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Stereoselective Synthesis of Tetracyclic Indolines via Gold-Catalyzed Cascade Cyclization Reactions

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General Methods. ^{1}H-NMR spectra were recorded on Varian 200 (200 MHz), Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = duplet, pd = pseudo duplet, t = triplet, pt = pseudo triplet, q = quartet, pq = pseudo quartet, br = broad, bs = broad singlet, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on a Varian 200 (50 MHz), Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: δ 77.0 ppm). GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: *m/z* (rel. intense). LC-electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was done with 240-400 mesh silica gel. Elemental analyses were carried out by using a EACE 1110 CHNOS analyzer. Supplementary crystallographic data (CCDC 814206-814207) for **2c** and **5a** can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Materials. All reactions were carried out under inert gas and under anhydrous conditions, if not further specified. Anhydrous solvents were supplied by Fluka in Sureseal® bottles and used without any further purification.

Targeted tosyl-tryptamines were synthesized in variable yields (50-86%), from the commercially available tryptamines, following conventional protocols. tryptamines/TsCl/TEA (1/1.2/2), CH_2Cl_2, rt,4 h.[1] 2-(1*H*-indol-3ylmethyl)-malonic acid dialkyl esters were synthesized as previously described.[2] Propargylic bromide **A** was synthesized from monoprotected butyn-1,4-diol following a conventional protocol. In a three-necked round bottomed flask, equipped with a dropping funnel, under nitrogen atmosphere, 10 mmol of monoprotected butyn-1,4-diol and 11 mmol of NBS were dissolved in 25 ml of DCM. At the same time, 11 mmol of PPh_3 were dissolved in 15 ml of DCM in the adding funnel and then the solution dropped at 0 °C. The suspension was allowed to warm up to r.t. and stirred for 2 hs. DCM was then removed under vacuum. The crude was then treated with 30 ml of pentane and stirred for 1 h. Afterwards the organic layer was filtered with a Gooch funnel and pentane removed under vacuum to afford propargylic bromide **A** with yields greater than 90% and NMR purity > 95%.

Synthesis of indolyl propargylic silyl ethers 1a'-j'

To a solution of 2-(2,5-disubstituted-1*H*-indole-3-ylmethyl) malonic acid dialkyl ester (1eq) in THF, NaH (60% suspension in mineral oil, 2 eq.) was added at 0 °C. The suspension was stirred for 30 min at 0 °C, then **2** (1.2 eq) was added drop-wise. The reaction was warmed up to room temperature and stirred for 3 h. After extractive work-up (H_2O/EtOAc) the organic layer was separated, dried with Na_2SO_4, filtrated and concentrated under vacuum. The residue

was purified by flash chromatography. Compounds **1f'**, **1g'** and **1i'** were not isolated and deprotected as reaction crudes.

1a': Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 8:2). Yield = 77%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.15 (s, 6H); 0.92 (s, 9 H); 1.23 (t, J = 7.2 Hz, 6H); 2.83 (s, 2H); 3.57 (s, 2H); 4.12-4.21 (m, 4H); 4.46 (s, 2H); 7.07-7.18 (m, 3H); 7.33 (d, J = 8.4 Hz, 1H); 7.67 (d, J = 7.6 Hz, 1H); 8.08 (s, 1H). LC-MS: 472 (M+1). 494 (M+Na).

1b': Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 8:2). Yield = 48%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.02 (s, 6H); 0.96 (s, 9H); 2.86 (s, 2H); 3.66 (s, 2H); 3.67 (s, 6H); 4.43 (t, J = 2.0 Hz , 2H); 6.99 (d, J = 2.0, Hz, 1H); 7.10 (ddd, J_1 = 18.0 Hz, J_2 = 8.0, Hz, J_3 = 1.2 Hz, 2H); 7.28 (d, J = 8.0 Hz, 1H); 7.59 (d, J = 8.0 Hz, 1H); 8,31 (s, 1H). LC-MS: 444 (M+1), 466 (M+Na).

1c': Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 8:2). Yield = 56%. ^{1}H-NMR (400 MHz,$CDCl_3$) δ: 0.10 (s, 6H); 0.87 (s, 9H); 1.43 (s, 9H); 2.75 (s, 2H); 3.47 (s, 2H); 4,36 (s, 2H); 7.05 (s, 1H); 7.09 (pt, J = 6.8 Hz, 1H); 7.16 (pt, J = 7.2 Hz, 1H); 7.32 (d, J = 8.0 Hz, 1H); 7.79 (d, J = 8.0 Hz, 1H); 8.10 (s,1H). LC-MS: 550 (M+Na).

1d': Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 8:2). Yield = 58%.^{1}H-NMR (400 MHz,$CDCl_3$) δ: 0.13-0.15 (m, 6H); 0.92-0.94 (m, 9H); 1.23-1.27 (m, 6H); 2.83 (t, J = 2.0 Hz, 2H); 3.55 (s, 2H); 4.12-4.21 (m, 4H); 4.38 (s, 2H); 6.99 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H); 7.03 (d, J = 2.4 Hz, 1H); 7.16 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H); 7.97 (s, 1H). LC-MS 486 (M); 509 (M+ Na).

1e'. Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 8:2). Yield = 60%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.13 (s, 6H); 0.90 (s, 9H); 1.26 (t, J = 7.2 Hz, 6H); 2.85 (s, 2H); 3.54 (s, 2H); 3.86 (s, 3H); 4.17 (q, J = 7.2 Hz, 4H); 4.35 (s, 2H); 6.83 (d, J = 8.8 Hz, 1H); 7.01 (d, J = 2.8 Hz, 1H); 7.19-7.27 (m, 2H); 7.95 (s, 1H). LC-MS: 502 (M+1).

1h'. Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 8:2). Yield = 46%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.14 (s, 6H); 0.91 (s, 9H); 1.27 (t, J = 7.2 Hz, 6H); 2.81 (s, 2H); 3.53 (s, 2H); 4.17 (q, J = 7.2 Hz, 4H); 4.39 (s, 2H); 7.10 (d, J = 2.4 Hz, 1H); 7.23-7.27 (m, 2H); 7.75 (d, J = 2.0 Hz, 1H); 8.13 (s, 1H). LC-MS: 552 (M+1), 573 (M+Na).

1j'. Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 8:2). Yield = 30%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.15 (s, 6H); 0.92 (s, 9H); 1.22 (t, J = 7.2 Hz, 6H); 2.40 (s, 3H); 2.81 (s, 3H); 3.51 (s, 2H); 4.15 (q, J = 7.2 Hz, 4H); 4.37 (t, J = 2.0 Hz, 2H); 7.01-7.10 (m, 2H); 7.22 (d, J = 8.4 Hz, 1H); 7.60 (d, J = 7.6 Hz, 1H); 7.80 (s, 1H). LC-MS: 486 (M+1).

Synthesis of indolyl propargylic alcohols 1a-j.

In a one-necked round bottom flask, the desired silyloxy compound **1'** was dissolved in 10 ml of reagent grade THF and then TBAF (1 eq.) was added at the reaction mixture. After stirring for 2-3 h, the reaction was monitored by TLC analysis and judged complete. After extractive work-up (H_2O/AcOEt), the collected organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude was purified by flash-chromatography.

1a. Yellow solid. Flash chromatography (CH_2Cl_2:MeOH = 95:5). Yield = 80%. Mp: 80- 82 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.23 (t, J = 7.2 Hz, 6H); 2.82 (s, 2H); 3.57 (s, 2H); 4.10-4.29 (m, 4H); 4.30 (s, 2H); 7.03 (d, J = 2.0 Hz,1H); 7.11 (ddd, J_1 = 18.6 Hz, J_2 = 8.0 Hz, J_3 = 1.2 Hz, 2H); 7.32 (d, J = 1.2 Hz, 1H); 7.64 (d, J = 8.0 Hz, 1H); 8.28 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9(2C), 23.1, 27.3, 50.9, 58.2, 61.6(2C), 81.4, 82.0, 109.4, 111.1, 118.7, 119.3, 121.9, 123.6, 128.0, 135.8, 170.3(2C). LC-MS: 340 (M-H_2O); 358 (M+1); 380 (M+Na). Anal. calcd for ($C_{20}H_{23}NO_5$: 357.40): C, 67.21; H, 6.49; N: 3.92. Found: C, 67.15; H, 6.50; N: 3.88.

1b. Viscous yellow oil. Flash chromatography (DCM:MeOH = 95:5). Yield = 90%. ^{1}H-NMR (400 MHz,$CDCl_3$) δ: 2.86 (s, 2H); 3.56 (s, 2H); 3.67 (s, 6H); 4.27 (t, J = 2.0 Hz, 2H); 7.00 (d, J = 2.0 Hz, 1H); 7.10 (ddd, J_1 = 18.0 Hz, J_2 = 8.0 Hz, J_3 = 1.2 Hz, 2H); 7.28 (d, J = 8.0 Hz, 1H); 7.59 (d, J = 8.0 Hz ,1H); 8,31 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 23.1, 27.5, 51.0, 52.7, 52.8(2C), 81.1, 82.1, 109.1, 111.1, 118.6, 119.4, 121.9, 123.6, 127.9, 135.8, 170.7(2C). LC-MS: 330 (M+1); 352 (M+Na). Anal. calcd for ($C_{18}H_{19}NO_5$: 329.35): C, 65.64; H, 5.81; N: 4.25. Found: C, 65.55; H, 5.70; N: 4.10.

1c. White solid. Flash chromatography (DCM:MeOH = 95:5). Yield = 72%. Mp: 117-119 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.44 (s, 18H); 2.76 (s, 2H); 3.48 (s, 2H); 4,28 (s, 2H); 7.04 (s, 2H); 7.13 (ddd, J_1 = 17.0 Hz, J_2 = 8.0 Hz, J_3 = 1.2 Hz, 2H); 7.31 (dd, J = 8.0 Hz, J_2 = 1.2 Hz, 1H); 7.77 (d, J = 8.0 Hz, 1H); 8.13 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 23.2, 26.7, 27.8(6C), 51.3, 52.8, 81.6(2C), 81.8, 82.2, 110.1, 110.9, 119.3, 121.9(2C), 123.2, 128.4, 135.7, 169.5(2C). LC-MS: 302 (M-CO_2tBu); 436 (M+Na). Anal. calcd for ($C_{24}H_{31}NO_5$: 413.51): C, 69.71; H, 7.56; N: 3.39. Found: C, 69.68; H, 7.43; N: 3.25.

1d. Yellow amorphous solid. Flash chromatography (DCM:MeOH = 95:5). Yield = 91%. ^{1}H-NMR (400 MHz,$CDCl_3$) δ: 1.26 (t, J = 7.2 Hz, 6H); 2.44 (s, 3H); 2.83 (t, J = 2.0 Hz, 2H); 3.55 (s, 2H); 4.12-4.24 (m, 4H); 4.31 (s, 2H); 6.99-7.01 (m, 2H); 7.22 (d, J = 8.4 Hz, 1H); 7.45 (s,

1H); 7.96 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.1(2C), 21.6, 23.2, 27.4, 51.3, 58.2, 61.8 (2C), 81.6, 82.2, 108.9, 110.9, 118.6, 123.6, 123.8, 128.4, 128.6, 134.3, 170.5(2C). LC-MS: 372 (M+1), 394 (M+Na). Anal. calcd for ($C_{21}H_{25}NO_5$: 371.43): C, 67.91; H, 6.78; N: 3.77. Found: C, 67.80; H, 6.66; N: 3.85.

1e. Viscous orange oil. Flash chromatography (DCM:MeOH = 95:5). Yield = 45%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.23 (t, J = 7.2 Hz, 6H); 2.8 (s, 2H); 3.53 (s, 2H); 3.86 (s, 3H); 4.16 (q, J = 7.2 Hz, 4H); 4.30 (s, 2H); 6.83 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H); 6.97 (d, J = 2.4 Hz, 1H); 7.20 (dd, J_1 = 5.8 Hz, J_2 = 2.8 Hz 2H); 8.10 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9, 14.1, 30.9, 51.1, 55.8, 58.5, 60.4, 61.6(2C), 81.7, 82.0, 100.9, 109.4, 111.7, 112.2, 124.1, 128.7, 131.0, 154.0, 170.2(2C). LC-MS: 388 (M+1), 410 (M+Na). Anal. calcd for ($C_{21}H_{25}NO_6$: 387.43): C, 65.10; H, 6.50; N: 3.62. Found: C, 65.01; H, 6.45; N: 3.70.

1f. Viscous yellow oil. Flash chromatography (DCM:MeOH = 95:5). Yield = 51% .^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.80 (t, J = 2.0 Hz, 2H); 3.54 (s, 2H); 3.74 (s, 6H); 4.33 (t, J = 2.4 Hz, 2H); 7.07 (d, J = 2.4 Hz, 1H); 7.13 (d, J = 2.0 Hz, 1H); 7.26 (d, J = 2.0 Hz, 1H); 7.62 (d, J = 2.0 Hz, 1H); 8.10 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 23.1, 27.3, 51.3, 52.8, 58.0(2C), 81.3, 82.3, 109.4, 112.1, 118.5, 122.4, 124.9, 125.4, 134.2, 159.0, 170.4(2C). LC-MS: 364 (M+1), 386 (M+Na). Anal. calcd for ($C_{18}H_{18}ClNO_5$: 363.79): C, 59.43; H, 4.99; N: 3.85. Found: C, 59.27; H, 5.06; N: 3.66.

1g. White solid. Flash chromatography (DCM:MeOH = 95:5). Yield = 60%. Mp = 107-109°C ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.26 (t, J = 7.2 Hz, 6H); 2.79 (t, J = 2.0 Hz, 2H); 4.12 (s, 2H); 4.12-4.24 (m, 4H); 4.33 (dt, J_1 = 4.0 Hz, J_2 = 2.0 Hz, 2H), 7.08 (d, J = 2.4 Hz, 1H), 7.12 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H); 7.14 (s, 1H); 7.26 (d, J = 2.8 Hz, 1H); 7.65 (d, J = 2.0 Hz, 1H); 8.12 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.0(2C), 23.0, 27.1, 51.3, 57.9, 61.8(2C), 81.5, 82.2, 112.1, 118.5, 122.3, 124.8, 125.3, 129.2, 132.0, 134.1, 170.1(2C). LC-MS: 392 (M+1), 414 (M+Na). Anal. calcd for ($C_{20}H_{22}ClNO_5$: 391.85): C, 61.30; H, 5.66; N: 3.57. Found: C, 61.19; H, 5.70; N: 3.40.

1h. Yellow solid. Flash chromatography (DCM:MeOH = 95:5). Yield = 74%. Mp = 124-126 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.27 (t, J = 7.2 Hz, 6H); 2.79 (s, 2H); 3.53 (s, 2H); 4.12-4.22 (m, 4H); 4.33 (s, 2H); 7.05 (d, J = 2.4 Hz, 1H); 7.22 (dd, J_1 = 20.8 Hz, J_2 = 8.0 Hz, 2H); 7.79 (s, 1H); 8.24 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9(2C), 22.9, 27.0, 51.2, 57.8, 61.8(2C), 81.3, 82.2, 109.2, 112.5, 112.7, 121.6, 124.7, 124.7, 129.8, 134.4, 170.1(2C). LC-MS: 436 (M), 437(M+1), 438 (M+2). Anal. calcd for ($C_{20}H_{22}BrNO_5$: 436.30): C, 55.06; H, 5.08; N: 3.21. Found: C, 55.11; H, 5.12; N: 3.10.

1i. Viscous white oil. Flash chromatography (DCM:MeOH = 95:5). Yield = 60%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.24 (t, J = 7.2 Hz, 6H); 2.81 (t, J = 1.6 Hz, 2H), 3.53 (s, 2H); 4.12-4.24

(m, 4H); 4.31 (s, 2H); 7.04 (d, J = 2.0 Hz, 1H); 7.07 (dd, J_1 = 8.4 Hz, J_2= 1.6 Hz, 1H); 7.33 (d, J = 1.6 Hz, 1H); 7.56 (d, J = 8.0 Hz, 1H); 8.12 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.0(2C), 23.1, 27.2, 51.3, 58.1, 61.7(2C), 81.4, 82.1, 109.9, 111.0, 119.8, 120.3, 124.1, 126.7, 128.0, 136.2, 170.1(2C). LC-MS: 414 (M+Na). Anal. calcd for ($C_{20}H_{22}ClNO_5$: 391.85): C, 61.30; H, 5.66; N: 3.57. Found: C, 61.33; H, 5.75; N: 3.51.

1j. Viscous orange oil. Flash chromatography (DCM:MeOH = 95:5). Yield = 74%. ^{1}H-NMR (400 MHz $CDCl_3$) δ: 1.15 (t, J = 7.2 Hz, 6H); 2.27 (s, 3H); 2.73 (s, 3H); 3.44 (s, 2H); 4.12 (q, J = 7.2 Hz, 4H); 4.22 (s, 2H); 6.96-7.00 (m, 2H); 7.13 (d, J = 8.0 Hz, 1H); 7.50 (d, J = 8.0 Hz, 1H); 7.85 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 12.0, 13.9(2C), 23.1, 26.8, 51.2, 58.6, 61.6(2C), 81.9, 82.0, 105.5, 110.0, 118.3, 119.1, 121.1, 129.3, 133.6, 135.2, 170.5(2C). LC-MS: 371 (M+1); 394 (M+Na). Anal. calcd for ($C_{21}H_{25}NO_5$: 371.43): C, 67.91; H, 6.78; N: 3.77. Found: C, 67.95; H, 6.70; N: 3.67.

Synthesis of indolyl alcohols 4.

In a Schlenk tube equipped with a magnetic stirring bar, (4-bromo-but-2-ynyloxy)-*tert*-butyl-dimethyl-silane **A** (1.2 eq.), was added to the corresponding *N*-tosyl tryptamine (1 eq.), K_2CO_3 (2 eq.) dissolved in 5 ml of acetone.[3] The reaction mixture was stirred at 60 °C for 12 h, and then quenched with water. The aqueous layer was extracted with ethyl acetate (3× 15 ml). The combined organic layers were dried with Na_2SO_4 and the solvents evaporated under vacuum. The residue was purified by flash-chromatography.

4a'. Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 80:20). Yield = 50%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.05 (s, 6H); 0.87 (s, 9H); 2.40 (s, 3H); 3.08 (t, J = 7.6 Hz, 2H); 3.51 (t, J = 7.6 Hz, 2H); 4.08 (s, 2H); 4.20 (s, 2H); 7.10-7.24 (m, 5H); 7.37 (d, J = 8.1 Hz, 1H); 7.62 (d, J = 7.6 Hz, 1H); 7.73 (d, J = 8.0 Hz, 2H); 8.01 (s, 1H). LC-MS: 497 (M+1).

4b'. Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 80:20). Yield = 35%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.05 (s, 6H); 0.87 (s, 9H); 2.41 (s, 3H); 3.02 (t, J = 7.2 Hz, 2H); 3.48 (t, J = 7.2 Hz, 2H); 4.11 (t, J = 2.0 Hz, 2H); 4.19 (t, J = 2.0 Hz, 2H); 7.15 (pt, J = 2.0 Hz, 2H); 7.26-7.28 (m, 4H); 7.52 (d, J = 2.0 Hz, 1H); 7.33 (d, J = 8.0 Hz, 1H); 8.07 (s, 1H). LC-MS: 533 (M+1).

4c'. Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 90:10). Yield = 37%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.048 (s, 6H); 0.88 (s, 9H); 2.40 (s, 3H); 3.31 (t, J = 8.4 Hz, 2H); 3.49 (t, J = 8.4 Hz, 2H); 3.88 (s, 3H); 3.96 (t, J = 2.0

Hz, 2H); 4.18 (t, J = 2.0 Hz, 2H); 6.87 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H); 7.07 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H); 7.24-7.28 (m, 3H); 7.72 (d, J = 7.2 Hz, 2H); 7.92 (br, 1H). LC-MS: 527 (M+1), 549 (M+Na).

4d'. Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 91:9). Yield = 44%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.048 (s, 6H); 0.88 (s, 9H); 2.40 (s, 3H); 3.06 (t, J = 7.2 Hz, 2H); 3.49 (t, J = 7.2 Hz, 2H); 3.75 (s, 3H); 4.08 (t, J = 2.0 Hz, 2H); 4.21 (t, J = 2.0 Hz, 2H); 6.94 (s, 1H); 7.09-7.13 (m, 1H); 7.22-7.31 (m, 5H); 7.60 (d, J = 8.0 Hz, 2H); 7.71 (d, J = 8.0 Hz, 2H). LC-MS: 533 (M+Na).

The cleavage of the silyl protecting group was performed in analogy to the previously described method for **1'**.

4a. White solid. Flash-chromatography (DCM:MeOH = 95:5). Yield: 70%. Mp = 109-111 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.32 (s, 3H); 2.99 (t, J = 7.6 Hz, 2H); 3.43 (t, J = 7.6 Hz, 2H); 3.90 (s, 2H); 4.08 (s, 2H); 7.00-7.13 (m, 5H); 7.28 (d, J = 7.2 Hz, 1H); 7.52 (d, J = 7.2 Hz, 1H); 7.64 (dd, J_1 = 6.6 Hz, J_2 = 2.0 Hz, 2H); 8.01 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 21.5, 24.4, 37.1, 47.1, 50.7, 78.8, 83.7, 111.2, 112.3, 118.6, 119.4, 122.1, 122.3, 127.2, 127.8(2C), 129.4(2C), 135.9, 136.2, 143.5. LC-MS: 383 (M+1),405 (M+Na). Anal. calcd for ($C_{21}H_{22}N_2O_3S$: 382.48): C, 65.95; H, 5.80; N: 7.32. Found: C, 65.88; H, 5.89; N: 7.22.

4b. Pale yellow wax. Flash-chromatography (DCM:MeOH = 95:5). Yield: 60%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.41 (s, 3H); 2.99 (t, J = 8.0 Hz, 2H); 3.48 (t, J = 8.0 Hz, 2H); 4.05 (s, 2H); 4.16 (s, 2H); 7.11 (s, 1H); 7.13 (d, J = 2.0 Hz, 1H); 7.26-7.28 (m, 3H); 7.51 (d, J = 1.6 Hz, 1H); 7.71 (d, J = 8.0 Hz, 2H); 8.27 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 21.6, 24.2, 37.1, 46.9, 50.9, 78.8, 84.1, 112.2, 112.4, 118.2, 122.5, 123.9, 125.3, 127.9 (2C), 128.5, 129.6 (2C), 134.6, 135.9, 143.7. LC-MS: 439 (M+Na). Anal. calcd for ($C_{21}H_{21}ClN_2O_3S$: 416.92): C, 60.50; H, 5.08; N: 6.72. Found: C, 60.41; H, 5.00; N: 6.85.

4c. Yellow viscous oil. Flash-chromatography (*c*Hex:EtOAc = 60:40). Yield: 71%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.40 (s, 3H); 3.04 (t, J = 8.0 Hz, 2H); 3.50 (t, J = 8.0 Hz, 2H); 3.87 (s, 3H); 4.00 (s, 2H); 4.19 (s, 2H); 6.87 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H); 7.06 (d, J = 2.4 Hz, 1H); 7.14 (d, J = 2.4 Hz, 1H); 7.25-7.27 (m, 3H); 7.73 (d, J = 8.0 Hz, 2H); 8.00 (br, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 21.4, 24.4, 37.1, 46.8, 50.6, 56.1, 78.6, 84.0, 101.4, 111.6, 111.9, 111.9, 123.2, 127.7(2C), 129.4(2C), 131.5, 135.9, 143.5, 153.8. LC-MS: 413 (M+1), 435 (M+Na). Anal. calcd for ($C_{22}H_{24}N_2O_3S$: 412.50): C, 64.06; H, 5.86; N: 6.79. Found: C, 64.15; H, 5.79; N: 6.71.

4d. White wax. Flash-chromatography (DCM:MeOH = 95:5). Yield: 43%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.41 (s, 3H); 3.07 (t, J = 7.2 Hz, 2H); 3.50 (t, J = 7.2 Hz, 2H); 3.76 (s, 3H); 3.99 (s, 2H); 4.19 (t, J = 1.6 Hz, 2H); 6.96 (s, 1H); 7.11 (ddd, J_1 = 8.0 Hz, J_2 = 7.2 Hz, J_3 = 1.2 Hz, 1H); 7.23-7.51 (m, 4H); 7.60 (d, J = 8.0 Hz, 1H); 7.73 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 1H). ^{13}C-NMR

(100 MHz, $CDCl_3$) δ: 24.3, 29.7, 37.1, 47.2, 50.8, 78.9, 83.7, 109.3 110.7, 118.7, 118.9, 121.7, 127.0, 127.7, 127.9, 129.3(2C); 136.0, 137.0, 143.5. LC-MS: 397 (M+1). Anal. calcd for ($C_{22}H_{24}N_2O_3S$: 396.50): C, 66.64; H, 6.10; N: 7.07. Found: C, 66.55; H, 6.01; N: 7.15.

General procedure for the gold-catalyzed diastereoselective domino cyclization.

In a 10 ml two-necked round bottomed flask, substrate **1/4** (0.2 mmol) was dissolved 1.0 ml of dry, followed by the addition of catalyst **3b** (5 mol%). The mixture was stirred overnight at rt, then the crude directly charged into a plug of silica for flash-chromatography purification.

2a. White wax. Flash chromatography (*c*Hex:AcOEt = 7:3). Yield = 74%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.18-1.21 (m, 6H); 2.37 (d, J = 14.4 Hz, 1H); 2.89 (d, J =14.0 Hz, 1H); 3.03 (d, J = 15.2 Hz, 1H); 3.62 (dd, J_1 = 15.3 Hz, J_2 = 3.6 Hz, 1H); 4.08 (s, 2H); 4.18-4.37 (m, 4H); 4.97 (s, 1H); 5.71 (t, J = 3.6 Hz, 1H); 6.68 (d, J = 8.0 Hz, 1H); 6.73 (pt, J = 8.0 Hz, 1H); 7.06 (dd, J_1 = 14.4 Hz, J_2 = 7.5 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9, 14.0, 41.0, 45.1, 52.3, 57.8, 61.1, 61.8, 61.9, 93.4, 109.6, 119.3, 119.6, 123.2, 127.9, 135.0, 137.5, 148.4, 171.5, 171.7. LC-MS: 358 (M+1); 380 (M+23). Anal. calcd for ($C_{20}H_{23}NO_5$: 357.40): C, 67.21; H, 6.49; N: 3.92. Found: C, 67.40; H, 6.31; N: 3.92.

2b. Pale yellow oil. Flash chromatography (*c*Hex:AcOEt = 6:4). Yield = 75%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ2.41 (d, J = 14.4 Hz, 1H); 2.87 (d, J = 14.0 Hz, 1H); 3.05 (d, J = 15.6 Hz, 1H); 3.63 (dd, J_1 = 15.6 Hz, J_2 = 3.2 Hz, 1H); 3.71 (s, 3H); 3.76 (s, 3H); 4.08 (dd, J_1 = 5.2 Hz, J_2 = 2.8 Hz, 2H); 4.96 (s, 1H); 5.72 (d, J = 2.8 Hz, 1H); 6.66 (d, J = 0.8 Hz, 1H); 6.74 (t, J = 6.4 Hz, 1H); 7.03-7.07 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 41.0, 45.1, 52.3, 53.0, 53.1, 61.1, 93.3, 109.6, 119.4, 119.6, 123.1, 127.9, 134.8, 137.3, 148.4, 156.3, 171.9, 172.2. LC-MS: 330 (M+1), 352 (M+Na).Anal. calcd for ($C_{18}H_{19}NO_5$: 329.36): C, 65.64; H, 5.81; N: 4.25. Found: C, 65.60; H, 5.96; N: 4.19.

2c. White solid. Flash chromatography (*c*Hex:AcOEt = 85:15). Yield = 81%.[4] Mp = 155-157 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.28 (s, 9H); 1.41 (s, 9H); 2.25 (d, J = 14.0 Hz, 1H); 2.82 (d, J = 14.0 Hz, 1H); 2.91 (d, J = 15.2 Hz, 1H); 3.55 (dd, J_1 = 15.2 Hz, J_2 = 2.4 Hz, 1H); 4.08 (s, 2H); 4.95 (s, 1H); 5.67 (t, J = 2.4 Hz, 1H); 6.71 (dt; J_1 = 15.2 Hz, J_2 = 8.0 Hz, 2H); 7.01-7.10 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 27.7(3C), 27.8(3C), 40.8, 44.9, 52.3, 59.1, 61.2, 81.6, 93.4, 109.6, 118.8, 119.6, 123.3, 127.7, 135.2, 137., 170.5, 170.9. LC-MS: 414 (M+1); 436 (M+Na). Anal. calcd for ($C_{24}H_{31}NO_5$: 412.51): C, 69.71; H, 7.56; N: 3.39. Found: C, 69.75; H, 7.44; N: 3.21.

2d. Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 7:3). Yield = 70%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.20 (t, J = 7.2 Hz, 6H); 2.31 (d, J = 14.0 Hz, 1H); 2.89 (d, J = 14.0, Hz, 1H); 3.02 (d, J = 15.6 Hz, 1H); 3.61 (dd, J_1 = 15.6 Hz, J_2 = 2.0 Hz, 1H); 3.73 (s, 3H); 4.13-4.93 (m, 4H); 4.24 (s, 2H); 4.90 (s, 1H); 5.70 (t, J = 2.0 Hz, 1H); 6.61 (d, J = 1.6 Hz, 2H); 6.73 (pt, J = 1.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9, 14.0, 20.9, 41.1, 44.9, 52.3, 57.9, 61.3, 61.7, 61.8, 93.6, 109.4, 119.3, 123.9, 128.2, 128.9, 135.3, 137.6, 146.0, 171.4, 171.7. LC-MS: 372 (M+1), 394 (M+Na). Anal. calcd for ($C_{21}H_{25}NO_5$: 371.43): C, 67.91; H, 6.78; N: 3.77. Found: C, 67.83; H, 6.69; N: 3.60.

2e. Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 7:3). Yield = 45%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.20 (t, J = 7.2 Hz, 6H); 2.31 (d, J = 14.0 Hz, 1H); 2.89 (d, J = 14.0 Hz, 1H); 3.02 (d, J = 15.6 Hz, 1H); 3.61 (dd, J_1 = 15.6 Hz, J_2 = 2.0 Hz, 1H); 3.73 (s, 3H); 4.12-4.22 (m, 4H); 4.24 (s, 2H); 4.90 (s, 1H); 5.70 (t, J = 2.0 Hz, 1H); 6.61 (d, J = 1.6 Hz, 2H); 6.73 (pt, J = 1.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9, 14.0, 40.9, 44.6, 52.8, 55.9, 57.7, 61.5, 61.8, 61.9, 93.9, 110.1, 110.4, 112.7, 119.3, 136.3, 137.1, 142.0, 153.9, 171.4, 171.7. LC-MS: 388 (M+1). Anal. calcd for ($C_{21}H_{25}NO_6$: 387.43): C, 65.10; H, 6.50; N: 3.62. Found: C, 65.23; H, 6.41; N: 3.78.

2f. White wax. Flash chromatography (*c*Hex:AcOEt = 6:4). Yield = 75%.^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.38 (d, J = 14.0 Hz, 1H); 2.85 (d, J = 14.0 Hz, 1H); 3.08 (d, J = 15.6 Hz, 1H); 3.57 (dt, J_1 = 16.0 Hz, J_2 = 2.8 Hz, 1H); 3.76 (s, 6H); 4.08 (t, J = 2.8 Hz, 2H); 4.93 (s, 1H); 5.74 (t, J = 2.8 Hz, 1H); 6.59 (d, J = 8.0 Hz, 1H); 7.01 (d, J = 10.4 Hz, 1H); 7.27 (d, J = 3.2 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 30.9, 40.9, 44.9, 52.5, 53.1, 61.4, 65.8, 93.5, 110.4, 119.9, 123.6, 124.1, 127.7(2C), 136.7, 147.9, 171.7, 172.2. LC-MS: 364 (M+1); 386 (M+Na). Anal. calcd for ($C_{18}H_{18}ClNO_5$: 363.79): C, 59.43; H, 4.88; N: 3.85. Found: C, 59.33; H, 4.97; N: 3.73.

2g. Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 7:3). Yield = 75%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.27 (t, J = 7.2 Hz, 6H); 2.36 (d, J = 14.4 Hz, 1H); 2.87 (d, J = 14.0 Hz, 1H); 3.06 (d, J = 15.6 Hz, 1H); 3.56 (dd, J_1 = 15.6 Hz, J_2 = 2.8 Hz, 1H); 4.07-4.09 (m, 2H); 4.17-4.25 (m, 4H); 4.93 (s, 1H); 5.73 (dd, J_1 = 5.4 Hz, J_2 = 2.4 Hz, 1H); 6.58-6.60 (m, 1H); 6.99-7.02 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9, 14.0, 40.9, 44.8, 52.5, 57.8, 61.4, 61.9, 62.0, 93.5, 110.4(2C), 119.8, 123.6, 124.1, 127.7, 136.9, 147.1, 171.2, 171.6. LC-MS: 414 (M +Na). Anal. calcd for ($C_{20}H_{22}ClNO_5$: 391.85): C, 61.30; H, 5.66; N: 3.57. Found: C, 61.21; H, 5.54; N: 3.45.

2h. White solid. Flash chromatography (*c*Hex:AcOEt = 7:3). Yield = 75%. Mp = 155-157 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.24 (t, J = 7.2 Hz, 6H); 2.36 (d, J = 14.4 Hz, 1H); 2.86 (d, J = 14.4 Hz, 1H); 3.06 (d, J = 15.6 Hz, 1H); 3.55 (dd, J_1 = 15.6 Hz, J_2 = 2.4 Hz, 1H); 4.08 (s, 2H); 4.17-4.26 (m, 4H); 4.93 (s, 1H); 5.73 (s, 1H); 6.55 (dd, J_1 = 6.4 Hz, J_2 = 2.0 Hz, 1H); 7.15 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9, 14.0, 40.9, 42.7, 44.8, 52.5, 57.8, 61.3, 61.9, 93.4, 111.0, 119.8,

126.4, 130.5, 136.9, 137.2, 147.6, 169.2, 171.2, 171.6. LC-MS: 436 (M); 437 (M+1); 438 (M+2). Anal. calcd for ($C_{20}H_{22}BrNO_5$: 436.30): C, 55.06; H, 5.08; N: 3.21. Found: C, 55.17; H, 4.99; N: 3.12.

2i. Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 6:4). Yield = 78%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.27 (t, J = 7.2 Hz, 6H); 2.33 (d, J = 14.0 Hz, 1H); 2.87 (d, J = 14.8 Hz, 1H); 3.02 (d, J = 15.6 Hz, 1H); 3.58 (dd, J_1 = 15.8 Hz, J_2 = 2.8 Hz, 1H); 4.06 (s, 2H); 4.12-4.22 (m, 4H); 4.97 (s, 1H); 5.72 (d, J = 2.8 Hz, 1H); 6.65 (s, 1H); 6.68 (d, J = 8.0 Hz, 1H); 6.96 (d, J = 8.0 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.0, 14.1, 40.8, 45.0, 51.8, 57.7, 61.1(2C), 61.9, 93.5, 109.8, 119.3, 119.5, 124.0, 133.6, 135.6, 137.2, 149.7, 171.4, 171.6. LC-MS: 414 (M+Na). Anal. calcd for ($C_{20}H_{22}ClNO_5$: 391.85): C, 61.30; H, 5.66; N: 3.57. Found: C, 61.35; H, 5.73; N: 3.46.

2j. Viscous yellow oil. Flash chromatography (*c*Hex:AcOEt = 7:3). Yield = 58%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.20 (t, J = 7.2 Hz, 6H); 1.53 (s, 3H); 2.36 (d, J = 14.0 Hz, 1H); 2.94 (d, J = 14.0 Hz, 1H); 3.02 (d, J = 15.6 Hz, 1H); 3.62 (d, J = 16.0 Hz, 1H); 4.03 (d, J = 16.0 Hz, 1H); 4.13-4.26 (m, 5H); 5.62 (pt, J = 3.8 Hz, 1H); 6.64 (d, J = 8.0 Hz, 1H); 6.70 (pt, J = 7.2 Hz, 1H); 7.01-7.08 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9, 14.0, 18.8, 40.7, 42.8, 54.6, 57.1, 60.9, 61.8(2C), 95.2, 109.7, 117.5, 119.5, 123.2, 127.6, 136.8, 137.4, 147.4, 171.7, 172.0. LC-MS: 371 (M+1); 394 (M+Na). Anal. calcd for ($C_{21}H_{25}NO_5$: 371.43): C, 67.91; H, 6.78; N: 3.77. Found: C, 67.85; H, 6.59; N: 3.71.

5a. White solid. Flash-chromatography (*c*Hex:AcOEt = 7:3). Yield: 76%. Mp = 109-111 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.85 (dt, J_1 = 12.6 Hz, J_2 = 3.6 Hz, 1H); 2.00 (td, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H); 2.34 (s, 3H); 3.27 (dt, J_1 = 12.6 Hz, J_2 = 3.6 Hz, 1H); 3.53 (td, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H); 3.77 (dd, J_1 = 16.4 Hz, J_2 = 4.0 Hz, 1H); 4.10 (dd, J_1 = 16.4 Hz, J_2 = 5.6 Hz, 1H); 4.21 (s, 2H); 5.05 (s, 1H); 5.68 (t, J = 5.6 Hz, 1H); 6.61 (d, J = 7.6 Hz, 1H); 6.74 (pt, J = 7.6 Hz, 1H); 7.06 (pt, 8.0 Hz, 1H); 7.19-7.28 (m, 2H); 7.41 (d, J = 7.6 Hz, 1H); 7.63(d, J = 8.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 21.5, 29.7, 32.6, 45.5, 59.1, 72.2, 100.9, 109.7, 117.5, 119.6, 126.6, 127.3(2C), 128.9, 129.4, 129.8(2C), 136.1, 143.5, 146.5, 148.5. LC-MS: 383 (M+1), 405 (M+Na). Anal. calcd for ($C_{21}H_{22}N_2O_3S$: 382.48): C, 65.95; H, 5.80; N: 7.32. Found: C, 65.88; H, 5.69; N: 7.22.

5b.White solid. Flash-chromatography (*c*Hex:AcOEt = 7:3). Yield: 60.[4] Mp = 100-103 °C.^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.94 (dt, J_1 = 14.0 Hz, J_2 = 3.6 Hz, 1H); 2.07 (dd, J_1 = 14.0 Hz, J_2 = 4.8 Hz, 1H); 2.46 (s, 3H); 3.38 (dt, J_1 = 9.6 Hz, J_2 = 4.0 Hz, 1H); 3.58 (dt, J_1 = 12.8 Hz, J_2 = 2.8 Hz, 1H); 3.88 (dd, J_1 = 15.2 Hz, J_2 = 4.8 Hz, 1H); 4.14-4.19 (m, 1H); 4.29-3.30 (m, 2H); 4.73 (s, 1H); 5.15 (s, 1H); 5.77-5.80 (m, 1H); 6.60 (d, J = 8.0 Hz, 1H); 7.09 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H); 7.35 (d, J = 7.6 Hz, 2H); 7.46 (d, J = 2.0 Hz, 1H); 7.72 (d, J = 7.6 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 21.5, 23.3, 32.6, 45.4, 45.6, 55.1, 59.1, 72.2, 73.5, 79.4, 86.7, 101.2, 110.5, 118.3, 126.7, 127.3(2C), 128.8, 129.8(2C), 131.4, 143.6, 147.1. LC-MS: 417 (M+1), 439 (M+Na). Anal. calcd for ($C_{21}H_{21}ClN_2O_3S$: 416.92): C, 60.50; H, 5.08; N: 6.72. Found: C, 60.41; H, 5.19; N: 6.62.

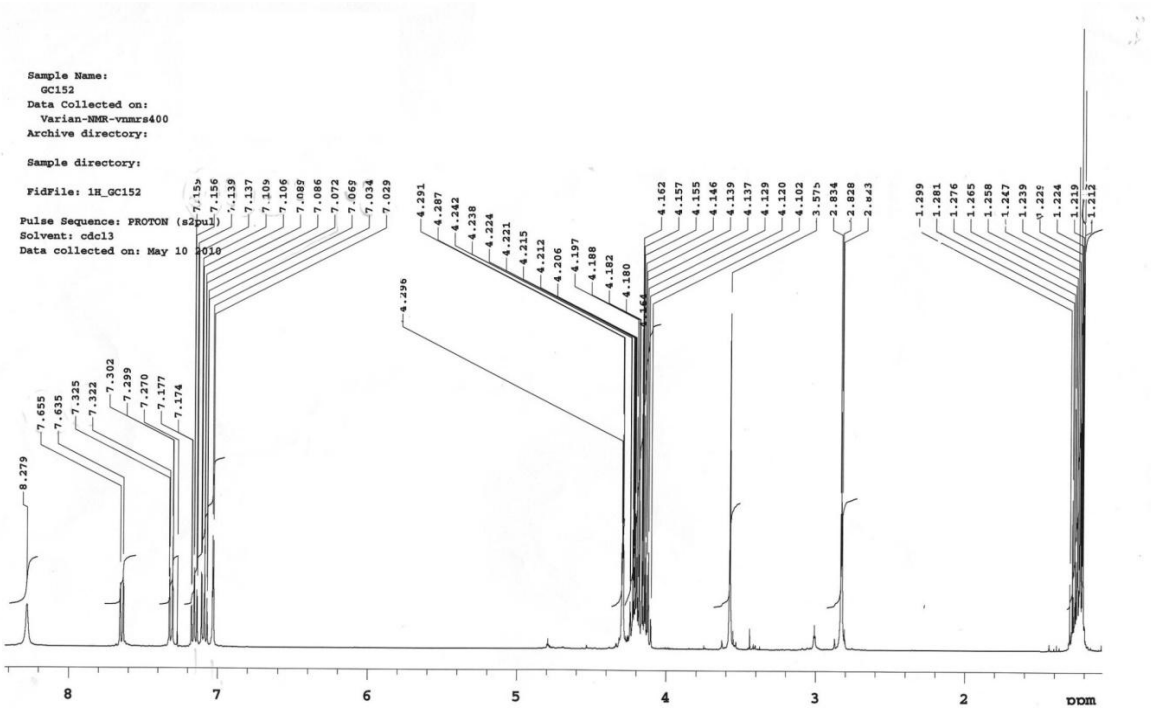
5c. White solid. Flash-chromatography (*c*Hex:AcOEt = 65:35). Yield: 52%.[4] Mp = 72-74 °C (mixture of isomers). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.99 (dq, J_1 = 14.0 Hz, J_2 = 3.2 Hz, 1H); 2.01 (dd, J_1 = 7.2 Hz, J_2 = 5.2 Hz, 1H); 2.46 (s, 3H); 3.05-3.15 (m, 1H); 3.19 (dp, J_1 = 14.0 Hz, J_2 = 7.2 Hz, 1H); 3.51 (dd, J_1 = 8.0 Hz, J_2 = 5.2 Hz, 1H); 3.68-3.72 (m, 1H); 3.82 (s, 3H); 4.21 (m, 2H); 5.23 (s, 1H); 5.67-5.69 (m, 1H); 6.61 (d, J = 8.8 Hz, 1H); 6.67 (dd, J_1 = 8.8 Hz, J_2 = 6.4 Hz, 1H); 6.85 (s, 1H); 7.35 (d, J = 7.6 Hz, 2H); 7.70 (d, J = 7.6 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 21.5, 26.9, 32.1, 45.3, 45.4, 56.1, 72.2, 101.6, 110.6, 112.3, 115.2, 117.9, 127.4(2C), 129.6, 129.8(2C), 142.3, 143.6, 146.1, 154.1. LC-MS: 413 (M+1), 435 (M+Na). Anal. calcd for ($C_{22}H_{24}N_2O_3S$: 412.50): C, 64.06; H, 5.86; N: 6.79. Found: C, 64.00; H, 5.85; N: 6.85.

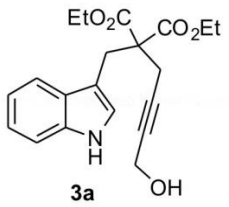
5d. White solid. Flash-chromatography (*c*Hex:AcOEt = 8:2). Yield of **5d**: 53. Mp = 160-162 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.85 (dt, J_1 = 14.0 Hz, J_2 = 3.6 Hz, 1H); 1.98 (td, J_1 = 11.6 Hz, J_2 = 3.6 Hz, 1H); 2.38 (s, 3H); 2.88 (s, 3H); 3.26-3.29 (m, 1H); 3.54 (td, J_1 = 12.4 Hz, J_2 = 4.0 Hz, 1H); 3.78 (dd, J_1 = 16.4 Hz, J_2 = 4.0 Hz, 1H); 4.09-4.13 (m, 2H); 4.17-4.21 (m, 1H); 4.92 (s, 1H); 5.66 (t, J = 4.8 Hz, 1H); 6.41 (d, J = 7.6 Hz, 1H); 6.67 (pt, J = 7.6 Hz, 1H); 7.10 (t, J = 7.6 Hz, 1H); 7.27 (d, J = 7.6 Hz, 1H); 7.35 (d, J = 6.4 Hz, 1H); 7.63 (d, J = 8.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 24.3, 26.7, 37.1, 47.2, 50.8, 54.1, 78.9, 83.7, 109.3, 110.7, 118.6, 118.9, 121.7, 127.0, 127.6, 127.9(2C), 129.3(2C), 136.7, 140.0, 143.4. LC-MS: 397 (M+1). Anal. calcd for ($C_{22}H_{24}N_2O_3S$: 396.50): C, 66.64; H, 6.10; N: 7.07. Found: C, 66.41; H, 6.00; N: 7.01.

X-ray data.

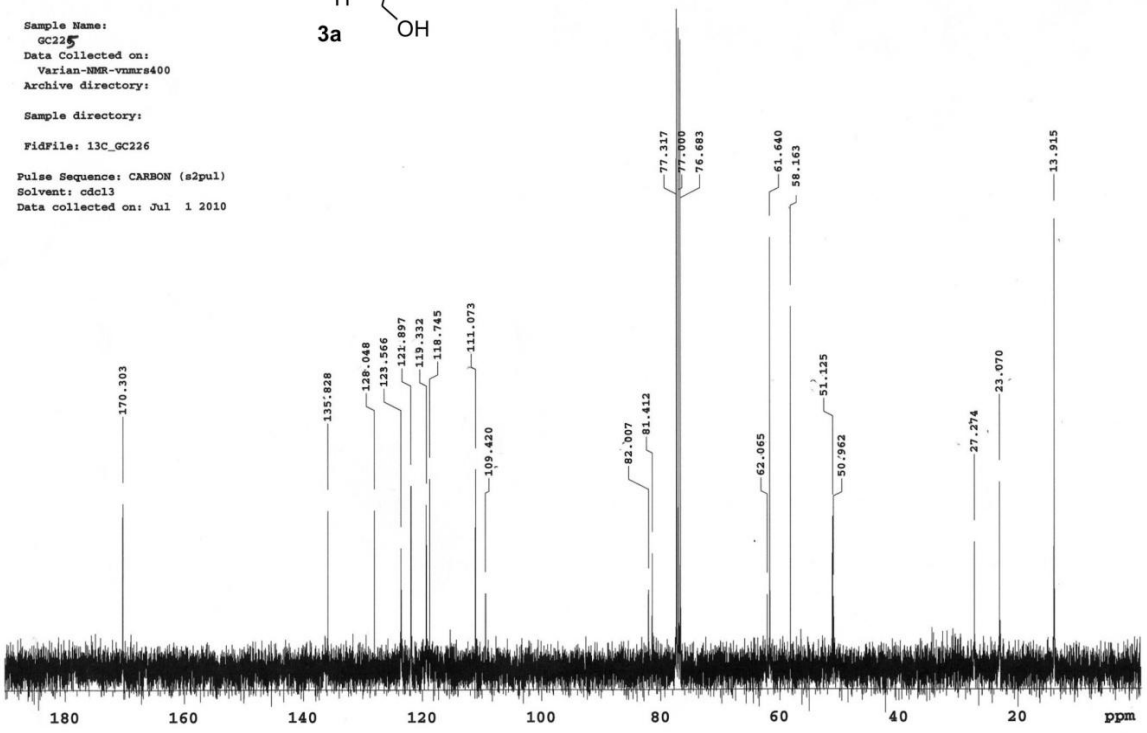
Crystal data for **2c**: $C_{24}H_{31}NO_5$, *M* = 413.50, colorless plate, 0.30 x 0.20 x 0.15 mm, monoclinic, space group *C2* (No. 5), *a* = 17.796(6), *b* = 6.252(2), *c* = 20.307(6) Å, β = 90.601(4)°, *V* = 2259(1) Å^3, *Z* = 4, *D*c = 1.216 g/cm^3, *F*(000) = 888, CCD area detector Smart ApexII, MoK$_\alpha$ radiation, λ = 0.71073 Å, *T* = 293(2)K, $2\theta_{max}$ = 50.8º, 10746 reflections collected, 4162 unique (R_{int} = 0.0321). The structure was solved and refined using the programs SIR-97[5] and SHELXTL,[6] respectively. Final *GooF* = 1.029, *R1* = 0.0381, *wR2* = 0.0897, *R* indices based on 3442 reflections with I >2σ (I) (refinement on F^2), 278 parameters, 1 restraint. Lp and absorption corrections applied, μ= 0.085 mm^{-1}.

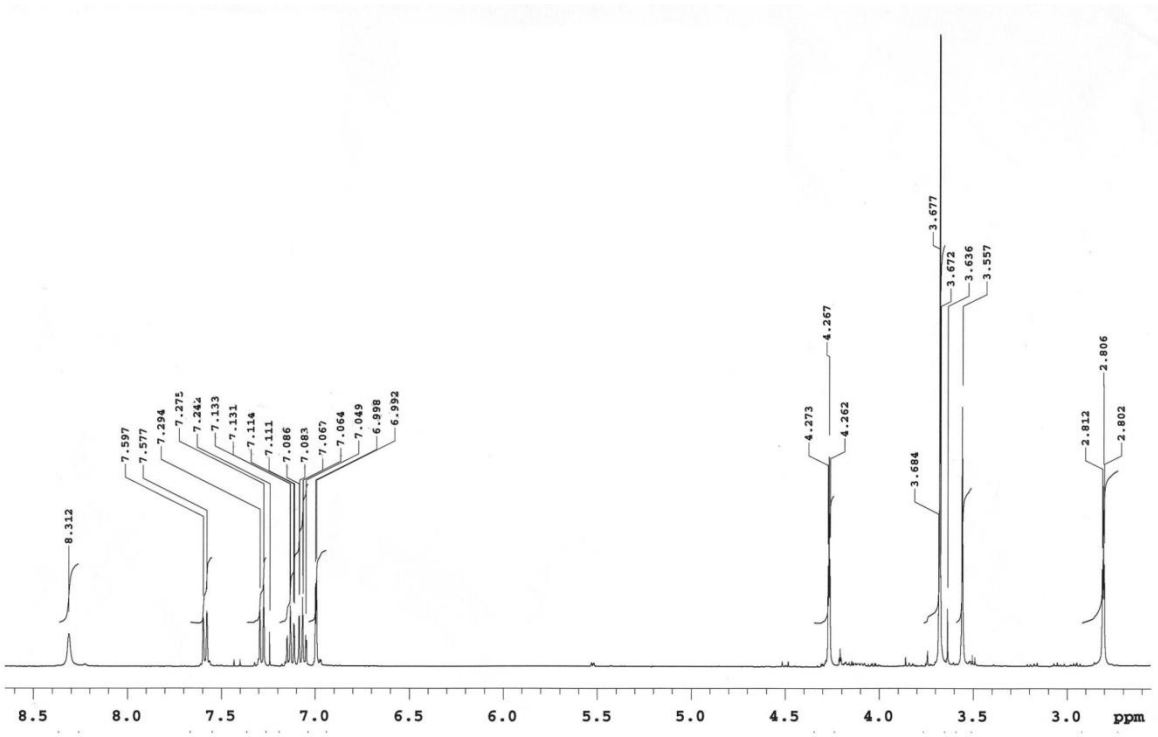
Crystal data for **5a**: $C_{21}H_{22}NO_5S$, *M* = 382.47, colorless plate, 0.25 x 0.15 x 0.07 mm, monoclinic, space group *C2/c* (No. 15), *a* = 16.779(4), *b* = 13.615(4), *c* = 16.919(4) Å, β =100.050(5)°, *V* = 3806(2) Å^3, *Z* = 8, *D*c = 1.335 g/cm^3, *F*(000) = 1616, CCD area detector Smart ApexII, MoK$_\alpha$ radiation, λ = 0.71073 Å, *T* = 293(2)K, $2\theta_{max}$ = 49.76º, 16998 reflections collected, 3298 unique (R_{int} = 0.1056). The structure was solved and refined using the programs SIR-97[5] and SHELXTL,[6] respectively. Final *GooF* = 1.087, *R1* = 0.0949, *wR2* = 0.1530, *R* indices based on 1363 reflections with I >2σ(I) (refinement on F^2), 245 parameters, 1 restraint. Lp and absorption corrections applied, μ = 0.194 mm^{-1}.


Sample Name:
GC152
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: 1H_GC152
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 10 2010
8.279
7.655
7.635
7.325
7.322
7.302
7.299
7.270
7.177
7.174
4.291
4.287
4.242
4.238
4.224
4.221
4.215
4.212
4.206
4.197
4.188
4.182
4.180
4.162
4.157
4.155
4.146
4.139
4.137
4.129
4.120
4.102
3.575
2.834
2.828
2.823
1.299
1.281
1.276
1.265
1.258
1.247
1.239
1.224
1.219
1.212
8
7
6
5
4
3
2
ppm


EtO2C
CO2Et
N
H
OH

3a


Sample Name:
GC225
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: 13C_GC226
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jul 1 2010
170.303
135.828
128.048
123.566
121.897
119.332
118.745
111.073
109.420
82.907
81.412
77.317
77.000
76.683
62.065
61.640
58.163
51.125
50.962
27.274
23.070
13.915
180
160
140
120
100
80
60
40
20
ppm



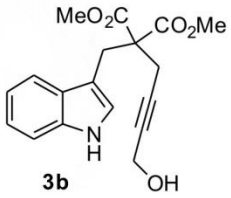
STANDARD CARBON PARAMETERS

Sample Name:
MB4325
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:

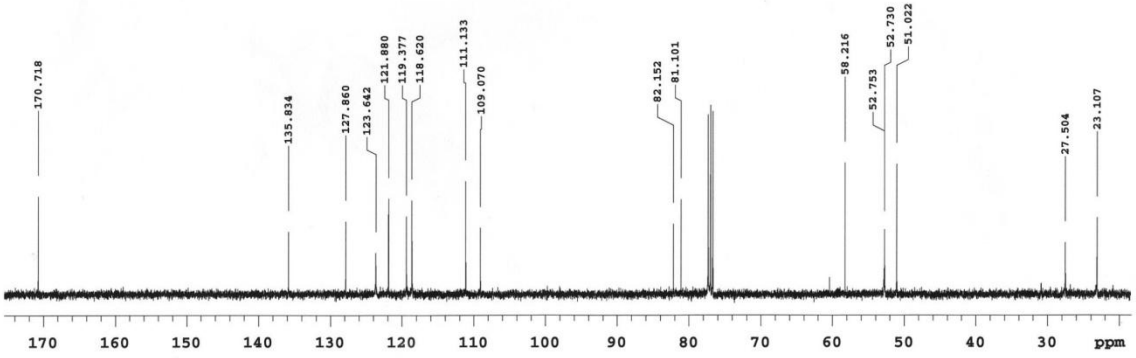
Sample directory:

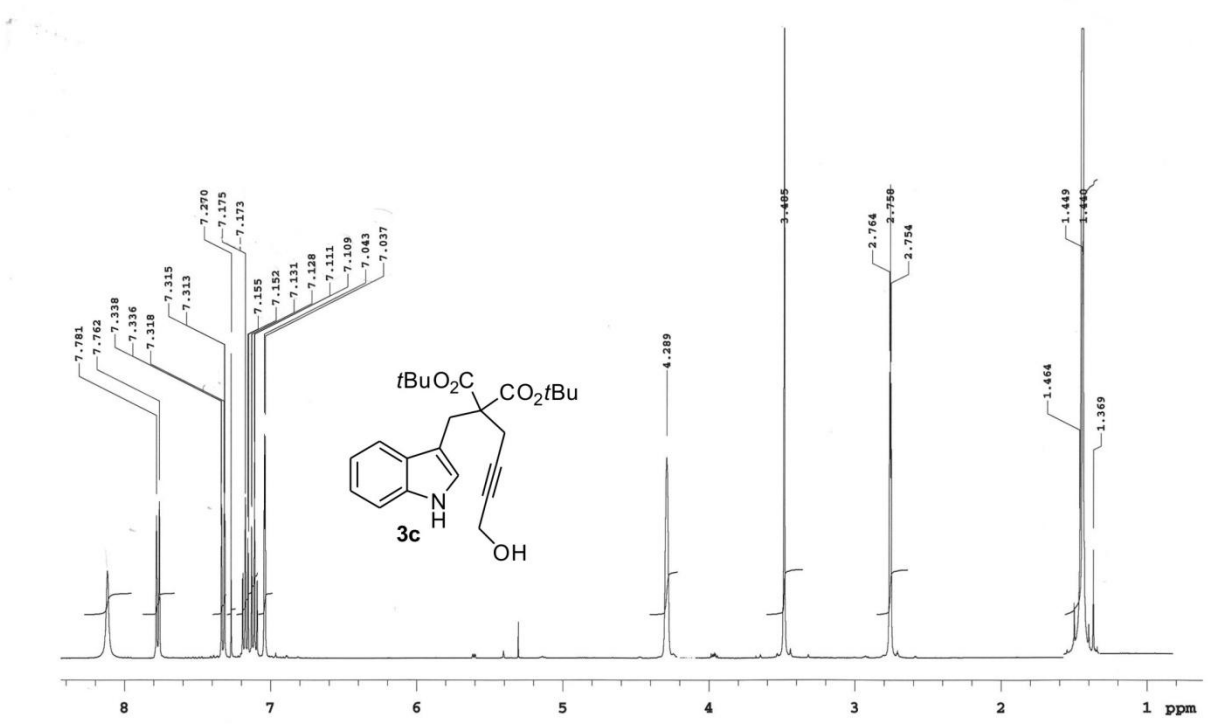
FidFile: CARBON

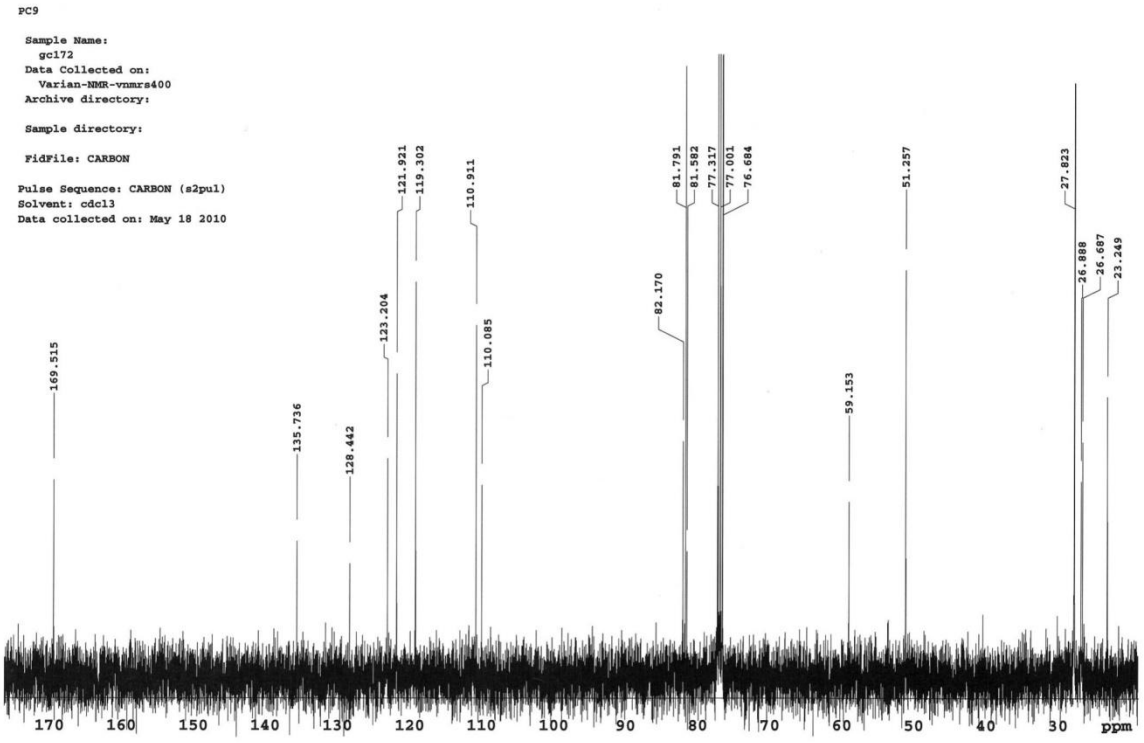
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 7 2010

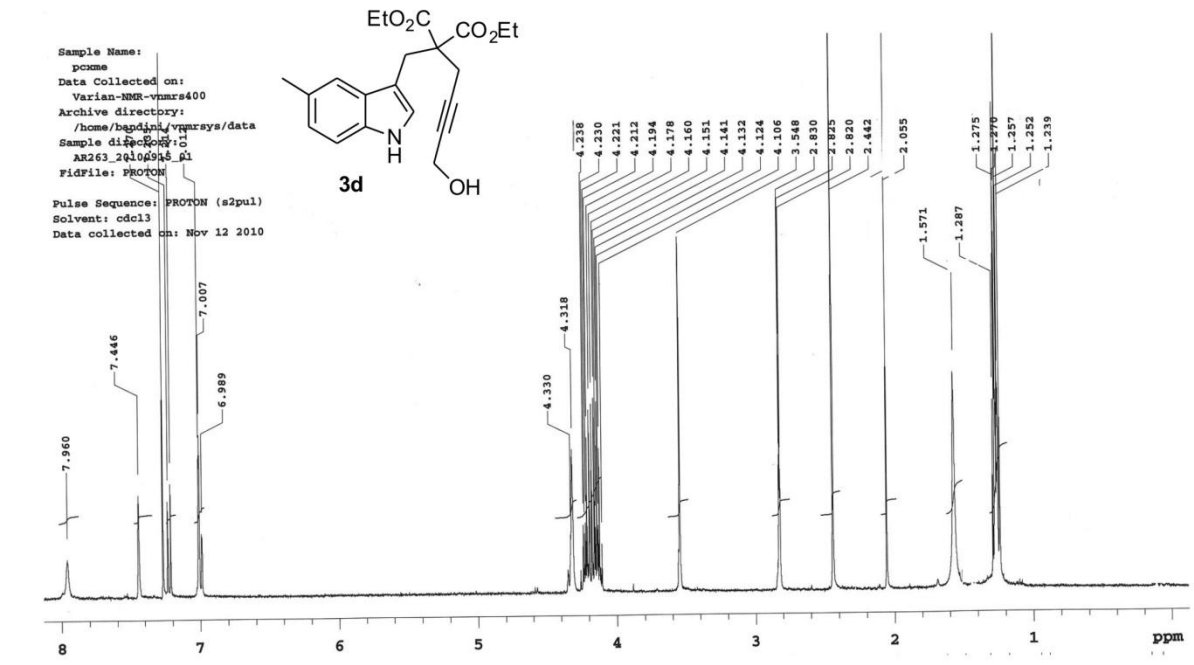


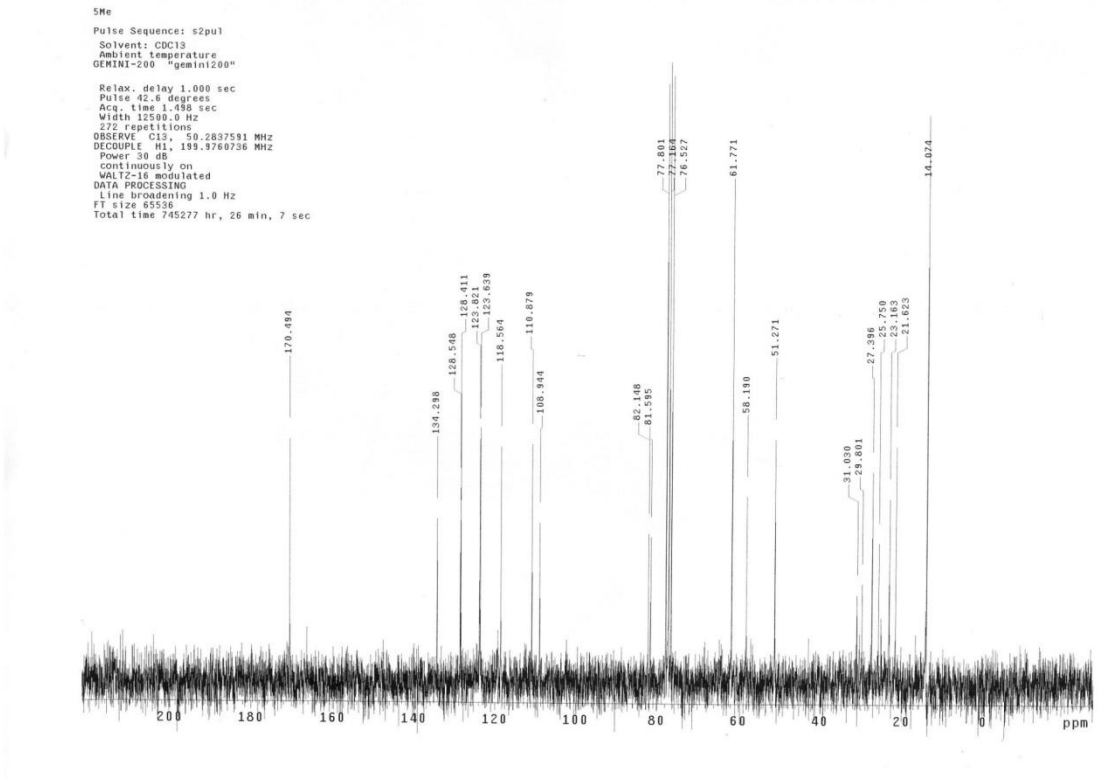
3b

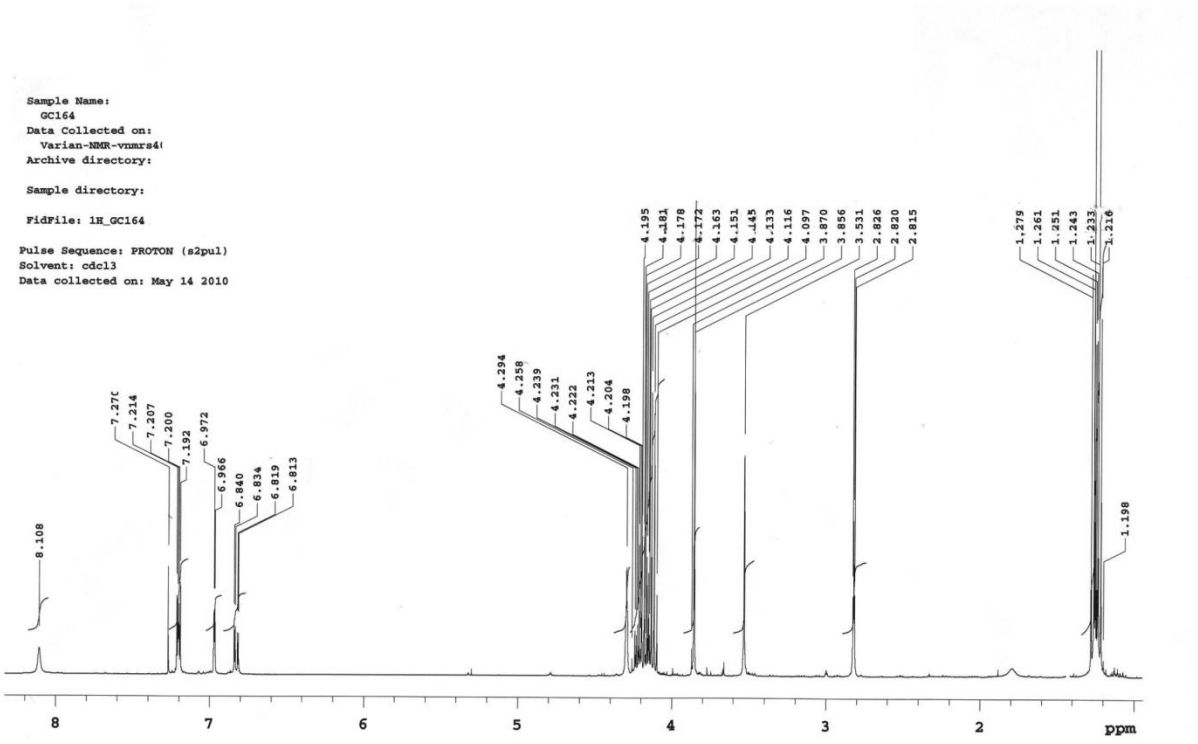


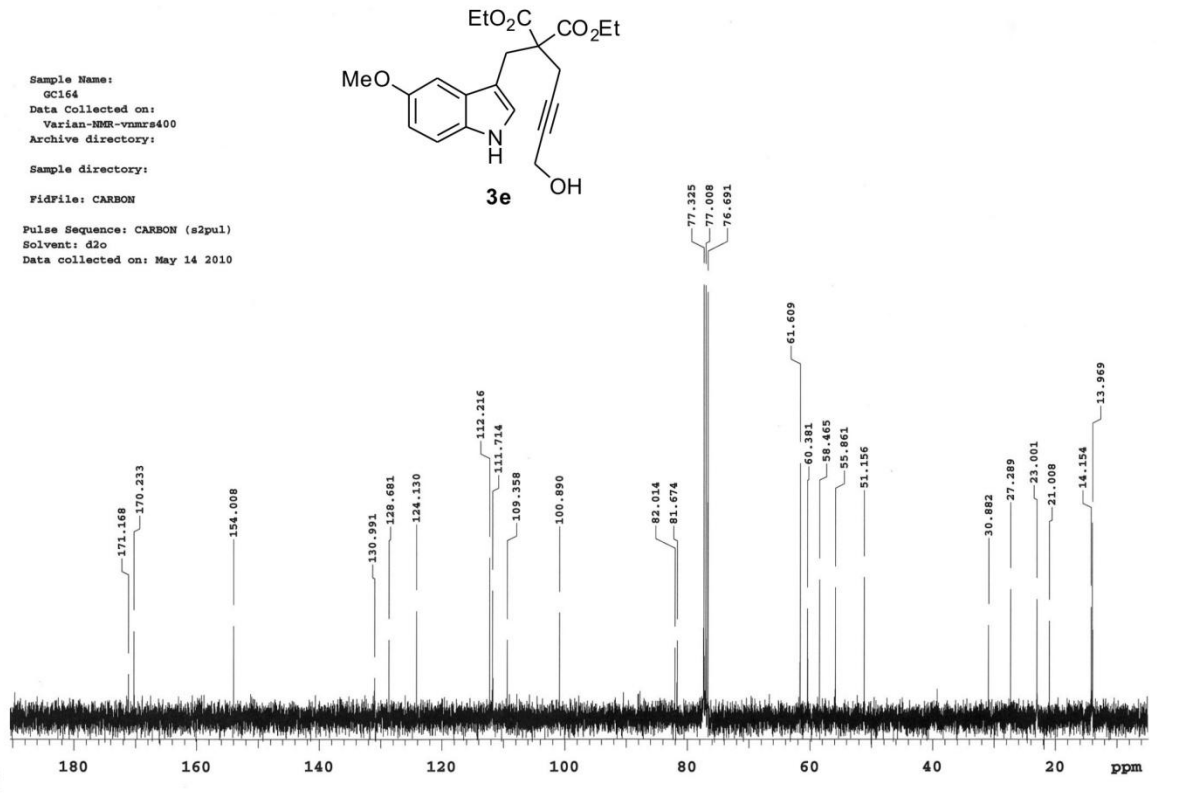

7.781
7.762
7.338
7.336
7.318
7.315
7.313
7.270
7.175
7.173
7.155
7.152
7.131
7.128
7.111
7.109
7.043
7.037
4.289
3.485
2.764
2.758
2.754
1.464
1.449
1.369
tBuO2C
CO2tBu
N
H
OH
3c
8
7
6
5
4
3
2
1 ppm

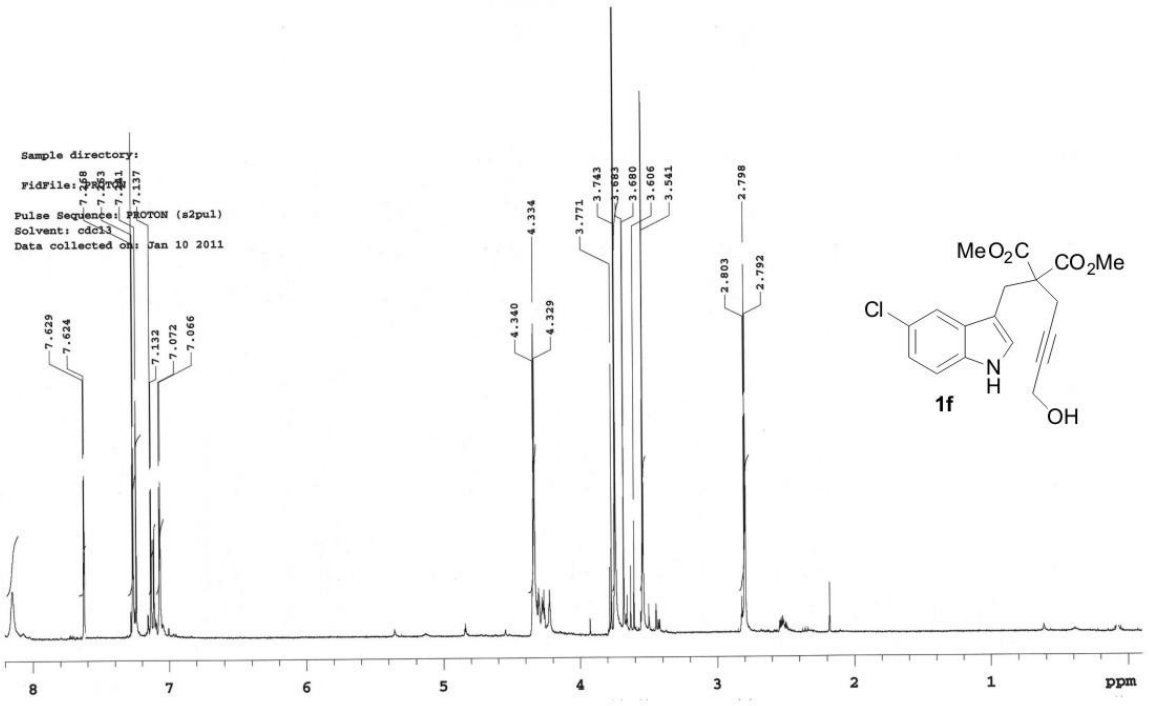

PC9
Sample Name:
gc172
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 18 2010
169.515
135.736
128.442
123.204
121.921
119.302
110.911
110.085
82.170
81.791
81.582
77.317
77.001
76.684
59.153
51.257
27.823
26.888
26.687
23.249
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

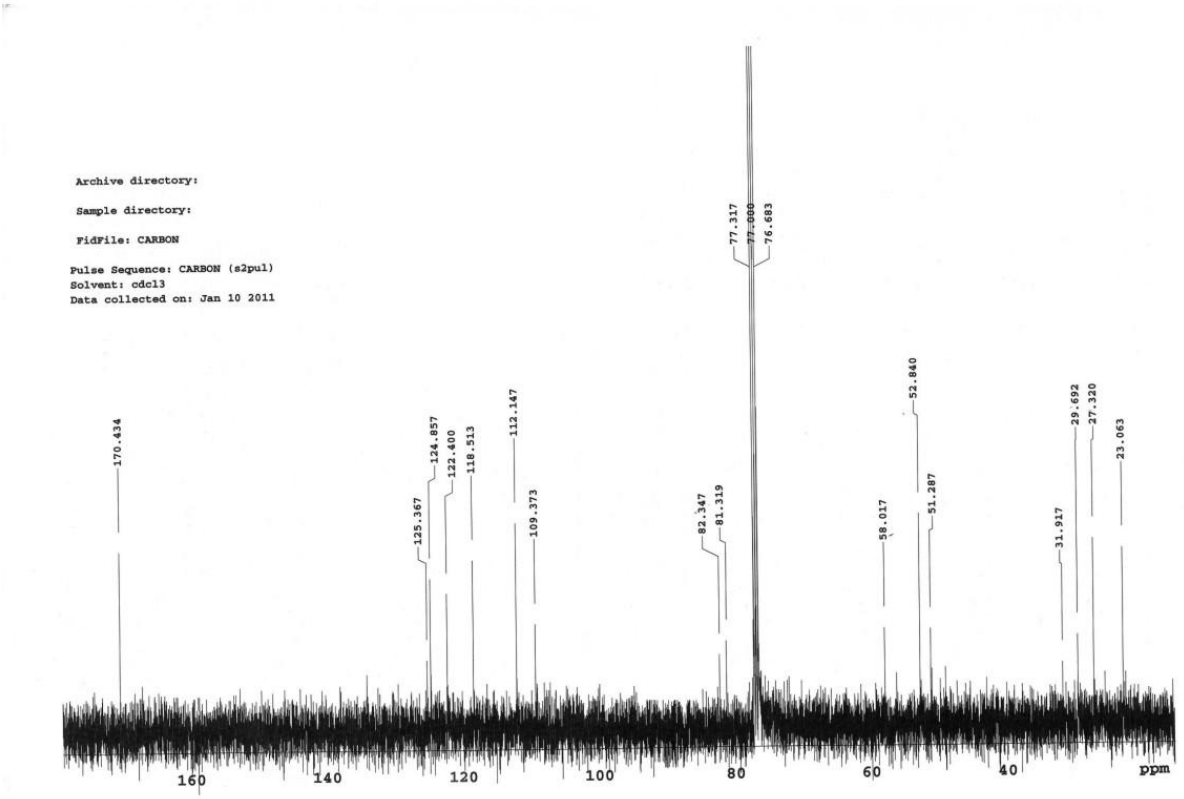

Sample Name:
pcxme
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
/home/bandini/vnmrsys/data
Sample directory:
AR263_20100915_01
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 12 2010
EtO2C
CO2Et
N
H
OH
3d
7.960
7.446
7.007
6.989
4.330
4.318
4.238
4.230
4.221
4.212
4.194
4.178
4.160
4.151
4.141
4.132
4.124
4.106
3.548
2.830
2.825
2.820
2.442
2.055
1.571
1.287
1.275
1.270
1.257
1.252
1.239
8
7
6
5
4
3
2
1
ppm

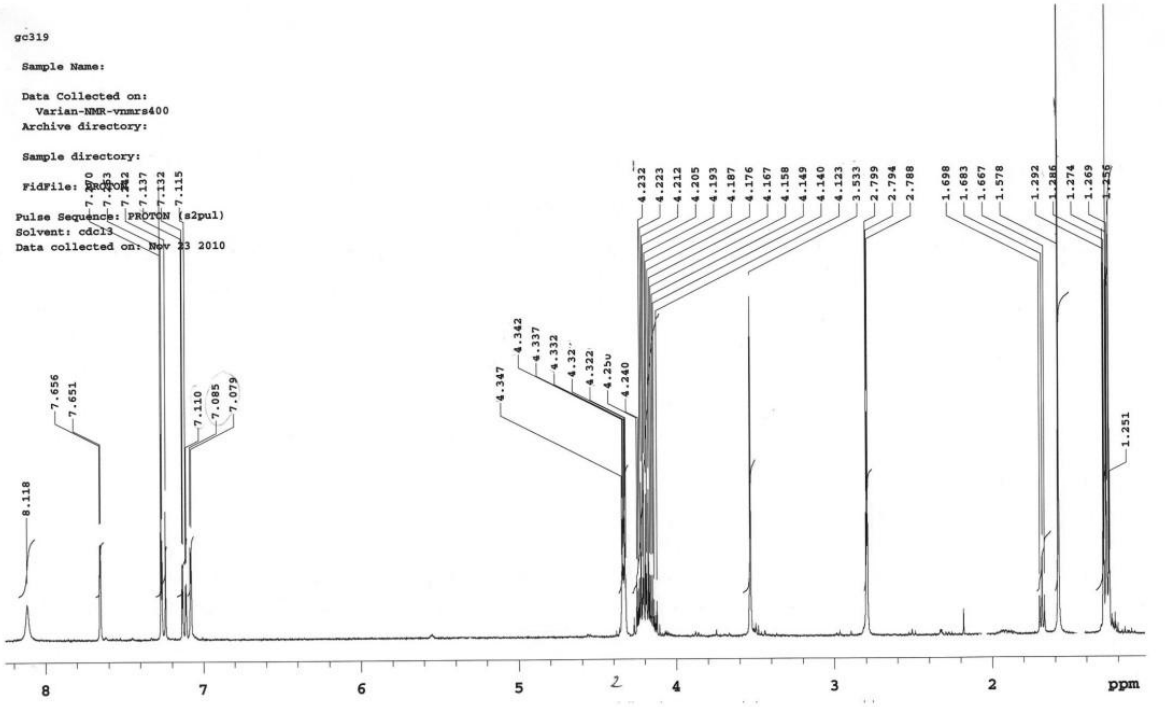

5Me
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-200 "gemini200"
Relax. delay 1.000 sec
Pulse 42.6 degrees
Acq. time 1.498 sec
Width 12500.0 Hz
272 repetitions
OBSERVE C13, 50.2837591 MHz
DECOUPLE H1, 199.9760736 MHz
Power 30 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 745277 hr, 26 min, 7 sec
170.494
134.238
128.548
128.411
123.821
123.639
118.564
110.879
108.944
82.148
81.585
77.801
77.164
76.527
61.771
58.190
51.271
31.030
29.801
27.396
25.750
23.163
21.623
14.074
200
180
160
140
120
100
80
60
40
20
0
ppm

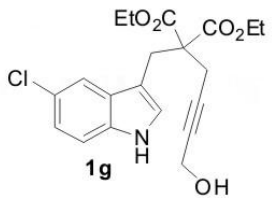

Sample Name:
GC164
Data Collected on:
Varian-NMR-vnmrs4(
Archive directory:
Sample directory:
FidFile: 1H_GC164
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 14 2010
8.108
7.276
7.214
7.207
7.200
7.192
6.972
6.966
6.840
6.834
6.819
6.813
4.294
4.258
4.239
4.231
4.222
4.213
4.204
4.198
4.195
4.181
4.178
4.172
4.163
4.151
4.145
4.133
4.116
4.097
3.870
3.856
3.531
2.826
2.820
2.815
1.279
1.261
1.251
1.243
1.233
1.216
1.198
8
7
6
5
4
3
2
ppm


Sample Name:
GC164
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: d2o
Data collected on: May 14 2010
EtO2C
CO2Et
MeO
N
H
OH
3e
77.325
77.008
76.691
171.168
170.233
154.008
130.991
128.681
124.130
112.216
111.714
109.358
100.890
82.014
81.674
61.609
60.381
58.465
55.861
51.156
30.882
27.289
23.001
21.008
14.154
13.969
180
160
140
120
100
80
60
40
20
ppm

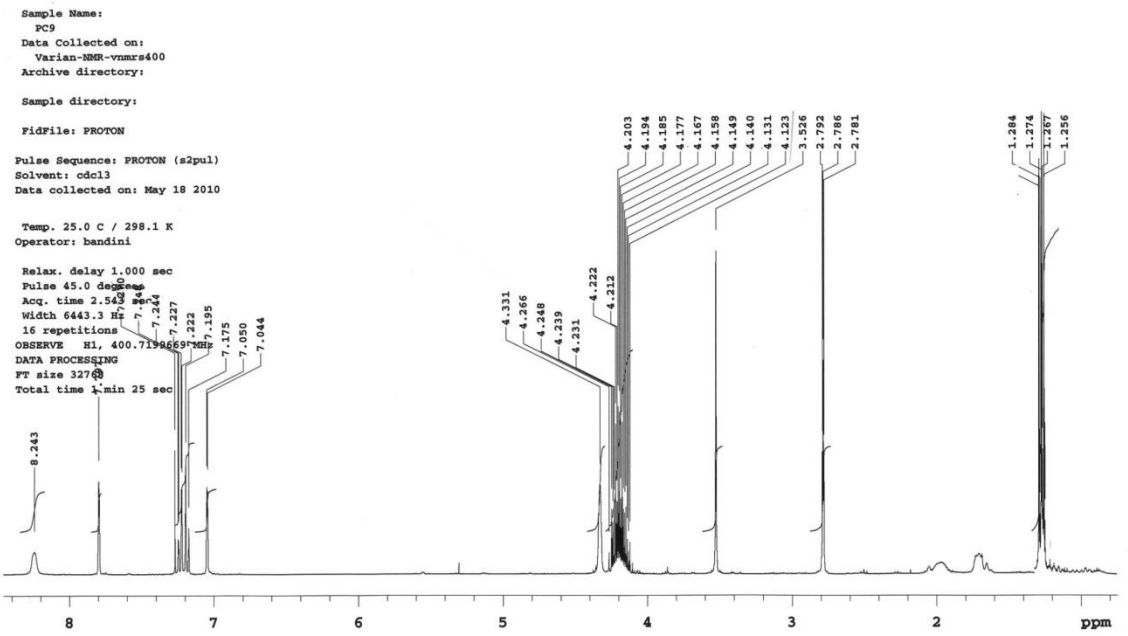

Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 10 2011
7.629
7.624
7.137
7.132
7.072
7.066
4.340
4.329
4.334
3.771
3.743
3.683
3.680
3.606
3.541
2.803
2.792
2.798
MeO2C
CO2Me
Cl
N
H
OH
1f
8
7
6
5
4
3
2
1
ppm

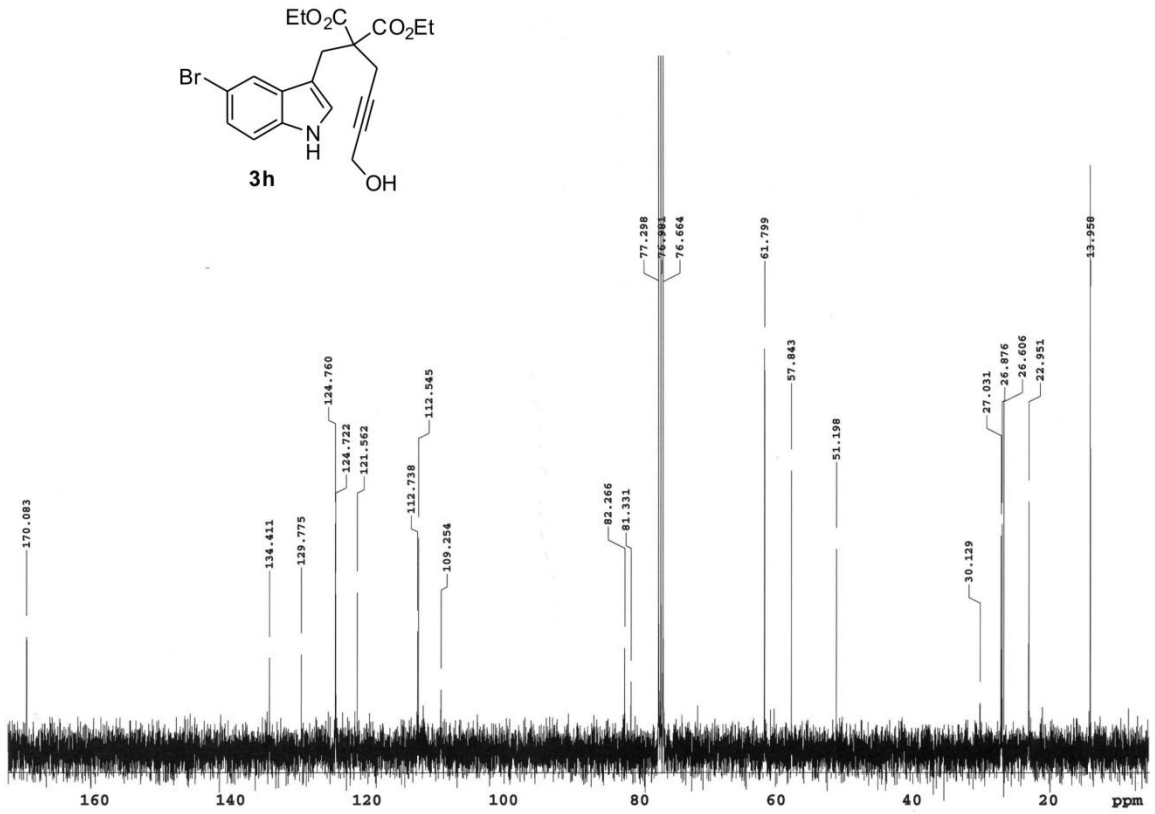

Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 10 2011
170.434
125.367
124.857
122.400
118.513
112.147
109.373
82.347
81.319
77.317
77.000
76.683
58.017
52.840
51.287
31.917
29.692
27.320
23.063
160
140
120
100
80
60
40
ppm

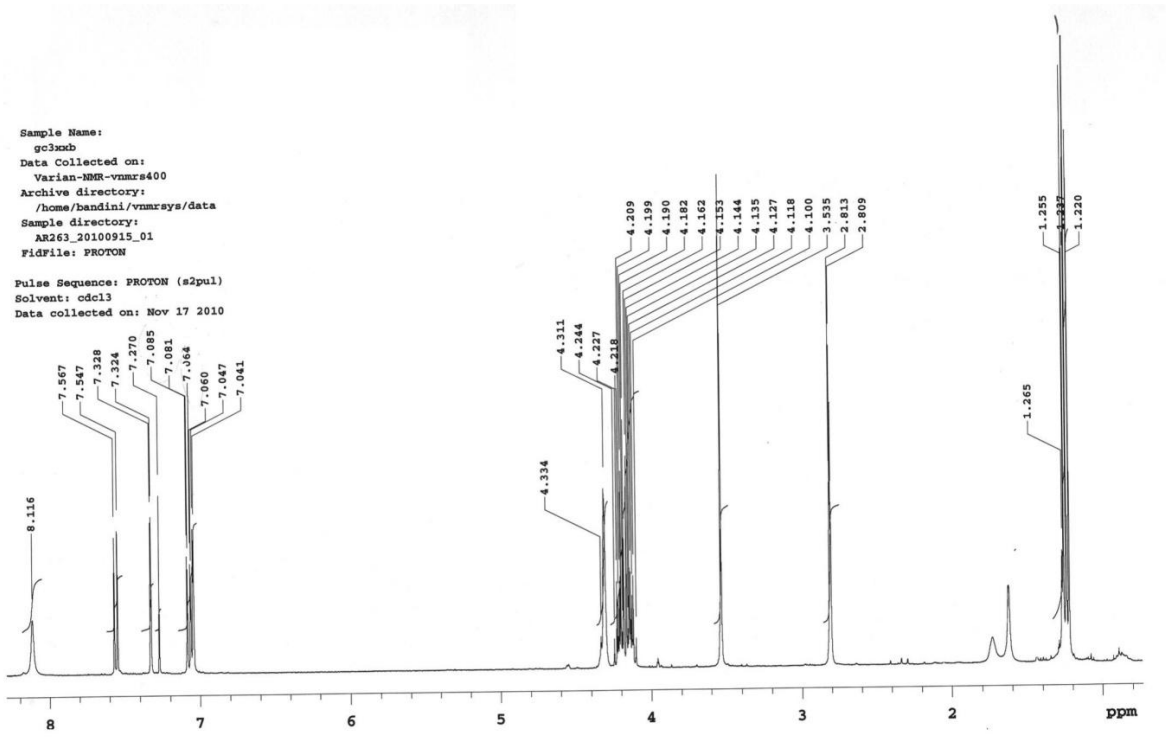

gc319
Sample Name:
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 23 2010
8.118
7.656
7.651
7.110
7.085
7.079
4.347
4.342
4.337
4.332
4.322
4.240
4.232
4.223
4.212
4.205
4.193
4.187
4.176
4.167
4.158
4.149
4.140
4.123
3.533
2.799
2.794
2.788
1.698
1.683
1.667
1.578
1.292
1.286
1.274
1.269
1.256
1.251
8
7
6
5
4
3
2
ppm

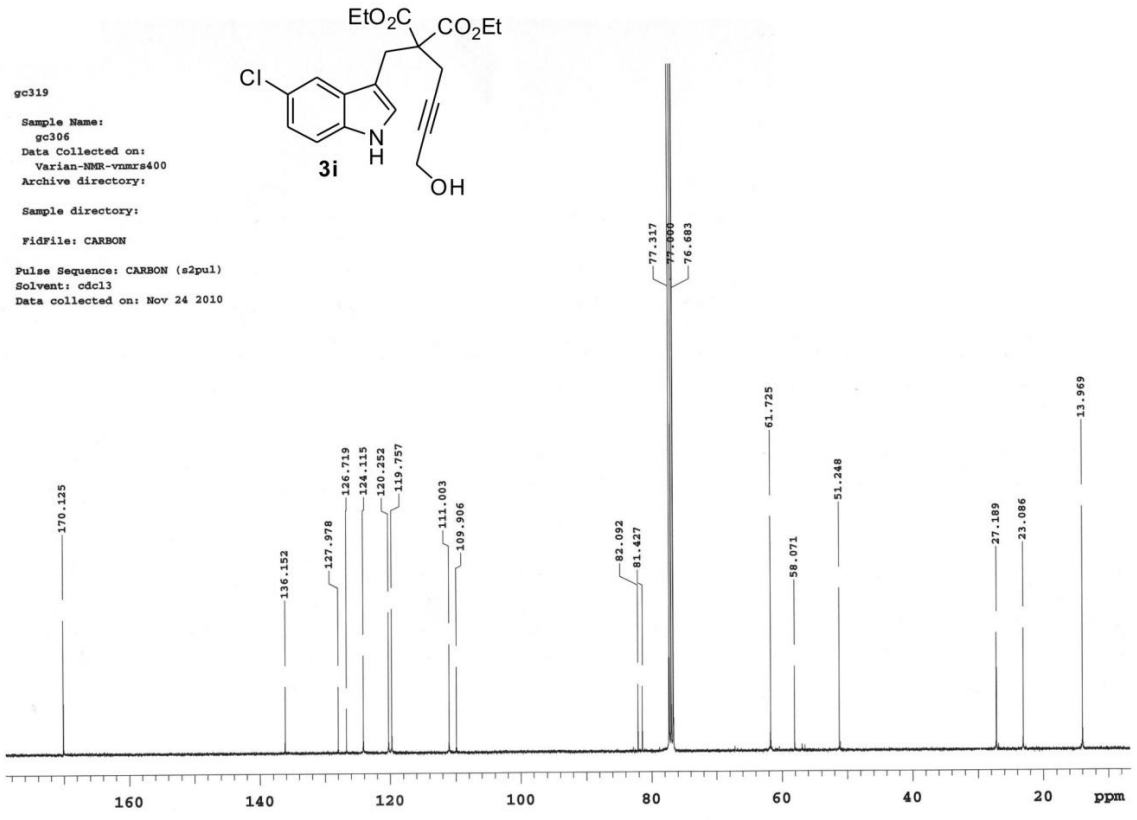

EtO2C
CO2Et
Cl
N
H
OH
1g

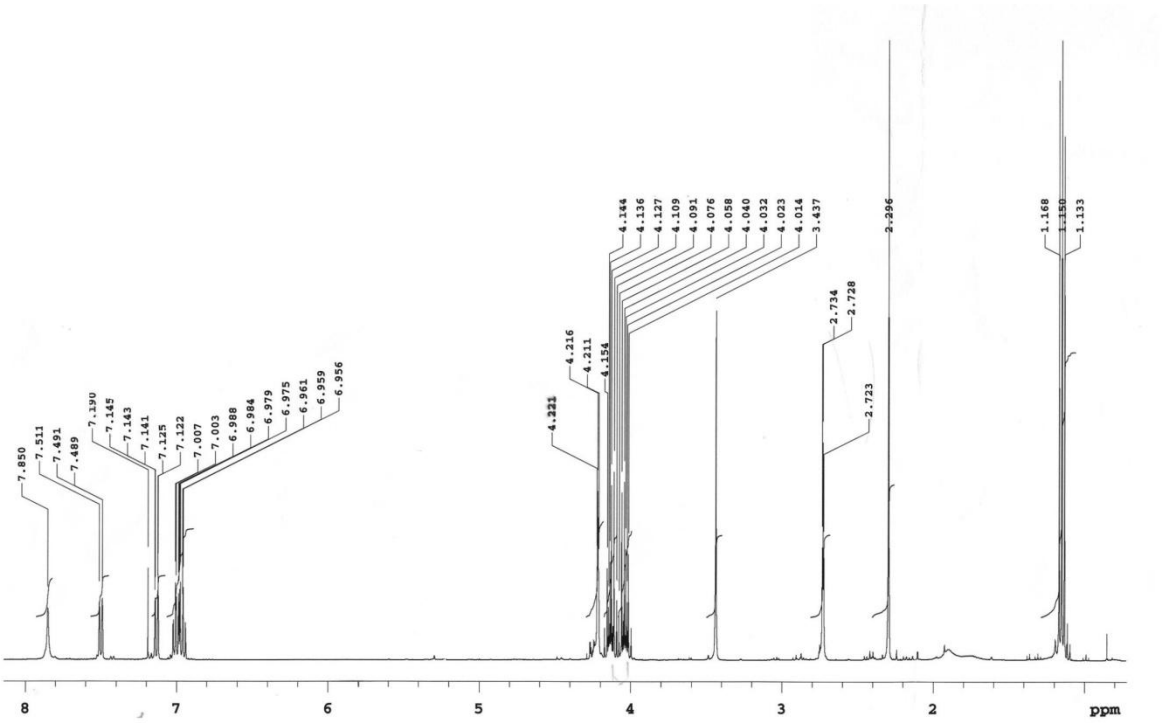
mb4479
Sample Name:
gc50L
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 10 2011
170.055
148.144
134.159
132.003
129.207
125.289
124.833
122.346
118.544
112.093
82.223
81.497
77.317
77.000
76.683
73.639
69.884
68.547
65.457
61.779
57.916
51.295
27.073
22.993
13.984
160
140
120
100
80
60
40
20
ppm

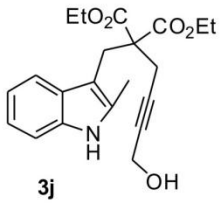

Sample Name:
PC9
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 18 2010
Temp. 25.0 C / 298.1 K
Operator: bandini
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.543 sec
Width 6443.3 Hz
16 repetitions
OBSERVE H1, 400.7198659 MHz
DATA PROCESSING
FT size 32768
Total time 1 min 25 sec
8.243
7.260
7.244
7.227
7.222
7.195
7.175
7.050
7.044
4.331
4.266
4.248
4.239
4.231
4.222
4.212
4.203
4.194
4.185
4.177
4.167
4.158
4.149
4.140
4.131
4.123
3.526
2.792
2.786
2.781
1.284
1.274
1.267
1.256
8
7
6
5
4
3
2
ppm


EtO2C
CO2Et
Br
N
H
OH
3h
170.083
134.411
129.775
124.760
124.722
121.562
112.738
112.545
109.254
82.266
81.331
77.298
76.981
76.664
61.799
57.843
51.198
30.129
27.031
26.876
26.606
22.951
13.950
160
140
120
100
80
60
40
20
ppm

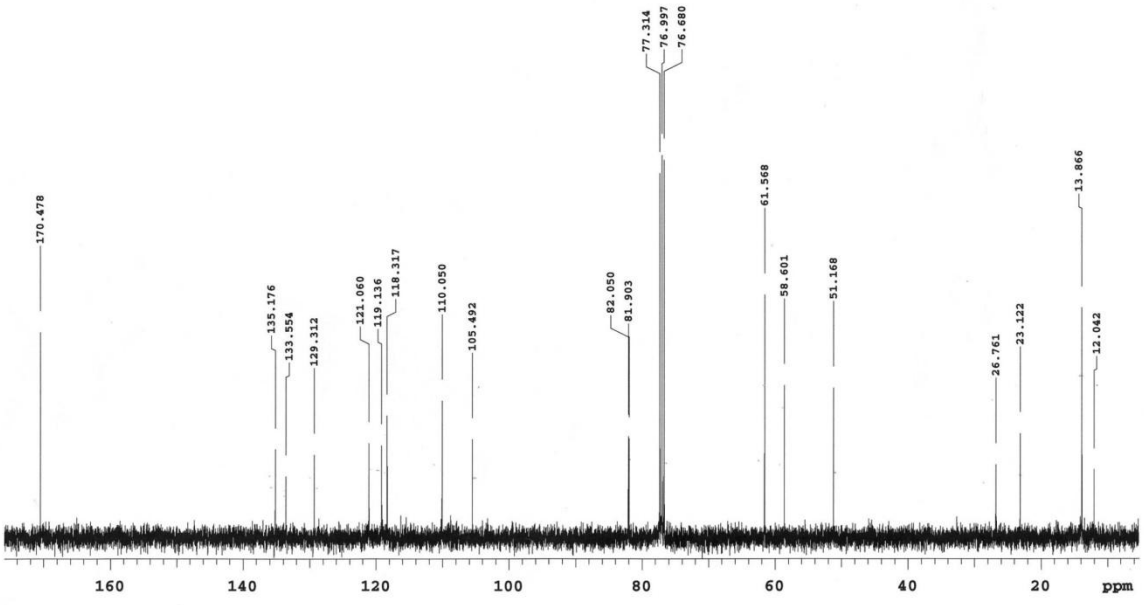

Sample Name:
gc3xxb
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
/home/bandini/vnmrsys/data
Sample directory:
AR263_20100915_01
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 17 2010
8.116
7.567
7.547
7.328
7.324
7.270
7.085
7.081
7.064
7.060
7.047
7.041
4.334
4.311
4.244
4.227
4.218
4.209
4.199
4.190
4.182
4.162
4.153
4.144
4.135
4.127
4.118
4.100
3.535
2.813
2.809
1.265
1.255
1.237
1.220
8
7
6
5
4
3
2
ppm

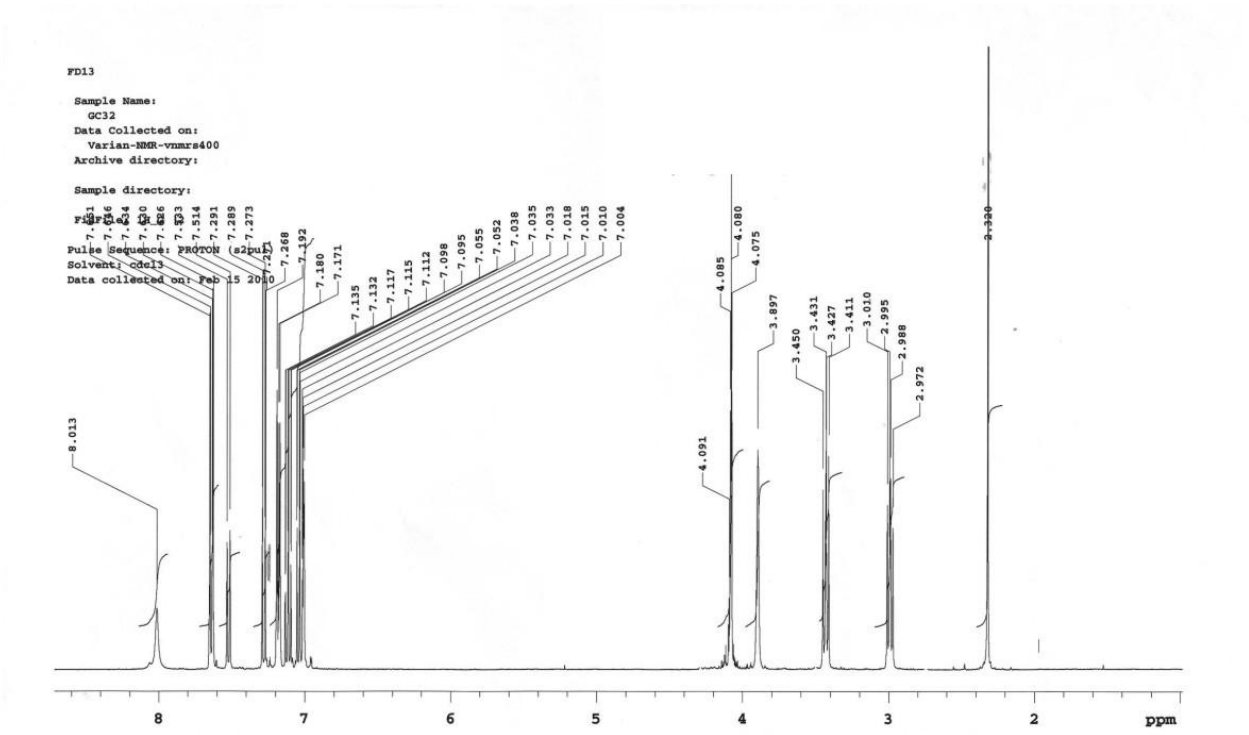

EtO2C
CO2Et
Cl
N
H
OH
3i
gc319
Sample Name:
gc306
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 24 2010
170.125
136.152
127.978
126.719
124.115
120.252
119.757
111.003
109.906
82.092
81.427
77.317
77.000
76.683
61.725
58.071
51.248
27.189
23.086
13.969
160
140
120
100
80
60
40
20
ppm

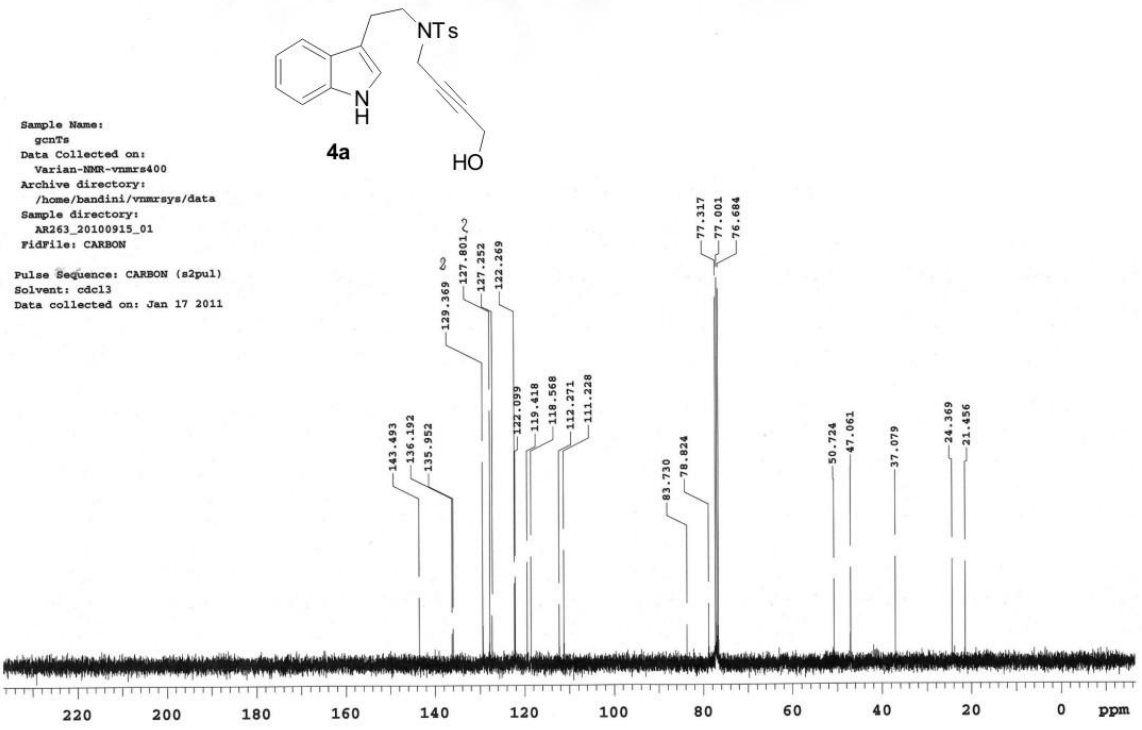

7.850
7.511
7.491
7.489
7.190
7.145
7.143
7.141
7.125
7.122
7.007
7.003
6.988
6.984
6.979
6.975
6.961
6.959
6.956
4.221
4.216
4.211
4.154
4.144
4.136
4.127
4.109
4.091
4.076
4.058
4.040
4.032
4.023
4.014
3.437
2.734
2.728
2.723
2.296
1.168
1.150
1.133
8
7
6
5
4
3
2
ppm

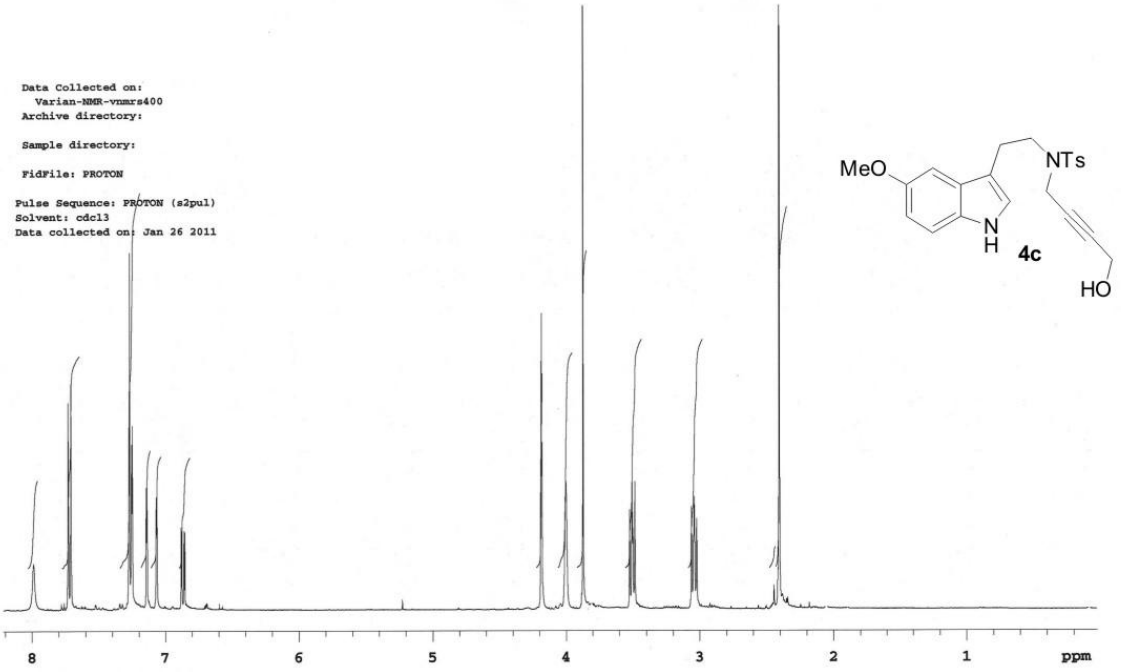

EtO2C
CO2Et
N
H
OH

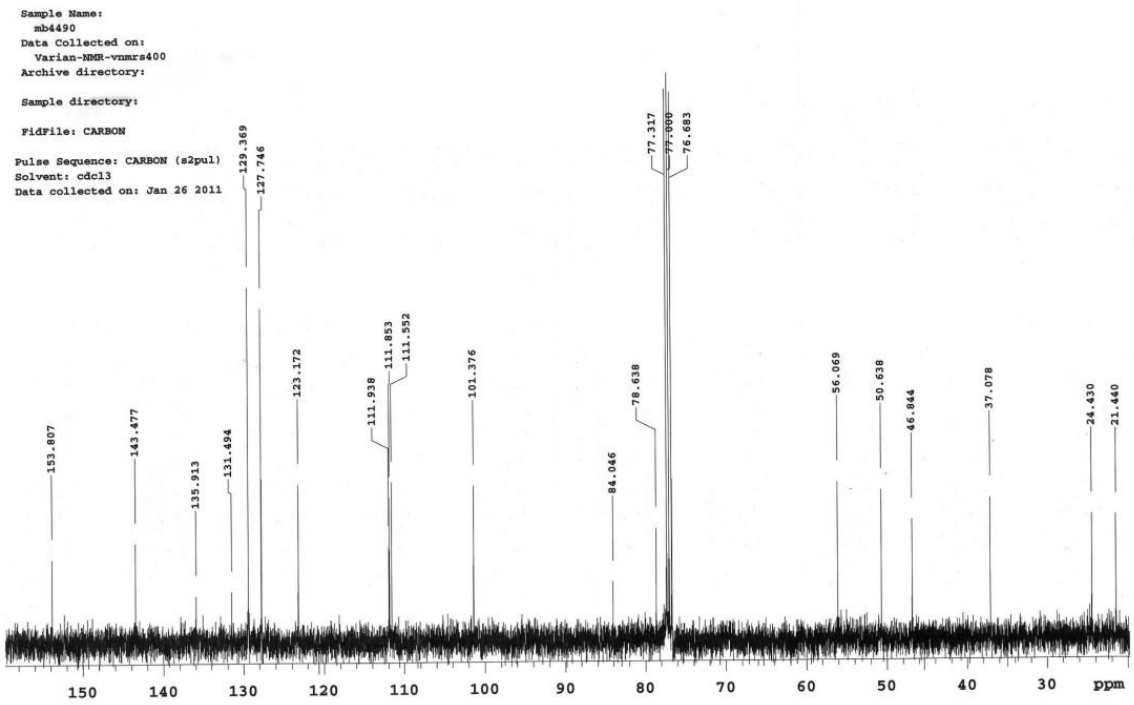
3j

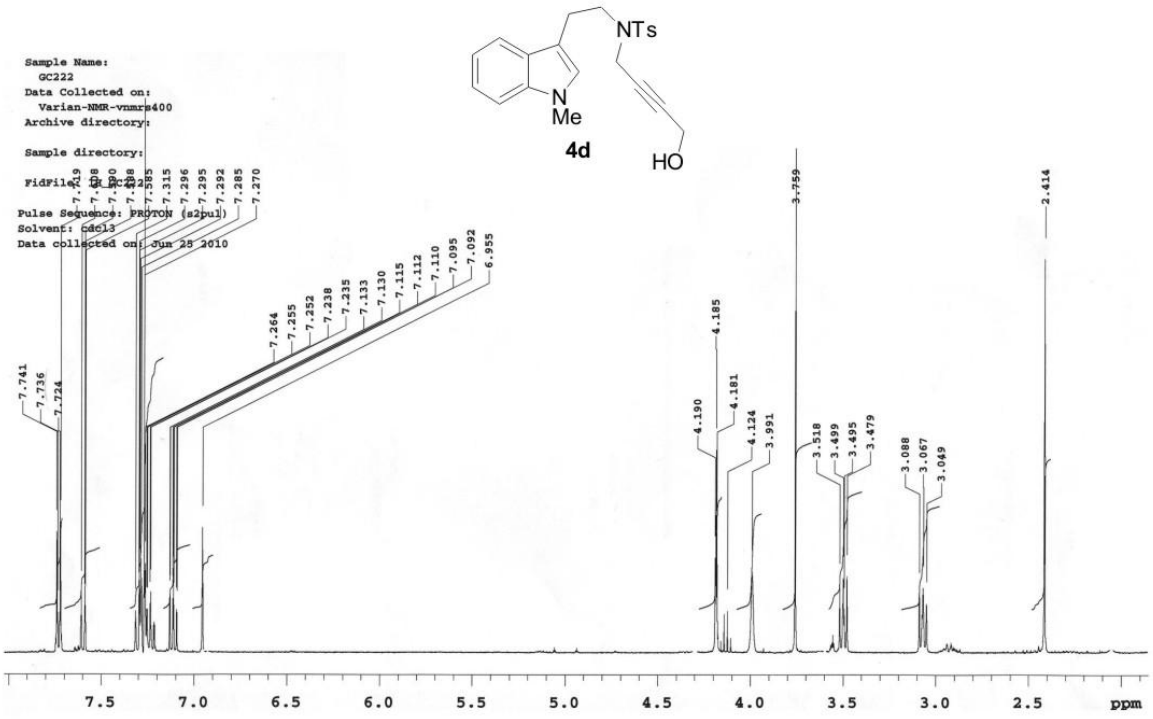

170.478
135.176
133.554
129.312
121.060
119.136
118.317
110.050
105.492
82.050
81.903
77.314
76.997
76.680
61.568
58.601
51.168
26.761
23.122
13.866
12.042
160
140
120
100
80
60
40
20
ppm

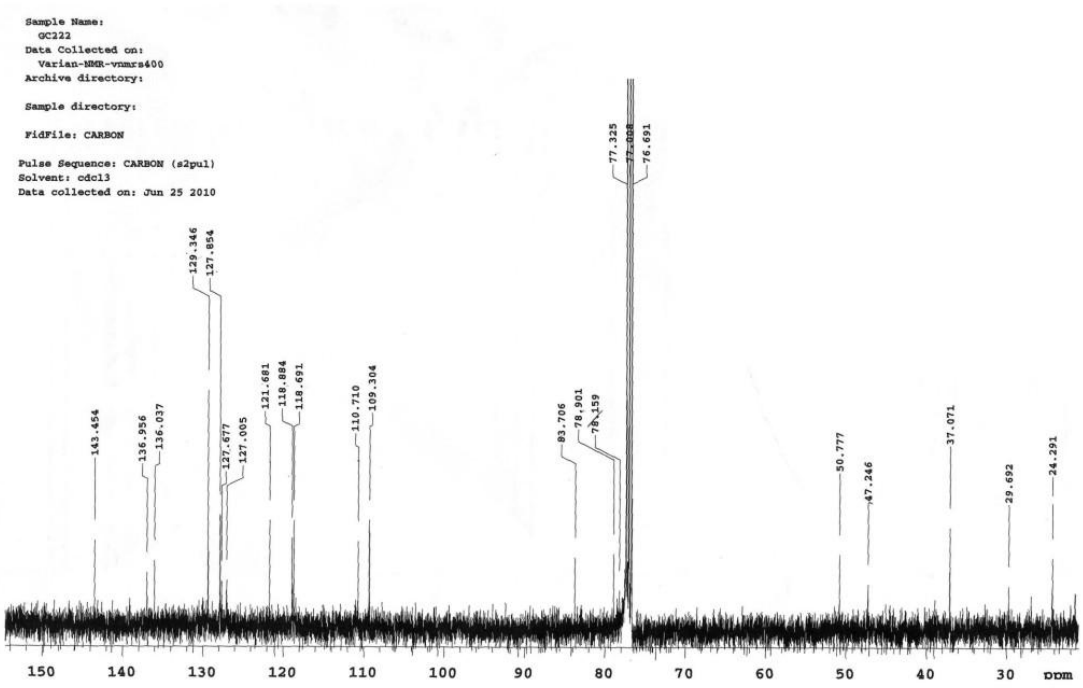

FD13
Sample Name:
GC32
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 15 2010
8.013
7.514
7.291
7.289
7.273
7.268
7.192
7.180
7.171
7.135
7.132
7.117
7.115
7.112
7.098
7.095
7.055
7.052
7.038
7.035
7.033
7.018
7.015
7.010
7.004
4.091
4.085
4.080
4.075
3.897
3.450
3.431
3.427
3.411
3.010
2.995
2.988
2.972
2.330
8
7
6
5
4
3
2
ppm

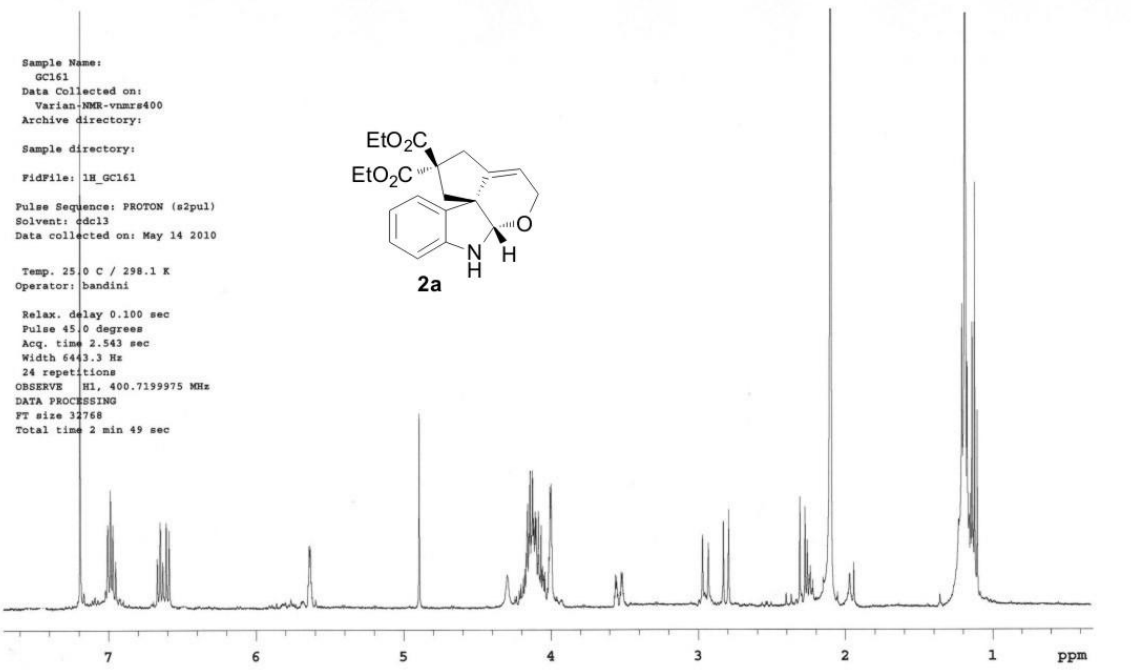

NTs
N
H
4a
HO
Sample Name:
gcnTs
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
/home/bandini/vnmrsys/data
Sample directory:
AR263_20100915_01
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 17 2011
143.493
136.192
135.952
129.369
127.801
127.252
122.269
122.099
119.418
118.568
112.271
111.228
83.730
78.824
77.317
77.001
76.684
50.724
47.061
37.079
24.369
21.456
220
200
180
160
140
120
100
80
60
40
20
0
ppm

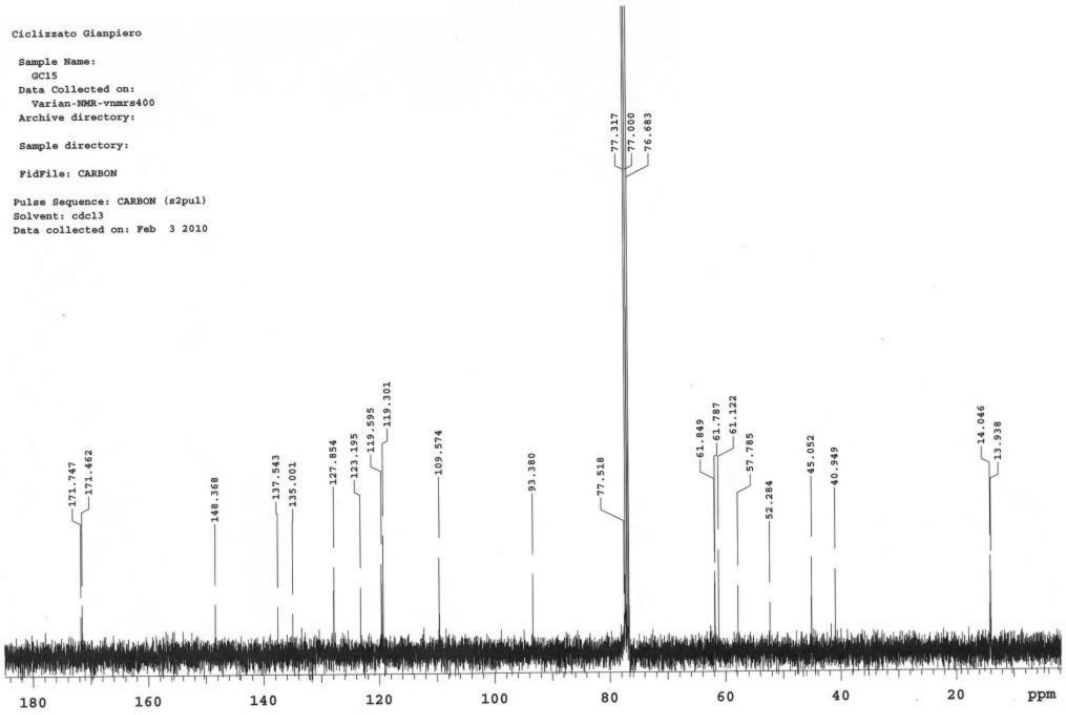

Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 26 2011
MeO
NTs
N
H
4c
HO
8
7
6
5
4
3
2
1
ppm

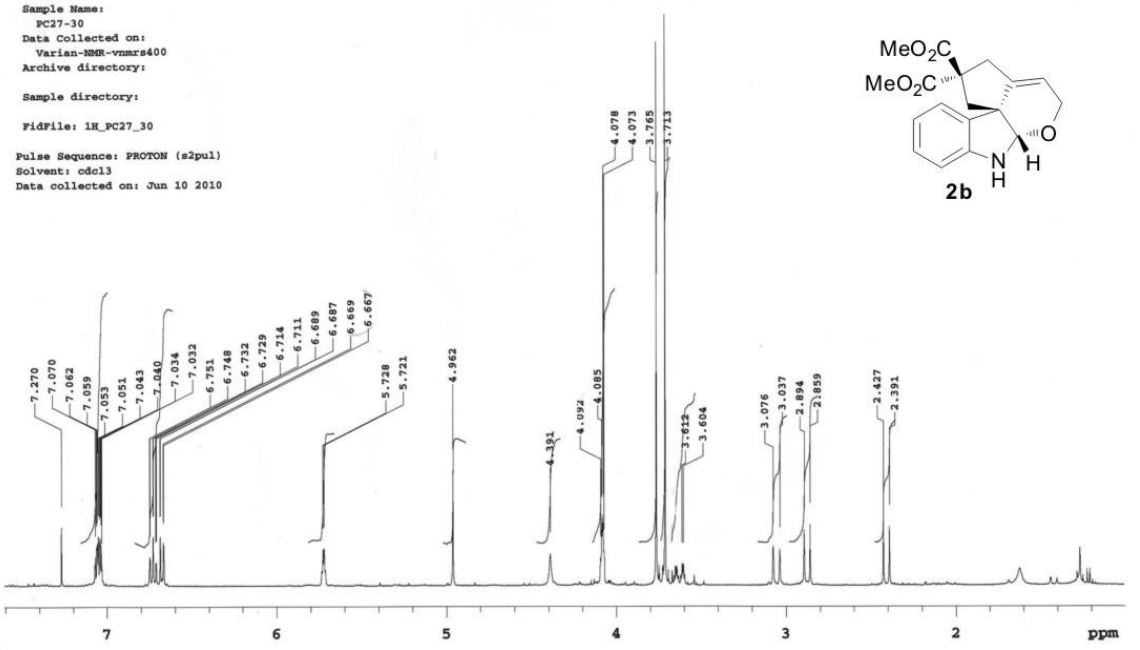

Sample Name:
mb4490
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 26 2011
153.807
143.477
135.913
131.494
129.369
127.746
123.172
111.938
111.853
111.552
101.376
84.046
78.638
77.317
77.000
76.683
56.069
50.638
46.844
37.078
24.430
21.440
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

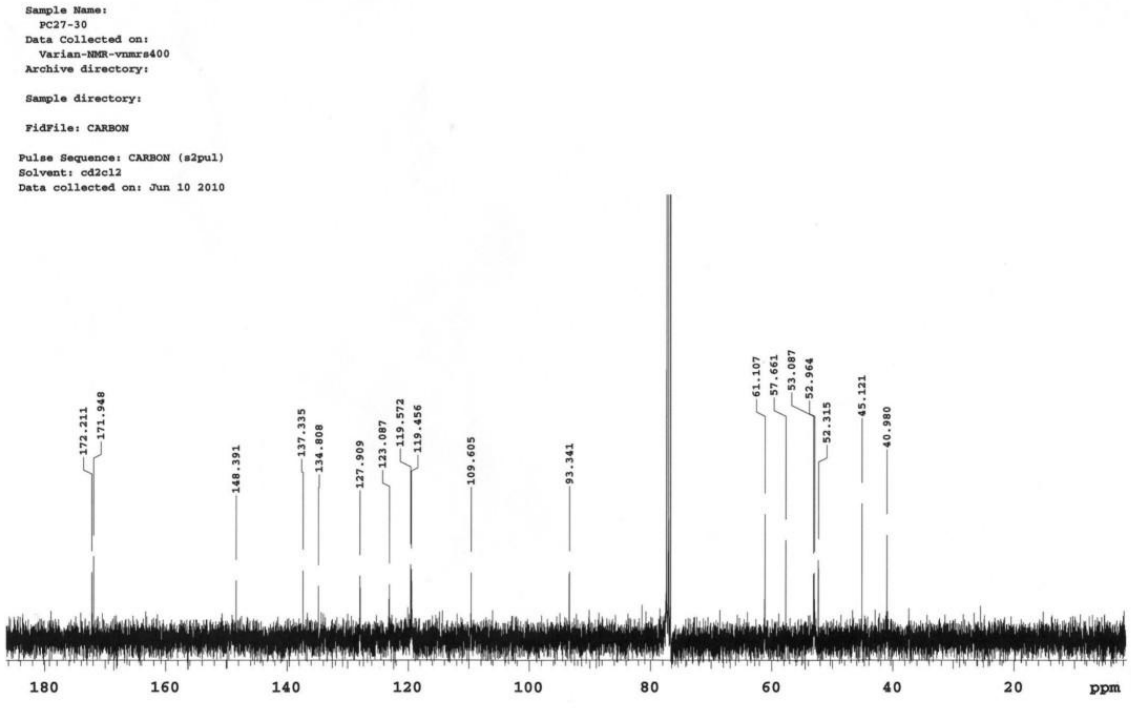

Sample Name:
GC222
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 25 2010
NTs
N
Me
4d
HO
ppm

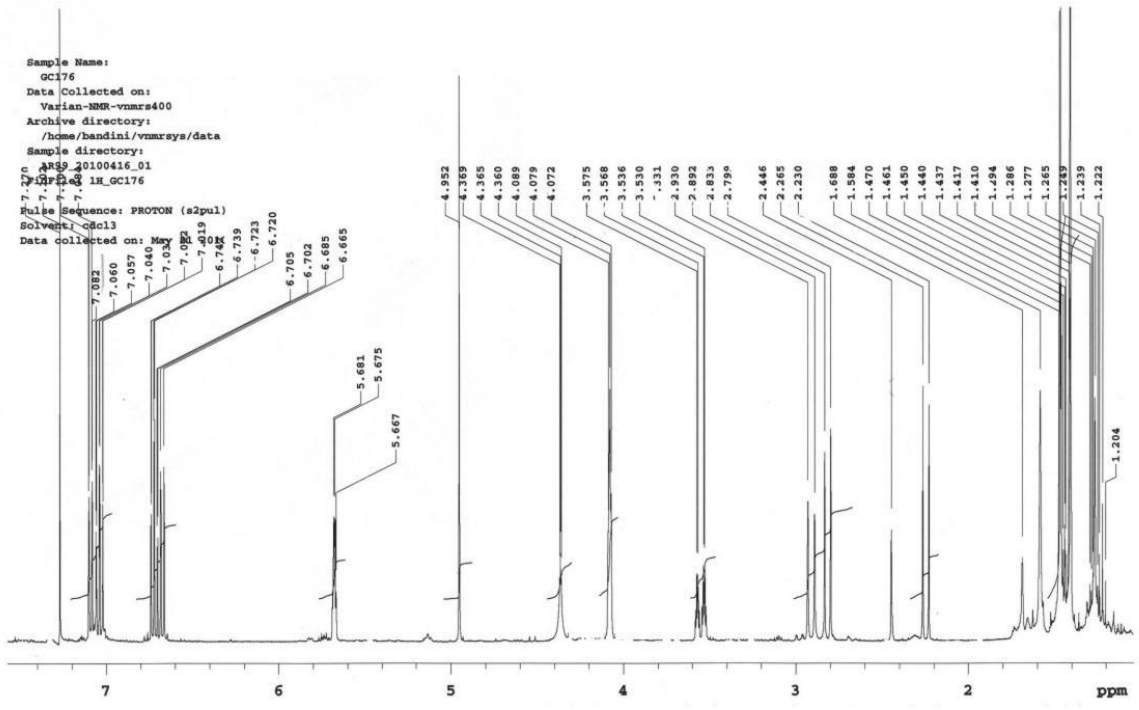

Sample Name:
GC222
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 25 2010
ppm

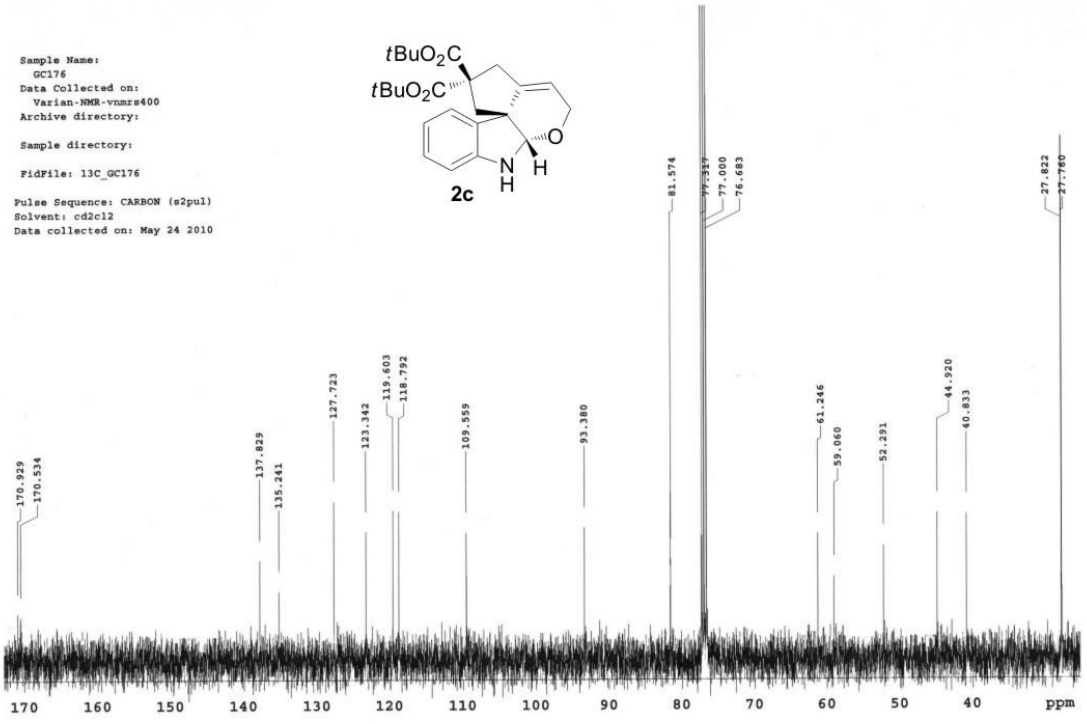

Sample Name:
GC161
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: 1H_GC161
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 14 2010
Temp. 25.0 C / 298.1 K
Operator: bandini
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.543 sec
Width 6443.3 Hz
24 repetitions
OBSERVE H1, 400.7199975 MHz
DATA PROCESSING
FT size 32768
Total time 2 min 49 sec
EtO2C
EtO2C
O
N
H
H
2a
7
6
5
4
3
2
1
ppm

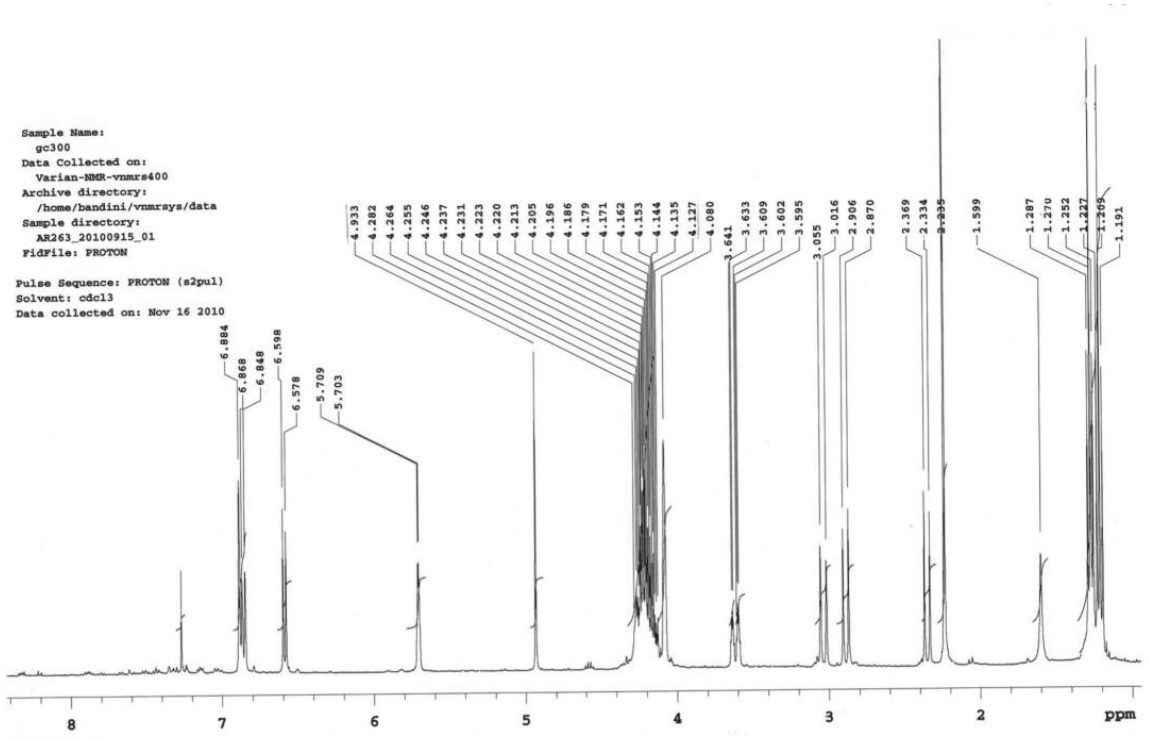

Ciclizzato Gianpiero
Sample Name:
GC15
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 3 2010
171.747
171.462
148.368
137.543
135.001
127.854
123.195
119.595
119.301
109.574
93.380
77.518
77.317
77.000
76.683
61.849
61.787
61.122
57.785
52.284
45.052
40.949
14.046
13.938
180
160
140
120
100
80
60
40
20
ppm

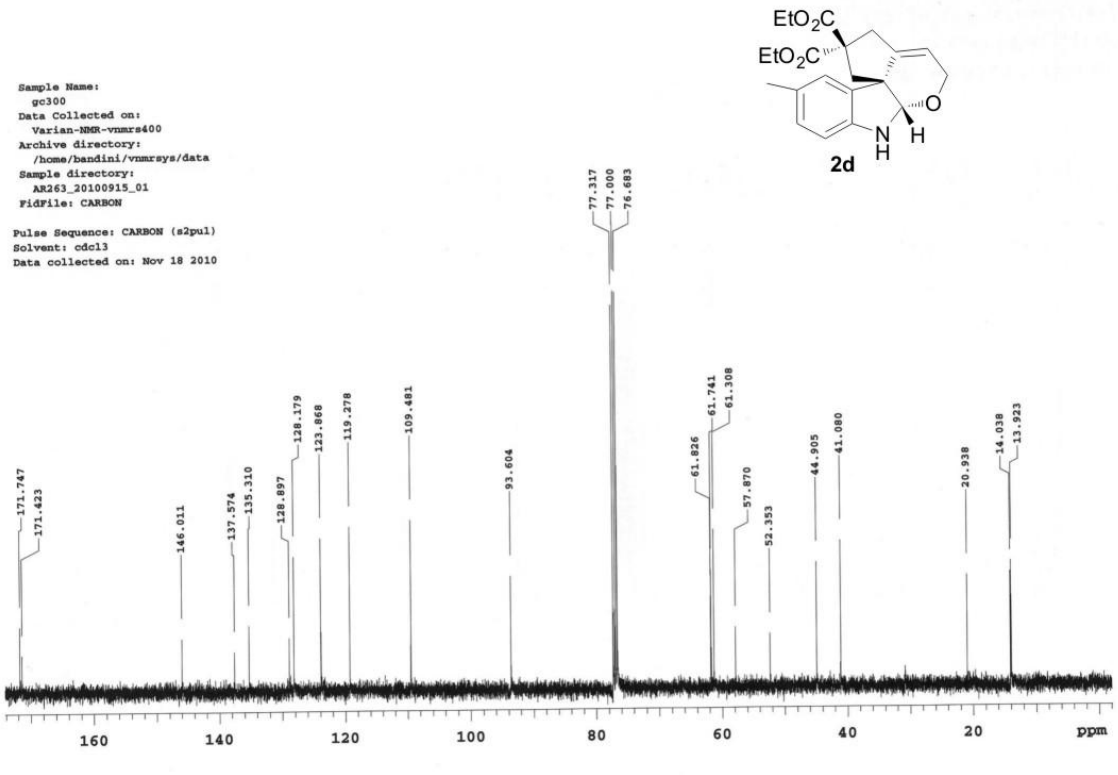

Sample Name:
PC27-30
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: 1H_PC27_30
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 10 2010
MeO2C
MeO2C
O
N H
H
2b
7.270
7.070
7.062
7.059
7.053
7.051
7.043
7.040
7.034
7.032
6.751
6.748
6.732
6.729
6.714
6.711
6.689
6.687
6.669
6.667
5.728
5.721
4.962
4.391
4.092
4.085
4.078
4.073
3.765
3.713
3.612
3.604
3.076
3.037
2.894
2.859
2.427
2.391
7
6
5
4
3
2
ppm


Sample Name:
PC27-30
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 10 2010
172.211
171.948
148.391
137.335
134.808
127.909
123.087
119.572
119.456
109.605
93.341
61.107
57.661
53.087
52.964
52.315
45.121
40.980
180
160
140
120
100
80
60
40
20
ppm


Sample Name:
GC176
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
/home/bandini/vnmrsys/data
Sample directory:
ARS9_20100416_01
FidFile: 1H_GC176
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 24 2010
7.270
7.082
7.060
7.057
7.040
7.032
7.022
7.019
7.001
6.743
6.739
6.723
6.720
6.705
6.702
6.685
6.665
5.681
5.675
5.667
4.952
4.369
4.365
4.360
4.089
4.079
4.072
3.575
3.568
3.536
3.530
3.331
2.930
2.892
2.833
2.790
2.446
2.265
2.230
1.688
1.584
1.470
1.461
1.450
1.440
1.437
1.417
1.410
1.294
1.286
1.277
1.265
1.249
1.239
1.222
1.204
7
6
5
4
3
2
ppm

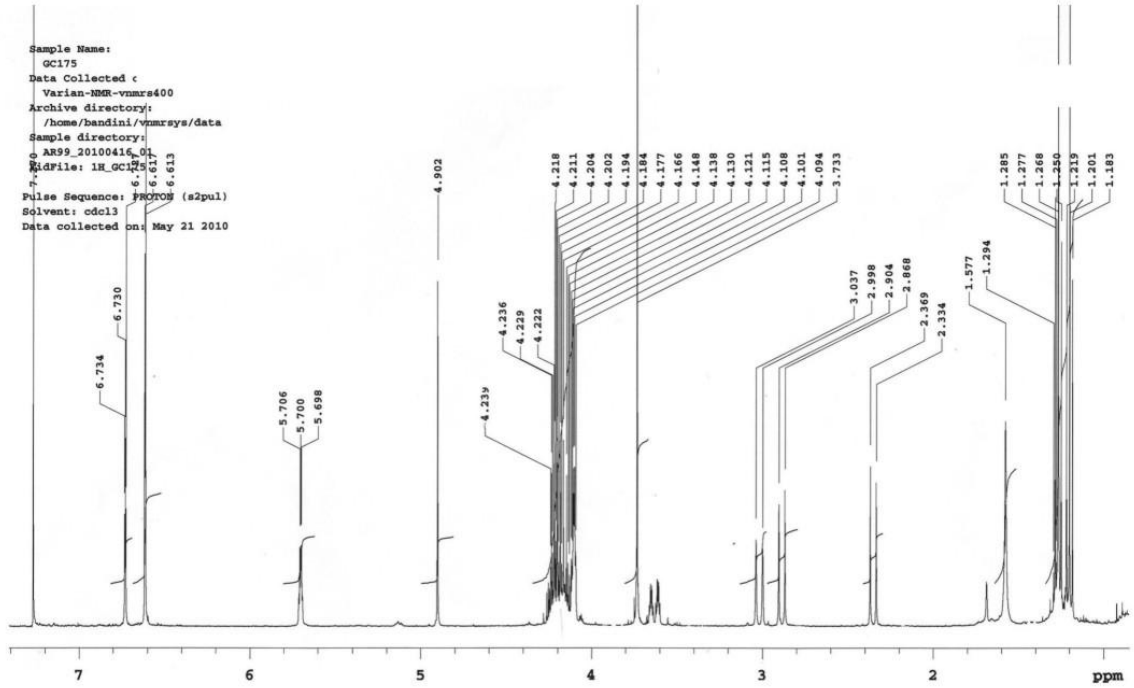

Sample Name:
GC176
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: 13C_GC176
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: May 24 2010
tBuO2C
tBuO2C
O
N
H
H
2c
170.929
170.534
137.829
135.241
127.723
123.342
119.603
118.792
109.559
93.380
81.574
77.317
77.000
76.683
61.246
59.060
52.391
44.920
40.833
27.822
27.760
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

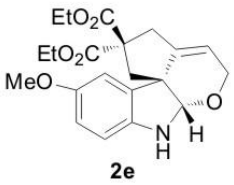

Sample Name:
gc300
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
/home/bandini/vnmrsys/data
Sample directory:
AR263_20100915_01
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 16 2010
6.884
6.868
6.848
6.598
6.578
5.709
5.703
4.933
4.282
4.264
4.255
4.246
4.237
4.231
4.223
4.220
4.213
4.205
4.196
4.186
4.179
4.171
4.162
4.153
4.144
4.135
4.127
4.080
3.641
3.633
3.609
3.602
3.595
3.055
3.016
2.906
2.870
2.369
2.334
2.035
1.599
1.287
1.270
1.252
1.227
1.269
1.191
8
7
6
5
4
3
2
ppm


Sample Name:
gc300
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
/home/bandini/vnmrsys/data
Sample directory:
AR263_20100915_01
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 18 2010
171.747
171.423
146.011
137.574
135.310
128.897
128.179
123.668
119.278
109.481
93.604
77.317
77.000
76.683
61.826
61.741
61.308
57.870
52.353
44.905
41.080
20.938
14.038
13.923
160
140
120
100
80
60
40
20
ppm

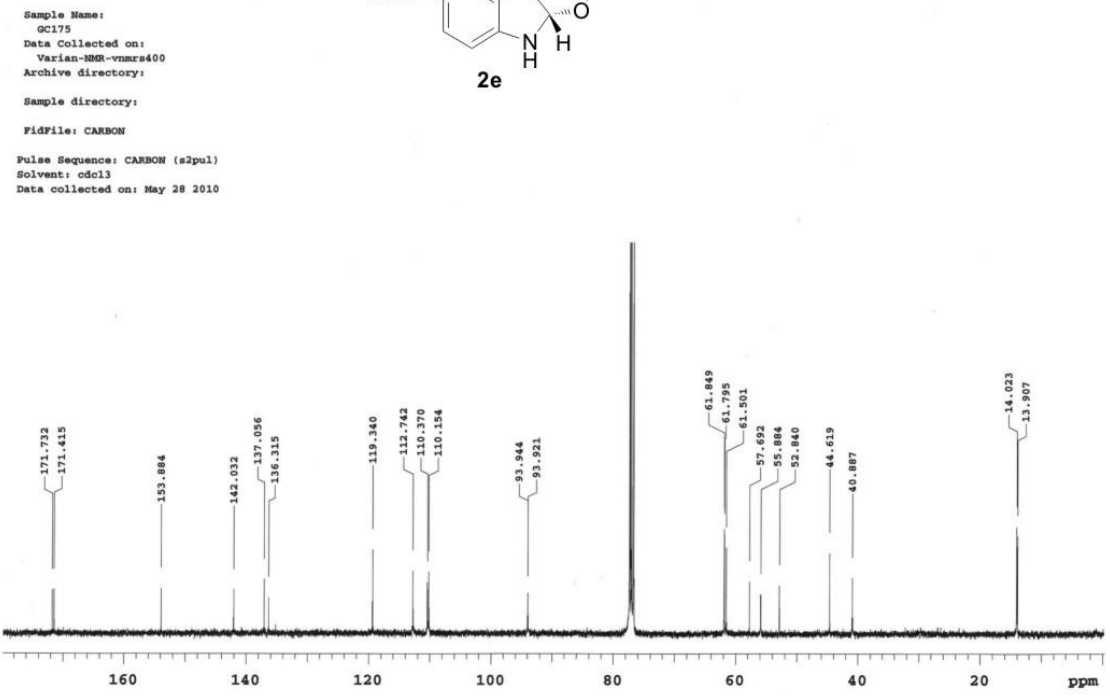
EtO2C
EtO2C
O
N
H
H

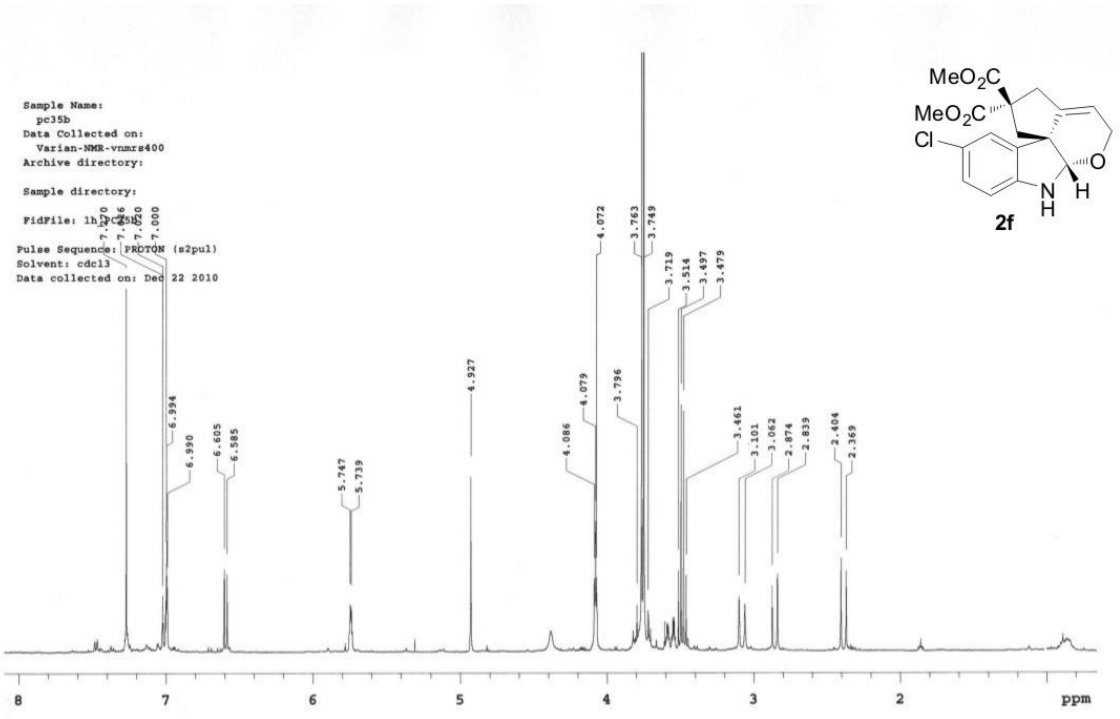
2d

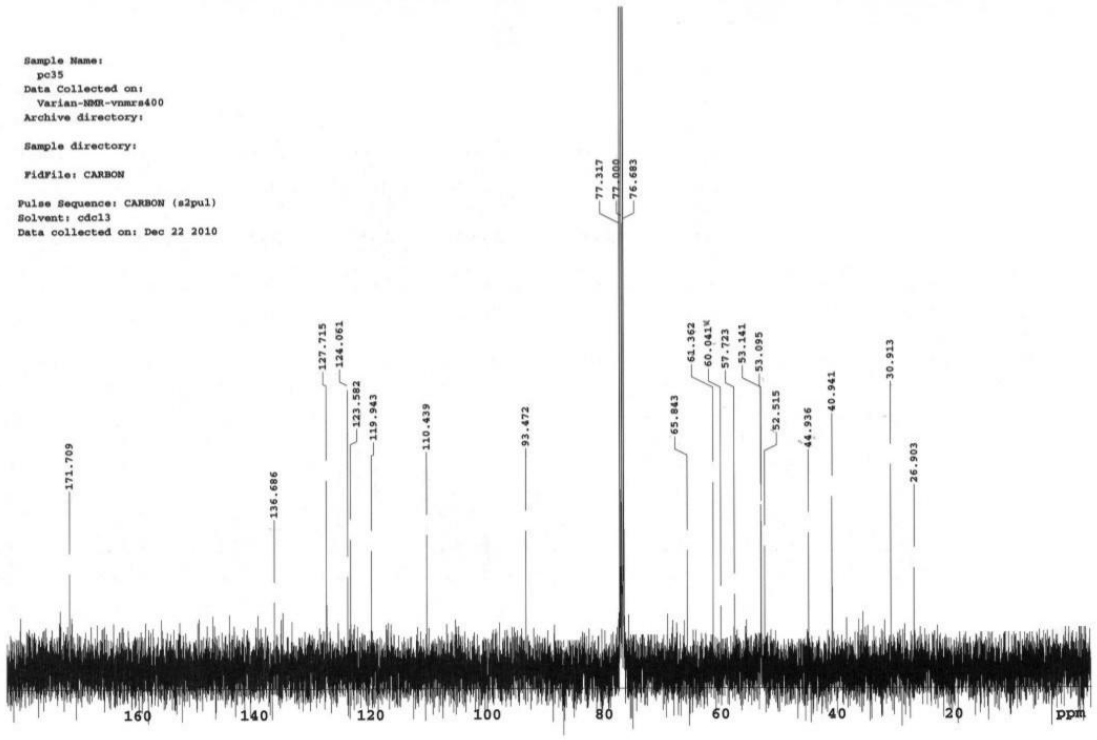

Sample Name:
GC175
Data Collected c
Varian-NMR-vnmrs400
Archive directory:
/home/bandini/vnmrsys/data
Sample directory:
AR99_20100416_01
FidFile: 1H_GC175
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 21 2010
6.734
6.730
6.617
6.613
5.706
5.700
5.698
4.902
4.239
4.236
4.229
4.222
4.218
4.211
4.204
4.202
4.194
4.184
4.177
4.166
4.148
4.138
4.130
4.121
4.115
4.108
4.101
4.094
3.733
3.037
2.998
2.904
2.868
2.369
2.334
1.577
1.294
1.285
1.277
1.268
1.250
1.219
1.201
1.183
7
6
5
4
3
2
ppm

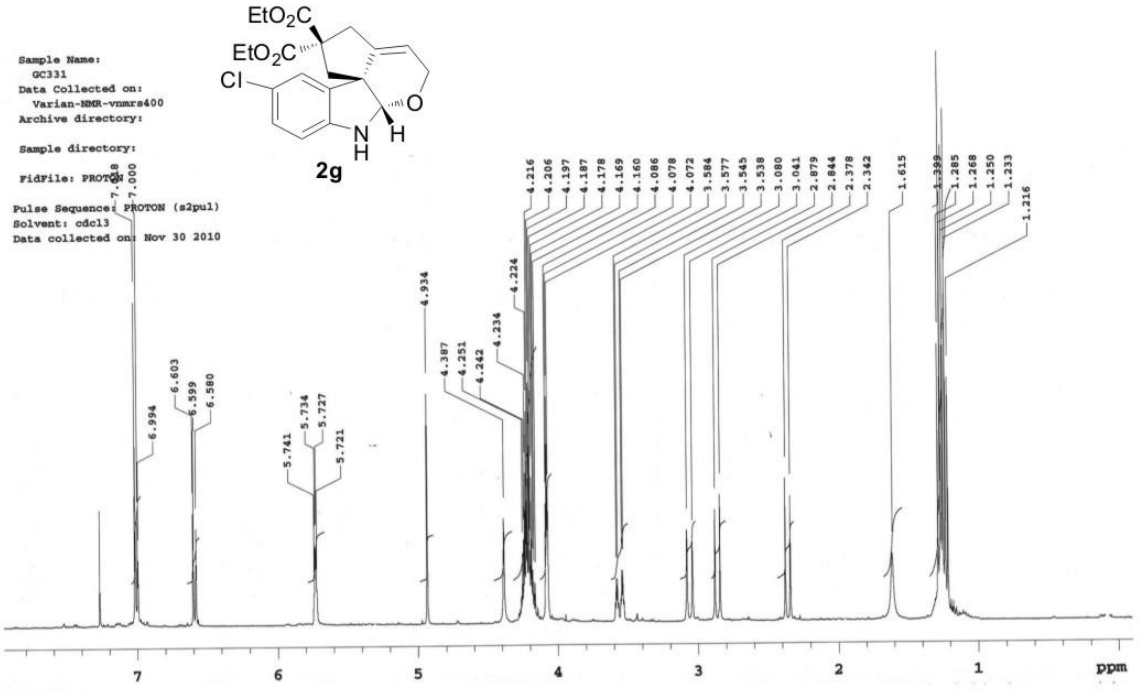

EtO2C
EtO2C
MeO
O
N
H
H

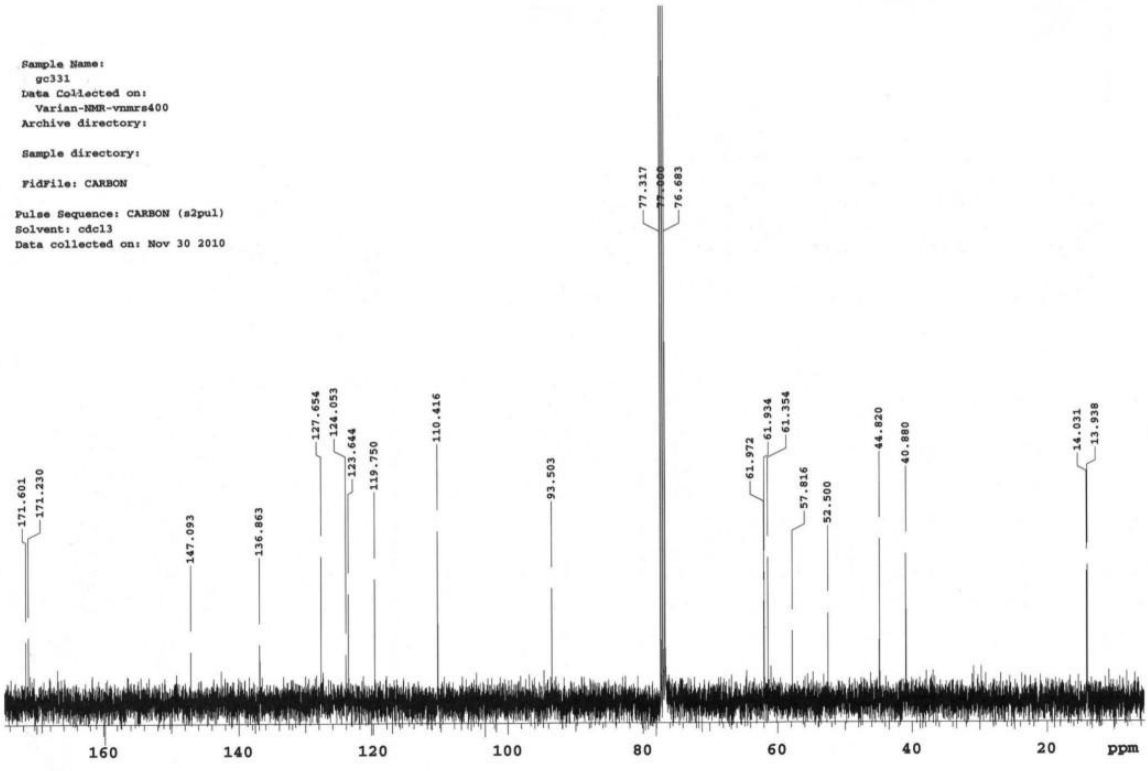
2e

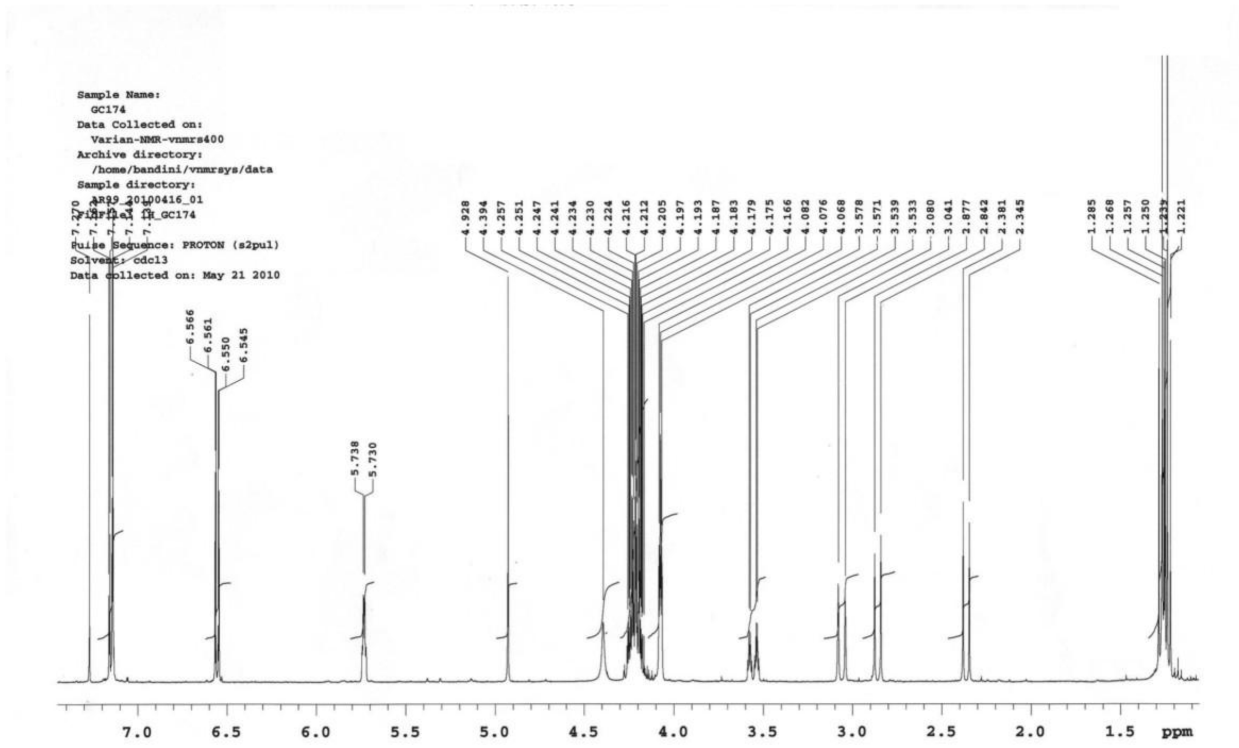

Sample Name:
GC175
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 28 2010
171.732
171.415
153.884
142.032
137.056
136.315
119.340
112.742
110.370
110.154
93.944
93.921
61.849
61.795
61.501
57.692
55.884
52.840
44.619
40.887
14.023
13.907
160
140
120
100
80
60
40
20
ppm

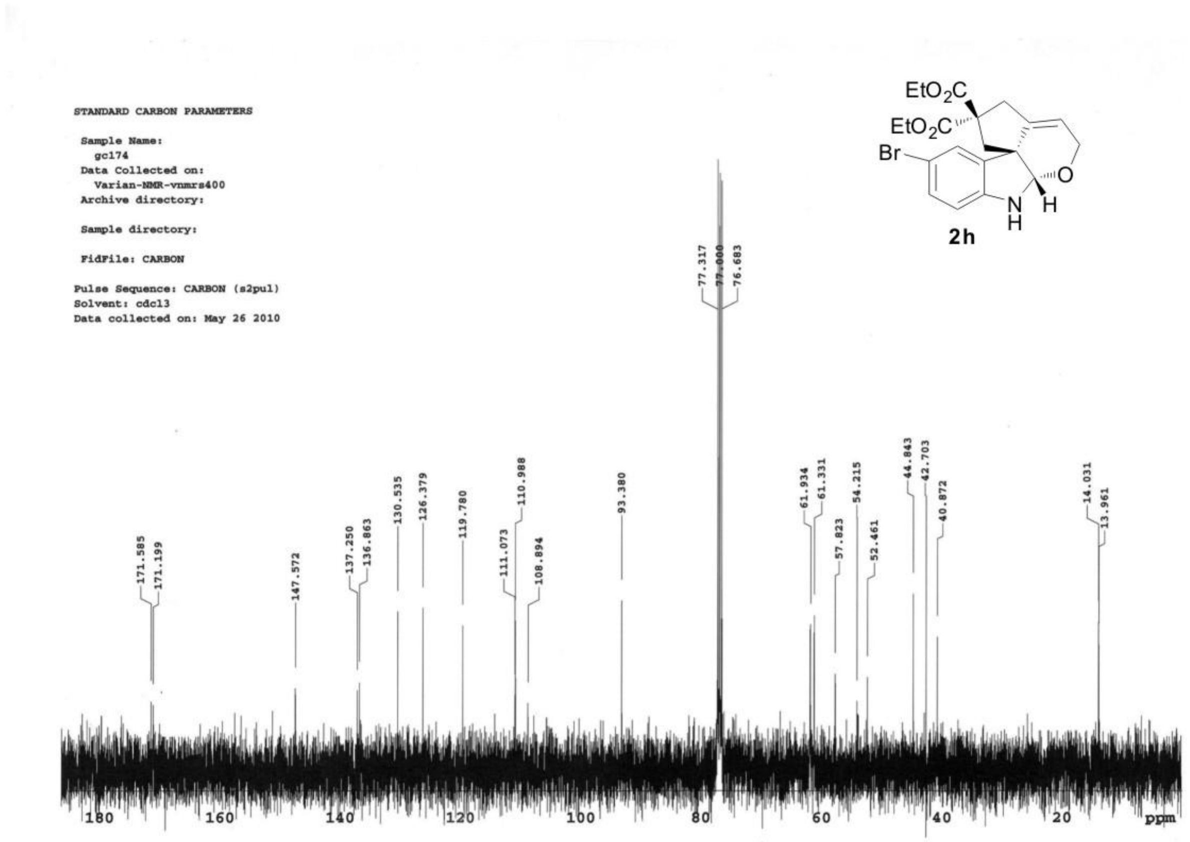

Sample Name:
pc35b
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: 1h_pc35b
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 22 2010
7.770
7.746
7.600
7.000
6.594
6.990
6.605
6.585
5.747
5.739
4.927
4.086
4.079
4.072
3.796
3.763
3.749
3.719
3.514
3.497
3.479
3.461
3.101
3.062
2.874
2.839
2.404
2.369
8
7
6
5
4
3
2
ppm
MeO2C
MeO2C
Cl
O
N
H
H
2f

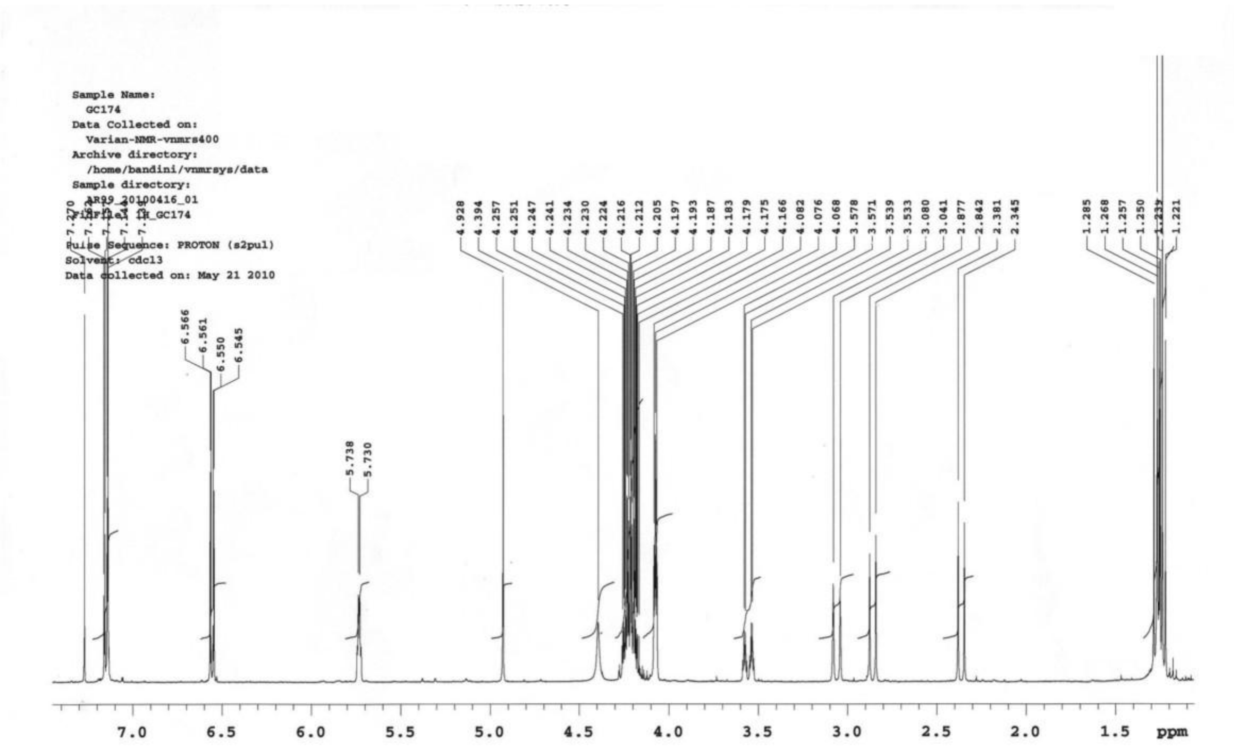

Sample Name:
pc35
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 22 2010
171.709
136.686
127.715
124.061
123.582
119.943
110.439
93.472
77.317
77.058
76.683
65.843
61.362
60.041
57.723
53.141
53.095
52.515
44.936
40.941
30.913
26.903
160
140
120
100
80
60
40
20
ppm

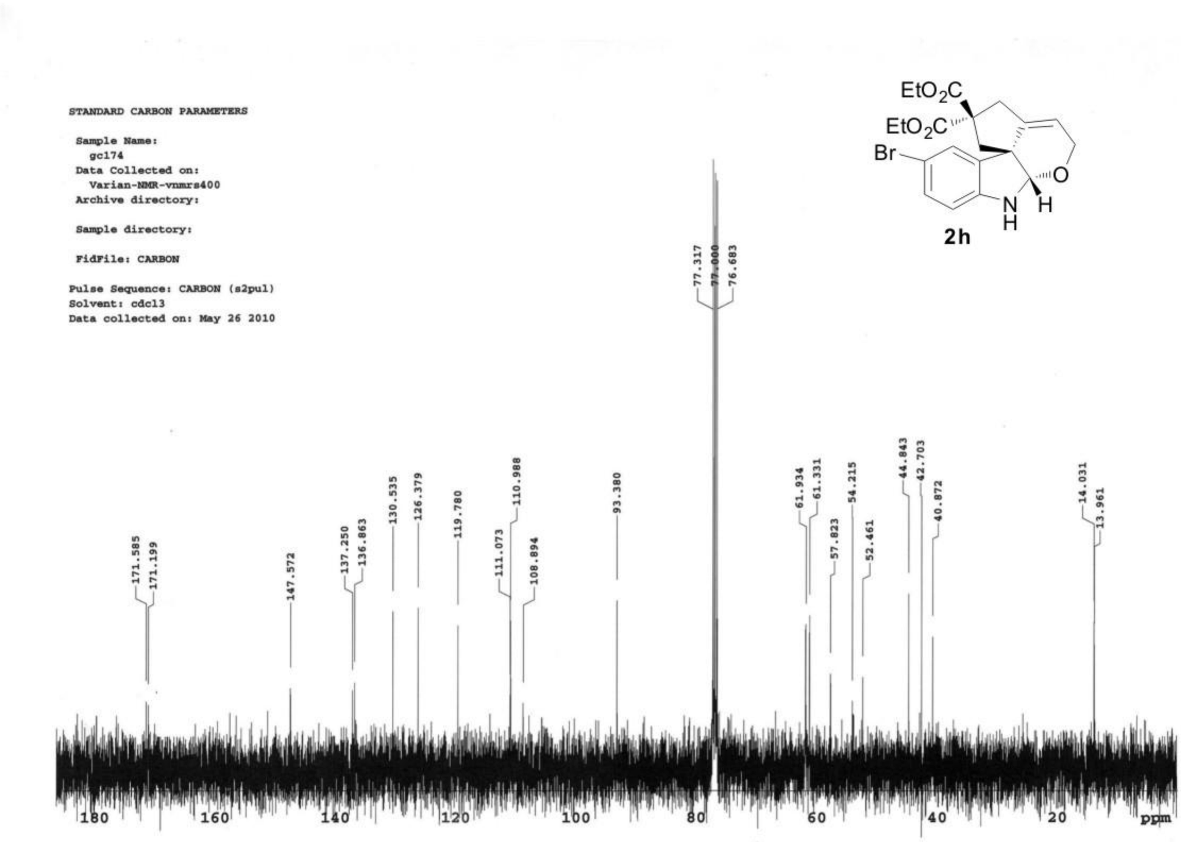

EtO2C
EtO2C
Cl
O
N
H
2g
Sample Name:
GC331
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 30 2010
7.268
7.000
6.994
6.603
6.599
6.580
5.741
5.734
5.727
5.721
4.934
4.387
4.251
4.242
4.234
4.224
4.216
4.206
4.197
4.187
4.178
4.169
4.160
4.086
4.078
4.072
3.584
3.577
3.545
3.538
3.080
3.041
2.879
2.844
2.378
2.342
1.615
1.399
1.285
1.268
1.250
1.233
1.216
7
6
5
4
3
2
1
ppm


Sample Name:
gc331
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 30 2010
171.601
171.230
147.093
136.863
127.654
124.053
123.644
119.750
110.416
93.503
77.317
77.000
76.683
61.972
61.934
61.354
57.816
52.500
44.820
40.880
14.031
13.938
160
140
120
100
80
60
40
20
ppm

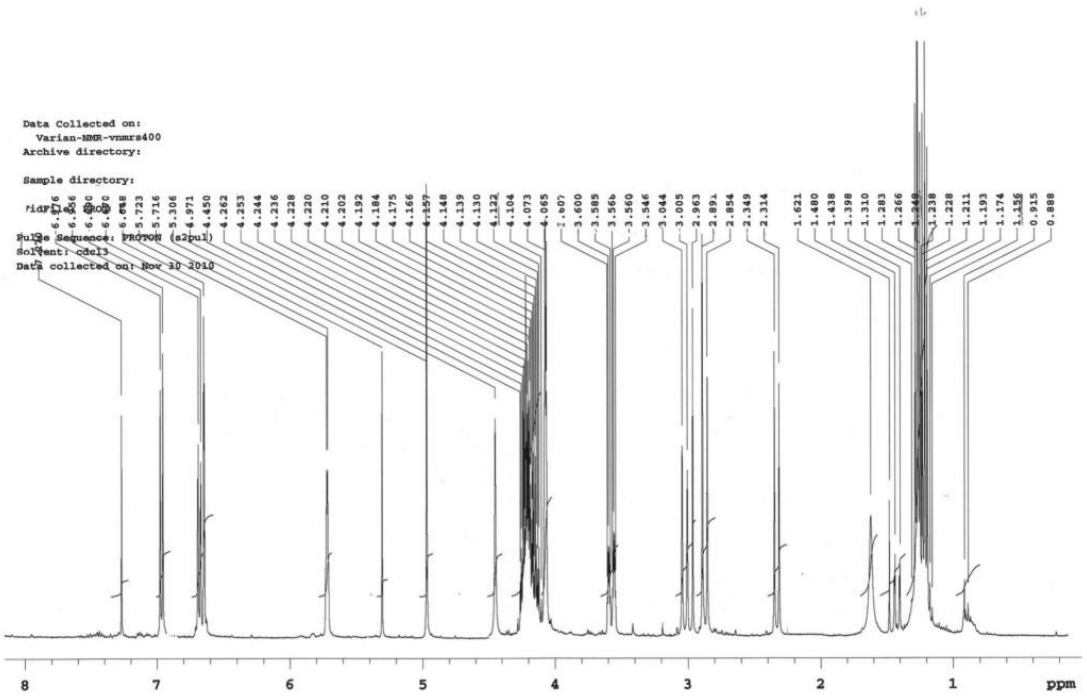

Sample Name:
GC174
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
/home/bandini/vnmrsys/data
Sample directory:
AR99_20100416_01
FidFile: 1H_GC174
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 21 2010
ppm

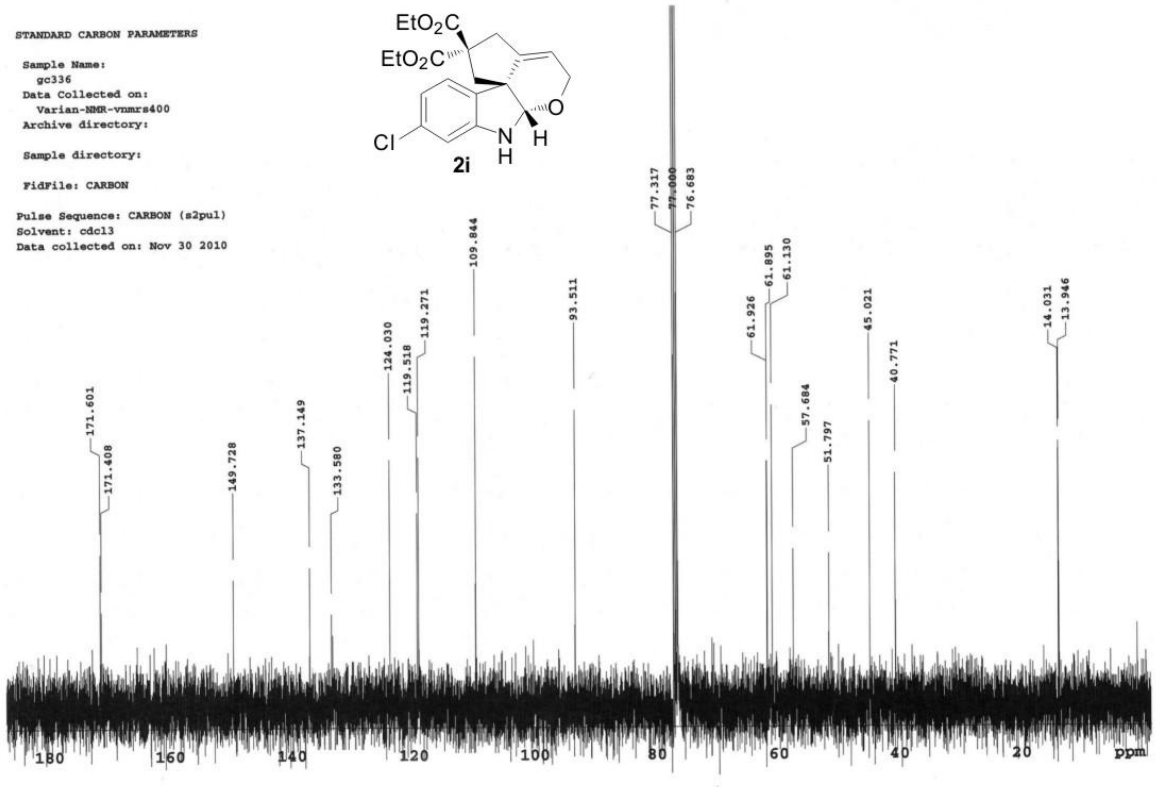

STANDARD CARBON PARAMETERS
Sample Name:
gc174
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 26 2010
EtO2C
EtO2C
Br
O
N
H
H
2h
ppm

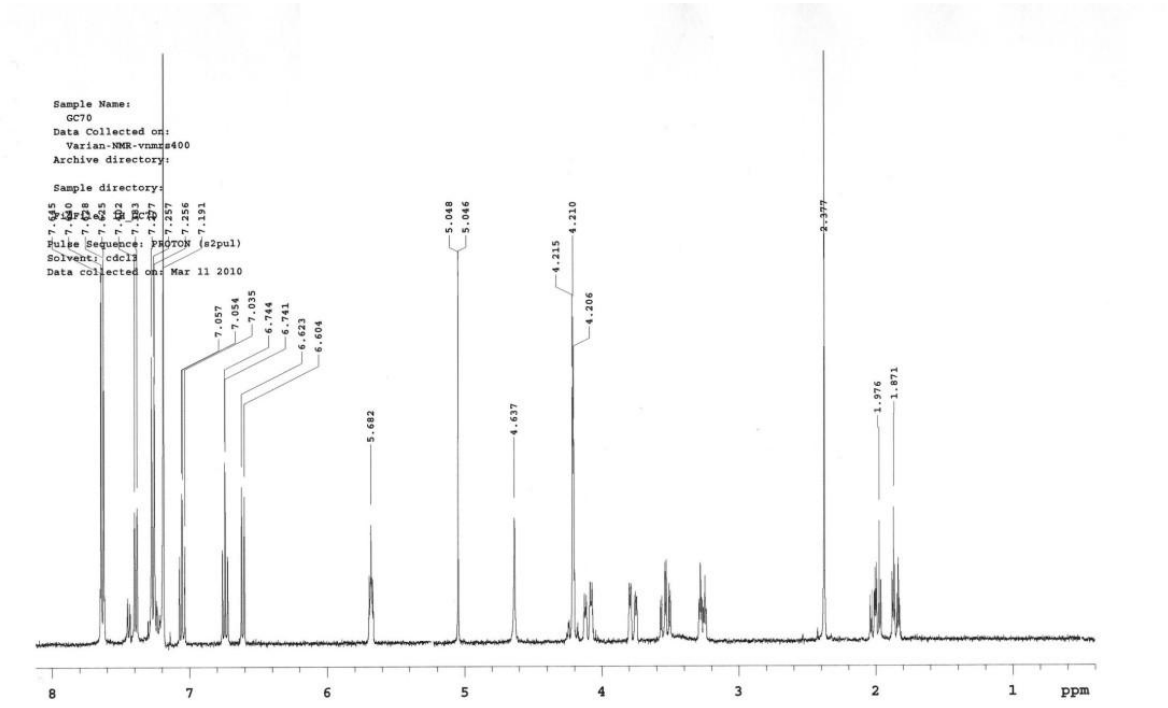


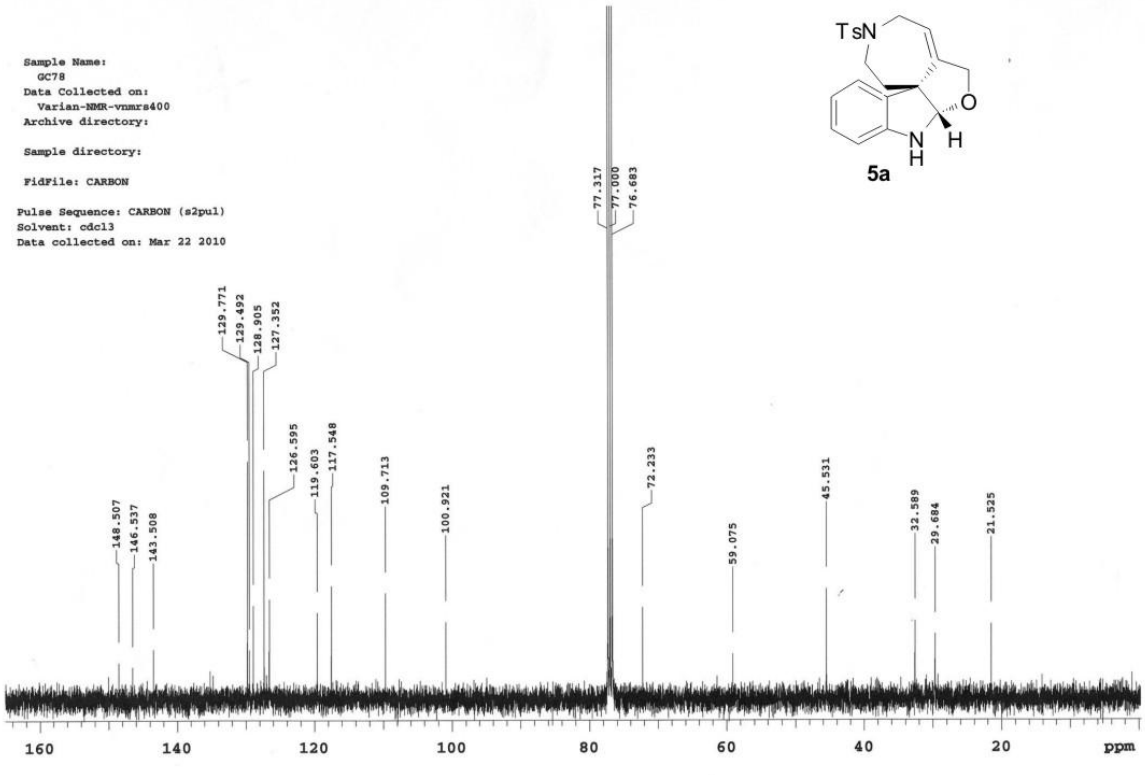


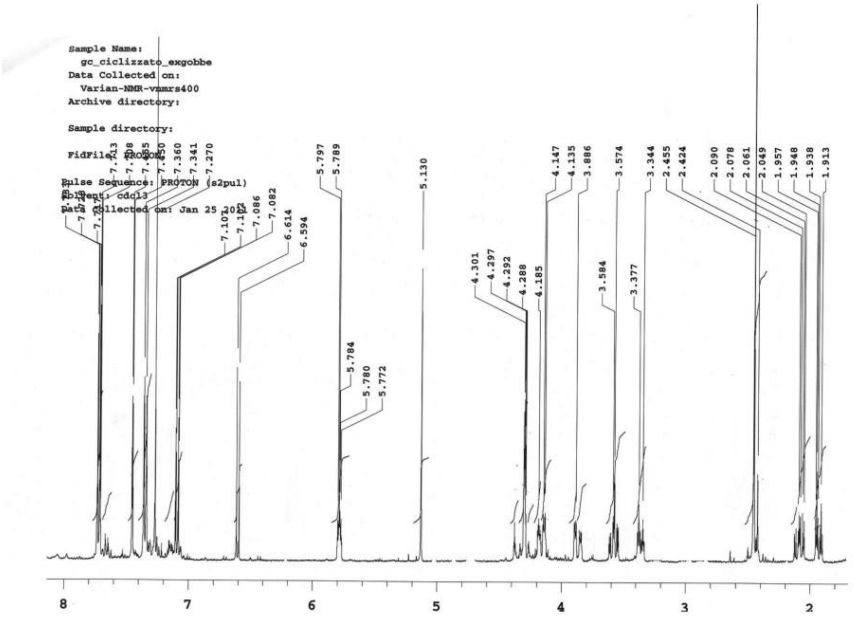
2h

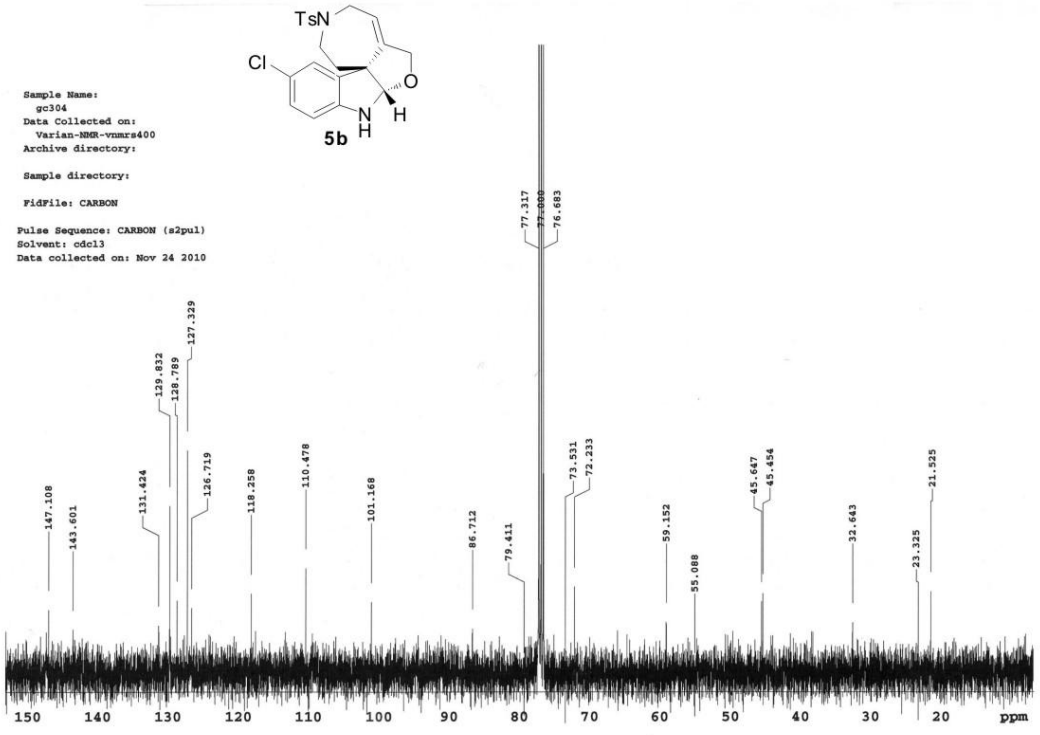

Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 30 2010
8
7
6
5
4
3
2
1
ppm

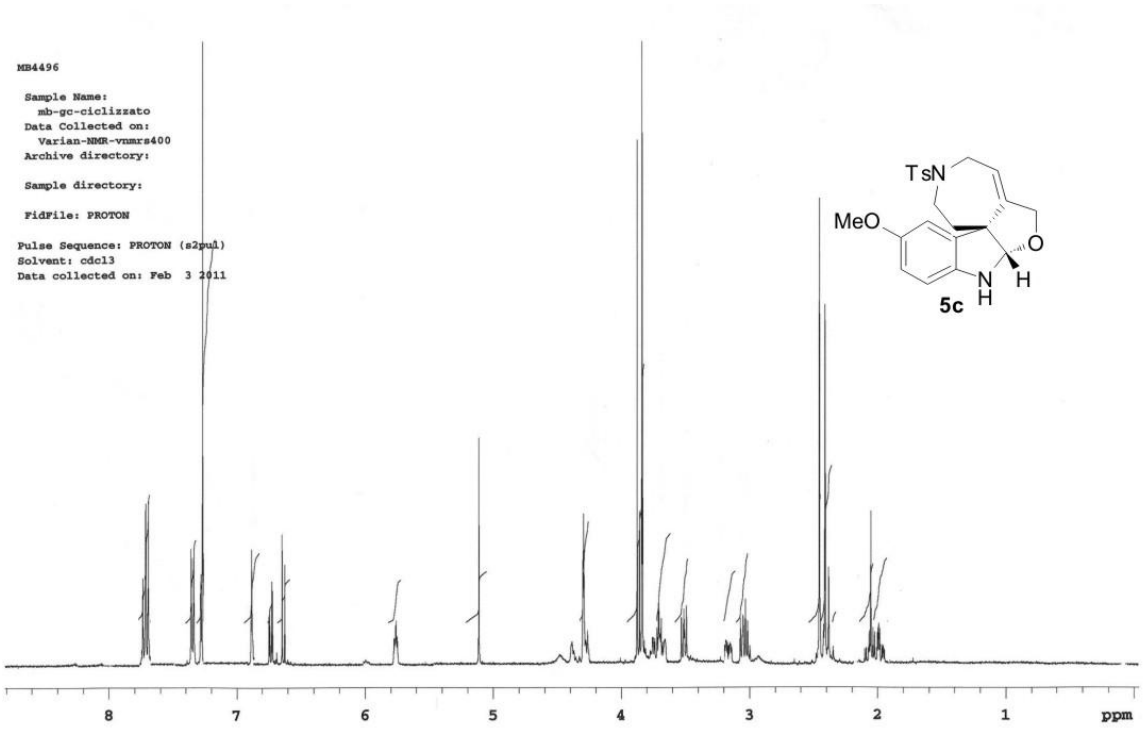

STANDARD CARBON PARAMETERS
Sample Name:
gc336
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 30 2010
EtO2C
EtO2C
Cl
N
H
O
H
2i
171.601
171.408
149.728
137.149
133.580
124.030
119.518
119.271
109.844
93.511
77.317
77.000
76.683
61.926
61.895
61.130
57.684
51.797
45.021
40.771
14.031
13.946
180
160
140
120
100
80
60
40
20
ppm

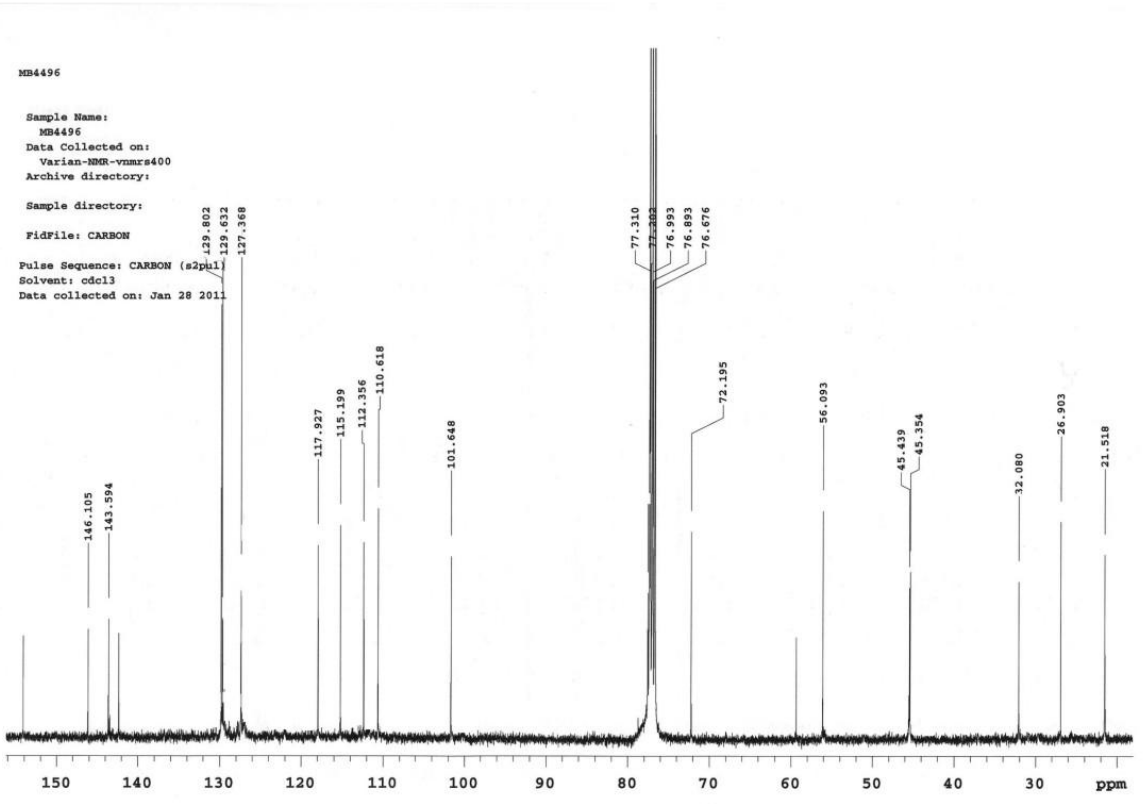

Sample Name:
GC70
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 11 2010
7.645
7.640
7.628
7.625
7.622
7.613
7.257
7.256
7.191
7.057
7.054
7.035
6.744
6.741
6.623
6.604
5.682
5.048
5.046
4.637
4.215
4.210
4.206
2.377
1.976
1.871
8
7
6
5
4
3
2
1
ppm

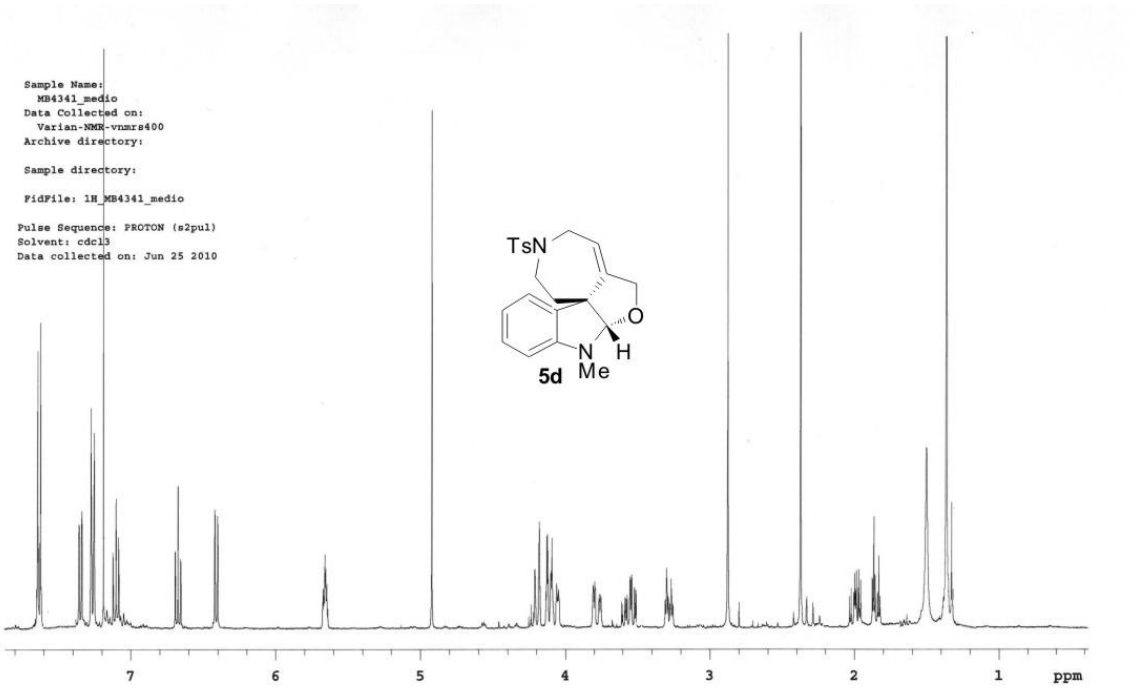

Sample Name:
GC78
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 22 2010
TsN
O
N
H
H
5a
77.317
77.000
76.683
129.771
129.492
128.905
127.352
126.595
119.603
117.548
109.713
100.921
72.233
59.075
45.531
32.589
29.684
21.525
148.507
146.537
143.508
160
140
120
100
80
60
40
20
ppm

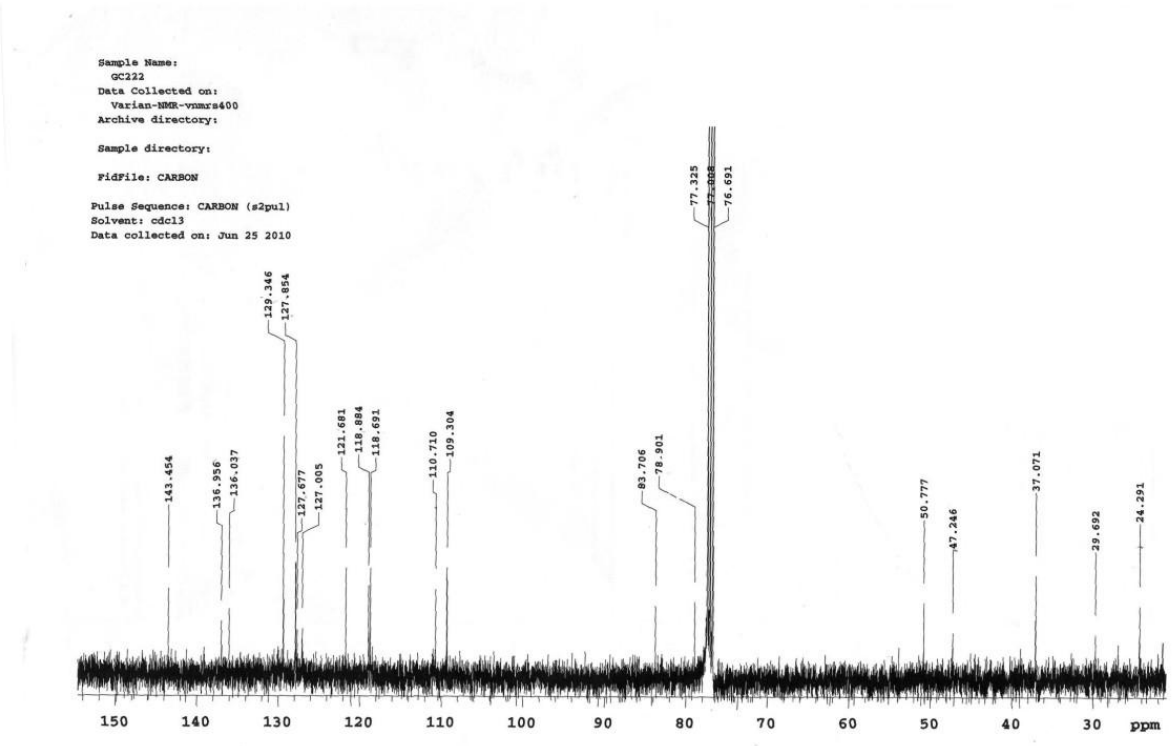

Sample Name:
gc_ciclizzato_exgobbe
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data Collected on: Jan 25 2011
7.360
7.341
7.270
7.086
7.082
6.614
6.594
5.797
5.789
5.784
5.780
5.772
5.130
4.301
4.297
4.292
4.288
4.185
4.147
4.135
3.886
3.584
3.574
3.377
3.344
2.455
2.424
2.090
2.078
2.061
2.049
1.957
1.948
1.938
1.913
8
7
6
5
4
3
2


TsN
Cl
O
N
H
5b
Sample Name:
gc304
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 24 2010
147.108
143.601
131.424
129.832
128.789
127.329
126.719
118.358
110.478
101.168
86.712
79.411
77.317
77.000
76.683
73.531
72.233
59.152
55.088
45.647
45.454
32.643
23.325
21.525
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


MB4496
Sample Name:
mb-gc-ciclizzato
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 3 2011
TsN
MeO
O
N
H
H
5c
8
7
6
5
4
3
2
1
ppm


MB4496
Sample Name:
MB4496
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 28 2011
129.802
129.632
127.368
146.105
143.594
117.927
115.199
112.356
110.618
101.648
77.310
77.202
76.993
76.893
76.676
72.195
56.093
45.439
45.354
32.080
26.903
21.518
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


Sample Name:
MB4341_medio
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: 1H_MB4341_medio
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 25 2010
TsN
O
N
H
Me
5d
7
6
5
4
3
2
1
ppm


Sample Name:
GC222
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 25 2010
143.454
136.956
136.037
129.346
127.854
127.677
127.005
121.681
118.884
118.691
110.710
109.304
83.706
78.901
77.325
77.008
76.691
50.777
47.246
37.071
29.692
24.291
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

References

[1] S. S. Kinderman, M. M. T. Wekking, J. H. van Maarseveen, H. E. Schoemaker, H. Hiemstra, F. P. J. T. Rutjes, *J.Org.Chem.* **2005**, **70**, 5519.

[2] D. T. Jones, G. D. Artman, R. M. Williams and M. Robert, *Tetrahedron Lett*. 2007, **48**, 1291.

[3] S. S. Kinderman, M. M. T. Wekking, J. H. van Maarseveen, H. E. Schoemaker, H. Hiemstra, F. P. J. T. Rutjes, *J. Org. Chem.* **2005**, **70**, 5519.

[4] With 10 mol% of catalyst.

[5] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni,. G. Polidori and R. Spagna, *J. Appl. Cryst*., 1999**, 32**, 115.

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