Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Spectroscopic Characterization of Diiodomethylzinc Iodide: Application to the Stereoselective Synthesis and Functionalization of Iodocyclopropanes.

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Table of contents

General Experimental Conditions

General: Unless stated otherwise, all reactions were run under an argon atmosphere with thoroughly flame-dried glassware using standard techniques for manipulating air-sensitive compounds.[i] CH_2Cl_2 and Et_2O were obtained by filtration through drying columns (packed with alumina), *tert*-amyl alcohol was distilled over calcium hydride under argon prior to use. Flash column chromatography was performed using an automatic purification system (Teledyne Isco Combiflash® Rf or Sq16x). Prepacked normal phase silica gel columns were used for separation of products using Teledyne Isco Redi*Sep*® Rf High Performance Gold or Silicycle Silia*Sep*TM High Performance columns (12 g, 24 g, 40 g, or 80 g). Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm), or using potassium permanganate and/or cerium ammonium molybdate stains.
Melting points were obtained on a Buchi melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on either a 400 or 500 MHz spectrometers (Bruker Ultrashield 400 or Bruker Ultrashield 500 plus) at 293 K. The corresponding chemical shifts for ^{1}H NMR and ^{13}C NMR spectra are reported in parts per million relative to the chemical shift of tetramethylsilane and recorded in $CDCl_3$, using the residual $CHCl_3$ as reference (^{1}H: δ7.26 ppm, ^{13}C: δ77.16 ppm). The corresponding chemical shifts of ^{19}F NMR spectra are recorded in parts per million relative to the chemical shift of $CFCl_3$ and recorded in $CDCl_3$, using α,α,α-trifluorotoluene (^{19}F: -63.72 ppm) as reference. The data is reported as follows: chemical shift (ppm), multiplicity (s = singlet, br = broad singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, dtd = doublet of triplet of doublets, t = triplet, app. t = apparent triplet, q = quadruplet, quin = quintet, sext = sextet and m = multiplet), coupling constant in Hz, integration. For new compounds, DEPT135 experiments were conducted to assign the substitution pattern for each cabon (Cq, CH, CH_2, CH_3). Infrared spectra were recorded on a Bruker Vertex Series FTIR and are reported in reciprocal centimeters (cm^{-1}). High resolution mass spectra and SFC chromatography experiments were performed by the Centre regional de spectroscopie de masse de l'Université de Montréal. Optical rotation values were recorded on a Anton Parr MCP200 apparatus using a 0.5 dm quartz cell at a 589 nm wavelength and 20 °C.

Reagents: Commercially available reagents were used as supplied or purified by standard techniques where necessary. Non-commercial starting materials were synthesized according to literature procedures. The chiral (R,R)-dioxaborolane was synthetized as previously reported in the literature.[ii]

Compound Handling/Storage: During all handling, exposure of the iodocyclopropanes to light should be minimized. The iodocyclopropanes products may be stored for prolonged periods below 0 °C in the dark without noticeable decomposition.

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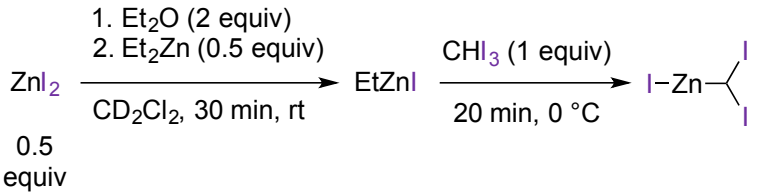
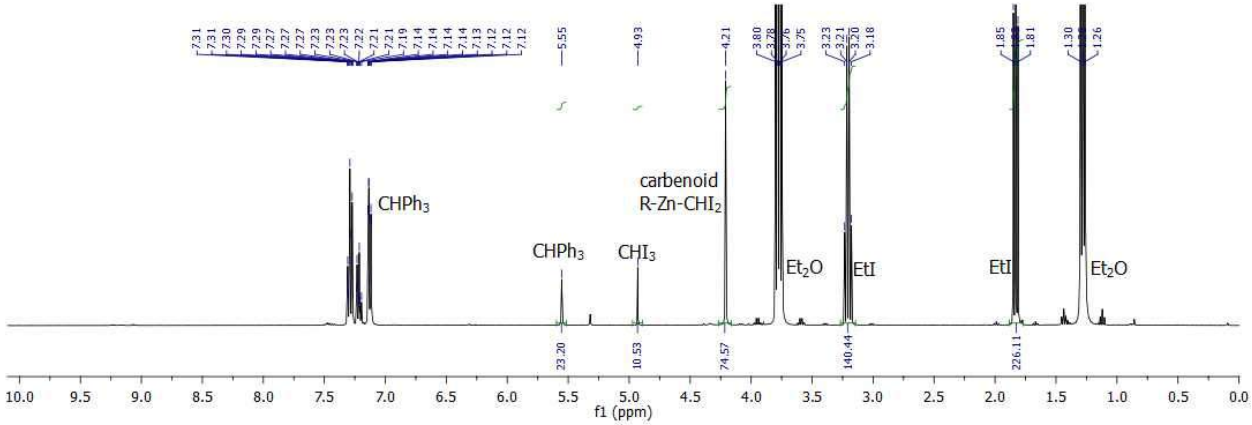
[i] Shriver, D. F. & Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; 2nd Edition; Wiley: New York, 1986.
[ii] Charette, A.B.; Lebel, H. *Org. Synth*. **1999**, *76*, 86.

Carbenoid Experiments

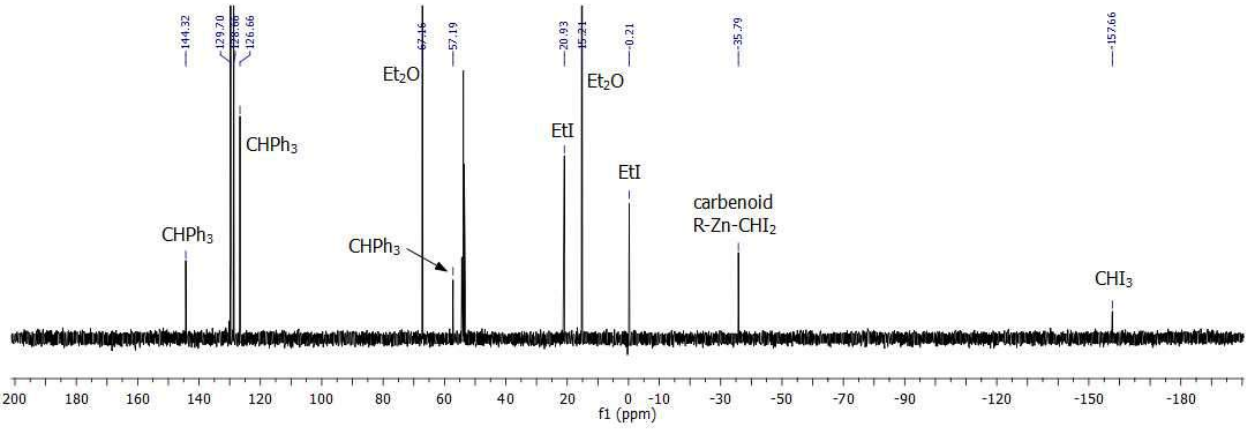
In a round-bottomed flask, iodoform (307.5 mg, 0.78 mmol, 1.0 equiv) was suspended in CD_2Cl_2 (0.7mL) under strong stirring. In a glovebox, another round-bottomed flask was charged with zinc iodide (124.7 mg, 0.39 mmol, 0.5 equiv), equipped with a septum and removed. To this was then added triphenylmethane (44.3 mg, 0.18 mmol, 0.23 equiv), Et_2O (165 µL, 1.59 mmol, 2.0 equiv) and CD_2Cl_2 (0.7 mL). Diethylzinc (40 µL, 0.39 mmol, 0.5 equiv) was added neat under strong stirring. Upon dissolution (partial, about 30 minutes), this mixture was cannulated over the vial containing the iodoform suspension at 0 °C. After 20 minutes, an aliquot was cannulated into a flame-dried NMR tube under argon, and the spectra were recorded immediately (given below). It is worthy to note that the solution is heterogeneous.



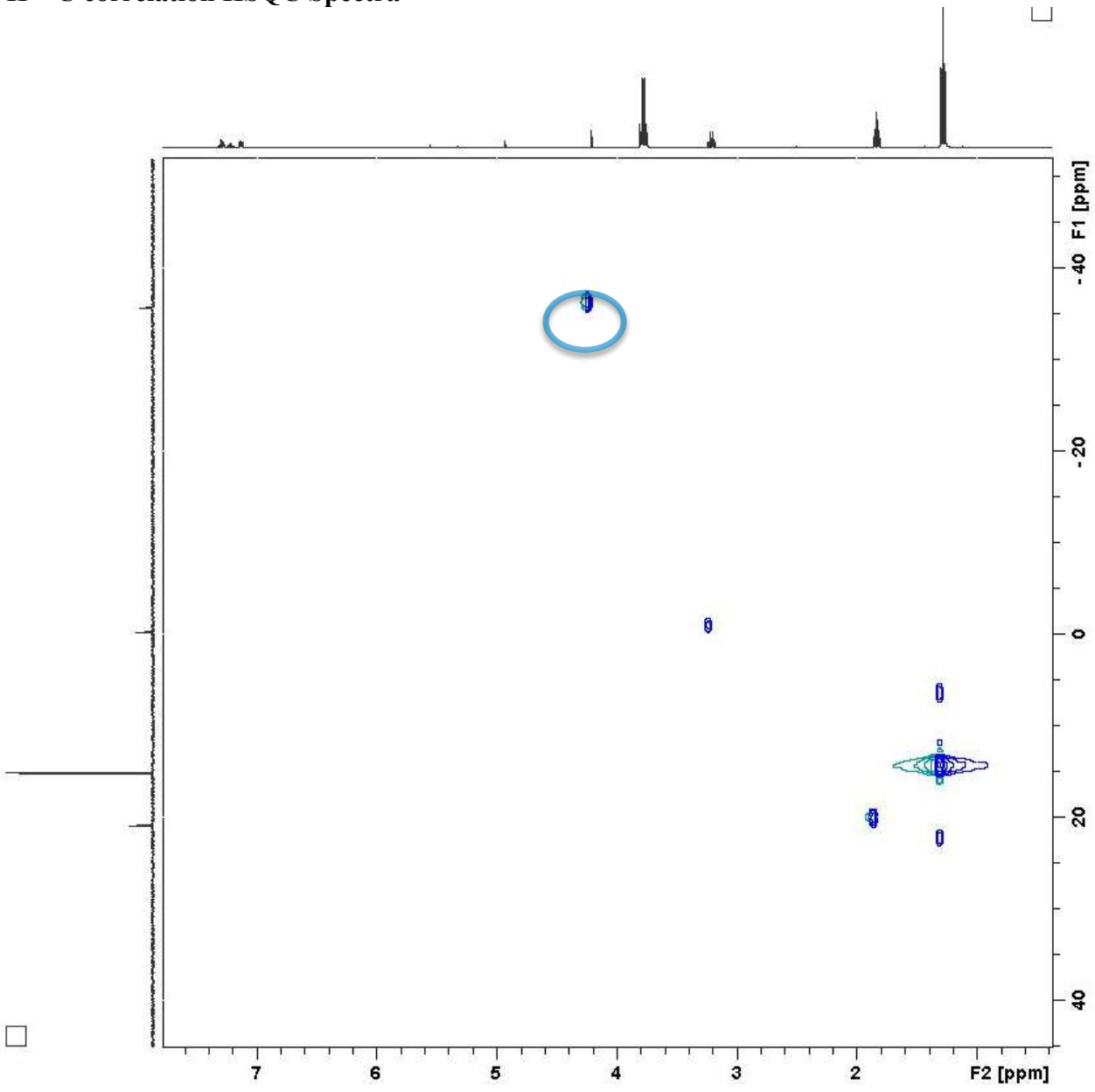
^{1}H NMR Spectra



^{13}C NMR Spectra

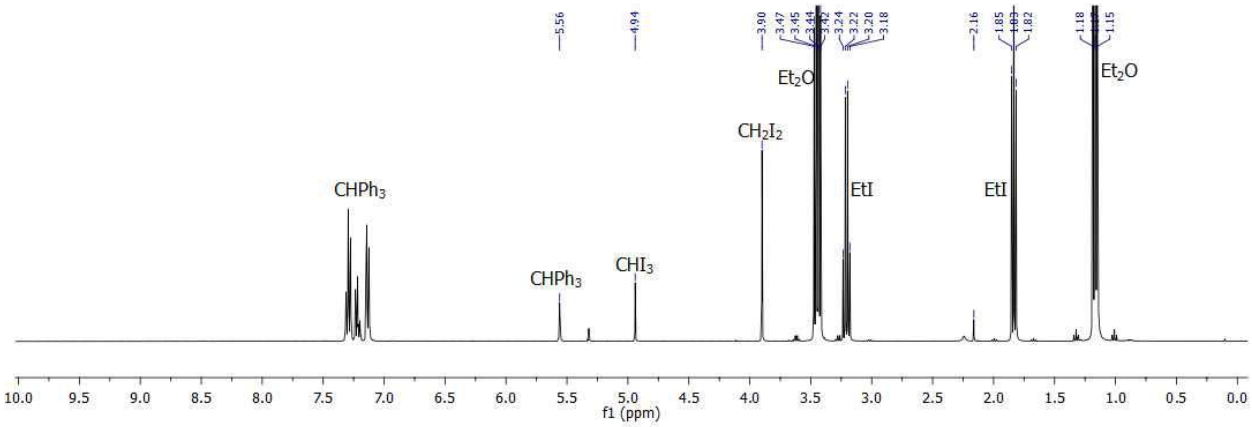


^{1}H-^{13}C correlation HSQC Spectra



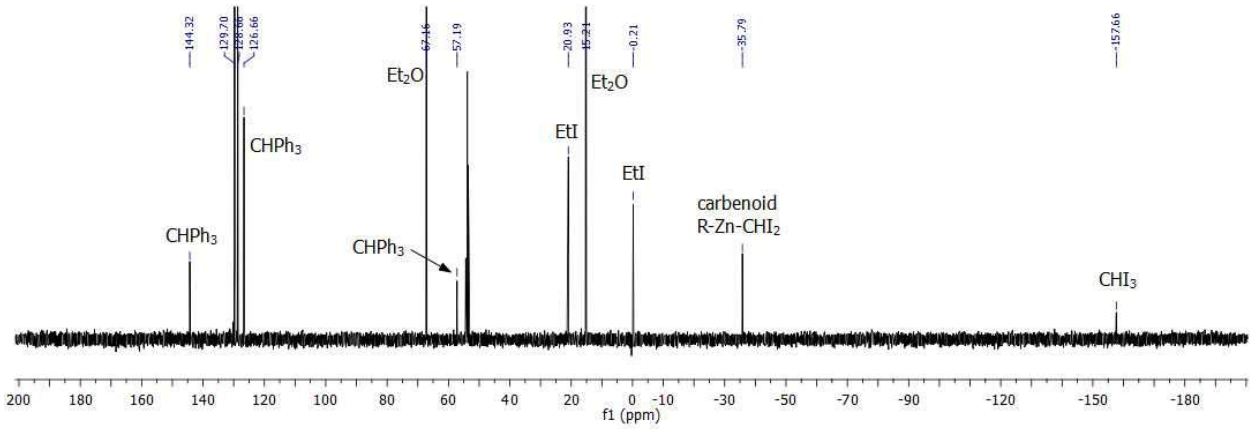
The remaining of the solution was then quenched with HCl 1M and the layers were allowed to separate. The organic one was passed through an anhydrous $MgSO_4$ pad and directly introduced into a NMR tube. Spectra were recorded immediately, given below.

^{1}H NMR Spectra



Signal at 2.16 corresponds to iodomethane, signaling the formation of traces of a gem-dizinc carbenoid.

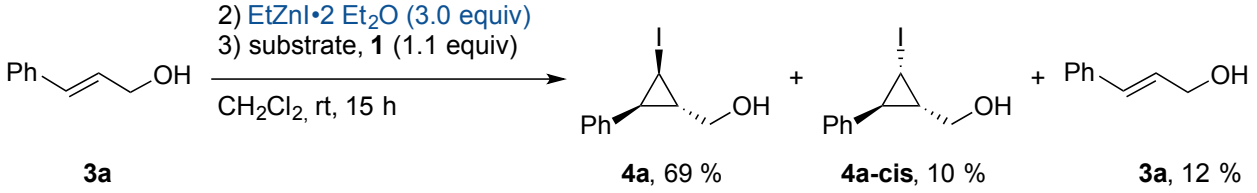
^{13}C NMR Spectra



Optimizations

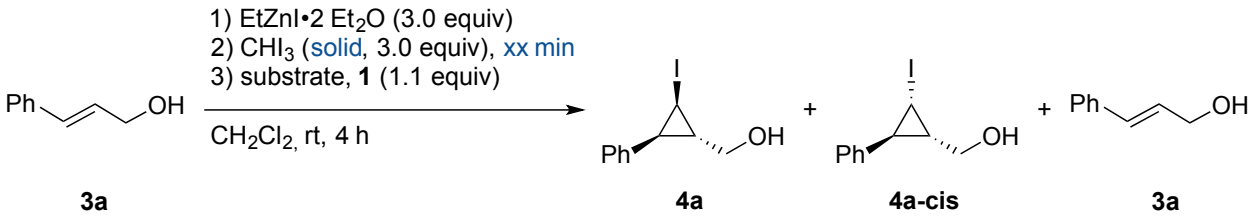
Iodocyclopropanation

Reaction Conditions: Addition of the EtZnI•2Et$_2$O Solution Over the CHI$_3$ Suspension.



Remaining EtZnI•2 Et$_2$O was observed on the vial after cannulation, meaning a loss of reagent. To overcome this, we decided to do a reverse addition procedure where the iodoform would be added as a solid to the EtZnI solution.

Reaction Conditions: Addition of the CHI$_3$ as a Solid Over the EtZnI•2Et$_2$O Solution.

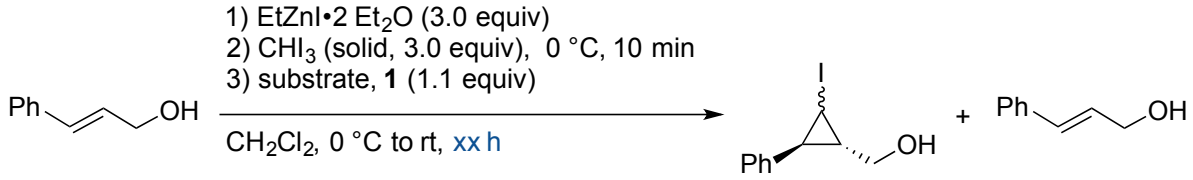


Entry	xx (min)	Color of the carbenoid sln[a]	3a (%)[b]	4a + 4a-*cis* (%)[b]	d.r.[b]
1	10	Cream Brown	6	82	7 : 1
2	30	Dark Green	47	44	7 : 1

[a] Color observed just before the addition of the substrate and 1. [b]Determined by ^{1}H NMR using Ph$_3$CH as internal standard.

Those results indicate that the carbenoid is not stable over time at room temperature. We decided to do this step at 0 °C instead in order to allow the formation of the carbenoid but prevent its degradation

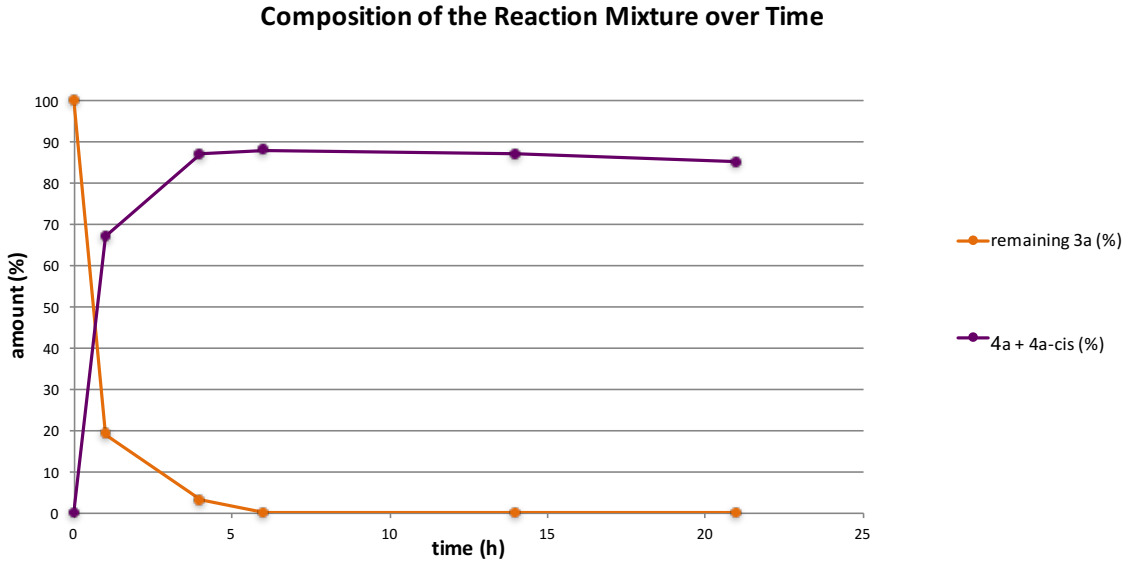
Timerange of the Reaction



3a **4a + 4a-*cis*** **3a**

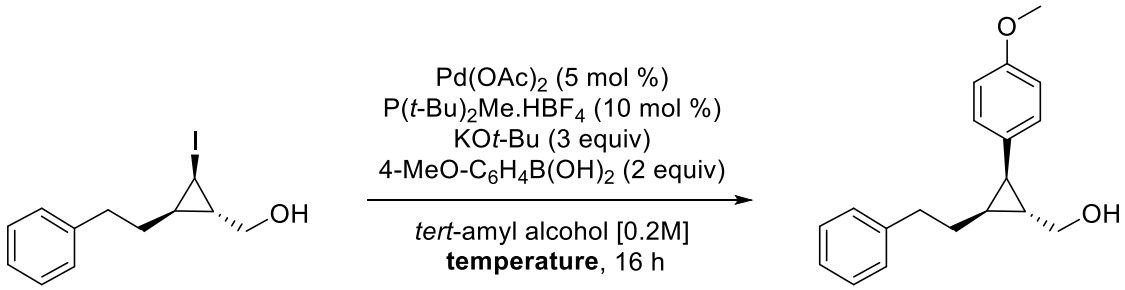
Time (h)	Remaining 3a (%)[a]	4a + 4a-cis (%)[b]
1	19	67
4	3	87
6	0	88
14	0	87
21	0	85

[a] ^{1}H NMR yields using Ph_3CH as internal standard.
[b] Combined ^{1}H NMR yields of both diastereoisomers



Suzuki-Miyaura Cross-Coupling

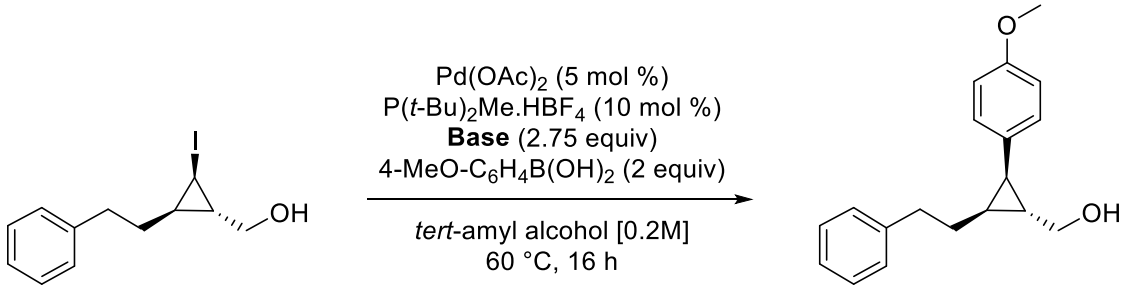
Temperature Screening



Entry	Temperature (°C)	Yield (%)[a]	SM (%)[a]
1	rt	0	100
2	45 °C	0	100
3	**60 °C**	**85**	**0**

[a]Average of two runs. Determined by ^{1}H NMR (Ph_3CH used as internal standard).

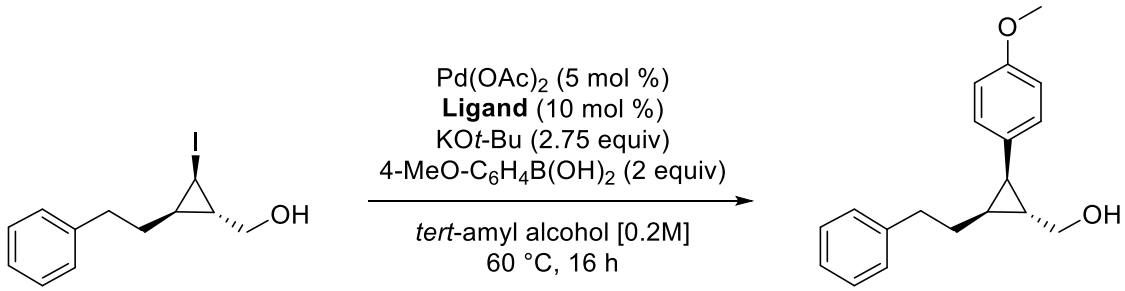
Base Screening



Entry	Base	Yield (%)[a]	SM (%)[a]
1	**KO*t*-Bu**	**90**	**0**
2	KOH	52	30
3	Cs_2CO_3	0	100
4	K_3PO_4	0	100

[a]Average of two runs. Determined by ^{1}H NMR (Ph_3CH used as internal standard).

Ligand Screening



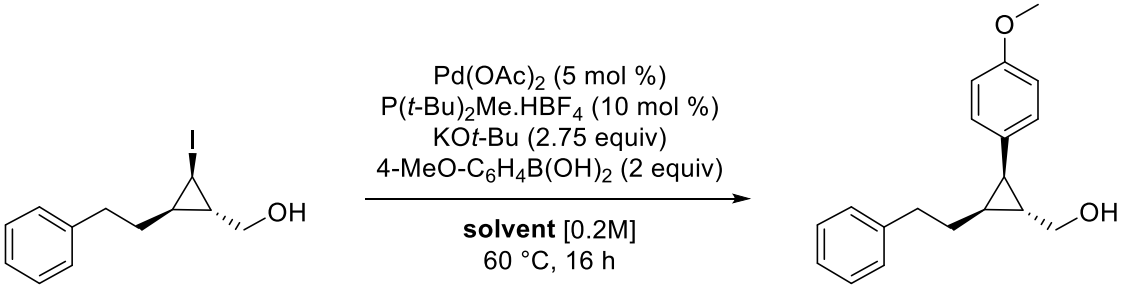
Entry	Ligand	Yield (%)[a]	SM (%)[a]
1	**P(*t*-Bu)$_2$Me.HBF$_4$**	**90**	**0**
2	P(*t*-Bu)$_3$.HBF$_4$	0	54
3	PCy$_3$	66	0
4	PPh$_3$	20	10
5	XPhos	80	0
6	SPhos	76	0
7	PhDavePhos	62	0

[a]Average of two runs. Determined by ^{1}H NMR (Ph$_3$CH used as internal standard).

Entry	Pd/L ratio	Yield (%)[a]	SM (%)[a]
1	**1:2**	**90**	**0**
2	1:1	78	0
3	1:3	67	14

[a]Average of two runs. Determined by ^{1}H NMR (Ph$_3$CH used as internal standard).

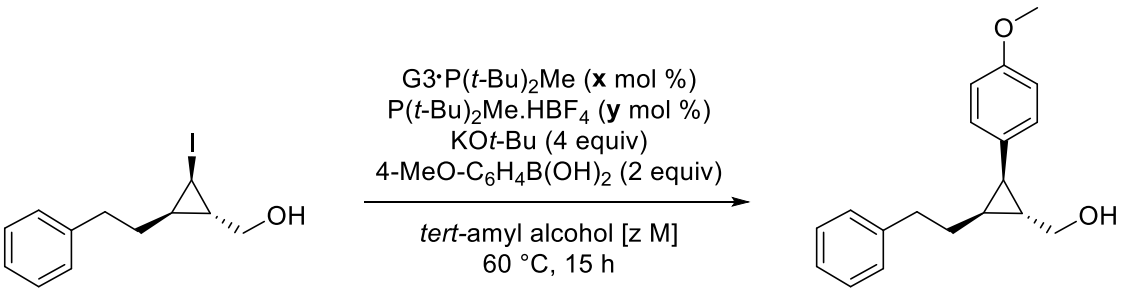
Solvent Screening



Entry	Solvent	Yield (%)[a]	SM (%)[a]
1	***tert*-amyl-alcohol**	**90**	**0**
2	*tert*-butanol	88	0
3	n-butanol	44	44
4	methanol	0	90

[a] Average of two runs. Determined by ^{1}H NMR (Ph$_3$CH used as internal standard).

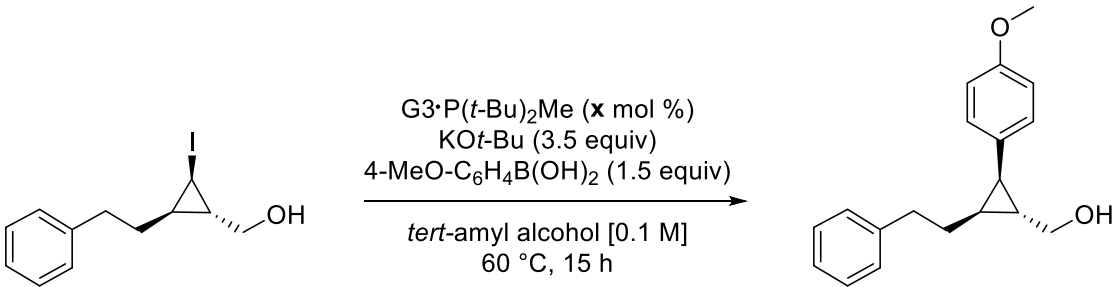
Use of the 3rd Generation of Buchwald Precatalyst as the Palladium Source



Entry	x (mol %)	y (mol %)	Pd/L ratio	z [M]	Yield (%)[a]	SM (%)[a]
1	5 mol %	-	1:1	0.2M	72	0
2	5 mol %	5 mol %	1:2	0.2M	78	0
3	5 mol %	10 mol %	1:3	0.2M	67	0
4	10 mol %	10 mol %	1:2	0.2M	74	0
5	5 mol %	5 mol %	1:2	0.1M	84	0
6	5 mol %	5 mol %	1:2	0.05M	83	0
7	**5 mol %**	**-**	**1:1**	**0.1M**	**82**	**0**

[a]Average of two runs. Determined by ^{1}H NMR (Ph_3CH used as internal standard).

Final optimization



Entry	x (mol %)	Yield (%)[a]	SM (%)[a]
1	5 mol %	80	0
2	2.5 mol %	80	0

[a]Average of two runs. Determined by ^{1}H NMR (Ph_3CH used as internal standard).

Synthetic Procedures

Procedure A: Enantioselective Iodocyclopropanation

In a round-bottomed flask was added the chosen substrate (1.0 mmol, 1.0 equiv), dioxaborolane (298 mg, 1.1 mmol, 1.1 equiv), and anhydrous CH_2Cl_2 (2 mL). In a glovebox, a round-bottomed flask was charged with zinc iodide (479 mg, 1.5 mmol, 1.5 equiv), sealed and removed, and to this was added Et_2O (0.63 mL, 6.1 mmol, 6.1 equiv) and CH_2Cl_2 (6 mL). Diethylzinc (154 µL, 1.5 mmol, 1.5 equiv) was then added neat. Upon observation of full dissolution of the reaction mixture (about 1 hour), the flask was cooled down to 0 °C with a water/ice bath, briefly opened and iodoform (1.18 g, 3.0 mmol, 3.0 equiv) was added in one portion. The mixture was stirred at this temperature for 10 minutes and the content of the first flask (mixture of the substrate and dioxaborolane in CH_2Cl_2) was then added via cannula. After 5 minutes, the bath was removed and the reaction mixture was allowed to warm up to room temperature and stirred for 14 hours. Upon reaction completion, it was quenched with 10% aqueous HCl, and diluted with Et_2O. The layers were separated, and the aqueous one was extracted with Et_2O (2 x 20 mL). The organic layers were combined and a solution of 6 mL of hydrogen peroxide (30% in water) and 18 mL of NaOH 2M was added. The mixture was stirred for 5 minutes and the organic layer was separated and washed successively with 10% aqueous HCl, saturated $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The crude product was then purified by dihydroxylation (to destroy the starting alkene, if needed) and silica-gel chromatography.

Procedure B: Racemic Iodocyclopropanation

Racemic compounds for all products except product **4h** were synthetized following procedure **A**, omitting the dioxaborolane auxiliary. Racemic compound for product **4h** was synthetized following procedure **A** using racemic dioxaborolane.

Procedure C: Dihydroxylation

The crude reaction mixture was dissolved in acetone (2 mL) and water (2 mL). To this stirred solution was added potassium osmate dihydrate (0.005 mmol), followed by a solution of NMO (N-methyl morpholine oxide) in water (0.1 mL, 0.4 mmol, 50 wt%). The reaction mixture was stirred overnight, and upon completion was quenched with saturated Na_2SO_3 (aq., 5 mL) and extracted with Et_2O (2 x 30 mL). The organic layers were combined and washed with 10% aqueous HCl and brine, dried over anhydrous $MgSO_4$, and the solvent removed under vacuum. The product was purified by silica-gel chromatography.

General procedure D: Suzuki-Miyaura Cross-Coupling

In a 10 mL round-bottomed flask was weighted the chosen substrate (0.4 mmol, 1.0 equiv), the chosen boronic acid (0.6 mmol, 1.5 equiv), the pre-catalyst (0.01 mmol, 0.025 equiv) and the KOt-Bu (1.4 mmol, 3.5 equiv). The flask was then flushed with argon during 20 minutes and then freshly distilled and degassed *tert*-amyl alcohol (4 mL) was added. The resulting heterogeneous

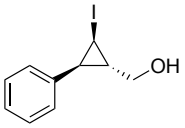
mixture was stirred under an argon atmosphere at 60 °C for 15 hours. Upon completion, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and diluted with Et_2O. The layers were separated, and the aqueous one extracted twice with Et_2O. The organic layers were combined and a solution of 5 mL of hydrogen peroxide (30% in water) and 15 mL of NaOH 2M was added in one portion. The bi-phasic mixture was vigorously stirred for 5 minutes and the organic layer was separated and washed successively with HCl 2M, saturated $NaHCO_3$ and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered over a short pad of a mixture celite/silica with copious washing (Et_2O or EtOAc) and concentrated under vacuum. The crude product was then purified by silica-gel chromatography.

Procedure E: Synthesis of Pre-catalyst **2**

The compound **2** was synthetized according to a modified procedure described by Buchwald *et al*.[1] In a glove-box, a 10 mL round-bottomed flask equipped with a magnetic stir bar was charged with the μ-OMs dimer – 2-ammoniumbiphenyl mesylate (1.0 equiv) and P(*t*-Bu)$_2$Me (1.0 equiv). The flask was removed from the glovebox, freshly distilled THF was added and the reaction mixture was stirred overnight at room temperature. The solvent was then removed under vacuum until ~10% remained. The residue was then triturated with pentane and the resulting solid was isolated *via* filtration and dried under vacuum overnight.

Compounds characterizations

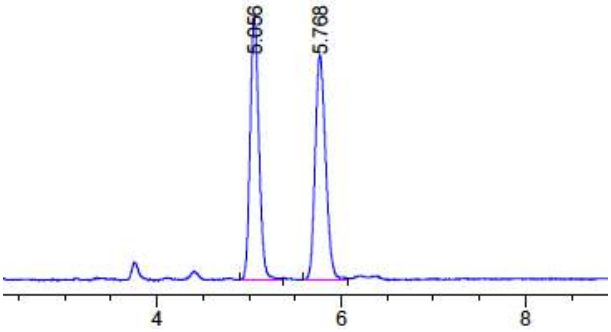
Iodocyclopropanes



((1S,2R,3S)-2-iodo-3-phenylcyclopropyl)methanol (4a): Synthesized according to general procedure **A** using (*E*)-cinnamyl alcohol (134.7 mg, 1.0 mmol) as starting material. Purified by flash column chromatography using a gradient from 15:5 CH_2Cl_2/Hexanes to 15:4:1 CH_2Cl_2/Hexanes/Et_2O as eluent. The product was isolated as an orange oil in 75% yield (206.0 mg, 0.75 mmol). The diastereomeric ratio (8:1) was determined by ^{1}H NMR on the crude mixture. The enantiomeric excess (98% *ee*) was determined by chiral SFC (Chiralpak AD-H 25 cm, 10% MeOH, 30 °C, 150 bar): t.r.$_{min}$ 5.0 min; t.r.$_{maj}$ 5.7 min. The characterization data match the literature.[2]

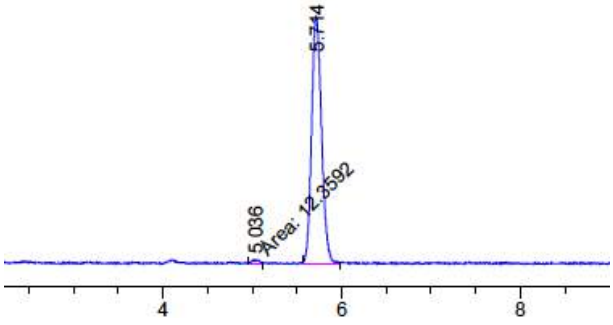
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 3H), 7.22 – 7.14 (m, 2H), 3.82 (dd, *J* = 11.4, 6.0 Hz, 1H), 3.77 (dd, *J* = 11.4, 6.1 Hz, 1H), 2.92 (dd, *J* = 8.3, 4.7 Hz, 1H), 2.08 – 1.99 (m, 1H), 1.92 (qd, *J* = 6.1, 4.8 Hz, 1H), 1.55 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.5, 129.0, 128.2, 127.2, 64.7, 30.5, 26.1, -2.6.

Racemate

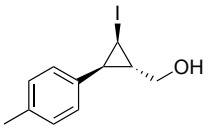


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.056	VB	0.1037	1815.68689	272.74869	49.6523
2	5.768	BV	0.1221	1841.11707	233.13054	50.3477

Enantiopure



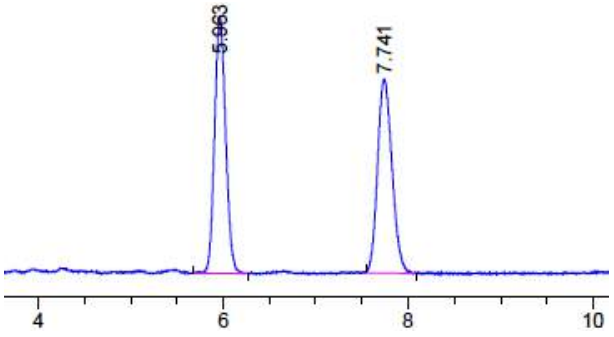
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.036	MM	0.0838	12.35921	2.45668	1.0435
2	5.714	BB	0.1200	1172.03259	151.96381	98.9565



((1S,2R,3S)-2-iodo-3-(*p*-tolyl)cyclopropyl)methanol (4b): Synthesized according to general procedure **A** using (*E*)-3-(p-tolyl)prop-2-en-1-ol[3] (147.9 mg, 1.0 mmol) as starting material. Purified by flash column chromatography using a gradient from 15:5 CH_2Cl_2/Hexanes to 15:4:1 CH_2Cl_2/Hexanes/ Et_2O as eluent. The product was isolated in 73% (210.4 mg, 0.73 mmol) yield as an off-white solid. The diastereomeric ratio (9:1) was determined by ^{1}H NMR on the crude mixture. The enantiomeric excess (96% *ee*) was determined by chiral SFC (Chiralpak AD-H 25 cm, 10% MeOH, 30 °C, 150 bar): $t.r._{min}$ 6.0 min; $t.r._{maj}$ 7.7 min. The characterization data match the literature.[2]

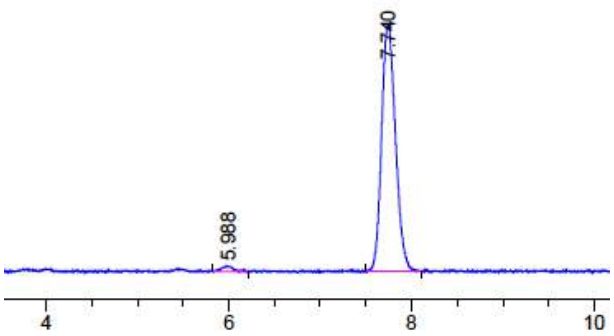
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 3.80 (dd, *J* = 11.4, 6.0 Hz, 1H), 3.74 (dd, *J* = 11.4, 6.2 Hz, 1H), 2.89 (dd, *J* = 8.2, 4.7 Hz, 1H), 2.35 (s, 3H), 2.04 – 1.94 (m, 1H), 1.92 – 1.82 (m, 1H), 1.65 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.7, 135.4, 128.9, 128.8, 64.7, 30.4, 25.8, 21.3, -2.2.

Racemate

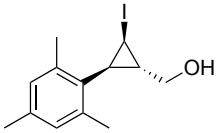


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.963	BB	0.1316	836.67291	100.02502	50.3195
2	7.741	BB	0.1691	826.04840	75.84184	49.6805

Enantiopure



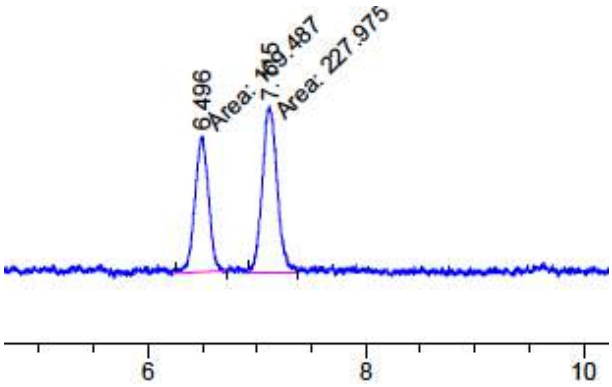
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.988	BB	0.1159	17.19355	1.85956	1.7937
2	7.740	BB	0.1651	941.38440	89.22548	98.2063



((1S,2R,3S)-2-iodo-3-mesitylcyclopropyl)methanol (4c) : Synthesized according to general procedure **A** using (*E*)-3-mesitylprop-2-en-1-ol[4] (177.4 mg, 1.0 mmol) as starting material. Purified by flash column chromatography using a gradient from 15:5 CH_2Cl_2/Hexanes to 15:4:1 CH_2Cl_2/Hexanes/Et_2O as eluent. The product was isolated in 82% yield (262 mg, 0.83 mmol) as an off-white solid. The diastereomeric ratio (>20:1) was determined by ^{1}H NMR on the crude mixture. The enantiomeric excess (99% *ee*) was determined by chiral SFC (Chiralpak OJ-H 25 cm, 4% MeOH, 35 °C, 150 bar): t.r.$_{min}$ 6.5 min; t.r.$_{maj}$ 7.1 min. The characterization data match the litterature.[2]

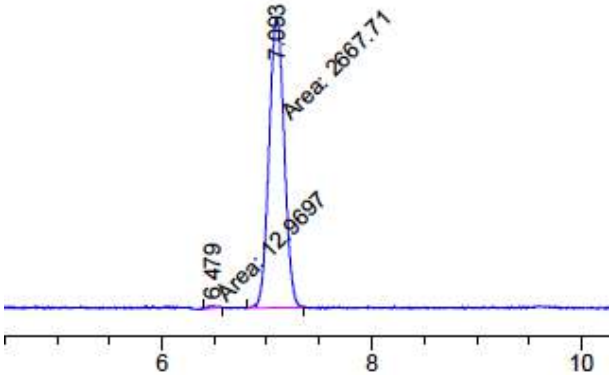
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 3.99 (dd, *J* = 11.5, 5.4 Hz, 1H), 3.74 (dd, *J* = 11.5, 6.5 Hz, 1H), 2.92 (dd, *J* = 7.7, 4.3 Hz, 1H), 2.33 (s, 6H), 2.27 (s, 3H), 1.99 – 1.89 (m, 1H), 1.73 (app. t, J = 7.5 Hz, 1H), 1.54 (br s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 136.5, 132.8, 129.5, 65.0, 34.6, 23.3, 21.2, 21.1, -3.0.

Racemate

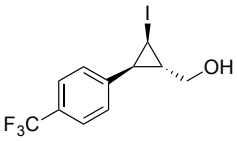


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.496	MM	0.1440	169.48746	19.61032	42.6424
2	7.115	MM	0.1597	227.97493	23.79104	57.3576

Enantiopure

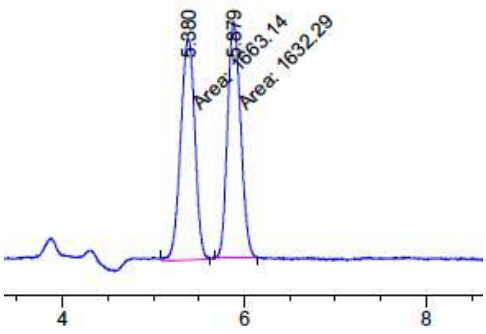


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.479	MM	0.1053	12.96966	2.05368	0.4838
2	7.093	MM	0.1679	2667.71094	264.77679	99.5162



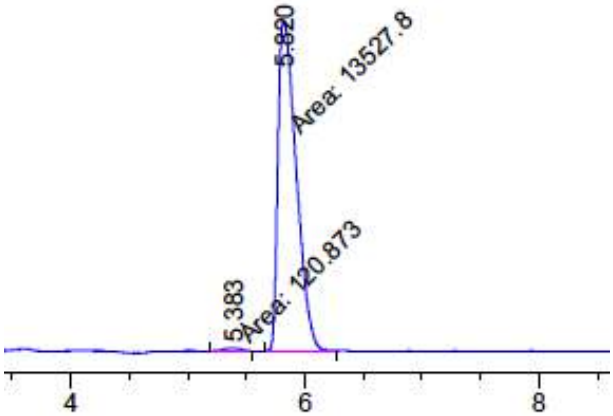
((1*S*,2*R*,3*S*)-2-iodo-3-(4-(trifluoromethyl)phenyl)cyclopropyl)methanol (4d) : Synthesized according to general procedure **A** using (*E*)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol[5] (200.9 mg, 1.0 mmol) as starting material. Purified by dihydroxilation (general procedure **C**) and flash column chromatography using a gradient from 15:5 CH_2Cl_2/Hexanes to 15:4:1 CH_2Cl_2/Hexanes/Et_2O as eluent. The product was isolated in 64% yield (217.5 mg, 0.64 mmol) as a clear yellow oil. The diastereomeric ratio (11:1) was determined by ^{1}H NMR on the crude mixture. The enantiomeric excess (98% *ee*) was determined by chiral SFC (Chiralpak AD-H 25cm, 5% MeOH, 30 °C, 150 bar): tr_{min}: 5.4 min; tr_{maj}: 5.8 min.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 3.84 (dd, J = 9.9, 4.3 Hz, 1H), 3.81 (dd, J = 9.9, 4.3 Hz, 1H), 2.96 (dd, J = 8.3, 4.8 Hz, 1H), 2.14 – 2.06 (m, 1H), 1.98 – 1.86 (m, 1H), 1.82 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.7 (Cq), 129.3 (CH), 126.2 (Cq), 125.1 (q, CH, *J* = 3.7 Hz), 122.6 (Cq), 64.1 (CH_2), 30.9 (CH), 25.7 (CH), -3.6 (CH). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.48. **FTIR (cm^{-1}) (neat):** 3311, 2928, 2874, 1617, 1322, 1111, 844, 596. **HRMS (ESI, Pos)** calculated for $C_{11}H_{10}F_3IONa$ $[M+Na]^+$: 364.96206 m/z, found 364.96111 m/z. **$[a]_D^{20}$** = +42.8 (c 0.73, $CHCl_3$). **Rf =** 0.24 (30% AcOEt in Hexanes).

Racemate

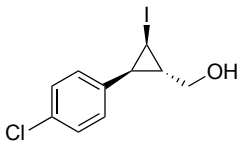


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.380	MM	0.1816	1663.14441	152.63048	50.4681
2	5.879	MM	0.1672	1632.28931	162.67099	49.5319

Enantiopure



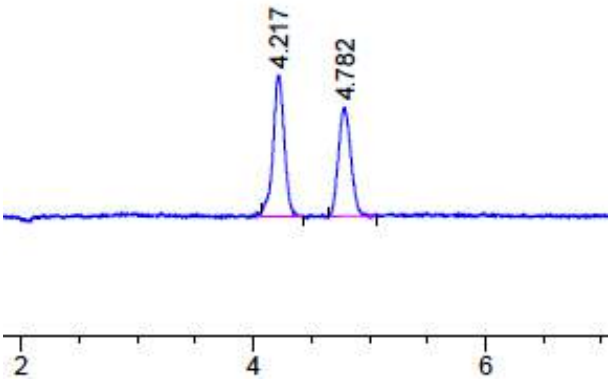
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.383	MM	0.1624	120.87253	12.40739	0.8856
2	5.820	MM	0.1807	1.35278e4	1247.82654	99.1144



((1S,2R,3S)-2-iodo-3-(4-chlorophenyl)cyclopropyl)methanol (4e): Synthesized according to general procedure **A** using (*E*)-3-(4-chlorophenyl)prop-2-en-1-ol[6] (167.2 mg, 1.0 mmol) as starting material. Purified by flash column chromatography using a gradient from 15:5 CH_2Cl_2/Hexanes to 15:4:1 CH_2Cl_2/Hexanes/Et_2O as eluent. The product was isolated as a clear oil in 78% yield (239.3 mg, 0.78 mmol). The diastereomeric ratio (11:1) was determined by ^{1}H NMR on the crude mixture. The enantiomeric excess (98% *ee*) was determined by chiral SFC (Chiralpak AD-H 25 cm, 15% MeOH, 30 °C, 150 bar): t.r.$_{min}$ 4.8 min; t.r.$_{maj}$ 4.2 min. The characterization data match the literature.[2]

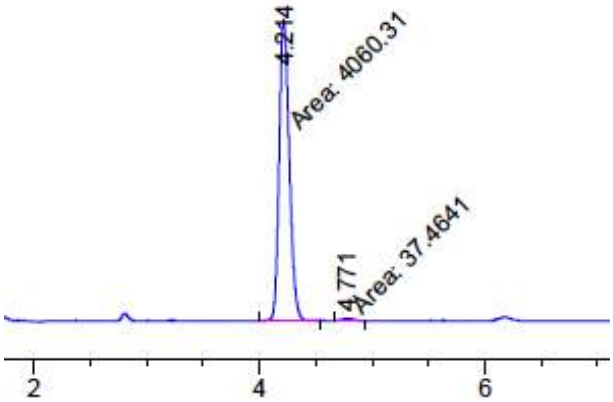
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 3.82 – 3.72 (m, 2H), 2.90 (dd, *J* = 8.2, 4.8 Hz, 1H), 2.07 – 1.93 (m, 1H), 1.84 (dt, *J* = 12.1, 6.0 Hz, 1H), 1.77 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.1, 132.9, 130.33, 128.35, 64.3, 30.7, 25.4, -3.0.

Racemate

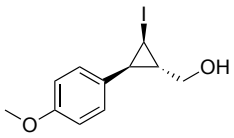


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.217	BB	0.1027	123.21451	18.26631	53.9075
2	4.782	BB	0.1153	105.35188	14.08072	46.0925

Enantiopure



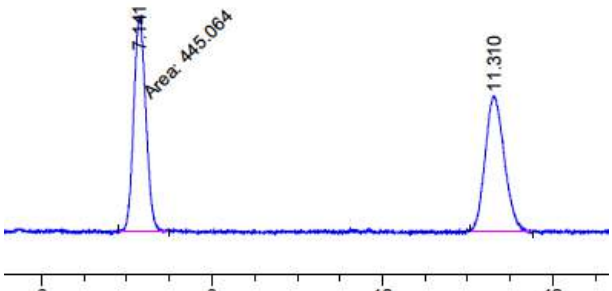
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.214	MM	0.1044	4060.31445	648.35876	99.0857
2	4.771	MM	0.1177	37.46406	5.30538	0.9143



((1S,2R,3S)-2-iodo-3-(4-methoxyphenyl)cyclopropyl)methanol (4f): Synthesized according to general procedure **A** using (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol[6] (166.2 mg, 1.0 mmol) as starting material. Purified by flash column chromatography using a gradient from 15:5 CH_2Cl_2/Hexanes to 15:4:1 CH_2Cl_2/Hexanes/Et_2O as eluent. The product was isolated in 67% yield (204.8 mg, 0.67 mmol) as a dark-green oil. The diastereomeric ratio (9:1) was determined by ^{1}H NMR on the crude mixture. The enantiomeric excess (>99% *ee*) was determined by chiral SFC (Chiralpak AD-H 25 cm, 10% MeOH, 30 °C, 150 bar): t.r.$_{min}$ 11.3 min ; t.r.$_{maj}$ 7.3 min. The characterization data match the literature.[2]

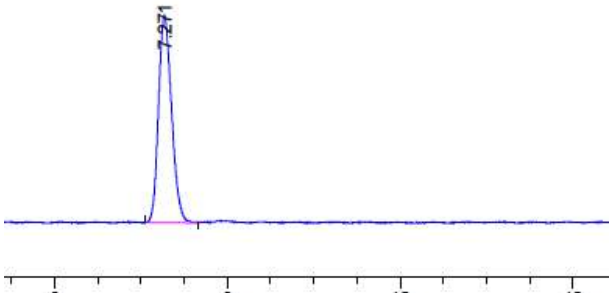
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 3.85 – 3.77 (m, 4H), 3.74 (dd, J = 11.4, 6.1 Hz, 1H), 2.88 (dd, J = 8.1, 4.7 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.84 (qd, J = 6.2, 4.7 Hz, 1H), 1.61 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.7, 130.7, 130.1, 113.6, 64.8, 55.4, 30.6, 25.4, -1.9.

Racemate



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.141	MM	0.1662	445.06360	44.64054	50.1111
2	11.310	BB	0.2120	443.08978	28.09781	49.8889

Enantiopure

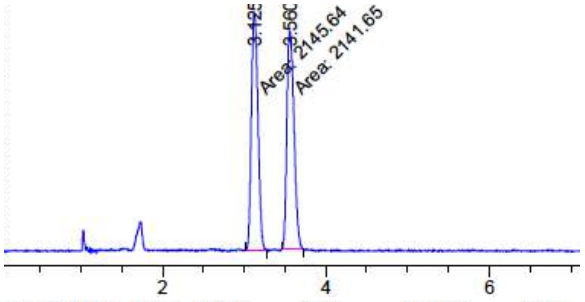


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.271	BB	0.1611	3078.40405	291.67294	100.0000

((1S,2R,3R)-2-iodo-3-propylcyclopropyl)methanol (4g): Synthesized according to general procedure **A** using (*E*)-2-Hexen-1-ol (0.12 mL, 1.0 mmol) as starting material. Purified by flash column chromatography using a gradient from 15:5 CH_2Cl_2/Hexanes to 15:4:1 CH_2Cl_2/Hexanes/Et_2O as eluent. The product was isolated in 65 % yield (157.1 mg, 0.65 mmol) as a yellow oil. The diastereomeric ratio (6:1) was determined by ^{1}H NMR on the crude mixture. The enantiomeric excess (94% *ee*) was determined by chiral SFC (Chiralpak AD-H 25 cm, 8% iPrOH, 30 °C, 150 bar): $t.r._{min}$ 3.1 min ; $t.r._{maj}$ 3.6 min. The characterization data match the literature.[2]

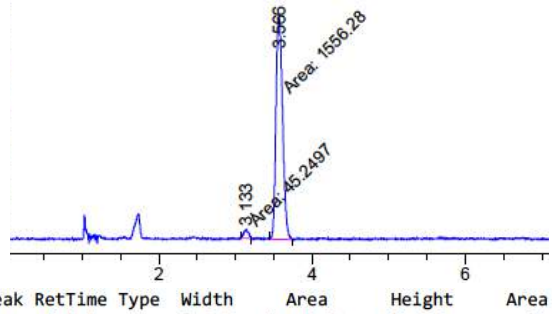
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.59 (dd, *J* = 11.4, 6.4 Hz, 1H), 3.54 (dd, *J* = 11.4, 6.6 Hz, 1H), 2.54 (dd, *J* = 7.8, 4.3 Hz, 1H), 1.63 – 1.33 (m, 5H), 1.13 (qd, *J* = 6.3, 4.4 Hz, 1H), 0.97 (t, *J* = 7.0 Hz, 3H), 0.54 – 0.41 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 65.3, 36.5, 31.7, 21.9, 20.9, 14.0, -4.0.

Racemate



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.125	MM	0.0938	2145.63843	381.23080	50.0465
2	3.560	MM	0.1019	2141.65210	350.12872	49.9535

Enantiopure

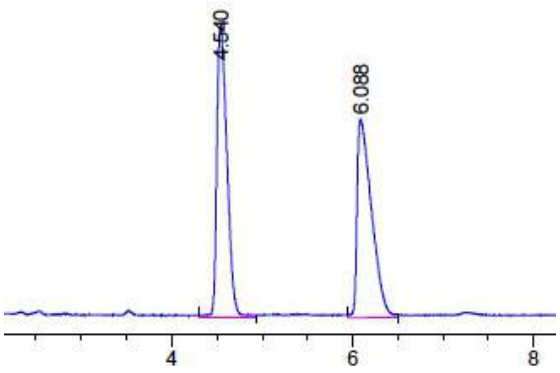


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.133	MM	0.0784	45.24966	9.62254	2.8254
2	3.566	MM	0.1005	1556.28479	258.05676	97.1746

((1*S*,2*R*,3*S*)-2-iodo-3-propylcyclopropyl)methanol (4h): Synthesized according to general procedure **A** using (*Z*)-Hex-2-en-1-ol (0.12 mL, 1.0 mmol) as starting material. Purified by flash column chromatography using a gradient from 0 to 30% Et_2O in Hexanes as eluent. The product was isolated in 50% yield (121.3 mg, 0.50 mmol) as an orange oil. The diastereomeric ratio (3:1) was determined by ^{1}H NMR on the crude mixture. The enantiomeric excess (>99% *ee*) was determined by SFC (Chiralpak AD-H 25 cm, 5% iPrOH, 30 °C, 150 bar): $t.r._{min}$ 6.1 min; $t.r._{maj}$ 4.5 min. The characterization data match the literature.[2]

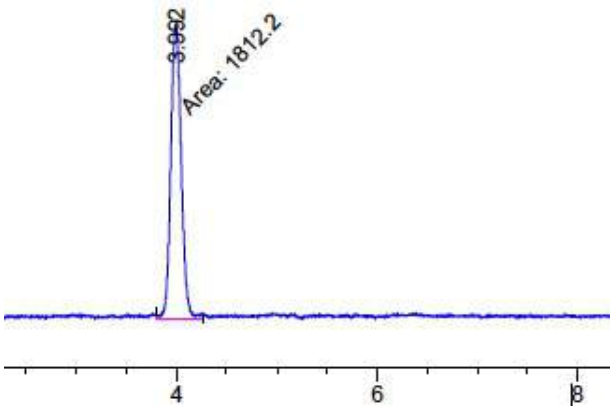
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (dd, *J* = 11.6, 6.9 Hz, 1H), 3.62 (dd, *J* = 11.6, 7.8 Hz, 1H), 2.05 (app. t, *J* = 4.1 Hz, 1H), 1.59 – 1.19 (m, 8H), 0.96 (dd, *J* = 9.5, 4.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 61.5, 30.2, 29.8, 28.4, 22.6, 14.1, -11.9.

Racemate

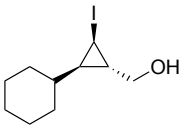


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.540	VV	0.1220	5836.49902	740.48187	51.0328
2	6.088	VV	0.1625	5600.26123	500.50427	48.9672

Enantiopure



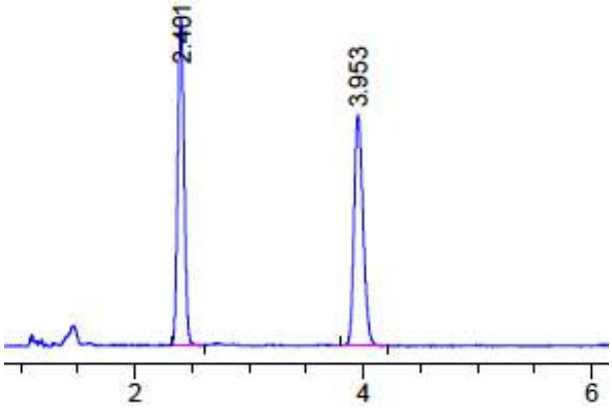
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.992	MM	0.1205	1812.20093	250.71072	100.0000



((1S,2R,3R)-2-iodo-3-cyclohexylcyclopropyl)methanol (4i): Synthesized according to general procedure A using (*E*)-3-cyclohexylprop-2-en-1-ol[6] (145.6 mg, 1.0 mmol) as starting material. Purified by flash column chromatography using a gradient from 15:5 CH_2Cl_2/Hexanes to 15:4:1 CH_2Cl_2/Hexanes/Et_2O as eluent. The product was isolated in 56% yield (163.8 mg, 0.58 mmol) as an orange oil. The diastereomeric ratio (5:1) was determined by ^{1}H NMR on the crude mixture. The enantiomeric excess (95% *ee*) was determined by chiral SFC-MS (Chiralpak AD-H 25 cm, 15% MeOH, 30 °C, 150 bar): t.r.$_{min}$ 4.0 min ; t.r.$_{maj}$ 2.4 min. The characterization data match the literature.[2]

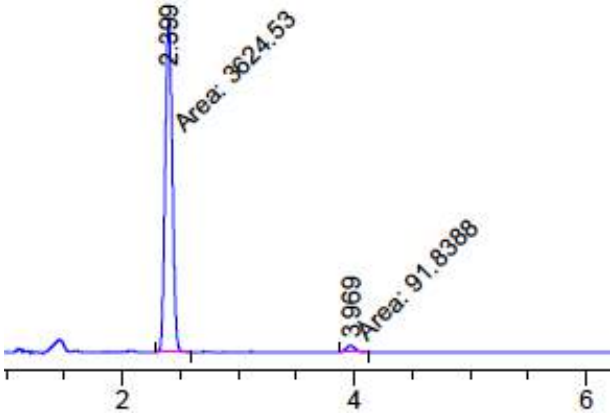
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 – 3.46 (m, 2H), 2.52 (dd, *J* = 7.7, 4.3 Hz, 1H), 2.02 – 1.88 (m, 1H), 1.85 – 1.60 (m, 4H), 1.38 (s, 1H), 1.34 – 1.10 (m, 5H), 1.05 – 0.89 (m, 2H), 0.21 (ddd, *J* = 9.2, 7.8, 6.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 65.5, 42.9, 32.6, 31.8, 30.8, 27.1, 26.5, 26.3, 25.8, -5.1.

Racemate

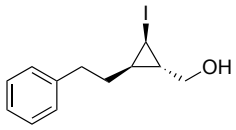


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.401	BB	0.0620	1102.15503	279.83282	50.4479
2	3.953	VB	0.0860	1082.58496	197.37300	49.5521

Enantiopure

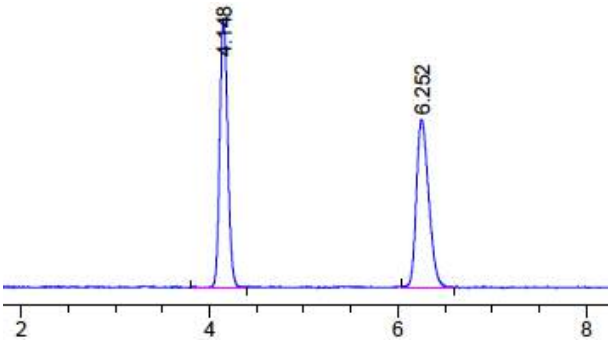


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.399	MM	0.0716	3624.53369	844.14752	97.5288
2	3.969	MM	0.0900	91.83877	17.01105	2.4712



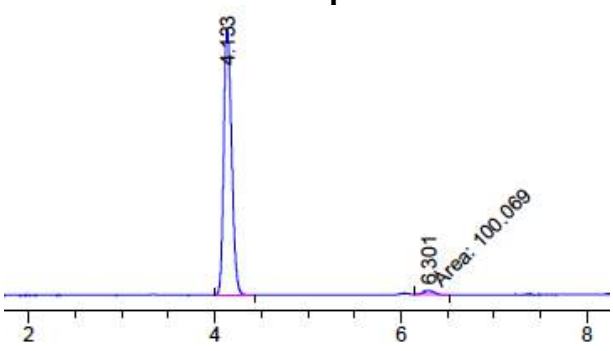
((1S,2R,3S)-2-iodo-3-phenethylcyclopropyl)methanol (4j): Synthesized according to general procedure **A** using (*E*)-5-phenylpent-2-en-1-ol[6] (161.0 mg, 1.0 mmol) as starting material. Purified by flash column chromatography using a gradient from 15:5 CH_2Cl_2/Hexanes to 15:4:1 CH_2Cl_2/Hexanes/Et_2O as eluent. The product was isolated in 61% yield (184.0 mg, 0.61 mmol) as a yellow oil. The diastereomeric ratio (4:1) was determined by ^{1}H NMR on the crude mixture. The enantiomeric excess (96% *ee*) was determined by chiral SFC (Chiralpak AD-H 25cm, 15% MeOH, 30 °C, 150 bar): tr_{min}: 6.3 min; tr_{maj}: 4.1 min.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (dd, *J* = 15.8, 7.3 Hz, 3H), 3.52 (dd, *J* = 11.4, 6.4 Hz, 1H), 3.48 (dd, *J* = 11.4, 6.5 Hz, 1H), 2.86 (dt, *J* = 14.2, 7.3 Hz, 1H), 2.71 (dt, *J* = 13.7, 8.0 Hz, 1H), 2.54 (dd, *J* = 7.8, 4.3 Hz, 1H), 1.79 (dd, *J* = 14.9, 7.3 Hz, 2H), 1.35 (br s, 1H), 1.11 (qd, *J* = 6.3, 4.4 Hz, 1H), 0.49 (dt, *J* = 13.8, 6.9 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.7 (Cq), 128.7 (CH), 128.5 (CH), 126.1 (CH), 65.0 (CH_2), 36.3 (CH_2), 34.7 (CH_2), 31.8 (CH), 20.55 (CH), -4.6 (CH). **FTIR (cm^{-1}) (neat):** 3318, 2921, 2855, 1601, 1450, 1232, 1021, 745, 698. **HRMS (ESI, Pos)** calculated for $C_{12}H_{15}IONa$ $[M+Na]^+$: 325.00598 m/z, found 325.00522 m/z. **$[a]_D^{20}$** = –9.9 (c 0.97, $CHCl_3$). **Rf** = 0.31 (30% AcOEt in Hexanes).

Racemate



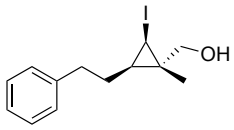
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.148	BB	0.0922	1655.94458	283.14999	50.7410
2	6.252	BB	0.1400	1607.58228	177.00897	49.2590

Enantiopure



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.133	BB	0.0926	4531.39258	770.73126	97.8394
2	6.301	MM	0.1419	100.06880	11.75647	2.1606

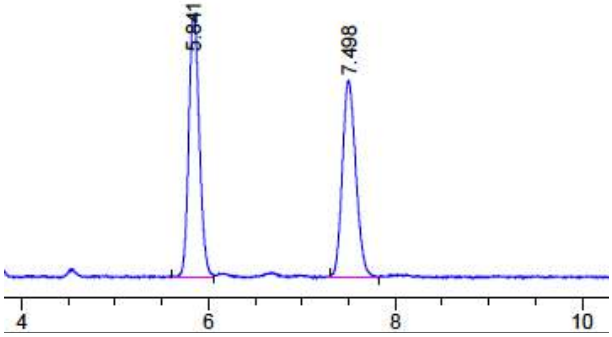
This product was also synthesized on a gram-scale using (E)-5-phenylpent-2-en-1-ol (1.005 g, 6.2 mmol). The product was isolated in 56% yield (1.04 g, 3.4 mmol).



((1S,2R,3R)-2-iodo-1-methyl-3-phenethylcyclopropyl)methanol (4k): Synthesized according to general procedure **A** using (*E*)-2-methyl-5-phenylpent-2-en-1-ol[7] (178.6 mg, 1.0 mmol) as starting material. Purified by flash column chromatography using a gradient from 15:5 CH_2Cl_2/Hexanes to 15:4:1 CH_2Cl_2/Hexanes/Et_2O as eluent. The product was isolated in 64% yield (205.0 mg, 0.65 mmol) as a clear orange oil. The diastereomeric ratio (20:1) was determined by ^{1}H NMR on the crude mixture. The enantiomeric excess (92% *ee*) was determined by chiral SFC (Chiralpak AD-H 25cm, 10% MeOH, 30 °C, 150 bar): tr_{min}: 7.5 min; tr_{maj}: 5.8 min. The characterization data match the literature.[2]

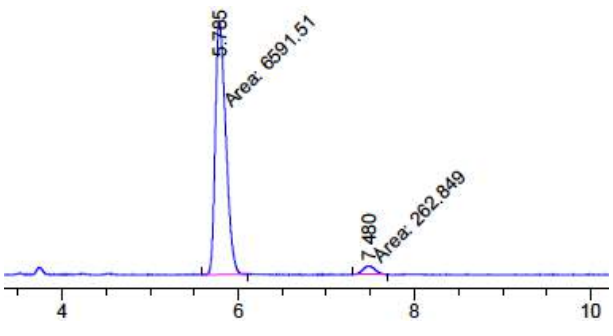
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 3.51 – 3.30 (m, 2H), 2.84 (d, *J* = 8.2 Hz, 1H), 2.81 – 2.73 (m, 1H), 2.64 (ddd, *J* = 13.6, 8.9, 7.1 Hz, 1H), 1.74 – 1.54 (m, 2H), 1.44 (s, 1H), 1.08 (s, 3H), 0.71 (dd, *J* = 15.0, 7.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.9, 128.7, 128.5, 126.1, 70.3, 34.9, 31.8, 25.0, 23.2, 16.8, 8.0.

Racemate



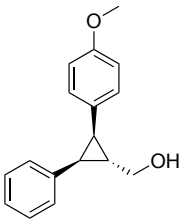
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.841	BV	0.1240	1087.57434	137.90685	51.0530
2	7.498	BV	0.1600	1042.71094	103.11959	48.9470

Enantiopure

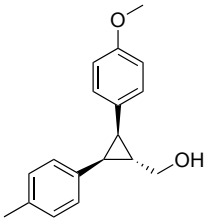


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.785	MM	0.1379	6591.51123	796.68549	96.1652
2	7.480	MM	0.1610	262.84909	27.21029	3.8348

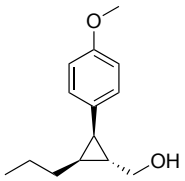
Cross-coupling Products



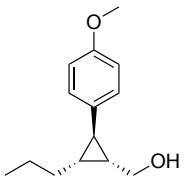
((1R,2R,3S)-2-(4-methoxyphenyl)-3-phenylcyclopropyl)methanol (5a): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-phenylcyclopropyl)methanol (**4a**) (104.4 mg, 0.38 mmol) as starting material. Purified by flash column chromatography using a gradient from 10% to 20% of EtOAc in Hexanes as eluent. The product was isolated in 52% yield (47.0 mg, 0.18 mmol) as a yellowish solid (**mp:** 88-90 °C).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.02 (m, 3H), 6.95 – 6.89 (m, 2H), 6.89 – 6.83 (m, 2H), 6.70 – 6.61 (m, 2H), 3.84 (d, *J* = 6.6 Hz, 2H), 3.71 (s, 3H), 2.45 – 2.28 (m, 2H), 2.11 – 1.94 (m, 1H), 1.62 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.92 (Cq), 137.74 (Cq), 130.20 (CH), 129.33 (Cq), 128.92 (CH), 127.92 (CH), 125.88 (CH), 113.44 (CH), 66.57 (CH_2), 55.26 (CH_3), 29.34 (CH), 29.16 (CH), 28.06 (CH). **FTIR (cm^{-1}) (neat):** 3285, 2912, 2833, 1513, 1458, 1247, 1018, 737, 696, 541. **HRMS (ESI, Pos)** calculated for $C_{17}H_{18}O_2Na$ $[M+Na]^+$: 277.1199 m/z, found 277.12108 m/z. **$[\alpha]_D^{20}$** = + 22.1 (c 0.51, $CHCl_3$). **Rf** = 0.10 (20% AcOEt in Hexanes).



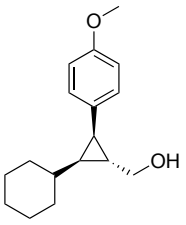
((1R,2R,3S)-2-(4-methoxyphenyl)-3-(p-tolyl)cyclopropyl)methanol (5b): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-(p-tolyl)cyclopropyl)methanol (**4b**) (110.1 mg, 0.38 mmol) as starting material. Purified by flash column chromatography using a gradient from 10% to 20% of EtOAc in Hexanes as eluent. The product was isolated in 38% yield (39.0 mg, 0.15 mmol) as an orange oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 7.9 Hz, 2H), 6.89 – 6.84 (m, 2H), 6.80 (d, *J* = 8.1 Hz, 2H), 6.70 – 6.63 (m, 2H), 3.86 – 3.77 (m, 2H), 3.72 (s, 3H), 2.37 – 2.25 (m, 2H), 2.23 (s, 3H), 2.03 – 1.92 (m, 1H), 1.67 (br, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.87 (Cq), 135.32 (Cq), 134.56 (Cq), 130.16 (CH), 129.54 (Cq), 128.79 (CH), 128.66 (CH), 113.43 (CH), 66.66 (CH_2), 55.26 (CH_3), 29.06 (CH), 29.02 (CH), 28.11 (CH), 21.10 (CH_3). **FTIR (cm^{-1}) (neat):** 3336, 3005, 2921, 1513, 1245, 1031, 827, 767, 526. **HRMS (ESI, Pos)** calculated for $C_{18}H_{20}O_2Na$ $[M+Na]^+$: 291.13555 m/z, found 291.13599 m/z. **$[\alpha]_D^{20}$** = + 14.7 (c 0.46, $CHCl_3$). **Rf** = 0.12 (20% AcOEt in Hexanes).



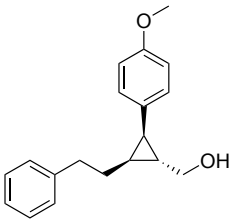
((1R,2R,3S)-2-(4-methoxyphenyl)-3-propylcyclopropyl)methanol (5g): Synthesized according to general procedure **D** using ((1S,2R,3R)-2-iodo-3-propylcyclopropyl)methanol (**4g**) (93.3 mg, 0.39 mmol) as starting material. Purified by flash column chromatography using a gradient from 10% to 20% of EtOAc in Hexanes as eluent. The product was isolated in 74% yield (63.0 mg, 0.29 mmol) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.63 (d, *J* = 6.9 Hz, 2H), 2.01 – 1.89 (m, *J* = 9.0, 5.2 Hz, 1H), 1.47 (s, 1H), 1.38 – 1.24 (m, 3H), 1.19 (dd, *J* = 13.7, 8.0 Hz, 1H), 1.02 – 0.86 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.94 (Cq), 130.61 (Cq), 130.05 (CH), 113.54 (CH), 67.03 (CH_2), 55.38 (CH_3), 30.10 (CH_2), 26.52 (CH), 25.94 (CH), 24.45 (CH), 22.71 (CH_2), 14.07 (CH_3). **FTIR (cm^{-1}) (neat):** 3348, 2955, 2927, 1512, 1244, 1031, 830. **HRMS (ESI, Pos)** calculated for $C_{14}H_{20}O_2Na$ $[M+Na]^+$: 243.13555 m/z, found 243.13639 m/z. **$[\alpha]_D^{20}$** = - 94.6 (c 1.15, $CHCl_3$). **Rf** = 0.19 (20% AcOEt in Hexanes).



((1R,2R,3R)-2-(4-methoxyphenyl)-3-propylcyclopropyl)methanol (5h): Synthesized according to general procedure **D** using ((1*S*,2*R*,3*S*)-2-iodo-3-propylcyclopropyl)methanol (**4h**) (74.6 mg, 0.31 mmol) as starting material. Purified by flash column chromatography using a gradient from 10% to 20% of EtOAc in Hexanes as eluent. The product was isolated in 39% yield (27.0 mg, 0.12 mmol) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.95 (m, 2H), 6.84 – 6.77 (m, 2H), 3.83 (dd, *J* = 11.4, 6.7 Hz, 1H), 3.78 (s, 3H), 3.75 – 3.66 (m, 1H), 1.65 – 1.54 (m, 1H), 1.54 – 1.41 (m, 5H), 1.42 – 1.32 (m, 1H), 1.22 – 1.11 (m, 1H), 0.95 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.81 (Cq), 134.98 (Cq), 127.03 (CH), 113.96 (CH), 62.79 (CH_2), 55.48 (CH_3), 30.74 (CH_2), 29.14 (CH), 27.87 (CH), 27.43 (CH), 23.28 (CH_2), 14.19 (CH_3). **FTIR (cm^{-1}) (neat):** 3342, 2955, 2870, 1513, 1463, 1243, 1031, 824, 524. **HRMS (ESI, Pos)** calculated for $C_{14}H_{20}O_2Na$ $[M+Na]^+$: 243.13555 m/z, found 243.1363 m/z. **$[\alpha]_D^{20}$** = - 11.1 (c 0.20, $CHCl_3$). **Rf** = 0.17 (20% AcOEt in Hexanes).

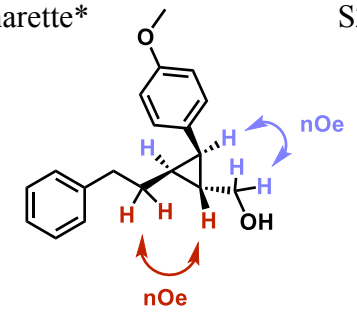


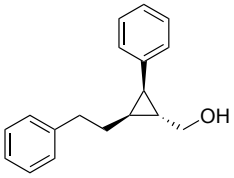
((1R,2S,3R)-2-cyclohexyl-3-(4-methoxyphenyl)cyclopropyl)methanol (5i): Synthesized according to general procedure **D** using ((1S,2R,3R)-2-iodo-3-cyclohexylcyclopropyl)methanol (**4i**) (91.0 mg, 0.32 mmol) as starting material. Purified by flash column chromatography using a gradient from 10% to 20% of EtOAc in Hexanes as eluent. The product was isolated in 74% yield (54.0 mg, 0.21 mmol) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.65 (dd, *J* = 11.2, 6.8 Hz, 1H), 3.54 (dd, *J* = 11.2, 7.1 Hz, 1H), 1.99 (dd, *J* = 9.1, 5.3 Hz, 1H), 1.81 – 1.59 (m, 2H), 1.59 – 1.34 (m, 5H), 1.20 – 1.00 (m, 3H), 0.98 – 0.79 (m, 2H), 0.74 (td, *J* = 9.6, 5.2 Hz, 1H), 0.68 – 0.50 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.85 (Cq), 130.49 (Cq), 129.73 (CH), 113.50 (CH), 67.10 (CH_2), 55.37 (CH_3), 35.77 (CH), 33.51 (CH_2), 32.57 (CH_2), 32.01 (CH), 26.51 (CH_2), 26.29 (CH_2), 26.22 (CH), 25.99 (CH_2), 25.02 (CH). **FTIR (cm^{-1}) (neat):** 3251, 2919, 2845, 1512, 1246, 1034, 831. **HRMS (ESI, Pos)** calculated for $C_{17}H_{24}O_2Na$ $[M+Na]^+$: 283.16685 m/z, found 283.16704 m/z. **$[\alpha]_D^{20}$ = -** 76.1 (c 0.53, $CHCl_3$). **Rf =** 0.20 (20% AcOEt in Hexanes).



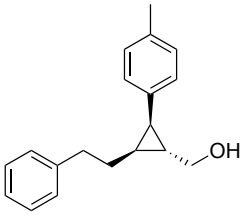
((1R,2R,3S)-2-(4-methoxyphenyl)-3-phenethylcyclopropyl)methanol (5j): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-phenethylcyclopropyl)methanol (**4j**) (117.4 mg, 0.39 mmol) as starting material. Purified by flash column chromatography using a gradient from 10% to 20% of EtOAc in Hexanes as eluent. The product was isolated in 80% yield (88.0 mg, 0.31 mmol) as a yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, J = 11.9, 4.5 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.16 – 7.11 (m, 2H), 7.08 (d, J = 7.0 Hz, 2H), 6.88 – 6.82 (m, 2H), 3.82 (s, 3H), 3.65 (dd, J = 11.2, 6.7 Hz, 1H), 3.56 (dd, J = 11.2, 7.0 Hz, 1H), 2.75 – 2.49 (m, 2H), 2.01 (dd, J = 9.2, 5.2 Hz, 1H), 1.55 (dq, J = 8.3, 6.4 Hz, 1H), 1.46 – 1.23 (m, 3H), 1.07 – 0.97 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.03 (Cq), 142.25 (Cq), 130.23 (Cq), 130.01 (CH), 128.56 (CH), 128.41 (CH), 125.89 (CH), 113.64 (CH), 66.76 (CH_2), 55.40 (CH_3), 35.64 (CH_2), 29.98 (CH_2), 26.53 (CH), 25.74 (CH), 24.12 (CH). **FTIR (cm^{-1}) (neat):** 3359, 2927, 2856, 1512, 1454, 1244, 1171, 1030, 833, 749, 698. **HRMS (ESI, Pos)** calculated for $C_{19}H_{22}O_2Na$ $[M+Na]^+$: 305.1512 m/z, found 305.15185 m/z. **$[\alpha]_D^{20}$ = -** 73.0 (c 0.65, $CHCl_3$). **Rf =** 0.12 (20% AcOEt in Hexanes).

The relative stereochemistry was verified by NOE experiment:

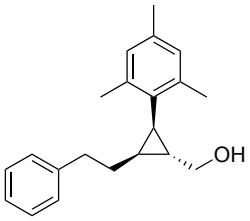




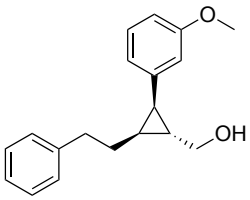
((1R,2S,3R)-2-phenethyl-3-phenylcyclopropyl)methanol (6a): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-phenethylcyclopropyl)methanol (**4j**) (92.1 mg, 0.31 mmol) as starting material. Purified by flash column chromatography using 4% of Et_2O in CH_2Cl_2 as eluent. The product was isolated in 75% yield (58.0 mg, 0.23 mmol) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.13 (m, 8H), 7.06 (d, J = 7.0 Hz, 2H), 3.66 (dd, J = 11.2, 6.6 Hz, 1H), 3.57 (dd, J = 11.2, 7.0 Hz, 1H), 2.67 – 2.51 (m, 2H), 2.07 (dd, J = 9.3, 5.3 Hz, 1H), 1.55 (td, J = 14.2, 6.8 Hz, 1H), 1.45 (ddd, J = 11.6, 5.7, 4.2 Hz, 1H), 1.41 – 1.32 (m, 2H), 1.08 (ddd, J = 12.9, 9.2, 7.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.19 (Cq), 138.29 (Cq), 129.02 (CH), 128.56 (CH), 128.42 (CH), 128.18 (CH), 126.08 (CH), 125.91 (CH), 66.67 (CH_2), 35.59 (CH_2), 29.88 (CH_2), 26.55 (CH), 26.42 (CH), 24.49 (CH). **FTIR (cm^{-1}) (neat):** 3344, 2922, 2857, 1601, 1495, 1451, 1023, 743, 696. **HRMS (ESI, Pos)** calculated for $C_{18}H_{24}N_1O_1$ $[M+NH_4]^+$: 270.18524 m/z, found 270.18469 m/z. **$[\alpha]_D^{20}$** = - 86.0 (c 0.59, $CHCl_3$). **Rf** = 0.17 (20% AcOEt in Hexanes).



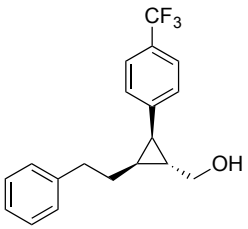
((1R,2S,3R)-2-phenethyl-3-(p-tolyl)cyclopropyl)methanol (6b): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-phenethylcyclopropyl)methanol (**4j**) (109.1 mg, 0.36 mmol) as starting material. Purified by flash column chromatography using 4% of Et_2O in CH_2Cl_2 as eluent. The product was isolated in 79% yield (76.0 mg, 0.29 mmol) as a yellow solid (**mp:** 50-52 °C).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.22 – 7.16 (m, 1H), 7.15 – 7.04 (m, 6H), 3.66 (dd, *J* = 11.2, 6.7 Hz, 1H), 3.56 (dd, *J* = 11.2, 7.0 Hz, 1H), 2.69 – 2.53 (m, 2H), 2.36 (s, 3H), 2.03 (dd, *J* = 9.3, 5.2 Hz, 1H), 1.64 – 1.50 (m, 1H), 1.45 – 1.26 (m, 4H), 1.11 – 0.97 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.25 (Cq), 135.57 (Cq), 135.12 (Cq), 128.91 (CH), 128.89 (CH), 128.59 (CH), 128.41 (CH), 125.90 (CH), 66.78 (CH_2), 35.62 (CH_2), 29.87 (CH_2), 26.47 (CH), 26.16 (CH), 24.31 (CH), 21.14 (CH_3). **FTIR (cm^{-1}) (neat):** 3320, 2925, 2860, 1448, 1021, 820, 746, 696, 563, 476. **HRMS (ESI, Pos)** calculated for $C_{19}H_{22}O_1Na$ $[M+Na]^+$: 289.156286 m/z, found 289.15728 m/z. **$[\alpha]_D^{20}$** = - 83.4 (c 0.92, $CHCl_3$). **Rf** = 0.19 (20% AcOEt in Hexanes).



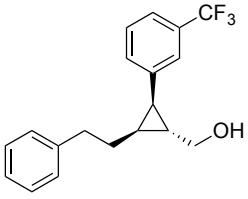
((1R,2R,3S)-2-mesityl-3-phenethylcyclopropyl)methanol (6c): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-phenethylcyclopropyl)methanol (**4j**) (111.3 mg, 0.37 mmol) as starting material. Purified by flash column chromatography using 4% of Et_2O in CH_2Cl_2 as eluent. The product was isolated in 74% yield (80.0 mg, 0.27 mmol) as a yellow solid (**mp:** 98-100 °C).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.24 – 7.12 (m, 3H), 6.84 (s, 2H), 3.93 (dd, J = 11.3, 5.6 Hz, 1H), 3.46 (dd, J = 11.3, 7.8 Hz, 1H), 2.80 – 2.61 (m, 2H), 2.36 (s, 6H), 2.27 (s, 3H), 1.92 (dtd, J = 10.7, 7.5, 3.4 Hz, 1H), 1.73 (dd, J = 8.5, 6.4 Hz, 1H), 1.39 (s, 1H), 1.27 – 1.18 (m, 1H), 1.18 – 1.07 (m, 1H), 0.79 – 0.64 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.15 (Cq), 138.54 (Cq), 135.47 (Cq), 131.87 (Cq), 129.09 (CH), 128.63 (CH), 128.49 (CH), 126.00 (CH), 67.01 (CH_2), 35.98 (CH_2), 30.44 (CH_2), 29.85 (CH), 23.61 (CH), 23.52 (CH), 20.92 (CH_3). **FTIR (cm^{-1}) (neat):** 3365, 2930, 1601, 1445, 1017, 743, 697. **HRMS (ESI, Pos)** calculated for $C_{21}H_{30}N_1O_1$ $[M+NH_4]^+$: 312.23219 m/z, found 312.2315 m/z. **$[\alpha]_D^{20}$** = -103.2 (c 0.56, $CHCl_3$). **Rf** = 0.26 (20% AcOEt in Hexanes).



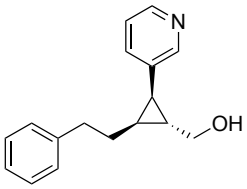
((1R,2R,3S)-2-(3-methoxyphenyl)-3-phenethylcyclopropyl)methanol (6d): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-phenethylcyclopropyl)methanol (**4j**) (85.2 mg, 0.28 mmol) as starting material. Purified by flash column chromatography using 4% of Et_2O in CH_2Cl_2 as eluent. The product was isolated in 65% yield (52.0 mg, 0.18 mmol) as an orange oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.14 (m, 4H), 7.08 (d, *J* = 7.1 Hz, 2H), 6.86 – 6.72 (m, 3H), 3.83 (s, 3H), 3.65 (dd, *J* = 11.3, 6.6 Hz, 1H), 3.55 (dd, *J* = 11.2, 7.0 Hz, 1H), 2.69 – 2.53 (m, 2H), 2.04 (dd, *J* = 9.3, 5.2 Hz, 1H), 1.59 (td, *J* = 14.3, 6.5 Hz, 1H), 1.50 – 1.25 (m, 3H), 1.07 (dt, *J* = 14.3, 7.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.53 (Cq), 142.18 (Cq), 140.02 (Cq), 129.11 (CH), 128.58 (CH), 128.42 (CH), 125.91 (CH), 121.46 (CH), 115.02 (CH), 111.28 (CH), 66.61 (CH_2), 55.30 (CH_3), 35.62 (CH_2), 29.83 (CH_2), 26.60 (CH), 26.55 (CH), 24.53 (CH). **FTIR (cm^{-1}) (neat):** 3365, 2925, 2856, 1602, 1582, 1491, 1453, 1315, 1254, 1152, 1040, 747, 696. **HRMS (ESI, Pos)** calculated for $C_{19}H_{22}O_2Na$ $[M+Na]^+$: 305.1512 m/z, found 305.15168 m/z. **$[\alpha]_D^{20}$** = - 82.8 (c 0.60, $CHCl_3$). **Rf** = 0.13 (20% AcOEt in Hexanes).



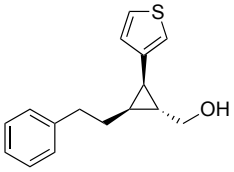
((1R,2S,3R)-2-phenethyl-3-(4-(trifluoromethyl)phenyl)cyclopropyl)methanol (6e): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-phenethylcyclopropyl)methanol (**4j**) (100.5 mg, 0.33 mmol) as starting material. Purified by flash column chromatography using 4% of Et_2O in CH_2Cl_2 as eluent. The product was isolated in 84% yield (89.0 mg, 0.28 mmol) as a yellowish solid (**mp:** 68-70 °C).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.1 Hz, 2H), 7.33 – 7.23 (m, 4H), 7.23 – 7.14 (m, 1H), 7.08 – 7.00 (m, 2H), 3.66 (dd, J = 11.3, 6.6 Hz, 1H), 3.60 (dd, J = 11.3, 6.8 Hz, 1H), 2.60 (t, J = 7.5 Hz, 2H), 2.11 (dd, J = 9.4, 5.3 Hz, 1H), 1.54 (td, J = 13.9, 7.1 Hz, 1H), 1.50 – 1.44 (m, 1H), 1.36 (dq, J = 14.1, 7.8 Hz, 2H), 1.21 – 1.10 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.81 (Cq), 141.83 (Cq), 129.18 (CH), 128.51 (CH), 128.20 (Cq), 126.06 (CH), 125.09 (q, CH, *J* =3.7 Hz), 123.39 (Cq), 66.24 (CH_2), 35.53 (CH_2), 29.73 (CH_2), 26.82 (CH), 26.38 (CH), 24.93 (CH). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.29. **FTIR (cm^{-1}) (neat):** 3352, 2927, 1617, 1322, 1107, 742, 696. **HRMS (ESI, Pos)** calculated for $C_{19}H_{18}F_3$ $[M+H-H_2O]^+$: 303.13550 m/z, found 303.13612 m/z. **$[\alpha]_D^{20}$** = - 81.8 (c 1.07, $CHCl_3$). **Rf** = 0.13 (20% AcOEt in Hexanes).



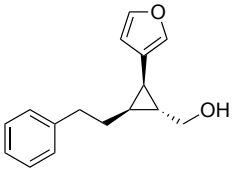
((1R,2S,3R)-2-phenethyl-3-(3-(trifluoromethyl)phenyl)cyclopropyl)methanol (6f): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-phenethylcyclopropyl)methanol (**4j**) (108.6 mg, 0.36 mmol) as starting material. Purified by flash column chromatography using 4% of Et_2O in CH_2Cl_2 as eluent. The product was isolated in 72% yield (83.0 mg, 0.26 mmol) as a yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.44 – 7.36 (m, 2H), 7.30 – 7.23 (m, 2H), 7.19 (ddd, *J* = 7.3, 3.9, 1.2 Hz, 1H), 7.10 – 7.02 (m, 2H), 3.66 (dd, *J* = 11.3, 6.6 Hz, 1H), 3.61 (dd, *J* = 11.3, 6.8 Hz, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.11 (dd, *J* = 9.3, 5.3 Hz, 1H), 1.54 (td, *J* = 14.0, 7.0 Hz, 1H), 1.50 – 1.43 (m, 1H), 1.40 (br, 1H), 1.37 – 1.31 (m, 1H), 1.14 (dddd, *J* = 9.3, 7.8, 6.5, 5.3 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.84 (Cq), 139.57 (Cq), 132.31 (CH), 130.57 (q, Cq), 128.61 (CH), 128.51 (CH), 128.49 (CH), 126.04 (CH), 125.66 (d, *J* = 3.7 Hz, CH), 123.26 (Cq), 122.94 (d, *J* = 3.8 Hz, CH), 66.23 (CH_2), 35.53 (CH_2), 29.80 (CH_2), 26.68 (CH), 26.31 (CH), 24.63 (CH). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.56. **FTIR (cm^{-1}) (neat):** 3329, 2925, 1603, 1453, 1324, 1119, 1019, 746, 698. **HRMS (ESI, Pos)** calculated for $C_{19}H_{18}F_3$ $[M+H-H_2O]^+$: 303.13550 m/z, found 303.13658 m/z. **$[\alpha]_D^{20}$** = - 75.1 (c 0.58, $CHCl_3$). **Rf** = 0.13 (20% AcOEt in Hexanes).



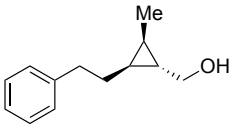
((1R,2S,3R)-2-phenethyl-3-(pyridin-3-yl)cyclopropyl)methanol (6g): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-phenethylcyclopropyl)methanol (**4j**) (100.2 mg, 0.33 mmol) as starting material. Purified by flash column chromatography using a gradient from 0% to 10% of MeOH in CH_2Cl_2 as eluent. The product was isolated in 82% yield (69.0 mg, 0.27 mmol) as a yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 – 8.23 (m, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.08 (m, 4H), 7.07 – 6.96 (m, 2H), 3.66 – 3.54 (m, 2H), 2.60 – 2.53 (m, J = 7.6 Hz, 2H), 2.48 (br, 1H), 1.99 (dd, J = 9.2, 5.3 Hz, 1H), 1.49 (td, J = 14.0, 7.1 Hz, 1H), 1.44 – 1.37 (m, 1H), 1.32 (dq, J = 14.1, 7.8 Hz, 1H), 1.16 – 1.06 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.39 (CH), 147.10 (CH), 141.74 (Cq), 136.27 (CH), 134.39 (Cq), 128.48 (CH), 128.46 (CH), 126.02 (CH), 123.07 (CH), 65.97 (CH_2), 35.50 (CH_2), 29.82 (CH_2), 26.37 (CH), 24.39 (CH), 23.97 (CH). **FTIR (cm^{-1}) (neat):** 3286, 2923, 2855, 1451, 1415, 1025, 732, 698. **HRMS (ESI, Pos)** calculated for $C_{17}H_{20}N_1O_1$ $[M+H]^+$: 254.15394 m/z, found 254.15325 m/z. **$[\alpha]_D^{20}$** = - 77.5 (c 0.42, $CHCl_3$). **Rf**= 0.41 (10% MeOH in CH_2Cl_2).



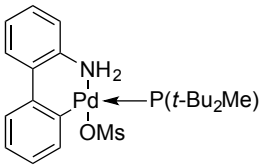
((1R,2S,3R)-2-phenethyl-3-(thiophen-3-yl)cyclopropyl)methanol (6h): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-phenethylcyclopropyl)methanol (**4j**) (103.8 mg, 0.34 mmol) as starting material. Purified by flash column chromatography using 4% of Et_2O in CH_2Cl_2 as eluent. The product was isolated in 79% yield (70.0 mg, 0.27 mmol) as an orange oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (ddd, *J* = 7.6, 4.6, 1.6 Hz, 3H), 7.20 (ddd, *J* = 7.3, 3.8, 1.3 Hz, 1H), 7.12 – 7.04 (m, 2H), 6.98 (dd, *J* = 4.9, 1.3 Hz, 1H), 6.95 – 6.90 (m, 1H), 3.65 (dd, *J* = 11.2, 6.7 Hz, 1H), 3.56 (dd, *J* = 11.2, 6.9 Hz, 1H), 2.70 – 2.52 (m, 2H), 2.01 (dd, *J* = 9.0, 5.1 Hz, 1H), 1.62 – 1.43 (m, 2H), 1.40 – 1.27 (m, 2H), 1.03 (dtd, *J* = 9.0, 7.1, 5.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.21 (Cq), 139.50 (Cq), 129.00 (CH), 128.55 (CH), 128.44 (CH), 125.92 (CH), 125.20 (CH), 120.78 (CH), 66.54 (CH_2), 35.65 (CH_2), 30.02 (CH_2), 27.88 (CH), 24.24 (CH), 21.84 (CH). **FTIR (cm^{-1}) (neat):** 3340, 2922, 2856, 1451, 1018, 781, 747, 696. **HRMS (ESI, Pos)** calculated for $C_{16}H_{18}O_1S_1Na$ $[M+Na]^+$: 281.09706 m/z, found 281.09721 m/z. **$[\alpha]_D^{20}$** = - 54.7 (c 0.30, $CHCl_3$). **Rf** = 0.15 (20% AcOEt in Hexanes).



((1R,2R,3S)-2-(furan-3-yl)-3-phenethylcyclopropyl)methanol (6i): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-phenethylcyclopropyl)methanol (**4j**) (115.3 mg, 0.38 mmol) as starting material. Purified by flash column chromatography using 20% of EtOAc in petroleum ether as eluent. The product was isolated in 34% yield (31.0 mg, 0.13 mmol) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 1.6 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.20 (dt, J = 1.7, 0.9 Hz, 1H), 7.17 (ddd, J = 7.3, 3.9, 1.3 Hz, 1H), 7.09 (dd, J = 7.8, 1.0 Hz, 2H), 6.25 (dd, J = 1.7, 0.7 Hz, 1H), 3.59 (dd, J = 11.2, 6.7 Hz, 1H), 3.50 (dd, J = 11.3, 7.0 Hz, 1H), 2.71 – 2.52 (m, 2H), 1.72 (dd, J = 8.9, 5.0 Hz, 1H), 1.62 – 1.43 (m, 2H), 1.23 (br, 1H), 1.11 (tt, J = 6.8, 5.1 Hz, 1H), 0.95 (dtd, J = 9.0, 7.1, 5.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.78 (CH), 142.22 (Cq), 140.09 (CH), 128.57 (CH), 128.47 (CH), 125.96 (CH), 122.67 (Cq), 111.88 (CH), 66.54 (CH_2), 35.66 (CH_2), 30.04 (CH_2), 27.50 (CH), 23.43 (CH), 16.82 (CH). **FTIR (cm^{-1}) (neat):** 3353, 3024, 2923, 1497, 1457, 1021, 748, 697, 597. **HRMS (ESI, Pos)** calculated for $C_{16}H_{18}O_2$ $[M+H]^+$: 243.13796 m/z, found 243.13829 m/z. **$[\alpha]_D^{20}$** = - 31.5 (c 0.33, $CHCl_3$). **Rf** = 0.13 (20% AcOEt in Hexanes).



((1S,2R,3S)-2-methyl-3-phenethylcyclopropyl)methanol (6j): Synthesized according to general procedure **D** using ((1S,2R,3S)-2-iodo-3-phenethylcyclopropyl)methanol (**4j**) (109.1 mg, 0.36 mmol) as starting material. Purified by flash column chromatography using 4% of Et_2O in CH_2Cl_2 as eluent. The product was observed in 36% yield (determined by ^{1}H NMR) and isolated along with the dehalogenation byproduct.
^{1}H NMR (400 MHz, $CDCl_3$) (peaks corresponding to the desired product **6j**) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 3.50 – 3.31 (m, 2H), 2.81 – 2.61 (m, 2H), 1.73 (ddd, *J* = 20.9, 8.4, 6.5 Hz, 1H), 1.68 – 1.48 (m, 1H), 1.32 (br, 1H), 1.06 (d, *J* = 6.2 Hz, 3H), 0.71 (ddt, *J* = 12.3, 10.9, 6.1 Hz, 1H), 0.65 – 0.54 (m, 1H), 0.54 – 0.42 (m, 1H).



Precatalyst (2): Synthesized following procedure **E** using the μ-OMs dimer – 2-ammoniumbiphenyl mesylate (209.3 mg, 0.57 mmol), P(*t*-Bu)$_2$Me (90.7 mg, 0.57 mmol) and 2.8 mL of THF. The compound **2** was isolated in 89% yield (268.0 mg, 0.51 mmol) as a brown solid (**mp:** 180-184 °C).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.16 (dd, *J* = 12.2, 4.7 Hz, 2H), 7.09 (td, *J* = 7.3, 1.1 Hz, 1H), 7.03 (td, *J* = 7.4, 1.4 Hz, 1H), 4.15 (br, 1H), 2.82 (s, 3H), 1.38 (d, *J* = 14.0 Hz, 9H), 1.03 (d, *J* = 13.9 Hz, 9H), 0.80 (d, *J* = 9.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.93, 139.97, 139.17, 138.35, 138.29, 136.55, 136.53, 128.45, 127.65, 127.63, 127.11, 125.90, 125.47, 125.00, 120.33, 40.11, 34.90, 34.74, 34.67, 34.53, 29.05, 29.02, 28.99, 28.95, 5.64, 5.42. (Observed complexity due to P-C splitting). **^{31}P NMR (202 MHz, $CDCl_3$)** δ 45.95. **FTIR (cm^{-1}) (neat):** 3280, 2944, 1571, 1494, 1416, 1366, 1252, 1138, 1035, 772.

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X-Ray Data

X-Ray Data for Compound **2**

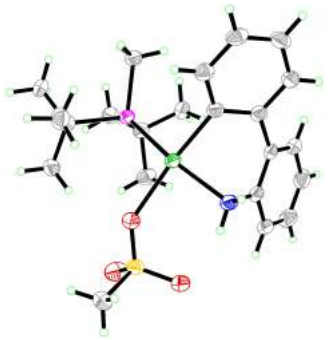
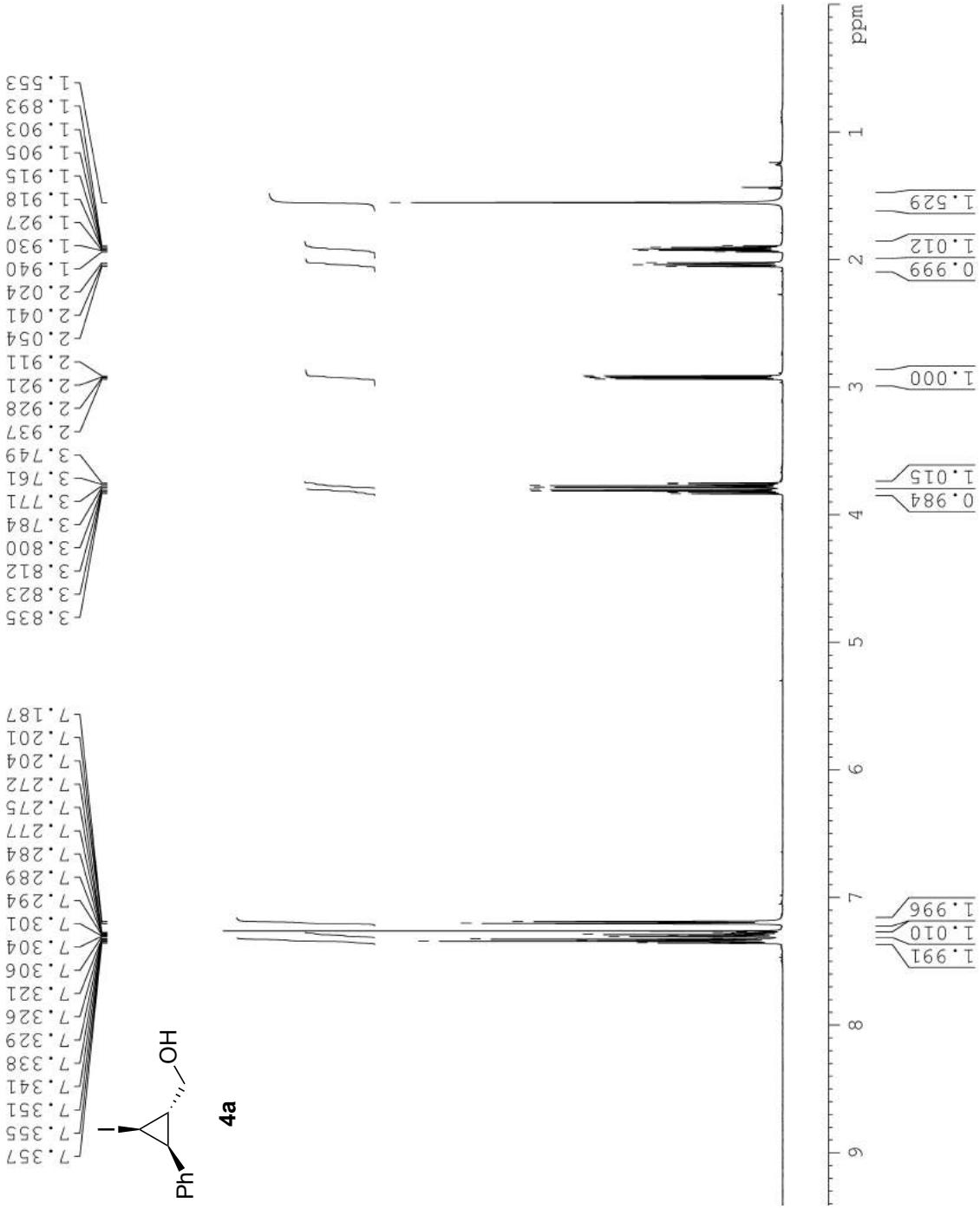


Table 1 Crystal data and structure refinement for SYLV22.

Identification code	SYLV22
Empirical formula	$C_{22}H_{34}NO_3PSPd$
Formula weight	529.93
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	9.1931(5)
b/Å	11.6107(6)
c/Å	12.2025(6)
α/°	76.780(2)
β/°	86.549(2)
γ/°	67.313(2)
Volume/Å^3	1169.28(11)
Z	2
ϱ_{calc}g/cm^3	1.505
μ/mm^{-1}	5.353
F(000)	548.0
Crystal size/mm^3	0.2 × 0.16 × 0.02
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.476 to 108.058
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	27434
Independent reflections	4278 [R_{int} = 0.0501, R_{sigma} = 0.0300]
Data/restraints/parameters	4278/0/276
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0259, wR_2 = 0.0659
Final R indexes [all data]	R_1 = 0.0264, wR_2 = 0.0663
Largest diff. peak/hole / e Å^{-3}	1.18/-0.42

NMR Spectra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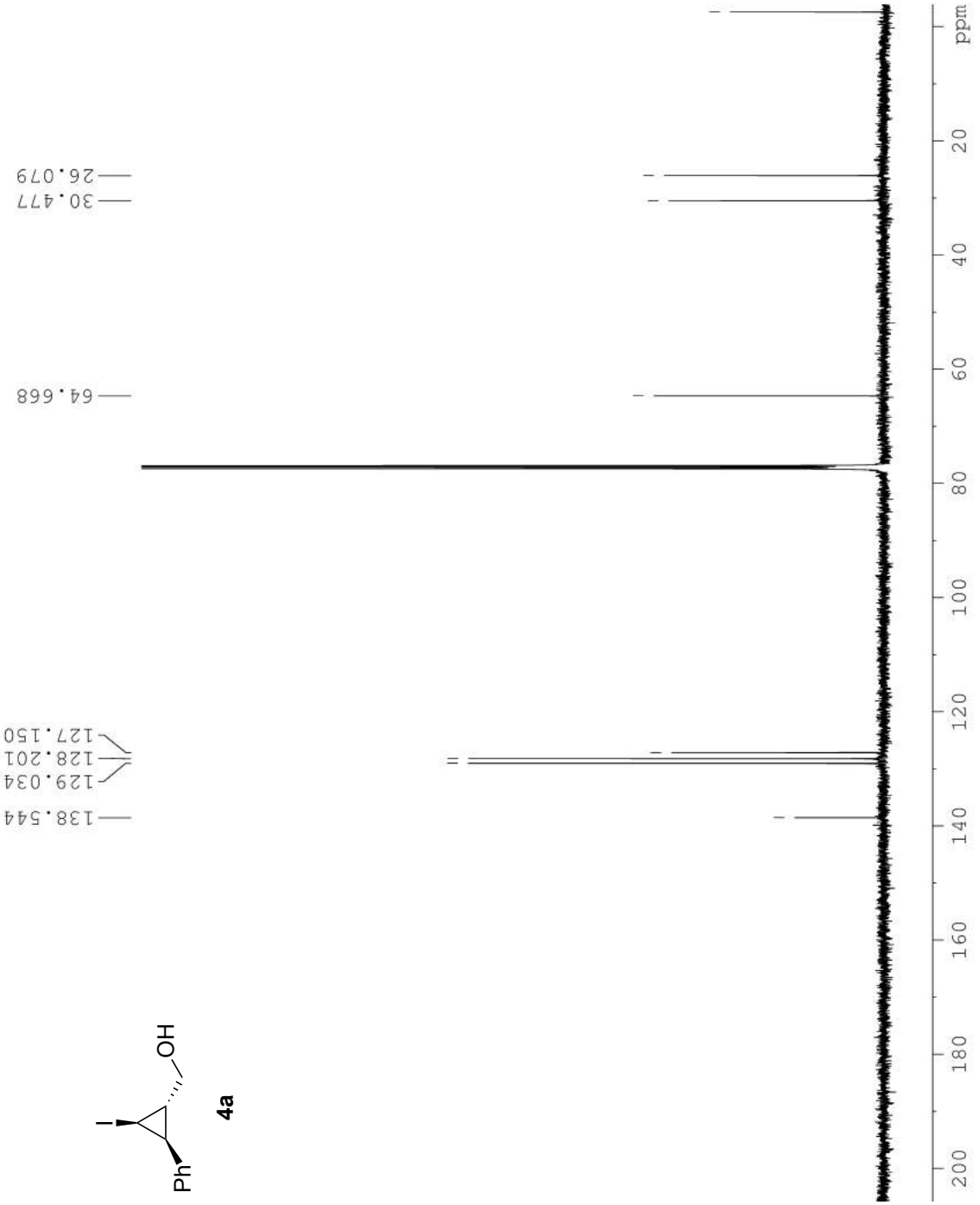
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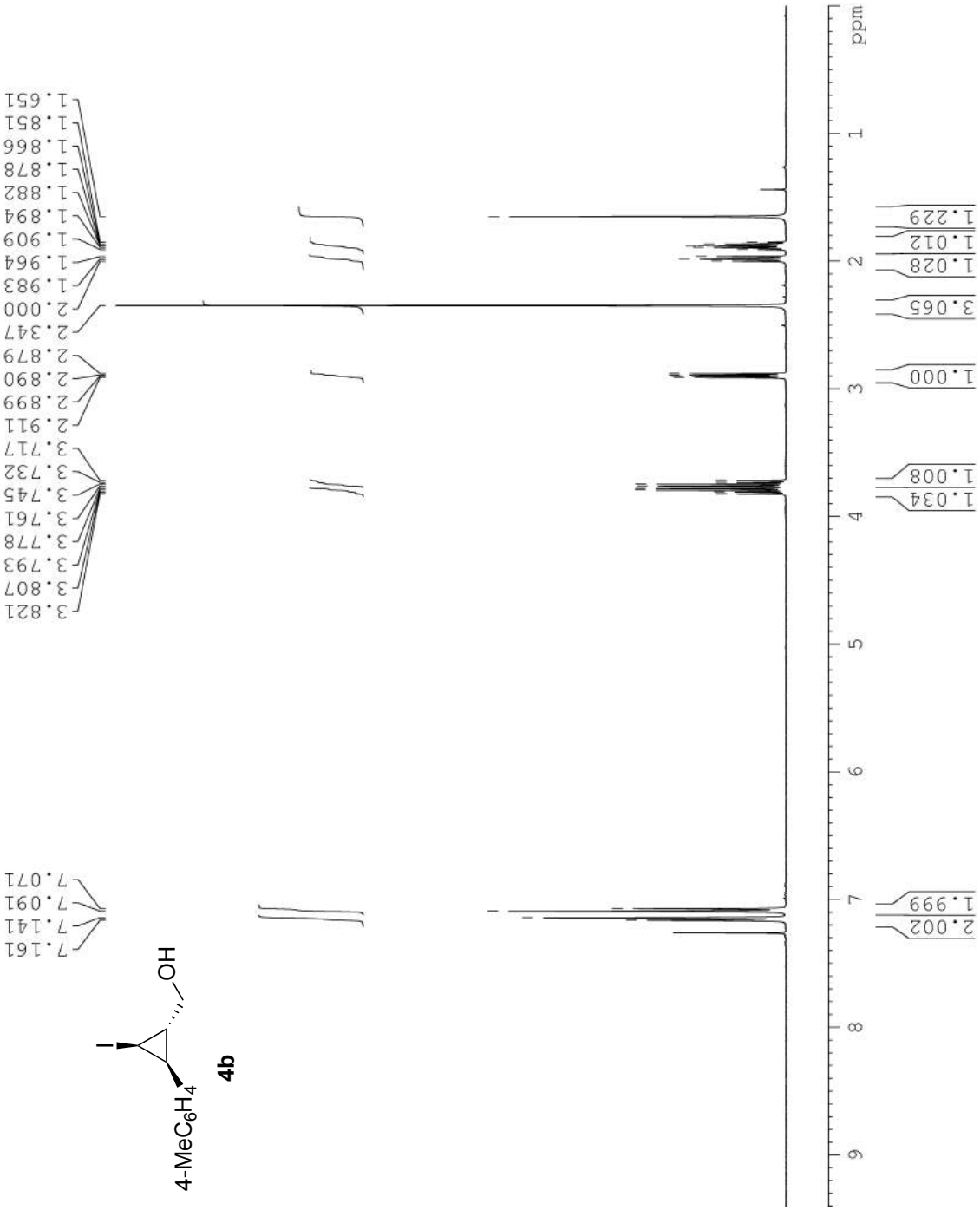
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3.732
3.717
2.911
2.899
2.890
2.879
2.347
2.000
1.983
1.964
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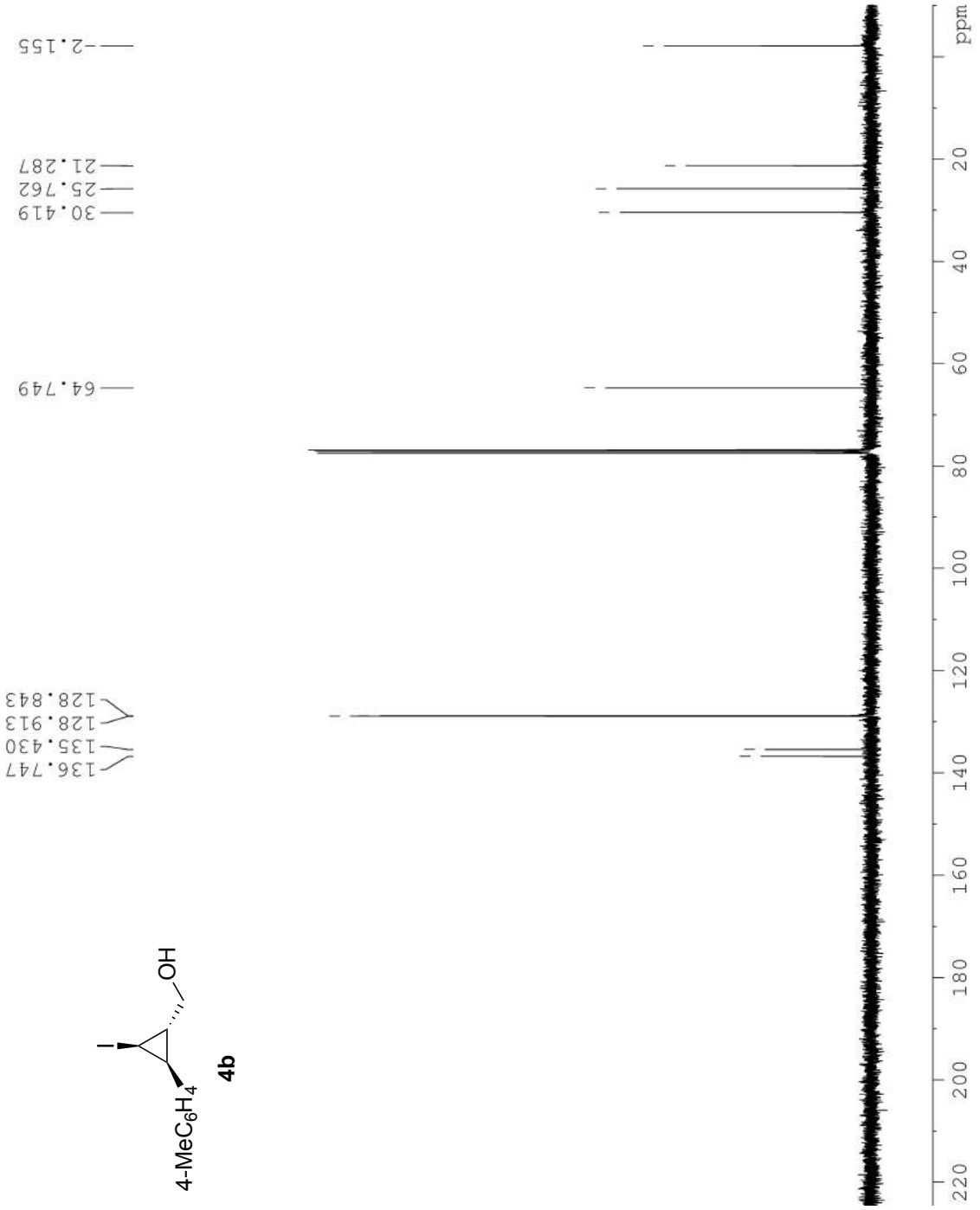
1.894
1.882
1.878
1.866
1.851
1.651
OH
I
4-MeC6H4
4b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25.762
30.419
64.749
128.843
128.913
135.430
136.747
ppm
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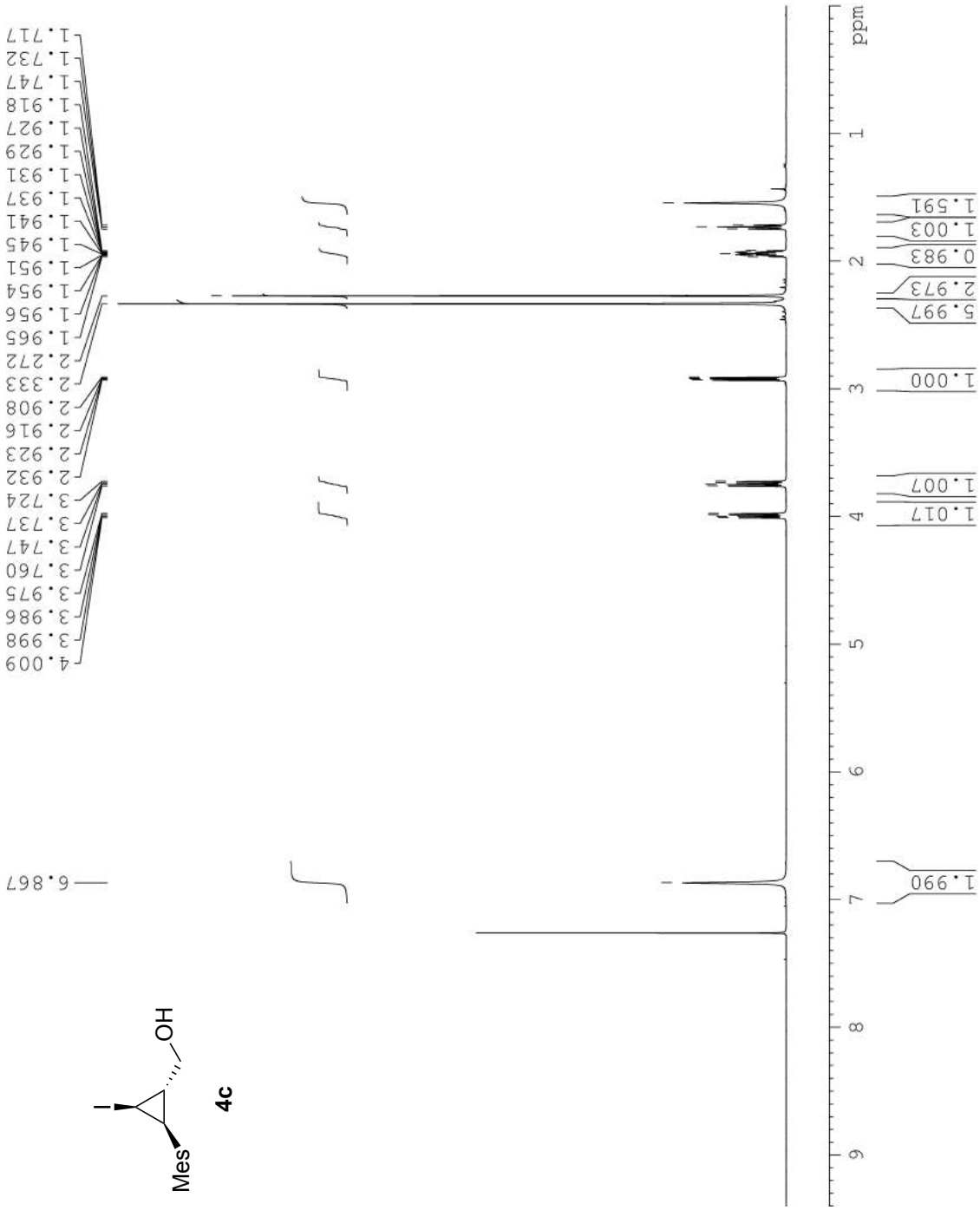
40
60
80
100
120
140
160
180
200
220
OH
I
4-MeC6H4
4b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1.732
1.747
1.918
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1.929
1.931
1.937
1.941
1.945
1.951
1.954
1.956
1.965
2.272
2.333
2.908
2.916
2.923
2.932
3.724
3.737
3.747
3.760
3.975
3.986
3.998
4.009
6.867
1.591
1.003
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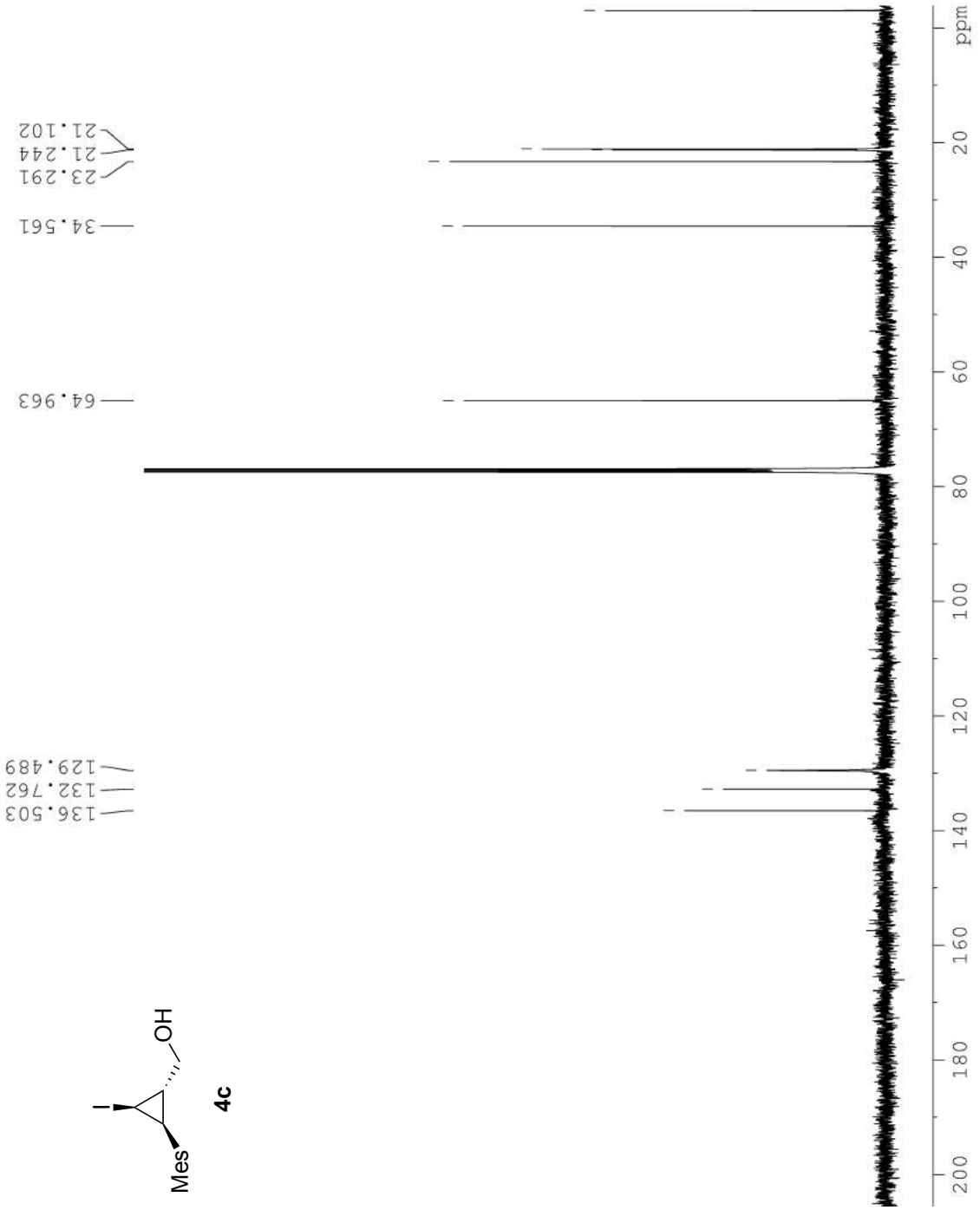
2.973
5.997
1.000
1.007
1.017
1.990
ppm
OH
I
Mes
4c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21.244
23.291
34.561
64.963
129.489
132.762
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ppm
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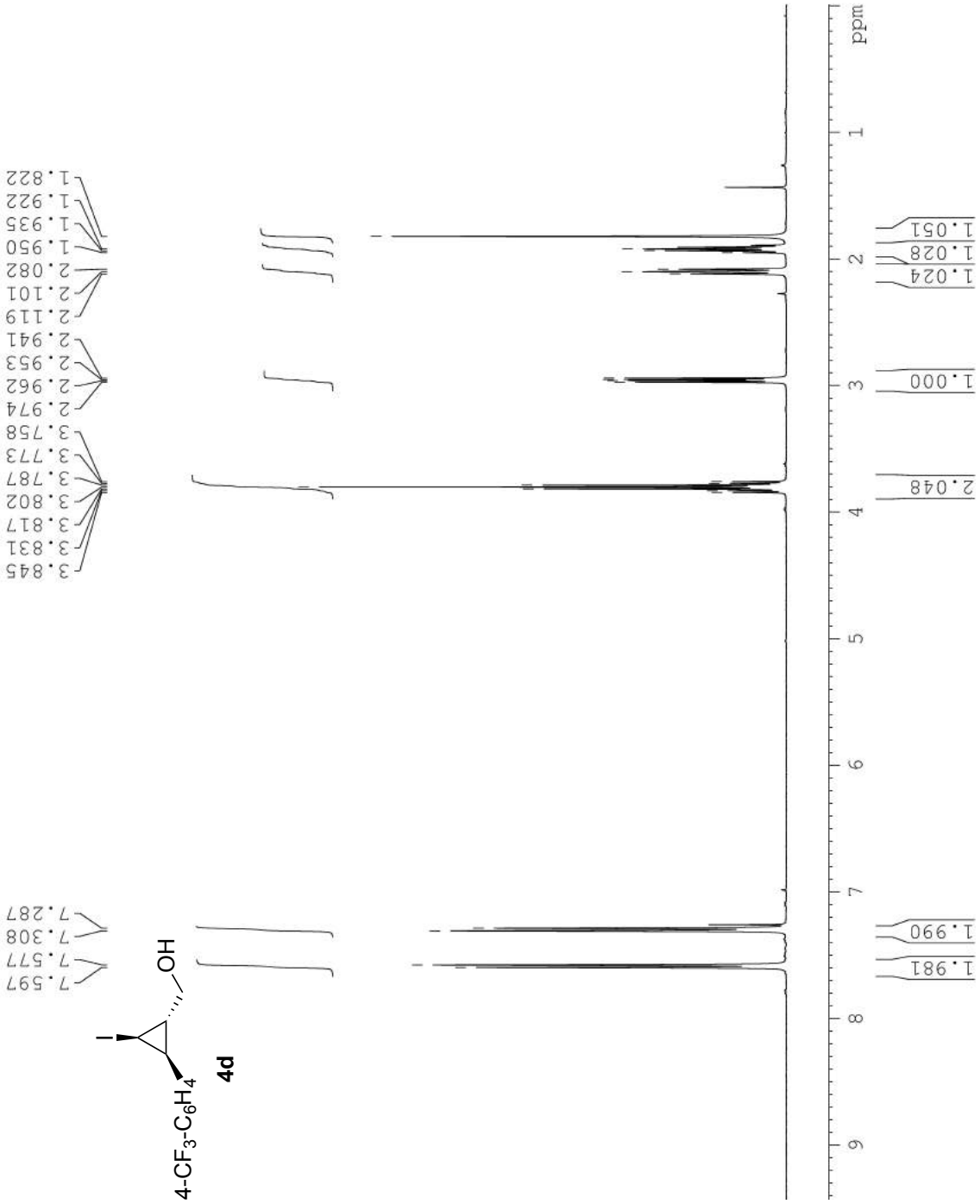
40
60
80
100
120
140
160
180
200
OH
I
Mes
4c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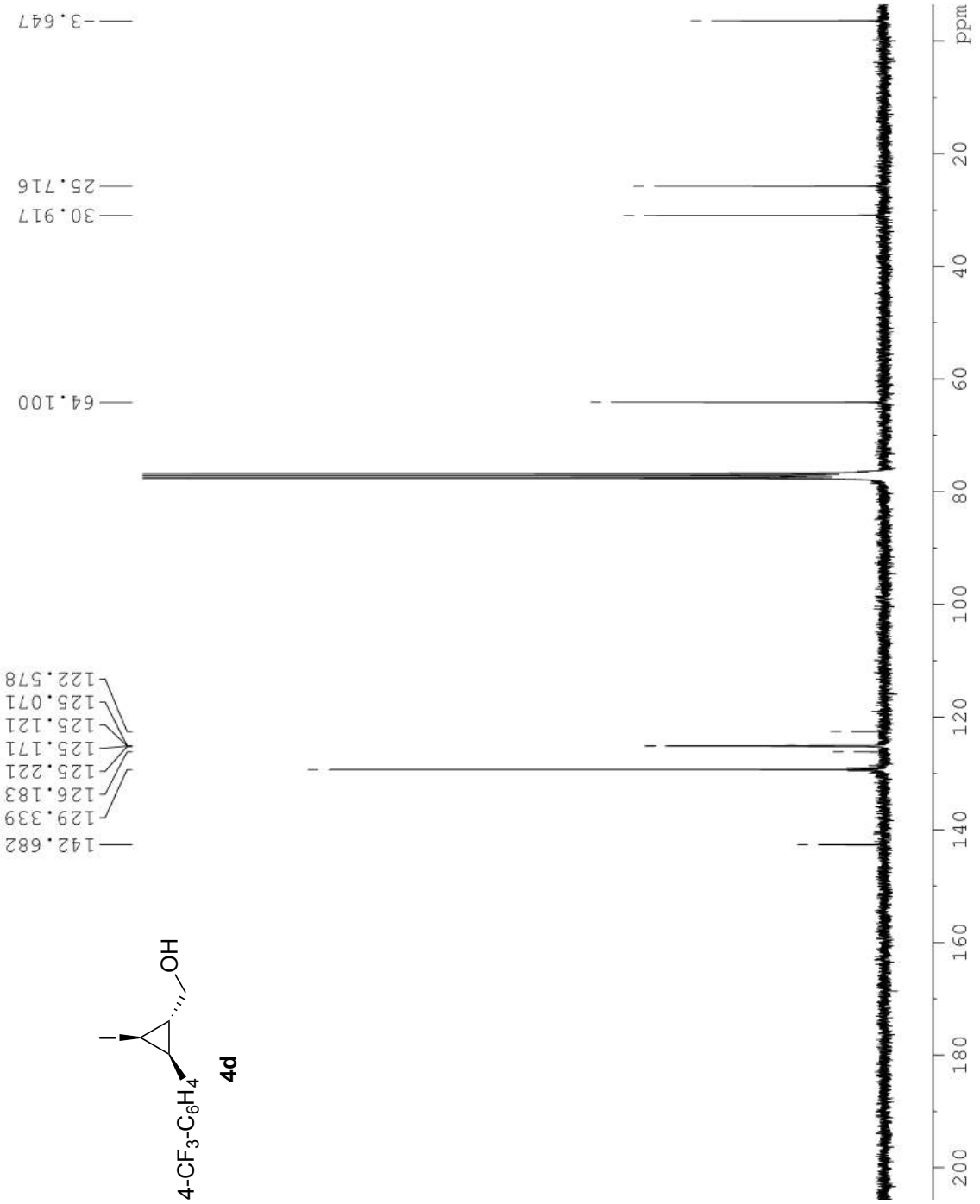
7.577
7.308
7.287
3.845
3.831
3.817
3.802
3.787
3.773
3.758
2.974
2.962
2.953
2.941
2.119
2.101
2.082
1.950
1.935
1.922
1.822
1.990
1.981
2.048
1.000
1.051
1.028
1.024
ppm
OH
I
4-CF3-C6H4
4d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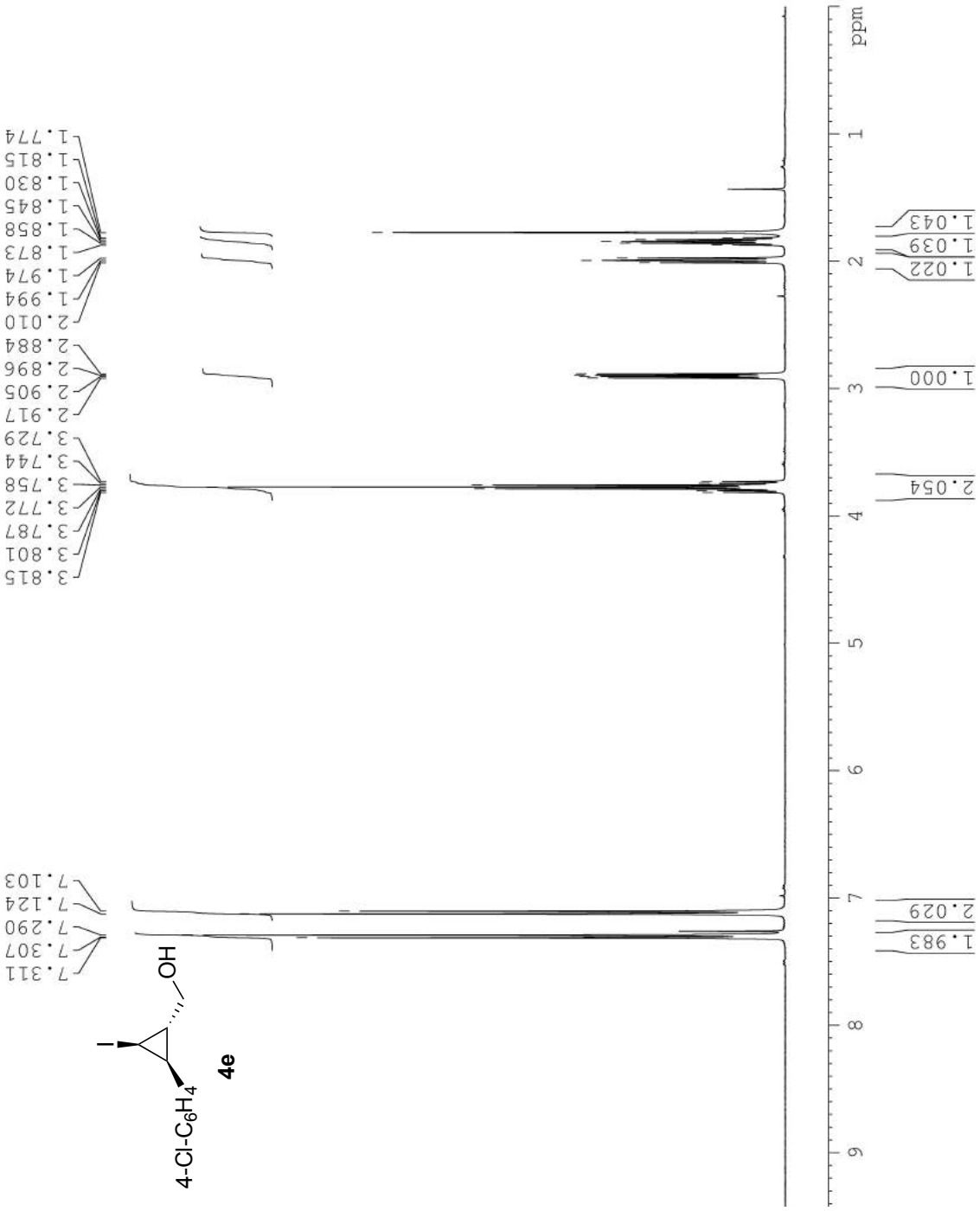
129.339
126.183
125.221
125.171
125.121
125.071
122.578
64.100
30.917
25.716
3.647
ppm
20
40
60
80
100
120
140
160
180
200
OH
4-CF3-C6H4
4d


7.311
7.307
7.290
7.124
7.103
3.815
3.801
3.787
3.772
3.758
3.744
3.729
2.917
2.905
2.896
2.884
2.010
1.994
1.974
1.873
1.858
1.845
1.830
1.815
1.774
ppm
1 2 3 4 5 6 7 8 9
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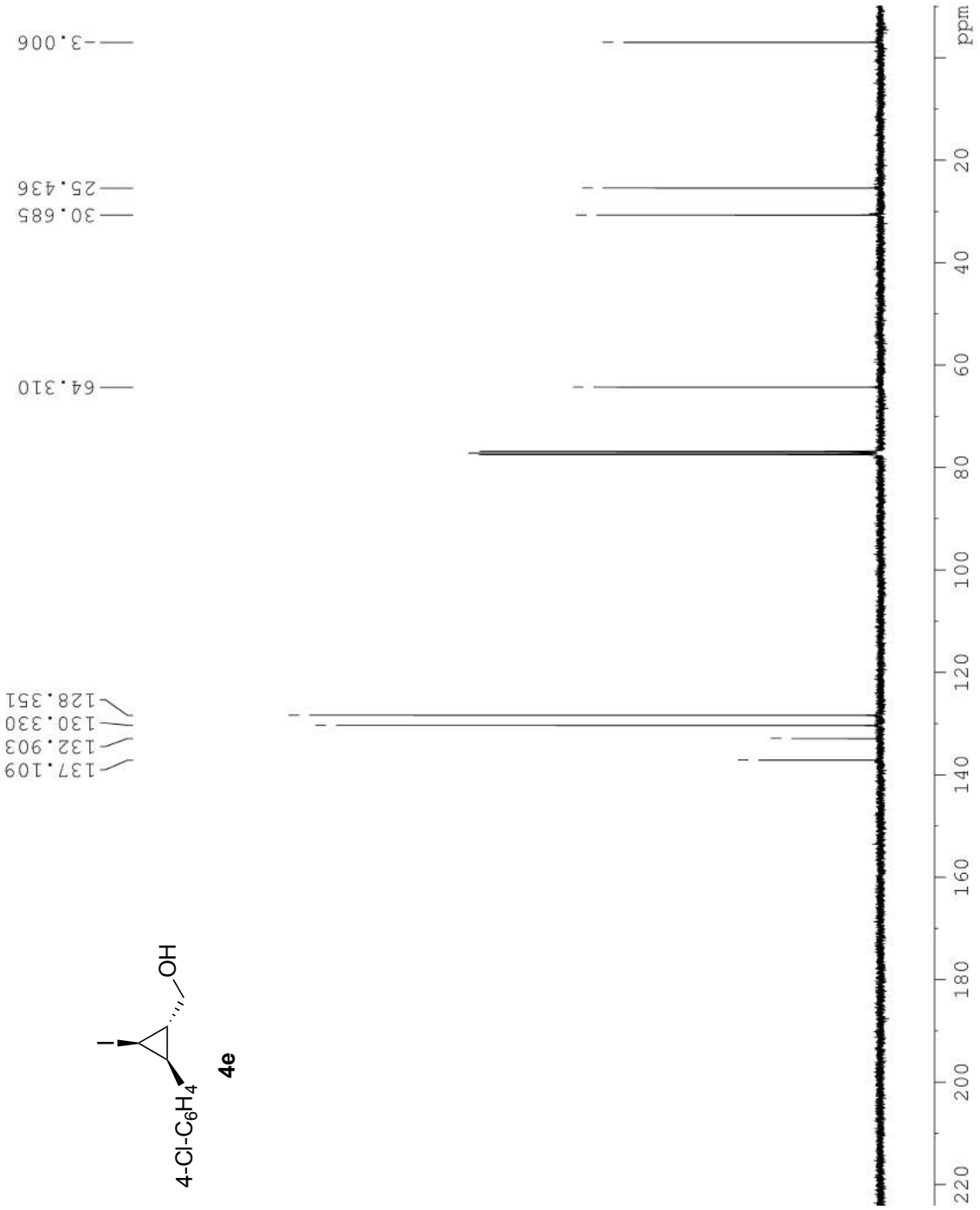
1.983
1.043
1.039
1.022
1.000
2.054
OH
I
4-Cl-C6H4
4e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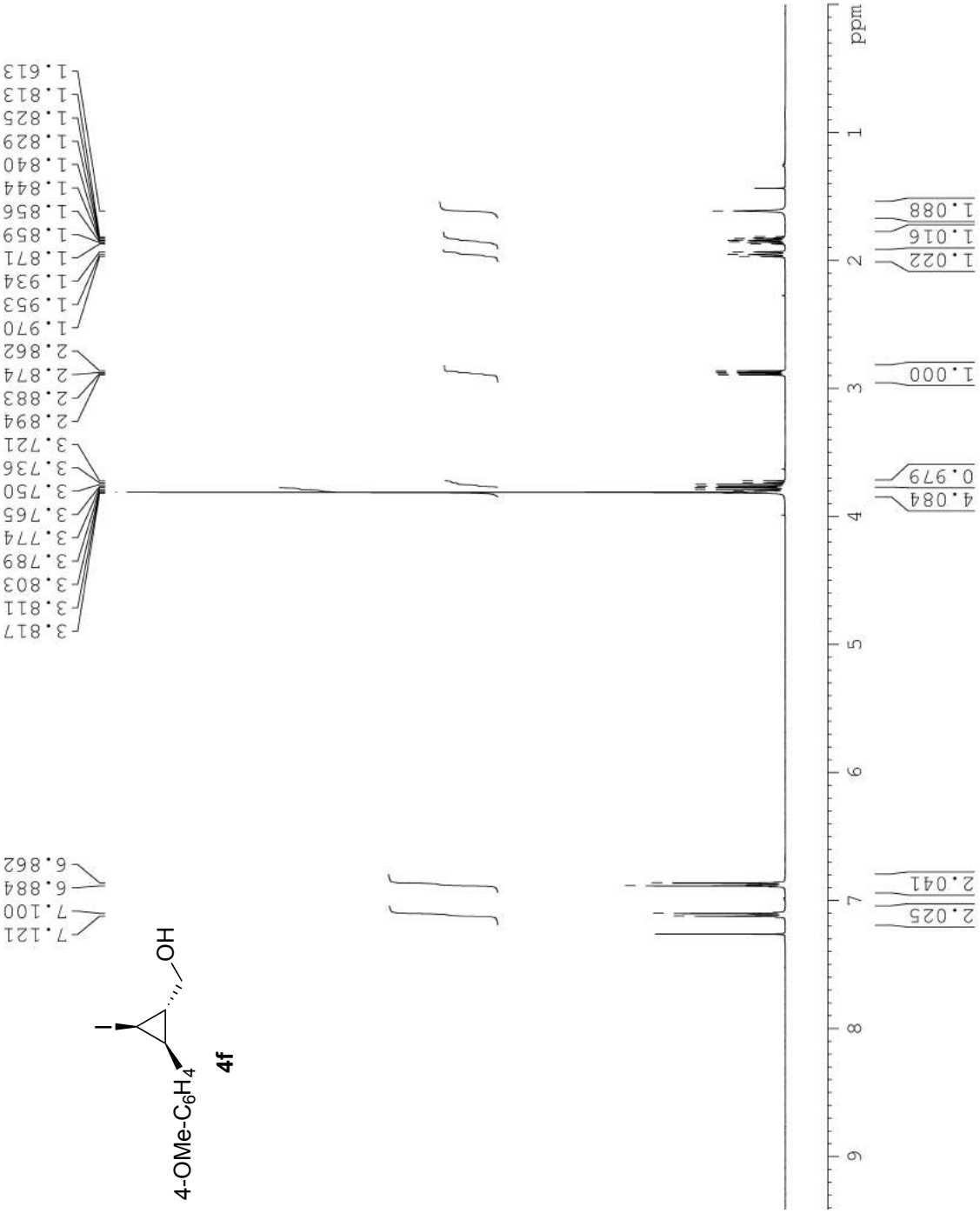
80
100
120
140
160
180
200
220
OH
I
4-Cl-C6H4
4e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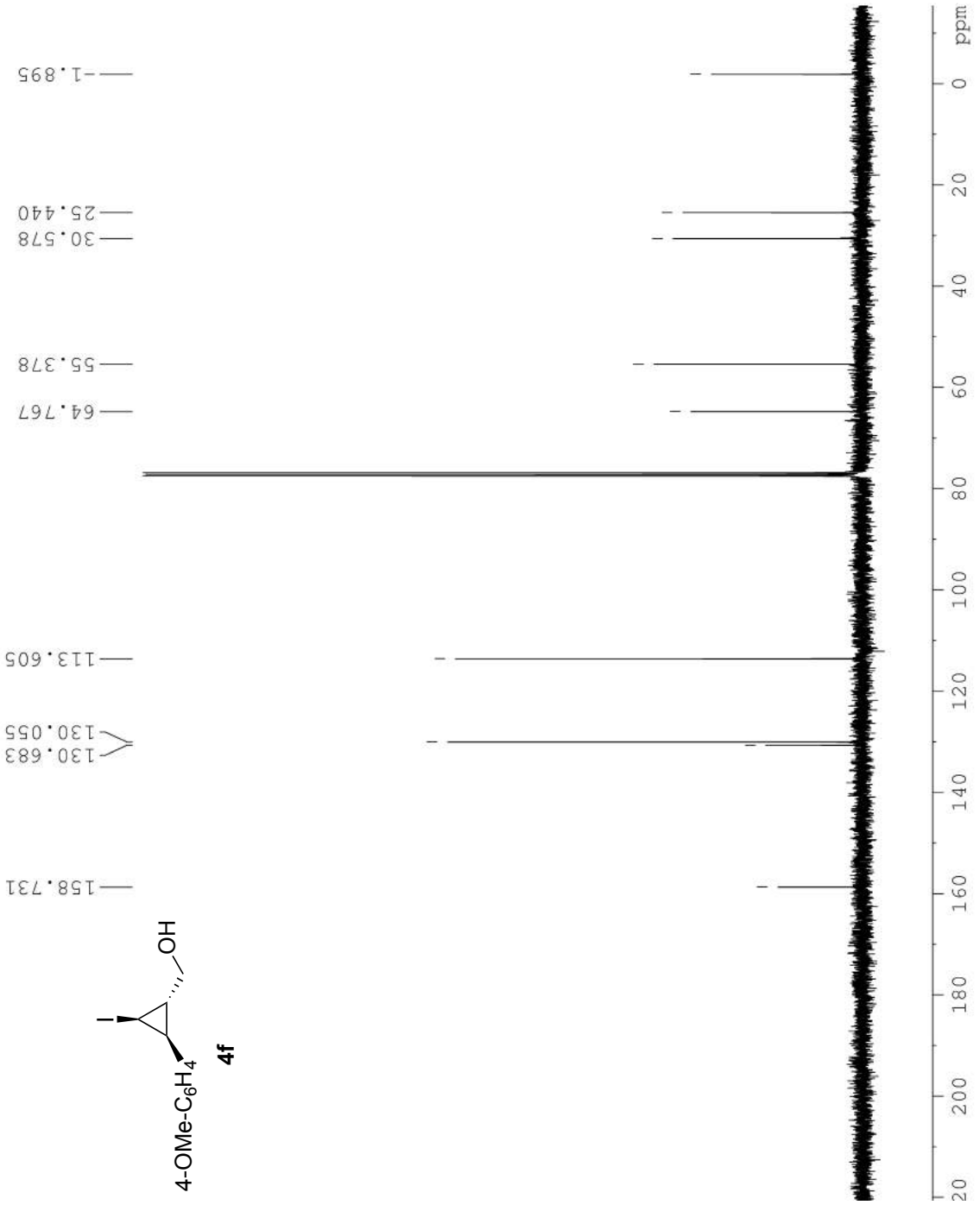
1
2
3
4
5
6
7
8
9
1.088
1.016
1.022
1.000
0.979
4.084
2.041
2.025
1.613
1.813
1.825
1.829
1.840
1.844
1.856
1.859
1.871
1.934
1.953
1.970
2.862
2.874
2.883
2.894
3.721
3.736
3.750
3.765
3.774
3.789
3.803
3.811
3.817
6.862
6.884
7.100
7.121
OH
4-OMe-C6H4
4f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30.578
55.378
64.767
113.605
130.055
130.683
158.731
ppm
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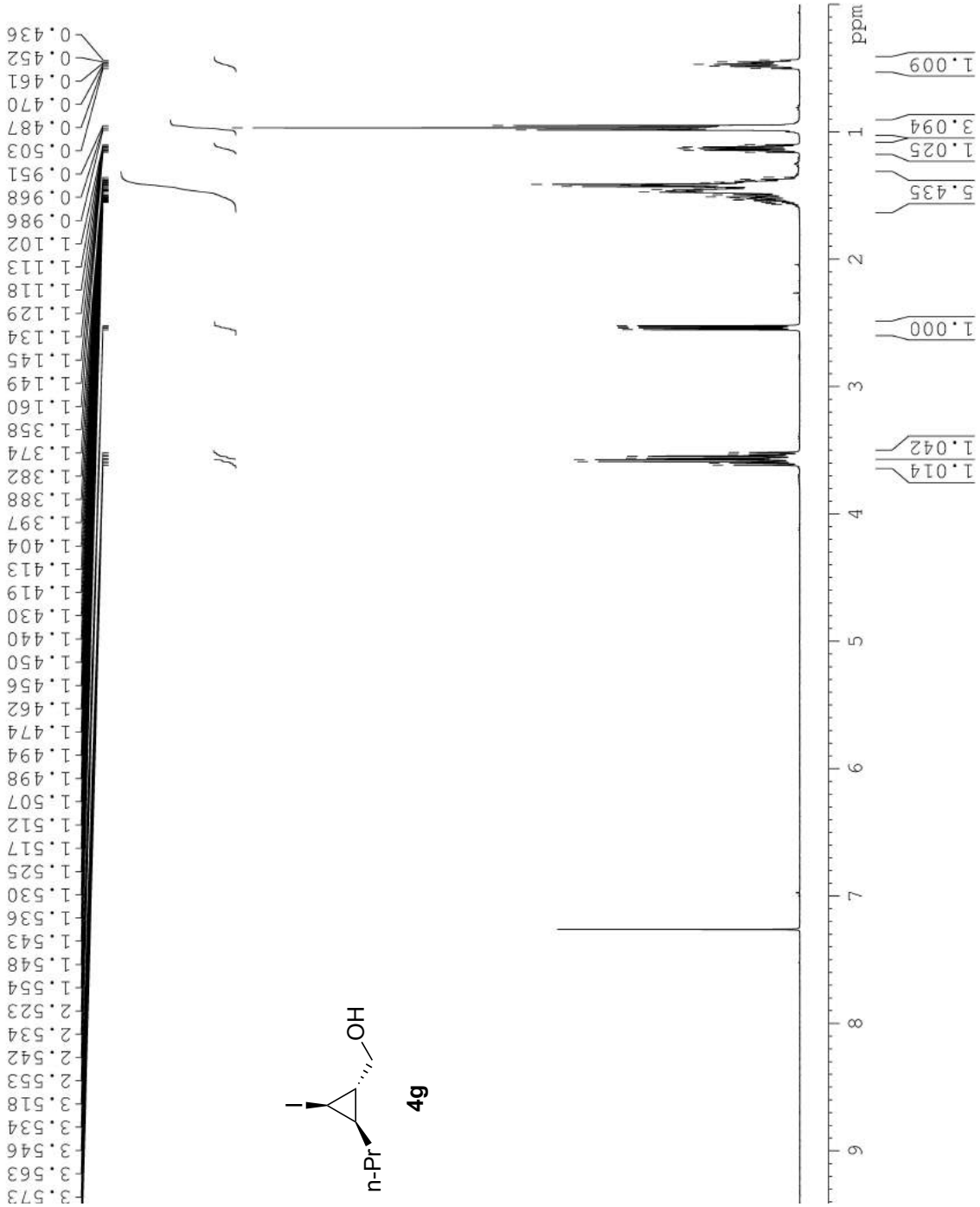
20
40
60
80
100
120
140
160
180
200
220
OH
4-OMe-C6H4
4f


ppm
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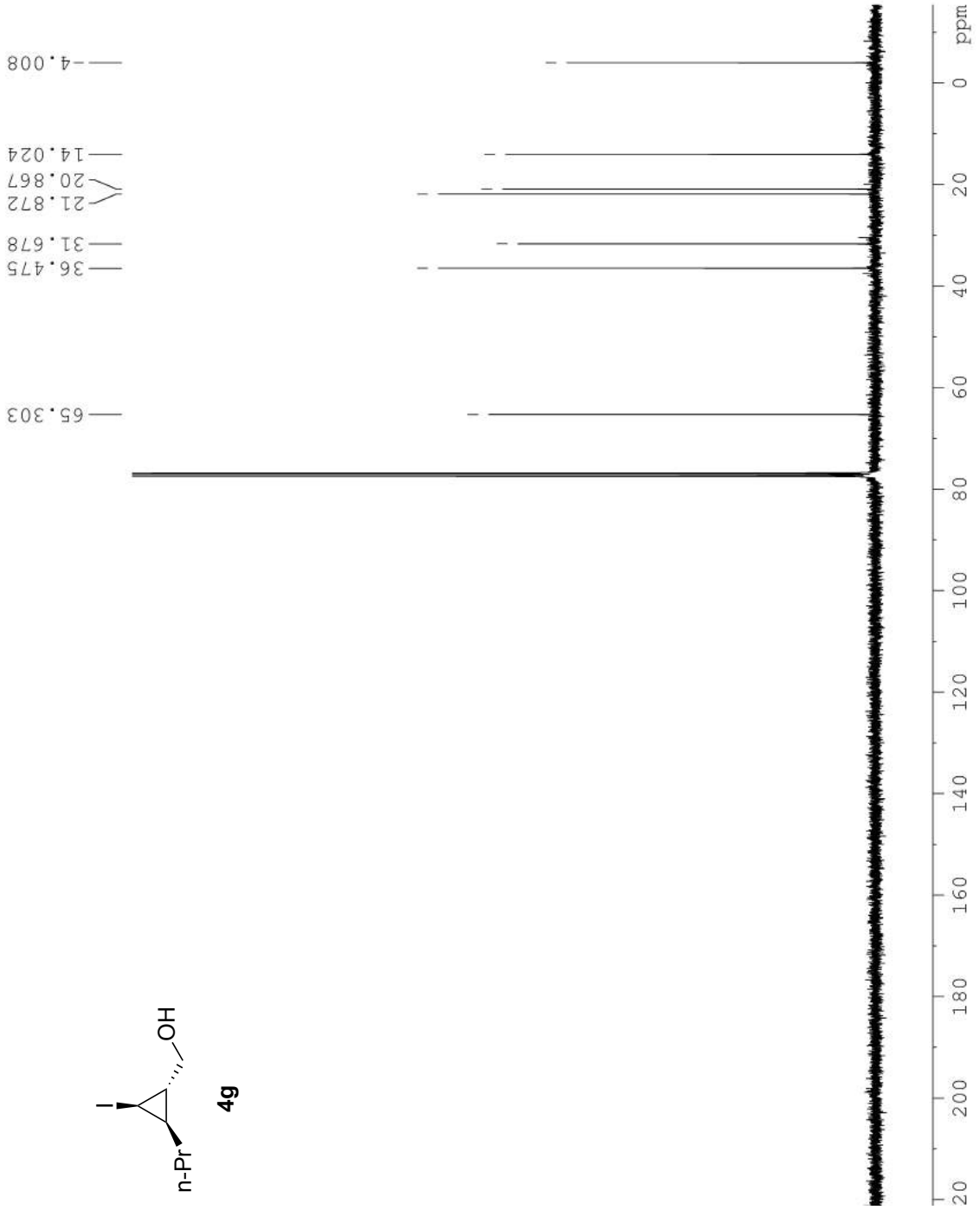
3.094
1.025
5.435
1.000
1.042
1.014
OH
I
n-Pr
4g


4.008
14.024
20.867
21.872
31.678
36.475
65.303
ppm
0
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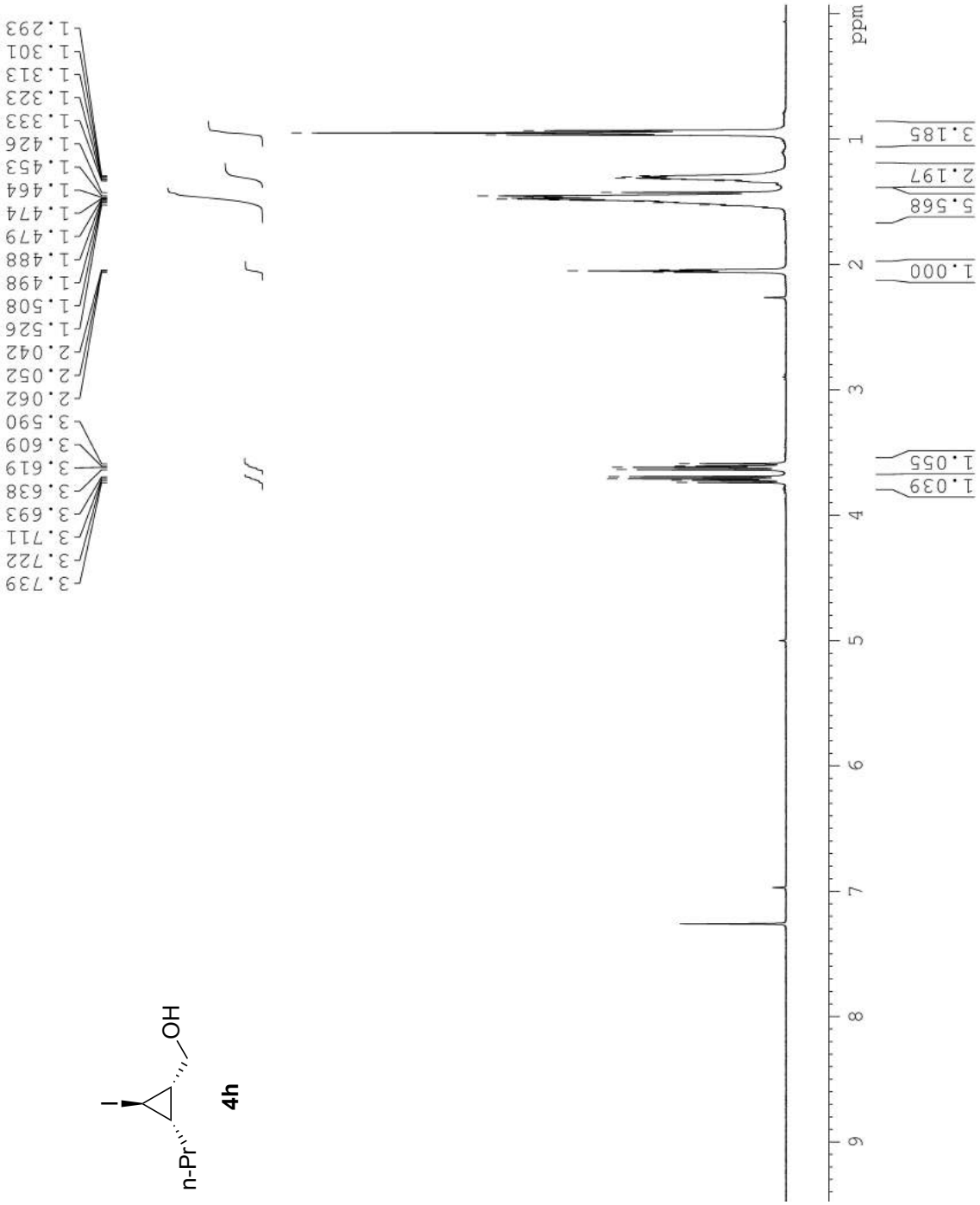
40
60
80
100
120
140
160
180
200
220
OH
I
n-Pr

4g


4h
n-Pr
OH
ppm
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2.197
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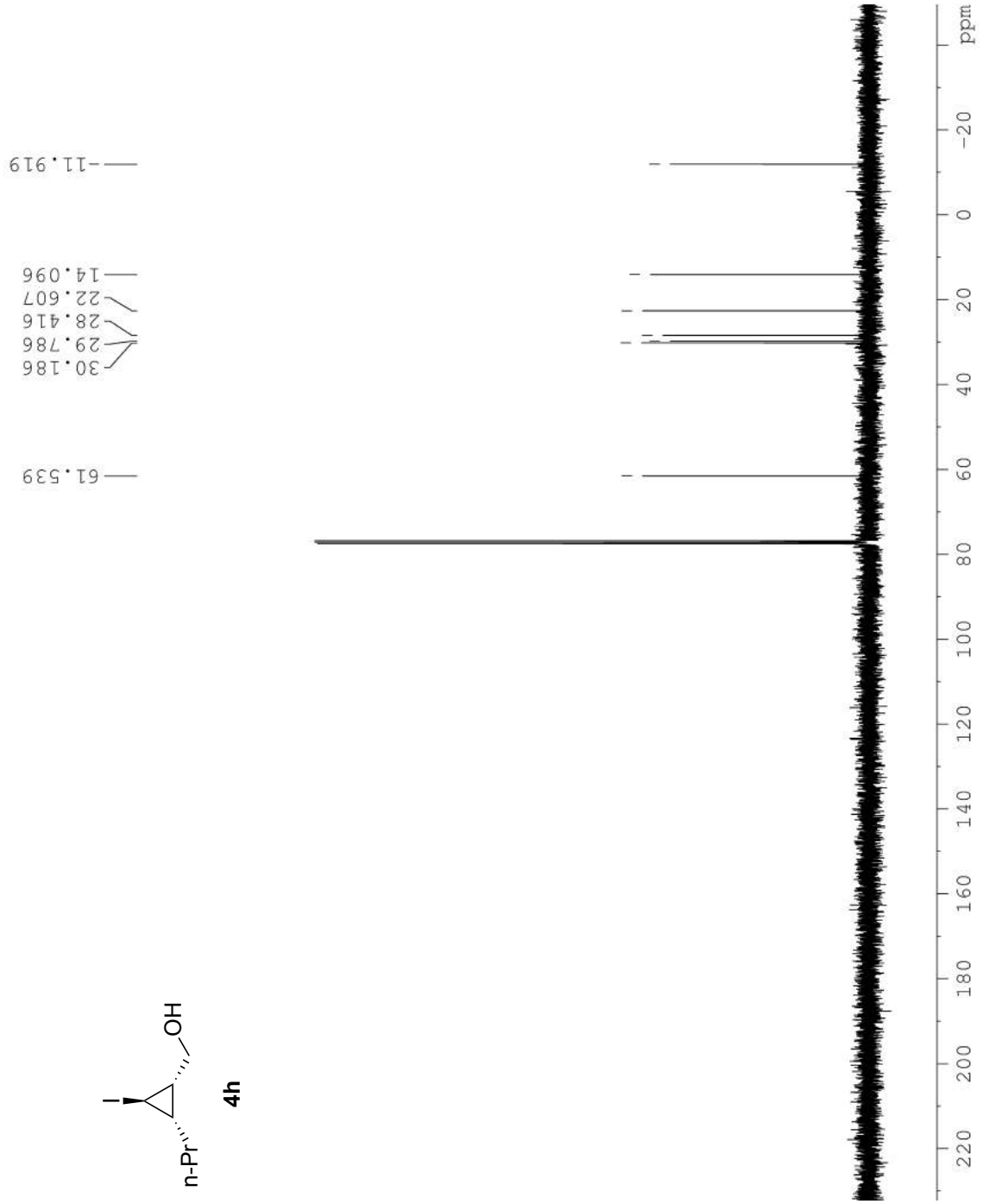
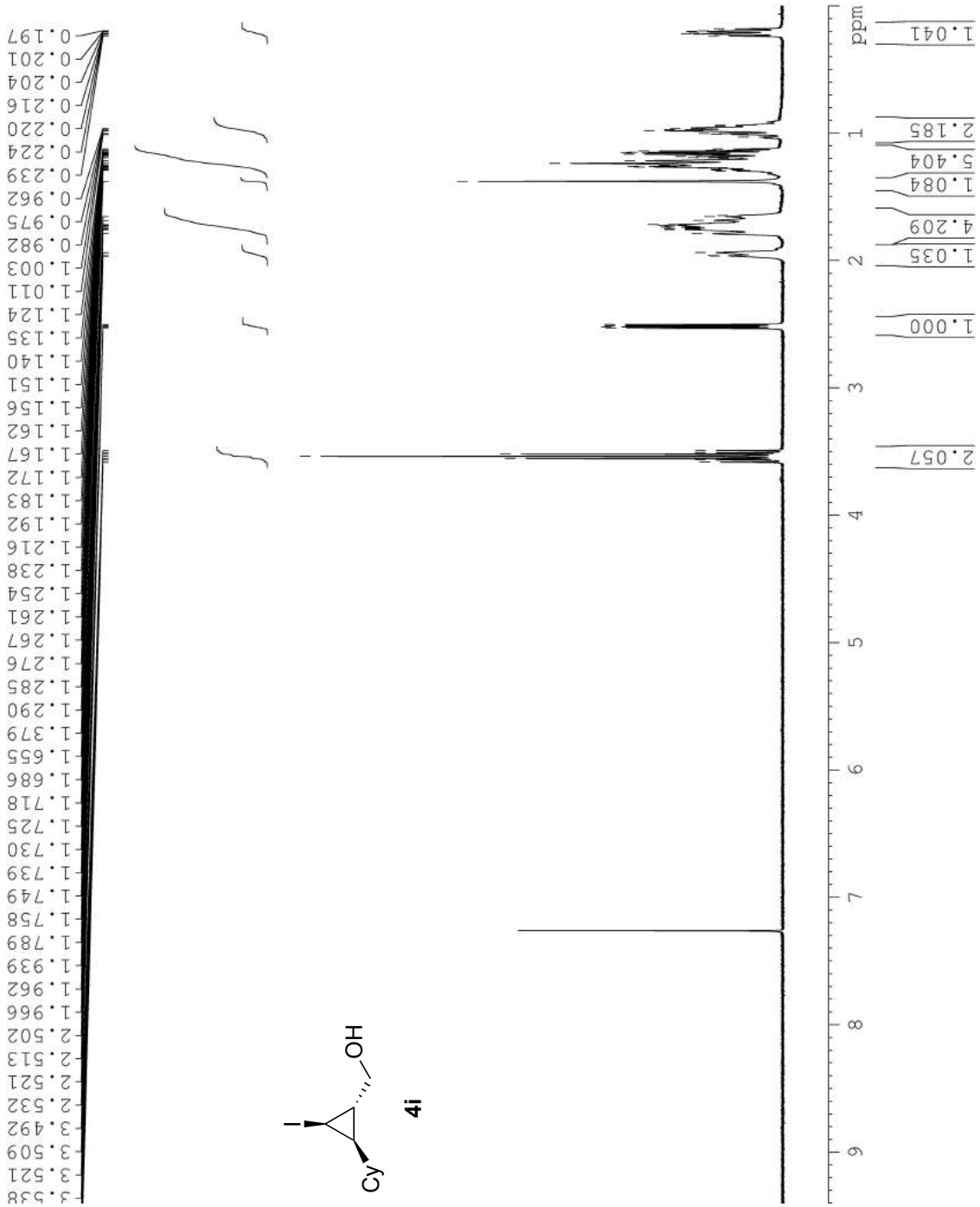
1.000
1.039
1.055


11.919
14.096
22.607
28.416
29.786
30.186
61.539
ppm
-20
0
20
40
60
80
100
120
140
160
180
200
220
OH
n-Pr
4h


ppm
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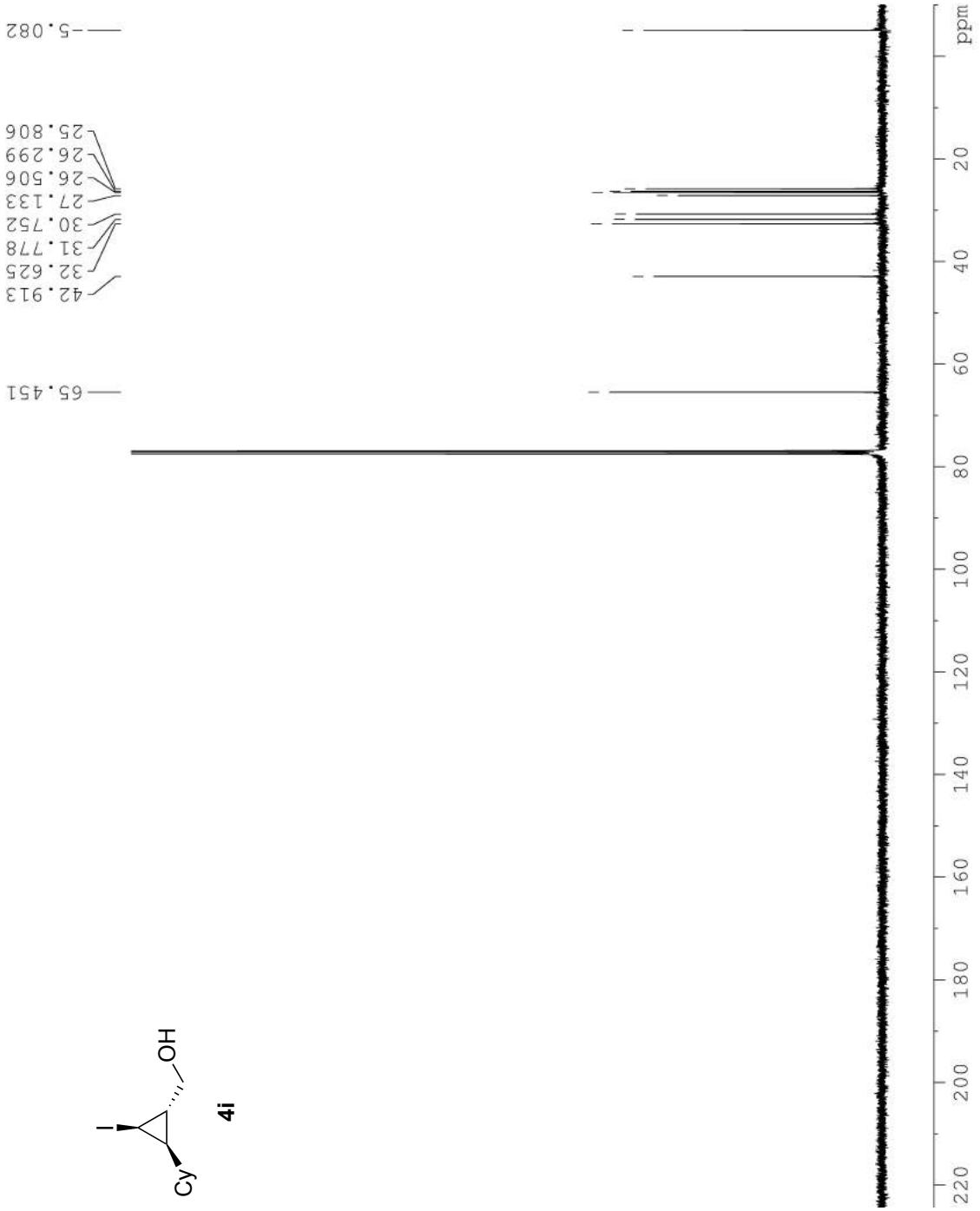
5.404
1.084
4.209
1.035
1.000
2.057
OH
I
Cy
4i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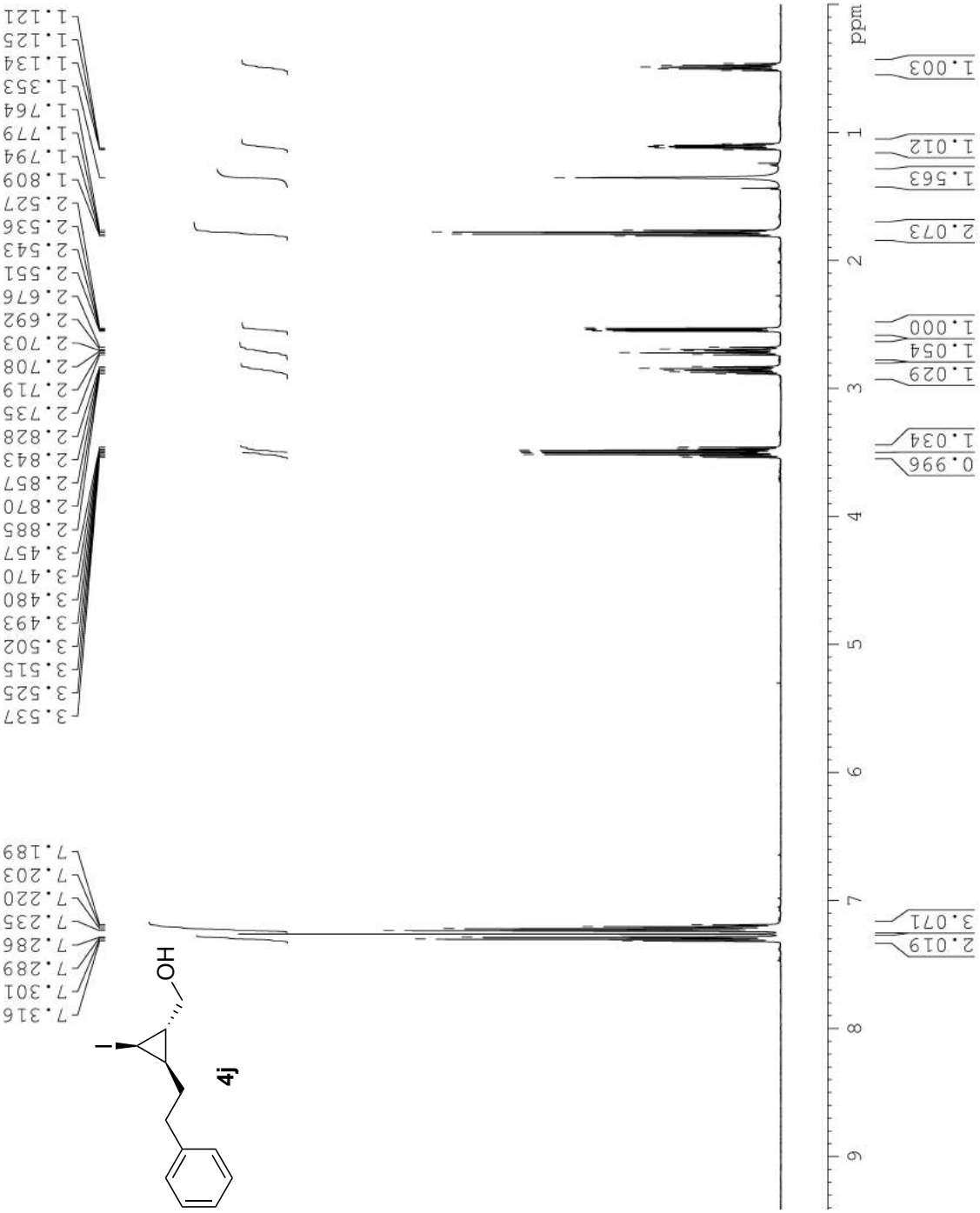
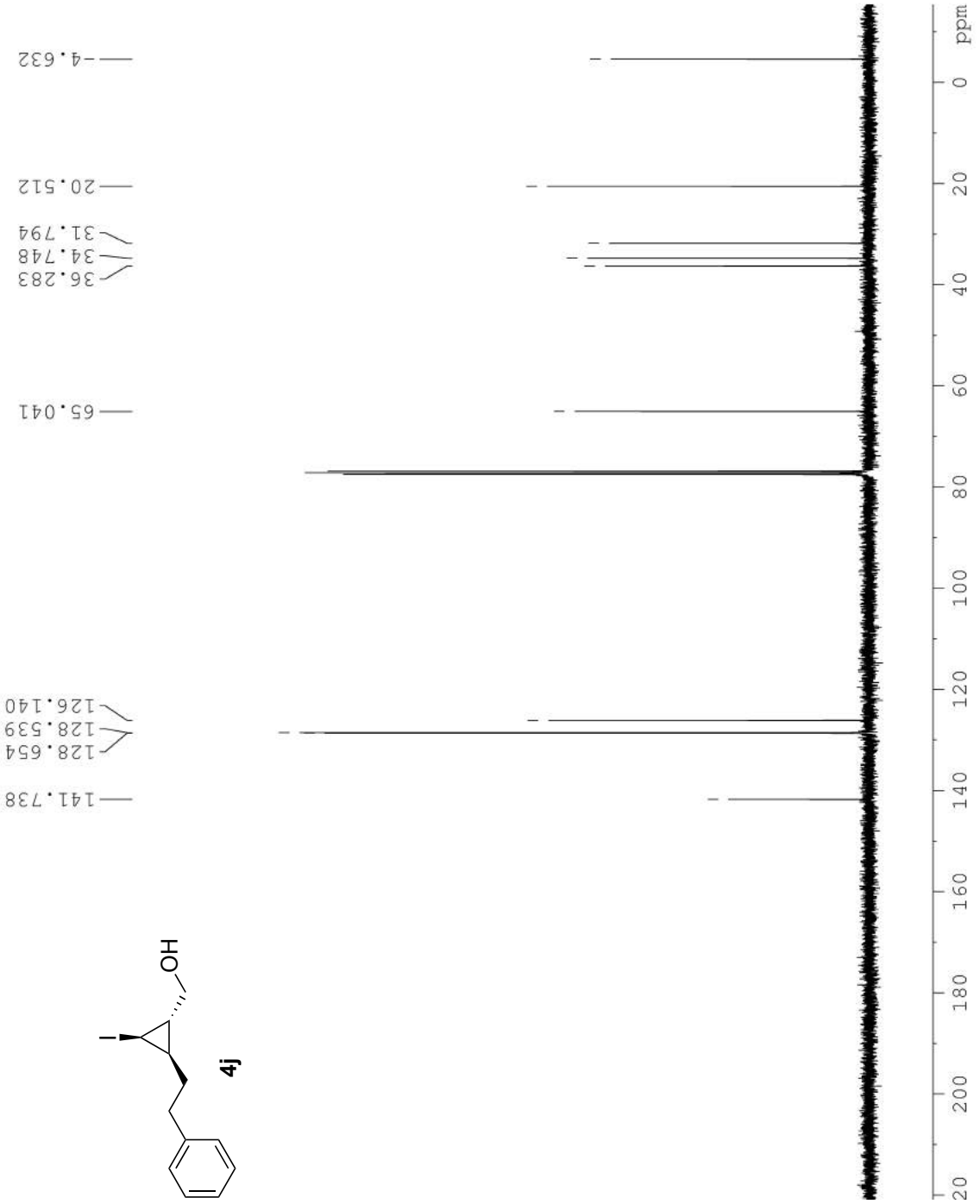
25.806
26.299
26.506
27.133
30.752
31.778
32.625
42.913
65.451
ppm
20
40
60
80
100
120
140
160
180
200
220
OH
Cy
I
4i


4j
OH
ppm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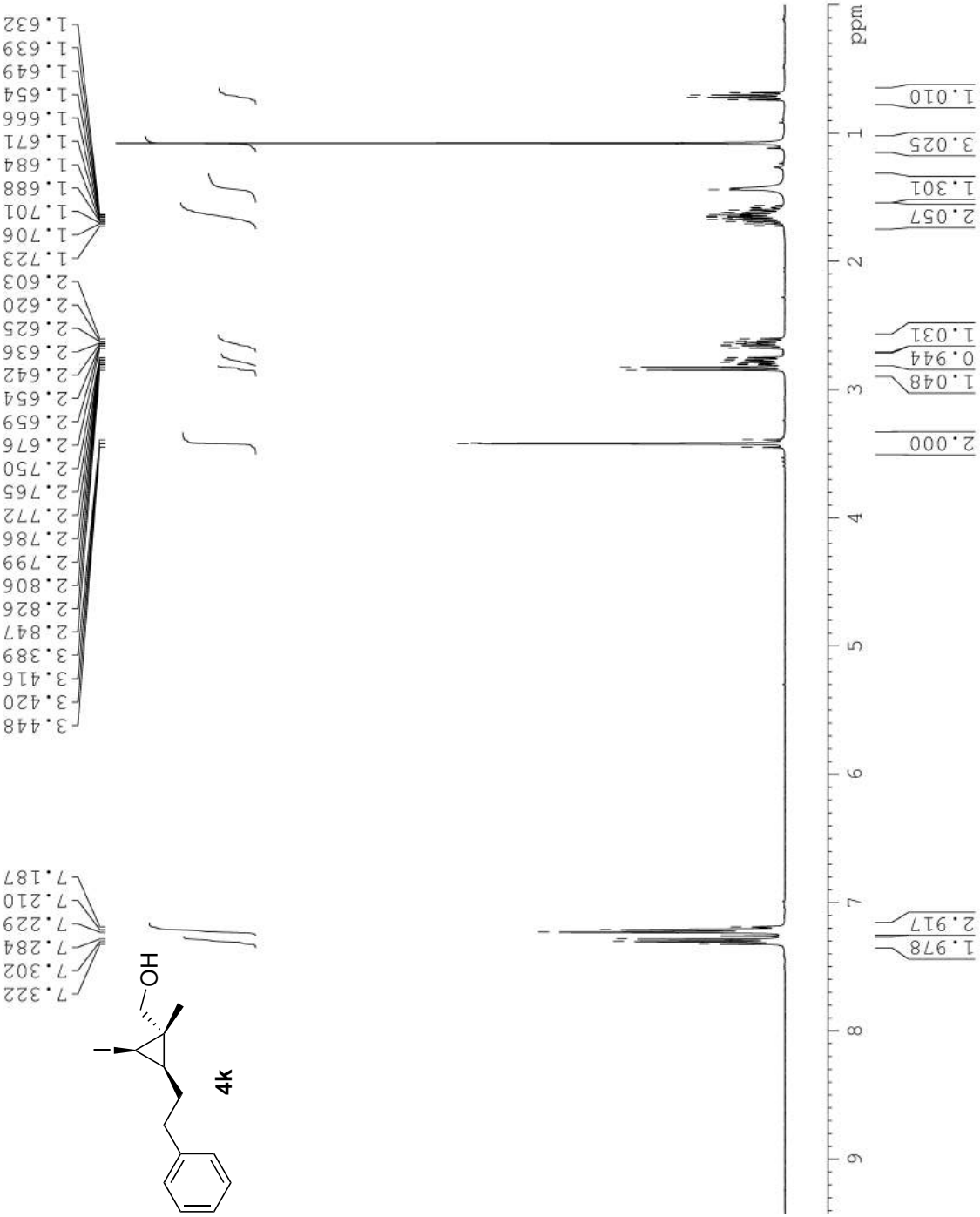
31.794
34.748
36.283
65.041
126.140
128.539
128.654
141.738
ppm
0
20
40
60
80
100
120
140
160
180
200
220
OH
4j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1.639
1.649
1.654
1.666
1.671
1.684
1.688
1.701
1.706
1.723
2.603
2.620
2.625
2.636
2.642
2.654
2.659
2.676
2.750
2.765
2.772
2.786
2.799
2.806
2.826
2.847
3.389
3.416
3.420
3.448
7.187
7.210
7.229
7.284
7.302
7.322
OH
4k
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1.301
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1.031
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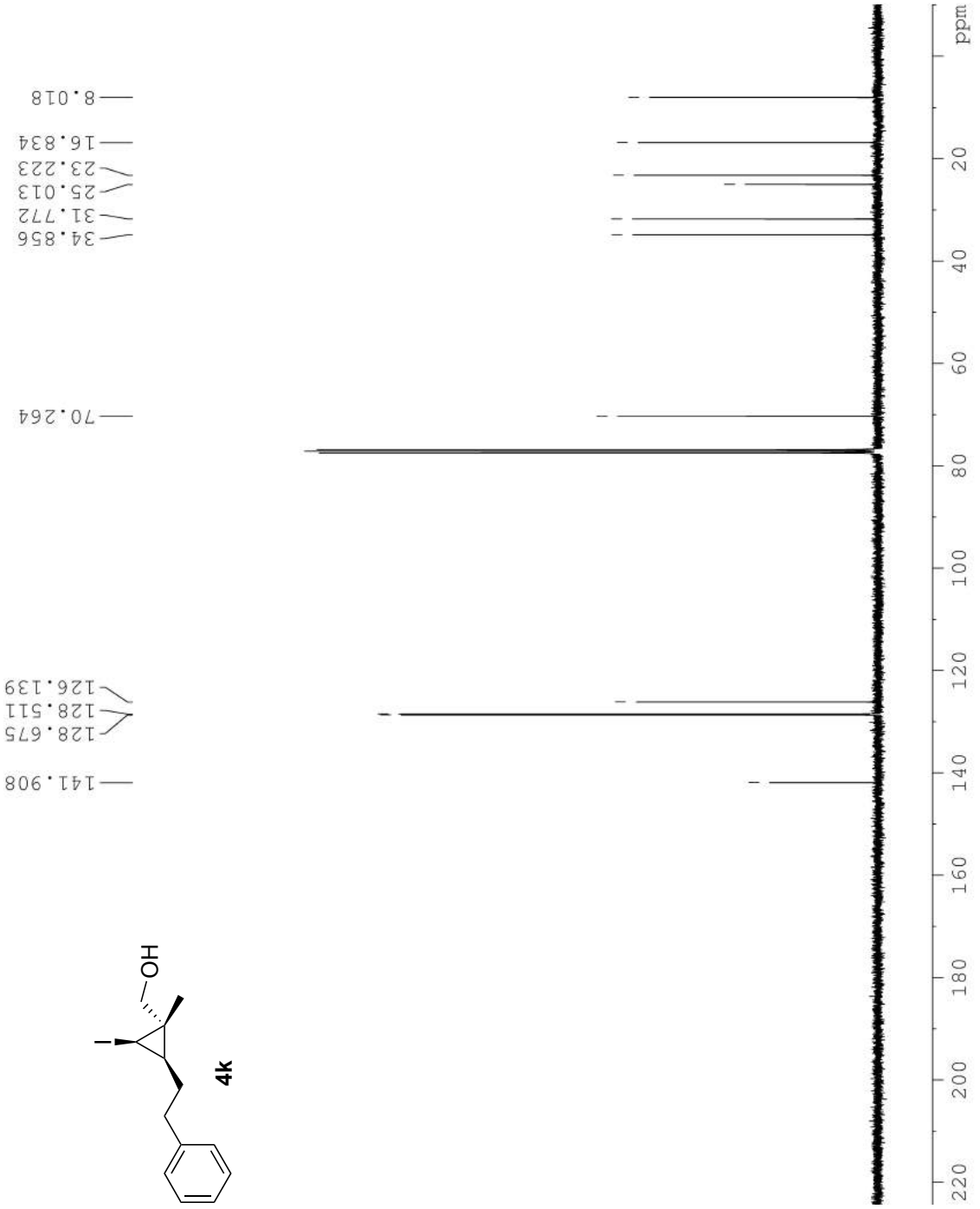
2.000
2.917
1.978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16.834
23.223
25.013
31.772
34.856
70.264
126.139
128.511
128.675
141.908
ppm
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80
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120
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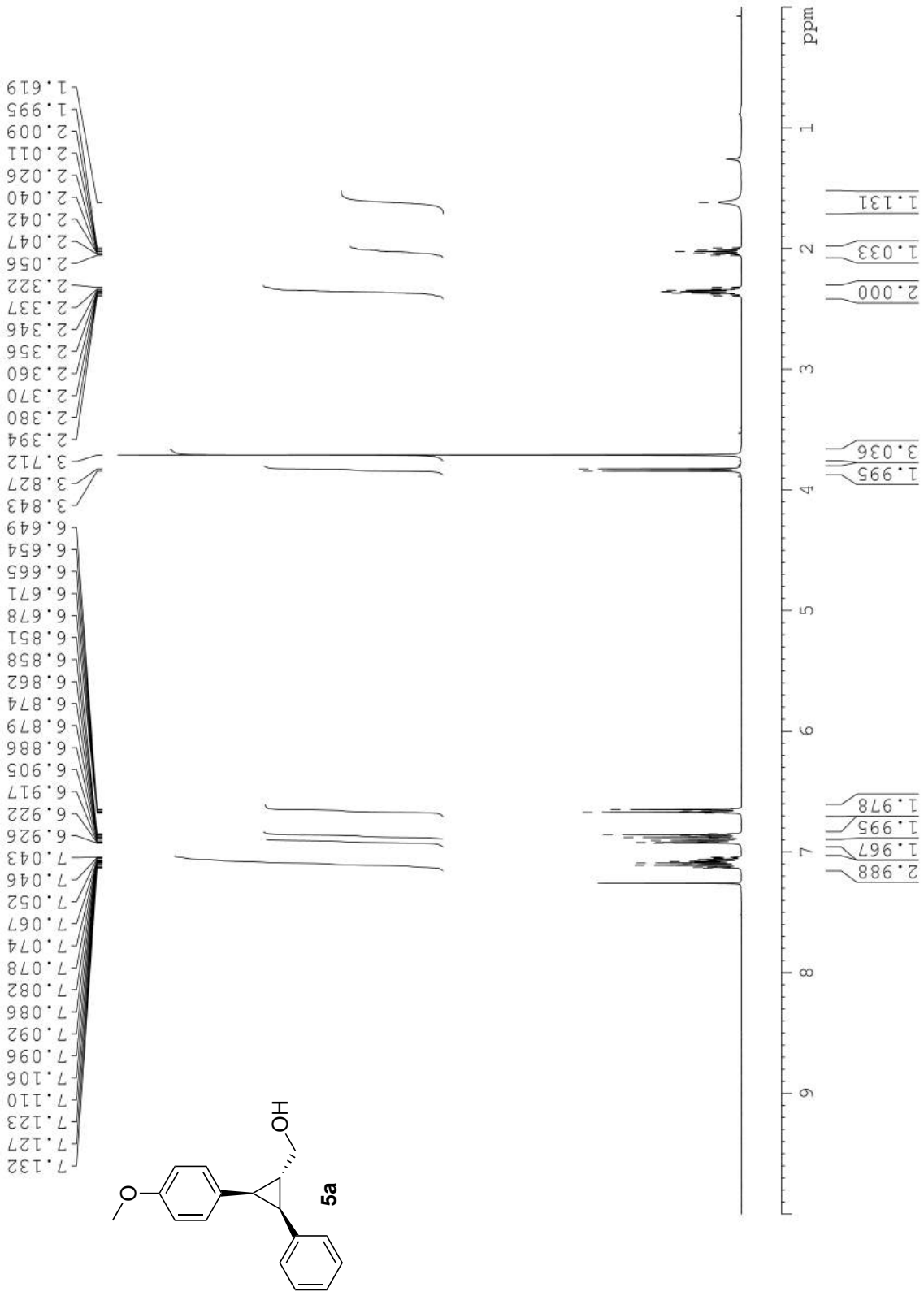
180
200
220
OH
4k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2.009
2.011
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2.040
2.042
2.047
2.056
2.322
2.337
2.346
2.356
2.360
2.370
2.380
2.394
3.712
3.827
3.843
6.649
6.654
6.665
6.671
6.678
6.851
6.858
6.862
6.874
6.879
6.886
6.905
6.917
6.922
6.926
7.043
7.046
7.052
7.067
7.074
7.078
7.082
7.086
7.092
7.096
7.106
7.110
7.123
7.127
7.132
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2.000
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1.995
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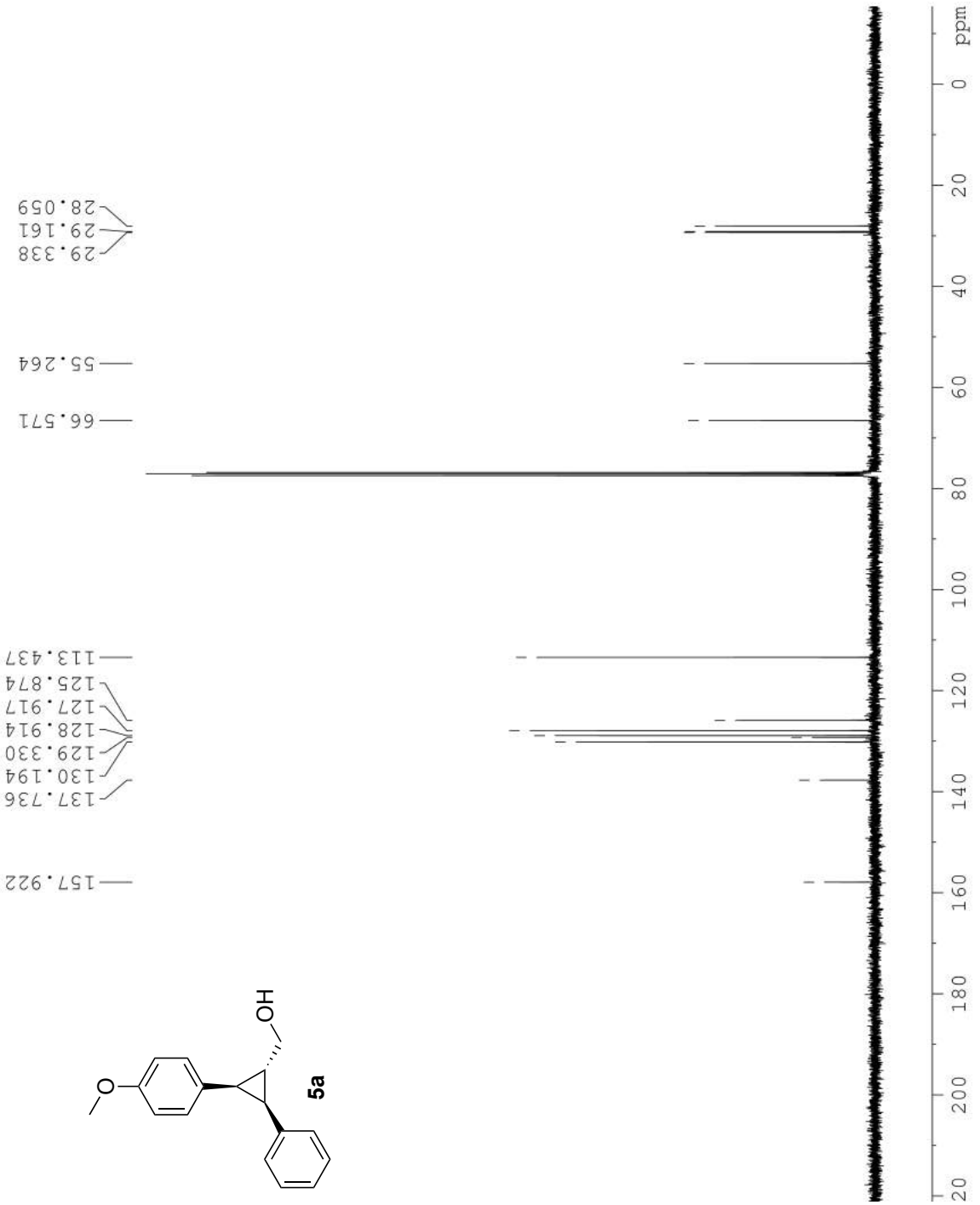
O
5a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127.917
128.914
129.330
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137.736
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ppm
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60
80
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120
140
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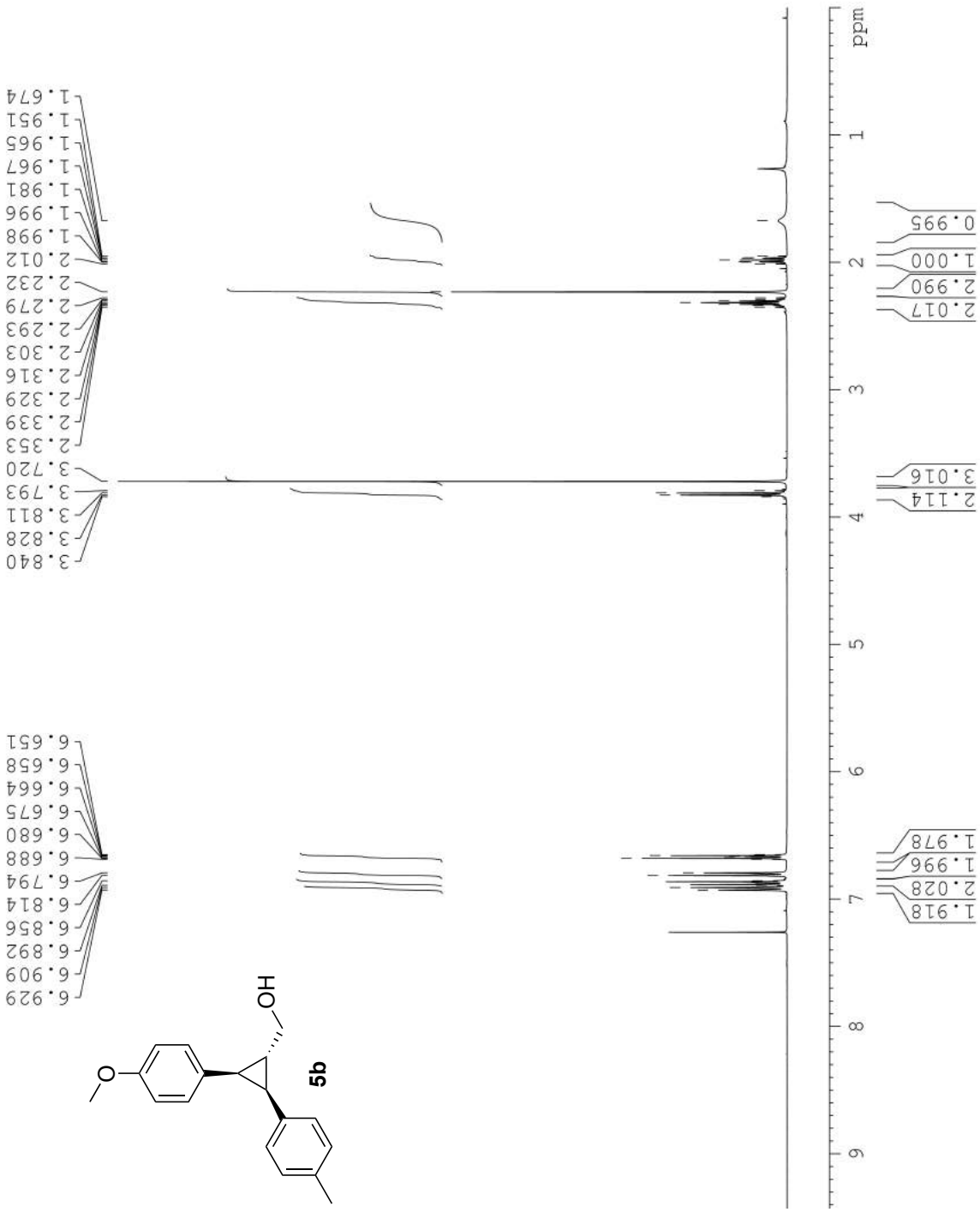
200
OH
O
5a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3
4
5
6
7
8
9
0.995
1.000
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2.017
3.016
2.114
1.978
1.996
2.028
1.918
6.929
6.909
6.892
6.856
6.814
6.794
6.688
6.680
6.675
6.664
6.658
6.651
3.840
3.828
3.811
3.793
3.720
2.353
2.339
2.329
2.316
2.303
2.293
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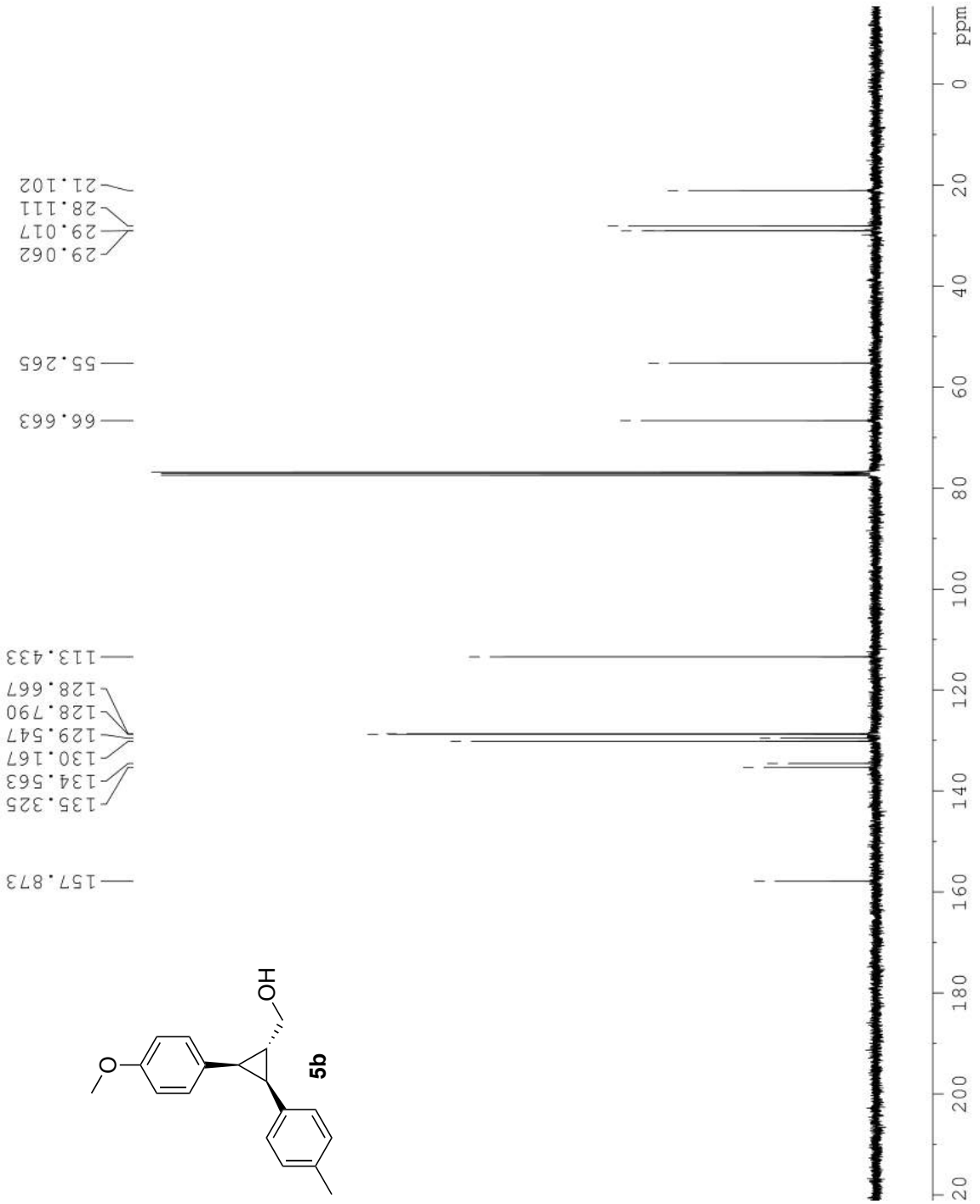
OH
O
5b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66.663
113.433
128.667
128.790
129.547
130.167
134.563
135.325
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ppm
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60
80
100
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140
160
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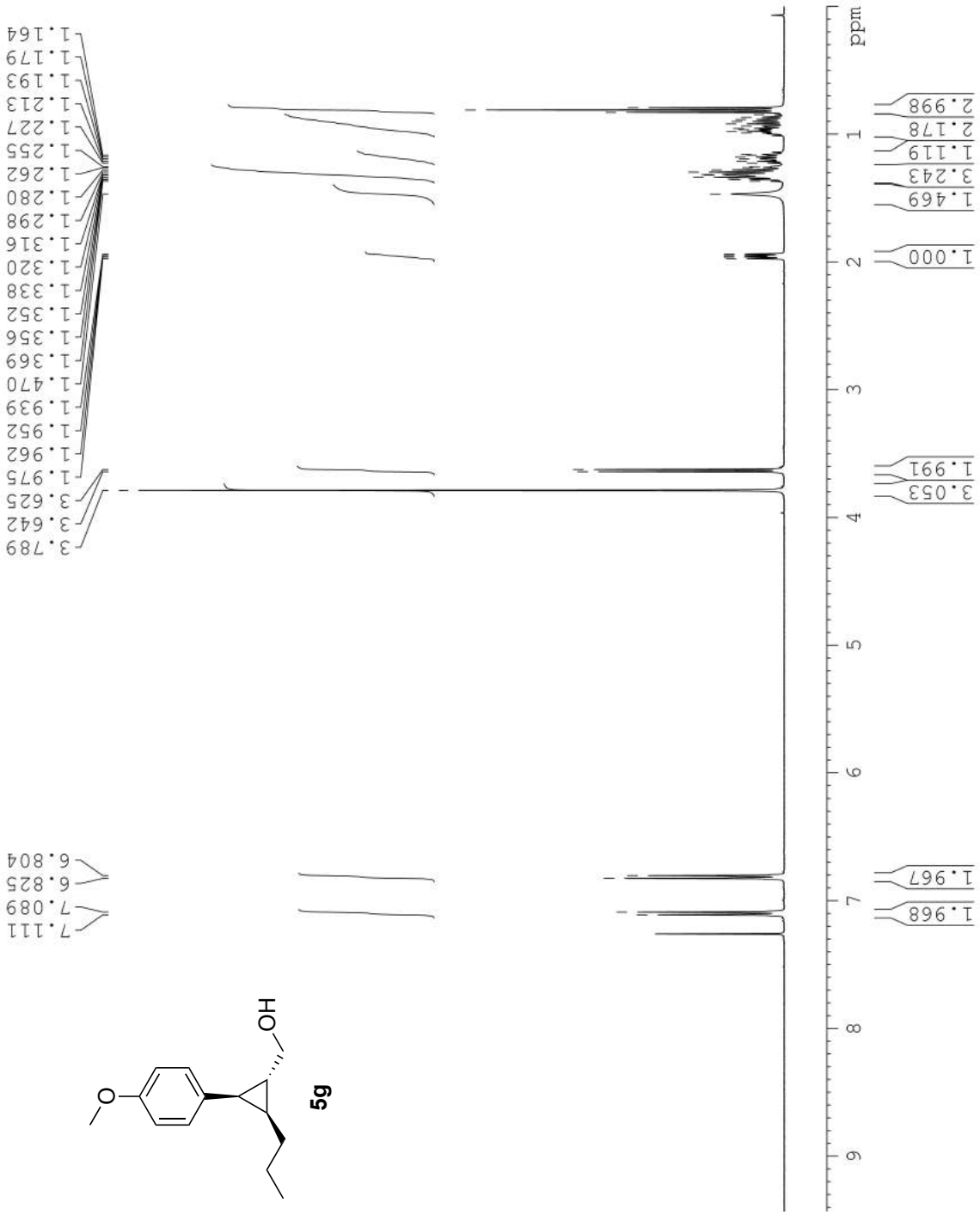
200
220
OH
O
5b


ppm
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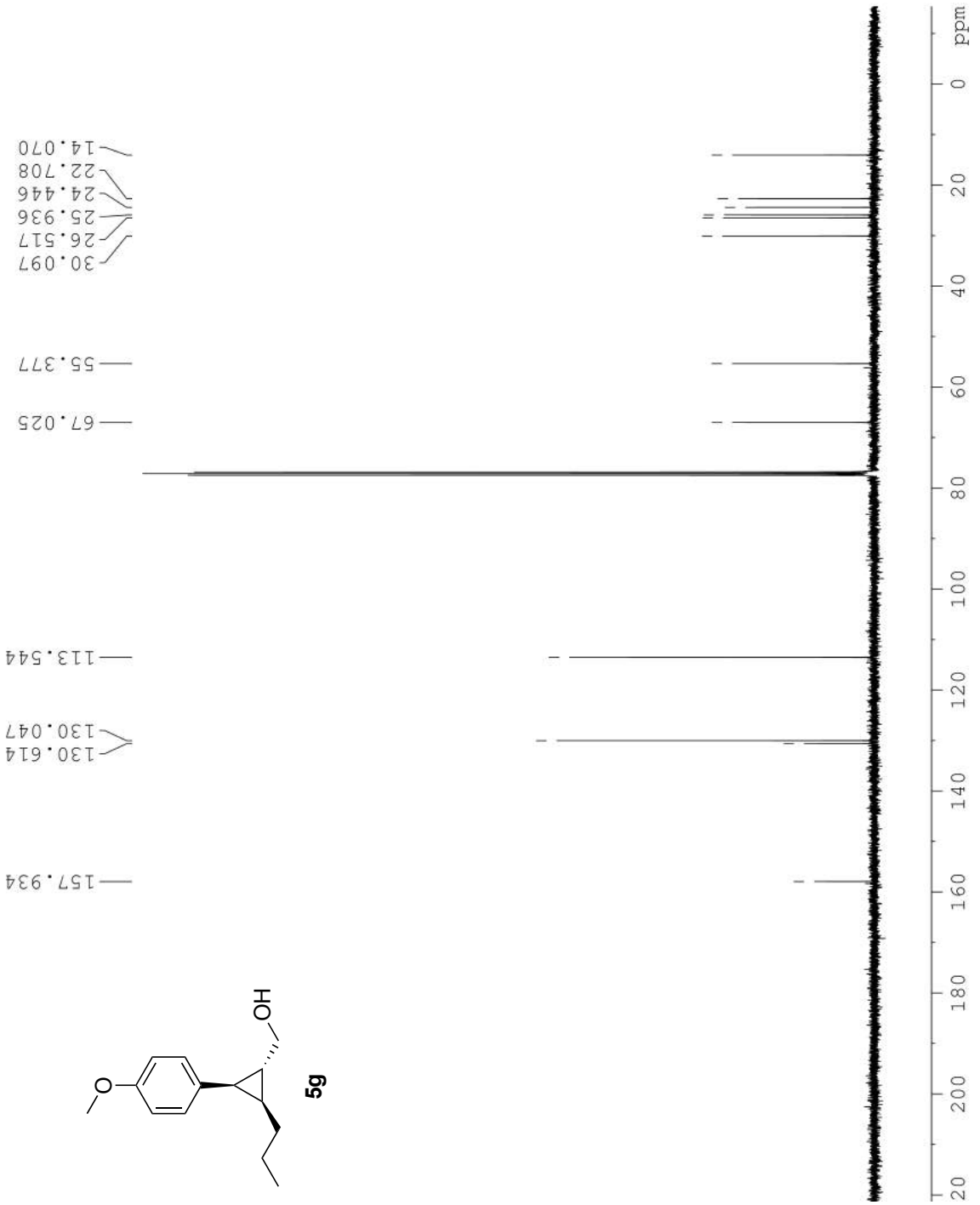
2
3
4
5
6
7
8
9
2.998
2.178
1.119
3.243
1.469
1.000
1.991
3.053
1.967
1.968
3.789
3.642
3.625
1.975
1.962
1.952
1.939
1.470
1.369
1.356
1.352
1.338
1.320
1.316
1.298
1.280
1.262
1.255
1.227
1.213
1.193
1.179
1.164
7.111
7.089
6.825
6.804
OH
O
5g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30.097
55.377
67.025
113.544
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130.614
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ppm
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100
120
140
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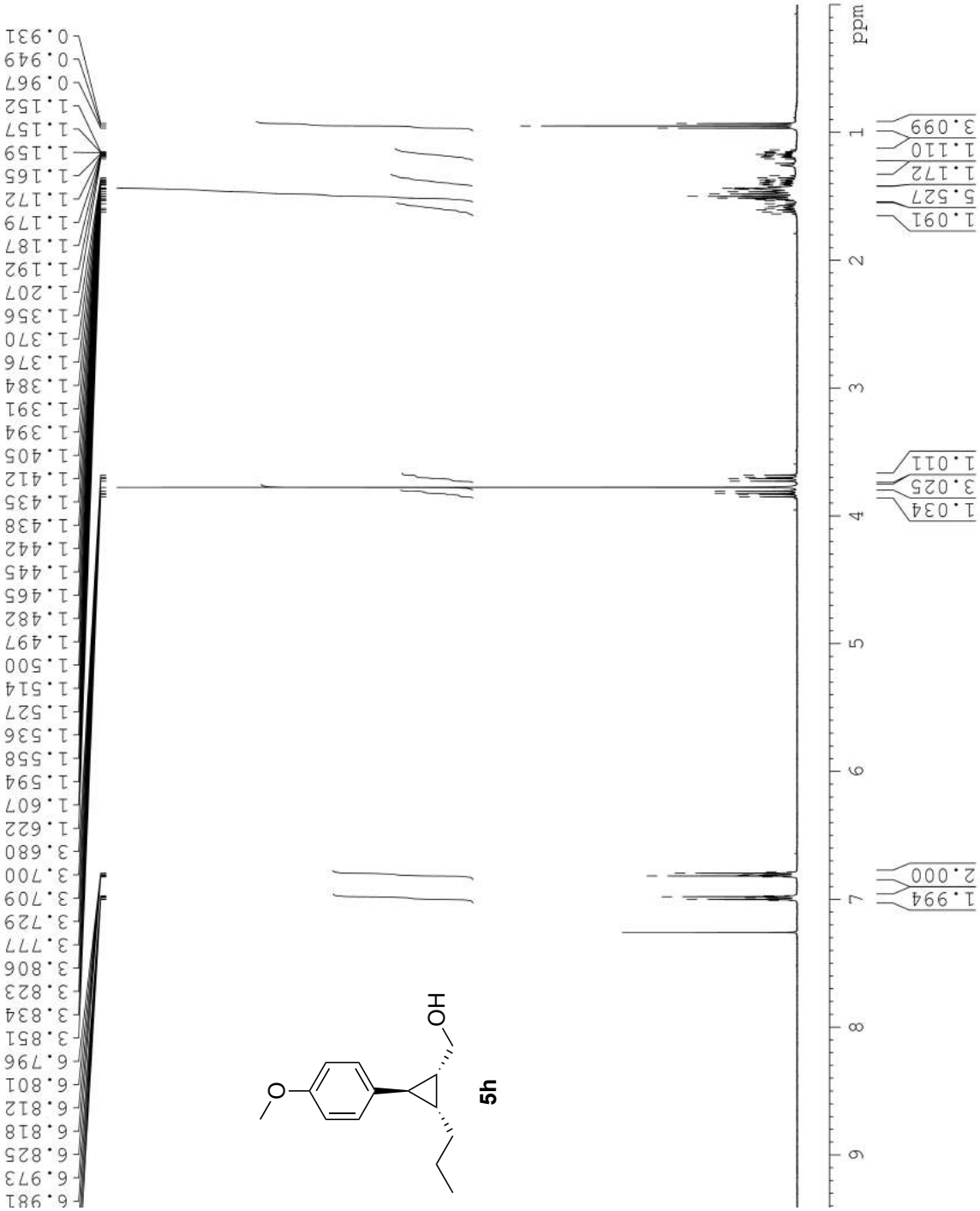
180
200
OH
O
5g


ppm
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2
3
4
5
6
7
8
9
3.099
1.110
1.172
5.527
1.091
1.011
3.025
1.034
1.994
2.000
0.931
0.949
0.967
1.152
1.157
1.159
1.165
1.172
1.179
1.187
1.192
1.207
1.356
1.370
1.376
1.384
1.391
1.394
1.405
1.412
1.435
1.438
1.442
1.445
1.465
1.482
1.497
1.500
1.514
1.527
1.536
1.558
1.594
1.607
1.622
3.680
3.700
3.709
3.729
3.777
3.806
3.823
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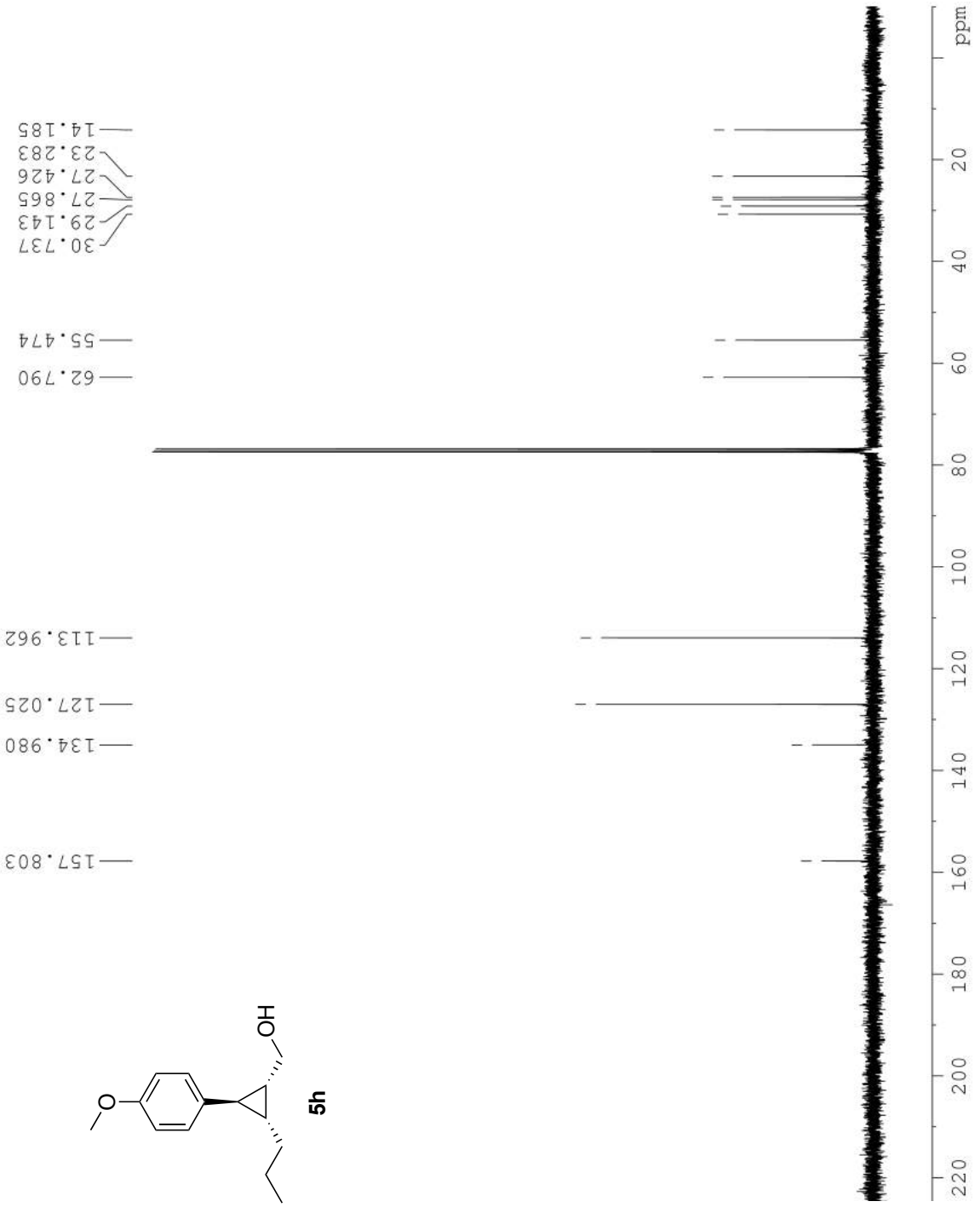
3.851
6.796
6.801
6.812
6.818
6.825
6.973
6.981
OH
O
5h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23.283
27.426
27.865
29.143
30.737
55.474
62.790
113.962
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134.980
157.803
ppm
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60
80
100
120
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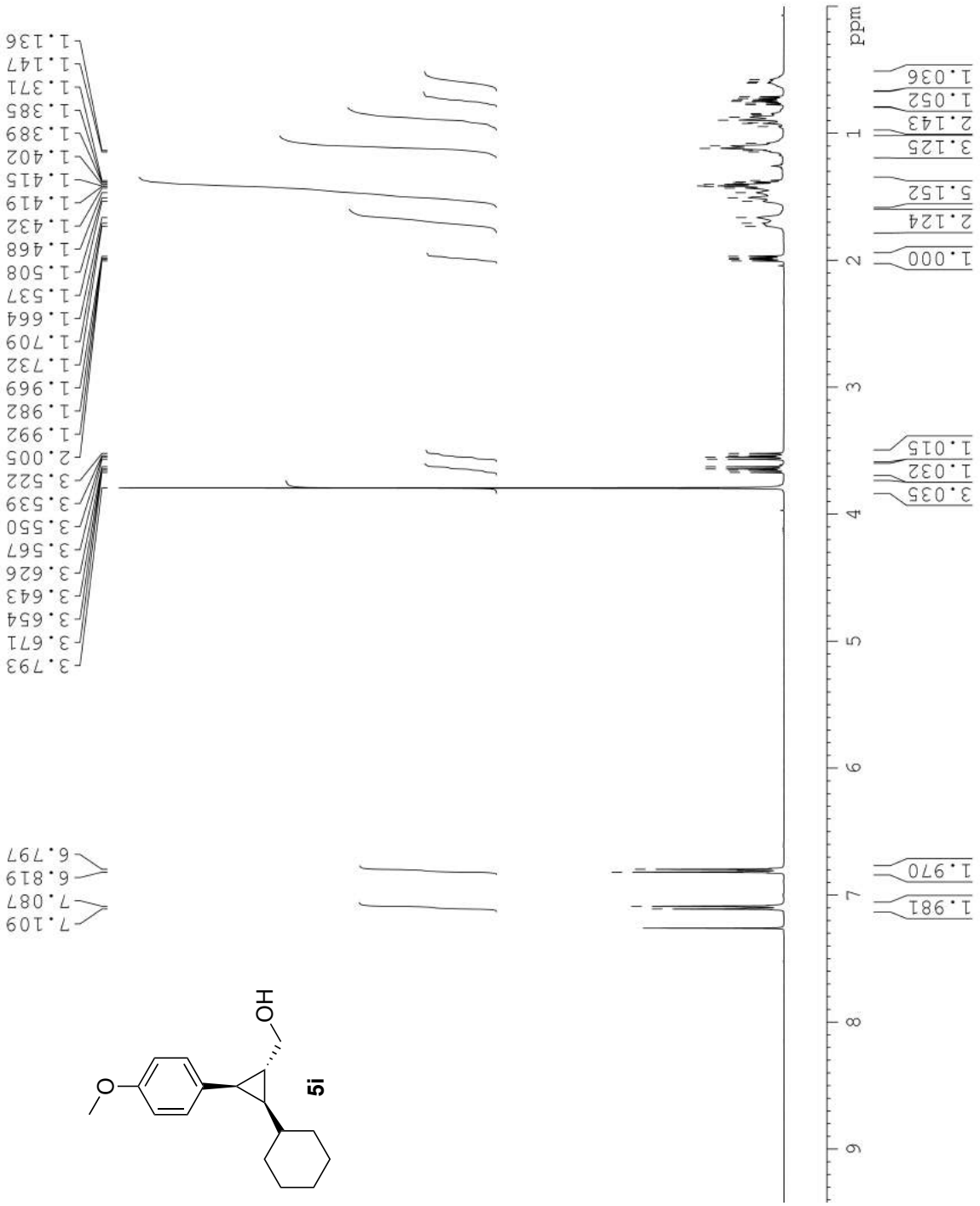
200
220
OH
O
5h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3.125
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3.035
1.032
1.015
1.970
1.981
1.136
1.147
1.371
1.385
1.389
1.402
1.415
1.419
1.432
1.468
1.508
1.537
1.664
1.709
1.732
1.969
1.982
1.992
2.005
3.522
3.539
3.550
3.567
3.626
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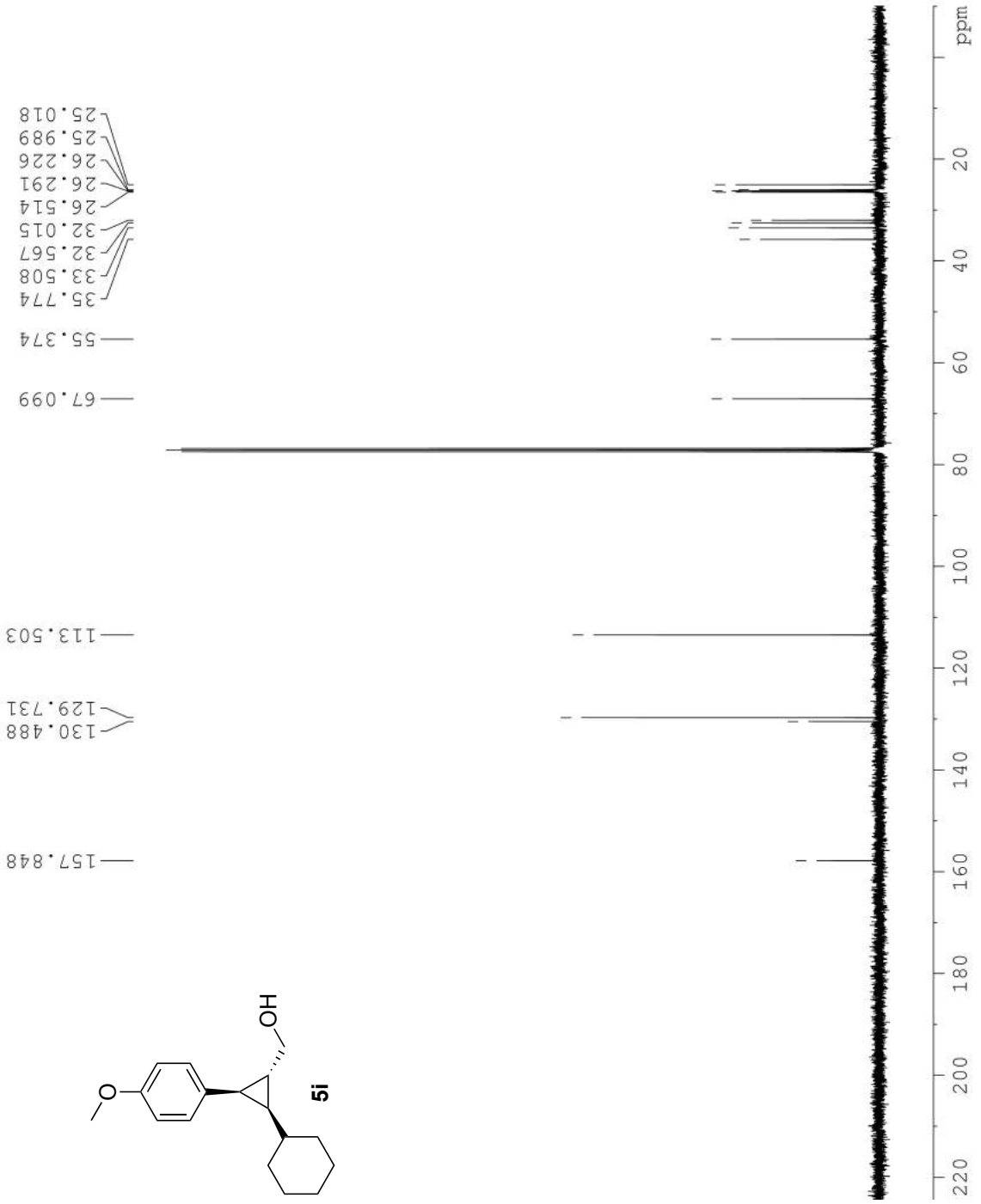
3.654
3.671
3.793
6.797
6.819
7.087
7.109
OH
O
5i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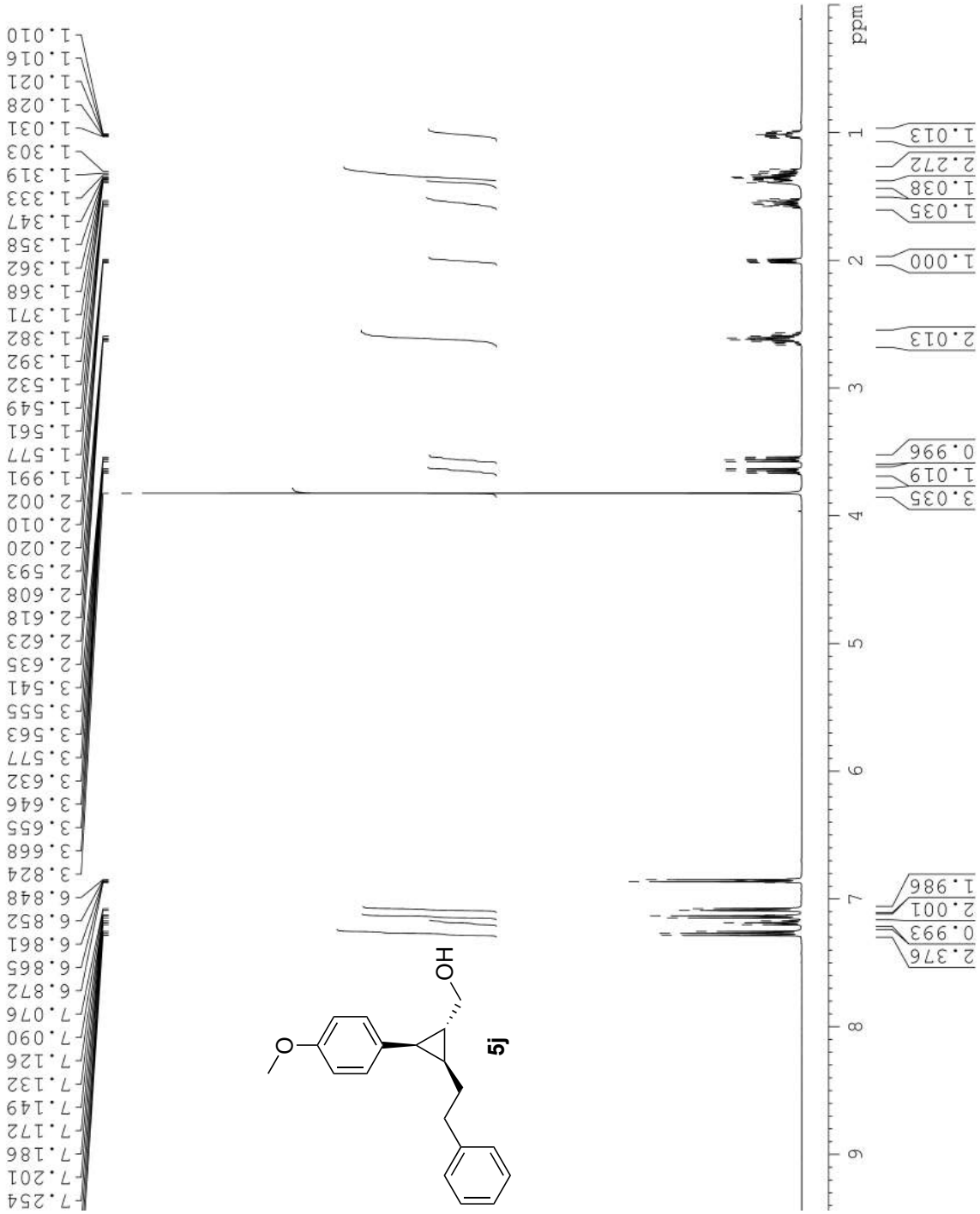
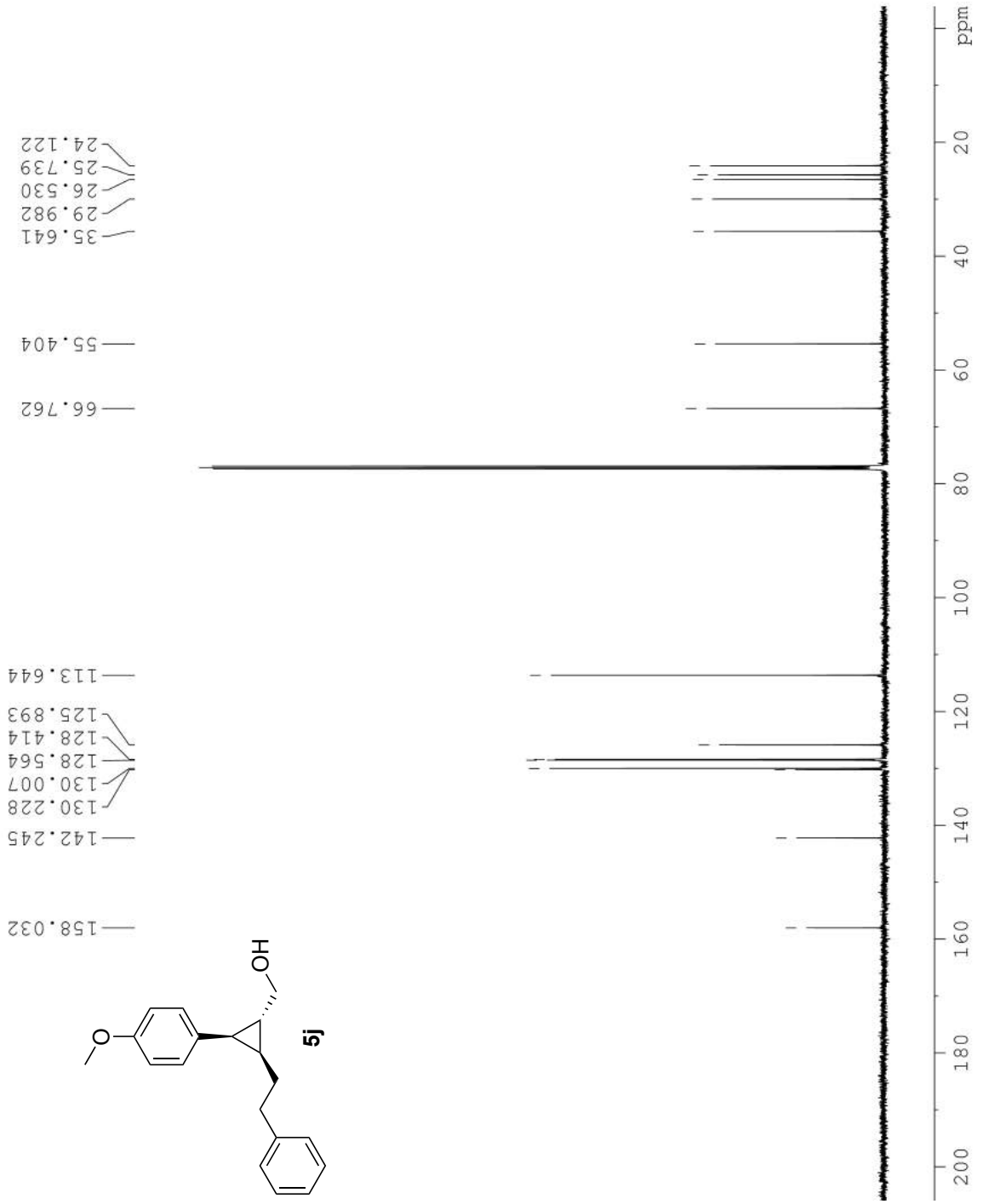
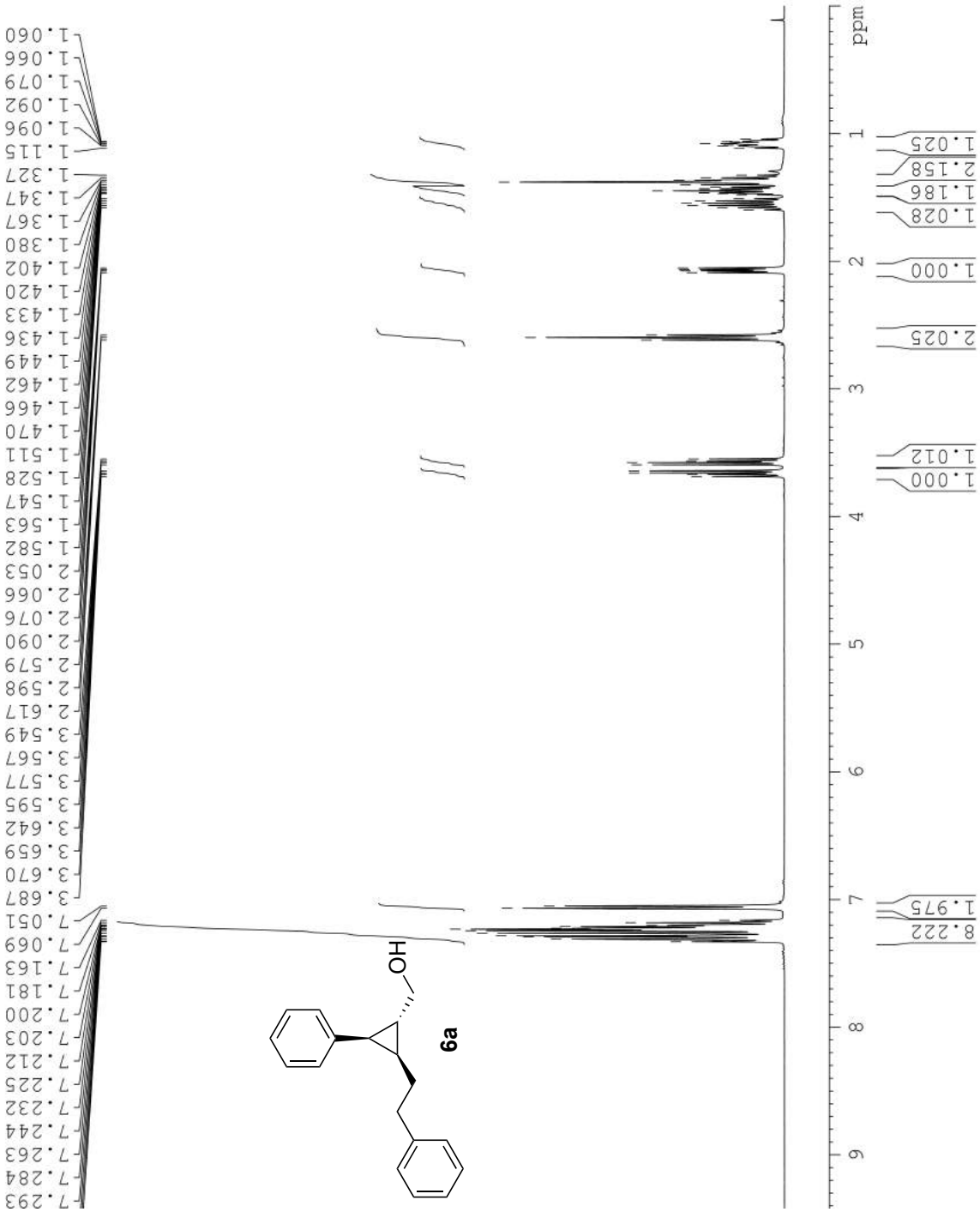
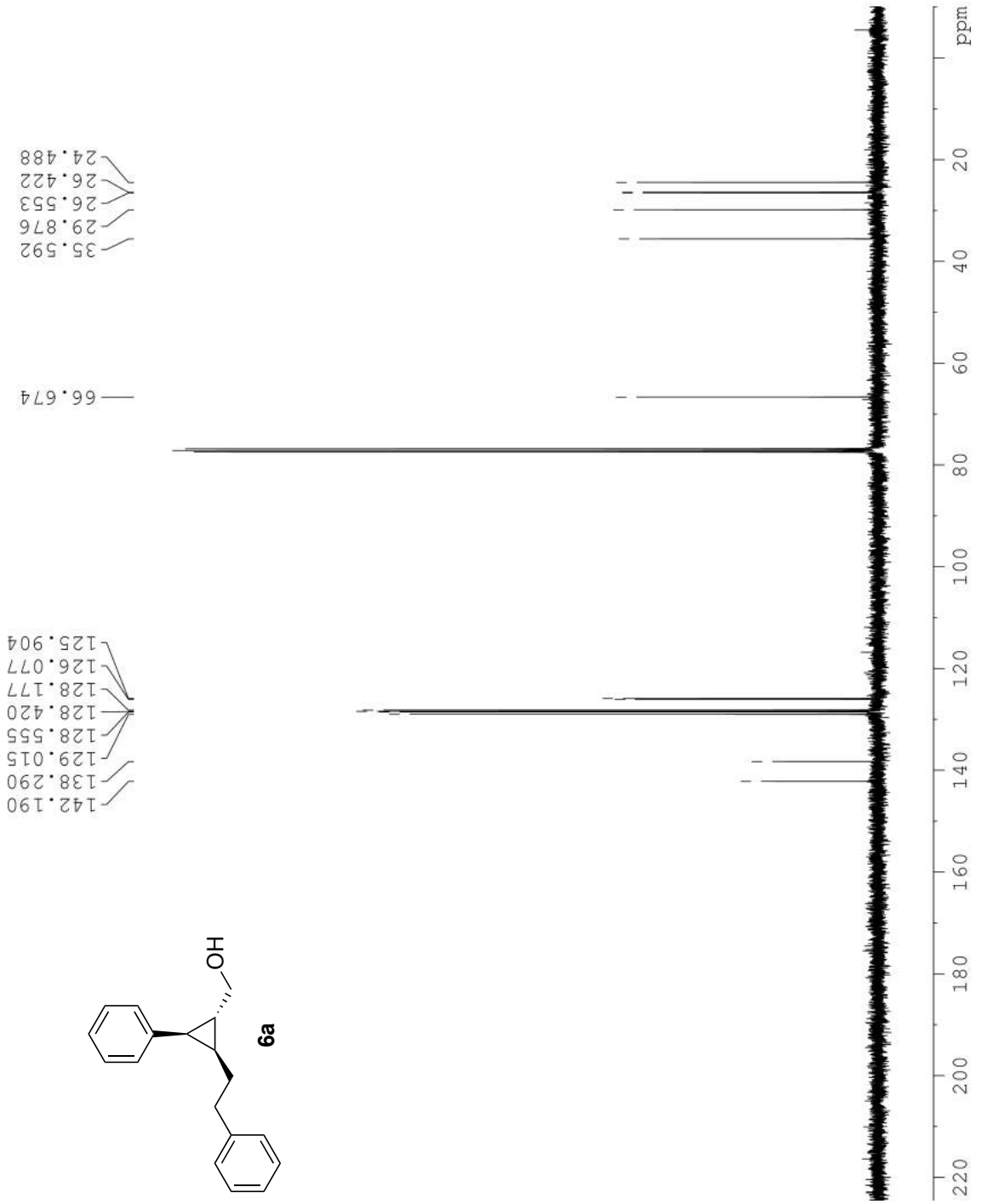
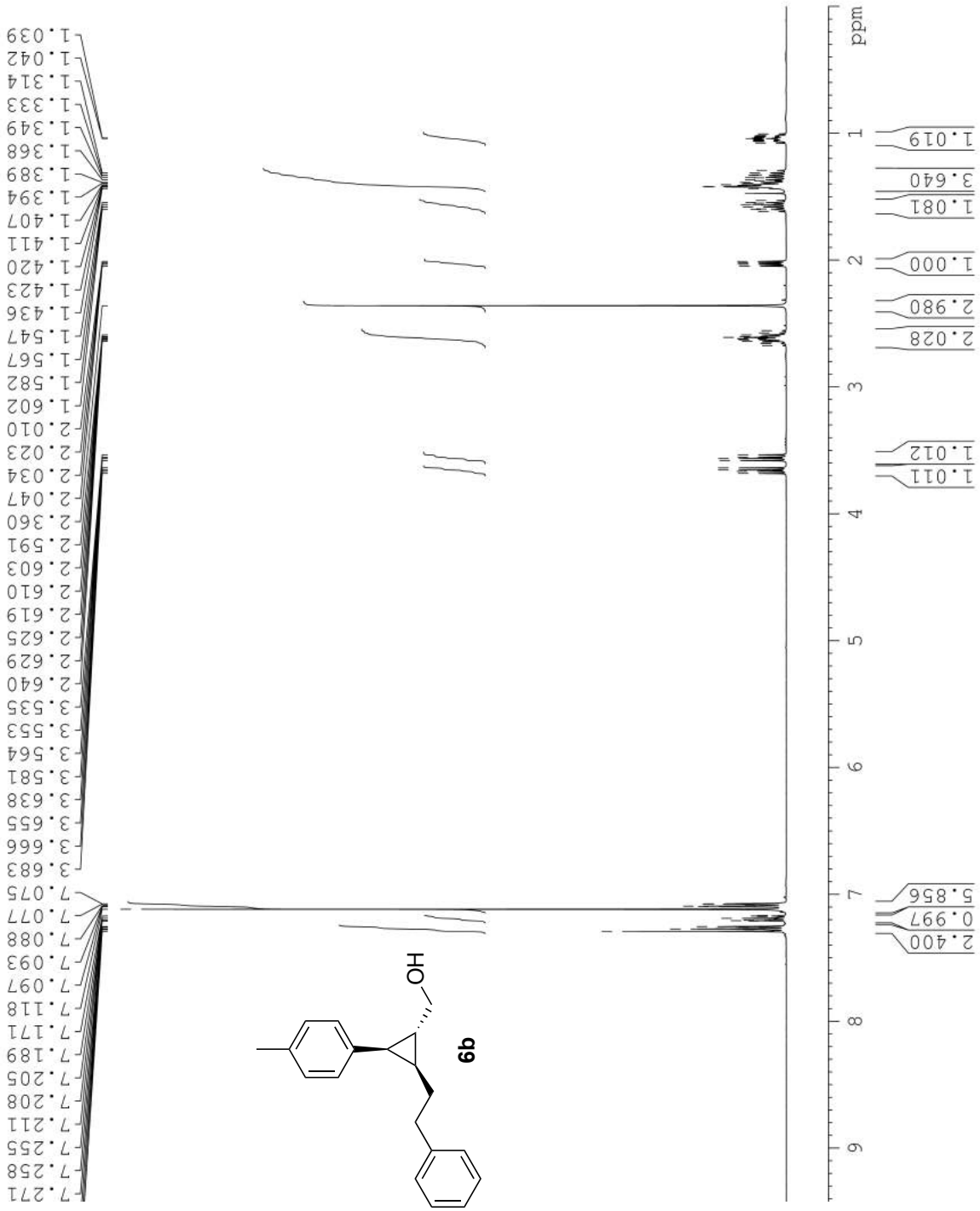
26.291
26.514
32.015
32.567
33.508
35.774
55.374
67.099
113.503
129.731
130.488
157.848
ppm
20
40
60
80
100
120
140
160
180
200
220
OH
O
5i

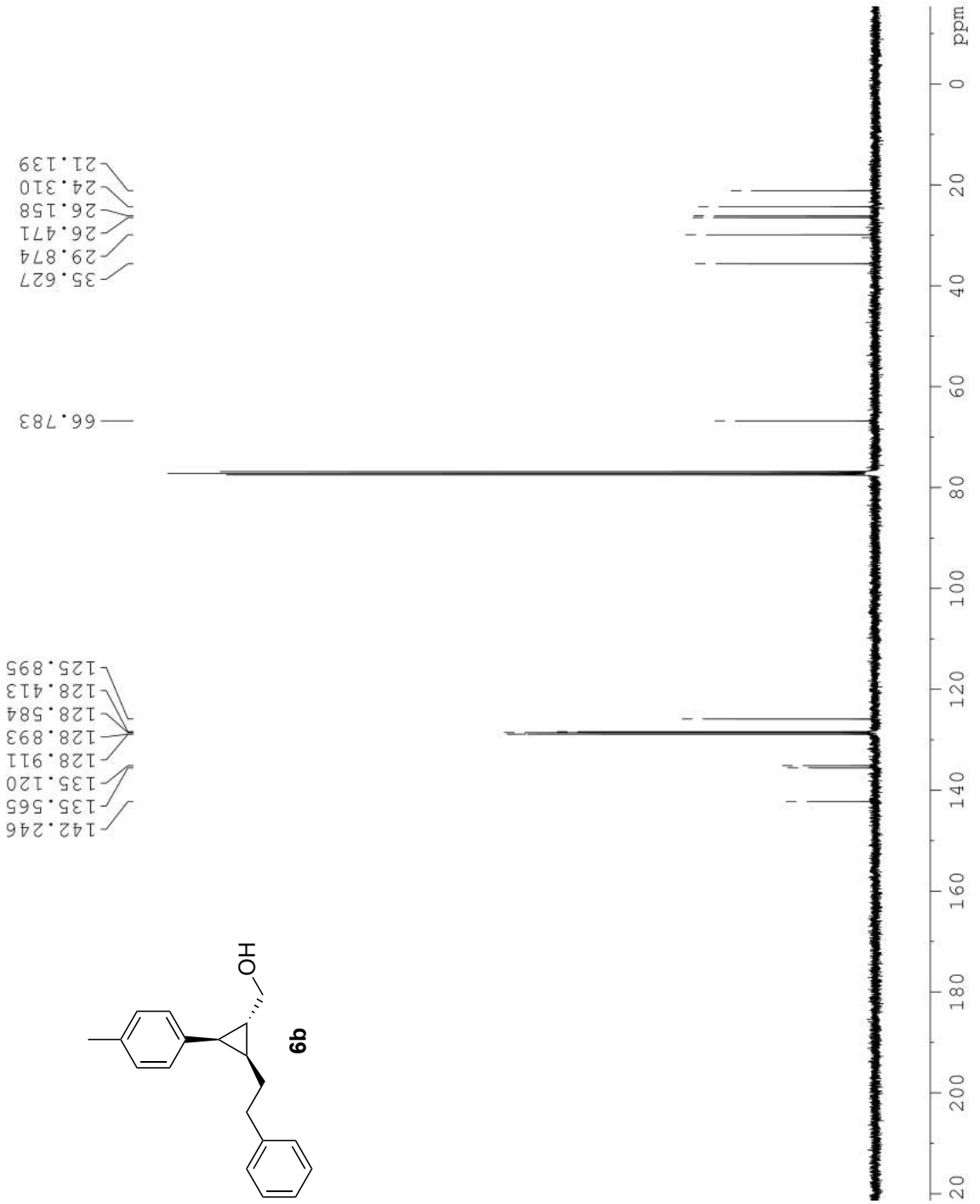

ppm
1
2
3
4
5
6
7
8
9
1.013
2.272
1.038
1.035
1.000
2.013
0.996
1.019
3.035
1.986
2.001
0.993
2.376
OH
O
5j

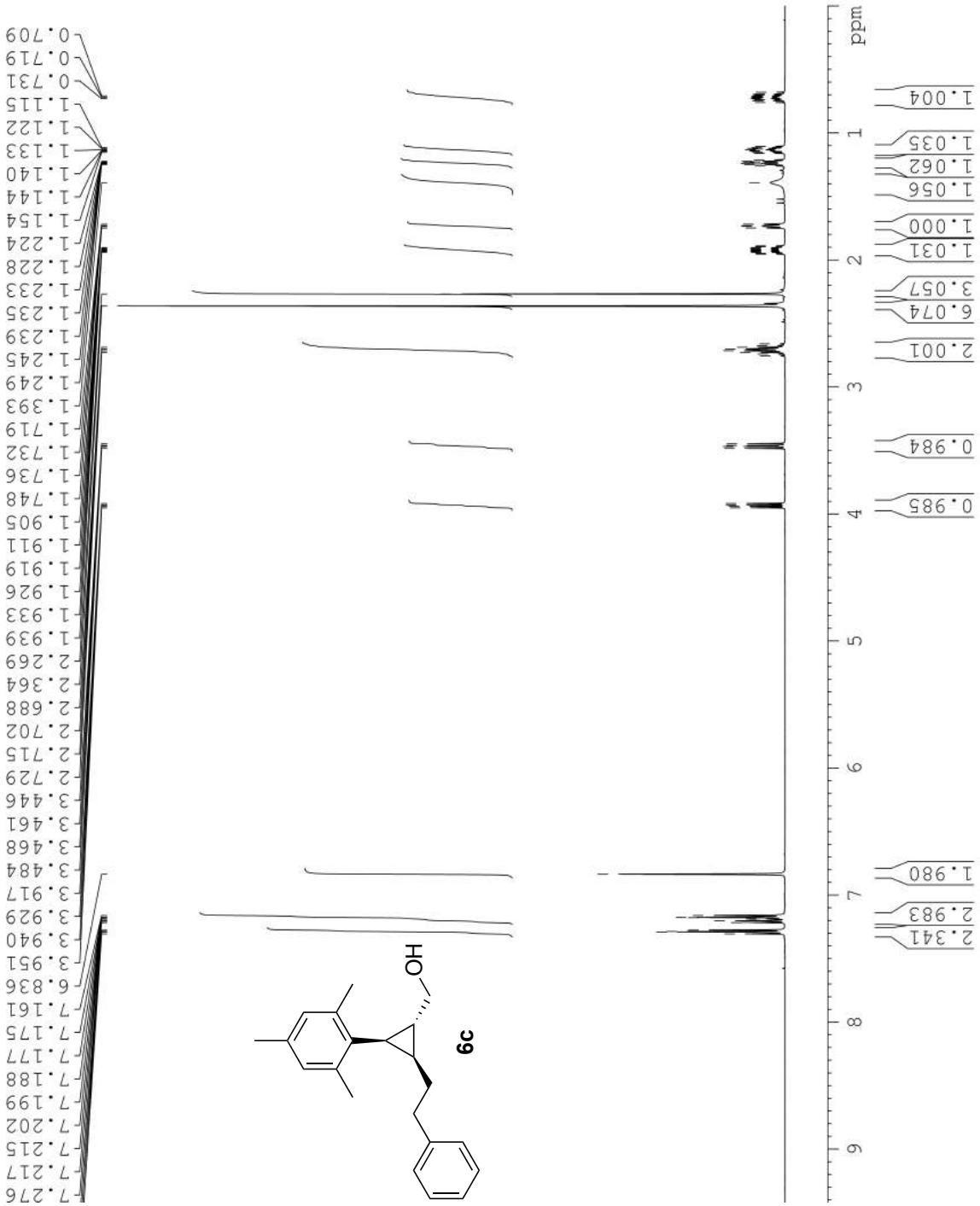

158.032
142.245
130.228
130.007
128.564
128.414
125.893
113.644
66.762
55.404
35.641
29.982
26.530
25.739
24.122
ppm
20
40
60
80
100
120
140
160
180
200
OH
O
5j

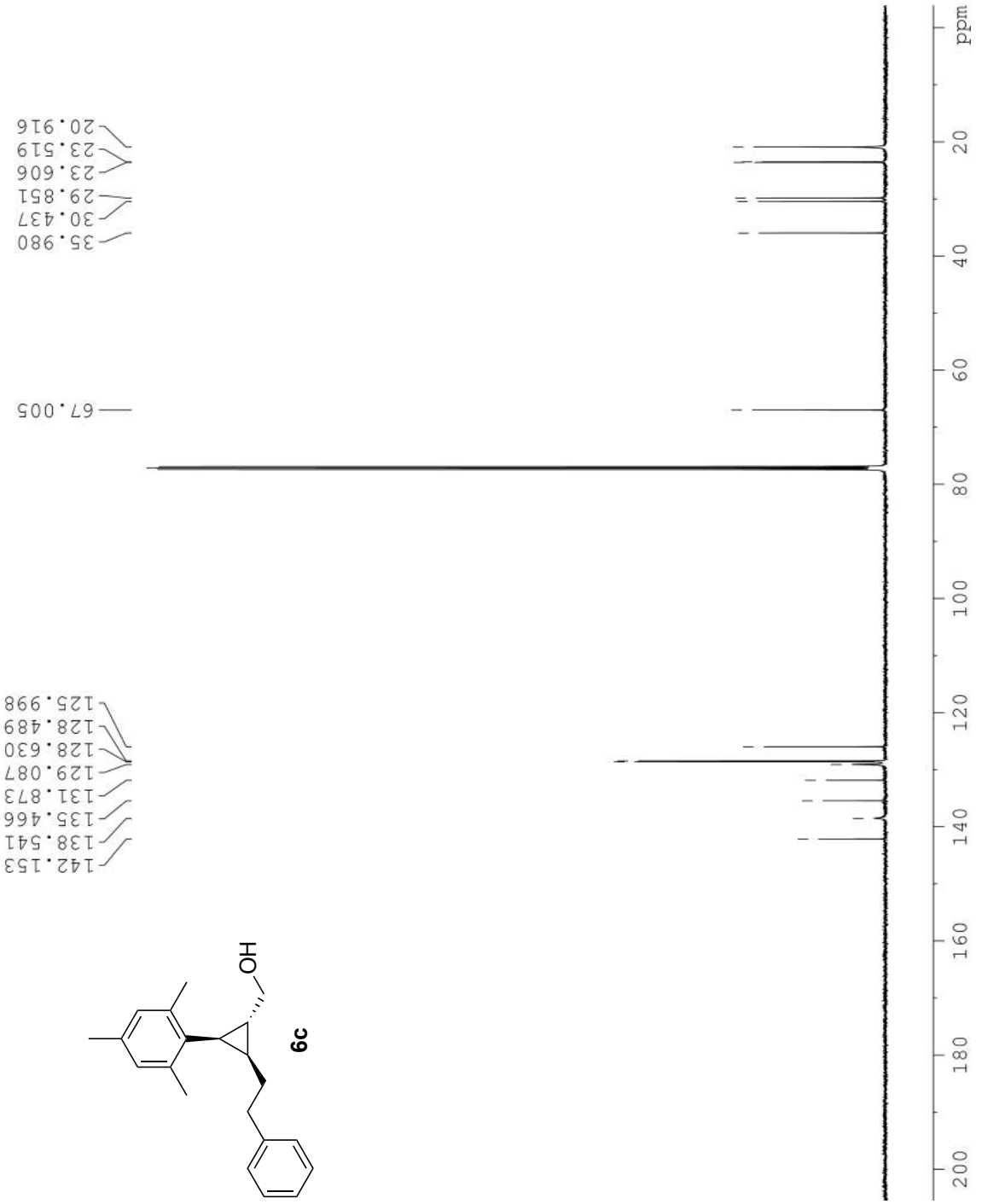

OH
6a
ppm
1.025
2.158
1.186
1.028
1.000
2.025
1.012
1.000
1.975
8.222

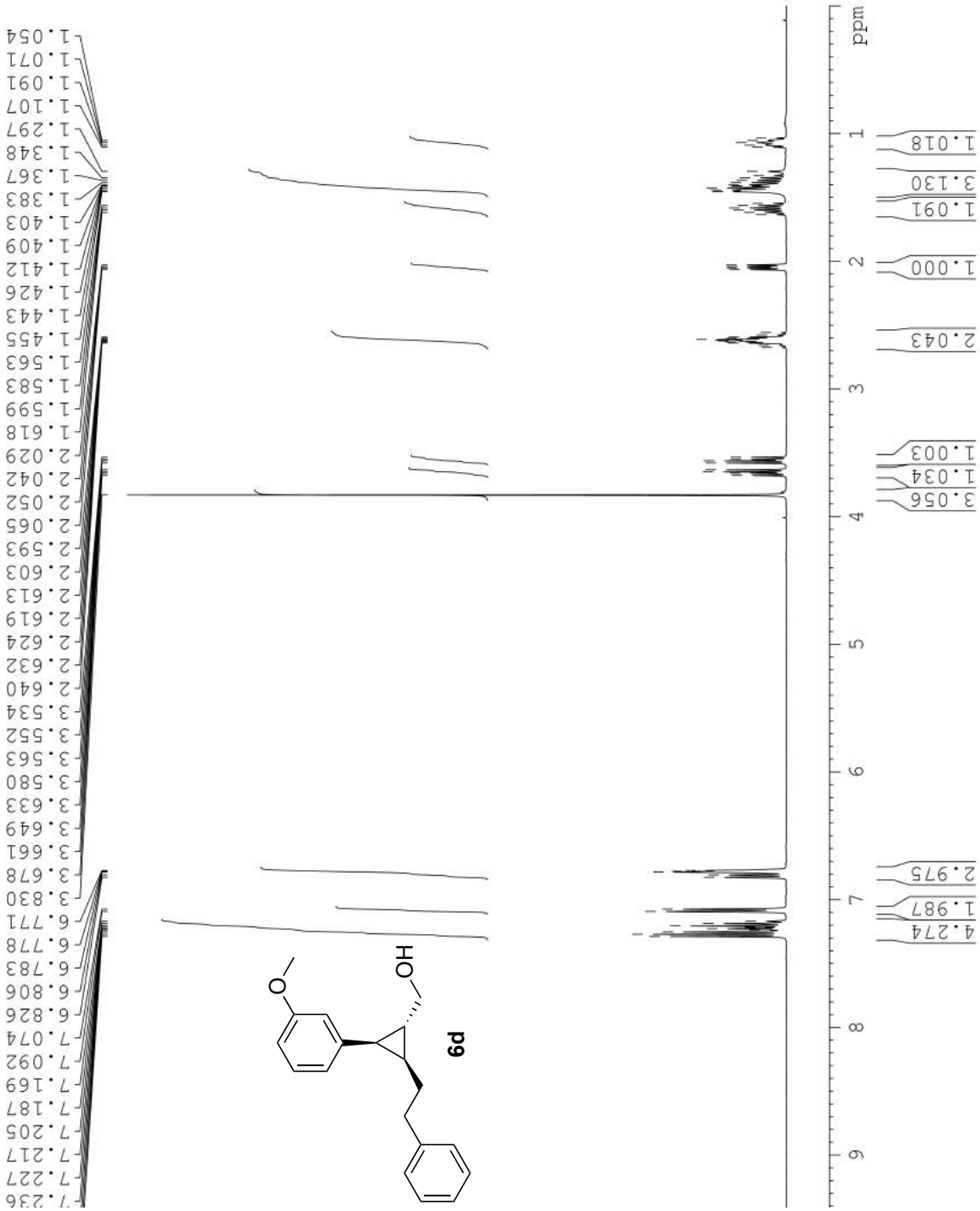

ppm
20
40
60
80
100
120
140
160
180
200
220
24.488
26.422
26.553
29.876
35.592
66.674
125.904
126.077
128.177
128.420
128.555
129.015
138.290
142.190
OH
6a

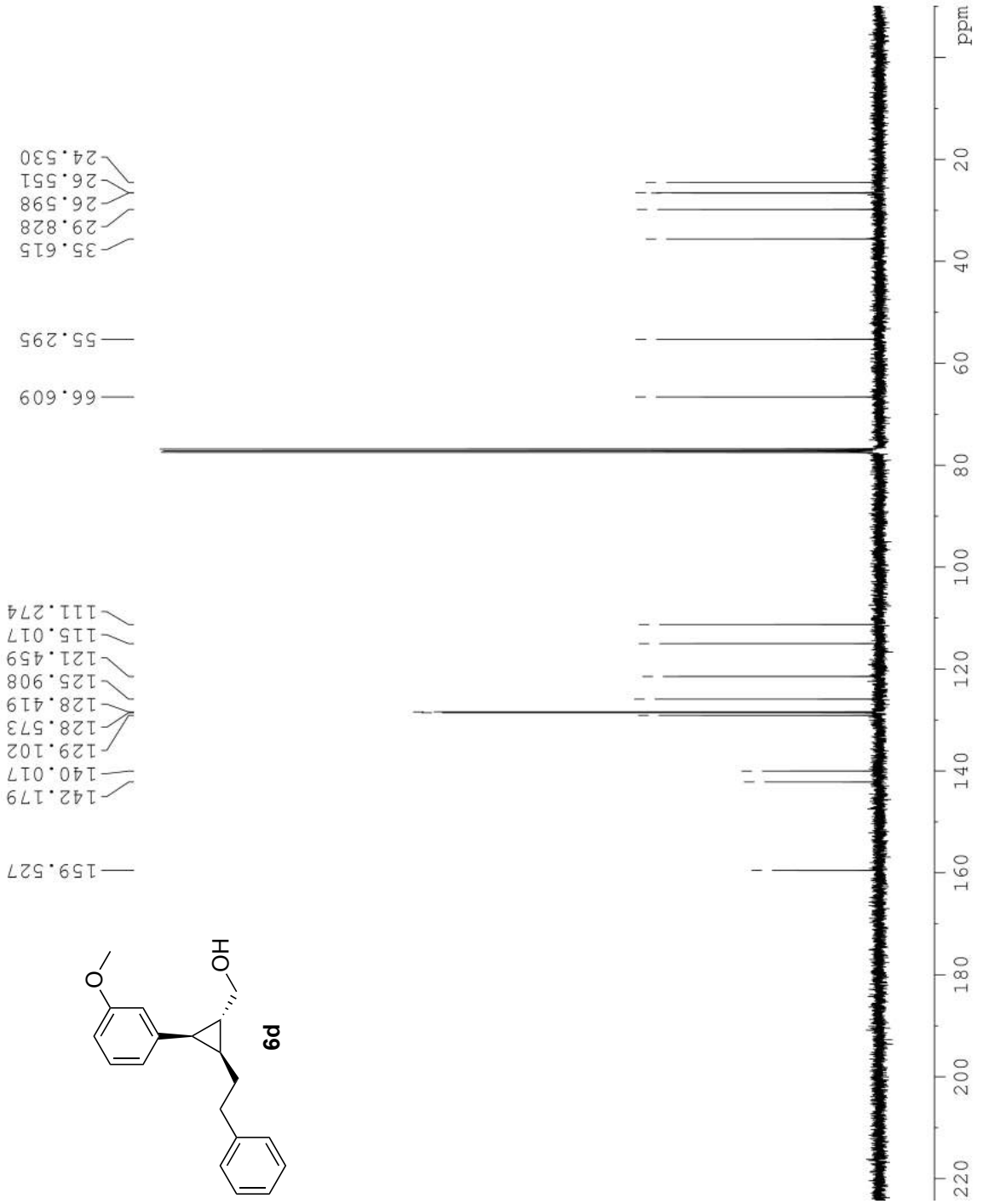

ppm
1.019
3.640
1.081
1.000
2.980
2.028
1.012
1.011
5.856
0.997
2.400
OH
6b

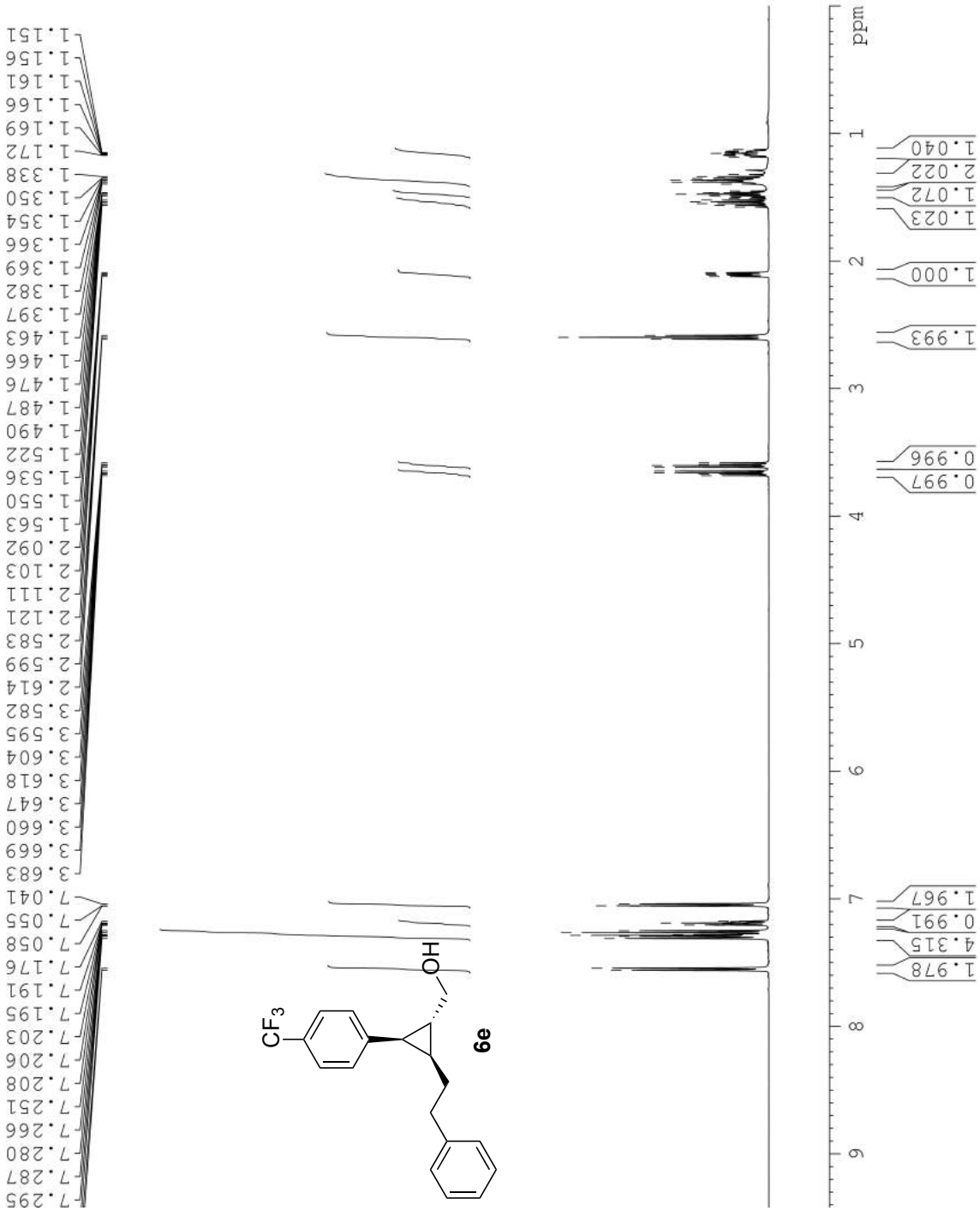

21.139
24.310
26.158
26.471
29.874
35.627
66.783
125.895
128.413
128.584
128.893
128.911
135.120
135.565
142.246
OH
6b
ppm
0
20
40
60
80
100
120
140
160
180
200

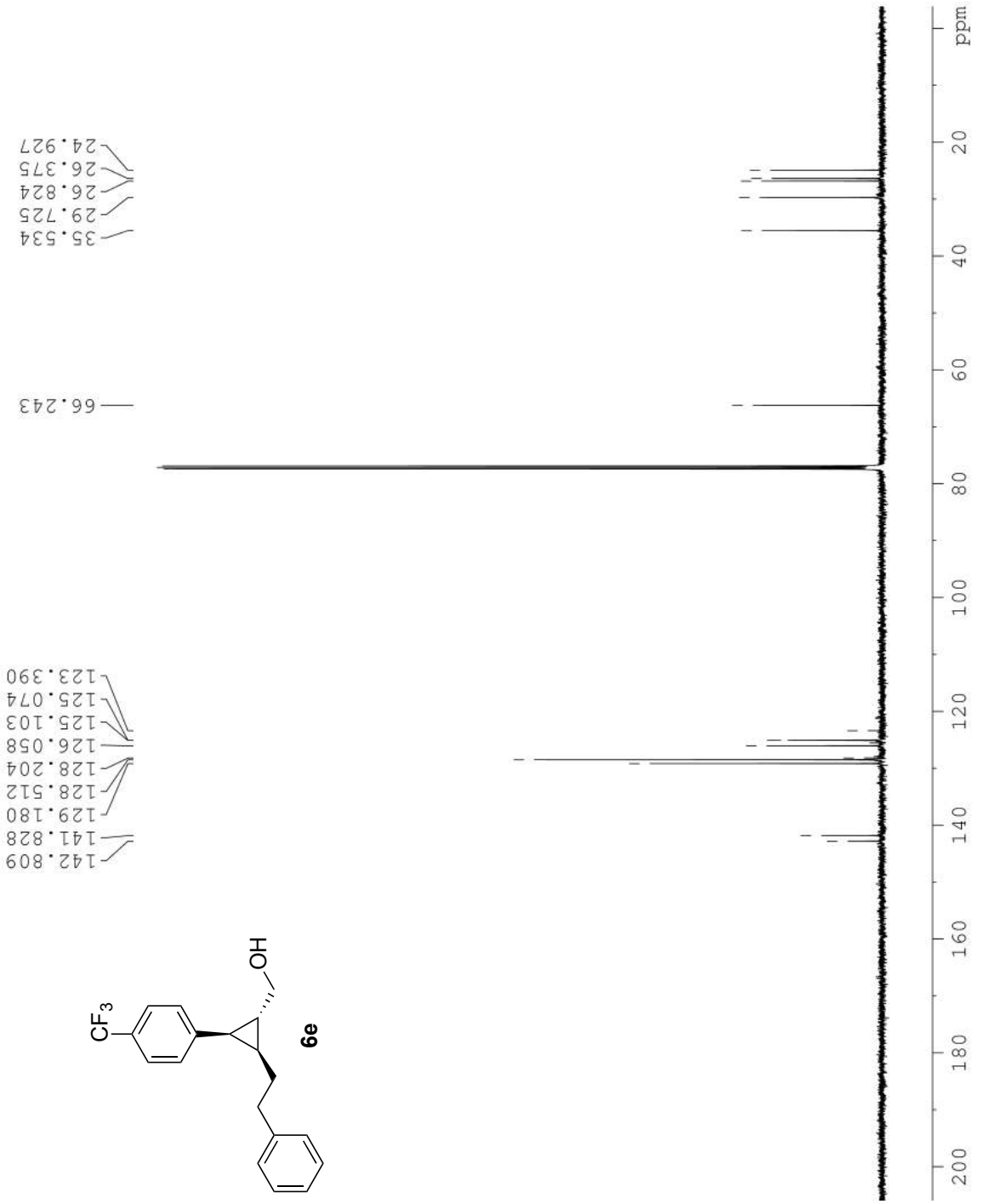

ppm
1.004
1.035
1.062
1.056
1.000
1.031
3.057
6.074
2.001
0.984
0.985
1.980
2.983
2.341
OH
6c

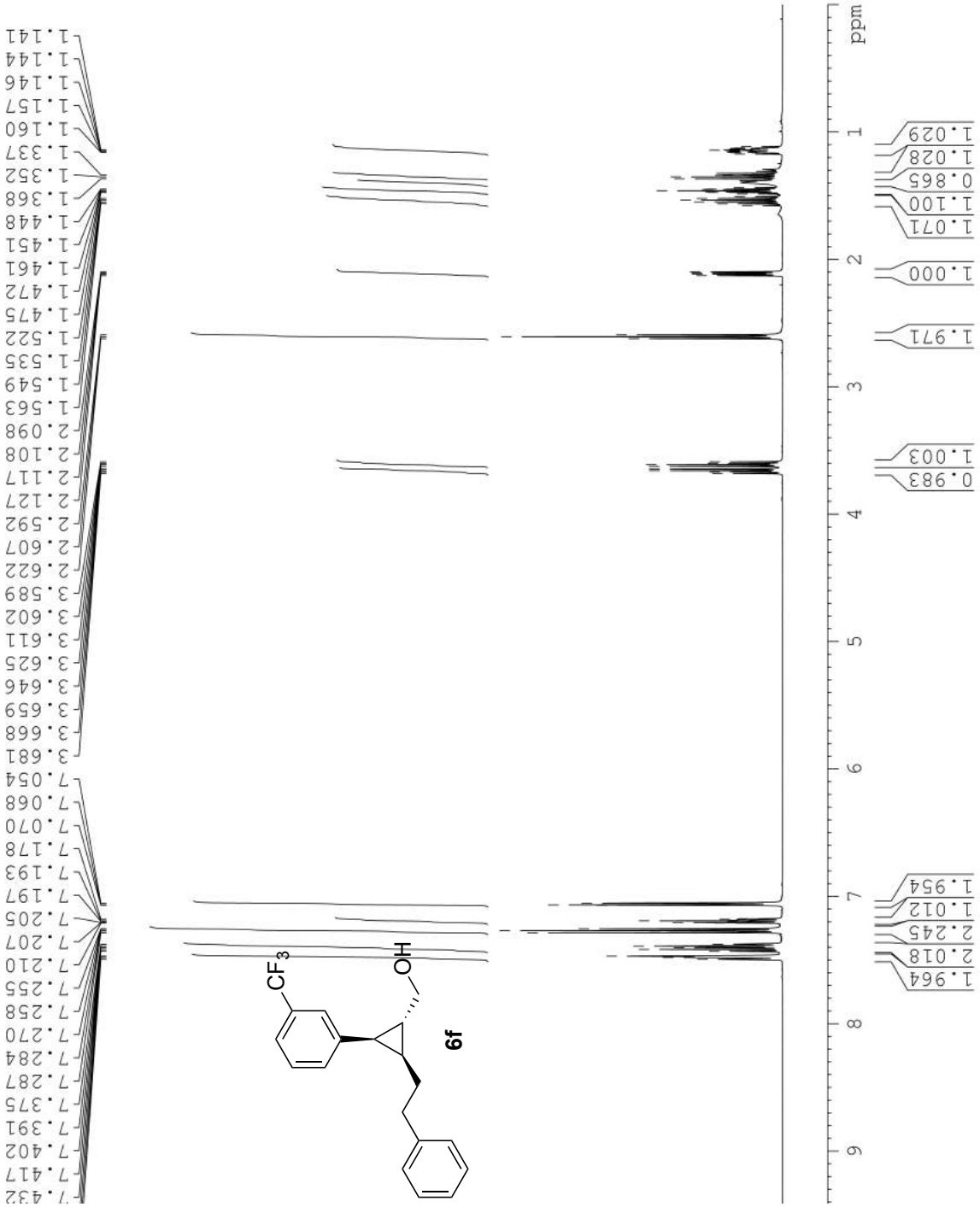

142.153
138.541
135.466
131.873
129.087
128.630
128.489
125.998
67.005
35.980
30.437
29.851
23.606
23.519
20.916
ppm
20
40
60
80
100
120
140
160
180
200
OH
6c

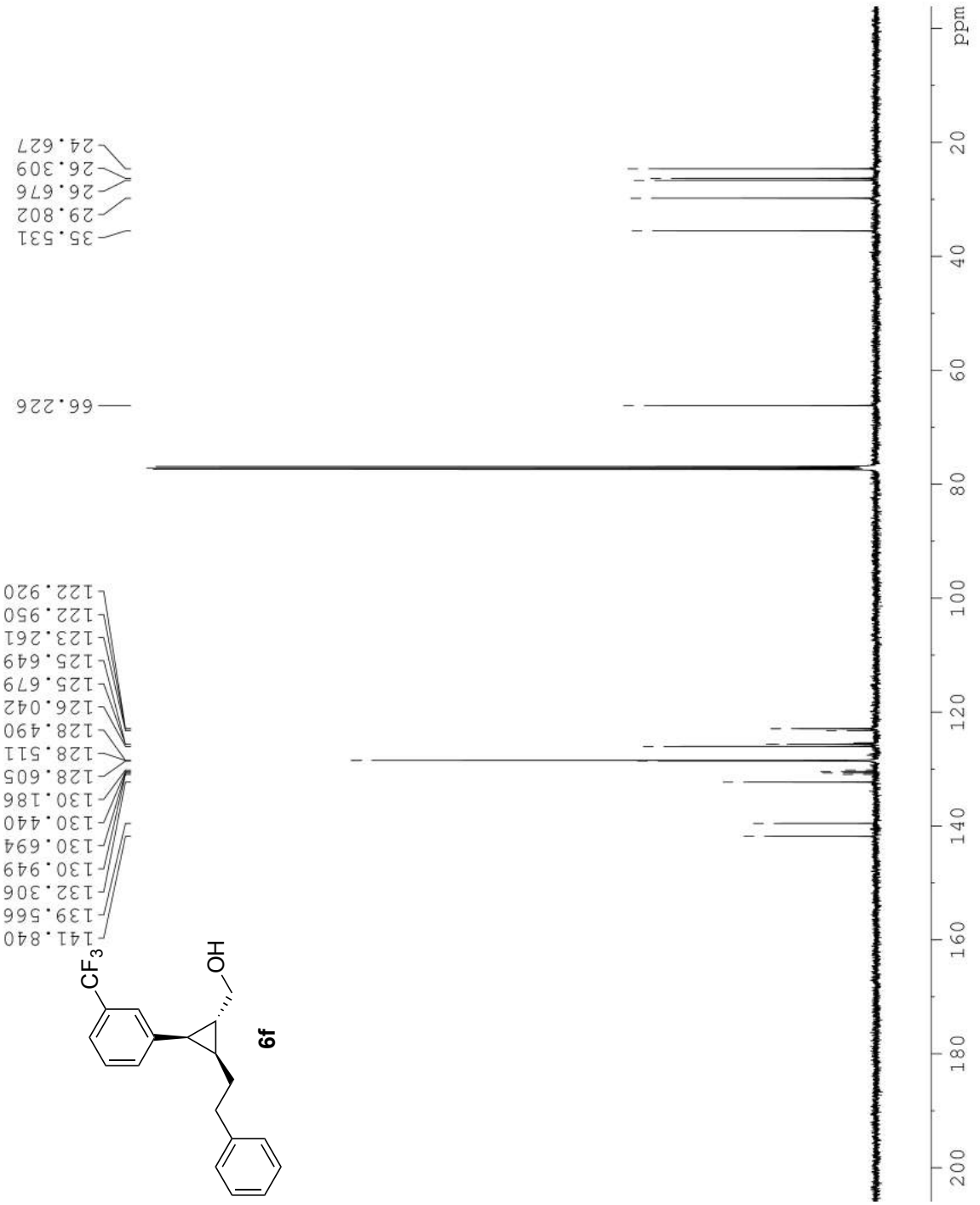

ppm
1.018
3.130
1.091
1.000
2.043
1.003
1.034
3.056
4.274
1.987
2.975
6d
OH
O

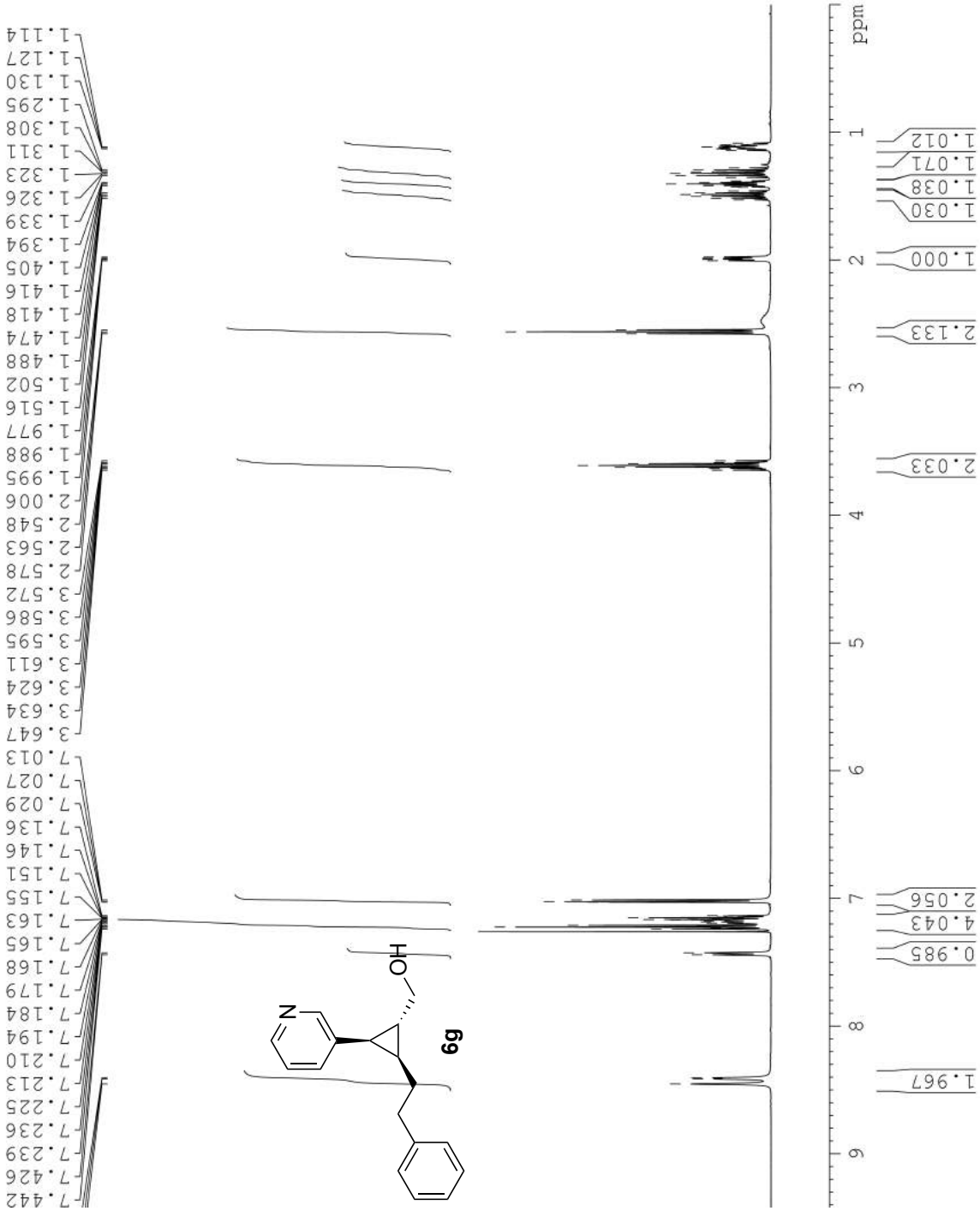

24.530
26.551
26.598
29.828
35.615
55.295
66.609
111.274
115.017
121.459
125.908
128.419
128.573
129.102
140.017
142.179
159.527
ppm
20
40
60
80
100
120
140
160
180
200
220
O
OH
6d

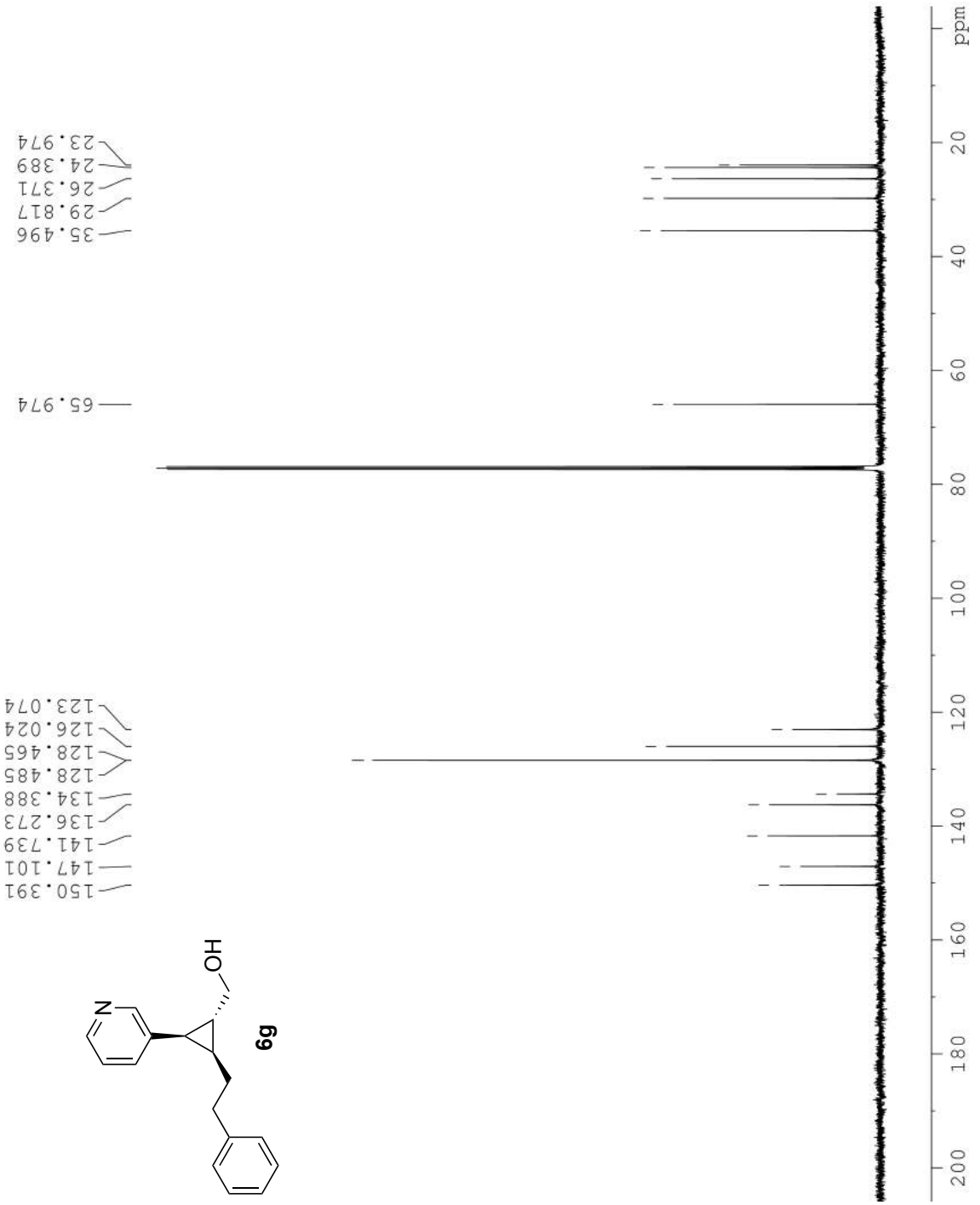

1.040
2.022
1.072
1.023
1.000
1.993
0.996
0.997
1.967
0.991
4.315
1.978
ppm
OH
CF3
6e

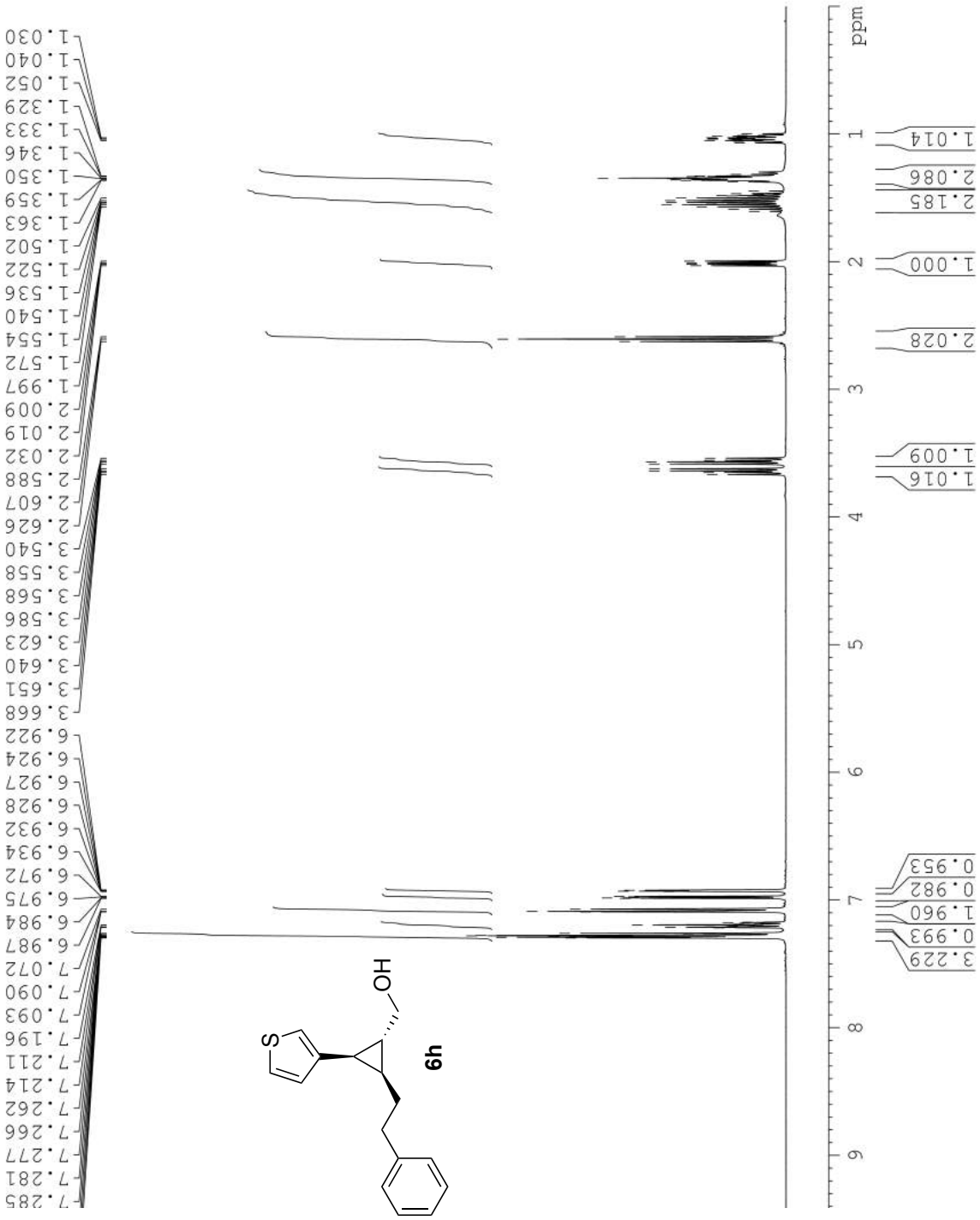

24.927
26.375
26.824
29.725
35.534
66.243
123.390
125.074
125.103
126.058
128.204
128.512
129.180
141.828
142.809
ppm
20
40
60
80
100
120
140
160
180
200
OH
CF3
6e

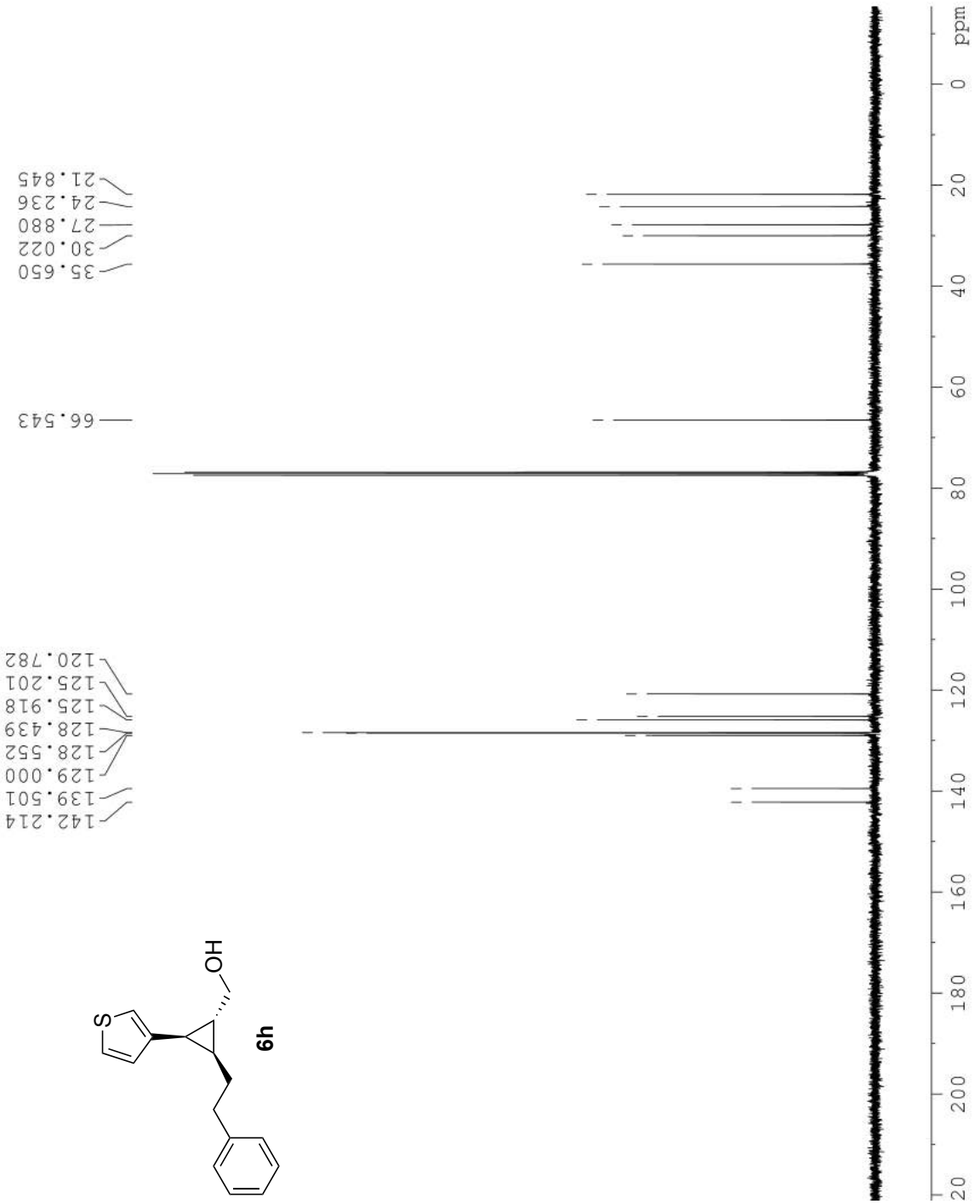

CF3
OH
6f
ppm
1.029
1.028
0.865
1.100
1.071
1.000
1.971
1.003
0.983
1.954
1.012
2.245
2.018
1.964

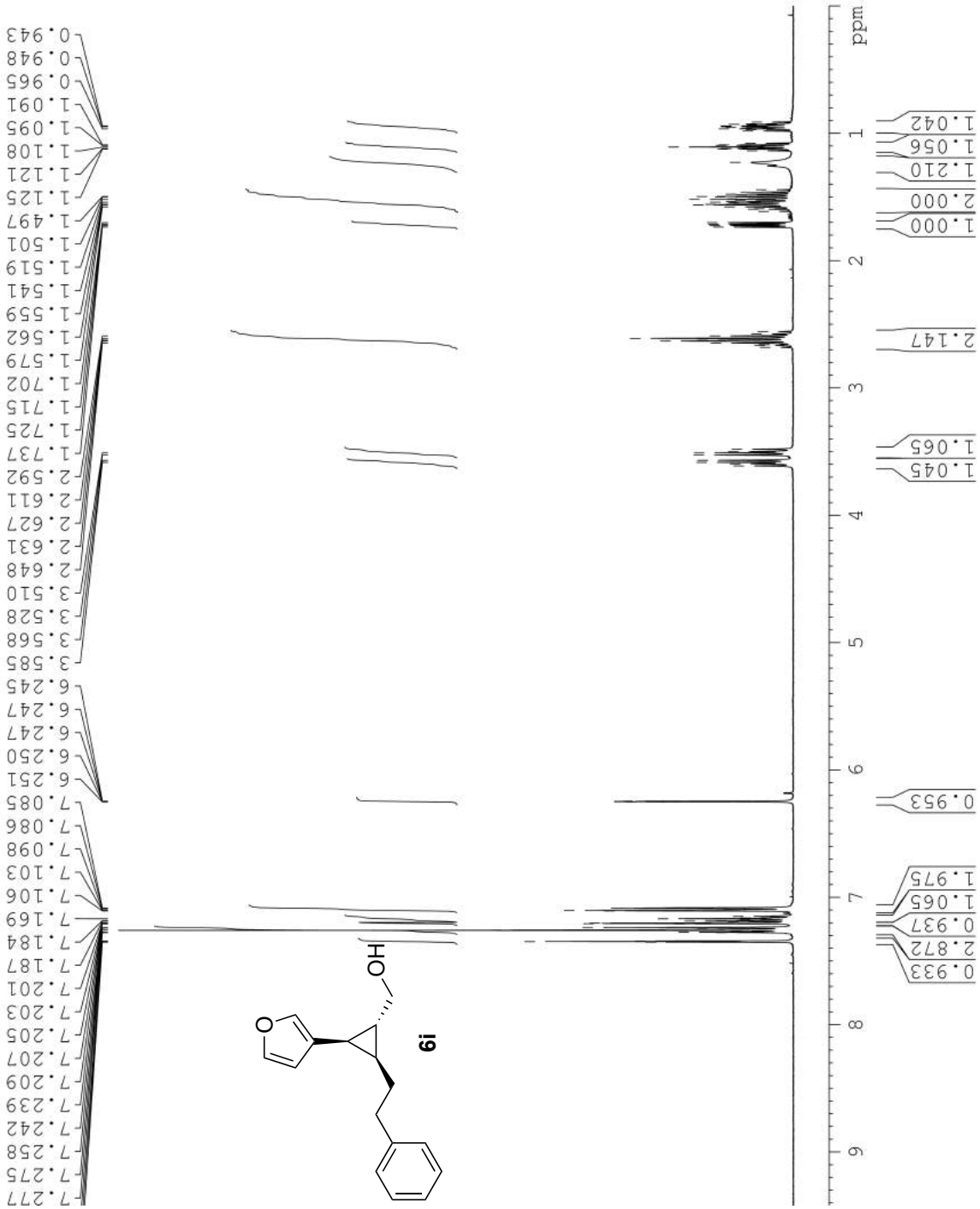

24.627
26.309
26.676
29.802
35.531
66.226
122.920
122.950
123.261
125.649
125.679
126.042
128.490
128.511
128.605
130.186
130.440
130.694
130.949
132.306
139.566
141.840
CF3
OH
6f
ppm
20
40
60
80
100
120
140
160
180
200

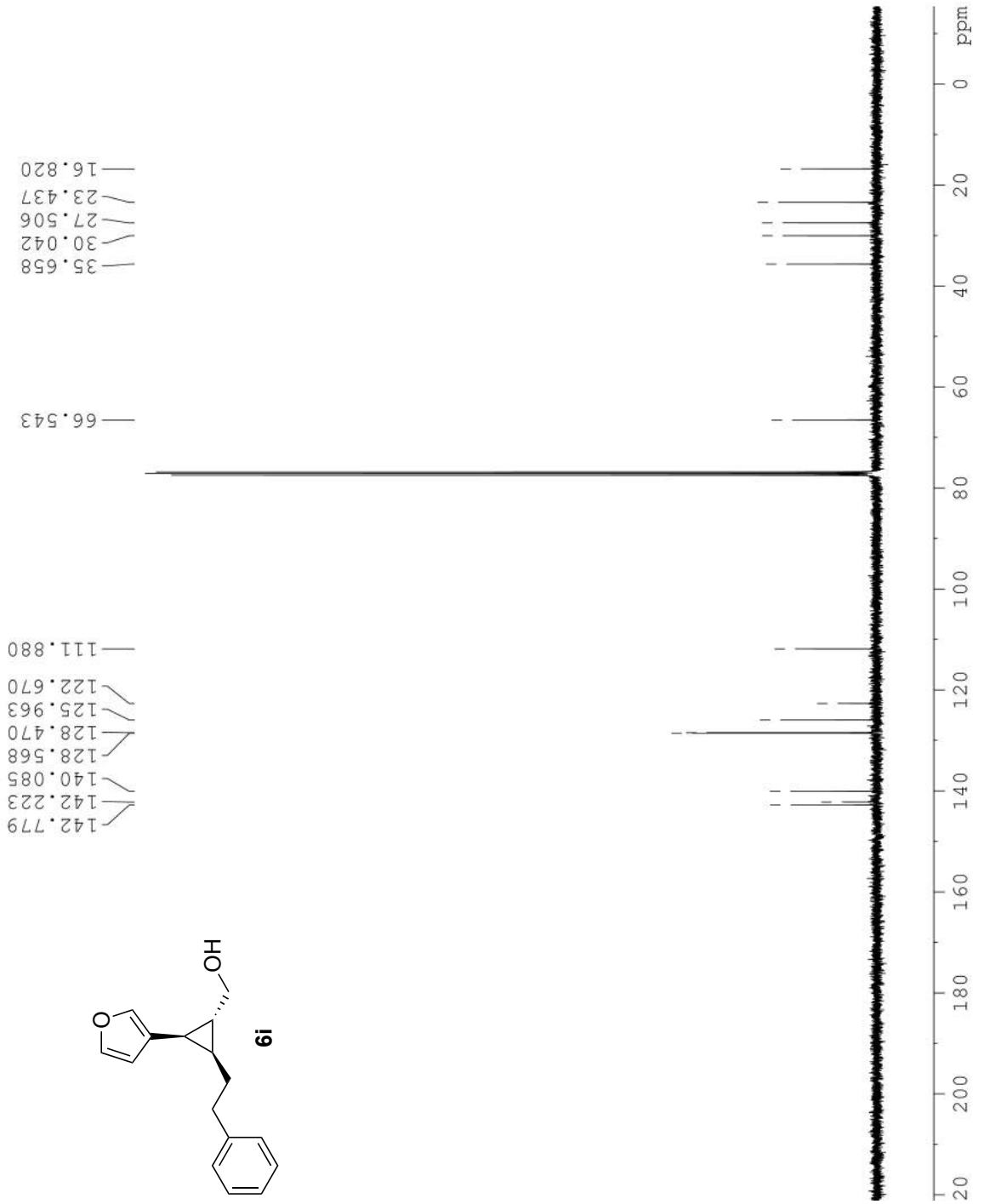

ppm
1.012
1.071
1.038
1.030
1.000
2.133
2.033
0.985
4.043
2.056
1.967
6g
OH
N

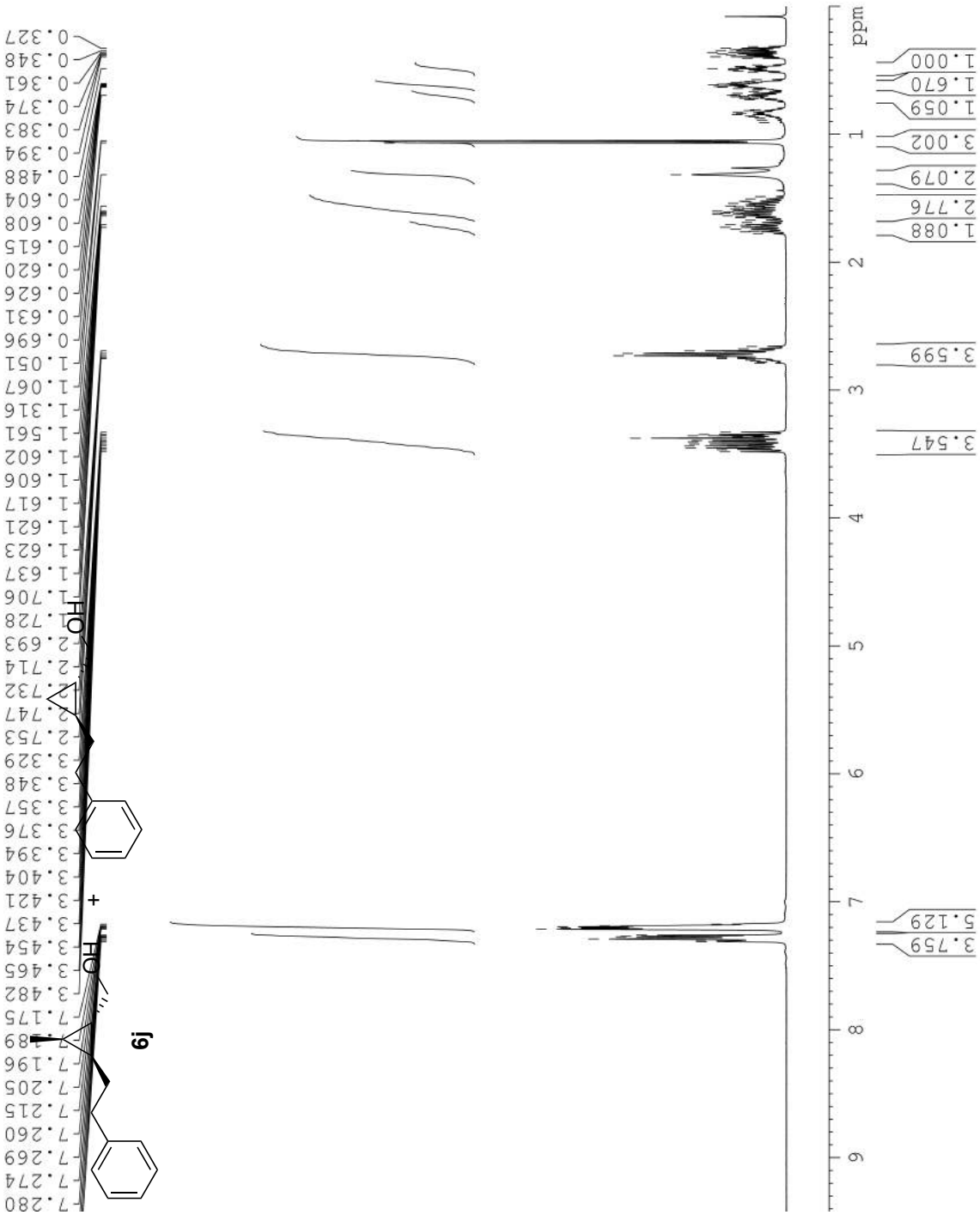

150.391
147.101
141.739
136.273
134.388
128.485
128.465
126.024
123.074
65.974
35.496
29.817
26.371
24.389
23.974
ppm
20
40
60
80
100
120
140
160
180
200
N
OH
6g

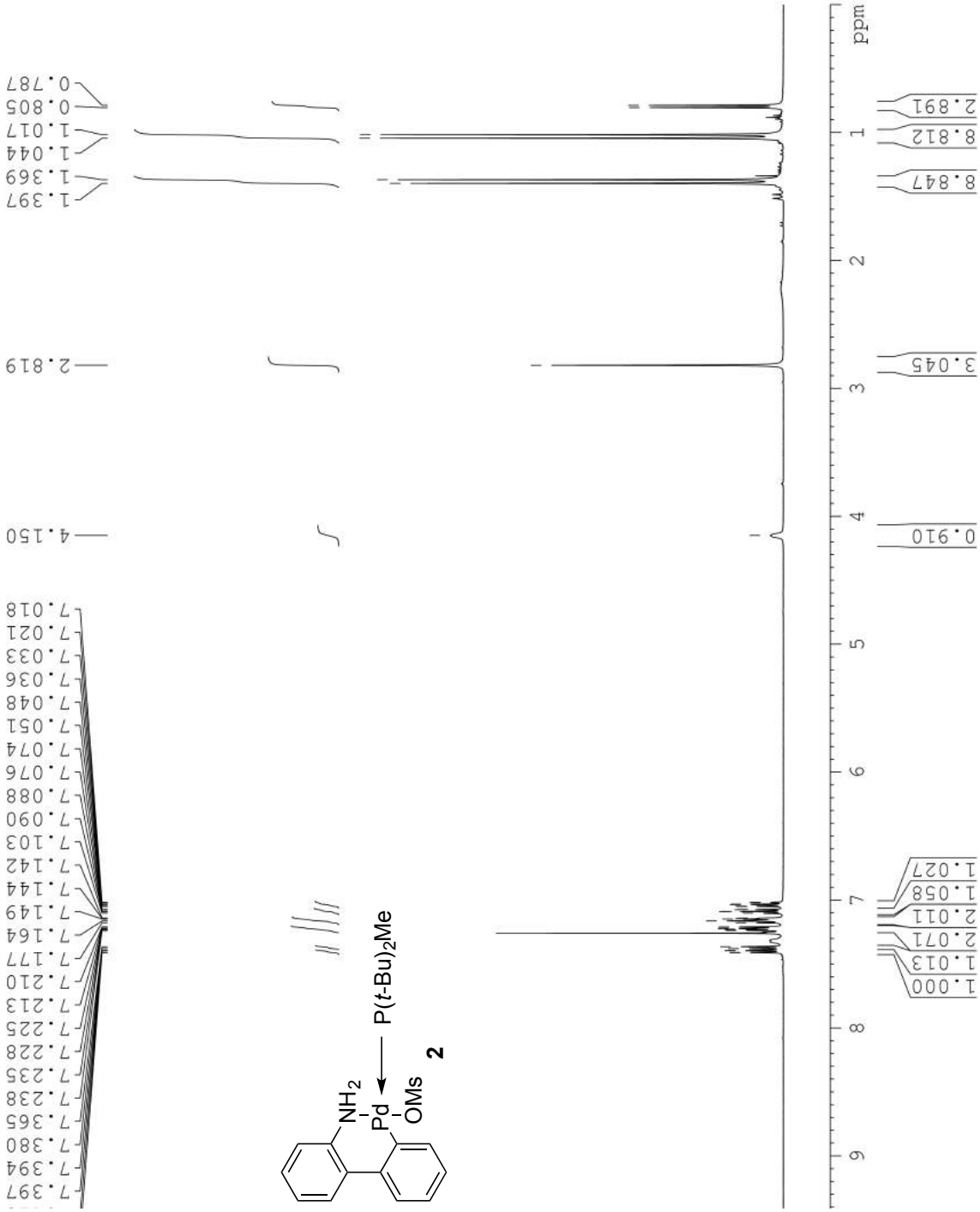

ppm
1.014
2.086
2.185
1.000
2.028
1.009
1.016
3.229
0.993
1.960
0.982
0.953
OH
S
6h

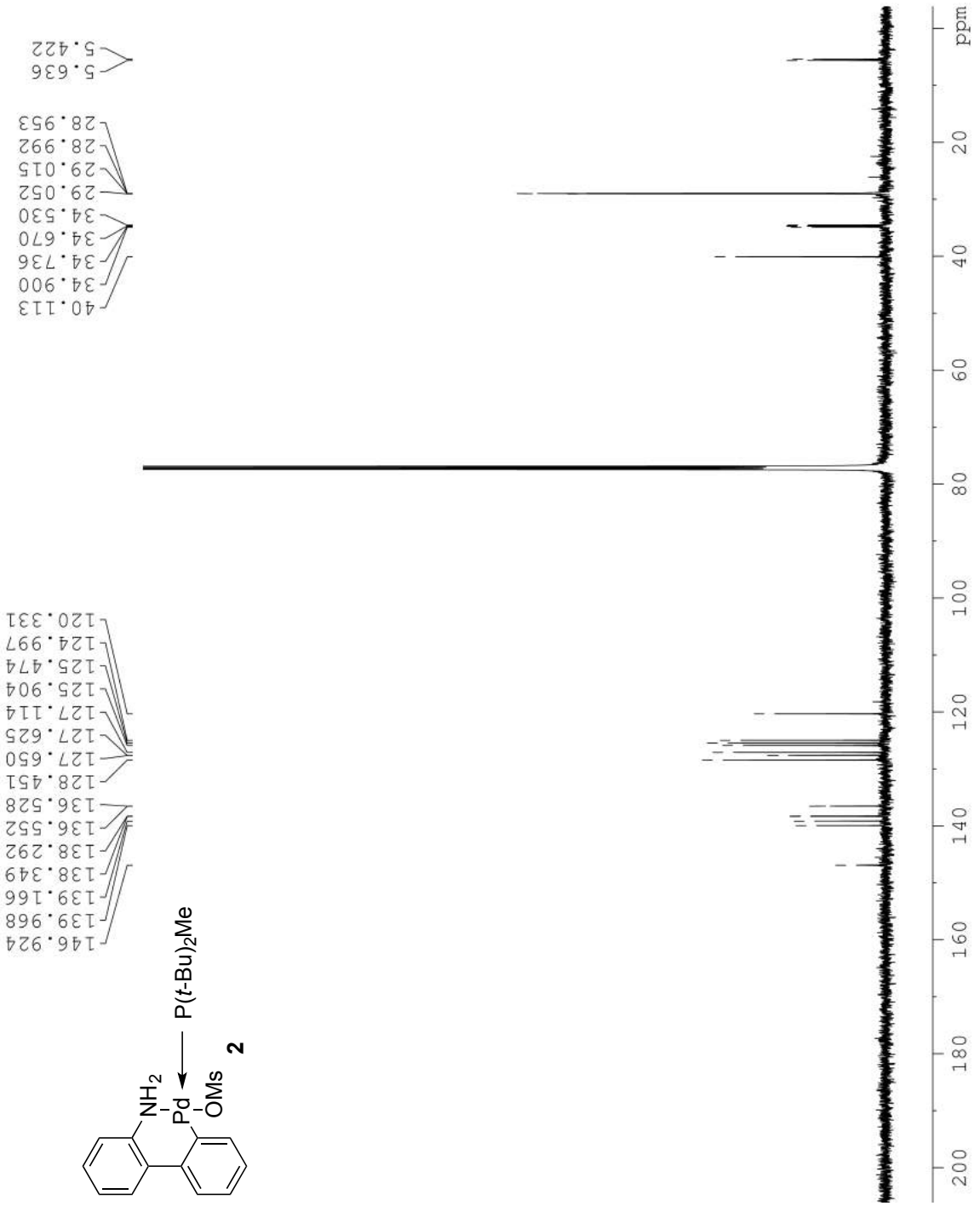

142.214
139.501
129.000
128.552
128.439
125.918
125.201
120.782
66.543
35.650
30.022
27.880
24.236
21.845
ppm
0
20
40
60
80
100
120
140
160
180
200
220
OH
S
6h


ppm
1.042
1.056
1.210
2.000
1.000
2.147
1.045
1.065
0.953
1.975
1.065
0.937
2.872
0.933
7.277
7.275
7.258
7.242
7.239
7.209
7.207
7.205
7.203
7.201
7.187
7.184
7.169
7.106
7.103
7.098
7.086
7.085
6.251
6.250
6.247
6.247
6.245
3.585
3.568
3.528
3.510
2.648
2.631
2.627
2.611
2.592
1.737
1.725
1.715
1.702
1.579
1.562
1.559
1.541
1.519
1.501
1.497
1.125
1.121
1.108
1.095
1.091
0.965
0.948
0.943
OH
O
6i


16.820
23.437
27.506
30.042
35.658
66.543
111.880
122.670
125.963
128.470
128.568
140.085
142.223
142.779
ppm
0
20
40
60
80
100
120
140
160
180
200
220
OH
O
6i


ppm
1.000
1.670
1.059
3.002
2.079
2.776
1.088
3.599
3.547
5.129
3.759
HO
HO
6j


ppm
1.000
1.013
2.071
2.011
1.058
1.027
0.910
3.045
8.847
8.812
2.891
4.150
2.819
1.397
1.369
1.044
1.017
0.805
0.787
7.018
7.021
7.033
7.036
7.048
7.051
7.074
7.076
7.088
7.090
7.103
7.142
7.144
7.149
7.164
7.177
7.210
7.213
7.225
7.228
7.235
7.238
7.365
7.380
7.394
7.397
NH2
Pd
OMs
P(t-Bu)2Me
2


5.422
5.636
28.953
28.992
29.015
29.052
34.530
34.670
34.736
34.900
40.113
120.331
124.997
125.474
125.904
127.114
127.625
127.650
128.451
136.528
136.552
138.292
138.349
139.166
139.968
146.924
ppm
20
40
60
80
100
120
140
160
180
200
NH2
Pd
OMs
P(t-Bu)2Me
2