Electronic Supporting Information

Generation of molecular complexity from cyclooctatetraene using dienyliron and olefin metathesis methodology

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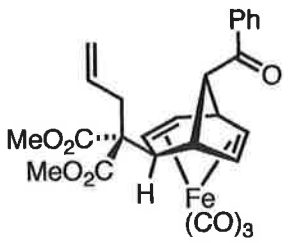
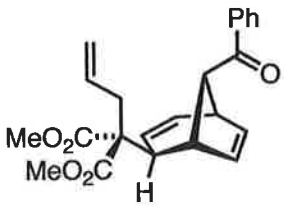
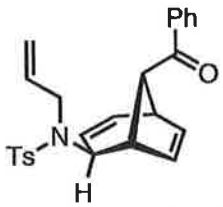


Tricarbonyl[1,3-dimethyl 2-[(3,4,6,7-η^4)-8-benzoylbicyclo[3.2.1]octa-3,6-dien-2-yl]-2-(2-propen-1-yl)propanedioate]iron. To a solution of sodium dimethyl allylmalonate, freshly prepared from dimethyl allylmalonate (0.157 g, 0.809 mmol) and excess NaH in THF (15 ml), at 0 °C under N_2 was added solid cation **2** (0.200 g, 0.404 mmol) and the reaction mixture stirred for 1 h. Water (15 mL) was added and the mixture was extracted several times with ethyl acetate. The combined extracts were dried ($MgSO_4$), concentrated, and the residue was purified by column chromatography (SiO_2, hexane-ethyl acetate = 10:1 to 5:1

gradient elution) to afford a golden-yellow oil (0.200 g, 95%). IR (Neat) 2954, 2033, 1968, 1715, 1681 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.61 (dd, J = 8.6, 14.8 Hz, 1H), 2.73 (m, 1H), 2.80 (dd, J = 6.8, 14.8 Hz, 1H), 3.26 (m, 4H), 3.41 (m, 2H), 3.74 (br m, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 5.08 (d, J = 17.4 Hz, 1H), 5.14 (d, J = 10.2 Hz, 1H), 5.68 (dtd, J = 7.4, 8.6, 15.4 Hz, 1H), 7.49 (m, 2H), 7.59 (m, 1H), 7.87 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.0, 36.5, 37.9, 38.9, 42.8, 52.7, 52.9, 53.5, 57.4, 62.4 (2 signals overlapping), 69.7, 119.8, 128.4, 128.9, 131.9, 133.3, 136.1, 170.9, 172.0, 199.0, 215.0. FAB-HRMS m/z 521.0903 (calcd for $C_{26}H_{25}O_8Fe$ ($M + H^+$) m/z 521.0899).

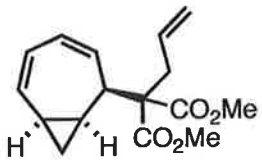


Dimethyl 2-[(3,4,6,7-η⁴)-8-benzoylbicyclo[3.2.1]octa-3,6-dien-2-yl]-2-(2-propen-1-yl)propanedioate (7). To a solution of the above iron complex (0.160 g, 0.307 mmol) in methanol was added cerium ammonium nitrate (0.336 g, 0.614 mmol) in one portion. The reaction mixture was stirred for 1 h at room temperature. Water (20 mL) was added and the mixture was extracted several times with ethyl acetate. The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane–ethyl acetate = 10:1) to afford **7** (0.096 g, 82%) as a colorless oil. IR (Neat) 3058, 3005, 1712, 1362 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.79 (t, J = 2.8 Hz, 1H), 2.84 (m, 2H), 3.17 (m, 2H), 3.31 (s, 1H), 3.63 (s, 3H), 3.71 (s, 3H), 5.09 (m, 2H), 5.52 (td, J = 2.6, 9.8 Hz, 1H), 5.67 (dtd, J = 7.6, 10.1, 17.6 Hz, 1H), 5.88 (dd, J = 3.1, 5.5 Hz, 1H), 5.99 (dd, J = 2.9, 5.6 Hz, 1H), 6.28 (ddd, J = 2.8, 6.5, 9.8 Hz, 1H), 7.43 (m, 2H), 7.52 (m, 1H), 7.91 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 38.1, 41.3, 42.1, 43.7, 52.4 (two signals overlapped), 55.1, 60.9, 119.4, 125.2, 128.5, 128.7, 131.2, 132.3, 132.9, 134.9, 136.1, 136.5, 170.9, 171.1, 199.7. This material was used in the next step without further characterization.



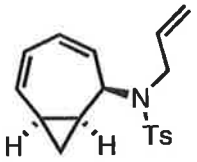
***N*-(8-Benzoylbicyclo[3.2.1]octa-3,6-dien-2-yl)-4-methyl-*N*-2-propen-1-yl-benzenesulfonamide (8).** To a solution of **2** (0.20 g, 0.40 mmol) in acetonitrile (15 mL) under N_2, was added the potassium salt of tosyl allylamine (0.250 g, 1.00 mmol). The mixture was stirred at room temperature for 3 h, at which time monitoring by TLC indicated the disappearance of **2**. The reaction mixture was filtered under vacuum and the filter bed washed with acetonitrile. To the combined filtrates was added cerium ammonium nitrate (0.42 g, 0.77 mmol). The mixture was stirred under nitrogen for 2 h, and then filtered through a short column of silica gel, using

CH_2Cl_2 to complete the elution. The combined filtrates were concentrated and the residue purified by column chromatography (SiO_2, hexanes–ethyl acetate = 4:1) to give **8** (0.117g, 70%) as a colorless solid. mp 137-138 °C; IR (CH_2Cl_2) 1676, 1330, 1157 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 3H), 3.11 (br s, 1H), 3.22 (dd, *J* = 3.0, 6.6 Hz, 1H), 3.88 (s, 1H), 3.98 (dd, *J* = 6.4, 16.8 Hz, 1H), 4.13 (br dd, *J* = 5.0, 16.8 Hz, 1H), 4.27-4.30 (m, 1H), 5.04-5.11 (m, 2H), 5.23 (dd, *J* = 1.2, 17.6 Hz, 1H), 5.86-5.93 (m, 2H), 6.18 (dd, *J* = 3.2, 5.6 Hz, 1H), 6.39 (ddd, *J* = 2.5, 6.4, 9.2 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.55 (tt, *J* = 1.6, 7.6 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.89 (dd, *J* = 1.6, 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 42.9, 47.3, 48.9, 55.3, 57.2, 117.5, 124.6, 127.3, 128.5, 128.8, 129.9, 130.0, 133.1, 135.9, 136.2, 137.9, 138.5, 140.4, 143.6, 199.4. Anal. Calcd for $C_{25}H_{25}NO_3S \cdot ½\ H_2O$: C, 70.07; H, 6.11. Found: C, 70.29; H, 5.90.

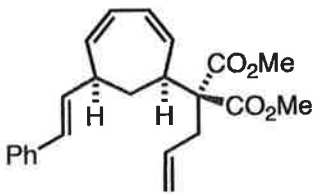


Dimethyl 2-(bicyclo[5.1.0]octa-3,5-dien-2-yl)-2-(2-propen-1-yl)propanedioate (9): To a cold solution of dimethyl allylmalonate (0.25 mL, 1.5 mmol) in dry ether (10 mL) was added a solution of methyl lithium (1.0 mL, 1.6 M in ether, 1.6 mmol). The mixture was stirred for 15 min at room temperature, at which time cation **3** (0.573 g, 1.01 mmol) was added in one portion. After 1 h, the reaction mixture was quenched with water (15 mL). The biphasic solution was extracted several times with ethyl acetate, and the combined extracts were dried ($MgSO_4$) and concentrated to ca. 15 mL. (Complete concentration resulted in spontaneous decomposition of the crude complex to give $(COT)Fe(CO)_2PPh_3$ and dimethyl allylmalonate). The solution of the crude complex was diluted with acetonitrile (10 mL) and CAN (1.186 g, 2.131 mmol) was added in one portion. The solution was stirred for 30 min, poured onto water (25 mL) and extracted several times with ethyl acetate. The combined extractions were washed with water, followed by brine, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate = 30:1) to give **9** (0.186 g, 67%) as a pale yellow oil. IR (neat) 3017, 2954, 1731, 1640, 1435, 1220 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.64 (dddd, *J* = 0.8, 4.4, 8.2, 8.8 Hz, 1H), 1.11-1.22 (m, 1H), 1.85 (dddd, *J* = 0.5, 4.4, 5.3, 5.9 Hz, 1H), 1.96-2.06 (m, 1H), 2.70-2.86 (m, 2H), 3.33-3.80 (m, 1H), 3.74 (s, 3H), 3.75 (s, 3H), 5.03-5.14 (m, 2H), 5.30 (tdd, *J* = 0.8, 5.0, 10.9 Hz, 1H), 5.57 (tdd, *J* = 0.9, 5.3, 11.6 Hz, 1H), 5.74-5.89 (m, 2H), 6.14 (tdd, *J* = 0.5, 7.7, 11.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 6.4, 15.9,

39.6, 42.4, 42.5, 52.67, 52.71, 61.8, 118.4, 123.1, 126.9, 127.6, 132.8, 134.6, 170.4, 170.5. GC/MS *m/z* 276. EI-HRMS *m/z* 276.1357 (calcd for $C_{16}H_{20}O_4$ *m/z* 276.1362).

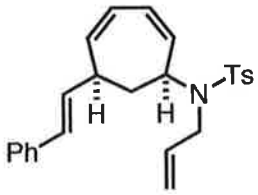


***N*-(Bicyclo[5.1.0]octa-3,5-dien-2-yl)-4-methyl-*N*-2-propen-1-yl-benzene-sulfonamide (10)**: To a stirring suspension of **3** (1.00 g, 1.77 mmol) in water-saturated ether (60 mL) was added the potassium salt of *N*-tosyl allylamine (2.76 g, 11.1 mmol). After 30 min the orange ethereal layer was decanted from any solid and additional moist ether (60 mL) was added to the solid and the mixture stirred for 10 min. This was repeated until the mother liquor was colorless. The collected ethereal layers were combined and concentrated to give a yellow solid (1.10 g, 90%): mp 108-109 °C. To a stirring solution of complex (0.30 g, 0.44 mmol) in dry acetonitrile (20 mL) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.11 g, 0.48 mmol). After 1 h, the starting material had been consumed as indicated by TLC monitoring. The reaction mixture was passed through short column of silica gel and the column flushed with CH_2Cl_2 until no further product appeared by TLC monitoring. These fractions were combined and concentrated, and the residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate = 4:1) to give **10** (81 mg, 58%) as a faint yellow oil. IR (CH_2Cl_2) 1346, 1162 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.77 (dt, *J* = 4.5, 8.4 Hz, 1H), 1.11-1.19 (m, 1H), 1.71 (dt, *J* = 4.8, 5.6 Hz, 1H), 1.79 (q, *J* = 8.4 Hz, 1H), 2.35 (s, 3H), 3.75 (dd, *J* = 6.2, 16.2 Hz, 1H), 3.95 (dd, *J* = 5.8, 16.2 Hz, 1H), 4.96 (br d, *J* = 11.6 Hz, 1H), 5.07 (dd, *J* = 2.0, 10.4 Hz, 1H), 5.08-5.12 (br s, 1H), 5.21 (dd, *J* = 1.6, 18.8 Hz, 1H), 5.44 (dd, *J* = 6.0, 11.6 Hz, 1H), 5.60 (ddd, *J* = 2.8, 6.4, 11.6 Hz, 1H), 5.93 (tdd, *J* = 6.2, 10.0, 17.2 Hz, 1H), 6.10 (dd, *J* = 7.2, 12.0 Hz, 1H), 7.25 and 7.70 (AB_q, *J* = 8.4 Hz, 4H total); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 8.4, 14.8, 21.7, 44.1, 48.1, 57.6, 117.1, 122.6, 126.6, 127.5, 127.9, 129.8, 135.3, 136.1, 137.7, 143.3. ESI-HRMS *m/z* 338.1180 (calcd for $C_{18}H_{21}NO_2SNa$ ($M+Na^+$) *m/z* 338.1191).



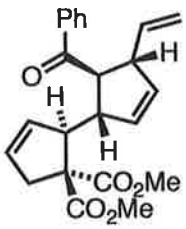
Dimethyl (6-styryl-2,4-cycloheptadien-1-yl)propandioate (11): To a cold solution of dimethyl allylmalonate (1.00 mL, 6.16 mmol) in freshly distilled dry ether (120 mL) was added dropwise a solution of n-butyl lithium (4.5 mL, 1.6 M in hexanes, 7.1 mmol). The mixture was stirred for 1 h and warmed to room temperature. Solid cation **4** (2.00 g, 4.74 mmol) was added and the mixture stirred for 3 h. The reaction mixture was quenched with water and extracted several times with ether. The combined ether extracts were washed with brine, dried

(Na_2SO_4), concentrated and the residue purified by column chromatography (SiO_2, hexanes–ethyl acetate = 4:1) to give a yellow oil which was used in the next step without further characterization. The mixture (2.608 gm) was dissolved in methanol (100 mL) and cerium ammonium nitrate (7.50 gm, 13.7 mmol) was added. The mixture was stirred for 1 h, then concentrated and the residue was partitioned between water and ether. The combined ether extracts were washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate = 20:1) to give **11** (1.17 gm, 67%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.55-1.68 (m, 1H), 2.09 (dd, *J* = 13.3, 5.4 Hz, 1H), 2.60-2.78 (dd, *J* = 10.4, 8.2 Hz, 2H), 3.11 (br d, *J* = 8.7 Hz, 1H), 3.38-3.48 (m, 1H), 3.72 (s, 6H), 5.05 (br s, 1H), 5.08 (d, *J* = 7.5 Hz, 1H), 5.69-5.87 (br m, 5H), 6.11 (ddd, *J* = 15.7, 8.1, 1.1 Hz, 1H), 6.41 (d, *J* = 15.9 Hz, 1H), 7.15-7.34 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.9, 38.8, 43.0, 47.4, 52.5, 61.7, 119.1, 124.4, 124.7, 126.3, 127.3, 128.7, 129.6, 132.8, 133.2, 134.3, 137.0, 137.6, 171.4. ESI-HRMS *m/z* 389.1728 (calcd for $C_{23}H_{26}O_4Na$ *m/z* 389.1729).

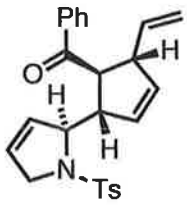


N-(6-styryl-2,4-cycloheptadien-1-yl)-4-methyl-N-2-propen-1-yl-benzenesulfonamide (12). To a solution of **4** (0.10 g, 0.24 mmol) in acetonitrile (10 mL), under N_2, was added the potassium salt of tosyl allylamine (0.140 g, 0.562 mmol). The mixture was stirred for 2 h, at which time TLC indicated the disappearance of **4**. The reaction mixture was dried under reduced pressure and the solid residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate = 4:1) to give the product (0.113 g, 86%) as a yellow foam. mp 47-48 °C; IR (CH_2Cl_2) 2047, 1965, 1338, 1157 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.14 (q, *J* = 12.4 Hz, 1H), 1.55 (br d, *J* = 13.2 Hz, 1H), 1.91 (d, *J* = 7.2 Hz, 1H), 2.40 (s, 3H), 2.82-2.92 (m, 2H), 3.68 (dd, *J* = 6.0, 16.8 Hz, 1H), 3.93 (dd, *J* = 5.2, 16.8 Hz, 1H), 4.38 (dd, *J* = 3.6, 12.0 Hz, 1H), 5.14 (d, *J* = 10.4 Hz, 1H), 5.22-5.33 (m, 3H), 5.80-5.94 (m, 2H), 6.33 (d, *J* 15.2 Hz, 1H), 7.20-7.38 (m, 7H), 7.77 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 36.4, 44.0, 46.2, 57.1, 58.6, 61.5, 88.3, 88.6, 117.0, 126.3, 127.3, 127.6, 128.8, 129.1, 130.1, 135.2, 136.5, 137.1, 137.9, 143.8. This compound was utilized in the next step without further characterization. To the prior complex (0.277 g, 0.509 mmol) in acetonitrile (15 mL), under N_2, was added cerium ammonium nitrate (0.47 g, 0.858 mmol). The mixture was stirred at room temperature for 1 h, at which time TLC indicated complete disappearance of starting material. The reaction mixture was filtered through a short column of silica gel, which was washed with CH_2Cl_2 until all of the product was eluted.

These fractions were combined, concentrated, and the residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate = 17:3) to give **12** (0.106 g, 51%) as a faint yellow oil. IR (CH_2Cl_2) 1336, 1162 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.96 (br d, J = 12.6 Hz, 1H), 2.08 (td, J = 10.9, 12.6 Hz, 1H), 2.42 (s, 3H), 3.30-3.42 (m, 1H), 3.73 (dd, J = 6.0, 16.5 Hz, 1H), 3.85 (dd, J = 6.0, 16.5 Hz, 1H), 4.85-4.94 (m, 1H), 5.13 (dd, J = 0.9, 8.7 Hz, 1H), 5.23 (dd, J = 1.5, 16.8 Hz, 1H), 5.39 (br d, J = 11.1 Hz, 1H), 5.64-5.75 (m, 3H), 5.91 (tdd, J = 6.0, 10.5, 17.1 Hz, 1H), 6.11 (dd, J = 8.4, 15.9 Hz, 1H), 6.39 (d, J = 15.9 Hz, 1H), 7.20-7.38 (m, 7H), 7.77 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.7, 39.0, 43.2, 47.9, 59.1, 117.6, 123.9, 125.1, 126.3, 127.4, 127.5, 128.8, 129.8, 129.9, 132.6, 134.4, 136.1, 137.3, 137.6, 137.9, 143.5. ESI-HRMS m/z 428.1657 (calcd for $C_{25}H_{27}NO_2SNa$ ($M+Na^+$) m/z 428.1660).

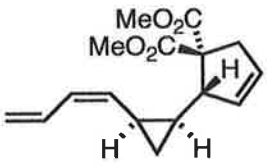


4-Benzoyl-5-[5',5'-bis(methoxycarbonyl)-2'-cyclopenten-1'-yl]-3-ethenylcyclopentene (13). To a solution of **8** (0.096 g, 0.25 mmol) in dichloromethane (18 mL) was added Grubbs' 1st generation catalyst (0.011 g, 0.013 mmol, 5 mol%) and the mixture was stirred for 5 h. Monitoring by ^1H NMR spectroscopy showed the completion of the reaction during this time. The reaction mixture was filtered through a pad of silica and the filtrate was collected and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane–ethyl acetate = 10:1 to 5:1, gradient elution) to afford **13** (0.060 g, 62%) as a brown oil. IR (Neat) 3059, 2954, 1731, 1683, 1266 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.75 (dt, J = 2.2, 18.0 Hz, 1H), 3.05-3.09 (br m, 1H), 3.23 (dd, J = 2.5, 17.8 Hz, 1H), 3.38 (t, J = 4.1 Hz, 1H), 3.57 (s, 3H), 3.69 (s, 3H), 3.75-3.77 (m, 1H), 3.94 (td, J = 2.5, 4.4 Hz, 1H), 4.82 (d, J = 16.9 Hz, 1H), 4.98 (dd, J = 1.6, 10.0 Hz, 1H), 5.42 (dt, J = 2.4, 5.6 Hz, 1H), 5.54-5.58 (m, 1H), 5.72-6.02 (m, 3H), 7.44 (t, J = 7.4 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.91 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 41.4, 48.6, 51.3, 52.9, 53.1, 53.7, 56.9, 62.1, 115.9, 128.5, 128.9, 129.1, 130.6, 131.4, 132.9, 134.5, 136.5, 140.1, 170.5, 172.9, 200.7. FAB-HRMS m/z 381.1701 (calcd for $C_{23}H_{25}O_5$ ($M + H^+$) m/z 381.1702).

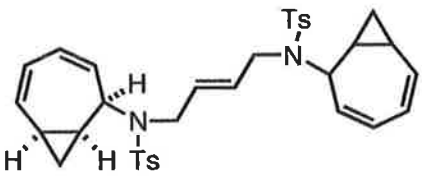


2-(5-Benzoyl-4-ethenyl-2-cyclopenten-1-yl)-2,5-dihydro-1-[(4-methylphenyl)sulfonyl]-1*H*-pyrrole (14): To a solution of **11** (45 mg, 0.11 mmol) in freshly distilled dichloromethane (25 mL), under N_2, was added Grubbs' 1st generation catalyst (5 mg, 0.006 mmol, 5 mol%). The reaction progress was monitored by ^1H NMR spectroscopy, which revealed that no starting material was

left after 90 min. The whole reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate = 4:1) to give **14** (36 mg, 80%) as a colorless oil. IR (CH_2Cl_2) 1678, 1340, 1162 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3H), 3.39-3.46 (br m, 1H), 3.76 (tdd, J = 2.4, 4.8, 15.2 Hz, 1H), 3.80-3.85 (m, 1H), 4.02-4.10 (m, 2H), 4.63-4.68 (m, 1H), 4.93 (d, J = 16.8 Hz, 1H), 5.01 (dd, J = 1.4, 9.4 Hz, 1H), 5.54 (qd, J = 2.0, 6.2 Hz, 1H), 5.59 (td, J = 2.2, 6.0 Hz, 1H), 5.65-5.70 (m, 2H), 5.91 (ddd, J = 8.8, 10.2, 17.0 Hz, 1H), 7.22 (t, J = 8.0 Hz, 2H), 7.46 (t, J = 7.4 Hz, 2H), 7.56 (br t, J = 7.6 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 8.00 (dd, J = 2.0, 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 52.1, 55.0, 56.0, 56.3, 69.5, 115.9, 126.7, 127.7, 128.6, 128.7, 129.2, 129.8, 129.9, 133.1, 133.9, 134.5, 137.4, 140.3, 143.7, 202.3. ESI-HRMS m/z 442.1451 (calcd for $C_{25}H_{25}NO_3S$ $(M+Na^+)$ m/z 442.1453).

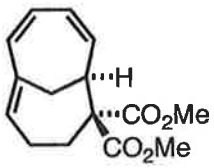


2-[2-(1*Z*,3-Butadien-1-yl)cyclopropyl]-3-cyclopentene-1,1-dicarboxylic acid dimethyl ester (15). To a solution of **9** (0.1301 g, 0.4708 mmol) in CH_2Cl_2 (35 mL) was added Grubbs' 1st generation catalyst (19.6 mg, 0.0238 mmol). The solution was heated at reflux for 22 h, during which time additional Grubbs' catalyst (38.5 mg, 0.0468 mmol) was added in portions when product conversion ceased, as indicated by ^1H NMR spectroscopic monitoring. The dark reaction solution was cooled to room temperature, filtered through a bed of silica gel and the filter bed washed with ethyl acetate. The combined filtrate and washings were concentrated and the residue was purified by preparative TLC (SiO_2, hexanes–ethyl acetate = 10:1) to give **15** (96.0 mg, 74%) as a white solid. mp 52-55 °C; IR (KBr) 3090, 3038, 2954, 1727, 1640, 1452, 1433, 1266 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.34-0.41 (m, 1H), 0.92 (dddd, J = 6.2, 7.9, 8.5, 11.1 Hz, 1H), 1.09 (dt, J = 4.7, 8.5 Hz, 1H), 1.77-1.90 (m, 1H), 2.78-2.87 (m, 1H), 3.33 (br d, J = 11.2 Hz, 1H), 3.37-3.47 (m, 1H), 3.60 (s, 3H), 3.73 (s, 3H), 5.05-5.31 (m, 3H), 5.61-5.70 (m, 2H), 6.04 (dt, J = 0.9, 10.9 Hz, 1H), 6.71 (dddd, J = 0.9, 10.2, 11.3, 16.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.6, 16.9, 20.9, 41.0, 50.8, 53.1, 53.2, 62.9, 116.5, 126.8, 128.4, 131.4, 132.1, 132.5, 170.1, 171.9. Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.29. Found: C, 69.27; H, 7.37.

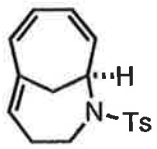


Self metathesis dimer (16): To a solution of **10** (248 mg, 0.786 mmol) in freshly distilled CH_2Cl_2 (100 mL) under N_2 was added Grubbs' 1st generation catalyst (39 mg, 0.047 mmol, 6 mol%). The mixture was heated at reflux and the

reaction progress was monitored by NMR spectroscopy. After 6 h additional Grubbs' I (39 mg, 0.047 mmol, 6 mol %) was added and heating continued for 12 h. A final portion of Grubbs' catalyst (20 mg, 0.024 mmol, 3 mol %) was added and heating continued for 12 h. The reaction mixture was concentrated and purified by column chromatography (SiO_2, hexanes–ethyl acetate = 7:3) to afford a mixture of diastereomeric dimers **16** (180 mg, 76%) as a colorless solid. mp 162-163 °C; IR (CH_2Cl_2) 1336, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.81-0.87 (m, 2H), 1.12-1.22 (m, 2H), 1.73-1.85 (m, 4H), 2.42 (s, 6H), 3.73 (dd, J = 2.4, 16.0 Hz, 2H), 3.92 (br d, J = 14.8 Hz, 2H), 4.94 (dt, J = 2.8, 12.0 Hz, 2H), 5.05-5.10 (br s, 2H), 5.46 (dd, J = 6.2, 11.4 Hz, 2H), 5.61 (dtd, J = 2.8, 6.0, 12.0 Hz, 2H), 5.83 (q, J = 3.2 Hz, 2H), 6.14 (dd, J = 7.4, 11.4 Hz, 2H), 7.29 and 7.72 (AB_q, J = 8.0 Hz, 8H total); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 8.2, 14.7, 21.7, 44.1, 46.9, 57.6, 122.6, 126.7, 127.5, 127.7, 129.9, 130.5, 135.3, 137.5, 143.4. Anal. Calcd for $C_{34}H_{38}N_2O_4S_2$: C, 67.75; H, 6.35. Found: C, 67.29; H, 5.92.

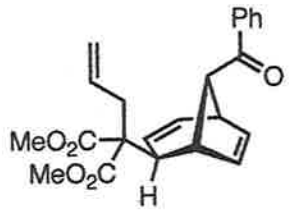


Bicyclo[4.4.1]undeca-5,7,9-triene-2,2-dicarboxylic acid dimethyl ester (17): To a stirring solution of **11** (30 mg, 0.082 mmol) in CH_2Cl_2 (2 mL) at room temperature was added Grubbs 1st generation catalyst (3 mg, 5 mol%). The reaction mixture was stirred for 45 min, concentrated and the residue purified by column chromatography (SiO_2, hexanes–ethyl acetate = 20:1) to give **17** (19 mg, 88%) as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.27 (dd, J = 1.2, 14.2 Hz, 1H), 2.55 (dd, J = 14.2, 1.5 Hz, 1H), 2.85-2.75 (m, 1H), 2.96-2.89 (m, 2H), 3.33-3.25 (dq, J = 17.3, 2 Hz, 1H), 3.66 (s, 3H), 3.75 (s, 3H), 3.84-3.76 (m, 1H), 5.66-5.57 (m, 2H), 6.21-6.18 (m, 1H), 6.31-6.26 (m, 1H), 6.44-6.39 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.8, 40.3, 43.6, 50.6, 52.5, 52.9, 63.0, 127.4, 128.4, 131.4, 132.5, 132.9, 146.8, 171.1, 173.0. ESI-HRMS m/z 262.1198 (calcd for $C_{15}H_{18}O_4$ m/z 262.1205).

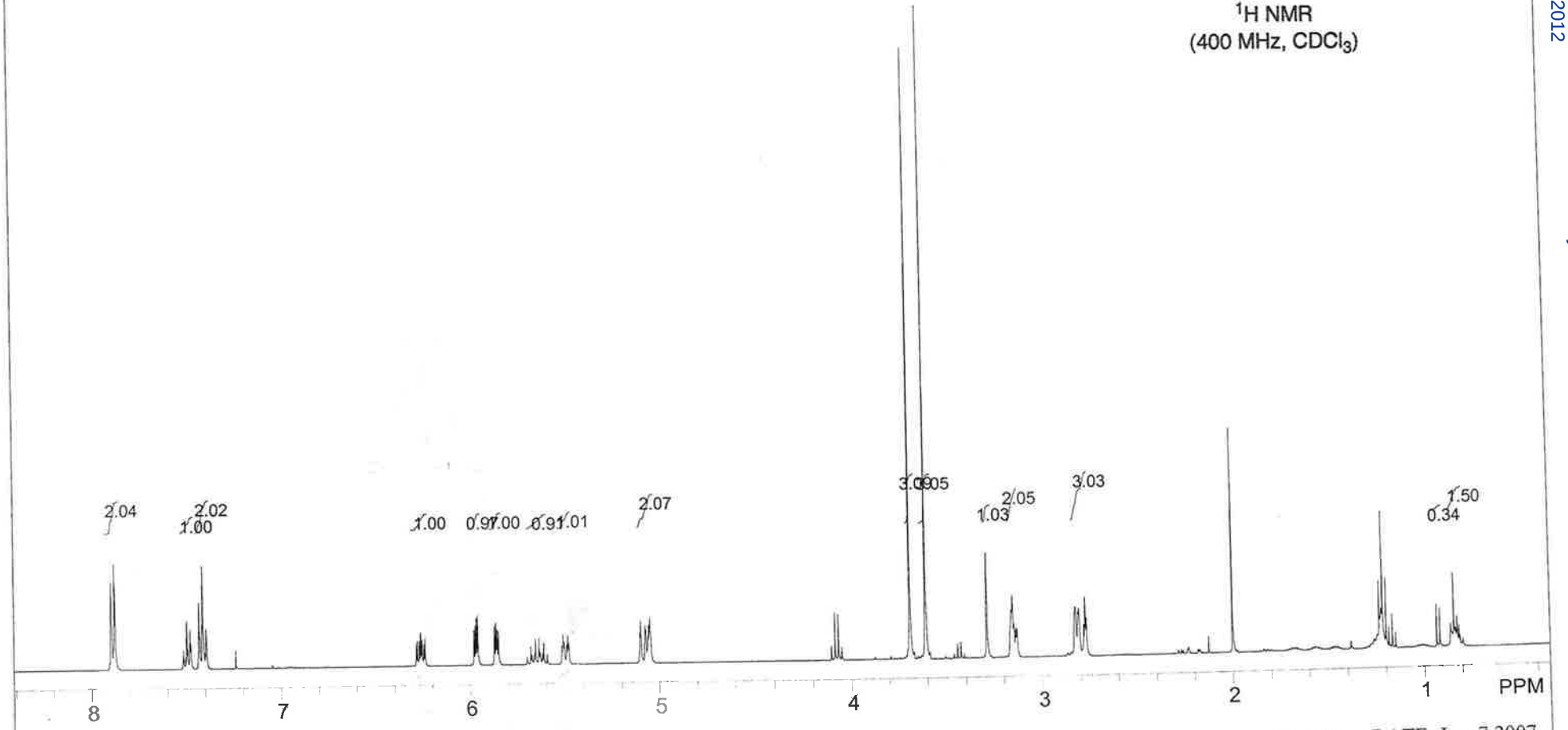


***N*-Toluenesulfonyl-2-Azabicyclo[4.4.1]undeca-5,7,9-triene (18):** To a solution of **12** (60 mg, 0.15 mmol) in freshly distilled dichloromethane (20 mL), was added Grubbs' 2nd generation catalyst (7 mg, 0.008 mmol, 5 mol %). The reaction mixture was stirred under N_2 and the reaction progress was monitored by ^1H NMR spectroscopy. After 4 h all signals for the starting material had disappeared. The reaction mixture was concentrated under a flow of N_2, and the residue purified by column chromatography (SiO_2, hexanes–ethyl acetate = 4:1) to afford **18** as a colorless oil (37 mg, 82%). ^1H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 3H), 2.81 (ddd, J = 1.2, 8.8, 14.4 Hz, 1H), 2.97-2.99 (narrow m, 2H), 3.06, ddd,

J = 1.2, 3.6, 14.4 Hz, 1H), 4.06-4.09 (narrow m, 2H), 4.59 (td, J = 4.0, 8.4 Hz, 1H), 5.56-5.60 (narrow m, 2H), 6.20-6.24 (m, 1H), 6.30 (qd, J = 1.2, 5.4 Hz, 1H), 6.43 (qd, J = 2.0, 5.4 Hz, 1H), 7.31 and 7.73 (ABq, J_{AB} = 8.2 Hz, 4H total); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 38.0, 44.6, 55.9, 67.6, 125.0, 127.6, 129.5, 130.0, 130.1, 131.9, 132.6, 134.8, 143.7, 144.5. This compound decomposed upon standing and thus a satisfactory HRMS was not obtained.



(±)-**7**
^{1}H NMR
(400 MHz, $CDCl_3$)



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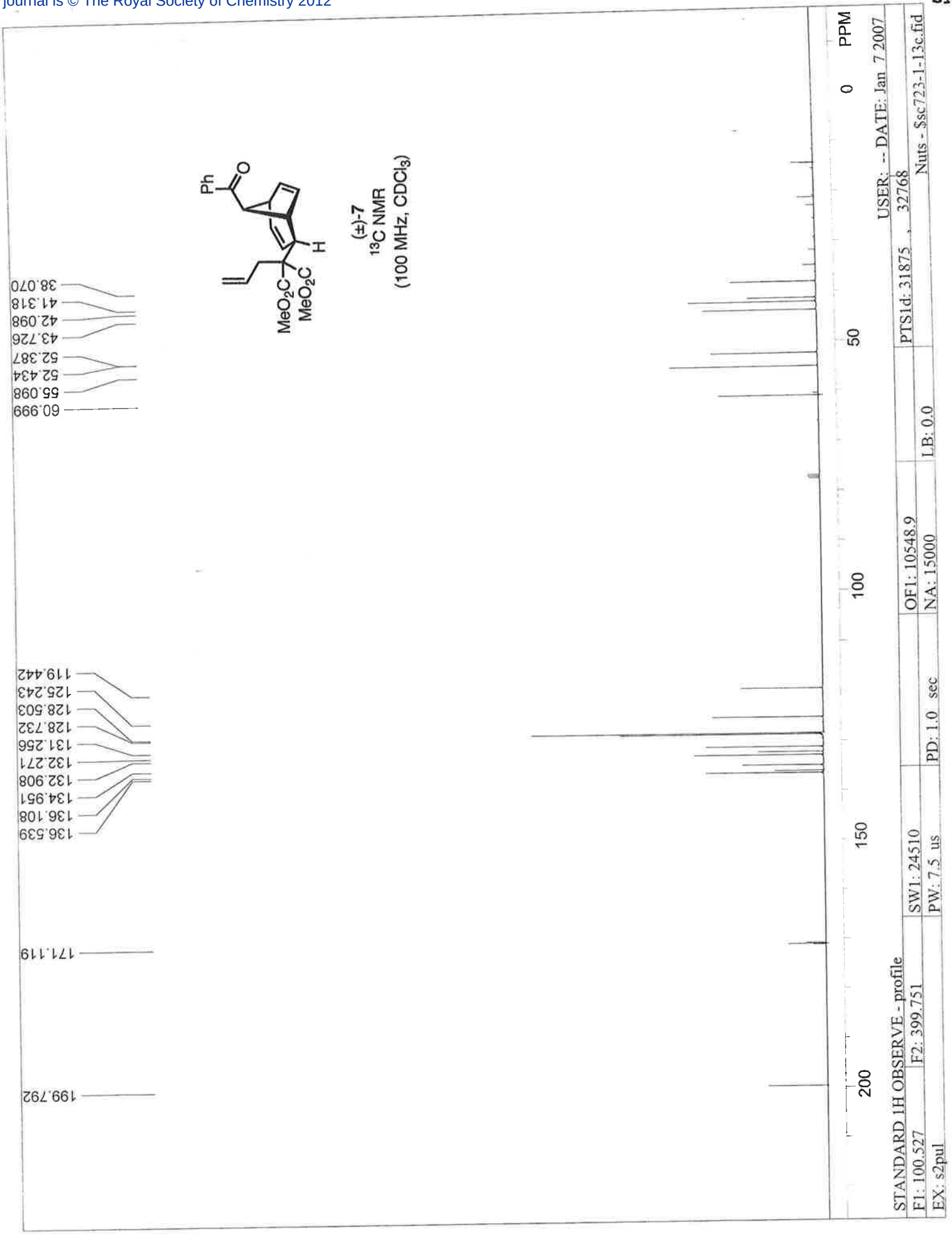

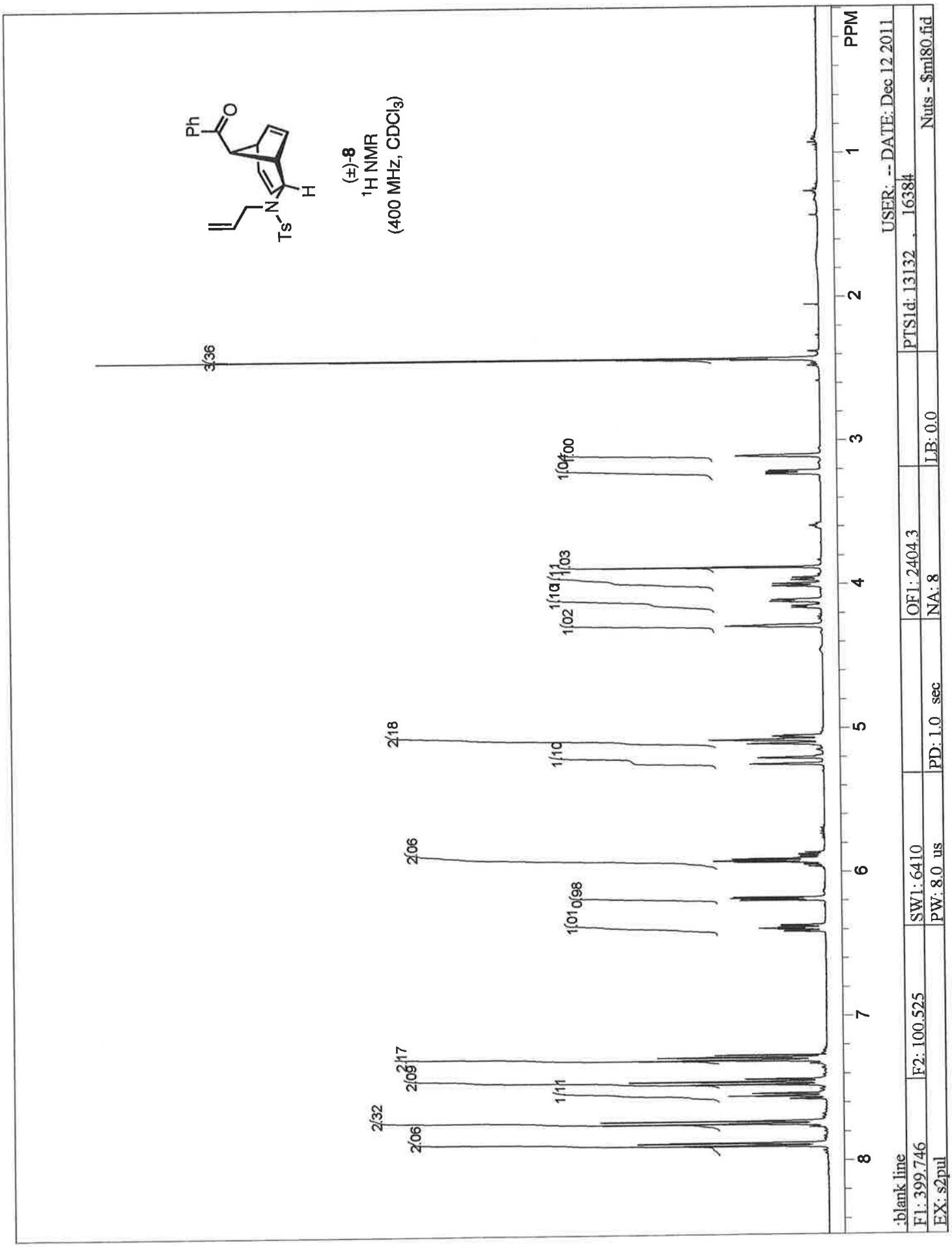
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H
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(400 MHz, CDCl$_3$)
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2.06
2.32
2.06
2.09
2.17
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1.02
1.03
1.00
1.01
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USER: -- DATE: Dec 12 2011
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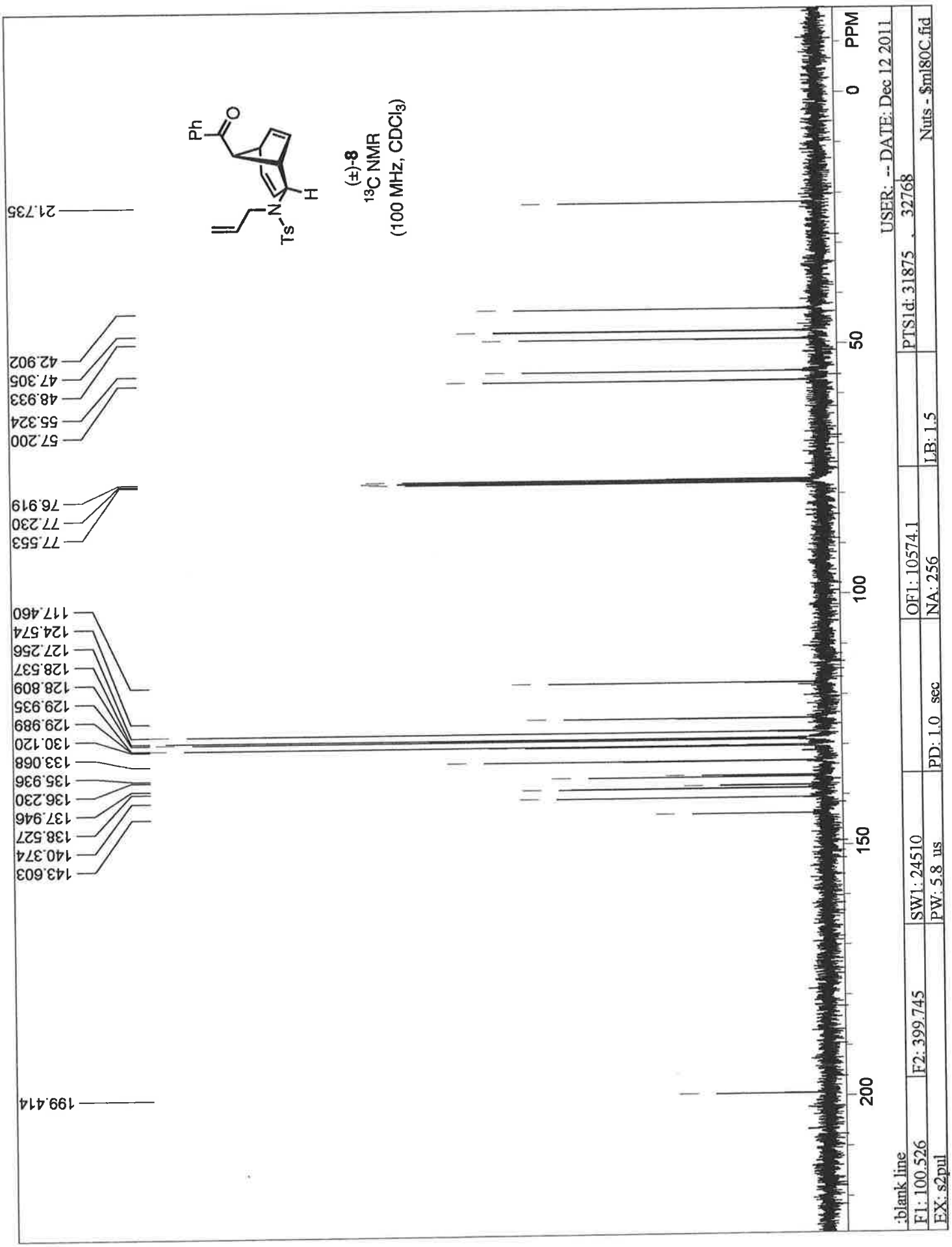

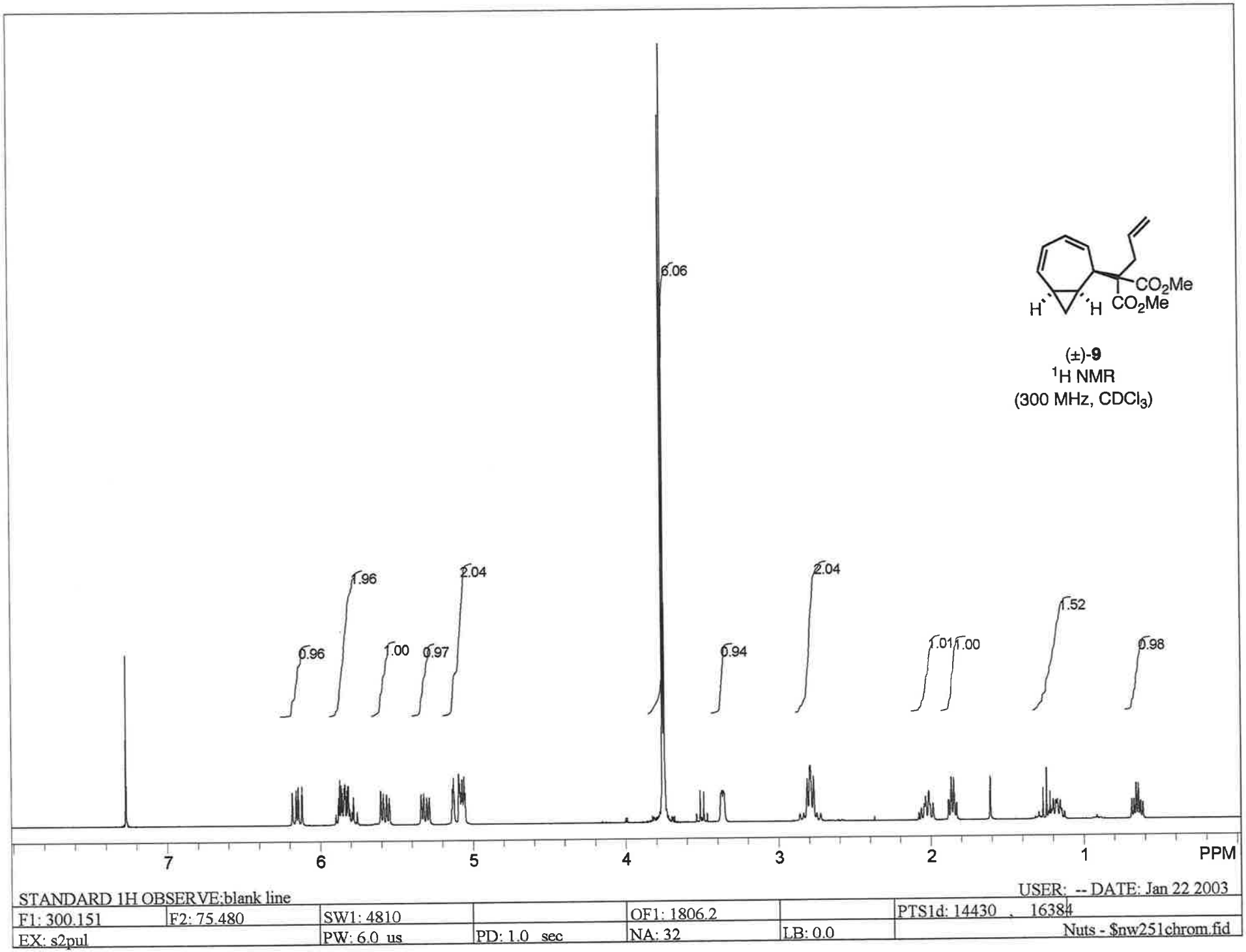

(±)-**9**
^{1}H NMR
(300 MHz, $CDCl_3$)

STANDARD 1H OBSERVE;blank line — USER: -- DATE: Jan 22 2003

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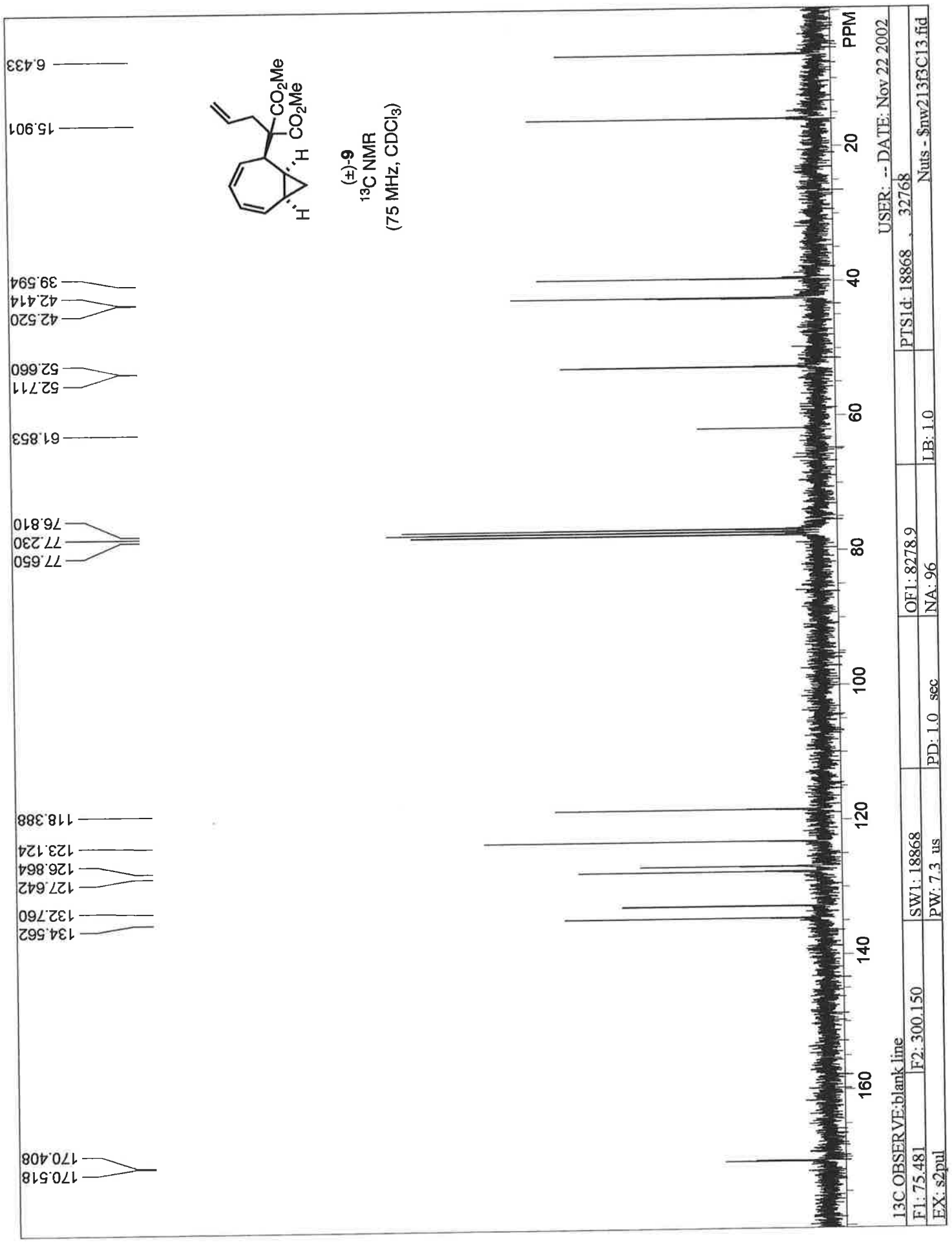
(±)-9
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(75 MHz, CDCl$_3$)
CO$_2$Me
CO$_2$Me
H
H
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15.901
39.594
42.414
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52.660
52.711
61.853
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77.230
77.650
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123.124
126.864
127.642
132.760
134.562
170.518
170.408
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40
60
80
100
120
140
160
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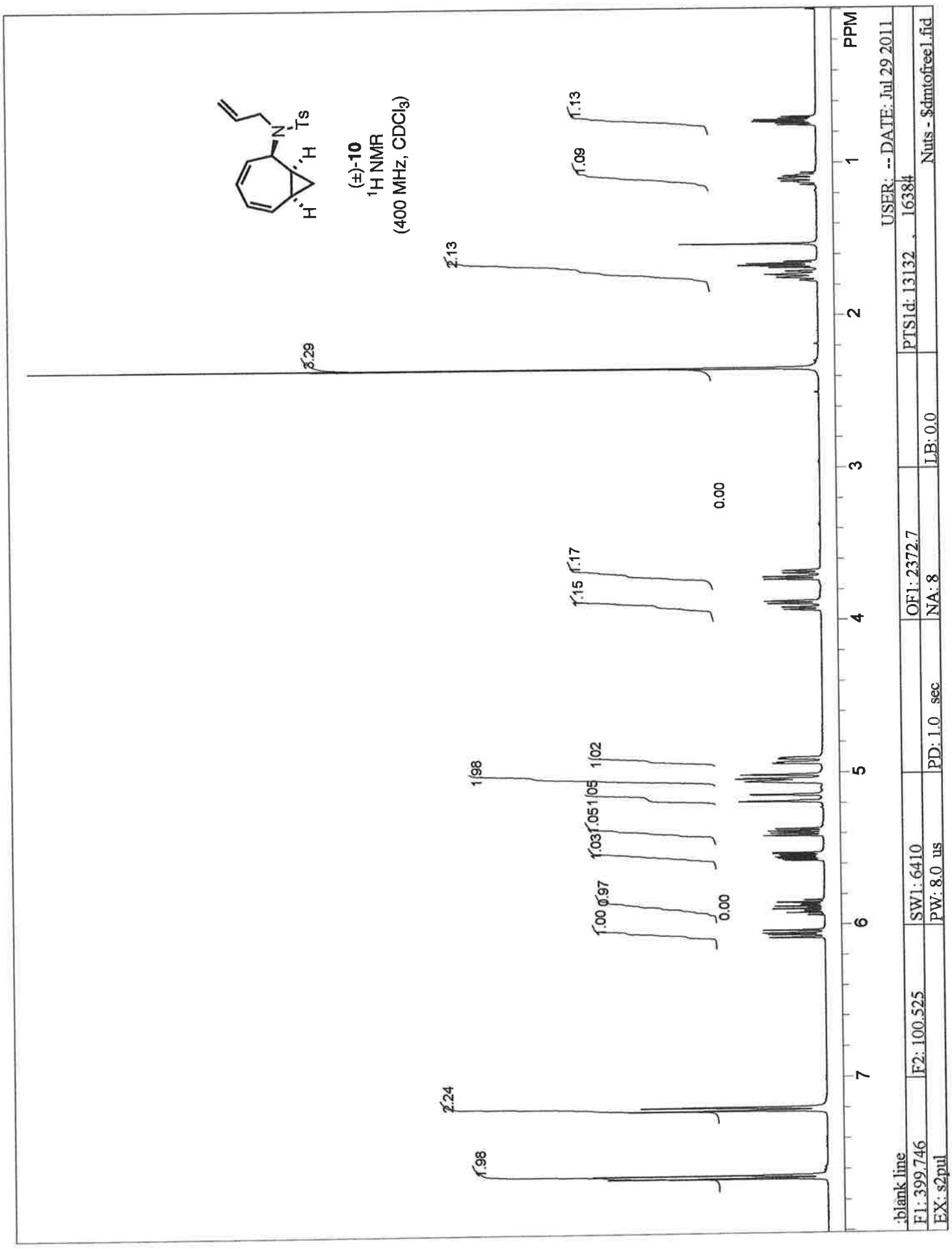
(±)-10
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(400 MHz, CDCl$_3$)
Ts
N
H
H
PPM
USER: -- DATE: Jul 29 2011
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PD: 1.0 sec
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LB: 0.0
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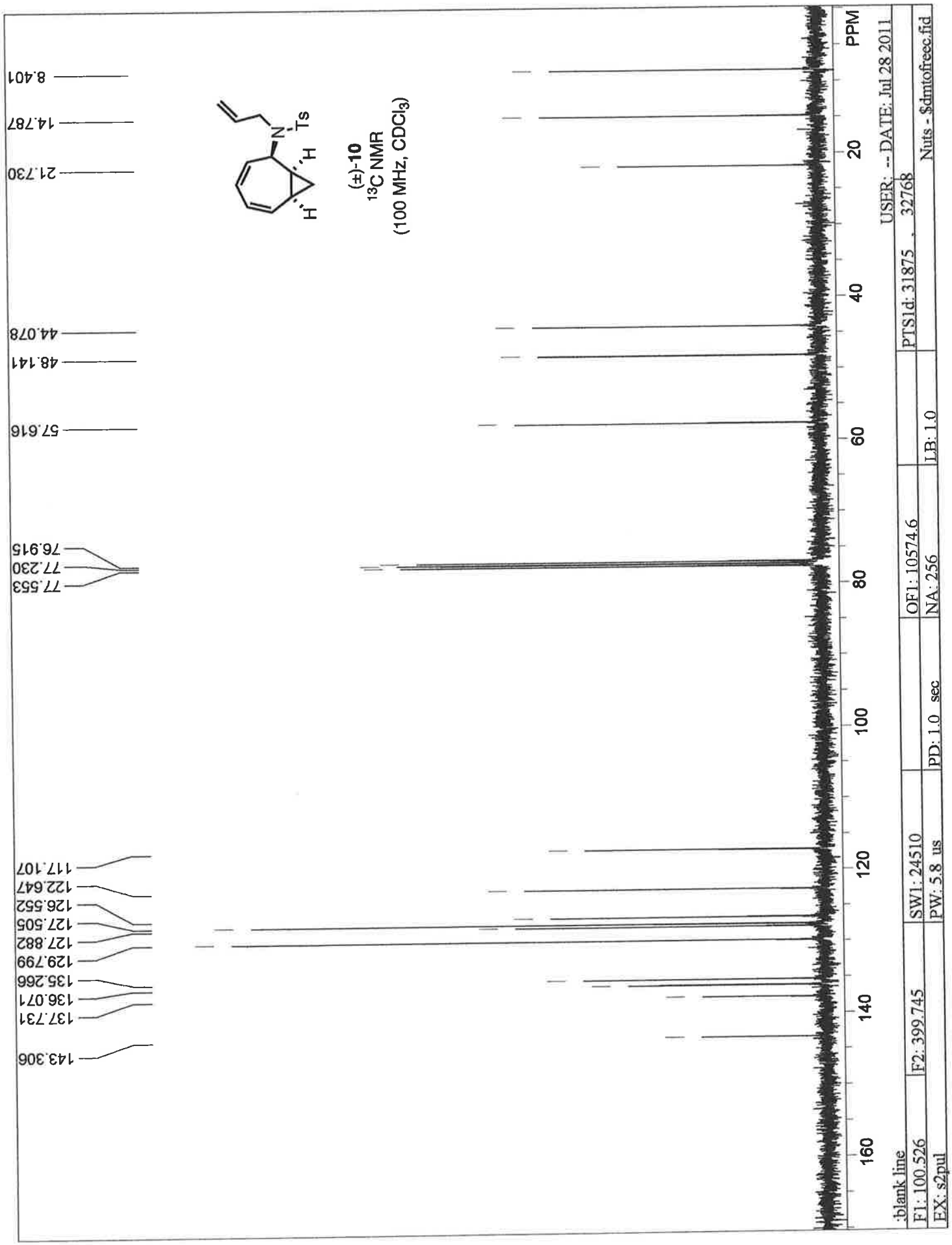
2.13
1.13
1.09
1.17
1.15
0.00
1.98
1.02
1.05
1.03
1.00
0.97
0.00
2.24
1.98


(±)-10
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(100 MHz, CDCl$_3$)
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76.915
77.230
77.553
117.107
122.647
126.552
127.505
127.882
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143.306
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EX: s2pul
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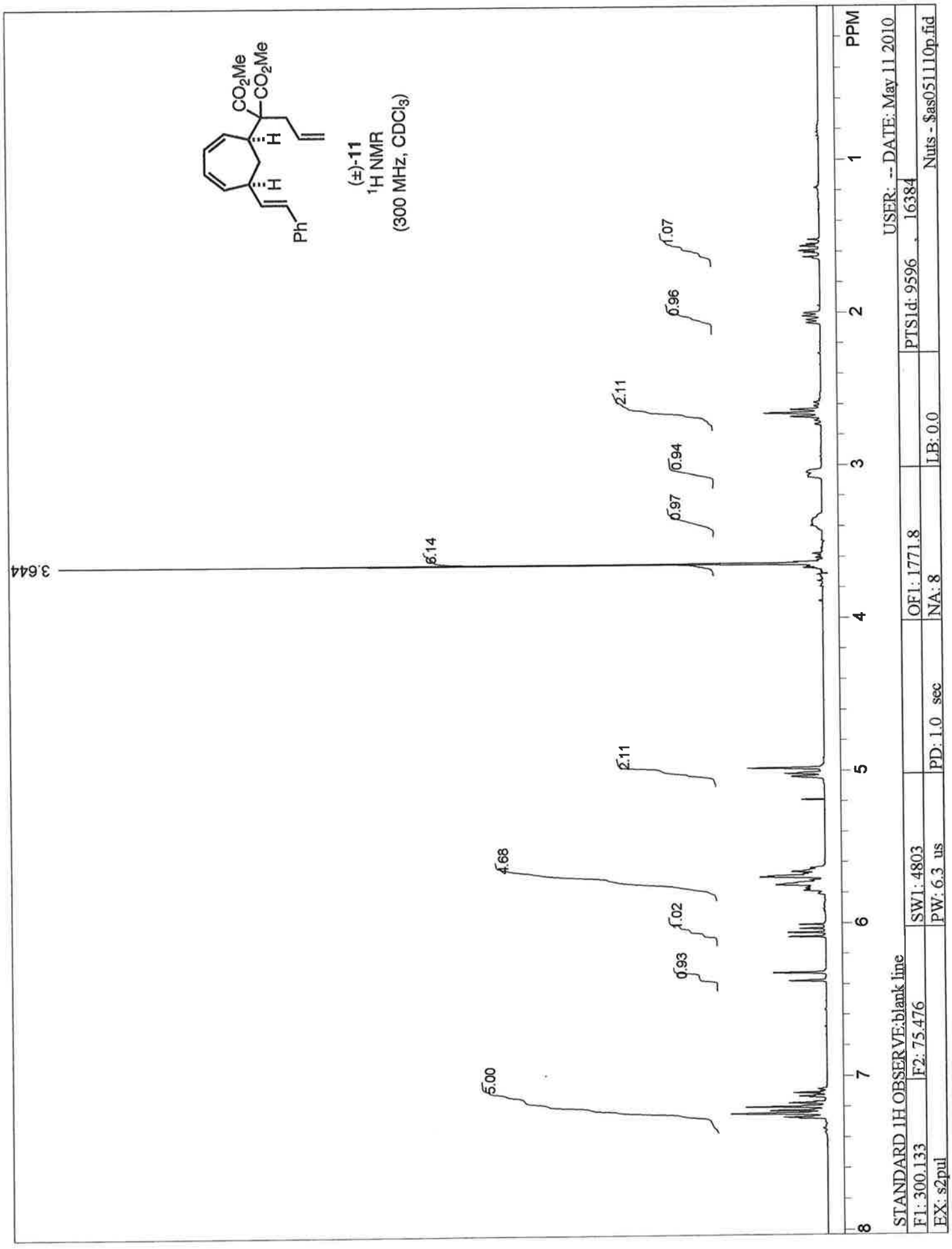

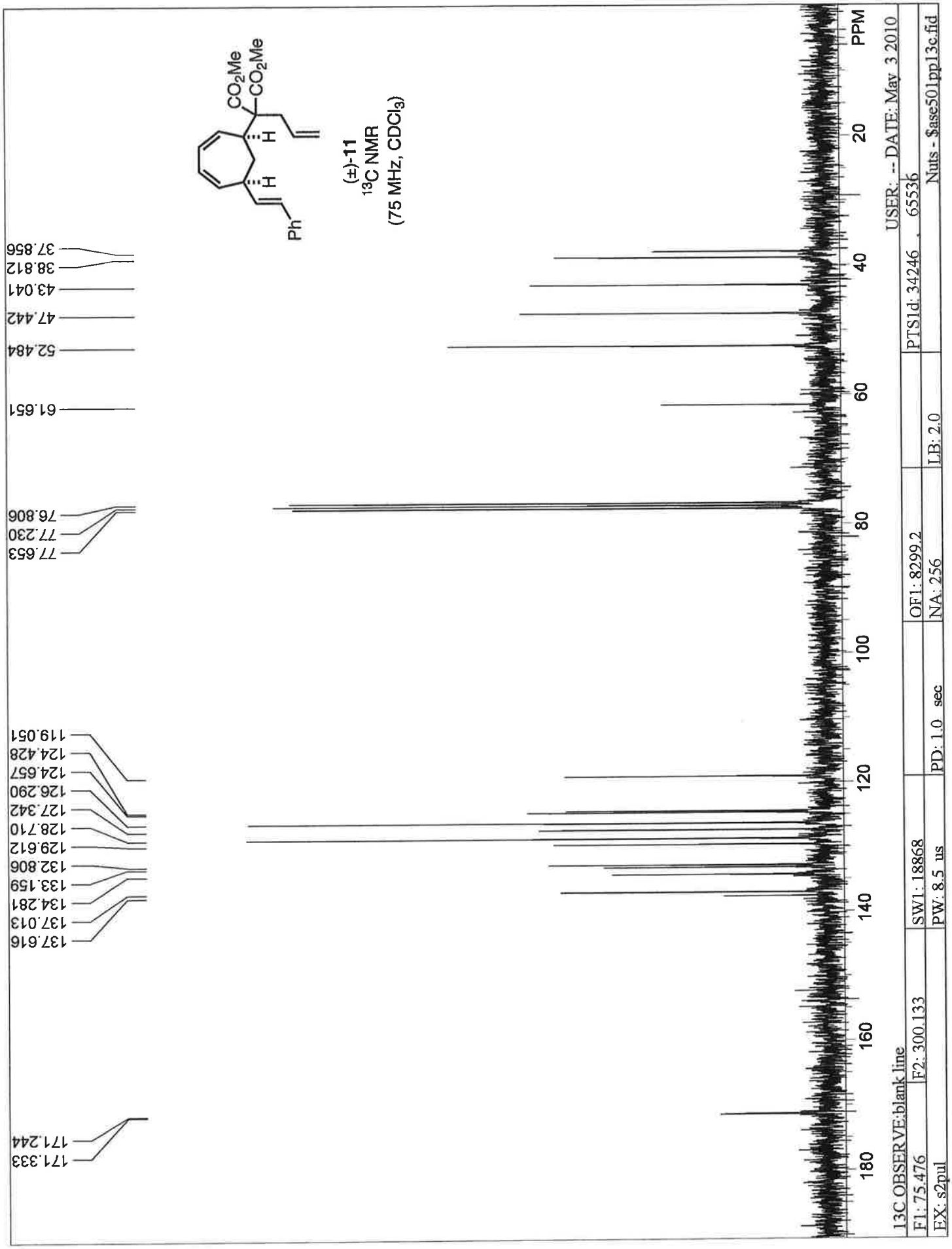

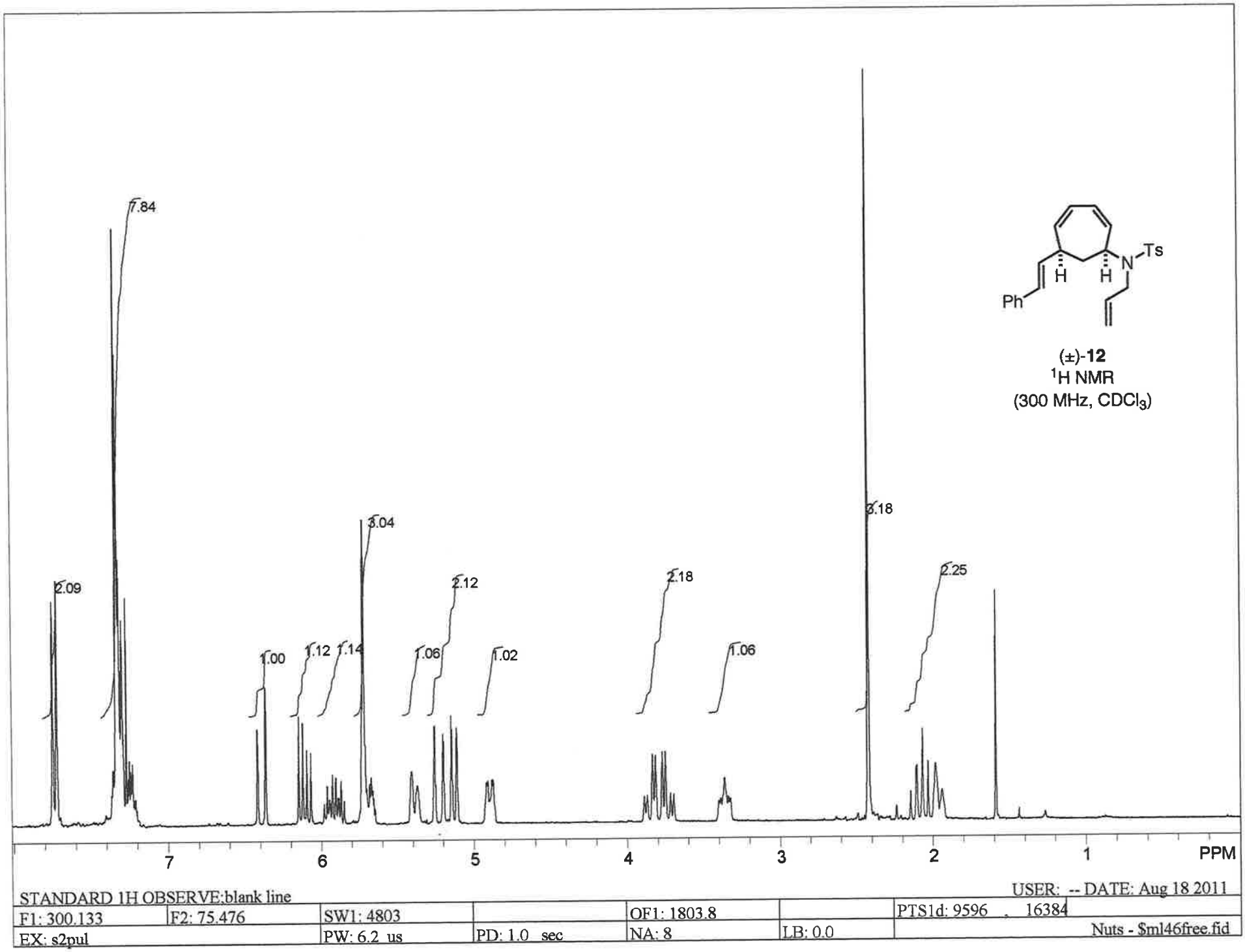

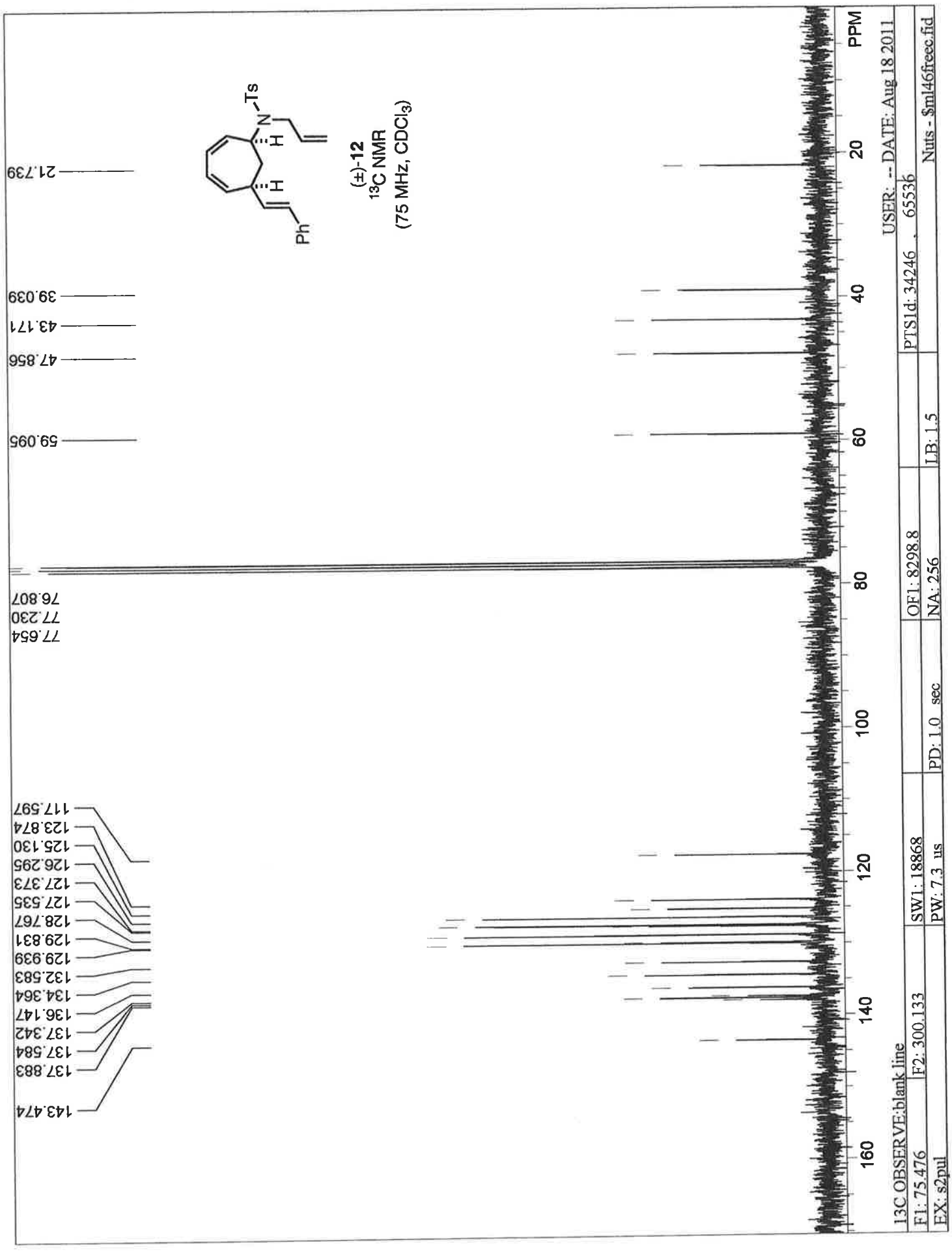

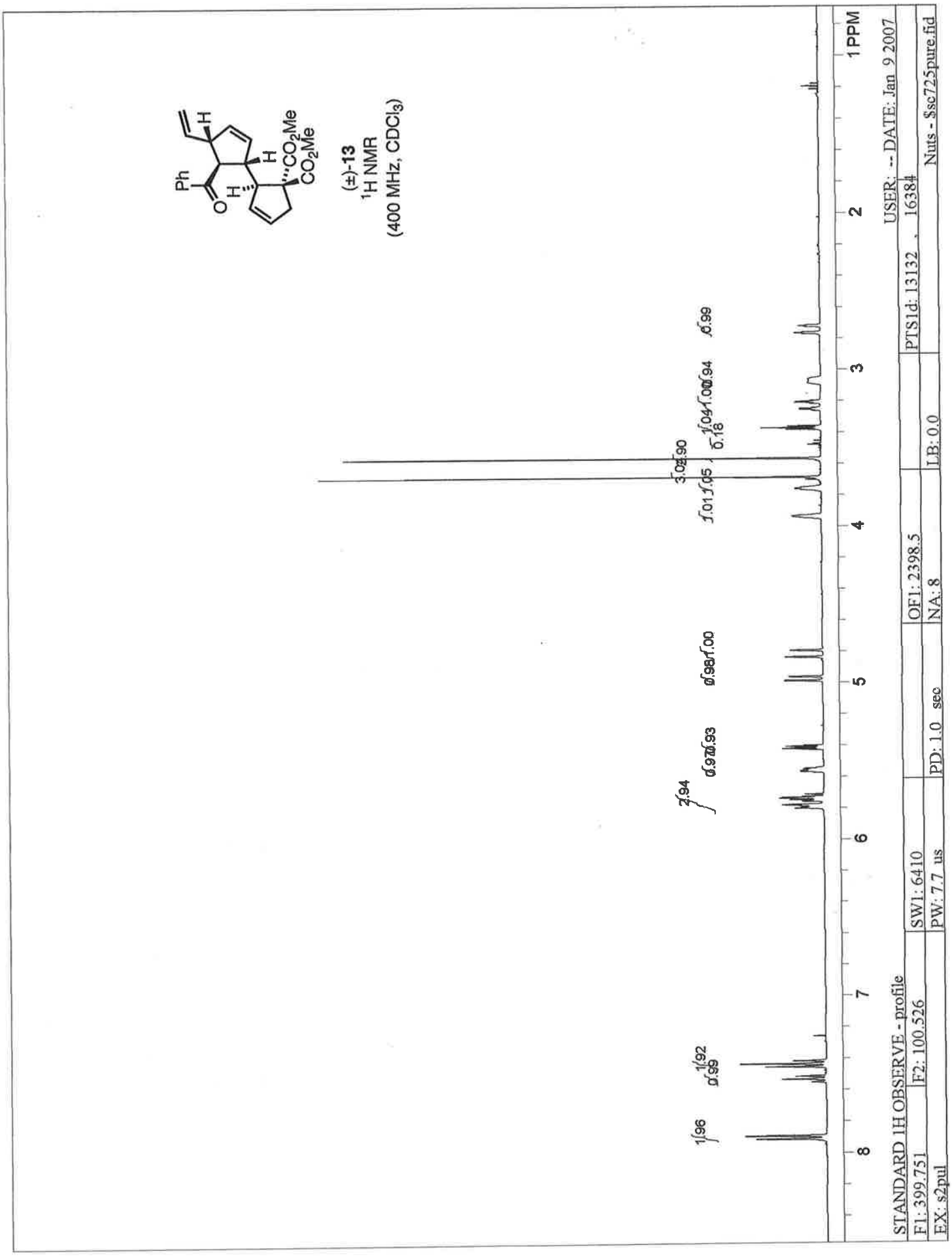

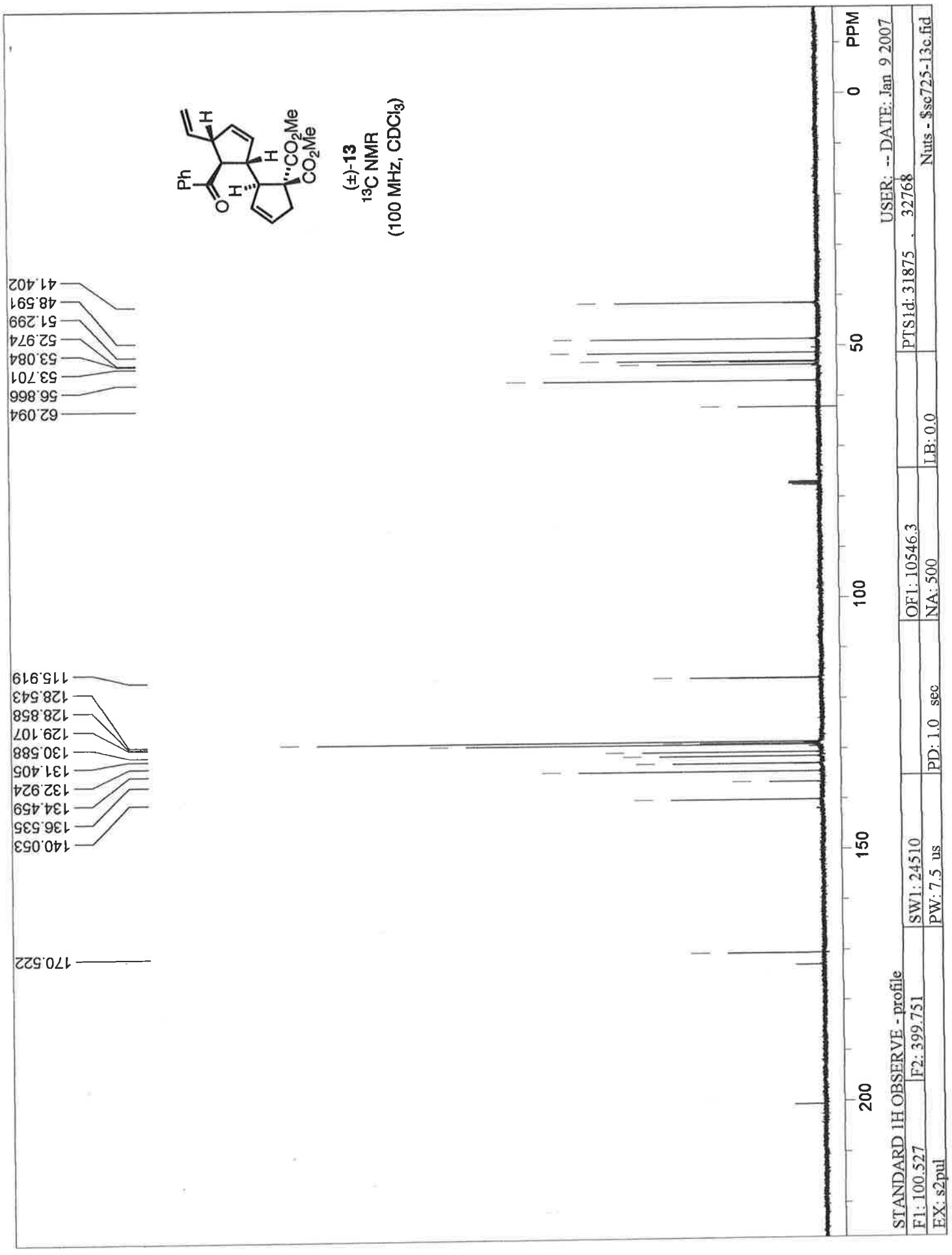

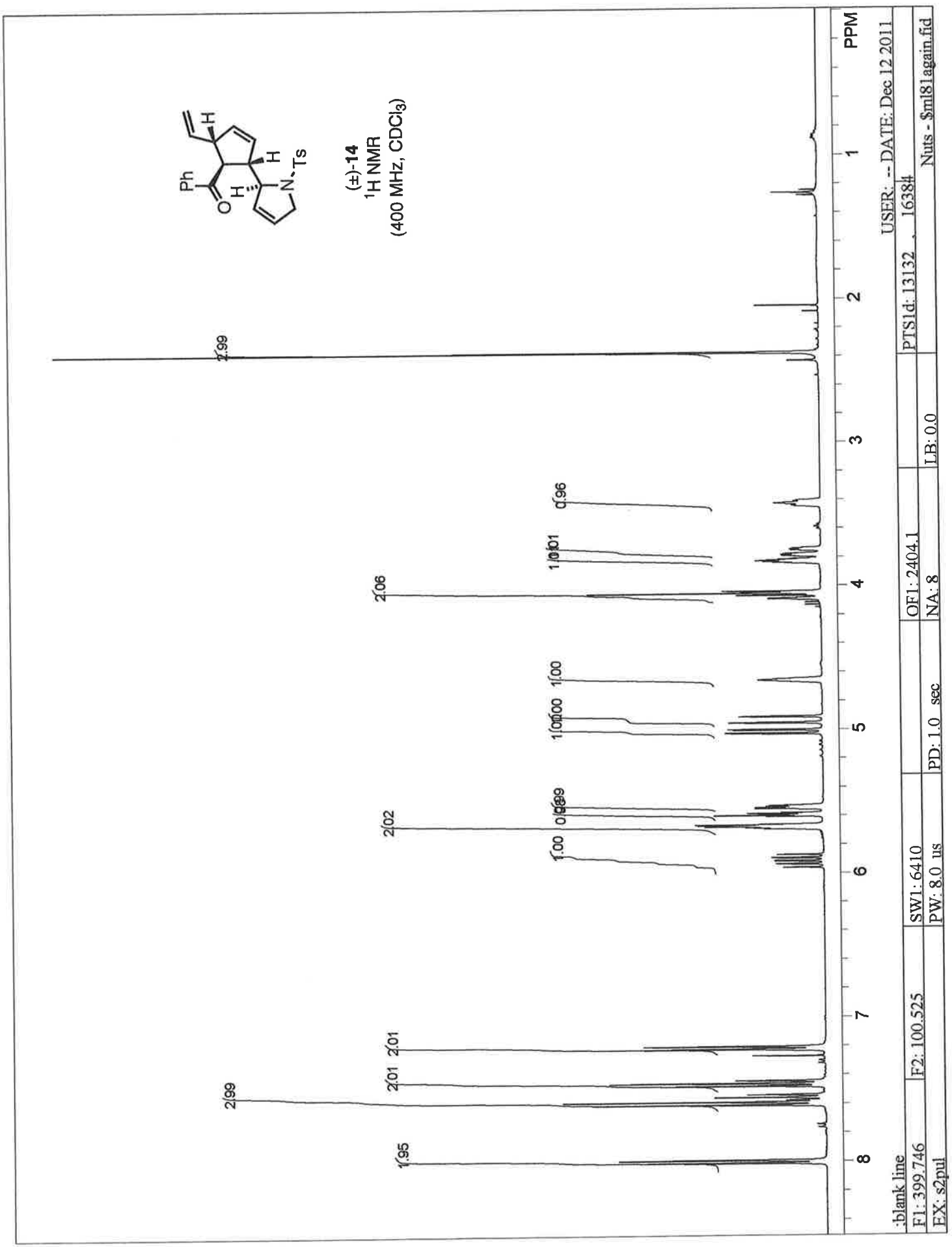

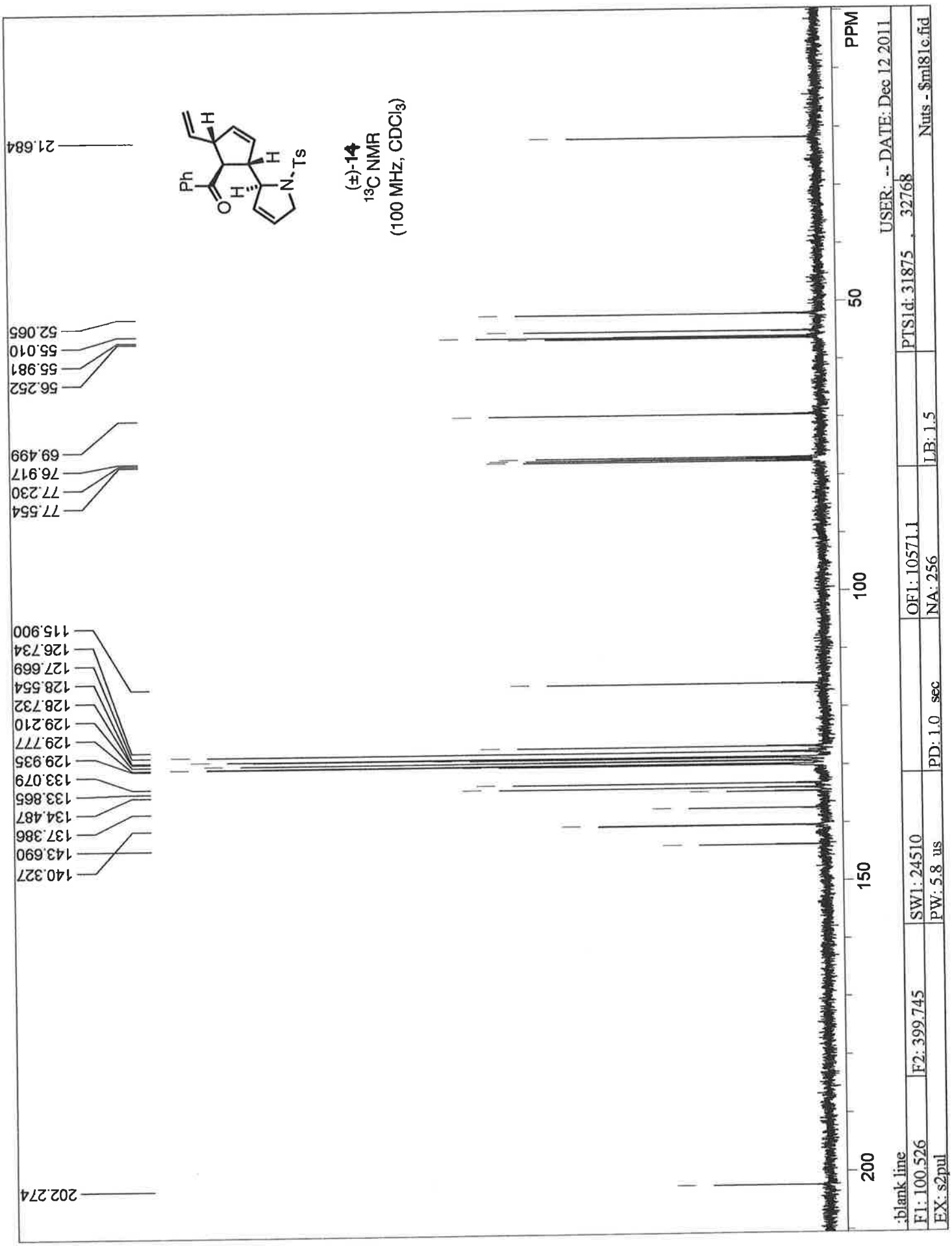

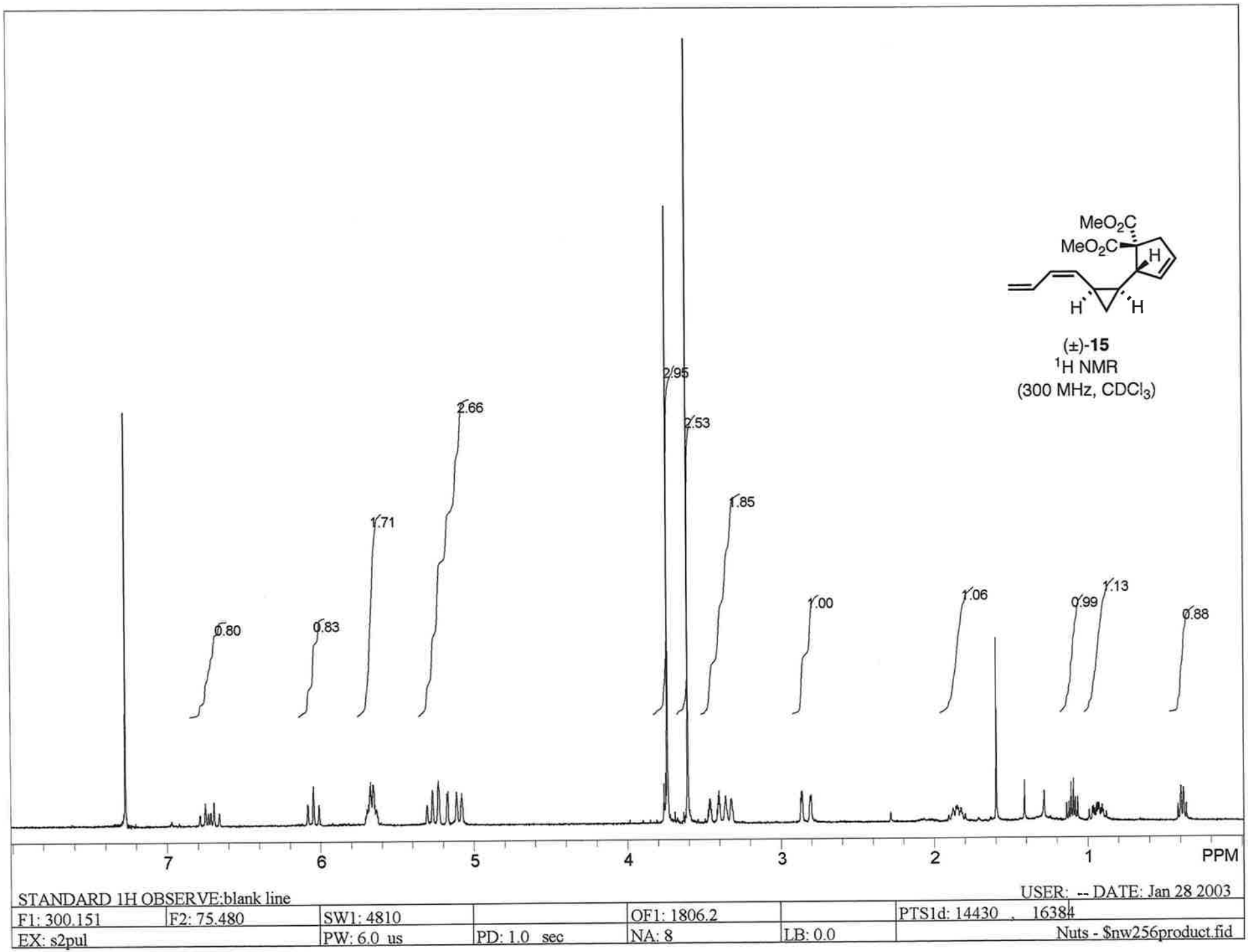

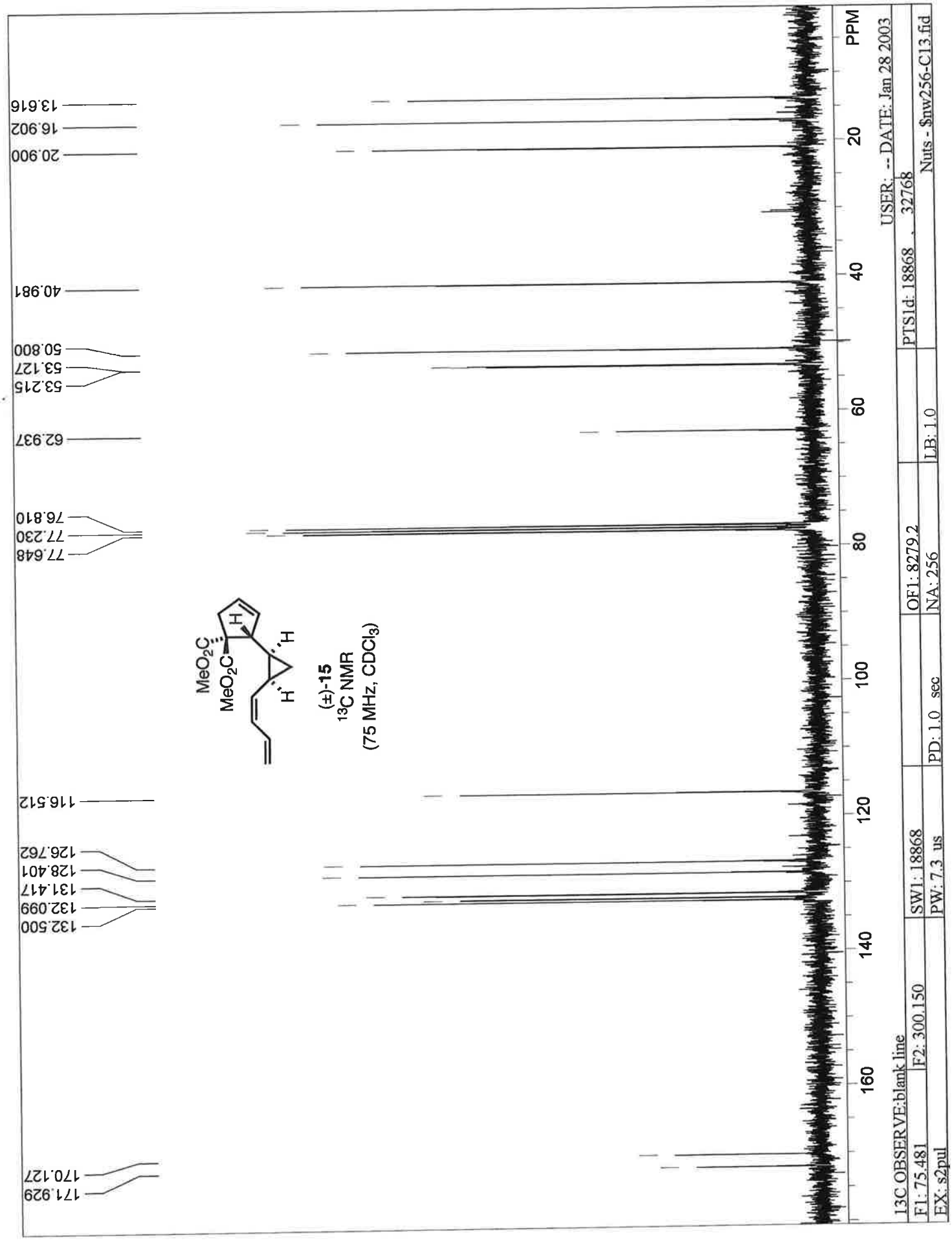

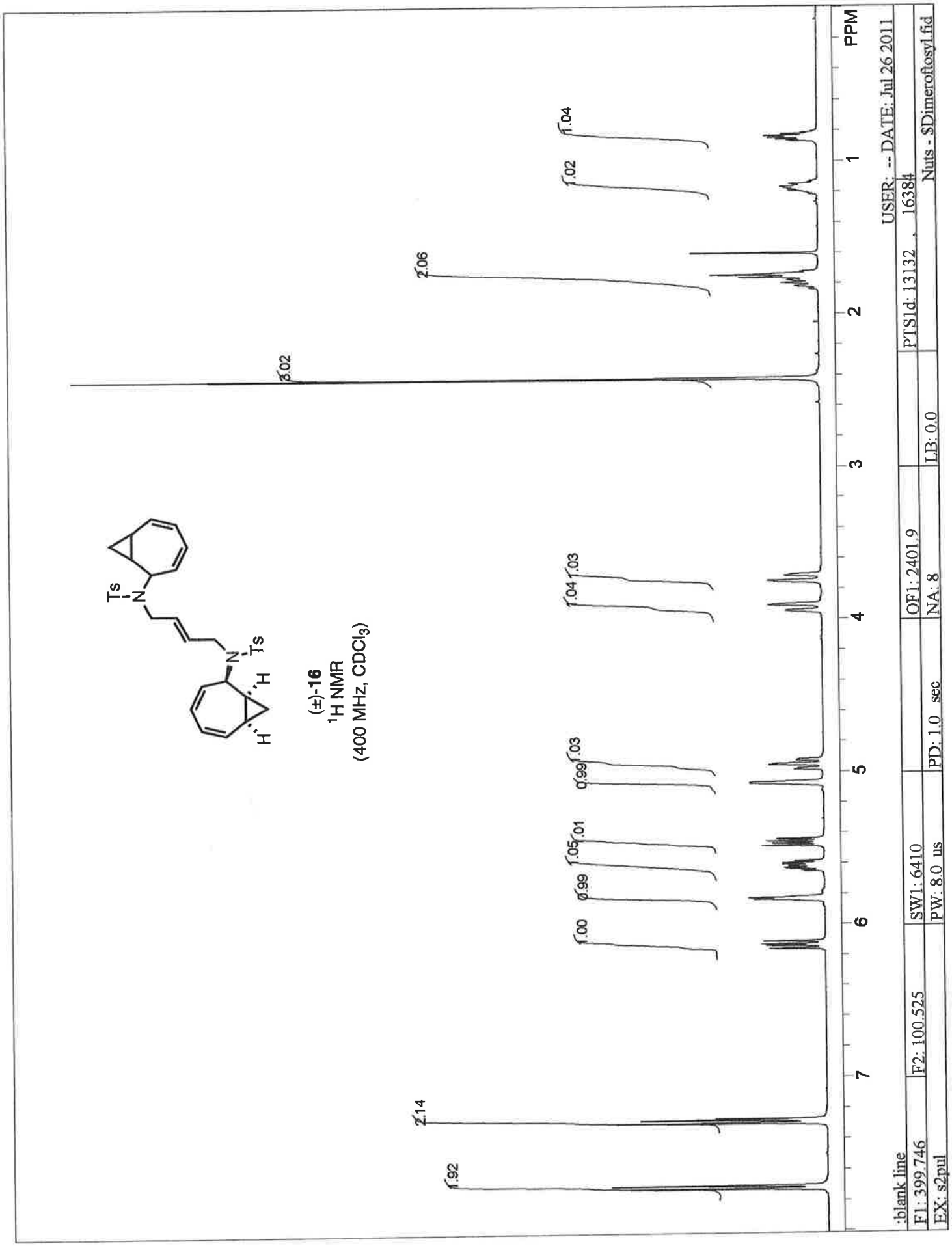

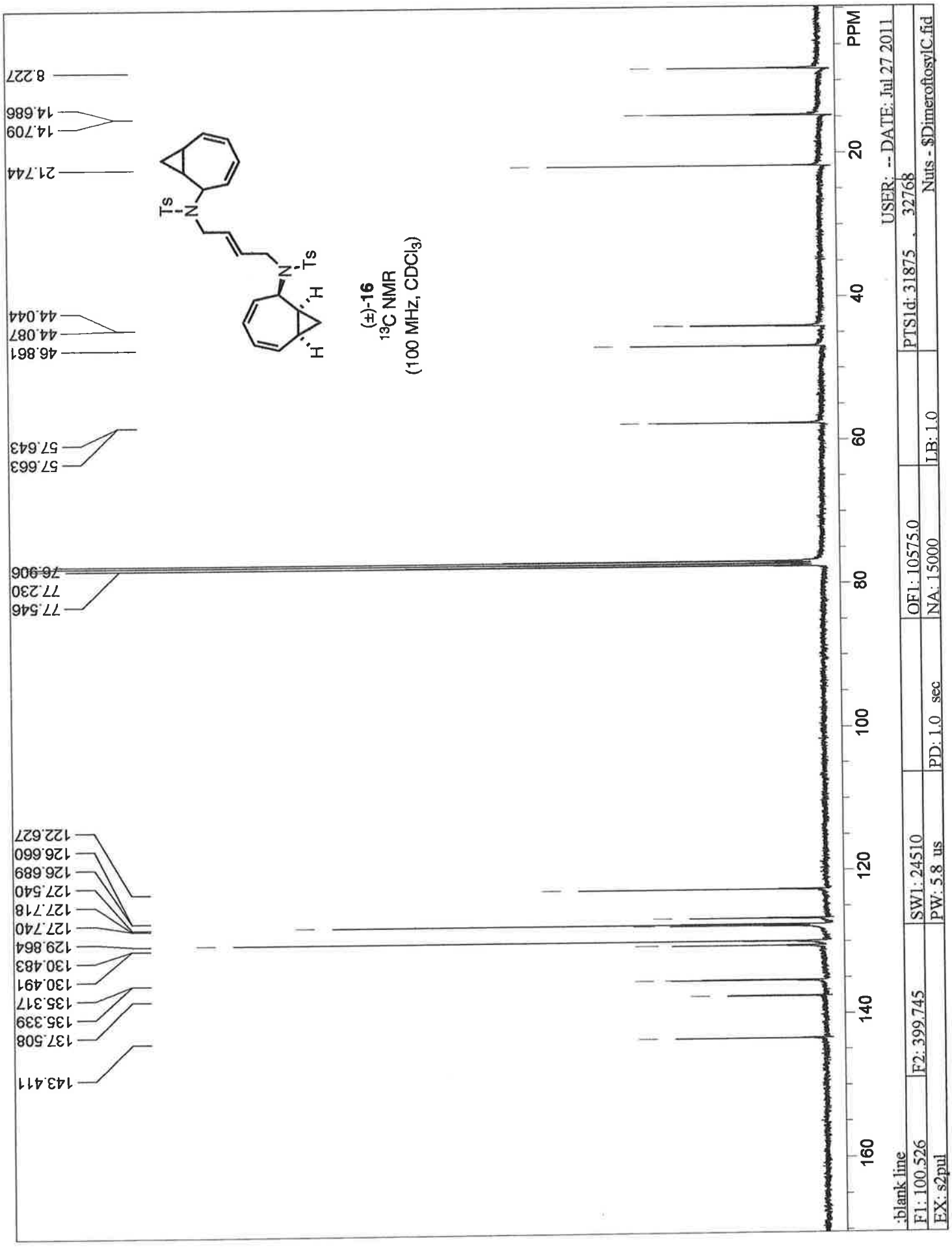
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(100 MHz, CDCl$_3$)
Ts
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Ts
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H
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14.686
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130.491
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160
USER: -- DATE: Jul 27 2011
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PW: 5.8 us
PD: 1.0 sec
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F1: 100.526
EX: s2pul
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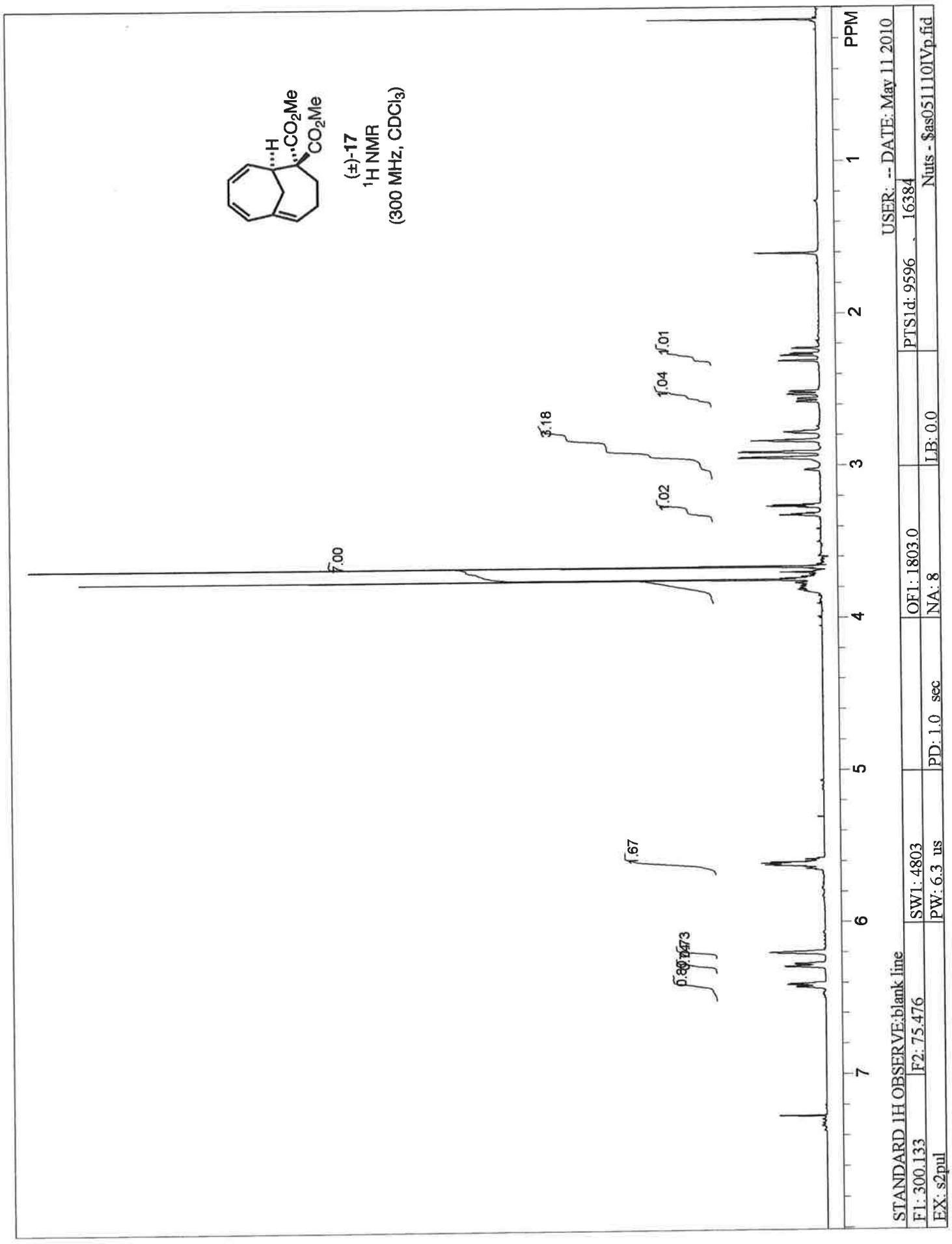
(±)-17
^{1}H NMR
(300 MHz, CDCl$_3$)
CO$_2$Me
CO$_2$Me
H
7.00
3.18
1.04
1.01
1.02
1.67
PPM
1
2
3
4
5
6
7
USER: -- DATE: May 11 2010
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PTS1d: 9596
16384
LB: 0.0
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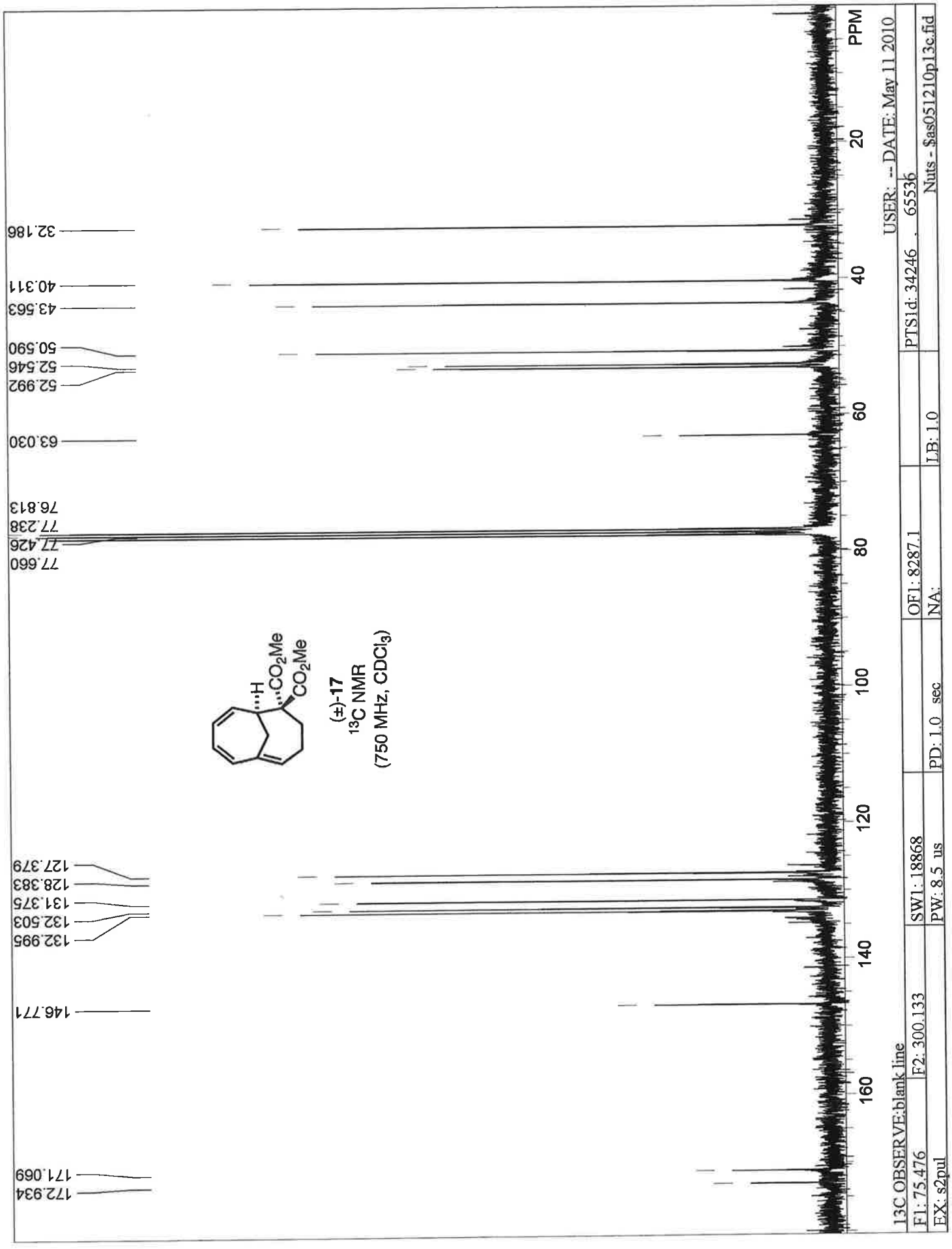

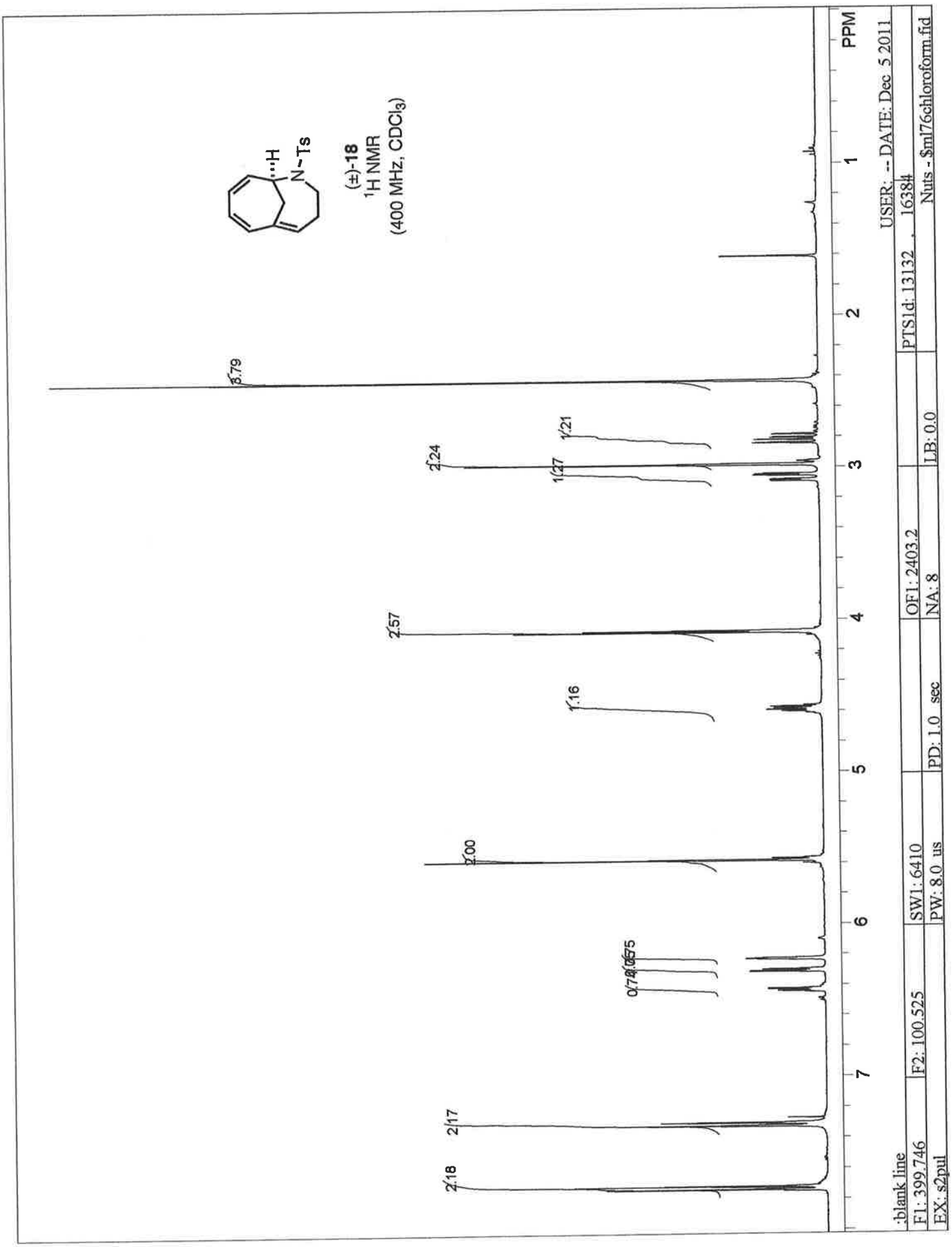
(±)-18
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(400 MHz, CDCl$_3$)
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1.21
1.27
2.57
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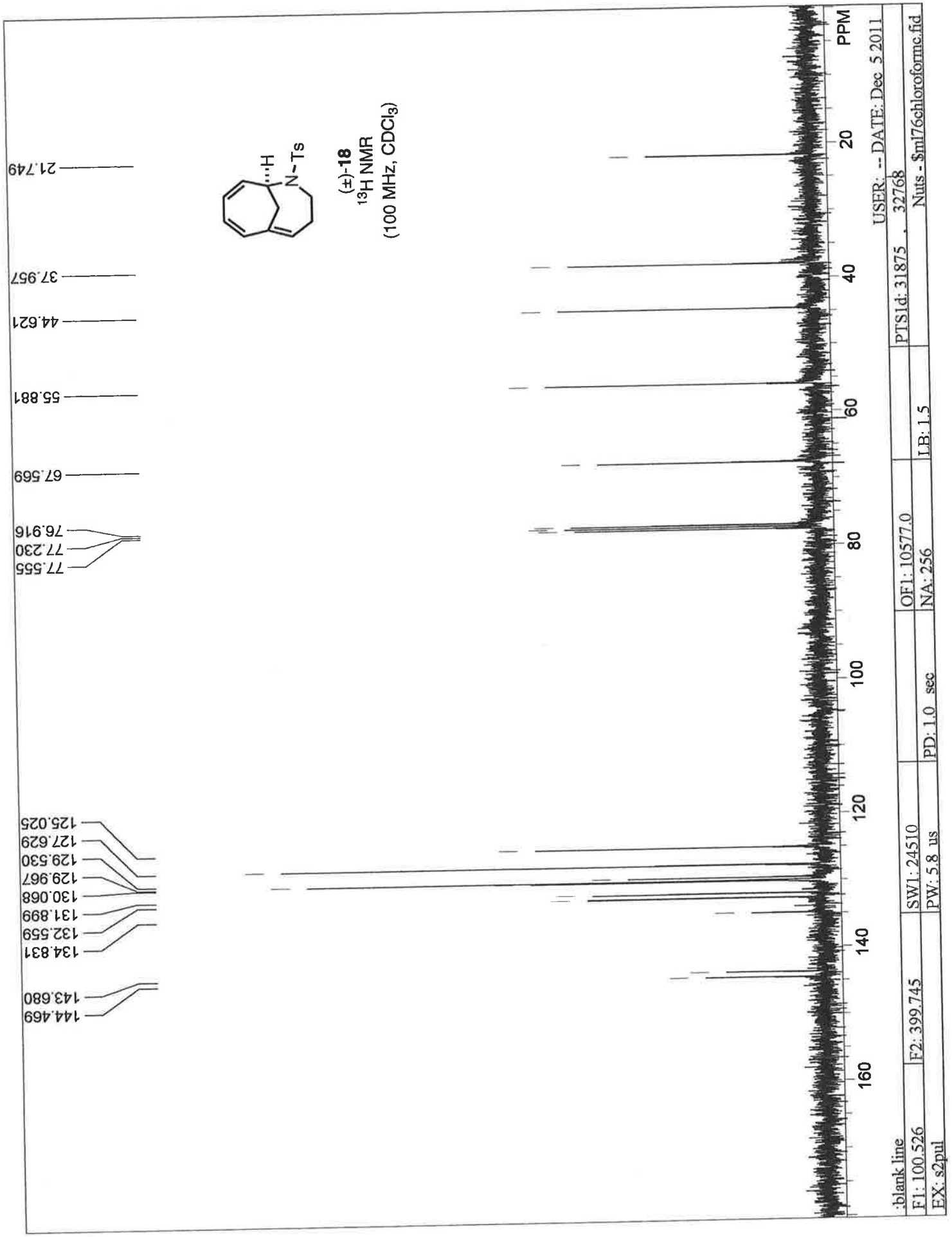
2.00
0.78
0.75
2.17
2.18
PPM
1
2
3
4
5
6
7
USER: -- DATE: Dec 5 2011
PTS1d: 13132 , 1638
Nuts - $ml76chloroform.fid
OF1: 2403.2
NA: 8
LB: 0.0
SW1: 6410
PD: 1.0 sec
PW: 8.0 us
F2: 100.525
F1: 399.746
EX: s2pul
blank line


(±)-18
^{13}H NMR
(100 MHz, CDCl$_3$)
N-Ts
21.749
37.957
44.621
55.881
67.569
76.916
77.230
77.555
125.025
127.629
129.530
129.967
130.068
131.899
132.559
134.831
143.680
144.469
PPM
20
40
60
80
100
120
140
160
USER: -- DATE: Dec 5 2011
PTS1d: 31875 32768
Nuts - $ml76chloroformc.fid
OF1: 10577.0
LB: 1.5
NA: 256
SW1: 24510
PD: 1.0 sec
PW: 5.8 us
F2: 399.745
F1: 100.526
:blank line
EX: s2pul