Supplementary information

Synthesis and properties of fluorous benzoquinones and their application in deprotection of silyl ethers

Hiroshi Matsubara,[a]* Takahiko Maegawa,[a] Yasuaki Kita,[a] Takato Yokoji[a] and Akihiro Nomoto[b]

[1]*Department of Chemistry, Graduate School of Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan*
[2]*Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan*

matsu@c.s.osakafu-u.ac.jp

Contents

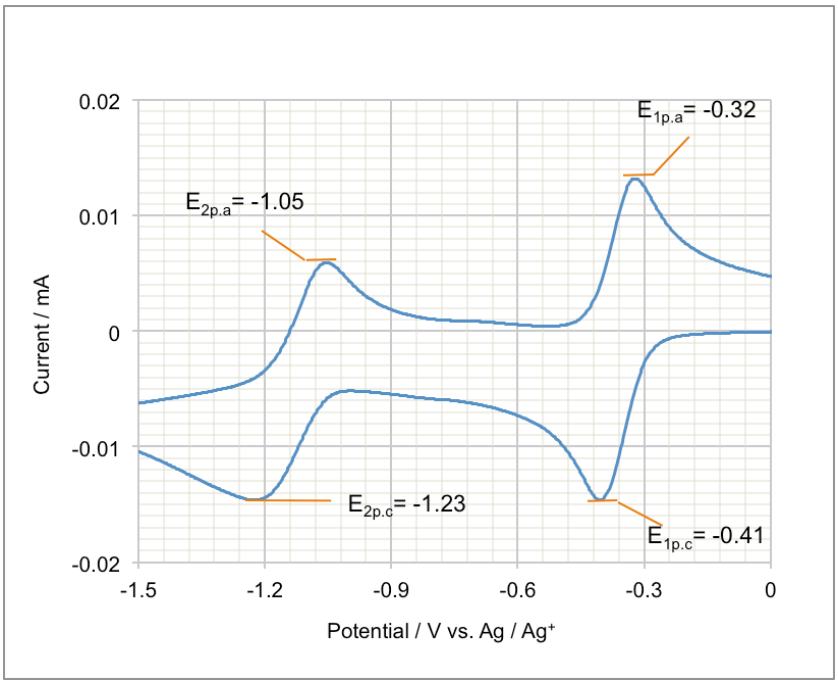


Fig. S1 CV of compound **3a**.

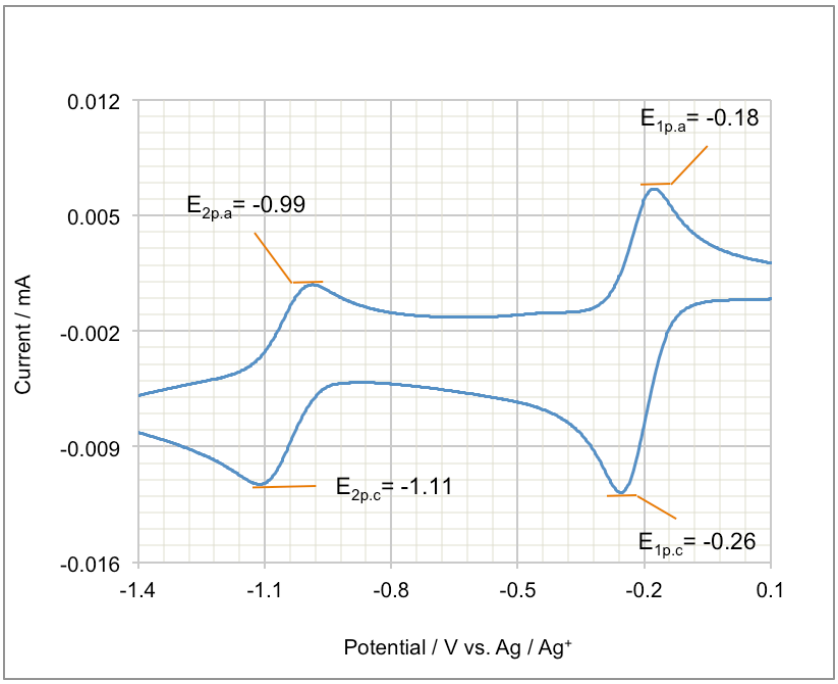


Fig. S2 CV of compound **3c**.

Table S1 Deprotection of silyl ethers using chloranil

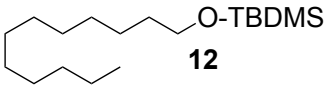
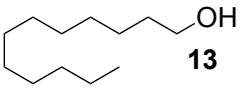
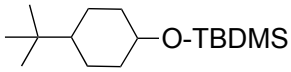
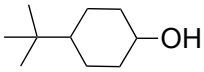
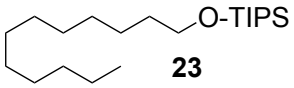
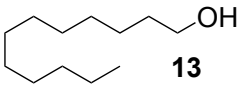
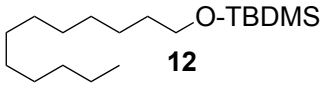
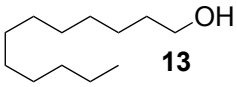
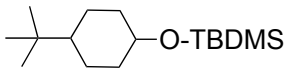
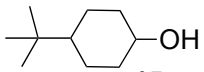
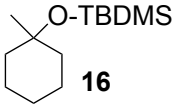
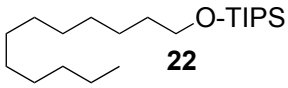
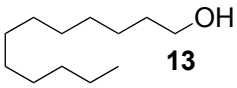
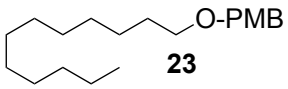
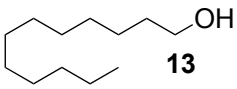
Substrate	Product	Temp.(°C)	Yield(%)
 **12**	 **13**	r.t. 50 °C 70 °C	nr nr 80%
 **14**	 **15**	r.t. 50 °C 70 °C	nr nr 96%
 **23**	 **13**	r.t. 50 °C 70 °C	nr nr nr

Table S2 Deprotection of silyl ethers using DDQ

Substrate	Product	Temp.(°C)	Yield(%)
 **12**	 **13**	r.t.	65%[1]
 **14**	 **15**	r.t.	96%[1]
 **16**	———	r.t.	nr
 **22**	 **13**	r.t.	81%
 **23**	 **13**	r.t.	93%

[1]Data taken from K. Tanemura, T. Suzuki, T. Horaguchi, *J. Chem. Soc. Perkin Trans. 1*, 1992, 2997.

General Information

Melting points were obtained with Yanako micro melting point apparatus and are not corrected. Products were purified by flash chromatography on silica gel (Kanto Chemical Co., Inc., Silica Gel 60N (spherical, neutral), 63-210 μm). ^{1}H NMR spectra were recorded with a JEOL-ECP-500 (500 MHz) spectrometer in $CDCl_3$ or $(CD_3)_2CO$. Chemical shifts were reported in parts per million (δ) referenced to the solvent peak at 7.26 or 2.04 ppm. ^{13}C NMR spectra were recorded with a JEOL-ECP-500 (126 MHz) spectrometer in $CDCl_3$ or $(CD_3)_2CO$ and referenced to the solvent peak at 77.0 or 206.5 ppm. Coupling constants, *J*, were reported in Hertz (Hz), and splitting patterns were designated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), brs (broad singlet), dd (double doublet) and m (multiplet). IR spectra were obtained on a JASCO FT/IR-4100 or a JASCO FT/IR-5300 spectrometer; absorptions were reported in reciprocal centimeters. Conventional mass spectra were recorded with a SHIMADZU GCMS-QP2010Plus or a JEOL MS-700 spectrometer and high-resolution mass spectra were recorded with a JEOL MS-700 spectrometer. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

1,4-diiodo-2,5-dimethoxybenzene (5)[1]

A mixture of 1,4-dimethoxybenzene (**4**, 4.14 g, 30.0 mmol), iodine (8.38 g, 33.0 mmol), iodic acid (2.64 g, 15.0 mmol), acetic acid (41 mL), water (8.1 mL), and sulfuric acid (1.2 mL) was heated to 60 °C for 5 h. After cooling to room temperature, the reaction mixture was poured into 10% aqueous $NaHSO_3$ (250 mL) and crystals separated were collected by filtration using a glass filter. The crystals were then washed with water and dried in vacuo to yield **5** (9.51 g, 76%) as white crystals. Mp 172-174 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 3.82 (s, 6H, OCH_3), 7.19 (s, 2H, ArH). ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 57.2, 85.4, 121.5, 153.3.

1,4-bis(trifluoromethyl)-2,5-dimethoxybenzene (6a)[2]

A mixture of **5** (3.90 g, 10.0 mmol), sodium trifluoroacetate (10.9 g, 80.0 mmol), copper (I) iodide (7.62 g, 40.0 mmol), and dry toluene (40 mL) was heated at 140 °C under N_2 with a Dean-Stark apparatus. After removing azeotropes from the reaction mixture, DMA (60 mL) was then added and the reaction mixture was heated at 170 °C for 4 h. After cooling to room temperature, water was added with cooling using an ice bath. The mixture was filtered through a pad of Celite and the pad was washed with diethyl ether. The aqueous layer was separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/chloroform = 1/2) to yield **2** (1.39 g, 51%) as light brown crystals. Sublimation point 116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 3.90 (s, 6H, OCH_3), 7.22 (s, 2H, ArH). ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 56.7, 111.6, 119.4-126.0, 122.2-122.9, 150.7.

2,5-bis(trifluoromethyl)-1,4-hydroquinone (7a)[2]

A mixture of ethanethiol (960 mg, 15.5 mmol), sodium hydride, 60% oil dispersion (620 mg, 15.5 mmol), and DMF

(15 mL) was stirred at room temperature under N_2 for 1 h. **6a** (834 mg, 3.04 mmol) dissolved in DMF (10 mL) was added and the reaction mixture was heated at 70 °C for 4 h. After cooling to room temperature, 2 M HCl was added until pH of the mixture reached to neutral. The aqueous layer was then separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure to afford crude solid (870 mg). A mixture of the crude product (870 mg) and dichloromethane (25 mL) was stirred under N_2 and cooled to -15 °C by an ice-salt bath. Boron tribromide (1.0 mL, 11 mmol) was added dropwise, and the mixture was warmed slowly to room temperature. After stirring for 4 h, the mixture was quenched by adding water dropwise at 0 °C. The aqueous layer was then separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/diethyl ether=3/1) to yield **7a** (770 mg, 94%) as lemon-yellow crystals. Sublimation point 118 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.26 (2H, s, ArH), 9.20 (2H, s, OH); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 116.2, 121.5, 124.1, 148.7.

2,5-bis(trifluoromethyl)-1,4-benzoquinone (3a)[2]

A mixture of **7a** (148 mg, 0.600 mmol), acetone (4.5 mL), and water (0.5 mL) was stirred at 0 °C for 10 min. Chromium(VI) oxide (42 mg, 0.42 mmol) dissolved in 33% aq H_2SO_4 (1.0 mL) was slowly added and stirred at room temperature for 1 h. The aqueous layer was then separated and extracted with diethyl ether. The combined organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure to yield **3a** (128 mg, 87%) as yellow crystals. Sublimation point 110 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.21 (s); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 116.6-123.2, 135.1, 135.5, 180.0.

Preparation of silyl ethers

Silyl ethers were prepared on the base of procedures reported previously.[3]

***tert*-Butyldimethylsilyl dodecyl ether (12)**

To a mixture of 1-dodecanol (**13**, 1.86 g, 10.0 mmol) and imidazole (681 mg, 10.0 mmol) in DMF (10 mL), *tert*-butyldimethylchlorosilane (1.51 g, 10.0 mmol) was added. After stirring for 6 h at room temperature, water was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane) to yield silyl ether **12** (1.79 g, 63%) as colorless liquid. ν_{max}/cm^{-1} (neat) 2955, 2926, 2855, 1464, 1254, 1103, 836, 775; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.05 (6H, s), 0.86-0.90 (3H, m), 0.88 (9H, s), 1.26-1.31 (18H, m), 1.50 (2H, m), 3.60 (2H, t, *J* 6.4); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C -5.3, 14.1, 18.4, 22.7, 25.8, 26.0, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 32.9, 63.3; LRMS (EI) 300(M^+, 0.3%), 244(23), 243(100), 111(13), 97(21), 89(11), 83(14), 75(39), 69(13); HRMS (EI) Found: [M^+] 300.2846. $C_{18}H_{40}OSi^+$ requires 300.2848).

4-*tert*-Butylcyclohexyl *tert*-butyldimethylsilyl ether (14)

To a mixture of 4-*tert*-butylcyclohexanol (**15**, 1.56 g, 10.0 mmol), triethylamine (3.0 mL, 22 mmol), and 4-dimethylaminopyridine (DMAP, 61 mg, 0.50 mmol) in DMF (10 mL), *tert*-butyldimethylchlorosilane (1.81 g, 12.0 mmol) was added. After stirring for 15 hours at room temperature, water was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane) to yield silyl ether **14** (903 mg, 34%) as colorless liquid. ν_{max}/cm^{-1} (neat): 2951, 2930, 2859, 1251, 1097, 876, 859, 836, 774; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.05 (6H, s), 0.83 (9H, s), 0.88 (9H, s), 0.91-1.04 (3H, m), 1.24 (2H, m), 1.74 (2H, m), 1.88 (2H, m), 3.47 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C -4.6, 18.3, 25.8, 25.9, 27.6, 32.3, 36.4, 47.2, 72.1; LRMS (EI) 270(M^+, 2%), 255(3), 214(18), 213(100), 137(43), 131(10), 123(6), 119(7), 81(10), 75(77). HRMS (EI) (Found: [M^+] 270.2371. $C_{14}H_2F_{18}O_2^+$ requires 270.2349).

1-Methylcyclohexyl *tert*-butyldimethylsilyl ether (16)[4]

To a mixture of 1-methylcyclohexanol (1.14 g, 10.0 mmol) and 2,6-lutidine (2.14 g, 20.0 mmol) in dichloromethane (10 mL), *tert*-butyldimethylsilyl trifluoromethanesulfonate (3.96 g, 15.0 mmol) was added. After stirring for one day at room temperature, water was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane) to yield silyl ether **16** (2.44 g, quant) as colorless liquid. ν_{max}/cm^{-1} (neat): 2956, 2931, 2857, 1254, 1170, 1065, 1028, 1005, 835, 771; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.06 (6H, s), 0.87 (9H, s), 1.19 (3H, s), 1.27-1.67 (10H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C -1.91, 18.3, 22.5, 25.9, 26.0, 30.5, 40.5, 72.6.

8-(*tert*-Butyldimethylsiloxy)-2,6-dimethyl-oct-2-ene (17)

To a mixture of citronellol (**18**, 1.56 g, 10.0 mmol) and imidazole (2.72 g, 40.0 mmol) in DMF (20 mL), *tert*-butyldimethylchlorosilane (1.51 g, 10.0 mmol) was added. After stirring for one day at room temperature, water was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane) to yield silyl ether **17** (2.74 g, quant) as colorless liquid. ν_{max}/cm^{-1} (neat) 2956, 2928, 2857, 1471, 1463, 1378, 1254, 1097, 836, 811, 775; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.05 (6H, s), 0.86-0.91 (12H, m), 1.15 (1H, m), 1.33 (2H, m), 1.50-1.65 (2H, m), 1.60 (3H, s), 1.68 (3H, s), 1.97 (2H, m), 3.64 (2H, m), 5.10 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C -5.2, 17.7, 18.4, 19.7, 25.6, 25.8, 26.0, 29.2, 37.3, 40.0, 61.5, 125.0, 131.1; LRMS (EI) 270(M^+, 2%), 213(46), 185(15), 157(18), 137(21), 95(72), 75(100); HRMS (EI) (Found: [M^+] 270.2374. $C_{16}H_{34}OSi^+$ requires 270.2379).

***dl*-*tert*-Butyldimethylsilyl-menthyl ether (19)**

To a mixture of *dl*-menthol (**20**, 1.56 g, 10.0 mmol) and imidazole (851 mg, 12.5 mmol) in DMF (10 mL), *tert*-butyldimethylchlorosilane (1.51 g, 10.0 mmol) was added. After stirring for 12 h at room temperature, water

was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane) to yield silyl ether **19** (2.46 g, 97%) as colorless liquid. ν_{max}/cm^{-1} (neat) 2956, 2928, 2857, 1471, 1463, 1255, 1108, 1083, 1069, 874, 834, 773; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.05 (6H, d, *J* 6.9), 0.72 (3H, d, *J* 6.9), 0.80-1.01 (18H, m), 1.12 (1H, m), 1.36 (1H, m), 1.60 (2H, m), 1.85 (1H, d, *J* 11.9), 2.21 (1H, m), 3.37 (1H, t, *J* 10.1); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C -4.7, -3.6, 15.8, 18.2, 21.4, 22.5, 22.8, 25.1, 26.0, 31.8, 34.7, 45.4, 50.3, 72.4; LRMS (EI) 270(M^+, 3%), 255(7), 213(100), 137(88), 95(71); HRMS (EI) (Found: [M^+] 270.2379. $C_{16}H_{34}OSi^+$ requires 270.2378).

***tert*-Butyldimethylsilyl *p*-xylyl ether (21)**

To a mixture of *p*-cresol (**33**, 1.08 g, 10.0 mmol) and imidazole (1.70 g, 25.0 mmol) in DMF (10 mL), *tert*-butyldimethylchlorosilane (1.51 g, 10.0 mmol) was added. After stirring for 4 h at room temperature, water was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane) to yield silyl ether **21** (1.90 g, 92%) as colorless liquid. ν_{max}/cm^{-1} (neat) 2957, 2929, 2859, 1613, 1510, 1472, 1257, 916, 839, 823, 780; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.18 (6H, s), 0.98 (9H, s), 2.28 (3H, s), 6.74 (2H, d, *J* 8.3), 7.02 (2H, d, *J* 8.3); ^{13}C NMR (126 MHz, $CDCl_3$): δ_C -4.5, 18.2, 20.6, 25.7, 119.8, 129.8, 130.4, 153.3; LRMS (EI) 222(M^+, 53%), 166(100), 91(66); HRMS (EI) (Found: [M^+] 222.1436. $C_{13}H_{22}OSi^+$ requires 222.1440).

Triisopropylsilyl dodecyl ether (22)

To a mixture of 1-dodecanol (**13**, 932 mg, 5.00 mmol) and imidazole (851 mg, 12.5 mmol) in DMF (6 mL), triisopropylsilyl chloride (1.12 g, 5.81 mmol) was added. After stirring for 20 h at room temperature, water was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane) to yield silyl ether **22** (1.74 g, 98%) as colorless liquid. ν_{max}/cm^{-1} (neat) 2925, 2865, 1465, 1381, 1107, 882, 681; ^1H NMR (500 MHz, $CDCl_3$): δ_H 0.88 (3H, t, *J* 6.9), 1.02-1.12 (22H, m), 1.26 (17H, m), 1.53 (2H, quint, *J* 7.0), 3.66 (2H, t, *J* 6.9); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 12.0, 14.1, 18.0, 22.7, 25.8, 29.4, 29.5, 29.6, 29.7, 31.9, 33.1, 63.5; LRMS (EI) 342 (M^+, 0.3%), 301(17), 300(69), 299(100), 271(31), 243(9); HRMS (EI) (Found: [M^+] 342.3320. $C_{21}H_{46}OSi^+$ requires 342.3318).

***tert*-Butyldiphenylsilyl dodecyl ether (23)**

To a mixture of 1-dodecanol (**13**, 932 mg, 5.00 mmol) and imidazole (477 mg, 7.01 mmol) in DMF (5 mL), *tert*-butyldiphenylchlorosilane (1.37 g, 4.98 mmol) was added. After stirring for 15 hours at room temperature, water was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane) to yield silyl ether **23** (2.02 g, 90%) as colorless liquid. ν_{max}/cm^{-1} (neat) 2955, 2926, 2855,

1465, 1428, 1389, 1111, 1030, 823, 739, 701, 613; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.93 (3H, t, *J* 6.9), 1.10 (9H, s), 1.30-1.40 (18H, m), 1.60 (2H, quint, *J* 7.0), 3.70 (2H, t, *J* 7.0), 7.39-7.47 (6H, m), 7.72 (4H, dd, *J* 7.8, 1.8); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 14.1, 19.2, 22.7, 25.8, 26.9, 29.4, 29.7, 31.9, 32.6, 64.0, 127.5, 129.5, 134.2, 135.6. LRMS (EI) 424(M^+, 0.3%), 368(31), 367(100), 201(12), 199(55), 183(24), 181(12), 123(10), 75(10); HRMS (EI) (Found: [M^+] 424.3152. $C_{28}H_{44}OSi^+$ requires 424.3161).

***p*-Methoxybenzyl dodecyl ether (24)**[5]

To a mixture of 1-dodecanol (**13**, 932 mg, 5.00 mmol) and sodium hydride, 60% oil dispersion (240 mg, 6.00 mmol) in DMF (5 mL) under N_2, 4-methoxybenzyl chloride (940 mg, 6.00 mmol) was added. After stirring for one day at room temperature, water was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/diethyl ether=6/1) to yield benzyl ether **24** (1.46 g, 95%) as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.88 (3H, t, *J* 6.9), 1.25-1.36 (18H, m), 1.58 (2H, quint, *J* 6.9), 3.43 (2H, t, *J* 6.9), 3.81 (3H, s), 4.43 (2H, s), 6.88 (2H, d, *J* 8.7), 7.27 (2H, d, *J* 8.7); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 13.9, 22.7, 26.2, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.2, 55.2, 70.2, 72.5, 113.7, 129.2, 130.8, 159.0.

4-(*tert*-Butyldimethylsiloxymethyl)-triisopropylsiloxymethylcyclohexane (25)

To a mixture of 1,4-cyclohexanedimethanol (8.65 g, 60.0 mmol) and imidazole (4.08 g, 60.0 mmol) in DMF (60 mL), triisopropylsilyl chloride (2.89 g, 15.0 mmol) was added. After stirring for 12 hours at room temperature, water was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane, hexane/diethyl ether=2/1) to yield siloxy alcohol **26** (1.30 g, 21%) as colorless liquid. ν_{max}/cm^{-1} (neat) 3334, 2940, 2920, 2865, 1464, 1119, 1094, 1061, 882, 682; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.91-1.08 (25H, m), 1.35-1.52 (2H, m), 1.80 (4H, m), 2.18 (1H, brs), 3.41 (2H, d, *J* 6.4), 3.47 (2H, d, *J* 6.0), 3.50 (d, *J* 7.4, minor stereoisomer), 3.54 (d, *J* 6.4, minor stereoisomer); ^{13}C NMR (126 MHz) δ_C 12.0, 18.1, 25.3, 25.6, 29.1, 38.0, 38.5, 40.8, 41.0, 65.9, 66.7, 68.6, 69.0; LRMS (EI) 300(M^+, 1%), 257(18), 183(19), 131(47), 109(100), 103(78); HRMS (EI) (Found: [M^+] 300.2493. $C_{17}H_{36}O_2Si^+$ requires 300.2485).

To a mixture of siloxy alcohol **26** (992 mg, 3.30 mmol) and imidazole (851 mg, 12.5 mmol) in DMF (10 mL), *tert*-butyldimethylchlorosilane (754 mg, 5.00 mmol) was added. After stirring for 4 h at room temperature, water was added and the mixture was then extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/diethyl ether=5/1) to yield silyl ether **25** (1.33 g, 95%) as colorless liquid. ν_{max}/cm^{-1} (neat) 2942, 2926, 2864, 1464, 1254, 1123, 1088, 1070, 882, 775; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.03 (6H, s), 0.89 (9H, s), 1.02-1.50 (27H, m), 1.80 (4H, m), 3.40 (2H, d, *J* 6.4), 3.48 (2H, d, *J* 6.4), 3.49 (d, *J* = 5.5 Hz, minor stereoisomer), 3.56 (d, *J* = 6.4 Hz, minor stereoisomer); ^{13}C NMR (126 MHz, $CDCl_3$): δ_C -5.3, 12.1, 18.1, 18.5, 25.5, 25.6, 26.1, 29.2, 40.8, 41.1, 68.9, 69.1; LRMS (EI) 414(M^+, 1%), 371(24), 203(22), 129(74), 109(100); HRMS (EI)

(Found: [M^+] 414.3347. $C_{23}H_{50}O_2Si_2^+$ requires 414.3349).

4-(*tert*-Butyldimethylsiloxy)-triisopropylsiloxycyclohexane (27)

To a mixture of 1,4-cyclohexanediol (6.97 g, 60.0 mmol) and imidazole (851 mg, 12.5 mmol) in DMF (60 mL), triisopropylsilyl chloride (2.89 g, 15.0 mmol) was added. After stirring for 15 h at room temperature, water was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/diethyl ether=3/1, hexane/diethyl ether=2/1) to yield siloxy alcohol **28** (2.94 g, 22%) as colorless liquid. ν_{max}/cm^{-1} (neat) 3348, 2941, 2866, 1464, 1372, 1109, 1053, 1017, 965, 882, 682; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.01 (21H, s), 1.27-1.91 (8H, m), 2.54 (1H, brs), 3.61-3.88 (2H, m); ^{13}C NMR (126 MHz) δ_C 12.2, 18.0, 30.0, 31.6, 32.4, 32.8, 66.6, 69.0, 69.1, 69.9; LRMS (EI) 272(M^+, 0.6%), 229(59), 131(26), 103(36), 97(100), 81(49), 61(41); HRMS (EI) (Found: [M^+] 272.2164. $C_{15}H_{32}O_2Si^+$ requires 272.2172).

To a mixture of siloxy alcohol **28** (1.37 g, 6.00 mmol) and imidazole (1.02 g, 15.0 mmol) in DMF (6 mL), *tert*-butyldimethylchlorosilane (904 mg, 6.00 mmol) was added. After stirring for 15 h at room temperature, water was added and the mixture was then extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/diethyl ether=3/1) to yield silyl ether **27** (1.92 g, 84%) as colorless liquid. ν_{max}/cm^{-1} (neat) 2942, 2892, 2865, 1463, 1379, 1254, 1101, 1052, 1017, 882, 835, 774, 679; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.05 (6H, s), 0.90 (9H, m), 1.06 (21H, m), 1.34-1.50 (4H, m), 1.76-1.88 (4H, m), 3.69-3.82 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C -4.6, 12.4, 18.2, 25.9, 31.2, 31.5, 32.4, 32.6, 68.2, 68.9, 69.7; LRMS (EI) 386(M^+, 0.2%), 344(22), 343(72), 329(19), 253(23), 245(19), 211(91), 205(22), 203(27), 147(29), 133(23), 81(100), 75(47), 73(26); HRMS (EI) (Found: [M^+] 386.3035. $C_{21}H_{46}O_2Si_2^+$ requires 386.3036).

8-(*tert*-Butyldimethylsiloxy)-(4-methoxybenzyloxy)octane (29)

To a mixture of 1,8-octanediol (8.77 g, 60.0 mmol) and imidazole (4.08 g, 60.0 mmol) in DMF (60 mL), *tert*-butyldimethylchlorosilane (2.26 g, 15.0 mmol) was added. After stirring for 17 h at room temperature, water was added and the mixture was then extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/diethyl ether=2:1) to yield 8-(*tert*-butyldimethylsiloxy)octanol[6] (**S1**, 2.92 g, 19%) as colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.04 (6H, s), 0.89 (9H, s), 1.31 (8H, m), 1.49-1.58 (4H, m), 3.59 (2H, t, *J* 6.9), 3.64 (2H, dt, *J* 6.4, 6.0); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C -5.4, 18.2, 25.6, 25.8, 29.2, 29.3, 32.5, 32.7, 62.4, 63.2.

To a mixture of siloxy alcohol **S1** (1.82 g, 7.00 mmol) and sodium hydride, 60% oil dispersion (288 mg, 7.20 mmol) in DMF (10 mL) under N_2, 4-methoxybenzyl chloride (1.11 g, 7.09 mmol) was added. After stirring for 22 h at room temperature, water was added and the mixture was then extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by

column chromatography on silica gel (eluent: hexane/diethyl ether=6/1) to yield silyl ether **29** (910 mg, 34%) as colorless liquid. ν_{max}/cm^{-1} (neat) 2929, 2855, 1613, 1514, 1464, 1249, 1099, 1039, 836, 775; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.05 (6H, s), 0.89 (9H, s), 1.29 (8H, m), 1.50 (2H, m), 1.59 (2H, m), 3.43 (2H, t, *J* 7.5), 3.59 (2H, t, *J* 6.5), 3.80 (3H, s), 4.43 (2H, s), 6.88 (2H, d, *J* 8.3), 7.26 (2H, d, *J* 8.3); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C -5.3, 18.4, 25.7, 26.0, 26.1, 29.4, 29.5, 29.7, 32.9, 55.2, 63.3, 70.2, 72.5, 113.7, 129.2, 130.8, 159.1; LRMS (EI) 380(M^+, 0.2%), 323(4), 195(11), 147(6), 122(10), 121(100), 75(5), 58(8); HRMS (EI) (Found: [M^+] 380.2745. $C_{22}H_{40}O_3Si^+$ requires 380.2747).

1-Adamantyl *tert*-butyldimethylsilyl ether (31)[7]

To a mixture of 1-adamantanol (**32**, 1.52 g, 10.0 mmol) and 2,6-lutidine (2.14 g, 20.0 mmol) in dichloromethane (10 mL), *tert*-butyldimethylsilyl trifluoromethanesulfonate (3.96 g, 14.9 mmol) was added. After stirring for 5 hours at room temperature, water was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane) to yield silyl ether **31** (2.65 g, 99%) as colorless liquid. ν_{max}/cm^{-1} (neat) 2955, 2912, 2851, 1353, 1254, 1128, 1093, 1015, 850, 832, 774; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.07 (6H, s), 0.85 (9H, s), 1.58 (6H, m), 1.72 (6H, d, *J* 2.8), 2.09 (3H, brs); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C -1.7, 17.9, 25.8, 30.9, 36.3, 46.1, 70.7; LRMS (EI) 266(M^+, 0.9%), 210(18), 209(97), 135(100), 75(34); HRMS (EI) (Found: [M^+] 266.2069.$C_{16}H_{30}OSi^+$ requires 266.2066).

1-Dodecanol (13)[8]

^1H NMR (500 MHz, $CDCl_3$) δ_H 0.85 (3H, m), 1.23 (18H, m), 1.52 (2H, m), 2.54 (1H, s), 3.57 (2H, m). ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 14.0, 22.6, 25.7, 29.3, 29.4, 29.6, 31.9, 32.7, 62.7.

4-*tert*-Butylcyclohexanol (15)[9]

^1H NMR (500 MHz, $CDCl_3$) δ_H 0.84 (9H, s,), 0.93-2.00 (9H, m), 3.50 (1H, m), 4.02 (s, minor stereoisomer). ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 20.9, 25.5, 27.5, 27.6, 32.3, 33.3, 36.0, 47.1, 48.0, 65.8, 71.2.

Citronellol (18)[10]

^1H NMR (500 MHz, $CDCl_3$) δ_H 0.87 (d, *J* = 6.5 Hz, 3H), 1.16 (m, 1H), 1.33 (m, 2H), 1.52-1.67 (m, 8H), 1.95 (m, 2H), 2.31 (brs, 1H), 3.61 (m, 2H), 5.06 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 17.5, 19.4, 25.4, 25.6, 29.1, 37.1, 39.7, 60.9, 124.6, 131.1.

Menthol (20)[11]

^1H NMR (500 MHz, $CDCl_3$) δ_H 0.80 (3H, d, *J* 6.9), 0.86-1.00 (8H, m), 1.10 (2H, m), 1.44 (2H, m), 1.61 (2H, m), 1.95 (1H, d, *J* 11.9), 2.16 (1H, m), 3.39 (1H, m). ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 16.1, 21.0, 22.2, 23.1, 25.8, 31.6, 34.5, 45.0, 50.1, 71.5.

8-(4-Methoxybenzyloxy)octanol (30)

Colorless liquid; ν_{max}/cm^{-1} (neat) 3388, 2931, 2855, 1613, 1514, 1464, 1248, 1096, 1037, 821; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.30 (8H, m), 1.55 (4H, m), 3.42 (2H, t, *J* 6.9), 3.60 (2H, t, *J* 6.4), 3.79 (3H, s), 4.42 (2H, s), 6.86 (2H, d, *J* 8.7), 7.25 (2H, d, *J* 8.7); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 25.6, 26.1, 29.3, 29.4, 29.7, 55.2, 62.9, 70.1, 72.4, 113.7, 129.2, 130.7, 159.0; LRMS (EI) 266(M^+, 7%), 136(91), 121(100), 107(14); HRMS (EI) (Found: [M^+] 266.1875. $C_{16}H_{26}O_3Si^+$ requires 266.1900).

1-Adamantanol (32)[12]

^1H NMR (500 MHz, $CDCl_3$) δ_H 1.46 (1H, s), 1.60 (6H, q, *J* 12.4), 1.70 (6H, s), 2.15 (3H, s). ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 30.7, 36.0, 45.3, 68.2.

***p*-Cresol (33)**[13]

^1H NMR (500 MHz, $CDCl_3$) δ_H 2.29 (3H, s), 4.80 (1H, s), 6.75 (2H, d, *J* 7.8), 7.05 (2H, d, *J* 7.8). ^{13}C NMR (126 MHz) δ_C 20.4, 115.1, 130.1, 153.1.

Cyclic voltammetry

Cyclic Voltammetry (CV) was applied to a 1.0 mM solution of samples in 0.1 M tetra-*n*-butylammonium perchlorate/acetonitrile (working electrode: glassy carbon (GC), counter electrode: platinum wire electrode, reference electrode: $Ag/AgNO_3$) system using a multichannel Potentiostat/Galvanostat (VSP, Bio-logic). The voltammogram was recorded at scan speed of 20-50 mV/s at room temperature. Potentials were corrected using ferrocene (Fc/Fc^+) as an internal standard.

References

1 A. Schaate, P. Roy, T. Preuße, S. J. Lohmeier, A. Godt and P. Behrens, *Chem. Eur. J.,* 2011, **17**, 9320.

2 S. Hünig, R. Bau, M. Kemmer, H. Meixner, T. Metzenthin, K. Peters, K. Sinzger and J. Gulbis, *Eur. J. Org. Chem.,* 1998, 335.

3 For TBDMS: using TBDMS chloride with imidazole: E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.,* 1972, **94**, 6190; with DMAP and triethylamine: S. K. Chaudhary and O. Hernandez, *Tetrahedron Lett.,* 1979, **20**, 99; using TBDMS triflate with 2,6-lutidine: E. J. Corey, H. Cho, C. Rücker and D. H. Hua, *Tetrahedron Lett.,* 1981, **22**, 3455. For TIPS: R. F. Cunico and L. Bedell, *J. Org. Chem.,* 1980, **45**, 4797. For TBDPS: S. Hanessian, and P. Lavallee, *Can. J. Chem.,* 1975, **53**, 2975; 1977, **55**, 562.

4 E. Brehm and R. Breinbauer, *Org. Biomol. Chem.,* 2013, **11**, 4750.

5 K. Manabe, S. Iimura, X.-M. Sun and S. Kobayashi, *J. Am. Chem. Soc*.. 2002, **124**, 11971.

6 M. R. Detty and M. D. Seidler, *J. Org. Chem.,* 1981, **46**, 1283.

7 A. Iida, A. Horii, T. Misaki and Y. Tanabe, *Synthesis,* 2005, **16**, 2677.

8 Y. Koshikari, A. Sakurai and K; Ishihara, *Org. Lett.* 2012, **14**, 3194.

9 N. Sakai, K. Nagasawa, R. Ikeda, Y. Nakaikea and T. Konakahara, *Tetrahedron Lett.,* 2011, **52**, 3133.

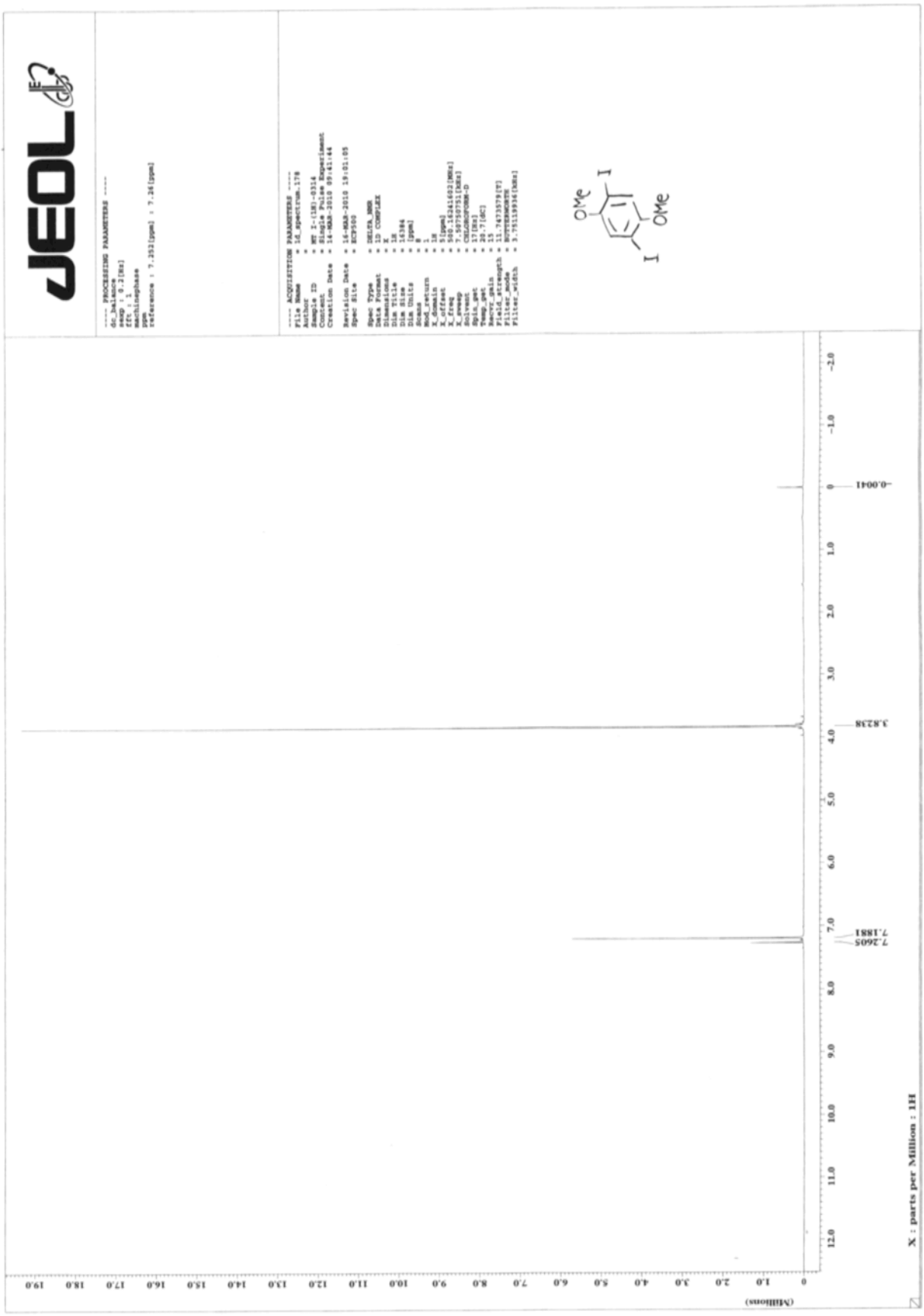
10 K. Oh and W. E. Knabe, *Tetrahedron,* 2009, **65**, 2966.

11 J. Yang, L. Dai, X. Wang and Y. Chen, *Tetrahedron,* 2011, **67**, 1456.

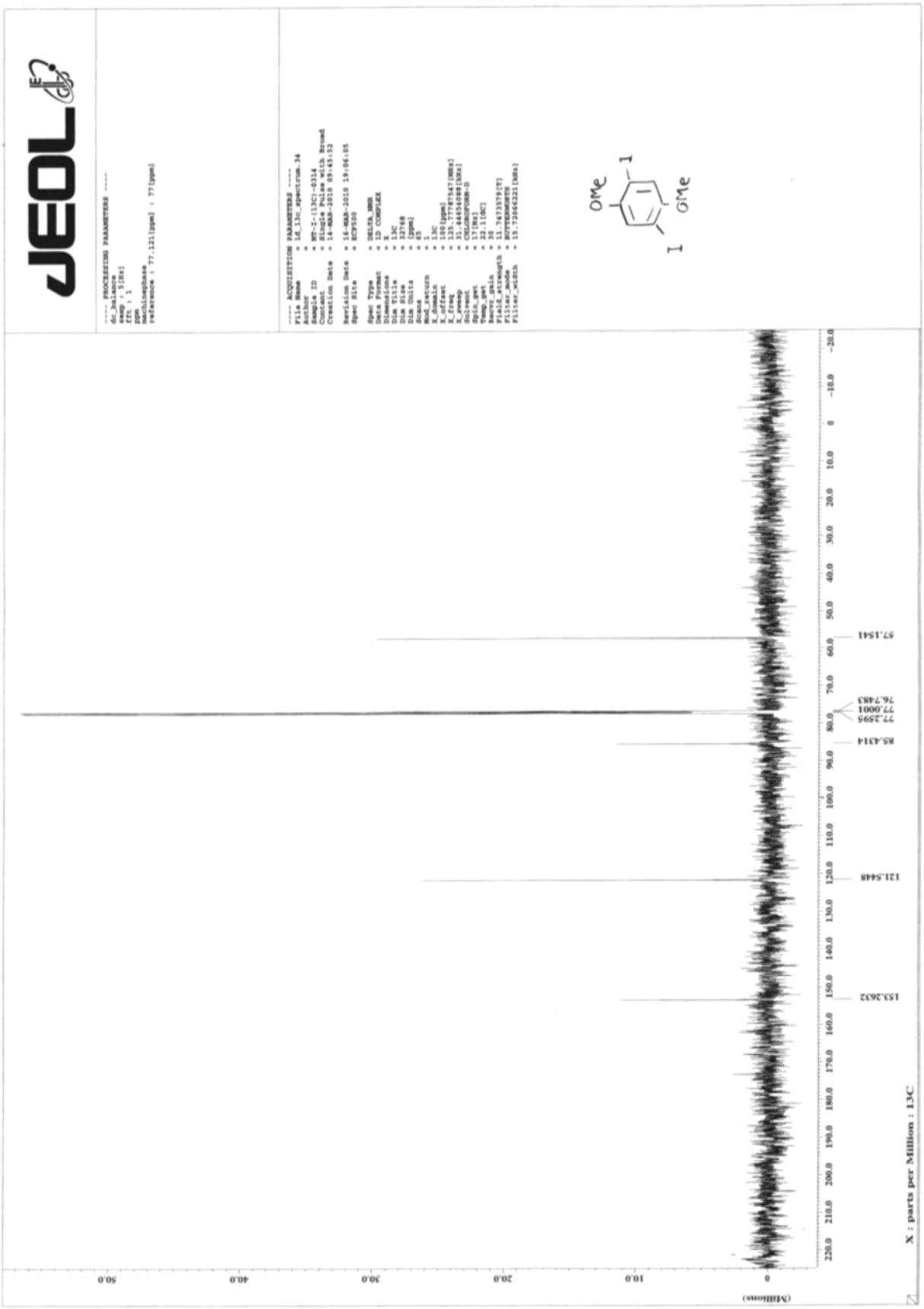
12 K. Lam and I. E. Markó, *Org. Lett.,* 2009, **11**, 2752.

13 K. Inamoto, K. Nozawa, M. Yonemoto and Y. Kondo, *Chem. Commun.,* 2011, **47**, 11775.

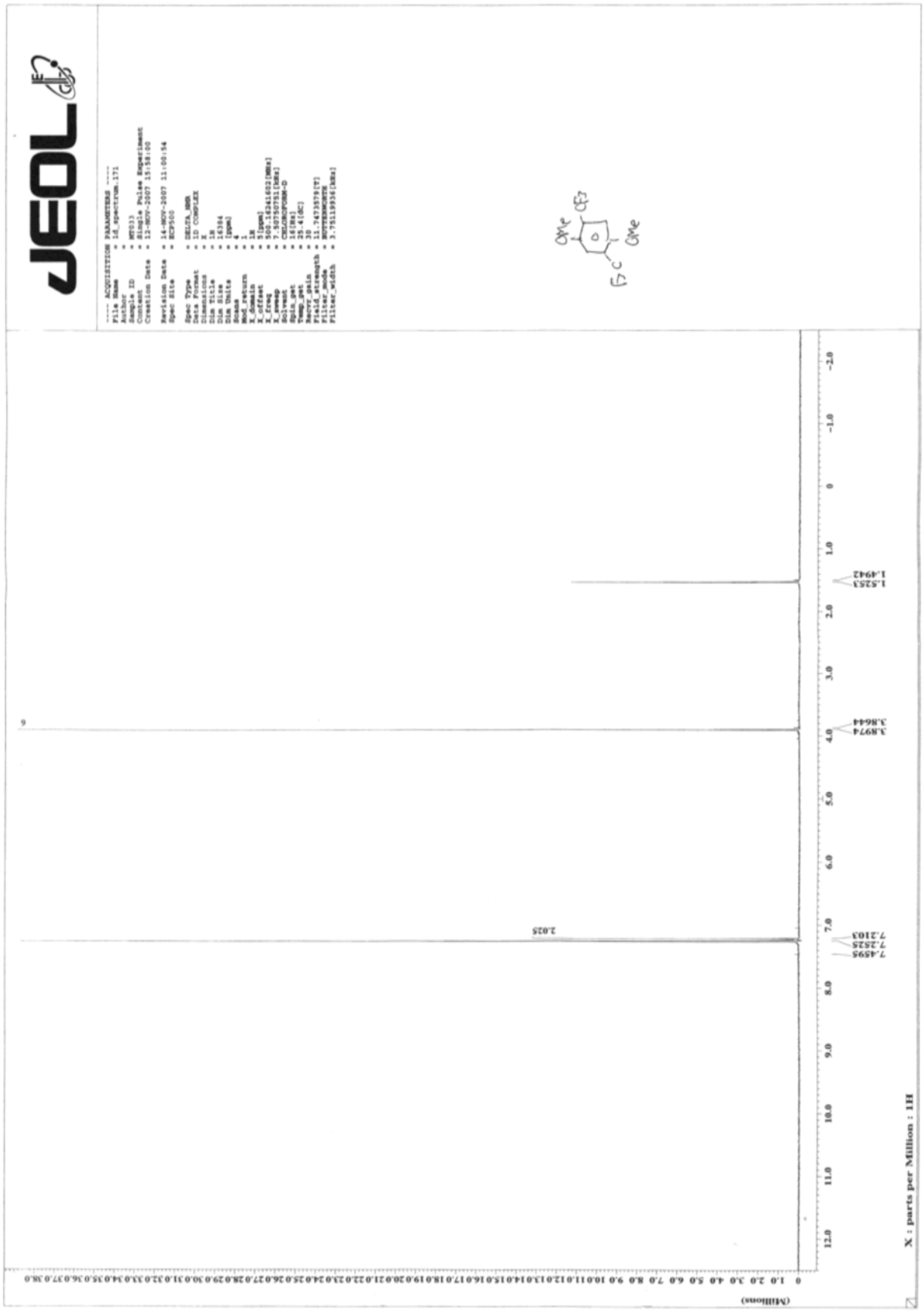
^{1}H NMR of 2,5-diiodo-1,4-dimethoxybenzene (**5**)



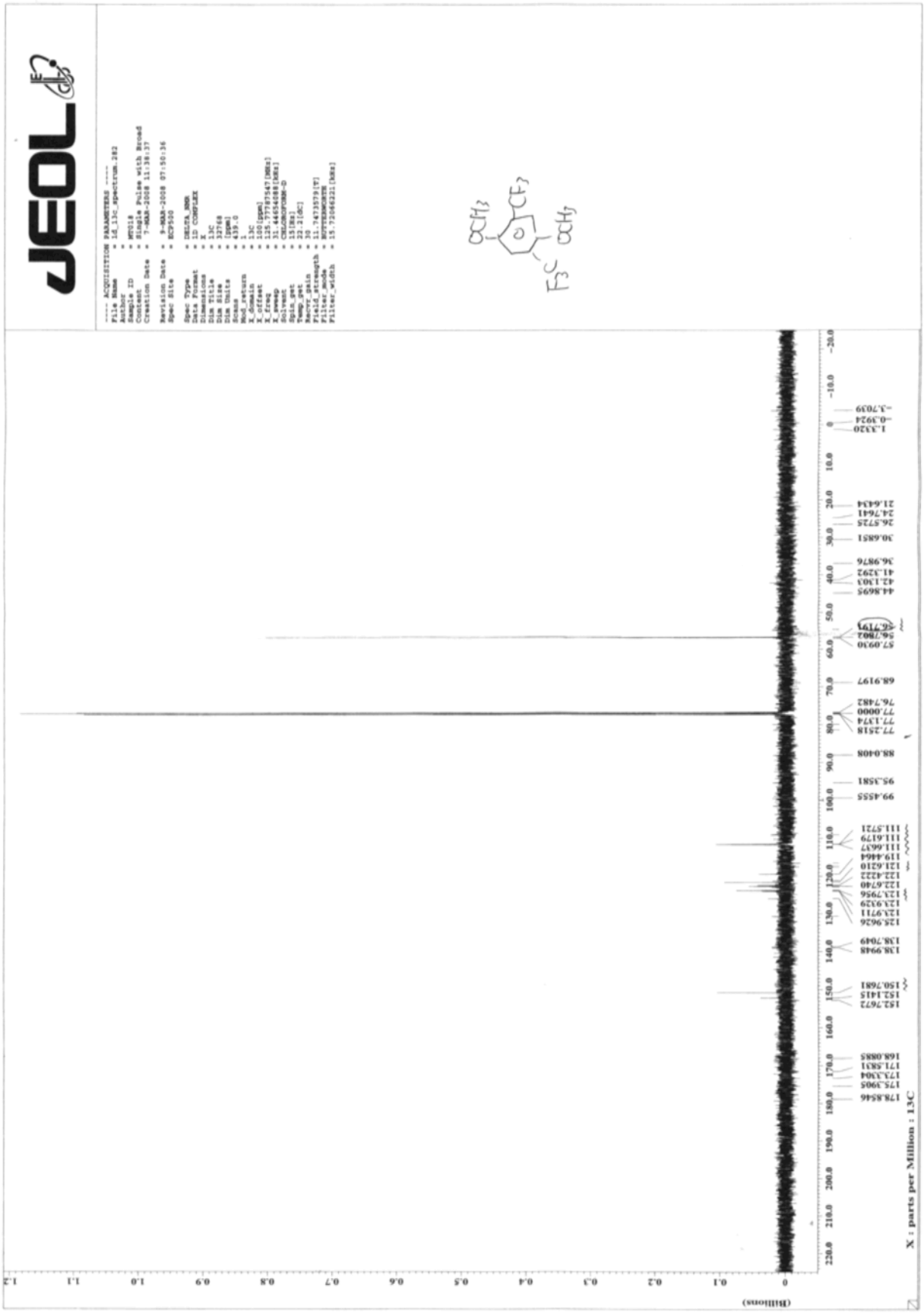
^{13}C NMR of 2,5-diiodo-1,4-dimethoxybenzene (**5**)



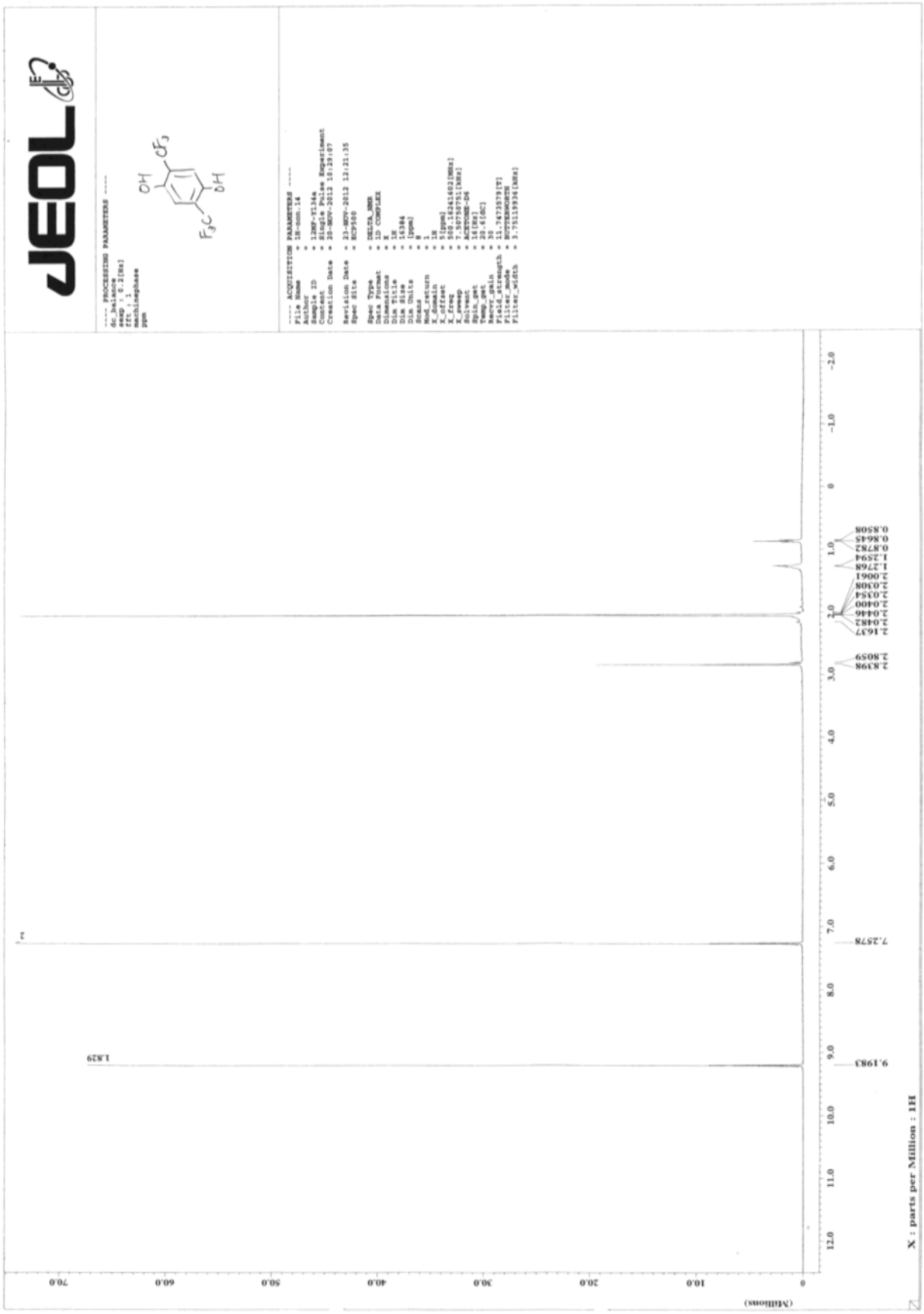
^{1}H NMR of 2,5-bis(trifluoromethyl)-1,4-dimethoxybenzene (**6a**)



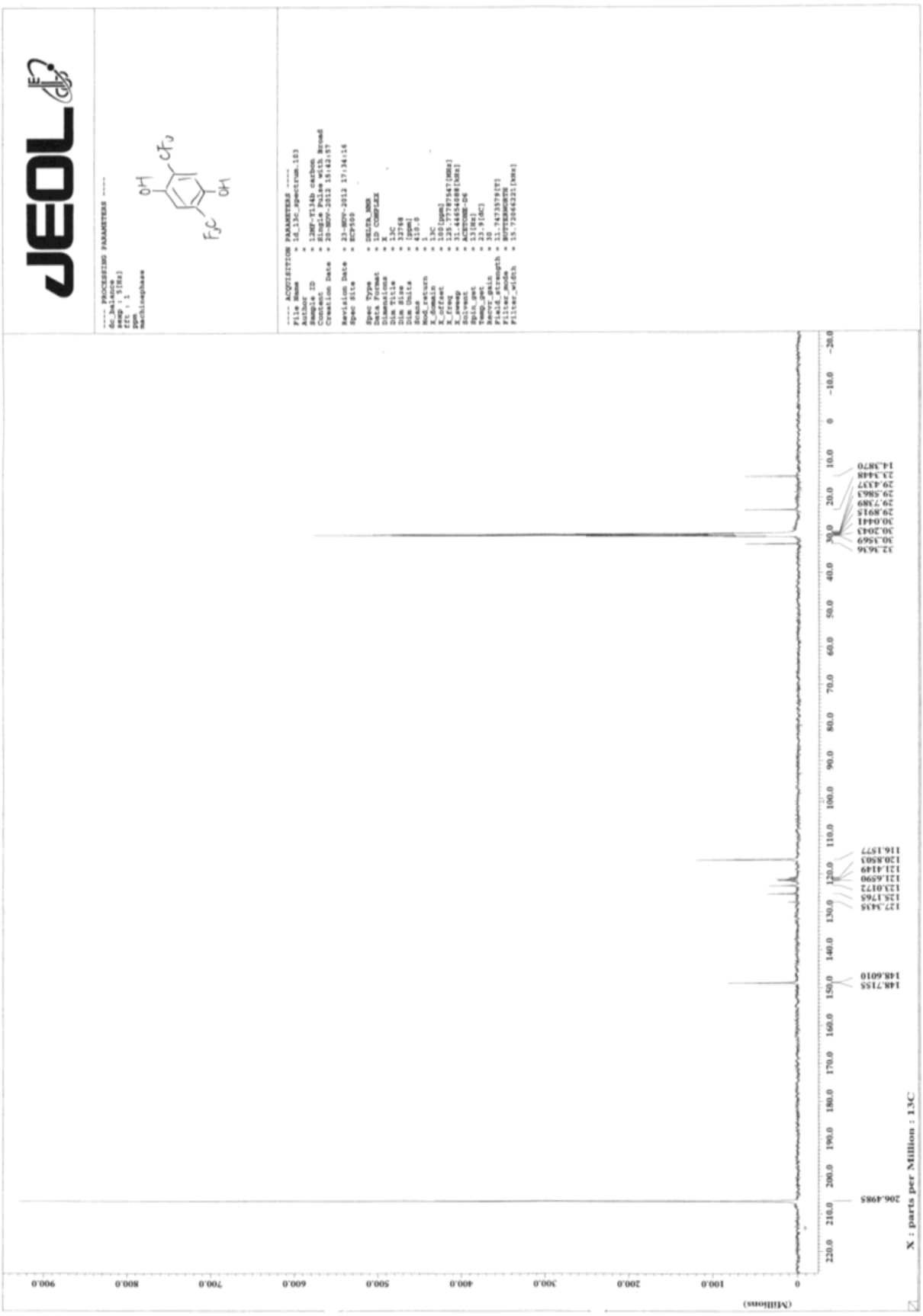
^{13}C NMR of 2,5-bis(trifluoromethyl)-1,4-dimethoxybenzene (**6a**)



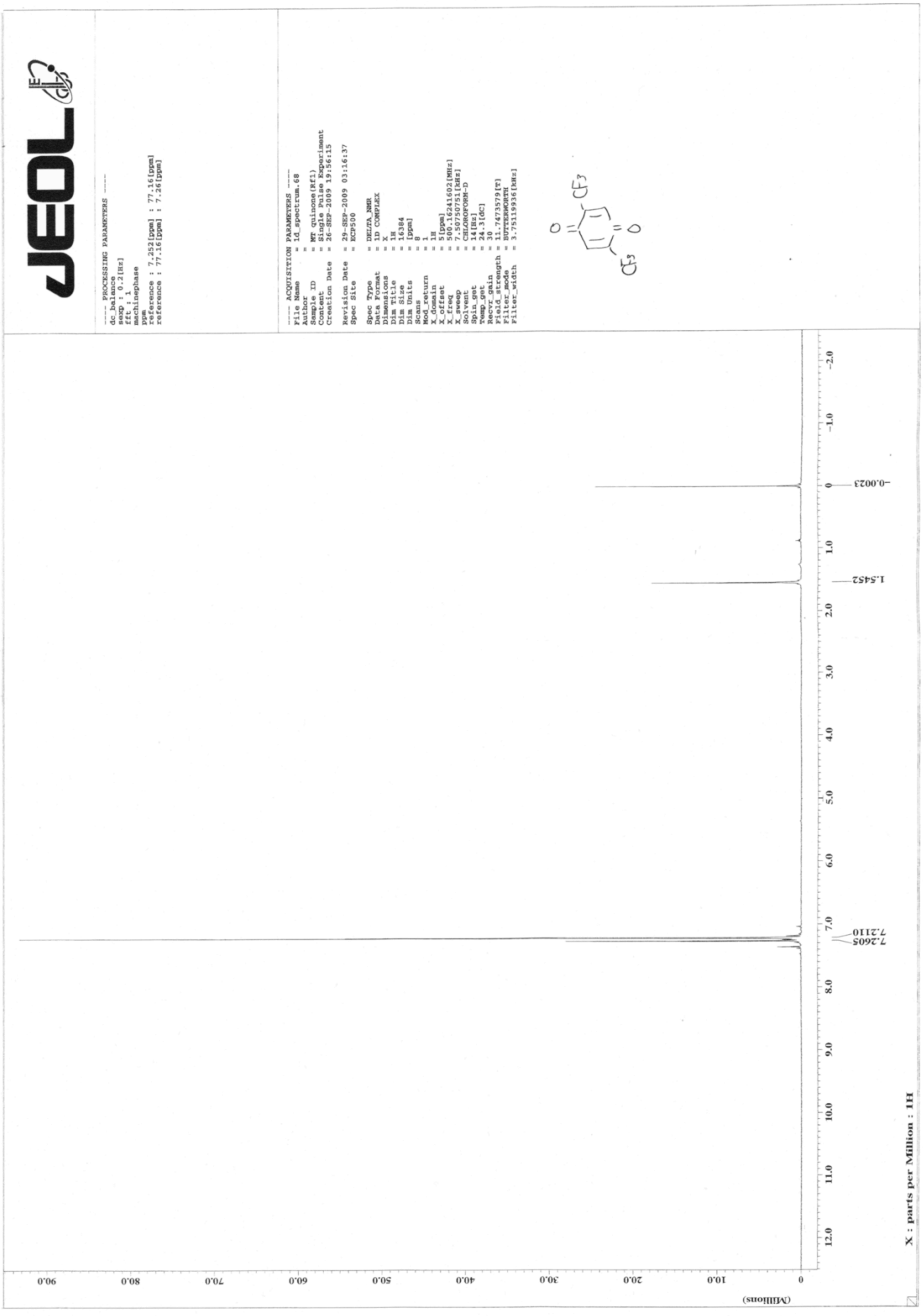
^{1}H NMR of 2,5-bis(trifluoromethyl)-1,4-hydroquinone (**7a**)



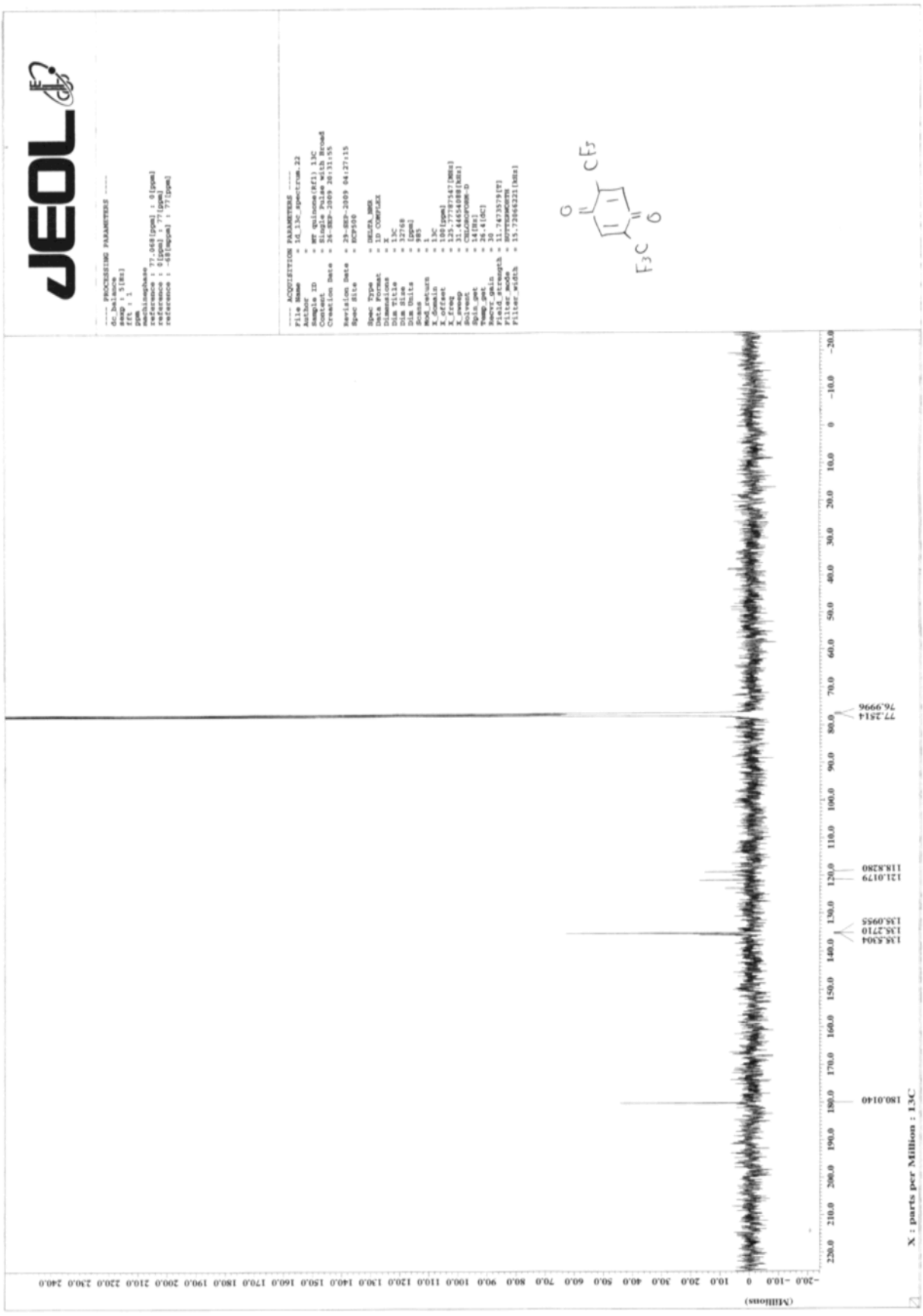
^{13}C NMR of 2,5-bis(trifluoromethyl)-1,4-hydroquinone (**7a**)



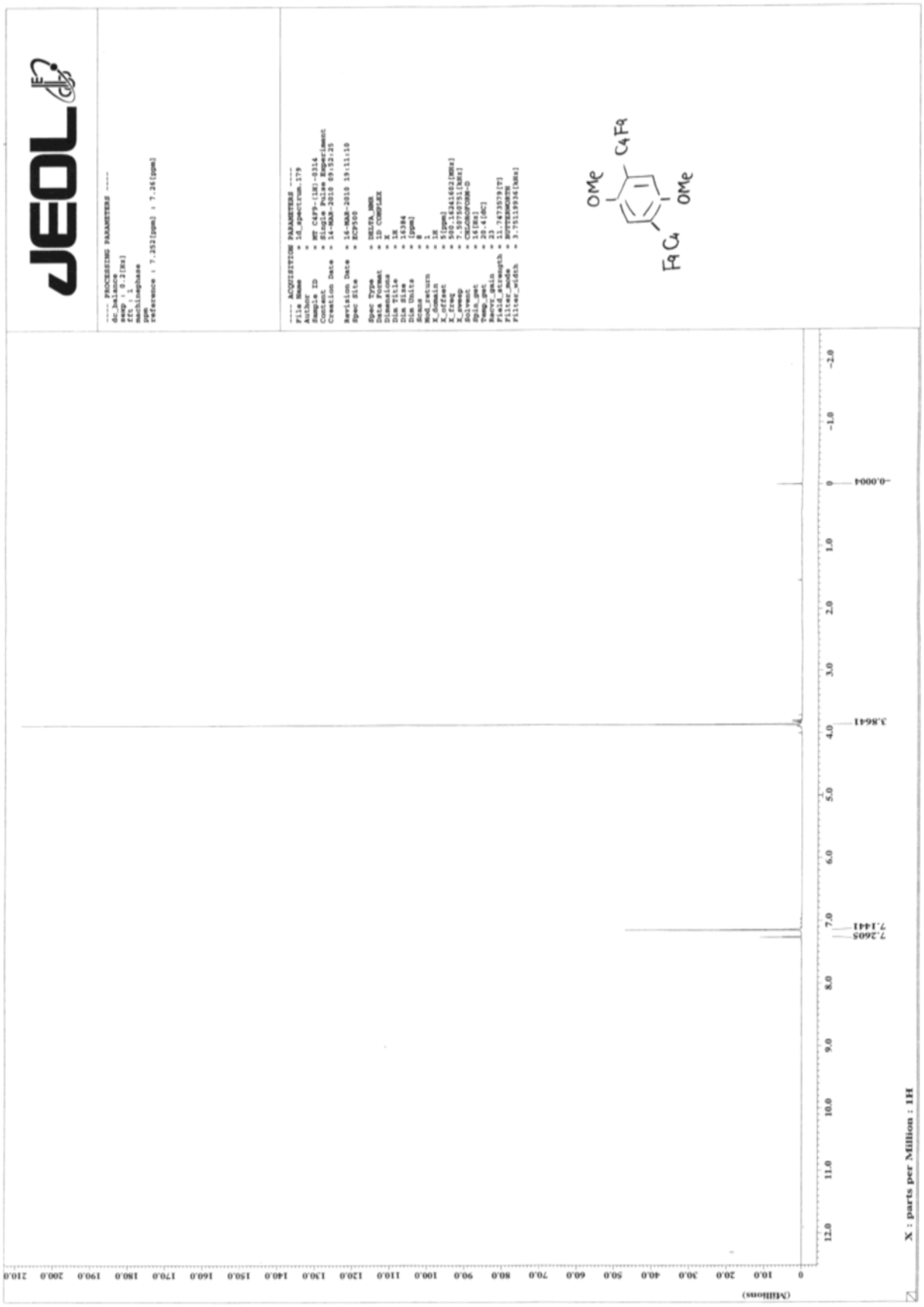
^{1}H NMR of 2,5-bis(trifluoromethyl)-1,4-benzoquinone (**3a**)



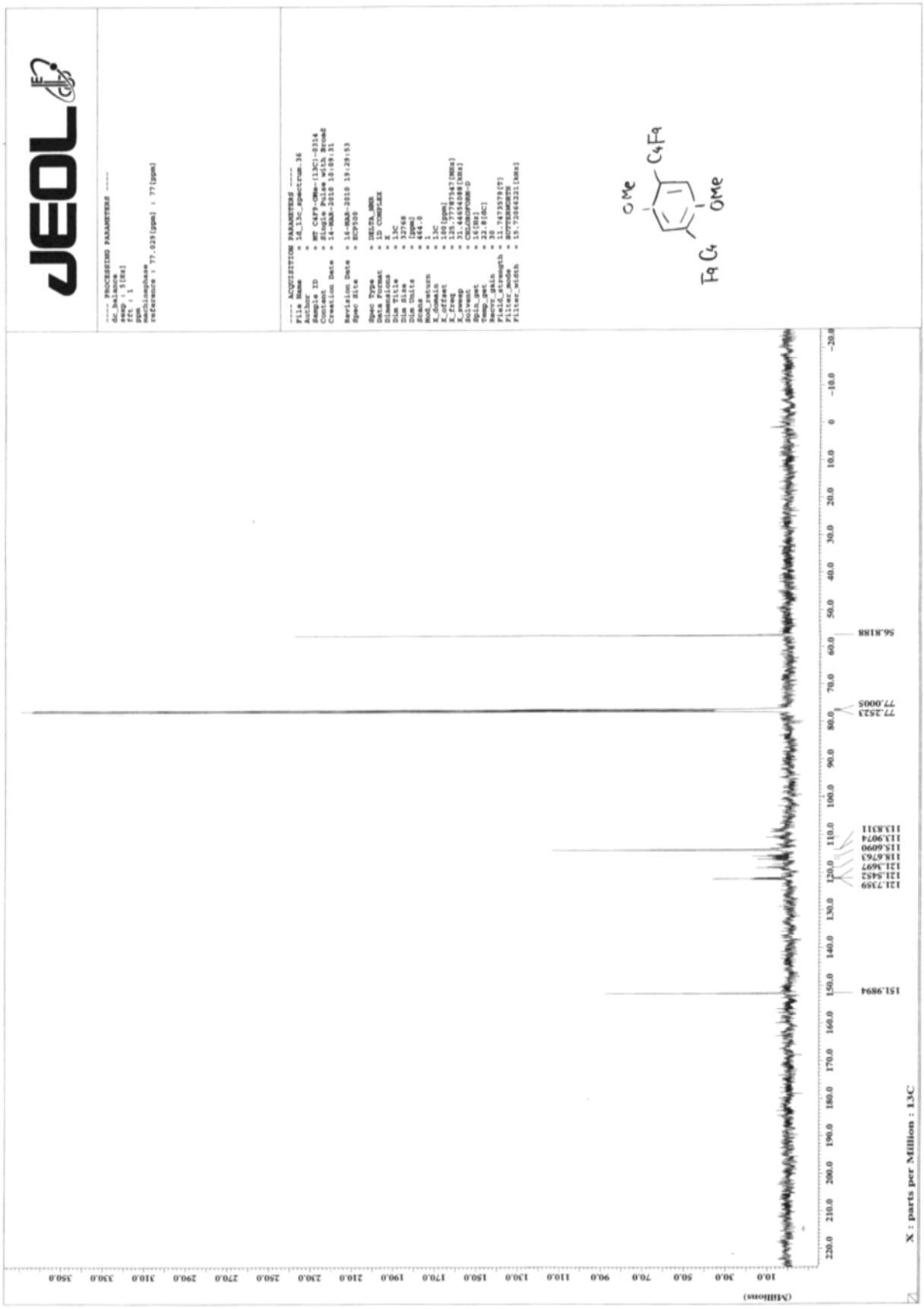
^{13}C NMR of 2,5-bis(trifluoromethyl)-1,4-benzoquinone (**3a**)



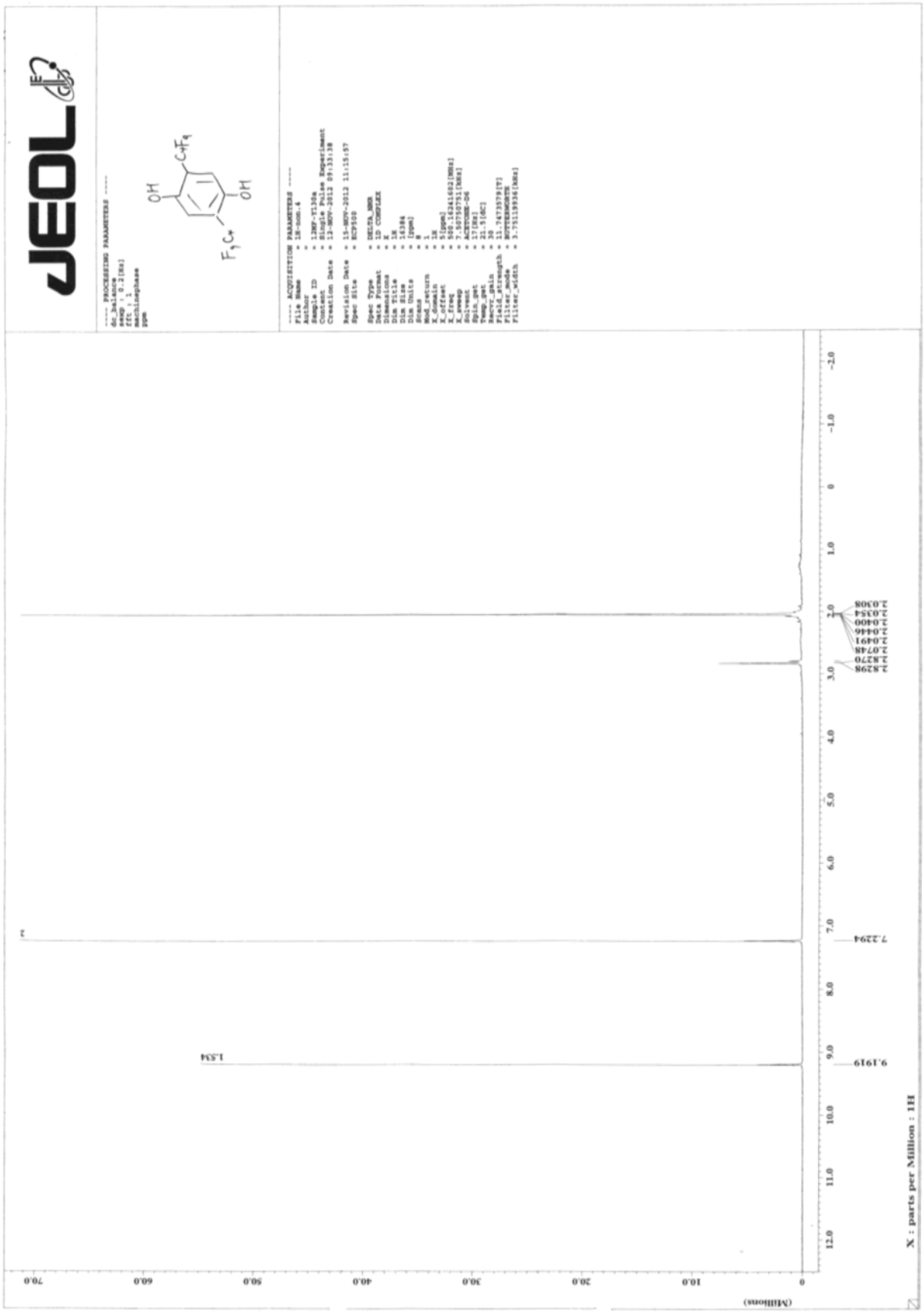
^{1}H NMR of 2,5-bis(perfluorobutyl)-1,4-dimethoxybenzene (**6b**)



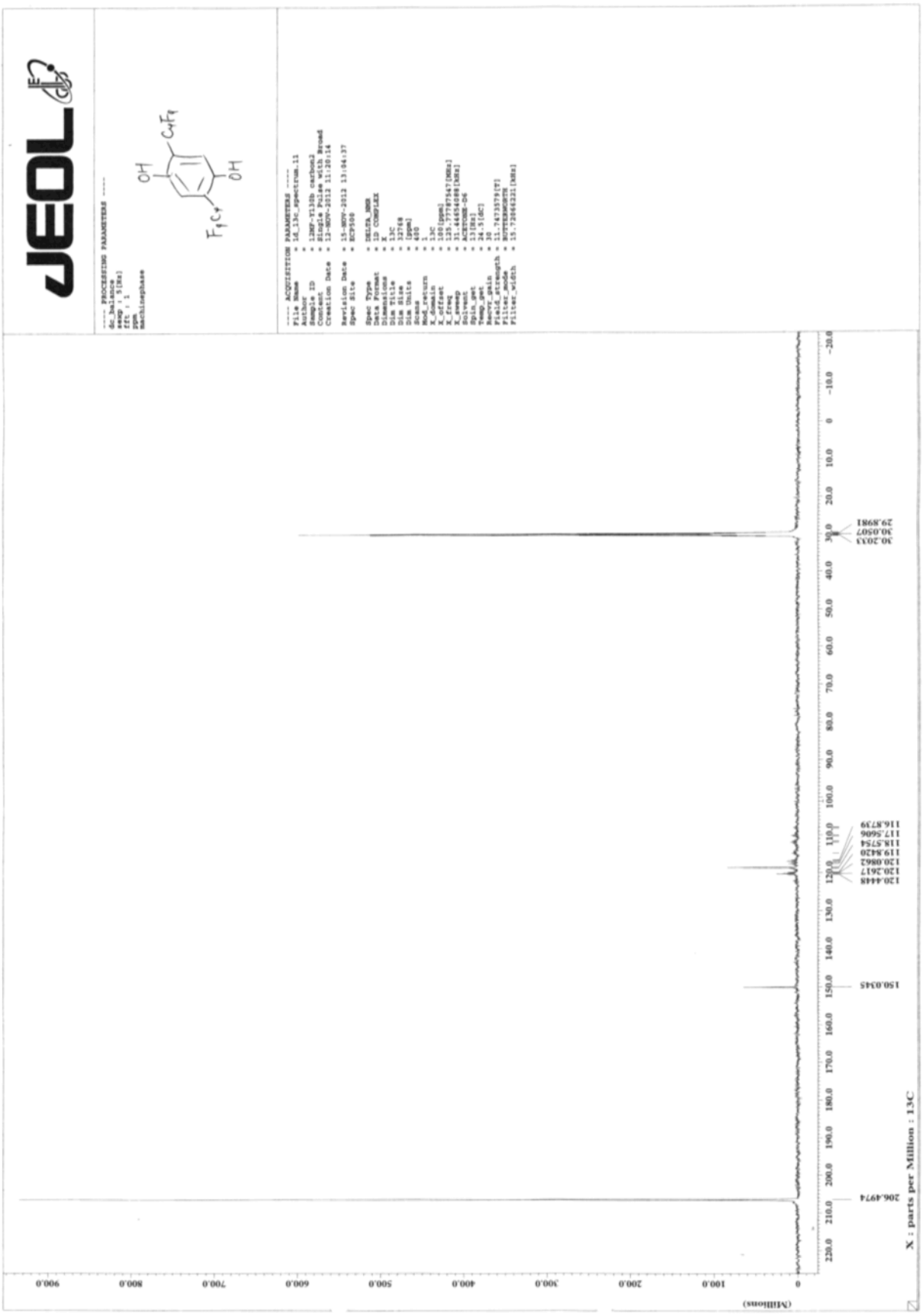
^{13}C NMR of 2,5-bis(perfluorobutyl)-1,4-dimethoxybenzene (**6b**)



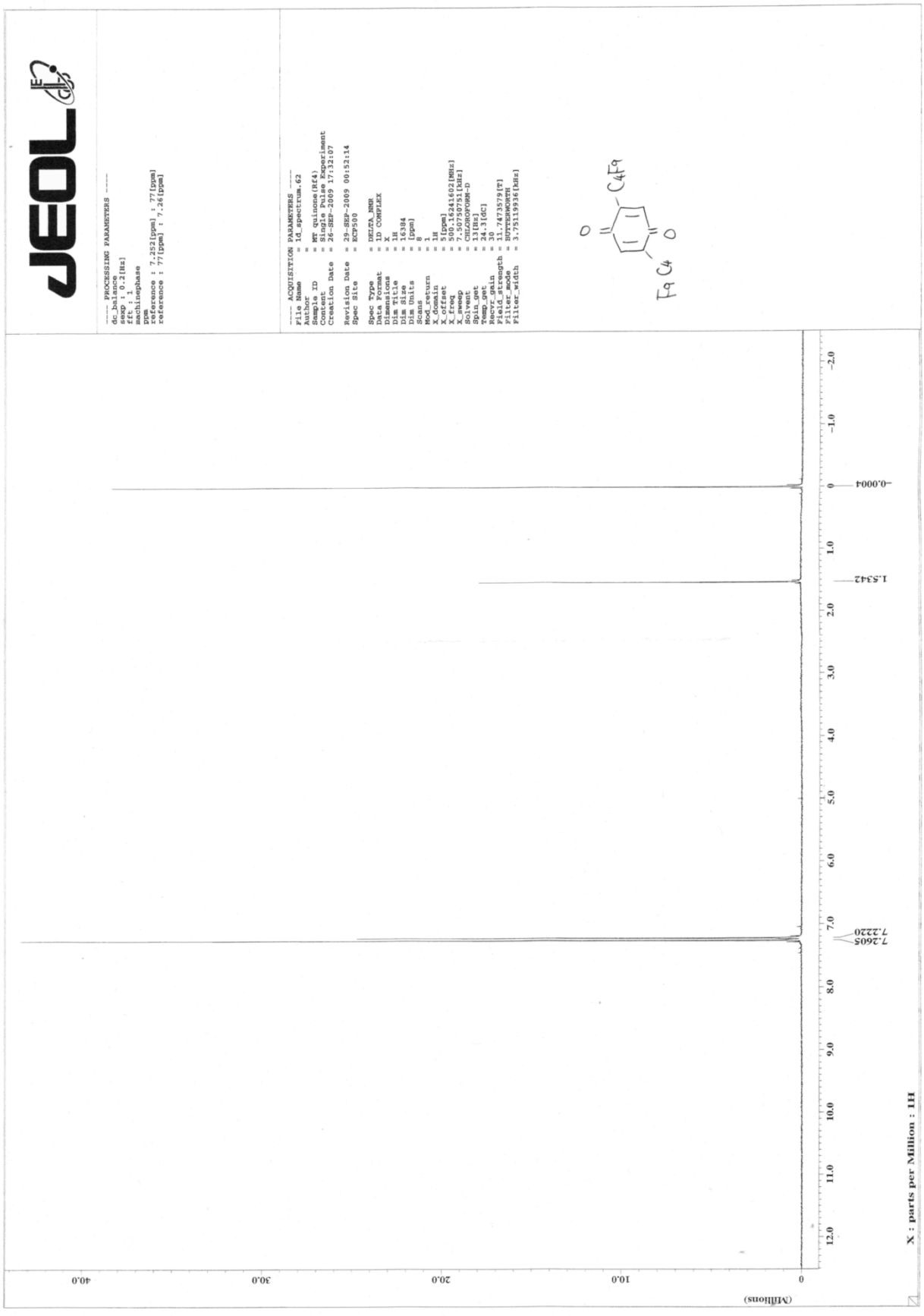
^{1}H NMR of 2,5-bis(perfluorobutyl)-1,4-hydroquinone (**7b**)



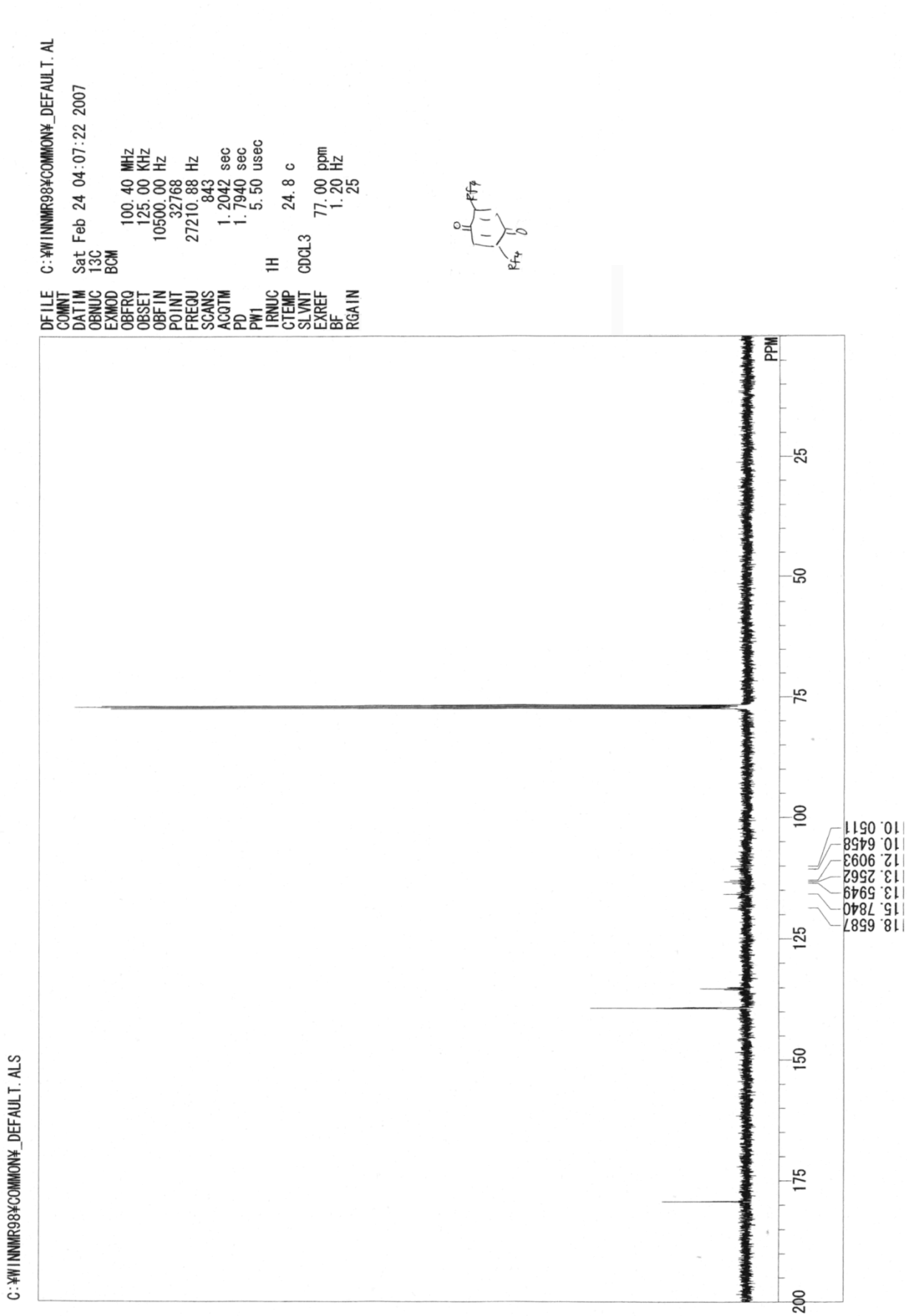
^{13}C NMR of 2,5-bis(perfluorobutyl)-1,4-hydroquinone (**7b**)



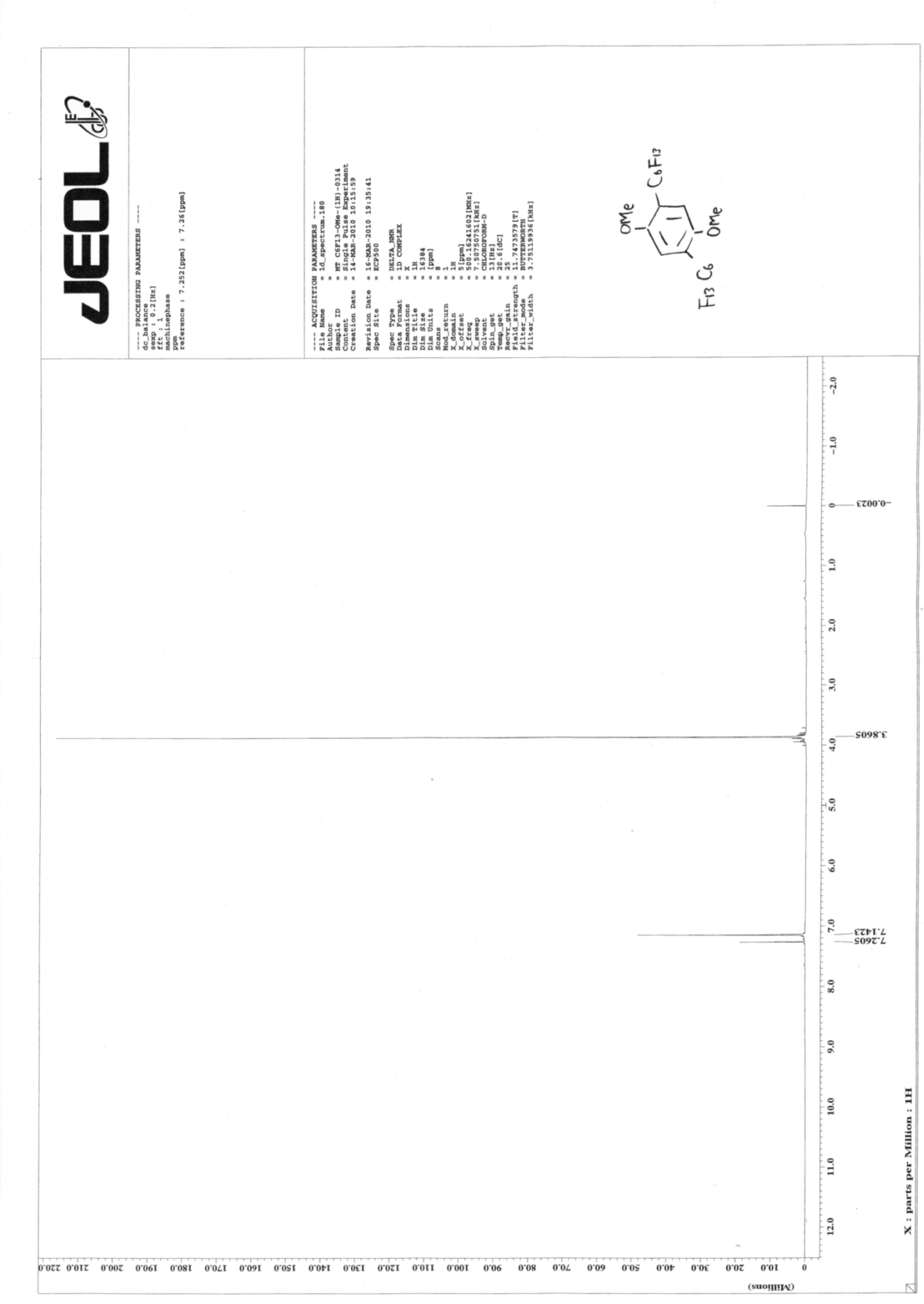
^{1}H NMR of 2,5-bis(perfluorobutyl)-1,4-benzoquinone (**3b**)



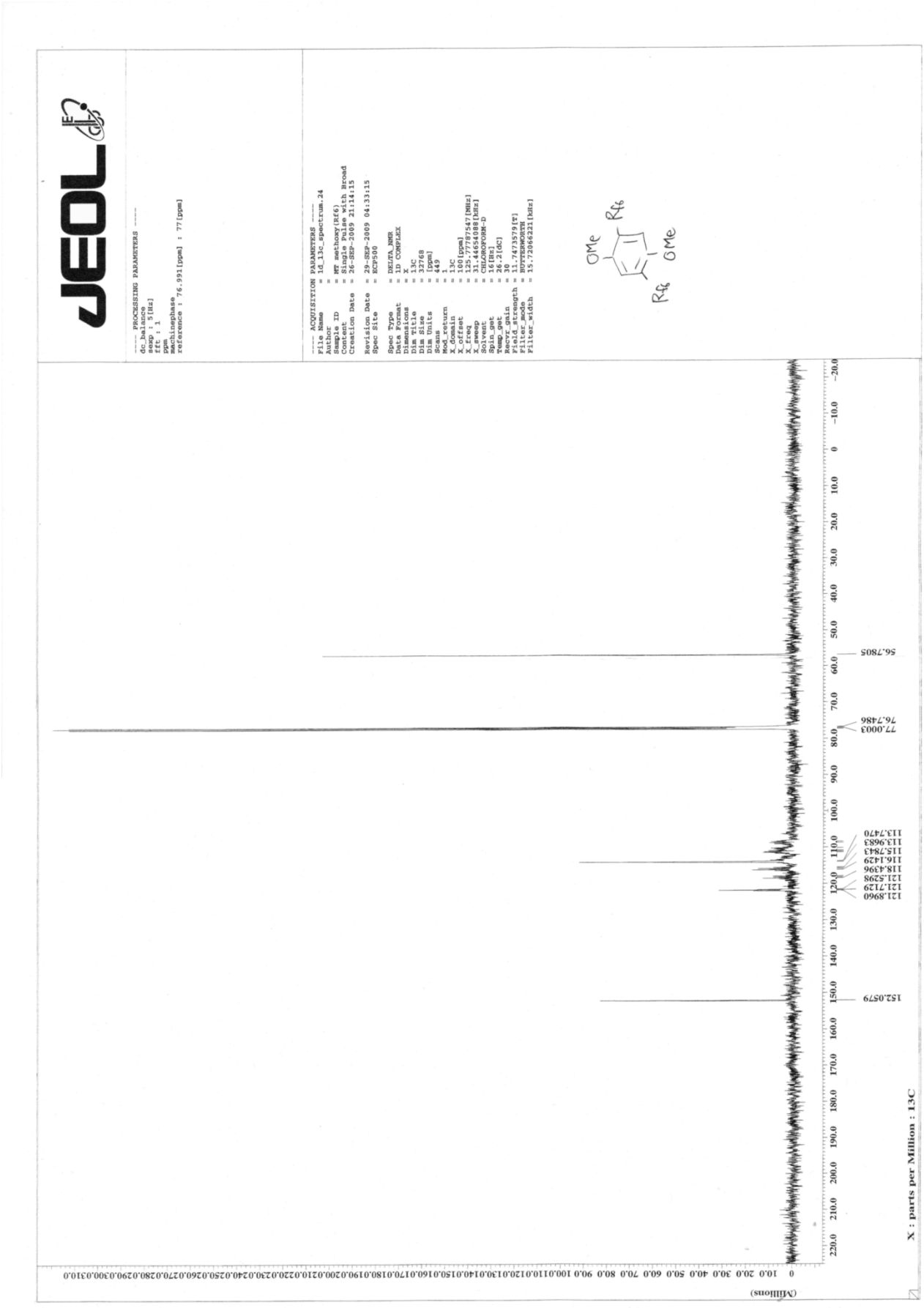
^{13}C NMR of 2,5-bis(perfluorobutyl)-1,4-benzoquinone (**3b**)



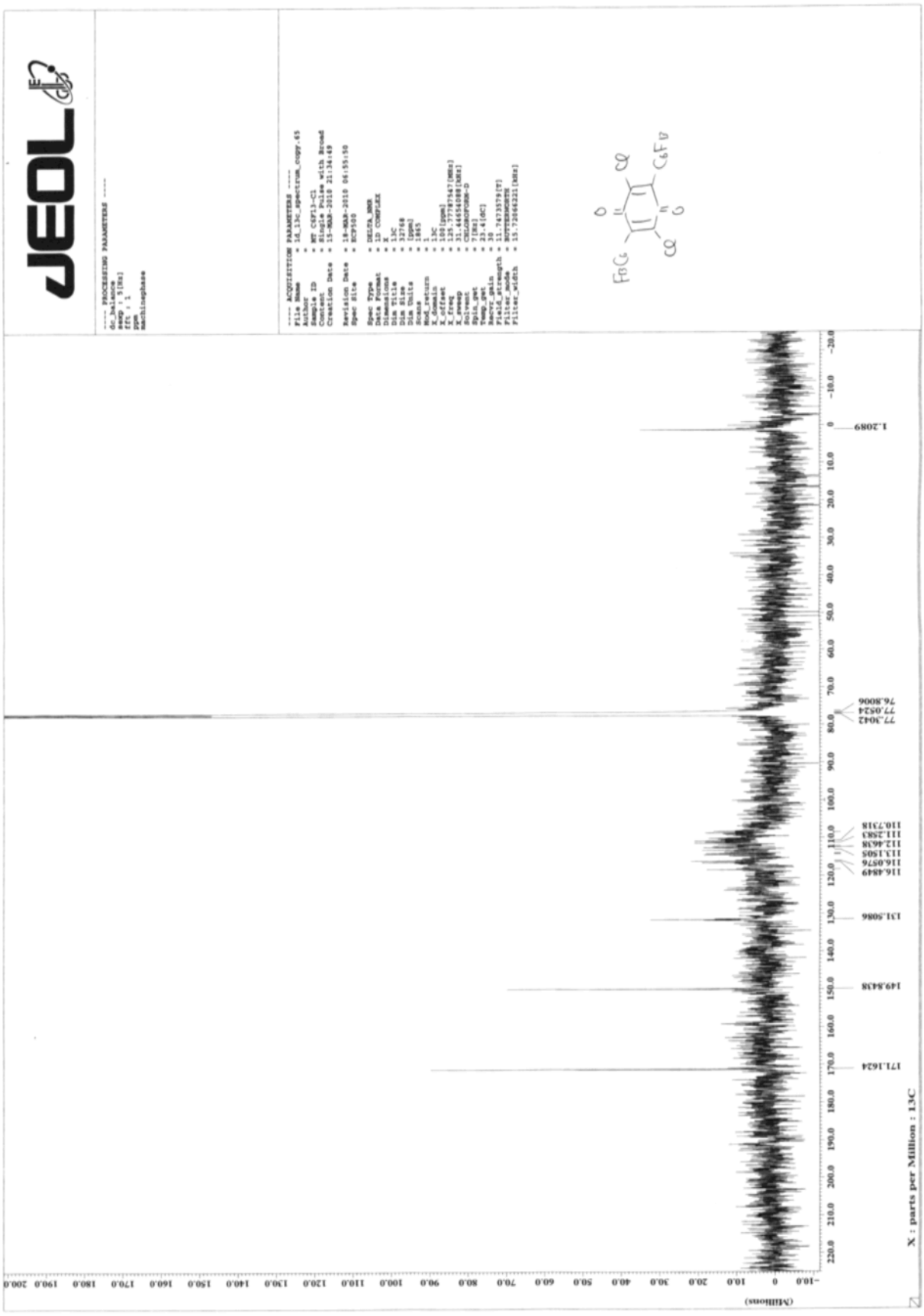
^{1}H NMR of 2,5-bis(perfluorohexyl)-1,4-dimethoxybenzene (**8**)



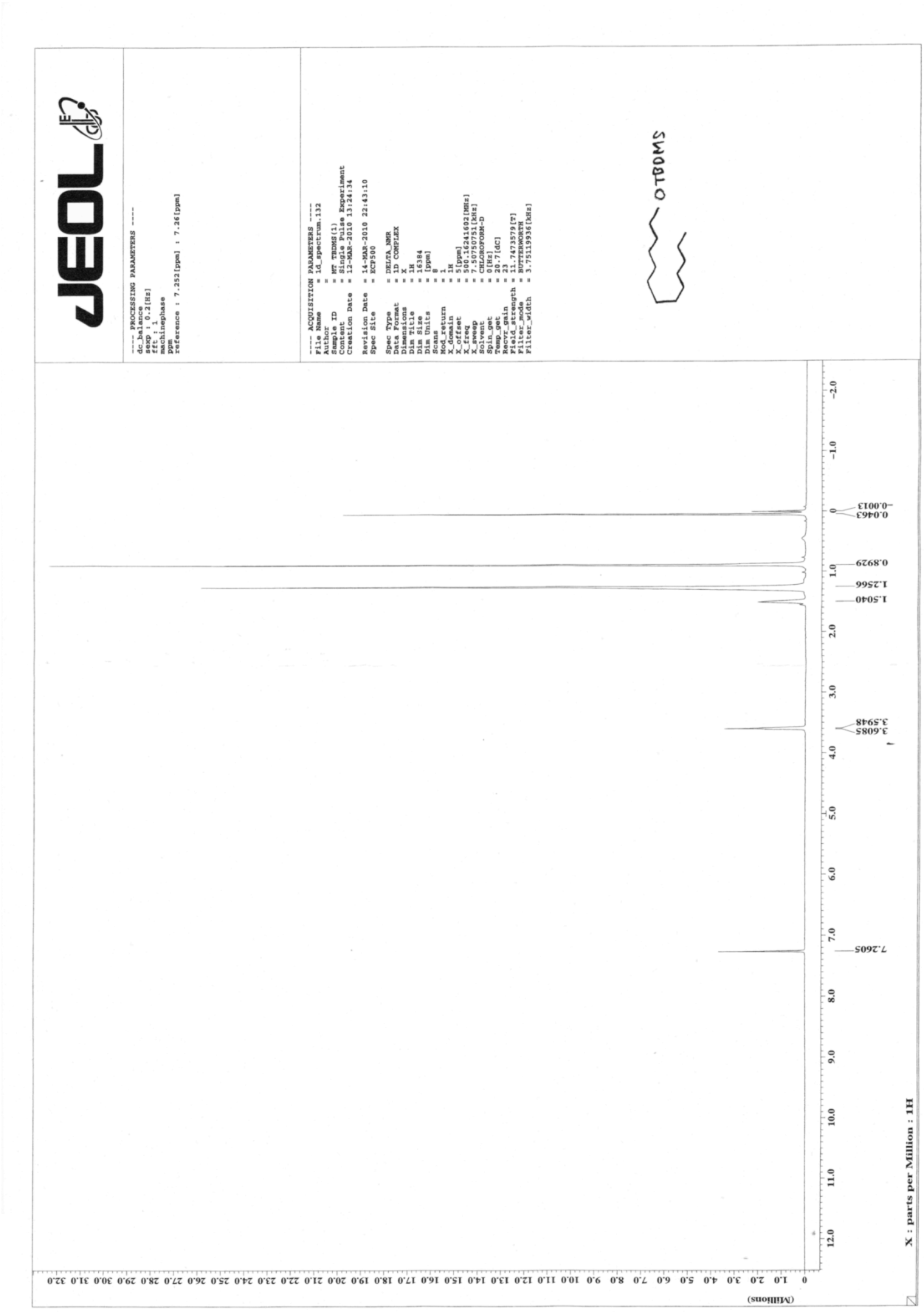
^{13}C NMR of 2,5-bis(perfluorohexyl)-1,4-dimethoxybenzene (**8**)



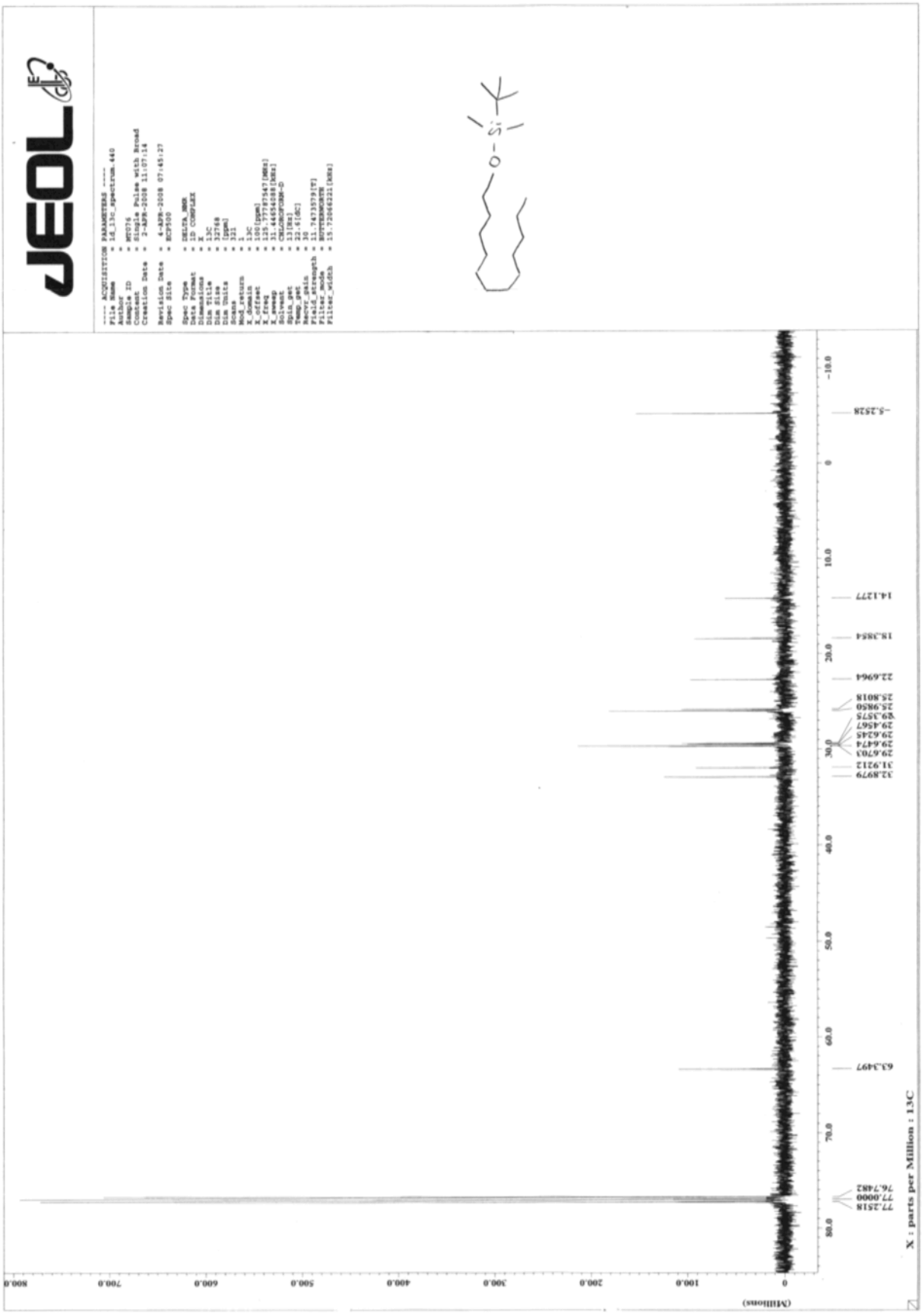
^{13}C NMR of 2,5-bis(perfluorohexyl)-3,6-dichloro-1,4-benzoquinone (**3c**)



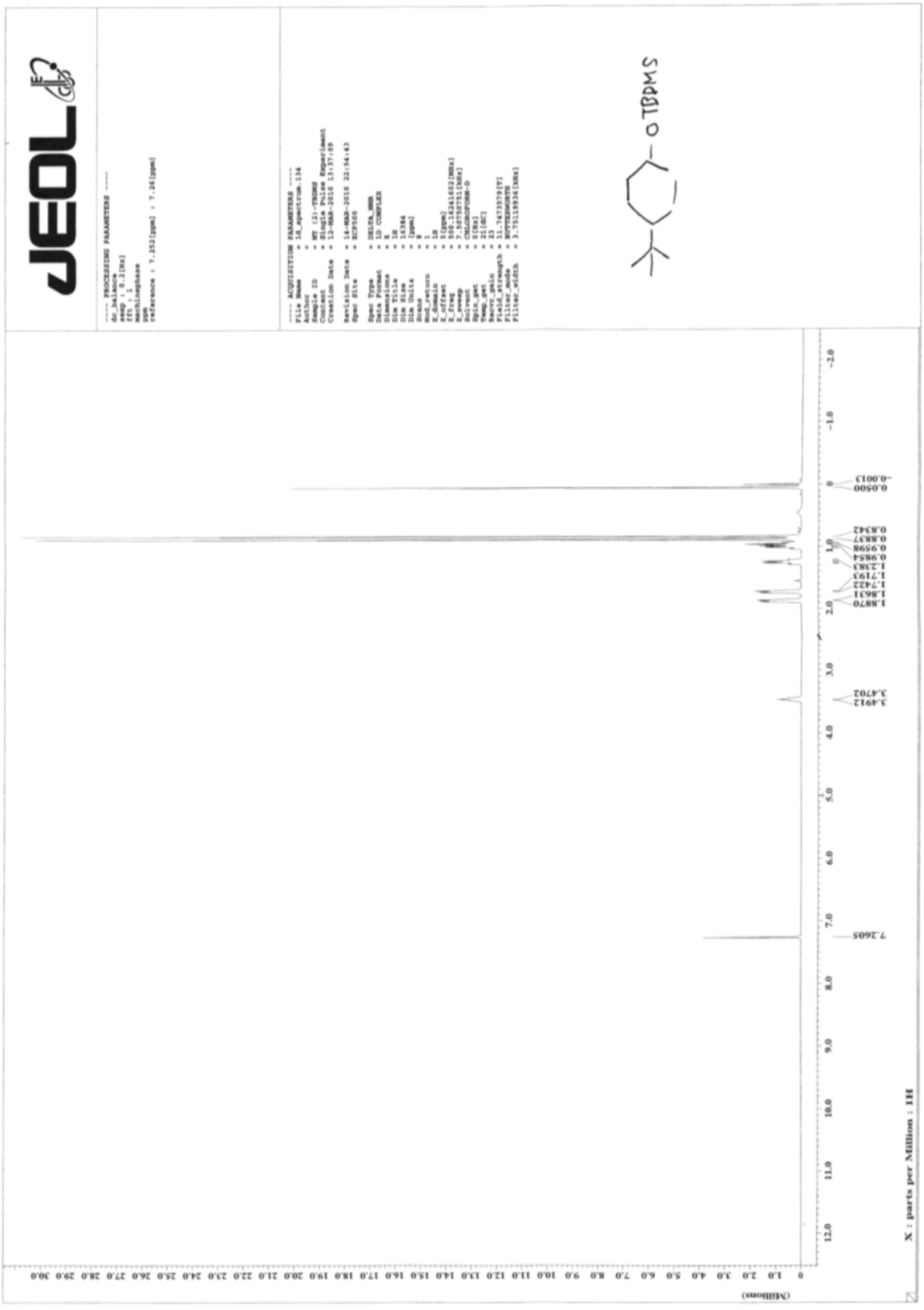
^{1}H NMR of *tert*-Butyldimethylsilyl dodecyl ether (**12**)



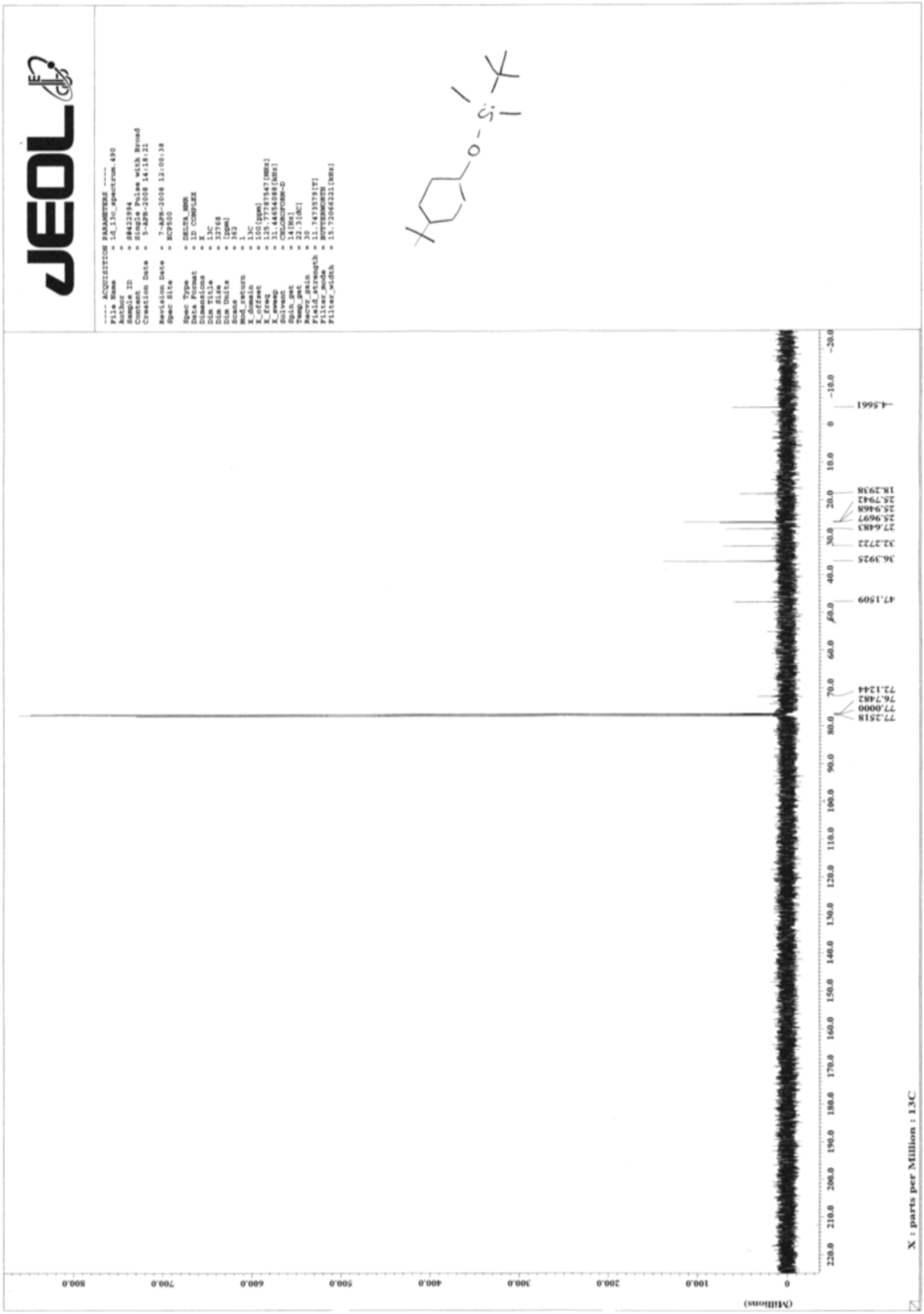
^{13}C NMR of *tert*-Butyldimethylsilyl dodecyl ether (**12**)



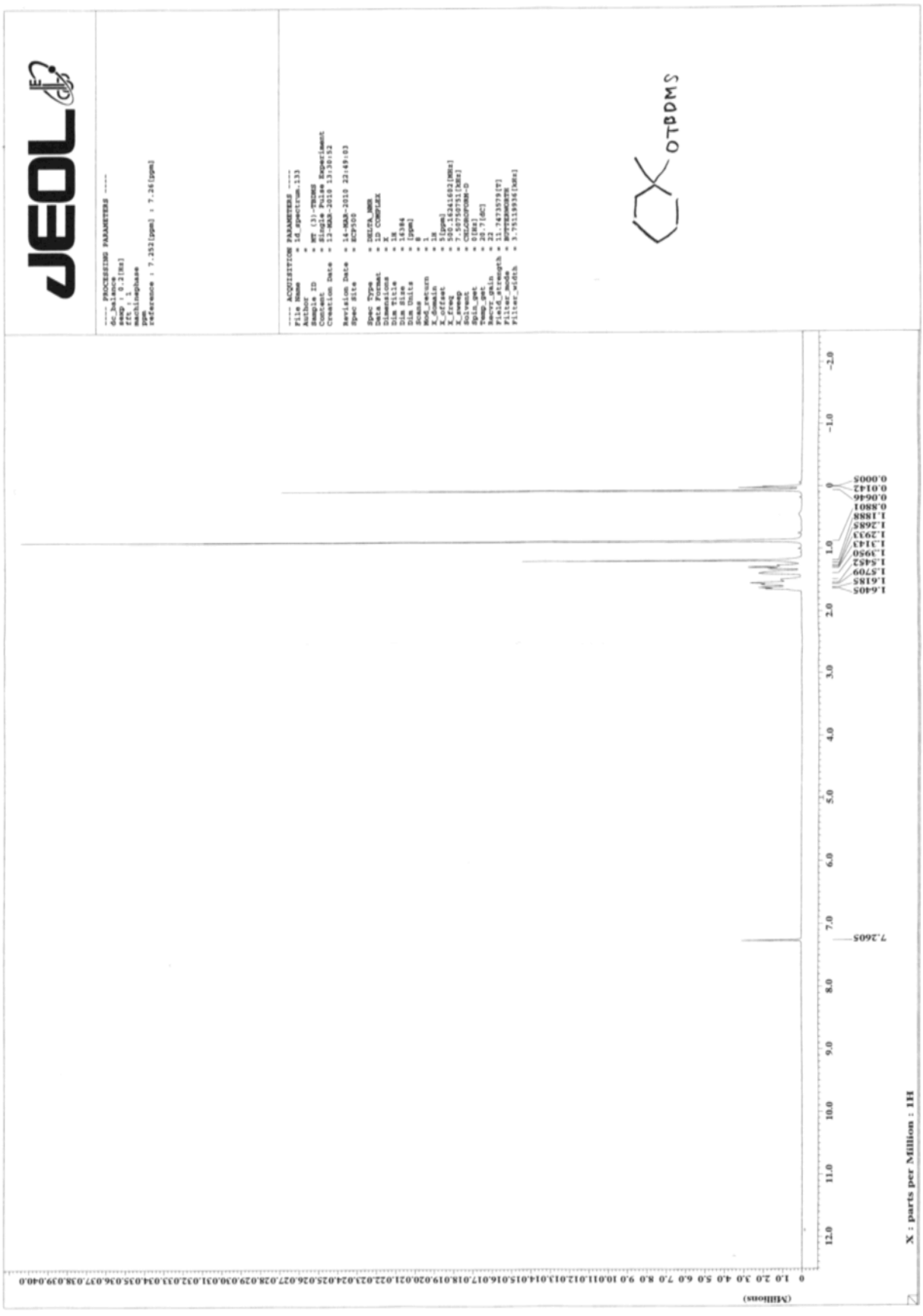
^{1}H NMR of 4-*tert*-butylcyclohexyl *tert*-butyldimethylsilyl ether (**14**)



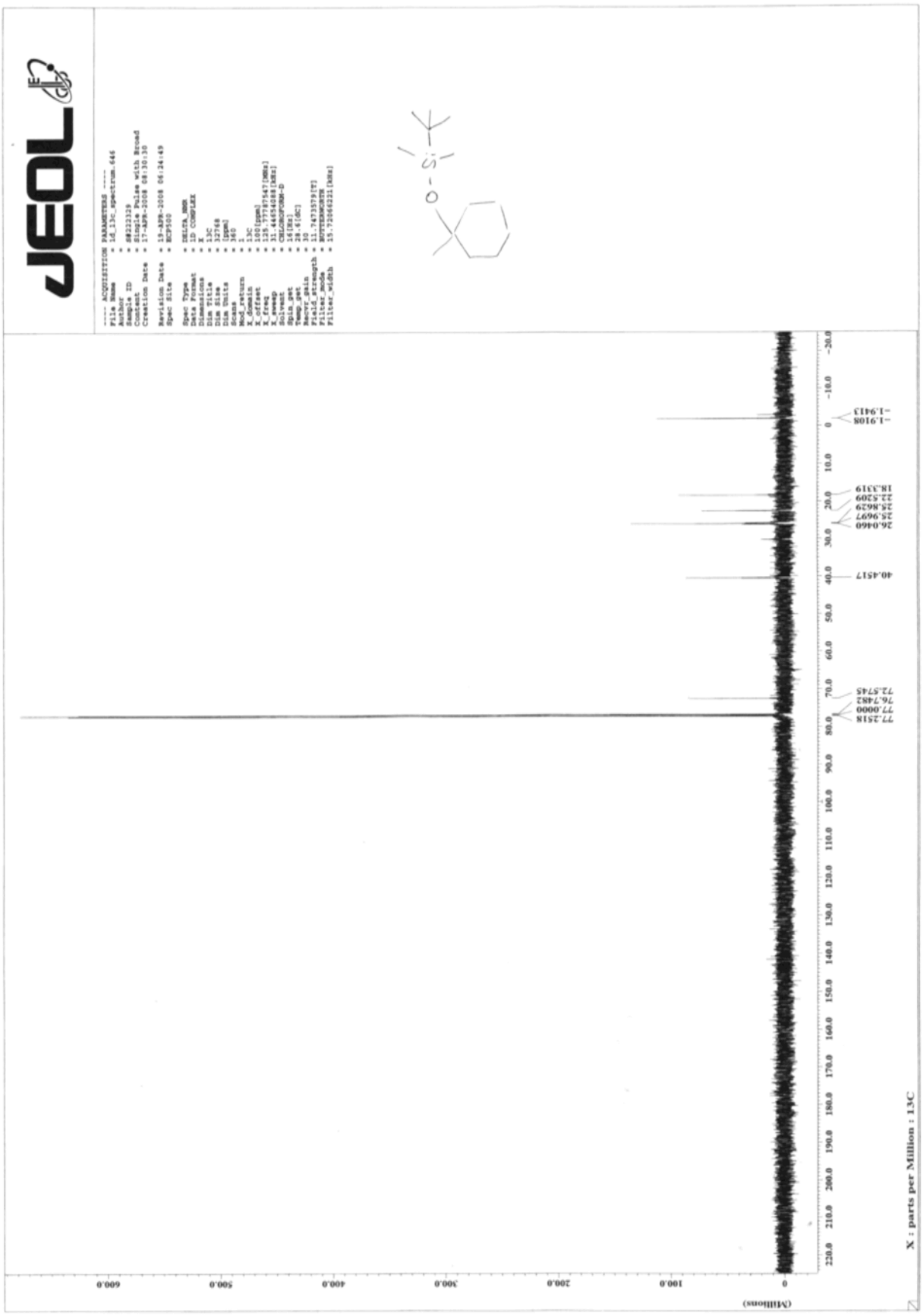
^{13}C NMR of 4-*tert*-butylcyclohexyl *tert*-butyldimethylsilyl ether (**14**)



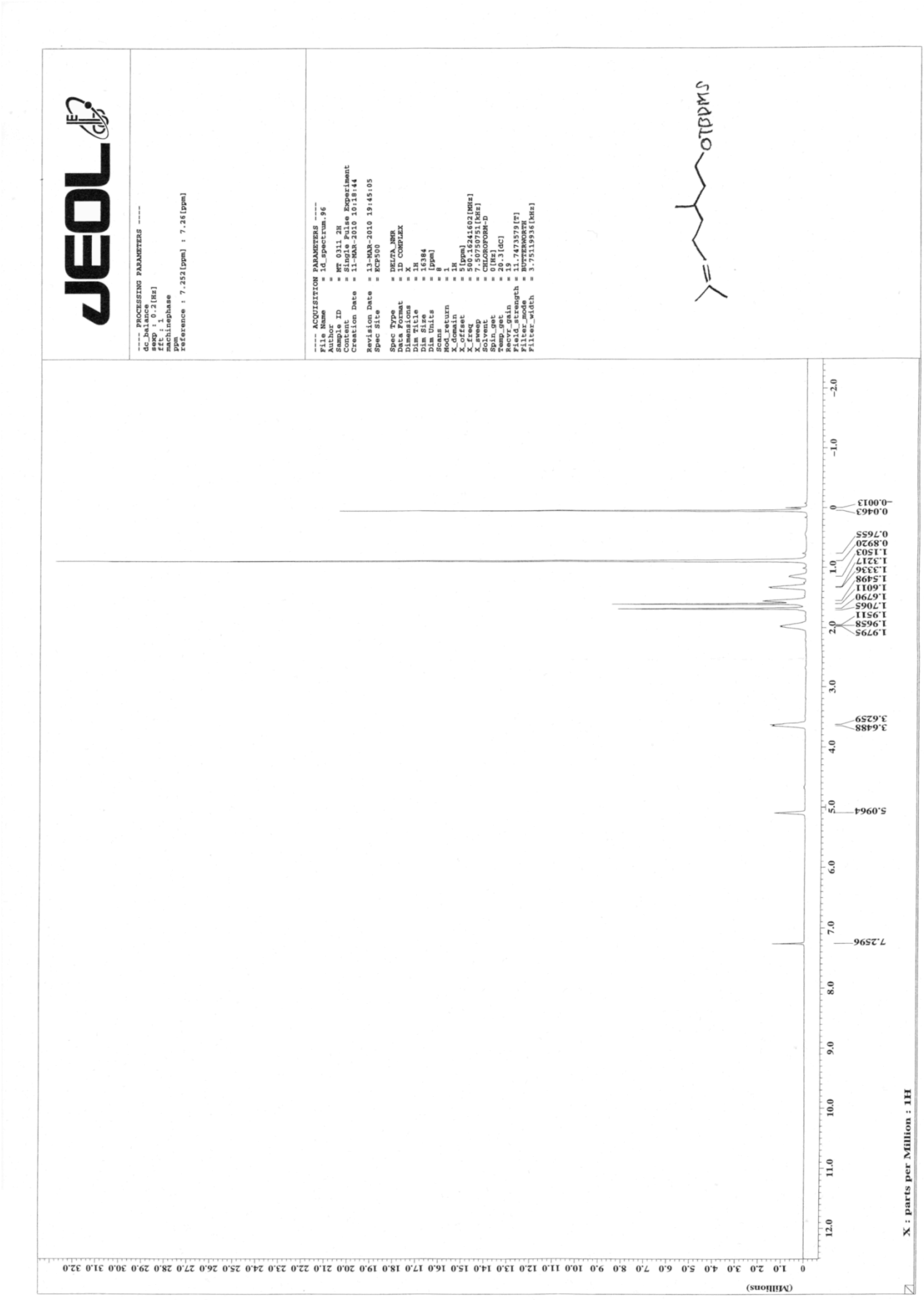
^{1}H NMR of 1-methylcyclohexyl *tert*-butyldimethylsilyl ether (**16**)



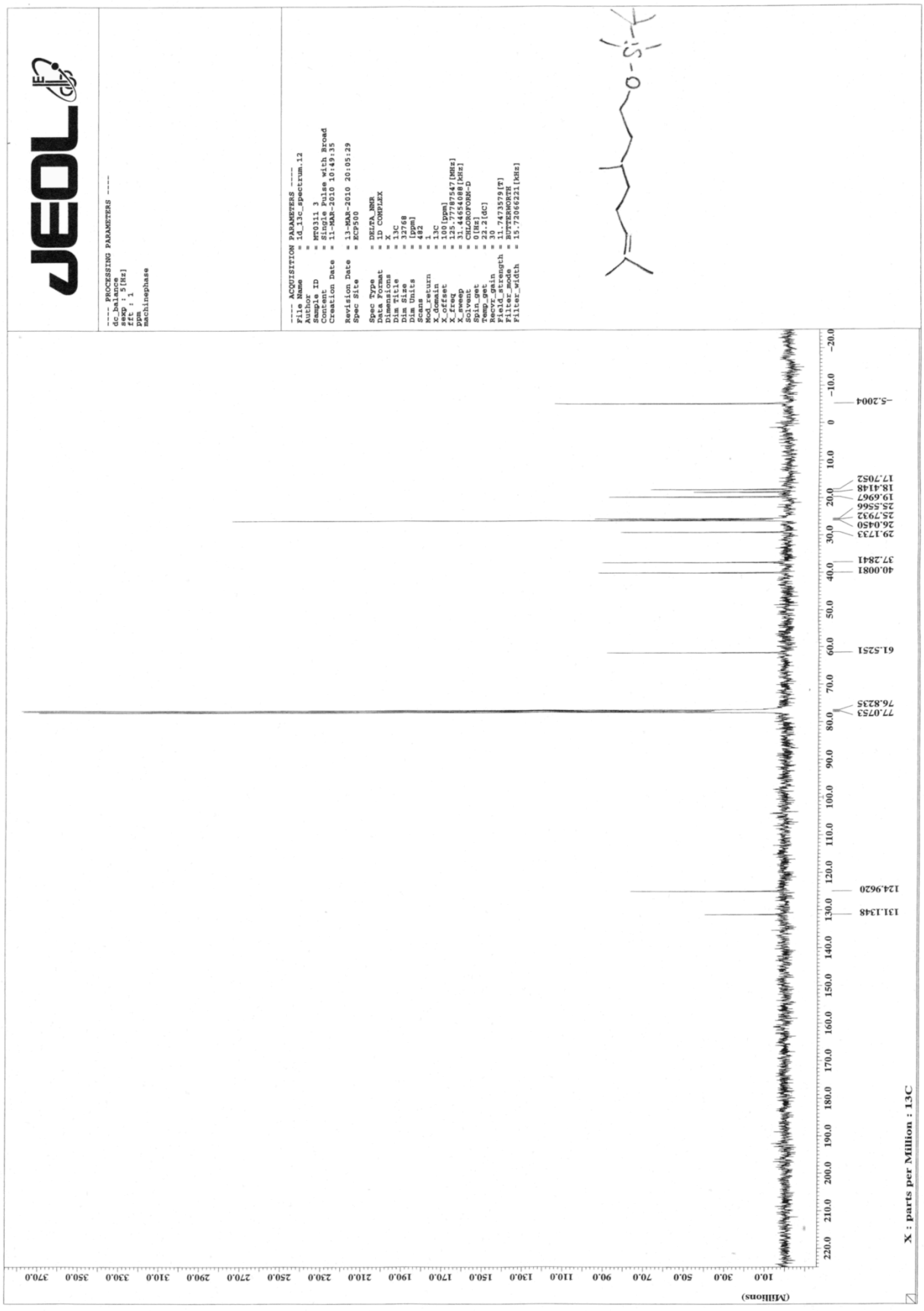
^{13}C NMR of 1-methylcyclohexyl *tert*-butyldimethylsilyl ether (**16**)



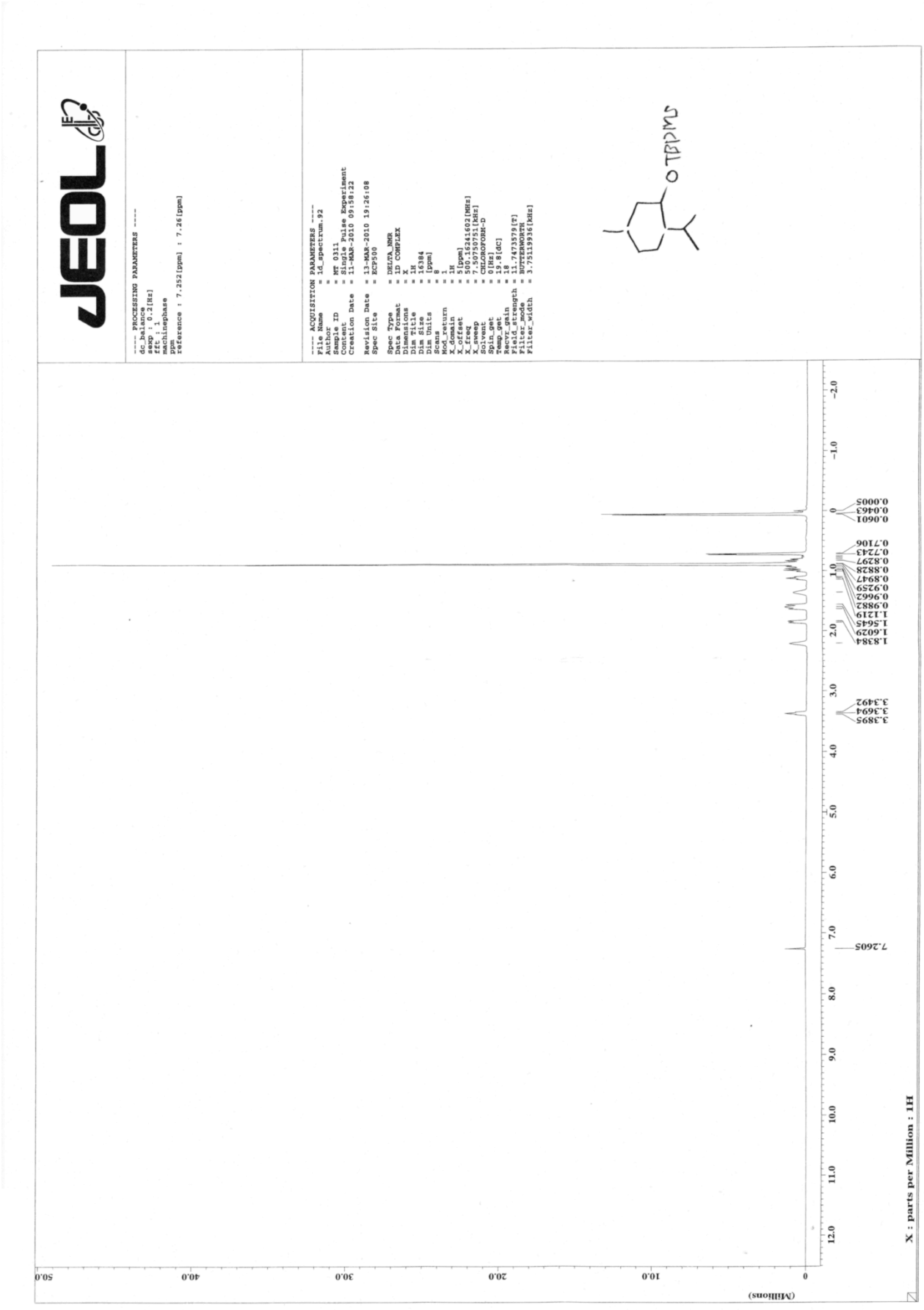
^{1}H NMR of 8-(*tert*-butyldimethylsiloxy)-2,6-dimethyl-oct-2-ene (**17**)



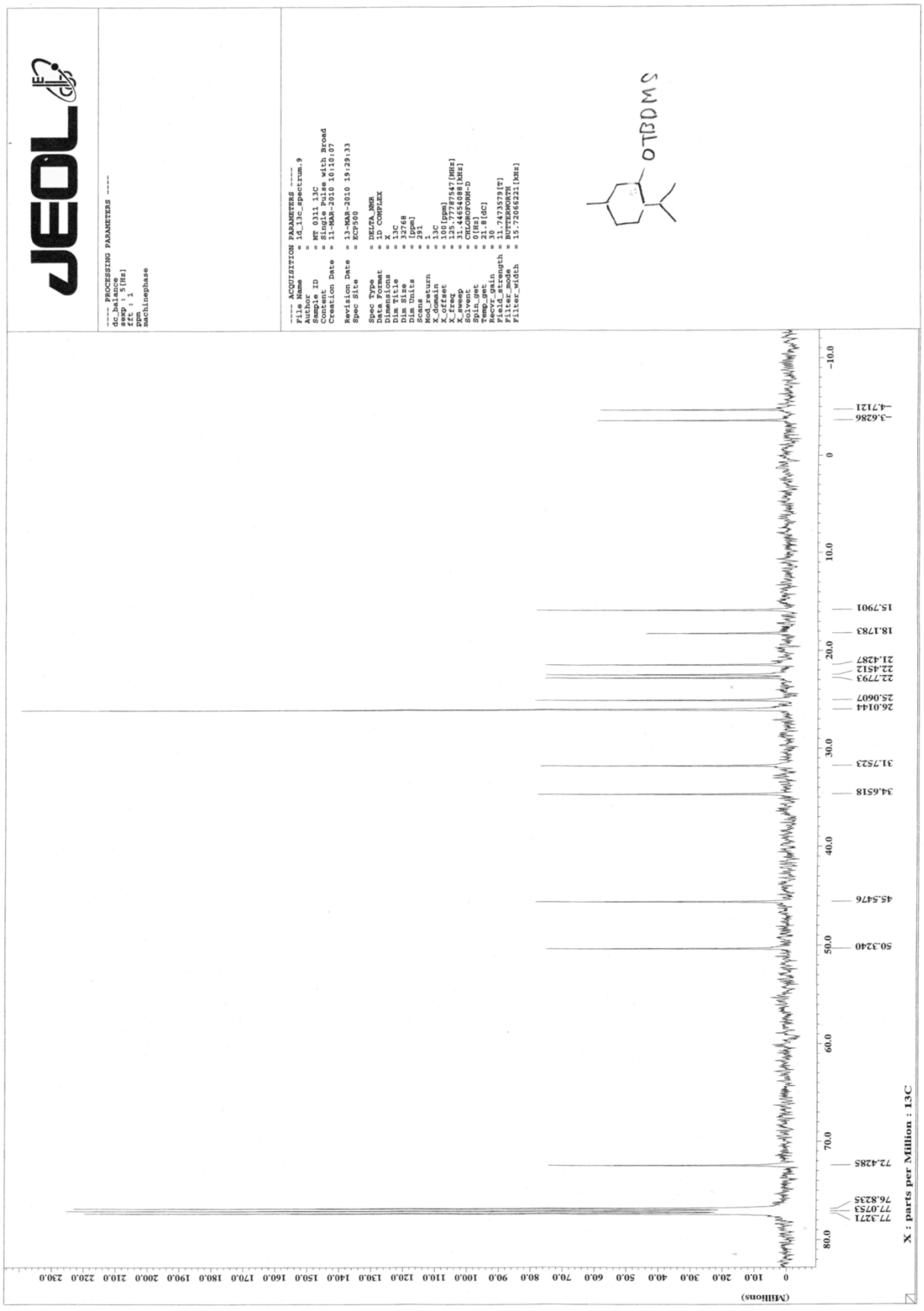
^{13}C NMR of 8-(*tert*-butyldimethylsiloxy)-2,6-dimethyl-oct-2-ene (**17**)



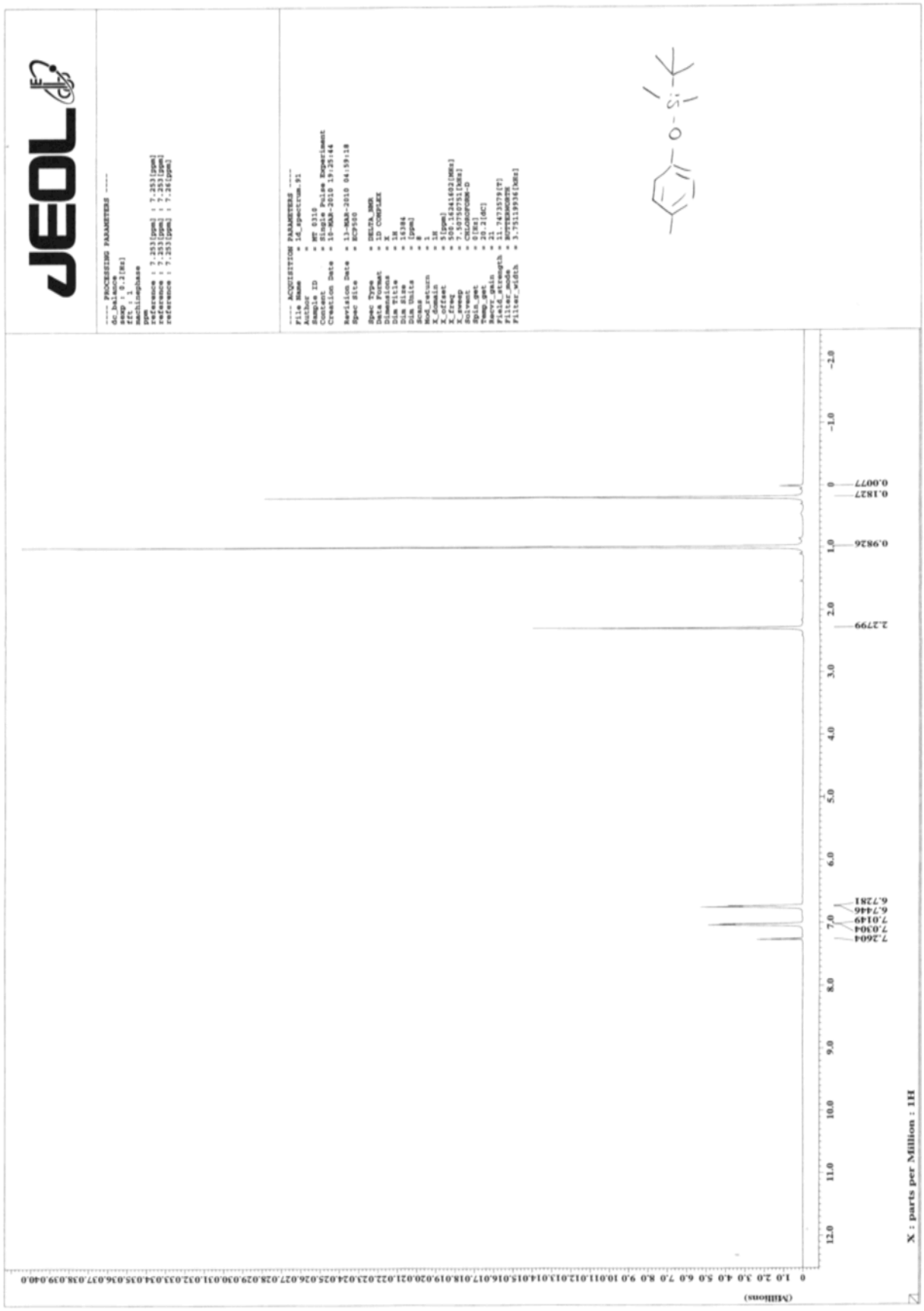
^{1}H NMR of *dl-tert*-butyldimethylsilyl-menthyl ether (**19**)



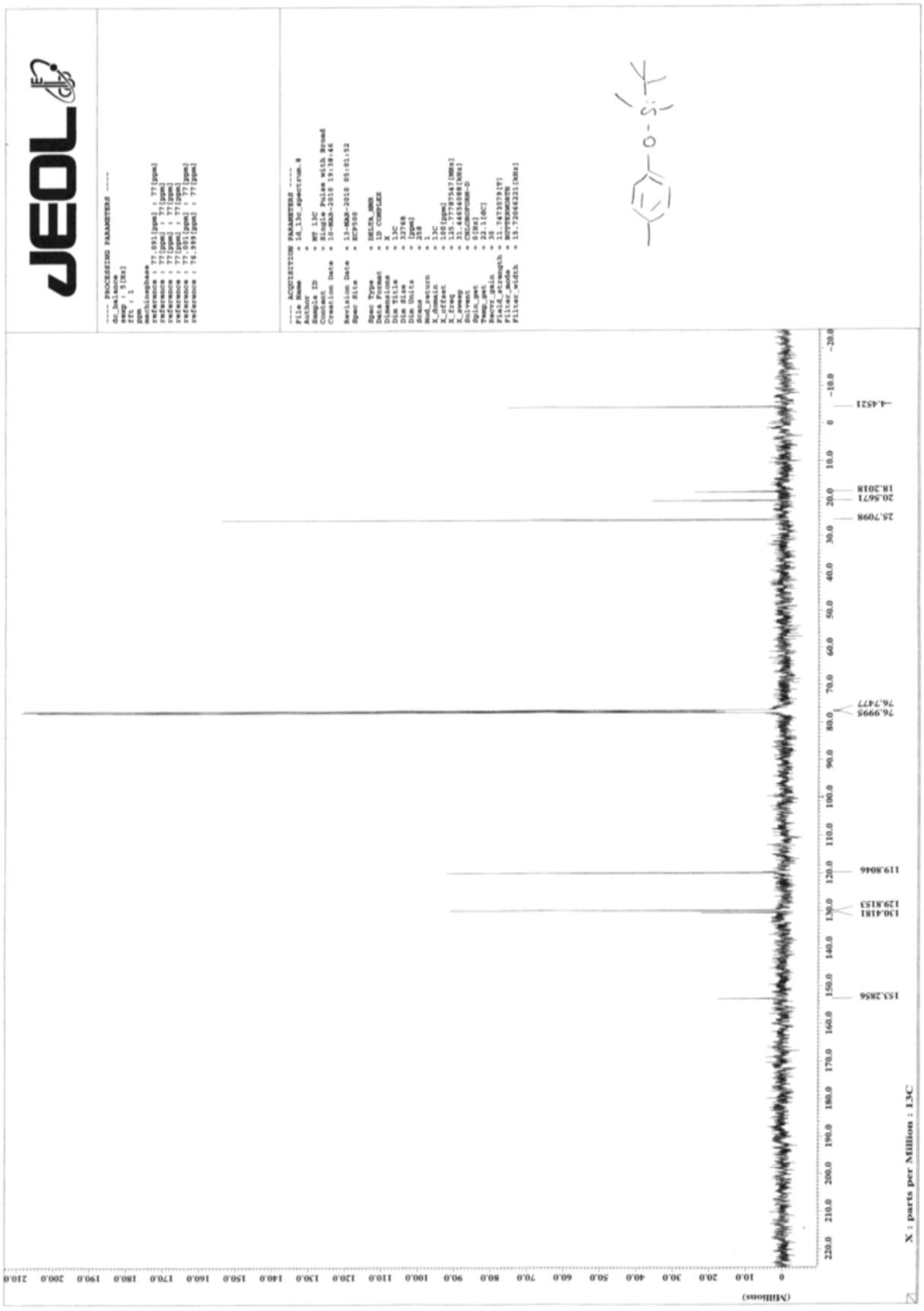
^{13}C NMR of *dl-tert*-butyldimethylsilyl-menthyl ether (**19**)



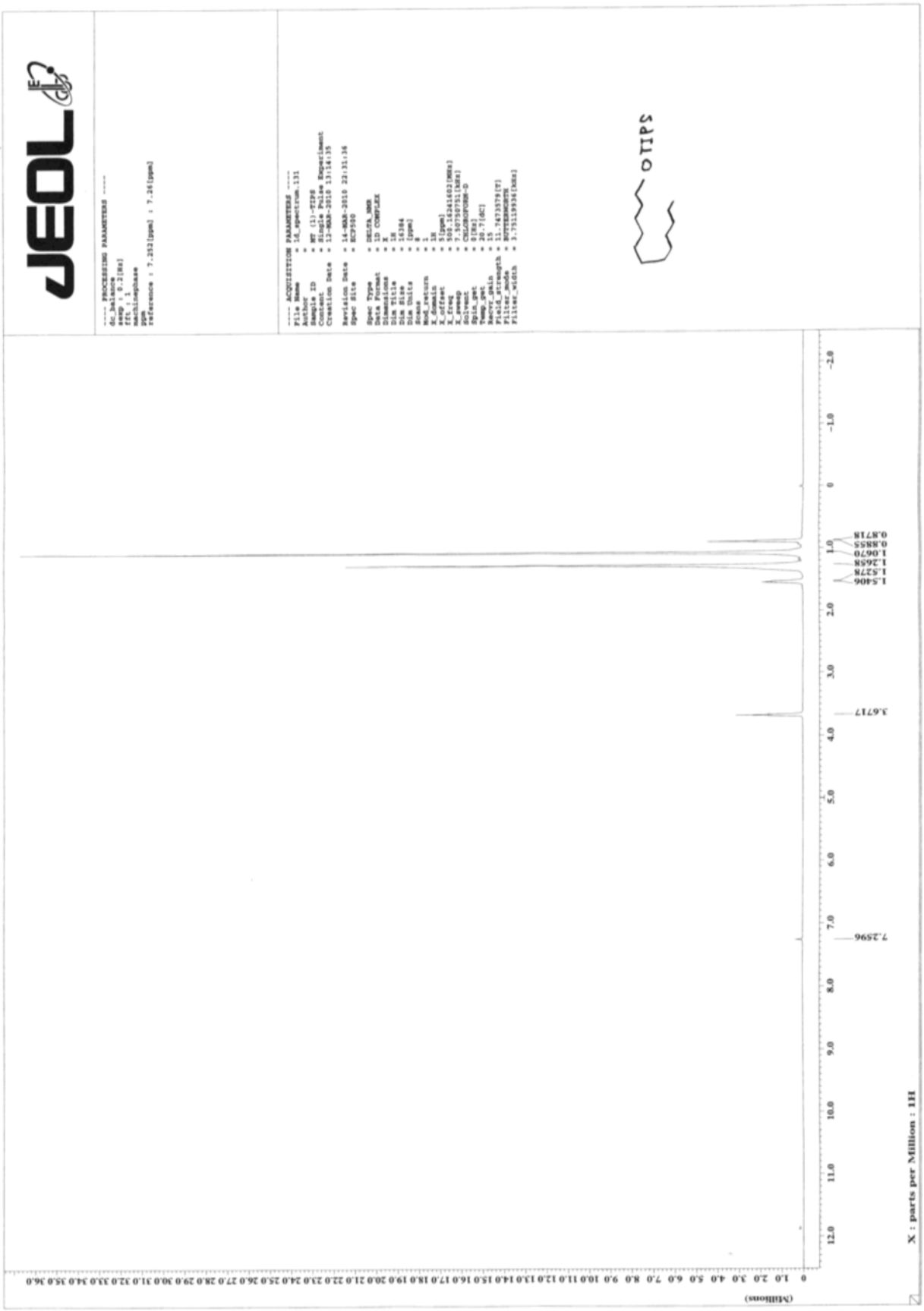
^{1}H NMR of *tert*-butyldimethylsilyl *p*-xylyl ether (**21**)



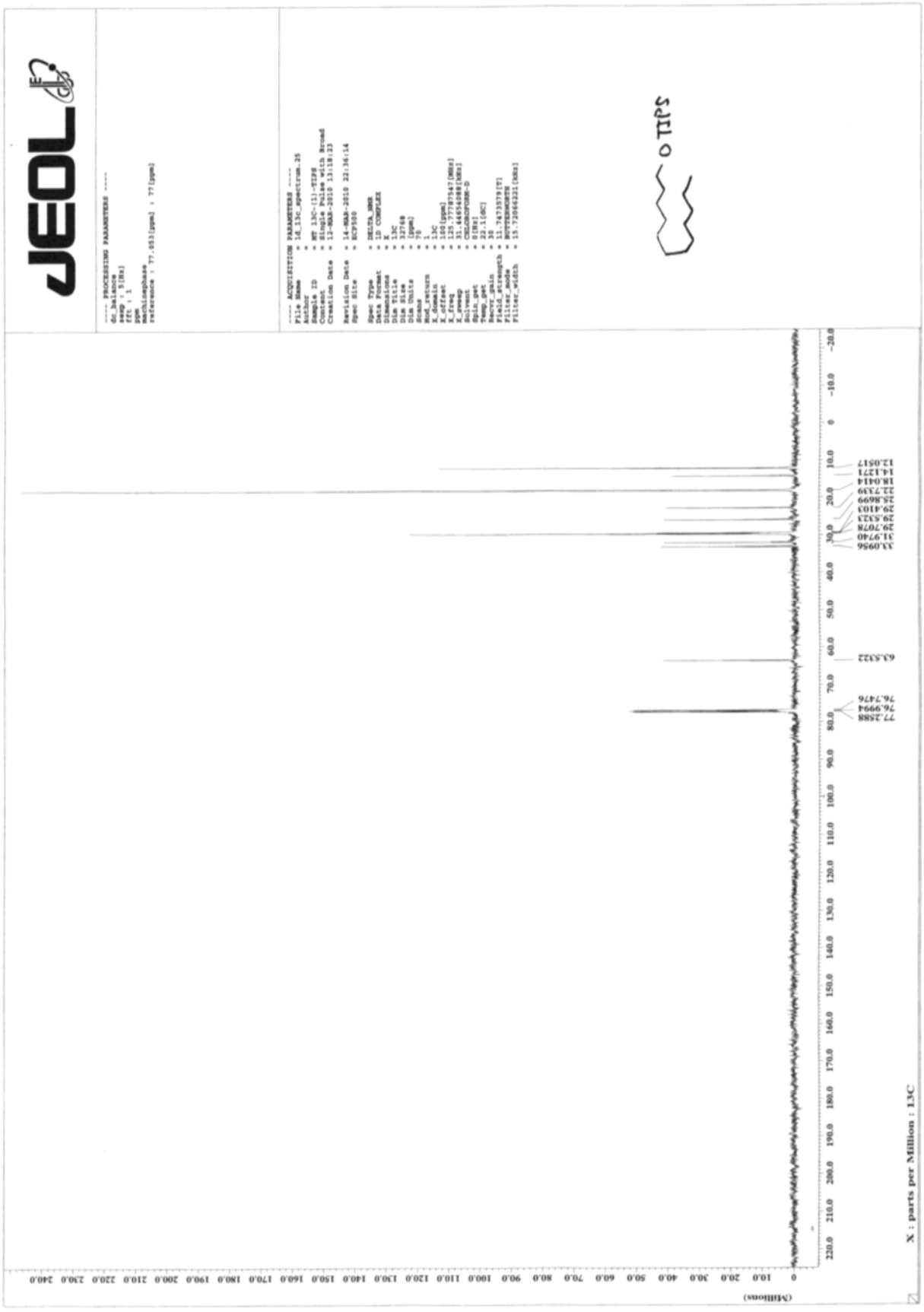
^{13}C NMR of *tert*-butyldimethylsilyl *p*-xylyl ether (**21**)



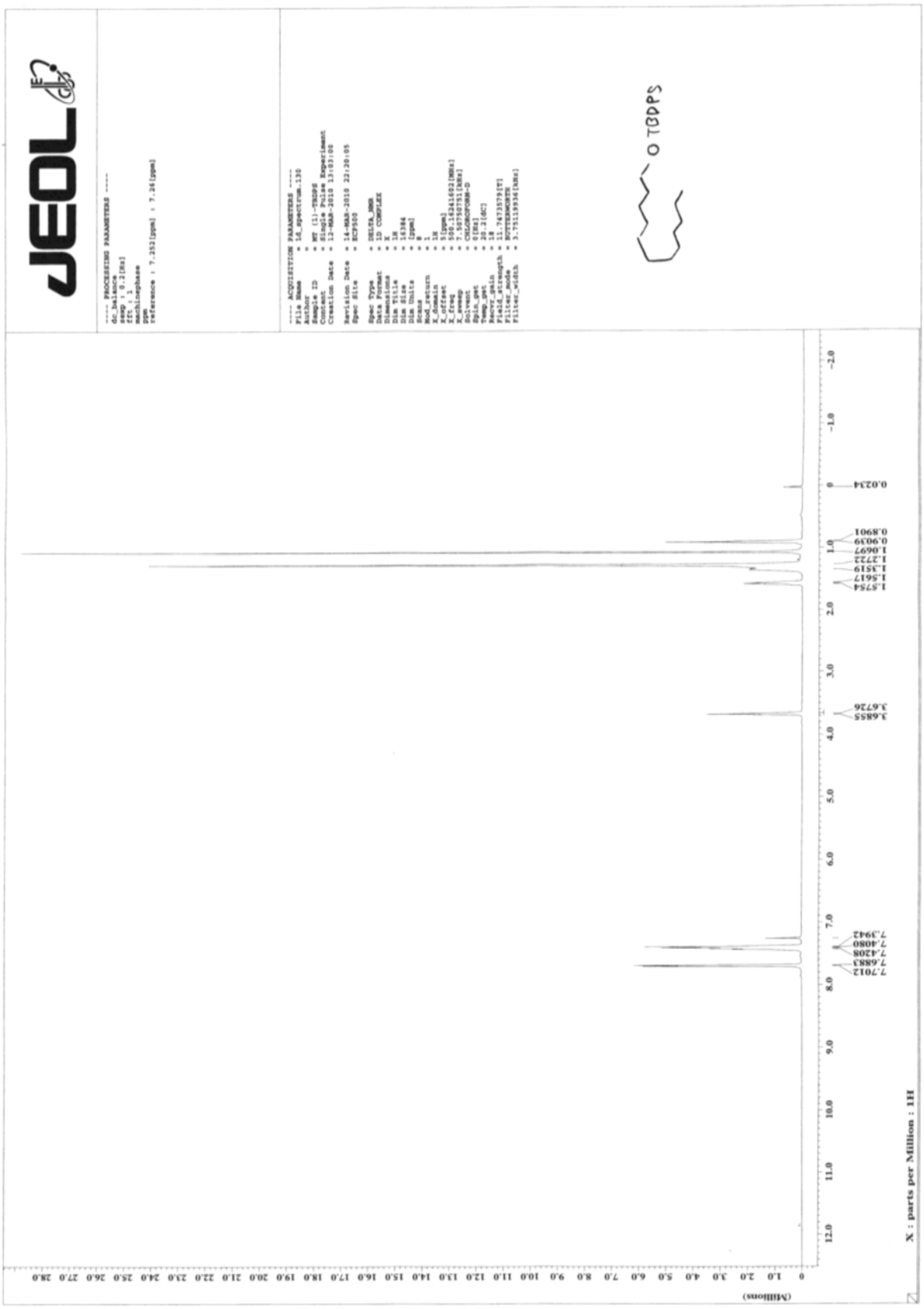
^{1}H NMR of triisopropylsilyl dodecyl ether (**22**)



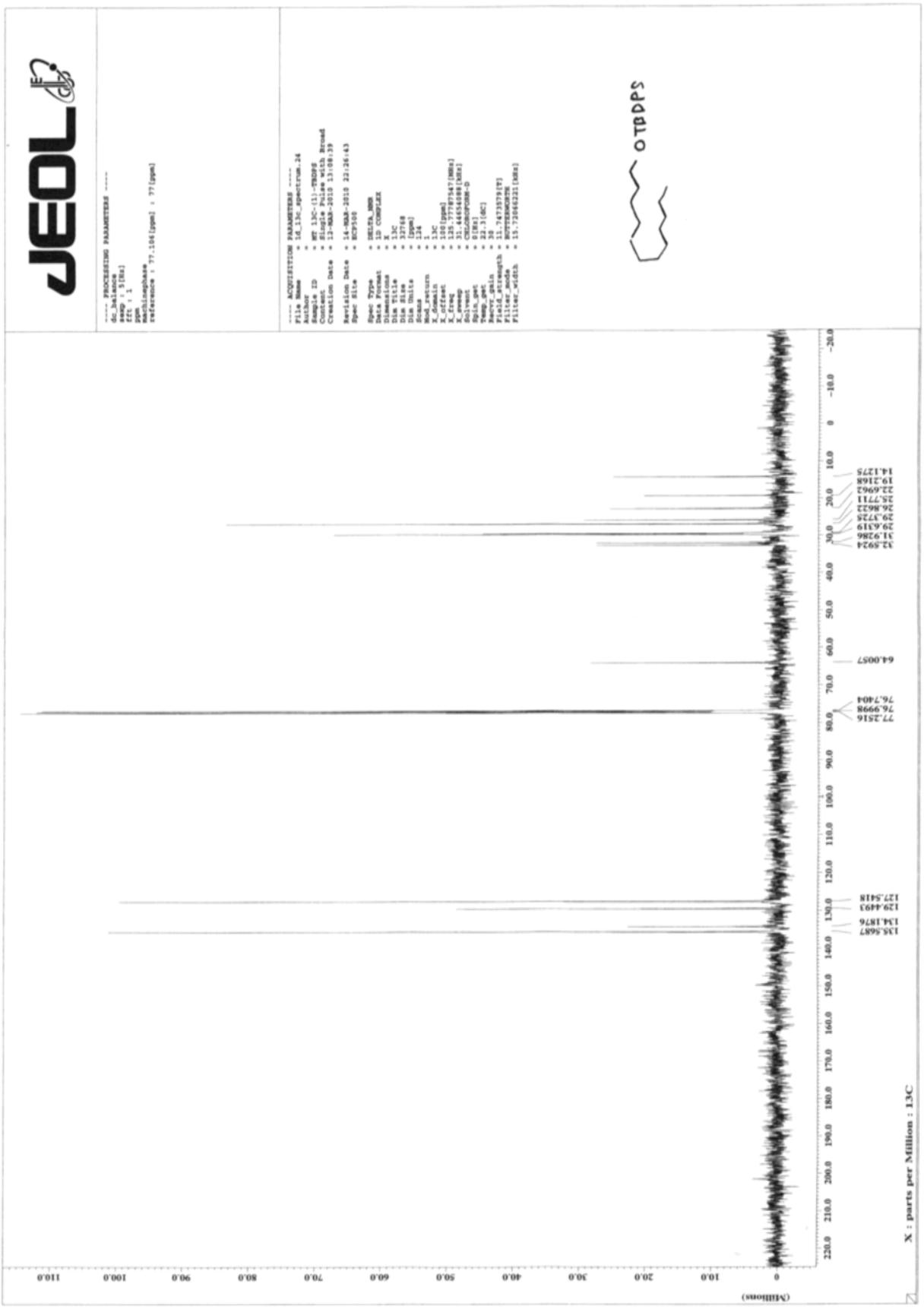
^{13}C NMR of triisopropylsilyl dodecyl ether (**22**)



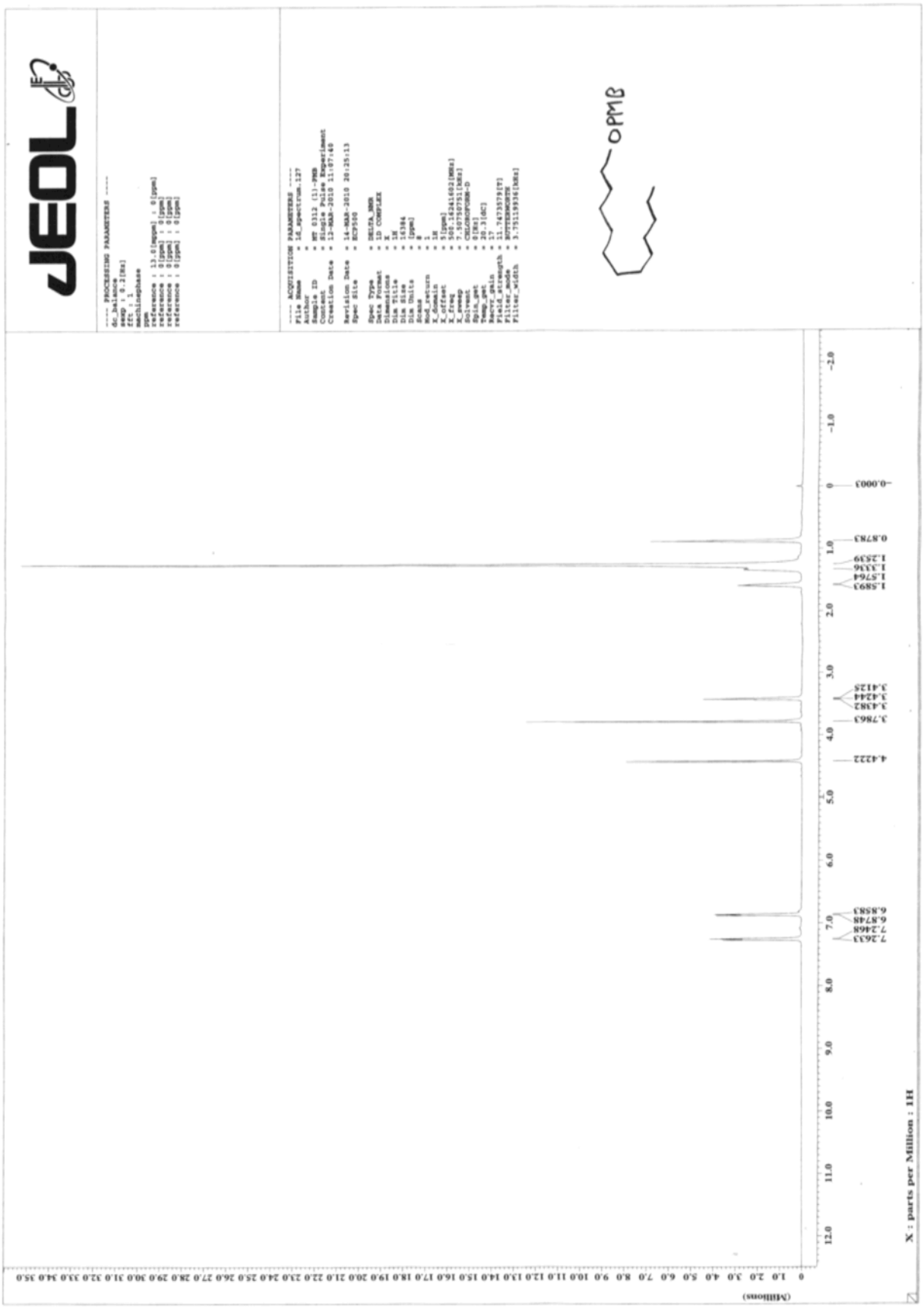
^{1}H NMR of *tert*-butyldiphenylsilyl dodecyl ether (**23**)



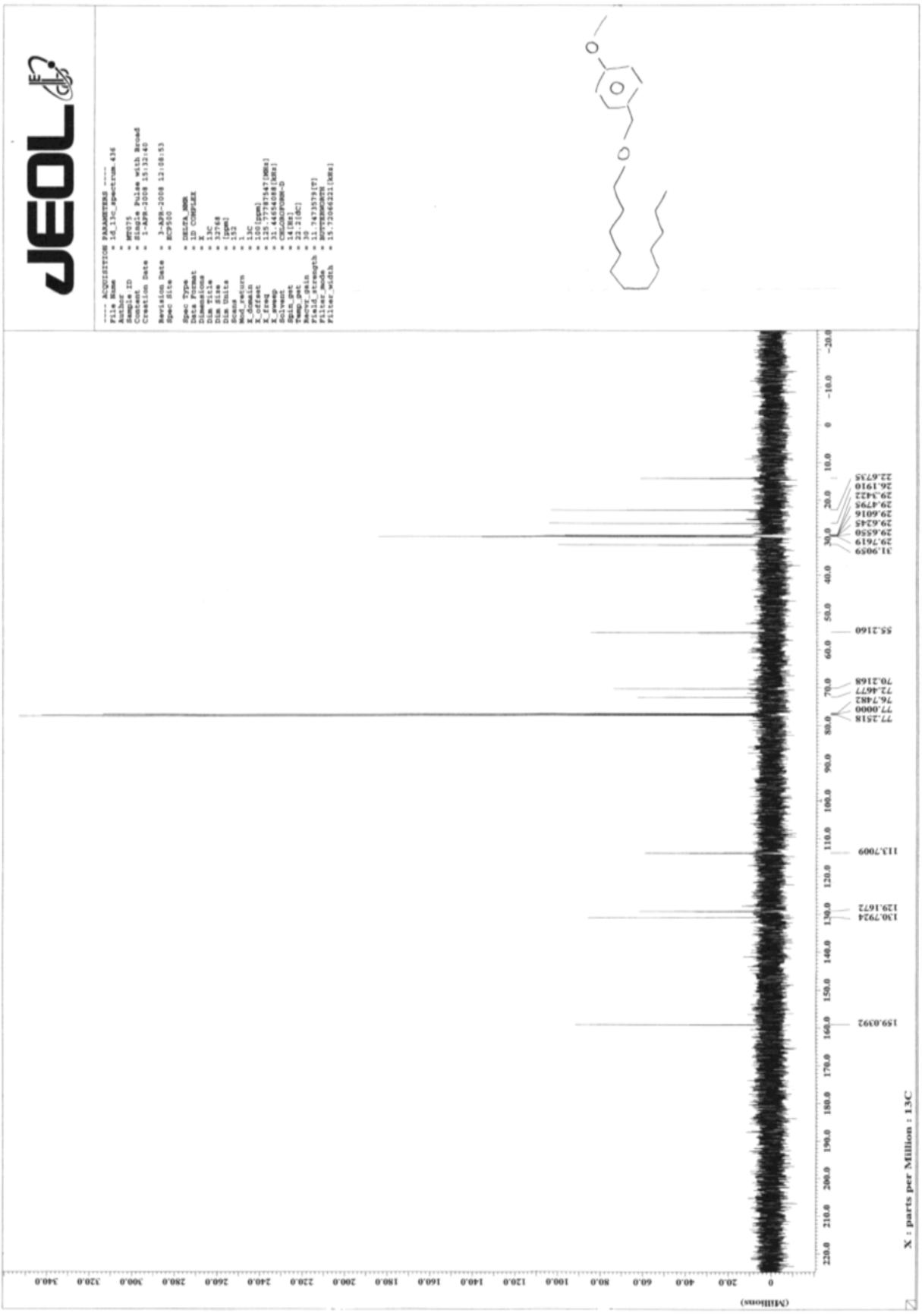
^{13}C NMR of *tert*-butyldiphenylsilyl dodecyl ether (**23**)



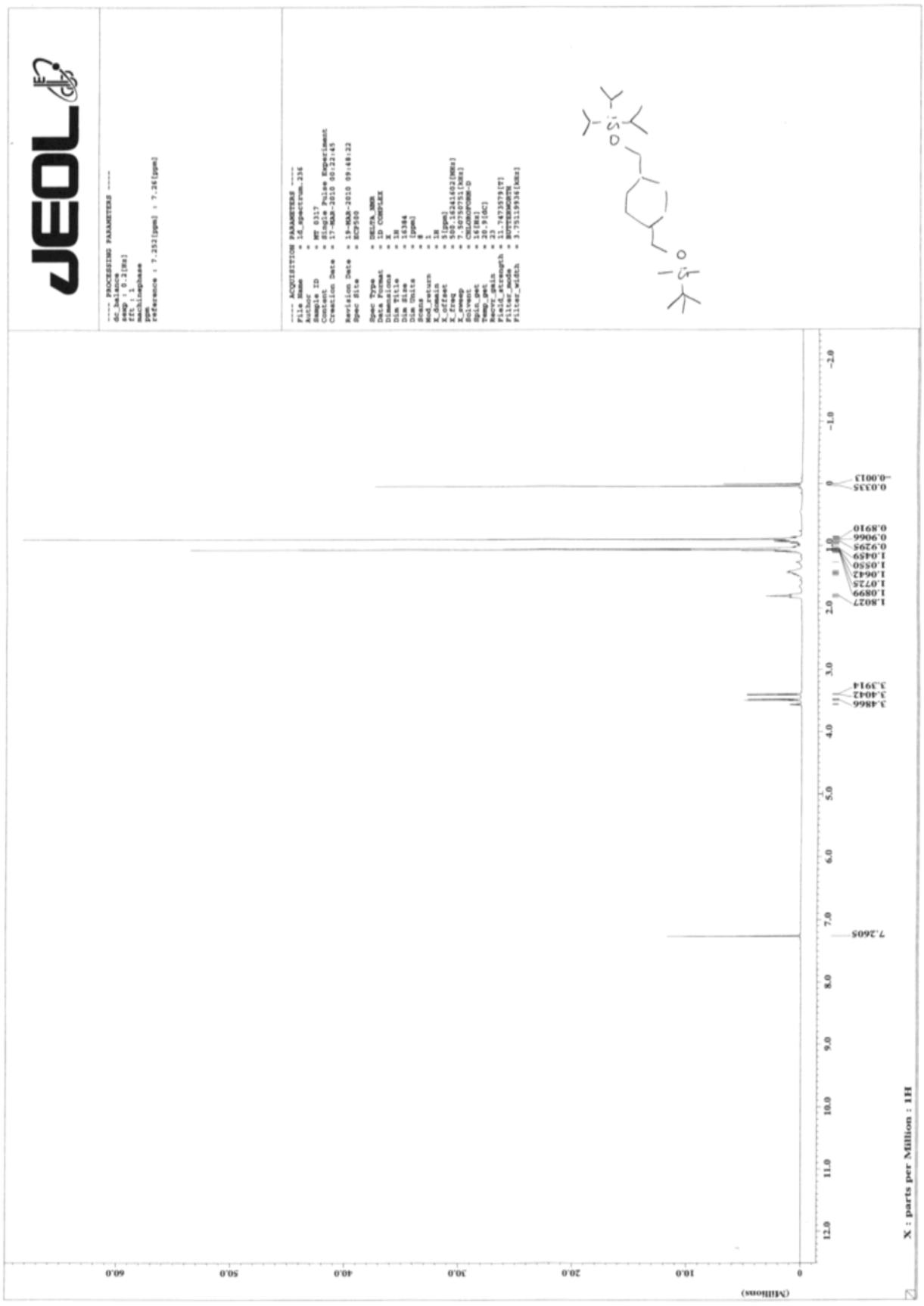
^{1}H NMR of *p*-methoxybenzyl dodecyl ether (**24**)



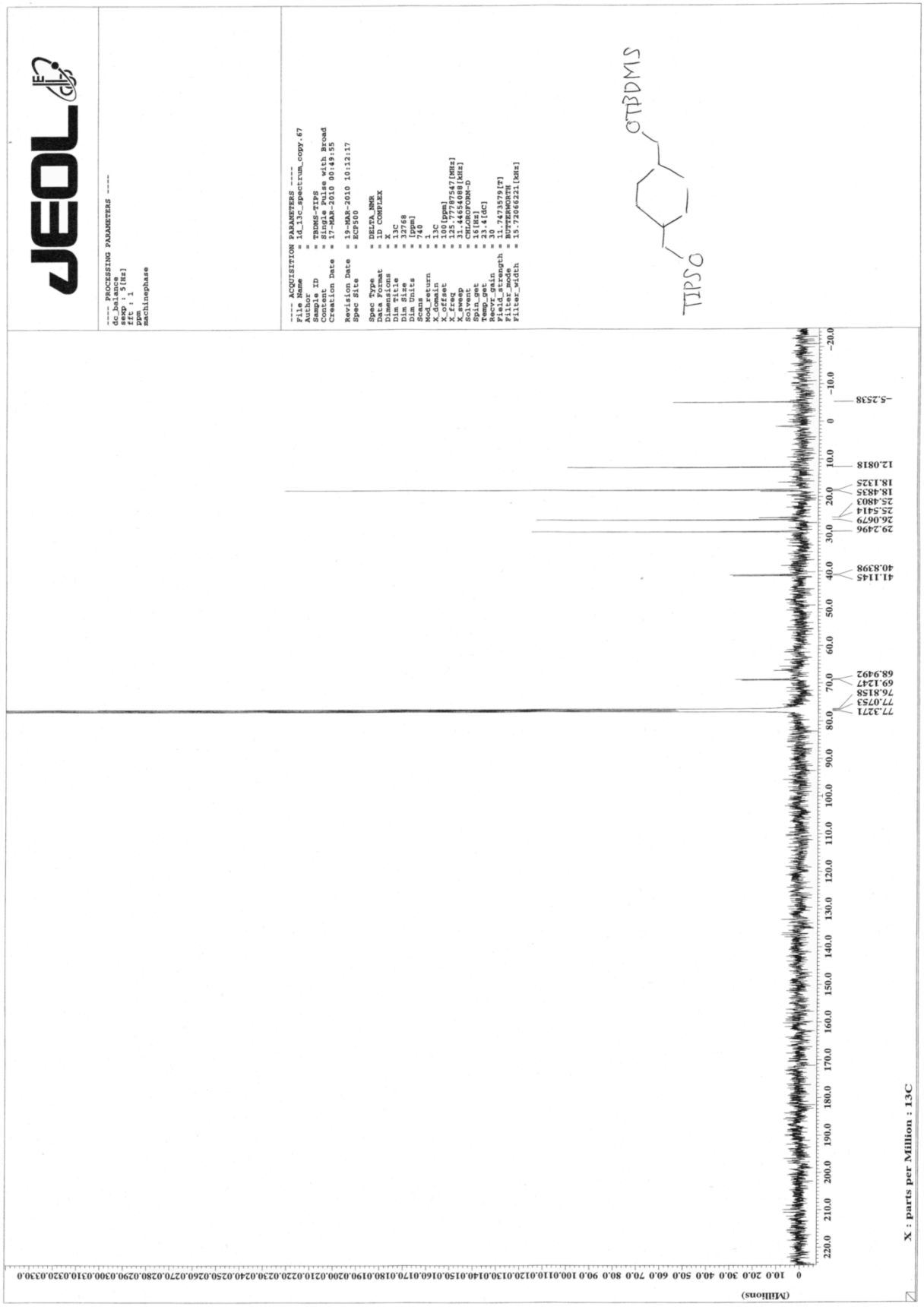
^{13}C NMR of *p*-methoxybenzyl dodecyl ether (**24**)



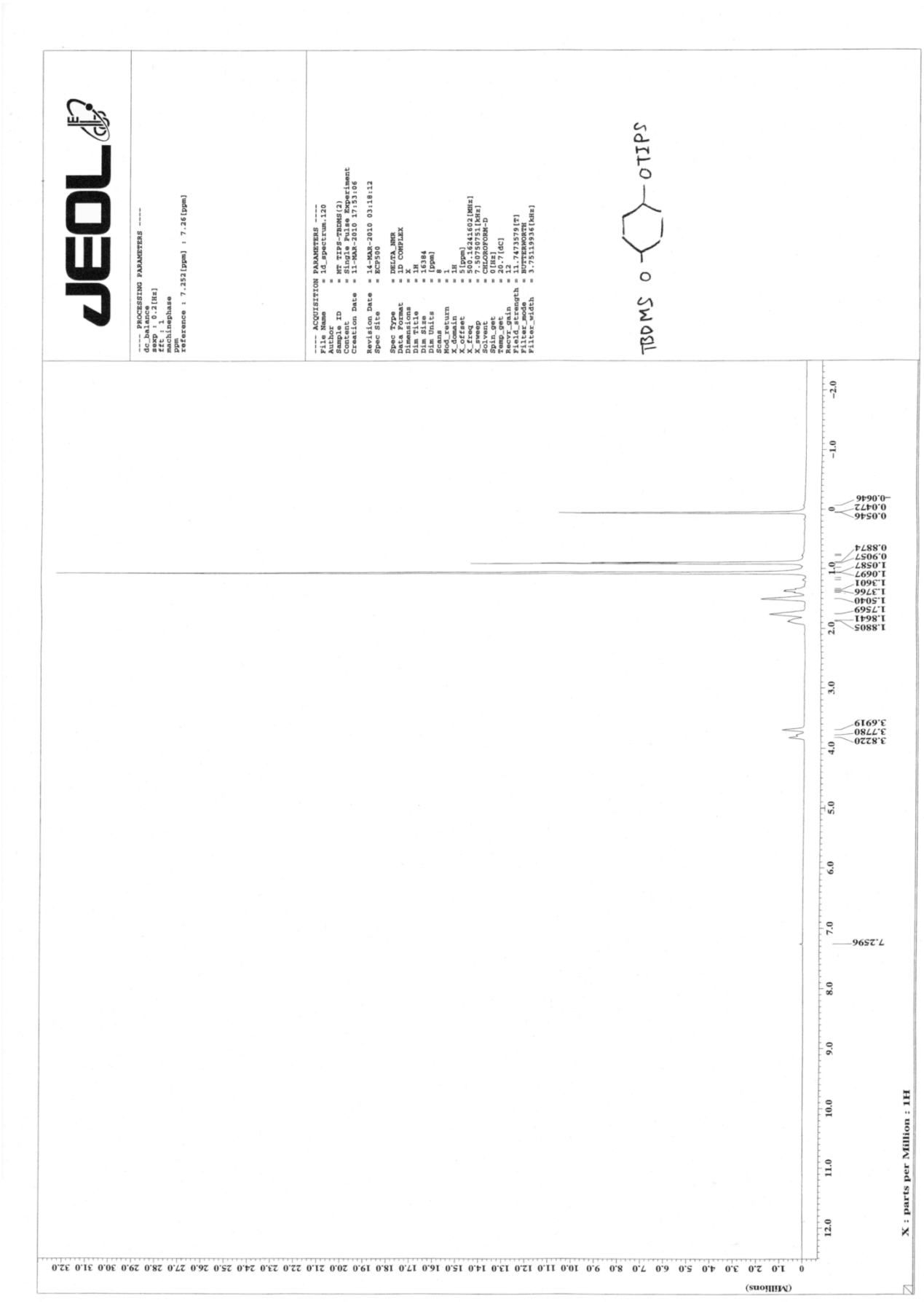
^{1}H NMR of 4-(*tert*-butyldimethylsiloxymethyl)-triisopropylsiloxymethylcyclohexane (**25**)



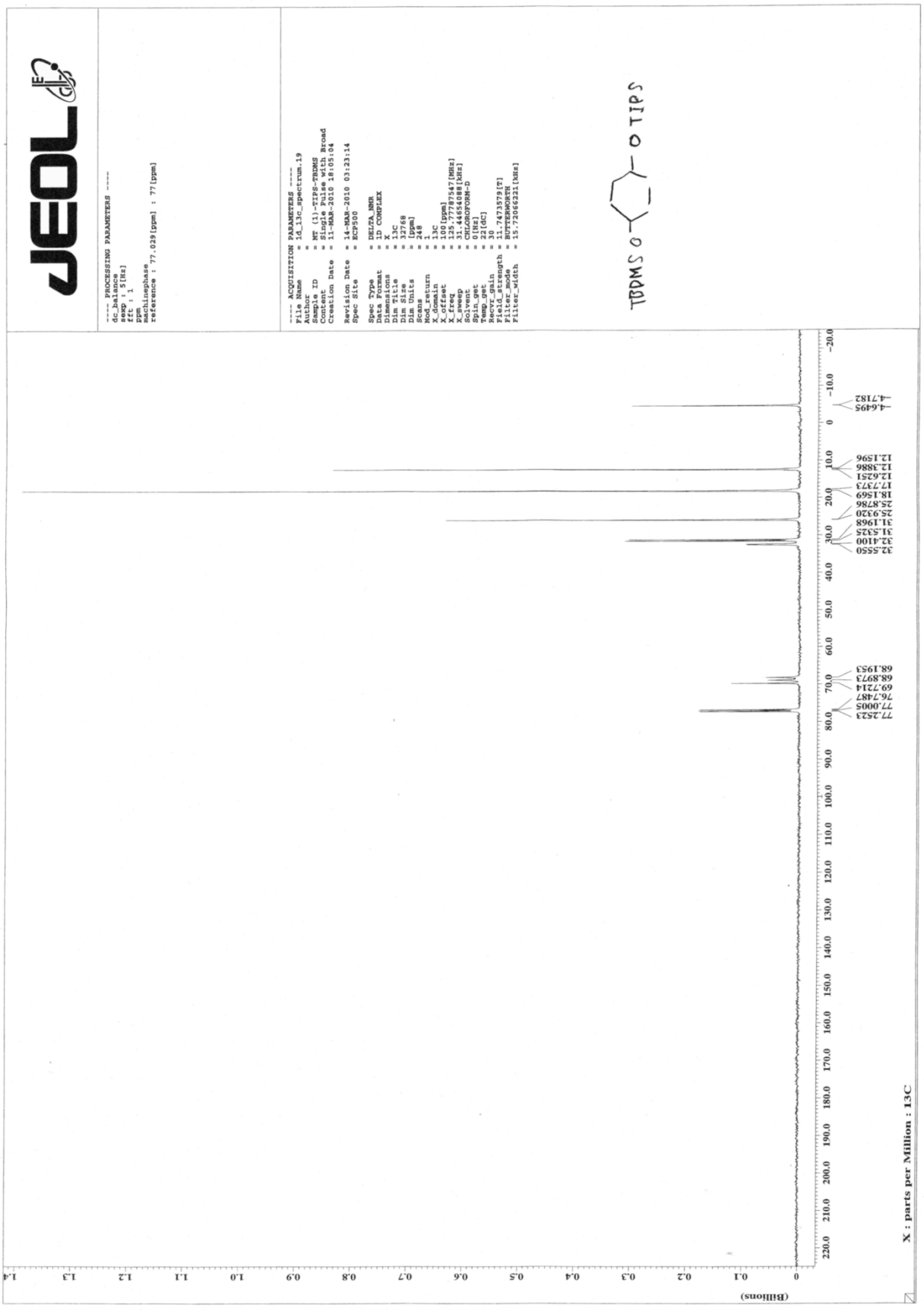
^{13}C NMR of 4-(*tert*-butyldimethylsiloxymethyl)-triisopropylsiloxymethylcyclohexane (**25**)



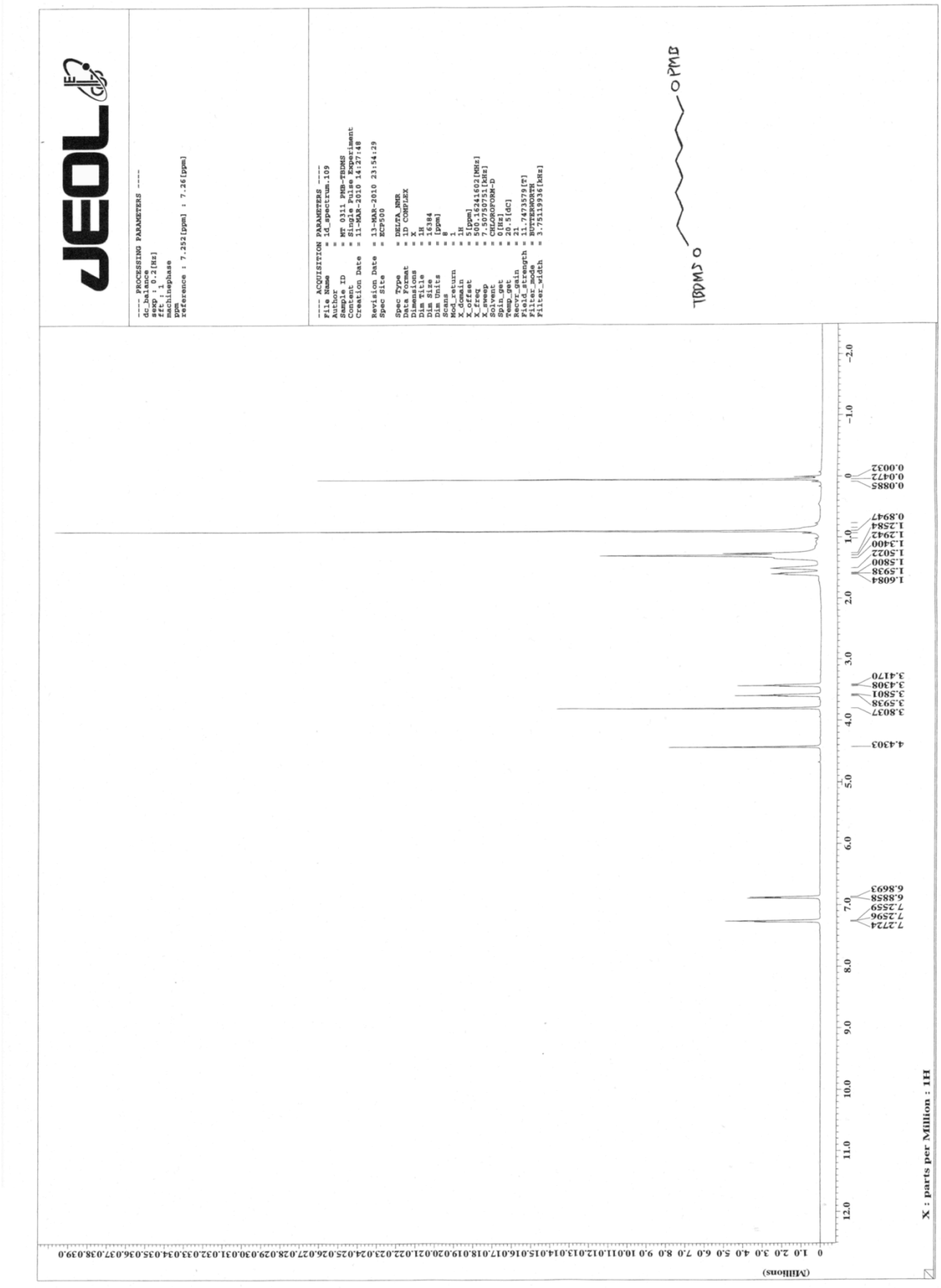
^{1}H NMR of 4-(*tert*-butyldimethylsiloxy)-triisopropylsiloxycyclohexane (**27**)



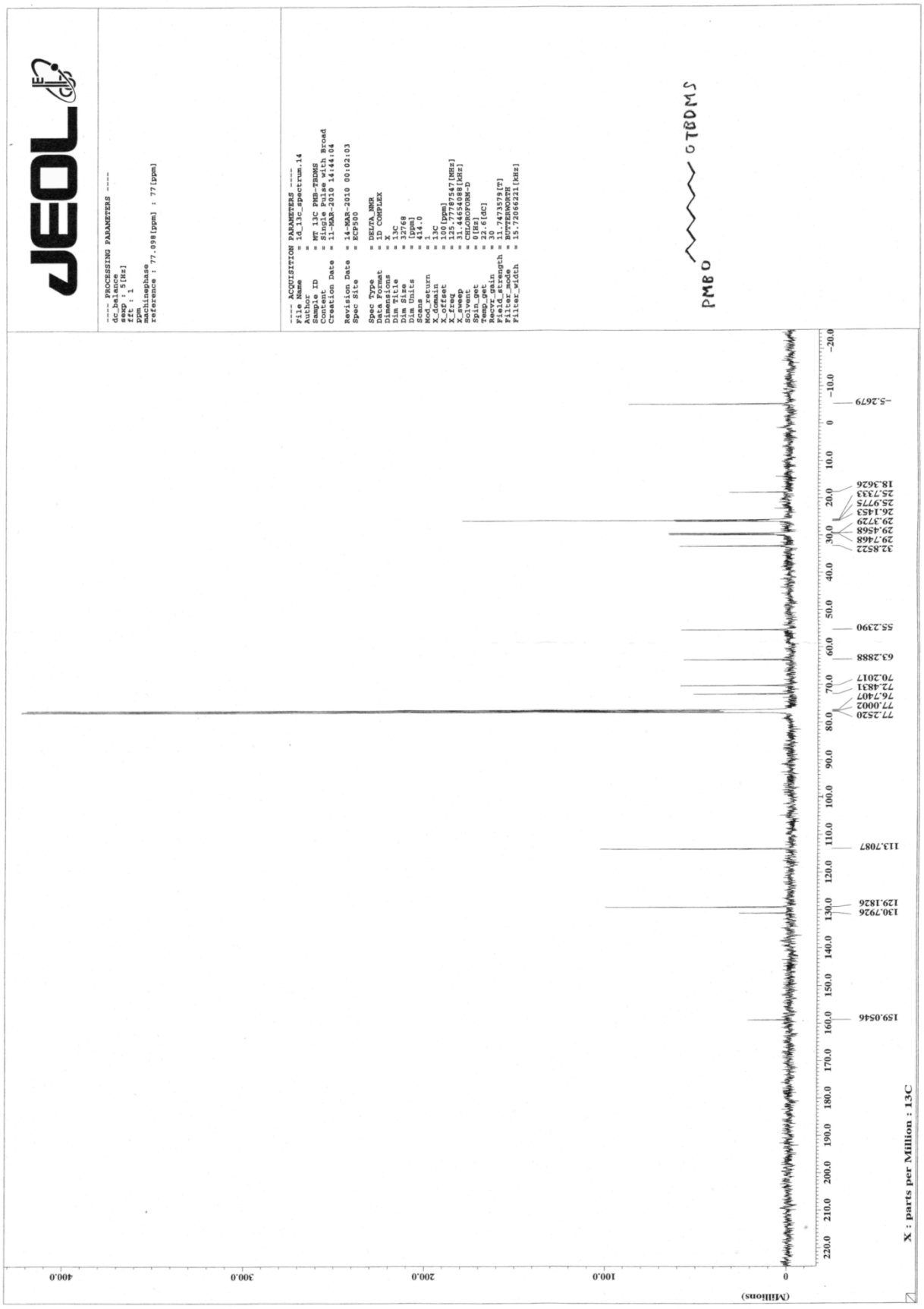
^{13}C NMR of 4-(*tert*-butyldimethylsiloxy)-triisopropylsiloxycyclohexane (**27**)



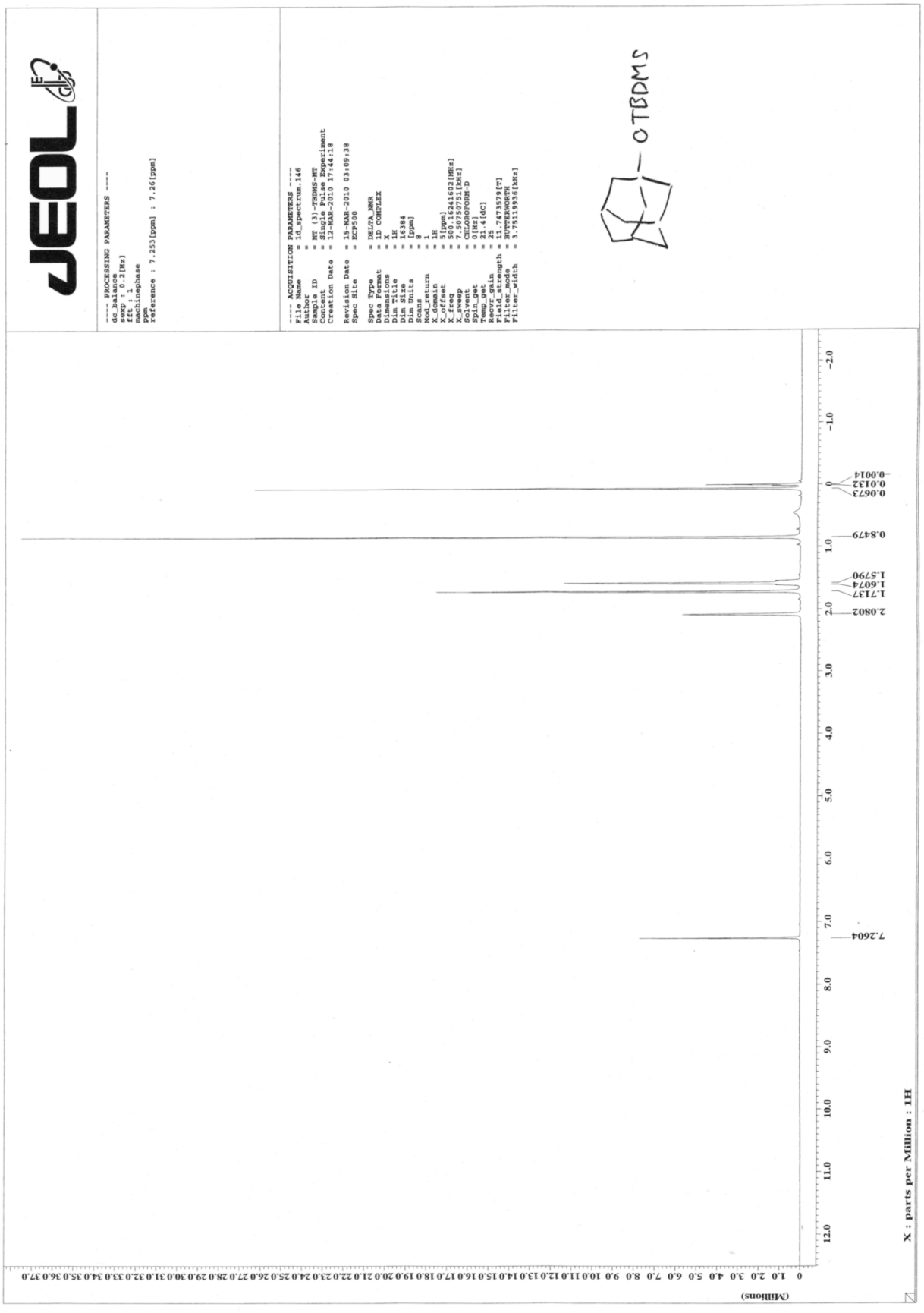
^{1}H NMR of 8-(*tert*-butyldimethylsiloxy)-(4-methoxybenzyloxy)octane (**29**)



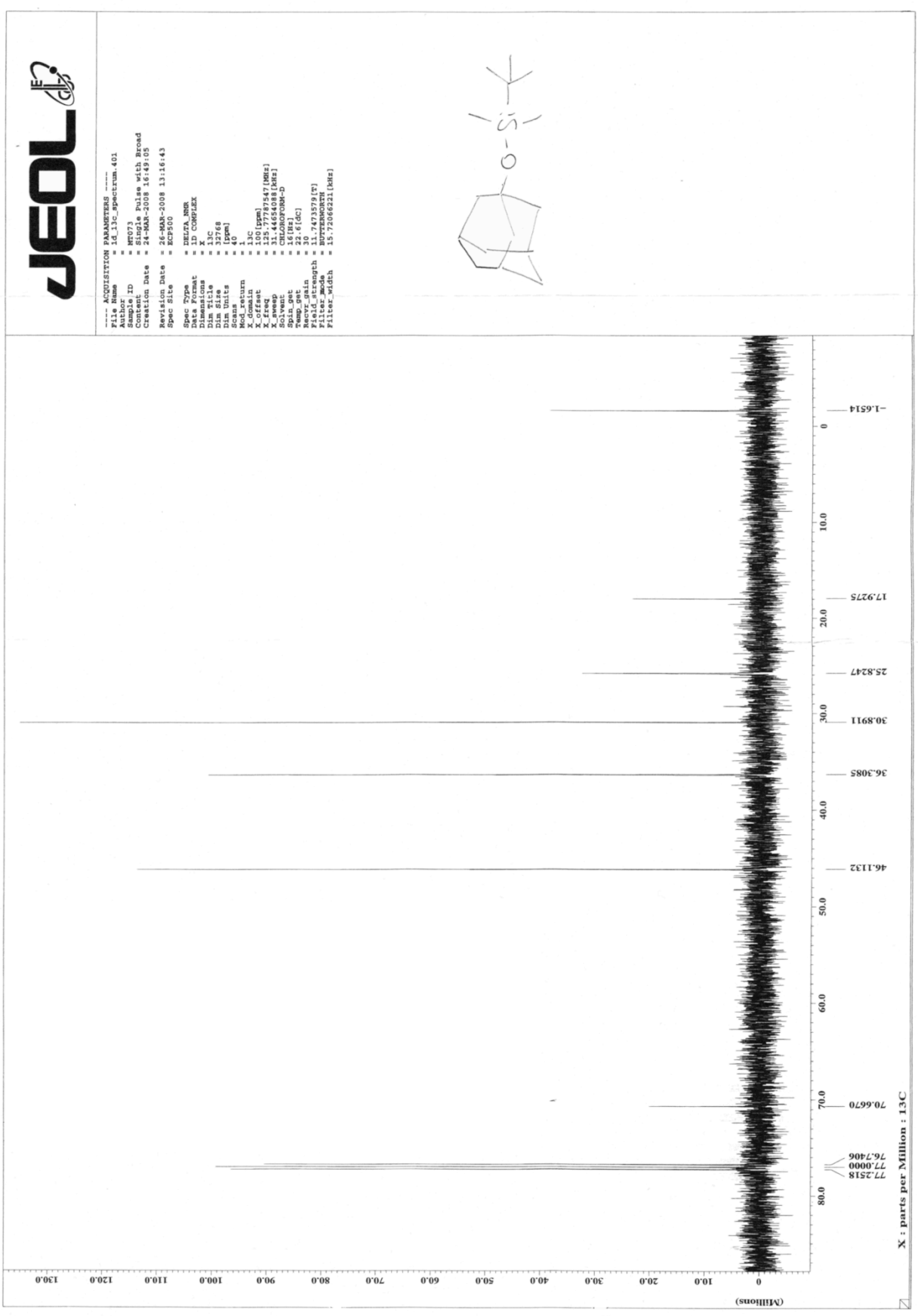
^{13}C NMR of 8-(*tert*-butyldimethylsiloxy)-(4-methoxybenzyloxy)octane (**29**)



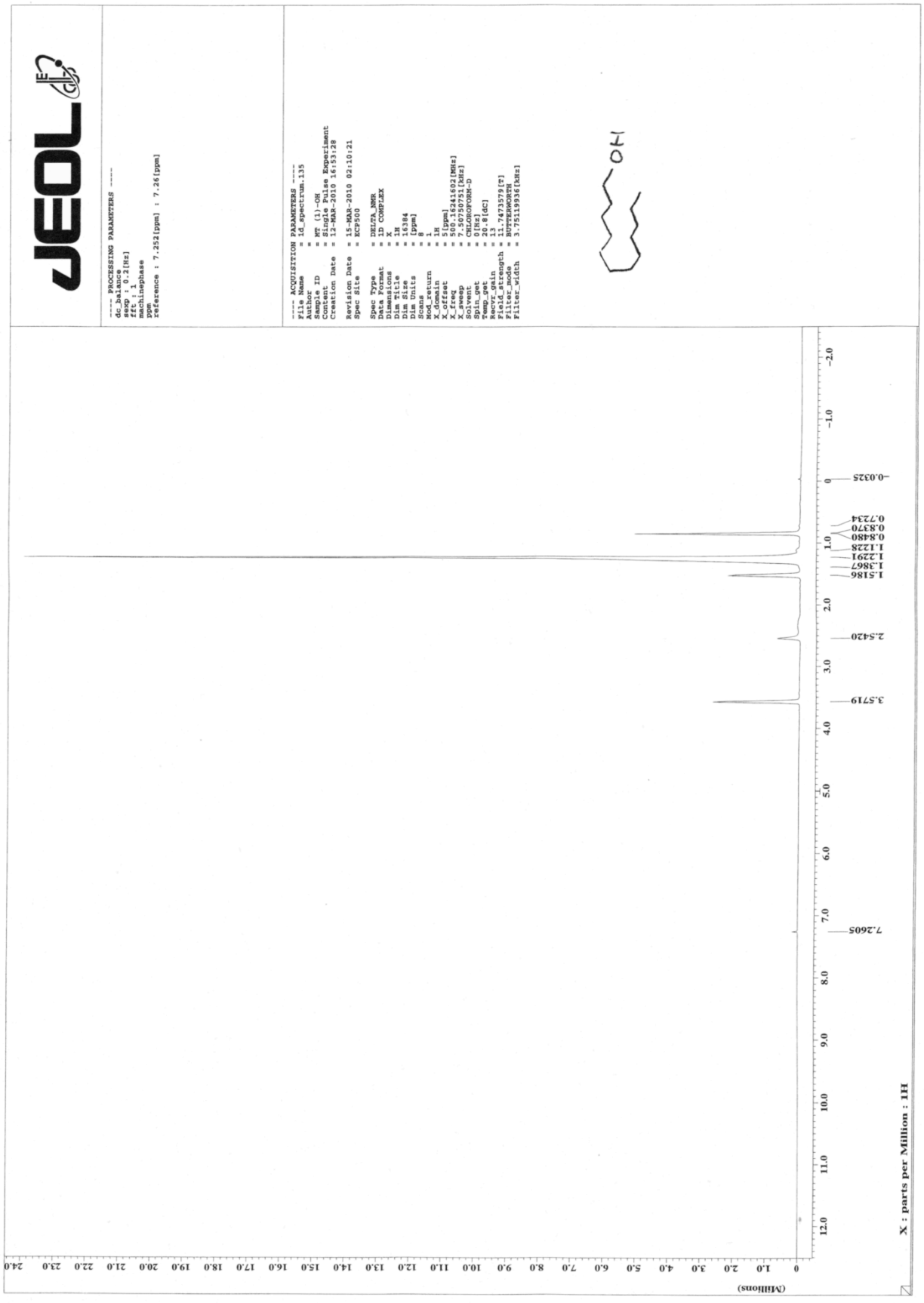
^{1}H NMR of 1-adamantyl *tert*-butyldimethylsilyl ether (**31**)



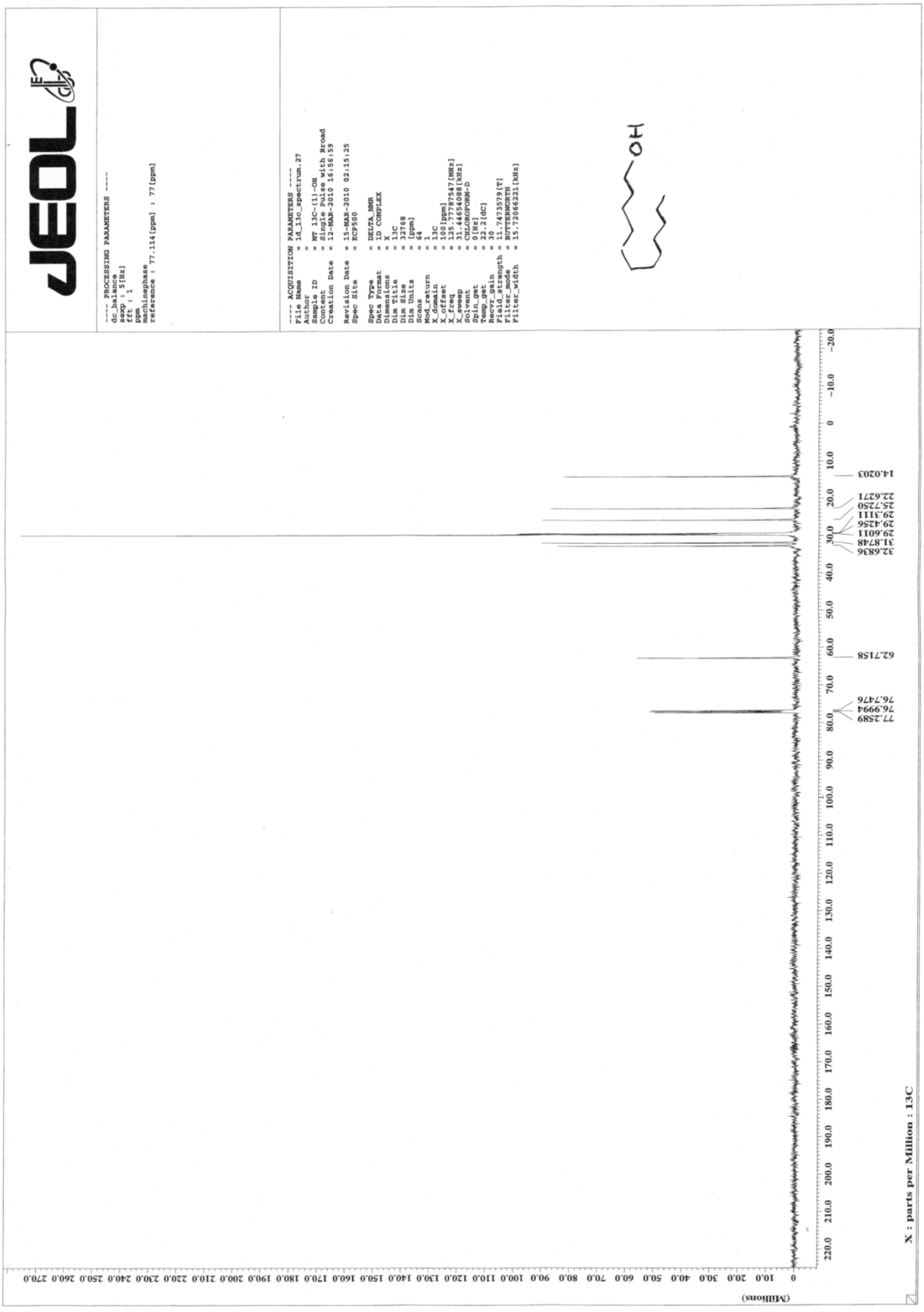
^{13}C NMR of 1-adamantyl *tert*-butyldimethylsilyl ether (**31**)



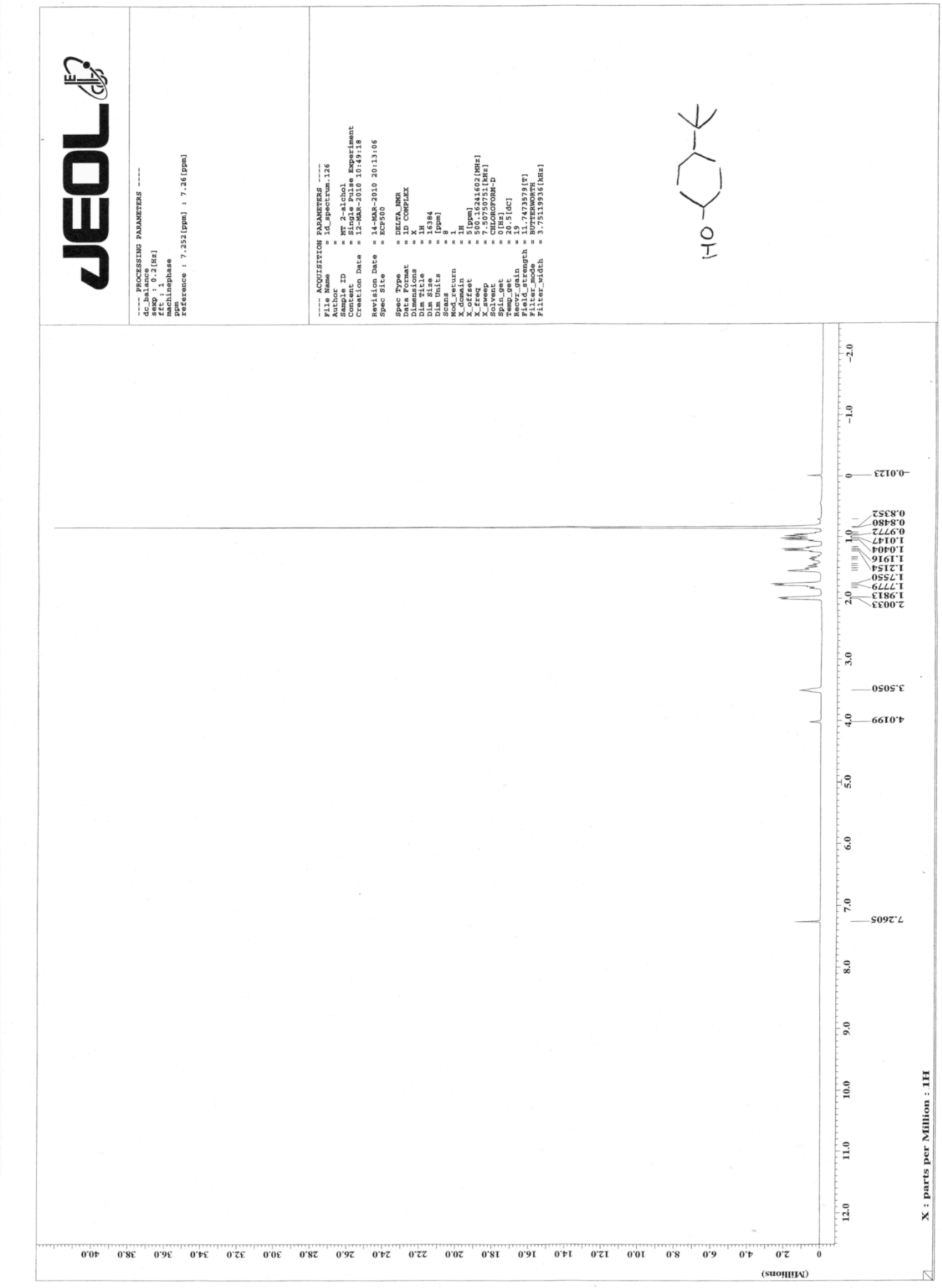
^{1}H NMR of 1-dodecanol (**13**)



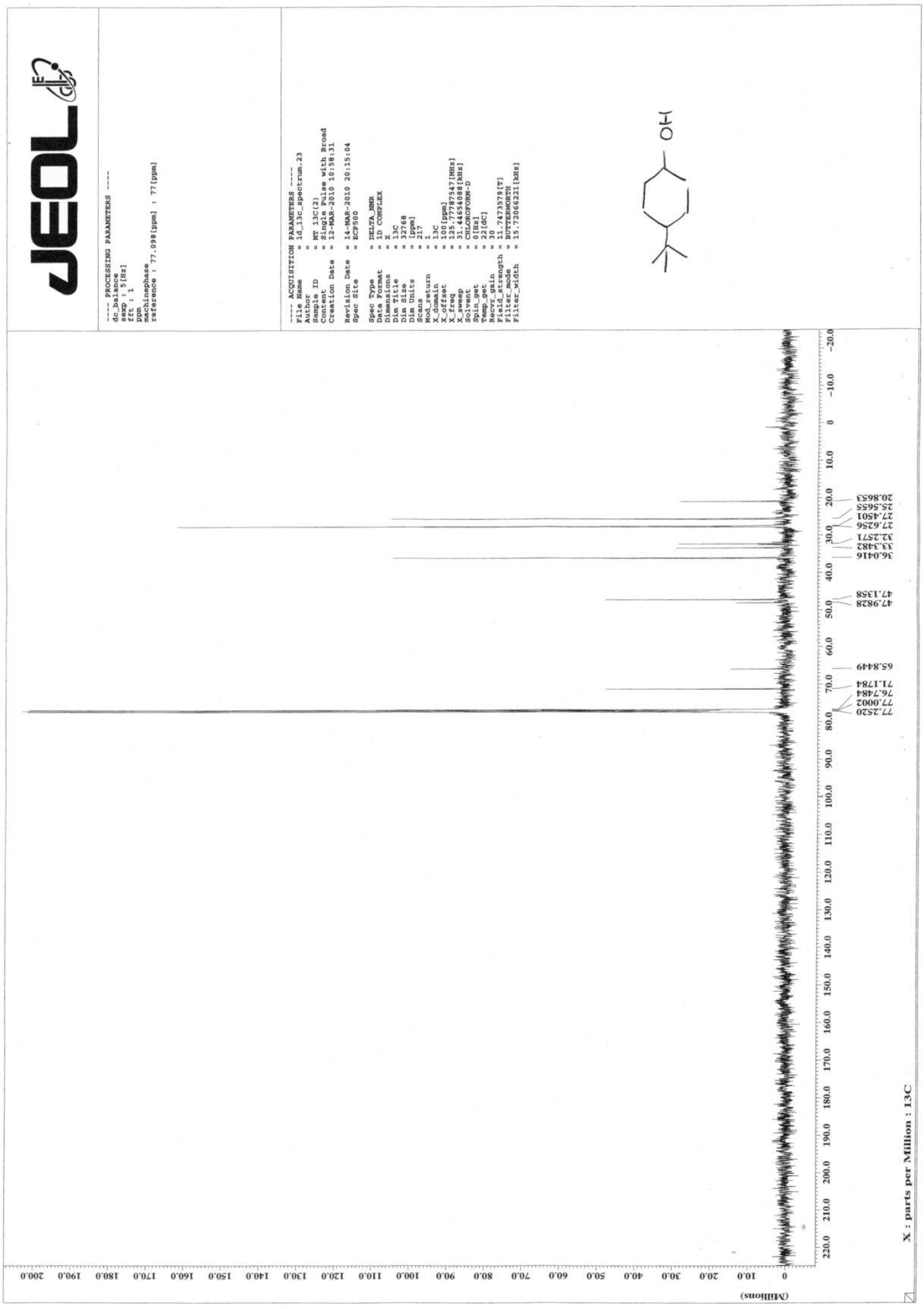
^{13}C NMR of 1-dodecanol (**13**)



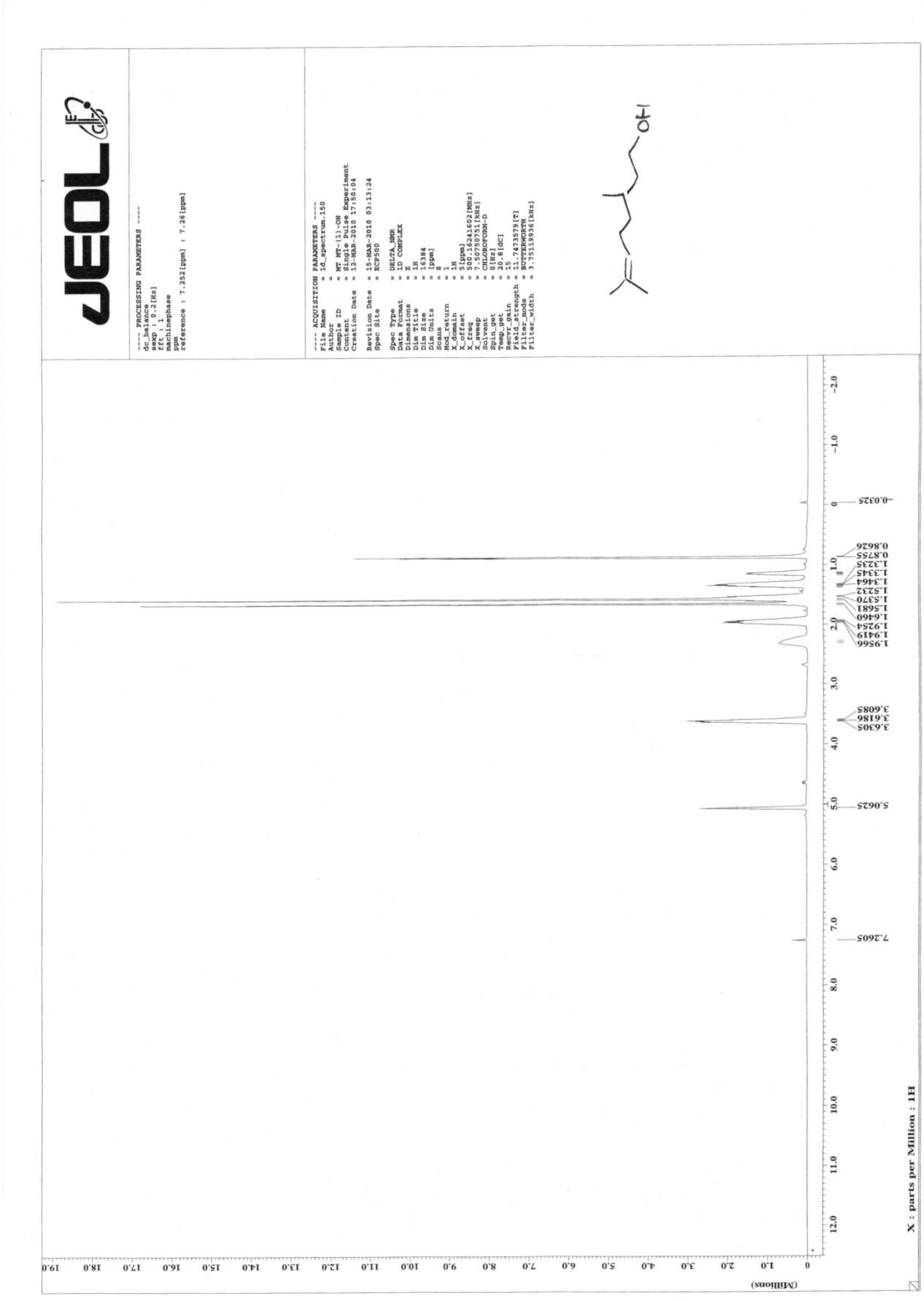
^{1}H NMR of 4-*tert*-butylcyclohexanol (**15**)



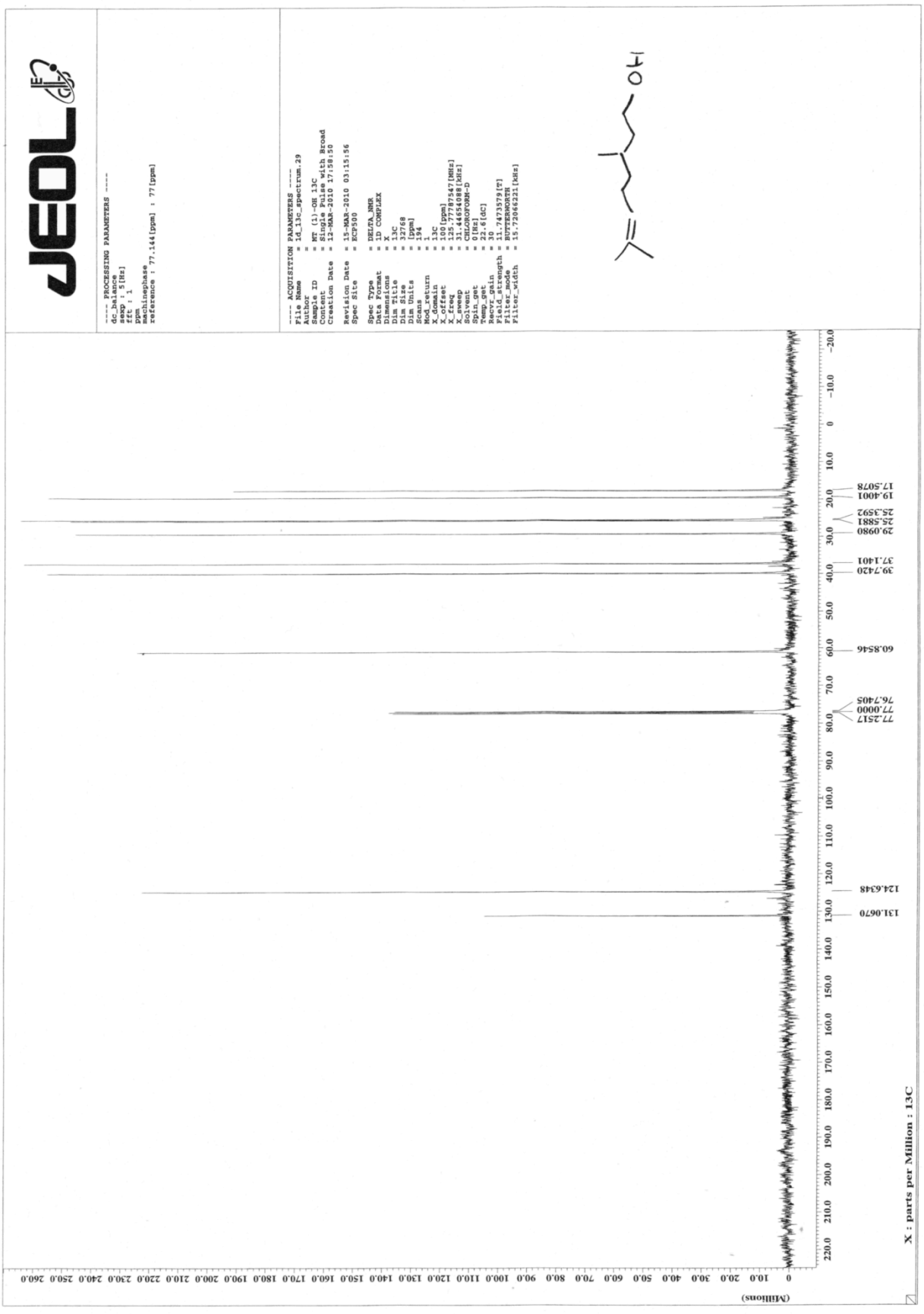
^{13}C NMR of 4-*tert*-butylcyclohexanol (**15**)



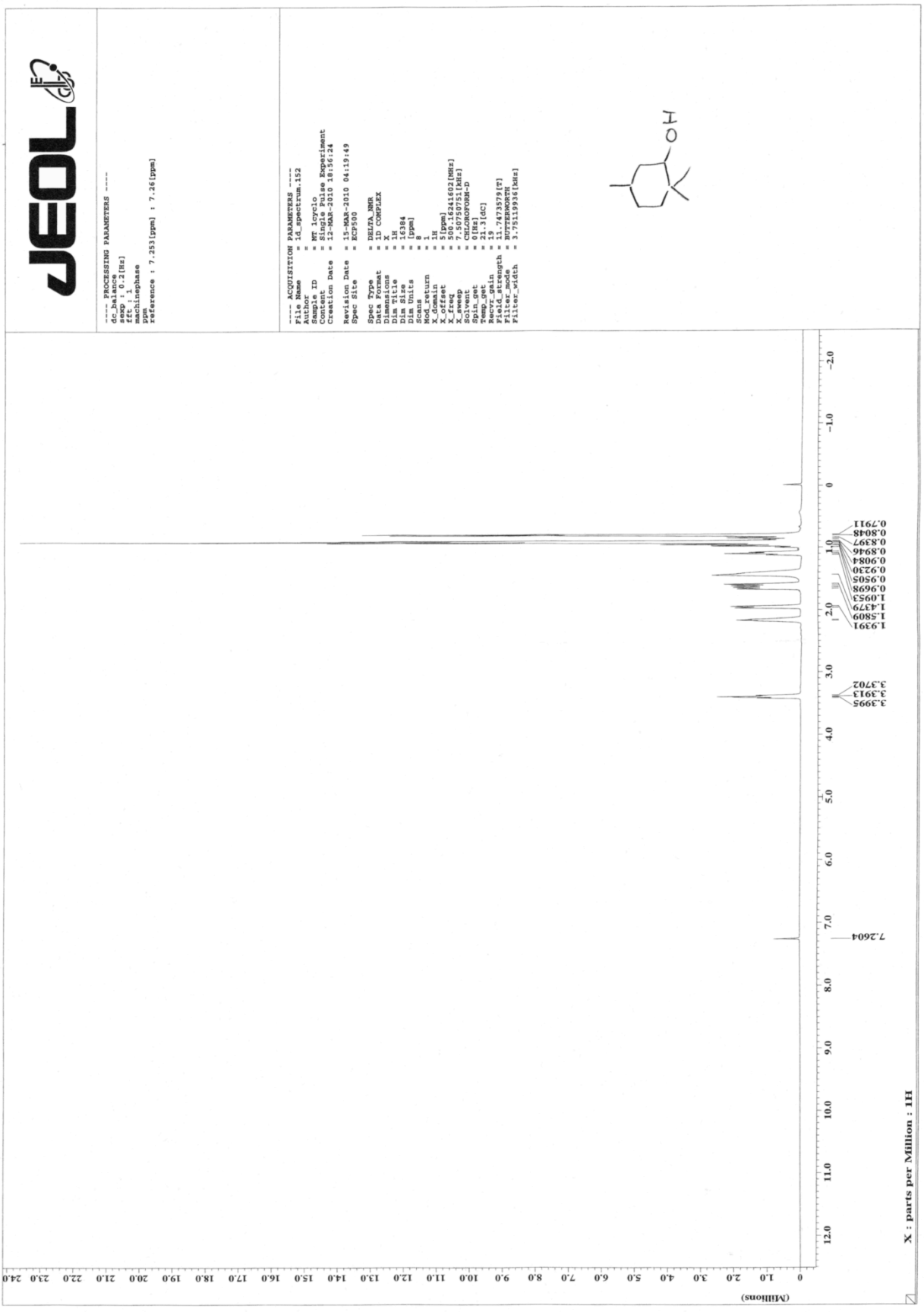
^{1}H NMR of citronellol (**18**)



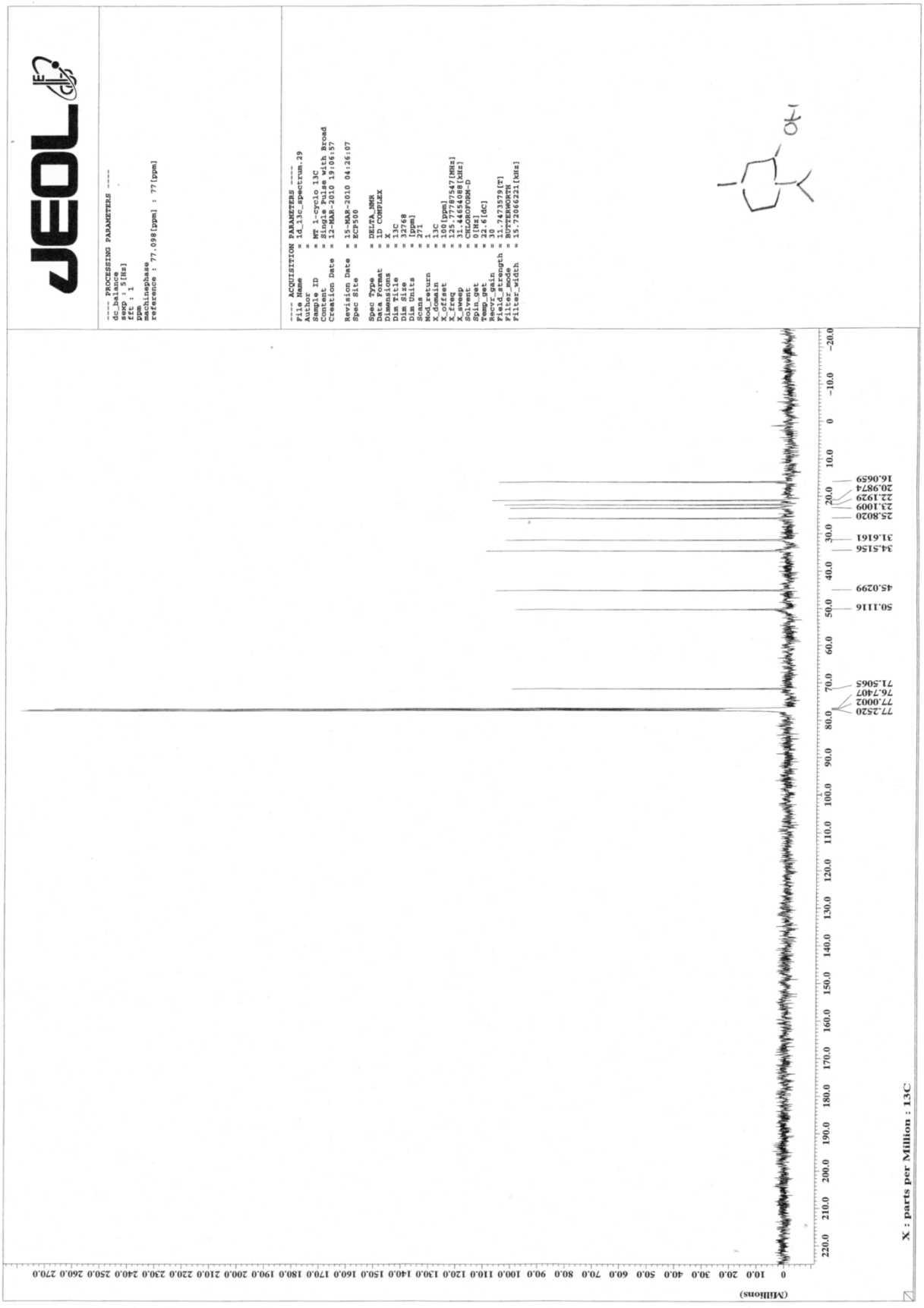
^{13}C NMR of citronellol (**18**)



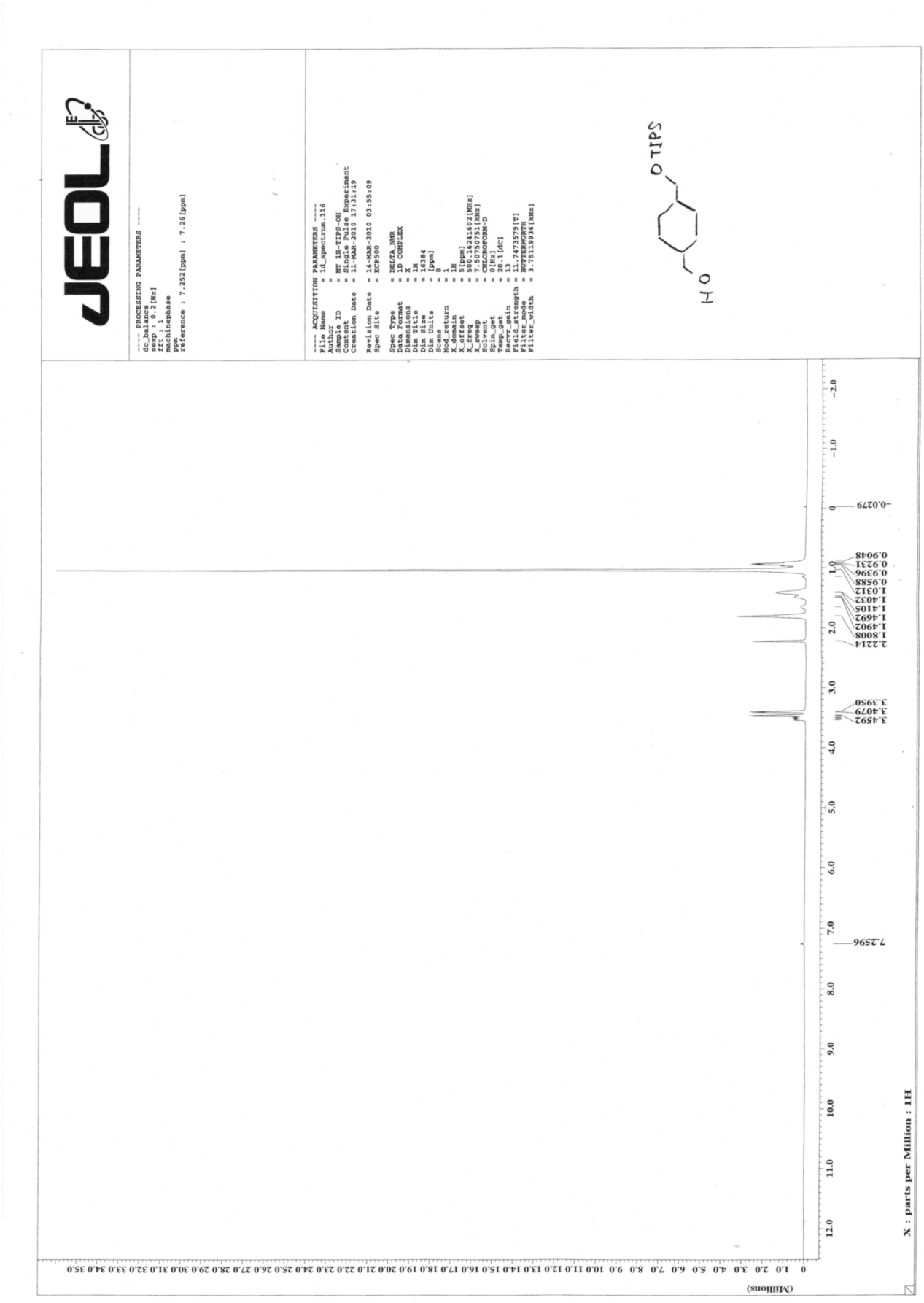
^{1}H NMR of *dl*-menthol (**20**)



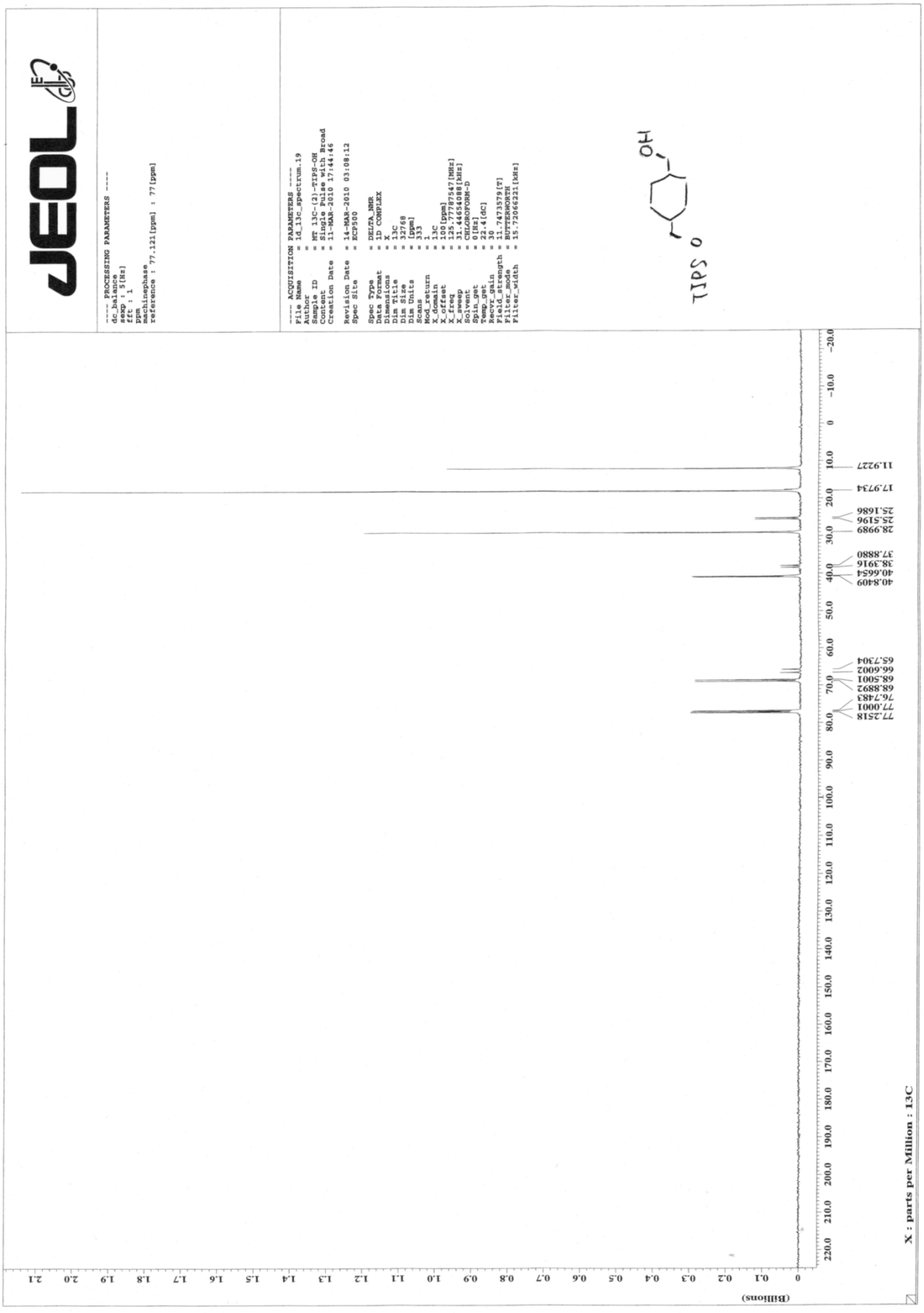
^{13}C NMR of *dl*-menthol (**20**)



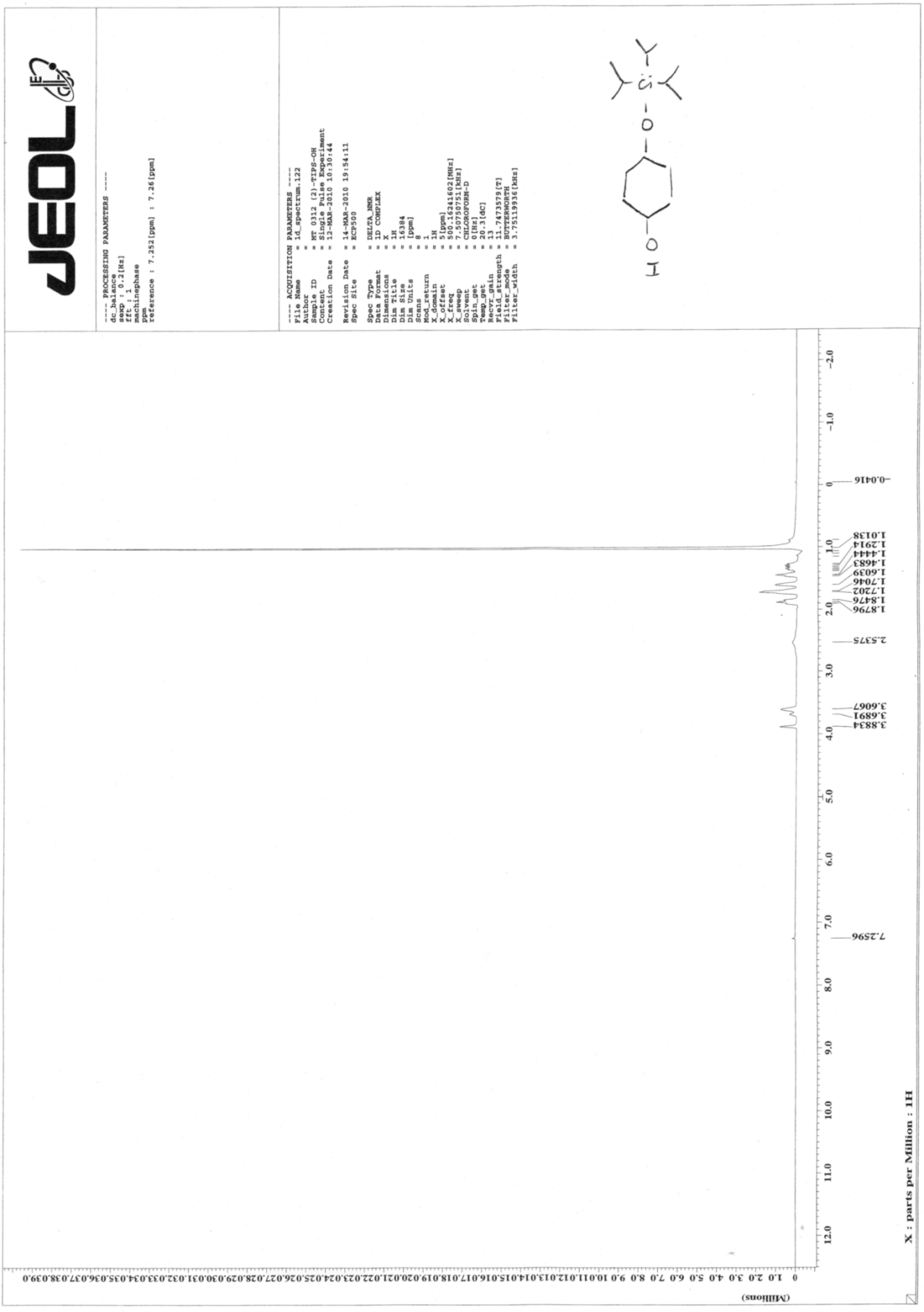
^{1}H NMR of 4-(triisopropylsiloxymethyl)cyclohexylmethanol (**26**)



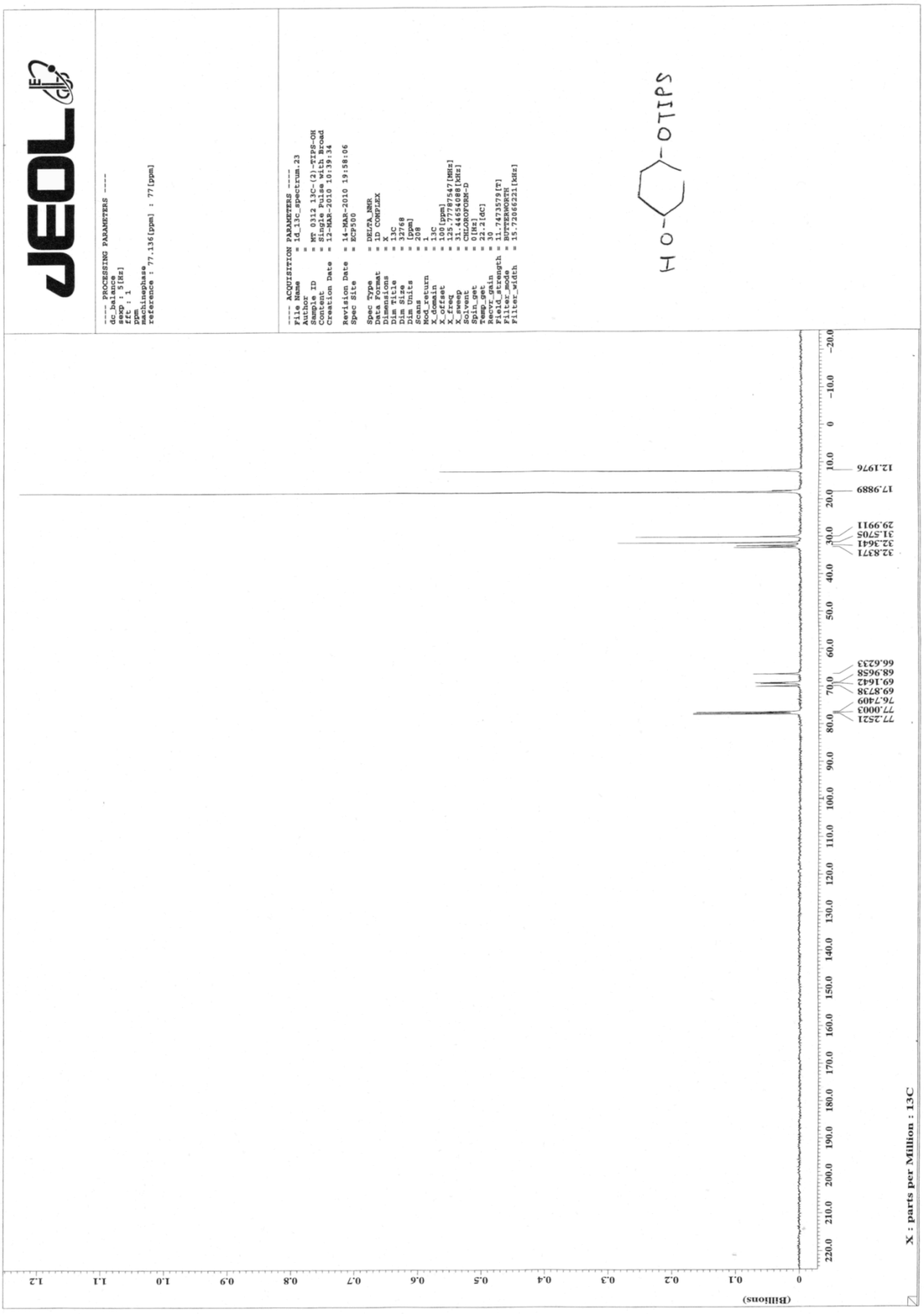
^{13}C NMR of 4-(triisopropylsiloxymethyl)cyclohexylmethanol (**26**)



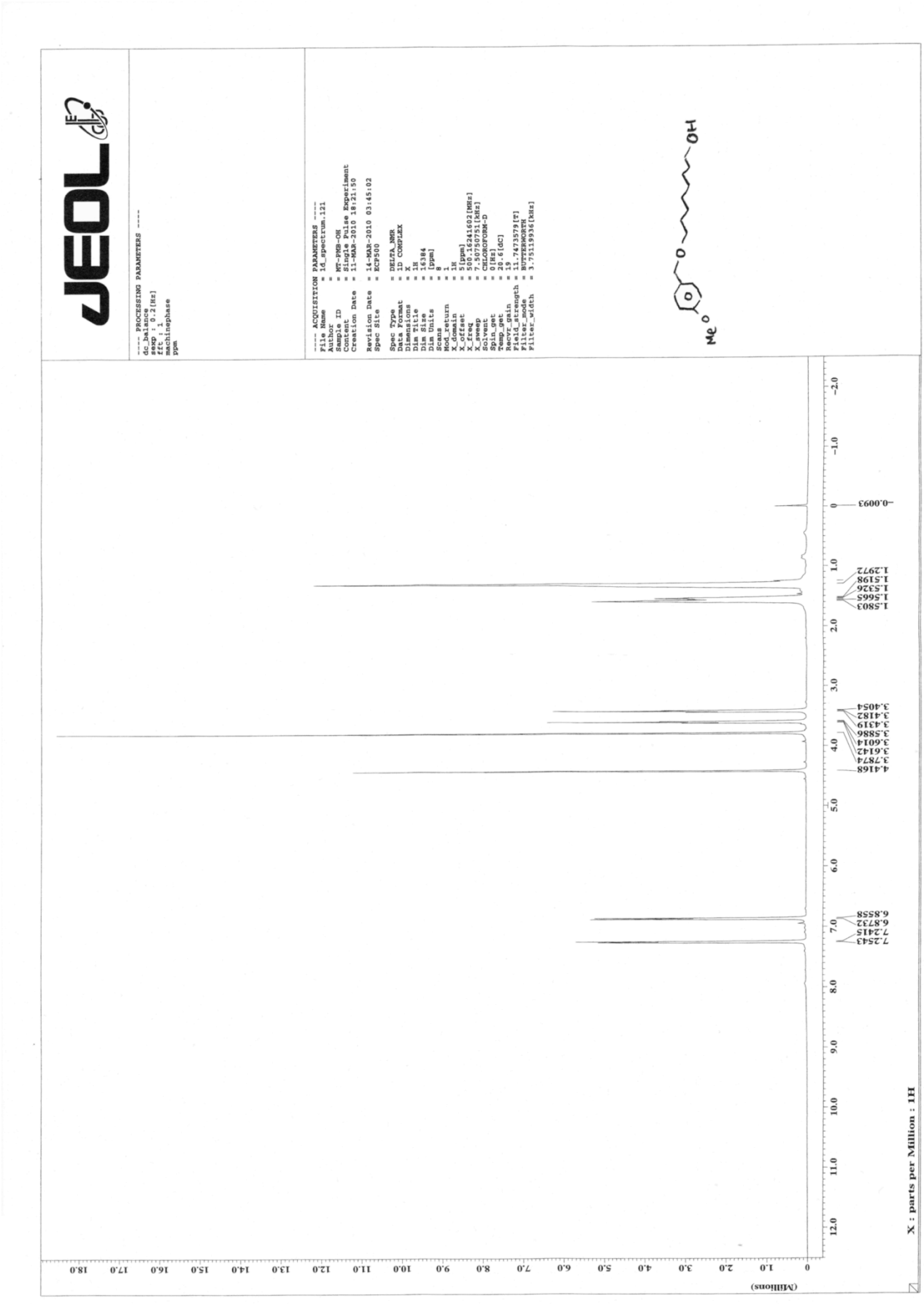
^{1}H NMR of 4-(triisopropylsiloxy)cyclohexanol (**28**)



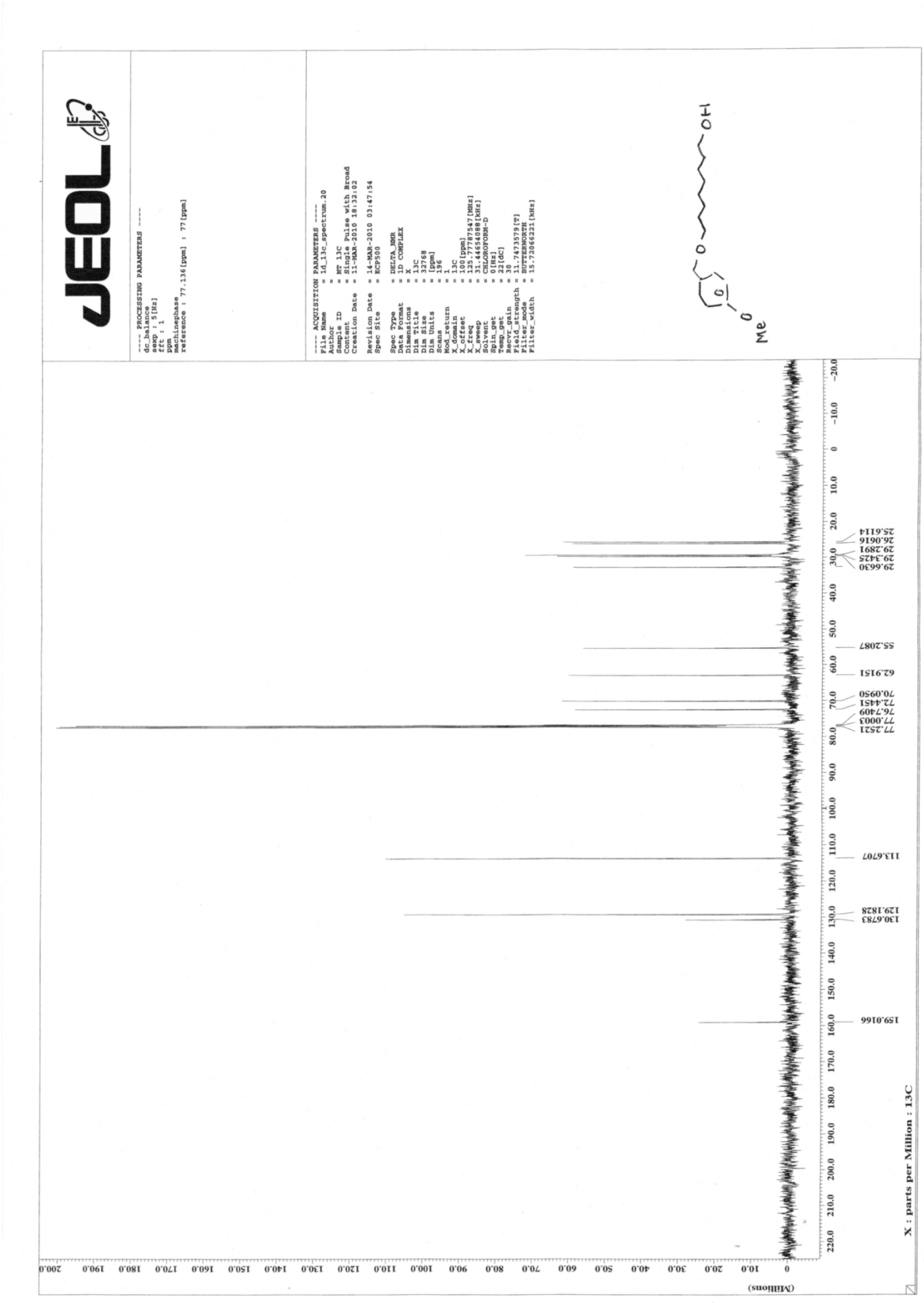
^{13}C NMR of 4-(triisopropylsiloxy)cyclohexanol (**28**)



^{1}H NMR of 8-(4-methoxybenzyloxy)octanol (**30**)

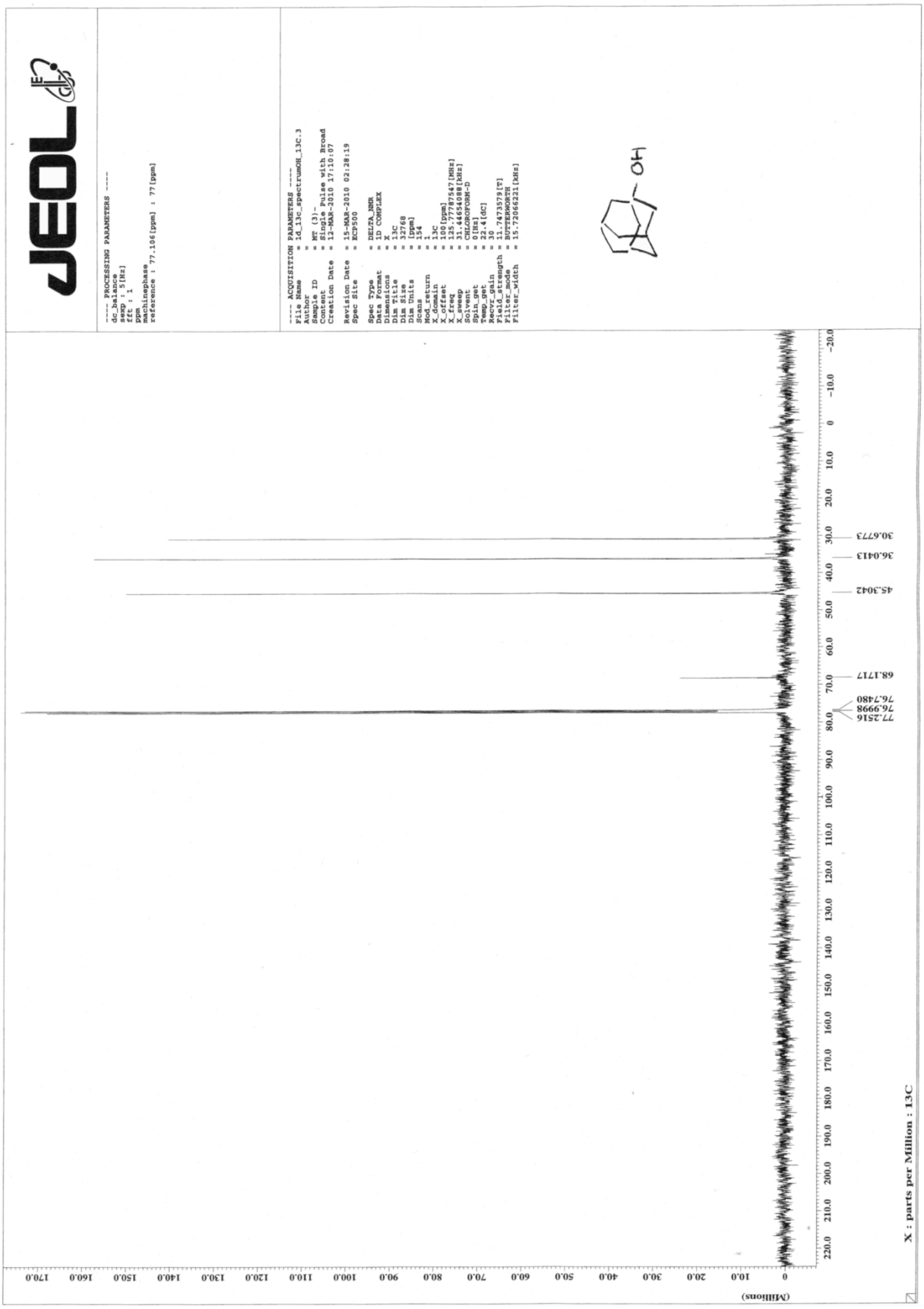


^{13}C NMR of 8-(4-methoxybenzyloxy)octanol (**30**)

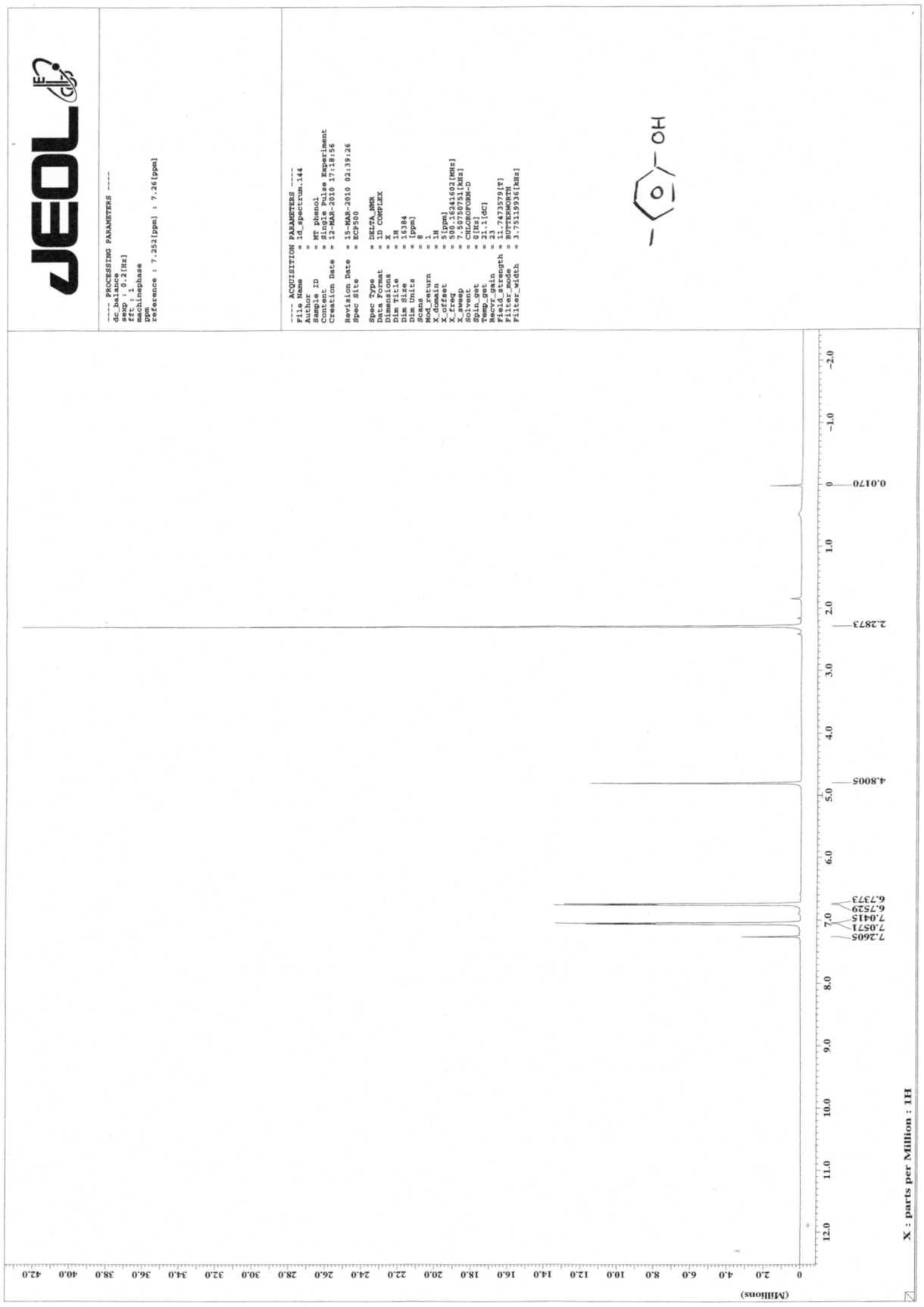


^{1}H NMR of 1-adamanthanol (**32**)

^{1}H NMR of 1-adamanthanol (**32**)



^{1}H NMR of *p*-cresol (**33**)



^{13}C NMR of *p*-cresol (**33**)