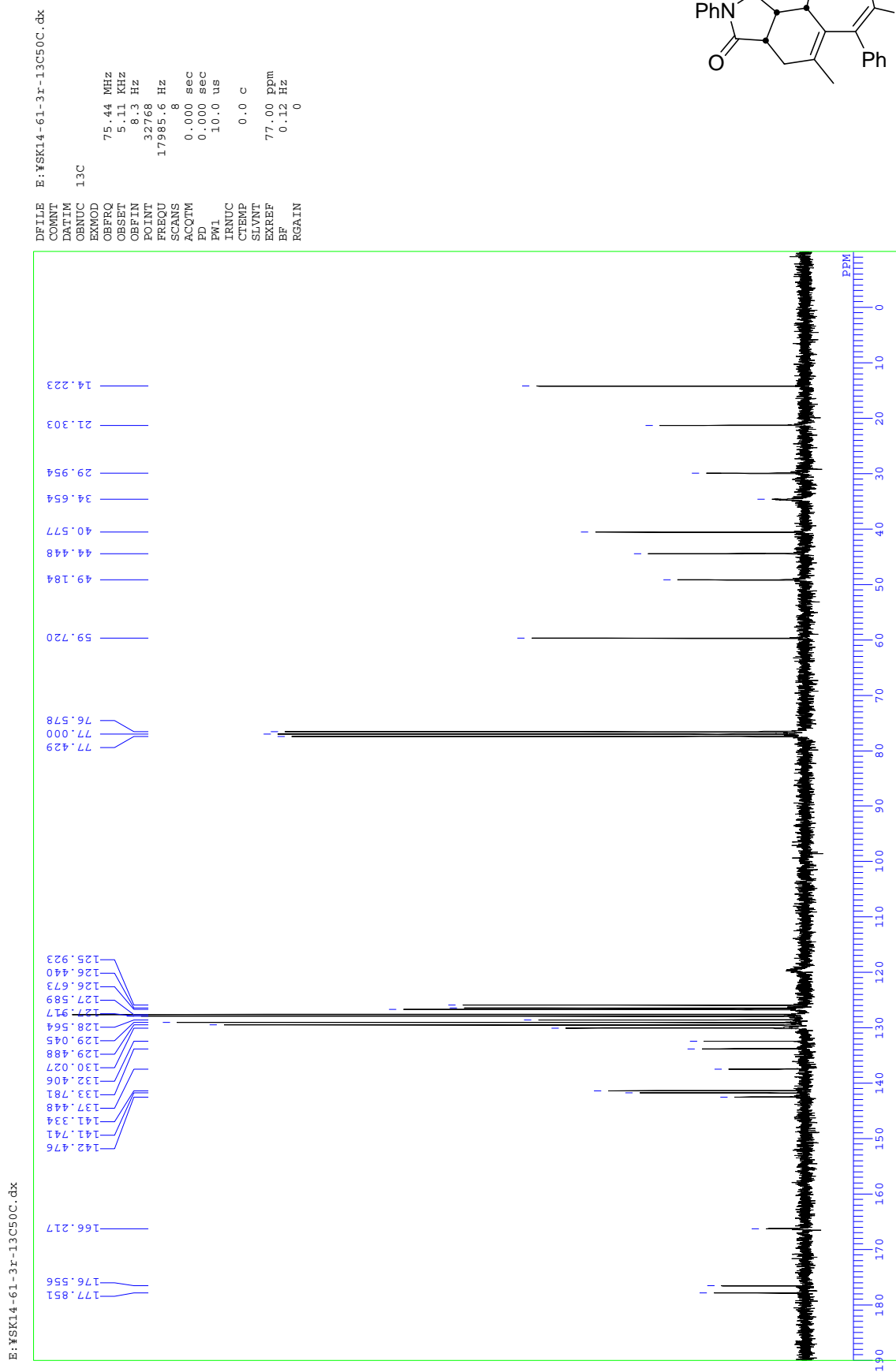
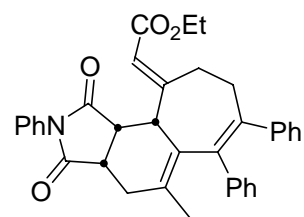
DFILE E:\SK12-71-3-13C.ALS
 COMNT SK12-71-3-13C
 DATIM Mon Dec 03 17:27:04 2007
 OBNUC 13C
 EXMOD BCM
 OBFREQ 75.45 MHz
 OBSSET 124.00 KHz
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 447
 ACQTM 1.606 sec
 PD 1.394 sec
 PWL 4.1 us
 IRNUC 1H
 CTEMP 20.8 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 22



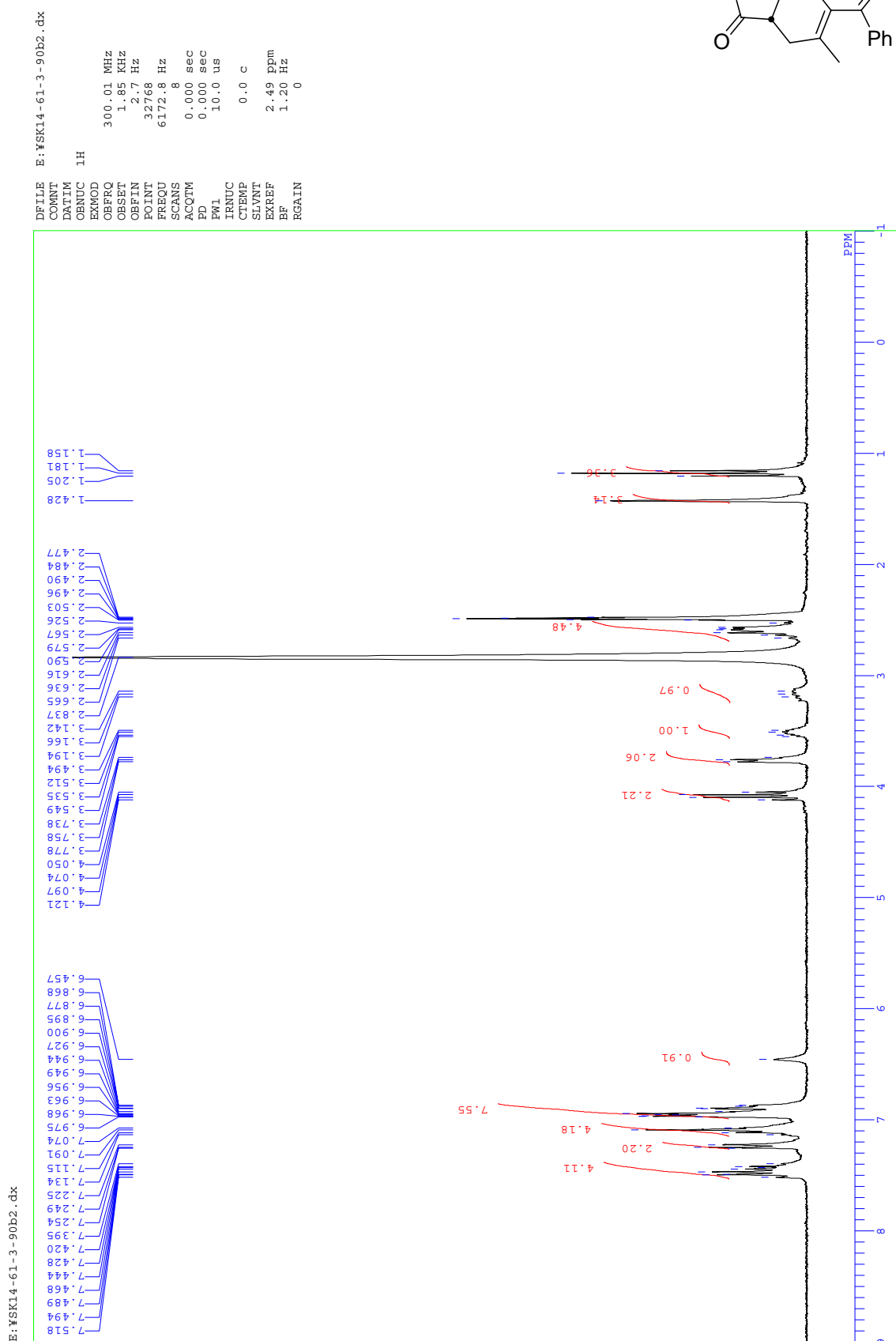
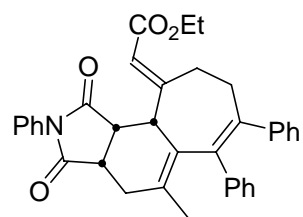
¹H NMR spectrum of *endo*-14c (CDCl₃, at 50 °C)



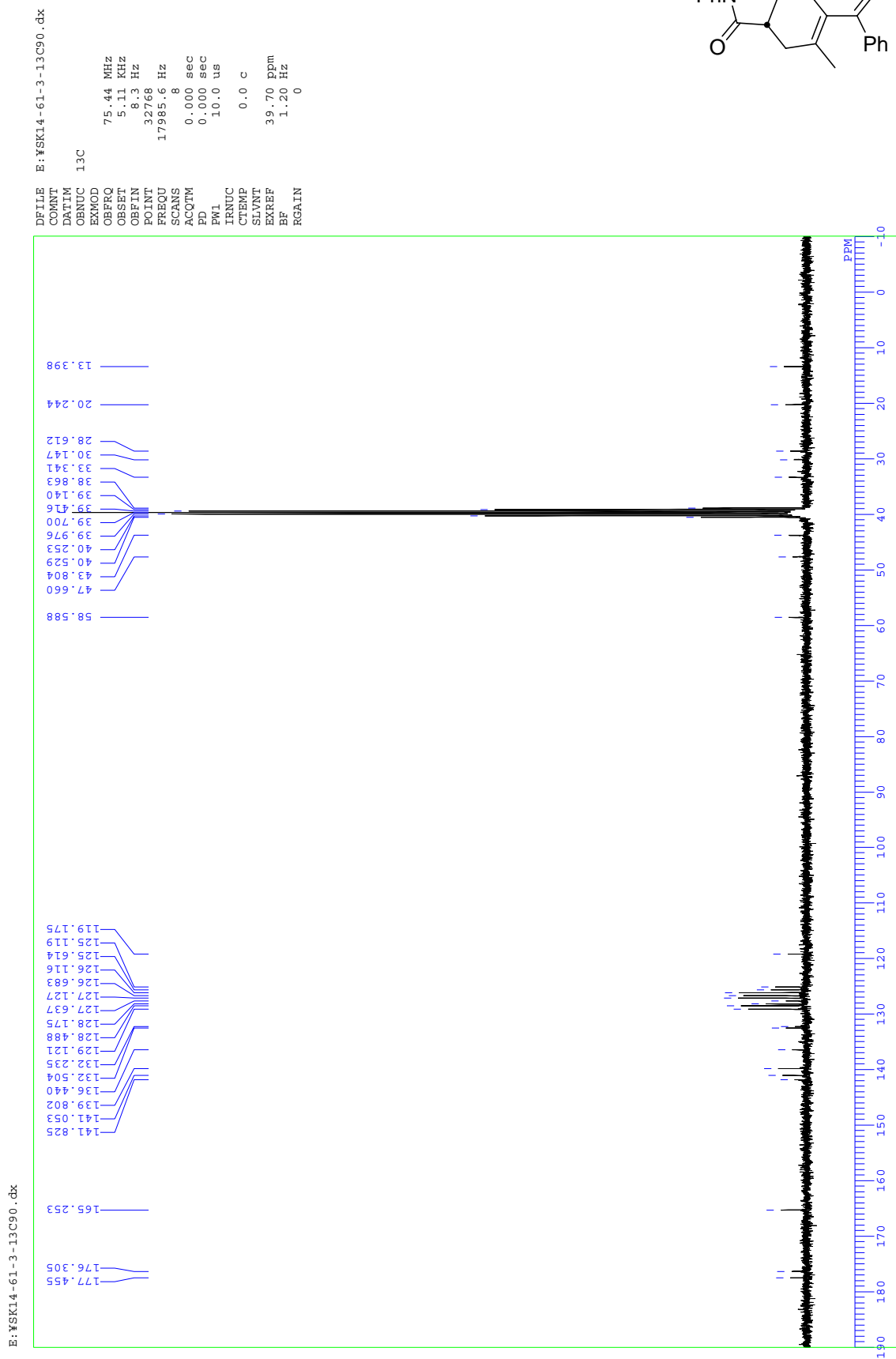
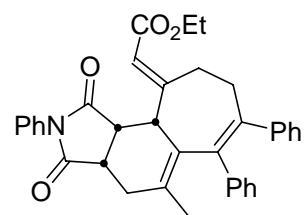
¹²C NMR spectrum of *endo*-14c (CDCl₃, at 50 °C)



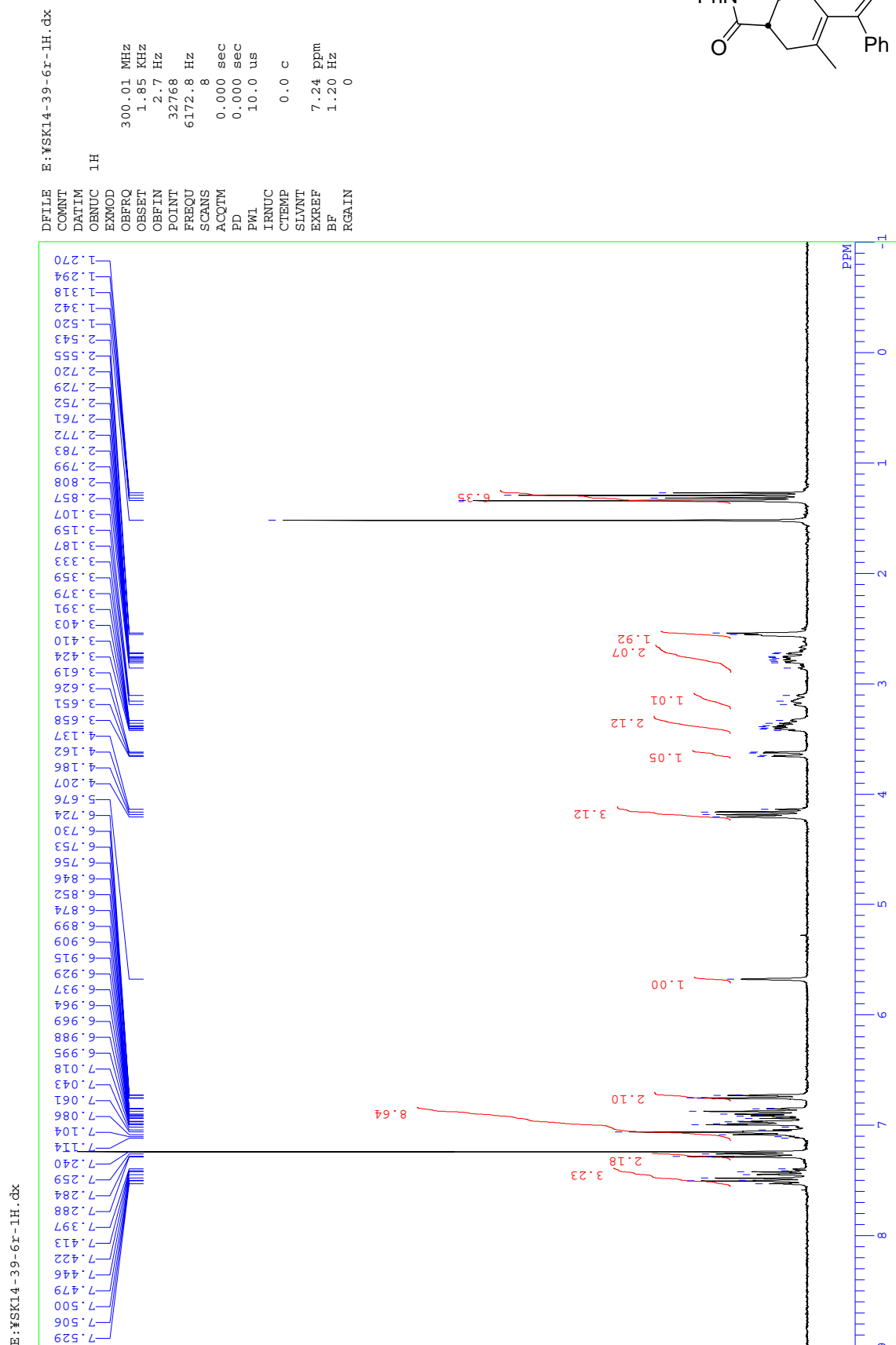
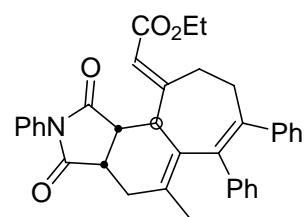
¹H NMR spectrum of *endo*-14c (DMSO-d₆, at 90 °C)



¹³C NMR spectrum of *endo*-14c (DMSO-d₆, at 90 °C)



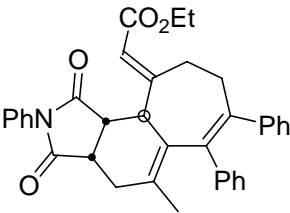
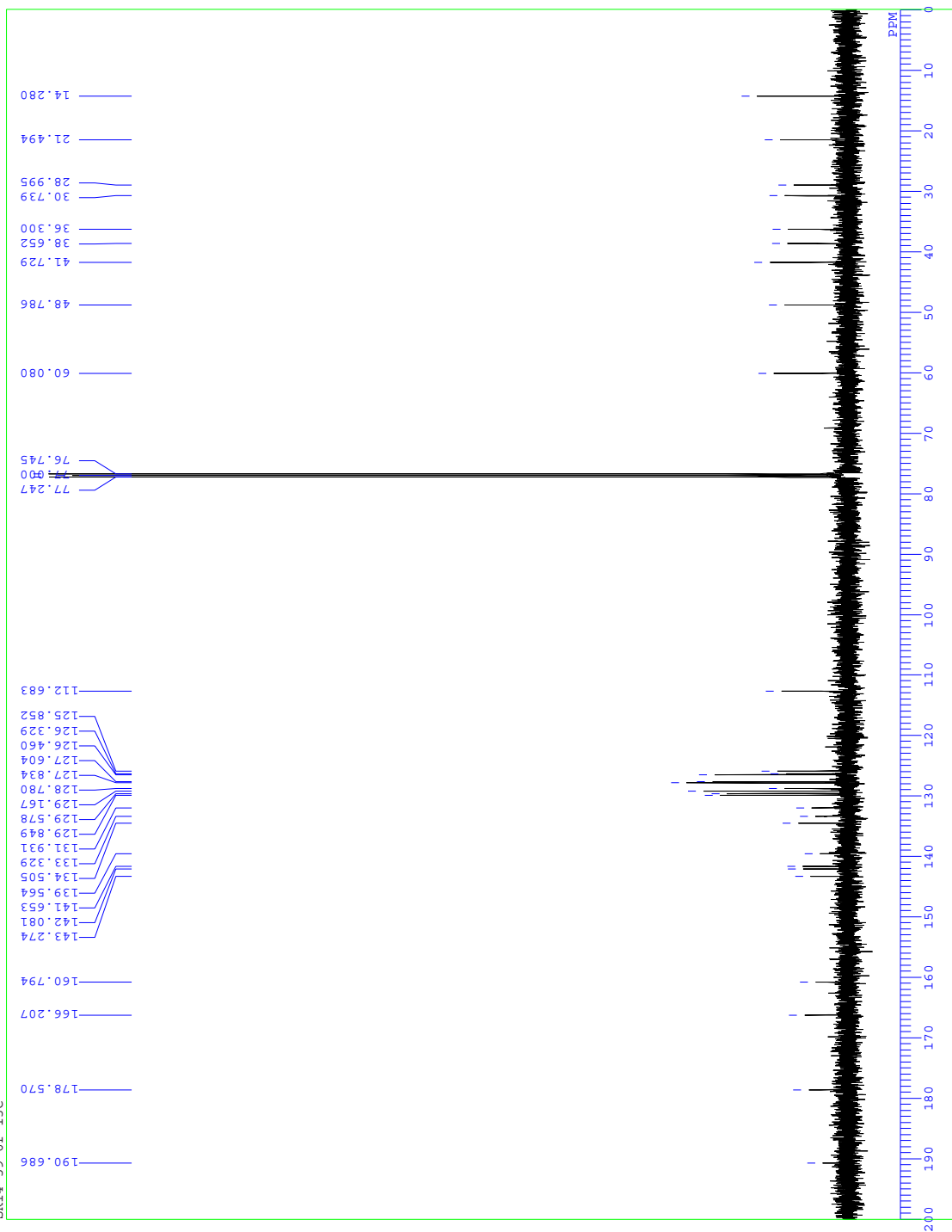
¹H NMR spectrum of *exo*-14c



¹²C NMR spectrum of *exo*-14c

Z:\Koma\Nmrdata\SK14-39-6r-13C.als
SK14-39-6r-13C

DFILE SK14-39-6r-13C
COMNT SK14-39-6r-13C
DATIM Tue Oct 07 16:35:10 2008
CHNOC 13C
EXMOD bcm
OBFRO 125.65 MHz
OBFSEI 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 708
ACQTM 0.967 sec
PD 2.033 sec
PW1 5.1 us
IRNUC 1H
CTEMP 25.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 30



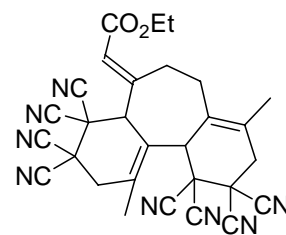
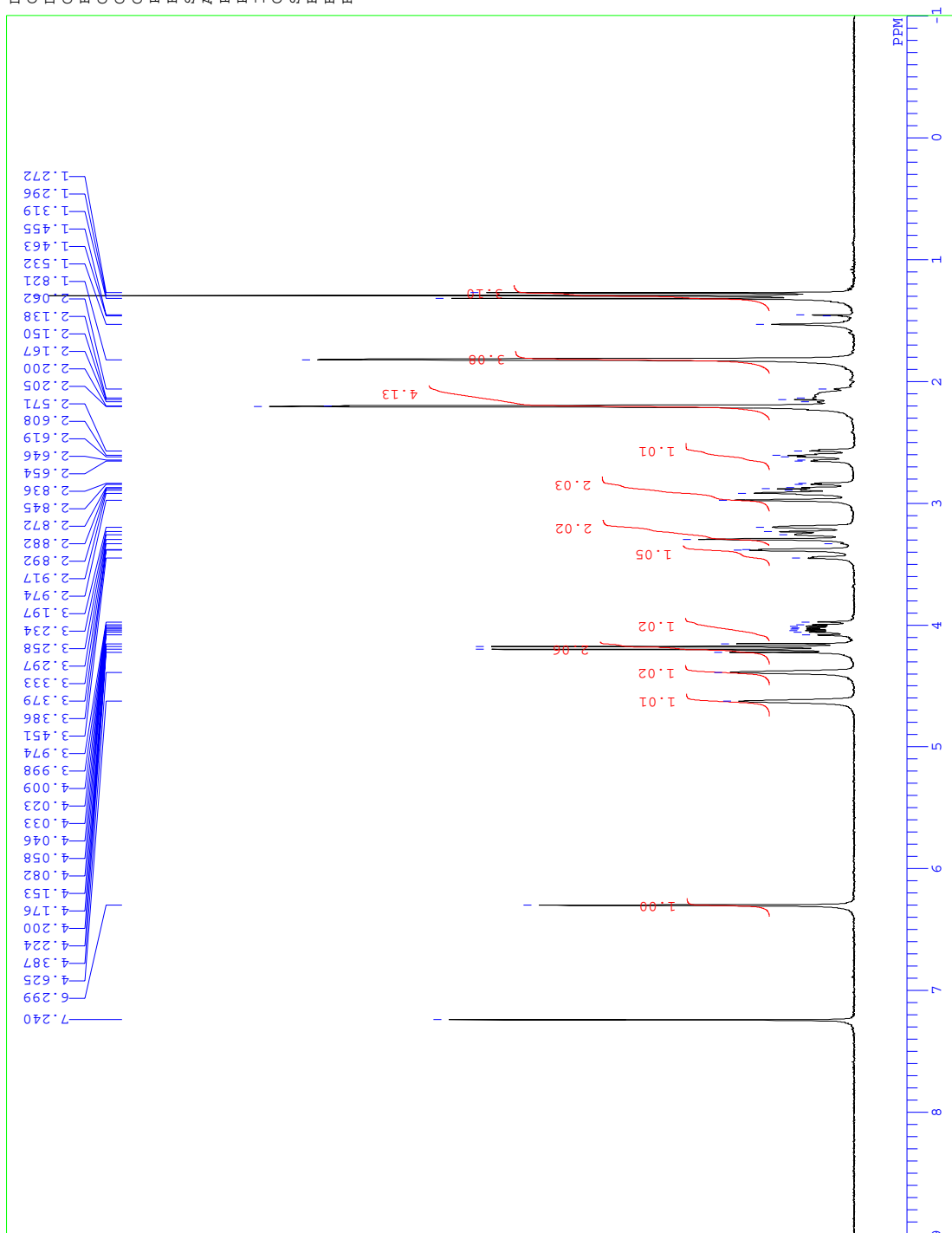
¹H NMR spectrum of 15b

L:\koma\nmrdata\SK12-75-3r-1H.als

DFILE
COMNT
DATIM
OENUC
EXMOD
OEFRO
OBSFQ
OBFIN
POINT
FREQU
SCANS
AQUTM
PD
PWL
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

L:\koma\nmrdata\SK12-75-3r-1H

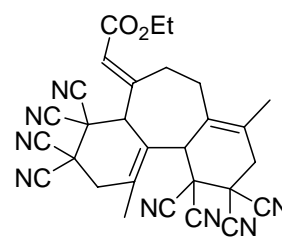
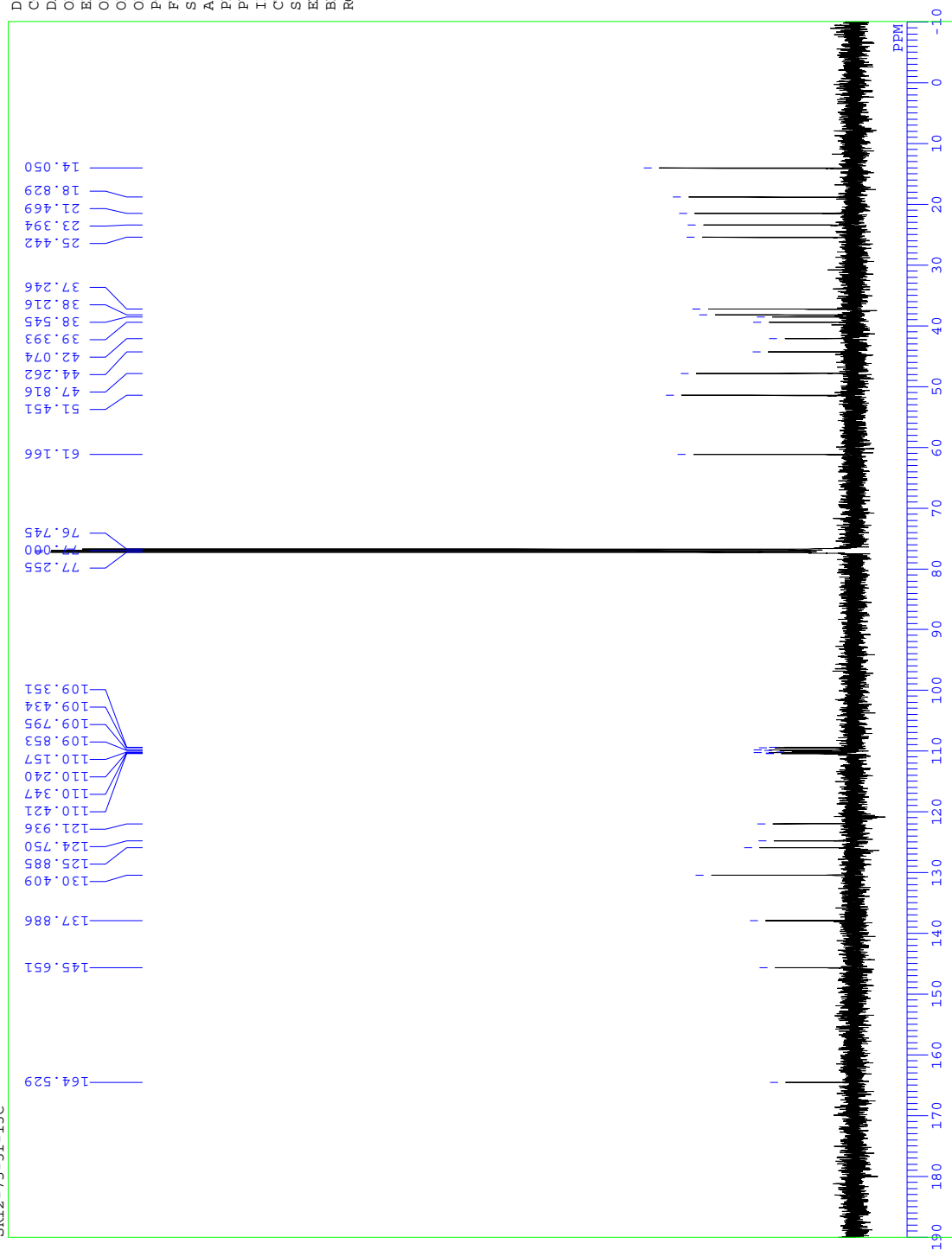
300.01 MHz
1.85 KHz
2.7 Hz
32768
6172.8 Hz
8
0.000 sec
0.000 sec
10.0 us
0.0 C
7.24 ppm
1.20 Hz
0



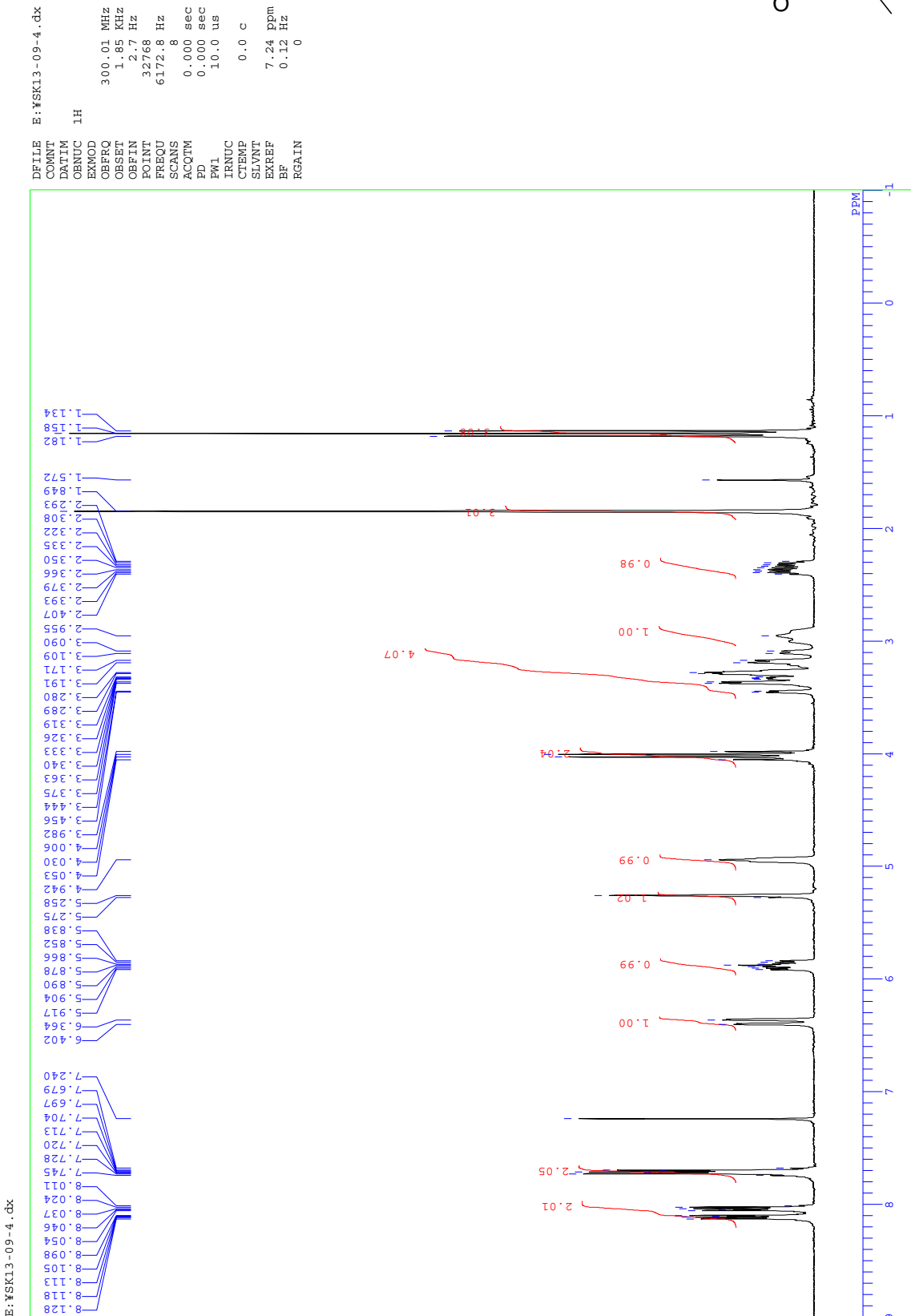
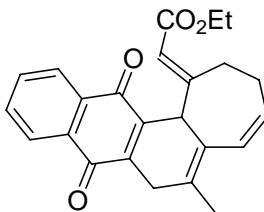
¹³C NMR spectrum of 15b

E:\MSK12-75-3r-13C.ALS
SK12-75-3r-13C

DFILE E:\MSK12-75-3r-13C.ALS
COMNT SK12-75-3r-13C
DATIM Fri Dec 07 15:52:15 2007
OBNUC 13C
EXMOD bcm
OBFREQ 125.65 MHz
OBSSET 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 604
AQTM 0.967 sec
PD 2.033 sec
PWL 5.1 us
IRNUC 1H
CTEMP 25.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 31



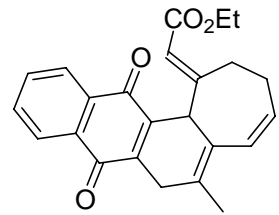
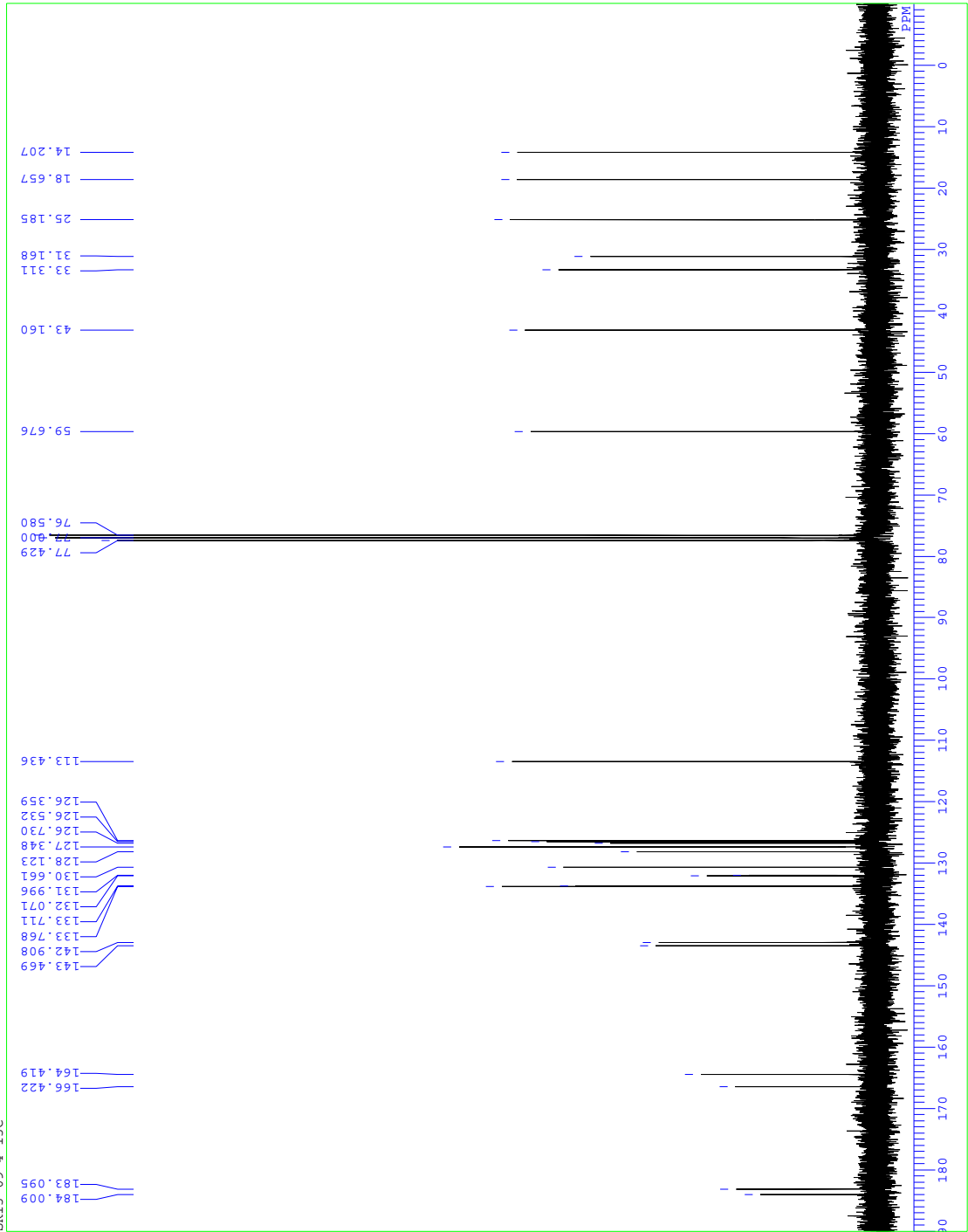
¹H NMR spectrum of 16d



¹³C NMR spectrum of 16d

L:\Koma\nmrdata\SK13-09-4-13C.als
SK13-09-4-13C

DFILE L:\Koma\nmrdata\SK13-09-4-13C.als
COMNT SK13-09-4-13C
DATIM Thu Jan 24 13:53:05 2008
ORNUC 13C
EXMOD BCM
OBFRO 75.45 MHz
OBSEI 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 408
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.1 us
IRNUC 1H
CTEMP 20.3 C
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 22



NOESY spectrum of *endo*-12a

