Quinine/Selectfluor Combination Induced Asymmetric Semipinacol Rearrangement of Allylic Alcohols: An Effective and Enantioselective Approach to α–Quaternary β–Fluoro Aldehydes

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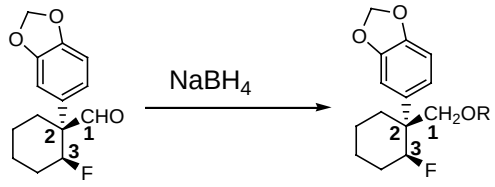
1. Determining the Absolute Configuration of 2a

Scheme 1. Determining the Absolute Configuration of **2a** Using Mosher's Method



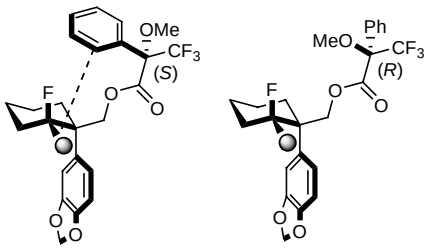
2a

3a R = H
4a R = (-)-MTPA
5a R = (+)-MTPA

The stereoselective of the β–fluoro aldehyde was determined by 1D NOE experiments of the product of entry **1** in Table **2**. The absolute configuration at C-3 of **2a** was achieved by ^{1}H-NMR analysis of (+) and (–)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA) esters [Mosher's (^{1}H) method]. The alcohol **3a**, obtained by reduction of **2a** with $NaBH_4$, was treated with an excess of (–) -MTPA and (+)-MTPA-Cl to yield (–)-MTPA (**4a**) and (+)-MTPA (**5a**) esters, respectively (Scheme 2). The fluoro proton signals of (+)-MTPA ester appear at δ (5.29) while in the spectrum of the (–)-MTPA ester they appear at δ (5.13). The stable conformation of the Mosher ester was depicted in Figure **1**. These observations are in agreement with an *S* configuration for **3a** at C-3 position, indicating that the absolute configuration of **2a** is (2*R*, 3*S*). Although we have not examined the

stereochemistry of all of the products in Table 2 one by one, we assume that the other products would have the same absolute configuration.

Figure 1. The Stable Conformation of the Mosher Ester



4a **5a**

Preparation of 3a.

A solution of 3.8mg (0.1mmol) of sodium borohydride in 1 mL of methanol was added to a stirring solution of 25mg (0.1 mmol) of the **2a** in methanol (2ml) at an ice bath temperature. After an additional 20 min the excess hydride was decomposed by addition of two drops of acetic acid. The solvent was evaporated under reduced pressure and the residue was taken up in ether. After washing the organic layer with water and brine and drying over Na_2SO_4, the solvent was evaporated. The residue was purified on a silica-gel layer chromatography to give 23mg (91%) of **3a**.

^{1}H NMR (300 MHz, $CDCl_3$): 6.87-6.81 (m, 3H), 5.96 (s, 2H), 5.24 (dd, ^1J= 47.4Hz, ^2J= 3.9Hz, 1H), 3.80 (J= 11.1Hz, 1 H), 3.51 (dd, ^1J= 11.1Hz, ^2J= 1.8Hz, 1H), 1.92-1.39 (m, 8H);

Note: ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on Varian Mercury-300 or Bruker ApexII 400 MHz. The MS data were obtained with EI (70 eV), and the relative intensity (%) is given in brackets. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of the SIMS or ESI technique.

Preparation of the Mosher Esters 4a and 5a.

Compound **3a** (4 mg) was esterified with (–)-α-methoxy-α-(trifluoromethyl)phenylacetic acid and DMAP (5mg) in dry CH_2Cl_2 (1 mL) at room temperature. After an additional 20 min, the solvent was evaporated under reduced pressure and the residue filtered through a short silica gel column with ether. The solvent was removed under

reduced pressure to give a crude oil, which was purified by preparative TLC on silica-gel to give **4a**.

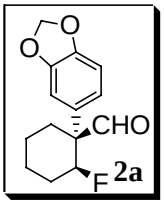
^{1}H NMR (400 MHz, $CDCl_3$): 7.37-7.21 (m, 5H), 6.75-6.68 (m, 3H), 5.93 (m, 2H), 5.13 (dd, *J*= 47.4Hz, 1H), 4.50 (d, *J*= 10.4Hz, 1H), 4.13 (dd, ^1J= 10.4Hz, ^2J= 2.4Hz, 1H), 3.37 (s, 3H), 2.17 (m, 2H), 2.00-1.57 (m, 6H);

Compound **3a** (4 mg) was esterified with (+)-α-methoxy-α-(trifluoromethyl) phenylacetyl chloride and DMAP (5mg) in dry toluene (3 mL) at refulx. After 24h, the solvent was evaporated under reduced pressure and the residue filtered through a short silica gel column with ether. The solvent was removed under reduced pressure to give a crude oil, which was purified by preparative TLC on silica-gel to give **5a**.

^{1}H NMR (400 MHz, $CDCl_3$): 7.54-6.68 (m, 5H), 6.75-6.68 (m, 3H), 5.96 (m, 2H), 5.29 (m, 1H), 4.48-4.16 (m, 2H), 3.50-3.38 (m, 3H), 2.17-1.30 (m, 8H);

2. Experimental Procedures and Spectroscopic and Analytical Data of the Products

Note: ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on Varian Mercury-300 or Bruker ApexII 400 MHz. The MS data were obtained with EI (70 eV), and the relative intensity (%) is given in brackets. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of the SIMS or ESI technique. Enantiometric determination was accomplished by Agilent 1100 HPLC using Chiralpak Ascolumn.

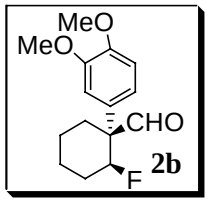


A typical experimental procedure for the fluorination of 1 a

A solution of **1a** (46.4 mg, 0.20 mmol) in CH_3CN (1ml) and K_2CO_3 (16.6 mg, 0.12 mmlol) were added to Quinine/Selectfluor combination [prepared in situ from quinine (90.7mg, 0.28mmol) and Selectfluor (95%, 99.1 mg, 0.28 mmol) in CH_3CN (2 ml) at room temperature for 30 minutes] in sequence at room temperature under Ar atmosphere. After stirring for 6 days, water was added to the reaction mixture and extracted with AcOEt. The organic phase washed with sat. NH_4Cl, sat. $NaHCO_3$, brine and dried over Na_2SO_4. The solvent was removed

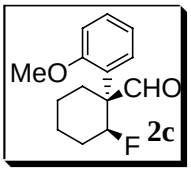
under reduced pressure to give a crude oil, which was purified by preparative TLC on silica-gel elute with 12% AcOEt in petro (60-90^{0}C) to give **2a** (18.5 mg, 39%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.59 (s, 1H), 6.85-6.78 (m, 3H), 5.96 (s, 2H), 5.32 (ddd, ^1J= 47.3Hz, ^2J= 7.6Hz, ^3J= 3.2Hz, 1H), 2.31-2.23 (m, 1H), 1.95-1.72 (m, 4H), 1.61-1.39 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 199.6, 148.4, 146.9, 129.5, 121.1, 108.6, 107.8, 101.2, 92.4 (d, ^1J= 176.0Hz), 57.7 (d, ^2J= 15.5 Hz), 28.6, 28.3 (d, ^2J= 19.8Hz), 21.7 (d, ^3J= 7.3Hz), 21.1; **MS** (70 eV): *m*/*z* (%): 250 (28) $[M]^+$, 221(13), 191(13), 153(33), 135(100), 115(14), 99(10), 55(11); **HRMS** (SIMS): *m*/*z* calcd for $C_{14}H_{19}NFO_3$: 268.1343; found: 268.1338$[M+NH_4]^+$ **; HPLC:** Chiralpak AS column, hexane/^{i}PrOH 95:5 1 mL/min, t_1= 14.3min(minor), t = 19.6 min(major) (74% ee)



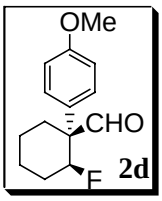
Fluorination of **1b** (49.6 mg, 0.20 mmol) in CH_3CN (1ml) and K_2CO_3 (16.6 mg, 0.12 mmlol) were added to Quinine/Selectfluor combination [prepared *in situ* from quinine (90.7 mg, 0.28 mmol) and Selectfluor (95%, 99.1 mg, 0.20 mmol) in CH_3CN (2 ml) at room temperature for 30 minutes] in sequence at room temperature under Ar atmosphere gave **2b** (22.3 mg, 42%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.62 (s, 1H), 6.94-6.83 (m, 3H), 5.37 (ddd, ^1J= 45.1Hz, ^2J= 7.6Hz, ^3J= 3.2Hz, 1H), 3.89-3.83(m, 3H), 2.36-2.28 (m, 1H), 2.10-1.93 (m, 1H), 1.92-1.81 (m, 2H), 1.80-1.75(m, 1H), 1.64-1.41 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 199.8, 149.3, 148.5, 128.2, 120.0, 111.4, 110.7, 92.5 (^1J= 176.0Hz), 57.7 (^2J= 17.5 Hz), 55.9, 55.8, 28.7, 28.5(^2J=19.9 Hz), 21.8 (^3J= 6.1Hz), 21.2; **MS** (70 eV): *m*/*z* (%): 266 (29) $[M]^+$, 237(100), 169(30), 151(83), 115(8.0), 99(12), 77(13), 55(9); **HRMS** (SIMS): *m*/*z* calcd for $C_{15}H_{23}NFO_3$: 284.1656 found:284.1652$[M+NH_4]^+$**; HPLC:** Chiralpak AS column, hexane/^{i}PrOH 95:5 1 mL/min, t_1= 12.7min(minor), t_2= 17.4 min(major) (73% ee)



Fluorination of **1c** (43.6 mg, 0.20 mmol) in CH_3CN (1ml) and K_2CO_3 (16.6 mg, 0.12 mmlol) were added to Quinine/Selectfluor combination [prepared *in situ* from quinine (90.7 mg, 0.28 mmol) and Selectfluor (95%, 99.1 mg, 0.20 mmol) in CH_3CN (2 ml) at room temperature for 30 minutes] in sequence at room temperature under Ar atmosphere gave **2c** (23.6 mg, 50%) as colorless crystal.

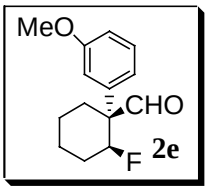
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s, 1H), 7.43-5.37 (m, 4H), 5.44 (ddd, ^1J= 47.6Hz, ^2J= 7.6Hz, ^3J= 3.6Hz, 1H), 3.77 (s, 3H), 2.39-2.33 (m, 1H), 1.94-1.81 (m, 4H), 1.74-1.68 (m, 1H), 1.61-1.55 (m, 1H), 1.47-1.40 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 202.8, 157.2, 129.0, 128.0, 121.3, 112.0, 92.6 (^1J= 175.6Hz), 56.1 (^2J= 16.8 Hz), 55.4, 29.1, 28.4 (^2J= 19.4 Hz), 22.1 (^3J= 8.0 Hz), 21.5; **MS** (70 eV): *m*/*z* (%): 236 (11) $[M]^+$, 188(49), 159(14), 145(19), 131(22), 121(100), 91(72), 77(36), 55(12); **HRMS** (SIMS): *m*/*z* calcd for $C_{14}H_{21}NFO_2$: 254.1551; found: 254.1552$[M+NH_4]^+$**; HPLC:** Chiralpak AS column, hexane/^{i}PrOH 95:5 1 mL/min, t_1= 8.6min(minor), t_2= 10.4 min(major) (71% ee)



Fluorination of **1d** (43.6 mg, 0.20 mmol) in CH_3CN (1ml) and K_2CO_3 (16.6 mg, 0.12 mmlol) were added to Quinine/Selectfluor combination [prepared *in situ* from quinine (90.7 mg, 0.28 mmol) and Selectfluor (95%, 99.1 mg, 0.20 mmol) in CH_3CN (2 ml) at room temperature for 30 minutes] in sequence at room temperature under Ar atmosphere gave **2d** (19.4 mg, 41%) as colorless oil.

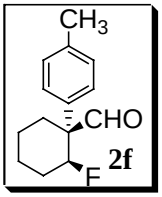
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.60 (s, 1H), 7.27-7.24, 6.93-6.90 (AA'BB', 4H), 5.38 (ddd, ^1J= 46.8 Hz, ^2J= 6.8 Hz, ^3J= 4.0Hz, 1H), 3.80 (s, 3H), 2.32-2.24 (m, 1H), 2.16-1.84 (m, 3H), 1.80-1.72 (m, 1H), 1.62-1.56 (m, 1H), 1.55-1.40 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 199.9, 158.9, 128.7, 127.7, 114.5, 92.5 (^1J= 175.7 Hz), 57.5 (^2J= 17.5 Hz), 55.2, 28.4 (^2J= 20.6 Hz), 21.8 (^3J= 5.7 Hz), 21.2; **MS** (70 eV): *m*/*z* (%): 236 (12) $[M]^+$,

207(86), 139(34), 121(100), 91(11), 77(14), 55(77); **HRMS** (SIMS): *m*/*z* calcd for $C_{14}H_{21}NFO_2$: 254.1551; found: 254.1548$[M+NH_4]^+$**; HPLC:** Chiralpak AS column, hexane/^{i}PrOH 95:5 1 mL/min, t_1= 10.6min(minor), t_2= 13.3 min(major) (76% ee)



Fluorination of **1e** (43.6 mg, 0.20 mmol) in CH_3CN (1ml) and K_2CO_3 (16.6 mg, 0.12 mmlol) were added to Quinine/Selectfluor combination [prepared *in situ* from quinine (90.7 mg, 0.28 mmol) and Selectfluor(95%, 99.1 mg, 0.20 mmol) in CH_3CN (2 ml) at room temperature for 30 minutes] in sequence at room temperature under Ar atmosphere gave **2e** (22.7 mg, 48%) as colorless oil.

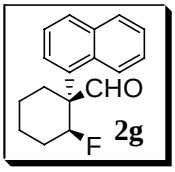
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.65 (s, 1H), 7.35-6.82 (m, 4H), 5.40 (ddd, ^1J= 46.7 Hz, ^2J= 7.4 z, ^3J= 3.4 Hz, 1H), 3.82 (s, 3H), 2.32-2.25 (m, 1H), 1.95-1.86 (m, 3H), 1.77-1.73(m, 1H), 1.62-1.55 (m, 1H), 1.52-1.41 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 199.9, 160.2, 137.6, 130.1, 119.8, 114.0, 112.5, 92.4 (^1J= 175.6 Hz), 58.3 (^2J=17.9 Hz), 55.3, 28.6, 28.4, 21.8 (^3J=6.1 Hz), 21.3; **MS** (70 eV): *m*/*z* (%): 236 (13) $[M]^+$, 207(31), 187(13), 163(26), 135(75), 121(100), 91(38), 77(78), 55(58); **HRMS** (SIMS): *m*/*z* calcd for $C_{14}H_{21}NFO_2$: 254.1551; found: 254.1555$[M+NH_4]^+$**; HPLC:** Chiralpak AS column, hexane/^{i}PrOH 95:5 1 mL/min, t_1= 8.4 min(minor), t_2= 11.7 min(major) (54% ee)



Fluorination of **1f** (40.4 mg, 0.20 mmol) in CH_3CN (1ml) and K_2CO_3 (16.6 mg, 0.12 mmlol) were added to Quinine/Selectfluor combination [prepared *in situ* from quinine (90.7 mg, 0.28 mmol) and Selectfluor (95%, 99.1 mg, 0.20 mmol) in CH_3CN (2 ml) at room temperature for 30 minutes] in sequence at room temperature under Ar atmosphere gave **2f** (15.4 mg, 35%) as colorless crystal.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.63(s, 1H), 7.25-7.20(m, 4H), 5.41(ddd, ^1J= 46.9Hz, ^2J=6.8Hz, ^3J=4.0Hz, 1H),

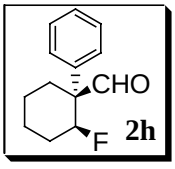
2.34 (s, 3H), 2.32-2.25 (m, 1H), 1.93-1.85 (m, 3H), 1.81-1.73 (m, 1H), 1.64-1.54 (m, 1H), 1.51-1.38 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 200.1, 137.5, 132.8, 129.9, 127.4, 92.4 (^1J=175.3 Hz), 57.9 (^2J= 17.1 Hz), 28.5, 28.3, 21.8 (^3J= 5.7 Hz), 21.2, 20.9; **MS** (70 eV): *m*/*z* (%): 220 (6) $[M]^+$, 191(56), 123(25), 105(100), 91(11), 77(9), 55(4); **HRMS** (SIMS): *m*/*z* calcd for $C_{14}H_{21}NFO$: 238.1602; found: 238.1606$[M+NH_4]^+$**; HPLC:** Chiralpak AS column, hexane/^{i}PrOH 95:5 1 mL/min, t_1 = 6.3min(minor), t_2= 7.8 min(major) (70% ee)



2g

Fluorination of **1g** (47.6 mg, 0.20 mmol) in CH_3CN (1ml) and K_2CO_3 (16.6 mg, 0.12 mmlol) were added to Quinine/Selectfluor combination [prepared *in situ* from quinine (90.7 mg, 0.28 mmol) and Selectfluor (95%, 99.1 mg, 0.20 mmol) in CH_3CN (2 ml) at room temperature for 30 minutes] in sequence at room temperature under Ar atmosphere gave **2g** (23.0 mg, 45%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.91 (s, 1H), 7.99-7.96 (m, 1H), 7.89-7.84 (m, 2H), 7.77-7.76 (m, 1H), 7.55-7.51 (m, 1H), 7.49-7.44 (m, 2H), 5.56 (ddd, ^1J= 46.1Hz, ^2J= 9.4 Hz, ^3J= 3.4 Hz, 1H), 2.79-2.75 (m, 1H), 2.17-2.10 (m, 1H), 2.08-1.95 (m, 2H), 1.93-1.78 (m, 2H), 1.52-1.44 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 203.7, 134.9, 133.8, 131.4, 129.6, 129.4, 126.2, 125.8, 125.5, 125.3, 124.9, 93.3 (^1J= 177.6 Hz), 59.1 (^2J= 16.4 Hz), 31.1, 28.8 (^2J= 20.4 Hz), 22.6 (^3J= 6.5 Hz), 21.5; **MS** (70 eV): *m*/*z* (%): 256 (18) $[M]^+$, 227(35), 207(22), 165141(100), 99(14), 77(15), 55(13); **HRMS** (SIMS): *m*/*z* calcd for $C_{17}H_{21}NFO$: 274.1602; found: 274.1599$[M+NH_4]^+$**; HPLC:** Chiralpak AS column, hexane/^{i}PrOH 99:1 0.5 mL/min, t_1 = 16.6min(minor), t_2= 18.6 min(major) (82% ee)

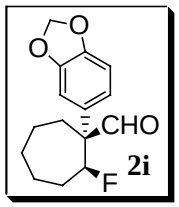


2h

Fluorination of **1h** (37.6 mg, 0.20 mmol) in CH_3CN (1ml) and K_2CO_3 (16.6 mg, 0.12 mmlol) were added to Quinine/Selectfluor combination [prepared *in situ* from quinine (90.7 mg, 0.28 mmol) and Selectfluor(95%, 99.1

mg, 0.20 mmol) in CH_3CN (2 ml) at room temperature for 30 minutes] in sequence at room temperature under Ar atmosphere gave **2h** (13.6 mg, 33%) as colorless oil.

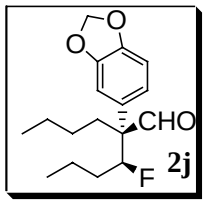
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.67 (s, 1H), 7.42-7.26(m, 5H), 5.43 (ddd, ^1J= 46.8 Hz, ^2J= 7.6 Hz, ^3J= 3.6Hz, 1H), 2.25-2.29 (m, 1H), 1.97-1.87 (m, 3H), 1.81-1.75 (m, 1H), 1.64-1.56 (m, 1H), 1.53-1.42 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 200.1, 136.1, 129.1, 127.7, 127.5, 92.5 (^1J= 176.4 Hz), 58.3 (^2J= 17.6 Hz), 28.7, 28.5 (^2J= 19.9 Hz), 21.9 (^3J= 6.1 Hz), 21.2, 20.9; **MS** (70 eV): *m*/*z* (%): 206 (6.0) $[M]^+$, 177(50), 158(28), 129(21), 115(27), 109(31), 91(100), 77(16), 55(4.0); **HRMS** (SIMS): *m*/*z* calcd for $C_{13}H_{19}NFO$: 224.1445; found: 224.1442$[M+NH_4]^+$**; HPLC:** Chiralpak AS column, hexane/^{i}PrOH 95:5 1 mL/min, t_1 = 6.6min(minor), t_2= 7.8 min(major) (67% ee)



2i

Fluorination of **1i** (49.2 mg, 0.20 mmol) in CH_3CN (1ml) and K_2CO_3 (16.6 mg, 0.12 mmlol) were added to Quinine/Selectfluor combination [prepared *in situ* from quinine (90.7 mg, 0.28 mmol) and Selectfluor(95%, 99.1 mg, 0.20 mmol) in CH_3CN (2 ml) at room temperature for 30 minutes] in sequence at room temperature under Ar atmosphere gave **2i** (18.0 mg, 34%) as colorless oil.

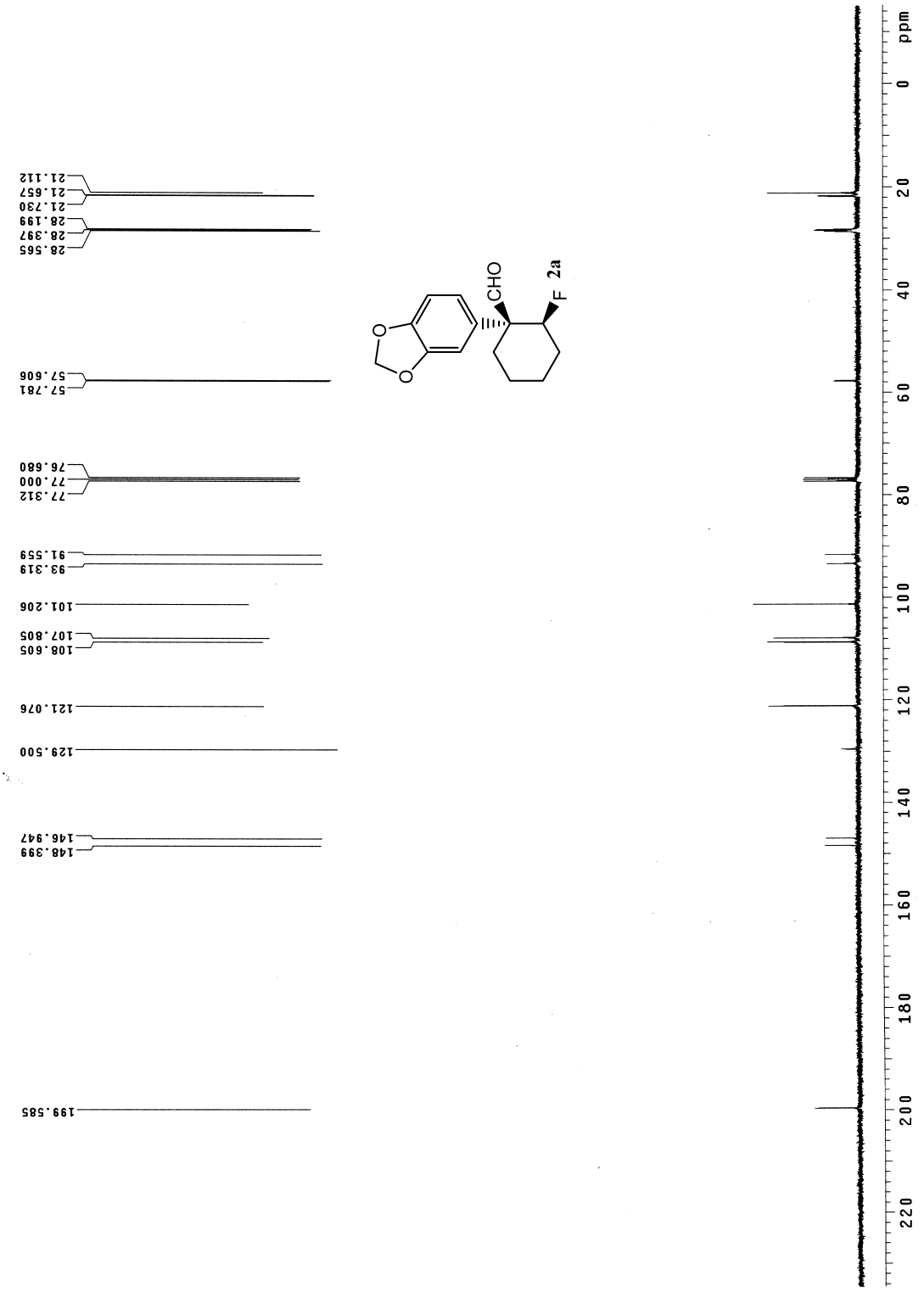
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.52 (s, 1H), 6.82-6.70 (m, 3H), 5.96 (s, 2H), 5.44 (ddd, ^1J= 45.3 Hz, ^2J= 8.0 Hz, ^3J= 2.0 Hz, 1H), 2.35-2.27 (m, 2H), 2.10-1.93 (m, 2H), 1.82-1.77 (m, 1H), 1.71-1.67 (m, 1H), 1.54-1.41(m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 199.1(^3J=9.1Hz), 148.4, 146.9, 130.7, 121.1, 108.7, 108.0, 101.3, 95.4(^1J= 171.9 Hz), 60.9 (^2J= 19.8 Hz), 30.7 (^2J= 21.3 Hz), 28.4, 27.6, 22.4 (^3J= 8.8 Hz), 22.1; **MS** (70 eV): *m*/*z* (%): 264 (9.0) $[M]^+$, 235(33), 177(11), 153(82), 135(100), 121(17), 91(14), 77(21), 55(18); **HRMS** (SIMS): *m*/*z* calcd for $C_{15}H_{21}NFO_3$: 282.1500; found: 282.1501$[M+NH_4]^+$**; HPLC:** Chiralpak AS column, hexane/^{i}PrOH 95:5 1 mL/min, t_1 = 14.9min(minor), t_2= 18.9 min(major) (65% ee)



Fluorination of **1j** (55.2 mg, 0.20 mmol) in CH_3CN (1ml) and K_2CO_3 (16.6 mg, 0.12 mmlol) were added to Quinine/Selectfluor combination [prepared *in situ* from quinine (90.7 mg, 0.28 mmol) and Selectfluor(95%, 99.1 mg, 0.20 mmol) in CH_3CN (2 ml) at room temperature for 30 minutes] and in sequence at room temperature under Ar atmosphere gave **2j** (21.8 mg, 37%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.69 (d, ^3J=4.8Hz, 1H), 6.82-6.57 (m, 3H), 5.97 (s, 2H), 4.96 (ddd, ^1J= 47.5 Hz, ^2J= 9.2 Hz, ^3J= 1.6 Hz, 1H), 2.14-2.07 (m, 1H), 1.93-1.87 (m, 1H), 1.56-1.48(m, 1H), 1.42-1.09 (m, 7H), 0.90-0.82 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 202.0, 148.2, 147.0, 130.1, 121.6, 108.5, 108.3, 101.2, 94.4 (^1J= 175.3 Hz), 60.7 (^2J= 19.4 Hz), 33.2 (^2J= 27.0Hz), 31.9 (^3J= 5.3 Hz), 26.1, 23.4, 19.2, 13.8, 13.7; **MS** (70 eV): *m*/*z* (%): 294 (6) $[M]^+$, 265(18), 209(21), 153(20), 135(100), 91(14), 55(16); **HRMS** (SIMS): *m*/*z* calcd for $C_{17}H_{27}NFO_3$: 312.1969; found: 312.1967$[M+NH_4]^+$**;** **HPLC:** Chiralpak AS column, hexane/^{i}PrOH 99:1 1 mL/min, t_1 = 5.7min(minor), t_2= 6.1 min(major) (61% ee)

3. Copies of NMR Spectra of the Products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101.206
107.805
108.605
121.076
129.500
146.947
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60
80
100
120
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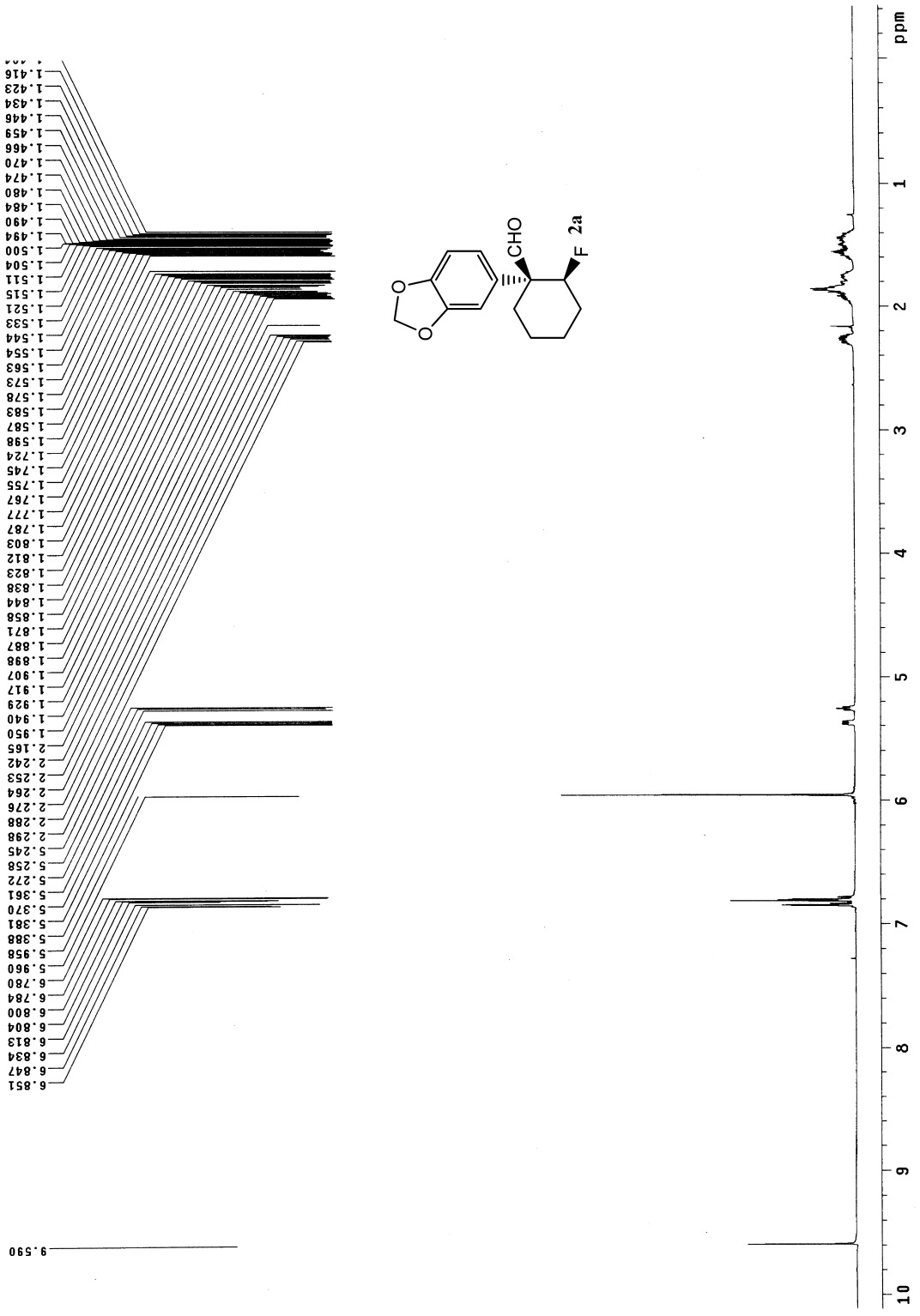
180
200
220
ppm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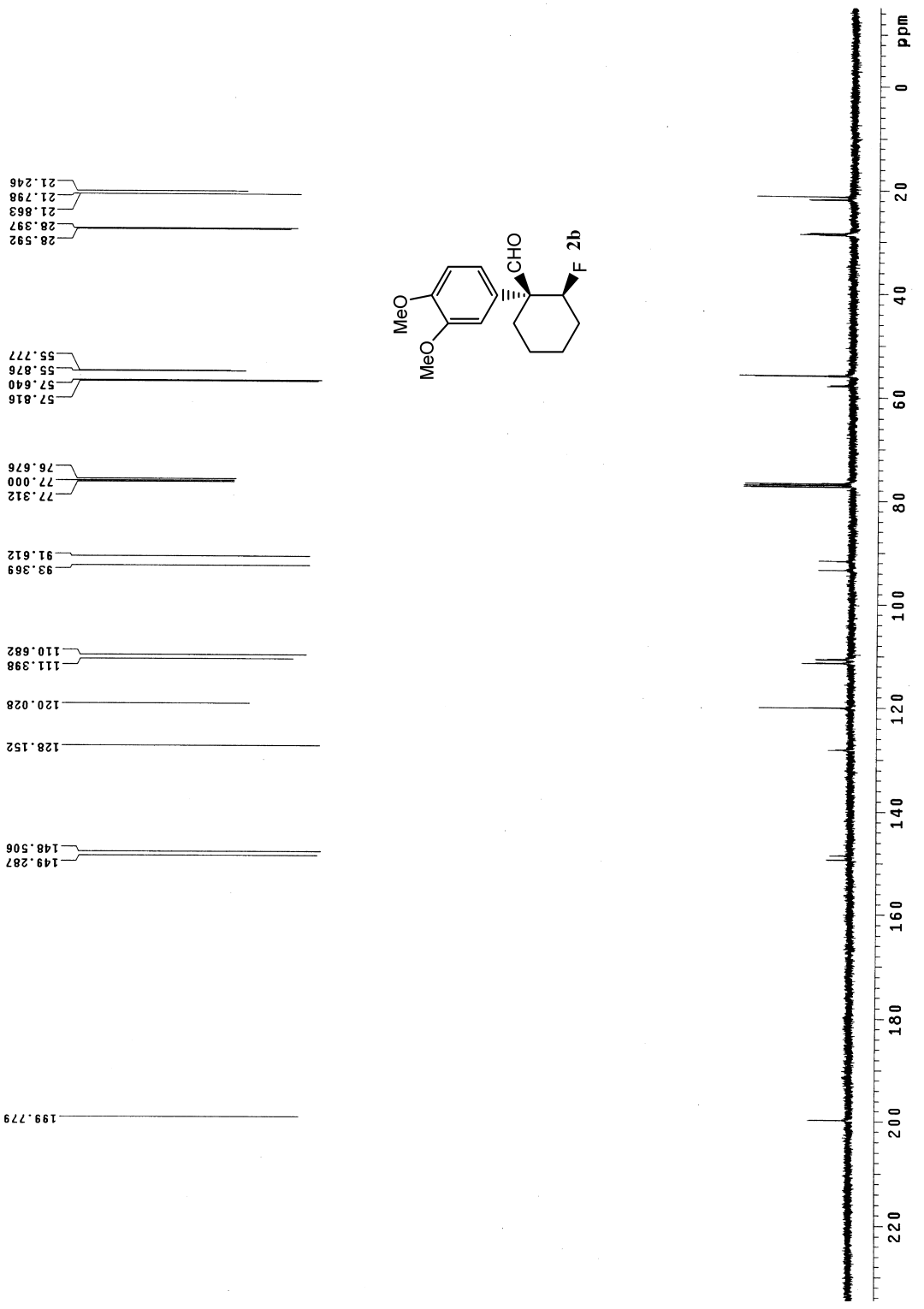
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93.369
110.682
111.398
120.028
128.152
148.506
149.287
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2b
ppm
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200
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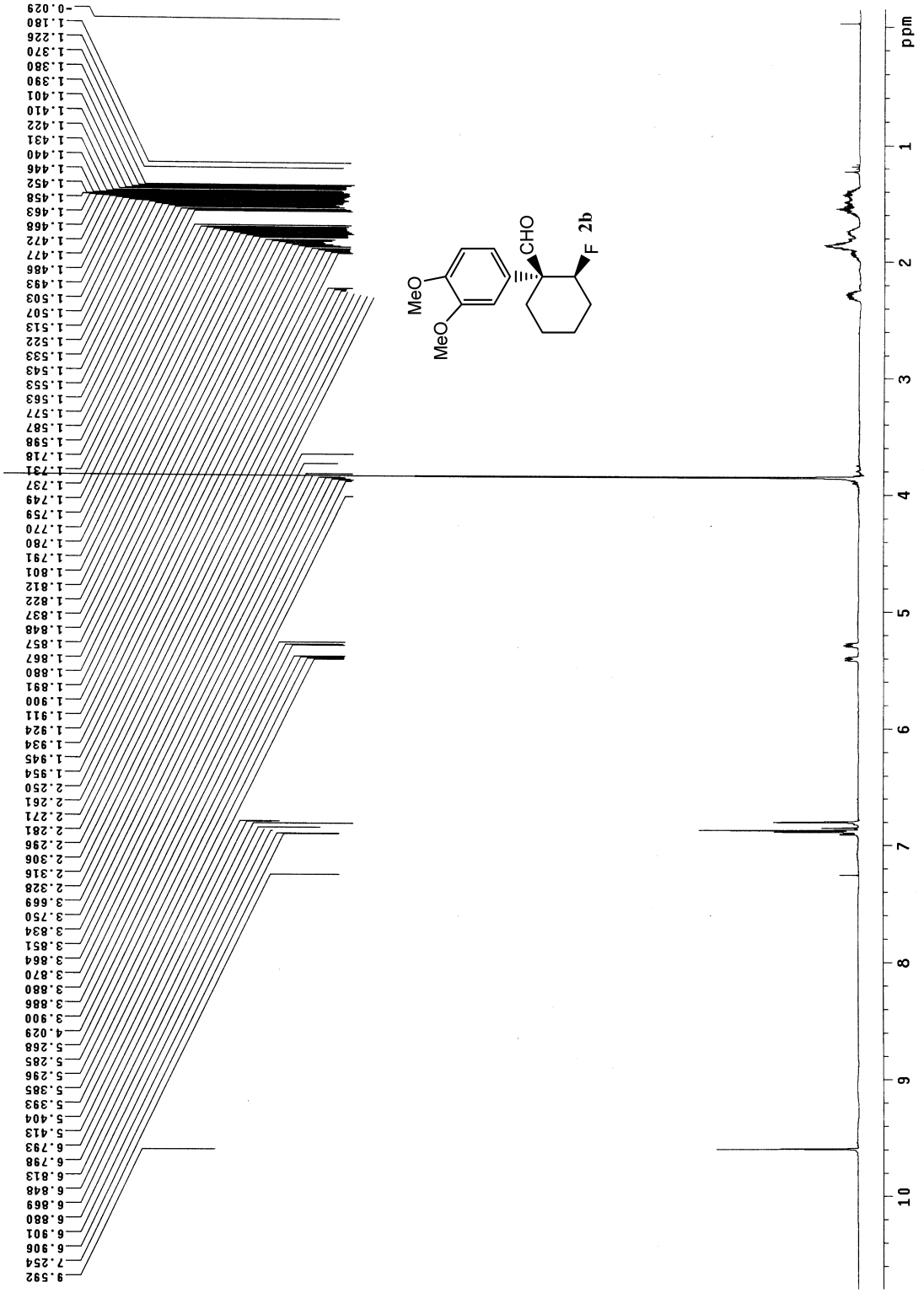
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MeO
CHO
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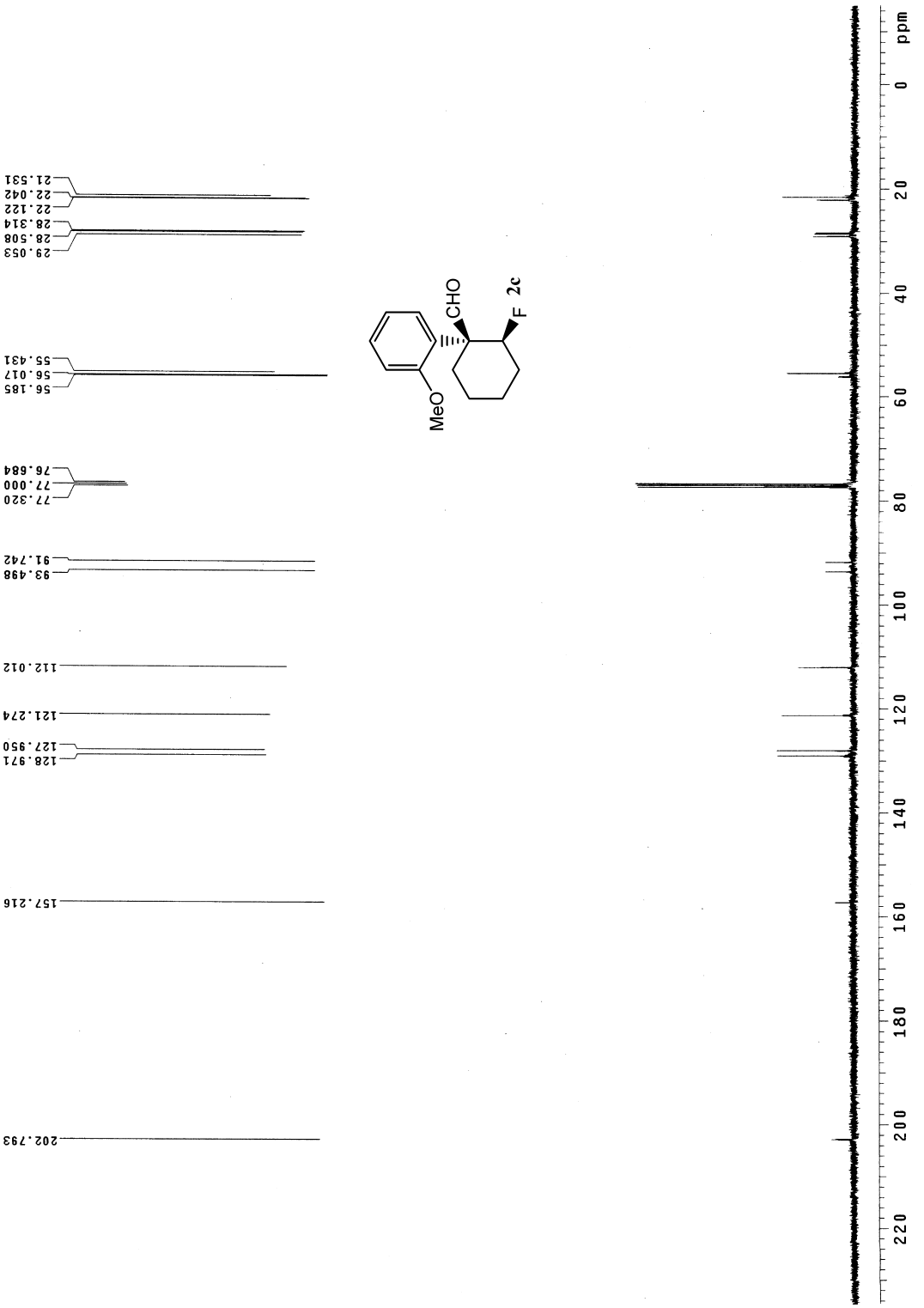
2b
ppm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80
100
120
140
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180
200
220
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28.314
28.508
29.053
55.431
56.017
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77.320
91.742
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112.012
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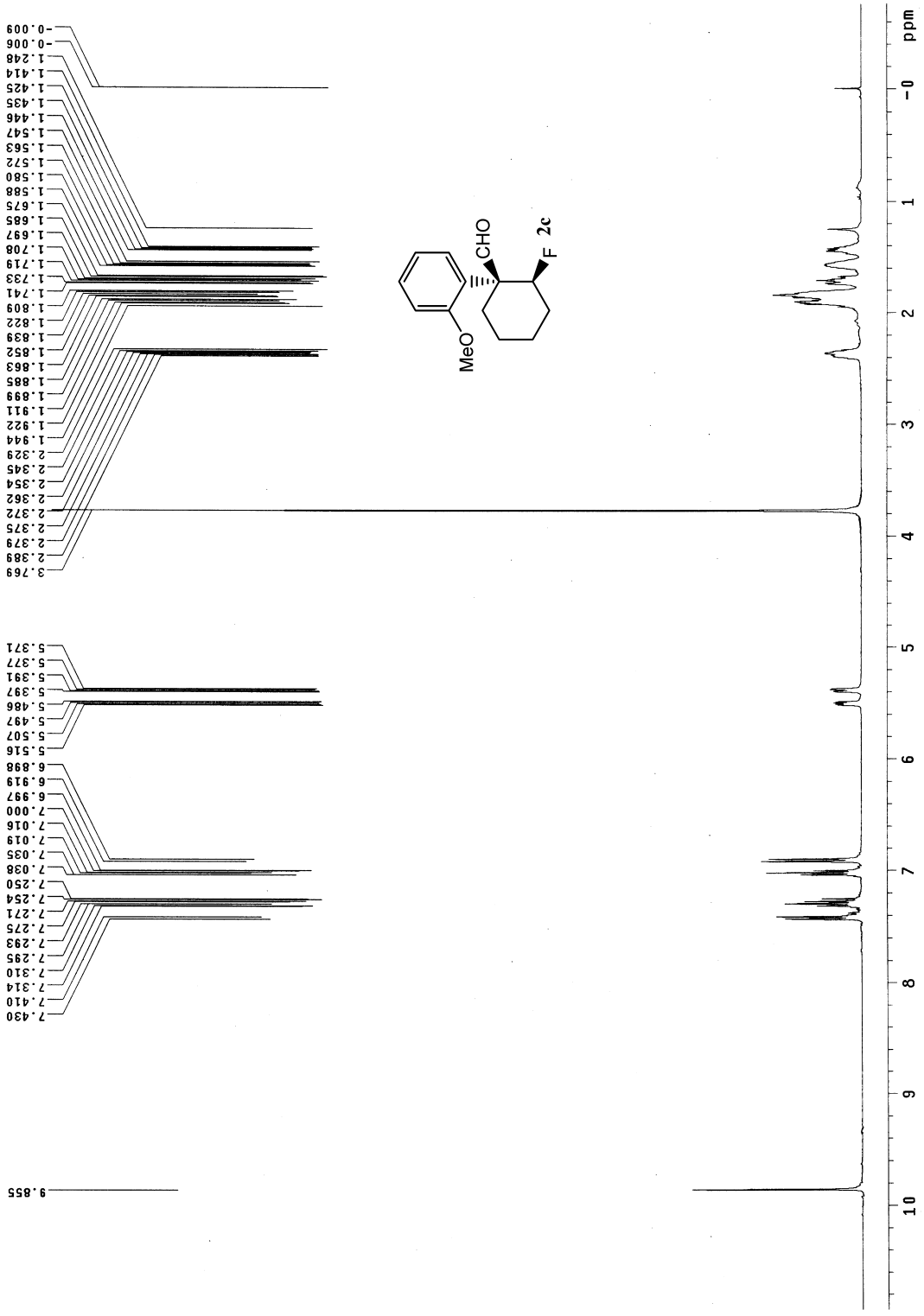
202.793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1.708
1.719
1.733
1.741
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1.822
1.839
1.852
1.863
1.885
1.899
1.911
1.922
1.944
2.329
2.345
2.354
2.362
2.372
2.375
2.379
2.389
3.769
5.371
5.377
5.391
5.397
5.486
5.497
5.507
5.516
6.898
6.919
6.997
7.000
7.016
7.019
7.035
7.038
7.250
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7.271
7.275
7.293
7.295
7.310
7.314
7.410
7.430
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F
2e
MeO
ppm
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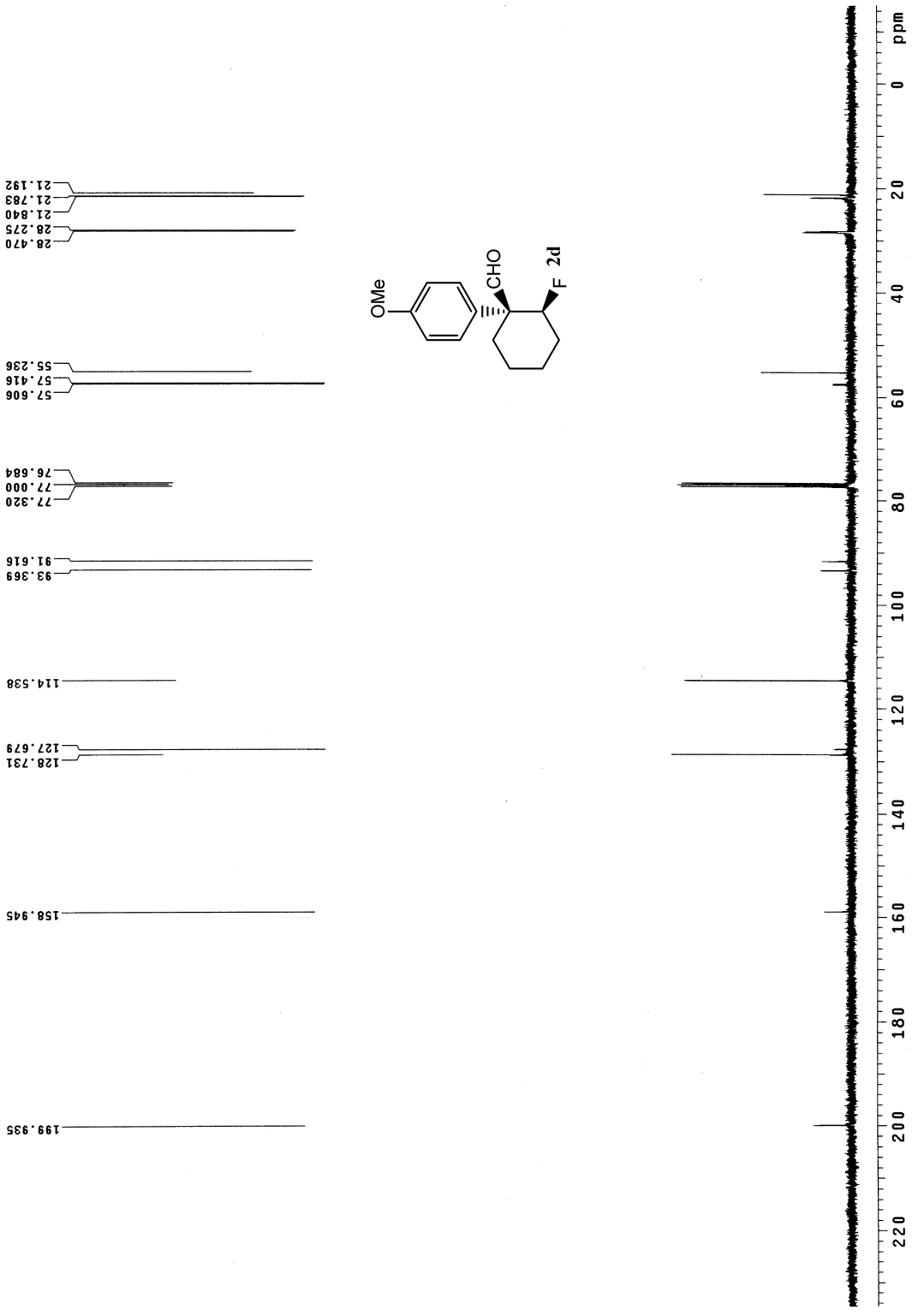
2
3
4
5
6
7
8
9
10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180
200
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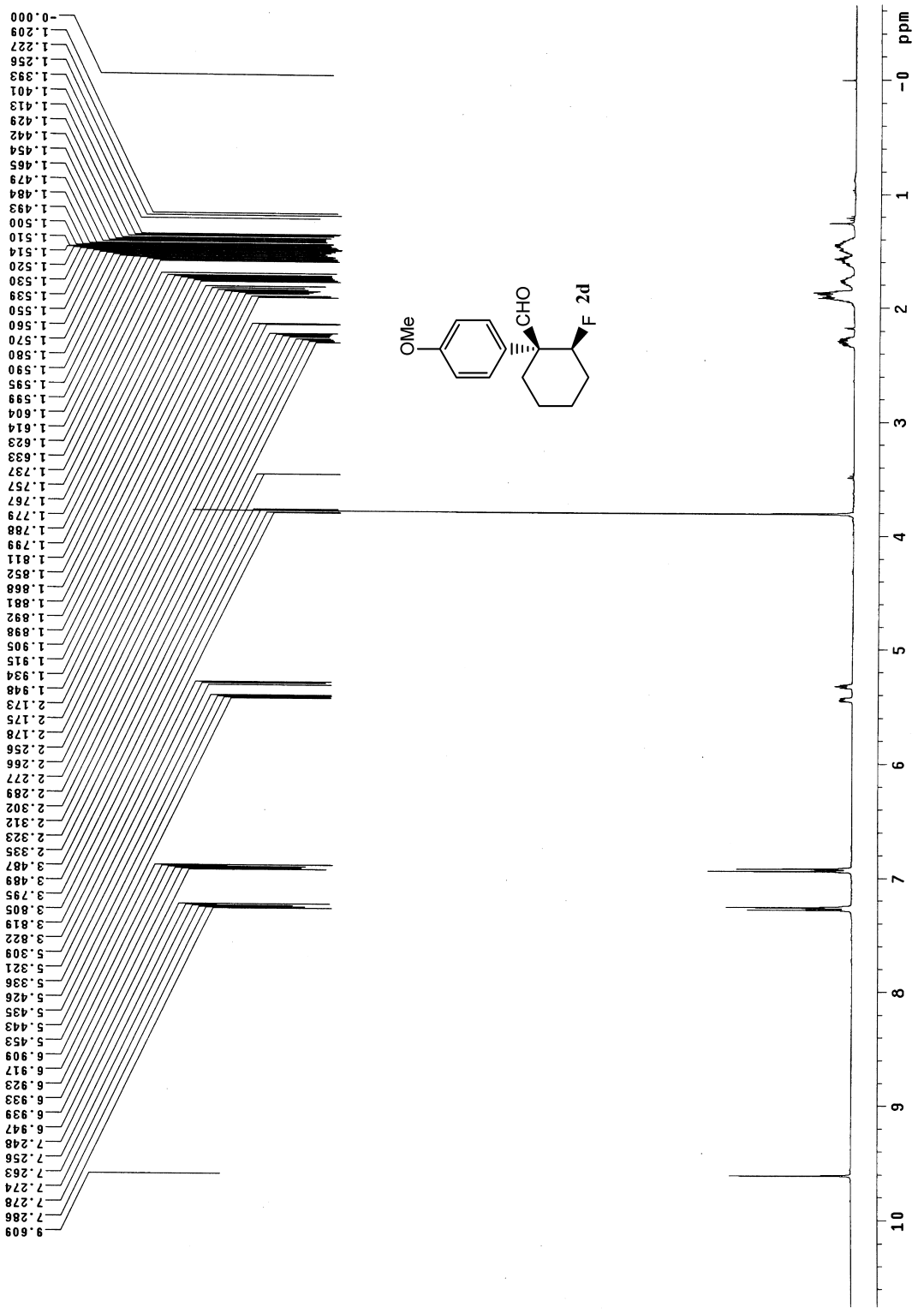
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2d
ppm

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114.046
119.765
130.102
137.616
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F
2e
ppm
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60
80
100
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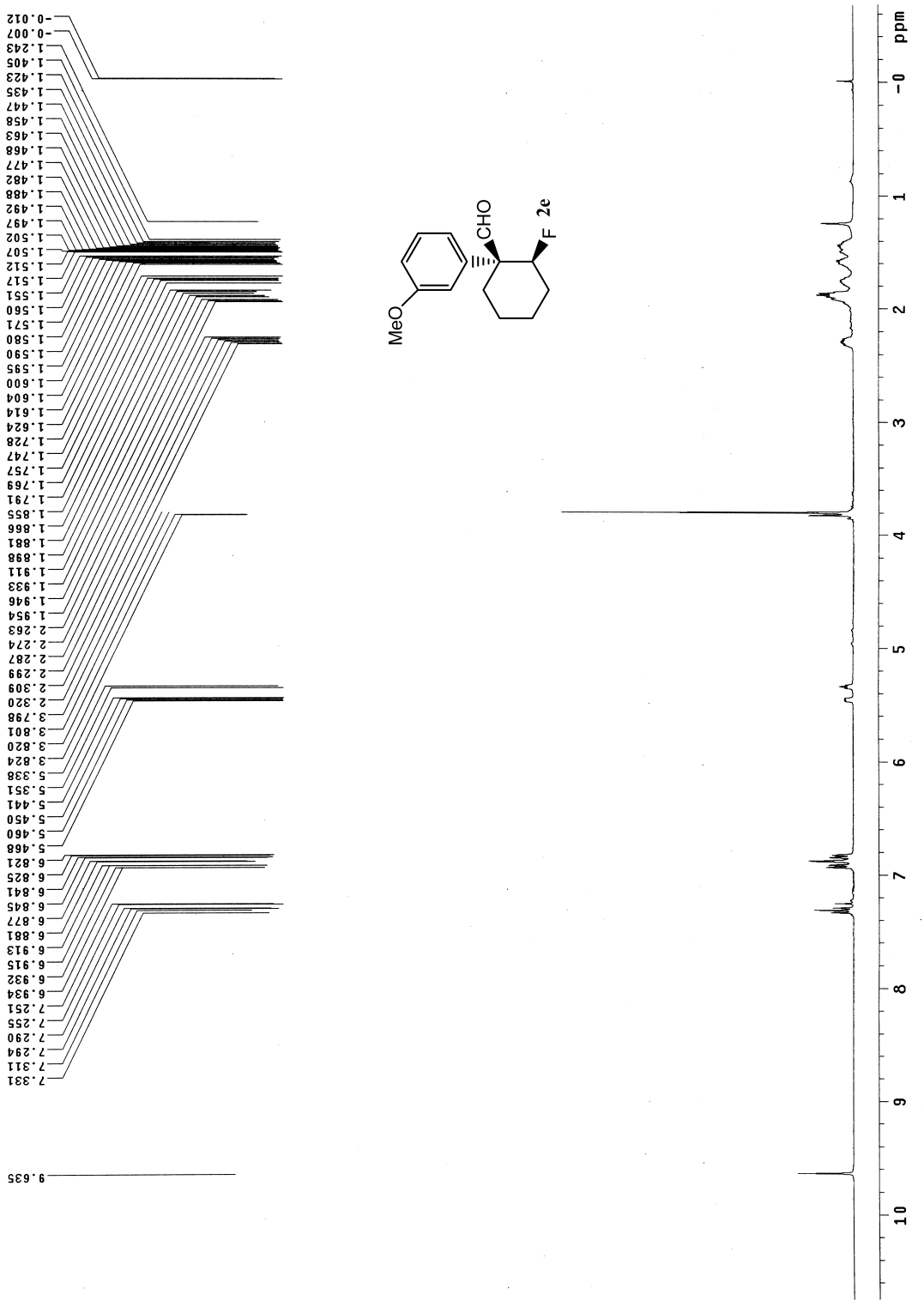
160
180
200
220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1.492
1.497
1.502
1.507
1.512
1.517
1.551
1.560
1.571
1.580
1.590
1.595
1.600
1.604
1.614
1.624
1.728
1.747
1.757
1.769
1.791
1.855
1.866
1.881
1.898
1.911
1.933
1.946
1.954
2.263
2.274
2.287
2.299
2.309
2.320
3.798
3.801
3.820
3.824
5.338
5.351
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5.450
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5.468
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6.825
6.841
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6.877
6.881
6.913
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6.934
7.251
7.255
7.290
7.294
7.311
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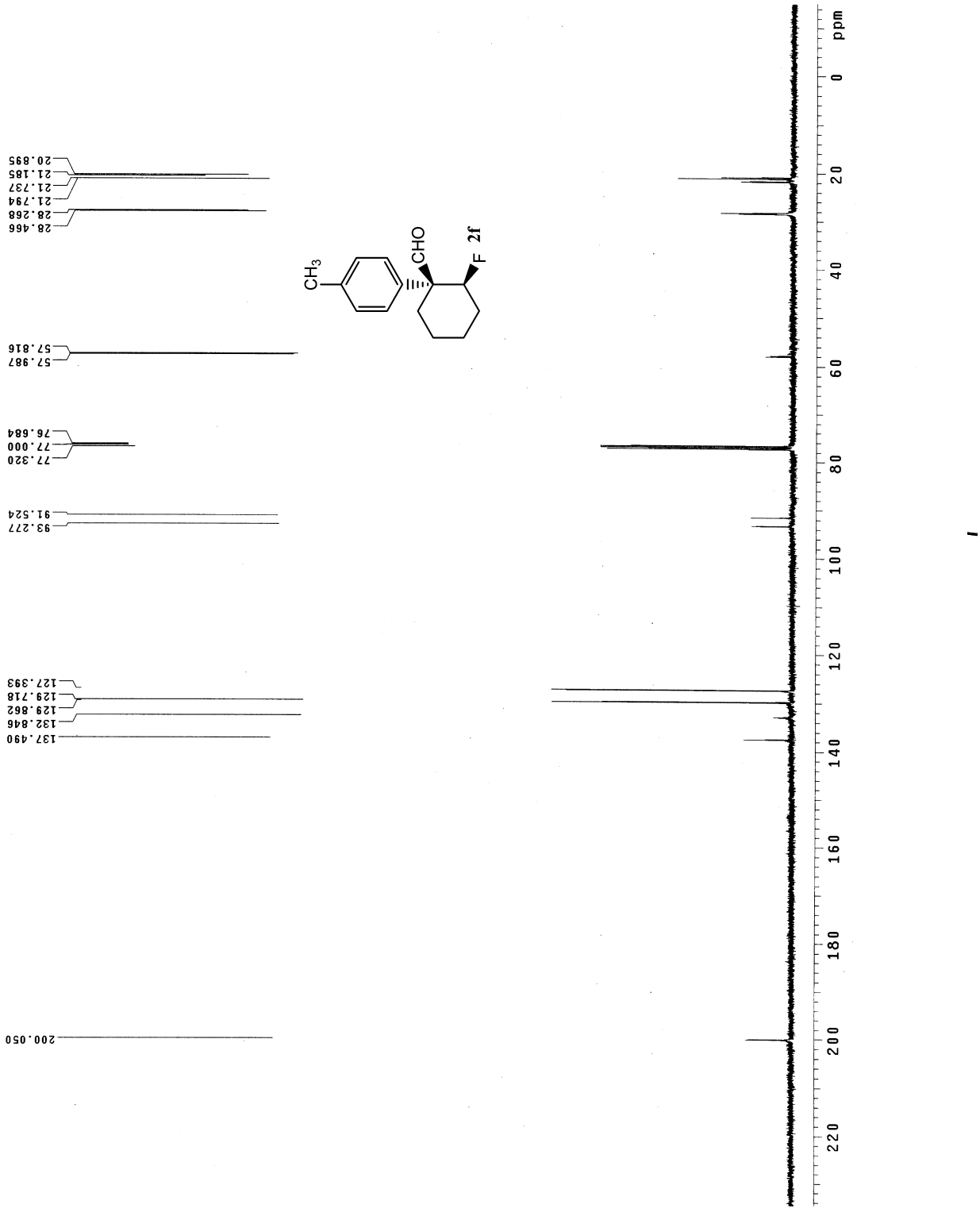
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129.718
129.862
132.846
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2f
CH3
ppm
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80
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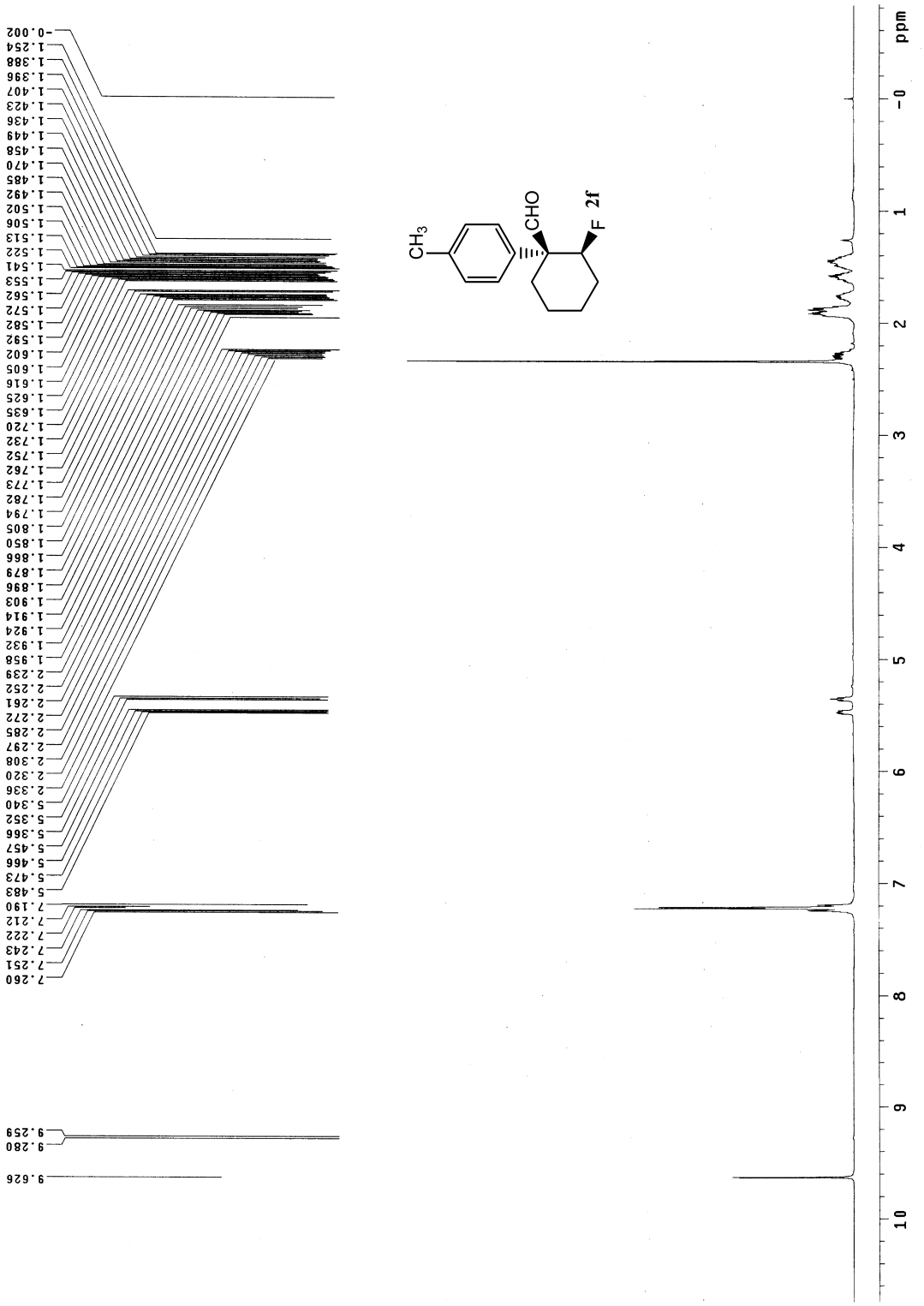
160
180
200
220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1.502
1.506
1.513
1.522
1.541
1.553
1.562
1.572
1.582
1.592
1.602
1.605
1.616
1.625
1.635
1.720
1.732
1.752
1.762
1.773
1.782
1.794
1.805
1.850
1.866
1.879
1.896
1.903
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1.924
1.932
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2.252
2.261
2.272
2.285
2.297
2.308
2.320
2.336
5.340
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5.366
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5.466
5.473
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7.251
7.260
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ppm
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7
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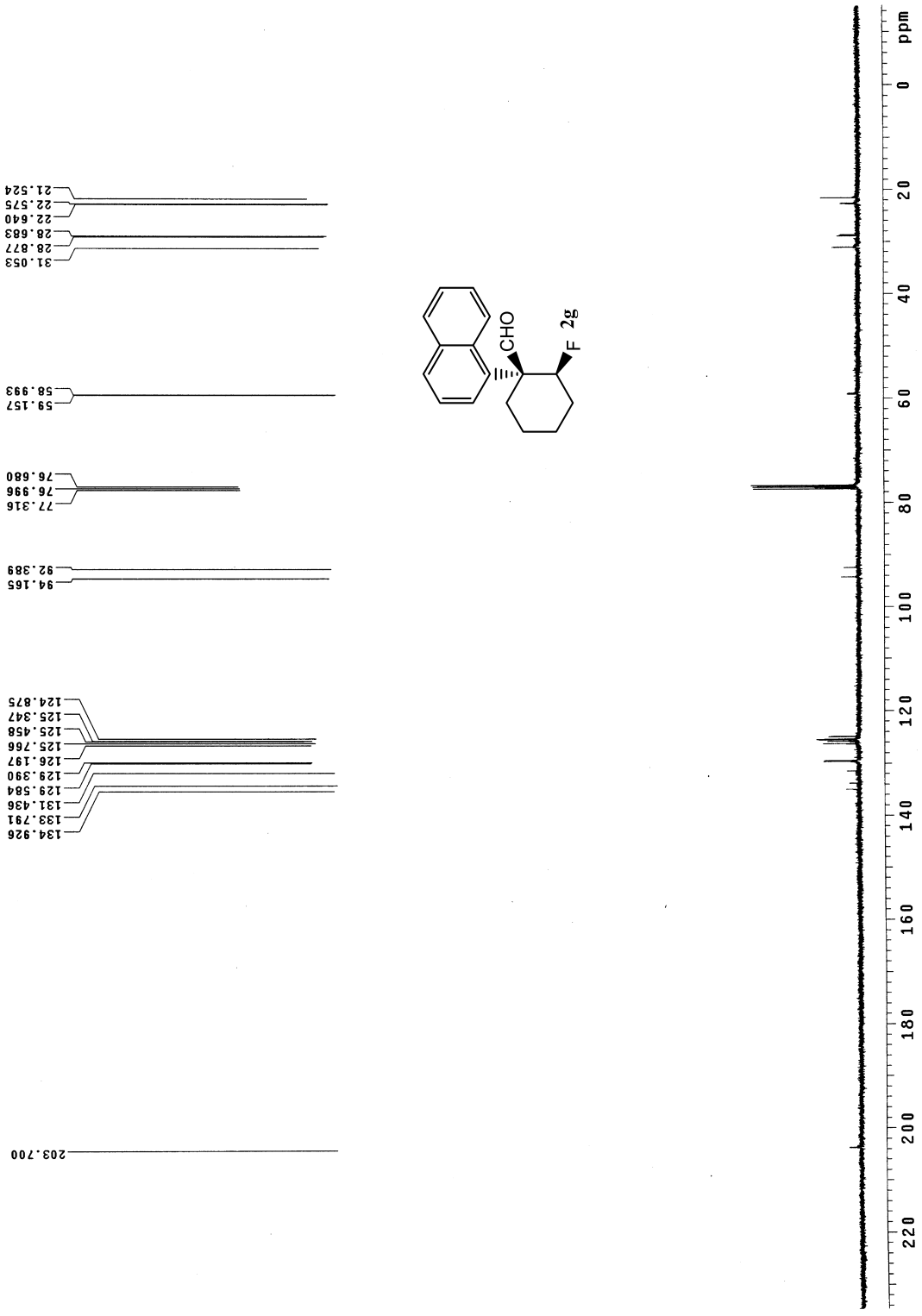
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133.791
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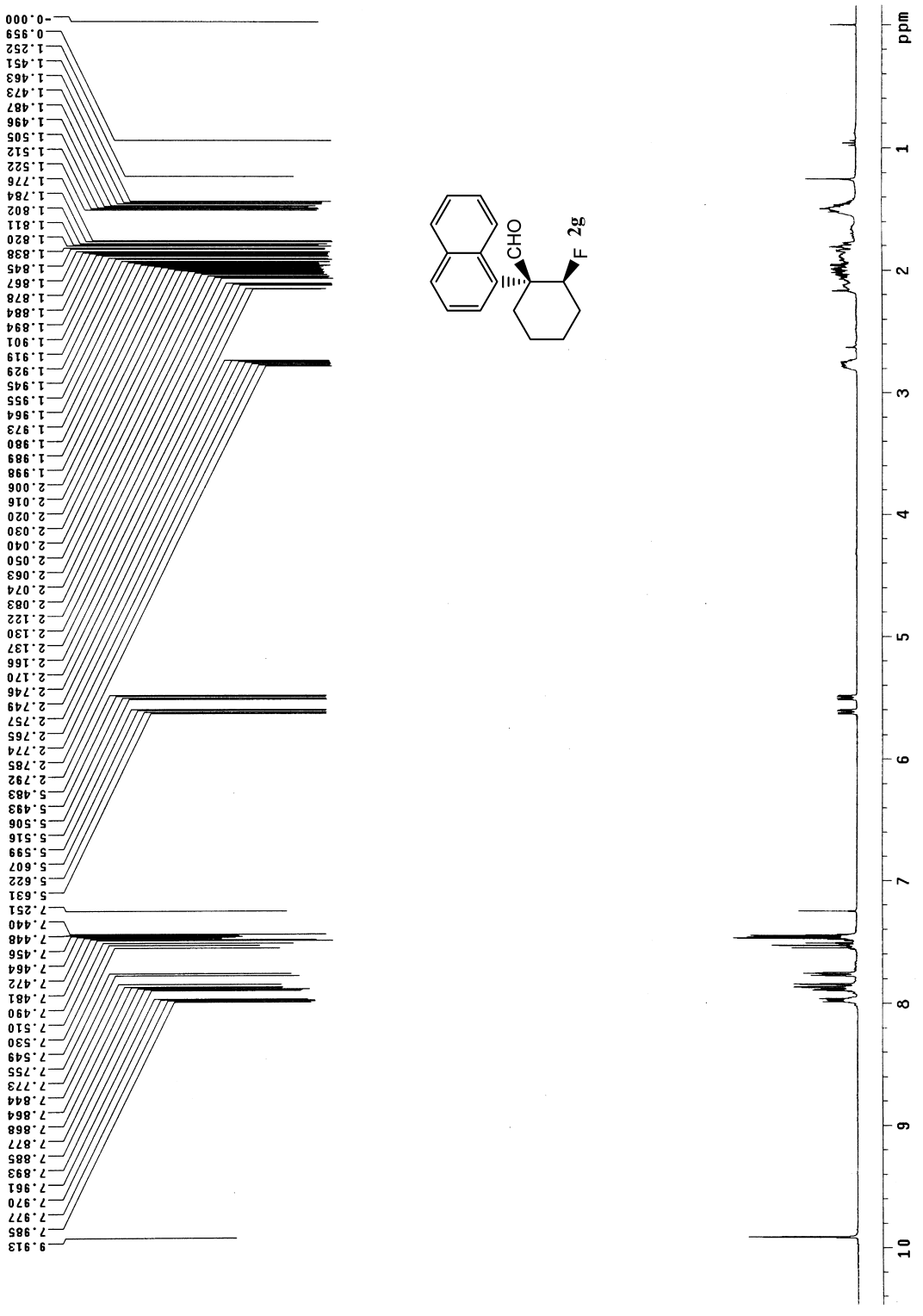
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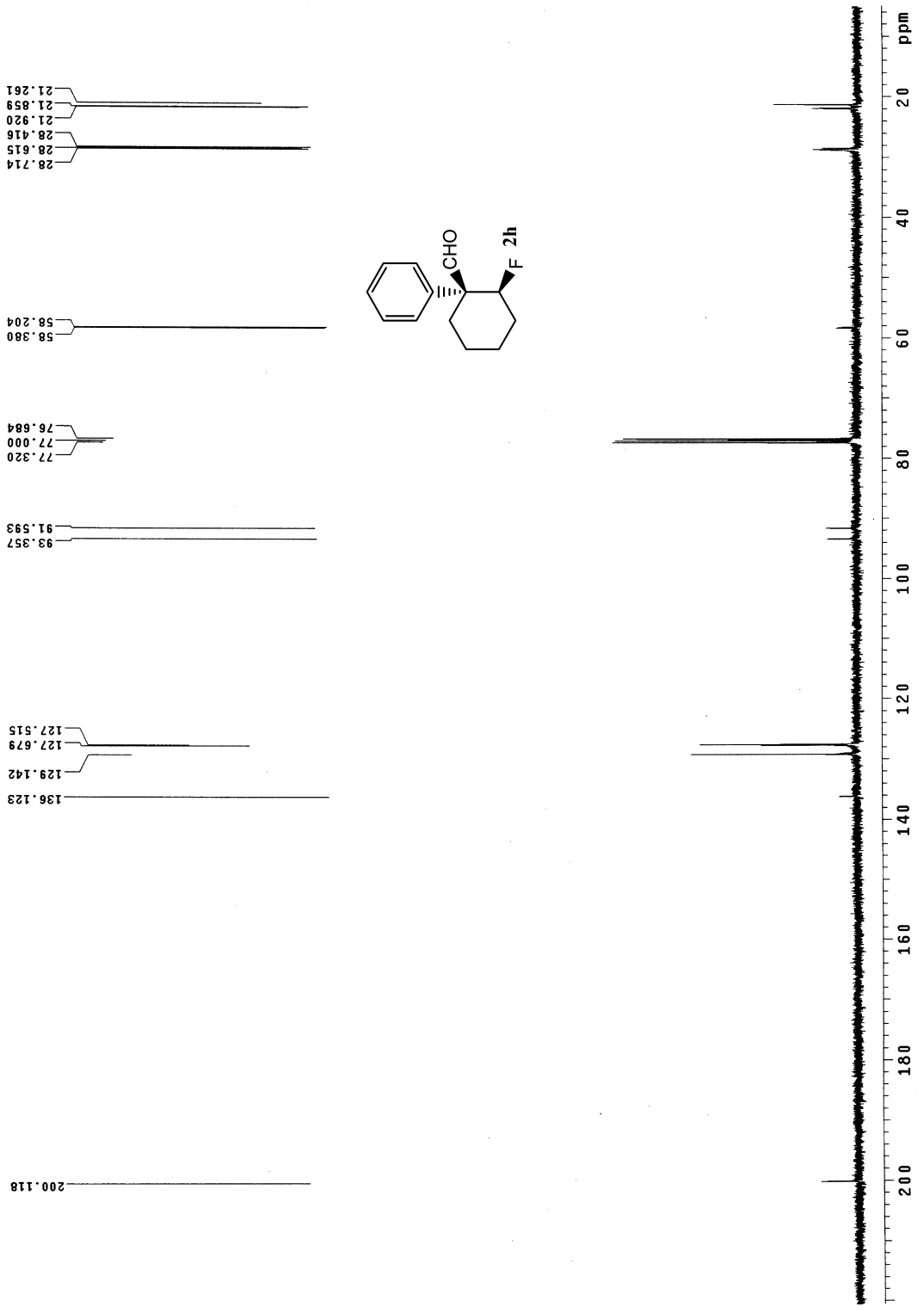
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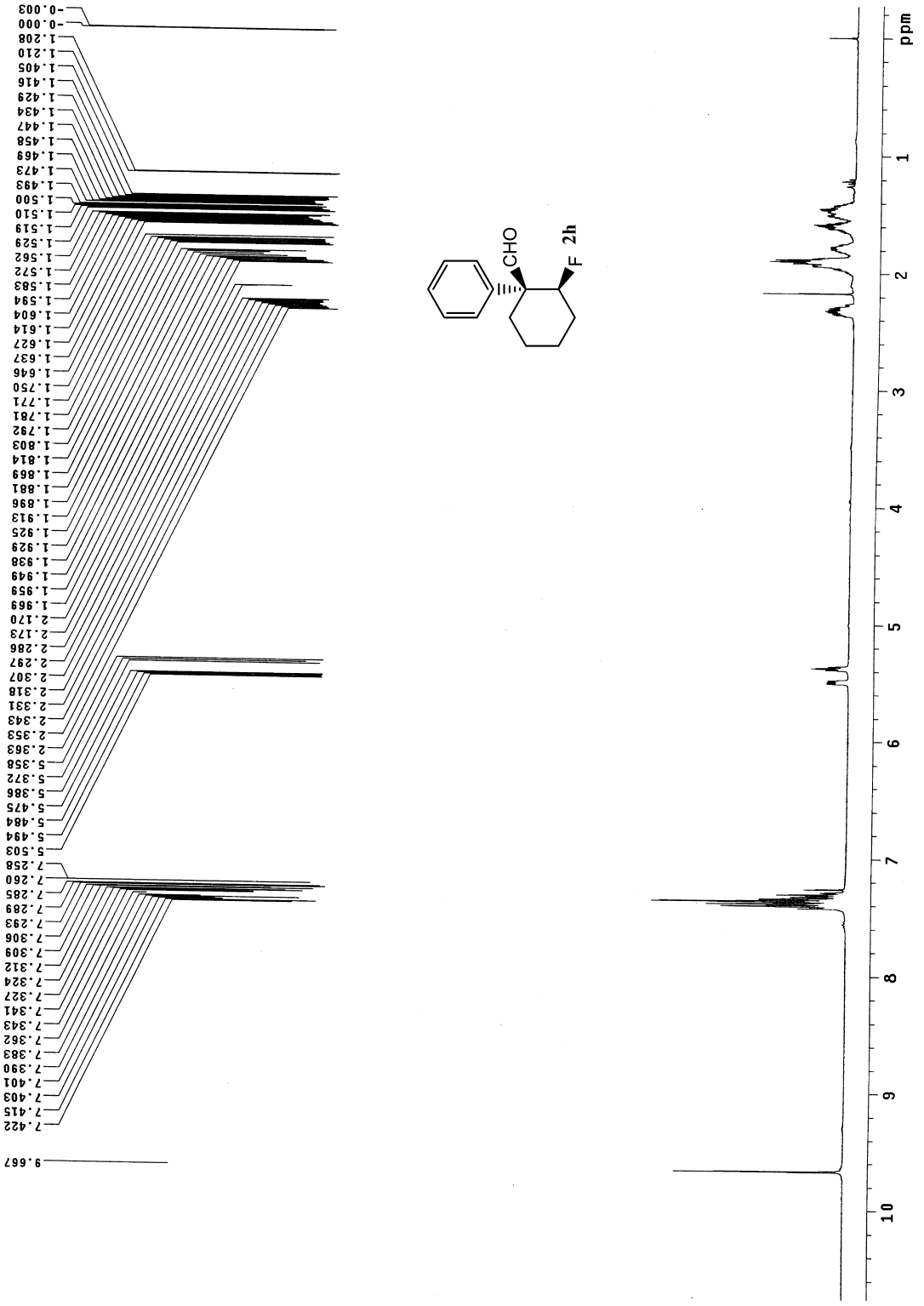
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1.913
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1.929
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1.949
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1.969
2.170
2.173
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2.297
2.307
2.318
2.331
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7.343
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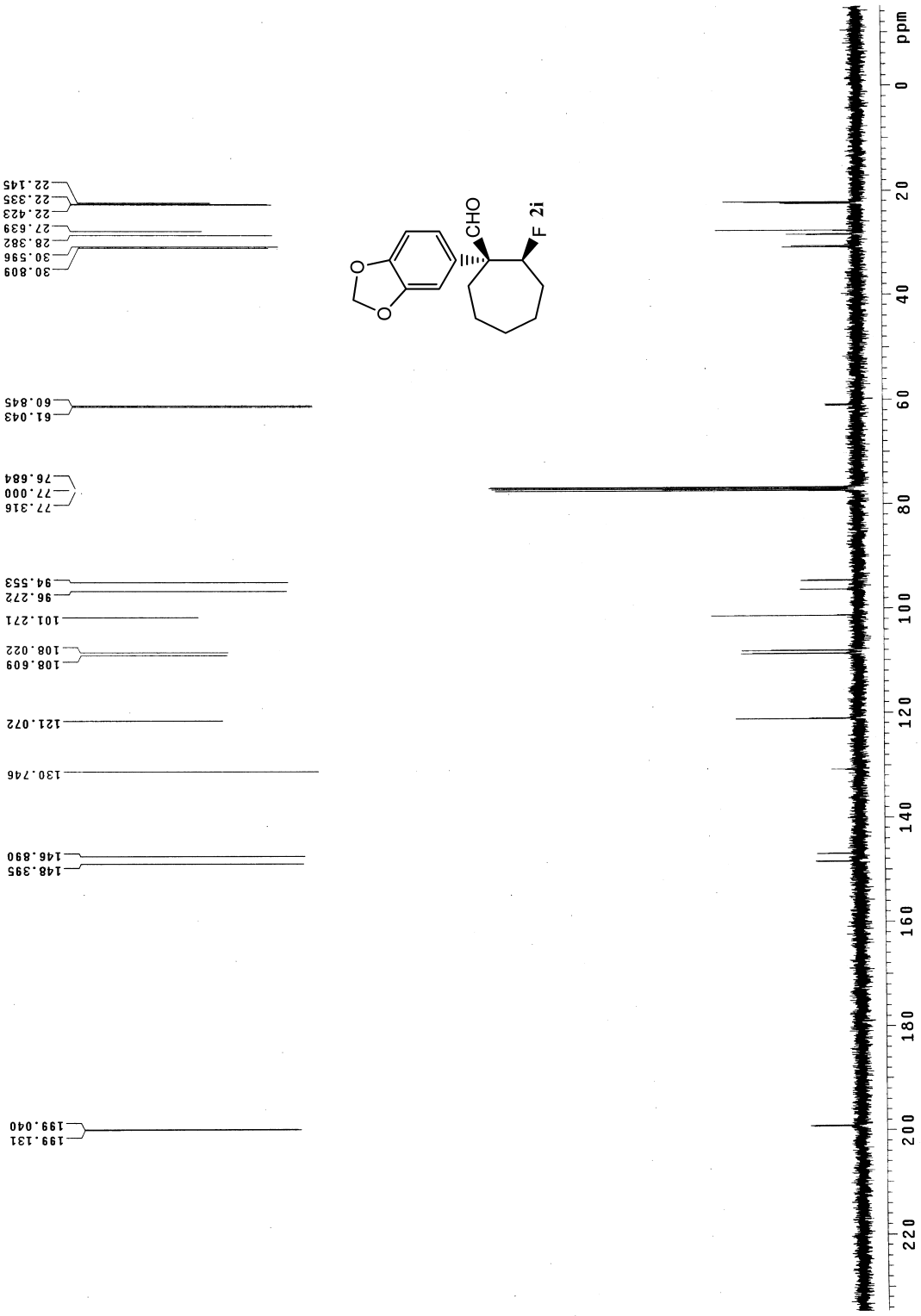
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101.271
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200
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CHO
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2i
ppm
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8
10
12

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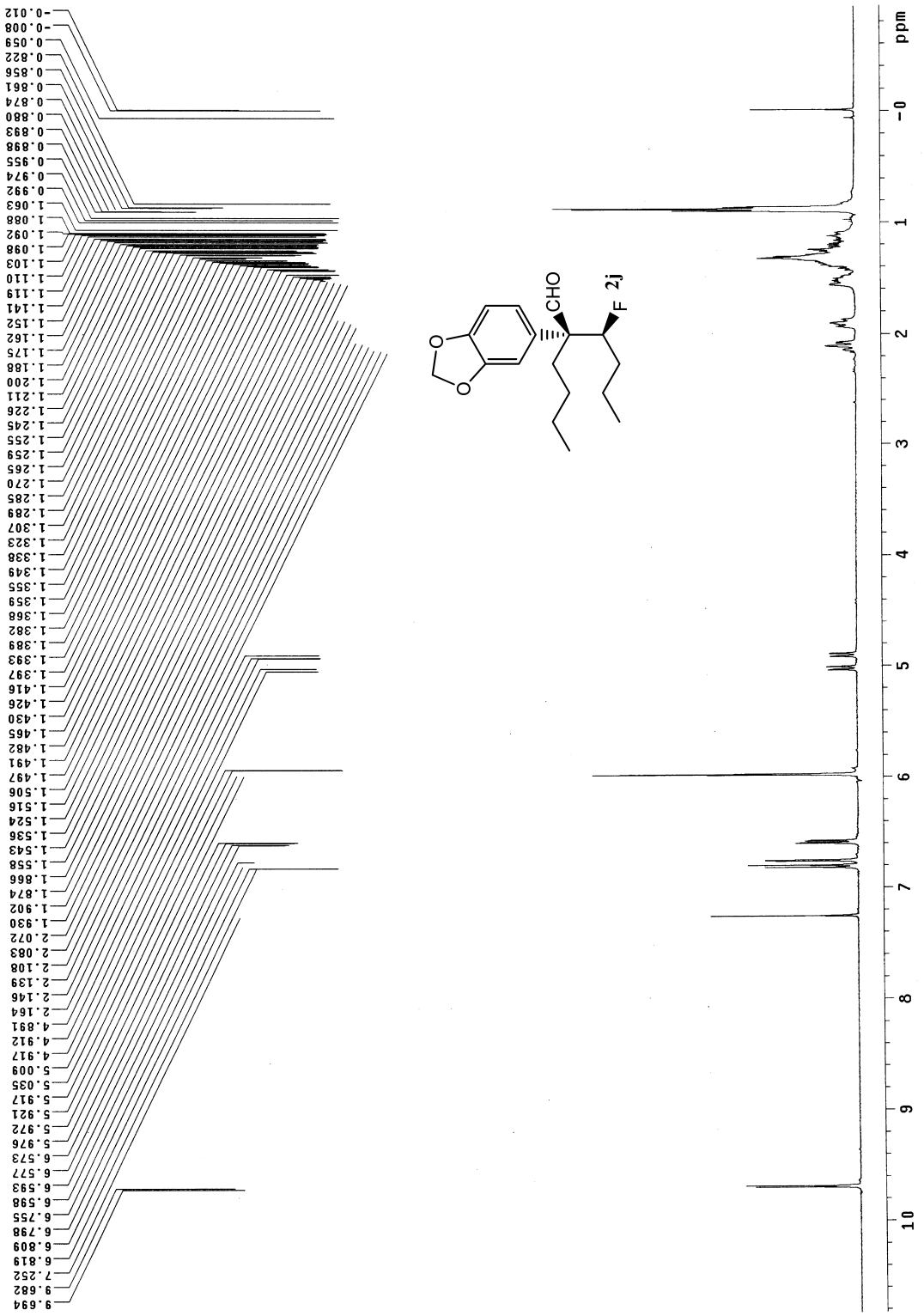
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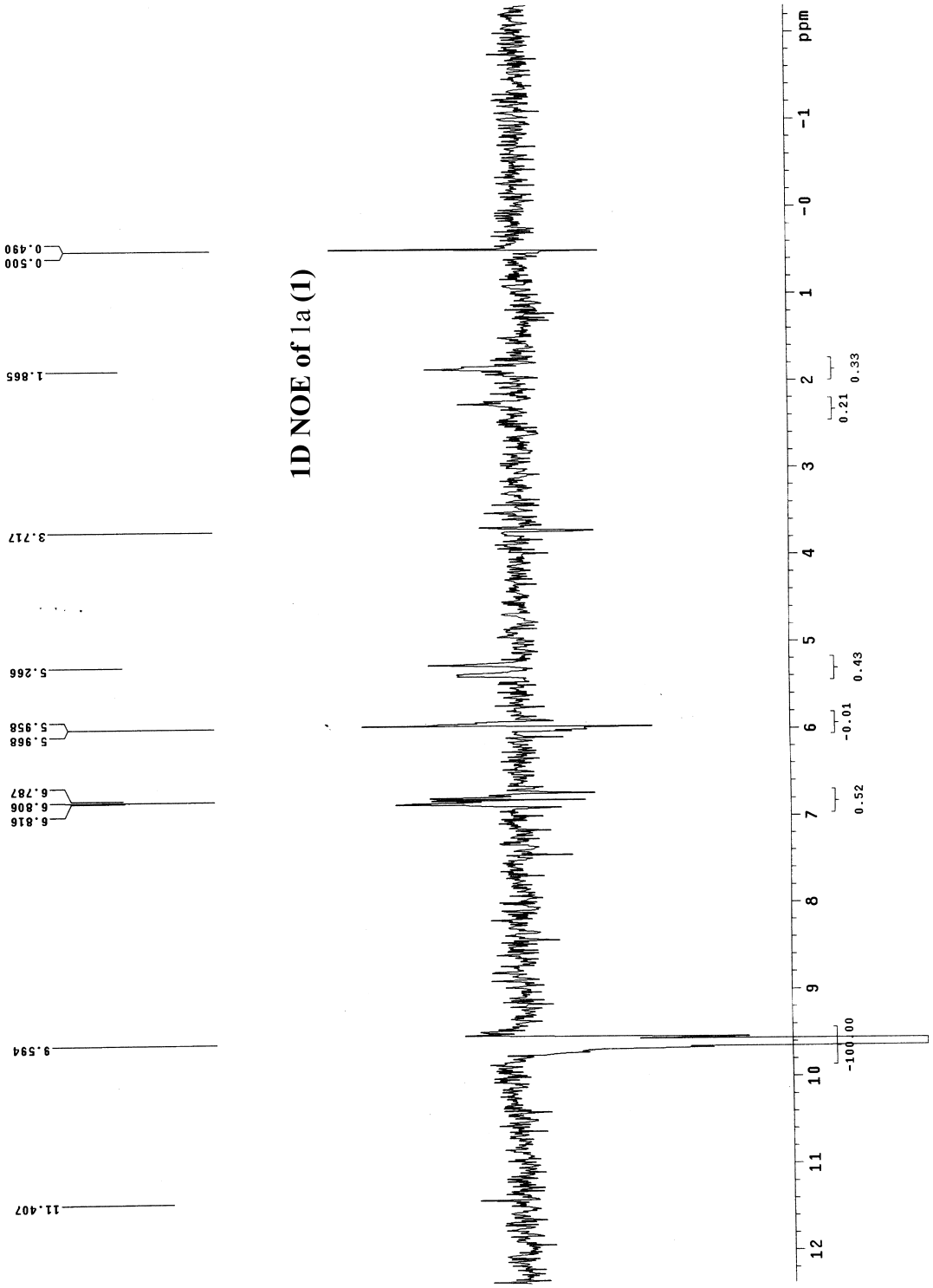
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6.787
6.806
6.816
9.594
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ppm
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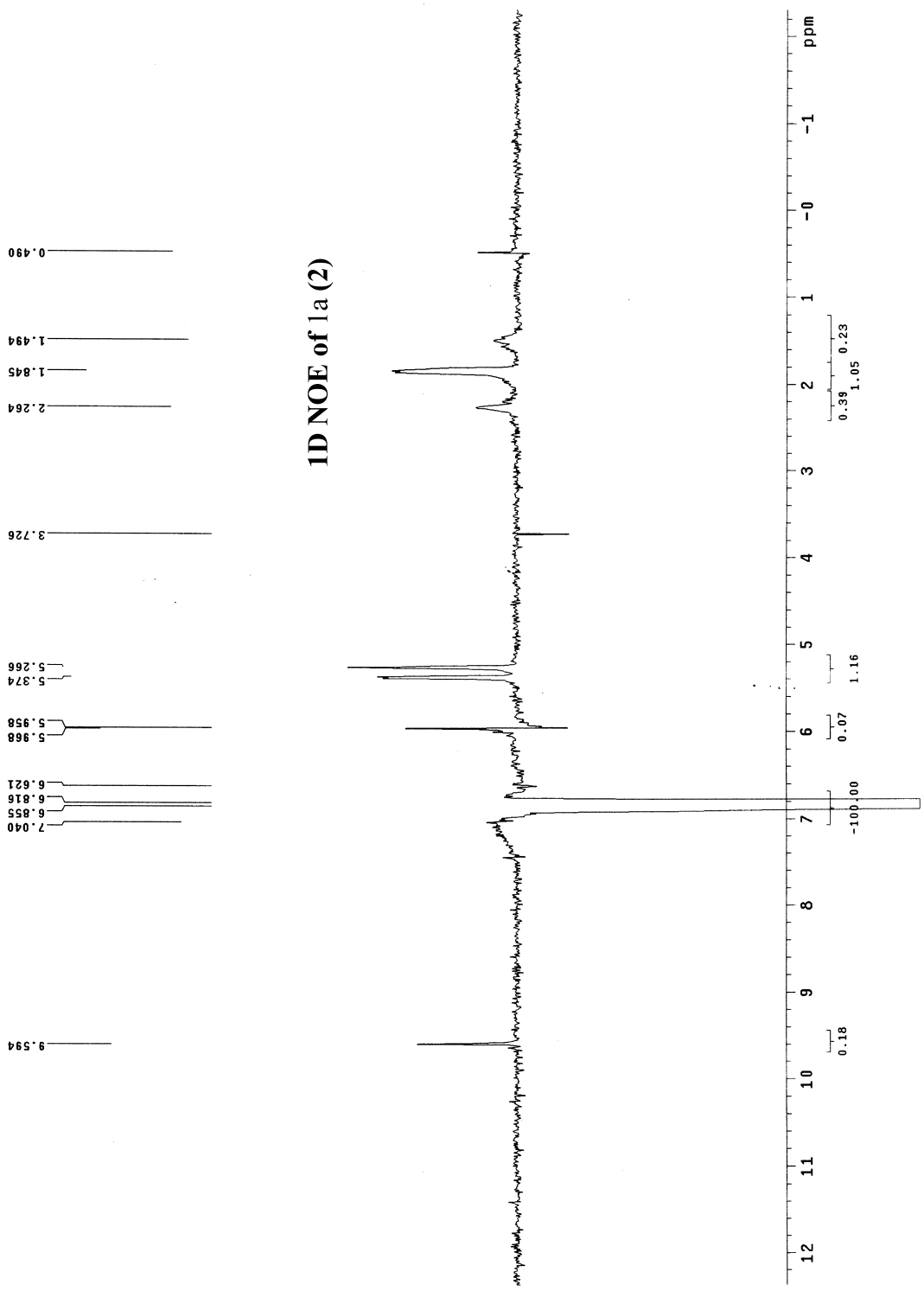
0.21
0.33

1D NOE of 1a **(2)**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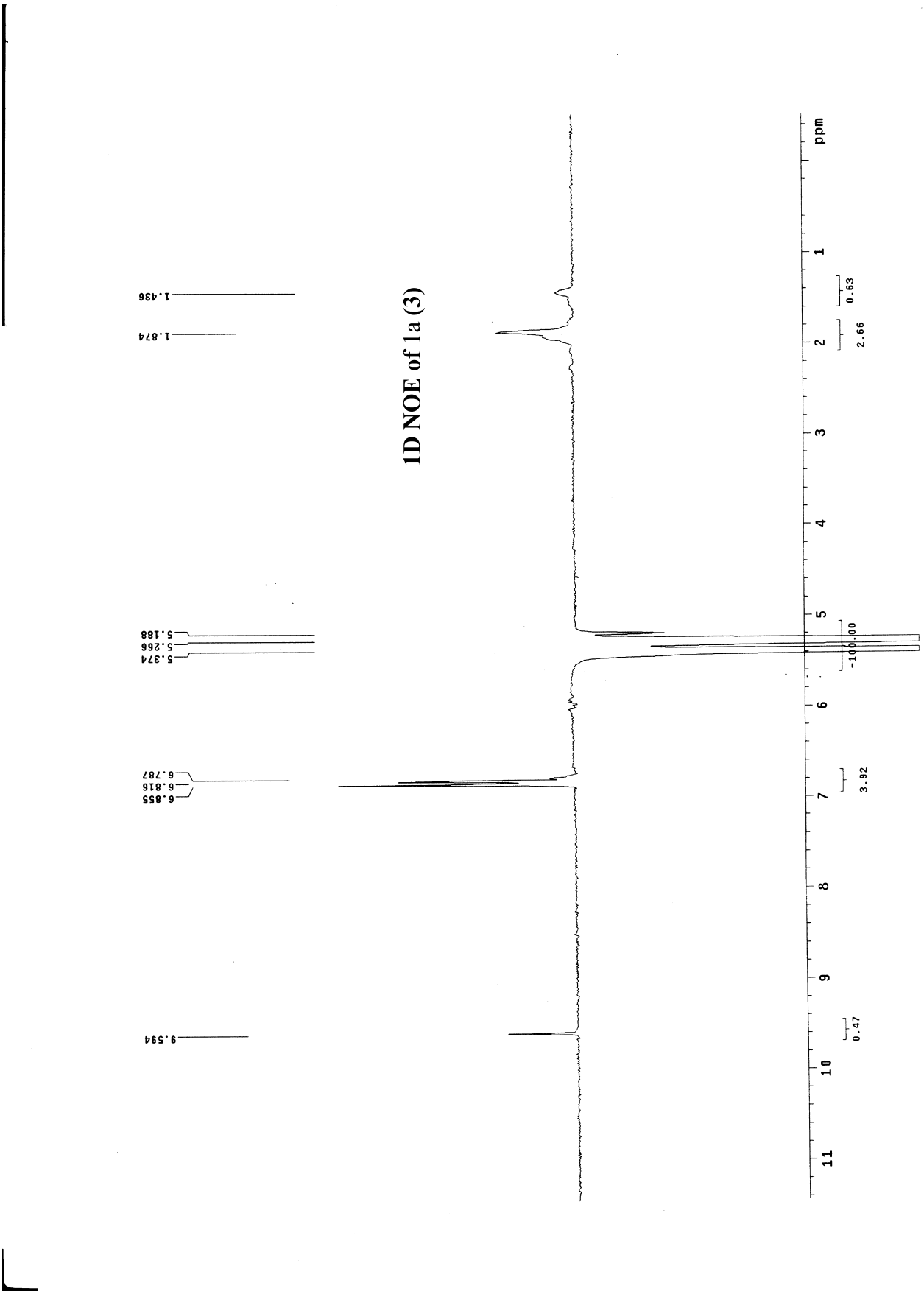
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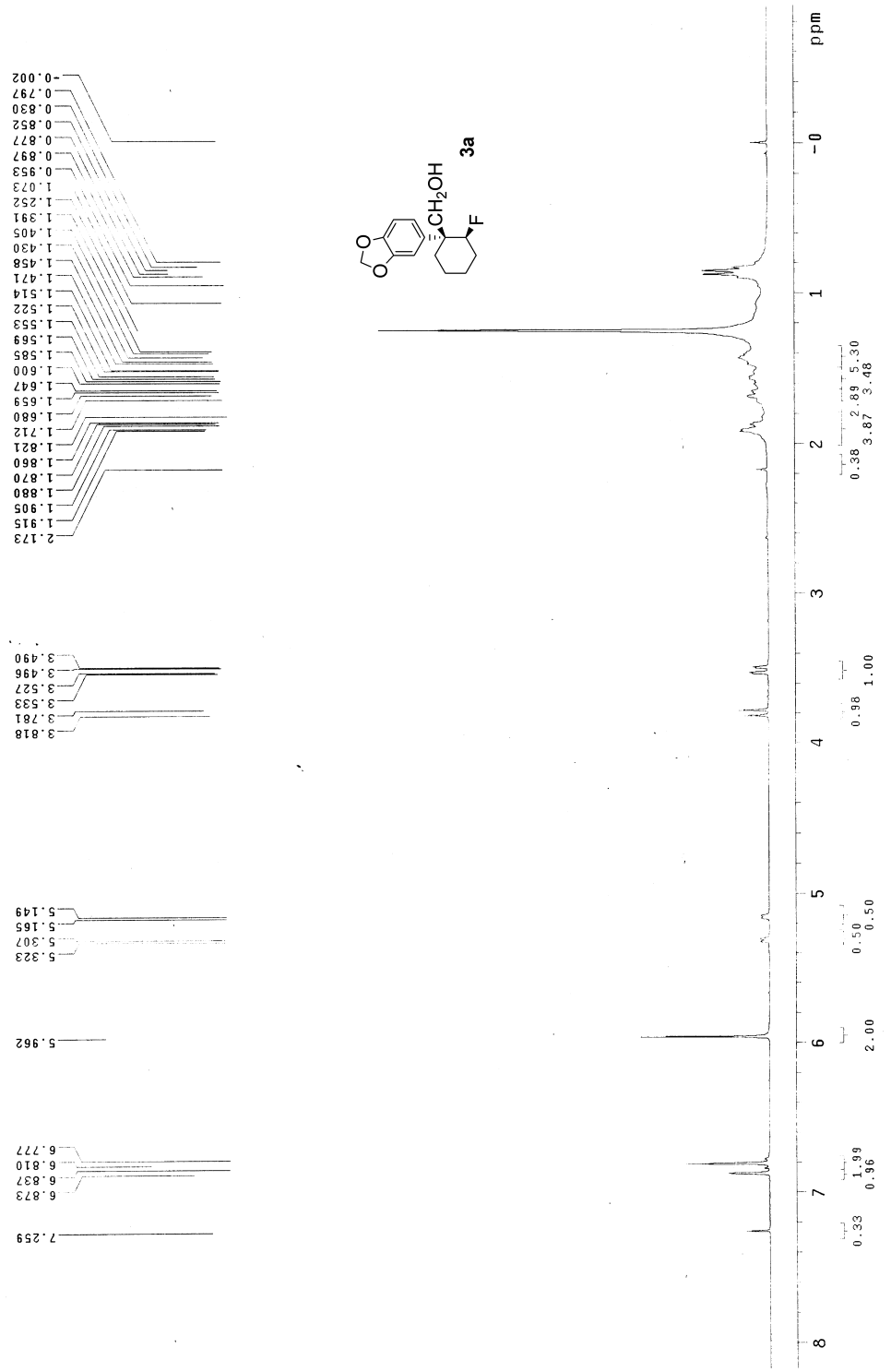
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1.553
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1.585
1.600
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1.659
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1.870
1.880
1.905
1.915
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3.533
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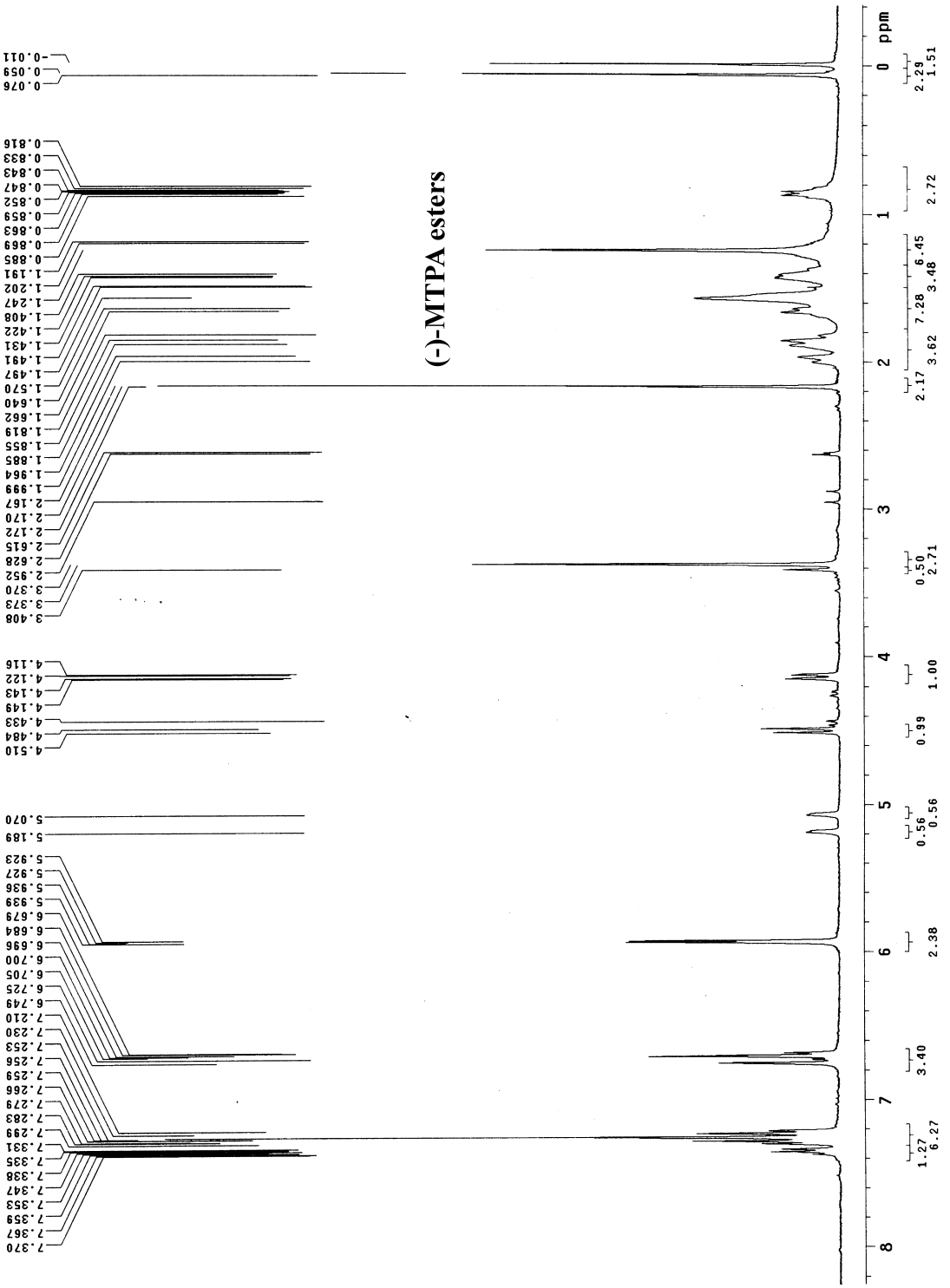
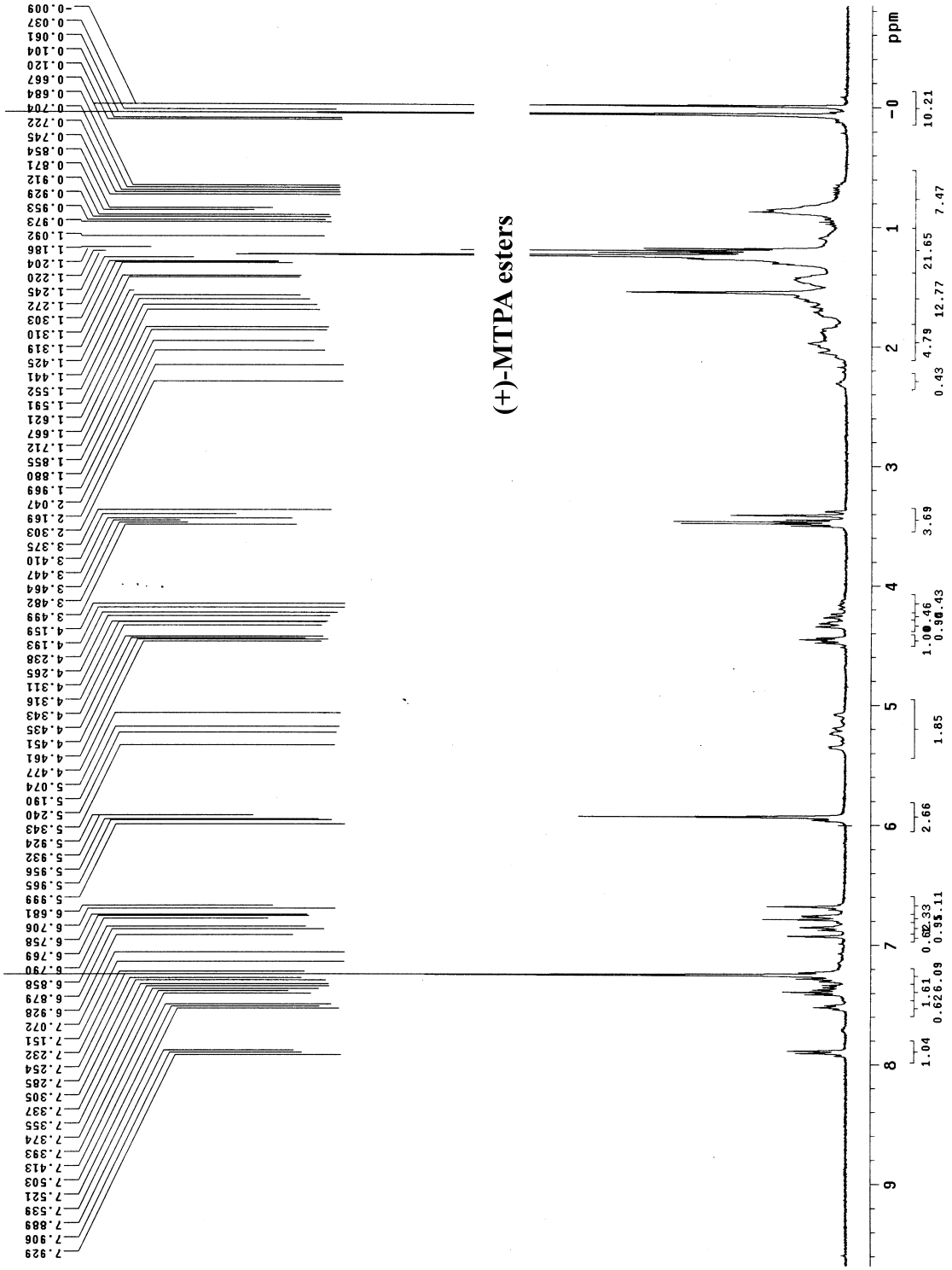

(-)-MTPA esters
ppm


(+)-MTPA esters
ppm