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Supporting Information

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An efficient approach to 1,5,7,8,9-pentahydrocyclopenta[*h*]-2-benzopyran-3-one derivatives via palladium-catalyzed tandem reaction of 2,7-alkadiynylic carbonates with 2,3-allenoic acids

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Materials and Methods

General Information. NMR spectra were taken with a Varian Mercury-300 spectrometer (300 MHz for ^{1}H NMR, 75.4 MHz for ^{13}C NMR) in $CDCl_3$. Chemical shifts were recorded in ppm relative to internal standard $CDCl_3$ and coupling constants were reported in Hz. The high resolution mass spectra were recorded on a Finnigan MAT 8430 spectrometer. Other mass spectra were obtained on a Shimadzu GCMS-2010 or Shimadzu LCMS-2010 spectrometer. Optical rotations were recorded on a PerkinElmer 341 (Manchester, U.K.) in a 10-cm cell. Melting points were measured on a X-4 melting point apparatus (Shanghai, China). IR studies were carried out on a Perkin-Elmer 983 spectrometer. X-ray intensity data were measured at 293 K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a fine-focus Mo-target X-ray tube (? = 0.71073 Å) operated at 1,500 W. The detector was placed at a distance of 6.042 cm for the crystal. The frames were integrated with the SAINT software package

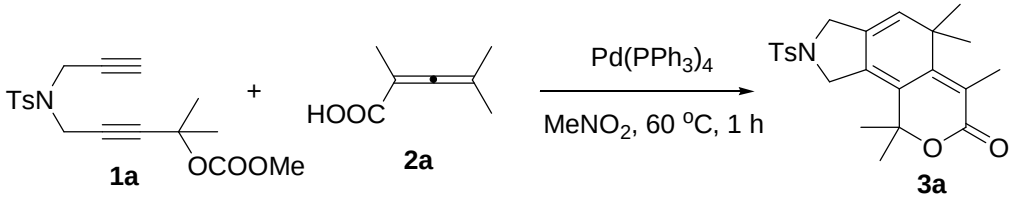
(Bruker, Billerica, MA) by using a narrow-frame integration algorithm. Enantiomeric excess (ee) was determined by HPLC with a Chiralpak AD, AD-H, or AB-H column (Daicel Chemical Industries, Ltd. Japan) and hexane/isopropanol as the eluent. All reactions were carried out in a oven dried Schlenk tube under Ar atmosphere. All solvents were distilled from the indicated drying reagents right before use: Toluene and THF (Na, benzophenone), $ClCH_2CH_2Cl$ (P_2O_5), and MeCN, $MeNO_2$ (this solvent was first distilled from CaH_2, then redistilled), DMSO, NMP, and DMF (CaH_2). The normal work-up procedure included extraction with Et_2O or EtOAc, drying over Na_2SO_4, and evaporation of solvent *in vacuo*. Purification by column chromatography was performed using Huanghai (Shandong, China) silica gel H (10-40 μ).

2,3-Allenoic acid 2 were prepared according to the literature procedure.[1]

General Procedure for the Preparation of the 1,5,7,8,9-Pentahydrocyclopenta[*h*]- 2-benzopyran-3-one Derivatives.

To a dried and degassed Schlenk tube were added 2,3-allenoic acid **2** (0.33 mmol), $Pd(PPh_3)_4$ (17 mg 5 mol%), 2,7-alkadiynoic carbonate **1** (0.3 mmol), and 3 mL of $MeNO_2$ sequentially under Ar atmosphere. The resulting mixture was stirred at 60 ^oC for 1h under Ar atmosphere. After the completion of the reaction (monitored by TLC), removal of the solvent by evaporation and purification by column chromatography on silica gel (eluent: CH_2Cl_2 or petroleum ether/diethyl ether) afforded the pure expected Pproduct **3** or **4**.

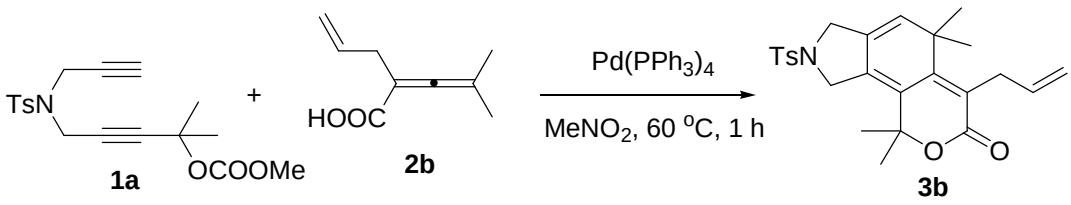
(1) Synthesis of 1,1,4,5,5-Pentamethyl-8-tosyl-1,5,7,9-tetrahydropyrrolo[3,4-*h*]-2-benzopyran-3-one **(3a)**.



The reaction of **1a** (110 mg, 0.3 mmol), **2a** (42 mg, 0.33 mmol), and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) in 3 mL of nitromethane afforded 109 mg of **3a** (87%) (eluent: CH_2Cl_2): Corlorless solid, m.p. 172-173 ^oC (acetone/ethyl ether); ^1H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 5.40 (s, 1 H), 4.16 (s, 2 H), 3.93 (s, 2 H), 2.43 (s, 3 H), 2.24 (s, 3 H), 1.53 (s, 6 H), 1.34 (s, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 16.7, 21.4, 26.6, 28.0, 38.6, 50.0, 52.3, 79.8, 122.8, 126.9, 127.6, 127.9, 129.8, 131.5, 132.2, 132.6, 144.1, 150.8, 165.4; MS(EI): *m/z* (%) 413 (M^+, 15.07), 398 (M^+-CH_3, 4.05), 91 (100); IR (film): 1783, 1698, 1597, 1347, 1163 cm^{-1}; Anal. calcd. for $C_{23}H_{27}NO_4S$, C 66.80, H 6.58, N 3.39; Found, C 66.78, H 6.47, N 3.31.

Crystal data for **3a:** Recrystallization from acetone and ethyl ether, $C_{23}H_{27}NO_4S$, MW = 413.52, Monoclinic, space group P2(1)/c, Mo Kα, final R indices [$I > 2\sigma(I)$], R1 = 0.0633, wR2 = 0.1486, R indices (all data): R1 = 0.0963, wR2 = 0.1647; a = 12.6156(17) Å, b = 7.5890(11) Å, c = 23.006(3) Å, *a* = 90^o, *b* = 100.518(3)^o, *g* = 90^o, V = 2165.6(5) Å^3, T = 293(2) K, wavelength: 0.71073 Å, Z = 4, reflections collected/unique 12125/4704 (R_{int} = 0.1281), number of observation [$I > 2\sigma(I)$] 2980, parameters 268. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. CCDC 675814.

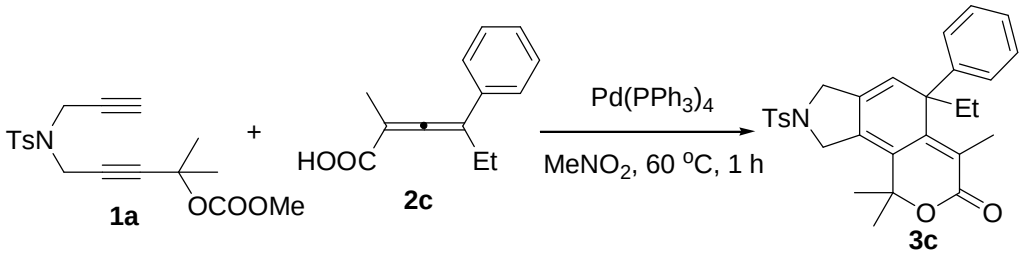
(2) Synthesis of 4-Allyl-1,1,5,5-tetramethyl-8-tosyl-1,5,7,9-tetrahydropyrrolo[3,4-*h*]-2-benzopyran-3-one **(3b)**.



The reaction of **1a** (110 mg, 0.3 mmol), **2b** (50 mg, 0.33 mmol), and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) in 3 mL of nitromethane afforded 101 mg of **3b** (77%) (eluent: CH_2Cl_2): Corlorless solid, m.p. 147-148 ^oC (acetone/ethyl ether); ^1H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2

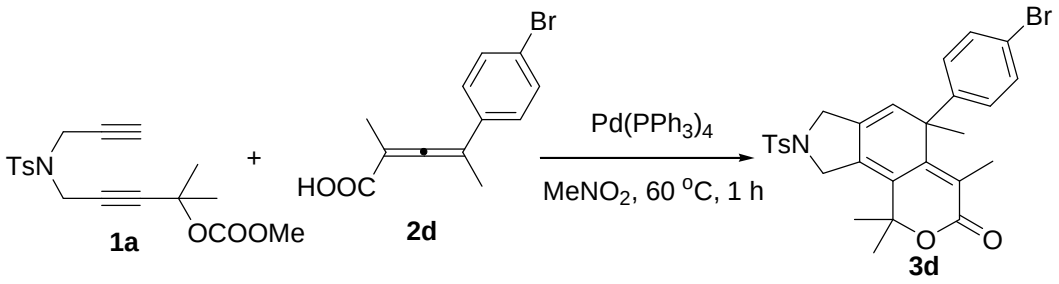
H), 5.95-5.80 (m, 1 H), 5.45 (s, 1 H), 5.08-4.97 (m, 2 H), 4.18 (s, 2 H), 3.94 (d, *J* = 1.8 Hz, 2 H), 3.51 (d, *J* = 5.4 Hz, 2 H), 2.43 (s, 3 H), 1.54 (s, 6 H), 1.31 (s, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.4, 28.0, 28.1, 33.4, 38.6, 50.0, 52.5, 79.7, 116.1, 125.5, 127.2, 127.7, 129.8, 132.2, 132.3, 132.9, 136.3, 144.2, 151.4, 164.5; MS(EI): *m/z* (%) 439 (M^+, 22.43), 424 (M^+-CH_3, 16.55), 91 (100); IR (KBr): 1695, 1638, 1598, 1345, 1165 cm^{-1}; Anal. calcd. for $C_{25}H_{29}NO_4S$, C 68.31, H 6.65, N 3.19; Found, C 68.17, H 6.87, N 3.26.

(3) Synthesis of 5-Ethyl-5-phenyl-1,1,4-trimethyl-8-tosyl-1,5,7,9-tetrahydropyrrolo[3,4-*h*]-2-benzopyran-3-one **(3c)**.



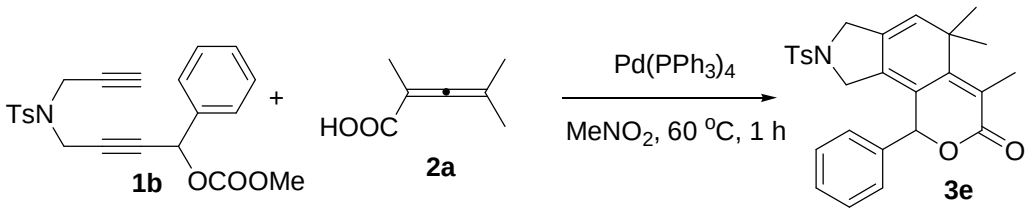
The reaction of **1a** (109 mg, 0.3 mmol), **2c** (67 mg, 0.34 mmol), and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) in 3 mL of nitromethane afforded 109 mg of **3c** (74%) (eluent: CH_2Cl_2): Corlorless solid, m.p. 188-189 ^{o}C (acetone/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.32-7.18 (m, 3 H), 7.11 (d, *J* = 7.2 Hz, 2 H), 5.30 (s, 1 H), 4.29 (d, *J* = 16.2 Hz, 1 H), 4.17 (d, *J* = 16.2 Hz, 1 H), 4.01 (dd, *J* = 13.2, 1.2 Hz, 1 H), 3.85 (dd, *J* = 13.2, 1.2 Hz, 1 H), 2.45 (s, 3 H), 2.50-2.38 (m, 1H), 1.99 (q, *J* = 7.2 Hz, 1 H), 1.64 (s, 3 H), 1.61 (s, 3 H), 1.58 (s, 3 H), 0.76 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 8.8, 15.9, 21.5, 28.4, 28.5, 29.7, 50.0, 51.6, 52.4, 80.3, 124.9, 126.0, 126.7, 127.6, 128.5, 128.8, 129.7, 129.9, 132.3, 132.4, 144.2, 145.8, 149.6, 165.0; MS(EI): *m/z* (%) 489 (M^+, 10.34), 460 (M^+-C_2H_5, 11.48), 91 (100); IR (film): 1694, 1683, 1455, 1351, 1163 cm^{-1}; Anal. calcd. for $C_{29}H_{31}NO_4S$, C 71.14, H 6.38, N 2.86; Found, C 71.02, H 6.54, N 2.75.

(4) Synthesis of 5-(4-bromophenyl)-5-methyl-1,1,4-trimethyl-8-tosyl-1,5,7,9-tetrahydropyrrolo-[3,4-*h*]-2-benzopyran-3-one **(3d)**



The reaction of **1a** (109 mg, 0.3 mmol), **2d** (86 mg, 0.33 mmol), and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) in 3 mL of nitromethane afforded 141 mg of **3d** (73%) (eluent: petrolem ether/ether 1 : 1): Corlorless solid, m.p. 204-205 ^{o}C (acetone/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.8 Hz, 2 H), 7.42 (d, *J* = 8.7 Hz, 2 H), 7.35 (d, *J* = 8.7 Hz, 2 H), 7.02 (d, *J* = 7.8 Hz, 2 H), 5.31 (s, 1 H), 4.26 (d, *J* = 15.9 Hz, 1 H), 4.19 (d, *J* = 15.9 Hz, 1 H), 4.26 (d, *J* = 13.5 Hz, 1 H), 4.26 (d, *J* = 13.5 Hz, 1 H), 2.45 (s, 3 H), 1.64 (s, 3 H), 1.58 (s, 3 H), 1.56 (s, 3 H), 1.53 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 16.2, 21.5, 22.9, 28.1, 28.2, 46.6, 50.0, 52.3, 80.2, 120.6, 124.3, 126.8, 127.0, 127.7, 129.9, 130.0, 131.5, 131.9, 132.2, 144.2, 144.4, 150.1, 164.9; MS(EI): *m/z* (%) 555 [(^{81}Br)M^+, 15.14], 553 [(^{79}Br)M^+, 13.59], 91 (100); IR (film): 1696, 1597, 1567, 1487, 1345, 1163, 1095 cm^{-1}; Anal. calcd. for $C_{28}H_{28}BrNO_4S$, C 60.65, H 5.09, N 2.53; Found, C 60.57, H 5.24, N 2.59.

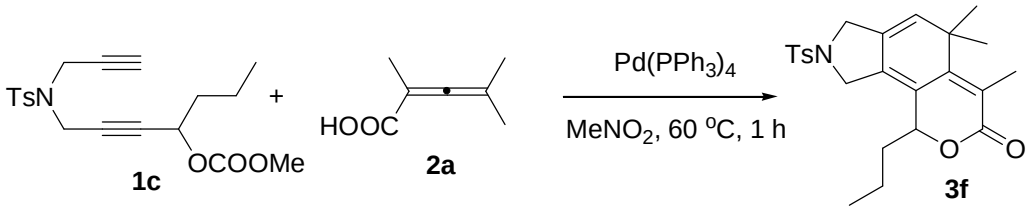
(5) Synthesis of 1-Phenyl-4,5,5-trimethyl-8-tosyl-1,5,7,9-tetrahydropyrrolo[3,4-*h*]-2-benzopyran-3-one **(3e)**.



The reaction of **1b** (122 mg, 0.3 mmol), **2a** (42 mg, 0.33 mmol), and $Pd(PPh_3)_4$ (19 mg, 0.016 mmol) in 3 mL of nitromethane afforded 119 mg of **3e** (86%) (eluent: CH_2Cl_2): Corlorless solid, m.p. 197-198 ^{o}C (acetone/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.8 Hz, 2 H), 7.40-7.20 (m, 7 H), 5.82 (s, 1 H), 5.47 (s, 1 H), 4.13-3.80 (m, 4 H), 2.42 (s, 3 H), 2.16 (s, 3 H), 1.42 (s, 3 H), 1.31 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 16.4, 21.5, 26.4, 26.7, 39.3, 50.4, 50.6, 120.5, 124.0, 126.2, 127.7, 127.8,

128.9, 129.8, 129.8, 132.4, 133.2, 134.5, 137.9, 144.1, 151.0, 165.1; MS(EI): *m/z* (%) 461 (M^+, 12.08), 446 (M^+-CH_3, 16.34), 91 (100); IR (film): 1737, 1365, 1353, 1229, 1217 cm^{-1}; Anal. calcd. for $C_{27}H_{27}NO_4S$, C 70.26, H 5.90, N 3.03; Found, C 69.89, H 5.84, N 2.84.

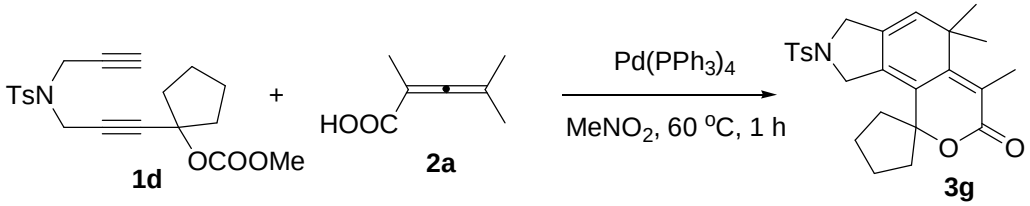
(6) Synthesis of 1-Propyl-4,5,5-trimethyl-8-tosyl-1,5,7,9-tetrahydropyrrolo[3,4-*h*]-2-benzopyran-3-one **(3f)**.



1c **2a** **3f**

The reaction of **1c** (112 mg, 0.3 mmol), **2a** (43 mg, 0.33 mmol), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) in 3 mL of nitromethane afforded 105 mg of **3f** (83%) (eluent: petroleum ether/ethyl ether = 1/1): Corlorless solid, m.p. 151-152 °C (acetone/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 5.35 (s, 1 H), 4.76 (dd, *J* = 3.9, 9.0 Hz, 1 H), 4.05-3.82 (m, 4 H), 2.37 (s, 3 H), 2.14 (s, 3 H), 1.82-1.65 (m, 1 H), 1.52-1.20 (m, 3 H), 1.37 (s, 3 H), 1.23 (s, 3 H), 0.87 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 13.6, 16.3, 18.3, 21.4, 26.0, 26.7, 37.6, 39.0, 50.0, 50.5, 75.7, 122.3, 122.9, 127.6, 127.7, 129.8, 131.8, 132.4, 144.1, 150.3, 165.2; MS(EI): *m/z* (%) 427 (M^+, 22.56), 412 (M^+-CH_3, 4.55), 91 (100); IR (film): 1737, 1719, 1701, 1698, 1460, 1376, 1350, 1164 cm^{-1}; Anal. calcd. for $C_{24}H_{29}NO_4S$, C 67.42, H 6.84, N 3.28; Found, C 67.30, H 6.91, N 3.13.

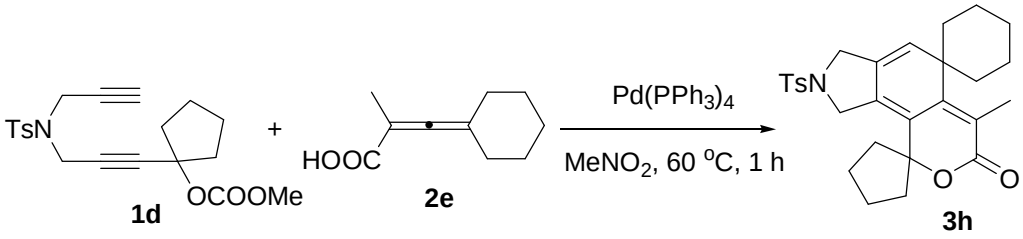
(6) Synthesis of Spiro[cyclopetane-1,1'-4',5',5'-trimethyl-8'-tosyl-1',5',7',9'-tetrahydropyrrolo[3,4-*h*] -2'-benzopyran -3'-one] **(3g)**.



1d **2a** **3g**

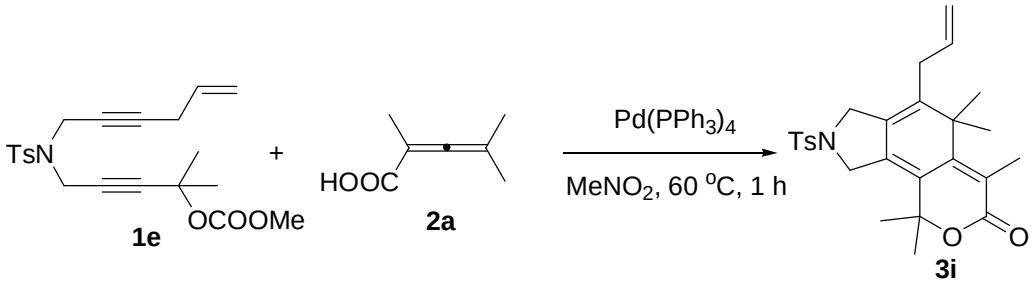
The reaction of **1d** (119 mg, 0.31 mmol), **2a** (43 mg, 0.33 mmol), and $Pd(PPh_3)_4$ (16 mg, 0.015 mmol) in 3 mL of nitromethane afforded 97 mg of **3g** (74%) (eluent: CH_2Cl_2): Corlorless solid, m.p. 183-184 ^oC (acetone/ethyl ether); ^1H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 5.35 (s, 1 H), 4.14 (s, 2 H), 3.87 (d, *J* = 1.5 Hz, 2 H), 2.37 (s, 3 H), 2.15 (s, 3 H), 2.18-1.65 (m, 8 H), 1.28 (s, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 16.7, 21.4, 22.8, 26.6, 38.65, 38.74, 49.9, 52.0, 90.0, 123.5, 125.2, 127.6, 128.6, 129.8, 130.6, 132.3, 132.5, 144.1, 152.5, 165.7; MS(EI): *m/z* (%) 439 (M^+, 16.83), 424 (M^+-CH_3, 9.59), 91 (100); IR (film): 1696, 1597, 1450, 1350, 1163, 1095 cm^{-1}; Anal. calcd. for $C_{25}H_{29}NO_4S$, C 68.31, H 6.65, N 3.19; Found, C 68.43, H 6.68, N 3.06.

(8) Synthesis of Dispiro[cyclopetane-1,1'-1'-methyl-8'-tosyl-1',5',7',9'-tetrahydro- pyrrolo[3,4-*h*]-2'-benzopyran -3'-one-5',1''-cyclohexane] **(3h)**.



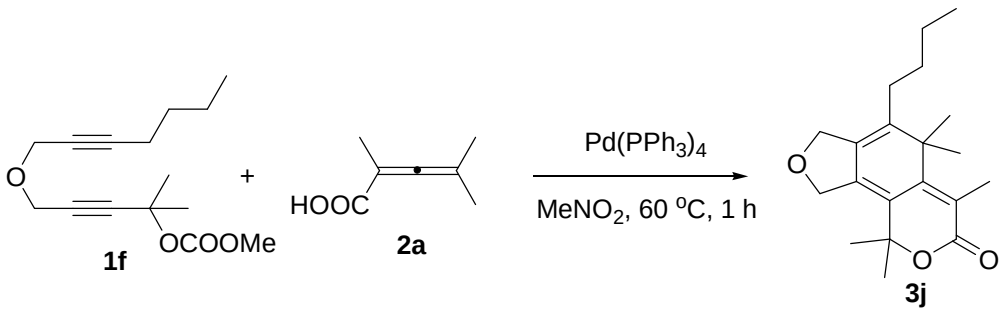
The reaction of **1d** (117 mg, 0.3 mmol), **2e** (54 mg, 0.33 mmol), and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) in 3 mL of nitromethane afforded 101 mg of **3h** (70%) (eluent: CH_2Cl_2): Corlorless solid, m.p. 253-254 ^oC (acetone/ethyl ether); ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 6.17 (s, 1 H), 4.20 (s, 2 H), 3.95 (s, 2 H), 2.42 (s, 3 H), 2.30 (s, 3 H), 2.20-1.25 (m, 18 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 17.6, 21.2, 21.4, 22.8, 24.5, 32.7, 38.7, 41.6, 50.3, 52.2, 89.7, 123.0, 126.2, 127.3, 127.7, 129.1, 129.8, 129.9, 132.4, 144.1, 152.9, 166.0; MS(EI): *m/z* (%) 479 (M^+, 6.78), 464 (M^+-CH_3, 2.43), 91 (100); IR (film): 1739, 1729, 1371, 1366, 1347, 1229, 1217, 1157 cm^{-1}; Anal. calcd. for $C_{28}H_{33}NO_4S$, C 70.12, H 6.93, N 2.92; Found, C 69.94, H 6.90, N 2.85.

(9) Synthesis of 6-Allyl-1,1,4,5,5-pentamethyl-8-tosyl-1, 5,7,9-tetrahydropyrrolo[3,4-*h*]-2-benzopyran-3-one **(3i)**.



The reaction of **1e** (119 mg, 0.3 mmol), **2a** (43 mg, 0.33 mmol), and $Pd(PPh_3)_4$ (18 mg, 0.015 mmol) in 3 mL of nitromethane afforded 83 mg of **3i** (61%) (eluent: CH_2Cl_2 ~ CH_2Cl_2/diethyl ether 20/1): Corlorless solid, m.p. 164-165 ^oC (acetone/ethyl ether); ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.1 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 5.70-5.55 (m, 1 H), 5.12-5.00 (m, 2 H), 4.17 (s, 2 H), 3.91 (s, 2 H), 2.88 (d, *J* = 6.0 Hz, 2 H), 2.43 (s, 3 H), 2.25 (s, 3 H), 1.53 (s, 6 H), 1.38 (s, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 17.5, 21.5, 24.9, 28.1, 34.3, 41.7, 49.4, 52.5, 79.6, 116.9, 121.7, 125.5, 127.60, 127.64, 129.9, 131.8, 132.5, 133.7, 139.5, 144.2, 153.1, 165.8; MS(EI): *m/z* (%) 453 (M^+, 6.87), 410 (M^+-allyl, 16.58), 384 (100); IR (film): 1755, 1694, 1597, 1556, 1456, 1348, 1164, 1095 cm^{-1}; Anal. calcd. for $C_{26}H_{31}NO_4S$, C 68.85, H 6.89, N 3.09; Found, C 68.74, H 6.77, N 3.06.

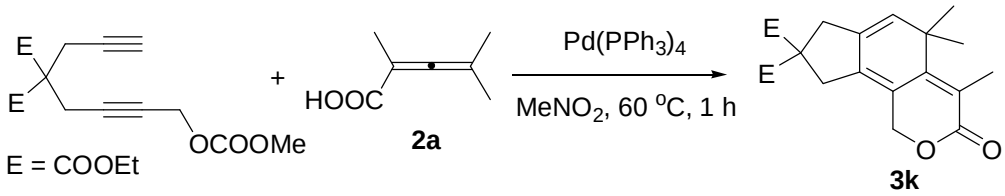
(10) Synthesis of 4-Butyl-1,1,4,5,5-pentamethyl-1,5,7,9-tetrahydrofuro[3,4-*h*]-2- benzopyran-3-one **(3j)**.



The reaction of **1f** (80 mg, 0.3 mmol), **2a** (41 mg, 0.33 mmol), $Pd(PPh_3)_4$ (18 mg, 0.015 mmol) in 3 mL of nitromethane afforded 66 mg of **3j** (68%) (eluent: petroleum ether/CH_2Cl_2 = 1/9): yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ 4.65 (s, 2 H), 4.47 (s, 2 H), 2.28 (s, 3 H), 2.10 (m, 2 H), 1.51 (s, 6 H), 1.47 (s, 6 H), 1.40-1.32 (m, 4 H), 0.92 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 13.7, 17.4, 23.3, 24.8, 27.9, 30.3, 31.7, 42.1, 69.3, 71.6, 79.5, 120.4, 123.1, 128.6, 135.7, 141.3, 154.2, 166.3; MS(EI): *m/z* (%)

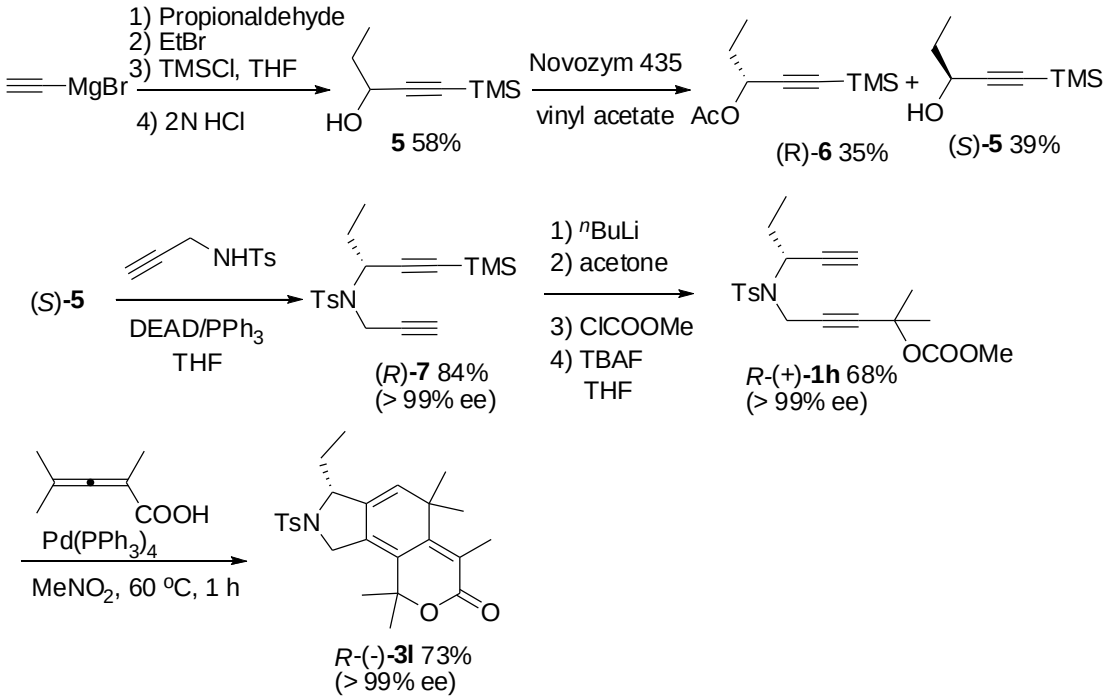
316 (M^+, 10.06), 301 (M^+-CH_3, 1.83), 231 (100); IR (film): 1757, 1696, 1554, 1461, 1344, 1226, 1122, 1071 cm^{-1}; HRMS: cacld. for $C_{20}H_{28}O_3$ [M^+] 316.2038; Found, 316.2029.

(11) Synthesis of 8,8-Bis(ethoxycarbonyl)-4,5,5-trimethyl-1,5,7,8,9-pentahydrocyclopenta[*h*]-2-benzopyran-3-one **(3k)**.



The reaction of **1g** (98 mg, 0.3 mmol), **2a** (42 mg, 0.33 mmol), and $Pd(PPh_3)_4$ (18 mg, 0.015 mmol) in 3 mL of nitromethane afforded 64 mg of **3k** (54%) (eluent: petroleum ether/ethyl ether = 1/1): Viscous solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.42 (s, 1 H), 4.84 (s, 2 H), 4.18 (q, *J* = 4.8 Hz, 4 H), 3.04 (s, 2 H), 3.00 (s, 2 H), 2.20 (s, 3 H), 1.36 (s, 6 H), 1.22 (t, *J* = 4.8 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 13.9, 16.3, 26.8, 37.2, 37.8, 39.2, 58.8, 61.9, 65.5, 118.2, 121.6, 130.6, 133.6, 136.8, 153.7, 166.6, 170.7; MS(EI): *m/z* (%) 374 (M^+, 35.06), 359 (M^+-CH_3, 8.57), 227 (100); IR (film): 1732, 1702, 1405, 1400, 1367, 1250, 1190, 1068 cm^{-1}; HRMS: cacld. for $C_{21}H_{26}O_6$ [M^+] 374.1729; Found, 374.1730.

(12) Synthesis of (*R*)-(-)-3-Ethyl-1,1,4,5,5-pentamethyl-8-tosyl-1, 5,7,9-tetrahydropyrrolo[3,4-*h*]-2-benzopyran-3-one **[*R*-(-)-3l]**.



Scheme 1

(a) **1-(Trimethylsilyl)pentyn-3-ol (5).**[2] To a stirred solution of ethynyl magnesium bromide (0.2 mol) in 200 mL of THF was added over 30 min a solution of propionaldehyde (11.654 g, 0.2 mol) in 30 mL of THF at 0 ^{o}C. The mixture was vigorously stirred at room temperature for 1 h and then heated to reflux for 30 min. To this mixture was slowly added over 30 min a solution of ethyl magnesium bromide (0.2 mol) in 200 mL of THF at 0 ^{o}C. Then the mixture allowed to warm to room temperature naturally and stirred at the temperature for another 1 h. A solution of chlorotrimethylsilane (TMSCl) (50.8 mL, *d* = 0.855, 43.463 g, 0.4 mol) in 30 mL of THF was added dropwise to the mixture at 0 ^{o}C. After the addition was complete, the mixture was stirred for an additional hour at room temperature. The mixture was cautiously poured into a 500 mL of 2 M HCl and the resulting mixture was stirred for half an hour. The organic phase was separated and the aqueous phase was extracted with ether (50 mL x 3). The combined organic layers were dried over sodium sulfate and concentrated. Flash chromatography (eluent: ether/petroleum ether = 5/1) afforded product **5** (18.030 g, 58%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.31 (q, *J* = 6.0 Hz, 1 H), 1.83 (bs, 1H), 1.78-1.63 (m, 2 H), 1.00 (t, *J* = 7.2 Hz, 3 H), 0.15 (s, 9 H).

(b) (*S*)-**1-(Trimethylsilyl)pent-1-yn-3-ol (*S*-5).**[3] Novozym 435 (1.021 g) was added to a solution of racemic **5** (6.552 g) in 100 mL of vinyl acetate. The suspension was stirred at room temperature for 100 hr as monitored by TLC. The reaction mixture was diluted with 100 mL of diethyl ether and filtered. Concentration and purification by flash chromatography on silica gel (petroleum ether/ether 5/1) afforded (*R*)-**6** (2.933 g, 35%) and (*S*)-**5** (2.539, 39%) as pale-yellow oil. (*S*)-**5**: $[\alpha]^{20}_{,D}$ = - 5.4 ^{o} (*c* = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): 4.37-4.25 (m, 1 H), 1.97 (bs, 1H), 1.78-1.63 (m, 2 H), 1.00 (t, *J* = 7.2 Hz, 3 H), 0.16 (s, 9 H); (*R*)-**6:** $[\alpha]^{20}_{,D}$ = + 126.5 ^{o} (*c* = 1.00, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$): 5.32 (t, *J* = 6.6 Hz, 1 H), 2.07 (s, 3H), 1.75 (m, 2 H), 0.98 (t, *J* = 7.5 Hz, 3 H), 0.16 (s, 9 H).

(c) (*R*)-***N*-(2-proparyl)-*N*-(1-trimethylsilyl-1-pentyn-3-yl)tosylamide (*R*-7).**[4] Diethyl azodicarboxylate (2.003 g, 11 mmol) was added dropwise to a solution of (*S*)-**5** (1.670 g, 10 mmol), triphenylphosphine (2.627 g, 10 mmol), and *N*-proparyl tosylamide (2.095 g, 10 mmol) in anhydrous THF (20 mL) at 0 ^{o}C. Then the resulting yellow solution was allowed to warm to room temperature and stirred for 5 hours. Then the solvent was evaporated and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl ether = 7/1) to afford (*R*)-**7** (2.939 g, 84%) as white solid (>99% ee, HPLC conditions: AB-H column; rate, 0.6 mL/min; eluent, hexane/*i*-PrOH 95/5. ? = 230 nm). $[\alpha]^{20}_{,D}$ = + 124.3 ^{o} (*c* = 1.00, $CHCl_3$). White solid, M.p. 61-62 ^{o}C (crystalization from petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.8 Hz, 2 H), 7.26 (d, *J* = 7.8 Hz, 2 H), 4.56 (t, *J* = 7.8 Hz, 1 H), 4.08 (dd, *J* = 18.3, 2.1 Hz, 1 H), 3.88 (dd, *J* = 18.3, 1.5 Hz, 1 H), 2.39 (s, 3 H), 2.19 (s, 1 H), 1.83 (dq, *J* = 7.8, 7.2 Hz, 2 H), 1.01 (t, *J* = 7.2 Hz, 3 H), -0.02 (s, 9 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ -0.5, 10.8, 21.5, 28.5, 33.5, 53.2, 72.0, 79.6, 90.9, 101.1, 127.6, 129.4, 135.9, 143.5; MS(ESI): *m/z* 402 (M+MeOH+Na^+), 370 (M+Na^+); IR (film): 3286, 2173, 1598, 1359, 1340, 1250, 1168 cm^{-1}; Anal. calcd. for $C_{18}H_{25}NO_2SSi$, C 62.21, H 7.25, N 4.03; Found, C 62.11, H 7.19, N 4.03.

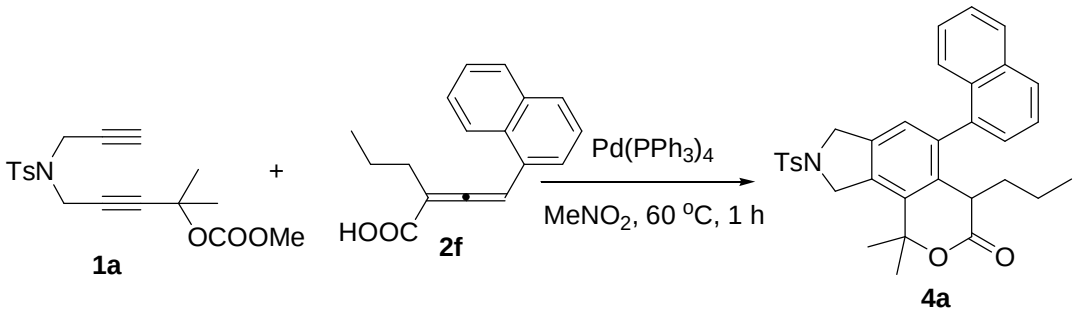
(d) (*R*)-***N*-(4-methyl-4-(methoxycarbonyloxy)pent-2-ynyl)-*N*-(1-pentyn-3-yl)-tosylamide (*R*-1h).**[5] To a solution of (*R*)-**7** (1.733 g, 5.0 mmol) in 20 mL of THF was added dropwise 2.4 mL of ^{n}BuLi (2.5 M in Hexane) at -78 ^{o}C. After lithiation for 20 min at -78 ^{o}C, anhydrous acetone (0.45 mL, 6.0 mmol) was added at this temperature. The reaction mixture was warmed up to room temperature and stirred for 30 min. Then methyl chloroformate (658 mg, 0.54 mL, 9 mmol) was added at -78 ^{o}C. The mixture was warmed to room temperature and quenched with aqueous NH_4Cl after 2 hours. The mixture was extracted with ethyl ether, and the combined organic phase was dried over $MgSO_4$ and concentrated. The residue was dissolved in 10 mL of THF and treated with TBAF (1.739 g, 6.0 mmol). The mixture was stirred for 30 min at room temperature. The mixture was diluted with 100 mL of ether and washed with water (30 mL x 2). The organic phase was dried over Na_2SO_4 and evaporated. Purification by flash chromatography on silica gel (eluent: petroleum ether/ethyl ether = 10/1) afforded (*S*)-**1h** (1.340 g, 68%). (>99% ee, HPLC conditions: AD column; rate, 0.6 mL/min; eluent, hexane/*i*-PrOH 90/10. ? = 230 nm). $[\alpha]^{20}_{,D}$ = + 63.5 ^{o} (*c* = 1.00, $CHCl_3$). White solid, M.p. 69-70 ^{o}C (crystalization from petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.1 Hz, 2 H), 7.26 (d, *J* = 7.8 Hz, 2 H), 4.63-4.55 (m 1 H), 4.22 (d, *J* = 18.3 Hz, 1 H), 4.03 (d, *J* = 18.3 Hz, 1 H), 3.71 (s, 3 H), 2.39 (s, 3 H), 2.17 (s, 1 H), 1.90-1.75 (m, 2 H), 1.56 (s, 6 H), 0.97 (t, *J* = 3.3 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): ?10.8, 21.4, 28.30, 28.34, 33.6, 52.0, 54.2, 73.9, 74.1, 80.0, 80.3, 83.8, 127.5, 129.4, 136.4, 143.5, 153.3; MS (ESI): *m/z* 414 ($M+Na^+$); IR (film): 3278, 1764, 1600, 1441, 1357, 1340, 1275, 1167, 1138, 1092 cm^{-1}; HRMS (ESI): cacld. for $C_{20}H_{25}NO_5SNa^+$ [$M+Na^+$] 414.1346; Found, 414.1348.

(e) Synthesis of *R*-(-)-**3l.**

Following the general procedure, the reaction of *R*-(+)-**1h** (116 mg, 0.3 mmol, 99.3% ee), **2a** (44 mg, 0.33 mmol), and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) in 3 mL of nitromethane afforded *R*-(-)-**3l** (93 mg, 73% yield) (eluent: petroleum/ethyl ether = 1/1) (>99% ee, HPLC conditions: AD-H column; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH 95/5. ? = 230 nm). $[\alpha]^{20}_{,D}$ = - 46.1 ^{o} (*c* = 1.00, $CHCl_3$). White solid, m.p.

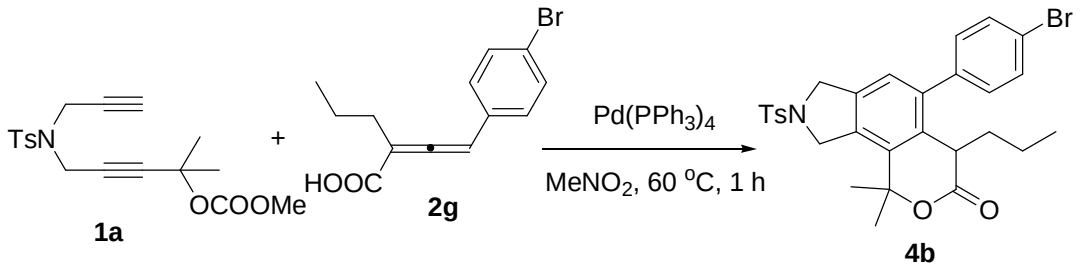
175-176 ^{o}C (acetone/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.1 Hz, 2 H), 7.21 (d, *J* = 8.1 Hz, 2 H), 5.19 (s, 1 H), 4.22 (d, *J* = 18.3 Hz, 1 H), 4.03 (d, *J* = 18.3 Hz, 1 H), 2.33 (s, 3 H), 2.15 (s, 3 H), 1.62 (m, 2 H), 1.53 (s, 3 H), 1.35 (s, 3 H), 1.32 (s, 3 H), 1.01 (s, 3 H), 0.90 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 9.1, 16.7, 21.3, 26.0, 26.8, 27.5, 28.29, 38.34, 51.7, 63.4, 79.7, 122.5, 126.6, 127.2, 129.6, 132.0, 132.1, 132.7, 134.4, 143.8, 150.8, 165.4; MS(EI): *m/z* (%) 441 (M^+, 17.3), 426 (M^+-CH_3, 3.84), 91 (100); IR (film): 1696, 1450, 1342, 1163, 1120, 1090, cm^{-1}; Anal. calcd. for $C_{25}H_{31}NO_4S$, C 68.00, H 7.08, N 3.17; Found, C 67.92, H 7.08, N 3.24.

(13) Synthesis of 1,1-Dimethyl-5-(naphthalen-1-yl)-4-propyl-8-tosyl-1,4,7,9- tetrahydropyrrolo[3,4-*h*]-2-benzopyran-3-one **(4a)**.



The reaction of **1a** (111 mg, 0.305 mmol), **2f** (85 mg, 0.337 mmol), and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) in 3 mL of nitromethane afforded 112 mg of **4a** (69%)(eluent: CH_2Cl_2). Corlorless solid, m.p. 203-204 ^{o}C (acetone/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95-7.82 (m, 2 H), 7.80 (d, *J* = 8.1 Hz, 2 H), 7.58-7.25 (m, 5 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.21 (d, *J* = 7.2 Hz, 1 H), 7.08 (s, 1 H), 4.34 (d, *J* = 10.2 Hz, 1 H), 4.80-4.62 (m, 2 H), 4.47 (d, *J* = 13.2 Hz, 1 H), 2.41 (s, 3 H), 1.79 (s, 3 H), 1.75 (s, 3 H), 1.36 (q, *J* = 9.3 Hz, 1 H), 1.05-0.95 (m, 2 H), 0.70-0.55 (m, 1 H), 0.01 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 12.2, 20.2, 21.4, 29.8, 30.2, 38.2, 40.3, 52.8, 54.2, 84.0, 125.1, 125.2, 125.3, 125.9, 126.2, 126.9, 127.6, 128.3, 128.4, 129.8, 130.1, 132.2, 132.95, 133.00, 133.8, 134.3, 136.0, 136.2, 139.5, 143.9, 171.2; MS(ESI): *m/z* 594 ($M+Na^+$+MeOH), 562 ($M+Na^+$); IR (film): 1736, 1460, 1365, 1352, 1229, 1217, 1164, 1097 cm^{-1}; Anal. calcd. for $C_{33}H_{33}NO_4S$, C 73.44, H 6.16, N 2.60; Found, C 73.30, H 6.24, N 2.49.

(14) Synthesis of 5-(4-Bromophenyl)-1,1-dimethyl-4-propyl-8-tosyl-1,4,7,9- tetrahydropyrrolo[3,4-*h*]-2-benzopyran-3-one **(4b)**.



The reaction of **1a** (111 mg, 0.3 mmol), **2g** (93 mg, 0.33 mmol), and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) in 3 mL of nitromethane afforded 92 mg of **4b** (59%) (eluent: CH_2Cl_2). White solid, m.p. 202-203 ^oC (acetone/ethyl ether); ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.4 Hz, 2 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.07 (d, *J* = 8.4 Hz, 2 H), 6.98 (s, 1 H), 4.80-4.55 (m, 3 H), 4.46 (d, *J* = 12.9 Hz, 1 H), 3.79 (dd, *J* = 3.3, 10.8 Hz, 1 H), 2.41 (s, 3 H), 1.75 (s, 3 H), 1.72 (s, 3 H), 1.51 (m, 1 H), 1.35-1.17 (m, 2 H), 1.12-0.95 (m, 1 H), 0.54 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 12.9, 20.4, 21.5, 29.8, 30.0, 38.8, 40.0, 52.8, 54.1, 84.1, 122.0, 124.2, 127.6, 129.9, 130.3, 130.7, 131.7, 131.8, 132.9, 134.2, 136.5, 138.2, 140.5, 144.1, 170.9; MS(EI): *m/z* (%) 569 [(^{81}Br)M^+, 5.38], 567 [(^{79}Br)M^+, 5.13], 91 (100); IR (film): 1732, 1597, 1492, 1448, 1349, 1285, 1163, 1098, 1011 cm^{-1}; Anal. calcd. for $C_{29}H_{30}BrNO_4S$, C 61.27, H 5.32, N 2.46; Found, C 60.96, H 5.37, N 2.43.

Crystal data for **4b**: Recrystallization from acetone and ethyl ether, $C_{29}H_{30}BrNO_4S$, MW = 568.51, Monoclinic, space group P2(1)/n, final R indices [$I > 2\sigma(I)$], R1 = 0.0424, wR2 = 0.0778, R indices (all data): R1 = 0.0984, wR2 = 0.0868; a = 17.4190(17) Å, b = 9.6103(10) Å, c = 31.794(3) Å, $a = 90^o$, $b = 93.815(2)^o$, $g = 90^o$, V = 5310.5(9) $Å^3$, T = 293(2) K, wavelength: 0.71073 Å, Z = 8, reflections collected/unique 27183/9845 (R_{int} = 0.0900), number of observation [$I > 2\sigma(I)$] 4485, parameters 657. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. CCDC 675815.

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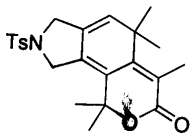
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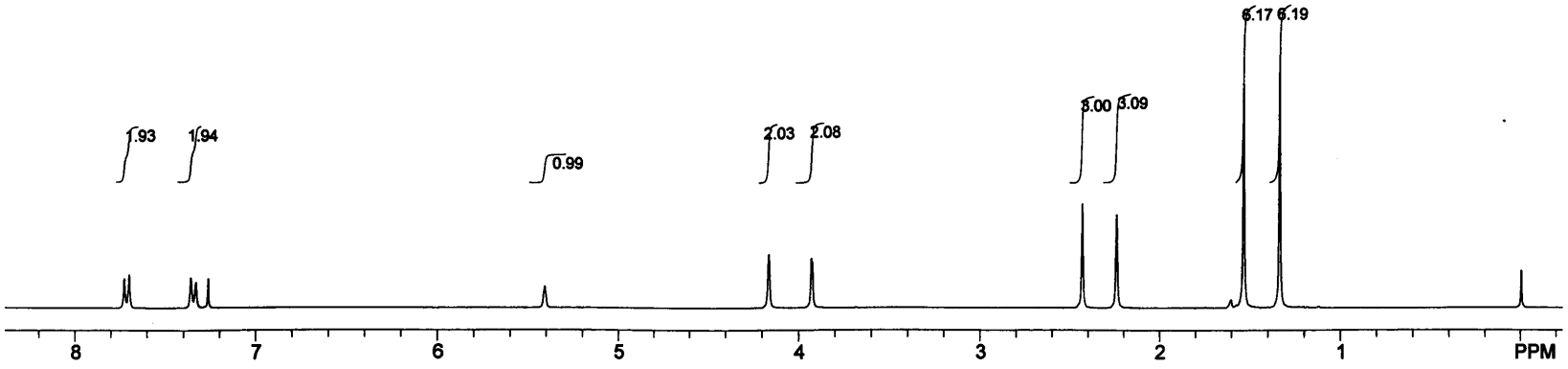
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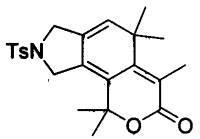

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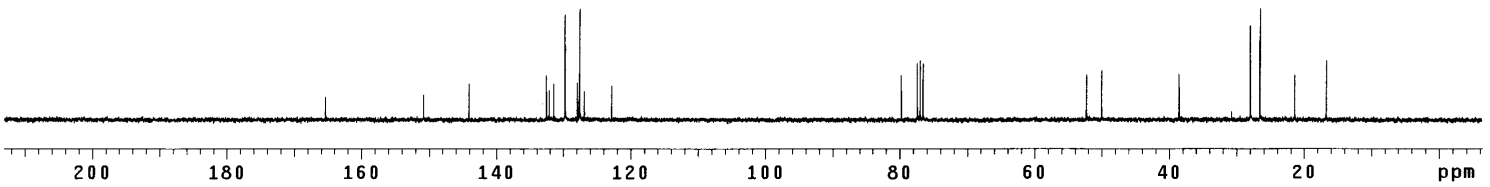

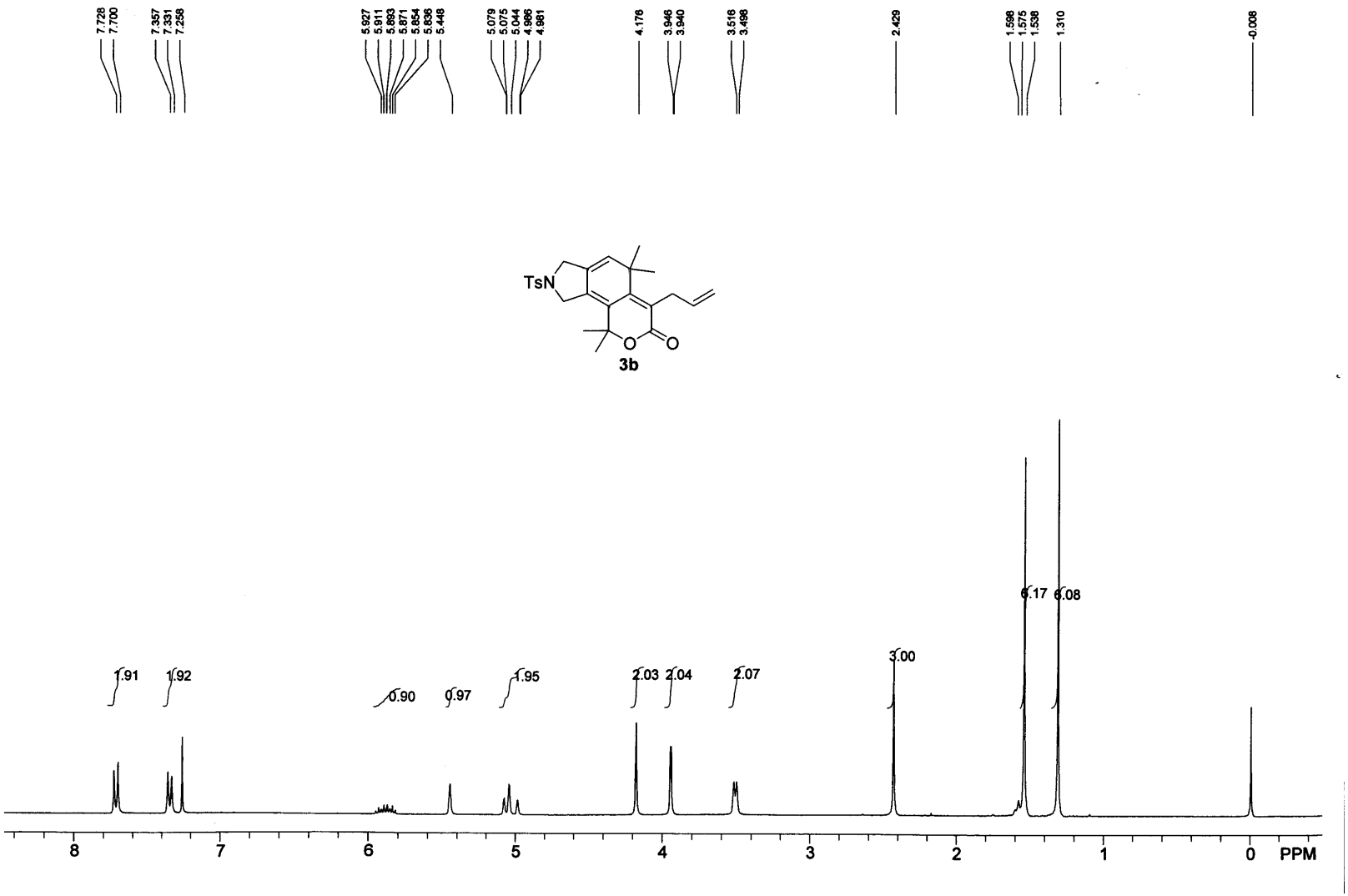
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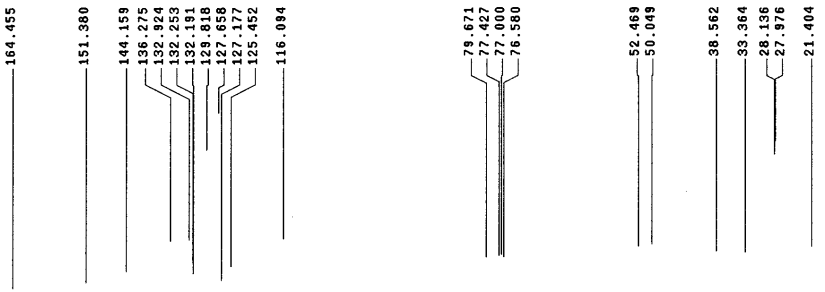

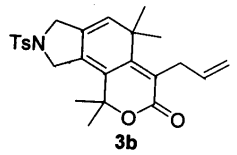

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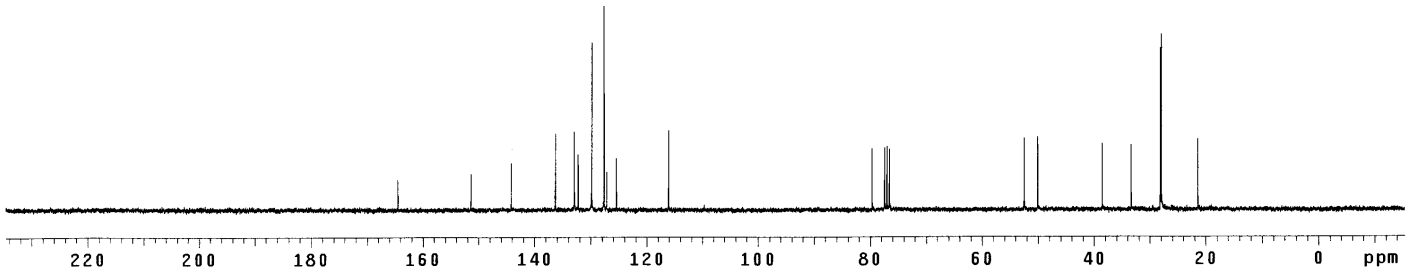

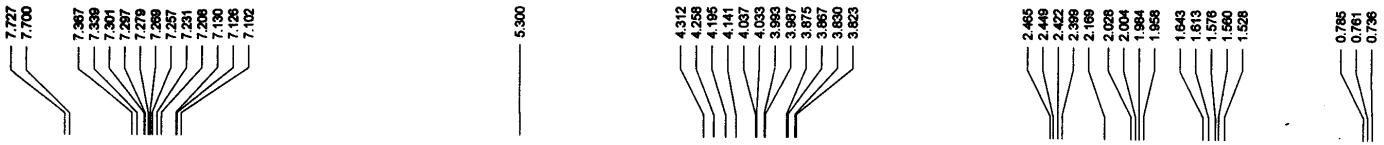
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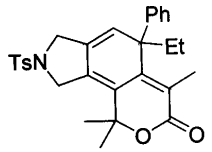
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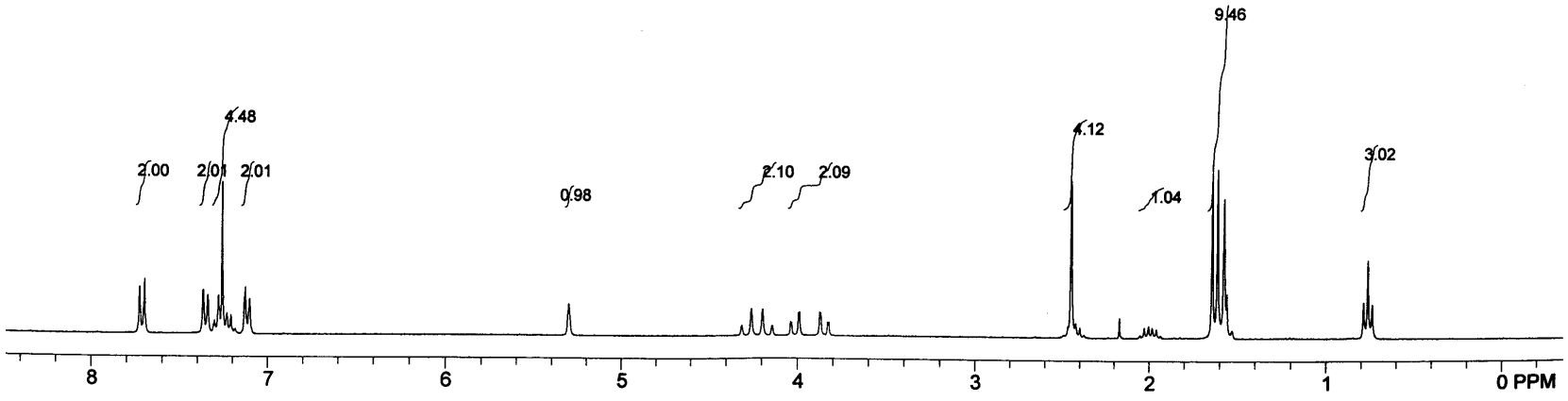
O
O

3c

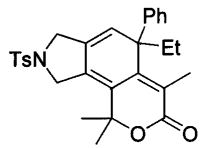

9.46
4.48
4.12
3.02
2.00
2.01
2.01
0.98
2.10
2.09
1.04
8
7
6
5
4
3
2
1
0 PPM

lxd-3-164-c

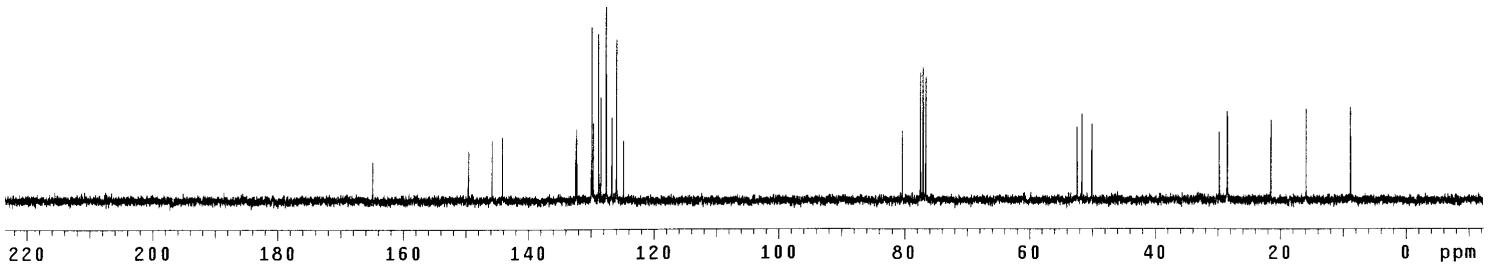
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

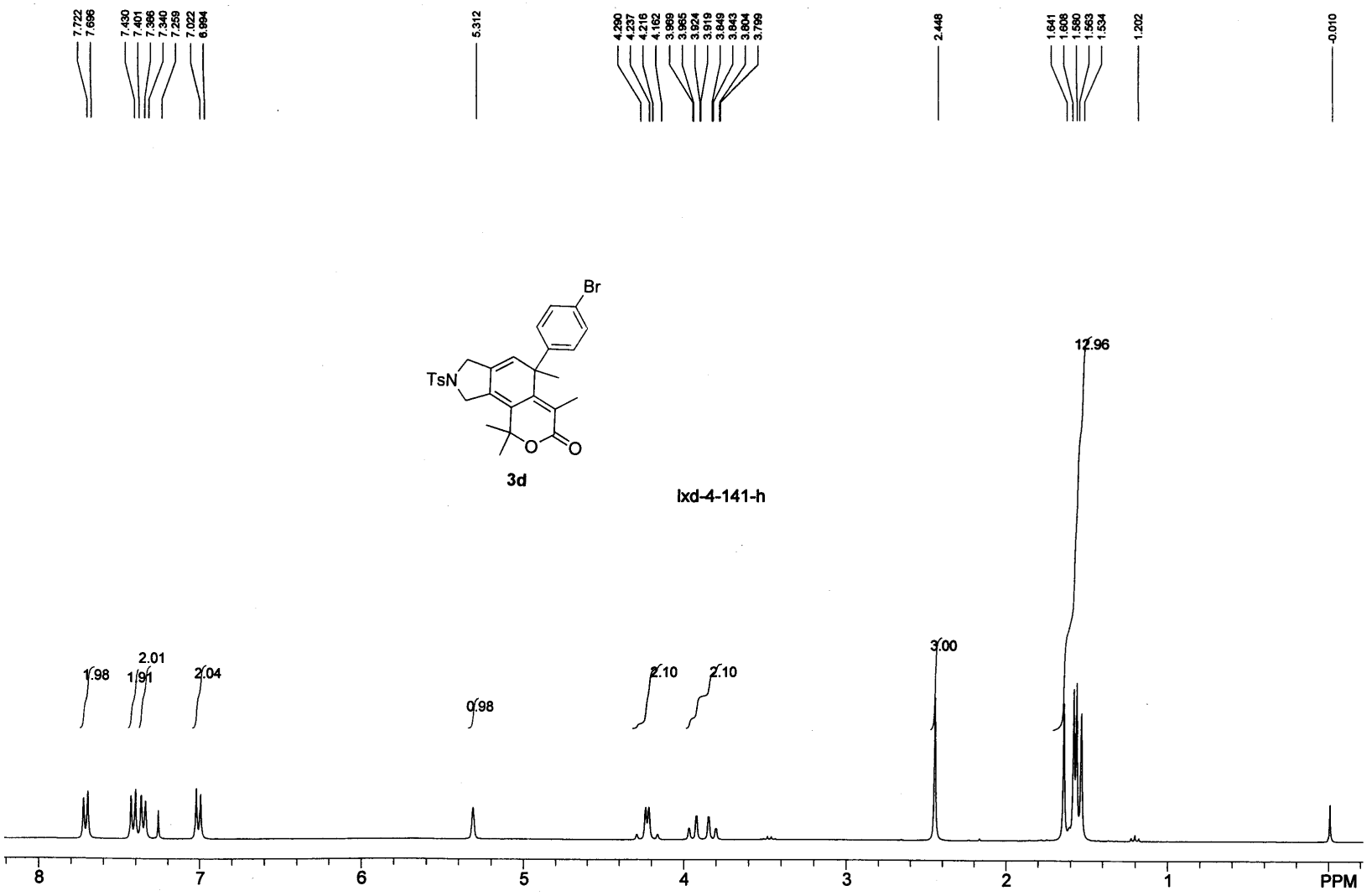
Pulse Sequence: s2pul

164.960
149.606
145.820
144.158
132.418
132.266
129.927
129.697
128.847
128.480
127.631
126.738
126.004
124.874
80.325
77.425
77.000
76.575
52.376
51.627
50.043
29.738
28.493
28.435
21.489
15.860
8.777



3c



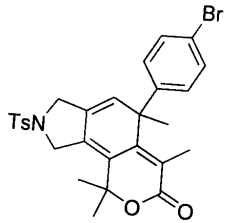

7.722
7.696
7.430
7.401
7.396
7.340
7.259
7.022
6.994
5.312
4.290
4.237
4.216
4.162
3.969
3.965
3.924
3.919
3.849
3.843
3.804
3.799
2.448
1.641
1.608
1.580
1.563
1.534
1.202
-0.010
Br
TsN
O
O
3d
lxd-4-141-h
1.98
2.01
1.91
2.04
0.98
2.10
2.10
3.00
12.96
8
7
6
5
4
3
2
1
PPM

lxd-4-140-c

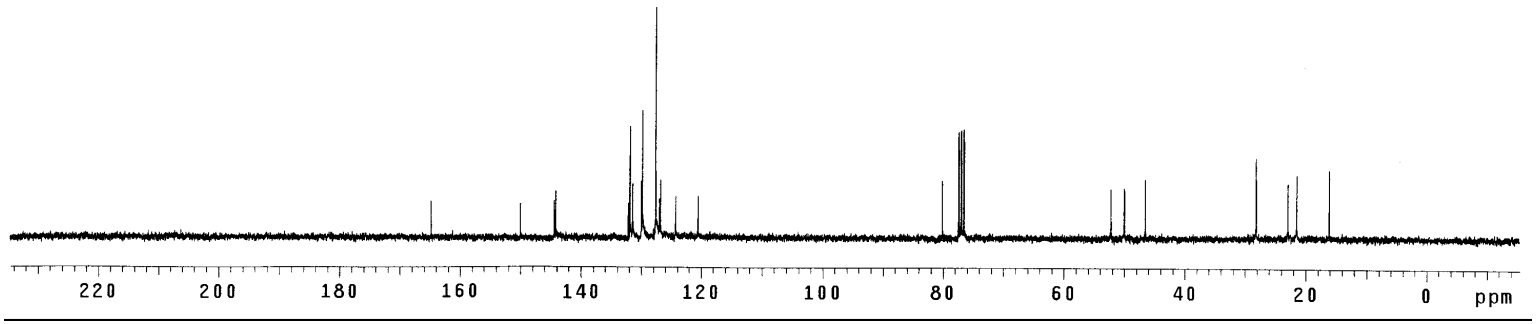
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

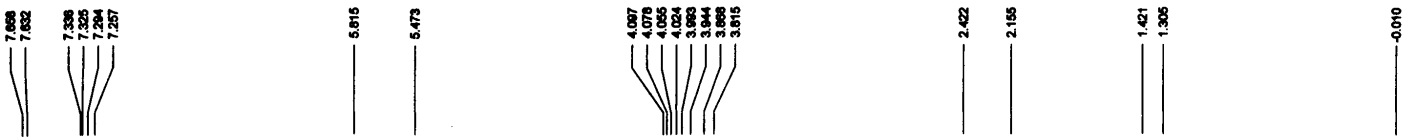
Pulse Sequence: s2pul

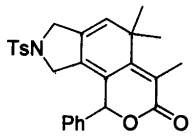
164.867
150.060
144.419
144.183
132.199
131.940
131.497
130.039
129.871
127.650
127.009
126.826
124.292
120.567
80.160
77.420
77.000
76.573
52.255
50.026
46.576
28.143
28.174
22.915
21.473
16.160



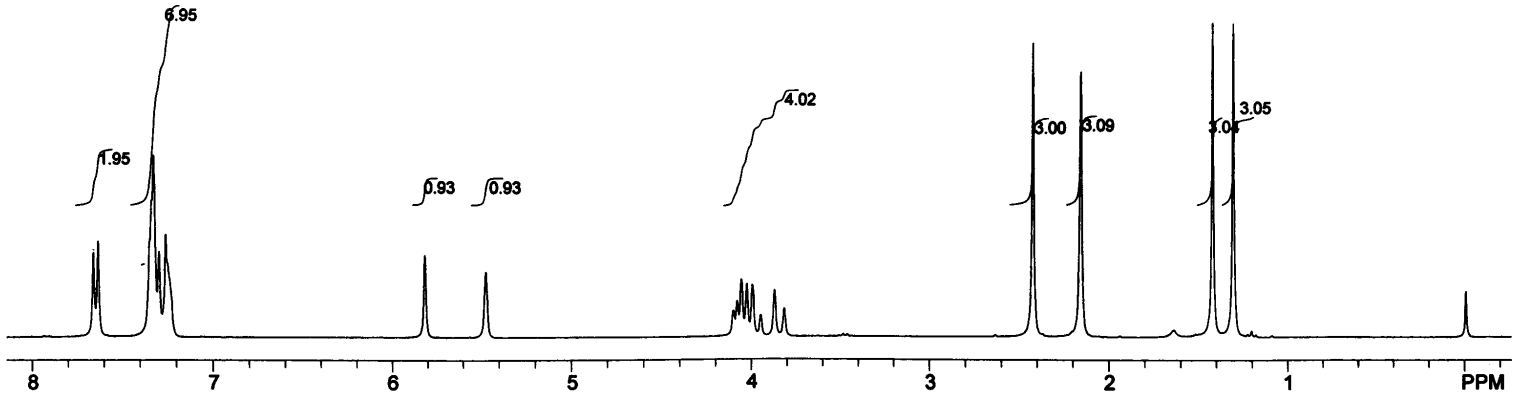
3d




7.668
7.652
7.336
7.325
7.294
7.257
5.815
5.473
4.087
4.078
4.055
4.024
3.993
3.944
3.866
3.815
2.422
2.155
1.421
1.305
0.010


TsN
Ph
O
O

3e

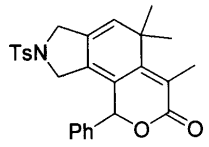

6.95
1.95
0.93
0.93
4.02
3.00
3.09
3.04
3.05
8
7
6
5
4
3
2
1
PPM

lxd-3-161-c

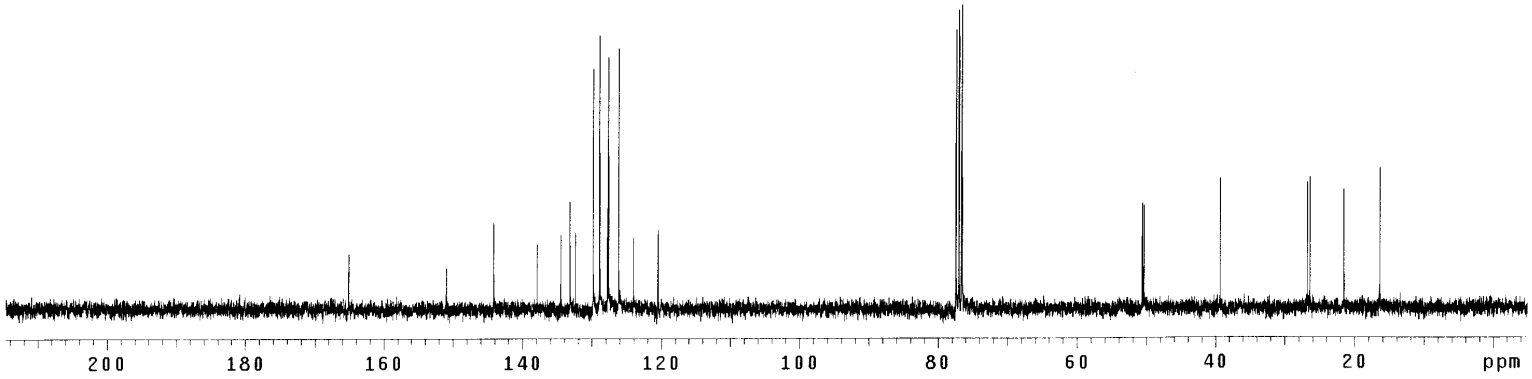
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

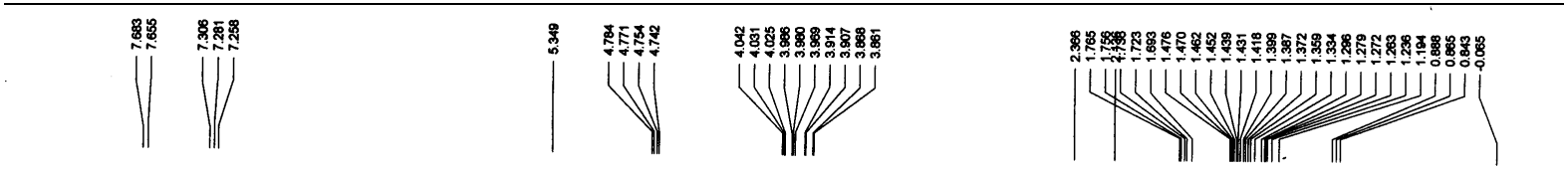
Pulse Sequence: s2pul

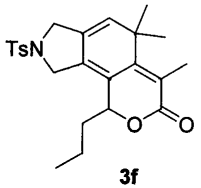
165.119
144.129
137.893
134.489
133.176
132.398
129.848
128.925
128.879
127.795
127.658
126.192
124.025
120.498
77.420
77.000
76.573
50.606
50.377
39.333
26.739
26.388
21.503
16.404



3e

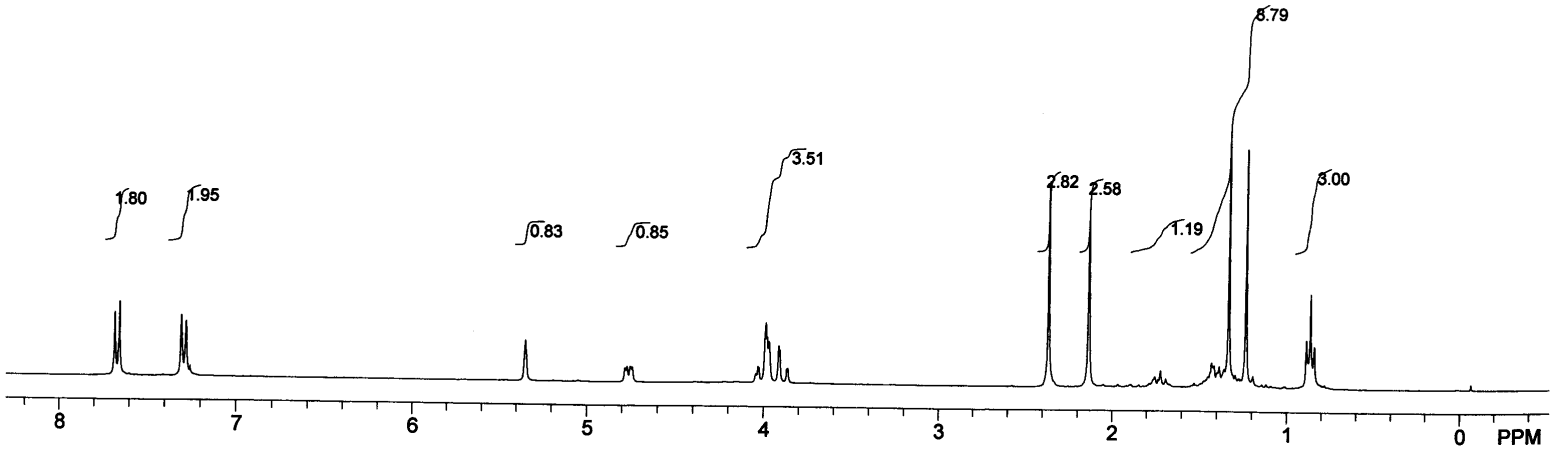



7.683
7.655
7.306
7.281
7.258
5.349
4.784
4.771
4.754
4.742
4.042
4.031
4.025
3.986
3.980
3.969
3.914
3.907
3.898
3.861
2.966
1.765
1.723
1.693
1.476
1.470
1.462
1.452
1.439
1.431
1.418
1.399
1.387
1.372
1.359
1.334
1.296
1.279
1.272
1.263
1.236
1.194
0.986
0.965
0.943
-0.065


TsN
O
O

3f

lxd-4-36-h

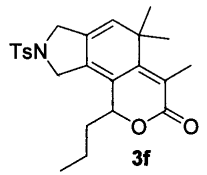

8.79
3.51
2.82
2.58
3.00
1.80
1.95
0.83
0.85
1.19
8
7
6
5
4
3
2
1
0
PPM

lxd-4-36-c

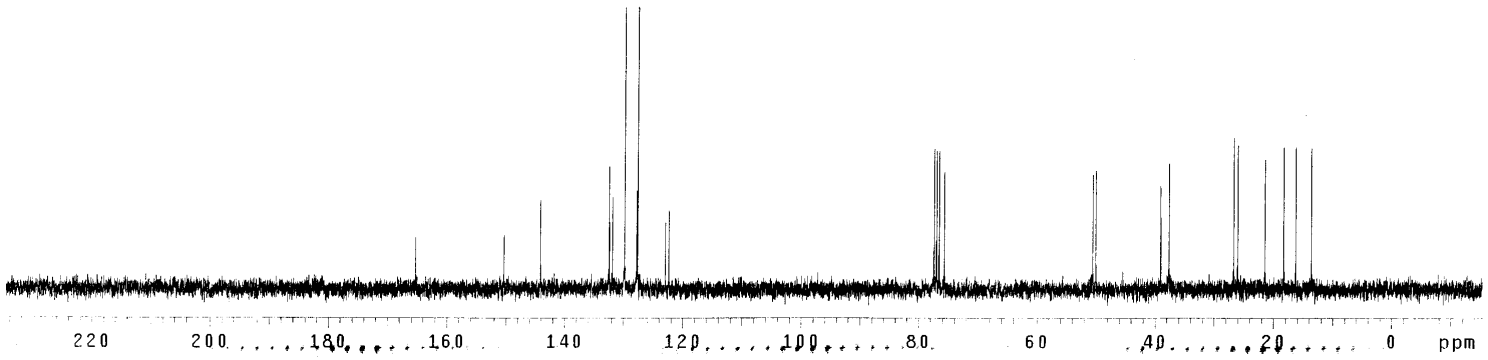
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

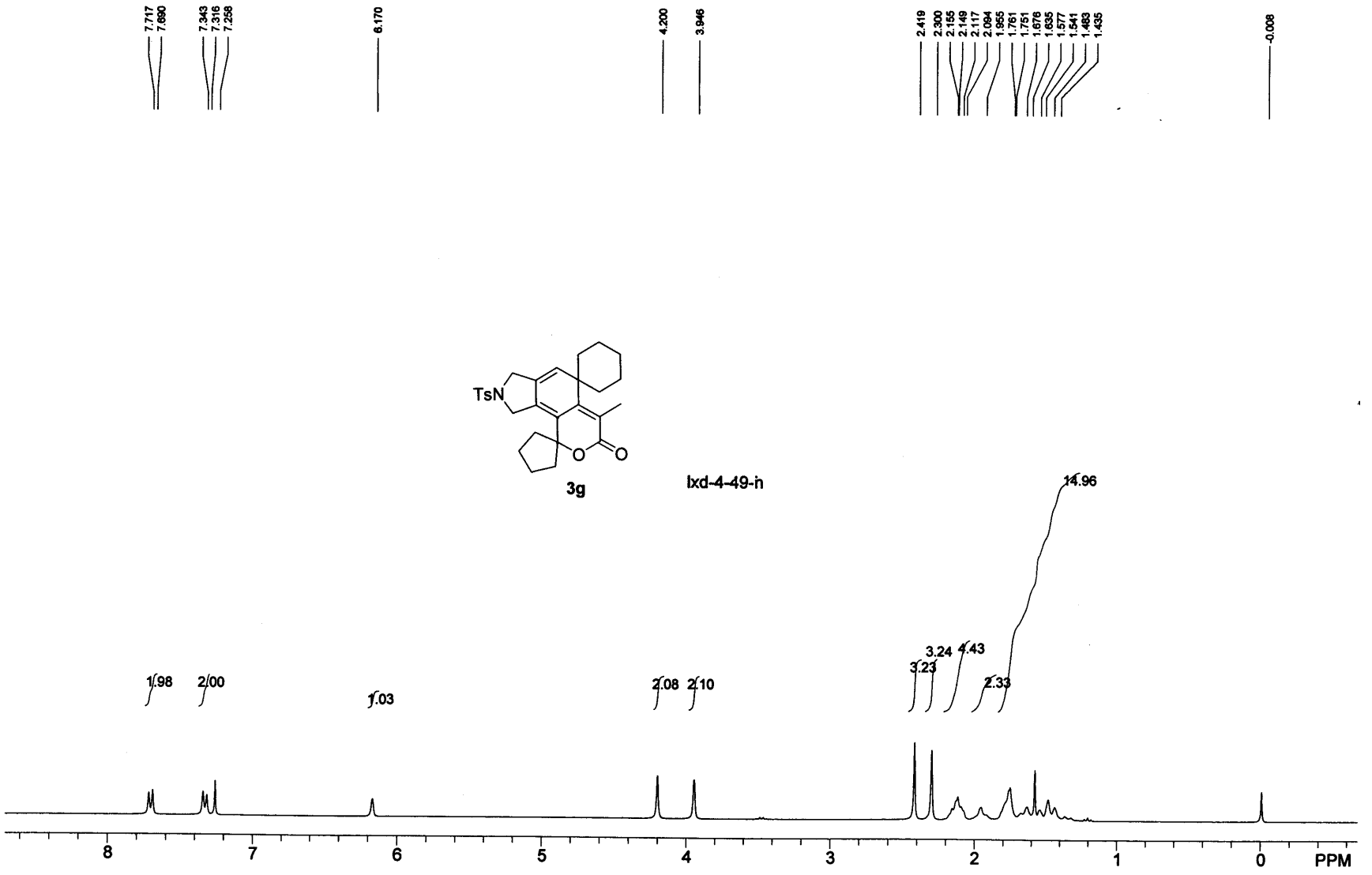
Pulse Sequence: s2pul

165.233
150.349
144.114
132.443
131.833
129.802
127.749
127.612
122.933
122.345
77.420
76.992
76.573
75.702
50.507
49.986
39.028
37.639
26.693
26.022
21.412
18.275
16.267
13.611



3f



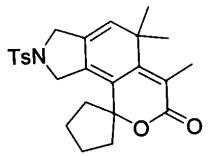

7.717
7.690
7.343
7.316
7.258
6.170
4.200
3.946
2.419
2.300
2.155
2.149
2.117
2.094
1.955
1.761
1.751
1.678
1.635
1.577
1.541
1.483
1.435
-0.008
TsN
O
O
3g
lxd-4-49-h
14.96
3.24
3.23
4.43
2.33
1.98
2.00
1.03
2.08
2.10
8
7
6
5
4
3
2
1
0
PPM

lxd-3-184-c

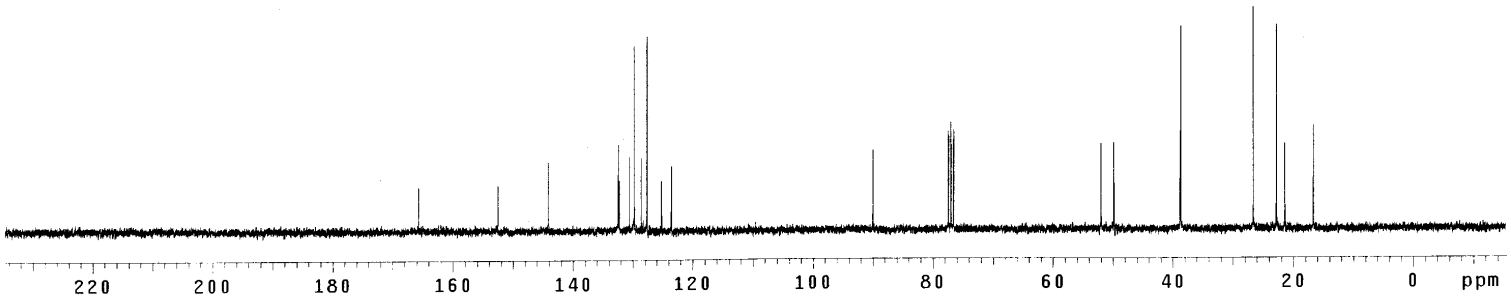
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

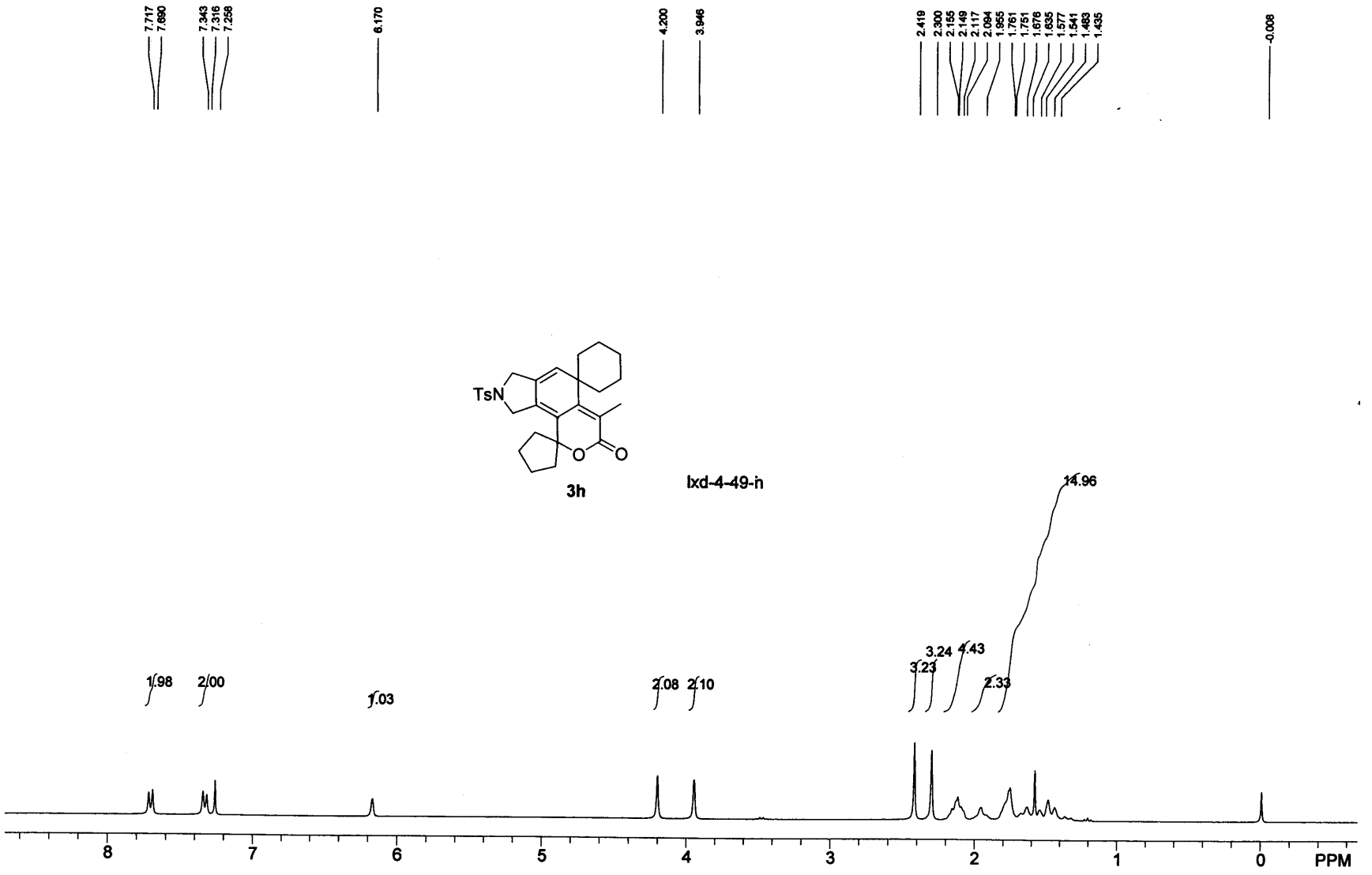
Pulse Sequence: s2pul

165.683
152.532
144.129
132.459
132.253
130.550
129.764
128.574
127.827
125.177
123.544
89.953
77.427
77.000
76.573
52.011
49.866
38.745
38.654
26.594
22.778
21.381
16.695



3g

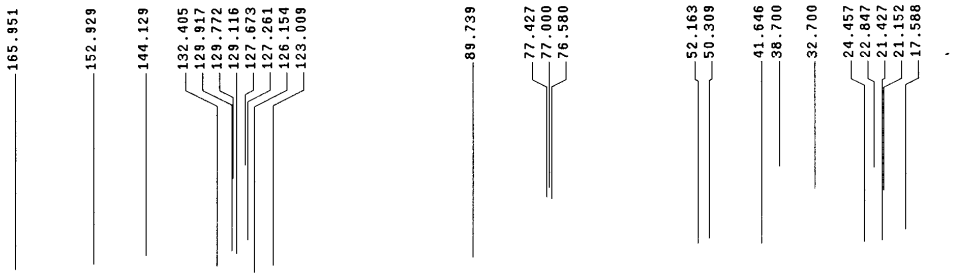


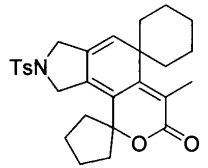

7.717
7.690
7.343
7.316
7.258
6.170
4.200
3.946
2.419
2.300
2.155
2.149
2.117
2.094
1.955
1.761
1.751
1.678
1.635
1.577
1.541
1.483
1.435
-0.008
TsN
O
O
3h
lxd-4-49-h
14.96
3.24
3.23
4.43
2.33
1.98
2.00
1.03
2.08
2.10
8
7
6
5
4
3
2
1
0
PPM

lxd-4-49-c

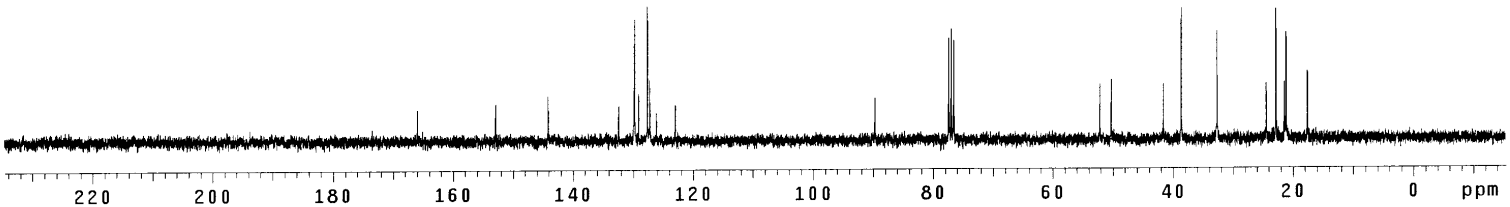
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

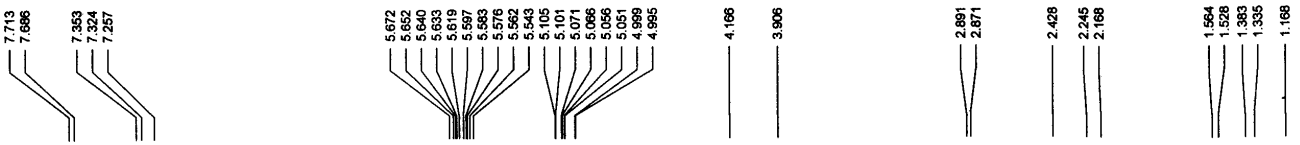
Pulse Sequence: s2pul

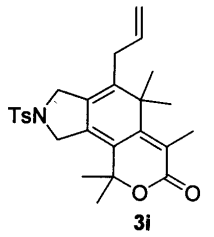




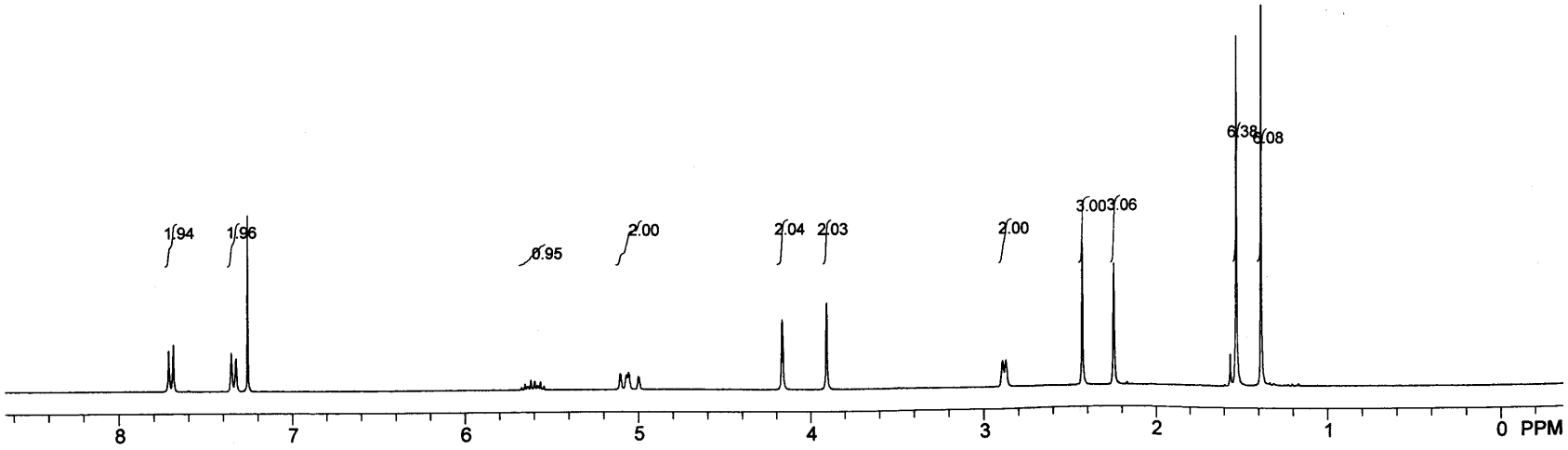
3h




7.713
7.686
7.353
7.324
7.257
5.672
5.652
5.640
5.633
5.619
5.597
5.583
5.576
5.562
5.543
5.105
5.101
5.071
5.066
5.056
5.051
4.999
4.995
4.166
3.906
2.891
2.871
2.428
2.245
2.168
1.564
1.528
1.383
1.335
1.166


TsN
O
O

3i

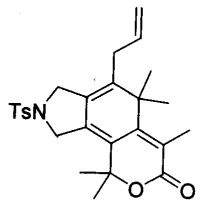

1.94
1.96
0.95
2.00
2.04
2.03
2.00
3.00
3.06
6.38
6.08
8
7
6
5
4
3
2
1
0 PPM

lxd-3-183-c

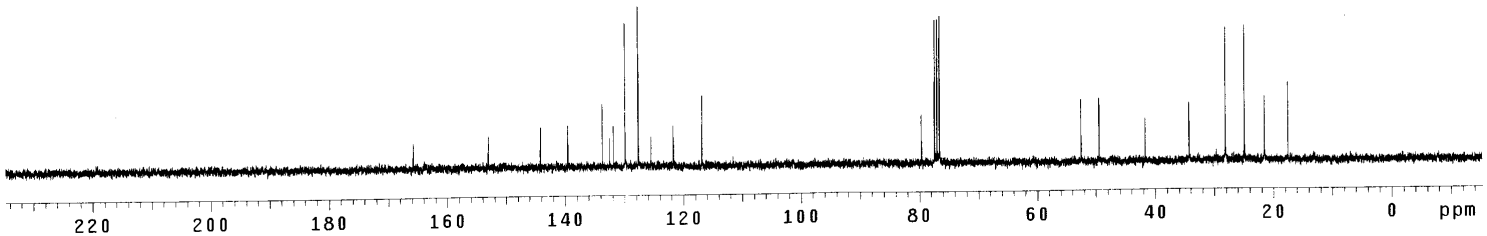
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

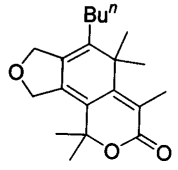
165.798
153.074
144.167
139.511
133.710
132.489
131.848
129.856
127.642
127.597
125.505
121.704
116.858
79.633
77.420
77.000
76.573
52.507
49.446
41.669
34.265
28.113
24.869
21.496
17.511



3i

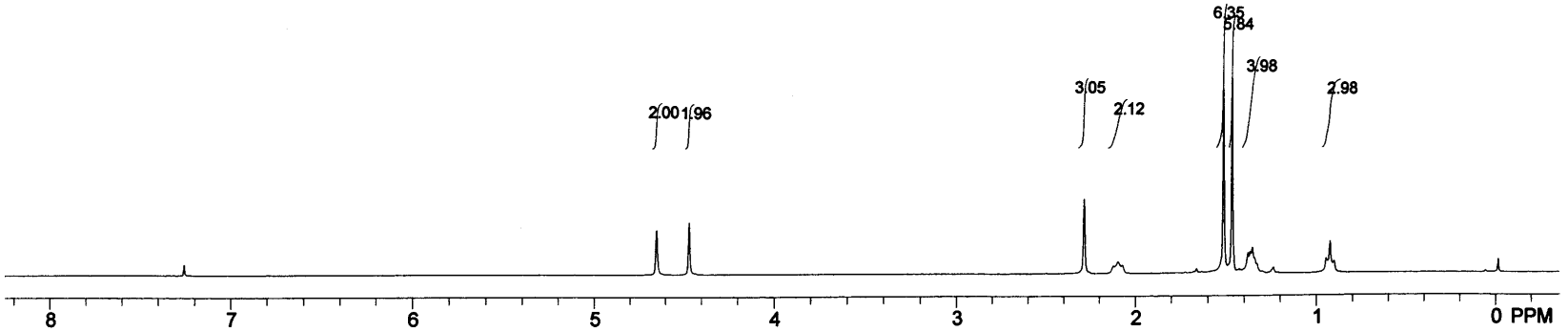



7.258
4.649
4.498
2.284
2.123
2.096
2.072
1.512
1.485
1.377
1.365
1.352
1.342
1.328
0.945
0.924
0.902
-0.017


Bu^n
O
O
O

3j

lxd-3-194-h

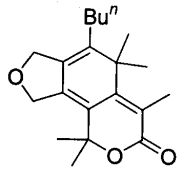

2.00
1.96
3.05
2.12
6.35
5.84
3.98
2.98
8
7
6
5
4
3
2
1
0 PPM

lxd-3-194-c

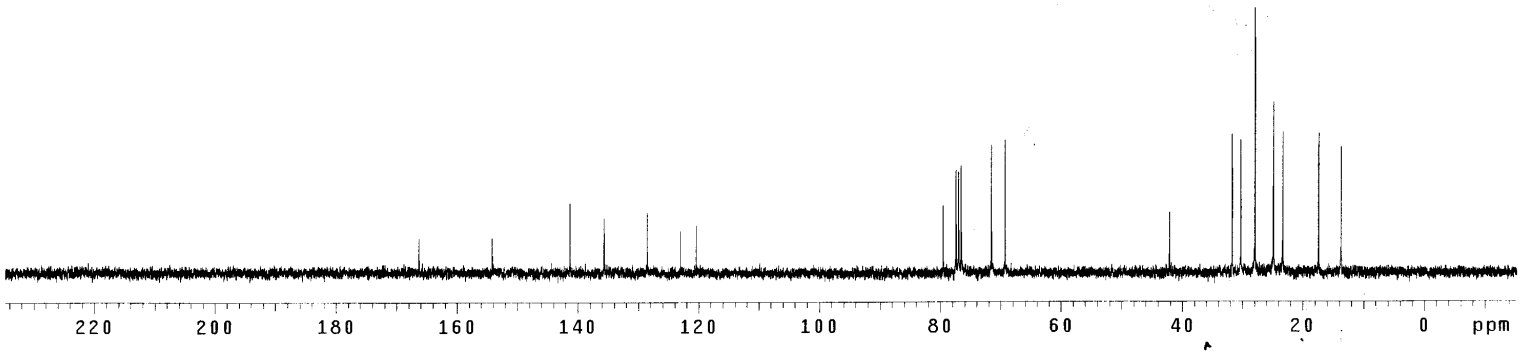
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

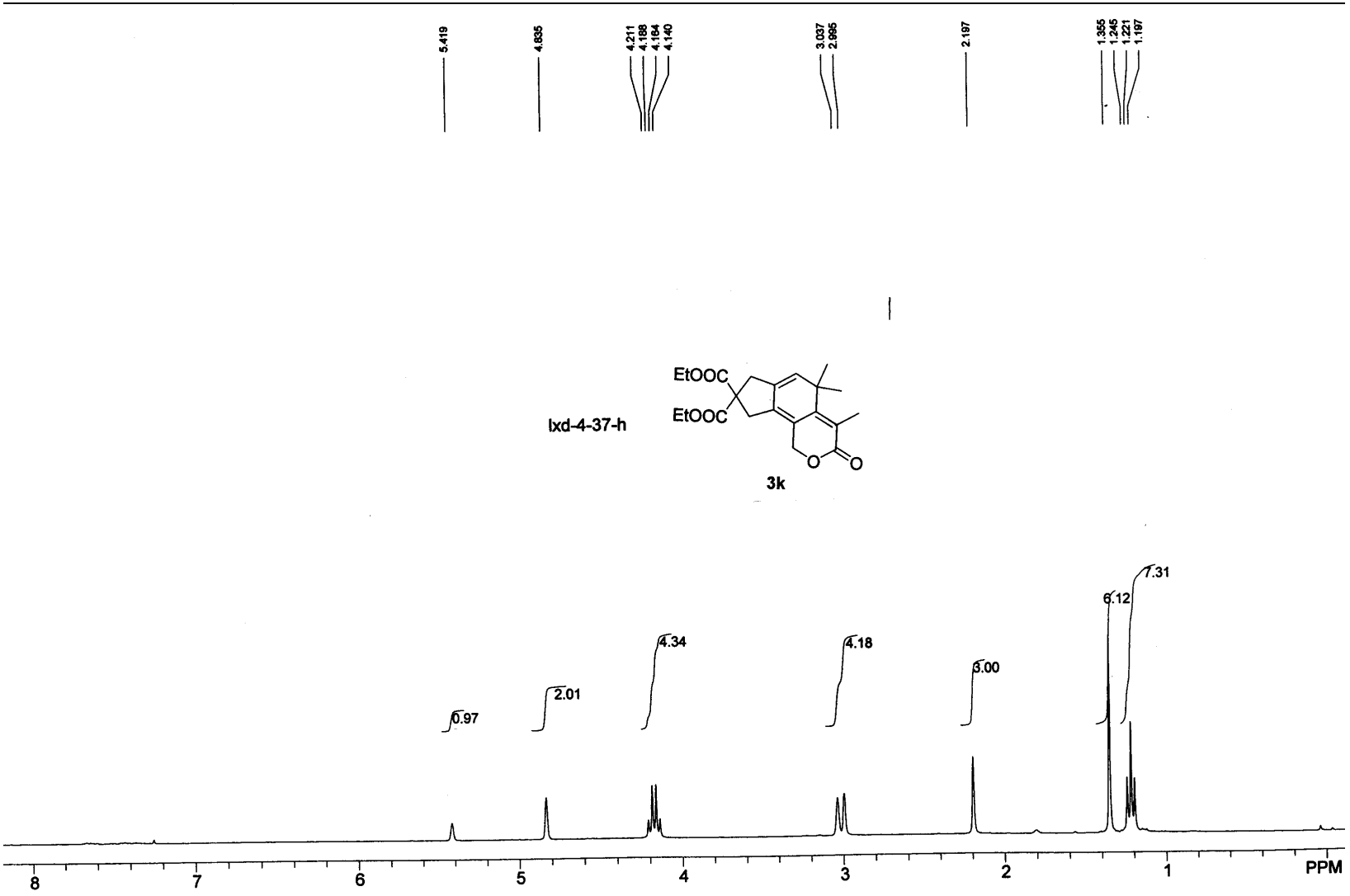
Pulse Sequence: s2pul

166.309
154.173
141.312
135.672
128.566
123.078
120.437
79.549
77.427
77.008
76.580
71.573
69.283
42.104
31.693
30.265
27.876
24.801
23.259
17.359
13.672



3j



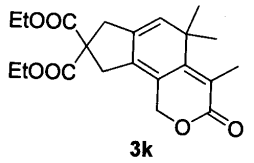

5.419
4.835
4.211
4.188
4.164
4.140
3.037
2.995
2.197
1.355
1.245
1.221
1.197
lxd-4-37-h
EtOOC
EtOOC
O
O
3k
0.97
2.01
4.34
4.18
3.00
6.12
7.31
8
7
6
5
4
3
2
1
PPM

lxd-4-37-c

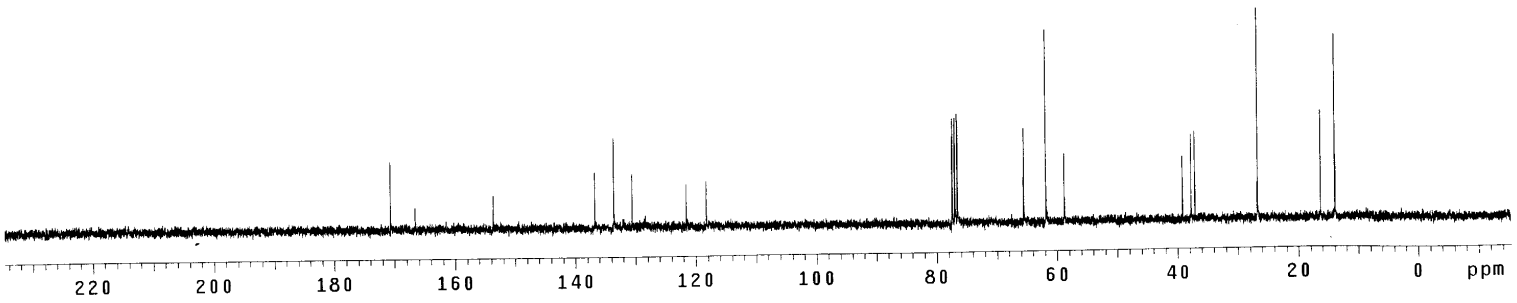
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

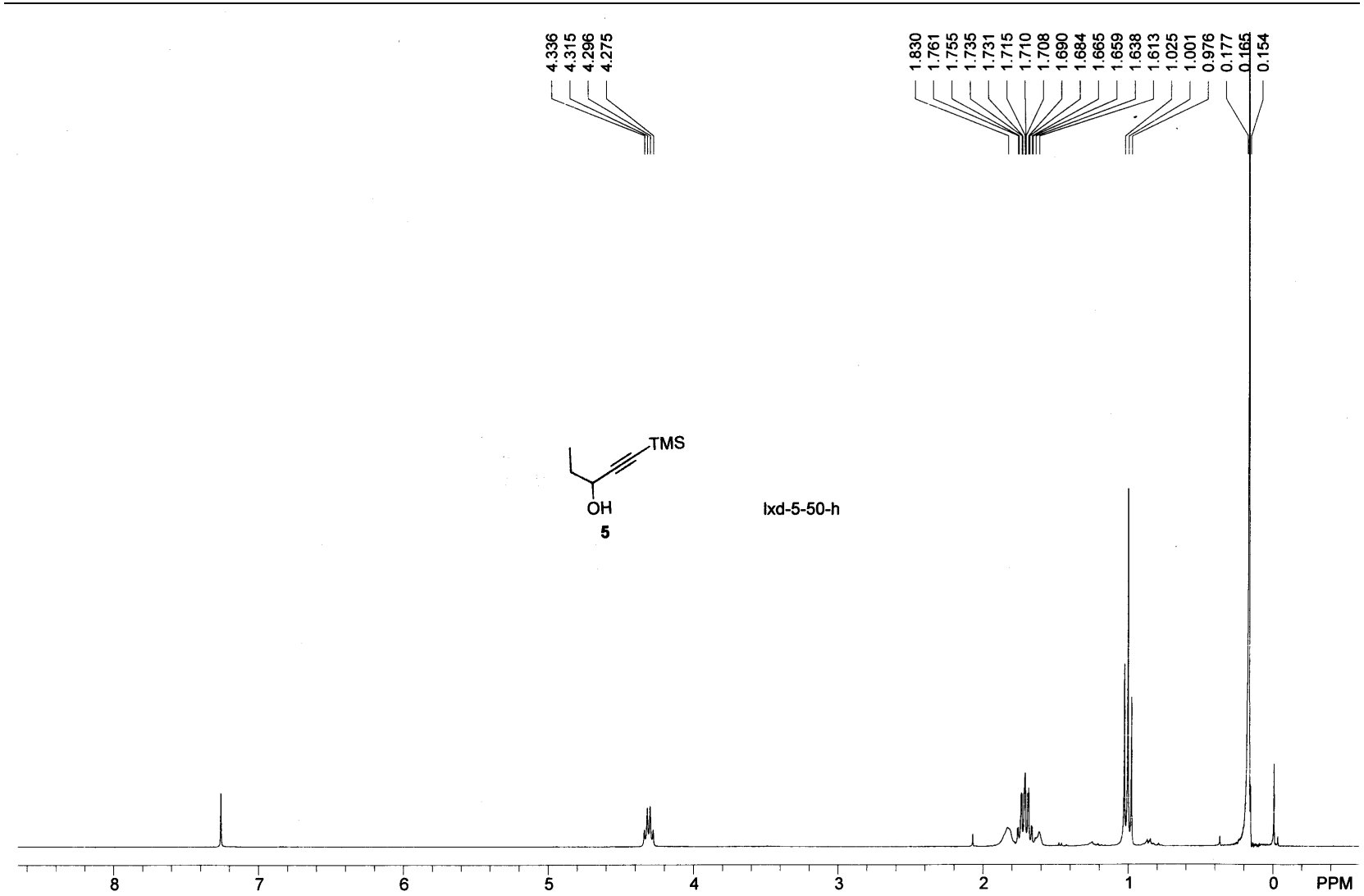
Pulse Sequence: s2pul

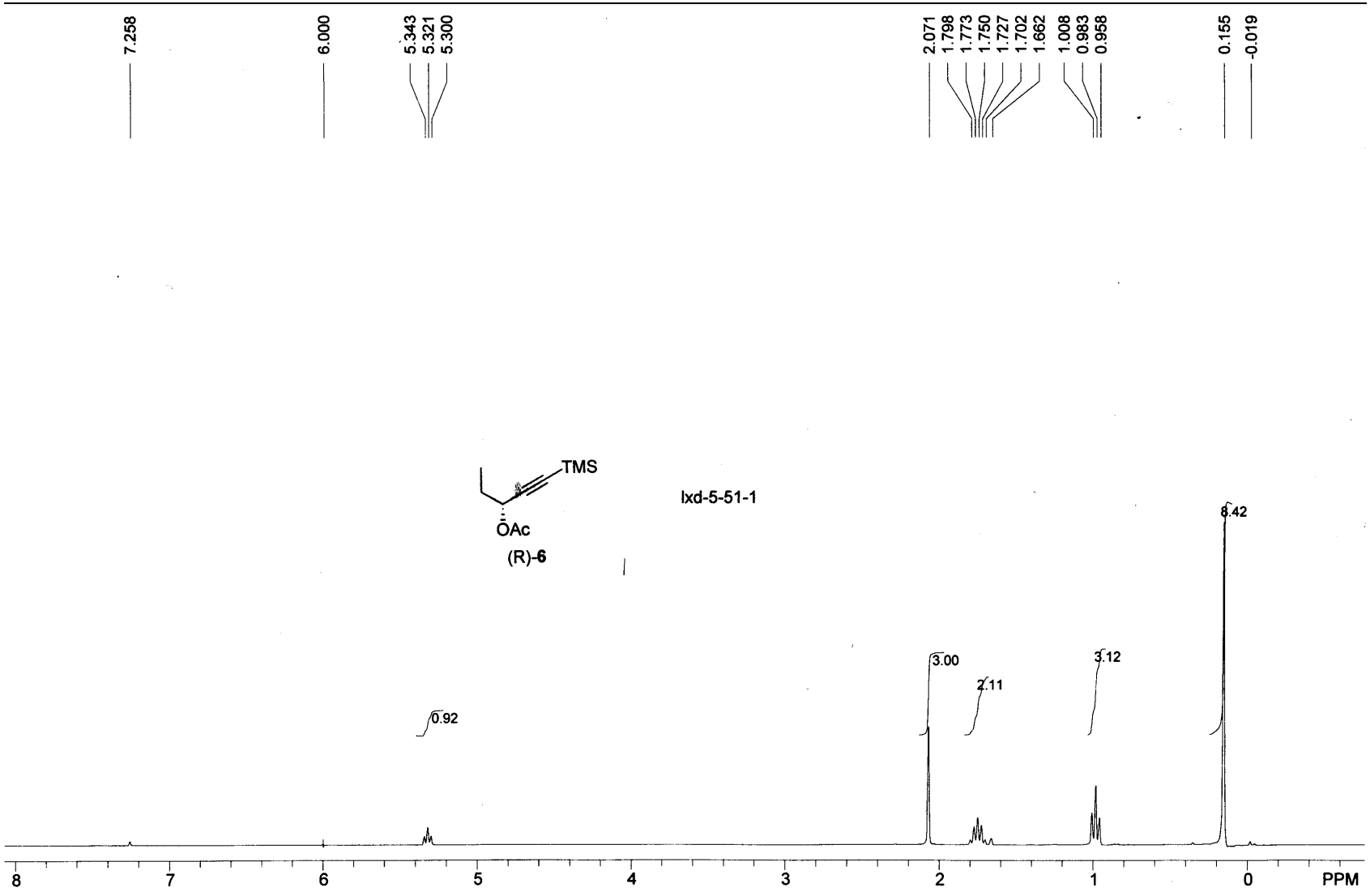
170.668
166.592
153.662
136.771
133.619
130.581
121.582
118.231
77.420
76.992
76.573
65.536
61.849
58.773
39.173
37.776
37.150
26.770
16.328
13.909

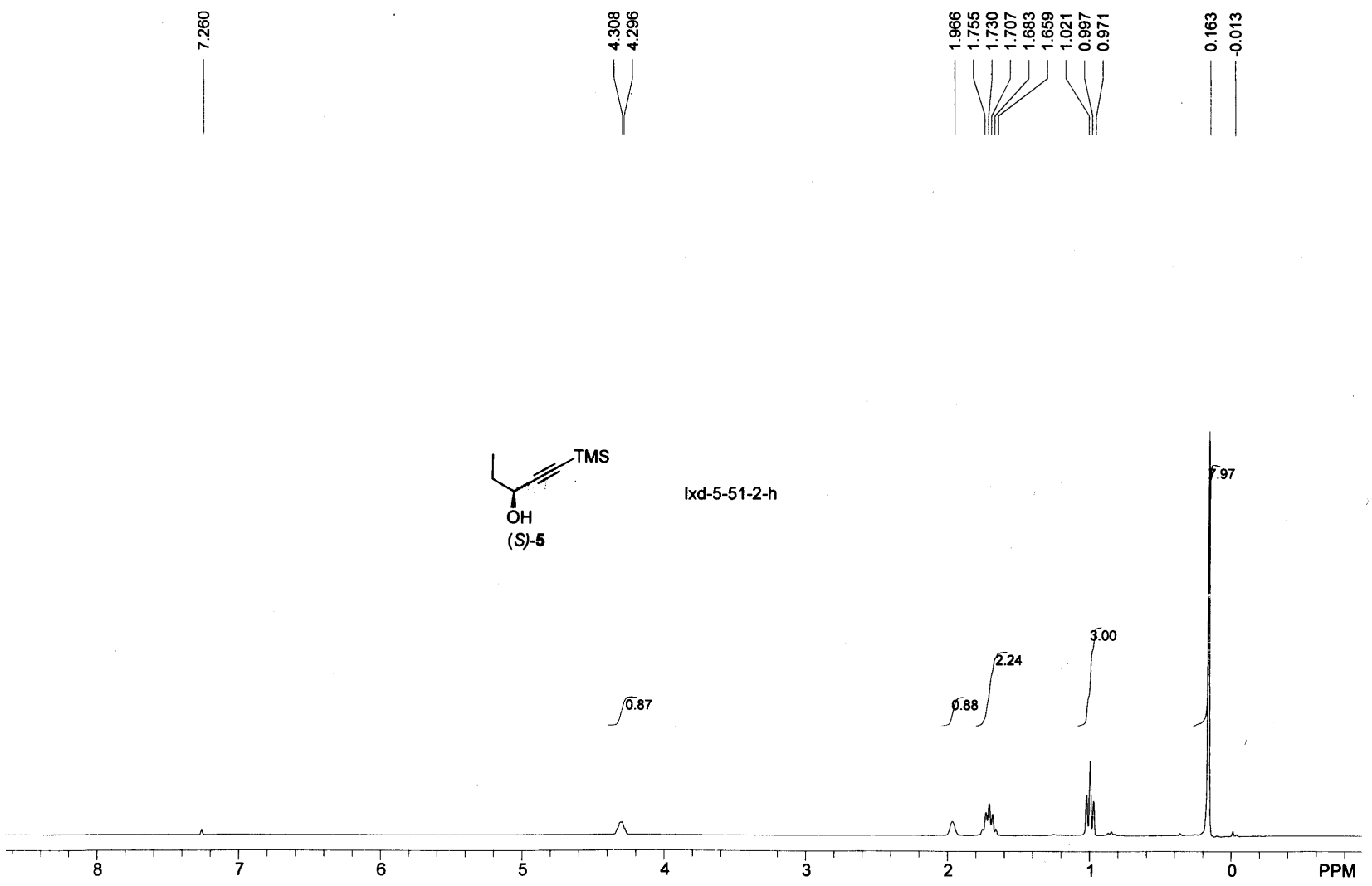


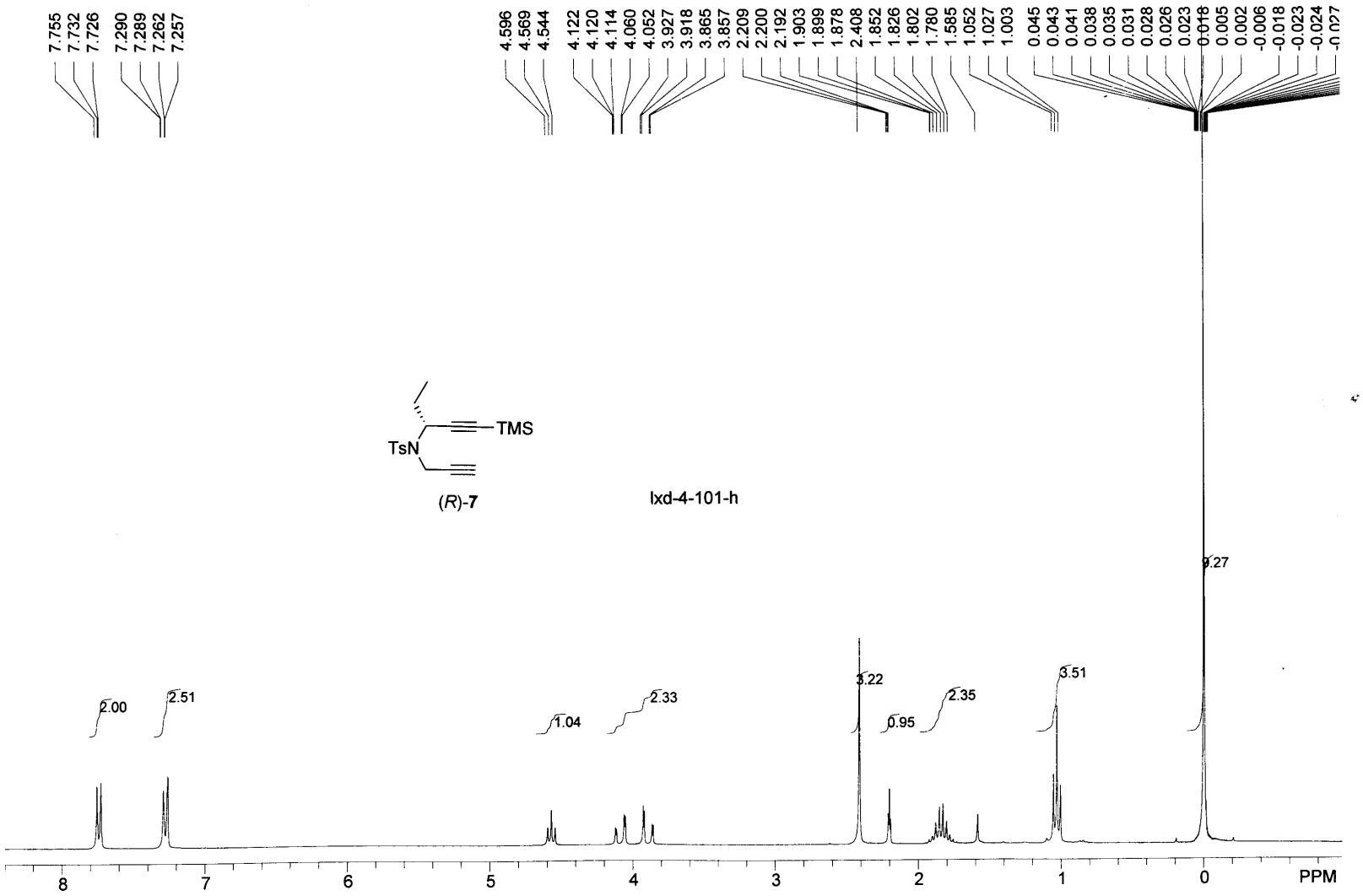
3k




4.336
4.315
4.296
4.275
1.830
1.761
1.755
1.735
1.731
1.715
1.710
1.708
1.690
1.684
1.665
1.659
1.638
1.613
1.025
1.001
0.976
0.177
0.165
0.154
TMS
OH
5
lxd-5-50-h
8
7
6
5
4
3
2
1
0
PPM


7.258
6.000
5.343
5.321
5.300
2.071
1.798
1.773
1.750
1.727
1.702
1.662
1.008
0.983
0.958
0.155
-0.019
TMS
OAc
(R)-6
lxd-5-51-1
0.92
3.00
2.11
3.12
8.42
8
7
6
5
4
3
2
1
0
PPM


7.260
4.308
4.296
1.966
1.755
1.730
1.707
1.683
1.659
1.021
0.997
0.971
0.163
-0.013
TMS
OH
(S)-5
lxd-5-51-2-h
0.87
0.88
2.24
3.00
7.97
8
7
6
5
4
3
2
1
0
PPM

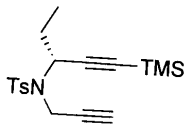

7.755
7.732
7.726
7.290
7.289
7.262
7.257
4.596
4.569
4.544
4.122
4.120
4.114
4.060
4.052
3.927
3.918
3.865
3.857
2.209
2.200
2.192
1.903
1.899
1.878
2.408
1.852
1.826
1.802
1.780
1.585
1.052
1.027
1.003
0.045
0.043
0.041
0.038
0.035
0.031
0.028
0.026
0.023
0.018
0.005
0.002
-0.006
-0.018
-0.023
-0.024
-0.027
TMS
TsN
(R)-7
lxd-4-101-h
9.27
2.00
2.51
1.04
2.33
3.22
0.95
2.35
3.51
8
7
6
5
4
3
2
1
0
PPM

lxd-4-112-cc

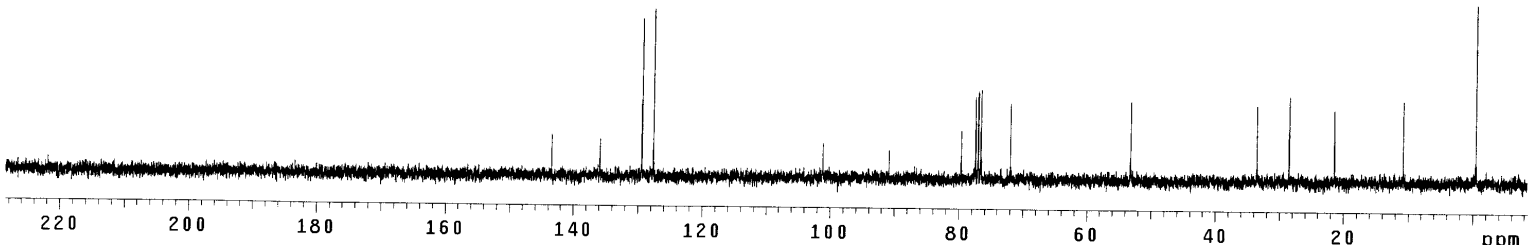
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

143.450
135.916
129.398
127.620
101.134
90.884
79.641
77.412
77.000
76.573
71.970
53.186
33.524
28.517
21.457
10.779
-0.464



(*R*)-**7**

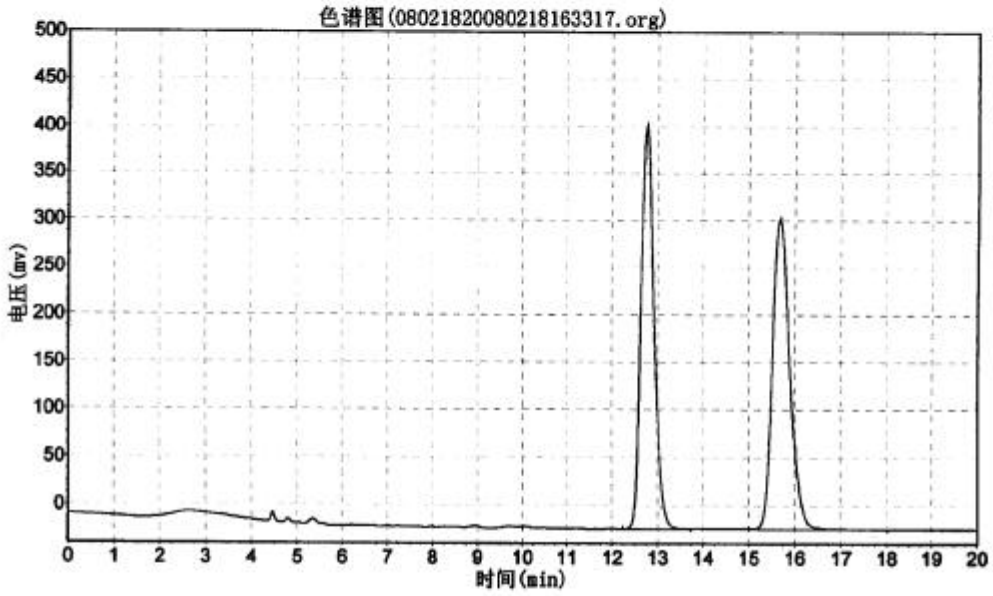


实验时间：2008-02-18,16:53:21
谱图文件:C:\浙大智达\N2000\样品\08021820080218163317.org

实验者：
报告时间：2008-02-18,17:01:55
积分方法:面积归一法

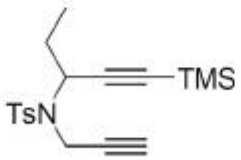
使用仪器类型:气相色谱　　检测器:FID　　进样器:分流

柱温:程序升温



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		12.765	422614.281	8477458.000	49.7305
2		15.698	325427.781	8569326.000	50.2695
总计			748042.063	17046784.000	100.0000



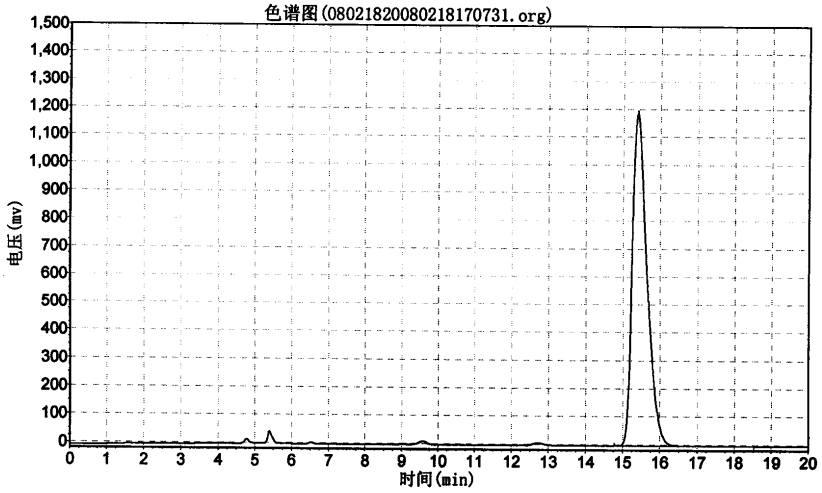
Condition;
AB-H, 0.6 mL/min.
95/5. λ=230.

实验时间：2008-02-18,17:39:22
谱图文件:C:\浙大智达\N2000\样品\08021820080218170731.org

实验者：
报告时间：2008-02-18,17:41:57
积分方法:面积归一法

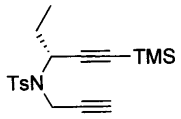
使用仪器类型:气相色谱　　检测器:FID　　进样器:分流

柱温:程序升温

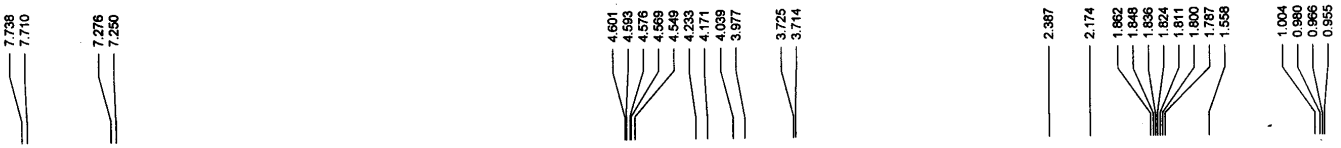


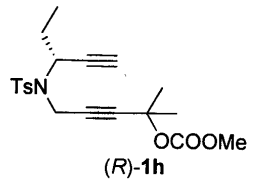
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		15.390	1187035.750	32605886.000	100.0000
总计			1187035.750	32605886.000	100.0000



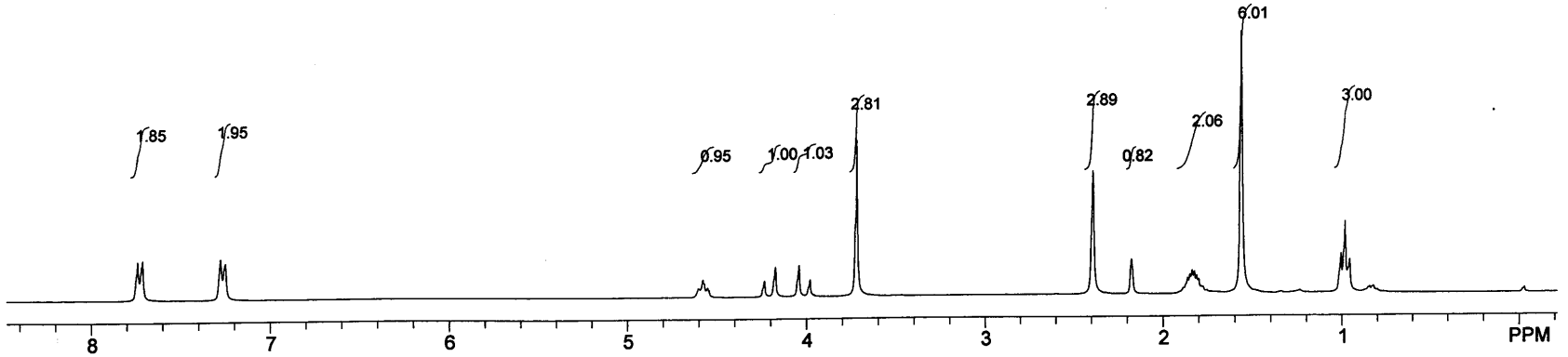
(*R*)-**7**





(*R*)-**1h**

lxd-4-120-h

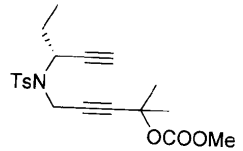


lxd-4-120-c

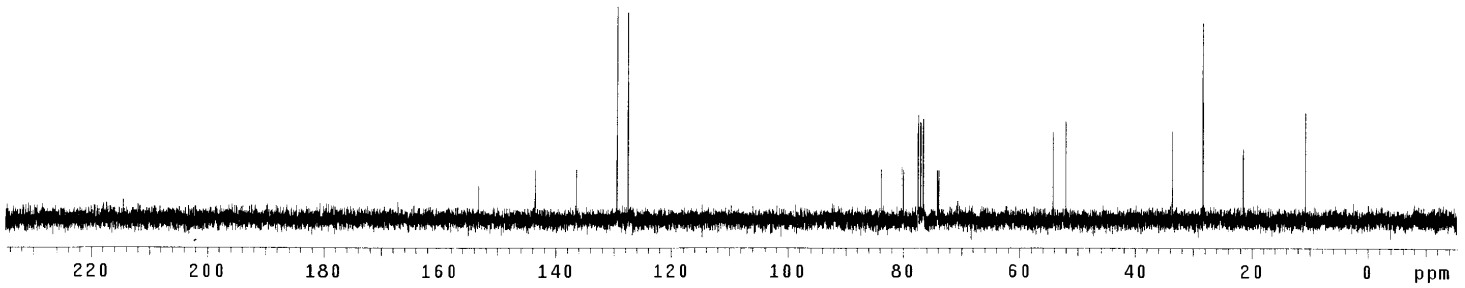
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

153.265
143.480
136.405
129.398
127.543
83.831
80.252
79.961
77.412
77.000
76.573
74.161
73.939
54.201
52.003
33.639
28.342
28.304
21.442
10.817



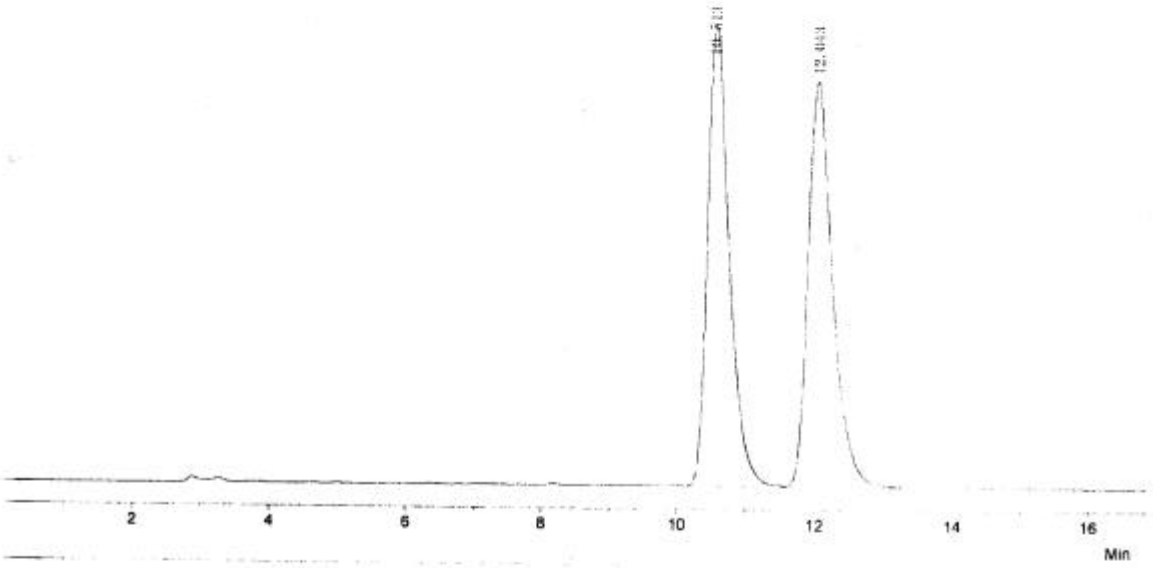
(*R*)-**1h**



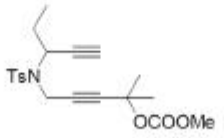
高效液相色谱分析报告

分析谱图
2008-01-03

样品文件名:lxd-4-104 ad 90.che
分析时间:14:39
流动相:
检测波长:



kNo	R.Time	PeakHeight	PeakArea	PerCent
1	10.543	545369.3	12149742.4	49.9840
2	12.043	486920.8	12157503.5	50.0160
		1032290.1	24307245.9	100.0000



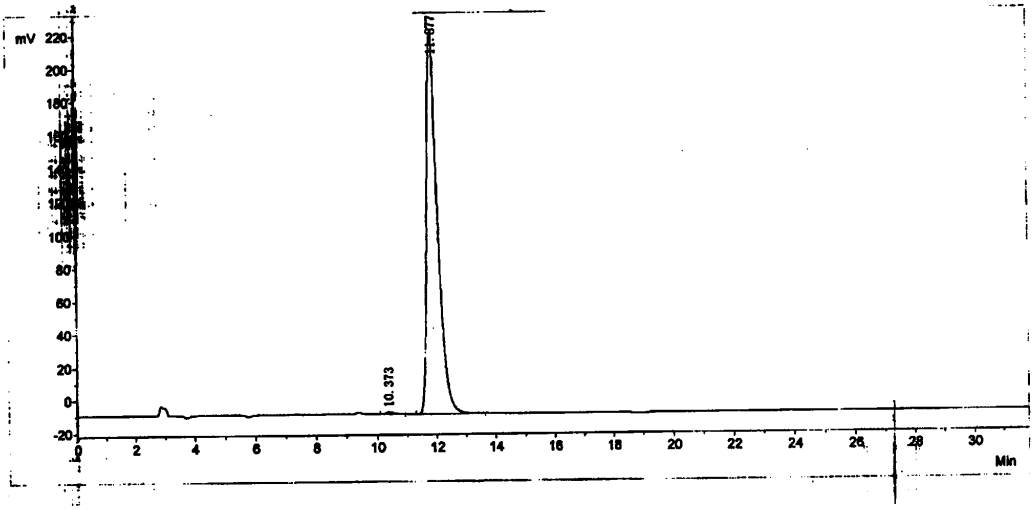
高效液相色谱分析报告

样品名称:分析谱图　　样品文件名:lxd-4-120..che

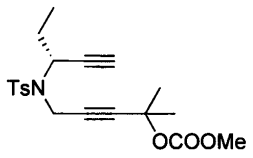
分析日期:2008-01-16　　分析时间:11:25

色谱柱:　　流动相:

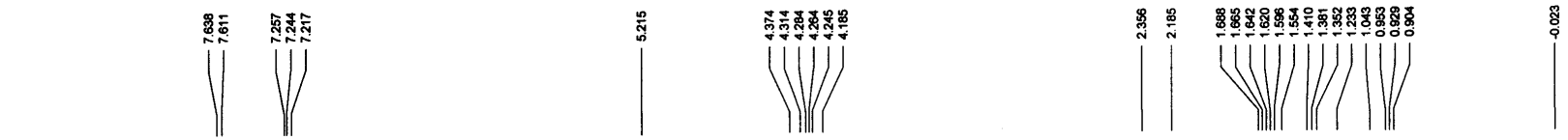
流速:　　检测波长:

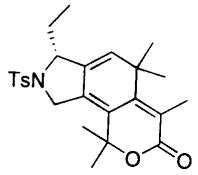


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	10.373	970.8	21020.7	0.3611
2	2	11.877	230584.8	5800198.7	99.6389
Total			231555.6	5821219.4	100.0000



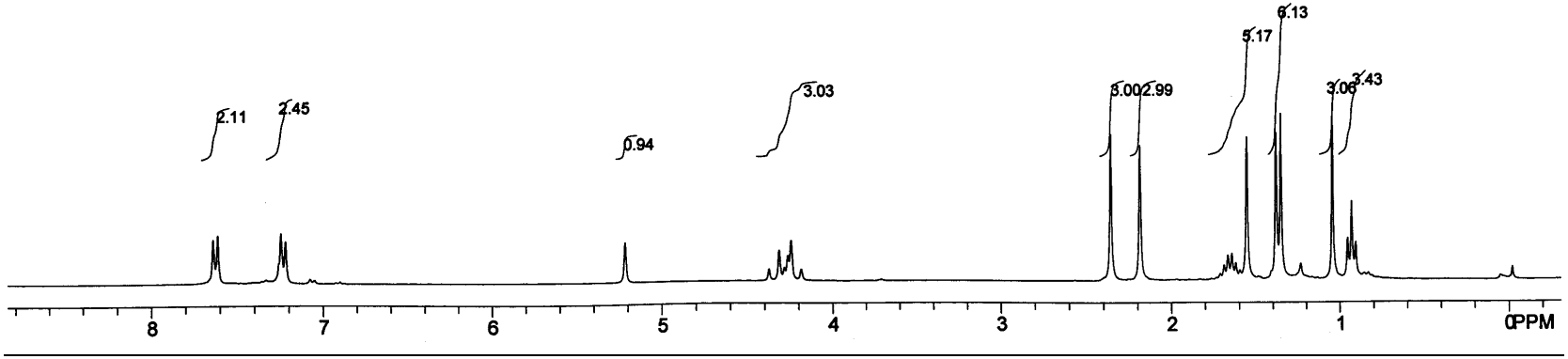
(*R*)-**1h**





R-(-)-**3l**

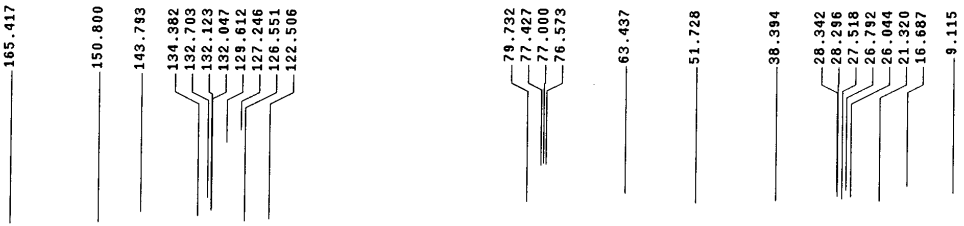
lxd-4-125-h

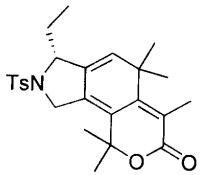


1xd-4-121-c

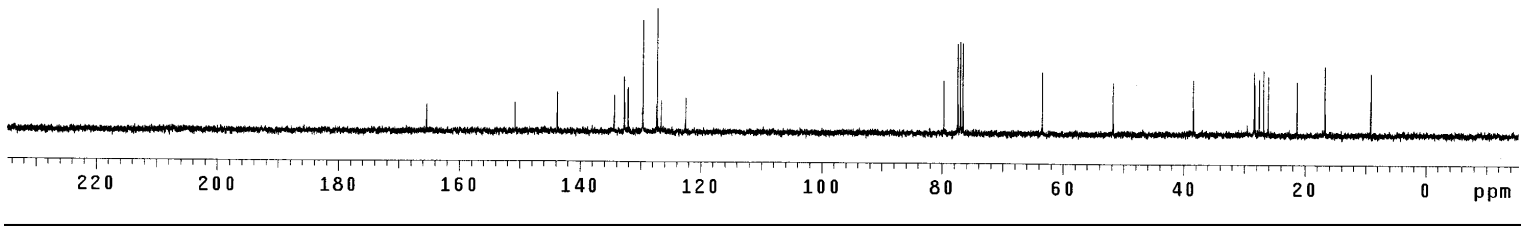
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul





R-(-)-**3l**

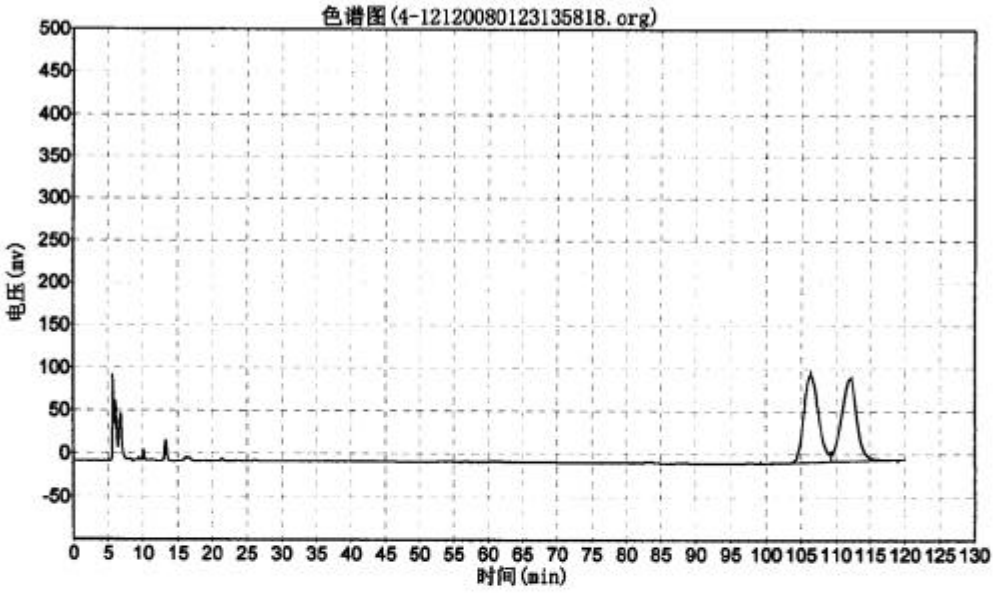


实验时间：2008-01-23,15:58:28
谱图文件:C:\浙大智达\N2000\样品\4-12120080123135818.org

实验者：
报告时间：2008-01-23,16:13:16
积分方法:面积归一法

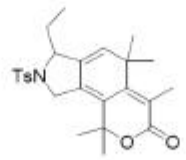
使用仪器类型:气相色谱　　检测器:FID　　进样器:分流

柱温:程序升温



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		106.390	100105.945	14643603.000	49.7497
2		112.257	95525.867	14790961.000	50.2503
总计			195631.813	29434564.000	100.0000

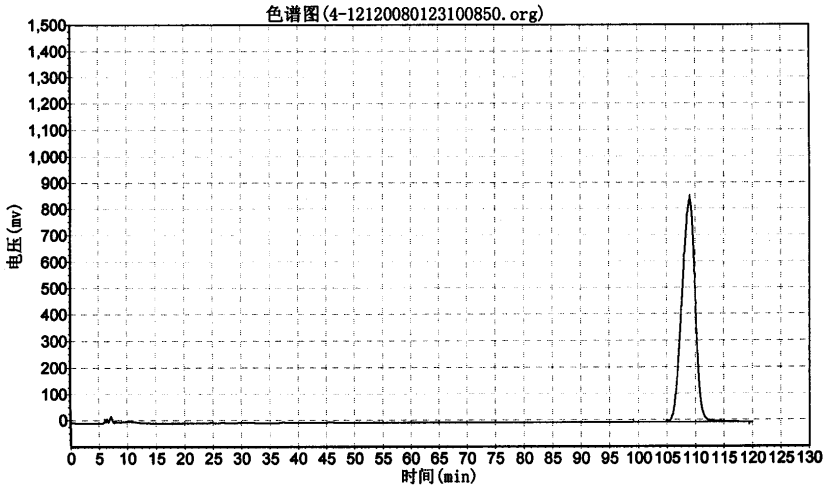


实验时间：2008-01-23,12:09:01
谱图文件:C:\浙大智达\N2000\样品\4-12120080123100850.org

实验者：
报告时间：2008-01-23,16:17:00
积分方法:面积归一法

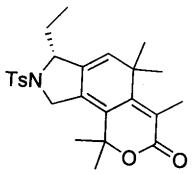
使用仪器类型:气相色谱　　检测器:FID　　进样器:分流

柱温:程序升温



分析结果表

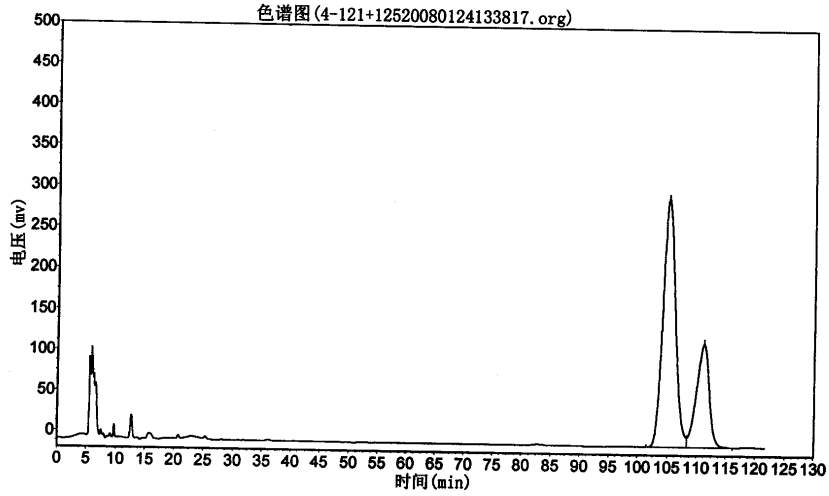
峰号	峰名	保留时间	峰高	峰面积	含量
1		109.065	836376.250	135473552.000	100.0000
总计			836376.250	135473552.000	100.0000



(*R*)-**3k**

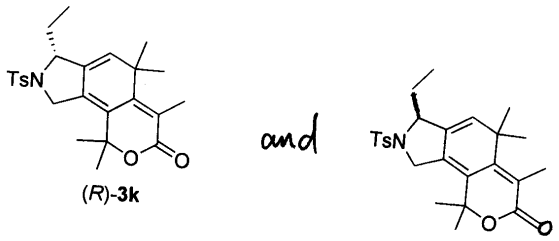
lxd-4-121-125

谱图文件:C:\浙大智达\N2000\样品\4-121+12520080124133817.org 报告时间：2008-04-04,16:40:52

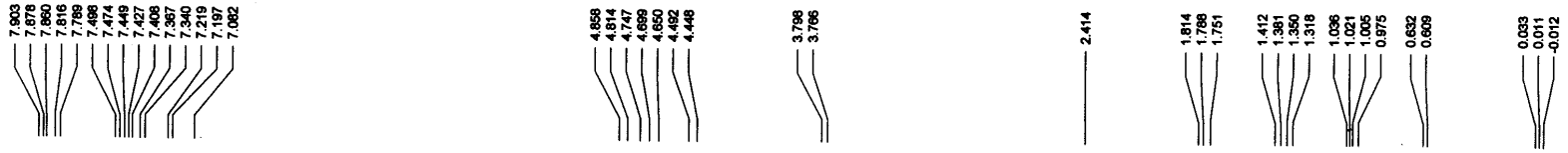


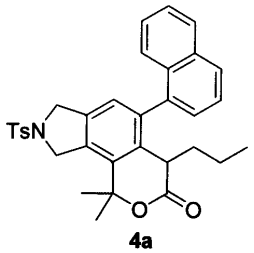
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		105.132	303517.531	44677504.000	69.9847
2		111.215	127228.805	19161484.000	30.0153
总计			430746.336	63838988.000	100.0000

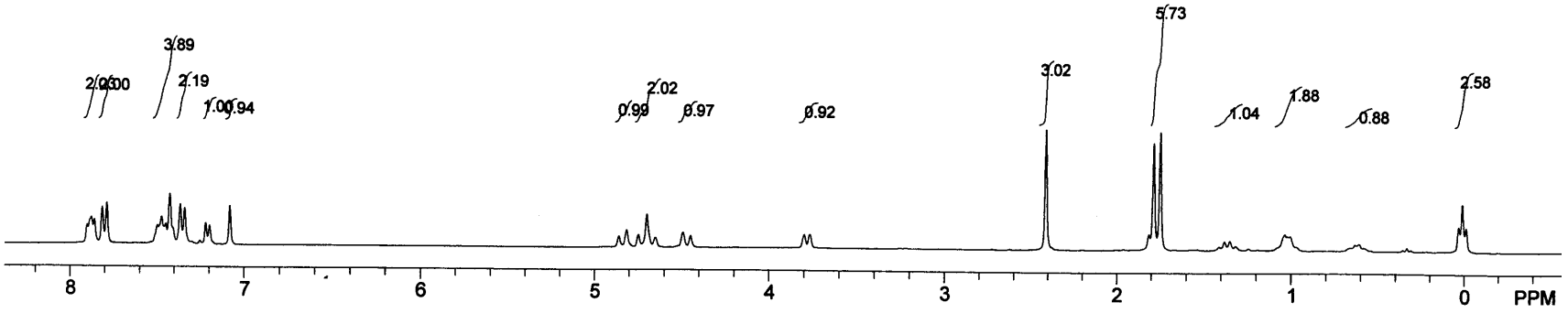


(*R*)-**3k**


7.903
7.878
7.860
7.816
7.789
7.498
7.474
7.449
7.427
7.408
7.367
7.340
7.219
7.197
7.062
4.858
4.814
4.747
4.699
4.650
4.492
4.448
3.798
3.766
2.414
1.814
1.788
1.751
1.412
1.381
1.350
1.318
1.036
1.021
1.005
0.975
0.632
0.609
0.033
0.011
-0.012


TsN
O
O

4a

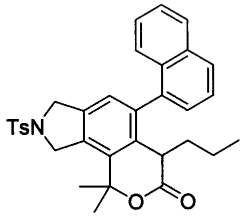

3.89
2.19
1.00
0.94
2.02
0.99
0.97
0.92
3.02
5.73
1.04
1.88
0.88
2.58
8
7
6
5
4
3
2
1
0
PPM

lxd-3-163-c

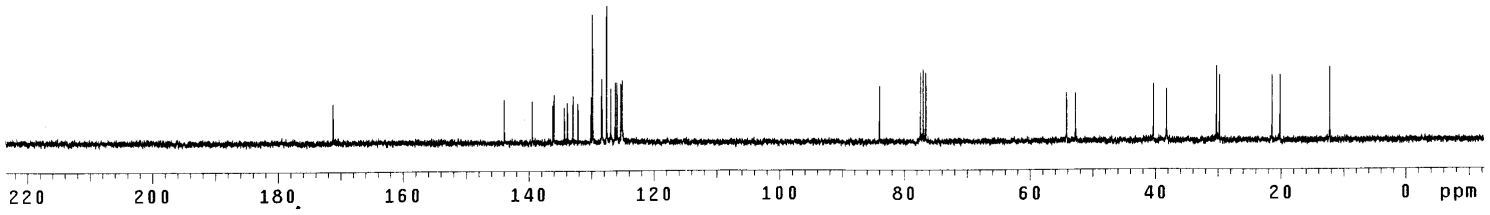
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

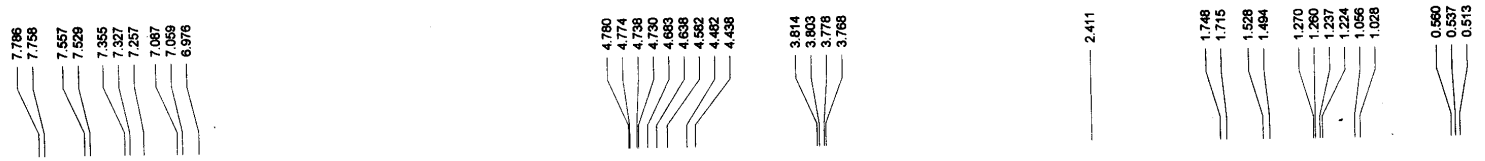
Pulse Sequence: s2pul

171.201
143.934
139.464
136.175
135.988
134.318
133.836
133.001
132.950
132.158
130.071
129.841
128.387
128.343
127.595
126.925
126.213
125.918
125.299
125.198
125.076
83.996
77.425
77.000
76.575
54.175
52.764
40.312
38.210
30.242
29.752
21.438
20.164
12.203

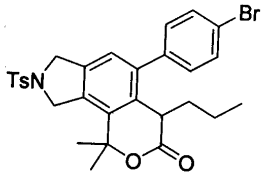


4a

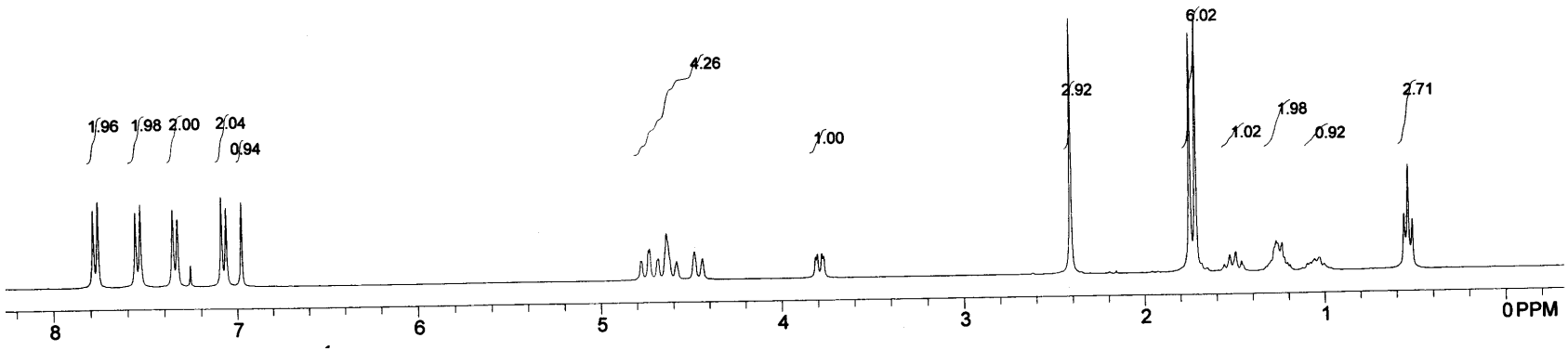



7.796
7.758
7.557
7.529
7.355
7.327
7.257
7.087
7.059
6.976
4.780
4.774
4.738
4.730
4.683
4.638
4.582
4.482
4.438
3.814
3.803
3.778
3.768
2.411
1.748
1.715
1.528
1.494
1.270
1.260
1.237
1.224
1.056
1.028
0.560
0.537
0.513

lxd-4-87-h


Br
TsN
O
O

4b

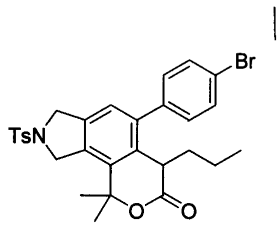

1.96
1.98
2.00
2.04
0.94
4.26
1.00
2.92
6.02
1.02
1.98
0.92
2.71
8
7
6
5
4
3
2
1
0 PPM

lxd-4-87-c

Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

170.866
144.053
140.511
138.244
136.542
134.207
132.940
131.802
131.749
130.673
130.253
129.932
127.612
124.246
122.033
84.068
77.427
77.008
76.580
54.117
52.782
39.997
38.753
30.036
29.830
21.503
20.358
12.909



4b