Supporting Information for

Asymmetric Synthesis of 3,3,5,5-Tetrasubstituted 1,2-Dioxolanes:

Total Synthesis of Epiplakinic Acid F

Xiang-Yin Tian,[a] Jian-Wei Han,[a] Qiong Zhao[a] and Henry N.C. Wong*[a,b,c]

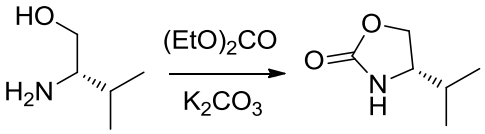
Table of Contents

General Information

All non-aqueous reactions were carried out using oven-dried glassware under a positive pressure of dry nitrogen unless otherwise noted. Solvents were predried over activated 4Å molecular sieves and were refluxed over magnesium (methanol), sodium (toluene, THF, Et_2O, benzene, dioxane, cyclohexane), or calcium hydride (DCM, DCE, EA, CH_3CN) under an argon atmosphere and collected by distillation. All evaporation of organic solvents was carried out with a rotary evaporator. Column chromatography was performed on silica gel 60 (Huanghai, 300-400mesh). Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. 1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 (300 MHz) or Bruker AM 400 (400 MHz) spectrometer. ^{1}H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane. Data are reported as follows: brs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz. HPLC analyses on a Agilent 1100 Series chromatograph. Infrared spectra were prepared as KBr pellets and were recorded on a Bio-Rad FTS-185 FT-IR spectrometer. Optical rotations were measured with a Perkin Elmer 241 polarimeter in a 1 dm cuvette. Mass spectra were recorded by the mass spectrometry service of Shanghai Institute of Organic Chemistry.

Experimental Details and Characteristic Data for Compounds

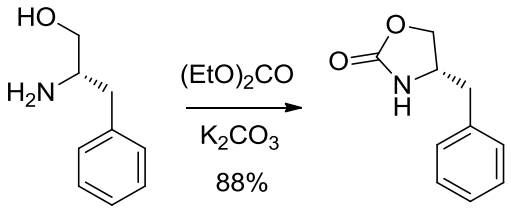
Synthesis of (*S*)-4-Isopropyloxazolidin-2-one (9a):[1]



S-1 **9a**

Into a 25-mL flask equipped with a 10 cm Vigreux column was added **S-1** (2 g, 19.5 mmol), diethyl carbonate (4.7 ml, 38.8 mmol), and anhydrous potassium carbonate (2.68 g, 19.5 mmol). The mixture was heated at 130-135 ^{o}C (oil temperature) and ethanol (1.8 g, 38.8 mmol) was distilled (ca. 1 hour). The resultant mixture was then cooled to room temperature and dissolved in CH_2Cl_2 (20 mL), and the mixture was washed with water (10 mL×2) and brine (10 mL), dried over Na_2SO_4, and concentrated. The residual was crystallized by EtOAc to give **9a** (white needles, 2.0g, 80%). **M.p.**: 73 ℃ (Lit[1]: 69-70 ℃).; **$[\alpha]_D^{25}$** = +11.3 (*c*, 0.5, $CHCl_3$), [Lit[2]: $[\alpha]_D^{25}$ = +13.0 (*c*, 2.6, $CHCl_3$)]; **IR** (Film): 3271, 2976, 2961, 2915, 2875, 1751, 1725, 1472, 1406, 1247, 1091, 1010, 936, 769, 710 cm^{-1}; **MS** (EI): *m/z* (relative intensity), 129 (M^+, 6); **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 7.00 (s, 1H), 4.42-4.48 (t, *J* = 8.4 Hz, 1H), 4.11 (dd, *J* =8.4, 6.3 Hz, 1H), 3.61 (q, *J* = 6.9 Hz, 1H), 1.70-1.76 (m, 1H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H).

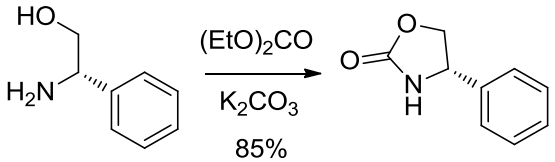
Synthesis of (*S*)-4-Benzyloxyzaolidin-2-one (9b):[1]



S-2 **9b**

Into a 25-mL flask equipped with a 10 cm Vigreux column was added **S-2** (1 g, 6.6 mmol), diethyl carbonate (1.6 ml, 13.2 mmol), and anhydrous potassium carbonate (0.91 g, 6.6 mmol). The mixture was heated at 130-135 ^{o}C and ethanol (0.60 g, 13.2 mmol) was distilled (ca. 1 hour). The resultant mixture was then cooled to room temperature and dissolved in CH_2Cl_2 (20 mL), and the mixture was washed with water (10 mL×2) and brine (10 mL), dried over Na_2SO_4, and concentrated. The residual was purified by flash chromatography (hexane/EtOAc, 2/1) to obtain **9b** (white solid, 1.03 g, 88 %). **M.p.**: 89 ℃ (Lit[3]: 89-90 ℃).; **$[\alpha]_D^{25}$** = -62.7 (*c*, 1.0, $CHCl_3$), [Lit[4]: $[\alpha]_D^{22}$ = -63.3 (*c*, 1.0, $CHCl_3$)]; **IR** (Film): 3281, 2924, 1751, 1709, 1404, 1245, 1096, 1063, 1021, 943, 758, 708, 618, 528 cm^{-1}; **MS** (EI): *m/z*, 177 (M^+); **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 7.13-7.42 (m, 5H), 5.82 (br, 1H), 4.45 (t, *J* = 7.5 Hz, 1H), 4.03-4.20 (m, 2H), 2.88 (d, *J* = 6.3 Hz, 2H).

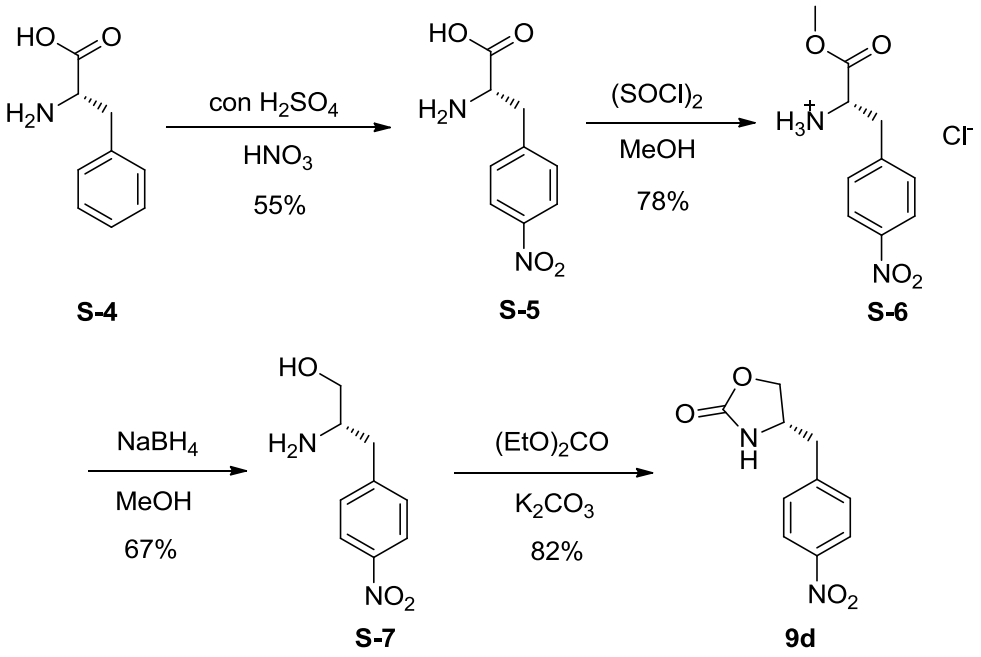
Synthesis of (*S*)-4-phenyloxazolidin-2-one (9c):[1]



S-3 **9c**

Into a 25-mL flask equipped with a 10 cm Vigreux column was added **S-3** (1 g, 7.3 mmol), diethyl carbonate (1.75 ml, 14.6 mmol), and anhydrous potassium carbonate (1.0 g, 7.3 mmol). The mixture was heated at 130-135 ℃ and ethanol (0.68 g, 14.6 mmol) was distilled (ca. 1 hour). The resultant mixture was then cooled to room temperature and dissolved in CH_2Cl_2 (20 mL), and the mixture was washed with water (10 mL × 2) and brine (10 mL), dried over Na_2SO_4, and concentrated. The residual was purified by flash chromatography (hexane/EtOAc, 1/1) to obtain **9b** (white solid, 1.01 g, 85 %). **M.p.**: 127-128 ℃ (Lit[5]: 124-126 ℃); **$[\alpha]_D^{25}$** = +47.6 (*c*, 1.2, $CHCl_3$), [Lit[5]: $[\alpha]_D^{23}$ = +48.1 (*c*, 1.0, $CHCl_3$)]; **IR** (Film): 3250, 3031, 1743, 1705, 1488, 1402, 1236, 1098, 1077, 1002, 967, 924, 768, 697 cm^{-1}; **MS** (ESI): *m/z*, 164.1 ($M+H^+$); **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 7.34-7.45 (m, 5H), 6.30 (s, 1H), 4.97 (t, *J* = 7.8 Hz, 1H), 4.74 (t, *J* = 8.7 Hz, 1H), 4.19 (t, *J* = 6.9 Hz, 1H).

Synthesis of (*S*)-4-(4-Nitrobenzyl)-1,3-oxazolidin-2-one (9d):[6]



S-4 **S-5** **S-6**

S-7 **9d**

Synthesis of (*S*)-2-amino-3-(4-nitrophenyl)propanoic acid (S-5):

To a stirring concentrated sulfuric acid (40 mL) at 0 ℃ was added **S-4** (30 g, 182 mmol), After **S-4** was dissolved, the concentrated nitric acid (21 mL, 364 mmol) was gradually added over 45 min. The reaction mixture was then stirred for another 30 min at 0 ℃ and was allowed to warm to room temperature and stirred for 1 hour. The reaction mixture was poured onto ice/water (200 L), and ammonia (26~28% in water) was added until adjust pH to 7~8. Then the solution was filtrated and the precipitate was washed by cooled water (20 mL 3), dried out to give the crude product. The crude

product was recrystallized from water (250 mL) to give **S-5** (white crystals, 21 g, 55%). **M.p.**: 236 ℃ (Lit[6]: 239-241 ℃); **$[\alpha]_D^{25}$** = +5.6 (*c*, 1.0, 3M HCl), [Lit[7]: $[\alpha]_D^{20}$ = +6.8 (*c*, 1.0, 3M HCl)]; **IR** (Film): 3293, 2895, 2651, 1700, 1647, 1616, 1571, 1538, 1516, 1419, 1350, 1332, 1312, 878, 863 cm^{-1}; **MS** (EI): *m/z* (relative intensity) 43 (100), 41(75), 94 (50), 120 (9), 105(8), 129(7), 144 (7); **^{1}H NMR** (300 MHz, MeOH): δ (ppm) 8.05 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 3.86 (t, *J* = 6.9 Hz, 1H), 3.05-3.25 (m, 2H).

Synthesis of (*S*)-Methyl 4-Nitrophenylalanate Hydrochloride (S-6):

To a solution of **S-5** (21 g, 100 mmol) in methanol (200 mL) was added thionyl chloride (10.6 mL, 150 mmol). And the reaction mixture was stirred for overnight at room temperature. Then the solvent was removed under reduced pressure and the residue was dried out to give **S-7** (white solid, 26 g, 100 %). **M.p.**: 219 ℃ (Lit[6]: 227-228 ℃); **MS** (ESI): *m/z* (relative intensity) 235($[M-Cl]^+$); **^{1}H NMR** (300MHz, MeOH): *δ* (ppm) 8.07 (d, *J* = 8.1Hz, 2H), 7.35 (d, *J* = 8.1Hz, 2H), 4.35 (t, *J* = 6.9Hz, 1H), 3.65 (s, 3H), 3.17-3.34 (m, 2H); **IR** (Film): 2800-3400(br), 2984, 2917, 2677, 2631, 1744, 1604, 1544, 1519, 1508, 1492, 1454, 1349, 1241, 1146, 752cm^{-1}; **$[\alpha]_D^{25}$** = +43.9 (*c*, 1.0, H_2O), [Lit[8]: $[\alpha]_D^{20}$ = +34.2 (*c*, 1.0, EtOH)];

Synthesis of (*S*)-2-Amino-3-(4-nitrophenyl)propanol (S-7):

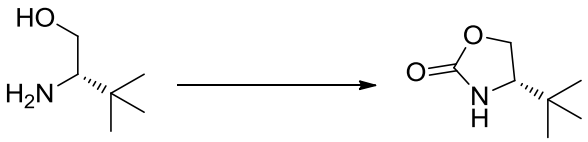
To a stirring solution of sodium borohydride (0.53 g, 14 mmol) in EtOH/water (1:1) (30 mL) at 0 ℃ was added the amino ester **S-7** (0.9 g, 3.5 mmol). The mixture was refluxed for 4 hours and then allowed to cool to room temperature. The solvent was filtrated and the precipitate was washed by EtOH. The filtrate was combined and the ethanol was then removed under vacuum. The remaining water was extracted with EtOAc (20 mL × 6) and the combined organic extracts was washed with brine (50 mL), dried over Na_2SO_4, and concentrated. The yellow solid was recrystallized from EtOH to give **S-7** (yellow crystals, 230 mg, 67 %). **M.p**: 145 ℃ (Lit[6]: 141-142 ℃); **$[\alpha]_D^{25}$** = -26.5 (*c*, 1.0, MeOH), [Lit[9]: $[\alpha]_D^{20}$ = -26.6 (*c*, 2.3, MeOH)]; **IR** (Film): 3352, 3297, 3106, 3079, 2944, 2905, 2837, 1607, 1596, 1585, 1515, 1344, 1109, 1058, 858, 703 cm^{-1}; **MS** (ESI): *m/z* (relative intensity) 197($M+H^+$); **^{1}H NMR** (300 MHz, $CDCl_3$): *δ* (ppm) 8.17 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 3.65 (dd, *J* = 3.9, 10.8 Hz, 1H), 3.41 (dd, *J* = 7.2, 10.8 Hz, 1H), 3.18 (m, 1H), 2.92 (dd, *J* = 3.9, 13.5 Hz, 1H), 2.67 (dd, *J* = 8.4, 13.5 Hz, 1H), 1.6 (br, 2H).

Synthesis of (*S*)-4-(4-Nitrobenzyl)-1,3-oxazolidin-2-one (9d):

Into a 50-mL flask equipped with a 10-cm Vigreux column was added **S-7** (5 g, 25.5 mmol), diethyl carbonate (6.19 ml, 51 mmol), and anhydrous potassium carbonate (3.52 g, 25.5 mmol). The mixture was heated at 130-135 ℃ (oil temperature) for 1 hour and ethanol was distilled. The resultant mixture was then cooled to room temperature and dissolved in CH_2Cl_2 (50 mL), and the mixture was washed with water (50 mL×2) and brine (50 mL), dried over Na_2SO_4, and concentrated. The residual was purified by flash chromatography (hexane/EtOAc, 3/1) to obtain **9d** (yellow solid, 4.63 g, 87 %). **M.p.**: 132 ℃; **$[\alpha]_D^{25}$** = -65.0 (*c*, 0.8, $CHCl_3$),

[Lit[10]: $[\alpha]_D^{20}$ = -63 (*c*, 5.5, $CHCl_3$)]; **IR** (Film): 3254, 3104, 3077, 3000, 2973, 2192, 2857, 1774, 1610, 1599, 1536, 1420, 1346, 1253, 1224, 1109, 703 cm^{-1}; **MS** (ESI): *m/z* (relative intensity) 223 ($M+H^+$); **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.21-8.24 (d, *J* = 8.7 Hz, 2H), 8.37-8.40 (d, *J* = 8.7 Hz, 2H), 5.57 (s, 1H), 4.51 (m, 1H), 4.17 (m, 2H), 3.01 (d, *J* = 6.0 Hz, 2H).

Synthesis of (*S*)-4-(tert-butyl)oxazolidin-2-one (9e):[1]



S-8 **9e**

Into a 25-mL flask equipped with a 10-cm Vigreux column was added **S-8** (800 mg, 6.8 mmol), diethyl carbonate (1.6 g, 13.7 mmol), and anhydrous potassium carbonate (1.9 g, 13.7 mmol). The mixture was heated at 130-135 ℃ for 1 hour and ethanol was distilled. The resultant mixture was then cooled to room temperature and dissolved in CH_2Cl_2 (20 mL), and the mixture was washed with water (10 mL×2) and brine (10 mL), dried over Na_2SO_4, and concentrated. The residual was purified by flash chromatography (hexane/EtOAc, 5/1) to obtain **9e** (white solid, 640 mg, 65 %). **M.p.**: 116-118 ℃ (Lit[11]: 120 ℃); $[\alpha]_D^{25}$ = +13.5 (*c*, 0.5, $CHCl_3$), [Lit[4]: $[\alpha]_D^{21}$ = +12.8 (*c*, 1.0, $CHCl_3$)]; **IR** (Film): 3299, 3244, 3008, 2970, 1744, 1717, 1480, 1401, 1238, 1101, 1052, 985, 962 cm^{-1}; **MS** (EI): *m/z*, 143 (M^+); **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 6.98 (br, 1H), 4.37 (t, *J* = 9.0 Hz, 1H), 4.20 (dd, *J* =9.0, 6.0 Hz, 1H), 3.61 (dd, *J* = 9.0, 6.0 Hz, 1H), 0.93 (s, 9H).

Tables for Feldman Reaction Conditions

Table S1. Solvent effective studies of the Feldman reaction of *trans*-**10a** and *trans*-**11a**

Entry[a]	Solvent	Yield %[b]	*trans*-12a/*trans*-13a/*cis*-14a [c]
1	DCM	quant	25/64/11
2	CH_3CN	quant	26/64/10
3	DMF	90%	26/64/10
4	Et_2O	quant	23/67/10
5	THF	99%	25/64/11
6	toluene	94%	23/67/10
7	EtOH	No product	complex

[a] Reaction conditions: 1:1 mixture of *trans*-**10**a and *trans*-**11**a (10 mg), Ph_2Se_2(0.2 equiv.), AIBN (0.4 equiv.), solvent(1 mL), 300 W sunlamp, room temperature. [b] Isolated yields of all diastereomers. [c] Determined by HPLC analysis.

Table S2. Additive effective studies of the Feldman reaction of *trans*-**10a** and *trans*-**11a**

Entry[a]	Additive (1 eq.)	Yield %[b]	*trans*-12a/*trans*-13a/*cis*-14a[c]
1	None	quant	26/66/9
2	LiCl	85	24/66/10
3	$Mg(ClO_4)_2$	96	22/63/15
4	$Ti(^iPrO)_4$	96	25/65/10
5	$Yb(OTf)_3$	86	21/67/12
6	$La(OTf)_3$	82	23/66/11
7	$Sc(OTf)_3$	92	16/76/8

[a] Reaction conditions: 1:1 mixture of *trans*-**10**a and *trans*-**11**a (10 mg), Ph_2Se_2(0.2 equiv.), AIBN (0.4 equiv.), ether (1 mL), Additive(1 equiv.), 300 W sunlamp, room temperature. [b] Isolated yields of all diastereomers. [c] Determined by HPLC analysis.

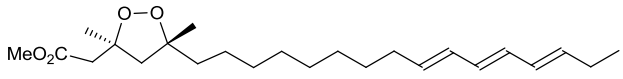
Table S3. Tempreture effective studies of the Feldman reaction of *trans*-**10a** and *trans*-**11a**

Entry[a]	Temp.	Yield %[b]	*trans*-12a/*trans*-13a/*cis*-14a[c]

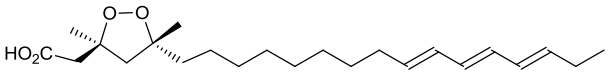
1	r.t.	quant	26/66/9
2	0℃	88	26/62/13
3	reflux	85	26/66/9

[a] Reaction conditions: 1:1 mixture of *trans*-**10**a and *trans*-**11**a (10 mg), Ph_2Se_2(0.2 equiv.), AIBN (0.4 equiv.), ether (1 mL), $Sc(OTf)_3$(1 equiv.), 300 W sunlamp. [b] Isolated yields of all diastereomers. [c] Determined by HPLC analysis.

Characterization Tables for Compounds 1 and 2



Epiplakinic acid F methyl ester (+)-**2**



Epiplakinic acid F (**1**)

Table S4. The data reported for natural Epiplakinic acid F methyl ester and the data for our Synthetic compound 2 (for comparison)

Epiplakinic acid F methyl ester						
Source	Natural Product[16]			synthetic compound		
HRMS	HR-EI-MS *m/z* 392.2918 (calcd for $C_{24}H_{40}O_4$ $[M]^+$, 392.2927).			HR-ESI-MS *m/z* 392.2911 (calcd for $C_{24}H_{40}O_4$ $[M]^+$, 392.2927).		
$[\alpha]_D^{25}$	$[\alpha]_D^{20}$= 34.4 (*c*, 1.0, $CHCl_3$)			$[\alpha]_D^{25}$= 32.39 (*c*, 0.5, $CHCl_3$)		
NMR($CDCl_3$)	^{1}H (500 MHz)	^{13}C (125 MHz)		^{1}H (500 MHz)	^{13}C (125 MHz)	
equipment	Bruker DRX-500			Bruker DRX-500		
H-1		C-1	171.1		C-1	171.3
H-2	2.76, α(d, 14.5) 2.65, β(d, 14.5)	C-2	44.0	2.76, α(d, 14.5) 2.64, β(d, 14.5)	C-2	44.2

H-3		C-3	83.9		C-3	84.2
H-4	2.22 α(d, 12.5) 2.46 β(d, 12.5)	C-4	55.4	2.46 α(d, 12.5) 2.22 β(d, 12.5)	C-4	55.6
H-5		C-5	86.5		C-5	86.7
H-6	1.69α(t, 12.5) 1.53α(t, 12.5)	C-6	39.6	1.69α(br, m) 1.53β(br, m)	C-6	39.9
H-7	1.28 α(br, s) 1.37 β(br, m)	C-7	24.5	1.33 α(br, s) 1.37 β(br, m)	C-7	24.4
H-8	1.28 (br, s)	C-8	29.5	1.33 (br, s)	C-8	29.7
H-9	1.28 (br, s)	C-9	29.4	1.33 (br, s)	C-9	29.6
H-10	1.28 (br, s)	C-10	29.3	1.33 (br, s)	C-10	29.6
H-11	1.28 (br, s)	C-11	30.0	1.33 (br, s)	C-11	30.2
H-12	1.37 (br, m)	C-12	29.1	1.37 (br, m)	C-12	29.4
H-13	2.05 (m)	C-13	32.8	2.07 (m)	C-13	33.0
H-14	5.65 (dt, 7.0,14.2)	C-14	134.5	5.68 (dt, 7.5,14.0)	C-14	134.7

H-15	6.03 (br, m)	C-15	130.4	6.02 (m)	C-15	130.7
H-16	6.10 (br, m)	C-16	130.9	6.10 (m)	C-16	131.1
H-17	6.08 (br, m)	C-17	130.8	6.08 (m)	C-17	130.0
H-18	6.06 (br, m)	C-18	129.5	6.05 (m)	C-18	129.7
H-19	5.71 (dt, 7.5,14.5)	C-19	135.9	5.70 (dt, 7.5,14.0)	C-19	136.1
H-20	2.08 (m)	C-20	25.8	2.09 (m)	C-20	26.0
H-21	0.97 (t, 7.4)	C-21	13.6	1.00 (t, 7.5)	C-21	13.8
H-22	1.43 (s)	C-22	24.1	1.44 (s)	C-22	24.8
H-23	1.28 (s)	C-23	23.3	1.28 (s)	C-23	23.5
$-OCH_3$	3.69 (s)	C-24	51.7	3.69 (s)	C-24	51.9

Table S5. The data reported for natural Epiplakinic acid F and the data for our Synthetic compound 1 (for comparison)

Epiplakinic acid F						
Source	Natural Product[17]			synthetic compound		
HRMS	HR-FAB-MS *m/z* 379.2816 (calcd for $C_{23}H_{39}O_4$ $[M+H]^+$, 379.2850).			HR-ESI-MS *m/z* 396.3102 (calcd for $C_{23}H_{42}O_4N$ $[M+NH_4]^+$, 396.3108).		
$[\alpha]_D^{25}$				$[a]_D^{25}$= 31.21 (c, 0.5, $CHCl_3$)		
NMR($CDCl_3$)	^1H (500 MHz)	^{13}C (125 MHz)		^1H (500 MHz)	^{13}C (125 MHz)	
equipment	Bruker AMX-500			Bruker DRX-500		
H-1		C-1	171.80		C-1	173.3
H-2	2.75 (s)	C-2	43.94	2.79 (dd, 14.5, 23.5)	C-2	43.1
H-3		C-3	83.68		C-3	83.4
H-4	2.40 α(d, 12.5) 2.25 β(d, 12.5)	C-4	55.51	2.46 α(d, 12.5) 2.28 β(d, 12.5)	C-4	55.2
H-5		C-5	86.86		C-5	86.2

H-6	1.65 (m) 1.28 (m)	C-6	38.77	1.72 (m) 1.30 (m)	C-6	39.3
H-7	1.16-1.53 (m)	C-7	24.86	1.39 α(br, s) 1.30 β(br, m)	C-7	24.0
H-8	1.16-1.53 (m)	C-8	29.70	1.30 (br, s)	C-8	29.0
H-9	1.16-1.53 (m)	C-9	29.42	1.30 (br, s)	C-9	28.8
H-10	1.16-1.53 (m)	C-10	29.12	1.30 (br, s)	C-10	28.7
H-11	1.16-1.53 (m)	C-11	30.02	1.30 (br, s)	C-11	29.5
H-12	1.39 (m)	C-12	29.70	1.39 (br, m)	C-12	29.0
H-13	2.05 (q, 7.2)	C-13	32.78	2.13 (m)	C-13	32.3
H-14	5.63 (dt, 7.2,14.1)	C-14	134.41	5.68 (dt, 7.5,14.0)	C-14	133.9
H-15	6.02 (m)	C-15	130.48	6.04 (m)	C-15	130.0
H-16	6.06 (m)	C-16	130.83	6.12 (m)	C-16	130.3
H-17	6.06 (m)	C-17	130.87	6.10 (m)	C-17	130.4
H-18	6.02 (m)	C-18	129.51	6.05 (m)	C-18	129.0

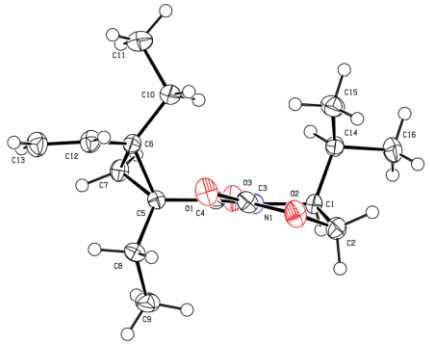
H-19	5.68 (dt, 7.2,14.4)	C-19	135.90	5.72 (dt, 7.5,14.0)	C-19	135.4
H-20	2.08 (q, 7.2)	C-20	25.81	2.12 (m)	C-20	25.3
H-21	0.97 (t, 7.5)	C-21	14.11	1.03 (t, 7.5)	C-21	13.1
H-22	1.45 (s)	C-22	24.75	1.50 (s)	C-22	23.2
H-23	1.28 (s)	C-23	23.69	1.28 (s)	C-23	22.6

Basic Crystal Data for Compounds *trans*-10a, *trans*-12a and *trans*-20a

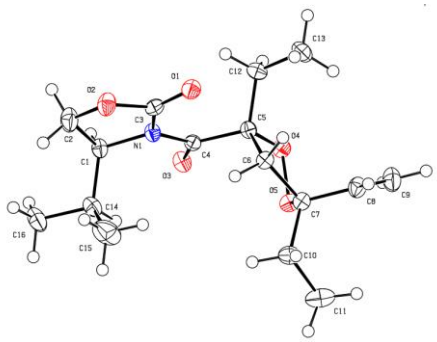
CCDC 978791 (*trans*-**10a**), CCDC 978789 (*trans*-**12a**), CCDC 978792 (*trans*-**20a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Deposition Number(s): 978791, 978789, 978792.

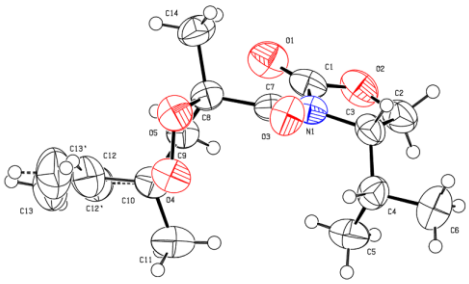
CIF files for these structures are attached to this message.



ORTEP diagram of compound *trans*-**10a**. Thermal ellipsoids were plotted at 30 % probability level. Hydrogen atoms are omitted for clarity.

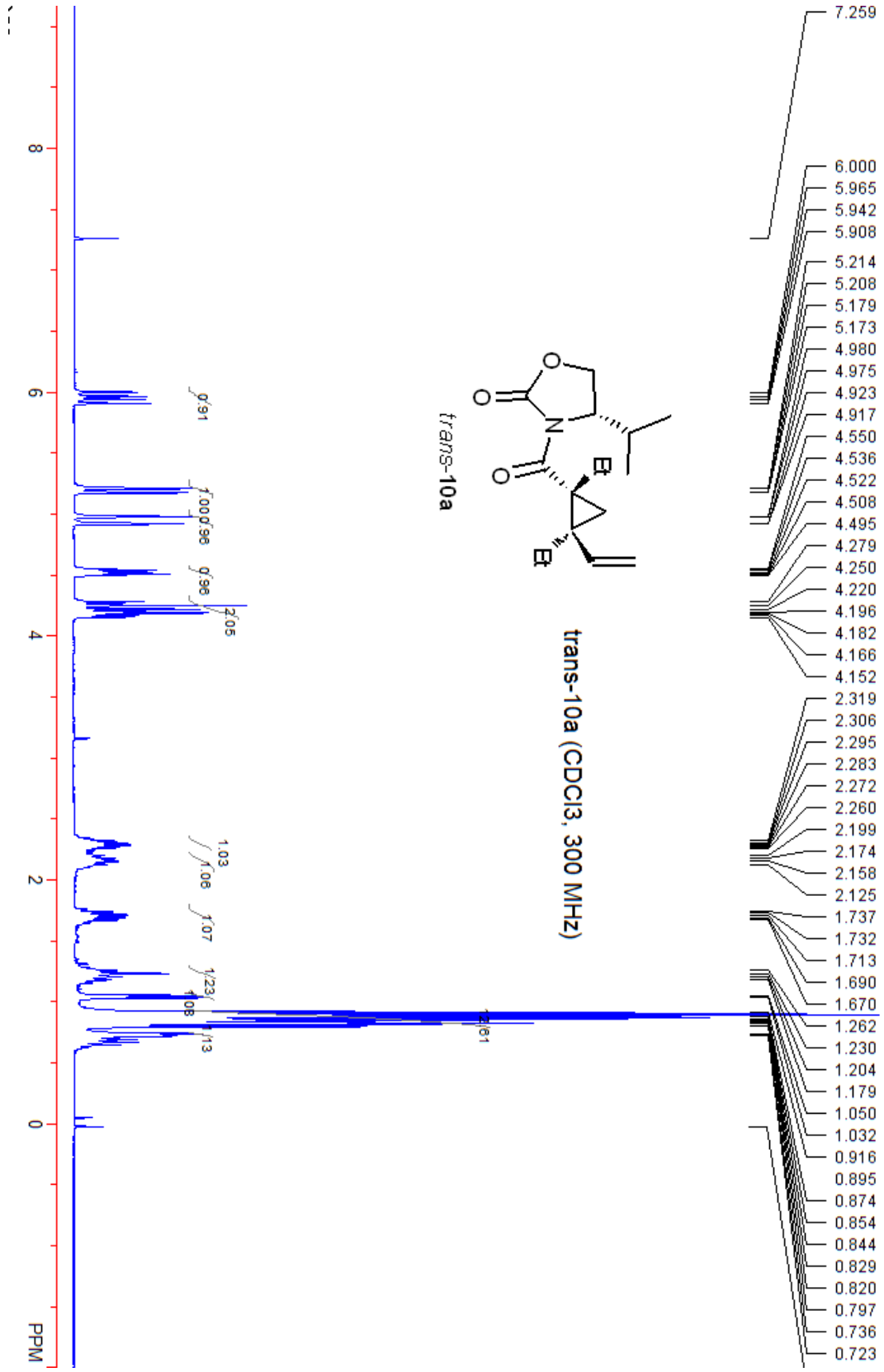


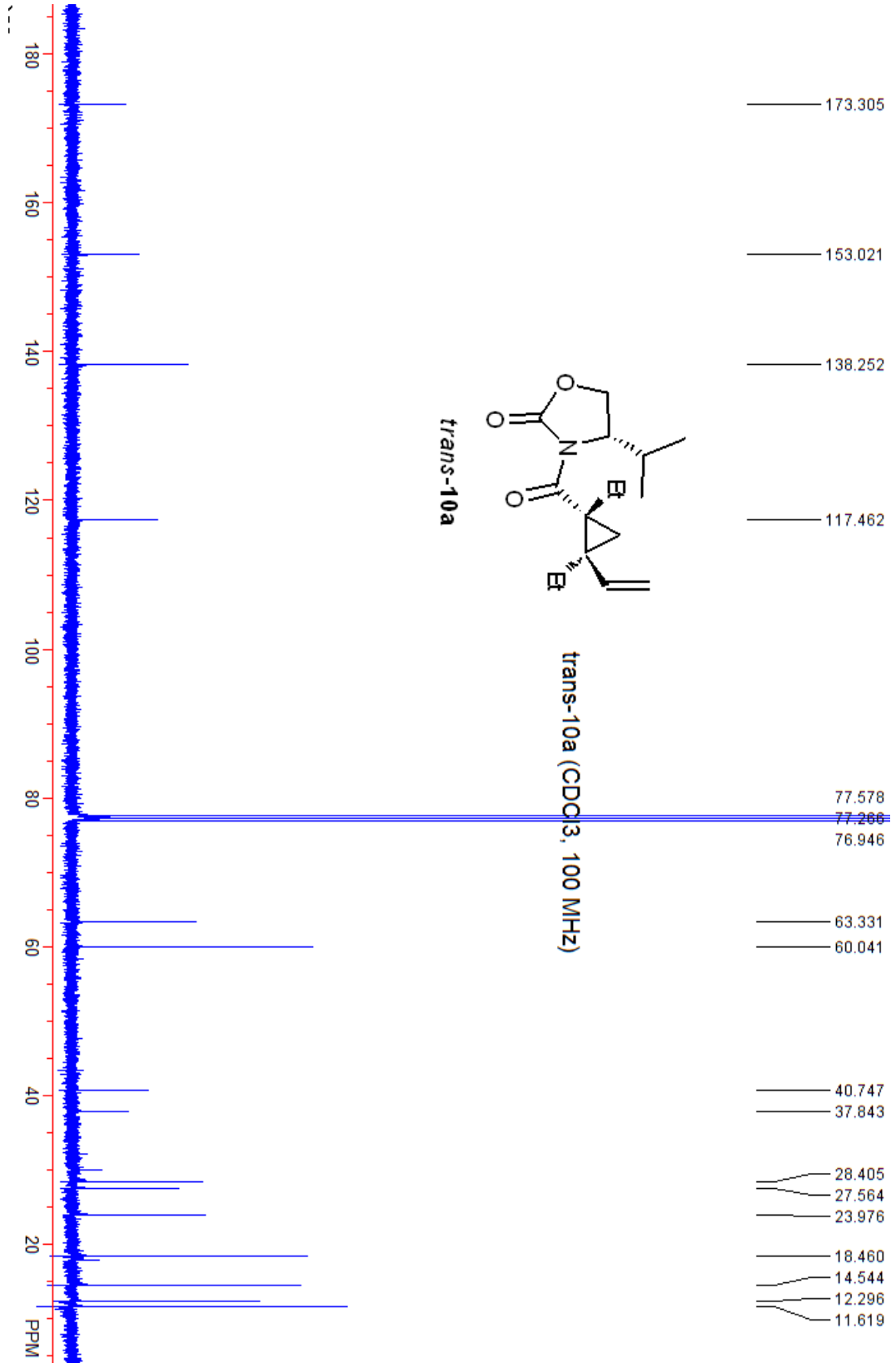
ORTEP diagram of compound *trans*-**12a**. Thermal ellipsoids were plotted at 30 % probability level. Hydrogen atoms are omitted for clarity.

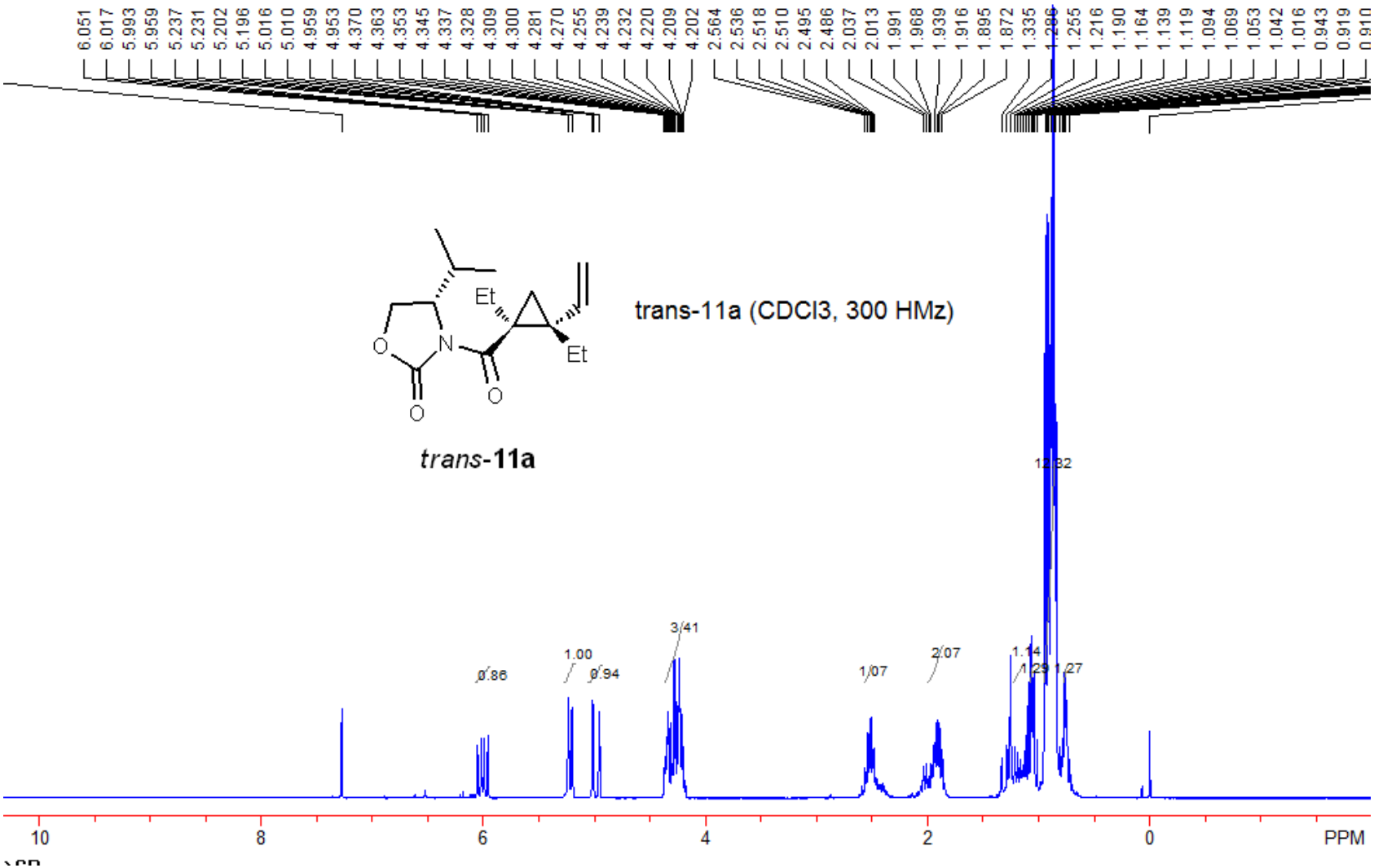


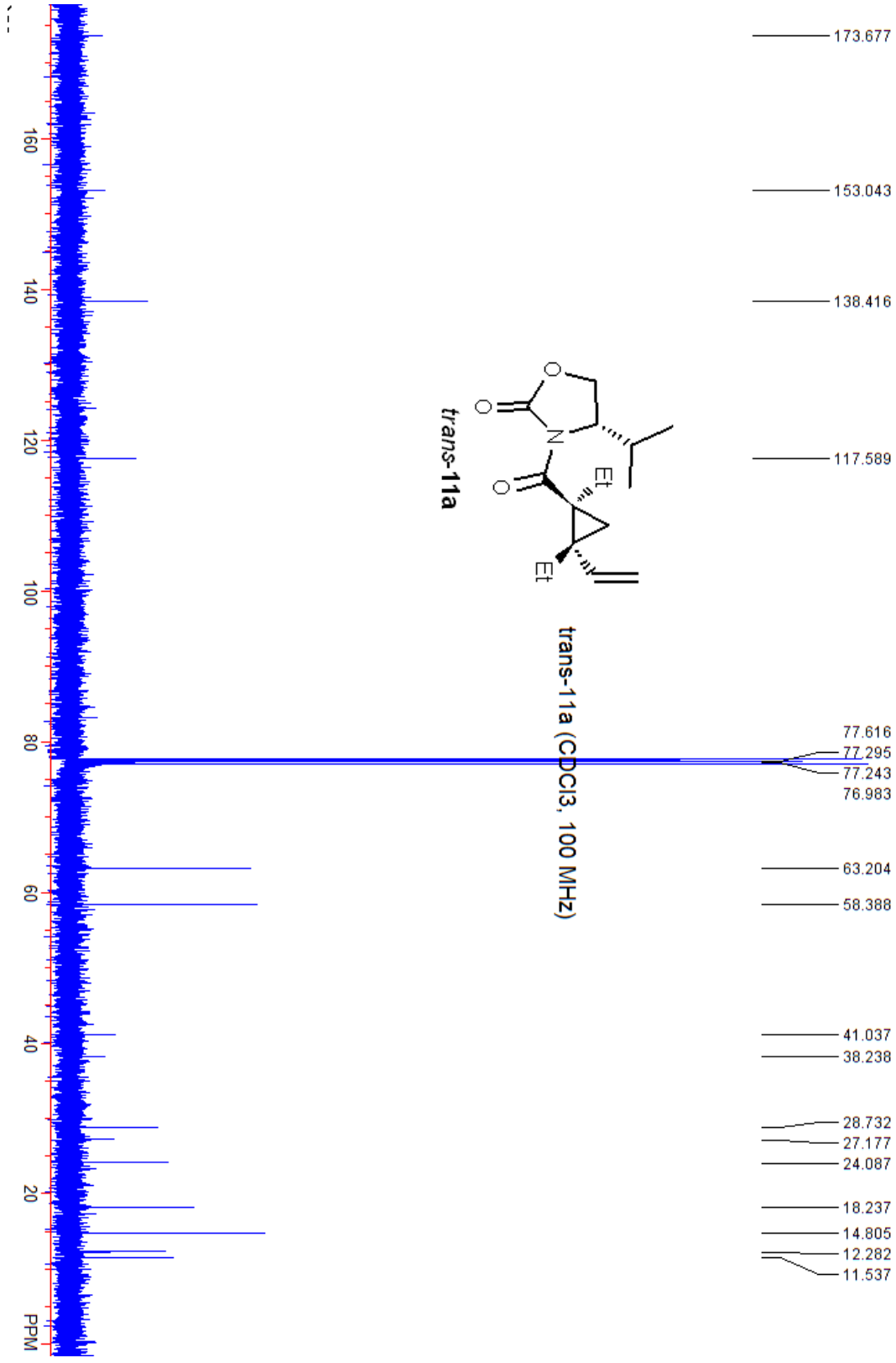
ORTEP diagram of compound *trans*-**20a**. Thermal ellipsoids were plotted at 30 % probability level. Hydrogen atoms are omitted for clarity.

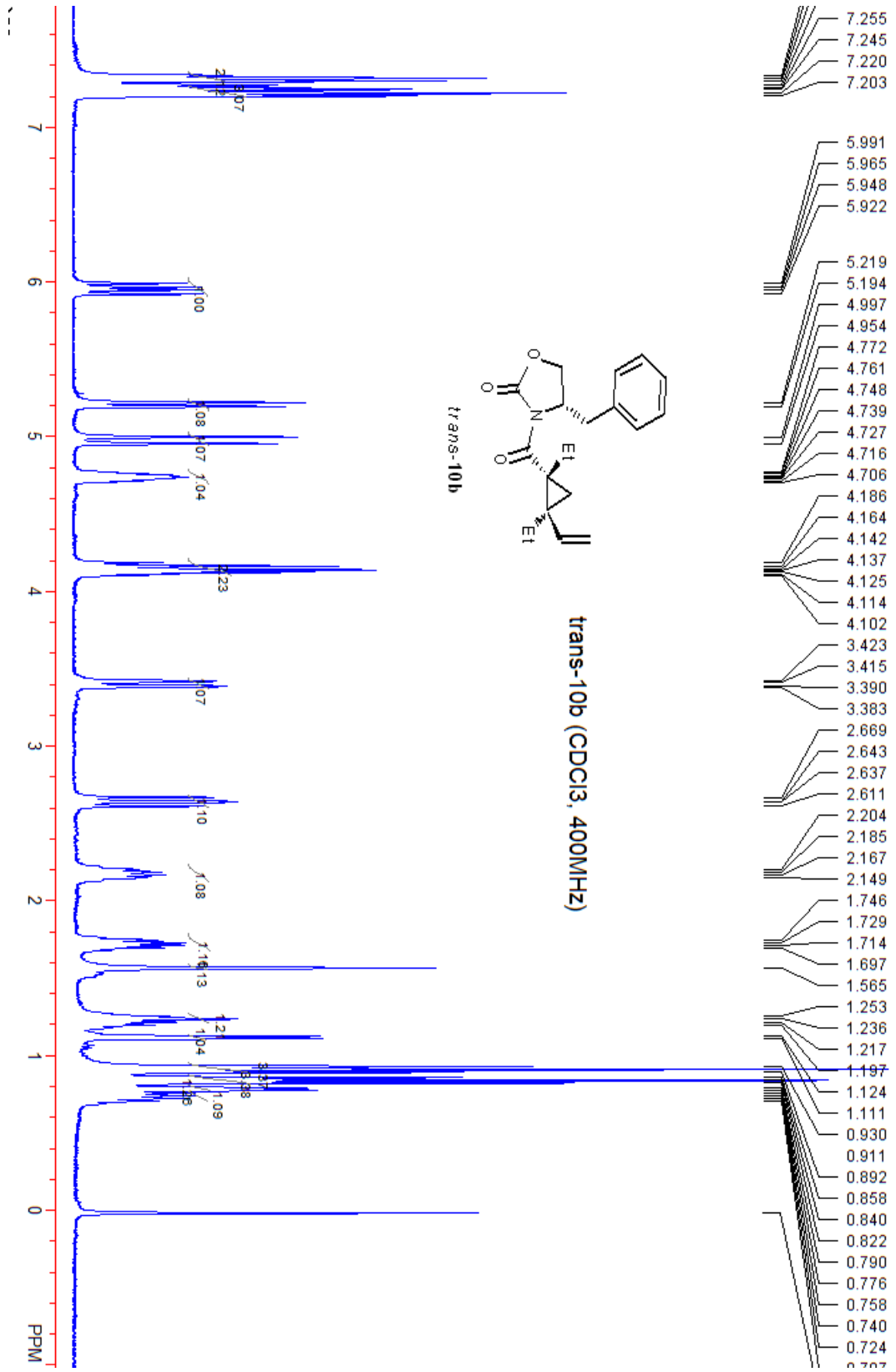
^{1}H and ^{13}C NMR Spectra

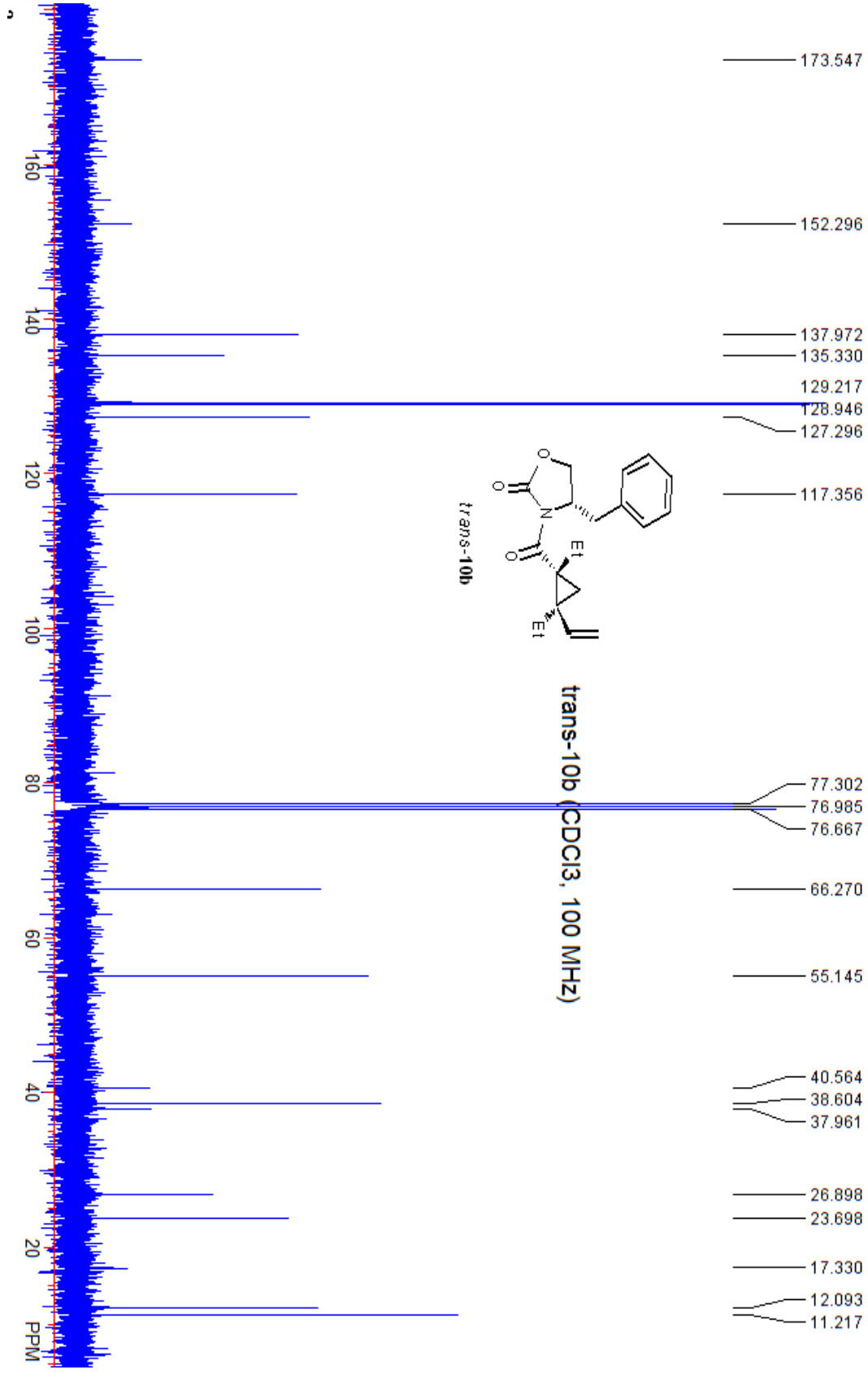


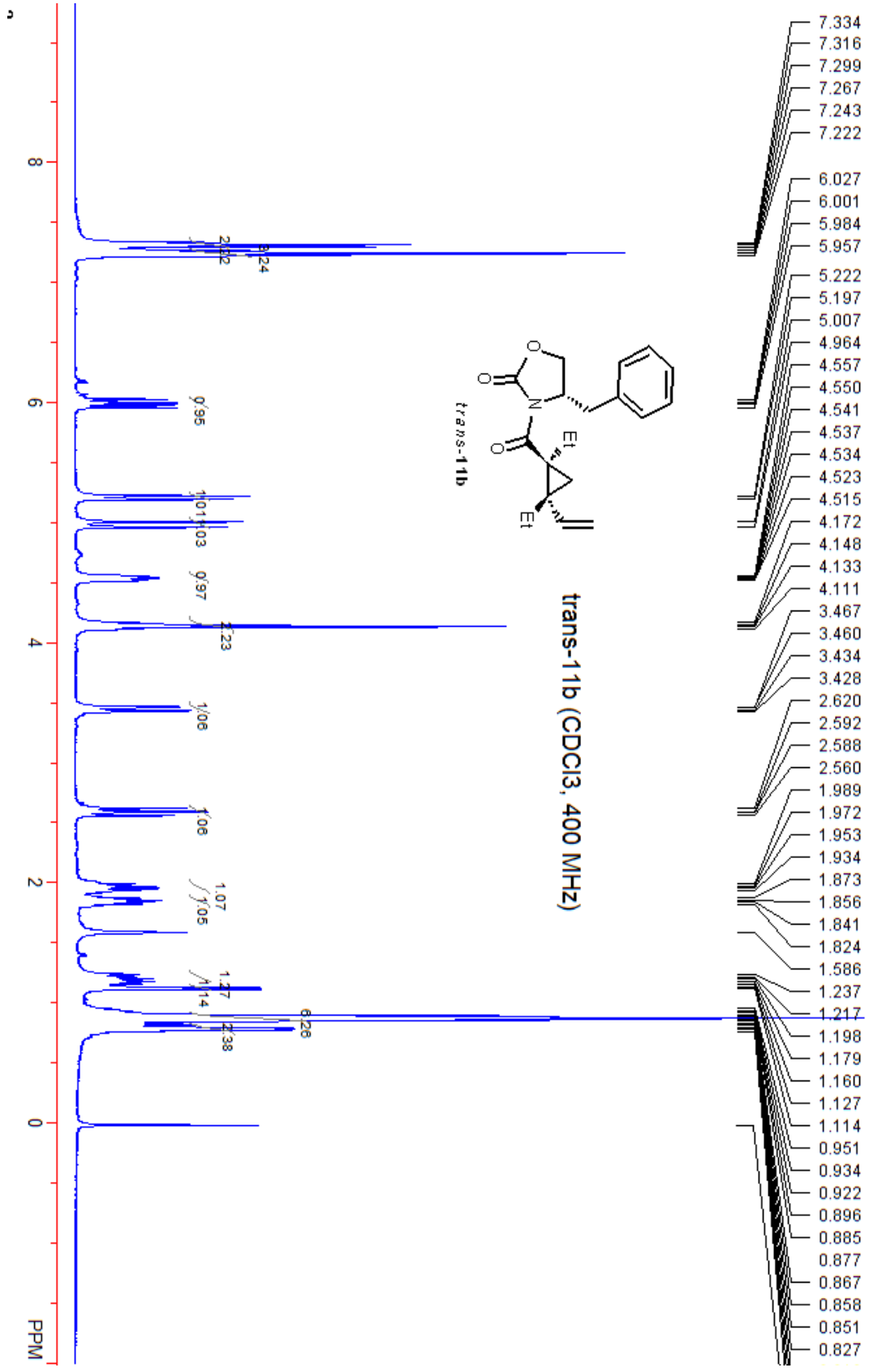

trans-10a (CDCl3, 100 MHz)
trans-10a
Et
Et
173.305
153.021
138.252
117.462
77.578
77.266
76.946
63.331
60.041
40.747
37.843
28.405
27.564
23.976
18.460
14.544
12.296
11.619
PPM

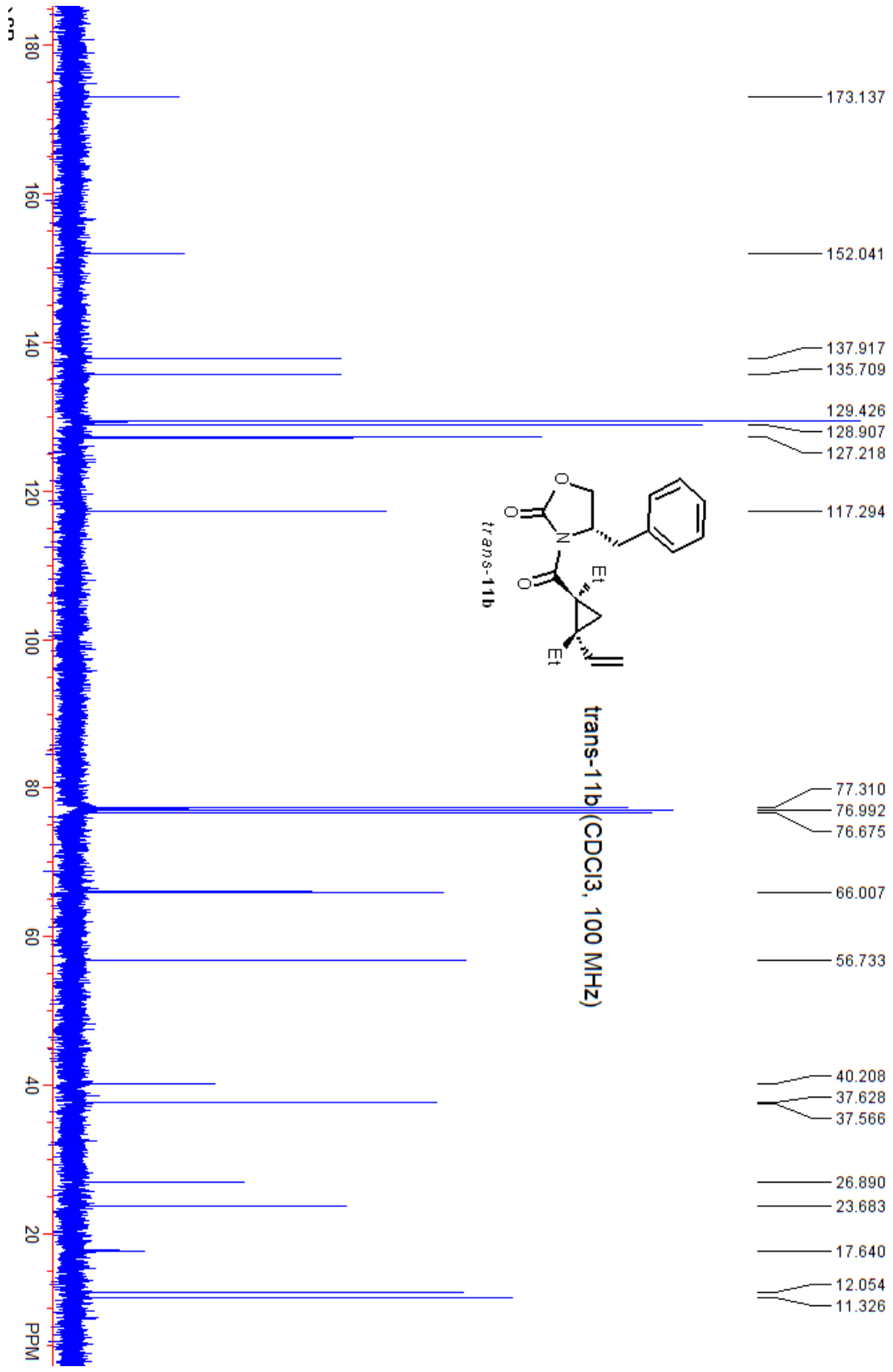

6.051
6.017
5.993
5.959
5.237
5.231
5.202
5.196
5.016
5.010
4.959
4.953
4.370
4.363
4.353
4.345
4.337
4.328
4.309
4.300
4.281
4.270
4.255
4.239
4.232
4.220
4.209
4.202
2.564
2.536
2.518
2.510
2.495
2.486
2.037
2.013
1.991
1.968
1.939
1.916
1.895
1.872
1.335
1.255
1.216
1.190
1.164
1.139
1.119
1.094
1.069
1.053
1.042
1.016
0.943
0.919
0.910
Et
Et
O
N
O
O
trans-11a (CDCl3, 300 HMz)
trans-11a
12.32
3.41
1.00
0.86
0.94
1.07
2.07
1.14
1.29
1.27
10
8
6
4
2
0
PPM

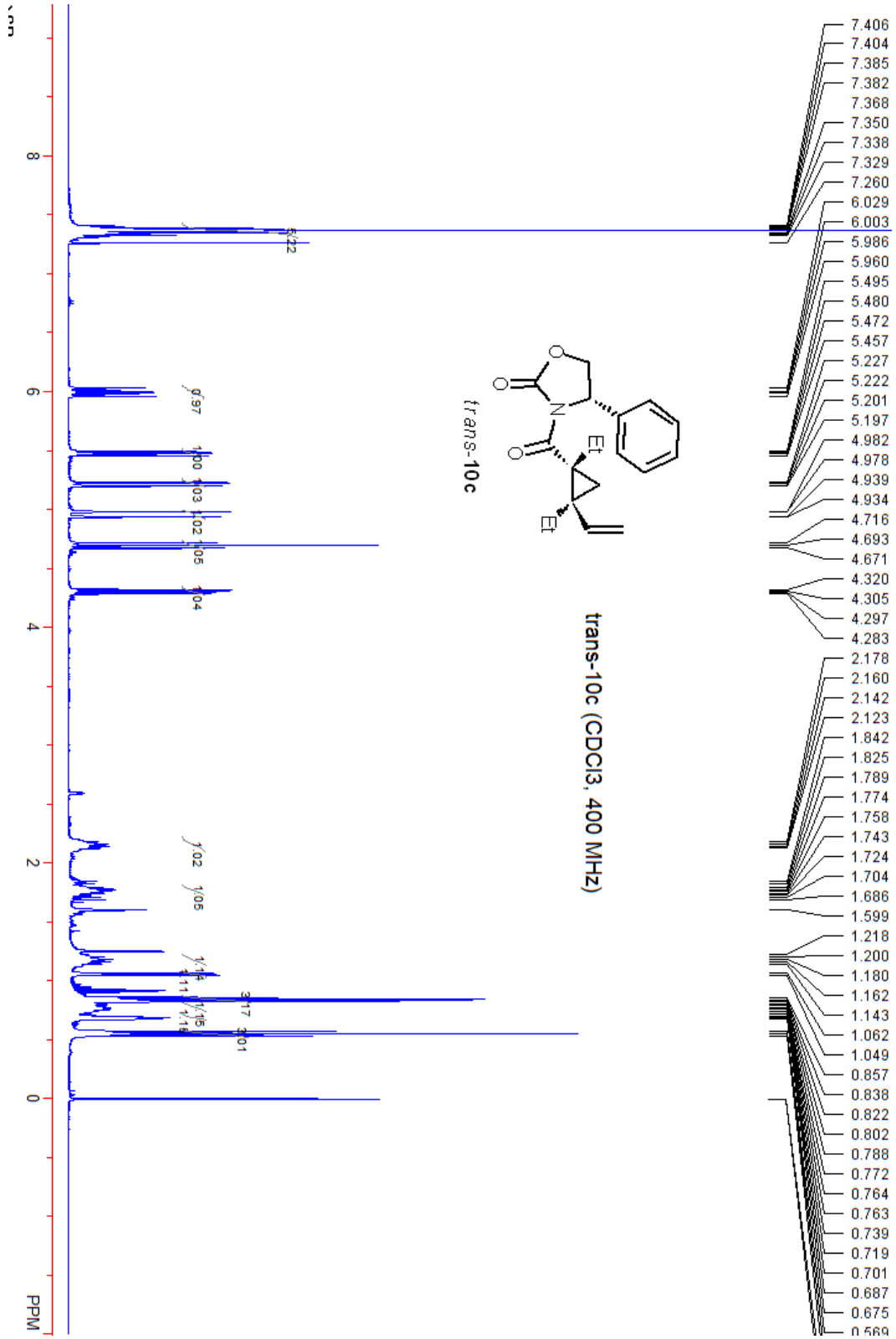

173.677
153.043
138.416
117.589
77.616
77.295
77.243
76.983
63.204
58.388
41.037
38.238
28.732
27.177
24.087
18.237
14.805
12.282
11.537
160
140
120
100
80
60
40
20
PPM
trans-11a
Et
Et
trans-11a (CDCl3, 100 MHz)

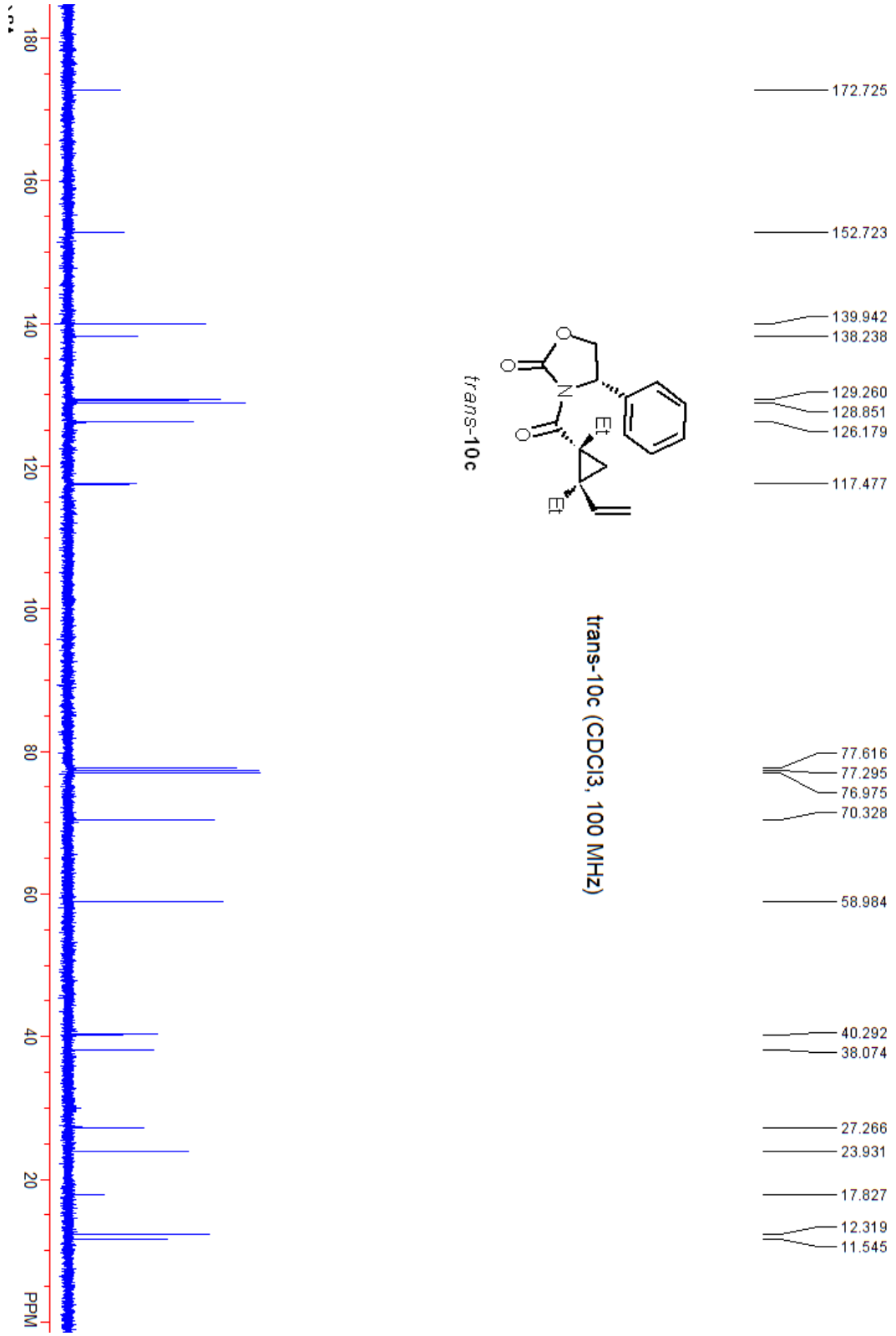

trans-10b (CDCl3, 400MHz)
trans-10b
Et
Et
7.255
7.245
7.220
7.203
5.991
5.965
5.948
5.922
5.219
5.194
4.997
4.954
4.772
4.761
4.748
4.739
4.727
4.716
4.706
4.186
4.164
4.142
4.137
4.125
4.114
4.102
3.423
3.415
3.390
3.383
2.669
2.643
2.637
2.611
2.204
2.185
2.167
2.149
1.746
1.729
1.714
1.697
1.565
1.253
1.236
1.217
1.197
1.124
1.111
0.930
0.911
0.892
0.858
0.840
0.822
0.790
0.776
0.758
0.740
0.724
PPM

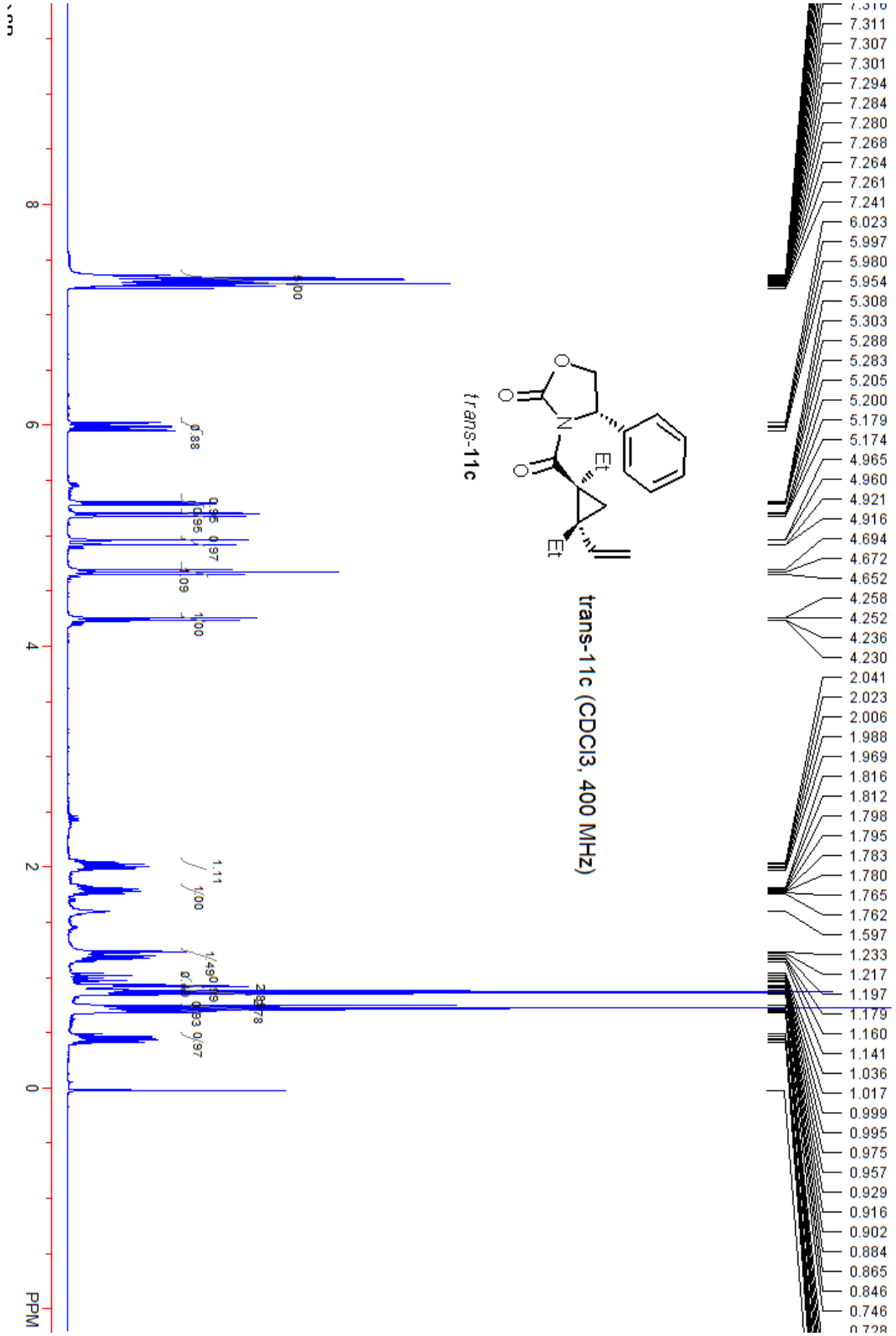

trans-10b (CDCl3, 100 MHz)
trans-10b
Et
Et
173.547
152.296
137.972
135.330
129.217
128.946
127.296
117.356
77.302
76.985
76.667
66.270
55.145
40.564
38.604
37.961
26.898
23.698
17.330
12.093
11.217
160
140
120
100
80
60
40
20
PPM

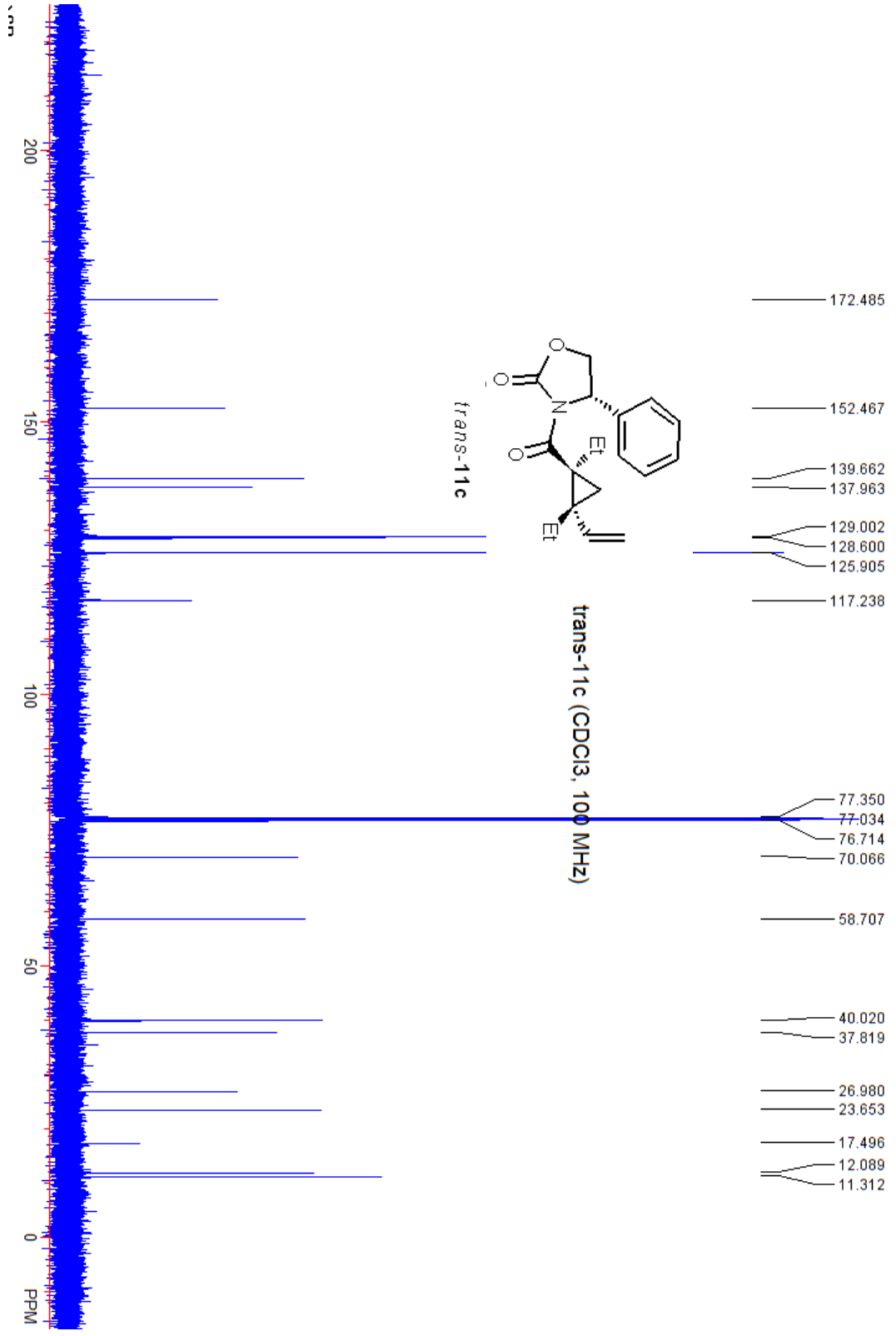

trans-11b (CDCl3, 400 MHz)
trans-11b
7.334
7.316
7.299
7.267
7.243
7.222
6.027
6.001
5.984
5.957
5.222
5.197
5.007
4.964
4.557
4.550
4.541
4.537
4.534
4.523
4.515
4.172
4.148
4.133
4.111
3.467
3.460
3.434
3.428
2.620
2.592
2.588
2.560
1.989
1.972
1.953
1.934
1.873
1.856
1.841
1.824
1.586
1.237
1.217
1.198
1.179
1.160
1.127
1.114
0.951
0.934
0.922
0.896
0.885
0.877
0.867
0.858
0.851
0.827
PPM

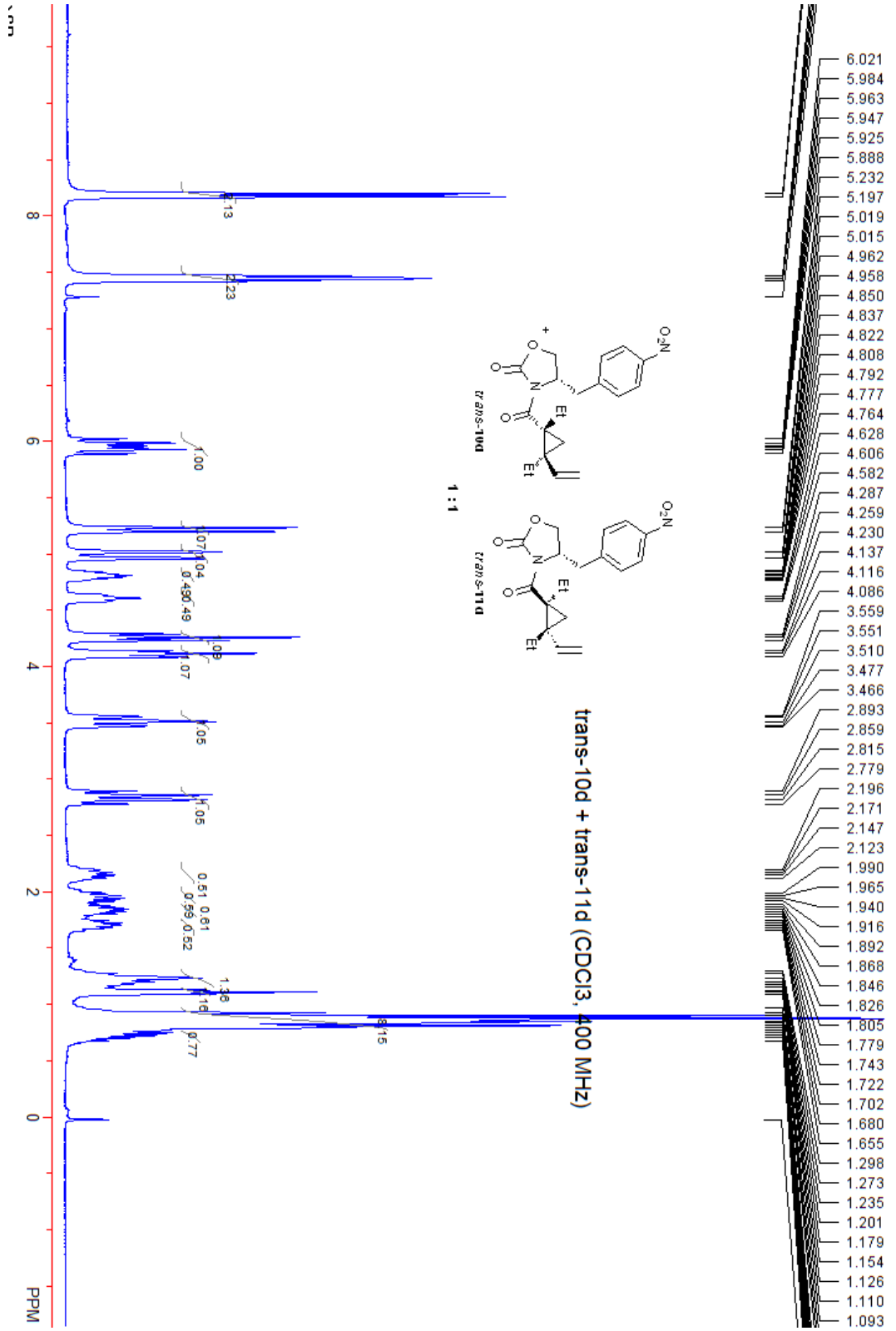

trans-11b (CDCl3, 100 MHz)
trans-11b
173.137
152.041
137.917
135.709
129.426
128.907
127.218
117.294
77.310
76.992
76.675
66.007
56.733
40.208
37.628
37.566
26.890
23.683
17.640
12.054
11.326
PPM

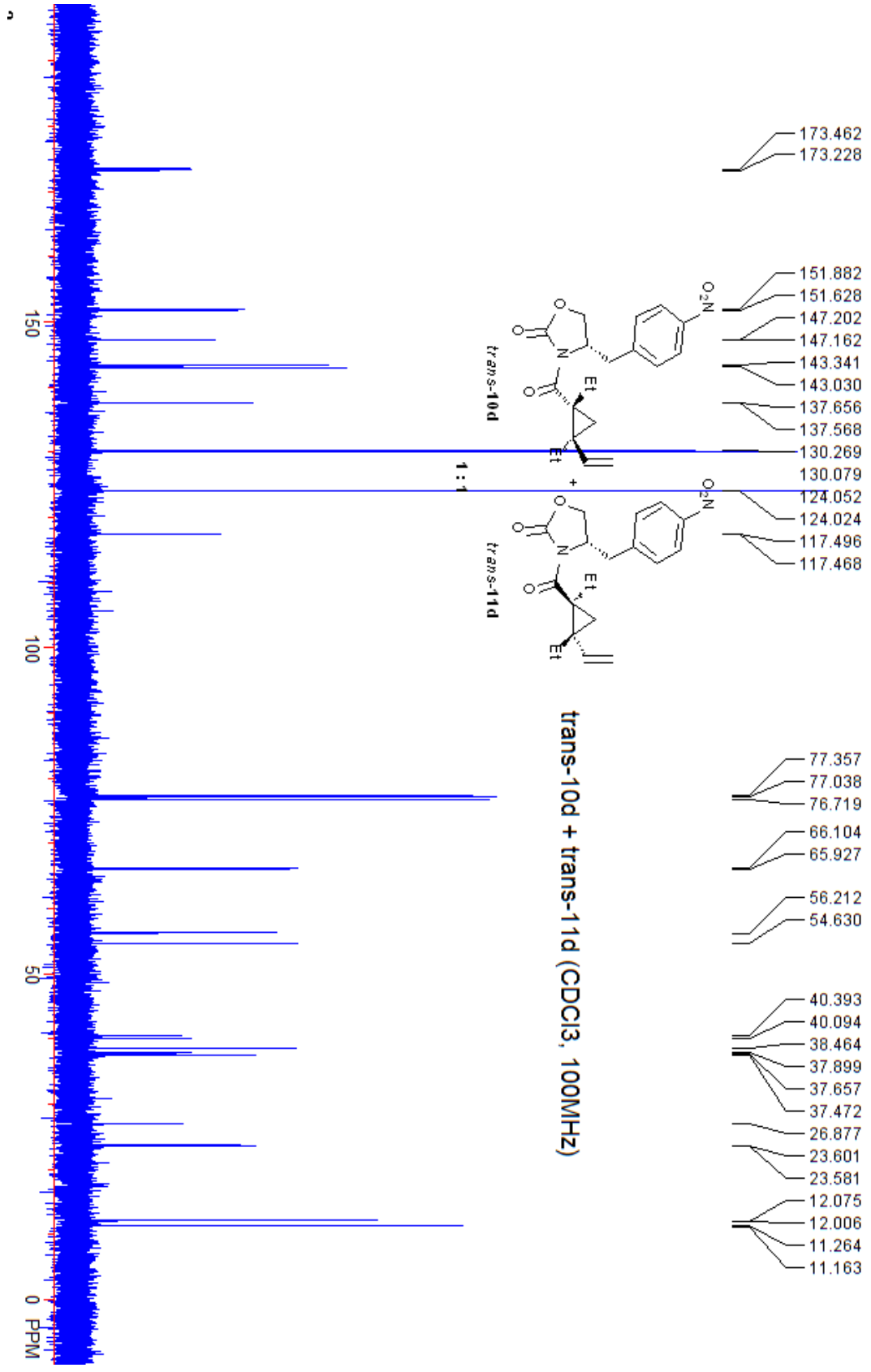

trans-10c (CDCl3, 400 MHz)
trans-10c
Et
Et
7.406
7.404
7.385
7.382
7.368
7.350
7.338
7.329
7.260
6.029
6.003
5.986
5.960
5.495
5.480
5.472
5.457
5.227
5.222
5.201
5.197
4.982
4.978
4.939
4.934
4.716
4.693
4.671
4.320
4.305
4.297
4.283
2.178
2.160
2.142
2.123
1.842
1.825
1.789
1.774
1.758
1.743
1.724
1.704
1.686
1.599
1.218
1.200
1.180
1.162
1.143
1.062
1.049
0.857
0.838
0.822
0.802
0.788
0.772
0.764
0.763
0.739
0.719
0.701
0.687
0.675
0.569
PPM

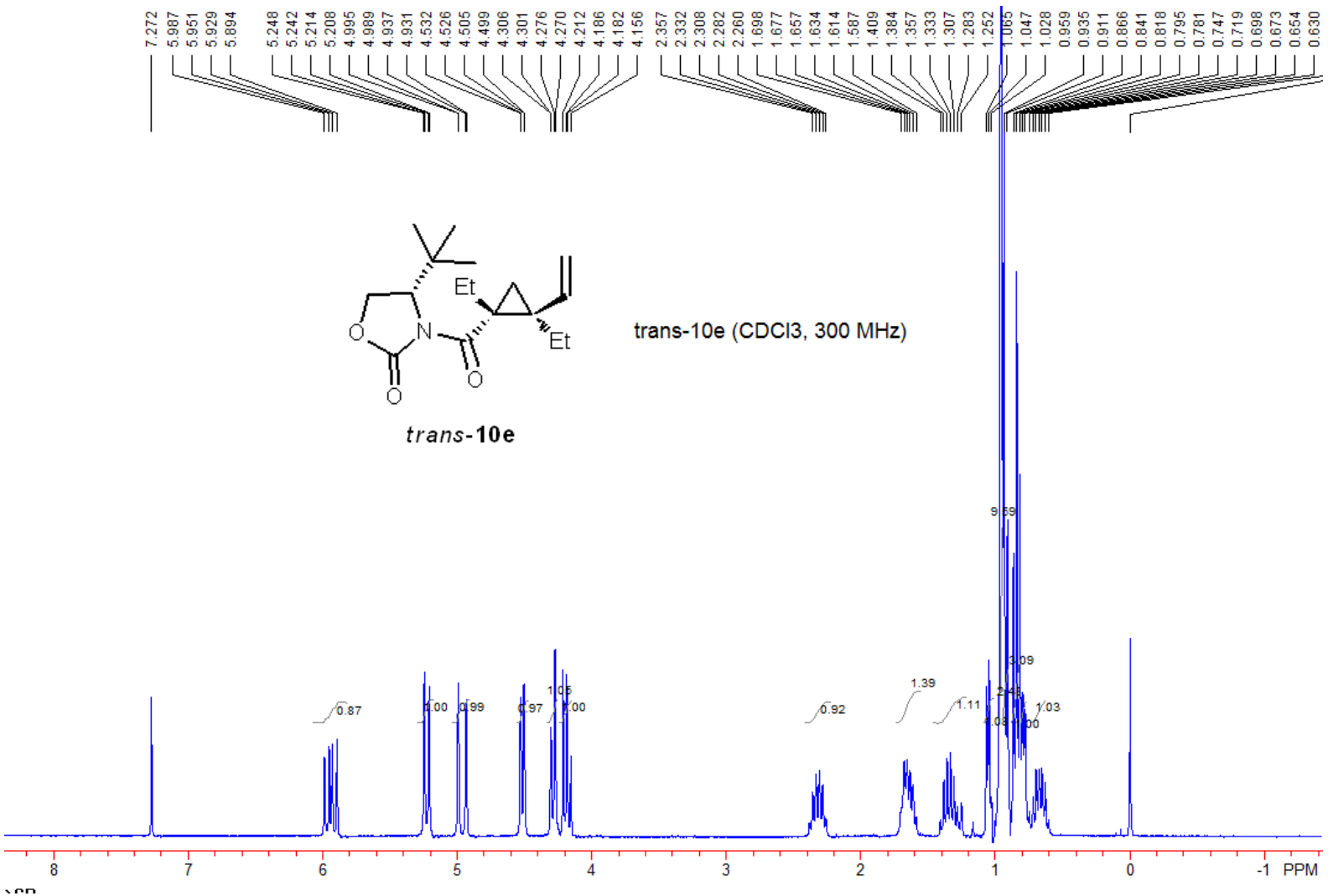

trans-10c
trans-10c (CDCl3, 100 MHz)
Et
Et
172.725
152.723
139.942
138.238
129.260
128.851
126.179
117.477
77.616
77.295
76.975
70.328
58.984
40.292
38.074
27.266
23.931
17.827
12.319
11.545
PPM

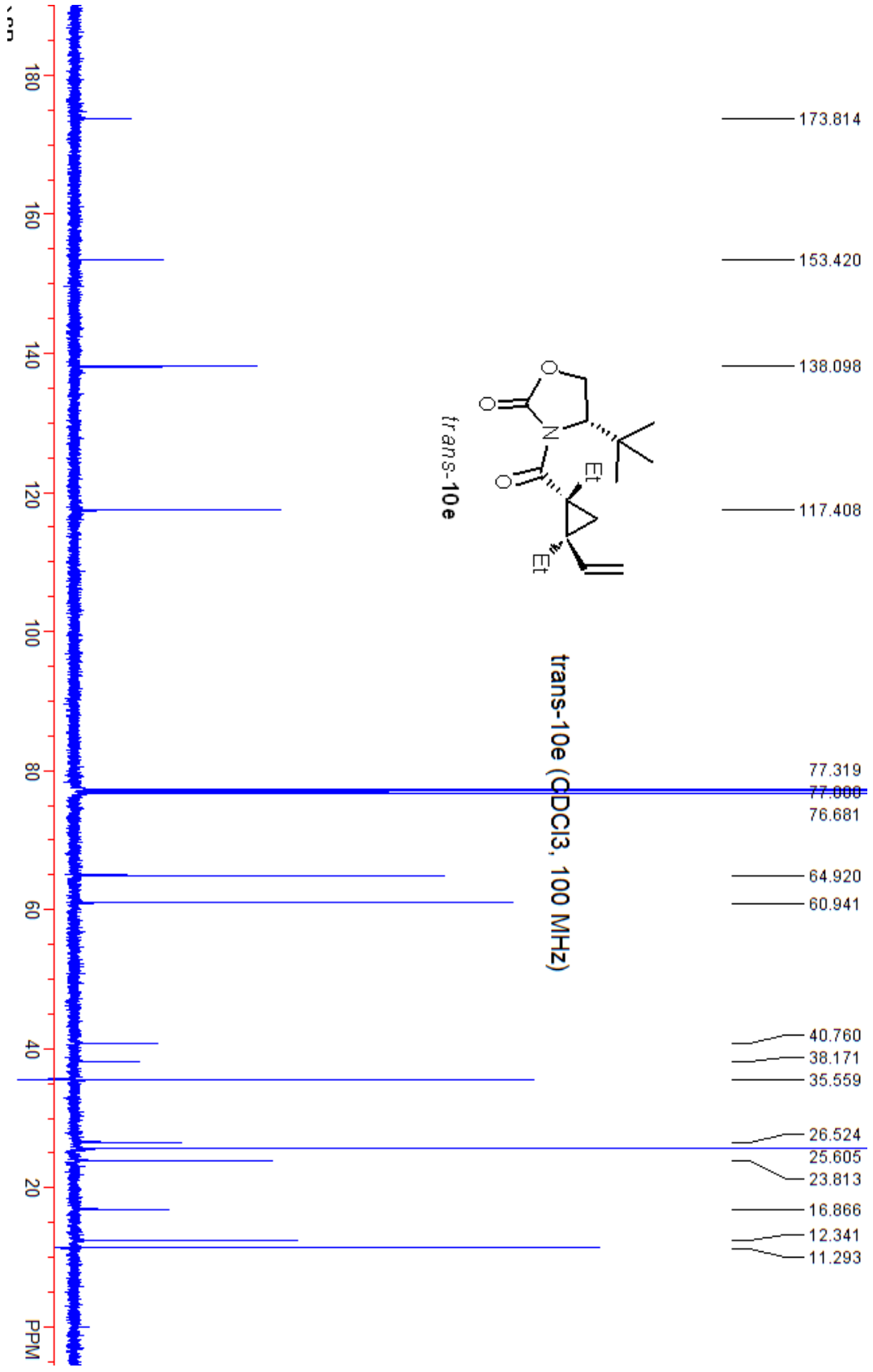

trans-11c (CDCl3, 400 MHz)
trans-11c
Et
Et
7.311
7.307
7.301
7.294
7.284
7.280
7.268
7.264
7.261
7.241
6.023
5.997
5.980
5.954
5.308
5.303
5.288
5.283
5.205
5.200
5.179
5.174
4.965
4.960
4.921
4.916
4.694
4.672
4.652
4.258
4.252
4.236
4.230
2.041
2.023
2.006
1.988
1.969
1.816
1.812
1.798
1.795
1.783
1.780
1.765
1.762
1.597
1.233
1.217
1.197
1.179
1.160
1.141
1.036
1.017
0.999
0.995
0.975
0.957
0.929
0.916
0.902
0.884
0.865
0.846
0.746
8
6
4
2
0
PPM

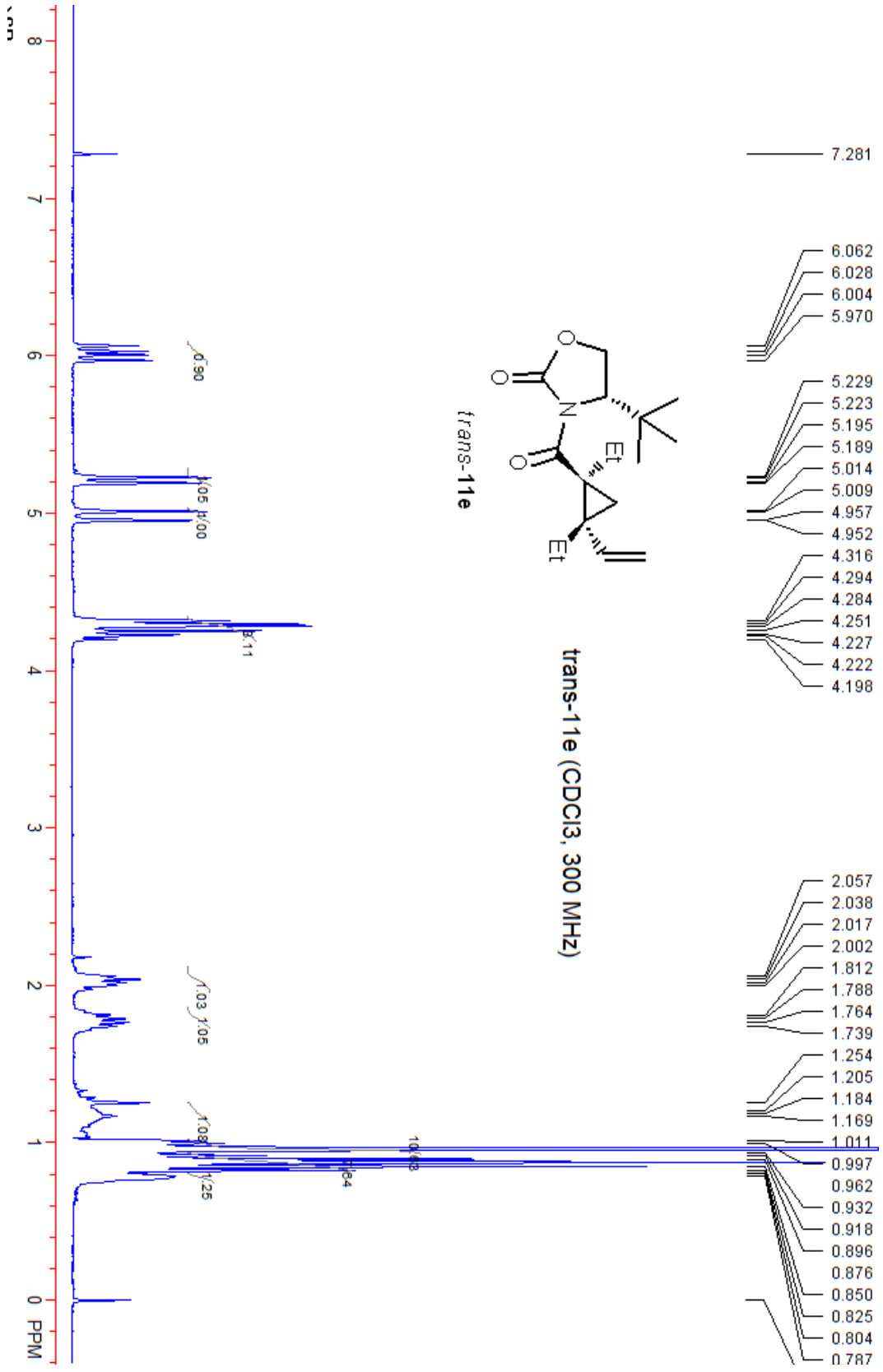

trans-11c (CDCl3, 100 MHz)
trans-11c
Et
Et
O
O
N
O
172.485
152.467
139.662
137.963
129.002
128.600
125.905
117.238
77.350
77.034
76.714
70.066
58.707
40.020
37.819
26.980
23.653
17.496
12.089
11.312
200
150
100
50
0
PPM

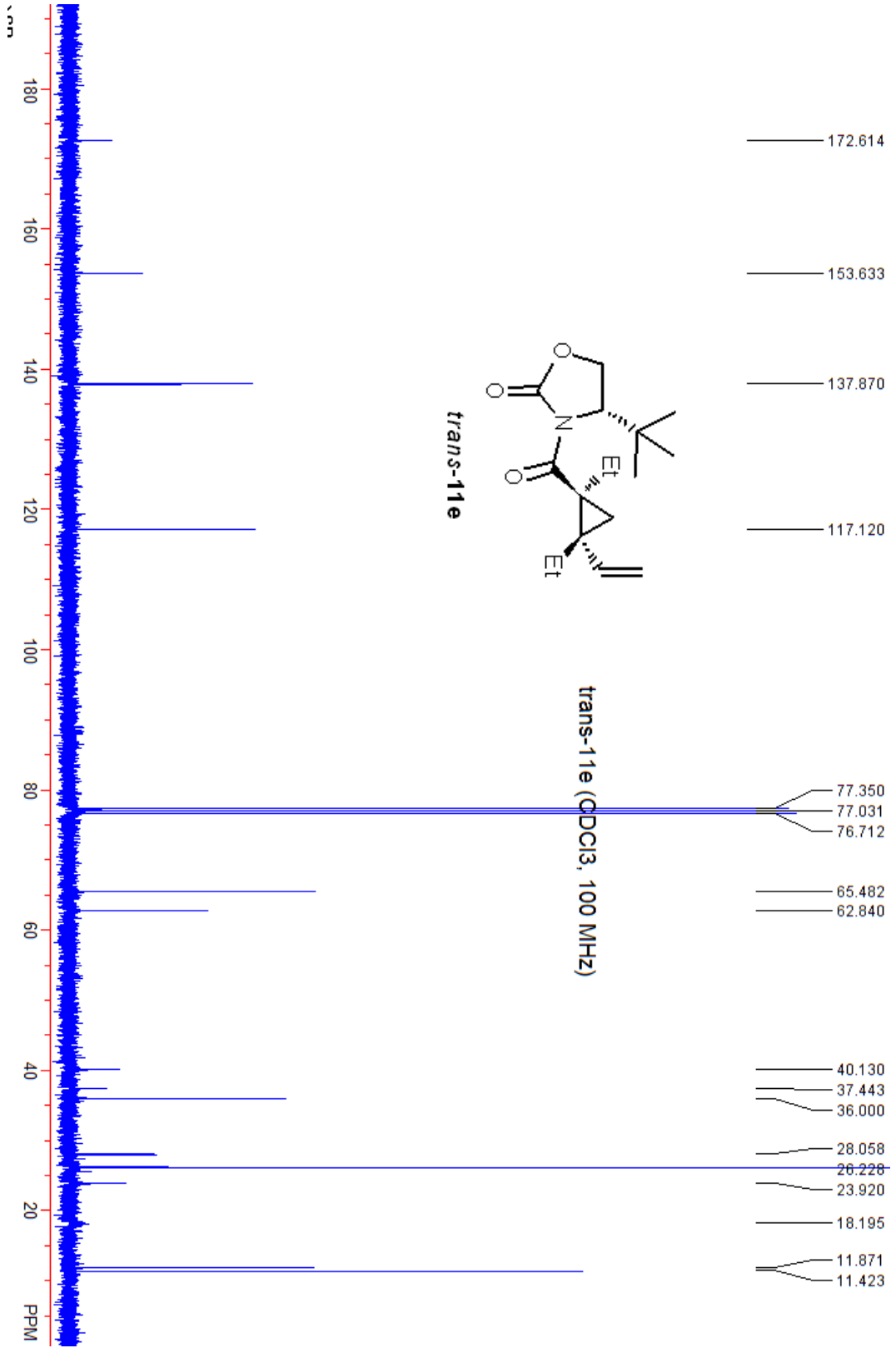

trans-10d + trans-11d (CDCl3, 400 MHz)
trans-10d
trans-11d
1 : 1
6.021
5.984
5.963
5.947
5.925
5.888
5.232
5.197
5.019
5.015
4.962
4.958
4.850
4.837
4.822
4.808
4.792
4.777
4.764
4.628
4.606
4.582
4.287
4.259
4.230
4.137
4.116
4.086
3.559
3.551
3.510
3.477
3.466
2.893
2.859
2.815
2.779
2.196
2.171
2.147
2.123
1.990
1.965
1.940
1.916
1.892
1.868
1.846
1.826
1.805
1.779
1.743
1.722
1.702
1.680
1.655
1.298
1.273
1.235
1.201
1.179
1.154
1.126
1.110
1.093
PPM

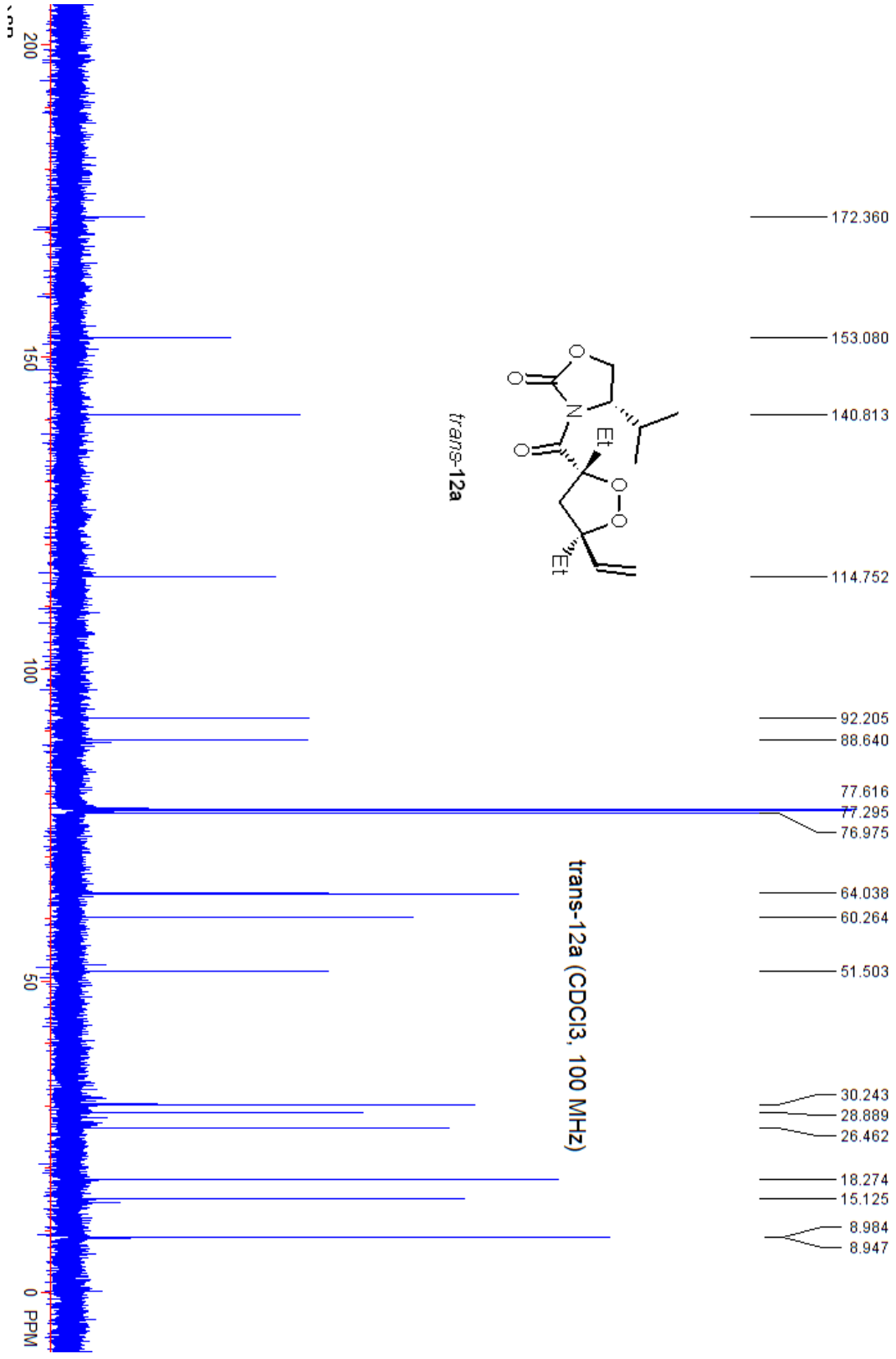

trans-10d + trans-11d (CDCl3, 100MHz)
trans-10d
trans-11d
1 : 1
173.462
173.228
151.882
151.628
147.202
147.162
143.341
143.030
137.656
137.568
130.269
130.079
124.052
124.024
117.496
117.468
77.357
77.038
76.719
66.104
65.927
56.212
54.630
40.393
40.094
38.464
37.899
37.657
37.472
26.877
23.601
23.581
12.075
12.006
11.264
11.163
150
100
50
0 PPM

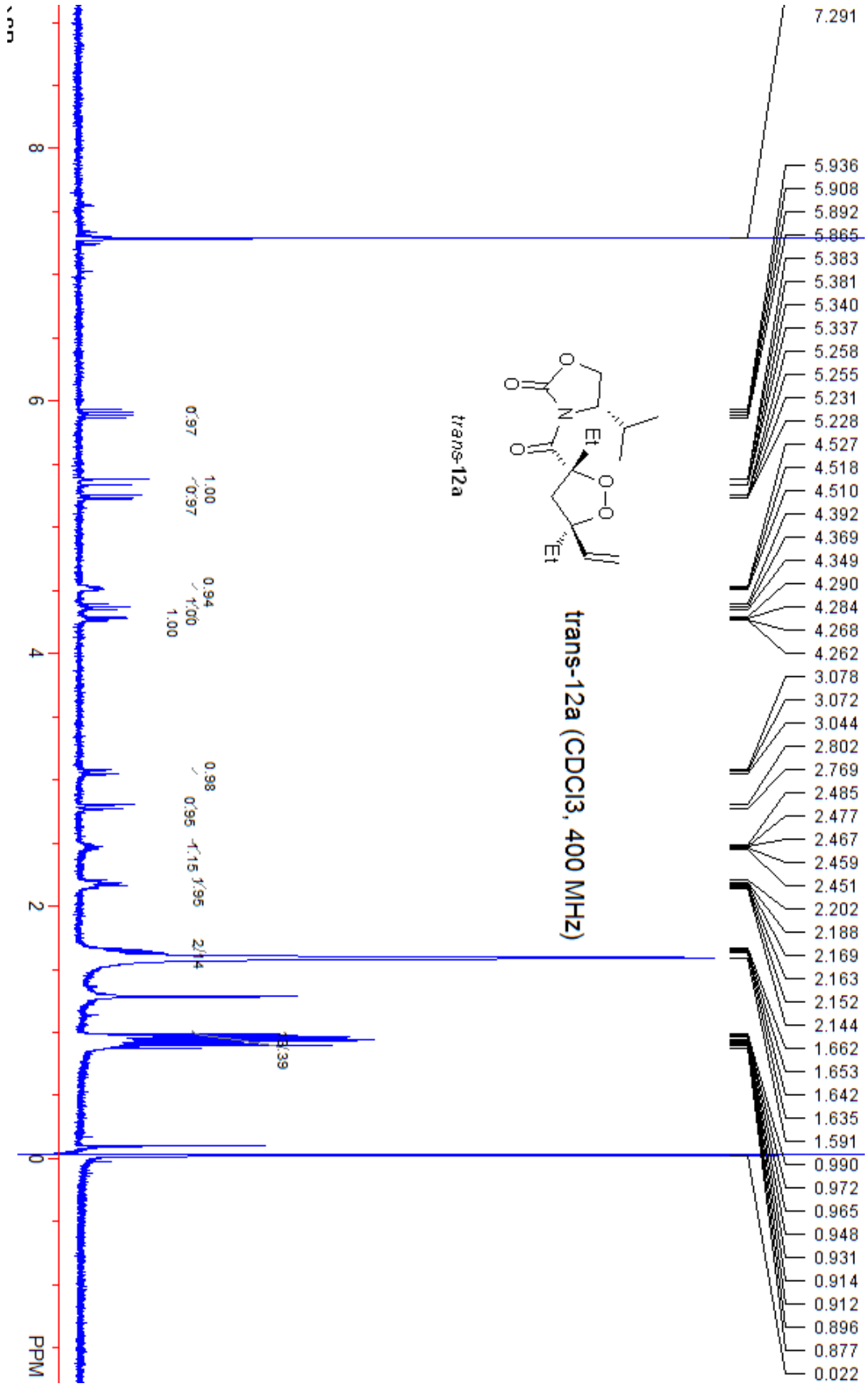

7.272
5.987
5.951
5.929
5.894
5.248
5.242
5.214
5.208
4.995
4.989
4.937
4.931
4.532
4.526
4.505
4.499
4.306
4.301
4.276
4.270
4.212
4.186
4.182
4.156
2.357
2.332
2.308
2.282
2.260
1.698
1.677
1.657
1.634
1.614
1.587
1.409
1.384
1.357
1.333
1.307
1.283
1.252
1.065
1.047
1.028
0.959
0.935
0.911
0.866
0.841
0.818
0.795
0.781
0.747
0.719
0.698
0.673
0.654
0.630
Et
Et
O
N
O
O
trans-10e (CDCl3, 300 MHz)
trans-10e
0.87
1.00
0.99
0.97
1.05
1.00
0.92
1.39
1.11
9.59
3.09
1.03
8
7
6
5
4
3
2
1
0
-1
PPM

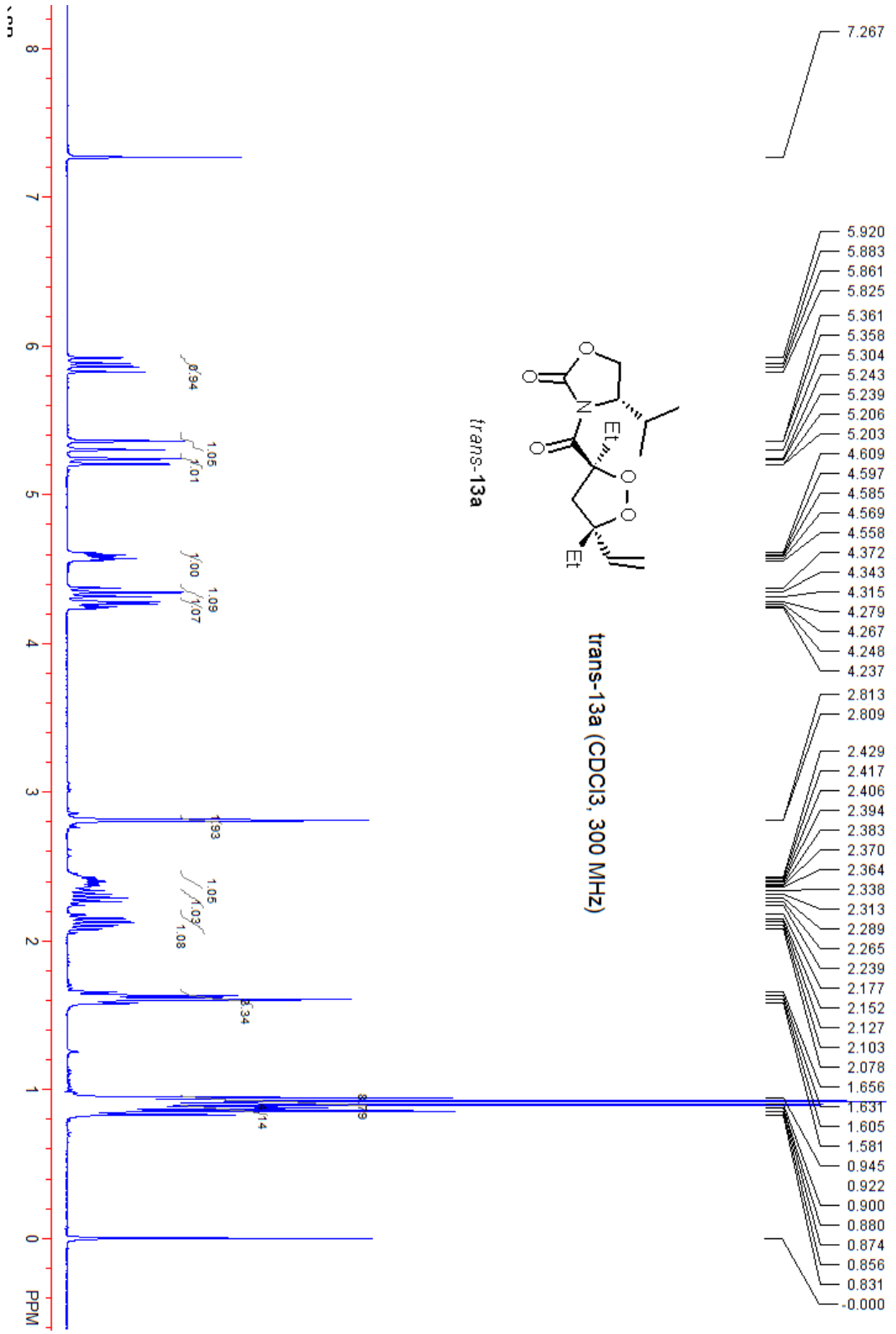

trans-10e (CDCl3, 100 MHz)
trans-10e
Et
Et
173.814
153.420
138.098
117.408
77.319
77.000
76.681
64.920
60.941
40.760
38.171
35.559
26.524
25.605
23.813
16.866
12.341
11.293
PPM

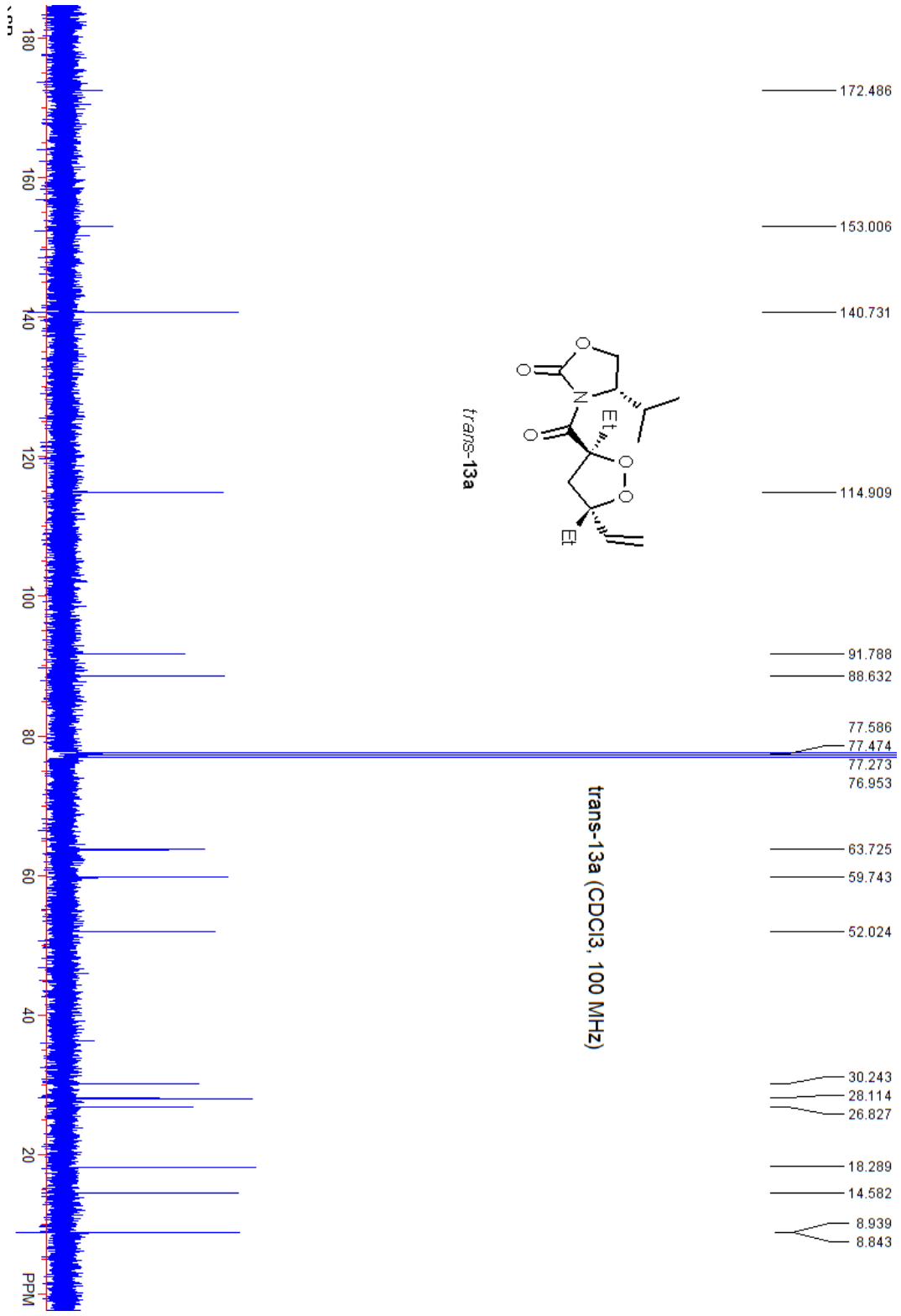

trans-11e (CDCl3, 300 MHz)
trans-11e
Et
Et
7.281
6.062
6.028
6.004
5.970
5.229
5.223
5.195
5.189
5.014
5.009
4.957
4.952
4.316
4.294
4.284
4.251
4.227
4.222
4.198
2.057
2.038
2.017
2.002
1.812
1.788
1.764
1.739
1.254
1.205
1.184
1.169
1.011
0.997
0.962
0.932
0.918
0.896
0.876
0.850
0.825
0.804
0.787
0.90
1.05
2.00
4.11
1.03
1.05
1.08
1.25
10.63
8.64
PPM

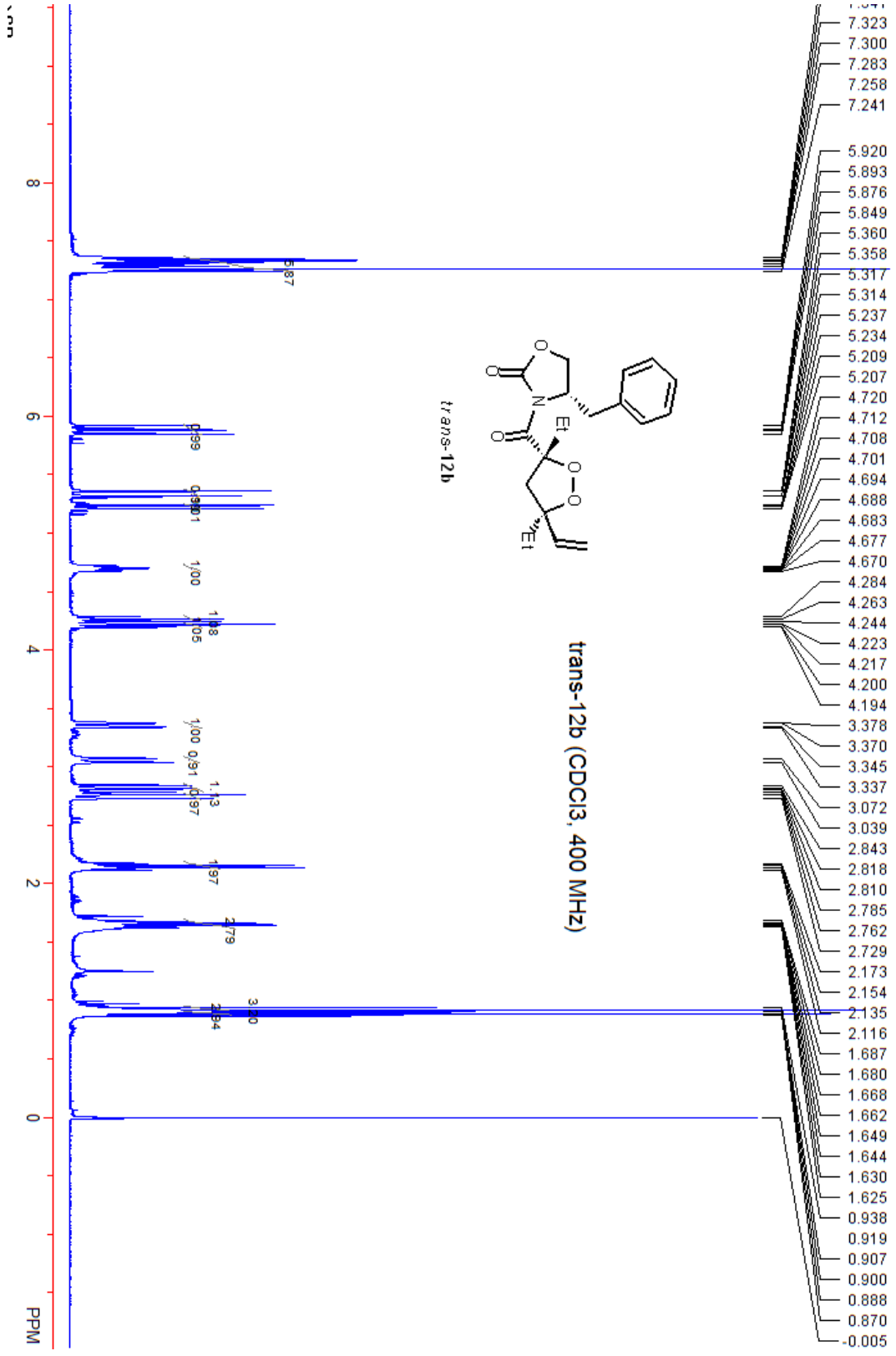

trans-11e (CDCl3, 100 MHz)
trans-11e
Et
Et
172.614
153.633
137.870
117.120
77.350
77.031
76.712
65.482
62.840
40.130
37.443
36.000
28.058
26.228
23.920
18.195
11.871
11.423
PPM

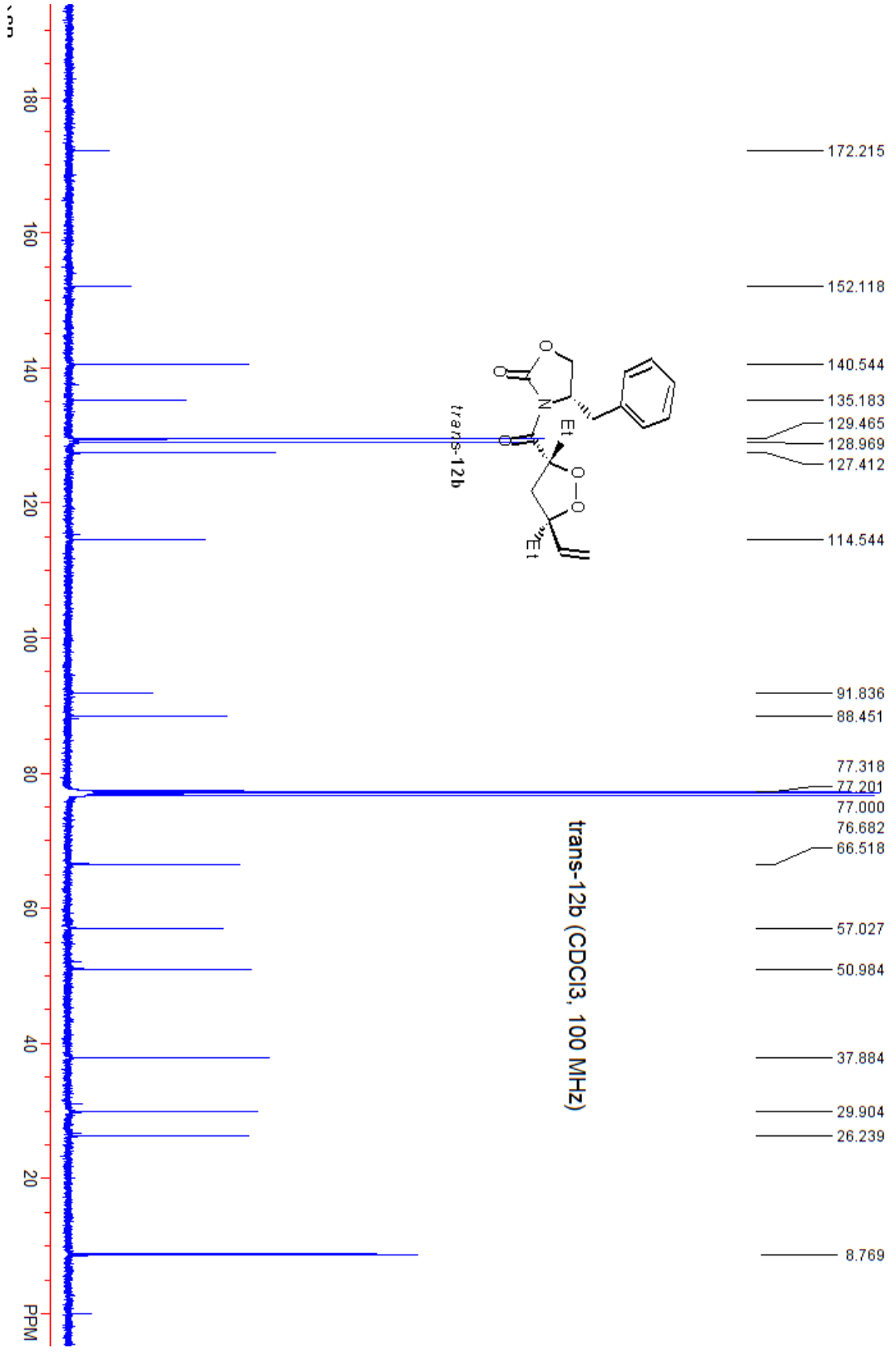

trans-12a
trans-12a (CDCl3, 100 MHz)
172.360
153.080
140.813
114.752
92.205
88.640
77.616
77.295
76.975
64.038
60.264
51.503
30.243
28.889
26.462
18.274
15.125
8.984
8.947
200
150
100
50
0
PPM

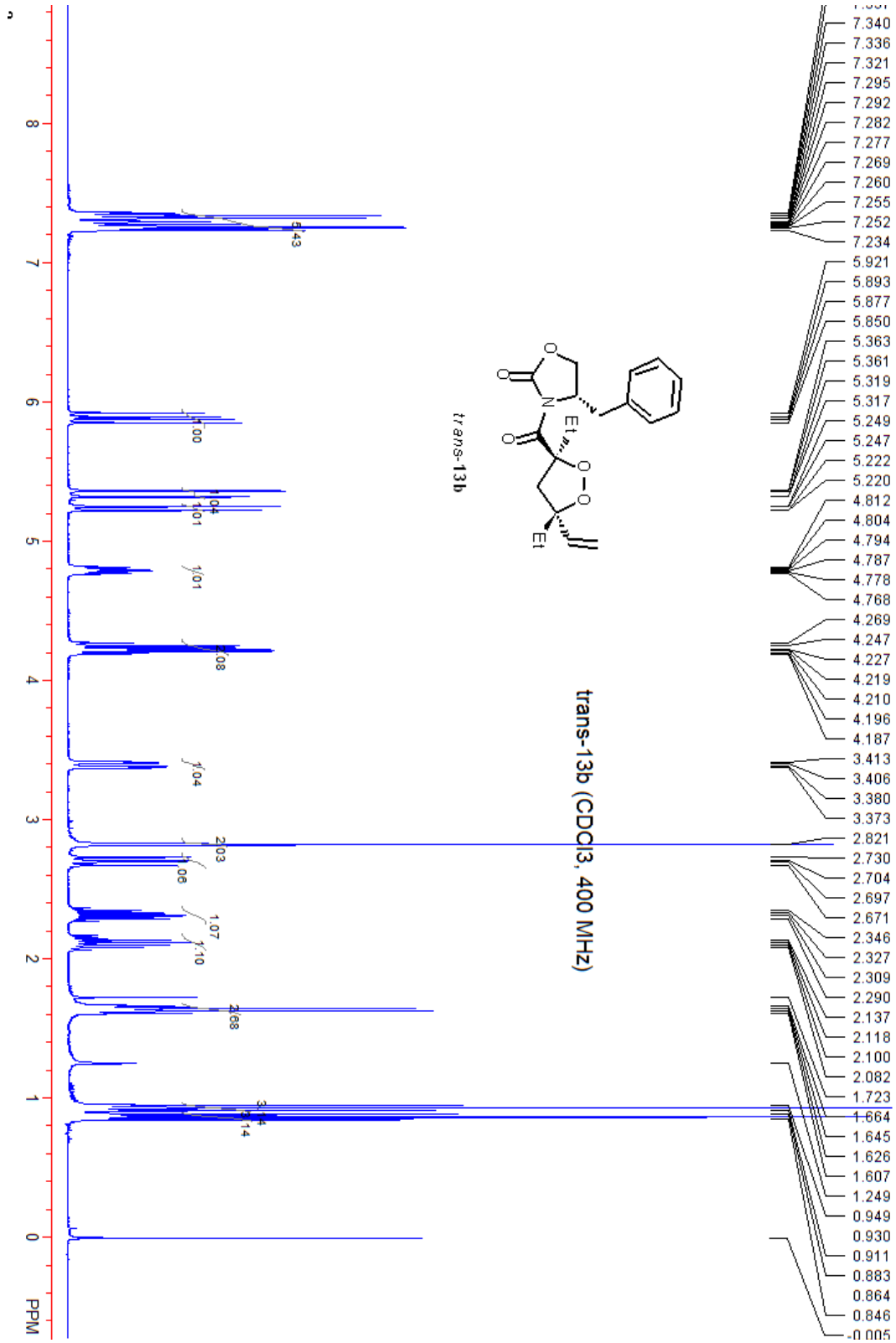

trans-12a (CDCl3, 400 MHz)
trans-12a
7.291
5.936
5.908
5.892
5.865
5.383
5.381
5.340
5.337
5.258
5.255
5.231
5.228
4.527
4.518
4.510
4.392
4.369
4.349
4.290
4.284
4.268
4.262
3.078
3.072
3.044
2.802
2.769
2.485
2.477
2.467
2.459
2.451
2.202
2.188
2.169
2.163
2.152
2.144
1.662
1.653
1.642
1.635
1.591
0.990
0.972
0.965
0.948
0.931
0.914
0.912
0.896
0.877
0.022
0.97
1.00
0.97
0.94
1.00
1.00
0.98
0.95
1.15
1.95
2.14
8.39
PPM

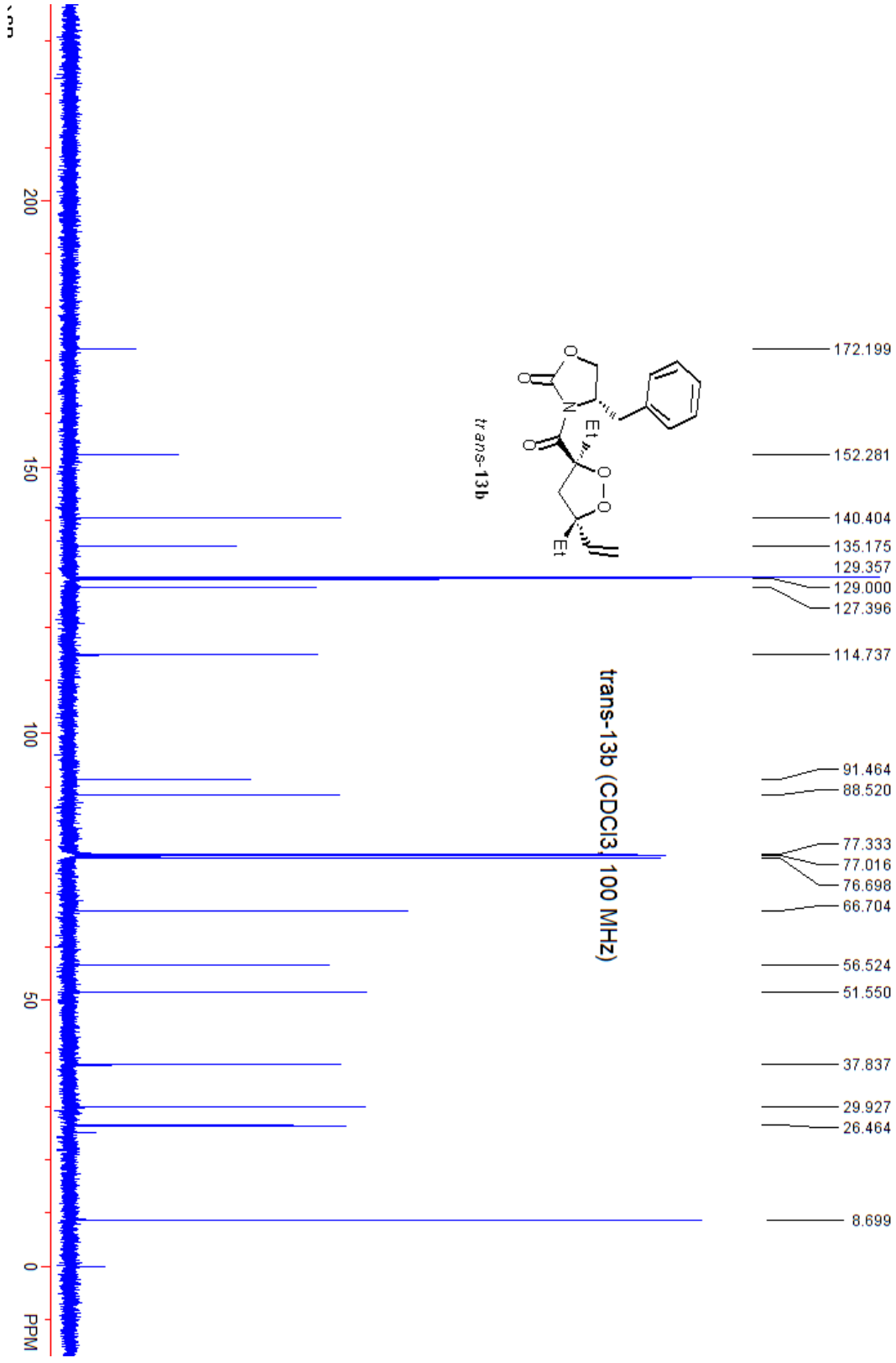

trans-13a (CDCl3, 300 MHz)
trans-13a
Et
Et
7.267
5.920
5.883
5.861
5.825
5.361
5.358
5.304
5.243
5.239
5.206
5.203
4.609
4.597
4.585
4.569
4.558
4.372
4.343
4.315
4.279
4.267
4.248
4.237
2.813
2.809
2.429
2.417
2.406
2.394
2.383
2.370
2.364
2.338
2.313
2.289
2.265
2.239
2.177
2.152
2.127
2.103
2.078
1.656
1.631
1.605
1.581
0.945
0.922
0.900
0.880
0.874
0.856
0.831
-0.000
0.94
1.05
1.01
1.00
1.09
1.07
1.93
1.05
1.03
1.08
2.34
8.19
3.14
PPM

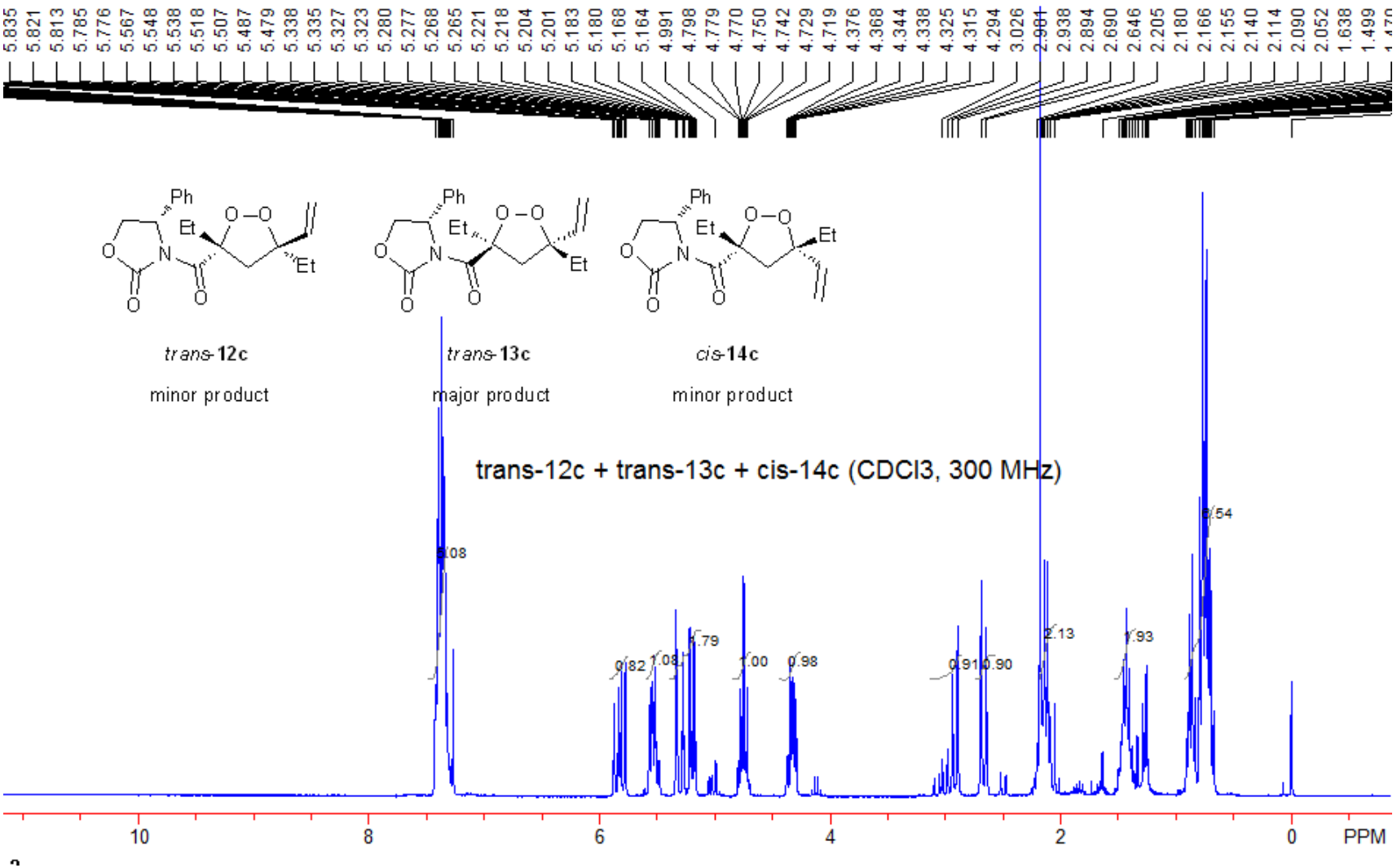

trans-13a
trans-13a (CDCl3, 100 MHz)
172.486
153.006
140.731
114.909
91.788
88.632
77.586
77.474
77.273
76.953
63.725
59.743
52.024
30.243
28.114
26.827
18.289
14.582
8.939
8.843
PPM

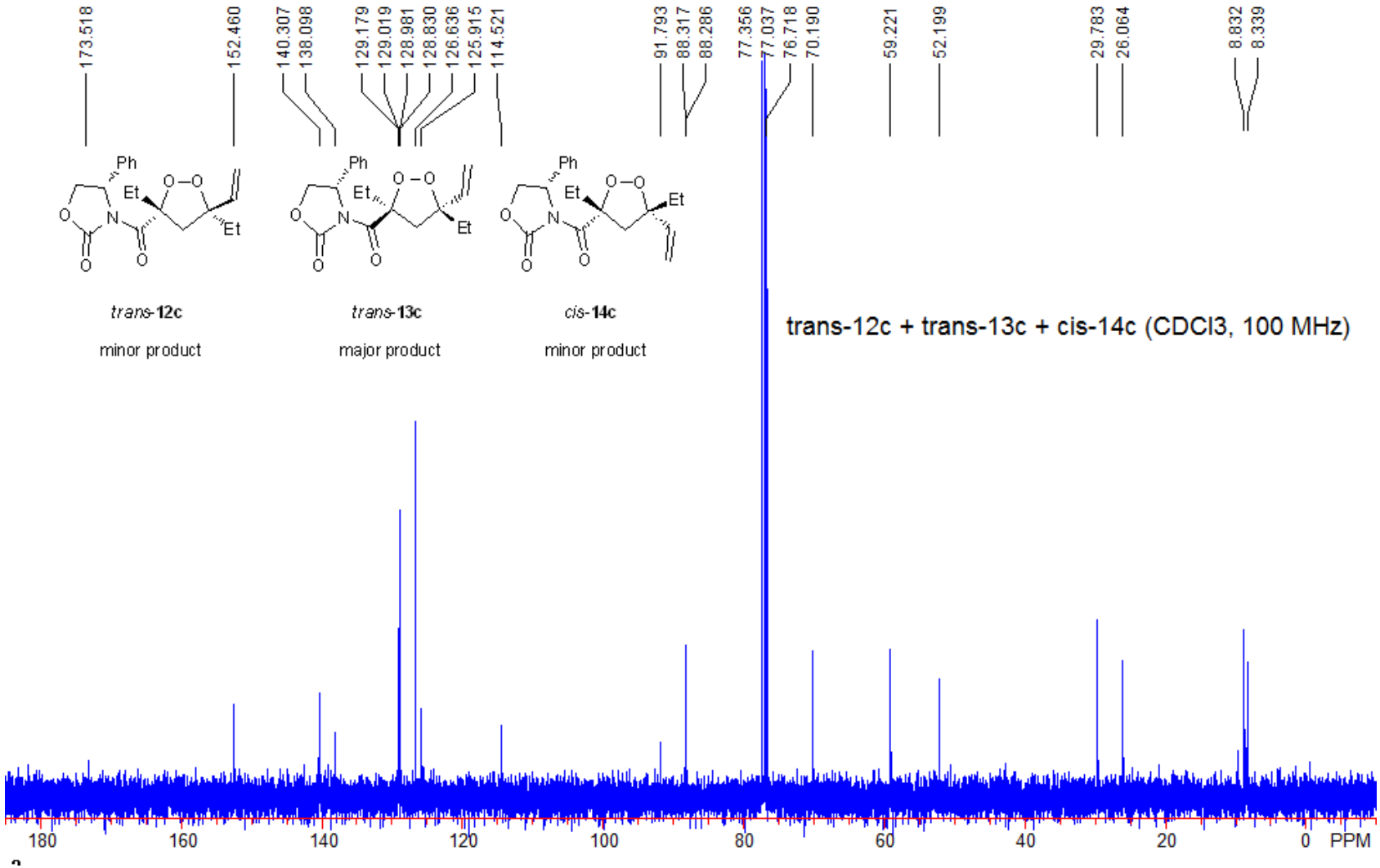

trans-12b (CDCl3, 400 MHz)
trans-12b
7.323
7.300
7.283
7.258
7.241
5.920
5.893
5.876
5.849
5.360
5.358
5.317
5.314
5.237
5.234
5.209
5.207
4.720
4.712
4.708
4.701
4.694
4.688
4.683
4.677
4.670
4.284
4.263
4.244
4.223
4.217
4.200
4.194
3.378
3.370
3.345
3.337
3.072
3.039
2.843
2.818
2.810
2.785
2.762
2.729
2.173
2.154
2.135
2.116
1.687
1.680
1.668
1.662
1.649
1.644
1.630
1.625
0.938
0.919
0.907
0.900
0.888
0.870
-0.005
PPM

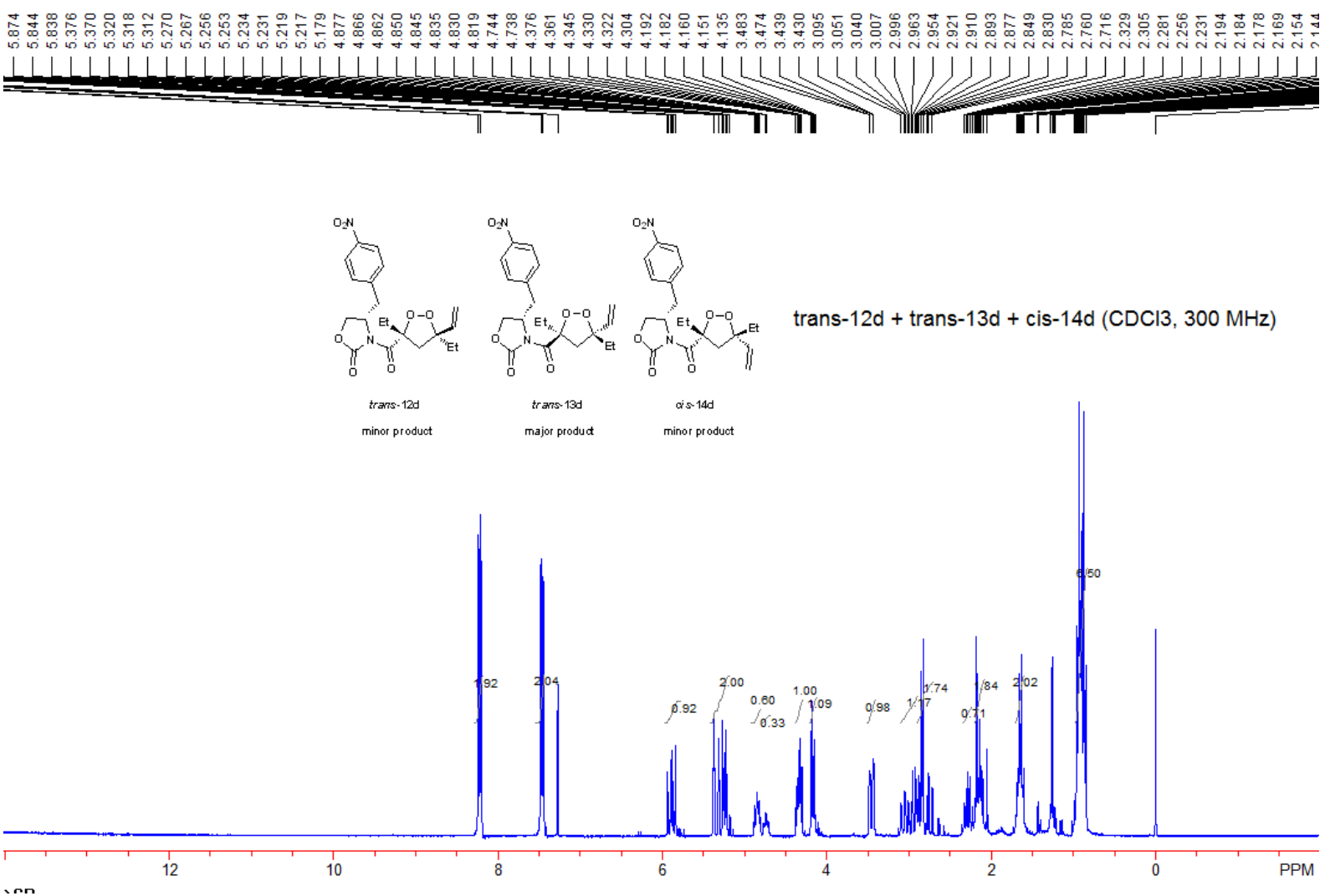

trans-12b
trans-12b (CDCl3, 100 MHz)
172.215
152.118
140.544
135.183
129.465
128.969
127.412
114.544
91.836
88.451
77.318
77.201
77.000
76.682
66.518
57.027
50.984
37.884
29.904
26.239
8.769
PPM

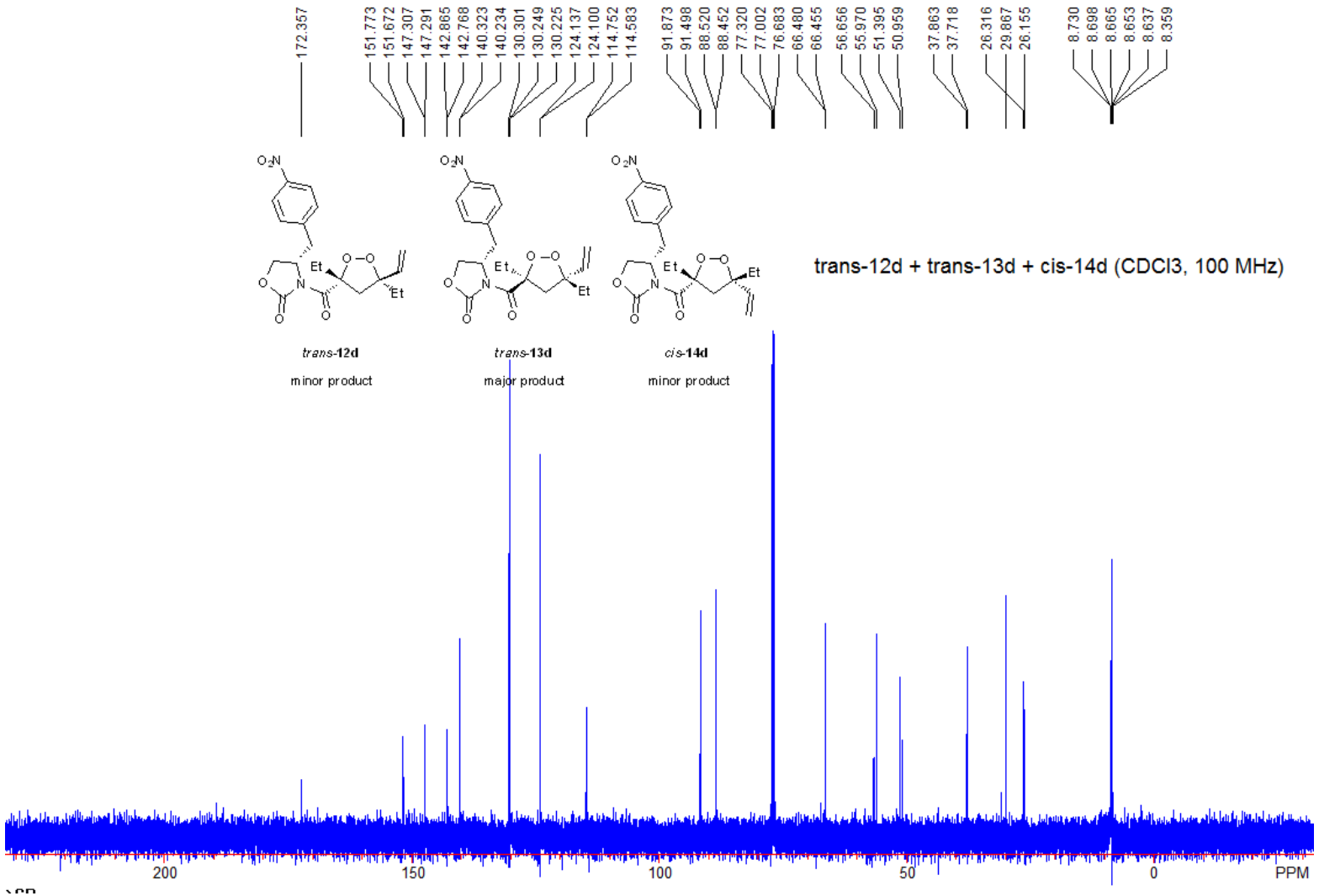

trans-13b (CDCl3, 400 MHz)
trans-13b
7.340
7.336
7.321
7.295
7.292
7.282
7.277
7.269
7.260
7.255
7.252
7.234
5.921
5.893
5.877
5.850
5.363
5.361
5.319
5.317
5.249
5.247
5.222
5.220
4.812
4.804
4.794
4.787
4.778
4.768
4.269
4.247
4.227
4.219
4.210
4.196
4.187
3.413
3.406
3.380
3.373
2.821
2.730
2.704
2.697
2.671
2.346
2.327
2.309
2.290
2.137
2.118
2.100
2.082
1.723
1.664
1.645
1.626
1.607
1.249
0.949
0.930
0.911
0.883
0.864
0.846
PPM

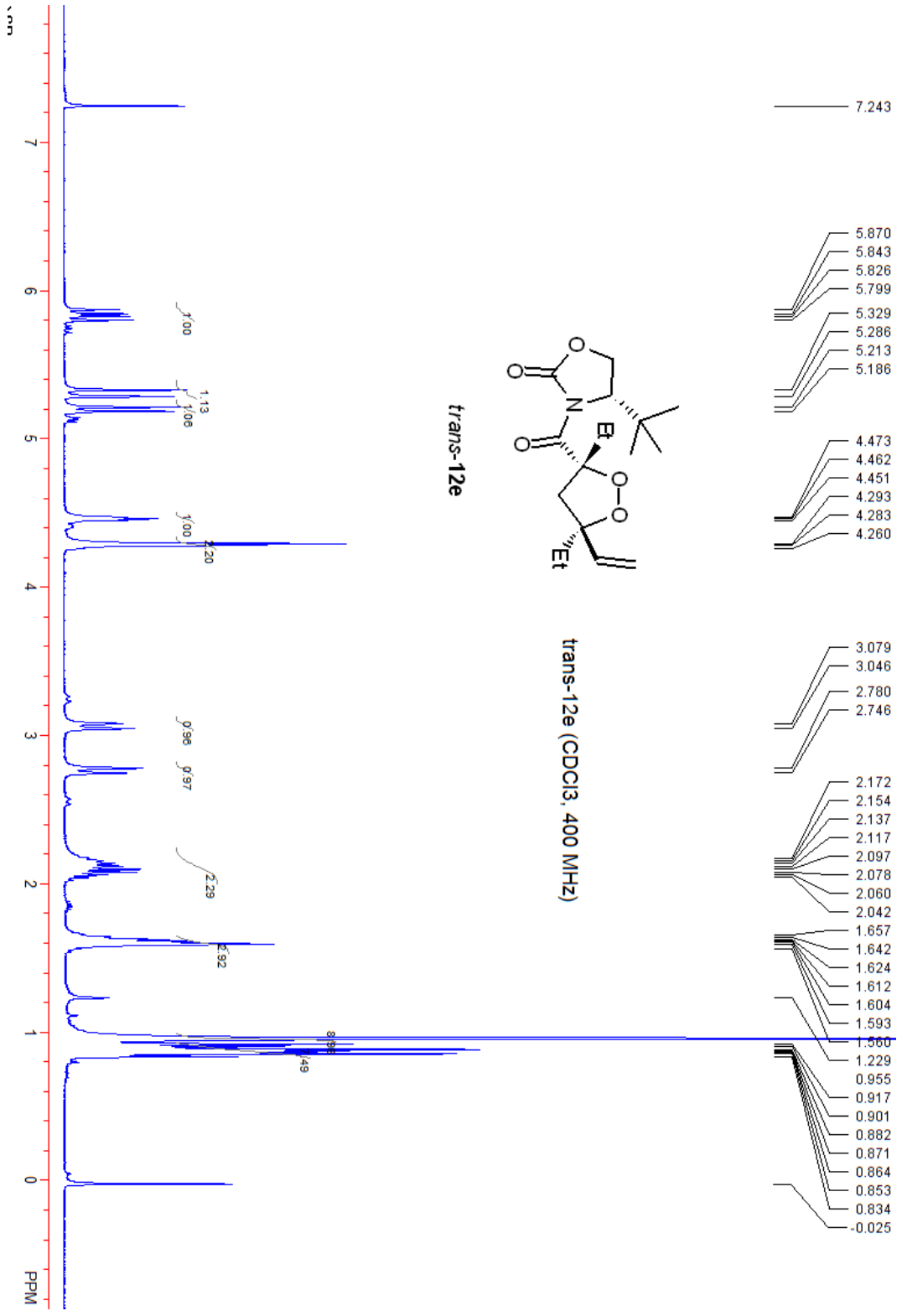

trans-13b
trans-13b (CDCl3, 100 MHz)
172.199
152.281
140.404
135.175
129.357
129.000
127.396
114.737
91.464
88.520
77.333
77.016
76.698
66.704
56.524
51.550
37.837
29.927
26.464
8.699
PPM

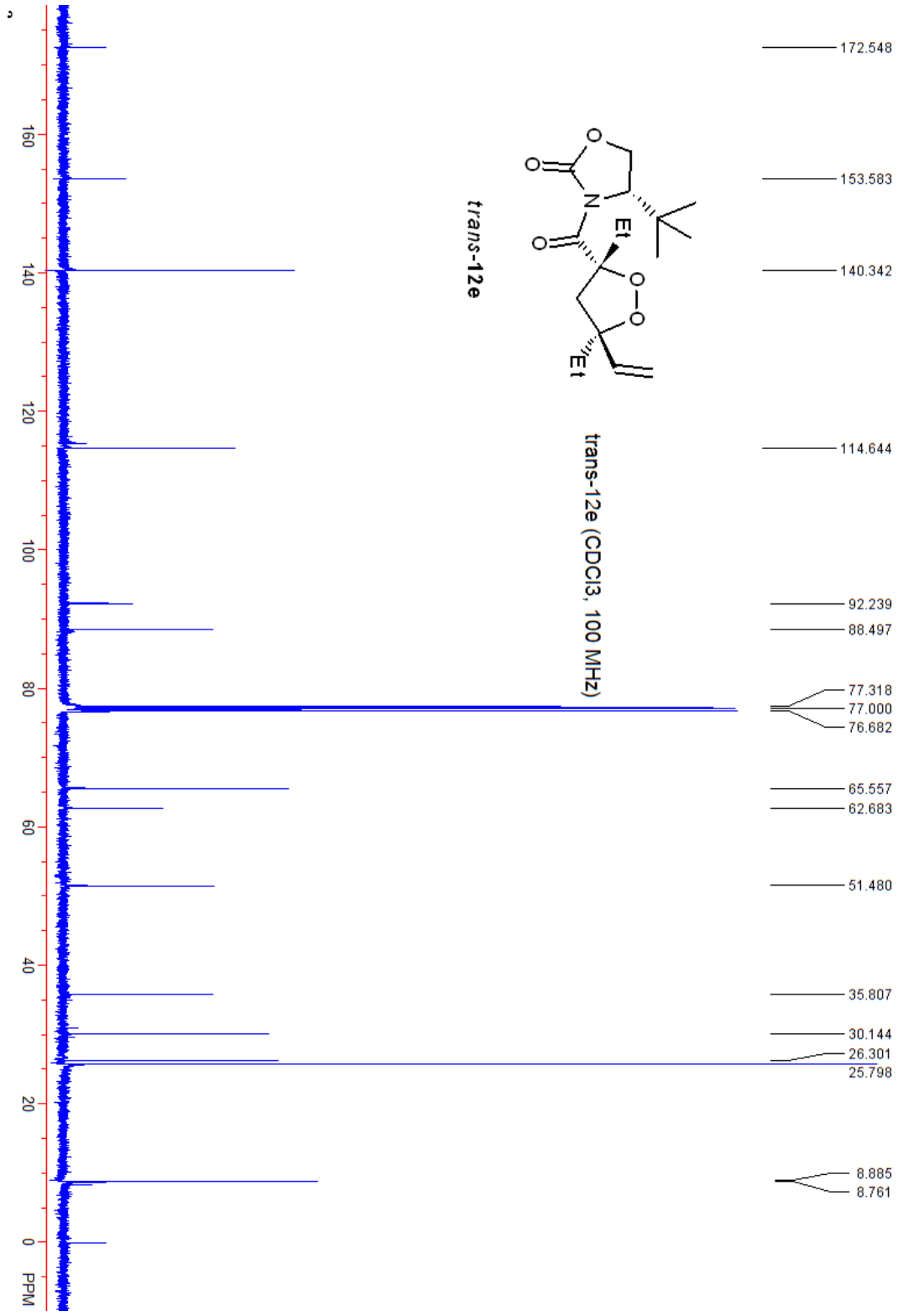

5.835
5.821
5.813
5.785
5.776
5.567
5.548
5.538
5.518
5.507
5.487
5.479
5.338
5.335
5.327
5.323
5.280
5.277
5.268
5.265
5.221
5.218
5.204
5.201
5.183
5.180
5.168
5.164
4.991
4.798
4.779
4.770
4.750
4.742
4.729
4.719
4.376
4.368
4.344
4.338
4.325
4.315
4.294
3.026
2.981
2.938
2.894
2.690
2.646
2.205
2.180
2.166
2.155
2.140
2.114
2.090
2.052
1.638
1.499
Ph
Et
O–O
Et
O
N
O
O
trans-12c
minor product
trans-13c
major product
cis-14c
minor product
trans-12c + trans-13c + cis-14c (CDCl3, 300 MHz)
3.08
0.82
1.08
1.79
1.00
0.98
0.91
0.90
2.13
1.93
0.54
10
8
6
4
2
0
PPM

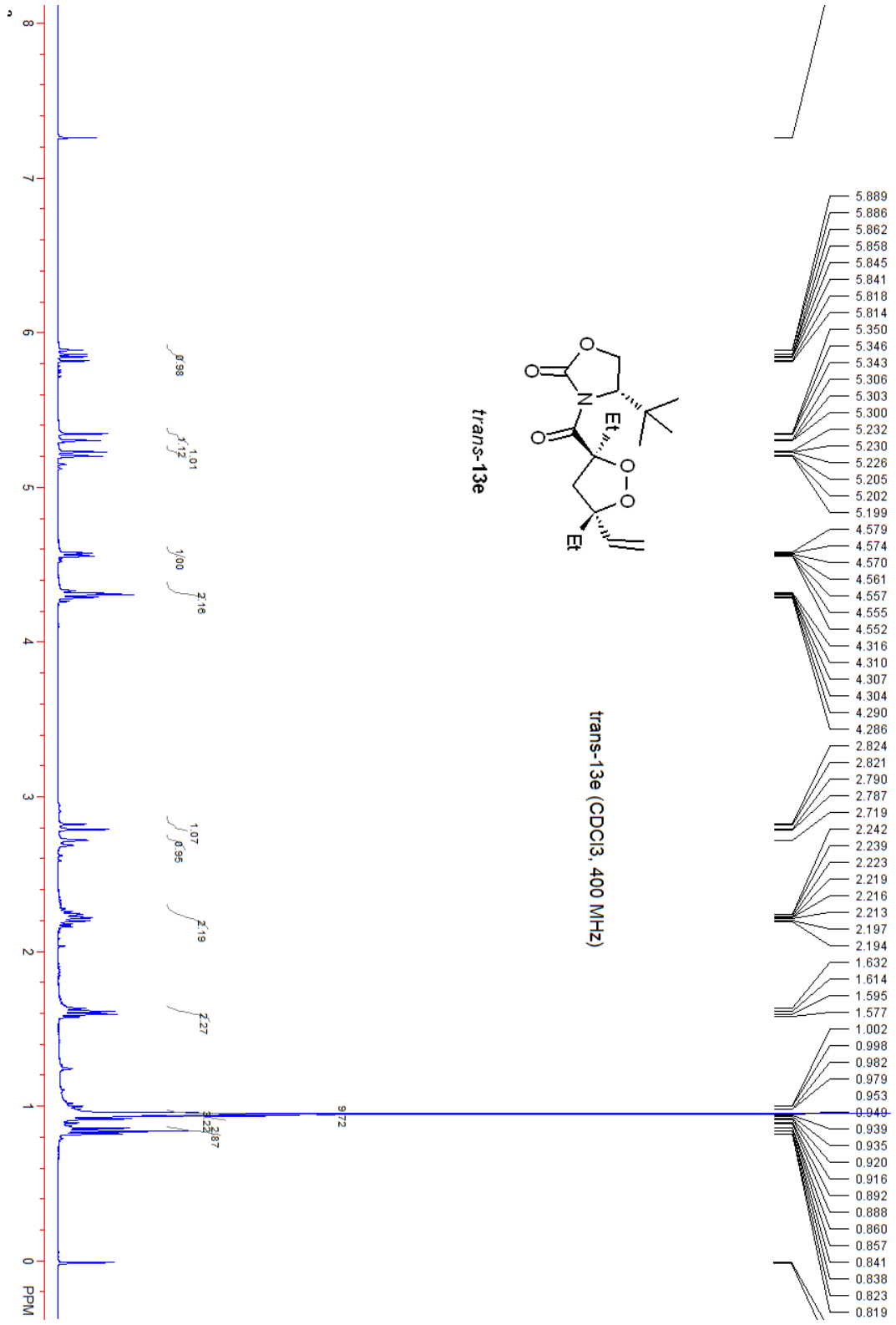

173.518
152.460
140.307
138.098
129.179
129.019
128.981
128.830
126.636
125.915
114.521
91.793
88.317
88.286
77.356
77.037
76.718
70.190
59.221
52.199
29.783
26.064
8.832
8.339
trans-12c
minor product
trans-13c
major product
cis-14c
minor product
trans-12c + trans-13c + cis-14c (CDCl3, 100 MHz)
180
160
140
120
100
80
60
40
20
0
PPM

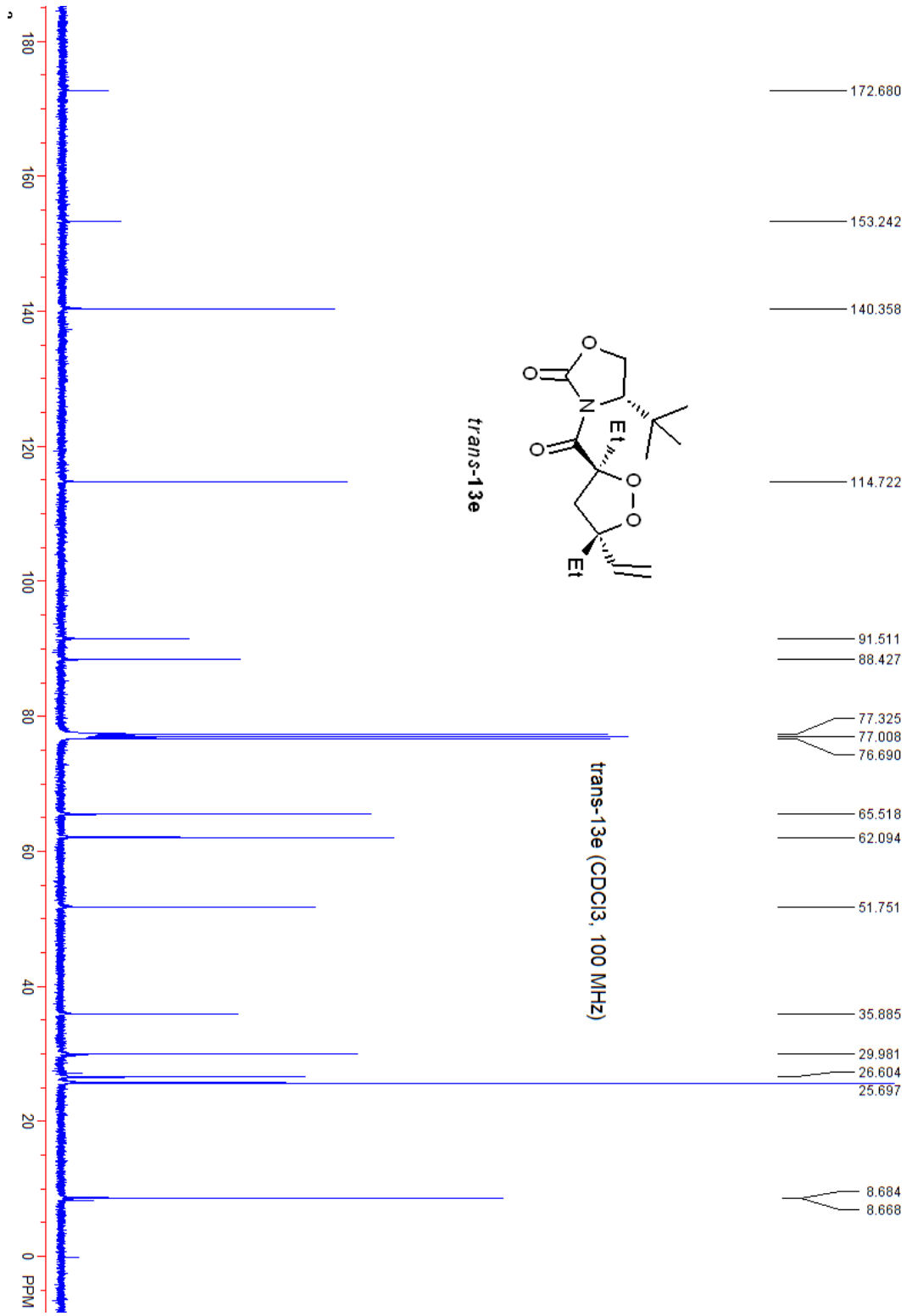

5.874
5.844
5.838
5.376
5.370
5.320
5.318
5.312
5.270
5.267
5.256
5.253
5.234
5.231
5.219
5.217
5.179
4.877
4.866
4.862
4.850
4.845
4.835
4.830
4.819
4.744
4.738
4.376
4.361
4.345
4.330
4.322
4.304
4.192
4.182
4.160
4.151
4.135
3.483
3.474
3.439
3.430
3.095
3.051
3.040
3.007
2.996
2.963
2.954
2.921
2.910
2.893
2.877
2.849
2.830
2.785
2.760
2.716
2.329
2.305
2.281
2.256
2.231
2.194
2.184
2.178
2.169
2.154
2.144
trans-12d
minor product
trans-13d
major product
cis-14d
minor product
trans-12d + trans-13d + cis-14d (CDCl3, 300 MHz)
1.92
2.04
0.92
2.00
0.60
0.33
1.00
1.09
0.98
1.17
0.74
0.71
0.84
2.02
6.50
12
10
8
6
4
2
0
PPM

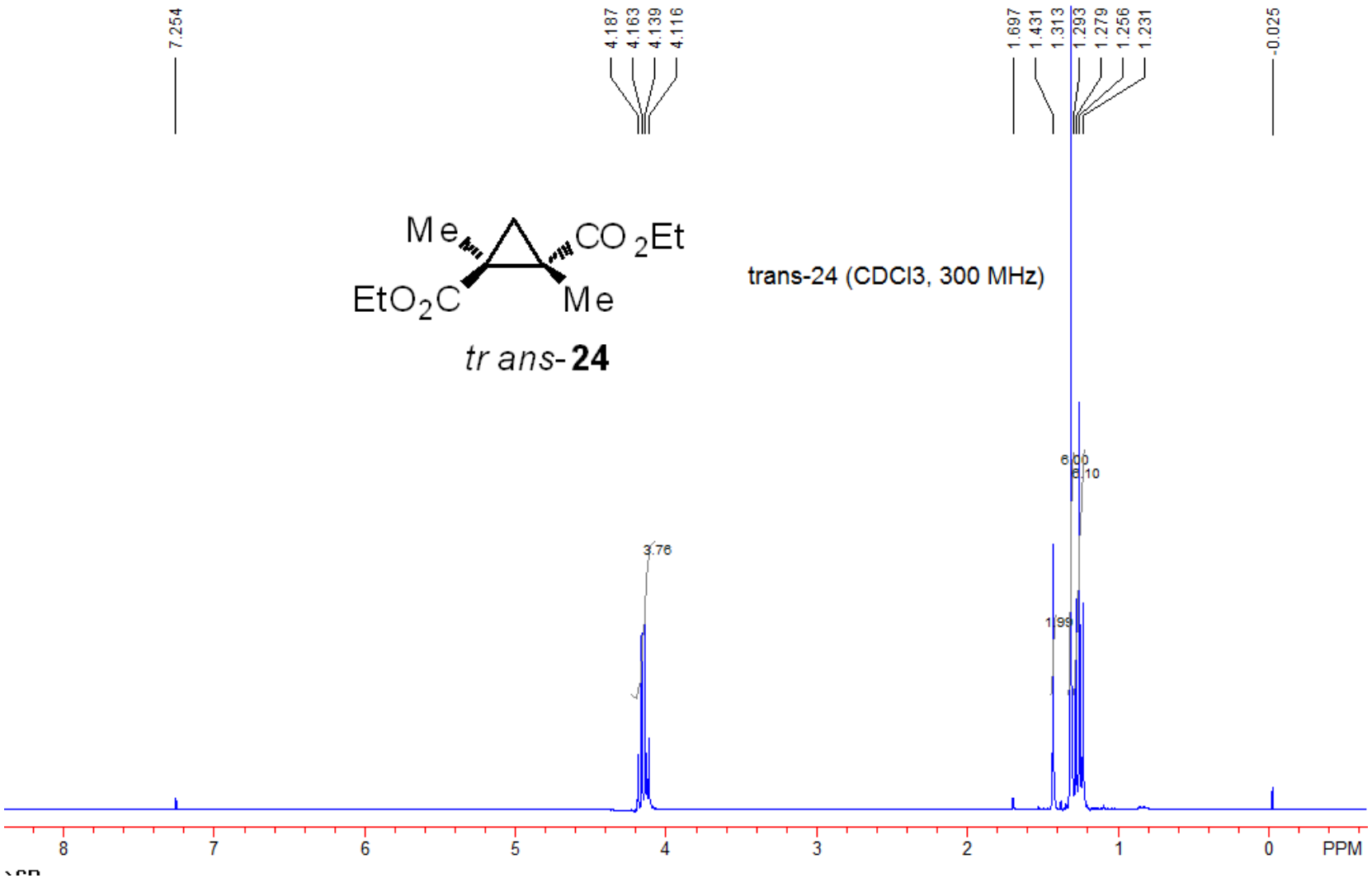

172.357
151.773
151.672
147.307
147.291
142.865
142.768
140.323
140.234
130.301
130.249
130.225
124.137
124.100
114.752
114.583
91.873
91.498
88.520
88.452
77.320
77.002
76.683
66.480
66.455
56.656
55.970
51.395
50.959
37.863
37.718
26.316
29.867
26.155
8.730
8.698
8.665
8.653
8.637
8.359
trans-12d + trans-13d + cis-14d (CDCl3, 100 MHz)
trans-12d
minor product
trans-13d
major product
cis-14d
minor product
200
150
100
50
0
PPM

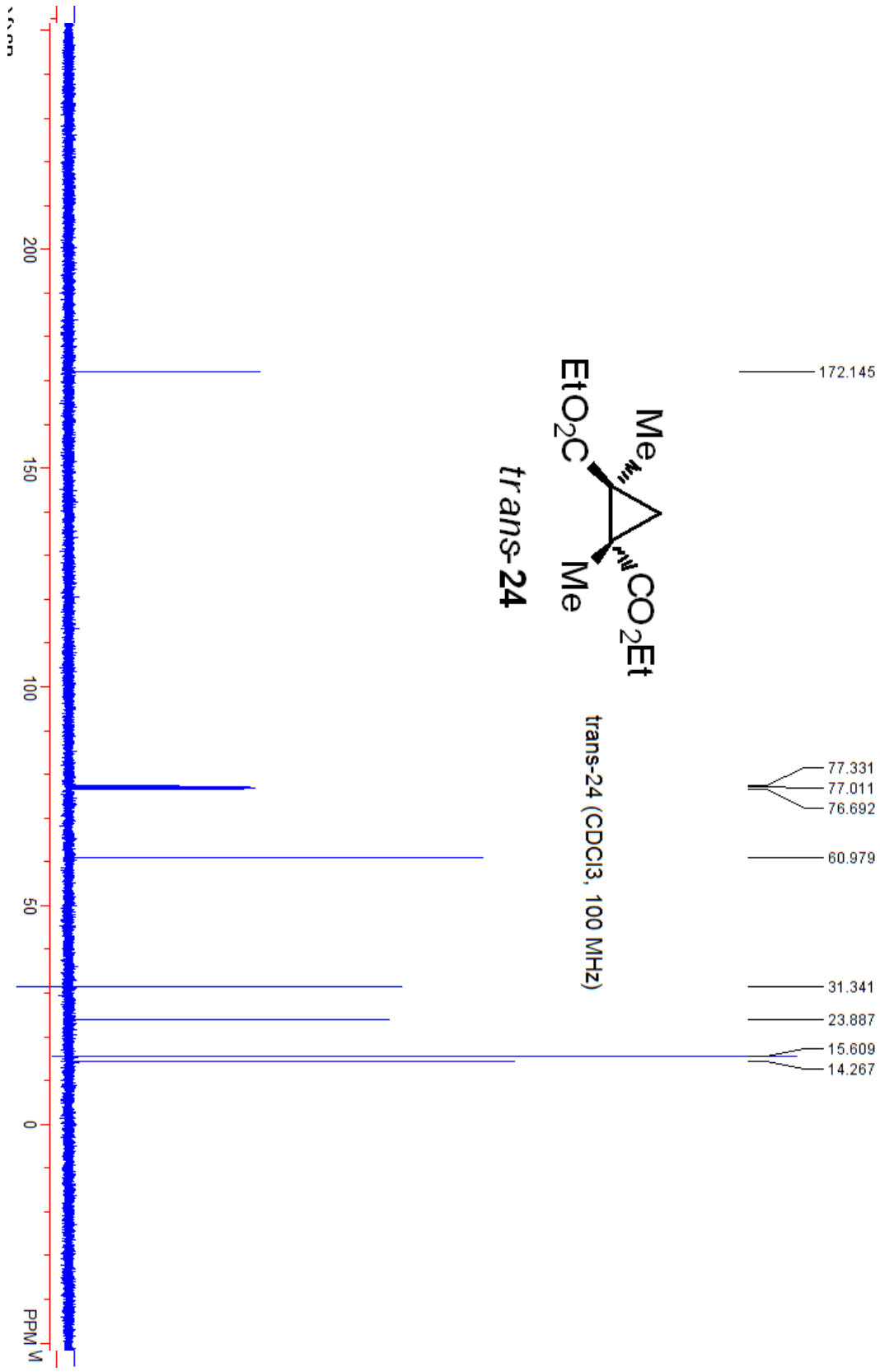

trans-12e (CDCl3, 400 MHz)
trans-12e
Et
Et
7.243
5.870
5.843
5.826
5.799
5.329
5.286
5.213
5.186
4.473
4.462
4.451
4.293
4.283
4.260
3.079
3.046
2.780
2.746
2.172
2.154
2.137
2.117
2.097
2.078
2.060
2.042
1.657
1.642
1.624
1.612
1.604
1.593
1.560
1.229
0.955
0.917
0.901
0.882
0.871
0.864
0.853
0.834
-0.025
1.00
1.13
1.06
1.00
2.20
0.96
0.97
2.29
2.92
8.49
PPM

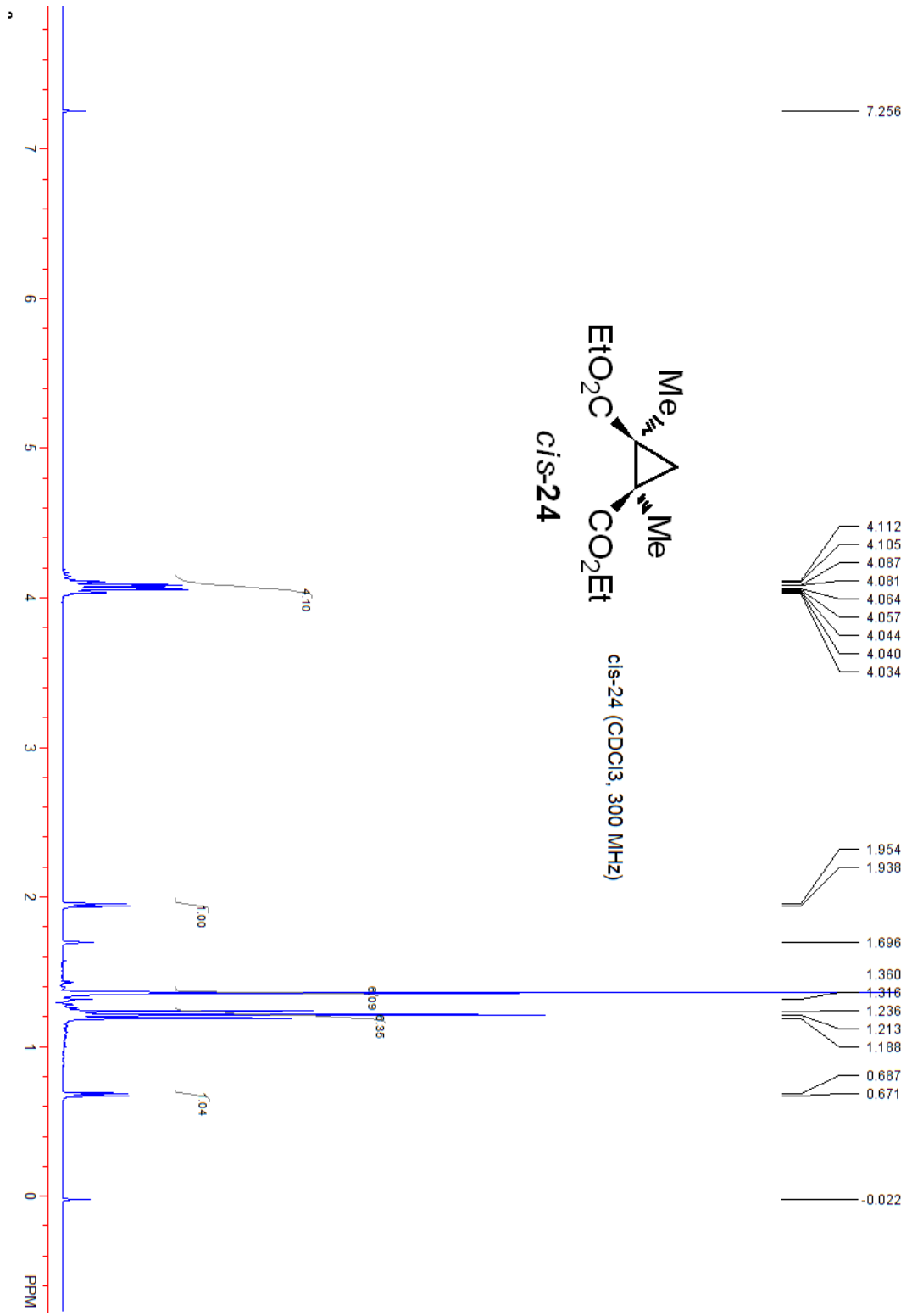

trans-12e
trans-12e (CDCl3, 100 MHz)
172.548
153.583
140.342
114.644
92.239
88.497
77.318
77.000
76.682
65.557
62.683
51.480
35.807
30.144
26.301
25.798
8.885
8.761
PPM

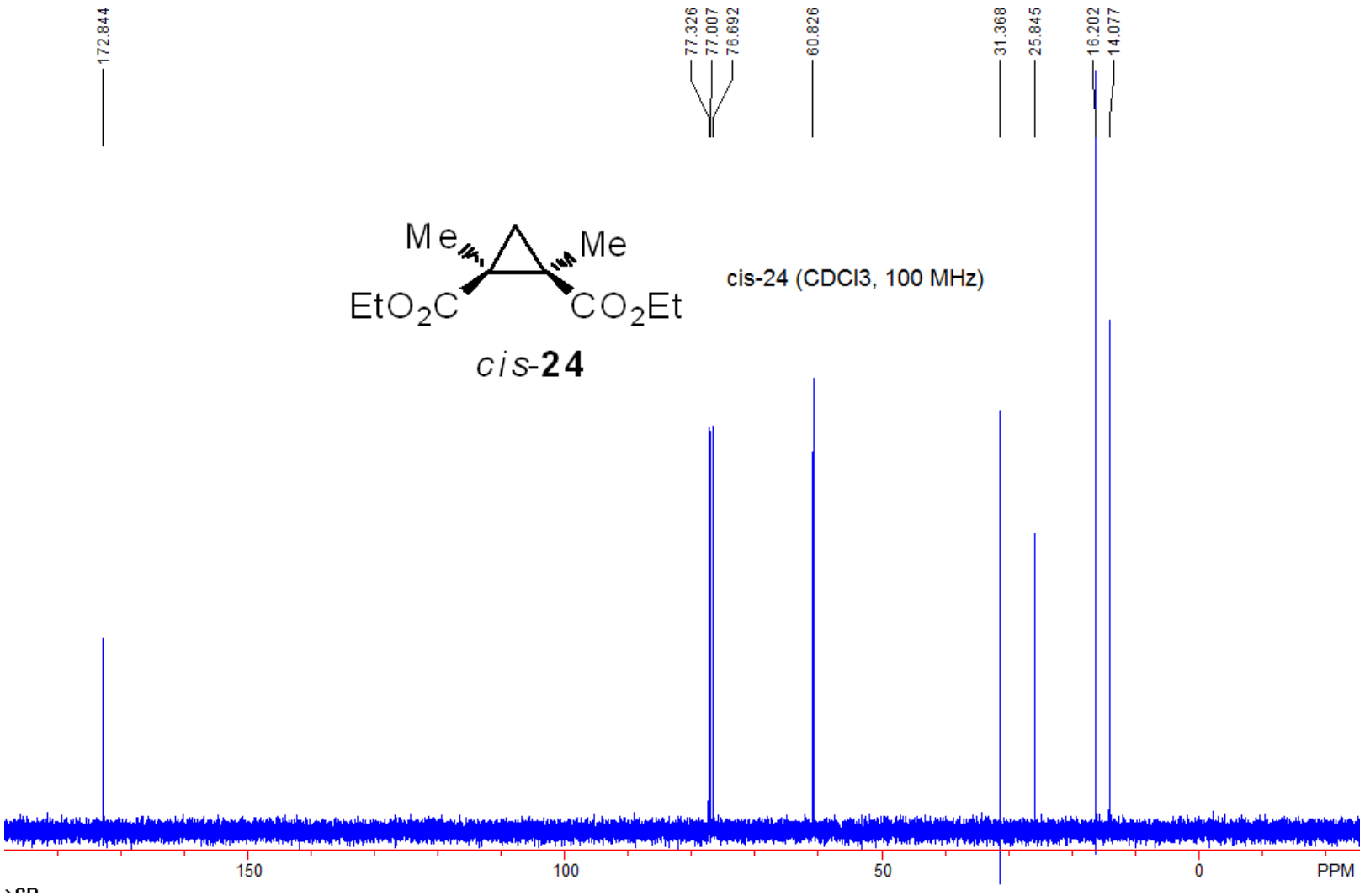

trans-13e
trans-13e (CDCl3, 400 MHz)
Et
Et
5.889
5.886
5.862
5.858
5.845
5.841
5.818
5.814
5.350
5.346
5.343
5.306
5.303
5.300
5.232
5.230
5.226
5.205
5.202
5.199
4.579
4.574
4.570
4.561
4.557
4.555
4.552
4.316
4.310
4.307
4.304
4.290
4.286
2.824
2.821
2.790
2.787
2.719
2.242
2.239
2.223
2.219
2.216
2.213
2.197
2.194
1.632
1.614
1.595
1.577
1.002
0.998
0.982
0.979
0.953
0.940
0.939
0.935
0.920
0.916
0.892
0.888
0.860
0.857
0.841
0.838
0.823
0.819
0.98
1.12
1.01
1.00
2.16
1.07
0.95
2.19
2.27
9.72
3.22
2.87
PPM

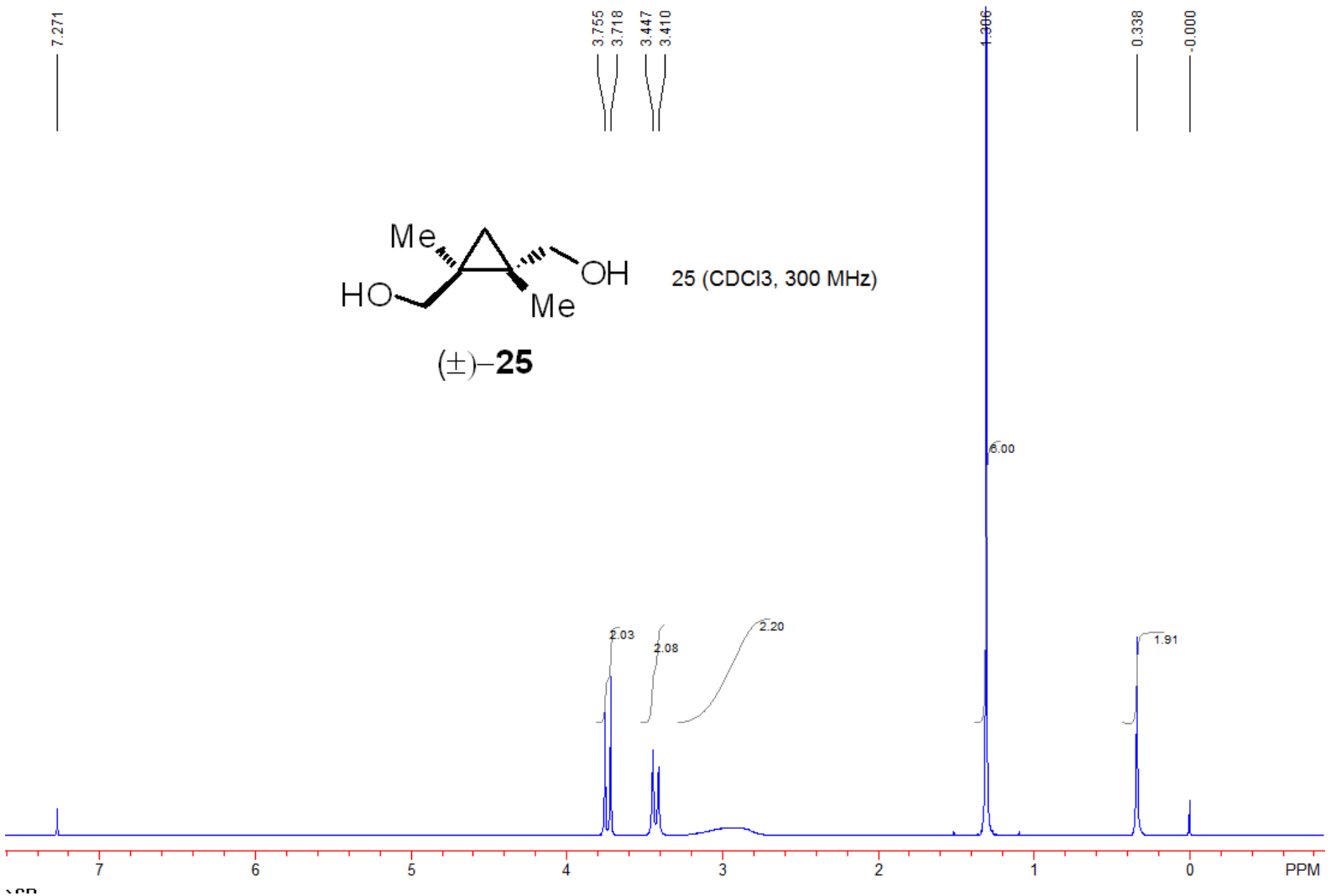

trans-13e
trans-13e (CDCl3, 100 MHz)
Et
Et
O
O
N
O
O
O
172.680
153.242
140.358
114.722
91.511
88.427
77.325
77.008
76.690
65.518
62.094
51.751
35.885
29.981
26.604
25.697
8.684
8.668
180
160
140
120
100
80
60
40
20
0
PPM

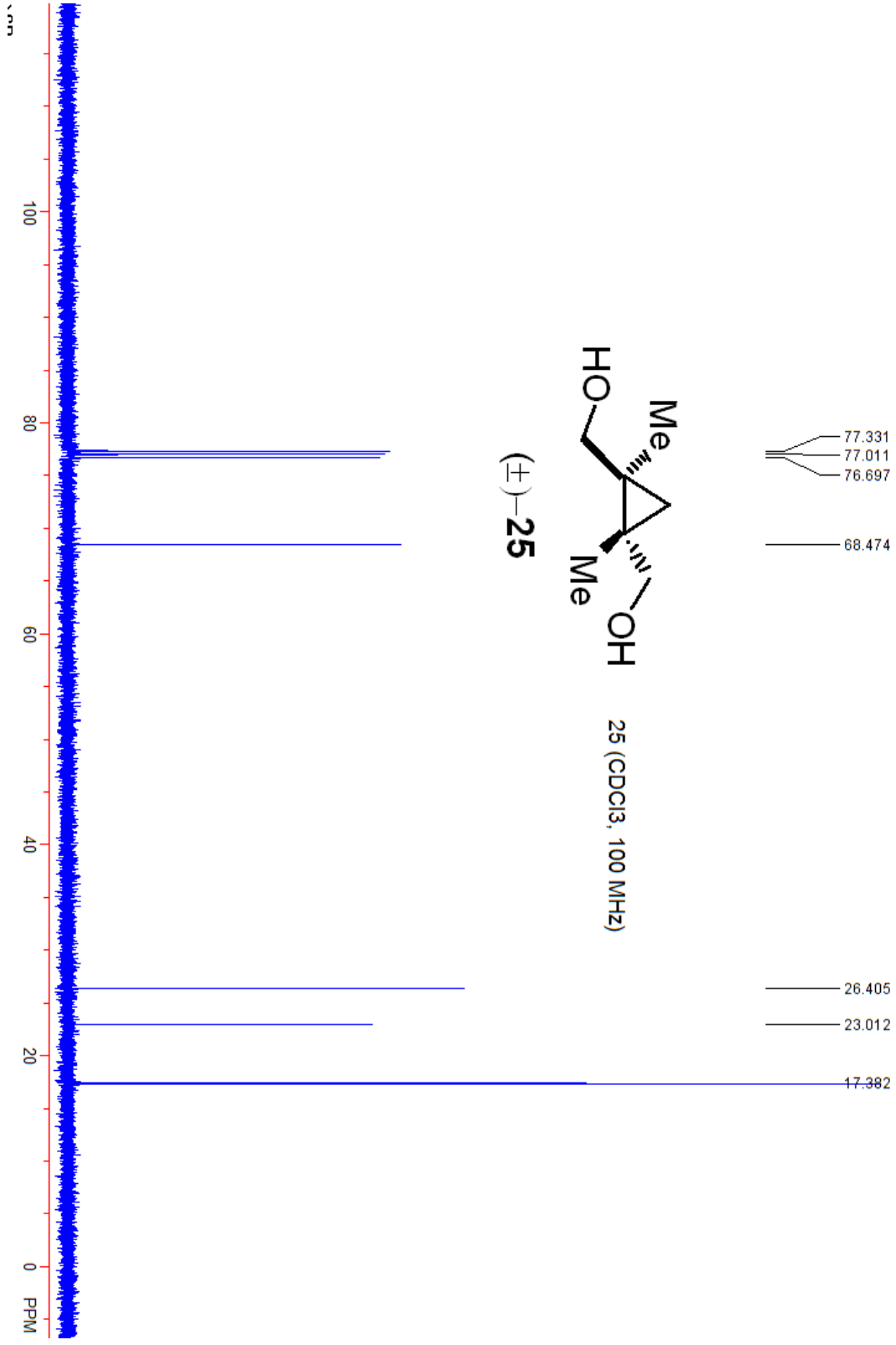

7.254
4.187
4.163
4.139
4.116
1.697
1.431
1.313
1.293
1.279
1.256
1.231
-0.025
Me
CO2Et
EtO2C
Me
trans-24
trans-24 (CDCl3, 300 MHz)
6.00
6.10
3.76
1.99
8
7
6
5
4
3
2
1
0
PPM

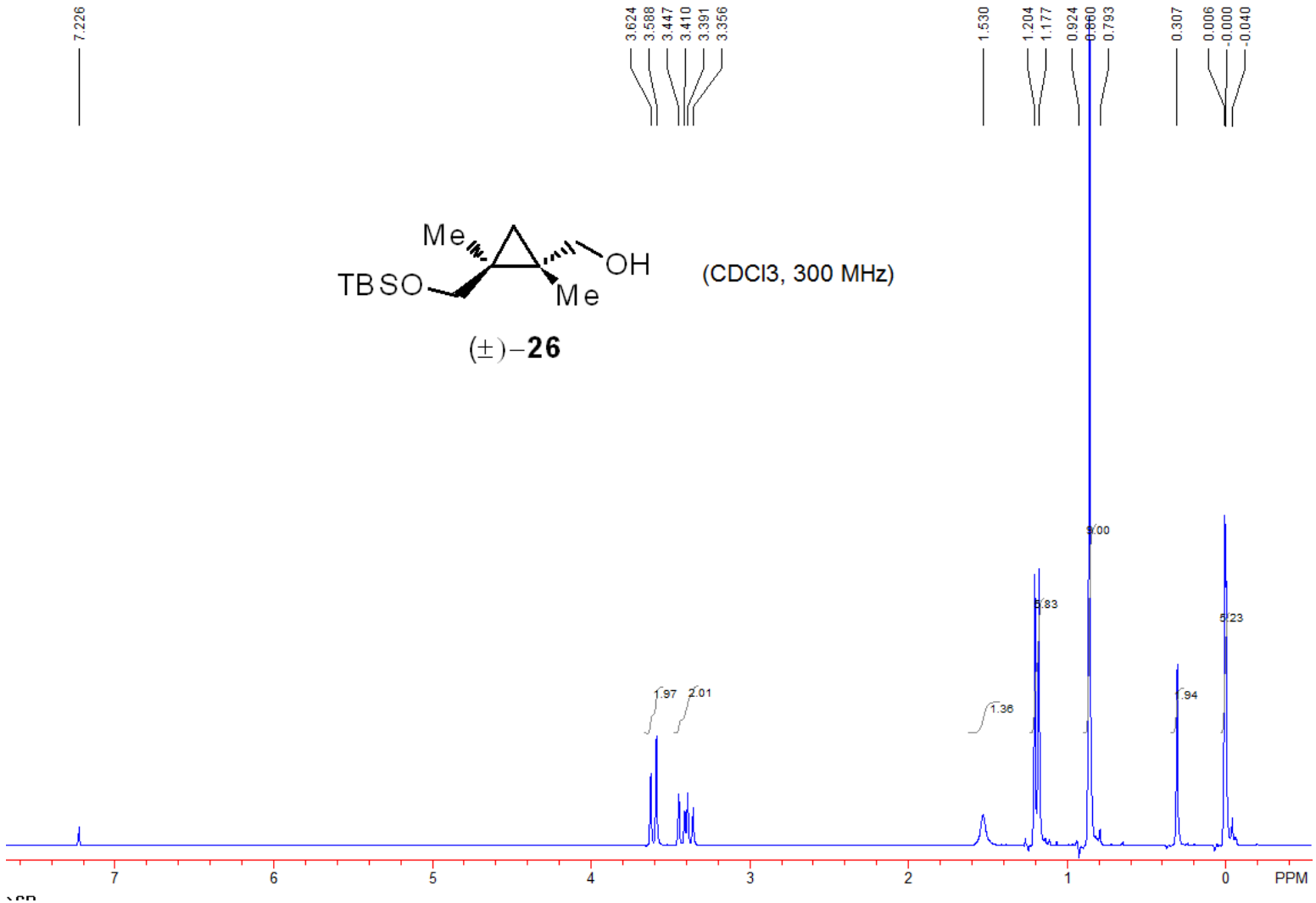

Me
EtO2C
CO2Et
Me
trans-24
trans-24 (CDCl3, 100 MHz)
172.145
77.331
77.011
76.692
60.979
31.341
23.887
15.609
14.267
200
150
100
50
0
PPM

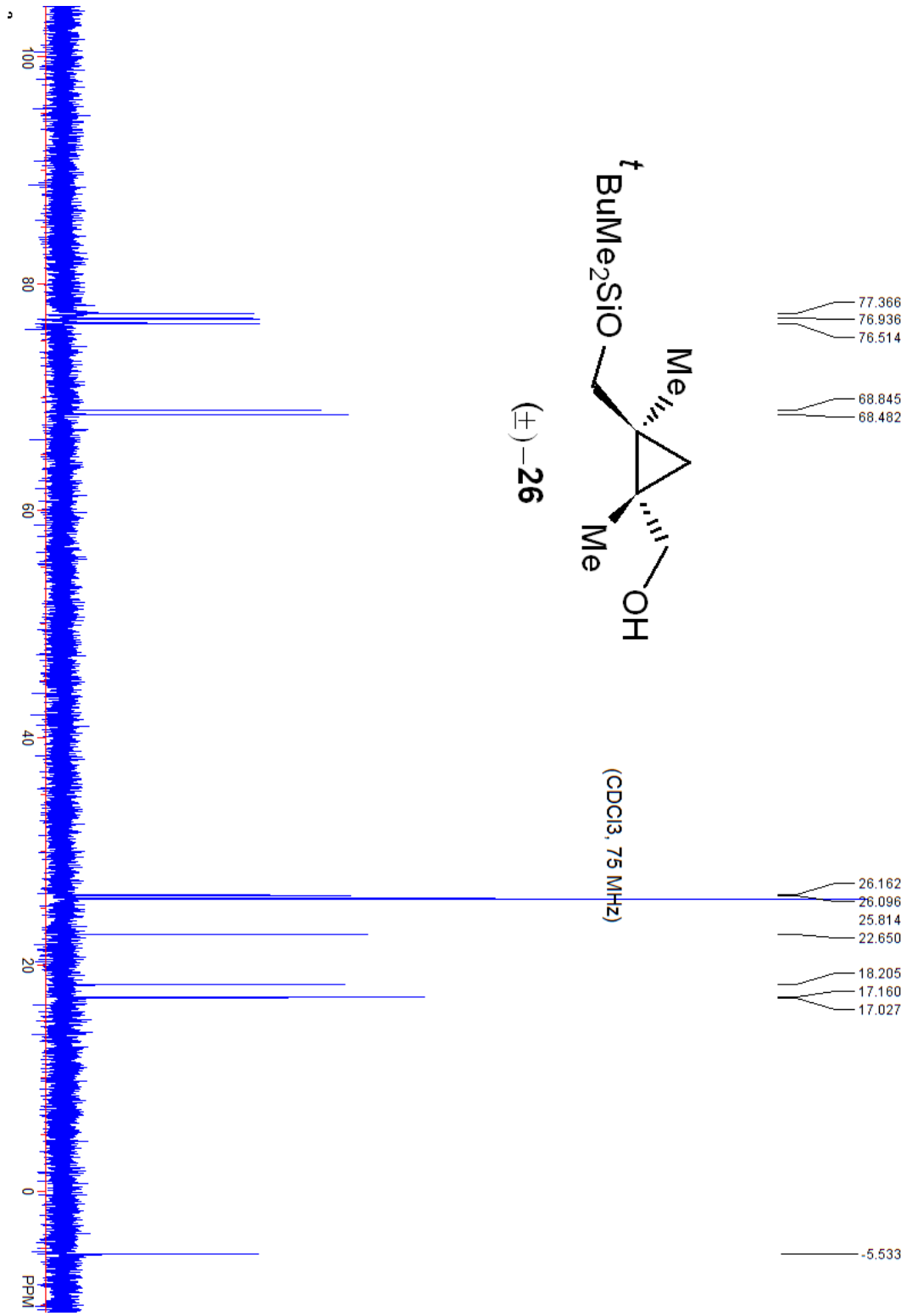

Me
EtO2C
CO2Et
Me
cis-24
cis-24 (CDCl3, 300 MHz)
7.256
4.112
4.105
4.087
4.081
4.064
4.057
4.044
4.040
4.034
1.954
1.938
1.696
1.360
1.316
1.236
1.213
1.188
0.687
0.671
-0.022
4.10
1.00
6.09
6.35
1.04
PPM

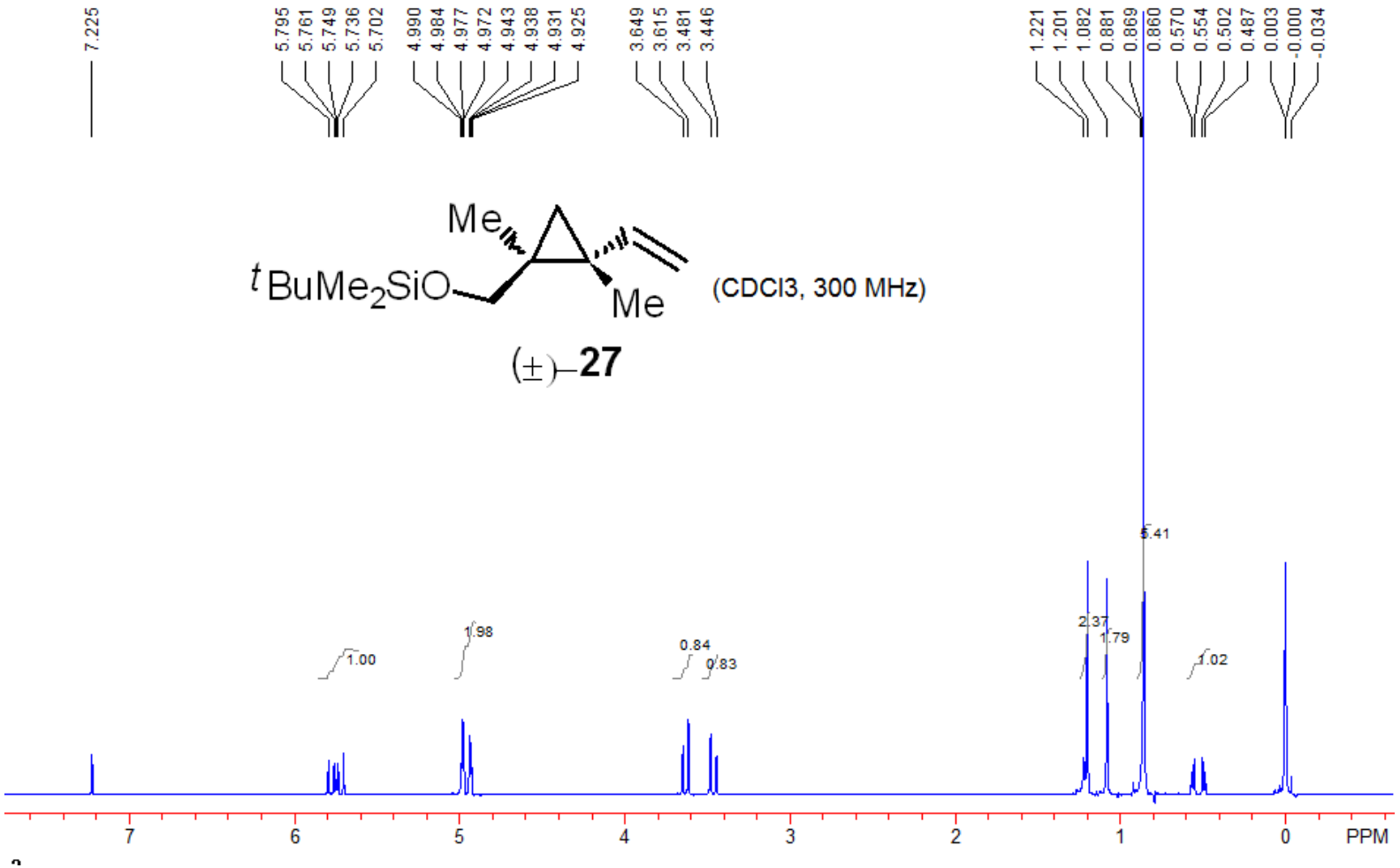

172.844
77.326
77.007
76.692
60.826
31.368
25.845
16.202
14.077
Me
Me
EtO2C
CO2Et
cis-24
cis-24 (CDCl3, 100 MHz)
150
100
50
0
PPM

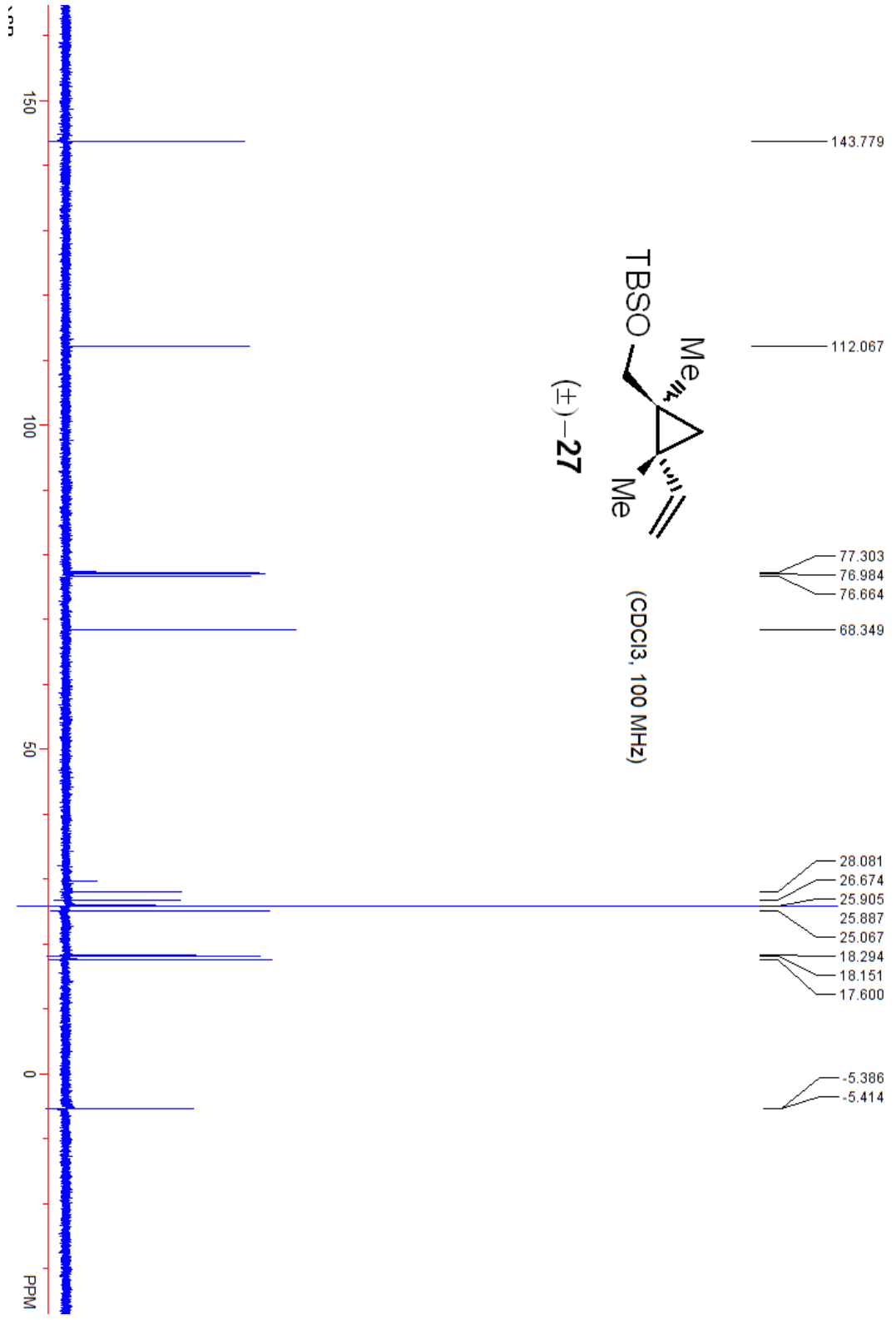

7.271
3.755
3.718
3.447
3.410
1.306
0.338
-0.000
Me
HO
OH
Me
25 (CDCl3, 300 MHz)
(±)–25
6.00
2.03
2.08
2.20
1.91
7
6
5
4
3
2
1
0
PPM

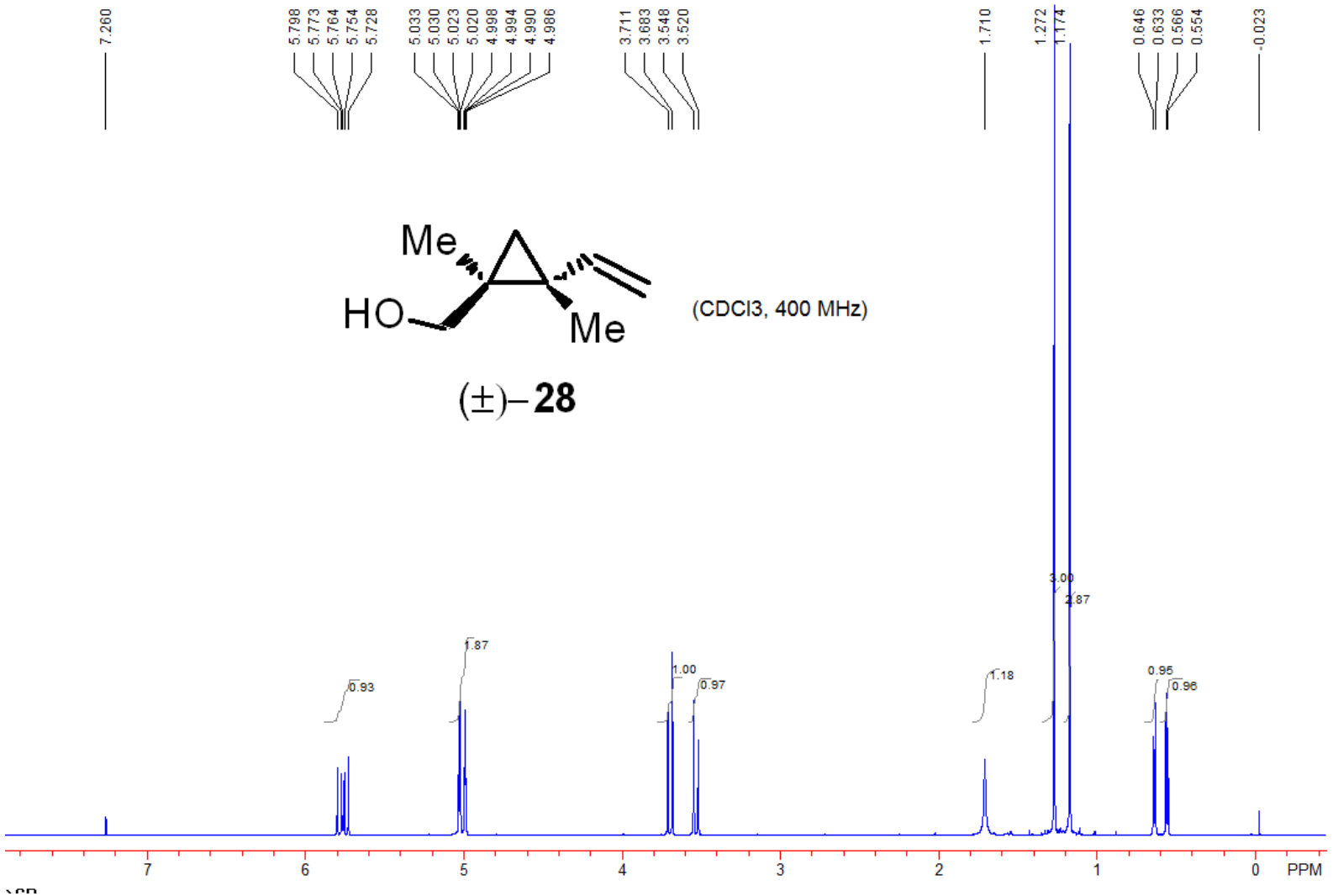

(±)-25
25 (CDCl3, 100 MHz)
HO
Me
Me
OH
77.331
77.011
76.697
68.474
26.405
23.012
17.382
100
80
60
40
20
0
PPM


7.226
3.624
3.588
3.447
3.410
3.391
3.356
1.530
1.204
1.177
0.924
0.880
0.793
0.307
0.006
-0.000
-0.040
Me
OH
TBSO
Me
(CDCl3, 300 MHz)
(±)−26
1.97
2.01
1.36
5.83
9.00
1.94
5.23
7
6
5
4
3
2
1
0
PPM

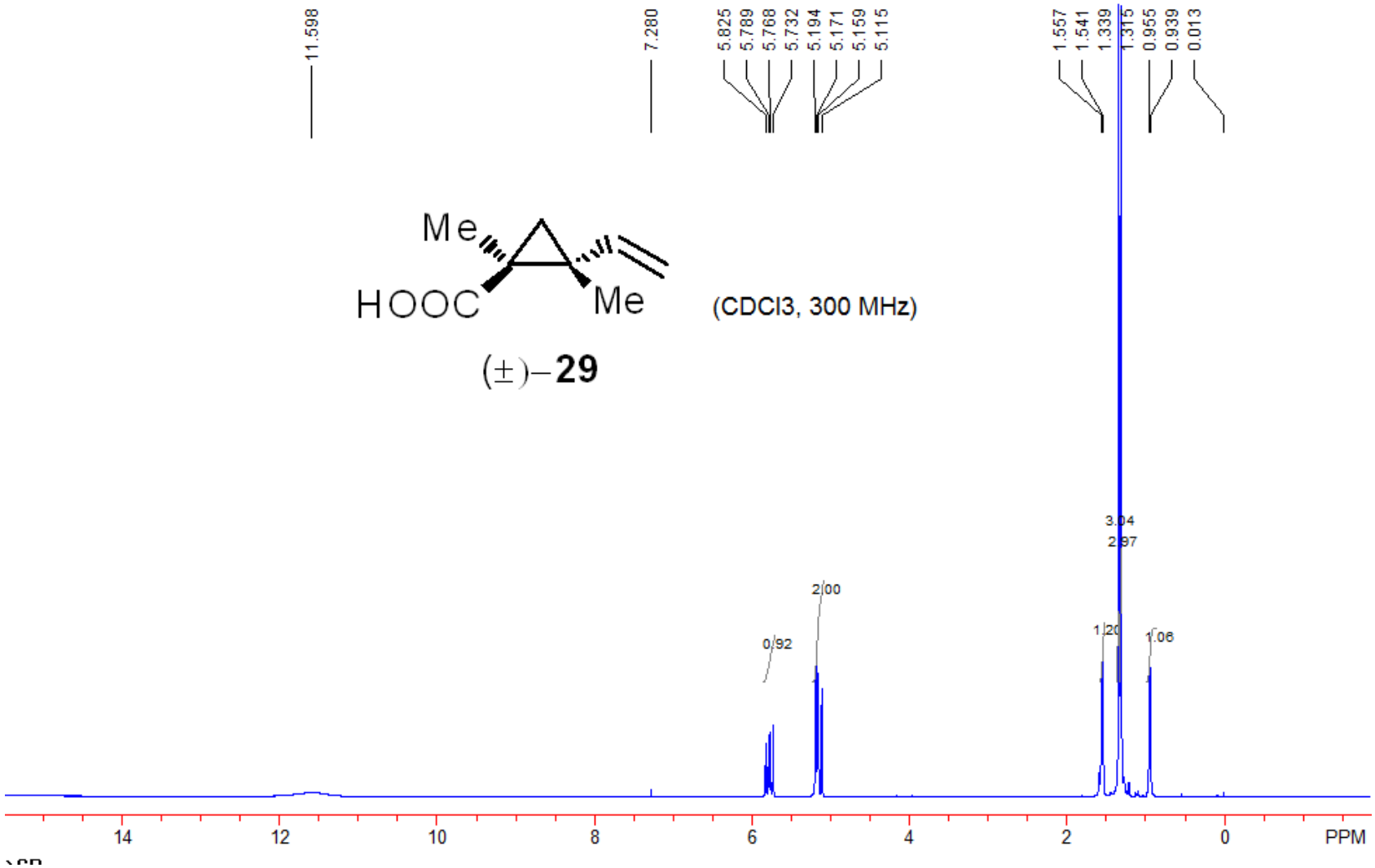

(±)−26
(CDCl3, 75 MHz)
77.366
76.936
76.514
68.845
68.482
26.162
26.096
25.814
22.650
18.205
17.160
17.027
-5.533
PPM

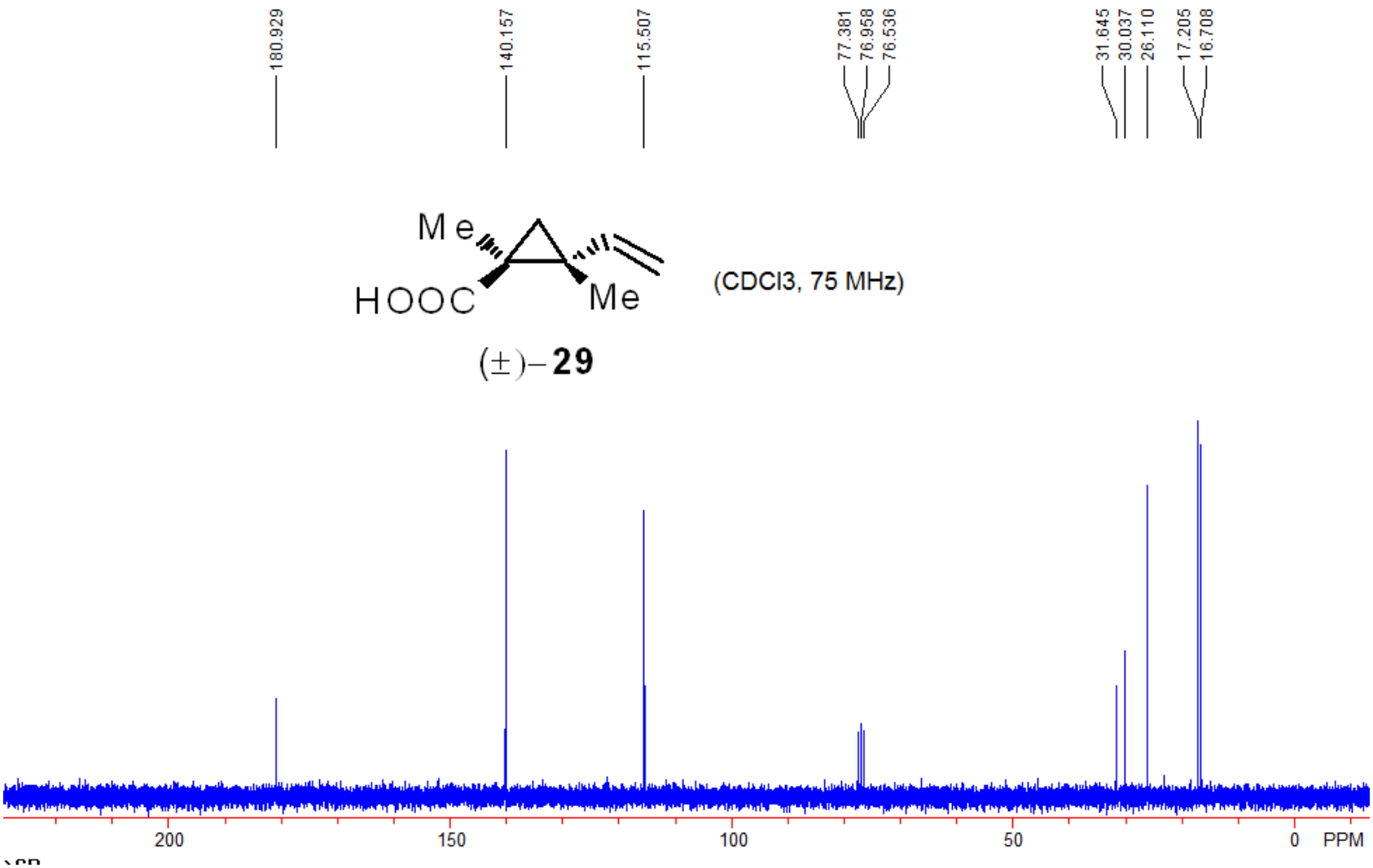

7.225
5.795
5.761
5.749
5.736
5.702
4.990
4.984
4.977
4.972
4.943
4.938
4.931
4.925
3.649
3.615
3.481
3.446
1.221
1.201
1.082
0.881
0.869
0.860
0.570
0.554
0.502
0.487
0.003
-0.000
-0.034
Me
tBuMe2SiO
Me
(CDCl3, 300 MHz)
(±)–27
1.00
1.98
0.84
0.83
6.41
2.37
1.79
1.02
7
6
5
4
3
2
1
0
PPM

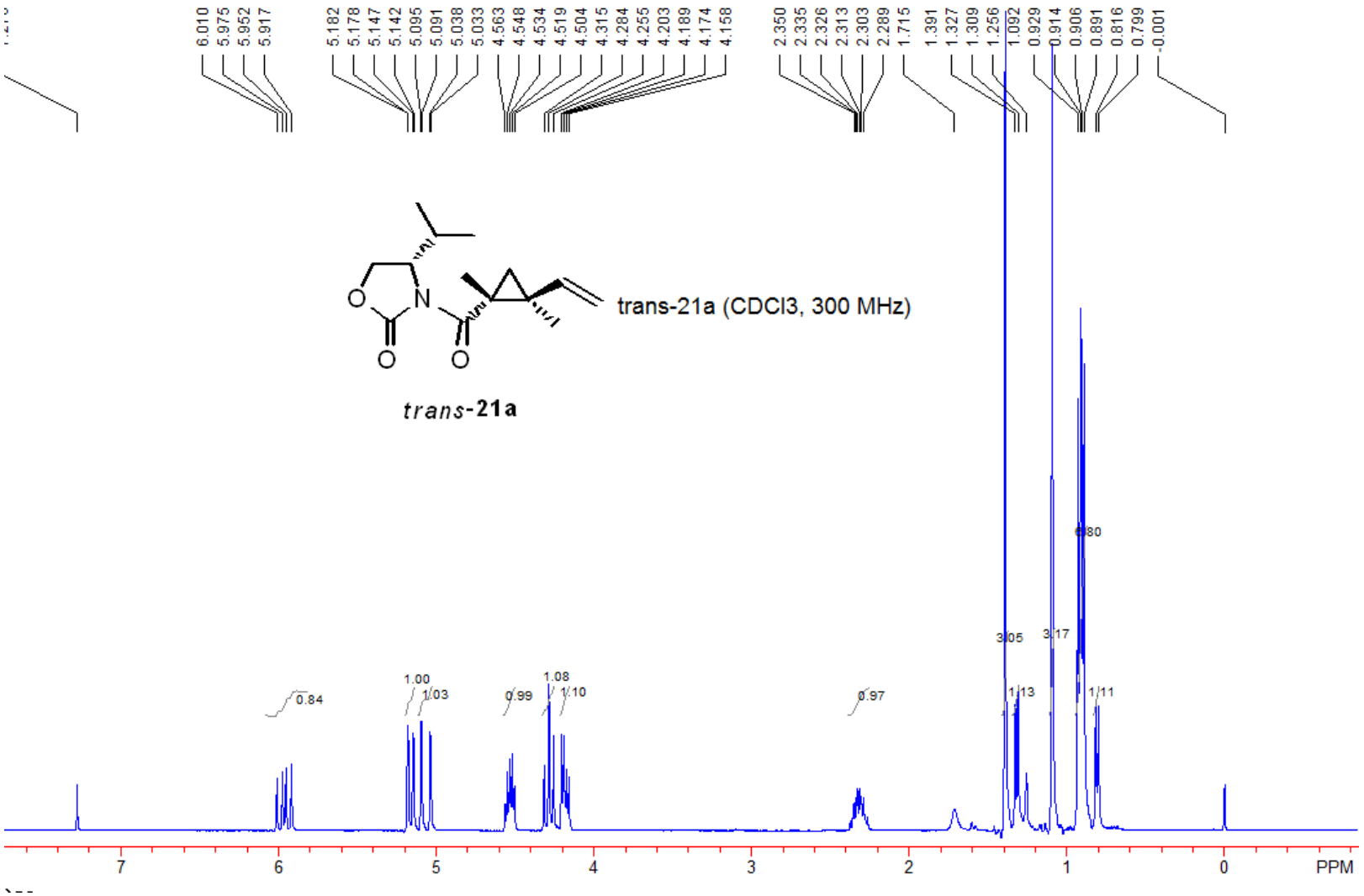

(±)–27
TBSO
Me
Me
(CDCl3, 100 MHz)
143.779
112.067
77.303
76.984
76.664
68.349
28.081
26.674
25.905
25.887
25.067
18.294
18.151
17.600
-5.386
-5.414
150
100
50
0
PPM

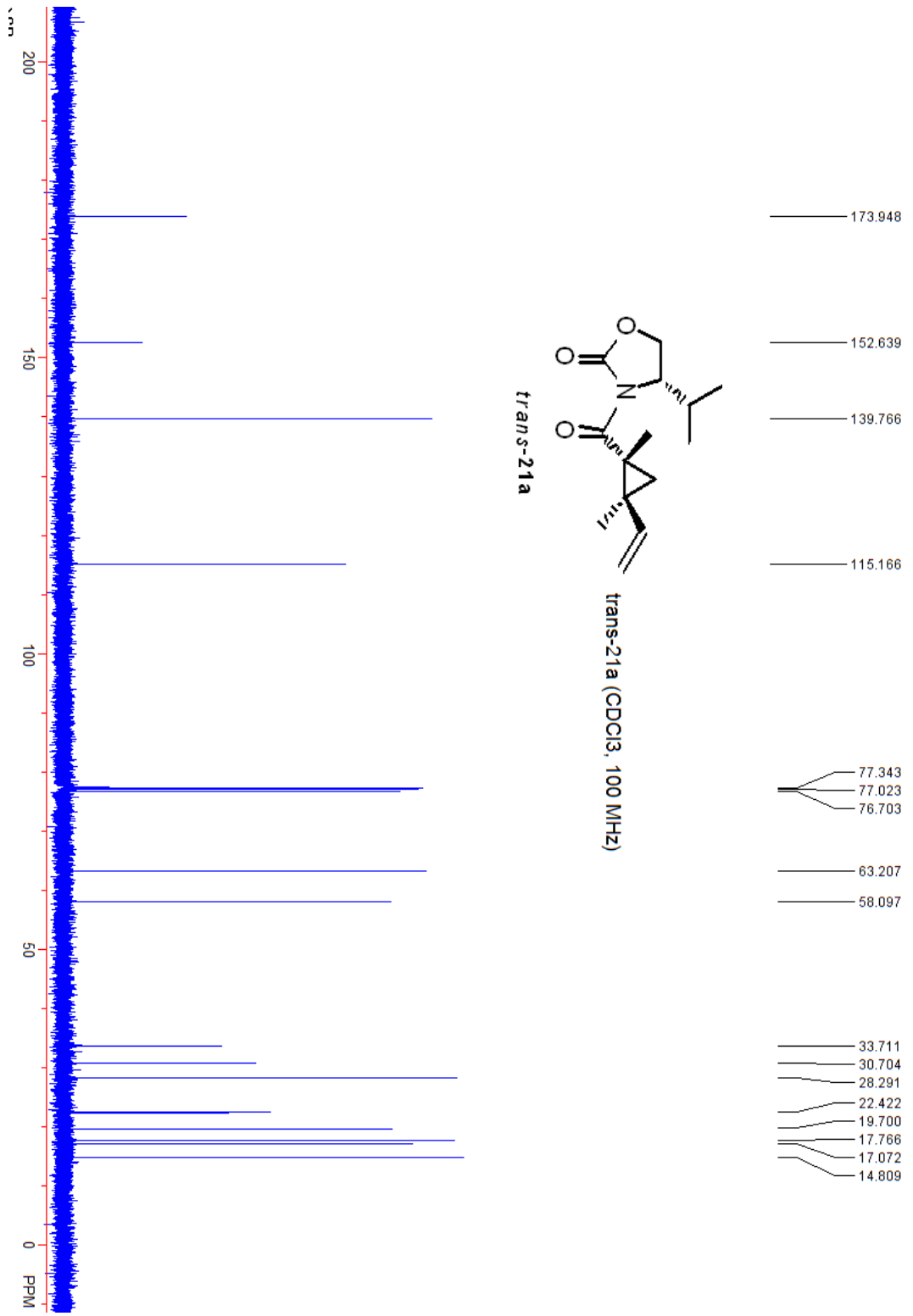

7.260
5.798
5.773
5.764
5.754
5.728
5.033
5.030
5.023
5.020
4.998
4.994
4.990
4.986
3.711
3.683
3.548
3.520
1.710
1.272
1.174
0.646
0.633
0.566
0.554
-0.023
Me
HO
Me
(CDCl3, 400 MHz)
(±)–28
0.93
1.87
1.00
0.97
1.18
3.00
2.87
0.95
0.96
7
6
5
4
3
2
1
0
PPM

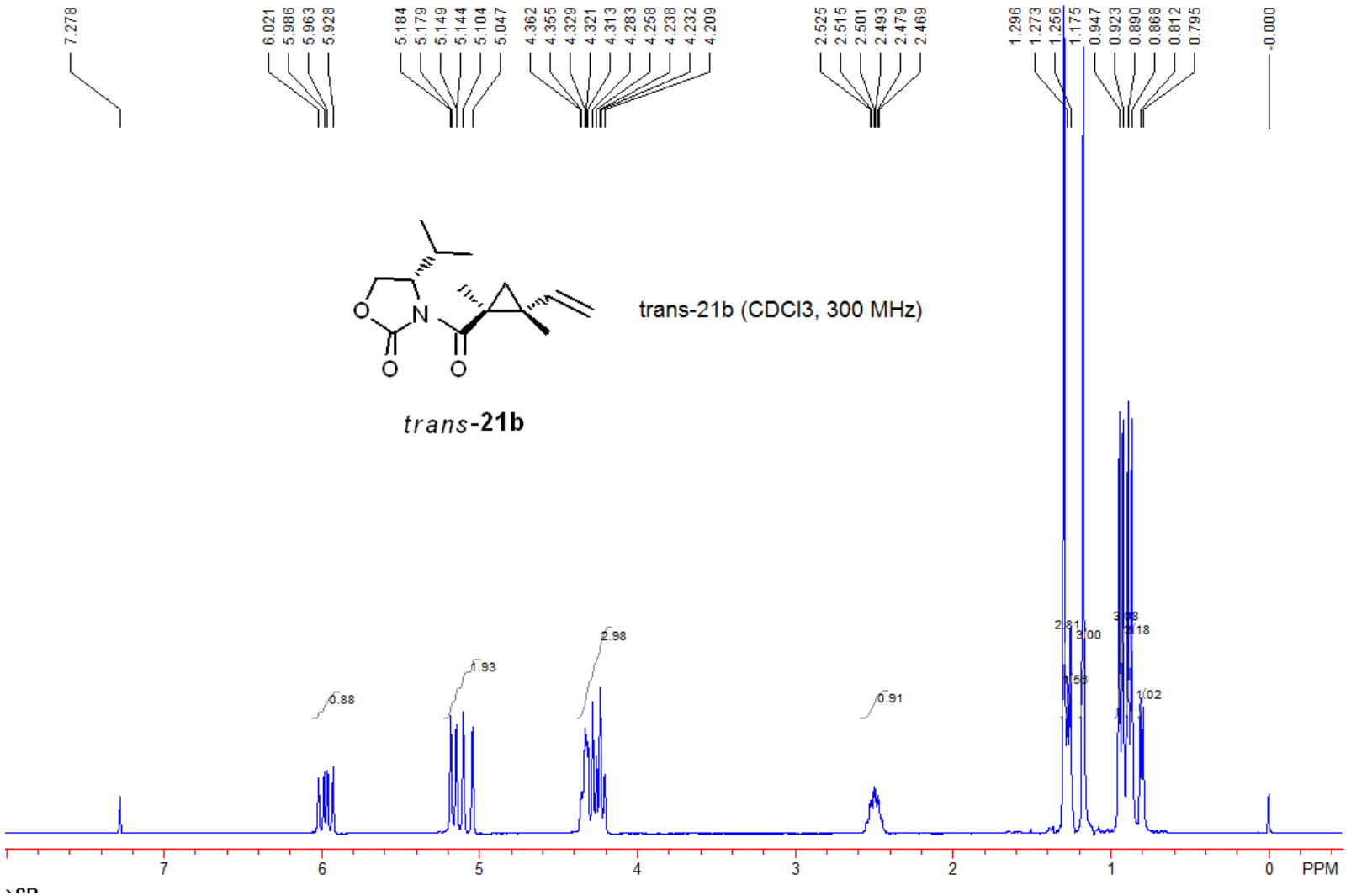
(±)–28
(CDCl3, 100 MHz)
HO
Me
Me
143.362
112.985
77.652
77.336
77.020
69.030
28.640
27.193
25.676
18.288
17.939
200
150
100
50
0
PPM

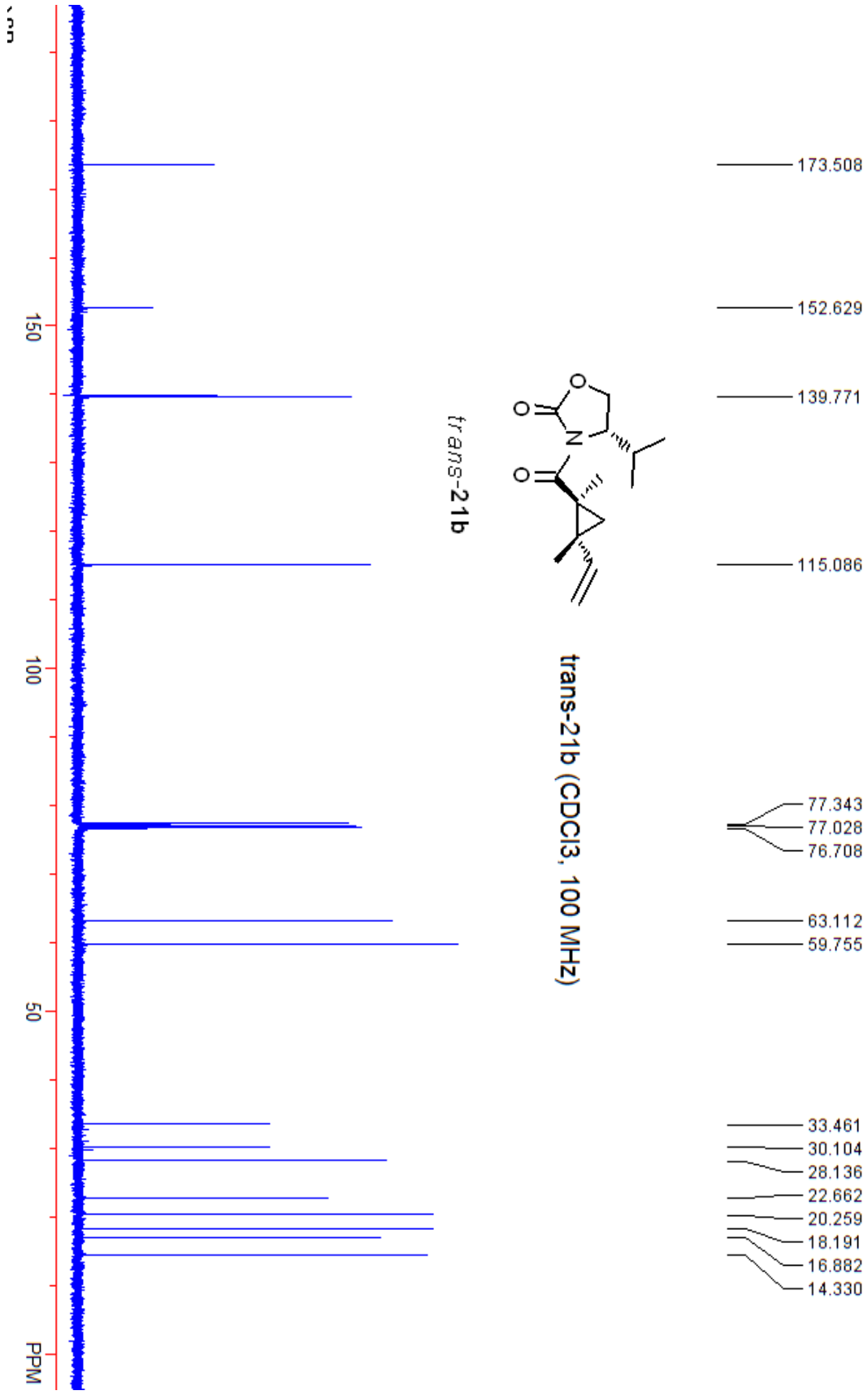

11.598
7.280
5.825
5.789
5.768
5.732
5.194
5.171
5.159
5.115
1.557
1.541
1.339
1.315
0.955
0.939
0.013
Me
HOOC
Me
(CDCl3, 300 MHz)
(±)–29
3.04
2.97
2.00
0.92
1.20
1.06
14
12
10
8
6
4
2
0
PPM

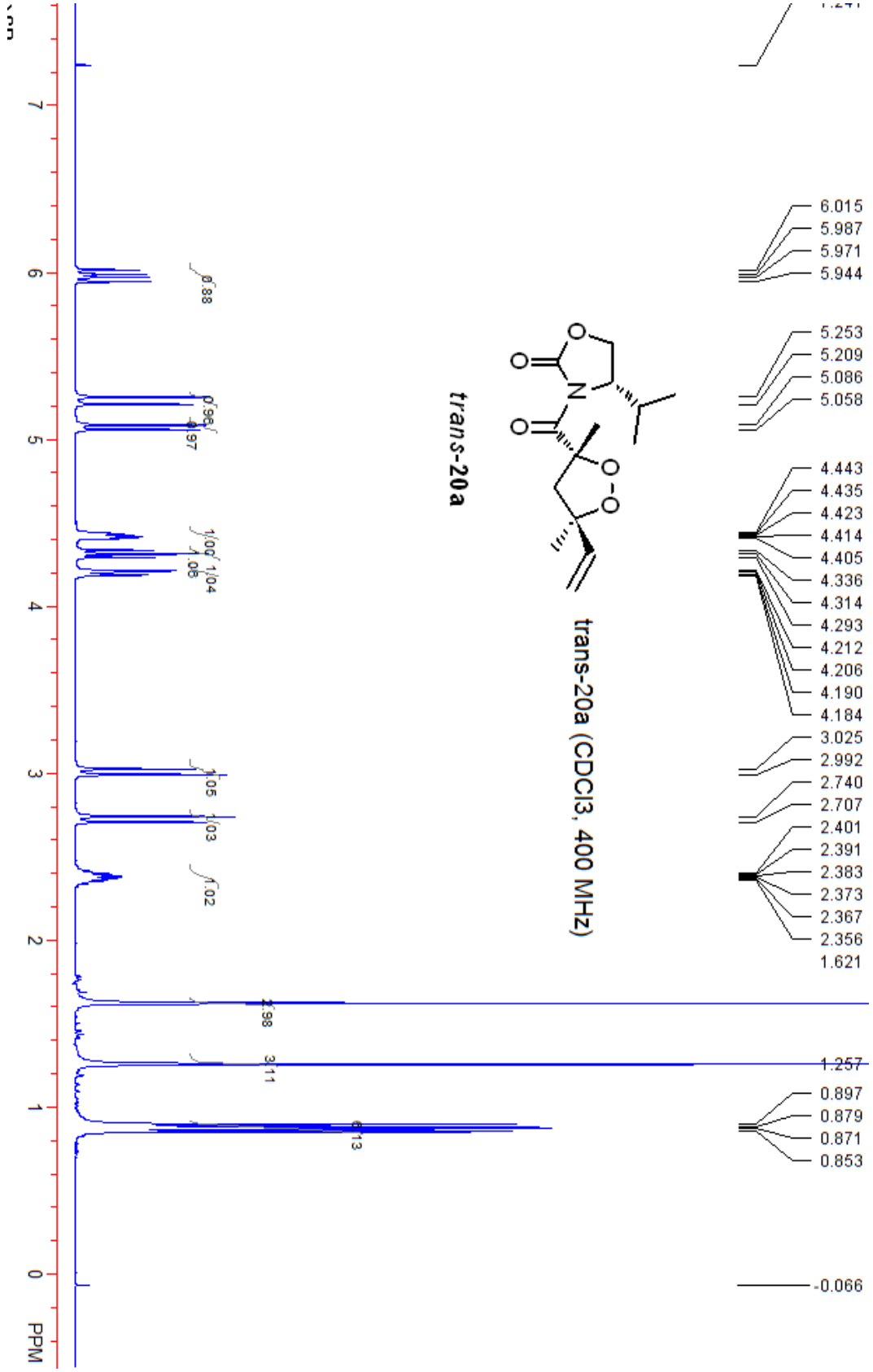

180.929
140.157
115.507
77.381
76.958
76.536
31.645
30.037
26.110
17.205
16.708
Me
HOOC
Me
(±)–29
(CDCl3, 75 MHz)
200
150
100
50
0
PPM

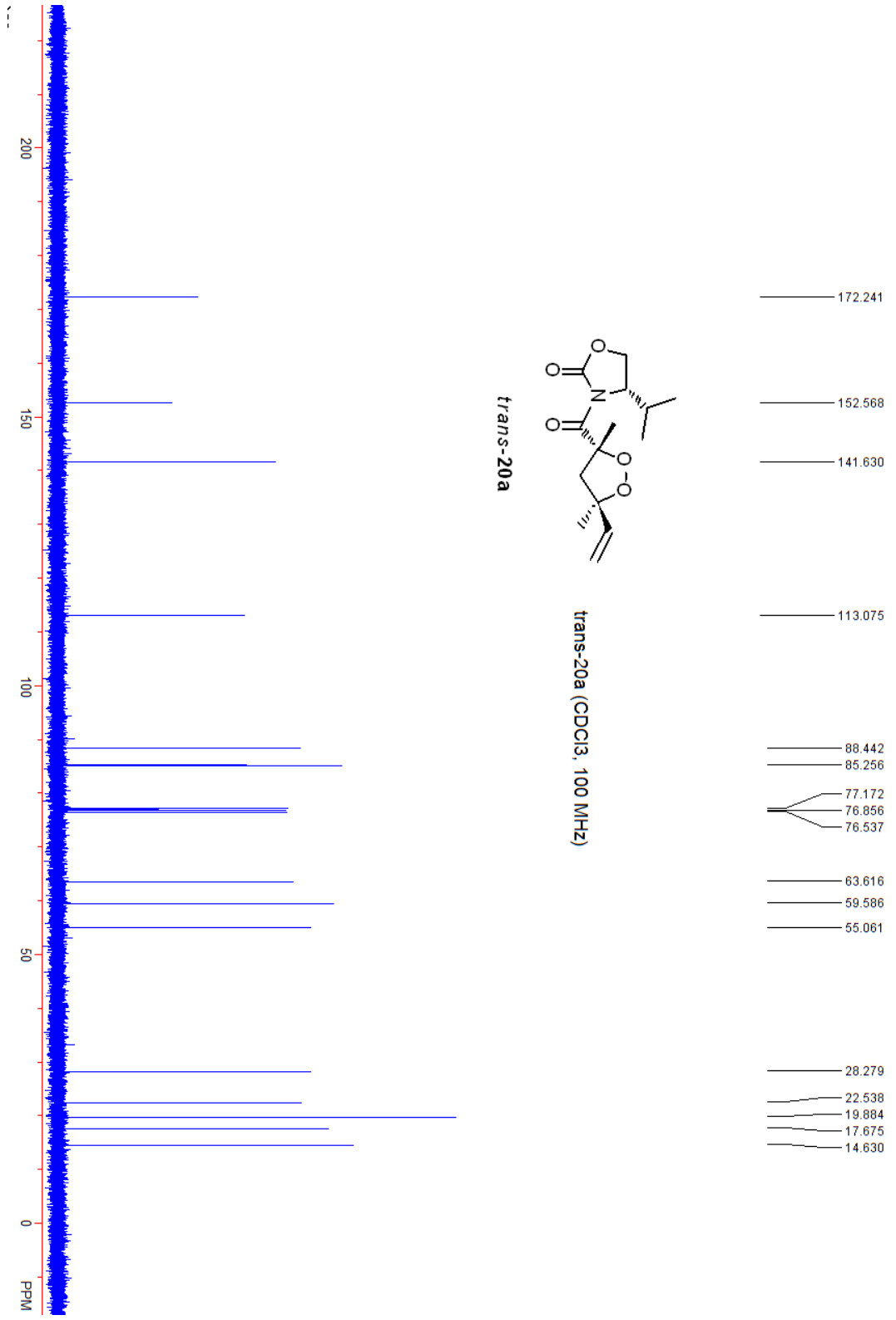

6.010
5.975
5.952
5.917
5.182
5.178
5.147
5.142
5.095
5.091
5.038
5.033
4.563
4.548
4.534
4.519
4.504
4.315
4.284
4.255
4.203
4.189
4.174
4.158
2.350
2.335
2.326
2.313
2.303
2.289
1.715
1.391
1.327
1.309
1.256
1.092
0.929
0.914
0.906
0.891
0.816
0.799
-0.001
trans-21a (CDCl3, 300 MHz)
trans-21a
0.84
1.00
1.03
0.99
1.08
1.10
0.97
3.05
1.13
3.17
6.80
1.11
7
6
5
4
3
2
1
0
PPM

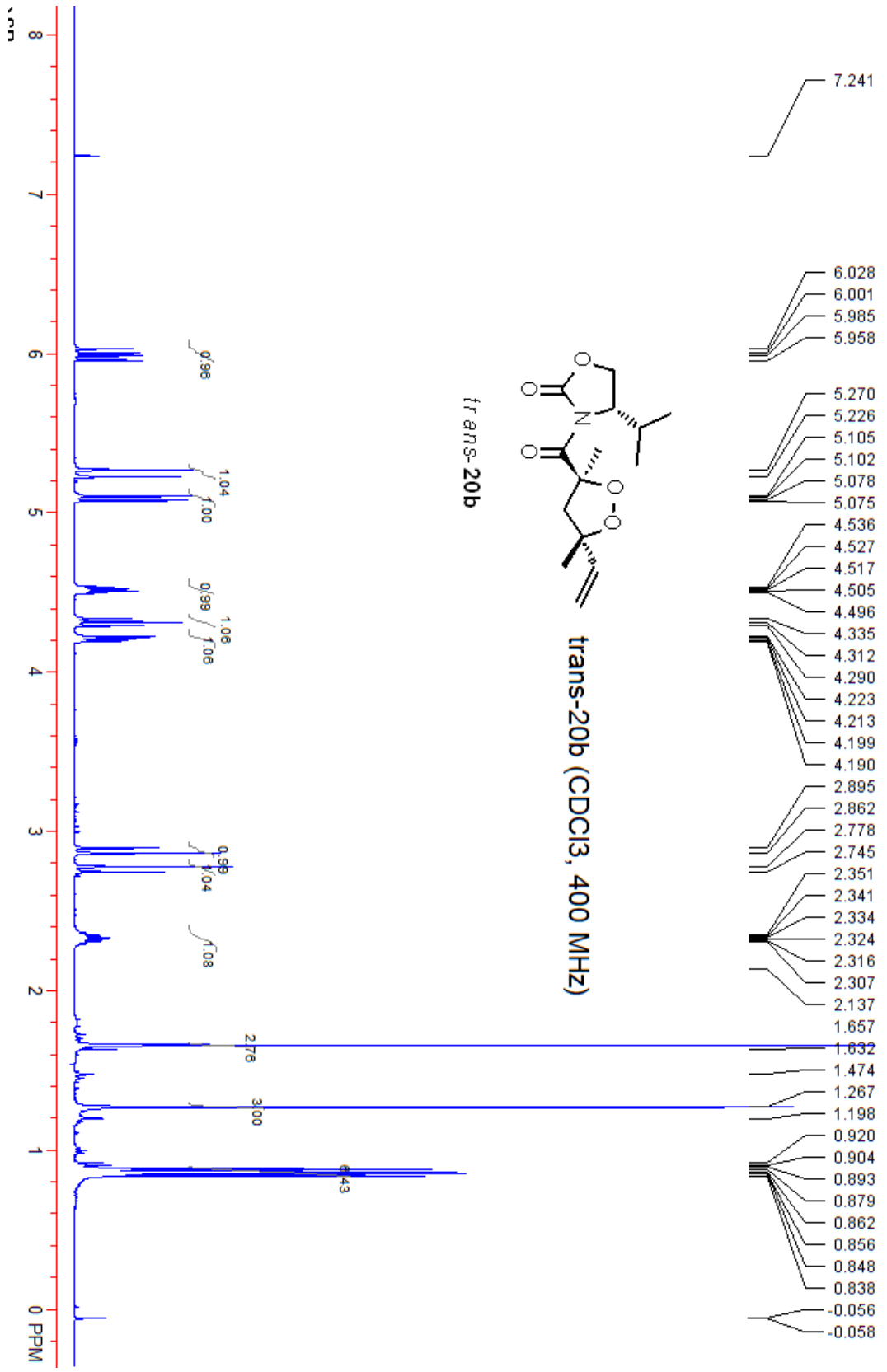

trans-21a
trans-21a (CDCl3, 100 MHz)
173.948
152.639
139.766
115.166
77.343
77.023
76.703
63.207
58.097
33.711
30.704
28.291
22.422
19.700
17.766
17.072
14.809
200
150
100
50
0
PPM

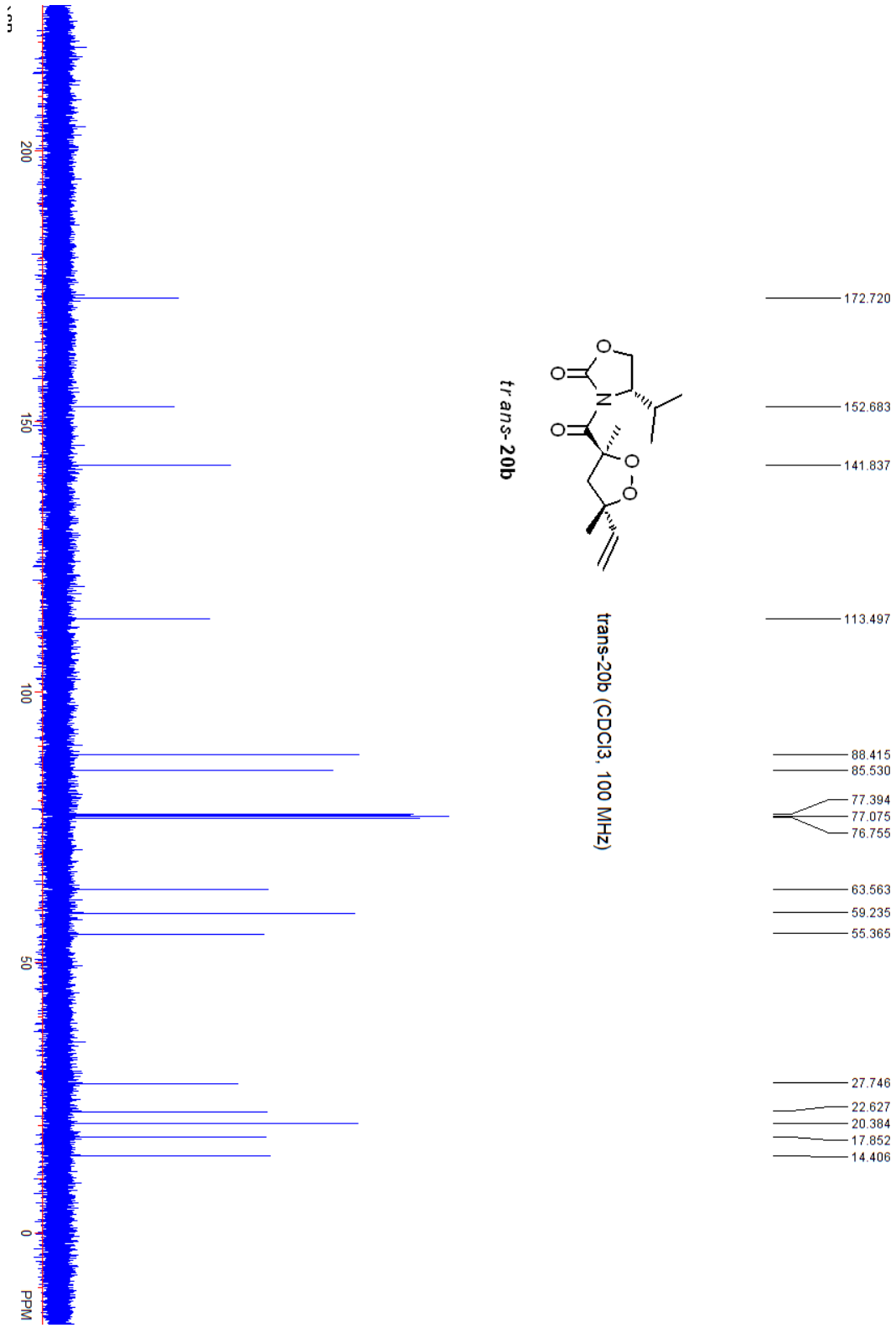

7.278
6.021
5.986
5.963
5.928
5.184
5.179
5.149
5.144
5.104
5.047
4.362
4.355
4.329
4.321
4.313
4.283
4.258
4.238
4.232
4.209
2.525
2.515
2.501
2.493
2.479
2.469
1.296
1.273
1.256
1.175
0.947
0.923
0.890
0.868
0.812
0.795
-0.000
trans-21b (CDCl3, 300 MHz)
trans-21b
0.88
1.93
2.98
0.91
2.81
3.00
1.02
PPM

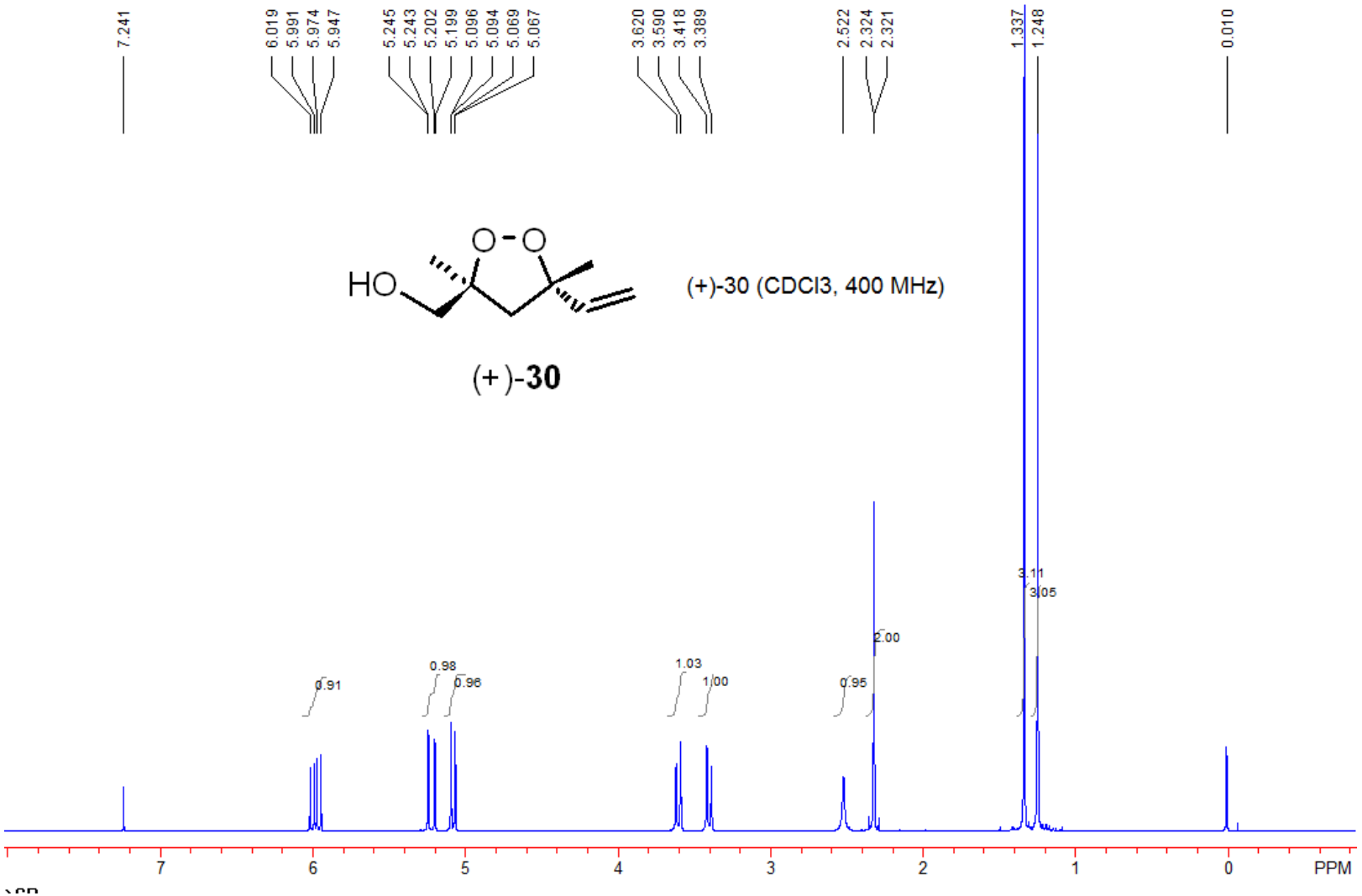

trans-21b
trans-21b (CDCl3, 100 MHz)
173.508
152.629
139.771
115.086
77.343
77.028
76.708
63.112
59.755
33.461
30.104
28.136
22.662
20.259
18.191
16.882
14.330
150
100
50
PPM

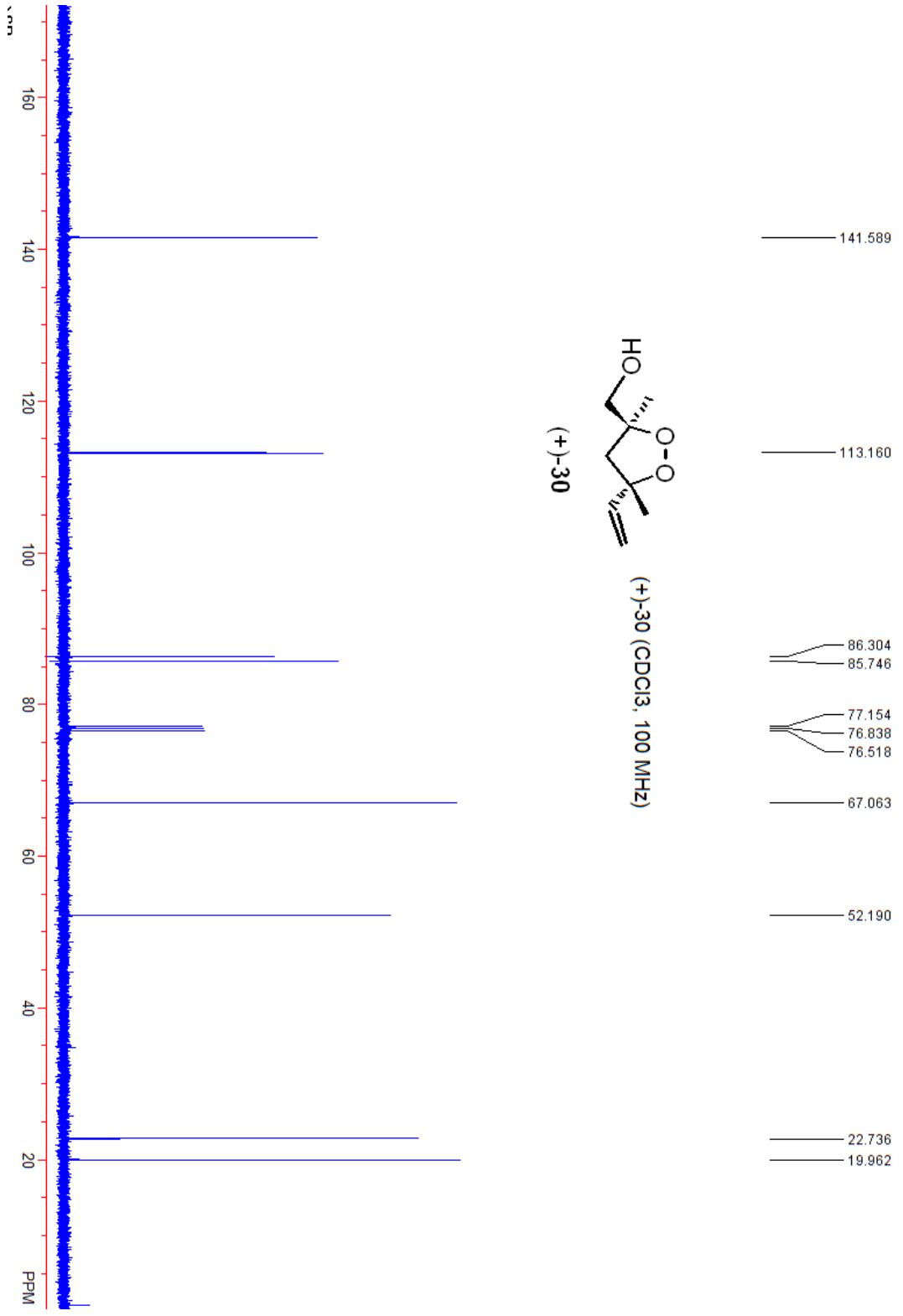

trans-20a (CDCl3, 400 MHz)
trans-20a
6.015
5.987
5.971
5.944
5.253
5.209
5.086
5.058
4.443
4.435
4.423
4.414
4.405
4.336
4.314
4.293
4.212
4.206
4.190
4.184
3.025
2.992
2.740
2.707
2.401
2.391
2.383
2.373
2.367
2.356
1.621
1.257
0.897
0.879
0.871
0.853
-0.066
PPM

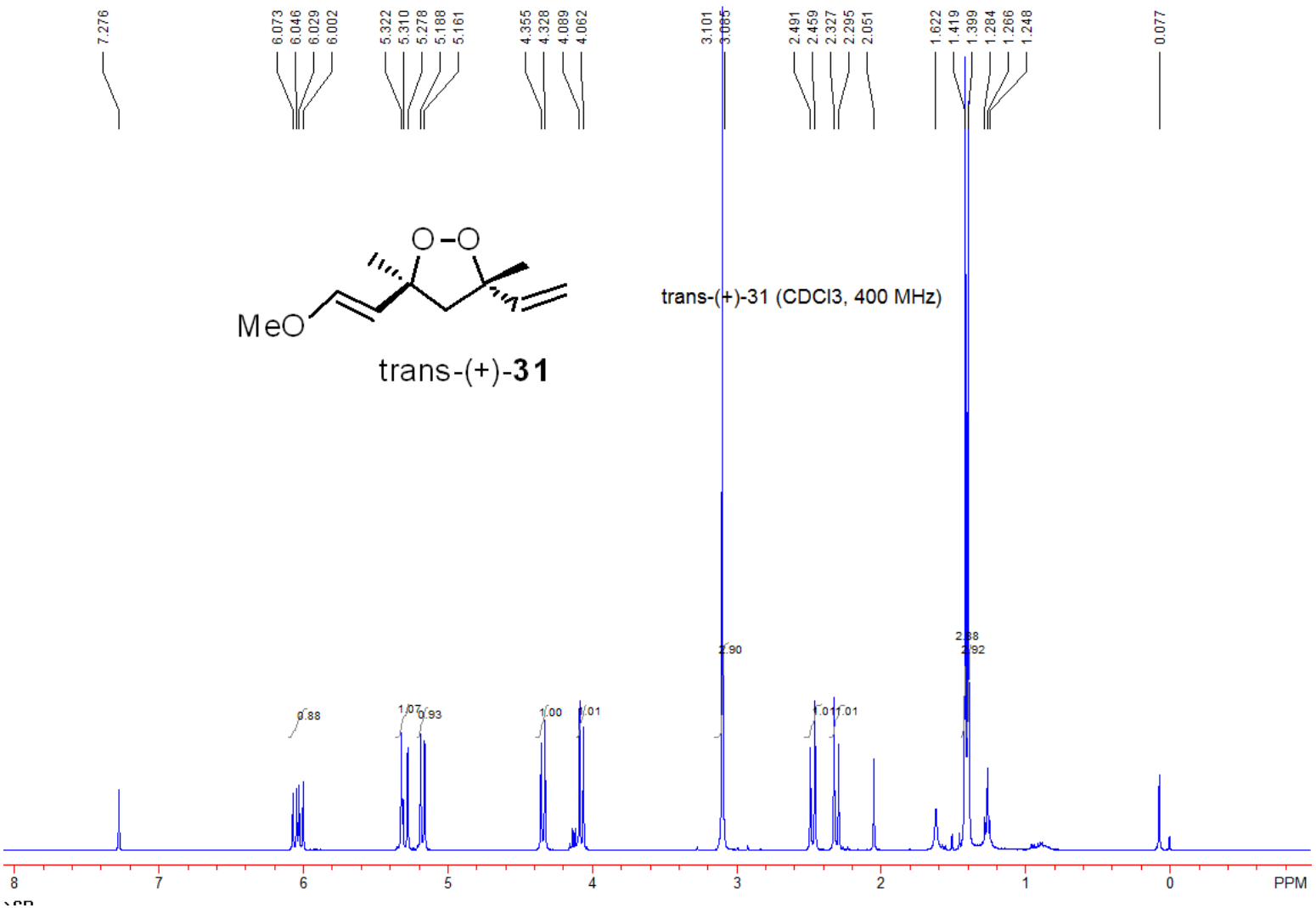

trans-20a
trans-20a (CDCl3, 100 MHz)
172.241
152.568
141.630
113.075
88.442
85.256
77.172
76.856
76.537
63.616
59.586
55.061
28.279
22.538
19.884
17.675
14.630
200
150
100
50
0
PPM

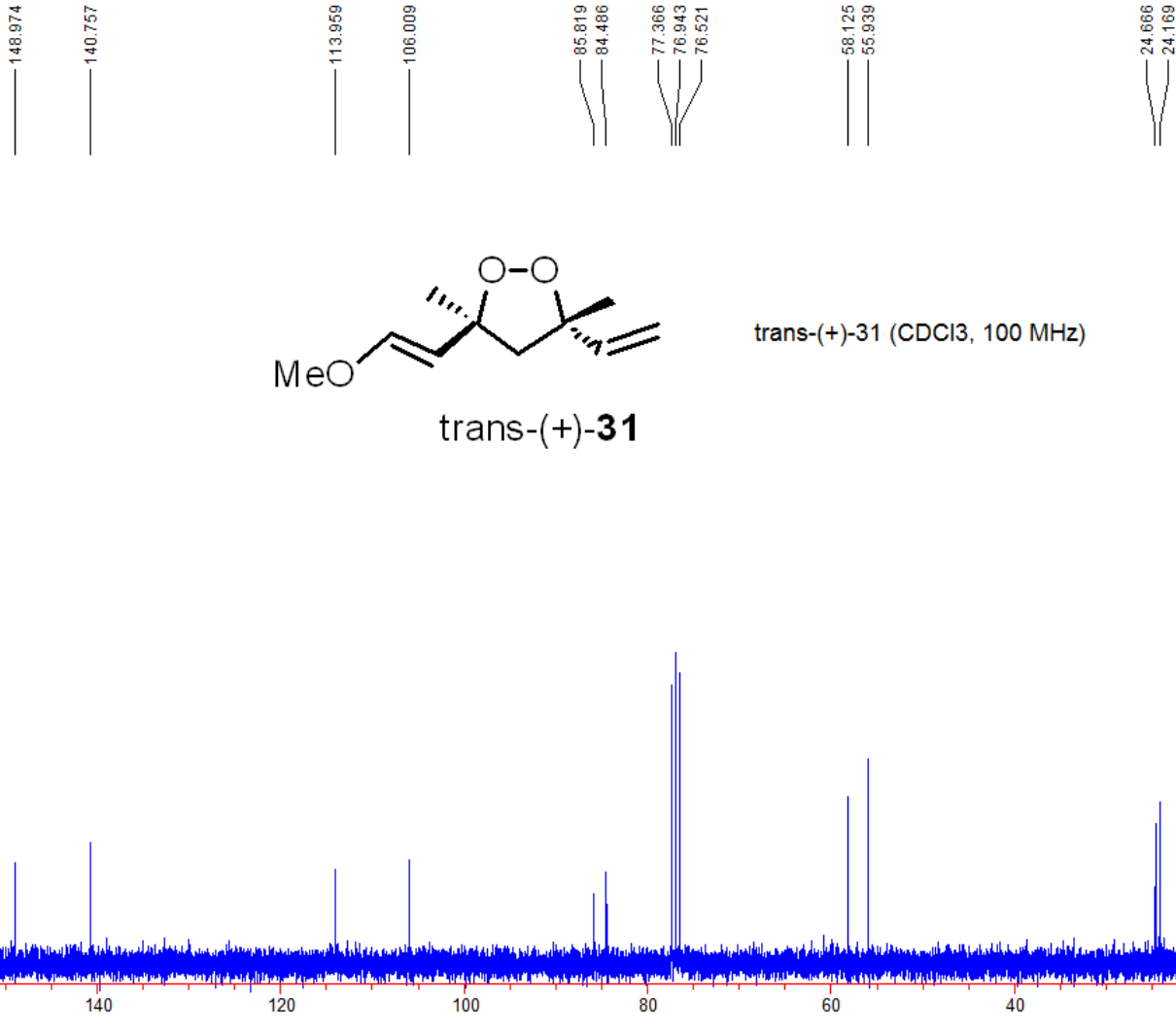

trans-20b (CDCl3, 400 MHz)
trans-20b
7.241
6.028
6.001
5.985
5.958
5.270
5.226
5.105
5.102
5.078
5.075
4.536
4.527
4.517
4.505
4.496
4.335
4.312
4.290
4.223
4.213
4.199
4.190
2.895
2.862
2.778
2.745
2.351
2.341
2.334
2.324
2.316
2.307
2.137
1.657
1.632
1.474
1.267
1.198
0.920
0.904
0.893
0.879
0.862
0.856
0.848
0.838
-0.056
-0.058
0.96
1.04
1.00
0.99
1.06
1.06
0.99
1.04
1.08
2.76
3.00
6.43
0 PPM

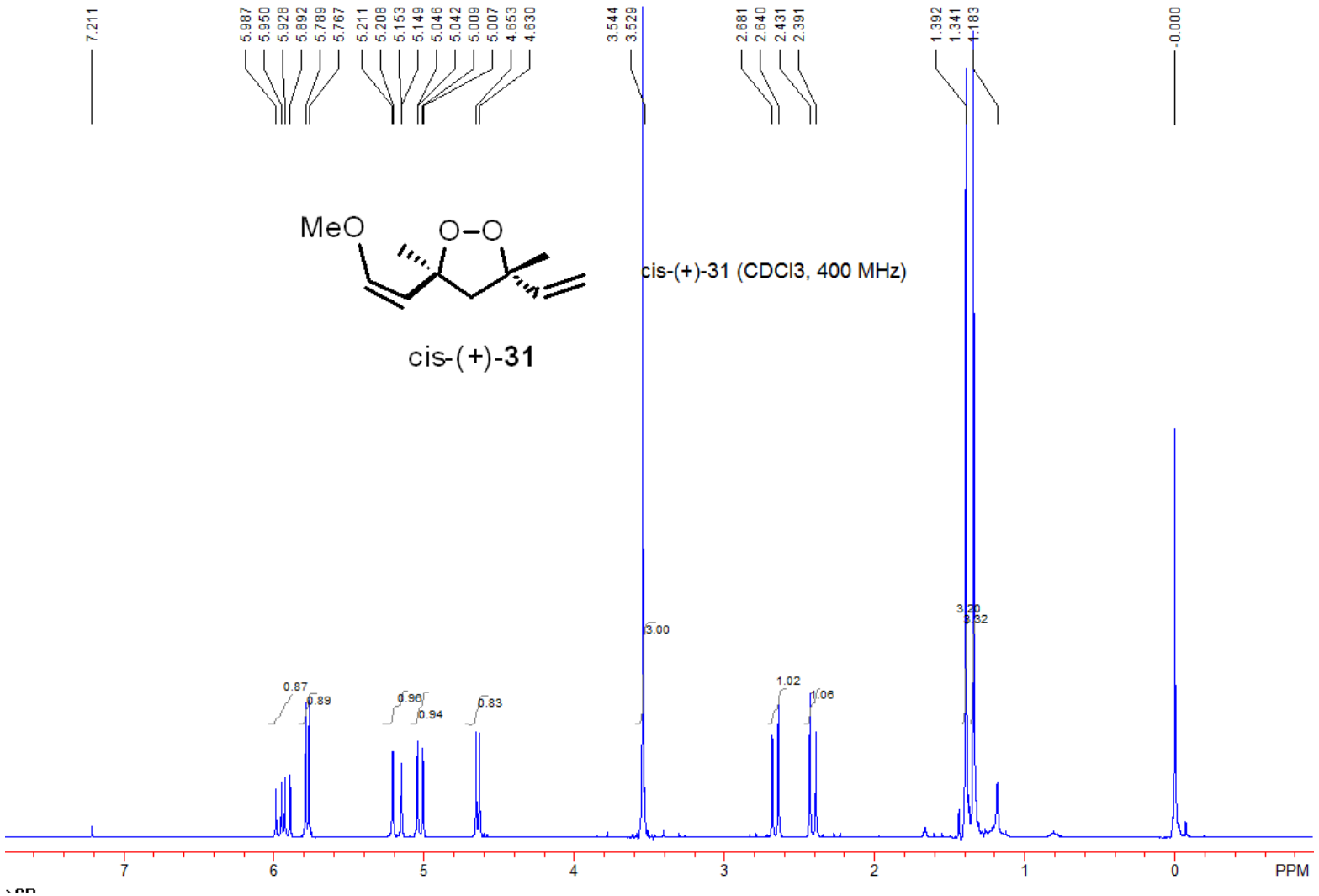

trans-20b
trans-20b (CDCl3, 100 MHz)
172.720
152.683
141.837
113.497
88.415
85.530
77.394
77.075
76.755
63.563
59.235
55.365
27.746
22.627
20.384
17.852
14.406
200
150
100
50
0
PPM

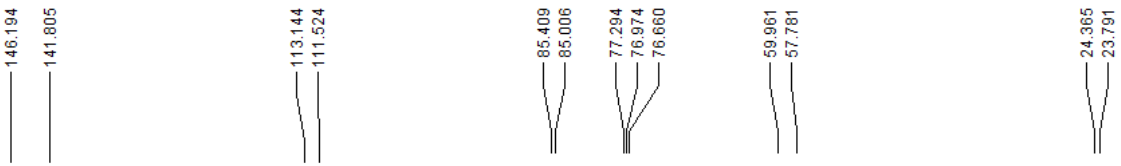

7.241
6.019
5.991
5.974
5.947
5.245
5.243
5.202
5.199
5.096
5.094
5.069
5.067
3.620
3.590
3.418
3.389
2.522
2.324
2.321
1.337
1.248
0.010
HO
O
O
(+)-30 (CDCl3, 400 MHz)
(+)-30
0.91
0.98
0.96
1.03
1.00
0.95
2.00
3.11
3.05
7
6
5
4
3
2
1
0
PPM

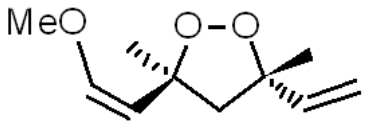

(+)-30
(+)-30 (CDCl3, 100 MHz)
141.589
113.160
86.304
85.746
77.154
76.838
76.518
67.063
52.190
22.736
19.962
160
140
120
100
80
60
40
20
PPM


7.276
6.073
6.046
6.029
6.002
5.322
5.310
5.278
5.188
5.161
4.355
4.328
4.089
4.062
3.101
3.085
2.491
2.459
2.327
2.295
2.051
1.622
1.419
1.399
1.284
1.266
1.248
0.077
O–O
MeO
trans-(+)-31 (CDCl3, 400 MHz)
trans-(+)-31
0.88
1.07
0.93
1.00
1.01
2.90
1.01
1.01
2.88
2.92
8
7
6
5
4
3
2
1
0
PPM


148.974
140.757
113.959
106.009
85.819
84.486
77.366
76.943
76.521
58.125
55.939
24.666
24.169
MeO
trans-(+)-31
trans-(+)-31 (CDCl3, 100 MHz)
160
140
120
100
80
60
40
20
PPM


7.211
5.987
5.950
5.928
5.892
5.789
5.767
5.211
5.208
5.153
5.149
5.046
5.042
5.009
5.007
4.653
4.630
3.544
3.529
2.681
2.640
2.431
2.391
1.392
1.341
1.183
0.000
MeO
O–O
cis-(+)-31 (CDCl3, 400 MHz)
cis-(+)-31
0.87
0.89
0.96
0.94
0.83
3.00
1.02
1.06
3.20
3.32
7
6
5
4
3
2
1
0
PPM

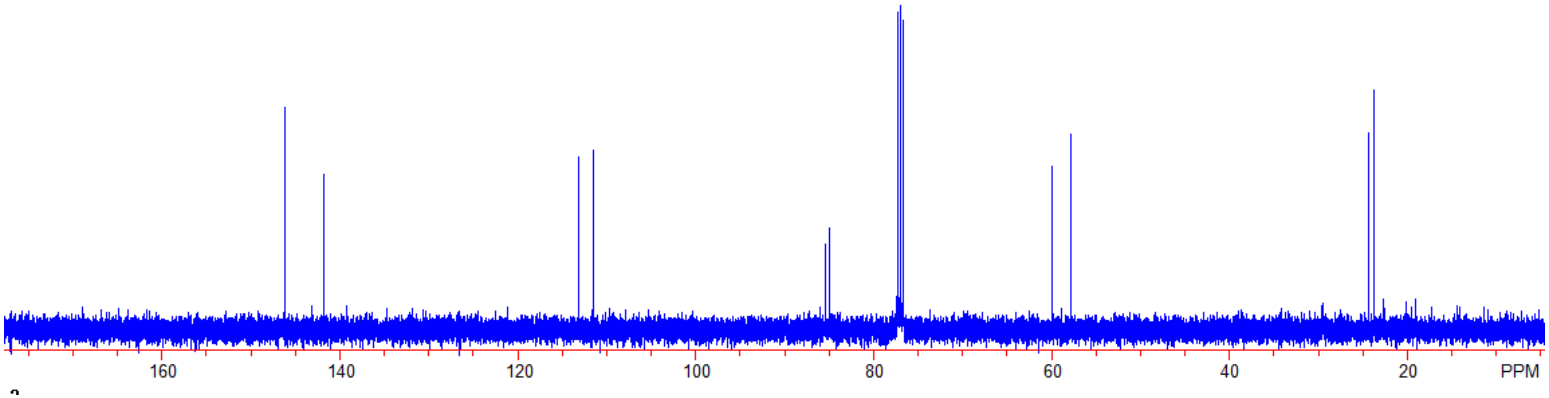


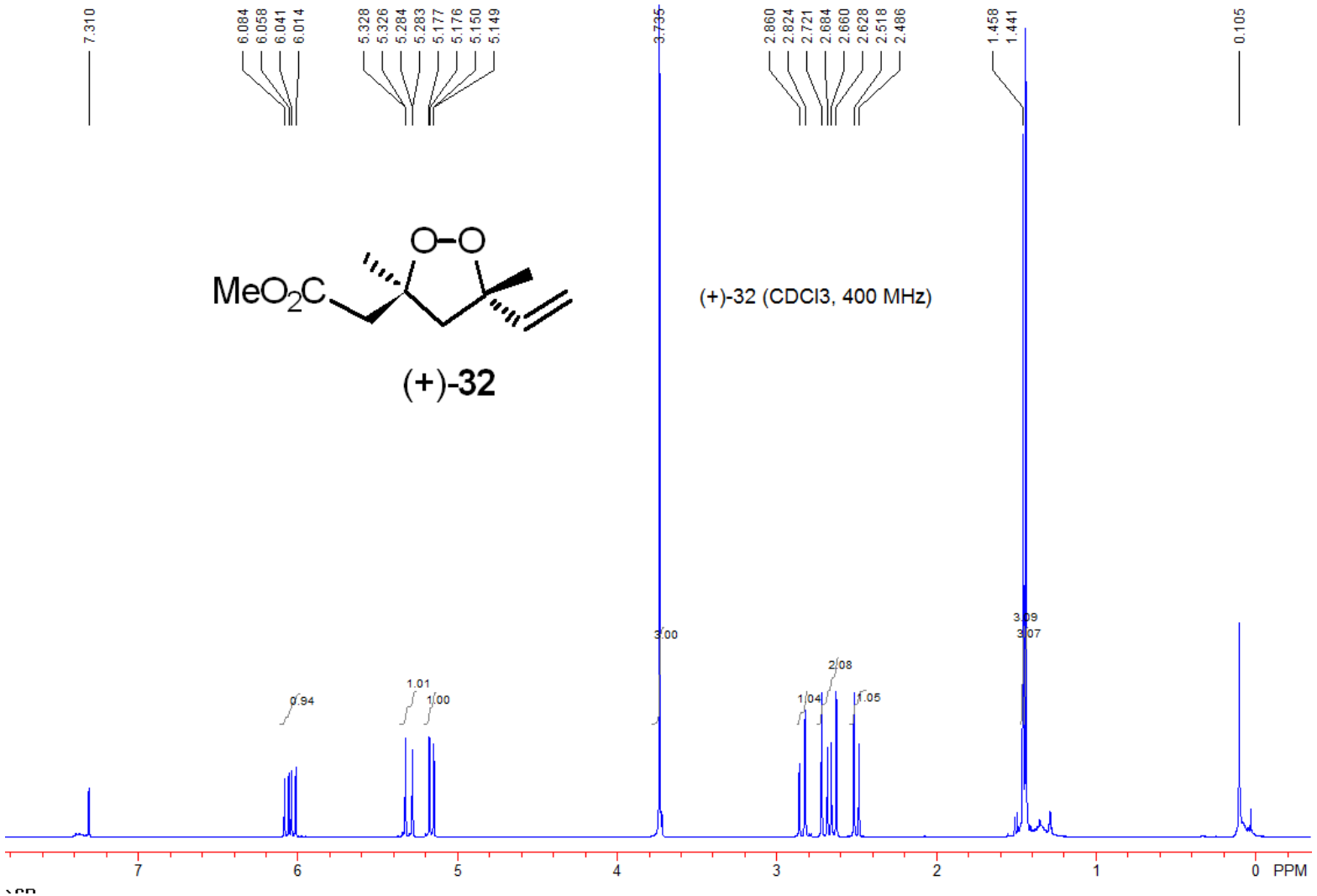


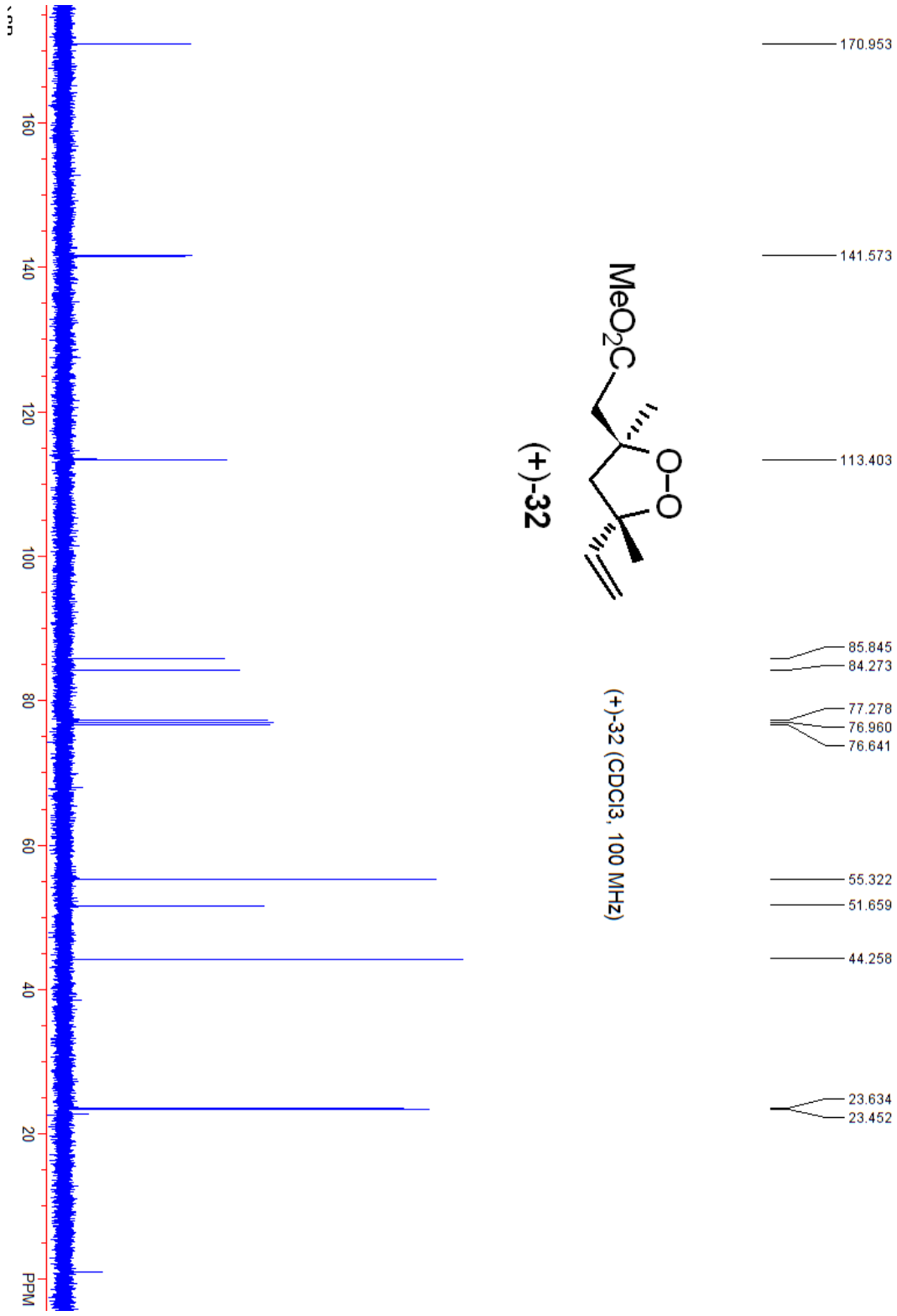
cis-(+)-31 (CDCl3, 100 MHz)

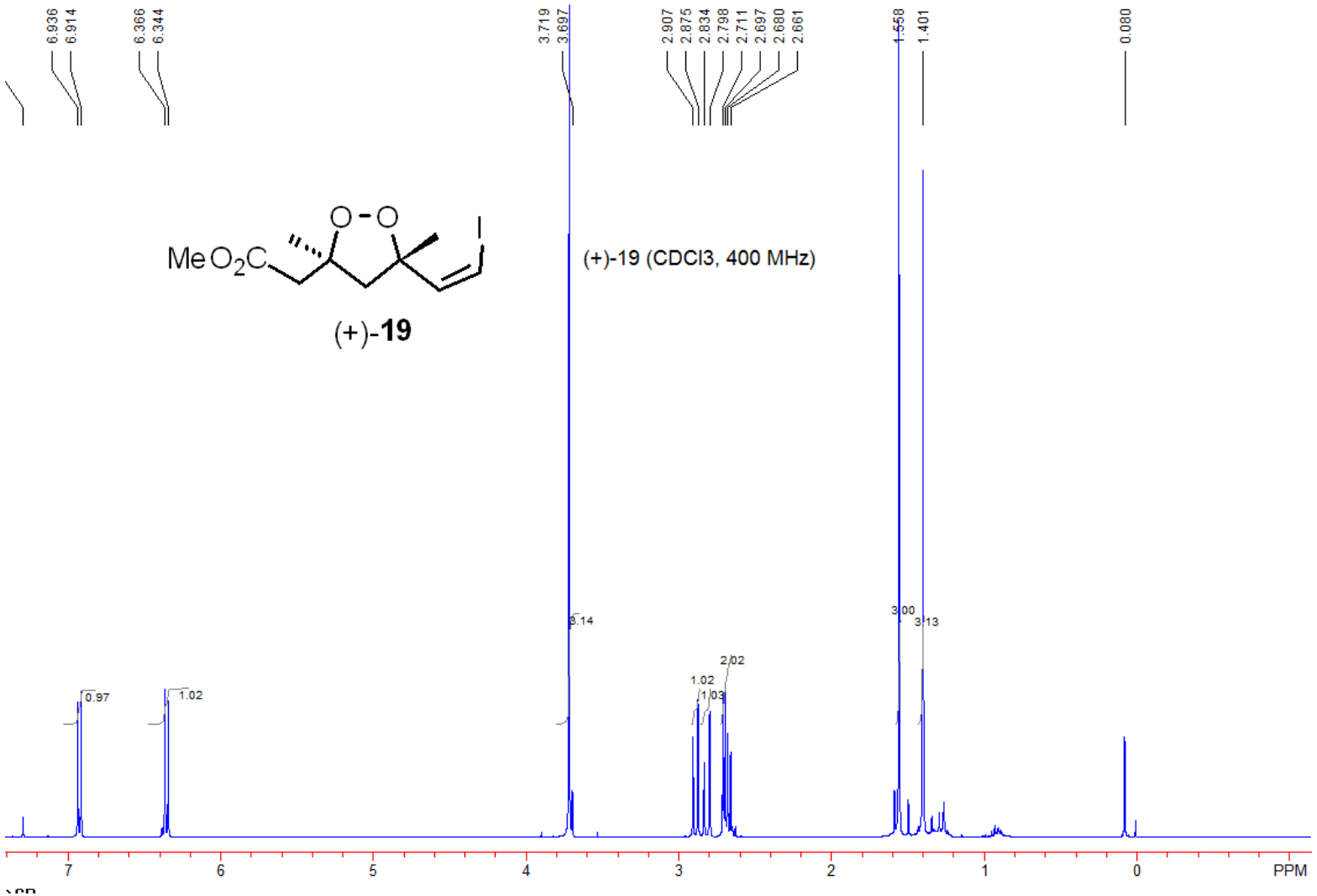
;blank line

cis-(+)-**31**

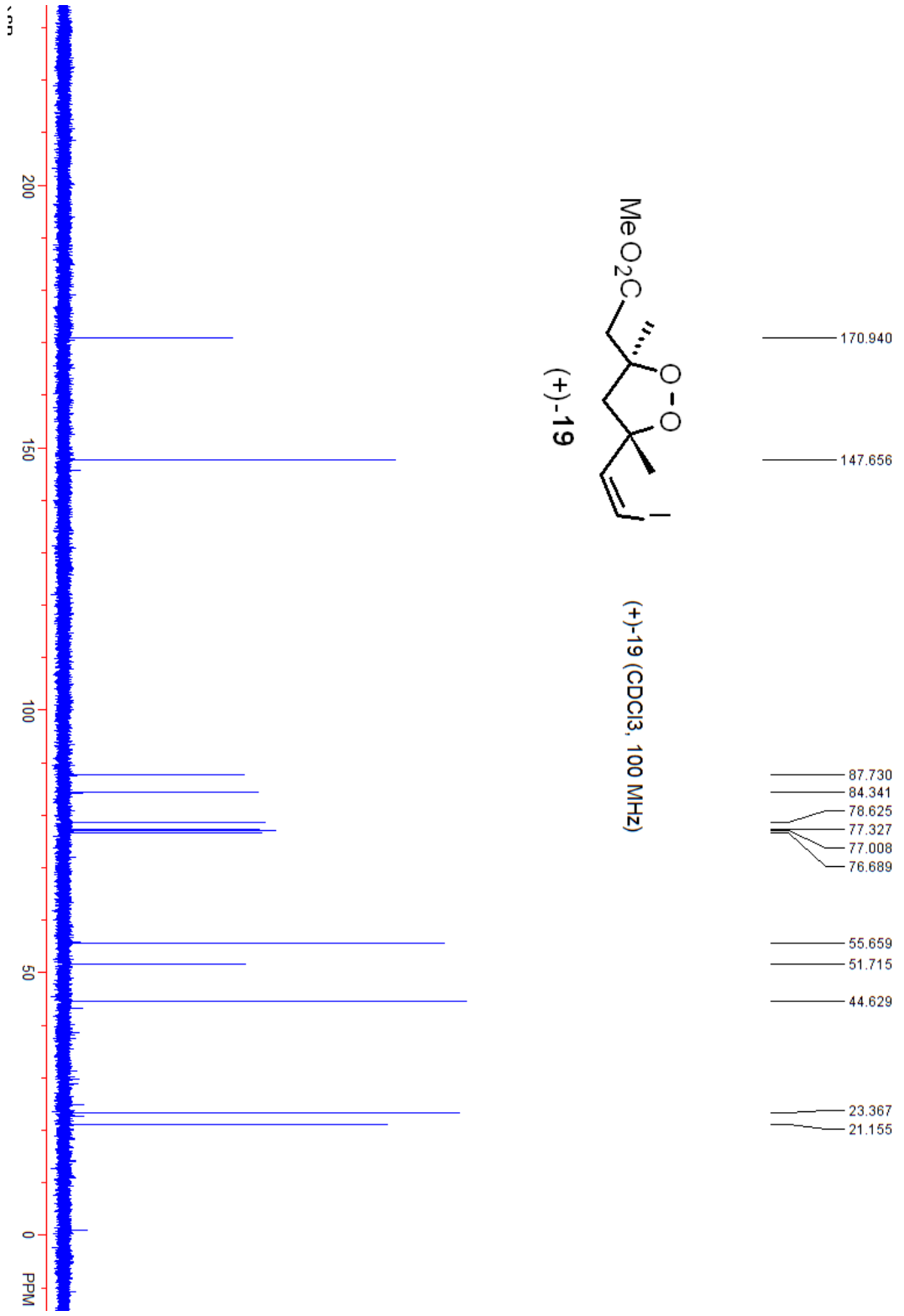


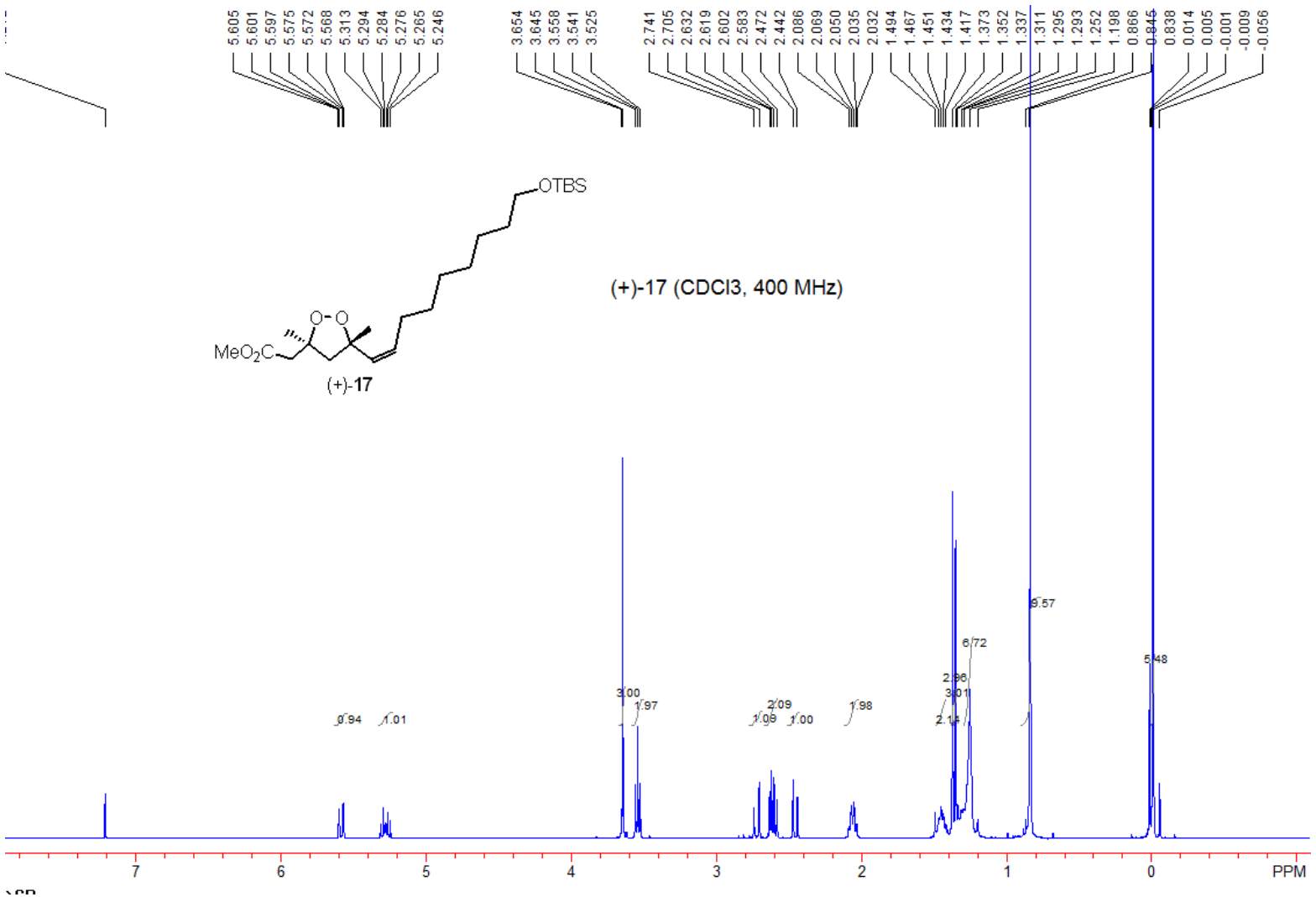

7.310
6.084
6.058
6.041
6.014
5.328
5.326
5.284
5.283
5.177
5.176
5.150
5.149
3.735
2.860
2.824
2.721
2.684
2.660
2.628
2.518
2.486
1.458
1.441
0.105
MeO2C
O–O
(+)-32
(+)-32 (CDCl3, 400 MHz)
0.94
1.01
1.00
3.00
1.04
2.08
1.05
3.09
3.07
7
6
5
4
3
2
1
0
PPM

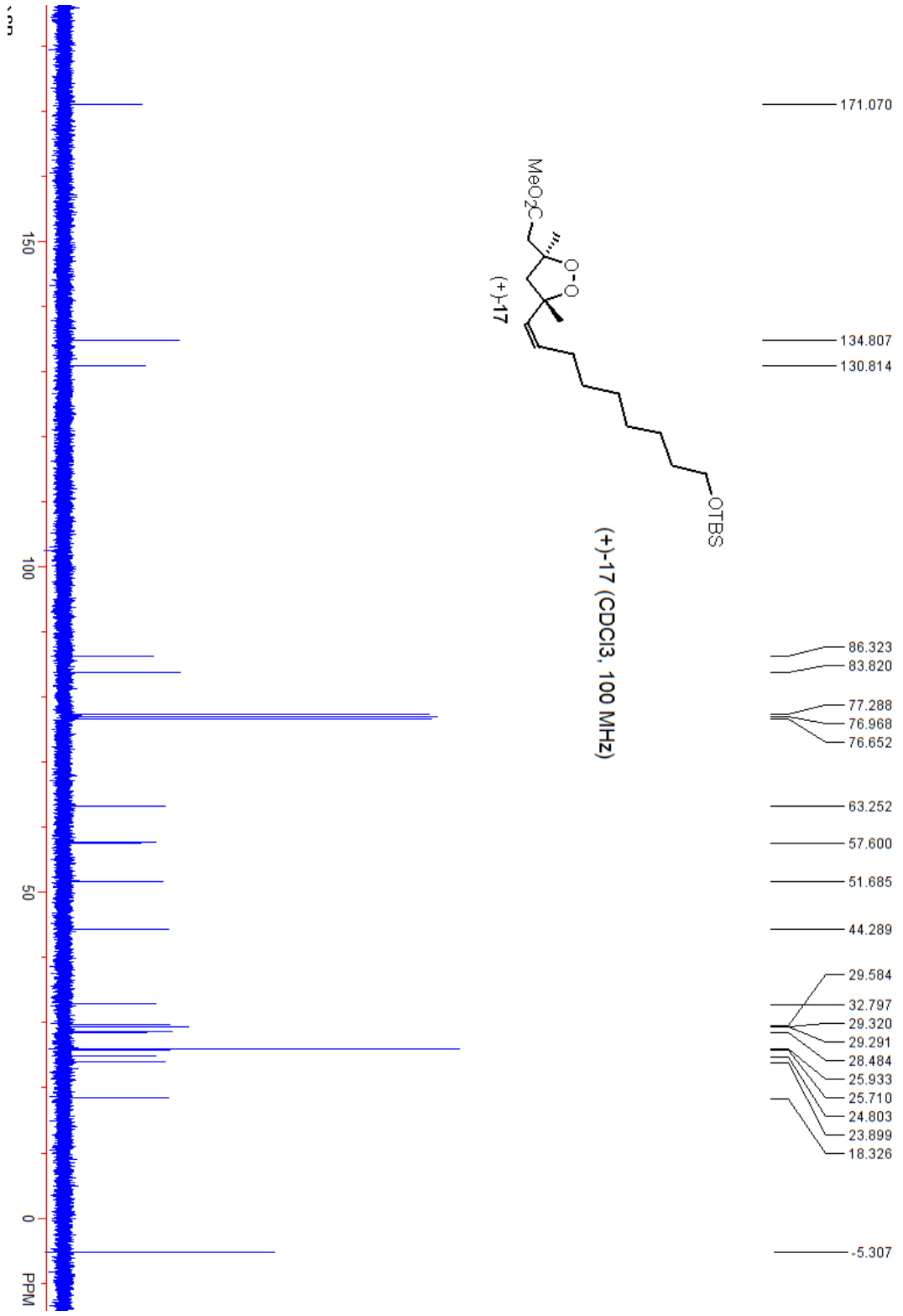

170.953
141.573
113.403
85.845
84.273
77.278
76.960
76.641
55.322
51.659
44.258
23.634
23.452
MeO2C
O–O
(+)-32
(+)-32 (CDCl3, 100 MHz)
160
140
120
100
80
60
40
20
PPM

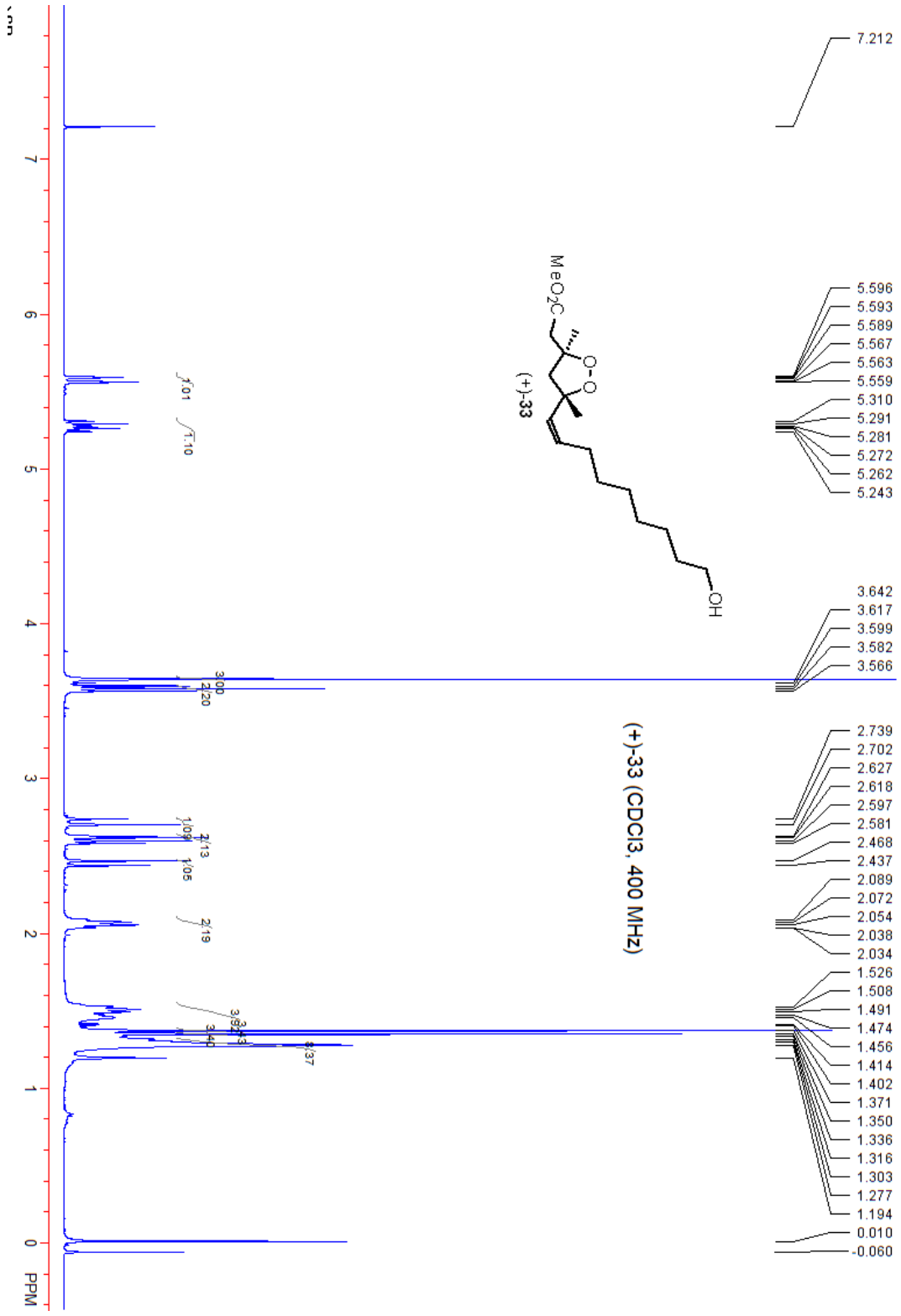

6.936
6.914
6.366
6.344
3.719
3.697
2.907
2.875
2.834
2.798
2.711
2.697
2.680
2.661
1.558
1.401
0.080
(+)-19 (CDCl3, 400 MHz)
0.97
1.02
3.14
1.02
1.03
2.02
3.00
3.13
7
6
5
4
3
2
1
0
PPM

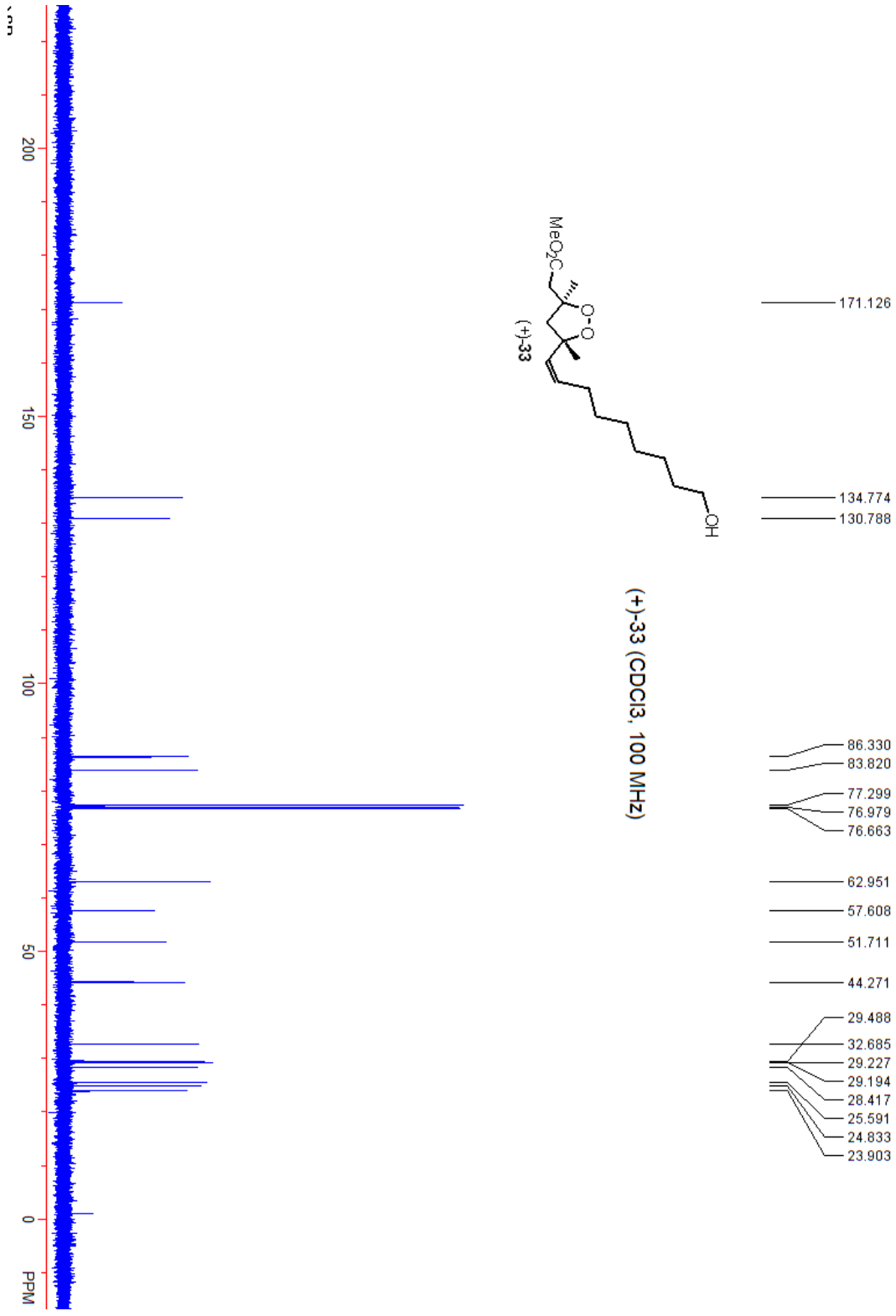
(+)-**19**

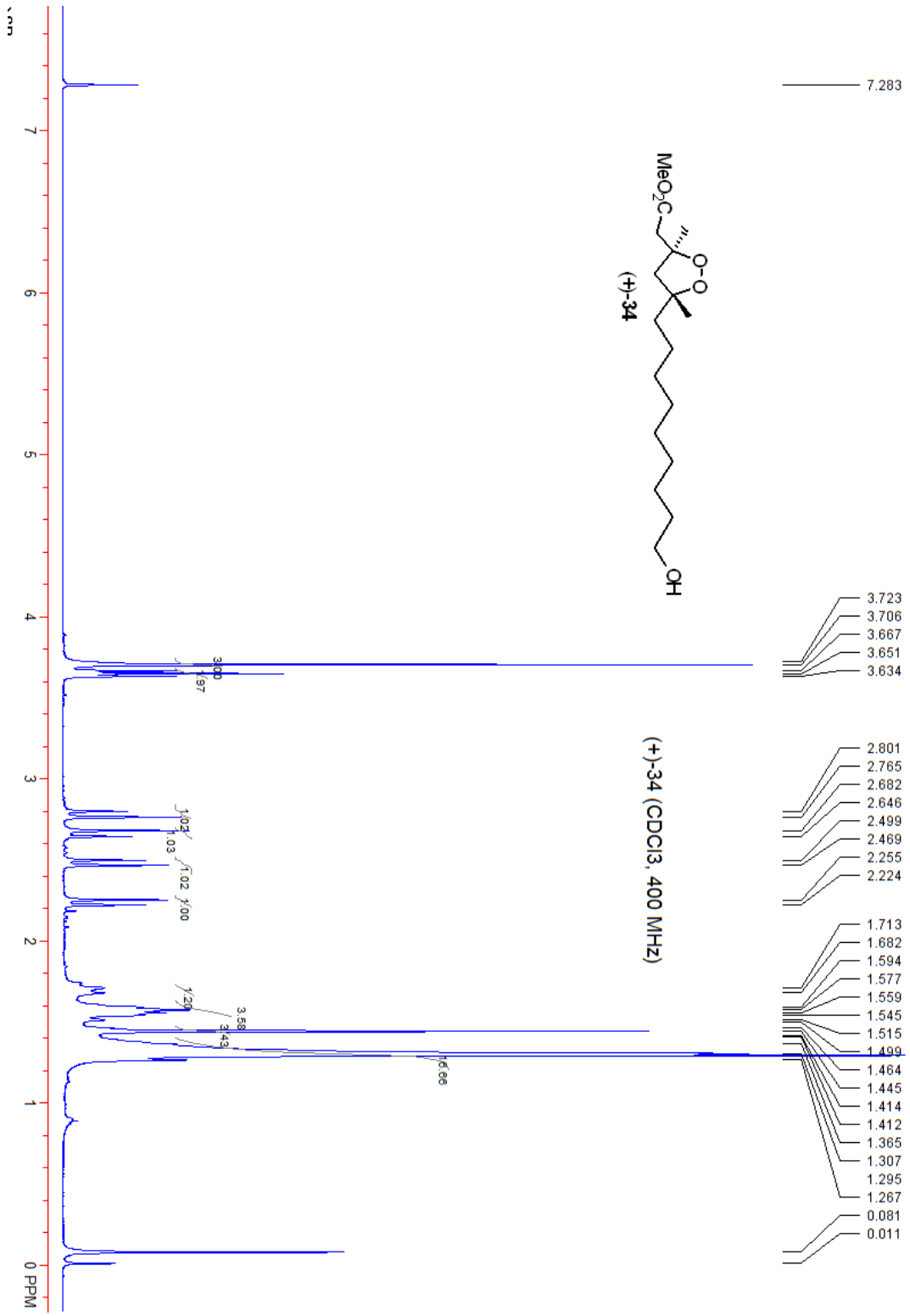

(+)-19
(+)-19 (CDCl3, 100 MHz)
170.940
147.656
87.730
84.341
78.625
77.327
77.008
76.689
55.659
51.715
44.629
23.367
21.155
200
150
100
50
0
PPM

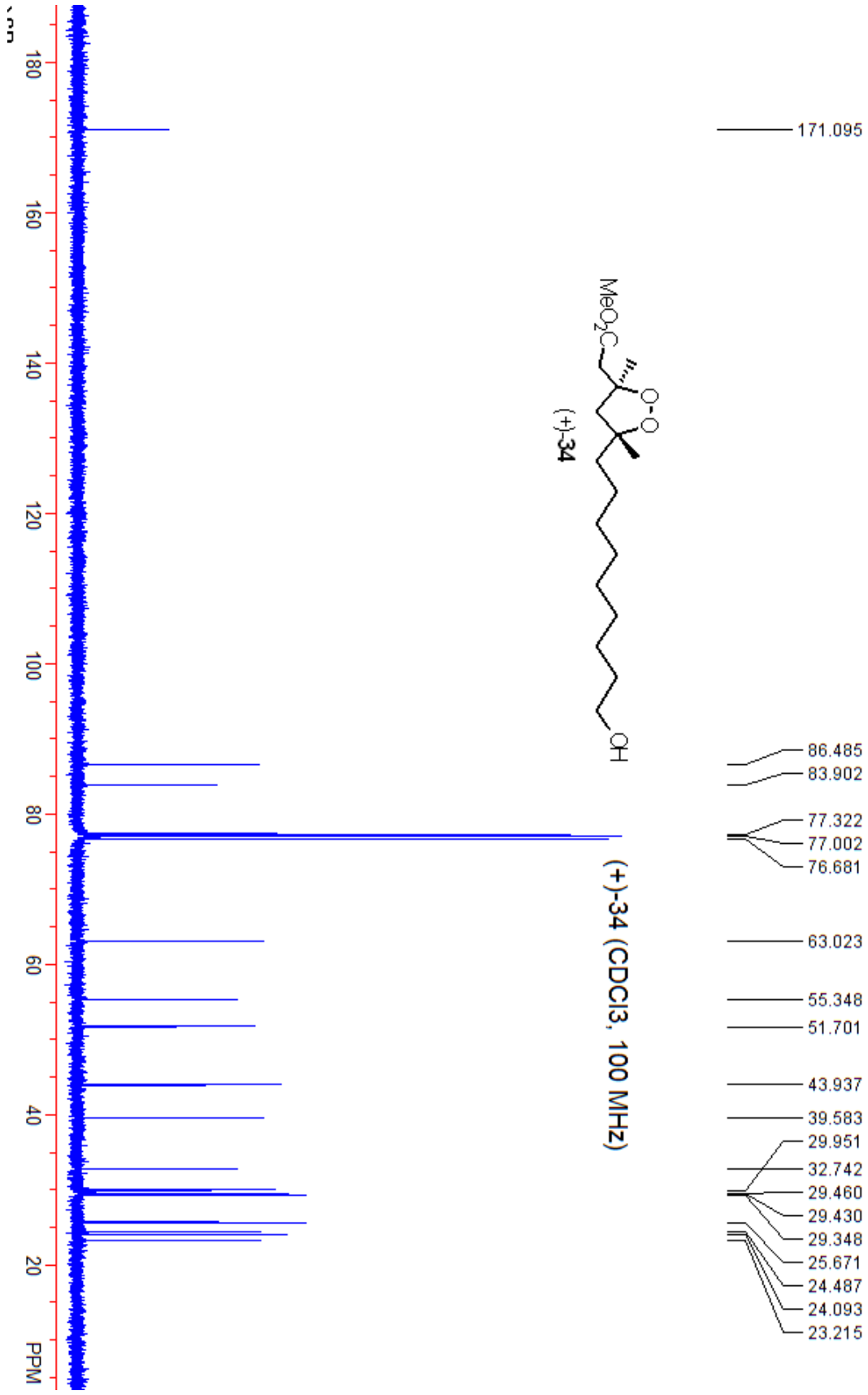

5.605
5.601
5.597
5.575
5.572
5.568
5.313
5.294
5.284
5.276
5.265
5.246
3.654
3.645
3.558
3.541
3.525
2.741
2.705
2.632
2.619
2.602
2.583
2.472
2.442
2.086
2.069
2.050
2.035
2.032
1.494
1.467
1.451
1.434
1.417
1.373
1.352
1.337
1.311
1.295
1.293
1.252
1.198
0.866
0.845
0.838
0.014
0.005
-0.001
-0.009
-0.056
OTBS
MeO2C
(+)-17
(+)-17 (CDCl3, 400 MHz)
9.57
6.72
5.48
3.00
1.97
2.09
1.98
2.96
3.01
0.94
1.01
1.09
1.00
2.13
7
6
5
4
3
2
1
0
PPM

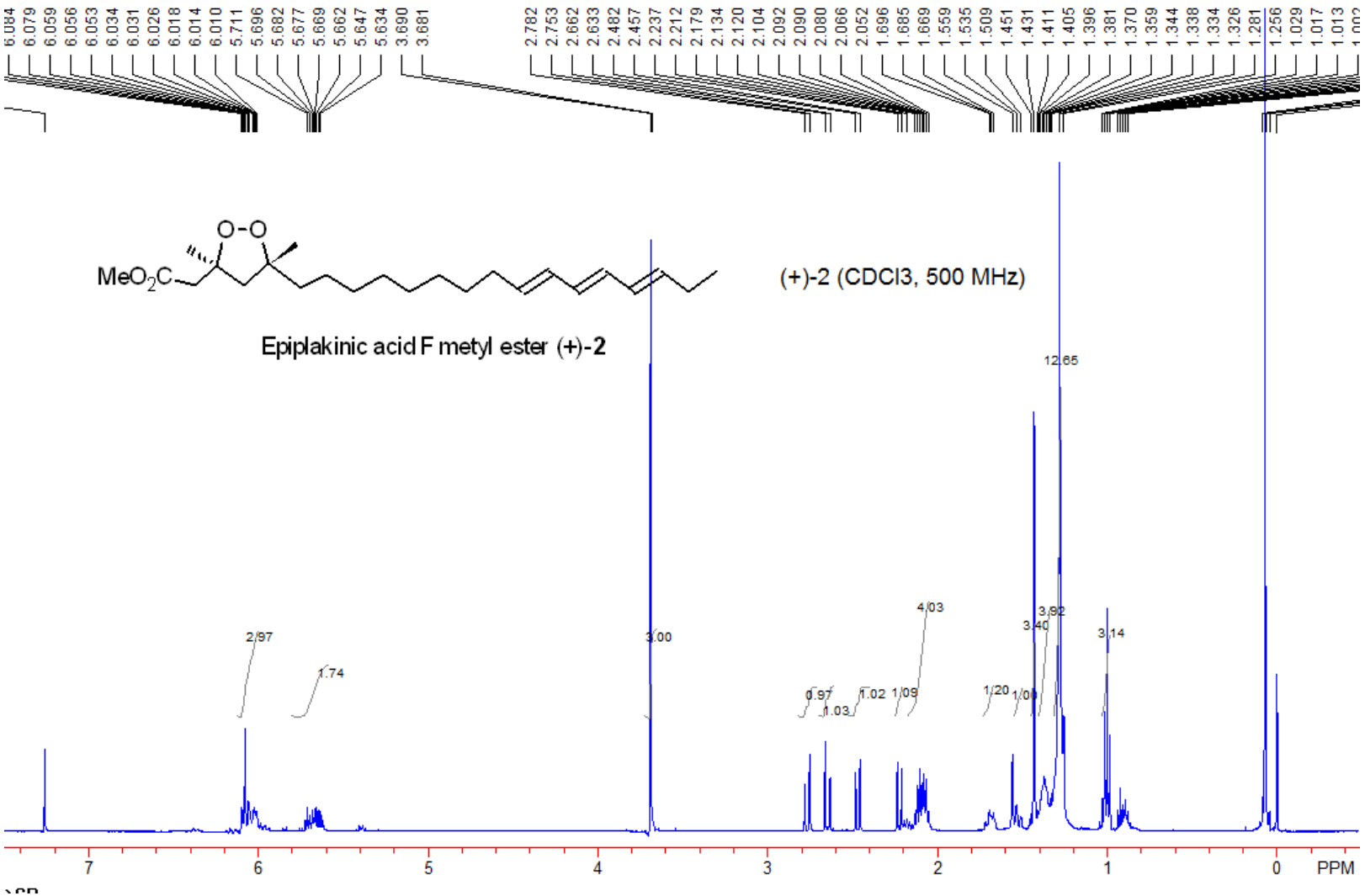

MeO2C
O-O
(+)-17
OTBS
(+)-17 (CDCl3, 100 MHz)
171.070
134.807
130.814
86.323
83.820
77.288
76.968
76.652
63.252
57.600
51.685
44.289
29.584
32.797
29.320
29.291
28.484
25.933
25.710
24.803
23.899
18.326
-5.307
150
100
50
0
PPM

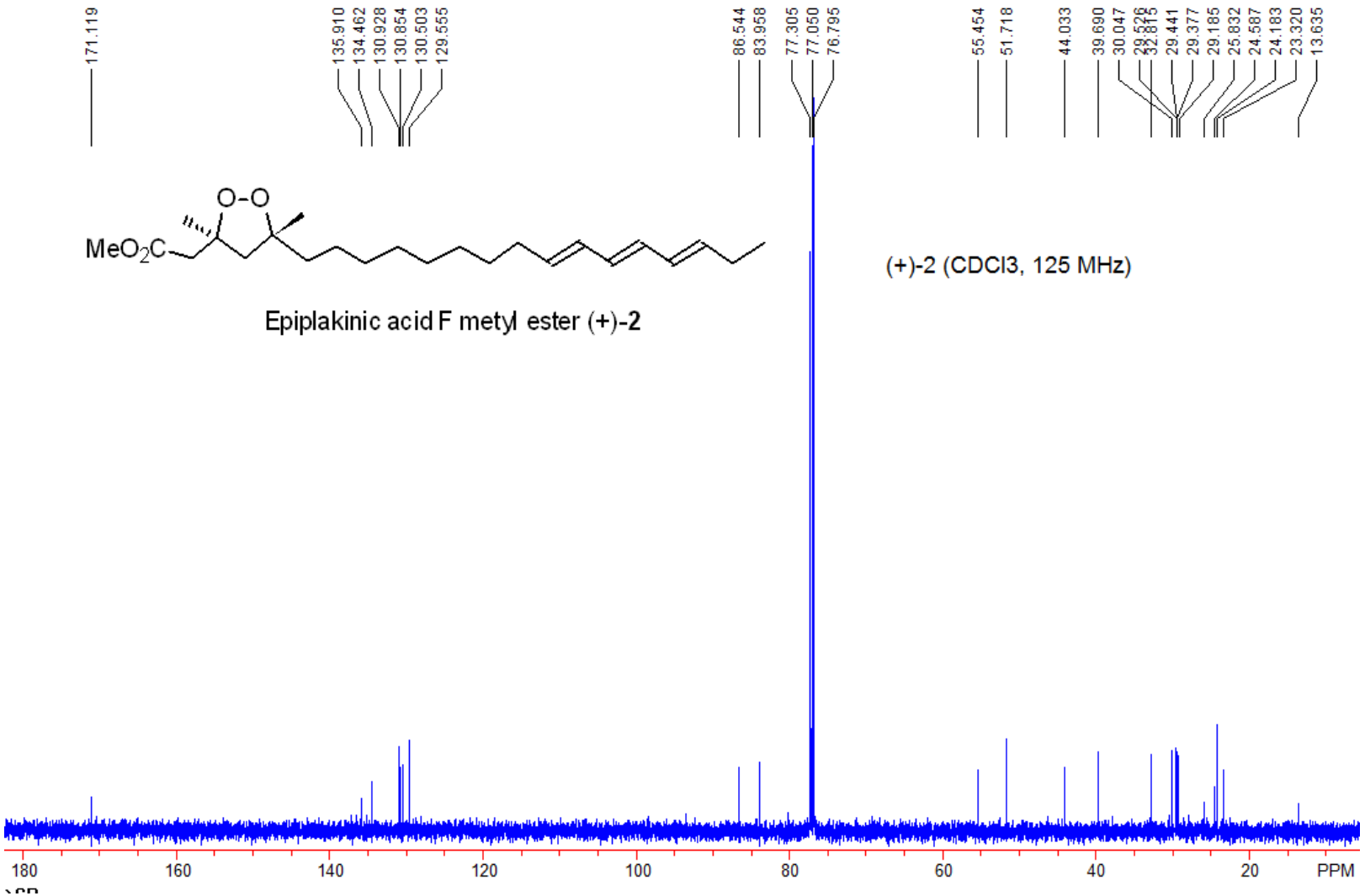

7.212
5.596
5.593
5.589
5.567
5.563
5.559
5.310
5.291
5.281
5.272
5.262
5.243
3.642
3.617
3.599
3.582
3.566
2.739
2.702
2.627
2.618
2.597
2.581
2.468
2.437
2.089
2.072
2.054
2.038
2.034
1.526
1.508
1.491
1.474
1.456
1.414
1.402
1.371
1.350
1.336
1.316
1.303
1.277
1.194
0.010
-0.060
MeO2C
O-O
(+)-33
OH
(+)-33 (CDCl3, 400 MHz)
PPM


200
150
100
50
0
PPM
MeO2C
O-O
(+)-33
OH
(+)-33 (CDCl3, 100 MHz)
171.126
134.774
130.788
86.330
83.820
77.299
76.979
76.663
62.951
57.608
51.711
44.271
29.488
32.685
29.227
29.194
28.417
25.591
24.833
23.903

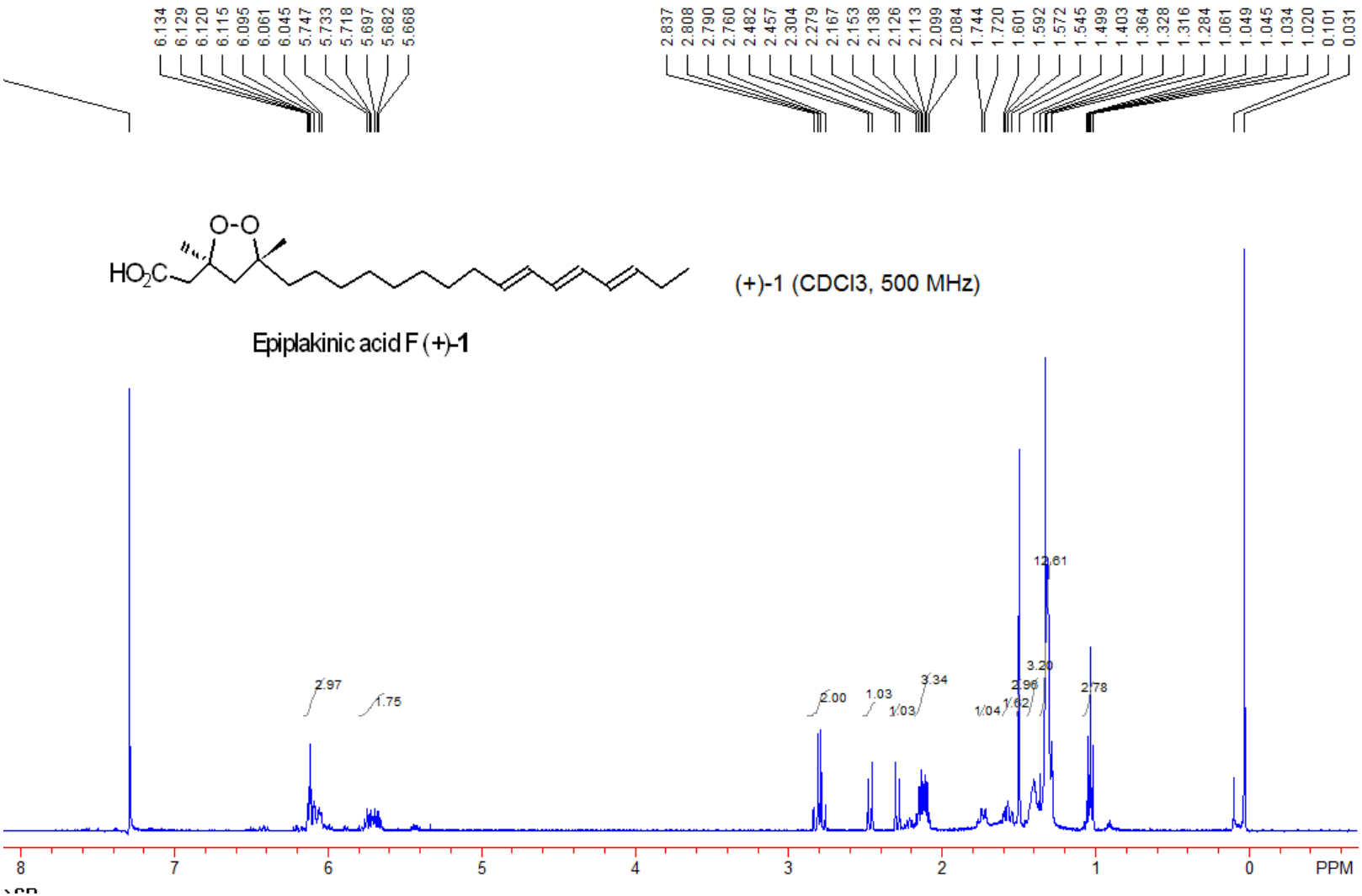

MeO2C
O-O
OH
(+)-34
(+)-34 (CDCl3, 400 MHz)
7.283
3.723
3.706
3.667
3.651
3.634
2.801
2.765
2.682
2.646
2.499
2.469
2.255
2.224
1.713
1.682
1.594
1.577
1.559
1.545
1.515
1.499
1.464
1.445
1.414
1.412
1.365
1.307
1.295
1.267
0.081
0.011
3.00
1.97
1.02
1.03
1.02
1.00
1.29
3.58
3.43
16.66
0 PPM

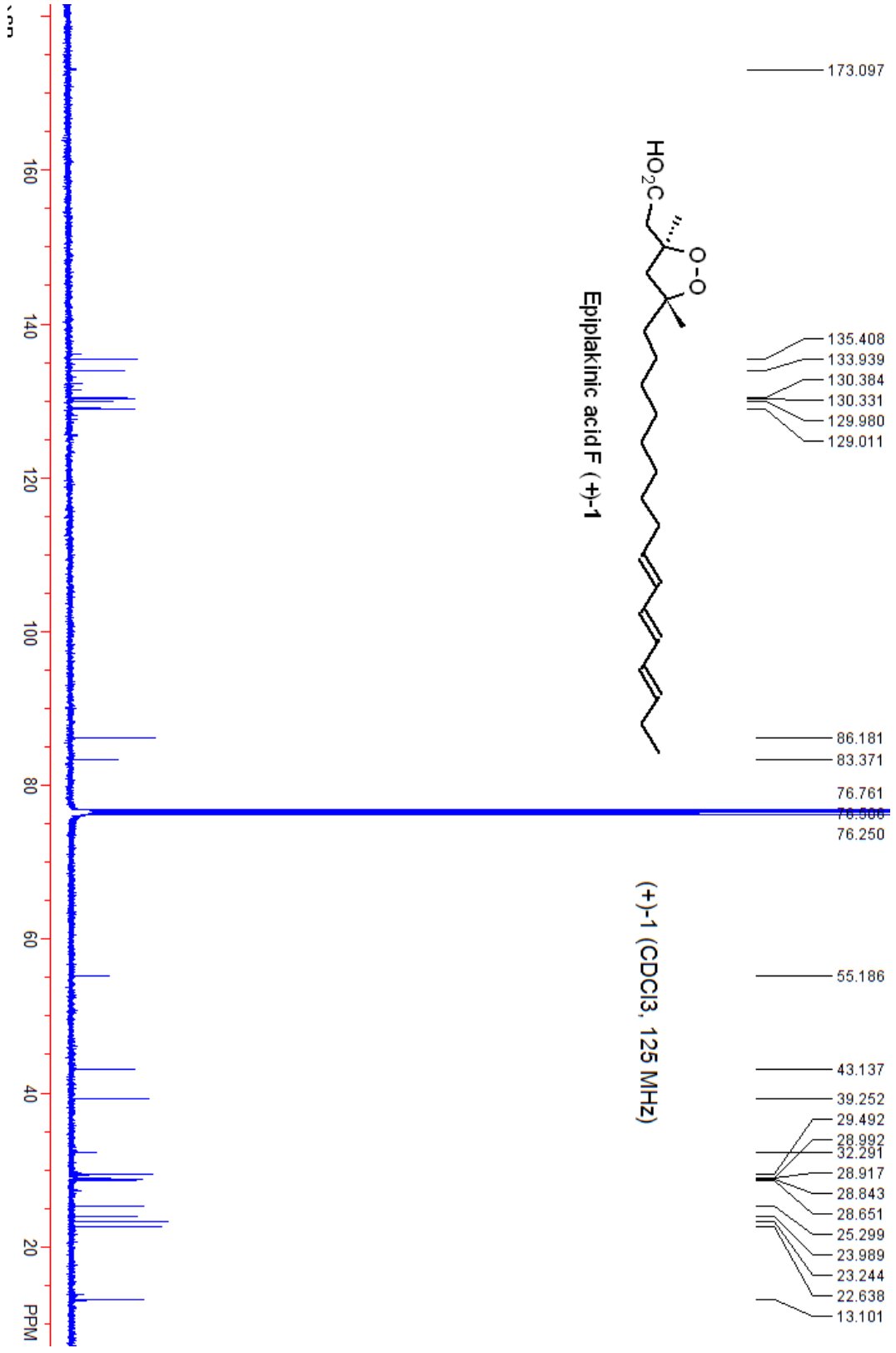

MeO2C
O-O
OH
(+)-34
(+)-34 (CDCl3, 100 MHz)
171.095
86.485
83.902
77.322
77.002
76.681
63.023
55.348
51.701
43.937
39.583
29.951
32.742
29.460
29.430
29.348
25.671
24.487
24.093
23.215
180
160
140
120
100
80
60
40
20
PPM


6.084
6.079
6.059
6.056
6.053
6.034
6.031
6.026
6.018
6.014
6.010
5.711
5.696
5.682
5.677
5.669
5.662
5.647
5.634
3.690
3.681
2.782
2.753
2.662
2.633
2.482
2.457
2.237
2.212
2.179
2.134
2.120
2.104
2.092
2.090
2.080
2.066
2.052
1.696
1.685
1.669
1.559
1.535
1.509
1.451
1.431
1.411
1.405
1.396
1.381
1.370
1.359
1.344
1.338
1.334
1.326
1.281
1.256
1.029
1.017
1.013
O-O
MeO2C
(+)-2 (CDCl3, 500 MHz)
Epiplakinic acid F metyl ester (+)-2
12.65
4.03
3.92
3.40
3.14
3.00
2.97
1.74
1.20
1.09
1.02
1.03
0.97
7
6
5
4
3
2
1
0
PPM



Epiplakinic acid F metyl ester (+)-**2**

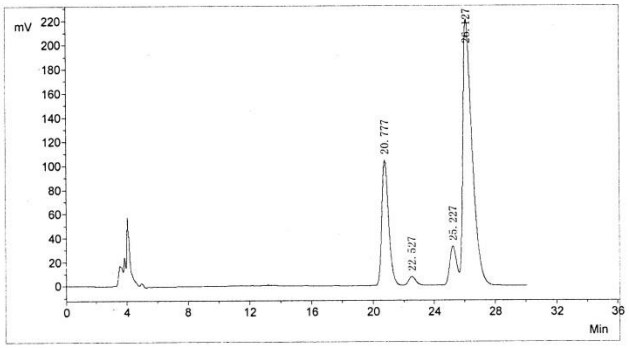

6.134
6.129
6.120
6.115
6.095
6.061
6.045
5.747
5.733
5.718
5.697
5.682
5.668
2.837
2.808
2.790
2.760
2.482
2.457
2.304
2.279
2.167
2.153
2.138
2.126
2.113
2.099
2.084
1.744
1.720
1.601
1.592
1.572
1.545
1.499
1.403
1.364
1.328
1.316
1.284
1.061
1.049
1.045
1.034
1.020
0.101
0.031
O-O
HO2C
(+)-1 (CDCl3, 500 MHz)
Epiplakinic acid F (+)-1
2.97
1.75
2.00
1.03
1.03
3.34
1.04
2.96
1.02
12.61
3.20
2.78
8
7
6
5
4
3
2
1
0
PPM


Epiplakinic acid F (+)-1
(+)-1 (CDCl3, 125 MHz)
HO2C
O-O
173.097
135.408
133.939
130.384
130.331
129.980
129.011
86.181
83.371
76.761
76.506
76.250
55.186
43.137
39.252
29.492
28.992
32.291
28.917
28.843
28.651
25.299
23.989
23.244
22.638
13.101
160
140
120
100
80
60
40
20
PPM

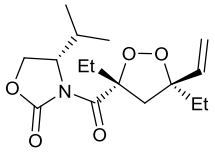
HPLC Report

Sample Name:
Operator:
Time:13:42

Data File:TXY.che
Date:2011-03-29

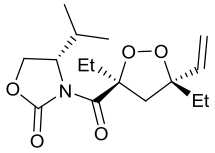


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	20.777	104082.9	3223432.0	23.4025
2	2	22.527	7302.6	242468.0	1.7603
3	3	25.227	32830.5	1018985.9	7.3980
4	4	26.127	220508.4	9288967.7	67.4391
Total			364724.6	13773853.5	100.0000



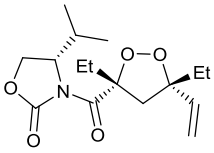
trans-**12a**

minor product



trans-**13a**

major product



cis-**14a**

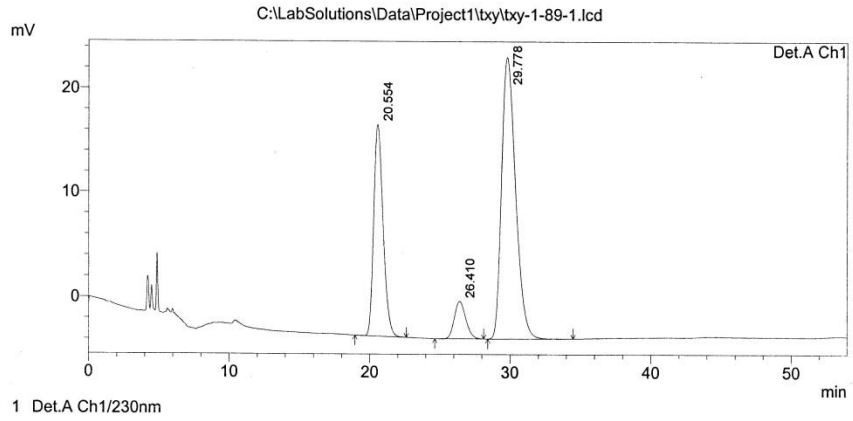
minor product

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\txy\txy-1-89-1.lcd

Acquired by	: Admin
Sample Name	: txy
method	:od-h,80/20,0.7,230
Injection Volume	: 1 uL
Data File Name	: txy-1-89-1.lcd
Method File Name	: 111.lcm
Report File Name	: Default.lcr
Data Acquired	: 2009-12-9 10:06:18
Data Processed	: 2009-12-9 11:00:20

<Chromatogram>

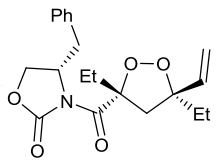


1 Det.A Ch1/230nm

PeakTable

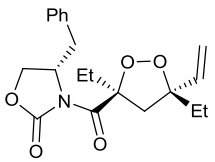
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.554	942934	20277	31.312	39.887
2	26.410	202276	3589	6.717	7.059
3	29.778	1866222	26971	61.971	53.054
Total		3011433	50837	100.000	100.000



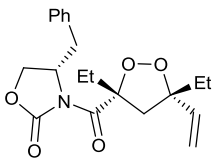
trans-**12b**

minor product



trans-**13b**

major product



cis-**14b**

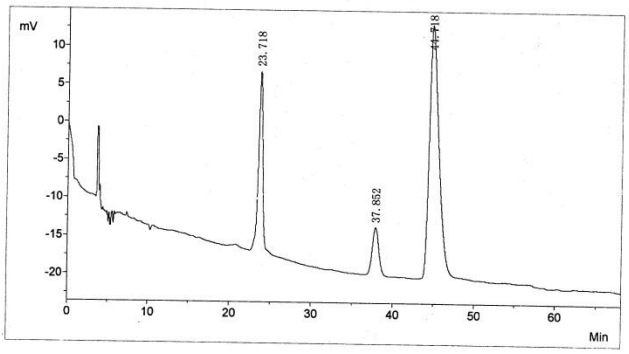
minor product

C:\LabSolutions\Data\Project1\txy\txy-1-89-1.lcd

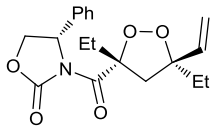
HPLC REPORT

Data File:TXY-2-32-2+- IC 82 214 0.7.che
Date:2010-01-05
Operator:

Sample name:
Time :14:15

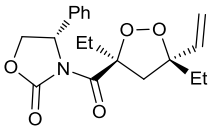


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		23.718	23875.2	874980.2	22.3477
2	2		37.852	6279.2	347357.8	8.8718
3	3		44.718	33244.7	2692962.9	68.7805
Total				63399.1	3915300.9	100.0000



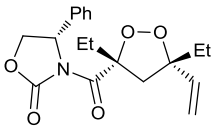
trans-**12c**

minor product



trans-**13c**

major product



cis-**14c**

minor product

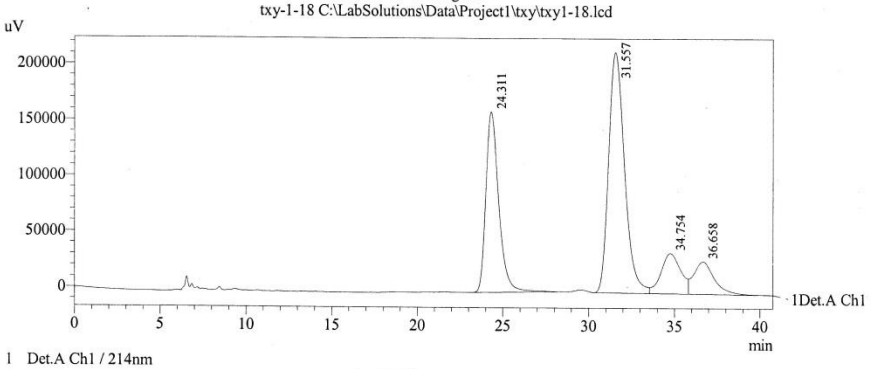
==== Shimadzu LCsolution Calibration Curve ====

Sample Information

Acquired by	: Admin
Sample Name	: ~~txy-1-18~~
Sample ID	: ic,50/50,0.5,214
Vail#	:
Injection Volume	: 1 uL
Data Filename	: txy1-18.lcd
Method Filename	: 111.lcm
Batch Filename	:
Report Filename	: Default.lcr

Chromatogram

txy-1-18 C:\LabSolutions\Data\Project1\txy\txy1-18.lcd

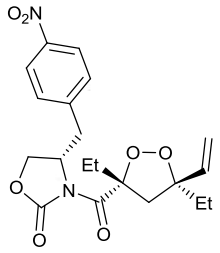


1 Det.A Ch1 / 214nm

PeakTable

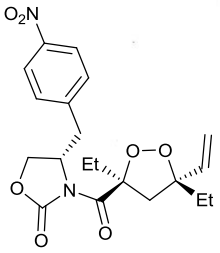
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.311	8438734	161197	30.550	36.549
2	31.557	13843914	214881	50.118	48.722
3	34.754	2870220	35925	10.391	8.145
4	36.658	2469886	29036	8.941	6.584
Total		27622754	441039	100.000	100.000



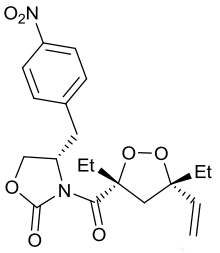
trans-**12d**

minor product



trans-**13d**

major product



cis-**14d**

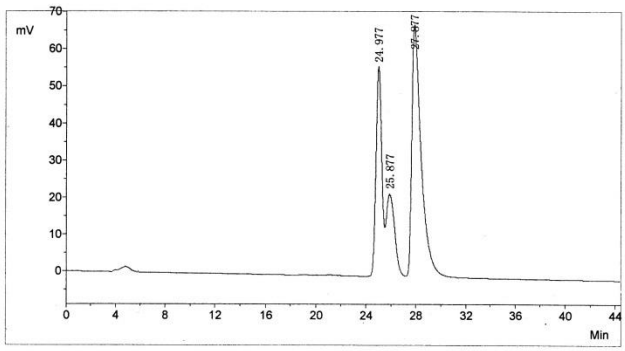
minor product

C:\LabSolutions\Data\Project1\txy\txy1-18.lcd

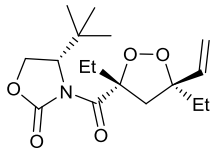
HPLC Report

Sample Name:
Operator:
Time:08:53

Data File:TXY4-60-1+-AD-H9820.7214.che
Date:2010-12-16

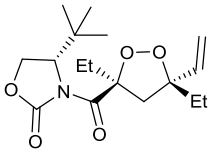


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		24.977	56416.9	1845525.2	28.5066
2	2		25.877	22314.3	1043026.9	16.1109
3	3		27.877	68027.4	3585480.1	55.3825
Total				146758.7	6474032.1	100.0000



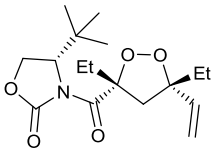
trans-**12e**

minor product



trans-**13e**

major product



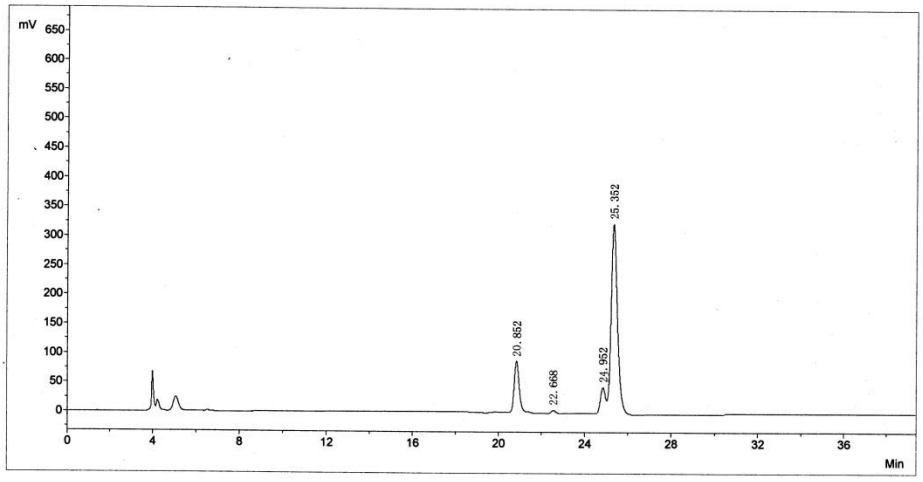
cis-**14e**

minor product

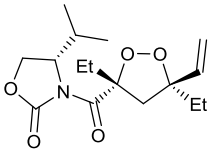
HPLC Report

Sample Name:
Operator:
Time:19:36

Data File:TXY-2-84-1.che
Date:2010-04-06

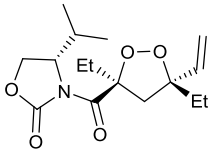


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		20.852	87958.1	1365530.2	15.5149
2	2		22.668	5273.3	80960.5	0.9199
3	3		24.952	45232.7	663641.1	7.5402
4	4		25.352	327329.6	6691255.6	76.0250
Total				465793.7	8801387.3	100.0000



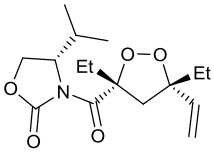
trans-**12a**

minor product



trans-**13a**

major product



cis-**14a**

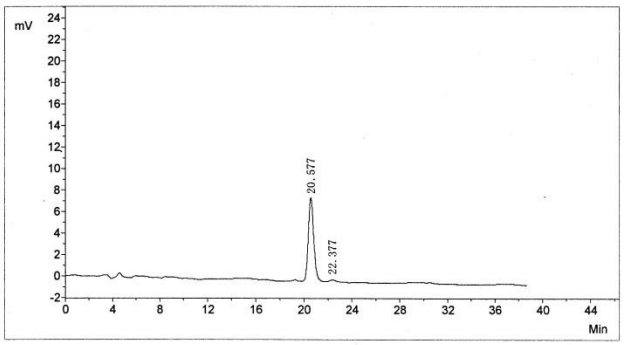
minor product

reaction in Et_2O as the solvent and in the presence of $Sc(OTf)_3$ as Lewis acid

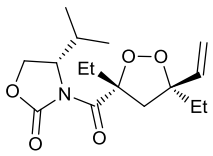
HPLC Report

Sample Name:
Operator:
Time:09:07

Data File:TXY2-74-2.che
Date:2011-05-30



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		20.577	7803.3	244751.8	97.3077
2	2		22.377	194.7	6771.8	2.6923
Total				7998.0	251523.6	100.0000



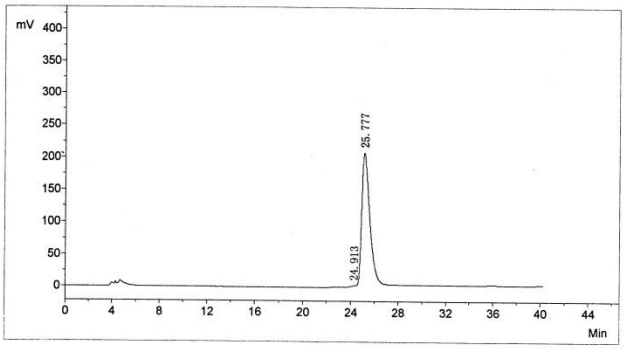
trans-**12a**

minor product

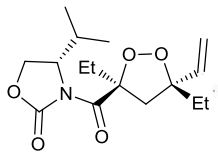
HPLC Report

Sample Name:
Operator:
Time:09:48

Data File:TXY-2-74-3.che
Date:2011-05-30



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		24.913	1126.1	29160.0	0.2948
2	2		25.777	206483.6	9863090.1	99.7052
Total				207609.6	9892250.1	100.0000



trans-**13a**

major product

HPLC Report

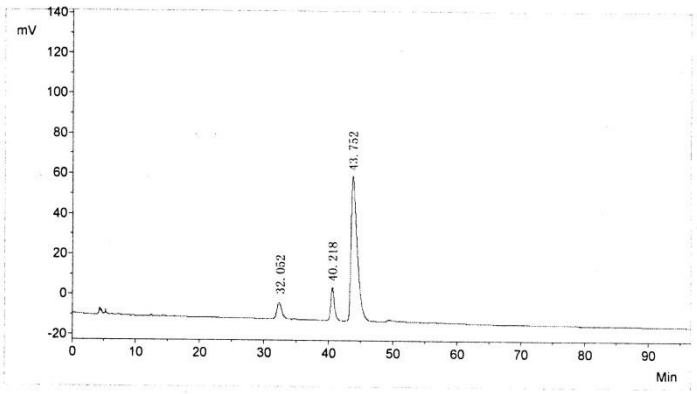
Sample Name:

Operator:

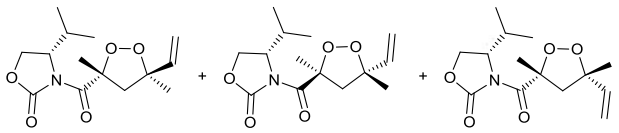
Time:10:02

Data File:TXY-6-3MIX AD-H 982 214 0.7.che

Date:2013-12-16



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		32.052	8212.7	427358.7	7.3014
2	2		40.218	16628.4	651801.0	11.1872
3	3		43.752	72058.7	4770949.9	81.5114
Total				96899.8	5853109.6	100.0000



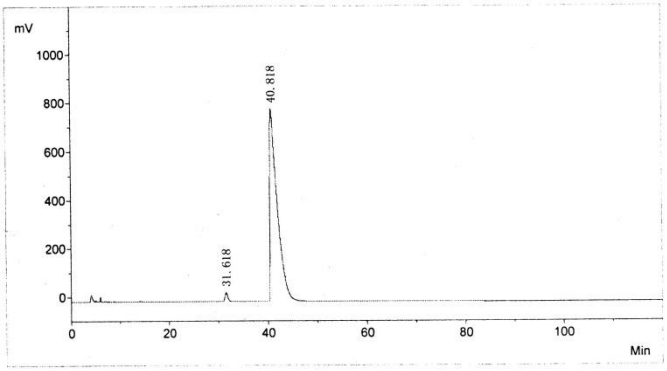
trans-**20a** + *trans*-**20b** + *cis*-**20c**

major product

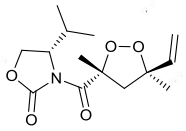
HPLC Report

Sample Name:
Operator:
Time:12:47

Data File:TXY-6-3-1.che
Date:2013-12-16



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		31.618	38031.2	1479995.2	1.7826
2	2		40.818	792953.4	81543572.7	98.2174
Total				830984.7	83023567.9	100.0000



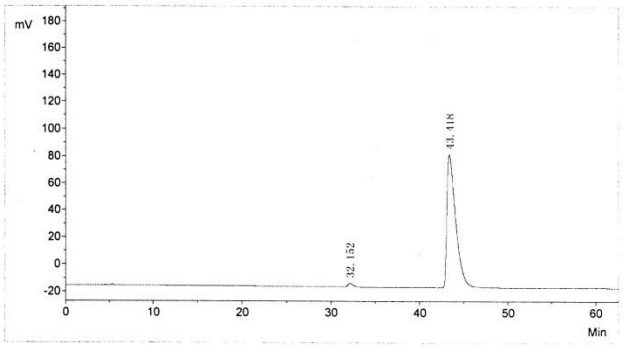
de > 96%

trans-**20a**

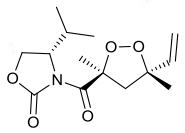
HPLC Report

Sample Name:
Operator:
Time:11:43

Data File:TXY-6-3-2.che
Date:2013-12-16



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		32.152	2779.3	107768.8	1.5657
2	2		43.418	98640.4	6775526.1	98.4343
Total				101419.7	6883291.9	100.0000



de > 96%

trans-**20b**

major product

References

1 D. A. Evans, D. J. Mathre, W. L. Scott, *J. Org. Chem*., **1985**, *50*, 1830-1835

2 N. A. Shaye, D. M. Benoit, S. Chavda, E. Coulbeck, M. Dingjan, J. Eames, Y. Yohannes, *Tetrahedron: Asymmetry*, **2011**, *22*, 413-438.

3 K. Orito, M. Miyazawa, T. Nakamura, A. Horibata, H. Ushito, H. Nagasaki, M. Yuguchi, S. Yamashita, T. Yamazaki, M. Tokuda, *J. Org. Chem.*, **2006**, *71*, 5951-5958.

4 S. W. Foo, Y. Takada, Y. Yamazaki, S. Saito, *Tetrahedron Lett.*, **2013**, *54*, 4717-4720.

5 C. J. MacNevin, R. L. Moore, D. C. Liotta, *J. Org. Chem.*, **2008**, *73*, 1264-1269.

6 G. P. Moloney, A. D. Robertson, G. R. Martin, S. MacLennan, N. Mathews, S. Dodsworth, S. P. Y., C. Knight, R. Glen, *J. Med. Chem.*, **1997**, *40*, 2347-2362.

7 N. Lakshminarayana, Y. Rajendra Prasad, L. Gharat, A. Thomas, P. Ravikumar, S. Narayanan, C. V. Srinivasan, B. Gopalan, *Eur. J. Med. Chem.*, **2009**, *44*, 3147-3157.

8 Y. Chen, K. B. Killday, P. J. McCarthy, R. Schimoler, K. Chilson, C. Selitrennikoff, S. A. Pomponi and A. E. Wright, *J. Nat. Prod.* **2001**, *64*, 262-264.

9 M. P. Bosch, F. Campos, I. Niubó, G. Rosell, J. L. Díaz, J. Brea, M. I. Loza, A. Guerrero, *J. Med. Chem.*, **2004**, *47*, 4041-4053.

10 S. Ahmed, S. Adat, A. Murrells, C. P. Owen, Y. Amanuel, *Bioorg. Chem.*, **2002**, *30*, 315-331.

11 L. F. Tietze, C. Schneider, A. Grote, *Chem. Eur. J.*, **1996**, *2*, 139-148.

Notes and References

[a]Shanghai-Hong Kong Joint Laboratory in Chemical Synthesis, The Chinese Academy of Sciences, 345 Ling Ling Road, Shanghai 200032, China.

[b]Shenzhen Municipal Key Laboratory of Chemical Synthesis of Medicinal Organic Molecules & Shenzhen Center of Novel Functional Molecules, Shenzhen Research Institute, The Chinese University of Hong Kong，No.10. 2nd Yuexing Road, Shenzhen 518507, China

[c]Department of Chemistry, Centre of Novel Functional Molecules and State Key Laboratory of Synthetic Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, China.

Fax: (+852) 26096329; E-mail: hncwong@cuhk.edu.hk.