Syntheses of the *Stemona* Alkaloids (±)-Stenine, (±)-Neostenine, and (±)-13-Epineostenine Using a Stereodivergent Diels–Alder/Azido-Schmidt Reaction

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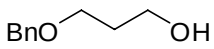
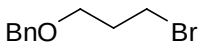
Experimental Section

General Procedures. All chemicals were purchased from commercial suppliers and used as received. Methylene chloride and THF were dried by being passed through two packed columns of neutral alumina under argon using a commercial solvent purification system prior to use. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz respectively in $CDCl_3$ (with 0.03% TMS as an internal standard). Chemical shifts are reported in parts per million (ppm) downfield from TMS. ^{13}C multiplicities were determined with the aid of an APT pulse sequence, differentiating the signals for methyl and methane carbons as "d" from methylene and quarternary carbons as "u". The infrared (IR) spectra were acquired as thin films on a FT-IR spectrometer and the absorbtion frequencies are reported in cm^{-1}. Melting points were determined on a capillary melting point apparatus and are uncorrected. Low resolution mass spectroscopic data (CI, chemical ionization or FAB^{+}, fast atom bombardment) were obtained with a quadrupole instrument. High resolution mass spectra (HRMS) [ESI+] were obtained using either a TOF or a double focusing spectrometer. Reaction flasks were oven or flame-dried and cooled under vacuum then purged with argon.

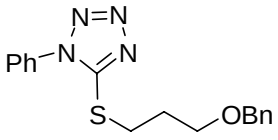


3-Benzyloxypropan-1-ol. Sodium hydride (60% dispersion in oil, 5.80 g, 116.0 mmol) was washed in triplicate with hexanes. After decanting the solvent the final time, dry DMF was added (150 mL). The mixture was cooled to 0 ºC, and 1,3-propanediol (8.0 g, 105 mmol) was added slowly. After stirring for 10 min, benzyl bromide (12.5 ml, 105 mmol) was added cautiously. The mixture was allowed to acclimate to room temperature

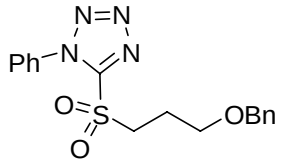
and stirred for 18 h. The reaction was quenched upon addition of water (200 mL) and subsequently extracted with EtOAc (6 x 100 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure to afford a yellow oil. Flash chromatography (25% EtOAc/hexane) gave the known 3-benzyloxypropan-1-ol[1] (17.3 g, 104.0 mmol, 92% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.86 (p, J = 6.1 Hz, 2H), 3.51 (br s, 1H) 3.61 (t, J = 6.1 Hz, 2H), 3.72 (m, 2H), 4.50 (s, 2H), 7.30 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 32.8, 60.9, 68.8, 73.5, 128.0, 128.8, 138.7; IR (neat) 3330, 2850, 1090 cm^{-1}; MS (CI) *m/z* 167 (M^++1), 91; HRMS calcd for $C_{10}H_{15}O_2$ (M^++1): 167.1072, found 167.1067.



3-Benzyloxy-1-bromopropane. To a solution of benzyloxypropan-1-ol (10.2 g, 61.4 mmol) in dry CH_2Cl_2 (150 mL) was added CBr_4 (25.4 g, 76.7 mmol). After cooling the solution to 0 ºC, PPh_3 (29.0 g, 110 mmol) was added in portions. The resulting red solution was stirred at room temperature for 18 h. The solvent was removed under reduced pressure, and the precipitate washed several times with ether (6 x 100 mL) and filtered. The collective ether extracts were concentrated to afford a yellow oil. Flash chromatography (3% EtOAc/hexane) gave the known 3-benzyloxy-1-bromopropane[2] (14.0 g, 61.1 mmol, 99% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (p, J = 6.3 Hz, 2H), 3.46 (t, J = 6.6 Hz, 2H), 3.53 (t, J = 5.8 Hz, 2H), 4.45 (s, 2H), 7.29 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 31.2, 33.5, 68.2, 73.6, 128.13, 128.15, 128.9, 138.8; IR (neat) 2820, 1090, 730, 690 cm^{-1}; MS (CI) *m/z* 228 (M^+-1), 91; HRMS calcd for $C_{10}H_{12}OBr$ (M^+-1): 227.0072, found 227.0067.



5-(3-Benzyloxypropylsulfanyl)-1-phenyl-1*H*-tetrazole. Sodium hydride (60% dispersion in oil, 3.70 g, 92.9 mmol) was washed in triplicate with hexanes. After decanting the solvent the final time, dry DMF was added (225 mL). The reaction mixture was cooled to 0 ºC, and 1-phenyl-1*H*-tetrazole-5-thiol (17.7 g, 77.4 mmol) was added slowly. After stirring for 10 min, 3-benzyloxy-1-bromopropane (13.8 g, 77.4 mmol) was added slowly, and the resulting solution was stirred for 18 h at room temperature. The reaction was quenched upon addition of water (500 mL) and subsequently extracted with EtOAc (6 x 100 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure to afford a yellow oil. Flash chromatography (25% EtOAc/hexane) gave 5-(3-benzyloxypropylsulfanyl)-1-phenyl-1*H*-tetrazole (25.0 g, 76.6 mmol, 99% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (p, J = 6.2 Hz, 2H), 3.53 (t, J = 7.0 Hz, 2H) 3.63 (t, J = 5.8 Hz, 2H), 4.52 (s, 2H), 7.32 (m, 5H), 7.56 (s, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.6, 30.8, 68.4, 73.5, 124.2, 128.11, 128.13, 128.8, 130.2, 130.5, 134.1, 138.5, 154.8; IR (neat) 2820, 1680, 1480 cm^{-1}; MS (CI) *m/z* 327 (M^++1), 173, 91, 84; HRMS calcd for $C_{17}H_{18}N_4OS$ (M^++1): 327.1280, found 327.1292.



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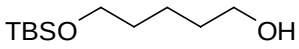
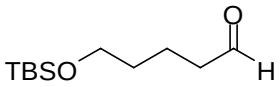
5-(3-Benzyloxy-propane-1-sulfonyl)-1-phenyl-1*H*-tetrazole 13. To a stirred solution of 5-(3-benzyloxypropylsulfanyl)-1-phenyl-1*H*-tetrazole (17.1 g, 52.4 mmol) in CH_2Cl_2 (400 mL) was added $NaHCO_3$ (13.2 g, 157 mmol) and *m*-CPBA (27.1 g, 157.0 mmol). The resulting mixture was stirred under an Ar atmosphere for 18 h and then quenched with 10% aq NaOH solution (150 mL). After extracting the aqueous layer with EtOAc (5 x 100 mL), the organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure to afford an orange oil. Flash chromatography (25% EtOAc/hexane) gave **13** (17.5 g, 48.8 mmol, 93% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25-2.32 (m, 2H), 3.65 (t, *J* = 5.8 Hz, 2H), 3.90 (m, 2H), 4.52 (s, 2H), 7.32-7.38 (m, 5H), 7.60-7.70 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.4, 54.0, 67.5, 73.4, 125.6, 128.2, 128.3, 128.9, 130.1, 131.9, 133.4, 138.2, 153.9; IR (neat) 2820, 1580, 1480, 1320, cm^{-1}; MS (CI) *m/z* 359 (M^++1), 131; HRMS calcd for $C_{17}H_{19}N_4O_3S$ (M^++1): 359.1178, found 359.1182.



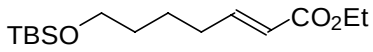
5-(*tert*-Butyldimethylsilanyloxy)-pentan-1-ol. Sodium hydride (60% dispersion in oil, 3.20 g, 63.4 mmol) was washed in triplicate with hexanes. After decanting the solvent the final time, dry THF was added (275 mL). The reaction mixture was cooled to 0 ºC, and 1,5-pentanediol was added slowly (6.0 g, 57.6 mmol). After stirring for 45 min at room temperature, the mixture was cooled to 0 ºC, and *tert*-butyldimethylchlorosilane

(8.60 g, 57.6 mmol) was added cautiously. The mixture was allowed to acclimate to room temperature and stirred for an additional 45 min. The reaction was quenched upon addition of 10% aq K_2CO_3 and subsequently extracted with ether (4 x 100 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure to afford a yellow oil. Flash chromatography (15% EtOAc/hexane) gave 5-(*tert*-Butyldimethylsilanyloxy)-pentan-1-ol[3] (12.6 g, 57.7 mmol, 99% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 6H), 0.90 (s, 9H), 1.37-1.45 (m, 2H), 1.52-1.63 (m, 4H), 1.71 (br s, 1H), 3.61-3.67 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ -4.9, 18.8, 22.4, 26.4, 32.8, 32.9, 63.3, 63.5; IR (neat) 3300, 2900, 1240 cm^{-1}; MS (CI) *m/z* 219 (M^++1), 161, 105, 92, 75, 69; HRMS calcd for $C_{11}H_{27}O_2Si$ (M^++1): 219.1780, found 219.1763.



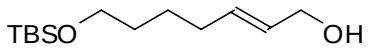
5-(*tert*-Butyldimethylsilanyloxy)-pentanal. A solution of oxalyl chloride (5.0 mL, 57.8 mmol) in dry CH_2Cl_2 (100 mL) was cooled to –78 ºC under an atmosphere of Ar. A solution of DMSO (8.20 mL, 116 mmol) in CH_2Cl_2 (10 mL) was added at a rate such that the reaction temperature remained below –65 ºC. After stirring for 5 min, a solution of 5-(*tert*-Butyldimethylsilanyloxy)-pentan-1-ol (12.6 g, 57.8 mmol) in CH_2Cl_2 (15 mL) was added slowly, and the resulting mixture was stirred for 15 min. Next, NEt_3 (40 mL, 289 mmol) was added slowly. After stirring the reaction for 10 additional min at –70 ºC, the cooling bath was removed and the reaction was allowed to warm for ca. 45 min. Upon reaching room temperature, water (100 mL) was added and stirring continued for 15 min. The reaction mixture was transferred to a separatory funnel, washed

successively with 5% HCl (100 mL), saturated $NaHCO_3$ solution (100 mL), and brine (50 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure to afford an oil. Flash chromatography (15% EtOAc/hexane) gave 5-(*tert*-butyldimethylsilanyloxy)-pentanal[4] (12.5 g, 57.8 mmol, 99% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 6H), 0.88 (s, 9H), 1.50-1.57 (m, 2H), 1.69 (p, *J* = 7.6 Hz, 2H), 2.45 (dt, *J* = 7.3 Hz, 1.6 Hz, 2H), 3.62 (t, *J* = 6.2 Hz, 2H), 9.76 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ -4.98, 18.7, 19.0, 26.3, 32.5, 44.0, 62.9, 203.0; IR (neat) 2940, 1730 cm^{-1}; MS (CI) *m/z* 217 (M^++1), 154, 136; HRMS calcd for $C_{11}H_{25}O_2Si$ (M^++1): 217.1624, found 217.1609.

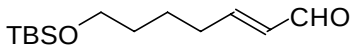


(*E*)-7-(*tert*-Butyldimethylsilanyloxy)-hept-2-enoic acid ethyl ester. A solution of 5-(*tert*-butyldimethylsilanyloxy)-pentanal (5.10 g, 23.6 mmol) and (carbethoxymethylene)triphenylphosphorane (8.20 g, 23.6 mmol) in CH_2Cl_2 (175 mL) was heated to reflux for 18 h. The reaction was cooled to room temperature, diluted with water and extracted with pentane. The organic extract was dried (Na_2SO_4), filtered, and concentrated under reduced pressure to afford a yellow oil. Flash chromatography (15% EtOAc/hexane) gave (*E*)-7-(*tert*-butyldimethylsilanyloxy)-hept-2-enoic acid ethyl ester[5] (6.6 g, 23.0 mmol, 98% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.84 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.50-1.54 (m, 4H), 2.19-2.24 (m, 2H), 3.59-3.62 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 5.83 (dd, *J* = 15.5 Hz, 1.3 Hz, 1H), 6.96 (dt, *J* = 15.6 Hz, *J* = 6.9 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ -4.9, 14.7, 18.7, 24.7, 26.3,

32.3, 32.6, 60.5, 63.1, 121.8, 149.5, 167.1; IR (neat) 2925, 1720, 1660 cm^{-1}; MS (CI) *m/z* 287 (M^++1), 229, 81; HRMS calcd for $C_{15}H_{31}O_3Si$ (M^++1): 287.2042, found 287.2063.

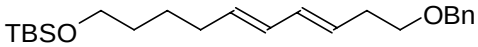


(*E*)-7-(*tert*-Butyldimethylsilanyloxy)-hept-2-en-1-ol. To a solution of (*E*)-7-(*tert*-butyldimethylsilanyloxy)-hept-2-enoic acid ethyl ester (11.2 g, 39.1 mmol) in diethyl ether (250 mL) was added DIBAL-H (1.0 M in hexanes, 86.0 mL, 86.1 mmol) at –78 ºC. The reaction was stirred at –20 ºC for 1 h and then warmed to room temperature. After stirring at room temperature for 2 h, an equal volume of saturated aq potassium sodium tartrate was added slowly, and the resulting voluminous mixture was stirred for an additional 18 h. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 x 150 mL). The organic extracts were combined, dried (Na_2SO_4), filtered, and concentrated to afford a colorless oil. Flash chromatography (15% EtOAc/hexane) gave (*E*)-7-(*tert*-butyldimethylsilanyloxy)-hept-2-en-1-ol[6] (9.5 g, 38.9 mmol, 99% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 6H), 0.90 (s, 9H), 1.42-1.56 (m, 5H), 2.07 (m, 2H), 3.62 (t, *J* = 6.4 Hz, 2H), 4.10 (d, *J* = 5.3 Hz, 2H), 5.61-5.74 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ -4.9, 18.8, 25.8, 26.4, 32.4, 32.7, 63.4, 64.2, 129.5, 133.7; IR (neat) 3330, 2930, 1470 cm^{-1}; MS (CI) *m/z* 245 (M^++1), 227, 187, 115; HRMS calcd for $C_{13}H_{29}O_2Si$ (M^++1): 245.1937, found 245.1930.



14

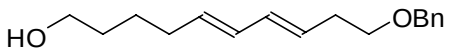
(*E*)-7-(*tert*-Butyldimethylsilanyloxy)-hept-2-enal 14. (*E*)-7-(*tert*-Butyldimethylsilyloxy)-hept-2-enal[7] **14** was prepared from (*E*)-7-(*tert*-butyldimethylsilanyloxy)-hept-2-en-1-ol using a Swern oxidation, as described above for 5-(*tert*-butyldimethylsilanyloxy)-pentanal. Flash chromatography (15% EtOAc/hexane) gave (*E*)-7-(*tert*-Butyldimethylsilanyloxy)-hept-2-enal **14** (7.1 g, 29.3 mmol, 99% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.89 (s, 9H), 1.57 (m, 4H), 2.35 (m, 2H), 3.63 (m, 2H), 6.12 (dd, *J* = 15.6 Hz, 7.9 Hz, 1H), 6.86 (dt, *J* = 15.6 Hz, 6.7 Hz, 1H), 9.51 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ -4.9, 18.7, 24.6, 26.3, 32.5, 32.9, 63.0, 133.4, 159.1, 194.5; IR (neat) 2900, 1670, 1080 cm^{-1}; MS (CI) *m/z* 243 (M^++1), 185, 111, 75; HRMS calcd for $C_{13}H_{27}O_2Si$ (M^++1): 242.1780, found 243.1775.



15

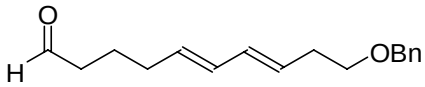
(5*E,7E*)-(10-Benzyloxy-deca-5,7-dienyloxy)-*tert*-butyldimethylsilane 15. A solution of sulfone **13** (10.0 g, 27.9 mmol) in THF (175 mL) was cooled to –78 ºC, and a solution of lithium bis(trimethylsilyl)amide (30.7 mL, 30.7 mmol) in THF (20 mL) was added slowly. The resulting solution was stirred at –65 ºC for 1 h, and then a solution of (*E*)-7-(*tert*-butyldimethylsilanyloxy)-hept-2-enal **14** (6.90 g, 28.5 mmol) in THF (20 mL) was added at a rate such that the temperature remained below –65 ºC. The orange solution was stirred for an additional hour at –65 ºC and then allowed to acclimate to room temperature over 18 h. Water (150 mL) was added and the resulting mixture stirred

for 1 h. The reaction was transferred to a separatory funnel, extracted with Et_2O (3 x 100 mL), dried (Na_2SO_4), filtered, and concentrated to afford a yellow oil. Flash chromatography (3% EtOAc/hexane) gave **15** (9.6 g, 25.6 mmol, 90% yield) as a pale yellow oil. The ratio of (5*E,7E*)-**15**/(5*E*,7*Z*)-**15** was determined to be ca. 85:15 by ^{1}H NMR. (5*E,7E*)-**15**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 6H), 0.93 (s, 9H), 1.37-1.49 (m, 2H), 1.52-1.59 (m, 2H), 2.08-2.13 (m, 2H), 2.39-2.44 (m, 2H), 4.55 (s, 2H), 5.57-5.65 (m, 2H), 6.01-6.14 (m, 2H), 7.28-7.37 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ -4.68, 18.8, 22.6, 26.4, 32.8, 33.1, 33.5, 63.6, 70.3, 73.3, 127.9, 128.0, 128.4, 128.7, 130.8, 132.7, 133.3, 138.9; IR (neat) 2900, 1450, 1090 cm^{-1}; MS (CI) *m/z* 375 (M^++1), 243, 91; HRMS calcd for $C_{23}H_{39}O_2Si$ (M^++1): 375.2719, found 375.2690. (5*E,7Z*)-**15**: ^{1}H NMR (400 MHz, $CDCl_3$, diagnostic peaks only) δ 2.51-2.56 (m, 2H), 4.56 (m, 2H), 5.33-5.42 (m, 1H), 5.65-5.75 (m, 1H), 6.34-6.42 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, diagnostic peaks only) δ 26.0, 28.8, 33.0, 63.4, 70.3, 125.7, 126.1, 128.0, 129.1, 130.9, 135.6.

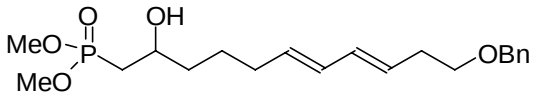


(5*E,7E*)-10-Benzyloxy-deca-5,7-dien-1-ol. To a stirred solution of diene **15** (5.70 g, 15.2 mmol) in ethanol (150 mL) was added pyridinium *p*-toluenesulfonate (1.10 g, 4.57 mmol). After stirring for 18 h, the solution was concentrated to give a viscous oil. Flash chromatography (25% EtOAc/hexane) gave (5*E,7E*)-10-Benzyloxy-deca-5,7-dien-1-ol (3.8 g, 14.6 mmol, 95% yield) as a colorless oil. The ratio of (5*E,7E*)-diene/(5*E*,7*Z*)-diene was determined to be ca. 85:15 by ^{1}H NMR. (5*E,7E*)-diene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41-1.63 (m, 5H), 2.11 (m, 2H), 2.40 (m, 2H), 3.53 (t, *J* = 6.8 Hz, 2H), 3.65 (t, *J* = 6.6 Hz, 2H), 4.54 (s, 2H), 5.62 (dt, *J* = 14.4 Hz, *J* = 6.9 Hz, 2H), 6.07 (m, 2H),

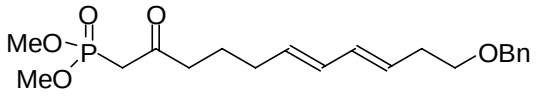
7.32 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 25.9, 32.6, 32.7, 33.5, 63.2, 70.3, 73.3, 128.0, 128.1, 128.6, 128.8, 130.9, 132.6, 133.0, 138.8; IR (neat) 3350, 2900, 1440, 1090 cm^{-1}; MS (CI) *m/z* 261 (M^++1), 243, 169, 91; HRMS calcd for $C_{17}H_{25}O_2$ (M^++1): 261.1855, found 261.1853. (5*E,7Z*)-diene: ^{1}H NMR (400 MHz, $CDCl_3$, diagnostic peaks only) δ 2.42 (m, 2H), 5.37 (m, 1H), 5.71 (m, 1H), 6.34 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, diagnostic peaks only) δ 25.8, 28.8, 33.0, 70.2, 126.0, 126.2, 128.1, 130.8, 135.3.



(5*E,7E*)-10-Benzyloxy-deca-5,7-dienal. The corresponding aldehyde was prepared from (5*E,7E*)-10-Benzyloxy-deca-5,7-dien-1-ol using a Swern oxidation, as described above. Flash chromatography (15% EtOAc/hexane) gave (5*E,7E*)-10-benzyloxy-deca-5,7-dienal (10.0 g, 38.7 mmol, 99% yield) as a yellow oil. The ratio of (5*E,7E*)-diene /(5*E*,7*Z*)-diene was determined to be ca. 85:15 by ^{1}H NMR. (5*E,7E*)-diene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62-1.71 (m, 2H), 1.97–2.10 (m, 2H), 2.32-2.38 (m, 4H), 3.47 (t, *J* = 6.7 Hz, 2H), 4.46 (s, 2H), 5.45-5.61 (m, 2H), 5.95-6.07 (m, 2H), 7.25 (m, 5H), 9.67 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.0, 32.2, 33.5, 43.5, 70.2, 73.2, 127.9, 128.0, 128.8, 129.2, 131.7, 131.8, 132.3, 139.0, 202.6; IR (neat) 2800, 1695, 1080 cm^{-1}; MS (CI) *m/z* 259 (M^++1), 154, 136; HRMS calcd for $C_{12}H_{23}O_2$ (M^++1): 259.1698, found 259.1689. (5*E,7Z*)- diene: ^{1}H NMR (400 MHz, $CDCl_3$, diagnostic peaks only) δ 2.49 (m, 2H), 5.33 (m, 1H), 6.33 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, diagnostic peaks only) δ 28.9, 32.5, 70.1, 126.6, 127.0, 127.9, 130.6, 134.1.

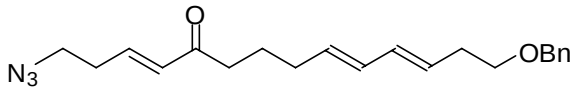


(6*E*,8*E*)-(11-benzyloxy-2-hydroxy-undeca-6,8-dienyl)-phosphonic acid dimethyl ester. To a cooled solution of dimethyl methyl phosphonate (2.60 mL, 23.8 mmol) in THF (25 mL) at -78 ºC was added *n*-butyllithium (1.6 M in hexanes, 15.5 mL, 23.3 mmol) slowly. The solution was stirred at -78 ºC for 1 h, and then (5*E,7E*)-10-benzyloxy-deca-5,7-dienal (2.80 g, 10.8 mmol) was added as a solution in THF (10 mL). Stirring was continued at -78 ºC for 3h and then at 0 ºC for an additional hour. The reaction mixture was quenched at 0 ºC with saturated aq NH_4Cl solution, transferred to a separatory funnel, and extracted with EtOAc (3 x 100 mL). The organic extracts were dried (Na_2SO_4), filtered, and concentrated to afford a yellow oil. Flash chromatography (100% EtOAc) gave β-hydroxyphosphonate (3.8 g, 9.9 mmol, 92% yield) as a pale yellow oil. The ratio of (6*E*,8E)-diene/(6*E*,8*Z*)-diene was determined to be ca. 85:15 by ^{1}H NMR. (6*E*,8E)-diene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39-1.56 (m, 4H), 1.90 (m, 1H), 1.95 (m, 1H), 2.01-2.14 (m, 2H), 2.33-2.40 (m, 2H), 3.48 (t, J = 6.8 Hz, 2H), 3.73 (d, J = 10.9 Hz, 6H), 3.87 (m, 1H), 3.96 (br s, 1H), 4.49 (s, 2H), 5.46-5.60 (m, 2H), 5.93-6.08 (m, 2H), 7.26 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 25.5, 32.7, 33.4, 38.1, 38.2, 52.6, 52.8, 66.5, 70.2, 73.2, 127.9, 128.0, 128.6, 128.7, 131.0, 132.9, 138.8; IR (neat) 3350, 2890, 1200 cm^{-1}; MS (CI) *m/z* 383 (M^++1), 357, 207, 91; HRMS calcd for $C_{20}H_{32}O_5P$ (M^++1): 383.198, found 383.1968. (6*E*,8*Z*)-diene: ^{1}H NMR (400 MHz, $CDCl_3$, diagnostic peaks only) δ 2.46 (dd, J = 13.3 Hz, 8.0 Hz, 2H), 4.50 (s, 2H), 5.33 (m, 1H), 5.60 (m, 1H), 6.34 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, diagnostic peaks only) δ 28.8, 32.7, 33.0, 33.7, 38.1, 38.3, 52.7, 52.8, 66.5, 70.2, 127.9.



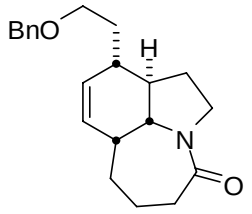
16

(6*E*,8*E*)-(11-Benzyloxy-2-oxo-undeca-6,8-dienyl)-phosphonic acid dimethyl ester 16. To a stirred solution of hydroxyphosphonate (2.90 g, 7.58 mmol) in dry CH_2Cl_2 (50 mL) was added activated 4Å sieves, *N*-morpholine-*N*-oxide (1.30 g, 11.4 mmol) and TPAP (0.13 g, 0.38 mmol). After stirring the resulting black mixture for 72 h, the reaction mixture was filtered through Celite and washed with EtOAc. Concentration of the filtrate provided a black oil. Flash chromatography (100% EtOAc) gave **16 (**2.2 g, 5.8 mmol, 75% yield) as a yellow oil. The ratio of (6*E*,8E)-**16**/(6*E*,8*Z*)-**16** was determined to be ca. 85:15 by ^{1}H NMR. (6*E*,8E)-**16**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64-1.73 (m, 2H), 2.05-2.19 (m, 2H), 2.36-2.41 (m, 2H), 2.59-2.63 (m, 2H), 3.05 (d, *J* = 22.7 Hz, 2H), 3.51 (t, *J* = 6.8 Hz, 2H), 3.75-3.77 (d, *J* = 11.2 Hz, 6H), 4.51 (s, 2H), 5.49-5.63 (m, 2H), 5.97-6.09 (m, 2H), 7.33 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.3, 32.0, 33.5, 41.1, 43.7, 53.4, 70.2, 73.3, 127.9, 128.1, 128.8, 129.1, 131.5, 132.0, 132.3, 138.8, 202.2; IR (neat) 2950, 1720, 1035 cm^{-1}; MS (CI) *m/z* 381 (M^++1), 345, 255, 91; HRMS calcd for $C_{20}H_{30}O_5P$ (M^++1): 381.1831, found 381.1836. (6*E*,8*Z*)-**16**: ^{1}H NMR (400 MHz, $CDCl_3$, diagnostic peaks only) δ 2.47-2.52 (m, 2H), 4.52 (s, 2H), 5.34-5.39 (m, 1H), 6.28-6.34 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, diagnostic peaks only) δ 28.8, 32.3, 42.4, 70.2, 126.4, 126.8, 130.5, 134.3.

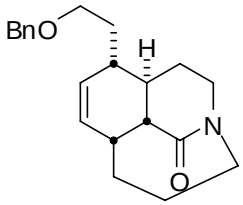


7

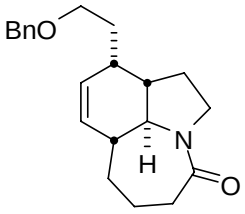
(3*E*,9*E*,11*E*)-1-Azido-14-benzyloxy-tetradeca-3,9,11-trien-5-one 7. Prior to use, $Ba(OH)_2 \bullet 8H_2O$ was dried in a 140 ºC oven for 2 h (NOTE: drying of the hydroxide for shorter or longer periods of time resulted in lower overall yields of **7**). Phosphonate **16** (1.30 g, 3.42 mmol) was placed in a 100 mL flask with THF (30 mL) and $Ba(OH)_2 \bullet 8H_2O$ (0.86 g, 2.74 mmol). The mixture was stirred for 30-45 min, causing it to turn white in color. 3-azidopropanal[8] (0.34 g, 3.42 mmol) was added slowly in 40:1 THF/H_2O (15 mL). After stirring the gelatinous material for 6 h, the solution was poured over saturated $NaHCO_3$ solution and extracted with EtOAc (4 x 100 mL). The extracts were dried (Na_2SO_4), filtered, and concentrated to give a yellow oil. Flash chromatography (15% EtOAc/Hex) afforded **7 (**1.0 g, 2.8 mmol, 85% yield) as a yellow oil. The ratio of (3*E*,9*E*,11*E*)-**7**/(3*E*,9*E*,11*Z*)-**7** was determined to be ca. 85:15 by ^{1}H NMR. (3*E*,9*E*,11*E*)-**7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67-1.76 (m, 2H), 2.02-2.16 (m, 2H), 2.39-2.43 (m, 2H), 2.43-2.55 (m, 4H), 3.39 (t, *J* = 6.7 Hz, 2H), 3.49 (t, *J* = 6.8 Hz, 2H), 4.50 (s, 2H), 5.45-5.70 (m, 2H), 5.97-6.09 (m, 2H), 6.14 (d, *J* = 16.0 Hz, 1H), 6.73 (dt, *J* = 16.0 Hz, *J* = 6.8 Hz, 1H), 7.26-7.33 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.9, 32.2, 32.3, 33.5, 39.9, 50.0, 70.2, 73.3, 127.9, 128.0, 128.1, 128.8, 129.0, 131.3, 132.3, 132.4, 132.7, 142.2, 200.2; IR (neat) 2050, 1700, 1650, 1600 cm^{-1}; MS (FAB$^+$) *m/z* 354 (M^++1), 154, 136; HRMS calcd for $C_{21}H_{28}N_3O_2$ (M^++1): 354.2182, found 354.2162. (3*E*,9*E*,11*Z*)-**7**: ^{1}H NMR (400 MHz, $CDCl_3$, diagnostic peaks only): δ 5.34-5.38 (m, 1H), 6.28-6.35 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, diagnostic peaks only) δ 14.6, 21.5, 27.4, 28.8, 32.6, 39.9, 60.8, 126.3, 126.8, 130.6, 134.6.



9



17



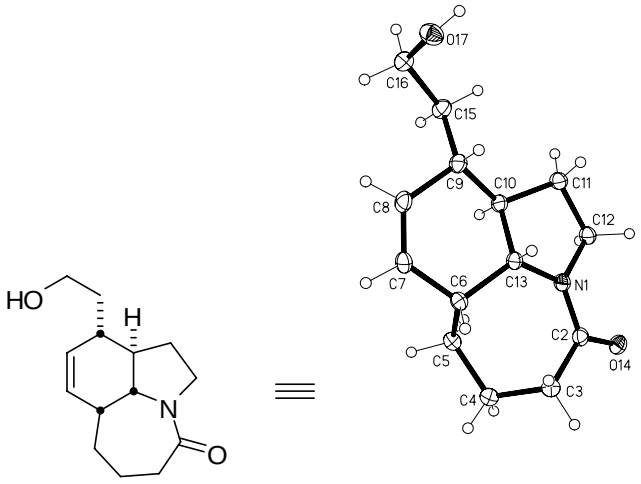
18

Lactams 9, 17 and 18. To a flame dried 50 mL flask was added azidotriene **7** (0.25 g, 0.71 mmol) in CH_2Cl_2 (35 mL) and $MeAlCl_2$ (0.71 mL, 1.0 M soln in toluene, 0.71 mmol). Refluxing the yellow solution for 48 h produced a dark greenish solution that was cooled to room temperature and then poured over saturated aq $NaHCO_3$ solution (100 mL). Upon shaking, the dark solution turned yellow in color. The mixture was extracted with EtOAc (3 × 100 mL), the combined organic layers dried (Na_2SO_4), filtered, and concentrated to afford a yellow oil. Flash chromatography (100% EtOAc) afforded the major lactam isomer **9** (100 mg, 0.31 mmol, 43% yield) as a viscous oil, the bridged lactam **17** (56 mg, 0.17 mmol, 24% yield) as a viscous oil, and the minor lactam isomer **18** (27 mg, 0.083 mmol, 12% yield as a white solid.

Major lactam **9** (R_f = 0.17): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39-1.48 (m, 3H), 1.54-1.64 (m, 2H), 1.72 (m, 2H), 1.85-1.93 (m, 2H), 2.13-2.16 (m, 1H), 2.28 (ddd, *J* = 13.2 Hz, 5.1 Hz, 1.7 Hz, 1H), 2.59 (m, 1H), 2.67 (m, 1H), 3.42 (m, 1H), 3.47-3.52 (m, 3H), 3.57 (t, *J* = 6.6 Hz, 1H), 4.51 (m, 2H), 5.53-5.59 (m, 1H), 5.63-5.66 (m, 1H), 7.31 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.2, 25.4, 26.8, 33.2, 33.4, 36.5, 38.0, 43.9, 45.9, 62.6, 68.0, 73.5, 128.01, 128.03, 128.8, 130.7, 130.9, 138.7, 171.5; IR (neat) 2840, 1625 cm^{-1}; MS (CI) *m/z* 326 (M^++1), 234, 91; HRMS calcd for $C_{21}H_{28}NO_2$ (M^++1): 326.2120, found 326.2129.

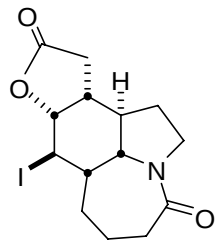
Bridged lactam **17** (R_f = 0.63): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40-1.64 (m, 4H), 1.72-2.01 (m, 5H), 2.19 (m, 1H), 2.36 (m, 1H), 2.48 (dt, *J* = 12.4 Hz, *J* = 4.8 Hz, 1H), 2.58 (dd, *J* = 10.0 Hz, *J* = 4.5 Hz, 1H), 2.89 (dt, *J* = 11.2 Hz, *J* = 4.2 Hz, 1H), 3.56 (t, *J* = 6.3 Hz, 2H), 3.69 (dt, *J* = 15.3 Hz, *J* = 4.2 Hz, 2H), 4.49 (m, 2H), 5.62-5.67 (m, 2H), 7.27-7.37 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.9, 25.4, 31.3, 32.2, 39.3, 39.9, 41.3, 53.4, 56.2, 56.8, 68.2, 73.6, 128.0, 128.1, 128.8, 132.6, 133.4, 138.8, 188.1; IR (neat) 2940, 1690 cm^{-1}; MS (FAB^+) *m/z* 326 (M^++1), 234, 91; HRMS calcd for $C_{21}H_{28}NO_2$ (M^++1): 326.2120, found 326.2122.

Minor lactam **18** (R_f = 0.25). Mp: 85-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20-1.26 (m, 1H), 1.44-1.47 (m, 1H), 1.57-1.63 (m, 2H), 1.76-1.79 (m, 1H), 1.86-1.91 (m, 2H), 1.95-1.99 (m, 1H), 2.08-2.17 (m, 2H), 2.31 (t, *J* = 13.9 Hz, 1H), 2.59-2.67 (m, 2H), 3.00 (dd, *J* = 10.7 Hz, *J* = 9.3 Hz, 1H), 3.20-3.27 (m, 1H), 3.55-3.61 (m, 2H), 3.90 (dd, *J* = 11.6 Hz, *J* = 8.0 Hz, 1H), 4.52 (m, 2H), 5.37 (m, 1H), 5.75-5.79 (m, 1H), 7.28-7.36 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.2, 25.7, 30.8, 34.4, 37.0, 38.8, 45.1, 46.8, 47.2, 60.1, 68.7, 73.5, 128.1, 128.8, 131.3, 138.7, 175.3; IR (neat) 2820, 1600, 1430 cm^{-1}; MS (FAB^+) *m/z* 326 (M^++1), 234, 91; HRMS calcd for $C_{21}H_{28}NO_2$ (M^++1): 326.2120, found 326.2102.



10-(2-Hydroxyethyl)-1,2,6,7,7a,10,10a,10b-octahydro-5*H*-azepino[3,2,1-*hi*]indol-4-one. Ammonia (10 mL) was condensed into a solution of lactam **9** (250 mg, 0.77 mmol) in THF (3 mL) at -78 ºC. Sodium was added, and upon stirring, the reaction mixture turned blue. The reaction was quenched with solid NH_4Cl, and the ammonia was allowed to evaporate. The resulting mixture was diluted with water (5 mL) and then extracted with CH_2Cl_2 (3 x 30mL). The organic extracts were dried (Na_2SO_4), filtered and concentrated under reduced pressure to afford a colorless oil. Flash chromatography (5% MeOH/CH_2Cl_2) afforded the tricyclic alcohol (180 mg, 0.76 mmol, 99% yield) as a white crystalline solid. Mp 158-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41-1.50 (m, 4H), 1.60-1.65 (m, 3H), 1.72-1.74 (m, 1H), 1.83-1.92 (m, 2H), 2.13-2.18 (m, 1H), 2.28 (ddd, *J* = 13.3 Hz, 5.1 Hz, 1.7 Hz, 1H), 2.64 (dt, *J* = 13.4 Hz, 6.7 Hz, 1H), 2.74 (m, 1H), 3.41-3.59 (m, 3H), 3.72-3.79 (m, 2H), 5.57-5.62 (m, 1H), 5.66-5.69 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.1, 25.4, 26.8, 33.1, 36.3, 36.5, 37.6, 43.9, 45.9, 60.4, 62.7, 130.7, 130.8, 171.6; IR (neat) 2920, 1600 cm^{-1}; MS (CI) *m/z* 236 (M^+-1), 111, 69; HRMS calcd for $C_{14}H_{22}NO_2$ (M^+-1): 236.1651, found 236.1640. Recrystallization from

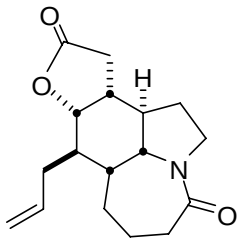
CH_2Cl_2/Hexanes gave white crystals (Mp 158-160 °C) that were subjected to single-crystal x-ray analysis.



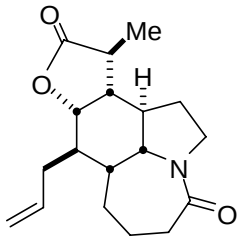
23

Iodolactam 23. Freshly prepared Jones reagent (8.0 N, 2.7 M) was added dropwise to an ice-cooled solution of tricyclic alcohol (100 mg, 0.43 mmol) in acetone (10 mL) until an orange color persisted. The solution was stirred for 3 h at 0 ºC and then 30 min at room temperature. After quenching with 2-propanol, the mixture was concentrated to afford a blue-green solid. To this material was added saturated aq $NaHCO_3$ solution (10 mL), THF (5 mL), Et_2O (5 mL), and solid $NaHCO_3$ (ca. 0.5 g). The mixture was cooled to 0 ºC, and then I_2 (0.32 g, 1.28 mmol) was added. The resulting reaction mixture was stirred for 2 h at 0 ºC and then at room temperature for 15 h. After adding saturated aq sodium thiosulfate solution, the solution was extracted with CH_2Cl_2 (3 × 50 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure to afford a yellow oil. Flash chromatography (5% MeOH/CH_2Cl_2) afforded **23** (128 mg, 0.34 mmol, 80% yield) as a white solid. Mp 187 °C (dec.), ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (m, 1H), 1.92 (m, 3H), 1.74-1.78 (m, 1H), 1.90-2.13 (m, 3H), 2.33-2.37 (m, 1H), 2.45 (dd, *J* = 18.0 Hz, 8.6 Hz, 1H), 2.64 (m, 2H), 2.88 (dd, *J* = 18.0 Hz, 10.0 Hz, 1H), 3.45 (m, 1H), 3.69 (dd, *J* = 11.6 Hz, 9.4 Hz, 1H), 3.78 (dd, *J* = 11.8 Hz, 9.0 Hz, 1H), 3.93 (t, *J* = 10.9 Hz, 1H), 4.94 (dd, *J* = 11.2 Hz, 9.5 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.2, 25.0,

27.9, 33.3, 33.6, 33.9, 38.0, 43.2, 44.2, 47.0, 60.6, 83.4, 171.4, 174.6; IR (neat) 1770, 1630 cm^{-1}; MS (EI) *m/z* 376 (M^++H), 248; HRMS calcd for $C_{14}H_{19}NO_2$ (M^++1): 376.0410, found 376.0405.

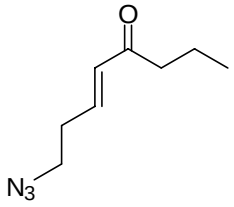


Allylated lactam. To a solution of lactam **23** (86 mg, 0.23 mmol) in degassed benzene (15 mL) was added allyltributyltin (0.14 mL, 0.459 mmol) and AIBN (8.0 mg, 0.0459 mmol). The solution was refluxed for 22 h, cooled to room temperature, and concentrated under reduced pressure to afford a colorless oil. Flash chromatography (5% MeOH/CH_2Cl_2) afforded the allylated lactam (62 mg, 0.21 mmol, 93% yield) of a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42-1.80 (m, 6H), 1.90-2.03 (m, 3H), 2.10-2.16 (m, 1H), 2.35-2.50 (m, 4H), 2.60 (m, 1H), 2.87 (dd, *J* = 17.9 Hz, 10.0 Hz, 1H), 3.48 (m, 2H), 3.77 (dd, *J* = 12.1 Hz, 9.1 Hz, 1H), 4.60 (dd, *J* = 11.9 Hz, 9.3 Hz, 1H), 5.84-5.94 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.6, 23.6, 28.2, 33.5, 33.6, 34.3, 35.3, 37.7, 42.2, 44.7, 47.1, 60.8, 81.2, 119.1, 134.3, 171.5, 176.3; IR (neat) 1760, 1620 cm^{-1}; MS (EI) *m/z* 290 (M^++1), 246, 84; HRMS calcd for $C_{17}H_{24}NO_3$ (M^++1): 290.1756, found 290.1755.

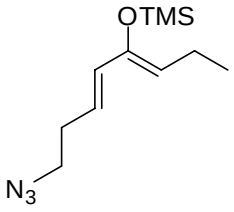


24

Methylated lactam 24. To a cooled solution of allylated lactam (0.16 g, 0.57 mmol) in THF (10 mL) at -78 ºC was added lithium bis(trimethylsilyl)amide (1.0 M in hexanes, 1.0 mL, 1.0 mmol) slowly. The solution was stirred at -78 ºC for 1 h, and then iodomethane (0.35 mL, 5.67 mmol) was added quickly. The yellow solution was stirred at -78 ºC for 40 min longer, and then the reaction was quenched with the addition of 20% aq HCl (ca. 6 mL). After warming to room temperature, the solution was extracted with CH_2Cl_2 (3 × 30mL). The organic extracts were dried (Na_2SO_4), filtered and concentrated under reduced pressure to afford an off-white solid. Flash chromatography (50% EtOAc/50% Hex) afforded **24** (0.13 g , 0.43 mmol, 77% yield) as a white crystalline solid. An analytical sample was furnished by reverse-phase prep HPLC (50% acetonitrile/50% water/0.1% TFA). Mp: 119-121 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (d, *J* = 7.1 Hz, 3H), 1.37-1.53 (m, 2H), 1.60-1.76 (m, 3H), 1.87-2.02 (m, 3H), 2.13-2.21 (m, 2H), 2.34-2.46 (m, 5H), 3.47 (m, 2H), 3.74 (dd, *J* = 12.2 Hz, *J* = 9.1 Hz, 1H), 4.43 (dd, *J* = 12.3 Hz, *J* = 9.4 Hz, 1H), 5.13 (m, 2H), 5.79-5.89 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 15.9, 22.5, 23.4, 28.2, 33.0, 34.1, 35.3, 40.2, 42.0, 44.7, 45.9, 47.5, 61.0, 78.7, 119.2, 134.2, 172.2, 178.9; IR (neat) 1779, 1639 cm^{-1}; MS (FAB$^+$) *m/z* 304 (M^++1), 154, 136; HRMS calcd for $C_{18}H_{26}NO_3$ (M^++1): 304.1908, found 304.1913.



(*E*)-8-Azidooct-5-en-4-one. To a solution of NaH (60%, 1.2 g, 30 mmol) in THF (60 mL) under Ar at −78 °C was added slowly β-keto phosphonate **25**[9] (5.90 g, 30 mmol) in THF (10 mL). The resulting solution was allowed to slowly warm up to −25 °C over 2 h to give a white gel-like suspension. This suspension was cooled in an ice bath followed by dropwise addition of 3-azidopropional[8b] (3.0 g, 30 mmol) in THF (10 mL). The mixture was stirred in an ice bath for 1 h and then quenched with water (50 mL). The reaction mixture was partitioned between water and Et_2O. The organic layer was dried (Na_2SO_4), filtered, and concentrated to give an oil. Chromatography (2-10% EtOAc/hexane) afforded (*E*)-8-azidooct-5-en-4-one (4.6 g, 27.5 mmol, 92% yield) as a colorless oil. R_f = 0.48 (15% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.8 Hz, 2H), 1.63 (h, *J* = 7.8 Hz, 2H), 2.50 (m, 4H), 3.43 (t, *J* = 7.7 Hz, 2H), 6.18 (d, *J* = 16.8 Hz, 1H), 6.75 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7, 17.7, 32.0, 42.3, 49.8, 132.5, 141.8, 200.2; IR (neat) 2100, 1697, 1674 cm^{-1}; MS (ES+) *m/z* 168 (M^++1); HRMS calcd for $C_8H_{14}N_3O$ (M^++H): 168.1137, found 168.1116.

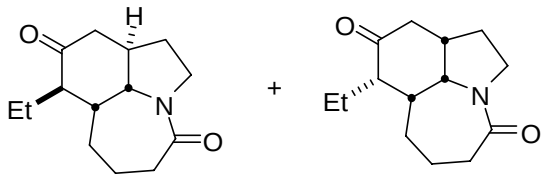


10

[(3*Z*,5*E*)-8-Azidoocta-3,5-dien-4-yloxy]trimethylsilane 10. To a solution of (*E*)-8-azidooct-5-en-4-one (1.67 g, 10.0 mmol) in anhydrous ethyl ether (35 mL) under Ar was added Et_3N (2.1 g, 20 mmol) at 0 °C followed by the addition of TMSOTf (3.3 g, 15 mmol). The resulting mixture was stirred at 0 °C for 30 min. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated under reduced pressure to give the diene **10 (**2.27 g, 9.5 mmol, 95% yield) as a light yellow oil. This diene was used directly for the next step. R_f = 0.75 (5:95 EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.23 (s, 9H), 0.99 (t, *J* = 7.0 Hz, 3H), 2.11 (m, 2H), 2.42 (m, 2H), 3.33 (t, *J* = 7.2 Hz, 2H), 4.75 (t, *J* = 7.6 Hz, 1H), 5.68 (m, 1H), 5.98 (d, *J* = 15.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 0.6, 14.1, 19.4, 31.7, 51.0, 117.1, 123.5, 131.7, 147.3; IR (neat) 2100 cm^{-1}; MS (ES+) *m/z* 240 (M^++1); HRMS calcd for $C_{11}H_{22}N_3OSi$ (M^++H): 240.1532, found 240.1519.

General procedure for the intermolecular Diels–Alder/intramolecular Schmidt reaction involving the diene 10. To a cooled (–78 ºC) solution of enone (5.0–10 mmol) in CH_2Cl_2 (20–40 mL) under Ar was added a Lewis acid such as $SnCl_4$ (1 equiv) followed by the addition of diene **10** (1.8 equiv). The resulting mixture was stirred at –78 ºC and allowed to warm to –55 ºC over 2 h. After slow addition of another portion of the same Lewis acid (1.5 equiv), the mixture was stirred at room temperature for 12 h and quenched with aqueous NH_4Cl. The mixture was partitioned between water and

CH_2Cl_2. The organic layer was collected, dried (Na_2SO_4), filtered, and concentrated to give an oil. Chromatography (10-50% EtOAc/hexane followed by 1-2% MeOH/ CH_2Cl_2) afforded the reaction products.



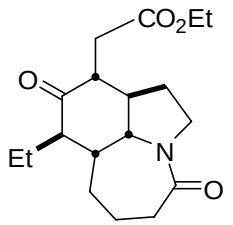
12 **26**

10-Ethyloctahydroazipino[3,2,1-*h,i*]indol-4,9(1*H*, 5*H*)dione 12 and **26**. 2-Cyclohexen-1-one (95%, 500 mg, 5.0 mmol) was reacted with **10** using $SnCl_4$ as Lewis acid to afford 820 mg (70%) of **12** and **26**, an oil, as a ca. 3: 1 (**12** : **26**) mixture of diastereomers based on HPLC/MS analysis. Repeated chromatography afforded pure **12** (600 mg, 2.55 mmol, 52% yield) and **26** (200 mg, 0.85 mmol, 17% yield) as brown syrups. Lactam **12**: R_f = 0.38 (1:10 MeOH/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.8 Hz, 3H), 1.45 (m, 2H), 1.62-2.70 (complex, 13H), 3.40 (dd, *J* = 8.9, 12.2 Hz, 1H), 3.53 (dt, *J* = 6.7, 11.2 Hz, 1H), 3.73 (dd, *J* = 8.9, 12.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.9, 21.0, 22.5, 24.9, 28.3, 32.9, 38.4, 38.7, 43.4, 46.9, 53.5, 62.2, 171.0, 212.0. IR (neat) 1707, 1612 cm^{-1}; MS (CI) *m/z* 236 (M^++1); HRMS calcd for $C_{14}H_{22}NO_2$ (M^++H): 236.1651, found 236.1634.

Lactam **26**: R_f = 0.32 (1:10 MeOH/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.03 (m, 1H), 1.26 (septet, *J* = 7.2 Hz, 1H), 1.52-2.54 (complex, 10H), 2.88 (sextet, *J* = 6.1 Hz, 1H), 3.40 (dt, *J* = 6.6, 11.9 Hz, 1H), 3.88 (dd, *J* = 9.6, 12.5 Hz, 1H), 4.40 (dd, *J* = 5.8, 9.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4, 19.3,

21.6, 21.9, 27.3, 33.3, 37.1, 37.7, 39.4, 44.8, 52.1, 59.9, 171.9, 211.2. IR (neat) 1713, 1624 cm^{-1}; MS (CI) *m/z* 236 (M^++1); HRMS calcd for $C_{14}H_{22}NO_2$ (M^++H): 236.1651, found 236.1644.

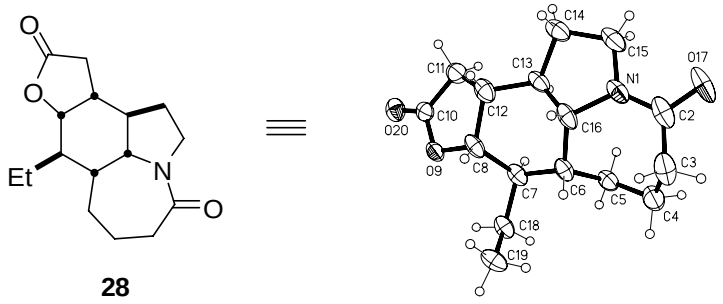
Compound **26** was obtained as the only product in 35% yield (415 mg) when BF_3•OEt_2 as Lewis acid; the physical and spectra data were identical as above.



27

Ethyl 10-ethyl-4,9-dioxo-dodecahydroazipino[3,2,1-*h,i*]indol-8-yl)acetate 27. Ketone **12** (500 mg, 2.12 mmol) in THF (10 mL) was added to a solution of LiHMDS (1 M, 3.8 mL, 3.8 mmol) in THF (30 mL) at –78 °C under Ar. After stirring at –78 °C for 1 h, ethyl 2-bromoacetate (1.78 g, 10.6 mmol) was added followed by HMPA (1.14 g, 6.4 mmol). The resulting mixture was stirred for 3.5 h and then quenched with aq 2 N HCl. After warming up to room temperature, the mixture was partitioned between water and CH_2Cl_2. The organic layer was collected, dried (Na_2SO_4), filtered, and concentrated to give an oil. Chromatography (10-50% EtOAc/hexane followed by 1-2% MeOH/EtOAc and finally1-2% MeOH/CH_2Cl_2) afforded **27** (500 mg, 1.56 mmol, 73% yield) as a yellow syrup. R_f = 0.42 (1:10 MeOH/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.26 (t, *J* = 6.8 Hz, 3H), 1.45 (m, 2H), 1.60-2.09 (complex, 7H), 2.30-2.47 (m, 4H), 2.57 (dd, *J* = 5.0, 16.4 Hz, 1H), 2.57 (dd, *J* = 5.0, 16.4 Hz, 1H), 2.73 (dd, *J* = 5.0, 16.4 Hz, 1H), 3.51 (m, 2H), 3.71 (dd, *J* = 9.2, 12.8 Hz, 1H), 4.13 (q, *J* = 6.8 Hz, 2H);

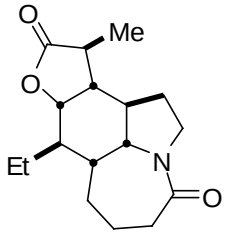
^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4, 14.2, 21.8, 22.4, 25.2, 26.8, 32.9, 34.7, 38.0, 42.6, 46.6, 49.2, 53.2, 60.9, 62.1, 171.0, 171.3, 213.0. IR (neat) 1732, 1713, 1632 cm^{-1}; MS (ES+) *m/z* 322 (M^++1); HRMS calcd for $C_{18}H_{28}NO_4$ (M^++H): 322.2018, found 322.2015.



28

(±)-**13-Desmethyl-5-oxostenine 28.** To a solution of ketoester **27** (400 mg, 1.25 mmol) in MeOH (30 mL) at 0°C was added $NaBH_4$ (118 mg, 3.8 mmol). The resulting mixture was stirred under for 1.5 h and then quenched with aq 2 N HCl. After concentration to ca 20 mL, the mixture was partitioned between water and CH_2Cl_2. The organic layer was collected, dried (Na_2SO_4), filtered, and concentrated to give a light yellow syrup. Chromatography (50% EtOAc/hexane followed by 2-5% MeOH/EtOAc and then 2-5% MeOH/ CH_2Cl_2) afforded **28** (220 mg, 0.79 mmol, 64% yield) as off-white crystalline solid. Mp 143-144 °C; R_f = 0.28 (1:10 MeOH/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.4 Hz, 3H), 1.37-1.75 (complex, 7H), 1.80-2.10 (complex, 4H), 2.26-2.59 (m, 4H), 2.78 (dd, *J* = 10.0, 17.8 Hz, 1H), 3.43 (m, 1H), 3.70 (dd, *J* = 9.0, 12.2 Hz, 1H), 4.56 (dd, *J* = 9.3, 11.7 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.2, 22.5, 23.0, 23.5, 27.8, 33.0, 33.1, 35.5, 37.4, 42.5, 44.2, 46.7, 60.6, 81.6, 171.1, 176.0. IR (neat) 1772, 1628 cm^{-1}; MS (ES+) *m/z* 278 (M^++1); HRMS calcd for $C_{16}H_{24}NO_3$ (M^++H):

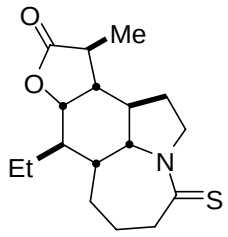
278.1756, found 278.1734. Crystals for X-ray crystallographic analysis were obtained by recrystallization from EtOAc/hexane.



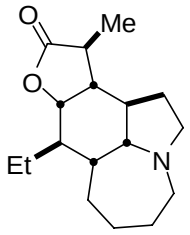
29

(±)-**5-Oxostenine 29.** To a solution of 56 mg (0.2 mmol) of lactone **28** in 10 mL of THF at −78 °C under Ar was added LiHMDS (1 M, 0.3 mL, 0.3 mmol). After stirring at −78 °C for 1 h, MeI (142 mg, 1 mmol) was added. The resulting mixture was stirred for 2 h and then quenched with aq 2 N HCl. After warming up to room temperature, the mixture was partitioned between water and CH_2Cl_2. The organic layer was collected, dried (Na_2SO_4), filtered, and concentrated to give a yellow syrup. Chromatography (10-50% EtOAc/hexane followed by, 1-2% MeOH/EtOAc) afforded **29** (46 mg, 0.16 mmol, 79% yield) as a light yellow crystalline solid. An analytical sample was furnished by reverse-phase preparative HPLC (50% acetonitrile/50%water/0.1% TFA). Mp 164-165 ºC; R_f = 0.34 (1:10 MeOH/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.5 Hz, 3H), 1.35 (d, *J* = 7.1 Hz, 3H), 1.40-1.75 (complex, 7H), 1.84-2.04 (complex, 4H), 2.14-2.21 (m, 2H), 2.31 (dd, *J* = 4.6, 12.8 Hz, 1H), 2.43 (m, 2H), 3.48 (m, 1H), 3.73 (dd, *J* = 9.2, 12.0 Hz, 1H), 4.46 (dd, *J* = 9.3, 12.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.2, 15.4, 22.5, 22.8, 23.4, 27.8, 33.0, 35.8, 39.8, 42.3, 44.3, 45.7, 46.9, 60.5, 79.2, 171.1, 178.7. IR (neat) 1763, 1634 cm^{-1}; MS (ES+) *m/z* 292 (M^++1); HRMS calcd for

$C_{17}H_{26}NO_3$ (M^++H): 292.1913, found 292.1906. ^1H and ^{13}C NMR spectra matched data reported by Wipf et al for (–)-**29**.[10]

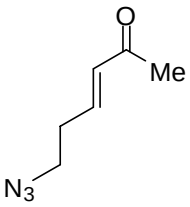


(±)-**5-Thiostenine.** To a solution of **29** (24 mg, 0.082 mmol) in 5 mL of CH_2C1_2 was added at room temperature 49 mg (0.123 mmol) of Lawesson's reagent. After 3 h, the reaction mixture was concentrated under reduced pressure and chromatographed on SiO_2 (EtOAC/hexane, 1: 3 to 1: 1) to give (±)-4-thiostenine (24 mg, 0.078 mmol, 93% yield) as a colorless solid. Mp 180-181 ºC; R_f = 0.49 (1:1 EtOAc/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.4 Hz, 3H), 1.37 (d, *J* = 7.1 Hz, 3H), 1.49-1.75 (complex, 7H), 2.00 (m, 2H), 2.20 (m, 3H), 2.46 (m, 2H), 2.87 (dt, *J* = 5.6, 13.0 Hz, 1H), 3.02 (dd, *J* = 3.9, 12.8 Hz, 1H), 3.73 (m, 2H), 4.14 (dd, *J* = 8.7, 13.9 Hz, 1H), 4.44 (dd, *J* = 8.9, 12.1 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.1, 15.6, 22.6, 23.2, 24.7, 27.8, 35.6, 39.7, 42.2, 42.7, 44.6, 45.5, 55.2, 65.8, 78.8, 178.4, 199.3. IR (neat) 1768 cm^{-1}; MS (ES+) *m/z* 308 (M^++1); HRMS calcd for $C_{17}H_{26}NSO_2$ (M^++H): 308.1684, found 308.1667.



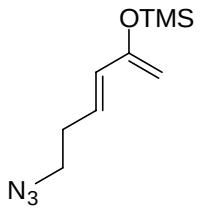
1

(±)**-Stenine 1.** A solution of 5-thiosteine (20 mg, 0.065 mmol) in 95% EtOH (10 mL) was treated at room temperature with Raney Ni (350 mg). The reaction mixture was shaken for 30 min and filtered through a cotton filter. The solvent was removed under reduced pressure, and the solid residue was chromatographed on SiO_2 (EtOAc) to give stenine **1 (**16 mg, 0.058 mmol, 89% yield) as a light yellow oil. R_f = 0.1 (1:10 MeOH/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.28 (d, *J* = 7.1 Hz, 3H), 1.30-1.75 (complex, 10H), 1.90 (m, 2H), 2.05-2.50 (m, 2H), 2.86 (dt, *J* = 4.2, 13.0 Hz, 1H), 3.17 (dt, *J* = 3.5, 9.0 Hz, 1H), 4.46 (dd, *J* = 9.2, 12.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 9.8, 15.0, 22.3, 26.2, 27.5, 29.5, 29.8, 39.8, 40.4, 42.5, 43.2, 47.4, 53.1, 55.0, 68.0, 80.5, 179.6. IR (neat) 1770 cm^{-1}; MS (ES+) *m/z* 278 (M^++1); HRMS calcd for $C_{17}H_{28}NO_2$ (M^++H): 278.2120, found 278.2106.



***(E)*-6-Azido-3-hexen-2-one.** To a solution of commercially-available dimethyl 2-oxopropylphosphonate (1.60 g, 10 mmol) in THF/H_2O (4:1, 40 mL) was added K_2CO_3 (2.10 g, 15 mmol). The resulting solution was cooled in an ice bath followed by dropwise addition of the 3-azidopropanal[8] (1.0 g, 10 mmol) in THF (4 mL). The mixture was

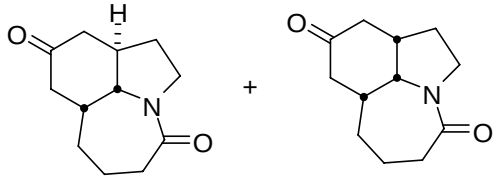
stirred in an ice bath for 1 h and then quenched with saturated aqueous $NaHCO_3$. The reaction mixture was partitioned between water and EtOAc. The organic layer was dried (Na_2SO_4), filtered, and concentrated to give an oil. Chromatography (10% EtOAc/hexane) afforded (*E)*-6-azido-3-hexen-2-one (940 mg, 6.76 mmol, 68% yield) as a colorless oil. R_f = 0.46 (25% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 2.51 (m, 2H), 3.44 (t, *J* = 6.7 Hz, 2H), 6.15 (d, *J* = 16.0 Hz, 1H), 6.74 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.5, 32.2, 50.0, 133.6, 143.4, 198.5; IR (neat) 1709, 1644 cm^{-1}; MS (CI) *m/z* 140 (M^++1); HRMS calcd for $C_6H_{10}N_3O$ (M^++H): 140.0824, found 140.0853.



30

(*E*)-6-Azido-2-trimethylsilyloxy-1,3-hexadiene 30. To a solution of (*E)*-6-azido-3-hexen-2-one (1.4 g, 10 mmol) in anhydrous ethyl ether (35 mL) under argon was added Et_3N (2.1 g, 20 mmol) at 0 °C followed by the addition of TMSOTf (3.3 g, 15 mmol). The resulting mixture was stirred at 0 °C for 30 min and then quenched with saturated aqueous $NaHCO_3$. The reaction mixture was partitioned between water and EtOAc. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated under reduced pressure to give **30** (2.18 g, 10.3 mmol, 98% yield) as a very light yellow oil oil. This diene was used directly for the next step without further purification. R_f = 0.52 (2% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 9H), 2.42 (m, 2H), 3.36 (t, *J* =

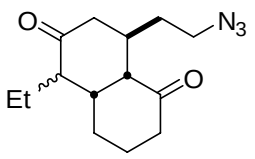
7.0 Hz, 2H), 4.31 (d, *J* = 3.5 Hz, 2H), 5.92 (m, 1H), 6.01 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ -0.1, 31.5, 50.7, 95.3, 126.4, 130.5, 154.3; IR (neat) 2098 cm^{-1}; MS (CI) *m/z* 212 (M^++1); HRMS calcd for $C_9H_{18}N_3OSi$ (M^++H): 212.1219, found 212.1196.



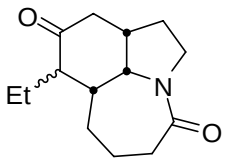
31 **32**

(±)-5-Octahydro-azipino[3,2,1-*h,i*]indol-4,9-dione 31 and **32.** To a cooled (-78 ºC) solution of 2-cyclohexenone (100 mg, 1.0 mmol) in CH_2Cl_2 (20 mL) under argon was added $SnCl_4$ (261 mg, 1.0 mmol) followed by the addition of diene **30** (380 mg, 1.8 mmol). The resulting mixture was stirred at -78 ºC for 2 h. After slow addition of another portion of $SnCl_4$ (391 mg, 1.5 mmol), the mixture was stirred at for 12 h, and then quenched with aqueous $NaHCO_3$. The mixture was partitioned between water and $CHCl_3$. The organic layer was collected, dried (Na_2SO_4), filtered, and concentrated to give an oil. Chromatography (10-50% EtOAc/hexane followed by 1-2% MeOH/$CHCl_3$) afforded a viscous oil of the desired lactams **31** and **32** (170 mg, 0.82 mmol, 82% yield) as a ca. 1:3.4 (**31**:**32**) mixture of diastereomers. The mixture solidified upon standing. R_f = 0.32 (1:10 MeOH/EtOAc); IR (neat) 1709, 1624 cm^{-1}; MS (CI) *m/z* 208 (M^++1); HRMS calcd for $C_{12}H_{18}NO_2$ (M^++H): 208.1338, found 208.1357. A pure sample of the major diastereomer was obtained after recrystallization from hexanes/EtOAc. Mp 131-133 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.54-1.84 (complex, 6H), 2.00 (m, 1H), 2.11 (d, *J* = 15.7 Hz, 1H), 2.24 (dd, *J* = 4.0, 15.9 Hz, 1H), 2.46 (m, 3H), 2.65 (m, 2H), 2.99 (m, 1H), 3.24

(two sets of t, J = 6.56, 11.9 Hz, 1H), 3.91 (m, 1H), 4.13 (d, 1H, J = 6.9 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 18.5, 31.2, 33.6, 35.7, 38.0, 39.3, 39.7, 43.3, 45.8, 59.7, 174.3, 211.2. Minor diastereomer (diagnostic peaks only, from the mixture): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (m), 3.75 (m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.1, 26.6, 28.4, 31.9, 39.7, 43.2, 45.6, 47.3, 62.6, 171.6, 211.5.



33

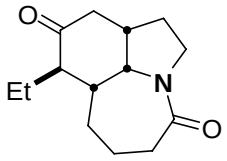


26a,**b**

10-Ethyloctahydroazepino[3,2,1]indole-4,9(1*H*,5*H*)-dione 26a,b. To a solution of 2-cyclohexen-1-one (562 mg, 5.85 mmol) and 4 Å molecular sieve pellets (7.00 g) in CH_2Cl_2 (80 mL) BF_3•OEt_2 (0.89 mL, 7.02 mmol, 1.20 equiv) was added at -78 °C. After stirring for 5 min, enol ether **11** (2.14 g, 8.77 mmol, 1.5 equiv) in CH_2Cl_2 (10 mL) was added portionwise over 15 min. The reaction was allowed to warm to room temperature and stirred overnight. Saturated aqueous NH_4Cl was added and the reaction extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated to yield a dark brown oil. Silica chromatography afforded a diastereomeric mixture of the ethyl tricylic ketoamides **26a,b** (587 mg, 2.50 mmol, 43% yield) as a light orange oil and ca. 0.32 g of a mixture of cyclohexenone and the azide-containing Diels-Alder adduct **33**. The diketoazide **33** mixture was dissolved in CH_2Cl_2 (50 mL), $TiCl_4$ (0.18 mL, 1.60 mmol, 1.30 equiv) was added, and the reaction stirred at room temperature overnight. The reaction was worked up and purified as above to yield an additional portion of mixed diastereomeric lactams **26a,b** as a light organge oil (166

mg, 0.71 mmol, 12% additional yield). The characterization of the major diastereomer of **26a** was in agreement with those previously reported.[11] R_f = 0.32 (1:10 MeOH/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.03 (m, 1H), 1.26 (septet, *J* = 7.2 Hz, 1H), 1.52-2.54 (complex, 10H), 2.88 (sextet, *J* = 6.1 Hz, 1H), 3.40 (dt, *J* = 6.6, 11.9 Hz, 1H), 3.88 (dd, *J* = 9.6, 12.5 Hz, 1H), 4.40 (dd, *J* = 5.8, 9.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4, 19.3, 21.6, 21.9, 27.3, 33.3, 37.1, 37.7, 39.4, 44.8, 52.1, 59.9, 171.9, 211.2. IR (neat) 1713, 1624 cm^{-1}; MS (CI) *m/z* 236 (M^++1); HRMS calcd for $C_{14}H_{22}NO_2$ (M^++H): 236.1651, found 236.1644.

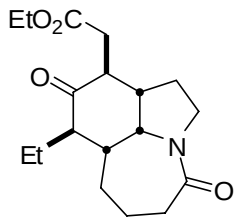
For the diketoazide **33**: R_f = 0.43 (25% EtOAc in hexanes); ^{1}H NMR (major isomer, 400 MHz) δ 0.83 (t, *J* = 7.3 hz, 3 H), 1.40-1.52 (m, 2 H), 1.64 (m, 1 H), 1.85 (m, 2 H), 1.92-2.08 (complex, 3 H), 2.19-2.34 (complex, 3 H), 2.49 (m, 2 H), 2.68 (dd, *J* = 11.1, 14.4 Hz, 1 H), 2.78 (m, 1 H), 2.92 (m, 1 H), 3.27 (m, 1 H), 3.36 (m, 1 H); ^{13}C NMR (major isomer, 100 MHz) δ d 11.9, 35.8, 42.3, 49.7, 55.1; u 19.7, 23.7, 25.3, 31.2, 41.3, 41.6, 49.2, 212.1, 213.0.



26b

10-Ethyloctahydroazepino[3,2,1]indole-4,9(1*H*,5*H*)-dione 26b.The collected diastereomeric ketolactams **26a**,**b** (3.80 g, 16.15 mmol) were epimerized by dissolution in MeOH (75 mL) followed by the addition of sodium methoxide (1.74 g, 32.3 mmol, 2.0 equiv) After stirring at room temperature for approximately 14 h, the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and filtered through Celite.

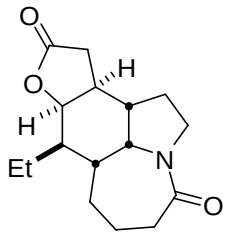
Silica gel chromatography afforded diastereomerically pure ketoamide **26b** (3.17 g, 13.5 mmol, 83% yield) as a light orange solid. For **26b** R_f = 0.58 (1:1 acetone:CH_2Cl_2) mp 92-95 °C; ^{1}H NMR (400 MHz) δ 0.85 (t, *J* = 7.5 Hz, 3 Hz), 1.45 (m, 1 H), 1.65-1.74 (complex, 4 H), 1.84 (m, 1 H), 1.92-1.99 (m, 1 H), 2.00-2.07 (m, 1 H), 2.17-2.18 (m, 1 H), 2.28-2.32 (m, 2 H), 2.43 (m, 1 H), 2.60-2.71 (m, 2 H), 2.97-3.03 (m, 1 H), 3.10 (dt, *J* = 6.3, 11.9 Hz, 1 H), 3.91 (dd, *J* = 8.4, 12.2 Hz, 1 H), 4.12 (d, *J* = 7.1 Hz, 1 H); ^{13}C NMR (100 MHz) δ d 10.2, 38.0, 39.1, 46.0, 60.2; u 17.8, 21.2, 30.4, 31.4, 38.1, 43.7, 46.0, 173.8, 213.9; IR 3554, 1707, 1618 cm^{-1}; HRMS calcd for $C_{14}H_{22}NO_2$ 236.1651, found 236.1639.



34

Ethyl 2-(10′-ethyl-4′,9′-dioxododecahydroazepino[3,2,1-hi]indol-8′-yl)acetate 34. To a solution of ketone **26b** (229 mg, 0.97 mmol) in THF (10.0 mL) and HMPA (0.52 mL, 3.00 mmol) at -78 °C was added LHMDS (2.5 mL, 1.0 M in THF, 2.50 mmol). The reaction was stirred for 1.75 h at -78 °C, then ethyl bromoacetate (0.54 mL, 4.86 mmol) was added neat. The cooling bath was removed and the reaction stirred for 3 h, then quenched with saturated NH_4Cl and extracted with EtOAc (1 × 20 mL) and CH_2Cl_2 (2 × 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The reaction residue was chromatographed on silica gel to yield the ketoester **34** as a light yellow oil (296 mg, 0.92 mmol, 95% yield). R_f = 0.49 (1:1 CH_2Cl_2:acetone); ^{1}H NMR

(400 MHz) δ 0.84 (t, *J* = 7.32 Hz, 3 H), 1.21 (t, *J* = 7.32 Hz, 3 H), 1.43-1.49 (m, 2 H), 1.51-1.57 (m, 2 H), 1.63-1.70 (m, 2 H), 1.80-1.90 (m, 1 H), 2.04-2.15 (m, 2 H), 2.34 (m, 1 H), 2.41 (dd, *J* = 3.2, 16.1 Hz, 1 H), 2.45-2.75 (complex, 5 H), 3.58 (m, 1 H), 3.93 (dd, *J* = 2.3, 5.2 Hz, 1 H), 4.00-4.12 (m, 3 H); ^{13}C NMR (100 MHz) δ d 11.5, 14.2, 41.3, 46.1, 46.8, 48.0, 62.1; u 17.8 (2 C), 28.3, 31.7, 33.5, 39.3, 47.3, 60.7, 172.0, 175.1, 210.0; IR 3450, 2935, 2878, 1719, 1643 (s) cm^{-1}; HRMS calcd for $C_{18}H_{28}NO_4$ 322.2018, found 322.2029.



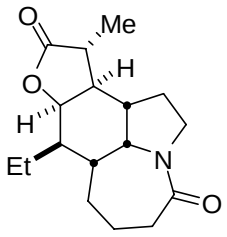
35a

8-Ethyldecahydroazepino[3,2,1-hi]furo[3,2-e]indole-4,10(31H,11bH)-dione

35a. A solution of the keto ester **34** (334 mg, 1.04 mmol) in CH_2Cl_2 (10 mL) was added to a slurry of anhydrous cerium trichloride (388 mg, 1.56 mmol) in CH_2Cl_2 (20 mL) at -78 °C. The mixture was stirred at -78 °C for 1 h and L-Selectride™ solution (2.1 mL, 1.0 M in THF, 2.10 mmol) was then added. The reaction was stirred for 15 h, slowly warming to rt. The reaction was filtered through a short plug of celite and the solvent removed in vacuo. The residue was purified by silica chromatography to give a mixture of two diastereomeric lactols **36** and a small amount of lactone **35a** (233 mg, 0.80 mmol, based on the lactol MW), which was used without further purification. For the lactol mixture **36**: ^{13}C NMR (100 MHz) δ d 11.0, 33.2, 33.5, 36.9, 43.3, 61.7, 80.0, 97.6, 98.2; u

17.6, 20.8, 28.3, 30.8, 38.5, 39.5, 47.4, 175.2, 176.4; HRMS calcd for $C_{16}H_{26}NO_3$ 280.1913, found 280.1896.

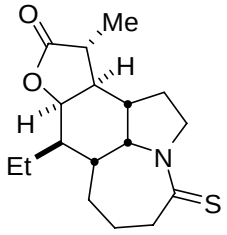
The mixture of the lactone **35a** and lactols **36** (233 mg, 0.80 mmol based on the lactol MW) were dissolved in CH_2Cl_2 (15 mL) and added to 4 Å molecular sieve pellets (1.50 g). To this mixture was successively added N-methylmorpholine N-oxide (187 mg, 1.60 mmol) then tetrapropylammonium perruthenate (28 mg, 0.08 mmol) as solids. The reaction was stirred for 1.5 h at room temperature, filtered through a plug of Celite and the solvent removed in vacuo. The residue was purified by silica chromatography to give lactone **35a** as a white solid (182 mg, 0.66 mmol, 63% yield over two steps). For **35a** R_f = 0.33 (1:1 acetone: CH_2Cl_2); mp 143-145 °C; ^{1}H NMR (400 MHz) δ 0.99 (t, *J* = 7.3 Hz, 3 H), 1.39 (m, 1 H), 1.48-1.71 (complex, 6 H), 1.85 (m, 1 H), 2.10 (m, 2 H), 2.14 (m, 2 H), 2.35 (d, *J* = 16.9 Hz, 2 H), 2.72 (dd, *J* = 7.0, 15.1 Hz, 1 H), 2.82 (dd, *J* = 7.1, 16.9 Hz, 1 H), 3.42 (dt, J = 6.0, 11.9 Hz, 1 H), 3.79 (dd, J = 2.0, 4.8 Hz, 1 H), 3.92 (dd, *J* = 8.3, 12.4 Hz, 1 H), 4.67 (dd, *J* = 2.5, 4.6 Hz, 1 H); ^{13}C NMR (100 MHz) δ d 11.0, 33.3, 33.5, 37.0, 43.3, 61.6, 80.0; u 17.6, 20.8, 28.3, 30.9, 38.5, 39.6, 47.3, 175.1, 176.3; IR 2935, 2253, 1772, 1615 cm^{-1}; HRMS calcd for $C_{16}H_{24}NO_3$ 278.1756, found 278.1756.



37

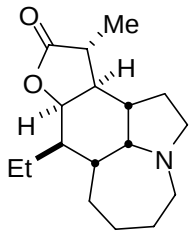
13-*Epi*-5-oxoneostenine 37. A mixture of lactone **35a** (40 mg, 0.14 mmol) and HMPA (0.10 mL, 0.56 mmol) in THF (2 mL) was cooled to -78 °C, a solution of

LHMDS (0.36 mL, 1.0 M in THF, 0.36 mmol, 2.5 equiv) was added, and the reaction stirred at -78 °C for 2 h. A solution of methyl iodide (102 mg, 0.72 mmol, 5 equiv) in THF (1 mL) was added and the reaction warmed to room temperature. The reaction mixture was quenched with aqueous saturated NH_4Cl and extracted with EtOAc (3 × 15 mL). The organics were dried with Na_2SO_4 and concentrated to a viscous oil. Silica gel chromatography gave the methylated lactone **37** (37 mg, 0.13 mmol, 92% yield) as a white solid. R_f = 0.49 (1:1 acetone: CH_2Cl_2); mp 154-156 °C; ^{1}H NMR (400 MHz) δ 1.03 (t, *J* = 7.3 Hz, 3 H), 1.37 (d, *J* = 7.6 Hz, 3 H), 1.52-1.67 (complex, 6 H), 1.84-1.93 (m, 2 H), 2.17 (m, 1 H), 2.38 (m, 1 H), 2.49 (dd, *J* = 1.8, 7.6 Hz, 1 H), 2.65 (d, *J* = 9.4 Hz, 1 H), 2.69 (m, 1 H), 3.43 (dt, *J* = 6.7, 10.5 Hz, 1 H), 3.82 (dd, *J* = 2.3, 5.6 Hz, 1 H), 3.87 (ddd, *J* = 2.0, 8.8, 12.3 Hz, 1 H), 4.81 (dd, *J* = 2.6, 5.6 Hz, 1 H); ^{13}C NMR (100 MHz) δ d 11.1, 15.4, 33.5, 34.0, 43.0, 43.7, 44.7, 60.9, 77.4; u 17.7, 20.7, 28.5, 30.2, 38.9, 46.9, 174.6, 179.2; IR 1769, 1630 cm^{-1}; HRMS calcd for $C_{17}H_{26}NO_3$ 292.1913, found 292.1932.



13-*Epi*-5-thioneostenine. Lactam **37** (37 mg, 0.12 mmol) and phosphorous pentasulfide (18 mg, 0.04 mmol) were combined in CH_2Cl_2 (1 mL). A solution of hexamethyldisiloxane (19 mg, 0.37 mmol) in CH_2Cl_2 (1 mL) was added and the reaction monitored by TLC. After 2 h, the reaction was filtered through a plug of silica gel and concentrated to a viscous oil. The crude mixture was purified by silica chromatography to

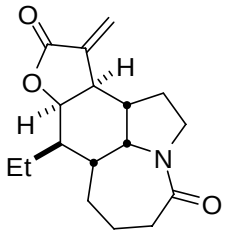
give the pure thioamide as an off-white solid (31 mg, 0.10 mmol, 84% yield). R_f = 0.84 (1:1 acetone:CH_2Cl_2); mp 192-196 °C; ^{1}H NMR (400 MHz) δ 1.00 (t, *J* = 7.3 Hz, 3 H), 1.37 (d, *J* = 7.3 Hz, 3 H), 1.50 (dt, *J* = 3.8, 15.5 Hz, 1 H), 1.58-1.80 (complex, 6 H), 1.88 (m, 1 H), 2.11 (dd, *J* = 7.3, 12.8 Hz, 1 H), 2.20 (m, 2 H), 2.52 (m, 2 H), 2.82 (m, 1 H), 3.42 (m, 1 H), 3.86 (m, 1 H), 4.13 (m, 1 H), 4.20 (t, *J* = 4.7 Hz, 1 H), 4.86 (dd, *J* = 2.9, 7.0 Hz, 1 H); ^{13}C NMR (100 MHz) δ d 11.1, 15.7, 33.8, 36.4, 41.8, 42.9, 43.0, 64.0, 76.5; u 19.8, 20.8, 28.3, 29.2, 46.9, 54.6, 178.8, 202.4; IR 2975, 2932, 2876, 1761, 1753 cm^{-1}; HRMS calcd for $C_{17}H_{26}NO_2S$ 308.1684, found 308.1700.



13-epineostenine **38**

13-*Epi*neostenine 38. To a solution of 13-epi-4-thioneostenine (31 mg, 0.10 mmol) in EtOH (2 mL) was added Raney nickel 2800 slurry in water (600 mg). The mixture was stirred vigorously for 2 h, filtered through a Celite plug and the solvents removed in vacuo. The residue was purified by chromatography on basic alumina to give 13-epineostenine **38** as a white solid (22 mg, 0.079 mmol, 93% yield). R_f = 0.20 (acetone); mp 106-108 °C; ^{1}H NMR (400 MHz) δ 0.98 (t, *J* = 7.3 Hz, 3 H), 1.29 (d, *J* = 7.0 Hz, 3 H), 1.33-1.43 (m, 2 H), 1.53-1.64 (complex, 4 H), 1.66-1.74 (m, 3 H), 1.83 (m, 2 H), 2.26-2.46 (complex, 5 H), 2.80 (dd, *J* = 4.6, 9.0 Hz, 1 H), 3.02 (dd, *J* = 4.1, 12.0 Hz, 1 H), 3.10 (t, *J* = 7.0 Hz, 1 H), 4.85 (dd, *J* = 4.1, 8.5 Hz, 1 H); ^{13}C NMR (100 MHz) δ d 11.4, 15.4, 35.1, 38.9, 39.4, 41.5, 42.8, 65.6, 77.4; u 19.8, 22.9, 31.2, 31.3, 56.0, 57.6,

179.8; IR 2930, 1772, 1634 cm^{-1}; HRMS calcd for $C_{17}H_{28}NO_2$ 278.2120, found 278.2124.

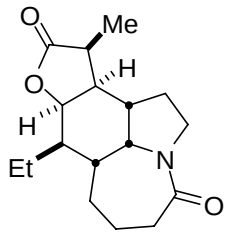


39

8-Ethyl-11-methylenedecahydroazepino[3,2,1-hi]furo[3,2-e]indole-4,10(31H,11bH)-dione 39. A mixture of lactone **35a** (52 mg, 0.19 mmol) and HMPA (0.10 mL, 0.56 mmol) in THF (2 mL) was cooled to -78 °C, a solution of LHMDS (0.47 mL, 1.0 M in THF, 0.47 mmol) was added, and the reaction stirred at -78 °C for 1 h. Carbon dioxide was then bubbled through the reaction for 15 min and the reaction warmed to room temperature. The reaction mixture was quenched with aqueous saturated NH_4Cl and extracted with EtOAc (3 × 15 mL). The organics were dried with Na_2SO_4 and the solvent removed in vacuo to give the β-carboxylic acid lactone as a yellow oil, which was used without further purification or characterization.

A methylenation reagent stock solution was prepared as described by Greene and coworkers[12] by combining N-methylaniline (5.2 mL), sodium acetate (600 mg), and aqueous formaldehyde solution (15 mL, 37% solution) in acetic acid (20 mL). The methylenation reagent stock solution (0.5 mL) was added to the crude β-carboxylic acid lactone. The reaction mixture stirred at rt for 2.5 h, diluted with water (20 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The organic layers were combined, dried with Na_2SO_4 and the solvent removed in vacuo. The crude product mixture was purified on

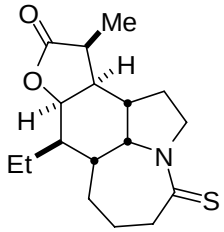
silica chromatography to give the methylene lactone as a white solid (27 mg, 0.09 mmol, 49% yield from **35a**). R_f = 0.46 (1:1 acetone: CH_2Cl_2); mp 149-151 °C; ^{1}H NMR (400 MHz) δ 1.00 (t, *J* = 7.3 Hz, 3 H), 1.23 (m, 1 H), 1.42 (m, 1 H), 1.57-1.83 (complex, 5 H), 1.99 (m, 1 H), 2.45 (m, 2 H), 2.65 (m, 1 H), 2.91 (t, *J* = 6.1, 1 H), 3.52 (m, 1 H), 3.82 (m, 1 H), 3.88 (dd, *J* = 2.5, 6.6 Hz, 1 H), 4.77 (dd, *J* = 3.0, 6.8 Hz, 1 H), 5.67 (d, *J* = 2.0 Hz, 1 H), 6.23 (d, *J* = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz) δ d 11.2, 33.7, 35.0, 40.2, 42.8, 59.5, 76.9; u 18.0, 20.4, 28.7, 29.2, 37.8, 46.3, 121.0, 140.7, 171.0, 174.1; IR 1753, 1625 cm^{-1}; HRMS calcd for $C_{17}H_{24}NO_3$ 290.1756, found 290.1779.



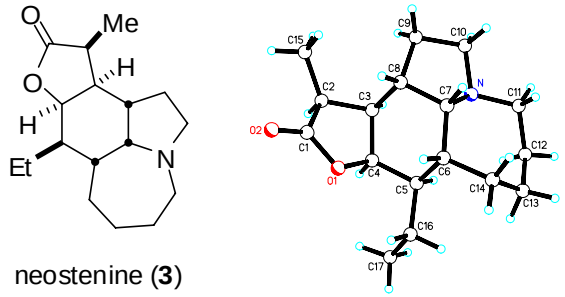
40

5-Oxoneostenine 40. Methylene lactone **39** (67 mg, 0.23 mmol) and platinum (IV) oxide (20 mg, 0.09 mmol) were suspended in methanol (1 mL) and acetic acid (1 mL). The mixture was stirred under a hydrogen atmosphere at 1 atmfor 16 h at room temperature, filtered through Celite and concentrated. The residue was purified by silica chromatography to give 5-oxoneostenine **40** (60 mg, 0.21 mmol, 91% yield) as a white solid. R_f = 0.56 (1:1 CH_2Cl_2:acetone); mp 203-205 °C; ^{1}H NMR (400 MHz) δ 0.99 (t, *J* = 7.3 Hz, 3 H), 1.28 (d, *J* = 7.3 Hz, 3 H), 1.37-1.69 (complex, 7 H), 1.87 (m, 1 H), 2.08 (m, 1 H), 2.17 (m, 3 H), 2.34 (m, 1 H), 2.71 (m, 1 H), 2.95 (m, 1 H), 3.40 (m, 1 H), 3.80 (m, 1 H), 3.93 (m, 1 H), 4.57 (m, 1 H); ^{13}C NMR (100 MHz) δ d 9.4, 11.0, 32.2, 33.3, 38.2,

40.5, 42.0, 61.9, 78.2; u 17.6, 20.5, 29.1, 30.9, 39.6, 47.2, 175.0, 178.6; IR 1759, 1636 cm^{-1}; HRMS calcd for $C_{17}H_{26}NO_3$ 292.1913, found 292.1932.

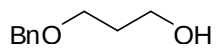


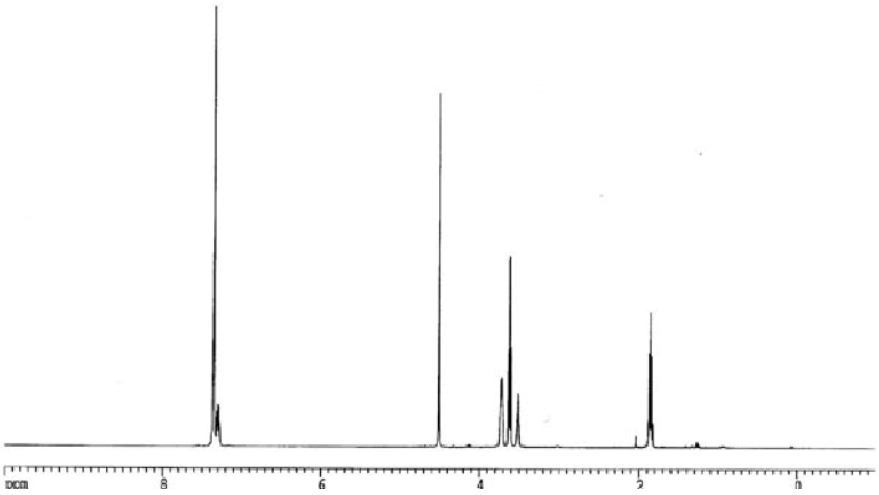
5-Thioneostenine. 5-Oxoneostenine **40** (63 mg, 0.23 mmol) and phosphorous pentasulfide (100 mg, 0.23 mmol) were combined in CH_2Cl_2 (1 mL). A solution of hexamethyldisiloxane (73 mg, 0.45 mmol) in CH_2Cl_2 (1 mL) was added and the reaction monitored by TLC. After 2 h, the reaction was filtered through a plug of silica gel and concentrated to give a viscous oil. The crude mixture was purified by silica chromatography to give the pure thioamide as a white solid (49 mg, 0.16 mmol, 70% yield). R_f = 0.45 (1:1 EtOAc:hexanes); mp 212-214 °C; ^{1}H NMR (400 MHz) δ 0.98 (t, *J* = 7.3 Hz, 3 H), 1.28 (d, *J* = 7.3 Hz, 3 H), 1.38 (m, 1 H), 1.49-1.64 (complex, 5 H), 1.72 (m, 1 H), 1.99 (m, 1 H), 2.12 (m, 1 H), 2.25 (m, 1 H), 2.33 (m, 1 H), 2.67 (m, 1 H), 2.98 (m, 1 H), 3.57 (dd, *J* = 7.6, 14.1 Hz, 1 H), 3.78 (dt, *J* = 6.3, 12.1 Hz, 1 H), 4.00 (d, *J* = 5.3 Hz, 1 H), 4.37 (dd, *J* = 7.8, 13.9 Hz, 1 H), 4.60 (dd, *J* = 2.3, 4.6, 1 H); ^{13}C NMR (100 MHz) δ d 9.4, 10.9, 33.1, 34.0, 38.9, 40.6, 41.8, 66.8, 77.8; u 19.2, 20.6, 29.6, 30.7, 49.4, 56.4, 178.3, 204.6; IR 2977, 2933, 2878, 1764, 1482 cm^{-1}; HRMS calcd for $C_{17}H_{26}NO_2S$ 308.1684, found 308.1691.



neostenine (**3**)

Neostenine 3. To a solution of 5-thioneostenine (26 mg, 0.085 mmol) in THF (1 mL) and EtOH (1 mL) was added Raney nickel 2800 slurry in water (230 mg). The mixture was stirred vigorously for 1.5 h, filtered through a Celite plug and the solvents removed in vacuo. The residue was purified by chromatography on basic alumina to give neostenine as a white solid (22 mg, 0.079 mmol, 93% yield). R_f = 0.31 (acetone); mp 126-128 °C (lit[13] 90-92 °C); ^{1}H NMR (400 MHz) δ 0.99 (t, *J* = 7.3 Hz, 3 H), 1.22 (d, *J* = 7.2 Hz, 3 H), 1.41 (m, 1 H), 1.56-1.91 (complex, 10 H), 1.98 (m, 1 H), 2.26 (m, 1 H), 2.33 (m, 1 H), 2.39-2.48 (m, 2 H), 2.86 (m, 1 H), 3.19 (m, 1 H), 4.51 (m, 1 H); ^{13}C NMR (100 MHz) δ d 10.6, 11.8, 34.8, 37.8, 38.0, 43.0, 43.5, 71.4, 79.9; u 21.6, 21.7, 28.6, 28.9, 30.7, 56.1, 56.4, 180.2; IR 2985, 2934, 1762, 1638 cm^{-1}; HRMS calcd for $C_{17}H_{28}NO_2$ 278.2120, found 278.2131. Except for the increased melting point, these data are in agreement with those obtained by Lin and coworkers[13].



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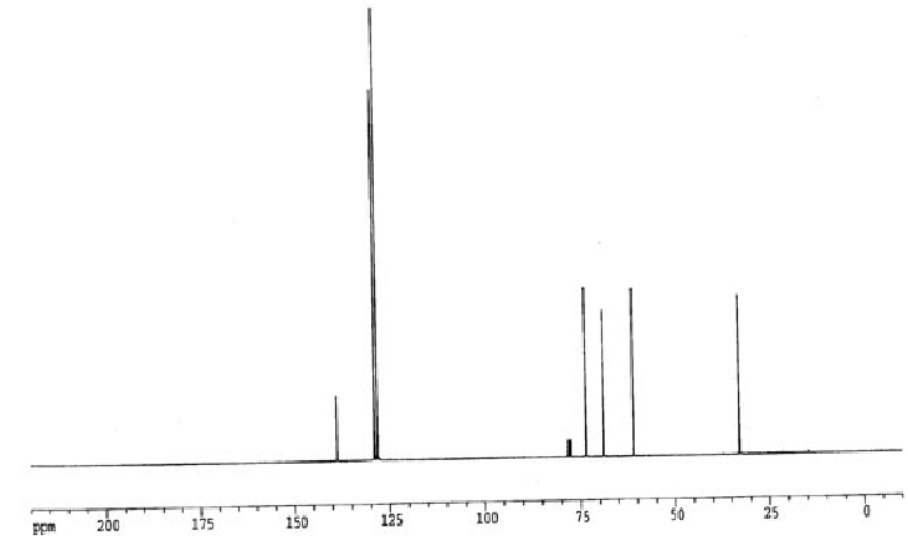
Current Data Parameters
NAME                  dc-VI-24
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20010629
Time                   14.42
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG                zg30
TD                      32768
SOLVENT                CDCl3
NS                         16
DS                          2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                         16
DW                  104.400 usec
DE                    4.50 usec
TE                    300.0 K
D1                 1.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                       7.70 usec
PL1                     -6.00 dB
SFO1             400.1320007 MHz

F2 - Processing parameters
SI                         16384
SF                400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                      20.00 cm
F1P                    10.000 ppm
F1                   4001.30 Hz
F2P                    -1.000 ppm
F2                   -400.13 Hz
PPMCM                 0.55000 ppm/cm
HZCM                220.07150 Hz/cm
```




```
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_              20010629
Time                   14.51
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG                zgpg30
TD                      65536
SOLVENT                CDCl3
NS                        309
DS                          2
SWH                23148.148 Hz
FIDRES              0.353213 Hz
AQ                  1.4156276 sec
RG                       4096
DW                   21.600 usec
DE                    4.50 usec
TE                    300.0 K
D1                 0.05000000 sec
d11                0.03000000 sec
d12                0.00002000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                   12.30 usec
PL1                   2.00 dB
SFO1             100.6232933 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                100.00 usec
PL2                     0.00 dB
PL12                   18.00 dB
PL13                   18.00 dB
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                100.6127290 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                      20.00 cm
F1P                   220.000 ppm
F1                  22134.80 Hz
F2P                   -10.000 ppm
F2                   -1006.13 Hz
PPMCM                11.50000 ppm/cm
HZCM                1157.04639 Hz/cm
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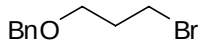

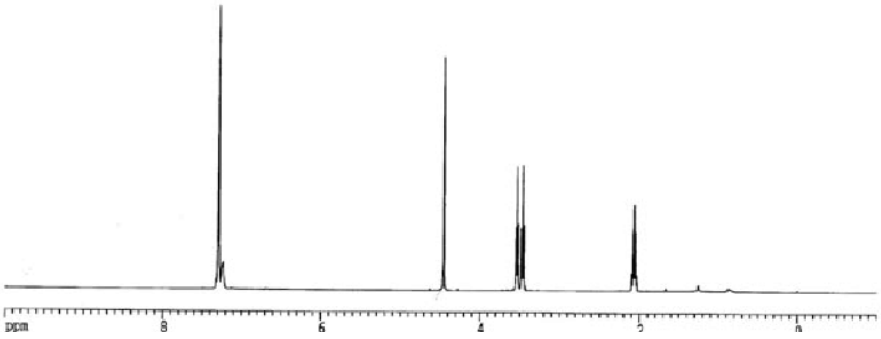


```
Current Data Parameters
NAME                  4c-VI-27
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20010630
Time                    13.30
INSTRUM                drx400
PROBHD      5 mm Multinu
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                        16
DW                  104.400 usec
DE                    4.50 usec
TE                    300.0 K
D1                  1.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     7.70 usec
PL1                   -6.00 dB
SFO1              400.1320007 MHz

F2 - Processing parameters
SI                        16384
SF                400.1300611 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        20.00 cm
F1P                       10.000 ppm
F1                      4001.30 Hz
F2P                       -1.000 ppm
F2                      -400.13 Hz
PPMCM                  0.55000 ppm/cm
HZCM                 220.07153 Hz/cm
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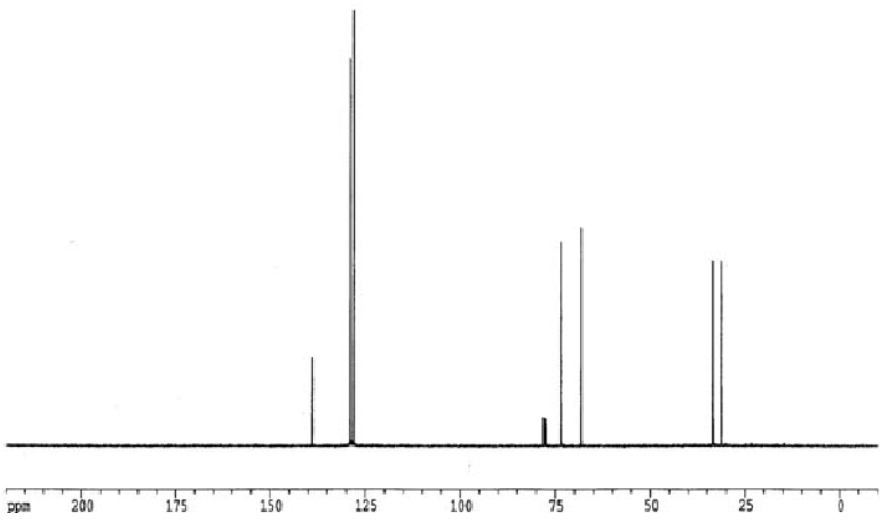


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Current Data Parameters
NAME                  4c-VI-27
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_               20010630
Time                    13.33
INSTRUM                drx400
PROBHD      5 mm Multinu
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        98
DS                         2
SWH                23148.148 Hz
FIDRES              0.353213 Hz
AQ                  1.4156276 sec
RG                     1824.6
DW                  21.600 usec
DE                    6.50 usec
TE                    309.0 K
D1                  0.05000000 sec
d11                 0.03000000 sec
d12                 0.00002000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                     12.30 usec
PL1                    2.00 dB
SFO1              100.6232933 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                100.00 usec
PL2                    0.00 dB
PL12                  18.00 dB
PL13                  18.00 dB
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                100.6127290 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40

1D NMR plot parameters
CX                        20.00 cm
F1P                      220.000 ppm
F1                     22134.80 Hz
F2P                      -10.000 ppm
F2                     -1006.13 Hz
PPMCM                 11.50000 ppm/cm
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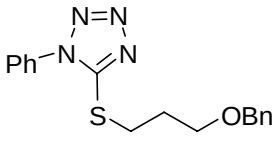

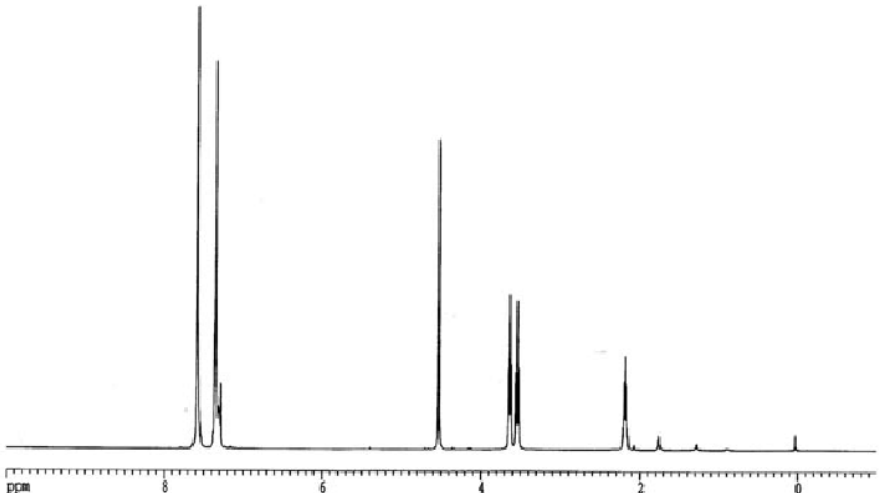


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Current Data Parameters
NAME                  4c-V-72b
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20010314
Time                    19.00
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG                 zg30
TD                     32768
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  4789.272 Hz
FIDRES               0.146157 Hz
AQ                   3.4210291 sec
RG                       101.6
DW                     104.400 usec
DE                       4.50 usec
TE                      300.0 K
D1                 1.00000000 sec

========== CHANNEL f1 ==========
NUC1                       1H
P1                       7.70 usec
PL1                     -6.00 dB
SFO1               400.1320007 MHz

F2 - Processing parameters
SI                       16384
SF                 400.1300000 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       20.00 cm
F1P                     10.000 ppm
F1                     4001.30 Hz
F2P                    -1.000 ppm
F2                     -400.13 Hz
PPMCM                  0.55000 ppm/cm
HZCM                 220.07150 Hz/cm
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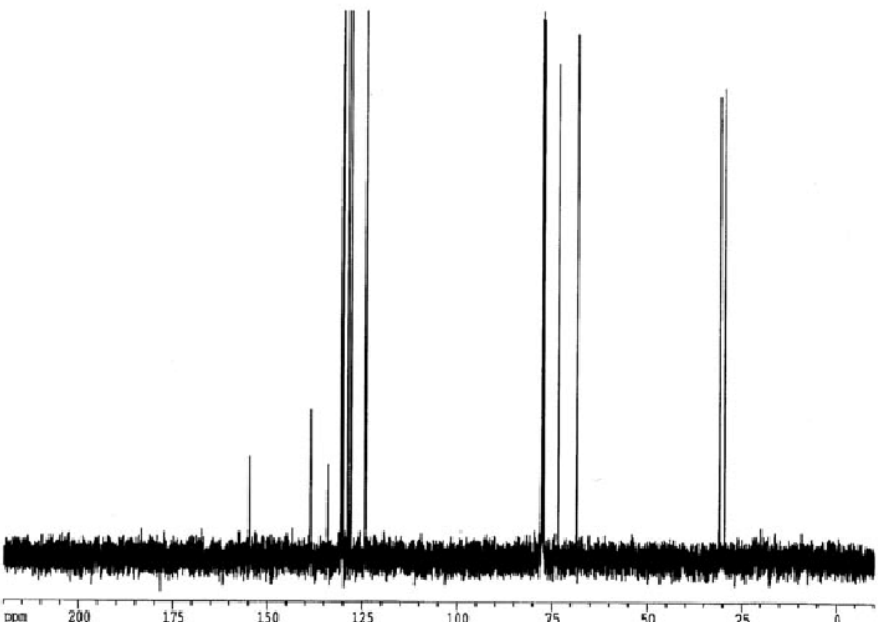


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Current Data Parameters
NAME                  4c-V-72b
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_              20010314
Time                    19.03
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG                 zgpg30
TD                       65536
SOLVENT                 CDCl3
NS                         127
DS                          2
SWH                 23148.148 Hz
FIDRES               0.353213 Hz
AQ                   1.4156276 sec
RG                        8192
DW                      21.600 usec
DE                       4.50 usec
TE                      300.0 K
D1                  0.05000000 sec
d11                 0.03000000 sec
d12                 0.00002000 sec

========== CHANNEL f1 ==========
NUC1                       13C
P1                       12.30 usec
PL1                       2.00 dB
SFO1               100.6232933 MHz

========== CHANNEL f2 ==========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                   100.00 usec
PL2                       0.00 dB
PL12                     18.00 dB
PL13                     18.00 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF                 100.6127290 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
F1P                     220.000 ppm
F1                     22134.80 Hz
F2P                    -10.000 ppm
F2                     -1006.13 Hz
PPMCM                 11.50000 ppm/cm
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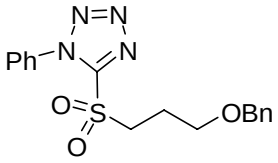
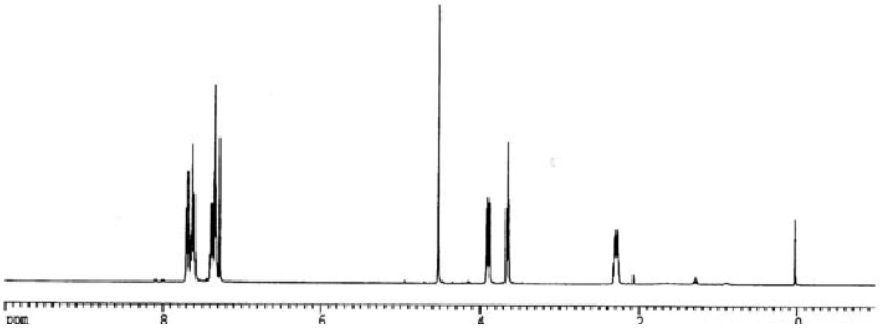


13



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Current Data Parameters
NAME                 4c-V-86a
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20010317
Time                   13.35
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG                zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                      203.2
DW                  104.400 usec
DE                    4.50 usec
TE                    300.0 K
D1                  1.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     7.70 usec
PL1                   -6.00 dB
SFO1             400.1320007 MHz

F2 - Processing parameters
SI                        16384
SF                  400.1300000 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        20.00 cm
F1P                       10.000 ppm
F1                      4001.30 Hz
F2P                       -1.000 ppm
F2                      -400.13 Hz
PPMCM                  0.55000 ppm/cm
HZCM                 220.07150 Hz/cm
```

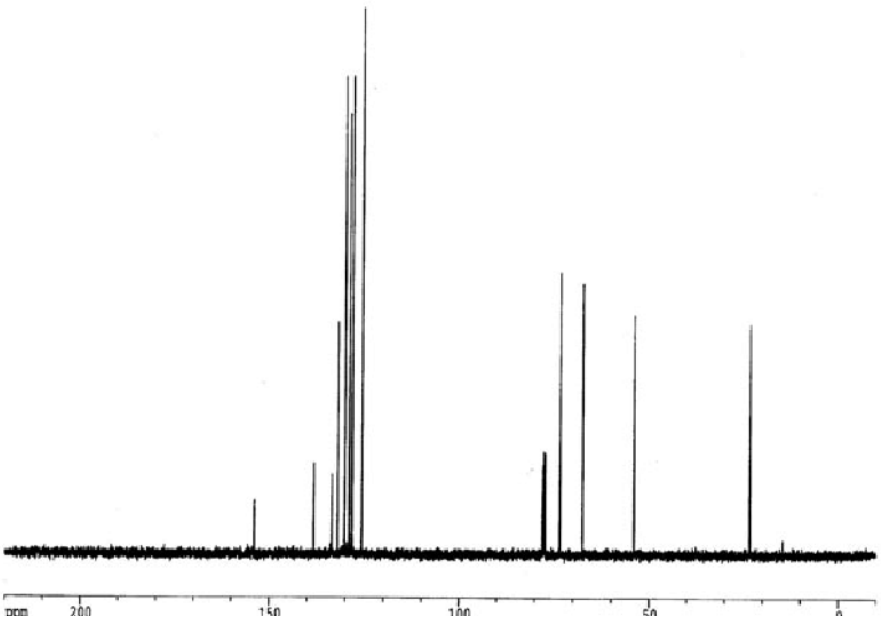

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Current Data Parameters
NAME                 4c-V-86a
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20010317
Time                   12.56
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        30
DS                         2
SWH                 23148.148 Hz
FIDRES              0.353213 Hz
AQ                  1.4156276 sec
RG                      2048
DW                  21.600 usec
DE                    4.50 usec
TE                    303.0 K
D1                  0.05000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                    12.30 usec
PL1                    2.00 dB
SFO1             100.6232933 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                100.00 usec
PL2                    0.00 dB
PL12                  18.00 dB
PL13                  18.00 dB
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                  100.6127290 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40

1D NMR plot parameters
CX                        20.00 cm
F1P                      220.000 ppm
F1                     22136.88 Hz
F2P                      -10.000 ppm
F2                     -1006.13 Hz
PPMCM                  11.50000 ppm/cm
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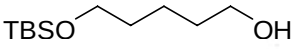

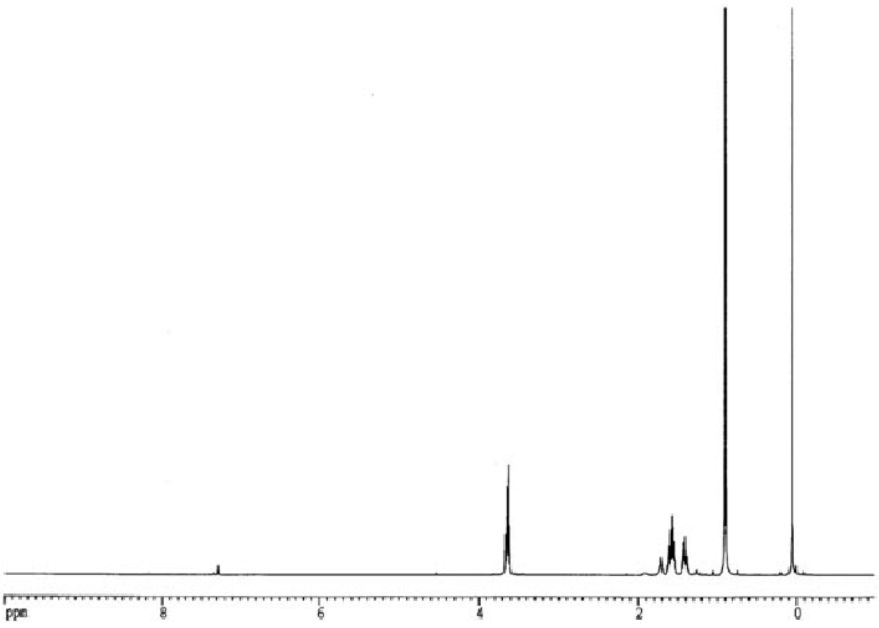


```
Current Data Parameters
NAME                  4c-VI-29
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20110701
Time                    14.29
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG                 zg30
TD                     32768
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                         64
DW                    104.400 usec
DE                      4.50 usec
TE                     300.0 K
D1                 1.00000000 sec

============ CHANNEL f1 ============
NUC1                       1H
P1                       7.70 usec
PL1                     -6.00 dB
SFO1               400.8320007 MHz

F2 - Processing parameters
SI                         16384
SF                 400.8300000 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00

1D NMR plot parameters
CX                         20.00 cm
F1P                        10.000 ppm
F1                       4001.30 Hz
F2P                        -1.000 ppm
F2                       -400.13 Hz
PPMCM                    0.55000 ppm/cm
HZCM                   220.07150 Hz/cm
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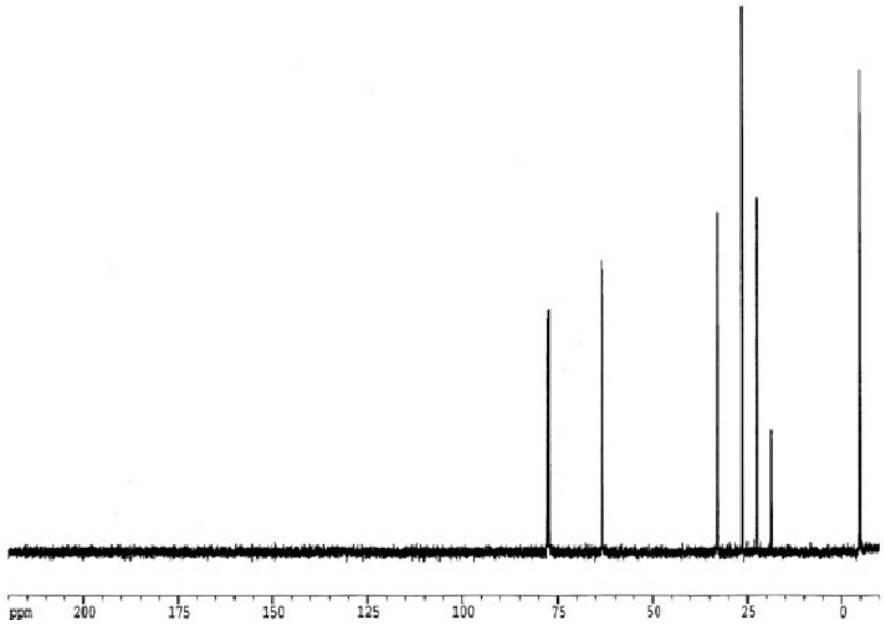


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Current Data Parameters
NAME                  4c-VI-29
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_              20110701
Time                    14.35
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG                 zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        197
DS                          2
SWH                23148.148 Hz
FIDRES              0.353213 Hz
AQ                  1.4156276 sec
RG                       8096
DW                    21.600 usec
DE                      4.50 usec
TE                     300.0 K
D1                 0.05000000 sec
d11                0.03000000 sec
d12                0.00001000 sec

============ CHANNEL f1 ============
NUC1                      13C
P1                      12.30 usec
PL1                      2.00 dB
SFO1               100.6232933 MHz

============ CHANNEL f2 ============
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  100.00 usec
PL2                      0.00 dB
PL12                    18.00 dB
PL13                    18.00 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                 100.6227290 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40

1D NMR plot parameters
CX                         20.00 cm
F1P                        220.000 ppm
F1                       22134.80 Hz
F2P                      -10.000 ppm
F2                       -1006.13 Hz
PPMCM                    11.50000 ppm/cm
HZCM                   1852.84638 Hz/cm
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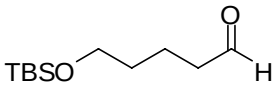

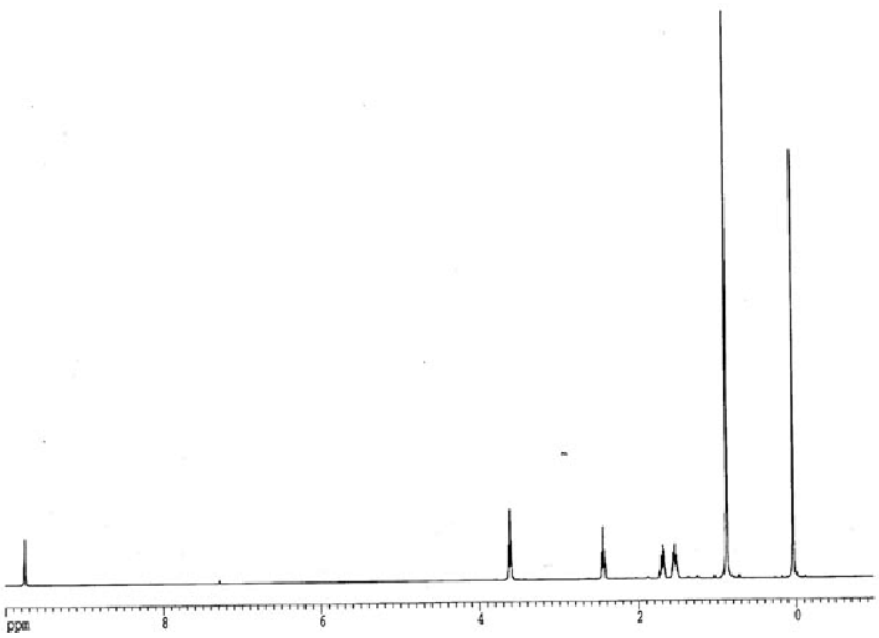


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NAME                4c-VI-42
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20010709
Time                   12.20
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG                zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                        32
DW                  104.400 usec
DE                    4.50 usec
TE                  300.0 K
D1                  1.00000000 sec

============ CHANNEL f1 ============
NUC1                      1H
P1                    7.70 usec
PL1                  -6.00 dB
SFO1           400.1320007 MHz

F2 - Processing parameters
SI                        16384
SF                 400.1300000 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                 10.000 ppm
F1                 4001.30 Hz
F2P                 -1.000 ppm
F2                  -400.13 Hz
PPMCM               0.55000 ppm/cm
HZCM              220.07150 Hz/cm
```
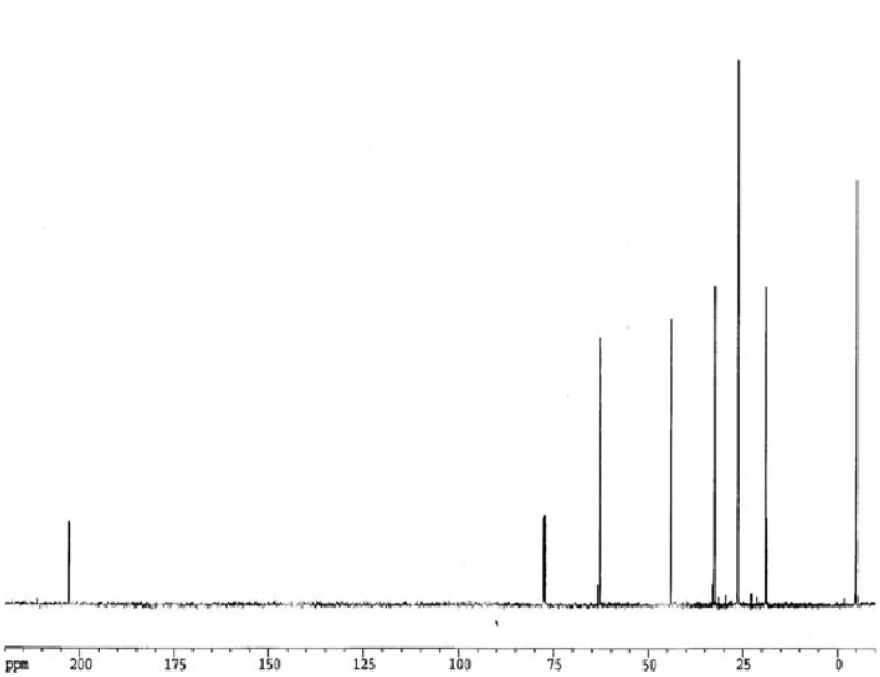
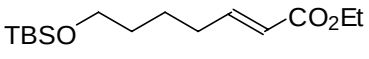
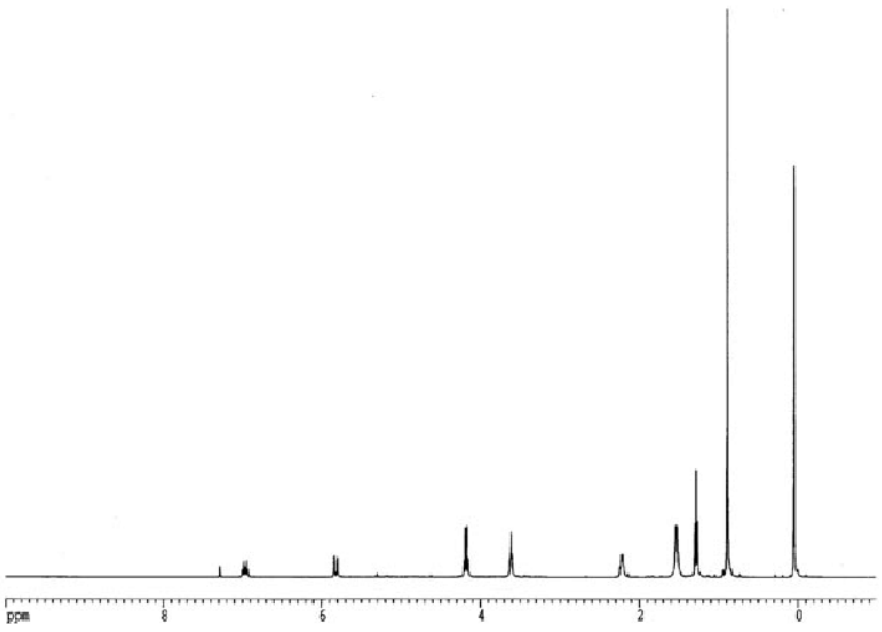
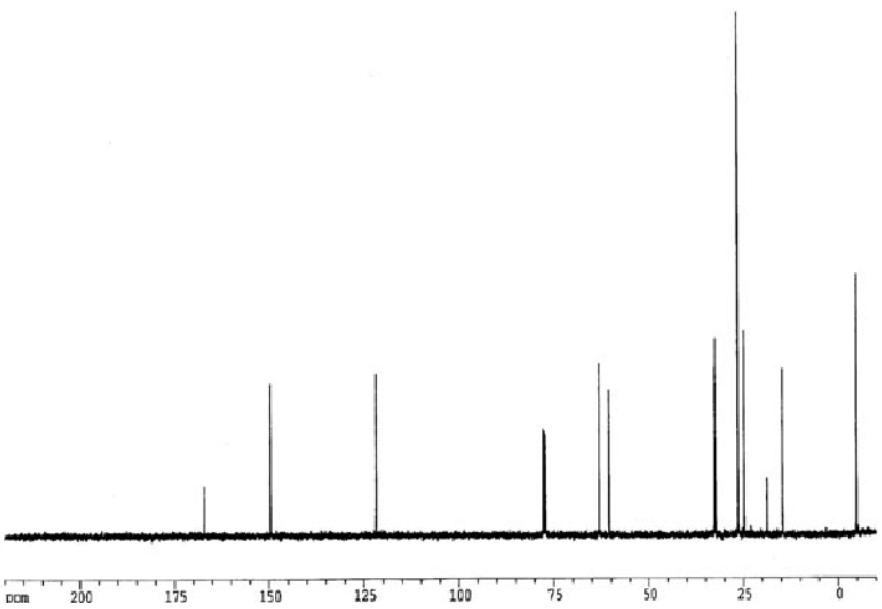




```
Current Data Parameters
NAME                4c-VI-42
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_               20010709
Time                   12.24
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG                zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        177
DS                         2
SWH                23148.148 Hz
FIDRES              0.353213 Hz
AQ                  1.4156276 sec
RG                      8192
DW                  21.600 usec
DE                    4.50 usec
TE                  300.0 K
D1                  0.05000000 sec
d11                 0.03000000 sec
d12                 0.00002000 sec

============ CHANNEL f1 ============
NUC1                      13C
P1                   12.30 usec
PL1                   2.00 dB
SFO1           100.6232933 MHz

============ CHANNEL f2 ============
CPDPRG2                waltz16
NUC2                      1H
PCPD2                100.00 usec
PL2                   0.00 dB
PL12                 18.00 dB
PL13                 18.00 dB
SFO2           400.1314005 MHz

F2 - Processing parameters
SI                        32768
SF                 100.6127290 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                 220.000 ppm
F1                 22134.80 Hz
F2P                 -10.000 ppm
F2                 -1006.13 Hz
PPMCM              11.50000 ppm/cm
```

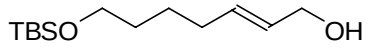


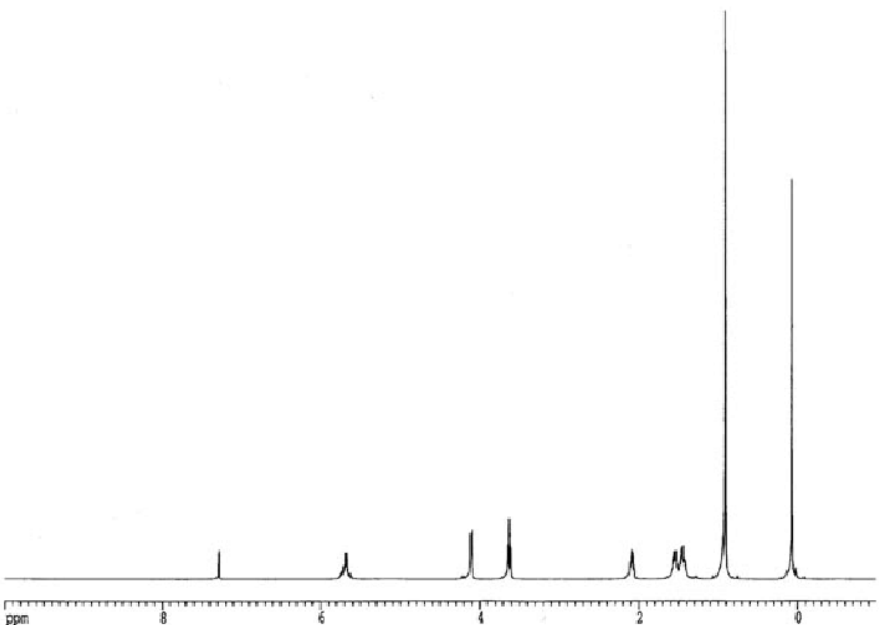



```
Current Data Parameters
NAME                 4c-IV-277
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20010123
Time                     15.45
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG                  zg30
TD                      32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                          32
DW                   104.400 usec
DE                     4.50 usec
TE                     300.0 K
D1                  1.00000000 sec

============ CHANNEL f1 ============
NUC1                        1H
P1                       7.70 usec
PL1                     -6.00 dB
SFO1               400.1320007 MHz

F2 - Processing parameters
SI                      16384
SF                 400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                      20.00 cm
F1P                     10.000 ppm
F1                    4001.30 Hz
F2P                     -1.000 ppm
F2                    -400.13 Hz
PPMCM                 0.55000 ppm/cm
HZCM                220.07150 Hz/cm
```

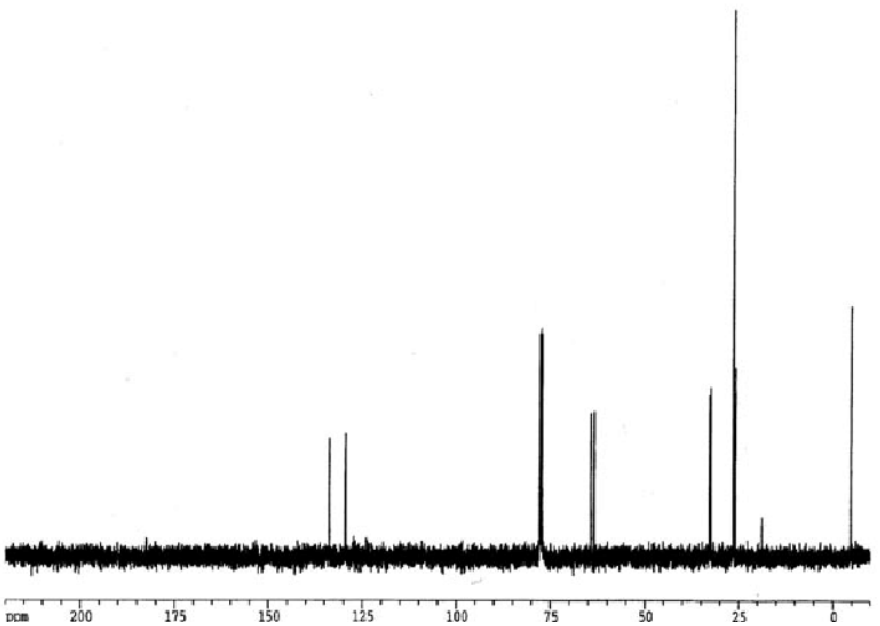



```
Current Data Parameters
NAME                 4c-IV-277
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_               20010123
Time                     15.49
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG                zgpg30
TD                      65536
SOLVENT                  CDCl3
NS                         125
DS                           2
SWH                23148.148 Hz
FIDRES              0.353213 Hz
AQ                  1.4156276 sec
RG                        1024
DW                   21.600 usec
DE                     4.50 usec
TE                     300.0 K
D1                  0.05000000 sec
d11                 0.03000000 sec
d12                 0.00002000 sec

============ CHANNEL f1 ============
NUC1                        13C
P1                      12.30 usec
PL1                      2.00 dB
SFO1               100.6232933 MHz

============ CHANNEL f2 ============
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                  100.00 usec
PL2                      0.00 dB
PL12                    18.00 dB
PL13                    18.00 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                      32768
SF                 100.6127290 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                      20.00 cm
F1P                    220.036 ppm
F1                   22138.42 Hz
F2P                    -10.036 ppm
F2                   -1009.73 Hz
PPMCM                11.54955 ppm/cm
HZCM                 1162.40747 Hz/cm
```

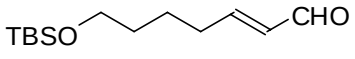




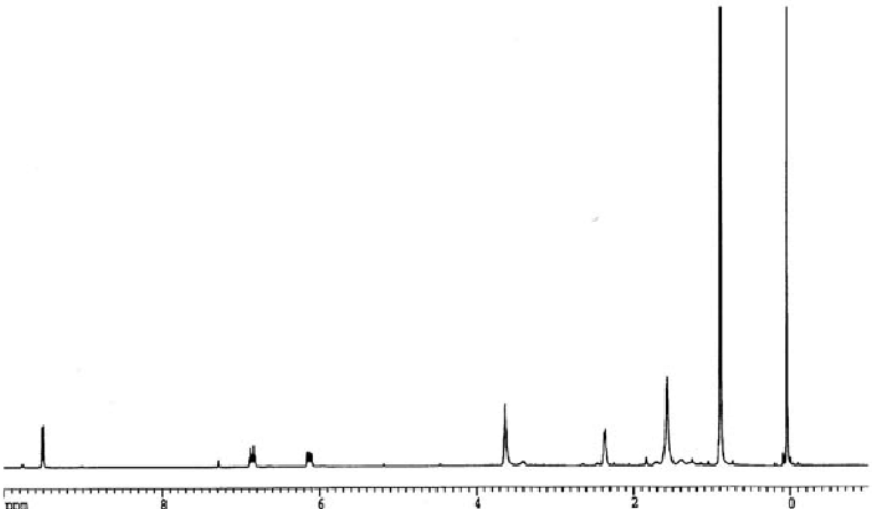

```
Current Data Parameters
NAME                  4c-IV-260
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20010118
Time                      14.11
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG                 zg30
TD                       32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                          64
DW                   104.400 usec
DE                     4.50 usec
TE                   300.0 K
D1                  1.00000000 sec

============ CHANNEL f1 ============
NUC1                        1H
P1                        7.70 usec
PL1                      -6.00 dB
SFO1              400.1320007 MHz

F2 - Processing parameters
SI                       16384
SF                400.1300000 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       20.00 cm
F1P                    10.000 ppm
F1                   4001.30 Hz
F2P                    -1.000 ppm
F2                   -400.13 Hz
PPMCM                 0.55000 ppm/cm
HZCM                220.07150 Hz/cm
```



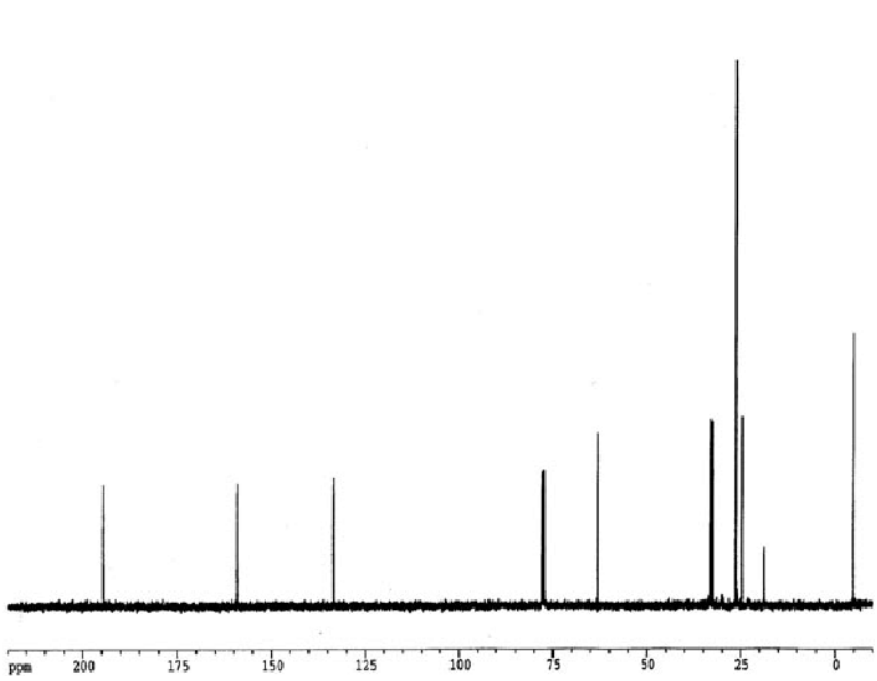

```
Current Data Parameters
NAME                  4c-IV-260
EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
Date_              1010118
Time                      14.15
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         122
DS                           2
SWH                23148.148 Hz
FIDRES              0.353213 Hz
AQ                  1.4156276 sec
RG                        2048
DW                   21.600 usec
DE                     4.50 usec
TE                   300.0 K
d11                 0.0300000 sec
d12                 0.0000200 sec
PL13                    18.00 dB
P4                  0.05000000 sec
CPDPRG2                waltz16
PCPD2                  100.00 usec
SFO2              400.1316005 MHz
NUC2                        1H
PL2                      0.00 dB
PL12                    18.00 dB
P1                       12.30 usec
DE                     4.50 usec
SFO1              100.6232933 MHz
NUC1                       13C
PL1                      2.00 dB

F2 - Processing parameters
SI                       32768
SF                100.6127290 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
F1P                   220.000 ppm
F1                   22134.80 Hz
F2P                   -10.000 ppm
F2                   -1006.13 Hz
PPMCM                 11.50000 ppm/cm
```



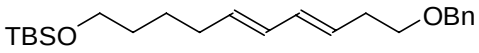
14



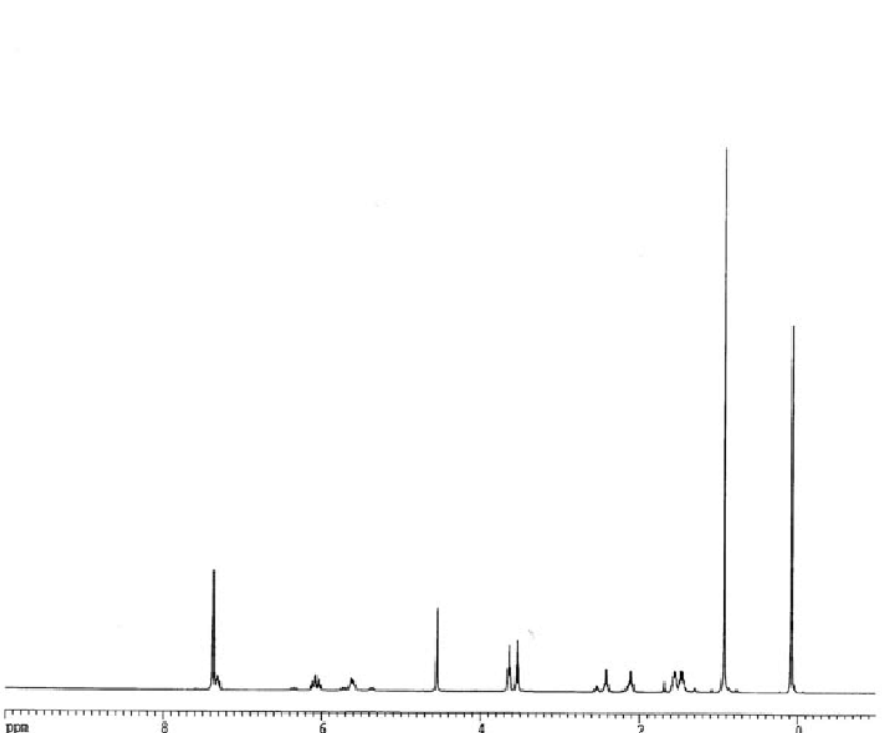
```
Current Data Parameters
NAME                 4c-VI-81b9
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               1010723
Time                     14.31
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                       65.3
DW                    104.400 usec
DE                      6.50 usec
TE                     300.0 K
D1                 1.00000000 sec
P1                      7.70 usec
DE                      6.50 usec
SFO1               400.1320009 MHz
NUC1                       1H
PL1                    -6.00 dB

F2 - Processing parameters
SI                       16384
SF                 400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                      20.00 cm
F1P                     10.000 ppm
F1                    4001.30 Hz
F2P                    -1.000 ppm
F2                    -400.13 Hz
PPMCM                 0.55000 ppm/cm
HZCM                220.07150 Hz/cm
```



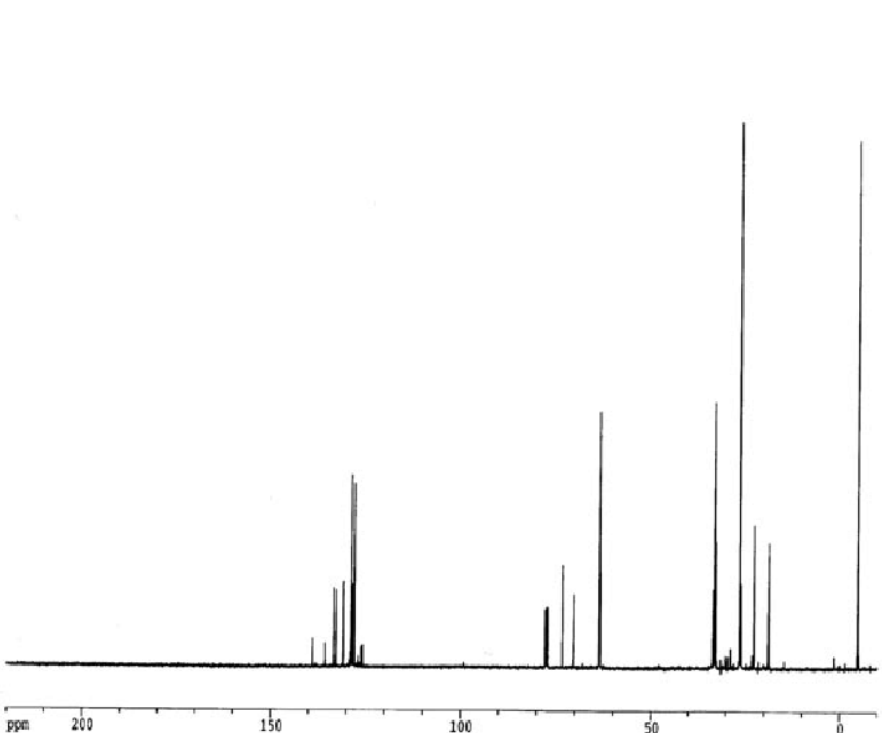
```
Current Data Parameters
NAME                 4c-VI-81b9
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_               1010723
Time                     14.34
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG                zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       115
DS                         2
SWH                23148.148 Hz
FIDRES              0.353213 Hz
AQ                  1.4156276 sec
RG                      8192
DW                    21.600 usec
DE                      6.50 usec
TE                     300.0 K
d11                 0.0300000 sec
d12                 0.0000200 sec
PL13                   18.00 dB
D1                  0.05000000 sec
CPDPRG2                waltz16
PCPD2                  100.00 usec
SFO2               400.1316005 MHz
NUC2                       1H
PL2                     0.00 dB
PL12                   18.00 dB
P1                     12.30 usec
DE                      6.50 usec
SFO1               100.6232933 MHz
NUC1                       13C
PL1                     2.00 dB

F2 - Processing parameters
SI                       32768
SF                 100.6127290 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                      20.00 cm
F1P                    220.000 ppm
F1                   22134.80 Hz
F2P                   -10.000 ppm
F2                   -1006.13 Hz
PPMCM                11.50000 ppm/cm
HZCM               1157.84639 Hz/cm
```



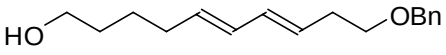
15 (85:15 *E*:*Z*)



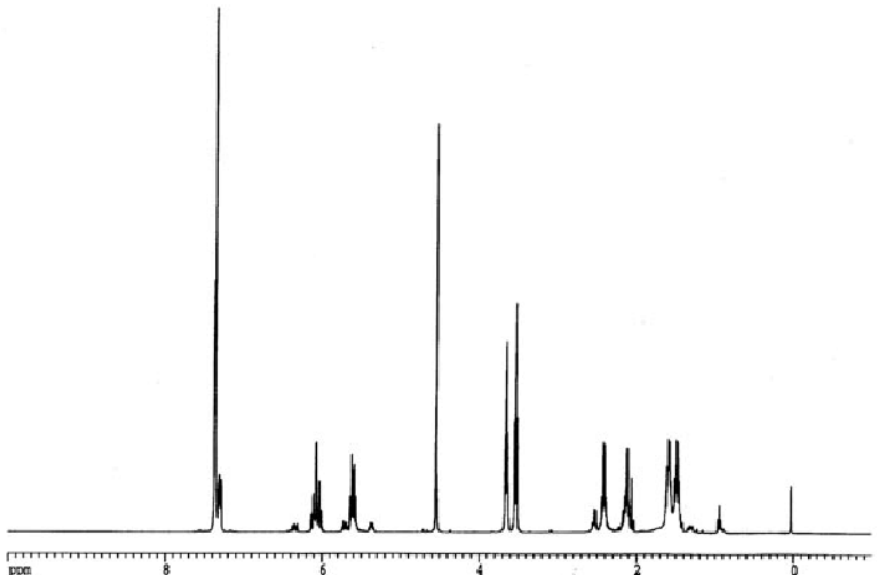

```
Current Data Parameters
NAME                  4c-V1-20
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20010627
Time                    13.48
INSTRUM                drx400
PROBHD      5 mm Multinu
PULPROG                zg30
TD                    32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                        64
DW                  104.400 usec
DE                    4.50 usec
TE                   300.0 K
D1                1.00000000 sec

========== CHANNEL f1 ==========
NUC1                      1H
P1                      7.70 usec
PL1                    -6.00 dB
SFO1              400.1320007 MHz

F2 - Processing parameters
SI                        16384
SF                400.1300000 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        20.00 cm
F1P                       10.000 ppm
F1                      4001.30 Hz
F2P                       -1.000 ppm
F2                      -400.13 Hz
PPMCM                  0.55000 ppm/cm
HZCM                 220.07150 Hz/cm
```



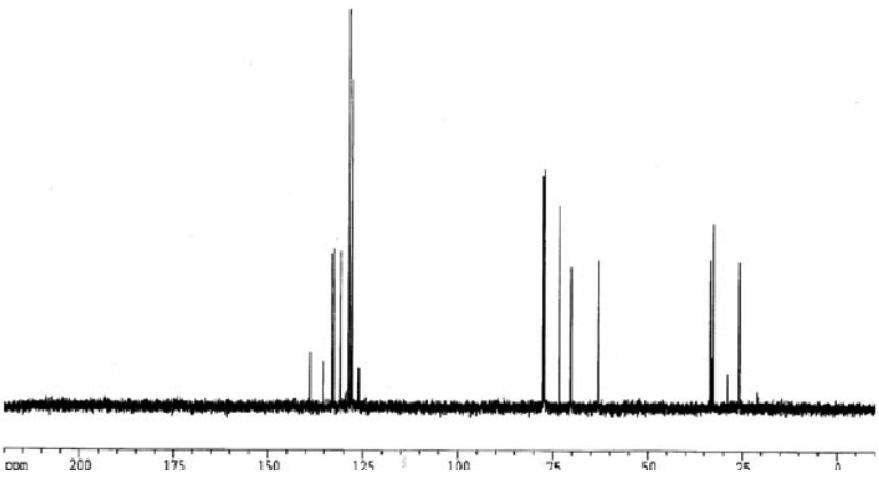

```
Current Data Parameters
NAME                  4c-V2-147
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_              20010825
Time                    16.01
INSTRUM                drx400
PROBHD      5 mm Multinu
PULPROG                zgpg30
TD                    65536
SOLVENT                CDCl3
NS                       506
DS                         2
SWH                23148.148 Hz
FIDRES              0.353213 Hz
AQ                  1.4156276 sec
RG                       2048
DW                  21.600 usec
DE                    4.50 usec
TE                   300.0 K
D1                0.05000000 sec
d11               0.03000000 sec
d12               0.00002000 sec

========== CHANNEL f1 ==========
NUC1                      13C
P1                      12.30 usec
PL1                     2.00 dB
SFO1              100.6232913 MHz

========== CHANNEL f2 ==========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                 100.00 usec
PL2                      0.00 dB
PL12                    18.00 dB
PL13                    18.00 dB
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                100.6127290 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40

1D NMR plot parameters
CX                        20.00 cm
F1P                     220.000 ppm
F1                    22134.80 Hz
F2P                     -10.000 ppm
F2                    -1006.13 Hz
PPMCM                 11.50000 ppm/cm
```



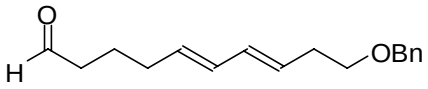
(85:15 *E*:*Z*)



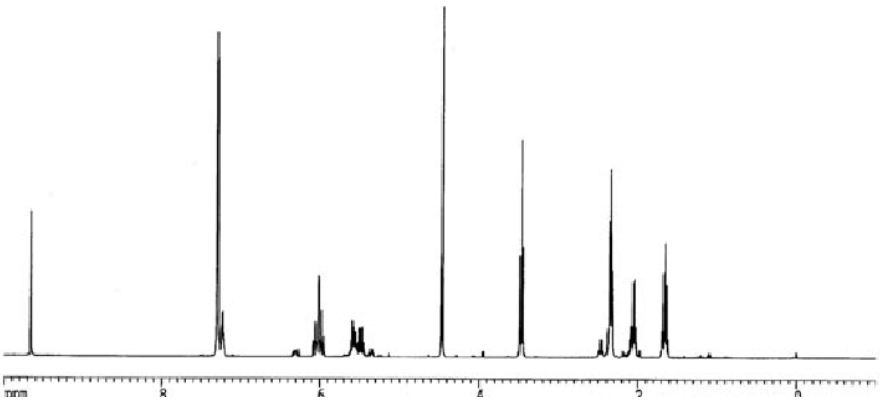

```
Current Data Parameters
NAME                  4c-VI-21
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20100627
Time                   17.47
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG                zg30
TD                    32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH               4789.272 Hz
FIDRES            0.146157 Hz
AQ                3.4210291 sec
RG                       64
DW                 104.400 usec
DE                   4.50 usec
TE                  300.0 K
D1                1.00000000 sec
P1                   7.70 usec
DE                   4.50 usec
SFO1             400.1320007 MHz
NUC1                     1H
PL1                  +6.00 dB

F2 - Processing parameters
SI                       16384
SF                400.1300000 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       20.00 cm
F1P                      10.000 ppm
F1                     4001.30 Hz
F2P                      -1.999 ppm
F2                     -400.13 Hz
PPMCM                  0.55000 ppm/cm
HZCM                 220.07150 Hz/cm
```



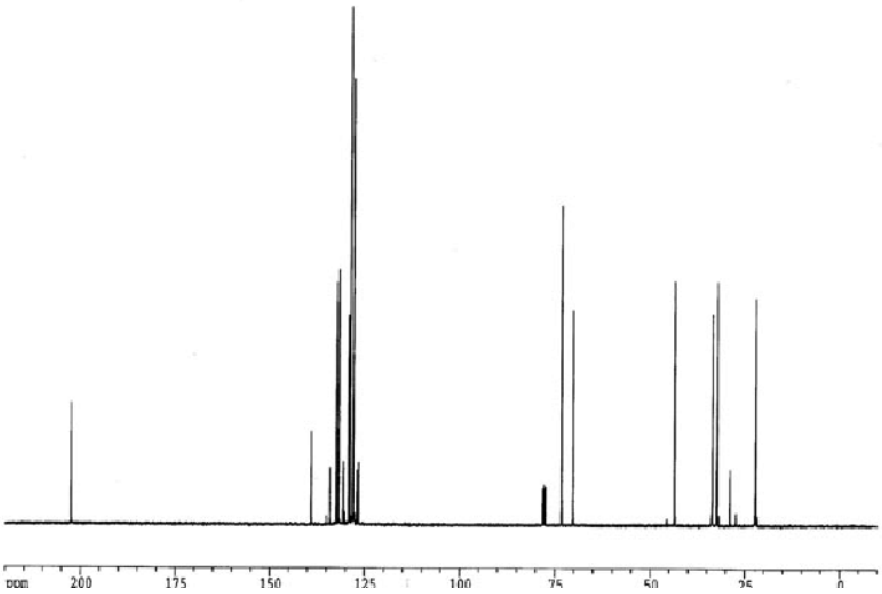

```
Current Data Parameters
NAME                  4c-VI-21
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_              20010627
Time                   17.57
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG             zgpg30
TD                    65536
SOLVENT                CDCl3
NS                       159
DS                         2
SWH              23148.148 Hz
FIDRES            0.353213 Hz
AQ                1.4156276 sec
RG                    9195.2
DW                  21.600 usec
DE                   4.50 usec
TE                  300.0 K
D1                0.05000000 sec
D11               0.03000000 sec
D12               0.00000000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                   12.30 usec
PL1                   2.00 dB
SFO1            100.6232933 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2               100.00 usec
PL2                   0.00 dB
PL12                 18.00 dB
PL13                 18.00 dB
SFO2            400.1314005 MHz

F2 - Processing parameters
SI                       32768
SF                100.6127290 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
F1P                     220.000 ppm
F1                     22134.80 Hz
F2P                    -10.000 ppm
F2                    -2006.13 Hz
PPMCM                 11.50000 ppm/cm
```



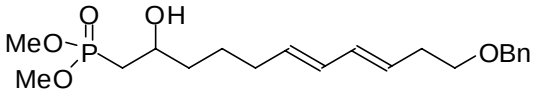
(85:15 *E*:*Z*)



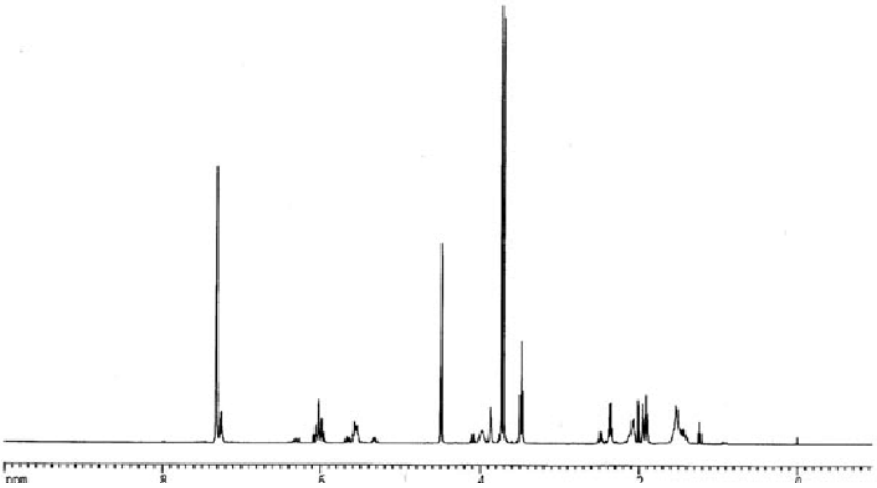
```
Current Data Parameters
NAME                 4c-VII-24
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20011104
Time                    14.17
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG                 zg30
TD                      32768
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  4789.272 Hz
FIDRES               0.146157 Hz
AQ                   3.4210291 sec
RG                         16
DW                   104.400 usec
DE                     4.50 usec
TE                     300.0 K
D1                  1.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                       7.70 usec
PL1                     -6.00 dB
SFO1                400.1320007 MHz

F2 - Processing parameters
SI                       16384
SF                  400.1300173 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       20.00 cm
F1P                      10.000 ppm
F1                     4001.30 Hz
F2P                      -1.000 ppm
F2                     -400.13 Hz
PPMCM                 0.55000 ppm/cm
HZCM                220.07150 Hz/cm
```



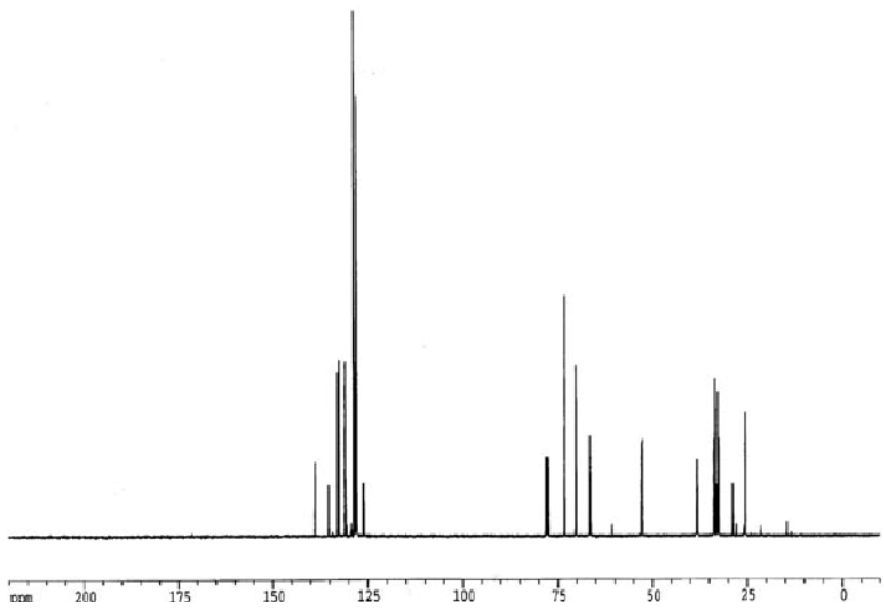
```
Current Data Parameters
NAME                 4c-VII-24
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_               20011104
Time                    14.22
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG                 zgpg30
TD                       65536
SOLVENT                 CDCl3
NS                         106
DS                          2
SWH                 23148.148 Hz
FIDRES               0.353213 Hz
AQ                   1.4154276 sec
RG                      1625.5
DW                   21.600 usec
DE                     4.50 usec
TE                     300.0 K
D1                  0.05000000 sec
d11                 0.03000000 sec
d12                 0.00002000 sec

======== CHANNEL f1 ========
NUC1                       13C
P1                      12.30 usec
PL1                      2.00 dB
SFO1               100.6232933 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                       1H
PCPD2                  100.00 usec
PL2                      0.00 dB
PL12                    18.00 dB
PL13                    18.00 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF                 100.6127290 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
F1P                     220.000 ppm
F1                     22134.80 Hz
F2P                     -10.000 ppm
F2                     -1006.13 Hz
PPMCM                11.50000 ppm/cm
```



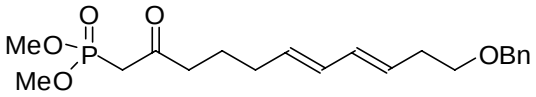
(85:15 *E*:*Z*)



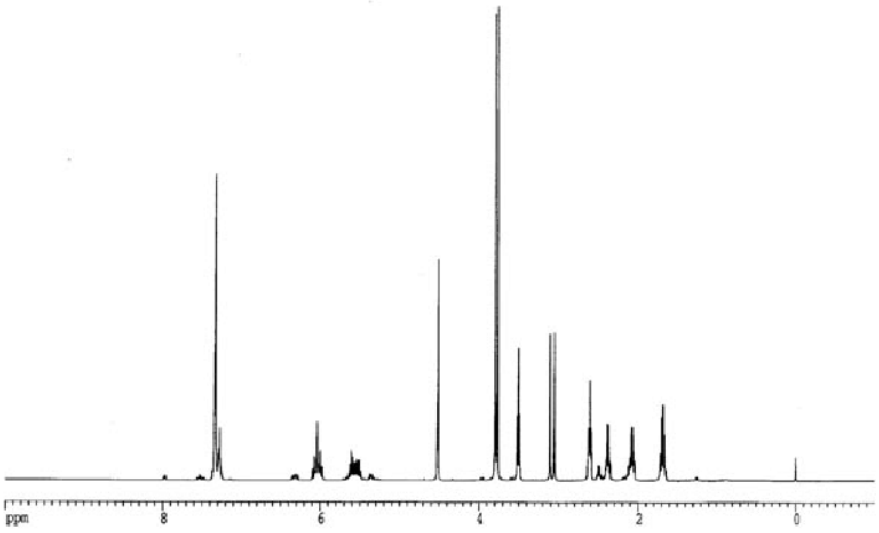
```
Current Data Parameters
NAME                  4C-VI-262
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20011014
Time                      12.35
INSTRUM                 drx400
PROBHD       5 mm Multina
PULPROG                 zg30
TD                       32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                          16
DW                   104.400 usec
DE                     4.50 usec
TE                    300.0 K
D1                 1.00000000 sec

========== CHANNEL f1 ==========
NUC1                       1H
P1                       7.70 usec
PL1                     -6.00 dB
SFO1              400.1320007 MHz

F2 - Processing parameters
SI                       16384
SF                400.1299831 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       20.00 cm
F1P                     10.000 ppm
F1                    4001.30 Hz
F2P                    -1.000 ppm
F2                    -400.13 Hz
PPMCM                 0.55000 ppm/cm
HZCM                220.07169 Hz/cm
```



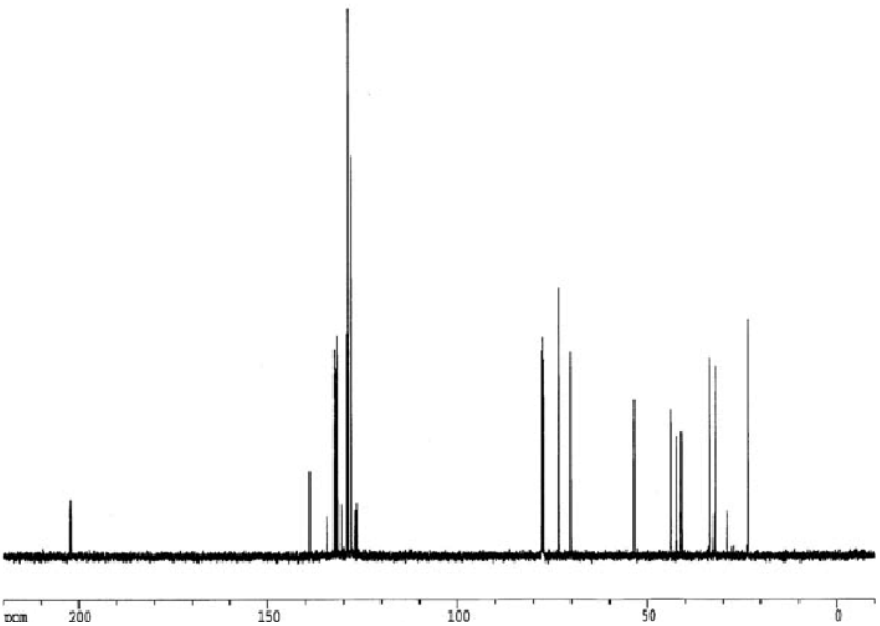
```
Current Data Parameters
NAME                  4C-VI-263
EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
Date_              20011014
Time                      12.43
INSTRUM                 drx400
PROBHD       5 mm Multinu
PULPROG              apgp30
TD                       65536
SOLVENT                  CDCl3
NS                         261
DS                           2
SWH                23148.148 Hz
FIDRES              0.353213 Hz
AQ                  1.4154276 sec
RG                        4096
DW                      21.600 usec
DE                      4.50 usec
TE                    300.0 K
D1                 0.05000000 sec
d11                0.03000000 sec
d12                0.00002000 sec

========== CHANNEL f1 ==========
NUC1                       13C
P1                       12.30 usec
PL1                       2.00 dB
SFO1              100.6232933 MHz

========== CHANNEL f2 ==========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  100.00 usec
PL2                       0.00 dB
PL12                     18.00 dB
PL13                     18.00 dB
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF                100.6127290 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
F1P                     220.000 ppm
F1                    22134.80 Hz
F2P                    -10.000 ppm
F2                    -1006.13 Hz
PPMCM                 11.50000 ppm/cm
```



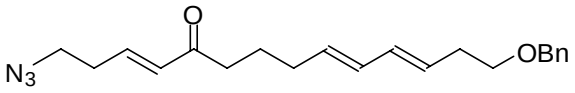
16 (85:15 *E*:*Z*)



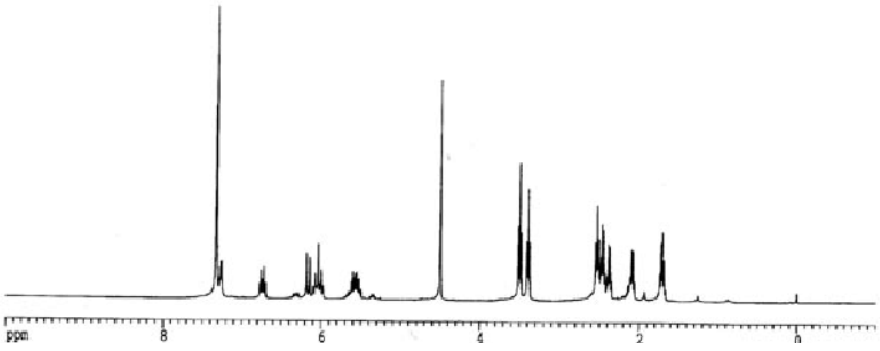

```
Current Data Parameters
NAME                  4c-VI-26
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20010702
Time                   14.47
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                4789.272 Hz
FIDRES             0.146157 Hz
AQ                 3.4210291 sec
RG                       64
DW                  104.400 usec
DE                    4.50 usec
TE                   300.0 K
D1                1.00000000 sec

========== CHANNEL f1 ==========
NUC1                     1H
P1                     7.70 usec
PL1                   -6.00 dB
SFO1           400.1320007 MHz

F2 - Processing parameters
SI                       16384
SF                 400.1300061 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       20.00 cm
F1P                      10.000 ppm
F1                     4001.30 Hz
F2P                      -1.000 ppm
F2                     -400.13 Hz
PPMCM                  0.55000 ppm/cm
HZCM                 220.07150 Hz/cm
```



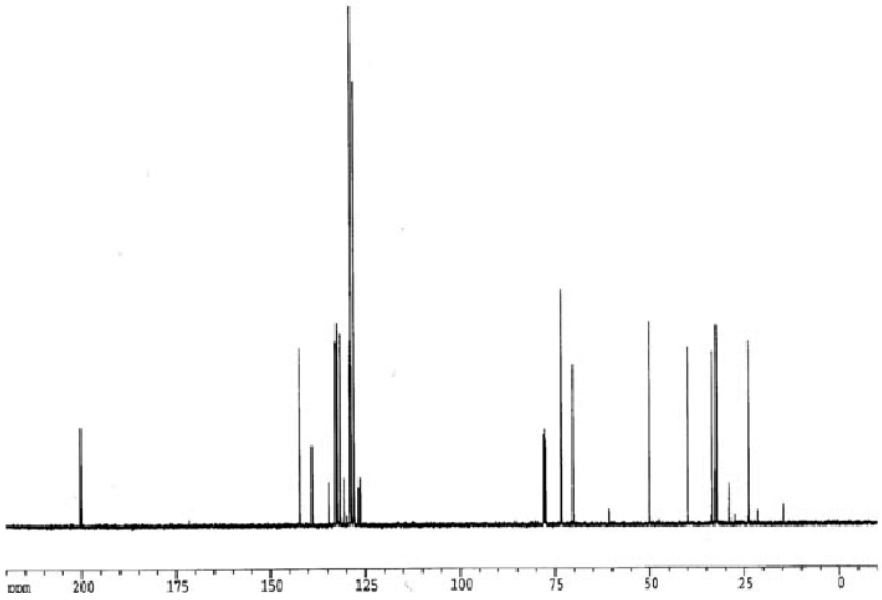

```
Current Data Parameters
NAME                 4c-VII-23
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_              20011109
Time                   10.20
INSTRUM                drx400
PROBHD     5 mm Multinu
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       212
DS                        2
SWH               23148.148 Hz
FIDRES             0.353213 Hz
AQ                 1.4154276 sec
RG                     8192
DW                   21.600 usec
DE                    4.50 usec
TE                   300.0 K
D1                0.05000000 sec
d11               0.03000000 sec
d12               0.00001000 sec

========== CHANNEL f1 ==========
NUC1                     13C
P1                    12.30 usec
PL1                    2.00 dB
SFO1           100.6232933 MHz

========== CHANNEL f2 ==========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                    0.00 dB
PL12                  18.00 dB
PL13                  18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF                 100.6127290 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
F1P                     220.000 ppm
F1                     22134.80 Hz
F2P                     -10.000 ppm
F2                     -1006.13 Hz
PPMCM                  11.50000 ppm/cm
```



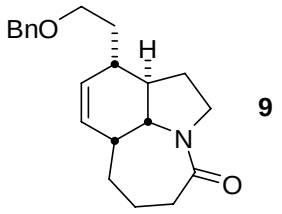
7 (85:15 *E*:*Z*)




```
Current Data Parameters
NAME                  4c-VI-37
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20010709
Time                    14.23
INSTRUM                 drx400
PROBHD       5 mm Multinu
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                4789.272 Hz
FIDRES             0.146157 Hz
AQ                 3.4210201 sec
RG                        32
DW                  104.400 usec
DE                    4.50 usec
TE                  300.0 K
D1                1.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     7.70 usec
PL1                   -6.00 dB
SFO1             400.1320007 MHz

F2 - Processing parameters
SI                       16384
SF                 400.1300097 MHz
WDW                         EM
SSB                          0
LB                      0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       20.00 cm
F1P                      10.000 ppm
F1                     4001.30 Hz
F2P                      -1.000 ppm
F2                     -400.13 Hz
PPMCM                  0.55000 ppm/cm
HZCM                 220.07150 Hz/cm
```




```
Current Data Parameters
NAME                  4c-VII-33
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_              20011108
Time                    18.58
INSTRUM                 drx400
PROBHD       5 mm Multinu
PULPROG                 zgpg30
TD                      65536
SOLVENT                CDCl3
NS                        171
DS                         2
SWH               21148.348 Hz
FIDRES             0.322813 Hz
AQ                 1.41562216 sec
RG                       8192
DW                  23.600 usec
DE                    4.50 usec
TE                  300.0 K
D1                0.05000000 sec
d11               0.03000000 sec
d12               0.00002000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                    13.30 usec
PL1                    2.00 dB
SFO1             100.6232931 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                100.00 usec
PL2                    0.00 dB
PL12                  18.00 dB
PL13                  18.00 dB
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF                 100.6227290 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
F1P                     220.000 ppm
F1                     22134.89 Hz
F2P                     -10.000 ppm
F2                     -1006.13 Hz
PPMCM                  11.50000 ppm/cm
HZCM                 1157.84639 Hz/cm
```



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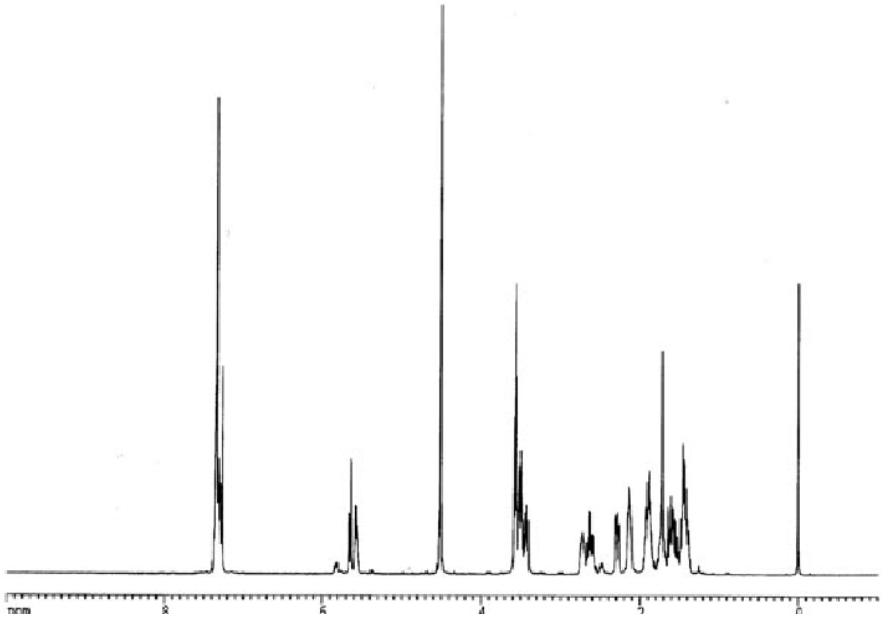
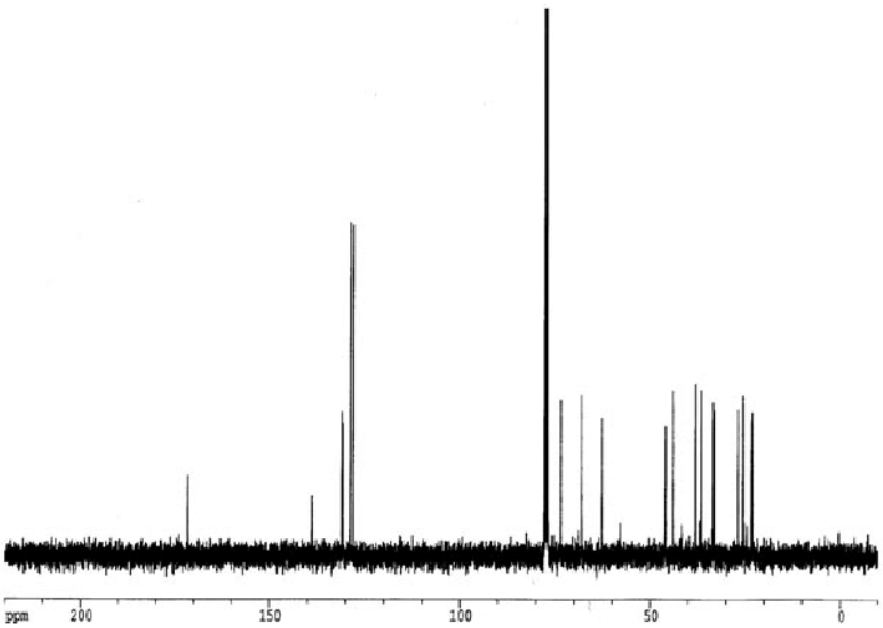
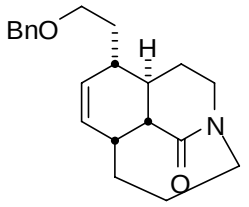


```
Current Data Parameters
NAME          4c-VII-17major
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20111124
Time                  16.07
INSTRUM               drx400
PROBHD     5 mm Multinu
PULPROG               zg30
TD                   32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                4789.272 Hz
FIDRES            0.146157 Hz
AQ                3.4210291 sec
RG                    143.7
DW                  104.400 usec
DE                    4.50 usec
TE                   300.0 K
D1                1.00000000 sec

============ CHANNEL f1 ============
NUC1                     1H
P1                     7.70 usec
PL1                   -6.00 dB
SFO1           400.1320007 MHz

F2 - Processing parameters
SI                       16384
SF             400.1300074 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       20.00 cm
F1P                     10.000 ppm
F1                    4001.30 Hz
F2P                    -1.000 ppm
F2                    -400.13 Hz
PPMCM                 0.55000 ppm/cm
HZCM                220.07150 Hz/cm
```



```
Current Data Parameters
NAME          4c-VII-17major
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20111124
Time                  20.42
INSTRUM               drx400
PROBHD     5 mm Multinu
PULPROG             zgpg30
TD                   65536
SOLVENT               CDCl3
NS                      380
DS                        2
SWH               23148.148 Hz
FIDRES            0.353213 Hz
AQ                1.4156276 sec
RG                    8192
DW                  21.600 usec
DE                    4.50 usec
TE                   300.0 K
D1                0.05000000 sec
d11               0.03000000 sec
d12               0.00002000 sec

============ CHANNEL f1 ============
NUC1                     13C
P1                    12.30 usec
PL1                    2.00 dB
SFO1           100.6232933 MHz

============ CHANNEL f2 ============
CPDPRG2              waltz16
NUC2                     1H
PCPD2                160.00 usec
PL2                    0.00 dB
PL12                  18.00 dB
PL13                  18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF             100.6127290 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
F1P                    220.000 ppm
F1                   22134.80 Hz
F2P                    -10.000 ppm
F2                   -1006.13 Hz
PPMCM                 11.50000 ppm/cm
```



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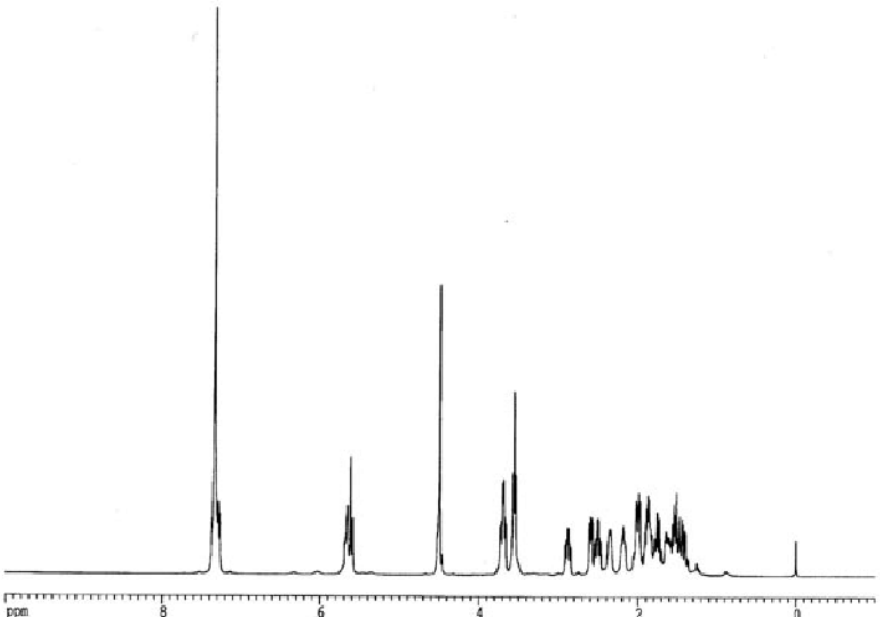
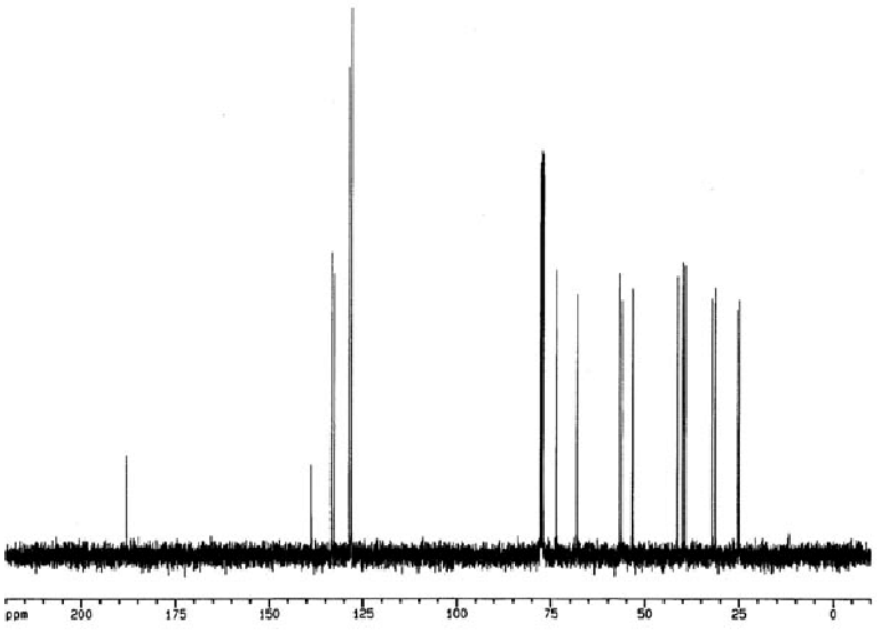
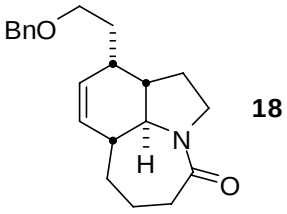


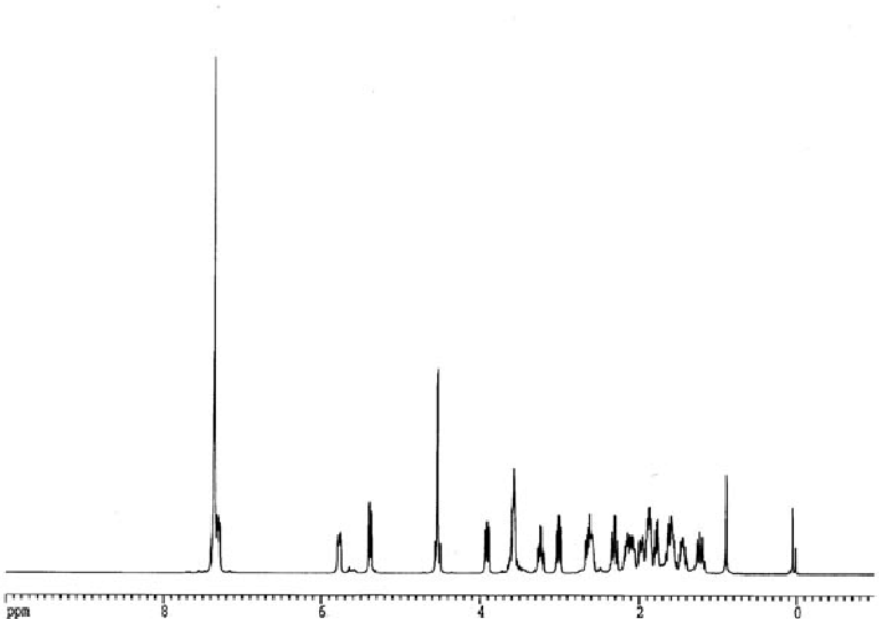

```
Current Data Parameters
NAME          4c-Vilactam
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_              20010724
Time                  17.21
INSTRUM             drx400
PROBHD     5 mm Multinu
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4789.272 Hz
FIDRES           0.146157 Hz
AQ               3.4210291 sec
RG                     64
DW                104.400 usec
DE                  4.50 usec
TE                 300.0 K
D1              1.00000000 sec

========== CHANNEL f1 ===========
NUC1                   1H
P1                   7.70 usec
PL1                 -6.00 dB
SFO1          400.1320007 MHz

F2 - Processing parameters
SI                     16384
SF            400.1300068 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                10.000 ppm
F1                 4001.30 Hz
F2P                -1.000 ppm
F2                 -400.13 Hz
PPMCM               0.55000 ppm/cm
HZCM              220.07150 Hz/cm
```



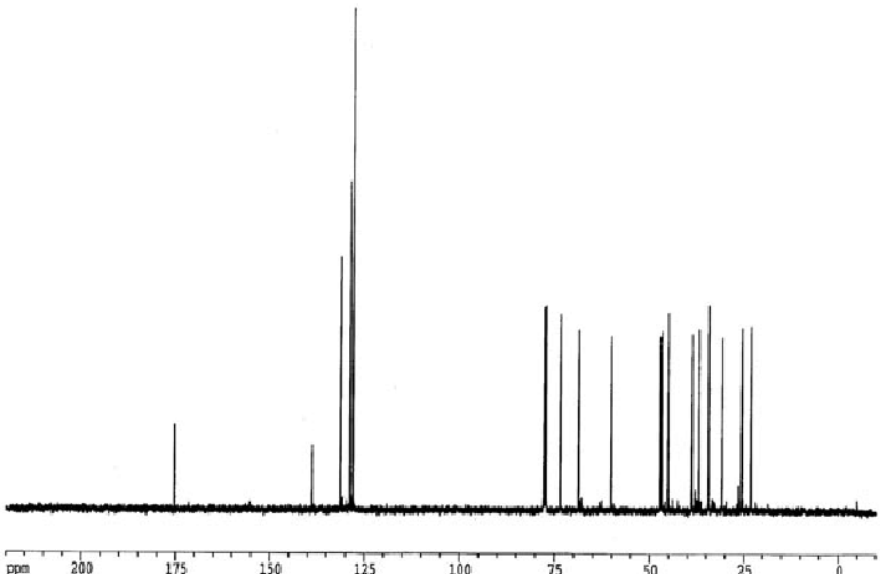

```
Current Data Parameters
NAME          4c-Vilactam
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_              1010724
Time                  17.26
INSTRUM             drx400
PROBHD     5 mm Multinu
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                    169
DS                      2
SWH             23148.148 Hz
FIDRES           0.353213 Hz
AQ               1.4156276 sec
RG                   4096
DW                 21.600 usec
DE                  4.50 usec
TE                 300.0 K
d11              0.0300000 sec
d12              0.0000200 sec
PL13                18.00 dB
D1               0.05000000 sec
CPDPRG2             waltz16
PCPD2              100.00 usec
SFO2          400.1316005 MHz
NUC2                   1H
PL2                 0.00 dB
PL12               18.00 dB
P1                 12.30 usec
DE                  4.50 usec
SFO1          100.6232933 MHz
NUC1                  13C
PL1                 2.00 dB

F2 - Processing parameters
SI                     32768
SF            100.6127290 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P               220.000 ppm
F1              22136.80 Hz
F2P               -10.000 ppm
F2              -1006.53 Hz
PPMCM              11.50000 ppm/cm
HZCM            1157.04639 Hz/cm
```



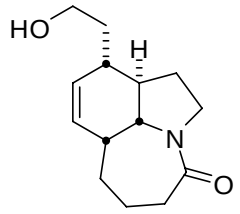
18

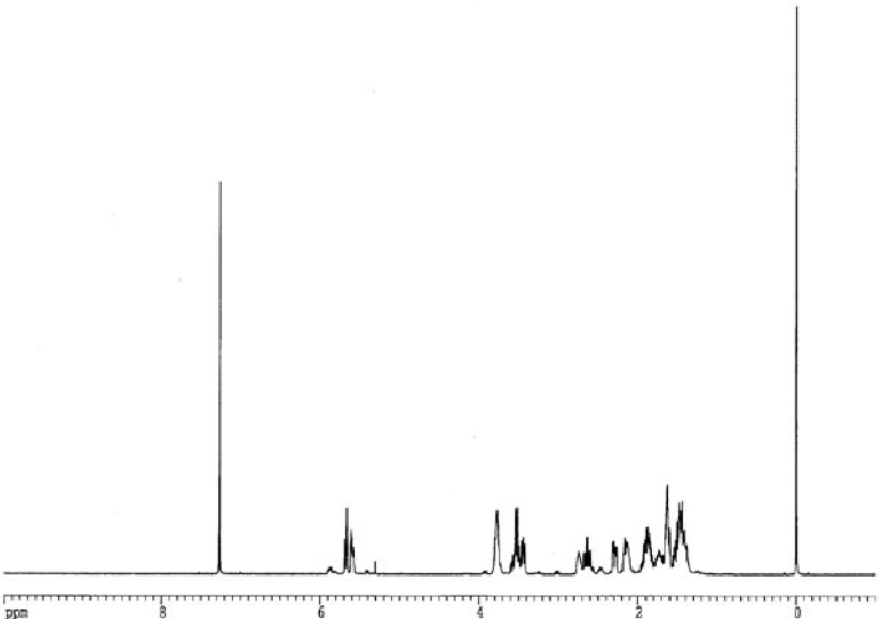



```
Current Data Parameters
NAME                  4c-VI-100a
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_               20010820
Time                      13.08
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG                 zg30
TD                         32768
SOLVENT                  CDCl3
NS                            16
DS                             2
SWH                  4789.272 Hz
FIDRES               0.146157 Hz
AQ                   3.4210291 sec
RG                            64
DW                     104.400 usec
DE                       4.50 usec
TE                      300.0 K
D1                   1.00000000 sec

========== CHANNEL f1 ==========
NUC1                          1H
P1                         7.70 usec
PL1                       -6.00 dB
SFO1                400.1320007 MHz

F2 - Processing parameters
SI                         16384
SF                  400.1300000 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00

1D NMR plot parameters
CX                         20.00 cm
F1P                        10.000 ppm
F1                       4001.30 Hz
F2P                        -1.000 ppm
F2                       -400.13 Hz
PPMCM                     0.55000 ppm/cm
HZCM                    220.07150 Hz/cm
```

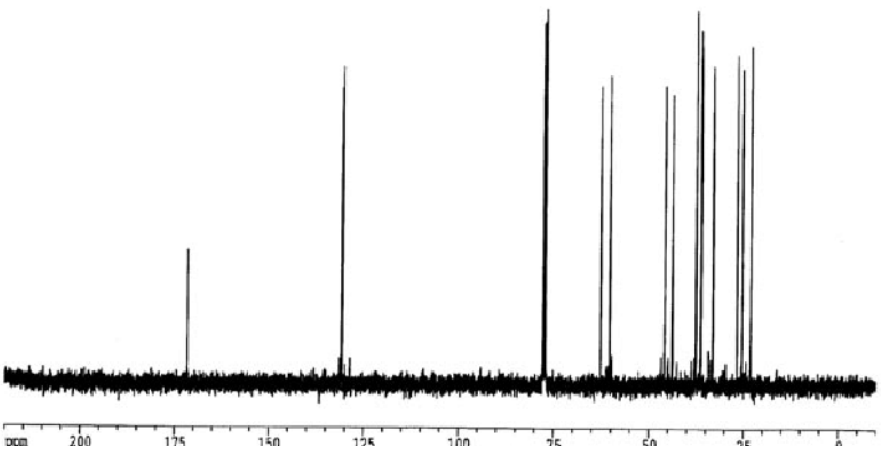



```
Current Data Parameters
NAME                  4c-VI-100a
EXPNO                          2
PROCNO                         1

F2 - Acquisition Parameters
Date_               20010820
Time                      13.12
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG                 zgpg30
TD                         65536
SOLVENT                  CDCl3
NS                           401
DS                             2
SWH                 23148.148 Hz
FIDRES               0.353213 Hz
AQ                   1.4154276 sec
RG                          8192
DW                      21.600 usec
DE                       4.50 usec
TE                      300.0 K
D1                   0.05000000 sec
d11                  0.03000000 sec
d12                  0.00002000 sec

========== CHANNEL f1 ==========
NUC1                          13C
P1                        12.30 usec
PL1                        2.00 dB
SFO1                100.6232933 MHz

========== CHANNEL f2 ==========
CPDPRG2                 waltz16
NUC2                          1H
PCPD2                    100.00 usec
PL2                        0.00 dB
PL12                      18.00 dB
PL13                      18.00 dB
SFO2                400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                  100.6127290 MHz
WDW                           EM
SSB                            0
LB                         3.00 Hz
GB                             0
PC                          1.40

1D NMR plot parameters
CX                         20.00 cm
F1P                       220.000 ppm
F1                      22136.80 Hz
F2P                       -10.000 ppm
F2                      -1006.13 Hz
PPMCM                    11.50000 ppm/cm
```

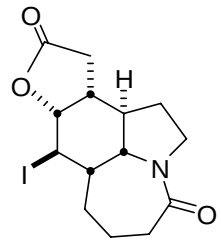





```
Current Data Parameters
NAME          4C-VII-56-8
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20011125
Time              17.11
INSTRUM          drx400
PROBHD     5 mm Multinu
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           4789.272 Hz
FIDRES        0.146157 Hz
AQ            3.4210291 sec
RG                 181
DW              104.400 usec
DE                4.50 usec
TE              300.0 K
D1            1.00000000 sec

============ CHANNEL f1 ============
NUC1                1H
P1                7.70 usec
PL1              -6.00 dB
SFO1        400.1320007 MHz

F2 - Processing parameters
SI                16384
SF          400.1300074 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P              10.000 ppm
F1              4001.30 Hz
F2P              -1.000 ppm
F2              -400.13 Hz
PPMCM          0.55000 ppm/cm
HZCM         220.07150 Hz/cm
```




```
Current Data Parameters
NAME          4c-VI-123a
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_          20010827
Time              14.50
INSTRUM          drx400
PROBHD     5 mm Multinu
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 193
DS                   2
SWH          23148.148 Hz
FIDRES        0.353213 Hz
AQ            1.4154276 sec
RG                4096
DW              21.600 usec
DE                4.50 usec
TE              300.0 K
D1            0.05000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1               12.30 usec
PL1               2.00 dB
SFO1        100.6232913 MHz

============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                1H
PCPD2          100.00 usec
PL2              0.00 dB
PL12            18.00 dB
PL13            18.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127290 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P             220.000 ppm
F1             22134.88 Hz
F2P             -10.000 ppm
F2             -1006.13 Hz
PPMCM         11.50000 ppm/cm
```



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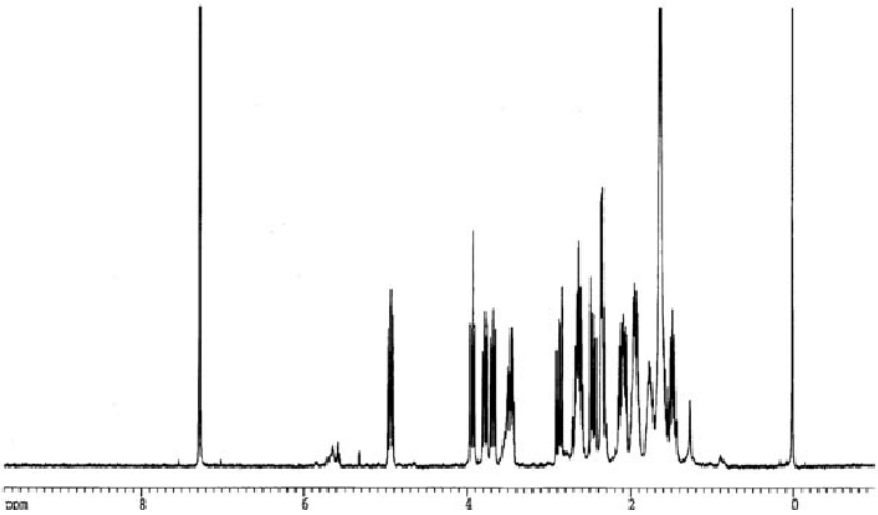
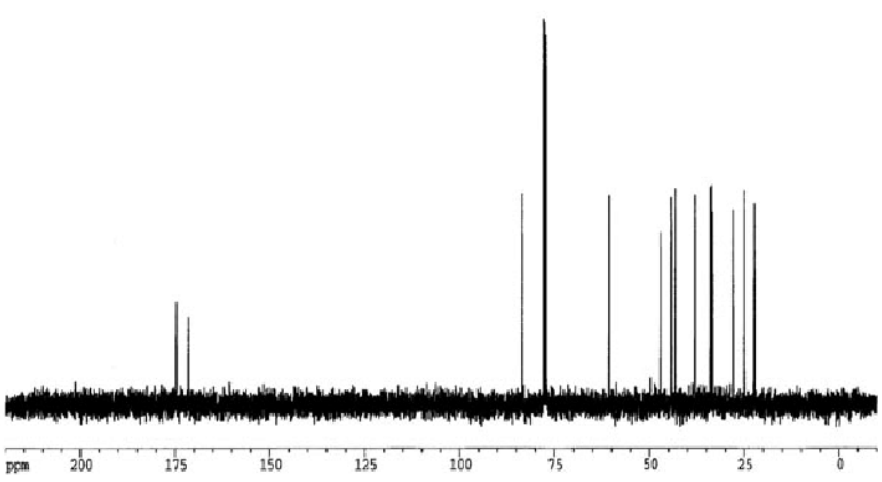
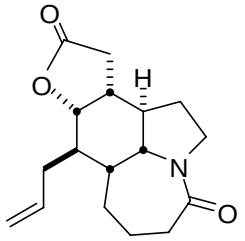
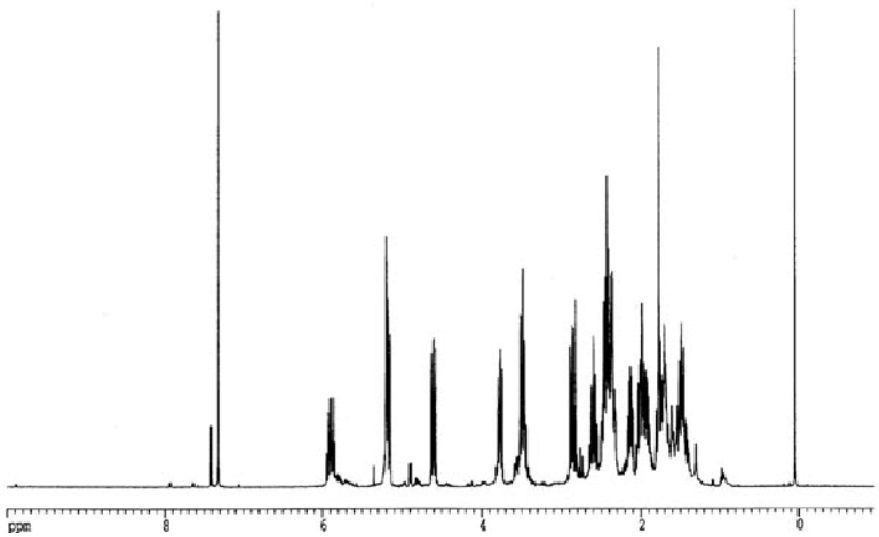



```
Current Data Parameters
NAME        4C-VII-67frac8
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20011204
Time                   8.59
INSTRUM              drx400
PROBHD     5 mm Multinu
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH               4789.272 Hz
FIDRES            0.146157 Hz
AQ                3.4210291 sec
RG                    203.2
DW                  104.400 usec
DE                    4.50 usec
TE                   300.0 K
D1                1.00000000 sec

========== CHANNEL f1 ==========
NUC1                    1H
P1                    7.70 usec
PL1                  -6.00 dB
SFO1          400.1320007 MHz

F2 - Processing parameters
SI                     16384
SF                400.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
F1P                    9.000 ppm
F1                  3881.26 Hz
F2P                   -1.000 ppm
F2                  -400.13 Hz
PPMCM                0.53500 ppm/cm
HZCM               214.06955 Hz/cm
```

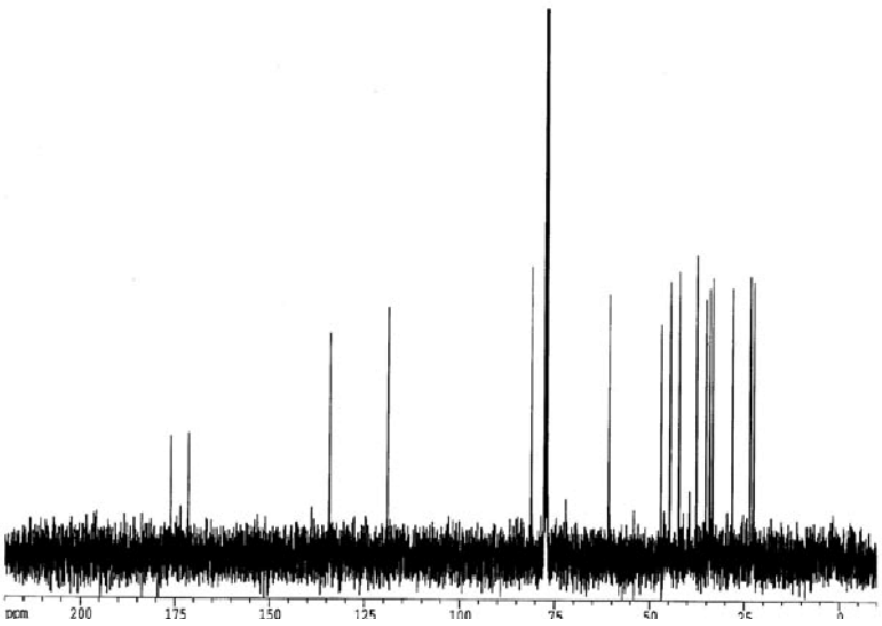



```
Current Data Parameters
NAME        4C-VII-59-b1
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20011126
Time                  11.41
INSTRUM              drx400
PROBHD     5 mm Multinu
PULPROG             apgp30
TD                   65536
SOLVENT              CDCl3
NS                      96
DS                       2
SWH              23148.148 Hz
FIDRES            0.353213 Hz
AQ                1.4156276 sec
RG                    8192
DW                  21.600 usec
DE                    4.50 usec
TE                   308.0 K
D1                0.05000000 sec
d11               0.03000000 sec
d12               0.00002000 sec

========== CHANNEL f1 ==========
NUC1                    13C
P1                   12.30 usec
PL1                   2.00 dB
SFO1          100.6232933 MHz

========== CHANNEL f2 ==========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                100.00 usec
PL2                   0.00 dB
PL12                 18.00 dB
PL13                 18.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                     32768
SF                100.6127290 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                     20.00 cm
F1P                  220.000 ppm
F1                 22134.80 Hz
F2P                  -10.000 ppm
F2                  -1006.13 Hz
PPMCM               11.50000 ppm/cm
HZCM              1157.04639 Hz/cm
```

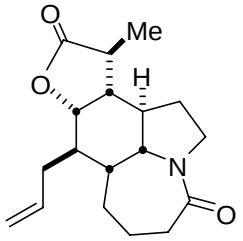





```
Current Data Parameters
NAME                  4C-VII-68
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20011205
Time                      17.32
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG                 zg30
TD                       32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                       143.7
DW                     104.400 usec
DE                       4.50 usec
TE                      300.0 K
D1                  1.00000000 sec

============ CHANNEL f1 ============
NUC1                        1H
P1                        7.70 usec
PL1                      -6.00 dB
SFO1               400.1320007 MHz

F2 - Processing parameters
SI                       16384
SF                 400.1299854 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       20.00 cm
F1P                      10.000 ppm
F1                     4001.30 Hz
F2P                      -1.000 ppm
F2                     -400.13 Hz
PPMCM                 0.55000 ppm/cm
HZCM                220.07149 Hz/cm
```




```
Current Data Parameters
NAME                  4C-VII-68
EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
Date_              20011205
Time                      17.37
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG              zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         358
DS                           2
SWH                23148.148 Hz
FIDRES              0.353213 Hz
AQ                  1.4156276 sec
RG                        8192
DW                     21.600 usec
DE                       4.50 usec
TE                      309.0 K
D1                  0.05000000 sec
d11                 0.03000000 sec
d12                 0.00002000 sec

============ CHANNEL f1 ============
NUC1                       13C
P1                       12.30 usec
PL1                       2.00 dB
SFO1               100.6232933 MHz

============ CHANNEL f2 ============
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                  100.00 usec
PL2                       0.00 dB
PL12                     18.00 dB
PL13                     18.00 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF                 100.6127290 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
F1P                     220.000 ppm
F1                     22136.80 Hz
F2P                     -10.000 ppm
F2                     -1006.13 Hz
PPMCM                 11.50000 ppm/cm
```



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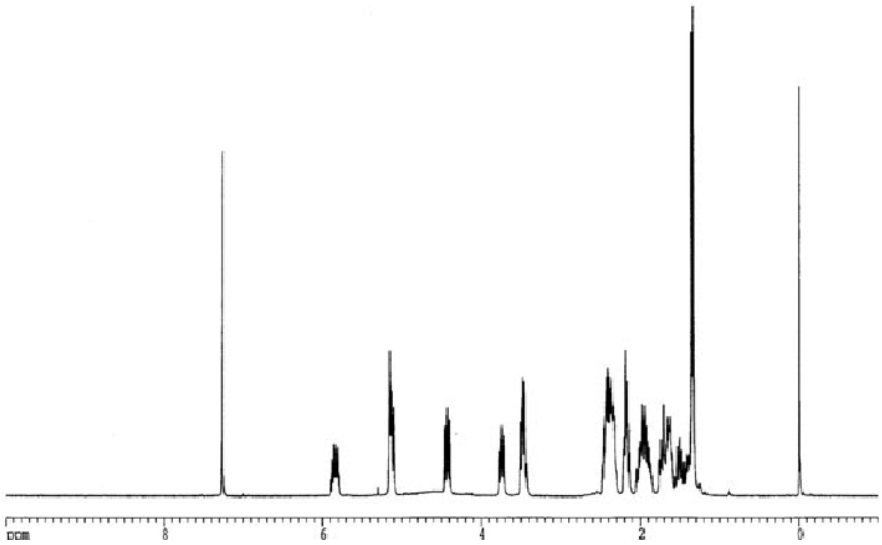
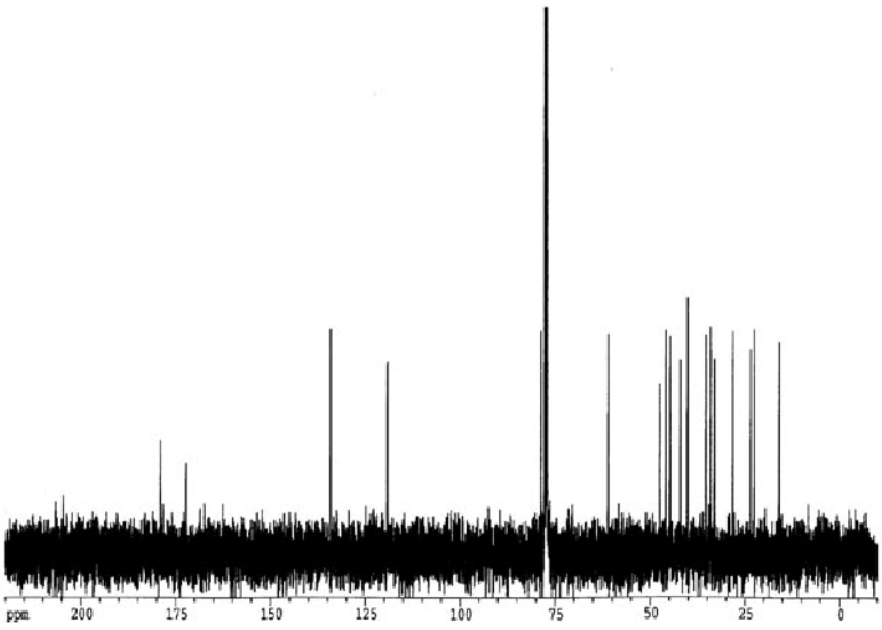
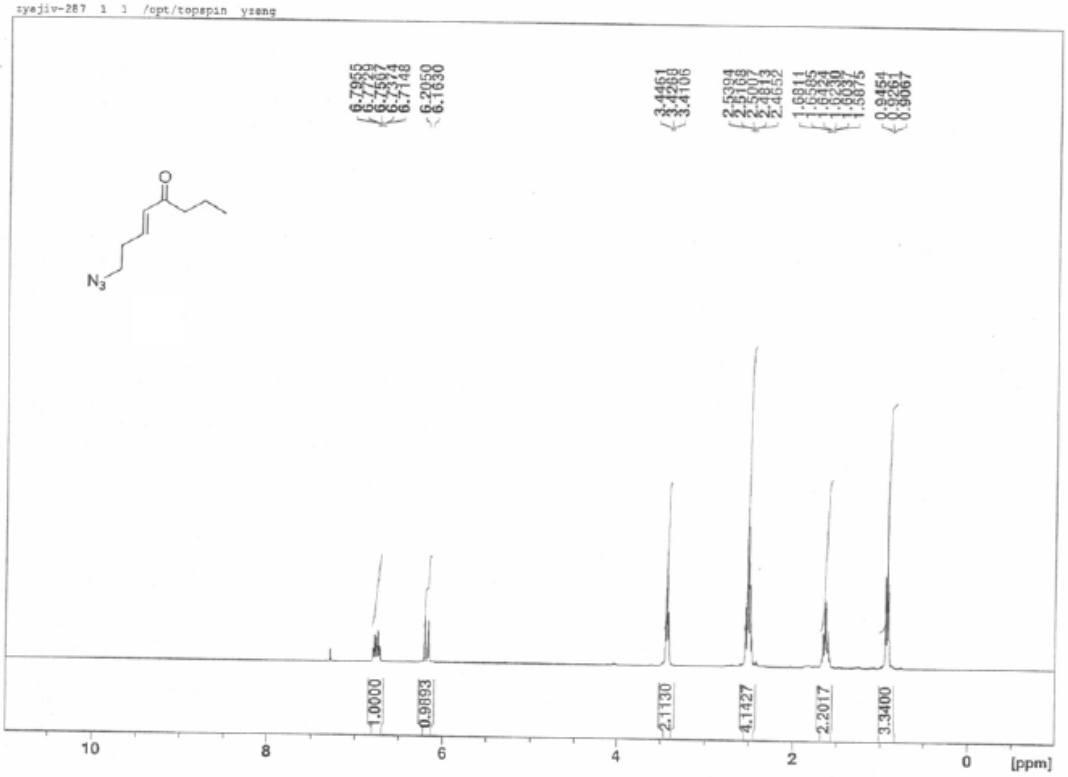
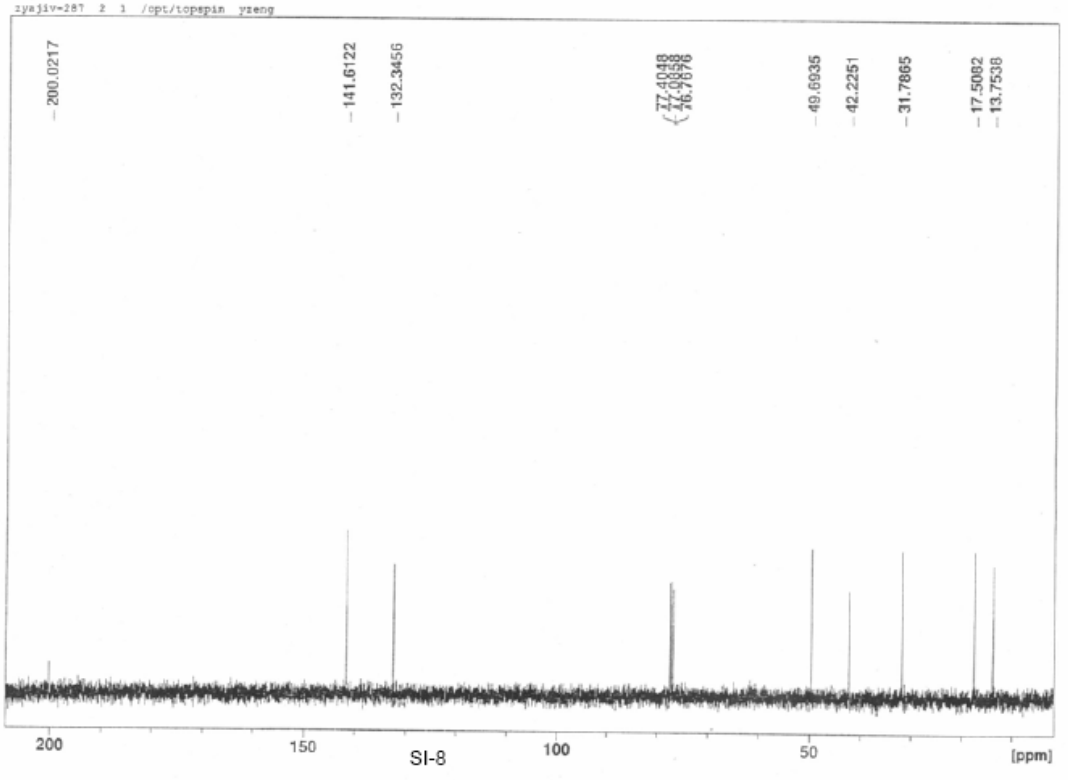


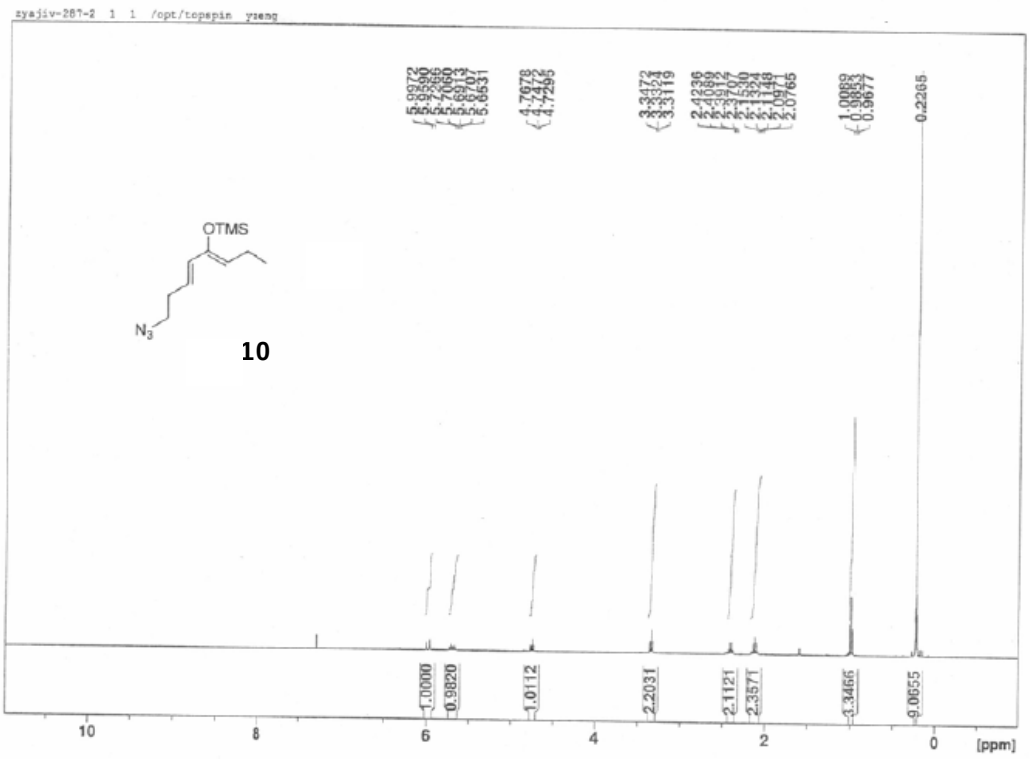

```
Current Data Parameters
NAME      4c-VII-168-new
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_         20020222
Time             11.25
INSTRUM         drx400
PROBHD     5 mm Multinu
PULPROG          zg30
TD              32768
SOLVENT          CDCl3
NS                 16
DS                  2
SWH           4789.272 Hz
FIDRES        0.146157 Hz
AQ            3.4210291 sec
RG                203.2
DW              104.400 usec
DE                4.50 usec
TE                300.0 K
D1            1.00000000 sec

============ CHANNEL f1 ============
NUC1               1H
P1                7.70 usec
PL1               -6.00 dB
SFO1        400.1320007 MHz

F2 - Processing parameters
SI                16384
SF          400.1300082 MHz
WDW                EM
SSB                 0
LB                0.30 Hz
GB                  0
PC                1.00

1D NMR plot parameters
CX                20.00 cm
F1P               10.000 ppm
F1                4001.30 Hz
F2P               -1.000 ppm
F2                -400.13 Hz
PPMCM             0.55000 ppm/cm
HZCM            220.07150 Hz/cm
```

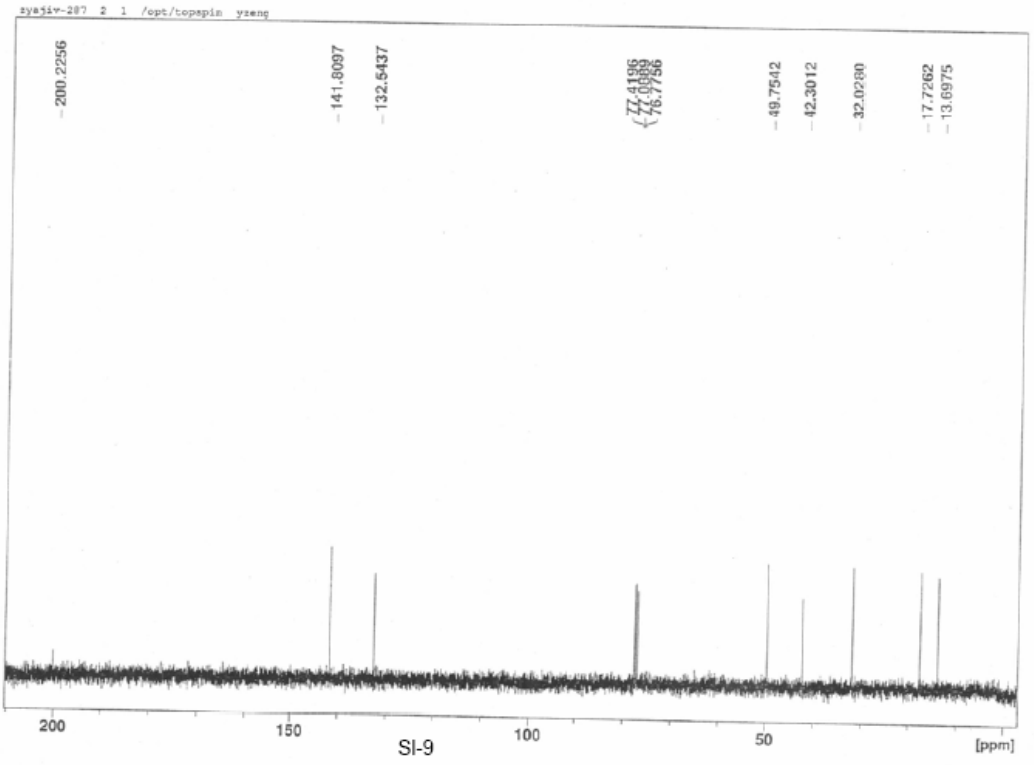


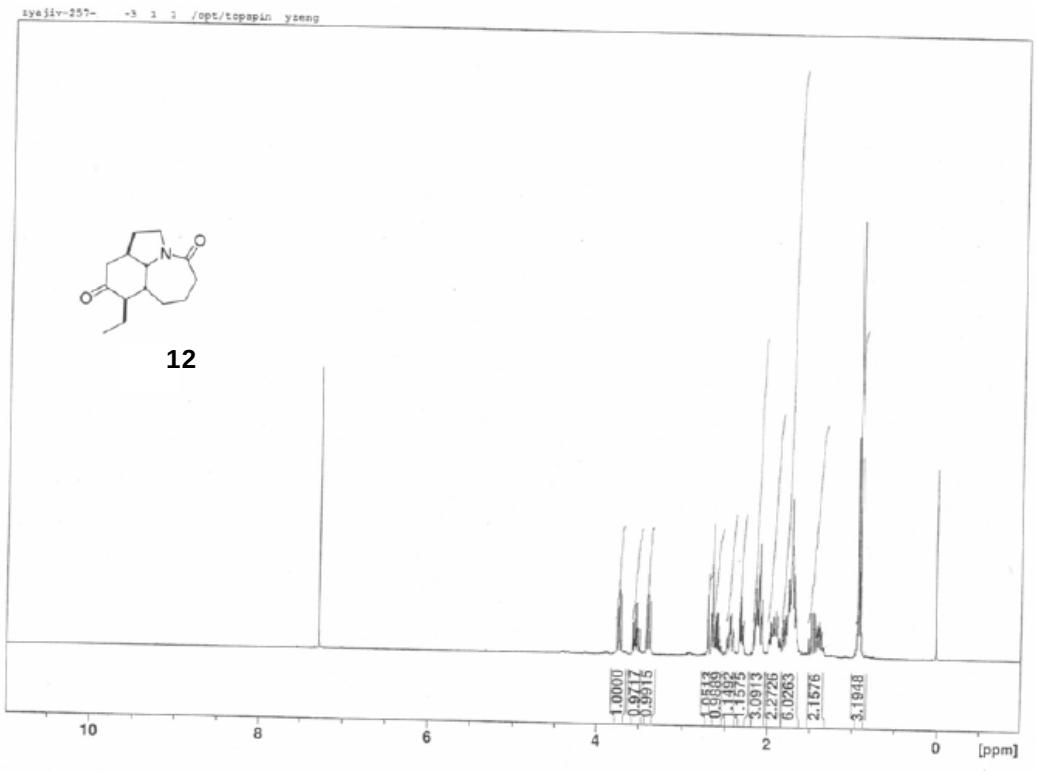

```
Current Data Parameters
NAME      4c-VII-168-new
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_         20020222
Time             14.20
INSTRUM         drx400
PROBHD     5 mm Multinu
PULPROG        zgpg30
TD              65536
SOLVENT          CDCl3
NS                391
DS                  2
SWH          23148.148 Hz
FIDRES        0.353213 Hz
AQ            1.4156276 sec
RG                4096
DW              21.600 usec
DE                4.50 usec
TE                300.0 K
D1            0.05000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 ============
NUC1               13C
P1                12.30 usec
PL1               2.00 dB
SFO1        100.6232933 MHz

============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2               1H
PCPD2           100.00 usec
PL2               0.00 dB
PL12             18.00 dB
PL13             18.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6123290 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40

1D NMR plot parameters
CX                20.00 cm
F1P              220.000 ppm
F1             22134.80 Hz
F2P              -10.000 ppm
F2             -1006.13 Hz
PPMCM         11.50000 ppm/cm
HZCM          1157.08630 Hz/cm
```

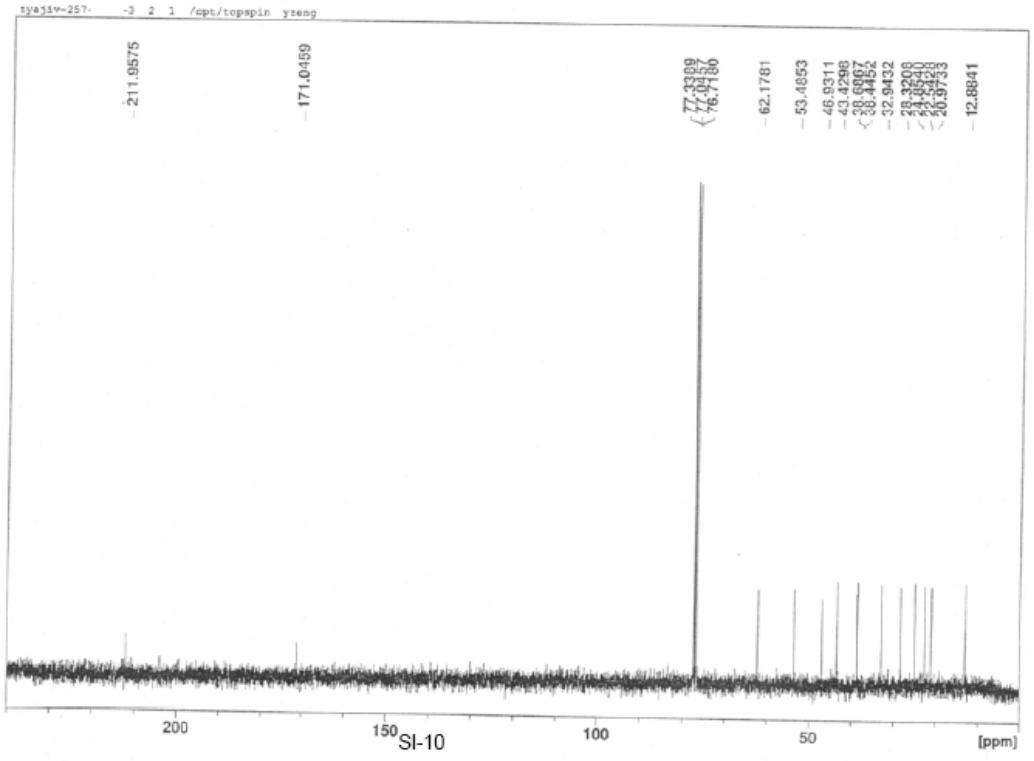

zyajiv-287 1 1 /opt/topspin yzeng
6.7955
6.7667
6.7514
6.7148
6.2050
6.1630
3.4461
3.4280
3.4106
2.5394
2.5169
2.5007
2.4813
2.4652
1.6811
1.6585
1.6424
1.6230
1.5937
1.5875
0.9454
0.9261
0.9067
1.0000
0.9893
2.1130
4.1427
2.2017
3.3400
10
8
6
4
2
0
[ppm]

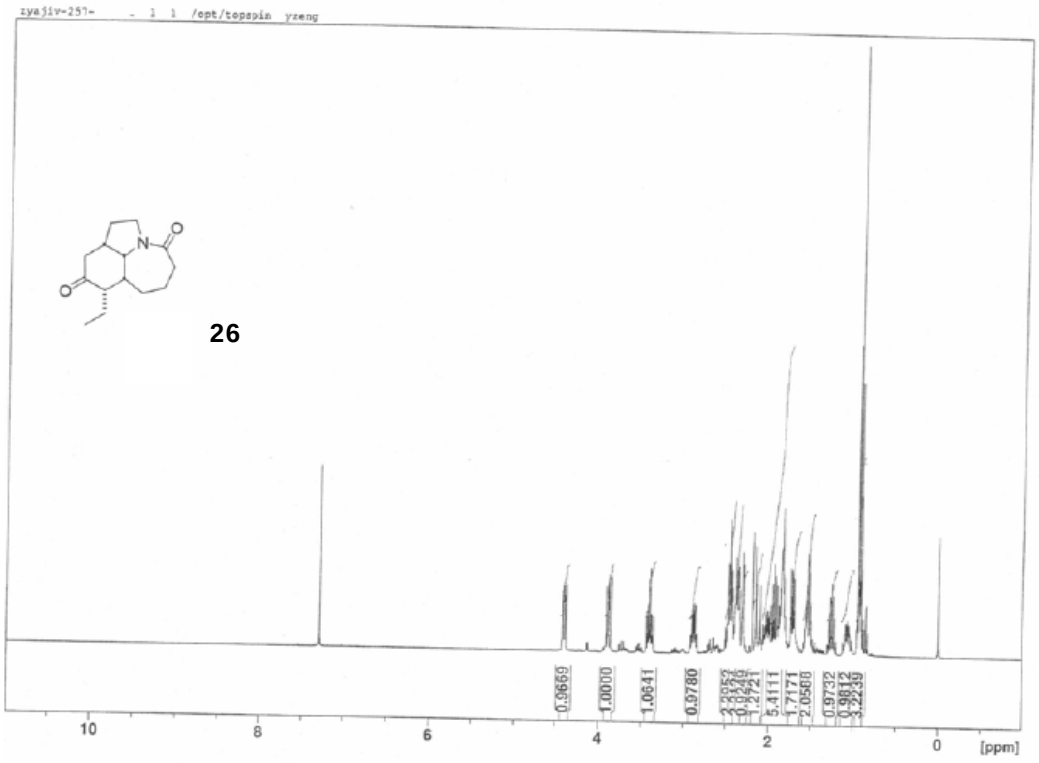

zyajiv-287 2 1 /opt/topspin yzeng
200.0217
141.6122
132.3456
77.4048
77.0858
76.7676
49.6935
42.2251
31.7865
17.5082
13.7538
200
150
100
50
[ppm]

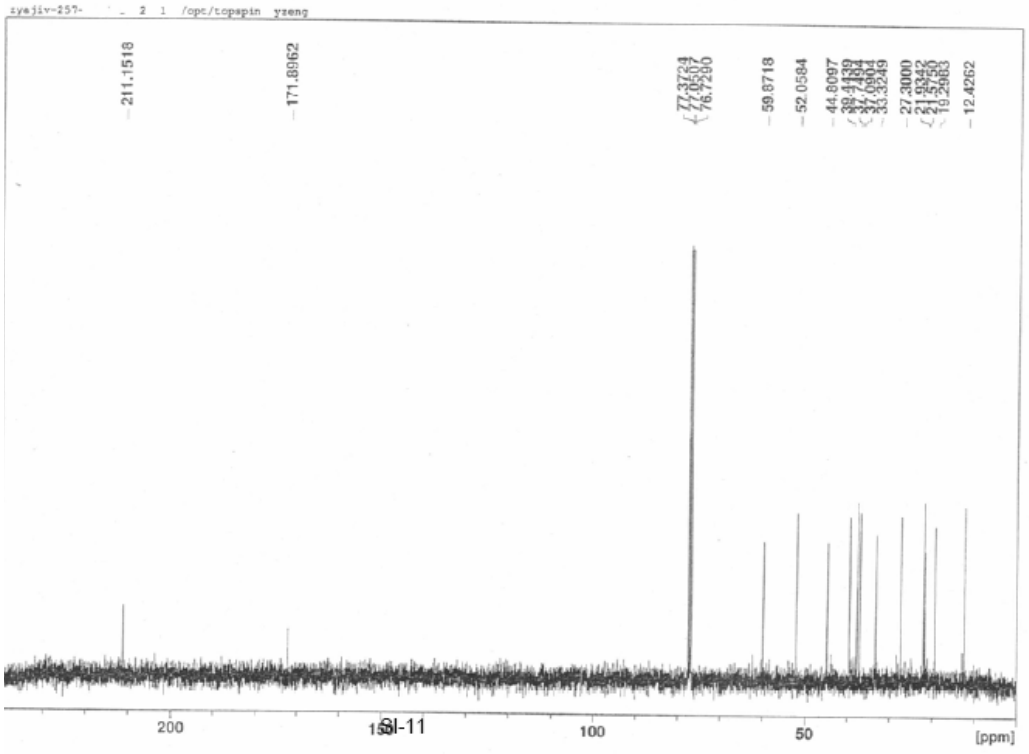

zyajiv-287-2 1 1 /opt/topspin yzeng
OTMS
N_3
10
[ppm]

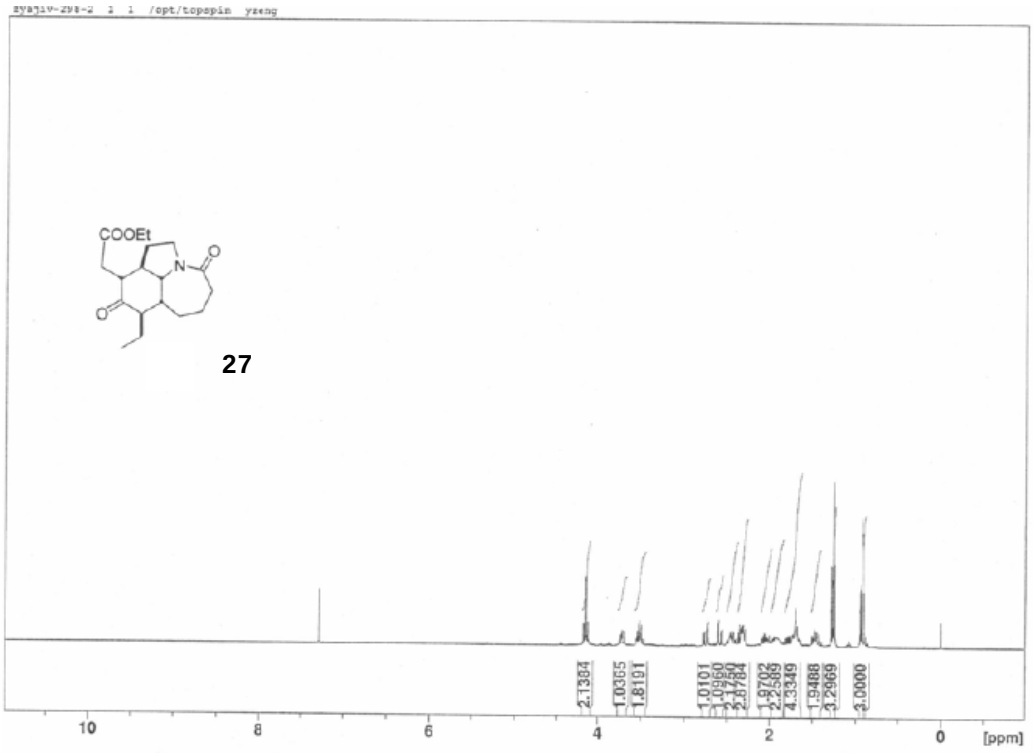

zyajiv-287 2 1 /opt/topspin yzeng
200.2256
141.8097
132.5437
77.4196
77.0000
76.7756
49.7542
42.3012
32.0280
17.7262
13.6975
[ppm]

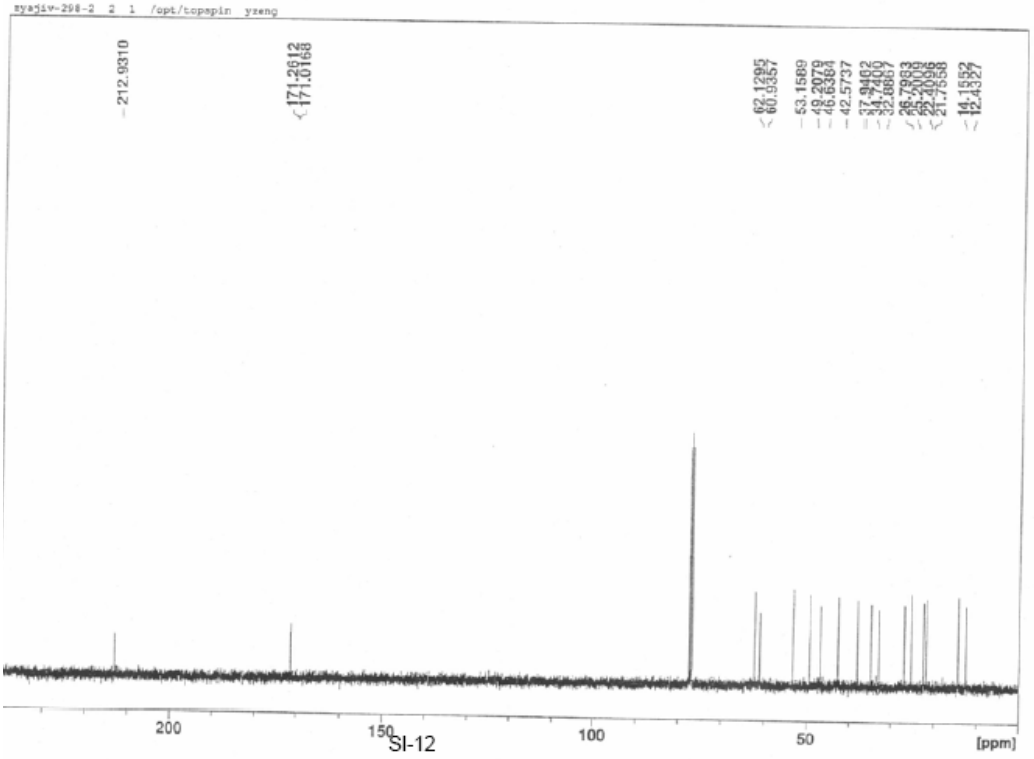

syajiv-257- -3 1 1 /opt/topspin yzeng
12
1.0000
0.9717
0.9915
1.0513
0.8869
1.1492
1.1575
3.0913
2.2726
6.0263
2.1576
3.1948
10
8
6
4
2
0
[ppm]

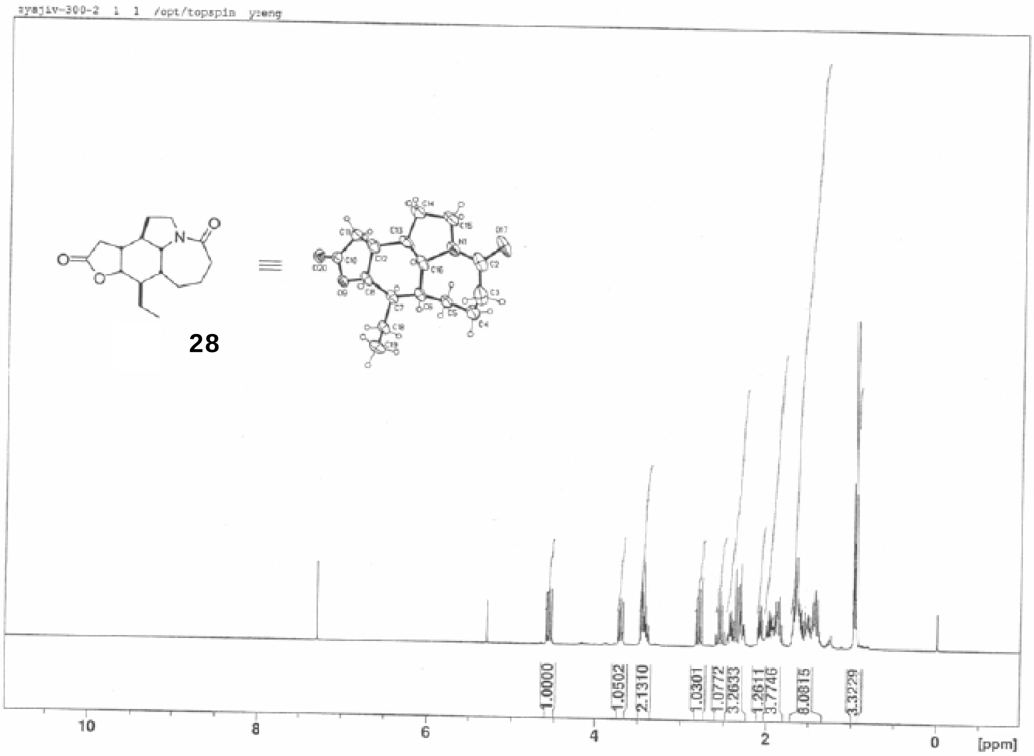

syajiv-257- -3 2 1 /opt/topspin yzeng
211.9575
171.0459
77.3389
77.0457
76.7180
62.1781
53.4853
46.9311
43.4296
38.6067
38.4452
32.9432
28.3208
21.8540
21.5428
20.9733
12.8841
200
150
100
50
[ppm]

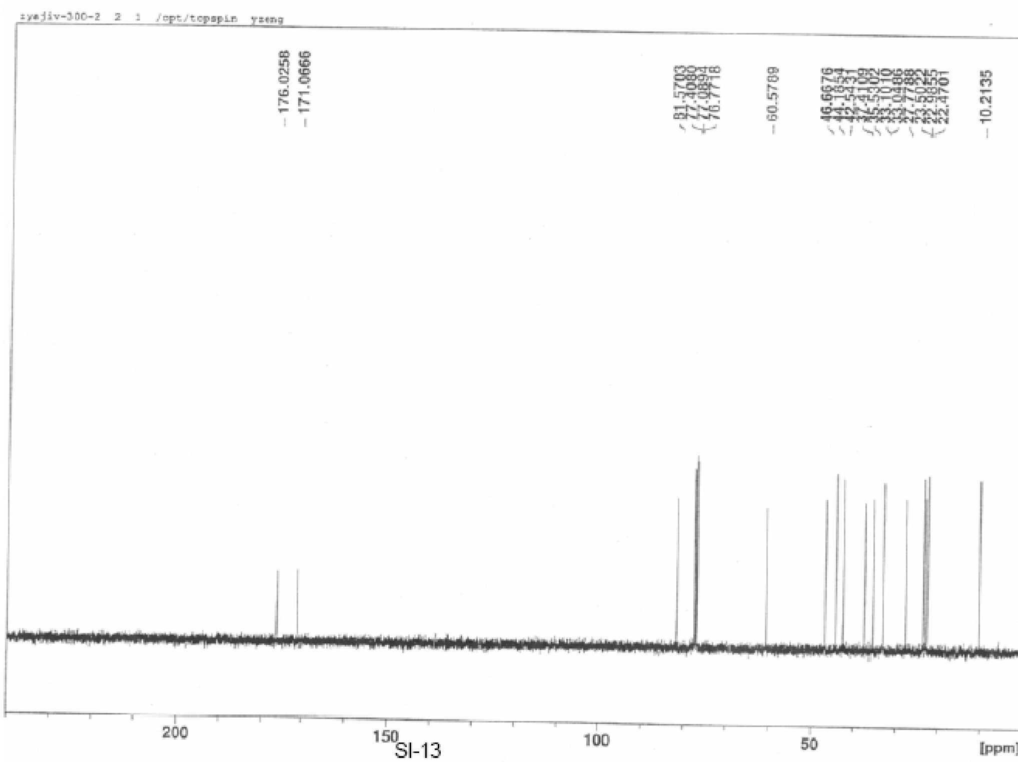

zyajiv-257-
/opt/topspin yzeng
26
0.9659
1.0000
1.0641
0.9780
5.4111
1.7171
2.0588
10
8
6
4
2
0
[ppm]


zyajiv-257-
/opc/topspin yzeng
211.1518
171.8962
77.3724
77.0507
76.7290
59.6718
52.0584
44.8097
27.3000
21.9342
21.5750
19.2983
12.4262
200
150
100
50
[ppm]

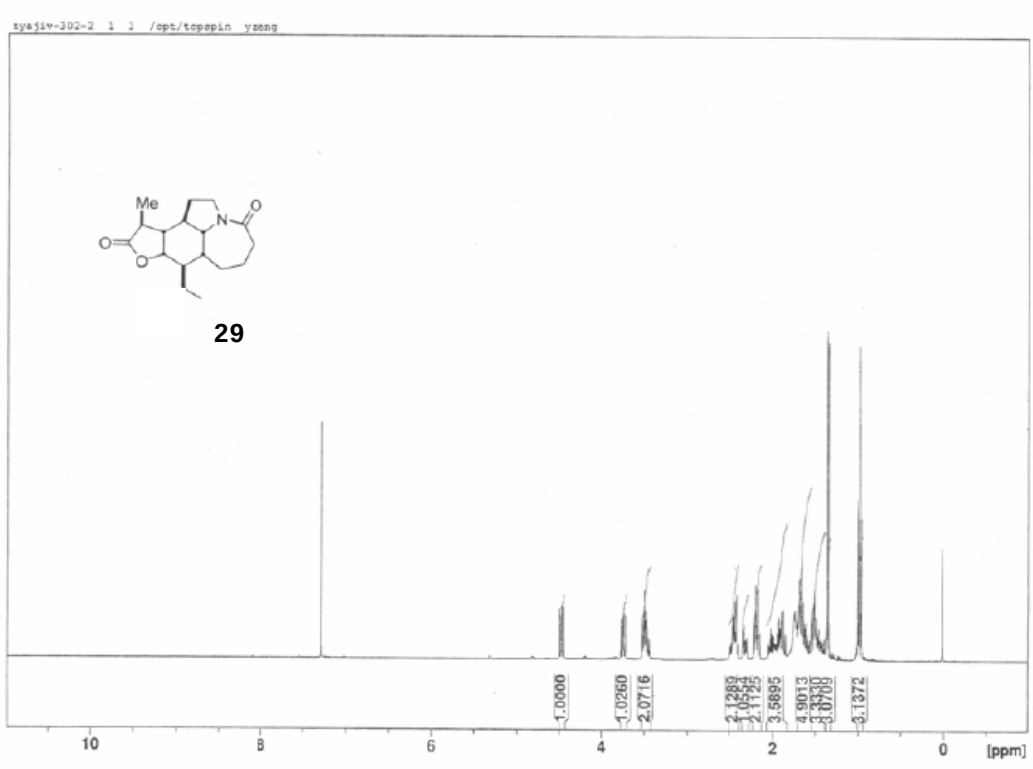

zyajiv-298-2 2 1 /opt/topspin yzeng
COOEt
O
N
O
O
27
2.1384
1.0365
1.8191
1.0101
1.0960
2.3784
1.9702
2.2589
4.3349
1.9488
3.2969
3.0000
10
8
6
4
2
0
[ppm]

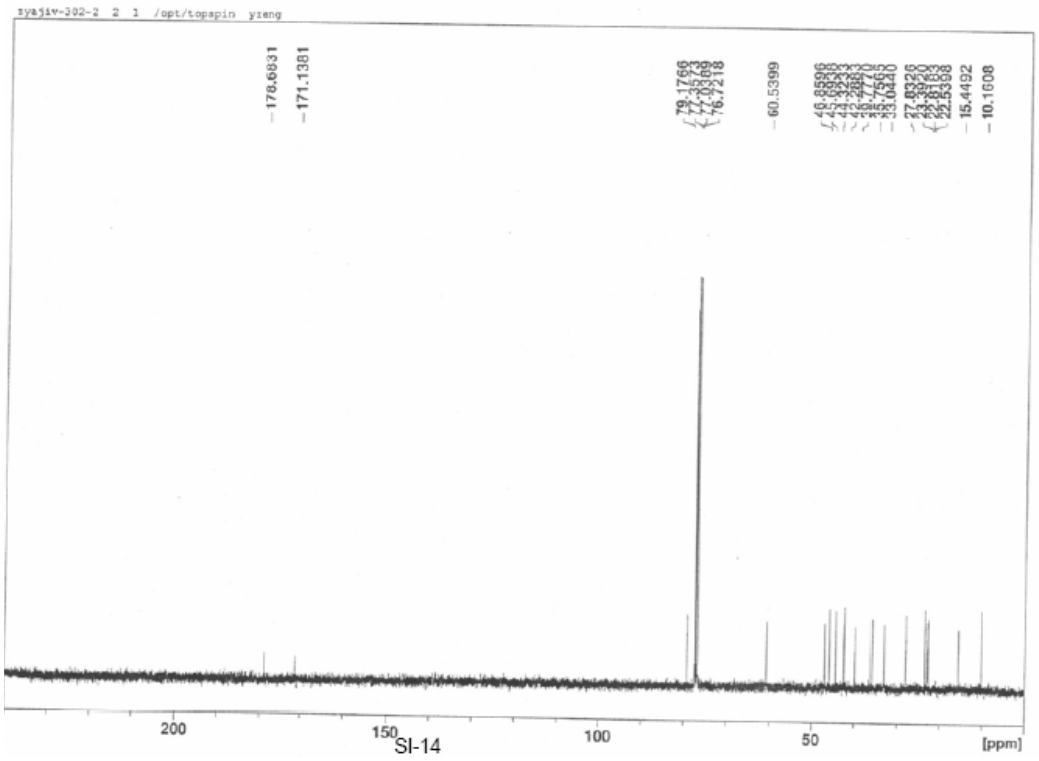

zyajiv-298-2 2 1 /opt/topspin yzeng
212.9310
171.2612
171.0168
62.1295
60.5357
53.1589
48.2079
46.6384
42.5737
37.9462
34.7400
32.8867
26.7983
25.2009
22.4096
21.7558
14.1552
12.4327
200
150
100
50
[ppm]

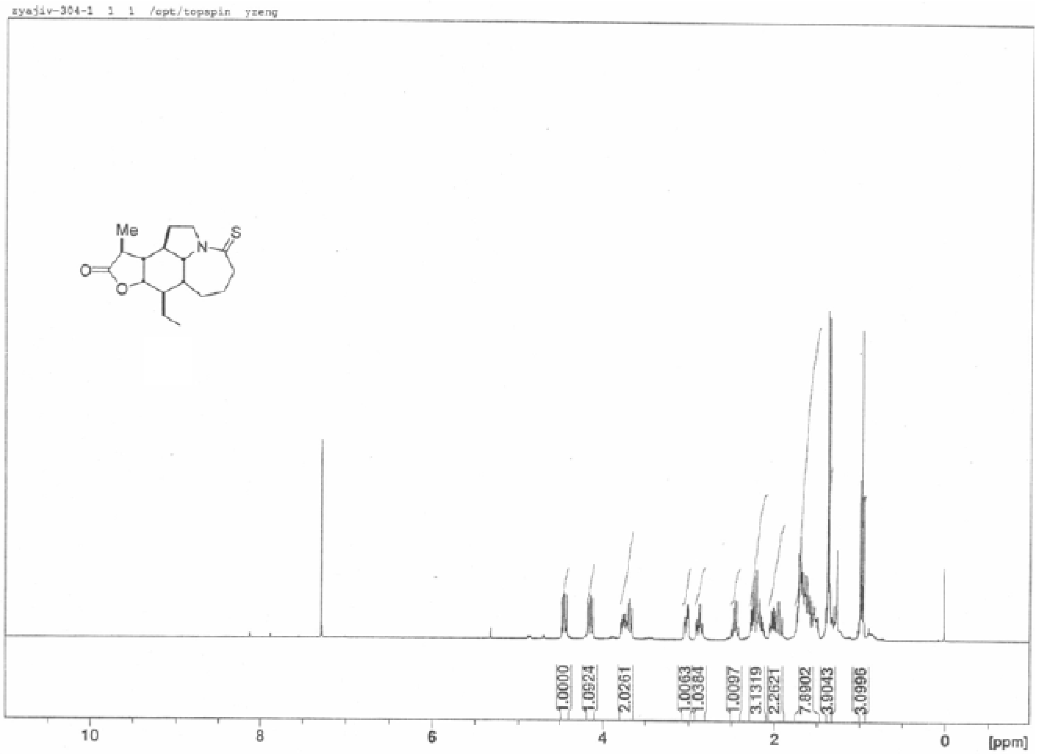

zysjiv-300-2 1 1 /opt/topspin yzeng
28
1.0000
1.0502
2.1310
1.0301
1.0772
3.2633
1.2611
3.7746
8.0815
3.3229
10
8
6
4
2
0
[ppm]

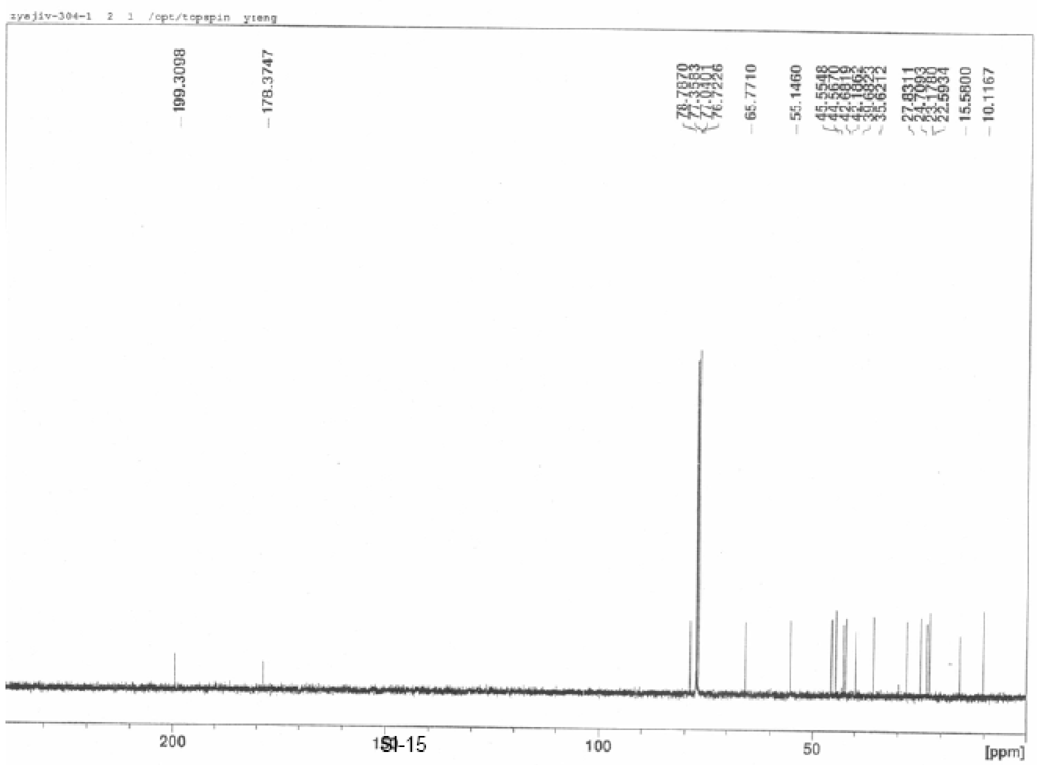

zysjiv-300-2 2 1 /opt/topspin yzeng
176.0258
171.0666
81.5703
60.5789
46.6676
10.2135
200
150
100
50
[ppm]

SI-13

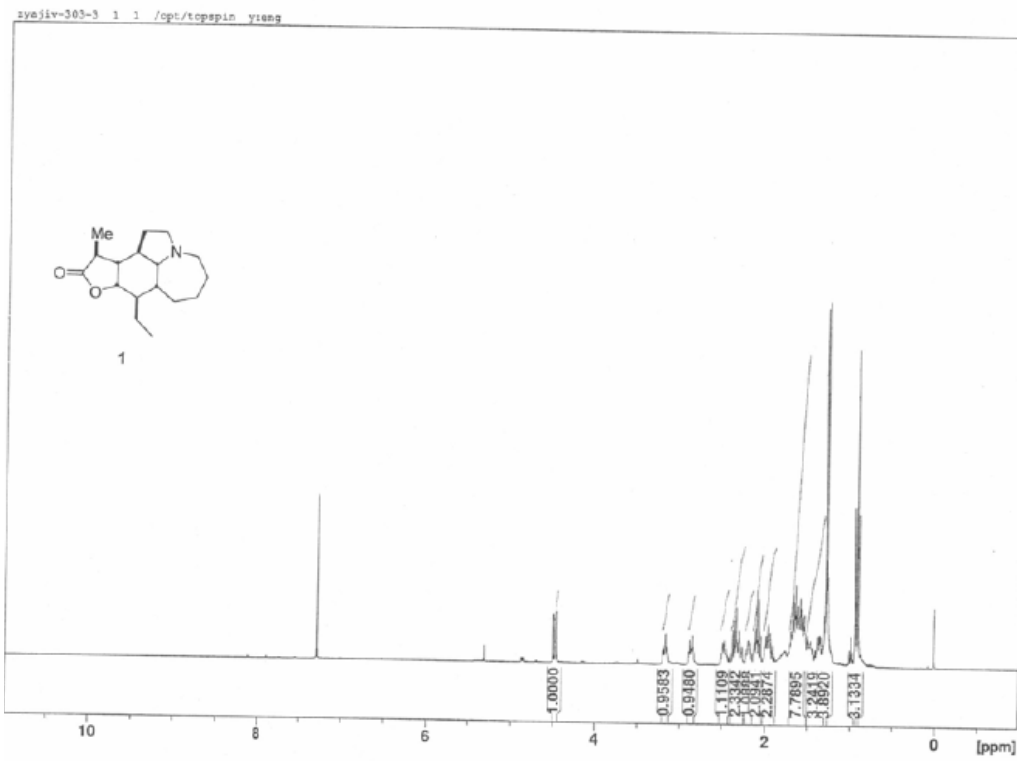

Me
O
O
O
N
O
29
1.0000
1.0260
2.0716
3.5895
4.9013
3.3330
3.0709
3.1372
10
8
6
4
2
0
[ppm]

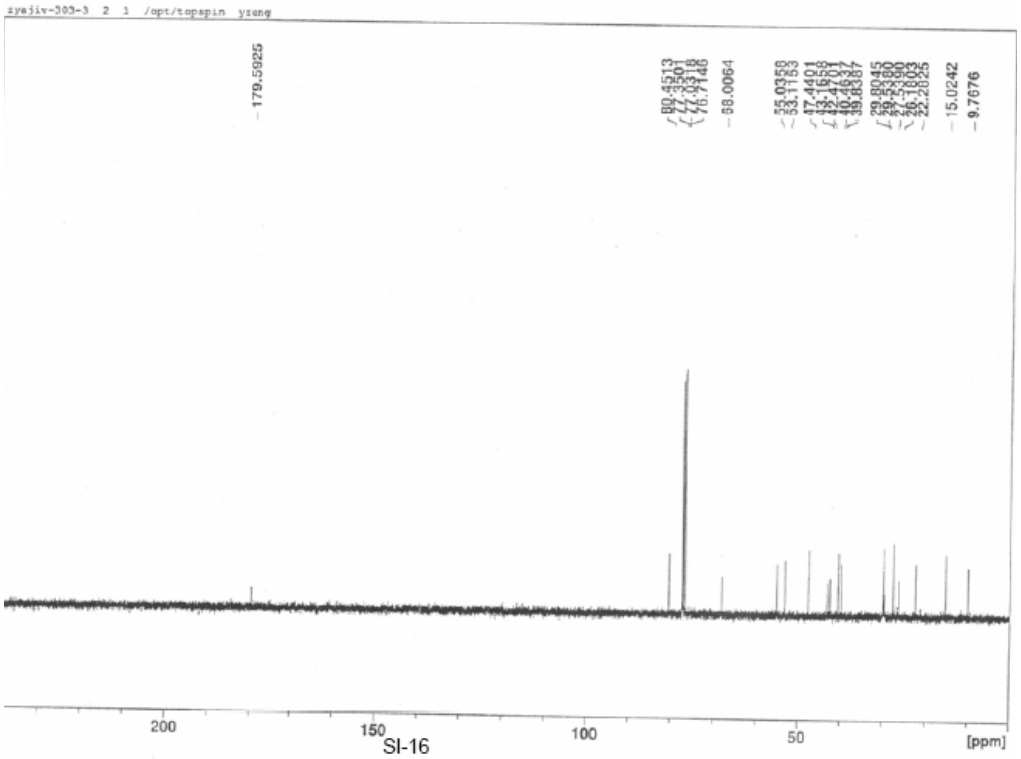

178.6831
171.1381
79.1766
77.3573
77.0369
76.7218
60.5399
46.8596
45.6938
44.2633
43.2683
35.7565
33.0440
27.8326
23.3950
22.8183
22.5398
15.4492
10.1608
200
150
100
50
[ppm]

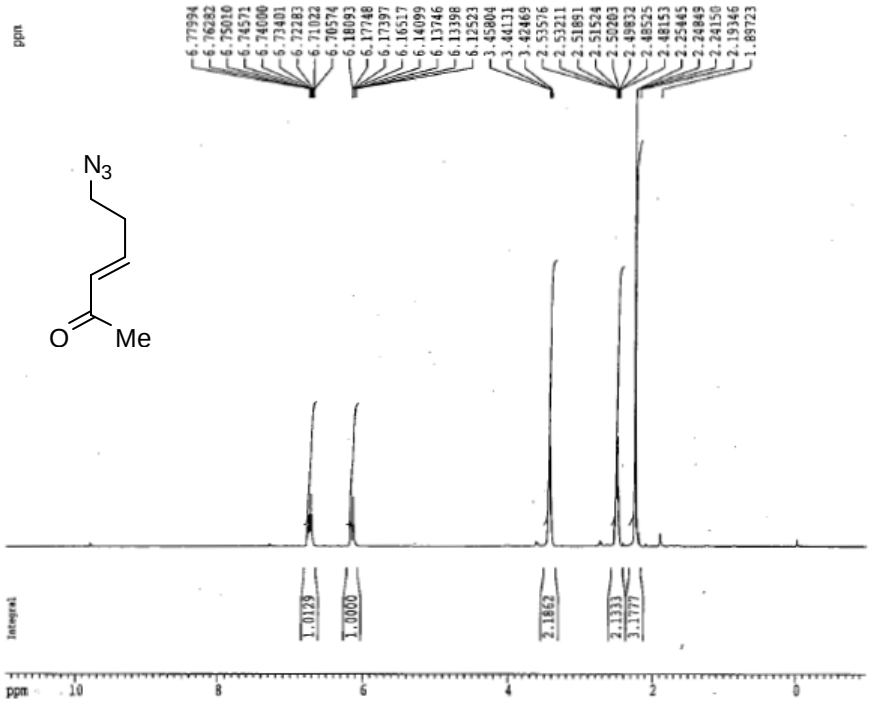

zyajiv-304-1 1 1 /opt/topspin yzeng
Me
O
N
S
1.0000
1.0924
2.0261
1.0063
1.0384
1.0097
3.1319
2.2621
7.8902
3.9043
3.0996
10
8
6
4
2
0
[ppm]


zyajiv-304-1 2 1 /opt/topspin yzeng
199.3098
178.3747
65.7710
55.1460
15.5800
10.1167
200
100
50
[ppm]

SI-15


zyajiv-303-3 1 1 /opt/topspin yzeng
Me
O
O
N
1
1.0000
0.9583
0.9480
1.1109
2.3342
2.1094
2.2874
7.7695
3.2410
3.8920
8.1334
10
8
6
4
2
0
[ppm]


zyajiv-303-3 2 1 /opt/topspin yzeng
179.5925
80.4513
77.3501
77.0318
76.7146
68.0064
55.0358
53.1153
47.4401
43.1658
42.4701
40.4637
39.8387
29.8045
29.5380
26.7803
25.2023
15.0242
9.7676
200
150
100
50
[ppm]



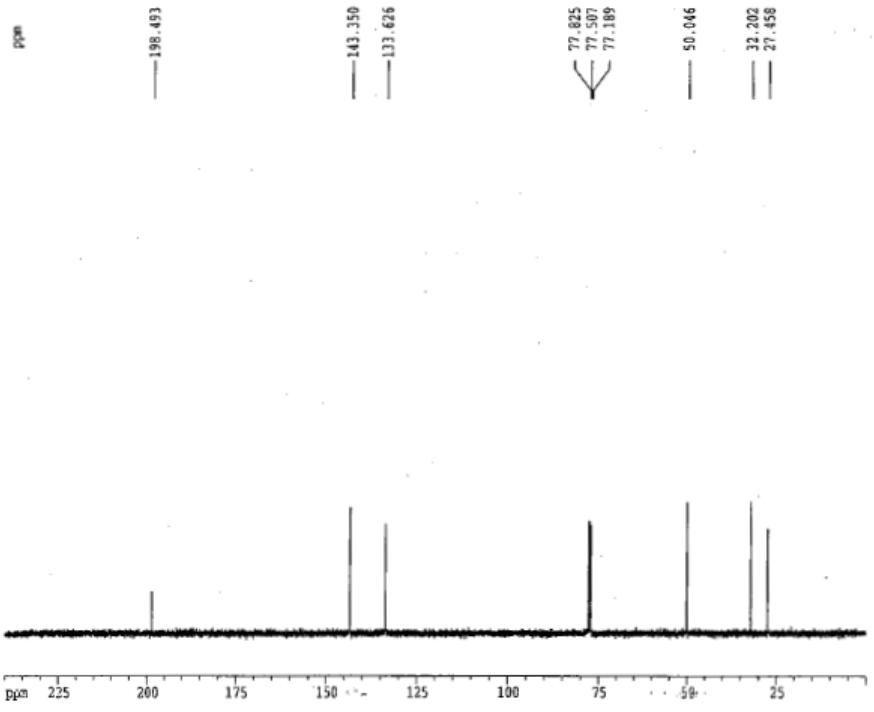
10

F2 - Acquisition Parameters
Date_ 20040530
Time 18.35
INSTRUM drx400
PROBHD 5 mm Multinucl
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 64
DW 104.400 usec
DE 5.50 usec
TE 679.6 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.70 usec
PL1 -6.00 dB
SFO1 600.1320007 MHz

F2 - Processing parameters
SI 32768
SF 600.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 10.985 ppm
F1 6595.28 Hz
F2P -0.985 ppm
F2 -593.99 Hz
PPMCM 0.59846 ppm/cm
HZCM 359.46362 Hz/cm



Current Data Parameters
NAME II-242
EXPNO 2
PROCNO 1

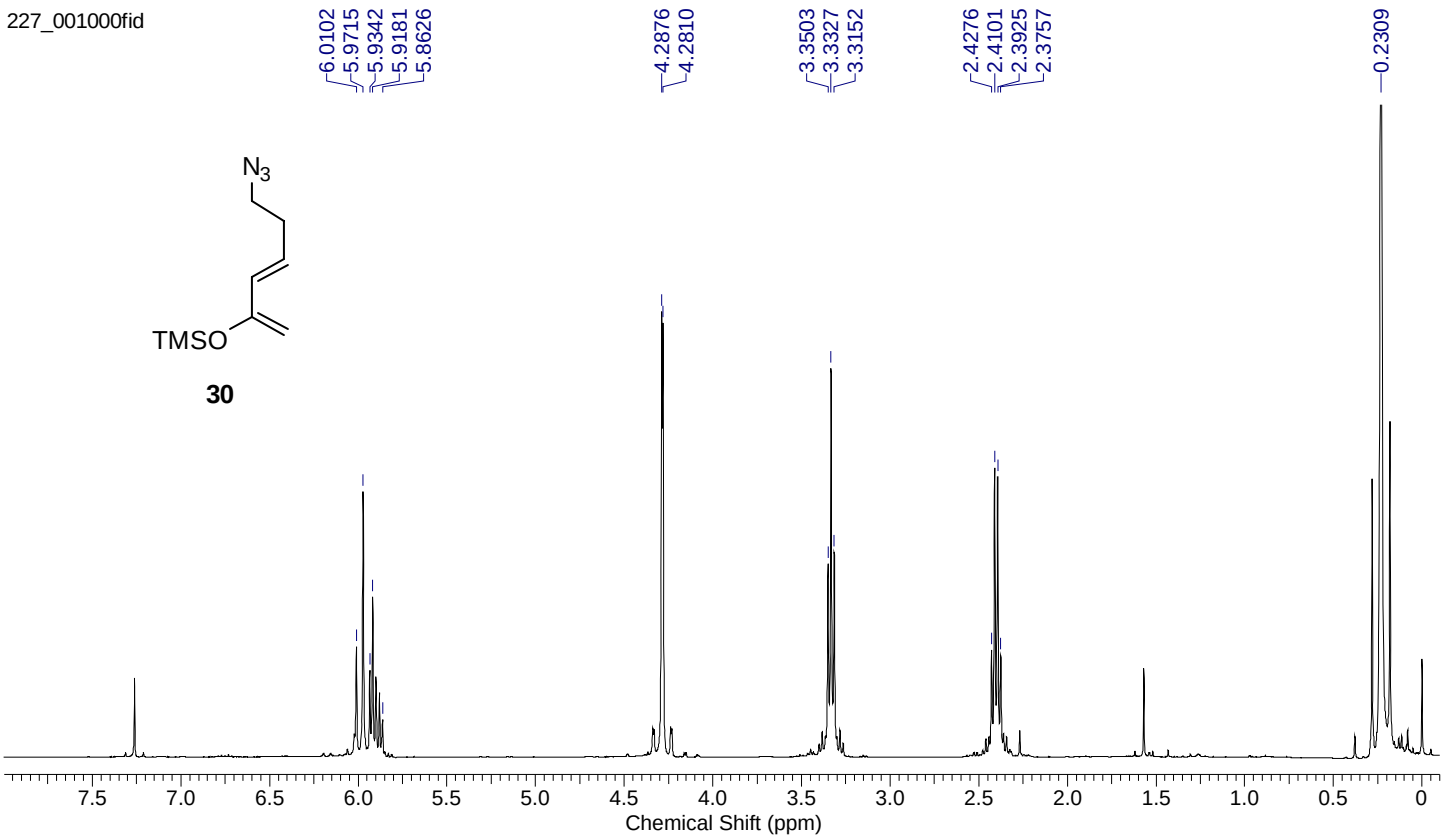
F2 - Acquisition Parameters
Date_ 20040530
Time 18.58
INSTRUM drx400
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 95
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 32768
DW 20.700 usec
DE 5.50 usec
TE 679.6 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 12.30 usec
PL1 2.00 dB
SFO1 150.6248025 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.00 dB
PL13 18.00 dB
SFO2 600.1316005 MHz

F2 - Processing parameters
SI 65536
SF 150.6127250 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 0.00 cm
F1P 240.037 ppm
F1 36150.82 Hz
F2P -0.037 ppm
F2 -5.77 Hz
PPMCM 12.08374 ppm/cm
HZCM 1819.38960 Hz/cm


227_001000fid
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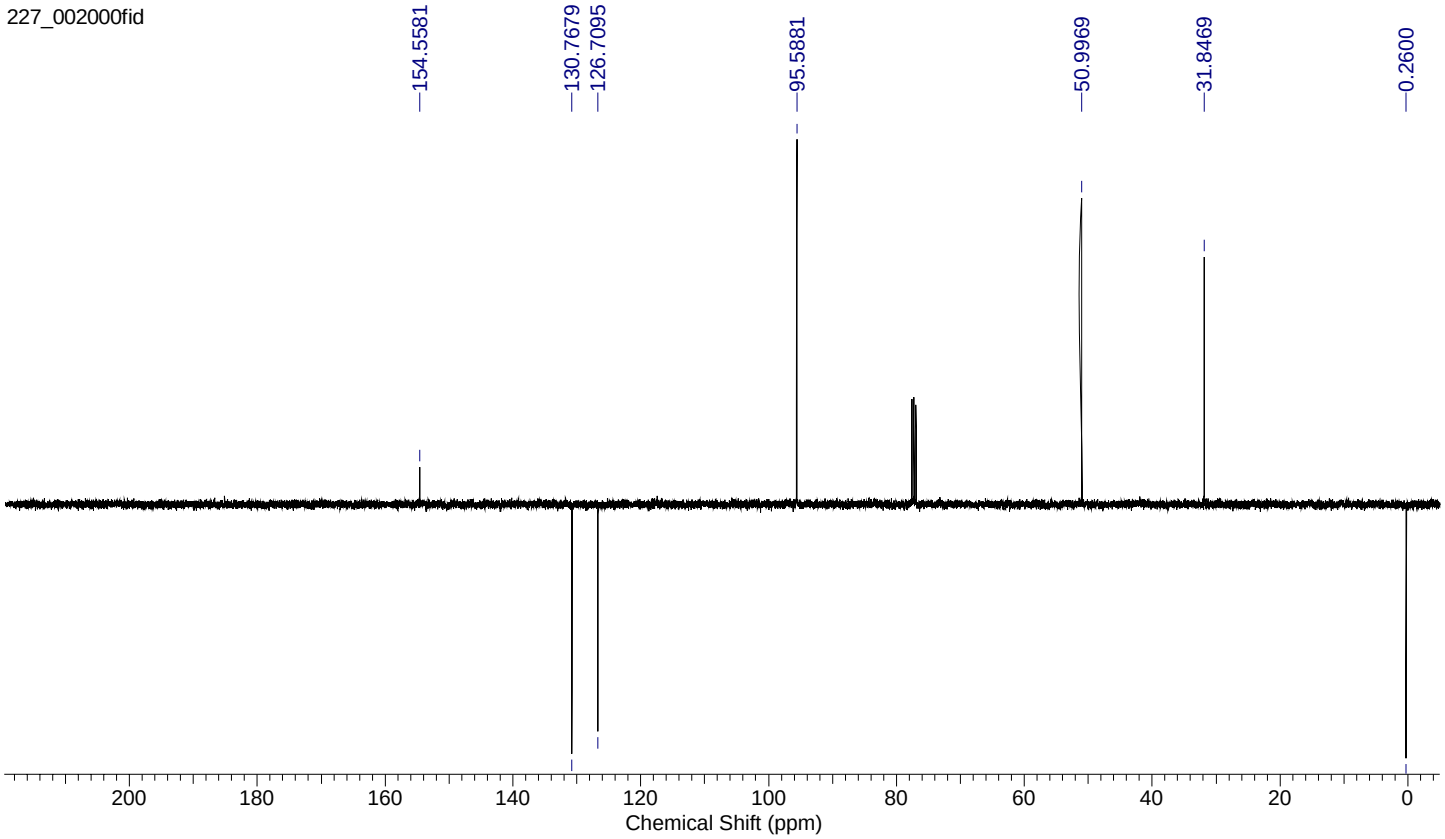
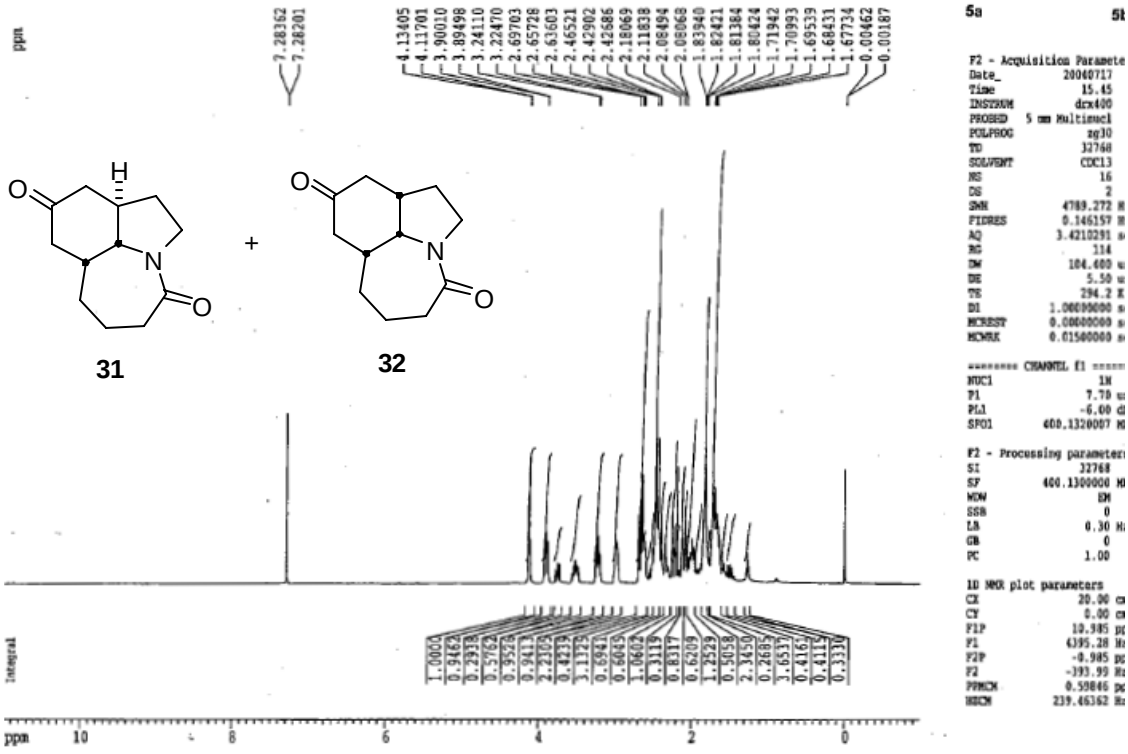
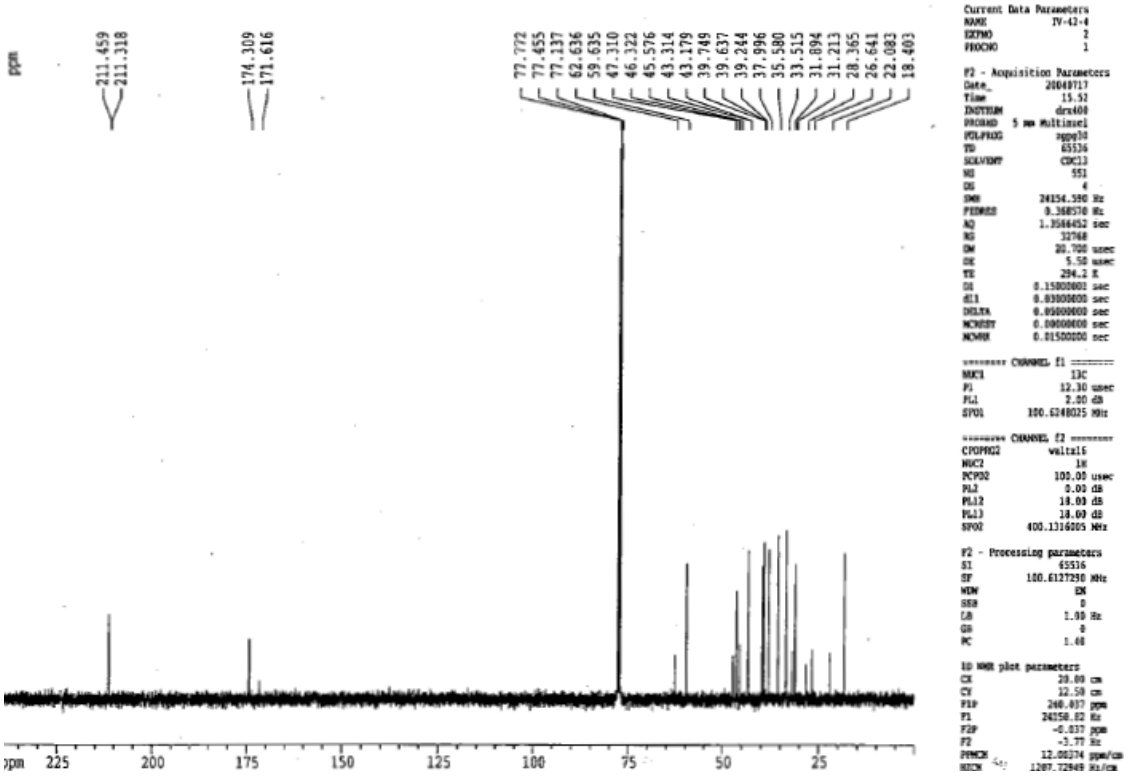
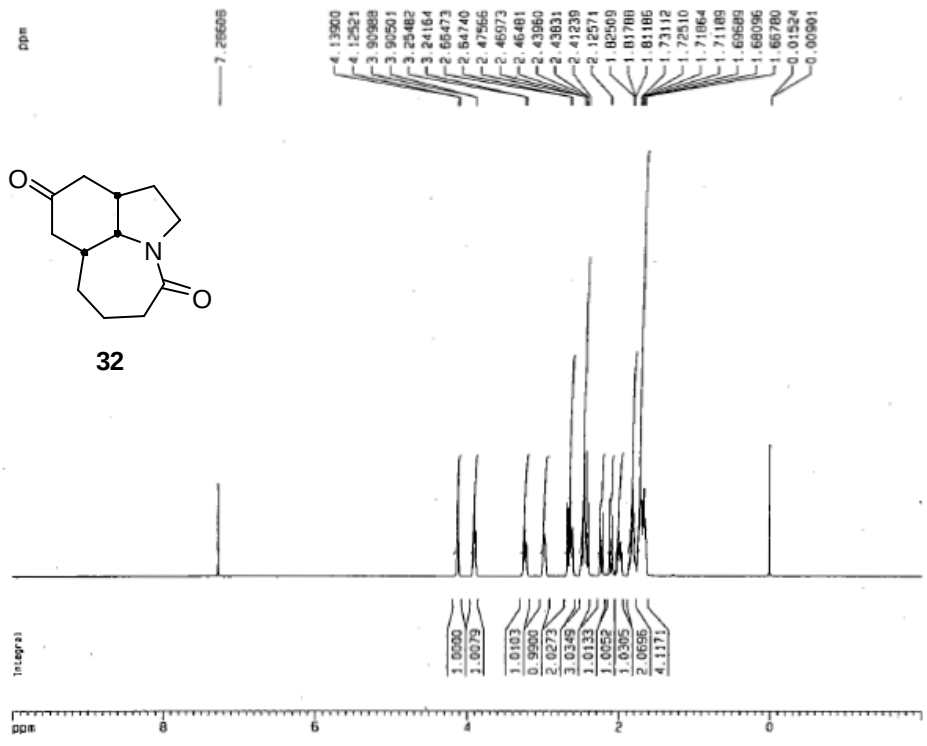
5.9715
5.9342
5.9181
5.8626
4.2876
4.2810
3.3503
3.3327
3.3152
2.4276
2.4101
2.3925
2.3757
0.2309
N3
TMSO
30
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


227_002000fid
154.5581
130.7679
126.7095
95.5881
50.9969
31.8469
0.2600
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


31
32
5a
ppm
Integral

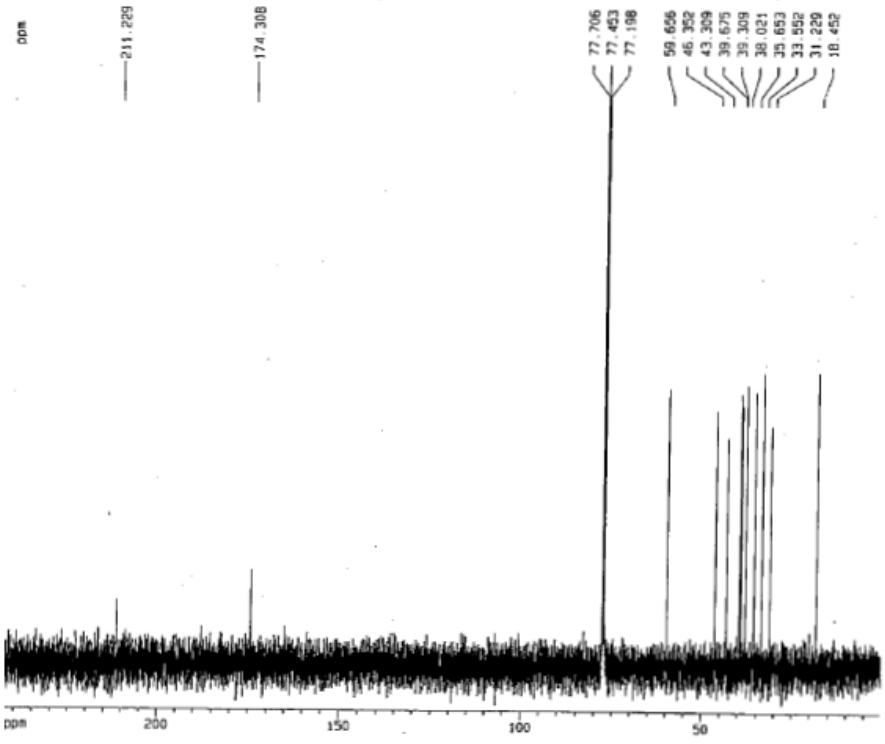

ppm



32

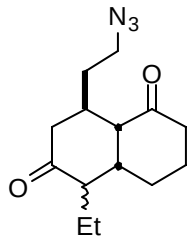
5a

F2 - Acquisition Parameters
Date_ 20040726
Time 15.16
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 9000.615 Hz
FIDRES 0.183795 Hz
AQ 2.7264305 sec
RG 287.5
DW 83.200 usec
DE 6.00 usec
TE 297.4 K
D1 0.03000000 sec
HDNEST 0.00200000 sec
HDWIN 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.70 usec
PL1 -4.60 dB
SFO1 500.1320005 MHz
F1 - Acquisition parameters
NDO 2
TD 256
SFO1 500.1325 MHz
FIDRES 23.475060 Hz
SW 12.016 ppm
FnMODE undefined
F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 QF
SF 500.1300000 MHz
WDW QSINE
SSB 0
LB 0.30 Hz
GB 0
1D NMR plot parameters
CX 20.00 cm
CY 0.00 cm
F1P 10.000 ppm
F1 5005.33 Hz
F2P -2.000 ppm
F2 -1004.20 Hz
PPMCM 0.58001 ppm/cm
HZCM 300.48877 Hz/cm



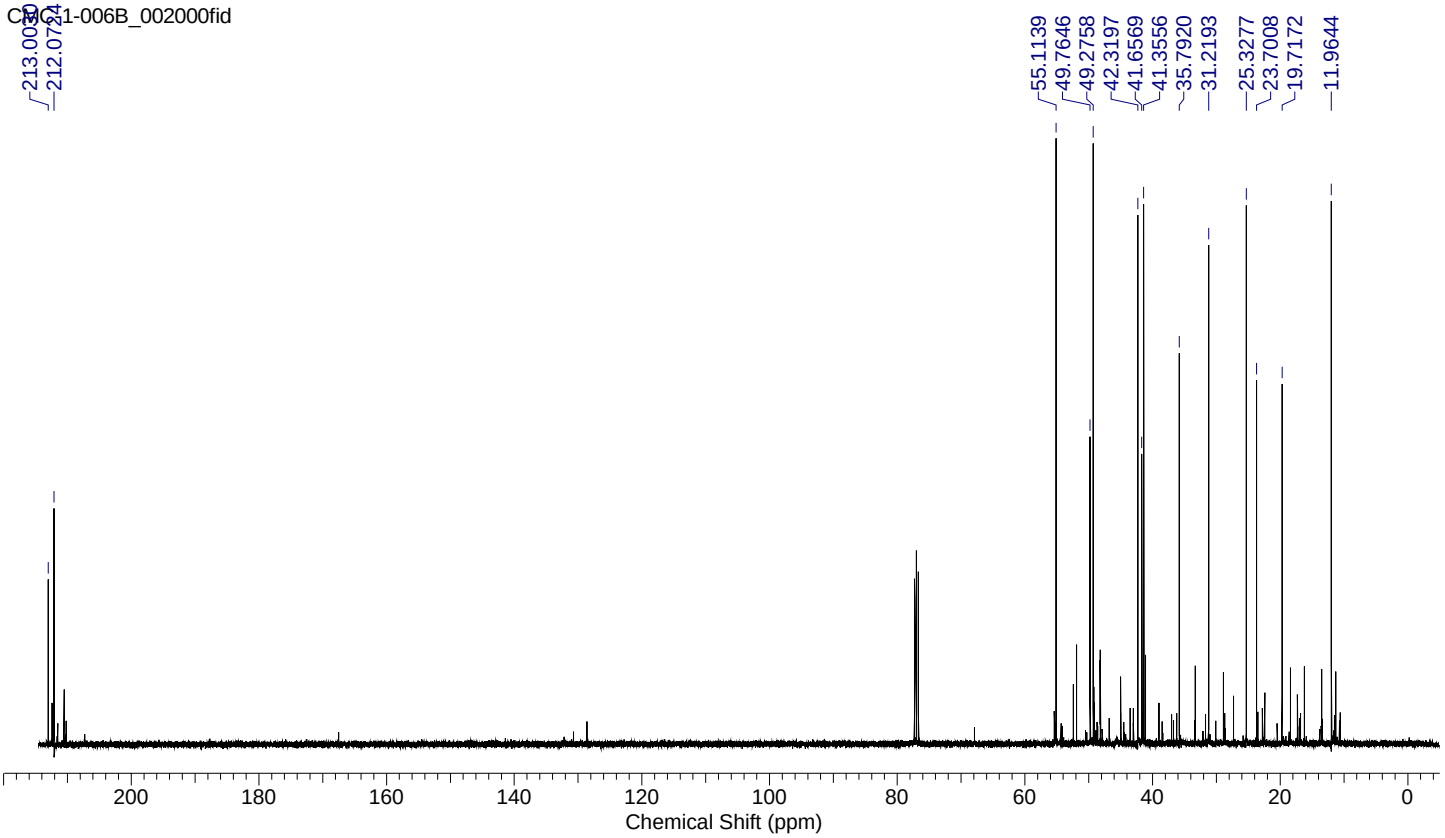
Current Data Parameters
NAME
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040726
Time 15.16
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 31446.541 Hz
FIDRES 0.479838 Hz
AQ 1.0429883 sec
RG 256
DW 15.900 usec
DE 6.00 usec
TE 297.0 K
D1 0.05000001 sec
D11 0.03000000 sec
DELTA 0.05000000 sec
HDNEST 0.00000000 sec
HDWIN 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 6.50 usec
PL1 5.00 dB
SFO1 125.7739087 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 20.00 dB
SFO2 500.1325000 MHz
F1 - Acquisition parameters
NDO 2
TD 256
SFO1 500.1325 MHz
FIDRES 23.475060 Hz
SW 12.016 ppm
FnMODE undefined
F2 - Processing parameters
SI 65536
SF 125.7577361 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
F1 - Processing parameters
SI 1024
MC2 QF
SF 500.1300000 MHz
WDW no
SSB 0
LB 0.30 Hz
GB 0
1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 242.567 ppm
F1 30496.41 Hz
F2P -2.538 ppm
F2 -648.51 Hz
PPMCM 12.50282 ppm/cm

CMC-1-006B_001000fid

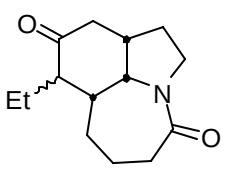


33

CMC-1-006B_002000fid

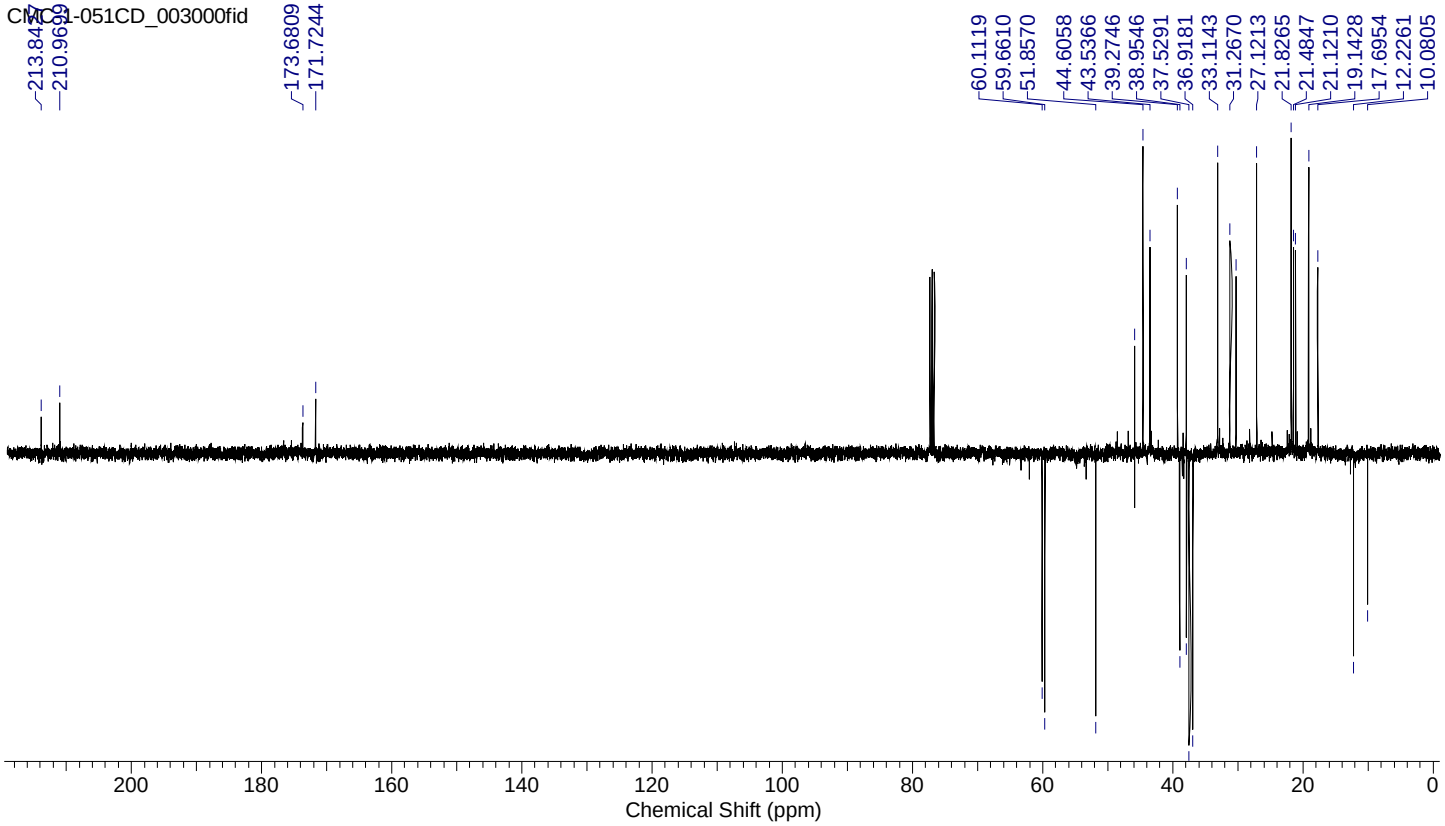


CMC-1-051CD_002000fid

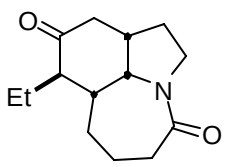


26a,b

CMC-1-051CD_003000fid

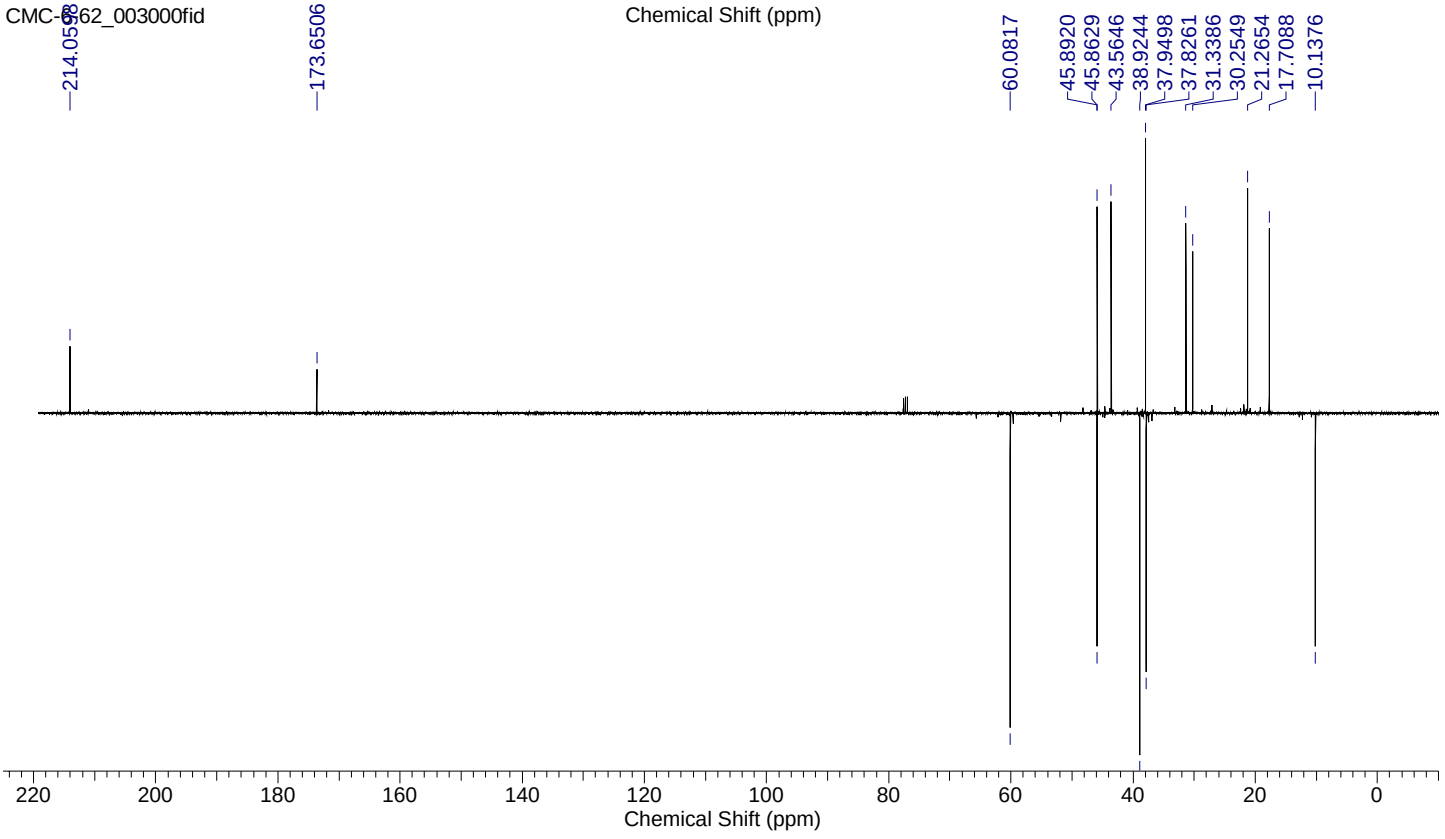


CMC-6-62_001000fid

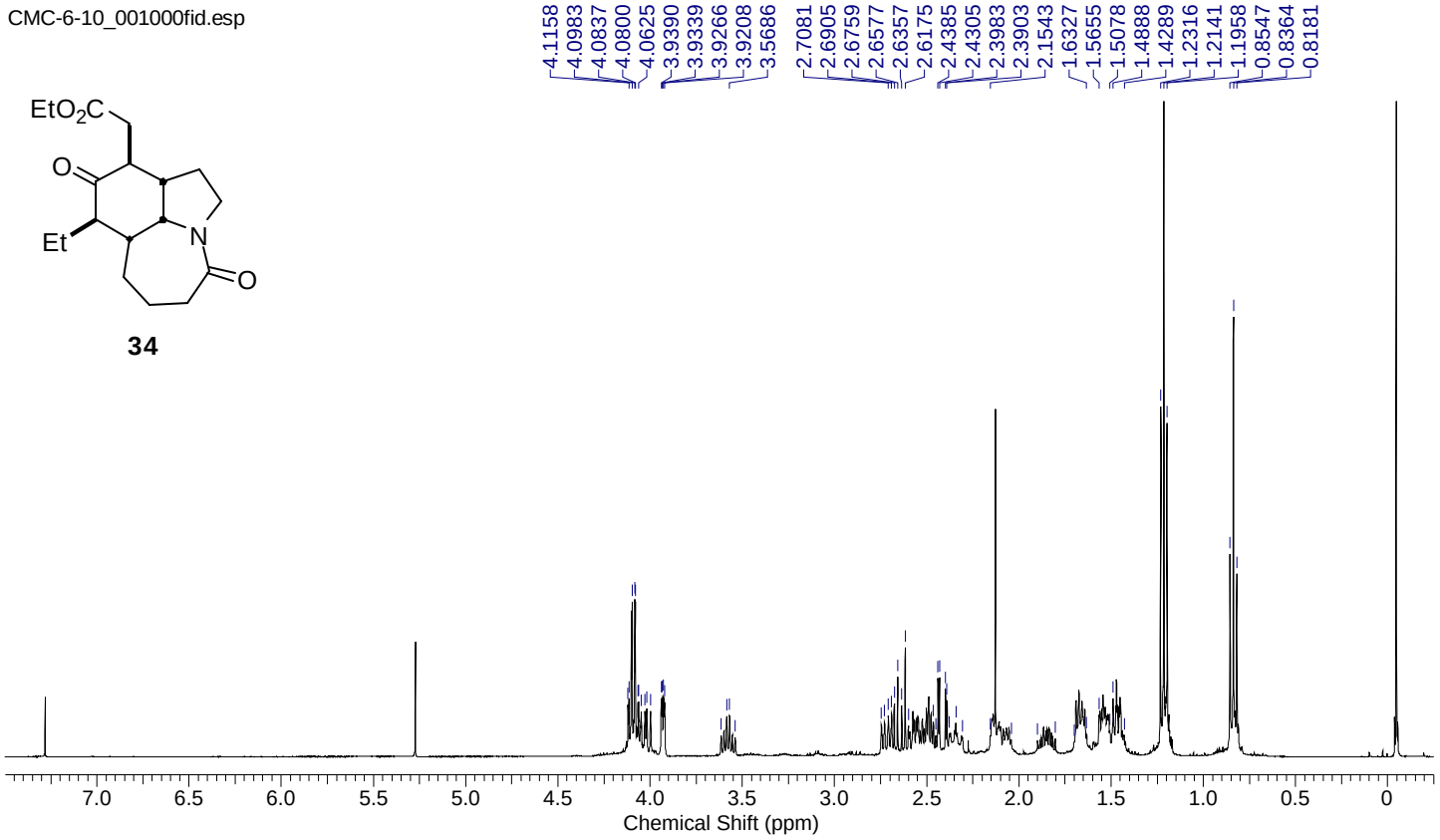


26b

CMC-6-62_003000fid

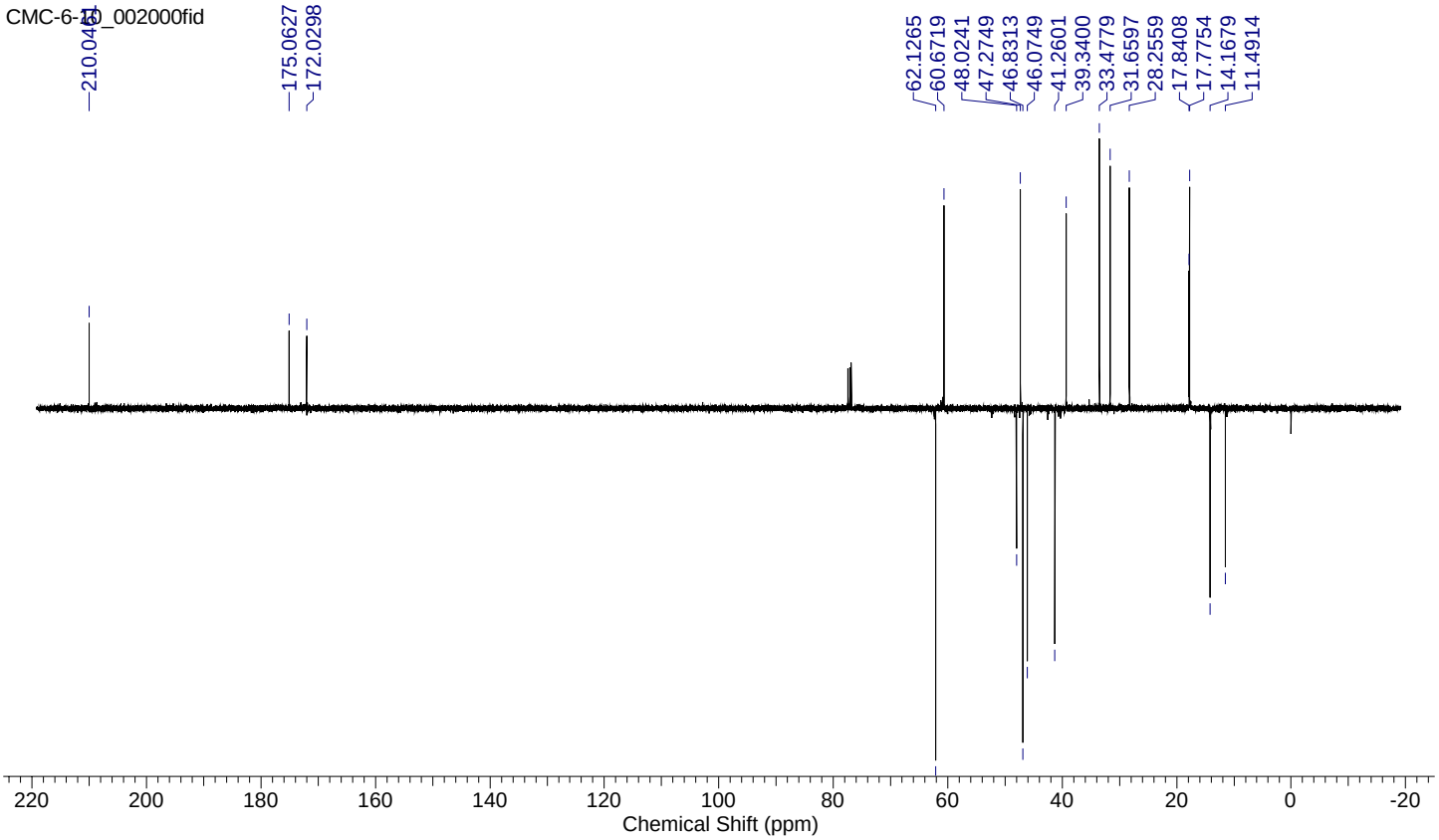


CMC-6-10_001000fid.esp

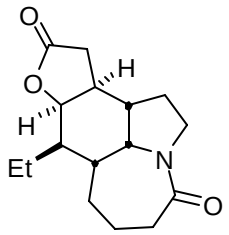


34

CMC-6-10_002000fid

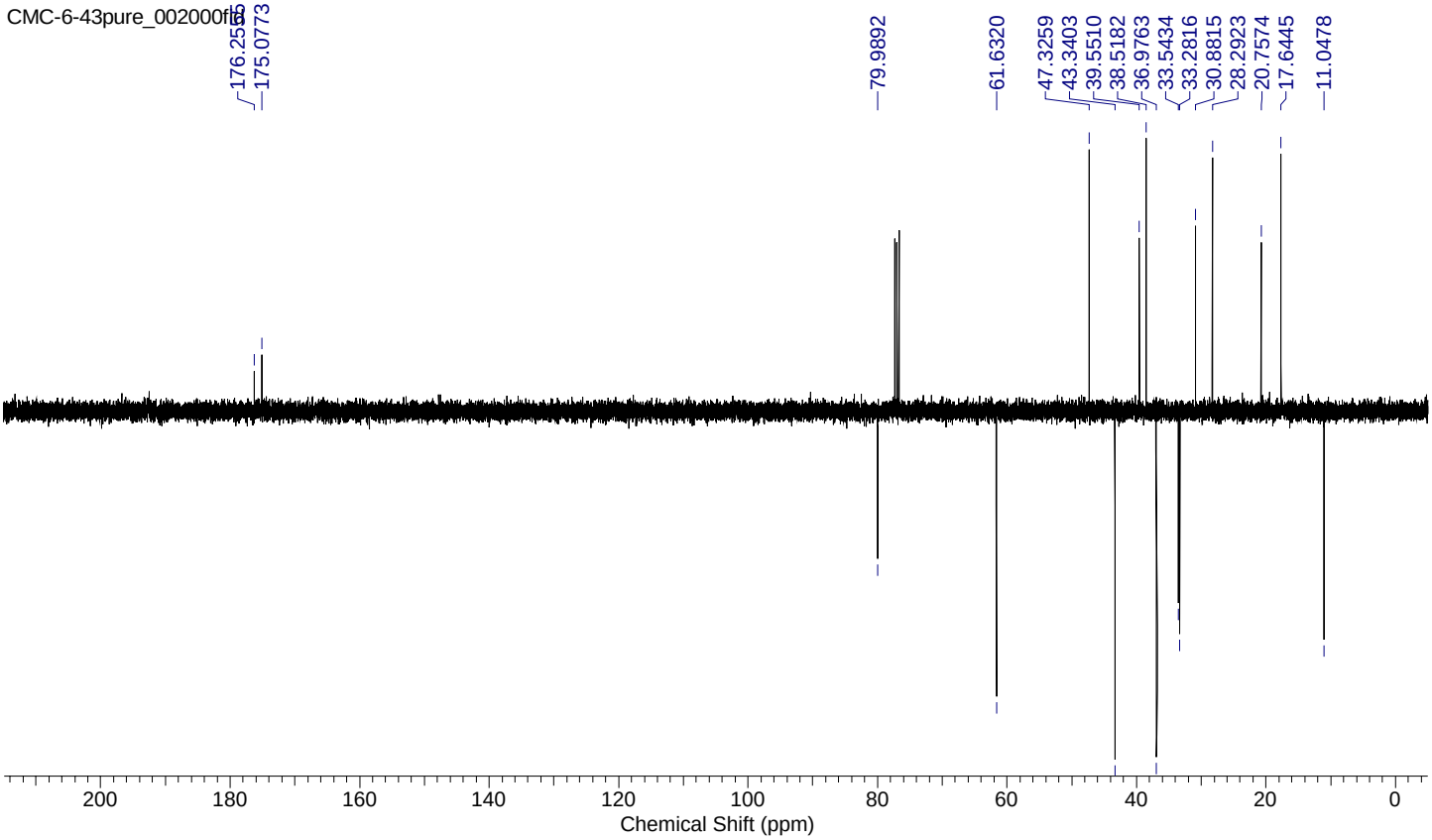


CMC-6-43pure_001000fid.esp

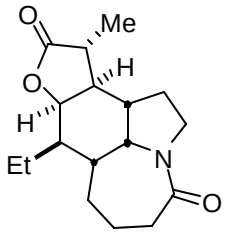


35a

CMC-6-43pure_002000fid

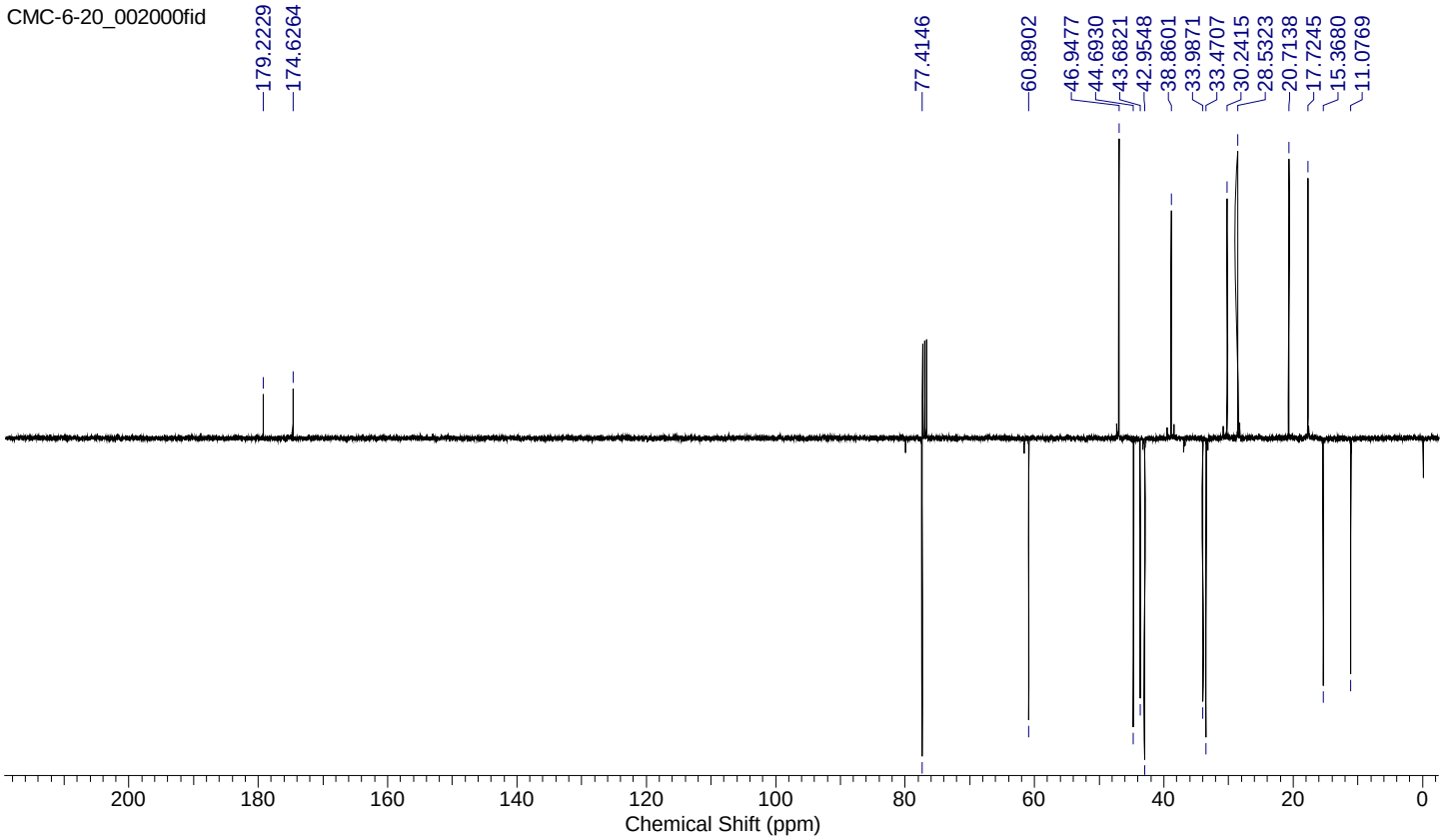


CMC-6-20_001000fid

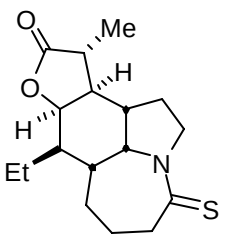


37

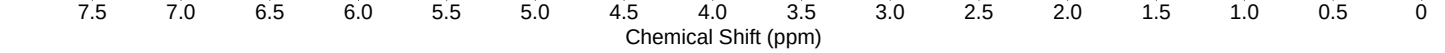
CMC-6-20_002000fid



CMC-2-22_001000fid



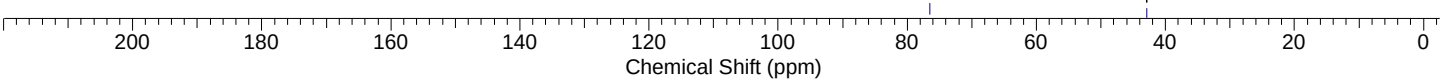
4.8756 4.8683 4.8581 4.8508 4.2152 4.2035 4.1882 4.1663 4.1320 3.8967 3.8785 3.8609 3.8434 3.8237 3.4350 3.3985 2.8221 2.5701 2.4627 2.2092 2.1953 2.1748 2.1368 2.1186 2.1047 2.0857 1.8855 1.8738 1.7986 1.4983 1.3800 1.3617 1.0191 1.0008 0.9833



Chemical Shift (ppm)

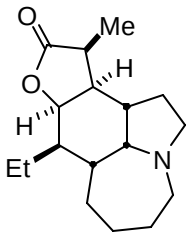
CMC-2-22_002000fid

202.3990 178.8011 76.4836 63.9594 54.6062 46.8822 42.9257 41.7911 36.4308 33.7616 29.1650 28.2850 20.8010 19.7828 15.6590 11.1206



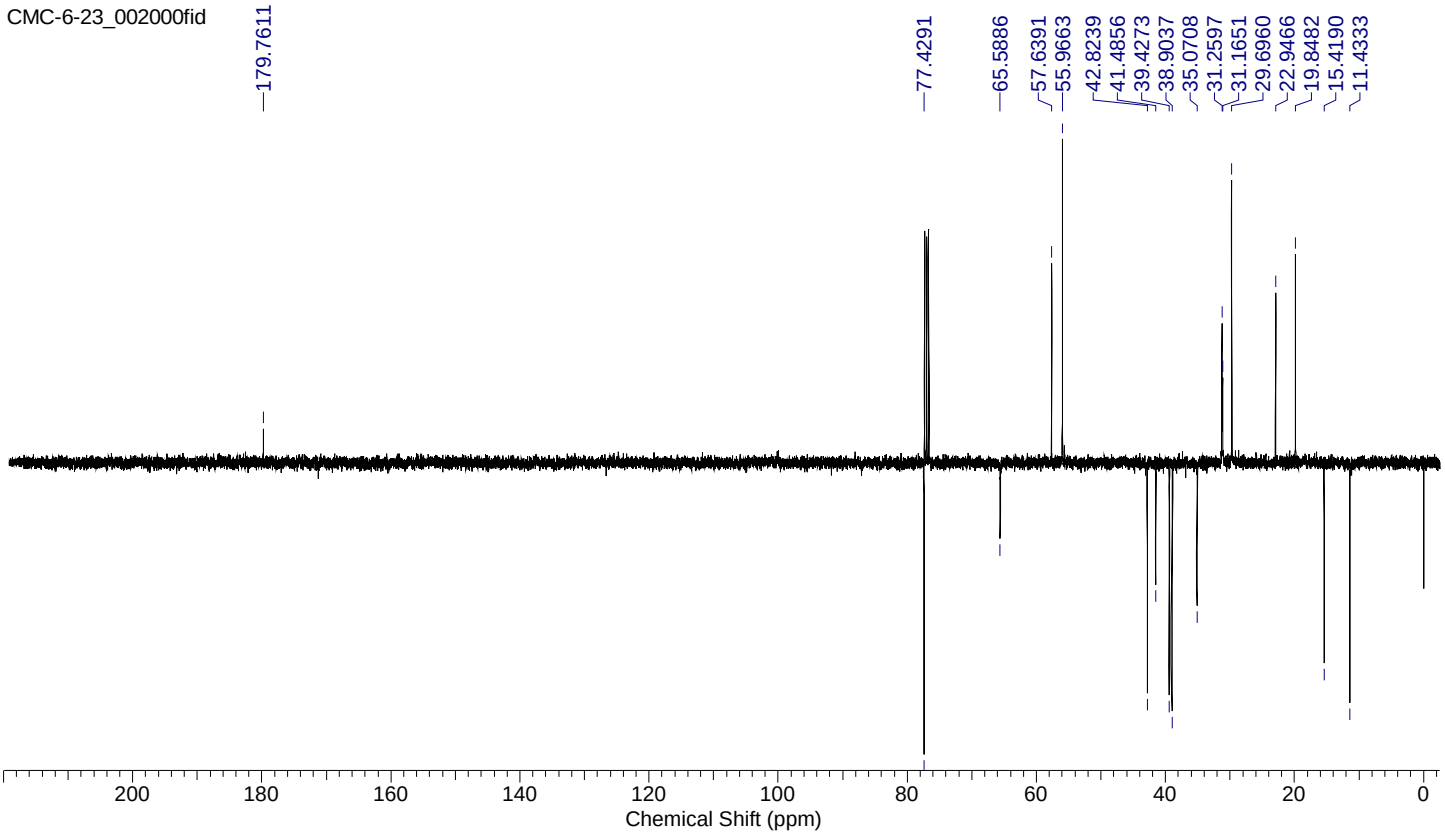
Chemical Shift (ppm)

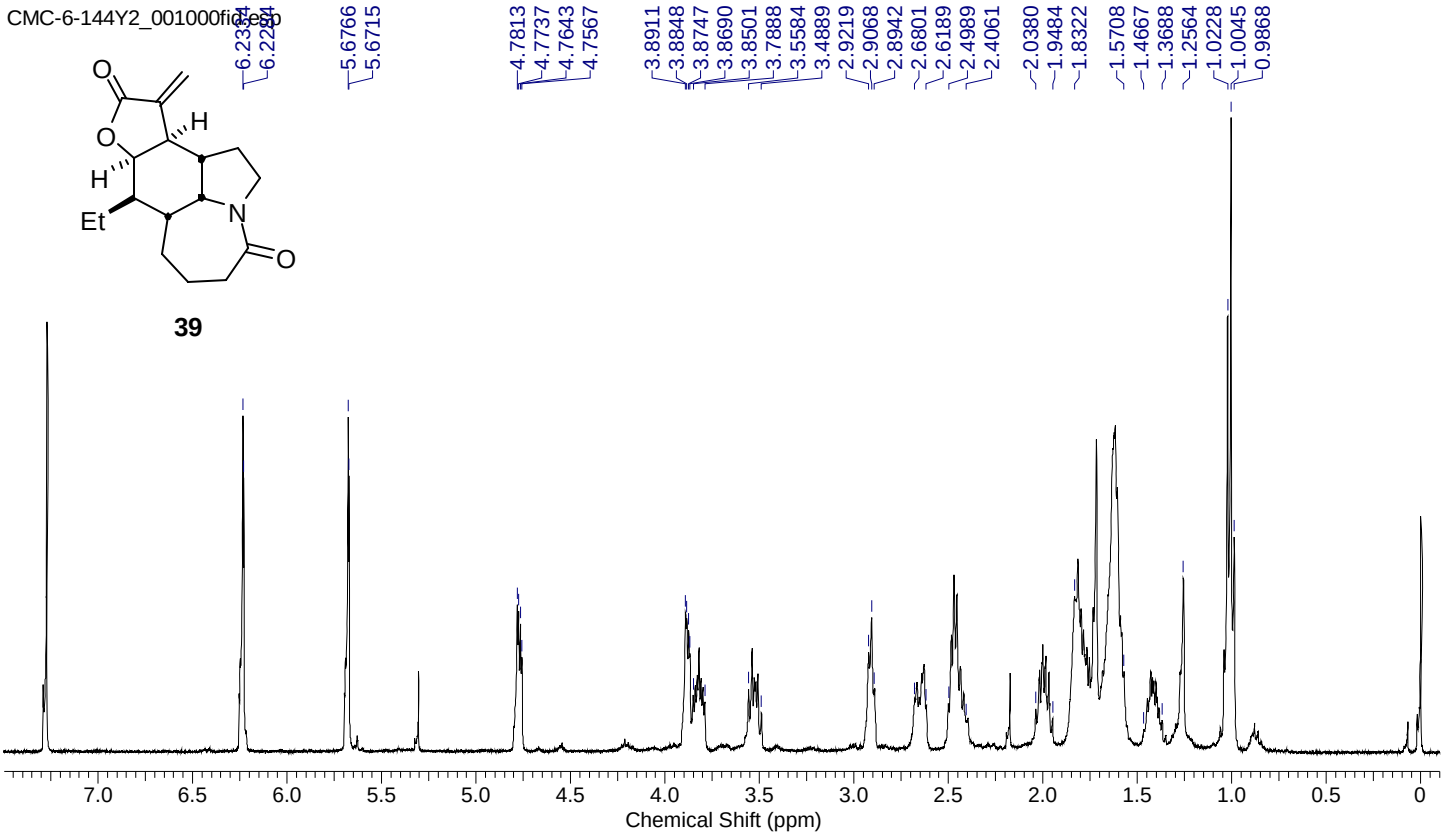
CMC-6-23_001000fid



13-epineostenine **38**

CMC-6-23_002000fid




CMC-6-144Y2_001000fid.esp
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6.2281
5.6766
5.6715
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4.7643
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3.8848
3.8747
3.8690
3.8501
3.7888
3.5584
3.4889
2.9219
2.9068
2.8942
2.6801
2.6189
2.4989
2.4061
2.0380
1.9484
1.8322
1.5708
1.4667
1.3688
1.2564
1.0228
1.0045
0.9868
O
O
H
H
Et
N
O
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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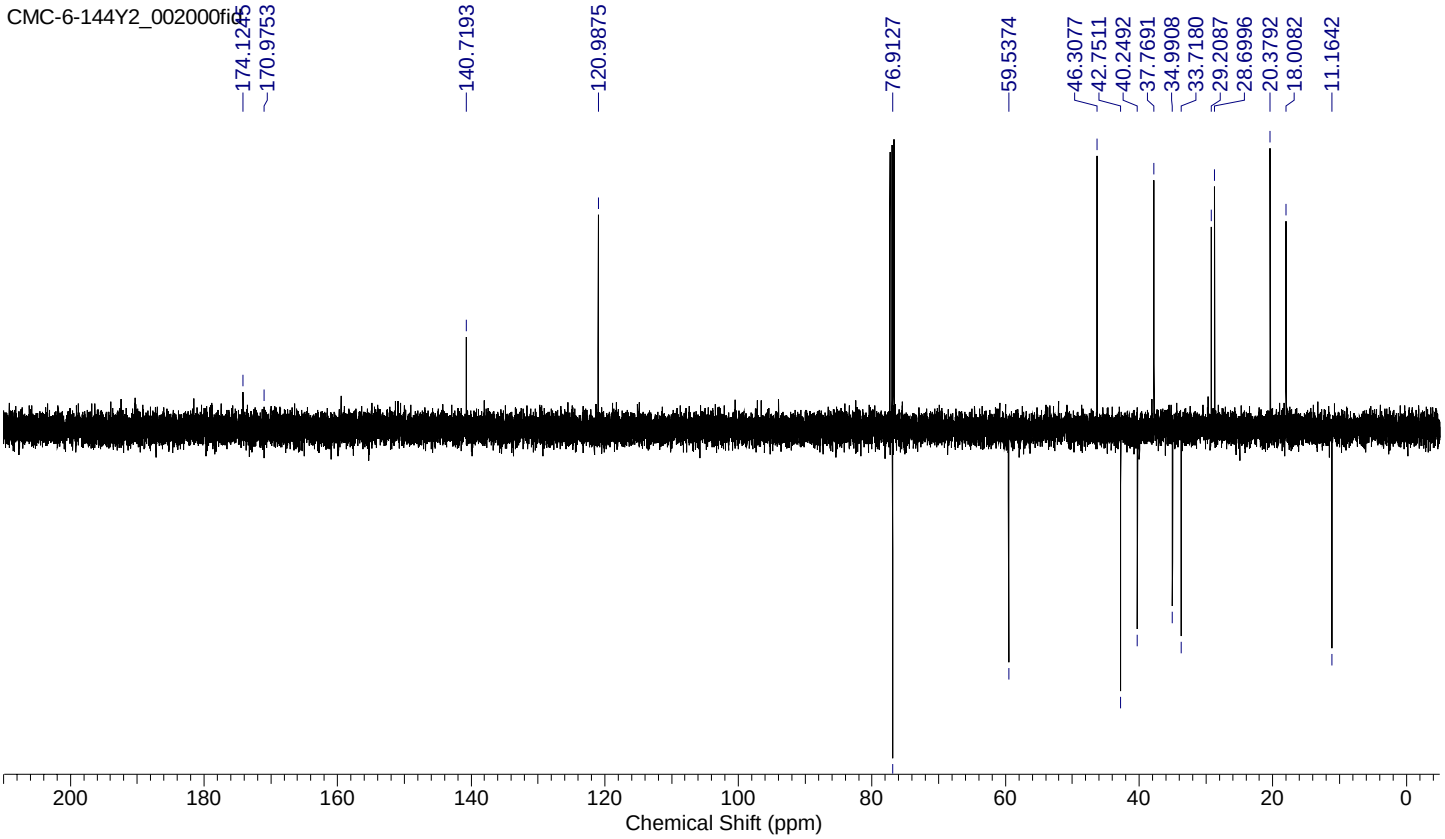
0
Chemical Shift (ppm)

39


CMC-6-144Y2_002000fid.esp
174.1245
170.9753
140.7193
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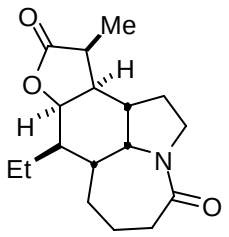
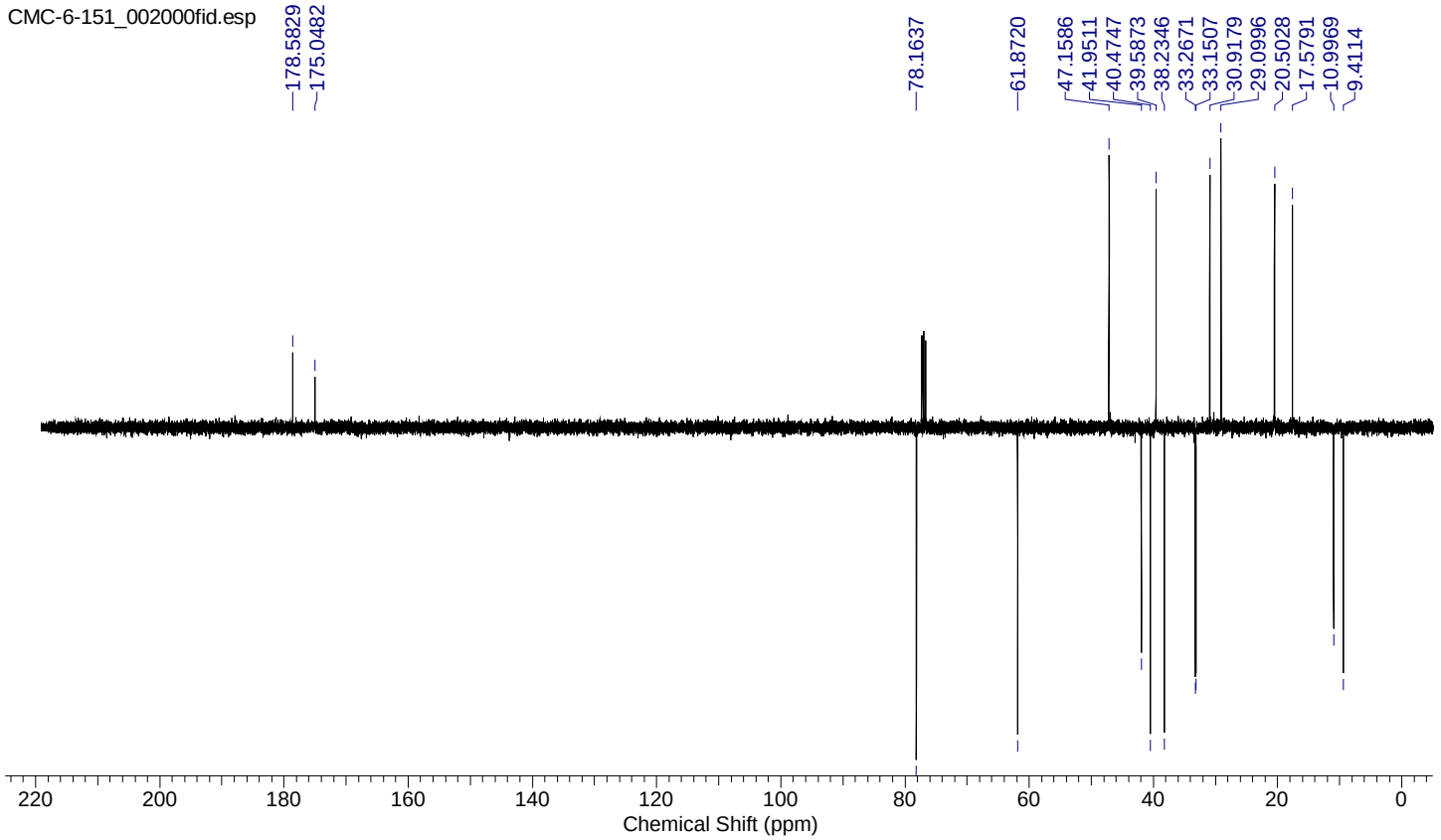
76.9127
59.5374
46.3077
42.7511
40.2492
37.7691
34.9908
33.7180
29.2087
28.6996
20.3792
18.0082
11.1642
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

CMC-6-151_001000fid.esp

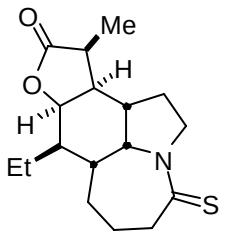


40

CMC-6-151_002000fid.esp



CMC-6-94_001000fid.esp



4.6052
4.5995
4.5938
4.5887
4.3987
4.3791
4.3646
4.3444
4.0079
3.9946
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2.9958
2.9781
2.9605
2.7010
2.6694
2.6391
2.3266
2.2546
2.1157
1.9945
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1.4862
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1.2987
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1.2602
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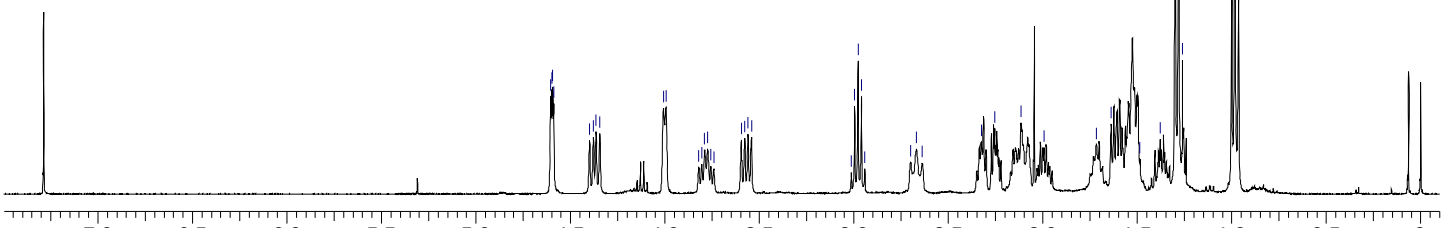
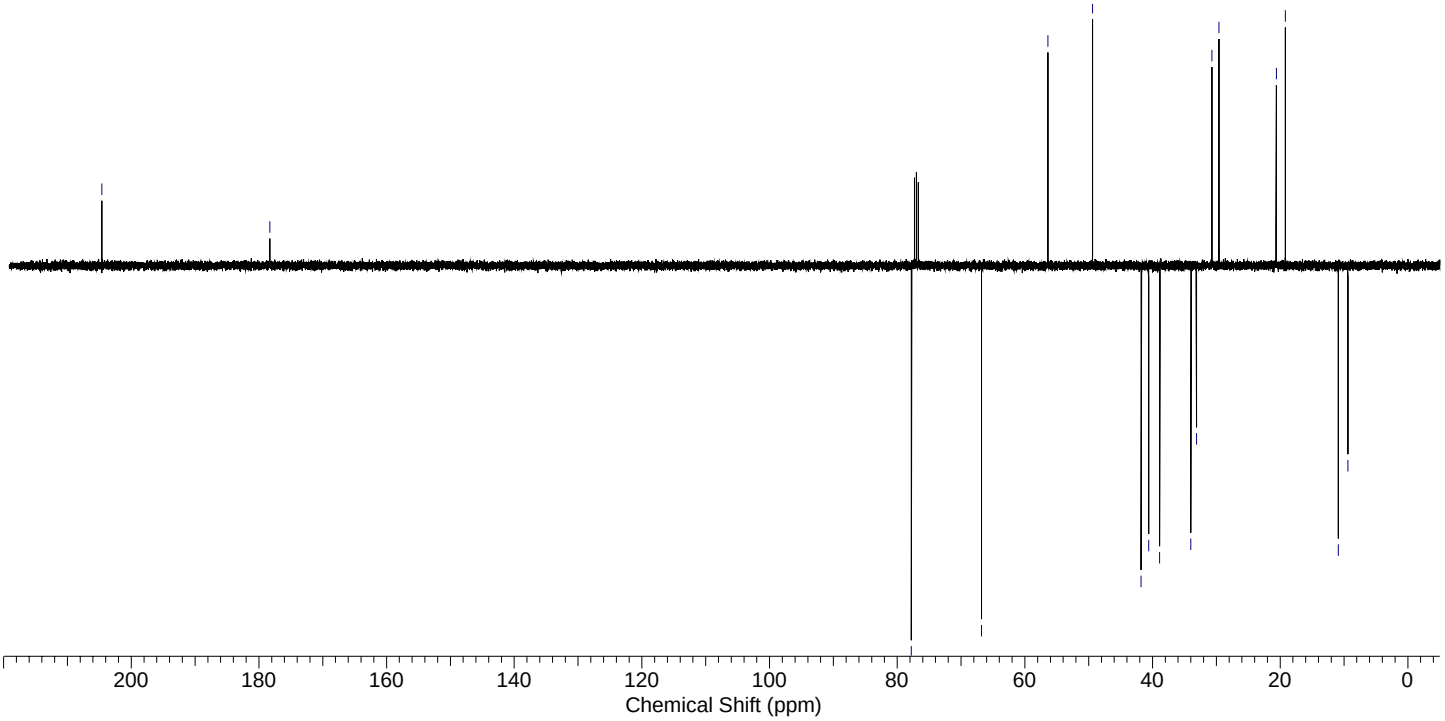
0.9824
0.9641

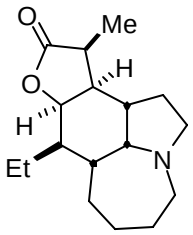


CMC-6-94_002000fid

204.5768
178.3138
77.7709
66.7959
56.3954
49.4133
41.7620
40.6274
38.8528
33.9580
33.1361
30.6997
29.5723
20.6410
19.2082
10.8806
9.4260



CMC-6-95_001000fid.esp



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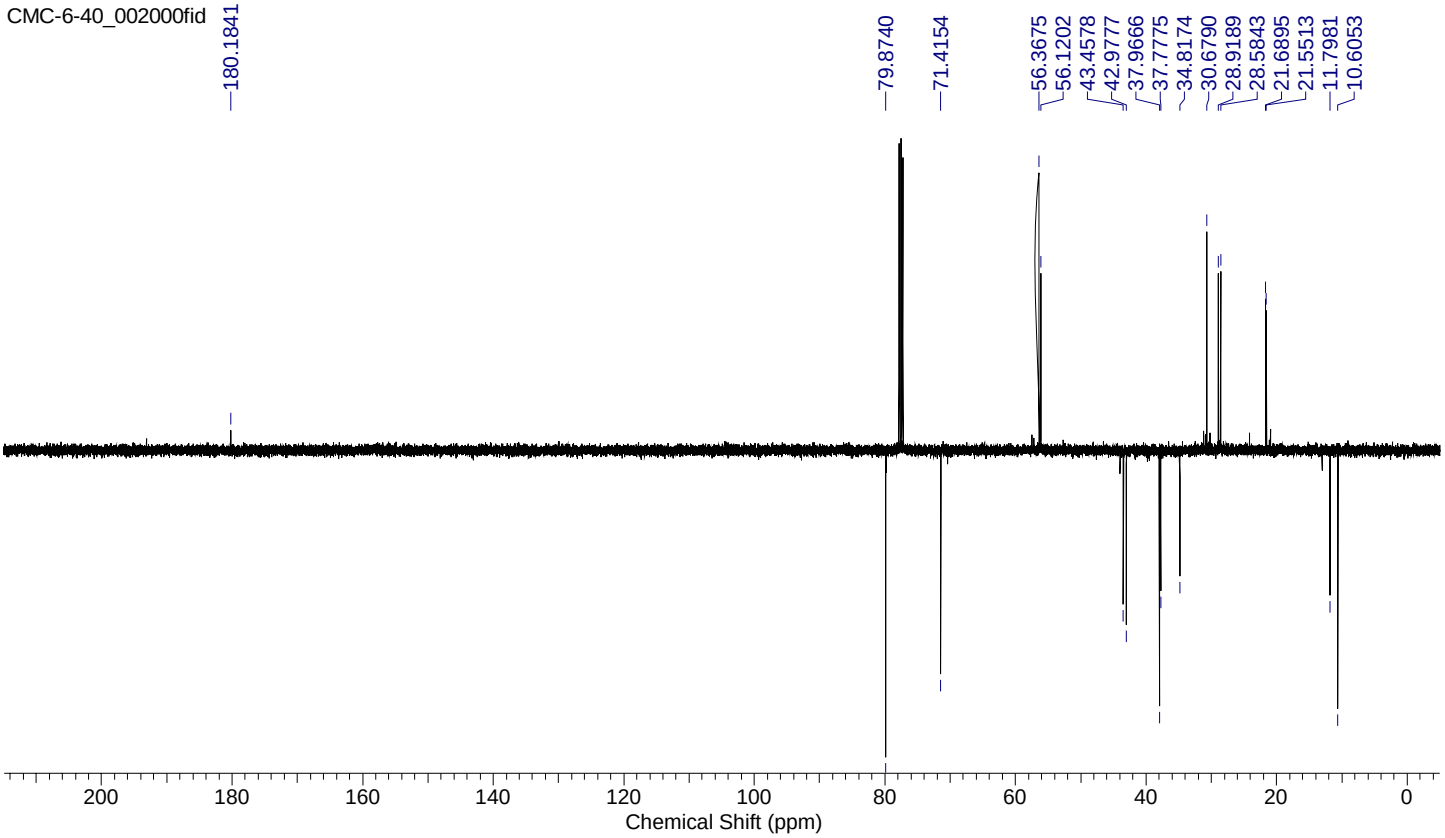
CMC-6-40_002000fid



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