Diastereoselective construction of *anti*-4,5-disubstituted-1,3-dioxolanes *via* a bismuth-mediated two-component hemiacetal oxa-conjugate addition of γ-hydroxy-α,β-unsaturated ketones with paraformaldehyde

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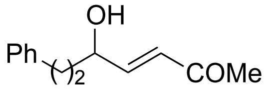
Contents of supporting information:

1. General information

All reactions were carried out under an ambient atmosphere with reagent grade solvents unless otherwise stated. Anhydrous dichloromethane, diethyl ether and tetrahydrofuran were obtained by passing degassed solvents through activated alumina columns in a Grubbs solvent purification system (PureSolv MD-6 of Innovative Technology Inc.). Anhydrous magnesium sulphate ($MgSO_4$) and sodium sulfate (Na_2SO_4) were used as drying agents; all other commercially available reagents (Aldrich, Alfa-Aesar, Acros) were purchased and used as received, unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on pre-coated 0.25 mm thick silica gel 60-F254 plates (Whatman PE SIL G/UV); Plates were visualized with UV light and spraying with Pancaldi reagent [$(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O] followed by heating. All compounds were purified by flash chromatography using silica gel 60 (40–63 μm, SiliCycle) and gave spectroscopic data consistent with being ≥95% the assigned structure. ^{1}H- and ^{13}C-NMR spectra were recorded on a *Bruker Avance DRX-500* spectrometer in the solvent indicated ($CDCl_3$ or C_6D_6) at ambient temperature; chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as the internal reference ($CDCl_3$: δ_H = 7.26 ppm and δ_C = 77.16 ppm; C_6D_6: δ_H = 7.16 ppm and δ_C = 128.06 ppm). ^{1}H-NMR data are reported as follows: chemical shift (multiplicity, 1st order spin system if available, coupling constant, integration). Coupling constants (*J*) are reported in Hz and the splitting patterns are designated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), app. (apparent) and combinations thereof. The reported chemical shifts for broad singlets and each part of the 1st order spin systems were averaged. ^{13}C-NMR spectra with complete proton decoupling were described with the aid of an APT sequence, separating methylene and quaternary carbons (e, even), from methyl and methine (o, odd). IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum 100 spectrometer; wavenumbers (ν) are given in cm^{-1}; the abbreviations w (weak, <33%), m (medium, 33-66%), s (strong, >66), vs (very strong, >95%) and br. (broad) are used to describe the relative intensities of the IR absorbance bands. High resolution chemical ionization (CI) and electrospray ionization (ESI) mass spectra were recorded on a *TermoFinnigan Mat 95 XP* spectrometer and a *VG 7070E* double focusing magnetic sector mass spectrometer equipped with solid probe inlet.

2. Representative experimental procedure and spectral data for the synthesis of γ-hydroxy-α,β-unsaturated ketones 1a-l. Hoveyda-Grubbs 2nd generation catalyst (0.25 mmol, 0.025 equiv.) was added to a stirred solution of allylic alcohol (10 mmol, 1 equiv.) and methyl vinyl ketone (50 mmol, 5 equiv.) in anhydrous dichloromethane (20 ml) at room temperature. The reaction mixture was refluxed under argon for *ca.* 4 hours (t.l.c. control) and then concentrated *in vacuo* to afford the crude product. Purification by flash chromatography (silica gel, eluting with diethyl ether/petroleum ether) furnished the desired *γ-hydroxy-α,β-unsaturated ketones* **1a-l**.



1a

(*E*)-5-Hydroxy-7-phenylhept-3-en-2-one (1a)[1]

Color and state: Brown oil.

FC (silica gel, eluting with 1:4 to 1:2 ethyl acetate/petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.22-7.19 (m, 3H), 6.76 (dd, *J* = 16.0, 5.0 Hz, 1H), 6.28 (dd, *J* = 16.0, 1.6 Hz, 1H), 4.34 (dtd, *J* = 12.3, 5.0, 1.7 Hz, 1H), 2.80 (ddd, A of

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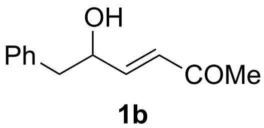
[1] T. J. Donohoe and J. F. Bower, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 3373.

ABXY, J_{AB} = 14.3 Hz, J_{AX} = 8.5 Hz, J_{AY} = 6.2 Hz, 1H), 2.74 (ddd, B of ABXY, J_{AB} = 15.2 Hz, J_{BX} = 7.7 Hz, J_{BY} = 6.5 Hz, 1H), 2.26 (s, 3H), 1.98-1.87 (m, 2H), 1.76 (d, J = 4.6 Hz, 1H).

IR (Neat) 3413 (br, w), 3027 (w), 2922 (w), 2854 (w), 1672 (s), 1630 (m), 1496 (w), 1455 (m), 1361 (m), 1257 (s), 979 (m), 733 (s), 700 (s) cm^{-1}.



1b

(*E*)-5-Hydroxy-6-phenylhex-3-en-2-one (1b)

Color and state: Colorless oil.

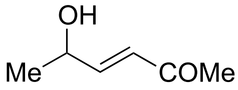
FC (silica gel, eluting with 1:3 to 1:2.5 ethyl acetate/petroleum ether).

^{1}H NMR (500 MHz, C_6D_6) δ 7.14-7.11 (m, 2H), 7.07-7.04 (m, 1H), 7.00-6.99 (m, 2H), 6.49 (dd, J = 15.9, 4.6 Hz, 1H), 6.18 (dd, J = 15.9, 1.6 Hz, 1H), 4.05 (dtd, J = 6.0, 4.5, 1.8 Hz, 1H), 2.56-2.47 (m, 2H), 1.81 (s, 3H), 1.56 (d, J = 4.5 Hz, 1H).

^{13}C NMR (125 MHz, C_6D_6) δ 196.78 (e), 147.36 (o), 137.71 (e), 129.81 (o), 129.37 (o), 128.76 (o), 126.96 (o), 71.85 (o), 43.57 (e), 27.18 (o).

IR (Neat) 3413 (br, w), 3026 (w), 2919 (w), 2858 (w), 1670 (s), 1627 (m), 1494 (w), 1452 (w), 1359 (m), 1254 (s), 980 (m), 746 (s) 699 (s) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{12}H_{15}O_2$ 191.1072, found 191.1062.



1c

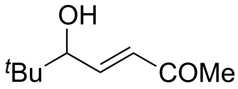
(*E*)-5-Hydroxyhex-3-en-2-one (1c)[2]

Color and state: Colorless oil.

FC (silica gel, eluting with 2:1 to 3:1 diethyl ether/pentane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (dd, J = 16.1, 4.8 Hz, 1H), 6.23 (dd, J = 16.1, 1.5 Hz, 1H), 4.48 (app. dtq, J = 6.6, 4.8, 1.7 Hz, 1H), 2.65 (d, J = 4.7 Hz, 1H), 2.25 (s, 3H), 1.32 (d, J = 6.7 Hz, 3H).

IR (neat) 3407 (br, m), 2976 (w), 2932 (w), 1691 (vs), 1629 (s), 1424 (m), 1362 (s), 1255 (vs), 1146 (s), 977 (vs) cm^{-1}.



1d

(*E*)-5-Hydroxy-6,6-dimethylhept-3-en-2-one (1d)

Color and state: Colorless oil.

FC (silica gel, eluting with 1:2 to 1:1 diethyl ether/petroleum ether).

^{1}H NMR (500 MHz, C_6D_6) δ 6.71 (dd, J = 16.0, 5.6 Hz, 1H), 6.24 (d, J = 15.9 Hz, 1H), 3.67-3.62 (m, 1H), 2.42 (br. s, 1H), 1.88 (s, 3H), 0.85 (s, 9H).

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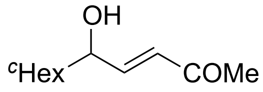
[2] T. Ishikawa, M. Senzaki, R. Kadoya, T. Morimoto, N. Miyake, M. Izawa, S. Saito and H. Kobayashi, *J. Am. Chem. Soc.*, 2001, **123**, 4607.

^{13}C NMR (125 MHz, C_6D_6) δ 197.55 (e), 146.84 (o), 130.99 (o), 78.93 (o), 35.60 (e), 27.14 (o), 25.89 (o).

IR (Neat) 3445 (br, w), 2955 (m), 2907 (w), 2869 (w), 1670 (vs), 1627 (s), 1466 (m), 1361 (s), 1257 (s), 1110 (s), 983 (s) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_9H_{17}O_2$ 157.1223, found 157.1216.



1e

(*E*)-5-Cyclohexyl-5-hydroxypent-3-en-2-one (1e)

Color and state: Colorless oil.

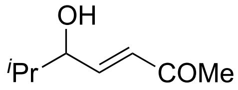
FC (silica gel, eluting with 1:3.5 to 1:3 ethyl acetate/petroleum ether).

^{1}H NMR (500 MHz, C_6D_6) δ 6.53 (dd, *J* = 16.0, 5.3 Hz, 1H), 6.18 (dd, *J* = 16.0, 1.5 Hz, 1H), 3.64 (td, *J* = 5.3, 1.1 Hz, 1H), 1.86 (s, 3H), 1.68-1.60 (m, 3H), 1.56-1.47 (m, 3H), 1.20 (app. dddt, *J* = 11.8, 6.3, 5.6, 3.1 Hz, 1H), 1.13-0.96 (m, 3H), 0.95-0.84 (m, 2H).

^{13}C NMR (125 MHz, C_6D_6) δ 196.82 (e), 147.67 (o), 130.06 (o), 75.44 (o), 43.83 (o), 29.23 (e), 28.13 (e), 27.21 (o), 26.70 (e), 26.49 (e), 26.41 (e).

IR (Neat) 3423 (br, w), 2922 (s), 2851 (m), 1669 (s), 1626 (s), 1448 (m), 1359 (m), 1253 (s), 1108 (m), 979 (s) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{11}H_{19}O_2$ 183.1380, found 183.1371.



1f

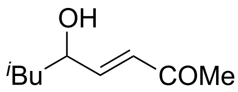
(*E*)-5-Hydroxy-6-methylhept-3-en-2-one (1f)[3]

Color and state: Volatile colorless oil.

FC (silica gel, eluting with 1:1 diethyl/petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.71 (dd, *J* = 16.0, 5.2 Hz, 1H), 6.18 (dd, *J* = 16.0, 1.3 Hz, 1H), 4.01 (app. qd, *J* = 5.0, 1.0 Hz, 1H), 3.17 (d, *J* = 4.8 Hz, 1H), 2.19 (s, 3H), 1.76 (octet, *J* = 6.6 Hz, 1H), 0.86 (d, *J* = 6.9 Hz, 6H).

IR (neat) 3424 (br, w), 2962 (m), 2875 (w), 1671 (vs), 1631 (s), 1468 (m), 1361 (s), 1255 (s), 1176 (m), 980 (vs) cm^{-1}.



1g

(*E*)-5-Hydroxy-7-methyloct-3-en-2-one (1g)

Color and state: Colorless oil.

FC (silica gel, eluting with 1:1 to 1.5:1 diethyl ether/petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.72 (dd, *J* = 16.0, 5.1 Hz, 1H), 6.20 (d, *J* = 16.0 Hz, 1H), 4.34-4.29 (m, 1H), 2.94 (d, *J* = 2.8 Hz, 1H), 2.21 (s, 3H), 1.75 (nonet, *J* = 6.7 Hz, 1H), 1.46 (ddd, A of

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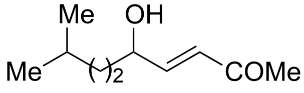
[3] A. Giardina, E. Marcantoni, T. Mecozzi and M. Petrini, *Eur. J. Org. Chem.*, 2001, 713.

ABXY, J_{AB} = 14.0 Hz, J_{AX} = 8.5 Hz, J_{AY} = 5.7 Hz, 1H), 1.32 (ddd, B of ABXY, J_{AB} = 13.7 Hz, J_{BX} = 8.4 Hz, J_{BY} = 5.2 Hz, 1H), 0.89 (d, J = 6.7 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.22 (e), 150.19 (o), 128.71 (o), 69.32 (o), 45.73 (e), 27.26 (o), 24.51 (o), 23.15 (o), 22.07 (o).

IR (Neat) 3412 (br, w), 2955 (m), 2925 (m), 2870 (w), 1671 (vs), 1628 (s), 1467 (m), 1360 (s), 1255 (s), 1147 (m), 980 (s) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_9H_{17}O_2$ 157.1223, found 157.1217.



1h

(*E*)-5-Hydroxy-8-methylnon-3-en-2-one (1h)

Color and state: Colorless oil.

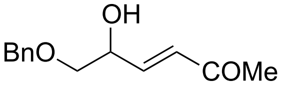
FC (silica gel, eluting with 1:2, 1:1 diethyl ether/petroleum ether).

^{1}H NMR (500 MHz, C_6D_6) δ 6.52 (dd, J = 16.0, 4.9 Hz, 1H), 6.22 (dd, J = 16.0, 1.4 Hz, 1H), 3.91-3.87 (m, 1H), 1.93 (br. s, 1H), 1.88 (s, 3H), 1.41 (nonet, J = 6.6 Hz, 1H), 1.40-1.29 (m, 2H), 1.24 (ddt, A of $ABXY_2$, J_{AB} = 12.9 Hz, J_{AX} = 9.8 Hz, J_{AY} = 6.5 Hz, 1H), 1.11 (ddt, B of $ABXY_2$, J_{AB} = 13.0 Hz, J_{BX} = 9.9 Hz, J_{BY} = 6.5 Hz, 1H), 0.84 (d, J = 6.6 Hz, 3H), 0.83 (d, J = 6.6 Hz, 3H).

^{13}C NMR (125 MHz, C_6D_6) δ 197.33 (e), 149.09 (o), 129.08 (o), 71.32 (o), 34.90 (e), 34.70 (e), 28.30 (o), 27.12 (o), 22.74 (o), 22.60 (o).

IR (Neat) 3420 (br, w), 2953 (m), 2933 (m), 2869 (m), 1671 (vs), 1628 (s), 1467 (m), 1361 (s), 1255 (s), 1171 (m), 977 (s) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{10}H_{19}O_2$ 171.1380, found 171.1371.



1i

(*E*)-6-(Benzyloxy)-5-hydroxyhex-3-en-2-one (1i)

Color and state: Colorless oil.

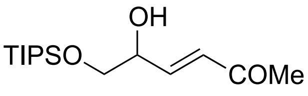
FC (silica gel, eluting with 1:3 to 1:2 ethyl acetate/petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.33-7.30 (m, 3H), 6.71 (dd, J = 16.0, 4.4 Hz, 1H), 6.39 (d, J = 16.0 Hz, 1H), 4.58 (s, 2H), 4.56-4.51 (m, 1H), 3.63 (dd, A of ABX, J_{AB} = 9.5 Hz, J_{AX} = 3.5 Hz, 1H), 3.41 (dd, B of ABX, J_{AB} = 9.4 Hz, J_{BX} = 7.8 Hz, 1H), 2.62 (d, J = 4.0 Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.31 (e), 144.26 (o), 137.46 (e), 130.55 (o), 128.70 (o), 128.20 (o), 128.01 (o), 73.65 (e), 73.05 (e), 70.13 (o), 27.79 (o).

IR (Neat) 3427 (br, w), 2920 (vs), 2851 (s), 1676 (m), 1633 (m), 1455 (m), 1361 (m), 1257 (m), 1103 (m), 981 (m), 739 (m) cm^{-1}.

HRMS (CI, $[M+NH_4]^+$) calcd for $C_{13}H_{20}NO_3$ 238.1443, found 238.1445.



1j

(*E*)-5-Hydroxy-6-((triisopropylsilyl)oxy)hex-3-en-2-one (1j)

Color and state: Colorless oil.

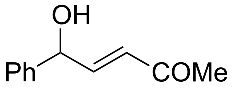
FC (silica gel, eluting with 1:6 to 1:5 ethyl acetate/petroleum ether).

^{1}H NMR (500 MHz, C_6D_6) δ 6.59 (dd, J = 16.0, 4.3 Hz, 1H), 6.43 (dd, J = 15.9, 0.9 Hz, 1H), 4.16-4.10 (m, 1H), 3.52 (dd, A of ABX, J_{AB} = 9.7 Hz, J_{AX} = 4.4 Hz, 1H), 3.40 (dd, B of ABX, J_{AB} = 9.7 Hz, J_{BX} = 7.1 Hz, 1H), 2.46 (d, J = 3.8 Hz, 1H), 1.88 (s, 3H), 1.06-1.00 (m, 18H), 0.98 (septet, J = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, C_6D_6) δ 196.29 (e), 144.31 (o), 130.60 (o), 71.82 (o), 67.18 (e), 27.28 (o), 18.08 (o), 12.22 (o).

IR (Neat) 3429 (br, w), 2941 (m), 2865 (m), 1675 (s), 1630 (m), 1462 (m), 1360 (m), 1252 (m), 1109 (s), 980 (s), 881 (s), 786 (s) cm^{-1}.

HRMS (ESI, $[M–H]^-$) calcd for $C_{15}H_{29}O_3Si$ 285.1891, found 285.1900.



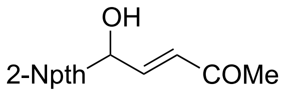
1k

(*E*)-5-Hydroxy-5-phenylpent-3-en-2-one (1k)[1]

FC (silica gel, eluting with 1:3 to 1:2 ethyl acetate/petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.31 (m, 5H), 6.86 (dd, J = 16.0, 5.0 Hz, 1H), 6.38 (dd, J = 16.0, 1.6 Hz, 1H), 5.38 (app. td, J = 3.4, 1.6 Hz, 1H), 2.39 (d, J = 3.6 Hz, 1H), 2.26 (s, 3H).

IR (Neat) 3395 (br, w), 3062 (w), 3031 (w), 2852 (w), 1672 (s), 1627 (m), 1453 (w), 1360 (m), 1256 (s), 1098 (m), 979 (s), 761 (m) cm^{-1}.



1l

(*E*)-5-Hydroxy-5-(naphthalen-2-yl)pent-3-en-2-one (1l)

FC (silica gel, eluting with 1:3 to 1:2.5 ethyl acetate/petroleum ether).

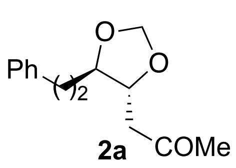
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85-7.82 (m, 3H), 7.80-7.78 (m, 1H), 7.52-7.48 (m, 2H), 7.44-7.42 (m, 1H), 6.90 (dd, J = 16.0, 5.0 Hz, 1H), 6.41 (dd, J = 16.0, 1.2 Hz, 1H), 5.51 (app. t, J = 3.7 Hz, 1H), 2.77 (d, J = 3.5 Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.94 (e), 147.53 (o), 138.39 (e), 133.39 (e), 133.31 (e), 129.20 (o), 128.92 (o), 128.11 (o), 127.86 (o), 126.58 (o), 126.49 (o), 125.56 (o), 124.35 (o), 73.81 (o), 27.45 (o).

IR (neat) 3383 (br, m), 3055 (w), 3024 (w), 1670 (s), 1627 (s), 1601 (m), 1508 (m), 1360 (s), 1253 (s), 1096 (s), 978 (s), 818 (vs), 749 (vs) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{15}H_{15}O_2$ 227.1072, found 227.1074.

3. General experimental procedure and spectral data for the synthesis of the *anti*-4,5-disubstituted-1,3-dioxolanes 2a-l. Bismuth(III) nitrate pentahydrate (0.05 mmol, 0.1 equiv.) was added to a stirred solution of the γ-hydroxy-α,β-unsaturated ketone (0.5 mmol, 1 equiv.) and paraformaldehyde (2.5 mmol, 5 equiv.) in dichloromethane (2 ml) at room temperature. The reaction mixture was then stirred at this temperature for *ca*. 36 hours (t.l.c. control), filtered through a pad of silica gel with diethyl ether and the crude material was concentrated *in vacuo* to afford the crude product. Purification by flash chromatography (silica gel, eluting with diethyl ether/pentane) furnished the *anti-4,5-disubstitted-1,3-dioxolanes* **2a-l**.



2a

1-((4*R,5*R**)-(5-Phenethyl-1,3-dioxolan-4-yl)propan-2-one (2a)**

Color and state: Colorless oil.

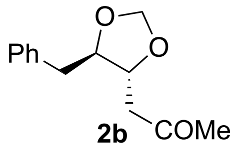
FC (silica gel, eluting with 1:2.5 diethyl ether/petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.22-7.18 (m, 3H), 5.02 (s, 1H), 4.99 (s, 1H), 4.06 (ddd, A of AMXY, $J_{AM} = 7.8$ Hz, $J_{AX} = 6.0$ Hz, $J_{AY} = 5.1$ Hz, 1H), 3.63 (app. q, M of AMXY, $J_{AM} = J_{MX} = J_{MY} = 6.3$ Hz, 1H), 2.86 (dt, A of ABX_2, $J_{AB} = 14.2$ Hz, $J_{AX} = 7.2$ Hz, 1H), 2.76 (dd, A of ABX, $J_{AB} = 16.6$ Hz, $J_{AX} = 7.8$ Hz, 1H), 2.71 (dt, B of ABX_2, $J_{AB} = 13.9$ Hz, $J_{BX} = 7.8$ Hz, 1H), 2.56 (dd, B of ABX, $J_{AB} = 16.7$ Hz, $J_{BX} = 4.8$ Hz, 1H), 2.18 (s, 3H), 1.91 (td, $J = 8.0$, 6.1 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.16 (e), 141.31 (e), 128.46 (o), 128.41 (o), 126.02 (o), 94.06 (e), 80.32 (o), 76.41 (o), 46.43 (e), 33.90 (e), 32.09 (e), 30.75 (o).

IR (neat) 3027 (w), 2920 (m), 2851 (m), 1714 (s), 1603 (w), 1497 (w), 1455 (m), 1358 (m), 1086 (s), 983 (m), 701 (s) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{14}H_{19}O_3$ 235.1334, found 235.1337.



2b

1-((4*R,5*R**)-5-Benzyl-1,3-dioxolan-4-yl)propan-2-one (2b)**

Color and state: Colorless oil.

FC (silica gel, eluting with 1:3 to 1:2 diethyl ether/pentane).

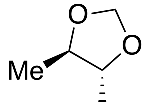
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.26-7.22 (m, 3H), 5.01 (s, 1H), 4.97 (s, 1H), 4.13 (ddd, A of AMXY, $J_{AM} = 7.9$ Hz, $J_{AX} = 6.4$ Hz, $J_{AY} = 4.5$ Hz, 1H), 3.85 (dt, M of AMX_2, $J_{AM} = 7.1$ Hz, $J_{MX} = 6.1$ Hz, 1H), 3.02 (dd, A of ABX, $J_{AB} = 14.0$ Hz, $J_{AX} = 7.4$

Hz, 1H), 2.89 (dd, B of ABX, J_{AB} = 13.9 Hz, J_{BX} = 5.6 Hz, 1H), 2.68 (dd, A of ABX, J_{AB} = 16.5 Hz, J_{AX} = 7.9 Hz, 1H), 2.34 (dd, B of ABX, J_{AB} = 16.5 Hz, J_{BX} = 4.5 Hz, 1H), 2.14 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 205.96 (e), 137.27 (e), 129.35 (o), 128.69 (o), 126.84 (o), 94.29 (e), 81.65 (o), 76.48 (o), 46.57 (e), 38.71 (e), 30.70 (o).

IR (neat) 3026 (w), 2919 (w), 2858 (w), 1712 (s), 1603 (w), 1495 (w), 1453 (w), 1358 (m), 1080 (s), 969 (s), 700 (s) cm^{-1}.

HRMS (ESI, [M+H]$^+$) calcd for $C_{13}H_{17}O_3$ 221.1172, found 221.1162.



2c

1-((4*R,5*R**)-(5-Methyl-1,3-dioxolan-4-yl)propan-2-one (2c)**

Color and state: Colorless oil.

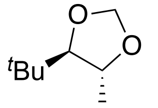
FC (silica gel, eluting with 1:2 diethyl ether/pentane).

^{1}H NMR (500 MHz, CDCl$_3$) δ 4.98 (s, 1H), 4.94 (s, 1H), 3.90 (ddd, A of AMXY, J_{AM} = 7.8 Hz, J_{AX} = 6.6 Hz, J_{AY} = 4.8 Hz, 1H), 3.70 (quintet, M of A_3MX, J_{AM} = J_{MX} = 6.3 Hz, 1H), 2.76 (dd, A of ABX, J_{AB} = 16.5 Hz, J_{AX} = 7.8 Hz, 1H), 2.58 (dd, B of ABX, J_{AB} = 16.5 Hz, J_{BX} = 4.8 Hz, 1H), 2.20 (s, 3H), 1.29 (d, J = 6.2 Hz, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 206.34 (e), 94.09 (e), 77.94 (o), 77.34 (o), 46.24 (e), 30.87 (o), 17.40 (o).

IR (neat) 2871 (w), 1714 (s), 1384 (m), 1361 (m), 1167 (m), 1091 (s), 974 (s), 730 (vs) cm^{-1}.

HRMS (CI, [M+NH$_4$]$^+$) calcd for $C_7H_{16}NO_3$ 162.1130, found 162.1134.



2d

1-((4*R,5*R**)-5-(*tert*-Butyl)-1,3-dioxolan-4-yl)propan-2-one (2d)**

Color and state: Colorless oil.

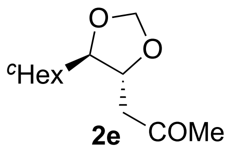
FC (silica gel, eluting with 1:3 diethyl ether/pentane).

^{1}H NMR (500 MHz, CDCl$_3$) δ 5.00 (s, 1H), 4.92 (s, 1H), 4.31 (ddd, A of AMXY, J_{AX} = 9.2 Hz, J_{AM} = 6.1 Hz, J_{AY} = 3.1 Hz, 1H), 3.33 (d, M of AM, J_{AM} = 6.0 Hz, 1H), 2.77 (dd, A of ABX, J_{AB} = 16.1 Hz, J_{AX} = 9.3 Hz, 1H), 2.50 (dd, B of ABX, J_{AB} = 16.1 Hz, J_{BX} = 3.1 Hz, 1H), 2.22 (s, 3H), 0.94 (s, 9H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 206.16 (e), 94.61 (e), 88.69 (o), 72.82 (o), 48.06 (e), 33.62 (e), 31.00 (o), 25.86 (o).

IR (neat) 2956 (m), 2908 (w), 2869 (w), 1715 (s), 1478 (w), 1362 (m), 1162 (m), 1087 (s), 968 (s) cm^{-1}.

HRMS (ESI, [M+H]$^+$) calcd for $C_{10}H_{19}O_3$ 187.1329, found 187.1319.


2e

1-((4*R,5*R**)-5-Cyclohexyl-1,3-dioxolan-4-yl)propan-2-one (2e)**

Color and state: Colorless oil.

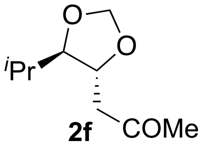
FC (silica gel, eluting with 1:5 to 1:4 diethyl ether/pentane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.93 (s, 1H), 4.92 (s, 1H), 4.21 (ddd, A of AMXY, J_{AM} = 8.8 Hz, J_{AX} = 5.9 Hz, J_{AY} = 3.6 Hz, 1H), 3.34 (app. t, M of AMX, $J_{AM} = J_{MX}$ = 6.6 Hz, 1H), 2.73 (dd, A of ABX, J_{AB} = 16.2 Hz, J_{AX} = 8.7 Hz, 1H), 2.54 (dd, B of ABX, J_{AB} = 16.2 Hz, J_{BX} = 3.6 Hz, 1H), 2.20 (s, 3H), 1.91-1.85 (m, 1H), 1.76-1.71 (m, 2H), 1.68-1.57 (m, 2H), 1.49 (dddd, J = 15.0, 11.5, 7.1, 3.6 Hz, 1H), 1.28-1.10 (m, 3H), 1.03 (app. qt, J = 12.2, 4.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.34 (e), 94.20 (e), 85.17 (o), 74.60 (o), 47.49 (e), 40.39 (o), 30.93 (o), 29.25 (e), 28.96 (e), 26.40 (e), 26.01 (e), 25.81 (e).

IR (neat) 2923 (s), 2851 (m), 1713 (s), 1449 (m), 1357 (m), 1163 (m), 1084 (s), 998 (s), 972 (s) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{12}H_{21}O_3$ 213.1485, found 213.1475.


2f

1-((4*R,5*R**)-(5-Isopropyl-1,3-dioxolan-4-yl)propan-2-one (2f)**

Color and state: Colorless oil.

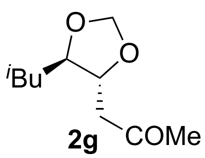
FC (silica gel, eluting with 1:5 to 1:4 diethyl ether/pentane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.93 (s, 1H), 4.91 (s, 1H), 4.17 (ddd, A of AMXY, J_{AM} = 8.9 Hz, J_{AX} = 5.7 Hz, J_{AY} = 3.8 Hz, 1H), 3.32 (app. t, M of AMX, $J_{AM} = J_{MX}$ = 6.5 Hz, 1H), 2.74 (dd, A of ABX, J_{AB} = 16.3 Hz, J_{AX} = 8.7 Hz, 1H), 2.54 (dd, B of ABX, J_{AB} = 16.3 Hz, J_{BX} = 3.8 Hz, 1H), 2.18 (s, 3H), 1.79 (octet, J = 6.8 Hz, 1H), 0.96 (d, J = 6.7 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.25 (e), 94.17 (e), 85.97 (o), 74.65 (o), 47.39 (e), 30.89 (o), 30.59 (o), 18.74 (o), 18.39 (o).

IR (neat) 2963 (w), 2876 (w), 1716 (m), 1470 (w), 1360 (w), 1167 (m), 1086 (s), 972 (m), 912 (s), 729 (vs) cm^{-1}.

HRMS (CI, $[M+NH_4]^+$) calcd for $C_9H_{20}NO_3$ 190.1443, found 190.1449.


2g

1-((4*R,5*R**)-5-Isobutyl-1,3-dioxolan-4-yl)propan-2-one (2g)**

Color and state: Colorless oil.

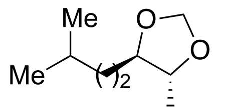
FC (silica gel, eluting with 1:5 to 1:4 diethyl ether/pentane).

^{1}H NMR (500 MHz, CDCl$_3$) δ 4.95 (s, 1H), 4.93 (s, 1H), 3.93 (ddd, A of AMXY, J_{AM} = 8.0 Hz, J_{AX} = 6.4 Hz, J_{AY} = 4.5 Hz, 1H), 3.64 (ddd, M of AMXY, J_{AM} = 9.5 Hz, J_{MX} = 6.3 Hz, J_{MY} = 3.4 Hz, 1H), 2.74 (dd, A of ABX, J_{AB} = 16.3 Hz, J_{AX} = 8.0 Hz, 1H), 2.56 (dd, B of ABX, J_{AB} = 16.3 Hz, J_{BX} = 4.5 Hz, 1H), 2.19 (s, 3H), 1.78 (app. dd of septet, J = 8.2, 6.6, 5.2 Hz, 1H), 1.53 (ddd, A of ABXY, J_{AB} = 14.2 Hz, J_{AX} = 9.2 Hz, J_{AY} = 5.3 Hz, 1H), 1.31 (ddd, B of ABXY, J_{AB} = 14.0 Hz, J_{BX} = 8.4 Hz, J_{BY} = 3.5 Hz, 1H), 0.93 (d, J= 6.7 Hz, 3H), 0.91 (d, J= 6.6 Hz, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 206.28 (e), 94.11 (e), 79.65 (o), 77.04 (o), 46.51 (e), 41.15 (e), 30.85 (o), 25.37 (o), 23.38 (o), 22.09 (o).

IR (neat) 2955 (m), 2928 (m), 2870 (m), 1713 (s), 1467 (w), 1364 (m), 1164 (m), 1084 (s), 985 (s) cm^{-1}.

HRMS (ESI, [M+H]$^+$) calcd for $C_{10}H_{19}O_3$ 187.1329, found 187.1320.



2h

1-((4*R,5*R**)-5-Isopentyl-1,3-dioxolan-4-yl)propan-2-one (2h)**

Color and state: Colorless oil.

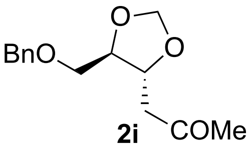
FC (silica gel, eluting with 1:5 diethyl ether/pentane).

^{1}H NMR (500 MHz, CDCl$_3$) δ 4.98 (s, 1H), 4.96 (s, 1H), 4.01 (ddd, A of AMXY, J_{AM} = 7.9 Hz, J_{AX} = 6.2 Hz, J_{AY} = 4.6 Hz, 1H), 3.58 (app. q, M of AMXY, J_{AM} = J_{MX} = J_{MY} = 6.3 Hz, 1H), 2.77 (dd, A of ABX, J_{AB} = 16.3 Hz, J_{AX} = 8.0 Hz, 1H), 2.59 (dd, B of ABX, J_{AB} = 16.3 Hz, J_{BX} = 4.5 Hz, 1H), 2.22 (s, 3H), 1.62-1.53 (m, 3H), 1.38 (ddt, A of ABXY$_2$, J_{AB} = 13.6 Hz, J_{AX} = 8.5 Hz, J_{AY} = 7.0 Hz, 1H), 1.24 (ddt, B of ABXY$_2$, J_{AB} = 13.9 Hz, J_{BX} = 9.4 Hz, J_{BY} = 7.1 Hz, 1H), 0.90 (d, J= 6.6 Hz, 3H), 0.90 (d, J= 6.7 Hz, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 206.27 (e), 94.15 (e), 81.62 (o), 76.71 (o), 46.76 (e), 35.04 (e), 30.89 (o), 30.18 (e), 28.11 (o), 22.63 (o), 22.52 (o).

IR (neat) 2953 (m), 2933 (m), 2868 (m), 1713 (s), 1467 (w), 1359 (m), 1163 (m), 1085 (vs), 975 (s) cm^{-1}.

HRMS (ESI, [M+H]$^+$) calcd for $C_{11}H_{21}O_3$ 201.1485, found 201.1480.



2i

1-((4*R,5*R**)-(5-(Benzyloxymethyl)-1,3-dioxolan-4-yl)propan-2-one (2i)**

Color and state: Colorless oil.

FC (silica gel, eluting with 1:1.5 to 1:1 diethyl ether/pentane).

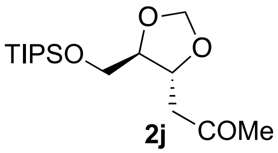
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35-7.26 (m, 5H), 5.00 (s, 1H), 4.97 (s, 1H), 4.58 (d, A of AB, J_{AB} = 12.5 Hz, 1H), 4.55 (d, B of AB, J_{AB} = 12.4 Hz, 1H), 4.22 (ddd, A of

AMXY, J_{AM} = 7.6 Hz, J_{AX} = 6.3 Hz, J_{AY} = 5.1 Hz, 1H), 3.82 (app. q, M of AMXY, J_{AM} = J_{MX} = J_{MY} = 5.6 Hz, 1H), 3.65 (dd, A of ABX, J_{AB} = 10.2 Hz, J_{AX} = 5.7 Hz, 1H), 3.59 (dd, B of ABX, J_{AB} = 10.2 Hz, J_{BX} = 4.9 Hz, 1H), 2.83 (dd, A of ABX, J_{AB} = 16.8 Hz, J_{AX} = 7.8 Hz, 1H), 2.67 (dd, B of ABX, J_{AB} = 16.8 Hz, J_{BX} = 4.9 Hz, 1H), 2.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.12 (e), 137.81 (e), 128.47 (o), 127.81 (o), 127.73 (o), 94.71 (e), 79.48 (o), 74.29 (o), 73.59 (e), 69.86 (e), 46.69 (e), 30.70 (o).

IR (neat) 2922 (w), 2864 (w), 1713 (s), 1497 (w), 1454 (w), 1360 (m), 1164 (m), 1085 (vs), 977 (s), 732 (vs), 698 (s) cm^{-1}.

HRMS (CI, $[M+NH_4]^+$) calcd for $C_{14}H_{22}NO_4$ 268.1549, found 268.1543.



2j

1-((4*R,5*R**)-5-(((Triisopropylsilyl)oxy)methyl)-1,3-dioxolan-4-yl)propan-2-one (2j)**

Color and state: Colorless oil.

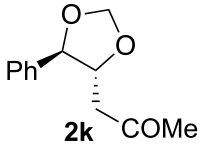
FC (silica gel, eluting with 1:6 diethyl ether/petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.01 (s, 1H), 4.96 (s, 1H), 4.32 (ddd, A of AMXY, J_{AM} = 8.0 Hz, J_{AX} = 6.1 Hz, J_{AY} = 4.6 Hz, 1H), 3.92 (dd, A of ABX, J_{AB} = 10.3 Hz, J_{AX} = 4.6 Hz, 1H), 3.79 (dd, B of ABX, J_{AB} = 10.3 Hz, J_{BX} = 5.9 Hz, 1H), 3.70 (dt, M of AMX_2, J_{AM} = 5.9 Hz, J_{MX} = 4.7 Hz, 1H), 2.83 (dd, A of ABX, J_{AB} = 16.5 Hz, J_{AX} = 8.1 Hz, 1H), 2.72 (dd, B of ABX, J_{AB} = 16.5 Hz, J_{BX} = 4.5 Hz, 1H), 2.20 (s, 3H), 1.14-1.00 (m, 21H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.14 (e), 95.04 (e), 80.74 (o), 74.74 (o), 63.90 (e), 47.21 (e), 30.65 (o), 18.04 (o), 11.98 (o).

IR (neat) 2941 (m), 2892 (m), 2865 (m), 1716 (m), 1462 (m), 1359 (m), 1135 (m), 1089 (s), 978 (m), 880 (s), 784 (m) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{16}H_{33}O_4Si$ 317.2143, found 317.2128.



2k

1-((4*R,5*R**)-5-Phenyl-1,3-dioxolan-4-yl)propan-2-one (2k)**

Color and state: Colorless oil.

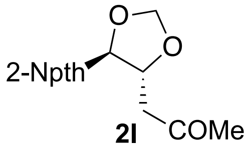
FC (silica gel, eluting with 1:3 to 1:2 diethyl ether/pentane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.32 (m, 5H), 5.29 (s, 1H), 5.20 (s, 1H), 4.54 (d, A of AM, J_{AM} = 7.1 Hz, 1H), 4.21 (ddd, M of AMXY, J_{AM} = 8.4 Hz, J_{MX} = 7.3 Hz, J_{MY} = 3.8 Hz, 1H), 2.83 (dd, A of ABX, J_{AB} = 16.4 Hz, J_{AX} = 8.6 Hz, 1H), 2.70 (dd, B of ABX, J_{AB} = 16.4 Hz, J_{BX} = 3.7 Hz, 1H), 2.20 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 205.88 (e), 137.77 (e), 128.87 (o), 128.69 (o), 126.61 (o), 95.73 (e), 82.77 (o), 79.31 (o), 45.27 (e), 30.83 (o).

IR (neat) 2918 (w), 2853 (w), 1713 (s), 1495 (w), 1456 (w), 1358 (m), 1162 (m), 1089 (s), 994 (s), 951 (s), 758 (s), 700 (vs) cm^{-1}.

HRMS (CI, $[M+NH_4]^+$) calcd for $C_{12}H_{18}NO_3$ 224.1287, found 224.1290.



2l

1-((4*R,5*R**)-5-(Naphthalen-2-yl)-1,3-dioxolan-4-yl)propan-2-one (2l)**

Color and state: Colorless oil.

FC (silica gel, eluting with 1:2.5 to 1:2 diethyl ether pentane).

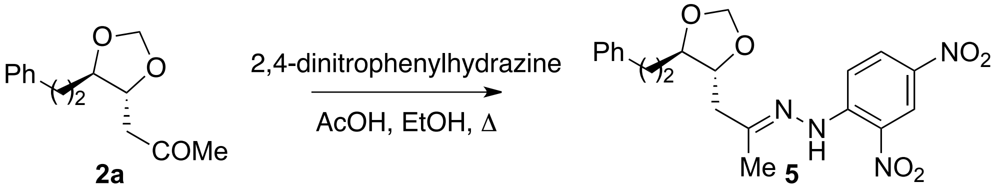
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.89-7.82 (m, 4H), 7.52-7.49 (m, 3H), 5.37 (s, 1H), 5.26 (s, 1H), 4.72 (d, A of AM, J_{AM} = 7.1 Hz, 1H), 4.32 (ddd, M of AMXY, J_{AM} = 8.2 Hz, J_{MX} = 7.4 Hz, J_{MY} = 3.6 Hz, 1H), 2.89 (dd, A of ABX, J_{AB} = 16.4 Hz, J_{AX} = 8.6 Hz, 1H), 2.75 (dd, B of ABX, J_{AB} = 16.4 Hz, J_{BX} = 3.6 Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 205.87 (e), 135.15 (e), 133.51 (e), 133.25 (e), 128.92 (o), 128.05 (o), 127.90 (o), 126.56 (o), 126.46 (o), 126.02 (o), 124.01 (o), 95.86 (e), 82.93 (o), 79.19 (o), 45.31 (e) 30.84 (o).

IR (neat) 3056 (w), 2856 (w), 1713 (s), 1602 (w), 1508 (w), 1357 (m), 1163 (m), 1087 (s), 961 (m), 860 (m), 820 (s), 749 (m) cm^{-1}.

HRMS (CI, $[M+NH_4]^+$) calcd for $C_{16}H_{20}NO_3$ 274.1443, found 274.1440.

4. Preparation of hydrazone 5

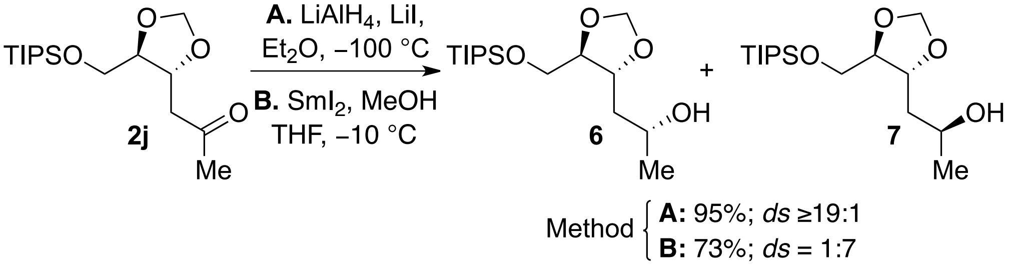


2a → 5

(*E*)-1-(2,4-Dinitrophenyl)-2-(1-((4*R,5*R**)-5-phenethyl-1,3-dioxolan-4-yl)propan-2-ylidene)hydrazine (5).** Acetic acid (2 drops) was added to a stirred solution of the 1,3-dioxolane **2a** (0.0512 g, 0.219 mmol) and (2,4-dinitrophenyl)hydrazine (0.087 g, 0.437 mmol) in ethanol (1 ml). The reaction mixture was then heated at reflux for *ca.* 6 hours (t.l.c. control), cooled to ambient temperature and concentrated *in vacuo* to afford the crude hydrazone. Purification by flush chromatography (silica gel, eluting with 1:200 diethyl ether/dichloromethane) afforded the *hydrazone* **5** (0.023 g, 25% yield) as yellow solid: **^{1}H NMR**

(500 MHz, $CDCl_3$) δ 11.05 (br. s, 1H), 9.13 (d, J = 2.6 Hz, 1H), 8.28 (dd, J = 9.5, 2.6 Hz, 1H), 7.88 (d, J = 9.6 Hz, 1H), 7.29-7.26 (m, 2H), 7.20-7.17 (m, 3H), 5.06 (s, 1H), 5.05 (s, 1H), 3.99 (ddd, A of AMXY, J_{AX} = 7.1 Hz, J_{AM} = 6.2 Hz, J_{AY} = 5.1 Hz, 1H), 3.73 (ddd, M of AMXY, J_{MX} = 8.9 Hz, J_{AM} = 6.1 Hz, J_{MY} = 3.8 Hz, 1H), 2.89 (ddd, A of ABXY, J_{AB} = 14.1 Hz, J_{AX} = 9.3 Hz, J_{AY} = 5.0 Hz, 1H), 2.74 (ddd, B of ABXY, J_{AB} = 14.0 Hz, J_{BX} = 9.2 Hz, J_{BY} = 7.3 Hz, 1H), 2.67 (dd, A of ABX, J_{AB} = 10.6 Hz, J_{AX} = 7.3 Hz, 1H), 2.63 (dd, B of ABX, J_{AB} = 15.0 Hz, J_{BX} = 5.0 Hz, 1H), 2.11 (s, 3H), 1.98 (dt, A of ABX_2, J_{AB} = 9.4 Hz, J_{AX} = 4.8 Hz, 1H), 1.91 (ddd, B of ABXY, J_{AB} = 9.8 Hz, J_{BX} = 7.2 Hz, J_{BY} = 3.9 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.82 (e), 145.16 (e), 141.29 (e), 138.10 (e), 130.16 (o), 129.40 (e), 128.64 (o), 128.50 (o), 126.26 (o), 123.59 (o), 116.57 (o), 94.40 (e), 80.33 (o), 78.53 (o), 41.97 (e), 34.24 (e), 32.27 (e), 16.78 (o); **IR** (neat) 3322 (w), 3105 (w), 3026 (w), 2923 (w), 2857 (w), 1616 (s), 1591 (s), 1498 (s), 1330 (s), 1310 (s), 1135 (m), 1084 (s), 978 (m), 832 (s), 743 (s), 700 (s) cm^{-1}; **HRMS** (ESI, $[M+H]^+$) calcd for $C_{20}H_{23}N_4O_6$ 415.1612, found 415.1622.

5. Stereodivergent 1,3-reduction of 1-((4*R**,5*R**)-5-(((triisopropylsilyl)oxy)methyl)-1,3-dioxolan-4-yl)propan-2-one (2j) – s*yn*- and *anti*-1,3-diol derivatives 6 and 7

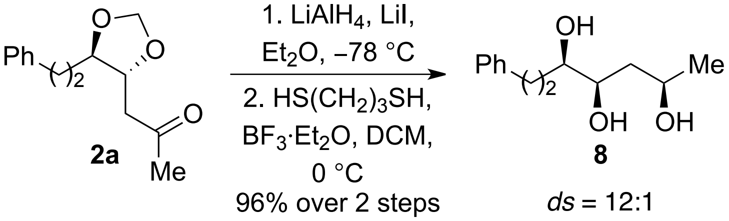


Method A: (*R*)-1-((4*R,5*R**)-5-(((Triisopropylsilyl)oxy)methyl)-1,3-dioxolan-4-yl)propan-2-ol (6).** Lithium iodide (0.169 g, 1.262 mmol) was added to a stirred solution of the 1,3-dioxolane **2j** (0.160 g, 0.505 mmol) in anhydrous diethyl ether (10 ml) at room temperature under an atmosphere of argon. The mixture was then stirred at this temperature for *ca.* 10 minutes before being cooled to −100 °C. $LiAlH_4$ (42.8 mg, 1.262 mmol) was added and the resulting mixture stirred at this temperature for *ca.* 2 hours (t.l.c. control). The reaction was then quenched with saturated aqueous NH_4Cl solution and partitioned between water and diethyl ether. The combined organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford the crude product. Purification by flash chromatography (silica gel, eluting with 1:2

diethyl ether/pentane) afforded the *syn-1,3-diol derivative* **6** (153 mg, 95% yield) as a colorless oil: *ds* ≥19:1; **^{1}H NMR** (500 MHz, CDCl$_3$) δ 5.03 (s, 1H), 4.96 (s, 1H), 4.07 (dd, A of ABX, J_{AB} = 8.3 Hz, J_{AX} = 5.3 Hz, 1H), 4.06 (dd, B of ABX, J_{AB} = 8.5 Hz, J_{BX} = 6.2 Hz, 1H), 3.90 (dd, A of ABX, J_{AB} = 10.2 Hz, J_{AX} = 4.4 Hz, 1H), 3.75 (dd, B of ABX, J_{AB} = 10.2 Hz, J_{BX} = 6.5 Hz, 1H), 3.69 (dt, M of AMX$_2$, J_{AM} = 6.4 Hz, J_{MX} = 4.6 Hz, 1H), 2.96 (br. s, 1H), 1.79-1.71 (m, 2H), 1.22 (d, J = 6.2 Hz, 3H), 1.15-1.07 (m, 3H), 1.06-1.05 (m, 18H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 94.77 (e), 81.16 (o), 79.28 (o), 67.39 (o), 63.78 (e), 41.79 (e), 23.44 (o), 18.05 (o), 11.98 (o); **IR** (neat) 3450 (br, w), 2940 (m), 2865 (s), 1461 (m), 1382 (w), 1132 (m), 1089 (s) 983 (m), 881 (s), 784 (s), 681 (s) cm^{-1}; **HRMS** (ESI, [M+H]$^+$) calcd for $C_{16}H_{35}O_4Si$ 319.2299, found 319.2284.

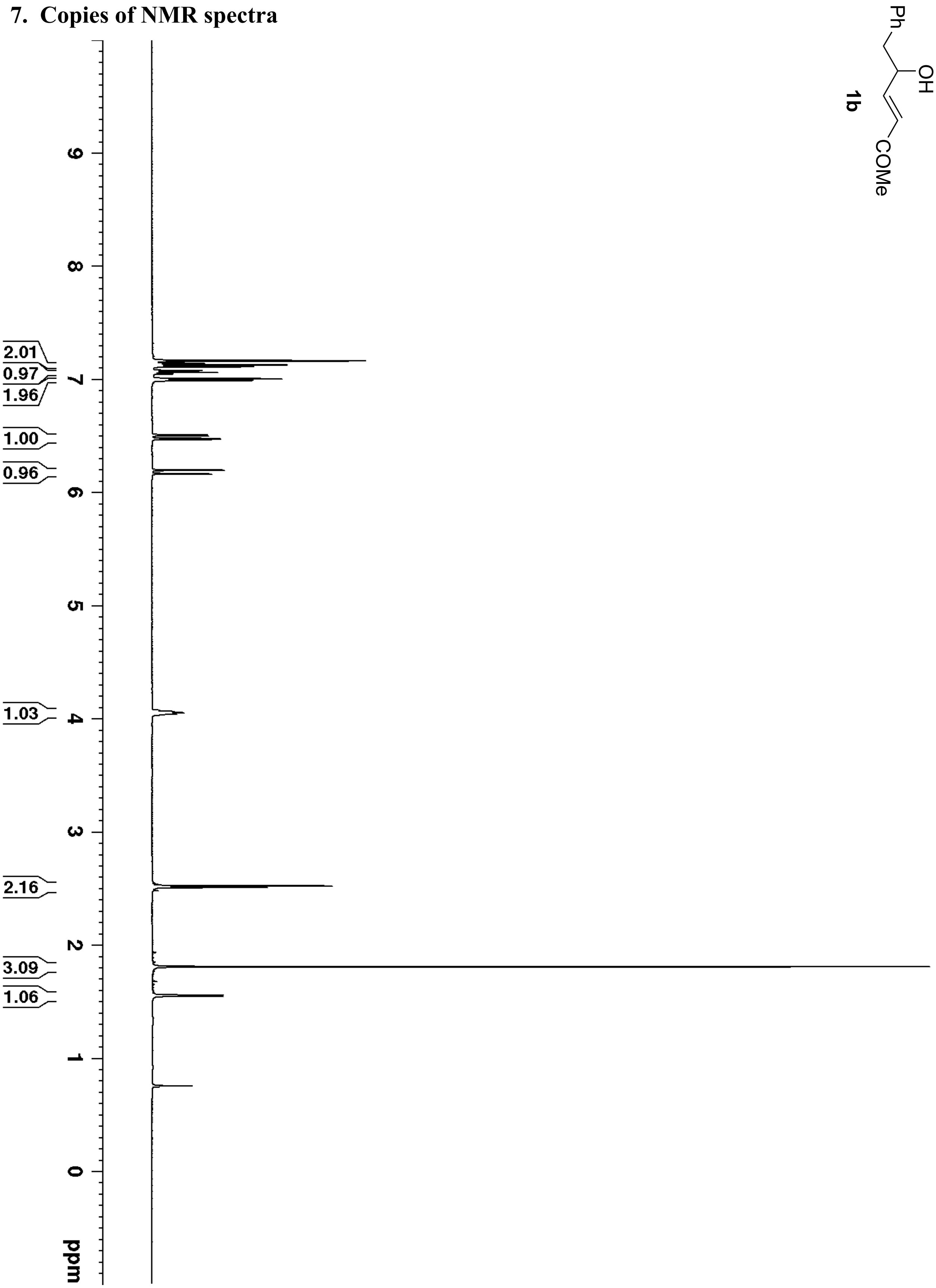
Method B: (*S*)-1-((4*R,5*R**)-5-(((Triisopropylsilyl)oxy)methyl)-1,3-dioxolan-4-yl)propan-2-ol (7).** Samarium(II) iodide (4.1 ml, 0.41 mmol, 0.1 M in THF) was cooled with stirring to –10 °C under an atmosphere of argon. The 1,3-dioxolane **2j** (42.8 mg, 0.135 mmol) in tetrahydrofuran (0.5 ml) was added dropwise followed by the addition of methanol (109 µl, 2.70 mmol) and the resulting mixture stirred at this temperature for *ca.* 40 hours (t.l.c. control). The reaction was then quenched with saturated aqueous NaCl solution and partitioned between water and diethyl ether. The combined organic phases were washed with saturated aqueous NaCl solution, dried (MgSO$_4$), filtered and concentrated *in vacuo* to afford the crude product. Purification by flash chromatography (silica gel, eluting with 1:2 diethyl/ether pentane) afforded the *anti-1,3-diol derivative* **7** (31.5 mg, 73 % yield) as a colorless oil: *ds* = 7:1; **^{1}H NMR** (500 MHz, CDCl$_3$) δ 5.03 (s, 1H), 4.92 (s, 1H), 4.13 (dd, A of ABX, J_{AB} = 11.7 Hz, J_{AX} = 6.6 Hz, 1H), 4.10-4.05 (m, 1H), 3.92-3.87 (m, 1H), 3.79-3.74 (m, 2H), 2.39 (d, J = 4.5 Hz, 1H), 1.81 (dd, J = 7.3, 4.0 Hz, 1H), 1.80 (dd, J = 7.5, 5.3 Hz, 1H), 1.25 (d, J = 6.3 Hz, 3H), 1.15-1.08 (m, 3H), 1.07-1.05 (m, 18H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 94.66 (e), 80.58 (o), 77.09 (o), 65.44 (o), 63.96 (e), 41.45 (e), 23.77 (o), 18.08 (o), 12.03 (o); **IR** (neat) 3456 (br, w), 2943 (m), 2866 (s), 1463 (m), 1384 (w), 1134 (s), 1090 (s), 984 (s), 882 (s), 785 (s), 682 (s) cm^{-1}; **HRMS** (ESI, [M+H]$^+$) calcd for $C_{16}H_{35}O_4Si$ 319.2299, found 319.2312.

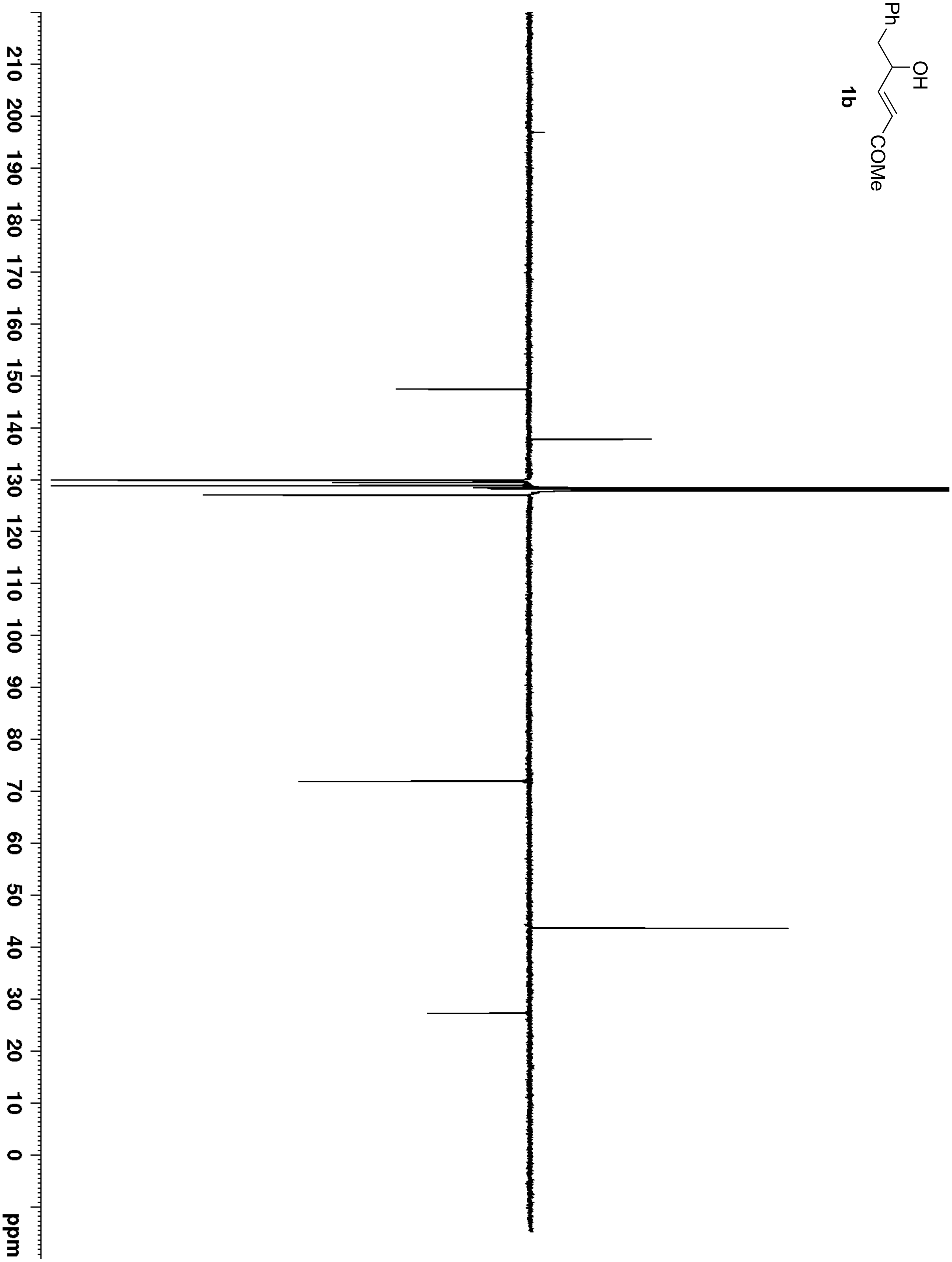
6. Mild deprotection of the 1,3-dioxolane 2a – *syn*,*syn*-1,2,4-triol 8



(2*R,4*R**,5*R**)-7-Phenylheptane-2,4,5-triol (8).** Lithium iodide (0.148 g, 1.104 mmol) was added to a stirred solution of the 1,3-dioxolane **2a** (0.1035 g, 0.442 mmol) in anhydrous diethyl ether (8.8 ml) at room temperature under an atmosphere of argon. The mixture was then stirred at this temperature for *ca.* 10 minutes before being cooled to –78 °C. $LiAlH_4$ (0.042 g, 1.104 mmol) was added and the resulting mixture stirred for *ca.* 2 hours (t.l.c. control). The reaction was then quenched with saturated aqueous NH_4Cl solution and partitioned between water and diethyl ether. The combined organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford the secondary alcohol (0.1017 g, 97% yield), which was used in the next step without purification. 1,3-Propanedithiol (0.068 ml, 0.677 mmol) and $BF_3·Et_2O$ (8.58 µl, 0.068 mmol) were sequentially added to a stirred solution of the crude *syn*-alcohol (0.008 g, 0.034 mmol) in dichloromethane (0.3 ml) at 0 °C. The reaction mixture was then stirred at this temperature for *ca.* 6 hours (t.l.c. control), before being quenched with saturated aqueous NH_4Cl solution and partitioned between water and ethyl acetate. The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to afford the crude triol. Purification by flush chromatography (silica gel, eluting with 1:30 methanol/dichloromethane) furnished the *triol* **8** (0.0075 g, 99% yield) as colorless oil: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.22-7.17 (m, 3H), 4.08 (sextet, J = 6.1 Hz, 1H), 3.71 (dt, M of AMX_2, J_{AM} = 8.2 Hz, J_{MX} = 4.2 Hz, 1H), 3.43 (dt, M of AMX_2, J_{AM} = 6.1 Hz, J_{MX} = 5.1 Hz, 1H), 2.85 (dt, A of ABX_2, J_{AB} = 14.2 Hz, J_{AX} = 7.2 Hz, 1H), 2.73-2.35 (m, 2H), 2.70 (dt, B of ABX_2, J_{AB} = 13.9 Hz, J_{BX} = 8.1 Hz, 1H), 1.81 (dq, J = 7.9, 1.6 Hz, 2H), 1.64-1.54 (m, 2H), 1.26 (br. s, 1H), 1.22 (d, J = 6.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.04 (e), 128.59 (o), 126.06 (o), 75.04 (o), 74.17 (o), 68.65 (o), 41.48 (e), 35.40 (e), 32.11 (e), 24.58 (o). **IR** (neat) 3336 (br, m), 3025 (w), 2921 (m), 2855 (w), 1602 (w), 1494 (w), 1452 (m), 1135 (m), 1050 (s), 932 (m), 746 (m), 698 (s) cm^{-1}. **HRMS** (ESI, $[M+H]^+$) calcd for $C_{13}H_{21}O_3$ 225.1485, found 225.1476.

7. Copies of NMR spectra

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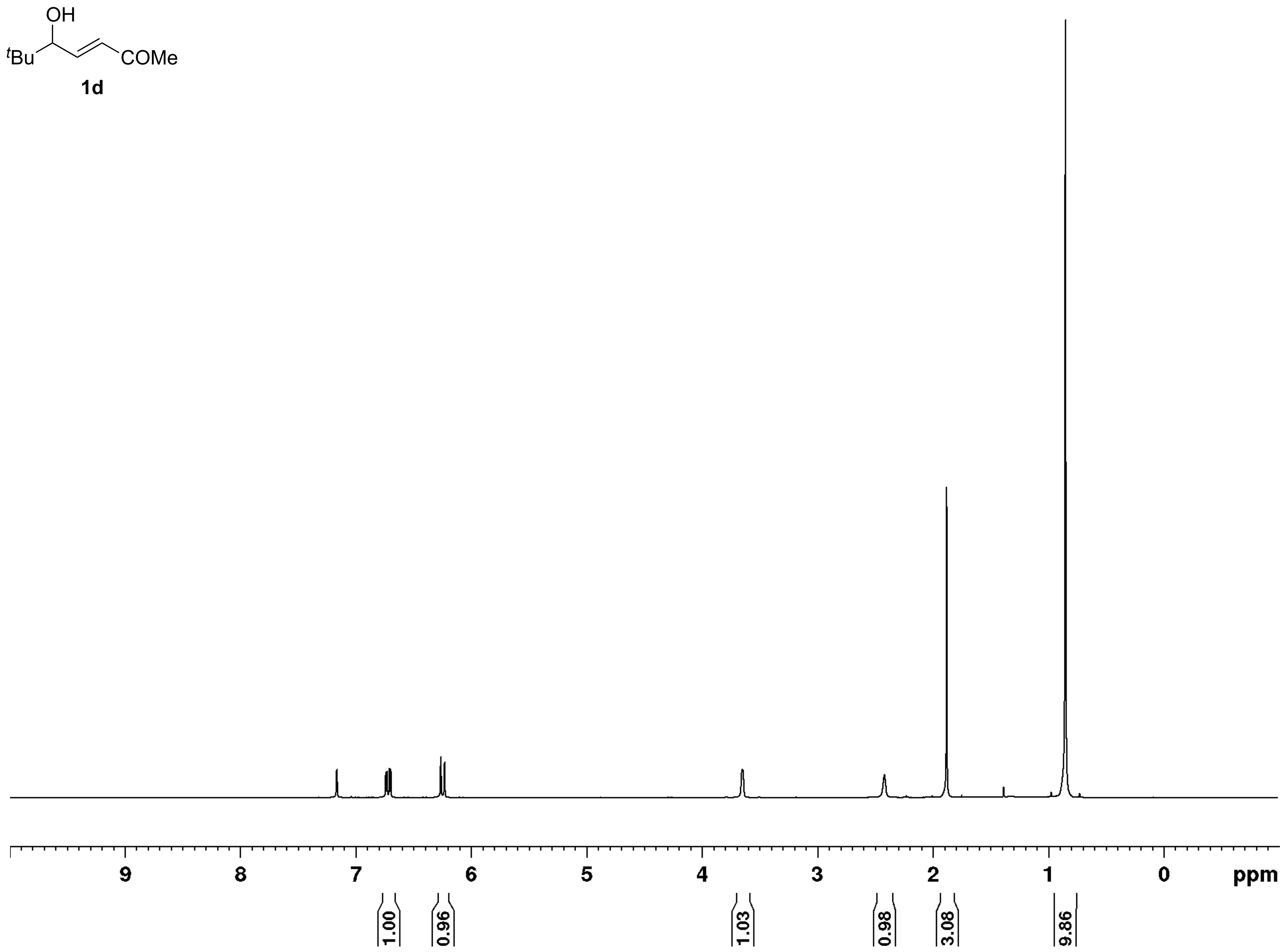

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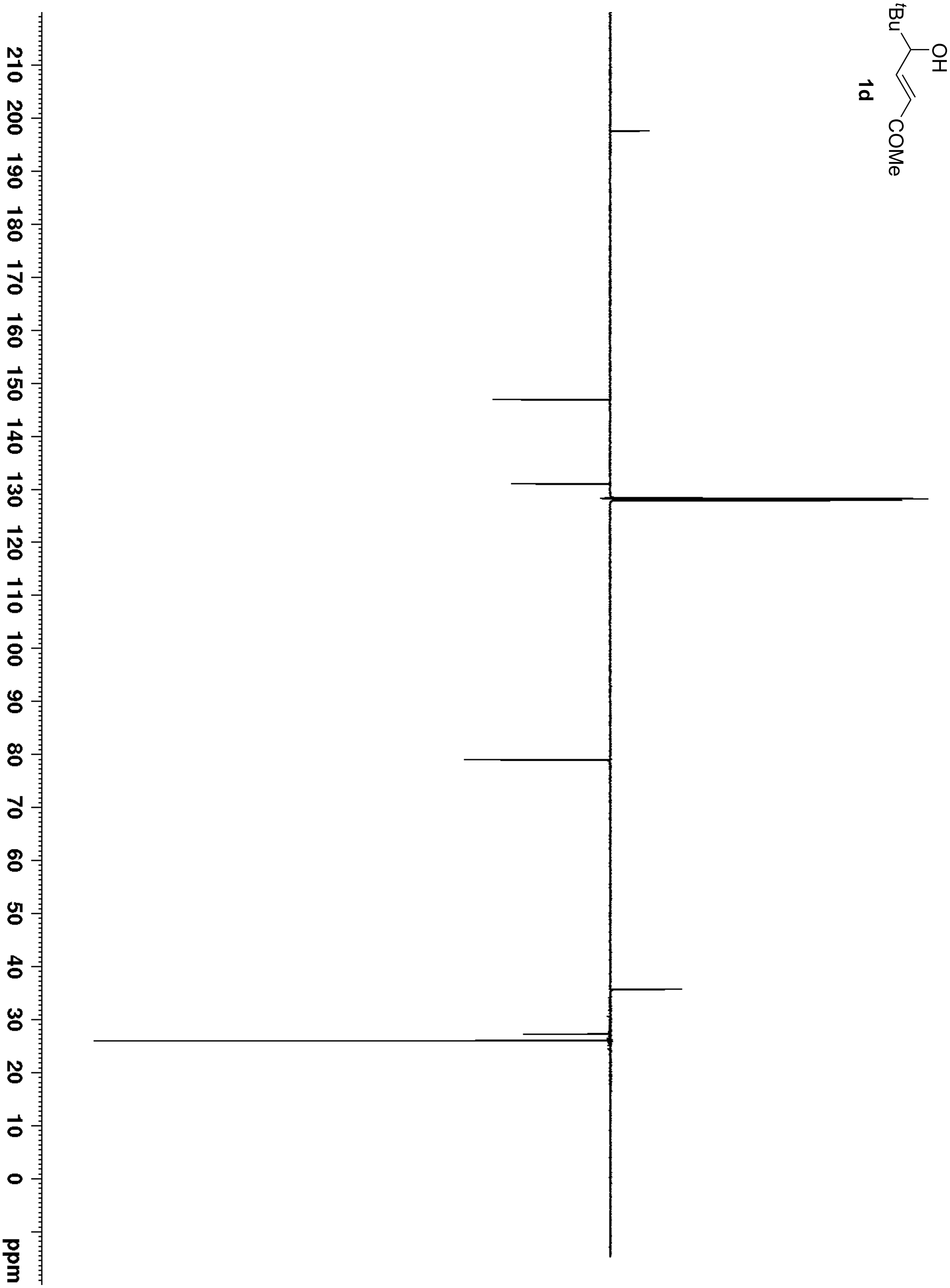
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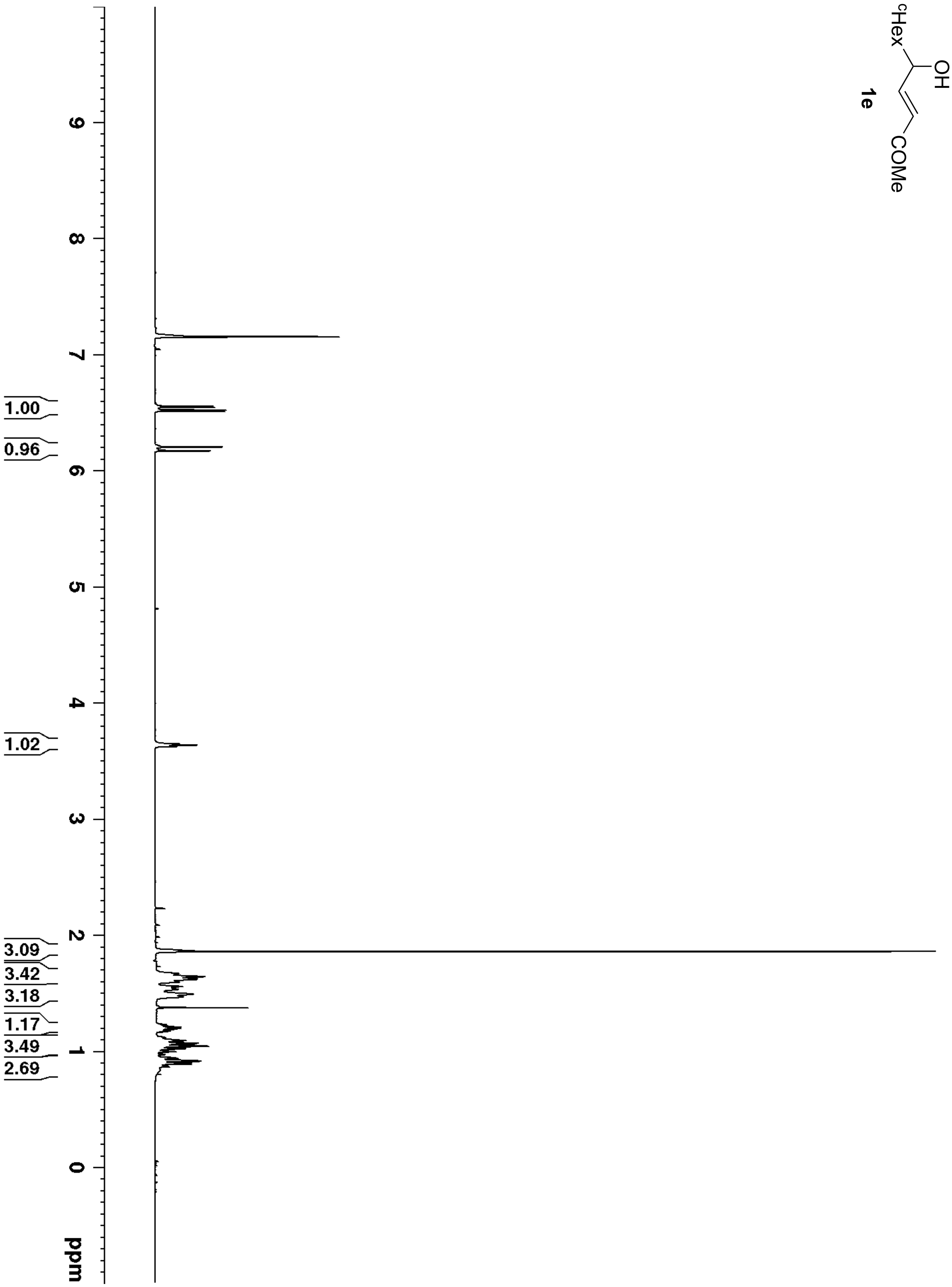

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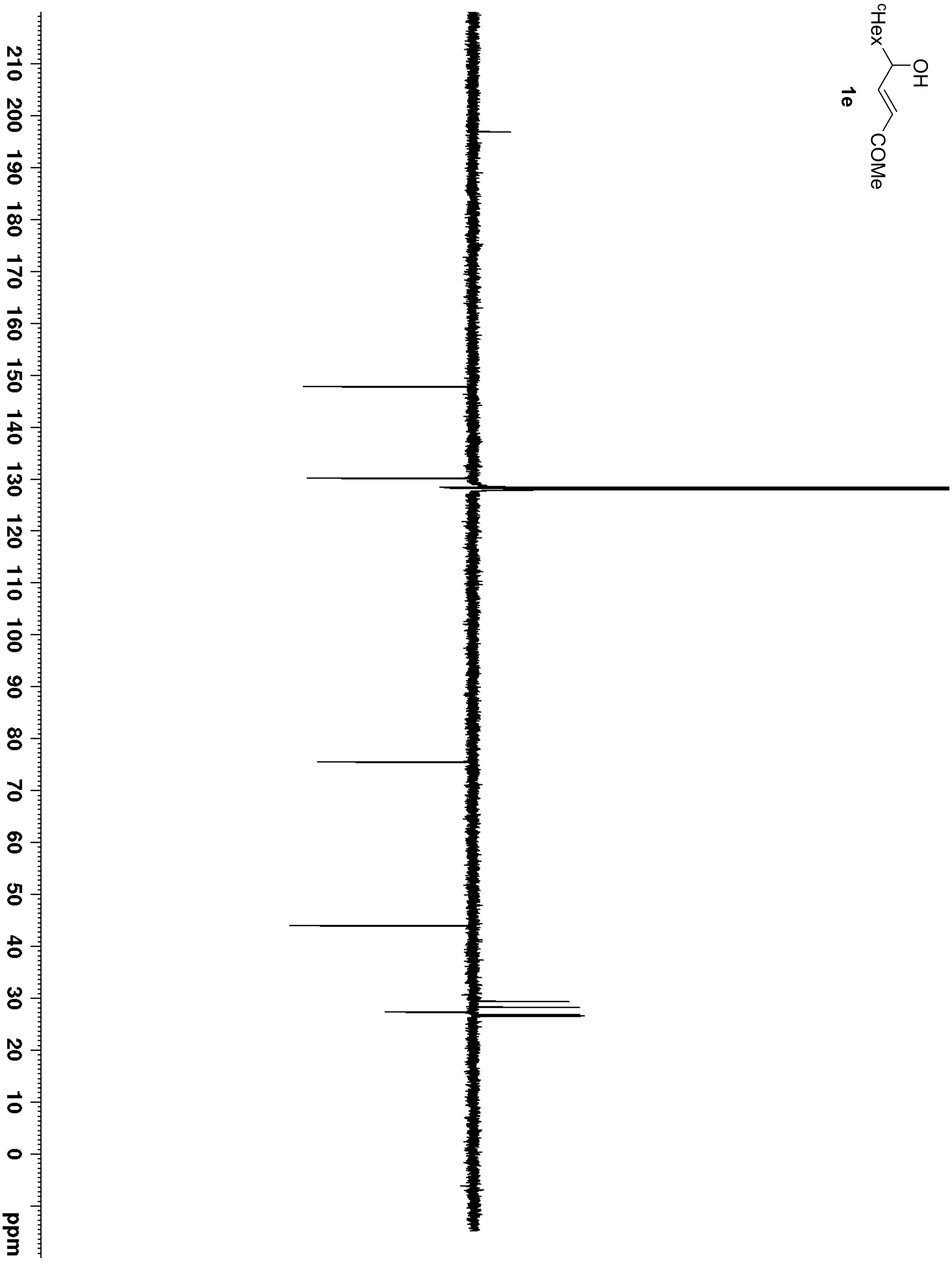

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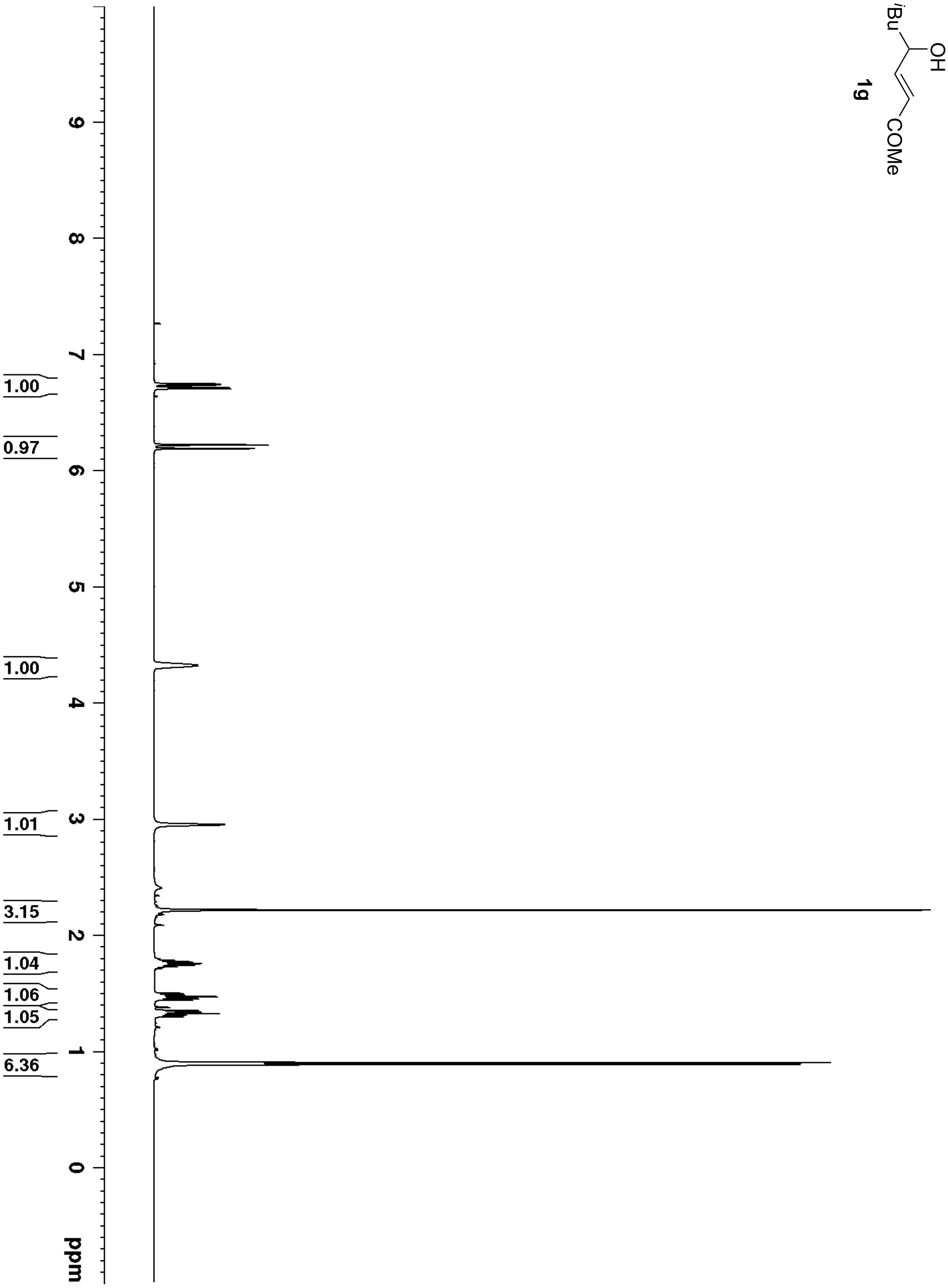

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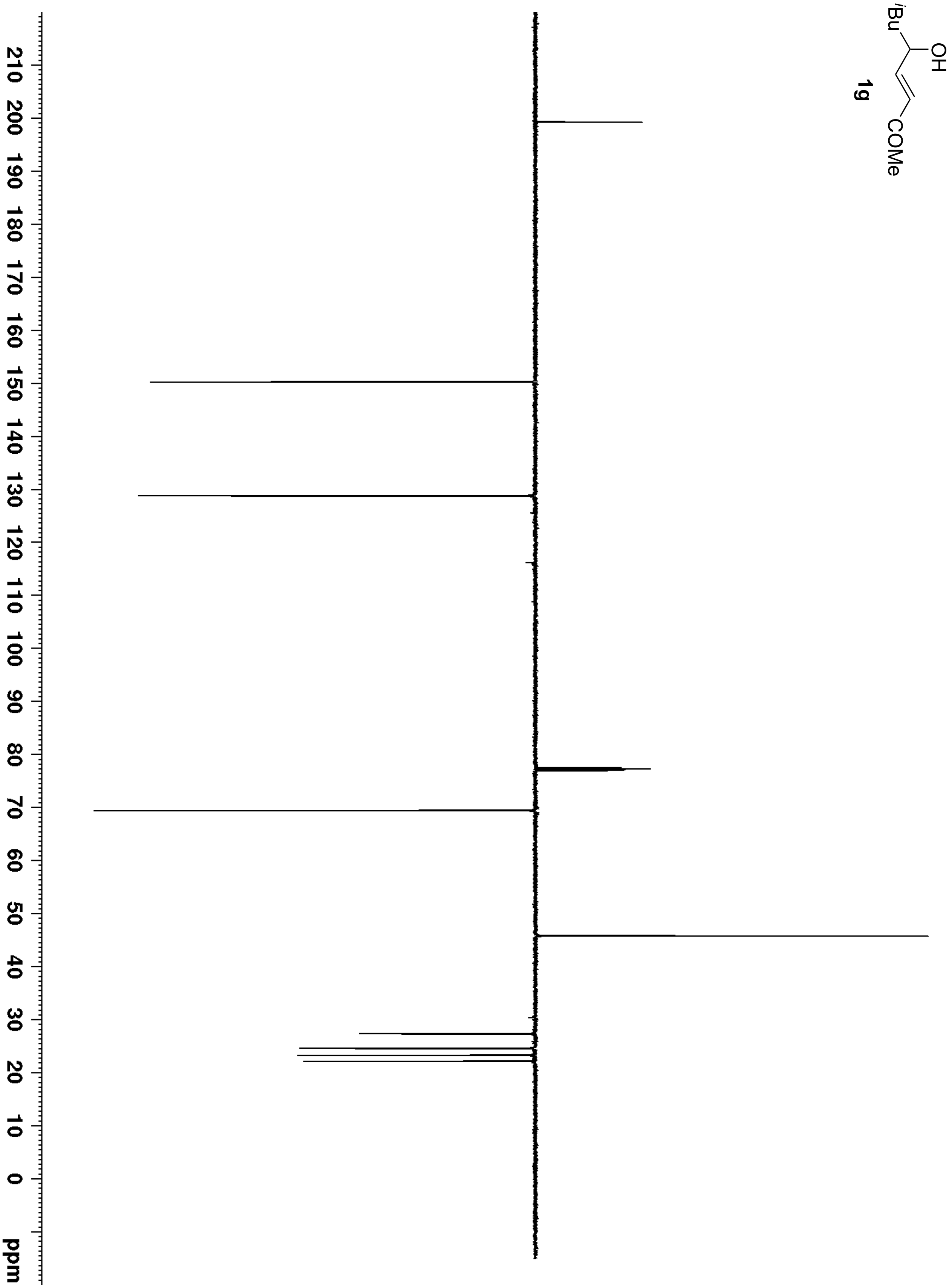
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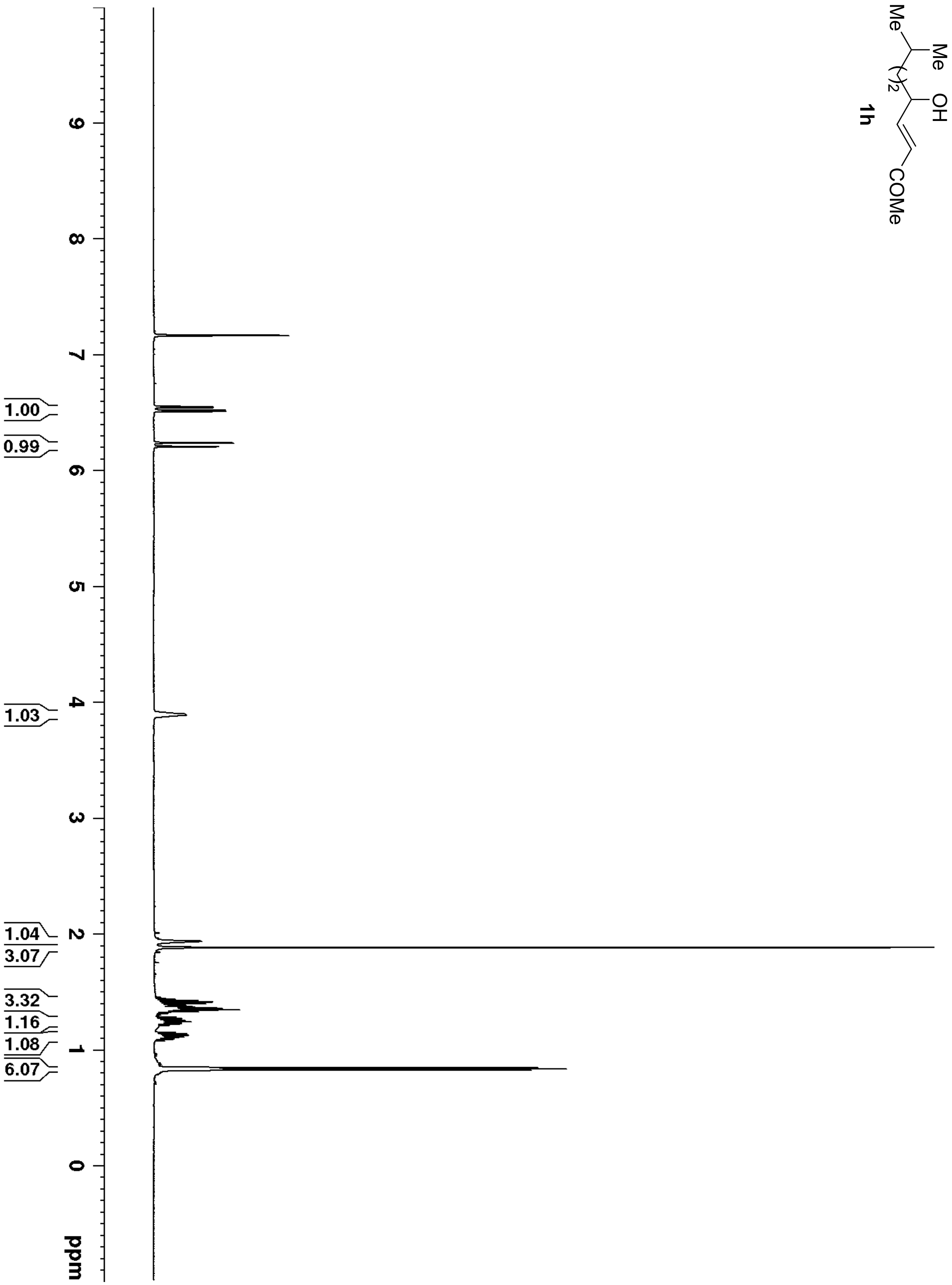
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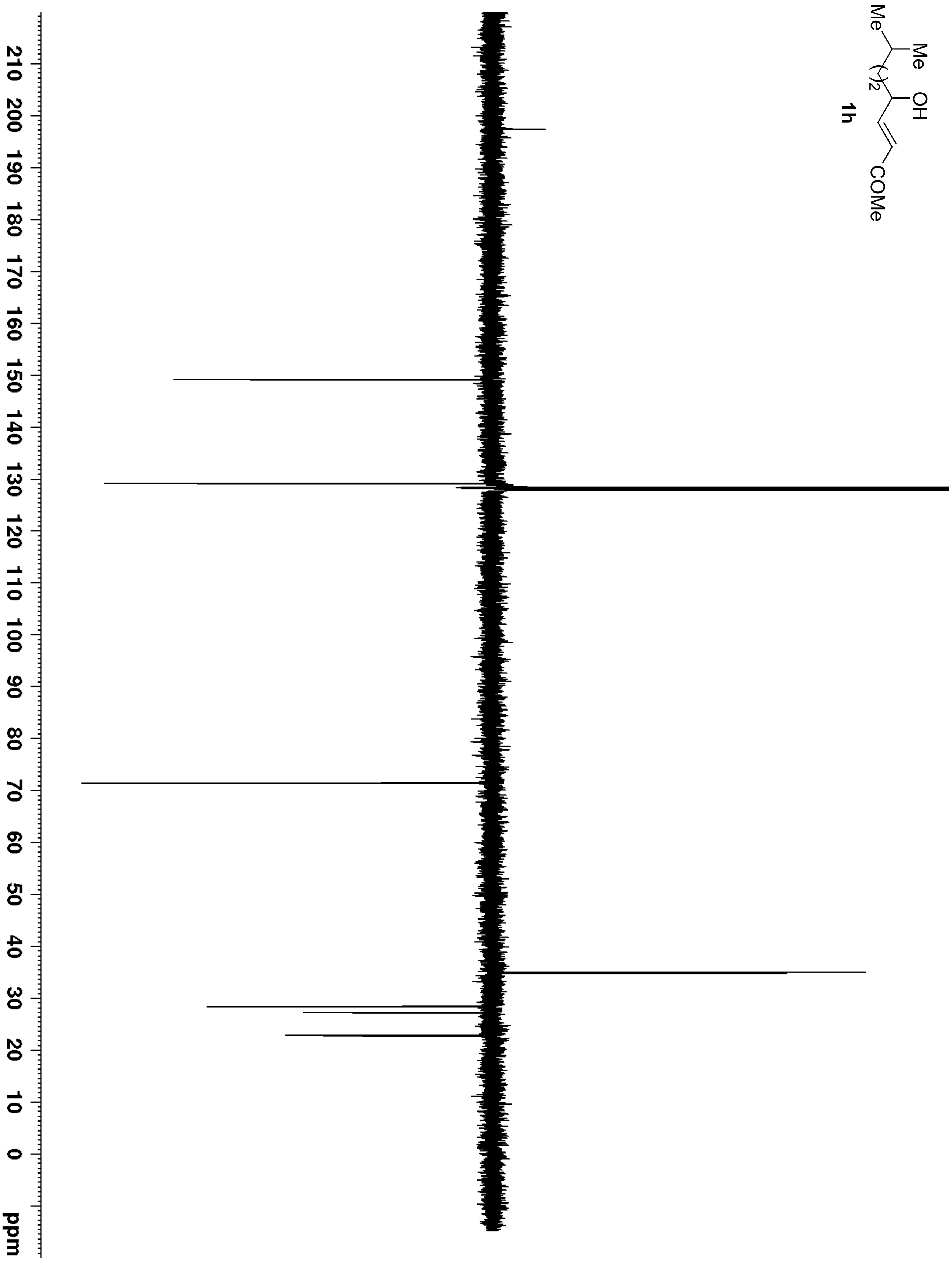

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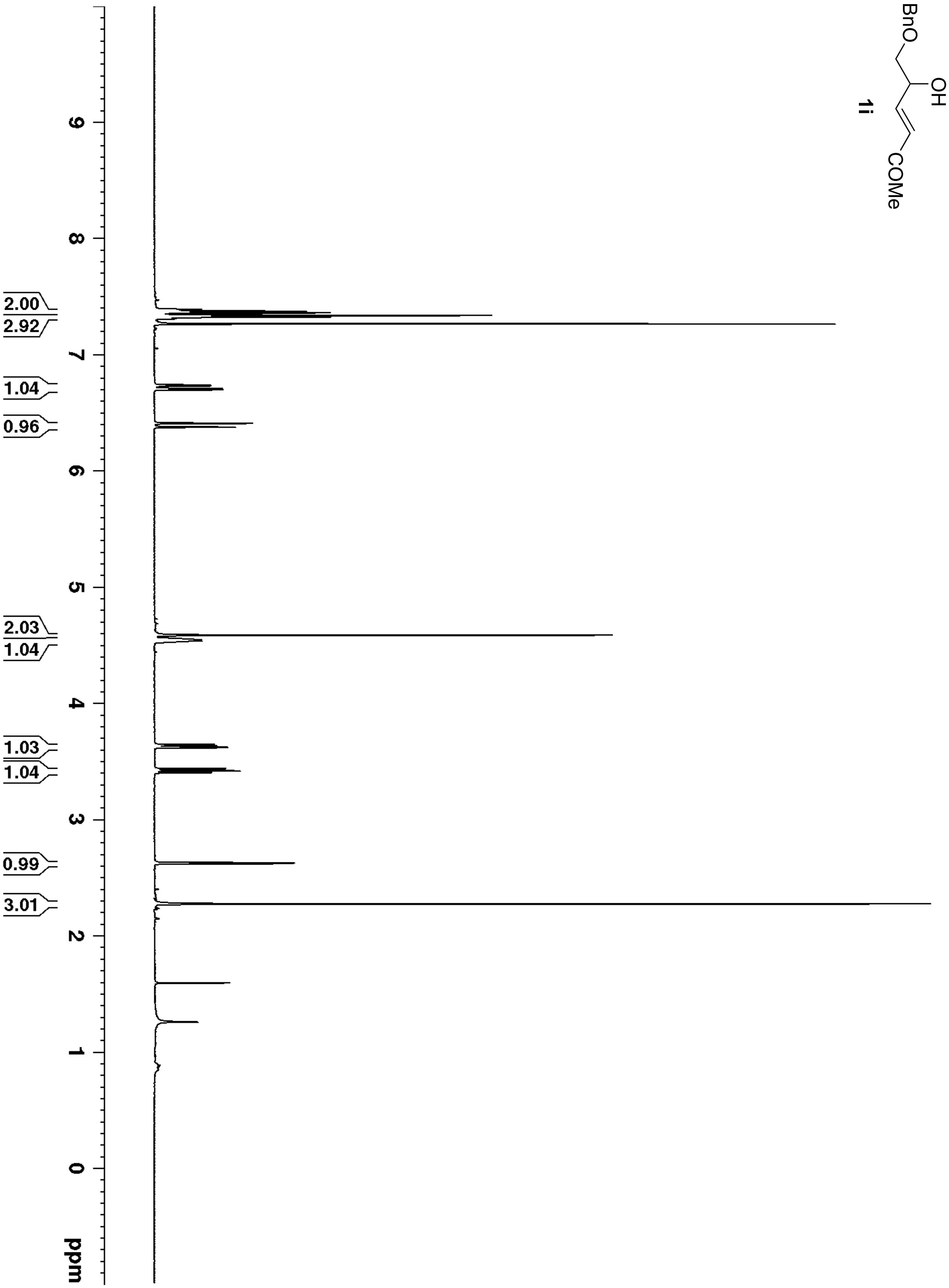

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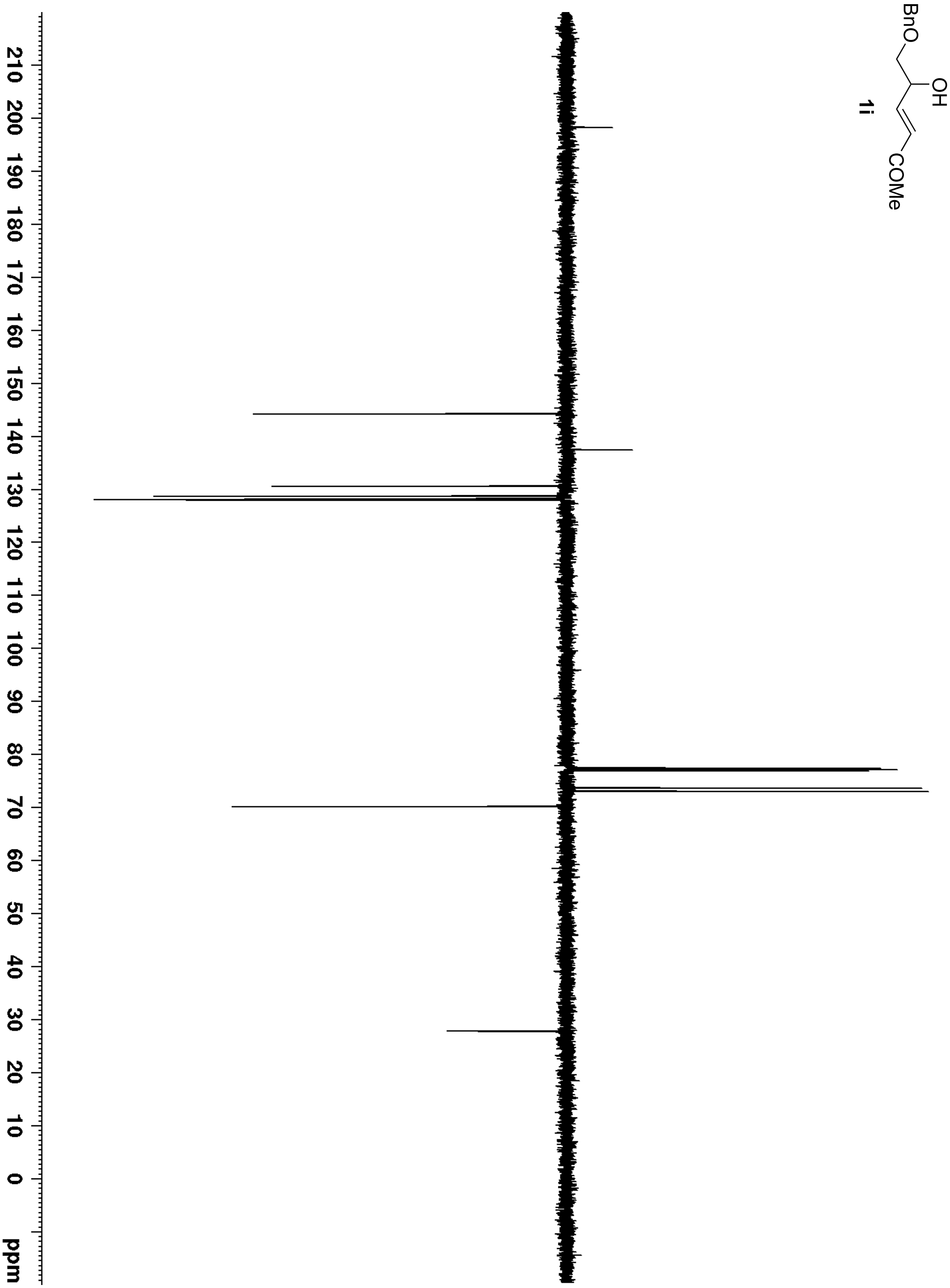
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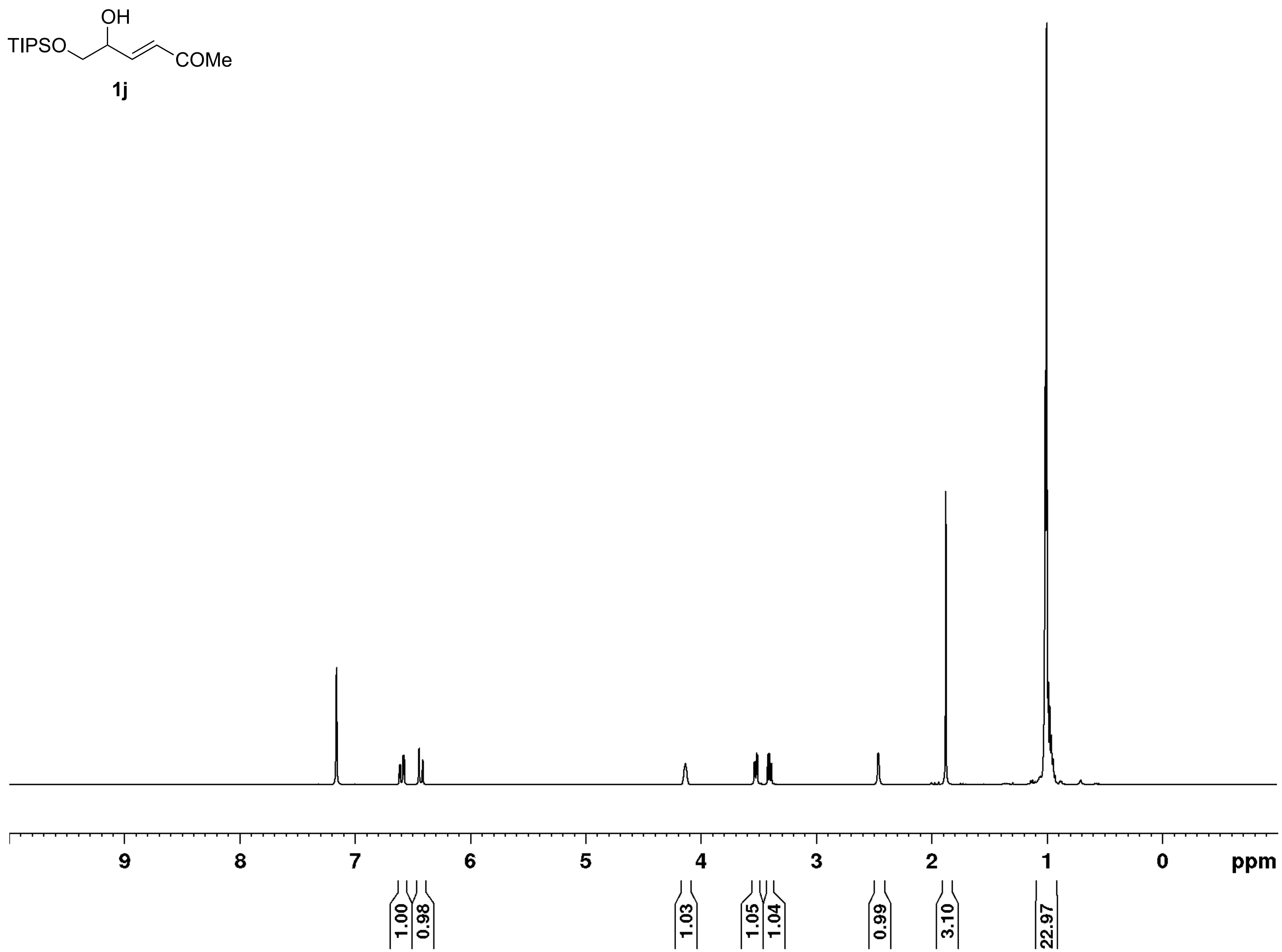

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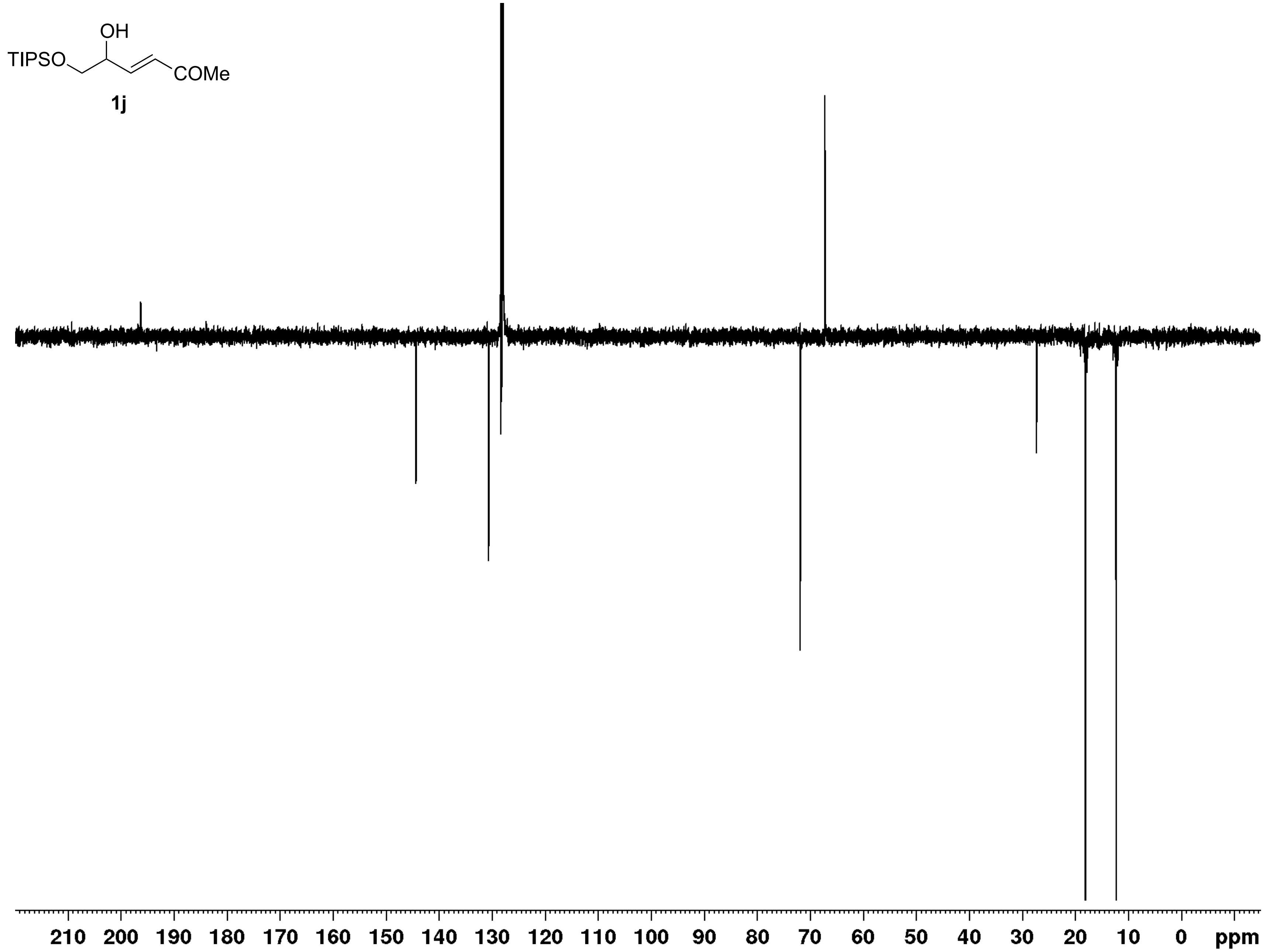

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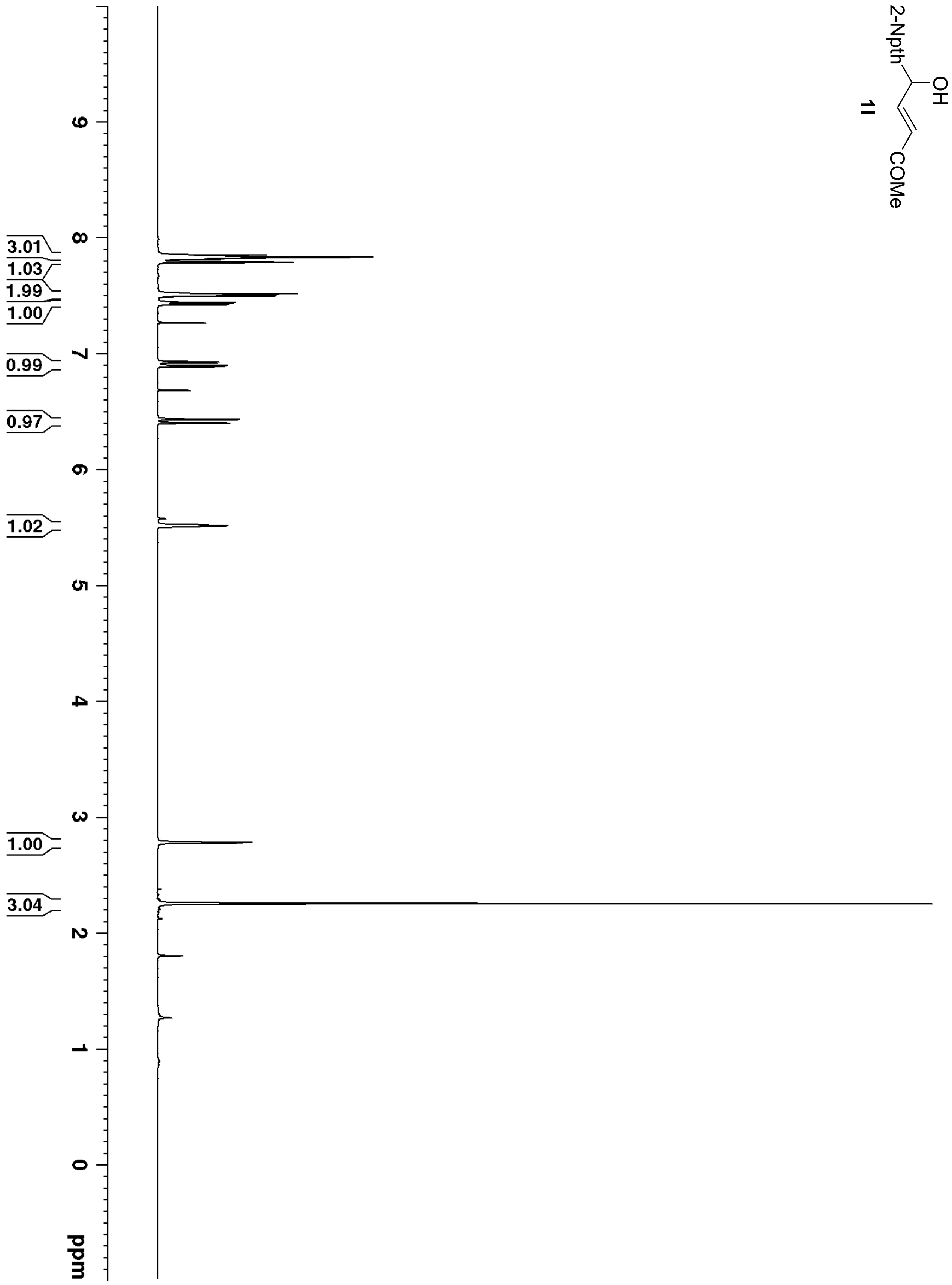

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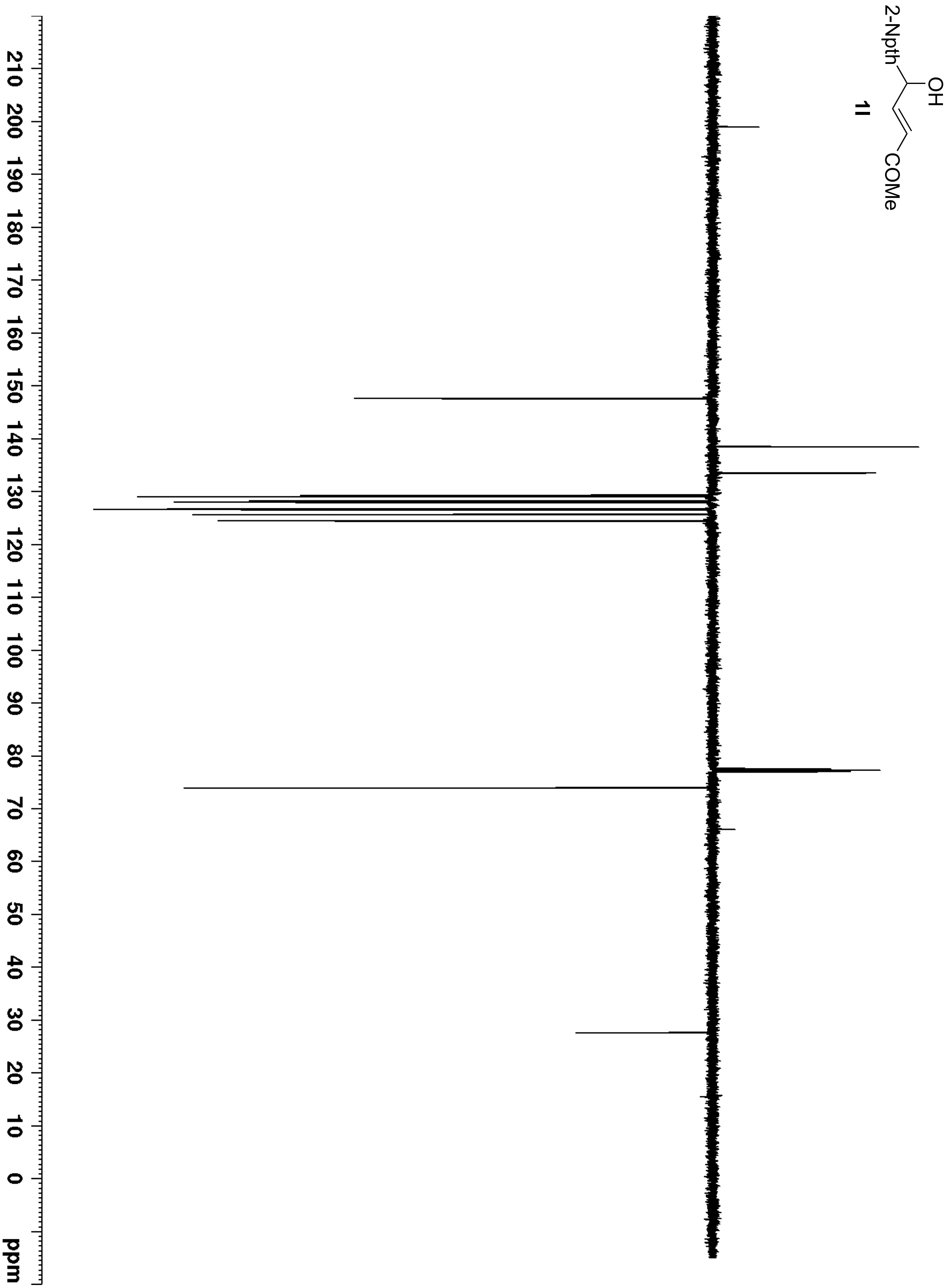
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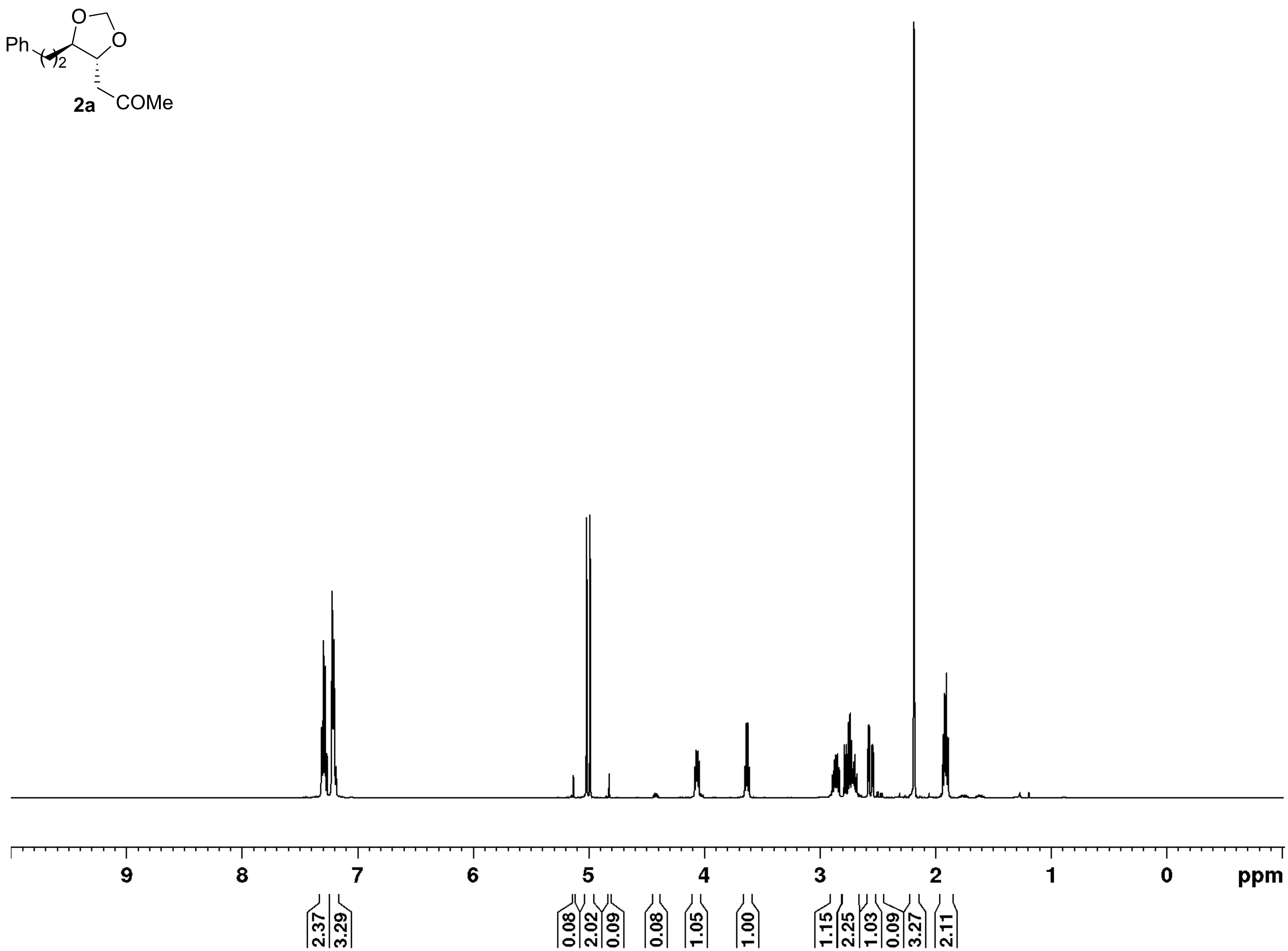
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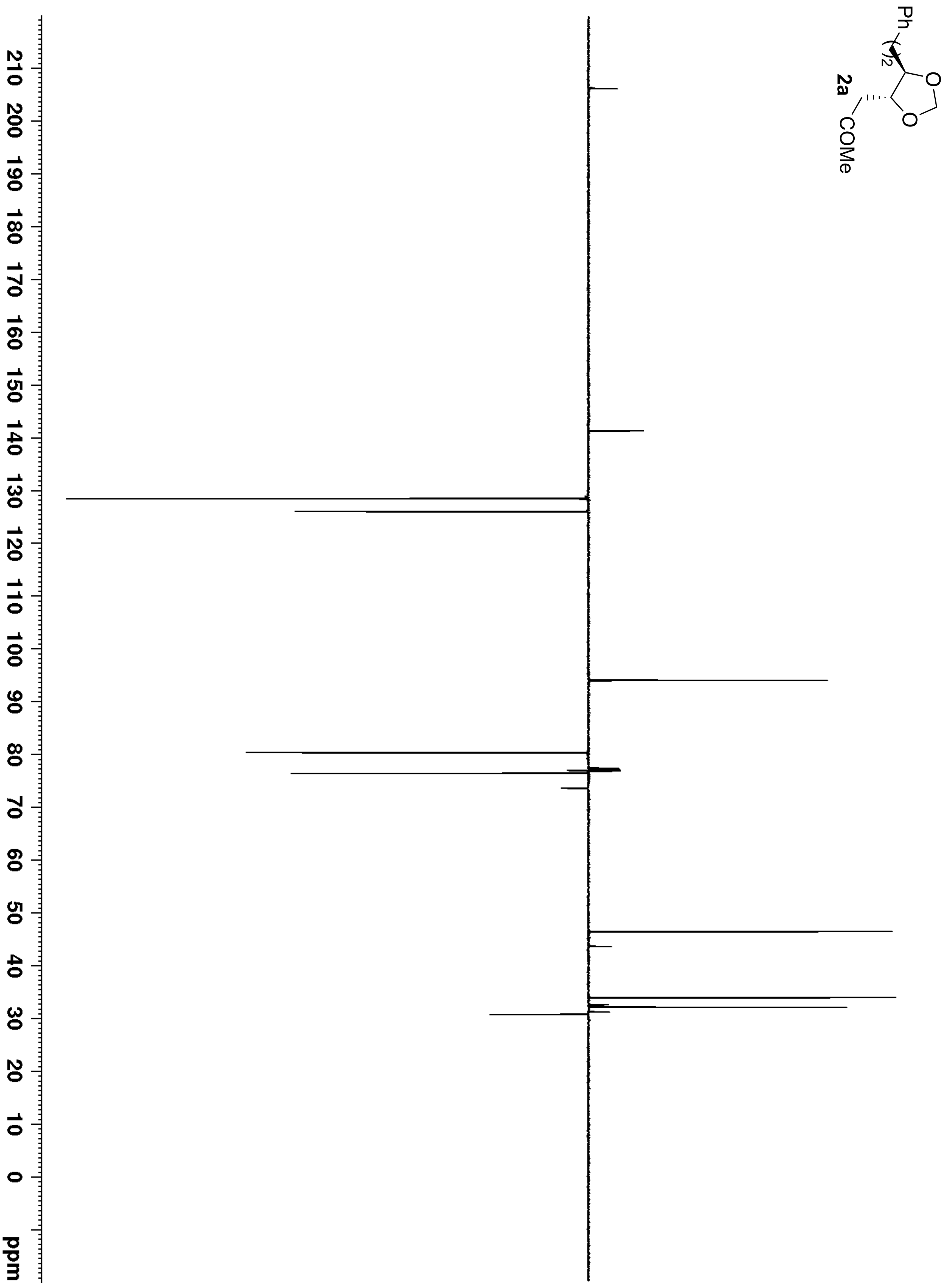

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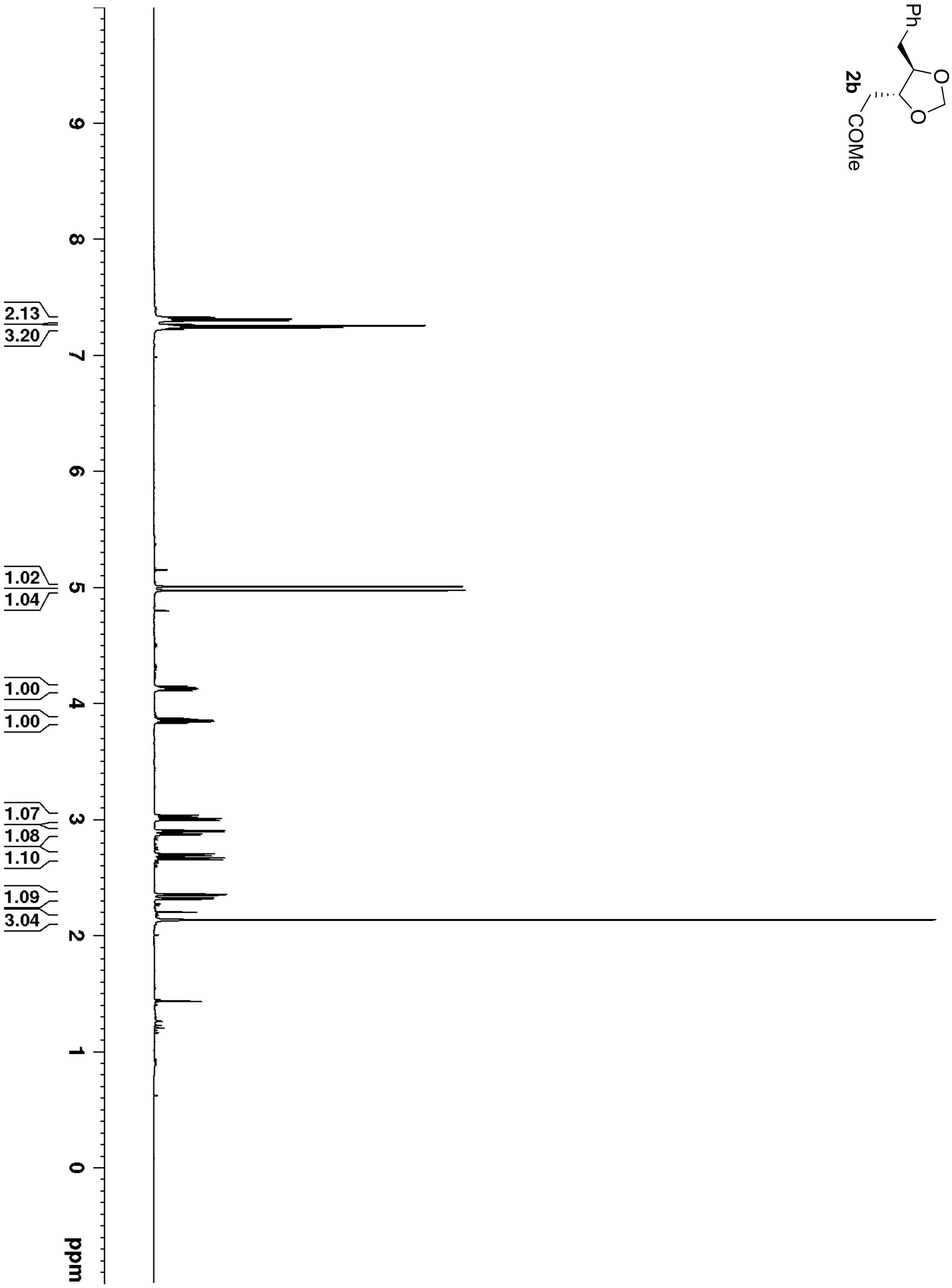

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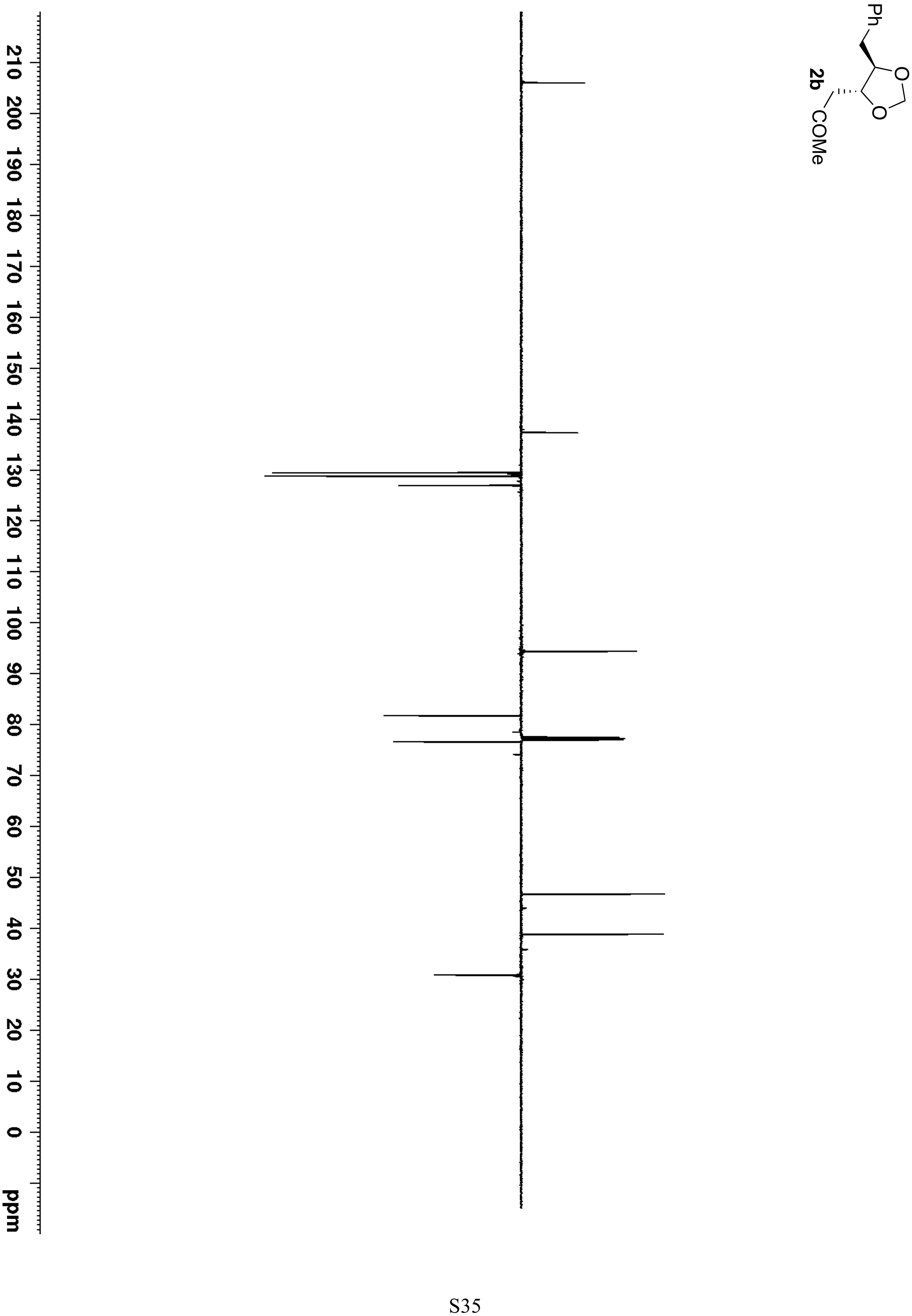
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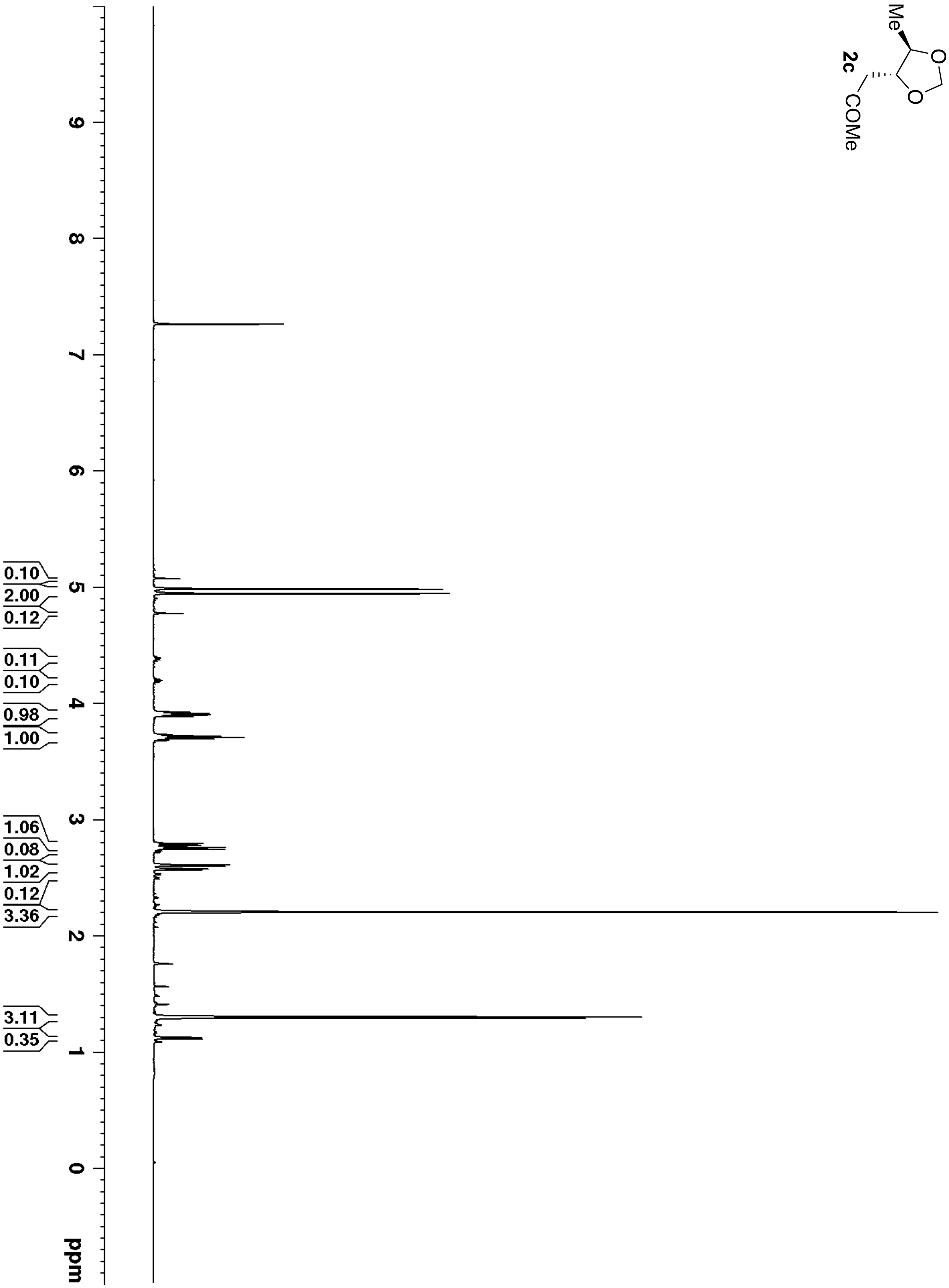
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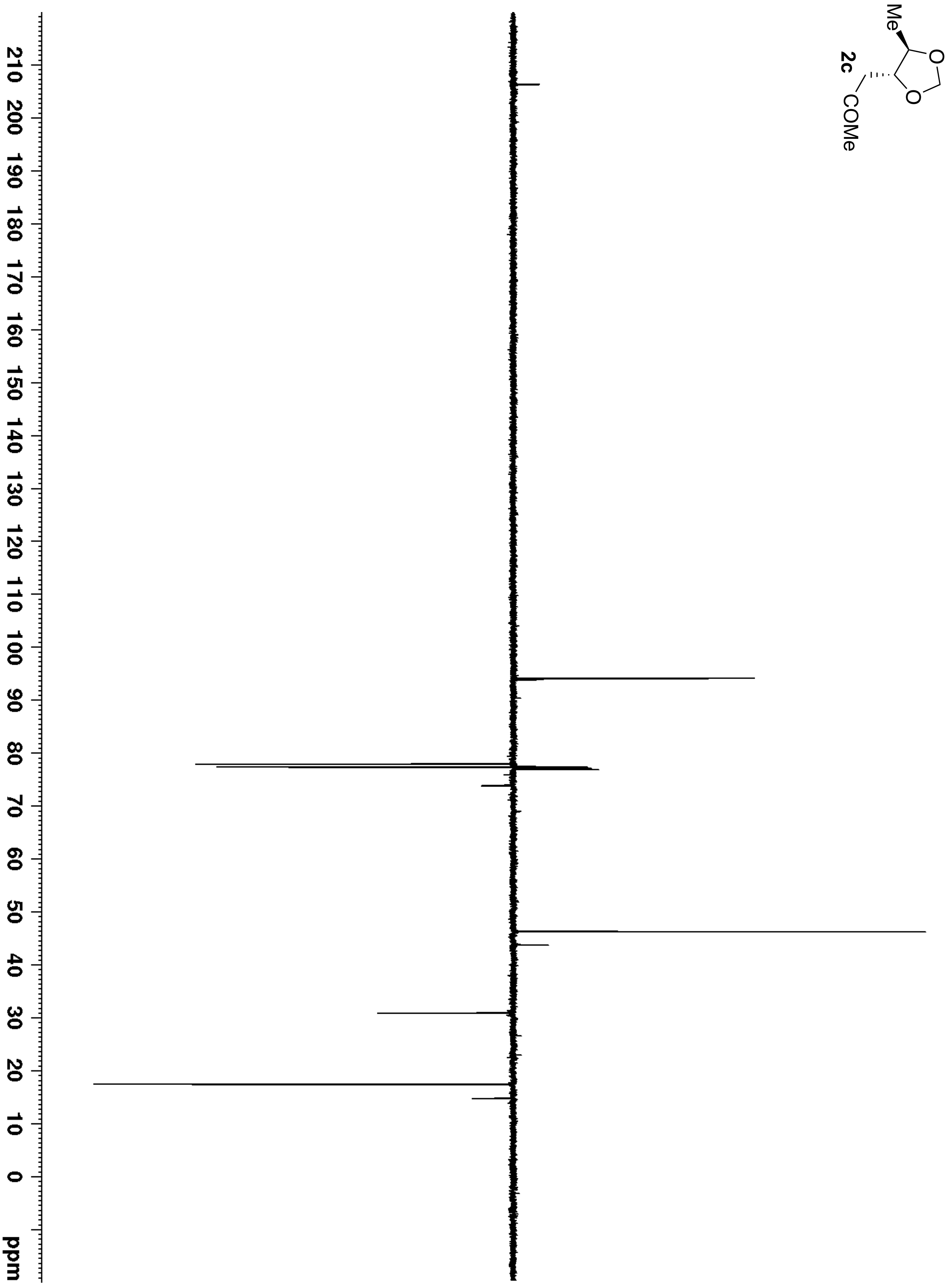
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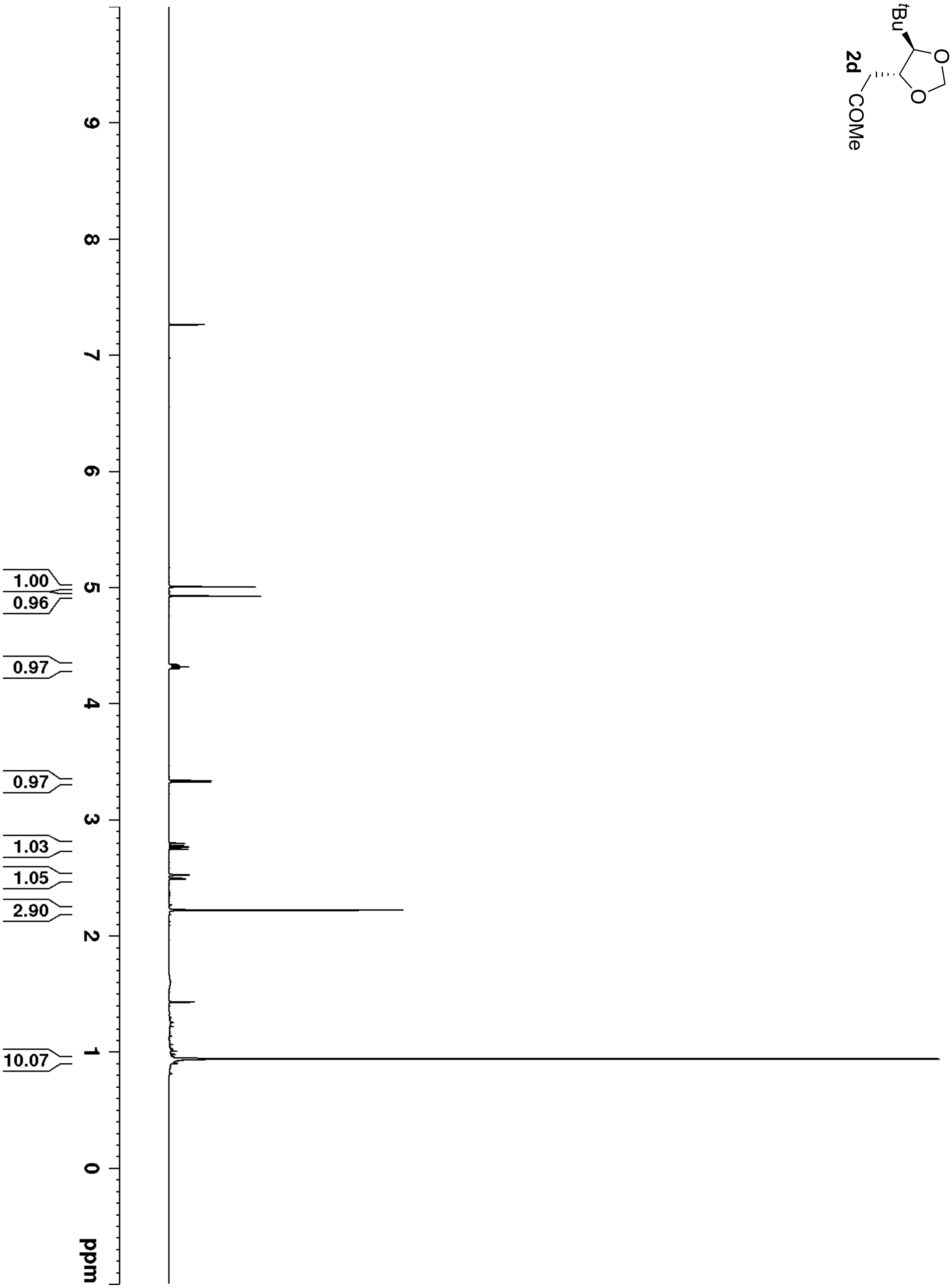

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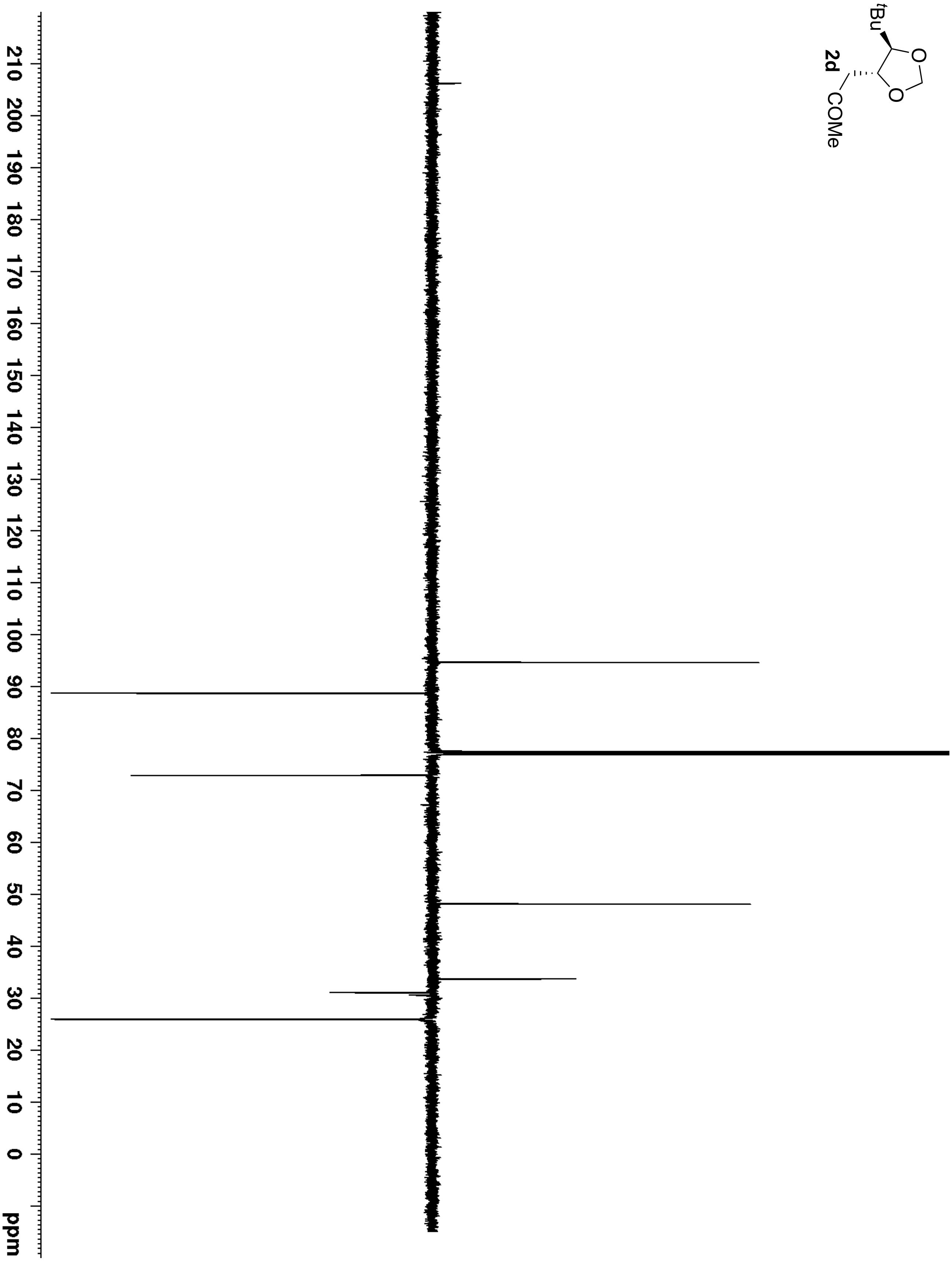

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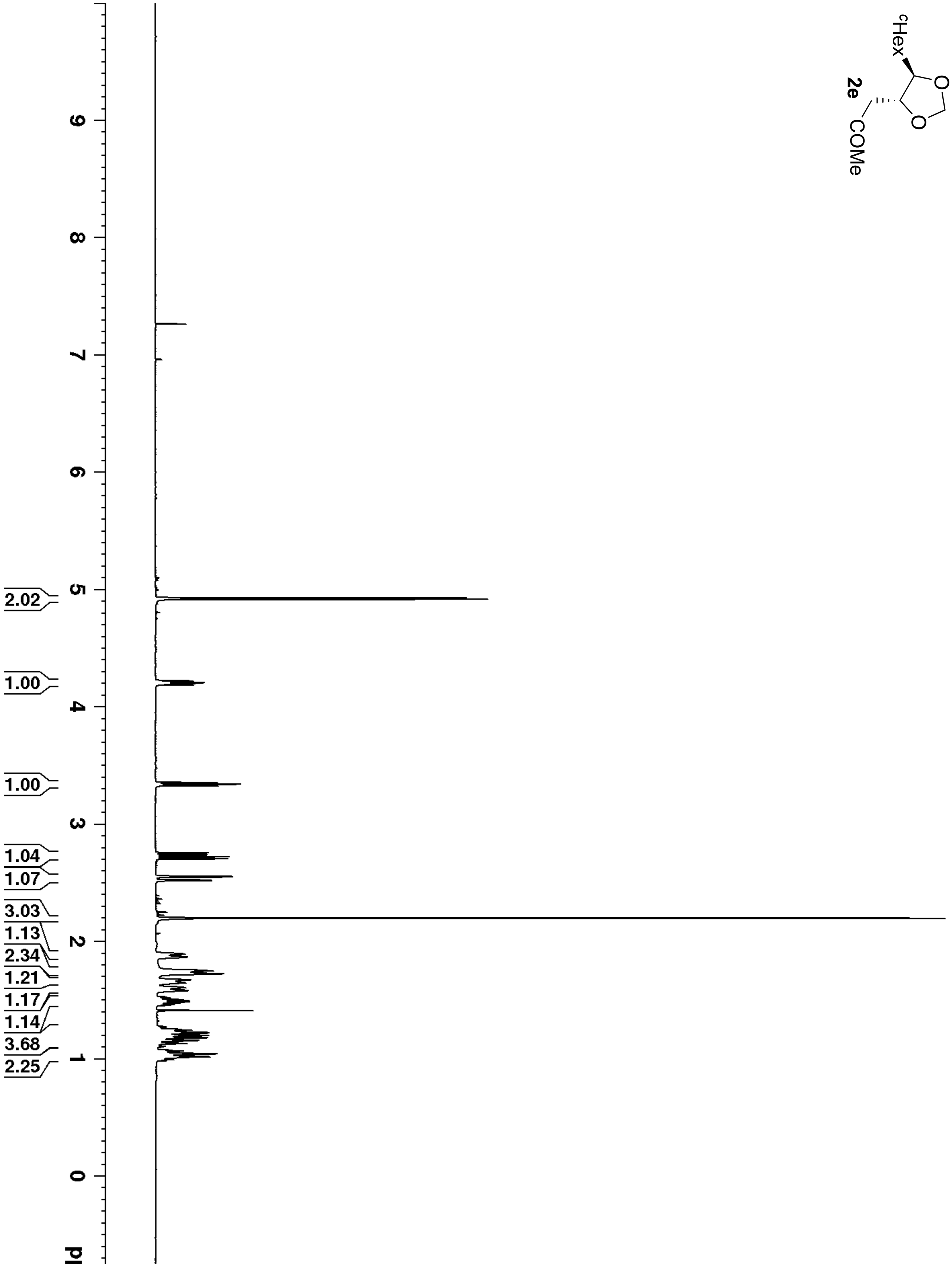
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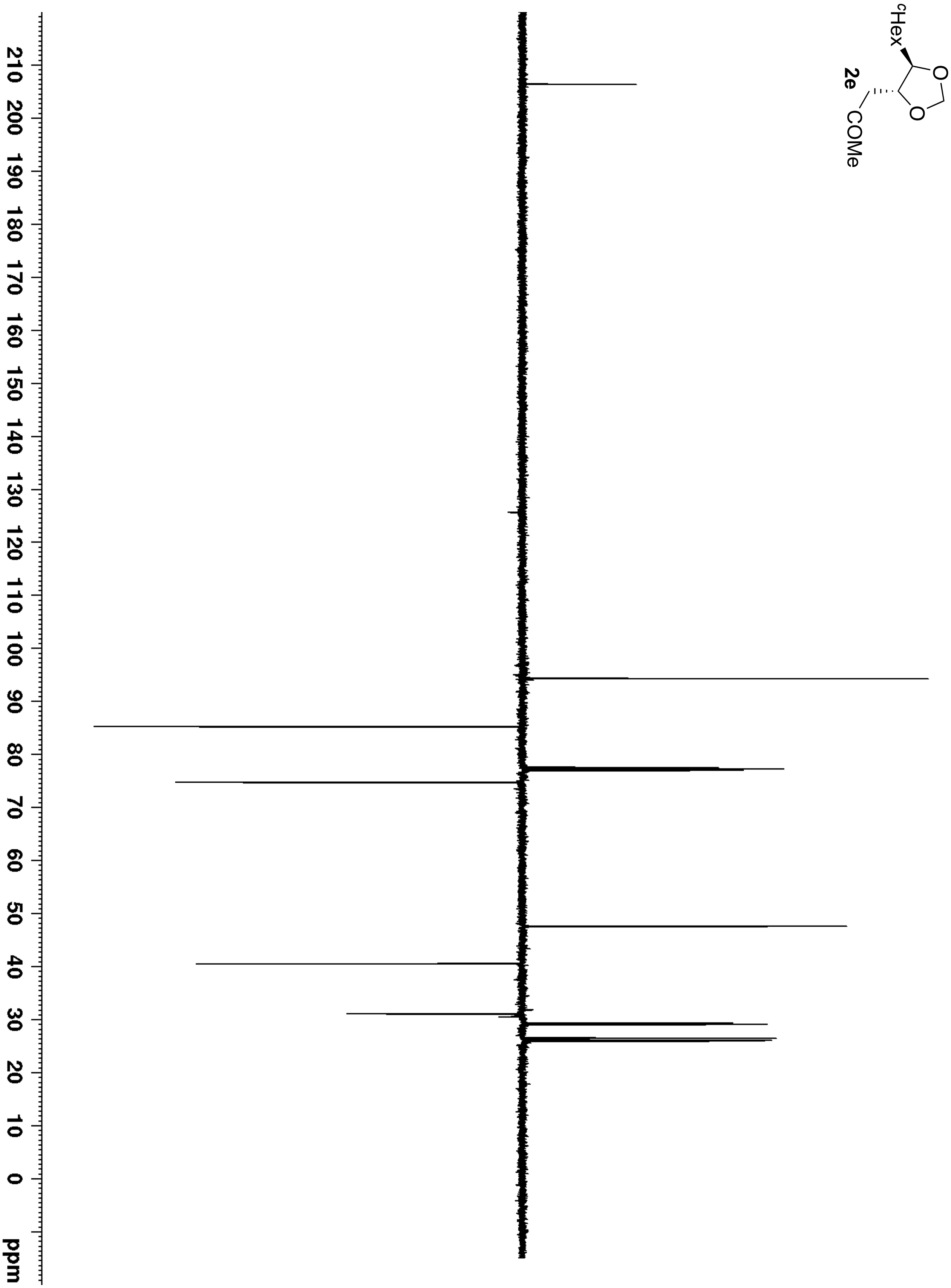
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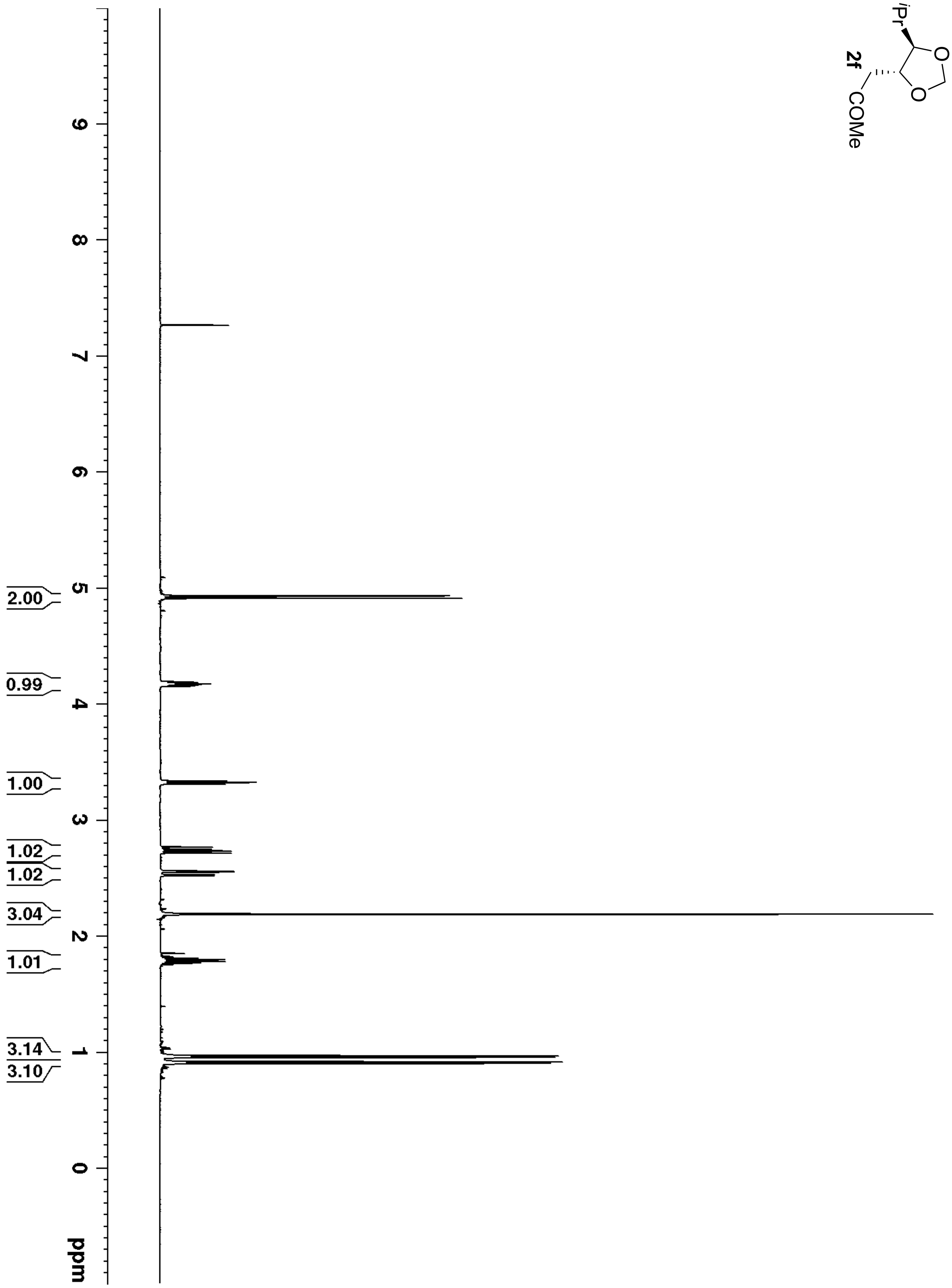

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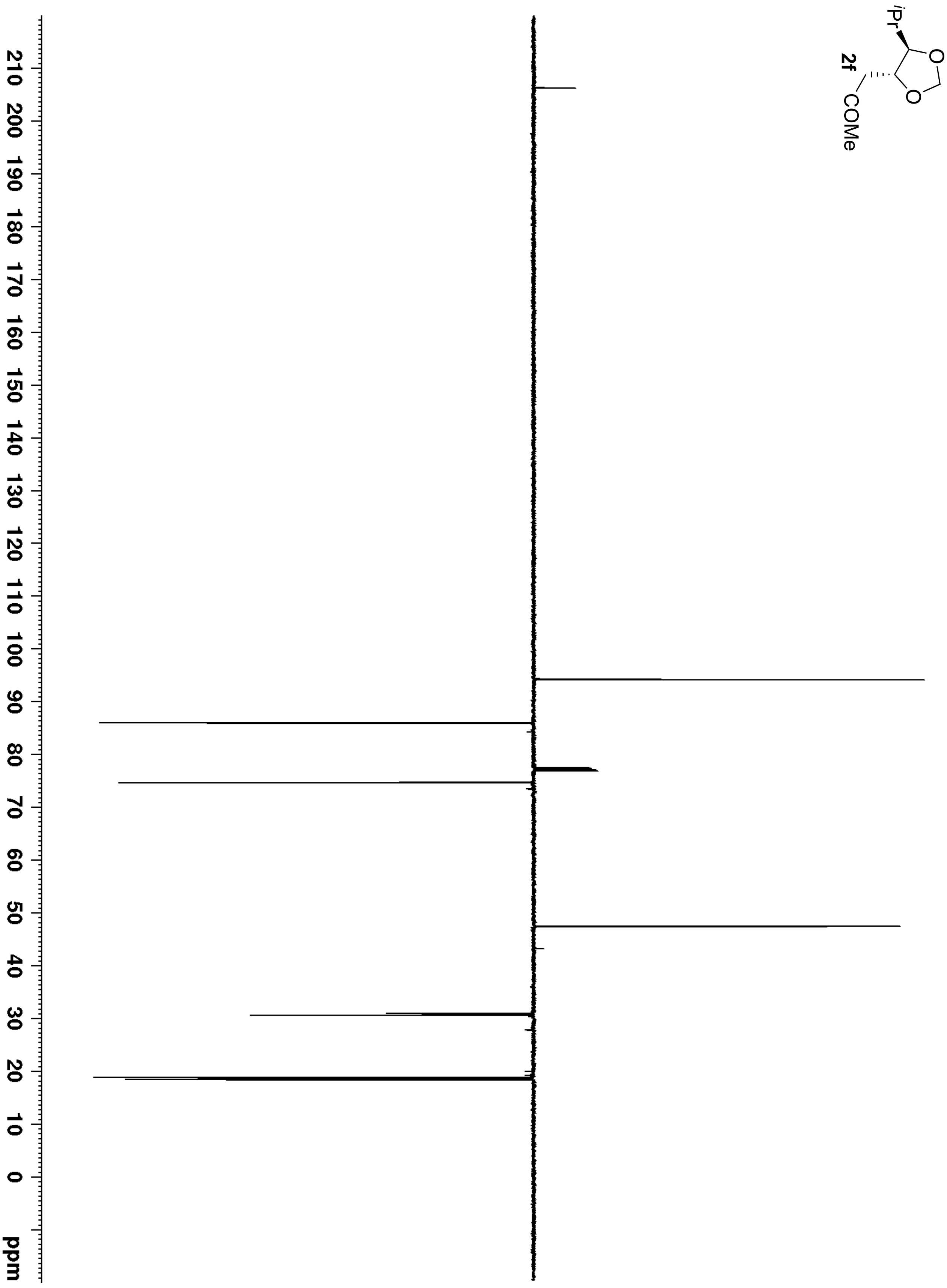
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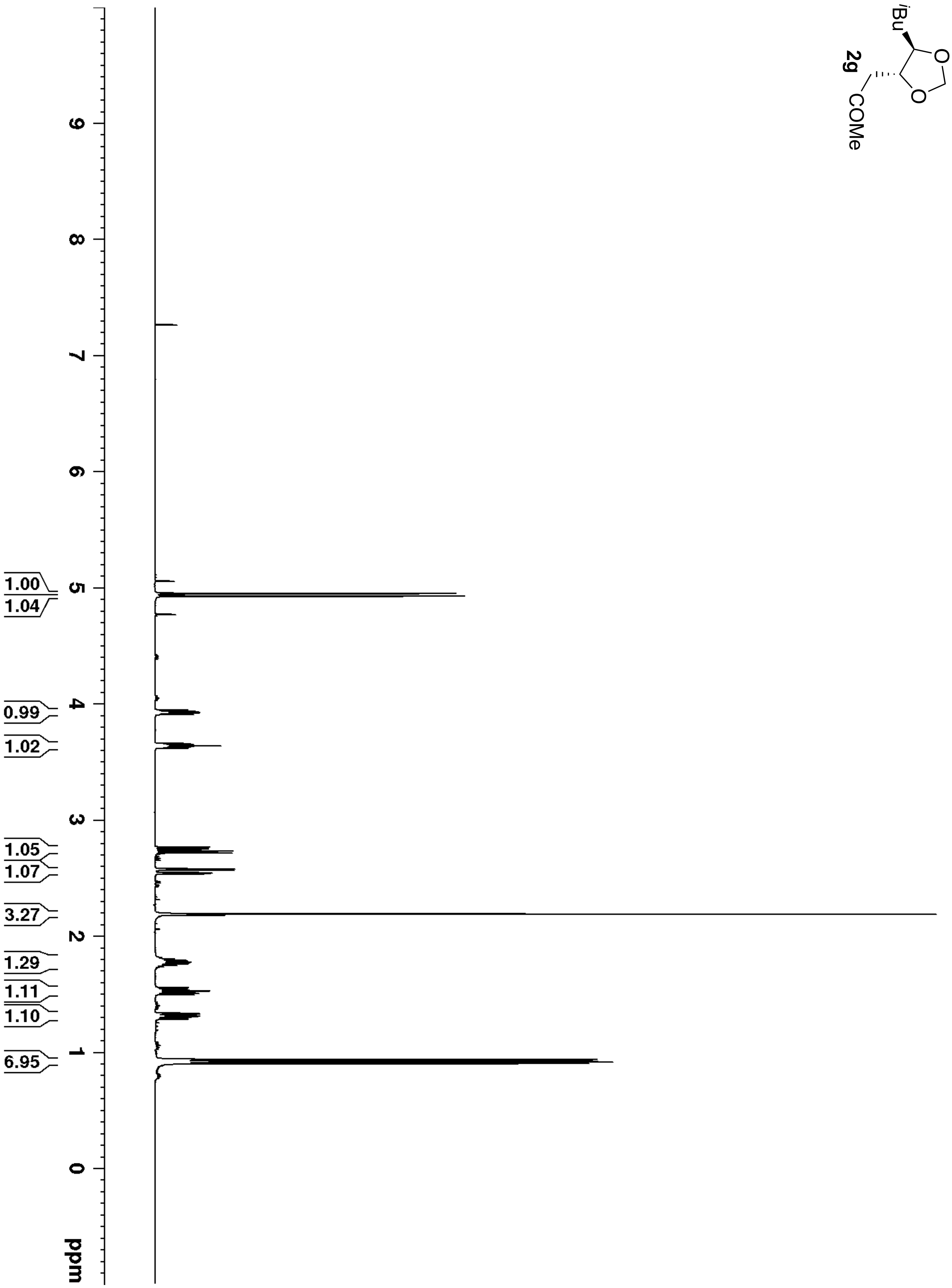

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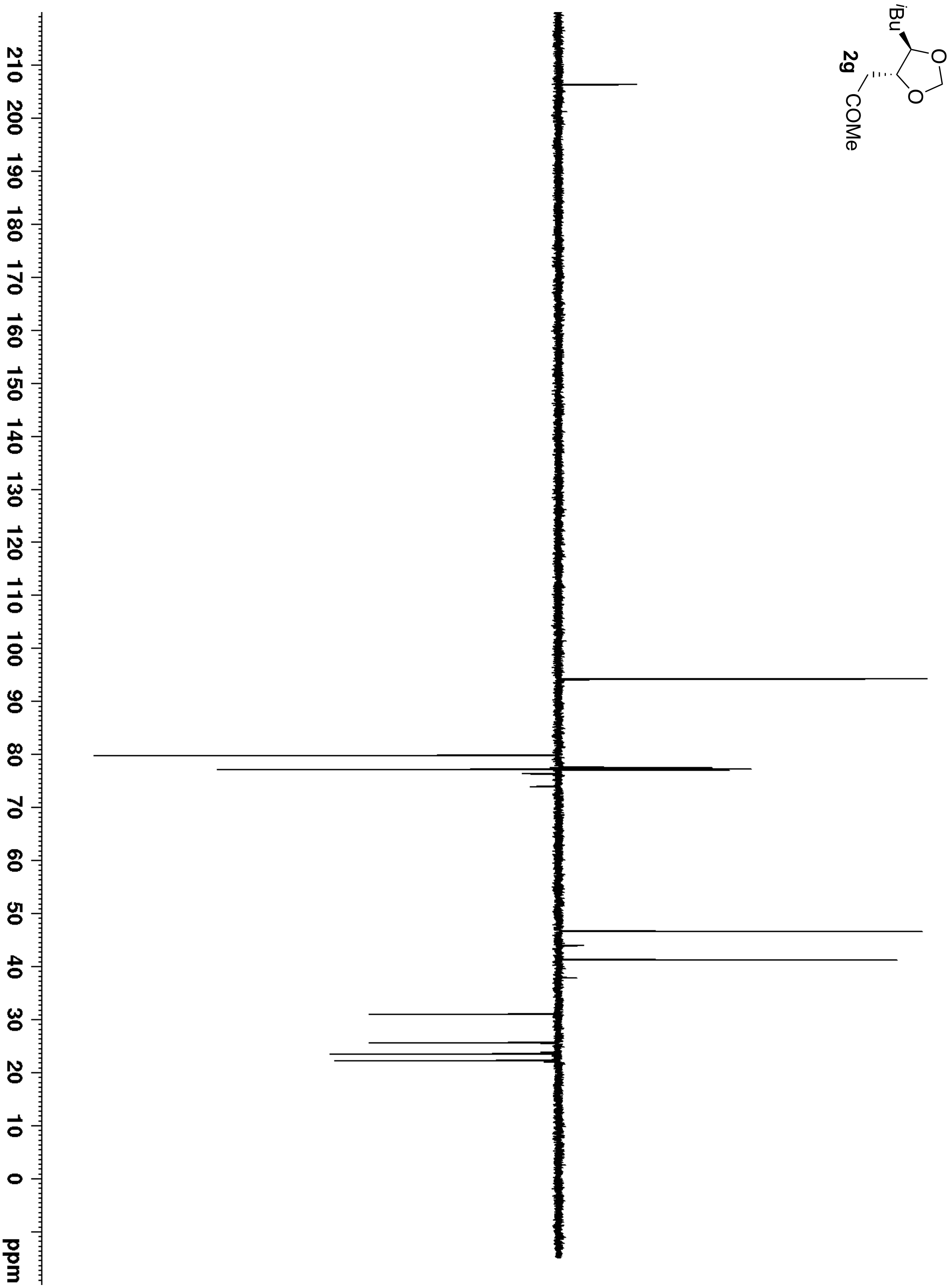

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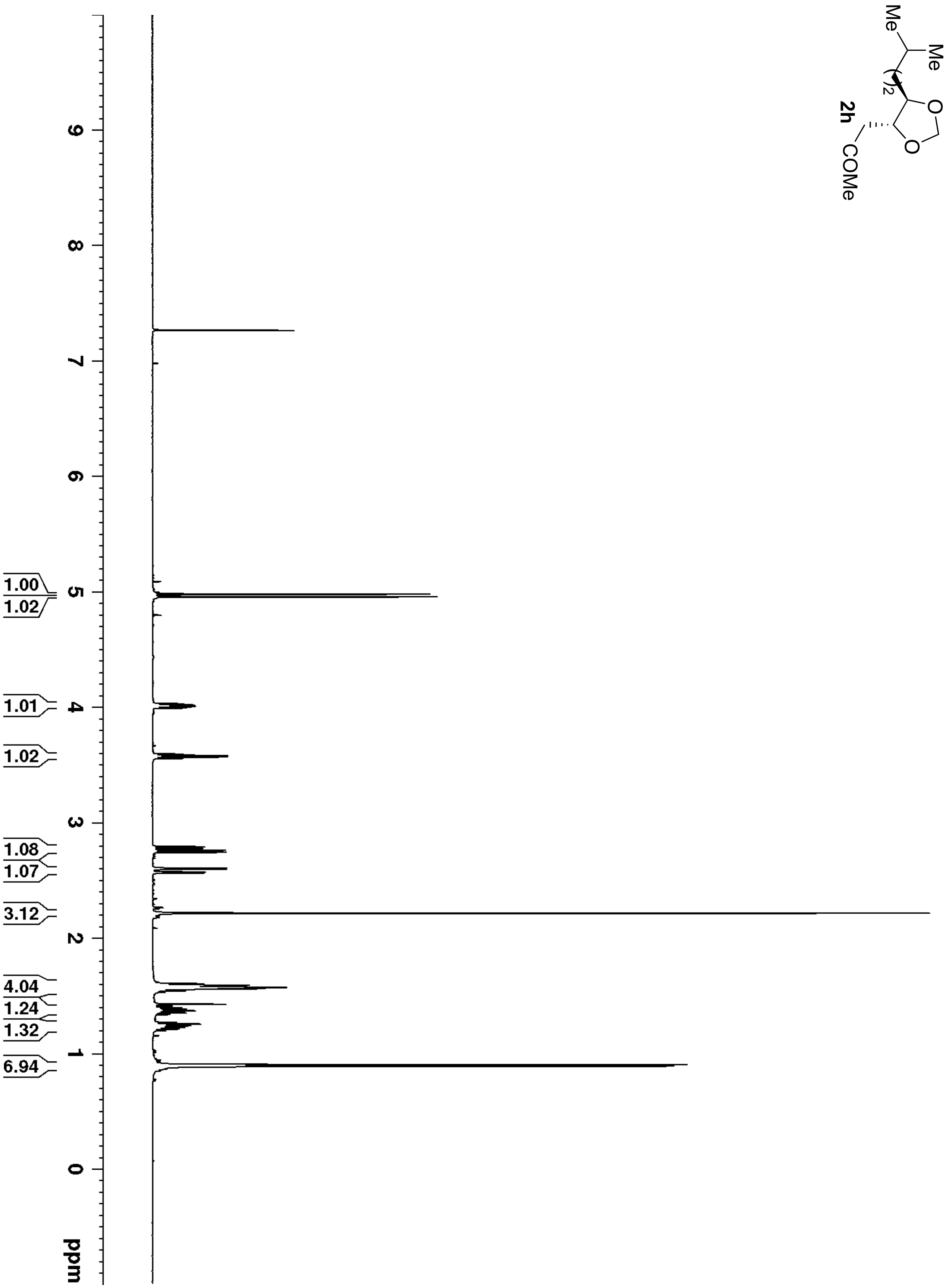
2g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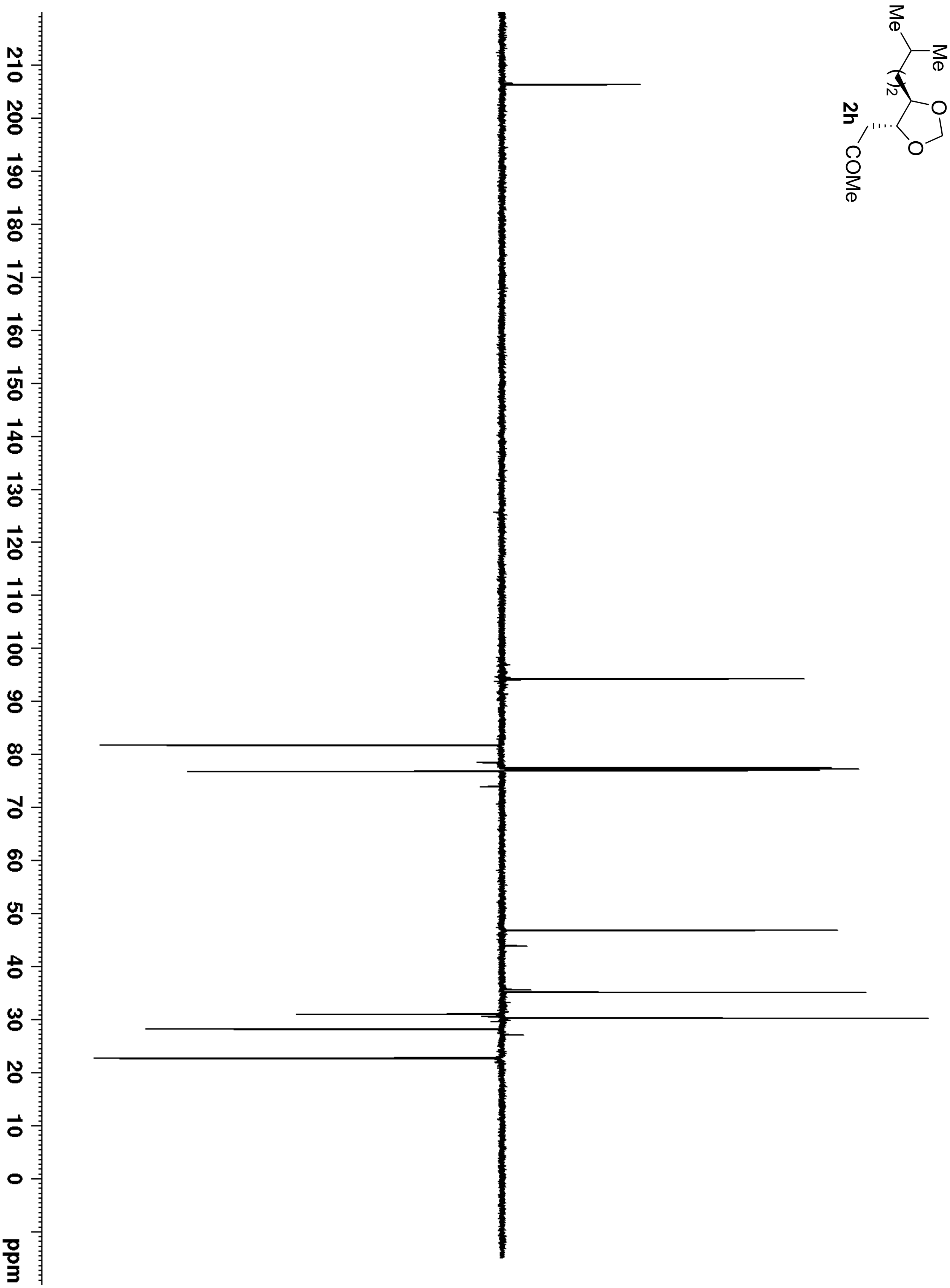
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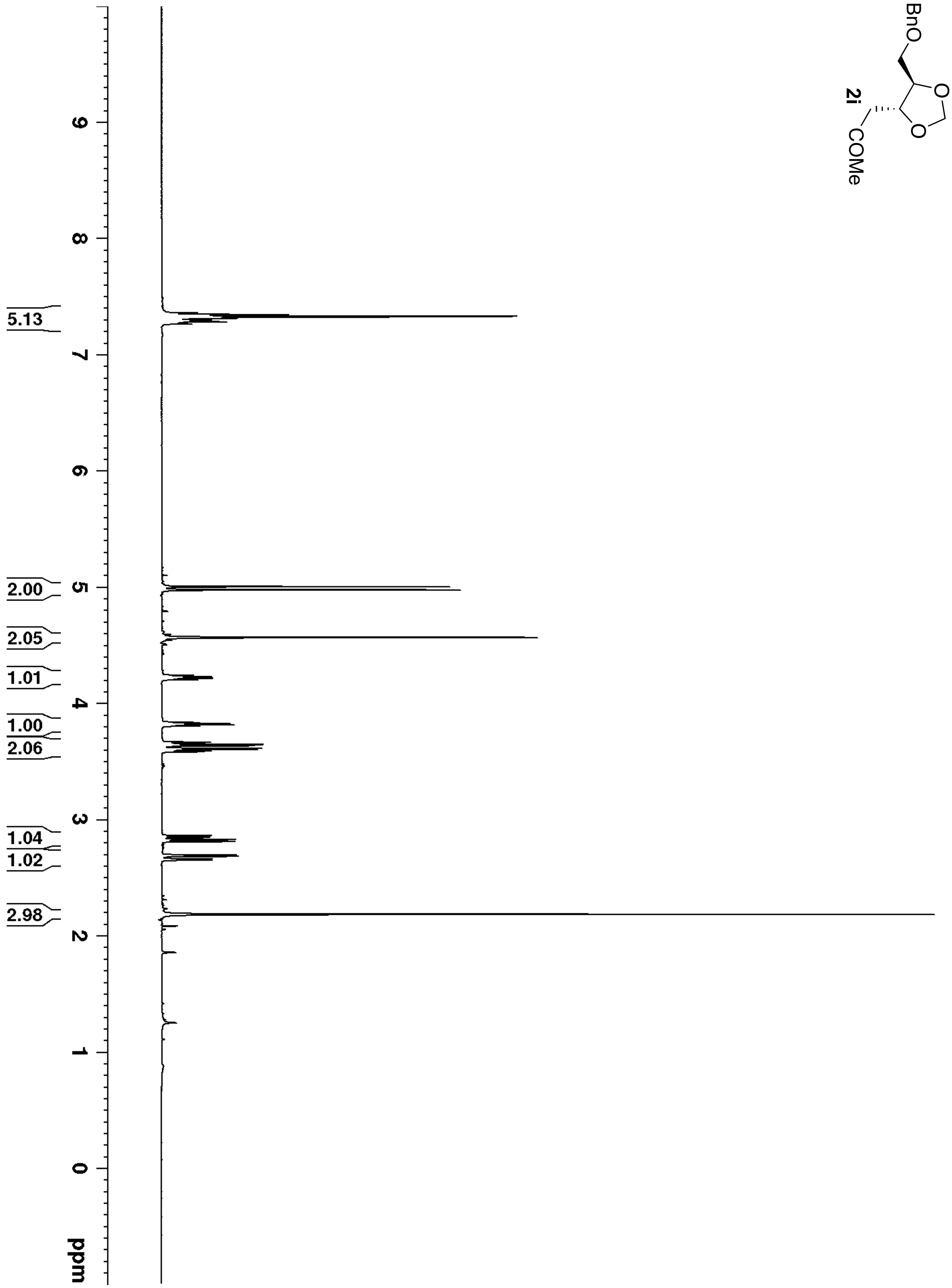
2h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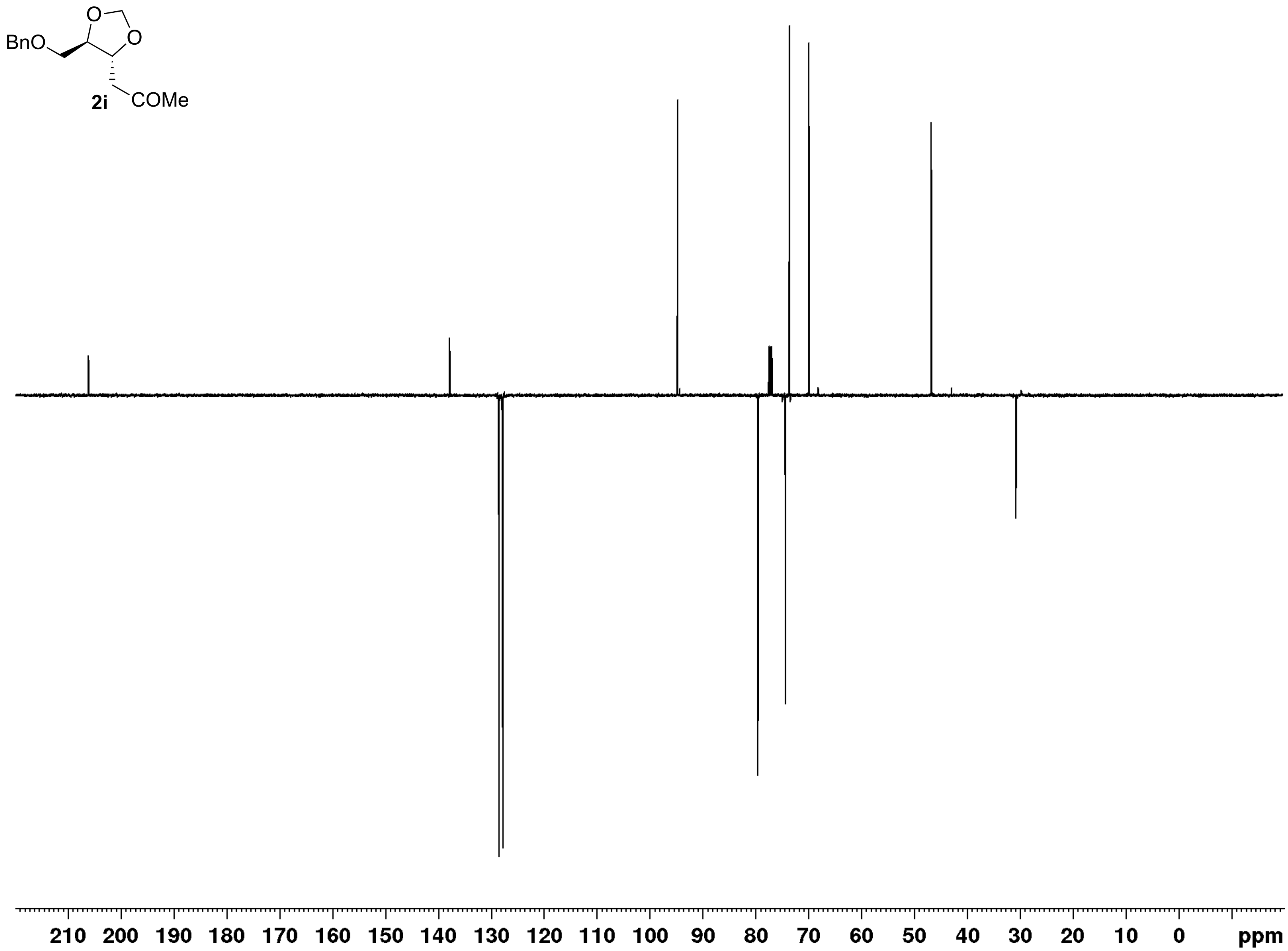
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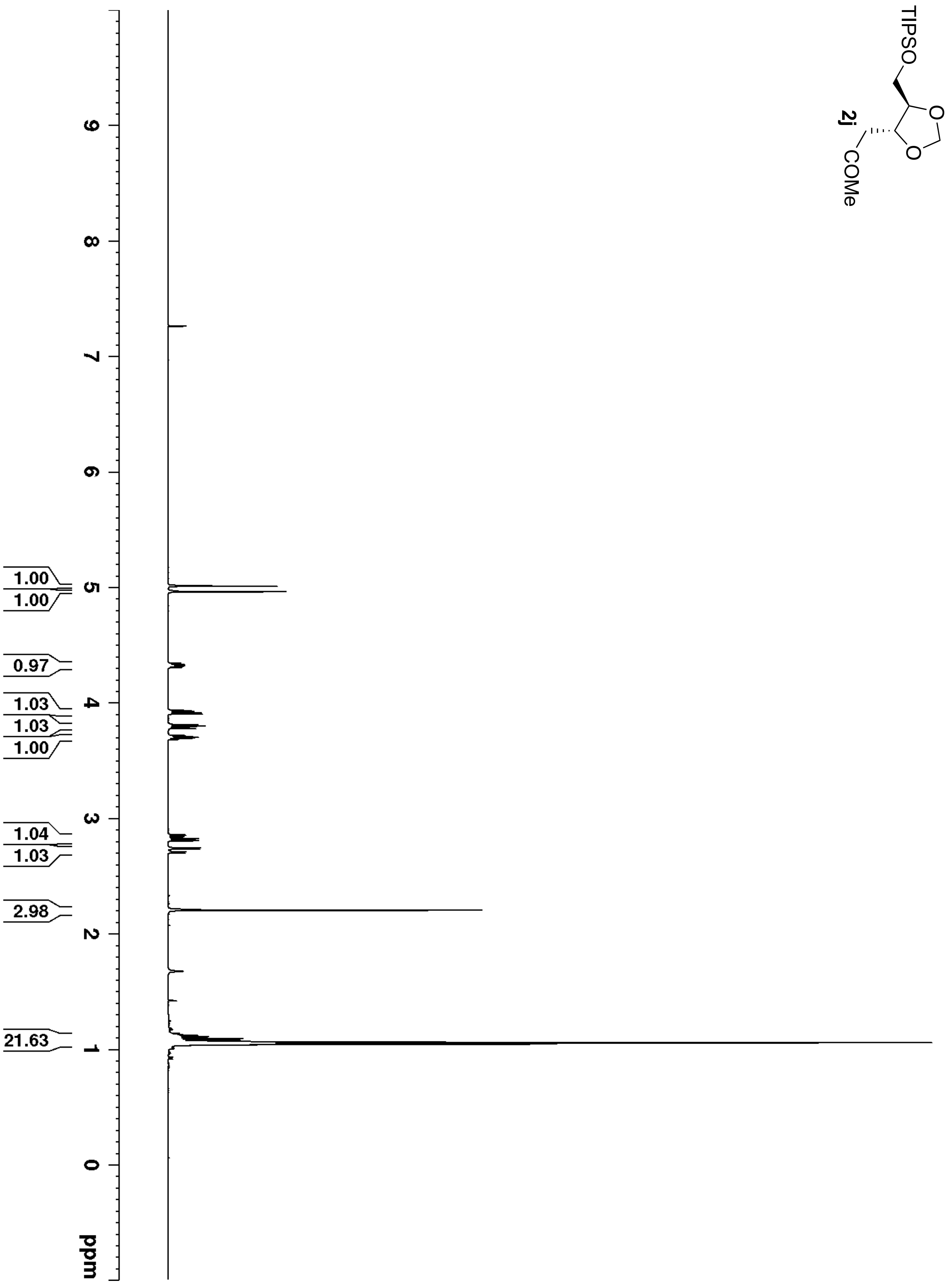
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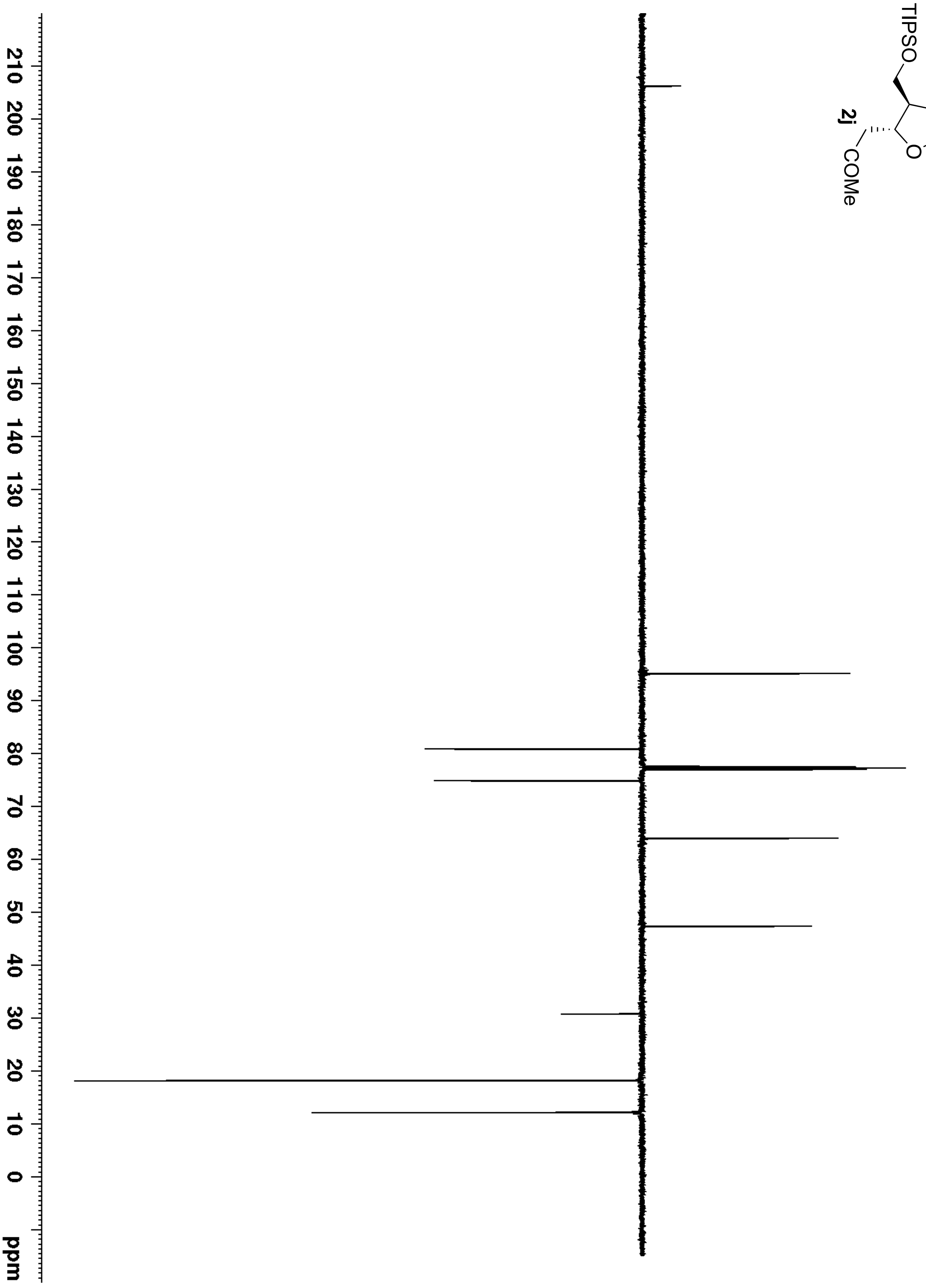
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O
COMe
2j
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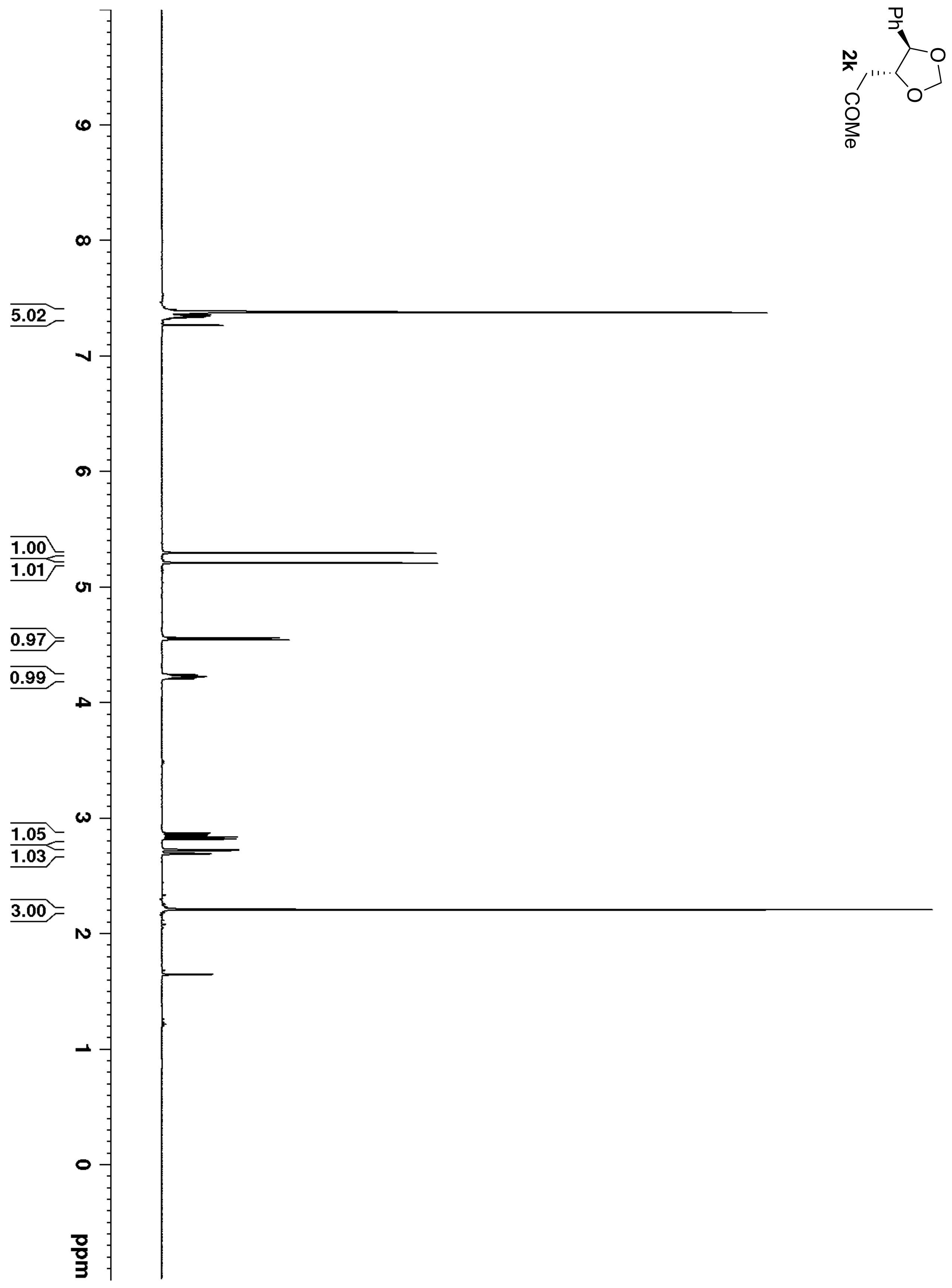
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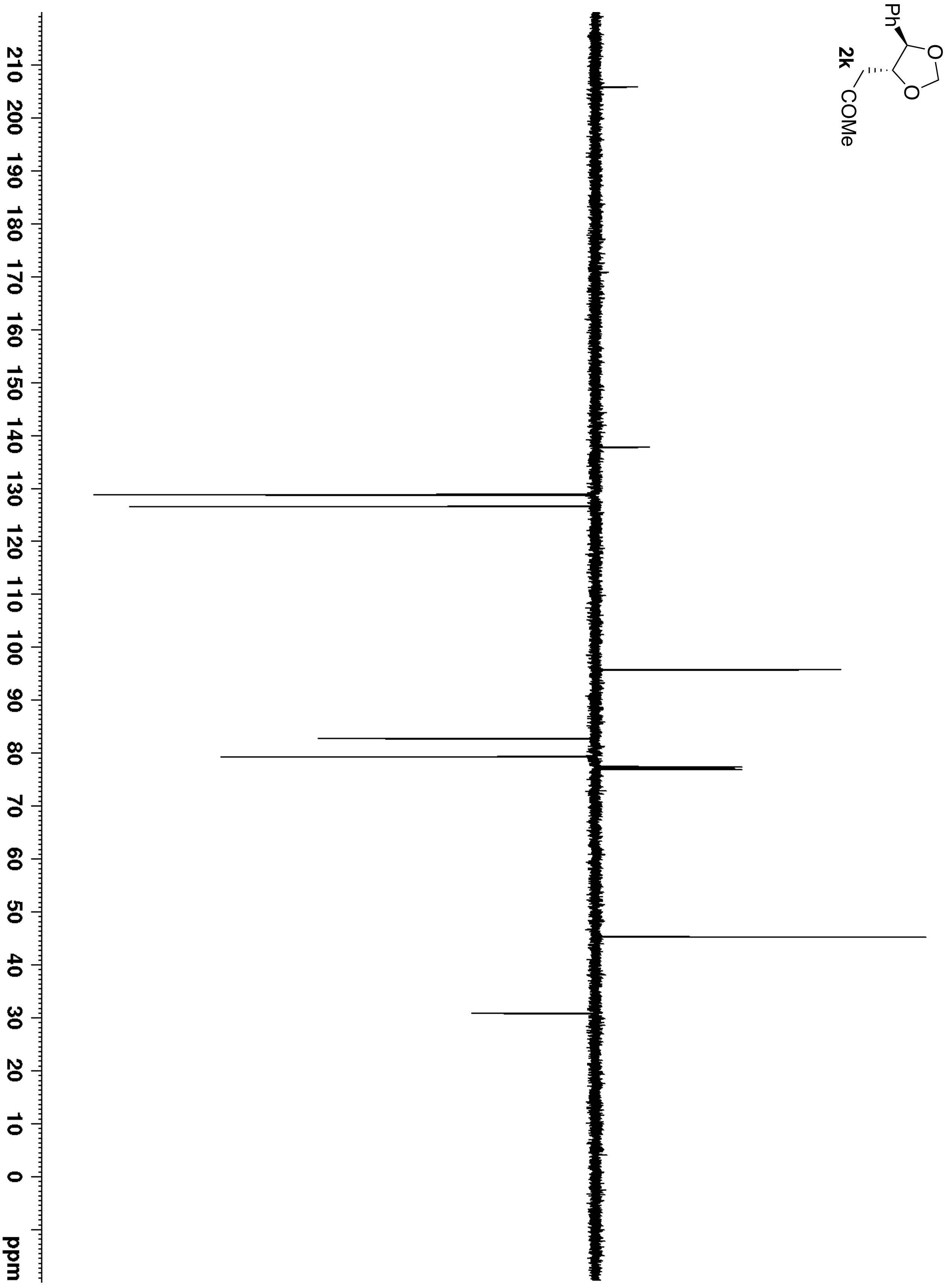
2k

Ph
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O
COMe
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120
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60
50
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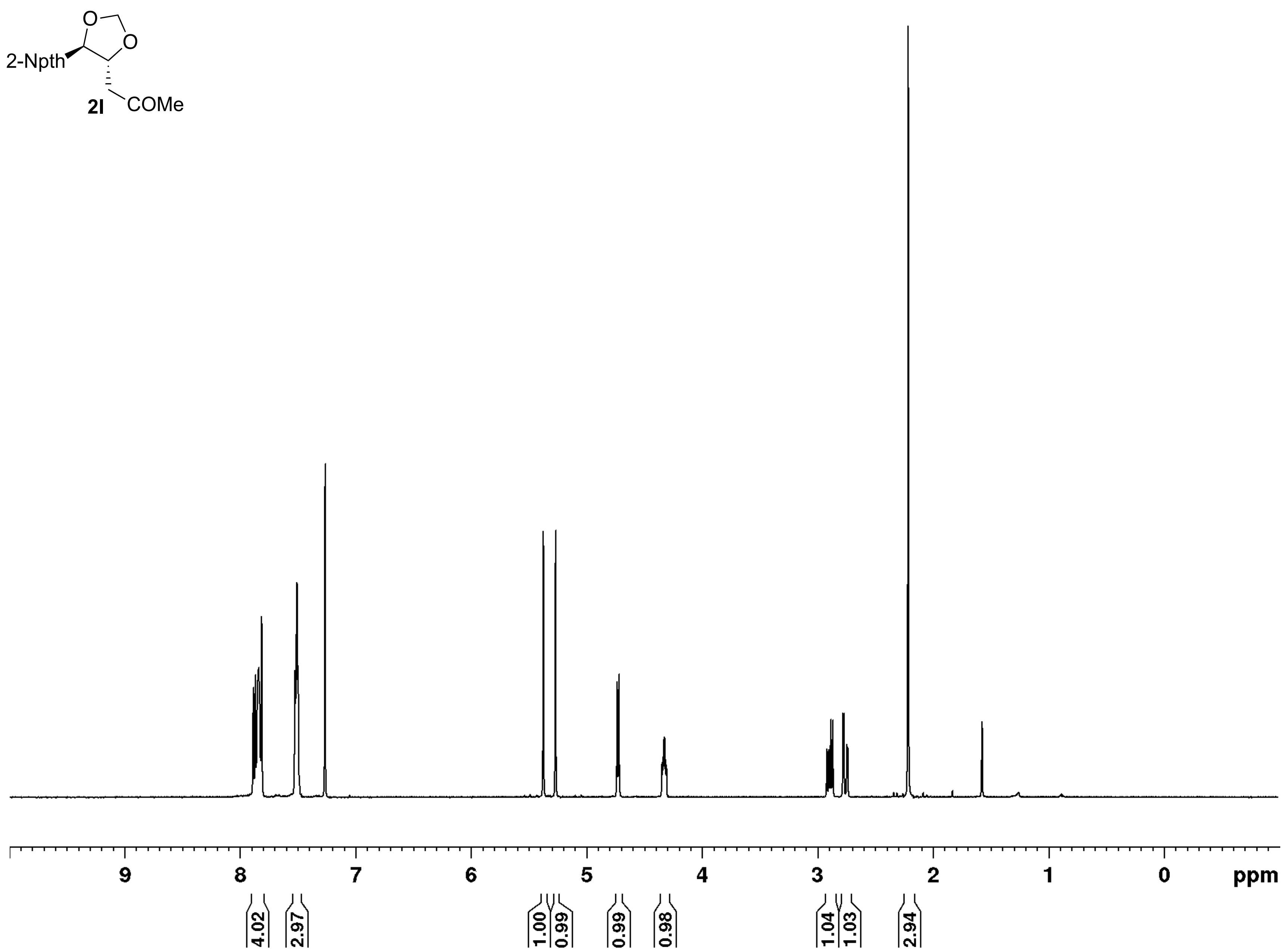
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O
2l
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8
7
6
5
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3
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1.00
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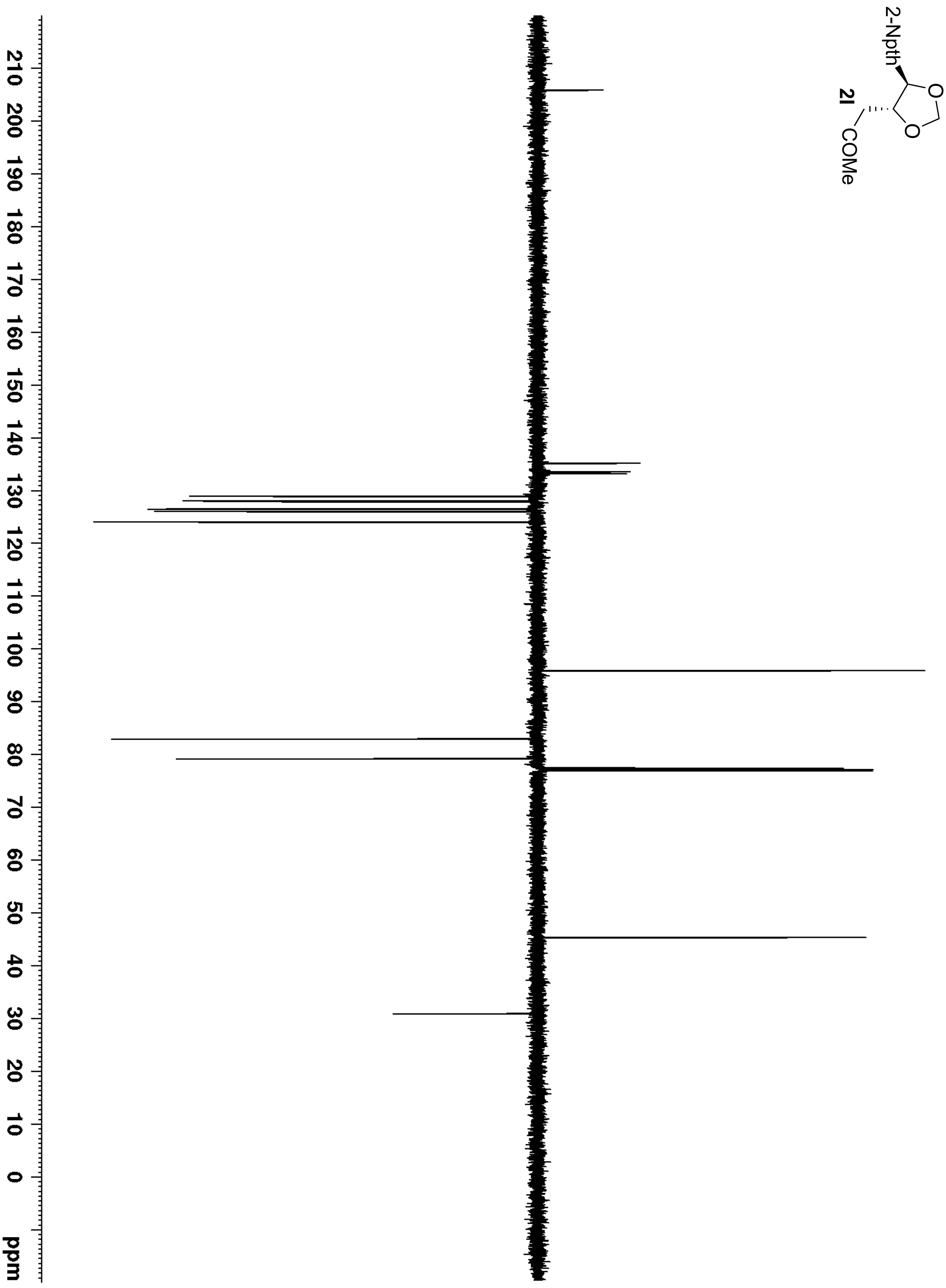
1.04
1.03
2.94


2-Npth
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O
COMe
2l
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200
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120
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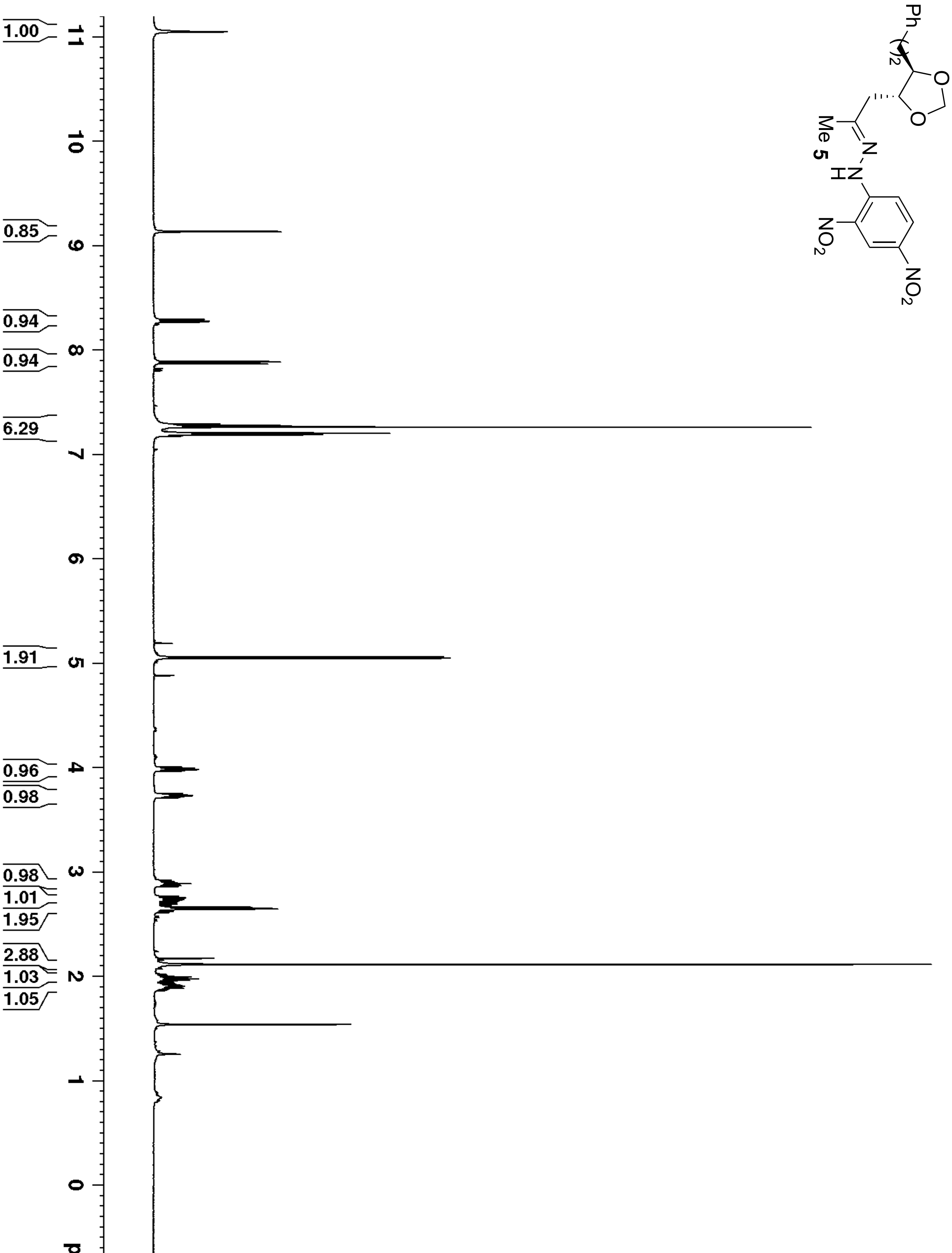
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H
Me
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NO2
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1.91
0.96
0.98
0.98
1.01
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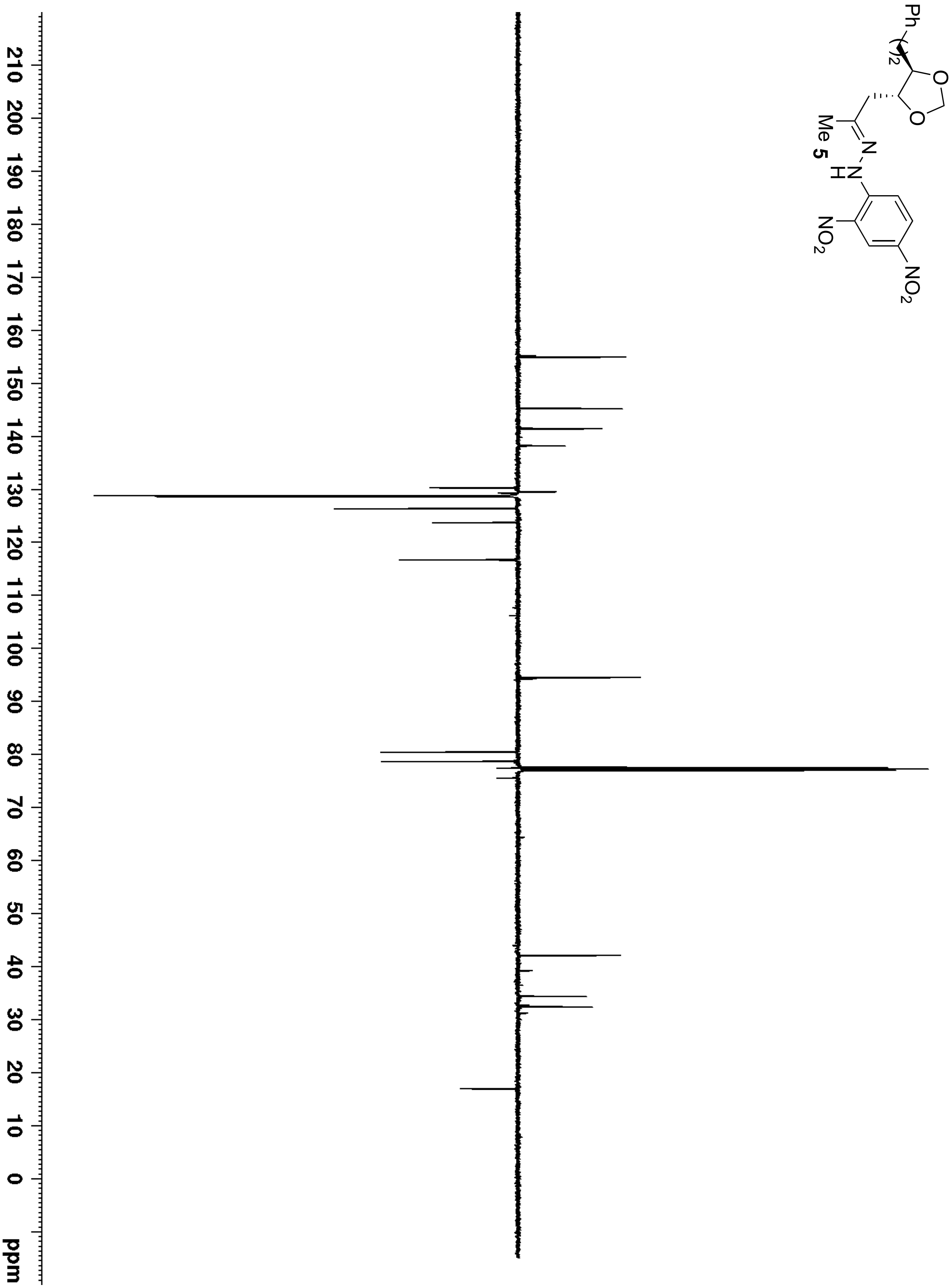
ppm



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N
N
H
Me
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NO2
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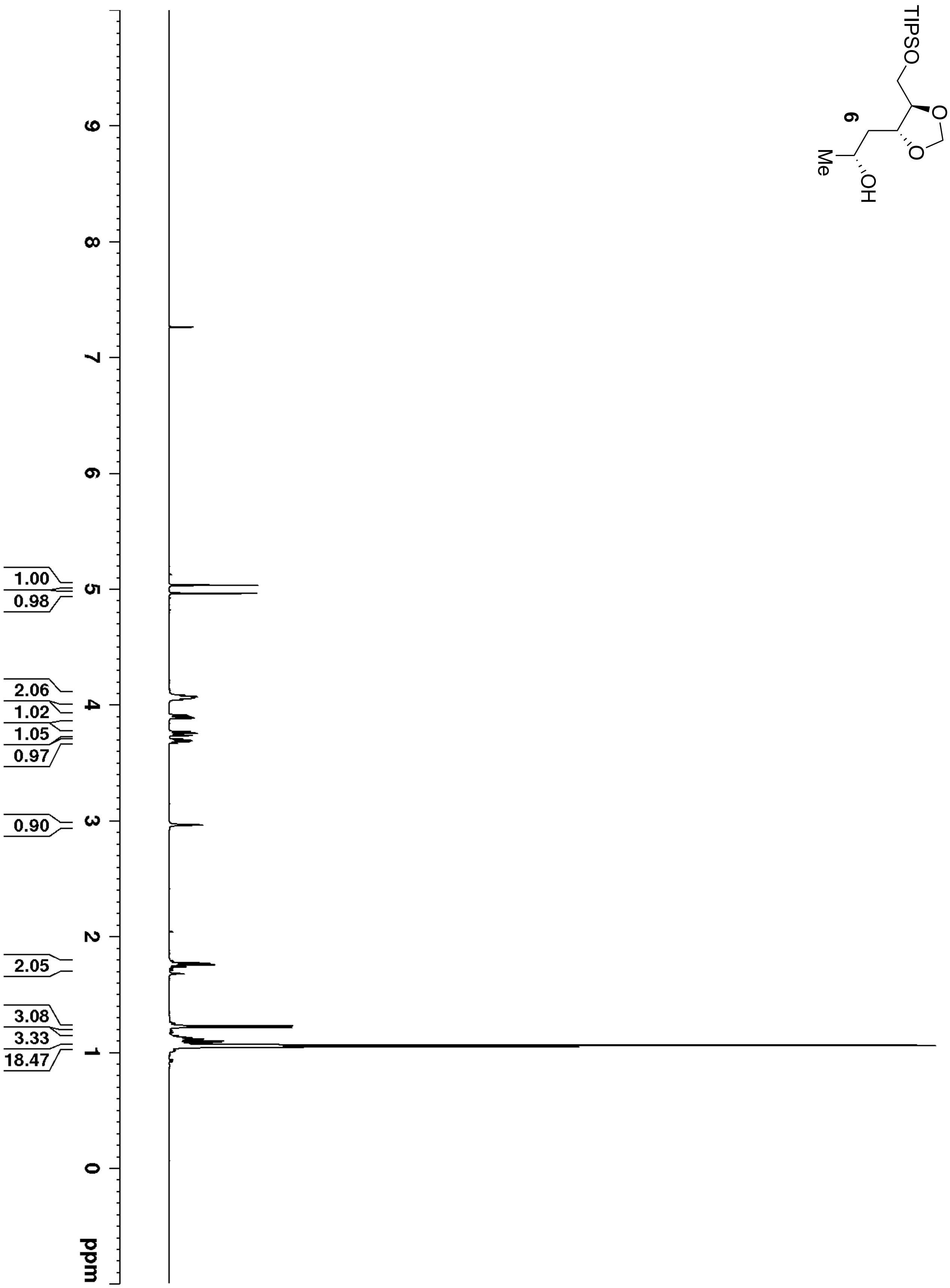
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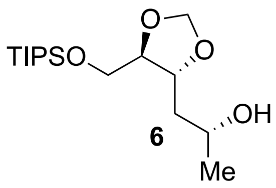
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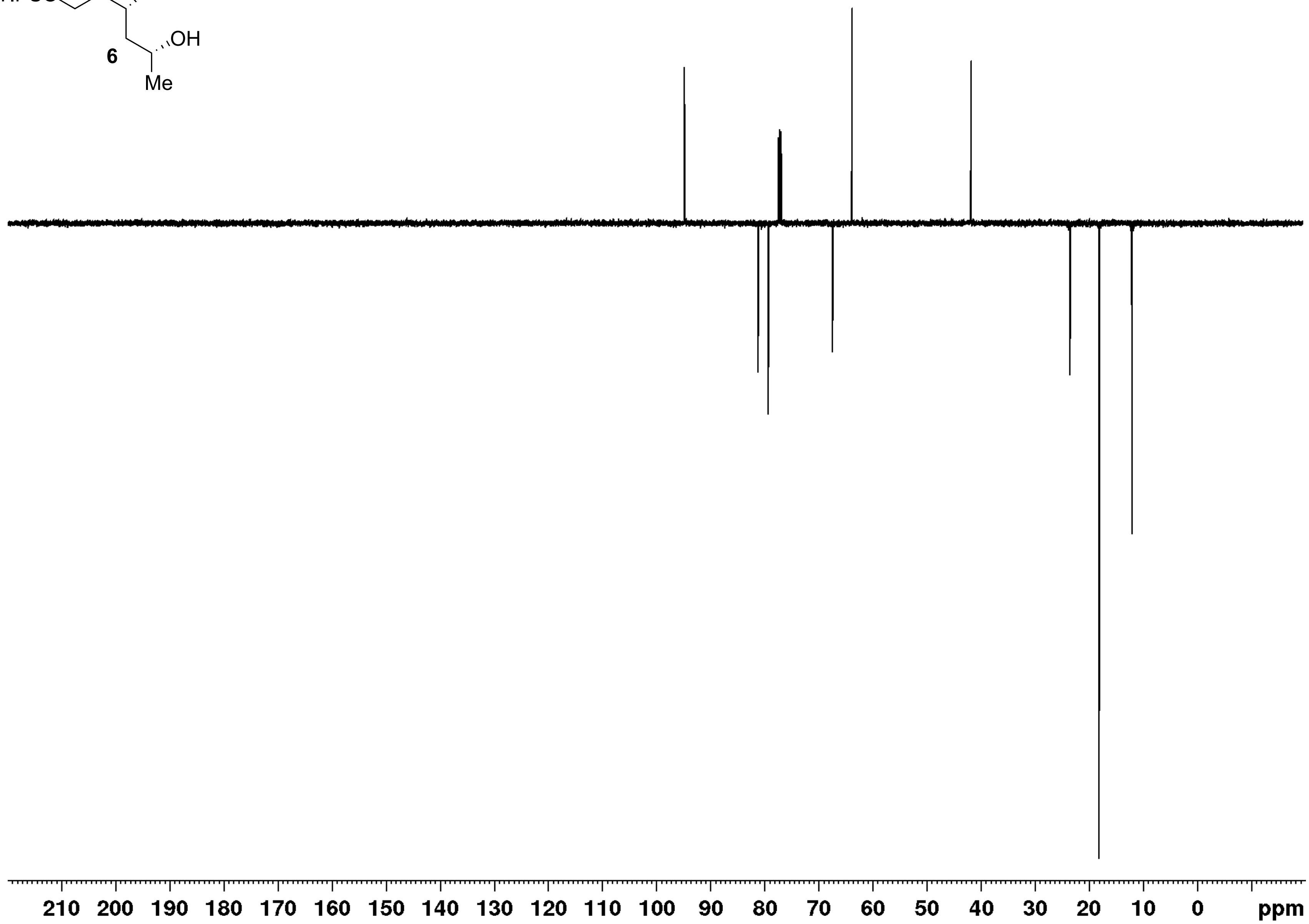
O
OH
Me

6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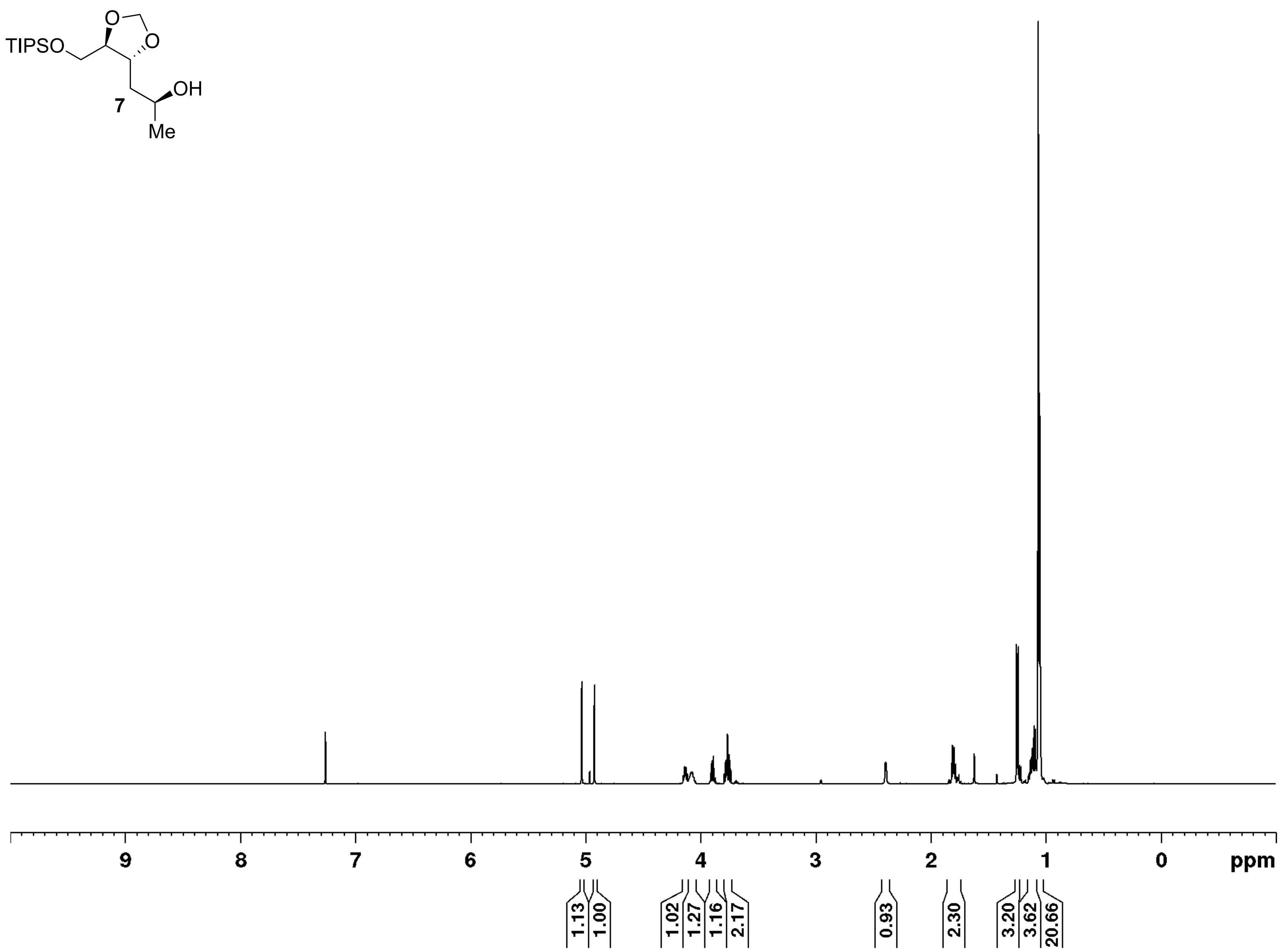
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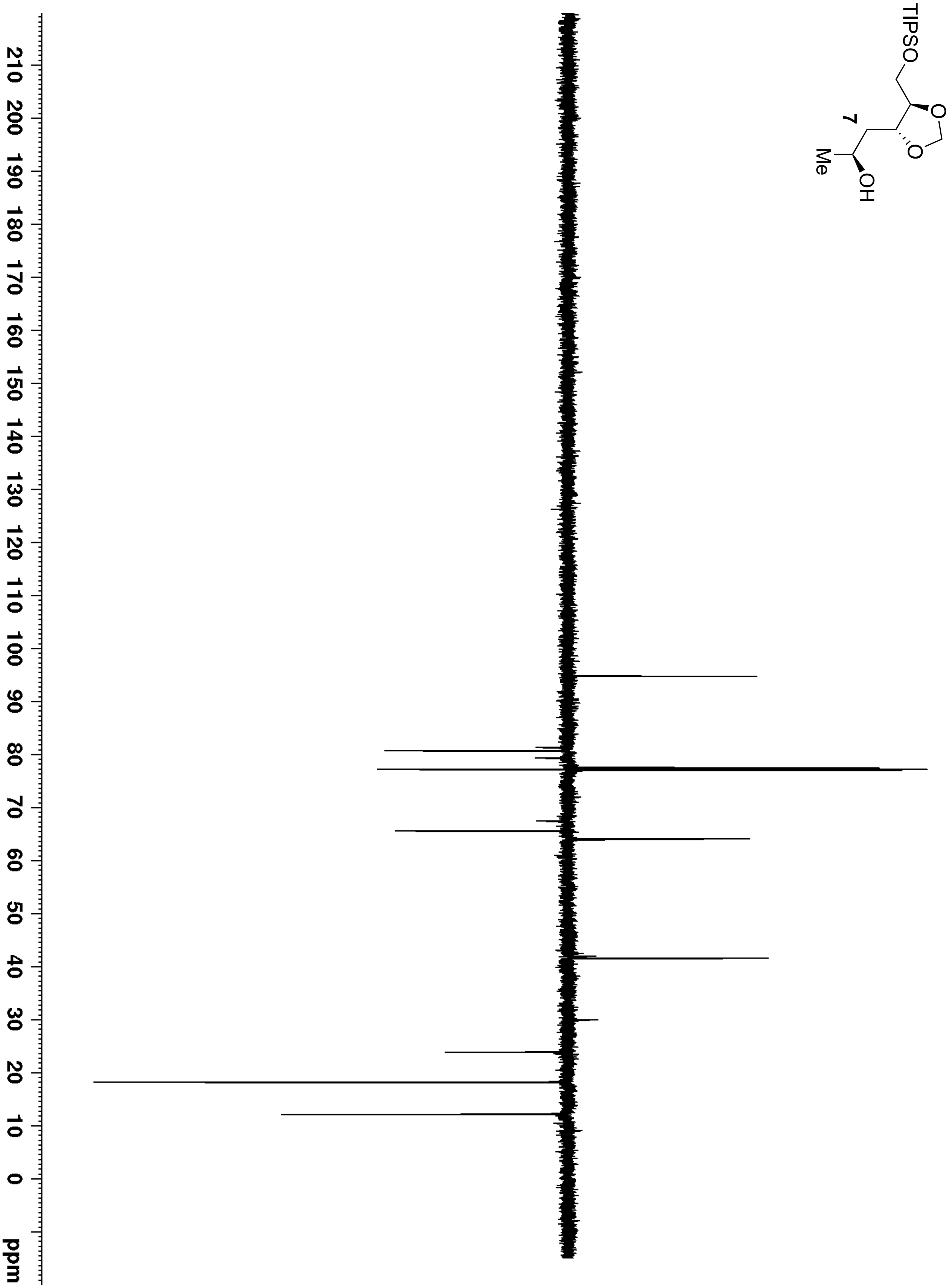
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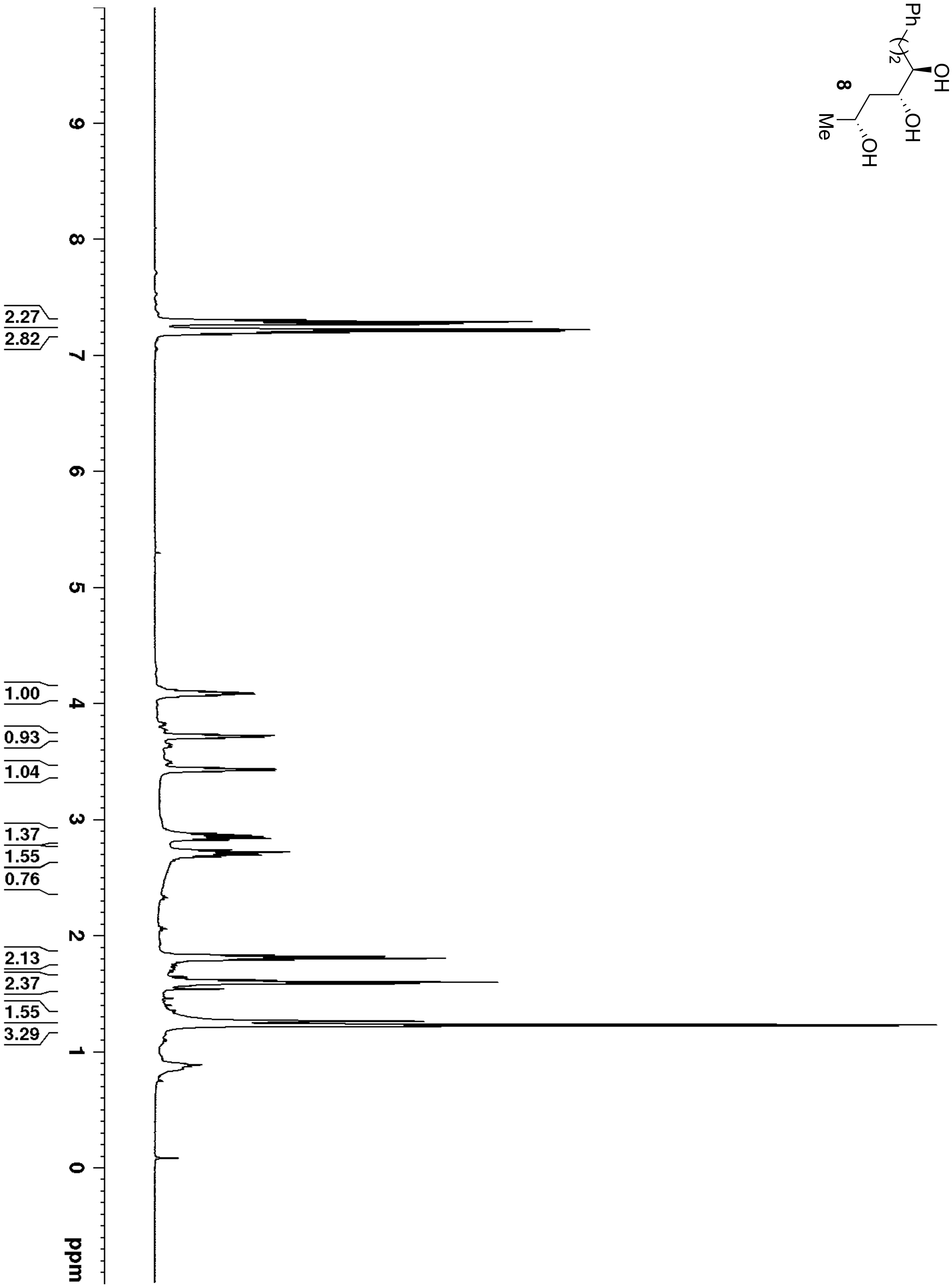
8

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OH
OH
Me
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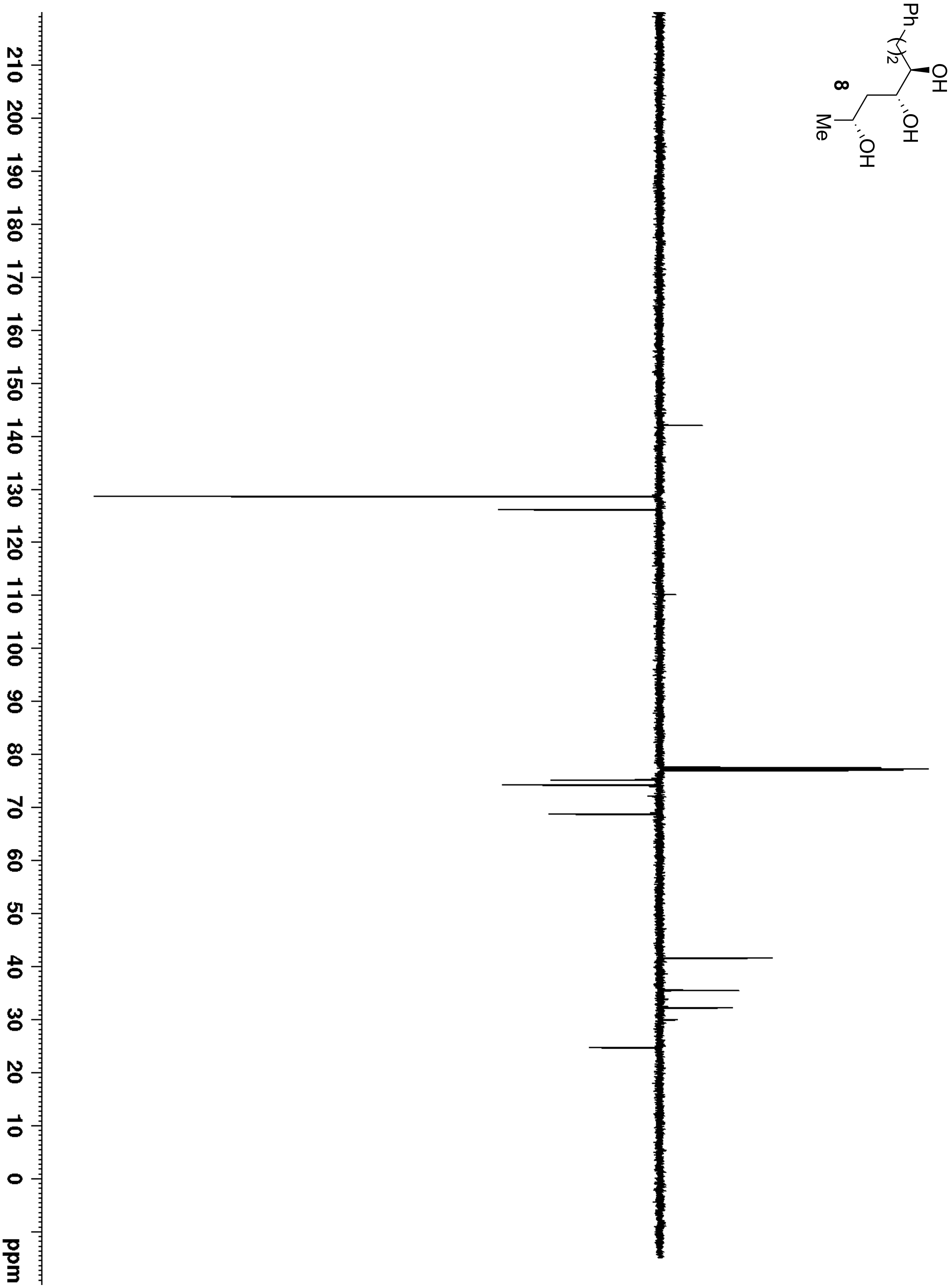
Ph
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OH
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130
120
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100
90
80
70
60
50
40
30
20
10
0
ppm

8

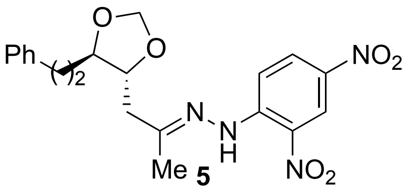
8. X-ray crystallographic data for hydrazone 5

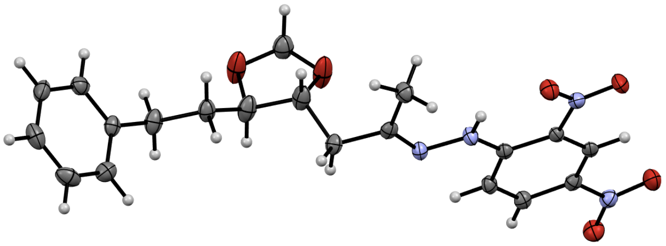
Structure report for (*E*)-1-(2,4-dinitrophenyl)-2-(1-((4*R*,5*R*)-5-phenethyl-1,3-dioxolan-4-yl)propan-2-ylidene)hydrazine (5)

John Bacsa

Crystal and Refinement Data

$C_{20}H_{22}N_4O_6$
$M = 414.41$
Colorless needle, 0.5 x 0.07 x 0.03 mm^3
monoclinic, space group $P2_1/n$
$a = 18.938(6)$ Å, $b = 5.2580(17)$ Å,
$c = 20.517(7)$ Å
$\beta = 108.760(5)°$
$V = 1934.4(11)$ Å^3, $Z = 4$, $D_{calc} = 1.423$ g/cm^{3c}
T = 100 (2) K
9510 reflections collected
3543 independent reflections
$R_{int} = 0.0600$
Final *GooF* = 1.022
$R_1 = 0.0510$, $wR_2 = 0.1117$
3270 data / 114 restraints / 272 parameters
$\mu = 0.107\ mm^{-1}$
CCDC deposition number - 1050168





Data collection, structure solution and refinement

A crystal with well-formed faces was selected from a sample submitted by Dr. Michael D. Ganton from the research group of Prof. P. A. Evans. A colourless needle-shaped crystal with dimensions 0.50 × 0.07 × 0.03 mm^3 was mounted on a loop with paratone oil. Data were collected using a Bruker APEX diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at $T = 100(2)$ K.

Data were measured using ω scans with a narrow frame width scans of 0.5 ° per frame for 40 s using MoK_α radiation (fine-focus sealed tube, 45kV, 40 mA). The resolution that was achieved was $\lambda = 25.3°$. Unit cell indexing was performed by using the **SMART V5.632** (Bruker, 2005)[4] software and the cell parameters were refined using **SAINT V6.45A** (Bruker, 2003)[5] on 2544 reflections, 27% of the observed reflections. Data reduction was performed using the SAINT (Bruker, V6.45A, 2003)[5] software. The final completeness is 99.7% out to 25.3° in θ. The absorption coefficient (μ) of this material is 0.107 mm^{-1} and the minimum and maximum transmissions are 0.5935 and 0.7455. The structure was solved by Direct Methods using the **ShelXS-97** (Sheldrick, 2008)[6] structure solution program with Olex2[7] and refined by Least Squares using version 2014/6 of **XL** (Sheldrick, 2008).[6] The structure was solved in the space group $P2_1/n$ (# 14). All non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated geometrically and refined using the riding model.

Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

---

[4] SMART v.5.632, Bruker axs, Madison, WI (2005).

[5] SAINT v6.45a, Software for the Integration of CCD Detector System Bruker Analytical X-ray Systems, Bruker axs, Madison, WI (2005).

[6] G. M. Sheldrick *Acta Cryst.*, 2008, **A64**, 112.

[7] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.