Supporting Information

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

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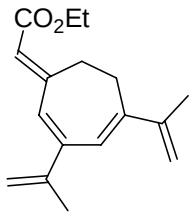
Table of contents

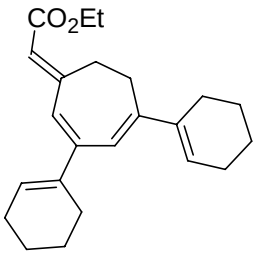
General Information

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) dichloride[11] were prepared as reported. Chemical shifts were reported in delta units (δ) relative to chloroform (7.24 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR) or dimethyl sulfoxide (2.49 ppm for ^{1}H 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/MSC, 1998) was used. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included as their calculated positions.

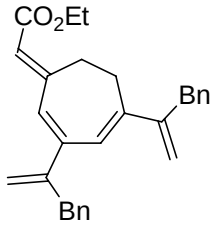
Nickel(0)-Catalyzed Cycloaddition of Ethyl Cyclopropylideneacetate (1) and Conjugated Enynes (Table 1). A Representative Procedure. To a dark red mixture of $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in dry toluene (0.5 mL) was added dropwise a solution of **1** (126 mg, 1 mmol) and **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**.



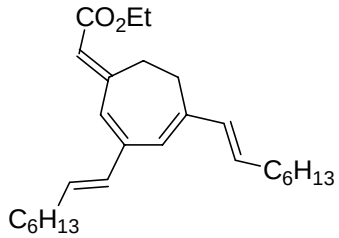
(*E*)-1-Ethoxycarbonylmethylene-3,5-(di-1-methylethenyl)-2,4-cycloheptadiene (3a): purified by silica gel column chromatography (hexane/AcOEt 30:1 and hexane/CH_2Cl_2 3:1); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 6.39 (s, 1H), 6.19 (s, 1H), 5.71 (s, 1H), 5.23 (s, 1H), 5.14 (s, 1H), 5.05 (s, 2H), 4.13 (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 $C_{17}H_{22}O_2$: 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/CH_2Cl_2 3:1); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (75 MHz, $CDCl_3$) 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 $(C_{23}H_{30}O_2)[M+Na]^+$: 361.2138. Found: 361.2138.

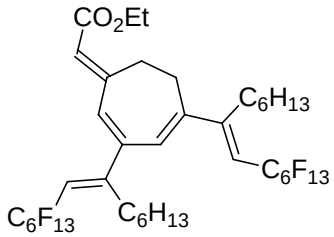


(*E*)-1-Ethoxycarbonylmethylene-3,5-(di-1-benzylethenyl)-2,4-cycloheptadiene (3c): purified by silica gel column chromatography (hexane/AcOEt 20:1); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.29-6.99 (m, 10H), 6.27 (s, 1H), 6.08 (s, 1H), 5.55 (s, 1H), 5.40 (s, 1H), 5.06 (s, 1H), 4.94 (s, 1H), 4.85 (s, 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $(C_{29}H_{30}O_2)[M+Na]^+$: 433.2138. Found: 433.2139.

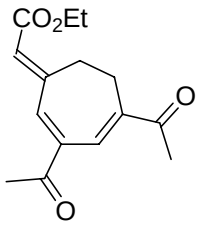


(*E*)-1-Ethoxycarbonylmethylene-3,5-(di-1-octenyl)-2,4-cycloheptadiene (3d): purified by silica gel column chromatography (hexane/ether 30:1); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 6.16-5.83 (m, 6H), 5.64 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.14-3.11 (m, 2H), 2.46-2.43 (m, 2H), 2.13 (quint, *J* = 6.8 Hz, 4H), 1.40-1.23 (m, 19H), 0.89-0.85 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $(C_{27}H_{42}O_2)[M+Na]^+$: 421.3077. Found: 421.3079.



(*E*)-1-Ethoxycarbonylmethylene-3,5-[di-1-hexyl-(2*E*)-perfluorohexyletenyl]-2,4-cycloheptadiene (3e): purified by silica gel column chromatography (hexane/AcOEt 30:1); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 166.4, 159.5 (t, $^3J_{CF}$ = 5 Hz), 155.4 (t, $^3J_{CF}$ = 5 Hz), 150.1, 143.1, 134.4, 124.6, 119.9, 114.3 (t, $^2J_{CF}$ = 23 Hz), 112.8 (t, $^2J_{CF}$ = 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 $C_{39}H_{40}F_{26}O_2$: C, 45.27; H, 3.90. Found: C, 45.08; H, 3.89.

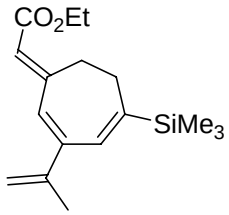


(*E*)-1-Ethoxycarbonylmethylene-3,5-(di-1-oxoethyl)-2,4-cycloheptadiene (4g): purified by silica gel column chromatography (hexane/AcOEt 3:1); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.57 (s, 1H), 7.31 (s, 1H), 6.03 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.09-3.05 (m, 2H), 2.64-2.61 (m, 2H), 2.47 (s, 3H), 2.42 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 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 $(C_{15}H_{18}O_4)[M+Na]^+$: 285.1097. Found: 285.1056.

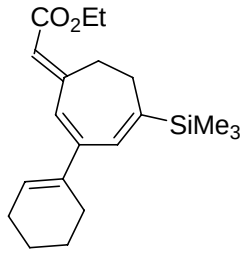
Nickel(0)-Catalyzed Three-Component Cycloaddition of Ethyl Cyclopropylideneacetate (1), Conjugated Enynes and (Trimethylsilyl)acetylene (5) (Table 2). A Representative Procedure. To a dark red mixture of $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in dry toluene (0.5 mL) was added dropwise a solution of **1** (126 mg, 1 mmol), **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 $Ni(PPh_3)_2Br_2$-Zn-PPh_3 System (entry 2, Table 2). A mixture of $Ni(PPh_3)_2Br_2$ (372 mg, 0.5 mmol), PPh_3 (262 mg, 1 mmol), and Zn dust (654 mg, 10 mmol) in dry toluene

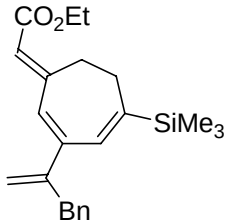
(2.5 mL) was stirred at room temperature over 1 h and changed color from green to dark red. To this mixture was added dropwise a solution of **1a** (630 mg, 5 mmol), **2a** (0.48 mL, 5 mmol), and **5** (2.1 mL, 15 mmol) in dry toluene (2.5 mL) at room temperature for 5 h under Ar. The mixture was stirred 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 (hexnane/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/CH_2Cl_2 3:1); pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 ($C_{17}H_{26}O_2Si$)[M+Na]$^+$: 313.1594. Found: 313.1594.

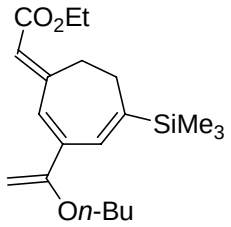


(*E*)-1-Ethoxycarbonylmethylene-3-(1-cyclohexenyl)-5-trimethylsilyl-2,4-cycloheptadiene (6b): purified by silica gel column chromatography (hexane/AcOEt 30:1); pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 6.30 (s, 1H), 5.91 (t, *J* = 4.0 Hz, 1H), 5.67 (s, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.07-3.03 (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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 ($C_{20}H_{30}O_2Si$)[M+Na]$^+$: 353.1907. Found: 353.1907.

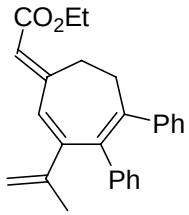


(*E*)-1-Ethoxycarbonylmethylene-3-(1-benzylethenyl)-5-trimethylsilyl-2,4-cycloheptadiene (6c): purified

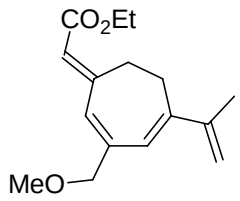
by silica gel column chromatography (hexane/AcOEt 25:1 and hexane/CH_2Cl_2 3:1); pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.28-7.13 (m, 5H), 6.34 (s, 1H), 6.26 (s, 1H), 5.58 (s, 1H), 5.23 (d, *J* = 1.3 Hz, 1H), 4.98 (d, *J* = 1.3 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.59 (s, 2H), 3.02-2.98 (m, 2H), 2.25-2.22 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 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 ($C_{22}H_{20}O$)[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; ^{1}H NMR (300 MHz, C_6D_6) 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, 7.3 Hz, 6.3 Hz, 2H), 1.31 (qt, 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); ^{13}C NMR (125 MHz, C_6D_6) 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 ($C_{20}H_{32}O_3Si$)[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/CH_2Cl_2 2:1); pale yellow solid; mp 86-87 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{26}H_{26}O_2$: C, 84.29; H, 7.07. Found: C, 84.15; H, 7.13.

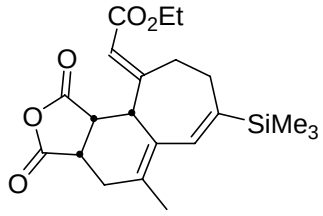


(*E*)-1-Ethoxycarbonylmethylene-3-methoxymethyl-5-(1-methylethenyl)-2,4-cycloheptadiene (10): purified by silica gel column chromatography (hexane/AcOEt 10:1); pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 6.29 (s, 1H), 6.00 (s, 1H), 5.66 (s, 1H), 5.23 (s, 1H), 5.06 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 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 $(C_{16}H_{22}O_3)[M+Na]^+$: 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**.

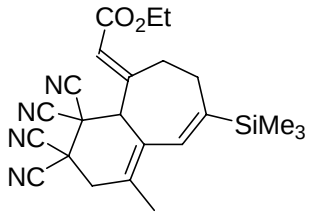
Diels-Alder Reaction of 5a and 6 in the presence of $TiCl_2$(O*i*-Pr)$_2$. A Representative Procedure. To a mixture of **6a** (145 mg, 0.5 mmol) and **11** (0.75 mmol) in toluene (2 mL) was added a solution of $TiCl_2$(O*i*-Pr)$_2$ (1.2 mL, 0.5 M in toluene, 0.6 mmol) at rt. After the reaction completed, 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 Ni(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%).

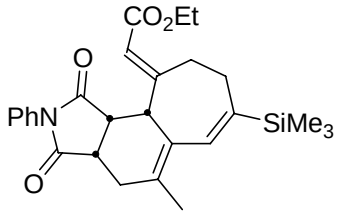


***endo*-12a:** purified by silica gel column chromatography (hexane/AcOEt 3:1); white solid; mp 67-68 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 6.39 (s, 1H), 5.92 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.61 (dd, *J* = 9.8, 5.8 Hz, 1H), 3.44 (ddd, *J* = 9.8, 6.7, 2.4 Hz, 1H), 3.32 (m, 1H), 3.04-2.99(m, 1H), 2.83-2.78 (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,

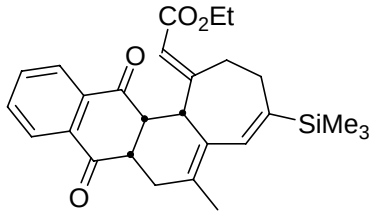
20.4, 14.2, -1.9; IR (KBr) 2955, 1844, 1779, 1704, 1650, 1248, 1179, 992, 937, 837 cm^{-1}. HR-MS (EI) Calcd for $C_{21}H_{28}O_5Si$: 388.1706. Found: 388.1714.



12b: purified by silica gel column chromatography (hexane/AcOEt 8:1); colorless solid; mp 156-158 °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 $C_{23}H_{26}N_4O_2Si$: C, 66.00; H, 6.26; N, 13.39. Found: C, 65.97; H, 6.26; N, 13.19.

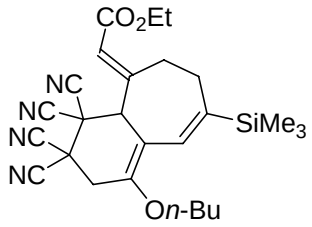


***endo*-12c:** purified by silica gel column chromatography (CH_2Cl_2/ether 20:1); white amorphous; mp 59-61 °C; ^1H NMR (300 MHz, $CDCl_3$) 7.45-7.16 (m, 5H), 6.47 (s, 1H), 5.97 (s, 1H), 4.13 (qd, *J* = 7.2, 1.3 Hz, 2H), 3.54-3.49 (m, 2H), 3.33-3.27 (m, 1H), 3.05-2.99 (m, 1H), 2.93-2.85 (m, 1H), 2.71 (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 $C_{27}H_{33}NO_4Si$: C, 69.94; H, 7.17; N, 3.02. Found: C, 69.71; H, 7.27; N, 3.06.

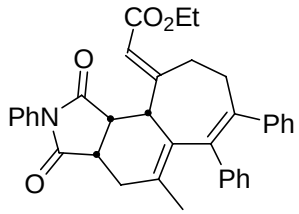


***endo*-12d:** purified by silica gel column chromatography (hexane/AcOEt 10:1); white solid; mp 141-142 °C; ^1H NMR (500 MHz, $CDCl_3$) 8.01-7.99 (m, 1H), 7.89-7.88 (m, 1H), 7.70-7.68 (m, 2H), 6.34 (s, 1H), 5.58 (s, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 3.80 (t, *J* = 5.2 Hz, 1H), 3.58-3.49 (m, 2H), 3.30 (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,

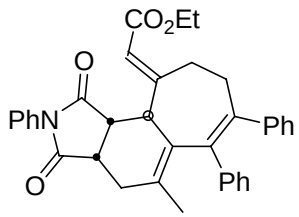
132.9, 130.5, 127.5, 126.8, 126.6, 116.3, 59.4, 55.0, 49.9, 48.5, 34.1, 32.3, 30.6, 20.2, 14.3, -1.8; IR (KBr) 2952, 1713, 1692, 1631, 1594, 1449, 1376, 1285, 1251, 1205, 1165, 1047, 967, 836 cm^{-1}. Anal. Calcd for $C_{27}H_{32}O_4Si$: C, 72.28; H, 7.19. Found: C, 72.05; H, 7.17.



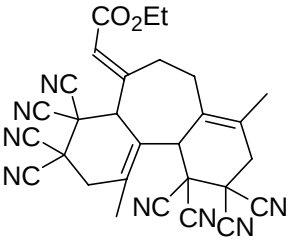
13b: purified by silica gel column chromatography (hexane/AcOEt 10:1); colorless solid; mp 133-134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 6.34 (s, 1H), 6.17 (s, 1H), 4.21 (qd, *J* = 7.2, 3.2 Hz, 2H), 3.97 (s, 1H), 3.82 (m, 2H), 3.64-3.59 (m, 1H), 3.26 (d, *J* = 18.0 Hz, 1H), 3.17 (d, *J* = 18.0 Hz, 1H), 2.67-2.46 (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 $C_{26}H_{32}N_4O_3Si$: C, 65.52; H, 6.77; N, 11.75. Found: C, 65.64; H, 6.79; N, 11.52.



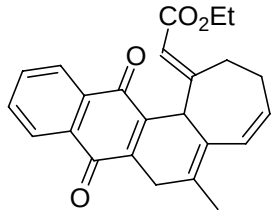
***endo*-14c:** purified by silica gel column chromatography (hexane/AcOEt 2:1); white solid; mp 181-182 °C; ^{1}H NMR (300 MHz, $CDCl_3$ at 50 °C) 7.47-6.83 (m, 15H), 6.33 (bs, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.68-3.62 (m, 1H), 3.64 (dd, *J* = 9.4, 6.3 Hz, 1H) 3.38-3.31 (m, 2H), 2.87-2.52 (m, 5H), 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; ^{1}H 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 $C_{36}H_{33}NO_4$: 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; ^{1}H 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 $C_{36}H_{33}NO_4$: 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.); ^{1}H 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 $C_{29}H_{22}N_8O_2$: 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; ^{1}H 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 $C_{24}H_{22}O_4$: 374.1518. Found: 374.1518.

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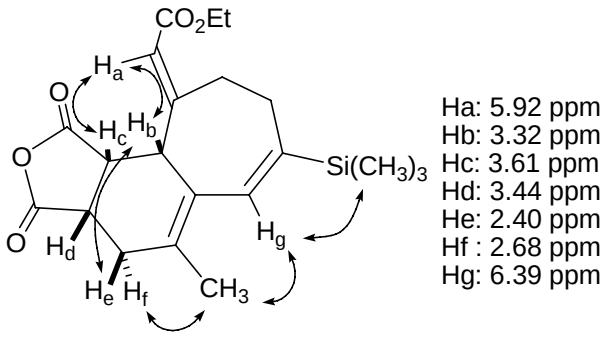


Figure S1. A NOESY experiment of **12a**.

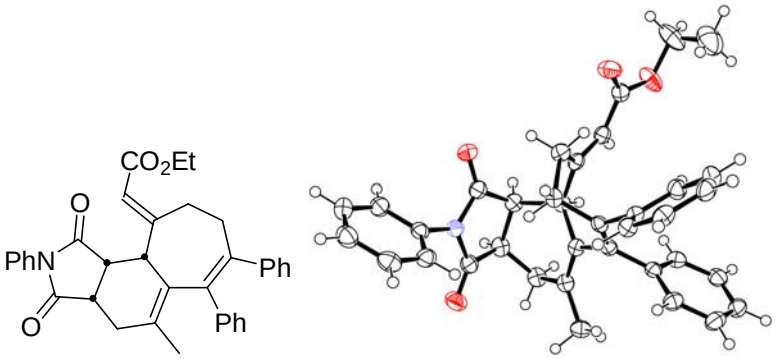


Figure S2. An ORTEP view of *endo*-**14c**. Crystal data for *endo*-**14c**: $C_{36}H_{33}NO_4$; M = 543.63 g mol^{-1}, monoclinic, $P2_1/c$, colorless prism measuring 0.40 × 0.30 × 0.30 mm, T = 150 K, a = 11.818 (1), b = 8.5654(7), c = 28.864(3) Å, β = 101.646(1)°, V = 2861.5 (4) Å^3, Z = 4, D_c = 1.262 Mg m^{-3}, μ(CuKα) = 0.082 mm^{-1}, T_{max} = 0.9759, T_{min} = 0.9681, *GOF* 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).

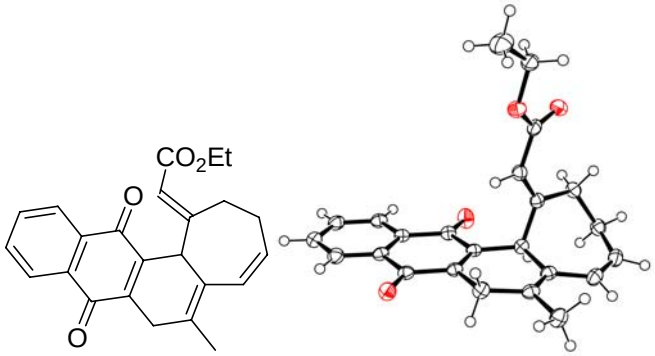
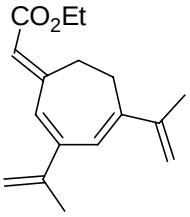
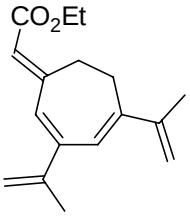


Figure S3. An ORTEP view of **16d**. Crystal data for **16d**: $C_{24}H_{22}O_4$; M = 374.42 g mol^{-1}, monoclinic, $P2_1/n$, colorless prism measuring 0.30 × 0.10 × 0.10 mm, T = 120 K, a = 8.319(3), b = 15.649(5), c = 14.325(4) Å, β = 93.669(2)°, V = 1861(1) Å^3, Z = 4, D_c = 1.336 Mg m^{-3}, μ(CuKα) = 0.090 mm^{-1}, T_{max} = 0.9910, T_{min} = 0.9734, GOF 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).

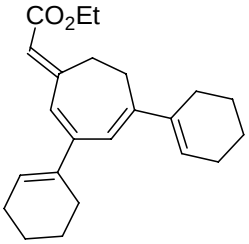
^{1}H NMR spectrum of 3a



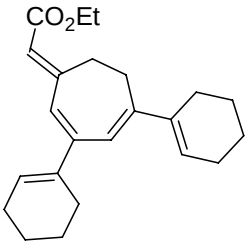
^{13}C NMR spectrum of 3a



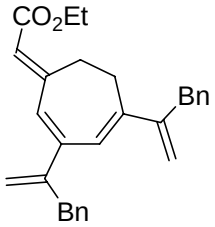
^{1}H NMR spectrum of 3b



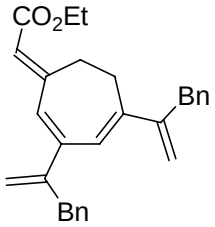
^{13}C NMR spectrum of 3b

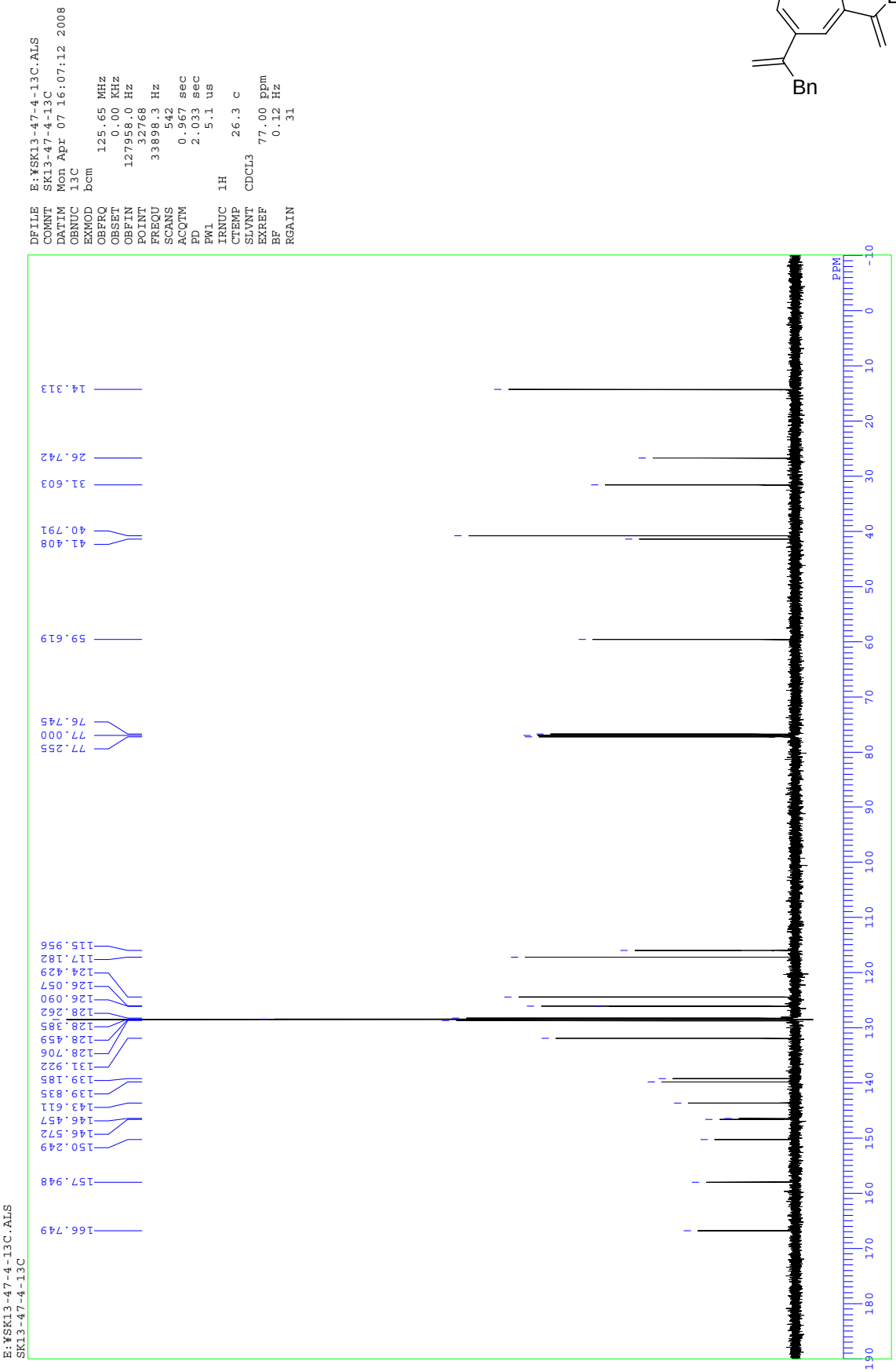


^{1}H NMR spectrum of 3c

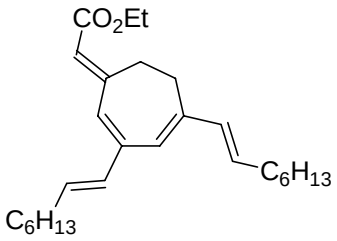


^{13}C NMR spectrum of 3c

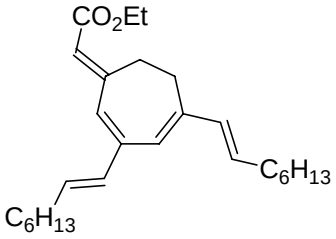




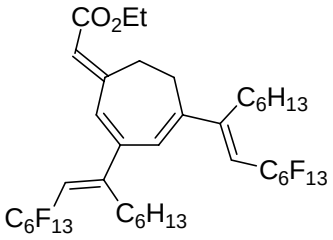
^{1}H NMR spectrum of 3d



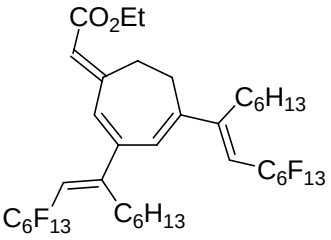
^{13}C NMR spectrum of 3d



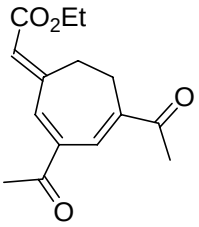
^{1}H NMR spectrum of 3e



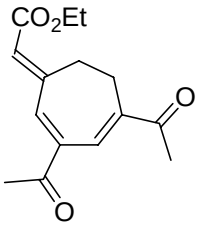
^{13}C NMR spectrum of 3e



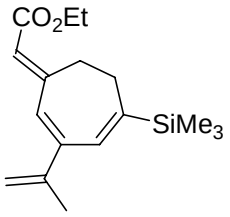
^{1}H NMR spectrum of 4g



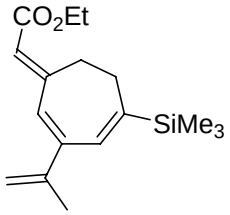
^{13}C NMR spectrum of 4g

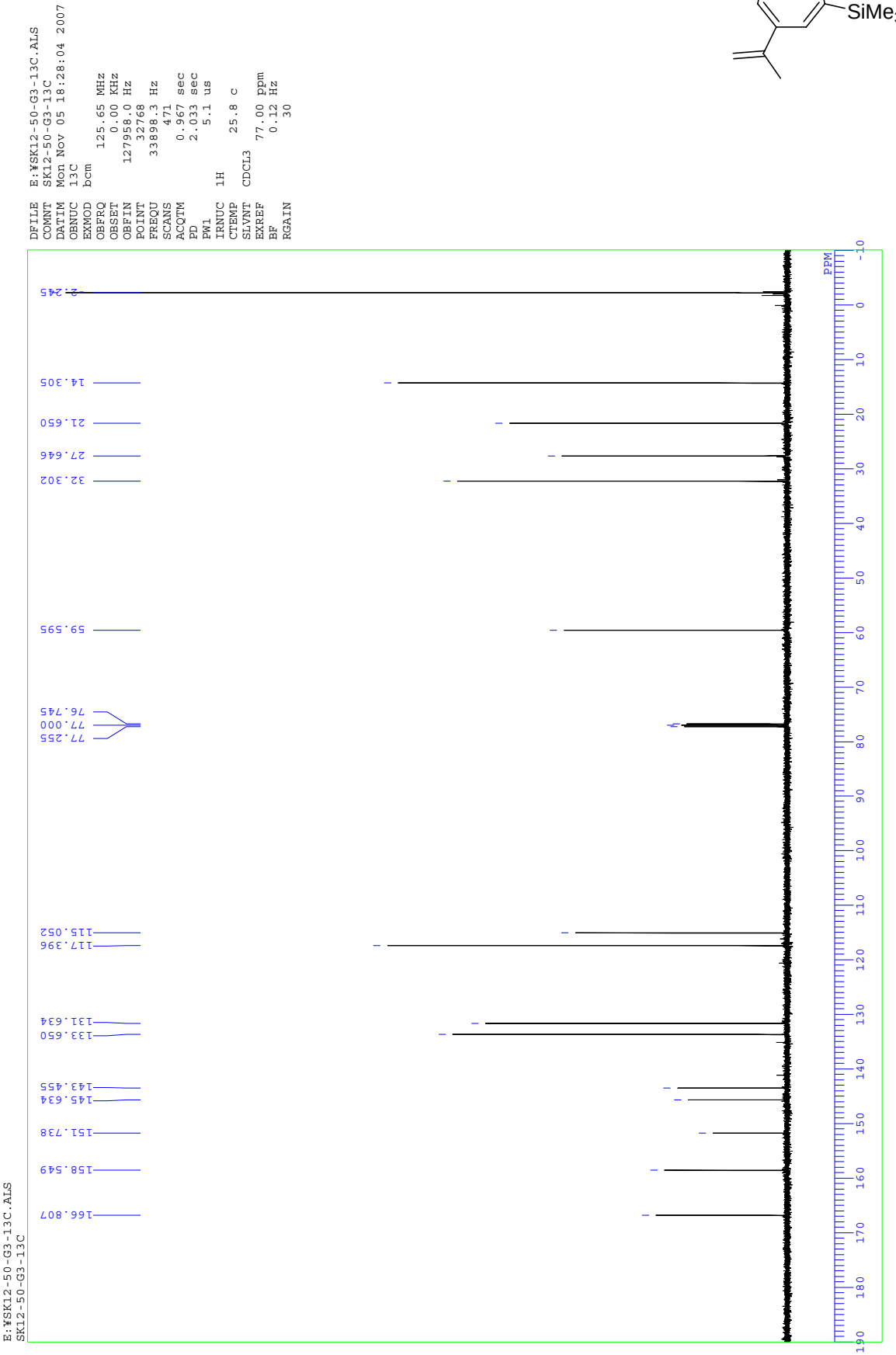


^{1}H NMR spectrum of 6a

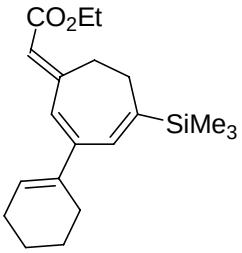


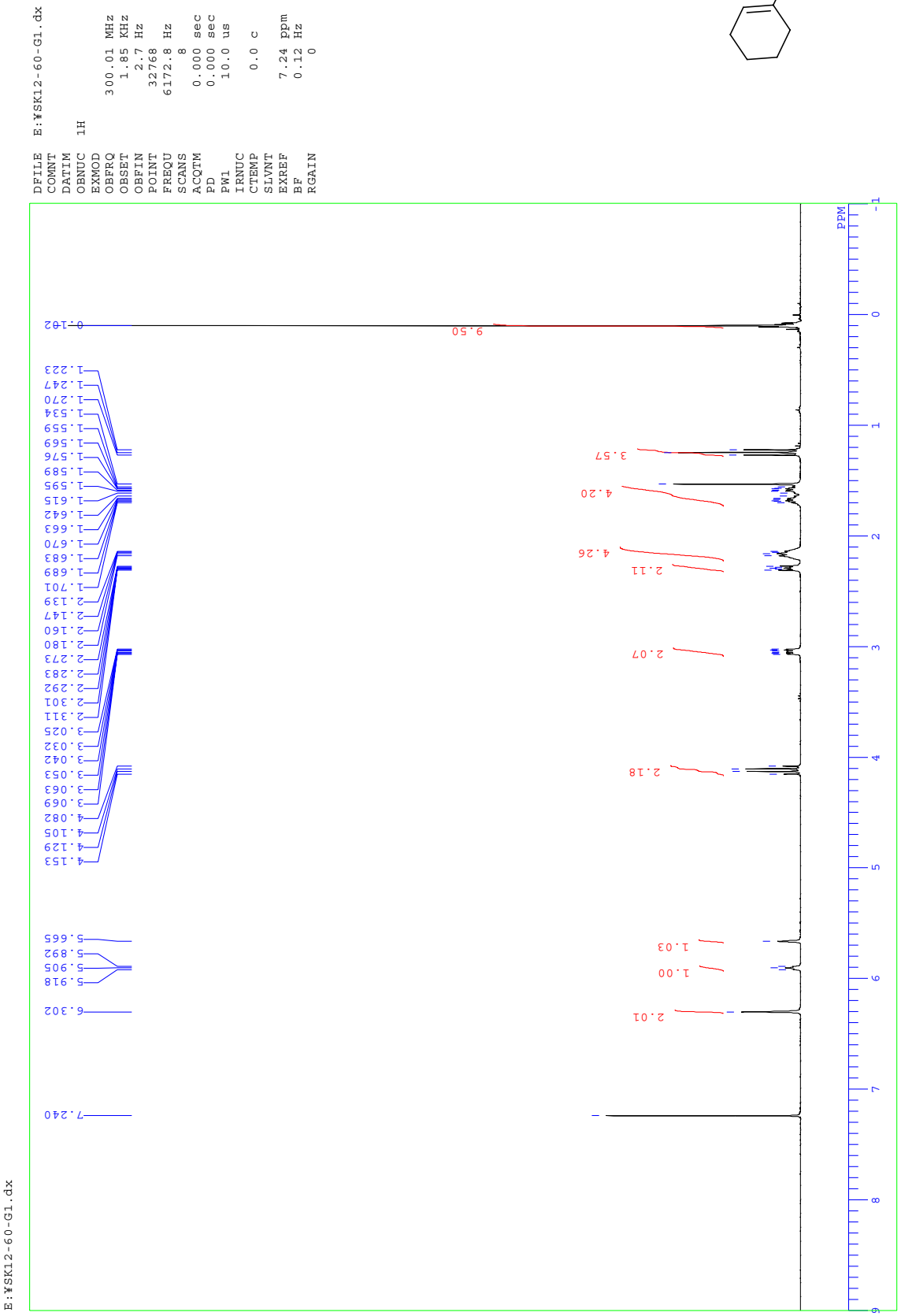
^{13}C NMR spectrum of 6a



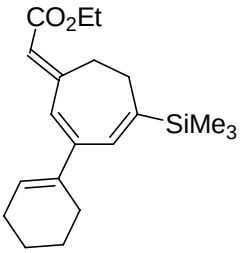


^{1}H NMR spectrum of 6b

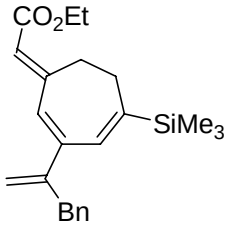




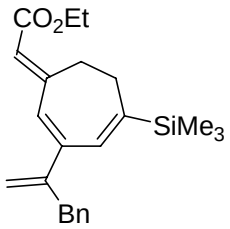
^{13}C NMR spectrum of 6b



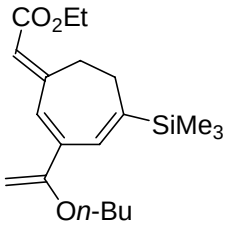
^{1}H NMR spectrum of 6c



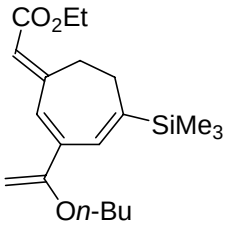
^{13}C NMR spectrum of 6c



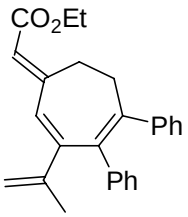
^{1}H NMR spectrum of 6g

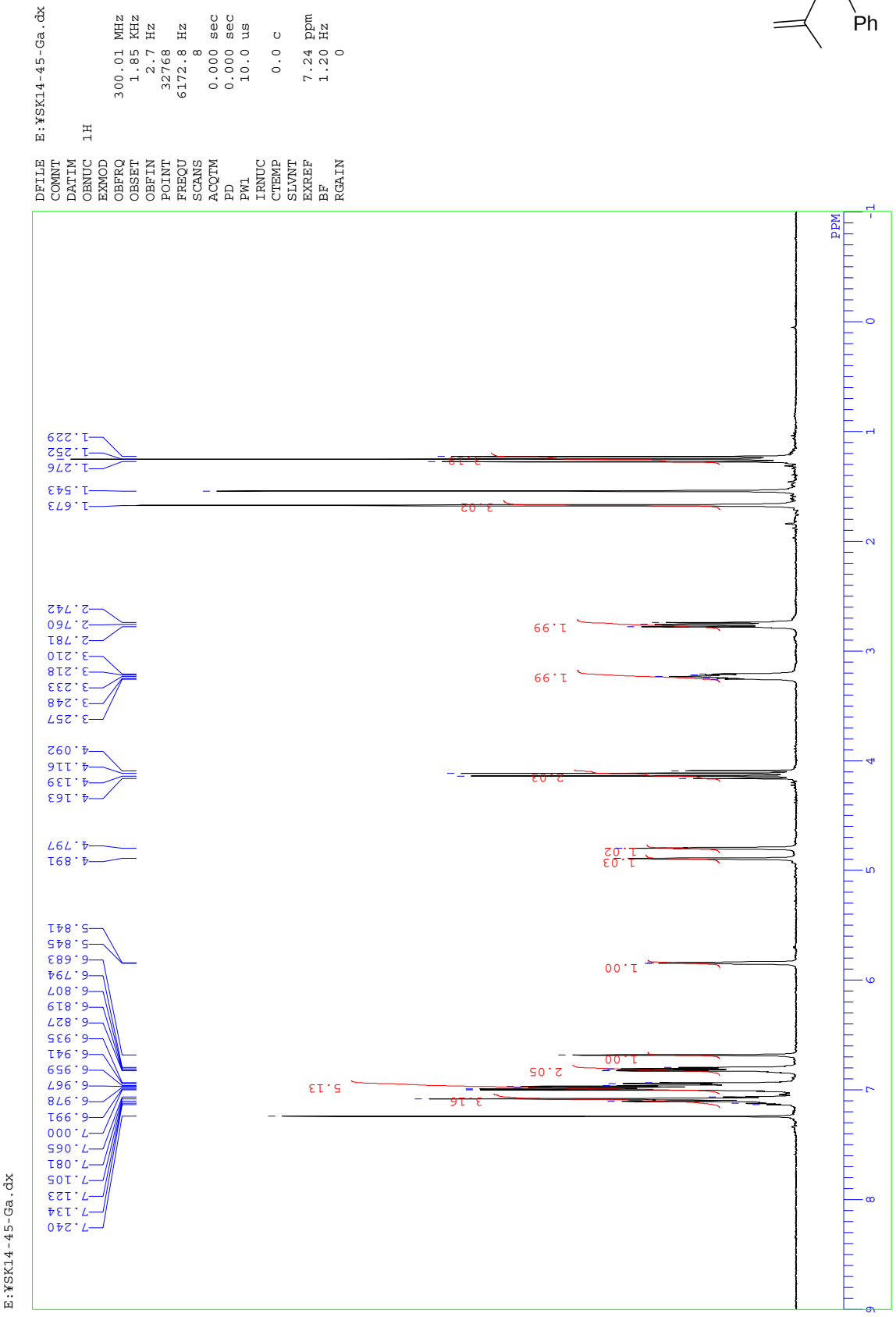


^{13}C NMR spectrum of 6g

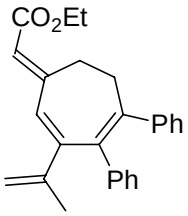


^{1}H NMR spectrum of 8

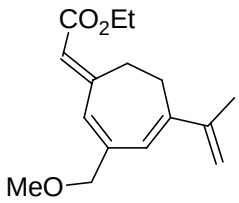


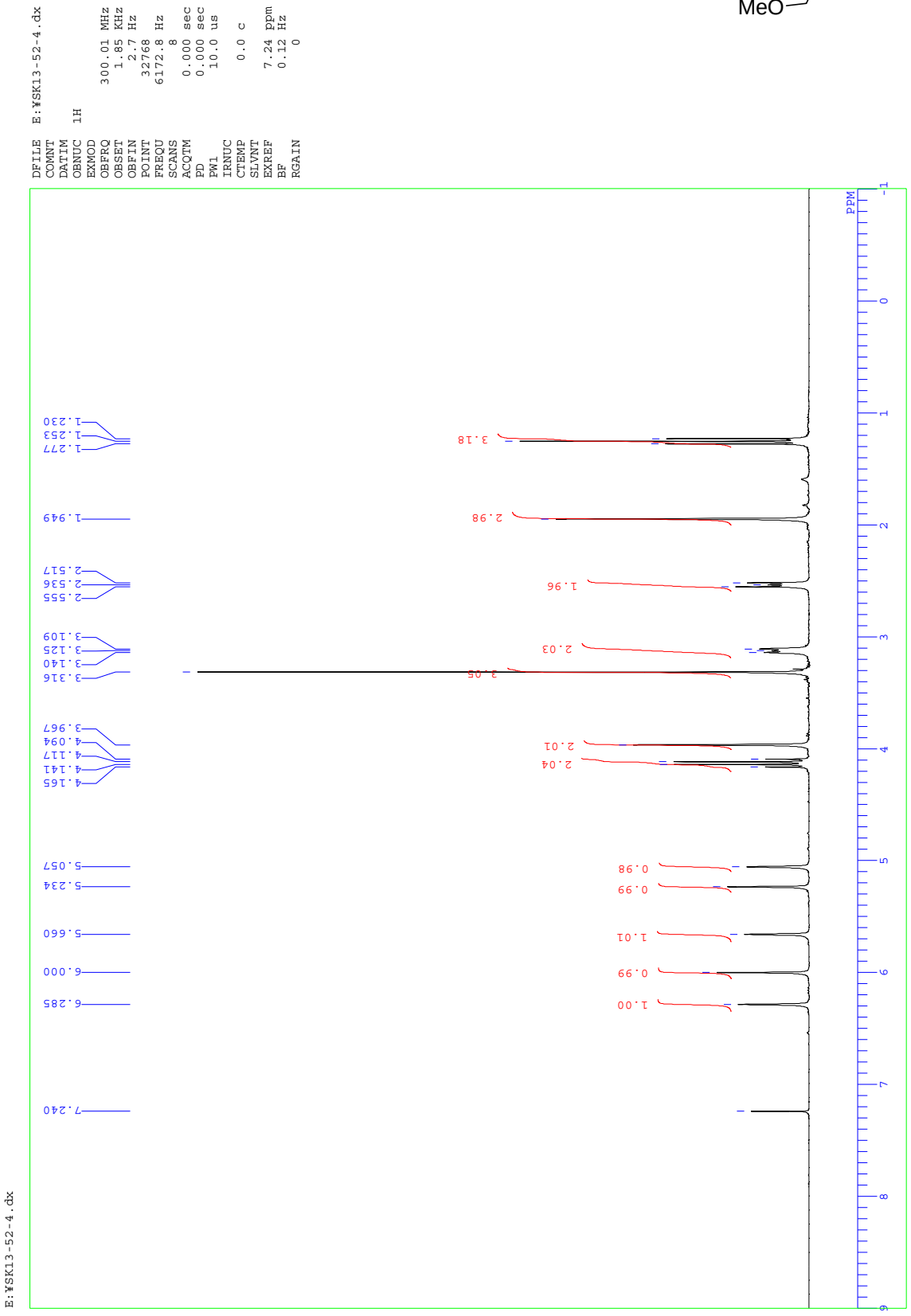


^{13}C NMR spectrum of 8

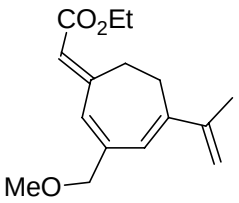


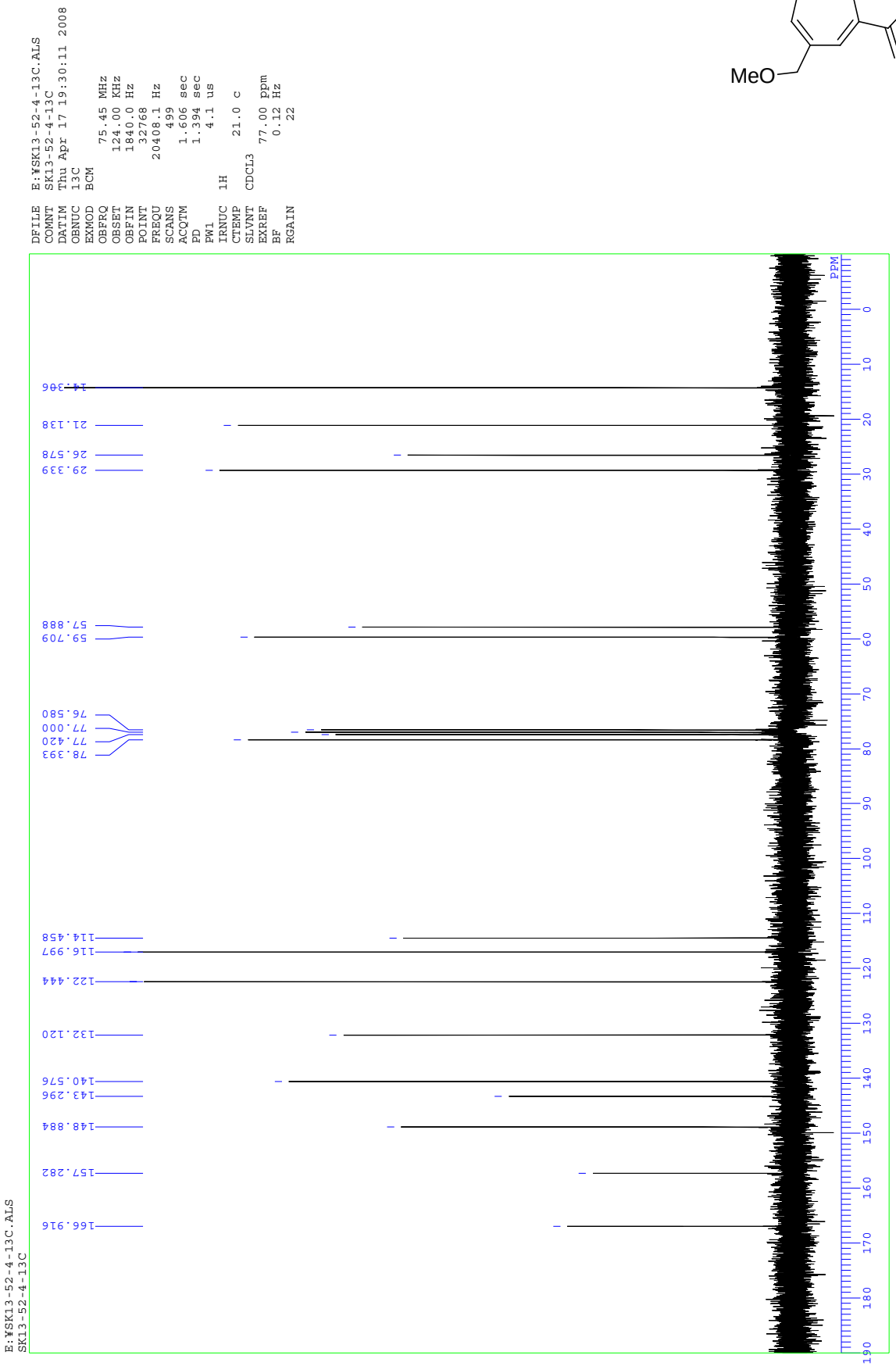
^{1}H NMR spectrum of 10



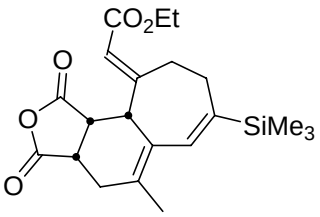


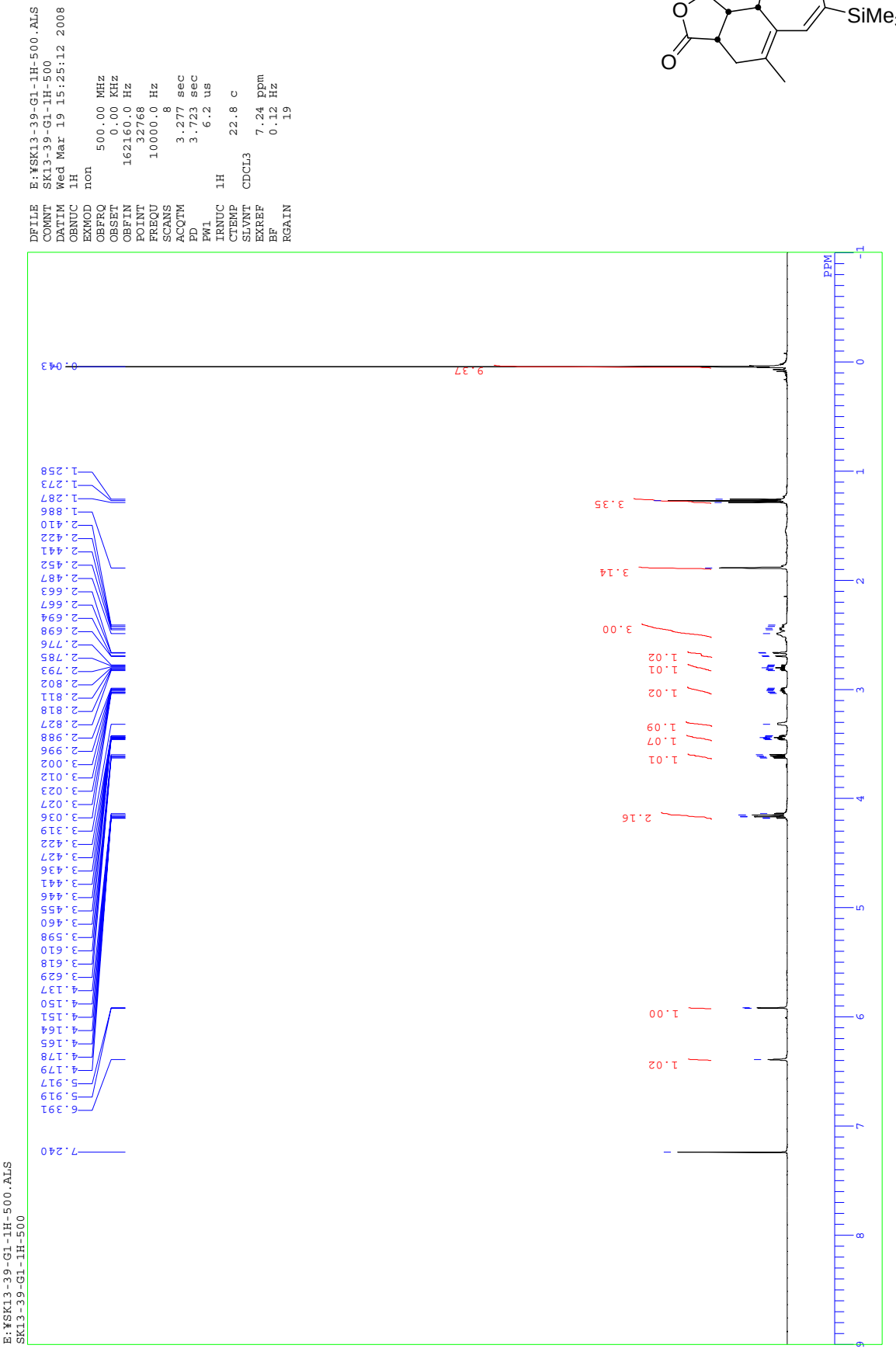
^{13}C NMR spectrum of 10



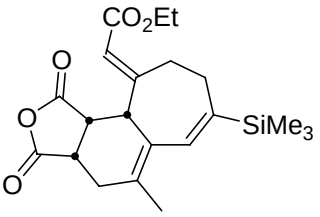


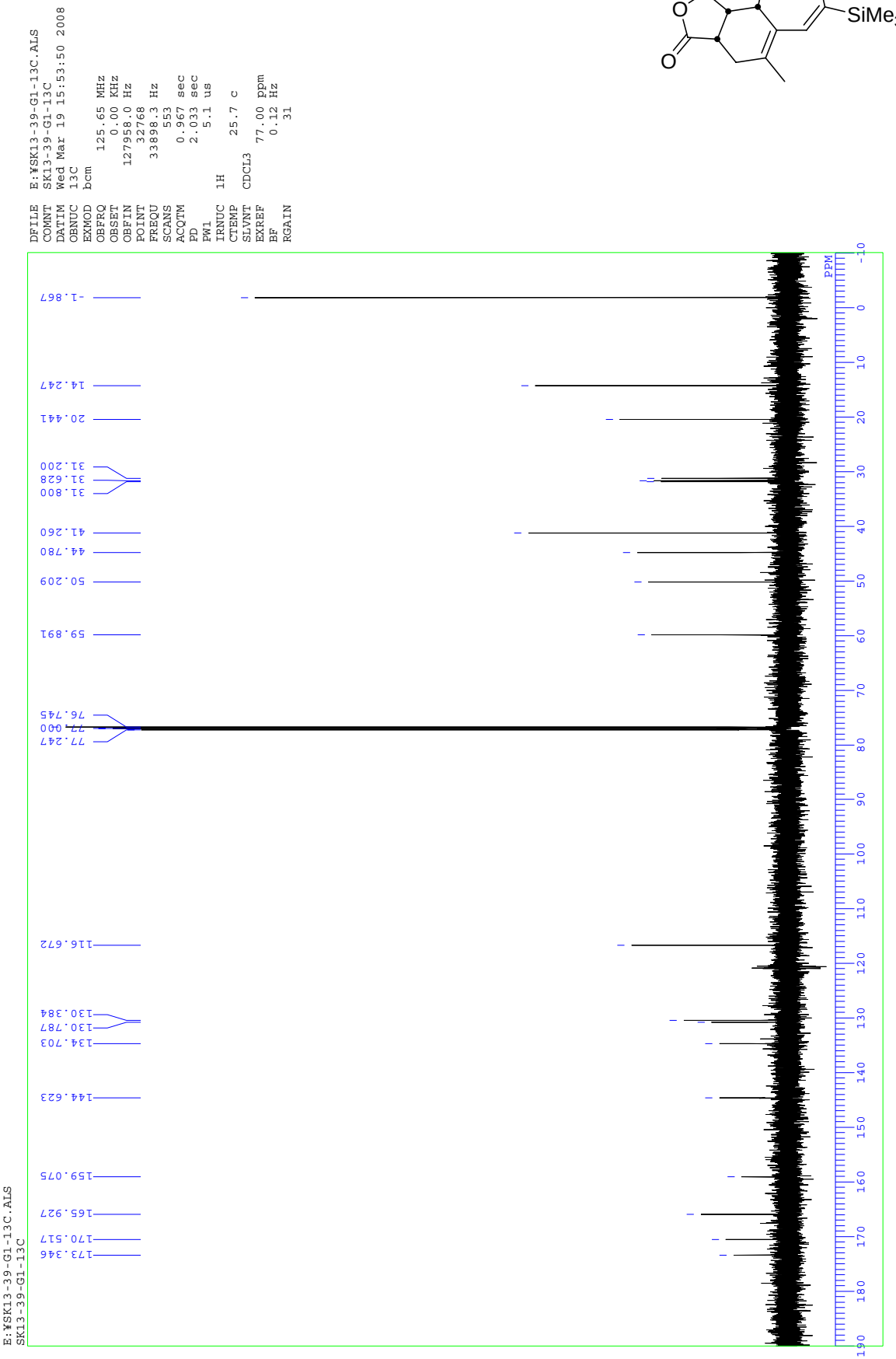
^{1}H NMR spectrum of *endo*-12a



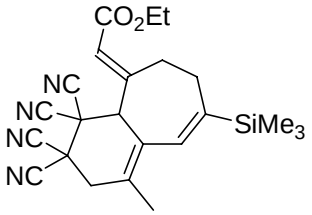


^{13}C NMR spectrum of *endo*-12a

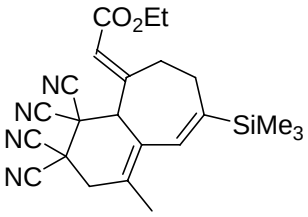




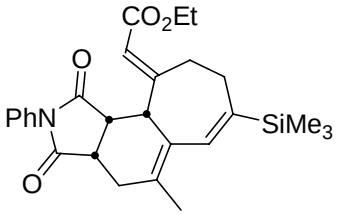
^{1}H NMR spectrum of 12b



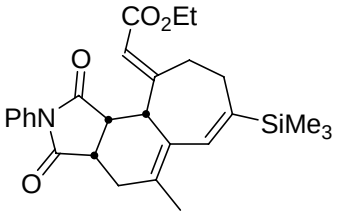
^{13}C NMR spectrum of 12b



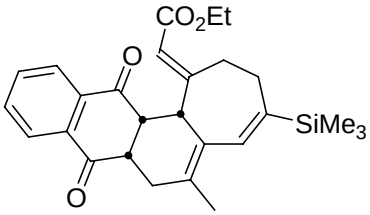
^{1}H NMR spectrum of *endo*-12c



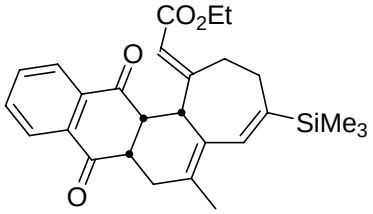
^{13}C NMR spectrum of *endo*-12c



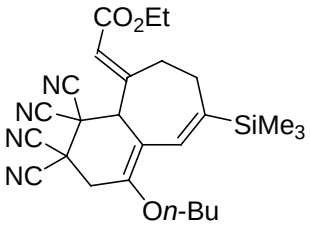
^{1}H NMR spectrum of *endo*-12d



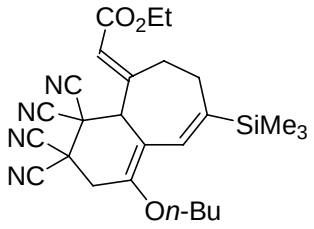
^{13}C NMR spectrum of *endo*-12d



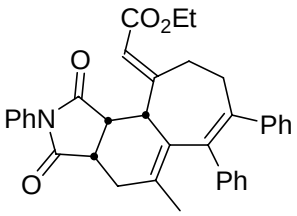
^{1}H NMR spectrum of 13b

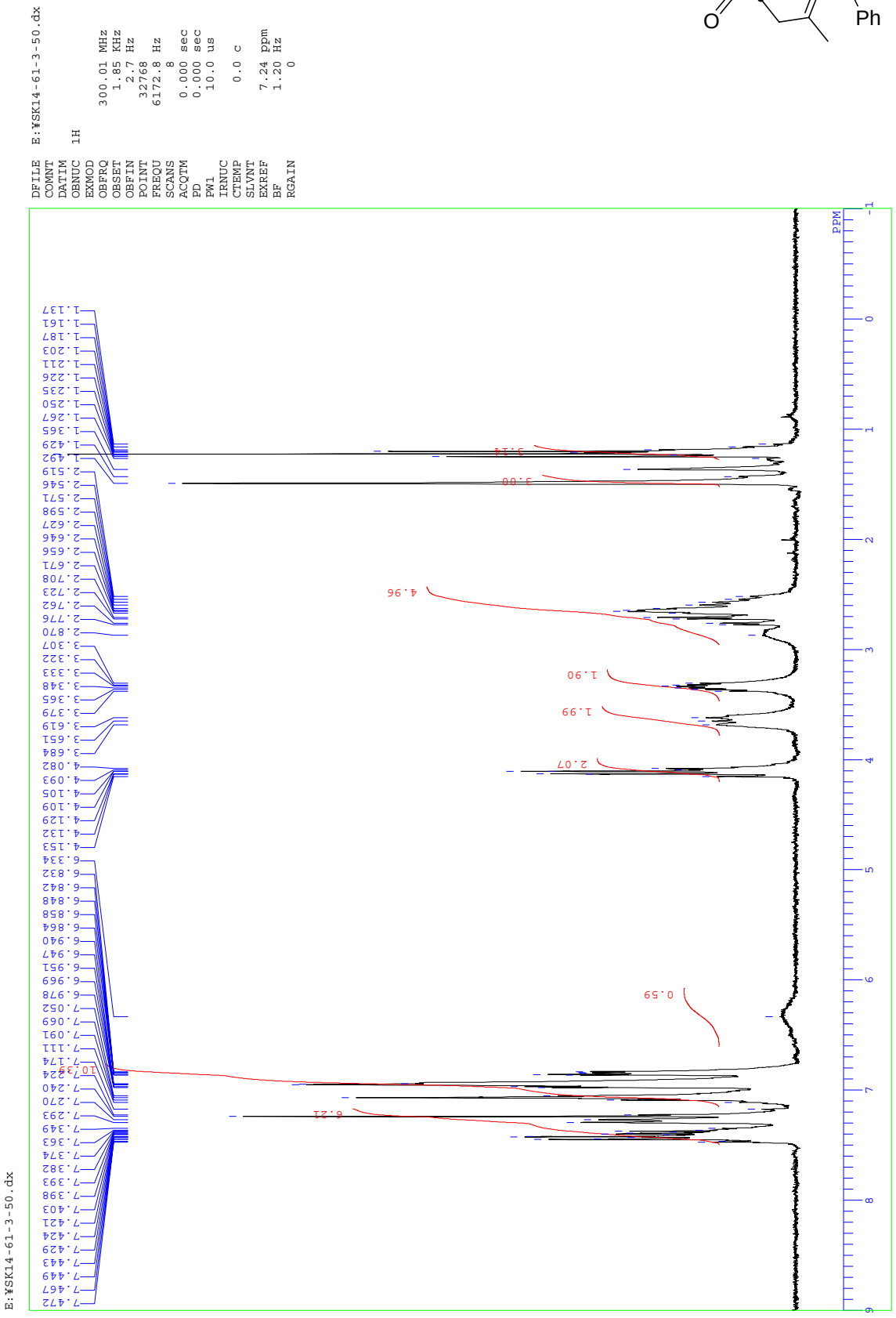


^{12}C NMR spectrum of 13b

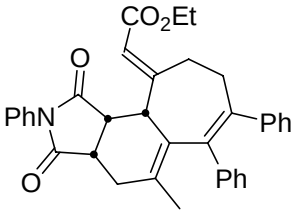


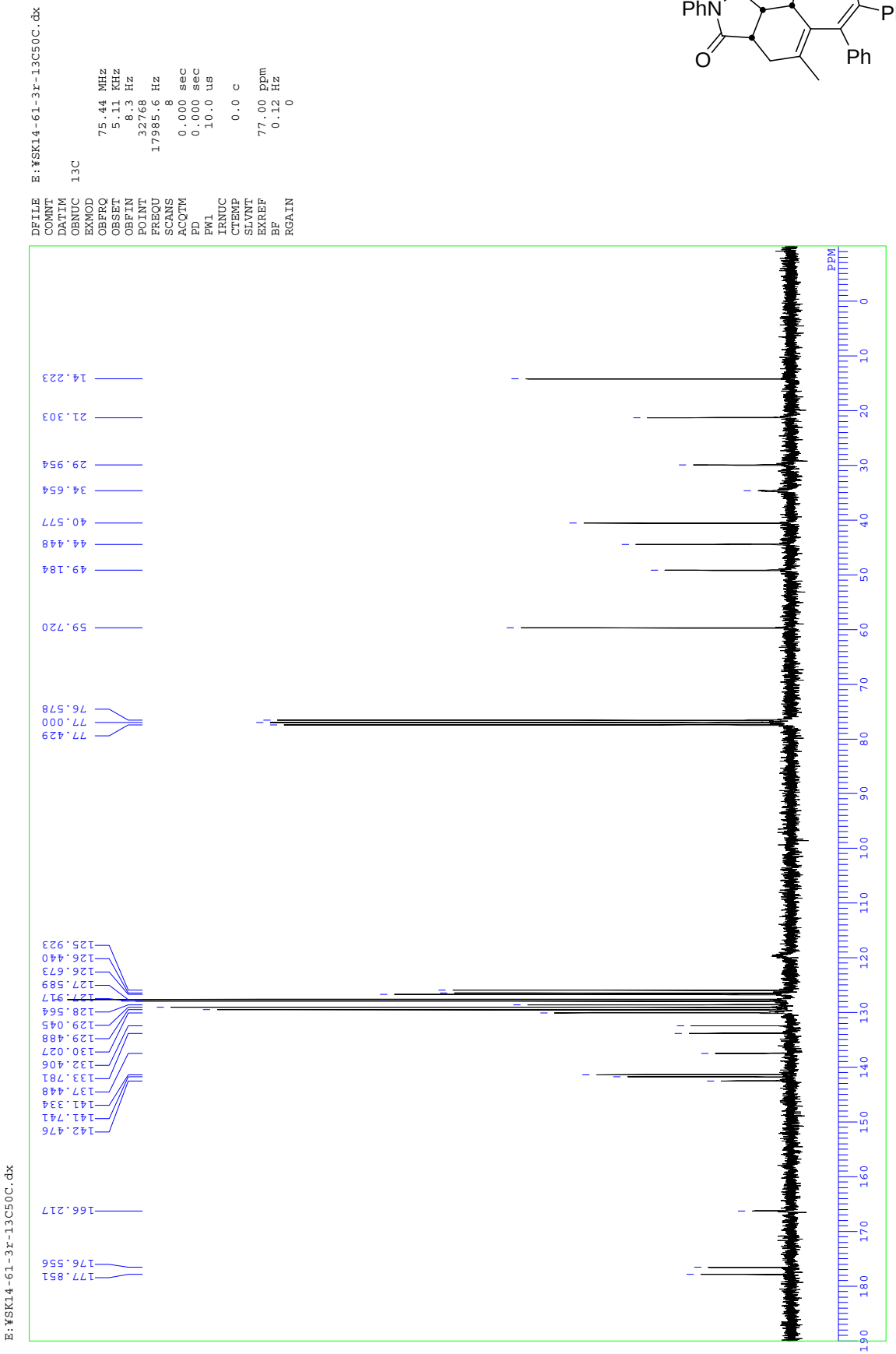
^{1}H NMR spectrum of *endo*-14c ($CDCl_3$, at 50 °C)



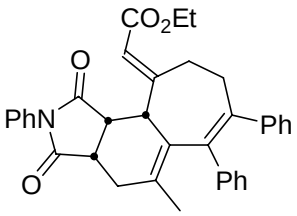


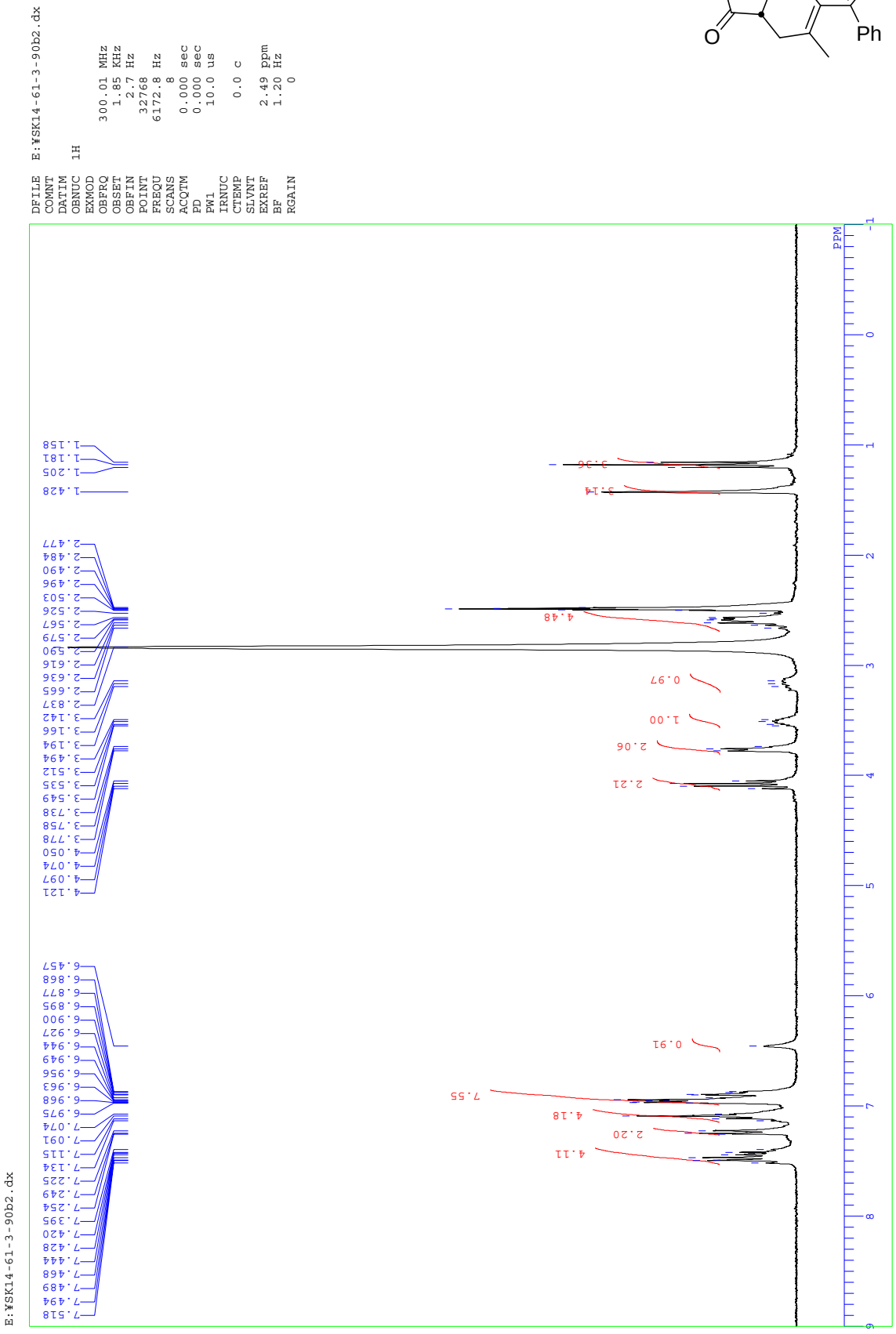
^{12}C NMR spectrum of *endo*-14c ($CDCl_3$, at 50 °C)



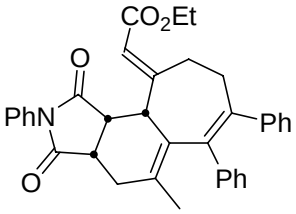


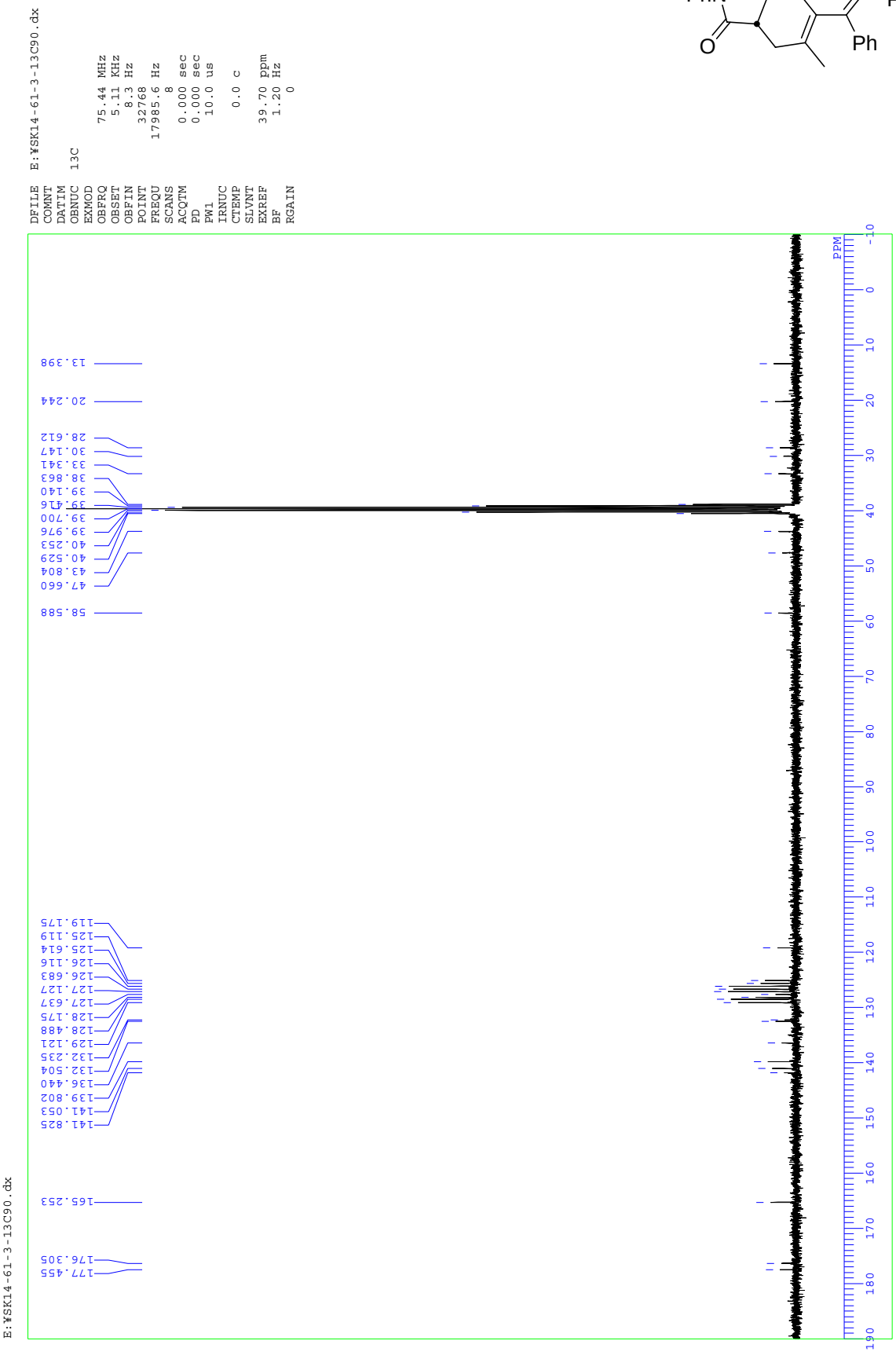
^{1}H NMR spectrum of *endo*-14c (DMSO-d_6, at 90 °C)



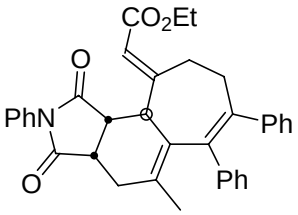


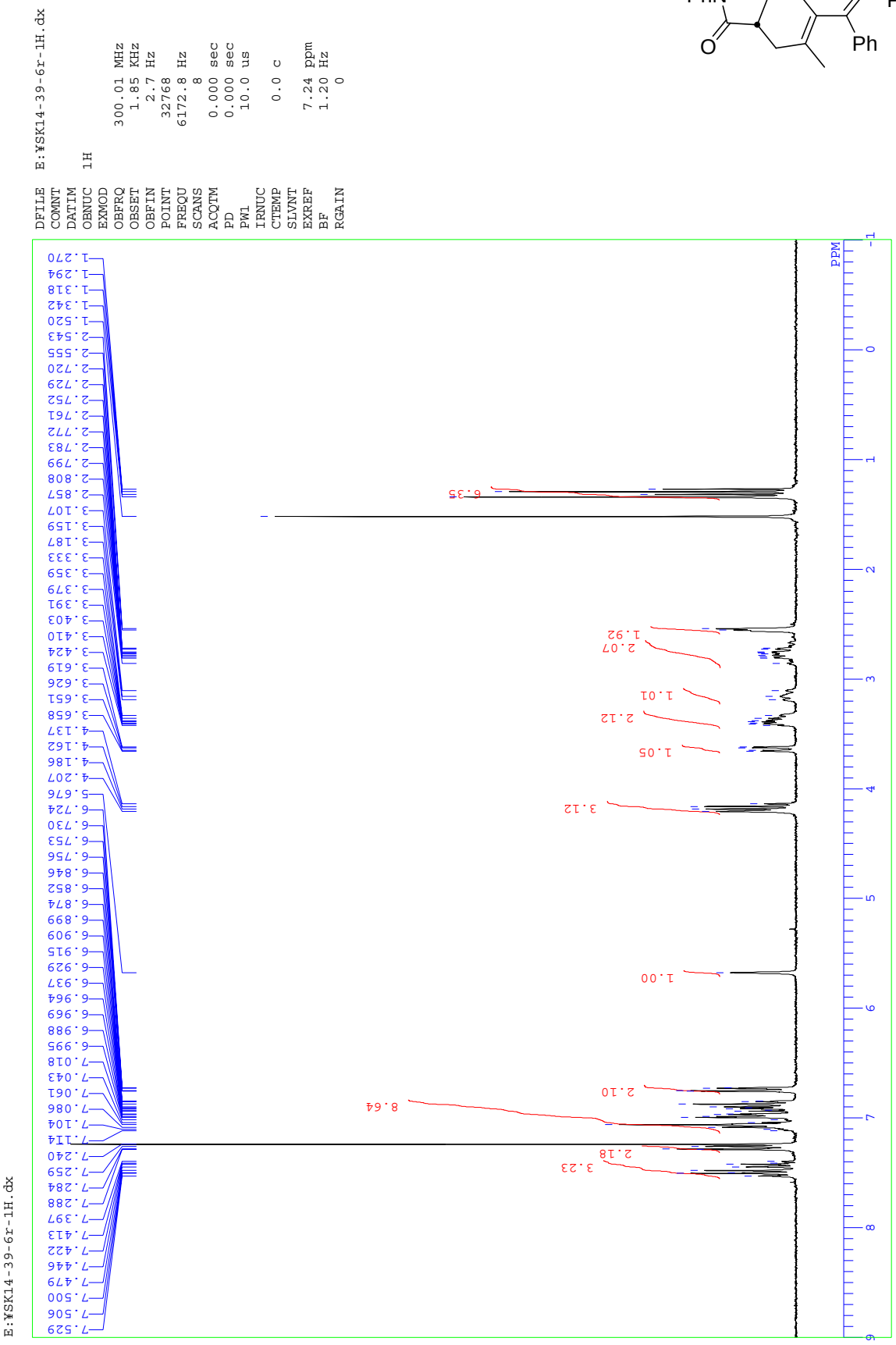
^{12}C NMR spectrum of *endo*-14c (DMSO-d_6, at 90 °C)



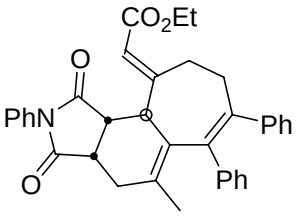


^{1}H NMR spectrum of *exo*-14c

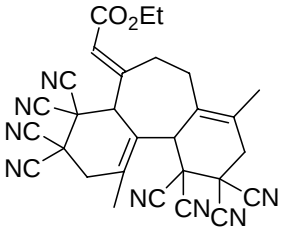




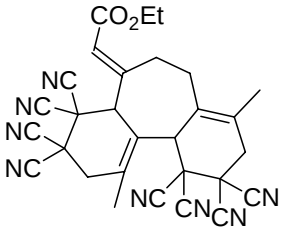
^{12}C NMR spectrum of *exo*-14c



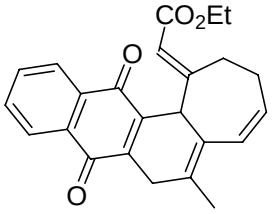
^{1}H NMR spectrum of 15b

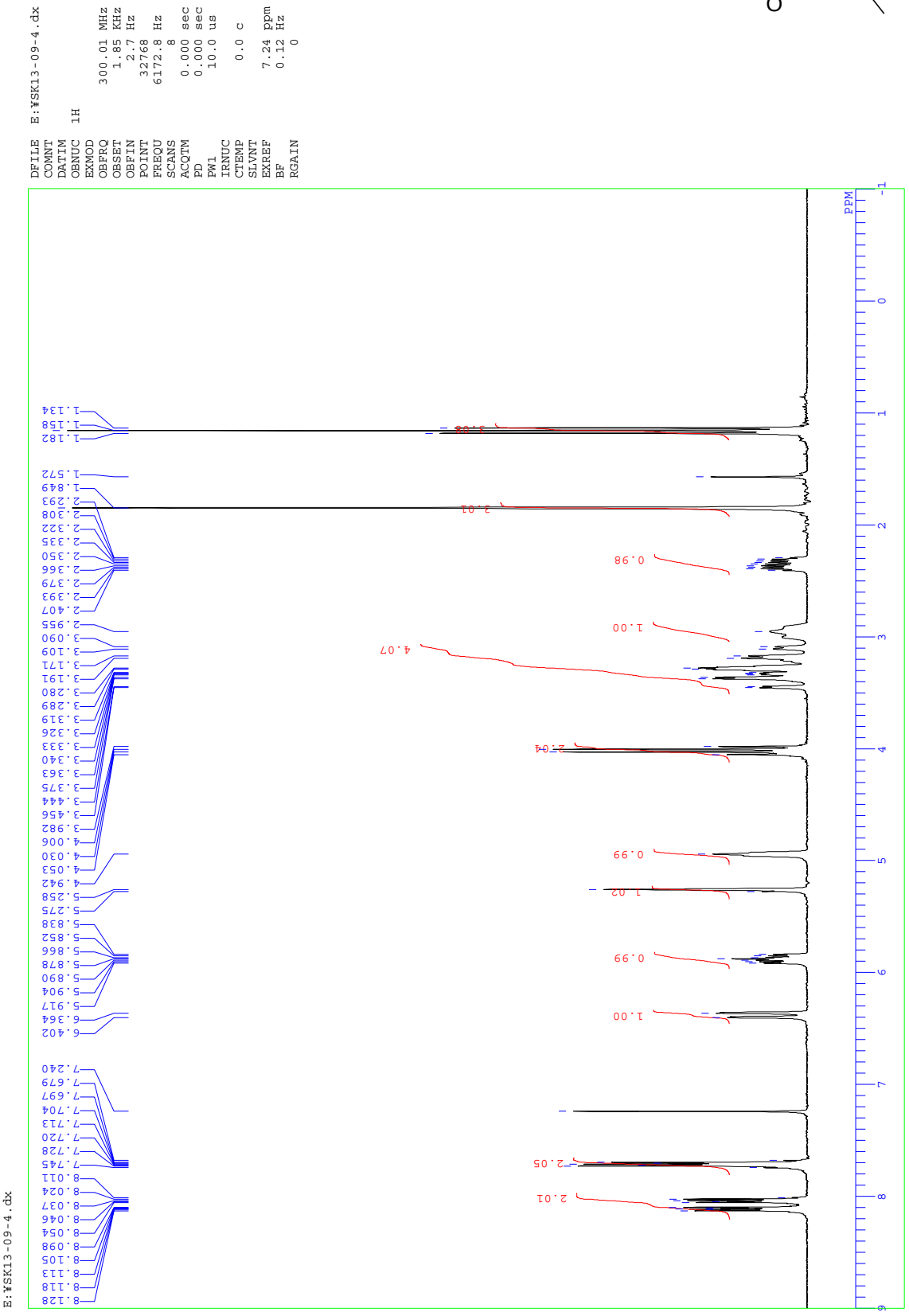


^{13}C NMR spectrum of 15b

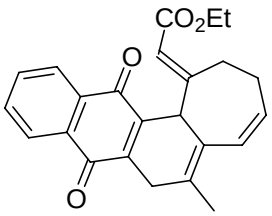


^{1}H NMR spectrum of 16d





^{13}C NMR spectrum of 16d



NOESY spectrum of *endo*-12a