Supporting Information

Organic synthesis using hypervalent iodine reagent: unexpected novel domino reaction leading to spiro cyclohexadienone lactone

Hiromichi Fujioka,* Hideyuki Komatsu, Taeko Nakamura, Akihito Miyoshi, Kayoko Hata, Jnashuara Ganesh, Kenichi Murai and Yasuyuki Kita*

Graduate School of Pharmaceutical Sciences, Osaka University, 1-6, Yamada-oka, Suita, Osaka, 565-0871 (Japan)
Tel: (+81) 6-6879-8229, Fax: (+81) 6-6879-8229, E-mail: fujioka@phs.osaka-u.ac.jp

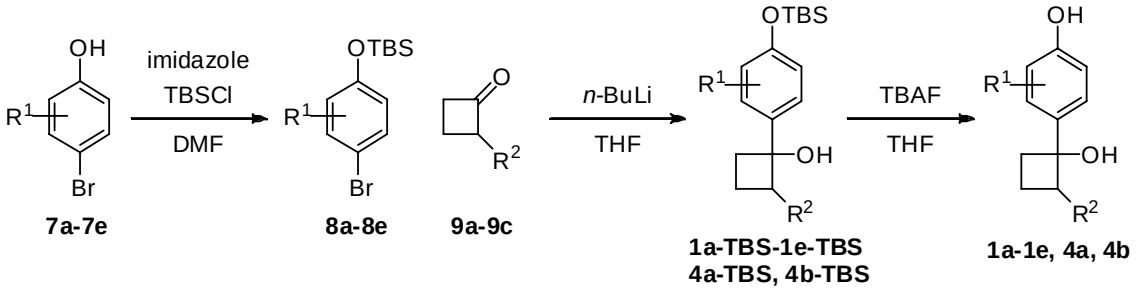
General

Melting points were measured by BÜCHI B-545 and all melting points were uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were measured by JEOL JNM-GX 500, JEOL JNM-ECS 400 or JEOL JNM-AL 300 spectrometers with tetramethylsilane as an internal standard. IR spectra were recorded by Shimadzu FTIR 8400 using a diffuse reflectance measurement of samples dispersed in KBr powder. High resolution mass spectra and elemental analysis were performed by the Elemental Analysis Section of Osaka University. Column chromatography was performed with SiO_2 (Merck Silica Gel 60 (230-400 mesh) or Kanto Chemical Silicagel 60 (spherical, 63-210 μm)).

Materials

Unless otherwise noted, materials were purchased from Aldrich Inc., Kanto Kagaku, Wako Chemicals, and other commercial suppliers and were used without purification.
2-Methylcyclobutanone **9b** was prepared according to the literature procedure.[1)] 2-isopropylcyclobutanone **9c** was prepared according to the literature procedure.[2)] 4-Bromophenols **7b** and **7c** were prepared according to the literature procedure.[3)] 4-Bromophenyl-TBS-ethers **8a-8e** were prepared according to the literature procedure.[4)]

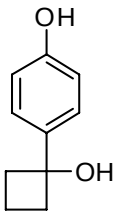
Preparation of 4-(1-Hydroxycyclobutyl)phenols (1a-1e, 4a, 4b)



Typical procedure for 4-(1-Hydroxycyclobutyl)phenol (1a)

To a solution of **8a** (R^1 = H), (2.30 g, 8.01 mmol) in THF (80 ml) was added *n*-butyl lithium in hexane (5.3 ml, 8.41 mmol) at -78 ^oC under N_2. After 1 h, cyclobutanone **9a** (R^2 = H) (0.69 ml, 8.81 mmol) was added to the reaction mixture. The completion of the reaction was checked by TLC. The mixture was quenched by the addition of sat. aq. NH_4Cl. The resulting solution was extracted with AcOEt. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by SiO_2 column chromatography (Hexane/AcOEt = 8/1) to give **1a-TBS** (1.53 g, 69%) as colorless oil. To a solution of **1a-TBS** (2.00 g, 7.18 mmol) in THF (70 ml) was added TBAF (2.25 g, 8.62 mmol) at 0 ^oC and the resulting mixture was stirred for 0.5 h at the same temperature. After the reaction was completed (judged by TLC), the mixture was quenched by the addition of sat. aq. NH_4Cl. The resulting solution was extracted with AcOEt. The organic layer was dried over Na_2CO_3 and evaporated in vacuo. The residue was purified by SiO_2 column chromatography (Hexane/AcOEt = 2/1) to give **1a** (1.03 g, 87%) as colorless solid.

4-(1-Hydroxycyclobutyl)phenol (1a)

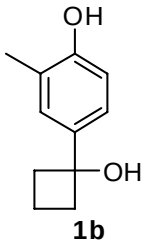


1a

1a-TBS: ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.20 (6H, s), 0.98 (9H, s), 1.60-1.72 (1H, m), 1.91-2.03 (1H, m), 2.32-2.39 (2H, m), 2.50-2.58 (2H, m), 6.83 (2H, dd, *J* = 6.6, 2.2 Hz), 7.35 ppm (2H, dd, *J* = 6.6, 2.2 Hz).

1a: m.p. 159-161 ^oC; ^{1}H-NMR (400 MHz, CD_3OD) δ: 1.58-1.64 (1H, m), 1.91-1.96 (1H, m), 2.26-2.33 (2H, m), 2.45-2.51 (2H, m), 6.66 (2H, d, *J* = 8.7 Hz), 7.22 ppm (2H, d, *J* = 8.7 Hz); ^{13}C-NMR (100 MHz, CD_3OD) δ: 13.7, 37.7, 77.2, 115.8, 127.5, 138.7, 157.4 ppm; IR (KBr): 2942, 1595, 1516 cm^{-1}; HRFABMS calcd for $C_{10}H_{12}O_2$ $[M]^+$ 164.0847, found 164.0842.

4-(1-Hydroxycyclobutyl)-2-methylphenol (1b)

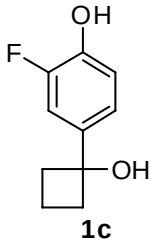


1b

1b-TBS: yield 46%; Reaction time: 5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 8/1. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.22 (6H, s), 1.02 (9H, s), 1.60-1.67 (1H, m), 1.90 (1H, s), 1.94-1.99 (1H, m), 2.22 (3H, s), 2.30-2.37 (2H, m), 2.51-2.58 (2H, m), 6.75 (1H, d, *J* = 8.6 Hz), 7.17 (1H, dd, *J* = 8.6, 2.6 Hz), 7.26 ppm (1H, d, *J* = 2.6 Hz).

1b: yield 81%; Reaction time: 10 min. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. colorless solid. m.p. 107-109 ^{o}C; ^{1}H-NMR (400 MHz, CD_3OD) δ: 1.56-1.63 (1H, m), 1.88-1.96 (1H, m), 2.19 (3H, s), 2.25-2.33 (2H, m), 2.45-2.51 (2H, m), 6.71 (1H, d, *J* = 8.2 Hz), 7.12 (1H, dd, *J* = 8.2, 2.3 Hz), 7.19 ppm (1H, d, *J* = 2.3 Hz); ^{13}C-NMR (100 MHz, CD_3OD) δ: 13.7, 16.4, 37.67, 37.72, 77.2, 115.1, 124.6, 125.0, 129.0, 138.4, 155.4 ppm; IR (KBr): 3361, 2943, 1610, 1506 cm^{-1}; *Anal*. Calcd for $C_{11}H_{14}O_2$: C 76.88, H 9.46; found: C 76.78, H 9.40.

2-Fluoro-4-(1-hydroxycyclobutyl)phenol (1c)

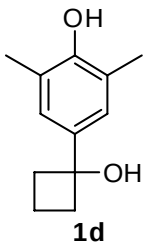


1c

1c-TBS: yield 62%; Reaction time: 5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 8/1. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.19 (6H, s), 1.00 (9H, s), 1.62-1.72 (1H, m), 1.94 (1H, s), 1.94-2.05 (1H, m), 2.28-2.39 (2H, m), 2.46-2.56 (2H, m), 6.89 (1H, t, *J* = 8.4), 7.11 (1H, dd, *J* = 8.4, 2.3 Hz), 7.18 ppm (1H, dd, *J* = 8.4, 2.3 Hz).

1c: yield 84%; Reaction time: 5 min. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 1/1. colorless solid. m.p. 94-96 ^{o}C; ^{1}H-NMR (400 MHz, CD_3OD) δ: 1.61-1.70 (1H, m), 1.91-2.00 (1H, m), 2.26-2.33 (2H, m), 2.42-2.48 (2H, m), 6.87 (1H, t, *J* = 8.7 Hz), 7.09-7.17 ppm (2H, m); ^{13}C-NMR (100 MHz, CD_3OD) δ: 13.7, 37.8, 76.9, 114.0 (d, $J_{C\text{-}F}$ = 19.2 Mz), 118.2 (d, $J_{C\text{-}F}$ = 2.9 Mz), 122.1 (d, $J_{C\text{-}F}$ = 3.8 Mz), 140.2 (d, $J_{C\text{-}F}$ = 4.8 Mz), 144.8 (d, $J_{C\text{-}F}$ = 13.4 Mz), 152.6 ppm (d, $J_{C\text{-}F}$ = 239.6 Mz); IR (KBr): 3316, 2942, 1620, 1514 cm^{-1}; *Anal*. Calcd for $C_{10}H_{11}FO_2$: C 65.92, H 6.09; found: C 66.00, H 6.11

2,6-Dimethyl-4-(1-hydroxycyclobutyl)phenol (1d)



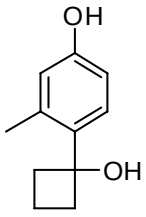
1d

1d-TBS: yield 36%; Reaction time: 5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 8/1. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.19 (6H, s), 1.03 (9H, s), 1.60-1.67 (1H, m), 1.91 (1H, s), 1.93-2.00 (1H, m), 2.28 (6H, s), 2.30-2.36 (2H, m), 2.51-2.58 (2H, m), 7.08 ppm (2H, s).

1d: yield 69%; Reaction time: 0.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. colorless solid. m.p. 142-144 ^{o}C; ^{1}H-NMR (400 MHz, CD_3OD) δ: 1.54-1.65 (1H, m), 1.87-1.97 (1H, m), 2.21 (6H, s), 2.24-2.31 (2H, m), 2.44-2.51 (2H, m), 7.03 ppm (2H, s); ^{13}C-NMR (100 MHz, CD_3OD) δ: 13.8, 16.8, 37.7, 77.2, 125.1, 126.4, 138.7, 153.2

ppm; IR (KBr): 3128, 1738, 1606, 1487 cm^{-1}; HRFABMS calcd for $C_{12}H_{16}O_2$ $[M+H]^+$ 192.1150, found 192.1142.

4-(1-Hydroxycyclobutyl)-3-methylphenol (1e)

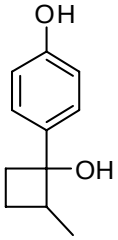


1e

1e-TBS: yield 67%; Reaction time: 5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 5/1. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.19 (6H, s), 0.98 (9H, s), 1.69-1.74 (1H, m), 1.79 (1H, s), 2.14-2.19 (1H, m), 2.35 (3H, s), 2.33-2.39 (2H, m), 2.61-2.68 (2H, m), 6.60 (1H, dd, *J* = 8.1, 2.8 Hz), 6.65 (1H, d, *J* = 2.8 Hz), 7.13 ppm (1H, d, *J* = 8.1 Hz).

1e: yield 26%; Reaction time: 0.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. colorless solid. m.p. 160-162 ^{o}C; ^{1}H-NMR (300 MHz, CD_3OD) δ: 1.59-1.68 (1H, m), 2.00-2.11 (1H, m), 2.32 (3H, s), 2.28-2.37 (2H, m), 2.55-2.64 (2H, m), 6.53 (1H, dd, *J* = 8.4, 2.4 Hz), 6.59 (1H, d, *J* = 2.4 Hz), 7.11 ppm (1H, d, *J* = 8.4 Hz); ^{13}C-NMR (75 MHz, CD_3OD) δ: 15.3, 20.6, 37.3, 79.1, 112.5, 119.2, 127.6, 135.6, 139.8, 157.5 ppm; IR (KBr): 3400, 2936, 1614, 1581, 1504 cm^{-1}; *Anal*. Calcd for $C_{11}H_{15}O_2$: C 74.13, H 7.92; found: C 73.77, H 7.88.

4-(1-Hydroxy-2-methylcyclobutyl)phenol (4a)

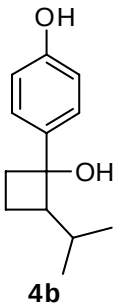


4a

4a-TBS: yield 78%; Reaction time: 8 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 8/1. colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.19 (6H, s), 0.98 (9H, s), 1.16 (3H, d, *J* = 7.0), 1.74 (1H, s), 1.68-1.81 (1H, m), 1.90-2.01 (1H, m), 2.14-2.23 (1H, m), 2.35-2.45 (1H, m), 2.65-2.75 (1H, m), 6.81 (2H, d, *J* = 8.4), 7.27 ppm (2H, d, *J* = 8.4).

4a: yield 85%; Reaction time: 0.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. colorless solid. m.p. 141-144 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.11 (3H, d, *J* = 4.6 Hz), 1.67-1.74 (1H, m), 1.89-1.95 (1H, m), 2.10-2.18 (1H, m), 2.29-2.36 (1H, m), 2.65-2.70 (1H, m), 6.81 (2H, d, *J* = 8.7 Hz), 7.31 ppm (2H, d, *J* = 8.7 Hz); ^{13}C-NMR (100 MHz, CD_3OD) δ: 14.7, 24.0, 34.7, 41.6, 79.1, 115.8, 127.3, 139.9, 157.2 ppm; IR (KBr): 3316, 2942, 1514 cm^{-1}; HRFABMS calcd for $C_{11}H_{14}NaO_2$ $[M+Na]^+$ 201.0891, found 201.0905.

4-(1-Hydroxy-2-isopropylcyclobutyl)-phenol (4b)



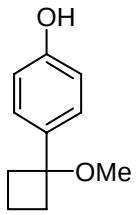
4b

4b-TBS: yield 69%; Reaction time: 8 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 10/1. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.19 (6H, s), 0.73 (3H, d, *J* = 6.6), 0.83 (3H, d, *J* = 6.6), 0.98 (9H, s), 1.78 (1H, s), 1.82-2.07 (4H, m), 2.24-2.32 (2H, m), 6.80 (2H, d, *J* = 8.4 Hz), 7.33 ppm (2H, d, *J* = 8.4 Hz).

4b: yield 77%; Reaction time: 5 min. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. colorless solid. m.p. 124-126 ^{o}C; ^{1}H-NMR (400 MHz, CD_3OD) δ:

0.70 (3H, d, *J* = 6.6 Hz), 0.81 (3H, d, *J* = 6.6 Hz), 1.80-2.00 (4H, m), 2.21-2.28 (2H, m), 6.71 (2H, d, *J* = 8.7 Hz), 7.30 ppm (2H, d, *J* = 8.7 Hz); ^{13}C-NMR (100 MHz, CD_3OD) δ: 20.0, 21.6, 22.0, 29.8, 35.9, 55.2, 79.9, 115.5, 127.1, 140.5, 156.8 ppm; IR (KBr): 3402, 3165, 2957, 1614, 1595, 1516, 1442 cm^{-1}; *Anal*. Calcd for $C_{13}H_{18}O_2$: C 74.13, H 7.92; found: C 74.03, H 7.97.

Preparation of 4-(1-Methoxycyclobutyl)phenol (1a-Me)



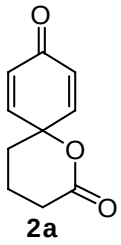
1a-Me

To a solution of **1a-TBS** (500 mg, 1.80 mmol) in THF (10 ml) was added NaH (108 mg, 2.69 mmol) at 0 ^{o}C under N_2. After 1 h, MeI (168 μl, 2.69 mmol) was added to the reaction mixture and the resulting solution was stirred at rt. The completion of the reaction was checked by TLC. The mixture was quenched by the addition of sat. aq. NH_4Cl. The resulting solution was extracted with AcOEt. The organic layer was dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by SiO_2 column chromatography (Hexane/AcOEt = 4/1) to give **1a-Me-TBS** (240 mg, 46%) as colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.21 (6H, m), 0.99 (9H, m), 1.61-1.68 (1H, m), 1.88-1.95 (1H, m), 2.29-2.41 (4H, m), 2.90 (3H, s), 6.83 (2H, d, *J* = 8.7 Hz), 7.26 ppm (2H, d, *J* = 8.7 Hz). Desilylation reaction was carried out according to the typical procedure for **1a**: **1a-Me-TBS** (240 mg, 0.82 mmol) and TBAF (0.82 ml, 0.82 mmol) in THF (8 ml) at 0 ^{o}C to give **1a-Me** (64 mg, 44%) as colorless solid. Reaction time: 10 min. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. m.p. 149-152 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.58-1.70 (1H, m), 1.88-1.97 (1H, m), 2.32-2.43 (4H, m), 2.94 (3H, s), 5.85 (1H, brs), 6.85 (2H, d, *J* = 8.7), 7.30 ppm (2H, d, *J* = 8.7); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 12.9, 32.8, 50.2, 81.4, 115.0, 127.9, 134.6, 155.1 ppm; IR (KBr): 3237, 2990, 1518 cm^{-1}; HRFABMS calcd for $C_{11}H_{14}O_2$ $[M]^+$ 178.0994, found 178.1006.

General Procedure for spiro cyclohexadienone lactone (2a)

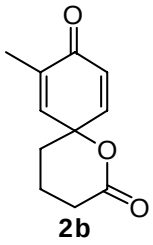
PIDA (118 mg, 0.366 mmol) was added to a stirred solution of **1a** (30 mg, 0.183 mmol) and $NaHCO_3$ (61.4 mg, 0.732 mmol) in HFIP/H_2O (V/V = 9/1, 2ml) at 0 ^{o}C under N_2 and the reaction mixture was stirred at the same temperature. The completion of the reaction was checked by TLC. The mixture was quenched by the addition of sat. aq. $NaHCO_3$. The resulting solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by SiO_2 column chromatography (Hexane/AcOEt = 2/1) to give **2a** (24.5 mg, 75%) as colorless solid.

1-Oxaspiro[5.5]undeca-7,10-diene-2,9-dione (2a)


2a

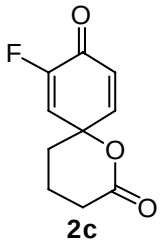
m.p. 125-127 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.98-2.01 (2H, m), 2.05-2.12 (2H, m), 2.68 (2H, t, J = 6.9 Hz), 6.24 (2H, dd, J = 10.4, 3.2 Hz), 6.93 ppm (2H, dd, J = 10.4, 3.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 17.5, 29.2, 32.2, 77.5, 128.6, 146.3, 168.7, 184.0 ppm; IR (KBr): 2960, 1737, 1678, 1633 cm^{-1}; HRFABMS calcd for $C_{10}H_{11}O_3$ $[M+H]^+$ 179.0708, found 179.0690; HRFABMS calcd for $C_{10}H_{11}O_2{}^{18}O$ $[M+H]^+$ 181.0751, found 181.0748.

8-Methyl-1-oxa-spiro[5.5]undeca-7,10-diene-2,9-dione (2b)


2b

Reaction was carried out according to the general procedure with PIDA (128.8 mg, 0.400 mmol), **1b** (35.4 mg, 0.200 mmol) and $NaHCO_3$ (67.2 mg, 0.800 mmol) in HFIP/H_2O (V/V = 9/1, 2 ml) at 0 ^{o}C to give **2b** (29.1 mg, 76%) as colorless solid. Reaction time: 0.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. m.p. 80-82 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.91 (3H,s), 1.92-1.98 (2H, m), 2.04-2.11 (2H, m), 2.66 (2H, t, J = 6.7 Hz), 6.23 (1H, d, J = 9.9 Hz), 6.70 (1H, m), 6.90 ppm (1H, dd, J = 9.9, 3.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.5, 17.4, 29.1, 32.2, 78.0, 128.5, 135.5, 141.6, 146.0, 169.1, 184.8 ppm; IR (KBr): 3155, 1730, 1680 cm^{-1}; HRFABMS calcd for $C_{11}H_{13}O_3$ $[M+H]^+$ 193.0865, found 193.0863.

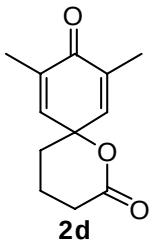
8-Fluoro-1-oxaspiro[5.5]undeca-7,10-diene-2,9-dione (2c)


2c

Reaction was carried out according to the general procedure with PIDA (128.8 mg, 0.400 mmol), **1c** (36.4 mg, 0.200 mmol) and $NaHCO_3$ (67.2 mg, 0.800 mmol) in HFIP/H_2O (V/V = 9/1, 2 ml) at 0 ^{o}C to give **2c** (25.2 mg, 64%) as colorless solid. Reaction time: 0.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. m.p. 138-140 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.04-2.17 (4H, m), 2.69 (2H, t, J = 6.3 Hz), 6.27 (1H, dd, J = 9.9, 3.0 Hz), 6.51 (1H, dd, J = 3.0, 2.7 Hz), 6.93 ppm (1H, dd, J = 9.9, 2.7 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 17.5, 29.1, 32.4 (d, $J_{C\text{-}F}$ = 1.9 Mz), 79.5 (d, $J_{C\text{-}F}$ = 9.5 Mz), 122.3 (d, $J_{C\text{-}F}$ = 13.3 Mz), 127.4 (d, $J_{C\text{-}F}$ = 3.8 Mz), 147.0 (d, $J_{C\text{-}F}$ = 2.9 Mz), 153.1 (d, $J_{C\text{-}F}$ = 269.8 Mz), 168.2, 177.1 (d, $J_{C\text{-}F}$ = 21.9 Mz) ppm; IR (KBr): 3153, 2961, 1746, 1666, 1219cm^{-1}; HRFABMS calcd for $C_{10}H_{10}FO_3$ $[M+H]^+$ 197.0614, found 197.0609.

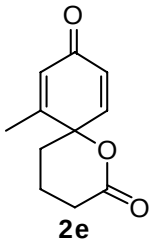
.

8,10-Dimethyl-1-oxaspiro[5.5]undeca-7,10-diene-2,9-dione (2d)


2d

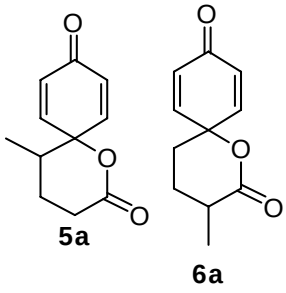
Reaction was carried out according to the general procedure with PIDA (128.8 mg, 0.400 mmol), **1d** (38.4 mg, 0.200 mmol) and $NaHCO_3$ (67.2 mg, 0.800 mmol) in HFIP/H_2O (V/V = 9/1, 2 ml) at 0 ^oC to give **2d** (31.7 mg, 77%) as colorless solid. Reaction time: 0.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. m.p. 122-124 ^oC; ^1H-NMR (400 MHz, $CDCl_3$) δ: 1.90 (6H, s), 1.91-1.95 (2H, m), 2.03-2.10 (2H, m), 2.65 (2H, t, *J* = 6.8 Hz), 6.65 ppm (2H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.8, 17.5, 29.2, 32.3, 77.9, 135.3, 141.3, 169.5, 185.6 ppm; IR (KBr): 3153, 1732, 1651 cm^{-1}. *Anal*. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84, found: C, 69.66, H, 6.87.

7-Methyl-1-oxaspiro[5.5]undeca-7,10-diene-2,9-dione (2e)


2e

Reaction was carried out according to the general procedure with PIDA (128.8 mg, 0.400 mmol), **1e** (35.6 mg, 0.200 mmol) and $NaHCO_3$ (67.2 mg, 0.800 mmol) in HFIP/H_2O (V/V = 9/1, 2 ml) at 0 ^oC to give **2e** (20.6 mg, 54%) as colorless solid. Reaction time: 0.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. m.p. 125-127 ^oC; ^1H-NMR (400 MHz, $CDCl_3$) δ: 1.80-1.84 (1H, m), 2.08 (3H, s), 2.05-2.19 (3H, m), 2.55-2.62 (1H, m), 2.76-2.82 (1H, m), 6.11 (1H, d, *J* = 1.8 Hz), 6.20 (1H, dd, *J* = 10.1, 1.8 Hz), 7.06 ppm (1H, d, *J* = 10.1 Hz); ^{13}C-NMR (67 MHz, $CDCl_3$) δ: 17.7, 18.1, 29.4, 31.8, 80.1, 127.1, 127.9, 146.6, 157.2, 168.9, 184.0 ppm; IR (KBr): 3153, 1732, 1674 cm^{-1}; HRFABMS calcd for $C_{11}H_{13}O_3$ $[M+H]^+$ 193.0865, found 193.0864.

5-Methyl-1-oxaspiro[5.5]undeca-7,10-diene-2,9-dione (5a) and 3-Methyl-1-oxaspiro [5.5]undeca-7,10-diene-2,9-dione (6a)

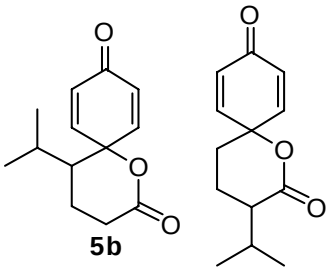

5a **6a**

Reaction was carried out according to the general procedure with PIDA (128.8 mg, 0.400 mmol), **4a** (37.2 mg, 0.200 mmol) and $NaHCO_3$ (67.2 mg, 0.800 mmol) in HFIP/H_2O (V/V = 9/1, 2 ml) at 0 ^oC to give **5a** (23.6 mg, 61%) as colorless solid and **6a** (3.9 mg, 10%) as colorless solid. Reaction time: 0.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. **5a**: polar; m.p. 110-112 ^oC; ^1H-NMR (400 MHz, $CDCl_3$) δ: 0.92 (3H, d, *J* = 6.9 Hz), 1.79-1.90 (1H, m), 1.98-2.05 (1H, m), 2.09-2.14 (1H, m), 2.65-2.74 (1H, m), 2.78-2.84 (1H, m), 6.31 (2H, m), 6.35 (1H, dd, *J* = 10.1, 1.8 Hz), 6.72 (1H, dd, *J* = 10.1, 3.2 Hz), 6.84 ppm (1H, dd, *J* = 10.1, 3.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.1, 25.4, 29.5, 35.2, 81.2, 129.7, 130.9, 142.5, 146.8, 168.9, 184.4 ppm; IR (KBr): 1732, 1673 cm^{-1}; HRFABMS calcd for $C_{11}H_{13}O_3$ $[M+H]^+$ 193.0865, found 193.0863.

6a: less polar; m.p. 108-110 ^oC; ^1H-NMR (500 MHz, $CDCl_3$) δ: 1.39 (3H, d, *J* = 6.9 Hz), 1.78-1.87 (1H, m), 1.97-2.01 (1H, m), 2.06-2.17 (2H, m), 2.62-2.69 (1H, m), 6.23 (2H, d, *J* = 9.9 Hz), 6.85

(1H, dd, *J* = 9.9, 3.0 Hz), 6.98 ppm (1H, dd, *J* = 9.9, 3.0 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 17.4, 25.9, 32.2, 35.2, 77.7, 128.4, 128.5, 145.9, 147.2, 172.4, 184.1 ppm; IR (KBr): 1738, 1676 cm^{-1}; HRFABMS calcd for $C_{11}H_{13}O_3$ $[M+H]^+$ 193.0865, found 193.0873.

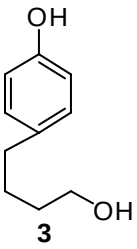
5-Isopropyl-1-oxaspiro[5.5]undeca-7,10-diene-2,9-dione (5b) and 3-Isopropyl-1-oxaspiro [5.5]undeca-7,10-diene-2,9-dione (6b)



Reaction was carried out according to the general procedure with PIDA (128.8 mg, 0.400 mmol), **4b** (41.2 mg, 0.200 mmol) and $NaHCO_3$ (67.2 mg, 0.800 mmol) in HFIP/H_2O (V/V = 9/1, 2 ml) at 0 °C to give **5b** (28.3 mg, 64%) as colorless solid and **6b** (4.2 mg, 10%) as colorless oil. Reaction time: 0.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. **5b**: polar; m.p. 89-91 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.81 (3H, d, *J* = 6.9 Hz), 0.97 (3H, d, *J* = 6.9 Hz), 1.66-1.75 (1H, m), 1.82-2.00 (3H, m), 2.59-2.68 (1H, m), 2.84-2.90 (1H, m), 6.30-6.35 (2H, m), 6.69-6.72 (1H, dd, *J* = 10.1, 3.2 Hz), 6.92-6.96 ppm (1H, dd, *J* = 10.1, 3.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 17.7, 18.5, 23.5, 26.3, 30.3, 46.6, 80.9, 129.96, 129.97, 143.3, 147.2, 168.9, 184.7 ppm; IR (KBr): 1736, 1674 cm^{-1}; HRFABMS calcd for $C_{13}H_{17}O_3$ $[M+H]^+$ 221.1178, found 221.1169.

6b: less polar; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.99 (3H, d, *J* = 6.9 Hz), 1.03 (3H, d, *J* = 6.9 Hz), 1.86-2.07 (4H, m), 2.50-2.64 (2H, m), 6.22-6.26 (2H, m), 6.82 (1H, dd, *J* = 10.1, 3.7 Hz), 6.94-7.00 ppm (1H, dd, *J* = 10.1, 3.7 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 17.7, 18.0, 19.8, 28.8, 32.4, 45.9, 77.2, 128.4, 128.7, 145.8, 147.6, 171.2, 184.1 ppm; IR (KBr): 1732, 1674 cm^{-1}; HRFABMS calcd for $C_{13}H_{17}O_3$ $[M+H]^+$ 221.1178, found 221.1183.

Preparation of 4-(4-hydroxyphenyl)butanol (3)



To a solution of **2a** (50.0 mg, 0.281 mmol) in THF (6 ml) was added lithium aluminum hydride (21.3 mg, 0.562 mmol) at 0 °C under N_2 and the solution was stirred at the same temperature. The completion of the reaction was checked by TLC. The mixture was quenched by the addition of 5% aq. HCl. The resulting solution was extracted with Et_2O. The organic layer was dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by SiO_2 column chromatography (Hexane/AcOEt = 1/1) to give **3** (33.7 mg, 71%) as colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.57-1.69 (4H, m), 2.58 (2H, t, *J* = 7.2 Hz), 3.67 (2H, brs), 6.74 (2H, d, *J* = 8.2 Hz), 7.04 ppm (2H, d, *J* = 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 27.7, 32.2, 34.7, 62.9, 115.1, 129.6, 134.5, 153.5 ppm; IR (KBr): 3190, 1514, 1238, 831 cm^{-1}; HRFABMS calcd for $C_{10}H_{14}O_2$ $[M]^+$ 166.0994, found 166.1001. HRFABMS calcd for $C_{10}H_{14}O^{18}O$ $[M]^+$ 168.1036, found 168.1047.

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1) a) O. H. Oldenziel, D. van Leusen, A. M. van Leusen, *J. Org. Chem.* **1977**, *42*, 3114-3118.

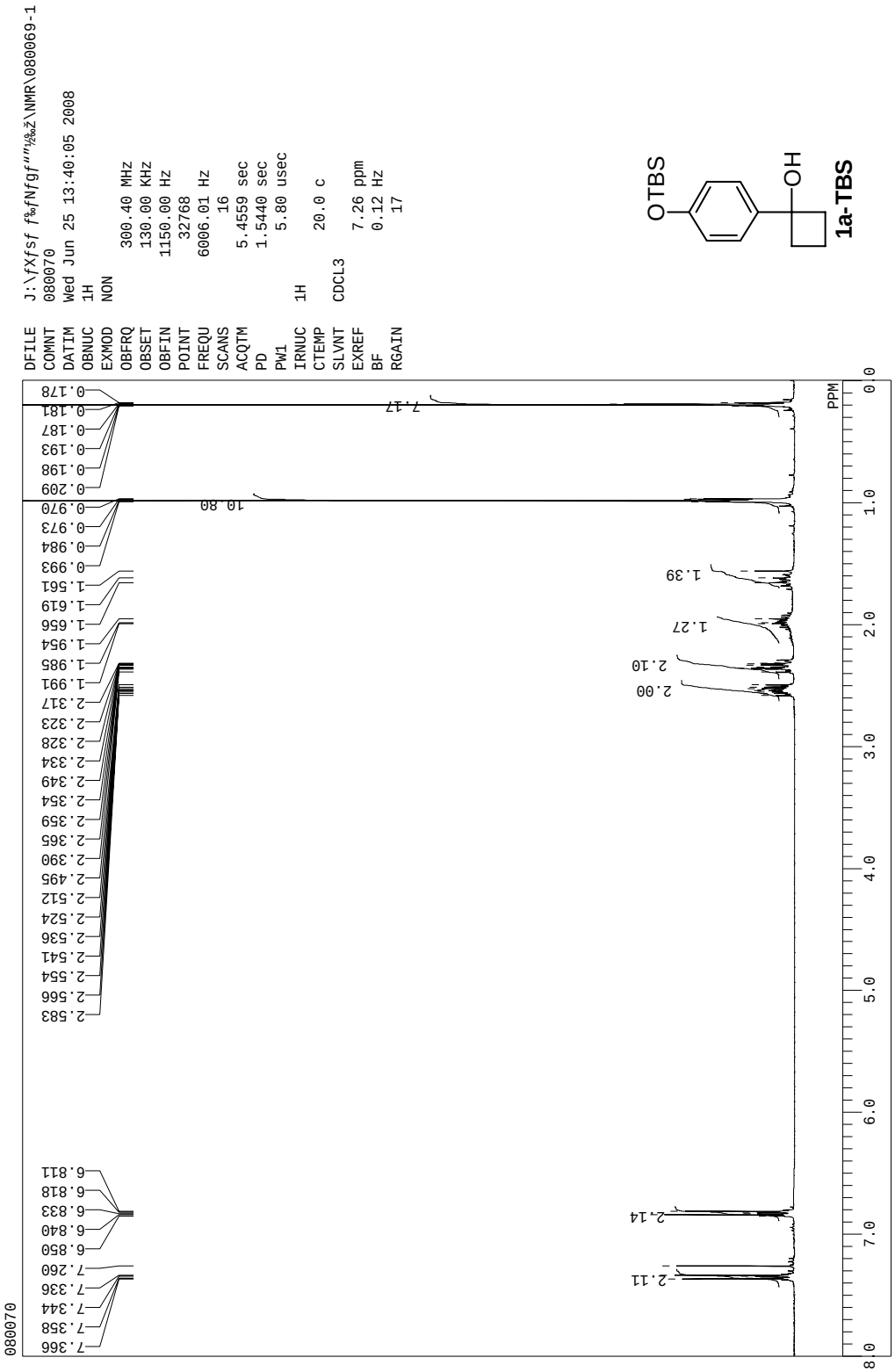
b) D. van Leusen, A. M. van Leusen, *Synthesis* **1980**, 325-326.

2) T. Nordvik, U. H. Brinker, *J. Org. Chem*. **2003**, *68*, 9394-9399.

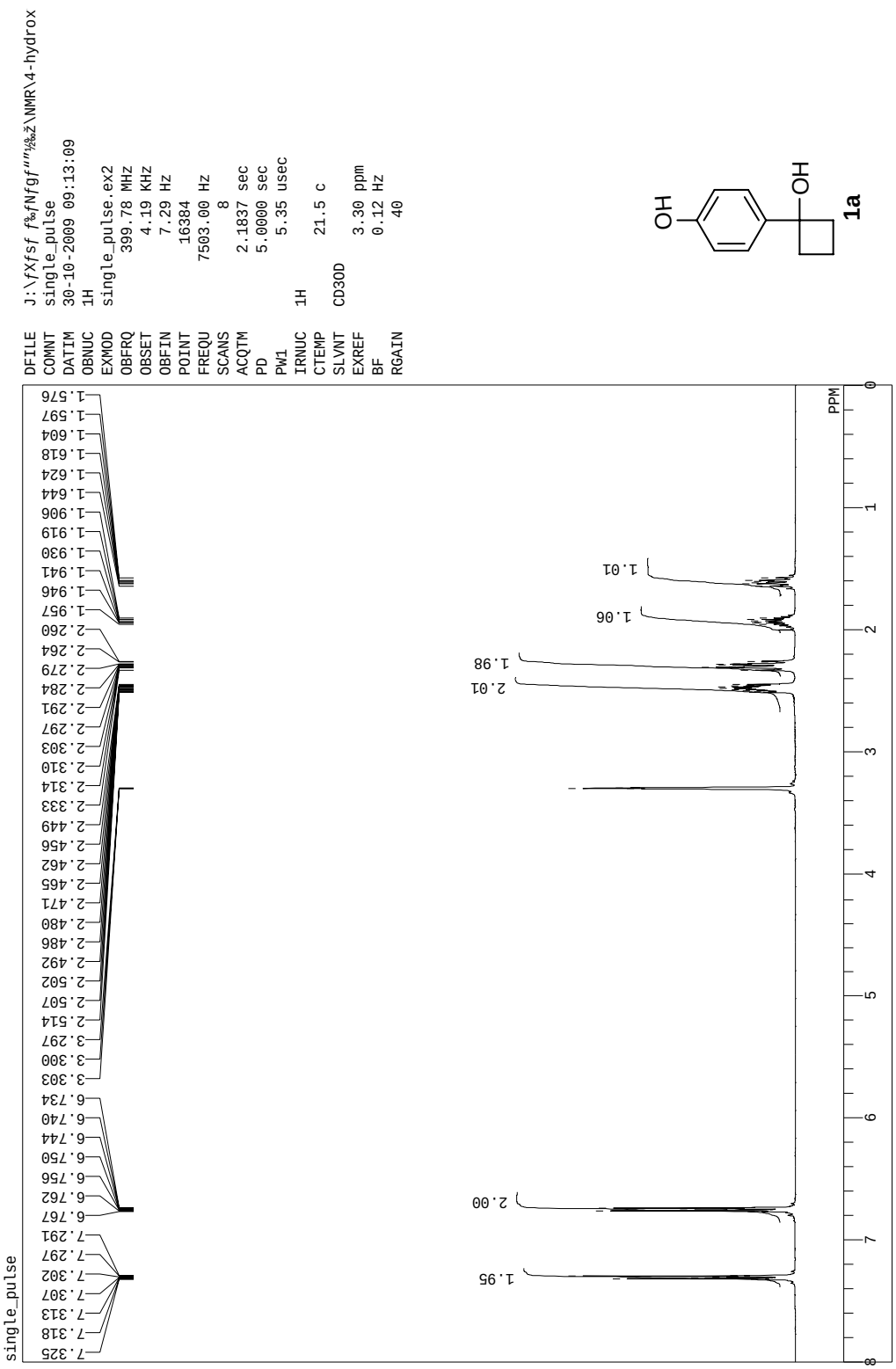
3) T. Oberhauser, *J. Org. Chem.* **1997**, *62*, 4504-4506.

4) M. Li, G. A. O'Doherty, *Org. Lett.* **2006**, *8*, 3897-3990.

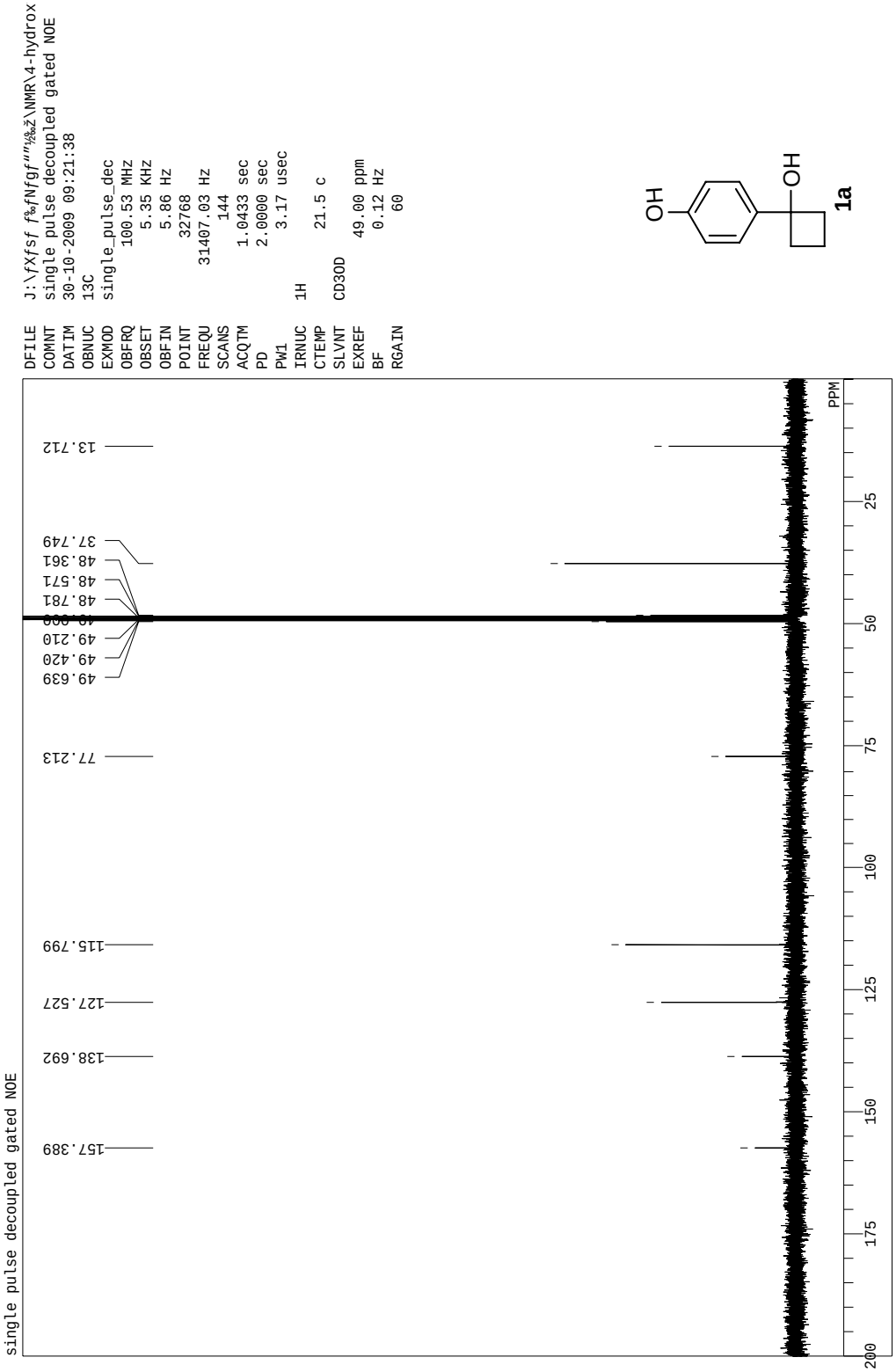
^{1}H NMR chart of Compound **1a-TBS**



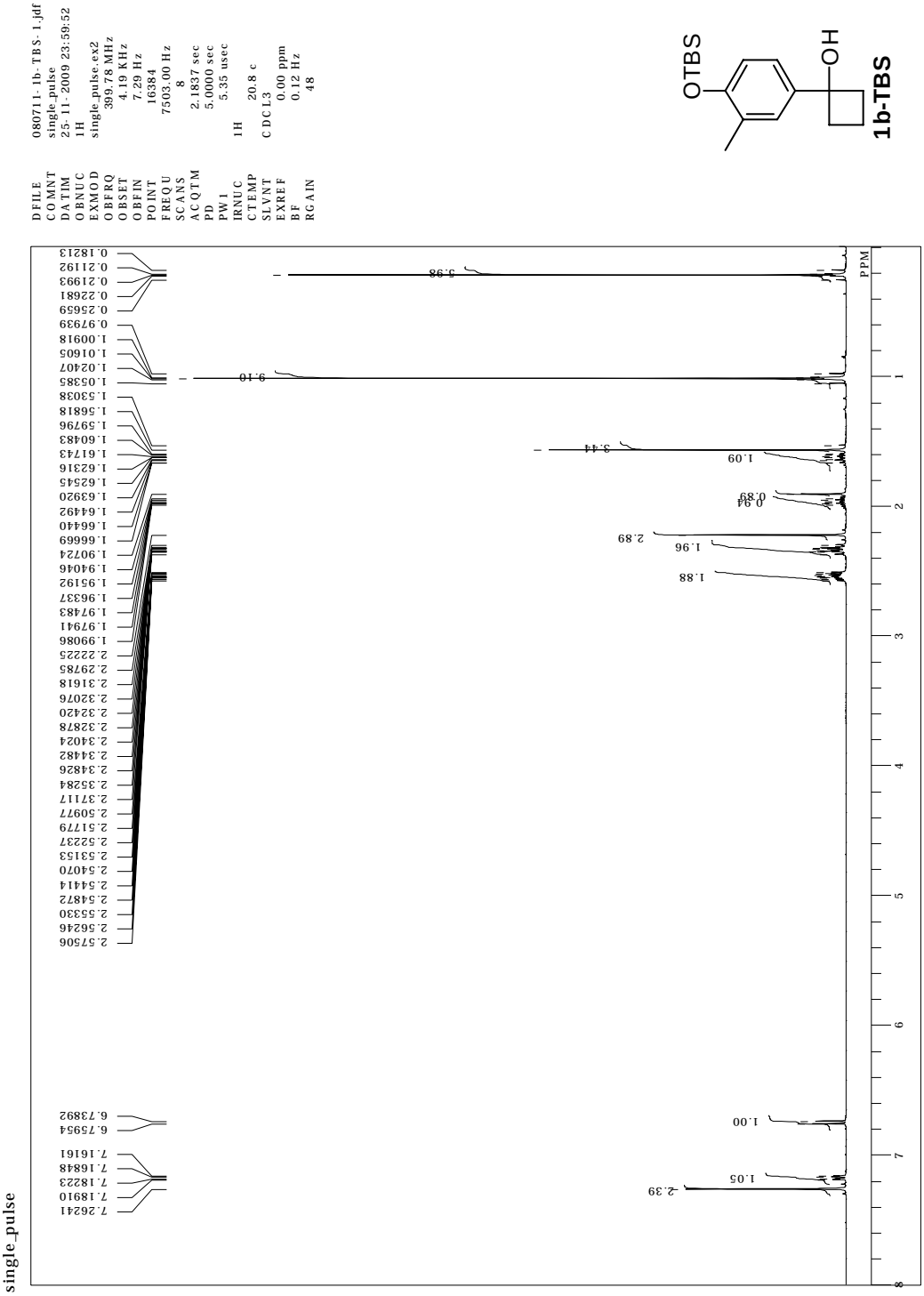
^{1}H NMR chart of Compound **1a**



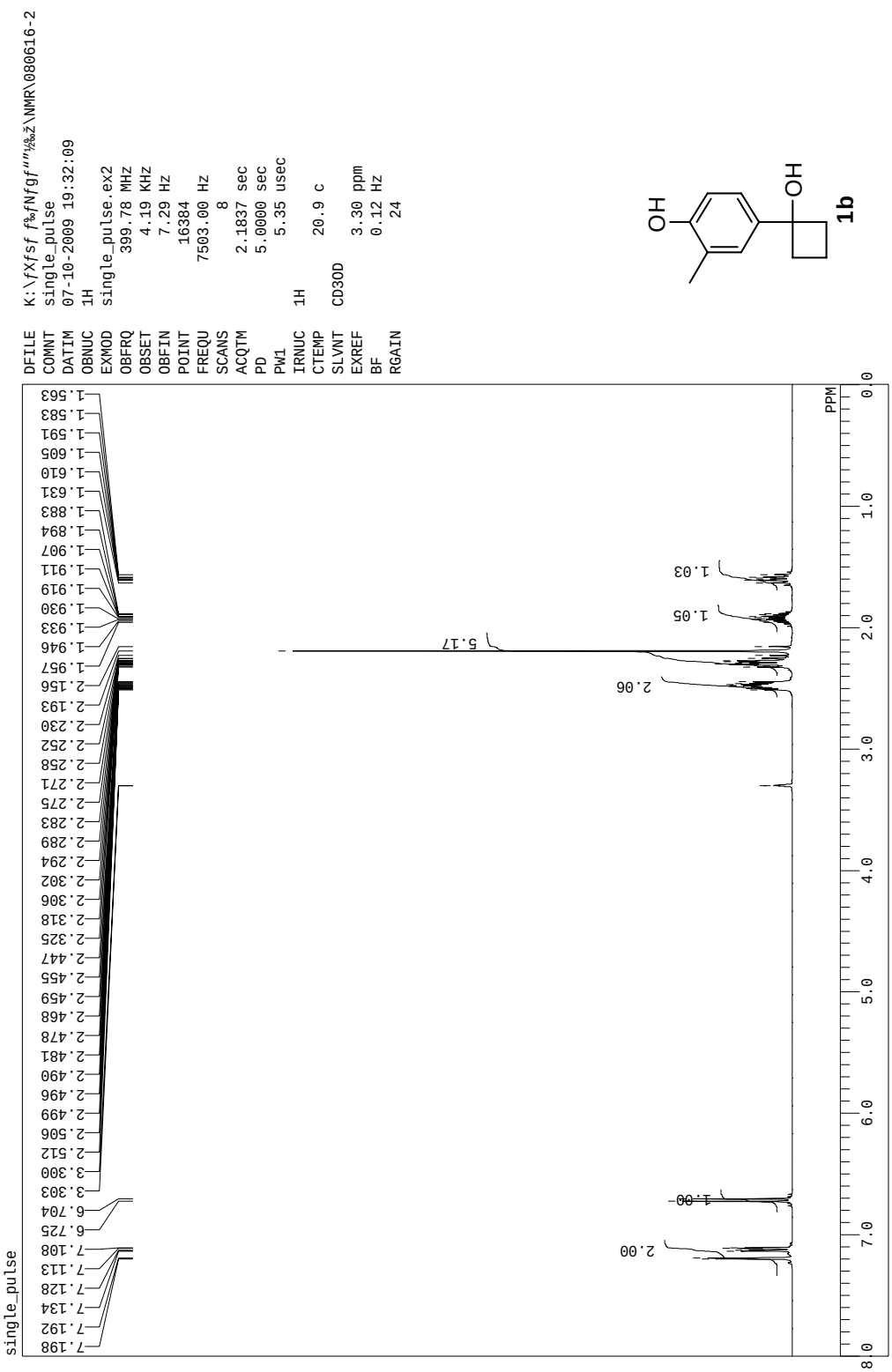
^{13}C NMR chart of Compound **1a**



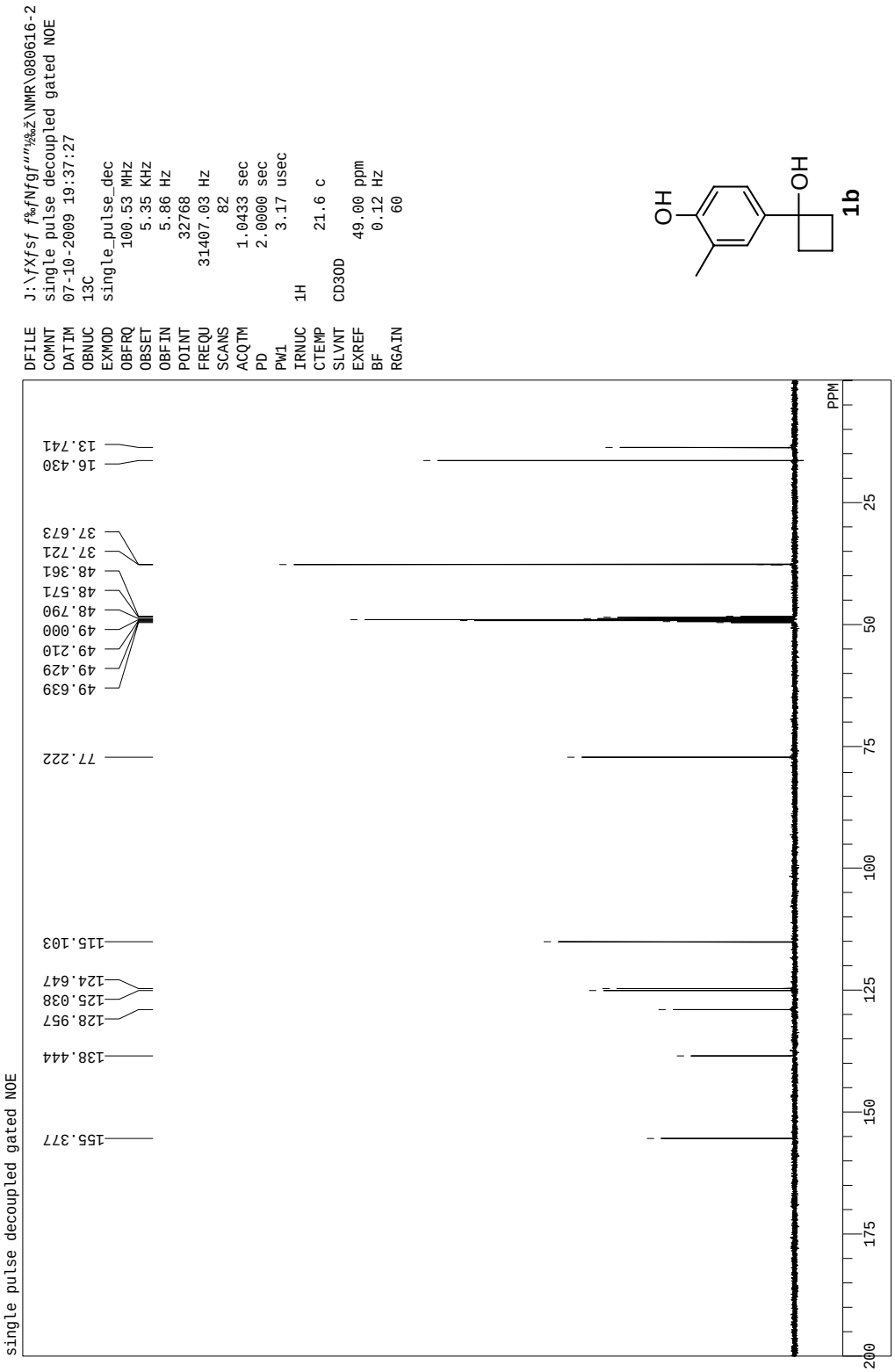
^{1}H NMR chart of Compound **1b-TBS**



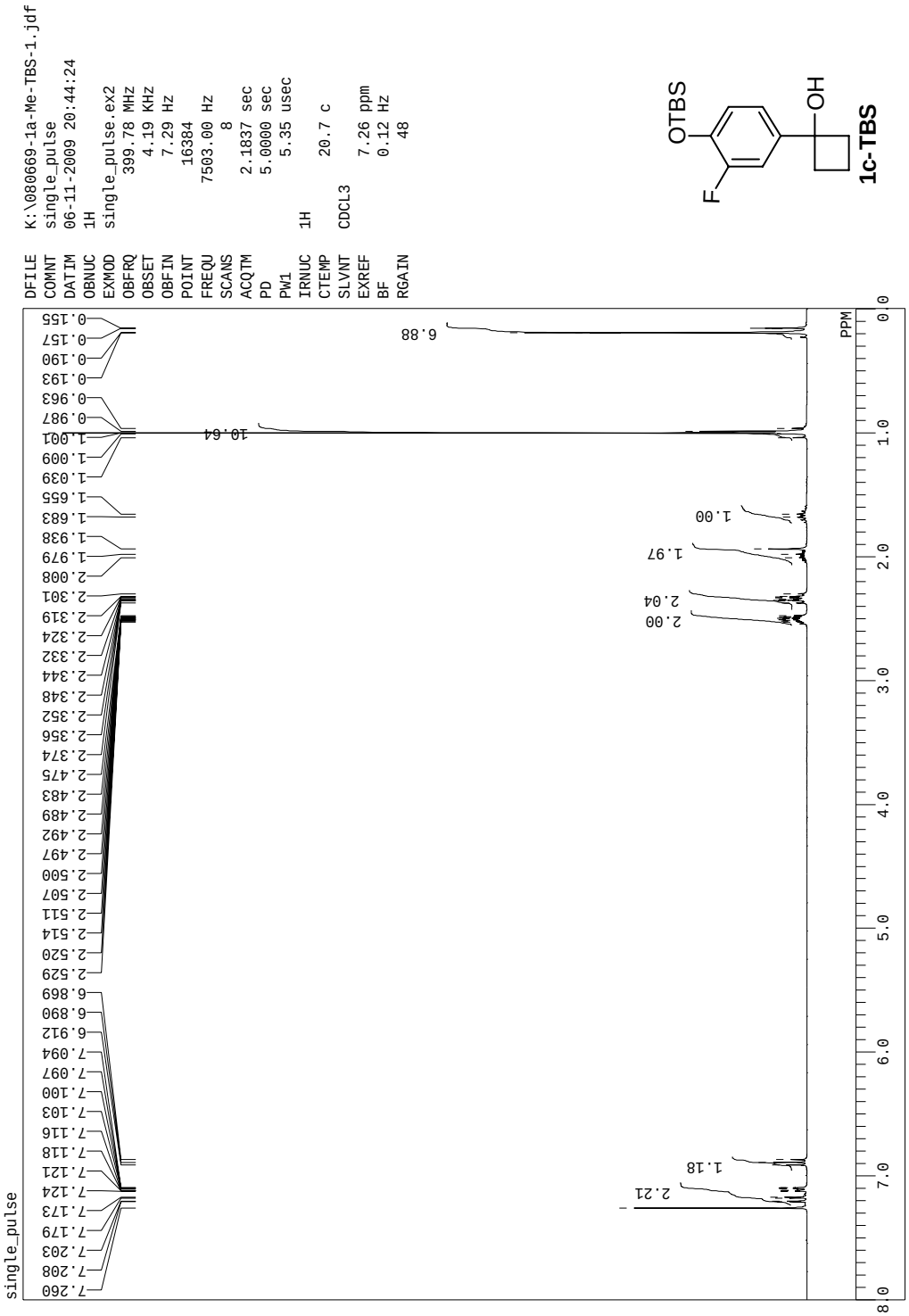
^{1}H NMR chart of Compound **1b**



^{13}C NMR chart of Compound **1b**



^{1}H NMR chart of Compound **1c-TBS**



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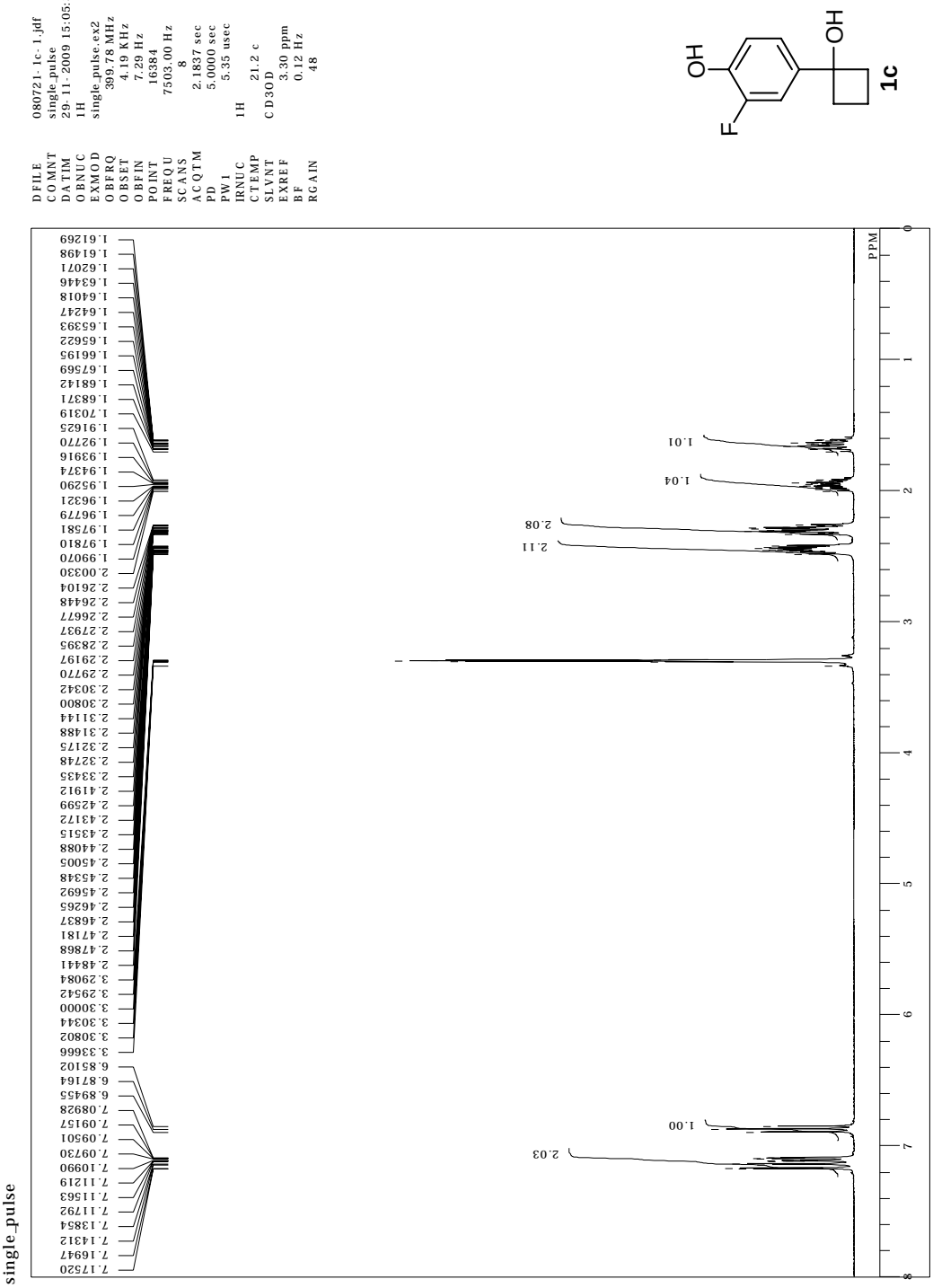
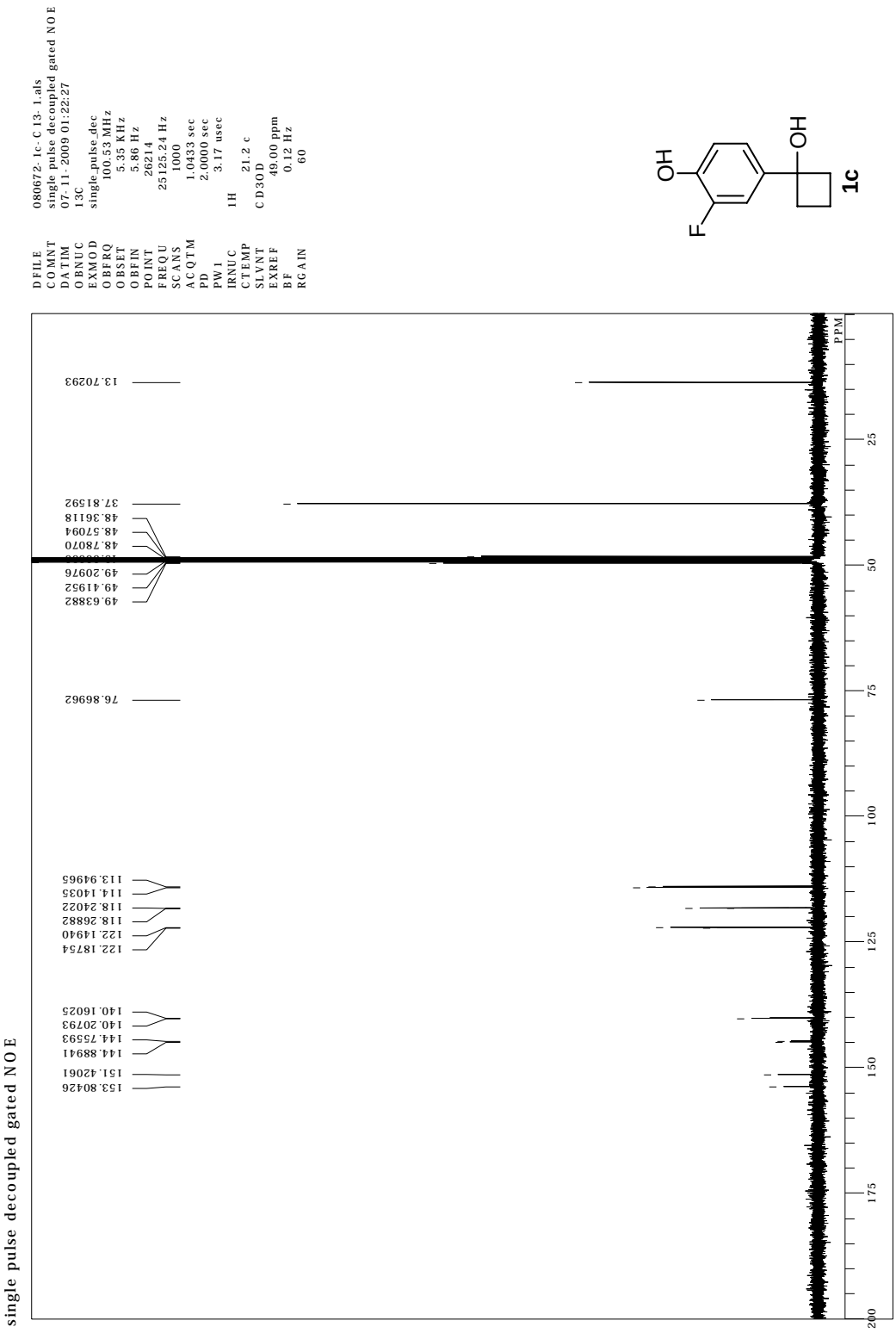
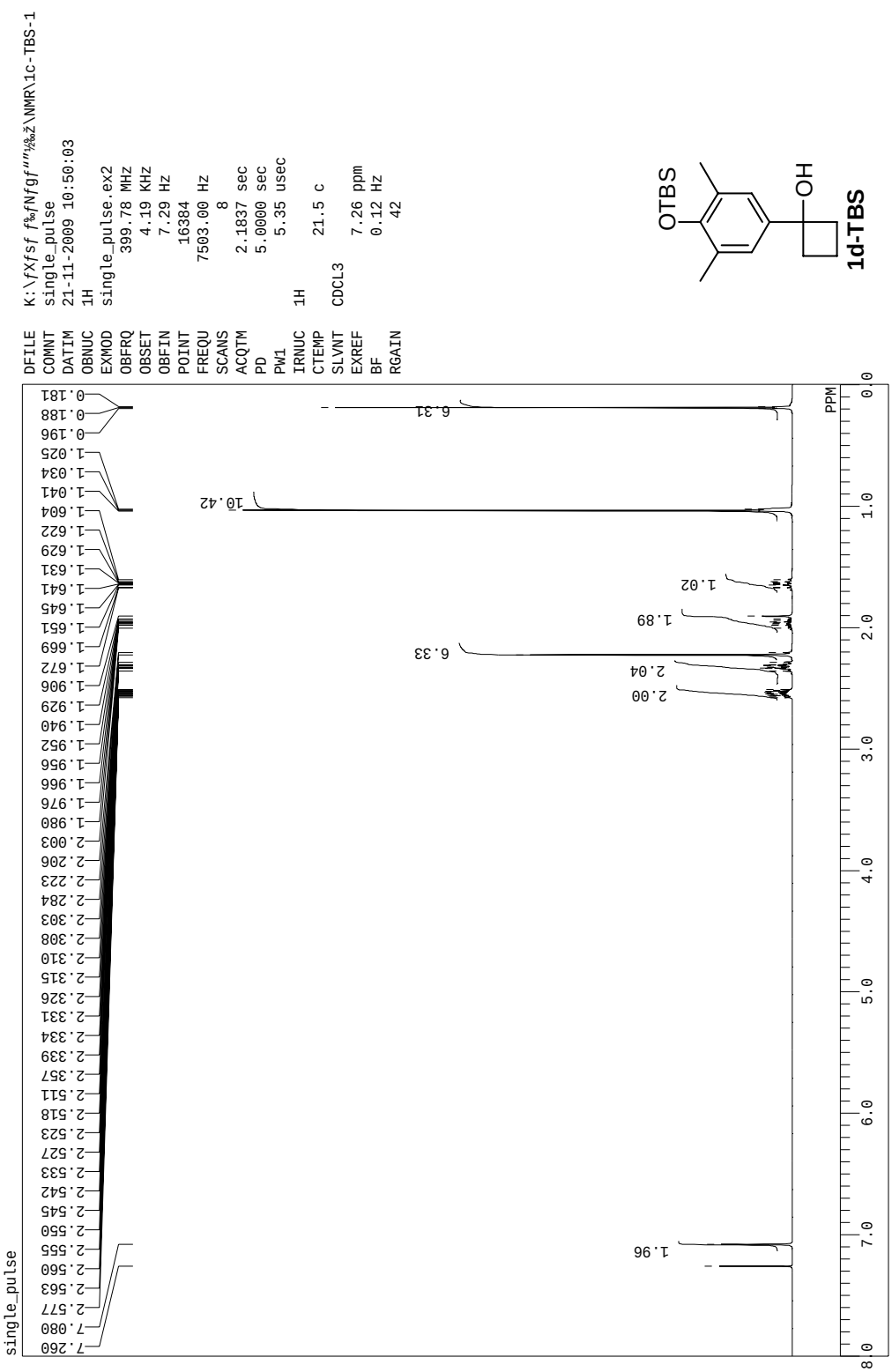


^{13}C NMR chart of Compound **1c**



^{1}H NMR chart of Compound **1d-TBS**



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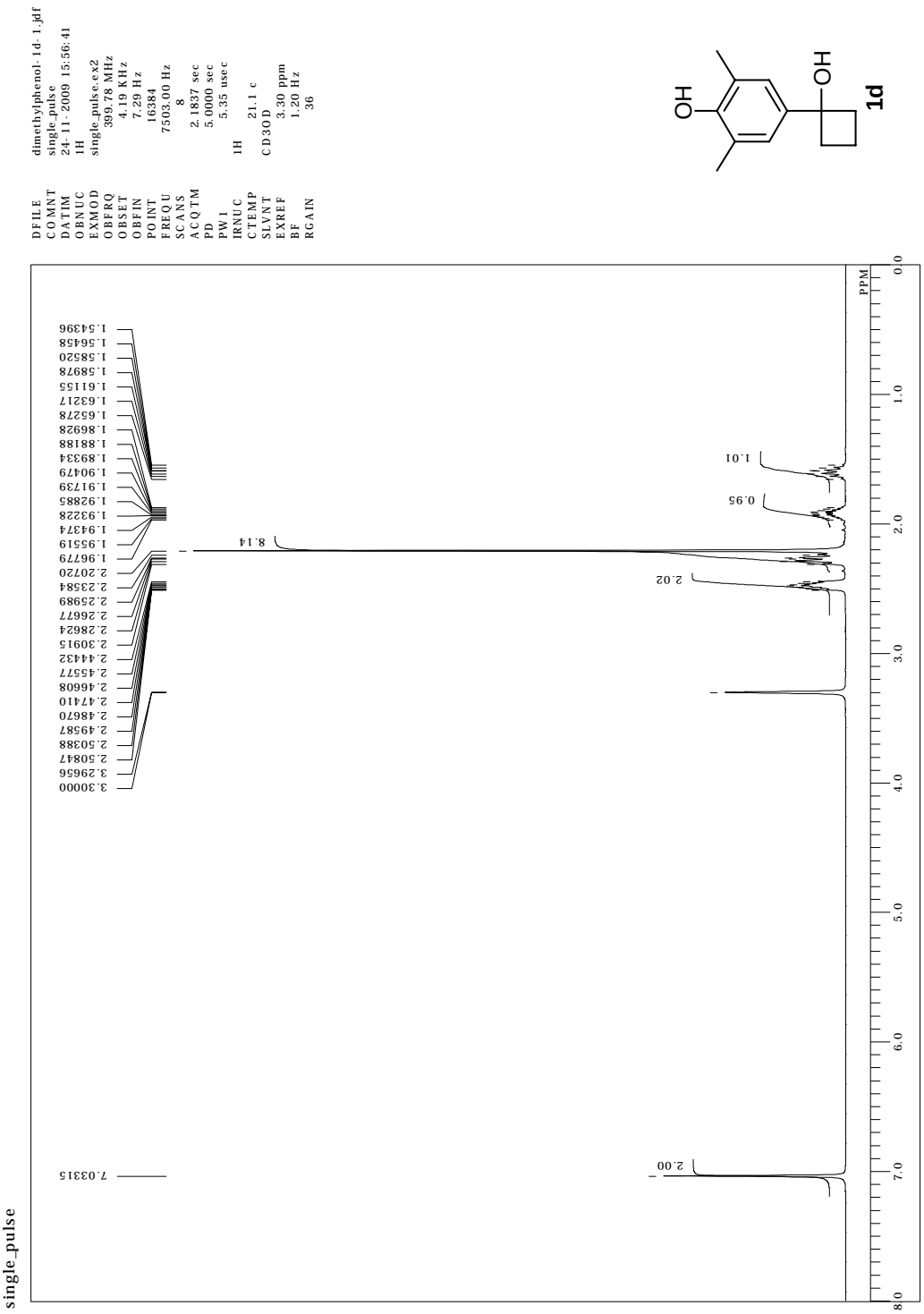
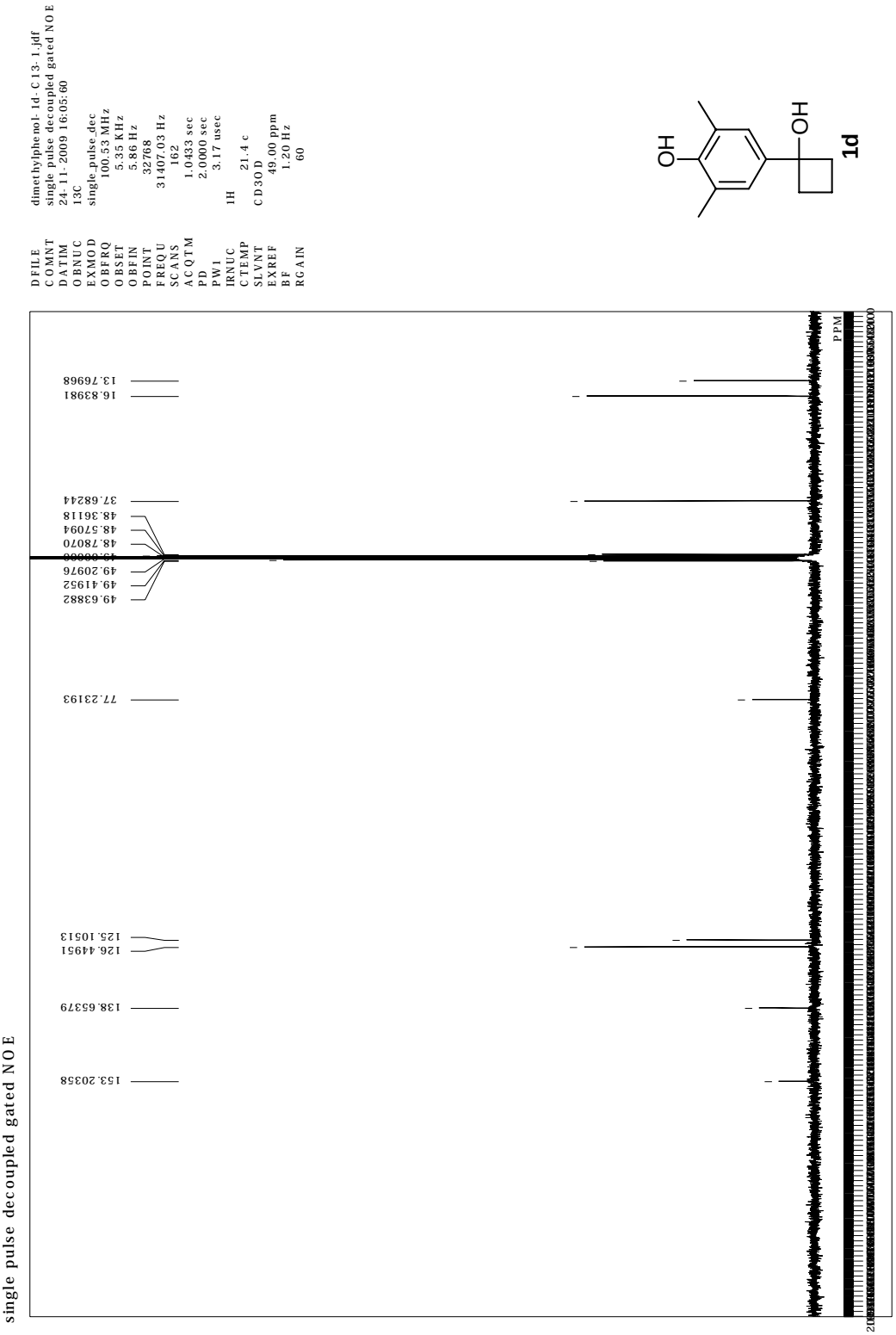
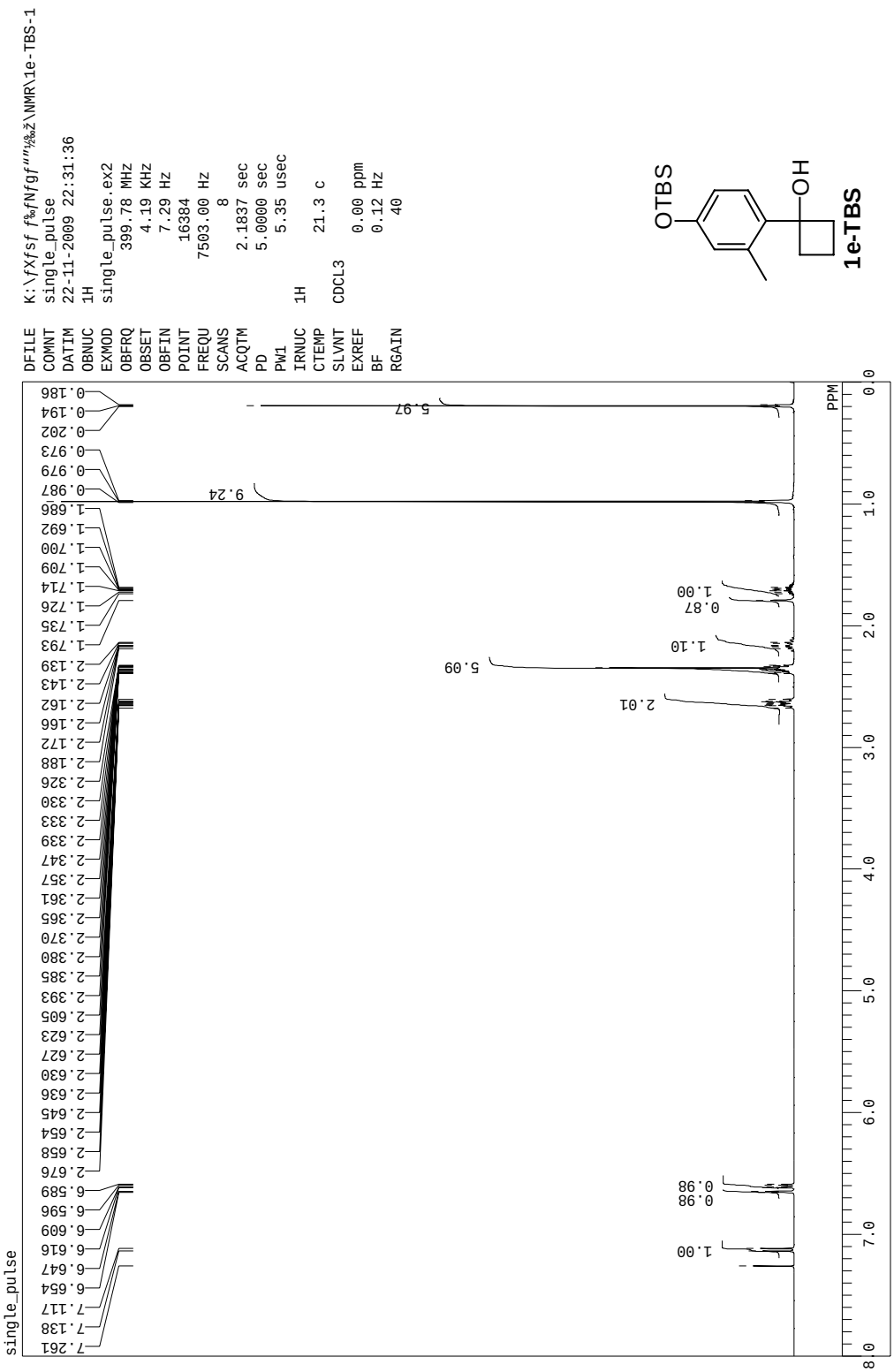


^{13}C NMR chart of Compound **1d**



^{1}H NMR chart of Compound **1e-TBS**



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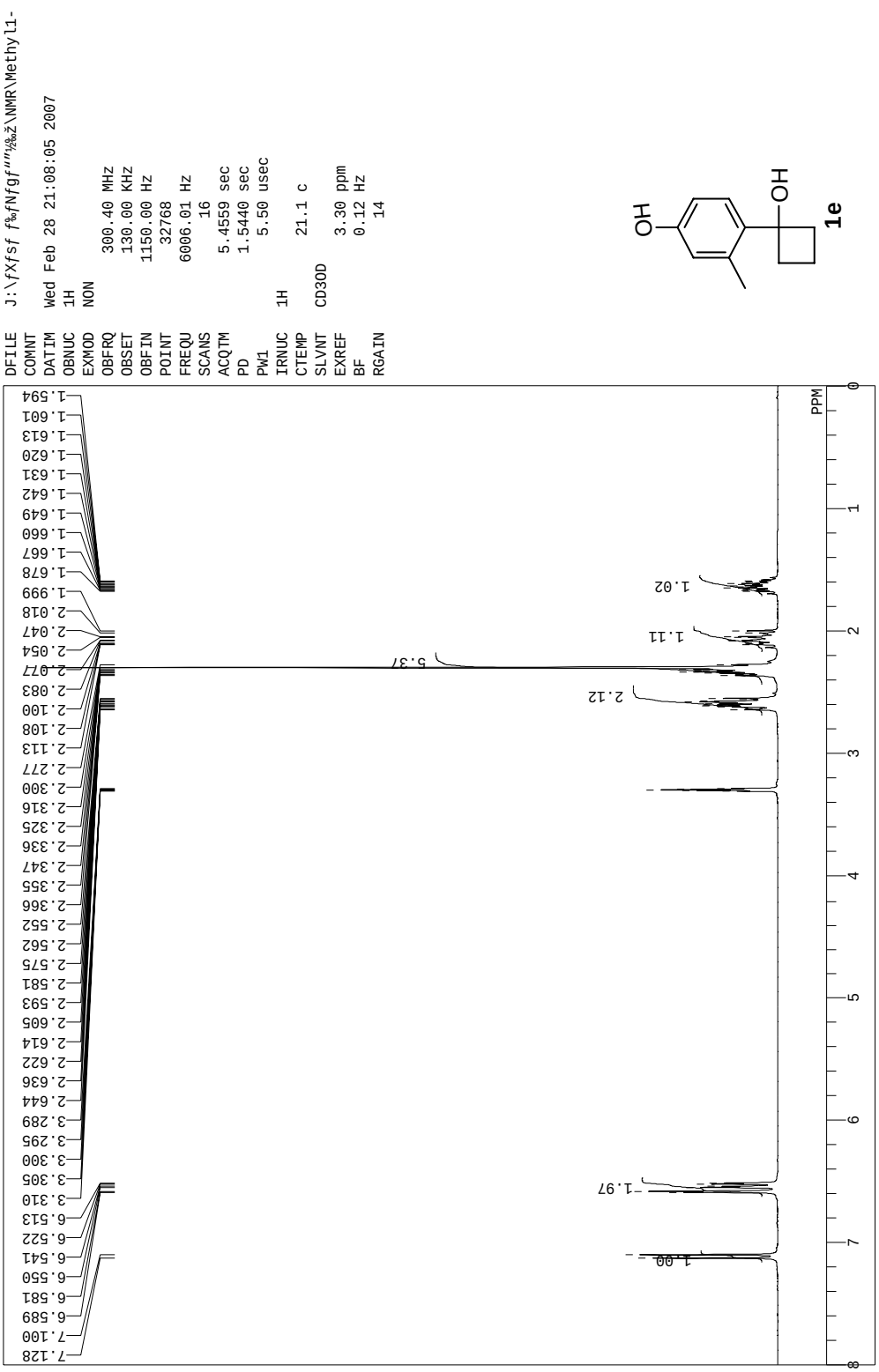

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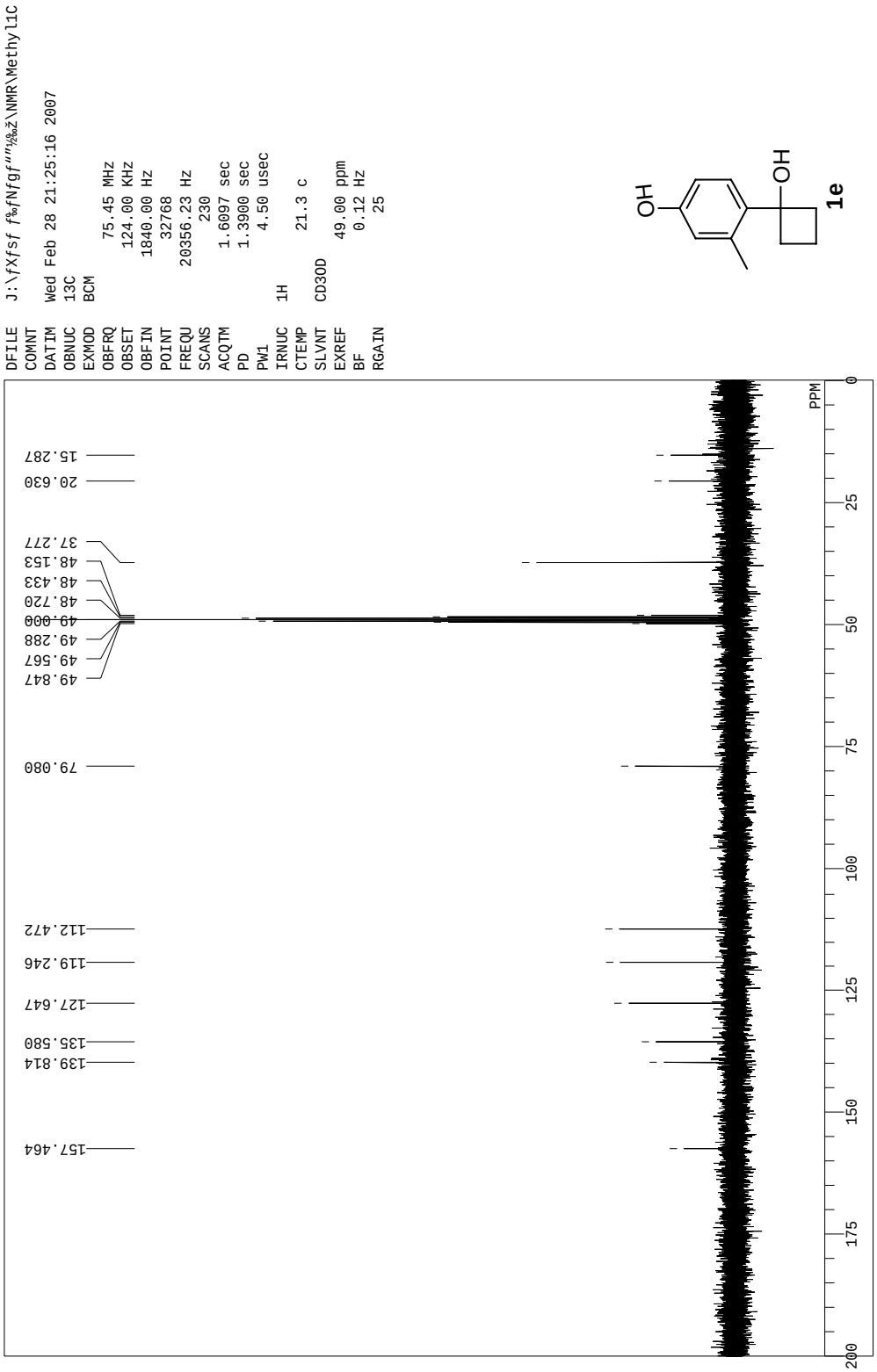
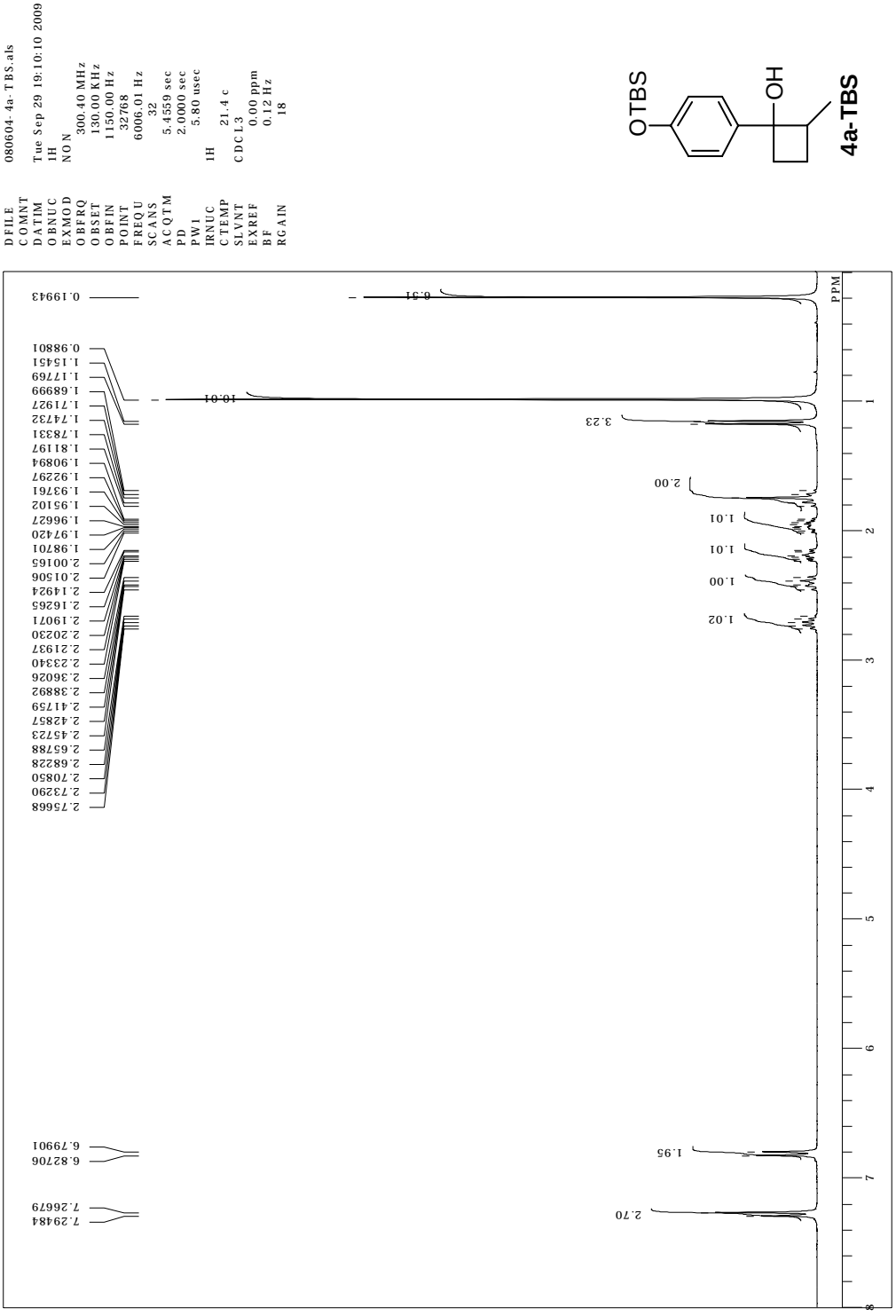


^{1}H NMR chart of Compound **4a-TBS**



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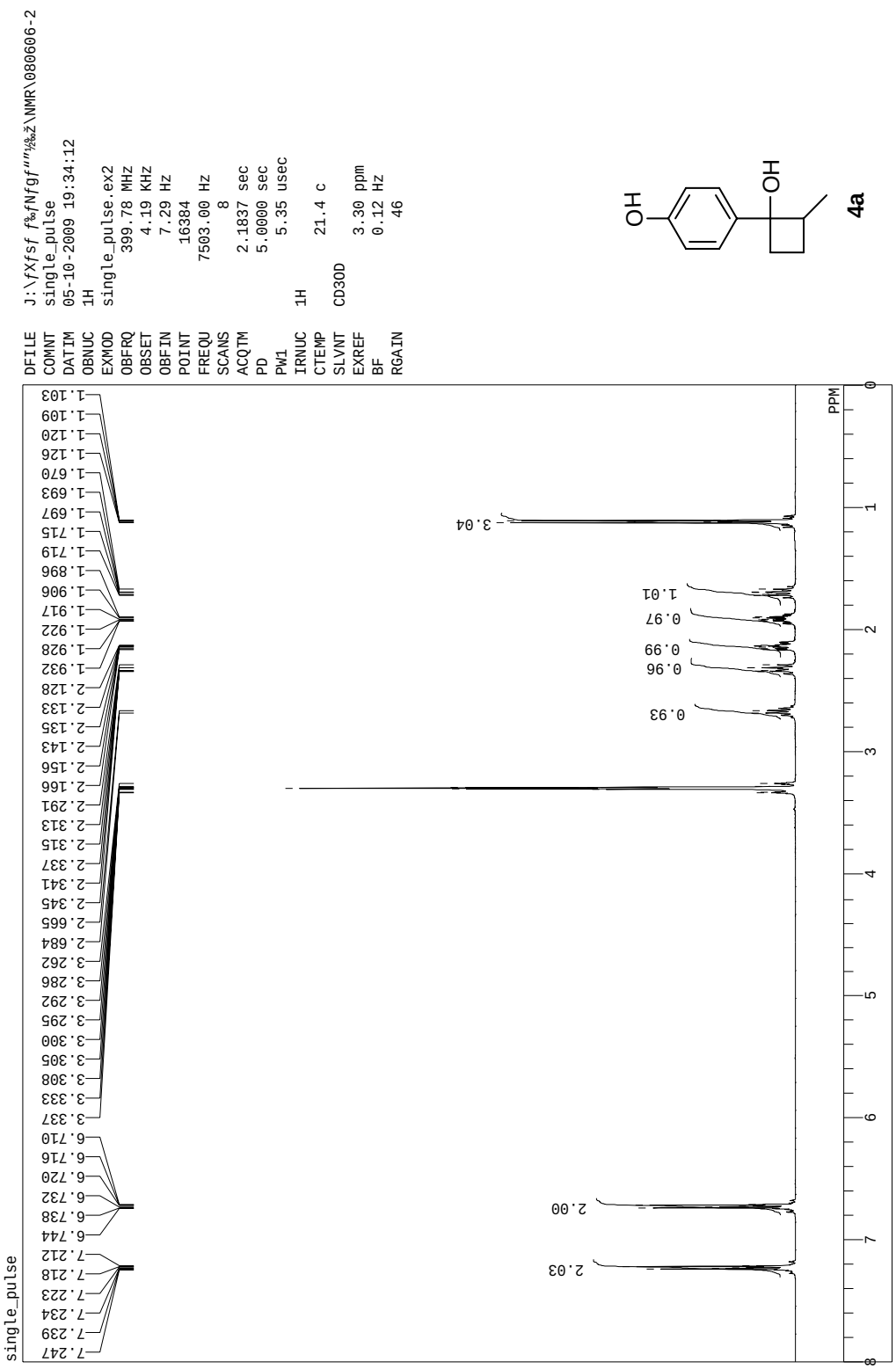

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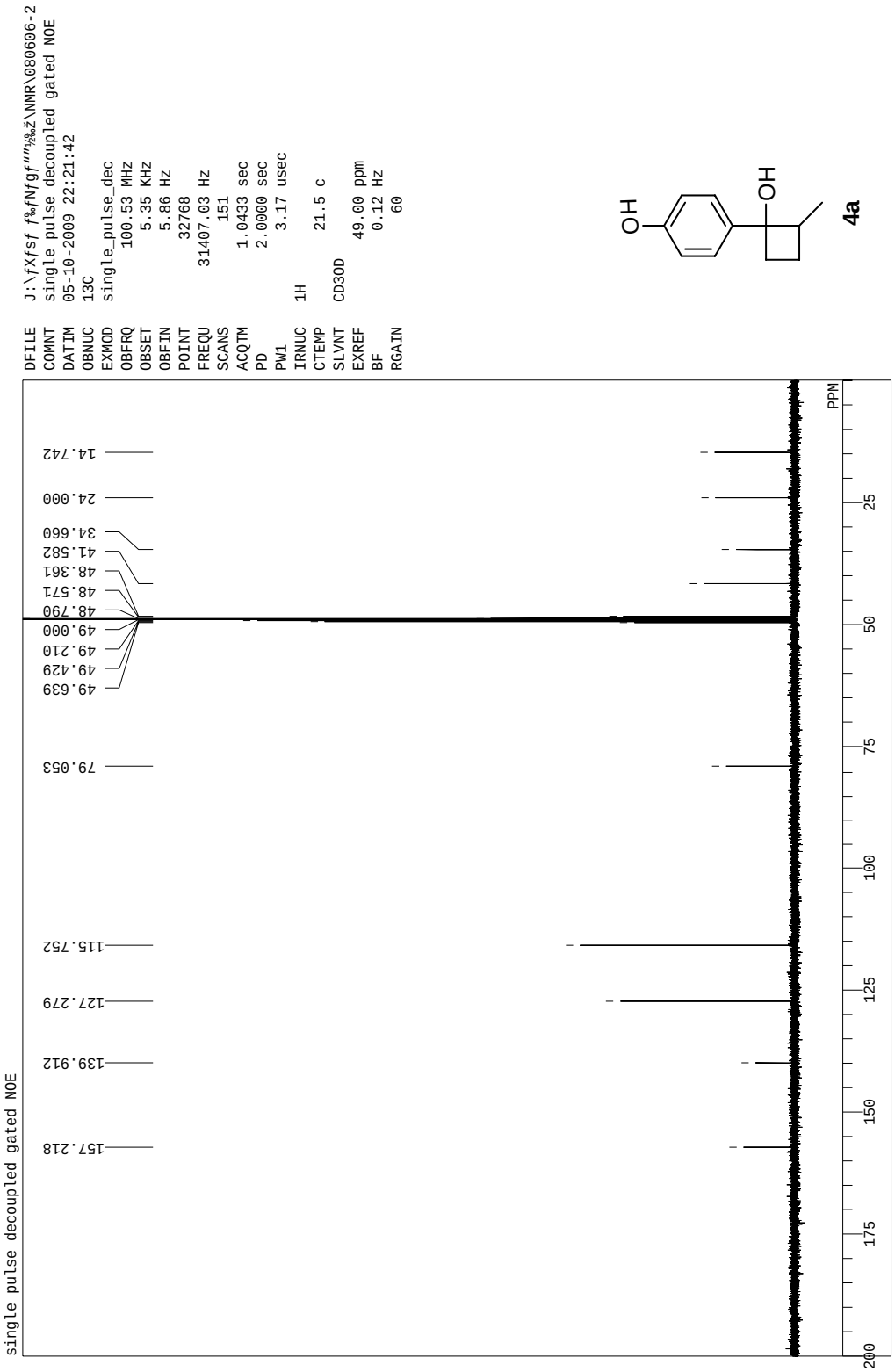
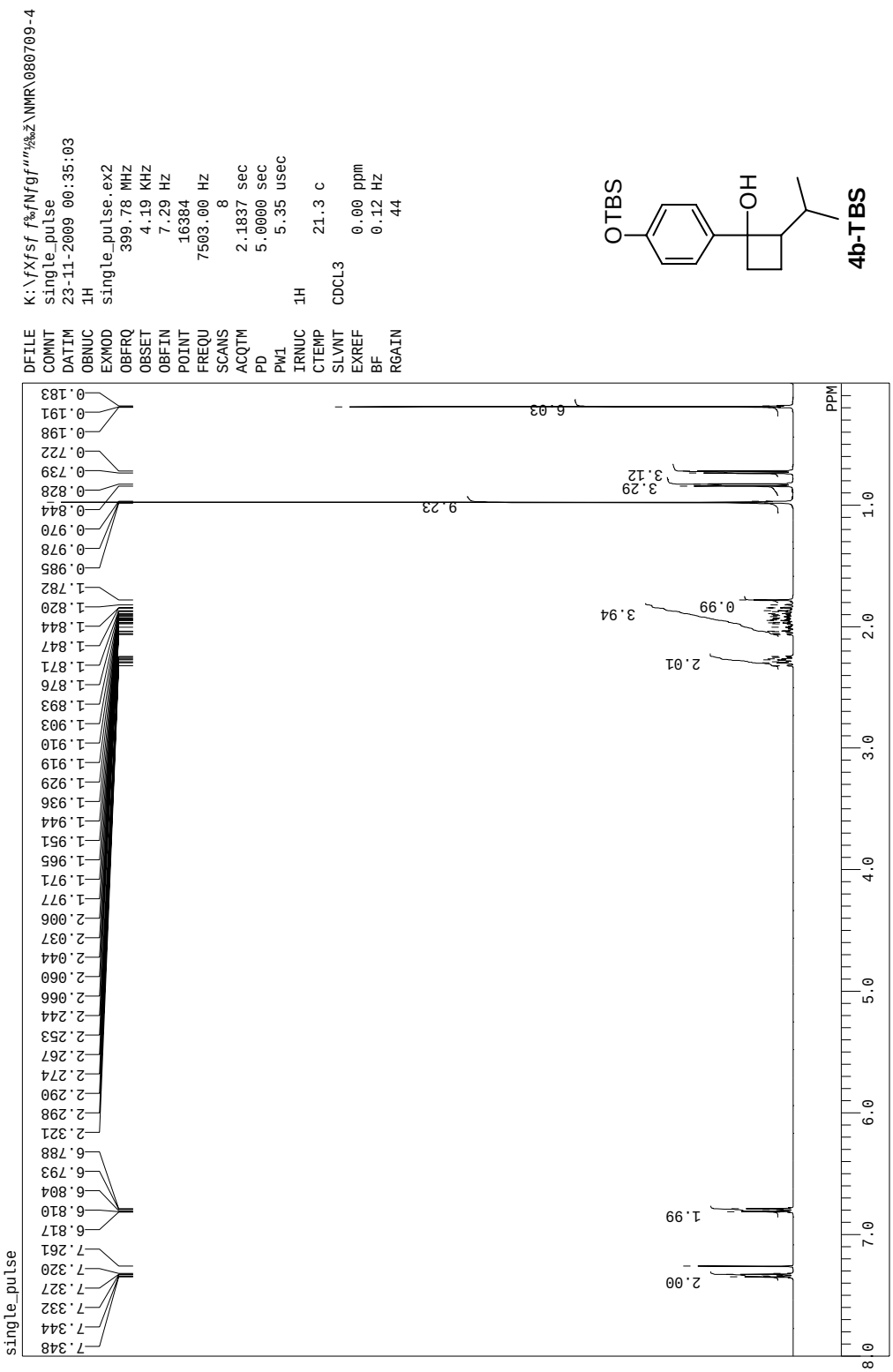


^{1}H NMR chart of Compound **4b-TBS**



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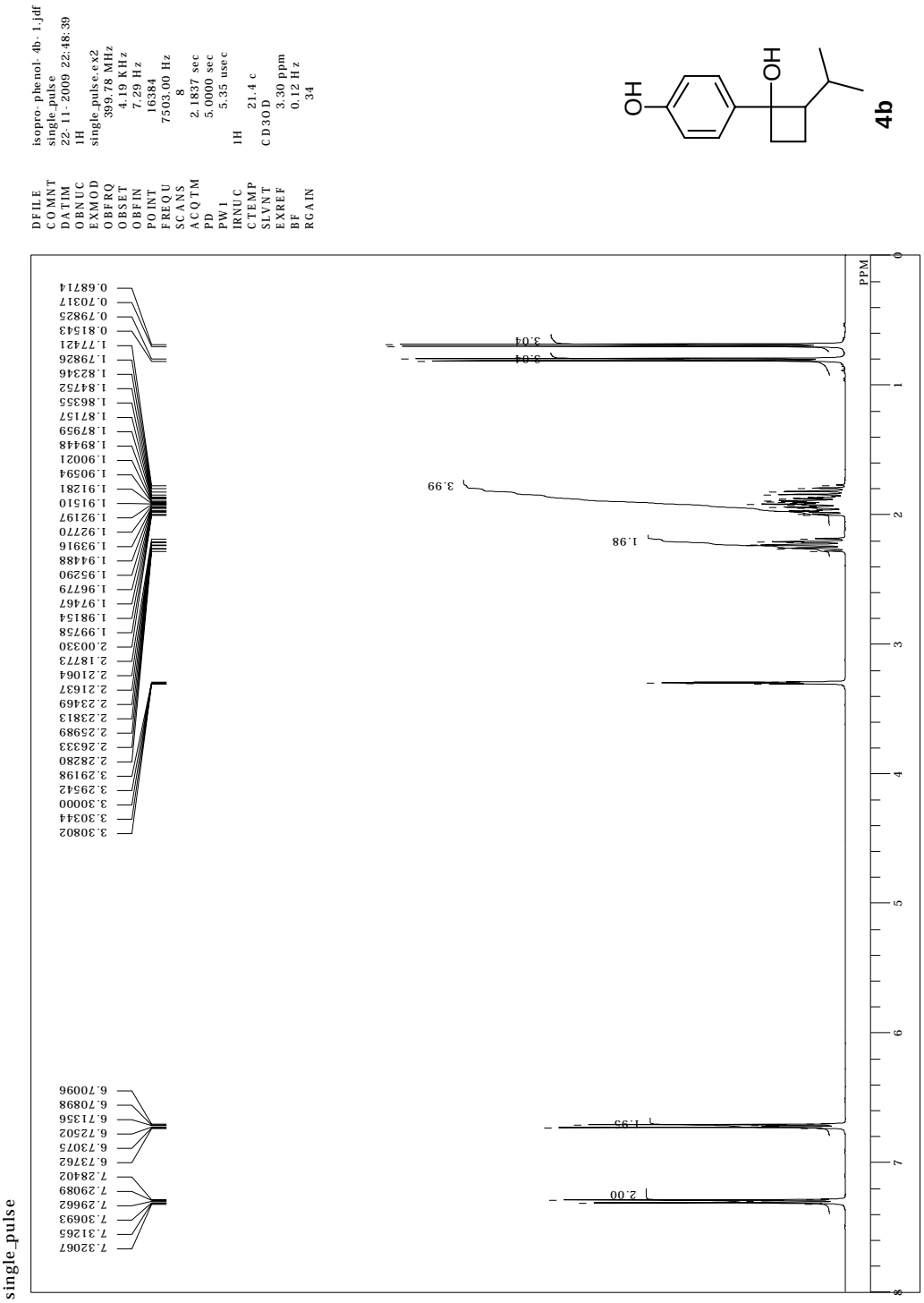

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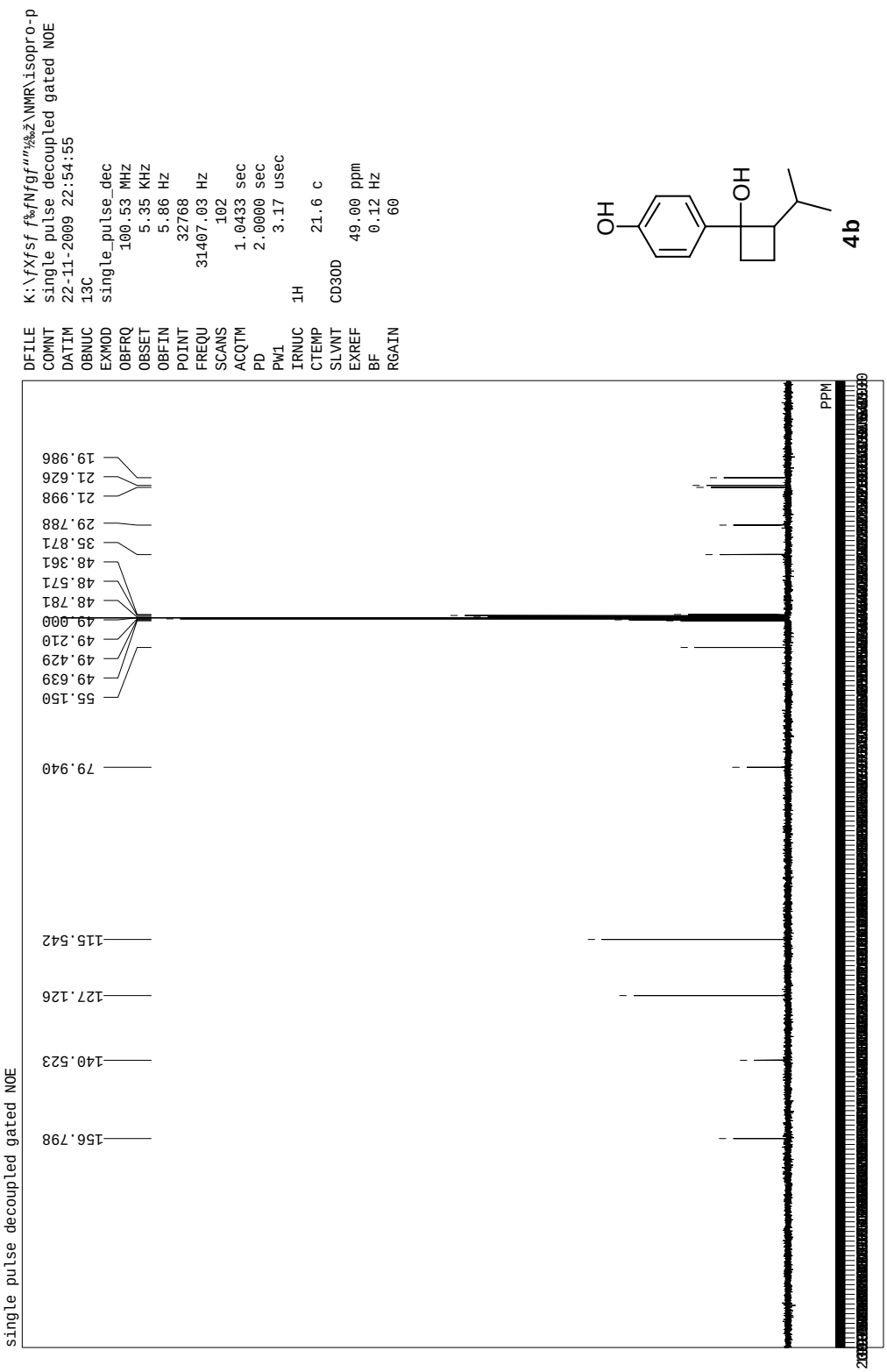
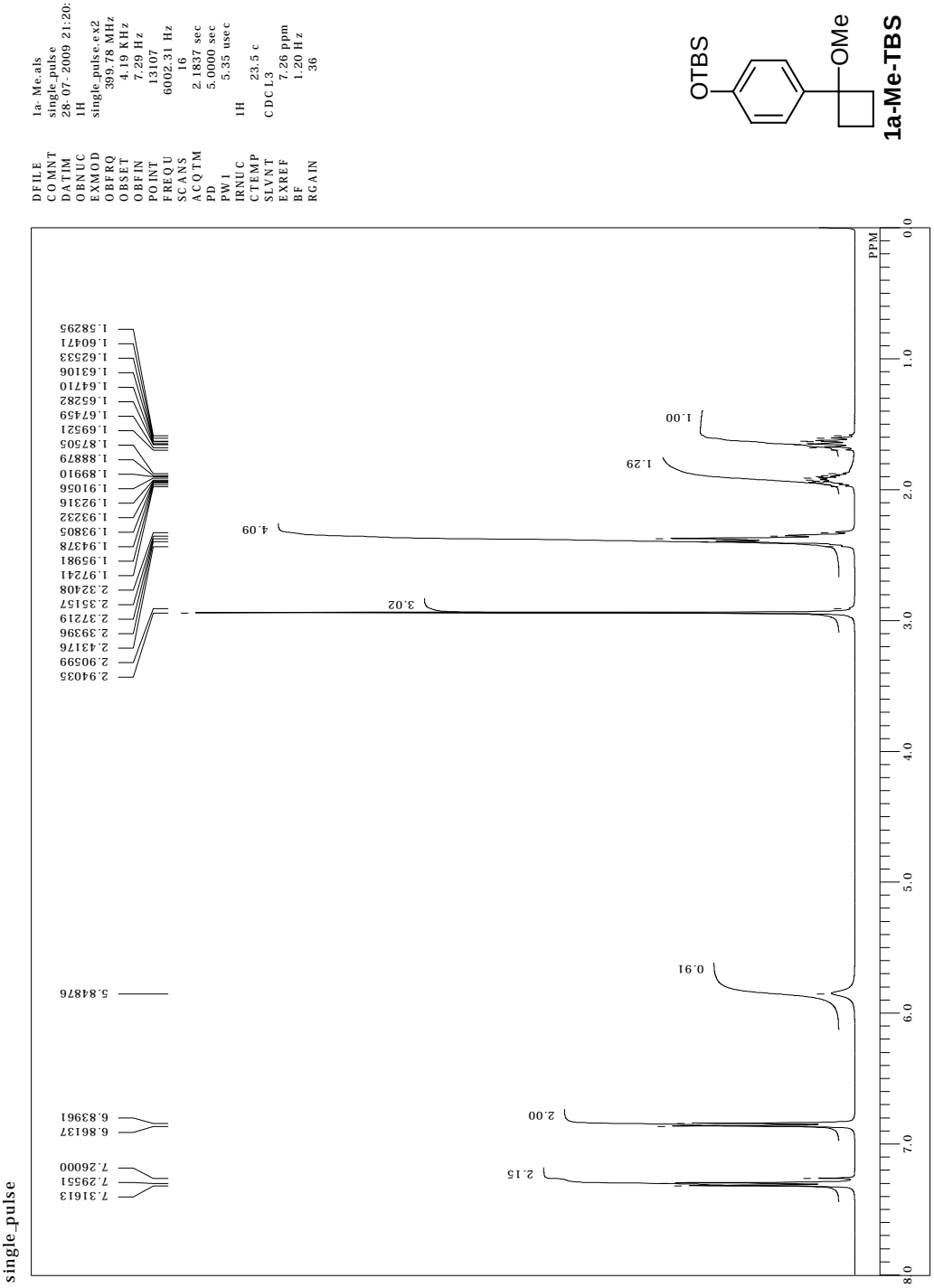
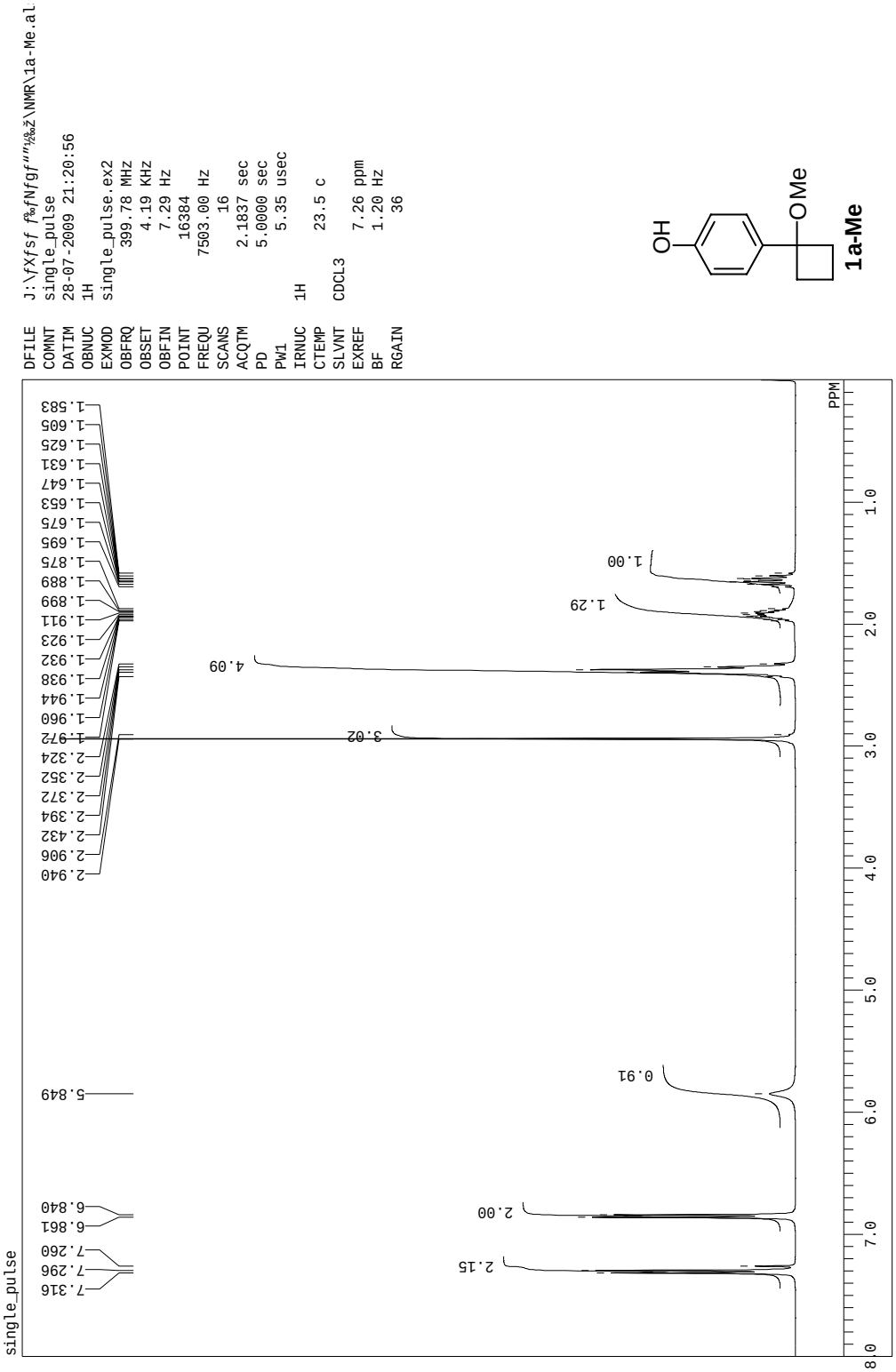


^{1}H NMR chart of Compound **1a-Me-TBS**



^{1}H NMR chart of Compound **1a-Me**



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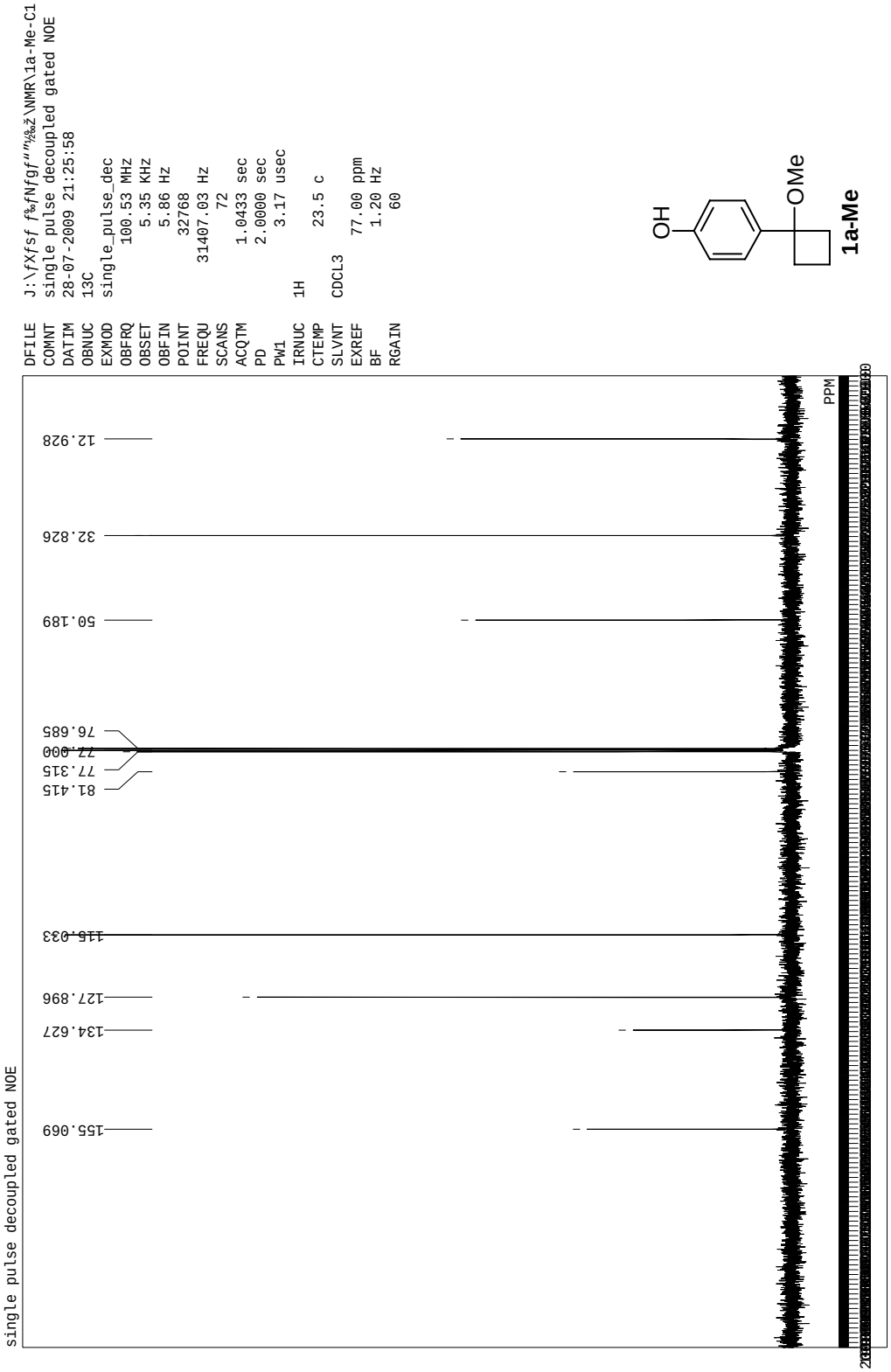
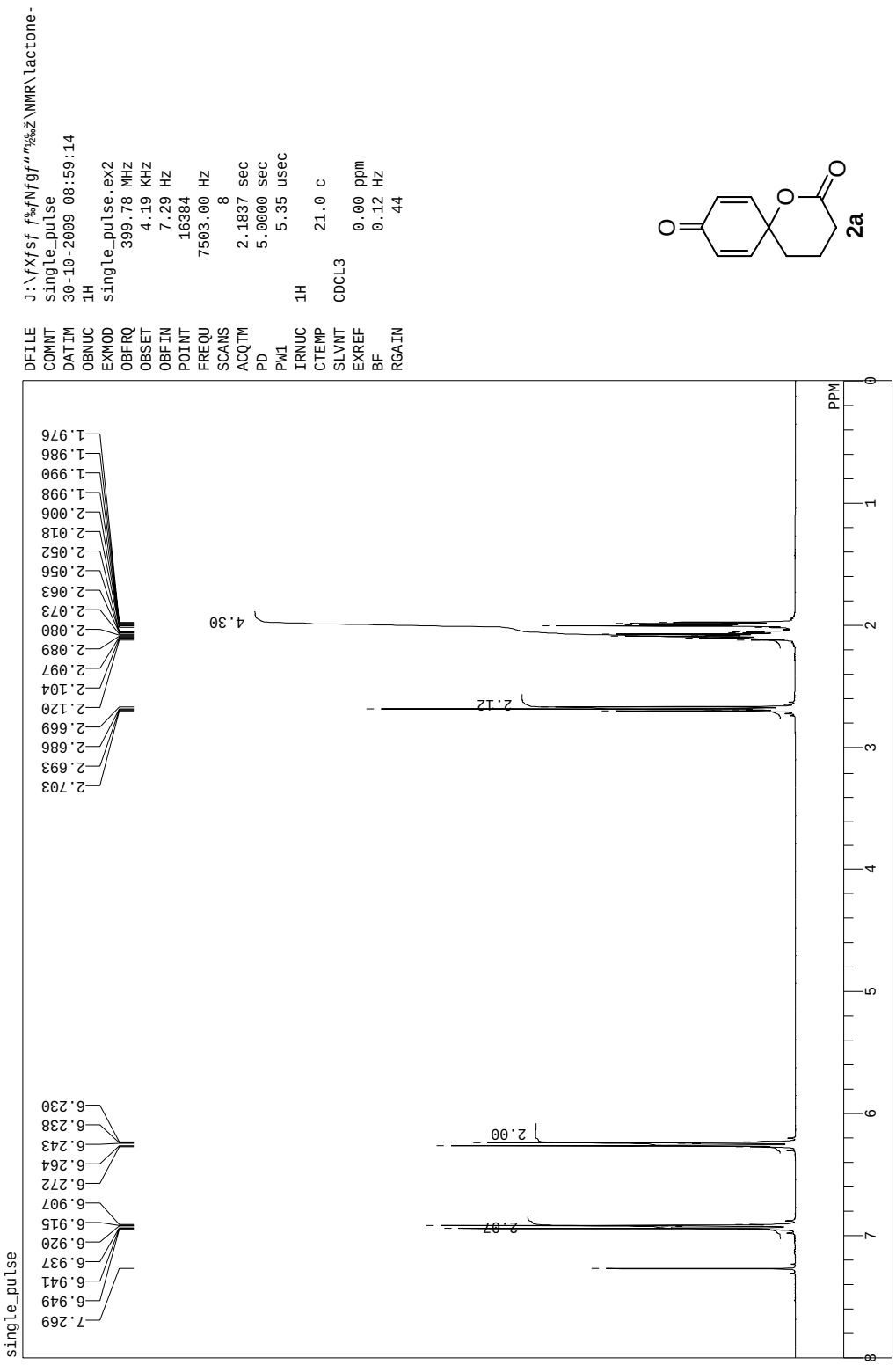


^{1}H NMR chart of Compound **2a**



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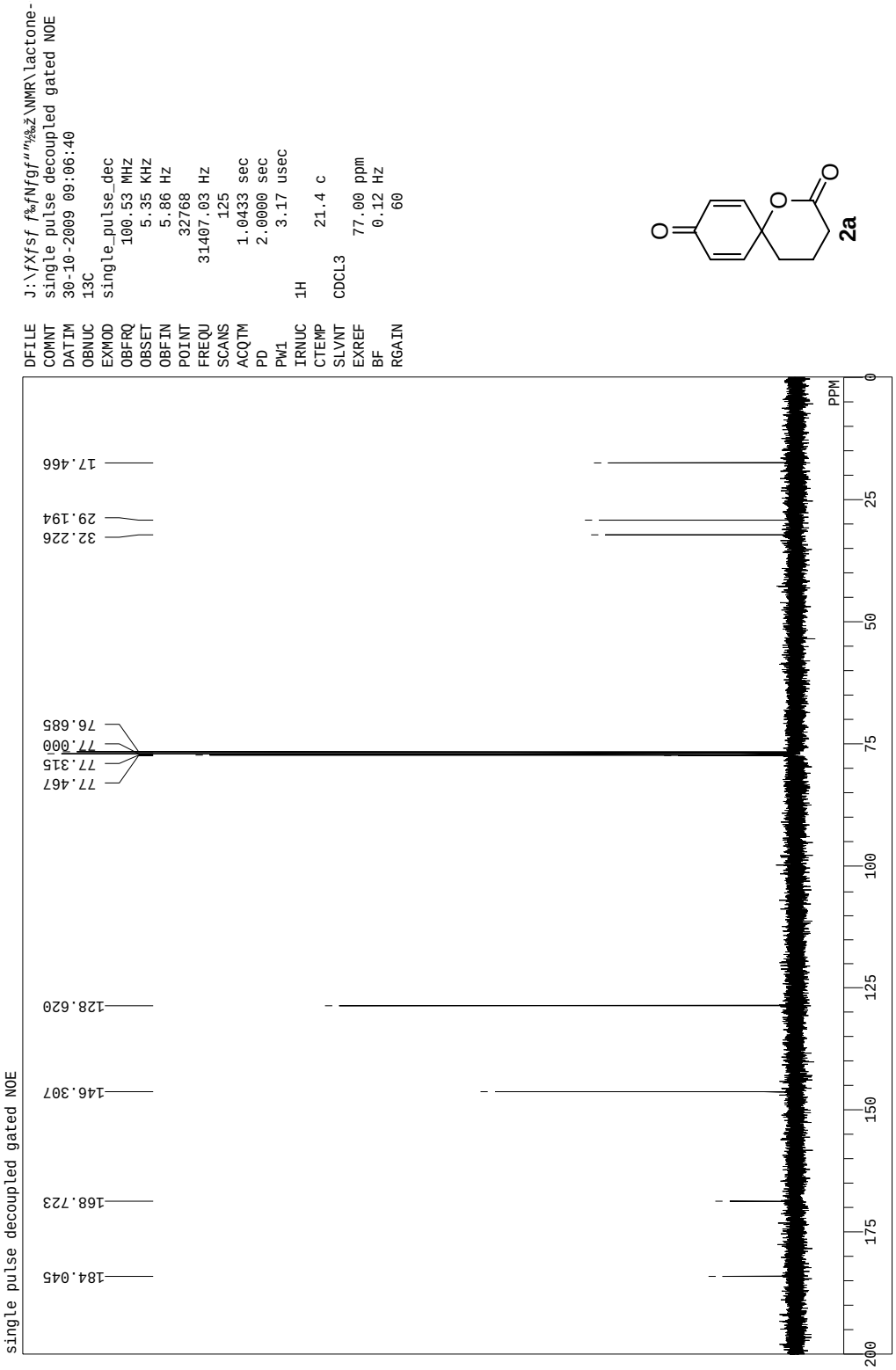
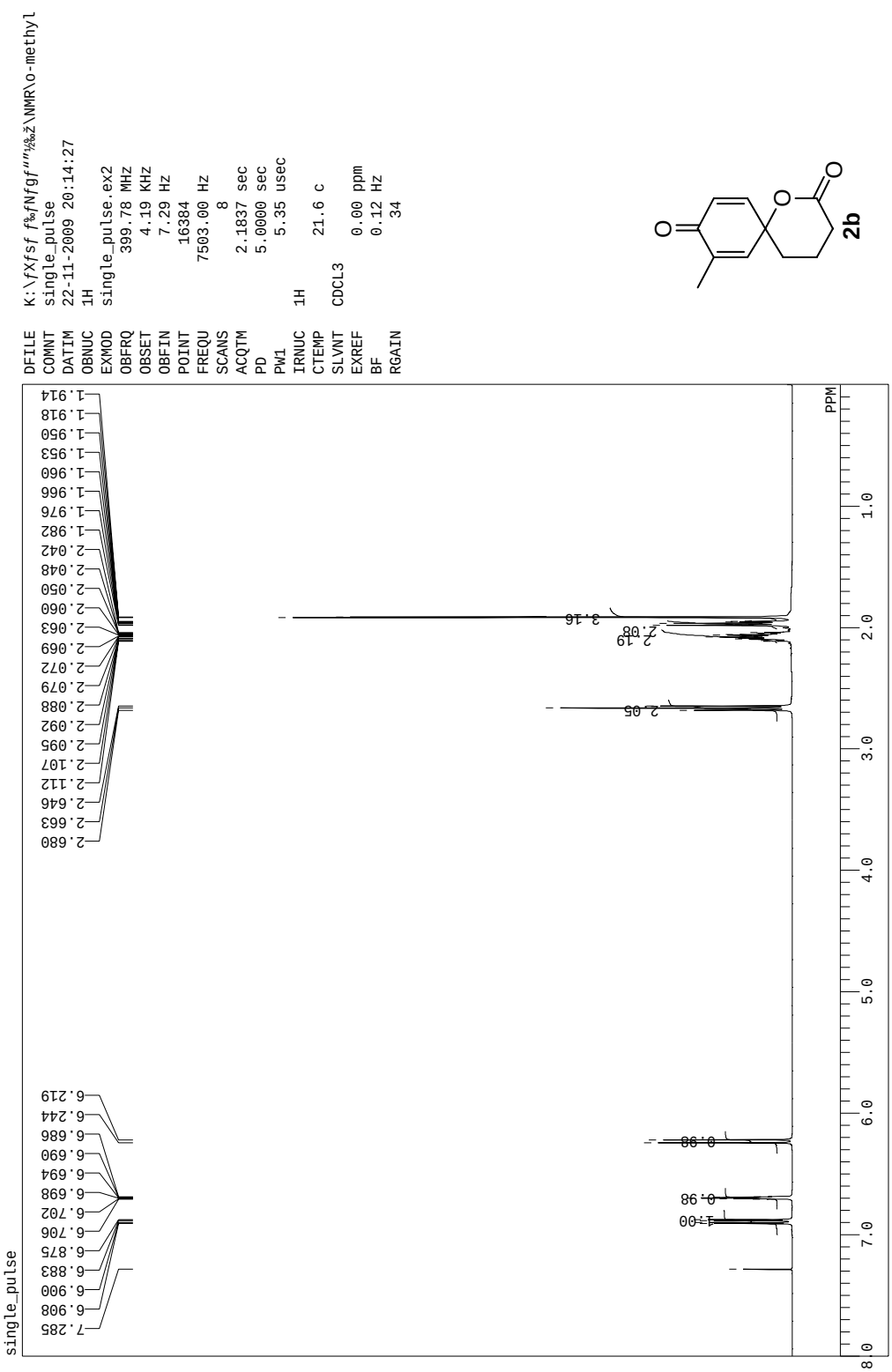
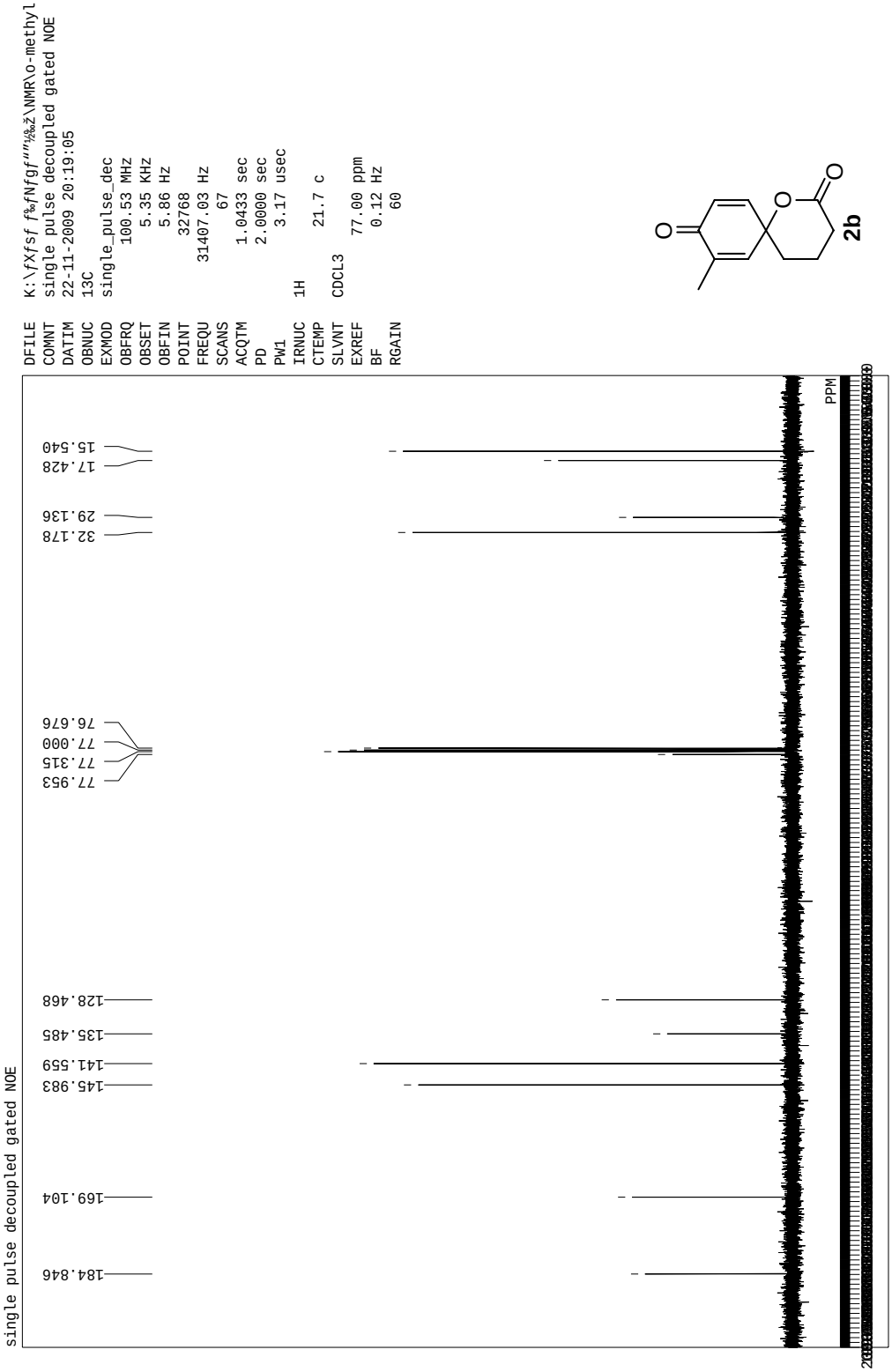


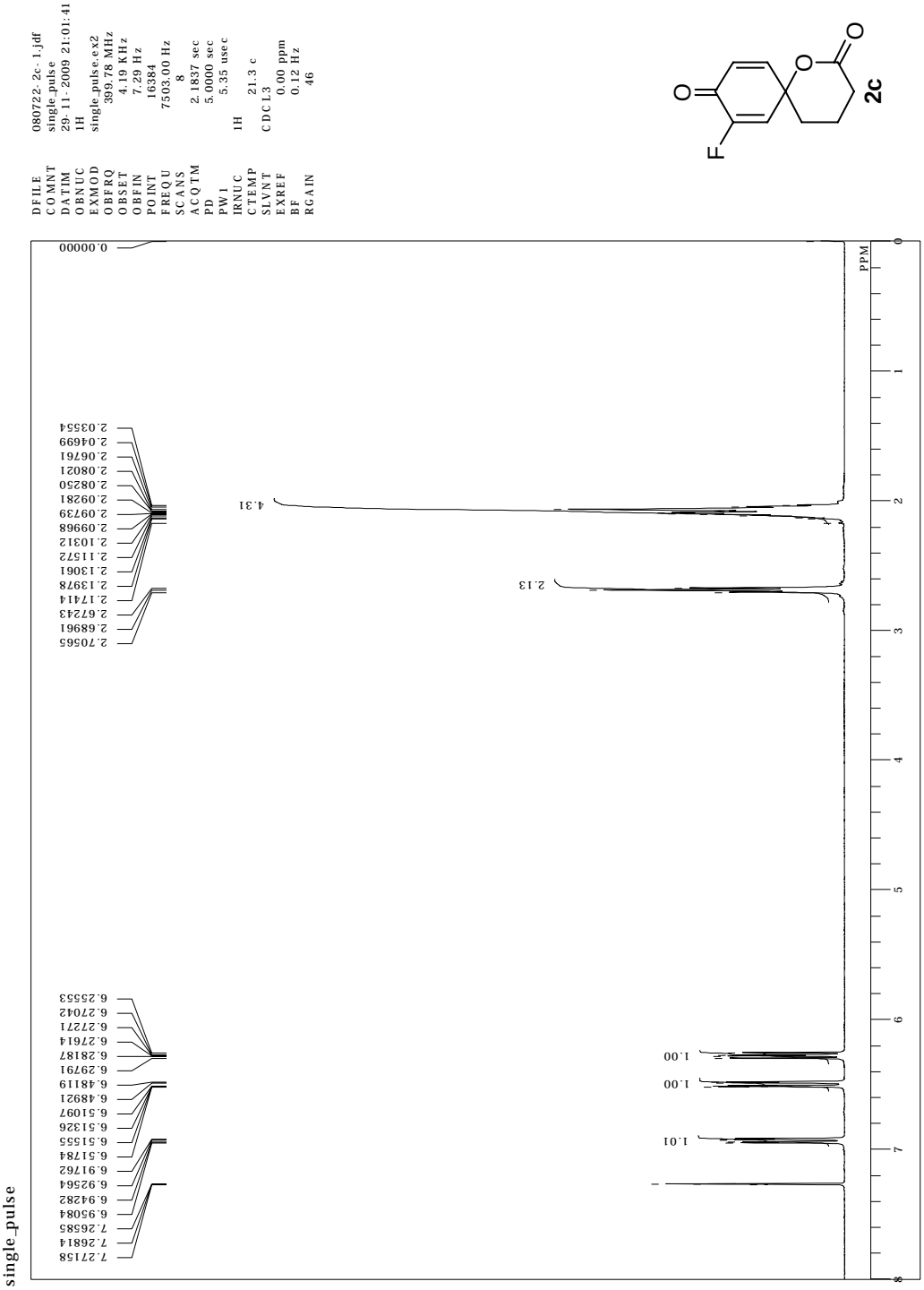
^{1}H NMR chart of Compound **2b**



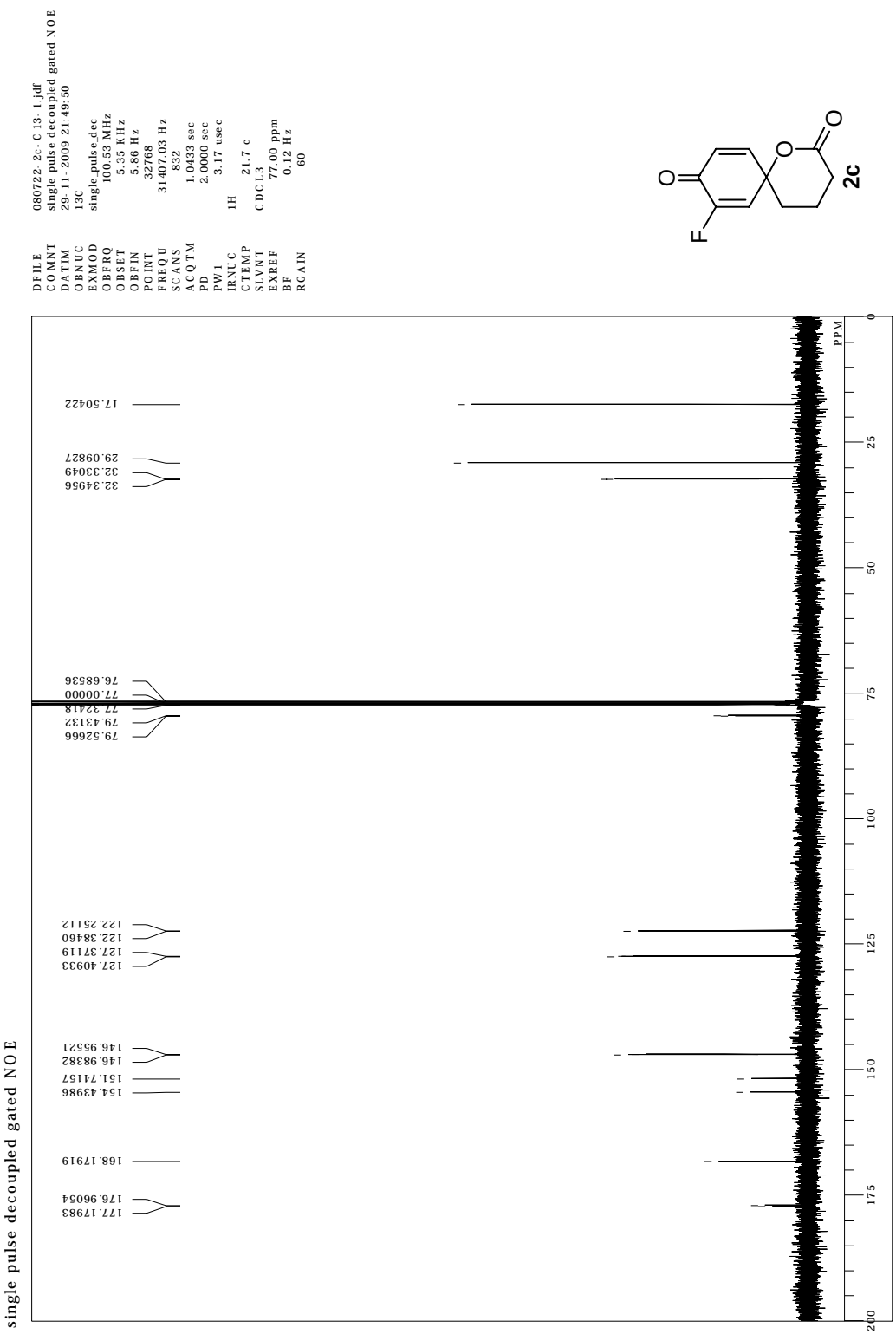
^{13}C NMR chart of Compound **2b**



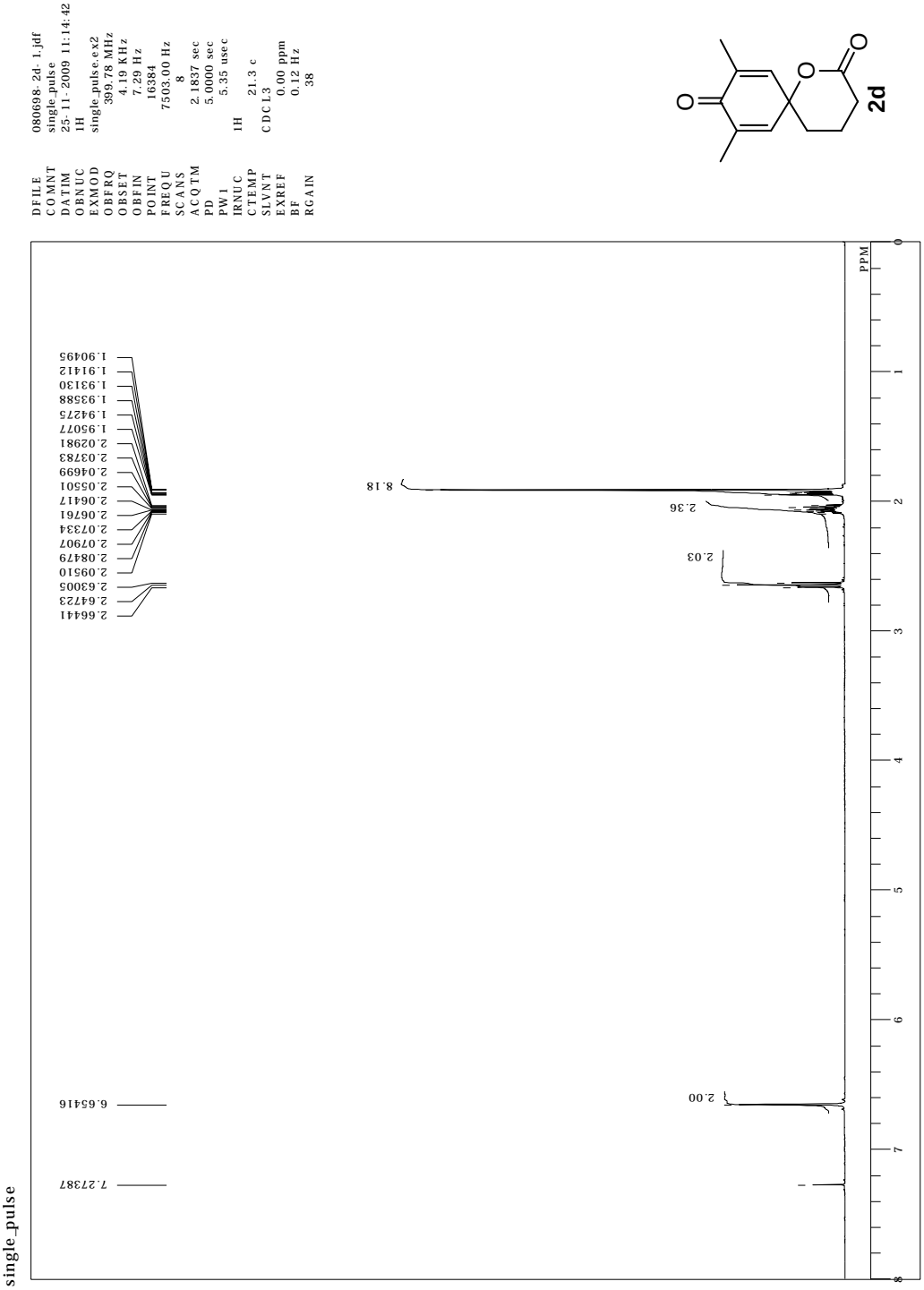
^{1}H NMR chart of Compound **2c**



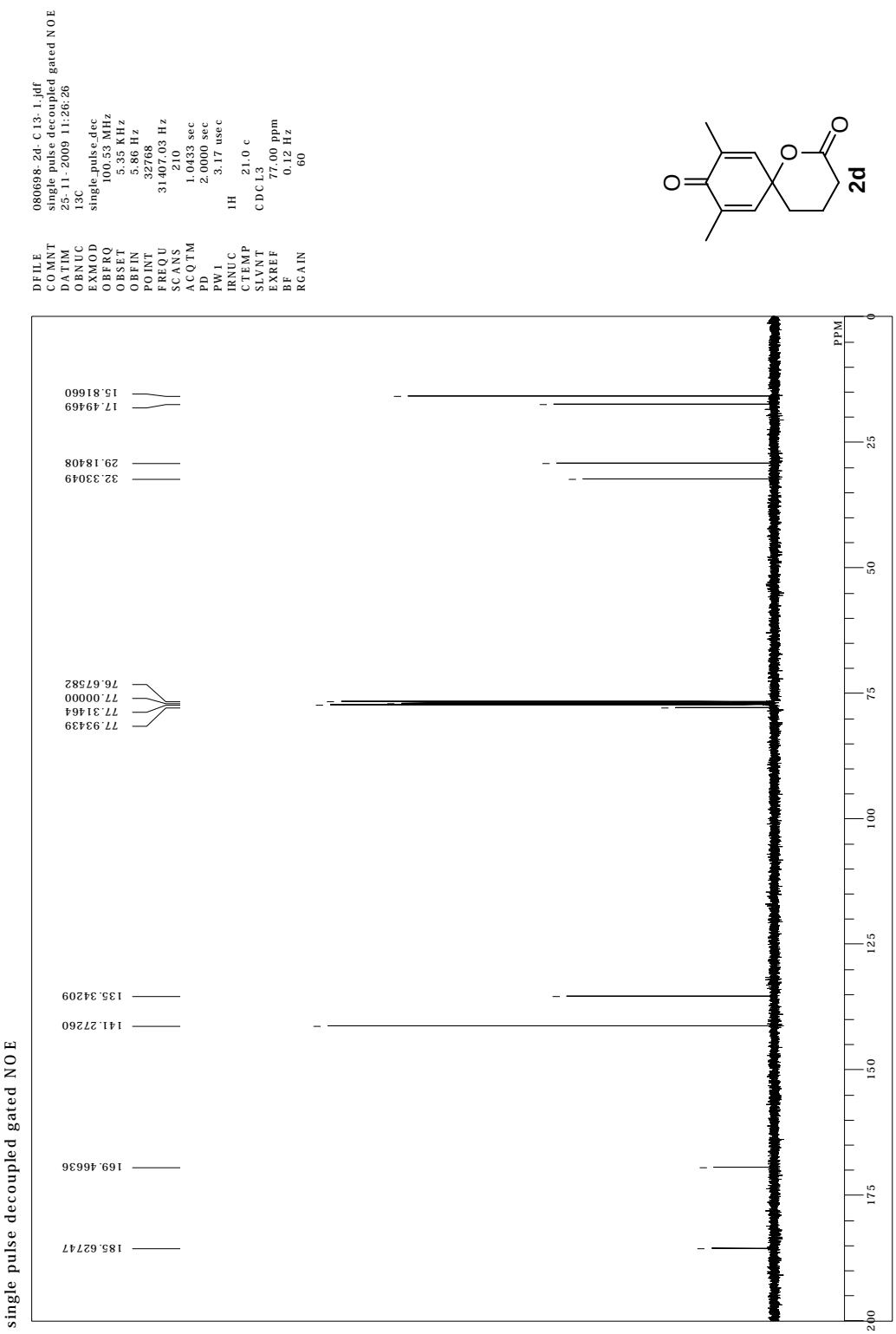
^{13}C NMR chart of Compound **2c**



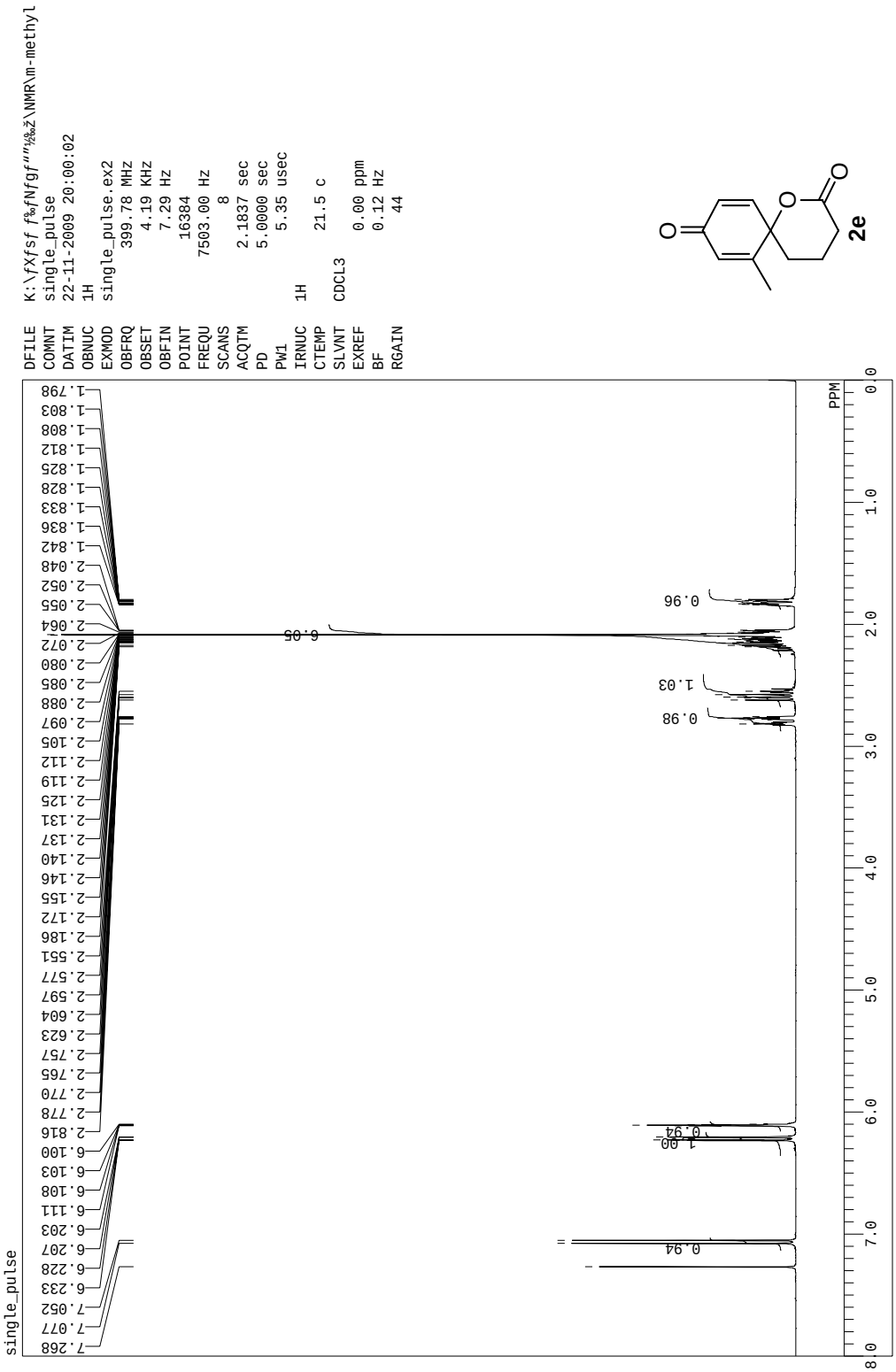
^{1}H NMR chart of Compound **2d**



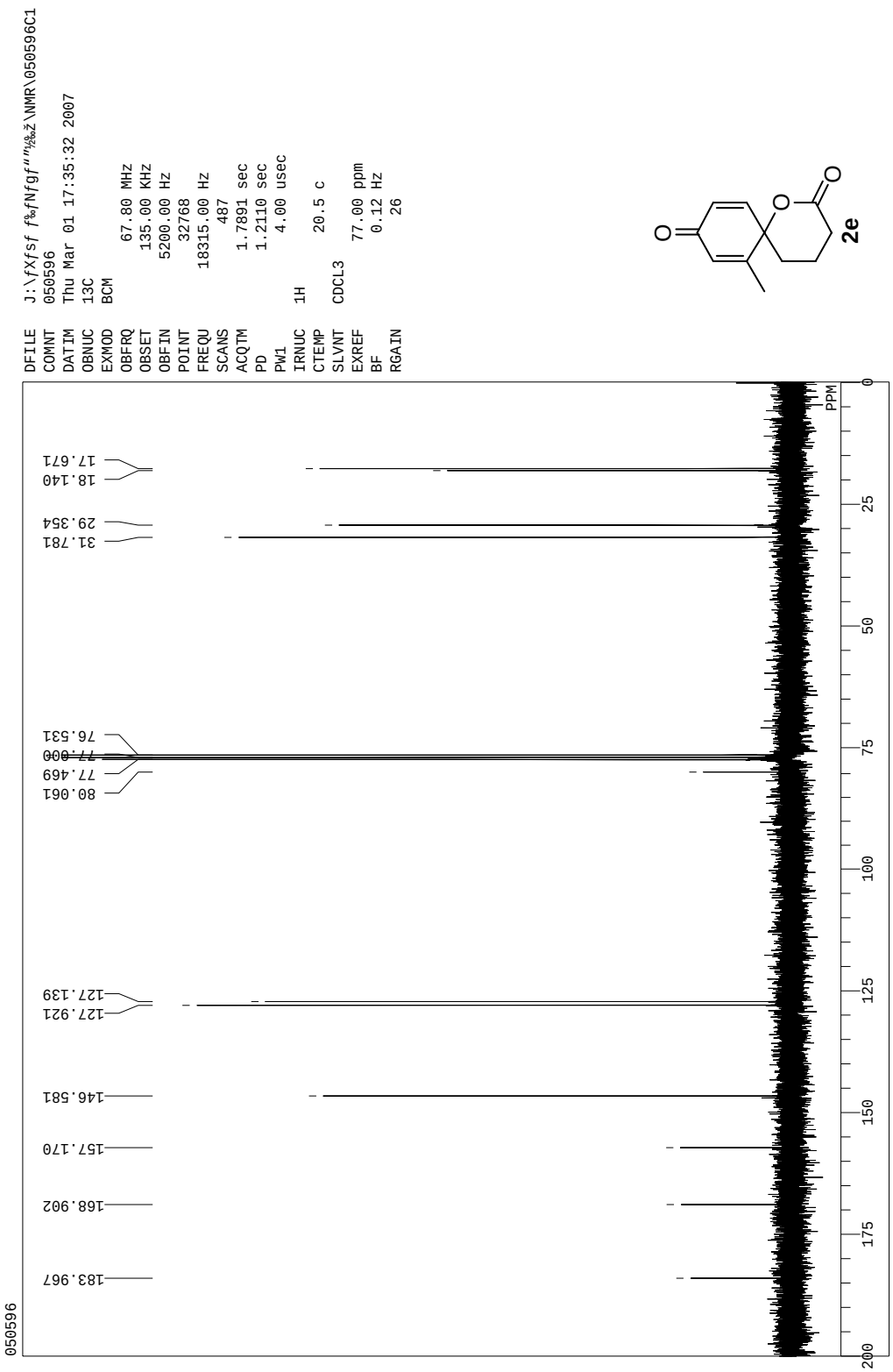
^{13}C NMR chart of Compound **2d**



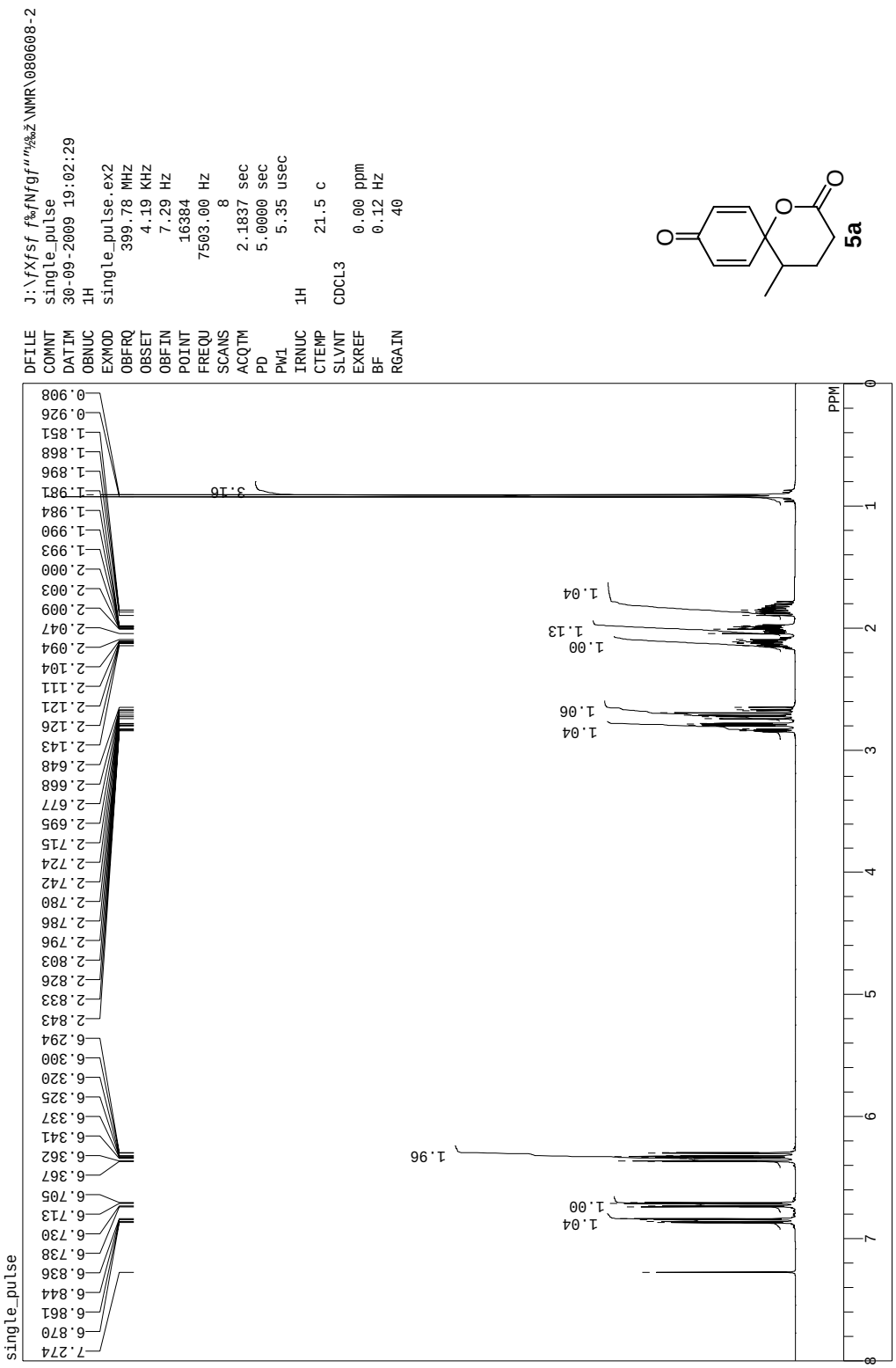
^{1}H NMR chart of Compound **2e**



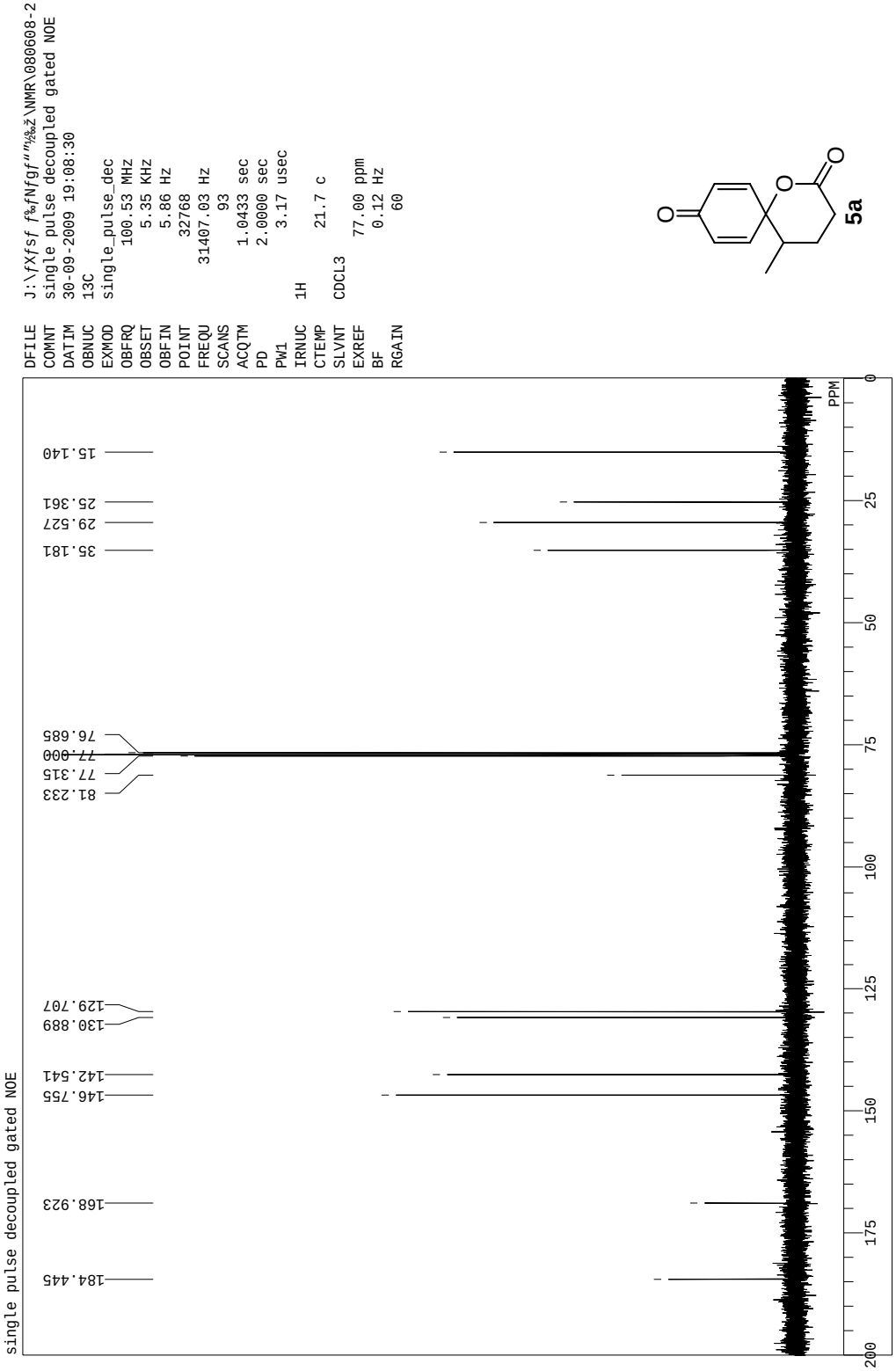
^{13}C NMR chart of Compound **2e**



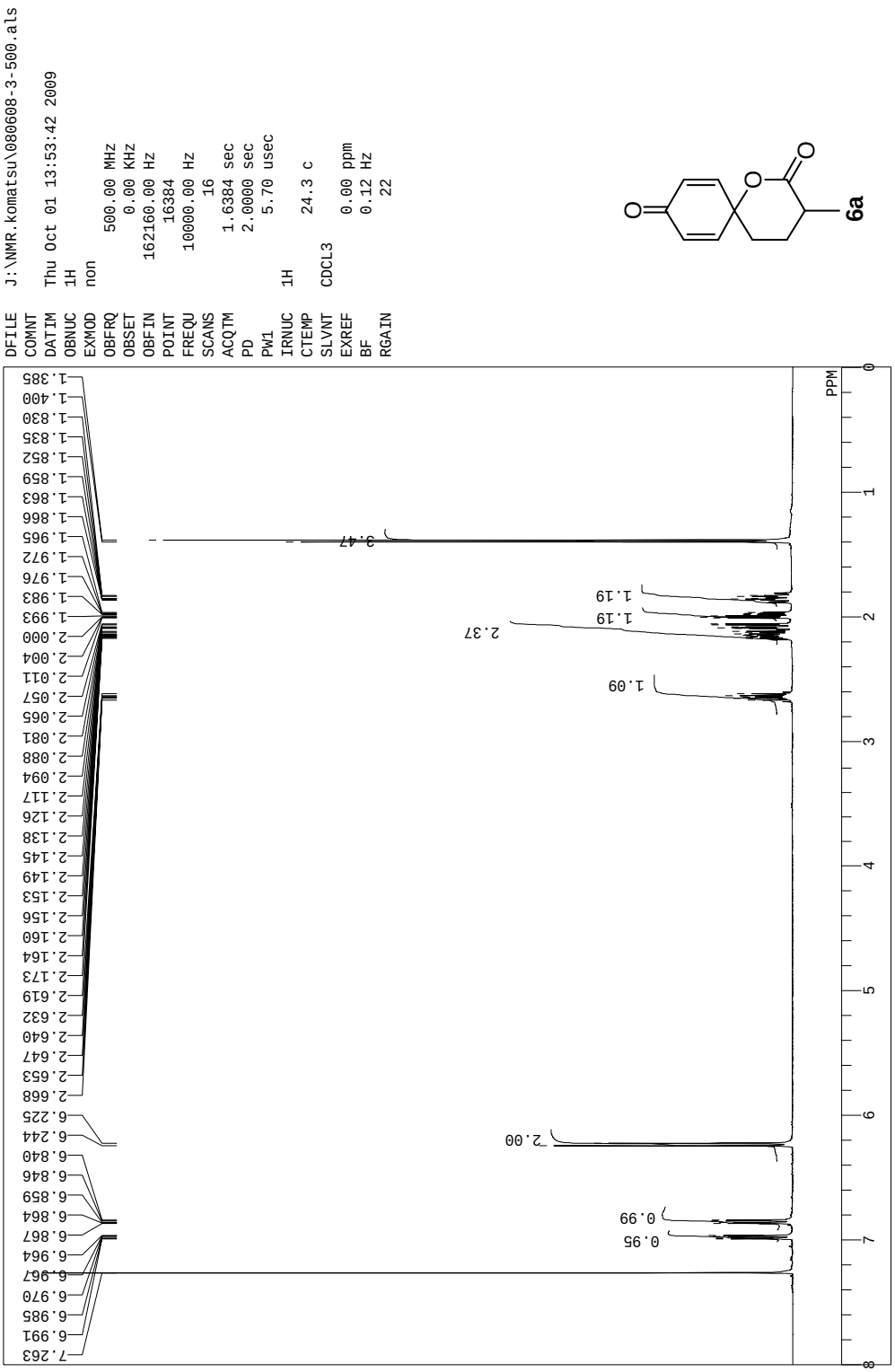
^{1}H NMR chart of Compound **5a**



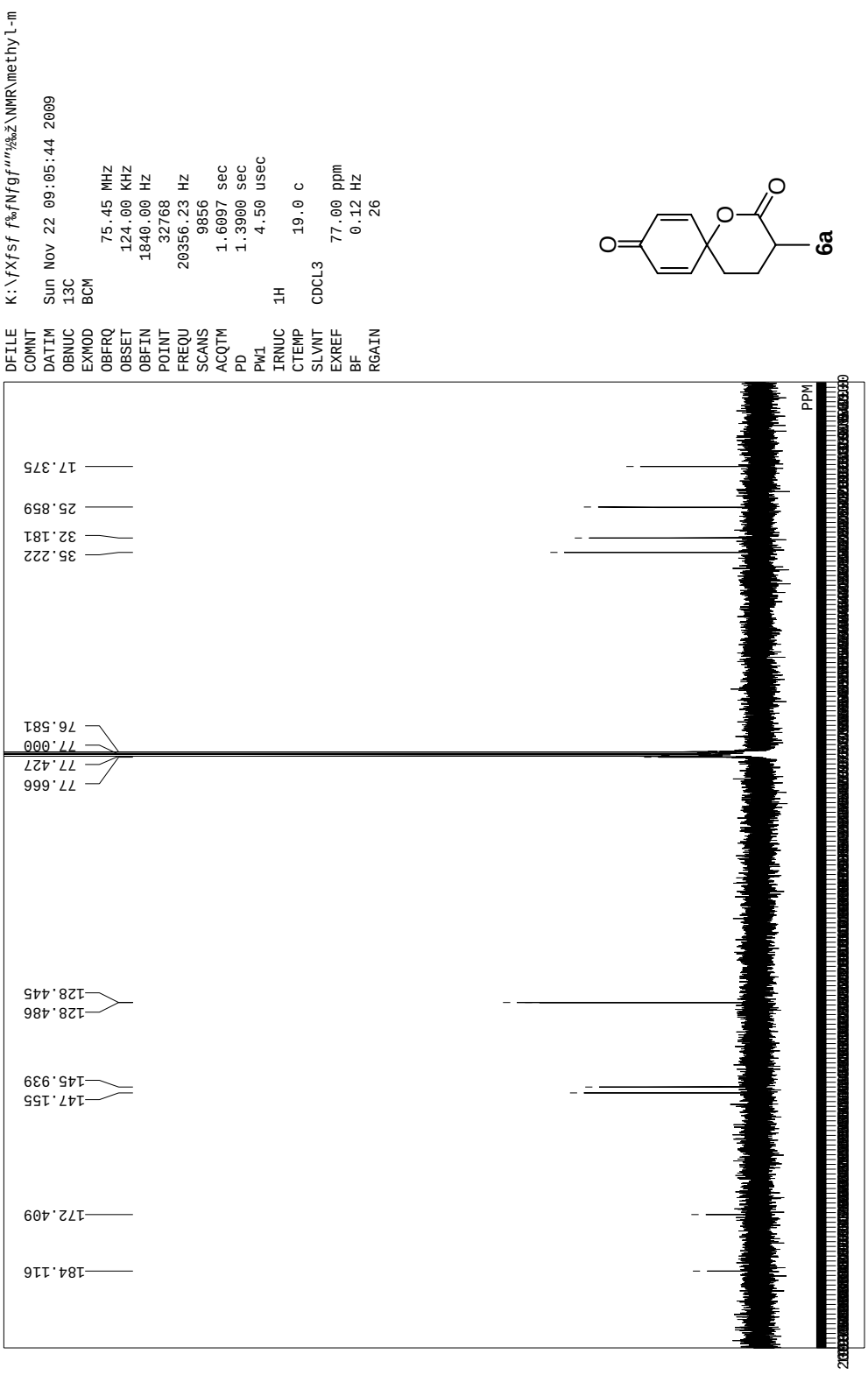
^{13}C NMR chart of Compound **4a**



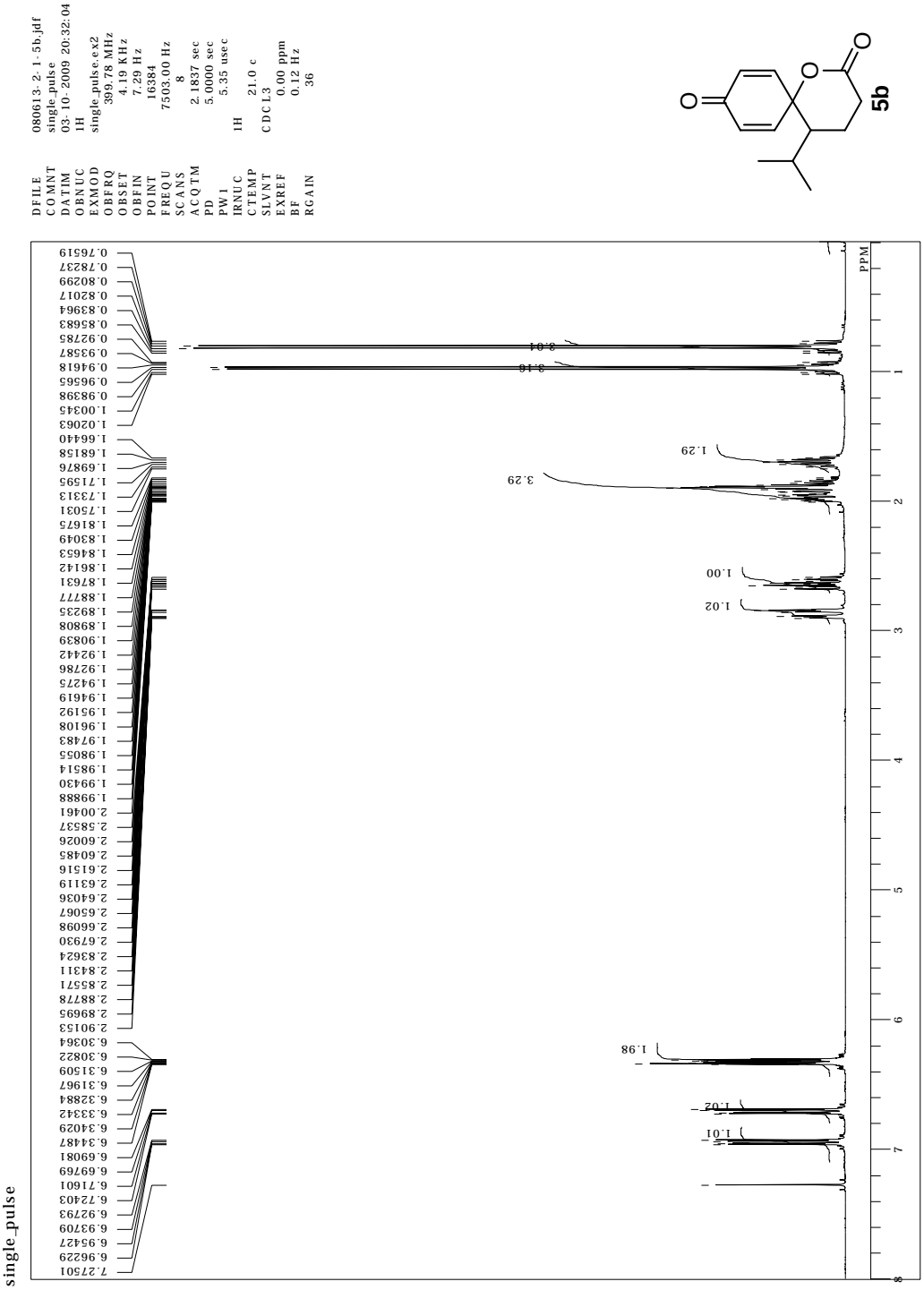
^{1}H NMR chart of Compound **6a**



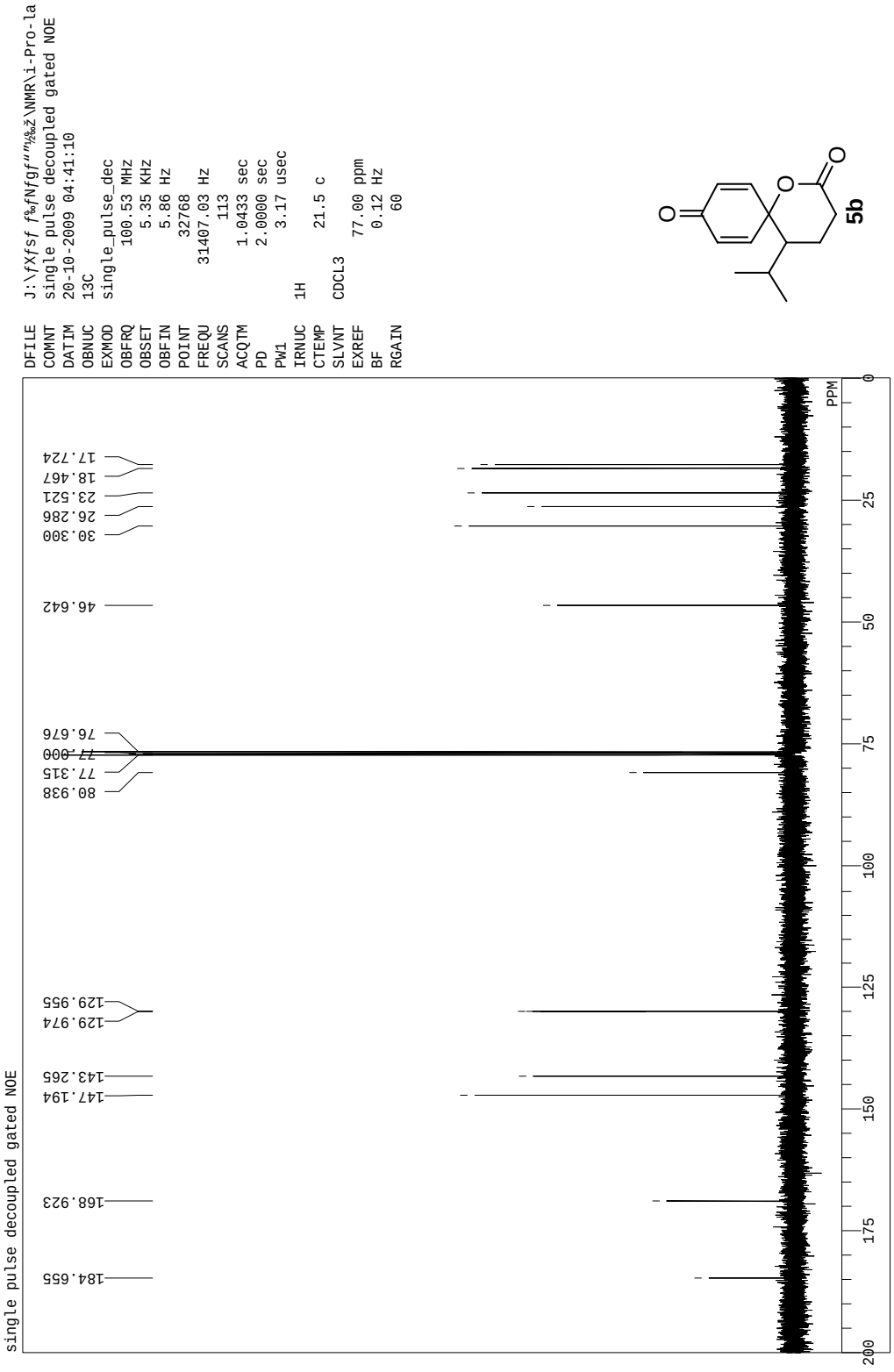
^{13}C NMR chart of Compound **6a**



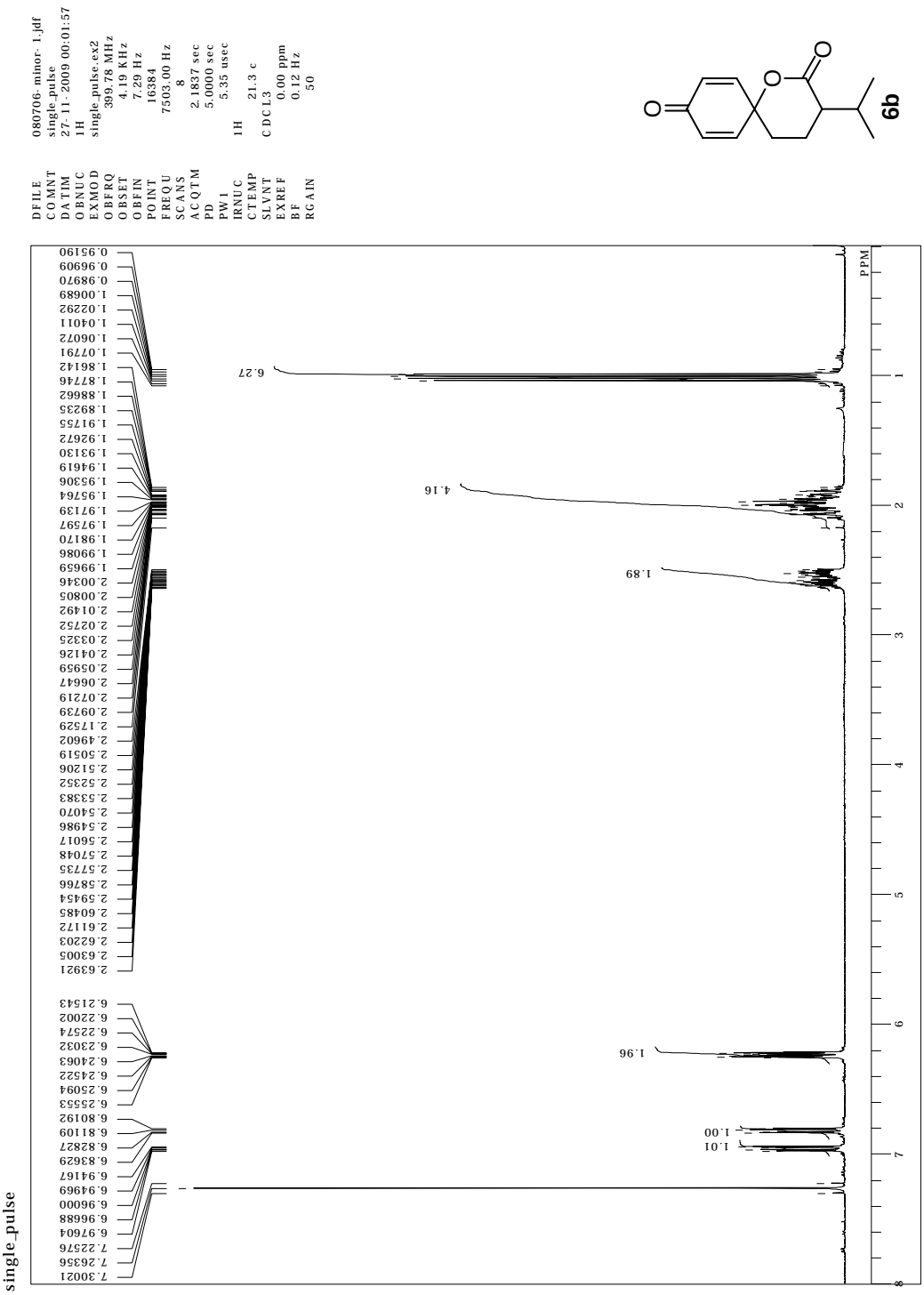
^{1}H NMR chart of Compound **5b**



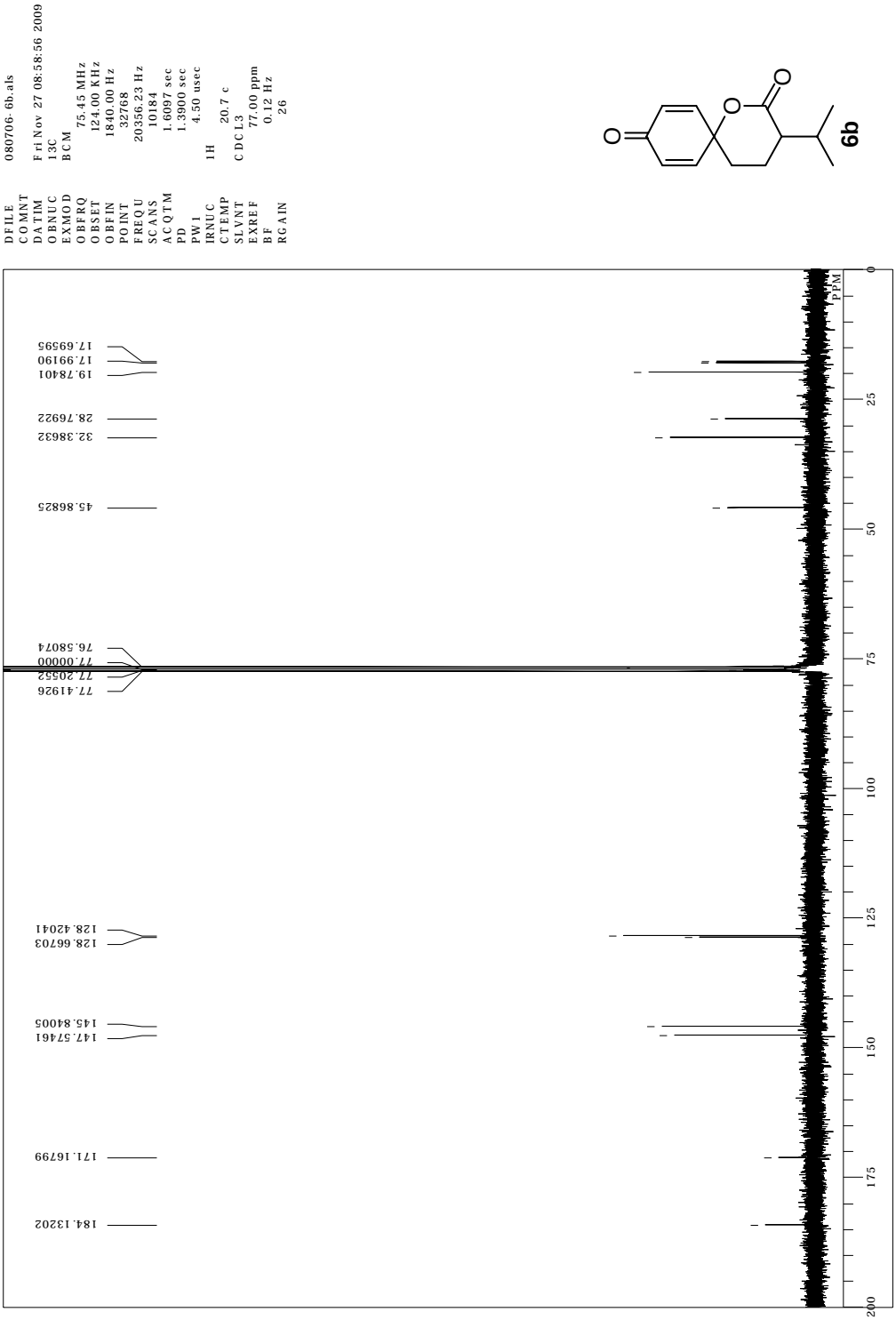
^{13}C NMR chart of Compound **5b**



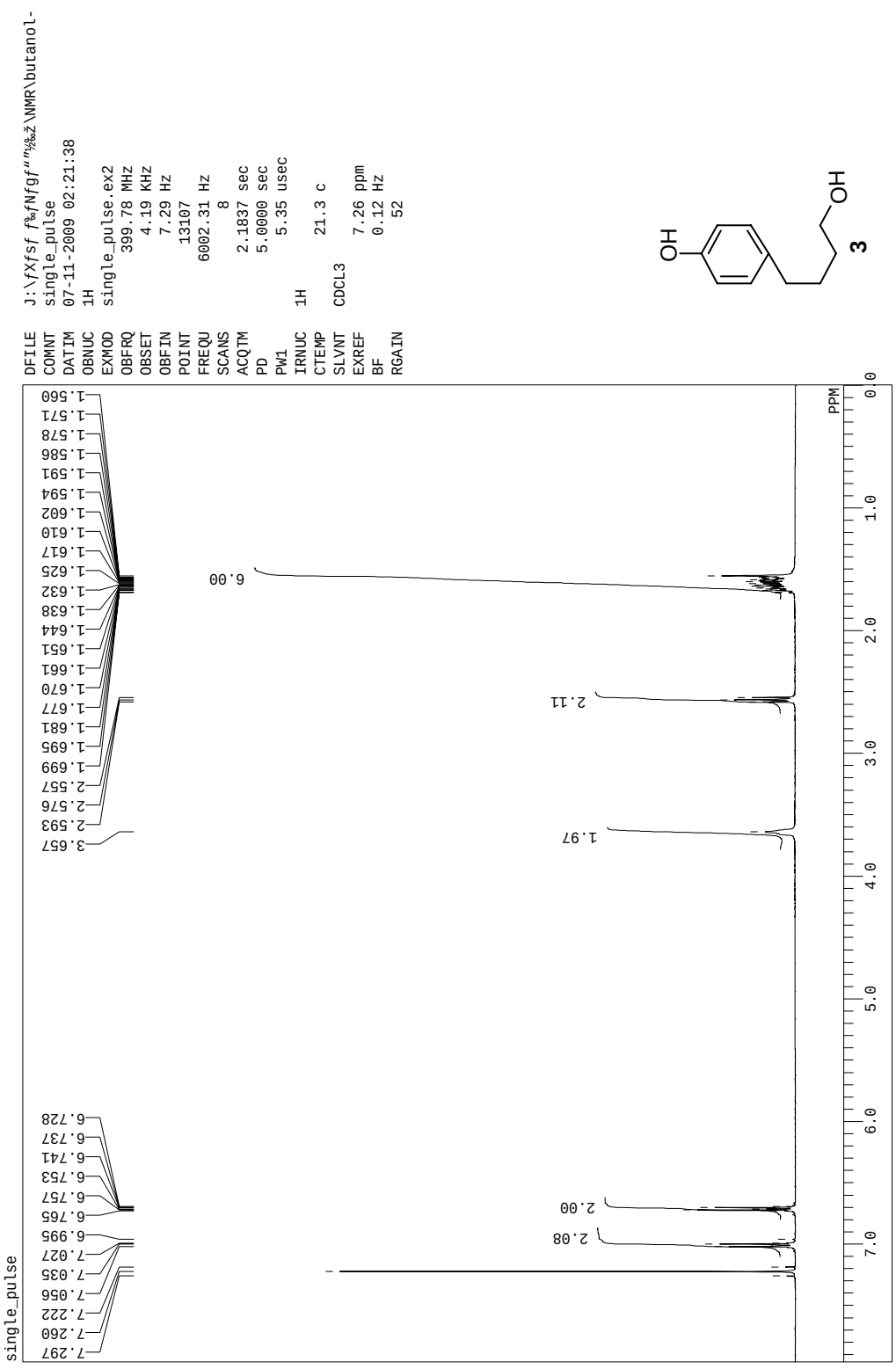
^{1}H NMR chart of Compound **6b**



^{13}C NMR chart of Compound **6b**



^{1}H NMR chart of Compound **3**



^{13}C NMR chart of Compound **3**