Supplementary Information

The Stereoselective Synthesis of α-Amino Aldols Starting from Terminal Alkynes

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General Methods: All reactions were carried out under a nitrogen atmosphere unless otherwise noted. The microwave irradiation was carried out with a Biotage® Initiator 2.5 microwave synthesizer. IR measurements were performed on a FTIR SHIMADZU DR-8000 spectrometer fitted with a Pike Technologies MIRacle Single Reflection ATR adapter. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-vx400 (^{1}H at 400.44 MHz and ^{13}C at 100.69 MHz) and a JEOL JNM-ECA600 (^{1}H at 600.17 MHz and ^{13}C at 150.92 MHz) spectrometer. NMR data were obtained in $CDCl_3$ unless otherwise noted. Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm ($CHCl_3$) and 7.16 ppm (C_6D_6). Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.0 ppm ($CDCl_3$) and 128.0 ppm (C_6D_6). High-resolution mass spectra were recorded on a Thermo Scientific Exactive (ESI) spectrometer or a JEOL JMS-T100CS (NSI) spectrometer. Preparative thin-layer chromatography was performed on silica gel plates with PF254 indicator (Merck). Flash column chromatography was performed with silica gel 60N (Kanto) and diol-silica gel DIOL MB 100–40/75 (Fuji Silysia Chemical Ltd.). Gel permeation chromatography (GPC) was carried out with a Japan Analytical Industry LC-9210 NEXT.

Materials: $Rh_2(OCOC_7H_{15})_4$ (Aldrich) was used as received from the commercial sources. $Rh_2(OCO1\text{-}Ad)_4$ was prepared according to the literature procedure.[1] Tetrahydrofuran and dichloromethane (Kanto, dehydrate) was used as received from commercial sources. Chloroform (Wako, super dehydrated, amylene as stabilizer) was distilled from phosphorus oxide(V). *tert*-Butyldimethylsilanol (Aldrich) was distilled from CaO. Terminal alkynes **1**, [phenylethyne (**1a**, Aldrich), (4-tolyl)ethyne (**1b**, TCI), (4-methoxyphenyl)ethyne (**1c**, Wako), (4-trifluoromethylphenyl)ethyne (**1d**, Aldrich), (3-thienyl)ethyne (**1e**, Aldrich), (*o*-tolyl)ethyne (**1j**, Aldrich), 1-pentyne (**1k**, Wako), and 4-methylpent-1-yne (**1l**, Aldrich)] were distilled at reduced pressure prior to use. (4-ethoxycarbonylphenyl)ethyne (**1h**) and (4-Acetylphenyl)ethyne (**1i**)[2] was prepared by Sonogashira coupling reaction between the corresponding iodo-compounds and 1-trimethylsilylethyne. Aldehydes **6**, [*p*-chlorobenzaldehyde (**6a**, Nacalai), bnezaldehyde (**6b**, Wako), *p*-bromobenzaldehyde (**6c**, Aldrich), *p*-nitrobenzaldehyde (**6d**, Aldrich), and enanthaldehyde (**6e**, Nacalai)] were distilled at reduced pressure prior to use. Titanium(IV) chloride (Wako) was used as receiver from commercial sources. 1,4-Disubstituted 1-sulfonyl-1,2,3-triazoles **3a**–**r** were prepared according to the literature procedure.[3] The analytical data of compounds **3a,**[3] **3g**,[4] **3h**,[5] **3k**,[6] **3m**,[7] **3n,**[3] **3o**,[3] **3p**,[3] **3q,**[8] and **3r**[9] have been already reported.

Typical procedure for the synthesis of 1-sulfonyl-1,2,3-triazole: To a solution of CuTC (95.2 mg, 0.5 mmol, 10 mol %) in toluene (10 mL) was added a solution of **1j** (600.2 mg, 5.2 mmol, 1.0 equiv) in toluene (5 mL) and tosyl azide (982.1 mg, 5.0 mmol, 1.0 equiv) in toluene (5 mL). After 15 h, the reaction mixture was diluted with saturated NH_4Cl aq (20 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organic phase was washed with brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 5:1), then reprecipitation (hexane/dichloromethane = 20:1) at –20 °C to give **3j** (1.01 g, 3.3 mmol, 65%) as a white powder.

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8 E. J. Yoo, M. Ahlquist, S. H. Kim, I. Bae, V. V. Fokin, K. B. Sharpless, S. Chang, *Angew. Chem. Int. Ed.* **2007**, *46*, 1730.

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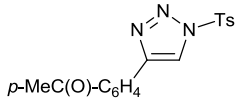
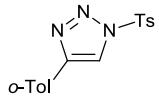
3i:



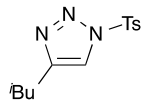
IR (ATR): 1680, 1394, 1190, 1169, 989 cm^{-1}; ^{1}H NMR: δ = 2.45 (s, 3H), 2.62 (s, 3H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 2H), 8.42 (s, 1H); ^{13}C NMR: δ = 21.8, 26.7, 119.9, 126.0, 128.7, 129.0, 130.5, 132.7, 133.2, 137.1, 146.1, 147.6, 197.4; HRMS (ESI^{+}): Calcd for $C_{17}H_{16}N_3O_3S$, $M+H^{+}$ 342.0907. Found m/z 342.0902.

3j:



IR (ATR): 1591, 1389, 1348, 1196, 1173, 986 cm^{-1}; ^{1}H NMR: δ = 2.448 (s, 3H), 2.453 (s, 3H), 7.23–7.33 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.73–7.77 (m, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 8.21 (s, 1H); ^{13}C NMR: δ = 21.3, 21.8, 120.8, 126.2, 128.1, 128.7, 128.9, 129.0, 130.4, 131.0, 133.0, 135.8, 146.6, 147.3; HRMS (ESI^{+}): Calcd for $C_{16}H_{16}N_3O_2S$, $M+H^{+}$ 314.0958. Found m/z 314.0950.

3l:

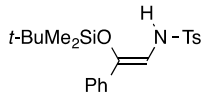


IR (ATR): 2957, 1595, 1387, 1192, 1175 cm^{-1}; ^{1}H NMR: δ = 0.89 (d, *J* = 6.8 Hz, 6H), 1.88–2.01 (m, 1H), 2.43 (s, 3H), 2.56 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.84 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ = 21.8, 22.1, 28.3, 34.3, 120.8, 128.5, 130.3, 133.2, 147.0, 147.1; HRMS (ESI^{+}): Calcd for $C_{13}H_{18}N_3O_2S$, $M+H^{+}$ 280.1114. Found m/z 280.1110.

Typical procedure for the one-pot reaction of terminal alkynes with silanol [Table 1, left column]: Phenylethyne **1a** (41.7 mg, 0.4 mmol), TsN_3 **2a** (79.4 mg, 0.4 mmol), CuTC (7.6 mg, 40 μmol), and $CHCl_3$ (2 mL) were added to an oven-dried 2–5 mL Biotage® microwave vial equipped with a stir bar. The vial was sealed with a cap containing an inner Teflon film. The reaction mixture was stirred at room temperature for 6 h. Then, the vial was taken inside the glove box. To the resulting mixtures were added silanol **4** (84.3 mg, 0.6 mmol), $Rh_2(OCOC_7H_{15})_4$ (3.2 mg, 4 μmol), 4 A MS (40 mg), and $CHCl_3$ (3 mL). The reaction mixture was heated to 100 °C for 15 min under microwave irradiation. After the reaction mixture was cooled and passed through a cotton stopper with $CHCl_3$, the filtrate was concentrated under reduced pressure. The residue was purified by gel permeation chromatography (GPC) to give the product **5a** as a white solid (121.6 mg, 0.3 mmol, 76%).

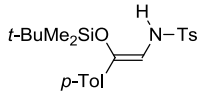
Typical procedure for the synthesis of silyl enol ethers [Table 2]: In a nitrogen-filled glove-box, $Rh_2(OCOC_7H_{15})_4$ (0.8 mg, 1 μmol), **3a** (61.0 mg, 0.20 mmol), 4 A MS (20 mg), silanol **4** (40.1 mg, 0.30 mmol), and $CHCl_3$ (4 mL) were added to an oven-dried 2-5 mL Biotage® microwave vial. The vial was sealed with a cap containing an inner Teflon film. The reaction mixture was heated to 100 °C for 15 min under microwave irradiation. After the reaction mixture was cooled and passed through a cotton stopper with $CHCl_3$, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography ($CHCl_3$) to give the product **5a** as a white solid (78.8 mg, 0.195 mmol, 96%).

5a:



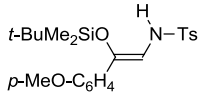
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3371, 2930, 1335, 1153 cm^{-1}; ^1H NMR: δ = –0.15 (s, 6H), 0.93 (s, 9H), 2.41 (s, 3H), 6.12 (d, *J* = 10.4 Hz, 1H), 6.21 (d, *J* = 10.8 Hz, 1H), 7.22–7.32 (m, 7H), 7.76 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ = –4.3, 18.2, 21.5, 25.7, 107.5, 125.3, 126.8, 127.8, 128.2, 129.8, 136.4, 137.0, 138.4, 143.7; HRMS (ESI^+): Calcd for $C_{21}H_{30}NO_3SSi$, $M+H^+$ 404.1710. Found m/z 404.1700.

5b:



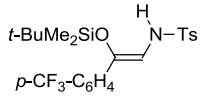
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3375, 2953, 1335, 1155 cm^{-1}; ^1H NMR: δ = –0.14 (s, 6H), 0.94 (s, 9H), 2.32 (s, 3H), 2.41 (s, 3H), 6.08 (d, *J* = 10.8 Hz, 1H), 6.21 (d, *J* = 10.8 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ = –4.3, 18.2, 21.1, 21.5, 25.7, 106.9, 125.3, 126.8, 128.8, 129.7, 133.5, 137.0, 137.7, 138.6, 143.6; HRMS (ESI^+): Calcd for $C_{22}H_{32}NO_3SSi$, $M+H^+$ 418.1867. Found m/z 418.1854.

5c:



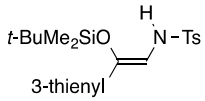
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3285, 2930, 1601, 1248, 1155 cm^{-1}; ^1H NMR: δ = –0.16 (s, 6H), 0.92 (s, 9H), 2.41 (s, 3H), 3.79 (s, 3H), 5.99 (d, *J* = 10.4 Hz, 1H), 6.14 (d, *J* = 10.8 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR: δ = –4.3, 18.1, 21.4, 25.7, 55.2, 106.2, 113.5, 126.7, 126.8, 128.8, 129.7, 136.9, 138.6, 143.6, 159.4; HRMS (ESI^+): Calcd for $C_{22}H_{32}NO_4SSi$, $M+H^+$ 434.1816. Found m/z 434.1821.

5d (reaction time, 20 h)**:**



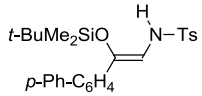
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3306, 2930, 1614, 1321, 1157 cm^{-1}; ^1H NMR: δ = –0.12 (s, 6H), 0.95 (s, 9H), 2.41 (s, 3H), 6.26 (d, *J* = 10.4 Hz, 1H), 6.30 (d, *J* = 10.8 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR: δ = –4.2, 18.2, 21.5, 25.7, 109.5, 124.0 (q, *J* = 270.1 Hz), 125.0, 125.3 (q, *J* = 3.7 Hz), 126.8, 129.5 (q, *J* = 32.2 Hz), 129.9, 136.4, 136.9, 140.0, 144.0; HRMS (ESI^-): Calcd for $C_{22}H_{27}F_3NO_4SSi$, $M–H^-$ 470.1438. Found m/z 470.1428.

5e:



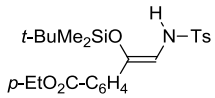
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3292, 2928, 1663, 1331, 1153 cm^{-1}; ^1H NMR: δ = –0.09 (s, 6H), 0.94 (s, 9H), 2.41 (s, 3H), 6.12 (d, *J* = 10.4 Hz, 1H), 6.17 (d, *J* = 10.8 Hz, 1H), 7.01 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.11 (dd, *J* = 2.4, 1.2 Hz, 1H), 7.23 (dd, *J* = 5.2, 2.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ = –4.3, 18.2, 21.5, 25.7, 107.1, 120.5, 125.0, 125.8, 126.7, 129.7, 134.5, 136.9, 137.8, 143.7; HRMS ($APCI^+$): Calcd for $C_{19}H_{28}NO_3S_2Si$, $M+H^+$ 410.1274. Found m/z 410.1268.

5g:



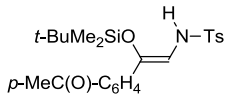
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3381, 2930, 1659, 1335, 1155 cm^{-1}; ^1H NMR: δ = –0.07 (s, 6H), 0.98 (s, 9H), 2.42 (s, 3H), 6.23 (d, *J* = 10.8 Hz, 1H), 6.30 (d, *J* = 10.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.34-7.38 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ = –4.2, 18.2, 21.5, 25.7, 107.6, 125.6, 126.7, 126.79, 126.80, 127.4, 128.7, 129.8, 135.2, 136.9, 137.9, 140.3, 140.5, 143.7; HRMS (ESI^+): Calcd for $C_{27}H_{34}NO_3SSi$, $M+H^+$ 480.2023. Found m/z 480.2031.

5h:



Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3277, 2932, 1713, 1339, 1273, 1151 cm^{-1}; ^1H NMR: δ = –0.13 (s, 6H), 0.94 (s, 9H), 1.37 (t, *J* = 7.2 Hz, 3H), 2.40 (s, 3H), 4.35 (q, *J* = 7.2 Hz, 2H), 6.28 (d, *J* = 10.8 Hz, 1H), 6.32 (d, *J* = 10.8 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ = –4.2, 14.3, 18.1, 21.5, 25.7, 60.9, 109.4, 124.6, 126.7, 129.4, 129.5, 129.8, 136.8, 136.9, 140.7, 143.9, 166.1; HRMS (ESI^+): Calcd for $C_{24}H_{34}NO_5SSi$, $M+H^+$ 476.1921. Found m/z 476.1930.

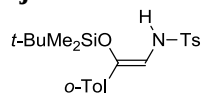
5i:



Purified by diol-silica gel column chromatography ($CHCl_3$); IR (ATR): 3290, 2930, 1680, 1601, 1339, 1256, 1157 cm^{-1}; ^1H NMR: δ = –0.13 (s, 6H), 0.95 (s, 9H), 2.41 (s, 3H), 2.58 (s, 3H), 6.32 (s, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR: δ = –4.2, 18.2, 21.5, 25.7, 26.5, 109.7, 124.7, 126.7, 128.4, 129.9, 136.0, 136.6, 136.8, 141.0, 144.0, 197.3; HRMS (ESI^+):

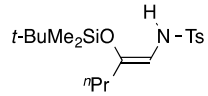
Calcd for $C_{23}H_{32}NO_4SSi$, $M+H^+$ 446.1816. Found m/z 446.1807.

5j:



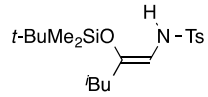
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3344, 2928, 1661, 1595, 1333, 1163 cm^{-1}; ^1H NMR: δ = –0.35 (s, 6H), 0.85 (s, 9H), 2.15 (s, 3H), 2.43 (s, 3H), 5.74 (d, *J* = 10.8 Hz, 1H), 6.21 (d, *J* = 10.8 Hz, 1H), 7.08–7.14 (m, 3H), 7.18–7.23 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ = –5.0, 18.0, 19.7, 21.5, 25.5, 108.5, 125.5, 126.9, 128.6, 129.2, 129.6, 130.2, 135.5, 136.7, 137.1, 139.7, 143.6; HRMS (ESI^+): Calcd for $C_{22}H_{32}NO_3SSi$, $M+H^+$ 418.1867. Found m/z 418.1861.

5k:



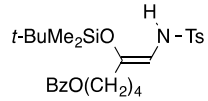
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3364, 2930, 1684, 1339, 1165 cm^{-1}; ^1H NMR: δ = –0.04 (s, 6H), 0.81 (t, *J* = 7.6 Hz, 3H), 0.85 (s, 9H), 1.38 (sext, *J* = 7.2 Hz, 2H), 1.91 (t, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 5.48 (d, *J* = 10.4 Hz, 1H), 5.89 (d, *J* = 10.4 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ = –4.3, 13.3, 18.1, 19.8, 21.5, 25.6, 35.5, 104.7, 126.8, 129.5, 136.8, 140.5, 143.4; HRMS (ESI^+): Calcd for $C_{18}H_{32}NO_3SSi$, $M+H^+$ 370.1867. Found m/z 370.1860.

5l:



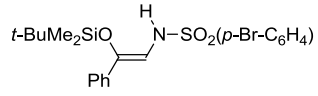
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3356, 2955, 1342, 1165, 781 cm^{-1}; ^1H NMR: δ = –0.05 (s, 6H), 0.76 (d, *J* = 6.4 Hz, 6H), 0.85 (s, 9H), 1.61–1.73 (m, 1H), 1.76 (d, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 5.48 (d, *J* = 10.4 Hz, 1H), 5.89 (d, *J* = 10.4 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ = –4.3, 18.1, 21.5, 22.0, 25.4, 25.6, 42.9, 105.6, 126.9, 129.5, 136.6, 139.7, 143.5; HRMS (ESI^+): Calcd for $C_{19}H_{34}NO_3SSi$, $M+H^+$ 384.2023. Found m/z 384.2024.

5m:



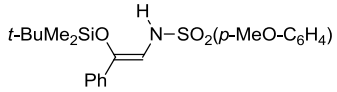
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3285, 2955, 1717, 1273, 1165 cm^{-1}; ^1H NMR: δ = –0.04 (s, 6H), 0.85 (s, 9H), 1.49–1.57 (m, 2H), 1.60–1.70 (m, 2H), 2.01 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 4.26 (t, *J* = 6.4 Hz, 2H), 5.53 (d, *J* = 10.4 Hz, 1H), 5.91 (d, *J* = 10.8 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR: δ = –4.3, 18.1, 21.5, 23.0, 25.6, 27.8, 33.1, 64.5, 105.1, 126.8, 128.3, 129.5, 129.6, 130.2, 132.9, 136.6, 139.9, 143.5, 166.6; HRMS (ESI^+): Calcd for $C_{26}H_{38}NO_5SSi$, $M+H^+$ 504.2234. Found m/z 504.2234.

5f:



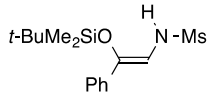
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3341, 2928, 1333, 1169, 1067 cm^{-1}; ^1H NMR: δ = –0.13 (s, 6H), 0.94 (s, 9H), 6.10 (d, *J* = 10.8 Hz, 1H), 6.27 (d, *J* = 10.4 Hz, 1H), 7.26-7.33 (m, 5H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ = –4.3, 18.2, 25.7, 106.9, 125.4, 127.9, 128.1, 128.2, 128.3, 132.4, 136.1, 138.8, 139.2; HRMS (ESI^+): Calcd for $C_{20}H_{27}BrNO_3SSi$, $M+H^+$ 468.0659. Found m/z 468.0670.

5n:



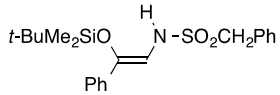
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3302, 2928, 1661, 1595, 1335, 1258, 1151 cm^{-1}; ^1H NMR: δ = –0.14 (s, 6H), 0.94 (s, 9H), 3.84 (s, 3H), 6.12 (d, *J* = 10.4 Hz, 1H), 6.22 (d, *J* = 10.8 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.23–7.32 (m, 5H), 7.81 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR: δ = –4.3, 18.2, 25.7, 55.6, 107.6, 114.3, 125.3, 127.8, 128.2, 128.9, 131.5, 136.3, 138.3, 163.0; HRMS (ESI^+): Calcd for $C_{21}H_{30}NO_4SSi$, $M+H^+$ 420.1659. Found m/z 420.1657.

5o:



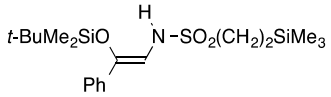
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3310, 2930, 1659, 1331, 1148 cm^{-1}; ^1H NMR: δ = 0.00 (s, 6H), 1.01 (s, 9H), 3.04 (s, 3H), 6.13 (s, 2H), 7.25–7.40 (m, 5H); ^{13}C NMR: δ = –4.0, 18.2, 25.8, 40.6, 107.4, 125.2, 128.0, 128.3, 136.2, 138.3; HRMS (ESI^+): Calcd for $C_{15}H_{26}NO_3SSi$, $M+H^+$ 328.1397. Found m/z 328.1395.

5p:



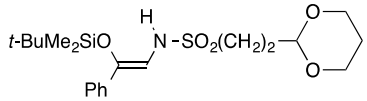
Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3346, 3287, 2930, 1661, 1323, 1146 cm^{-1}; ^1H NMR: δ = –0.06 (s, 6H), 0.88 (s, 9H), 4.31 (s, 2H), 6.00 (d, *J* = 11.2 Hz, 1H), 6.10 (d, *J* = 10.8 Hz, 1H), 7.27-7.43 (m, 10H); ^{13}C NMR: δ = –4.1, 18.1, 25.6, 58.4, 107.9, 125.1, 127.9, 128.3, 128.6, 128.8, 129.0, 130.7, 136.3, 137.7; HRMS (ESI^+): Calcd for $C_{21}H_{30}NO_3SSi$, $M+H^+$ 404.1710. Found m/z 404.1702.

5q:



Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3285, 2951, 1661, 1327, 1252, 1142 cm^{-1}; ^1H NMR: δ = 0.00 (s, 6H), 0.04 (s, 9H), 1.02 (s, 9H), 1.04-1.09 (m, 2H), 2.98-3.04 (m, 2H), 6.10 (s, 2H), 7.24-7.38 (m, 5H); ^{13}C NMR: δ = –4.0, –2.1, 10.6, 18.2, 25.7, 49.0, 108.0, 125.2, 127.9, 128.3, 136.3, 138.0; HRMS (ESI^+): Calcd for $C_{19}H_{36}NO_3SSi_2$, $M+H^+$ 414.1949. Found m/z 414.1954.

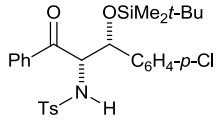
5r:



Purified by silica gel column chromatography ($CHCl_3$); IR (ATR): 3298, 2930, 2856, 1664, 1331, 1142 cm^{-1}; ^1H NMR: δ = 0.00 (s, 6H), 1.00 (s, 9H), 1.28‑1.37 (m, 1H), 1.95–2.15 (m, 3H) 3.23-3.30 (m, 2H), 3.74 (dt, *J* = 12.2, 2.4 Hz, 2H), 4.03‑4.10 (m, 2H) 4.69 (t, *J* = 4.4 Hz, 1H), 6.10 (d, *J* = 10.4 Hz, 1H), 6.14 (d, *J* = 10.4 Hz, 1H), 7.25-7.39 (m, 5H); ^{13}C NMR: δ = –4.0, 18.2, 25.4, 25.8, 29.2, 47.9, 66.7, 99.1, 107.7, 125.1, 127.7, 128.2, 136.3, 137.5; HRMS (ESI^+): Calcd for $C_{20}H_{34}NO_5SSi$, $M+H^+$ 428.1921. Found m/z 428.1917.

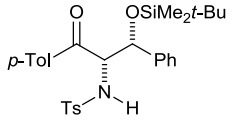
Typical procedure for the Mukaiyama-aldol reaction of silyl enol ether with aldehydes (Table 1, right column): Aldehyde **6a** (39.9 mg, 0.28 mmol), silyl enol ether **5a** (99.2 mg, 0.25 mmol), and dry CH_2Cl_2 (8 mL) were added to an oven-dried two-necked round bottom flask equipped with a stir bar. The reaction mixture was cooled to –78 °C. Then, $TiCl_4$ (31 μL, 0.28 mmol) was added dropwise via syringe. The resulting mixture was stirred at –78 °C for 13 h, and quenched with water (1 mL). The aqueous layer was repeatedly extracted with dichloromethane. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography ($CHCl_3$) to give the product **7aa** as a white solid (119.7 mg, 0.22 mmol, 88%).

7aa (reaction time, 13 h)**:**



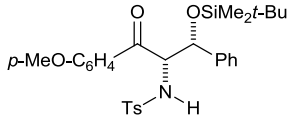
Purified by preparative thin-layer chromatography ($CHCl_3$); IR (ATR): 3290, 2928, 1692, 1340, 1165, 1084 cm^{-1}; ^1H NMR: δ = –0.35 (s, 3H), –0.29 (s, 3H), 0.75 (s, 9H), 2.30 (s, 3H), 4.94 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.04 (d, *J* = 2.8 Hz, 1H), 5.69 (d, *J* = 9.6Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.13-7.21 (m, 4H), 7.44–7.51 (m, 4H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ = –5.6, –4.9, 17.9, 21.4, 25.5, 63.4, 74.8, 126.8, 127.9, 128.2, 128.6, 128.8, 129.4, 133.8, 133.9, 134.7, 136.7, 138.3, 143.3, 195.2; HRMS (ESI^+): Calcd for $C_{28}H_{35}ClNO_4SSi$, $M+H^+$ 544.1739. Found m/z 544.1736.

7bb (reaction time, 18 h)**:**



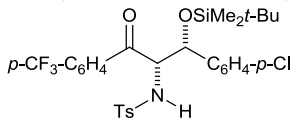
Purified by preparative thin-layer chromatography (hexane/ethyl acetate 4:1 then $CHCl_3$); IR (ATR): 3285, 2926, 1692, 1333, 1161, 1096 cm^{-1}; ^1H NMR: δ = –0.33 (s, 3H), –0.26 (s, 3H), 0.77 (s, 9H), 2.26 (s, 3H), 2.43 (s, 3H), 4.95 (dd, *J* = 9.8, 2.2 Hz, 1H), 5.04 (s, 1H), 5.67 (d, *J* = 9.2Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.22-7.30 (m, 7H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR(150 MHz): δ = –5.5, –4.9, 18.0, 21.3, 21.7, 25.6, 63.5, 75.5, 126.6, 126.8, 127.9, 128.0, 128.7, 129.316, 129.324, 132.3, 136.9, 139.8, 143.0, 144.7, 194.9; HRMS (ESI^+): Calcd for $C_{29}H_{38}NO_4SSi$, $M+H^+$ 524.2285. Found m/z 524.2272.

7cb (reaction time, 18 h)**:**



Purified by preparative thin-layer chromatography (hexane/ethyl acetate 4:1 then $CHCl_3$); IR (ATR): 3236, 2928, 1674, 1593, 1165, 1067 cm^{-1}; ^1H NMR: δ = –0.31 (s, 3H), –0.24 (s, 3H), 0.78 (s, 9H), 2.26 (s, 3H), 3.88 (s, 3H), 4.92 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.05 (d, *J* = 2.8 Hz, 1H), 5.71 (d, *J* = 9.6Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.22-7.30 (m, 5H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR(150 MHz): δ = –5.5, –4.9, 18.0, 21.3, 25.6, 55.5, 63.2, 75.8, 113.8, 126.6, 126.8, 127.7, 127.92, 127.94, 129.3, 130.9, 136.9, 139.9, 143.0, 163.9, 193.7; HRMS (ESI^+): Calcd for $C_{29}H_{38}NO_5SSi$, $M+H^+$ 540.2234. Found m/z 540.2222.

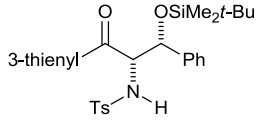
7da (reaction time, 65 h)**:**



Purified by preparative thin-layer chromatography (hexane/ethyl acetate 4:1) then GPC($CHCl_3$); IR (ATR): 3302, 2953, 1707, 1315, 1153, 1067 cm^{-1}; ^1H NMR: δ = –0.33 (s, 3H), –0.25 (s, 3H), 0.74 (s, 9H), 2.31 (s, 3H), 4.94 (dd, *J* = 9.4, 3.4 Hz, 1H), 5.01 (d, *J* = 3.2 Hz, 1H), 5.62 (d, *J* = 9.6Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR(150 MHz): δ = –5.4, –4.9, 17.9, 21.4, 25.5, 63.6, 74.8, 123.3 (q, *J* = 270.7 Hz),

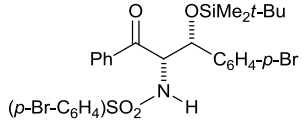
125.7 (q, *J* = 3.6 Hz) 126.8, 127.9, 128.3, 128.9, 129.5, 134.1, 134.9 (q, *J* = 32.3 Hz), 136.5, 137.7, 137.8, 143.6; HRMS (ESI$^+$): Calcd for $C_{29}H_{34}NO_4SSiF_3Cl$, M+H$^+$ 612.1613. Found m/z 612.1599.

7eb (reaction time, 18 h)**:**



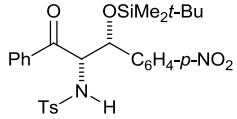
Purified by preparative thin-layer chromatography (hexane/ethyl acetate 3:1 then $CHCl_3$); IR (ATR): 3265, 2926, 1682, 1339, 1165, 1094 cm^{-1}; ^{1}H NMR: δ = –0.29 (s, 3H), –0.20 (s, 3H), 0.78 (s, 9H), 2.28 (s, 3H), 4.71 (dd, *J* = 9.2, 3.2 Hz, 1H), 5.08 (d, *J* = 3.2 Hz, 1H), 5.63 (d, *J* = 9.6Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.24 (s, 5H), 7.30 (dd, *J* = 4.8, 3.2 Hz, 1H), 7.40 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 8.02 (dd, *J* = 2.8, 1.2 Hz, 1H); ^{13}C NMR: δ = –5.5, –4.9, 18.0, 21.4, 25.6, 65.2, 75.7, 126.5, 126.6, 126.9, 127.0, 128.01, 128.04, 129.3, 133.3, 136.7, 139.6, 139.7, 143.1, 189.6; HRMS (ESI$^+$): Calcd for $C_{26}H_{34}NO_4S_2Si$, M+H$^+$ 516.1693. Found m/z 516.1683.

7fc (reaction time, 18 h)**:**



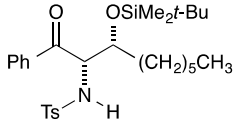
Purified by preparative thin-layer chromatography (dichloromethane/hexane 20:1 then 7:1); IR (ATR): 3292, 2926, 1690, 1342, 1167, 1084 cm^{-1}; ^{1}H NMR: δ = –0.35 (s, 3H), –0.31 (s, 3H), 0.76 (s, 9H), 4.95 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.05 (d, *J* = 2.4 Hz, 1H), 5.75 (d, *J* = 9.6 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.41 (s, 4H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR: δ = –5.6, –4.9, 17.9, 25.5, 63.7, 74.7, 122.2, 127.5, 128.2, 128.3, 128.6, 128.9, 131.2, 132.0, 134.1, 134.3, 138.8, 138.9, 194.8; HRMS (ESI$^+$): Calcd for $C_{27}H_{35}Br_2N_2O_4SSi$, M+$NH_4^+$ 669.0448. Found m/z 669.0435.

7ad (reaction time, 13 h)**:**



Purified by preparative thin-layer chromatography ($CHCl_3$); IR (ATR): 3275, 2928, 1697, 1528, 1340, 1165 cm^{-1}; ^{1}H NMR: δ = –0.36 (s, 3H), –0.31 (s, 3H), 0.76 (s, 9H), 2.25 (s, 3H), 4.99 (dd, *J* = 9.4, 2.4 Hz, 1H), 5.18 (d, *J* = 2.8 Hz, 1H), 5.77 (d, *J* = 9.2 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 7.42-7.52 (m, 6H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 8.08 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR: δ = –5.7, –4.9, 17.9, 21.3, 25.5, 63.2, 74.7, 123.2, 126.7, 127.5, 128.6, 128.9, 129.4, 134.17, 134.18, 136.5, 143.6, 147.2, 147.5, 194.5; HRMS (ESI$^+$): Calcd for $C_{28}H_{35}N_2O_6SSi$, M+H$^+$ 555.1980. Found m/z 555.1974.

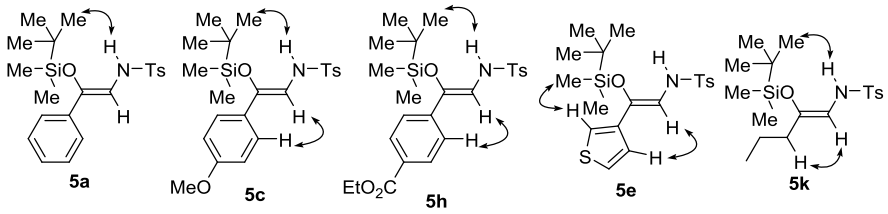
7ae (reaction time, 19 h)**:**



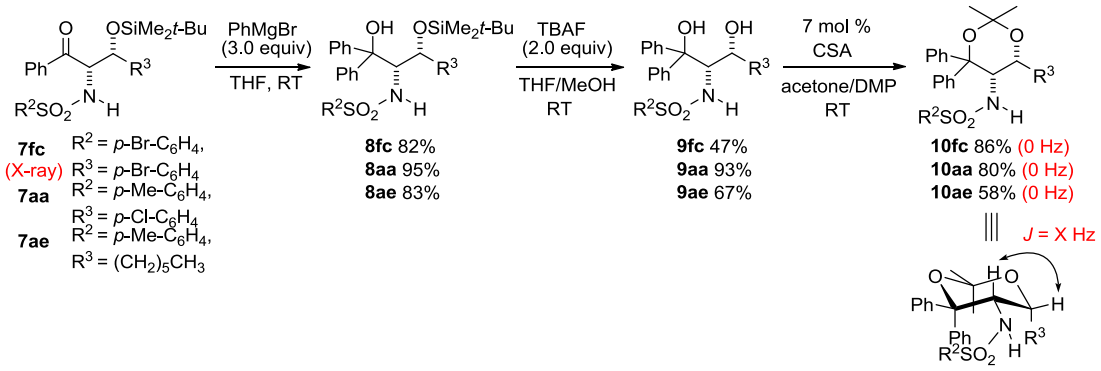
Purified by preparative thin-layer chromatography ($CHCl_3$); IR (ATR): 3287, 2926, 1697, 1333, 1163, 1080 cm^{-1}; ^{1}H NMR: δ = –0.36 (s, 3H), –0.16 (s, 3H), 0.76 (s, 9H), 0.91 (t, *J* = 3.2 Hz, 3H), 1.24-1.48 (m, 9H), 1.85-1.96 (m, 1H), 2.28 (s, 3H), 3.91-3.96 (m, 1H), 4.91 (d, *J* = 9.8 Hz, 1H), 5.63 (d, *J* = 10.0 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR: δ = –5.1, –4.5, 14.0, 17.8, 21.4, 22.6, 25.3, 25.6, 29.3, 31.7, 34.5, 60.3, 73.4, 127.0, 128.2, 128.7, 129.4, 133.6, 134.2, 137.0, 143.2, 195.4; HRMS (ESI$^+$): Calcd for $C_{28}H_{44}NO_4SSi$, M+H$^+$ 518.2755. Found m/z 518.2753.

Determination of Stereochemistries

The (*Z*)-stereochemistries of the silyl enol ethers (**5a**, **5c**, **5h**, **5e**, and **5k**) were determined by NOE experiments. Curved arrows shown below indicate the observed NOE. Other silyl enol ethers **5** were determined by analogy.

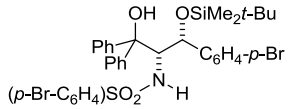


The relative stereochemistry of the aldol product **7fc** was unambiguously determined as *syn* by a single-crystal X-ray analysis. Other aldol products **7** were determined by NMR studies of its derivative.



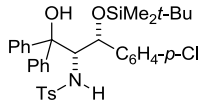
Typical procedure for the addition reaction of PhMgBr onto the aldol products 7: PhMgBr (0.3M in THF, 2.5 mL) and dry THF (3 mL) were added to an oven-dried two-necked round bottom flask equipped with a stir bar. The reaction mixture was cooled to 0 °C. Then, a solution of **7fc** (143.2 mg, 0.22 mmol) in THF (5 mL) was added dropwise via syringe. The resulting mixture was stirred at room temperature for 3 h, and quenched with sat. NH_4Cl (8 mL). The aqueous layer was repeatedly extracted with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate 5:1) to give the product **8fc** (130.8 mg, 0.18 mmol, 82%).

8fc:



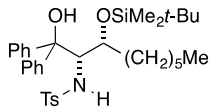
Purified by preparative thin-layer chromatography (hexane/ethyl acetate 5:1); IR (ATR): 3443, 2932, 2856, 1576, 1487, 1339, 1157, 1065 cm^{-1}; ^1H NMR (600 MHz): δ = –0.50 (s, 3H), –0.46 (s, 3H), 0.91 (s, 9H), 4.64 (dd, *J* = 9.3, 1.5 Hz, 1H), 4.70 (s, 1H), 5.31 (s, 1H), 5.47 (d, *J* = 9.6 Hz, 1H), 6.97–7.03 (m, 5H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.23–7.30 (m, 3H), 7.37 (d, *J* = 6.6 Hz, 2H), 7.38–7.43 (m, 4H), 7.70 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz): δ = –6.0, –3.8, 17.8, 25.8, 65.3, 75.2, 81.2, 122.3, 125.2, 125.6, 126.1, 126.8, 127.3, 127.4, 128.0, 128.70, 128.72, 131.1, 131.7, 139.4, 140.9, 143.4, 145.1; HRMS (APCI$^-$): Calcd for $C_{33}H_{36}Br_2NO_4SSi$, M-H$^-$ 728.0507. Found m/z 728.0522.

8aa:



Purified by silica gel column chromatography (hexane/ethyl acetate 3:1); IR (ATR): 3447, 2928, 1597, 1491, 1333, 1155 cm^{-1}; ^1H NMR: δ = –0.51 (s, 3H), –0.44 (s, 3H), 0.93 (s, 9H), 2.35 (s, 3H), 4.70 (dd, *J* = 9.0, 1.4 Hz, 1H), 4.79 (s, 1H), 5.33 (s, 1H), 5.46 (d, *J* = 9.2 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.98–7.18 (m, 9H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.51 (d, *J* =8.2 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR: δ = –6.1, –4.0, 17.7, 21.2, 25.8, 65.1, 75.0, 81.3, 125.4, 125.65, 125.71, 126.6, 127.2, 127.7, 127.9, 128.3, 128.6, 129.0, 133.6, 138.9, 139.0, 141.7, 143.3, 145.2; HRMS (ESI$^+$): Calcd for $C_{34}H_{40}ClNO_4SSiNa$, M+Na$^+$ 644.2028. Found m/z 644.2022.

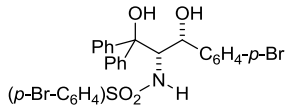
8ae:



Purified by preparative thin-layer chromatography (hexane/ethyl acetate 7:1); IR (ATR): 3437, 3306, 2924, 1431, 1321, 1157 cm^{-1}; ^1H NMR: δ = –0.08 (s, 3H), 0.03 (s, 3H), 0.89–1.00 (m, 12H), 1.18–1.42 (m, 8H), 1.58-1.70 (m, 1H), 1.88-2.00 (m, 1H), 2.33 (s, 3H), 4.11 (dd, *J* = 11.2, 4.0 Hz, 1H), 4.75 (s, 1H), 4.83 (d, *J* = 9.2 Hz, 1H), 5.10 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 7.02–7.14 (m, 3H), 7.18–7.26 (m, 3H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR: δ = -4.5, -3.3, 14.0, 17.9, 21.2, 22.6, 25.1, 25.9, 29.1, 31.7, 34.4, 59.7, 74.4, 81.3, 125.2, 125.3, 126.2, 126.3, 126.8, 127.9, 128.3, 129.0, 139.0, 142.0, 144.5, 145.9; HRMS (ESI$^-$): Calcd for $C_{34}H_{48}NO_4SSi$, M-H$^-$ 594.3079. Found m/z 594.3081.

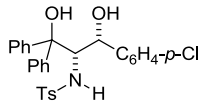
Typical procedure for the deprotection of *t*-butyldimethylsilyl group: Alcohol **8fc** (142.0 mg, 0.194 mmol), dry THF (6 mL), and dry MeOH (2 mL) were added to an oven-dried two-necked round bottom flask equipped with a stir bar. Then, TBAF solution (0.1 M in THF, 0.7 mL) was added dropwise via syringe. The resulting mixture was stirred at room temperature for 9 h, and diluted with water (8 mL). The aqueous layer was repeatedly extracted with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (chloroform/ethyl acetate/acetic acid 10:1:0.1) to give the product **9fc** (55.7 mg, 0.09 mmol, 47%).

9fc:



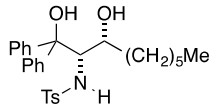
Purified by preparative thin-layer chromatography (chloroform/ethyl acetate/acetic acid 10:1:0.1); IR (ATR): 3360, 3024, 1576, 1448, 1327, 1153, 1067 cm^{-1}; ^1H NMR: δ = 3.18 (s, 1H), 4.746 (d, *J* = 8.8 Hz, 1H), 4.753 (s, 1H), 5.02 (s, 1H), 5.68 (d, *J* = 9.2 Hz, 1H), 6.94 (dt, *J* = 8.4, 2.8 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 7.06–7.15 (m, 3H), 7.21–7.32 (m, 5H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.47–7.54 (m, 2H), 7.67 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR: δ = 64.8, 72.8, 82.1, 121.9, 125.1, 125.5, 126.2, 127.14, 127.15, 127.3, 127.4, 128.1, 128.9, 131.3, 131.6, 139.4, 140.8, 143.1, 144.8; HRMS (APCI$^-$): Calcd for $C_{27}H_{22}Br_2NO_4S$, M-H$^-$ 613.9642. Found m/z 613.9649.

9aa:



Purified by GPC; IR (ATR): 3366, 3026, 1597, 1491, 1448, 1323, 1151 cm^{-1}; ^1H NMR: δ = 2.36 (s, 3H), 3.44 (d, *J* = 2.4 Hz, 1H), 4.72 (d, *J* = 8.8 Hz, 1H), 4.86 (s, 1H), 4.98 (d, *J* = 1.6 Hz, 1H), 5.56 (d, *J* = 9.2 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.4Hz, 2H), 6.98–7.17 (m, 7H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.55 (d, *J* =7.2 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR: δ = 21.3, 64.6, 72.6, 82.2, 125.2, 125.6, 125.7, 126.9, 127.0, 127.3, 127.9, 128.1, 128.8, 128.9, 133.3, 138.8, 139.0, 142.0, 143.1, 144.9; HRMS (ESI$^-$): Calcd for $C_{28}H_{25}ClNO_4S$, M-H$^-$ 506.1198. Found m/z 506.1200.

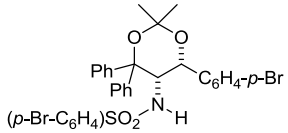
9ae:



Purified by preparative thin-layer chromatography (chloroform/ethyl acetate/acetic acid 10:1:0.1 then 10:1:0.05); IR (ATR): 3456, 3354, 2926, 1599, 1450, 1333, 1155 cm^{-1}; ^1H NMR: δ = 0.88 (t, *J* = 6.8 Hz, 3H), 1.14–1.40 (m, 8H), 1.48–1.72 (m, 2H), 2.33 (s, 3H), 2.61 (d, *J* = 5.2 Hz, 1H), 3.91–3.97 (m, 1H), 4.62 (d, *J* = 8.4 Hz, 1H), 4.74 (s, 1H), 5.51 (d, *J* = 8.8 Hz, 1H), 6.92–7.10 (m, 5H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR: δ = 14.0, 21.3, 22.6, 25.3, 29.0, 31.6, 35.0, 61.4, 72.4, 81.8, 125.1, 125.2, 126.3, 126.5, 127.0, 128.0, 128.5, 129.2, 138.5, 142.3, 144.1, 145.4; HRMS (ESI$^-$): Calcd for $C_{28}H_{34}NO_4S$, M-H$^-$ 480.2214. Found m/z 480.2219.

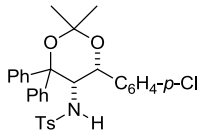
Typical procedure for the acetonide protection of 1,3-diol 9: 1,3-Diol **9fc** (142.0 mg, 0.194 mmol), 10-camphorsulfonic acid (CSA; 1.7 mg, 7.32 μmol), dry acetone (0.8 mL), and dry 2,2-dimethoxypropane (DMP; 0.2 mL) were added to an oven-dried two-necked round bottom flask equipped with a stir bar. The resulting mixture was stirred at room temperature for 6 h, and quenched with Et_3N (2 drops). Then, volatile materials were removed under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate 5:1) to give the product **10fc** (40.4 mg, 0.06 mmol, 86%).

10fc:



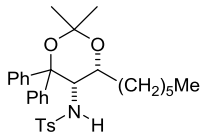
Purified by preparative thin-layer chromatography (hexane/ethyl acetate 5:1); IR (ATR): 3387, 2993, 1489, 1340, 1159, 1070 cm^{-1}; ^1H NMR: δ = 1.01 (s, 3H), 1.72 (s, 3H), 4.83 (d, *J* = 10.0 Hz, 1H), 4.89 (d, *J* = 9.6 Hz, 1H), 5.48 (s, 1H), 6.92 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.05–7.32 (m, 10H), 7.35 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (55 °C): δ = 24.2, 31.2, 57.6, 70.3, 81.9, 101.5, 122.0, 125.6, 126.2, 126.8, 127.2, 127.4, 127.6, 127.7, 127.9, 128.5, 131.3, 131.7, 137.4, 141.0, 144.1, 144.8; HRMS (APCI⁻): Calcd for $C_{30}H_{26}Br_2NO_4S$, M-H^- 653.9955. Found m/z 653.9967.

10aa:



Purified by preparative thin-layer chromatography (hexane/ethyl acetate 4:1); IR (ATR): 3391, 2989, 1599, 1491, 1339, 1155 cm^{-1}; ^1H NMR (C_6D_6): δ = 0.80 (s, 3H), 1.50 (s, 3H), 2.00 (s, 3H), 4.90 (d, *J* = 9.6 Hz, 1H), 5.02 (d, *J* = 9.6 Hz, 1H), 5.36 (s, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 6.94–7.20 (m, 12H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR: δ = 21.2, 24.2, 31.0, 57.5, 70.5, 82.4, 101.3, 126.3, 127.2, 127.6, 127.7, 127.9, 128.1, 128.4, 128.5, 128.6, 129.2, 133.7, 137.5, 140.4, 141.5, 144.9, 145.3; HRMS (ESI⁻): Calcd for $C_{31}H_{29}ClNO_4S$, M-H^- 546.1511. Found m/z 546.1524.

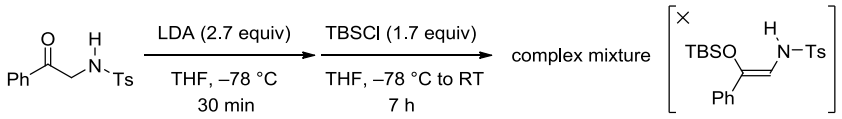
10ae:



Purified by preparative thin-layer chromatography (hexane/ethyl acetate 5:1); IR (ATR): 3287, 2926, 1429, 1327, 1157 cm^{-1}; ^1H NMR (600 MHz): δ = 0.91 (t, *J* = 6.6 Hz, 3H), 0.95 (s, 3H), 1.25–1.46 (m, 8H), 1.54–1.63 (m, 5H), 2.34 (s, 3H), 4.31 (dd, *J* = 7.2, 6.0 Hz, 1H), 4.57 (d, *J* = 9.6 Hz, 1H), 4.83 (d, *J* = 9.0 Hz, 1H), 6.93 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.97–7.02 (m, 4H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.18 (dt, *J* = 7.8, 1.2 Hz, 2H), 7.21 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz): δ = 14.0, 21.3, 22.6, 24.2, 25.1, 29.1, 31.1, 31.7, 32.4, 55.2, 69.7, 81.8, 100.9, 125.6, 126.2, 126.6, 127.2, 127.3, 128.2, 129.1, 139.1, 142.1, 144.9, 145.8; HRMS (ESI⁺): Calcd for $C_{31}H_{43}N_2O_4S$, M+NH_4^+ 539.2938. Found m/z 539.2924.

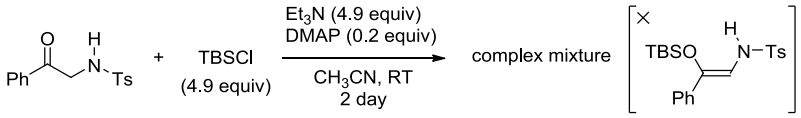
Experiments for the synthesis of the silyl enol ether from α-tosylamino acetophenone

i) Kinetic conditions using LDA as base according to the literature procedure.[4]



A solution of α-tosylamino acetophenone (62.1 mg, 0.215 mmol) in THF (1.0 mL) was added dropwise via syringe to a solution of LDA (0.39 M in THF, 1.5 mL) at –78°C. The resulting solution was further stirred for 30 min at –78°C, then a solution of *tert*-butyldimethylsilylchloride (55.2 mg, 0.366 mmol) in THF (1.0 mL) was added. The reaction mixture allowed to slowly warm to room temperature. After stirring for 7 h, the solution was filtrated through the patch of celite and removed under reduced pressure. The residue was checked by ^{1}H NMR, and a complex mixture was observed.

ii) Thermodynamic conditions using Et_3N as base according to the literature procedure.[5]

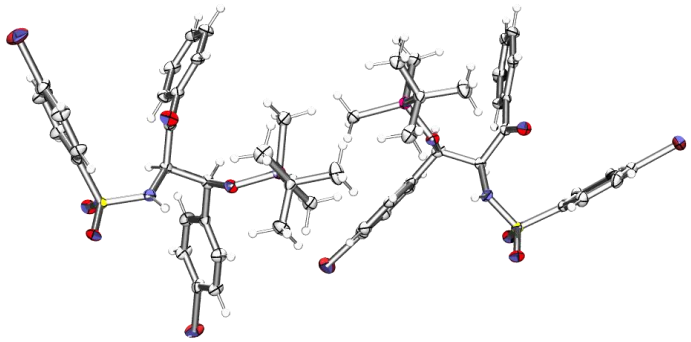


Et_3N (94.5 mg, 0.93 mmol) and DMAP (4.7 mg, 0.038 mmol) were added to a solution of α-tosylamino acetophenone (53.9 mg, 0.19 mmol) and *t*-butyldimethylsilylchloride (140.2 mg, 0.93 mmol) in dry acetonitrile (0.9 mL). The resulting solution was stirred at room temperature for 2 days. Then, volatile materials were removed under reduced pressure. The residue was checked by ^{1}H NMR, and a complex mixture was observed.

4 I. Fleming, I. Paterson, *Synthesis* **1979**, 736.
5 M. J. Crimmin, P. J. O' Hanlon, N. H. Rogers, F. M. Sime, G. Walker, *J. Chem. Soc. Perkin. Trans.1*. **1989**, 2059.

Detail of the Single-Crystal X-Ray Analysis (7fc).

The single crystal was mounted on a glass capillary. X-ray diffractions were collected on a Rigaku R-AXIS RAPID-F graphite-monochromated Mo Kα radiation diffractometer with imaging plate. A symmetry-related absorption correction was carried out by using the program ABSCOR.[1] The analysis was carried out with direct methods (SHELX-97[2] or SIR92[3]) using Yadokari-XG.[4] Details of crystal and data collection parameters are shown in ***Table S1–S5***.



ORTEP structure of **7fc**

Table S1. Crystal data and structure refinement.

Empirical formula	C27 H31 Br2 N O4 S Si	
Formula weight	653.50	
Temperature	296(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	p_21/a	
Unit cell dimensions	a = 18.9903(5) Å	α = 90°.
	b = 12.1460(3) Å	β = 108.1468(7)°.
	c = 26.2415(6) Å	γ = 90°.
Volume	5751.7(2) Å^3	
Z	8	
Density (calculated)	1.509 Mg/m^3	
Absorption coefficient	2.966 mm^{-1}	
F(000)	2656	
Crystal size	0.80 x 0.80 x 0.50 mm^3	
Theta range for data collection	3.12 to 27.49°.	
Index ranges	-24<=h<=24, -15<=k<=15, -33<=l<=28	
Reflections collected	53458	
Independent reflections	13126 [R(int) = 0.0794]	
Completeness to theta = 27.49°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3187 and 0.2001	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13126 / 0 / 659	
Goodness-of-fit on F^2	1.162	
Final R indices [I>2sigma(I)]	R1 = 0.0552, wR2 = 0.1320	
R indices (all data)	R1 = 0.0875, wR2 = 0.1860	
Largest diff. peak and hole	0.877 and -2.055 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-747(1)	5550(1)	3367(1)	34(1)

Br(2)	1508(1)	-1359(1)	-2123(1)	42(1)
Br(3)	617(1)	5544(1)	1673(1)	41(1)
Br(4)	3166(1)	-1479(1)	7142(1)	45(1)
S(5)	785(1)	1366(1)	5376(1)	19(1)
S(6)	407(1)	1365(1)	-426(1)	20(1)
Si(7)	1034(1)	-163(1)	3271(1)	21(1)
Si(8)	2626(1)	140(1)	1716(1)	21(1)
O(9)	505(2)	2499(2)	-518(1)	24(1)
O(17)	2029(2)	627(2)	1154(1)	20(1)
O(18)	918(2)	479(2)	3801(1)	21(1)
O(19)	1958(2)	-523(2)	4912(1)	27(1)
O(13)	-296(2)	955(2)	-418(1)	24(1)
O(14)	66(1)	1027(2)	5377(1)	22(1)
O(15)	1001(2)	2495(2)	5451(1)	24(1)
N(20)	984(2)	1043(3)	154(1)	20(1)
O(16)	1991(2)	-439(2)	28(1)	25(1)
C(83)	1165(2)	-550(4)	-1628(2)	29(1)
N(19)	850(2)	989(3)	4799(1)	20(1)
C(20)	1446(2)	597(3)	5876(1)	21(1)
C(21)	851(2)	3280(4)	1514(2)	27(1)
C(22)	1496(2)	1292(3)	4653(1)	18(1)
C(23)	4274(2)	192(4)	341(2)	25(1)
C(24)	2471(2)	-622(4)	6619(2)	30(1)
C(25)	2325(2)	-1328(3)	1727(2)	25(1)
C(26)	1029(2)	4329(4)	1407(2)	29(1)
C(27)	527(2)	-498(4)	-976(2)	26(1)
C(28)	3548(2)	-50(3)	298(1)	21(1)
C(29)	3008(2)	776(3)	172(1)	18(1)
C(30)	3324(2)	-76(3)	4706(1)	22(1)
C(31)	-428(2)	3268(4)	3419(2)	27(1)
C(32)	607(2)	4426(4)	3879(2)	28(1)
C(33)	-130(2)	4291(4)	3577(2)	26(1)
C(34)	1050(2)	1154(4)	-1216(2)	29(1)
C(35)	482(3)	-1461(3)	3221(2)	27(1)
C(36)	1811(2)	-1114(4)	6324(2)	30(1)
C(37)	671(2)	624(3)	-915(1)	20(1)
C(38)	763(2)	2456(3)	3870(1)	21(1)
C(39)	2240(2)	486(3)	141(1)	19(1)
C(40)	4011(2)	196(4)	4672(2)	25(1)
C(41)	2034(2)	-463(4)	3401(2)	31(1)
C(42)	-319(2)	-1173(4)	3182(2)	29(1)
C(43)	1755(2)	1387(3)	283(1)	18(1)
C(44)	1681(2)	2568(3)	1063(1)	19(1)
C(45)	1267(2)	1463(3)	4037(2)	20(1)
C(46)	2077(2)	1628(3)	893(1)	22(1)
C(47)	780(3)	-1097(4)	-1334(2)	31(1)
C(48)	1841(2)	3638(3)	948(2)	26(1)
C(49)	4468(2)	1257(4)	249(2)	26(1)
C(50)	488(3)	-2143(4)	2729(2)	38(1)
C(51)	1513(2)	4528(4)	1115(2)	30(1)
C(52)	2842(3)	-1949(4)	2209(2)	34(1)
C(53)	3113(2)	1813(4)	4880(2)	25(1)
C(54)	1533(3)	-1364(4)	1762(2)	34(1)
C(55)	1292(2)	-494(4)	5948(2)	26(1)
C(56)	2543(2)	927(4)	2301(2)	25(1)
C(57)	3938(2)	2081(4)	115(2)	28(1)
C(58)	1180(2)	2389(4)	1340(1)	24(1)
C(80)	2106(2)	410(3)	4812(1)	19(1)
C(60)	829(3)	-2148(4)	3732(2)	33(1)
C(61)	3808(2)	2076(4)	4862(2)	27(1)

C(62)	21(2)	2347(4)	3572(2)	26(1)
C(63)	3212(2)	1844(4)	87(1)	23(1)
C(64)	679(2)	728(4)	2668(2)	27(1)
C(65)	2858(2)	731(3)	4800(1)	21(1)
C(66)	1049(2)	3508(3)	4022(2)	26(1)
C(67)	2104(2)	1080(4)	6175(2)	31(1)
C(68)	4253(2)	1271(4)	4750(2)	28(1)
C(69)	1307(3)	551(4)	-1577(2)	34(1)
C(70)	3592(2)	265(4)	1701(2)	34(1)
C(72)	2623(3)	454(4)	6548(2)	38(1)
C(78)	2329(3)	-1905(4)	1205(2)	38(1)

Table S3. Bond lengths [Å] and angles [°].

Br(1)-C(33)	1.900(4)
Br(2)-C(83)	1.899(4)
Br(3)-C(26)	1.903(4)
Br(4)-C(24)	1.892(4)
S(5)-O(14)	1.426(3)
S(5)-O(15)	1.427(3)
S(5)-N(19)	1.622(3)
S(5)-C(20)	1.773(4)
S(6)-O(9)	1.421(3)
S(6)-O(13)	1.431(3)
S(6)-N(20)	1.622(3)
S(6)-C(37)	1.763(4)
Si(7)-O(18)	1.667(3)
Si(7)-C(41)	1.857(5)
Si(7)-C(64)	1.861(4)
Si(7)-C(35)	1.876(4)
Si(8)-O(17)	1.664(3)
Si(8)-C(70)	1.853(5)
Si(8)-C(56)	1.857(4)
Si(8)-C(25)	1.875(4)
O(17)-C(46)	1.412(5)
O(18)-C(45)	1.413(5)
O(19)-C(80)	1.215(5)
N(20)-C(43)	1.457(5)
O(16)-C(39)	1.219(5)
C(83)-C(69)	1.363(6)
C(83)-C(47)	1.385(7)
N(19)-C(22)	1.443(5)
C(20)-C(67)	1.382(5)
C(20)-C(55)	1.383(6)
C(21)-C(26)	1.371(6)
C(21)-C(58)	1.395(6)
C(22)-C(80)	1.538(5)
C(22)-C(45)	1.551(5)
C(23)-C(28)	1.379(6)
C(23)-C(49)	1.386(6)
C(24)-C(72)	1.364(6)
C(24)-C(36)	1.387(6)
C(25)-C(52)	1.535(5)
C(25)-C(54)	1.535(6)
C(25)-C(78)	1.541(5)
C(26)-C(51)	1.389(6)
C(27)-C(47)	1.388(6)
C(27)-C(37)	1.389(6)
C(28)-C(29)	1.400(5)

C(29)-C(63)	1.391(6)
C(29)-C(39)	1.476(5)
C(30)-C(40)	1.375(6)
C(30)-C(65)	1.394(6)
C(31)-C(33)	1.374(6)
C(31)-C(62)	1.388(6)
C(32)-C(66)	1.376(6)
C(32)-C(33)	1.388(6)
C(34)-C(37)	1.381(6)
C(34)-C(69)	1.401(6)
C(35)-C(42)	1.533(6)
C(35)-C(50)	1.536(5)
C(35)-C(60)	1.543(5)
C(36)-C(55)	1.380(6)
C(38)-C(62)	1.389(5)
C(38)-C(66)	1.396(6)
C(38)-C(45)	1.516(5)
C(39)-C(43)	1.549(5)
C(40)-C(68)	1.378(6)
C(43)-C(46)	1.553(5)
C(44)-C(58)	1.384(5)
C(44)-C(48)	1.389(6)
C(44)-C(46)	1.508(6)
C(48)-C(51)	1.383(6)
C(49)-C(57)	1.384(6)
C(53)-C(61)	1.375(6)
C(53)-C(65)	1.393(6)
C(57)-C(63)	1.390(6)
C(80)-C(65)	1.491(5)
C(61)-C(68)	1.382(6)
C(67)-C(72)	1.381(6)

O(14)-S(5)-O(15)	120.79(18)
O(14)-S(5)-N(19)	105.69(16)
O(15)-S(5)-N(19)	107.33(17)
O(14)-S(5)-C(20)	107.72(18)
O(15)-S(5)-C(20)	107.26(17)
N(19)-S(5)-C(20)	107.43(17)
O(9)-S(6)-O(13)	120.84(18)
O(9)-S(6)-N(20)	107.91(17)
O(13)-S(6)-N(20)	105.22(17)
O(9)-S(6)-C(37)	106.77(18)
O(13)-S(6)-C(37)	108.12(18)
N(20)-S(6)-C(37)	107.35(17)
O(18)-Si(7)-C(41)	109.41(17)
O(18)-Si(7)-C(64)	109.26(18)
C(41)-Si(7)-C(64)	110.5(2)
O(18)-Si(7)-C(35)	103.65(17)
C(41)-Si(7)-C(35)	111.4(2)
C(64)-Si(7)-C(35)	112.41(19)
O(17)-Si(8)-C(70)	110.99(17)
O(17)-Si(8)-C(56)	109.81(17)
C(70)-Si(8)-C(56)	108.3(2)
O(17)-Si(8)-C(25)	103.04(16)
C(70)-Si(8)-C(25)	112.8(2)
C(56)-Si(8)-C(25)	111.84(19)
C(46)-O(17)-Si(8)	127.4(2)
C(45)-O(18)-Si(7)	126.6(2)
C(43)-N(20)-S(6)	119.0(3)
C(69)-C(83)-C(47)	122.6(4)

C(69)-C(83)-Br(2)	118.4(4)
C(47)-C(83)-Br(2)	119.0(3)
C(22)-N(19)-S(5)	119.6(3)
C(67)-C(20)-C(55)	121.4(4)
C(67)-C(20)-S(5)	120.2(3)
C(55)-C(20)-S(5)	118.4(3)
C(26)-C(21)-C(58)	119.3(4)
N(19)-C(22)-C(80)	112.4(3)
N(19)-C(22)-C(45)	109.0(3)
C(80)-C(22)-C(45)	108.6(3)
C(28)-C(23)-C(49)	119.8(4)
C(72)-C(24)-C(36)	122.0(4)
C(72)-C(24)-Br(4)	119.8(3)
C(36)-C(24)-Br(4)	118.2(3)
C(52)-C(25)-C(54)	108.9(4)
C(52)-C(25)-C(78)	109.3(4)
C(54)-C(25)-C(78)	108.4(4)
C(52)-C(25)-Si(8)	111.1(3)
C(54)-C(25)-Si(8)	109.7(3)
C(78)-C(25)-Si(8)	109.4(3)
C(21)-C(26)-C(51)	121.6(4)
C(21)-C(26)-Br(3)	119.2(3)
C(51)-C(26)-Br(3)	119.2(4)
C(47)-C(27)-C(37)	119.7(4)
C(23)-C(28)-C(29)	120.5(4)
C(63)-C(29)-C(28)	119.1(4)
C(63)-C(29)-C(39)	122.2(3)
C(28)-C(29)-C(39)	118.7(4)
C(40)-C(30)-C(65)	120.7(4)
C(33)-C(31)-C(62)	118.9(4)
C(66)-C(32)-C(33)	118.7(4)
C(31)-C(33)-C(32)	121.8(4)
C(31)-C(33)-Br(1)	118.8(3)
C(32)-C(33)-Br(1)	119.4(3)
C(37)-C(34)-C(69)	119.8(4)
C(42)-C(35)-C(50)	109.5(4)
C(42)-C(35)-C(60)	109.1(4)
C(50)-C(35)-C(60)	109.0(4)
C(42)-C(35)-Si(7)	109.6(3)
C(50)-C(35)-Si(7)	111.3(3)
C(60)-C(35)-Si(7)	108.4(3)
C(55)-C(36)-C(24)	118.9(4)
C(34)-C(37)-C(27)	120.7(4)
C(34)-C(37)-S(6)	119.6(3)
C(27)-C(37)-S(6)	119.6(3)
C(62)-C(38)-C(66)	118.9(4)
C(62)-C(38)-C(45)	121.7(4)
C(66)-C(38)-C(45)	119.4(3)
O(16)-C(39)-C(29)	122.4(4)
O(16)-C(39)-C(43)	119.6(4)
C(29)-C(39)-C(43)	117.9(3)
C(30)-C(40)-C(68)	119.8(4)
N(20)-C(43)-C(39)	111.8(3)
N(20)-C(43)-C(46)	109.7(3)
C(39)-C(43)-C(46)	108.0(3)
C(58)-C(44)-C(48)	119.5(4)
C(58)-C(44)-C(46)	121.7(4)
C(48)-C(44)-C(46)	118.8(4)
O(18)-C(45)-C(38)	112.3(3)
O(18)-C(45)-C(22)	106.6(3)

C(38)-C(45)-C(22)	110.8(3)
O(17)-C(46)-C(44)	113.2(3)
O(17)-C(46)-C(43)	105.9(3)
C(44)-C(46)-C(43)	112.1(3)
C(83)-C(47)-C(27)	118.6(4)
C(51)-C(48)-C(44)	120.8(4)
C(57)-C(49)-C(23)	120.5(4)
C(48)-C(51)-C(26)	118.6(4)
C(61)-C(53)-C(65)	120.4(4)
C(36)-C(55)-C(20)	119.1(4)
C(49)-C(57)-C(63)	119.6(4)
C(44)-C(58)-C(21)	120.1(4)
O(19)-C(80)-C(65)	122.5(4)
O(19)-C(80)-C(22)	120.2(3)
C(65)-C(80)-C(22)	117.2(3)
C(53)-C(61)-C(68)	120.0(4)
C(31)-C(62)-C(38)	120.7(4)
C(57)-C(63)-C(29)	120.4(4)
C(53)-C(65)-C(30)	118.7(4)
C(53)-C(65)-C(80)	122.2(4)
C(30)-C(65)-C(80)	119.0(4)
C(32)-C(66)-C(38)	120.9(4)
C(72)-C(67)-C(20)	119.3(4)
C(40)-C(68)-C(61)	120.3(4)
C(83)-C(69)-C(34)	118.6(4)
C(24)-C(72)-C(67)	119.3(4)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$).
The anisotropic displacement factor exponent takes the form: $-2p^2\ [h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	32(1)	20(1)	43(1)	5(1)	1(1)	5(1)
Br(2)	38(1)	55(1)	31(1)	-13(1)	6(1)	17(1)
Br(3)	42(1)	29(1)	51(1)	-13(1)	12(1)	7(1)
Br(4)	41(1)	48(1)	38(1)	19(1)	0(1)	12(1)
S(5)	19(1)	17(1)	22(1)	2(1)	6(1)	2(1)
S(6)	16(1)	19(1)	22(1)	-1(1)	4(1)	1(1)
Si(7)	23(1)	18(1)	22(1)	0(1)	6(1)	1(1)
Si(8)	22(1)	20(1)	20(1)	0(1)	5(1)	2(1)
O(9)	26(2)	17(2)	27(1)	1(1)	7(1)	2(1)
O(17)	20(1)	16(2)	23(1)	2(1)	4(1)	0(1)
O(18)	23(1)	17(2)	25(1)	-2(1)	9(1)	0(1)
O(19)	27(2)	15(2)	40(2)	3(1)	14(1)	-1(1)
O(13)	17(1)	24(2)	31(1)	1(1)	5(1)	-1(1)
O(14)	15(1)	26(2)	30(1)	1(1)	13(1)	-1(1)
O(15)	27(2)	13(2)	32(1)	-1(1)	10(1)	0(1)
N(20)	17(2)	28(2)	15(1)	1(1)	4(1)	-3(1)
O(16)	23(2)	20(2)	31(1)	-3(1)	7(1)	-3(1)
C(83)	25(2)	36(3)	21(2)	-4(2)	3(2)	6(2)
N(19)	18(2)	20(2)	22(2)	-2(1)	5(1)	1(1)
C(20)	22(2)	21(2)	19(2)	1(1)	8(2)	0(2)
C(21)	24(2)	24(2)	30(2)	-4(2)	5(2)	1(2)
C(22)	16(2)	17(2)	22(2)	0(1)	7(1)	-3(2)
C(23)	22(2)	27(2)	29(2)	0(2)	10(2)	5(2)
C(24)	32(2)	33(3)	21(2)	9(2)	4(2)	4(2)
C(25)	32(2)	22(2)	22(2)	-1(2)	8(2)	4(2)
C(26)	26(2)	29(3)	29(2)	-6(2)	4(2)	4(2)
C(27)	28(2)	27(2)	25(2)	-2(2)	8(2)	-4(2)

C(28)	23(2)	23(2)	18(2)	-2(1)	7(1)	-2(2)
C(29)	20(2)	19(2)	16(2)	2(1)	9(1)	2(2)
C(30)	19(2)	19(2)	25(2)	-1(2)	4(2)	1(2)
C(31)	25(2)	24(2)	27(2)	1(2)	2(2)	0(2)
C(32)	32(2)	16(2)	30(2)	2(2)	1(2)	-2(2)
C(33)	31(2)	22(2)	22(2)	2(2)	5(2)	3(2)
C(34)	35(2)	24(2)	30(2)	-1(2)	11(2)	0(2)
C(35)	34(2)	20(2)	22(2)	-3(2)	3(2)	-2(2)
C(36)	32(2)	21(2)	35(2)	8(2)	8(2)	-1(2)
C(37)	16(2)	23(2)	19(2)	1(1)	3(1)	1(2)
C(38)	26(2)	22(2)	16(2)	2(1)	8(1)	1(2)
C(39)	24(2)	15(2)	18(2)	1(1)	4(1)	2(2)
C(40)	21(2)	23(2)	32(2)	-1(2)	10(2)	5(2)
C(41)	31(2)	31(3)	27(2)	-2(2)	5(2)	4(2)
C(42)	24(2)	28(3)	40(2)	-3(2)	17(2)	-4(2)
C(43)	20(2)	13(2)	21(2)	-2(1)	5(1)	-2(2)
C(44)	13(2)	19(2)	22(2)	-2(1)	1(1)	-1(2)
C(45)	23(2)	15(2)	24(2)	1(1)	10(2)	-3(2)
C(46)	23(2)	15(2)	24(2)	2(2)	3(2)	-2(2)
C(47)	39(3)	22(2)	25(2)	-7(2)	0(2)	-2(2)
C(48)	27(2)	23(2)	25(2)	0(2)	4(2)	-3(2)
C(49)	24(2)	29(3)	27(2)	2(2)	11(2)	-2(2)
C(50)	58(3)	24(3)	37(2)	-10(2)	22(2)	-8(2)
C(51)	32(2)	23(2)	29(2)	0(2)	3(2)	0(2)
C(52)	46(3)	22(2)	31(2)	2(2)	9(2)	5(2)
C(53)	23(2)	21(2)	30(2)	-3(2)	6(2)	1(2)
C(54)	40(3)	27(3)	31(2)	2(2)	5(2)	-7(2)
C(55)	21(2)	26(2)	29(2)	3(2)	4(2)	-3(2)
C(56)	24(2)	25(2)	24(2)	-1(2)	6(2)	-2(2)
C(57)	26(2)	27(3)	34(2)	5(2)	15(2)	-6(2)
C(58)	19(2)	26(2)	24(2)	-2(2)	0(2)	-3(2)
C(80)	18(2)	20(2)	20(2)	-1(1)	6(1)	-1(2)
C(60)	40(3)	23(3)	37(2)	7(2)	12(2)	-4(2)
C(61)	23(2)	19(2)	35(2)	0(2)	3(2)	-5(2)
C(62)	23(2)	19(2)	32(2)	-3(2)	5(2)	-4(2)
C(63)	20(2)	21(2)	28(2)	1(2)	8(2)	2(2)
C(64)	26(2)	28(3)	27(2)	1(2)	9(2)	-2(2)
C(65)	20(2)	20(2)	22(2)	1(2)	6(2)	2(2)
C(66)	23(2)	23(2)	29(2)	0(2)	5(2)	-5(2)
C(67)	26(2)	29(3)	34(2)	6(2)	1(2)	-8(2)
C(68)	21(2)	29(3)	32(2)	1(2)	6(2)	-3(2)
C(69)	36(3)	40(3)	29(2)	-2(2)	14(2)	-1(2)
C(70)	31(2)	48(3)	23(2)	4(2)	7(2)	5(2)
C(72)	30(2)	38(3)	36(2)	4(2)	-4(2)	-2(2)
C(78)	54(3)	26(3)	34(2)	-3(2)	15(2)	5(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(61)	837	675	382	24
H(62)	501	610	4582	24
H(1)	515	3163	1702	32
H(57)	1694	1986	4831	22
H(9)	4633	-357	431	30
H(10)	263	-846	-777	32
H(11)	3417	-768	352	25
H(12)	3169	-806	4665	26
H(2)	-923	3194	3214	32
H(3)	799	5125	3983	33

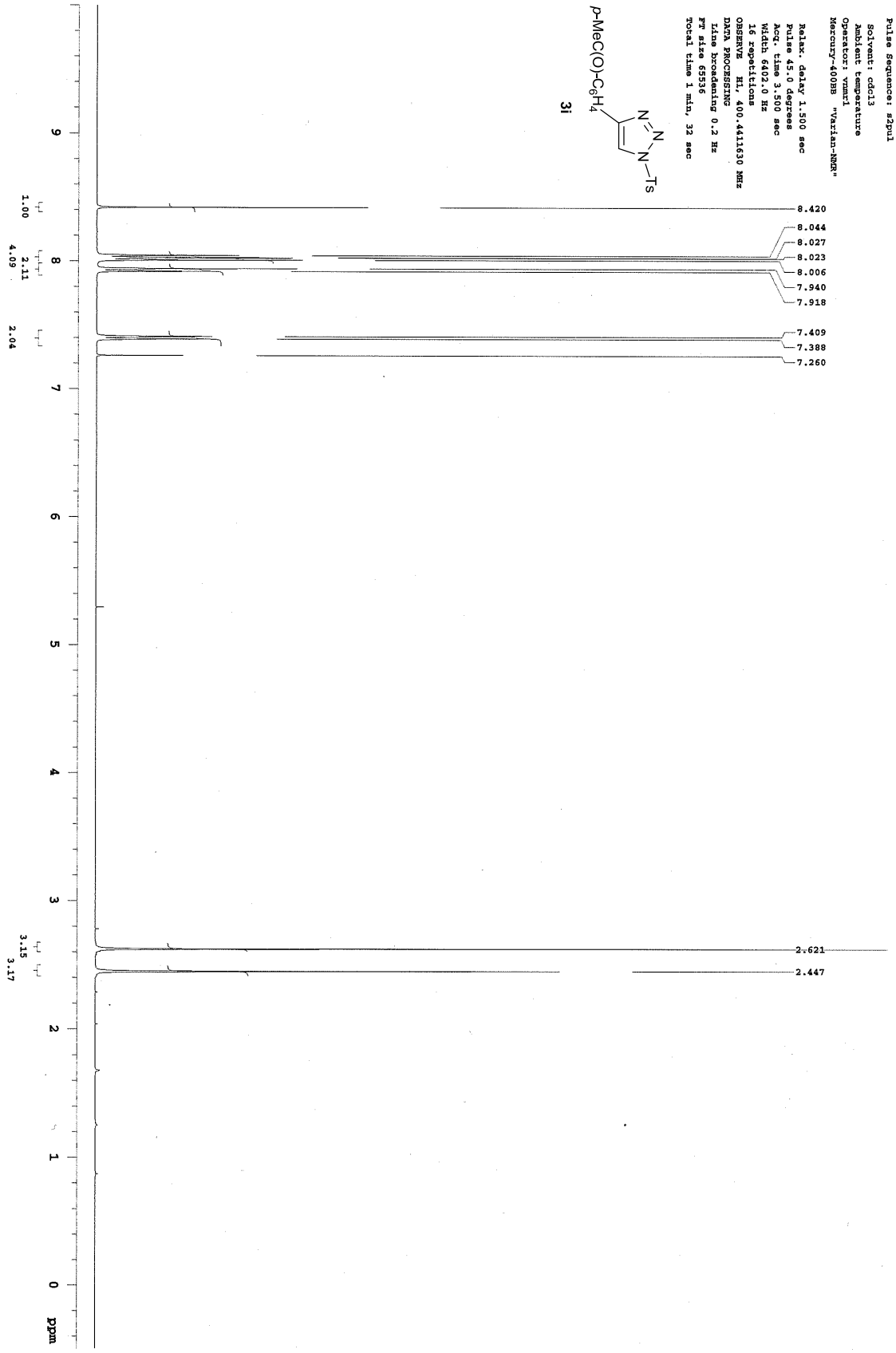
H(13)	1133	1908	-1178	35
H(14)	1719	-1850	6378	36
H(15)	4312	-344	4596	30
H(27)	2308	214	3460	46
H(28)	2101	-839	3098	46
H(29)	2209	-920	3714	46
H(30)	-536	-740	2865	43
H(31)	-323	-761	3493	43
H(32)	-599	-1839	3162	43
H(58)	1780	2059	82	22
H(59)	1713	1579	3932	24
H(60)	2601	1824	974	26
H(16)	693	-1850	-1377	37
H(4)	2172	3758	757	31
H(17)	4957	1419	278	31
H(33)	990	-2306	2748	57
H(34)	254	-1732	2408	57
H(35)	222	-2818	2723	57
H(5)	1615	5243	1033	36
H(36)	2668	-2691	2211	50
H(37)	2846	-1586	2534	50
H(38)	3334	-1959	2182	50
H(18)	2810	2360	4947	30
H(39)	1208	-961	1468	51
H(40)	1526	-1039	2094	51
H(41)	1370	-2115	1747	51
H(19)	846	-806	5745	31
H(42)	2624	1695	2252	38
H(43)	2906	668	2621	38
H(44)	2056	826	2330	38
H(20)	4068	2789	43	33
H(6)	1062	1674	1411	29
H(45)	524	-2781	3729	50
H(46)	862	-1707	4042	50
H(47)	1316	-2384	3743	50
H(21)	3979	2797	4924	33
H(7)	-177	1650	3473	31
H(22)	2859	2402	11	28
H(48)	171	915	2620	41
H(49)	713	339	2358	41
H(50)	970	1388	2716	41
H(8)	1545	3589	4222	31
H(23)	2195	1818	6126	38
H(24)	4718	1456	4729	33
H(25)	1570	895	-1778	41
H(51)	3653	-176	1414	51
H(52)	3927	15	2036	51
H(53)	3696	1021	1645	51
H(26)	3072	763	6748	45
H(54)	2814	-1852	1167	57
H(55)	1976	-1555	905	57
H(56)	2199	-2665	1218	57

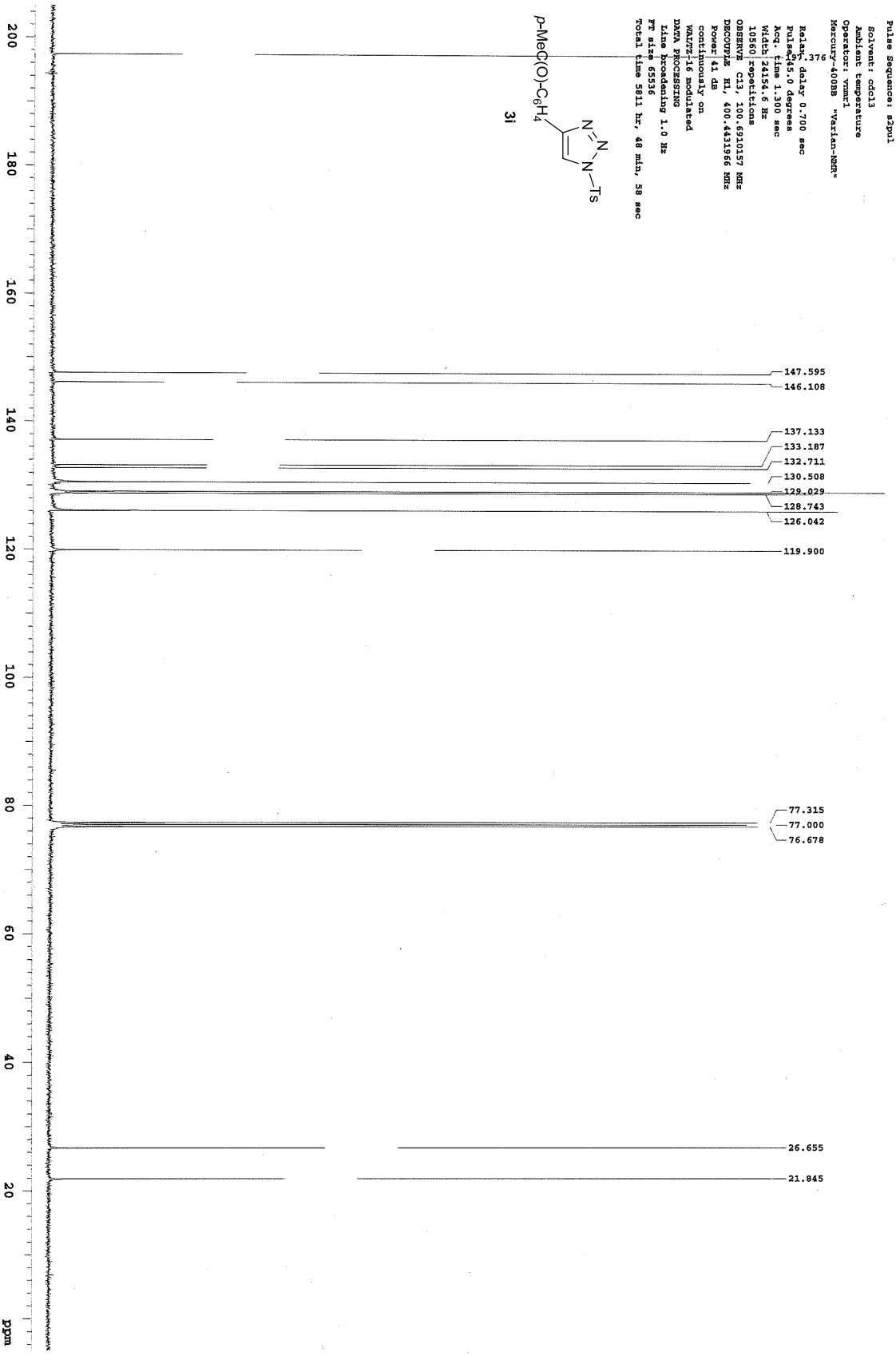
(1) Higashi, T. *ABSCOR. Program for Absorption Correction*.; Rigaku Corporation: Japan, 1995.

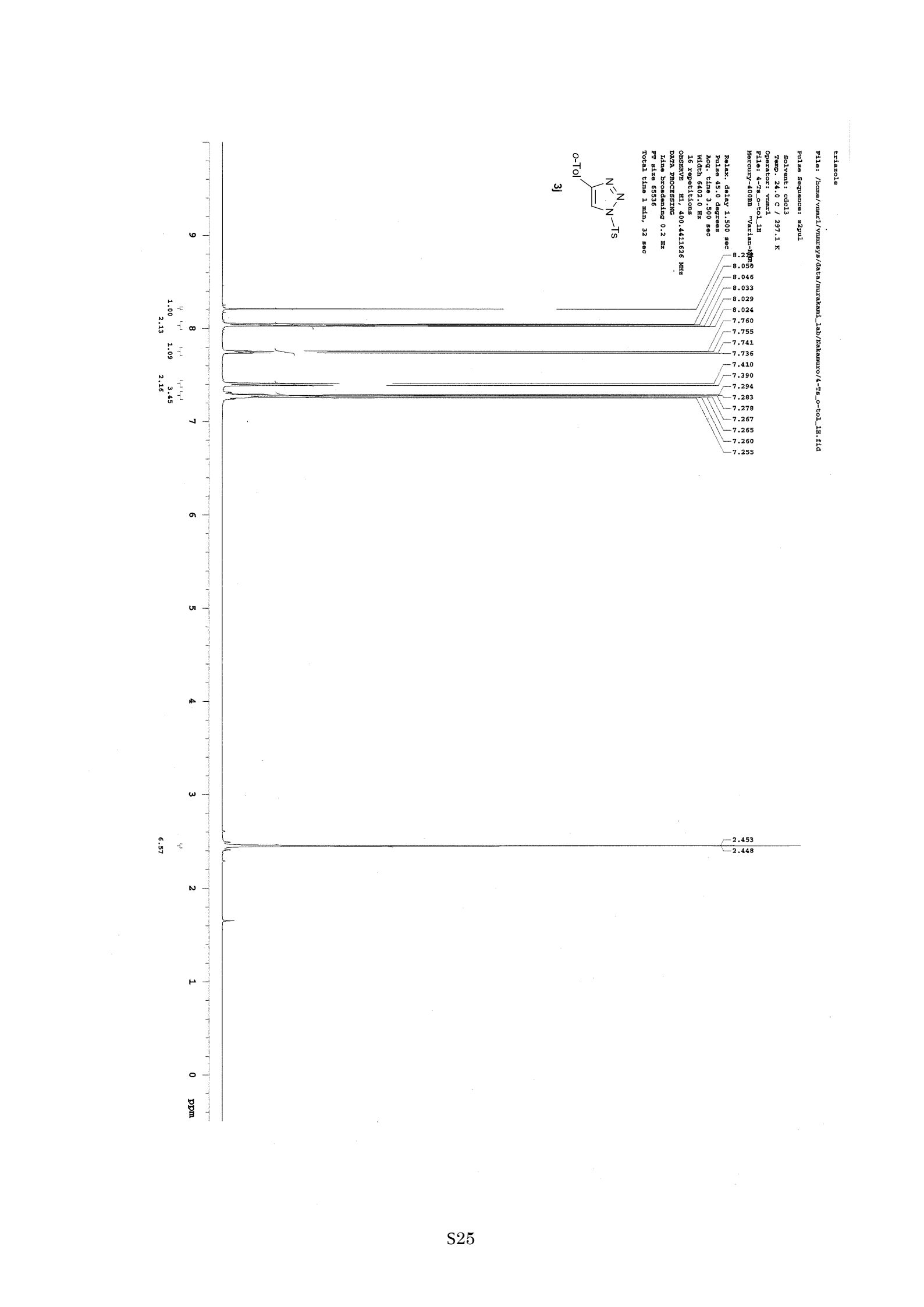
(2) Sheldrick, G. M. *SHELX-97. Programs for Crystal Structure Analysis.*; University of Göttingen: Germany, 1997.

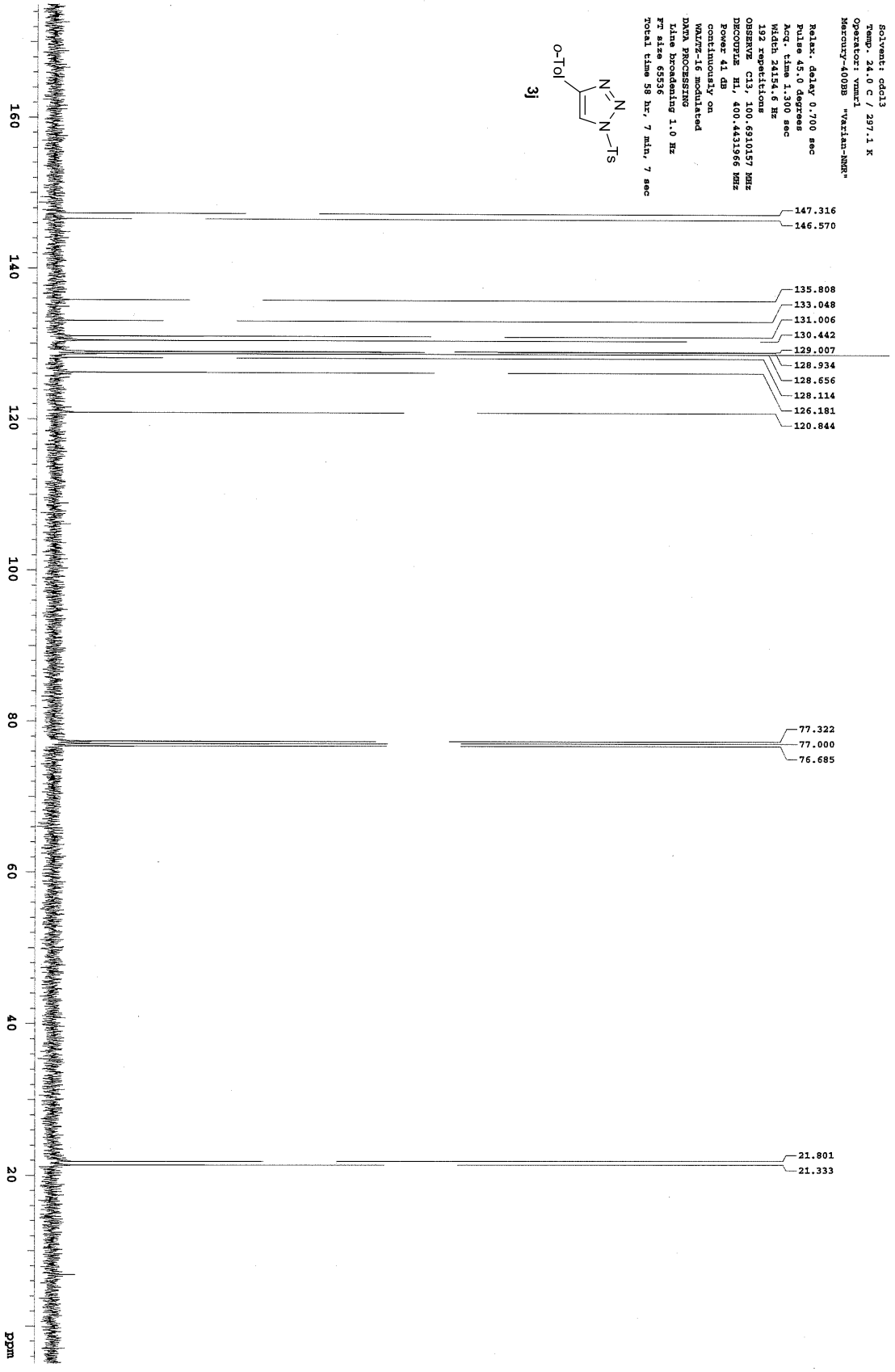
(3) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115–119.

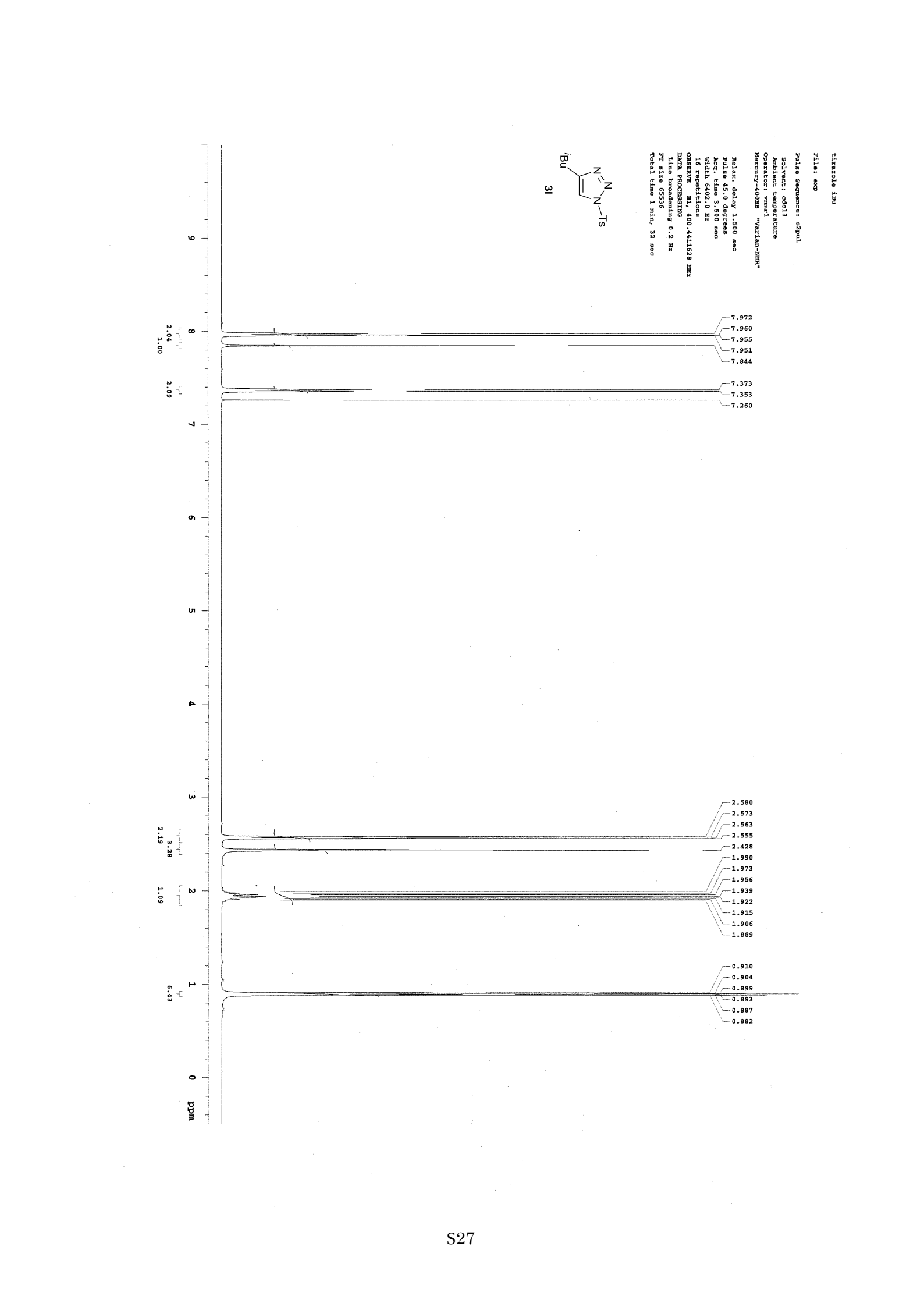
(4) Wakita, K. *Yadokari-XG. Program for Crystal Structure Analysis*.; 2000.

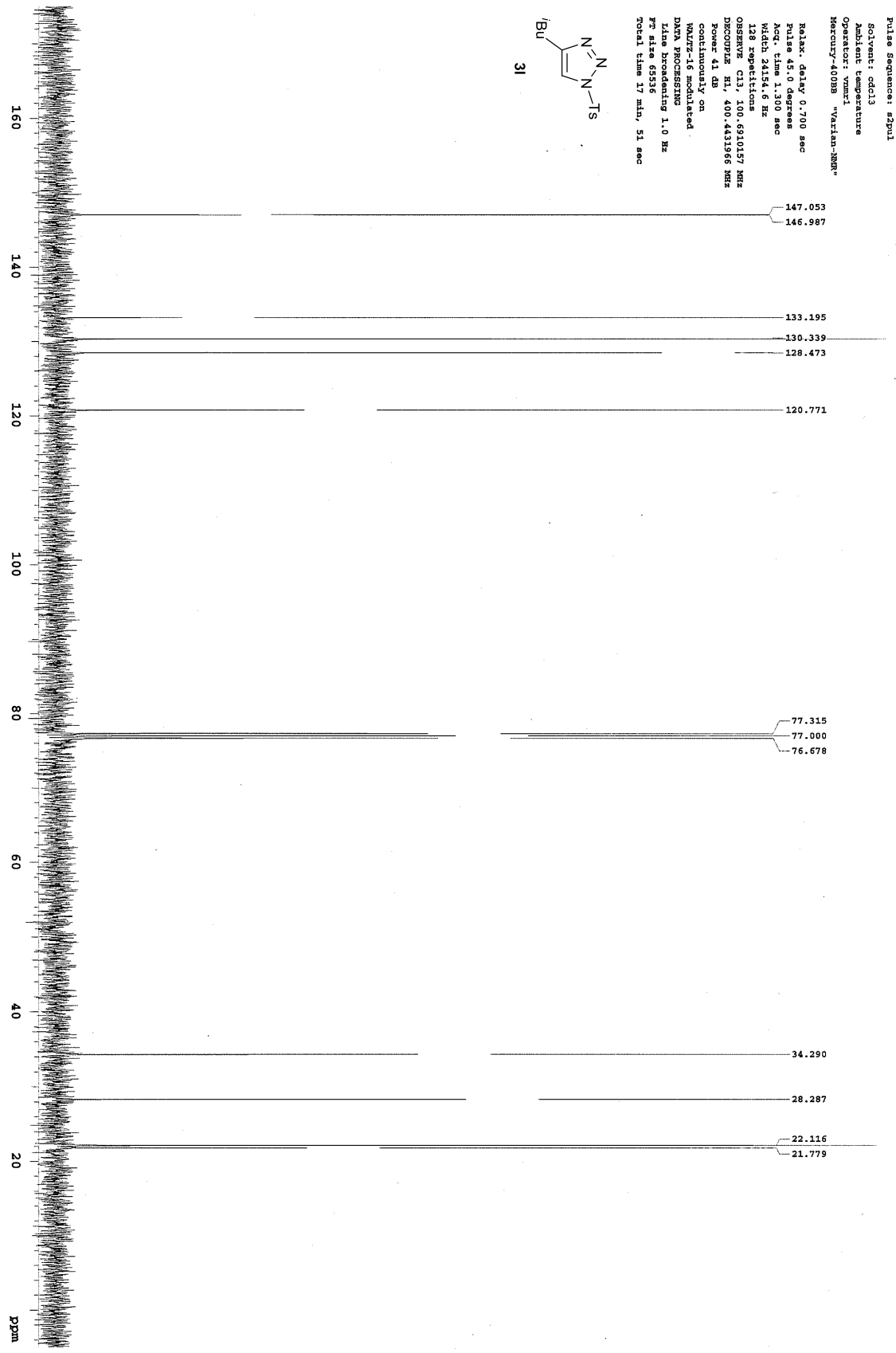

triazole Ac
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
p-MeC(O)-C6H4
N
N
N
Ts
3i
8.420
8.044
8.027
8.023
8.006
7.940
7.918
7.409
7.388
7.260
2.621
2.447
1.00
2.11
4.09
2.04
3.15
3.17
ppm

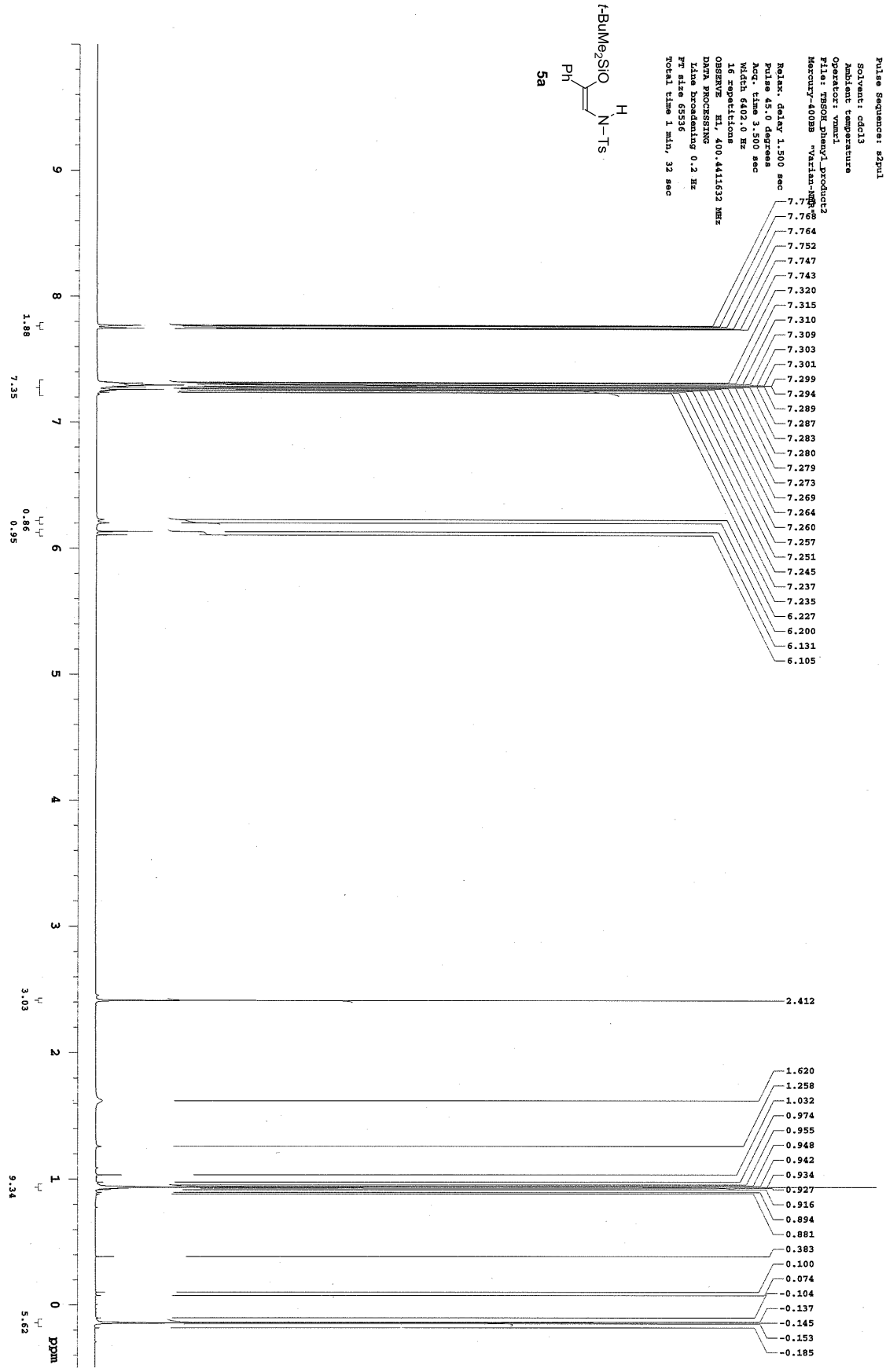

triazole Ac
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"
97.376
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
10560 repetitions
OBSERVE C13, 100.6910157 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 5811 hr, 48 min, 58 sec
p-MeC(O)-C6H4
Ts
3i
147.595
146.108
137.133
133.187
132.711
130.508
129.029
128.743
126.042
119.900
77.315
77.000
76.678
26.655
21.845
200
180
160
140
120
100
80
60
40
20
ppm


triazole
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/4-Ts_o-tol_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 24.0 C / 297.1 K
Operator: vnmr1
File: 4-Ts_o-tol_1H
Mercury-400BB "Varian-400
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411626 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
o-Tol
N
N
N
Ts
3j
8.221
8.051
8.046
8.033
8.029
8.024
7.760
7.755
7.741
7.736
7.410
7.390
7.294
7.283
7.278
7.267
7.265
7.260
7.255
2.453
2.448
1.00
2.13
1.09
3.45
2.16
6.57
9
8
7
6
5
4
3
2
1
0
ppm


1038-pu
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 24.0 C / 297.1 K
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
192 repetitions
OBSERVE C13, 100.6910157 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 58 hr, 7 min, 7 sec
o-Tol
Ts
3j
147.316
146.570
135.808
133.048
131.006
130.442
129.007
128.934
128.656
128.114
126.181
120.844
77.322
77.000
76.685
21.801
21.333
160
140
120
100
80
60
40
20
ppm


tirazole iBu
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrl
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.900 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411620 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
3l
7.972
7.960
7.955
7.951
7.844
7.373
7.353
7.260
2.580
2.573
2.563
2.555
2.428
1.990
1.973
1.956
1.939
1.922
1.915
1.906
1.889
0.910
0.904
0.899
0.893
0.887
0.882
2.04
2.09
3.28
1.09
6.43
1.00
2.19
ppm


tirazole iBu
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910157 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
3l
iBu
Ts
147.053
146.987
133.195
130.339
128.473
120.771
77.315
77.000
76.678
34.290
28.287
22.116
21.779
160
140
120
100
80
60
40
20
ppm

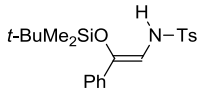

Selectfluor F
File: /home/vnmrs1/vnmrsys/data/murakami_lab/Nakamuro/TBSOH_phenyl_product2.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: TBSOH_phenyl_product2
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411632 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
Ph
H
N–Ts
5a
7.772
7.768
7.764
7.752
7.747
7.743
7.320
7.315
7.310
7.309
7.303
7.301
7.299
7.294
7.289
7.287
7.283
7.280
7.279
7.273
7.269
7.264
7.260
7.257
7.251
7.245
7.237
7.235
6.227
6.200
6.131
6.105
2.412
1.620
1.258
1.032
0.974
0.955
0.948
0.942
0.934
0.927
0.916
0.894
0.881
0.383
0.100
0.074
-0.104
-0.137
-0.145
-0.153
-0.185
1.88
7.35
0.86
0.95
3.03
9.34
5.62
ppm

File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/Triazole_Silanol/TBSOH_phenyl_product_13C.fid

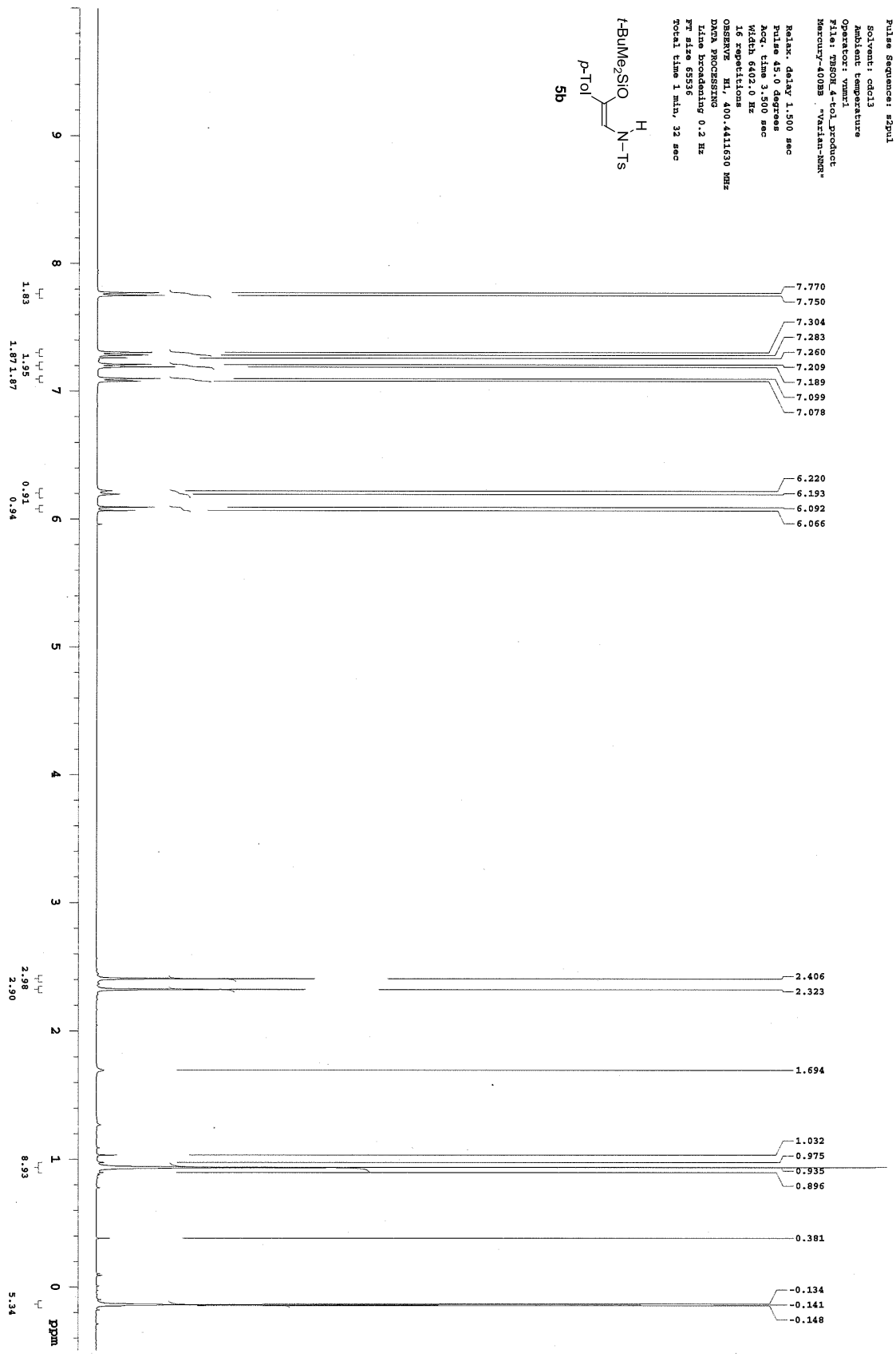
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: TBSOH_phenyl_product_13C
Mercury-400BB "Varian-NMR"

Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910127 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec



5a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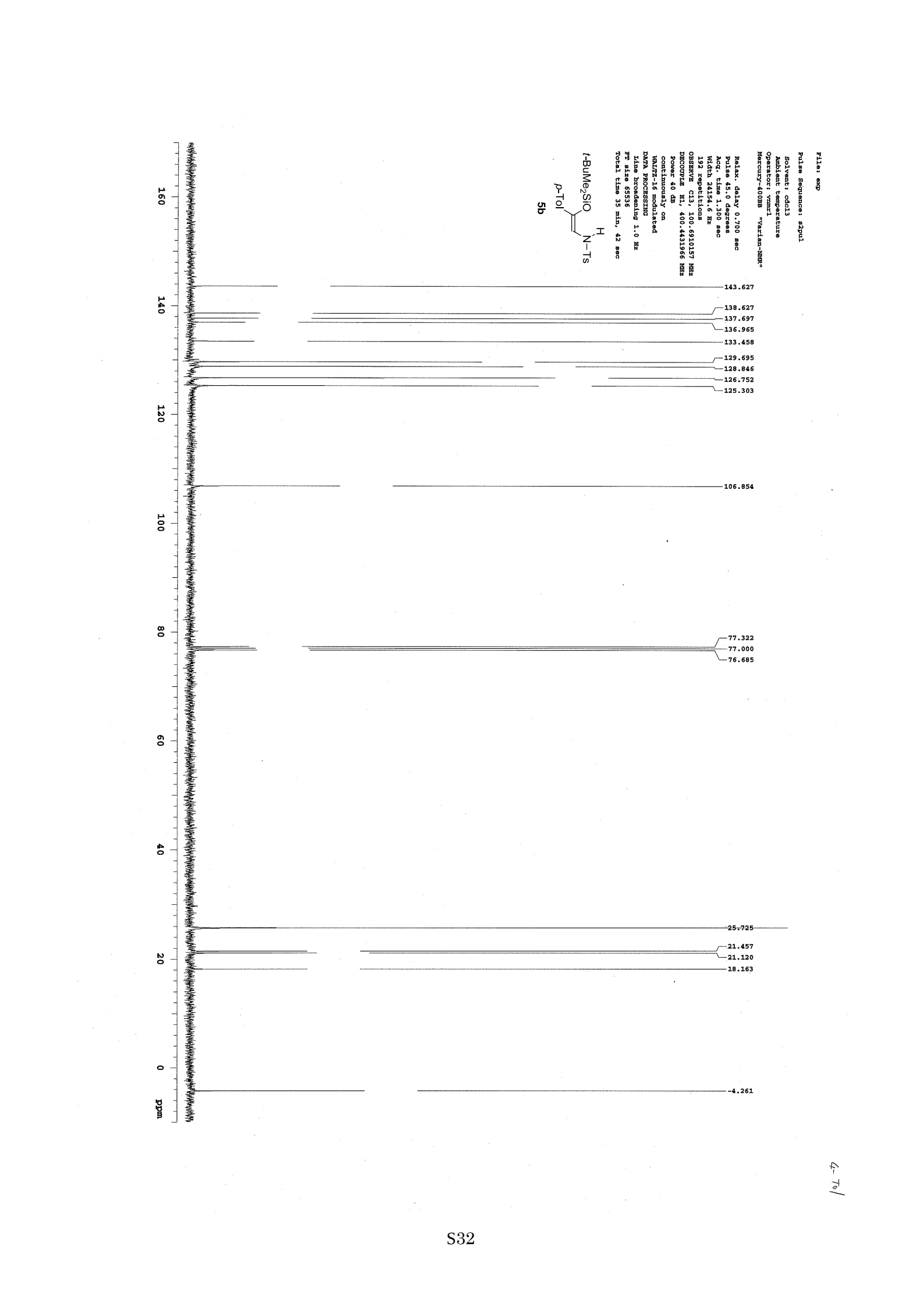
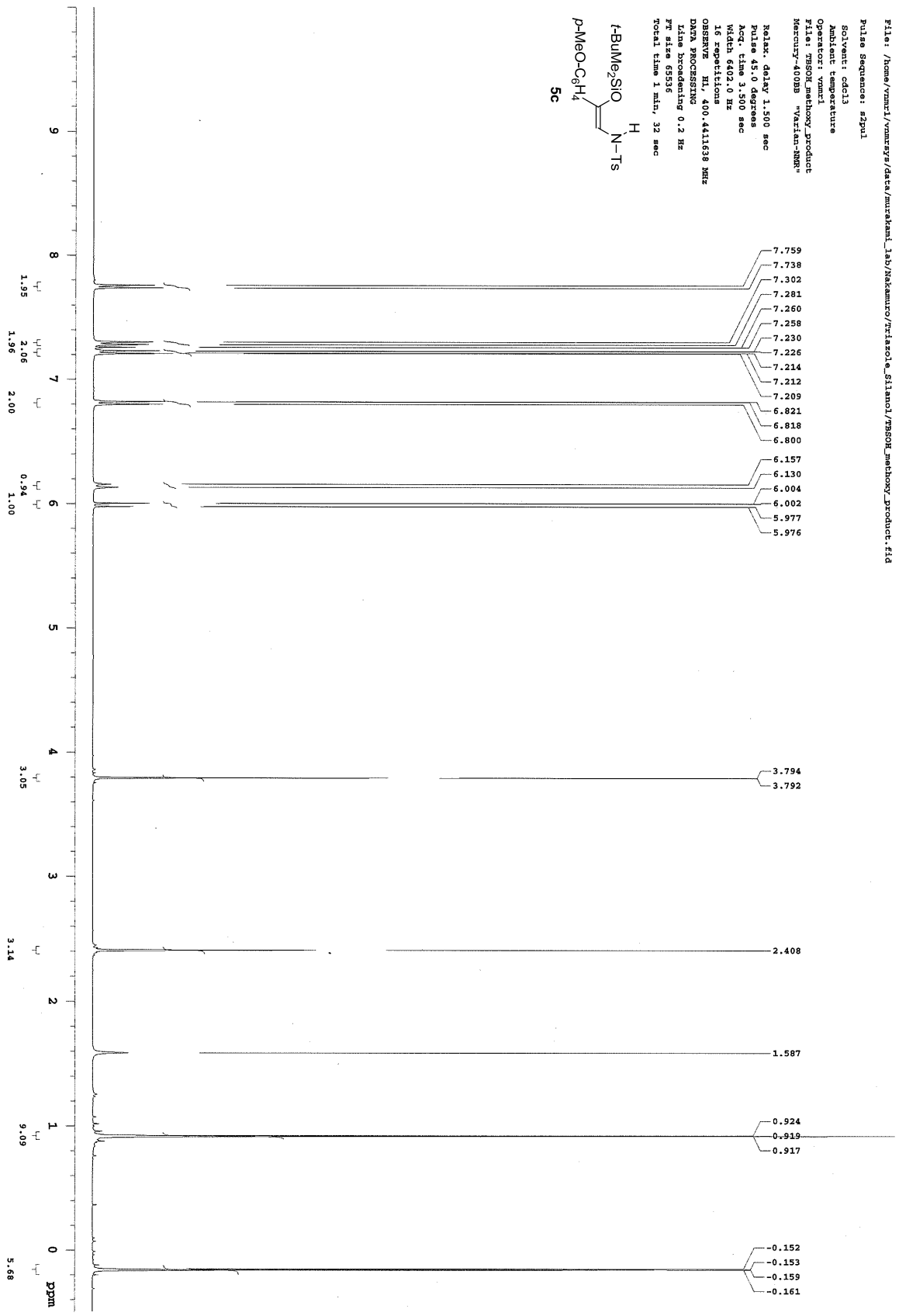
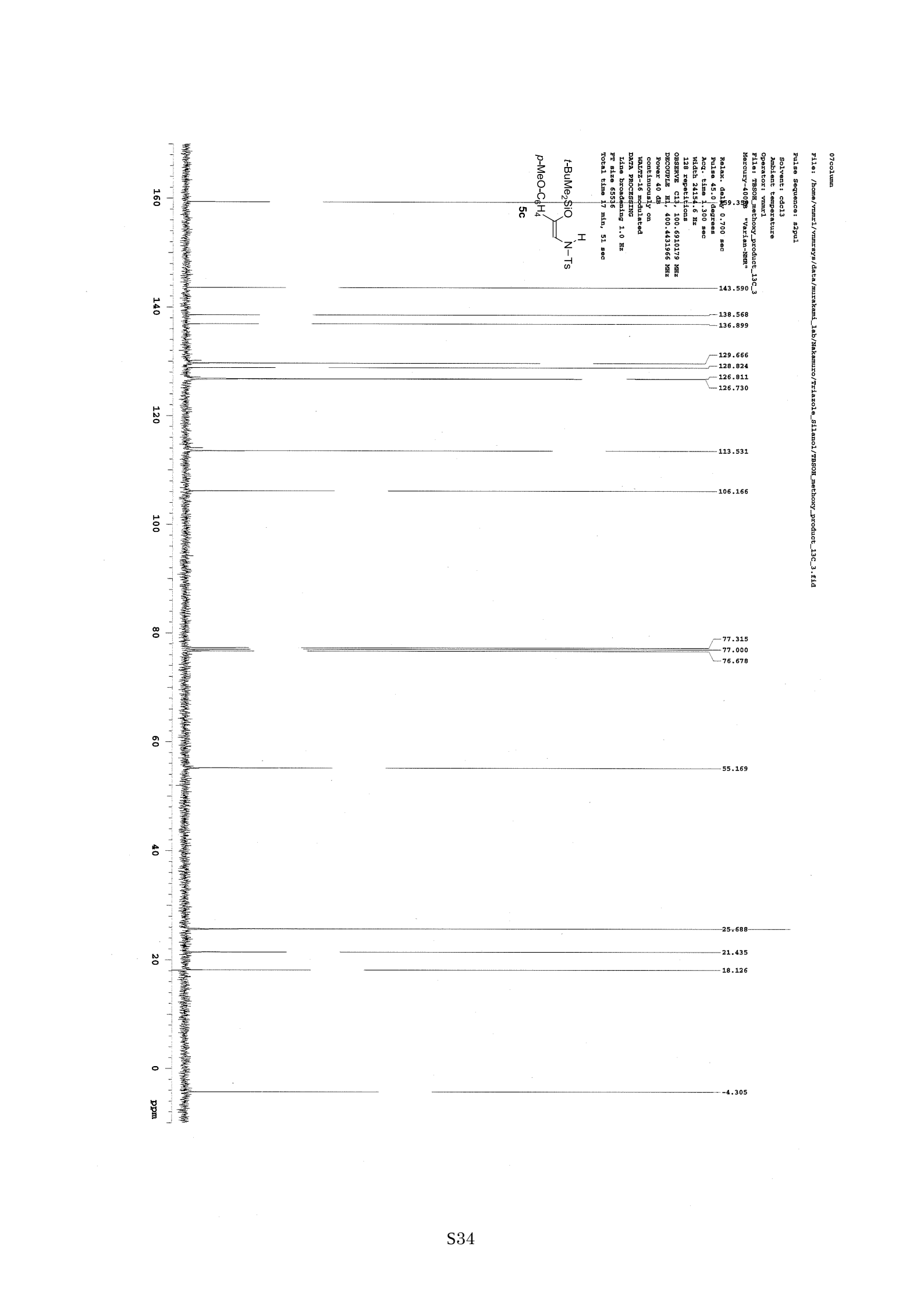
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrj
File: TBSOH_4-tol_product
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
p-Tol
H
N–Ts
5b
7.770
7.750
7.304
7.283
7.260
7.209
7.189
7.099
7.078
6.220
6.193
6.092
6.066
2.406
2.323
1.694
1.032
0.975
0.935
0.896
0.381
-0.134
-0.141
-0.148
1.83
1.95
1.87
1.87
0.91
0.94
2.98
2.90
8.93
5.34
ppm


File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
192 repetitions
OBSERVE C13, 100.6910157 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec
t-BuMe2SiO
H
N-Ts
p-Tol
5b
143.627
138.627
137.697
136.965
133.458
129.695
128.846
126.752
125.303
106.854
77.322
77.000
76.685
25.725
21.457
21.120
18.163
-4.261
160
140
120
100
80
60
40
20
0
ppm

4-Tol


new experiment
File: /home/vnmrj/vnmrsys/data/murakami_lab/Nakamuro/triazole_silanol/TBSOH_methoxy_product.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrj
File: TBSOH_methoxy_product
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411638 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
H
N–Ts
p-MeO-C6H4
5c
7.759
7.738
7.302
7.281
7.260
7.258
7.230
7.226
7.214
7.212
7.209
6.821
6.818
6.800
6.157
6.130
6.004
6.002
5.977
5.976
3.794
3.792
2.408
1.587
0.924
0.919
0.917
-0.152
-0.153
-0.159
-0.161
1.95
2.06
1.96
2.00
0.94
1.00
3.05
3.14
9.09
5.68
ppm


07column
File: /home/vnmrj/vnmrsys/data/murakami_lab/Nakamuro/Triazole_Silanol/TBSOH_methoxy_product_13C_3.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrj
File: TBSOH_methoxy_product_13C_3
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910179 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
t-BuMe2SiO
H
N–Ts
p-MeO-C6H4
5c
159.387
143.590
138.568
136.899
129.666
128.824
126.811
126.730
113.531
106.166
77.315
77.000
76.678
55.169
25.688
21.435
18.126
-4.305
160
140
120
100
80
60
40
20
0
ppm

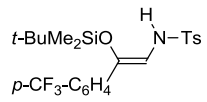
4

File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/Triazole_Silanol/TBSOH_trifluoro_product.fid

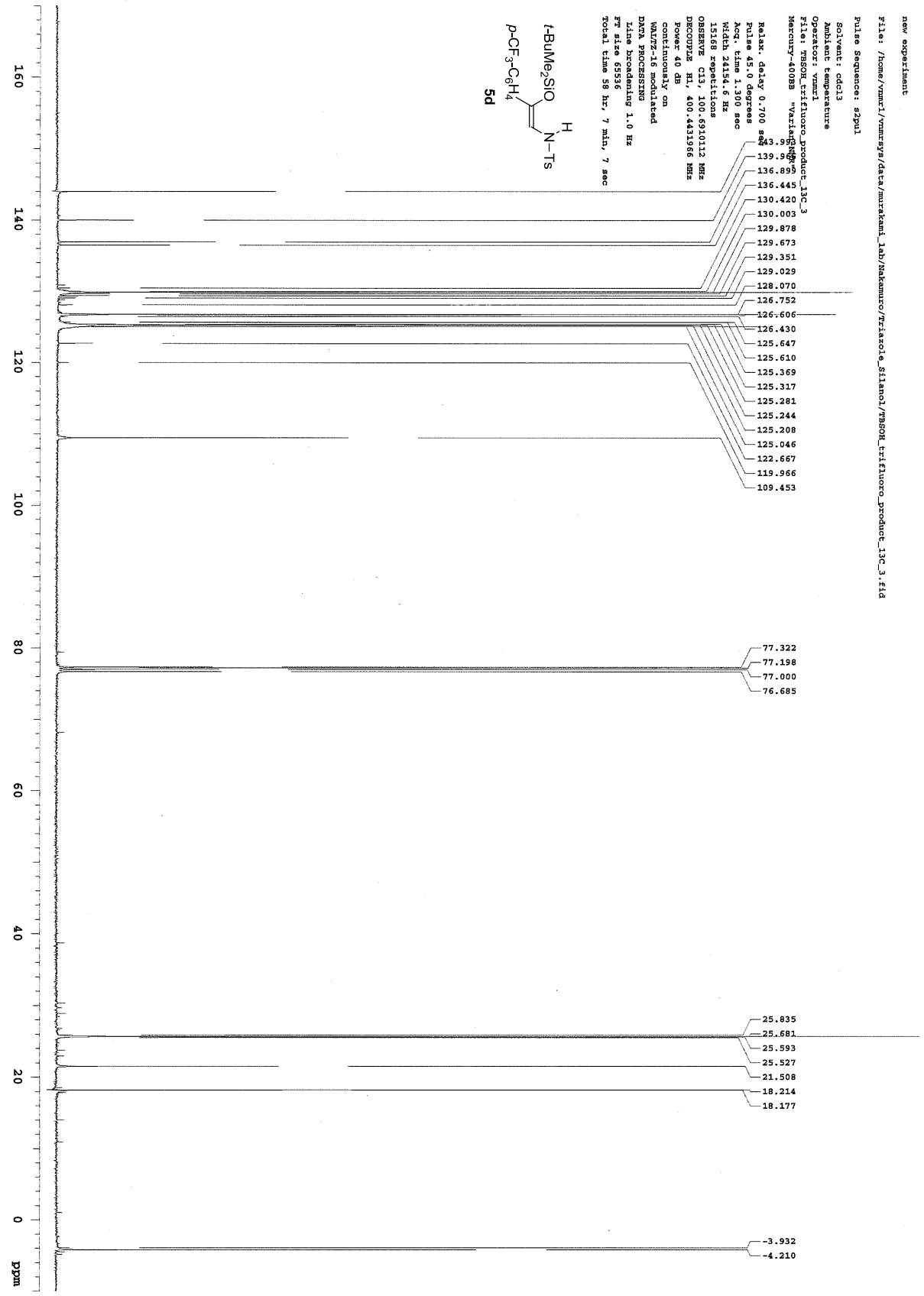
Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: TBSOH_trifluoro_product
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



5d


new experiment
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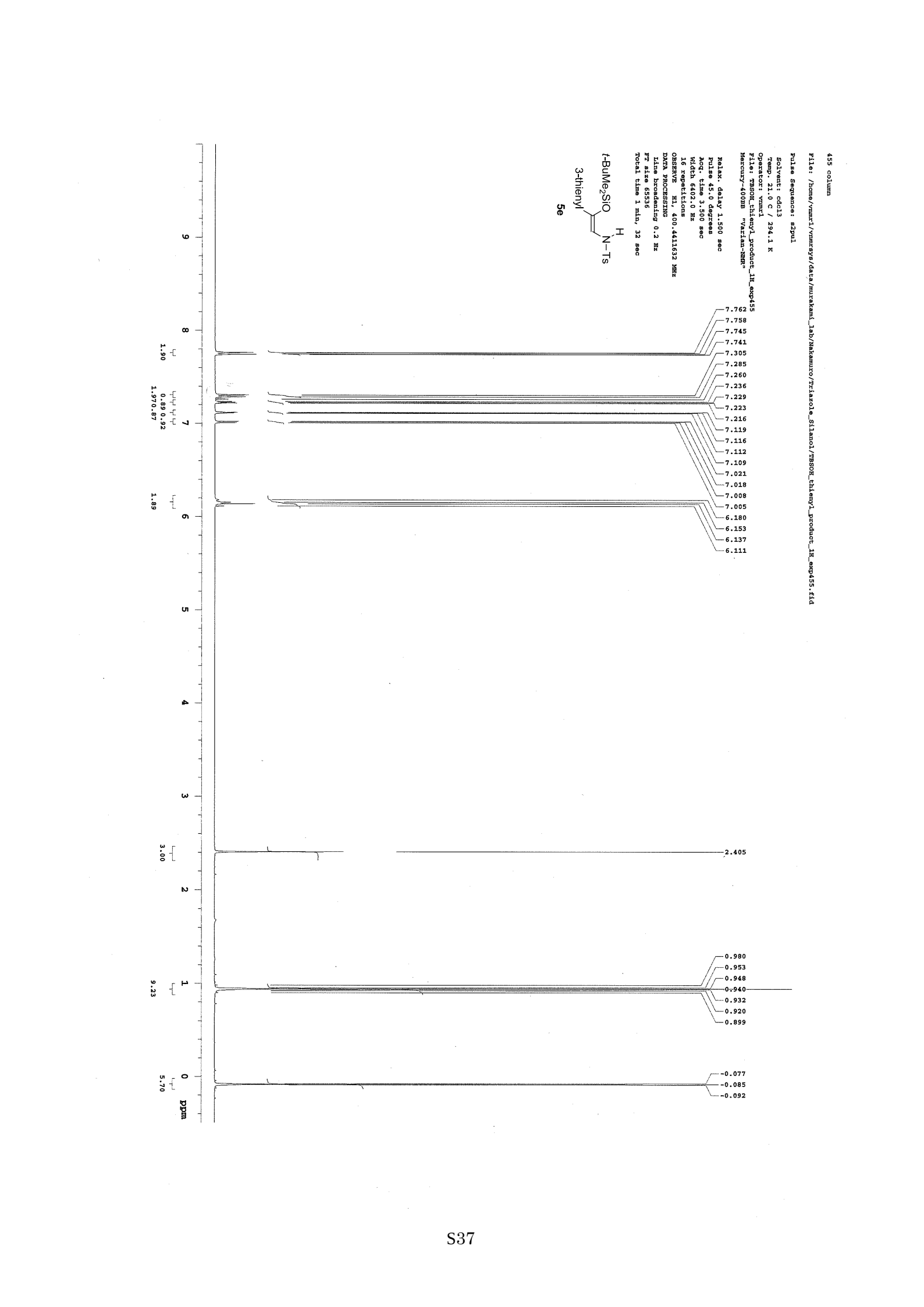
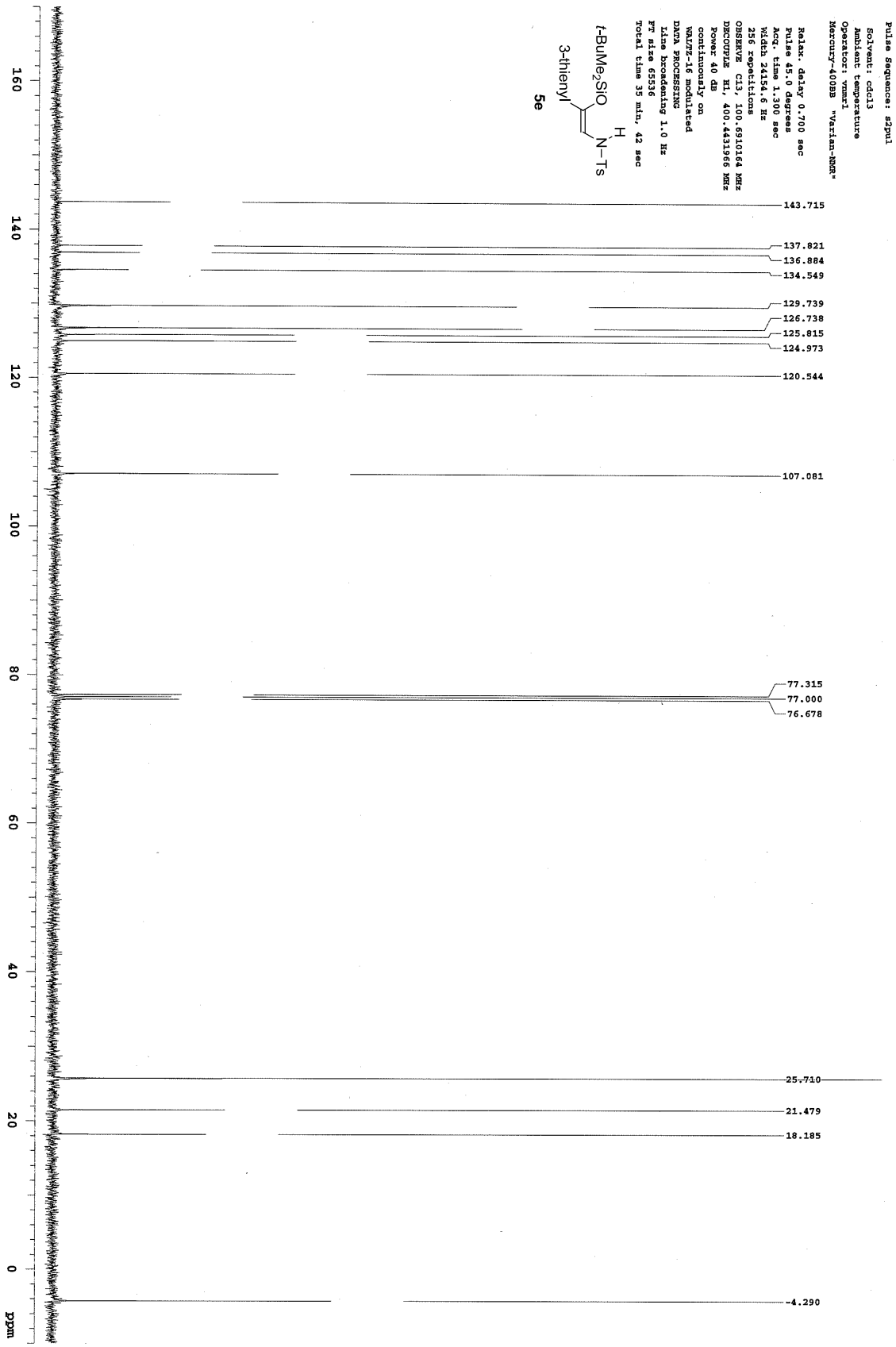
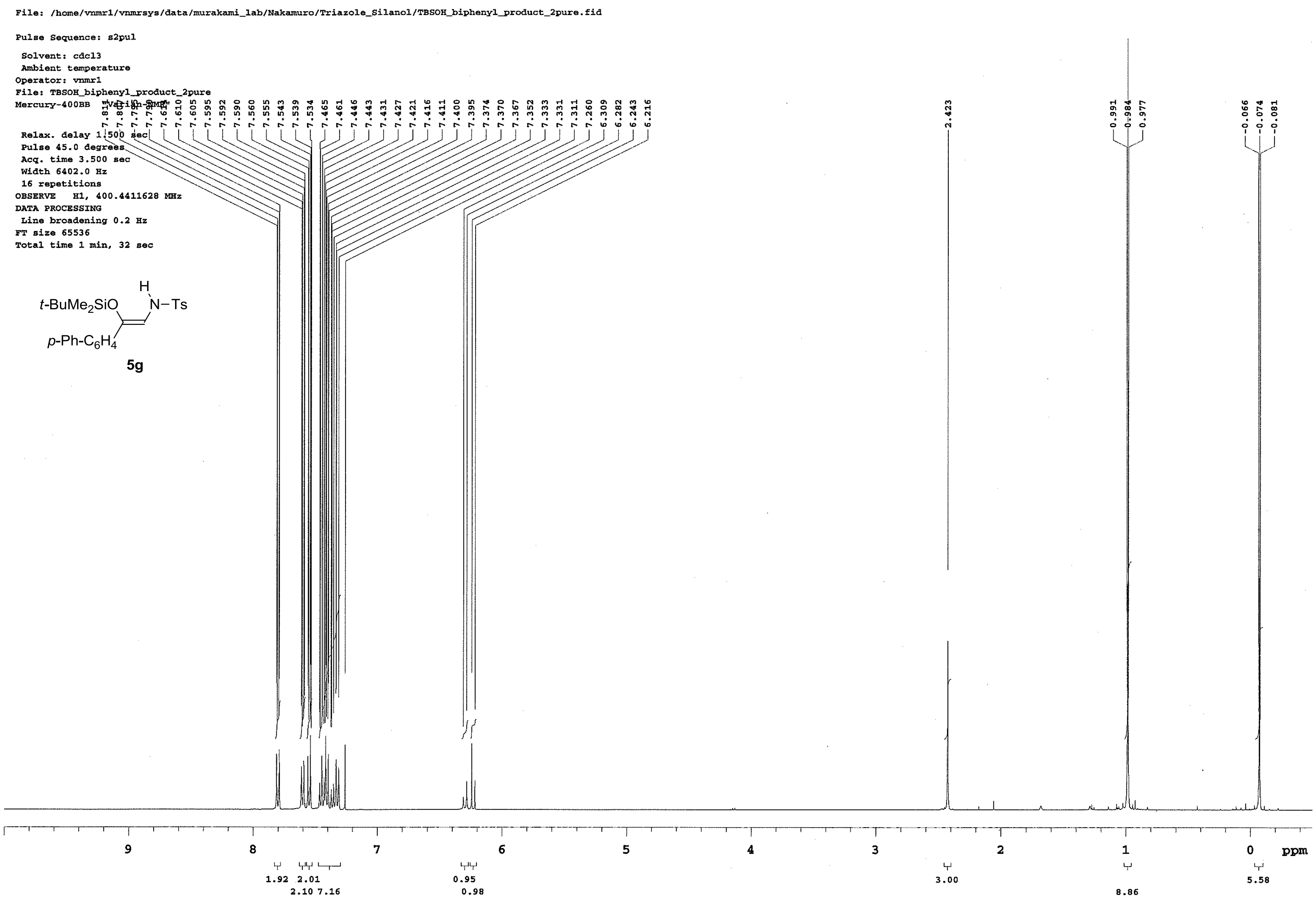
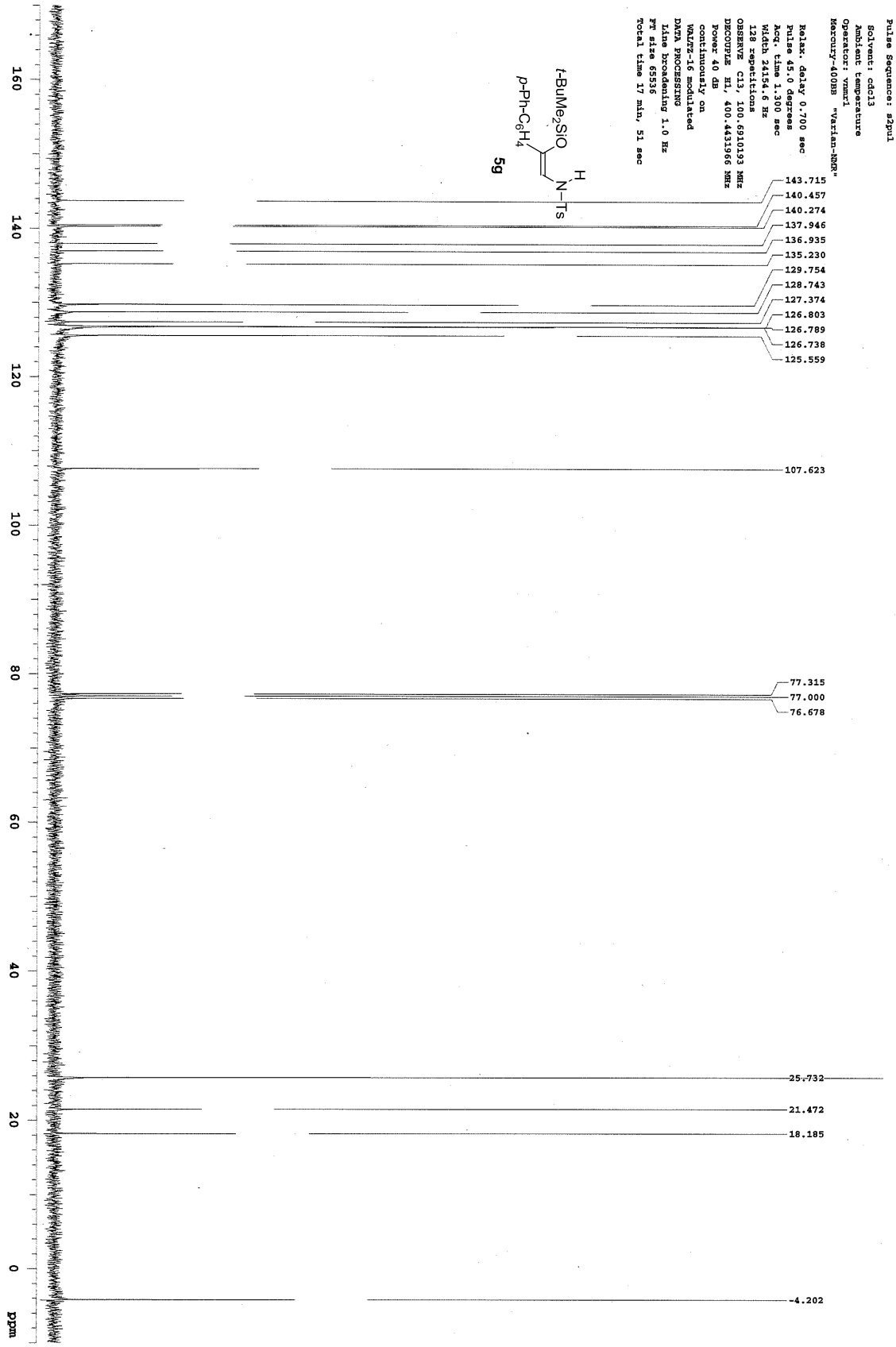
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: TBSOH_trifluoro_product_13C_3
Mercury-400BB "VarianMercury
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
15168 repetitions
OBSERVE C13, 100.6910112 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 58 hr, 7 min, 7 sec
t-BuMe2SiO
H
N–Ts
p-CF3-C6H4
5d
143.997
139.963
136.899
136.445
130.420
130.003
129.878
129.673
129.351
129.029
128.070
126.752
126.606
126.430
125.647
125.610
125.369
125.317
125.281
125.244
125.208
125.046
122.667
119.966
109.453
77.322
77.198
77.000
76.685
25.835
25.681
25.593
25.527
21.508
18.214
18.177
-3.932
-4.210
160
140
120
100
80
60
40
20
0
ppm


455 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/Triazole_Silanol/TBSOH_thienyl_product_1H_exp455.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 21.0 C / 294.1 K
Operator: vnmr1
File: TBSOH_thienyl_product_1H_exp455
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411632 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
H
N–Ts
3-thienyl
5e
7.762
7.758
7.745
7.741
7.305
7.285
7.260
7.236
7.229
7.223
7.216
7.119
7.116
7.112
7.109
7.021
7.018
7.008
7.005
6.180
6.153
6.137
6.111
2.405
0.980
0.953
0.948
0.940
0.932
0.920
0.899
-0.077
-0.085
-0.092
1.90
0.89
0.92
1.97
0.87
1.89
3.00
9.23
5.70
ppm


34crude is
file: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrl
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
256 repetitions
OBSERVE C13, 100.6910164 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec
t-BuMe2SiO
H
N–Ts
3-thienyl
5e
143.715
137.821
136.884
134.549
129.739
126.738
125.815
124.973
120.544
107.081
77.315
77.000
76.678
25.710
21.479
18.185
-4.290
160
140
120
100
80
60
40
20
0
ppm


File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/Triazole_Silanol/TBSOH_biphenyl_product_2pure.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: TBSOH_biphenyl_product_2pure
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411628 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
7.610 7.605 7.595 7.592 7.590 7.560 7.555 7.543 7.539 7.534 7.465 7.461 7.446 7.443 7.431 7.427 7.421 7.416 7.411 7.400 7.395 7.374 7.370 7.367 7.352 7.333 7.331 7.311 7.260 6.309 6.282 6.243 6.216
2.423
0.991 0.984 0.977
-0.066 -0.074 -0.081
t-BuMe2SiO
H
N–Ts
p-Ph-C6H4
5g
9 8 7 6 5 4 3 2 1 0 ppm
1.92 2.01 2.10 7.16
0.95 0.98
3.00
8.86
5.58


File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910193 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
t-BuMe2SiO
p-Ph-C6H4
H
N
Ts
5g
143.715
140.457
140.274
137.946
136.935
135.230
129.754
128.743
127.374
126.803
126.789
126.738
125.559
107.623
77.315
77.000
76.678
25.732
21.472
18.185
-4.202
160
140
120
100
80
60
40
20
0
ppm

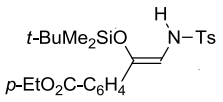
3

File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/Triazole_Silanol/TBSOH_CO2Et_product.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: TBSOH_CO2Et_product
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411626 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



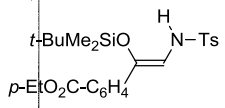
5h

3

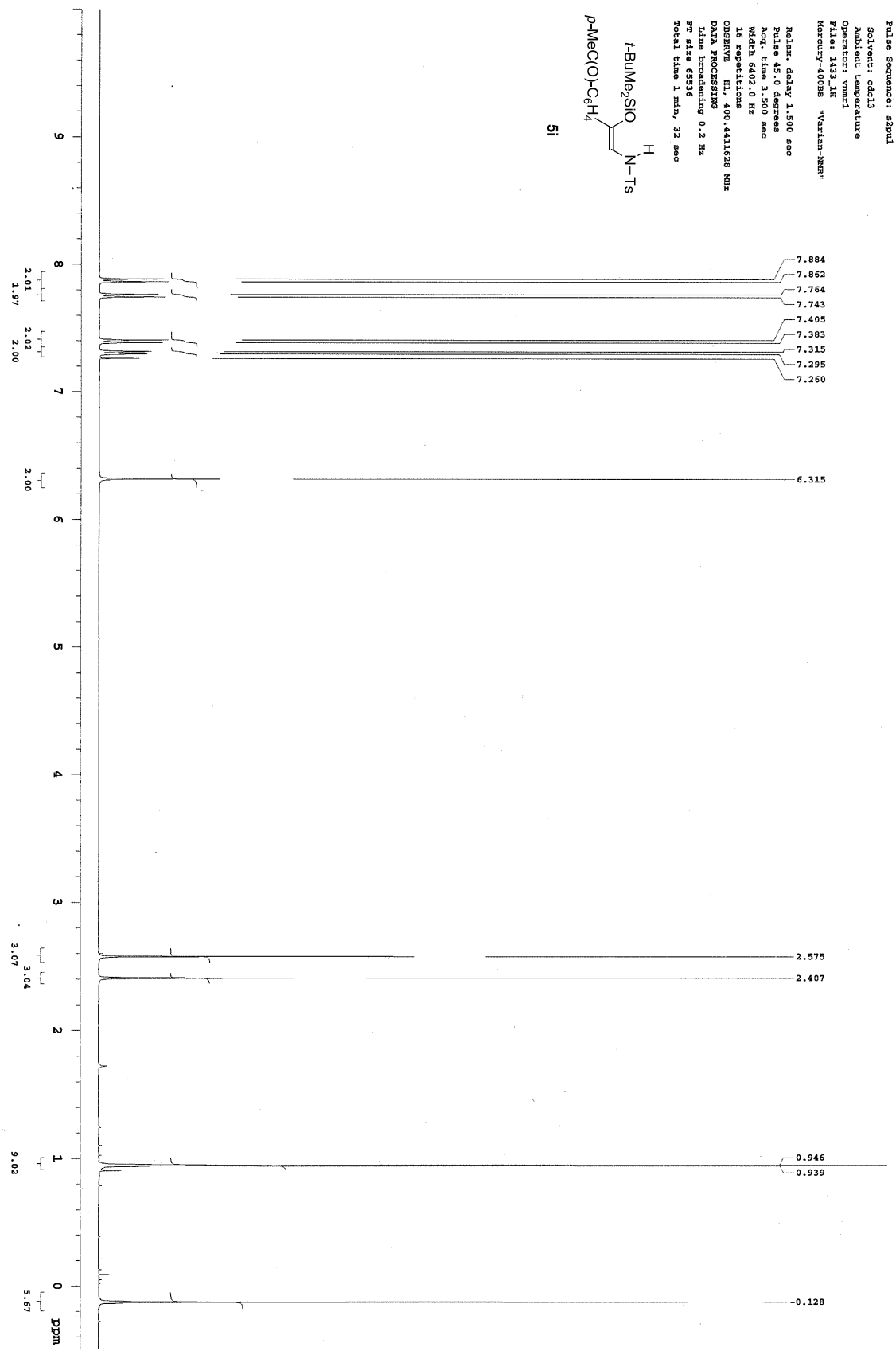
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/Triazole_Silanol/TBSOH_CO2Et_product_13C.fid

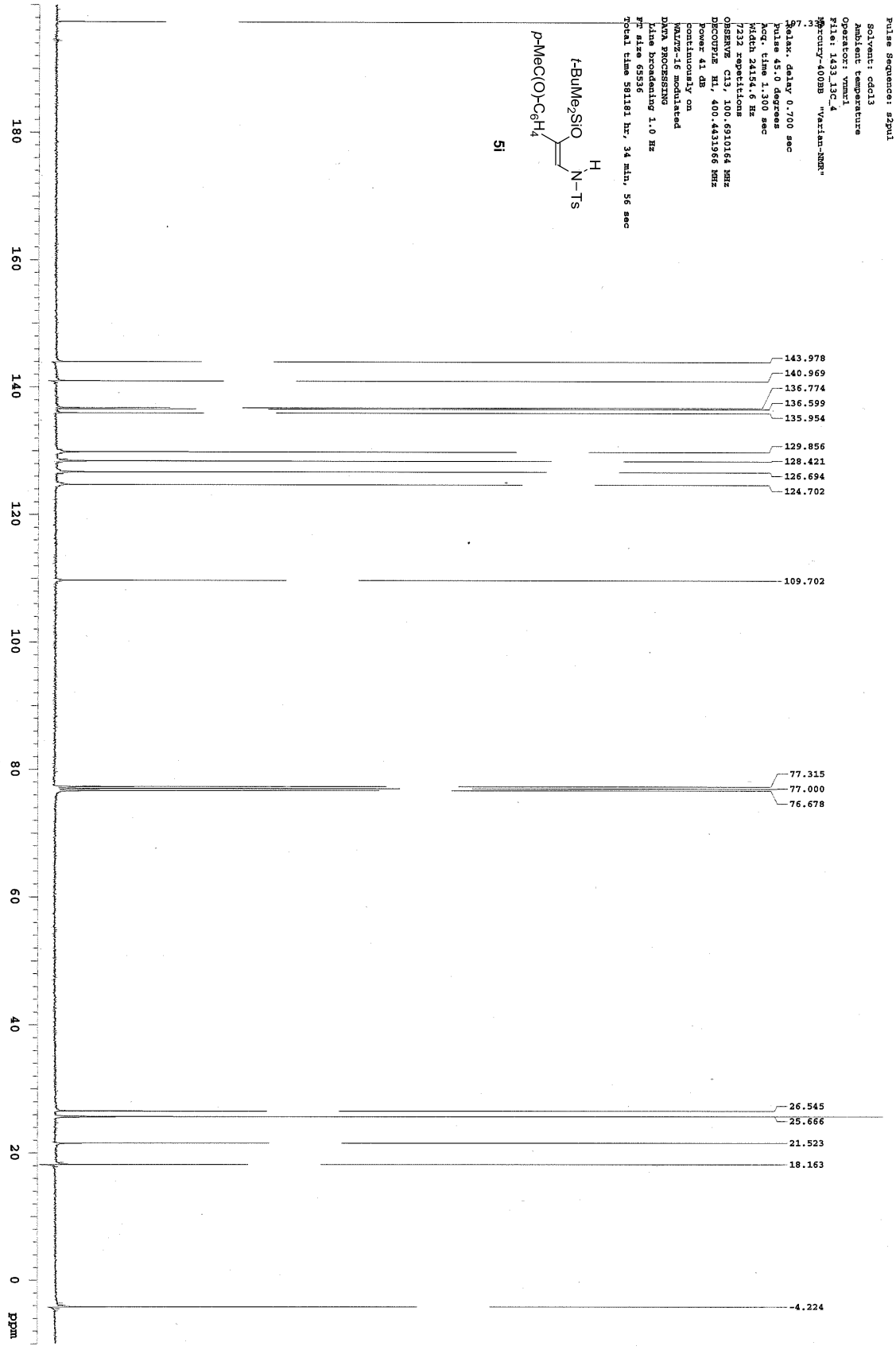
Pulse Sequence: s2pul

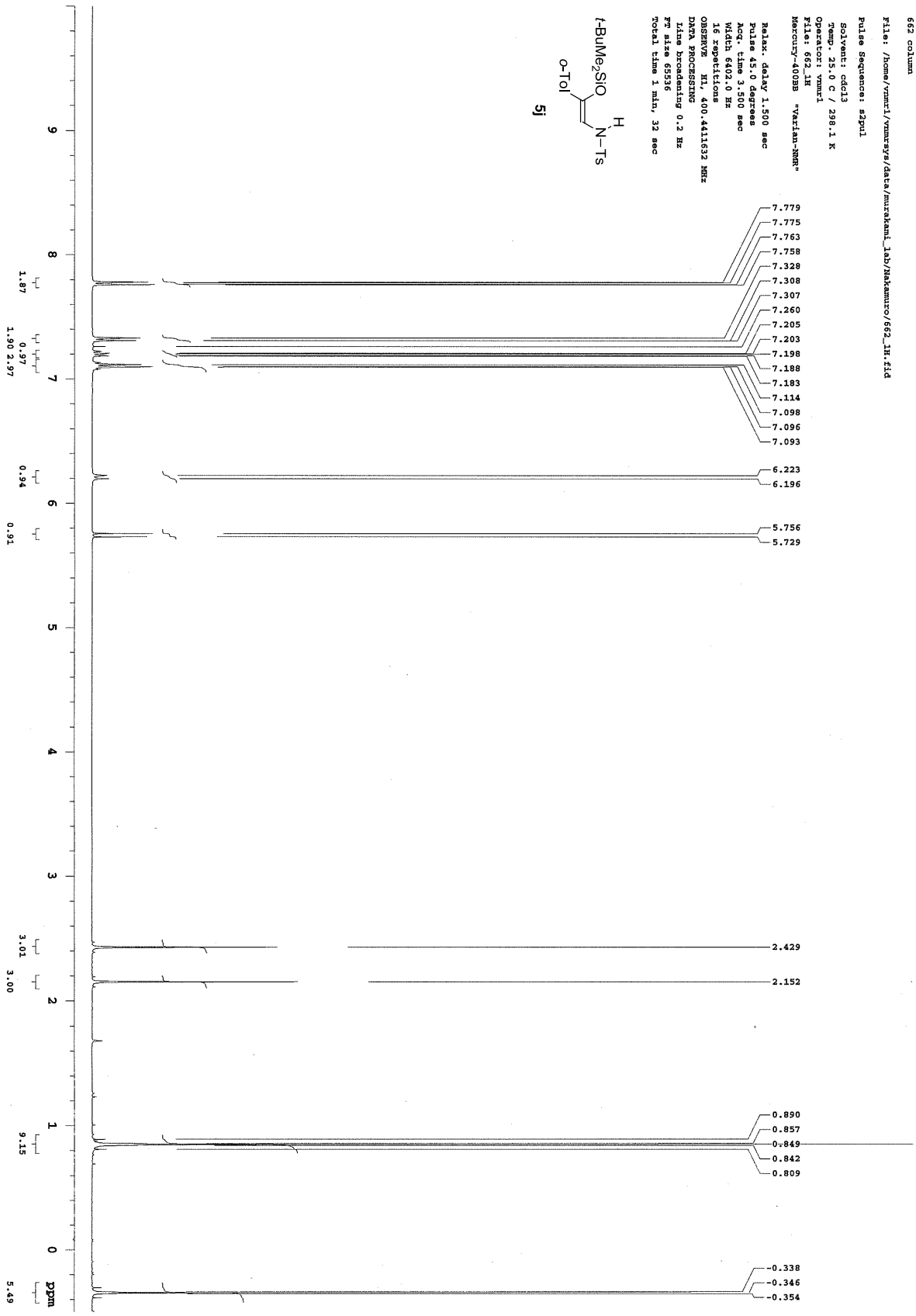
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: TBSOH_CO2Et_product_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
448 repetitions
OBSERVE C13, 100.6910157 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec

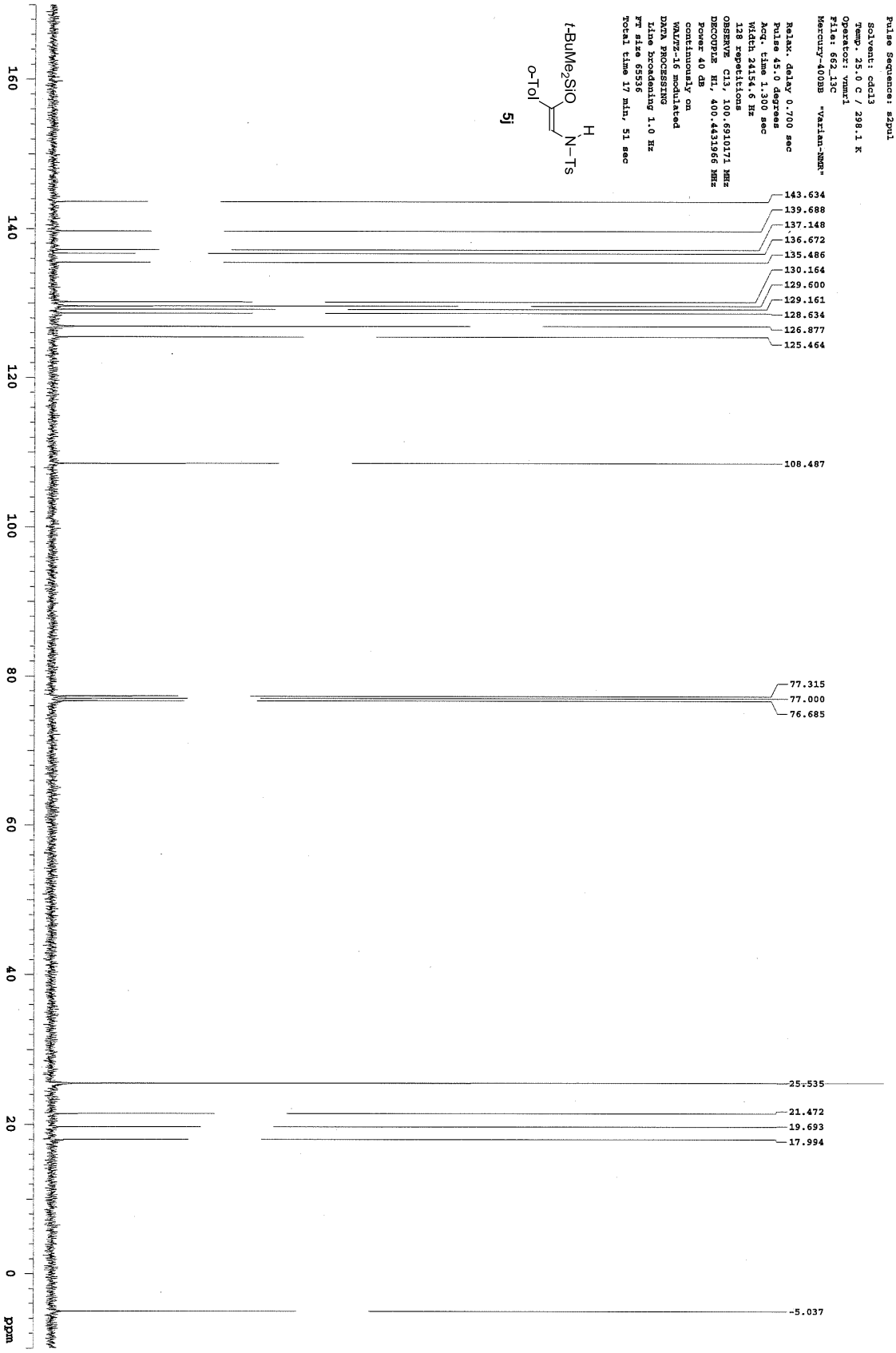


5h


1433 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/1433_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 1433_1H
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411628 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
H
N–Ts
p-MeC(O)-C6H4
5i
7.884
7.862
7.764
7.743
7.405
7.383
7.315
7.295
7.260
6.315
2.575
2.407
0.946
0.939
-0.128
2.01
1.97
2.02
2.00
2.00
3.07
3.04
9.02
5.67
ppm


File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/1433_13C_4.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 1433_13C_4
MERCURY-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
7232 repetitions
OBSERVE C13, 100.6910164 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 581181 hr, 34 min, 56 sec
t-BuMe2SiO
H
N–Ts
p-MeC(O)-C6H4
5i
143.978
140.969
136.774
136.599
135.954
129.856
128.421
126.694
124.702
109.702
77.315
77.000
76.678
26.545
25.666
21.523
18.163
-4.224
ppm


662 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/662_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: 662.1H
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411632 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
o-Tol
H
N–Ts
5j
7.779
7.775
7.763
7.758
7.328
7.308
7.307
7.260
7.205
7.203
7.198
7.188
7.183
7.114
7.098
7.096
7.093
6.223
6.196
5.756
5.729
2.429
2.152
0.890
0.857
0.849
0.842
0.809
-0.338
-0.346
-0.354
1.87
0.97
1.90 2.97
0.94
0.91
3.01
3.00
9.15
5.49
ppm


662 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/662_13C.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: 662_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910171 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
t-BuMe2SiO
H
N–Ts
o-Tol
5j
143.634
139.688
137.148
136.672
135.486
130.164
129.600
129.161
128.634
126.877
125.464
108.487
77.315
77.000
76.685
25.535
21.472
19.693
17.994
-5.037
160
140
120
100
80
60
40
20
0
ppm

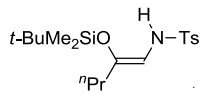
851 column

File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/851.fid

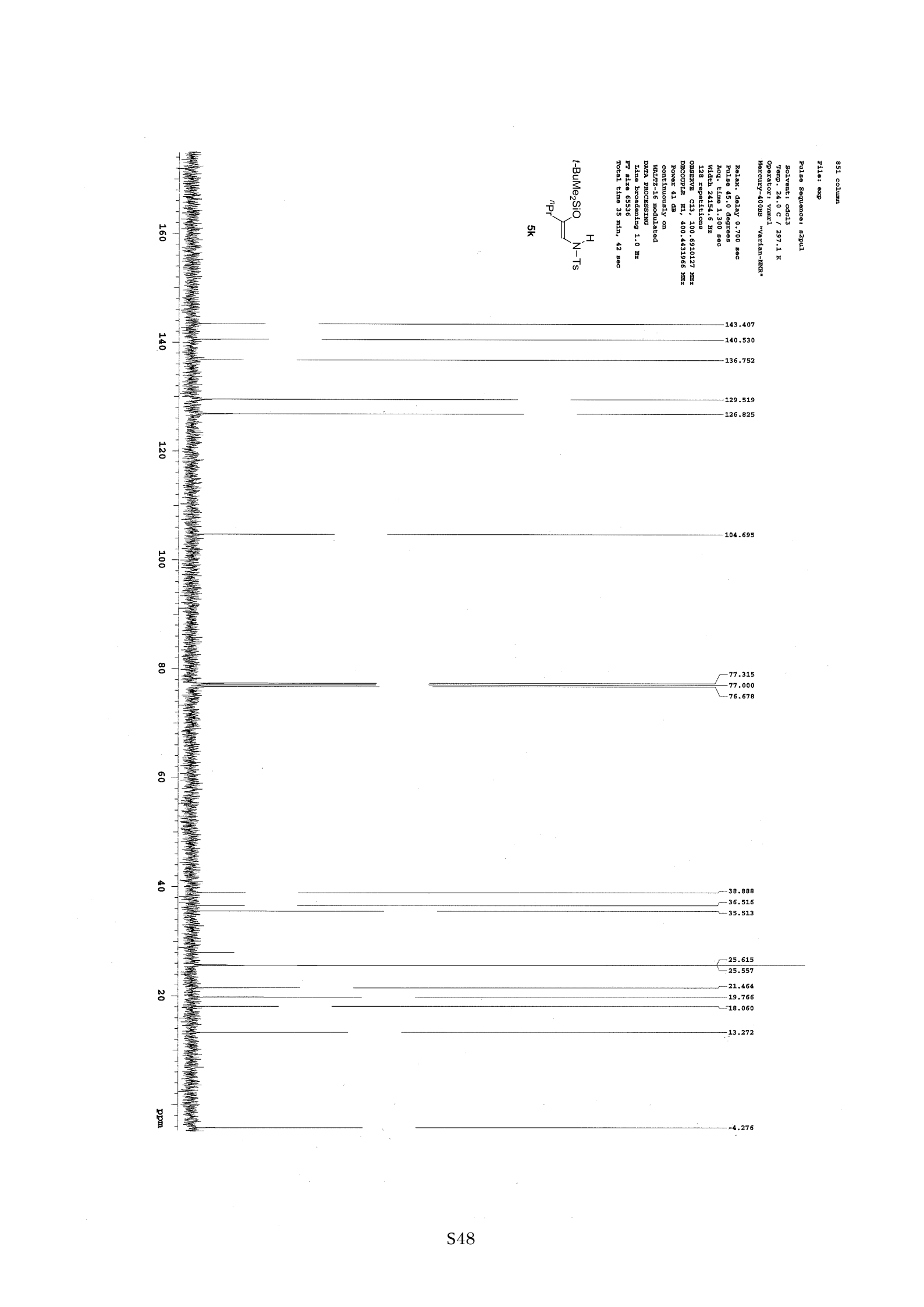
Pulse Sequence: s2pul

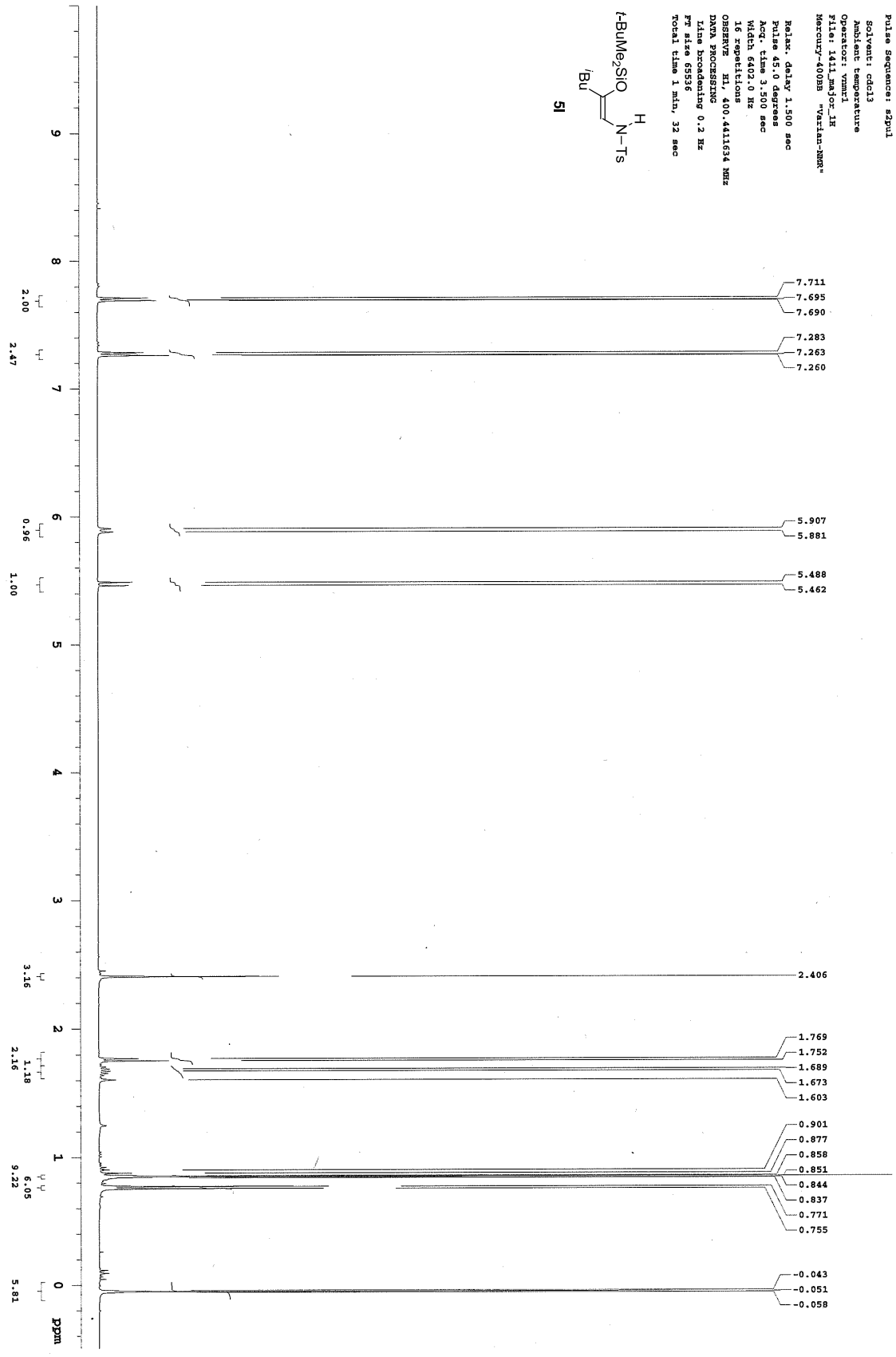
Solvent: cdcl3
Temp. 24.0 C / 297.1 K
Operator: vnmr1
File: 851
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



5k


851 column
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 24.0 C / 297.1 K
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910127 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec
t-BuMe2SiO
nPr
H
N
Ts
5k
143.407
140.530
136.752
129.519
126.825
104.695
77.315
77.000
76.678
38.888
36.516
35.513
25.615
25.557
21.464
19.766
18.060
13.272
-4.276
160
140
120
100
80
60
40
20
ppm


1411 column major
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/1411_major_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 1411_major_1H
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411634 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
iBu
H
N–Ts
5l
7.711
7.695
7.690
7.283
7.263
7.260
5.907
5.881
5.488
5.462
2.406
1.769
1.752
1.689
1.673
1.603
0.901
0.877
0.858
0.851
0.844
0.837
0.771
0.755
-0.043
-0.051
-0.058
2.00
2.47
0.96
1.00
3.16
1.18
2.16
6.05
9.22
5.81
ppm

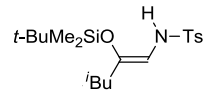
1411 column major

File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/1411_major_13C.fid

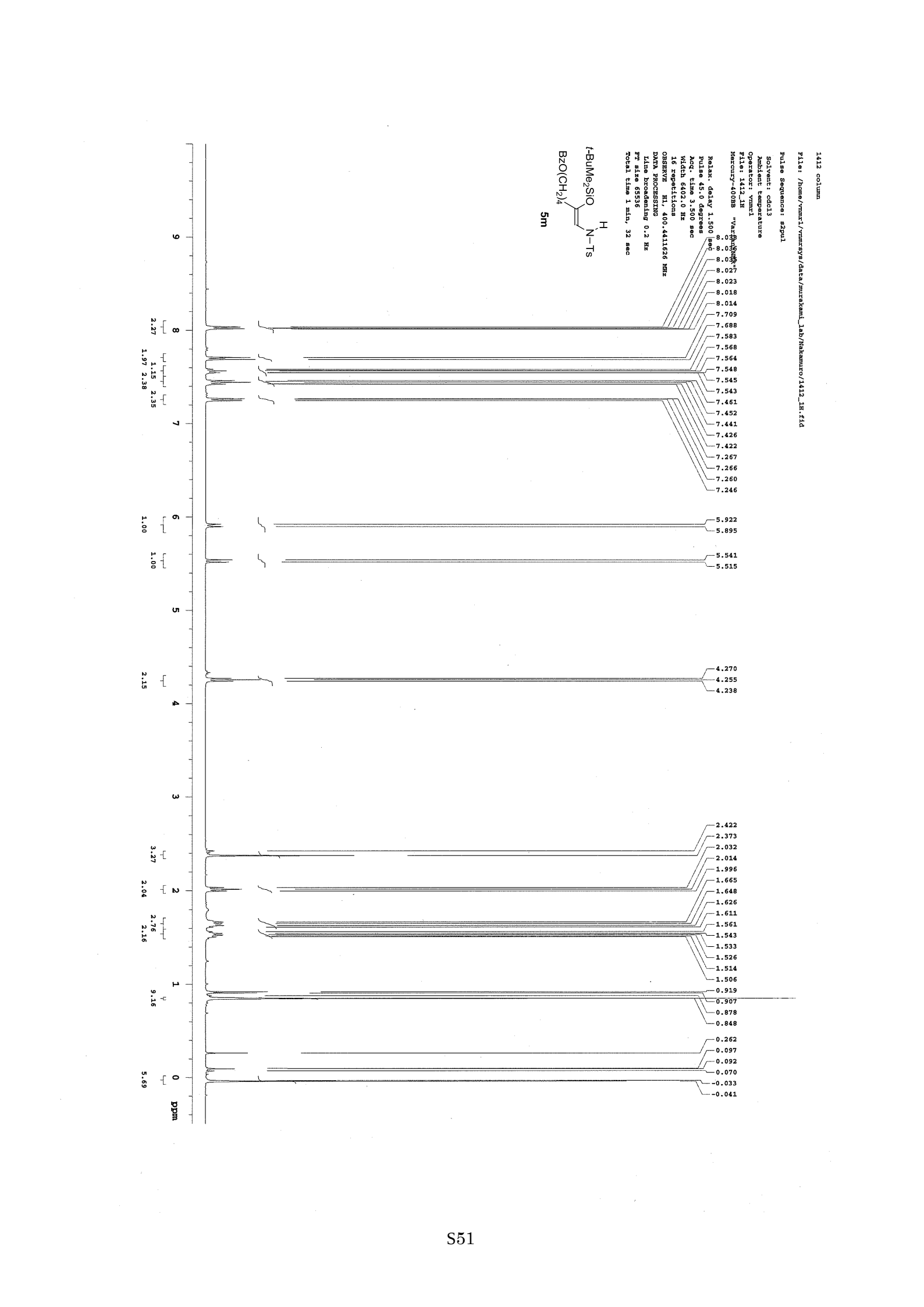
Pulse Sequence: s2pul

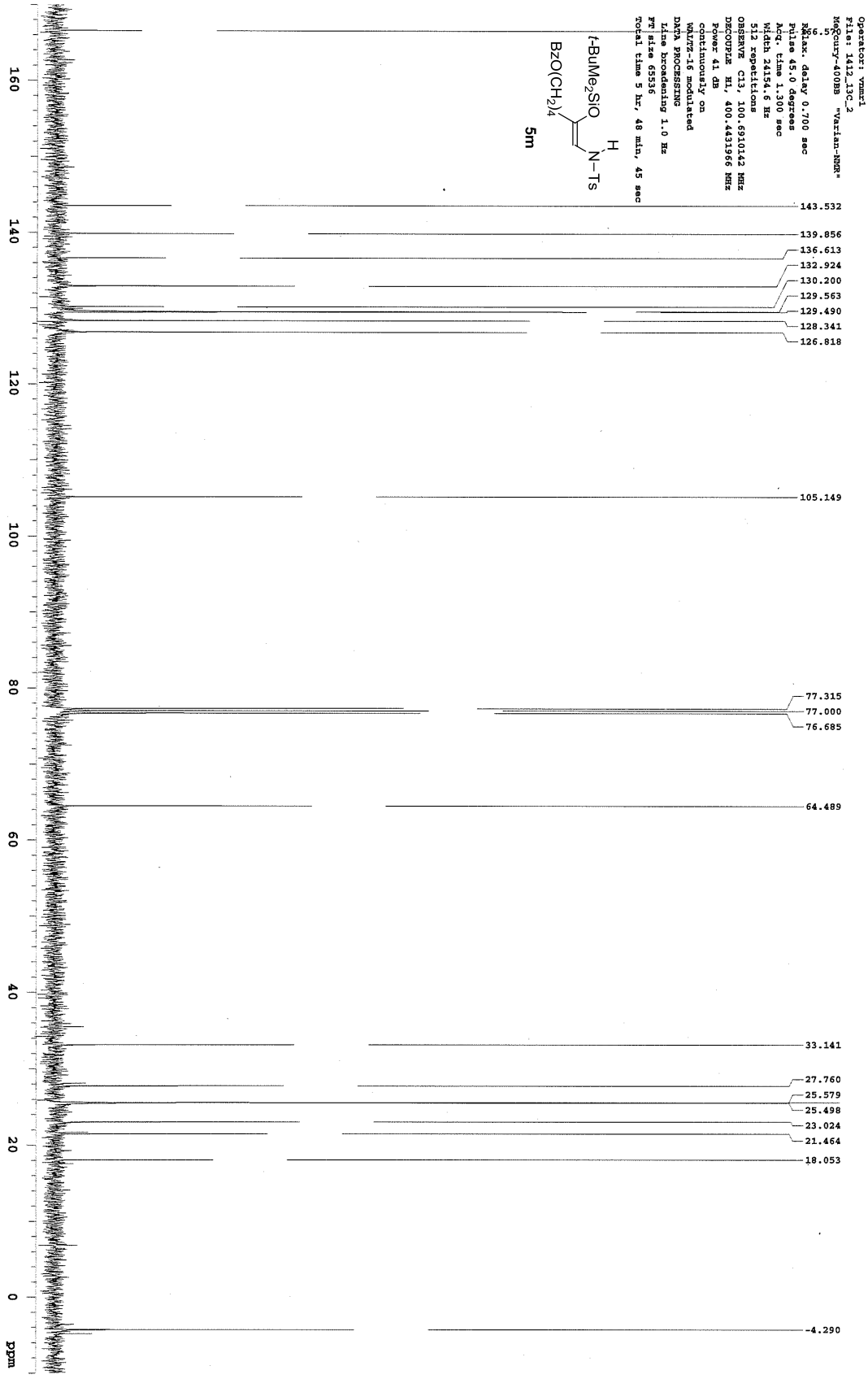
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 1411_major_13C
Mercury-400BB "Varian-NMR"

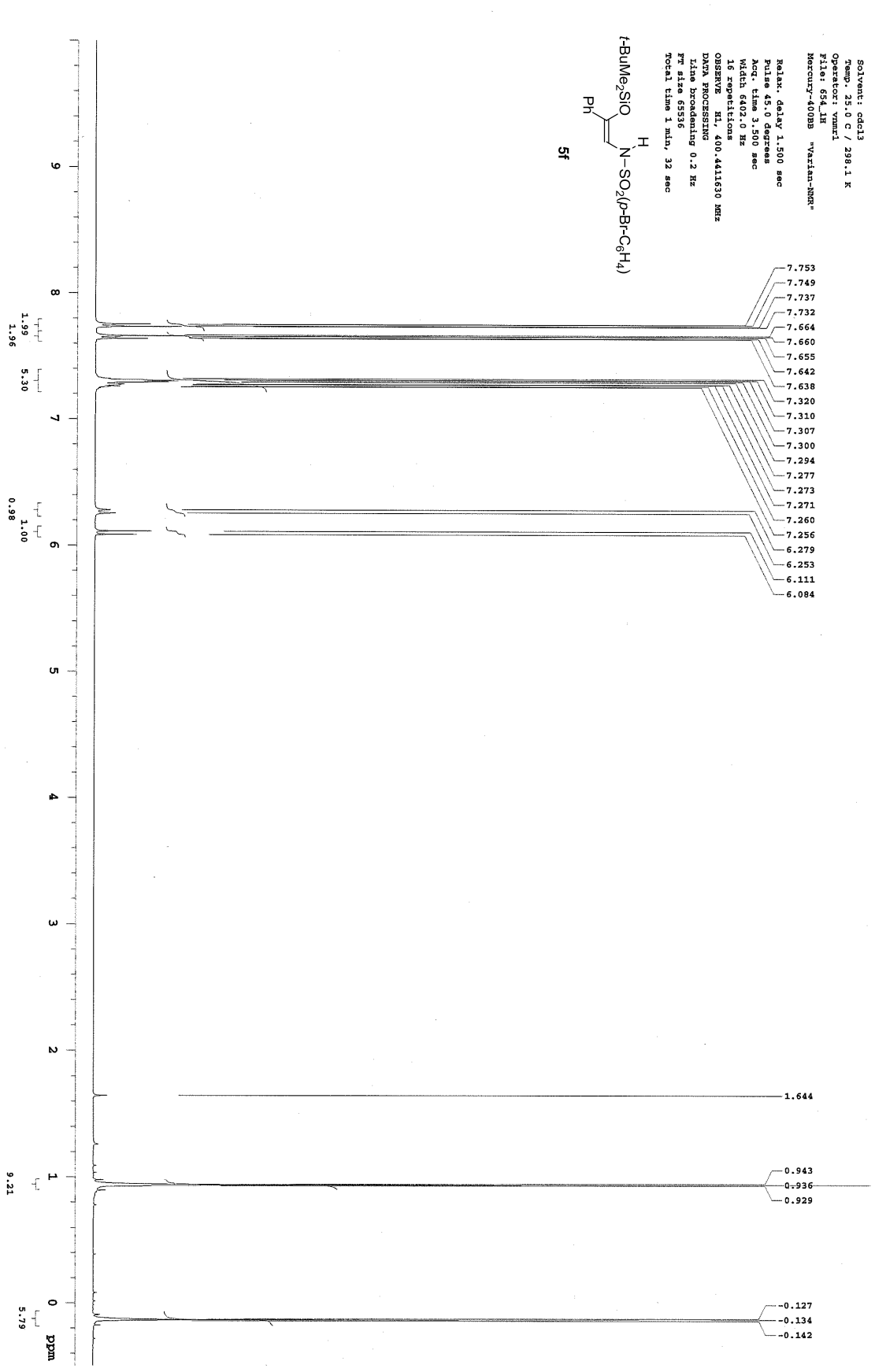
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
192 repetitions
OBSERVE C13, 100.6910134 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 5 hr, 48 min, 45 sec

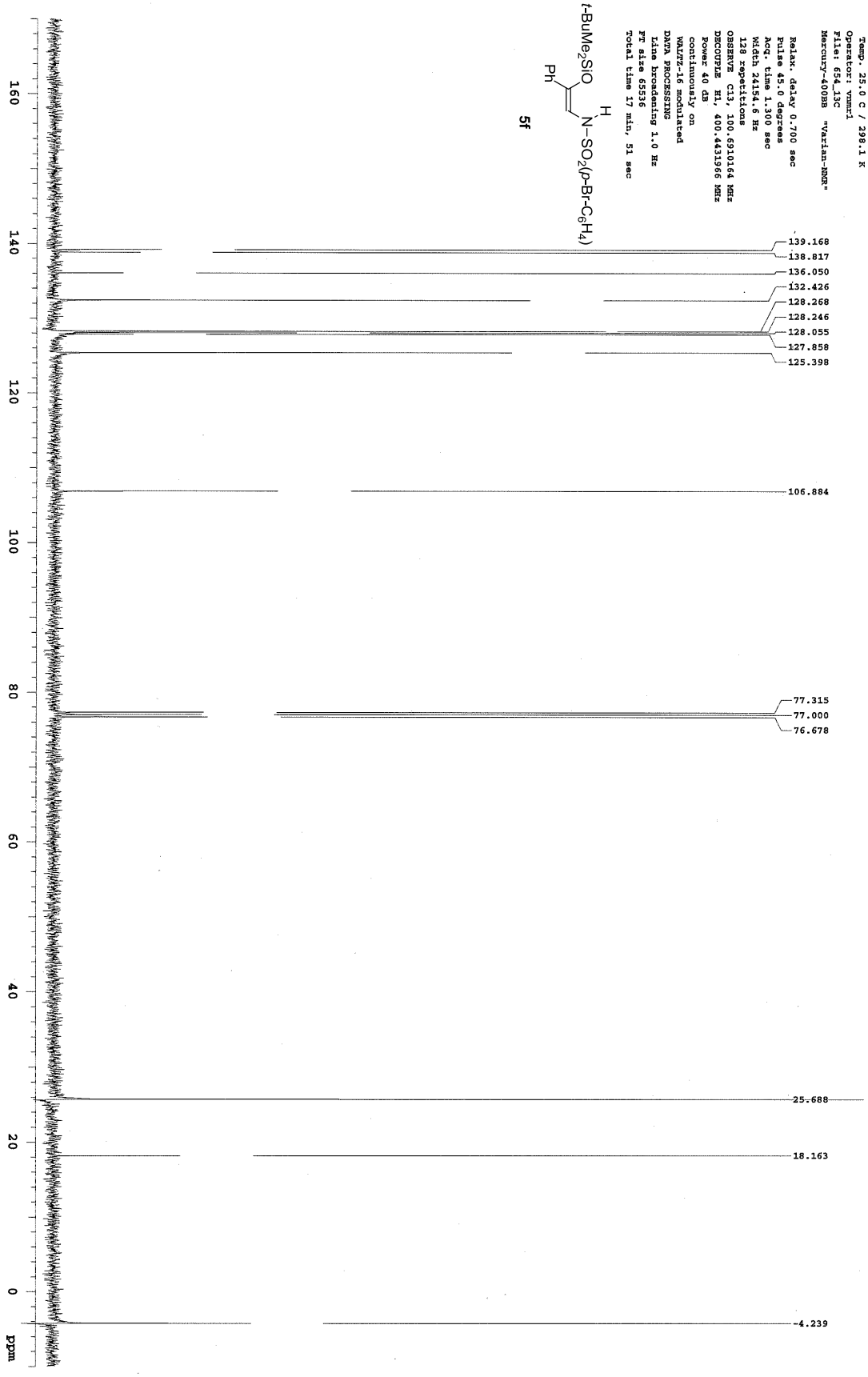


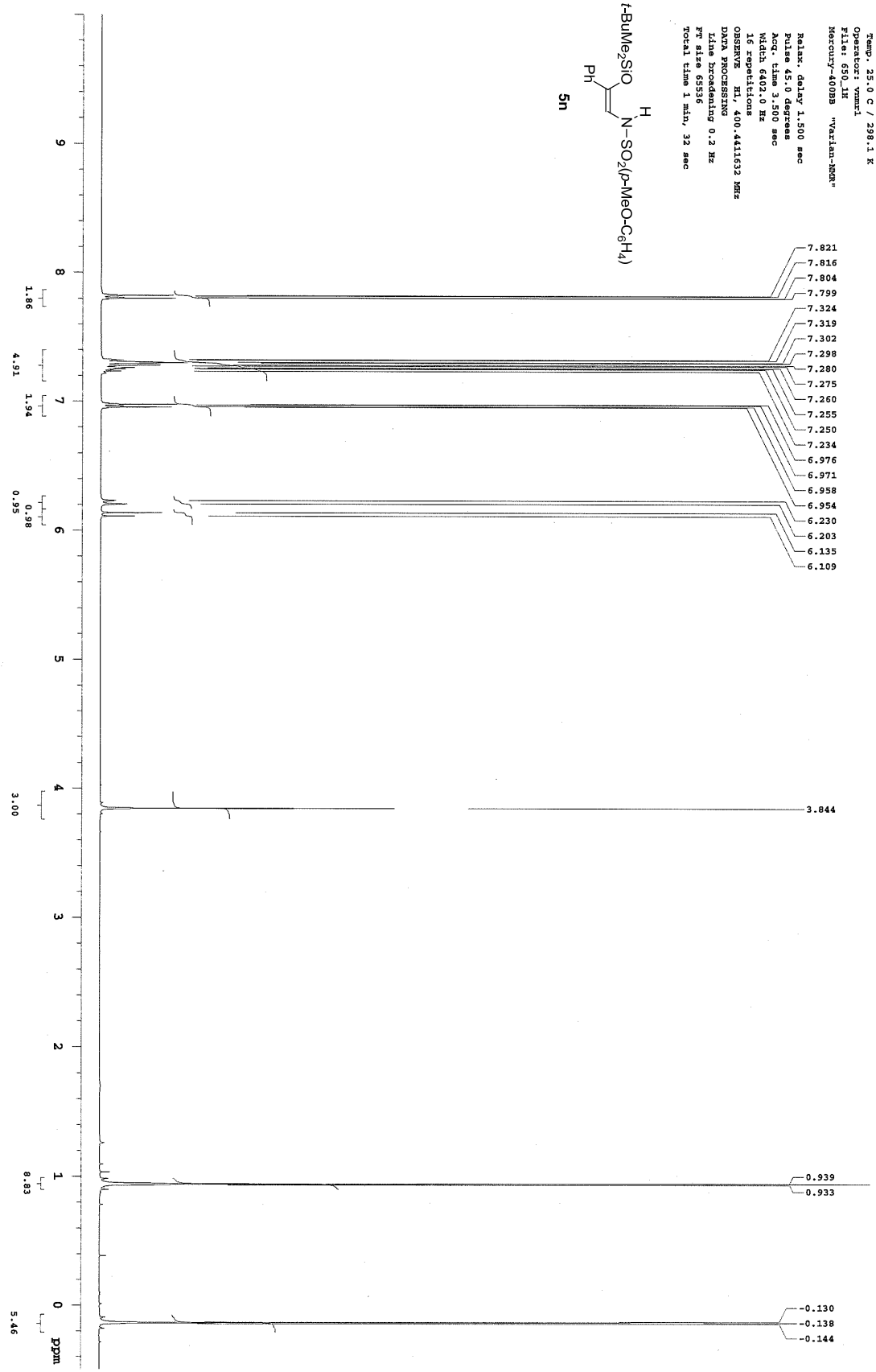
5l

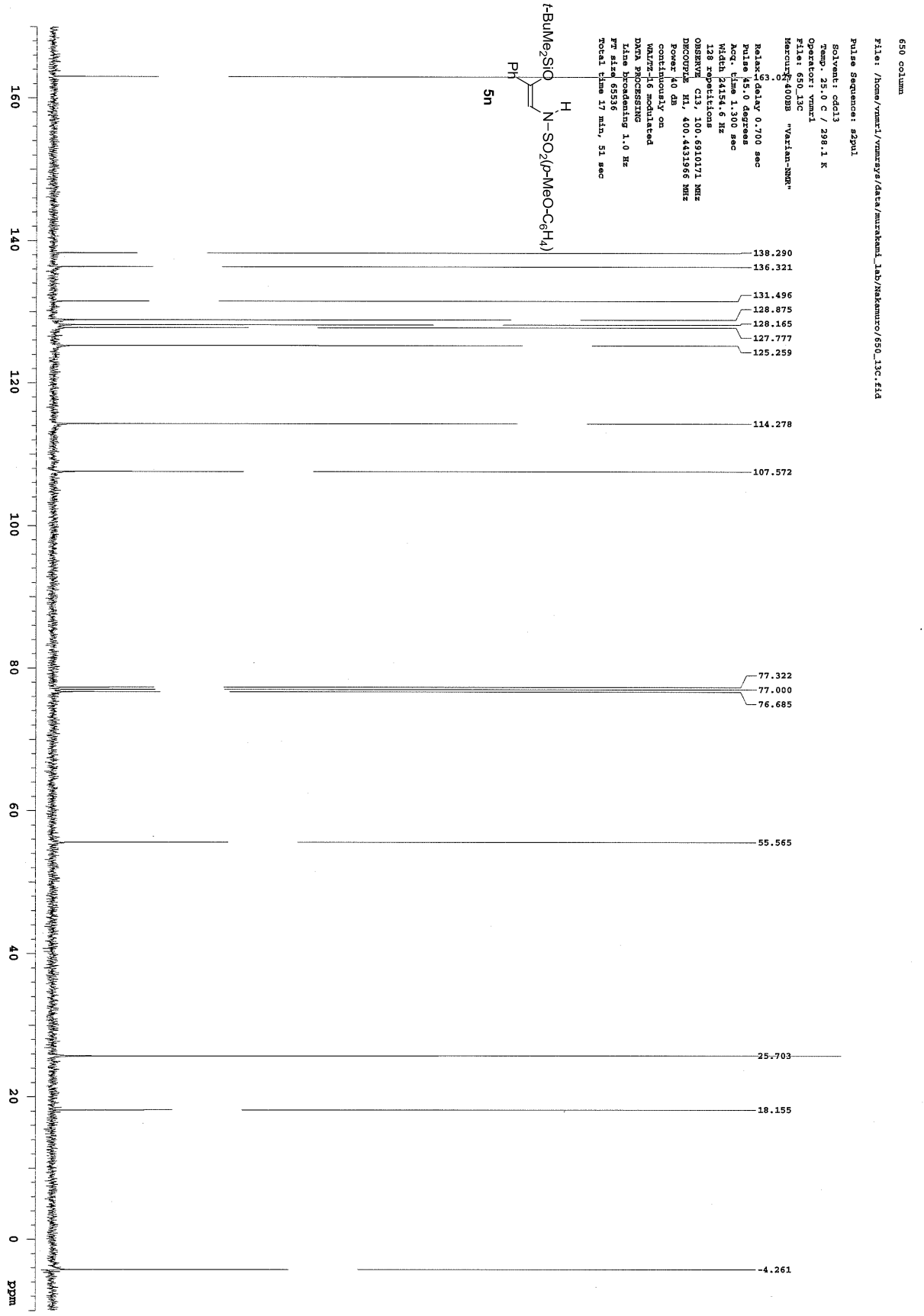

1412 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/1412_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 1412_1H
Mercury-400BB "VarianUser"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411626 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
BzO(CH2)4
H
N–Ts
5m
8.031
8.027
8.023
8.018
8.014
7.709
7.688
7.583
7.568
7.564
7.548
7.545
7.543
7.461
7.452
7.441
7.426
7.422
7.267
7.266
7.260
7.246
5.922
5.895
5.541
5.515
4.270
4.255
4.238
2.422
2.373
2.032
2.014
1.996
1.665
1.648
1.626
1.611
1.561
1.543
1.533
1.526
1.514
1.506
0.919
0.907
0.878
0.848
0.262
0.097
0.092
0.070
-0.033
-0.041
2.27
1.15
2.35
1.97
2.38
1.00
1.00
2.15
3.27
2.04
2.76
2.16
9.16
5.69
ppm

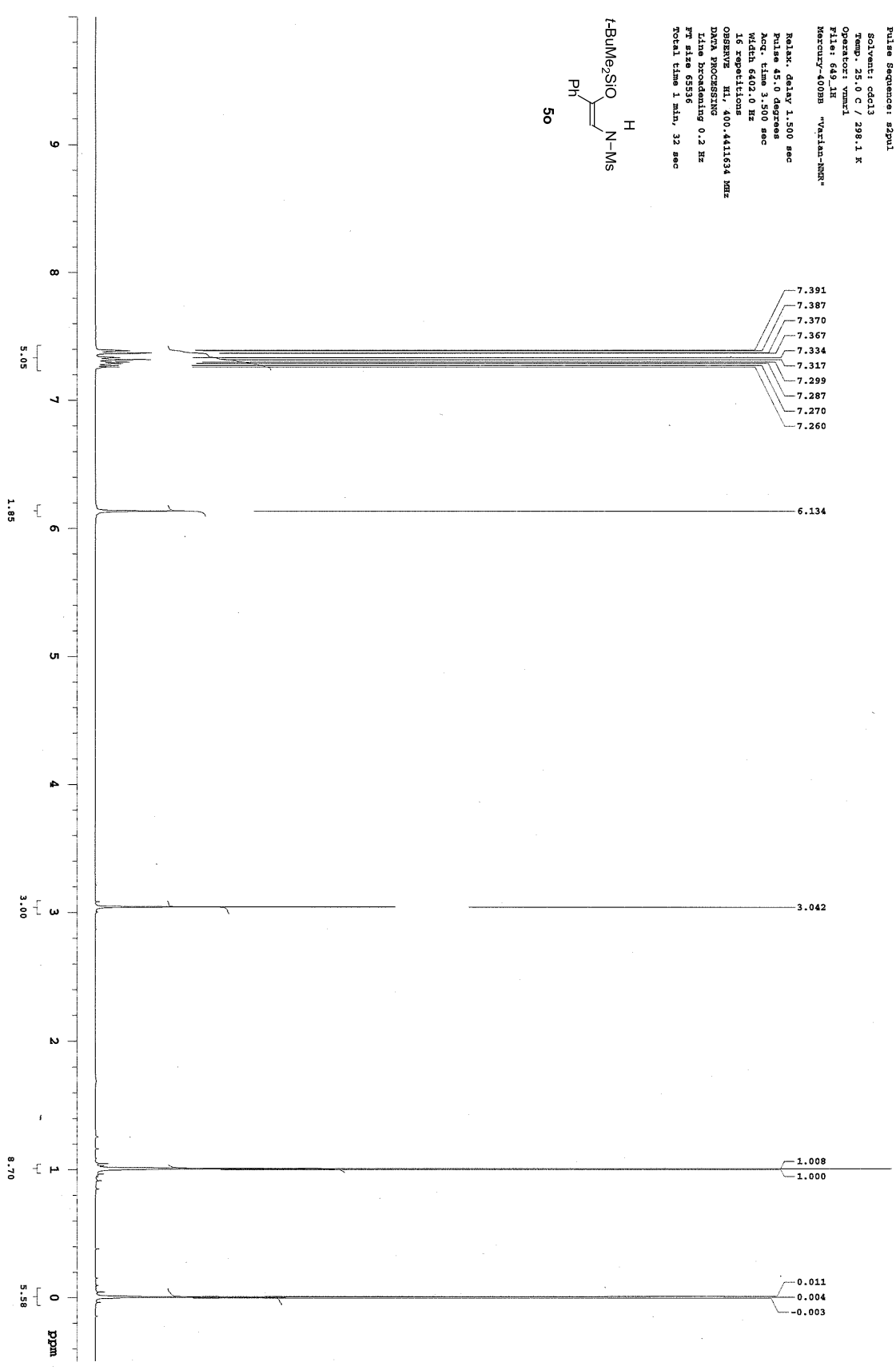

1412 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/1412_13C_2.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 1412_13C_2
Mercury-400BB "Varian-NMR"
6.5
NMax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
512 repetitions
OBSERVE C13, 100.6910142 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 5 hr, 48 min, 45 sec
t-BuMe2SiO
BzO(CH2)4
H
N
Ts
5m
143.532
139.856
136.613
132.924
130.200
129.563
129.490
128.341
126.818
105.149
77.315
77.000
76.685
64.489
33.141
27.760
25.579
25.498
23.024
21.464
18.053
-4.290
160
140
120
100
80
60
40
20
0
ppm

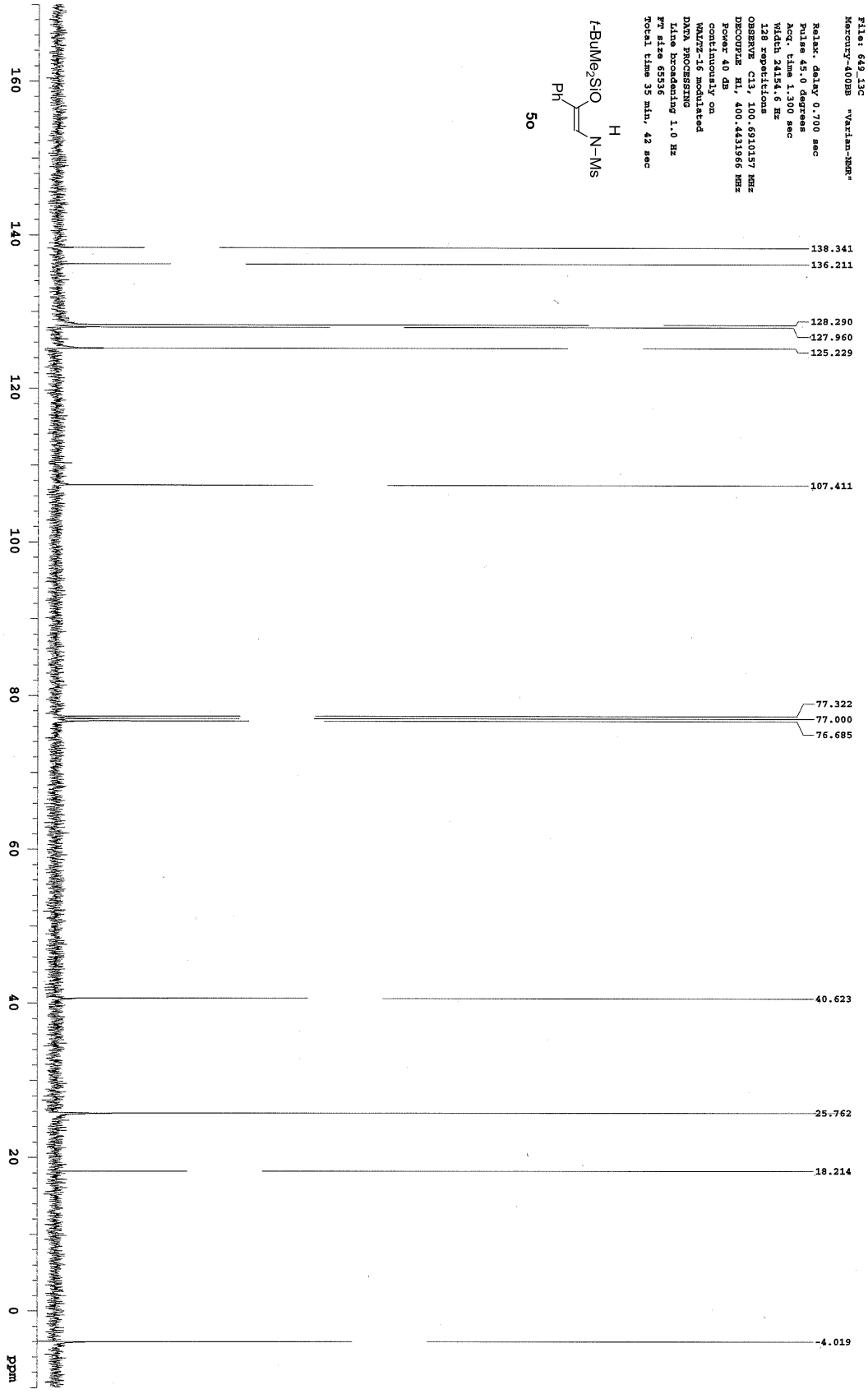

654 column
file: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/654_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: 654_1H
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
Ph
H
N–SO2(p-Br-C6H4)
5f
7.753
7.749
7.737
7.732
7.664
7.660
7.655
7.642
7.638
7.320
7.310
7.307
7.300
7.294
7.277
7.273
7.271
7.260
7.256
6.279
6.253
6.111
6.084
1.644
0.943
0.936
0.929
-0.127
-0.134
-0.142
1.99
5.30
1.96
1.00
0.98
9.21
5.79
ppm

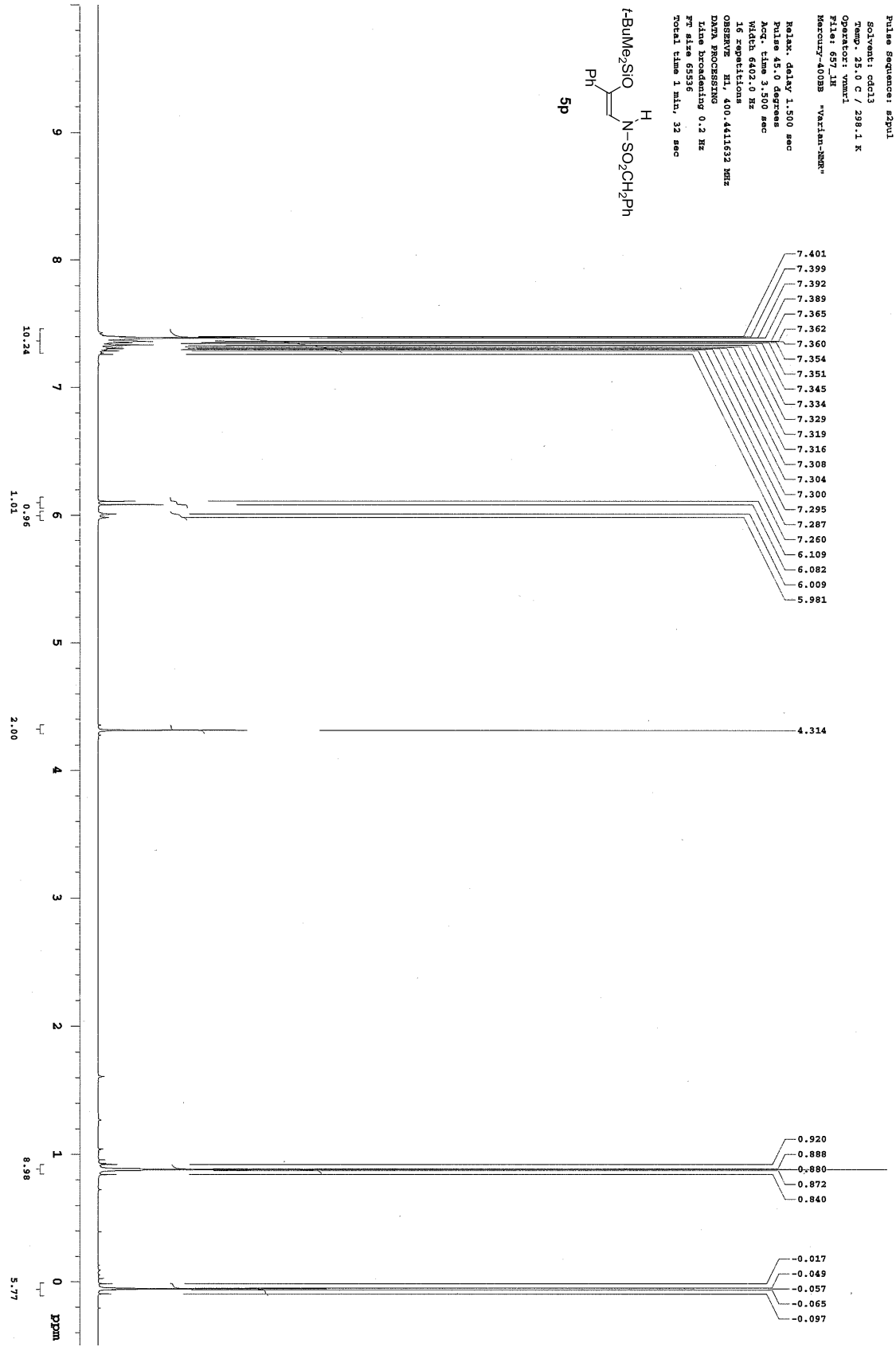

654 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/654_13C.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: 654_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910164 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
t-BuMe2SiO
Ph
H
N–SO2(p-Br-C6H4)
5f
139.168
138.817
136.050
132.426
128.268
128.246
128.055
127.858
125.398
106.884
77.315
77.000
76.678
25.688
18.163
-4.239
160
140
120
100
80
60
40
20
0
ppm

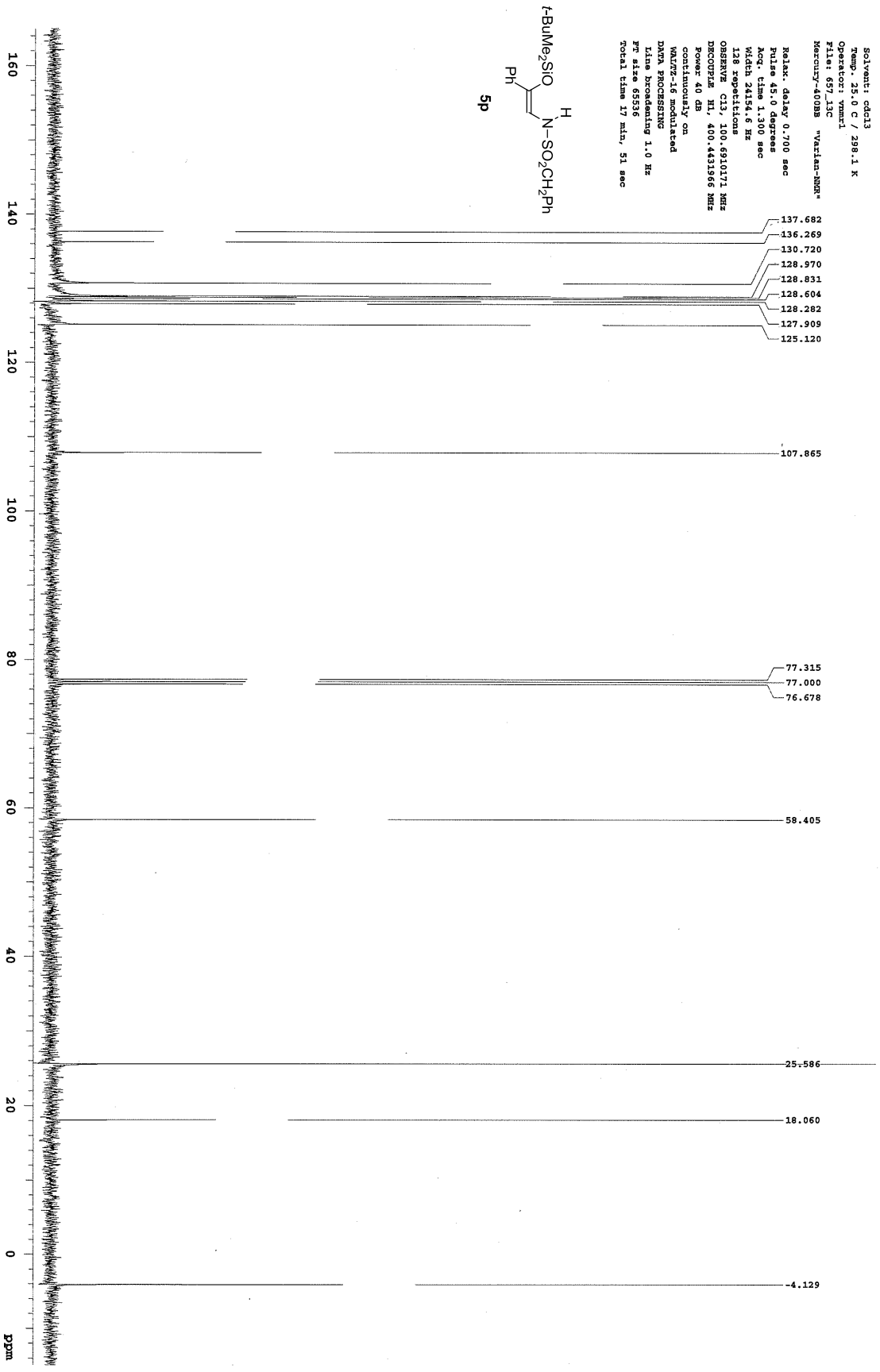

650 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/650_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: 650_1H
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411632 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
Ph
H
N–SO2(p-MeO-C6H4)
5n
7.821
7.816
7.804
7.799
7.324
7.319
7.302
7.298
7.280
7.275
7.260
7.255
7.250
7.234
6.976
6.971
6.958
6.954
6.230
6.203
6.135
6.109
3.844
0.939
0.933
-0.130
-0.138
-0.144
1.86
4.91
1.94
0.98
0.95
3.00
8.83
5.46
ppm

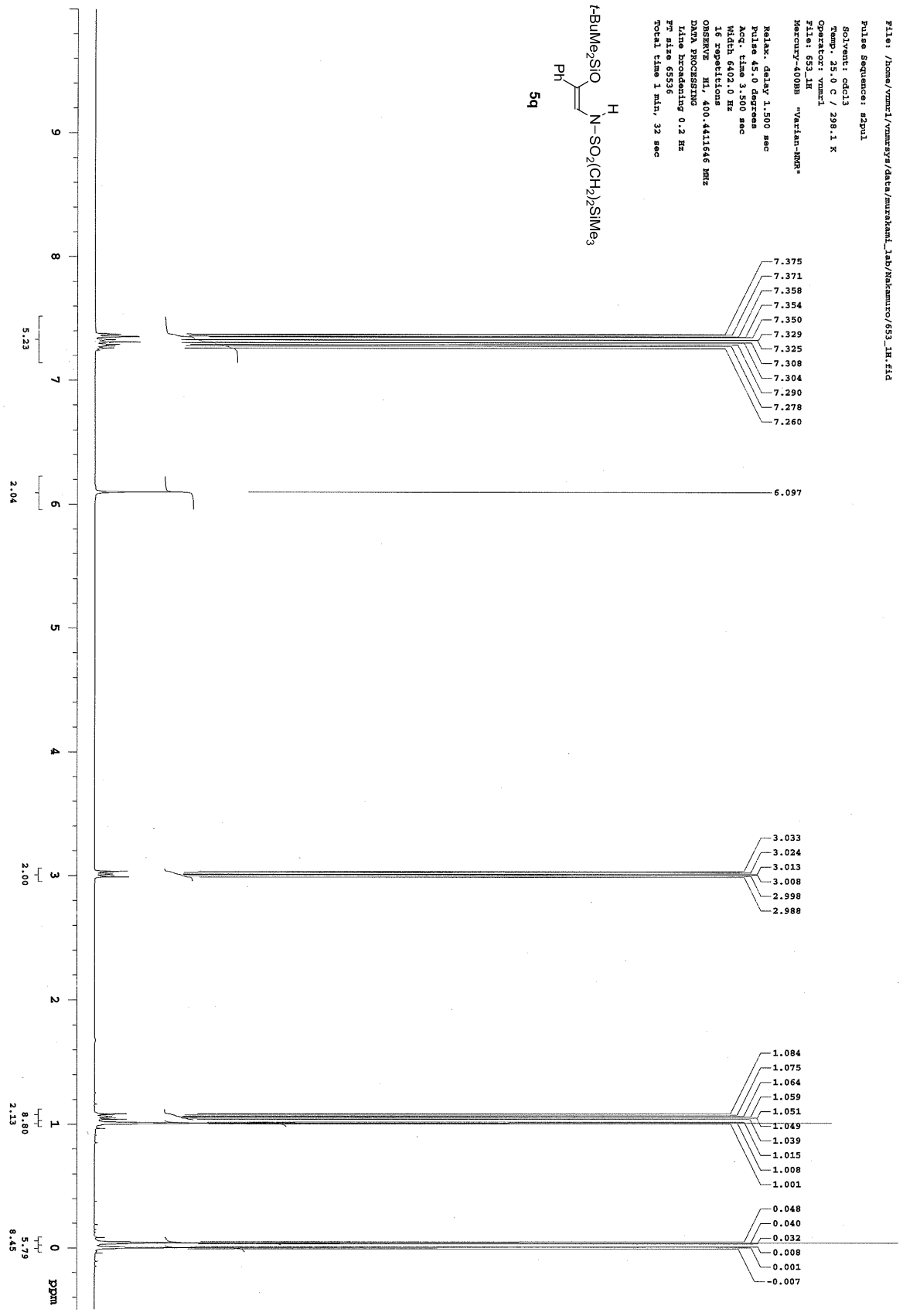

650 column
File: /home/vnmrj/vnmrsys/data/murakami_lab/Nakamuro/650_13C.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmrj
File: 650_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910171 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
t-BuMe2SiO
Ph
H
N–SO2(p-MeO-C6H4)
5n
163.078
138.290
136.321
131.496
128.875
128.165
127.777
125.259
114.278
107.572
77.322
77.000
76.685
55.565
25.703
18.155
-4.261
160
140
120
100
80
60
40
20
0
ppm

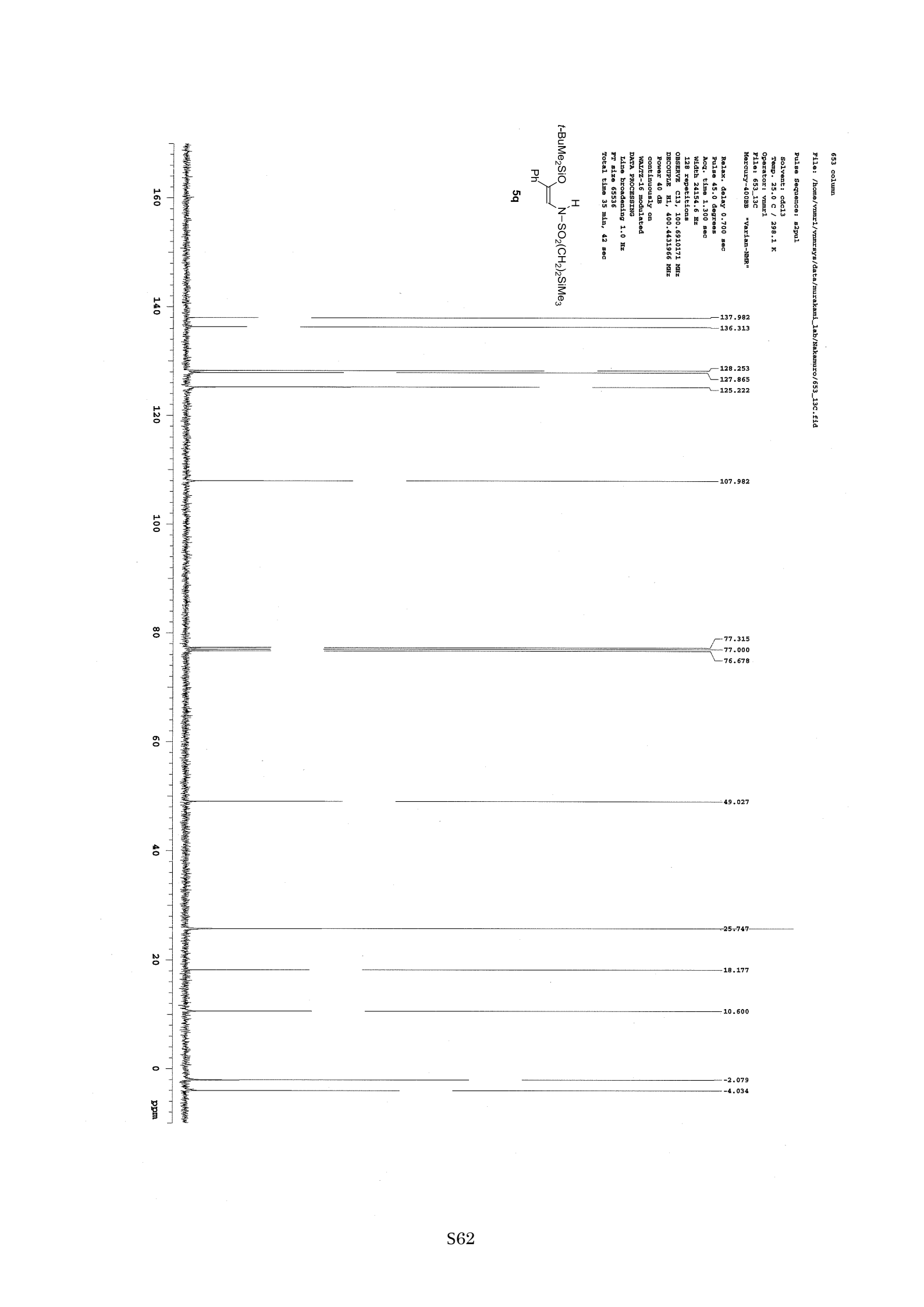

649 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/649_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: 649_1H
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411634 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
Ph
H
N–Ms
5o
7.391
7.387
7.370
7.367
7.334
7.317
7.299
7.287
7.270
7.260
6.134
3.042
1.008
1.000
0.011
0.004
-0.003
5.05
1.85
3.00
8.70
5.58
ppm

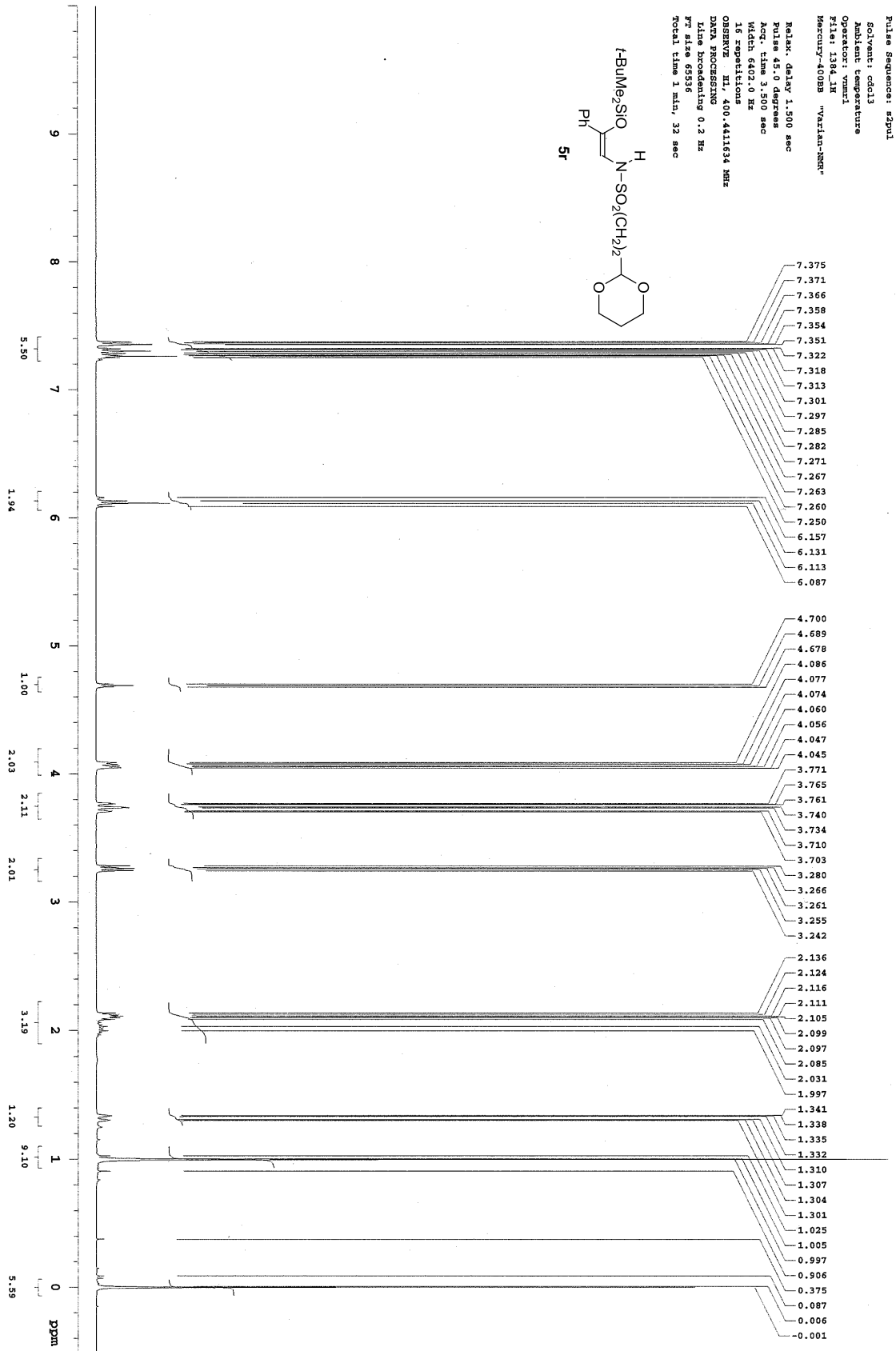

649 column
File: /home/vnmrj1/vnmrsys/data/murakami_lab/Nakamuro/649_13C.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmrj
File: 649_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910157 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec
t-BuMe2SiO
Ph
H
N–Ms
5o
138.341
136.211
128.290
127.960
125.229
107.411
77.322
77.000
76.685
40.623
25.762
18.214
-4.019
160
140
120
100
80
60
40
20
0
ppm

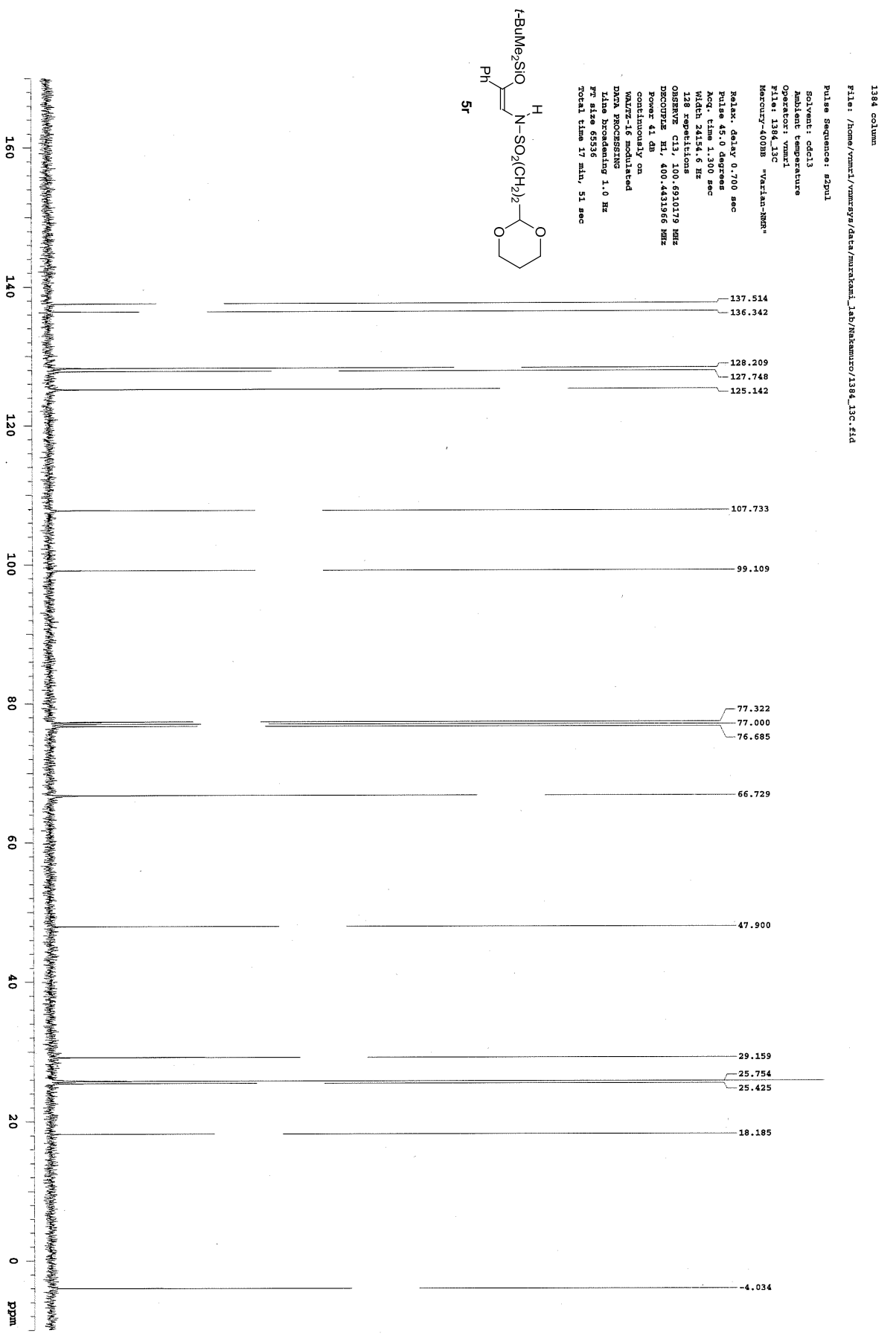

657 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/657_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: 657_1H
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411632 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
Ph
H
N–SO2CH2Ph
5p
7.401
7.399
7.392
7.389
7.365
7.362
7.360
7.354
7.351
7.345
7.334
7.329
7.319
7.316
7.308
7.304
7.300
7.295
7.287
7.260
6.109
6.082
6.009
5.981
4.314
0.920
0.888
0.880
0.872
0.840
-0.017
-0.049
-0.057
-0.065
-0.097
10.24
0.96
1.01
2.00
8.98
5.77
ppm

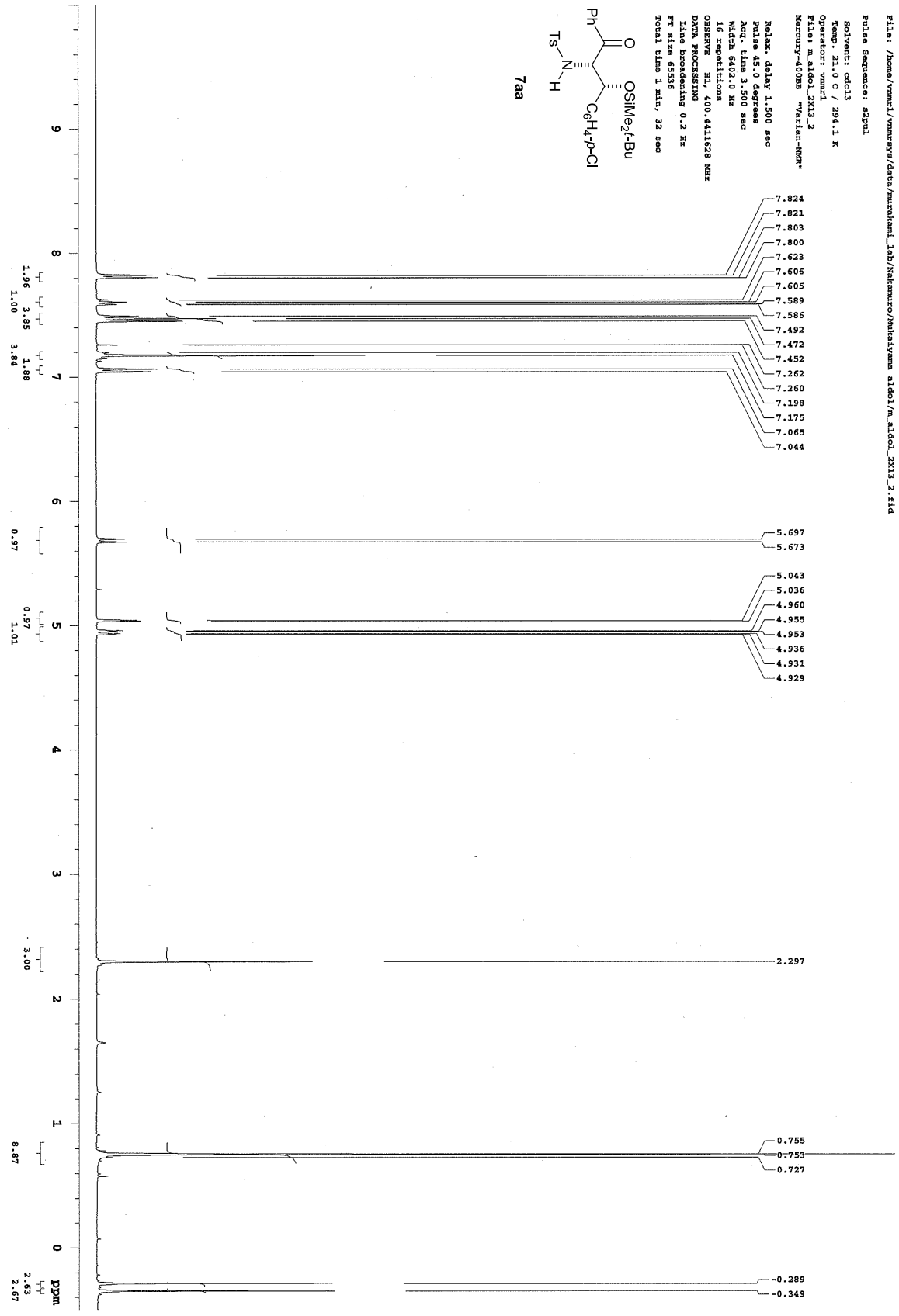

657 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/657_13C.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: 657_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910171 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
t-BuMe2SiO
Ph
H
N–SO2CH2Ph
5p
137.682
136.269
130.720
128.970
128.831
128.604
128.282
127.909
125.120
107.865
77.315
77.000
76.678
58.405
25.586
18.060
-4.129
160
140
120
100
80
60
40
20
0
ppm

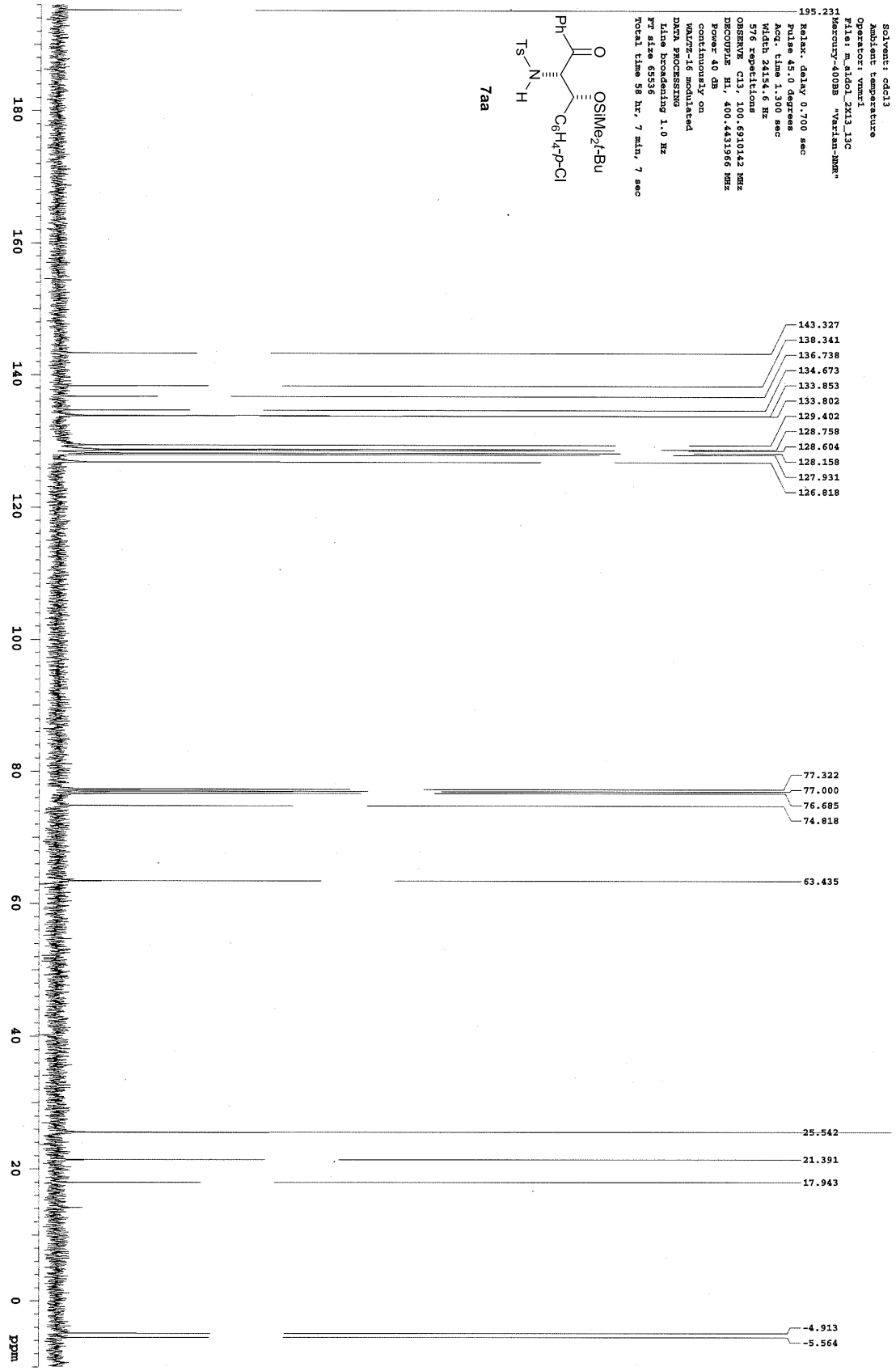

653 column
File: /home/vnmrl/vnmrsys/data/murakami_lab/Nakamuro/653_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmrl
File: 653_1H
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411646 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
Ph
H
N–SO2(CH2)2SiMe3
5q
7.375
7.371
7.358
7.354
7.350
7.329
7.325
7.308
7.304
7.290
7.278
7.260
6.097
3.033
3.024
3.013
3.008
2.998
2.988
1.084
1.075
1.064
1.059
1.051
1.049
1.039
1.015
1.008
1.001
0.048
0.040
0.032
0.008
0.001
-0.007
5.23
2.04
2.00
8.80
2.13
5.79
8.45
ppm

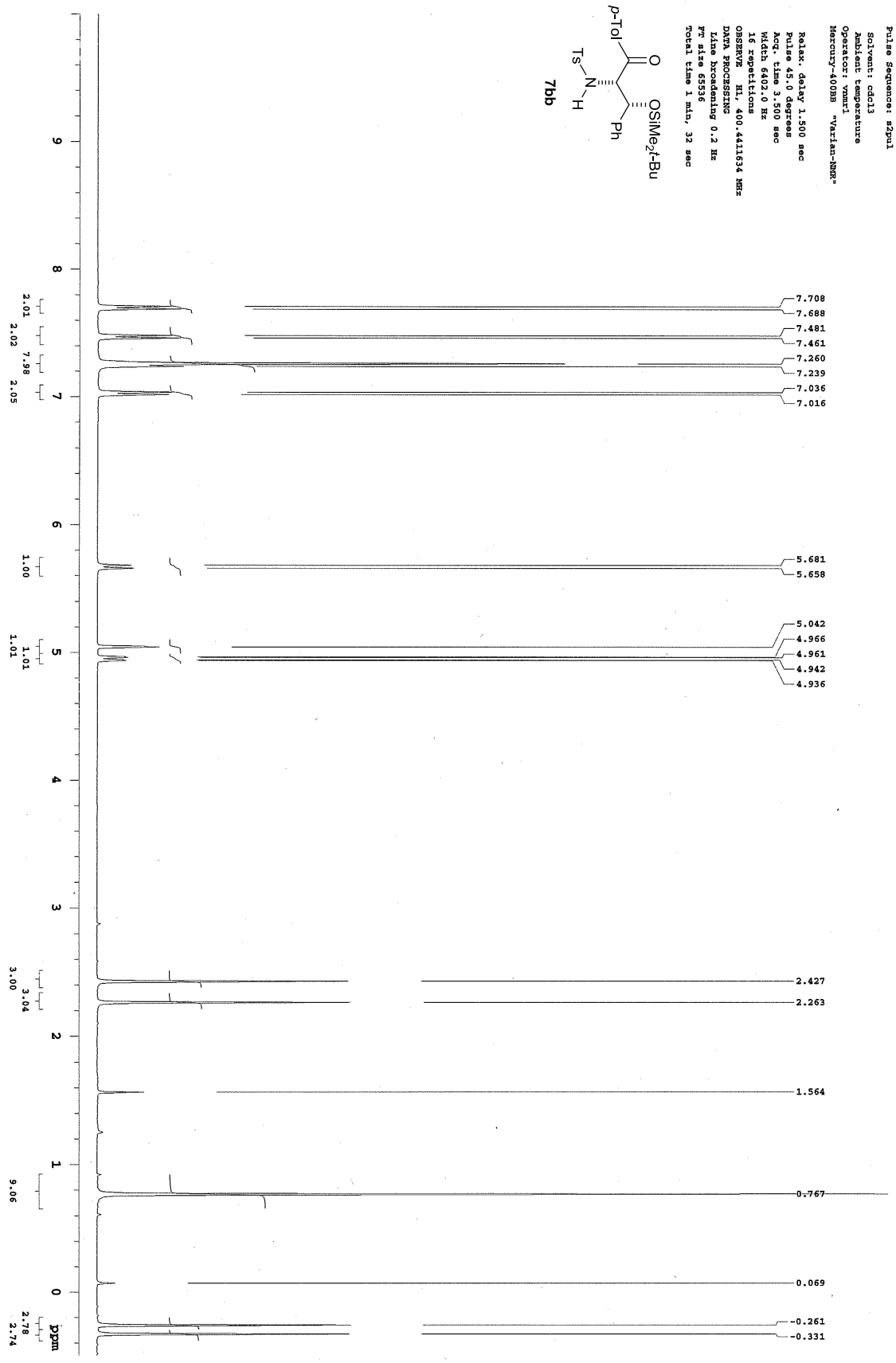

653 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/653_13C.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: 653_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910171 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec
t-BuMe2SiO
Ph
H
N–SO2(CH2)2SiMe3
5q
137.982
136.313
128.253
127.865
125.222
107.982
77.315
77.000
76.678
49.027
25.747
18.177
10.600
-2.079
-4.034
160
140
120
100
80
60
40
20
0
ppm

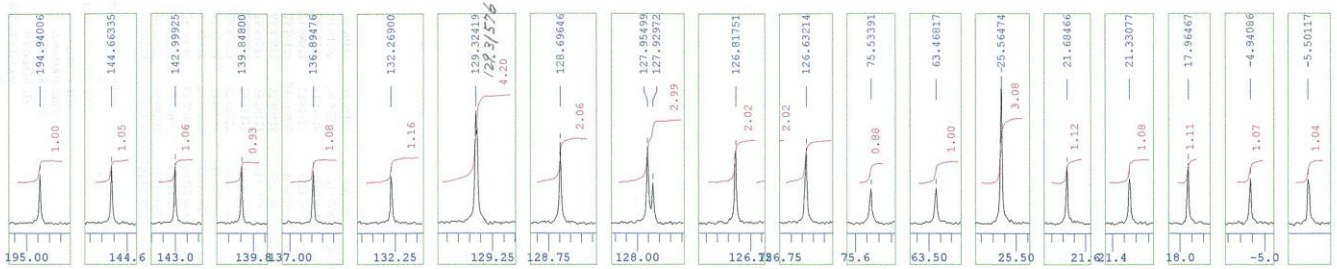

1384 column
File: /home/vnmrs1/vnmrsys/data/murakami_lab/Nakamuro/1384_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 1384_1H
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411634 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
t-BuMe2SiO
Ph
H
N–SO2(CH2)2
O
O
5r
7.375
7.371
7.366
7.358
7.354
7.351
7.322
7.318
7.313
7.301
7.297
7.285
7.282
7.271
7.267
7.263
7.260
7.250
6.157
6.131
6.113
6.087
4.700
4.689
4.678
4.086
4.077
4.074
4.060
4.056
4.047
4.045
3.771
3.765
3.761
3.740
3.734
3.710
3.703
3.280
3.266
3.261
3.255
3.242
2.136
2.124
2.116
2.111
2.105
2.099
2.097
2.085
2.031
1.997
1.341
1.338
1.335
1.332
1.310
1.307
1.304
1.301
1.025
1.005
0.997
0.906
0.375
0.087
0.006
-0.001
5.50
1.94
1.00
2.03
2.11
2.01
3.19
1.20
9.10
5.59
ppm

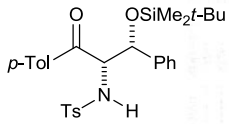

1384 column
File: /home/vnmrj/vnmrsys/data/murakami_lab/Nakamuro/1384_13c.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrj
File: 1384_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910179 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
t-BuMe2SiO
Ph
H
N–SO2(CH2)2
O
O
5r
137.514
136.342
128.209
127.748
125.142
107.733
99.109
77.322
77.000
76.685
66.729
47.900
29.159
25.754
25.425
18.185
-4.034
160
140
120
100
80
60
40
20
0
ppm


20-2
file: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/Mukaiyama aldol/m_aldol_2x13_2.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 21.0 C / 294.1 K
Operator: vnmr1
File: m_aldol_2x13_2
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411628 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Ph
O
OSiMe2t-Bu
Ts
N
H
C6H4-p-Cl
7aa
7.824
7.821
7.803
7.800
7.623
7.606
7.605
7.589
7.586
7.492
7.472
7.452
7.262
7.260
7.198
7.175
7.065
7.044
5.697
5.673
5.043
5.036
4.960
4.955
4.953
4.936
4.931
4.929
2.297
0.755
0.753
0.727
-0.289
-0.349
1.96
3.85
1.88
1.00
3.84
0.97
0.97
1.01
3.00
8.87
2.63
2.67
ppm


20-2
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/Mukaiyama aldol/m_aldol_2x13_13C.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: m_aldol_2x13_13C
Mercury-400BB "Varian-NMR"
195.231
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
576 repetitions
OBSERVE C13, 100.6910142 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 58 hr, 7 min, 7 sec
O
OSiMe2t-Bu
Ph
C6H4-p-Cl
Ts
N
H
7aa
143.327
138.341
136.738
134.673
133.853
133.802
129.402
128.758
128.604
128.158
127.931
126.818
77.322
77.000
76.685
74.818
63.435
25.542
21.391
17.943
-4.913
-5.564
180
160
140
120
100
80
60
40
20
0
ppm

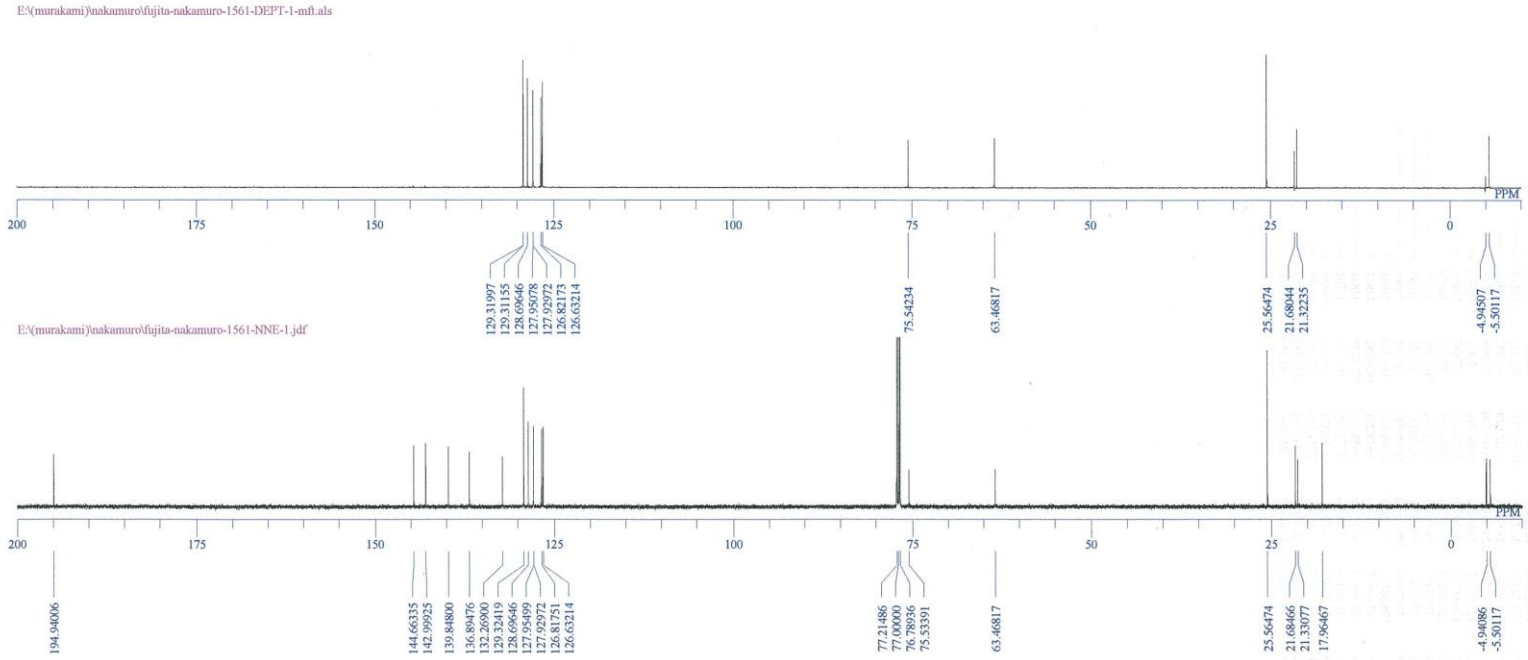

File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrl
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411634 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
p-Tol
O
OSiMe2t-Bu
Ts
N
H
Ph
7bb
7.708
7.688
7.481
7.461
7.260
7.239
7.036
7.016
5.681
5.658
5.042
4.966
4.961
4.942
4.936
2.427
2.263
1.564
0.767
0.069
-0.261
-0.331
2.01
2.02
7.98
2.05
1.00
1.01
1.01
3.00
3.04
9.06
2.78
2.74
ppm





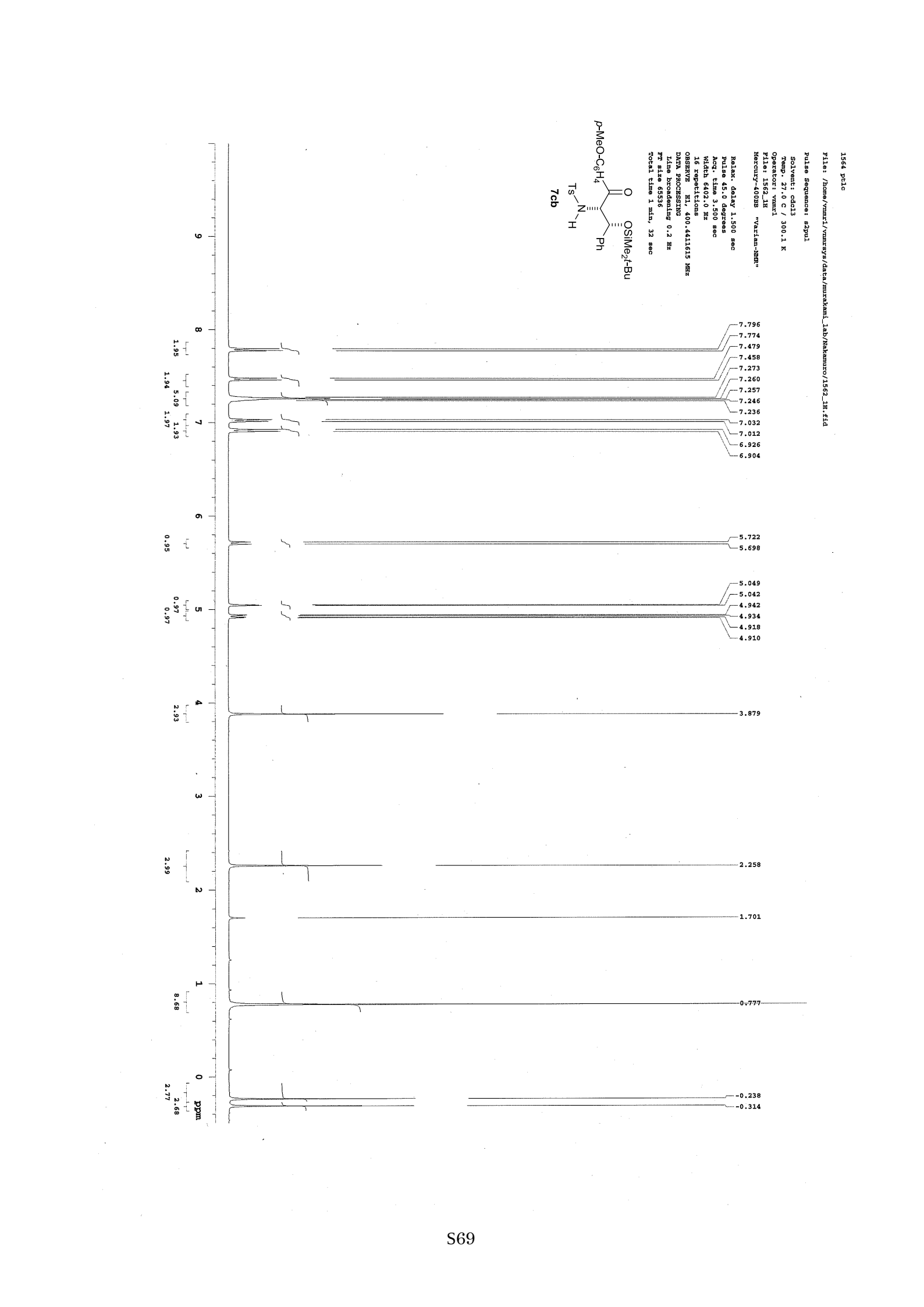
7bb

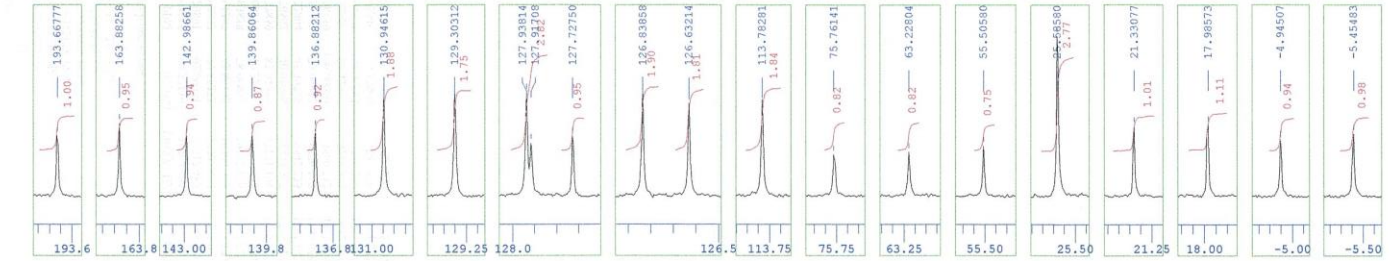
130448

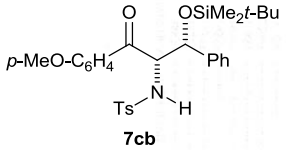



```
DFILE   fujita-nakamuro-1561-DEPT-1-mft.als
COMNT   DEPT with decoupling
DATIM   2014-02-24 15:37:38
OBNUC   13C
EXMOD   dept.ex2
OBFRQ     150.92 MHz
OBSET       8.52 KHz
OBFIN       1.74 Hz
POINT      65536
FREQU   41666.67 Hz
SCANS       1000
ACQTM     1.5729 sec
PD        1.0000 sec
PW1         11.30 usec
IRNUC   1H
CTEMP       20.8 c
SLVNT   CDCL3
EXREF       77.00 ppm
BF          0.60 Hz
RGAIN       60
```

```
DFILE   fujita-nakamuro-1561-NNE-1.jdf
COMNT   single pulse decoupled gated NO-NOE
DATIM   2014-02-24 14:53:32
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ     150.92 MHz
OBSET       8.52 KHz
OBFIN       1.74 Hz
POINT      65536
FREQU   41666.67 Hz
SCANS         153
ACQTM     1.5729 sec
PD        9.1000 sec
PW1         3.77 usec
IRNUC   1H
CTEMP       20.2 c
SLVNT   CDCL3
EXREF       77.00 ppm
BF          0.60 Hz
RGAIN       60
```

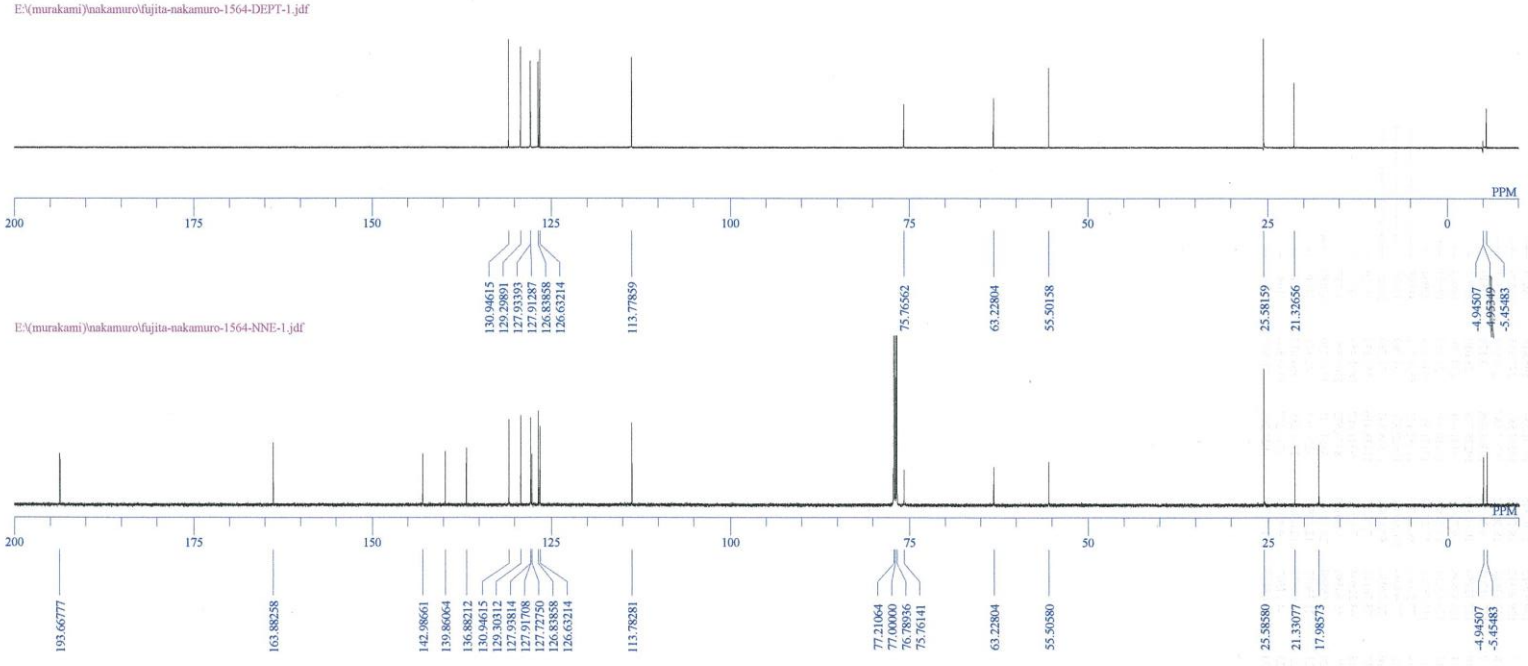

1564 plc
File: /home/vnmrs1/vnmrsys/data/murakami_lab/Nakamuro/1562_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 27.0 C / 300.1 K
Operator: vnmrs1
File: 1562_1H
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411615 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
p-MeO-C6H4
Ts
N
H
O
OSiMe2t-Bu
Ph
7cb
7.796
7.774
7.479
7.458
7.273
7.260
7.257
7.246
7.236
7.032
7.012
6.926
6.904
5.722
5.698
5.049
5.042
4.942
4.934
4.918
4.910
3.879
2.258
1.701
0.777
-0.238
-0.314
1.95
5.09
1.93
1.94
1.97
0.95
0.97
0.97
2.93
2.99
8.68
2.77
2.68
ppm





7cb

130449

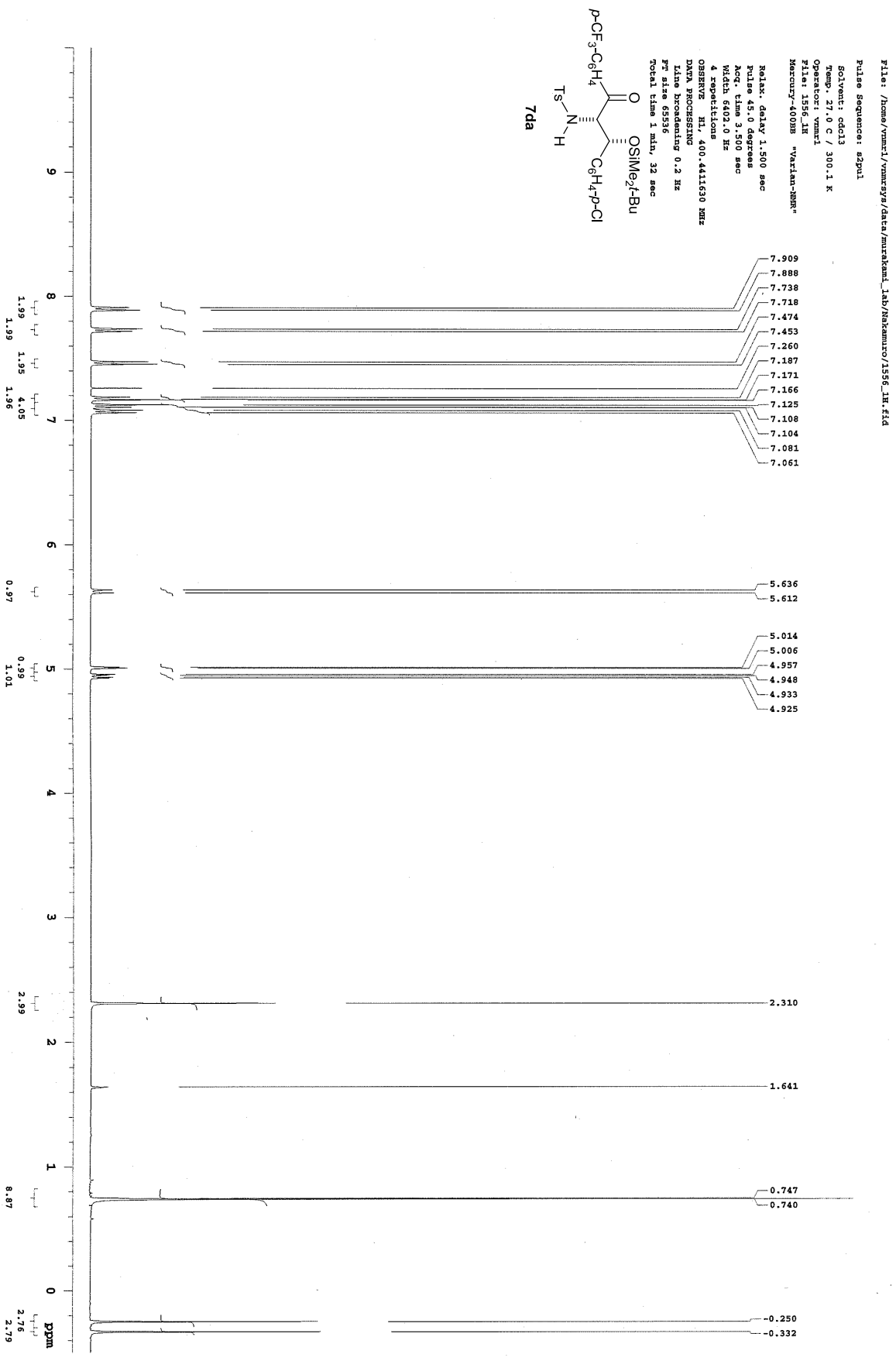


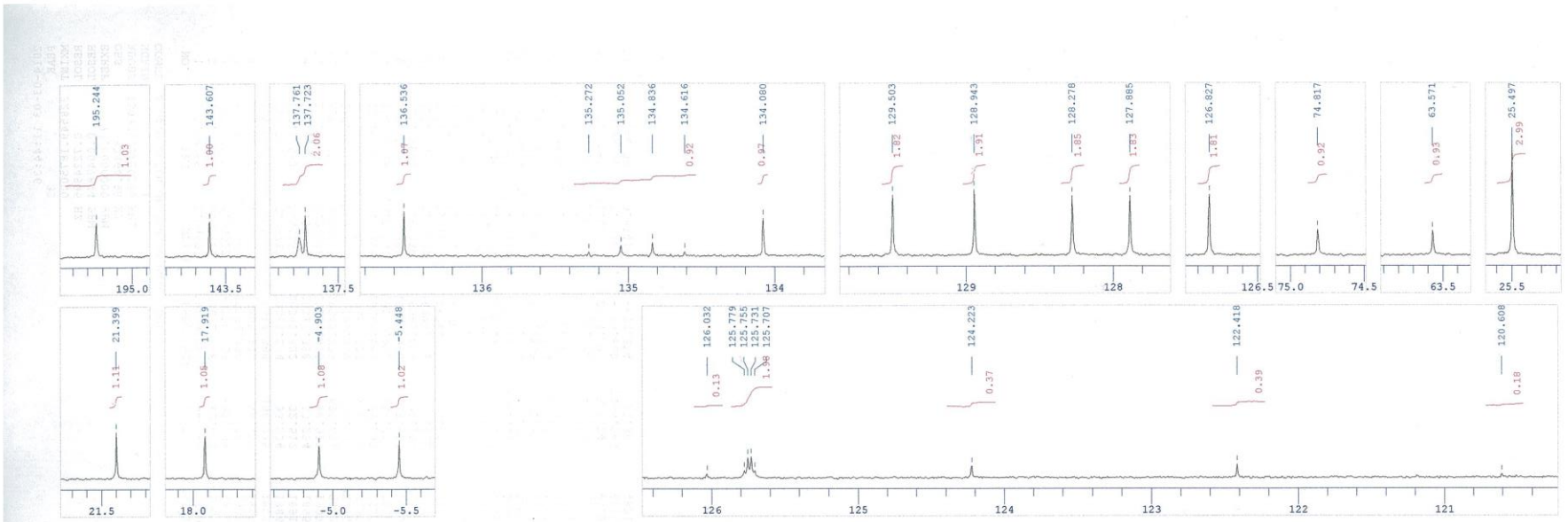
DEPT with decoupling

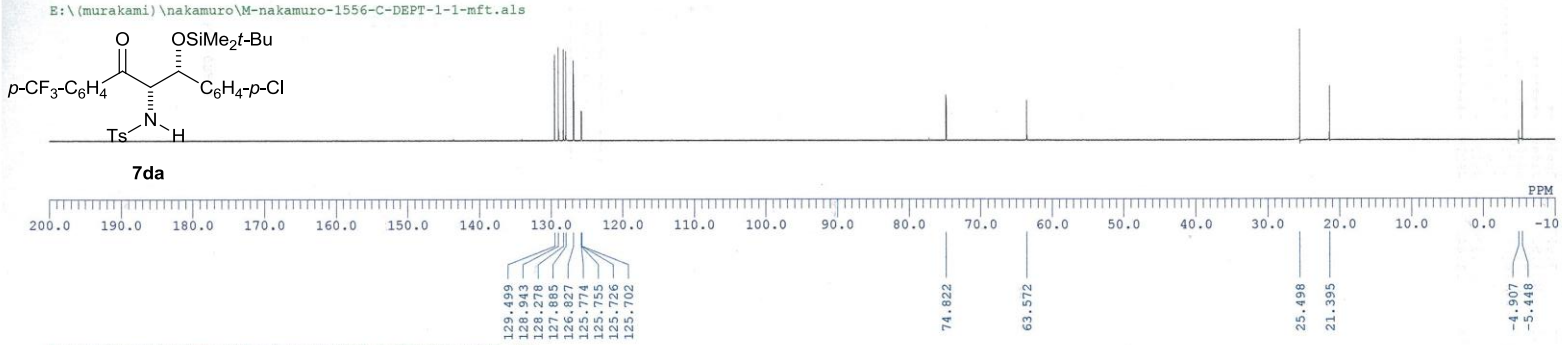
DFILE	fujita-nakamuro-1564-DEPT-1.jdf
COMNT	DEPT with decoupling
DATIM	2014-02-24 10:48:04
OBNUC	13C
EXMOD	dept.ex2
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	65536
FREQU	41666.67 Hz
SCANS	361
ACQTM	1.5729 sec
PD	1.0000 sec
PW1	11.30 usec
IRNUC	1H
CTEMP	20.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.60 Hz
RGAIN	60

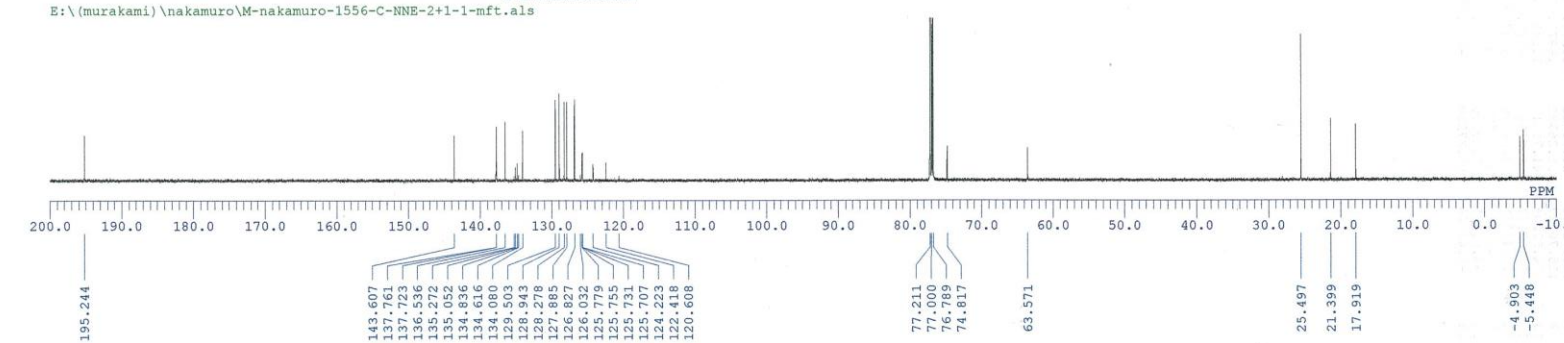
single pulse decoupled gated NO-NOE

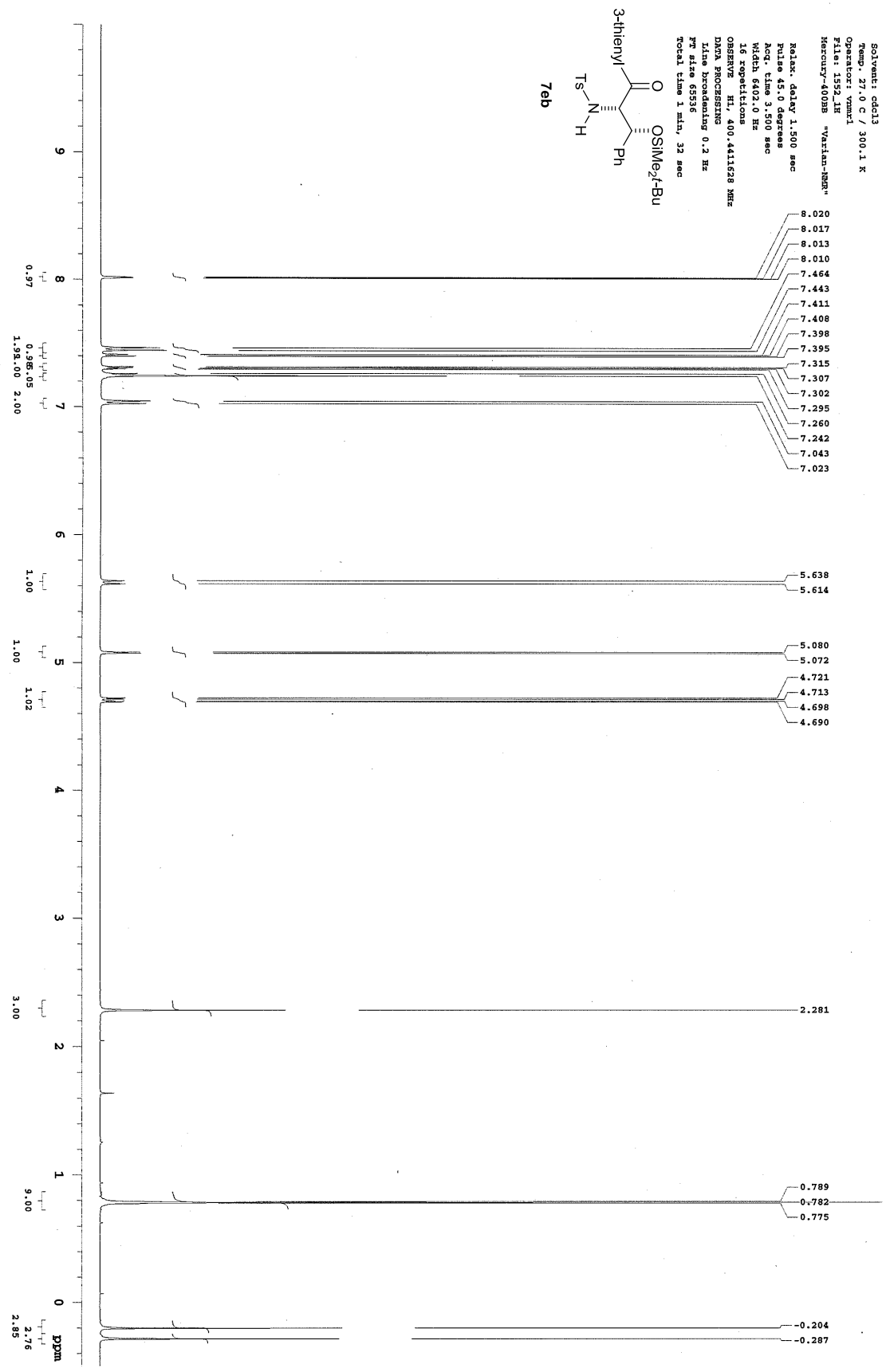
DFILE	fujita-nakamuro-1564-NNE-1.jdf
COMNT	single pulse decoupled gated NO-NOE
DATIM	2014-02-24 10:31:34
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	65536
FREQU	41666.67 Hz
SCANS	401
ACQTM	1.5729 sec
PD	9.1000 sec
PW1	3.77 usec
IRNUC	1H
CTEMP	19.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.60 Hz
RGAIN	60

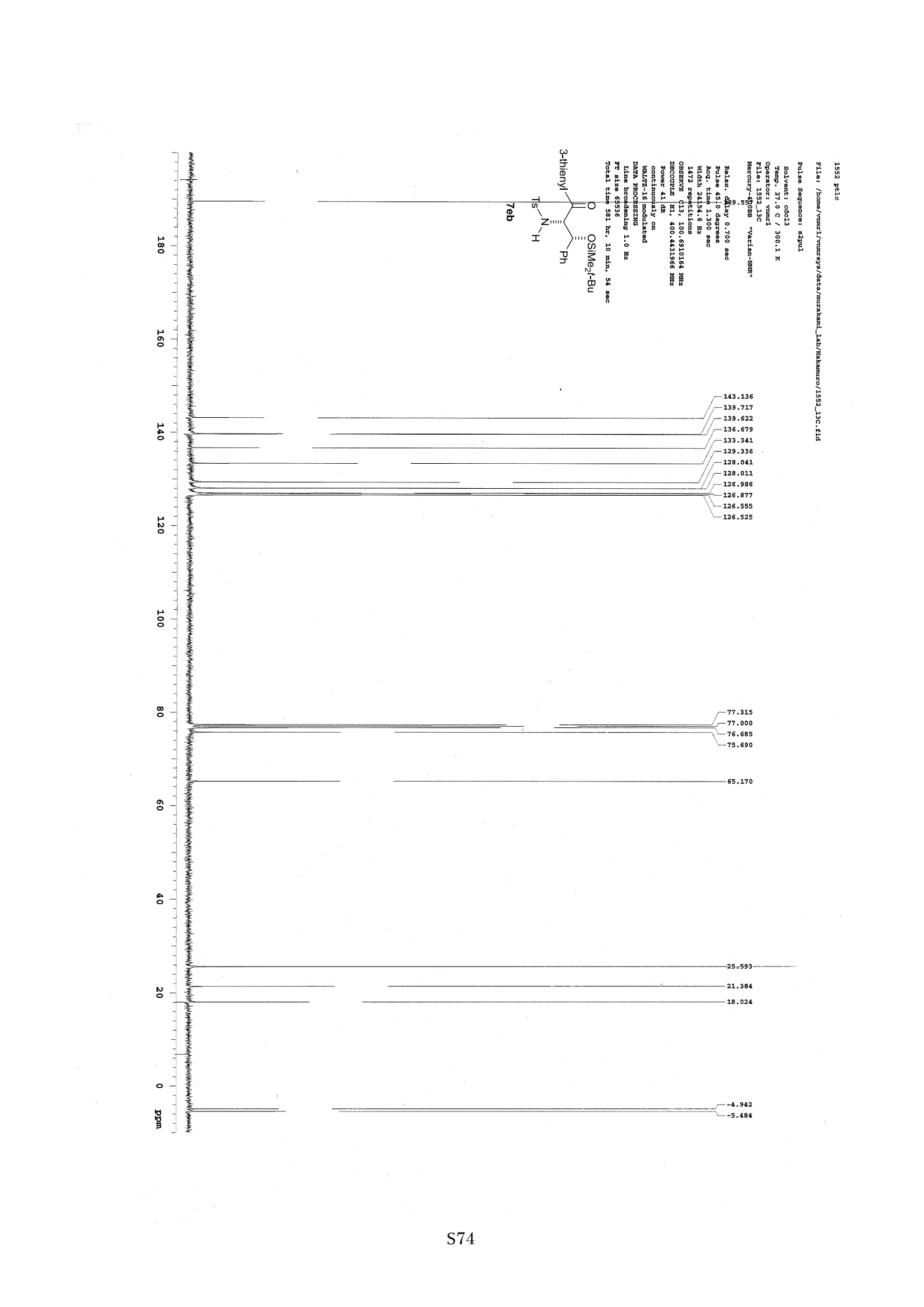

new experiment
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/1556_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 27.0 C / 300.1 K
Operator: vnmr1
File: 1556_1H
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
4 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
p-CF3-C6H4
O
OSiMe2-t-Bu
Ts
N
H
C6H4-p-Cl
7da
7.909
7.888
7.738
7.718
7.474
7.453
7.260
7.187
7.171
7.166
7.125
7.108
7.104
7.081
7.061
5.636
5.612
5.014
5.006
4.957
4.948
4.933
4.925
2.310
1.641
0.747
0.740
-0.250
-0.332
1.99
1.99
1.95
4.05
1.96
0.97
0.99
1.01
2.99
8.87
2.76
2.79
ppm

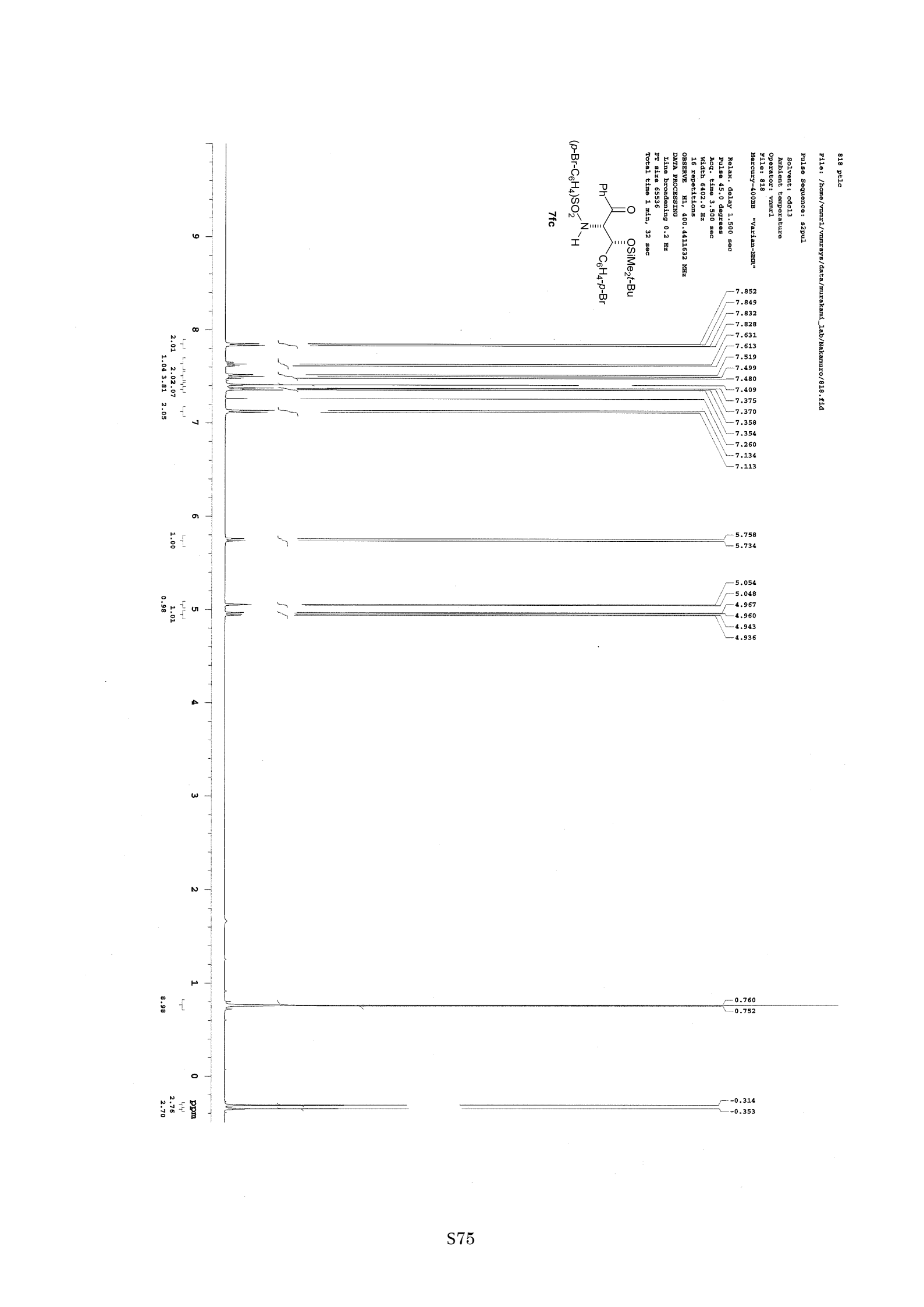

195.244
143.607
137.761
137.723
136.536
135.272
135.052
134.836
134.616
134.080
129.503
128.943
128.278
127.885
126.827
74.817
63.571
25.497
21.399
17.919
-4.903
-5.448
126.032
125.779
125.755
125.731
125.707
124.223
122.418
120.608

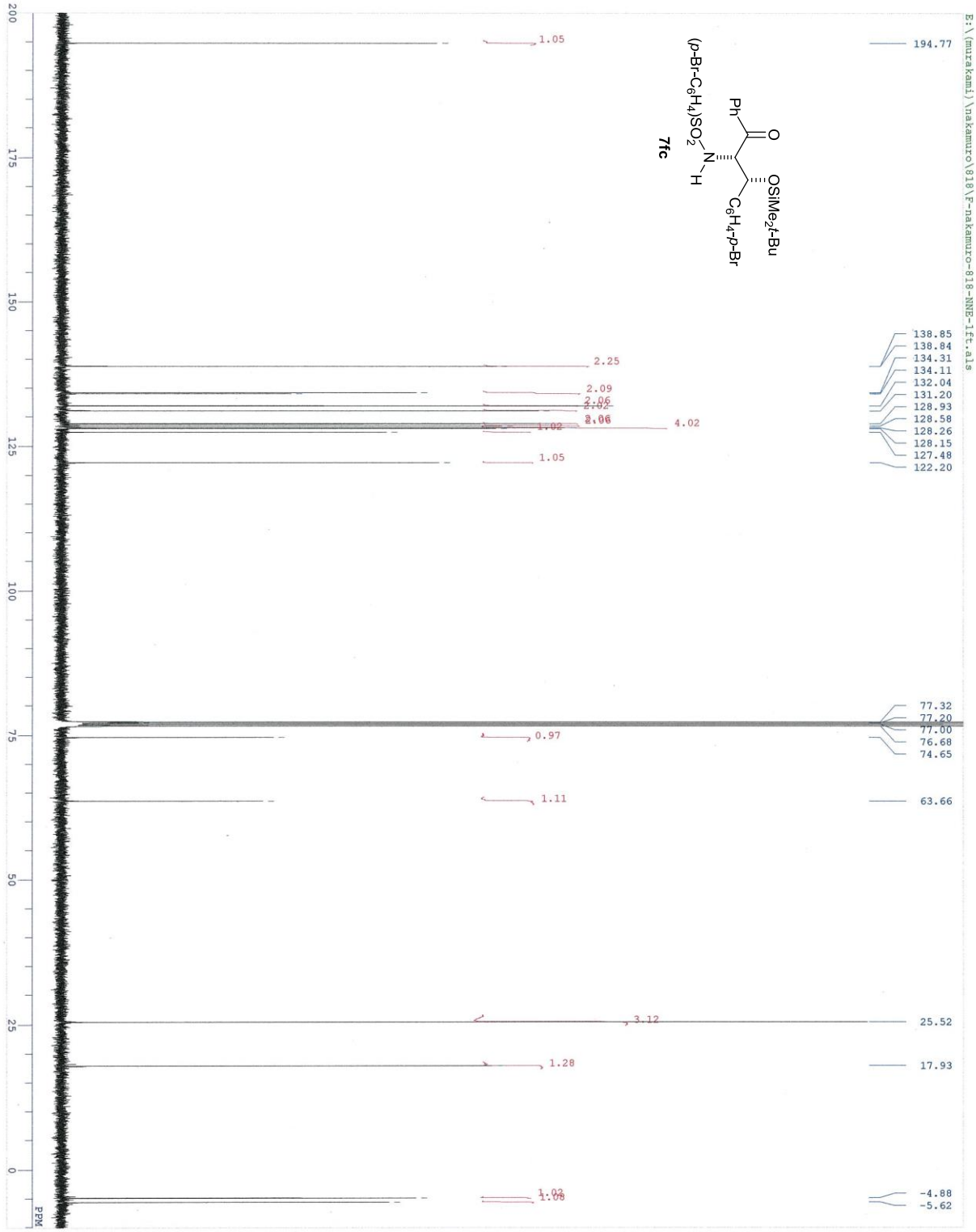

E:\(murakami)\nakamuro\M-nakamuro-1556-C-DEPT-1-1-mft.als
O
OSiMe2t-Bu
p-CF3-C6H4
C6H4-p-Cl
N
Ts
H
7da
PPM
129.499
128.943
128.278
127.885
126.827
125.774
125.755
125.726
125.702
74.822
63.572
25.498
21.395
-4.907
-5.448
DFILE M-nakamuro-1556-C-DEPT-1-1-mft.a
COMNT DEPT with decoupling
DATIM 2014-03-03 12:56:04
OBNUC 13C
EXMOD dept.ex2
OBFRQ 150.92 MHz
OBFIN 1.74 Hz
POINT 52428
FREQU 37878.21 Hz
SCANS 1200
ACQTM 1.3841 sec
PD 2.0000 sec
PW1 11.30 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF -5.45 ppm
BF 0.70 Hz
RGAIN 60

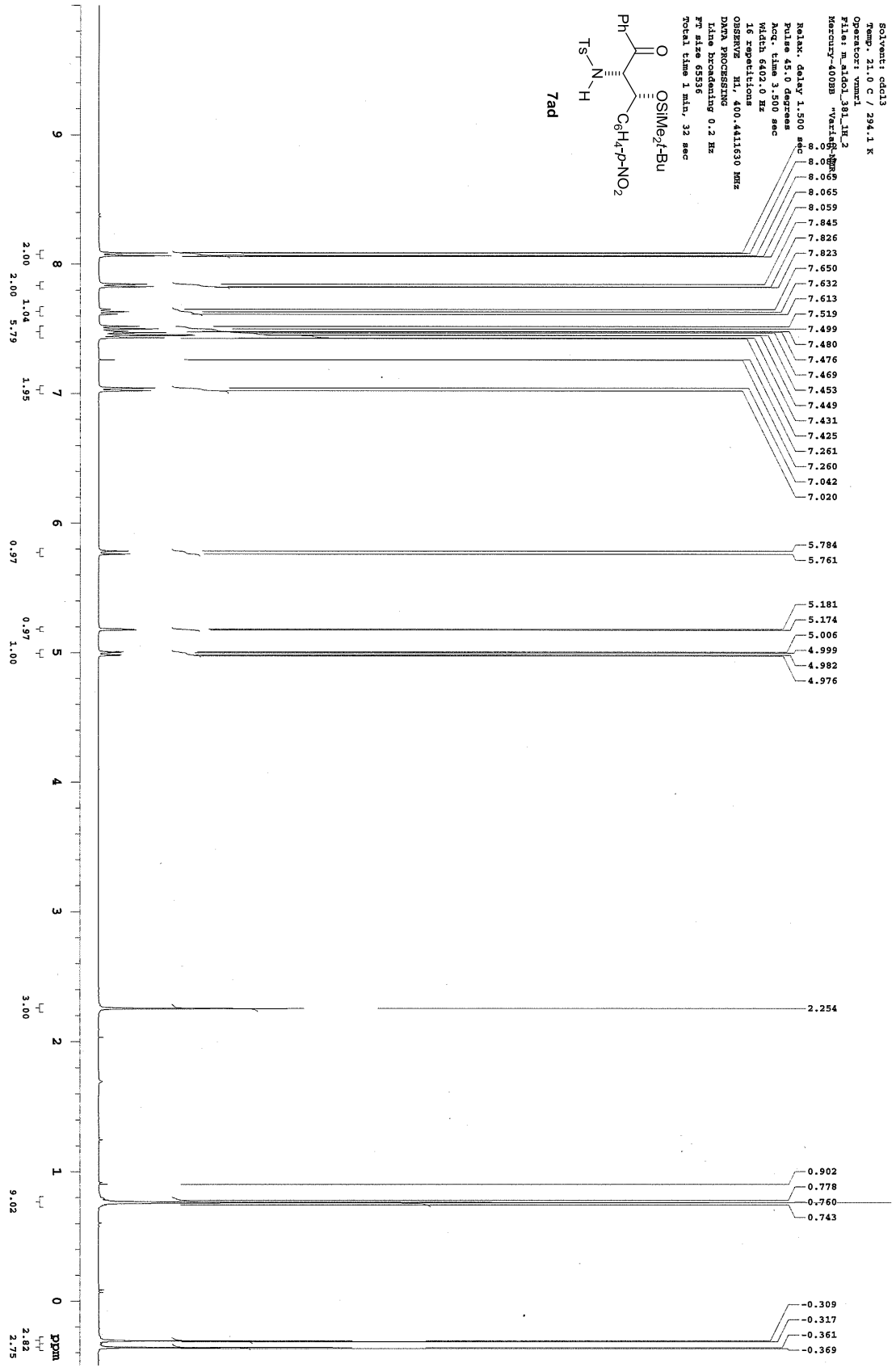

E:\(murakami)\nakamuro\M-nakamuro-1556-C-NNE-2+1-1-mft.als
PPM
195.244
143.607
137.761
137.723
136.536
135.272
135.052
134.836
134.616
134.080
129.503
128.943
128.278
127.885
126.827
126.032
125.779
125.755
125.731
125.707
124.223
122.418
120.608
77.211
77.000
76.789
74.817
63.571
25.497
21.399
17.919
-4.903
-5.448
DFILE M-nakamuro-1556-C-NNE-2+1-1-mft.
COMNT single pulse decoupled gated NOE
DATIM 2014-03-03 11:44:36
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBFIN 1.74 Hz
POINT 52428
FREQU 37878.21 Hz
SCANS 542
ACQTM 1.3841 sec
PD 9.0000 sec
PW1 3.77 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.70 Hz
RGAIN 60

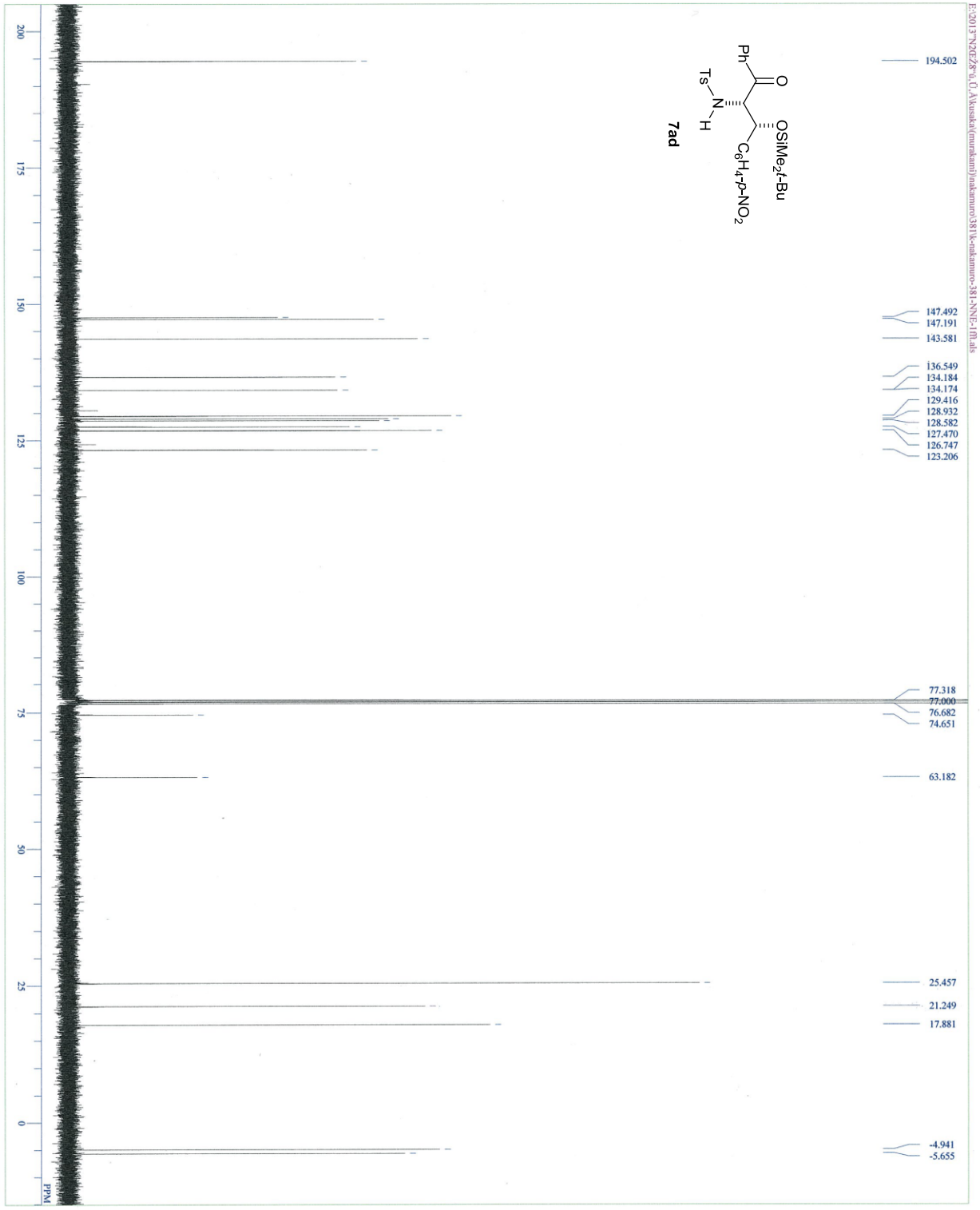

1552 ptlc
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/1552_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 27.0 C / 300.1 K
Operator: vnmr1
File: 1552_1H
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411628 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
3-thienyl
Ts
N
H
O
OSiMe2t-Bu
Ph
7eb
8.020
8.017
8.013
8.010
7.464
7.443
7.411
7.408
7.398
7.395
7.315
7.307
7.302
7.295
7.260
7.242
7.043
7.023
5.638
5.614
5.080
5.072
4.721
4.713
4.698
4.690
2.281
0.789
0.782
0.775
-0.204
-0.287
0.97
0.98
0.98
2.00
1.98.00
2.00
1.00
1.00
1.02
3.00
9.00
2.76
2.85
ppm


1552 ptlc
File: /home/vnmrs1/vnmrsys/data/murakami_lab/Nakamuro/1552_13C.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 27.0 C / 300.1 K
Operator: vnmr1
File: 1552_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1472 repetitions
OBSERVE C13, 100.6910164 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 581 hr, 10 min, 54 sec
3-thienyl
OSiMe2t-Bu
Ts
N
H
Ph
7eb
143.136
139.717
139.622
136.679
133.341
129.336
128.041
128.011
126.986
126.877
126.555
126.525
77.315
77.000
76.685
75.690
65.170
25.593
21.384
18.024
-4.942
-5.484
180
160
140
120
100
80
60
40
20
0
ppm


818 ptlc
File: /home/vnmrj/vnmrsys/data/murakami_lab/Nakamuro/818.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrj
File: 818
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411632 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Ph
OSiMe2-t-Bu
C6H4-p-Br
(p-Br-C6H4)SO2
N
H
7fc
7.852
7.849
7.832
7.828
7.631
7.613
7.519
7.499
7.480
7.409
7.375
7.370
7.358
7.354
7.260
7.134
7.113
5.758
5.734
5.054
5.048
4.967
4.960
4.943
4.936
0.760
0.752
-0.314
-0.353
2.01
2.02
2.07
1.04
3.81
2.05
1.00
1.01
0.98
8.98
2.76
2.70
ppm


E:\(murakami)\nakamuro\818\F-nakamuro-818-NNE-1ft.als
Ph
O
OSiMe2t-Bu
C6H4-p-Br
N
H
(p-Br-C6H4)SO2
7fc
194.77
138.85
138.84
134.31
134.11
132.04
131.20
128.93
128.58
128.26
128.15
127.48
122.20
77.32
77.20
77.00
76.68
74.65
63.66
25.52
17.93
-4.88
-5.62
1.05
2.25
2.09
2.06
4.02
1.05
0.97
1.11
3.12
1.28
1.02
PPM
DFILE F-nakamuro-818-NNE-1ft.als
COMNT single pulse decoupled gate
DATIM 14-06-2013 21:41:54
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBFIN 1.83 Hz
POINT 52428
FREQU 23147.79 Hz
SCANS 1000
ACQTM 2.2649 sec
PD 12.2000 sec
PW1 2.67 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.48 Hz
RGAIN 60


File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/Mukaiyama aldol/m_aldol_381_1H_2.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 21.0 C / 294.1 K
Operator: vnmr1
File: m_aldol_381_1H_2
Mercury-400BB "Varian 5 mm
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
7ad
8.071
8.069
8.065
8.059
7.845
7.826
7.823
7.650
7.632
7.613
7.519
7.499
7.480
7.476
7.469
7.453
7.449
7.431
7.425
7.261
7.260
7.042
7.020
5.784
5.761
5.181
5.174
5.006
4.999
4.982
4.976
2.254
0.902
0.778
0.760
0.743
-0.309
-0.317
-0.361
-0.369
2.00
1.04
5.79
1.95
0.97
0.97
1.00
3.00
9.02
2.82
2.75
ppm



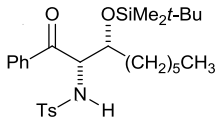
DFILE k-nakamuro-381-NNE-1ffl.als
COMNT single pulse decoupled gated NO NOE
DATIM 2012-12-03 11:36:21
ONUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 249712
FREQU 25125.24 Hz
SCANS 241
ACQTM 2.0867 sec
PD 5.4000 sec
PW1 2.67 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.06 Hz
RGAIN 60

File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/Mukaiyama aldol/m_aldol_2Y07_323_1H.fid

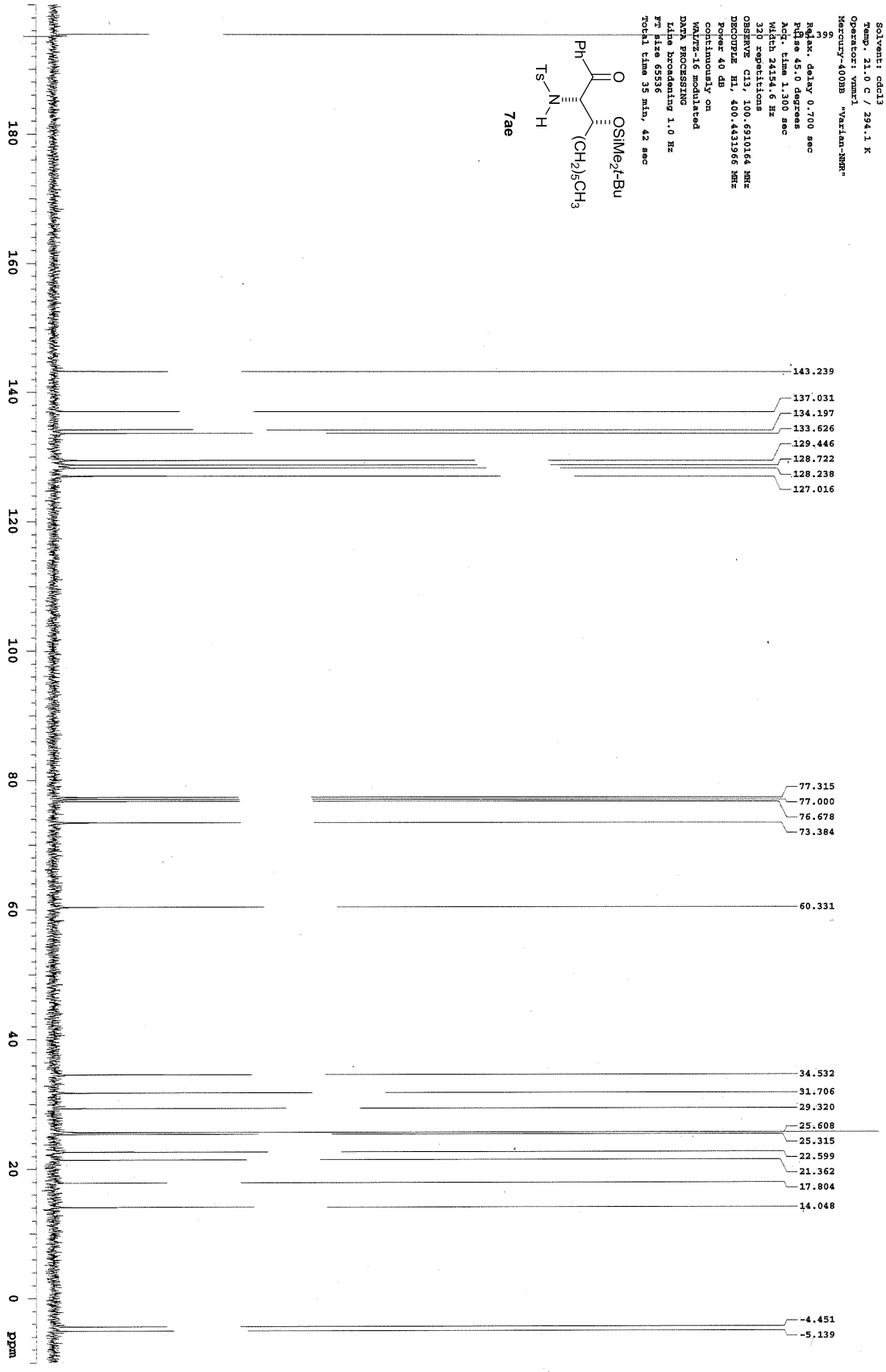
Pulse Sequence: s2pul

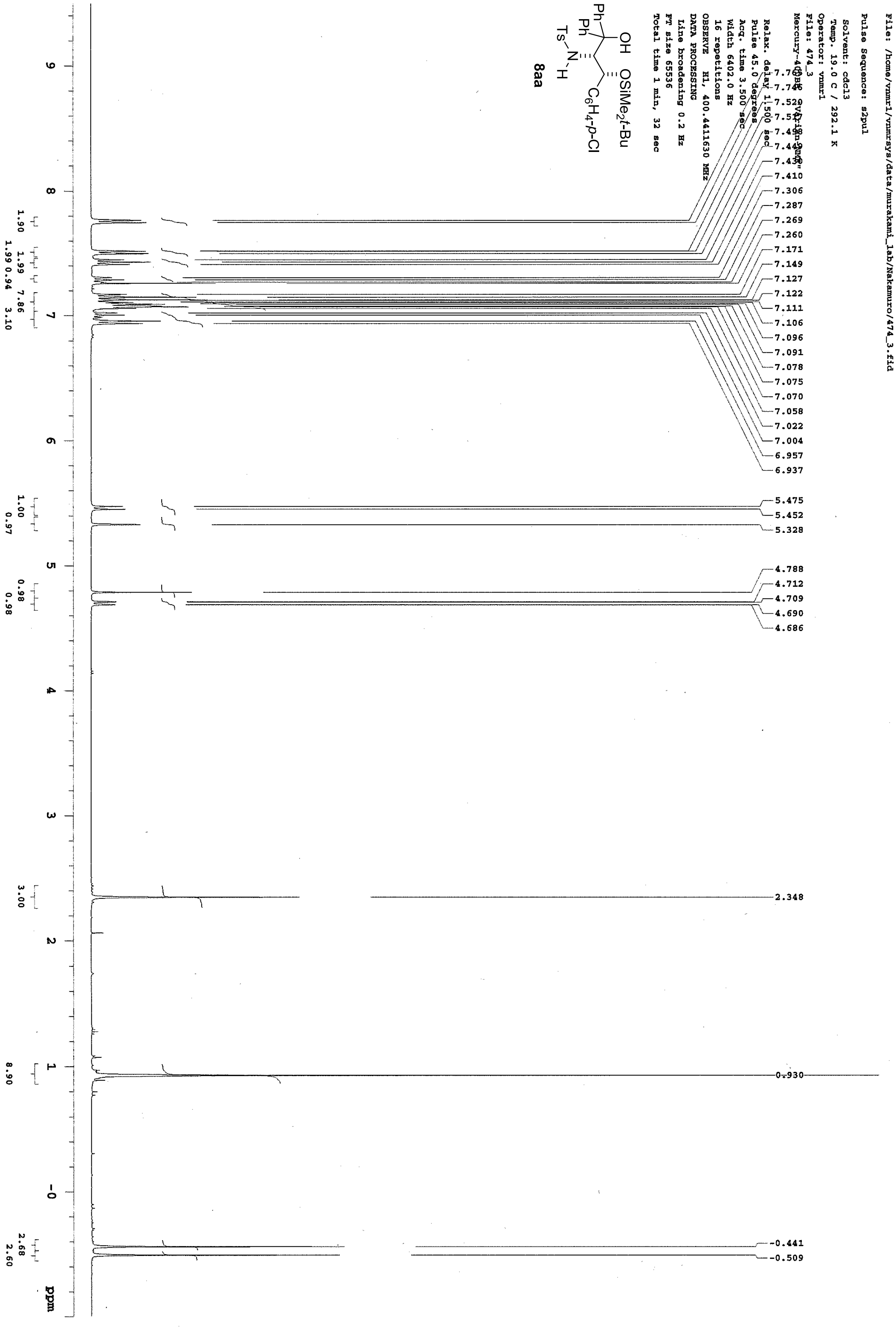
Solvent: cdcl3
Temp. 21.0 C / 294.1 K
Operator: vnmr1
File: m_aldol_2Y07_323_1H
Mercury-400BB "Varian-NMR"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411642 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec



7ae


new experiment
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 21.0 C / 294.1 K
Operator: vnmr1
Mercury-400BB "Varian-NMR"
399
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
320 repetitions
OBSERVE C13, 100.6910164 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 42 sec
Ph
O
OSiMe2t-Bu
Ts
N
H
(CH2)5CH3
7ae
143.239
137.031
134.197
133.626
129.446
128.722
128.238
127.016
77.315
77.000
76.678
73.384
60.331
34.532
31.706
29.320
25.608
25.315
22.599
21.362
17.804
14.048
-4.451
-5.139
180
160
140
120
100
80
60
40
20
0
ppm


474
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/474_3.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 19.0 C / 292.1 K
Operator: vnmr1
File: 474_3
Mercury-400BB
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
OH OSiMe2t-Bu
Ph
Ph
C6H4-p-Cl
Ts N H
8aa
7.7
7.74
7.520
7.5
7.49
7.449
7.430
7.410
7.306
7.287
7.269
7.260
7.171
7.149
7.127
7.122
7.111
7.106
7.096
7.091
7.078
7.075
7.070
7.058
7.022
7.004
6.957
6.937
5.475
5.452
5.328
4.788
4.712
4.709
4.690
4.686
2.348
0.930
-0.441
-0.509
1.90
1.99
1.99
0.94
7.86
3.10
1.00
0.97
0.98
0.98
3.00
8.90
2.68
2.60
9
8
7
6
5
4
3
2
1
-0
ppm

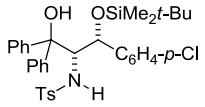
474

File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/474_3_13C.fid

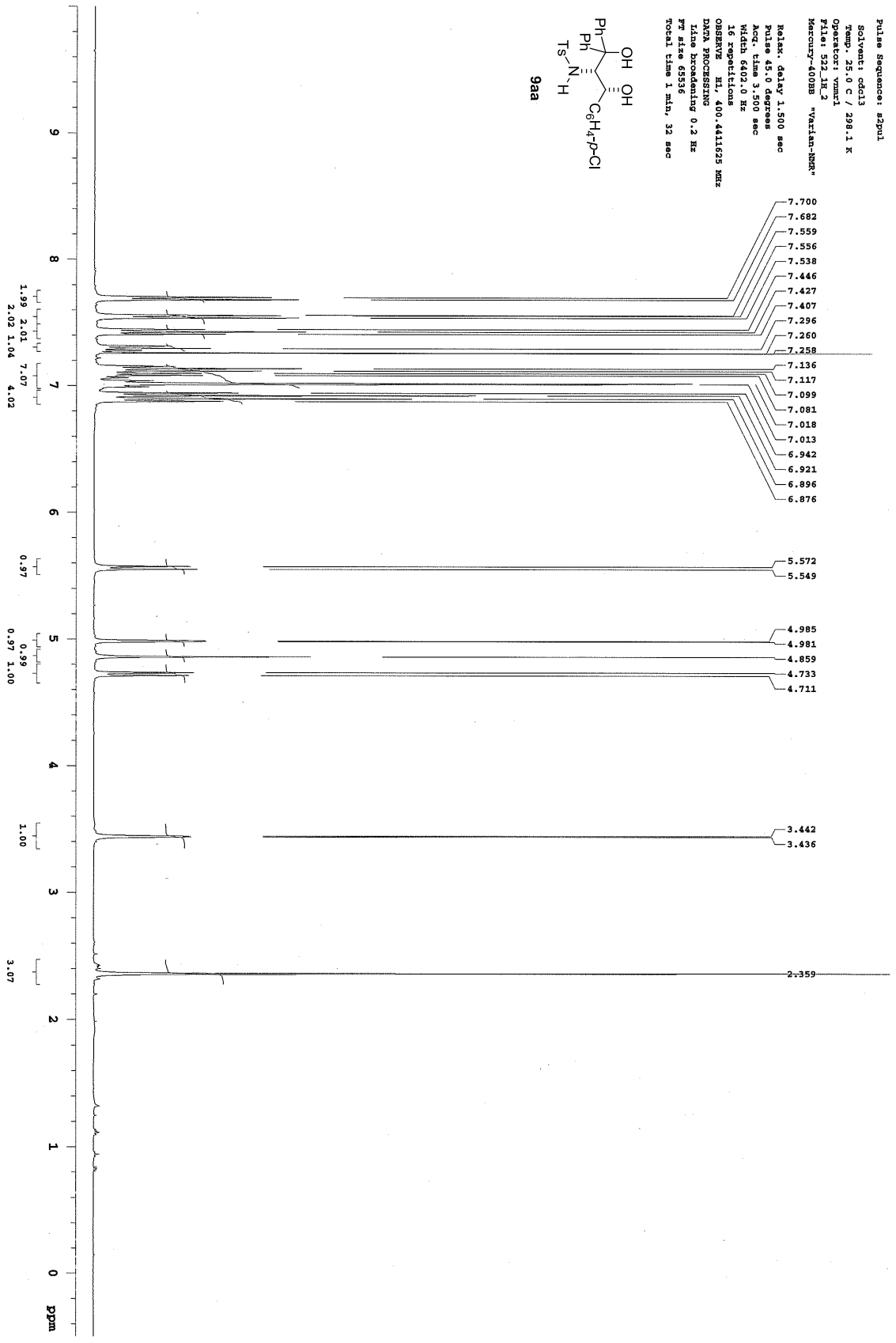
Pulse Sequence: s2pul

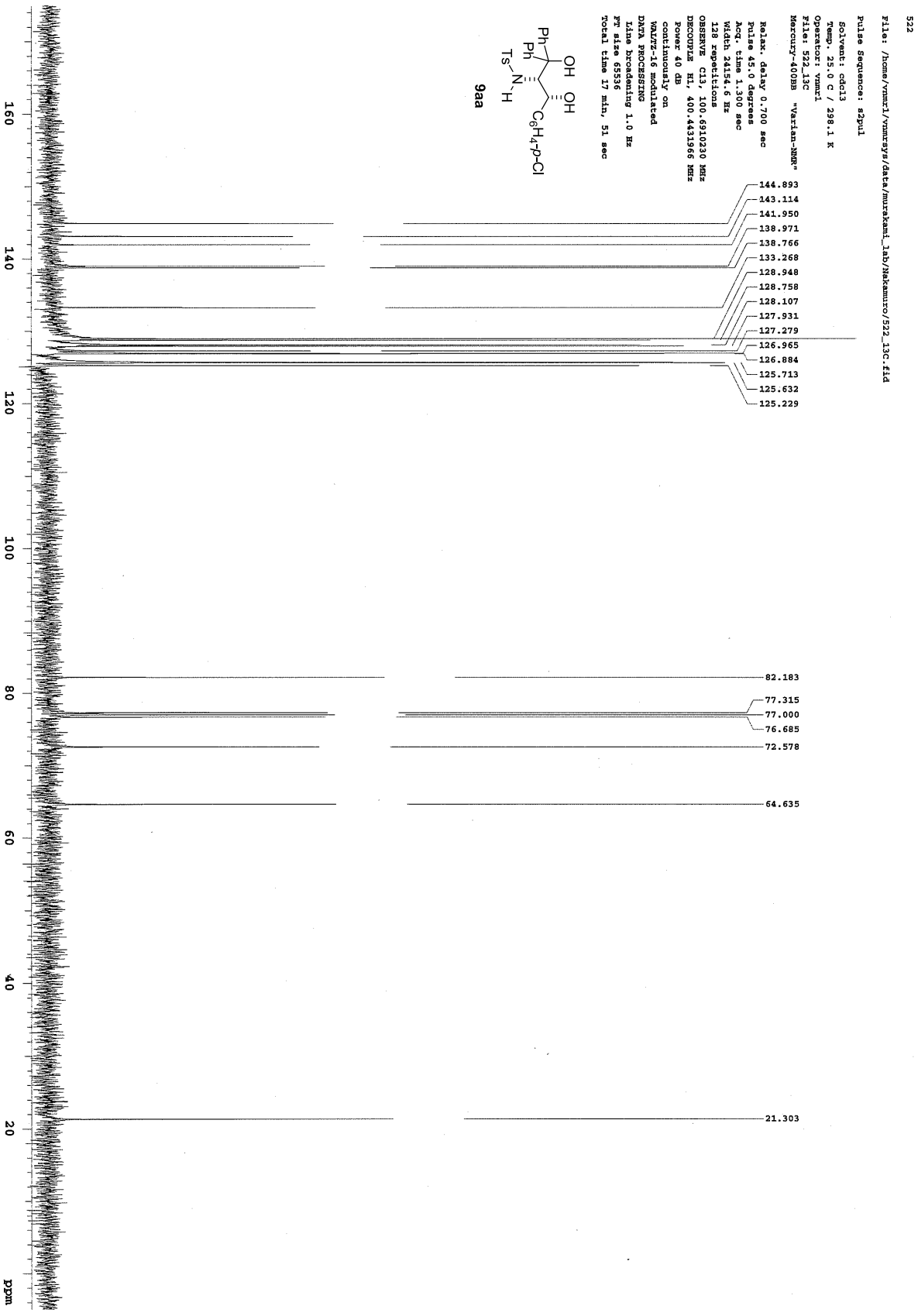
Solvent: cdcl3
Temp. 19.0 C / 292.1 K
Operator: vnmr1
File: 474_3_13C
Mercury-400BB "VarianNMR"

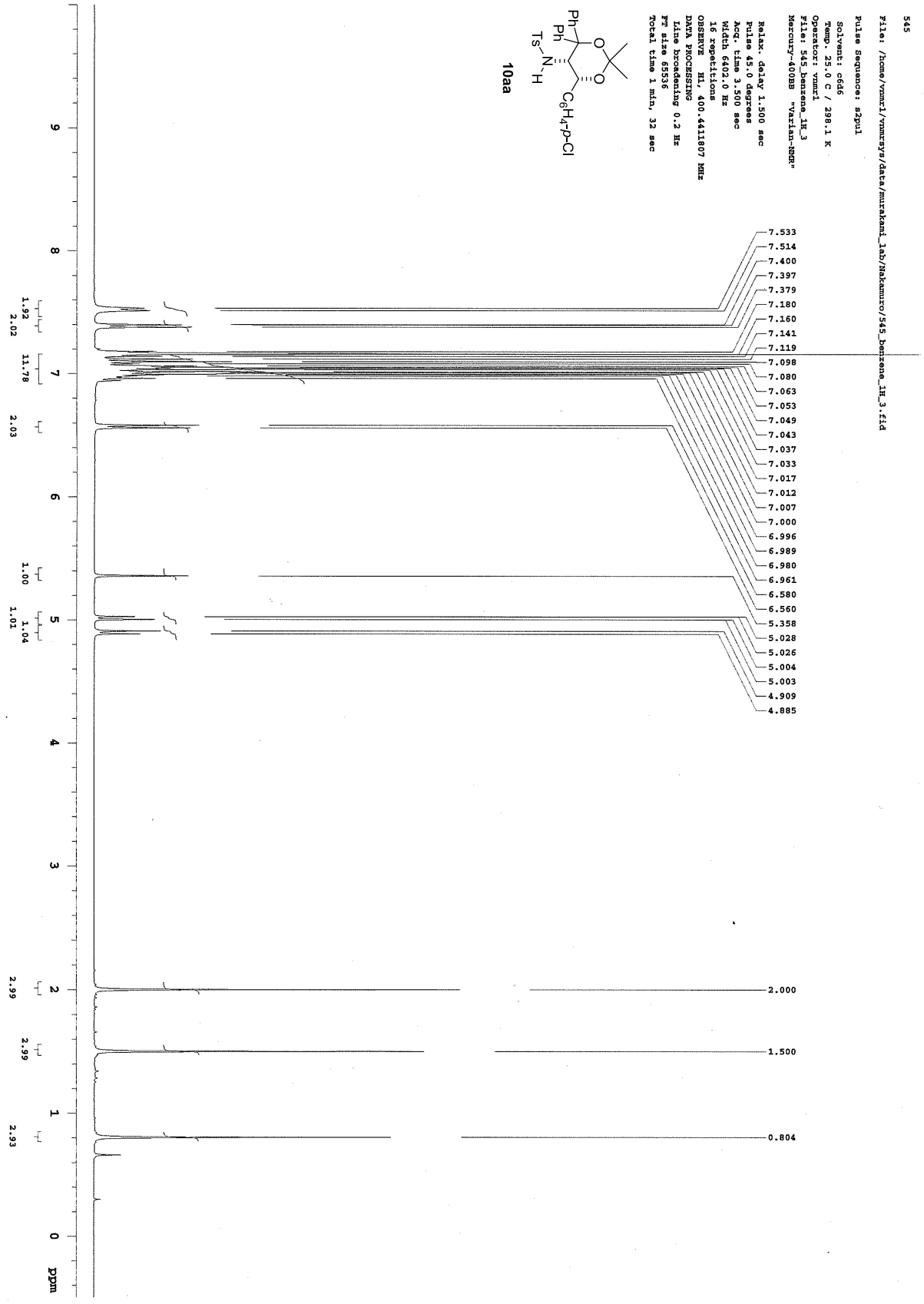
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910289 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec

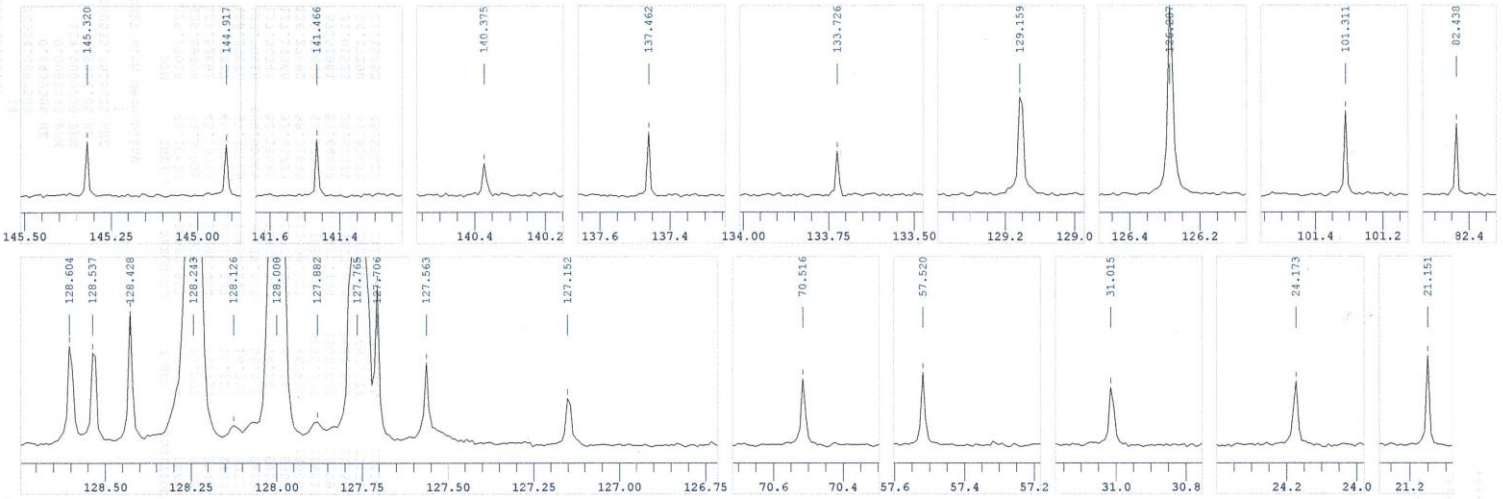


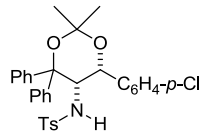
8aa


522
File: /home/vnmrj/vnmrsys/data/murakami_lab/Nakamuro/522_1H_2.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: 522_1H_2
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411625 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
9aa
7.700
7.682
7.559
7.556
7.538
7.446
7.427
7.407
7.296
7.260
7.258
7.136
7.117
7.099
7.081
7.018
7.013
6.942
6.921
6.896
6.876
5.572
5.549
4.985
4.981
4.859
4.733
4.711
3.442
3.436
2.359
1.99 2.01 2.02 1.04 7.07 4.02
0.97
0.97 1.00 0.99
1.00
3.07
ppm

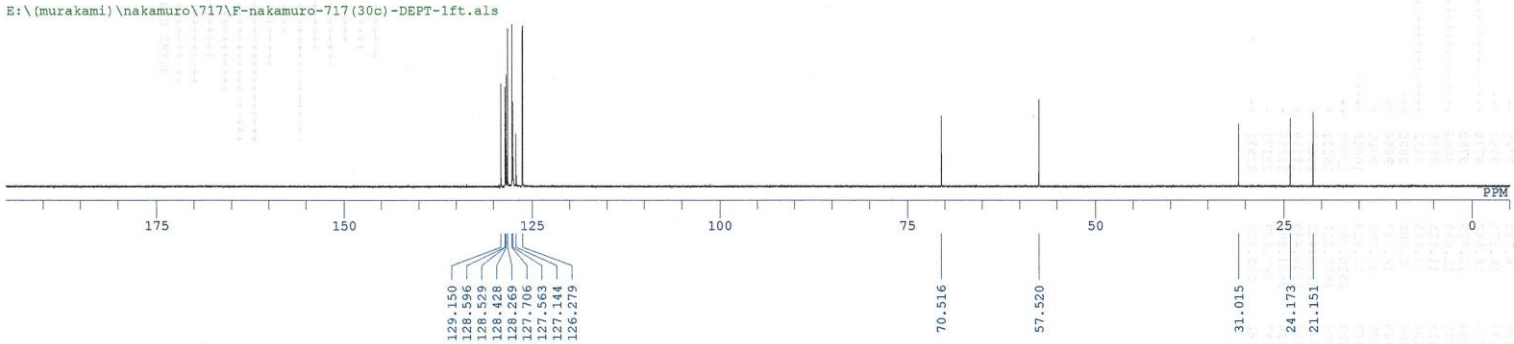

522
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/522_13C.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: 522_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910230 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
9aa
144.893
143.114
141.950
138.971
138.766
133.268
128.948
128.758
128.107
127.931
127.279
126.965
126.884
125.713
125.632
125.229
82.183
77.315
77.000
76.685
72.578
64.635
21.303
160
140
120
100
80
60
40
20
ppm


545
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/545_benzene_1H_3.fid
Pulse Sequence: s2pul
Solvent: c6d6
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: 545_benzene_1H_3
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411807 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Ph
Ph
Ts
N
H
O
O
C6H4-p-Cl
10aa
7.533
7.514
7.400
7.397
7.379
7.180
7.160
7.141
7.119
7.098
7.080
7.063
7.053
7.049
7.043
7.037
7.033
7.017
7.012
7.007
7.000
6.996
6.989
6.980
6.961
6.580
6.560
5.358
5.028
5.026
5.004
5.003
4.909
4.885
2.000
1.500
0.804
1.92
2.02
11.78
2.03
1.00
1.04
1.01
2.99
2.99
2.93
ppm

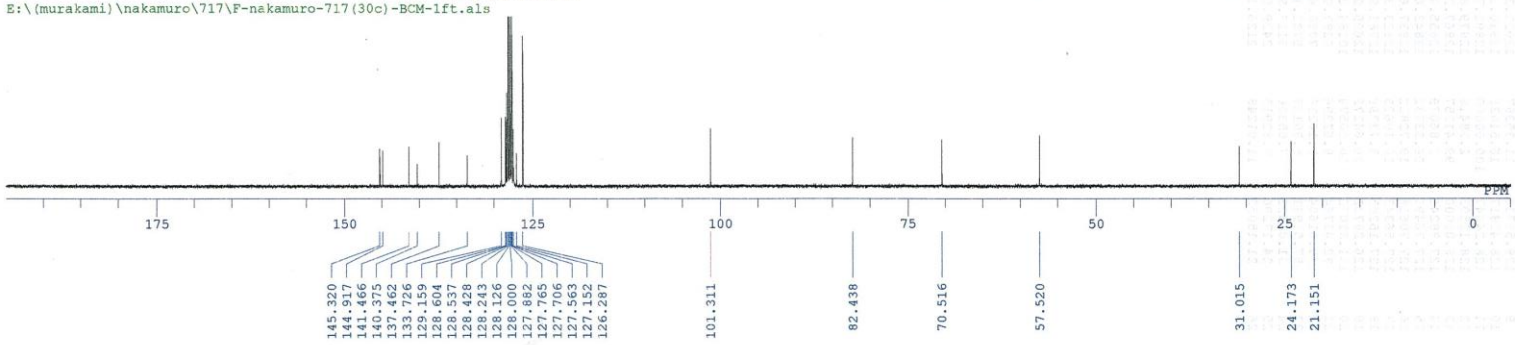




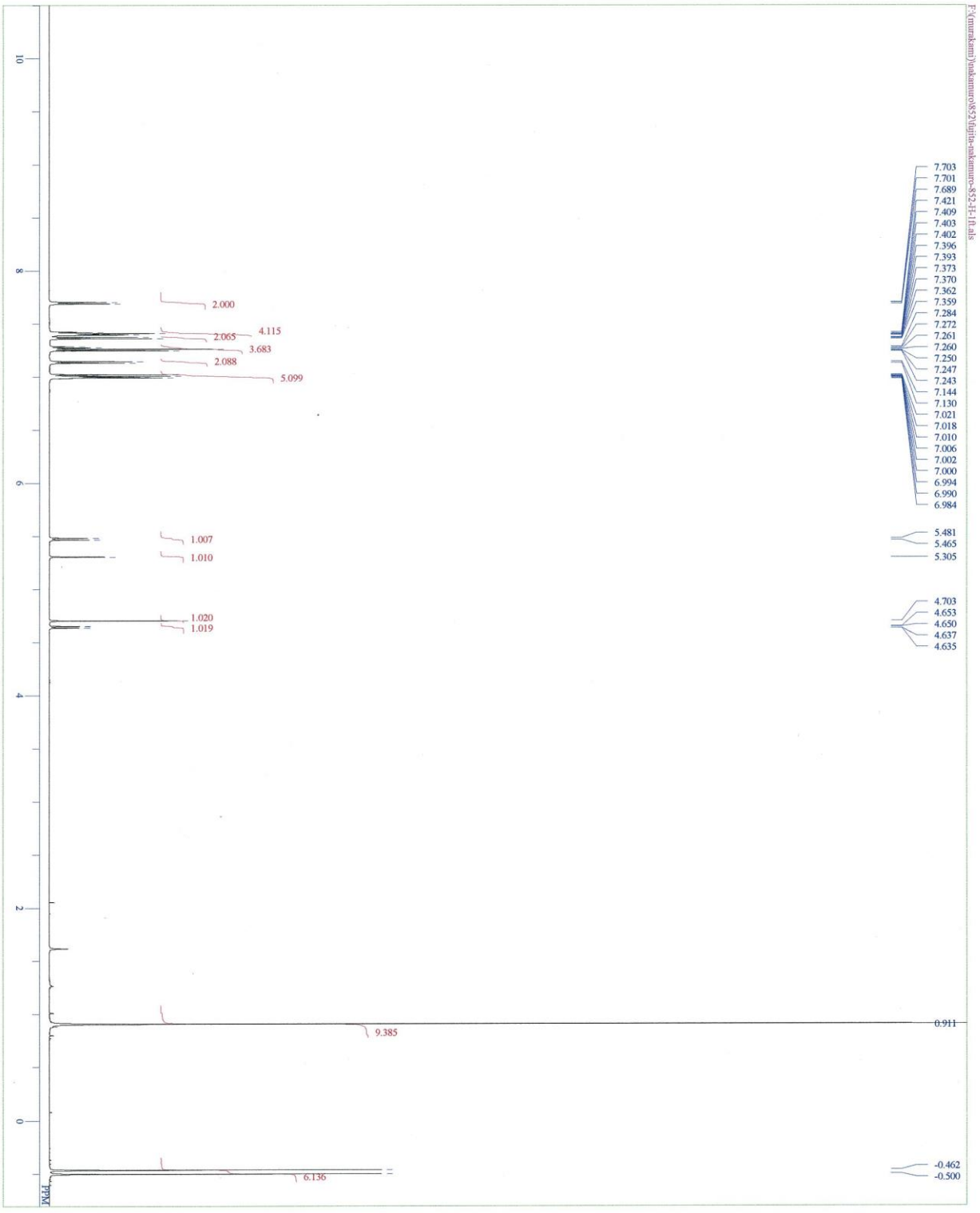
10aa

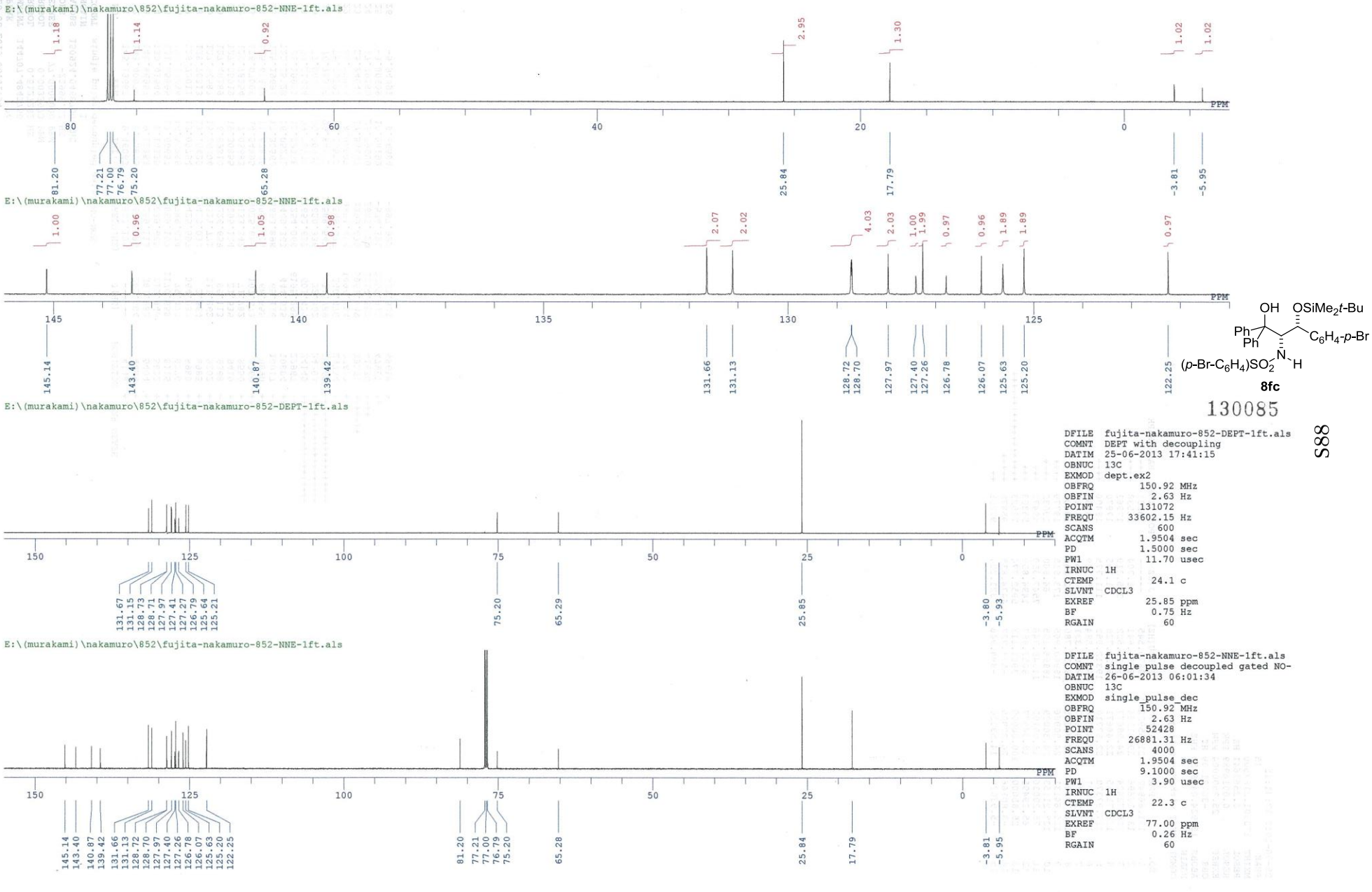



```
DFILE  F-nakamuro-717(30c)-DEPT-1ft.als
COMNT  DEPT with decoupling
DATIM  19-04-2013 23:19:43
OBNUC  13C
EXMOD  dept.ex2
OBFRQ        100.53 MHz
OBFIN          5.86 Hz
POINT         26214
FREQU      22123.56 Hz
SCANS           512
ACQTM        1.1849 sec
PD           1.2000 sec
PW1            8.00 usec
IRNUC  1H
CTEMP         30.0 c
SLVNT  C6D6
EXREF        128.00 ppm
BF             0.42 Hz
RGAIN            60
```

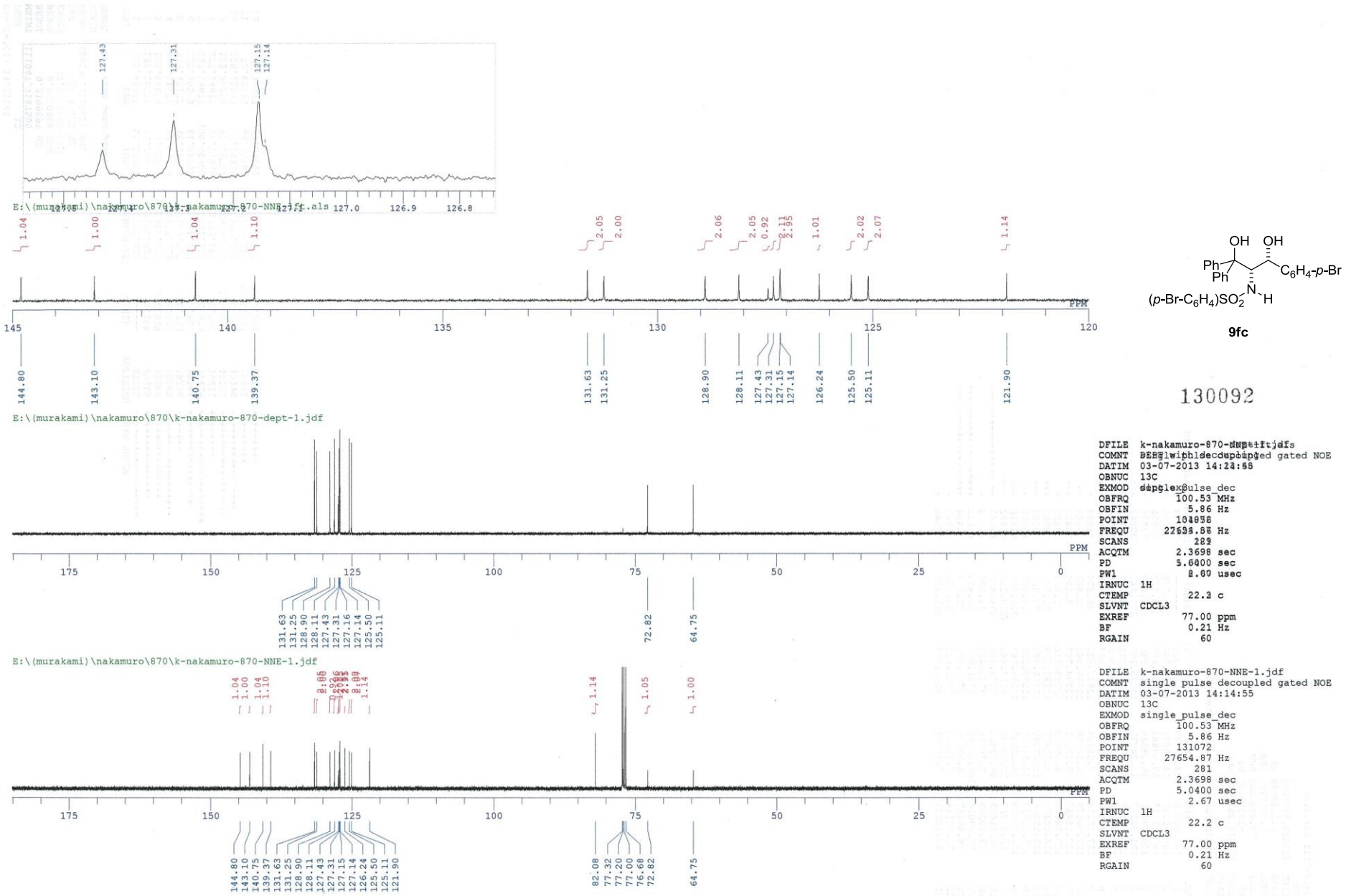


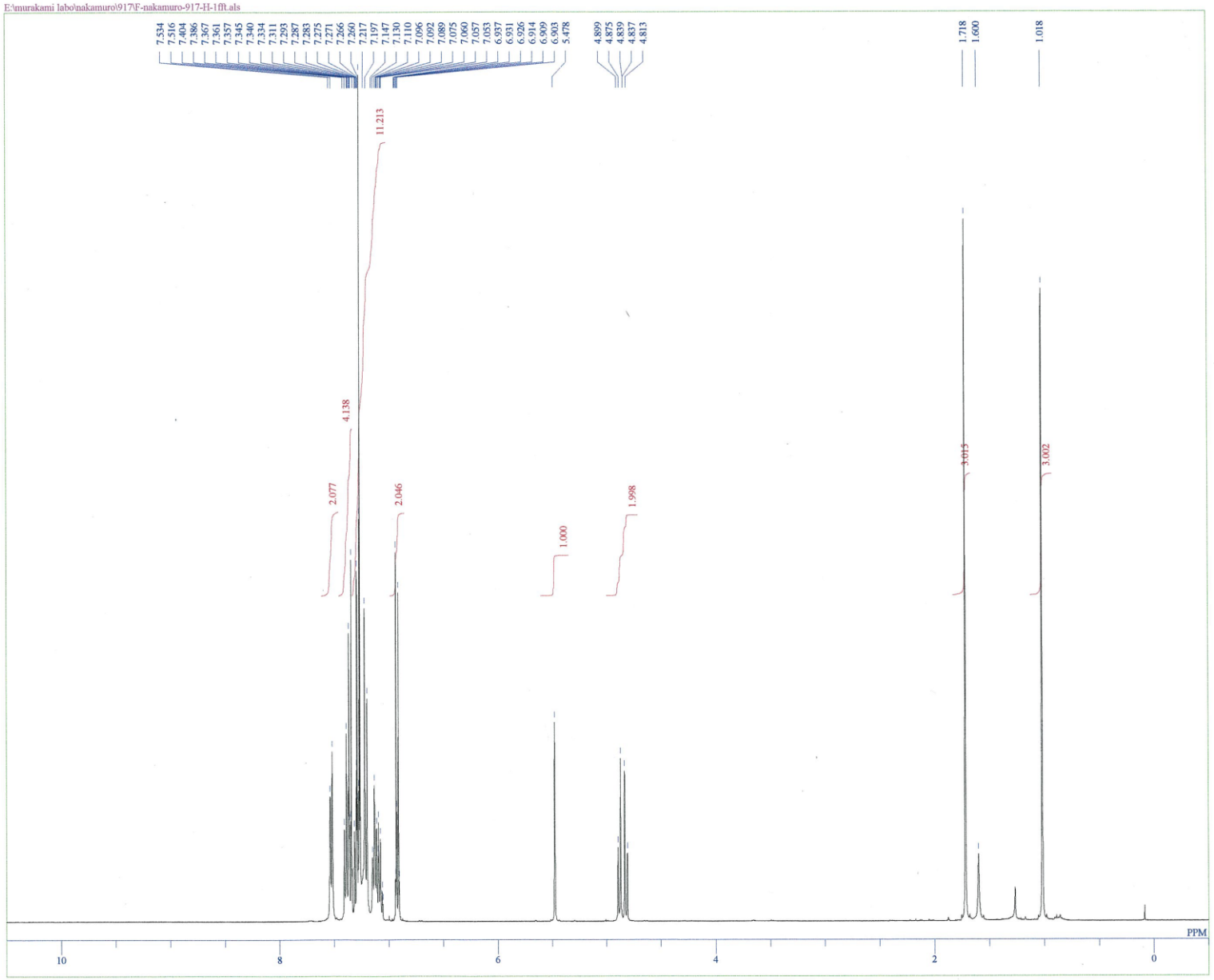

```
DFILE  F-nakamuro-717(30c)-BCM-1ft.als
COMNT  single pulse decoupled gated NOE
DATIM  19-04-2013 14:57:17
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBFIN          5.86 Hz
POINT         26214
FREQU      22123.56 Hz
SCANS           201
ACQTM        1.1849 sec
PD           1.2000 sec
PW1            2.67 usec
IRNUC  1H
CTEMP         30.0 c
SLVNT  C6D6
EXREF        128.00 ppm
BF             0.42 Hz
RGAIN            60
```


F:\(murakami)\nakamuro0852\fujita-nakamuro-852-H-1f.als
7.703
7.701
7.689
7.421
7.409
7.403
7.402
7.396
7.393
7.373
7.370
7.362
7.359
7.284
7.272
7.261
7.260
7.250
7.247
7.243
7.144
7.130
7.021
7.018
7.010
7.006
7.002
7.000
6.994
6.990
6.984
5.481
5.465
5.305
4.703
4.653
4.650
4.637
4.635
2.000
4.115
2.065
3.683
2.088
5.099
1.007
1.010
1.020
1.019
9.385
0.911
6.136
-0.462
-0.500
ppm
DFILE fujita-nakamuro-852-H-1f.als
COMNT single_pulse
DATIM 25-06-2013 16:47:50
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 26214
FREQU 7204.50 Hz
SCANS 8
ACQTM 3.6386 sec
PD 5.5000 sec
PW1 6.75 usec
IRNUC 1H
CTEMP 23.4 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.13 Hz
RGAIN 40
Ph
Ph
OH
OSiMe2t-Bu
C6H4-p-Br
(p-Br-C6H4)SO2
N
H
8fc

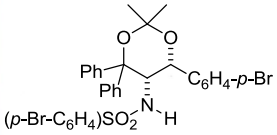

E:\(murakami)\nakamuro\852\fujita-nakamuro-852-NNE-1ft.als
E:\(murakami)\nakamuro\852\fujita-nakamuro-852-DEPT-1ft.als
E:\(murakami)\nakamuro\852\fujita-nakamuro-852-NNE-1ft.als
PPM
OH
OSiMe2t-Bu
Ph
Ph
C6H4-p-Br
(p-Br-C6H4)SO2
N
H
8fc
130085
S88
DFILE fujita-nakamuro-852-DEPT-1ft.als
COMNT DEPT with decoupling
DATIM 25-06-2013 17:41:15
OBNUC 13C
EXMOD dept.ex2
OBFRQ 150.92 MHz
OBFIN 2.63 Hz
POINT 131072
FREQU 33602.15 Hz
SCANS 600
ACQTM 1.9504 sec
PD 1.5000 sec
PW1 11.70 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 25.85 ppm
BF 0.75 Hz
RGAIN 60
DFILE fujita-nakamuro-852-NNE-1ft.als
COMNT single pulse decoupled gated NO-
DATIM 26-06-2013 06:01:34
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBFIN 2.63 Hz
POINT 52428
FREQU 26881.31 Hz
SCANS 4000
ACQTM 1.9504 sec
PD 9.1000 sec
PW1 3.90 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.26 Hz
RGAIN 60

F:\(murakami)\nakamuro\870k-nakamuro-870-H-1fnals.als
7.682
7.679
7.661
7.515
7.510
7.500
7.495
7.491
7.435
7.417
7.396
7.294
7.290
7.282
7.277
7.273
7.264
7.260
7.248
7.244
7.231
7.227
7.221
7.136
7.127
7.114
7.099
7.096
7.088
7.028
7.007
6.946
6.942
6.929
6.925
6.918
5.687
5.664
5.021
4.757
4.753
4.749
4.735
4.732
3.181
1.752
2.077
2.070
2.056
5.963
3.119
2.049
2.040
0.995
1.000
2.024
1.037
10
8
6
4
2
0
PPM
DFILE k-nakamuro-870-H-1fnals.als
COMNT single_pulse
DATIM 03-07-2013 13:37:36
OBNUC 1H
EXMOD single_pulse.exp2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 26214
FREQU 4798.39 Hz
SCANS 8
ACQTM 5.4631 sec
PD 5.0000 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.09 Hz
RGAIN 30
OH
OH
Ph
Ph
N
H
(p-Br-C6H4)SO2
C6H4-p-Br
9fc

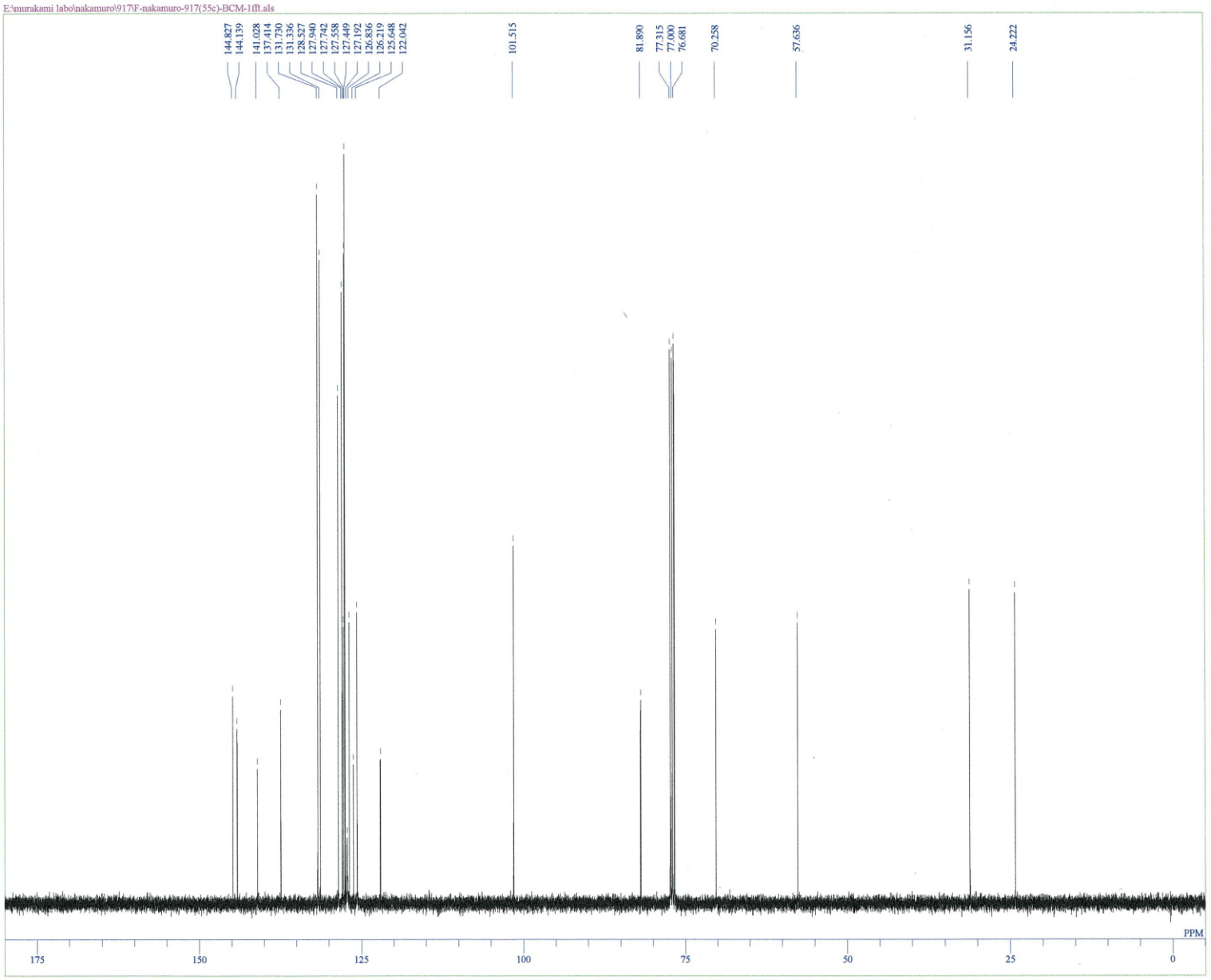

127.43
127.31
127.15
127.14
E:\(murakami)\nakamuro\870\k-nakamuro-870-NNE-1.jdf.als
1.04
1.00
1.04
1.10
2.05
2.00
2.06
2.05
0.92
2.11
2.05
1.01
2.02
2.07
1.14
PPM
144.80
143.10
140.75
139.37
131.63
131.25
128.90
128.11
127.43
127.31
127.15
127.14
126.24
125.50
125.11
121.90
E:\(murakami)\nakamuro\870\k-nakamuro-870-dept-1.jdf
72.82
64.75
E:\(murakami)\nakamuro\870\k-nakamuro-870-NNE-1.jdf
82.08
77.32
77.20
77.00
76.68
72.82
64.75
OH
OH
Ph
Ph
C6H4-p-Br
(p-Br-C6H4)SO2
N
H
9fc
130092
DFILE k-nakamuro-870-NNE-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 03-07-2013 14:14:55
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBFIN 5.86 Hz
POINT 131072
FREQU 27654.87 Hz
SCANS 281
ACQTM 2.3698 sec
PD 5.0400 sec
PW1 2.67 usec
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.21 Hz
RGAIN 60



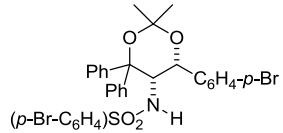
DFILE	F-nakamuro-917-H-1fft.als
COMNT	single_pulse
DATIM	11-07-2013 10:36:47
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	26214
FREQU	4798.39 Hz
SCANS	8
ACQTM	5.4631 sec
PD	5.0000 sec
PW1	5.40 usec
IRNUC	1H
CTEMP	23.4 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.09 Hz
RGAIN	30



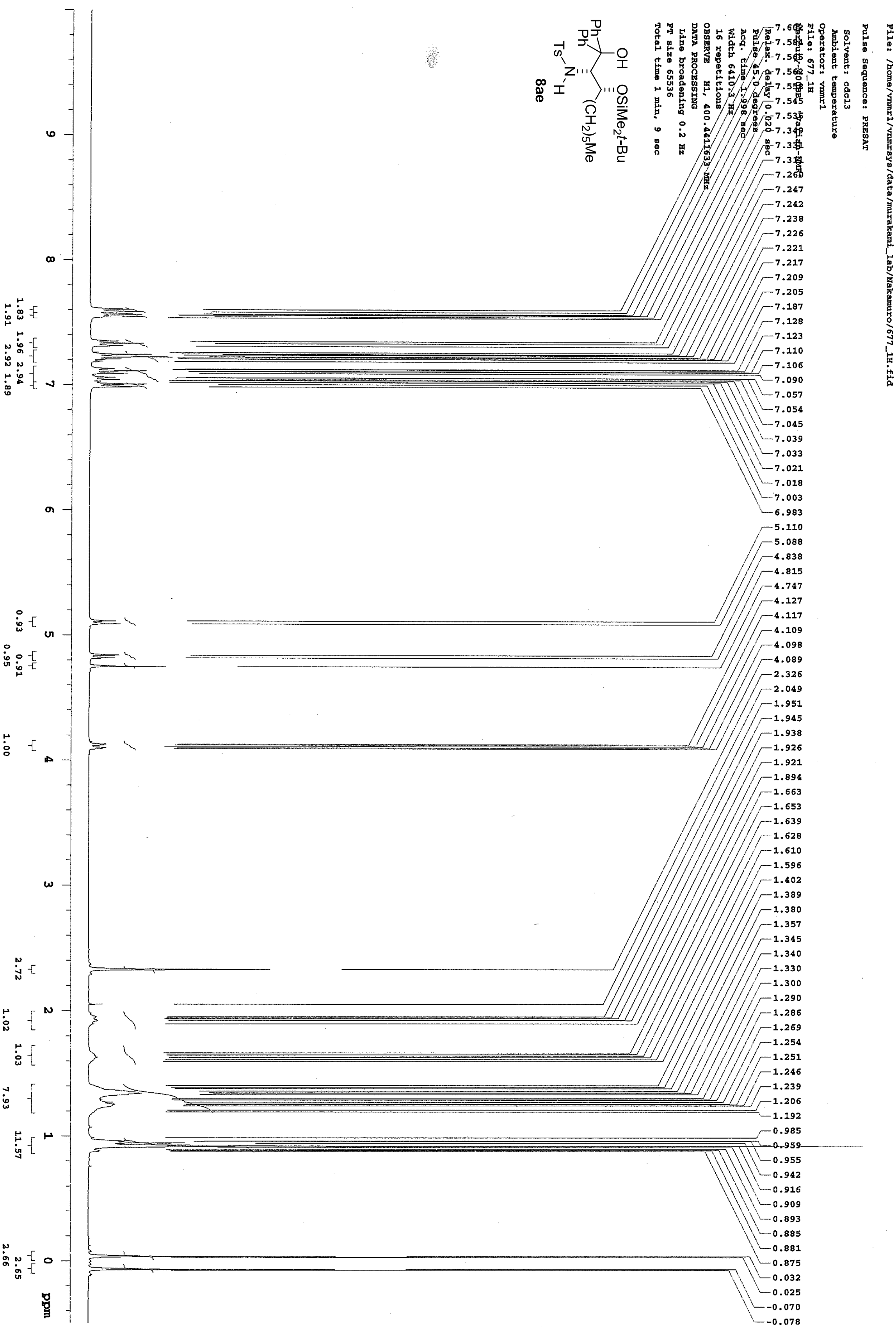
10fc

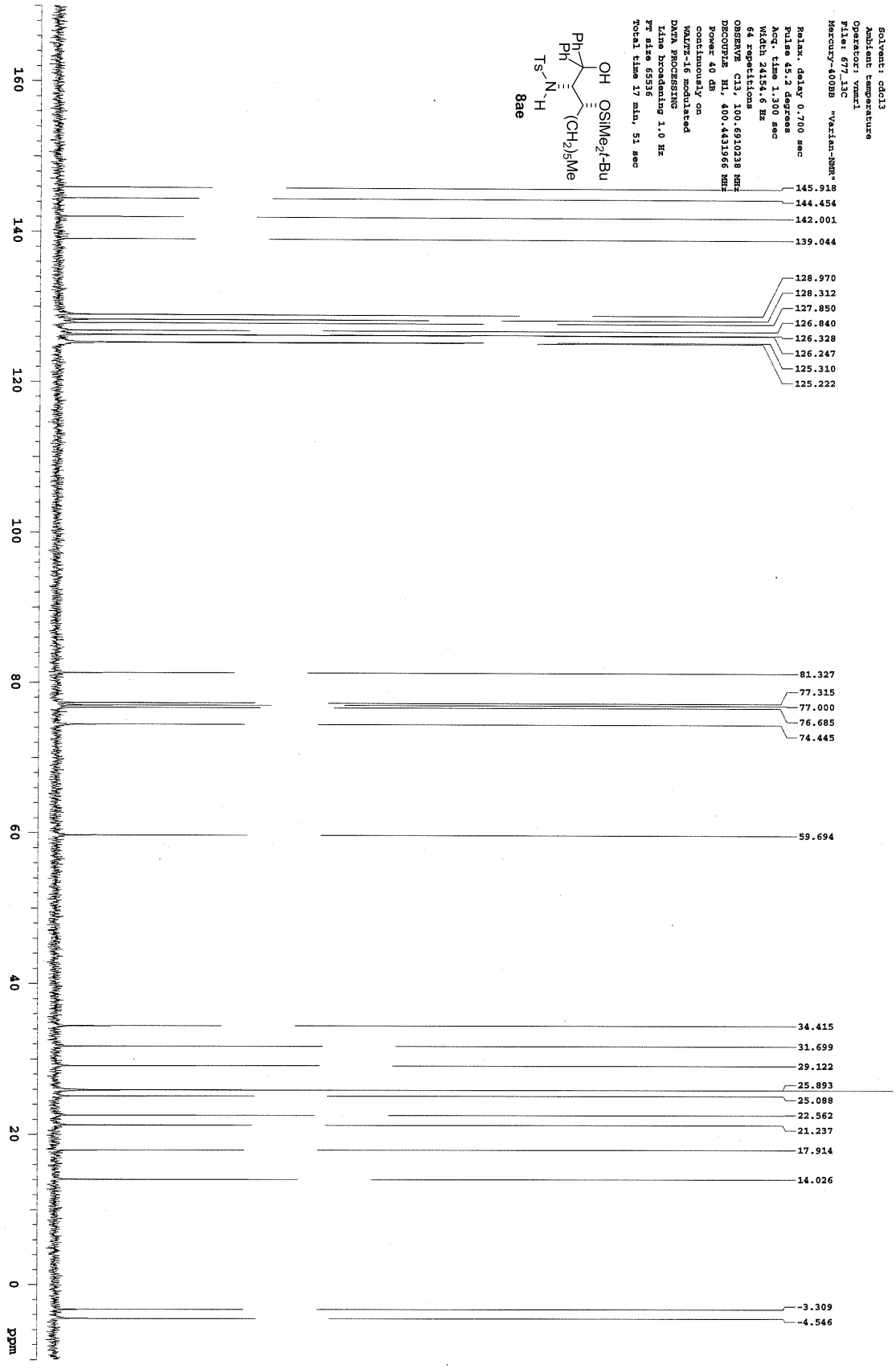


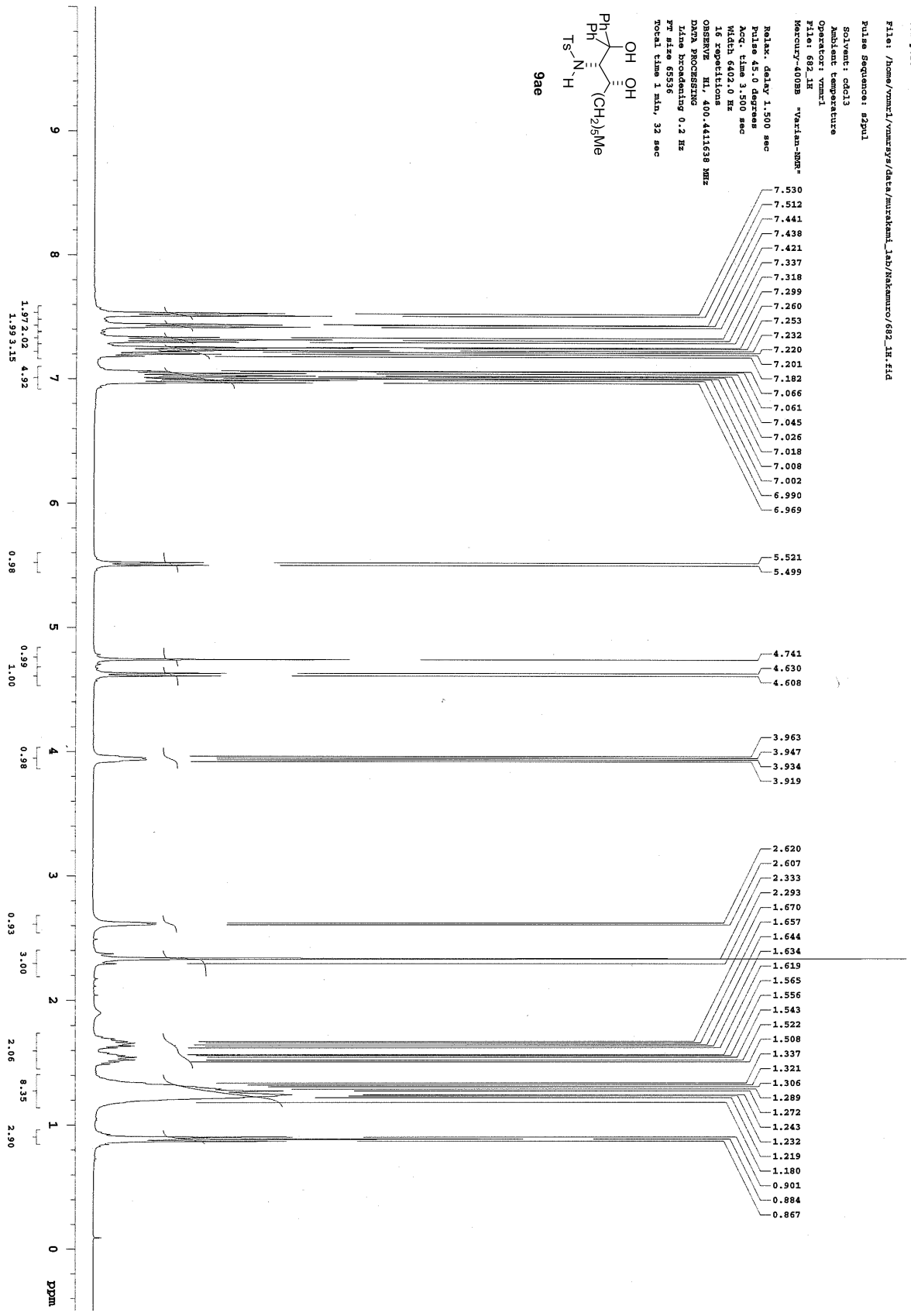
DFILE F-nakamuro-917(55c)-BCM-1fft.als
COMNT single pulse decoupled gated NOE
DATIM 12-07-2013 10:14:57
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 52428
FREQU 22123.56 Hz
SCANS 457
ACQTM 1.1849 sec
PD 1.2000 sec
PW1 2.67 usec
IRNUC 1H
CTEMP 55.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.11 Hz
RGAIN 60

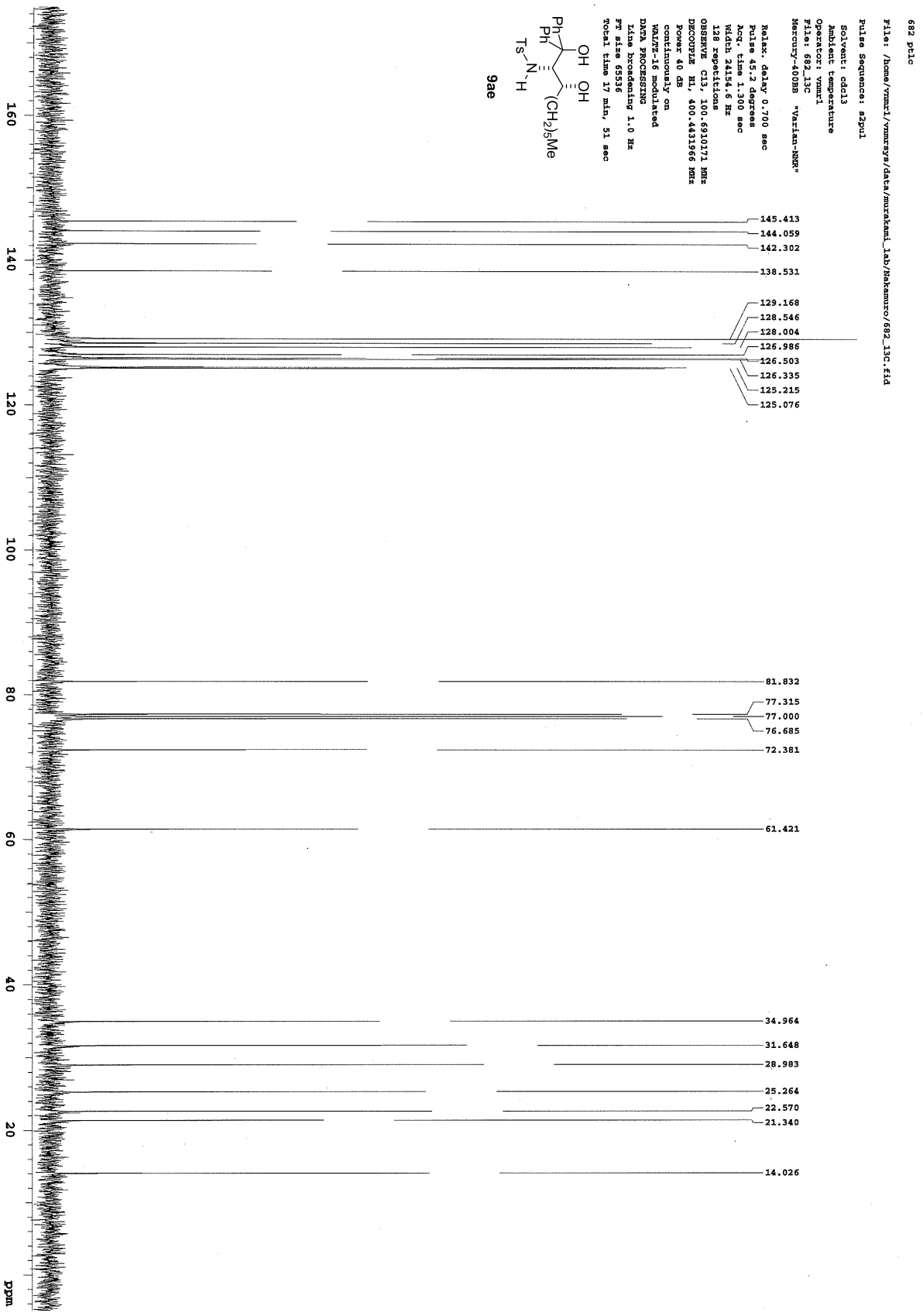


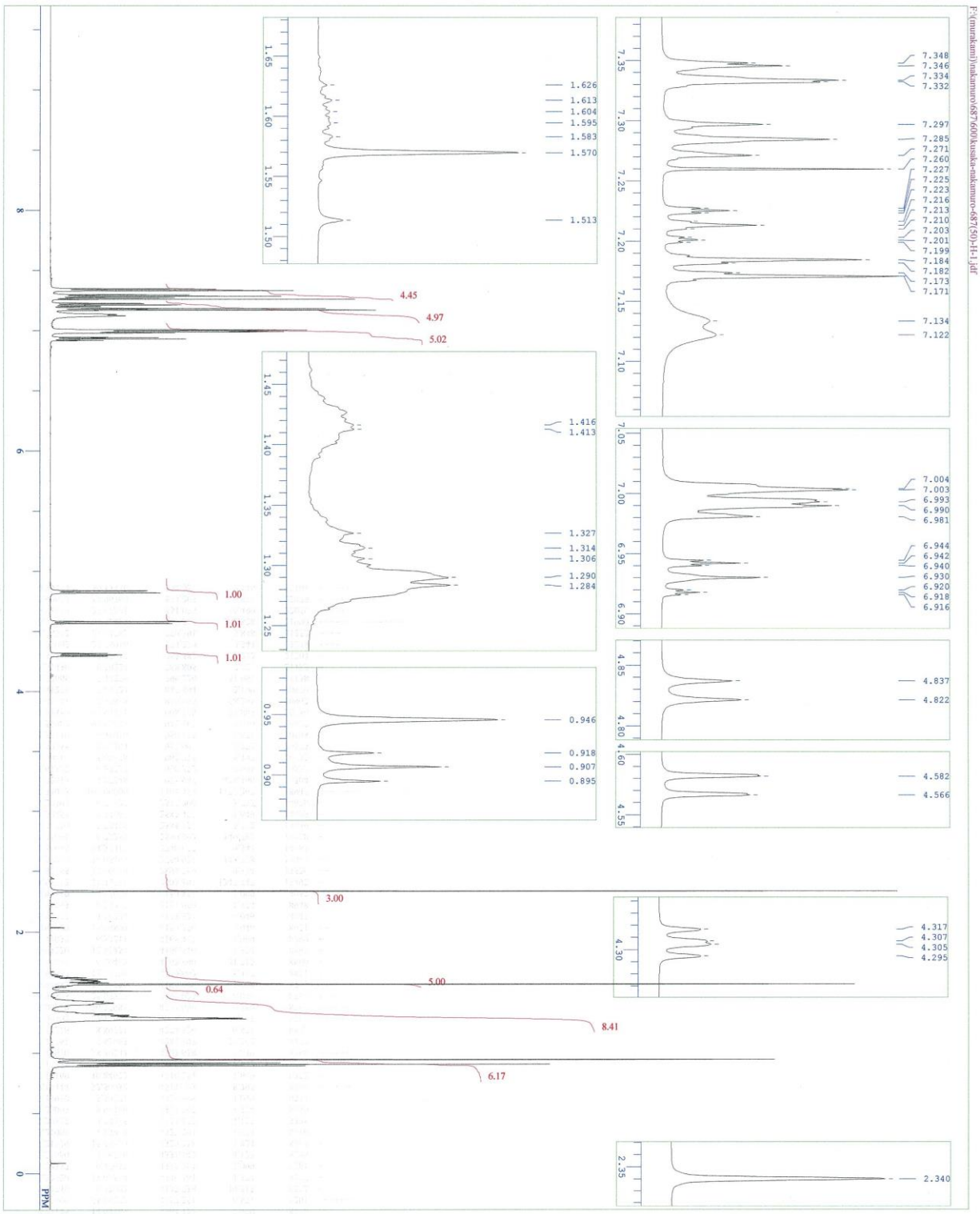
10fc

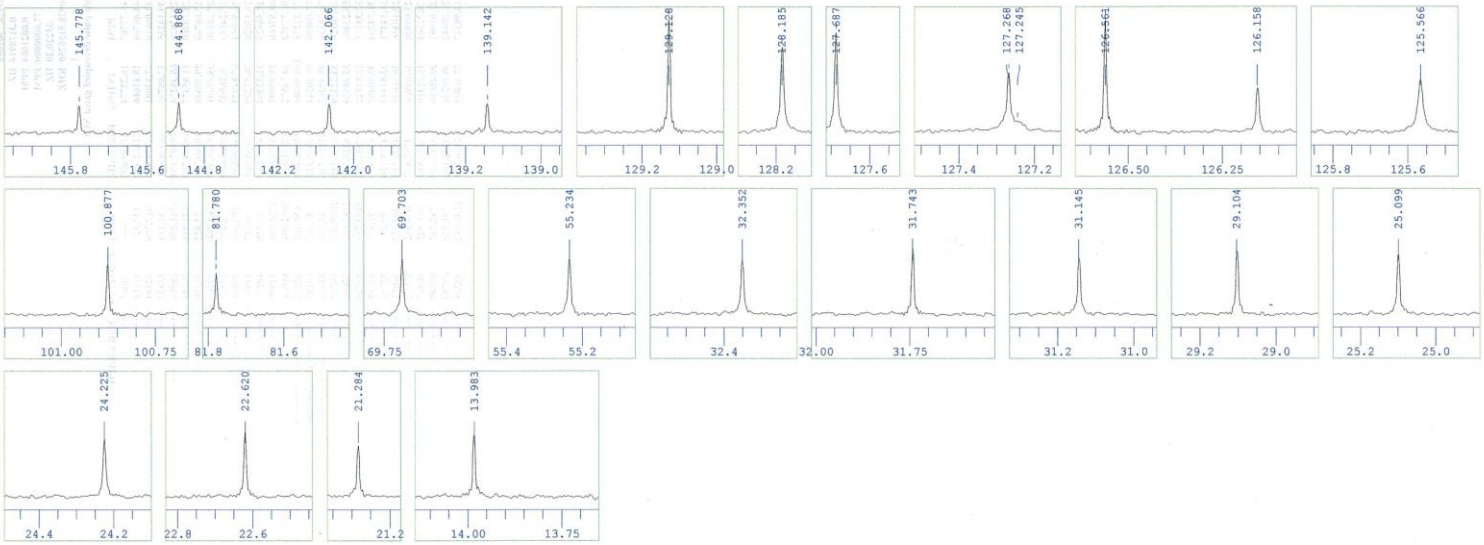

667 column
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/677_1H.fid
Pulse Sequence: PRESAT
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 677_1H
16 repetitions
OBSERVE H1, 400.4411633 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 9 sec
OH OSiMe2t-Bu
Ph
Ph
Ts
N
H
(CH2)5Me
8ae
7.260
7.247
7.242
7.238
7.226
7.221
7.217
7.209
7.205
7.187
7.128
7.123
7.110
7.106
7.090
7.057
7.054
7.045
7.039
7.033
7.021
7.018
7.003
6.983
5.110
5.088
4.838
4.815
4.747
4.127
4.117
4.109
4.098
4.089
2.326
2.049
1.951
1.945
1.938
1.926
1.921
1.894
1.663
1.653
1.639
1.628
1.610
1.596
1.402
1.389
1.380
1.357
1.345
1.340
1.330
1.300
1.290
1.286
1.269
1.254
1.251
1.246
1.239
1.206
1.192
0.985
0.959
0.955
0.942
0.916
0.909
0.893
0.885
0.881
0.875
0.032
0.025
-0.070
-0.078
ppm

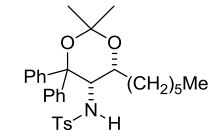

667 column
File: /home/vnmrj/vnmrsys/data/murakami_lab/Nakamuro/677_13c.fid
Pulse Sequence: s2pul
solvent: cdcl3
Ambient temperature
Operator: vnmrj
File: 677_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.2 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
64 repetitions
OBSERVE C13, 100.6910238 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
OH
OSiMe2t-Bu
Ph
Ph
(CH2)5Me
Ts
N
H
8ae
145.918
144.454
142.001
139.044
128.970
128.312
127.850
126.840
126.328
126.247
125.310
125.222
81.327
77.315
77.000
76.685
74.445
59.694
34.415
31.699
29.122
25.893
25.088
22.562
21.237
17.914
14.026
-3.309
-4.546
160
140
120
100
80
60
40
20
0
ppm


682 ptlc
File: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/682_1H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 682_1H
Mercury-400BB "Varian-MMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411638 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
OH
OH
Ph
Ph
Ts
N
H
(CH2)5Me
9ae
7.530
7.512
7.441
7.438
7.421
7.337
7.318
7.299
7.260
7.253
7.232
7.220
7.201
7.182
7.066
7.061
7.045
7.026
7.018
7.008
7.002
6.990
6.969
5.521
5.499
4.741
4.630
4.608
3.963
3.947
3.934
3.919
2.620
2.607
2.333
2.293
1.670
1.657
1.644
1.634
1.619
1.565
1.556
1.543
1.522
1.508
1.337
1.321
1.306
1.289
1.272
1.243
1.232
1.219
1.180
0.901
0.884
0.867
1.97 2.02 4.92
1.99 3.15
0.98
0.99
1.00
0.98
0.93
3.00
2.06
8.35
2.90
ppm

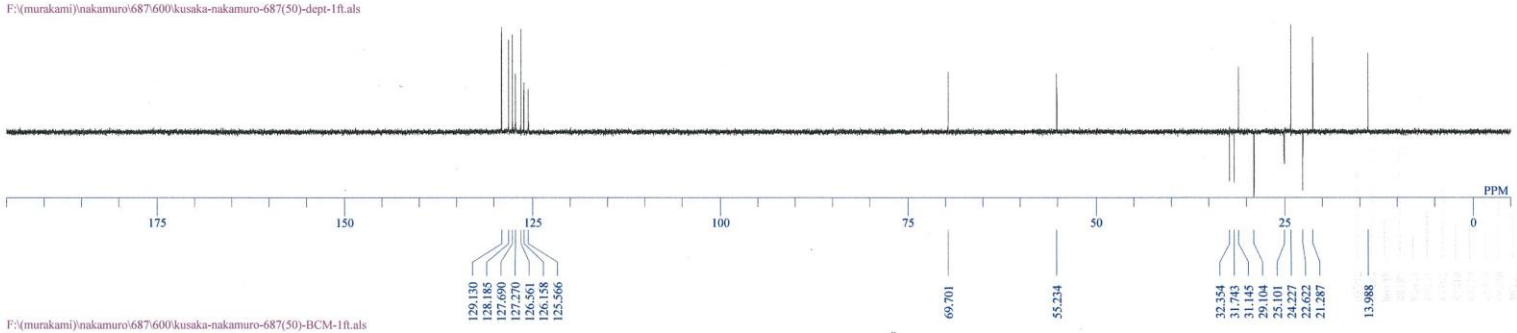

682 ptlc
file: /home/vnmr1/vnmrsys/data/murakami_lab/Nakamuro/682_13C.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 682_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.2 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6910171 MHz
DECOUPLE H1, 400.4431966 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
9ae
145.413
144.059
142.302
138.531
129.168
128.546
128.004
126.986
126.503
126.335
125.215
125.076
81.832
77.315
77.000
76.685
72.381
61.421
34.964
31.648
28.983
25.264
22.570
21.340
14.026
160
140
120
100
80
60
40
20
ppm


F:\(murakami)\nakamuro\687600\kusaka-nakamuro-687(50)-H-1.jdf
7.348
7.346
7.334
7.332
7.297
7.285
7.271
7.260
7.227
7.225
7.223
7.216
7.213
7.210
7.203
7.201
7.199
7.184
7.182
7.173
7.171
7.134
7.122
7.004
7.003
6.993
6.990
6.981
6.944
6.942
6.940
6.930
6.920
6.918
6.916
4.837
4.822
4.582
4.566
4.317
4.307
4.305
4.295
2.340
1.626
1.613
1.604
1.595
1.583
1.570
1.513
1.416
1.413
1.327
1.314
1.306
1.290
1.284
0.946
0.918
0.907
0.895
4.45
4.97
5.02
1.00
1.01
1.01
3.00
5.00
0.64
8.41
6.17
PPM
DFILE kusaka-nakamuro-687(50)-H-1.jdf
COMNT single_pulse
DATIM 2013-04-12 11:25:10
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 32768
FREQU 9005.76 Hz
SCANS 8
ACQTM 3.6386 sec
PD 5.0000 sec
PW1 6.75 usec
IRNUC 1H
CTEMP 50.0 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.13 Hz
RGAIN 44
Ph
Ph
Ts
N
H
O
O
O
(CH2)5Me
10ae

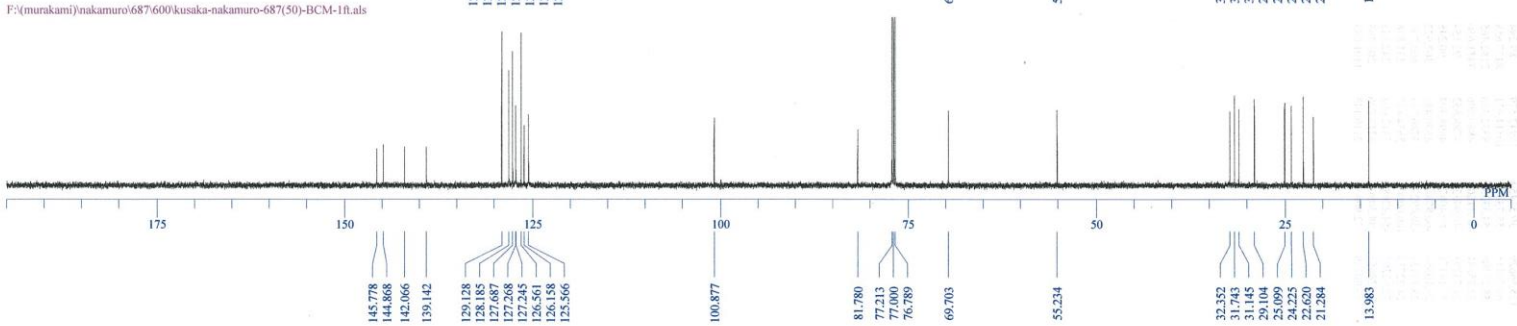




10ae



DFILE kusaka-nakamuro-687(50)-dept-1ft.als
COMNT DEPT with decoupling
DATIM 2013-04-12 11:43:19
OBNUC 13C
EXMOD dept.ex2
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 131072
FREQU 41666.67 Hz
SCANS 128
ACQTM 0.7864 sec
PD 2.0000 sec
PW1 11.70 usec
IRNUC 1H
CTEMP 50.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.63 Hz
RGAIN 60



DFILE kusaka-nakamuro-687(50)-BCM-1ft.als
COMNT single pulse decoupled gated NOE
DATIM 2013-04-12 11:36:42
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 131072
FREQU 41666.67 Hz
SCANS 193
ACQTM 0.7864 sec
PD 2.0000 sec
PW1 3.90 usec
IRNUC 1H
CTEMP 50.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.63 Hz
RGAIN 60