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# Supporting Information



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**Highly Enantio- and Diastereoselective Mukaiyama Aldol Reactions of *N,O*-Silyl Ketene Acetals Catalyzed by Hydrogen Bonding**

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## EXPERIMENTAL PROCEDURES and CHARACTERIZATION DATA

**General Experimental.** All reactions were carried out in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. All liquid aldehydes were distilled prior to use. All solid aldehydes were recrystallized prior to use. (2*R*,3*R*)-α,α,α',α'-tetra(1-naphthyl)-1,4-Dioxaspiro[4.5]decane-2,3-dimethanol was synthesized by literature methods and pure material was obtained by recrystallization from a solution of hexanes and ethyl acetate. (4*S*-*trans*)-2,2-Dimethyl-α,α,α',α'-tetra(1-naphthyl)-1,3-dioxolane-4,5-dimethanol (Aldrich) was used as received. All other reagents were used as received (Acros, Aldrich). (*Z*)-1-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-*N*,*N*-dimethyl-1-propen-1-amine (**2**) was synthesized according to literature precedent for such enolization/silylations.[1] $PhCH_3$ and $CH_2Cl_2$ were degassed by purging with nitrogen and dried over activated alumina. $^1H$ and $^{13}C$ NMR were recorded at 500 or 400 MHz and 125 or 100 MHz respectively on a Bruker DRX-500 spectrometer. Proton chemical shifts were internally referenced to the residual proton resonance in $CDCl_3$ (δ 7.26). Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (δ

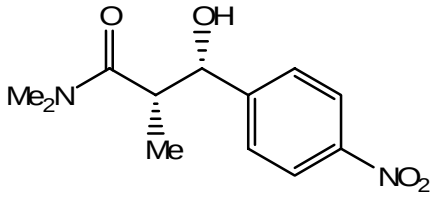
77.36). Infrared spectra were obtained on a Nicolet 20 SXB FT-IR spectrometer. TLCs were run on Whatman Partisil K6F thin layer chromatography plates (250 μm, 60 Å). Silica gel (60 Å, 230-400 mesh) was obtained from Silicycle and used as received. All enantiomeric excesses were determined by Chiral High-performance liquid chromatography (HPLC) and were run on an Agilent 1100 Series equipped with a variable wavelength detector using Diacel chiral stationary columns. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. Absolute stereochemistry of a amide aldol product **3a** was assigned based on chemical correlation to (1*S*,2*R*)-1-phenyl-2-methylpropane-1,3-diol, synthesized by literature precedent.[2] Stereochemistry for the remaining products was tentatively assigned.

**General Procedure for Enantioselective Mukaiyama Aldol Reactions: Isolation of β-Hydroxy Amide Products (Scheme 1 and Table 1)**

To a solution of catalyst **1a** or **1b** (0.025 mmol) in $PhCH_3$ (500 μL) at room temperature under an atmosphere of Argon was added aldehyde (0.5 mmol) in one portion. The mixture was cooled to -40 or -80 °C (temp. of cooling bath) and (*Z*)-1-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-*N*,*N*-dimethyl-1-propen-1-amine (**2**) was added dropwise (5-10 sec/drop) with vigorous stirring. The reaction was maintained at the temperature specified in Table 1 for 48 hours. To the stirring mixture was added HF (500 μL, 5% aq., prepared by dilution of Fischer 49% aq. HF with $CH_3CN$) and the rapidly stirring mixture was allowed to warm to room temperature. Stirring was continued at room temperature until the disappearance of the initially formed silyl ether product is

observed by TLC. The reaction mixture was then diluted by $CH_2Cl_2$ (4 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (5 mL). The aqueous layer was extracted with $CH_2Cl_2$ (3 × 5 mL), the combined organics were dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. $^1$H NMR of the crude reaction mixture was used to determine the ratio of *syn* to *anti* **3** prior to further purification. The products were purified by flash chromatography on silica gel (2:1 EtOAc:hexanes) to afford the corresponding separated diastereomeric products *syn*- and *anti*-**3**.

**(2*S*,3*S*)-3-Hydroxy-*N*,*N*,2-trimethyl-3-(4-nitrophenyl)propanamide (3b)**

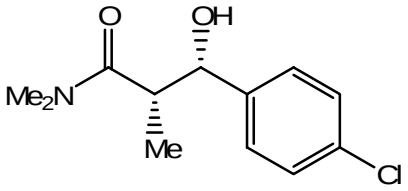



***Syn*-3b** isolated in 86% yield as a pale yellow solid: 94% ee [Chiralcel OD-H, hexane:*i*-propanol = 80:20, 0.8 mL/min, $t_R$ (minor) = 7.9 min, $t_R$ (major) = 10.5 min]; $[\alpha]_D^{28}$ = -2.2° (*c* 0.71, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.20 (2H, d, *J* = 9.0 Hz), 7.55 (2H, d, *J* = 8.5 Hz), 5.47 (1H, bs), 5.19 (1H, d, *J* = 1.5 Hz), 3.05 (3H, s), 2.99 (3H, s), 2.87 (1H, dq, *J* = 7.0, 2.0 Hz), 0.98 (3H, d, *J* = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 177.11, 149.58, 147.41, 127.24, 123.72, 72.83, 41.24, 37.71, 35.83, 9.58; IR (neat) υ 3377, 2936, 1622, 1519, 1401, 1348 cm$^{-1}$.

***Anti*-3b** isolated in 7% yield as a yellow oil: 82% ee [Chiralcel OD-H, hexane:*i*-propanol = 80:20, 0.8 mL/min, $t_R$ (major) = 8.4 min, $t_R$ (minor) = 14.7 min]; $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.17 (2H, d, *J* = 9.0 Hz), 7.51 (2H, d, *J* = 9.0 Hz), 5.18 (1H, bs), 4.84 (1H, d, *J* =

5.0 Hz), 3.02-3.08 (1H, m), 2.86 (3H, s), 2.84 (3H, s), 1.27 (3H, d, $J$ = 8.5 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 175.62, 151.22, 147.54, 127.24, 123.80, 76.22, 42.26, 37.55, 35.66, 15.68; IR (neat) υ 3300, 2936, 1624, 1518, 1401, 1348 cm$^{-1}$.

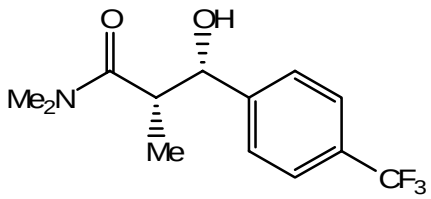
**(2*S*,3*S*)-3-(4-Chlorophenyl)-3-hydroxy-*N*,*N*,2-trimethylpropanamide (3c)**




***Syn*-3c** isolated in 82% yield as a white solid: 97% ee [Chiralcel OD-H, hexane:*i*-propanol = 90:10, 0.8 mL/min, $t_R$ (minor) = 8.0 min, $t_R$ (major) = 11.9 min]; $[\alpha]_D^{29}$ = -10.3° (*c* 0.62, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.31 (4H, s), 5.17 (1H, bs), 5.07 (1H, d, $J$ = 2.5 Hz), 3.03 (3H, s), 2.98 (3H, s), 2.81 (1H, dq, $J$ = 7.0, 2.5 Hz), 1.01 (3H, d, $J$ = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 177.50, 140.59, 133.05, 128.57, 127.74, 72.90, 41.63, 37.68, 35.76, 9.68; IR (neat) υ 3388, 2935, 1622, 1492, 1401 cm$^{-1}$; HRMS calcd for $C_{12}H_{16}ClNO_2Na^+$: 264.0762; found *m/z* = 264.0760, error = 1.0 ppm.

***Anti*-3c** not isolated via the general experimental procedures. Characteristic data included for **rac-*anti*-3c** isolated as an off-white solid: $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.26-7.31 (4H, m), 4.78 (1H, bs), 4.74 (1H, d, $J$ = 6.0 Hz), 2.96-3.01 (1H, m), 2.87 (6H, s), 1.19 (3H, d, $J$ = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 175.90, 142.00, 133.31, 128.64, 127.79, 76.28, 42.67, 37.51, 35.65, 15.52; IR (neat) υ 3311, 2979, 1614, 1491, 1417 cm$^{-1}$.

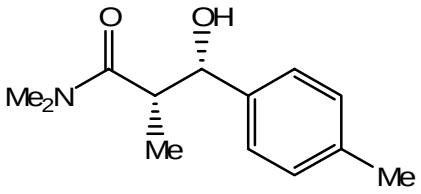
**(2S,3S)-3-(4-(trifluoromethyl)phenyl)-3-hydroxy-*N*,*N*,2-trimethylpropanamide (3d)**




***Syn*-3d** isolated in 84% yield as a white solid: 96% ee [Chiralcel OD-H, hexane:*i*-propanol = 90:10, 1 mL/min, $t_R$ (minor) = 5.9 min, $t_R$ (major) = 9.1min]; $[\alpha]_D^{28}$ = -24.4° (*c* 0.32, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.61 (2H, d, *J* = 8.2 Hz), 7.50 (2H, d, *J* = 8.2 Hz), 5.30 (1H, s), 5.16 (1H, bs), 3.05 (3H, s), 3.00 (3H, s), 2.85 (1H, dq, *J* = 7.1, 2.2 Hz), 1.00 (3H, d, *J* = 7.1 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 177.06, 145.75, 129.30 (q), 126.35, 125.04 (q), 123.10, 72.63, 41.13, 37.33, 35.44, 9.24; IR (neat) υ 3386, 2939, 1620, 1415, 1326 $cm^{-1}$.

***Anti*-3d** not isolated via the general experimental procedures. Characteristic data included for **rac-*anti*-3d** isolated as a yellow solid: $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.59 (2H, d, *J* = 8.1 Hz), 7.46 (2H, d, *J* = 8.1 Hz), 4.91 (1H, d, *J* = 7.0 Hz), 4.82 (1H, dd, *J* = 5.7, 6.2 Hz), 3.05-2.99 (1H, m), 2.86 (3H, s), 2.85 (3H, s), 1.24 (3H, d, *J* = 7.1 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 175.42, 147.24, 129.48 (q), 126.38, 125.10, 122.98, 76.03, 42.14, 37.10, 35.26, 15.18; IR (neat) υ 3384, 2934, 1621, 1418, 1326 $cm^{-1}$.

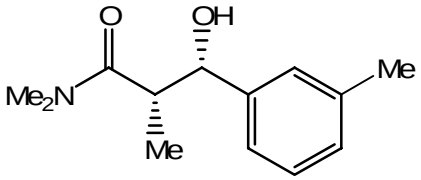
**(2S,3S)-3-hydroxy-*N*,*N*,2-trimethyl-3-*p*-tolylpropanamide (3e)**




***Syn*-3e** isolated in 77% yield as a pale yellow residue: 97% ee [Chiralcel OD-H, hexane:*i*-propanol = 90:10, 0.8 mL/min, $t_R$ (minor) = 8.0 min, $t_R$ (major) = 11.7 min]; $[\alpha]_D^{28}$ = -15.6° (*c* 1.5, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.25 (2H, d, *J* = 7.97 Hz), 7.15 (2H, d, *J* = 7.92 Hz), 5.06 (1H, d, *J* = 2.1 Hz), 5.00 (1H, br s), 3.01 (3H, s), 2.97 (3H, s), 2.88 (1H, dq, *J* = 7.14, 2.5 Hz), 2.34 (3H, s), 1.04 (3H, d, *J* = 7.15 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 177.48, 138.70, 136.63, 128.76, 125.88, 73.04, 41.56, 37.32, 35.40, 21.08, 9.48; IR (neat) υ 3395, 2928, 1622 $cm^{-1}$; HRMS calcd for $C_{13}H_{19}NO_2Na^+$: 244.1308; found *m/z* = 244.1316, error = 3.3 ppm.

***Anti*-3e** not isolated via the general experimental procedures. Characteristic data included for **rac-*anti*-3e** isolated as a yellow residue: $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.20 (2H, d, *J* = 7.97 Hz), 7.12 (2H, d, *J* = 7.89 Hz), 4.73 (1H, t, *J* = 6.05 Hz), 4.38 (1H, d, *J* = 6.2 Hz), 2.99 (1H, m), 2.87 (3H, s), 2.85 (3H, s), 2.32 (3H, s), 1.14 (3H, d, *J* = 7.04 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 175.82, 139.88, 136.96, 128.85, 125.99, 76.45, 42.56, 37.15, 35.31, 21.03, 15.16; IR (neat) υ 3381, 2933, 1624 $cm^{-1}$.

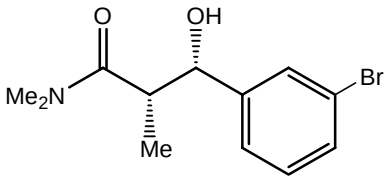
**(2S,3S)-3-hydroxy-*N*,*N*,2-trimethyl-3-*m*-tolylpropanamide (3f)**




Compound ***syn*-3f** isolated in 70% yield as a pale yellow oil: 96% ee [Chiralcel OD-H, hexane:*i*-propanol = 90:10, 0.8 mL/min, $t_R$ (minor) = 7.9 min, $t_R$ (major) = 12.3 min]; $[\alpha]_D^{28}$ = -20.5° (*c* 1.02, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.23 (1H, t, *J* = 7.6 Hz), 7.20 (1H, s), 7.14 (1H, d, *J* = 7.6 Hz), 7.07 (1H, d, J = 7.38 Hz), 5.30 (1H, s), 5.06 (1H, bs), 3.03 (3H, s), 2.98 (3H, s), 2.87 (1H, dq, *J* = 7.1, 2.2 Hz), 2.36 (3H, s), 1.04 (3H, d, *J* = 7.1 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 177.54, 141.62, 137.72, 127.98, 127.80, 126.67, 123.03, 73.08, 41.45, 37.35, 35.42, 21.51, 9.42; IR (neat) υ 3396, 2926, 1620 $cm^{-1}$.

***Anti*-3f** isolated in 7% yield as a yellow residue: 73% ee [Chiralcel OD-H, hexane:*i*-propanol = 90:10, 0.8 mL/min, $t_R$ (major) = 7.8 min, $t_R$ (minor) = 12.2 min]; $[\alpha]_D^{28}$ = -17.1° (*c* 0.32, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.18 (1H, t, *J* = 7.55 Hz), 7.13 (1H, s), 7.08 (1H, d, *J* = 7.6 Hz), 7.04 (1H, d, *J* = 7.45 Hz), 4.71 (1H, d, *J* = 6.1 Hz), 4.46 (1H, bs), 3.01 (1H, m), 2.86 (3H, s), 2.83 (3H, s), 2.32 (3H, s), 1.12 (3H, d, *J* = 7.1 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 175.76, 142.74, 137.74, 128.10, 127.99, 126.68, 123.19, 76.55, 42.51, 37.12, 35.28, 21.33, 15.11; IR (neat) υ 3390, 2933, 1623 $cm^{-1}$.

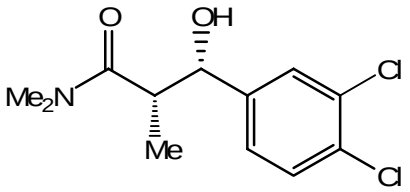
**(2S,3,S)-3-(3-bromophenyl)-3-hydroxy-*N*,*N*,2-trimethylpropanamide (3g)**




Compound ***syn*-3g** was isolated in 79% yield as an off-white solid: 95% ee [Chiralcel OD-H, hexane:*i*-propanol = 90:10, 1.0 mL/min, $t_R$ (minor) = 6.4 min, $t_R$ (major) = 8.4 min]; $[\alpha]_D^{28}$ = -16.6° (*c* 0.86, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.53 (1H, s), 7.38 (1H, d, J = 7.9 Hz), 7.29 (1H, d, J = 7.7 Hz), 7.21 (1H, t, J = 7.8 Hz), 5.25 (1H, s), 5.06 (1H, s), 3.04 (3H, s), 2.98 (3H, s), 2.83 (1H, dq, *J* = 7.1, 2.3 Hz), 1.00 (3H, d, *J* = 7.1 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 177.15, 144.09, 130.17, 129.70, 129.11, 124.65, 122.39, 72.44, 41.19, 37.37, 35.45, 9.28; IR (neat) υ 3393, 2929, 1619, 1476, 1417, 1157, 909 $cm^{-1}$.

***Anti*-3g** was isolated in 5% yield as a yellow residue: 67% ee [Chiralcel OD-H, hexane:*i*-propanol = 90:10, 1.0 mL/min, $t_R$ (major) = 6.4 min, $t_R$ (minor) = 11.8 min]; $\alpha]_D^{28}$ = -1.4° (*c* 0.4, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.50 (1H, t, *J* = 1.7 Hz), 7.40-7.38 (1H, m), 7.27-7.25 (1H, m), 7.19 (1H, t, *J* = 7.8 Hz) 4.75-4.70 (2H, m), 3.02-2.98 (1H, m), 2.88 (3H, s), 2.86 (3H, s), 1.21 (3H, d, *J* = 7.1 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 175.49, 145.49, 130.51, 129.81, 129.16, 124.83, 122.45, 76.05, 42.33, 37.22, 35.37, 15.23; IR (neat) υ 3373, 2935, 1623, 1475, 1417, 1264, 1047 $cm^{-1}$.

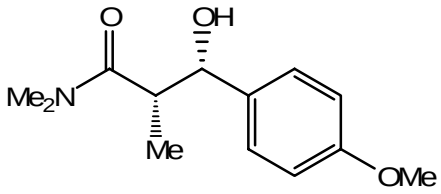
**(2S,3S)-3-(3,4-dichlorophenyl)-3-hydroxy-*N*,*N*,2-trimethylpropanamide (3h)**




***Syn*-3h** isolated in 71% yield as a yellow oil: 94% ee [Chiralcel OD-H, hexane:*i*-propanol = 95:5, 1 mL/min, $t_R$ (minor) = 10.1 min, $t_R$ (major) = 17.05 min]; $[\alpha]_D^{28}$ = -16.8° (*c* 1.04, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.48 (1H, d, *J* = 1.5 Hz), 7.41 (1H, d, *J* = 8.3 Hz), 7.20 (1H, dd, *J* = 8.2, 1.6 Hz), 5.33 (1H, s), 5.05 (1H, s), 3.04 (3H, s), 2.98 (3H, s), 2.81 (1H, dq, *J* = 7.1, 2.1 Hz), 0.99 (3H, d, *J* = 7.2 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 176.90, 142.00, 132.25, 130.82, 130.02, 128.03, 125.34, 71.95, 40.95, 37.32, 35.39, 9.16; IR (neat) υ 3390, 2928, 1621, 1031 $cm^{-1}$; HRMS calcd for.

***Anti*-3h** isolated in 6% yield as a white solid: 58% ee [Chiralcel OD-H, hexane:*i*-propanol = 90:10, 1.0 mL/min, $t_R$ (major) = 6.8 min, $t_R$ (minor) = 16.2 min]; $[\alpha]_D^{28}$ = -27.2° (*c* 0.12, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.43 (1H, d, *J* = 1.9 Hz), 7.37 (1H, d, *J* = 8.3 Hz), 7.15 (1H, dd, *J* = 8.3, 1.9 Hz), 4.96 (1H, d, *J* = 6.6 Hz), 4.69 (1H, t, J = 5.7 Hz), 2.95 (1H, m), 2.89 (3H, s), 2.86 (3H, s), 1.17 (3H, d, *J* = 7.1 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 175.38, 143.57, 132.28, 131.12, 130.10, 128.13, 125.56, 75.46, 42.14, 37.22, 35.35, 29.59, 15.12; IR (film) υ 3364, 2935, 1623, 1029 $cm^{-1}$.

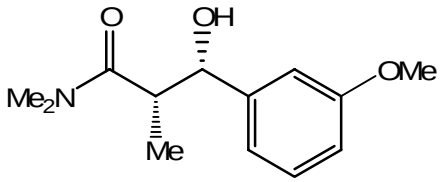
**(2*S*,3*S*)-3-Hydroxy-3-(4-methoxyphenyl)-*N*,*N*,2-trimethylpropanamide (3i)**




***Syn*-3i** isolated in 39% yield as a white solid: 87% ee [Chiralcel OD-H, hexane:*i*-propanol = 90:10, 0.8 mL/min, $t_R$ (minor) = 6.7 min, $t_R$ (major) = 9.1 min]; $[\alpha]_D^{31}$ = -14.4° (*c* 0.51, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.29 (2H, d, *J* = 12 Hz), 6.89 (2H, d, *J* = 12 Hz), 5.05 (1H, d, *J* = 2 Hz), 4.97 (1H, s), 3.81 (3H, s), 3.02 (3H, s), 2.98 (3H, s), 2.82 (1H, dq, *J* = 7.0, 2.5 Hz), 1.04 (3H, d, *J* = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 177.81, 159.01, 134.26, 127.45, 113.83, 73.20, 55.61, 42.00, 37.69, 35.76, 9.88; IR (neat) υ 3394, 2934, 1619, 1513, 1248, 1033 $cm^{-1}$; HRMS calcd for $C_{18}H_{31}NO_2SiNa^+$: 260.1263; found 2(*m/z*) – $H_2O$ = 479.2391, error = 8.4 ppm.

***Anti*-3i** isolated in 8% yield as a clear and colorless oil: 72% ee [Chiralcel OD-H, hexane:*i*-propanol = 90:10, 0.8 mL/min, $t_R$ (major) = 6.9 min, $t_R$ (minor) = 9.5 min]; $[\alpha]_D^{31}$ = -42.7° (*c* 0.28, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.26 (2H, d, *J* = 11.0 Hz), 6.88 (2H, d, *J* = 11.0 Hz), 4.74 (1H, dd, *J* = 6.5, 6.0 Hz), 4.30 (1H, d, *J* = 6.0 Hz), 3.79 (3H, s), 2.97-3.04 (1H, m), 2.90 (3H, s), 2.87 (3H, s), 1.15 (3H, d, *J* = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 176.24, 159.29, 135.41, 127.65, 113.99, 76.64, 55.60, 43.15, 37.57, 35.75, 15.54; IR (neat) υ 3385, 2933, 1622, 1512, 1248, 1033 $cm^{-1}$.

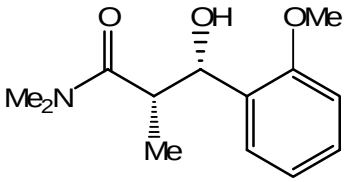
**(2S,3S)-3-hydroxy-3-(3-(methoxyphenyl)-*N*,*N*,2-trimethylpropanamide (3j)**




***Syn*-3j** isolated in 82% yield as a yellow oil: 94% ee [Chiralcel OD-H, hexane:*i*-propanol = 80:20, 0.8 mL/min, $t_R$ (minor) = 7.9 min, $t_R$ (major) = 10.5 min]; $[\alpha]_D^{28}$ = -16.4° (*c* 0.46, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.21 (2H, d, *J* = 9.0 Hz), 7.57 (2H, d, *J* = 8.5 Hz), 5.48 (1H, bs), 5.20 (1H, d, *J* = 1.5 Hz), 3.07 (3H, s), 3.00 (3H, s), 2.88 (1H, dq, *J* = 7.0, 2.0 Hz), 1.00 (3H, d, *J* = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 177.40, 159.54, 143.48, 129.06, 118.24, 112.55, 111.61, 72.96, 55.22, 41.44, 37.31, 35.40, 9.49; IR (neat) υ 3399, 2936, 1617, 1491, 1260, 1159, 1049 $cm^{-1}$; HRMS calcd for $C_{13}H_{19}NO_3Na^+$: 260.1257; found *m/z* = 260.1254, error = 1.2 ppm.

***Anti*-3j** not isolated via the general experimental procedures. Characteristic data included for **rac-*anti*-3j** isolated as a yellow residue : $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.20 (2H, d, *J* = 9.0 Hz), 7.54 (2H, d, *J* = 9.0 Hz), 5.21 (1H, bs), 4.86 (1H, d, *J* = 5.0 Hz), 3.06 (1H, m), 2.89 (3H, s), 2.86 (3H, s), 1.28 (3H, d, *J* = 8.5 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 175.81, 159.64, 144.71, 129.27, 118.51, 113.07, 111.52, 76.62, 55.23, 42.47, 37.21, 35.39, 15.32; IR (neat) υ 3378, 2936, 1622, 1456, 1260, 1155, 1046 $cm^{-1}$.

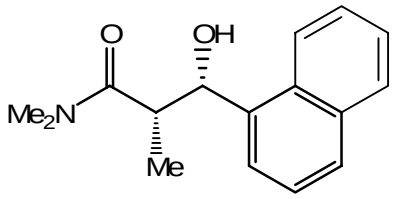
**(2S,3S)-3-hydroxy-3-(2-methoxyphenyl)-*N*,*N*,2-trimethylpropanamide (3k)**




***Syn*-3k** isolated in 50% yield as a pale yellow oil: 91% ee [Chiralcel AD, hexane:*i*-propanol = 98:2, 1.0 mL/min, $t_R$ (minor) = 52.2 min, $t_R$ (major) = 31.1 min]; $[\alpha]_D^{28}$ = -60.2° (*c* 0.31, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.56 (1H, d, J = 7.5, 0.8 Hz), 7.25-7.21 (1H, m), 6.98 (1H, d, *J* = 7.6 Hz), 6.84 (1H, d, *J* = 8.1 Hz), 5.27 (1H, d, *J* = 1.5 Hz), 4.98 (1H, s), 3.82 (3H, s), 3.12 (1H, dq, *J* = 7.1, 2.1 Hz), 3.05 (3H, s), 2.99 (3H, s), 0.98 (3H, d, *J* = 7.1 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 177.97, 155.37, 129.54, 127.82, 127.65, 120.47, 109.81, 68.43, 55.14, 37.86, 37.22, 35.40, 9.65; IR (neat) υ 3409, 2938, 1620, 1464, 1238, 1050 $cm^{-1}$; HRMS calcd for $C_{13}H_{19}NO_3Na^+$: 260.1257; found *m/z* = 260.1200, error = 1.6 ppm.

***Anti*-3k** isolated in 4% yield as a yellow residue: 58% ee [Chiralcel OD-H, hexane:*i*-propanol = 92:8, 1.0 mL/min, $t_R$ (major) = 11.0 min, $t_R$ (minor) = 13.00 min]; $[\alpha]_D^{28}$ = -87.1° (*c* 0.13, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.37 (1H, dd, *J* = 7.5, 1.4 Hz), 7.23-7.20 (1H, m), 6.95 (1H, t, J = 7.5 Hz), 6.84 (1H, d, *J* = 8.2 Hz), 5.05 (1H, d, *J* = 4.3 Hz), 3.84 (3H, s), 3.30 (1H, m), 2.79 (3H, s), 2.70 (3H, s), 1.29 (3H, d, *J* = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 176.28, 155.85, 131.37, 128.12, 126.86, 120.65, 109.92, 71.47, 55.32, 39.19, 37.01, 35.15, 15.44; IR (neat) υ 3392, 2936, 1620, 1463, 1238, 1049 $cm^{-1}$.

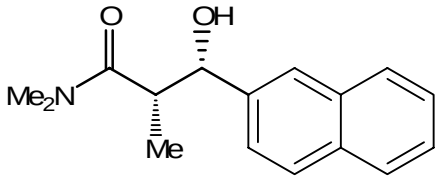
**(2*S*,3*S*)-3-Hydroxy-*N*,*N*,2-trimethyl-3-(naphthalene-1-yl)propanamide (3l)**




***Syn*-3l** isolated in 53% yield as a white solid: 90% ee [Chiralcel OD-H, hexane:*i*-propanol = 85:15, 1.0 mL/min, $t_R$ (major) = 10.0 min, $t_R$ (minor) = 19.4 min]; $[\alpha]_D^{31}$ = -40.6° (*c* 0.46, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.89 (1H, d, *J* = 8.0 Hz), 7.85 (2H, d, *J* = 7.5 Hz), 7.79 (1H, d, *J* = 8.5 Hz), 7.46-7.54 (3H, m), 5.90 (1H, s), 5.45 (1H, s), 3.10 (1H, dq, *J* = 7.0, 1.5 Hz), 3.04 (3H, s), 3.01 (3H, s), 1.01 (1H, d, *J* = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 178.25, 136.70, 134.02, 130.05, 129.59, 127.94, 126.29, 125.85, 125.47, 124.95, 122.38, 69.85, 39.67, 37.67, 35.87, 10.13; IR (neat) υ 3391, 2934, 1621 cm$^{-1}$; HRMS calcd for $C_{16}H_{19}NO_2Na^+$: 280.1308; found *m/z* = 280.1311, error = 1.1 ppm.

***Anti*-3l** isolated in 27% yield as a pale yellow solid: 86% ee [Chiralcel OD-H, hexane:*i*-propanol = 85:15, 1.0 mL/min, $t_R$ (major) = 6.4 min, $t_R$ (minor) = 22.3 min]; $[\alpha]_D^{31}$ = -90.3° (*c* 0.18, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.06 (1H, d, *J* = 8.5 Hz), 7.88 (1H, dd, *J* = 9.0, 1.5 Hz), 7.77 (1H, d, *J* = 8.0 Hz), 7.60 (1H, d, *J* = 7.0 Hz), 7.46-7.56 (3H, m), 5.59 (1H, dd, *J* = 5.5, 5.0 Hz), 4.99 (1H, d, *J* = 6.5 Hz), 3.37-3.42 (1H, m), 2.81 (3H, s), 2.48 (3H, s), 1.33 (3H, d, *J* = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 176.16, 138.79, 134.04, 130.70, 129.44, 128.28, 126.48, 125.80, 125.74, 124.11, 122.96, 73.79, 41.21, 37.36, 35.66, 16.10; IR (neat) υ 3375, 2931, 1621 cm$^{-1}$.

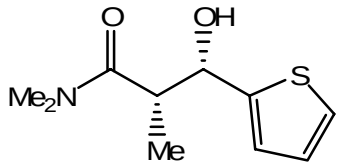
**(2S,3S)-3-hydroxy-*N*,*N*,2-trimethyl-3-(naphthalene-2-yl)propanamide (3m)**




***Syn*-3m** isolated in 50% yield as a pale yellow solid: 97% ee [Chiralcel OD-H, hexane:*i*-propanol = 85:15, 1.0 mL/min, $t_R$ (minor) = 7.8 min, $t_R$ (major) = 10.8 min]; $[\alpha]_D^{28}$ = -15.1° (*c* 0.72, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.91 (1H, s), 7.86-7.81 (3H, m), 7.50-7.41 (3H, m), 5.28 (2H, s), 3.05 (3H, s), 3.00 (3H, s), 3.00-2.96 (1H, m), 1.05 (3H, d, *J* = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 177.49, 139.06, 133.26, 132.70, 128.03, 127.72, 127.60, 126.02, 125.64, 124.90, 124.11, 73.18, 41.27, 37.40, 35.46, 9.43; IR (neat) υ 3396, 3053, 2925, 1621, 1265 $cm^{-1}$; HRMS calcd for $C_{16}H_{19}NO_2Na^+$: 280.1308; found *m/z* = 280.1314, error = 2.2 ppm.

***Anti*-3m** isolated in 3% yield as a white solid: 78% ee [Chiralcel OD-H, hexane:*i*-propanol = 85:15, 1.0 mL/min, $t_R$ (major) = 7.3 min, $t_R$ (minor) = 11.2 min]; $[\alpha]_D^{28}$ = -22.0° (*c* 0.12, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.84-7.80 (4H, m), 7.49-7.44 (3H, m), 4.95 (1H, t, J = 6.1 Hz), 4.74 (1H, d, *J* = 6.5 Hz), 3.17-3.12 (1H, m), 2.85 (3H, s), 2.82 (3H, s), 1.23 (3H, d, *J* = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 175.78, 140.42, 133.18, 132.86, 127.97, 127.57, 126.03, 125.72, 125.05, 124.09, 76.74, 42.37, 37.20, 35.34, 15.38; IR (neat) υ 3377, 3057, 2930, 1622 $cm^{-1}$.

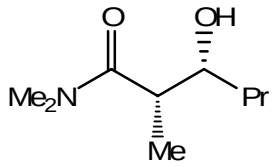
**(2*S*,3*S*)-3-Hydroxy-*N*,*N*,2-trimethyl-3-(thiophen-2-yl)propanamide (3n)**




***Syn*-3n** isolated in 80% yield as a pale yellow solid: 95% ee [Chiralcel OD-H, hexane:*i*-propanol = 90:10, 0.8 mL/min, $t_R$ (minor) = 8.8 min, $t_R$ (minor) = 11.0 min]; $[\alpha]_D^{28}$ = +0.7° (*c* 0.81, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 500 MHz) δ 7.21 (1H, dd, *J* = 5.0, 0.8 Hz), 6.93-6.98 (2H, m), 5.33 (1H, d, *J* = 2.4 Hz), 3.04 (3H, s), 2.96 (3H, s), 2.94 (1H, dq, *J* = 7.1, 2.8 Hz), 1.15 (3H, d, *J* = 7.1 Hz); $^{13}C$ NMR ($CDCl_3$, 125 MHz) δ 177.14, 146.08, 126.91, 124.18, 123.22, 70.94, 42.45, 37.66, 35.70, 10.41; IR (neat) υ 3306, 2962, 1607 $cm^{-1}$.

***Anti*-3n** isolated in 8% yield as a yellow oil: 48% ee [Chiralcel OD-H, hexane:*i*-propanol = 90:10, 0.8 mL/min, $t_R$ (minor) = 9.0 min, $t_R$ (minor) = 14.4 min]; $[\alpha]_D^{31}$ = -42.0° (*c* 0.19, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 500 MHz) δ 7.23 (1H, dd, *J* = 5.0, 1.0 Hz), 6.95-7.00 (2H, m), 5.02 (1H, dd, *J* = 6.0, 6.5 Hz), 4.83 (1H, d, *J* = 7.0 Hz), 3.05-3.14 (1H, m), 3.01 (3H, s), 2.93 (3H, s), 1.24 (3H, d, *J* = 7.0 Hz); $^{13}C$ NMR ($CDCl_3$, 125 MHz) δ 176.19, 147.52, 126.95, 124.83, 124.41, 73.45, 43.13, 37.64, 35.79, 15.48; IR (neat) υ 3364, 2927, 1622 $cm^{-1}$.

**(2*S*,3*R*)-3-Hydroxy-*N*,*N*,2-trimethylhexanamide (3o)**




***Syn*-3o** isolated in 42% yield (co-elutes with ***anti*-3o** on flash purification, 47% total yield) as a pale yellow oil: 91% ee [Chiralcel OD-H, hexane:*i*-propanol = 99:1, 1.0 mL/min, $t_R$ (minor) = 20.0 min, $t_R$ (minor) = 22.7 min]; $[\alpha]_D^{29}$ = +6.4° (*c* 1.61, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 500 MHz) δ 4.51 (1H, s), 3.86-3.88 (1H, m), 3.04 (3H, s), 2.94 (3H, s), 2.62 (1H, dq, 7.5, 2.0 Hz), 1.46-1.57 (2H, m), 1.23-1.36 (2H, m), 2.13 (3H, d, *J* = 7.5 Hz), 0.92 (3H, t, *J* = 7.0 Hz); $^{13}C$ NMR ($CDCl_3$, 125 MHz) δ 178.22, 71.20, 39.07, 37.66, 36.27, 35.67, 19.57, 14.40, 9.87; IR (neat) υ 3423, 2958, 2872, 1624 $cm^{-1}$; HRMS calcd for $C_9H_{19}NO_2Na^+$: 196.1308; found *m/z* = 196.1308, error = 1.0 ppm.

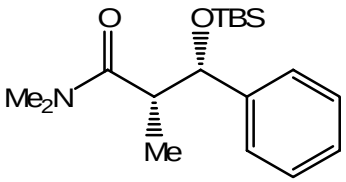
***Anti*-3o** not isolated via the general experimental procedures. Characteristic data included for **rac-*anti*-3c**, isolated as a clear and colorless oil: $^1H$ NMR ($CDCl_3$, 500 MHz) δ 4.00 (1H, d, *J* = 7.5 Hz), 3.58-3.63 (1H, m), 3.05 (3H, s), 2.95 (3H, s), 2.67-2.72 (1H, m), 1.31-1.60 (4H, m), 1.21 (3H, d, *J* = 7.0 Hz) 0.92 (3H, t, *J* = 7.0 Hz); $^{13}C$ NMR ($CDCl_3$, 125 MHz) 177.12, 74.39, 40.55, 38.07, 37.68, 35.64, 19.55, 15.45, 14.42; δ IR (neat) υ 3411, 2958, 2872, 1624 $cm^{-1}$.

**General Procedure for Enantioselective Mukaiyama Aldol Reactions: Isolation of β-Silyloxy Amide Products (Scheme 2)**

Following the general procedure outlined for isolation of β-hydroxy amide products now using **1b** (0.2 mmol), aldehyde (4.0 mmol), and **2** (2.0 mmol) in $PhCH_3$ (7

mL) over a 48 hour reaction time, after which HF (5% aq, 1 mL) was added at -40 or -80 °C (temp. of cooling bath) followed by immediate removal of the reaction mixture from the cooling bath. The reaction mixture was stirred vigorously for an additional 5 min prior to dilution by $CH_2Cl_2$ (20 mL) and washing with a saturated aqueous solution of $NaHCO_3$ (40 mL). The aqueous layer was extracted with $CH_2Cl_2$ (3 × 15 mL), the combined organics were dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography on silica gel (4:1 hexanes:EtOAc) to afford the corresponding silyloxy amide product **4** with an increased ratio of *syn* to *anti* product at the expense of isolated yield, due to incomplete separation of the silyloxy diastereomers by flash chromatography. Values reported for the diastereomer ratio of products **4a-c** correspond to ratios determined by $^1$H NMR after flash chromatography purification.

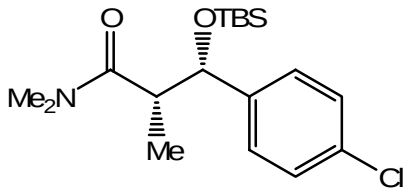
**(2*S*,3*S*)-3-phenyl-3-((*tert*-butyl)dimethylsilyloxy)-*N*,*N*,2-trimethylpropanamide (4a)**




**4a** isolated in 72% yield (35:1 syn:anti) as a white solid: $[\alpha]_D^{29}$ = +5.8° (*c* 0.55, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.16-7.30 (5H, m), 4.67 (1H, d, *J* = 10.0 Hz), 2.94-3.00 (1H, m), 2.64 (3H, s), 2.44 (3H, s), 1.28 (3H, d, *J* = 10.0 Hz), 0.86 (9H, s), 0.03 (3H, s), -0.23 (3H, s); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 174.57, 144.24, 128.05, 127.59, 126.80, 77.89, 46.10, 37.14, 35.50, 26.14, 18.49, 15.83, -4.28, -4.68; IR (neat) υ 2930, 2857,

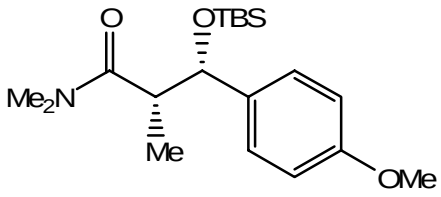
1645, 1061 $cm^{-1}$; HRMS calcd for $C_{18}H_{31}NO_2SiNa^+$: 344.2016; found *m/z* = 344.2029, error = 3.6 ppm.

**(2*S*,3*S*)-3-(4-Chlorophenyl)-3-((*tert*-butyl)dimethylsilyloxy)-*N*,*N*,2-trimethylpropanamide (4b)**




**4b** isolated in 68% yield (24:1 syn:anti) after flash chromatography as a white solid: $[\alpha]_D^{29}$ = +5.5° (*c* 0.47, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 500 MHz) δ 7.22-7.28 (4H, m), 4.70 (1H, d, *J* = 5.0 Hz), 2.91-2.99 (1H, m), 2.69 (3H, s), 2.56 (3H, s), 1.29 (3H, d, *J* = 5.0 Hz), 0.87 (9H, s), 0.05 (3H, s), -0.22 (3H, s); $^{13}C$ NMR ($CDCl_3$, 125 MHz) δ 174.38, 143.01, 133.19, 128.30, 128.28, 77.15, 46.17, 37.29, 35.59, 26.12, 18.46, 15.84, -4,25, -4.66; IR (neat) υ 2931, 2857, 1645, 1258, 1067, 874 $cm^{-1}$; HRMS calcd for $C_{18}H_{30}ClNO_2SiNa^+$: 378.1627; found *m/z* = 378.1617, error = 2.5 ppm.

**(2*S*,3*S*)-3-(4-methoxyphenyl)-3-((*tert*-butyl)dimethylsilyloxy)-*N*,*N*,2-trimethylpropanamide (4c)**

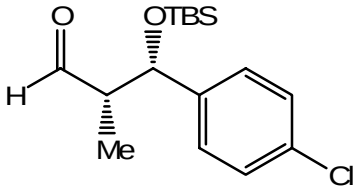


**4c** isolated in 34% yield (>50:1 syn:anti) after flash chromatography as a white solid: $[\alpha]_D^{31}$ = +1.3° (*c* 0.32, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 500 MHz) δ 7.22 (2H, d, *J* = 8.5 Hz), 6.78 (2H, d, *J* = 8.5 Hz), 4.64 (1H, d, *J* = 9.5 Hz), 3.79 (3H, s), 2.94-2.99 (1H, m), 2.68 (3H, s), 2.52 (3H, s), 1.28 (3H, d, *J* = 10.0 Hz), 0.86 (9H, s), 0.04 (3H, s), -0.22 (3H, s); $^{13}C$ NMR ($CDCl_3$, 125 MHz) δ 174.77, 159.04, 136.53, 127.96, 113.37, 77.50, 55.49, 46.19, 37.29, 35.59, 26.18, 18.53, 15.90, -4.21, -4.65; IR (neat) υ 2931, 2857, 1644, 1512, 1250, 1066, 876, 837, 778 $cm^{-1}$; HRMS calcd for $C_{18}H_{31}NO_2SiNa^+$: 344.2016; found *m/z* (– $C_6H_{14}Si$) = 260.1263, error = 4.4 ppm.

**General Procedure for Reduction of Amide Aldol Products to Aldehydes Using Schwartz's Reagent**

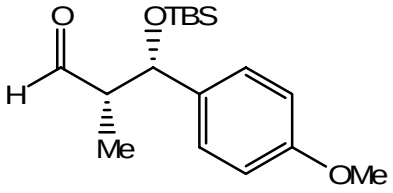
To a stirring mixture of bis(cyclopentadienyl)zirconium chloride hydride (0.6 mmol, Schwartz's reagent, Acros) in $CH_2Cl_2$ (3 mL) at room temperature under an atmosphere of argon was added a $CH_2Cl_2$ (1 mL) solution of amide **4** (0.2 mmol) in one portion. Stirring was continued at room temperature 15-80 min until complete consumption of amide is observed by TLC. To the reaction was added silica gel (~1g, 60 Å, 230-400 mesh) in one portion and the mixture was concentrated *in vacuo* to give a dry powder, which was loaded directly onto a column for flash chromatography on silica gel (hexanes:EtOAc 50:1) to afford the corresponding aldehyde product **5**. Reported diastereomer ratios for products **5a-c** correspond to values determined by $^1H$ NMR after flash chromatography.

**(2*S*,3*S*)-3-(4-Chlorophenyl)-3-((*tert*-butyl)dimethylsilyloxy)-*N*,*N*,2-trimethylpropanal (5b)**



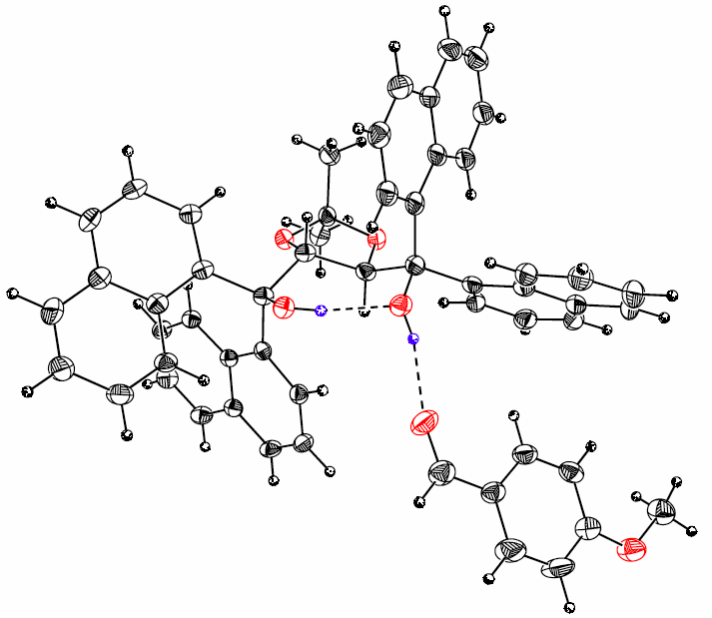

**5b** isolated in 84% yield (24:1 syn:anti) as a clear and colorless oil: $[\alpha]_D^{30}$ = -21.9° (*c* 0.22, $CHCl_3$); $^1$H NMR ($CDCl_3$, 500 MHz) δ 9.75 (1H, s), 7.31 (2H, d, *J* = 8.0 Hz), 7.24 (2H, d, *J* = 8.0 Hz), 5.15 (1H, d, *J* = 5.0 Hz), 2.54-2.56 (1H, m), 1.04 (3H, d, *J* = 5.0 Hz), 0.88 (9H, s), 0.04 (3H, s), -0.17 (3H, s); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 204.17, 141.29, 133.51, 128.73, 127.95, 73.89, 54.95, 26.06, 18.45, 8.28, -4.17, -4.90; IR (neat) υ 2930, 2858, 1729, 1490, 1254, 1090, 838 $cm^{-1}$.

**(2*S*,3*S*)-3-(4-methoxyphenyl)-3-((*tert*-butyl)dimethylsilyloxy)-*N*,*N*,2-trimethylpropanal(5c)**



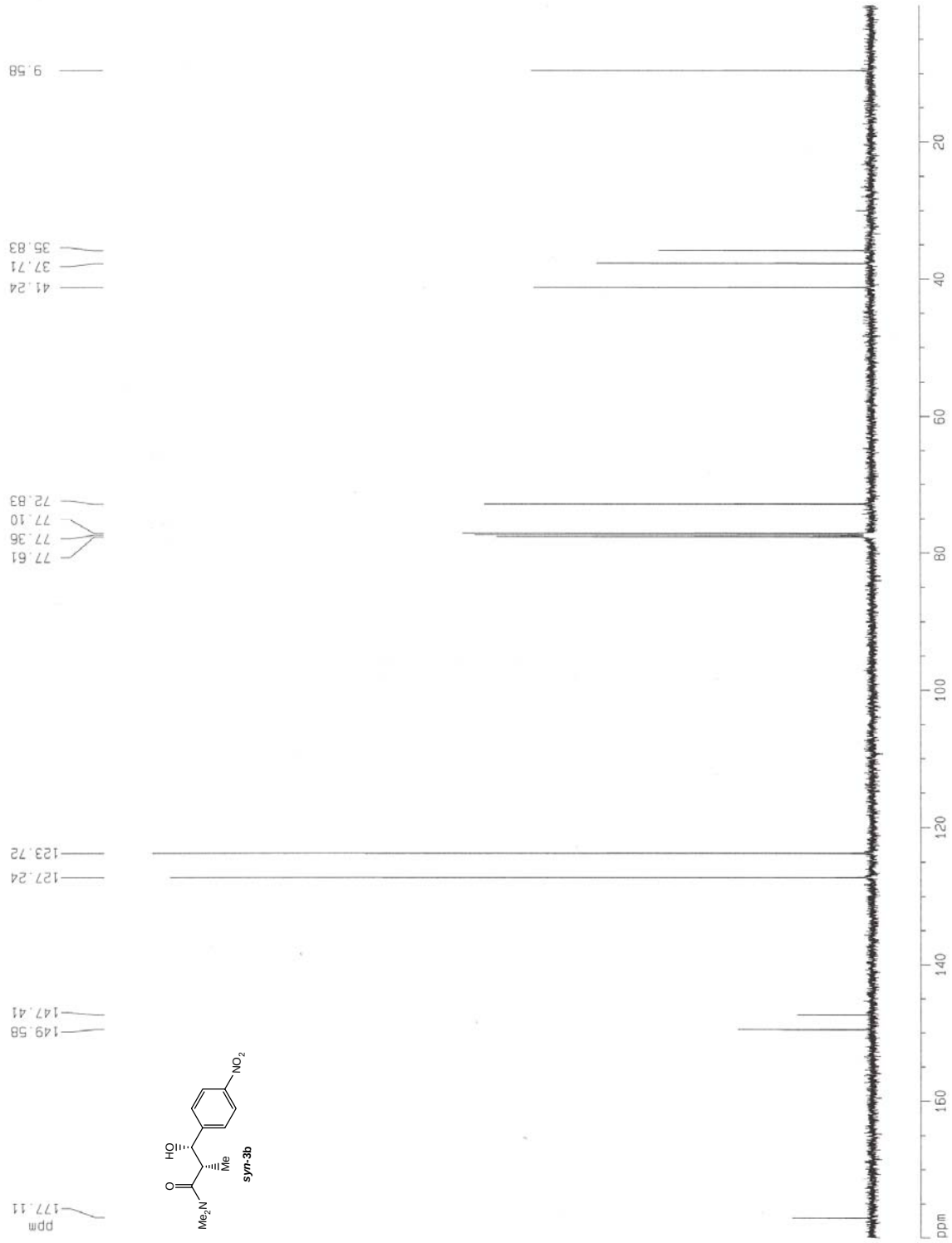

**5c** isolated in 85% yield (>50:1 syn:anti) as a clear and colorless oil: $[\alpha]_D^{31}$ = -48.8° (*c* 0.19, $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz) δ 9.74 (1H, d, *J* = 1.2 Hz), 7.20 (2H, d, *J* = 8.6 Hz), 6.85 (2H, d, *J* = 8.7 Hz), 5.07 (1H, d, *J* = 4.5 Hz), 3.80 (3H, s), 2.54-2.63 (1H, m), 1.03 (3H, d, *J* = 7.0 Hz), 0.88 (9H, s), 0.02 (3H, s), -0.18 (3H, s); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 204.91, 159.19, 134.69, 127.71, 113.81, 74.36, 55.53, 55.25, 26.07, 18.44,

8.60, -4.18, -4.94; IR (neat) υ 2931, 2857, 1727, 1613, 1513, 1251, 1035, 837 $cm^{-1}$; HRMS calcd for $C_{17}H_{28}O_3SiNa^+$: 331.1700; found *m/z* = 331.1705, error = 1.4 ppm.



**X-ray Structure of rac-1a-Anisaldehyde Complex.**

8.205
8.187
7.556
7.539
5.188
5.184
3.054
2.990
2.875
2.871
2.861
2.856
0.985
0.971
ppm
syn-3b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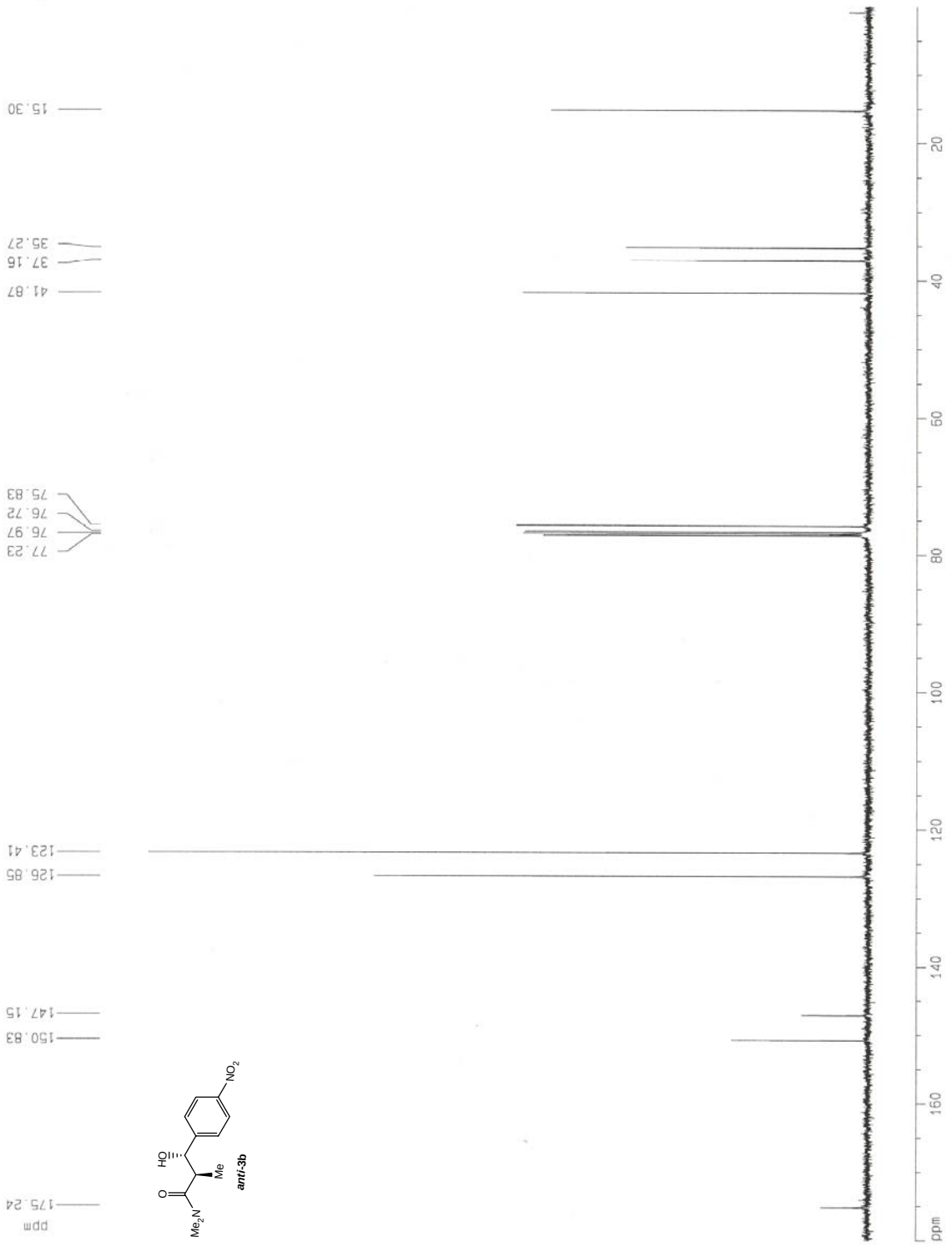
77.10
77.36
77.61
123.72
127.24
147.41
149.58
177.11
ppm
20
40
60
80
100
120
140
160
ppm
NO2
HO
Me
O
Me2N
syn-3b

1.261
1.275
2.836
2.861
4.834
4.844
7.504
7.521
8.162
8.180
ppm
anti-3b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37.16
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76.72
76.97
77.23
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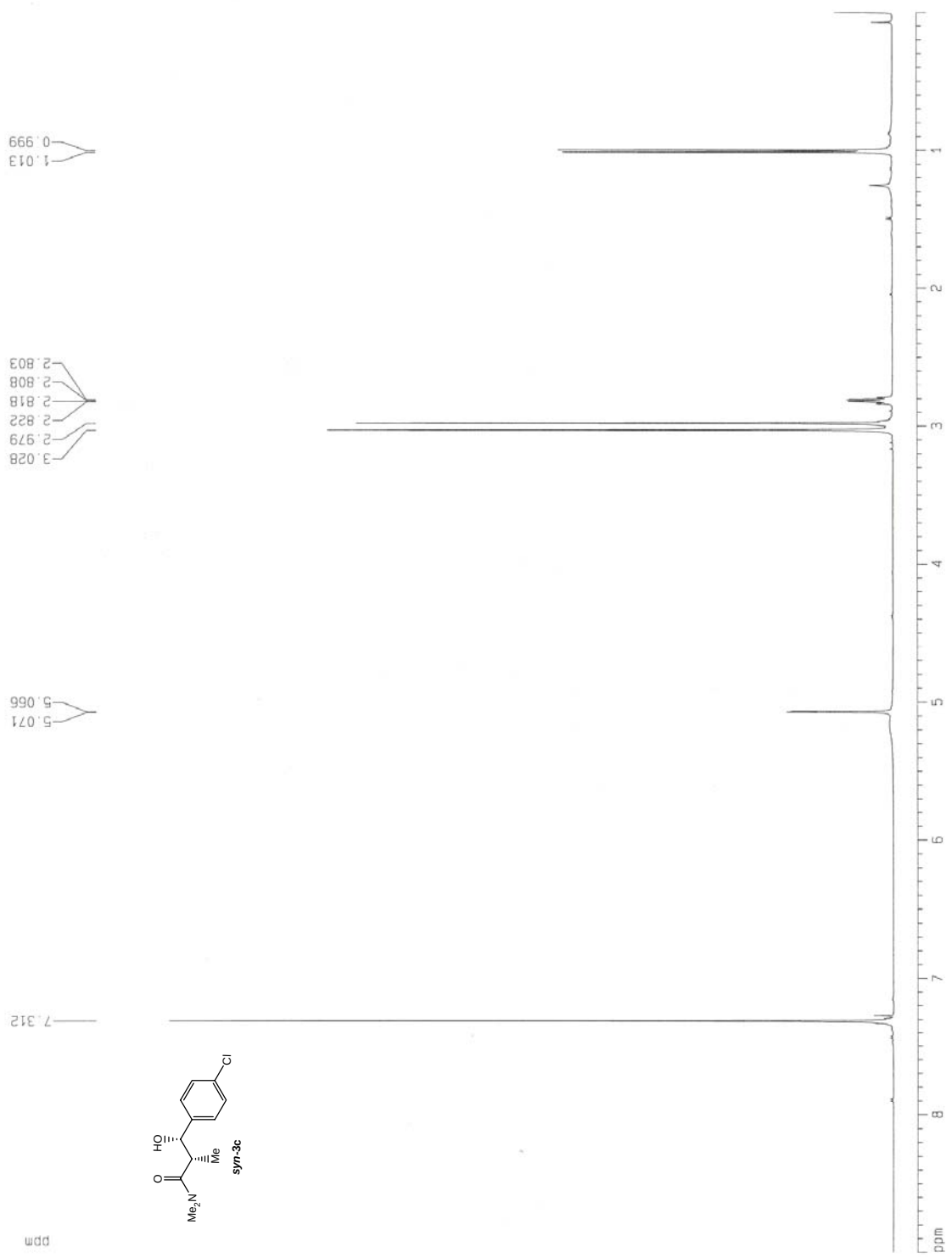
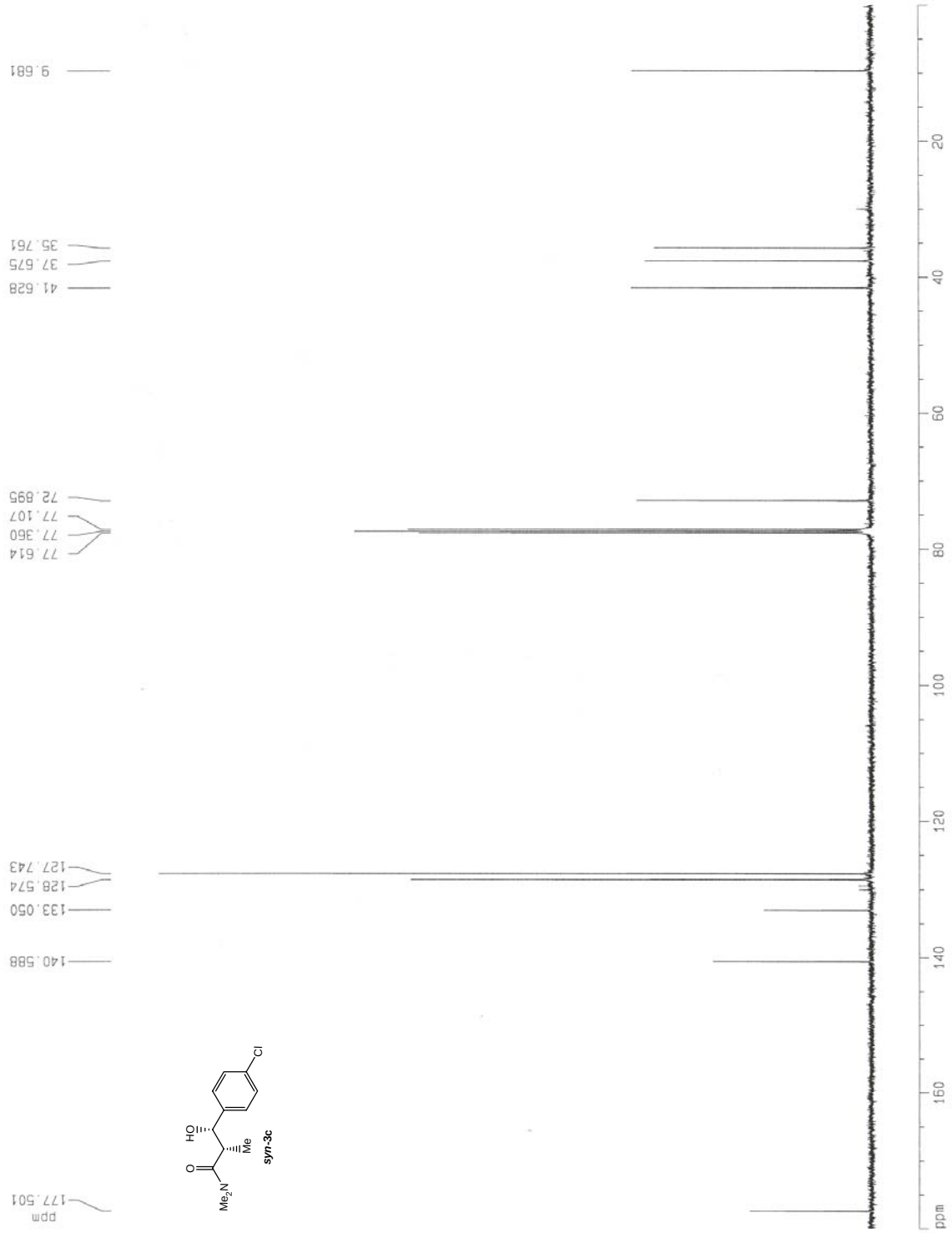
126.85
147.15
150.83
175.24
ppm
20
40
60
80
100
120
140
160
ppm
HO
Me
O
Me2N
NO2
anti-3b


syn-3c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77.360
77.614
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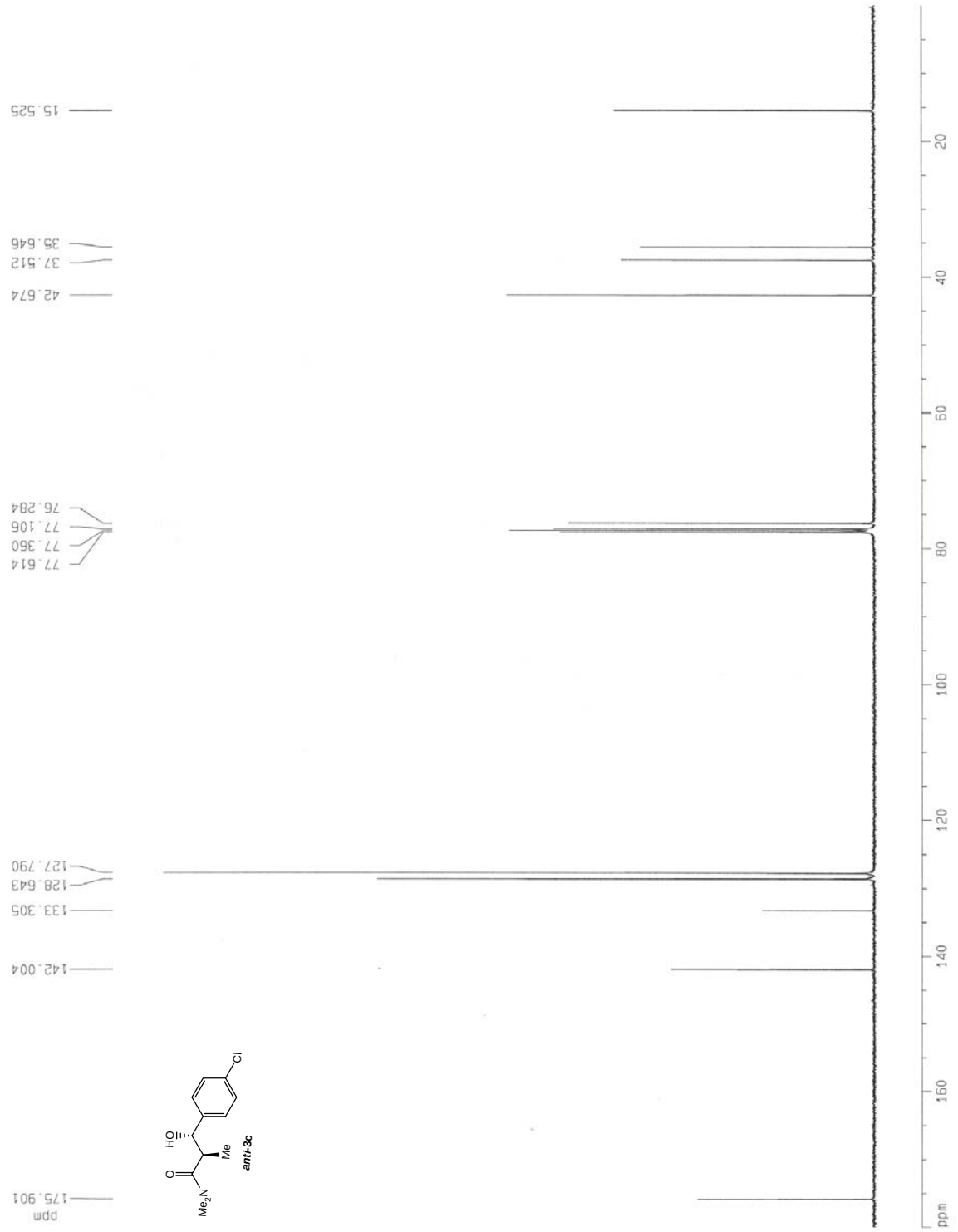
128.574
133.050
140.588
177.501
ppm
20
40
60
80
100
120
140
160
ppm
Cl
HO
Me
O
Me2N
syn-3c

1.179
1.193
2.866
2.871
2.974
2.987
3.000
4.732
4.744
7.262
7.279
7.290
7.307
ppm
1
2
3
4
5
6
7
8
Cl
HO
O
Me
Me2N
anti-3c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37.512
42.674
76.284
77.106
77.360
77.614
127.790
128.643
133.305
142.004
175.901
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20
40
60
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120
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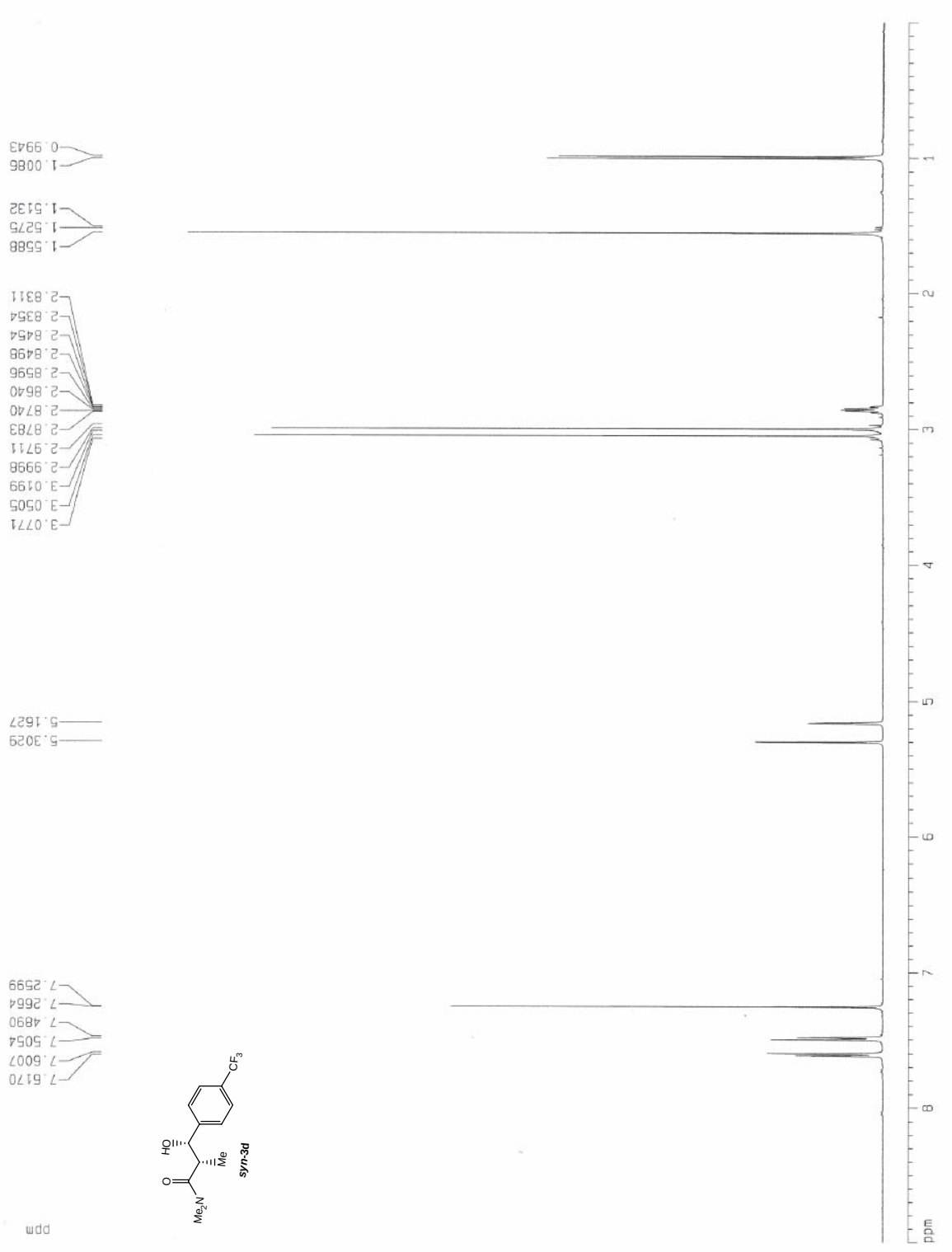
ppm
Cl
HO
Me
O
Me2N
anti-3c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1.5132
1.5275
1.5588
2.8311
2.8354
2.8454
2.8498
2.8596
2.8640
2.8740
2.8783
2.9711
2.9998
3.0199
3.0505
3.0771
5.1627
5.3029
7.2599
7.2664
7.4890
7.5054
7.6007
7.6170
ppm
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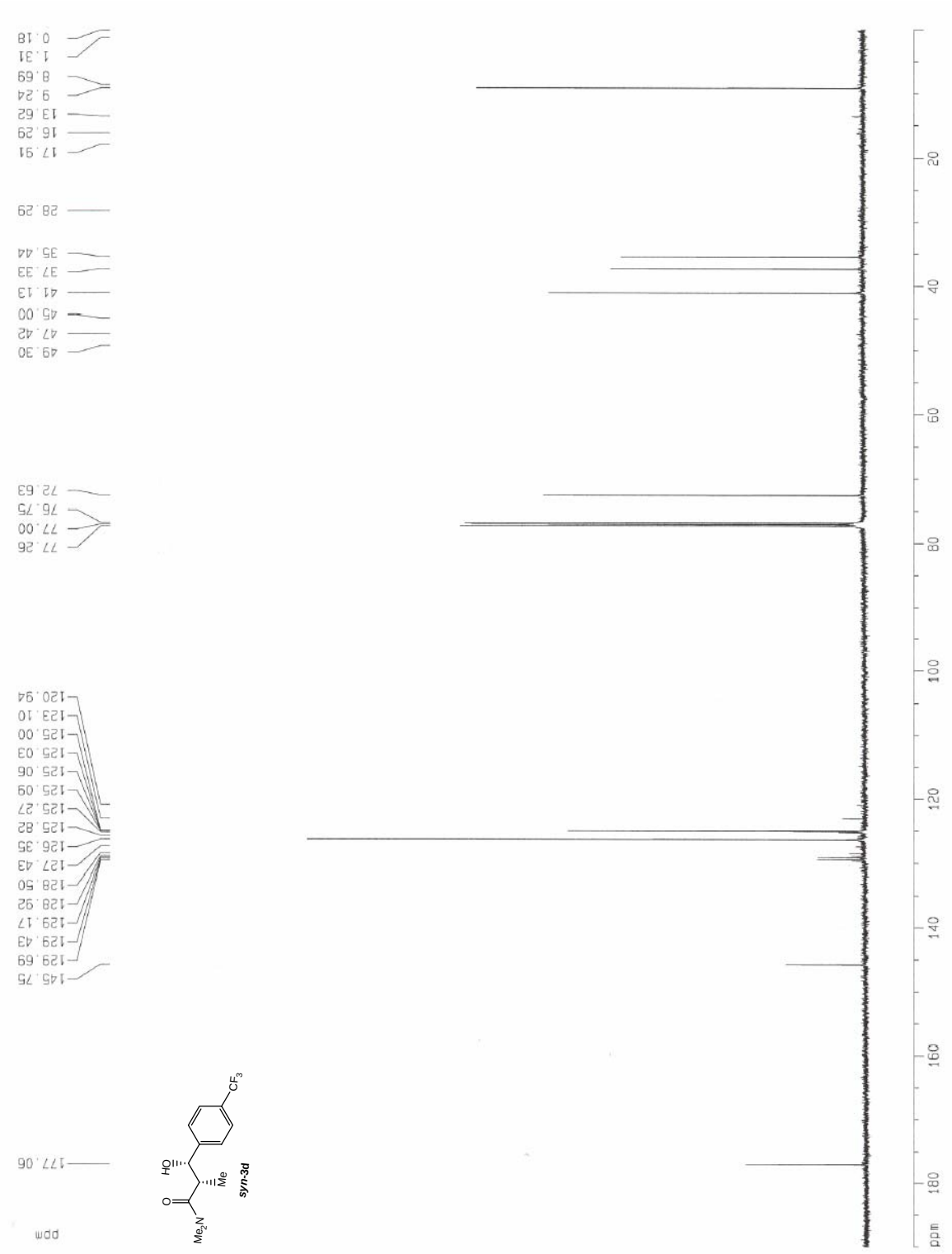
2
3
4
5
6
7
8
HO
Me
O
Me2N
CF3
syn-3d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9.24
13.62
16.29
17.91
28.29
35.44
37.33
41.13
45.00
47.42
49.30
72.63
76.75
77.00
77.26
120.94
123.10
125.00
125.03
125.06
125.09
125.27
125.82
126.35
127.43
128.50
128.92
129.17
129.43
129.69
145.75
177.06
ppm
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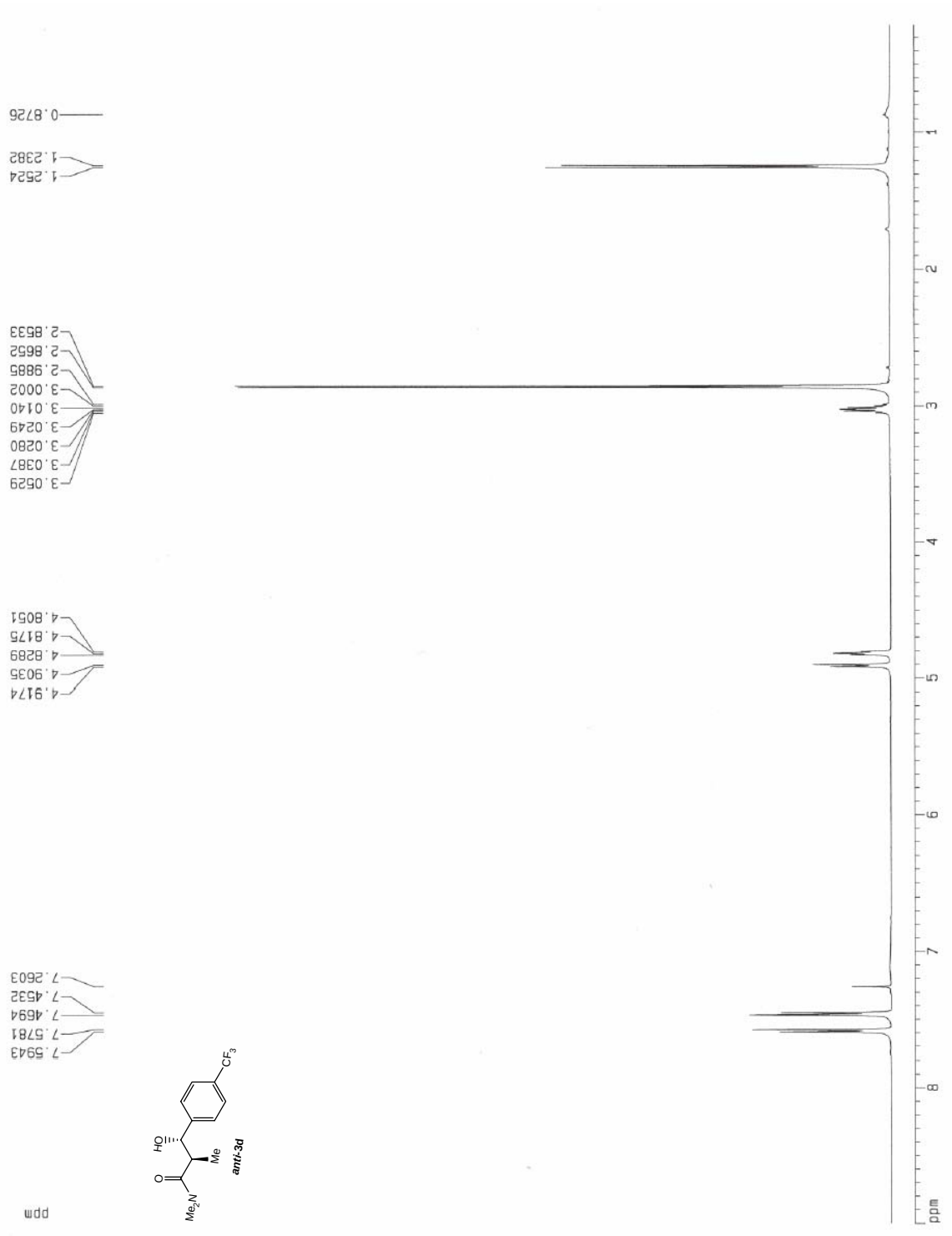
60
80
100
120
140
160
180
ppm
HO
Me
O
Me2N
CF3
syn-3d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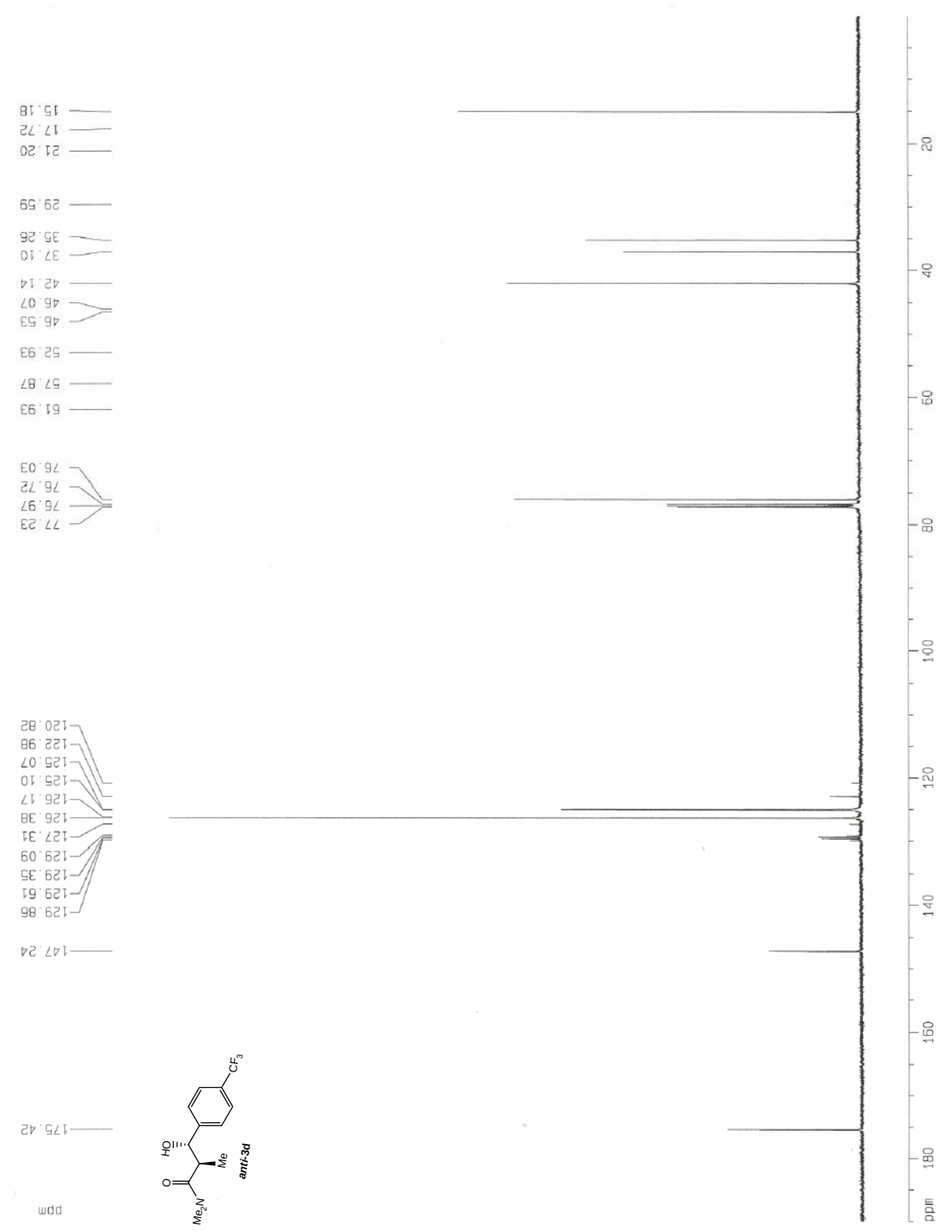
1.2382
2.8533
2.8652
2.9885
3.0002
3.0140
3.0249
3.0280
3.0387
3.0529
4.8051
4.8175
4.8289
4.9035
4.9174
7.2603
7.4532
7.4694
7.5781
7.5943
ppm
HO
Me
Me2N
O
CF3
anti-3d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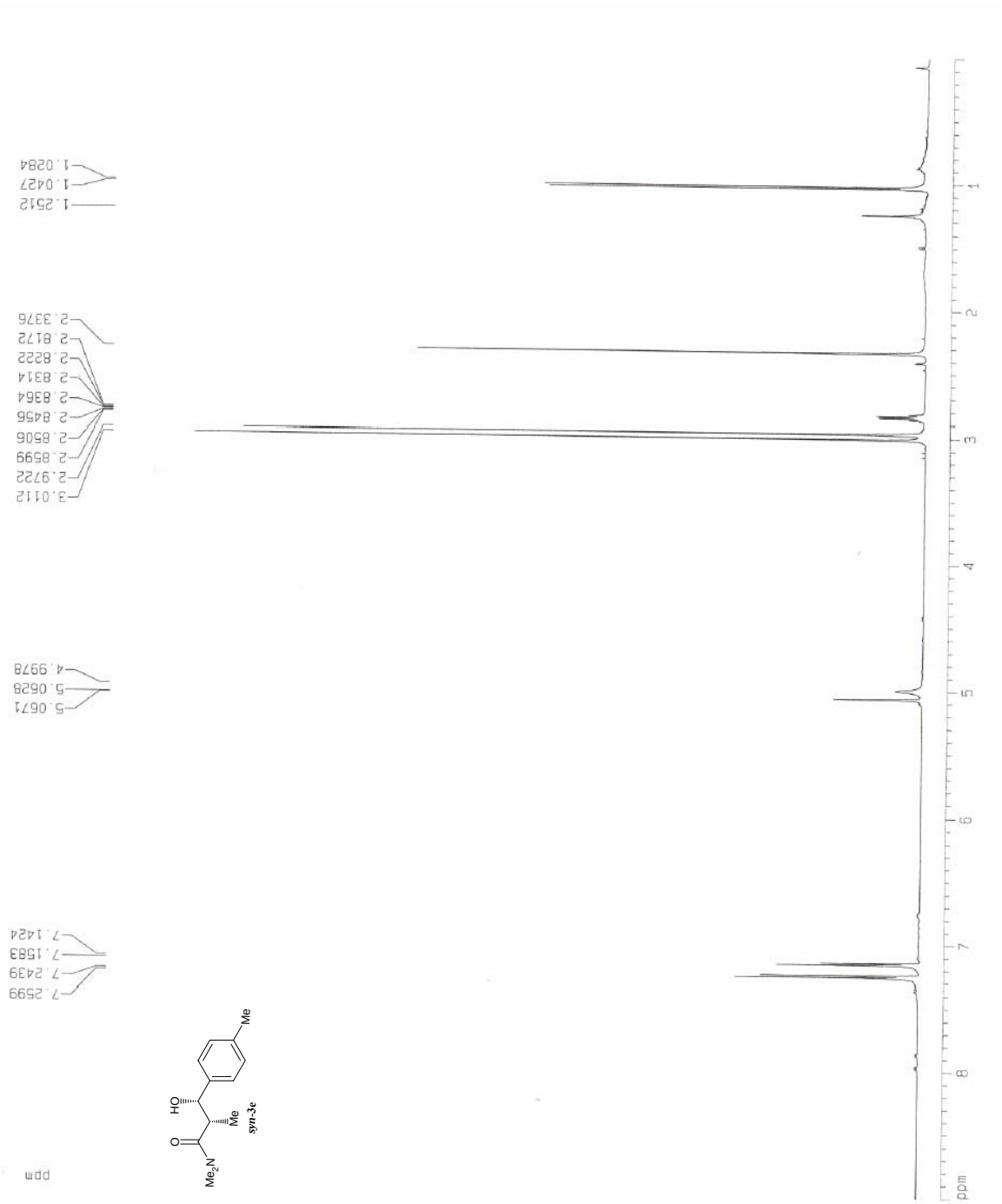
17.72
21.20
29.59
35.26
37.10
42.14
46.07
46.53
52.93
57.87
61.93
76.03
76.72
76.97
77.23
120.82
122.98
125.07
125.10
126.17
126.38
127.31
129.09
129.35
129.61
129.86
147.24
175.42
ppm
HO
Me
Me2N
O
CF3
anti-3d
20
40
60
80
100
120
140
160
180
ppm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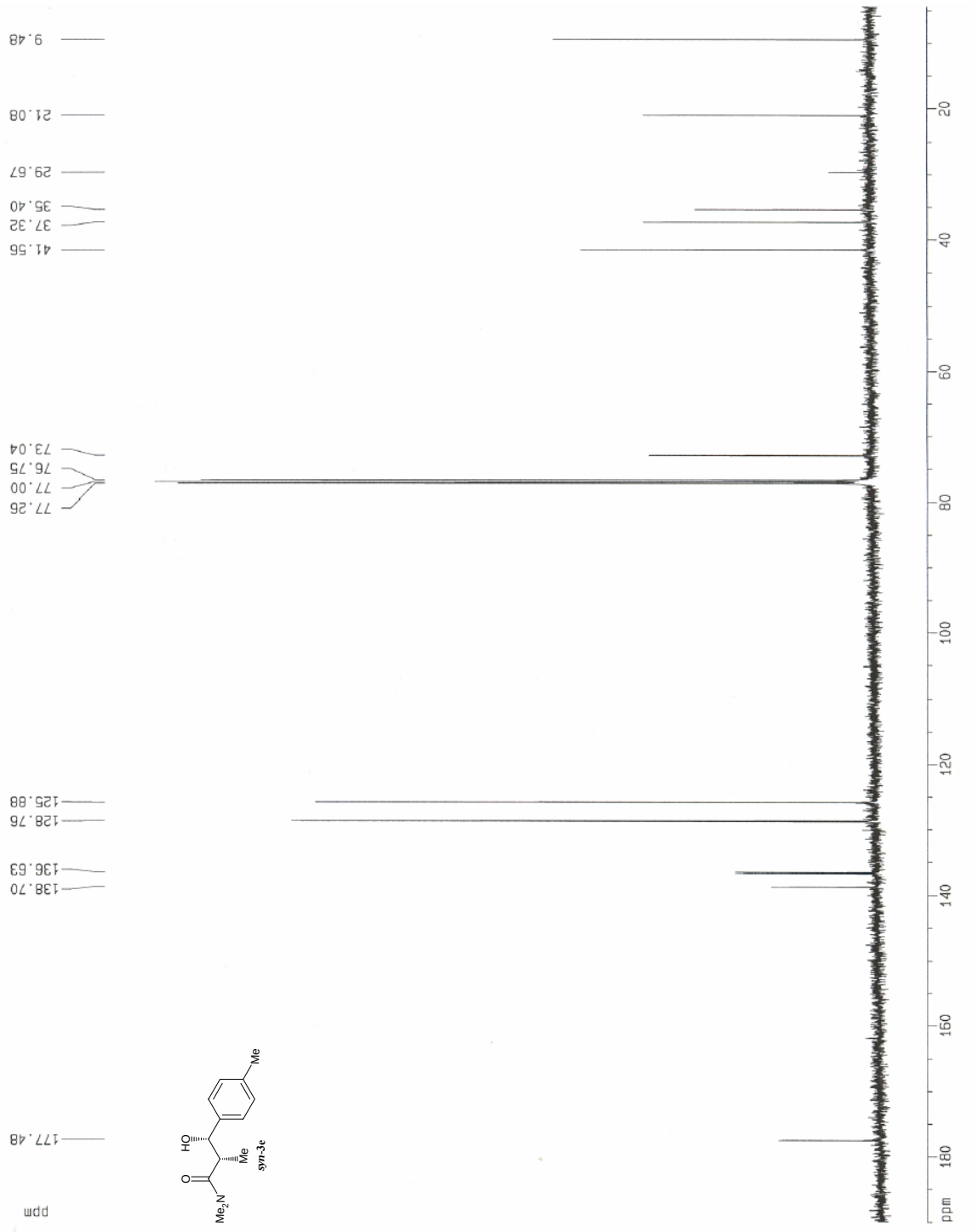
7.2439
7.1583
7.1424
5.0671
5.0628
4.9978
3.0112
2.9722
2.8599
2.8506
2.8456
2.8364
2.8314
2.8222
2.8172
2.3376
1.2512
1.0427
1.0284
ppm
Me
HO
Me
O
Me2N
syn-3e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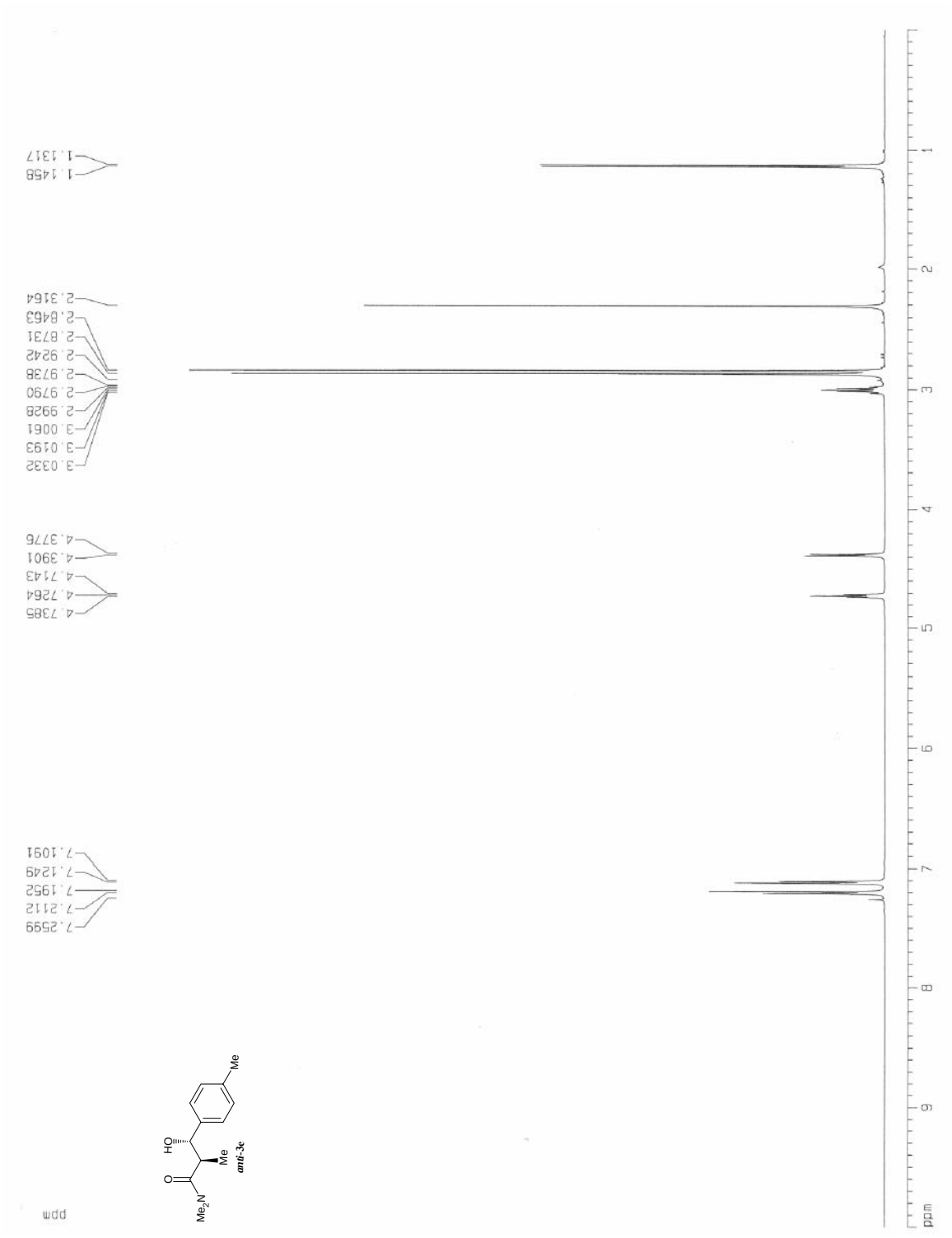
37.32
41.56
73.04
76.75
77.00
77.25
125.88
128.76
136.63
138.70
177.48
ppm
20
40
60
80
100
120
140
160
180
ppm
Me
HO
Me
syn-3e
O
Me2N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2.3164
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2.8731
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2.9738
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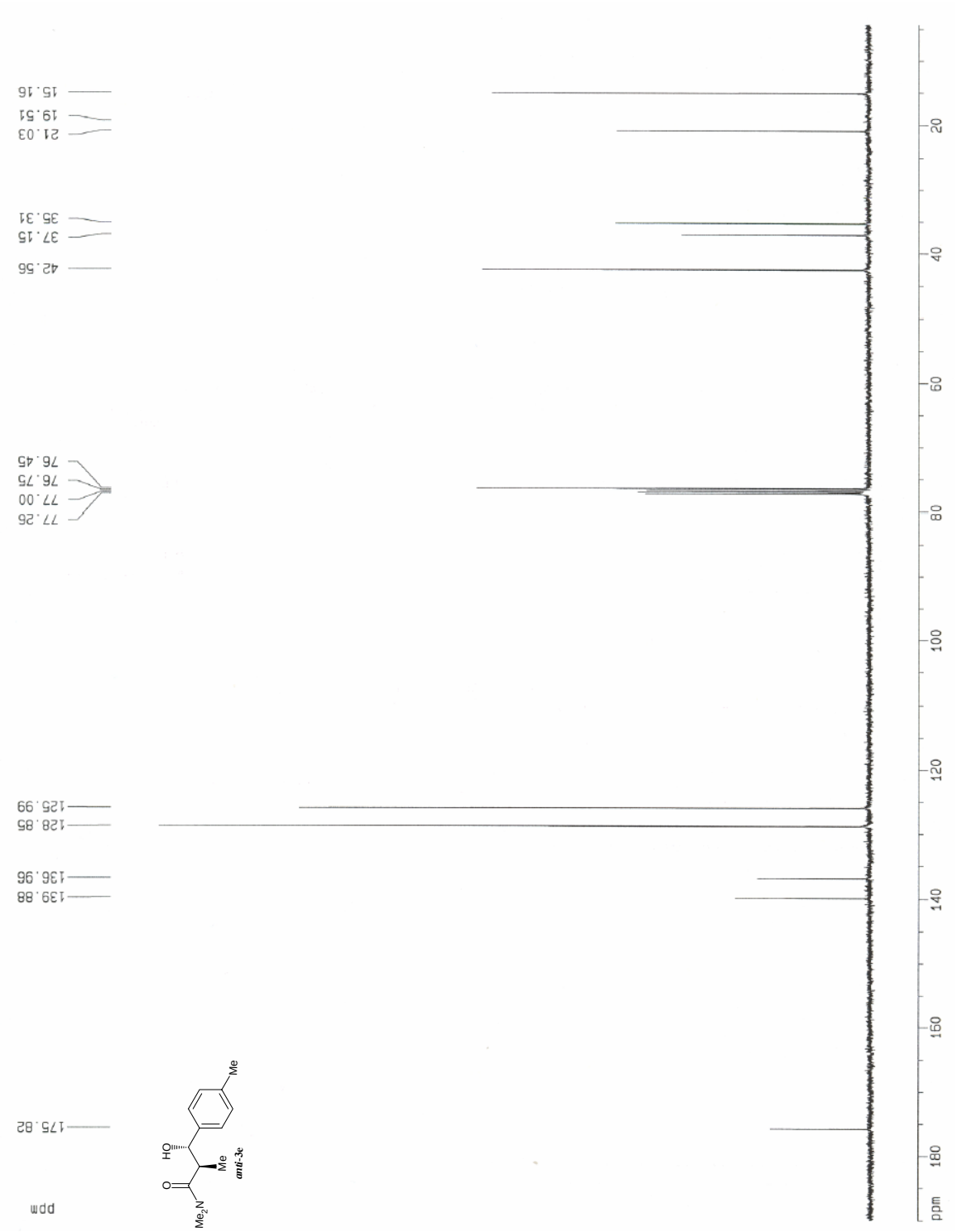
2.9928
3.0061
3.0193
3.0332
4.3776
4.3901
4.7143
4.7264
4.7385
7.1091
7.1249
7.1952
7.2112
7.2599
ppm
Me
HO
Me
anti-3c
O
Me2N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19.51
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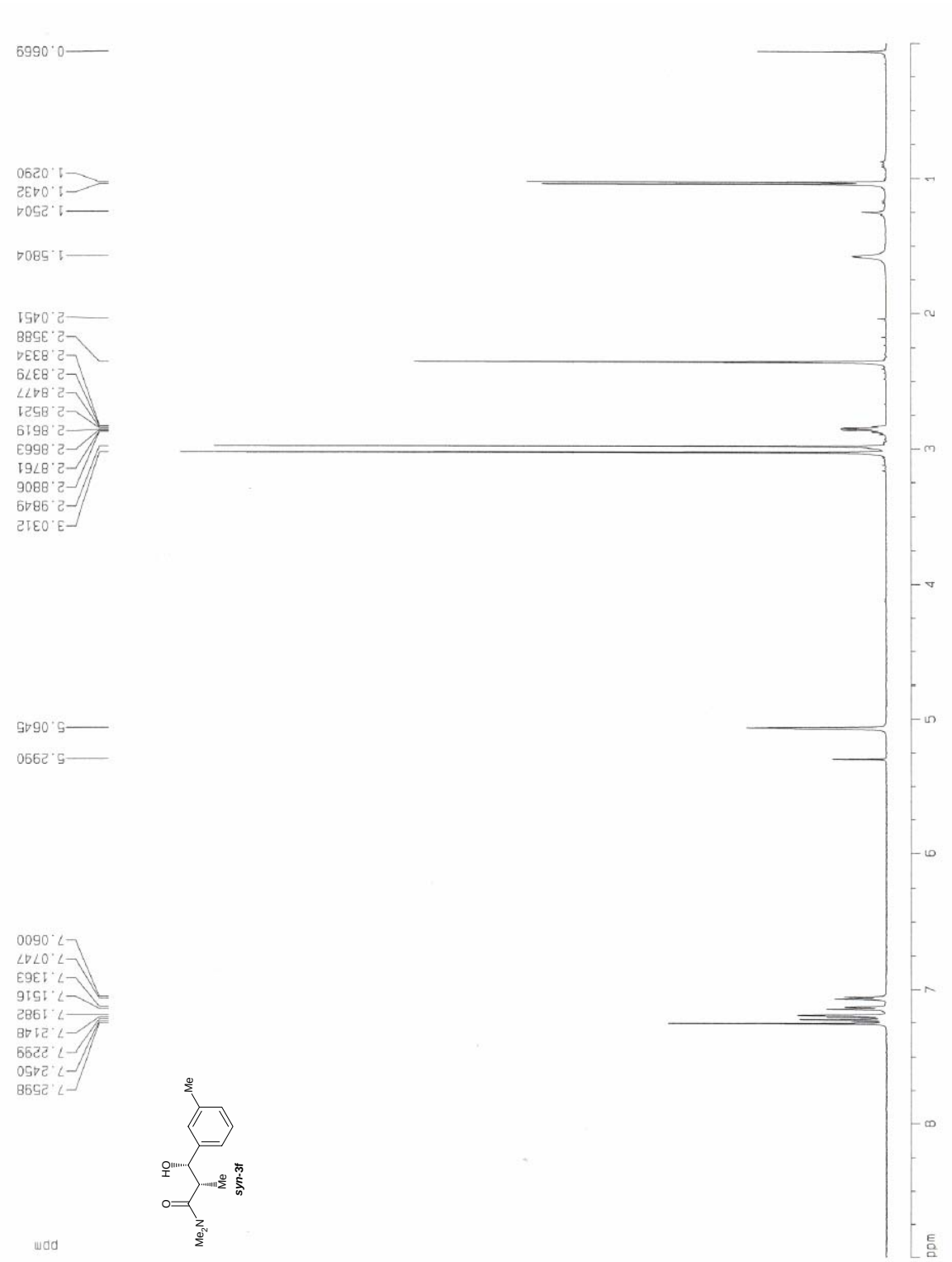
37.15
42.56
76.45
76.75
77.00
77.26
125.99
128.85
136.96
139.88
175.82
ppm
20
40
60
80
100
120
140
160
180
ppm
Me
HO
Me
O
Me2N
anti-3e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1.5804
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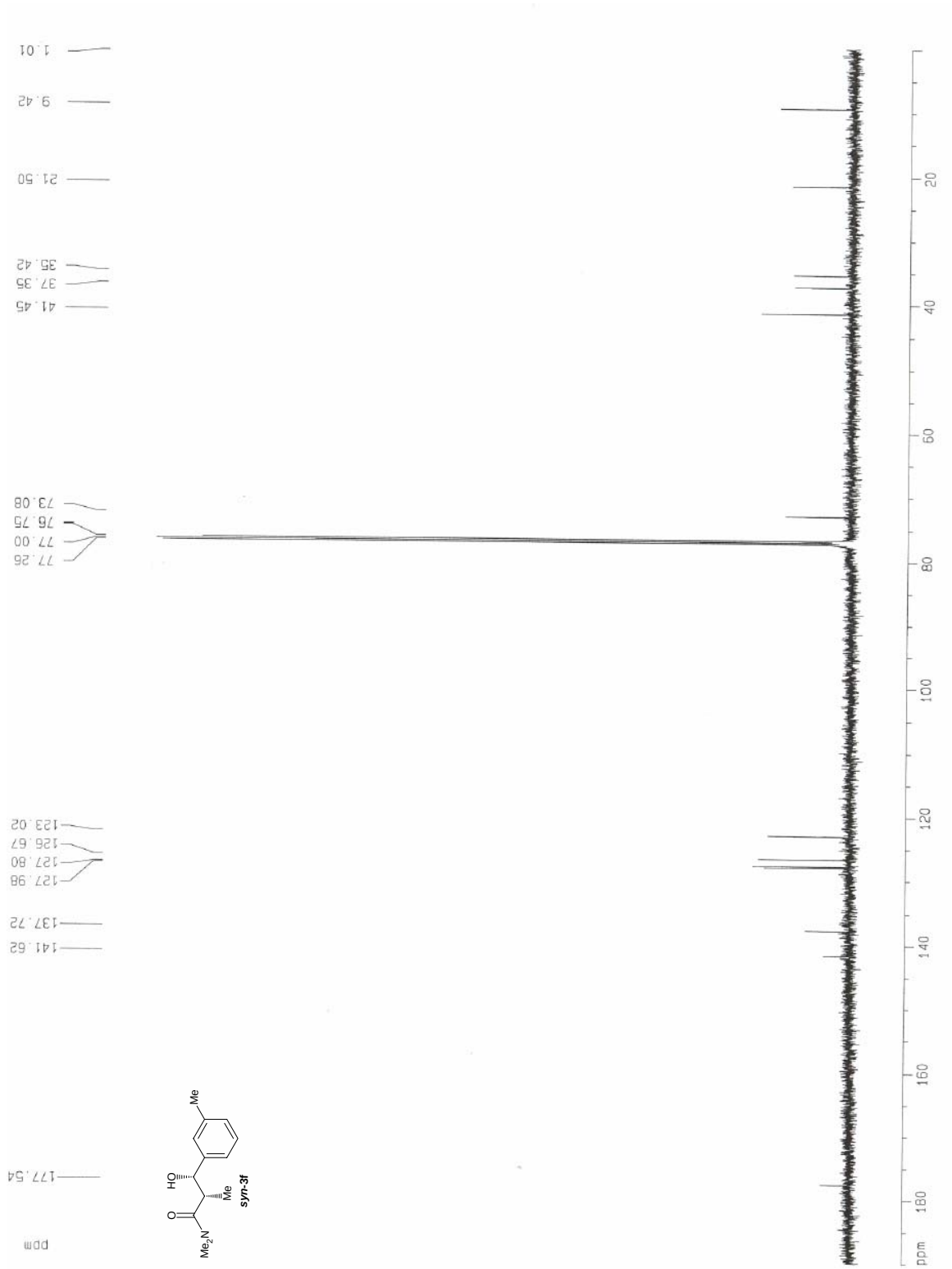
2.3588
2.8334
2.8379
2.8477
2.8521
2.8619
2.8663
2.8761
2.8806
2.9849
3.0312
5.0645
5.2990
7.0600
7.0747
7.1363
7.1516
7.1982
7.2148
7.2299
7.2450
7.2598
Me
HO
Me
O
Me2N
syn-3f
ppm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35.42
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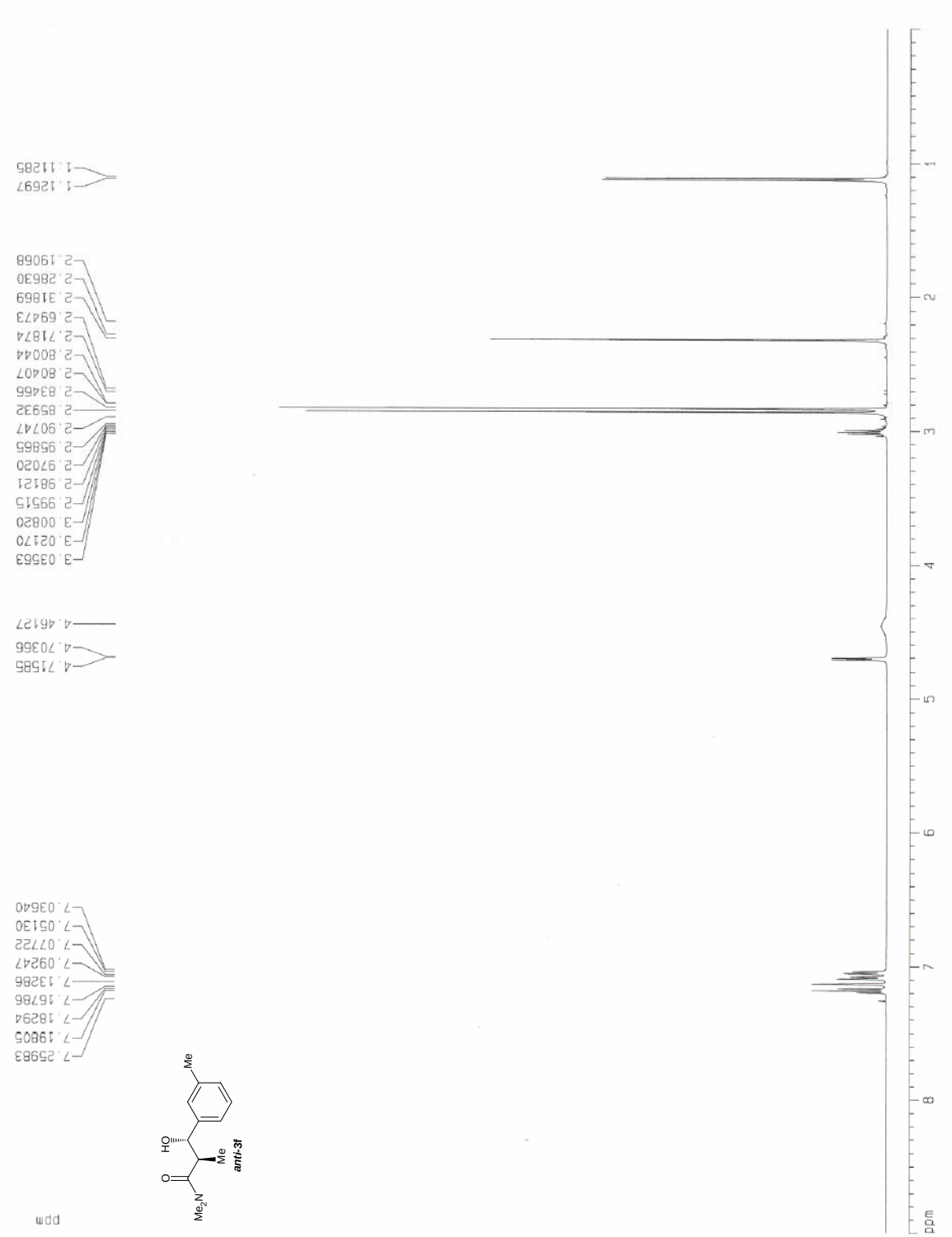
41.45
73.08
76.75
77.00
77.26
123.02
126.67
127.80
127.98
137.72
141.62
177.54
ppm
Me
HO
Me
O
Me2N
syn-3f
20
40
60
80
100
120
140
160
180
ppm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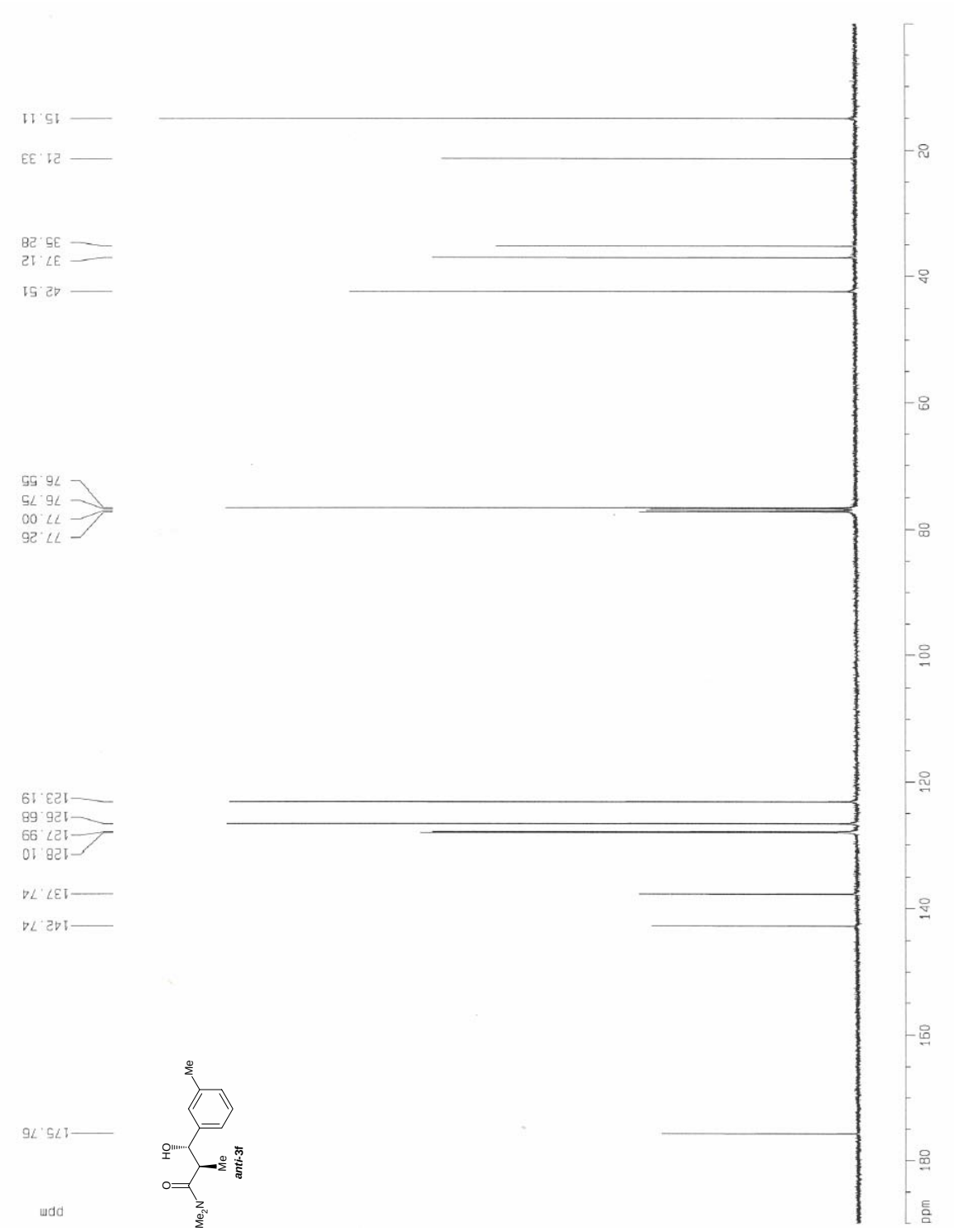
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137.74
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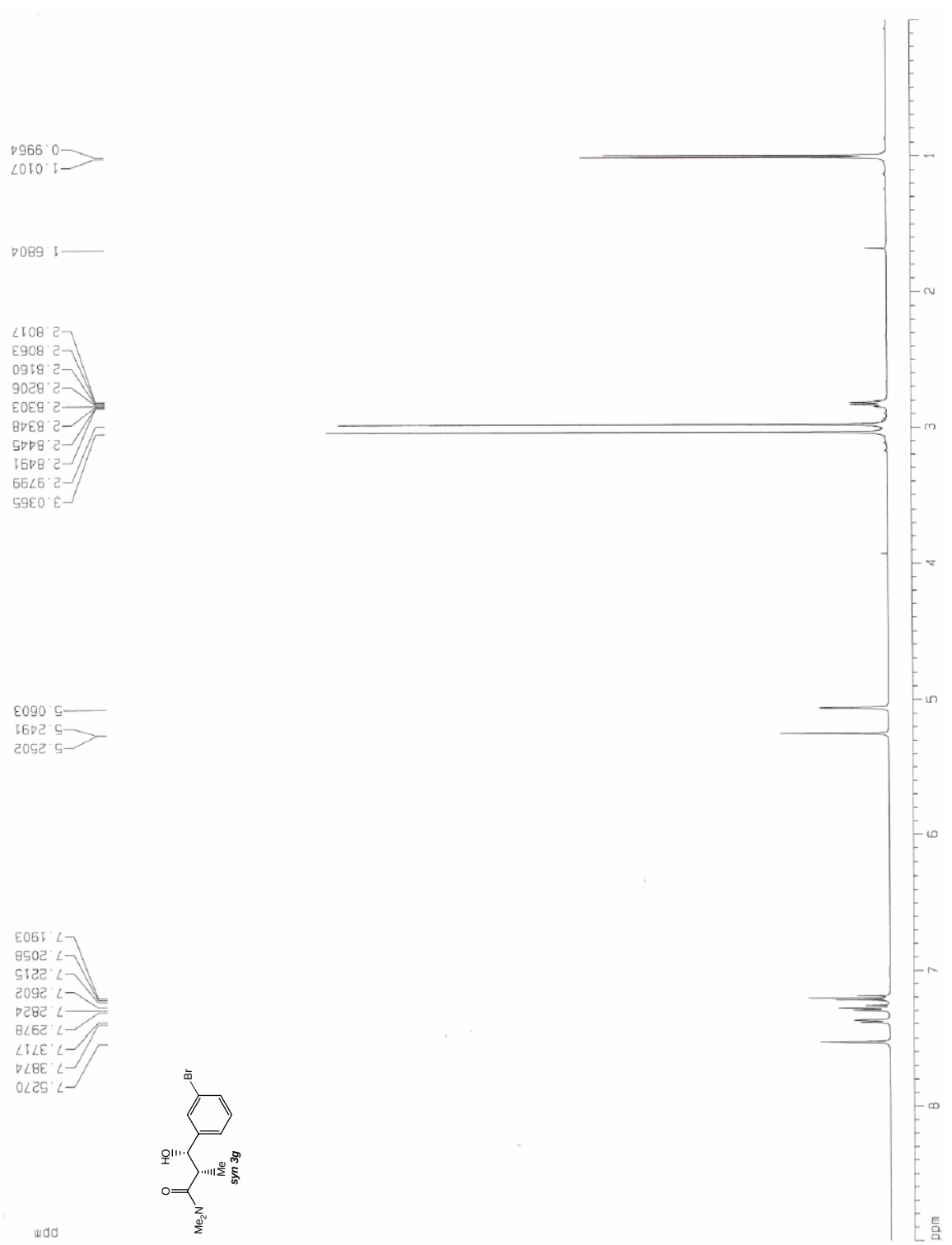
40
60
80
100
120
140
160
180
Me
HO
Me
O
Me2N
anti-3t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2.8491
2.9799
3.0365
5.0603
5.2491
5.2502
7.1903
7.2058
7.2215
7.2602
7.2824
7.2978
7.3717
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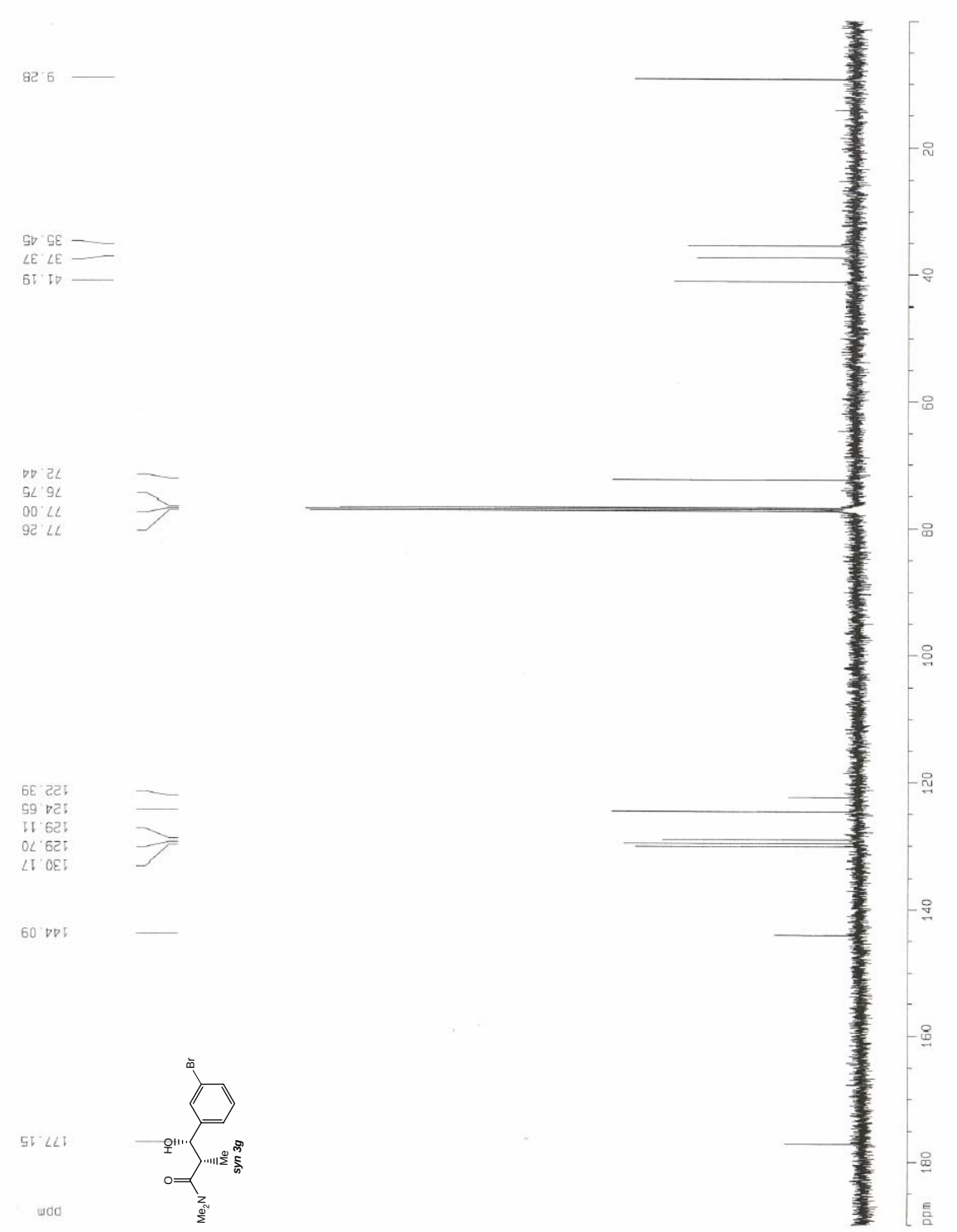
Br
HO
Me
O
Me2N
syn 3g
ppm
1
2
3
4
5
6
7
8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129.11
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130.17
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20
40
60
80
100
120
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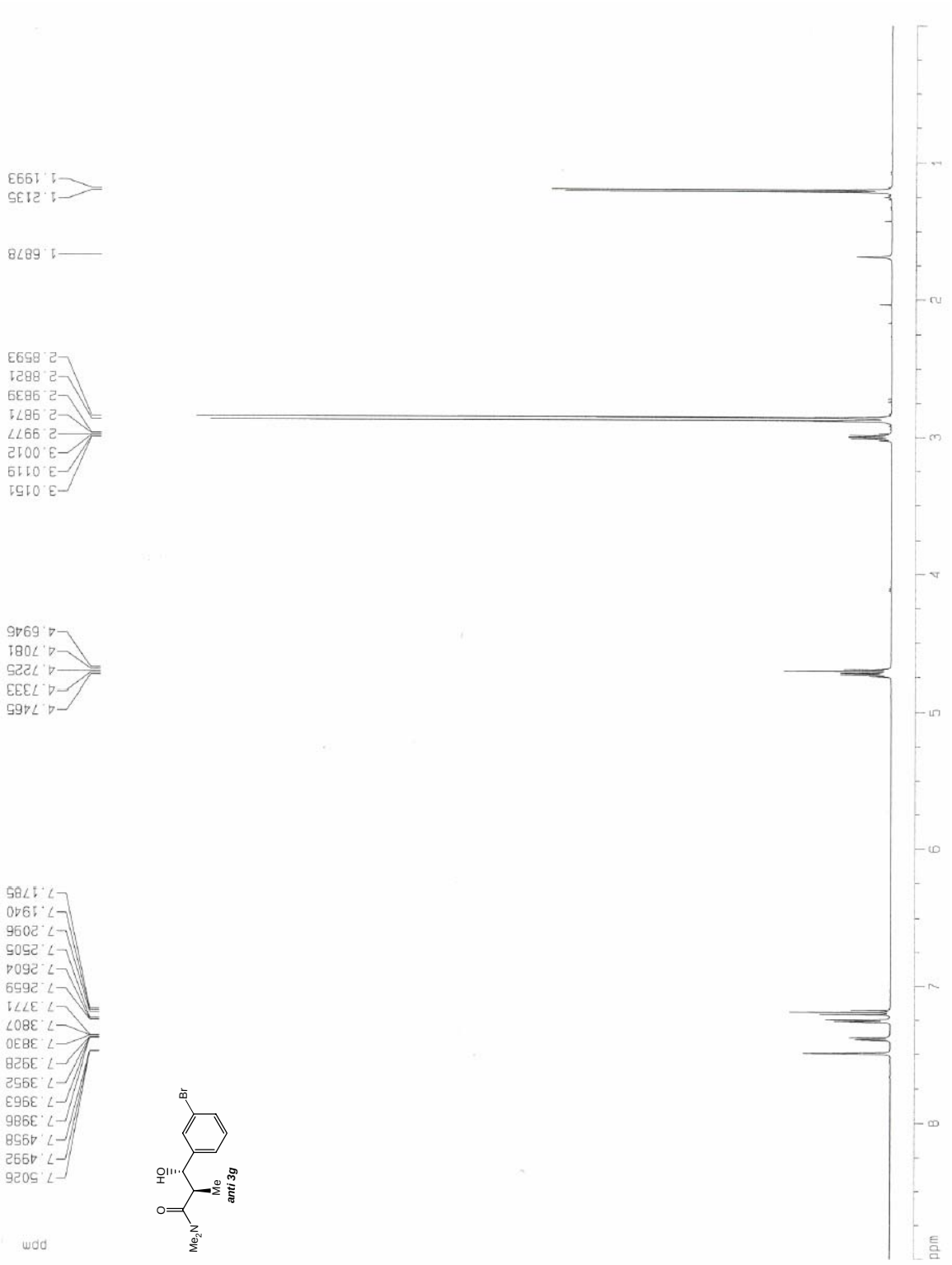
160
180
Br
HO
Me
O
Me2N
syn 3g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4.6946
4.7081
4.7225
4.7333
4.7465
7.1785
7.1940
7.2096
7.2505
7.2604
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7.3771
7.3807
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O
anti 3g
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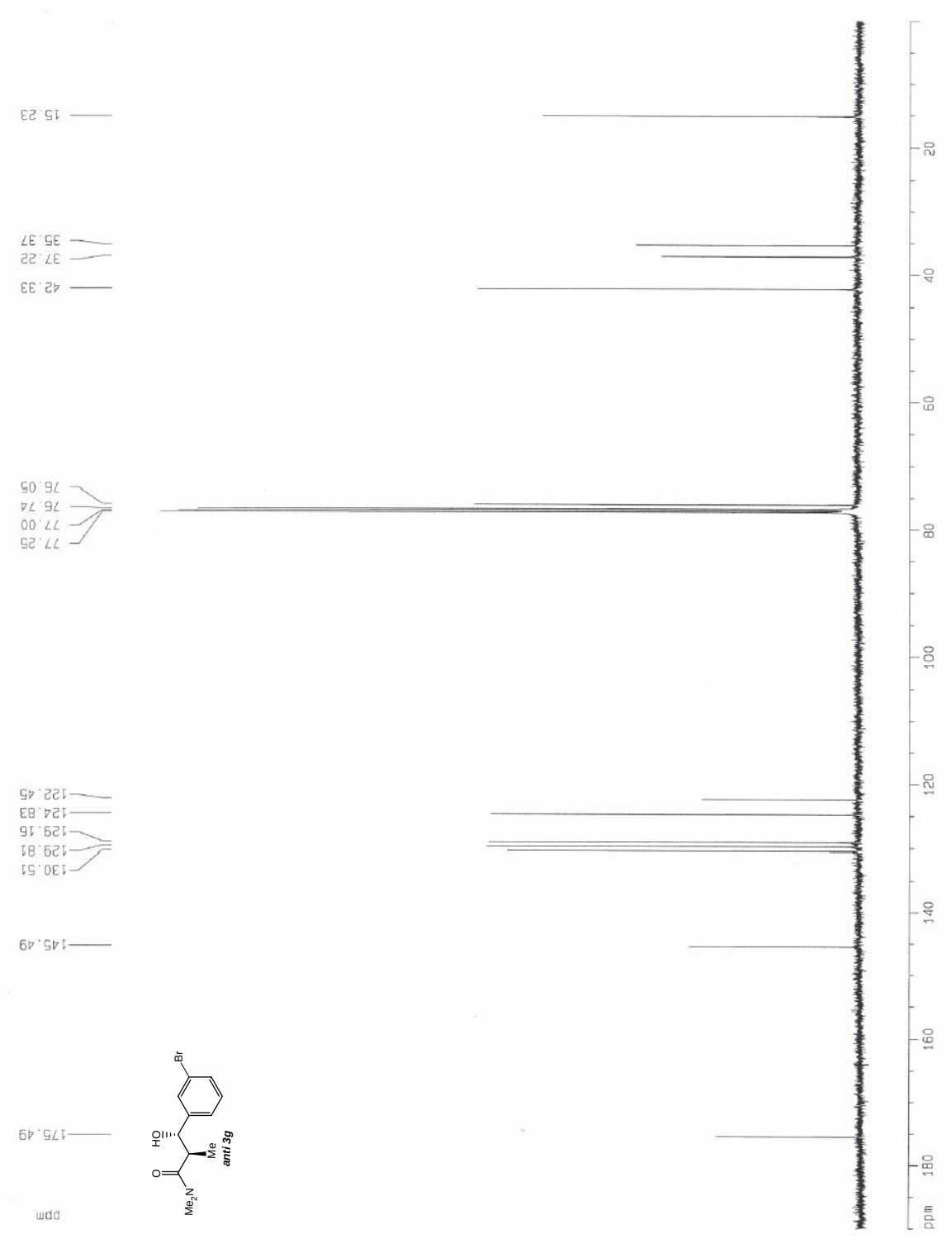
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130.51
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40
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180
Br
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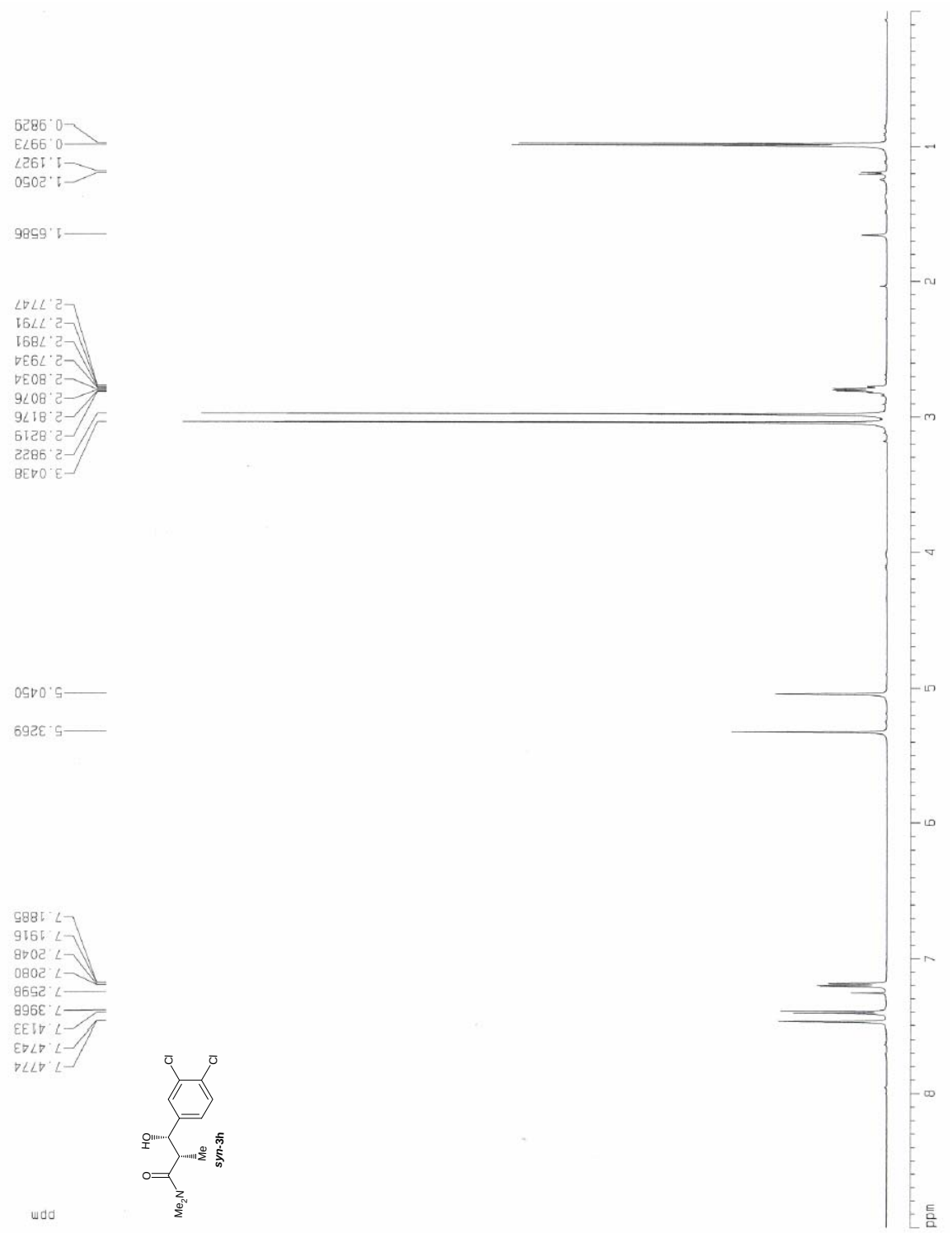
O
Me2N
anti 3g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2.8076
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2.8219
2.9822
3.0438
5.0450
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7.1916
7.2048
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Cl
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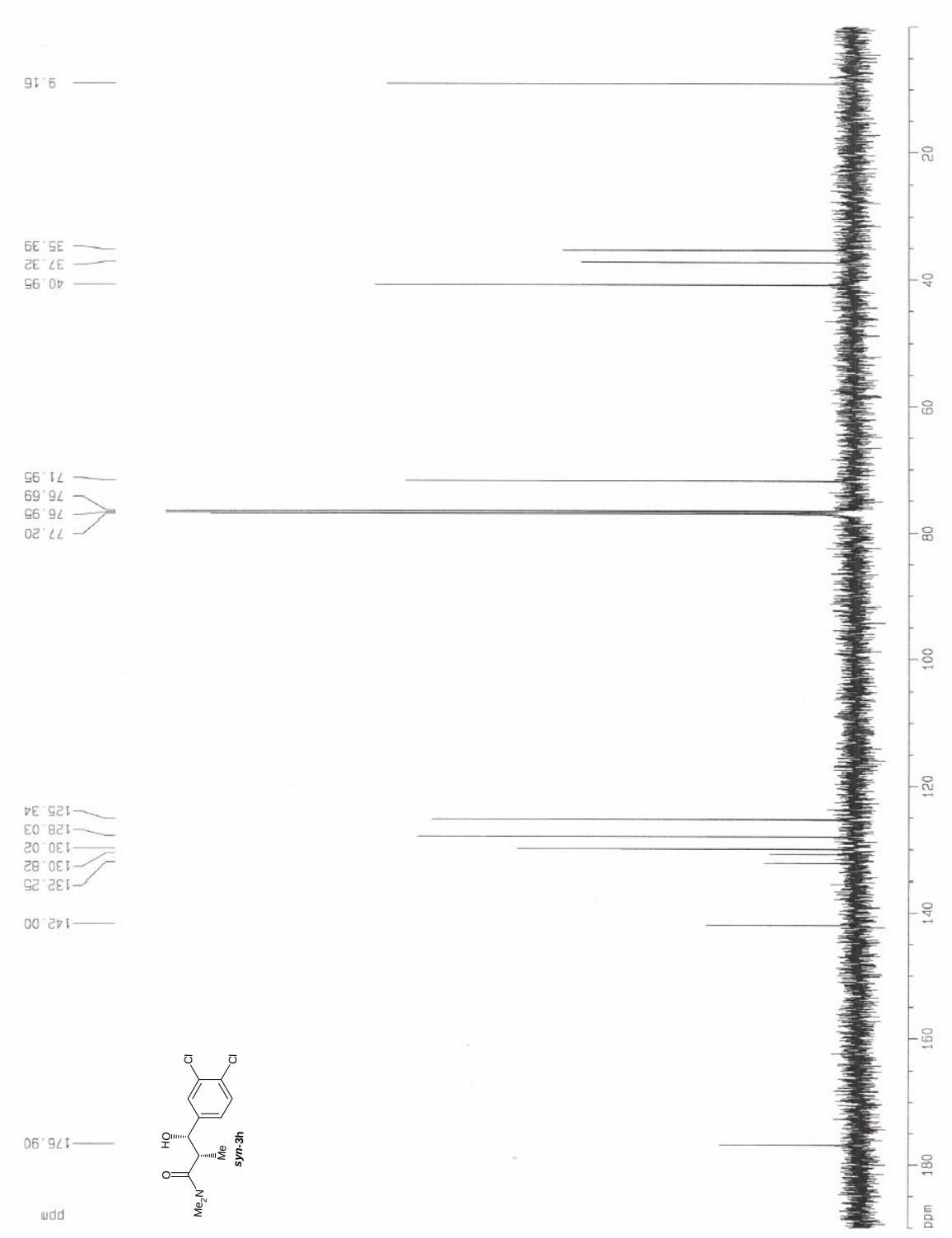
Me
O
Me2N
syn-3h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Cl
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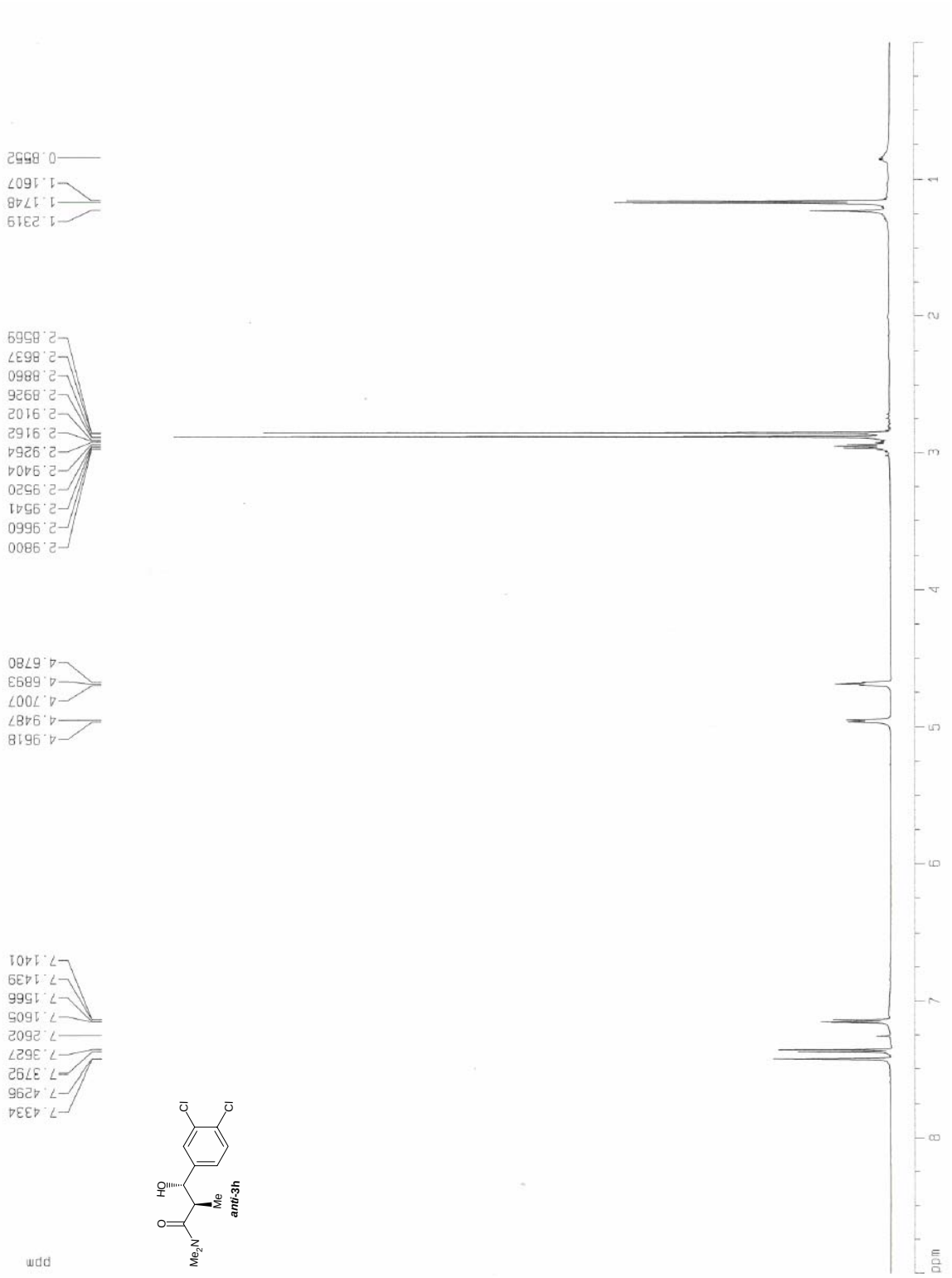
Me
O
Me2N
syn-3h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2.9404
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7.1439
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O
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anti-3h
ppm
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2
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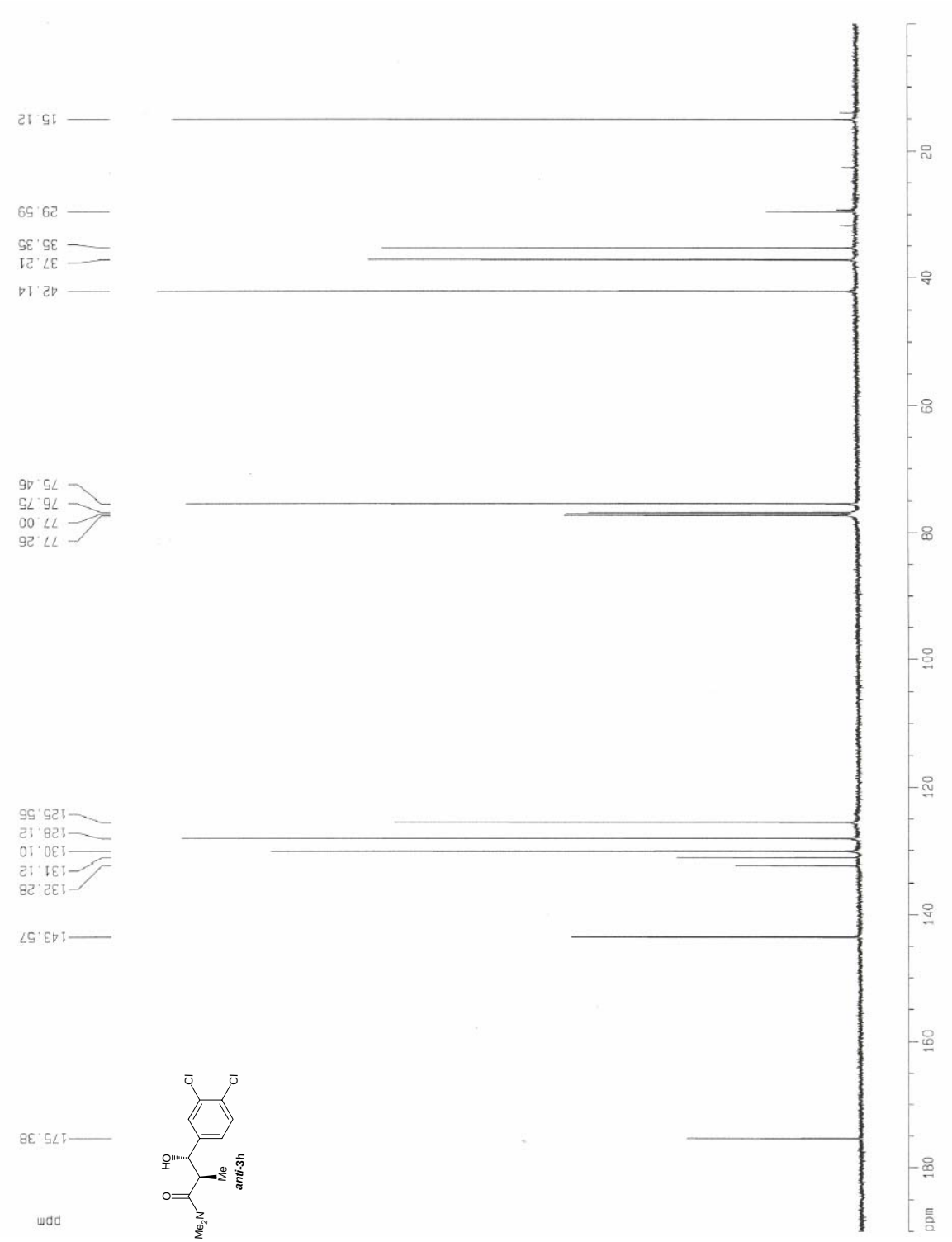
6
7
8
ppm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132.28
143.57
175.38
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60
80
100
120
140
160
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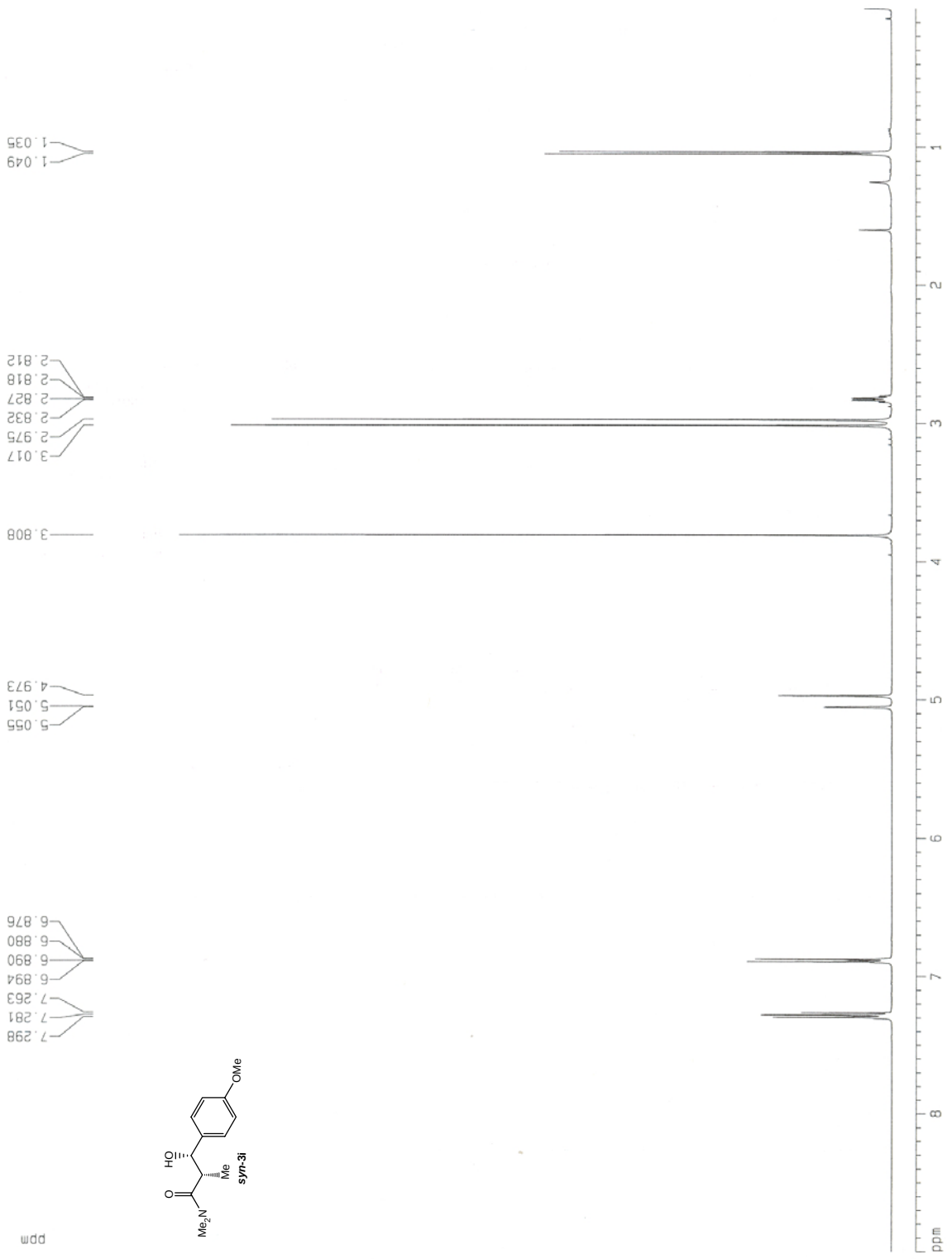
ppm
Cl
Cl
HO
Me
O
Me2N
anti-3h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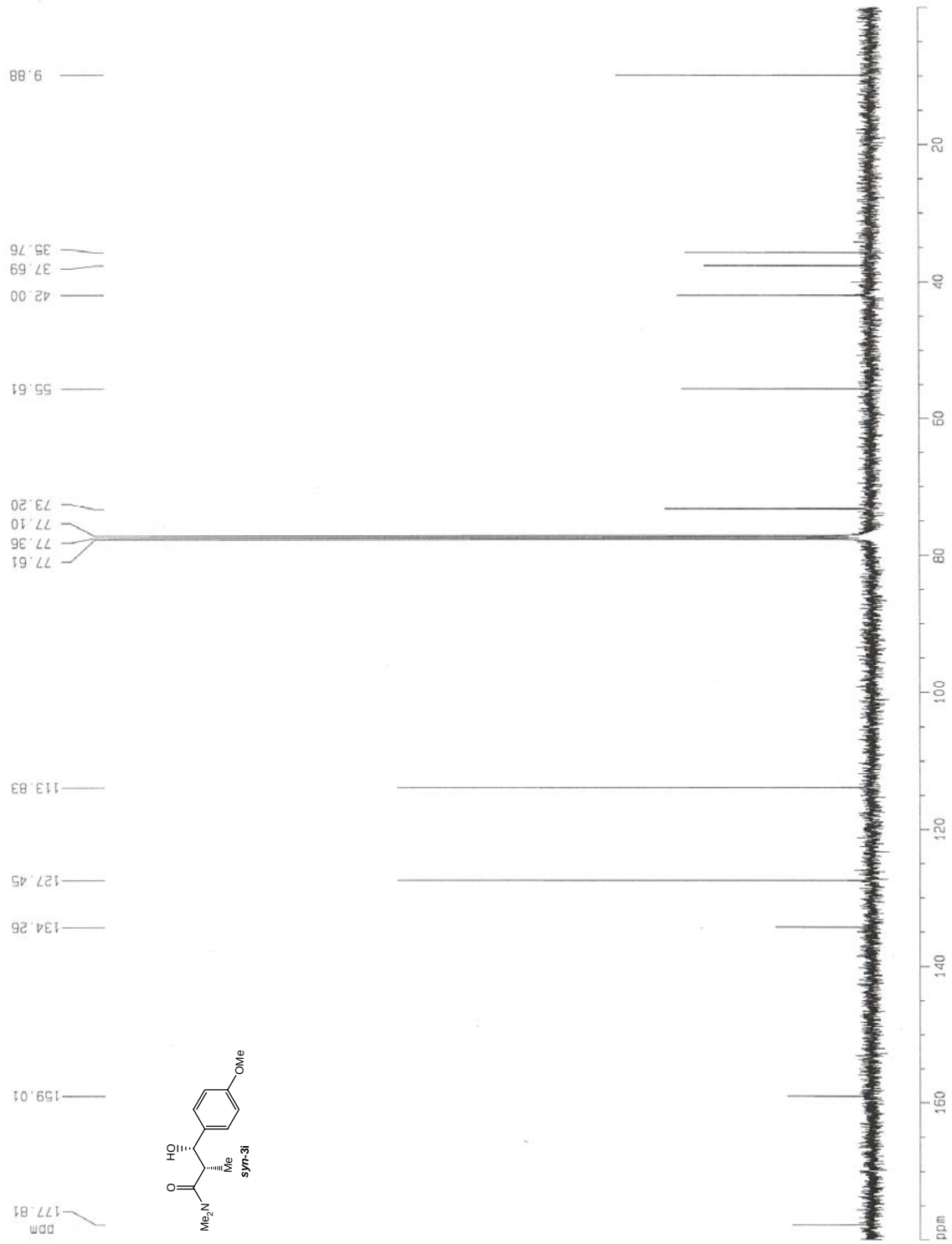
6.876
6.880
6.890
6.894
7.263
7.281
7.298
ppm
OMe
HO
Me
O
Me2N
syn-3i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134.26
159.01
177.81
DDM
ppm
20
40
60
80
100
120
140
160
OMe
HO
Me
O
Me2N
syn-3i

1.140
1.154
2.874
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2.999
3.013
3.791
3.797
4.293
4.305
4.742
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6.859
6.869
6.873
7.246
7.260
7.264
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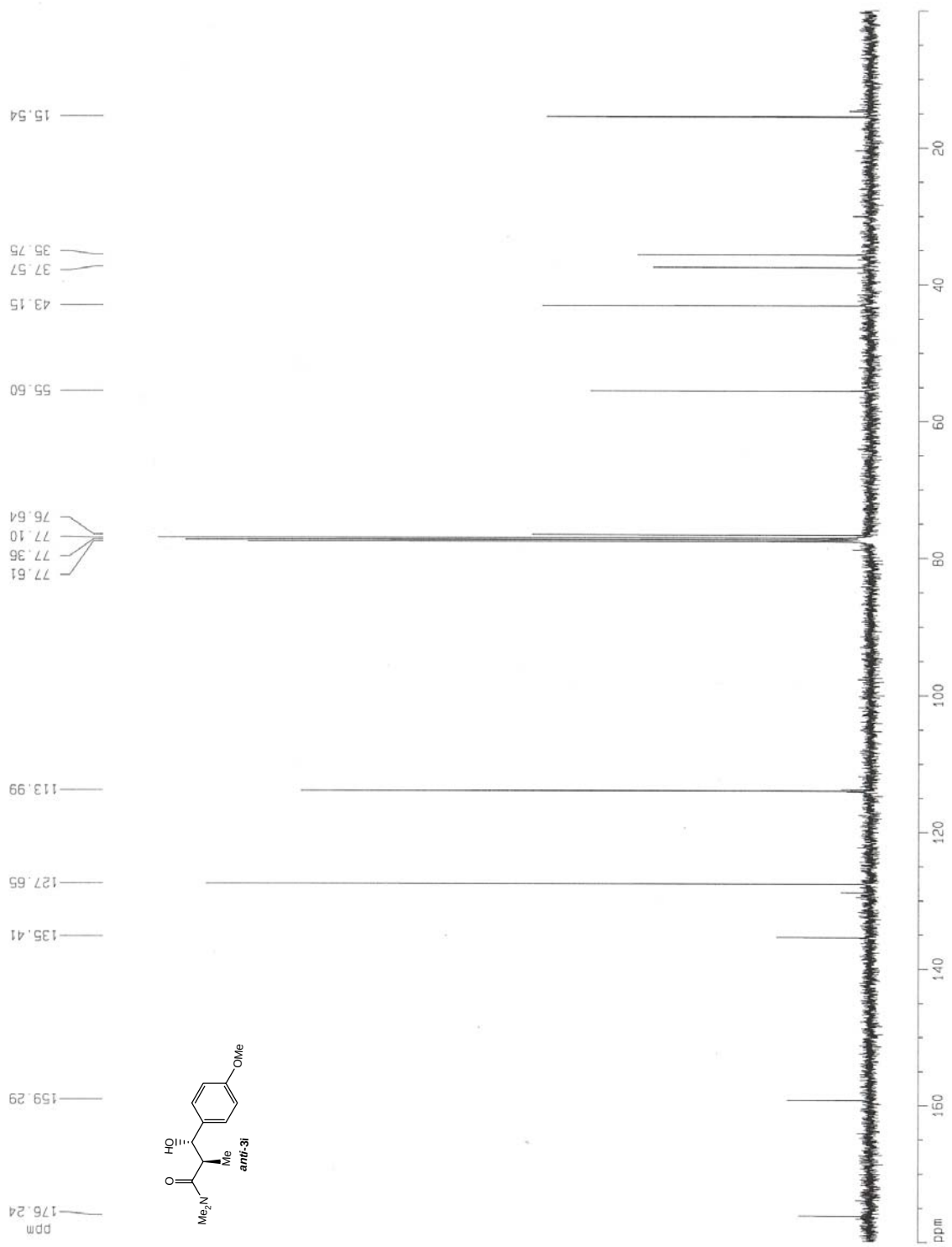
HO
Me
O
Me2N
anti-3i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159.29
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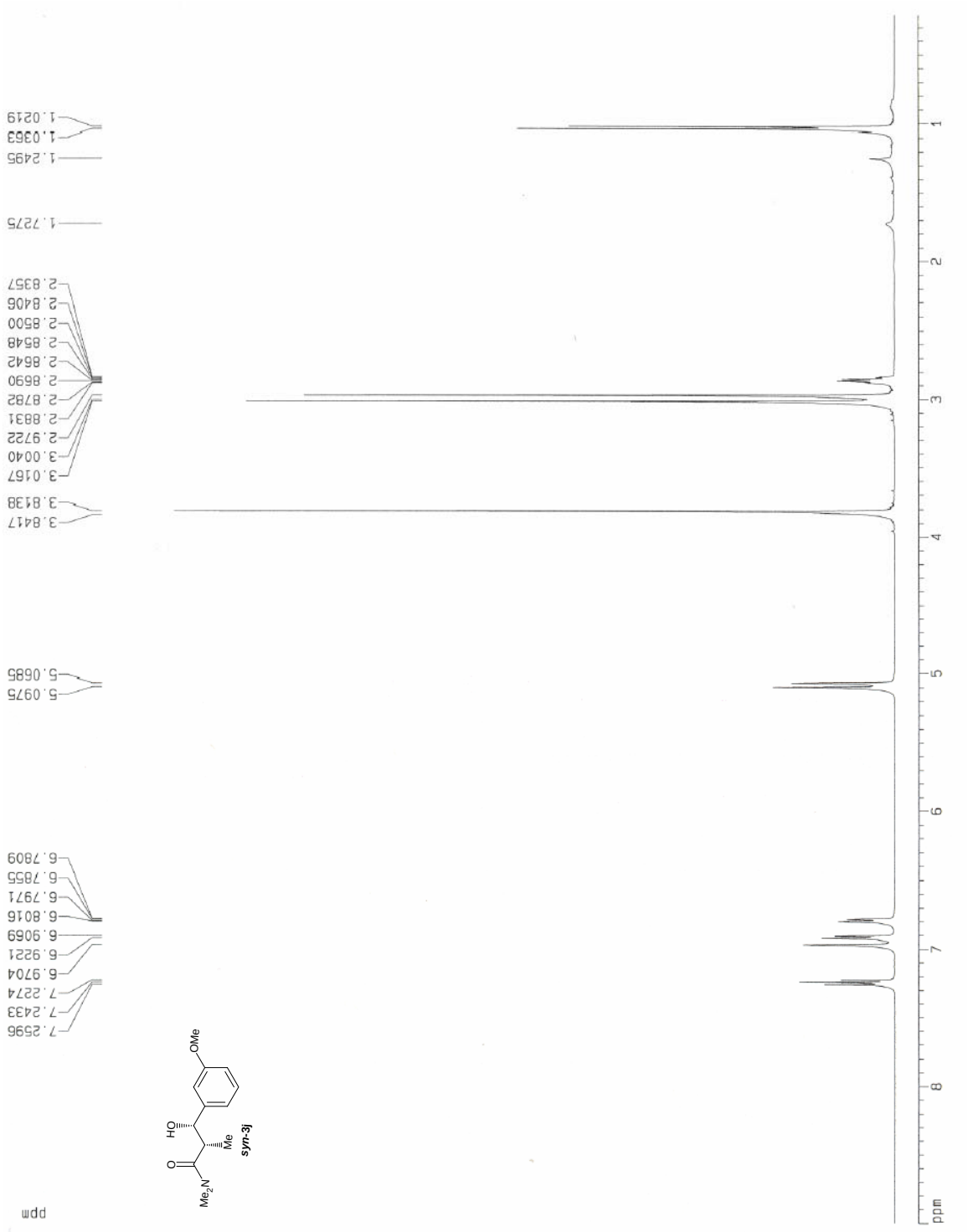
OMe
HO
Me
O
Me2N
anti-3i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6.7971
6.8016
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ppm
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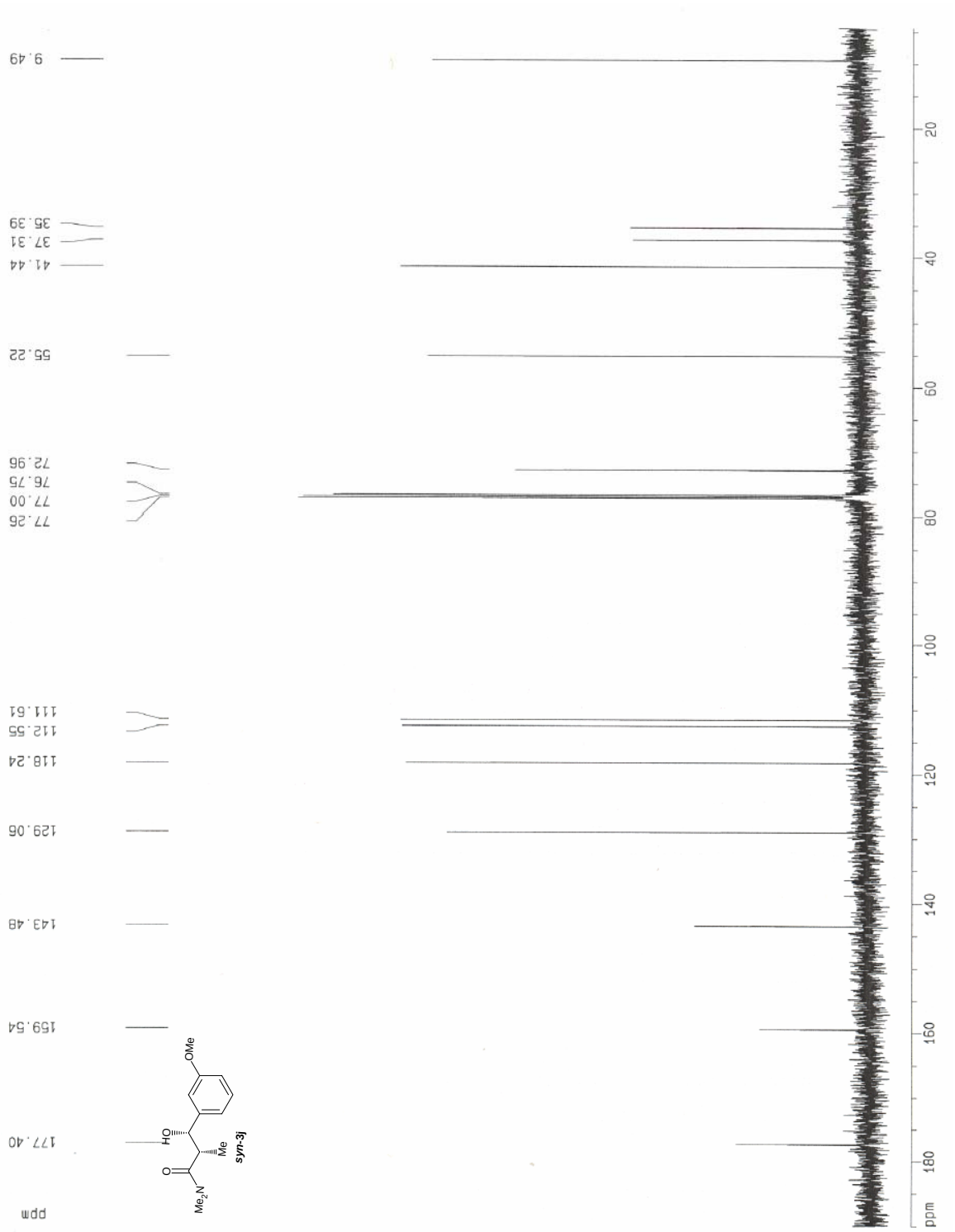
HO
Me
O
Me2N
syn-3j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143.48
159.54
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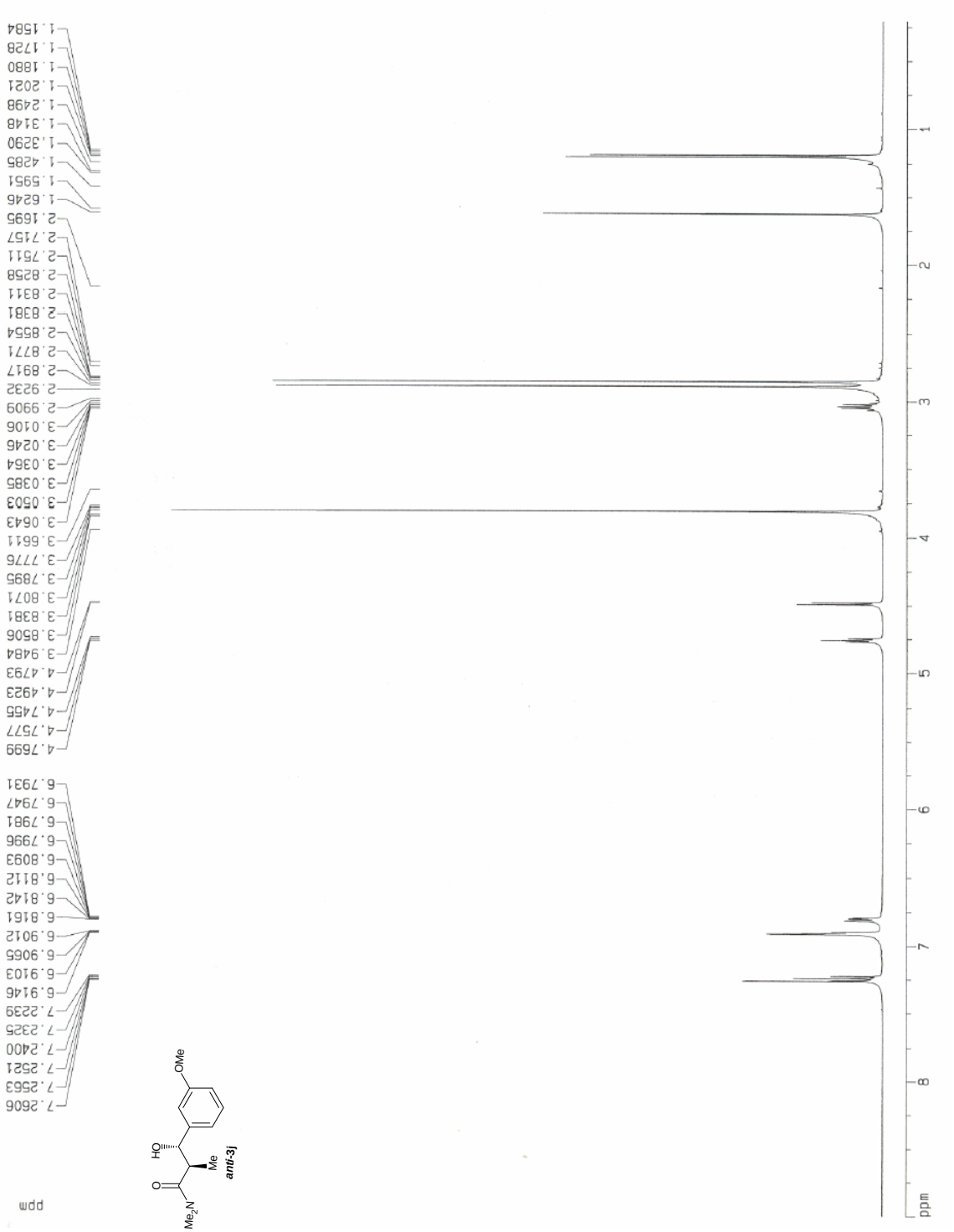
OMe
HO
Me
O
Me2N
syn-3j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anti-3j
Me2N
O
ppm

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159.64
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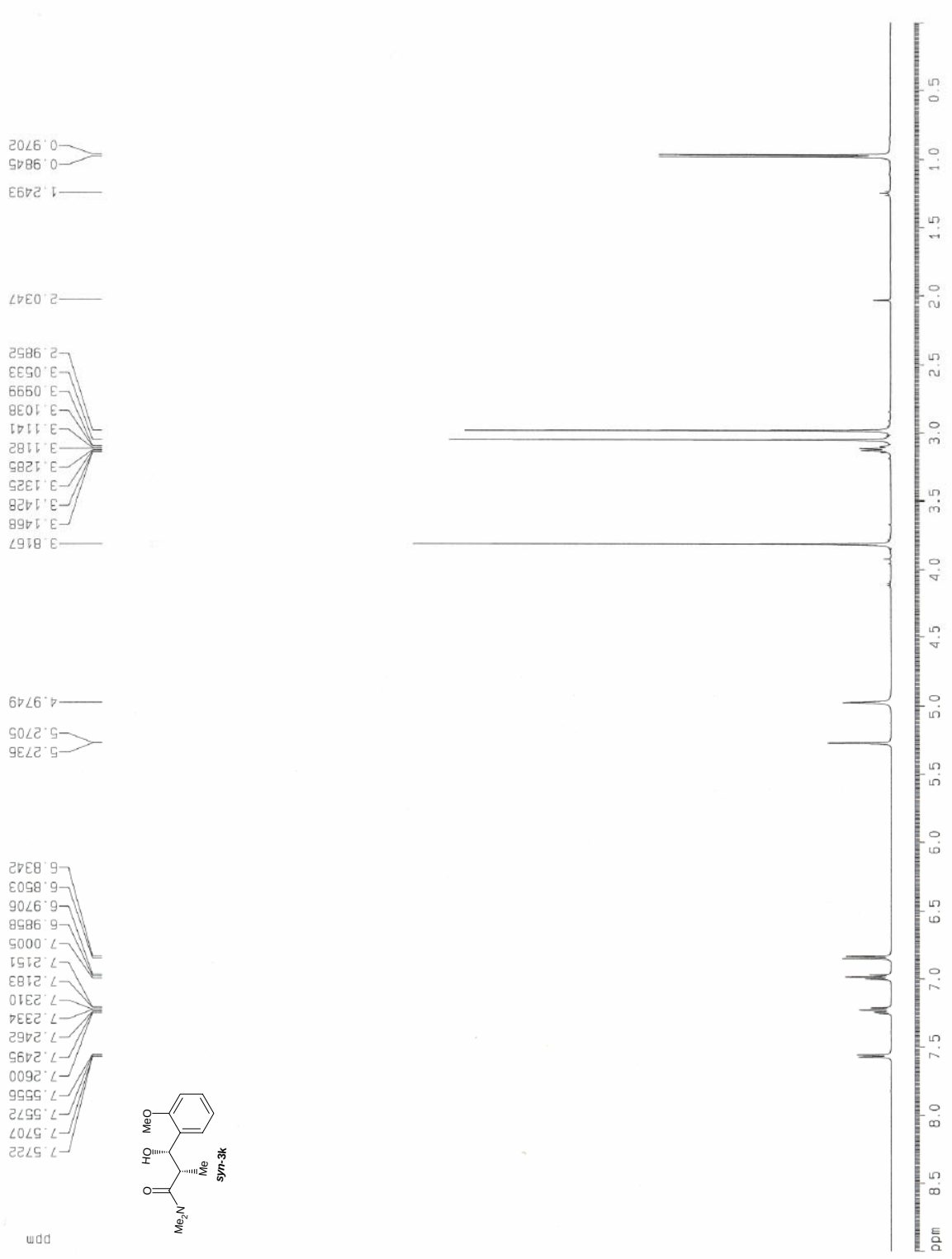
OMe
HO
Me
O
Me2N
anti-3j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3.8167
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5.2705
5.2736
6.8342
6.8503
6.9706
6.9858
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7.2151
7.2183
7.2310
7.2334
7.2462
7.2495
7.2600
7.5556
7.5572
7.5707
7.5722
ppm
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
4.5
4.0
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2.0
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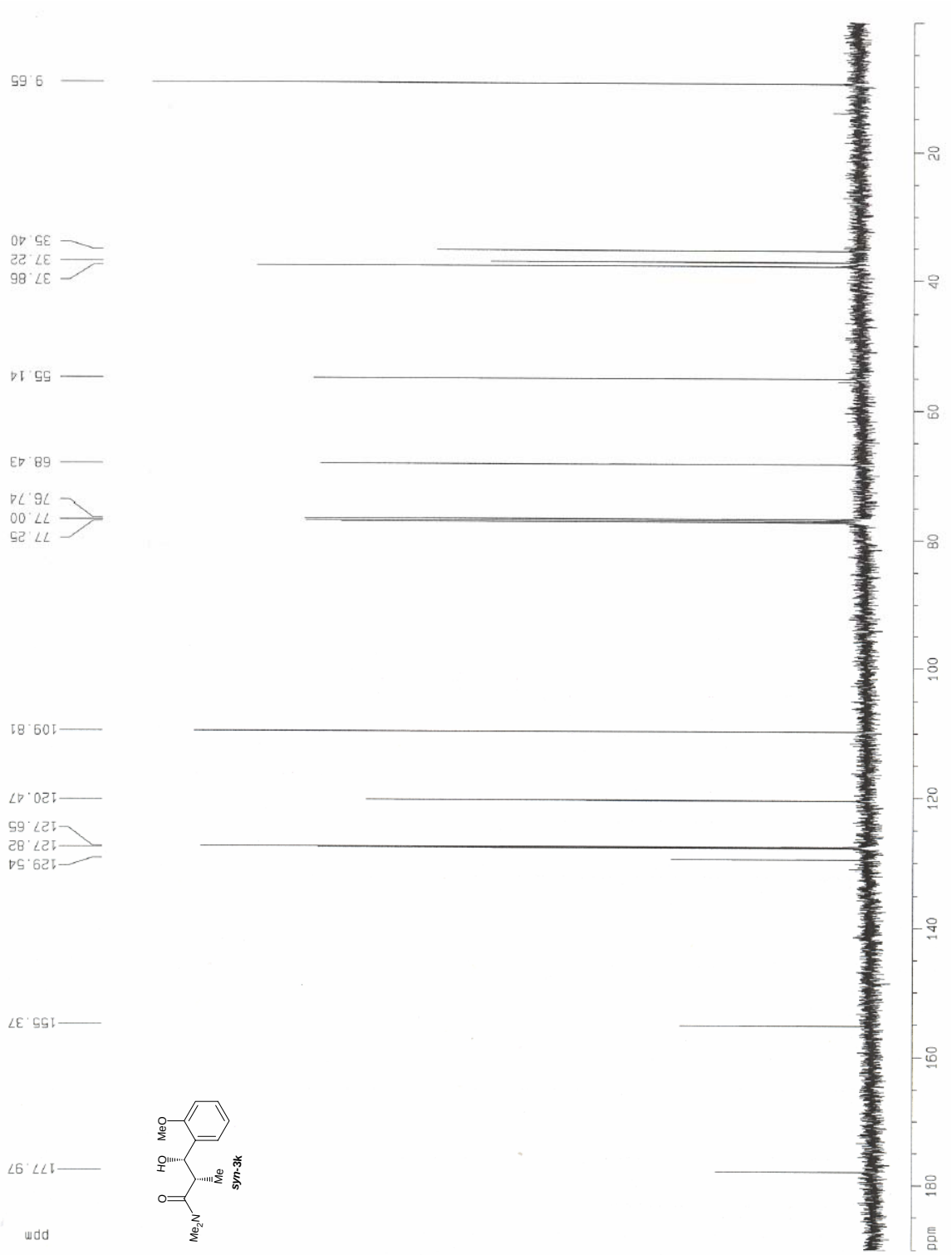
MeO
HO
Me
O
Me2N
syn-3k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77.00
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127.82
129.54
155.37
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60
80
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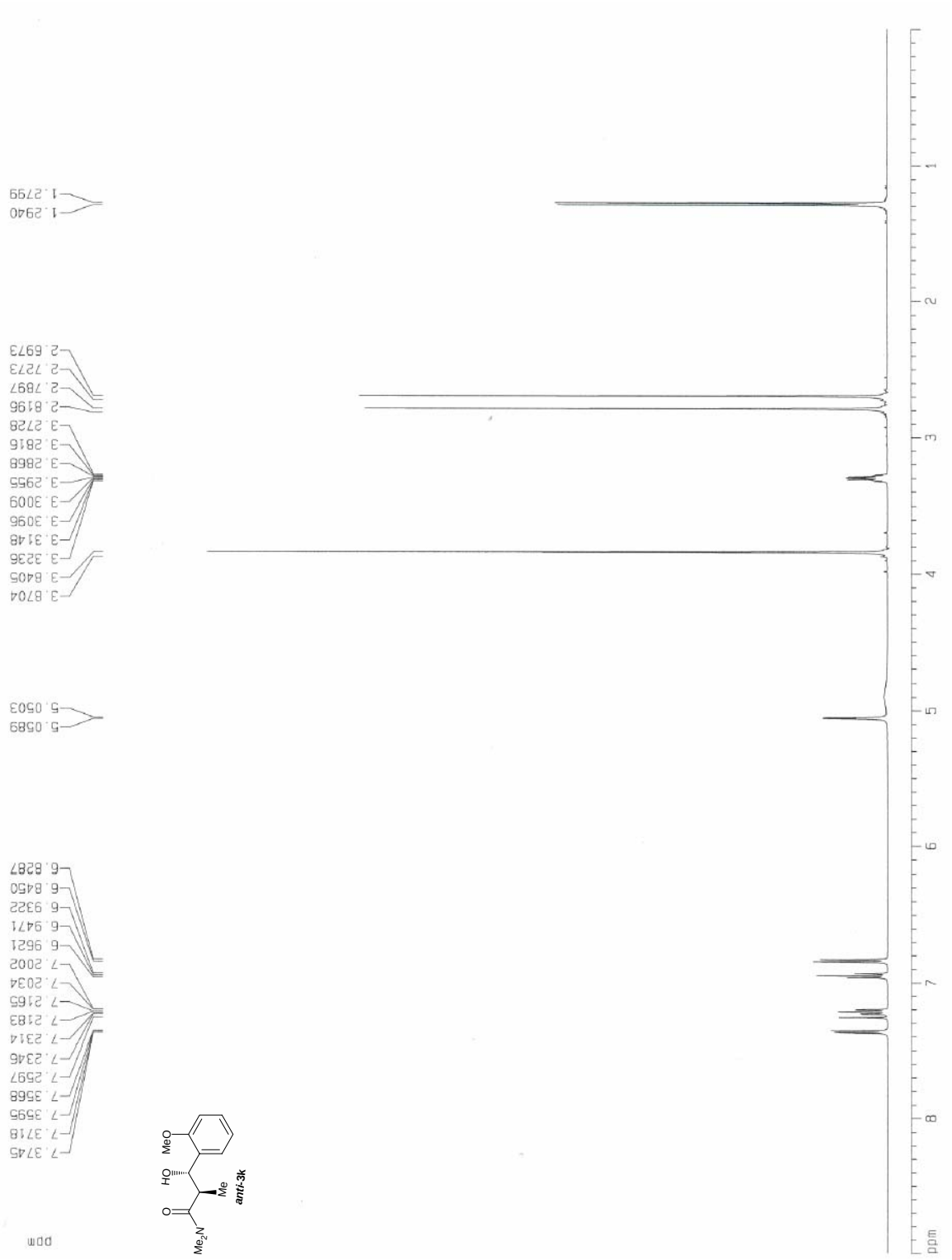
120
140
160
180
MeO
HO
Me
O
Me2N
syn-3k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3.3096
3.3148
3.3236
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3.8704
5.0503
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6.9471
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7.2183
7.2314
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ppm
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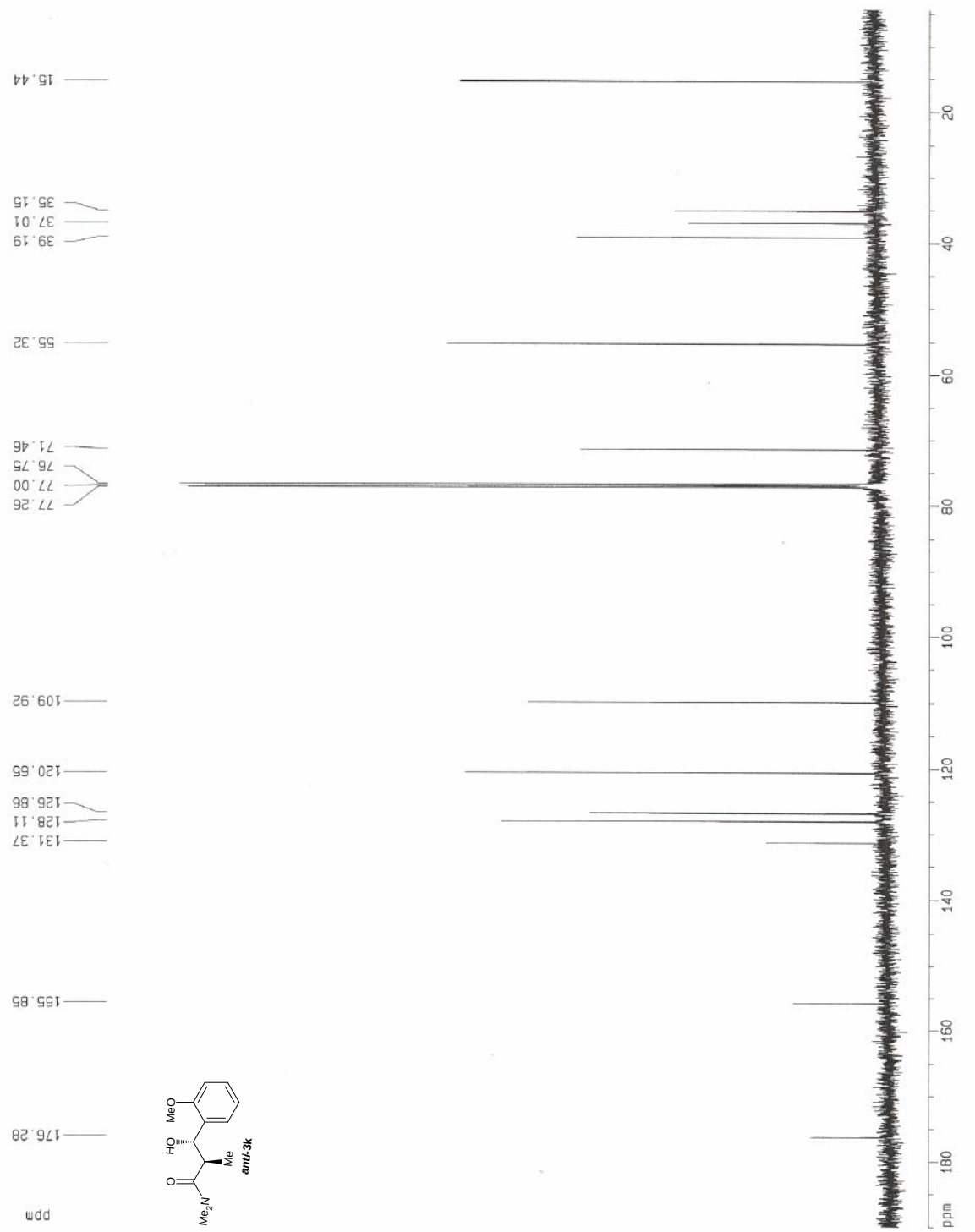
HO
Me
O
Me2N
anti-3k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128.11
131.37
155.85
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40
60
80
100
120
140
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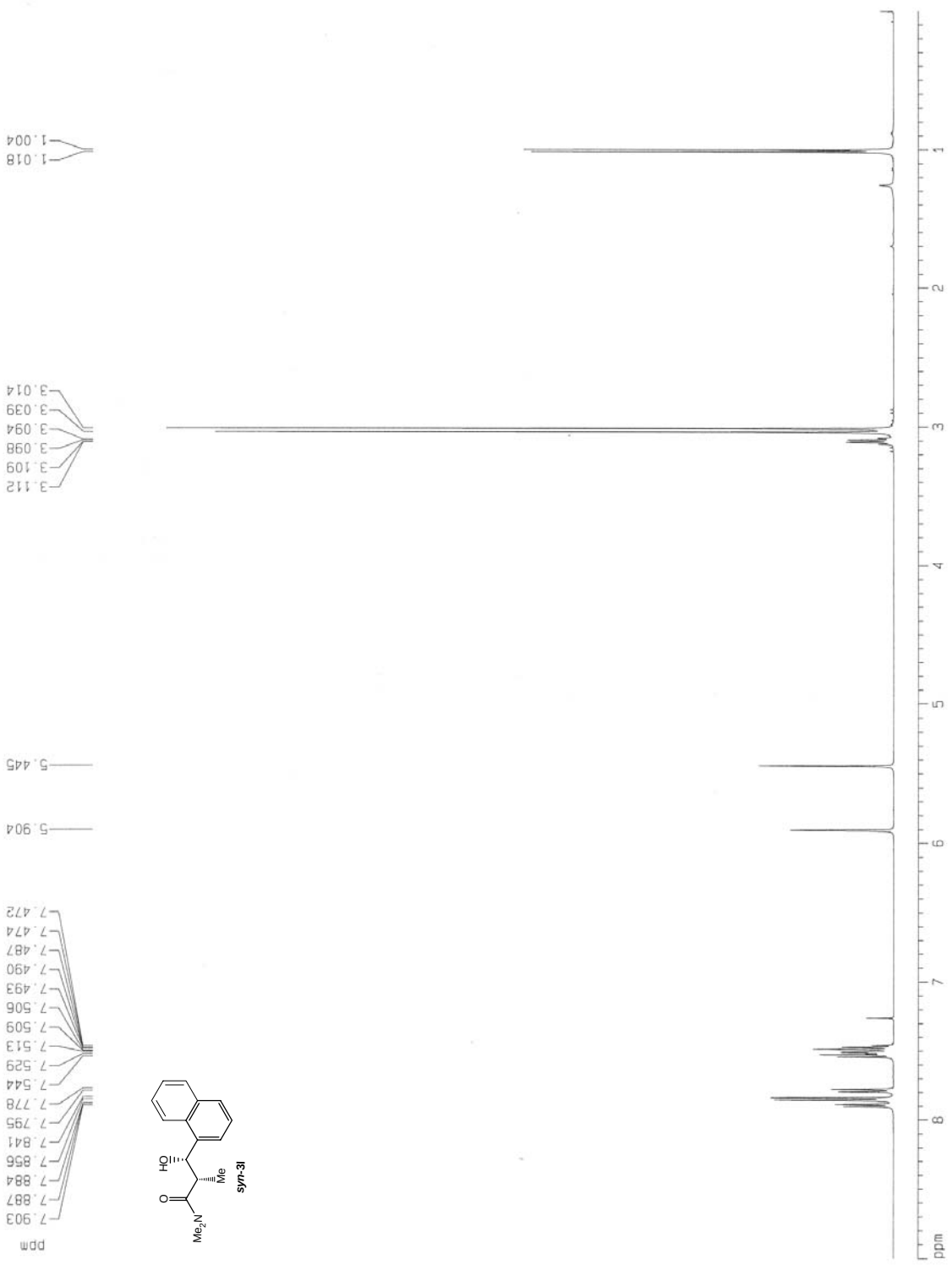
MeO
HO
Me
O
Me2N
anti-3k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3.109
3.112
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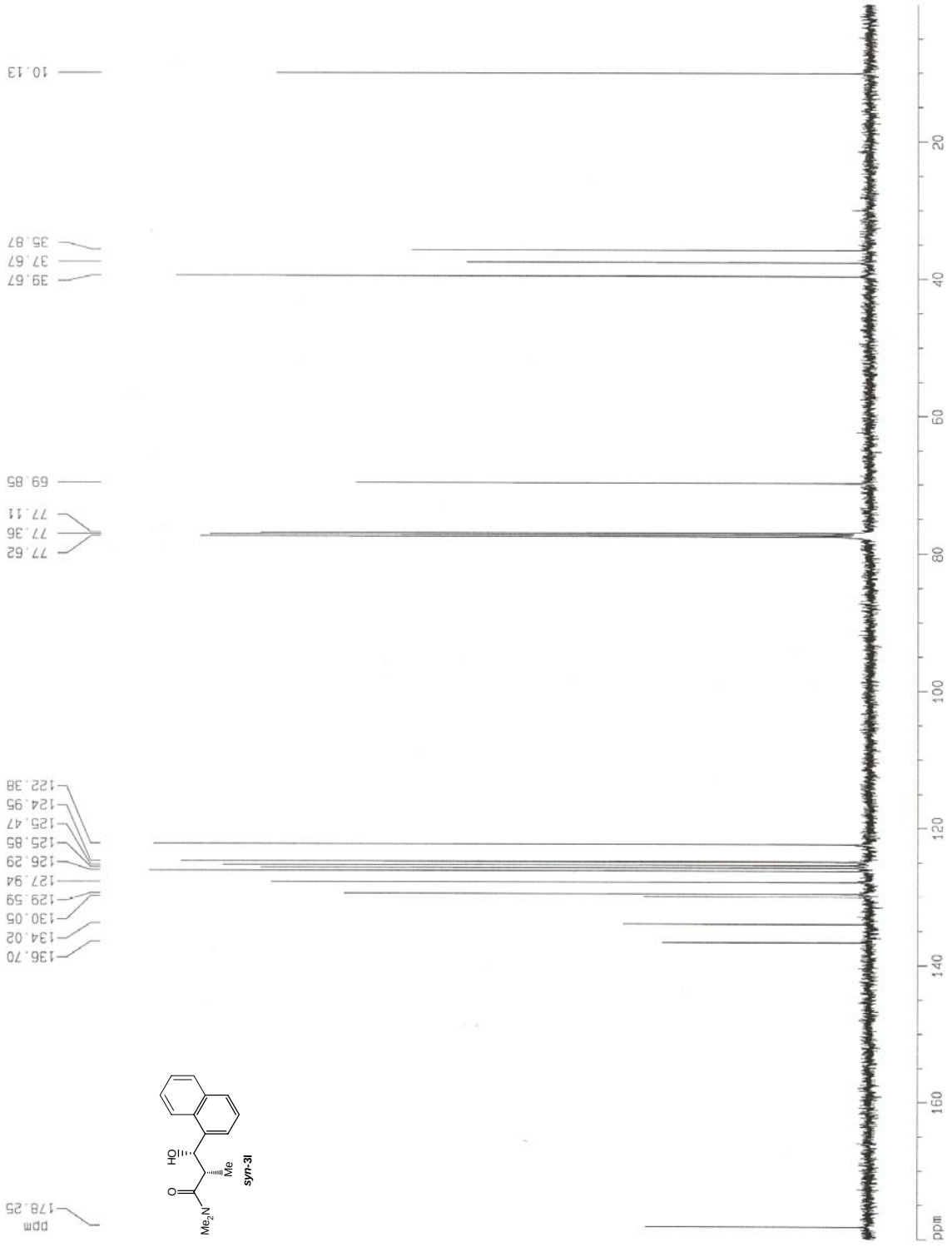
7.474
7.487
7.490
7.493
7.506
7.509
7.513
7.529
7.544
7.778
7.795
7.841
7.856
7.884
7.887
7.903
ppm
HO
O
Me2N
Me
syn-3l
1
2
3
4
5
6
7
8
ppm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124.95
125.47
125.85
126.29
127.94
129.59
130.05
134.02
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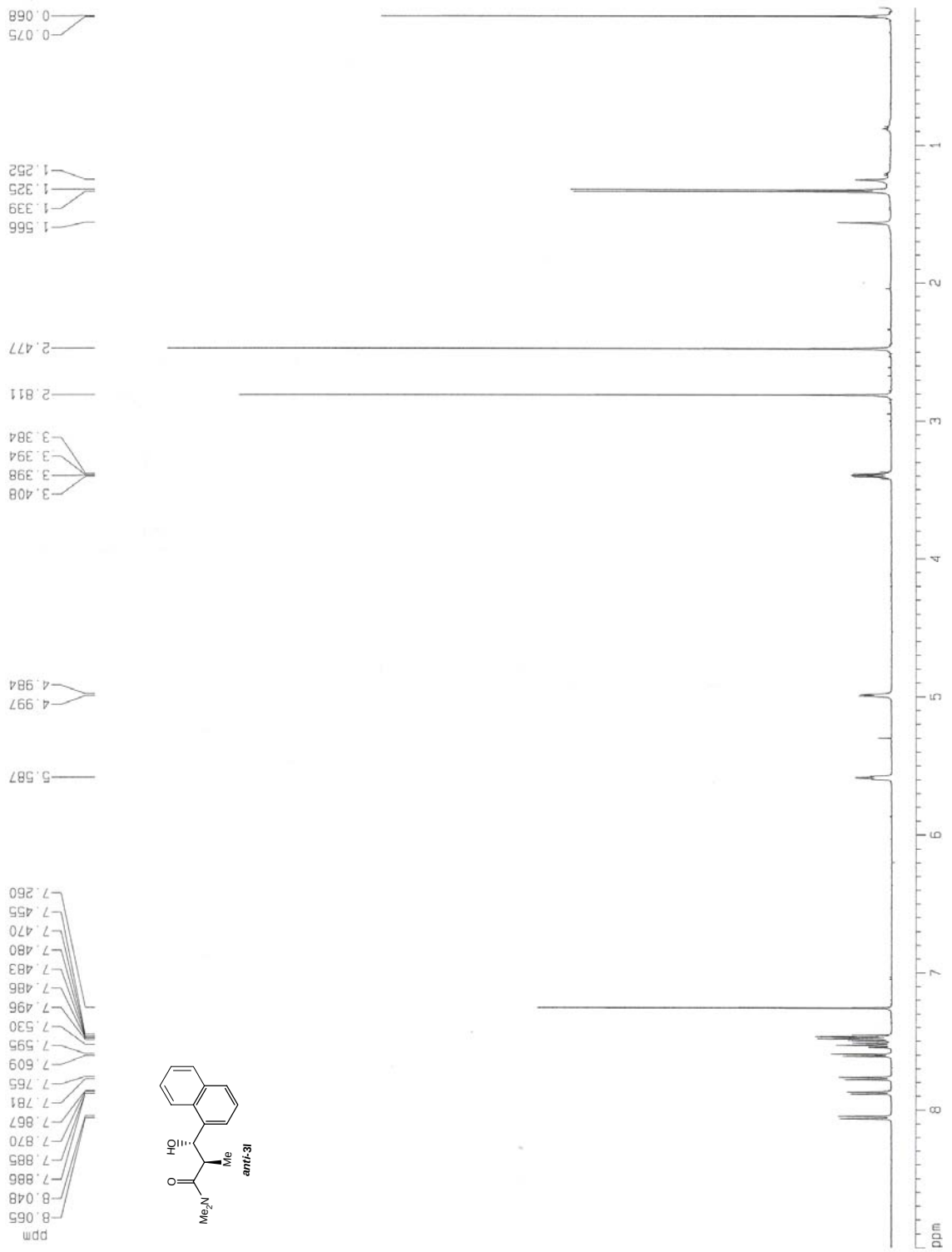
ppm
20
40
60
80
100
120
140
160
ppm
HO
Me
O
Me2N
syn-3l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4.997
5.587
7.260
7.455
7.470
7.480
7.483
7.486
7.496
7.530
7.595
7.609
7.765
7.781
7.867
7.870
7.885
7.886
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ppm
HO
Me
Me2N
O
anti-3l
1
2
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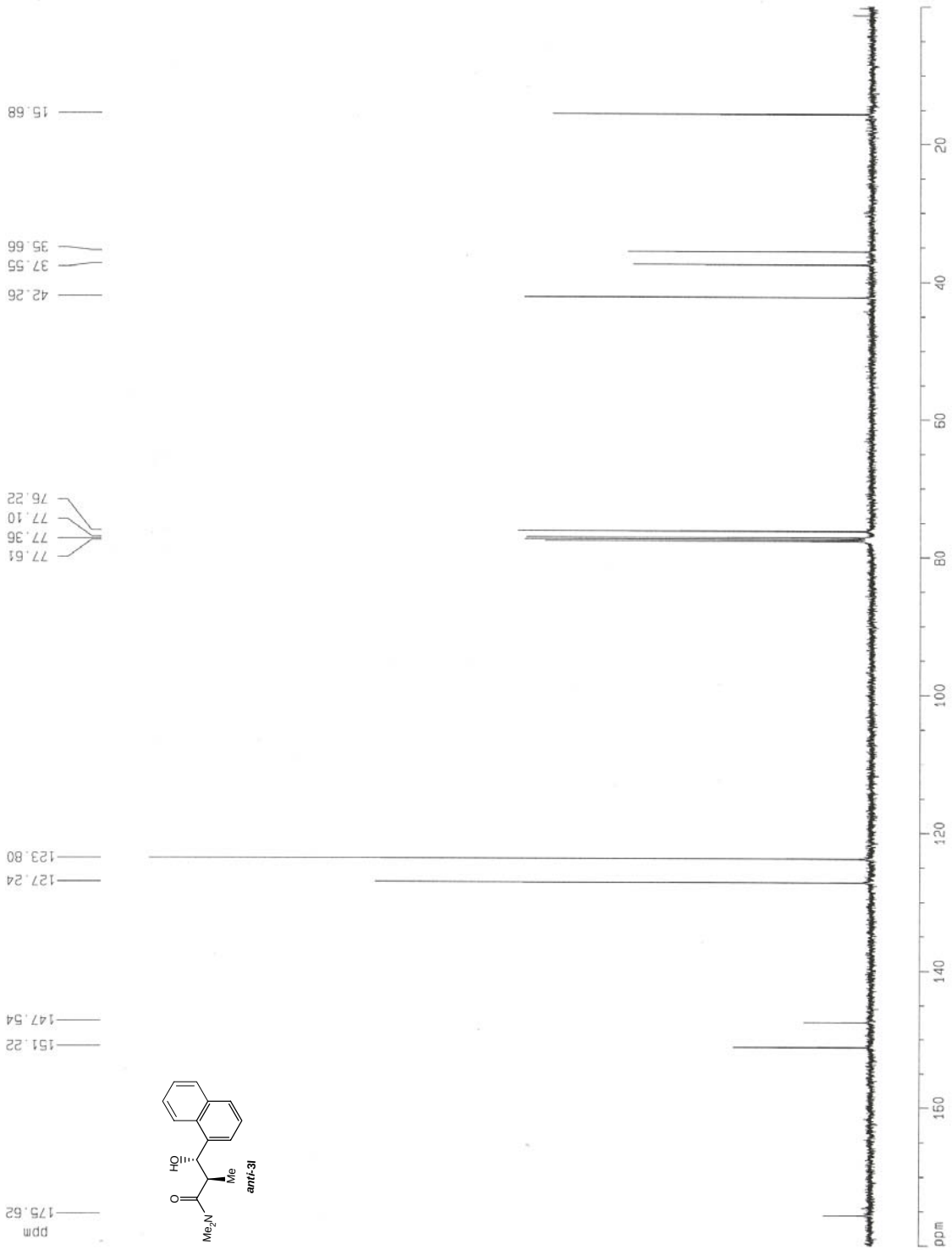
ppm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ppm
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40
60
80
100
120
140
160
ppm
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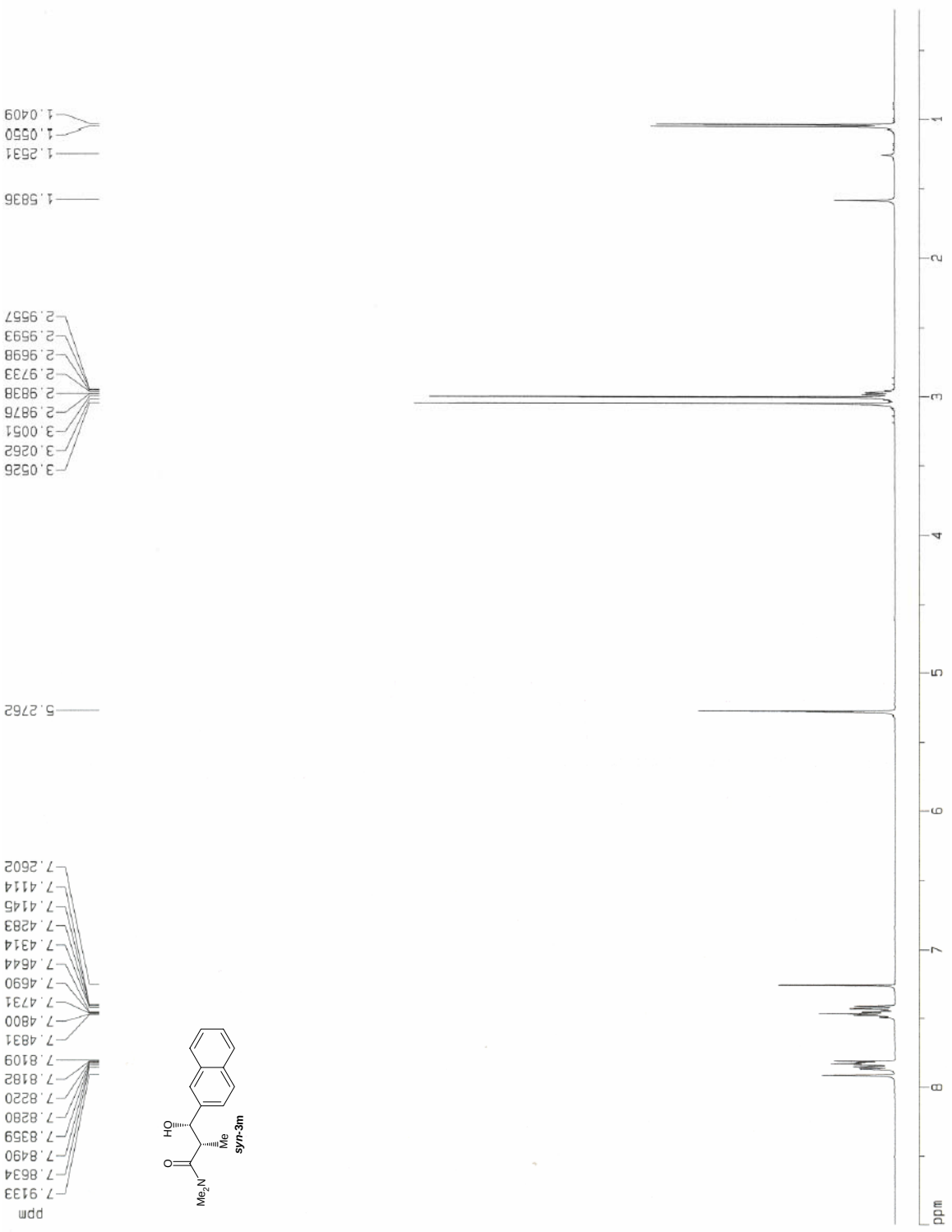
Me
O
Me2N
anti-3l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7.4731
7.4690
7.4644
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7.4283
7.4145
7.4114
7.2602
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3.0262
3.0051
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ppm
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Me
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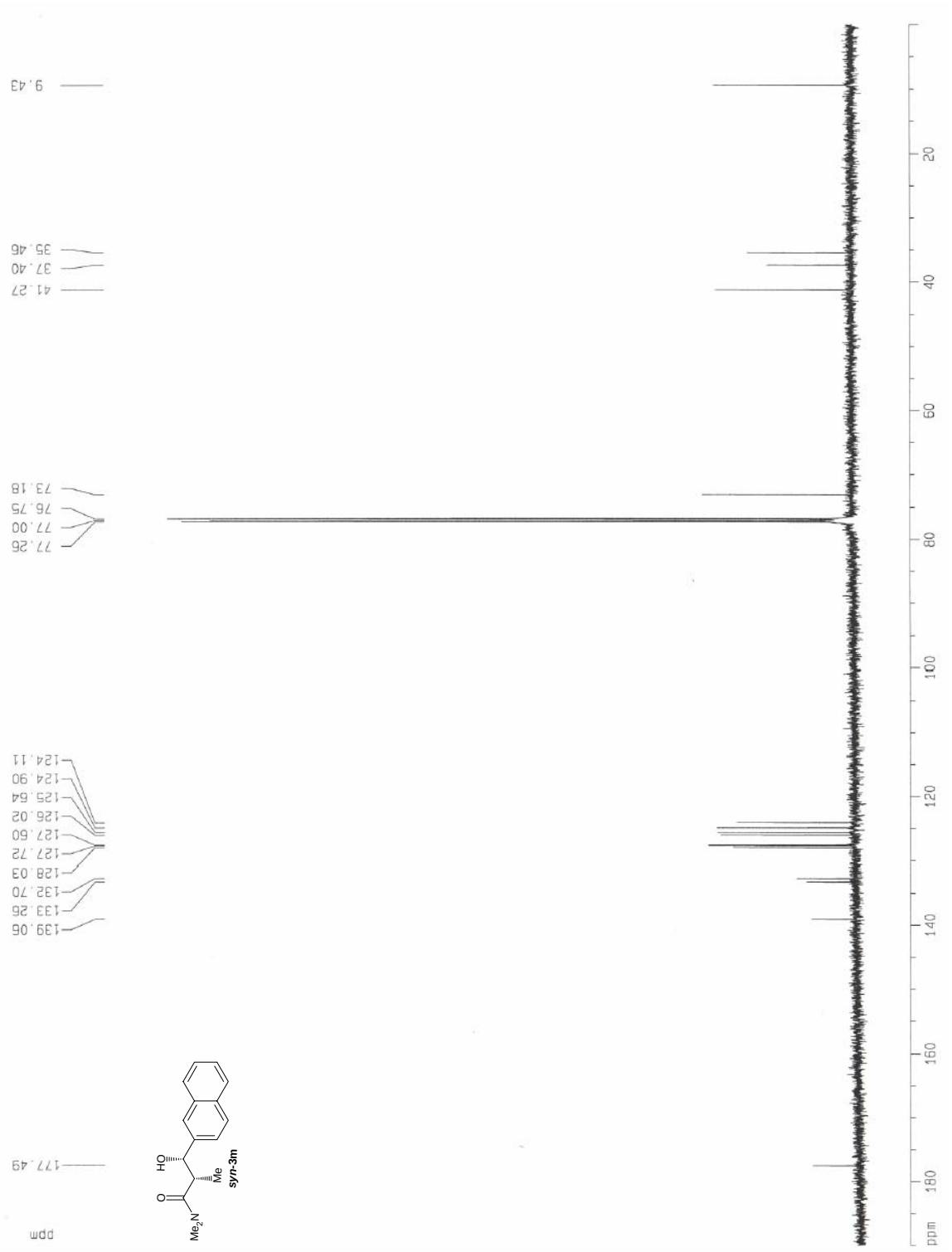
O
Me2N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77.26
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125.64
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127.60
127.72
128.03
132.70
133.26
139.06
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ppm
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Me
syn-3m
O
Me2N
20
40
60
80
100
120
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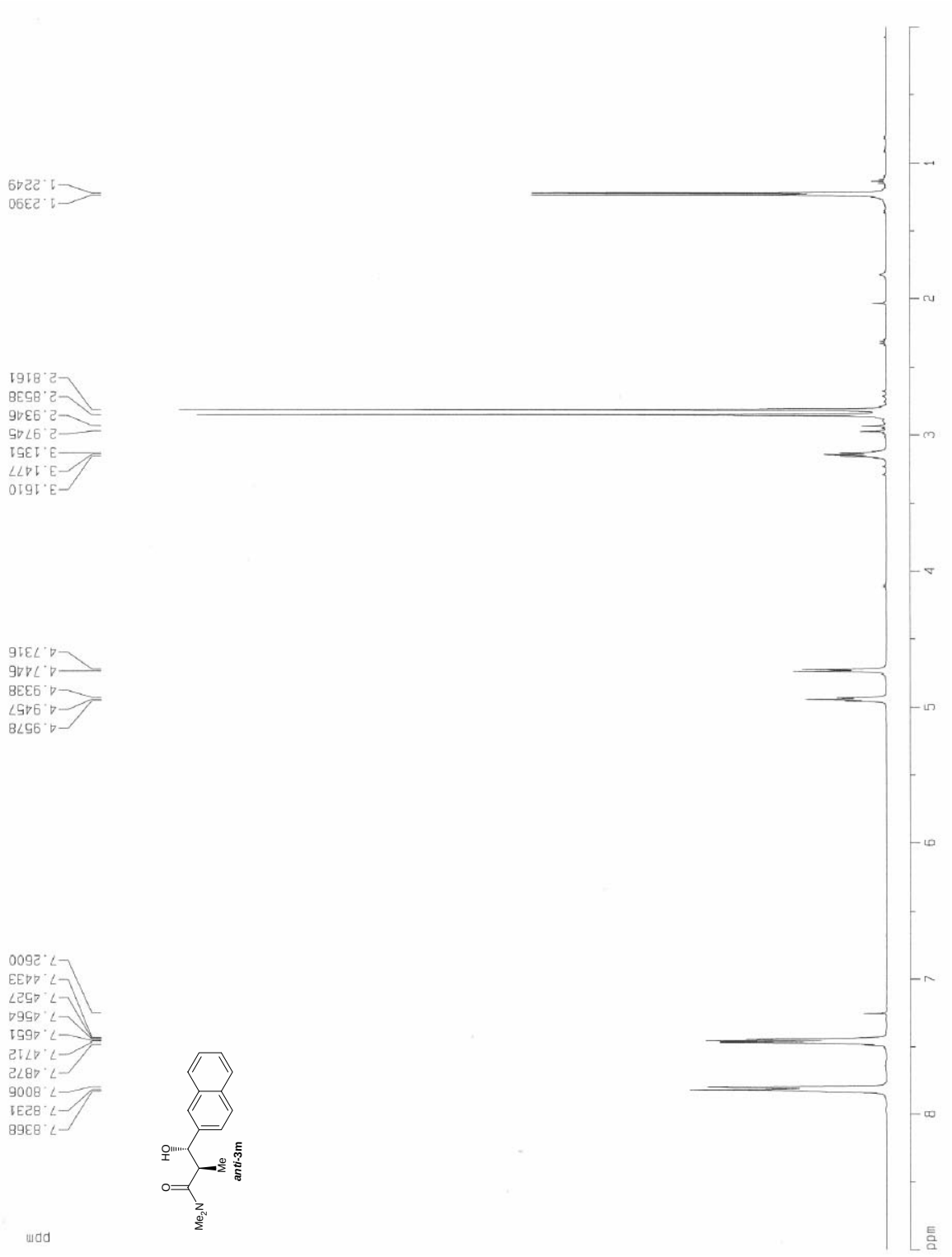
ppm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HO
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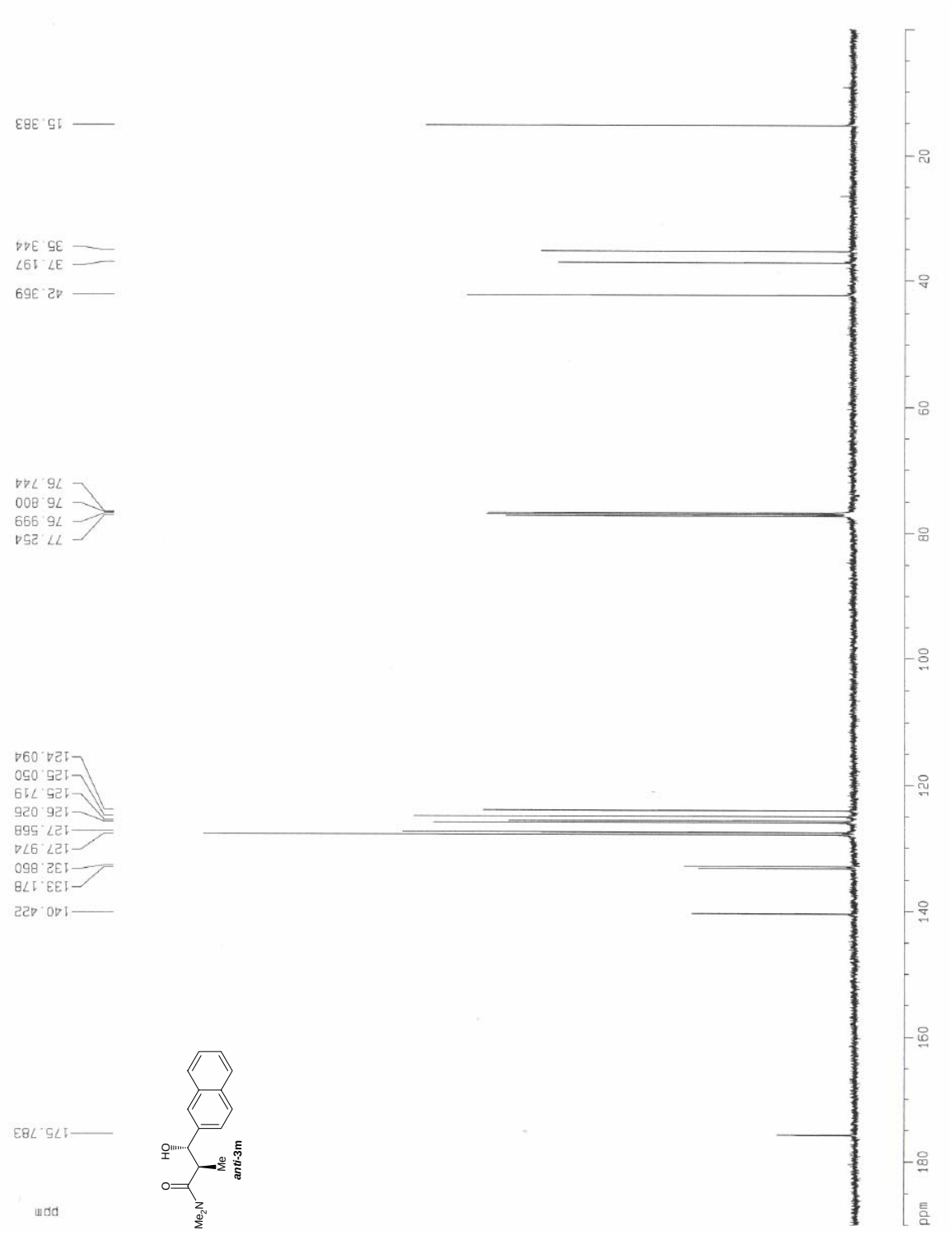
O
Me2N
anti-3m
ppm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127.974
132.860
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140.422
175.783
ppm
HO
Me
anti-3m
O
Me2N
20
40
60
80
100
120
140
160
180
ppm

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1.1547
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2.9341
2.9429
2.9484
2.9585
3.0355
5.3264
5.3312
6.9344
6.9413
6.9665
6.9738
6.9764
6.9835
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7.2097
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ppm
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4
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S
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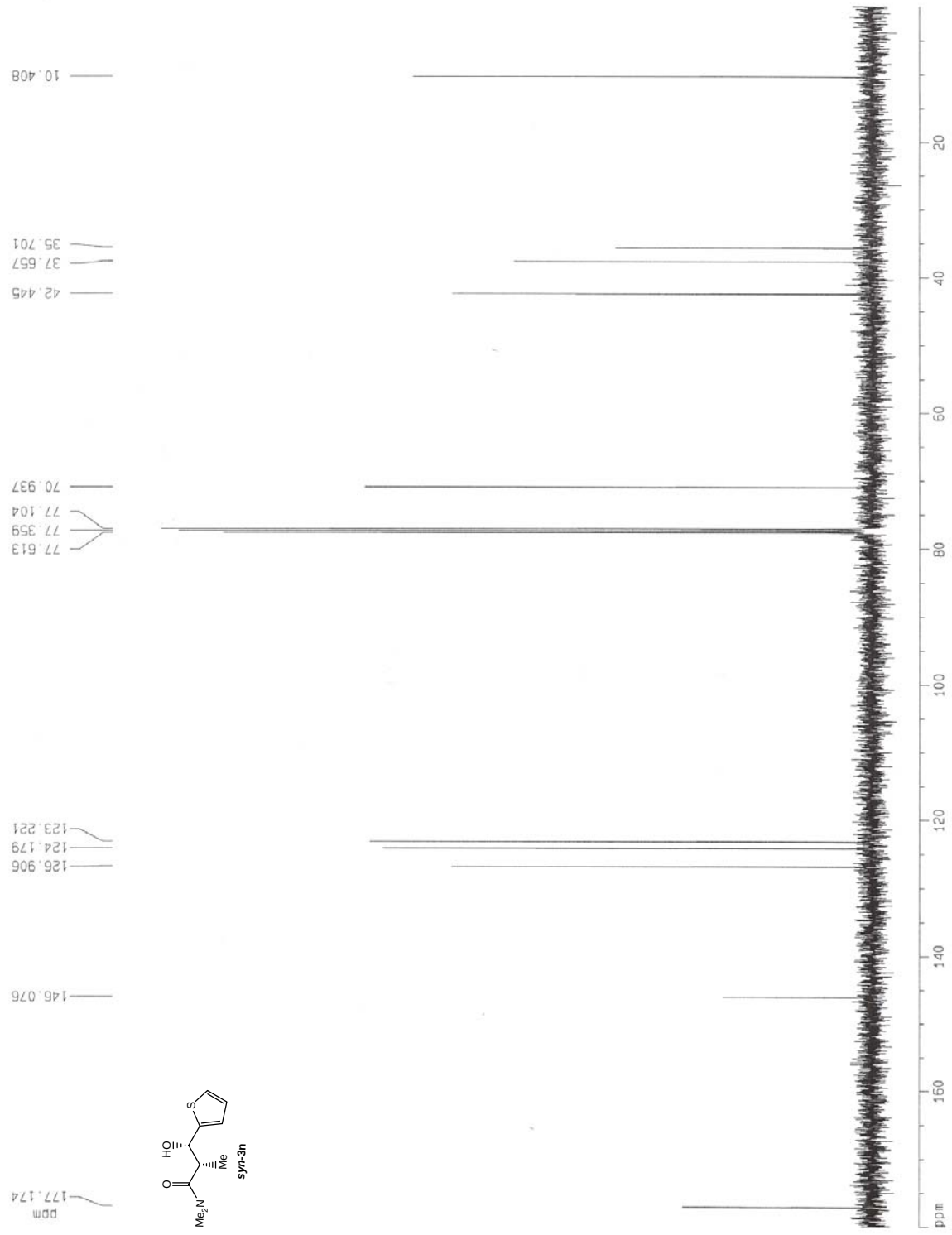
Me
O
Me2N
syn-3n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40
60
80
100
120
140
160
ppm
HO
Me
O
$Me_2N$
S
syn-3n

1.232
1.246
2.928
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3.078
3.089
3.092
3.103
4.822
4.836
5.006
5.019
5.031
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6.953
6.955
6.962
6.973
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6.979
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7.225
7.233
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ppm
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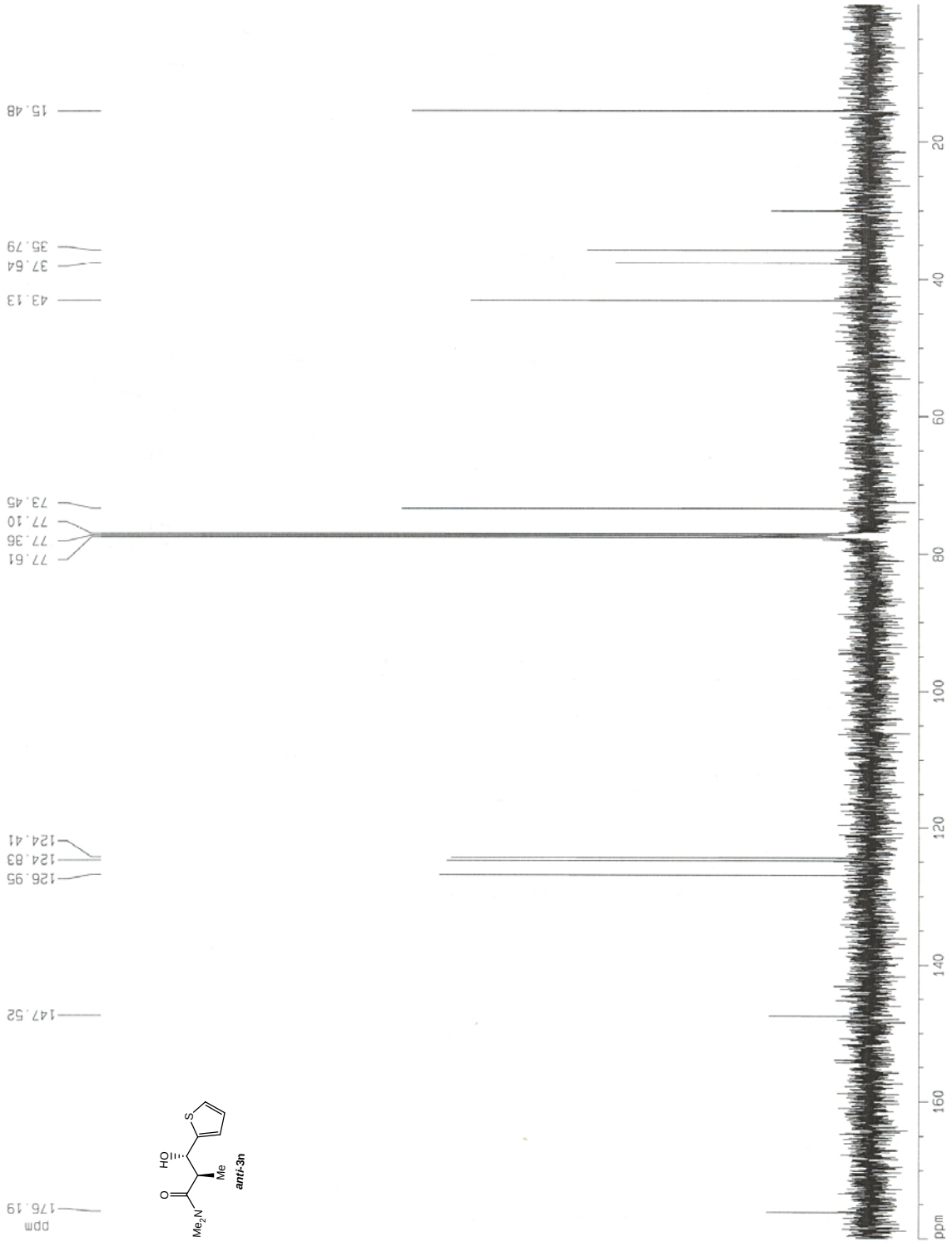
anti-3n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ppm
20
40
60
80
100
120
140
160
ppm
S
HO
Me
O
Me2N
anti-3n

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1.245
1.251
1.261
1.281
1.341
1.479
1.515
1.528
1.536
1.545
1.553
1.555
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2.615
2.625
2.629
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3.857
3.860
3.862
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3.870
3.873
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ppm
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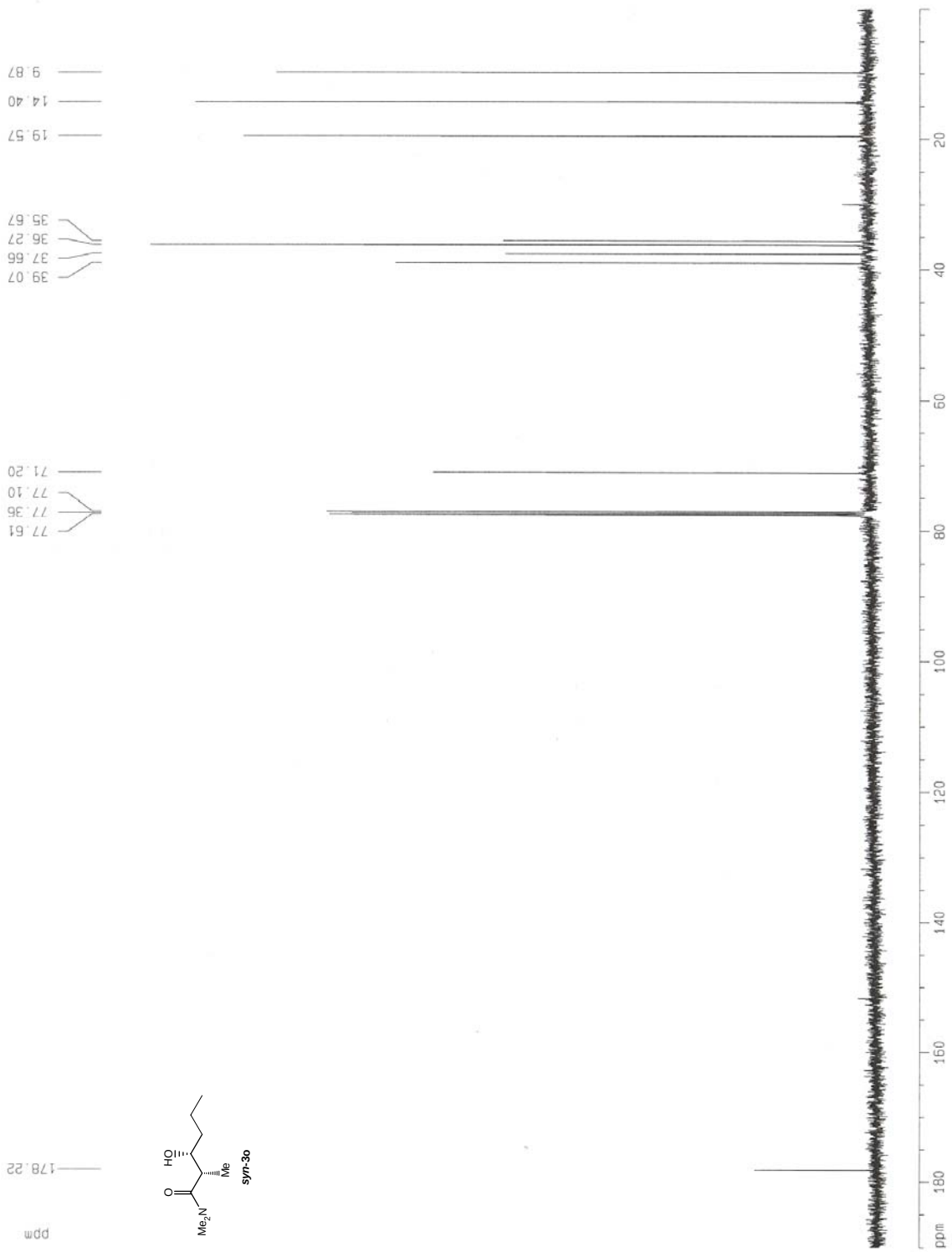
Me
O
Me2N
syn-3o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77.61
178.22
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20
40
60
80
100
120
140
160
180
ppm
HO
Me
O
Me2N
syn-3o

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0.03
0.86
1.27
1.29
2.44
2.64
4.66
4.68
7.21
7.22
7.29
7.30
ppm
0
1
2
3
4
5
6
7
8
ppm
TBSO
Me
O
Me2N
4a

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-4.28
15.83
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26.14
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37.14
46.10
77.11
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77.89
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128.05
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ppm
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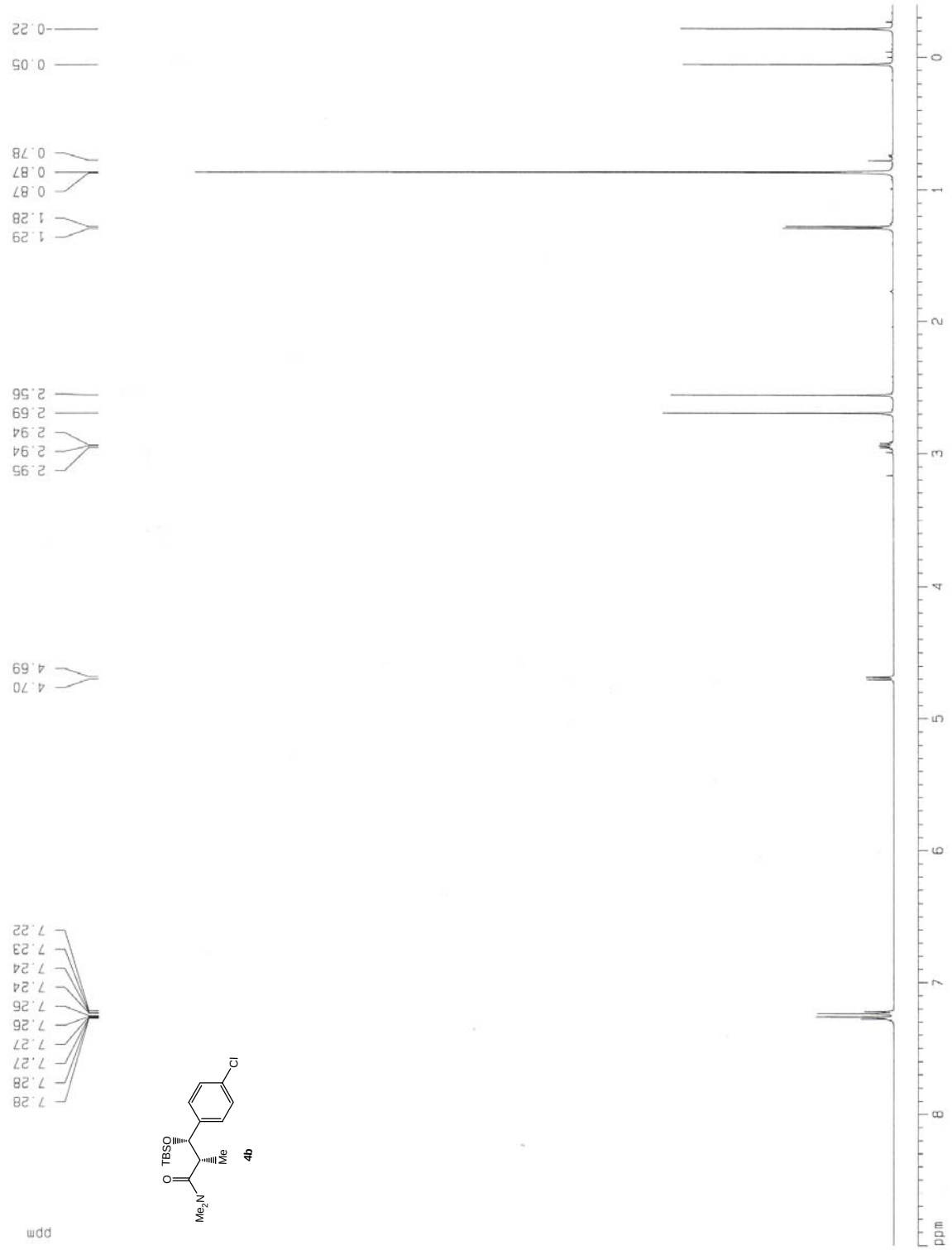
4a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4.70
7.22
7.23
7.24
7.24
7.26
7.26
7.27
7.27
7.28
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Me2N
O
Cl
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2
3
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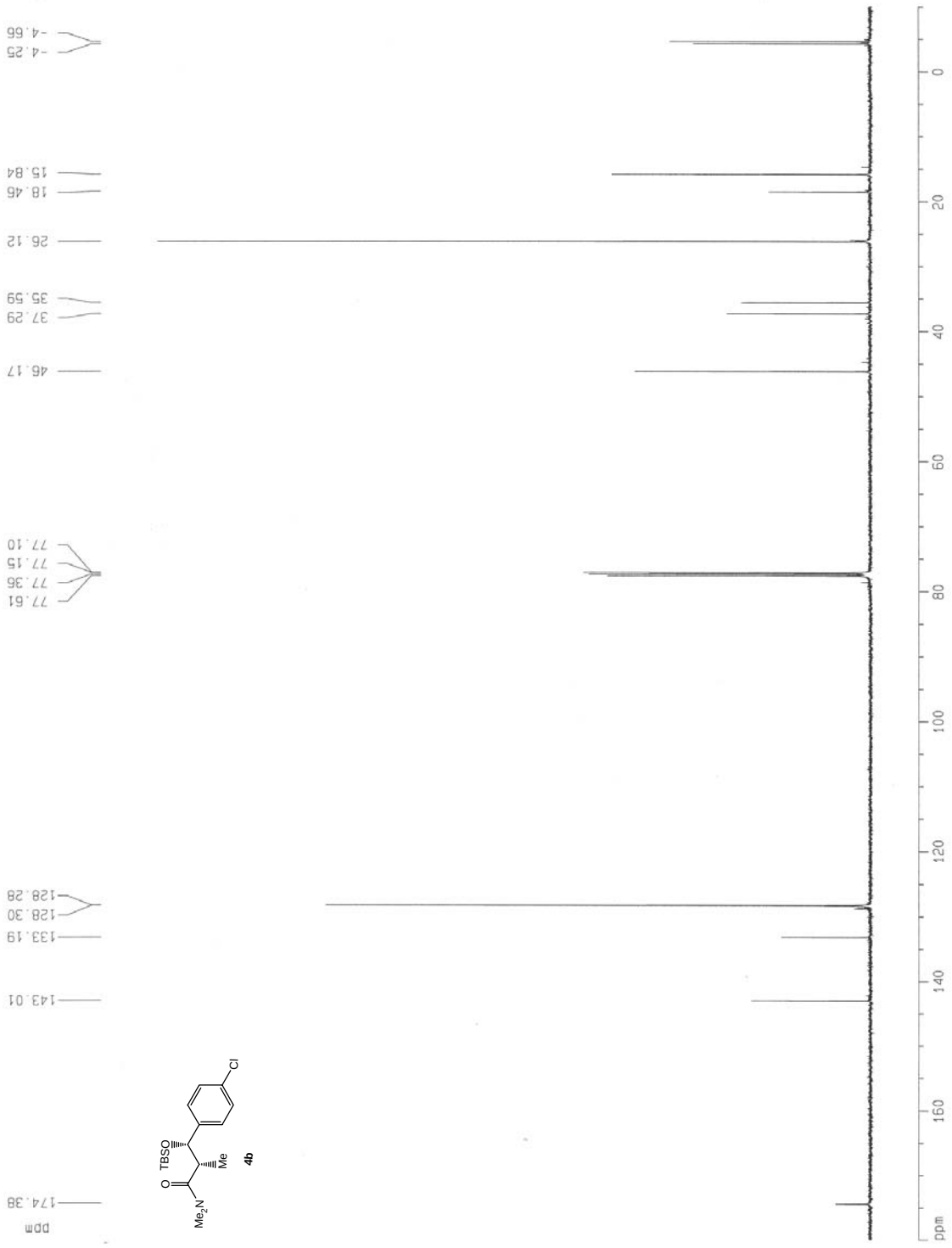
8
ppm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128.30
133.19
143.01
174.38
ppm
0
20
40
60
80
100
120
140
160
ppm
Cl
TBSO
Me
O
Me2N
4b

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0.86
1.27
1.29
2.52
2.68
3.79
6.79
7.26
ppm
0
1
2
3
4
5
6
7
8
ppm
TBS
O
Me
OMe
O
Me2N
4c


-4.65
-4.21
15.90
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26.18
35.59
37.29
46.19
55.49
77.10
77.36
77.50
77.61
113.37
127.96
136.53
159.04
174.77
ppm
0
20
40
60
80
100
120
140
160
ppm
OMe
TBS
O
Me
4c
O
Me2N

-0.17
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1.04
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TBSO
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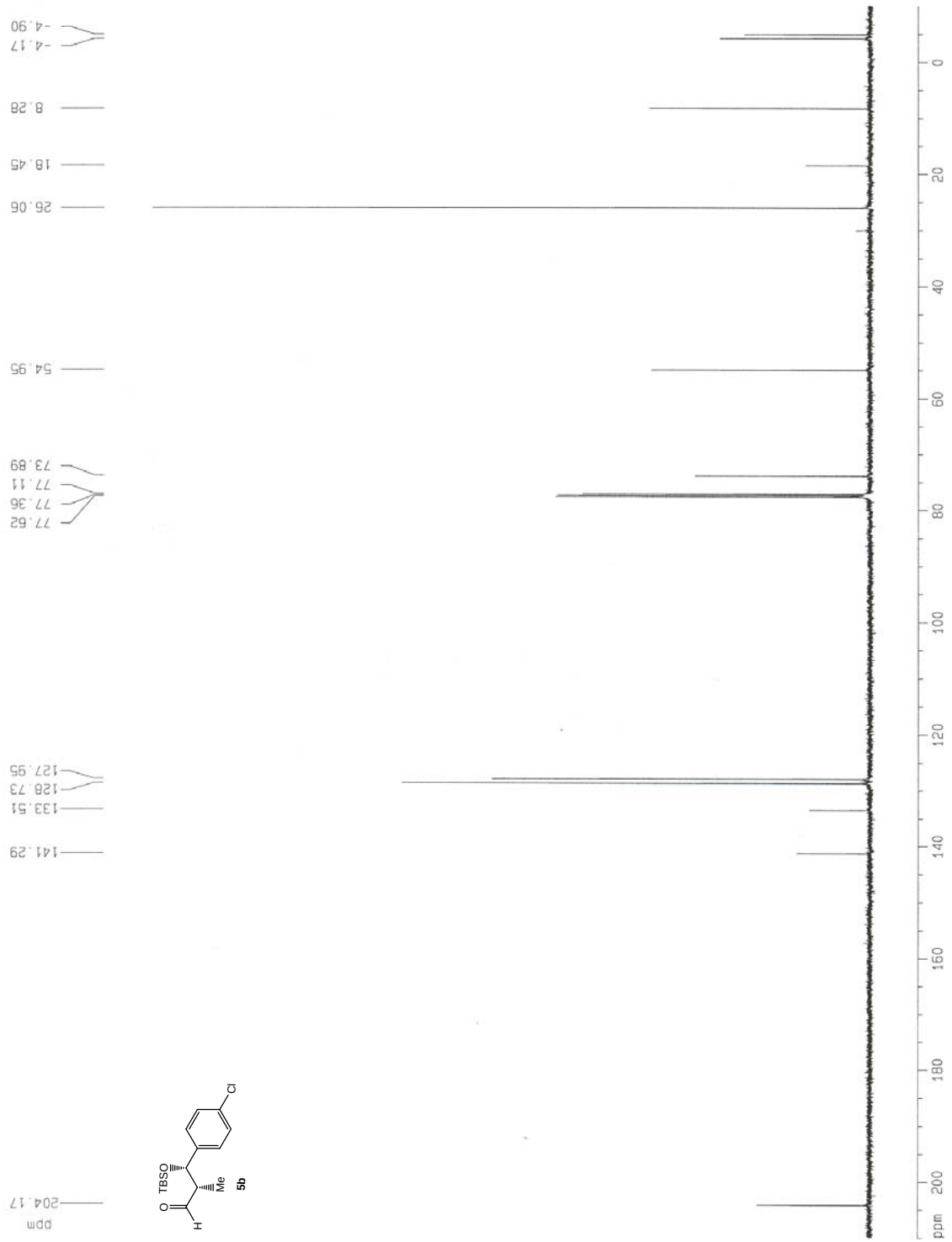
H
Me
Cl
5b
ppm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141.29
204.17
ppm
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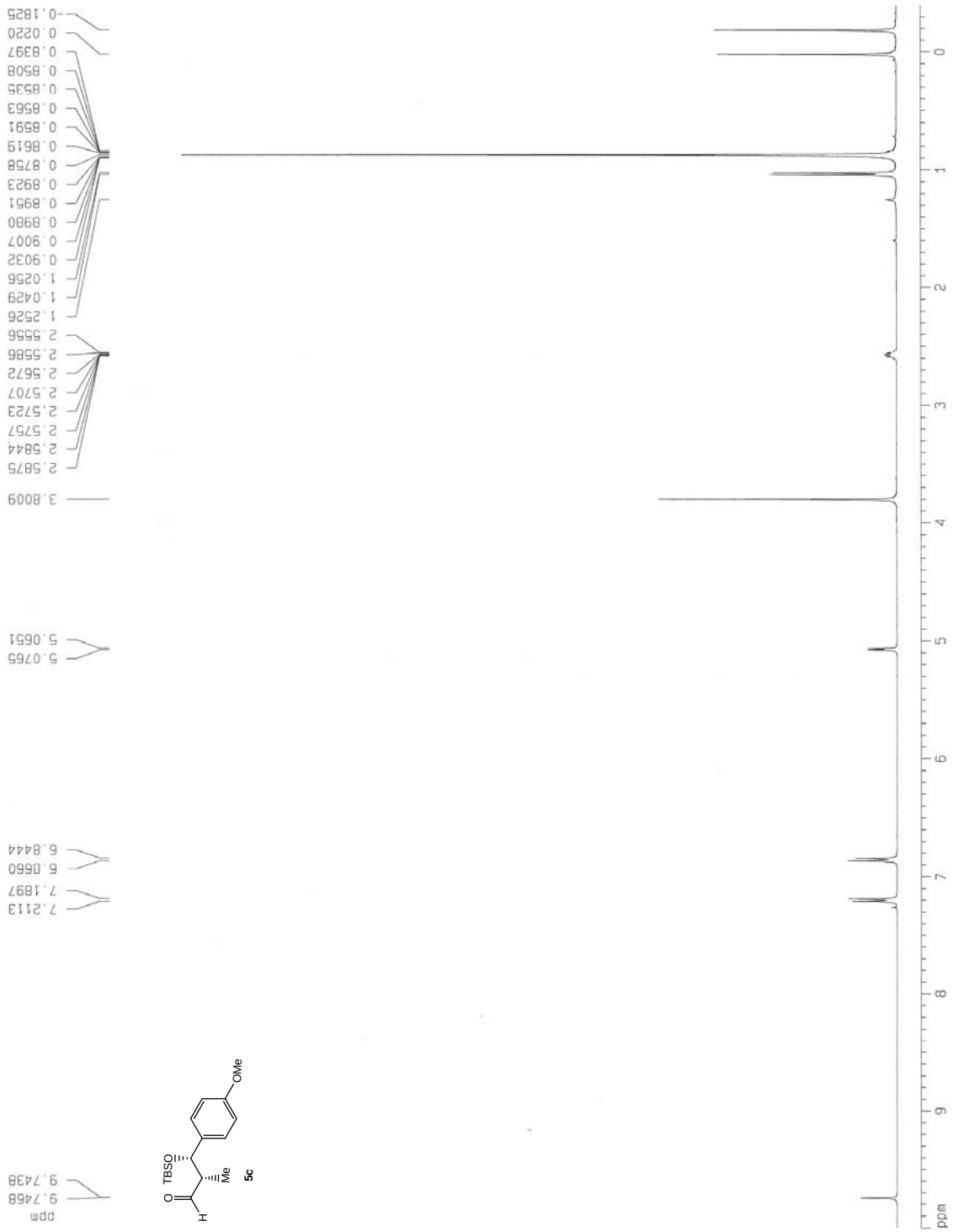
20
40
60
80
100
120
140
160
180
200
ppm
Cl
TBSO
O
H
Me
5b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0.0220
0.8397
0.8508
0.8535
0.8563
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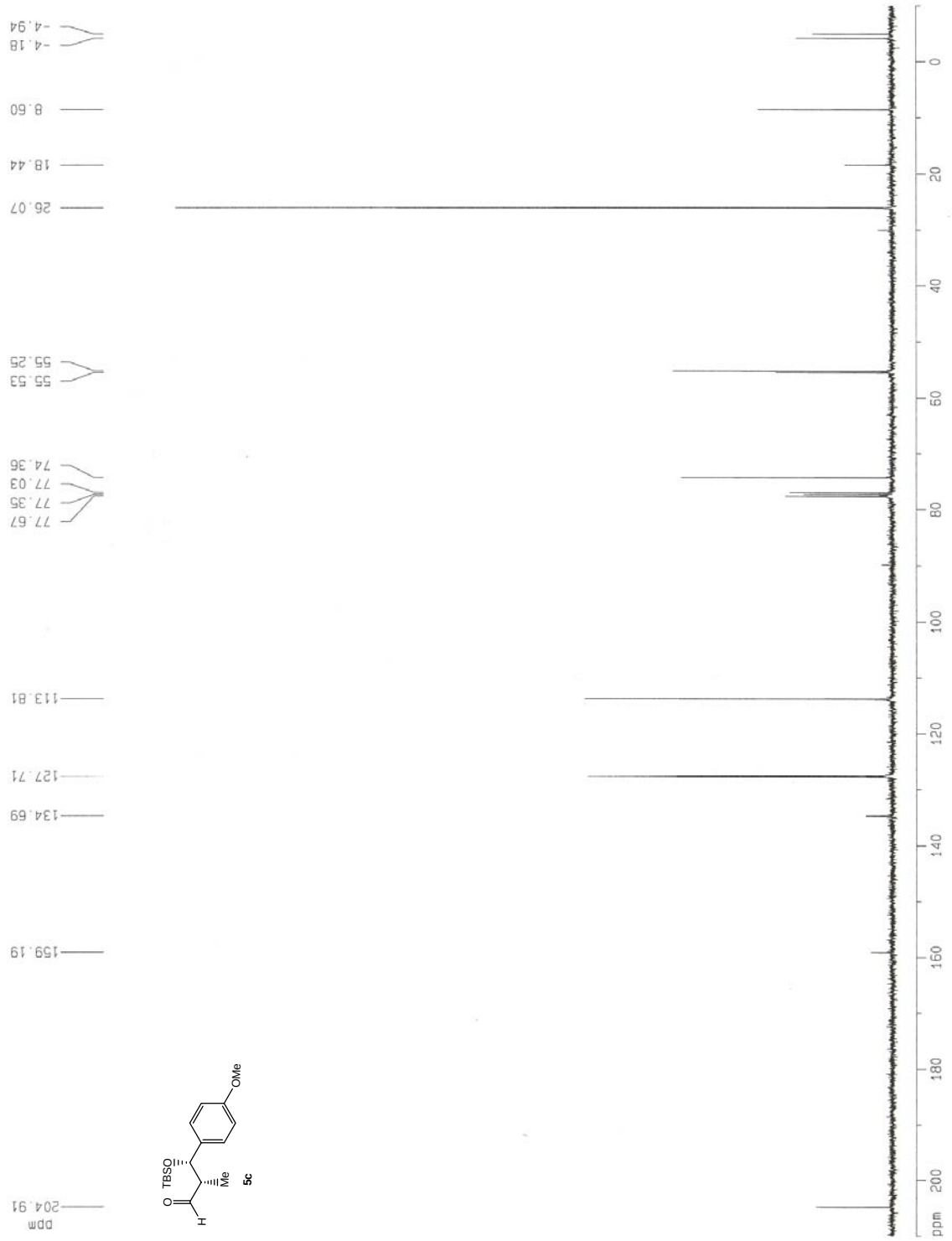
0.8923
0.8951
0.8980
0.9007
0.9032
1.0256
1.0429
1.2526
2.5556
2.5586
2.5672
2.5707
2.5723
2.5757
2.5844
2.5875
3.8009
5.0765
5.0651
6.8444
6.0660
7.1897
7.2113
9.7438
9.7468
ppm
TBSO
Me
OMe
H
O
5c
0
1
2
3
4
5
6
7
8
9
ppm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-4.18
8.60
18.44
26.07
55.25
55.53
74.36
77.03
77.35
77.67
113.81
127.71
134.69
159.19
204.91
ppm
0
20
40
60
80
100
120
140
160
180
200
OMe
TBSO
Me
O
H
5c

**References**

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