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Supporting Information

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Ni-Catalyzed Cascade Formation of C(sp^3)-C(sp^3) Bonds by Cyclization and Cross-coupling of Alkyl Iodides with Alkylzinc Halides

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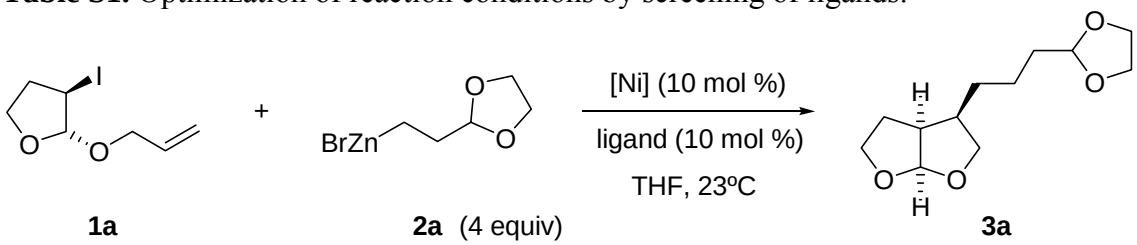
Iodoketals were synthesized by reaction of 2,3-dihydrofuran with the suitable allylic alcohol and NIS according to the described procedure.[1] Iodoethers were prepared in the same way from cyclopentene. 3-(2-iodoethoxy) cyclohex-1-ene[2], Dimethyl 2-allyl-2-(2-bromoethyl) malonate[3], *N*-(2-iodoethyl)-*N*-tosylprop-2-en-1-amine[4], **7a**[5], 8-Iodo-2, 6-dimethyl oct-2-ene,[6] 1-allyl-2-(iodomethyl) benzene[7], 6-iodohex-1-ene[8] and 3-(2-iodoethoxy)prop-1-ene[9] were previously described. The preparations of other starting compounds are described below.

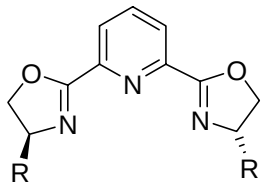
Table S1. Optimization of reaction conditions by screening of ligands.

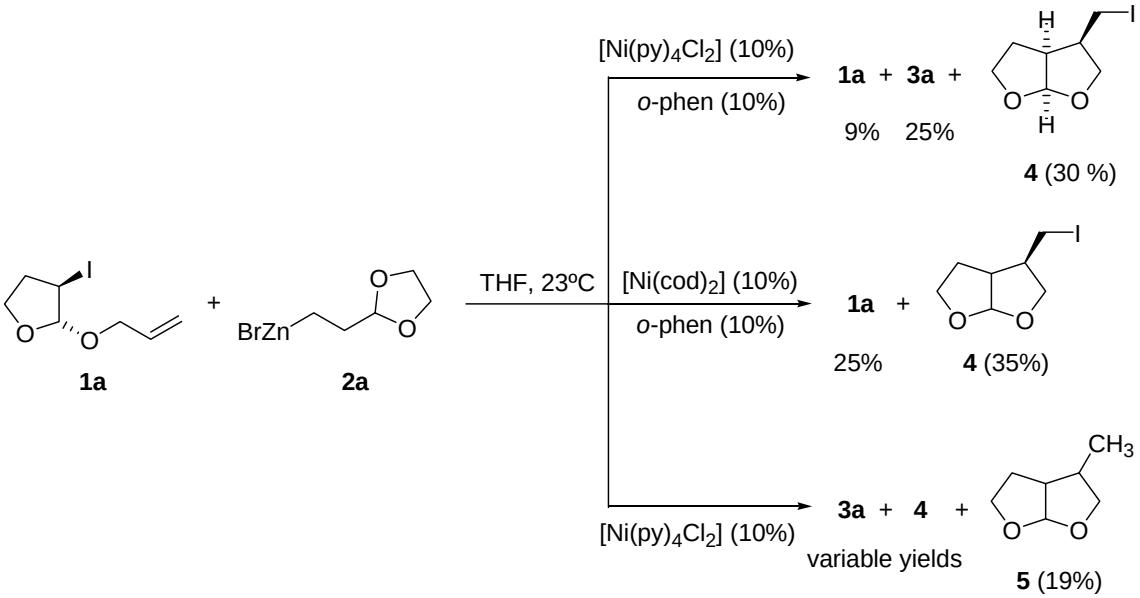


1a **2a** (4 equiv) **3a**

entry	catalyst	ligand	time (h)	yield (%)
1	$Ni(cod)_2$	terpyridine	48	24
2		bipyridine	48	19
3	$Ni(py)_4Cl_2$	terpyridine	27	57
4		*i*-Pr-Pybox	12	61

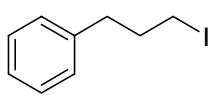
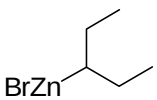
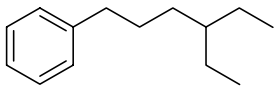
5		*t*-Bu-Pybox	14	34
6		Ph-Pybox	15	38
7		*s*-Bu-Pybox	7	79

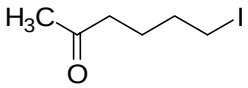
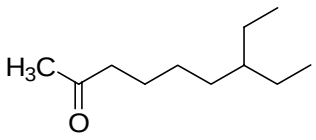
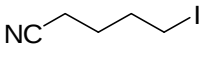
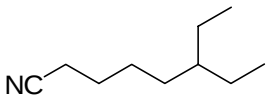
(*S*)-R-Pybox  R = *i*-Pr, *sec*-Bu, *t*-Bu, Ph



Scheme S1. Cross-coupling reactions in the presence of mono- and bidentate nitrogen ligands.

Table S2. Ni-catalyzed cross-couplings of additional alkyl iodides. Conditions: $[Ni(py)_4Cl_2]$ (10 mol %), (*S*)-(*s*-Bu)-Pybox (10 mol %), THF, 23ºC.

entry	substrate	RZnBr	product	t (h)	yield (%)[a]
1	 **6a**	 **2c**	 **7f**	18	61

2	 **6f**	 **7g**	11	66
3	 **6g**	 **7h**	11	71

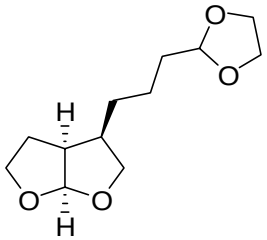
[a] Approximate yields. Pure compounds could not be obtained by column chromatography. In the case of entry 1, GC-MS indicates the presence of at least an isomer.

For full experimental details, see below.

General procedure for the cross-coupling reactions:

A 25 mL flask was charged with $Ni(py)_4Cl_2$ (17.5 mg, 0.039 mmol), (*S*)-(*s*-Bu)-Pybox [2] (12.9 mg, 0.039 mmol) and a stir bar in air. The flask was sealed with a septum and backfilled with Ar. A solution of the alkyl iodide[1] (0.393 mmol) in dry THF (2 mL) was added via syringe. After stirring for 3-4 min at rt, the resulting deep-blue solution was treated in turn with the corresponding alkylzinc bromide, (0.5 M THF solution, 0.787 mmol) was added, and the reaction mixture was stirred at room temperature for half of the total indicated reaction time. Then again alkylzinc bromide, (0.5 M THF solution, 0.787 mmol) was added, and the reaction mixture was then stirred for the rest of the total time. The reaction mixture was then transferred to a reparatory funnel with diethyl ether (20 mL), the product was extracted with ether (2×30 mL) and the combined organic extracts were washed with water (20 mL) and brine (20 mL). After drying (anhydrous Na_2SO_4), the solution was filtered and concentrated and the residue was purified by silica gel column chromatography (Hexane: EtOAc) which afforded the compounds as pale yellow oils. Modifications of this general procedure concerning the molar ratio for the reagents are indicated in every particular case below.

(3*R**, 3a*S**, 6a*R**)-3-[3-(1,3-dioxolan-2-yl)propyl]-hexahydrofuro [2, 3-*b*] furan (**3a**): 7 h, (Hexane: EtOAc = 6:4), Pale yellow oily liquid (71 mg, 79 %).



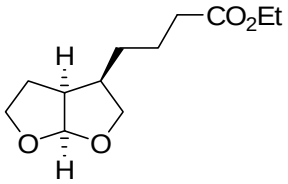
Procedure: General procedure described above.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.71 (d, *J* = 5.0 Hz, 1H), 4.84 (t, *J* = 4.7 Hz, 1H), 3.98-3.81 (m, 7H), 3.39 (dd, *J*= 11.4, 8.4 Hz, 1H), 2.83-2.72 (m, 1H), 2.35-2.21 (m, 1H), 1.89-1.76 (m, 2H), 1.70-1.61 (m, 2H), 1.49-1.36 (m, 4H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 109.91 (CH), 104.40 (CH), 72.70 (CH_2), 69.26 (CH_2), 65.05 (2·CH_2), 45.53 (CH), 42.37 (CH), 34.12 (CH_2), 27.69 (CH_2), 25.12 (CH_2), 23.10 (CH_2).

TOF MS EI+: Calcd. for $C_{12}H_{20}O_4$: 228.1362; Found: 228.1371

Ethyl 4-[(3*R**, 3a*S**, 6a*R**)-hexahydrofuro[2,3-b]furan-3-yl]butanoate (**3a´**)
13 h, (Hexane: EtOAc= 8:2), Pale yellow oily liquid (58 mg, 65 %).



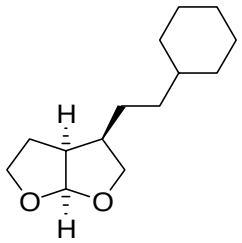
Procedure: General procedure described above.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.70 (d, *J* = 5.0 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.95-3.81(m, 3H), 3.39 (dd, *J*=11.4, 8.5 Hz, 1H) 2.84-2.73 (m, 1H), 2.34-2.23(m, 3H), 1.88-1.79 (m, 2H), 1.72-1.53 (m, 2H), 1.46-1.35 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (500MHz, $CDCl_3$, DEPT-135) δ 173.59 (C), 110.05 (CH_2), 72.74 (CH_2), 69.42 (CH_2), 60.66 (CH_2), 42.31 (CH), 42.31 (CH), 34.57 (CH_2), 27.35 (CH_2), 25.19 (CH_2), 24.09 (CH_2), 14.55 (CH_3).

TOF MS EI+: Calcd. for $C_{12}H_{19}O_4$ (M^+-1): 227.1283; Found: 227.1283.

(3*R**, 3a*S**, 6a*R**)-3-(2-cyclohexyl)-hexahydrofuro [2, 3-*b*] furan (**3a´´**)
15 h, (Hexane: EtOAc = 9:1), Colourless oily liquid (53 mg, 60 %).



Procedure: General procedure described above.

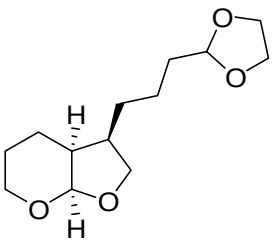
^{1}H NMR (300MHz, $CDCl_3$) δ 5.71 (d, *J* = 4.9 Hz, 1H), 3.95-3.81 (m, 3H), 3.39 (dd, *J* = 11.4, 8.4 Hz, 1H), 2.83-2.72 (m, 1H), 2.31-2.17 (m, 1H), 1.91-1.77 (m, 2H), 1.75-1.58 (m, 6H), 1.43-1.10 (m, 9H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ110.14 (CH), 73.12 (CH_2), 69.49 (CH_2), 45.77 (CH), 42.77 (CH), 38.23 (CH), 36.57 (CH_2), 33.78 (2·CH_2), 27.00 (2·CH_2), 26.70 (CH_2), 25.30 (CH_2), 25.15 (CH_2).

TOF MS EI+: Calcd. for $C_{14}H_{24}O_2$: 224.1776; Found: 224.1767.

(3*R**,3a*S**,7a*R**)-3-[3-(1,3-dioxolan-2-yl)propyl]-hexahydrofuro[2,3-*b*]pyran (**3b_major**)

8h, (Hexane: EtOAc= 7:3), Pale yellow oily liquid (76 %).



Procedure: Compound **3b_major** and **3b_major** are prepared by following the general procedure as described above, with the following amounts of reagents.

a) *trans*-3-Iodo-2-(2-propenyloxy) tetrahydropyran (100 mg, 0.373 mmol)
b) Organozinc reagent 4 equiv. (2+2), (1.5mL, 0.746 mmol) + (1.5mL, 0.746 mmol),
c) Ni $(py)_4 Cl_2$ (16.6 mg, 0.037 mmol),
d) *s*-Bu-Pybox (12.3 mg, 0.037 mmol).

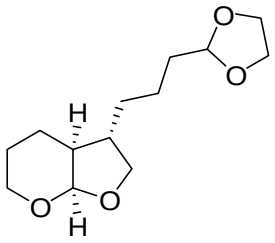
^{1}H NMR (300MHz, $CDCl_3$) *δ* 5.24, (d, *J* = 3.8 Hz, 1H), 4.81 (t, *J* = 4.7 Hz, 1H), 4.01-3.57 (m, 8H), 2.82-2.25 (m, 1H), 1.97-1.86 (m, 1H), 1.71-1.51 (m, 5H), 1.49-1.23 (m, 5H).

^{13}C NMR (500MHz, $CDCl_3$, DEPT-135) δ 104.59 (CH), 102.31 (CH), 70.30 (CH_2), 65.16 (2·CH_2), 61.23 (CH_2), 41.34 (CH), 36.74 (CH), 34.26 (CH_2), 27.30 (CH_2), 23.51 (CH_2), 23.00 (CH_2), 19.49 (CH_2).

EI+: Calcd. for $C_{13}H_{22}O_4$: 242.151809; Found: 242.151100.

(3*R**, 3a*R**, 7a*S**)-3-[3-(1, 3-dioxolan-2-yl) propyl]-hexahydrofuro [2, 3-*b*] pyran (**3b_minor**)

8h, (Hexane: EtOAc = 7:3), Pale yellow oily liquid (7%, mixture of two diastereomers).

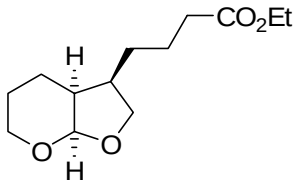


^{1}H NMR (300MHz, $CDCl_3$) δ 4.96 (d, *J* = 3.6 Hz, 1H), 4.26 (t, *J* = 8.2 Hz, 1H), 3.95-3.35 (m, 8H), 1.84-1.77 (m, 1H), 1.73-1.69 (m, 1H), 1.66-1.09 (m, 10H).

^{13}C NMR (500MHz, $CDCl_3$) δ Most signals overlap with those of the other major isomer.

Ethyl 4-[(3*R**, 3a*S**, 7a*R**)-hexahydro [2, 3-*b*] pyran-3-yl] butanoate (**3b´**)

16 h, (Hexane: EtOAc = 9:1), Pale yellow oily liquid (85 mg, 94%), (combined yield for both diastereoisomers).



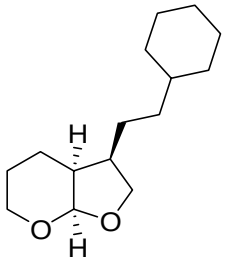
Procedure: Compound **3b´** was prepared according to the same procedure as described for **3b_major**, as a pale yellow oily liquid.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.25 (d, *J* = 3.6 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.94 (t, *J* = 8.2 Hz 1H), 3.77- 3.58 (m, 3H), 2.33-2.25 (m, 3H), 1.99-1.88 (m, 1H), 1.65-1.32 (m, 8H), 1.24 (t, J = 7.1 Hz, 3H).

^{13}C NMR (500MHz, $CDCl_3$) δ 173.3 (C), 102.05 (CH), 69.89 (CH_2), 61.1 (CH_2), 60.3 (CH_2), 40.9 (CH), 36.26 (CH), 39.5 (CH_2), 26.6 (CH_2), 23.6 (CH_2), 23.18 (CH_2), 19.3 (CH_2), 14.16 (CH_3).

(3*R**, 3a*S**, 7a*R**)-3-(2-cyclohexylethyl)-hexahydrofuro [2, 3-*b*] pyran (**3b´´**)

8h, (Hexane: EtOAc =20: 1), yellowish oily liquid (75 %)



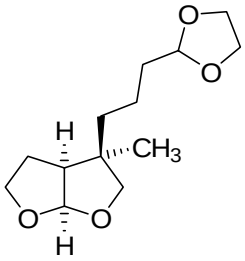
Procedure: Compound **3b´´** was prepared according to the same procedure as described for **3b_major**, as a pale yellow oily liquid.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.26 (d, *J* = 3.6 Hz, 1H), 3.93 (t, *J* = 7.8 Hz, 1H), 3.78-3.64 (m, 1H), 3.66-3.58 (m, 2H), 2.33-2.16 (m, 1H), 1.97-1.87 (m, 1H), 1.73-1.52 (m, 8H), 1.45-1.30 (m, 2H), 1.28-1.06 (m, 7H), 0.93-0.78 (m, 3H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 102.46 (CH), 70.58 (CH_2), 61.34 (CH_2), 41.67 (CH), 38.26 (CH), 36.87 (CH), 36.38 (CH_2), 33.80 (2·CH_2), 27.03 (CH_2), 26.73 (2·CH_2), 24.64 (CH_2), 23.66 (CH_2), 19.2 (CH_2).
EI+: Calcd. for $C_{15}H_{25}O_2$ (M^+-1): 237.185455; Found: 237.185500.

(3*R**, 3a*S**, 6a*R**)-3-[3-(1, 3-dioxolan-2-yl) propyl]-hexahydro3-methylfuro [2, 3-*b*] furan (**3c**)

8 h, (Hexane: EtOAc = 8:2), Pale yellow oily liquid (59 mg, 64 %).



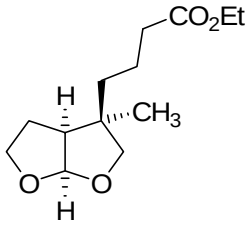
Procedure: Compound **3c** was prepared according to the general procedure as a pale yellow oily liquid, with the following amounts of reagents.

a) 2-(2-methylallyloxy)-tetrahydro -3-iodo furan (100 mg, 0.375 mmol)
b) Organozinc reagent 4 equiv. (2+2), (1.55mL, 0.752 mmol) + (1.55mL, 0.752 mmol),
c) Ni $(py)_4Cl_2$ (16.7 mg, 0.037 mmol),
d) *s*-Bu-Pybox (12.4 mg, 0.037 mmol).

^{1}H NMR (300MHz, $CDCl_3$) δ 5.74 (d, *J* = 4.8 Hz, 1H), 4.84 (t, *J* = 4.7 Hz, 1H), 4.02-3.76 (m, 6H), 3.54 (dd, *J* = 12.1, 8.4 Hz, 2H), 2.42-2.33 (m, 1H), 1.90-1.32 (m, 8H), 1.08 (s, 3H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 109.97 (CH), 104.63 (CH), 78.85 (CH_2), 69.15 (CH_2), 65.23 (2·CH_2), 52.90 (CH), 45.31 (C), 34.84 (2·CH_2), 26.49 (CH_2), 25.63 (CH_3), 19.93 (CH_2).
TOF MS EI+: Calcd. for $C_{13}H_{21}O_4$ (M^+-1): 241.1450; Found: 241.1440.

Ethyl 4-[(3*R**, 3a*S**, 6a*R**)-hexahydro3-methylfuro [2, 3-*b*] furan-3-yl] butanoate (**3c´**)
15 h, (Hexane: EtOAc = 7:3), Pale yellow oily liquid (62 mg, 68 %).



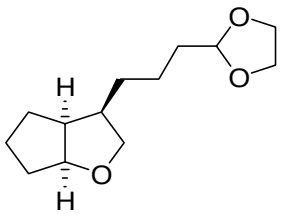
Procedure: Compound **3c´** was prepared according to the general procedure as a pale yellow oily liquid, with varying molar ratios of the reactant **3c**.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.76 (d, *J* = 4.9 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.96-3.77 (m, 2H), 3.55 (dd, *J* = 11.2, 8.3 Hz, 1H) 2.46-2.26 (m, 3H), 1.94-1.58 (m, 4H), 1.46-1.20 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H) 1.1 (s, 3H).

^{13}C NMR (500MHz, $CDCl_3$, DEPT-135) δ 173.67 (C), 109.98 (CH_2), 78.79 (CH_2), 69.16 (CH_2), 60.72 (CH_2), 52.79 (CH), 45.20 (C), 35.03 (CH_2), 34.31 (CH_2), 26.46 (CH_2), 25.58 (CH_3), 20.86 (CH_2), 14.61 (CH_3).

EI+: Calcd. for $C_{13}H_{21}O_4$ (M^+-1): 241.143984; Found: 241.143800.

Ethyl 4-[(3*R**,3a*S**,6a*S**)-3-(3-(1,3-dioxalan-2yl)propyl]-hexahydro-2*H*-cyclopenta [*b*] furan (**3d_major**):
9 h, (Hexane: EtOAc = 9:1), Pale yellow oily liquid (44 mg, 49 %).



Procedure: Compounds **3d_major** and **3d_minor** are prepared by following the general procedure as a pale yellow oily liquid, with the following amounts of reagents.

a) 1-(allyloxy)-2-iodocyclopentane (100 mg, 0.396 mmol),
b) Organozinc reagent 4 equiv. (2+2), (1.58mL, 0.793 mmol) + (1.58mL, 0.793 mmol),
c) Ni $(py)_4 Cl_2$ (17.6 mg, 0.039 mmol),
d) *s*-Bu-Pybox (13.0 mg, 0.039 mmol).

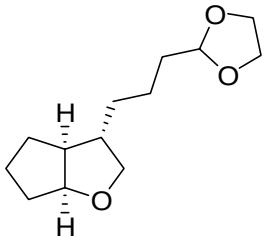
^{1}H NMR (300MHz, $CDCl_3$) δ 4.83 (t, *J* = 4.7 Hz, 1H), 4.53-4.46 (m, 1H), 3.93-3.79 (m, 5H), 3.29 (dtd, *J* = 8.4, 2.1, 1.7 Hz, 1H), 2.56-2.44 (m, 1H), 2.34-2.20 (m, 1H), 1.83-1.29 (m, 12H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 102.73 (CH), 86.25 (CH), 72.56 (CH_2), 65.12 (2.CH_2), 46.71 (CH), 43.50 (CH), 35.04 (CH_2), 34.38 (CH_2), 28.09 (CH_2), 26.26 (CH_2), 25.37 (CH_2), 23.61 (CH_2).

TOF MS EI+: Calcd. for $C_{13}H_{20}O_3$ (M^+-2): 226.1569; Found: 226.1576.

Ethyl 4-[(3*S**,3a*S**,6a*S**)-3-(3-(1,3-dioxalan-2yl)propyl]-hexahydro-2*H*-cyclopenta [*b*] furan (**3d_minor**).

9h, (Hexane: EtOAc = 9:1), Pale yellow oily liquid (25 mg, 27 %).



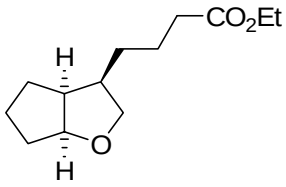
^{1}H NMR (300MHz, $CDCl_3$) δ 4.83 (t, *J* = 4.8 Hz, 1H), 4.42-4.35 (m, 1H), 4.01-3.78 (m, 5H), 3.17 (dt, *J* = 8.7 Hz, 1H) 2.24-2.12 (m, 1H), 1.84-1.31 (m, 13H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 104.83 (CH), 85.47 (CH), 73.98 (CH_2), 65.24 (2·CH_2), 50.10 (CH), 48.27 (CH), 34.51 (CH_2), 34.42 (CH_2), 33.26 (CH_2), 32.95 (CH_2), 24.24 (CH_2), 23.38 (CH_2).

TOF MS EI+: Calcd. for $C_{13}H_{22}O_3$: 226.1569; Found: 226.1566

Ethyl 4-[(3*R**,3a*S**,6a*S**)-hexahydro-2*H*-cyclopenta[*b*]furan-3-yl]butanoate (**3d_major**)

13 h, (Hexane: EtOAc = 9: 1), Pale yellow oily liquid (41 mg, 46%).



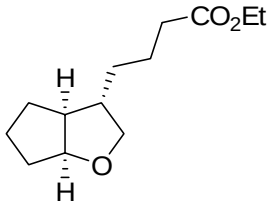
Procedure: Compounds **3d´_major** and **3d´_minor** are prepared by following the same procedure as described for **3d_major** as a pale yellow oily liquid.

^{1}H NMR (300MHz, $CDCl_3$) δ 4.49 (ddd, *J* = 5.8, 2.4 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.84(t, *J*= 7.7 Hz, 1H), 3.28 (dd, *J* = 10.6, 8.3 Hz, 1H) 2.56-2.44 (m, 1H), 2.33-2.19 (m, 3H), 1.83-1.29 (m, 10H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 173.83 (C), 86.33 (CH), 72.53 (CH_2), 60.61 (CH_2), 46.69 (CH), 43.33 (CH), 35.05 (CH_2), 34.82 (CH_2), 27.72 (CH_2), 26.31 (CH_2), 25.39 (CH_2), 24.55 (CH_2), 14.60 (CH_3).

TOF MS EI+: Calcd. for $C_{13}H_{20}O_3$ (M^+-2): 224.1412; Found: 224.1420.

Ethyl 4-[(3*S**,3a*S**,6a*S**)-hexahydro-2*H*-cyclopenta[*b*]furan-3-yl]butanoate (**3d´minor**)
13h, (Hexane: EtOAc = 9:1), Pale yellow oily liquid (32 mg, 35 %).

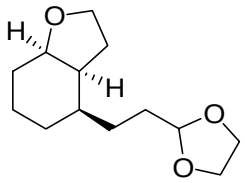


^{1}H NMR (300MHz, $CDCl_3$) δ 4.39 (t, *J* = 6.2 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.93 (dd, *J* = 8.5, 6.6 Hz, 1H), 3.17 (t, *J* = 8.6 Hz, 1H) 2.29 (t, *J* = 7.4 Hz, 2H), 2.23-2.13 (m, 1H), 1.90-1.32 (m, 11H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 173.87 (C), 85.48 (CH), 73.87 (CH_2), 60.64 (CH_2), 50.06 (CH), 48.04 (CH), 34.86 (CH_2), 34.39 (CH_2), 32.97 (CH_2), 32.81 (CH_2), 24.27 (CH_2), 24.24 (CH_2), 14.62 (CH_3).

TOF MS EI+: Calcd. for $C_{13}H_{20}O_3$ (M^+-2): 224.1412; Found: 224.1415.

(3a*S**, 4*R**, 7a*R**)-4-[2-(1, 3-dioxalan-2yl) ethyl]-octahydrobenzofuran (**3e**).
11 h, (Hexane: EtOAc = 9: 1), colourless oily liquid (44 mg, 46 %)



Procedure: Compound **3e** and **3e´** are prepared according to the general procedure as a colourless oily liquid, with varying molar ratios of the reactant.

a) 3-(2-iodoethoxy) cyclohex-1-ene, (100 mg, 0.423 mmol)
b) Organozinc reagent 4 equiv. (2+2), (1.69 mL, 0.847 mmol) + (1.69 mL, 0.847 mmol),
c) Ni (py) $_4$ Cl_2 (18.8 mg, 0.042 mmol),
d) *s*-Bu-Pybox (13.9 mg, 0.042 mmol).

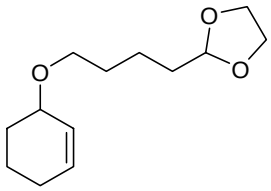
^{1}H NMR (300MHz, $CDCl_3$) δ 4.82 (t, *J* = 4.6 Hz, 1H), 3.99-3.73 (m, 7H), 2.09-1.39 (m, 11H), 1.19-0.75 (m, 3H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 105.19 (CH), 77.91 (CH), 66.27 (CH_2), 65.21 (2·CH_2), 43.97 (CH_2), 37.06 (CH), 31.64 (CH_2), 31.23 (CH_2), 30.33 (CH_2), 29.37 (CH_2), 28.62 (CH_2), 20.53(CH_2).

TOF MS EI+: Calcd. for $C_{13}H_{22}O_3$: 226.1569; Found: 226.1564.

2-[(4-cyclohex-2-enyloxy) butyl]-1, 3-dioxolane (**3e´**).

11 h, (Hexane: EtOAc = 9: 1), colourless oily liquid (35 mg, 36 %).



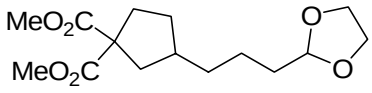
^{1}H NMR (300MHz, $CDCl_3$) δ 5.86-5.70 (m, 2H), 4.84 (t, *J* = 4.8 Hz, 1H), 3.98-3.77 (m, 5H), 3.54-3.38 (m, 2H), 2.11-1.41 (m, 12H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 130.92 (CH), 128.40 (CH), 104.92 (CH), 73.15 (CH), 68.35 (CH_2), 65.17 (2·CH_2), 34.06 (CH_2), 30.43 (CH_2), 28.69 (CH_2), 25.69 (CH_2), 21.22 (CH_2), 19.65 (CH_2).

TOF MS EI^+: Calc. for $C_{13}H_{22}O_3$: 226.1569; Found 225.1526.

Dimethyl 3-[3-(1, 3-dioxolan-2-yl)propyl]cyclopentane-1,1-dicarboxylate (**3f**)

6h, (Hexane: EtOAc = 9: 1), colourless oily liquid (58 mg, 64 %)



Procedure: Compound **3f** was prepared according to the general procedure with the following amounts of reagents.

a) Dimethyl 2-allyl-2-(2-iodoethyl) malonate (100 mg, 0.307 mmol), prepared by iodination (NaI/acetone) of Dimethyl 2-allyl-2-(2-bromoethyl) malonate[3]
b) Organozinc reagent 4 equiv. (2+2), (1.23 mL, 0.613 mmol) + (1.23 mL, 0.613 mmol),
c) Ni $(py)_4Cl_2$ (13.6 mg, 0.037 mmol),
d) *s*-Bu-Pybox (10.1 mg, 0.037 mmol).

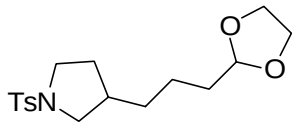
^{1}H NMR (300MHz, $CDCl_3$) δ 4.83 (t, *J* = 4.8 Hz, 1H), 3.99-3.80 (m, 4H), 3.71 (s, 3H), 3.70 (s, 3H), 2.51-2.41 (m, 1H), 2.35-2.05 (m, 2H), 2.00-1.80 (m, 2H), 1.74-1.59 (m, 3H), 1.47-1.21 (m, 5H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 173.52 (C), 173.51 (C), 104.83 (CH), 65.17 (2·CH_2), 60.23 (C), 50.95 (CH_3), 52.93 (CH_3), 41.14 (CH_2), 40.10 (CH_2), 35.49 (CH_2), 34.33 (CH_2), 34.23 (CH_2), 32.44 (CH_2), 23.32 (CH_2).

FAB$^+$ MS: Calcd. for $C_{15}H_{25}O_6$ (M^++1): 301.165114. Found: 301.164100

3-[3-(1,3-dioxolan-2-yl)propyl)]-1-tosylpyrrolidine (**3g**)

16 h, (Hexane: EtOAc = 7: 3), faint yellow oily liquid (66 mg, 83 %).



Procedure: Compound **3g** was prepared according to the general procedure with the following amounts of reagents.
a) *N*-(2-iodoethyl)-*N*-tosylprop-2-en-1-amine (100 mg, 0.274 mmol),
b) Organozinc reagent 4 equiv. (2+2), (1.1 mL, 0.549 mmol) + (1.1 mL, 0.549 mmol),
c) Ni (py) $_4$ Cl_2 (12.2 mg, 0.027 mmol),
d) *s*-Bu-Pybox (9.0 mg, 0.027 mmol).

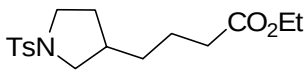
^{1}H NMR (300MHz, $CDCl_3$) δ 7.73-7.67 (m, 2H), 7.35-7.28 (m, 2H), 4.79 (t, *J* = 4.7 Hz, 1H), 3.98-3.79 (m, 4H), 3.43 (dd, *J* = 9.7, 7.5 Hz, 1H), 3.38-3.13 (m, 2H), 2.77 (dd, *J* = 9.8, 8.0 Hz, 1H), 2.43 (s, 3H), 2.05-1.85 (m, 2H), 1.63-1.52 (m, 2H), 1.45-1.21 (m, 5H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 143.62 (C), 134.23 (C), 129.94 (2·CH), 127.85 (2·CH), 104.55 (CH), 65.20 (2·CH_2), 53.55 (CH_2), 47.90 (CH_2), 39.13 (CH), 34.08 (CH_2), 33.29 (CH_2), 31.74 (CH_2), 22.83 (CH_2), 21.85(CH_3).

FAB$^+$: Calcd. for $C_{17}H_{26}NO_4S$ (M^++1): 340.158255. Found: 340.158400.

Ethyl 4-(1-tosylpyrrolidin-3-yl) butanoate (**3g´**)

19 h, (Hexane: EtOAc = 6: 4), faint yellow oily liquid (62 mg, 66 %).



Procedure:- Compound **3g´** was prepared according to the same procedure as used for the preparation of **3g**.

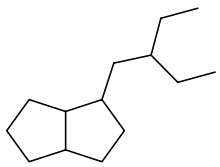
^{1}H NMR (300MHz, $CDCl_3$) δ 7.73-7.67 (m, 2H), 7.35-7.28 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.43 (dd, *J* = 9.3, 7.3 Hz, 1H), 3.38-3.12 (m, 2H), 2.77(dd, *J* = 9.8, 8.0 Hz, 1H), 2.43 (s, 3H), 2.23 (t, *J* = 7.4 Hz, 2H), 2.06-1.86 (m, 3H), 1.58-1.47 (m, 2H), 1.40-1.25 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 173.57 (C), 143.65 (C), 134.06 (C), 129.93 (2·CH), 127.80 (2·CH), 60.62 (CH_2), 53.43 (CH_2), 47.83 (CH_2), 38.87 (CH), 34.40 (CH_2), 32.78 (CH_2), 31.62 (CH_2), 23.69 (CH_2), 21.82 (CH_3), 14.53 (CH_3).

FAB$^+$-MS. Calcd. for $C_{17}H_{26}NO_4S$ (M^++1): 340.158255. Found: 340.159600.

1-(2-ethylbutyl)-octahydropentalene (**3h**):

22h, (Hexane only), colourless oily liquid (43 mg, 73 %).



Procedure: Compound **3h** was prepared according to the general procedure as a pale yellow oily liquid with the following amounts of reagents.

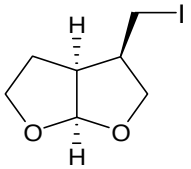
a) 1-(but-3-enyl)-2-iodocyclopentane[10.] (75mg, 0.3 mmol)
b) Organozinc reagent 4 equiv. (2+2), (1.2 mL, 0.6 mmol) + (1.2 mL, 0.6 mmol),
c) Ni (py)$_4$ Cl_2 (13.4 mg, 0.03 mmol),
d) *s*-Bu-Pybox (10 mg, 0.03 mmol).

^{1}H NMR (300MHz, $CDCl_3$) δ 2.47-2.21 (m, 1H),1.96-1.42 (m, 6H), 1.39-0.93 (m, 13H), 0.93-0.77 (m, 6H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 46.94 (CH), 42.90 (CH), 41.42 (CH), 39.62 (CH), 35.95 (CH_2), 34.65 (CH_2), 33.13 (2·CH_2), 31.98 (CH_2), 28.13 (CH_2), 28.03 (2·CH_2), 11.29 (2·CH_3).

(3*R**, 3a*S**, 6a*R*)-hexahydro-3-(iodomethyl)furo[2,3-*b*]furan (**4**):

4.5h, (Hexane: EtOAc = 8: 2), pale yellow oily liquid (220 mg, 91 %).



Procedure:

1 mmol of 2-(allyloxy)-3-iodo-tetrahydrofuran was taken in 10 ml of distilled water stirred of 5 min; flushed with argon, added 0.1 ml solution of Et_3B (1.0 M in hexanes), allowed to stir at rt for 4.5 hrs. Then extracted with ethyl acetate (2×20 ml), combined organic extracts dried over Na_2SO_4, concentrated and purified by silica gel chromatography.

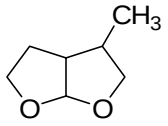
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (d, *J* = 4.86 Hz, 1H), 4.03 (dd, *J* = 7.13 Hz, 1H), 3.90 (dd, *J* = 6.21 Hz, 2H), 3.46 (dd, *J* = 8.66, 8.57 Hz, 1H), 3.17 (dd, *J* = 9.81, 7.60 Hz, 1H), 3.08 (dd, *J* = 9.81, 8.36 Hz, 1H), 2.97-2.72 (m, 2H), 2.01-1.76 (m, 2H).

^{13}C NMR (300 MHz, $CDCl_3$) δ 109.99 (CH), 72.38 (CH_2), 69.34 (CH_2), 46.89 (CH), 45.68 (CH), 24.78 (CH_2), 0.76 (CH_2).

TOF MS EI^+: Calcd. for $C_7H_{11}IO_2$: 253.9804; Found: 253.9800.

Hexahydro-3-methylfuro [2, 3-*b*] furan (**5**):

4.5h, (Hexane: EtOAc = 8: 2), pale yellow oily liquid (220 mg, 91 %).

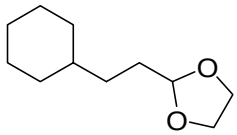


^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73 (d, *J* = 5.0 Hz, 1H), 3.96-3.79 (m, 3H), 3.37 (dd, *J* = 11.3, 8.5 Hz, 1H), 2.83-2.69 (m, 1H), 2.47-2.33 (m, 1H), 1.96-1.75 (m, 2H), 1.02 (d, *J* = 6.9, 3H).

^{13}C NMR (300 MHz, $CDCl_3$) δ 110.32 (CH), 74.21 (CH_2), 69.62 (CH_2), 46.90 (CH), 36.43 (CH), 25.47 (CH_2), 12.01 (CH_2).

2-(2-cyclohexylethyl)-1, 3-dioxolane (**7b**):

11h, (Hexane: EtOAc = 9: 1), colourless oily liquid (65 mg, 74 %).



Procedure: Compound **7b** was prepared according to the general procedure as a colourless oily liquid with the following amounts of reagents.

a) Cyclohexyl iodide (100 mg, 0.476 mmol) (commercial grade- Aldrich)
b) Organozinc reagent 4 equiv. (2+2), (1.9 mL, 0.952 mmol), + (1.9 mL, 0.952 mmol),
c) Ni $(py)_4Cl_2$ (21.2 mg, 0.047 mmol),
d) *s*-Bu-Pybox (15.6 mg, 0.047 mmol).

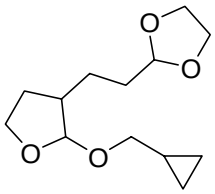
^{1}H NMR (300MHz, $CDCl_3$) δ 4.82 (t, *J* = 4.8 Hz, 1H), 4.02-3.86 (m, 4H), 1.76-1.57 (m, 7H), 1.34-1.07 (m, 6H), 0.95-0.77 (m, 2H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 105.30 (CH), 65.16 (2·CH_2), 37.88 (CH), 33.58 (2·CH_2), 31.90 (CH_2), 31.63 (CH_2), 26.98 (CH_2), 26.67 (2·CH_2).

TOF MS EI+: Calcd. for $C_{11}H_{19}O_2$ (M^+-1): 183.1385; Found: 183.1395.

2-(2-[(2*R**, 3*R**)-2-(cyclopropylmethoxy)-tetrahydrofuran-3-yl] ethyl)-1, 3-dioxolane (**7c_major**):

6h, (Hexane: EtOAc = 9: 1), colourless oily liquid (66 mg, 73 %)



Procedure: Compound **7c_major** and **7c_minor** was prepared according to the general procedure as a yellow oily liquid with the following amounts of reagents.

a) 2-(cyclopropyl methoxy) tetrahydro-3-iodofuran (100 mg, 0.373 mmol),
b) Organozinc reagent 4 equiv. (2+2), (1.49 mL, 0.746 mmol) + (1.49 mL, 0.746 mmol),
c) Ni $(py)_4Cl_2$ (16.6 mg, 0.037 mmol),
d) *s*-Bu-Pybox (11.2 mg, 0.037 mmol).

^{1}H NMR (300MHz, $CDCl_3$) δ 4.85 (t, *J* = 4.6 Hz, 1H), 4.81 (d, *J* = 1.5 Hz, 1H), 3.98-3.81 (m, 6H), 3.42 (dd, *J* = 10.4, 7.1 Hz, 1H), 3.25 (dd, *J* = 10.4, 6.9 Hz, 1H), 2.19-2.07 (m, 2H), 1.74-1.35 (m, 5H), 1.08-0.96 (m, 1H), 0.56-0.45 (m, 2H), 0.24-0.13 (m, 2H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 108.55 (CH), 104.56 (CH), 72.43 (CH_2), 66.88 (CH_2), 65.22 (2·CH_2), 45.59 (CH), 32.65 (CH_2), 30.90 (CH_2), 27.24 (CH_2), 10.89 (CH), 3.58 (CH_2), 3.16 (CH_2).

TOF MS EI+: Calcd. for $C_{13}H_{22}O_4$: 241.1440; Found: 241.1443.

2-(2-[(2*R**, 3*S**)-2-(cyclopropylmethoxy)-tetrahydrofuran-3-yl]ethyl)-1,3-dioxolane (**7c_minor**):

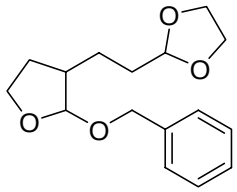
6h, (Hexane: EtOAc = 9: 1), colourless oily liquid, (Yield: 6 mg, 6 %)

^{1}H NMR (300MHz, $CDCl_3$) δ 4.85 (d, *J* = 4.9 Hz, 1H), 4.81 (t, *J* = 4.5 Hz, 1H), 3.98-3.78 (m, 6H), 3.47 (dd, *J* = 10.5, 6.6 Hz, 1H), 3.24 (dd, *J* = 10.6, 6.8 Hz, 1H), 1.79-1.59 (m, 2H), 1.79-1.58 (m, 4H), 1.08-0.78 (m, 2H), 0.55-0.40 (m, 2H), 0.26-0.11 (m, 2H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 105.01 (CH), 103.39 (CH), 71.72 (CH_2), 67.00 (CH_2), 65.25 (2·CH_2), 44.37 (CH), 33.15 (CH_2), 29.71 (CH_2), 23.55 (CH_2), 10.89 (CH), 3.55 CH_2), 2.94 (CH_2).

2-(2-[(2*R**, 3R*)-2-(benzyloxy)-tetrahydrofuran-3-yl] ethyl)-1, 3-dioxolane (**7d**):

16h, (Hexane: EtOAc = 8: 2), colourless oily liquid (66 mg, 72 %).



Procedure: Compound **7d** was prepared according to the general procedure as a yellow oily liquid with the following amounts of reagents.

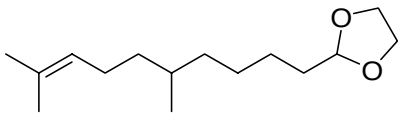
a) 2-(benzyl oxy)-tetrahydro-3-iodofuran (100 mg, 0.329 mmol)
b) Organozinc reagent 4 equiv. (2+2), (1.31 mL, 0.657 mmol), + (1.31 mL, 0.657 mmol),
c) Ni (py)$_4$ Cl$_2$ (14.6 mg, 0.032 mmol),
d) *s*-Bu-Pybox (10.8 mg, 0.032 mmol).

^{1}H NMR (300MHz, $CDCl_3$) δ 7.36-7.24 (m, 5H), 4.88 (d, J = 1.4 Hz, 1H), 4.84 (t, J = 4.6 Hz, 1H), 4.71 (d, J = 11.8 Hz, 1H), 4.46 (d, J = 11.8 Hz, 1H), 4.01-3.80 (m, 6H), 2.27-2.10 (m, 2H), 1.80-1.33 (m, 5H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 138.62 (C), 128.75 (2·CH), 128.62 (2·CH), 127.89 (CH), 108.21 (CH), 104.56 (CH), 69.43 (CH_2), 67.18 (CH_2), 65.27 (2·CH_2), 45.71 (CH), 32.65 (CH_2), 30.88 (CH_2), 27.18 (CH_2).

EI+: Calcd. for $C_{16}H_{21}O_4$ (M^+-1) 277.143984; Found: 277.143400.

2-(5, 9-dimethyldec-8-enyl)-1, 3-dioxolane (**7e**)
8h, (Hexane: EtOAc = 9: 1), colourless oily liquid (68 mg, 76 %)



Procedure: Compound **7e** was prepared according to the general procedure as a yellow oily liquid with the following amounts of reagents.

a) 8-iodo-2, 6-dimethyl oct-2-ene (100 mg, 0.375 mmol)
b) Organozinc reagent 4 equiv. (2+2), (1.5 mL, 0.751 mmol) + (1.5 mL, 0.751 mmol),
c) Ni (py)$_4$ Cl$_2$ (16.7 mg, 0.037 mmol),
d) *s*-Bu-Pybox (12.3 mg, 0.037 mmol).

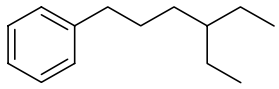
^{1}H NMR (300MHz, $CDCl_3$) δ 5.13-5.05 (m, 1H), 4.84 (t, J = 4.9 Hz, 1H), 3.99-3.81 (m, 4H), 2.06-1.84 (m, 2H), 1.67 (s, 3H), 1.59 (s, 3H), 1.71 (m, 3H), 1.47-1.03 (m, 8H), 0.85 (d, 3H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 131.29 (C), 125.40 (CH), 105.06 (CH), 65.18 (2·CH_2), 37.48 (CH_2), 37.20 (CH_2), 34.32 (CH_2), 32.66 (CH), 27.31 (CH_2), 26.06 (CH_2), 25.92 (CH_3), 24.77 (CH_2), 19.92 (CH_3), 17.97 (CH_3).

EI+: Calcd. for $C_{15}H_{28}O_2$: 240.208930; Found: 240.208800.

(4-ethylhexyl)benzene (**7f**):

18h, (Hexane only), pale yellow oily liquid (47 mg, not pure. GC-MS indicates de presence of isomers which could not be separated by column chromatography).



Procedure: Compound **7f** was prepared according to the general procedure as a pale yellow oily liquid with the following amounts of reagents.

a) (3-iodopropyl) benzene (100 mg, 0.406 mmol)
b) Organozinc reagent 4 equiv. (2+2), (1.62 mL, 0.815 mmol) + (1.62 mL, 0.815 mmol),
c) Ni (py) $_4$ Cl_2 (18.1 mg, 0.041 mmol),
d) *s*-Bu-Pybox (13.4 mg, 0.041 mmol).

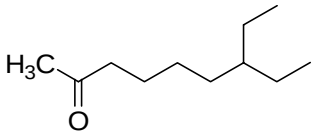
^{1}H NMR (300MHz, $CDCl_3$) δ 7.31-7.13 (m, 5H), 2.58 (t, *J* =7.8 Hz, 2H), 1.66-1.50 (m, 2H), 1.34-1.17 (m, 7H), 0.82 (t, *J*=7.2 Hz, 6H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 143.37 (C), 128.75 (2·CH), 128.60 (2·CH), 125.94 (CH), 40.66 (CH), 36.82 (CH_2), 32.86 (CH_2), 29.13 (CH_2), 25.79 (2·CH_2), 11.29 (2·CH_3).

TOF MS EI+: Calcd. for $C_{14}H_{22}$: 190.1722; Found: 190.1717.

7-ethylnonan-2-one (**7g**):

11h, (Hexane: EtOAc = 50: 1), colourless oily liquid (50 mg, not pure).



Procedure: Compound **7g** was prepared according to the general procedure as a colourless oily liquid with the following amounts of reagents.

a) 6-iodohexan-2-one (100 mg, 0.442 mmol)
b) Organozinc reagent 4 equiv. (2+2), (1.77 mL, 0.885 mmol) + (1.77 mL, 0.885 mmol),
c) Ni (py) $_4$ Cl_2 (19.7 mg, 0.044 mmol),
d) *s*-Bu-Pybox (14.5 mg, 0.044 mmol).

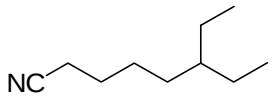
^{1}H NMR (300MHz, $CDCl_3$) δ 2.42 (t, *J* =7.5 Hz, 2H), 2.13 (s, 3H), 1.63-1.48 (m, 2H), 1.34-1.19 (m, 8H), 0.95-0.82 (m, 1H), 0.82 (t, *J*=7.2 Hz, 6H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 209.73 (C), 44.25 (CH_2), 40.59 (CH), 32.90 (CH_2), 30.22 (CH_3), 26.75 (CH_2), 25.76 (2·CH_2), 24.71 (CH_2), 11.25 (2·CH_3).

TOF MS EI+: Calcd. for $C_{11}H_{22}O$: 170.1671; Found: 170.1671.

6-ethyloctanenitrile (**7h**):

11h, (Hexane: EtOAc = 50: 1), colourless oily liquid (52 mg, not pure).



Procedure: Compound **7h** was prepared according to the general procedure as a colourless oily liquid with the following amounts of reagents.

a) 6-iodopentanenitrile (100 mg, 0.476 mmol)
b) Organozinc reagent 4 equiv. (2+2), (1.91 mL, 0.957 mmol) + (1.91 mL, 0.957 mmol),
c) Ni $(py)_4 Cl_2$ (21.3 mg, 0.048 mmol),
d) *s*-Bu-Pybox (15.7 mg, 0.048 mmol).

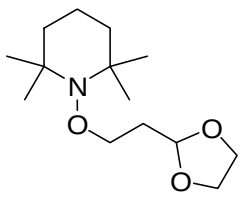
^{1}H NMR (300MHz, $CDCl_3$) δ 2.34 (t, *J* =7.1 Hz, 2H), 1.71-1.57 (m, 2H), 1.49-1.17 (m, 7H), 0.93-0.83 (m, 2H), 0.83 (t, *J*=7.2 Hz, 6H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 120.16 (C), 40.51 (CH), 32.26 (CH_2), 26.29 (CH_2), 26.17 (CH_2), 25.67 (2·CH_2), 17.49 (CH_2), 11.18 (2·CH_3).

TOF MS EI+: Calcd. for $C_{10}H_{19}N$ (M^+-1): 152.1439; Found: 152.1432.

1-[2-(1,3-dioxolan-2-yl)ethoxy]-2,2,6,6-tetramethylpiperidine (**8**).

20h, (Hexane: EtOAc = 20: 1), yellow oily liquid (68 mg, 60 %).

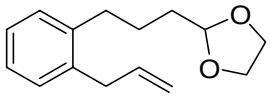


^{1}H NMR (300MHz, $CDCl_3$) δ 5.12 (t, *J* = 4.9 Hz, 1H), 4.10-3.90 (m, 6H), 1.97 (q, *J*=6.4 Hz, 2H), 1.61-1.31 (m, 6H), 1.24 (s, 6H), 1.16 (s, 6H).

(see ^{13}C NMR spectrum below).

ESI MS: Calcd. for $C_{14}H_{28}NO_3$ (M^++1): 258.2063; Found: 258.2060.

2-[3-(2-allylphenyl) propyl]-1, 3-dioxolane (**11a**):
3h, (Hexane: EtOAc = 20: 1), colourless oily liquid (71 mg, 82 %).



Procedure: Compound **11a** was prepared according to the general procedure as a yellow oily liquid with the following amounts of reagents.

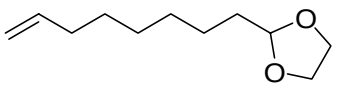
a) 1-allyl-2-(iodomethyl) benzene[7] (100 mg, 0.364 mmol)
b) Organozinc reagent 4 equiv. (2+2), (1.46 mL, 0.729 mmol) + (1.46 mL, 0.729 mmol),
c) Ni (py) $_4$ Cl_2 (16.2 mg, 0.036 mmol),
d) *s*-Bu-Pybox (12.0 mg, 0.036 mmol).

^1H NMR (300MHz, $CDCl_3$) δ 7.24-7.12 (m, 4H), 5.96 (ddt, *J* =16.5, 10.2, 6.3 Hz, 1H), 5.06 (dm, *J* = 10.0, 1.8 Hz, 1H), 5.00 (dm, *J* = 16.9, 1.8 Hz, 1H), 4.02-3.81 (m, 4H), 3.40 (dt, *J* = 6.4, 1.6 Hz, 2H), 2.71-2.62 (m, 2H), 1.78-1.68 (m, 4H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 140.59 (C), 137.88 (C), 137.70 (CH), 129.91 (CH), 129.56 (CH), 126.67 (CH), 126.41 (CH), 115.95 (CH_2), 104.77 (CH), 65.20 (2·CH_2), 37.36 (CH_2), 34.05 (CH_2), 32.81 (CH_2), 25.49 (CH_2).

TOF MS EI+: Calcd. for $C_{15}H_{20}O_2$: 232.1463; Found: 232.1470.

2-(oct-7-enyl)-1, 3-dioxolane (**11b**)
5 h, (Hexane: EtOAc = 20: 1), colourless oily liquid (36 mg, 41 %).



Procedure: Compound **11b** was prepared according to the general procedure as a yellow oily liquid with the following amounts of reagents.

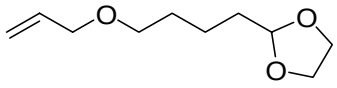
a) 6-iodohex-1-ene (100 mg, 0.476 mmol), prepared by iodination (NaI/acetone) of 6-bromohex-1-ene
b) Organozinc reagent 4 equiv. (2+2), (1.9 mL, 0.95 mmol), + (1.9 mL, 0.95 mmol),
c) Ni (py) $_4$ Cl_2 (21.2 mg, 0.047 mmol),
d) *s*-Bu-Pybox (14.1 mg, 0.047 mmol).

^{1}H NMR (300MHz, $CDCl_3$) δ 7.79 (ddt, *J* = 17.0, 10.1, 6.6 Hz, 1H), 5.02-4.87 (m, 2H), 4.83 (t, *J* = 4.8 Hz, 1H), 3.99-3.80 (m, 4H), 2.07-1.97 (m, 2H), 1.66-1.60 (m, 2H), 1.41-1.28 (m, 8H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 139.49 (CH), 114.54 (CH_2), 105.03 (CH), 65.19 (2·CH_2), 34.25 CH_2), 34.12 (CH_2), 29.74 (CH_2), 29.37 (CH_2), 29.14 (CH_2), 24.39 (CH_2).

2-[4-(allyloxy) butyl]-1, 3-dioxolane (**11c**)

11 h, (Hexane: EtOAc = 10: 1), faint yellow oily liquid (22 mg, 25 %).



Procedure: Compound **11c** was prepared according to the General procedure, with varying molar ratios of all reactants.

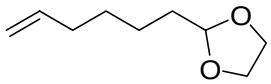
a) 3-(2-iodoethoxy)prop-1-ene[8] (100 mg, 0.472 mmol)
b) Organozinc reagent 4 equiv. (2+2), (1.9 mL, 0.943 mmol), + (1.9 mL, 0.943 mmol),
c) Ni (py) $_4$ Cl_2 (21.0 mg, 0.047 mmol),
d) *s*-Bu-Pybox (15.5 mg, 0.047 mmol).

^{1}H NMR (300MHz, $CDCl_3$) δ 5.90 (ddt, *J* =16.0, 10.4, 5.6 Hz, 1H), 5.25 (dm, *J* = 17.3, 1.6 Hz, 1H), 5.15 (dm, *J* = 10.4, 1.4 Hz, 1H), 4.84 (t, *J* = 4.7 Hz, 1H), 3.97-3.80 (m, 6H), 3.42 (t, *J* = 6.5 Hz, 2H), 1.66-1.44 (m, 4H), 0.95-0.80 (m, 2H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 135.41 (CH), 117.09 (CH_2), 104.92 (CH), 72.18 CH_2), 70.54 (CH_2), 65.21 (2·CH_2), 34.03 (CH_2), 29.97 (CH_2), 21.13 (CH_2).

2-(hex-5-enyl)-1,3-dioxolane (**11d**):

5h, (Hexane: EtOAc = 20: 1), colourless oily liquid (54 mg, 63 %).



Procedure:- same as General procedure, with varying molar ratios of all reactants.

a) (iodomethyl) cyclopropane (100 mg, 0.549 mmol), prepared by following the procedure described in reference number 6.
b) Organozinc reagent 4 equiv. (2+2), (2.2 mL, 1.09 mmol), + (2.2 mL, 1.09 mmol),
c) Ni (py) $_4$ Cl_2 (24.4 mg, 0.054 mmol),
d) *s*-Bu-Pybox (18.1 mg, 0.054 mmol).

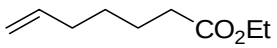
^{1}H NMR (300MHz, $CDCl_3$) δ 7.79 (ddt, *J* =17.0, 10.3, 6.7 Hz, 1H), 5.02 (dm, *J*=17.1, 1.7 Hz, 1H), 4.94 (dm, *J*=10.7, 1.2 Hz, 1H), 4.83 (t, *J* = 4.8 Hz, 1H), 3.98-3.80 (m, 4H), 2.11-2.01 (m, 2H), 1.07-1.61 (m, 2H), 1.48-1.40 (m, 4H).

^{13}C NMR (300MHz, $CDCl_3$, DEPT-135) δ 139.15 (CH), 114.4 (CH_2), 104.99 (CH), 65.2 (2·CH_2), 34.12 CH_2), 34.05 (CH_2), 29.20 (CH_2), 23.95 (CH_2).

TOF MS EI+: Calcd. for $C_9H_{16}O_2$: 156.1150; Found: 155.1136

Ethyl hept-6-enoate (**11d´**)

4h, (Hexane: EtOAc = 20: 1), colourless oily liquid(59 %).



Procedure: same as general procedure with same molar ratios as used for preparation of **11d**.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.78 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.03-4.91 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.29 (t, *J* = 7.5 Hz, 2H), 2.10-2.01 (m, 2H), 1.69-1.57 (m, 2H), 1.47-1.35 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (300MHz, $CDCl_3$) δ 174.07 (C), 138.81 (CH), 115.02 (CH_2), 60.55 (CH_2), 34.57 CH_2), 33.73 (CH_2), 28.73 (CH_2), 24.85 (CH_2), 14.61 (CH_3).

TOF MS EI+: Calcd. for $C_9H_{16}O_2$: 156.1150; Found: 155.1154.

Computational methods

Calculations were performed with Gaussian 03 at DFT level.[10a] The geometries of all complexes here reported were optimized using the B3LYP hybrid functional.[10b] For radical species UB3LYP was used. Optimizations were carried out using the standard 6-31G(d) basis set for C, H, and N. The LANL2DZ basis set, which includes the relativistic effective core potential (ECP) of Hay and Wadt and employs a split-valence (double-ζ) basis set, was used for Ni and I.[10c] Harmonic frequencies were calculated at the same level to characterize the stationary points and to determine the zero-point energies (ZPE). The starting approximate geometries for the transition states (TS) were graphically located. Intrinsic reaction coordinate (IRC) studies were performed to confirm the relation of the transition states with the corresponding minima.

I

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 Zero-point  correction=                                          0.306800
(Hartree/Particle)
 Thermal correction to Energy=                    0.326107
 Thermal correction to Enthalpy=                  0.327051
 Thermal correction to Gibbs Free Energy=         0.258803
 Sum of electronic and zero-point Energies=          -1028.030883
 Sum of electronic and thermal Energies=             -1028.011577
 Sum of electronic and thermal Enthalpies=           -1028.010633
 Sum of electronic and thermal Free Energies=        -1028.078880

---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1         28             0       -0.015129   -0.726435    0.032025
    2          7             0       -0.020972    1.097959    0.304284
    3          6             0        0.060355    3.770172   -0.181725
    4          6             0       -1.180700    1.713575   -0.063476
    5          6             0        1.218712    1.699953    0.256128
    6          6             0        1.248270    3.110764    0.060004
    7          6             0       -1.182011    3.089792   -0.283626
    8          1             0        2.205776    3.638073    0.085269
    9          1             0       -2.097209    3.626544   -0.544161
   10          1             0        0.064420    4.855274   -0.328558
   11          7             0        1.845787   -0.634647    0.200438
   12          6             0        3.116571   -1.459497    0.207109
   13          6             0        4.203921   -0.374445    0.356051
   14          8             0        3.549743    0.903146    0.350272
   15          6             0        2.197459    0.683348    0.264446
   16          1             0        3.105177   -2.147974    1.087350
   17          1             0        4.763939   -0.435841    1.304122
   18          1             0        4.930735   -0.353005   -0.473844
   19          7             0       -1.873528   -0.615911   -0.118647
   20          6             0       -3.149436   -1.435724   -0.134380
   21          6             0       -4.222502   -0.342246   -0.325222
   22          8             0       -3.538060    0.926213   -0.332656
   23          6             0       -2.203066    0.682127   -0.189222
   24          1             0       -3.130634   -2.149394   -0.995180
   25          1             0       -4.764566   -0.409517   -1.282988
   26          1             0       -4.961422   -0.294572    0.492946
   27          6             0        3.279846   -2.265754   -1.067369
   28          1             0        4.313684   -2.622334   -1.170065
   29          1             0        3.039120   -1.680242   -1.965481
   30          1             0        2.629429   -3.151427   -1.072137
   31          6             0       -3.312208   -2.200339    1.165835
   32          1             0       -4.314914   -2.644448    1.223693
   33          1             0       -3.182700   -1.554371    2.045639
   34          1             0       -2.584766   -3.019946    1.256194
   35          6             0        0.020447   -2.649320   -0.394760
   36          1             0        0.344702   -2.787264   -1.432568
   37          1             0       -0.983177   -3.070637   -0.266515
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II

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 Zero-point correction=                           0.356799
(Hartree/Particle)
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Thermal correction to Energy= 0.380404
Thermal correction to Enthalpy= 0.381349
Thermal correction to Gibbs Free Energy= 0.298076
Sum of electronic and zero-point Energies= -1081.264918
Sum of electronic and thermal Energies= -1081.241312
Sum of electronic and thermal Enthalpies= -1081.240368
Sum of electronic and thermal Free Energies= -1081.323641

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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3	1	0	0.080399	-0.008401	3.864765
4	1	0	1.433739	0.688585	2.965933
5	1	0	1.203676	-1.062577	2.999918
6	7	0	-0.696316	2.161646	1.030527
7	6	0	-1.058646	4.853625	0.399539
8	6	0	-1.508865	2.514909	-0.014154
9	6	0	-0.086653	3.123661	1.742390
10	6	0	-0.231039	4.476182	1.473777
11	6	0	-1.695348	3.872815	-0.340989
12	7	0	-1.811316	0.165156	-0.207580
13	6	0	-3.565874	0.358956	-2.355729
14	6	0	-2.359125	-0.972698	-0.744121
15	6	0	-2.138350	1.399414	-0.710414
16	6	0	-3.012828	1.514340	-1.788477
17	6	0	-3.237354	-0.894467	-1.822017
18	7	0	-1.078151	-2.036814	0.964254
19	6	0	-1.929156	-4.597529	0.260383
20	6	0	-0.652553	-3.114690	1.643100
21	6	0	-1.944477	-2.204970	-0.082902
22	6	0	-2.377669	-3.495225	-0.446825
23	6	0	-1.043028	-4.409510	1.337209
24	1	0	-1.199831	5.902169	0.152823
25	1	0	0.538630	2.770810	2.557447
26	1	0	0.283136	5.213870	2.080839
27	1	0	-2.338426	4.148184	-1.170232
28	1	0	-4.248259	0.434383	-3.196208
29	1	0	-3.270572	2.489132	-2.189185
30	1	0	-3.670024	-1.793249	-2.248954
31	1	0	-2.260737	-5.594837	-0.014677
32	1	0	0.028880	-2.907387	2.463101
33	1	0	-3.062663	-3.623289	-1.278229
34	1	0	-0.669993	-5.246419	1.918188
35	6	0	5.044256	-0.110439	-1.261571
36	6	0	3.957285	0.009870	-0.205324
37	6	0	4.051510	-1.019849	0.908276
38	1	0	5.036478	-1.098704	-1.732550
39	1	0	6.021265	0.025482	-0.776140
40	1	0	4.944058	0.647854	-2.042732
41	1	0	3.910734	1.022300	0.198501
42	1	0	3.250906	-0.900405	1.642049
43	1	0	5.014006	-0.889930	1.424149
44	1	0	4.015654	-2.040017	0.512061
45	53	0	1.947980	-0.153656	-1.196932

TS1

Zero-point correction= 0.355423
(Hartree/Particle)
Thermal correction to Energy= 0.379783
Thermal correction to Enthalpy= 0.380727
Thermal correction to Gibbs Free Energy= 0.296193
Sum of electronic and zero-point Energies= -1081.256210
Sum of electronic and thermal Energies= -1081.231850
Sum of electronic and thermal Enthalpies= -1081.230906
Sum of electronic and thermal Free Energies= -1081.315440

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	6	0	-0.088624	0.055268	-2.854307
3	1	0	-0.024716	-0.767271	-3.585245
4	1	0	0.719847	0.764966	-3.076834
5	1	0	-1.033279	0.587169	-3.031906
6	7	0	2.189929	-0.867172	-0.683696
7	6	0	4.876666	-1.143454	-0.013054
8	6	0	2.541413	-1.529355	0.449868
9	6	0	3.146184	-0.354423	-1.468830
10	6	0	4.501573	-0.466138	-1.179932
11	6	0	3.890780	-1.677433	0.806554
12	7	0	0.190179	-1.778207	0.727933
13	6	0	0.395584	-3.218559	3.085400
14	6	0	-0.935137	-2.237812	1.334249
15	6	0	1.416578	-2.050137	1.244030
16	6	0	1.546513	-2.766522	2.434300
17	6	0	-0.858512	-2.958993	2.526386
18	7	0	-2.031016	-1.185644	-0.511017
19	6	0	-4.581785	-1.878777	0.361338
20	6	0	-3.114536	-0.823902	-1.210805
21	6	0	-2.185633	-1.899840	0.635282
22	6	0	-3.463587	-2.256536	1.093193
23	6	0	-4.409000	-1.146086	-0.819725
24	1	0	5.924467	-1.251567	0.252139
25	1	0	2.792190	0.161998	-2.355535
26	1	0	5.240151	-0.034289	-1.847168
27	1	0	4.164878	-2.202094	1.715292
28	1	0	0.475722	-3.775852	4.013391
29	1	0	2.524396	-2.978453	2.852036
30	1	0	-1.755592	-3.320268	3.016740
31	1	0	-5.576071	-2.149167	0.705069
32	1	0	-2.916042	-0.253423	-2.112726
33	1	0	-3.580525	-2.821117	2.011714
34	1	0	-5.255845	-0.830910	-1.420333
35	6	0	0.340316	4.925928	1.836900
36	6	0	-0.091035	4.470579	0.475045
37	6	0	-1.466120	4.834121	0.002625
38	1	0	-0.394001	4.656350	2.605029
39	1	0	0.437697	6.026802	1.855098
40	1	0	1.308620	4.504086	2.121652
41	1	0	0.683183	4.478524	-0.288746
42	1	0	-1.712418	4.346832	-0.945142
43	1	0	-1.537383	5.925978	-0.153285
44	1	0	-2.230479	4.563249	0.740073
45	53	0	-0.100827	1.778473	0.647574

III

```
 Zero-point correction=                           0.354433
(Hartree/Particle)
 Thermal correction to Energy=                    0.379945
 Thermal correction to Enthalpy=                  0.380889
 Thermal correction to Gibbs Free Energy=         0.289353
 Sum of electronic and zero-point Energies=          -1081.270241
 Sum of electronic and thermal Energies=             -1081.244728
 Sum of electronic and thermal Enthalpies=           -1081.243784
 Sum of electronic and thermal Free Energies=        -1081.335320

---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
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    2          6             0       -0.253860    0.029326   -2.582842
    3          1             0       -0.273242   -0.735516   -3.377568
    4          1             0        0.563337    0.727612   -2.805632
    5          1             0       -1.187287    0.603956   -2.640378
    6          7             0        2.149886   -1.061038   -0.582495
    7          6             0        4.860177   -1.373935   -0.065765
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    9          6             0        3.055315   -0.360558   -1.269266
   10          6             0        4.426695   -0.482488   -1.045111
   11          6             0        3.916401   -2.103640    0.654578
   12          7             0        0.228554   -2.342313    0.675559
   13          6             0        0.559703   -4.110353    2.756749
   14          6             0       -0.853937   -2.898547    1.240374
   15          6             0        1.468931   -2.628915    1.099858
   16          6             0        1.672152   -3.524950    2.156087
   17          6             0       -0.720347   -3.801848    2.301387
   18          7             0       -2.068975   -1.557138   -0.333137
   19          6             0       -4.554985   -2.479620    0.492007
   20          6             0       -3.185022   -1.099731   -0.905421
   21          6             0       -2.154020   -2.470992    0.656726
   22          6             0       -3.391287   -2.957810    1.091309
   23          6             0       -4.455558   -1.531626   -0.524475
   24          1             0        5.919086   -1.499814    0.140349
   25          1             0        2.654058    0.320382   -2.012884
   26          1             0        5.128282    0.110413   -1.622468
   27          1             0        4.238550   -2.798223    1.422211
   28          1             0        0.690047   -4.803801    3.582183
   29          1             0        2.668738   -3.758586    2.511756
   30          1             0       -1.587860   -4.251103    2.770259
   31          1             0       -5.524924   -2.842862    0.818951
   32          1             0       -3.041219   -0.359977   -1.686218
   33          1             0       -3.452849   -3.693885    1.885023
   34          1             0       -5.337136   -1.129128   -1.012246
   35          6             0       -0.142361    6.562483    1.922370
   36          6             0       -0.245641    5.799534    0.642732
   37          6             0       -0.800068    6.437886   -0.588098
   38          1             0       -1.129613    6.720206    2.396894
   39          1             0        0.281800    7.565873    1.765659
   40          1             0        0.480491    6.040415    2.657699
   41          1             0       -0.151909    4.716490    0.671337
   42          1             0       -0.602969    5.835567   -1.482305
   43          1             0       -0.379014    7.441510   -0.751522
   44          1             0       -1.897012    6.573424   -0.531747
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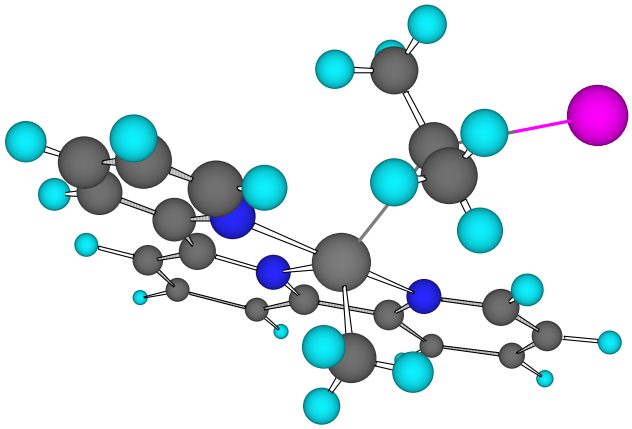
45	53	0	-0.168065	1.228428	1.053645

Transition state for the reaction of (tpy)NiMe with 2-iodopropane releasing atomic iodine:



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Sum of electronic and zero-point Energies= -1081.236351
Sum of electronic and thermal Energies= -1081.210703
Sum of electronic and thermal Enthalpies= -1081.209759
Sum of electronic and thermal Free Energies= -1081.299209

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	0.636498	-0.401846	0.176607
2	7	0	0.595625	0.117324	-1.937596
3	6	0	0.159745	0.588910	-4.645438
4	6	0	-0.656427	0.385355	-2.388172
5	6	0	1.614293	0.094417	-2.807883
6	6	0	1.444415	0.327664	-4.171518
7	6	0	-0.902723	0.619725	-3.745156
8	7	0	-1.272738	0.145024	-0.097122
9	6	0	-3.918204	0.815729	-0.478341
10	6	0	-2.098504	0.212729	0.975873
11	6	0	-1.706990	0.430747	-1.345562
12	6	0	-3.041674	0.767346	-1.568835
13	6	0	-3.446632	0.546435	0.804542
14	7	0	-0.123661	-0.376253	2.194523
15	6	0	-1.409191	-0.285276	4.668232
16	6	0	0.542573	-0.645237	3.326792
17	6	0	-1.447830	-0.064330	2.266077
18	6	0	-2.110687	-0.009614	3.501649

19	6	0	-0.050240	-0.612882	4.583654
20	6	0	1.042717	-2.356692	-0.017771
21	1	0	-0.015215	0.774246	-5.701094
22	1	0	2.601803	-0.088192	-2.396334
23	1	0	2.305588	0.315199	-4.830263
24	1	0	-1.907461	0.826114	-4.096573
25	1	0	-4.961304	1.074007	-0.631512
26	1	0	-3.400404	0.999129	-2.564766
27	1	0	-4.119647	0.598870	1.652759
28	1	0	-1.911334	-0.246399	5.630212
29	1	0	1.591683	-0.897625	3.207714
30	1	0	-3.163311	0.246787	3.548722
31	1	0	0.534652	-0.840744	5.468303
32	1	0	1.853053	-2.487360	-0.745102
33	1	0	0.146357	-2.872750	-0.379575
34	1	0	1.341130	-2.779249	0.948610
35	6	0	2.622133	2.104634	1.613176
36	6	0	2.912795	0.973562	0.676517
37	6	0	3.841188	-0.125070	1.096418
38	1	0	3.553260	2.593766	1.929674
39	1	0	2.123968	1.753242	2.532333
40	1	0	1.989059	2.864919	1.147242
41	1	0	2.454198	0.964764	-0.302019
42	1	0	3.469861	-0.656481	1.988724
43	1	0	4.823682	0.284243	1.366951
44	1	0	3.992046	-0.861676	0.303587
45	53	0	4.638857	2.294787	-1.401258

References:-

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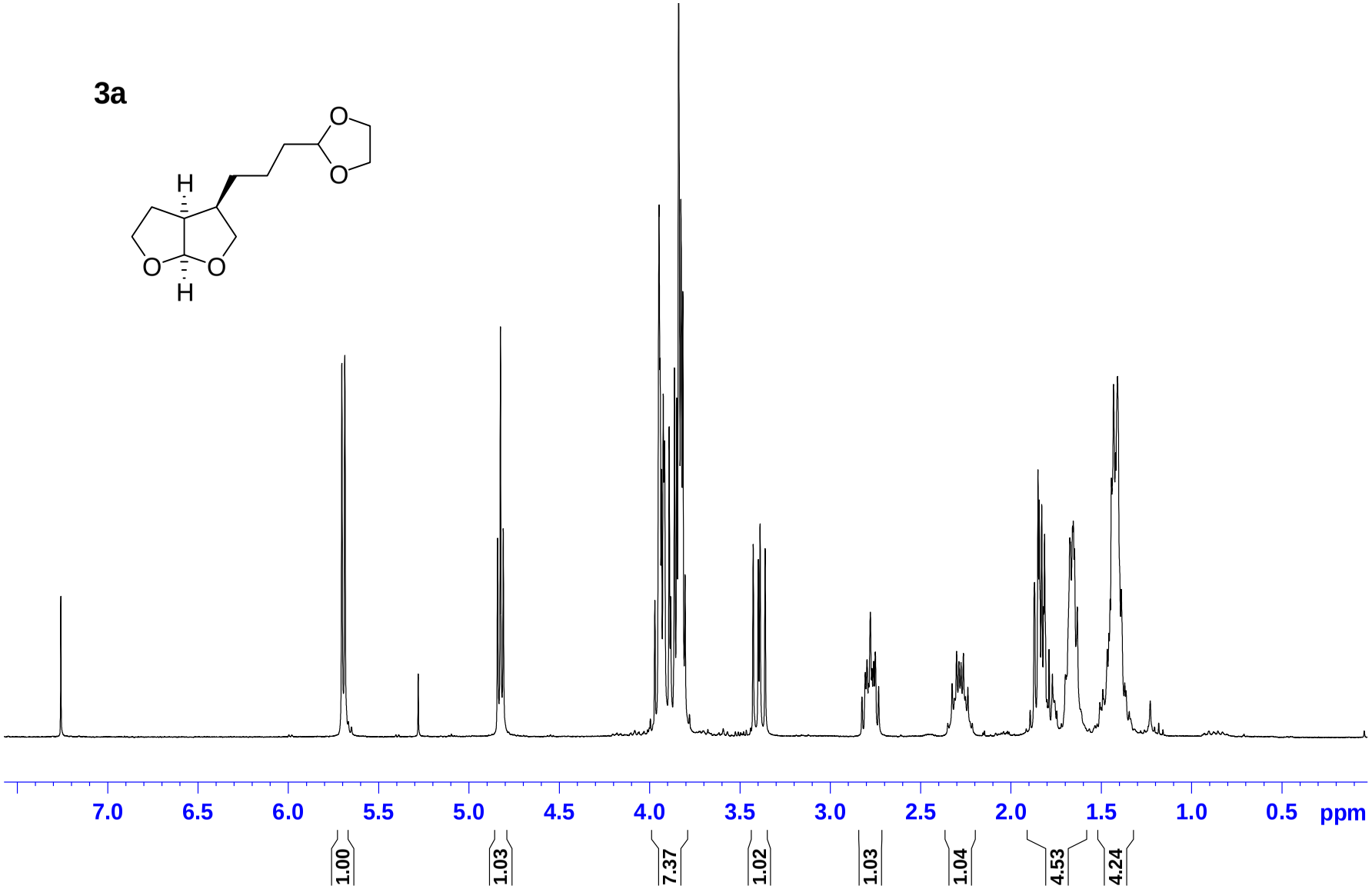
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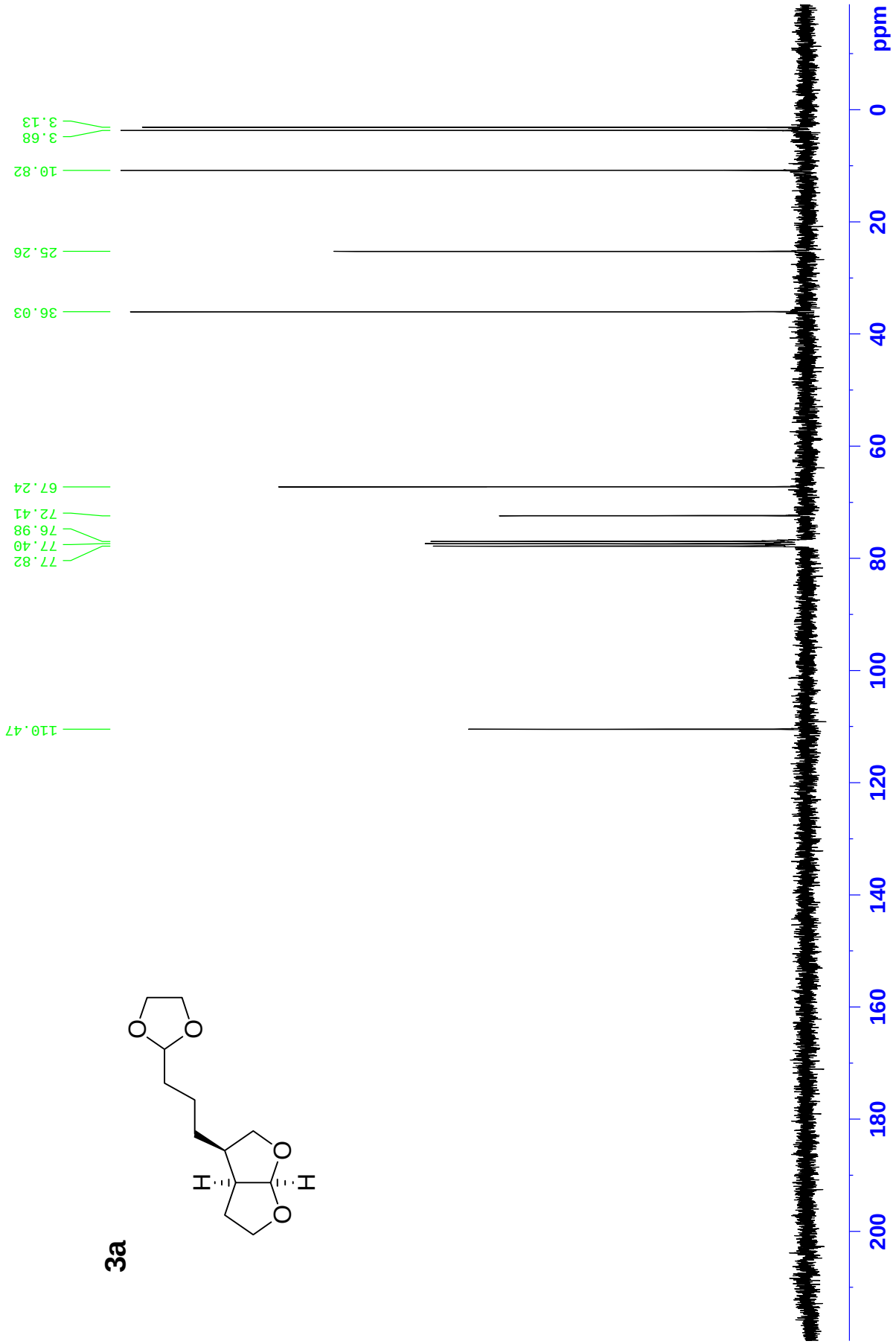
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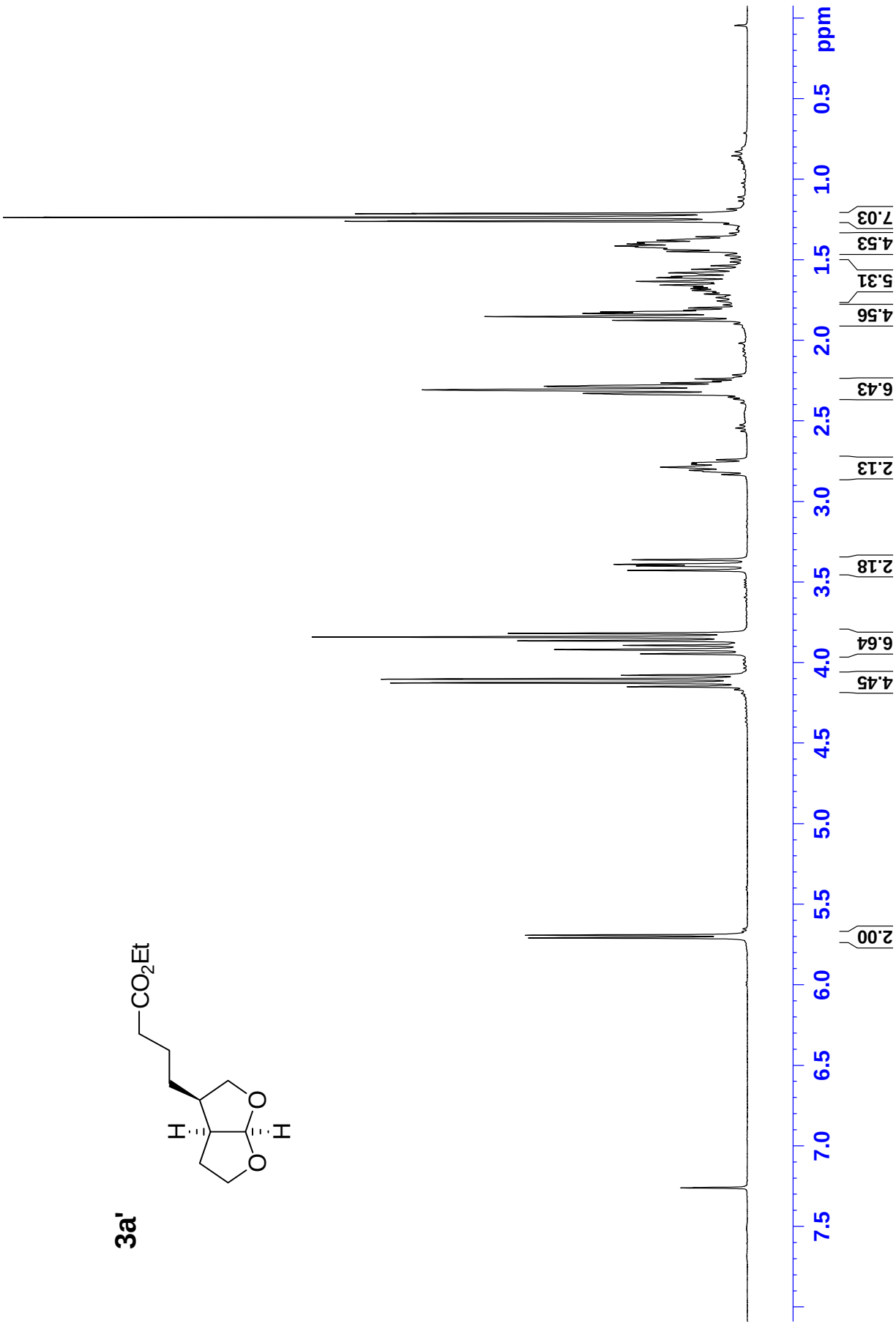
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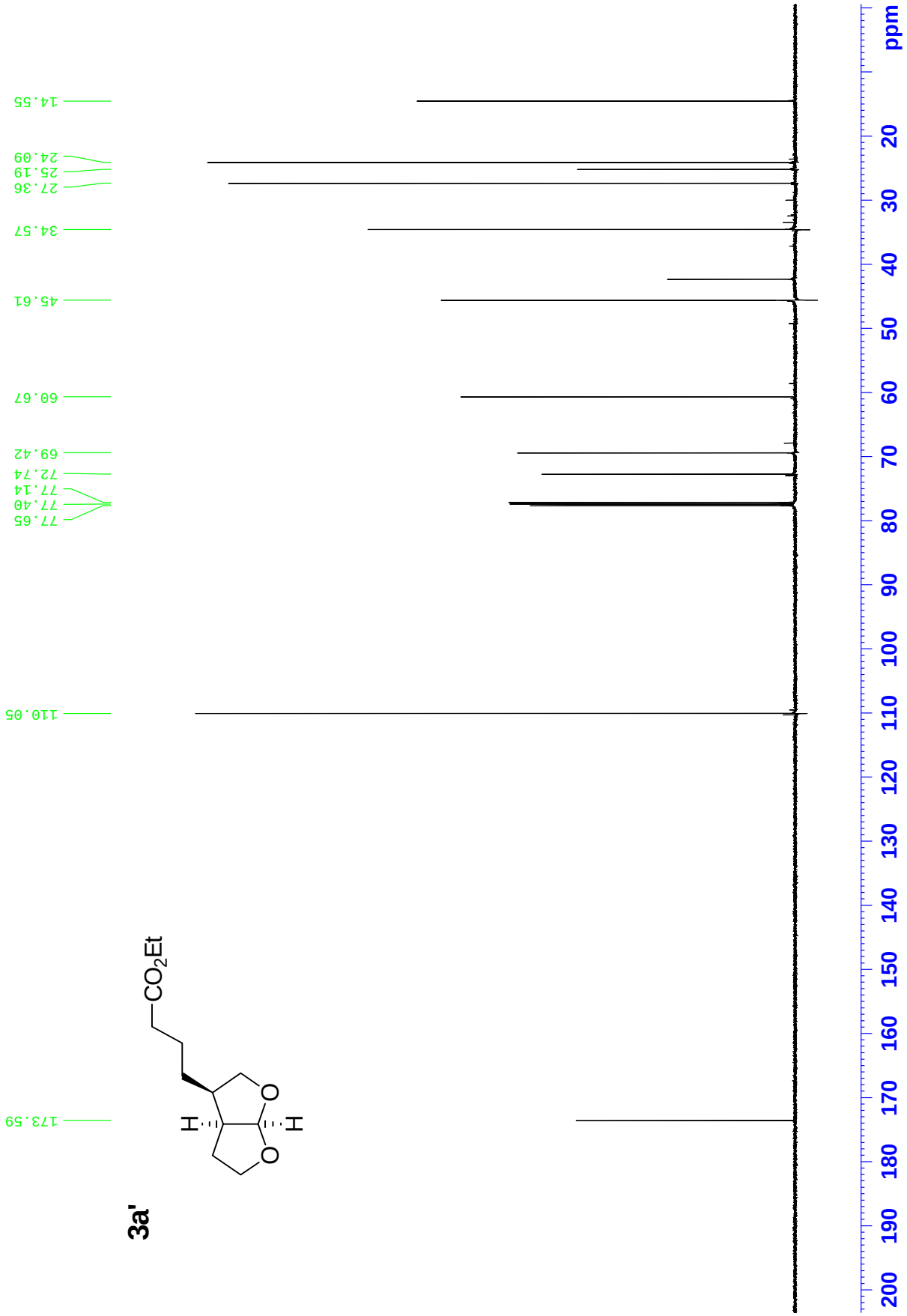
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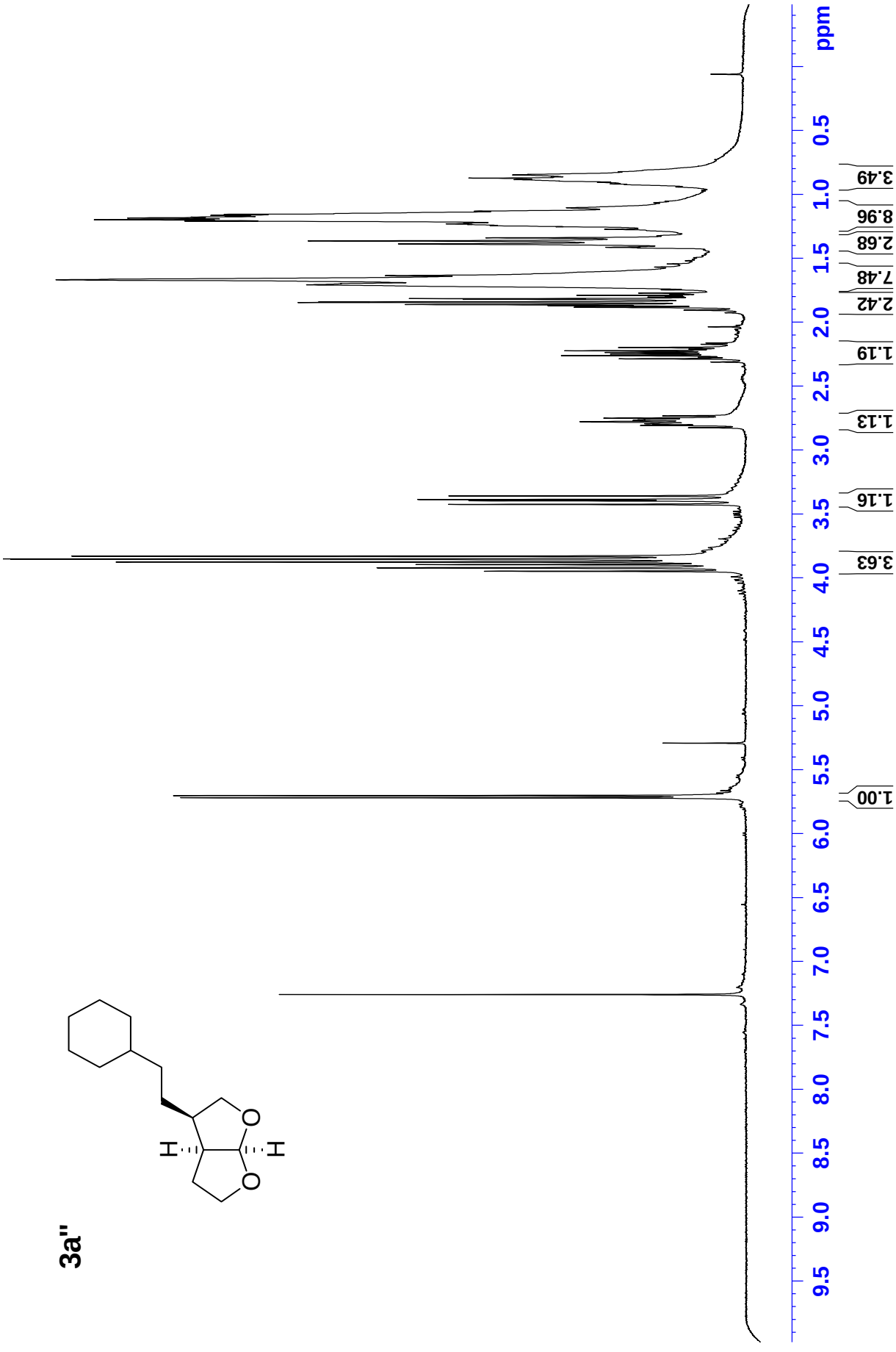
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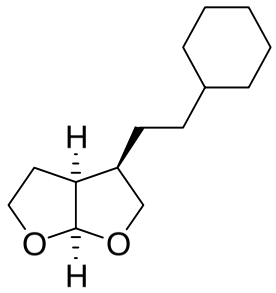
3a''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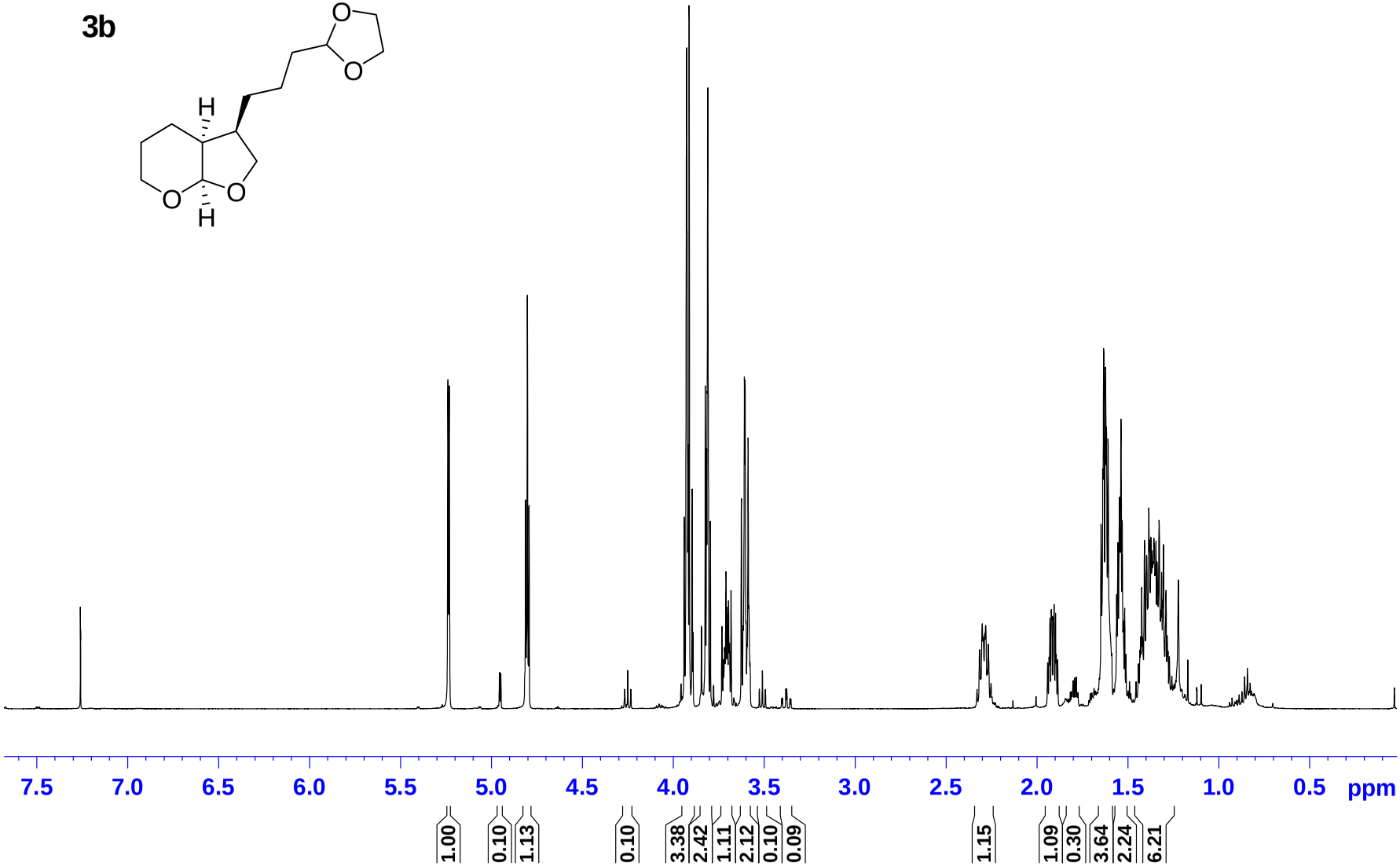
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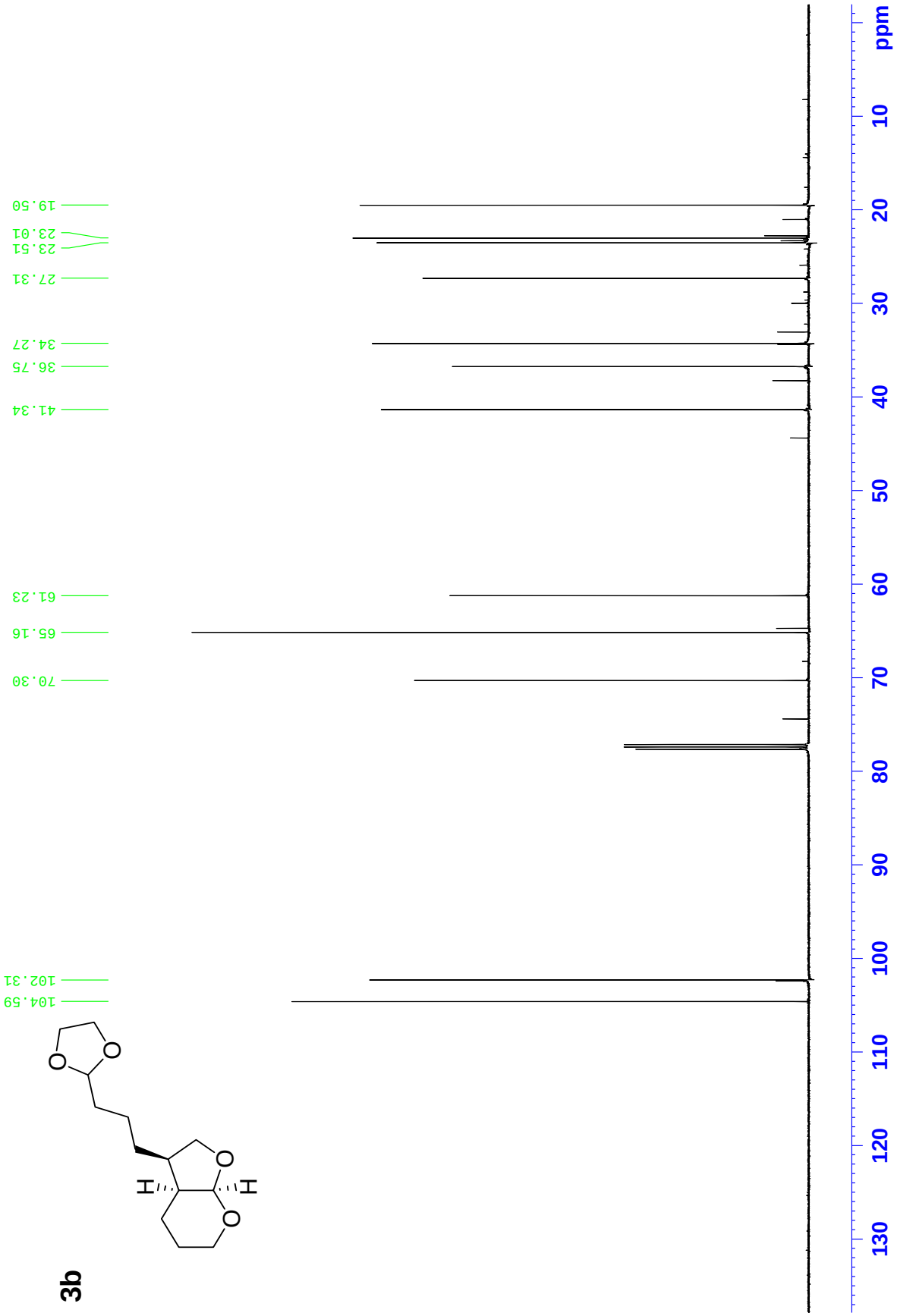
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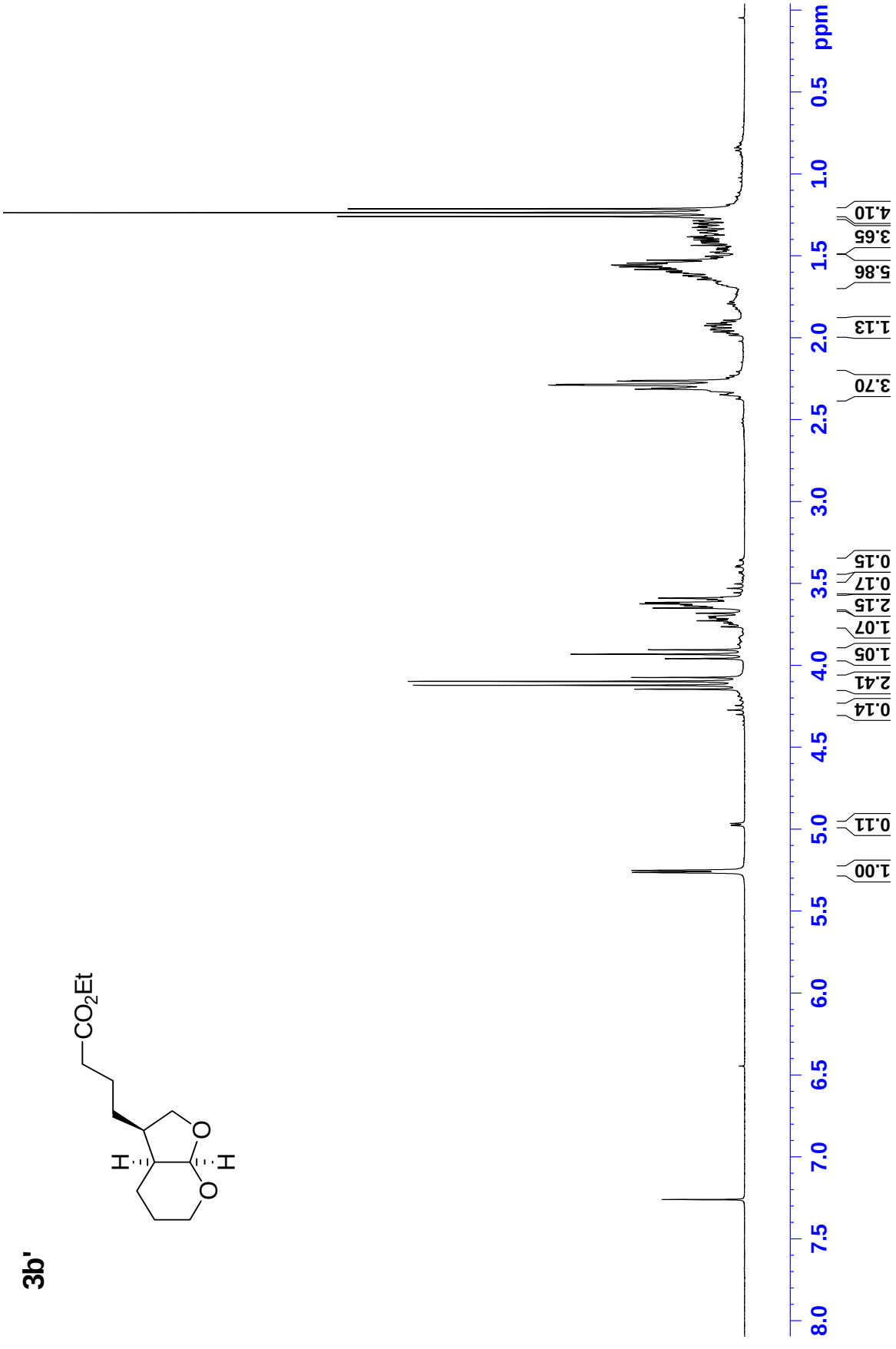
3b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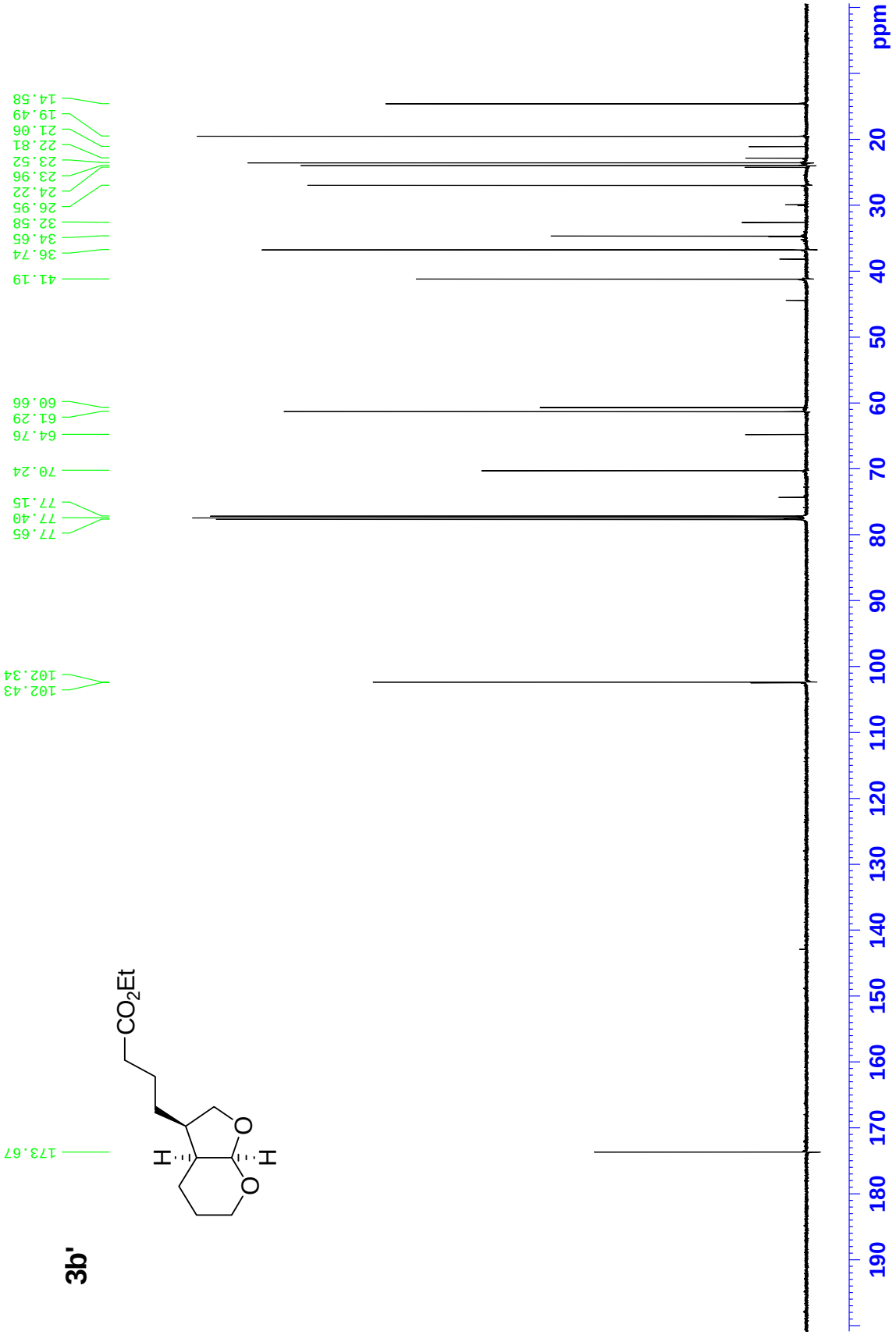
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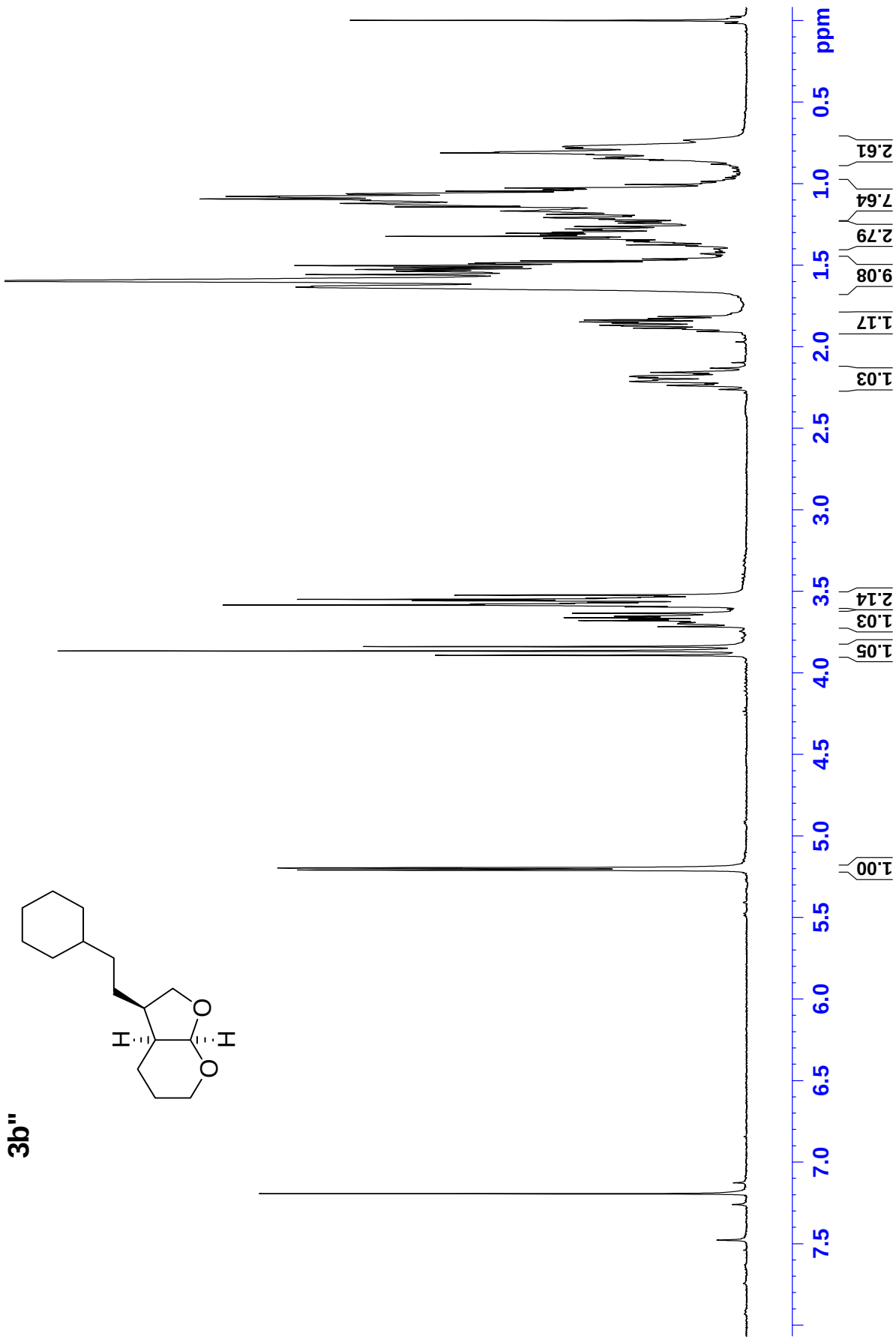
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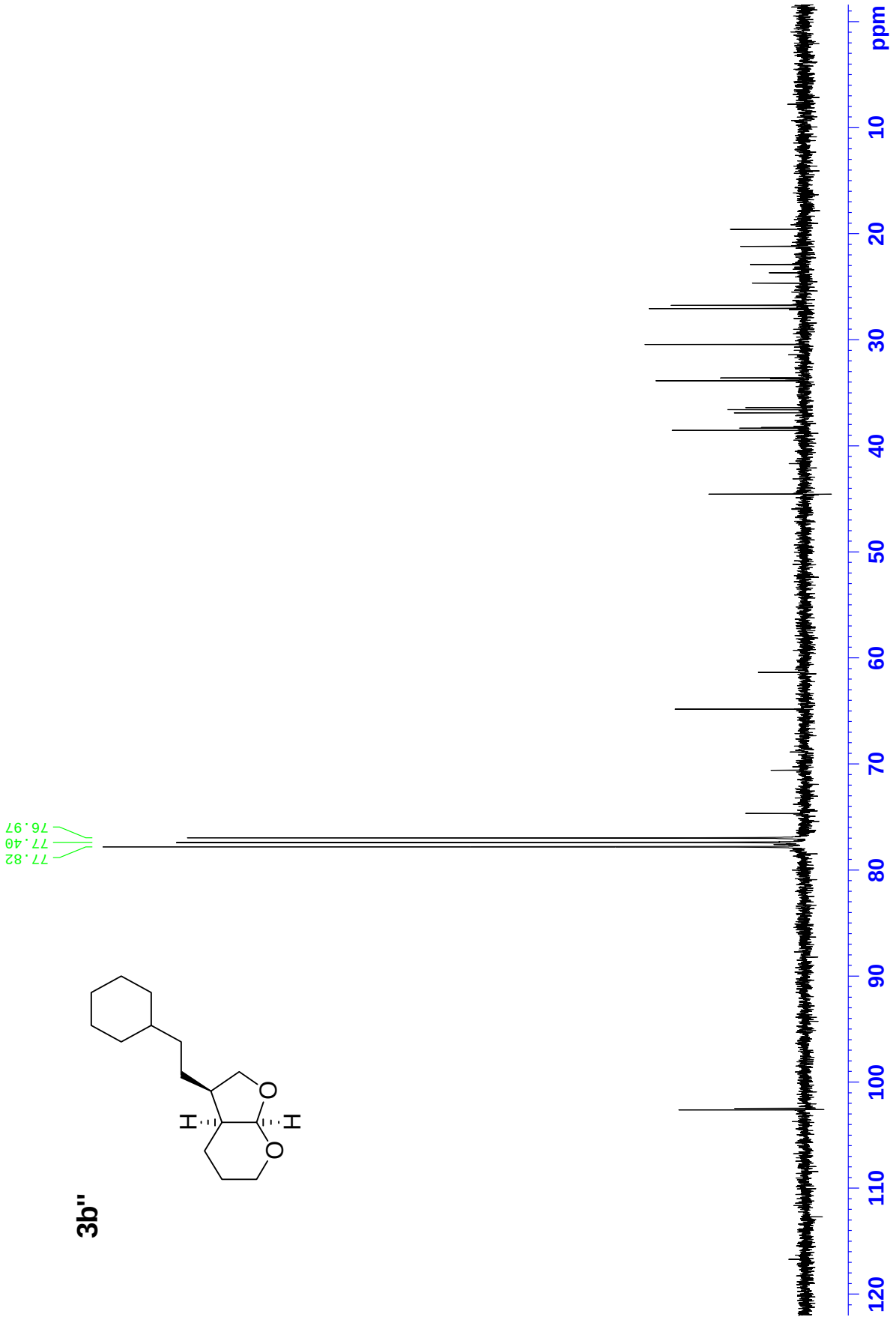
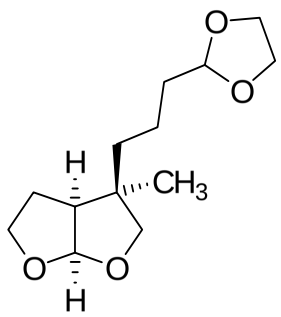
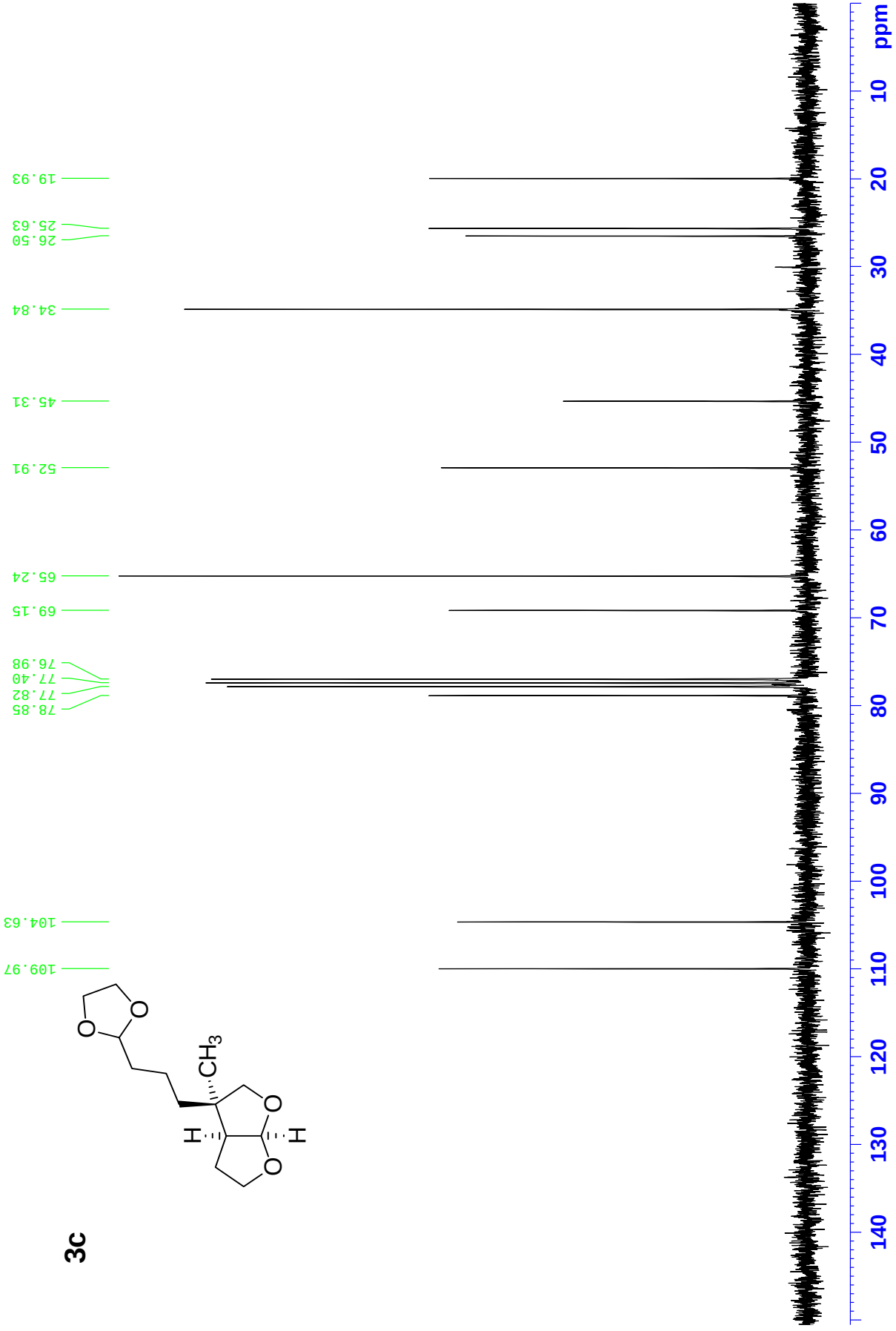
1.00


3b"
77.82
77.40
76.97
ppm
10
20
30
40
50
60
70
80
90
100
110
120

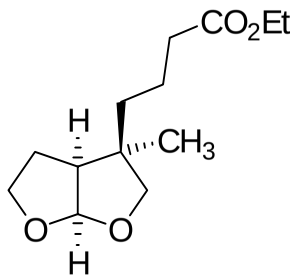
3c



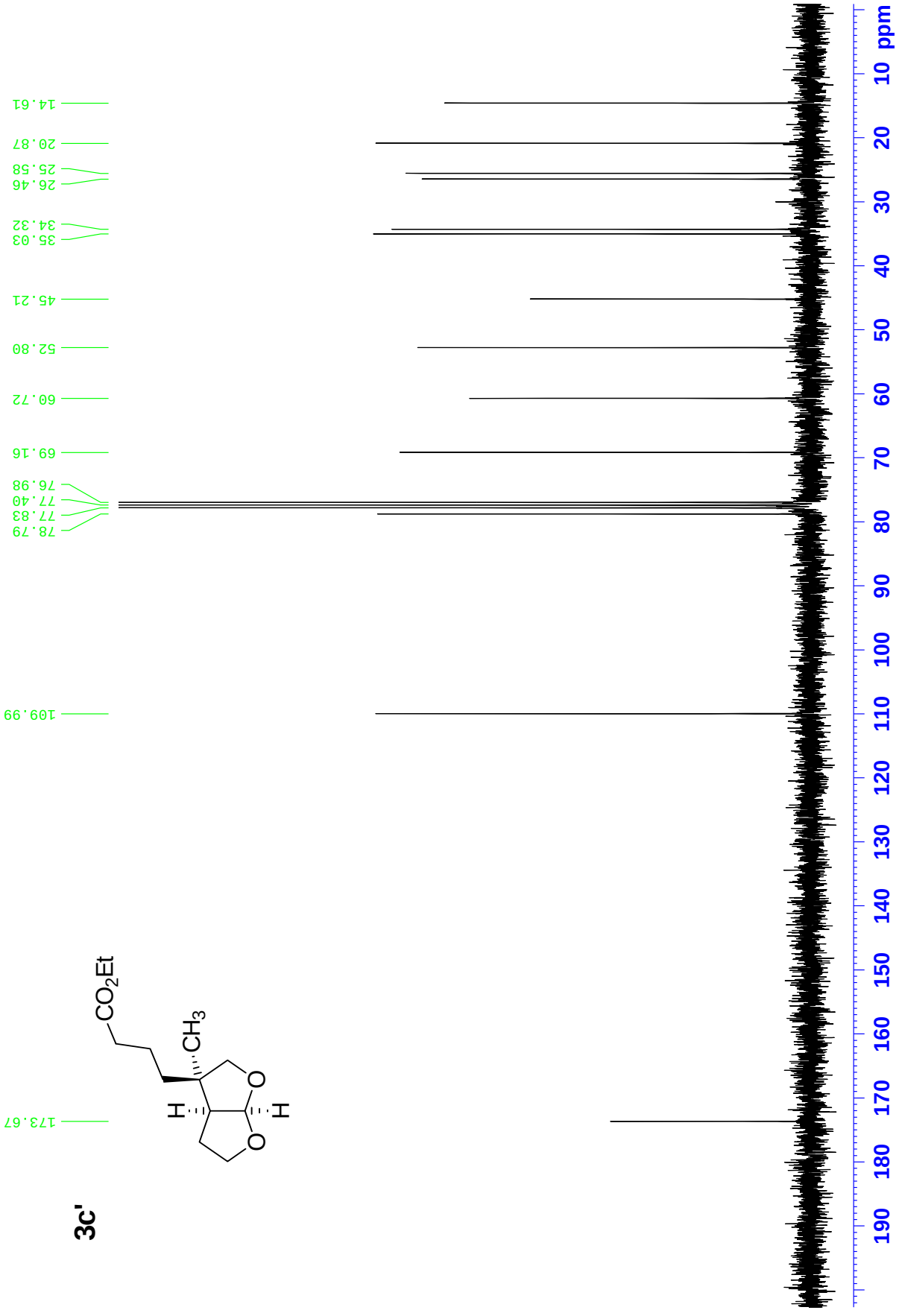

19.93
25.63
26.50
34.84
45.31
52.91
65.24
69.15
76.98
77.40
77.82
78.85
104.63
109.97
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
O
O
O
O
CH3
H
H

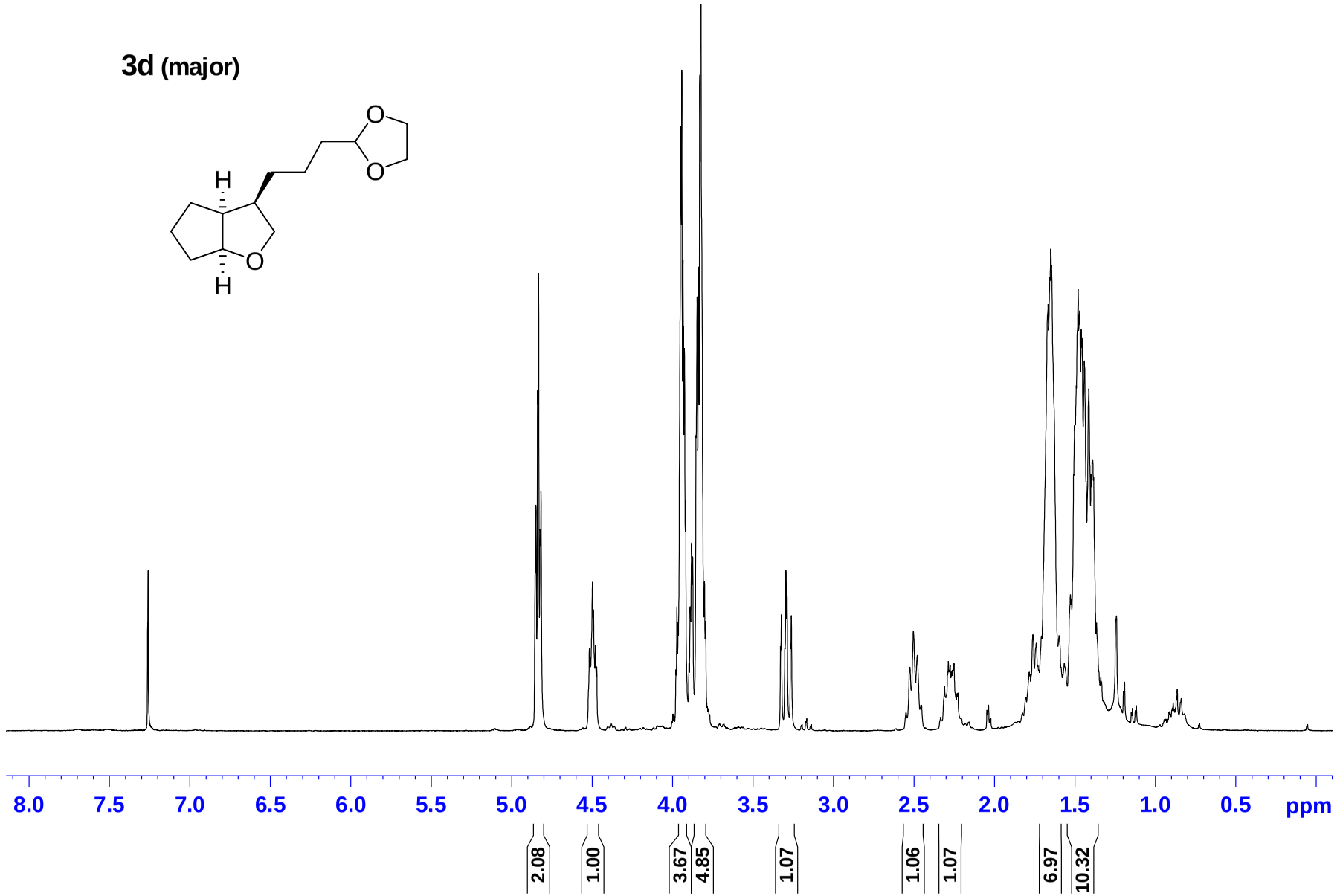
3c

3c'

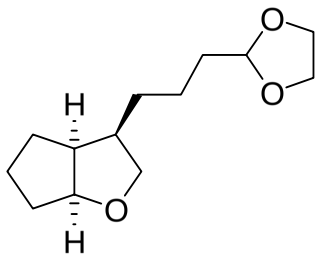

CO2Et
H
CH3
O
O
H

9
8
7
6
5
4
3
2
1
0
ppm
1.01
2.91
2.27
2.14
3.72
2.69
3.35
5.82
3.00

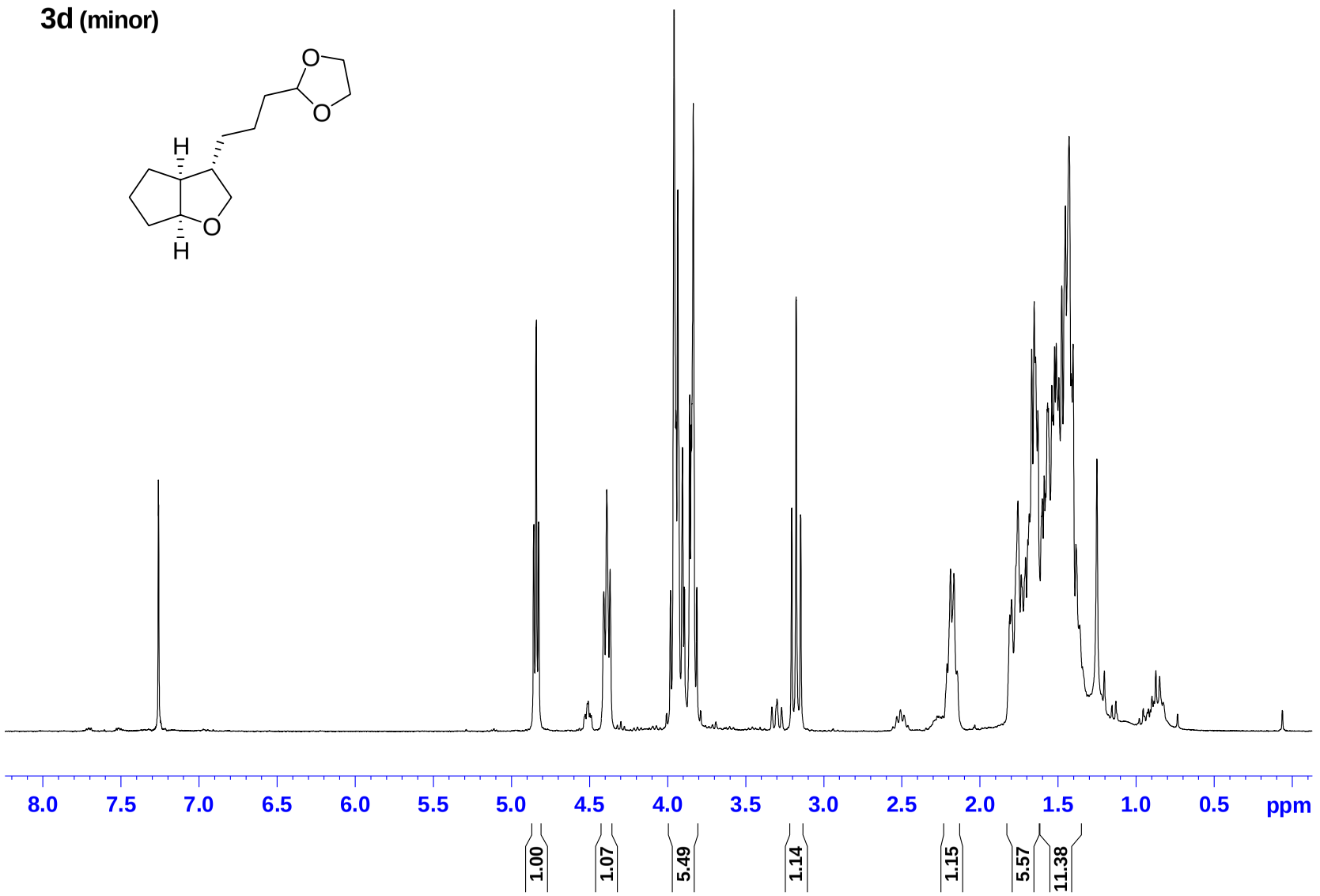

14.61
20.87
25.58
26.46
34.32
35.03
45.21
52.80
60.72
69.16
76.98
77.40
77.83
78.79
109.99
173.67
3c'
CO2Et
CH3
H
H
O
O
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

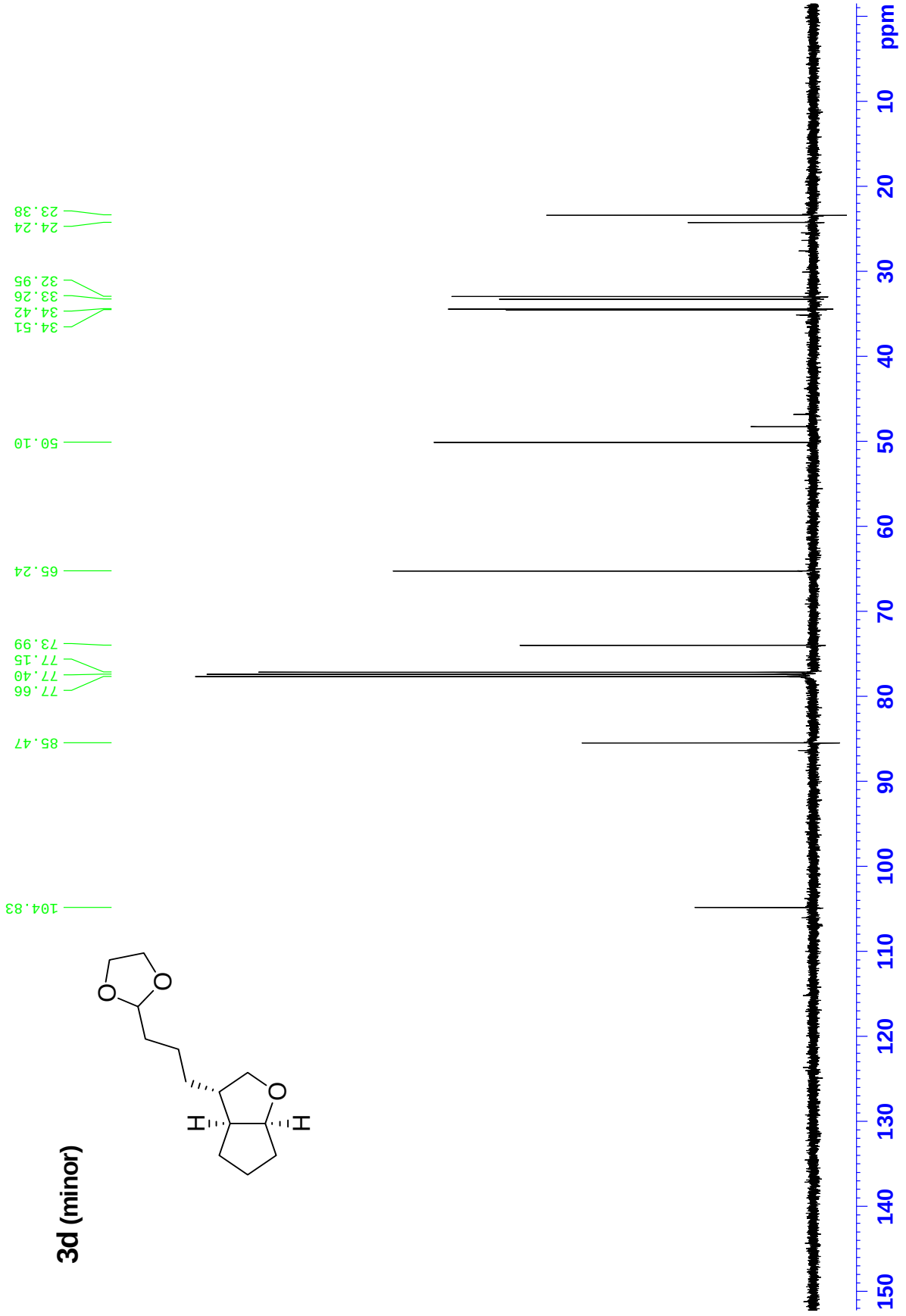

3d (major)
H
O
O
H
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.08
1.00
3.67
4.85
1.07
1.06
1.07
6.97
10.32

3d (major)

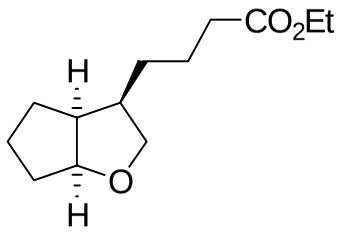

O
O
H
O
H

104.79
104.73
86.26
77.65
77.40
77.14
72.56
65.15
65.12
46.72
43.50
34.39
34.11
28.09
26.27
25.37
24.29
23.61
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

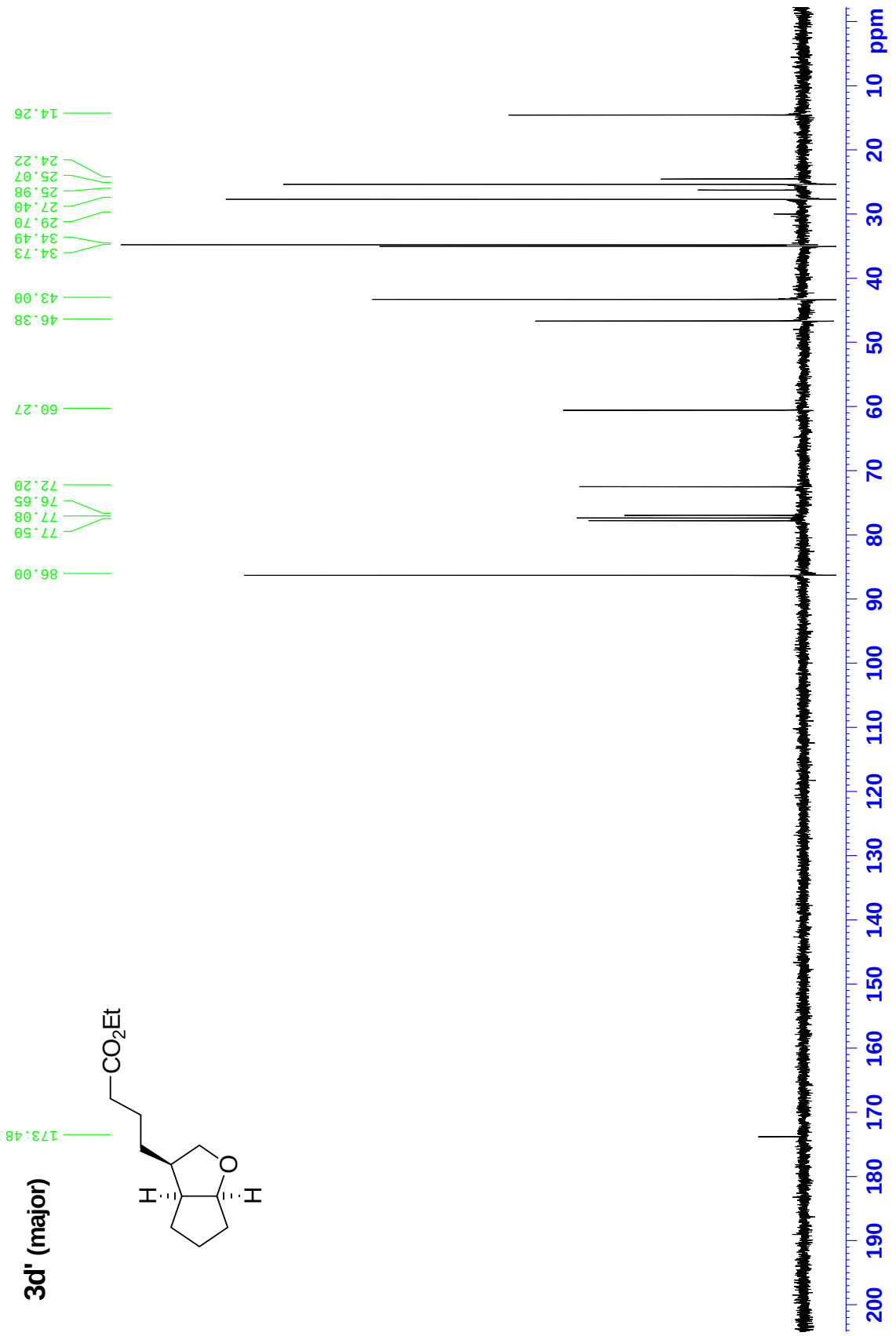

3d (minor)
O
O
H
O
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.07
5.49
1.14
1.15
5.57
11.38


3d (minor)
104.83
85.47
77.66
77.40
77.15
73.99
65.24
50.10
34.51
34.42
33.26
32.95
24.24
23.38
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

3d' (major)


CO2Et
H
O
H

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.08
1.03
1.01
1.01
3.11
5.51
3.20
2.08
3.49


3d' (major)
CO2Et
O
H
H
173.48
86.00
77.50
77.08
76.65
72.20
60.27
46.38
43.00
34.73
34.49
29.70
27.40
25.98
25.07
24.22
14.26
ppm
10
20
30
40
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60
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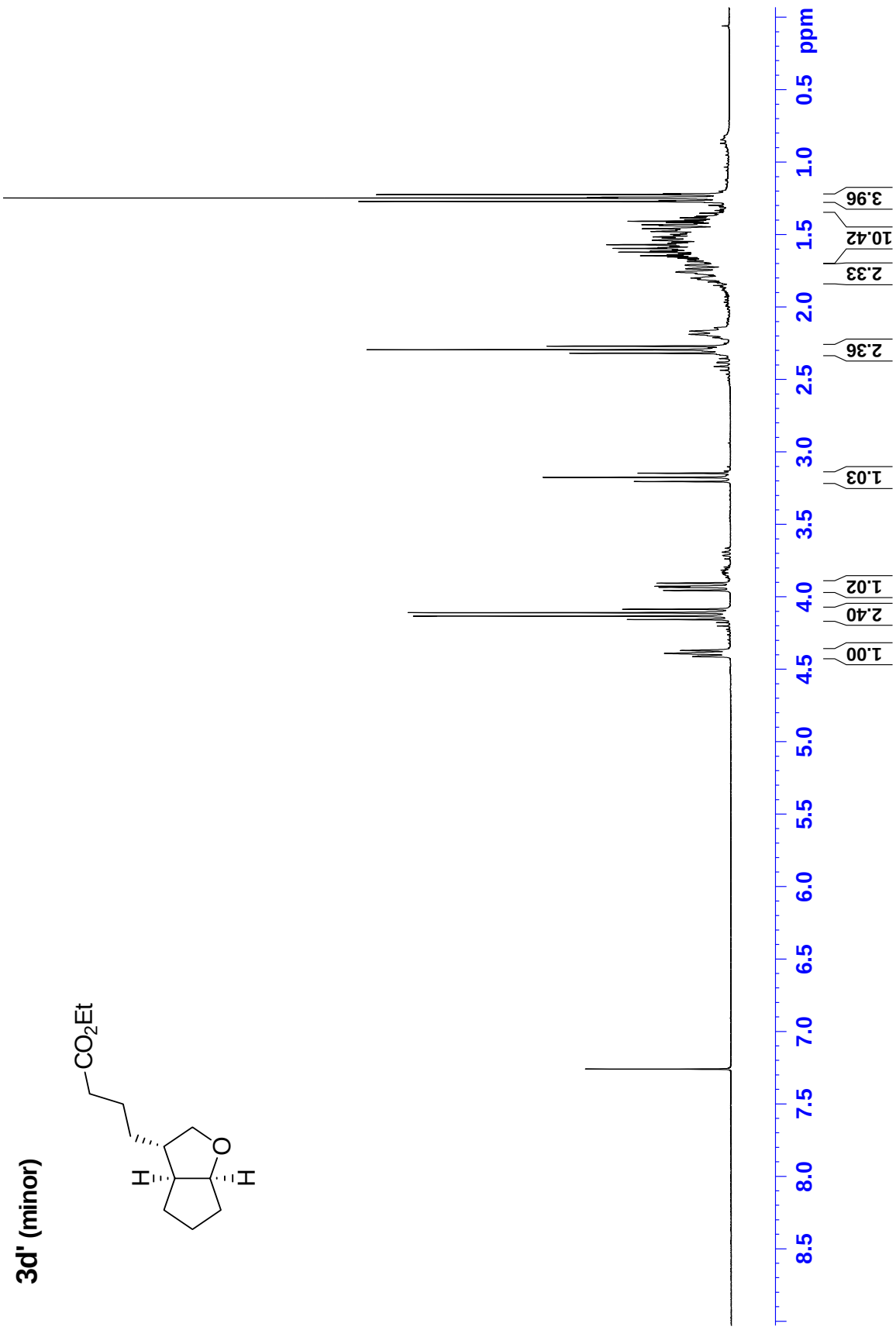
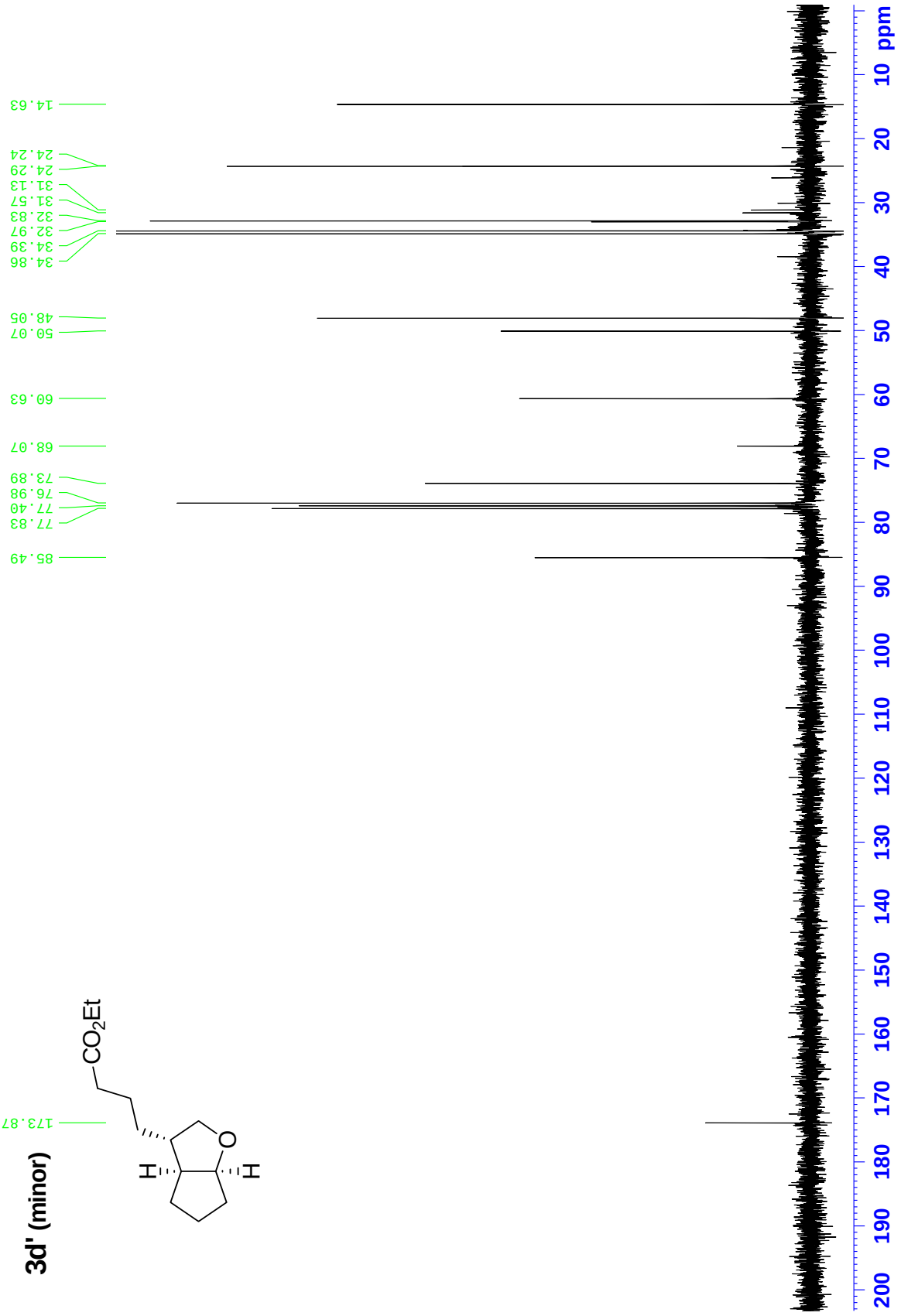
110
120
130
140
150
160
170
180
190
200


3d' (minor)
CO2Et
O
H
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.40
1.02
1.03
2.36
2.33
10.42
3.96


3d' (minor)
CO2Et
H
O
H
173.87
85.49
77.83
77.40
76.98
73.89
68.07
60.63
50.07
48.05
34.86
34.39
32.97
32.83
31.57
31.13
24.29
24.24
14.63
ppm
10
20
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50
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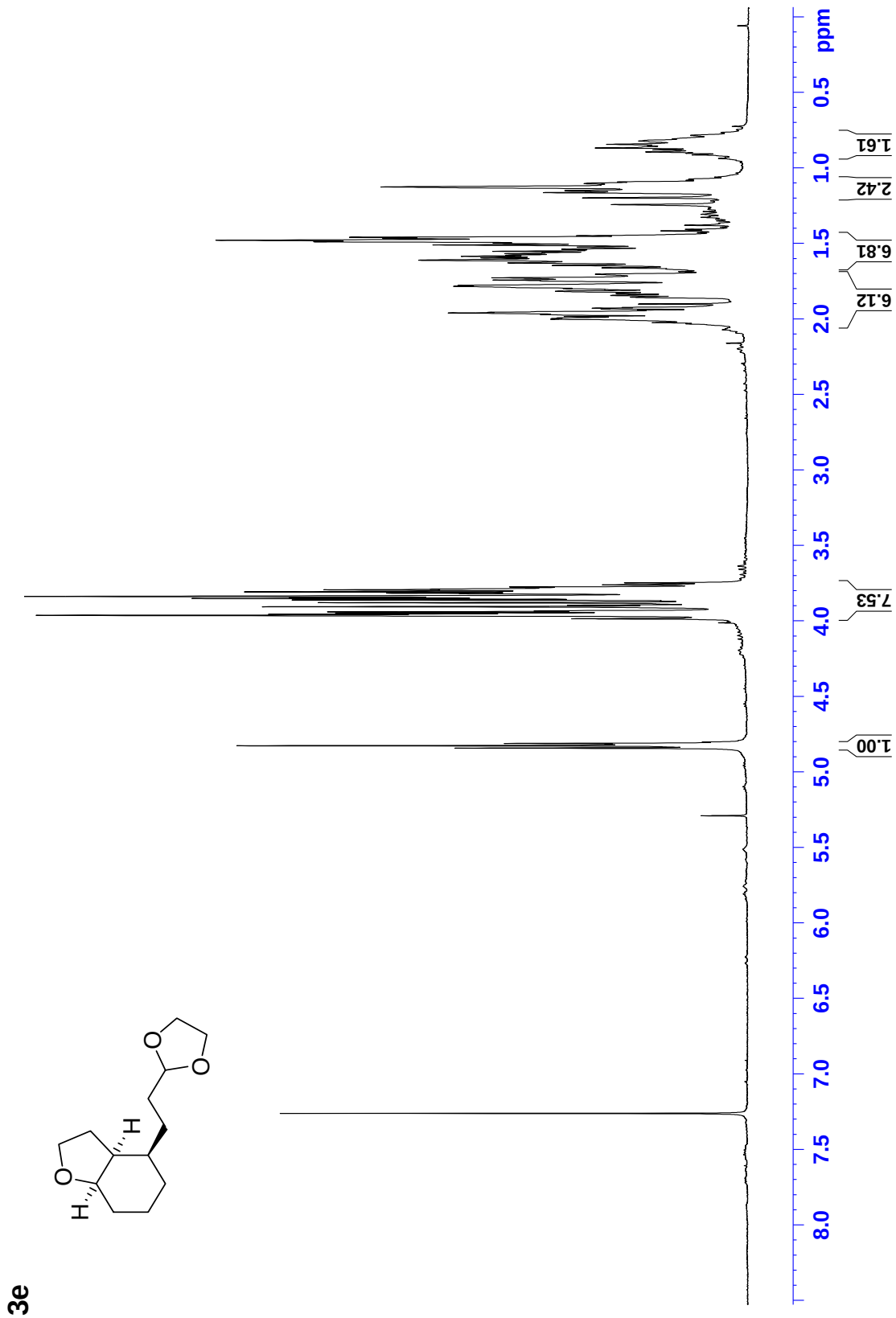
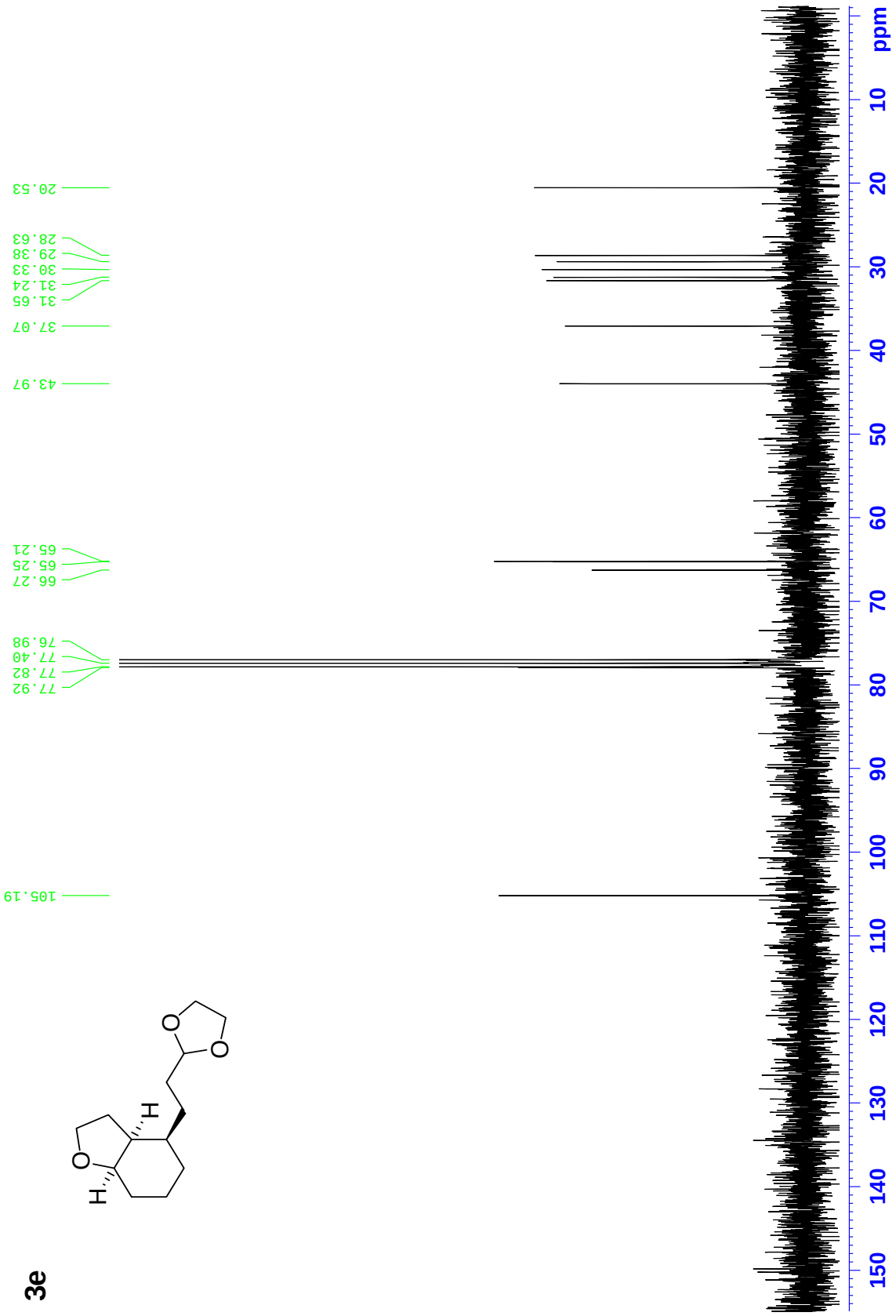
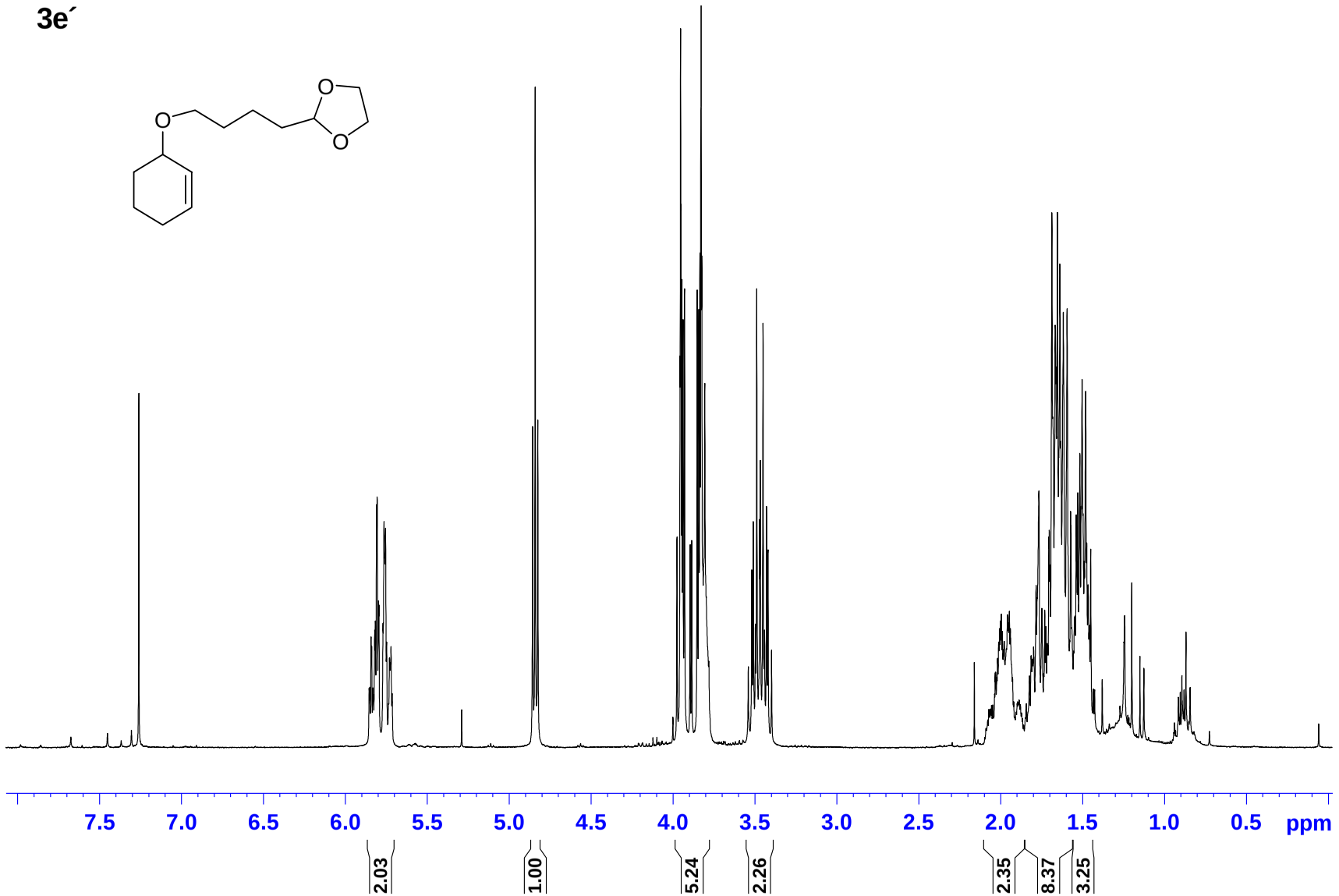
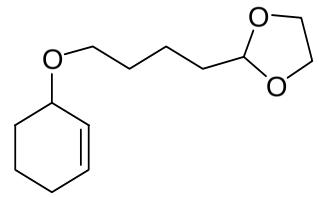
110
120
130
140
150
160
170
180
190
200


3e
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.00
7.53
6.12
6.81
2.42
1.61


3e
105.19
77.92
77.82
77.40
76.98
66.27
65.25
65.21
43.97
37.07
31.65
31.24
30.33
29.38
28.63
20.53
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

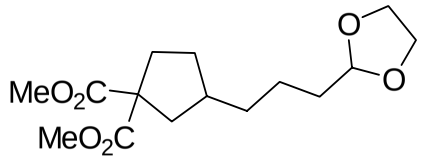

3e´
O
O
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
1.00
5.24
2.26
2.35
8.37
3.25

3e´


O
O
O

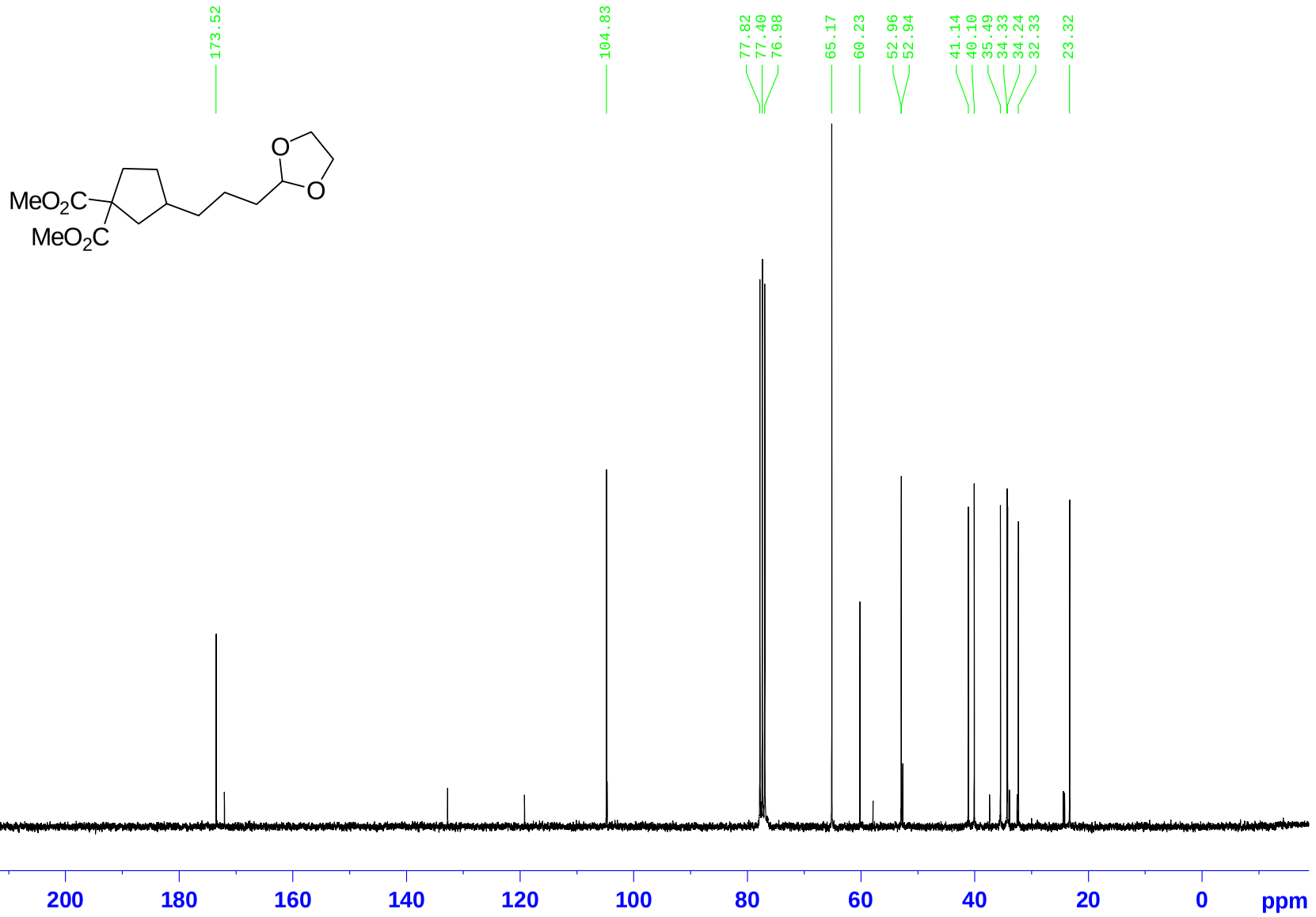
130.93
128.41
104.93
77.82
77.40
76.98
73.16
68.36
65.18
34.06
30.44
28.70
25.59
21.23
19.65
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

3f

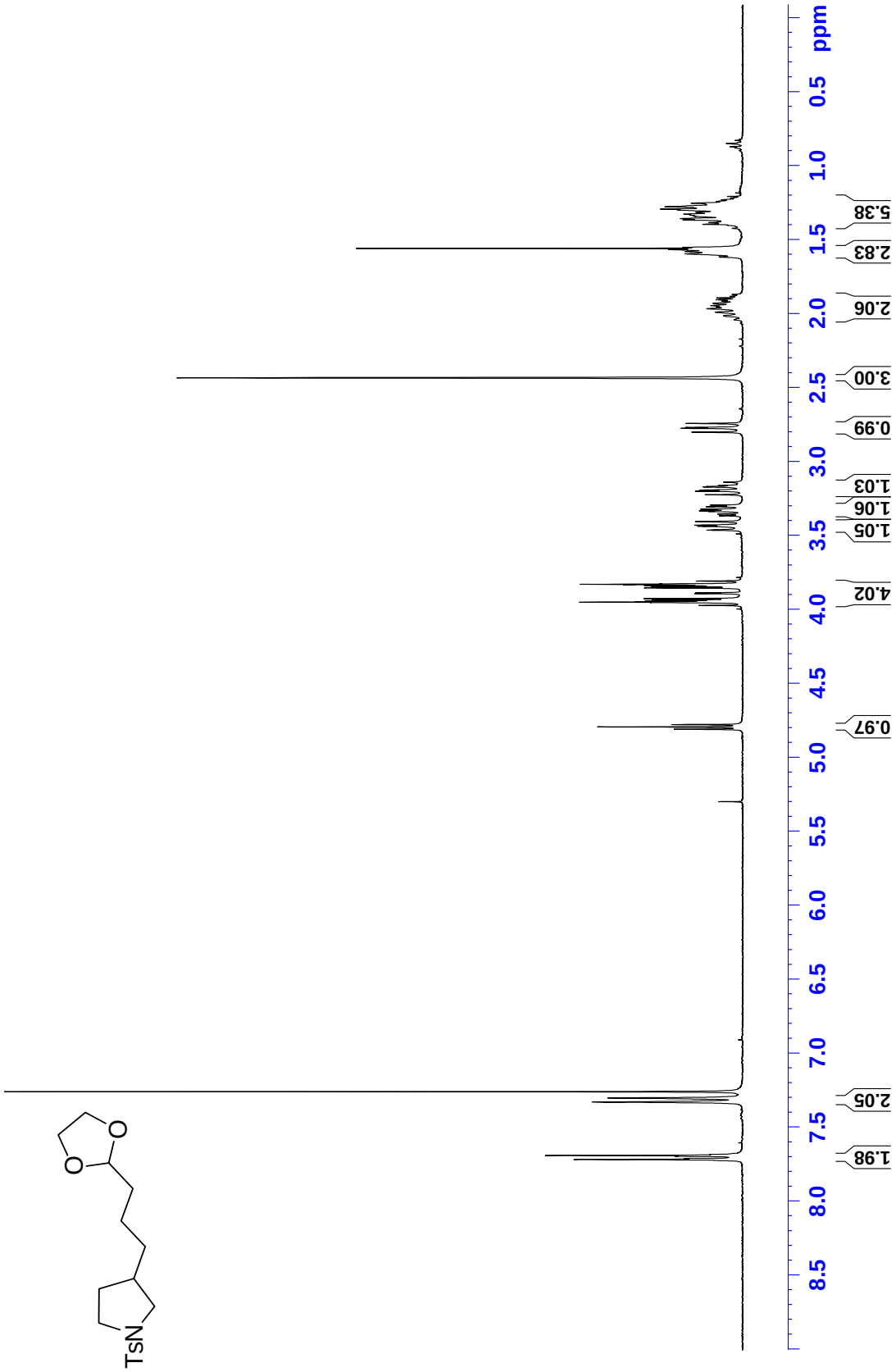

MeO2C
MeO2C
O
O

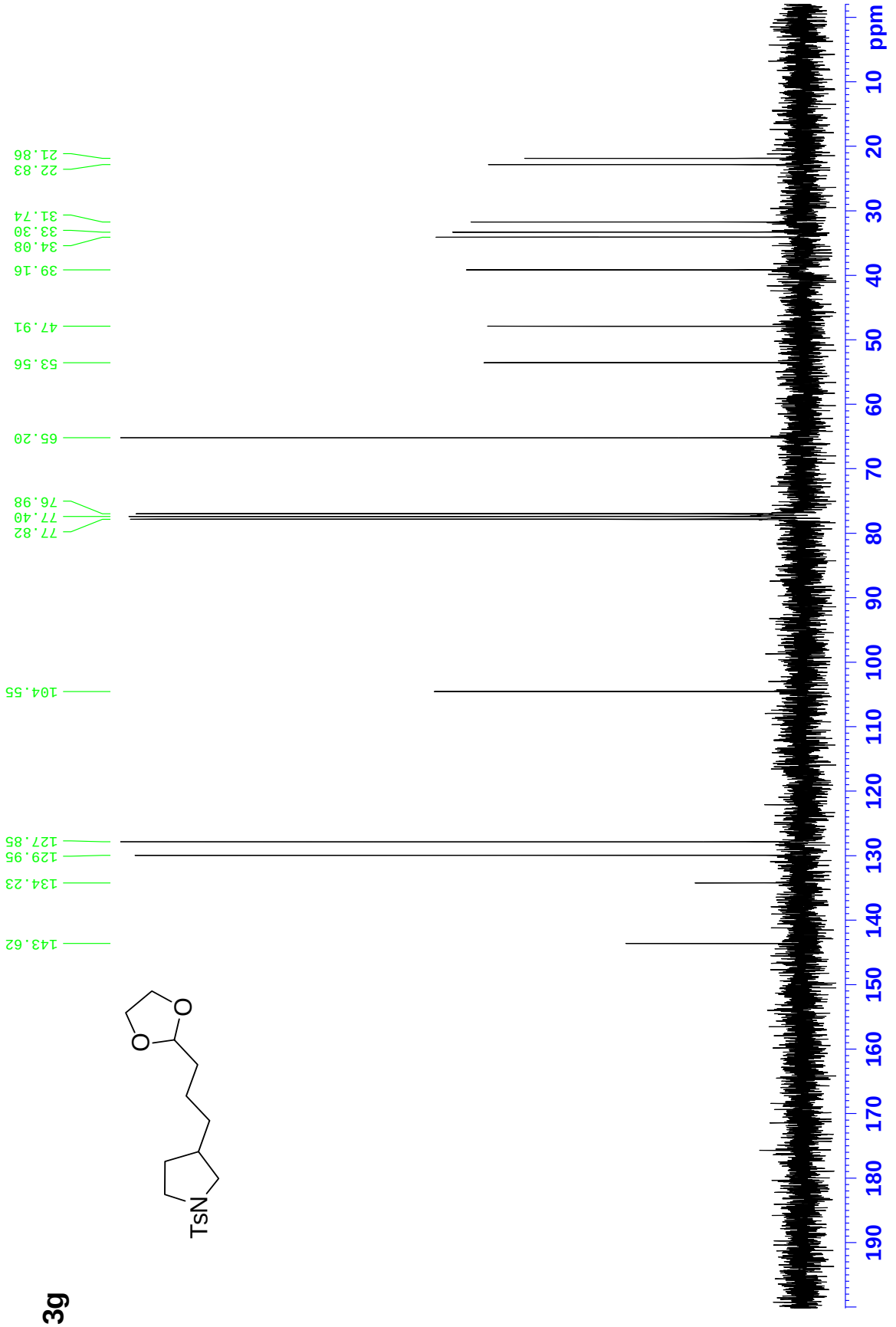
3.71
3.71
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.09
0.22
1.00
0.08
4.14
6.20
0.22
0.92
0.93
0.95
2.14
3.04
5.29

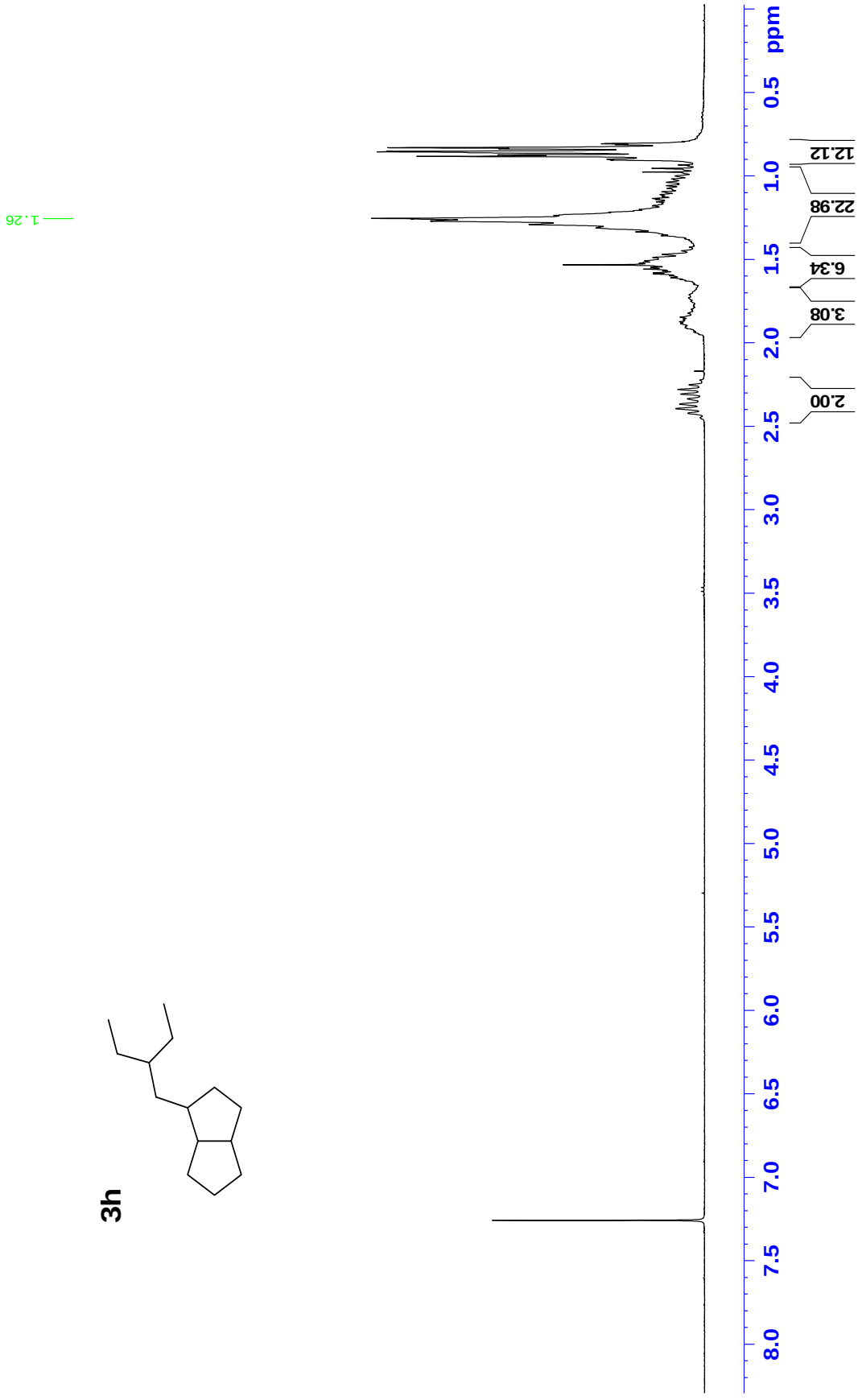
3f

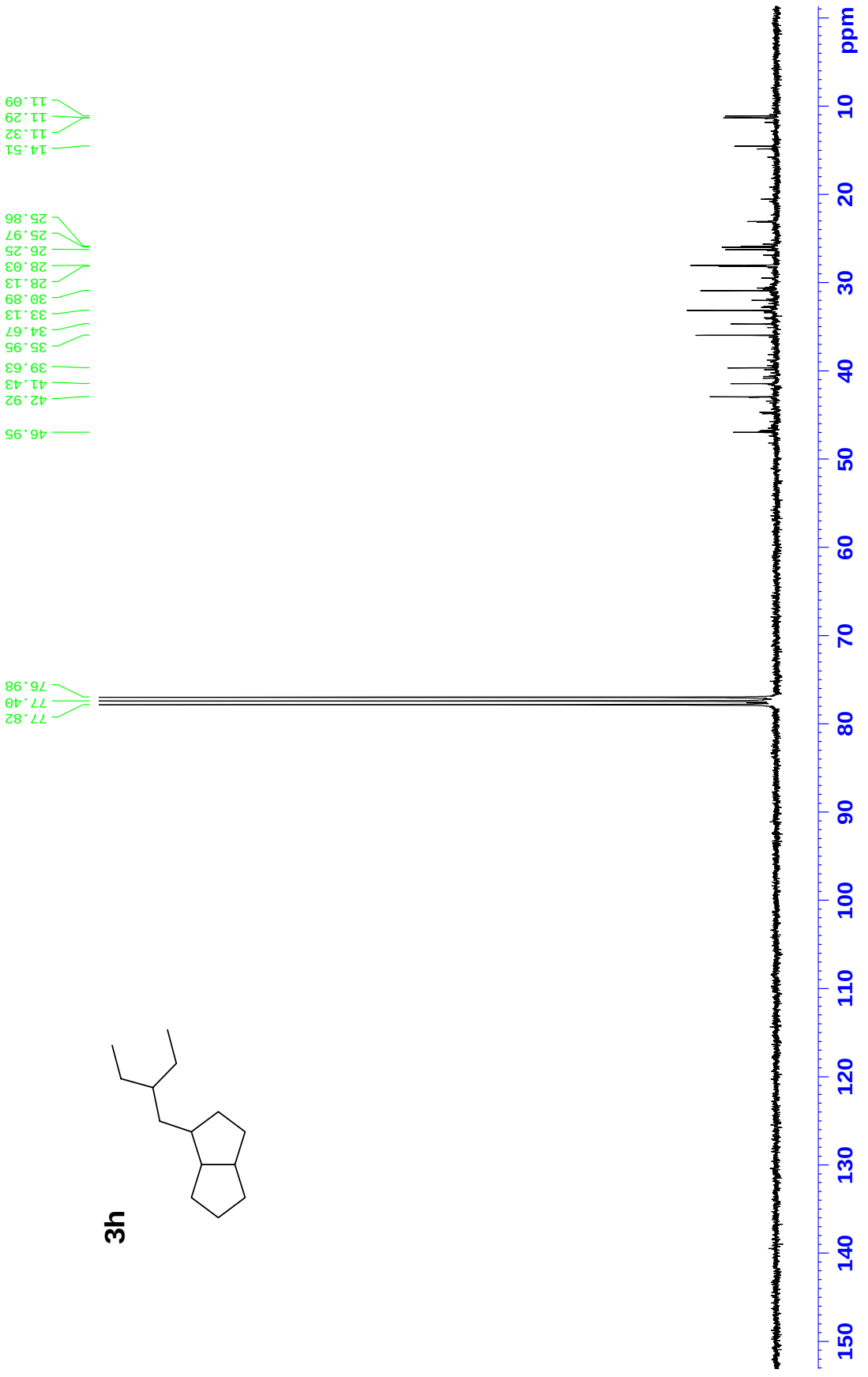

173.52
104.83
77.82
77.40
76.98
65.17
60.23
52.96
52.94
41.14
40.10
35.49
34.33
34.24
32.33
23.32
MeO2C
MeO2C
O
O
200
180
160
140
120
100
80
60
40
20
0
ppm

3g

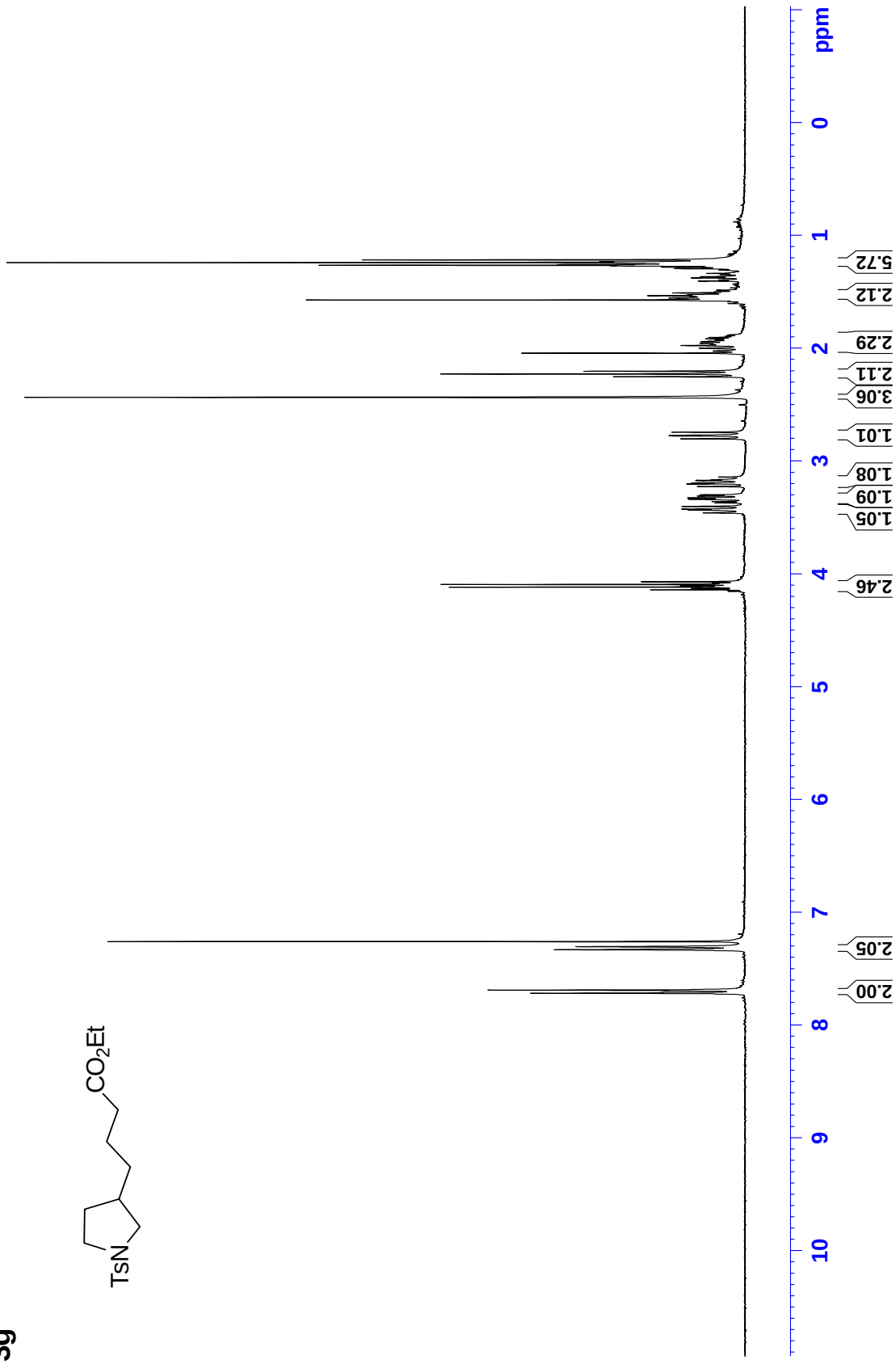

TsN
O
O
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
5.38
2.83
2.06
3.00
0.99
1.03
1.06
1.05
4.02
0.97
2.05
1.98

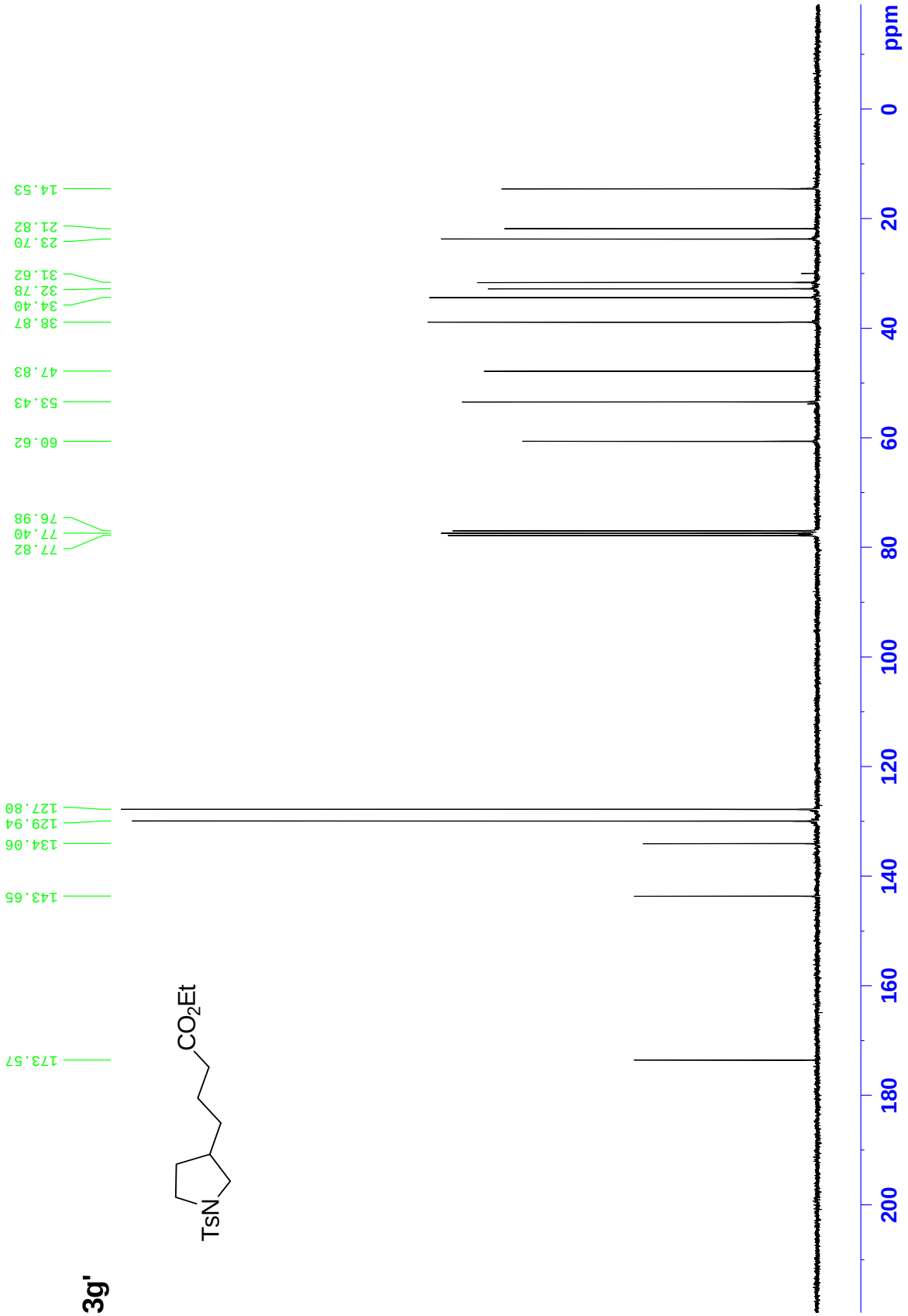

3g
TsN
O
O
21.86
22.83
31.74
33.30
34.08
39.16
47.91
53.56
65.20
76.98
77.40
77.82
104.55
127.85
129.95
134.23
143.62
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190


3h
1.26
12.12
22.98
6.34
3.08
2.00
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0

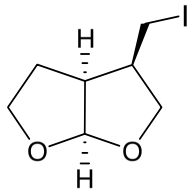

11.09
11.29
11.32
14.51
25.86
25.97
26.25
28.03
28.13
30.89
33.13
34.67
35.95
39.63
41.43
42.92
46.95
76.98
77.40
77.82
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
3h

3g'

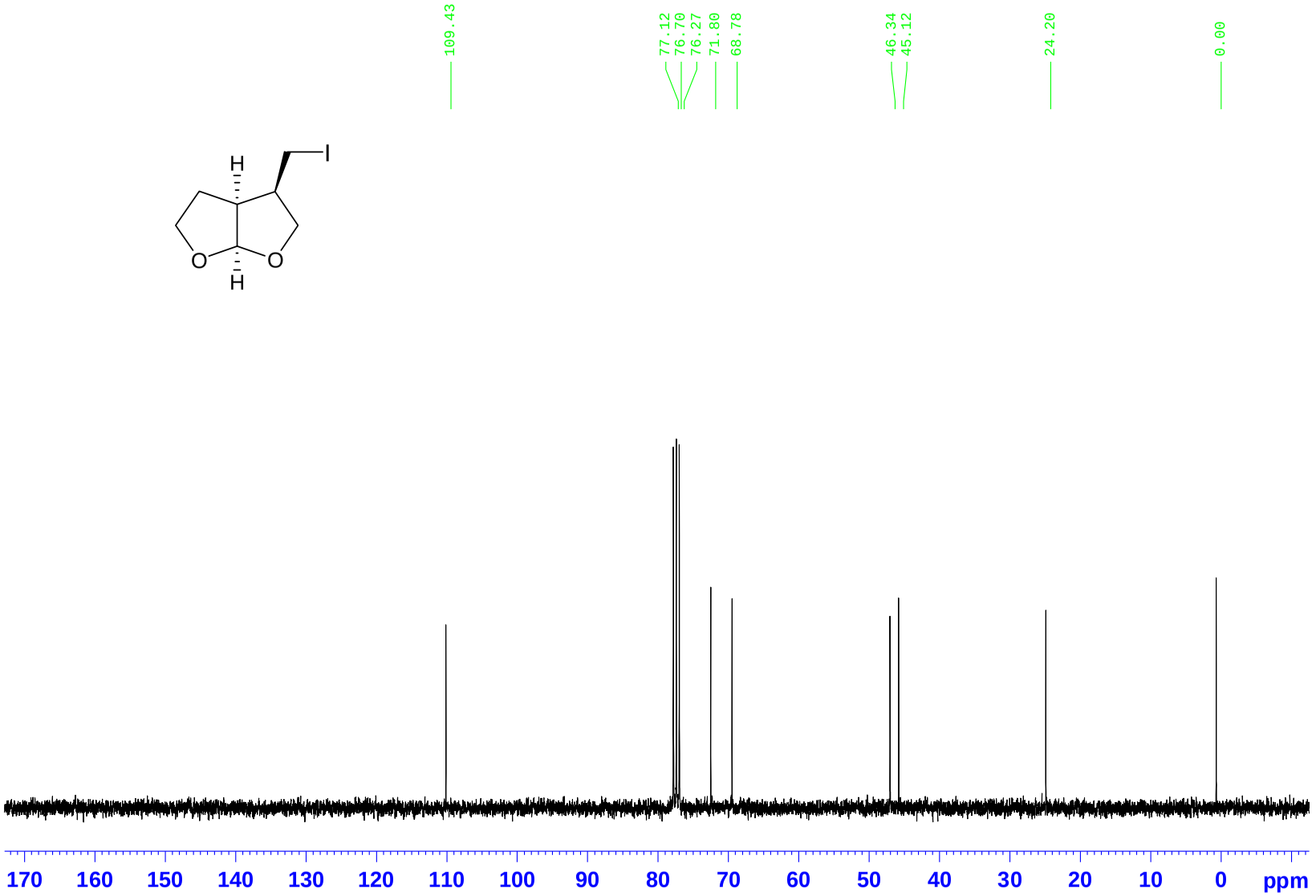

TsN
CO2Et
ppm
0
1
2
3
4
5
6
7
8
9
10
5.72
2.12
2.29
2.11
3.06
1.01
1.08
1.09
1.05
2.46
2.05
2.00

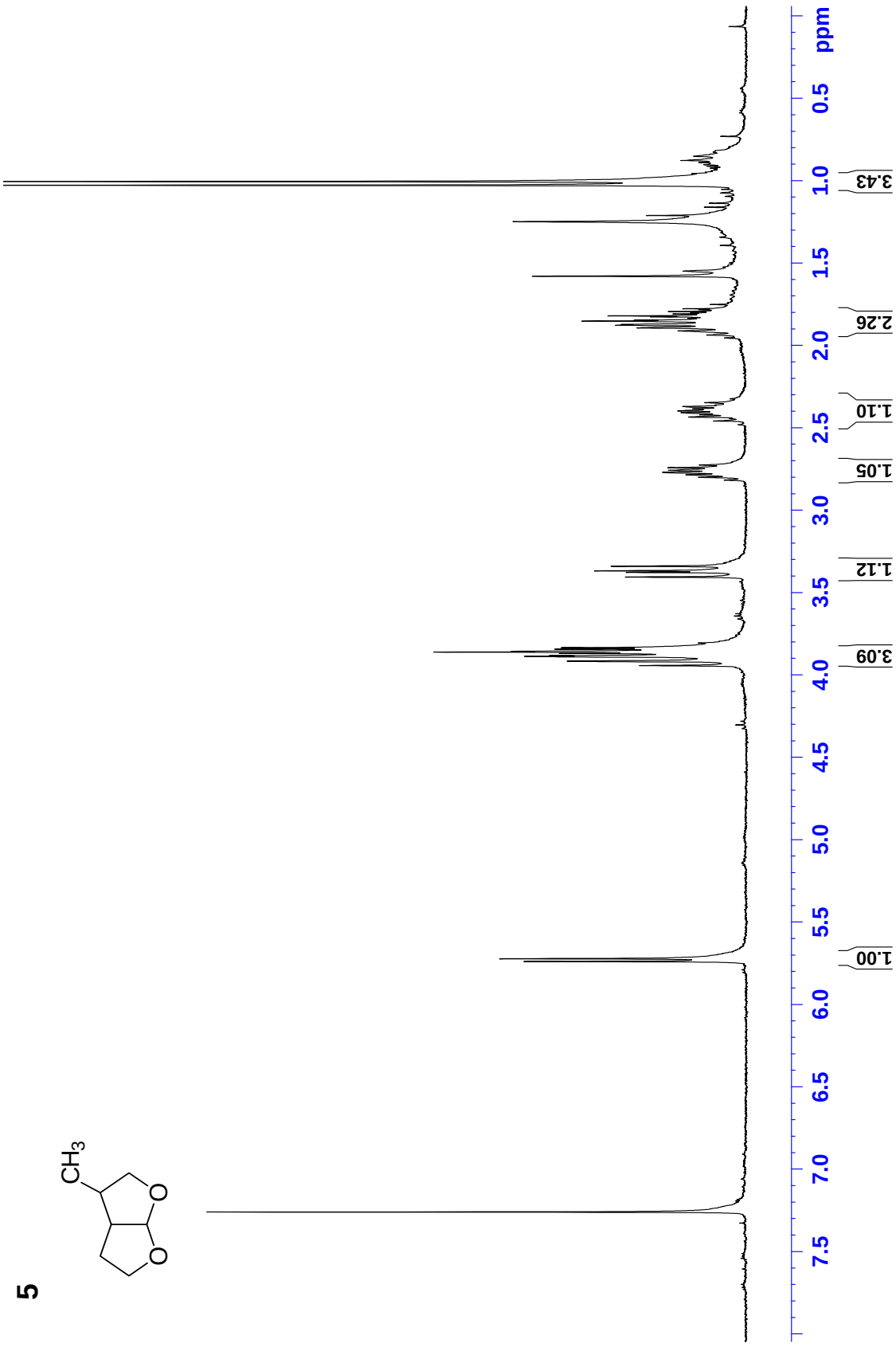

3g'
TsN
CO2Et
173.57
143.65
134.06
129.94
127.80
77.82
77.40
76.98
60.62
53.43
47.83
38.87
34.40
32.78
31.62
23.70
21.82
14.53
ppm
0
20
40
60
80
100
120
140
160
180
200

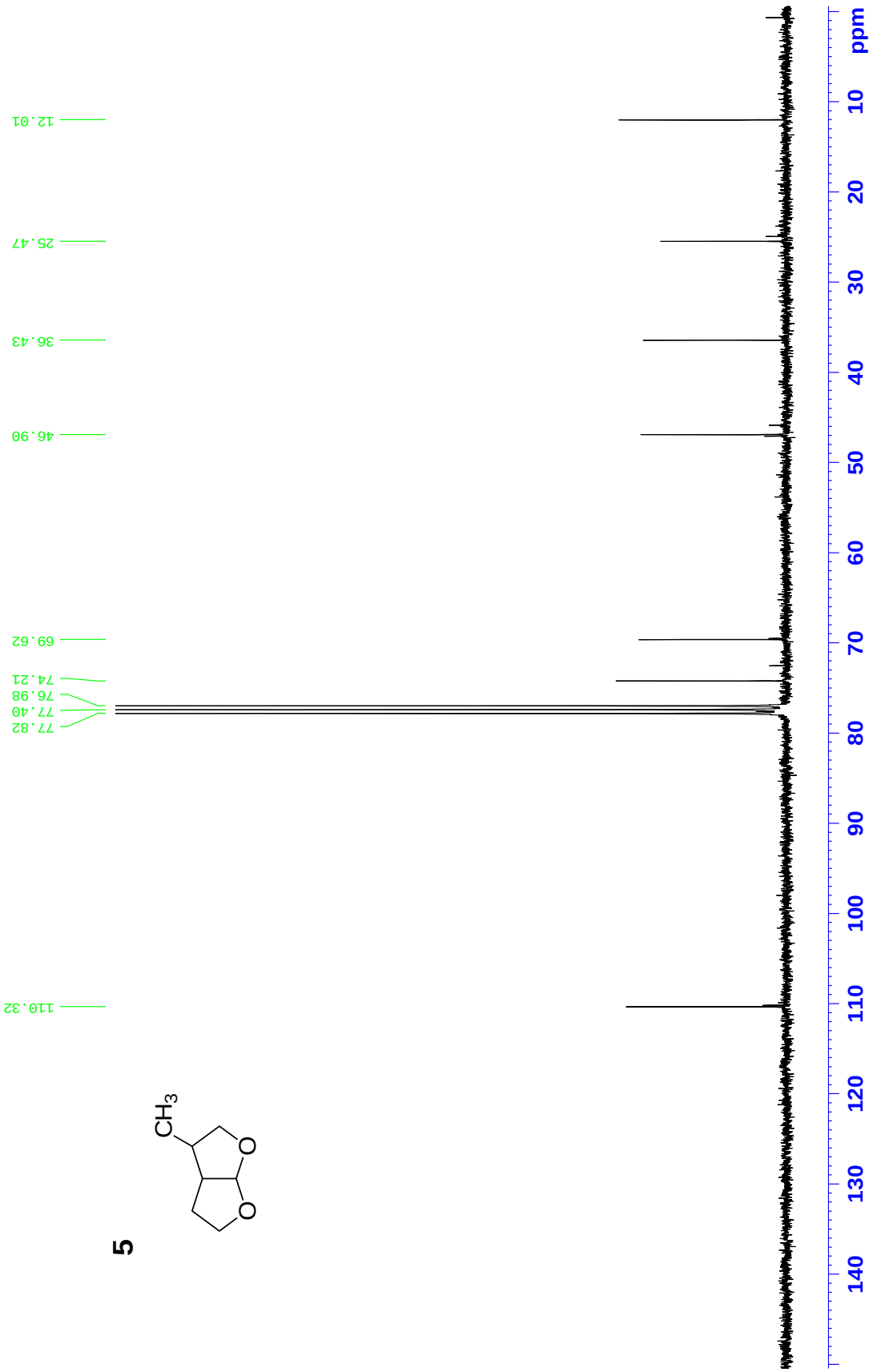
4


H
I
O
O
H

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.91
1.04
2.00
1.04
2.16
2.02
2.14

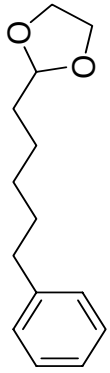

109.43
77.12
76.70
76.27
71.80
68.78
46.34
45.12
24.20
0.00
H
I
O
O
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

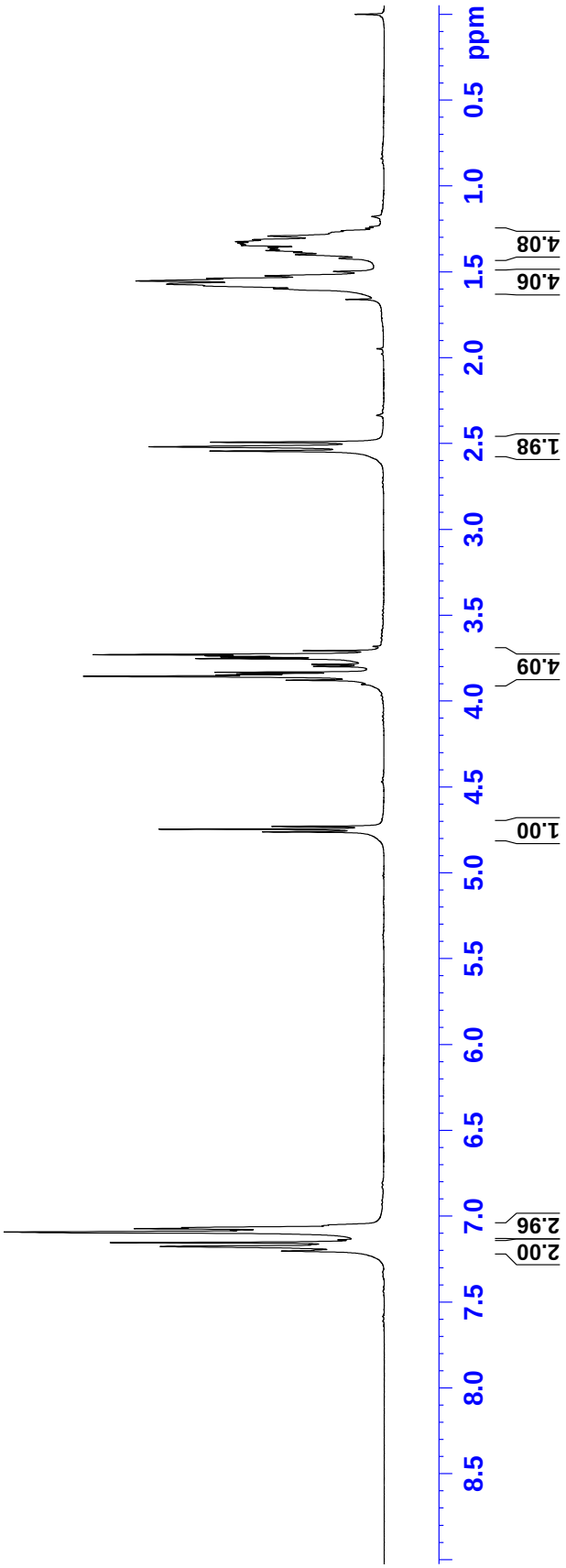

5
CH3
O
O
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.00
3.09
1.12
1.05
1.10
2.26
3.43

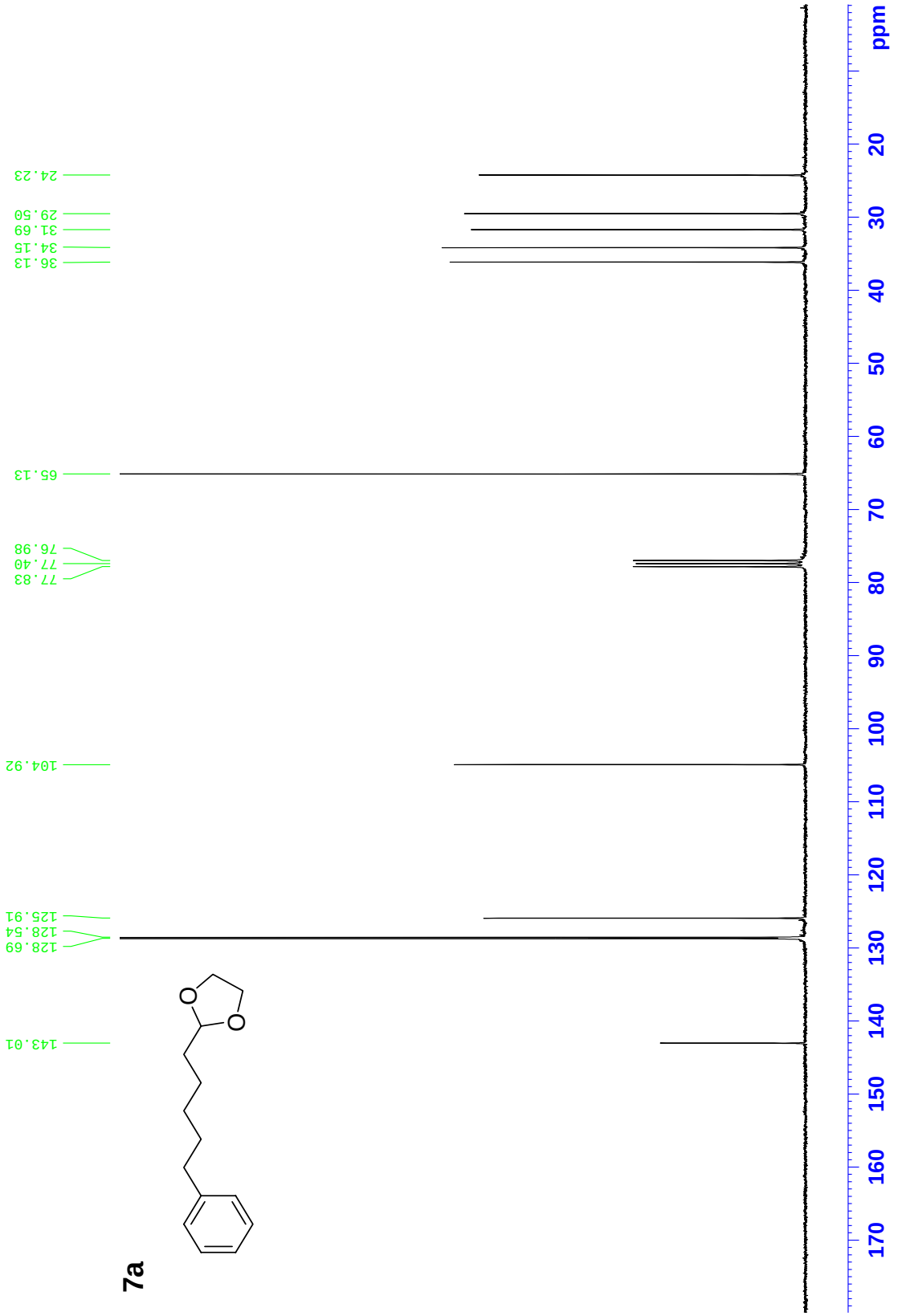

12.01
25.47
36.43
46.90
69.62
74.21
76.98
77.40
77.82
110.32
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
CH3
O
O

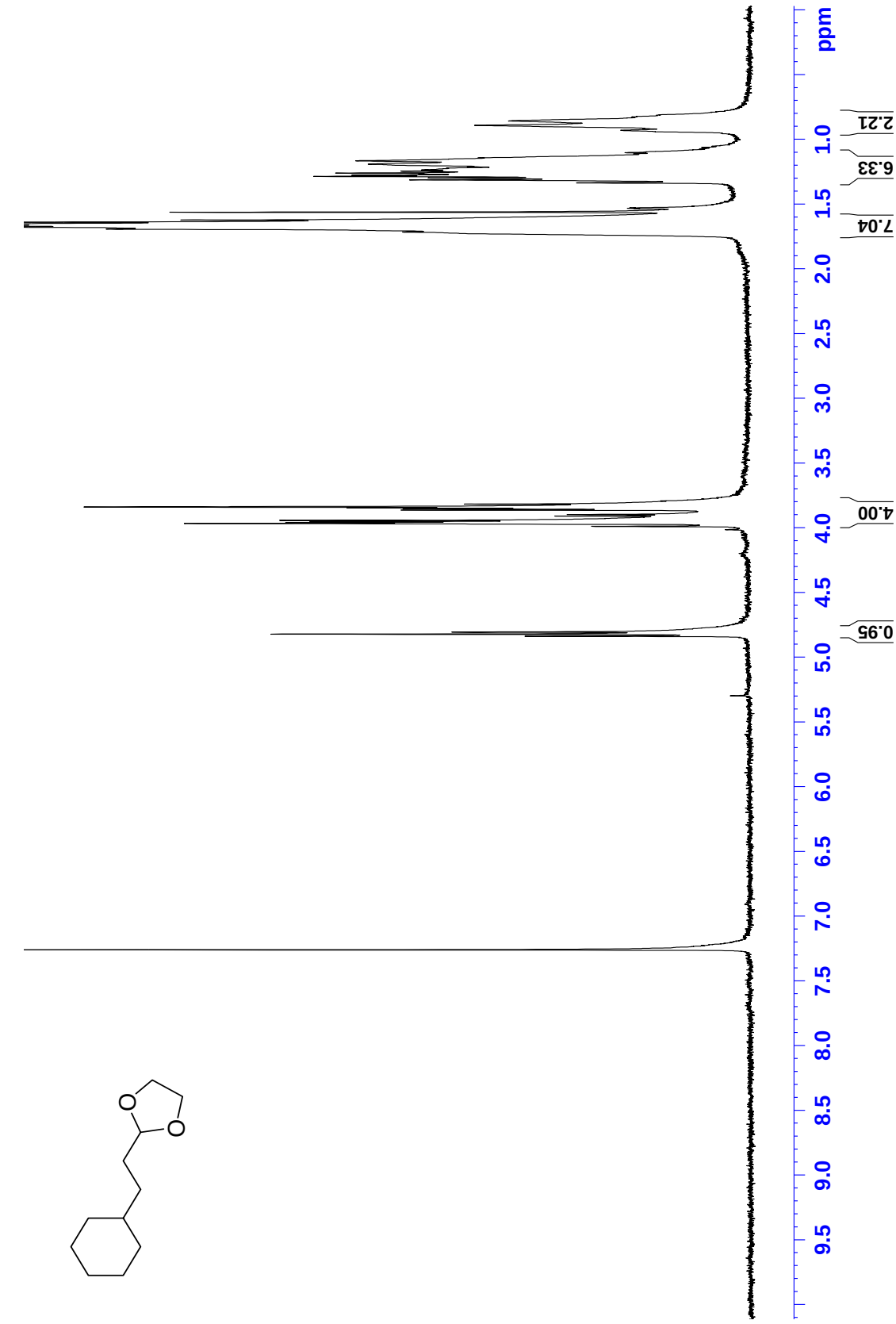
5

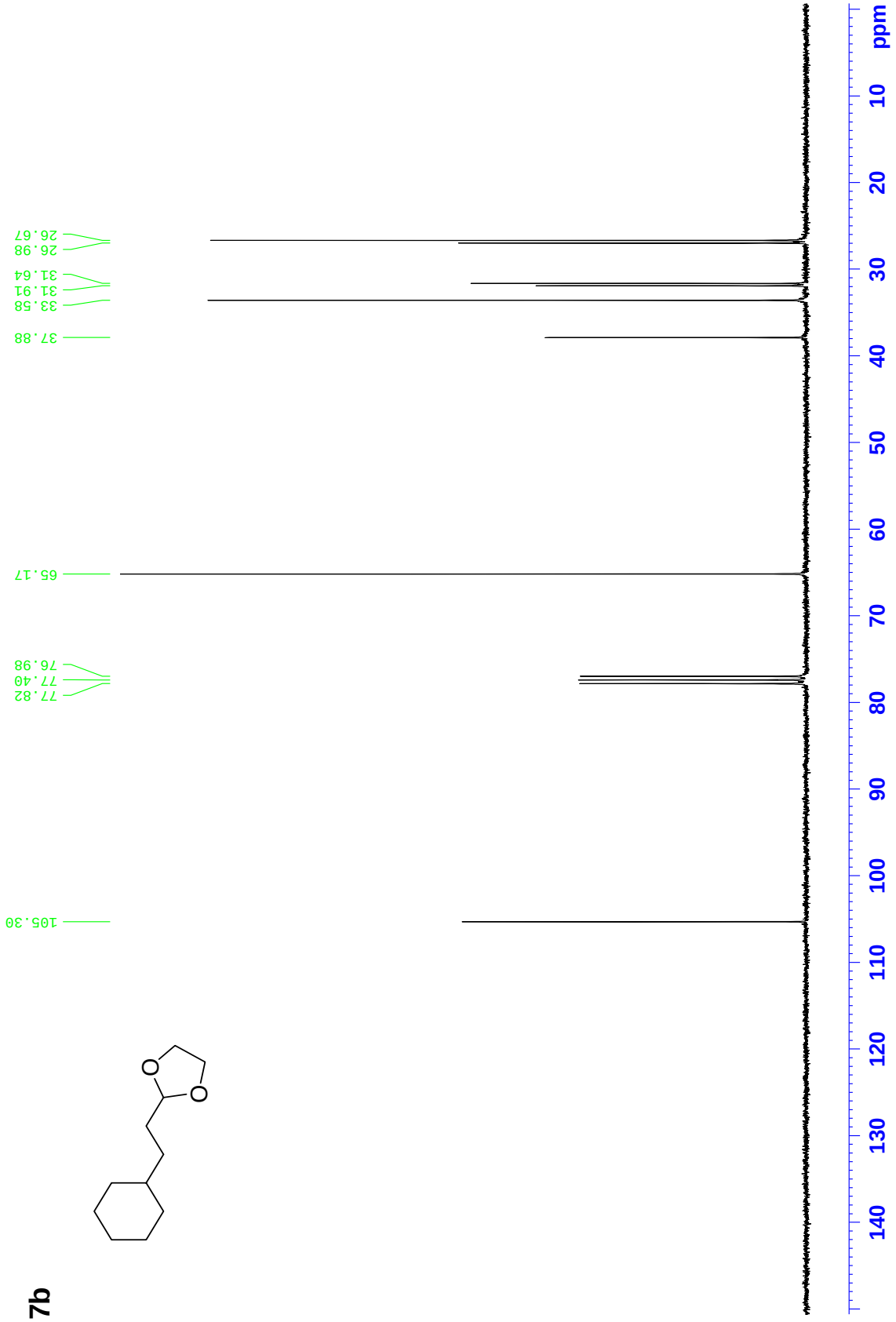
7a




ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
4.08
4.06
1.98
4.09
1.00
2.96
2.00

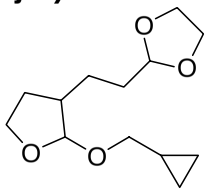

7a
143.01
128.69
128.54
125.91
104.92
77.83
77.40
76.98
65.13
36.13
34.15
31.69
29.50
24.23
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170


7b
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.95
4.00
7.04
6.33
2.21


7b
105.30
77.82
77.40
76.98
65.17
37.88
33.58
31.91
31.64
26.98
26.67
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140

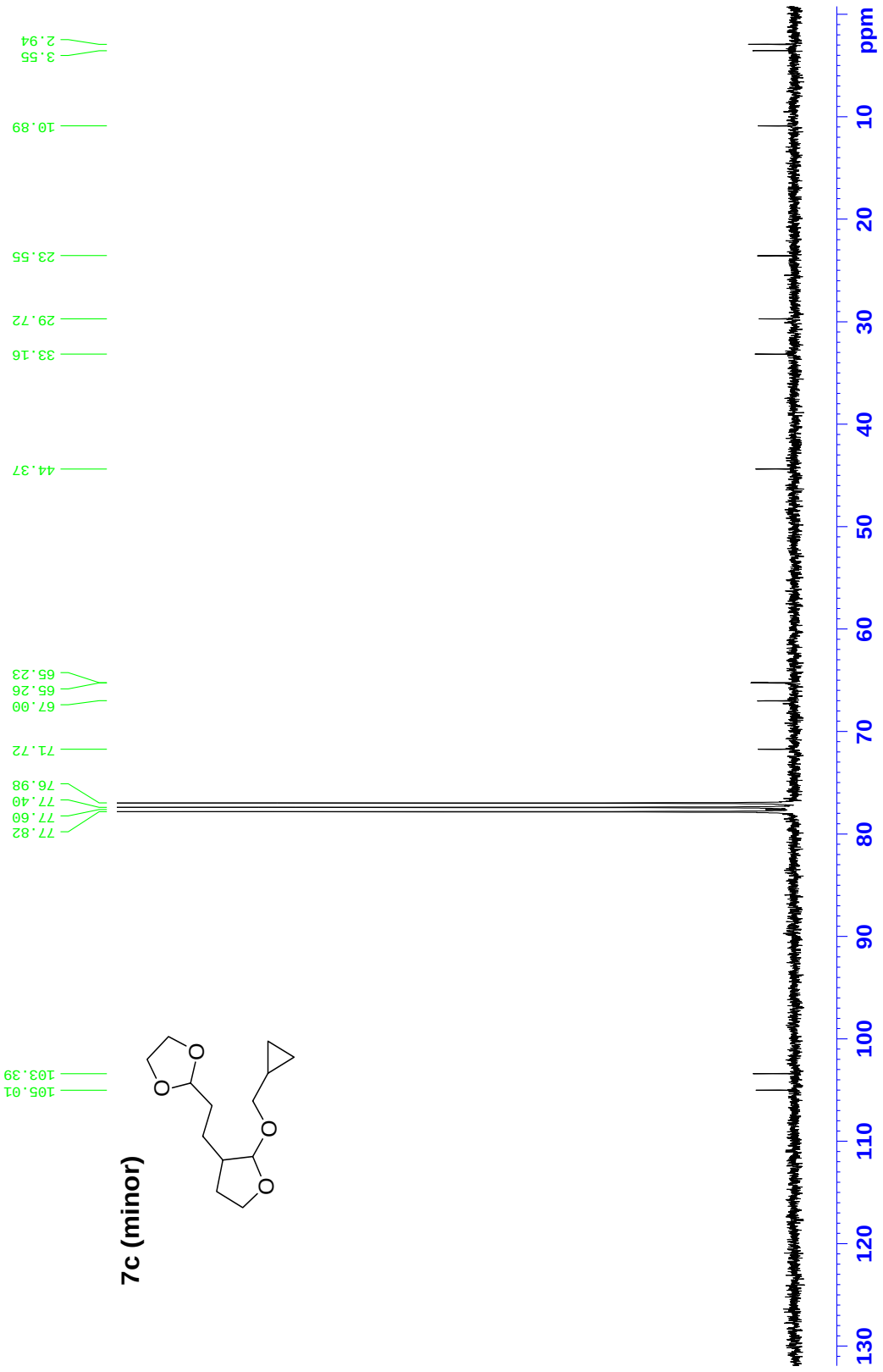
7c (major)
7.26
4.81
4.80
3.96
3.90
3.84
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
2.05
2.02
1.01
3.00
3.17
1.92
1.01
1.00
6.30
0.94
1.00

7c (major)

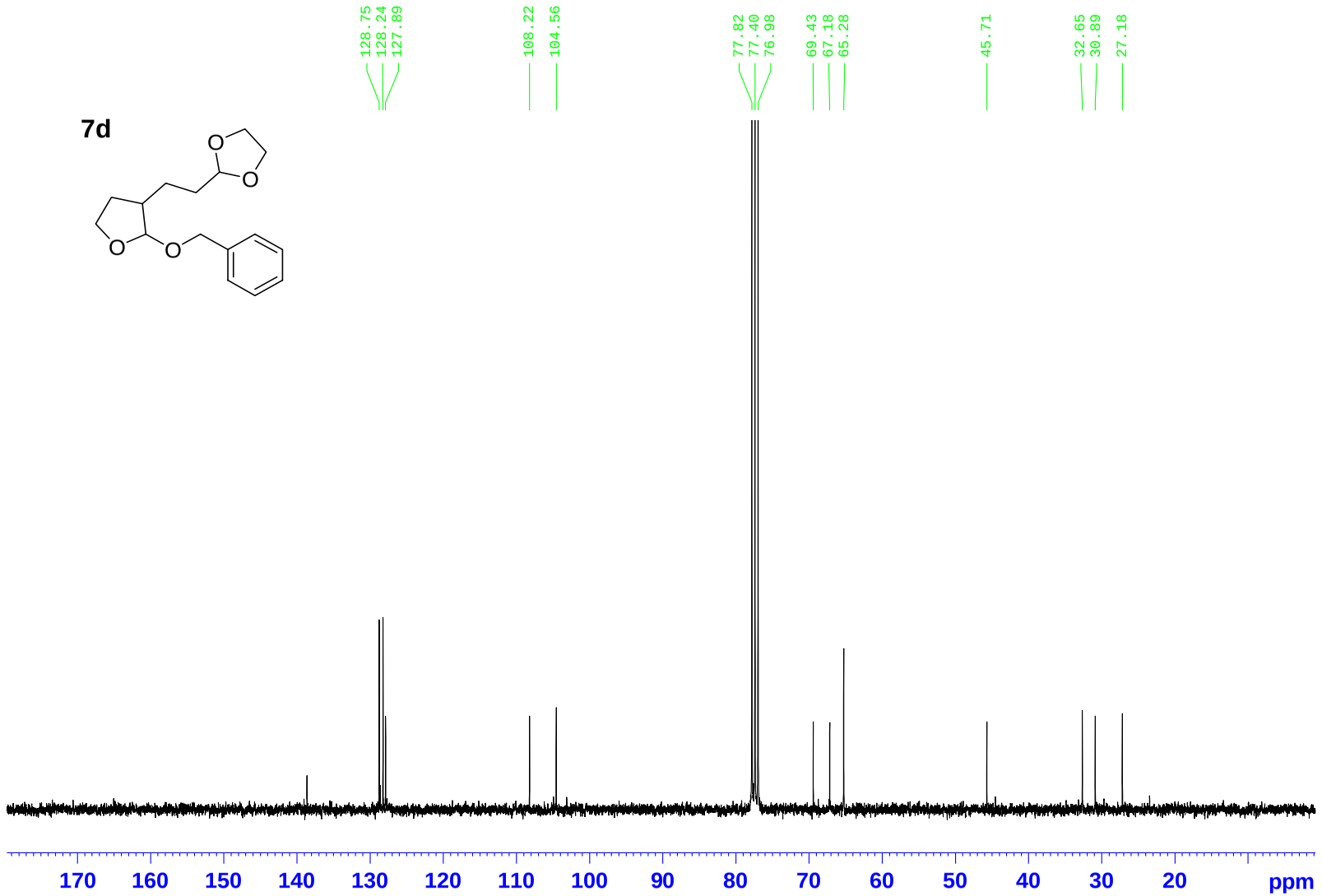


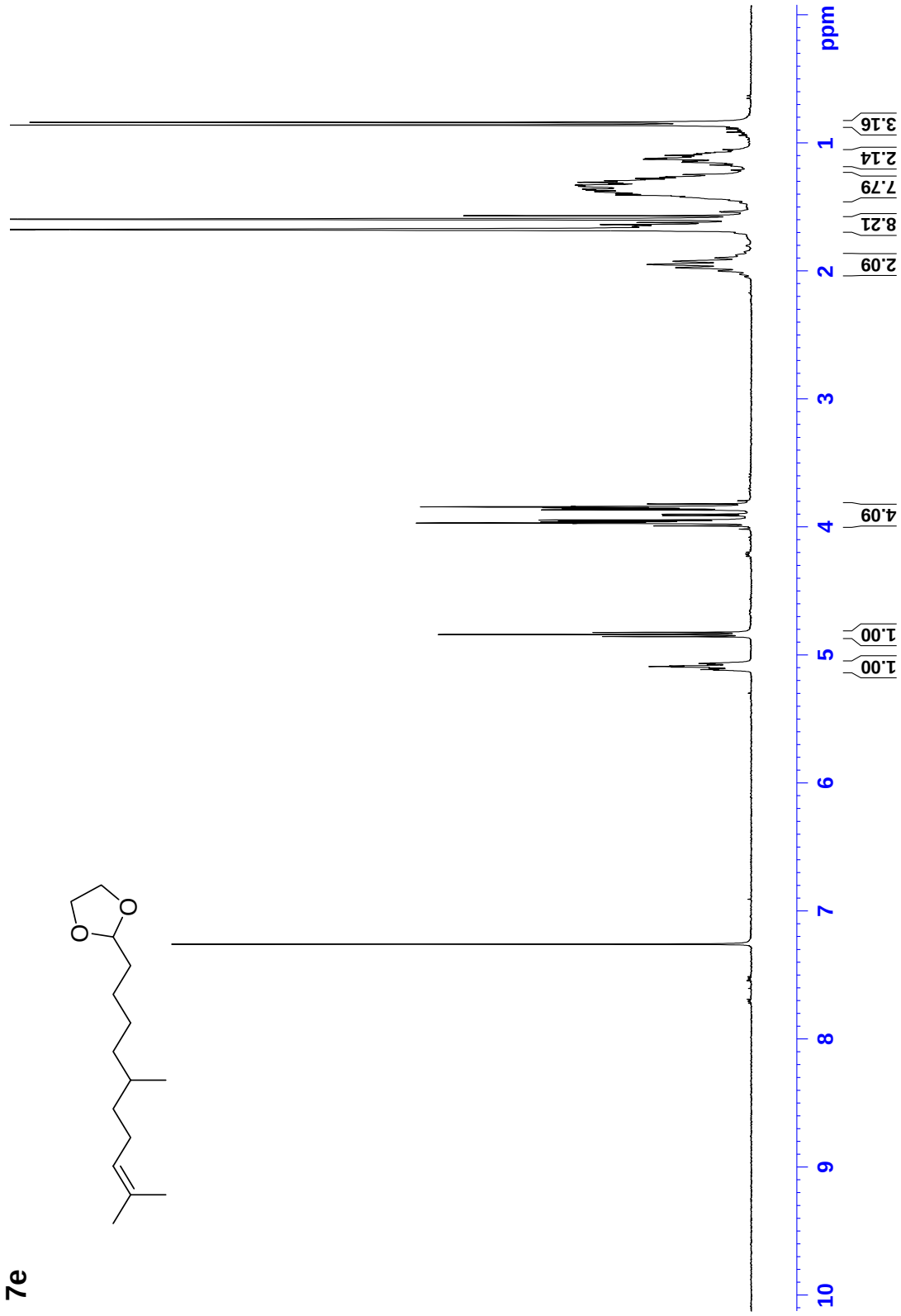
108.56
104.56
77.82
77.40
76.98
72.44
66.89
65.22
45.60
32.65
30.91
27.24
10.89
3.58
3.17
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

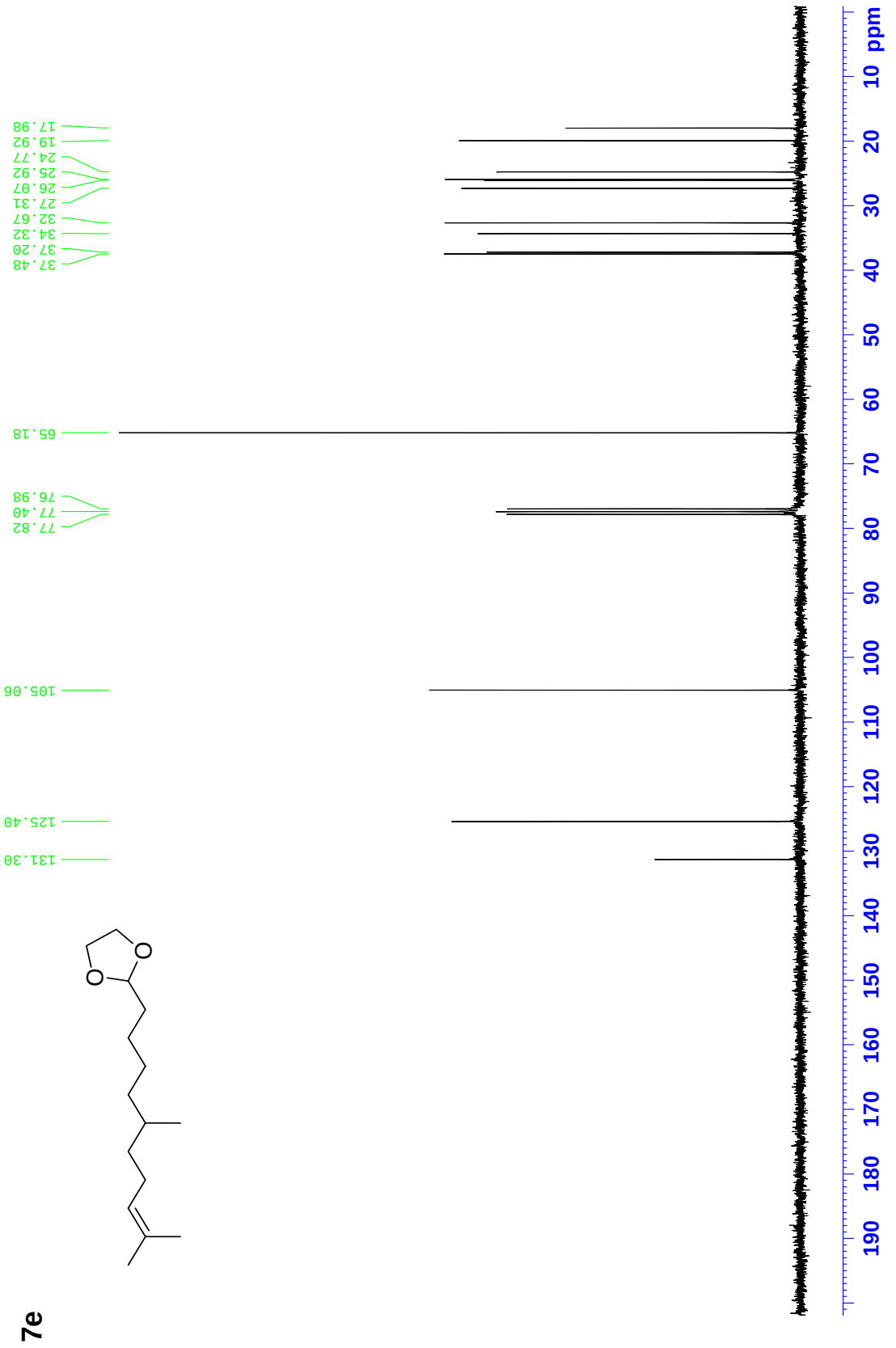
7c (minor)
7.26
1.00
1.01
6.07
1.08
1.06
2.14
4.94
2.14
1.24
0.69
2.14
2.13
ppm

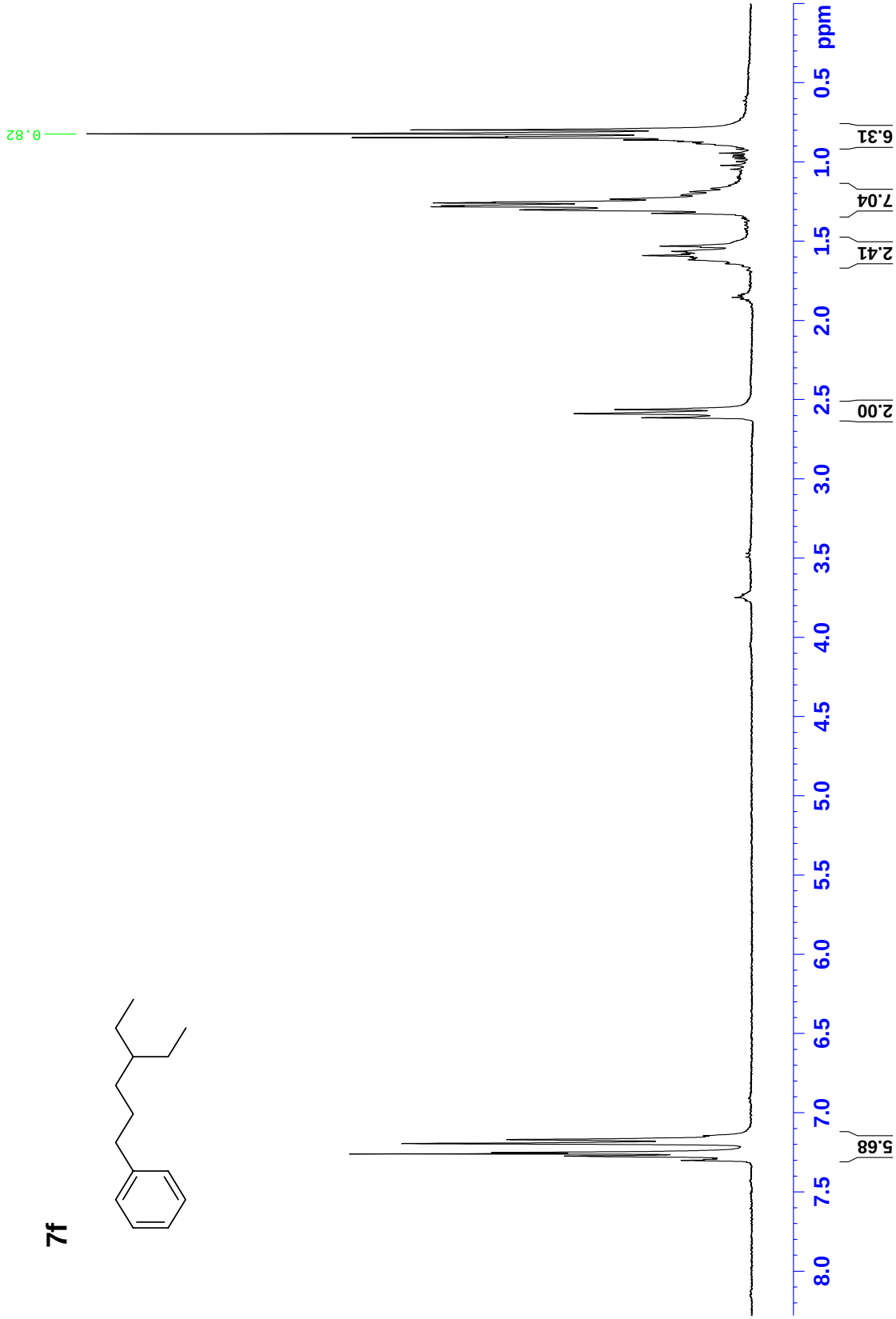

2.94
3.55
10.89
23.55
29.72
33.16
44.37
65.23
65.26
67.00
71.72
76.98
77.40
77.60
77.82
103.39
105.01
7c (minor)
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130

7.31
5.72
0.90
1.00
0.99
1.00
6.05
1.90
2.85
1.28
1.06
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
7d


7d
128.75
128.24
127.89
108.22
104.56
77.82
77.40
76.98
69.43
67.18
65.28
45.71
32.65
30.89
27.18
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

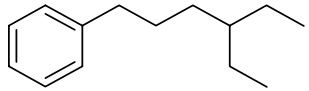

7e
ppm
1
2
3
4
5
6
7
8
9
10
3.16
2.14
7.79
8.21
2.09
4.09
1.00
1.00


7e
17.98
19.92
24.77
25.92
26.07
27.31
32.67
34.32
37.20
37.48
65.18
76.98
77.40
77.82
105.06
125.40
131.30
10 ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

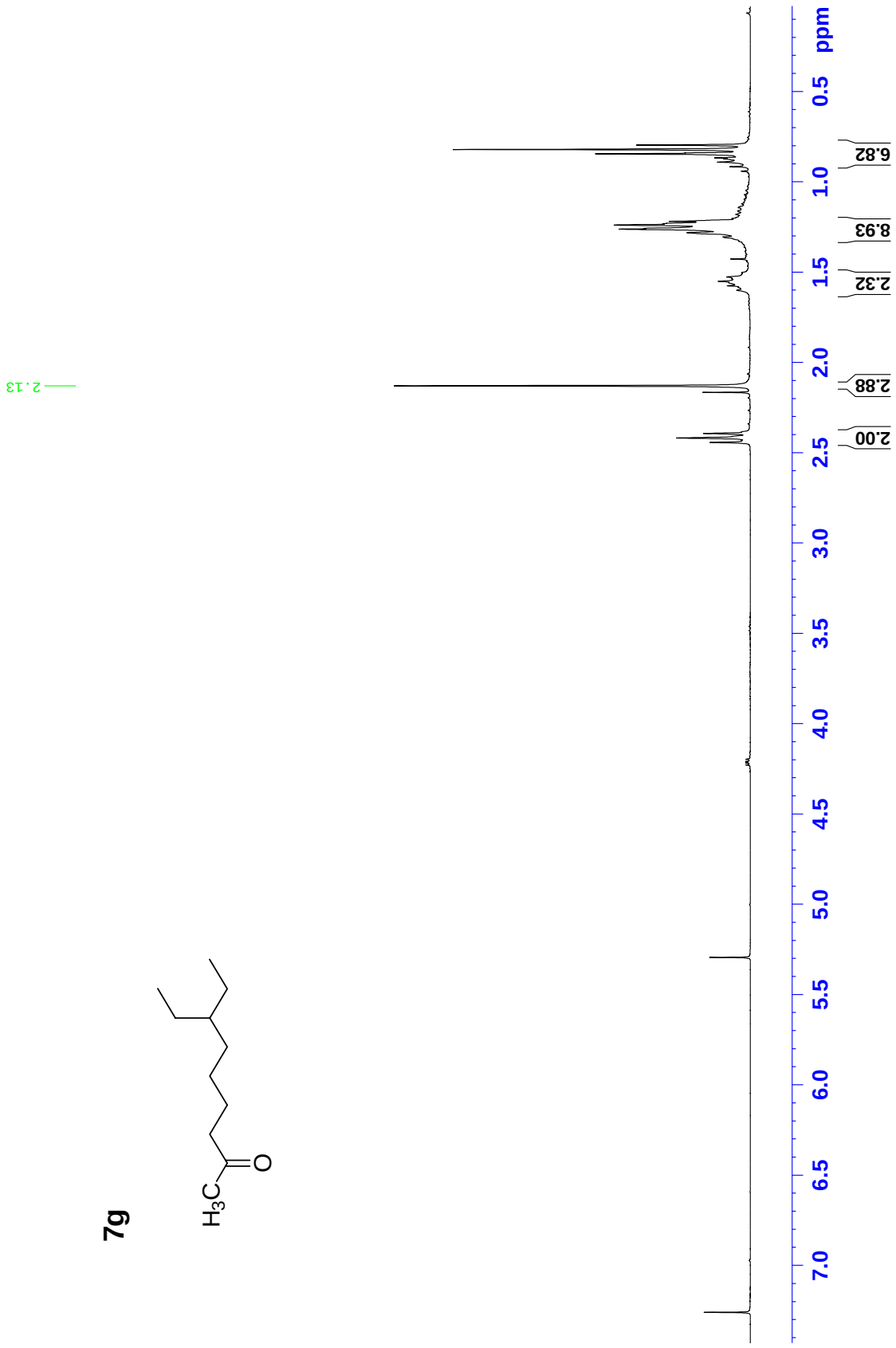

0.82
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
6.31
7.04
2.41
2.00
5.68

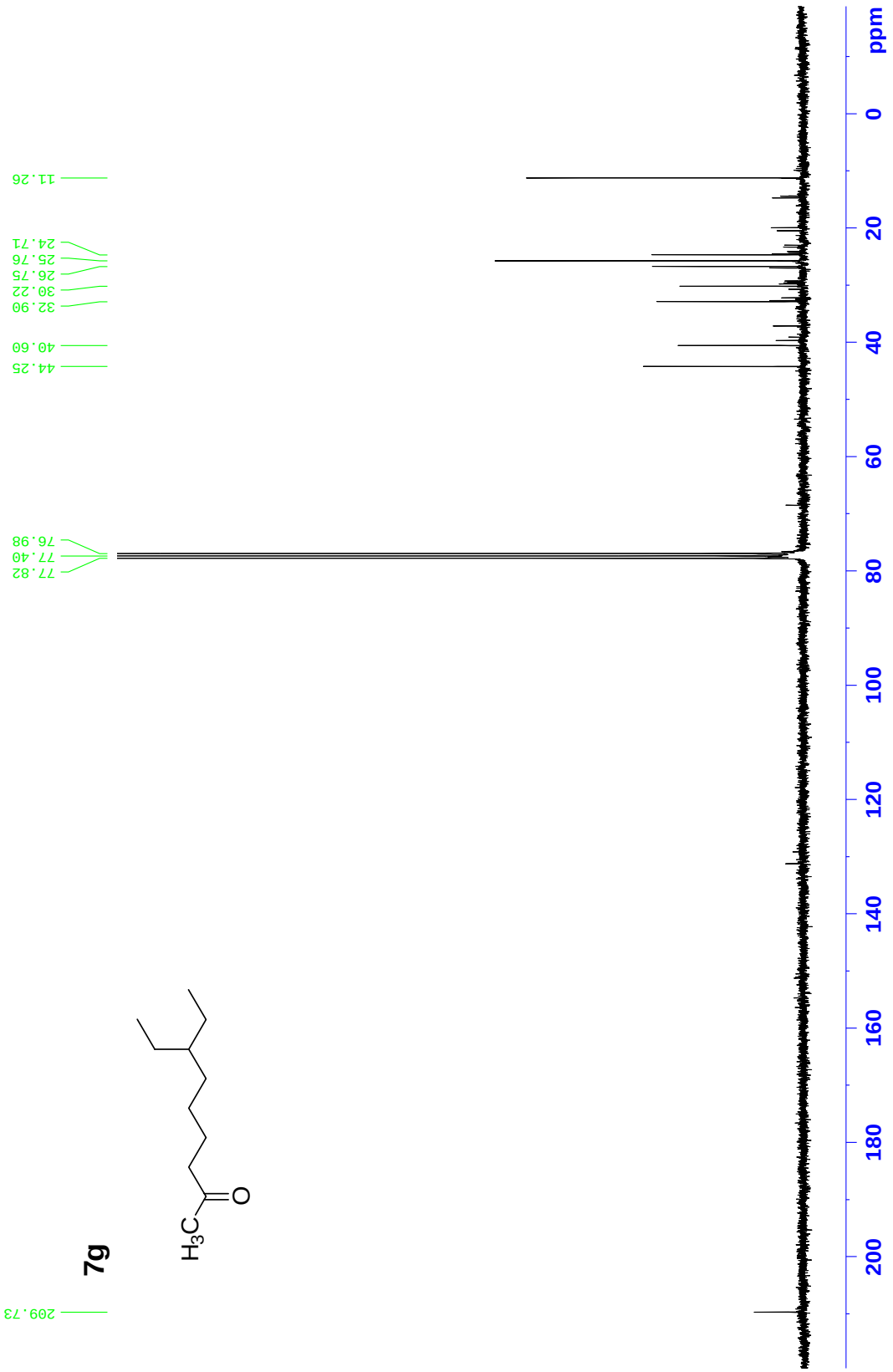
7f

7f

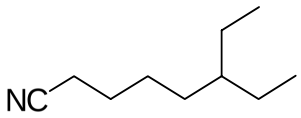


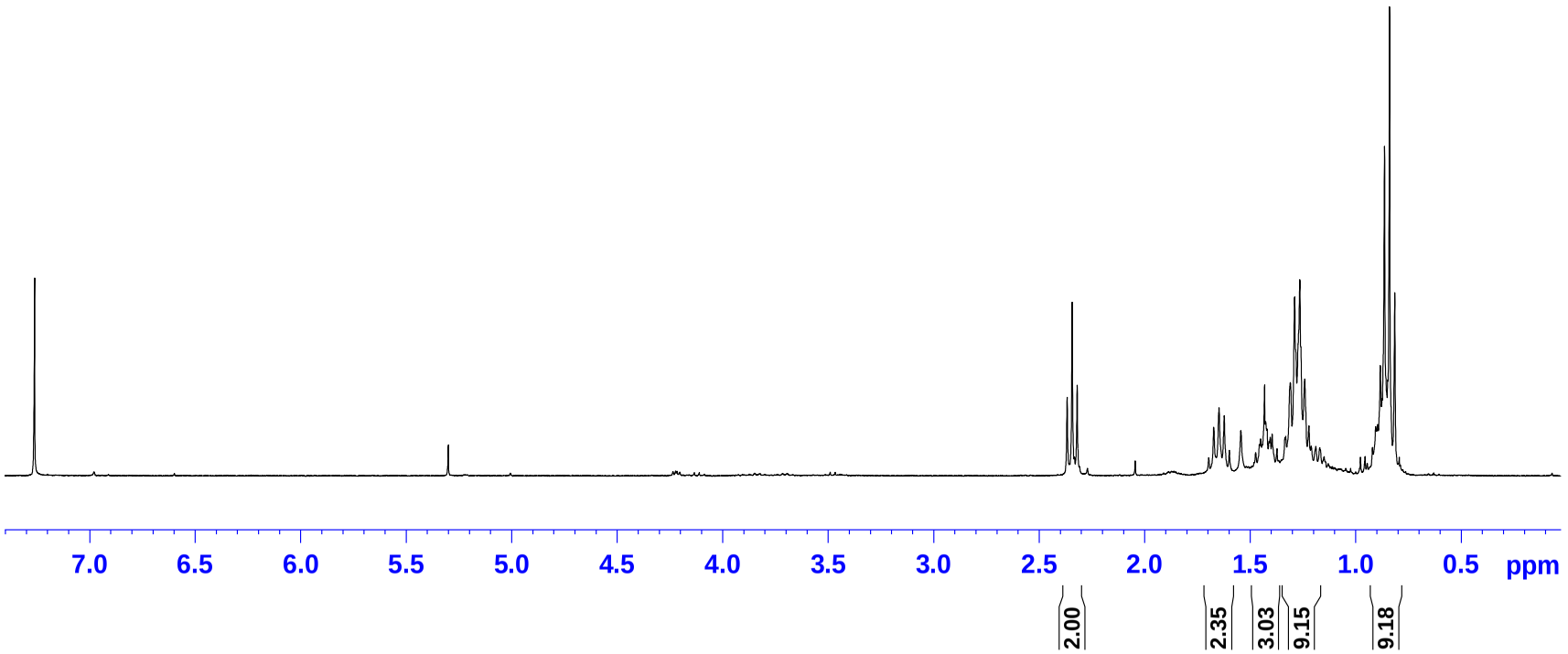
128.76
128.60
125.94
77.82
77.40
76.98
40.66
36.82
32.86
29.13
25.79
11.29
200
180
160
140
120
100
80
60
40
20
0
ppm

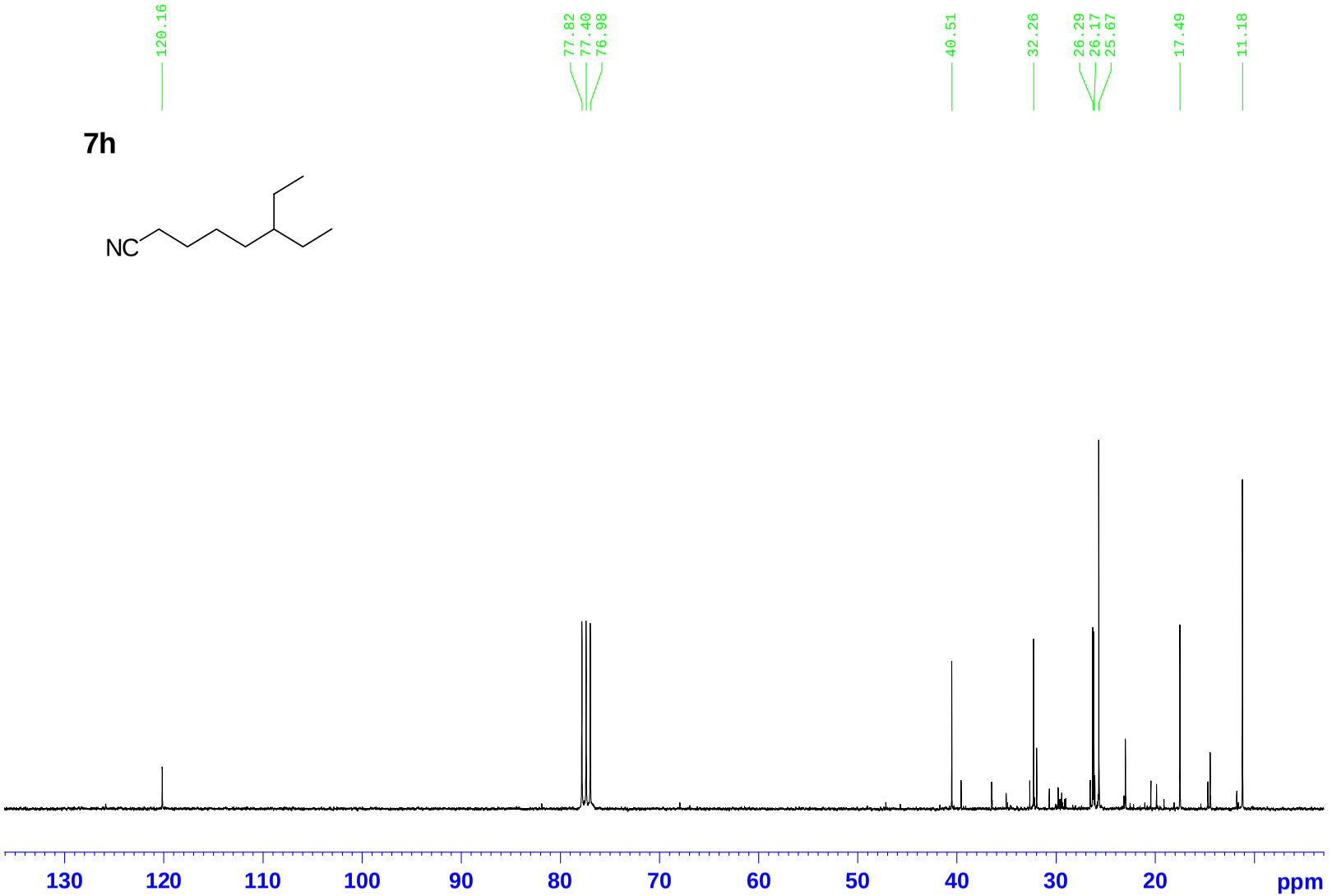

7g
H3C
O
2.13
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.88
2.32
8.93
6.82


7g
209.73
77.82
77.40
76.98
44.25
40.60
32.90
30.22
26.75
25.76
24.71
11.26
ppm
0
20
40
60
80
100
120
140
160
180
200

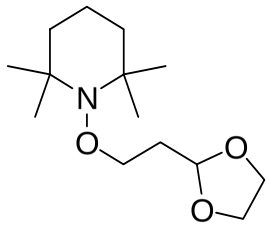
7h





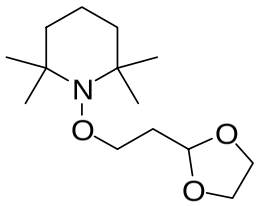

120.16
77.82
77.40
76.98
40.51
32.26
26.29
26.17
25.67
17.49
11.18
7h
NC
130
120
110
100
90
80
70
60
50
40
30
20
ppm

8


N
O
O
O

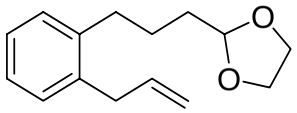
7.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
6.21
2.07
5.25
5.08
13.94

8


N
O
O
O

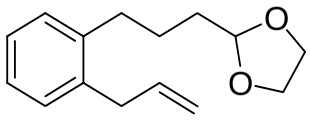
103.30
90.66
72.87
66.35
60.41
40.53
34.31
33.98
21.03
18.14
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

11a

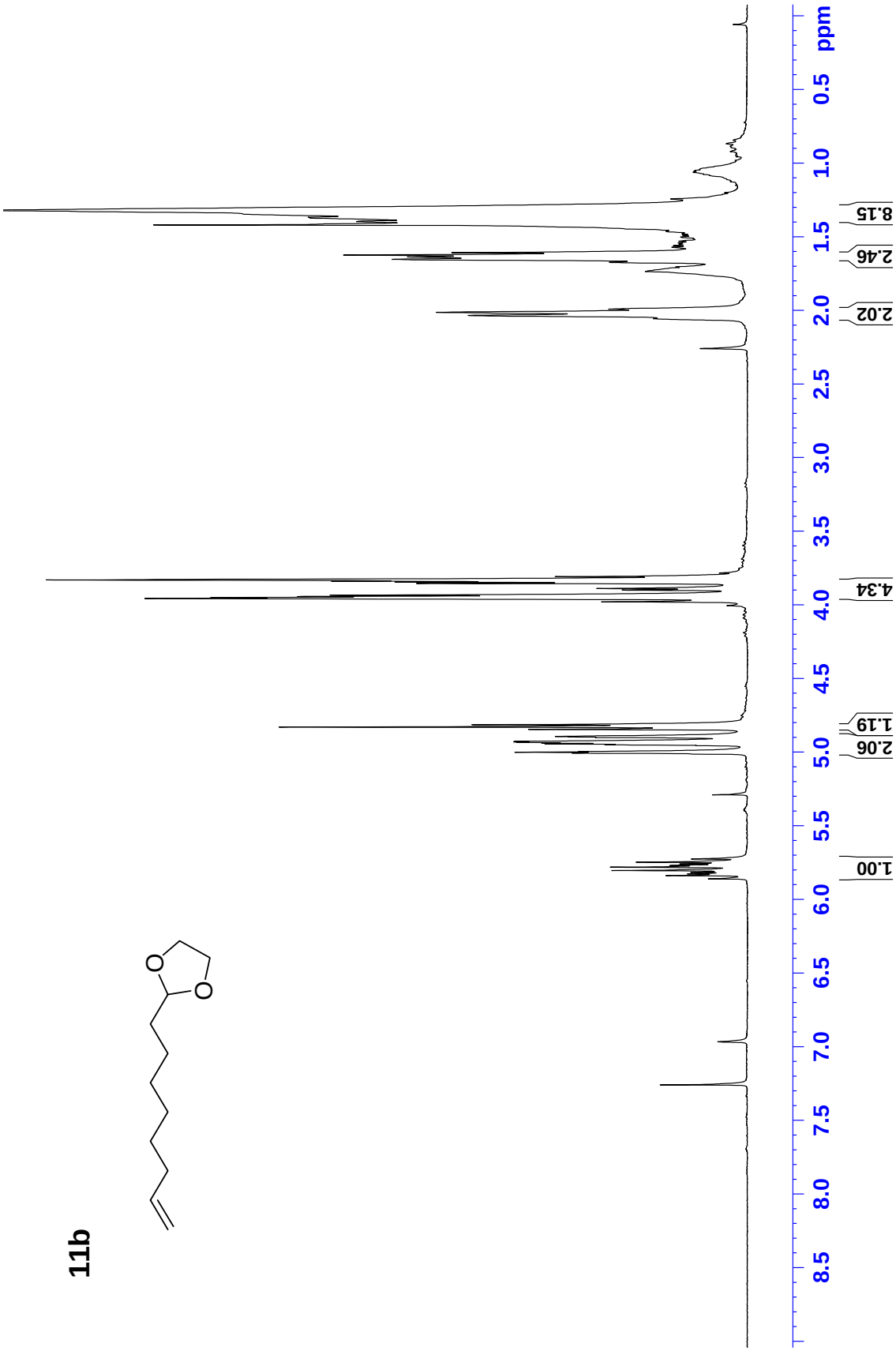

O
O

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.00
0.99
2.05
1.09
4.58
2.10
1.98
4.61

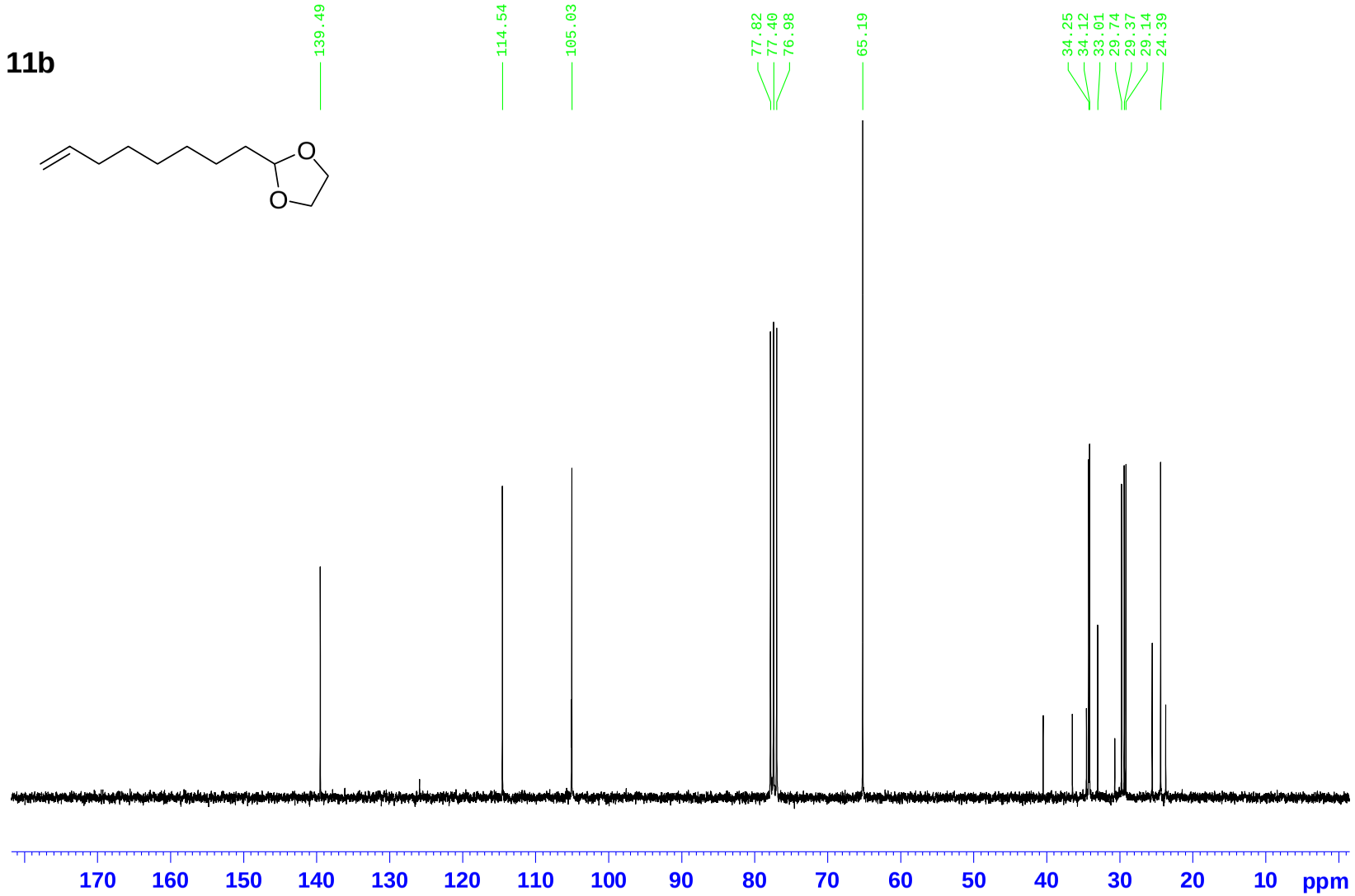
11a


O
O

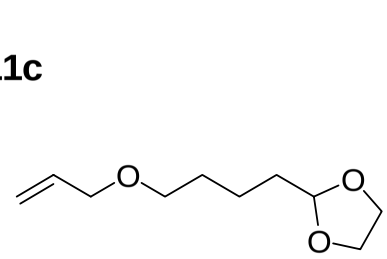
140.60
137.70
129.91
129.57
126.68
126.42
115.95
104.77
77.82
77.40
76.98
65.21
37.37
34.06
32.82
25.50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


11b
O
O
8.15
2.46
2.02
4.34
1.19
2.06
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

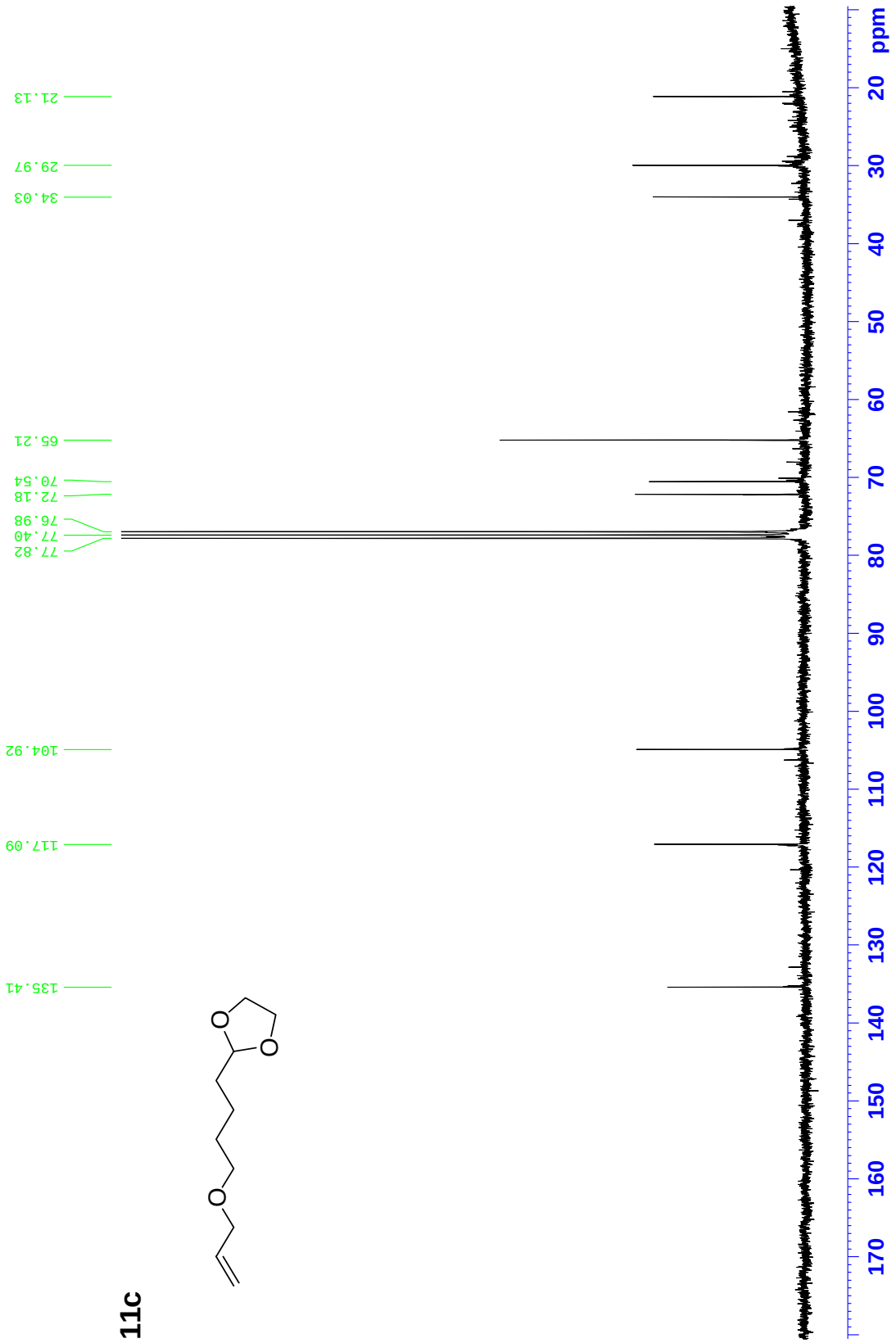
11b


139.49
114.54
105.03
77.82
77.40
76.98
65.19
34.25
34.12
33.01
29.74
29.37
29.14
24.39
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

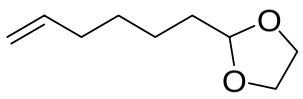
11c


O
O
O

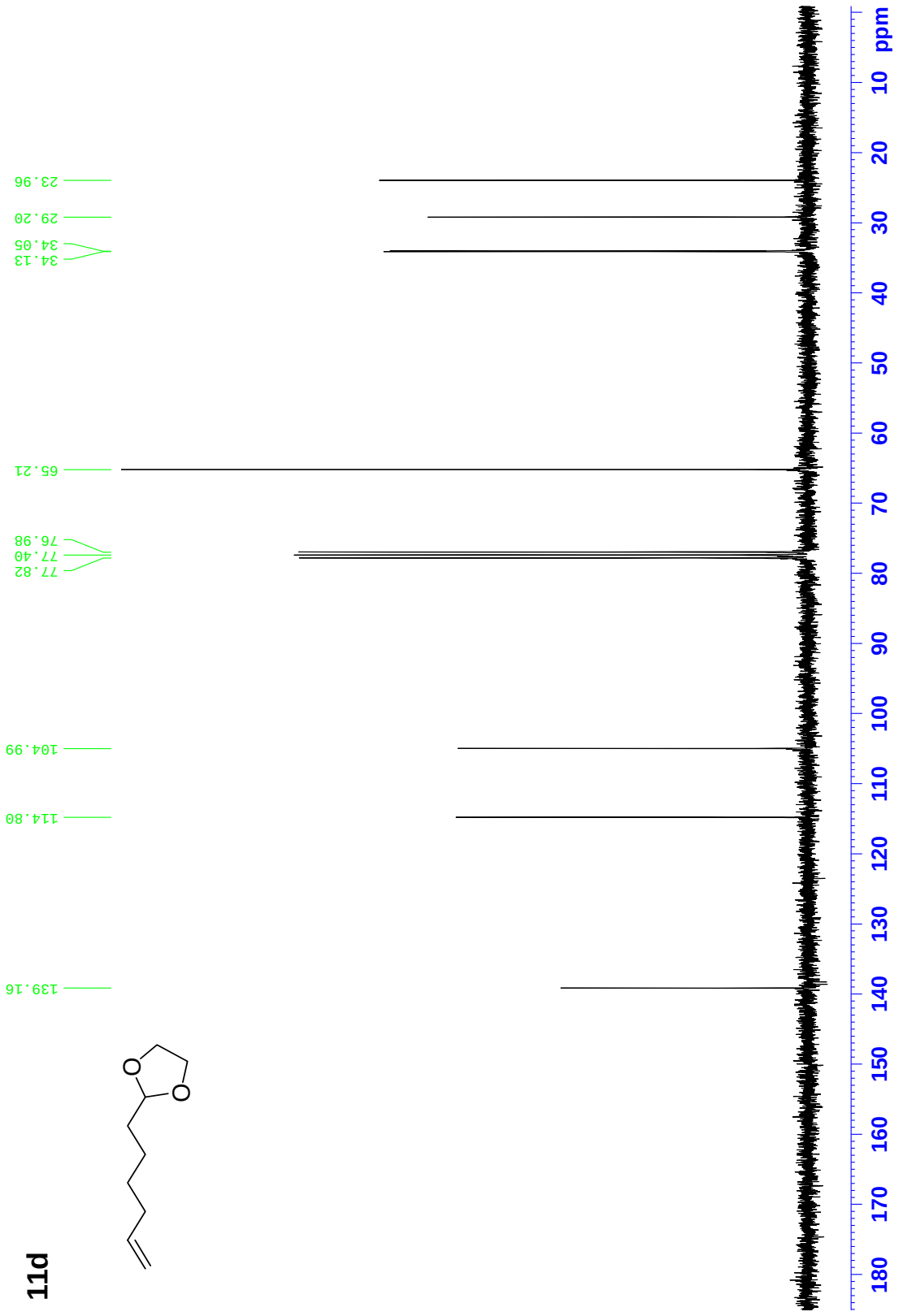
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.99
2.06
1.00
6.14
2.19
5.48
2.13

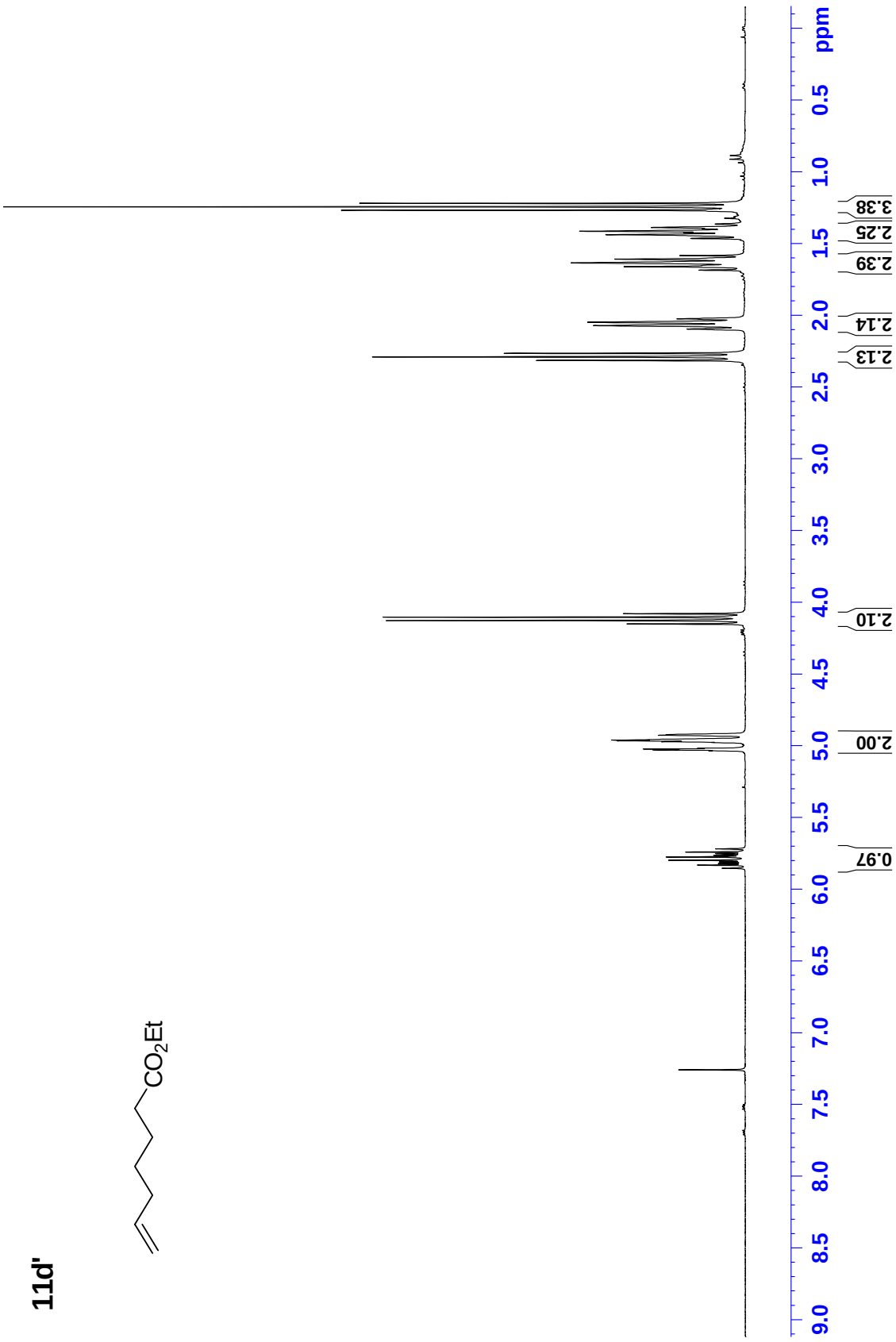

21.13
29.97
34.03
65.21
70.54
72.18
76.98
77.40
77.82
104.92
117.09
135.41
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
11c

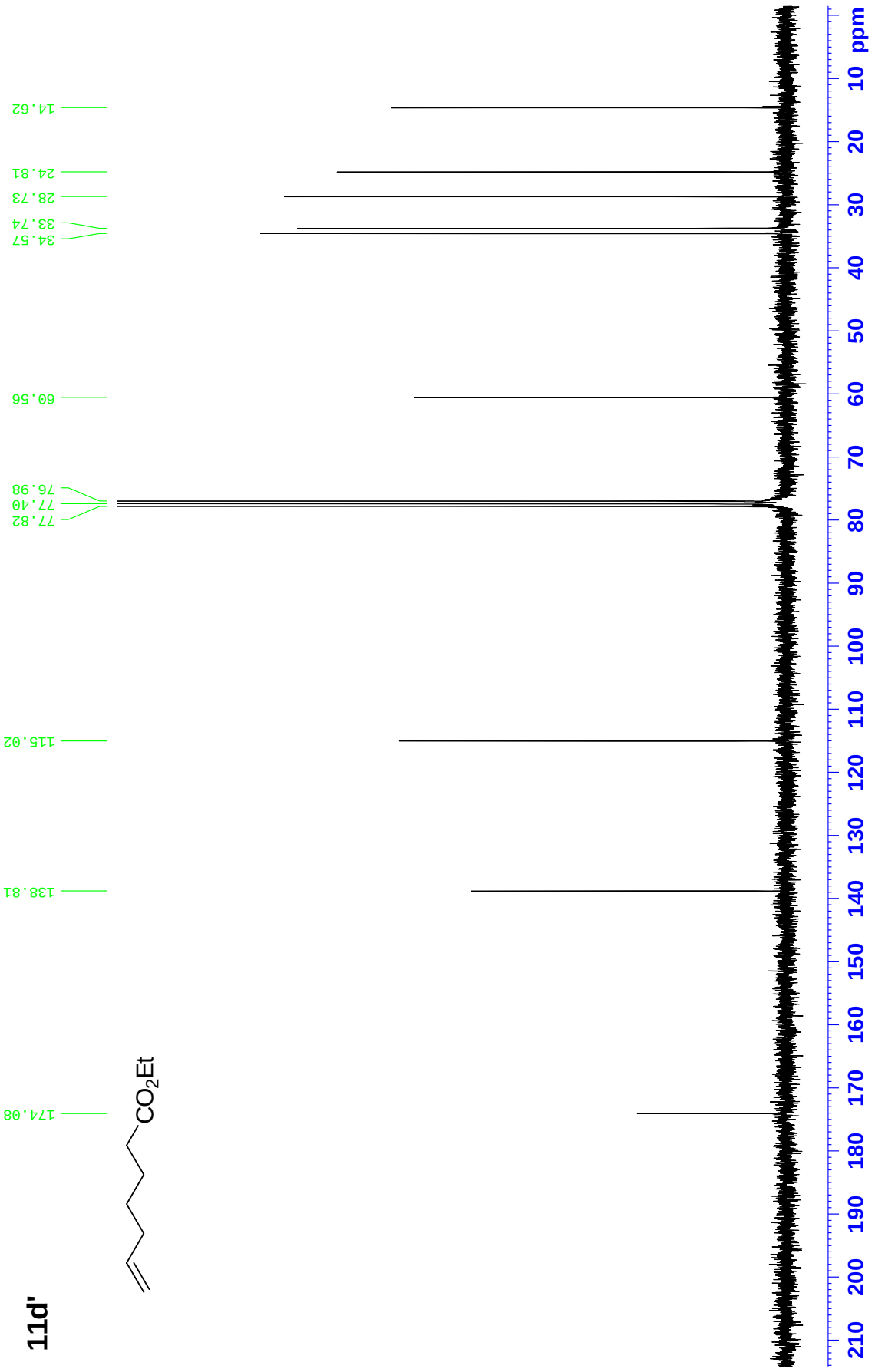
11d


O
O

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.96
2.00
1.06
4.38
2.14
2.36
4.10


11d
139.16
114.80
104.99
77.82
77.40
76.98
65.21
34.13
34.05
29.20
23.96
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180


11d'
CO2Et
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.97
2.00
2.10
2.13
2.14
2.39
2.25
3.38


11d'
CO2Et
14.62
24.81
28.73
33.74
34.57
60.56
76.98
77.40
77.82
115.02
138.81
174.08
ppm