SUPPORTING INFORMATION

FOR

Coupling of Alkenes and Alkynes: Synthesis of the C1-C11 and C18-C28 Fragments of Miyakolide

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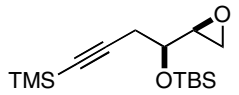
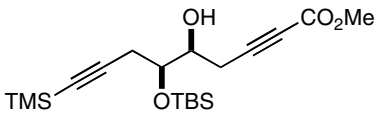
Experimental Procedures:

Solvents and reagents were reagent-grade and used without purification unless otherwise noted. Dichloromethane (CH_2Cl_2), triethylamine (Et_3N), and diisopropylamine were distilled from calcium hydride and stored under nitrogen. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were passed through a column of neutral alumina and stored under argon. Methanol (MeOH) and dimethylformamide (DMF) were passed through a column of molecular sieves and stored under argon. Toluene was passed through a column of Q5 reactant and stored under argon. All reactions were done in flame-dried glassware under nitrogen unless otherwise indicated. ^1H nuclear magnetic resonance (NMR) spectra were obtained at either 600, 500 or 400 MHz as solutions in $CDCl_3$. ^{13}C NMR were obtained at either 125, 100 or 75 MHz as solutions in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, d), and referenced from the solvent. Coupling constants are reported in Hertz (Hz). Spectral splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multplet; comp, complex; and br, broad. Infrared (IR) spectra were obtained using a Perkin-Elmer FTIR 1600 spectrophotometer using sodium chloride plates as indicated, and reported as wave numbers. Low resolution chemical ionization mass spectra were obtained with a Finnigan TSQ-70 instrument. High resolution measurements were made with a VG Analytical ZAB2-E instrument. Analytical thin layer chromatography was performed using Merck 250 micron 60F-254 silica gel plates. The plates were visualized with UV light, ninhydrin, phosphomolybdic acid, *p*-anisaldehyde, and potassium permanganate. Flash column chromatography was performed according to Still's procedure (Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923) using ICN Silitech 32-63 D 60A silica gel.



11

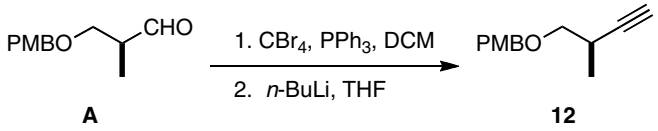
(*S*)-2-((*S*)-1-(*tert*-Butyldimethylsilyloxy)-4-(trimethylsilyl)but-3-ynyl)oxirane (11). ^{n}BuLi (2.5 M in hexanes, 0.46 mL, 1.16 mmol) was added dropwise to a stirred solution of trimethylsilylacetylene (125 mg, 1.27 mmol, 0.18 mL) in THF (6 mL) at –78 ˚C and stirred for 30 min. BF_3•OEt_2 (181 mg, 1.27 mmol, 0.16 mL) followed by a solution of **5** (100 mg, 1.16 mmol) in THF (6 mL) was added rapidly and the reaction stirred for 5 h. The mixture was diluted with saturated aqueous NH_4Cl (12 mL) and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 12 mL), and the combined organic fractions were dried (Na_2SO_4) and concentrated under reduced pressure. The crude residue was taken up in DMF (10 mL) and imidazole (291 mg, 4.26 mmol) then TBSCl (729 mg, 4.26 mmol) were added sequentially. The resulting mixture was stirred at room temperature for 12 h then diluted with saturated aqueous NH_4Cl (10 mL) and Et_2O (10 mL). The layers were separated and the aqueous phase extracted with Et_2O (10 mL). The combined organic fractions were washed with saturated aqueous NaCl (10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with petroleum ether/Et_2O (20:1) to give 248 mg (59%) of **11** as a clear colorless oil: R_f = 0.26 (20:1 Hexanes/Et_2O); $[\alpha]_D^{26.4}$ = –7.2˚ (*c* = 0.85, $CHCl_3$); ^{1}H NMR (500 MHz) δ 3.47 (app dt, *J* = 7.5, 6.0 Hz, 1 H), 3.01 (ddd, *J* = 6.5, 4.0, 2.5 Hz, 1 H), 2.82 (dd, *J* = 5.0, 4.5 Hz, 1 H), 2.69 (dd, *J* = 5.0, 2.5 Hz, 1 H), 2.50 (dd, *J* = 17.0, 7.0 Hz, 1 H), 2.46 (dd, *J* = 17.0, 6.5 Hz, 1 H), 0.91 (s, 9 H), 0.14 (s, 9 H), 0.12 (s, 3 H), 0.10 (s, 3 H); ^{13}C NMR (125 MHz) δ 102.9, 86.7, 73.2, 55.4, 45.2, 26.4, 25.8, 18.1, –0.07, –4.6, –4.9; IR (neat) 2957, 2930, 2180, 1463, 1251, 1103, 842, 779 cm^{-1}.



4

(5*S*,6*S*)-Methyl 6-(*tert*-butyldimethylsilyloxy)-5-hydroxy-9-(trimethylsilyl)nona-2,8-diynoate (4). ^{n}BuLi (2.31 M in hexanes, 2.8 mmol, 1.2 mL,) was added dropwise to a stirred solution of methyl propiolate (253 mg, 3.01 mmol, 0.27 mL) in THF (5 mL) at –78 ˚C and stirred for 30 min. BF_3•OEt_2 (143

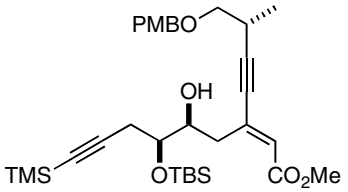
mg, 3.01 mmol, 0.13 mL) followed by a solution of **11** (300 mg, 1.0 mmol) in THF (5 mL) was added and the reaction stirred for 8 h. The resulting mixture was diluted with saturated aqueous $NaHCO_3$ (10 mL) and allowed to warm to room temperature. The layers were separated and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic fractions were dried (Na_2SO_4) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/EtOAc (10:1) to give 325 mg (85%) of **4** as a clear colorless oil: R_f = 0.11 (10:1 Hexanes/EtOAc); $[\alpha]_D^{26.4}$ = –15.2° (*c* = 0.74, $CHCl_3$); ^{1}H NMR (400 MHz) δ 3.94-3.89 (m, 2 H), 3.76 (s, 3 H), 2.61 (dd, *J* = 16.8, 6.0 Hz, 1 H), 2.59 (dd, *J* = 16.8, 7.2 Hz, 1 H), 2.52 (dd, *J* = 16.8, 7.2 Hz, 1 H), 2.39 (dd, *J* = 16.8, 5.2 Hz, 1 H), 0.91 (s, 9 H), 0.16 (s, 3 H), 0.15 (s, 9 H), 0.14 (s, 3 H); ^{13}C NMR (100 MHz) δ 153.9, 102.5, 87.7, 85.6, 74.4, 71.6, 70.7, 52.6, 25.8, 25.3, 24.3, 17.9, –0.09, –4.3, –4.9; IR (neat) 3519, 2956, 22410, 2178, 1719, 1252, 1075, 840 cm^{-1}; HRMS (EI) Calc'd for $C_{19}H_{34}O_4Si_2$: 382.1995; found: 382.1981.



A **12**

(*R*)-1-methoxy-4-((2-methylbut-3-ynyloxy)methyl)benzene (12). Carbon tetrabromide (4.417 g, 13.3 mmol) was added in one portion to a solution of PPh_3 (6.99 g, 26.6 mmol) in CH_2Cl_2 (33 mL) at 0 °C. The mixture was allowed to warm to rt by removal the cooling bath and stirred for 30 min. The reaction was recooled to 0 °C and a solution of **A** (1.387 g, 6.66 mmol) was added. The mixture was allowed to warm to rt by removal the cooling bath and stirred for an additional 2 h. The resulting solution was transferred to an Erlenmeyer flask containing pet. Et_2O (120 mL) and stirred for 1.5 h. The mixture was filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/Et_2O (5:1) to give 1.656 g (69%) of the dibromo olefin as a clear, pale yellow oil whose spectral data was consistent with that reported in the literature: R_f = 0.44 (5:1 Hexanes/Et_2O); ^{1}H NMR (500 MHz) δ 7.25 (dt, *J* = 9.0, 2.5 Hz, 2 H), 6.88 (dt, *J* = 9.0, 2.5 Hz, 2 H), 6.29 (d, *J* = 9.0 Hz, 1 H), 4.46 (d, *J* = 11.5 Hz, 1 H), 4.43 (d, *J* = 11.5 Hz, 1 H), 3.81 (s, 3 H), 3.35 (dd, *J* = 16.0, 9.0 Hz, 1 H), 3.34 (dd, *J* = 16.0, 9.5 Hz, 1 H), 2.81-2.73 (m, 1 H), 1.05 (d, *J* = 6.5 Hz, 3 H). *n*-Butyllithium (7.2 mL, 15.9 mmol, 2.22 M in hexanes) was added to a solution of dibromo olefin (2.321 g,

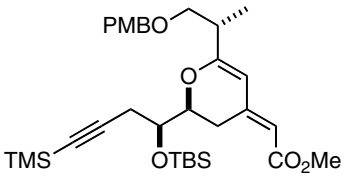
6.37 mmol) in THF (32 mL) at -78 ˚C and the reaction stirred for 1.5 h. The resulting solution was diluted with saturated aqueous $NaHCO_3$ (30 mL) and allowed to warm to rt by removal of the cooling bath. The layers were separated and the aqueous phase extracted with Et_2O (3 x 30 mL). The combined organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/EtOAc (10:1) to give 1.027 g (79%) of **100** as a clear, colorless oil: R_f = 0.25 (10:1 Hexanes/EtOAc); $[\alpha]_D^{26.4}$ = +3.63˚ (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz) δ 7.27 (dt, *J* = 7.2, 2.0 Hz, 2 H), 6.88 (dt, *J* = 9.0, 2.5 Hz, 2 H), 4.51 (d, *J* = 11.5 Hz, 1 H), 4.48 (d, *J* = 11.5 Hz, 1 H), 3.81 (s, 3 H), 3.49 (dd, *J* = 9.5, 6.5 Hz, 1 H), 3.35 (dd, *J* = 9.2, 7.5 Hz, 1 H), 2.73 (dddq, *J* = 7.0, 7.0, 7.0, 2.8 Hz, 1 H), 2.88 (app tq, *J* = 7.0, 7.0 Hz, 1 H), 2.66 (dd, *J* = 17.0, 6.5 Hz, 1 H), 2.42 (app dt, *J* = 13.5, 2.0 Hz, 1 H), 2.07 (d, *J* = 2.5 Hz, 1 H), 1.21 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz) δ 159.1, 130.1, 129.1, 113.6, 86.3, 73.4, 72.6, 68.9, 55.1, 26.4, 17.5; IR (neat) 3292, 2935, 2859, 1613, 1514, 1463, 1359, 1302, 1248, 1174, 1090, 1036, 818, 638 cm^{-1}.



13

(5*S*,6*S*,*E*)-methyl 3-((*R*)-4-(4-methoxybenzyloxy)-3-methylbut-1-ynyl)-6-(*tert*-butyldimethylsilyloxy)-5-hydroxy-9-(trimethylsilyl)non-2-en-8-ynoate (13). TDMPP (23 mg, 0.05 mmol) was added to a solution of $Pd(OAc)_2$ (24 mg, 0.10 mmol) in dry, degassed PhH (2.5 mL) at room temperature and stirred for 30 min. The resulting mixture was added *via* syringe to a solution of **4** (200 mg, 0.52 mmol) and **12** (128 mg, 0.62 mmol) in dry, degassed PhH (2.5 mL)at room temperature. The reaction was stirred for 10 h then concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with CH_2Cl_2/hexanes (3:1) and 2% Et_2O to give 196 mg (65%) of **13** as a clear, light brown oil: R_f = 0.37 (3:1 CH_2Cl_2/Hexanes + 2% Et_2O); $[\alpha]_D^{26.4}$ = +5.9˚ (*c* = 0.70, $CHCl_3$); ^{1}H NMR (500 MHz) δ 7.26 (dt, *J* = 8.5, 3.0 Hz, 2 H), 6.88 (dt, *J* = 8.5, 3.0 Hz, 2 H), 6.15 (s, 1 H), 4.49 (d, *J* = 11.5 Hz, 1 H), 4.46 (d, *J* = 11.5 Hz, 1 H), 3.95 (app dt, *J* = 11.0, 9.0, 2.5 Hz, 1 H), 3.84 (ddd, *J* = 9.0,

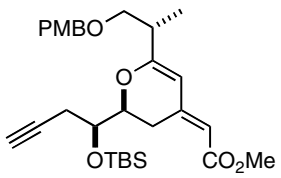
6.5, 3.0 Hz, 1 H), 3.81 (s, 3 H), 3.51 (dd, *J* = 9.0, 6.0 Hz, 1 H), 3.35 (dd, *J* = 9.0, 7.5 Hz, 1 H), 2.92 (d, *J* = 8.5 Hz, 1 H), 2.88 (app tq, *J* = 7.0, 7.0 Hz, 1 H), 2.66 (dd, *J* = 17.0, 6.5 Hz, 1 H), 2.42 (app dt, *J* = 13.5, 2.0 Hz, 1 H), 2.36 (dd, *J* = 17.0, 6.5 Hz, 1 H), 1.22 (d, *J* = 7.0 Hz, 3 H), 0.91 (s, 9 H), 0.14 (s, 3 H), 0.14 (s, 6 H), 0.12 (s, 3 H); ^{13}C NMR (125 MHz) δ 167.2, 159.2, 140.2, 130.1, 129.2, 125.0, 113.8, 104.3, 98.2, 86.3, 82.3, 73.9, 73.2, 72.7, 72.4, 55.2, 51.5, 36.4, 27.5, 25.9, 24.5, 18.1, 17.5, 0.01, –4.2, –4.7; IR (neat) 3484, 2955, 2857, 2178, 1715, 1613, 1513, 1249, 1171, 1038, 841, 779 cm^{-1}; HRMS (EI) Calc'd for $C_{32}H_{50}O_6Si_2$: 586.3145; found: 586.3146.



14

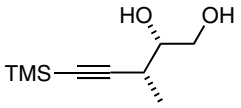
(*E*)-methyl 2-((*S*)-6-((*S*)-1-(4-methoxybenzyloxy)propan-2-yl)-2-((*S*)-1-(*tert*-butyldimethylsilyloxy)-4-(trimethylsilyl)but-3-ynyl)-2,3-dihydropyran-4-ylidene)acetate (14). TDMPP (2 mg, 4.6 μmol) was added to a solution of $PdCl_2(MeCN)_2$ (2 mg, 7.6 μmol) in dry, degassed THF (0.5 mL) at room temperature and stirred for 30 min. The resulting mixture was added *via* syringe to a solution of **13** (45 mg, 76 μmol) in dry, degassed THF (0.5 mL) at room temperature. The reaction was stirred for 2 h then concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with CH_2Cl_2/hexanes (3:1) and 2% Et_2O to give 25 mg (55%) of **14** as a clear, colorless oil. Upon scale up, when **101** (60 mg, 0.10 mmol) was treated with TDMPP (4.5 mg, 0.01 mmol) and $PdCl_2(MeCN)_2$ (5.3 mg, 0.02 mmol) in THF (1.0 mL) provided 35 mg (60%) of **14** as a clear, colorless oil: R_f = 0.29 (5:1 Hexanes/EtOAc); $[\alpha]_D^{26.4}$ = +4.4° (*c* = 1.12, $CHCl_3$); ^{1}H NMR (500 MHz) δ 7.27-7.23 (m, 2 H), 6.89-6.86 (m, 2 H), 5.45 (s, 1 H), 5.33 (s, 1 H), 4.45 (d, *J* = 11.5 Hz, 1 H), 4.42 (d, *J* = 11.5 Hz, 1 H), 4.00 (app dt, *J* = 13.5, 3.0 Hz, 1 H), 3.93 (ddd, *J* = 6.5, 6.5, 3.0 Hz, 1 H), 3.81 (s, 3 H), 3.68 (s, 3 H), 3.61 (dd, *J* = 17.0, 3.0 Hz, 1 H), 3.52 (dd, *J* = 9.0, 7.0 Hz, 1 H), 3.36 (dd, *J* = 9.5, 6.5 Hz, 1 H), 2.64 (dd, *J* = 17.0, 6.5 Hz, 1 H), 2.56 (dd, *J* = 14.0, 6.5 Hz, 1 H), 2.50 (dd, *J* = 16.5, 3.0 Hz, 1 H), 2.45 (dd, *J* = 16.5, 6.5 Hz, 1 H), 1.12 (d, *J* = 7.0 Hz, 3 H), 0.90 (s, 9 H), 0.14 (s, 3 H), 0.13 (s, 3 H), 0.12 (s, 9 H); ^{13}C NMR (125 MHz) δ 167.7, 165.9, 159.1, 150.2, 130.3, 129.3, 113.7, 108.0, 103.7, 102.3, 86.5, 77.4, 72.8, 72.1, 72.0, 55.2, 50.8, 39.4, 27.2, 25.8, 24.7, 18.1, 15.1, 0.00, –4.3, –4.6; IR (neat) 2956, 2361,

2178, 1720, 1610, 1514, 1461, 1251, 1170, 1112, 841 cm^{-1}; HRMS (EI) Calc'd for $C_{32}H_{50}O_6Si_2$: 586.3145; found: 586.3131.



3

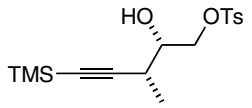
(*E*)-methyl 2-((*S*)-6-((*S*)-1-(4-methoxybenzyloxy)propan-2-yl)-2-((*S*)-1-(*tert*-butyldimethylsilyloxy)but-3-ynyl)-2,3-dihydropyran-4-ylidene)acetate (3). Solid K_2CO_3 (14 mg, 0.097 mmol) was added in one portion to a solution of **14** (19 mg, 0.03 mmol) in MeOH (0.5 mL) at rt. The resulting mixture was stirred for 2.5 h then diluted with H_2O (1 mL) and EtOAc (2 mL). The layers were separated, the aqueous phase was extracted with EtOAc (3 x 2 mL) and the combined organic fractions were washed with saturated aqueous NaCl (2 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/EtOAc (10:1) to give 16 mg (96%) of **3** as a clear, colorless oil: ^{1}H NMR (500 MHz) δ 7.23 (dt, *J* = 8.5, 2.0 Hz, 2 H), 6.87 (dt, *J* = 9.0, 2.0 Hz, 2 H), 5.45 (d, *J* = 2.0 Hz, 1 H), 5.35 (s, 1 H), 4.45 (d, *J* = 11.5 Hz, 1 H), 4.42 (d, *J* = 11.5 Hz, 1 H), 4.05 (dt, *J* = 13.5, 3.0 Hz, 1 H), 3.91 (ddd, *J* = 9.0, 6.0, 3.5 Hz, 1 H), 3.80 (s, 3 H), 3.68 (s, 3 H), 3.61 (dd, *J* = 17.0, 2.0 Hz, 1 H), 3.55 (dd, *J* = 9.5, 6.5 Hz, 1 H), 3.38 (dd, *J* = 9.5, 6.5 Hz, 1 H), 2.65 (ddd, *J* = 16.5, 7.5, 2.5 Hz, 1 H), 2.58 (dt, *J* = 13.5, 6.5 Hz, 1 H), 2.52 (ddd, *J* = 17.0, 14.0, 2.5 Hz, 1 H), 2.41 (ddd, *J* = 16.5, 5.5, 3.0 Hz, 1 H), 1.95 (t, *J* = 2.5 Hz, 1 H), 1.12 (d, *J* = 7.0 Hz, 3 H), 0.90 (s, 9 H), 0.13 (s, 3 H), 0.12 (s, 3 H); ^{13}C NMR (125 MHz) δ 167.7, 165.9, 159.1, 150.2, 130.4, 129.2, 113.7, 108.0, 102.5, 80.7, 72.8, 72.2, 72.0, 70.3, 55.2, 50.8, 39.3, 27.5, 25.8, 23.4, 18.1, 14.9, -4.5, -4.6; IR (neat) 3282, 2950, 2858, 1708, 1611, 1514, 1252, 1154, 1116, 1038, 837 cm^{-1}; HRMS (EI) Calc'd for $C_{29}H_{42}O_6Si$: 514.2751; found: 514.2749.



16

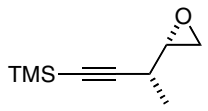
(2*S*,3*R*)-3-Methyl-5-(trimethylsilyl)pent-4-yne-1,2-diol (16). ^{n}BuLi (17.0 mmol, 6.81 mL, 2.5 M in hexanes) was added dropwise to a stirred solution of trimethylsilylacetylene (1.839 g, 18.7 mmol, 2.65 mL) in PhMe (45 mL) at –78 ˚C and stirred for 30 min. The –78 ˚C cooling bath was then

exchanged for a 0 ˚C cooling bath and stirring continued for an additional 15 min. Et_2AlCl (17.0 mmol, 17.0 mL, 1.0 M in PhMe) was added to the mixture and stirred for 30 min. A solution of **15** (500 mg, 5.67 mmol), prepared according to literature precedent,[6] in PhMe (15 mL) was then added at 0 ˚C and the reaction was allowed to warm to room temperature by removal of the cooling bath. Stirring was continued for 14 h at room temperature and the resulting white slurry was recooled to 0 ˚C. 1 M aqueous HCl (40 mL) was added slowly and the layers were separated. The aqueous phase was extracted with EtOAc (4 x 40 mL), and the combined organic fractions were washed with saturated aqueous $NaHCO_3$ (40 mL) and saturated aqueous NaCl (40 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with petroleum ether/EtOAc (1:1) to give 1.02 g (97%) of **16** as a clear, colorless oil: R_f = 0.47 (1:1 Hexanes/EtOAc); $[\alpha]_D^{26.4}$ = –18.3˚ (*c* = 0.79, $CHCl_3$); ^{1}H NMR (500 MHz) δ 3.85-3.83 (m, 1 H), 3.73-3.69 (m, 1 H), 3.60-3.55 (m, 1 H), 2.63 (dq, *J* = 14.5, 7.0 Hz, 1 H), 2.36 (br s, 1 H), 2.04 (br s, 1 H), 1.24 (d, *J* = 7.0 Hz, 3 H), 0.15 (s, 9 H); ^{13}C NMR (125 MHz) δ 107.4, 87.3, 74.6, 64.6, 30.8, 17.0, 0.03; IR (neat) 3384, 2960, 2167, 1455, 1250, 1061 cm^{-1}; HRMS (EI) Calc'd for $C_9H_{18}O_2Si$: 186.1076; found: 186.1073.



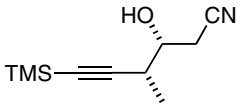
(2*S*,3*R*)-2-Hydroxy-3-methyl-5-(trimethylsilyl)pent-4-ynyl 4-methylbenzenesulfonate. Bu_2SnO (4 mg, 0.01 mmol), *p*-toluenesulfonyl chloride (57 mg, 0.29 mmol) and Et_3N (30 mg, 0.29 mmol, 0.04 mL) were added sequentially to a solution of **16** (50 mg, 0.26 mmol) in CH_2Cl_2 (3 mL) at room temperature and the resulting solution stirred for 16 h. The reaction was then diluted with H_2O (3 mL) and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 3 mL), and the combined organic fractions were washed with saturated aqueous NaCl (5 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with petroleum ether/EtOAc (3:1) to give 79 mg (90%) of the title compound as a clear, colorless oil. Upon scale up, when **16** (3.86 g, 20.7 mmol) was treated with Bu_2SnO (258 mg, 1.0 mmol), *p*-toluenesulfonyl chloride (4.345 g, 22.7 mmol) and Et_3N (2.308 g, 22.7 mmol, 3.2 mL) in CH_2Cl_2 (104 mL) provided 5.814 g (83%) of the title compound as a clear, colorless oil: R_f = 0.25 (3:1 Hexanes/EtOAc); $[\alpha]_D^{26.4}$ = –41.7˚ (*c* = 0.87, $CHCl_3$); ^{1}H NMR (400 MHz) δ 7.83-7.80 (m, 2 H), 7.37-7.35 (m, 2 H), 4.21 (dd, *J* = 9.6, 5.6 Hz, 1 H), 4.06 (dd, *J* = 9.6, 6.0 Hz, 1 H), 2.94-3.89 (m, 1 H), 2.79 (app q, *J* = 6.0 Hz, 1 H), 2.46 (s, 3 H), 1.93 (br d, *J* = 6.4 Hz, 1 H), 0.14 (s, 9 H); ^{13}C NMR (100 MHz) δ

145.1, 132.5, 129.9, 127.9, 106.3, 87.6, 72.4, 72.4, 30.3, 21.6, 16.8, –0.1; IR (neat) 3532, 2960, 2361, 2168, 1362, 1250, 1177, 844, 668 cm^{-1}; HRMS (EI) Calc'd for $C_{16}H_{24}O_4SSi$: 289.0719; found: 289.0765.



7

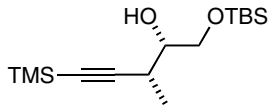
Trimethyl((*R*)-3-((*S*)-oxiran-2-yl)but-1-ynyl)silane (7). DBU (39 mg, 0.25 mmol, 0.04 mL) was added to a solution of (2*S*,3*R*)-2-hydroxy-3-methyl-5-(trimethylsilyl)pent-4-ynyl 4-methylbenzenesulfonate (43 mg, 0.12 mmol) in CH_2Cl_2 (1.5 mL) at room temperature and stirred for 4 h. The solution was then concentrated under reduced pressure and the resulting crude residue was purified by flash chromatography eluting with petroleum ether/Et_2O (5:1) to give 20 mg (99%) of **7** as a clear, colorless oil. Upon scale up, when (2*S*,3*R*)-2-hydroxy-3-methyl-5-(trimethylsilyl)pent-4-ynyl 4-methylbenzenesulfonate (2.382 g, 6.99 mmol) was treated with DBU (3.194 g, 20.9 mmol, 3.2 mL), in CH_2Cl_2 (25 mL) provided 760 mg (65%) of **7** as a clear, colorless oil: R_f = 0.63 (5:1 Hexanes/Et_2O); $[\alpha]_D^{26.4}$ = –71.8° (*c* = 1.25, $CHCl_3$); ^{1}H NMR (400 MHz) δ 2.92 (dq, *J* = 6.4, 2.4 Hz, 1 H), 2.80 (dd, *J* = 5.2, 4.0 Hz, 1 H), 2.70 (dd, *J* = 4.8, 2.4 Hz, 1 H), 2.45-2.38 (m, 1 H), 1.31 (d, *J* = 6.8 Hz, 3 H), 0.15 (s, 9 H); ^{13}C NMR (125 MHz) δ 105.8, 86.6, 54.8, 46.4, 30.1, 17.9, 0.1; IR (neat) 2961, 2170, 1250, 1179, 843 cm^{-1}; HRMS (EI) Calc'd for $C_9H_{16}OSi$: 167.0892; found: 167.0904.



17

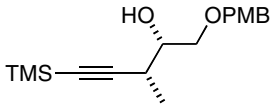
(3*R*,4*R*)-3-Hydroxy-4-methyl-6-(trimethylsilyl)hex-5-ynenitrile (17). Et_2AlCN (0.33 mmol, 0.33 mL, 1.0 M in PhMe) was added dropwise to a stirred solution of **7** (50 mg, 0.29 mmol) in THF (1.5 mL) at –10 °C and the reaction allowed to warm slowly to room temperature. After stirring for 2 d, the mixture was diluted with saturated aqueous $NaHCO_3$ (2 mL) and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 5 mL), and the combined organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with petroleum ether/EtOAc (2:1) to give 44 mg (78%) of **17** as a clear colorless oil: ^{1}H NMR (400

MHz) δ 3.82-3.76 (m, 1 H), 2.76 (dd, *J* = 16.8, 4.0 Hz, 1 H), 2.67-2.60 (comp, 3 H), 1.21 (d, *J* = 7.2 Hz, 3 H), 0.12 (s, 9 H); ^{13}C NMR (125 MHz) δ 117.9, 105.8, 88.5, 70.8, 33.5, 23.8, 16.7, –0.1; IR (neat) 3464, 2956, 2904, 2252, 2167, 1410, 1250, 1060, 841 cm^{-1}.



18

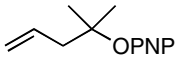
(2*S*,3*R*)-1-(*tert*-Butyldimethylsilyloxy)-3-methyl-5-(trimethylsilyl)pent-4-yn-2-ol (18). TBSCl (387 mg, 2.26 mmol) was added in one portion to a solution of **16** (384 mg, 2.06 mmol), DMAP (10 mg, 0.082 mmol) and Et_3N (229 mg, 2.26 mmol, 0.32 mL) in CH_2Cl_2 (21 mL) at room temperature. The resulting mixture was stirred for 24 h then diluted with saturated aqueous NH_4Cl (20 mL) and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 20 mL) and the combined organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/EtOAc (2:1) to give 492 mg (80%) of **18** as a clear, colorless oil: ^{1}H NMR (400 MHz) δ 3.81 (dd, *J* = 10.0, 3.5 Hz, 1 H), 3.69 (dd, *J* = 10.0, 5.5 Hz, 1 H), 3.42 (ddd, *J* = 5.5, 5.5, 3.5 Hz, 1 H), 2.50 (dq, *J* = 8.0, 7.0 Hz, 1 H), 1.22 (d, *J* = 7.0 Hz, 3 H), 0.88 (s, 9 H), 0.10 (s, 9 H), 0.06 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (100 MHz) δ 108.2, 86.3, 74.6, 65.0, 30.1, 25.9, 18.3, 17.2, 0.04.



19

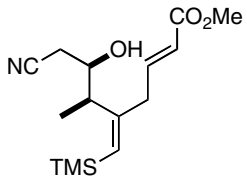
(2*S*,3*R*)-1-(4-Methoxybenzyloxy)-3-methyl-5-(trimethylsilyl)pent-4-yn-2-ol (19). A solution of Bu_2SnO (140 mg, 0.56 mmol) and **16** (100 mg, 0.53 mmol) in PhMe (10 mL) were warmed to reflux and stirred under azeotropic removal of water using a Dean-Stark apparatus for 12 h. After being allowed to cool to room temperature, *p*-methoxybenzyl chloride (118 mg, 0.75 mmol, 0.1 mL) and TBAI (297 mg, 0.80 mmol) were added, the mixture was again warmed to reflux and stirred for an additional 2 h. The mixture was allowed to cool to room temperature, diluted with H_2O (10 mL) and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 10 mL), and the combined organic fractions were washed sequentially with H_2O (10 mL) and saturated aqueous NaCl (10 mL), dried (Na_2SO_4) and

concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/EtOAc (5:1) to give 73 mg (47%) of **19** as a clear, colorless oil: R_f = 0.44 (5:1 Hexanes/EtOAc); $[\alpha]_D^{26.4}$ = –32.9° (*c* = 0.97, $CHCl_3$); ^{1}H NMR (400 MHz) δ 7.28-7.24 (m, 2 H), 6.90-6.86 (m, 2 H), 4.50 (app s, 2 H), 3.78 (s, 3 H), 3.70 (dd, *J* = 9.2, 2.8 Hz, 1 H), 3.52 (dd, *J* = 9.2, 6.8 Hz, 1 H), 3.64-3.60 (m, 1 H), 2.59 (dq, *J* = 6.8, 6.8 Hz, 1 H), 2.50 (br s, 1 H), 1.23 (d, *J* = 7.2 Hz, 3 H), 0.12 (s, 9 H); ^{13}C NMR (100 MHz) δ 159.2, 129.9, 129.4, 113.8, 107.9, 86.4, 73.3, 72.9, 71.9, 55.2, 30.6, 17.0, 0.01; IR (neat) 3446, 2958, 2167, 1700, 1611, 1514, 1464, 1250, 1172, 1089, 1036, 843, 760 cm^{-1}.



20

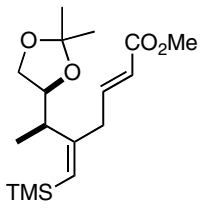
1-(2-methylpent-4-en-2-yloxy)-4-nitrobenzene (20). KHMDS (1.53 mmol, 3.30 mL, 0.46 M in THF) was added to a solution of 2-methylpent-4-en-2-ol (153 mg, 1.53 mmol) and 1-fluoro-4-nitrobenzene (196 mg, 1.39 mmol, 0.15 mL) in THF (14 mL) at 0 ˚C, and the mixture allowed to warm to room temperature. The reaction was stirred for 7 h then diluted with CH_2Cl_2 (30 mL) and washed with saturated aqueous $NaHCO_3$ (50 mL). The aqueous phase was extracted with CH_2Cl_2 (1 x 50 mL), and the combined organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with petroleum ether/Et_2O (2:1) to give 269 mg (87%) of **20** as a clear, colorless oil: ^{1}H NMR (400 MHz) δ 8.17-8.14 (m, 2 H), 7.08-7.05 (m, 2 H), 5.96-5.85 (m, 1 H), 5.16-5.10 (comp, 2 H), 2.50 (d, *J* = 7.2 Hz, 2 H), 1.41 (s, 6 H); ^{13}C NMR (100 MHz) δ 161.7, 142.4, 133.3, 125.1, 121.7, 118.5, 82.1, 46.5, 26.3; IR (neat) 3080, 2981, 2936, 1590, 1514, 1493, 1344, 1256, 1221, 1158, 1112, 896, 852 cm^{-1}.



22c

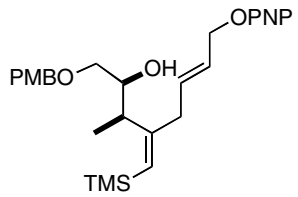
(2*E*,5*Z*,6*R*,7*R*)-Methyl 8-cyano-7-hydroxy-6-methyl-5-((trimethylsilyl)methylene)oct-2-enoate (22c). [$CpRu(MeCN)_3PF_6$] (11 mg, 0.02 mmol) was added in one portion to a solution of **17** (50 mg, 0.25 mmol) and **21** (128 mg, 1.27 mmol) in dry, degassed acetone (0.5 mL) at room temperature. The resulting mixture was stirred for 24 h then concentrated under reduced pressure. The crude residue

was purified by flash chromatography eluting with hexanes/EtOAc (5:1) to give 43 mg (57%) of **22c** as a clear, colorless oil: ^{1}H NMR (500 MHz) δ 6.88 (app dt, *J* = 15.5, 7.5 Hz, 1 H), 5.83 (app dt, 15.5, 1.5 Hz, 1 H), 5.30 (app t, *J* = 1.0, 1 H), 3.89 (dddd, *J* = 9.0, 8.5, 5.5, 3.0 Hz, 1 H), 3.73 (s, 3 H), 2.92 (dddd, *J* = 16.5, 7.0, 1.0, 1.0 Hz, 1 H), 2.78 (dddd, *J* = 16.5, 7.5, 1.0, 1.0 Hz, 1 H), 2.64 (d, *J* = 5.5 Hz, 1 H), 2.57 (dq, *J* = 7.0, 6.5 Hz, 1 H), 2.49 (dd, *J* = 17.0, 3.0 Hz, 1 H), 2.34 (d, *J* = 17.0, 8.5 Hz, 1 H), 1.15 (d, *J* = 7.0 Hz, 3 H), 0.10 (s, 9 H); ^{13}C NMR (125 MHz) δ 166.7, 154.9, 146.7, 130.5, 122.9, 118.1, 70.3, 51.6, 47.0, 35.8, 25.1, 15.5, 0.4; IR (neat) 3464, 2954, 2363, 2252, 2167, 1719, 1654, 1437, 1249, 853 cm^{-1}.



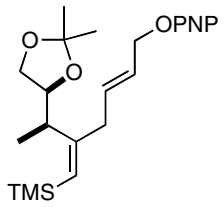
22d

(*R*,2*E*,5*Z*)-Methyl 6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-5-((trimethylsilyl)methylene)hept-2-enoate (36) (BLA-VI-85, procedure: BLA-VII-59). [CpRu(MeCN)$_3$]PF$_6$ (14 mg, 0.033 mmol) was added in one portion to a solution of **18** (100 mg, 0.33 mmol) and **21** (167 mg, 1.66 mmol) in dry, degassed acetone (1.0 mL) at room temperature. The resulting mixture was stirred for 36 h then concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/EtOAc (10:1) to give 100 mg (93%) of **22d** as a clear, colorless oil: R_f = 0.31 (5:1 Hexanes/EtOAc); ^{1}H NMR (400 MHz) δ 6.87 (app dt, *J* = 15.6, 7.2 Hz, 1 H), 5.79 (d, 15.6 Hz, 1 H), 5.20 (s, 1 H), 3.98 (ddd, *J* = 8.0, 6.4, 6.4 Hz, 1 H), 3.85 (dd, *J* = 8.4, 6.4 Hz, 1 H), 3.71 (s, 3 H), 3.57 (dd, *J* = 8.4, 6.4 Hz, 1 H), 2.91 (dd, *J* = 16.4, 6.8 Hz, 1 H), 2.78 (dd, *J* = 16.4, 6.8 Hz, 1 H), 2.60 (dq, *J* = 8.0, 6.8 Hz, 1 H), 1.39 (s, 3 H), 1.31 (s, 3 H), 1.12 (d, *J* = 6.8 Hz, 3 H), 0.08 (s, 9 H); ^{13}C NMR (125 MHz) δ 166.8, 156.1, 147.2, 128.8, 122.5, 109.3, 78.5, 67.6, 51.5, 44.8, 35.9, 27.1, 25.6, 16.0, 0.3; IR (neat) 2951, 2877, 1726, 1656, 1606, 1370, 1264, 1215, 1160, 1054, 856 cm^{-1}.



22f

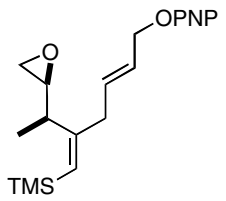
(2*S*,3*R*,4*Z*,6*E*)-1-(4-methoxybenzyloxy)-3-methyl-8-(4-nitrophenoxy)-4-((trimethylsilyl)methylene)oct-6-en-2-ol (22e). $[CpRu(MeCN)_3]PF_6$ (17 mg, 0.039 mmol) was added in one portion to a solution of **19** (60 mg, 0.195 mmol) and **8** (76 mg, 0.39 mmol) in dry, degassed acetone (1 mL) at room temperature. The resulting mixture was stirred for 36 h then concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/EtOAc (3:1) to give 12 mg (13%) of **22e** as a clear, colorless oil: R_f = 0.31 (3:1 Hexanes/EtOAc); ^{1}H NMR (400 MHz) δ 8.20 (d, *J* = 9.2 Hz, 2 H), 7.24 (d, *J* = 9.2 Hz, 2 H), 6.96 (d, *J* = 9.2 Hz, 2 H), 6.88 (d, *J* = 9.2 Hz, 2 H), 5.79 (dt, 15.6, 6.8 Hz, 1 H), 5.65 (dt, 15.6, 6.0 Hz, 1 H), 5.16 (s, 1 H), 4.62-4.60 (comp, 2 H), 3.81-3.75 (m, 1 H), 3.80 (s, 3 H), 3.42 (dd, *J* = 9.6, 2.4 Hz, 1 H), 3.24 (d, *J* = 9.2 Hz, 1 H), 2.86 (dd, *J* = 16.8, 6.8 Hz, 1 H), 2.71 (dd, *J* = 16.8, 6.8 Hz, 1 H), 2.59 (m, 1 H), 1.15 (s, 9 H); ^{13}C NMR (125 MHz) δ 163.6, 159.3, 157.9, 141.4, 134.2, 129.7, 129.4, 126.6, 126.2, 125.9, 125.6, 115.6, 114.6, 113.8, 73.0, 72.9, 72.3, 69.0, 60.4, 55.2, 44.1, 35.8, 29.7, 16.2, 14.2, 16.2, 0.45; IR (neat) 2928, 1711, 1608, 1592, 1513, 1341, 1250, 1173, 1112, 843 cm^{-1}.



22g

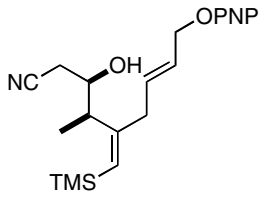
((1*Z*,4*E*)-2-((*R*)-1-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)ethyl)-6-(4-nitrophenoxy)hexa-1,4-dienyl)trimethylsilane (22g). $[CpRu(MeCN)_3]PF_6$ (6 mg, 0.01 mmol) was added in one portion to a solution of **16** (50 mg, 0.26 mmol) and **8** (104 mg, 0.53 mmol) in dry, degassed acetone (1 mL) at room temperature. The resulting mixture was stirred for 36 h then concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/EtOAc (10:1) to give 45 mg (42%) of **22g** as a clear, colorless oil: R_f = 0.50 (10:1 Hexanes/EtOAc); ^{1}H NMR (400 MHz) δ 8.20 (dt, *J* = 7.2, 2.8 Hz, 2 H), 6.98-6.95 (m, 2 H), 5.81 (app dt, *J* = 15.0, 7.5 Hz, 1 H), 5.69 (dt, *J* = 15.0, 6.0 Hz, 1

H), 5.22 (s, 1 H), 4.63 (dd, *J* = 6.0, 1.0 Hz, 2 H), 4.04 (app dt, *J* = 8.5, 6.0 Hz, 1 H), 3.88 (dd, *J* = 8.5, 1.5 Hz, 1 H), 3.61 (dd, *J* = 8.5, 6.5 Hz, 1 H), 2.87 (dd, *J* = 17.0, 6.5 Hz, 1 H), 2.71 (dd, *J* = 17.0, 7.5 Hz, 1 H), 2.64 (dq, *J* = 7.0, 6.5 Hz, 1 H), 1.43 (s, 3 H), 1.35 (s, 3 H), 1.17 (d, *J* = 7.0 Hz, 3 H), 0.11 (s, 9 H); ^{13}C NMR (125 MHz) δ 163.6, 157.6, 141.4, 134.2, 127.2, 125.8, 125.7, 114.7, 109.2, 78.6, 69.0, 67.6, 45.0, 35.9, 27.1, 25.7, 16.4, 0.37; IR (neat) 2948, 1593, 1515, 1342, 1262, 1112, 843 cm^{-1}.



22h

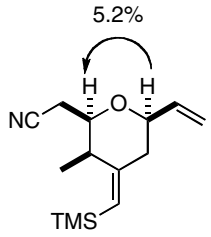
Trimethyl((1*Z*,4*E*)-6-(4-nitrophenoxy)-2-((*R*)-1-((*S*)-oxiran-2-yl)ethyl)hexa-1,4-dienyl)silane (22h). [CpRu(MeCN)$_3$]PF$_6$ (254 mg, 0.589 mmol) was added in one portion to a solution of **7** (993 mg, 5.89 mmol) and **8** (1.71 g, 8.83 mmol) in dry, degassed acetone (12 mL) at room temperature. The resulting mixture was stirred for 36 h then concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/EtOAc (10:1) to give 280 mg (81%, 93% based on recovered starting material) of **22h** as a clear, colorless oil: R_f = 0.16 (10:1 Hexanes/EtOAc); $[\alpha]_D^{26.4}$ = +15.1° (*c* = 0.69, $CHCl_3$); ^{1}H NMR (400 MHz) δ 8.17 (dt, *J* = 9.5, 3.5 Hz, 2 H), 6.95 (dt, *J* = 9.5, 3.5 Hz, 2 H), 5.85 (app dddt, *J* = 15.0, 7.0, 5.5, 1.0 Hz, 1 H), 5.69 (app dddt, *J* = 15.0, 7.0, 6.0, 1.0 Hz, 1 H), 5.19 (app t, *J* = 1.0 Hz, 1 H), 4.61 (dd, *J* = 5.5, 1.0 Hz, 2 H), 2.98-2.86 (comp, 3 H), 2.66 (dd, *J* = 4.5, 4.0 Hz, 1 H), 2.51-2.45 (comp, 3 H), 1.08 (d, *J* = 7.0 Hz, 3 H), 0.06 (s, 9 H); ^{13}C NMR (125 MHz) δ 163.6, 158.0, 141.4, 134.1, 126.3, 125.8, 125.6, 114.7, 69.0, 55.0, 45.4, 42.9, 36.7, 15.3, 0.38; IR (neat) 2956, 1608, 1529, 1514, 1496, 1341, 1250, 1176, 1112, 975, 843 cm^{-1}.



22e

(3*R*,4*R*,5*Z*,7*E*)-3-hydroxy-4-methyl-9-(4-nitrophenoxy)-5-((trimethylsilyl)methylene)non-7-enenitrile (22e). A 1.0 M solution of Et_2AlCN (1.06 mmol, 1.1 mL) in PhMe was added dropwise to a

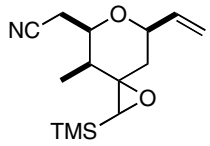
solution of **22h** (321 mg, 0.88 mmol) in PhMe (9 mL) at room temperature. The resulting mixture was stirred for 30 min, diluted with saturated aqueous Rochelle's salt (10 mL) and stirred rapidly for 3 h or until phase separation occurred. The layers were separated and the aqueous phase extracted with EtOAc (3 x 10 mL). The combined organic fractions were dried (Na_2SO_4) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/EtOAc (3:1) to give 243 mg (71%) of **22e** as a clear, colorless oil: R_f = 0.15 (3:1 Hexanes/EtOAc); $[\alpha]_D^{26.4}$ = –1.4° (*c* = 0.58, $CHCl_3$); ^{1}H NMR (500 MHz) δ 8.20 (dt, *J* = 9.5, 3.5 Hz, 2 H), 6.98 (dt, *J* = 9.5, 3.5 Hz, 2 H), 5.82 (app dt, *J* = 16.0, 6.5 Hz, 1 H), 5.72 (app dt, *J* = 15.5, 5.5 Hz, 1 H), 5.31 (s, 1 H), 4.64 (d, *J* = 5.0 Hz, 2 H), 3.94 (br t, *J* = 9.0 Hz, 1 H), 2.87 (dd, *J* = 16.0, 6.0 Hz, 1 H), 2.69 (dd, *J* = 16.5, 6.0 Hz, 1 H), 2.61-2.50 (comp, 3 H), 2.35 (dd, *J* = 17.0, 9.0 Hz, 1 H), 1.18 (d, *J* = 6.5 Hz, 3 H), 0.12 (s, 9 H); ^{13}C NMR (125 MHz) δ 163.5, 156.3, 141.4, 133.6, 129.0, 126.2, 125.9, 118.3, 114.7, 70.4, 68.8, 47.2, 35.8, 25.1, 15.9, 0.43; IR (neat) 3456, 2956, 1607, 1592, 1512, 1496, 1341, 1250, 1112, 843 cm^{-1}; HRMS (EI) Calc'd for $C_{20}H_{28}N_2O_4Si$: 250.1627; found: 250.1642.



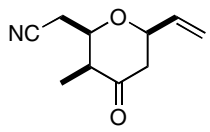
23

2-((2*R*,3*R*,6*R*,*Z*)-3-methyl-4-((trimethylsilyl)methylene)-6-vinyl-tetrahydro-2*H*-pyran-2-yl)acetonitrile (23). **(*S*,*S*)-L** (6.6 mg, 0.007 mmol) was added in one portion to a solution of $Pd_2(dba)_3$•$CHCl_3$ (2.7 mg, 0.0026 mmol) in CH_2Cl_2 (0.75 mL) at room temperature and the resulting yellow solution was stirred for 15 min. In a separate flask, ^{i}Pr_2NEt (19 mg, 0.14 mmol, 0.025 mL) was added to a solution of **22e** (50 mg, 0.128 mmol) in CH_2Cl_2 (0.75 mL) at room temperature and stirred for 10 min. Then the solution containing the $Pd_2(dba)_3$•$CHCl_3$/**(*S*,*S*)-L$_1$** mixture was added *via* syringe, the reaction stirred for 1 h at room temperature then concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/Et_2O (10:1) to give 29 mg (97%) of **23** as a mixture of *cis* and *trans* isomers (15:1), determined by comparison of δ 3.89-3.85 and δ 4.53 in the ^{1}H NMR spectra, as a clear, colorless oil: ***cis*-23:** R_f = 0.23 (10:1 Hexanes/Et_2O); $[\alpha]_D^{26.4}$ = –68.5° (*c* = 0.77, $CHCl_3$); ^{1}H NMR (500 MHz) δ 5.85 (ddd, *J* = 17.0, 10.5, 5.5 Hz, 1 H), 5.29 (s, 1 H), 5.27 (app dt, 16.0, 1.5 Hz, 1 H), 5.15 (app dt, 10.5, 1.5 Hz, 1 H), 3.89-3.85 (m, 1 H), 3.74 (ddd, *J* = 8.0, 6.5, 2.5 Hz, 1 H),

2.69 (dq, *J* = 6.5, 2.5 Hz, 1 H), 2.66 (dd, *J* = 16.5, 6.5 Hz, 1 H), 2.48 (dd, *J* = 17.0, 8.0 Hz, 1 H), 2.37 (ddd, *J* = 13.5, 12.0, 2.0 Hz, 1 H), 2.06 (dd, *J* = 13.5, 2.5 Hz, 1 H), 1.07 (d, *J* = 7.0 Hz, 3 H), 0.13 (s, 9 H); n.O.e. 1D ^{1}H NMR (600 MHz) 5.2% as indicated by irradiation of δ 3.89-3.85; ^{13}C NMR (125 MHz) δ 156.1, 137.7, 124.5, 117.1, 115.8, 79.9, 75.4, 40.1, 39.0, 21.4, 11.8, 0.14; IR (neat) 2953, 2253, 1621, 1426, 1249, 1117, 840 cm^{-1}; HRMS (EI) Calc'd for $C_{14}H_{23}NOSi$: 250.1627; found: 250.1654. ***trans*-23:** ^{1}H NMR (500 MHz) δ 5.87 (ddd, *J* = 17.0, 11.0, 4.5 Hz, 1 H), 5.31 (app dt, *J* = 17.0, 1.5 Hz, 1 H), 5.28 (s, 1 H), 5.27 (dd, *J* = 11.0, 1.5 Hz, 1 H), 4.53 (br t, *J* = 5.5 Hz, 1 H), 3.99 (ddd, *J* = 9.5, 7.0, 2.5 Hz, 1 H), 2.87 (ddd, *J* = 14.0, 7.0, 2.0 Hz, 1 H), 2.61 (dq, *J* = 6.5, 2.5 Hz, 1 H), 2.55 (dd, *J* = 16.5, 5.0 Hz, 1 H), 2.49 (dd, *J* = 17.0, 7.0 Hz, 1 H), 2.11 (dd, *J* = 14.0, 2.5 Hz, 1 H), 1.10 (d, *J* = 7.0 Hz, 3 H), 0.11 (s, 9 H); n.O.e. 1D ^{1}H NMR (600 MHz) 0.76% as indicated by irradiation of δ 4.53; ^{13}C NMR (125 MHz) δ 154.1, 136.0, 126.0, 118.7, 117.2, 74.5, 68.6, 39.5, 21.6, 11.8, 0.17.

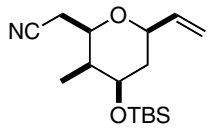


2-((2*R*,3*R*,6*R*,*Z*)-3-methyl-4-((trimethylsilyl)methyloxirane)-6-vinyl-tetrahydro-2*H*-pyran-2-yl)acetonitrile. *m*-CPBA (52 mg, 0.3 mmol) was added to a slurry of **23** (50 mg, 0.2 mmol) and Li_2CO_3 (8 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) at 0 ˚C and the mixture stirred for 2 h. The reaction was allowed to warm to room temperature by removal of the cooling bath and stirred for 3 h. The mixture was then diluted with saturated aqueous $Na_2S_2O_3$ (2 mL), stirred for 30 min and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 2 mL), and the combined organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/EtOAc (5:1) to give 50 mg (94%) of the title compound as a clear, colorless oil: R_f = 0.37 (5:1 Hexanes/EtOAc); $[\alpha]_D^{26.4}$ = –60.3˚ (*c* = 0.69, $CHCl_3$); ^{1}H NMR (500 MHz) δ 5.84 (ddd, *J* = 17.5, 10.5, 5.5 Hz, 1 H), 5.27 (app dt, *J* = 17.5, 1.5 Hz, 1 H), 5.15 (app dt, *J* = 10.5, 1.5 Hz, 1 H), 4.23 (ddddd, *J* = 11.5, 5.5, 3.0, 1.0, 1.0 Hz, 1 H), 4.12 (ddd, *J* = 9.5, 7.5, 2.5 Hz, 1 H), 2.66 (dd, *J* = 16.5, 7.0 Hz, 1 H), 2.45 (dd, *J* = 16.5, 7.5 Hz, 1 H), 2.14-2.09 (comp, 2 H), 1.49 (dq, *J* = 7.5, 1.5 Hz, 1 H), 1.08 (d, *J* = 7.5 Hz, 3 H), 1.07 (br s, 1 H), 0.17 (s, 9 H),; ^{13}C NMR (125 MHz) δ 137.4, 116.8, 115.8, 73.1, 64.8, 59.0, 37.3, 36.8, 21.1, 10.3, –1.8; IR (neat) 3445, 2957, 1728, 1412, 1251, 1125, 1083, 1028, 1007, 868, 842, 752, 699 cm^{-1}; HRMS (EI) Calc'd for $C_{14}H_{23}NO_2Si$: 264.1420; found: 264.1419.



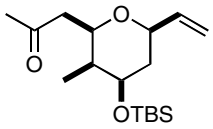
24

2-((2*R*,3*S*,6*R*)-3-methyl-4-oxo-6-vinyl-tetrahydro-2*H*-pyran-2-yl)acetonitrile (24). Periodic acid (86 mg, 0.36 mmol) was added to a solution of epoxide (25 mg, 0.09 mmol) in THF (1.75 mL) and H_2O (0.25 mL) at 0 ˚C and the mixture stirred for 1 h. The reaction was allowed to warm to room temperature by removal of the cooling bath and stirred for 2 h. The mixture was then diluted with H_2O (1 mL) and extracted Et_2O (3 x 2 mL). The combined organic fractions were washed sequentially with saturated aqueous $Na_2S_2O_3$ (2 mL) and H_2O (2 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with Et_2O/hexanes (2:1) to give 12 mg (74%) of **24** as a clear, colorless oil. Upon scale up, when epoxide (316 mg, 1.19 mmol) was treated with periodic acid (1.085 g, 4.76 mmol) in THF/H_2O (7:1 = 12 mL) provided 166 mg (78%) of **24** as a clear, colorless oil: R_f = 0.39 (2:1 Hexanes/Et_2O); $[\alpha]_D^{26.4}$ = –20.6˚ (*c* = 1.36, $CHCl_3$); ^{1}H NMR (500 MHz) δ 5.89 (ddd, *J* = 17.5, 10.5, 5.5 Hz, 1 H), 5.34 (app dt, *J* = 17.0, 1.5 Hz, 1 H), 5.25 (app dt, *J* = 10.5, 1.5 Hz, 1 H), 4.18 (ddddd, *J* = 11.0, 4.0, 3.0, 1.5, 1.5 Hz, 1 H), 4.05 (ddd, *J* = 9.0, 6.5, 2.5 Hz, 1 H), 2.77 (dd, *J* = 17.0, 7.5 Hz, 1 H), 2.60-2.51 (comp, 3 H), 2.37 (app dq, *J* = 7.5, 1.5 Hz, 1 H), 1.19 (d, *J* = 7.5 Hz, 3 H); ^{13}C NMR (125 MHz) δ 208.1, 136.0, 116.9, 116.4, 77.6, 74.0, 47.7, 43.1, 20.8, 10.4.



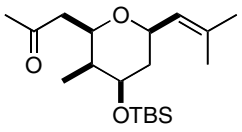
2-((2*R*,3*S*,4*R*,6*R*)-4-(*tert*-butyldimethylsilyloxy)-3-methyl-6-vinyl-tetrahydro-2*H*-pyran-2-yl)acetonitrile. $NaBH_4$ (4 mg, 0.09 mmol) was added to a solution of **24** (8 mg, 0.044 mmol) in EtOH (1 mL) at 0 ˚C and the mixture stirred for 15 min. The mixture was then diluted sequentially with saturated aqueous NH_4Cl (1 mL), H_2O (4 mL) and CH_2Cl_2 (5 mL). The layers were separated and the aqueous phase extracted with CH_2Cl_2 (3 x 5 mL) The combined organic fractions were dried (Na_2SO_4) and concentrated under reduced pressure. The crude alcohol was dissolved in DMF (2 mL) followed by the sequential addition of imidazole (10 mg, 0.13 mmol) and TBSCl (23 mg, 0.13 mmol) at room temperature. The mixture was stirred for 10 h then diluted with saturated aqueous NH_4Cl (2 mL), Et_2O (4

mL) and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 4 mL). The combined organic fractions were washed with saturated aqueous NaCl (4 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was purified by flash chromatography eluting with hexanes/EtOAc (5:1) to give 9 mg (70%) of the title compound as a clear, colorless oil: R_f = 0.41 (5:1 Hexanes/EtOAc); $[\alpha]_D^{26.4}$ = –18.5° (*c* = 0.87, $CHCl_3$); ^{1}H NMR (500 MHz) δ 5.83 (ddd, *J* = 17.0, 10.5, 5.5 Hz, 1 H), 5.27 (app dt, *J* = 17.0, 1.5 Hz, 1 H), 5.14 (app dt, *J* = 10.5, 1.5 Hz, 1 H), 3.91-3.85 (comp, 2 H), 3.75 (ddd, *J* = 9.5, 7.5, 2.5 Hz, 1 H), 2.66 (dd, *J* = 16.5, 7.5 Hz, 1 H), 2.47 (dd, *J* = 16.5, 7.0 Hz, 1 H), 1.96-1.91 (m, 1 H), 1.59 (dddd, *J* = 13.0, 4.5, 2.5, 0.5 Hz, 1 H), 1.50 (ddd, *J* = 13.5, 11.5, 11.0 Hz, 1 H), 0.91 (d, *J* = 7.0 Hz, 3 H), 0.89 (s, 9 H), 0.07 (s, 6 H); ^{13}C NMR (125 MHz) δ 137.4, 117.4, 115.7, 74.1, 70.5, 37.9, 35.0, 25.7, 21.5, 18.0, 4.5, –4.6, –4.8; IR (neat) 2954, 2930, 2857, 1648, 1472, 1379, 1254, 1114, 1072, 837, 776 cm^{-1}.



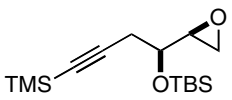
25

1-((2*R*,3*S*,4*R*,6*R*)-4-(*tert*-butyldimethylsilyloxy)-3-methyl-6-vinyl-tetrahydro-2*H*-pyran-2-yl)propan-2-one (25). A flask was charged with $CeCl_3 \bullet H_2O$ (167 mg, 0.44 mmol) and placed under vacuum. The flask was warmed to 160 ˚C slowly over 2 h, then maintained for an additional 10 h. After being allowed to cool to rt, THF (0.75 mL) was added to the dried $CeCl_3$ and stirred for 2 h. The slurry was cooled to –78 ˚C and MeLi (1.6 M solution in Et_2O, 0.21 mL, 0.33 mmol) was added via syringe and stirred for 1 h. A solution of nitrile (11 mg, 0.037 mmol) in THF (0.75 mL) was added to the mixture at –78 ˚C and the reaction stirred for 30 min. The reaction was diluted with saturated aqueous NH_4Cl (2 mL), allowed to warm to rt then stirred for 30 min. The mixture was diluted with Et_2O (2 mL), transferred to a separatory funnel and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 4 mL) and the combined organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure. The crude mixture was purified directly by flash chromatography eluting with hexanes/EtOAc (10:1) to give 8 mg (70%) of **25** as a clear, colorless oil: ^{1}H NMR (500 MHz) δ 5.82 (ddd, *J* = 17.5, 11.0, 5.5 Hz, 1 H), 5.22 (dt, *J* = 17.5, 1.5 Hz, 1 H), 5.08 (dt, *J* = 11.0, 1.5 Hz, 1 H), 3.93-3.87 (comp, 2 H), 3.85-3.81 (m, 1 H), 2.81 (dd, *J* = 16.0, 8.5 Hz, 1 H), 2.35 (dd, *J* = 16.0, 4.5 Hz, 1 H), 2.19 (s, 3 H), 1.77-1.74 (m, 1 H), 1.58-1.54 (m, 1 H), 1.51-1.47 (m, 1 H), 0.89-0.88 (m, 1 H), 0.88 (s, 9 H), 0.05 (s, 3 H), 0.05 (s, 3 H); HRMS (EI) Calc'd for $C_{17}H_{32}O_3Si$: 310.1964; found: 310.1958.



6

1-((2*R*,3*S*,4*R*,6*R*)-4-(*tert*-butyldimethylsilyloxy)-3-methyl-6-(2-methylprop-1-enyl)-tetrahydro-2*H*-pyran-2-yl)propan-2-one (6). Grubbs' second generation metathesis catalyst (10 mg, 1.6 μmol) was added to a solution of **25** (10 mg, 0.03 mmol) in 2-methyl-2-butene (0.3 mL) under an atmosphere of argon in a sealed vial. The resulting mixture was heated to 40 ˚C and stirred for 12 h. The crude mixture was purified directly by flash chromatography eluting with hexanes/EtOAc (10:1) to give 10 mg (quant.) of **6** as a clear, colorless oil: $[\alpha]_D^{26.4}$ = +0.60˚ (*c* = 1.14, $CHCl_3$); ^{1}H NMR (500 MHz) δ 5.17-5.14 (m, 1 H), 4.05-4.01 (m, 1 H), 3.92-3.88 (comp, 2 H), 2.80 (dd, *J* = 16.5, 8.5 Hz, 1 H), 2.35 (dd, *J* = 16.5, 4.5 Hz, 1 H), 2.17 (s, 1 H), 1.73-1.71 (m, 1 H), 1.71 (d, *J* = 1.0 Hz, 3 H), 1.67 (d, *J* = 1.0 Hz, 3 H), 1.51-1.48 (comp, 2 H), 0.88 (d, *J* = 6.5 Hz, 3 H), 0.88 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR (125 MHz) δ 207.2, 137.3, 125.1, 74.4, 73.1, 71.1, 46.8, 38.6, 35.8, 31.0, 25.8, 25.7, 18.4, 18.1, 5.3, -4.6, -4.7; HRMS (EI) Calc'd for $C_{19}H_{36}O_3Si$: 340.2434; found: 340.2441.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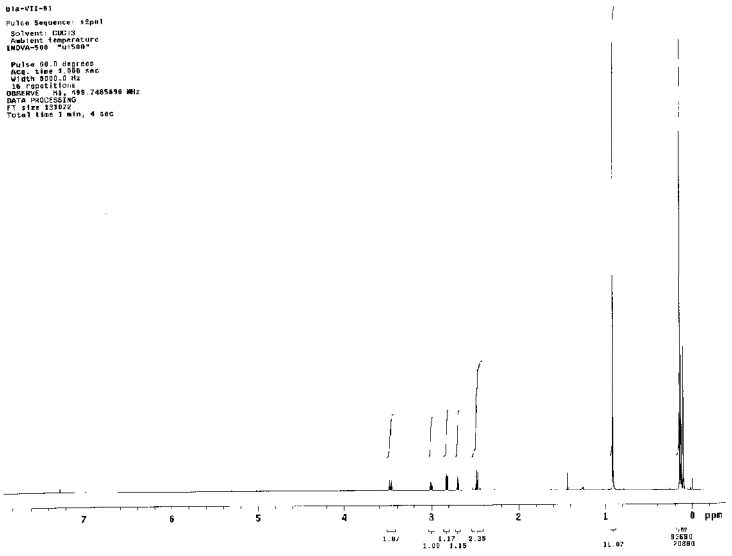
O

11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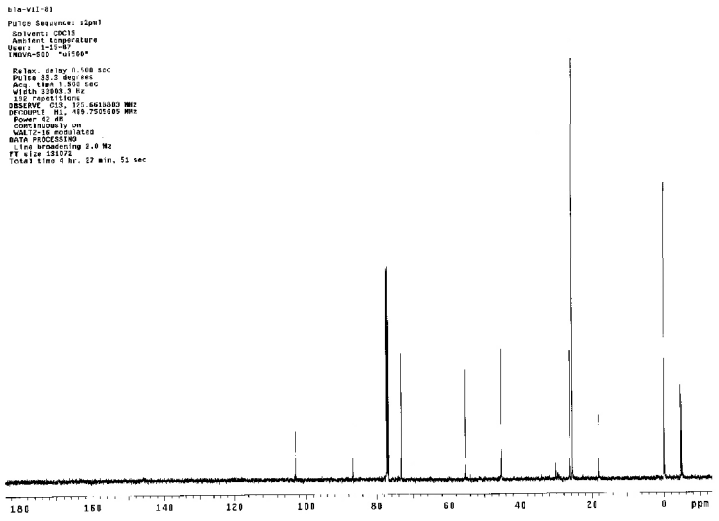
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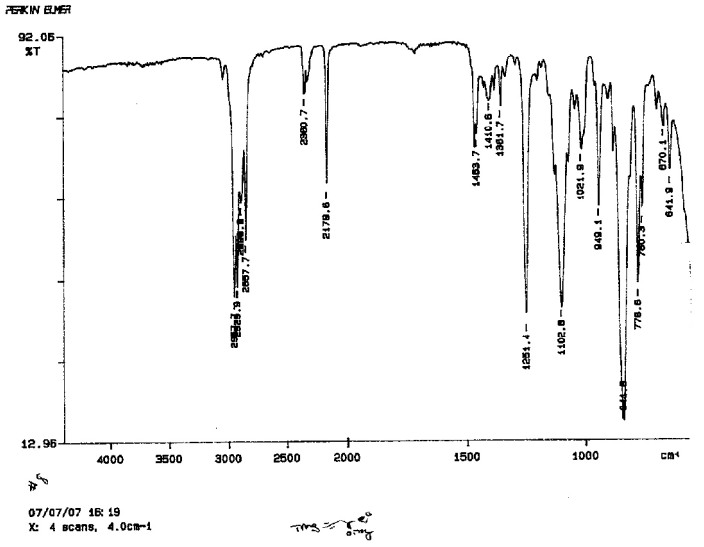
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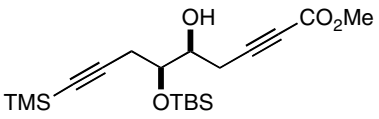
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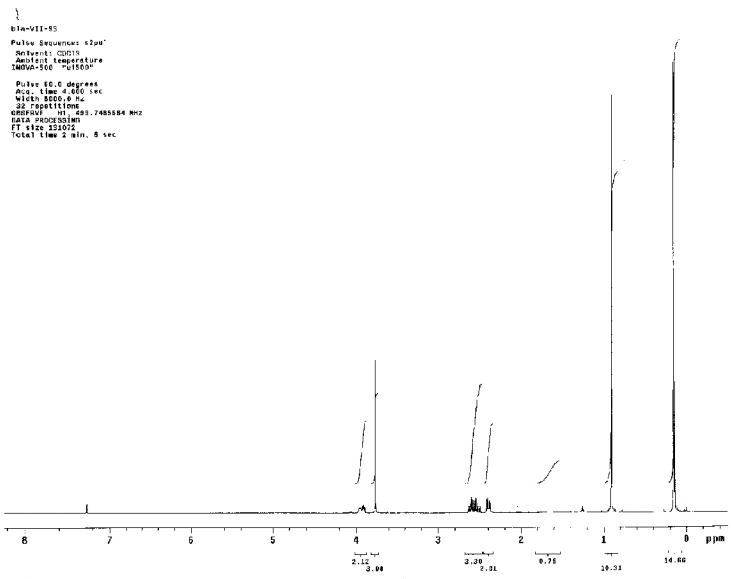
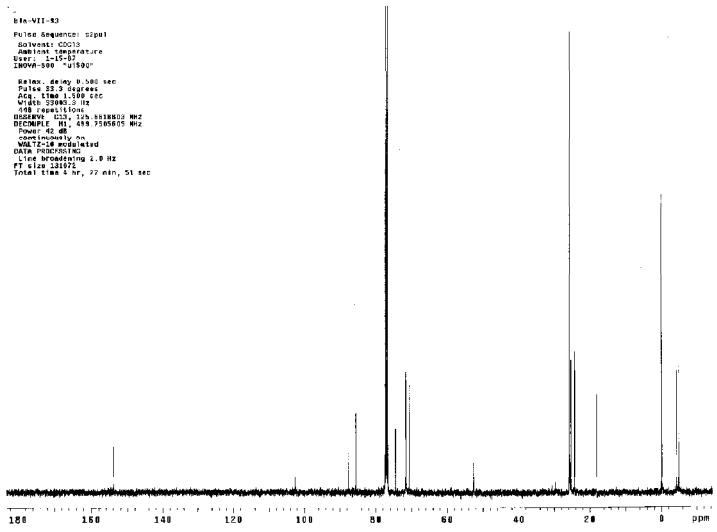
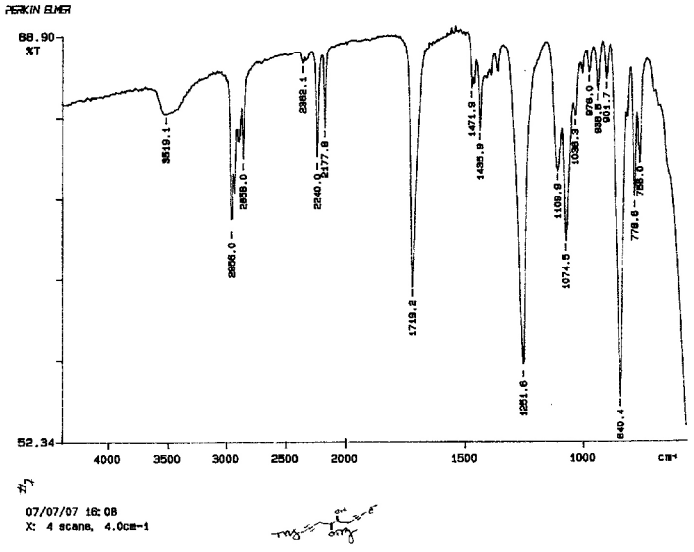
4



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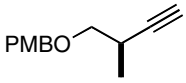
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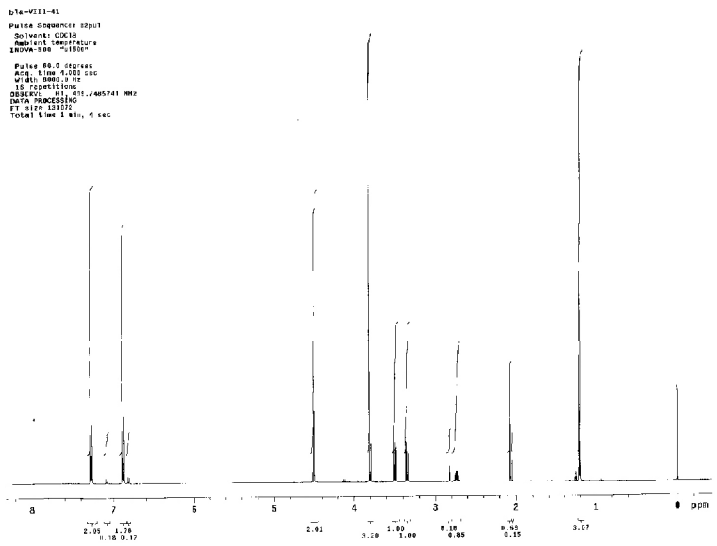
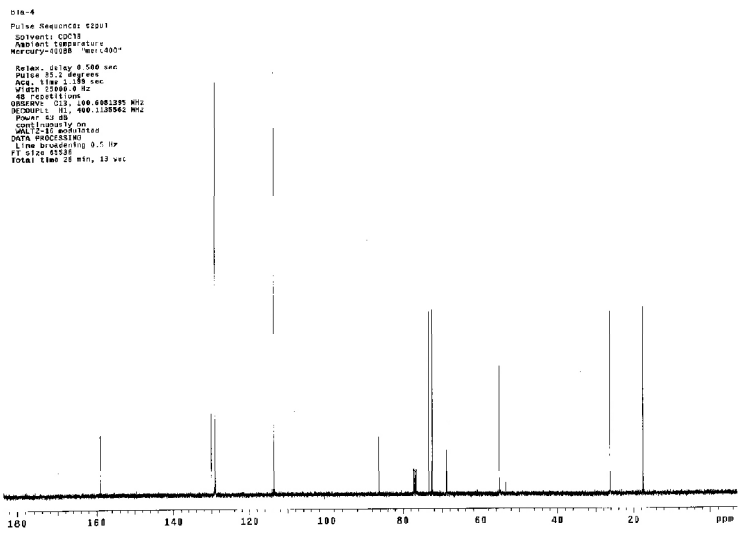
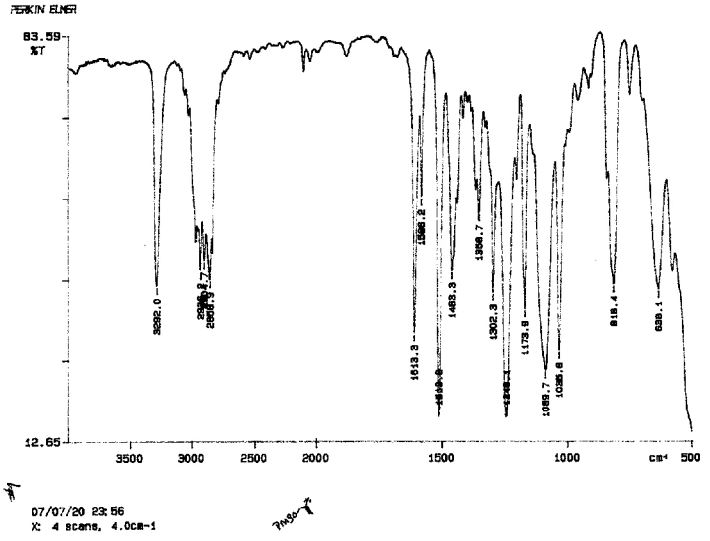
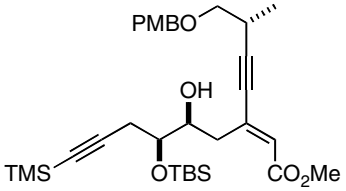
12

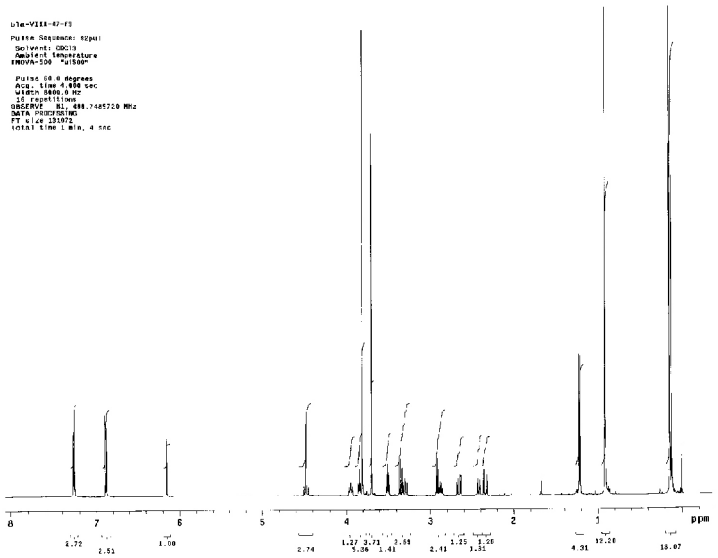


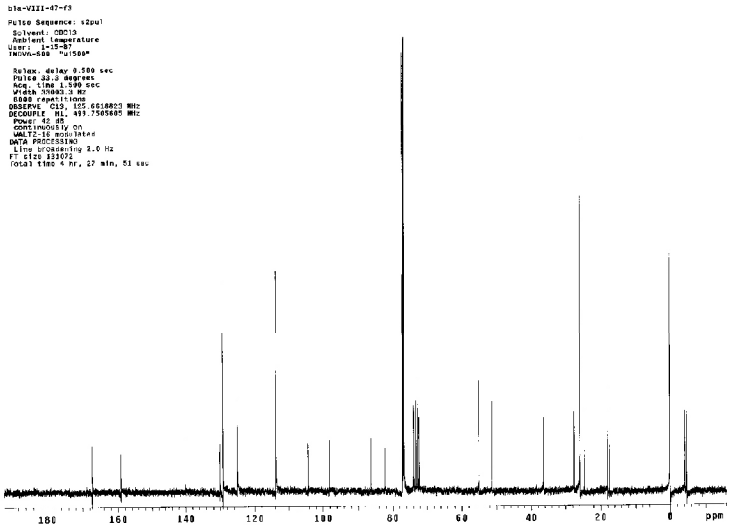


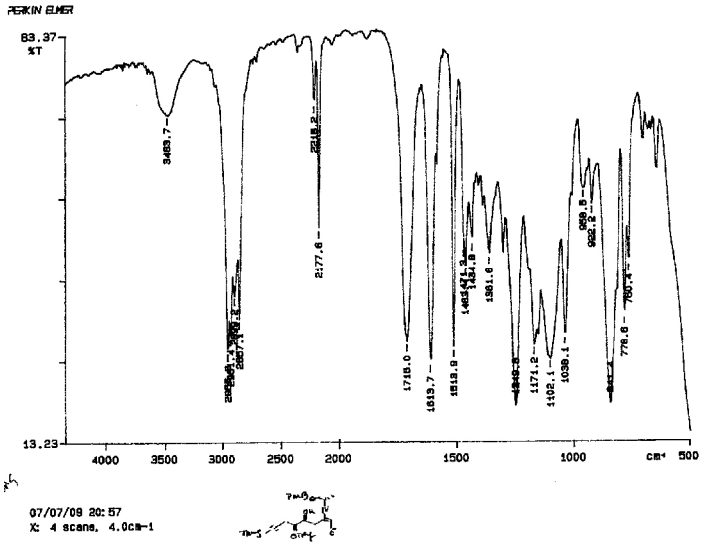

PERKIN ELMER
83.59
%T
12.65
3500
3000
2500
2000
1500
1000
cm-1
500
07/07/20 23:56
X: 4 scans, 4.0cm-1

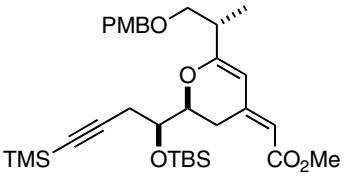

PMBO
OH
TMS
OTBS
CO_2Me

13

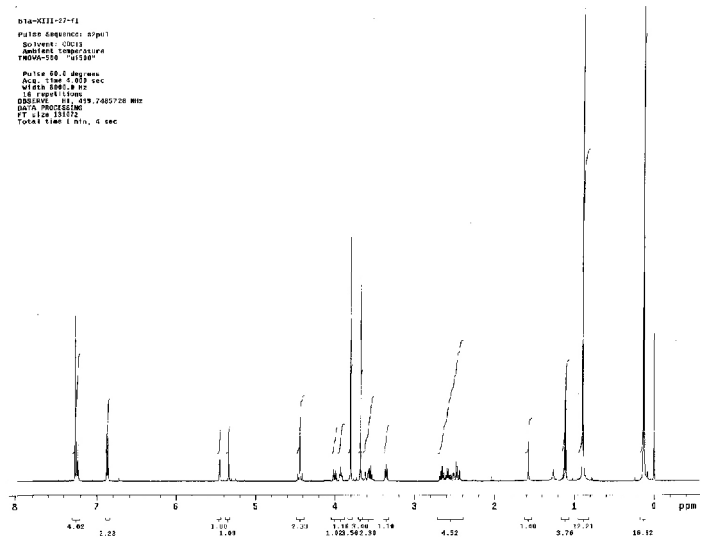


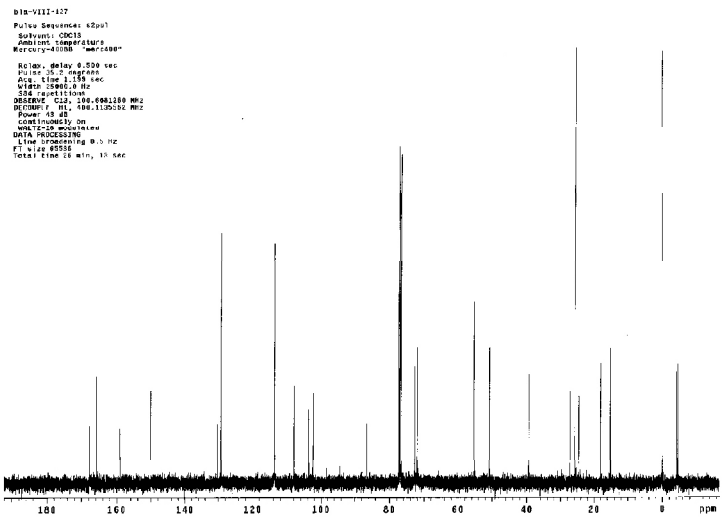


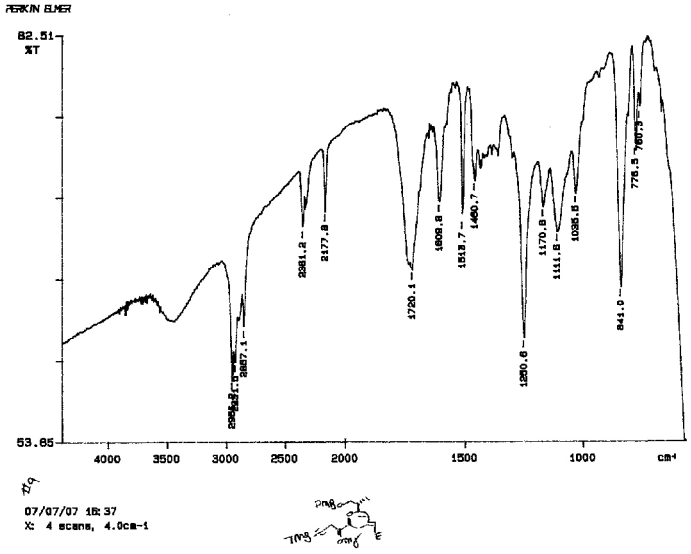

PERKIN ELMER
83.37
%T
13.23
3483.7
2977.6
1715.0
1613.7
1513.9
1391.6
1171.2
1102.1
1039.1
968.5
922.2
778.6
4000
3500
3000
2500
2000
1500
1000
cm-1
500
07/07/09 20:57
X: 4 scans, 4.0cm-1

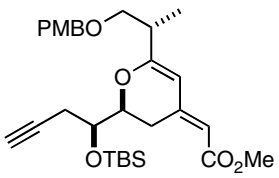

PMBO
O
TMS
OTBS
CO2Me

14

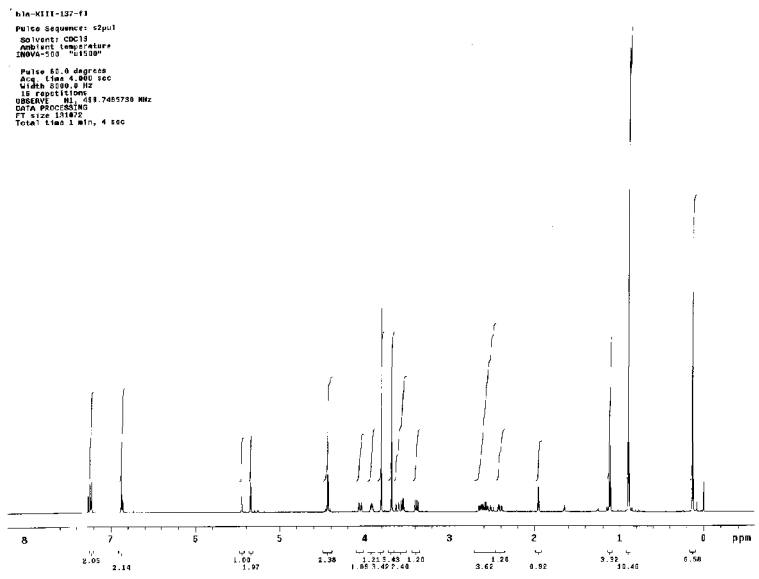


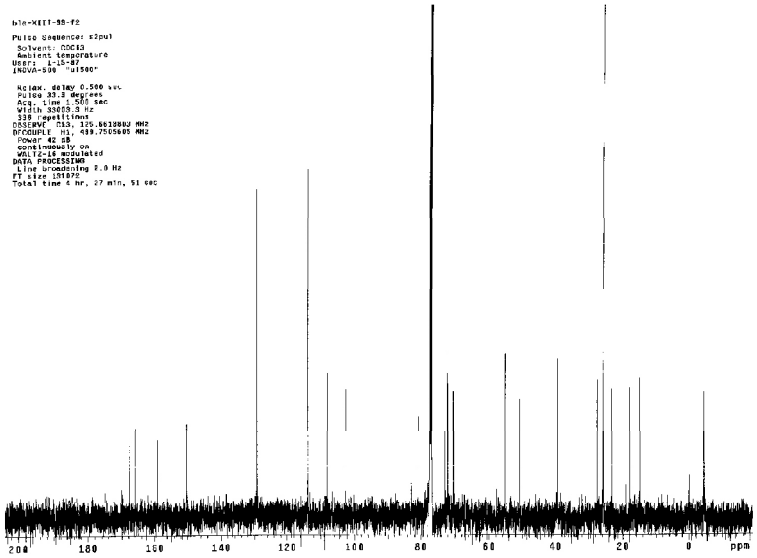


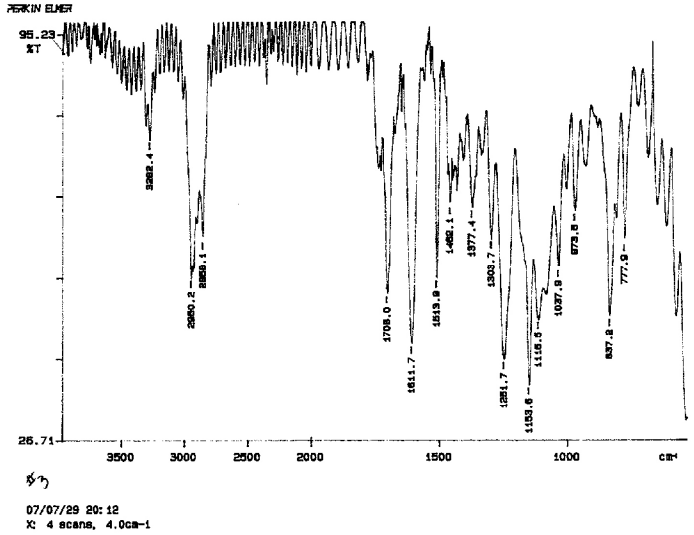

PERKIN ELMER
82.51
%T
53.85
4000
3500
3000
2500
2000
1500
1000
cm-1
2981.2
2877.1
2177.8
1720.1
1609.8
1513.7
1460.7
1380.6
1170.8
1111.8
1035.8
841.0
778.5
07/07/07 15:37
X: 4 scans, 4.0cm-1

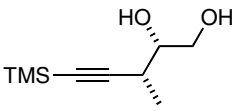

PMBO
O
OTBS
CO2Me

3

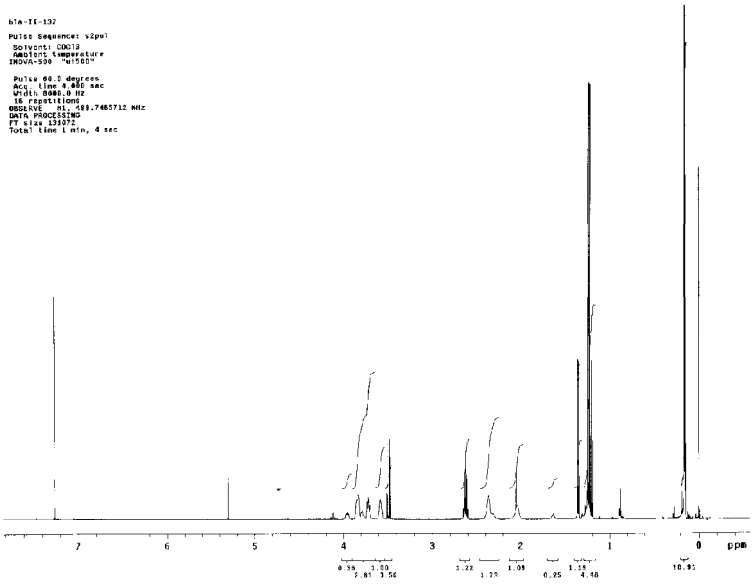

bla-XIII-137-f1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ul500"
Pulse 62.6 degrees
Acq. time 4.000 sec
Width 2200.9 Hz
16 repetitions
OBSERVE H1, 499.7485738 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec
ppm

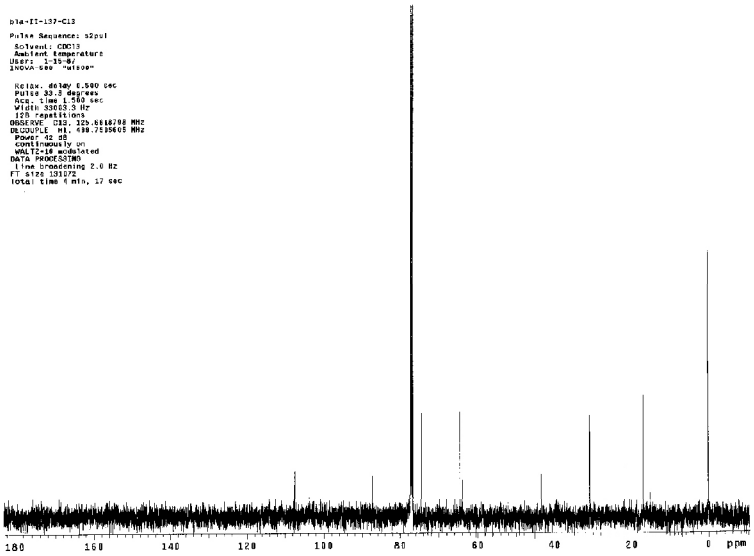

bla-XIII-98-f2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Users: L-15-87
INOVA-500 "ul500"
Relax. delay 0.500 sec
Pulse 33.8 degrees
Acq. time 1.500 sec
Width 33003.3 Hz
338 repetitions
OBSERVE C13, 125.6613880 MHz
DECOUPLE H1, 499.7505605 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 4 hr, 27 min, 51 sec
ppm

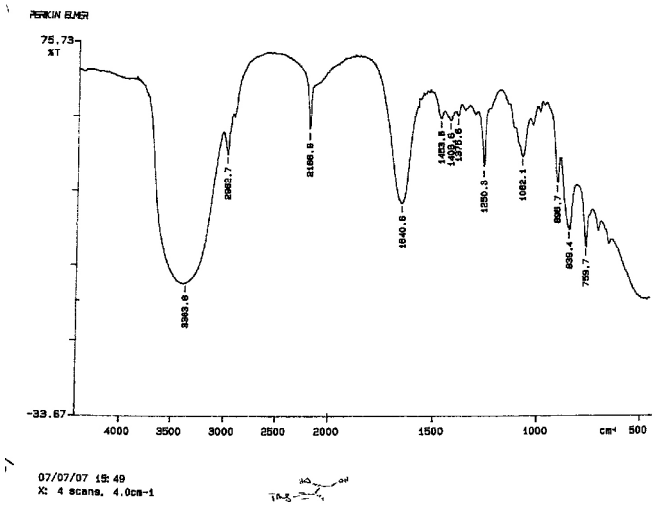

PERKIN ELMER
95.23
%T
25.71
3500
3000
2500
2000
1500
1000
cm-1
07/07/29 20:12
X: 4 scans, 4.0cm-1

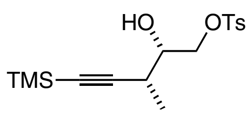

HO
OH
TMS

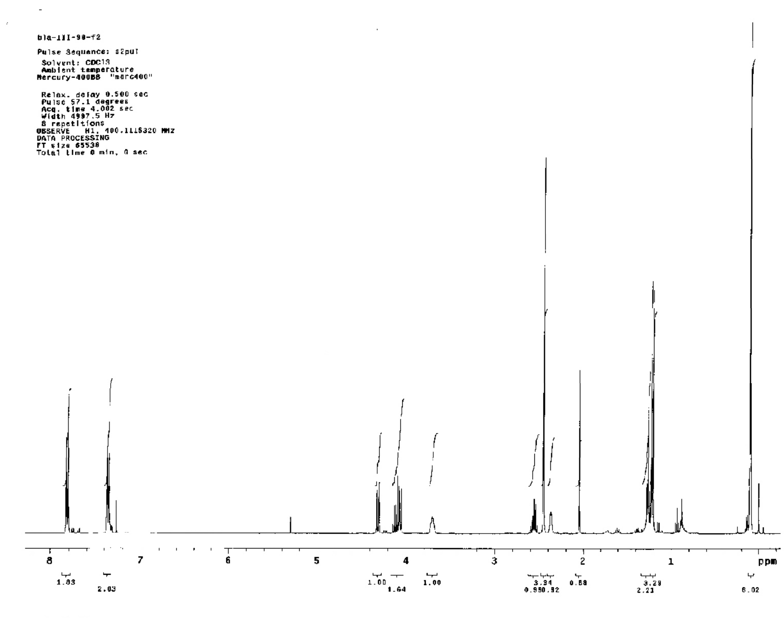
16

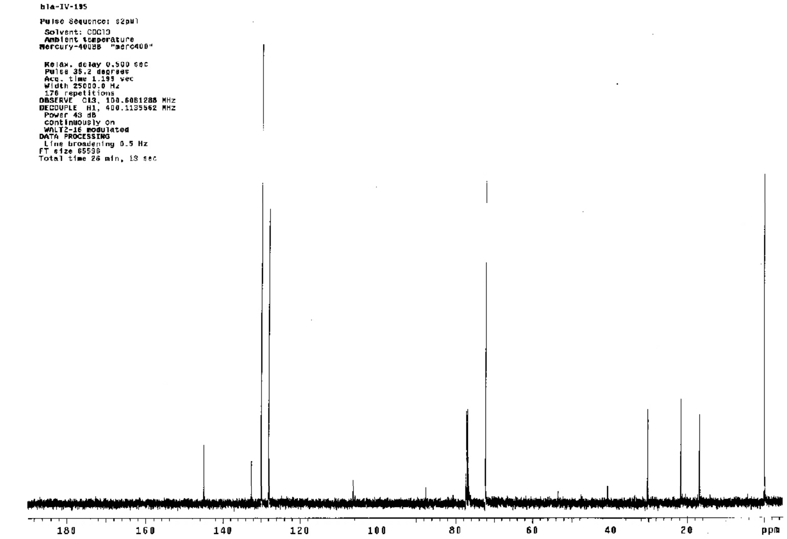


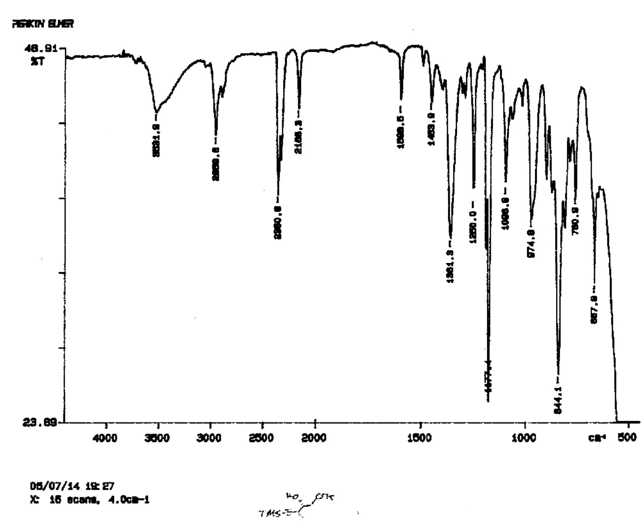


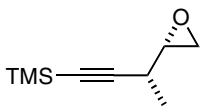

PERKIN ELMER
75.73
%T
-33.67
4000
3500
3000
2500
2000
1500
1000
cm-1
500
3343.0
2982.7
2166.8
1640.6
1250.3
1062.1
899.7
839.4
759.7
07/07/07 19:49
X: 4 scans, 4.0cm-1


HO
OTs
TMS

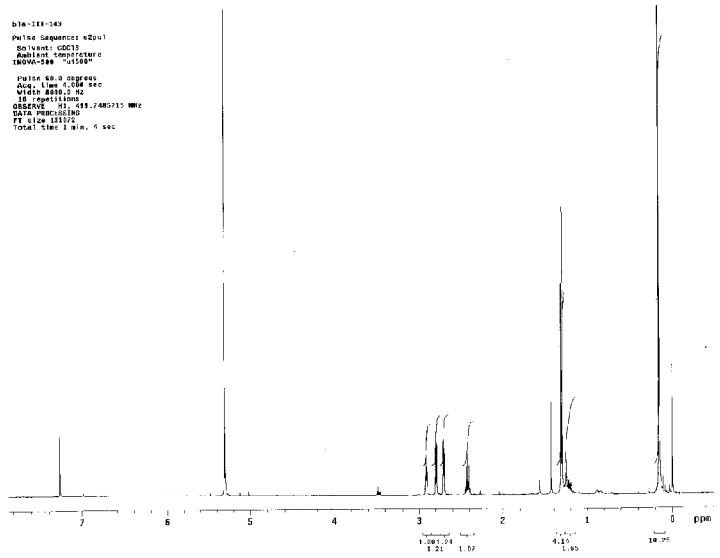


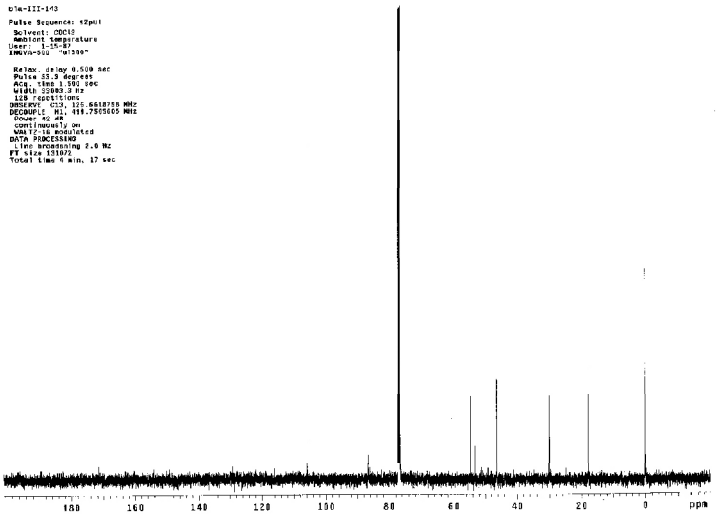


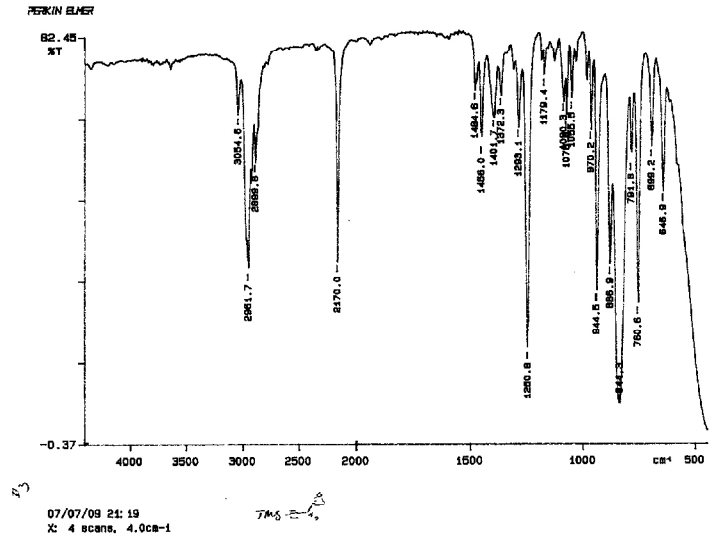


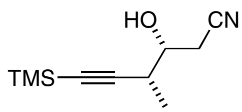

TMS
O

7

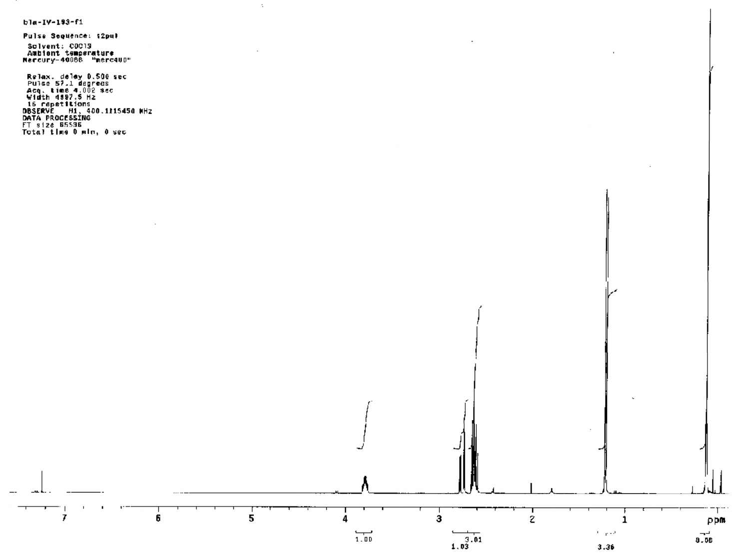

bla-III-143
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "u1500"
Pulse 60.0 degrees
Acq. time 4.008 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.7485715 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 6 sec
7
6
5
4
3
2
1
0
ppm

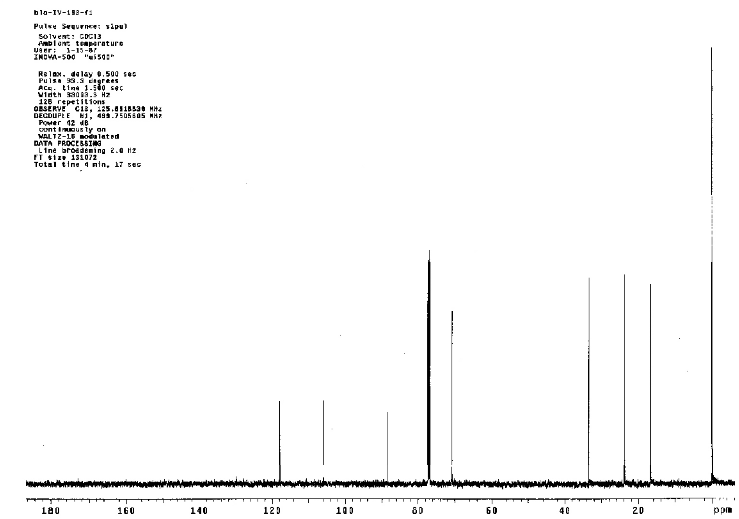

bla-III-143
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: l-15-87
INOVA-500 "u1500"
Relax. delay 0.500 sec
Pulse 33.9 degrees
Acq. time 1.592 sec
Width 22083.3 Hz
128 repetitions
OBSERVE C13, 125.6618758 MHz
DECOUPLE H1, 499.7505605 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 6 min, 17 sec
180
160
140
120
100
80
60
40
20
0
ppm

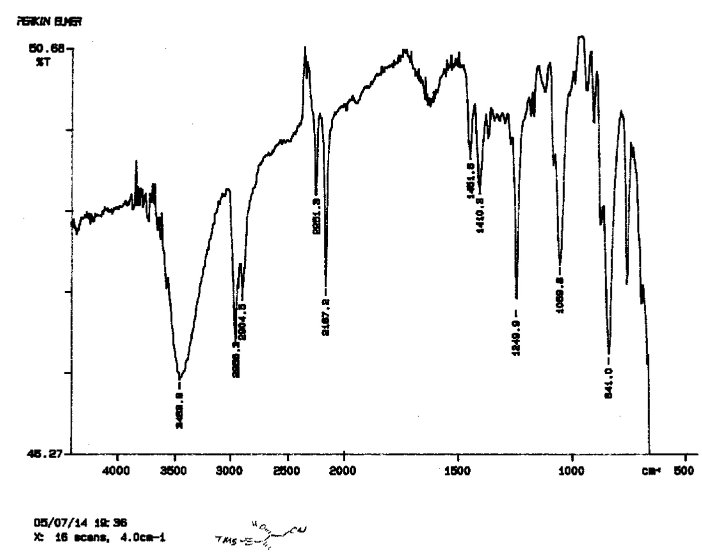

PERKIN ELMER
82.45
%T
-0.37
3054.6
2961.7
2868.7
2170.0
1458.0
1401.7
1372.9
1253.1
1179.4
1080.3
1065.8
870.2
844.5
795.9
760.6
650.2
646.9
1250.8
4000
3500
3000
2500
2000
1500
1000
500
cm-1
07/07/09 21:19
X: 4 scans, 4.0cm-1

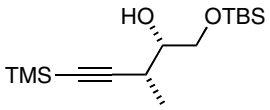


17

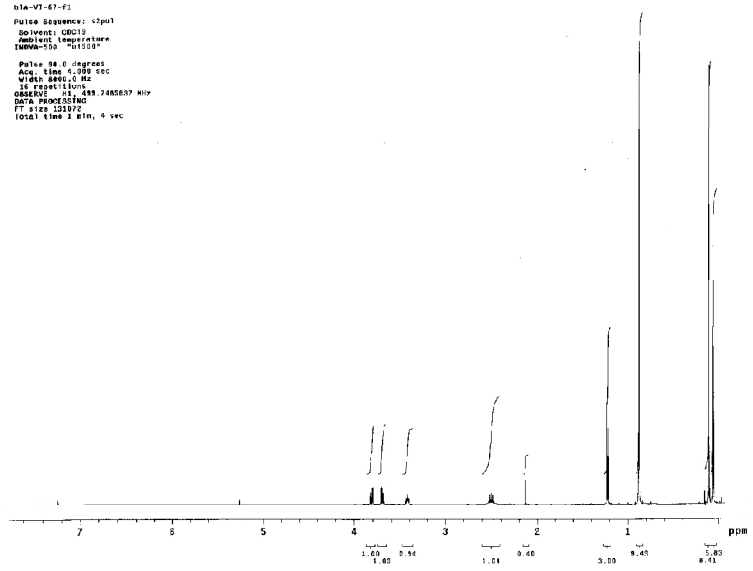


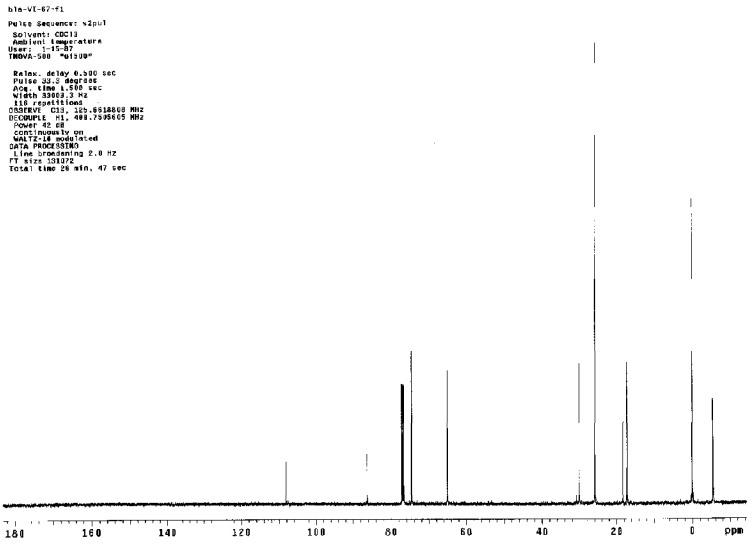


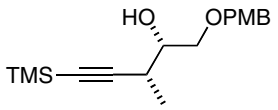



HO
OTBS
TMS

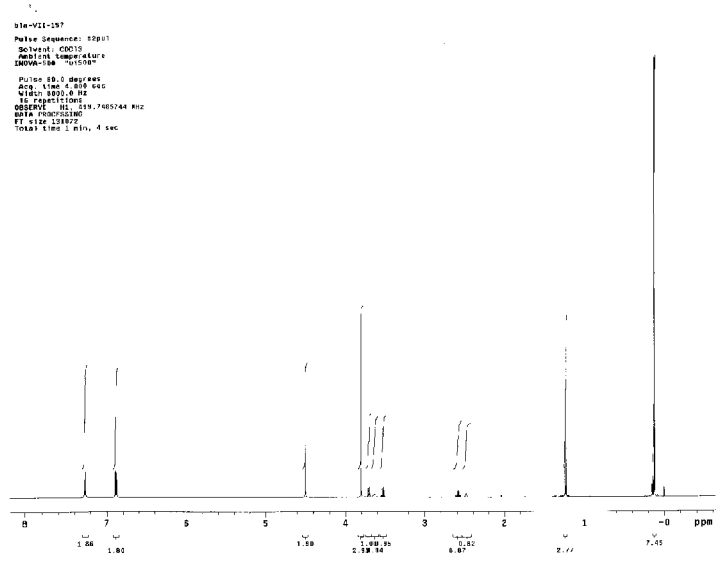
18

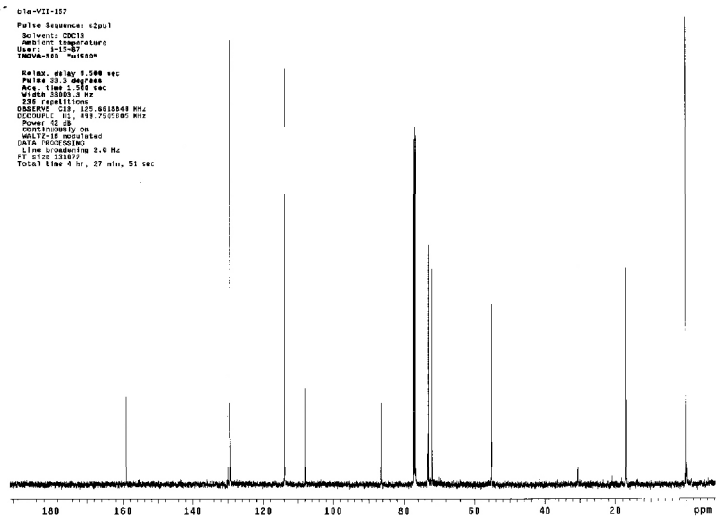

bla-VI-67-f1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ni500"
Pulse 90.0 degrees
Acq. time 4.099 sec
Width 6496.0 Hz
16 repetitions
OBSERVE H1, 499.7485837 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec
7
6
5
4
3
2
1
ppm
1.00
1.03
3.54
1.01
9.46
3.00
9.45
5.83
8.41

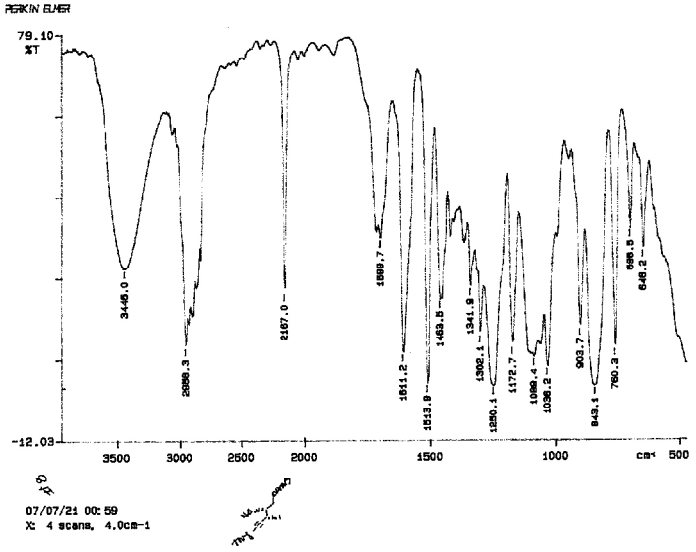

bla-VI-67-f1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: l-15-87
INOVA-500 "ni500"
Relax. delay 0.500 sec
Pulse 22.2 degrees
Acq. time 1.500 sec
Width 33603.3 Hz
118 repetitions
OBSERVE C13, 125.6518808 MHz
DECOUPLE H1, 499.7595605 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 26 min, 47 sec
180
160
140
120
100
80
60
40
20
0
ppm

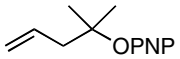

HO
OPMB
TMS

19

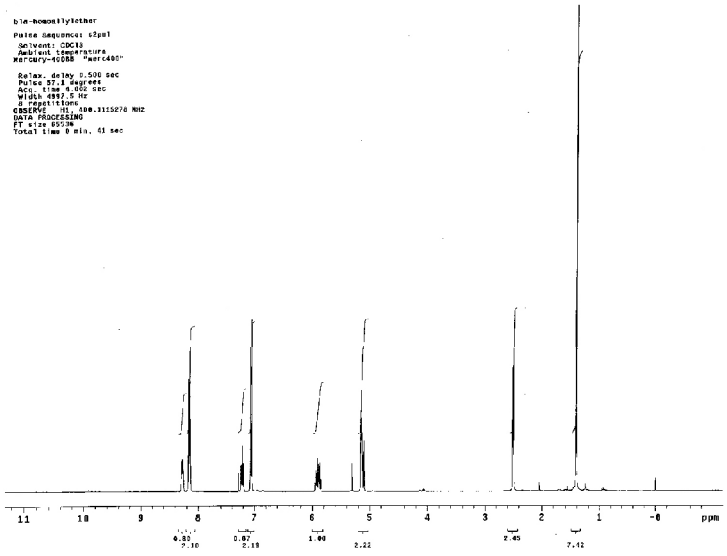


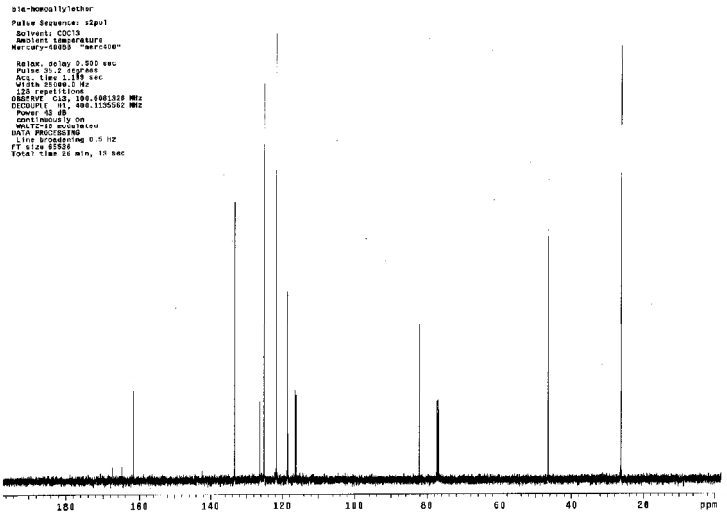


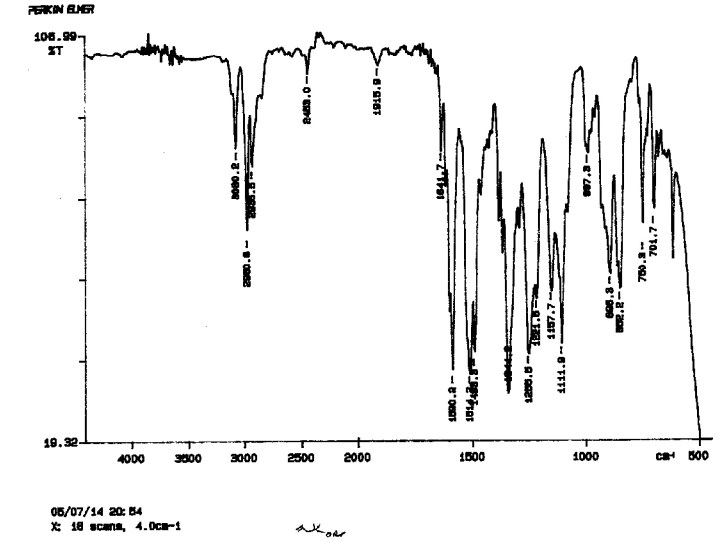

PERKIN ELMER
79.10
%T
-12.03
3445.0
2986.3
2187.0
1689.7
1611.2
1513.8
1463.5
1341.9
1302.1
1250.1
1172.7
1099.4
1038.2
903.7
849.1
760.3
696.5
648.2
3500
3000
2500
2000
1500
1000
cm-1
500
07/07/21 00:59
% 4 scans, 4.0cm-1

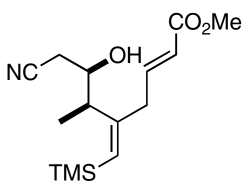

OPNP

20

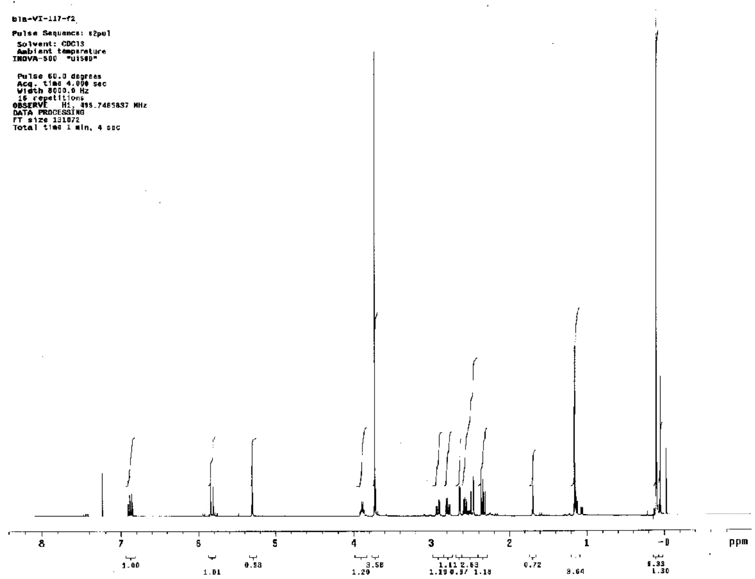

bis-homoallylether
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Relax. delay 0.500 sec
Pulse 37.1 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
8 repetitions
DATA PROCESSING
FT size 65536
Total time 0 min, 41 sec
ppm

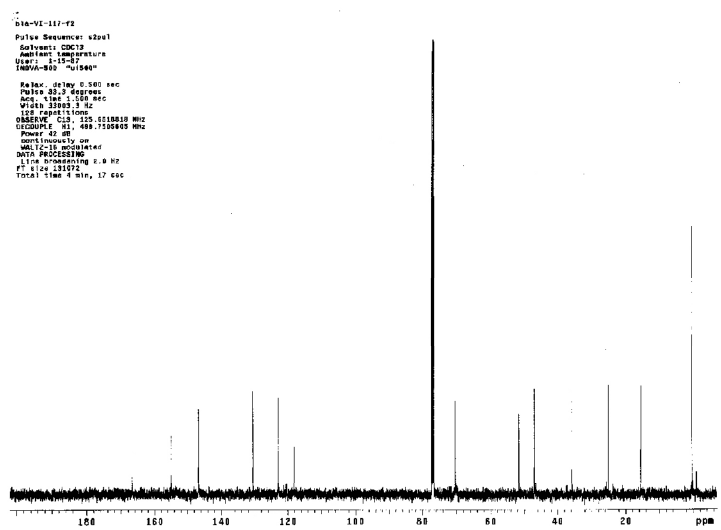

bis-homoallylether
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Relax. delay 0.500 sec
Pulse 35.2 degrees
Acq. time 1.119 sec
Width 25000.0 Hz
128 repetitions
Power 45 dB
continuously ON
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
ppm

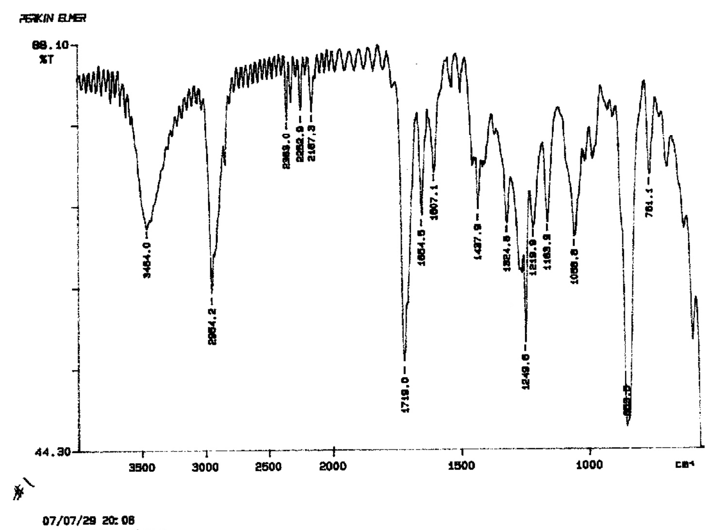

PERKIN ELMER
106.99
%T
19.32
cm-1
05/07/14 20:54
%: 16 scans, 4.0cm-1

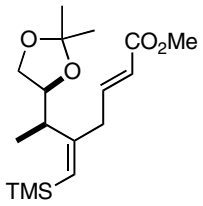


22c

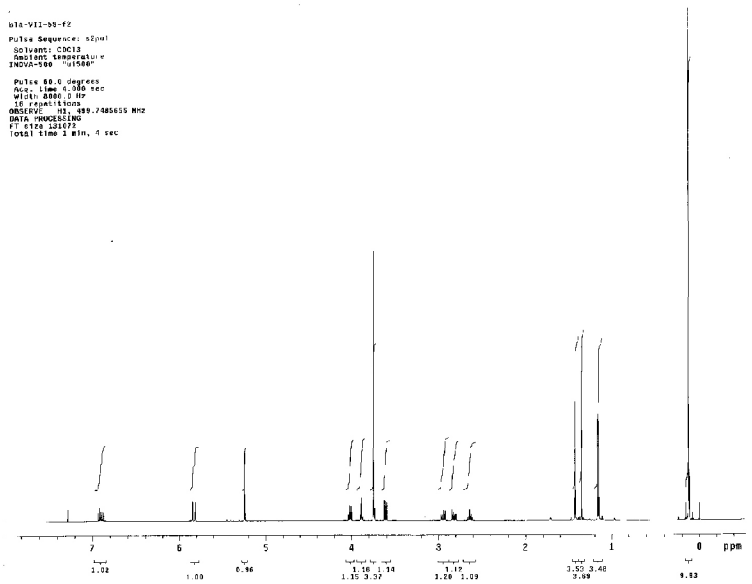


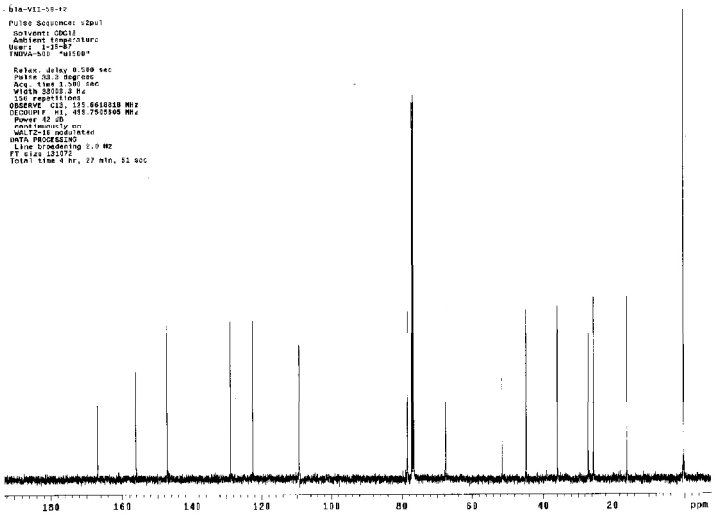


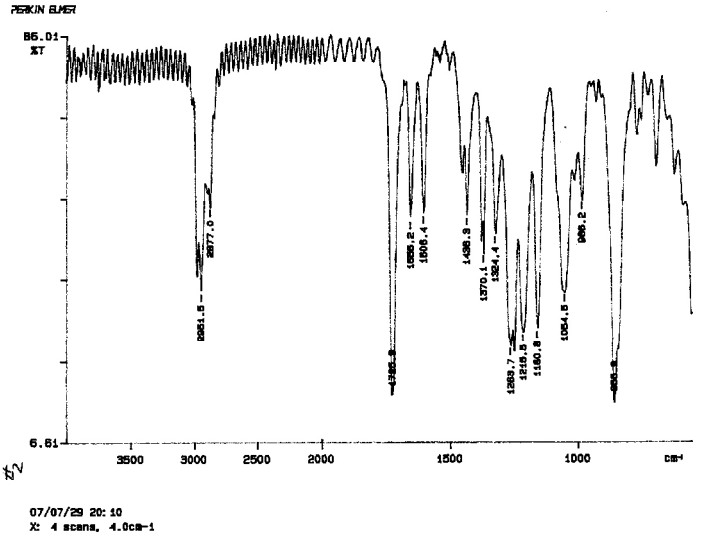




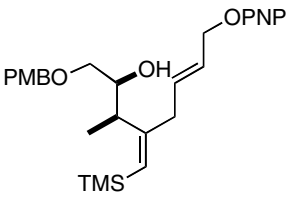
22d



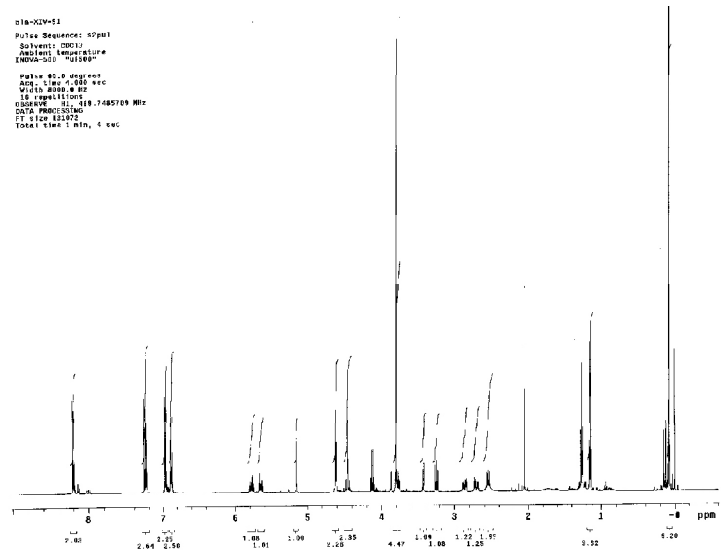


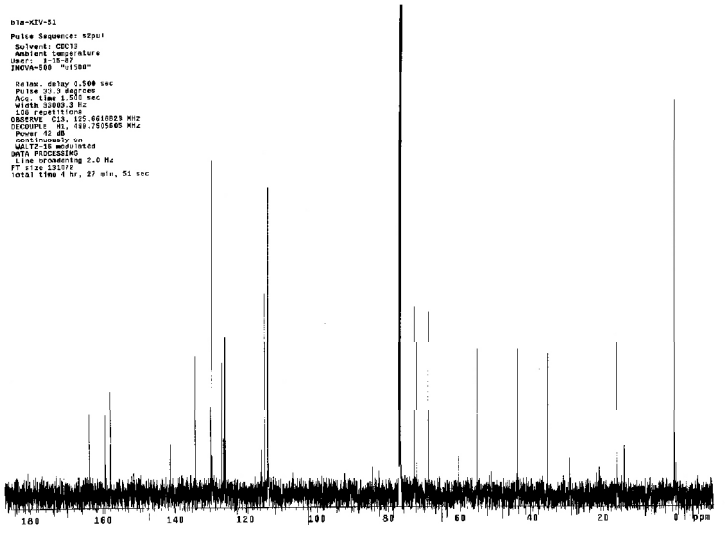


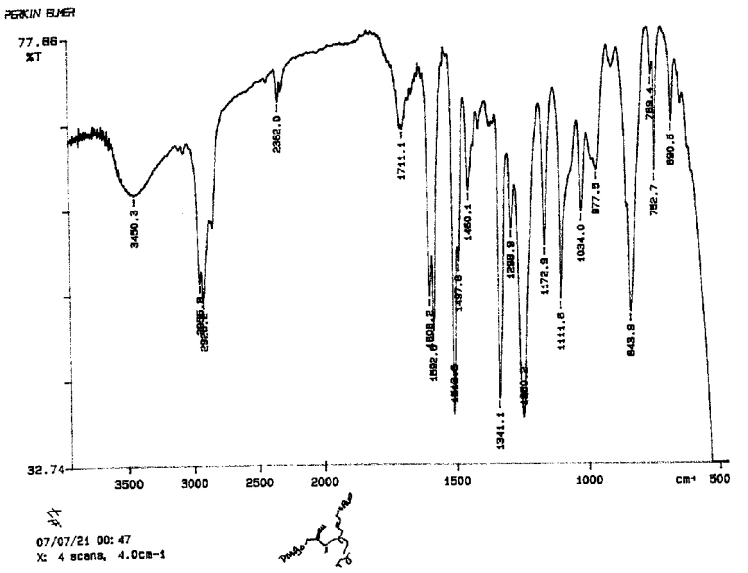
07/07/29 20:10
X: 4 scans, 4.0cm-1

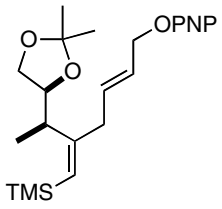

OPNP
PMBO
OH
TMS

22f

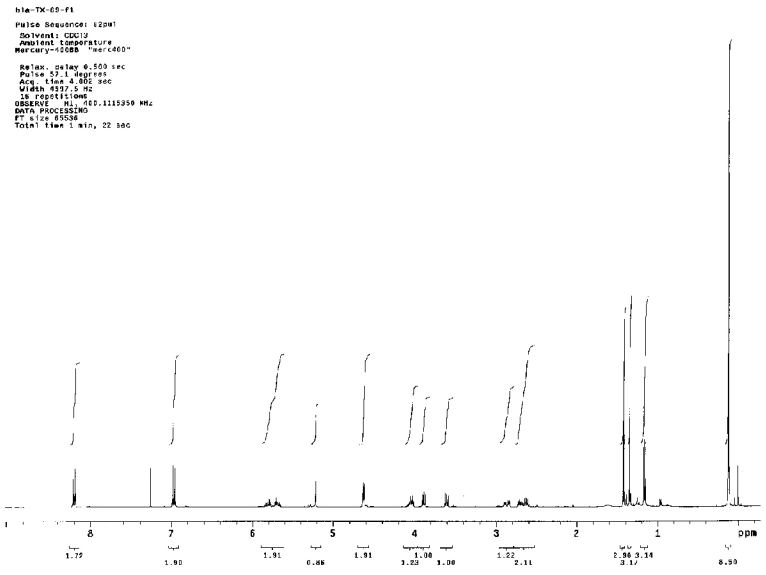


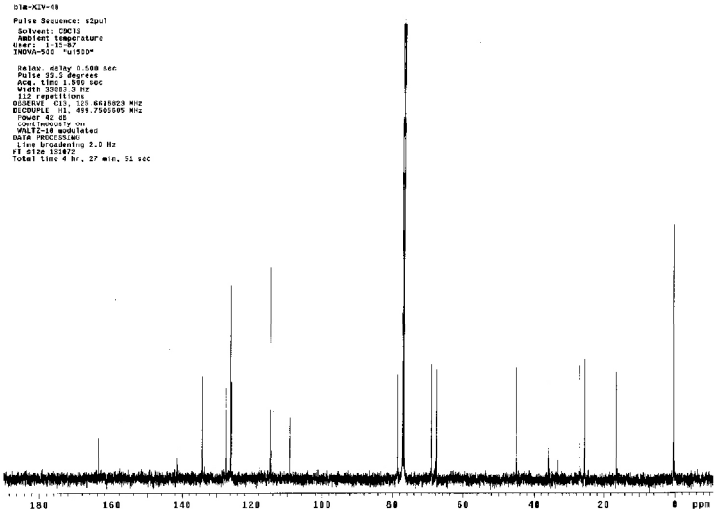


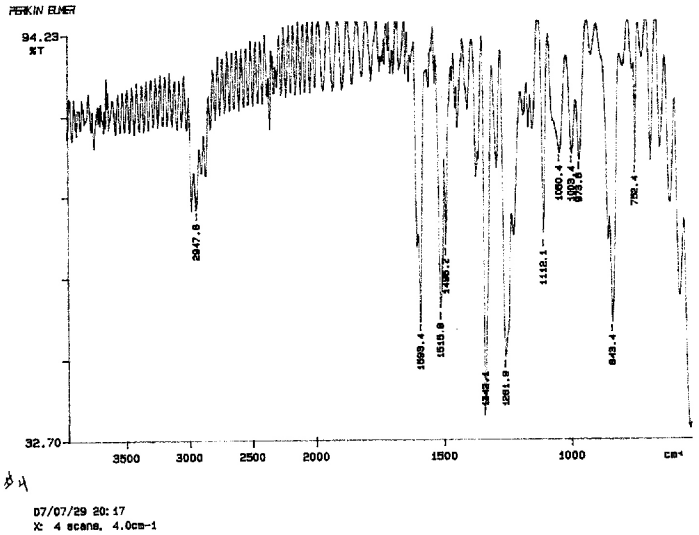

PERKIN ELMER
77.86
%T
32.74
3450.3
2362.0
1711.1
1460.1
1341.1
1034.0
877.5
643.8
890.6
3500
3000
2500
2000
1500
1000
cm-1
500
07/07/21 00:47
X: 4 scans, 4.0cm-1

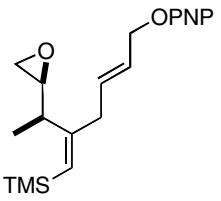

O
O
OPNP
TMS

22g

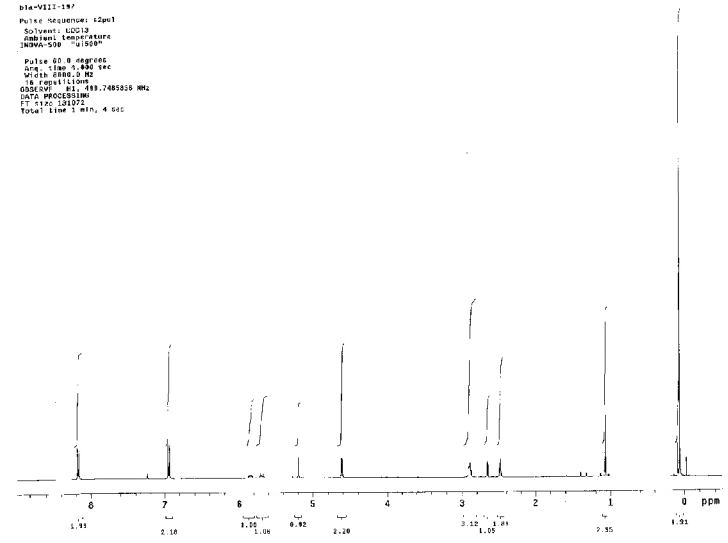

bla-TX-69-f1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 57.1 degrees
Acq. time 4.002 sec
Width 4197.5 Hz
16 repetitions
OBSERVE H1, 400.1115350 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 22 sec
8
7
6
5
4
3
2
1
ppm
1.79
1.90
1.91
0.86
1.91
1.08
1.23
1.00
1.22
2.11
2.36
3.14
3.17
8.90

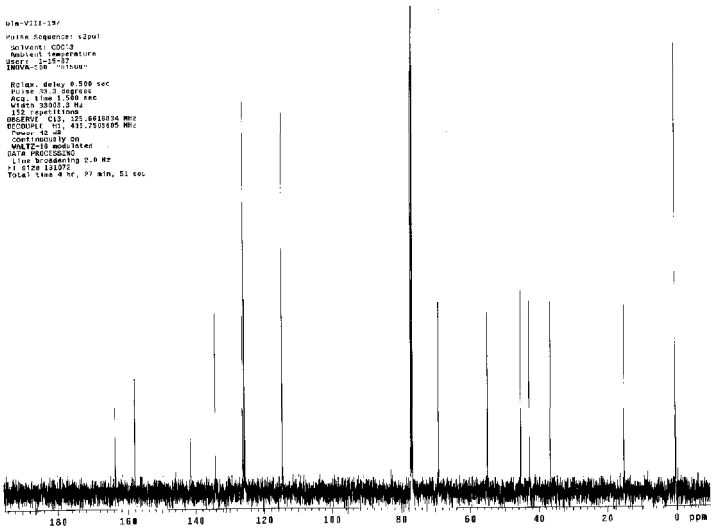

bla-XIV-69
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-12-07
INOVA-500 "u1500"
Relax. delay 0.500 sec
Pulse 30.0 degrees
Acq. time 1.990 sec
Width 33083.3 Hz
112 repetitions
OBSERVE C13, 125.6618828 MHz
DECOUPLE H1, 499.7902695 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
Data PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 4 hr, 27 min, 51 sec
180
160
140
120
100
80
60
40
20
0
ppm

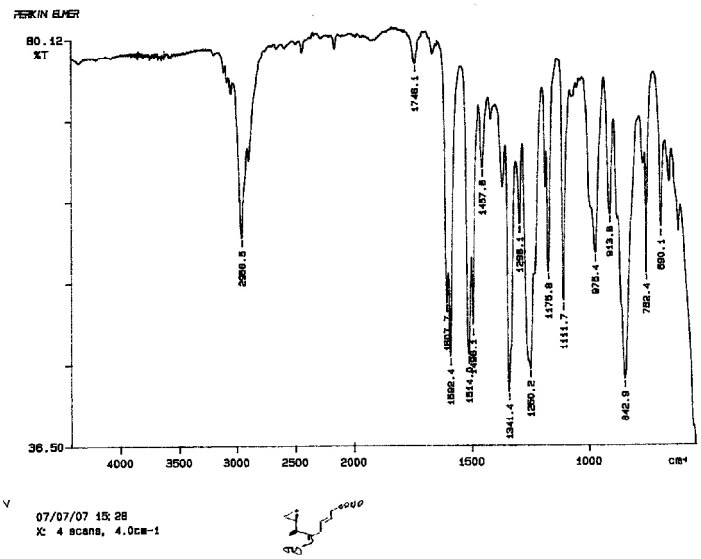

PERKIN ELMER
94.23
%T
32.70
2947.8
1599.4
1515.8
1468.7
1342.4
1261.9
1118.1
1060.4
1029.4
995.8
843.4
759.4
3500
3000
2500
2000
1500
1000
cm-1
07/07/29 20:17
X: 4 scans, 4.0cm-1

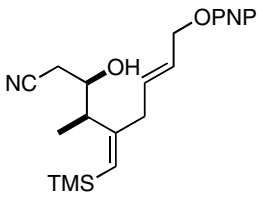

OPNP
O
TMS

22h

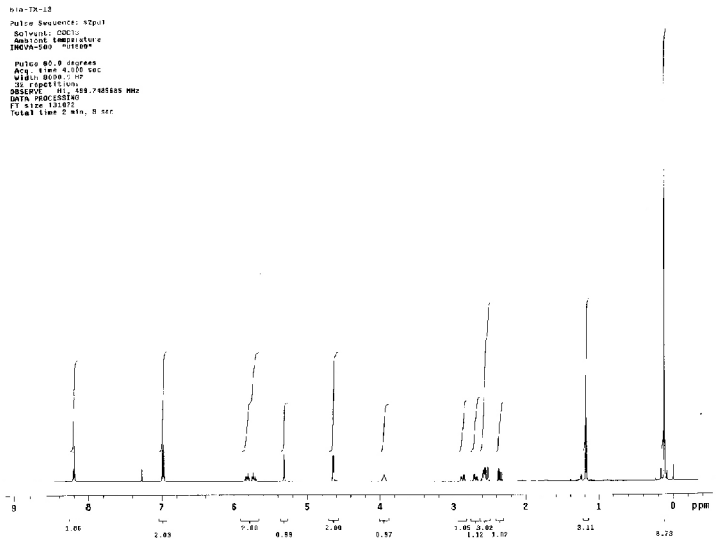


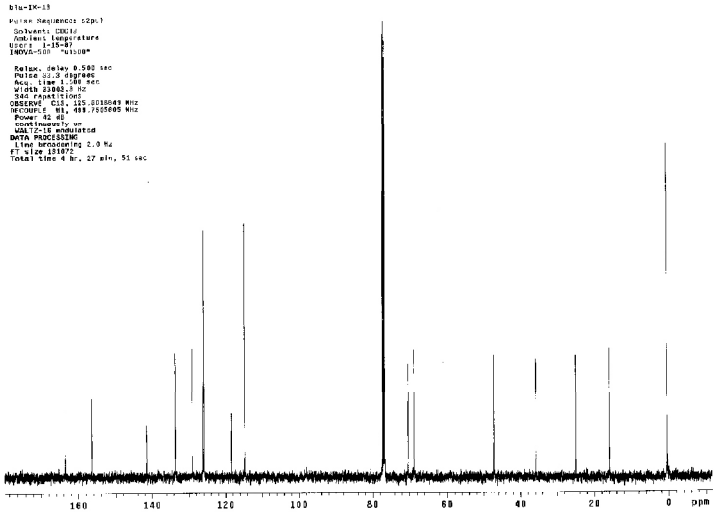


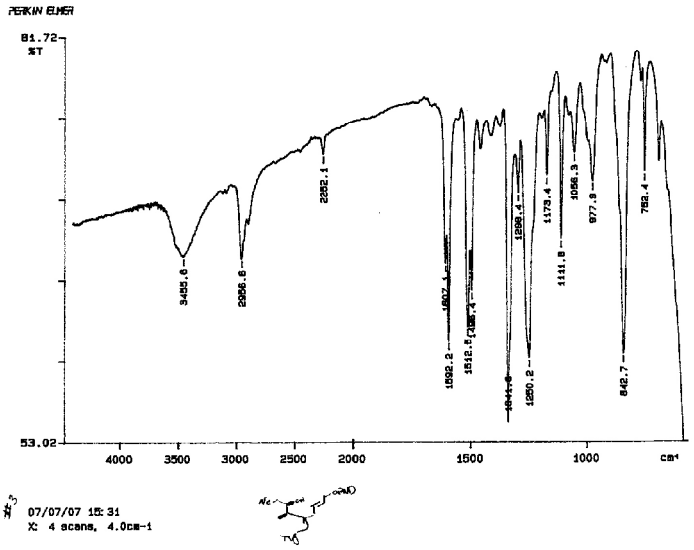

PERKIN ELMER
80.12
%T
36.50
4000
3500
3000
2500
2000
1500
1000
cm-1
2960.5
1748.1
1607.7
1582.4
1514.0
1457.8
1378.8
1341.4
1250.2
1111.7
915.8
842.9
782.4
680.1
07/07/07 15:28
4 scans, 4.0cm-1

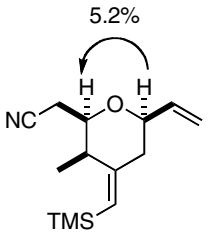

OPNP
OH
NC
TMS

22e

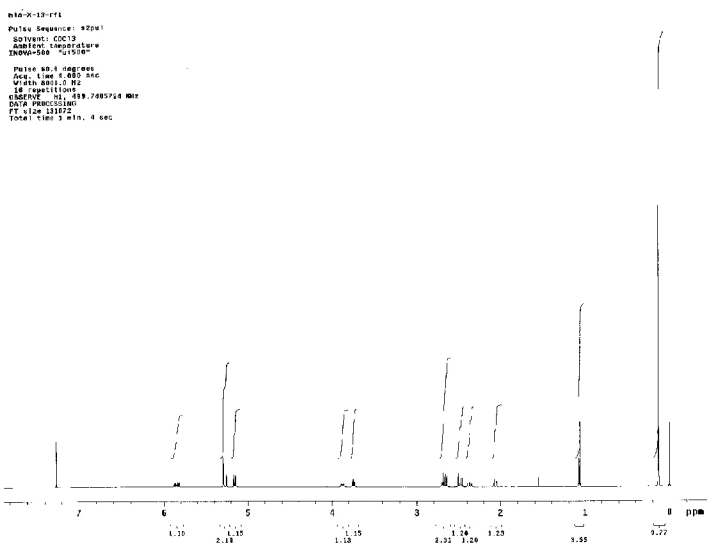

ppm

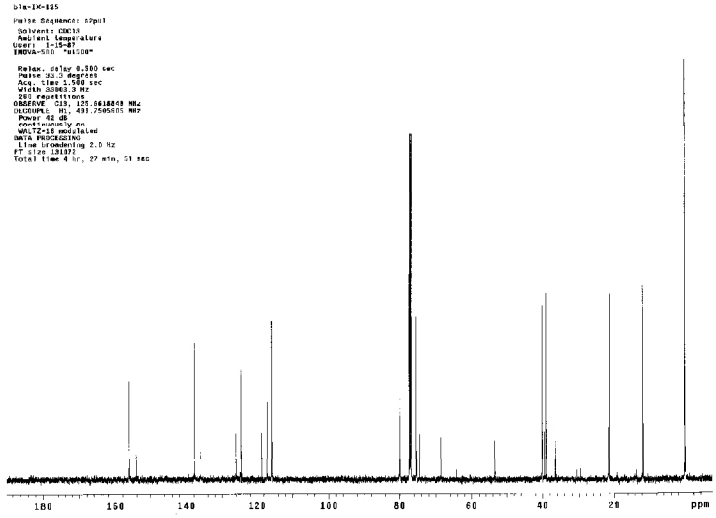

160
140
120
100
80
60
40
20
0
ppm

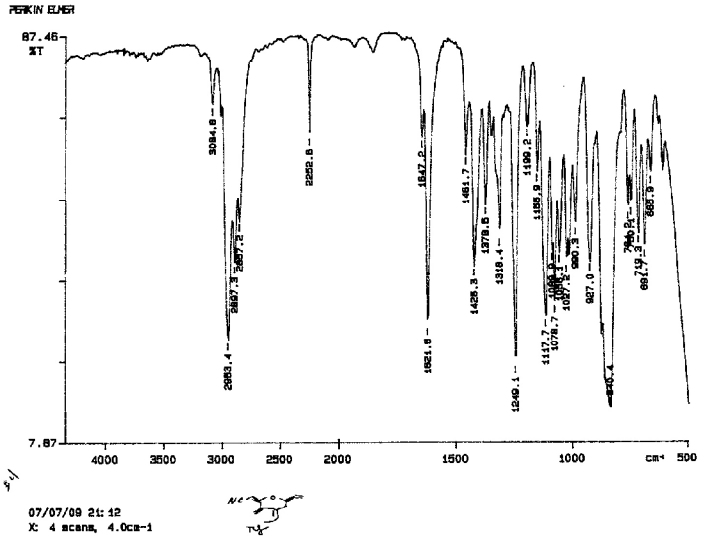

PERKIN ELMER
81.72
%T
53.02
3455.6
2956.8
2852.1
1602.2
1512.5
1250.2
1173.4
1056.3
977.8
842.7
782.4
4000
3500
3000
2500
2000
1500
1000
cm-1
07/07/07 15:31
X: 4 scans, 4.0cm-1

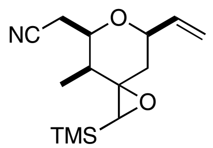

5.2%
H
H
O
NC
TMS

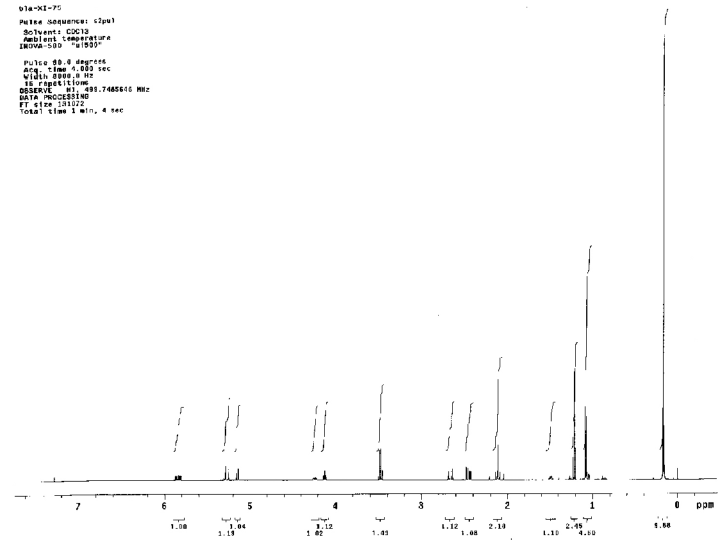
23

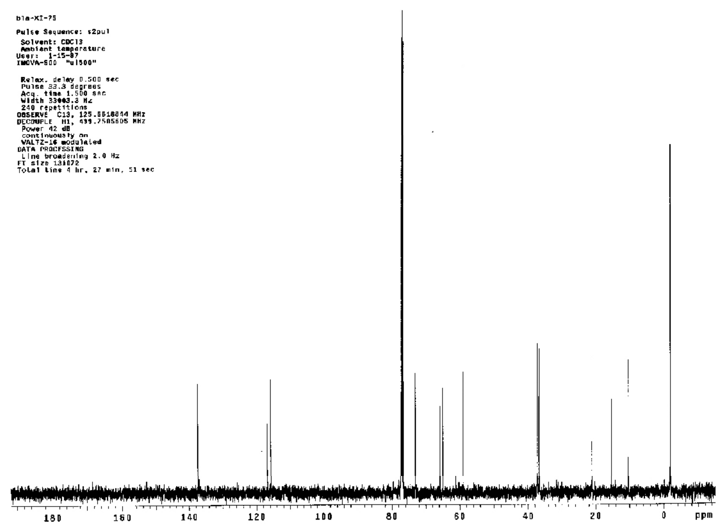


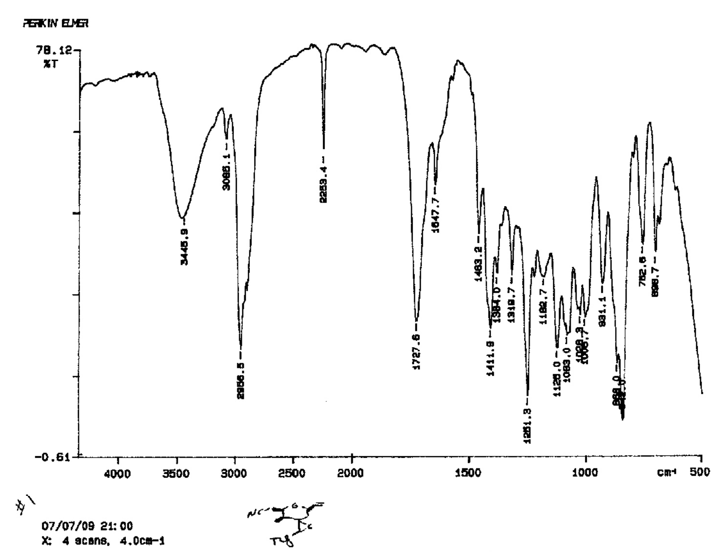


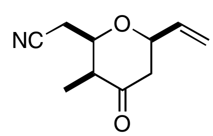

PERKIN ELMER
87.46
%T
7.87
4000
3500
3000
2500
2000
1500
1000
500
cm-1
3084.8
2967.3
2887.2
2083.4
2228.8
1647.2
1621.8
1481.7
1428.3
1378.6
1318.4
1249.1
1190.2
1155.9
1117.7
1076.7
1027.2
980.3
927.0
840.4
761.9
719.3
681.7
665.9
07/07/09 21:12
X: 4 scans, 4.0cm-1


NC
O
O
TMS

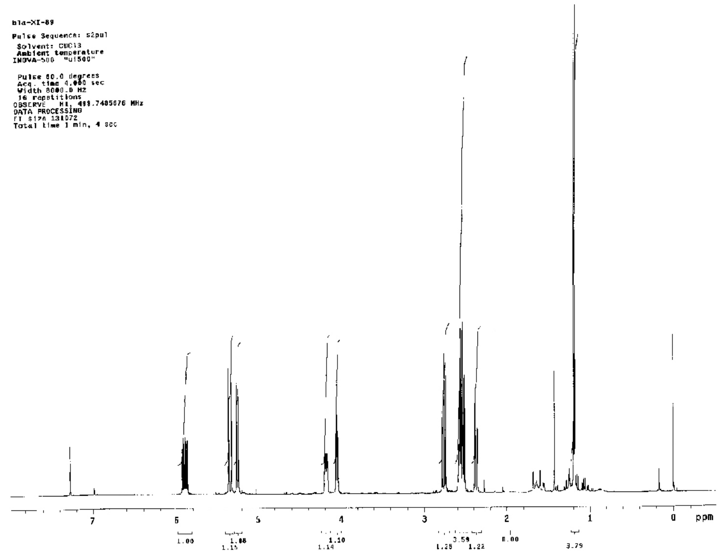


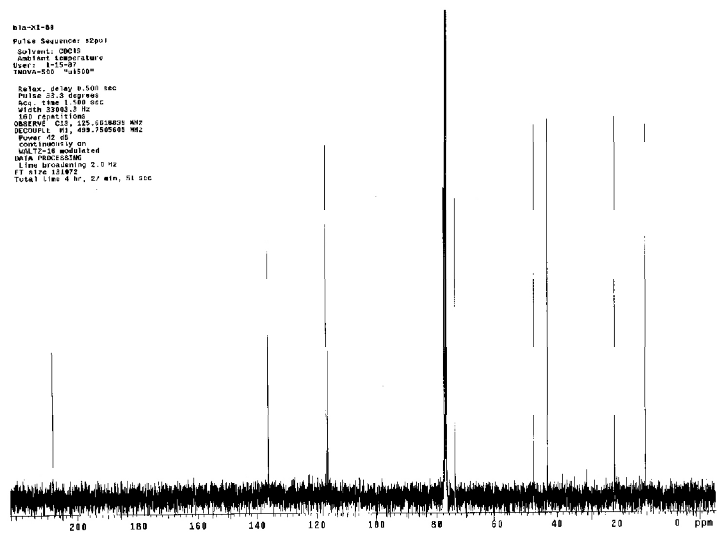


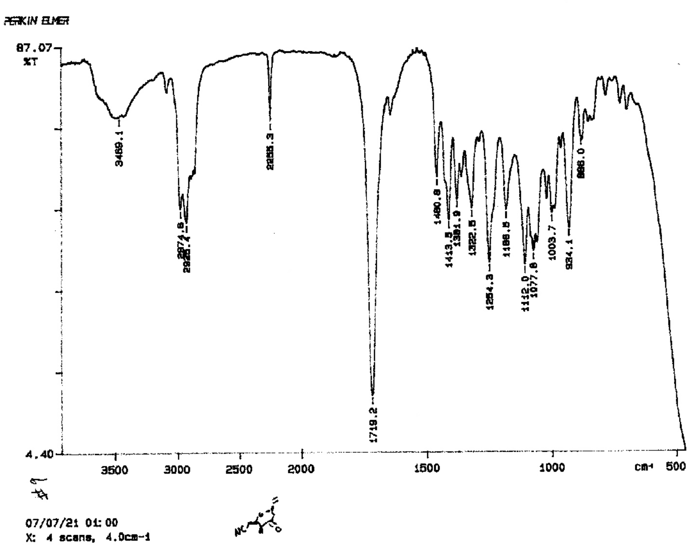

PERKIN ELMER
07/07/09 21:00
X: 4 scans, 4.0cm-1

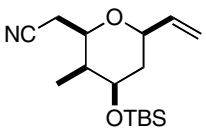

NC
O
O

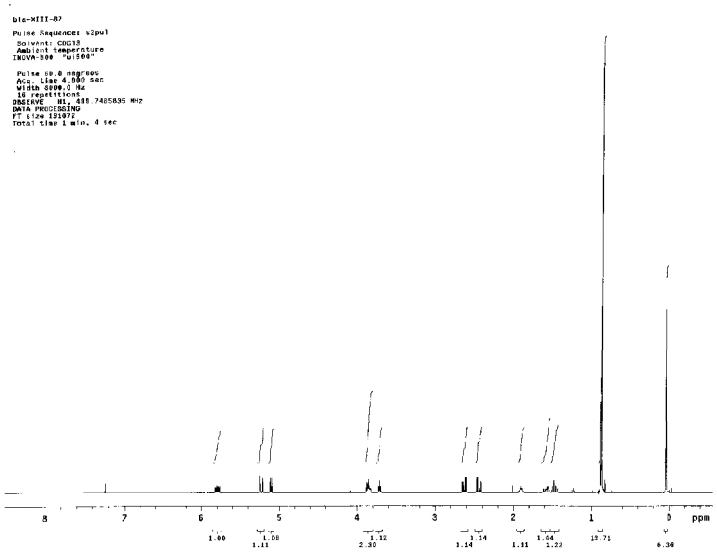
24

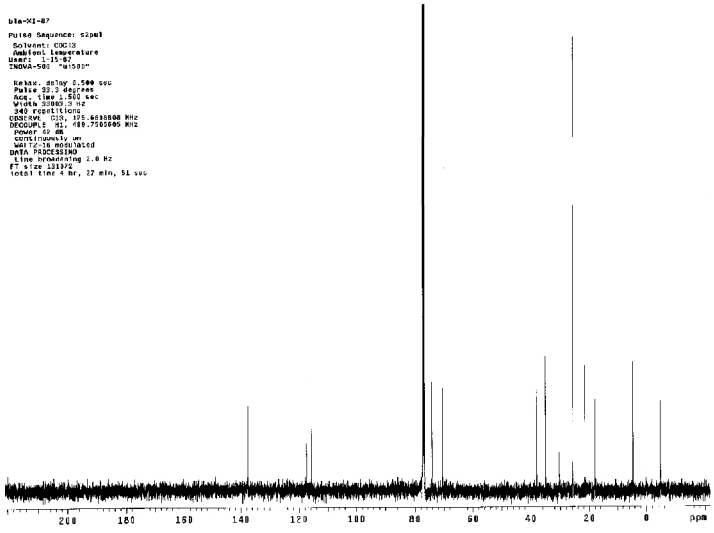

bla-XI-89
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "ui500"
Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.7485676 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec
7
6
5
4
3
2
1
0
ppm

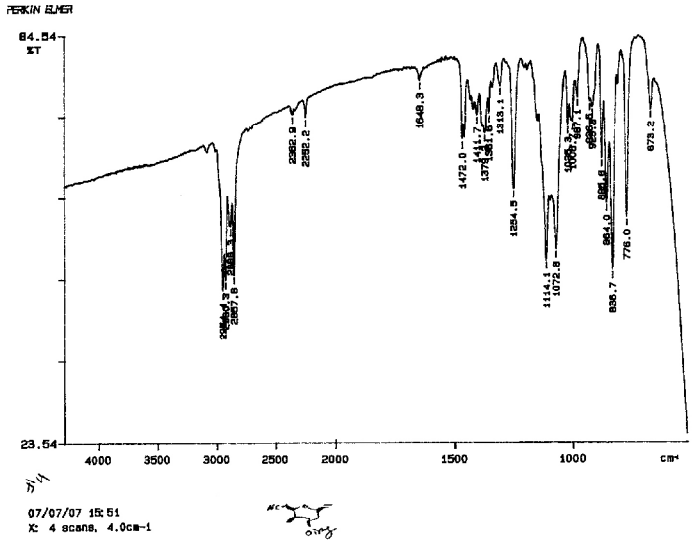

bla-XI-88
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-15-87
INOVA-500 "ui500"
Relax. delay 0.500 sec
Pulse 33.3 degrees
Acq. time 1.500 sec
Width 33003.3 Hz
160 repetitions
OBSERVE C13, 125.6618639 MHz
DECOUPLE H1, 499.7505605 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 4 hr, 27 min, 51 sec
200
180
160
140
120
100
80
60
40
20
0
ppm

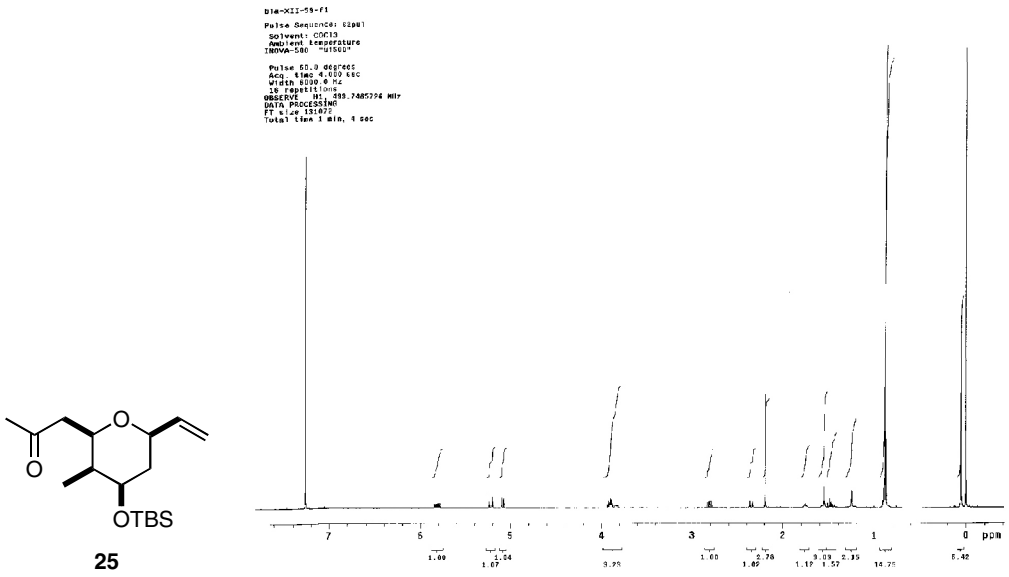

PERKIN ELMER
87.07
%T
3489.1
2974.8
2235.3
1719.2
1460.8
1413.5
1381.9
1322.5
1254.3
1188.5
1112.0
1077.8
1003.7
934.1
886.0
4.40
3500
3000
2500
2000
1500
1000
cm-1
500
07/07/21 01:00
X: 4 scans, 4.0cm-1


NC
O
OTBS

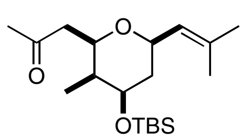

bla-XIII-87
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-300 "wi500"
Pulse 90.0 degrees
Acq. time 4.000 sec
Width 3000.0 Hz
16 repetitions
OBSERVE H1, 499.7485835 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec
8
7
6
5
4
3
2
1
0
ppm
1.00
1.08
1.11
1.32
2.30
3.14
1.14
1.64
1.11
1.64
1.22
19.71
6.30


bla-XI-87
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: l-15-07
INOVA-500 "wi500"
Relax. delay 2.500 sec
Pulse 32.3 degrees
Acq. time 1.500 sec
Width 33803.0 Hz
340 repetitions
OBSERVE C13, 125.6838868 MHz
DECOUPLE H1, 499.7505605 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 2.0 Hz
FT size 131072
total time 4 hr, 27 min, 51 sec
200
180
160
140
120
100
80
60
40
20
0
ppm


PERKIN ELMER
84.54
%T
23.54
4000
3500
3000
2500
2000
1500
1000
cm-1
2982.9
2892.2
1648.3
1472.0
1441.7
1381.6
1318.1
1254.5
1114.1
1072.8
1008.3
987.1
864.0
838.7
776.0
673.2
07/07/07 15:51
X: 4 scans, 4.0cm-1



25



6