Supporting Information

Chiral Substituted Poly-*N*-vinylpyrrolidinones and Bimetallic Nanoclusters in Catalytic Asymmetric Oxidation Reactions

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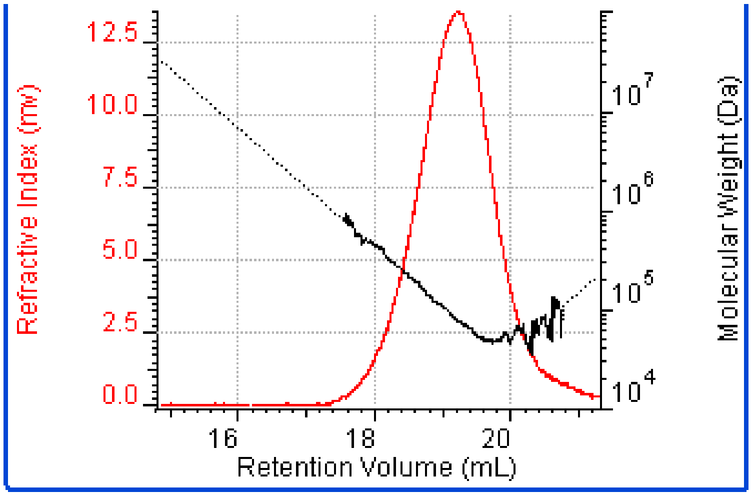
1. **Figure S1**. Molecular weight determination of polymer **17** by gel permeation chromatography using TSKgel GMHxl column and THF as solvent with a flow rate of 1 mL/min.

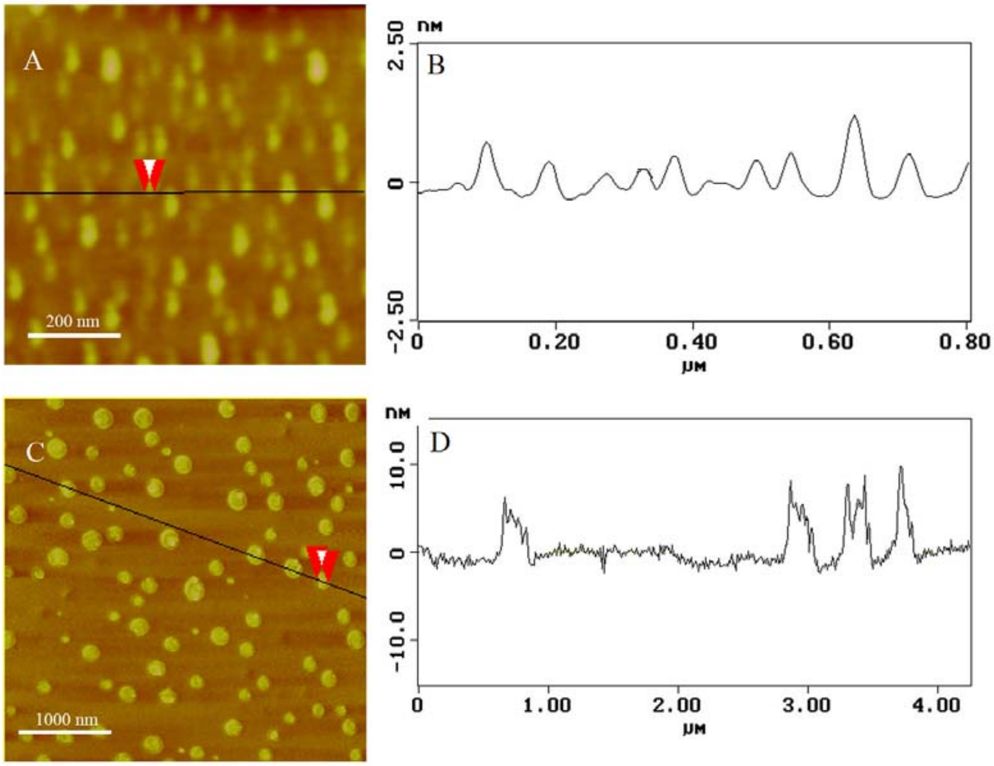


Method: Melania-0002.vcm

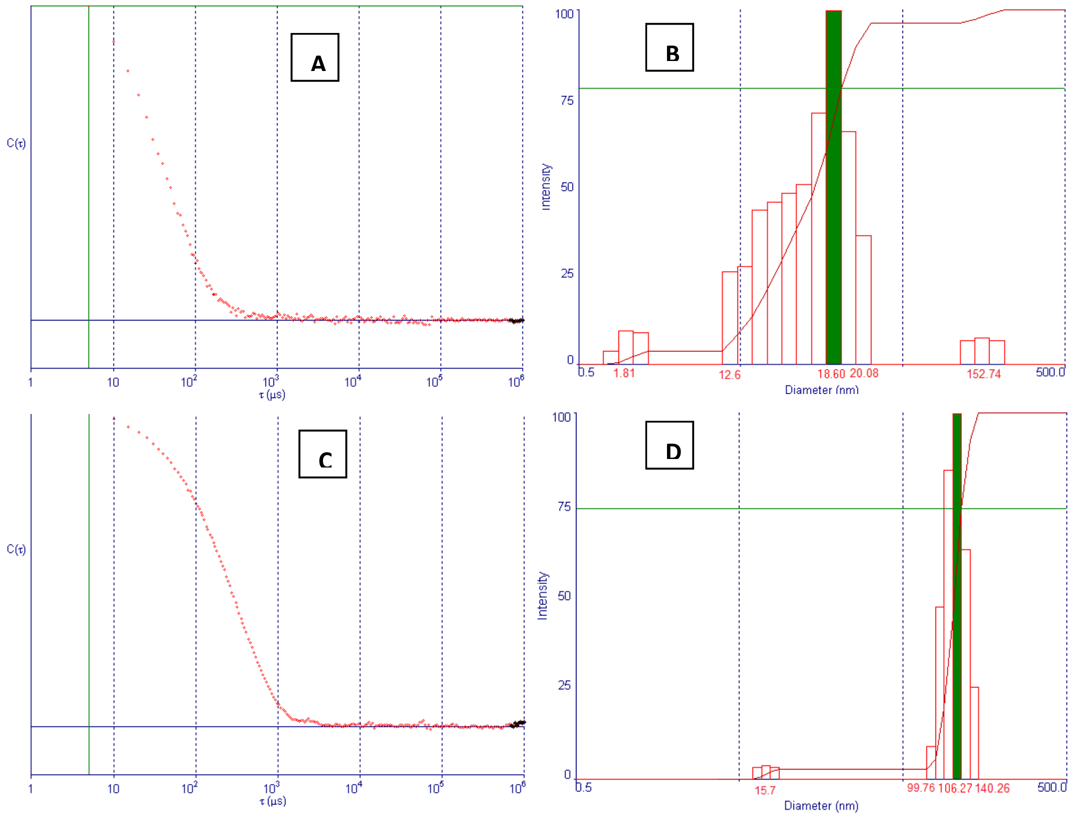
Peak RV - (ml)	19.183
Mn - (Daltons)	100,602
Mw - (Daltons)	106,184
Mz - (Daltons)	98,806
Mp - (Daltons)	100,812
Mw / Mn	1.06
Percent Above Mw:	100.000
Percent Below Mw:	0.000
IV - (dl/g)	0.3105
Rh(w) - (nm)	7.987
Wt Fr (Peak)	1.000
Mark-Houwink a	0.191
Mark-Houwink logK	-1.636
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	18.42
UV Area - (mvml)	0.00
RALS Area - (mvml)	47.62
LALS Area - (mvml)	0.00
IVDP Area - (mvml)	23.12

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.000	0.460
Sample Recovery (%)	0.000	45.972
dn/dc - (ml/g)	0.1470	0.0000
dA/dc - (ml/g)	1.0000	0.0000
Annotation		
Method File	Melania-0002.vcm	
Limits File		
Date Acquired	Jul 10, 2016 - 20:10:46	
Solvent	THF	
Acquisition Operator	autologin : autologin	
Calculation Operator	autologin : autologin	
Column Set	GMHxl	
System	System 1	
Flow Rate - (ml/min)	1.000	
Inj Volume - (μl)	100.0	
Volume Increment - (ml)	0.00333	
Detector Temp. - (deg C)	22.0	
Column Temp. - (deg C)	22.0	
OmniSEC Build Number	406	

2. **Figure S2**. Panel A: a representative AFM image of CSPVP **17**, and sizes of the polymer are ~20 - 30 nm. B: measurement of the height (Y axis) and width (X axis) of polymer **17**. C: representative image of nanocluster Pd/Au (3:1)-**17**. D: measurement of the height and width of the nanoclusters and the sizes are ~ 50 - 200 nm. The average height of the nanoparticles is 5.76 nm. For analysis, the crude nanocluster solution was filtered through a Vivaspin 20 centrifugal filter device (3,000 MWCO), and washed with deionized water twice to remove low MW inorganic materials. The resulting nanocluster was dissolved in water and subjected to AFM analysis. Images of polymers and nanocluster-polymers were randomly taken from the samples and representative images were displayed.



3. **Figure S3**. Dynamic light scattering studies of CSPVP **17** and Pd/Au (3:1)-**17**. A. Autocorrelation function over time of **17** in H_2O (deionized) solution with concentration of 0.12 mol/L. B. Size distribution graph of **17** in H_2O (same concentration as in A). C. Autocorrelation function over time of Pd/Au (3:1)-**17** in H_2O (deionized) solution with concentration of 4.36 mol/L Pd/Au (3:1) and 0.12 mol/L **17**. D. Size distribution graph of Pd/Au (3:1)-**17** in H_2O. The sizes of Pd/Au-**17** are ~5.7 times larger than those of polymer **17** alone. For analysis, the crude nanocluster solution was filtered through a Vivaspin 20 centrifugal filter device (3,000 MWCO), and washed with deionized water twice to remove low MW inorganic materials. The resulting nanocluster was dissolved in water and subjected to DLS analysis.

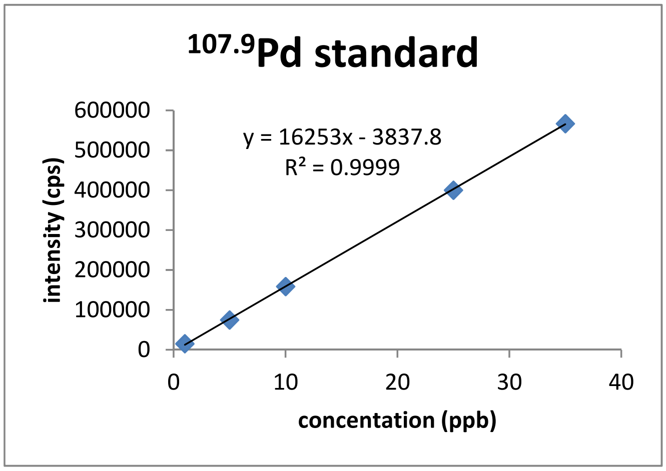


4. **Figure S4**. The appearance Pd/Au (3:1)-CSPVP **17** in deionized H_2O solution. Left cuvette: 2.18 M (1.63 M of Pd and 0.55 M of Au complexed with 0.06 M of **17**). Right cuvette: 4.23 M (3.17 M of Pd and 1.06 M of Au and 0.12 M of **17**).

5. **Inductively coupled plasma-mass spectrometry (ICP-MS)** measurement: An ICP-MS instrument, NexION® 300D from PerkinElmer was used to measure the concentrations of Pd, Au, and Cu in Pd/Au (3:1)-**17** and Cu/Au (3:1)-**17**. To a solution of 100 µg of Pd/Au (3:1)-

17 or Cu/Au (3:1)-**17** in 100 μL of deionized water was added 2 mL of aqua regia solution at 70°C under sonication for 3 h, and the solution was cooled to 25°C, diluted to 10 mL with a 1% HNO_3/2% HCl solution. A total of six separate experiments were conducted using different concentrations of the above solution. (1) Three similar experiments were carried out: in each experiment, 250 μL of the above Pd/Au (or Cu/Au) solution was removed and diluted to 5 mL of 1% HNO_3/2% HCl solution. The sample was subjected to the ICP mass spectrometer and intensities of Pd and Au (or Cu and Au) were obtained. (2) Three other similar experiments: in each experiment, 100 μL of the above Pd/Au (or Cu/Au) solution was removed and diluted to 5 mL of 1% HNO_3/2% HCl solution. The sample was subjected to the ICP mass spectrometer and intensities of Pd and Au (or Cu and Au) were obtained. Standard solutions for Au and Cu are commercially available, and standardized Pd solution was obtained from Na_2PdCl_4.

ICP-MS study of Pd/Au (3:1)-CSPVP 17 sample:



Standardized graph of intensities vs concentrations of standard $^{107.9}$Pd(II) from Na_2PdCl_4

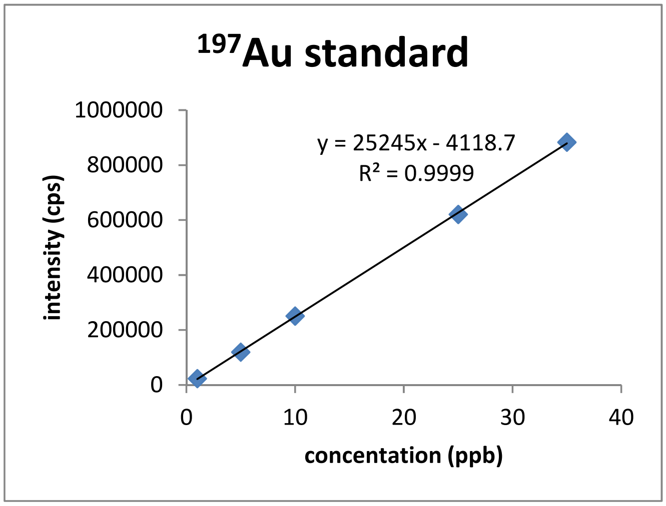
Pd/Au (3:1)-**17** sample measurements (from three experiments):

dilute times	intensity	concentration
2000	51927.9 ± 1079.1	3.43 ± 0.30
5000	19083.8 ± 838.0	1.41 ± 0.29

Concentration of $^{107.9}$Pd in Pd/Au (3:1)-**17** = 6.96 ± 1.03μg/mg

Concentration of total Pd in Pd/Au (3:1)-**17** = 26.3 ± 3.9μg/mg

Mole of Pd in Pd/Au (3:1)-**17** = 26.3/106.4 = 0.25 ± 0.037μmol/mg



Standardized graph of intensities vs concentrations of standard ^{197}Au.

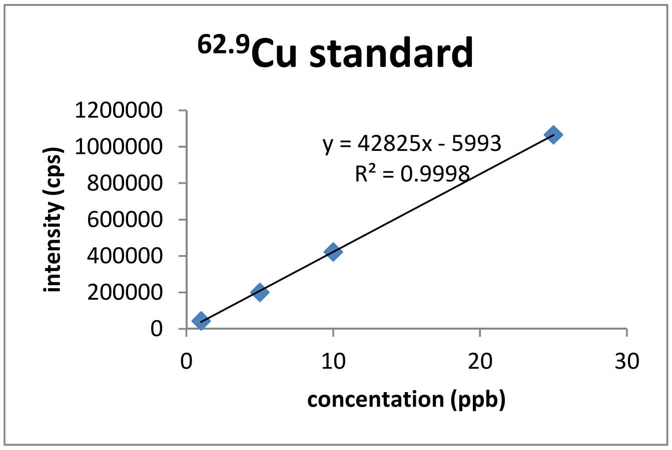
dilute times	intensity	concentration
2000	185915.2 ± 1359.2	7.53 ± 0.22
5000	78991.2 ± 1885.48	3.29 ± 0.24

Concentration of ^{197}Au in Pd/ Au (3:1)-**17** = 15.8 ± 0.82μg/mg

Mole of Au in Pd/Au (3:1)-**17** = 15.8/197 = 0.080 ± 0.004μmol/mg

The ratio of Pd/Au is: 0.25/0.08 = 3.12 ± 0.58

ICP-MS study of Cu/Au (3:1)-CSPVP 17 sample:

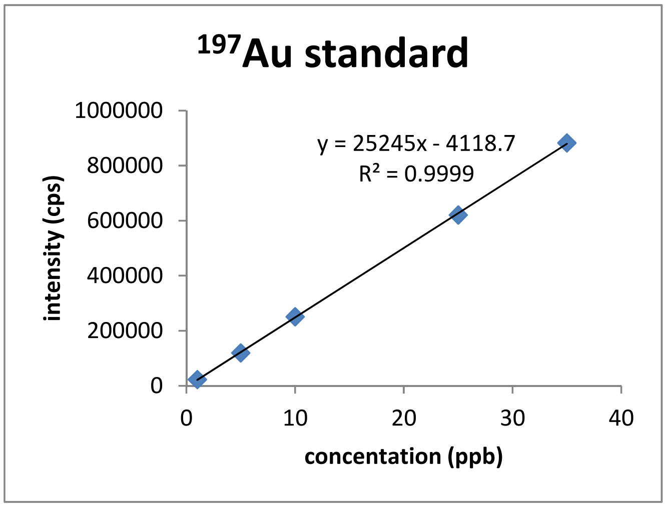


Standardized graph of intensities vs concentrations of standard $^{62.9}$Cu

Cu/Au (3:1)-**17** sample measurements (from three experiments):

dilute times	intensity	concentration
2000	222135.2 ± 332.3	5.33 ± 0.15
5000	90612.7 ± 6185.3	2.26 ± 0.28

Concentration of $^{62.9}$Cu in Cu/Au-**17** = 10.97 ± 0.85μg/mg
Concentration of Cu in Cu/Au (3:1)-**17** = 15.9 ± 1.2μg/mg
Mole of Cu in Cu/Au (3:1)-**17** = 15.9/63.6 = 0.25 ± 0.02μmol/mg



Standardized graph of intensities vs concentrations of standard ^{197}Au.

dilute times	intensity	concentration
2000	200274.2 ± 1541.6	8.10 ± 0.22
5000	79420.2 ± 1409.7	3.31 ± 0.22

Concentration of ^{197}Au in Cu/Au (3:1)-**17** =16.37 ± 0.77μg/mg
Mole of Au in Cu/Au (3:1)-**17** = 16.4/197 = 0.083 ± 0.004μmol/mg

The ratio of Cu/Au is: 0.25/0.083 = 3.0 ± 0.4

6. Transmission electron microscopy (TEM) images of Pd/Au (3:1)-17 and Cu/Au (3:1)-17:

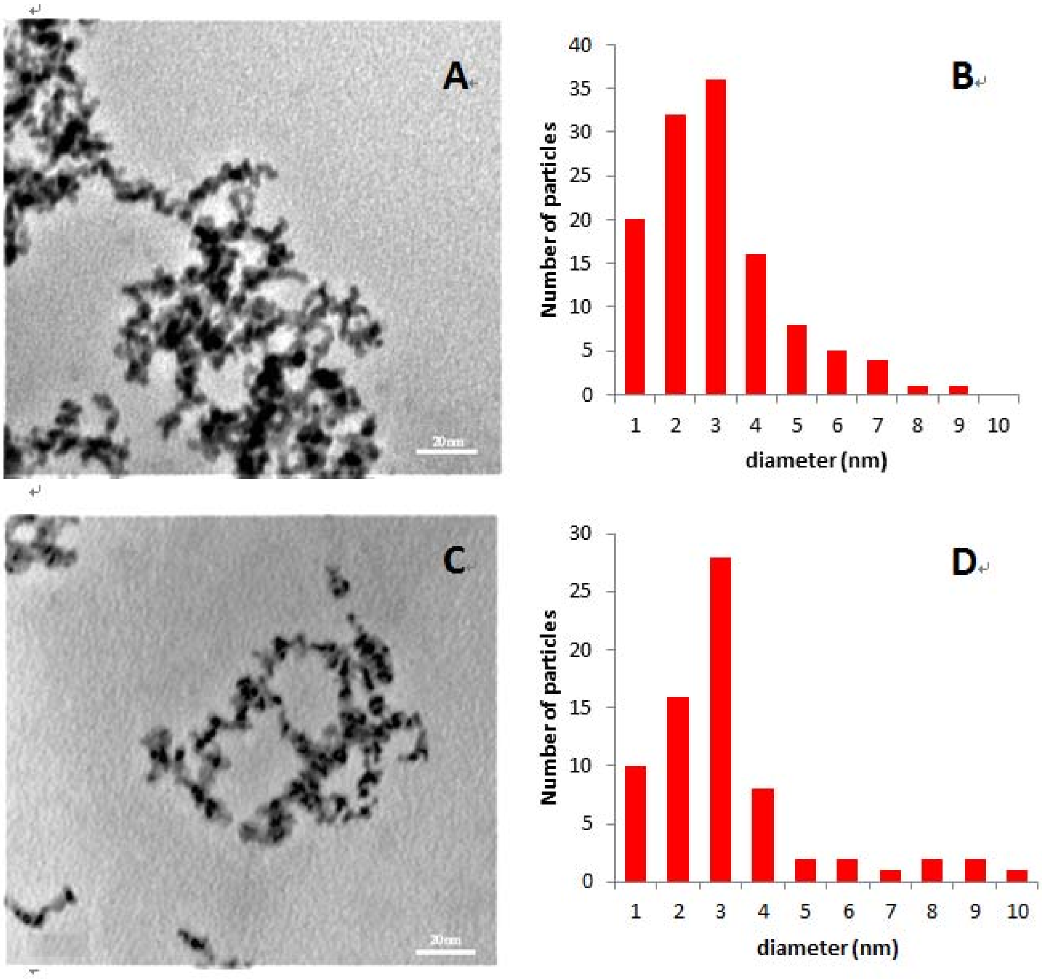


Figure S5. Panel A: a representative TEM image of nanocluster Pd/Au (3:1)-**17**. B: measurement of the diameter of the nanoclusters and the average size is 3.44 ± 1.63 nm. C: a representative TEM image of nanocluster Cu/Au (3:1)-**17**. D: measurement of the diameter of the nanoclusters and the average size is 3.66 ± 1.95 nm. Bars are 20 nm. For analysis, the crude nanocluster solution was filtered through a Vivaspin 20 centrifugal filter device (3,000 MWCO), and washed with deionized water twice to remove low MW inorganic materials. The resulting nanocluster was dissolved in ethanol and subjected to TEM analyses.

7. Calculation of the number of metal atoms (N) in each nanoparticle with the assumption that the nanoparticles have face-centered cubic close-packed structure.

For Pd/Au (3:1)-**17**: (diameters for Au and Pd are 0.288 and 0.275, respectively.)

Diameter d = (3 x 0.275 + 0.288) / 4 = 0.278
Nanocluster diameter: 12.3d = 3.44 nm (the diameter of Pd/Au is obtained from TEM)

The shell number: n = 6.5 (based on Poole, C.; Owens, F. Introduction to Nanotechnology, 2003, Wiley, New Jersey)
The number of atoms in a 3.44 nm nanocluster: $N = 1/3[10n^3 – 15n^2 + 11n – 3] = 727$ atoms
Mole of metals in each nanocluster: 1.21×10^{-21} mol
Mole of CSPVP in each nanocluster: $1.21 \times 10^{-21} \times 0.11 / 4 = 3.3 \times 10^{-23}$ mol
Number of CSPVP in each nanocluster: $3.3 \times 10^{-23} \times N_A$ (Avogadro number) = $3.3 \times 10^{-23} \times 6.022 \times 10^{23}$ = **20.0**

For Cu/Au (3:1)-**17**: (diameters for Au and Cu are 0.288 and 0.256, respectively.)

Diameter d = (3 x 0.256 + 0.288) / 4 = 0.264
Nanocluster diameter: 14d = 3.66 nm (the diameter of Cu/Au is obtained from TEM)
The shell number: n = 7.5
The number of atoms in a 3.66 nm nanocluster: $N = 1/3[10n^3 – 15n^2 + 11n – 3] = 1151$ atoms
Mole of metal in each nanocluster: 1.91×10^{-21}
Mole of CSPVP in each nanocluster: $1.91 \times 10^{-21} \times 0.11 / 4 = 5.3 \times 10^{-23}$
Number of CSPVP in each nanocluster: $5.3 \times 10^{-23} \times 6.022 \times 10^{23}$ = **32**

8. X-ray photoelectron spectroscopy (XPS) of Pd/Au (3:1)-17 and Cu/Au (3:1)-17:

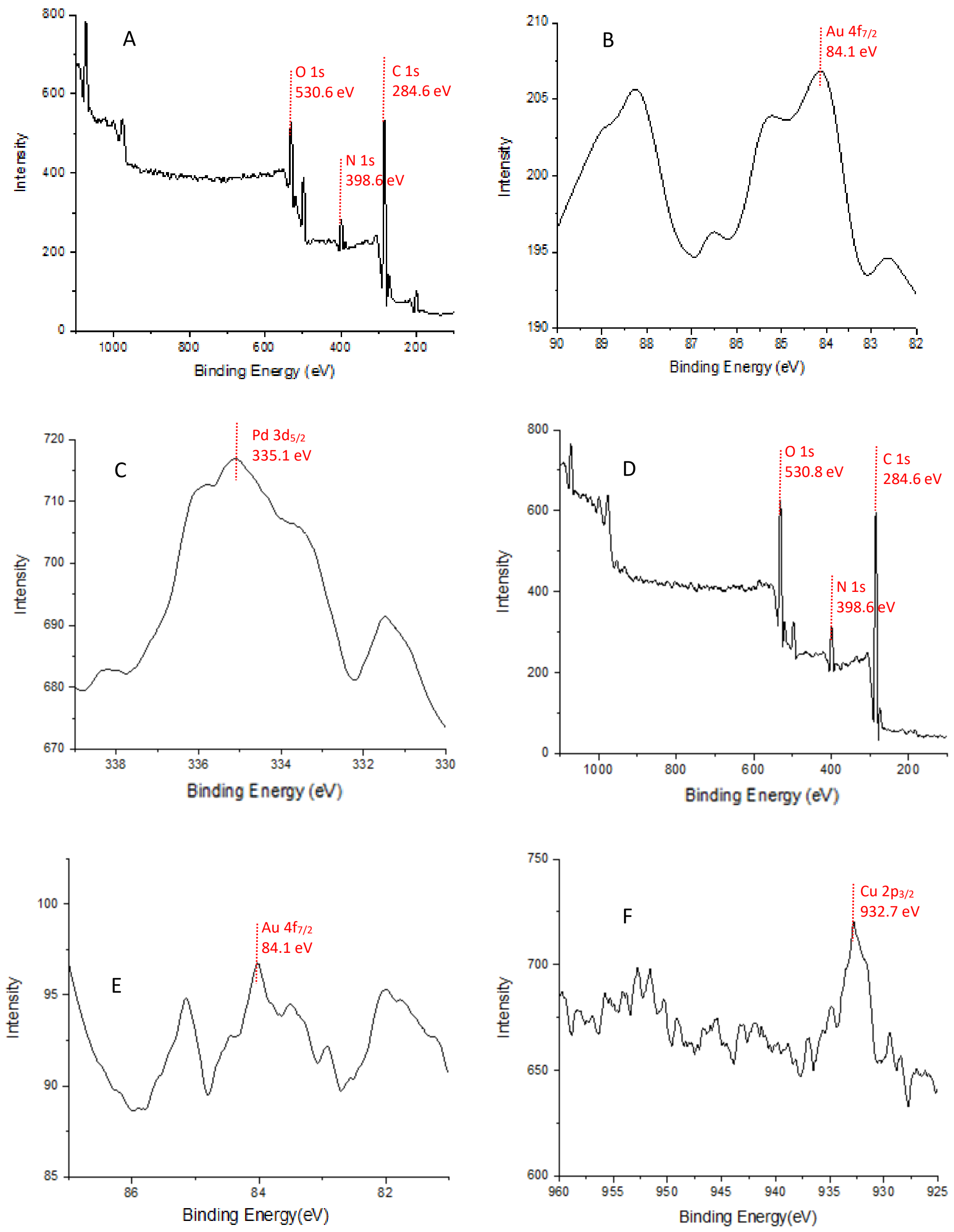


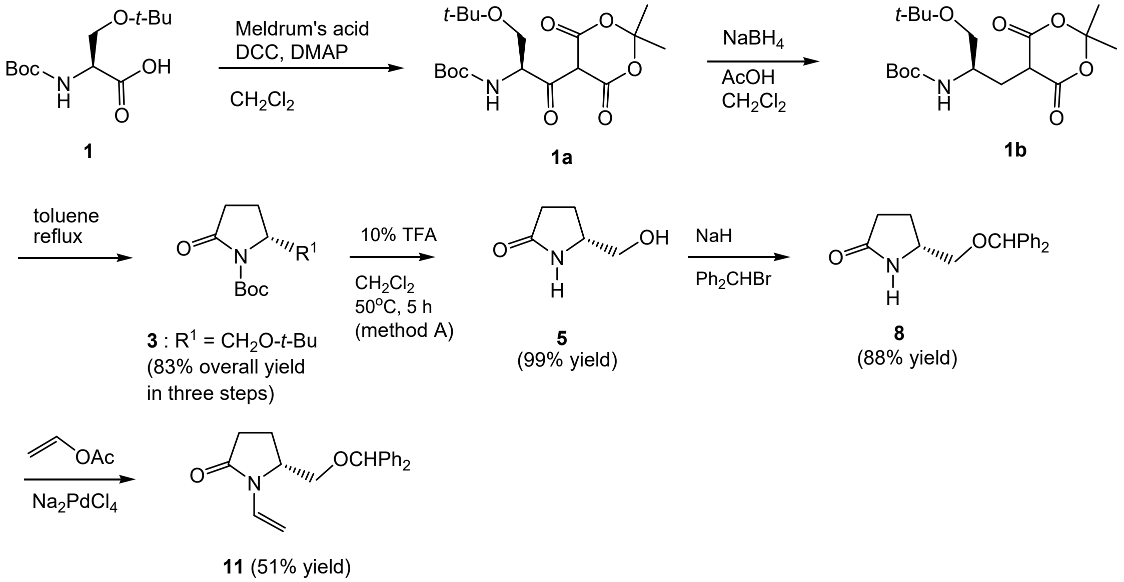
Figure S6. A. Wide-scan (or survey) XPS spectrum of Pd/Au (3:1)-**17** showing all elements present on the sample surface: major elements are carbon (C 1s at 284.6 eV), oxygen (O 1s at 530.6 eV), and nitrogen (N 1s at 398.6 eV) of the polymers. B. Detailed XPS spectrum of Pd/Au (3:1)-**17** in the range of the Au signals. The signal at 84.1 eV belongs to Au 4f$_{7/2}$. C. Detailed XPS spectrum of Pd/Au (3:1)-**17** in the range of the Pd signals. The signal at 335.1 eV belongs to Pd 3d$_{5/2}$. D. Wide-scan (or survey) XPS spectrum of Cu/Au (3:1)-**17** showing all elements present on the sample surface: major elements are carbon (C 1s at 284.6 eV), oxygen (O 1s at 530.8 eV), and nitrogen (N 1s at 398.6 eV) of the polymers. E. Detailed XPS spectrum of Cu/Au (3:1)-**17** in the range of the Au signals. The signal at 84.1 eV belongs to Au $4f_{7/2}$. F. Detailed XPS spectrum of Cu/Au (3:1)-**17** in the range of the Cu signals. The signal at 932.7 eV belongs to Cu $2p_{3/2}$.

9. Experimental Procedure

^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were measured from a solution in $CDCl_3$ unless otherwise mentioned. The chemical shift data for each signal on ^{1}H NMR are given in units of δ relative to TMS (δ = 0) or $CHCl_3$ (δ = 7.26). For ^{13}C NMR spectra, the chemical shifts are recorded relative to $CDCl_3$ (δ = 77.0). Low-resolution mass spectra were taken from an API 2000-triple quadrupole ESI-MS/MS mass spectrometer. High-resolution mass spectra were obtained using a LCT Premier time of flight mass spectrometer. IR spectra were measured directly in either solid or liquid form. Inductively coupled plasma-mass spectra (ICP-MS) were taken from a PerkinElmer NexION® 300D ICP-MS instrument. Transmission electron microscopy (TEM) images were taken from a FEI CM100 TEM instrument (Technical Sales Solutions Inc.). X-ray photoelectron spectroscopy (XPS) study was performed on a PHI 5400 XPS system (Physical Electronic Inc.). The purchased *N*-Boc-L-amino acids (from Chem-Impex International, Wood Dale, IL) were recrystallized twice from ethyl acetate and hexane to obtain pure amino acids before use. All *cis*-, and *trans*-1,2- and 1,3-cyclopentanes, -cyclohexanes, and –cycloheptanes, limonene, and sclareolide were purchased from Sigma-Aldrich or prepared by following the reported procedures.[1-3] 1,4-

Diisopropylcyclohexanes are commercially available from Alfa Aesar Co. as a mixture of inseparable *trans*- and *cis*-isomers. We prepared the *trans*-isomer **50** from a two-step sequence of reactions involving Birch reduction of 1,4-diisopropylbenzene followed by hydrogenation. Alcohols **52** – **54** and **58** were made from the addition reactions of isopropylmagnesium bromide with cycloalkanones in the presence of 0.2 equiv of $ZnCl_2$ in THF at 0°C.[4] Optical purities of various oxidized products were determined by HPLC using chiral column, Chiralpak AD(-H) column, size: 0.46 cm x 25 cm, from Daicel Chemical Industries, Exton, PA. AFM images were taken from a Nanoscope IIIa SPM atomic force microscope (Digital Instrument). Dynamic light scattering graphs were taken from a ZetaPALS zeta potential analyzer (Brookhaven Instrument Co.). High pressure reactions were conducted in a Parr Pressure Reactor (Parr Instrument Co., Moline, IL) under 2 atm. (or 30 psi) of oxygen. Vivaspin 20 centrifugal filter device with a 3,000 MWCO was purchased from Sartorius Inc.

Scheme S1. Synthesis of N-vinyl-5-benzhydryloxymethylpyrrolidinone (11).



(*S*)-*tert*-Butyl 3-*tert*-butoxy-1-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-1-oxopropan-2-ylcarbamate (1a).[5-7] A solution of 4.0 g (15.3 mmol) of *N*-Boc-*O*-*tert*-butyl-L-serine, 3.3 g (23 mmol) of Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione), and 2.8 g (22.9 mmol) of 4-(dimethylamino)pyridine (DMAP) in 80 mL of dichloromethane under argon was cooled to 0°C over an ice-water bath. To it, a solution of 3.47 g (16.8 mmol) of *N,N'*-dicyclohexylcarbodiimide (DCC) in 20 mL of dichloromethane was added dropwise. The mixture was stirred for 12 hours under argon and the precipitated (*N,N*'-dicyclohexylurea) was removed by filtration. The filtrate was washed with 50 mL of 5% HCl, and then water, dried (anhydrous Na_2SO_4), and concentrated to dryness leaving 5.83 g of compound **1a** as a white solid. This compound was used in the following step without further purification. ^{1}H NMR δ 5.67 – 5.63 (m, 1 H), 5.49 – 5.47 (m, 1 H), 3.74 – 3.70 (m, 2 H), 3.62 (s, 1 H, NH), 1.76 (s, 3 H), 1.73 (s, 3 H), 1.46 (s, 9 H), 1.26 (s, 9 H). ^{13}C NMR δ 206.8, 172.7, 152.3, 105.9, 79.0, 75.0, 62.0, 60.6, 59.9, 30.0 (3 C), 28.4 (3 C), 25.6 (2 C). MS (ESI, MeOH): *m/z* = 388.7 ($[M + H]^+$).

(*R*)-*tert*-Butyl 3-*tert*-butoxy-1-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)propan-2-ylcarbamate (1b). To a cold (0°C) solution of 5.80 g (15.2 mmol) of compound **1a** in 150 mL of dichloromethane under argon were added 5.51 g (91.8 mmol) of acetic acid and 1.51 g (39.8 mmol) of $NaBH_4$. The solution was stirred at 0°C for three hours and at 25°C for 12 hours, diluted with 30 mL of water, the dichloromethane layer was separated, and the water layer was extracted with dichloromethane three times. The combined organic layers were washed with water and brine, dried (anhydrous Na_2SO_4), concentrated to give a yellow oil, which was crystallized from diethyl ether to give 5.27 g of compound **1b** as a white solid. ^{1}H

NMR δ 5.08 – 5.09 (m, 1 H), 4.08 – 4.00 (m, 1 H), 3.62 (s, 1 H, NH), 3.45 – 3.41 (m, 2 H), 2.5 – 2.45 (m, 1 H), 2.16 – 2.01 (m, 1 H), 1.80 (s, 3 H), 1.72 (s, 3 H), 1.40 (s, 9 H), 1.05 (s, 9 H); ^{13}C NMR δ 208.0, 174.6, 151.0, 105.7, 79.3, 74.7, 69.8, 49.6, 47.1, 31.9, 28.4, 25.7. MS (ESI, MeOH): *m/z* = 374.0 ($[M + H]^+$), 299.9.

(*R*)-N-(*tert*-Butoxycarbonyl)-5-(*tert*-butoxymethyl)-pyrrolidin-2-one (3). A solution of 5.26 g (14.10 mmol) of compound **1b** in 40 mL of toluene under argon was heated to reflux for 6 hours, cooled to 25°C, concentrated under vacuum, and column chromatographed on silica gel using hexane and ethyl acetate (4:1) as eluent to give 3.44 g (83% overall yield in three steps) of compound **3** as a yellow oil. $[\alpha]_D^{22}$ = +80.7 (c 1.0, $CHCl_3$); ^{1}H NMR δ 4.09 – 4.07 (m, 1 H), 3.52 (dd, J = 10, 4 Hz, 1 H), 3.31 (dd, J = 10, 1.6 Hz, 1 H), 2.56 (dt, J = 17.6, 9.6 Hz, 1 H), 2.20 (dd, J = 17.6, 9.2 Hz, 1 H), 2.05 – 1.84 (m, 2 H), 1.40 (s, 9 H), 1.02 (s, 9 H). ^{13}C NMR δ 175.3, 150.1, 82.6, 73.2, 62.9, 58.0, 32.5, 28.2, 27.5, 21.7. MS (ESI, MeOH): *m/z* = 294.1 ($[M + Na]^+$), 272.0 ($[M+ H]^+$), 194.1, 172.1, 116.0. HRMS-ESI: *m/z* $[M + H]^+$ calcd for $C_{14}H_{26}NO_4$: 272.1862; found: 272.1887.

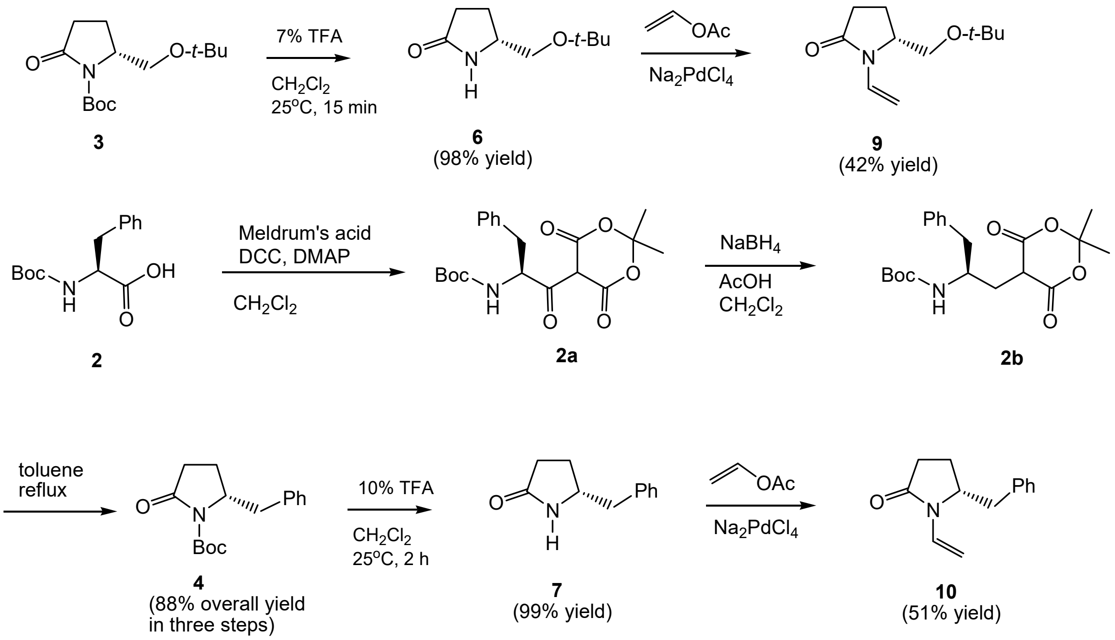
(*R*)-5-(Hydroxymethyl)pyrrolidin-2-one (5). A solution of 1.0 g (12.9 mmol) of compound **3** in 5 mL of 10% trifluoroacetic acid in dichloromethane was stirred at 50°C for 5 hours, cooled to 25°C, and diluted with dichloromethane. The solution was washed with an aqueous solution of $NaHCO_3$, then water and brine, dried ($MgSO_4$), concentrated to give 0.42 g (99% yield) of compound **5** as a brown oil. This material was used in the subsequent step without further purification. $[\alpha]_D^{22}$ = -60.2 (c 1.0, $CHCl_3$); ^{1}H NMR δ 6.7 – 6.6 (bs, 1 H, NH), 4.46 (dd, J = 11.2, 4 Hz, 1 H), 4.21 (dd, J = 11.2, 7.2 Hz, 1 H), 4.15 – 4.04 (m, 1 H), 2.54 – 2.32 (m, 4 H, CH_2 and OH), 1.98 – 1.87 (m, 1 H); ^{13}C NMR δ 181.6, 65.2, 57.5, 30.3, 22.3; MS (ESI, MeOH): *m/z* = 116.0 ([M + H]$^+$, 100%), 98.1. HRMS-ESI: *m/z* [M + Na]$^+$ calcd for $C_5H_9NO_2Na^+$: 138.0531 found: 138.0537.

(*R*)-5-(Benzhydryloxymethyl)pyrrolidin-2-one (8). To a cold (0°C) solution of 0.43 g (3.74 mmol) of compound **5** in 1 mL distilled THF under argon, was added 0.15 g (3.74 mmol) of NaH (60% in mineral oil; NaH was washed twice with dried diethyl ether). The mixture was stirred at 0°C for 30 minutes and added 1.11 g (4.48 mmol) of bromodiphenylmethane. The mixture was stirred at 50°C for 12 hours, diluted with 1 mL of H_2O, and the organic THF layer was separated and concentrated under vacuum and column chromatographed on silica gel using a gradient mixture of hexane and ethyl acetate as an eluent to give 0.93 g (88% yield) of compound **8** as a brown oil. $[\alpha]_D^{22}$ = -63.2 (c 1.0, $CHCl_3$); ^{1}H NMR δ 7.4 – 7.2 (m, 10 H, Ar), 6.06 – 5.98 (bs, 1 H, NH), 5.35 (s, 1 H), 3.95 – 3.88 (m, 1 H, CHN), 3.48 (dd, J = 9.6, 3.6 Hz, 1 H, CHO), 3.36 (dd, J = 9.6, 8 Hz, 1 H, CHO), 2.41 – 2.27 (m, 2 H, CH_2C=O), 2.24 – 2.14 (m, 1 H), 1.79 – 1.68 (m, 1 H); ^{13}C NMR δ 178.1, 141.8 (2 C), 128.7 (4 C), 127.9 (2 C), 127.1 (4 C), 84.1, 73.0, 54.1, 29.9, 23.4; MS (ESI, MeOH): *m/z* = 304.1 ([M + Na]$^+$), 194.0, 167.1. HRMS-ESI: *m/z* [M + Na]$^+$ calcd for $C_{18}H_{19}NO_2Na^+$: 304.1313; found: 304.1320.

(*R*)-5-(Benzhydryloxymethyl)-1-vinylpyrrolidin-2-one (11).[8] To a solution of 1.20 g (4.27 mmol) of compound **8** in 50 mL of vinyl acetate under argon, were added 4.0 g of 3 Å molecular sieves, 27 mg (0.34 mmol) of Na_2PdCl_4, and 1.06 g (7.69 mmol) of K_2CO_3. The mixture was stirred at 50°C under argon for 28 hours, cooled to 25°C, filtered, concentrated under vacuum, and column chromatographed on silica gel using a mixture of hexane and diethyl ether (1:1) as an eluent to give 0.67 g (51% yield) of pure compound **11** as a brown oil. $[\alpha]_D^{22}$ = +24.6 (c 1.0, $CHCl_3$); ^{1}H NMR δ 7.35 – 7.20 (m, 10 H), 6.98 (dd, J = 16.4, 9.2 Hz, 1 H, CH=), 5.31

(s, 1 H), 4.38 (d, J = 9.2 Hz, 1 H, =CH_2), 4.34 (d, J = 16.4 Hz, 1 H, =CH_2), 4.13 – 4.08 (m, 1 H), 3.68 (dd, J = 9.2, 4.8 Hz, 1 H), 3.52 (dd, J = 9.2, 2.8 Hz, 1 H), 2.70 (dt, J = 17, 10 Hz, 1 H), 2.42 – 2.34 (m, 1 H), 2.20 – 2.11 (m, 2 H); ^{13}C NMR δ 178.8, 142.5, 138.1, 128.7 (4 C), 127.9 (2 C), 127.1 (4 C), 96.8, 84.2, 73.6, 54.0, 30.2, 23.7. MS (ESI, MeOH): *m/z* = 330.1 ([M + Na]$^+$). HRMS-ESI: *m/z* [M + Na]$^+$ calcd for $C_{20}H_{21}NO_2Na^+$: 330.1470; found: 330.1490.

Scheme S2. Syntheses of N-vinyl 5-substituted pyrrolidinones 9 and 10.



(*R*)-5-(*t*-Butyloxymethyl)pyrrolidin-2-one (6). A solution of 10.2 g (37.5 mmol) of compound **3** in 100 mL of 7% trifluoroacetic acid (TFA) in dichloromethane was stirred at 25°C for 15 minutes and then diluted with 30 mL of saturated $NaHCO_3$. The mixture was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water, and brine, dried ($MgSO_4$), concentrated to give 6.28 g (98% yield) of compound **6** as a brown oil. This material was used in the subsequent step without further purification. $[\alpha]_D^{22}$ = -10.8 (c 1.0, $CHCl_3$); ^{1}H NMR δ 7.8 – 7.72 (bs, 1 H, NH), 3.94 – 3.86 (m, 1 H, CHN), 3.43 (dd, J = 9.0, 3.2 Hz, 1 H, CH_2O), 3.25 (dd, J = 9.0, 8.0 Hz, 1 H, CH_2O), 2.61

– 2.45 (m, 2 H, $CH_2C=O$), 2.28 – 2.18 (m, 1 H), 1.86 – 1.75 (m, 1 H), 1.18 (s, 9 H); ^{13}C NMR δ 175.5, 74.4, 65.2, 59.7, 32.4, 28.0 (3 C), 22.5. MS (ESI, MeOH): *m/z* = 194.1 ($[M + Na]^+$; 100%), 172.3. HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_9H_{17}NO_2Na^+$: 194.1157; found: 194.1172.

(*R*)-5-(*t*-Butyloxymethyl)-1-vinylpyrrolidin-2-one (9). To a solution of 2.0 g (11.6 mmol) of compound **6** in 35 mL of vinyl acetate under argon, were added 4.0 g of 3 Å molecular sieves, 0.27 g (0.9 mmol) of Na_2PdCl_4, and 2.25 g (16.3 mmol) of K_2CO_3. The mixture was stirred at 50°C under argon for 14 hours, cooled to 25°C, filtered, concentrated under vacuum, and column chromatographed on silica gel using a mixture of hexane and ethyl acetate (1:2) as an eluent to give 0.96 g (42% yield) of pure compound **9** as a yellow oil. $[\alpha]_D^{22}$ = +9.6 (c 1.0, $CHCl_3$); ^1H NMR δ 7.0 (dd, J = 16, 9 Hz, 1H, CH=), 4.45 (d, J = 9 Hz, 1 H, $=CH_2$), 4.44 (d, J = 16 Hz, 1 H, $=CH_2$), 4.06 – 4.00 (m, 1 H, CHN), 3.52 (dd, J = 9.2, 4.8 Hz, 1 H, CH_2O), 3.41 (dd, J = 9.2, 2.8 Hz, 1 H, CH_2O), 2.64 (dt, J = 17.2, 10.8 Hz, 1 H), 2.35 – 2.26 (m, 1 H), 2.14 – 2.05 (m, 2 H), 1.13 (s, 9 H); ^{13}C NMR δ 175.3, 139.7, 93.1, 74.6, 63.5, 58.8, 32.4, 28.2 (3 X), 20.8. MS (ESI, MeOH): *m/z* = 220.2 ($[M + Na]^+$), 198.2 ($M+H^+$), 187.1. HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_{11}H_{19}NO_2Na^+$: 220.1313; found: 220.1333.

(*S*)-*tert*-Butyl 1-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-1-oxo-3-phenylpropan-2-ylcarbamate (2a). [5-7] A solution of 1.33 g (5.0 mmol) of Boc-L-phenylalanine, 1.08 g (7.5 mmol) of Meldrum's acid, and 0.95 g (7.5 mmol) of 4-(dimethylamino)pyridine (DMAP) in 70 mL of dichloromethane under argon was cooled to 0°C over an ice-water bath. To it, a solution of 1.13 (5.5 mmol) g of *N,N'*-dicyclohexylcarbodiimide (DCC) in 15 mL of dichloromethane was added dropwise. The mixture was stirred for 12 hours under argon and the precipitated (*N,N'*-dicyclohexylurea) was removed by filtration. The filtrate was washed with 5% HCl twice, and then water, dried (anhydrous Na_2SO_4), and concentrated to dryness leaving 1.90 g of **2a**[5] as white solid. This compound was used in the following step without further purification. ^{1}H NMR δ 7.3 -7.15 (m, 5 H), 4.5 – 4.4 (m, 1 H), 4.3 – 4.2 (m, 1 H), 3.9 – 3.8 (m, 1 H), 2.8 – 2.7 (m, 2 H), 1.7 (s, 3 H), 1.65 (s, 3 H); ^{13}C NMR δ 207.5, 170.8, 153.1, 135.8, 129.6 (2 C), 128.9 (2 C), 127.4, 105.7, 80.3, 62.7, 60.3, 33.8, 28.4, 26.8.

(*R*)-*tert*-Butyl 1-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-3-phenylpropan-2-ylcarbamate (2b). To a cold (0°C) solution of 1.90 g (4.85 mmol) of compound **2a** in 25 mL of dichloromethane under argon were added 1.75 g (29.1 mmol) of acetic acid and 0.48 g (12.6 mmol) of $NaBH_4$. The solution was stirred at 0°C for three hours and at 25°C for 12 hours, diluted with 30 mL of water, the dichloromethane layer was separated, and the water layer was extracted with dichloromethane three times. The combined organic layers were washed with water and brine, dried ($MgSO_4$), concentrated to give 1.78 g of compound **2b**[5] as a white solid. This compound was used in the subsequent step without further purification. ^{1}H NMR δ 7.35 – 7.19 (m, 5 H), 4.48 – 4.43 (m, 1 H), 4.24 – 4.20 (m, 1 H), 3.92 – 3.90 (m, 1 H), 2.88 – 2.83 (m, 2 H), 2.31 – 2.11 (m, 2 H), 1.81 (s, 3 H), 1.77 (s, 3 H), 1.25 (s, 9 H); ^{13}C NMR δ 174.7, 150.2, 137.3, 129.6 (2 C), 129.0 (2 C), 127.1, 83.2, 59.2, 39.7, 31.3, 28.3 (3 C), 21.8. MS (ESI, MeOH): *m/z* = 400.2 ($[M + Na]^+$).

(*R*)-*N*-(*tert*-Butoxycarbonyl)-5-benzylpyrrolidin-2-one (4).[5] A solution of 0.35 g (0.93 mmol) of compound **2b** in 20 mL of toluene under argon was heated to reflux for 4 hours, cooled to 25°C, concentrated, and column chromatographed on silica gel using hexane and ethyl acetate (4:1) as eluent to give 0.23 g (88% overall yield in three steps) of compound **4**[5] as a yellow oil.

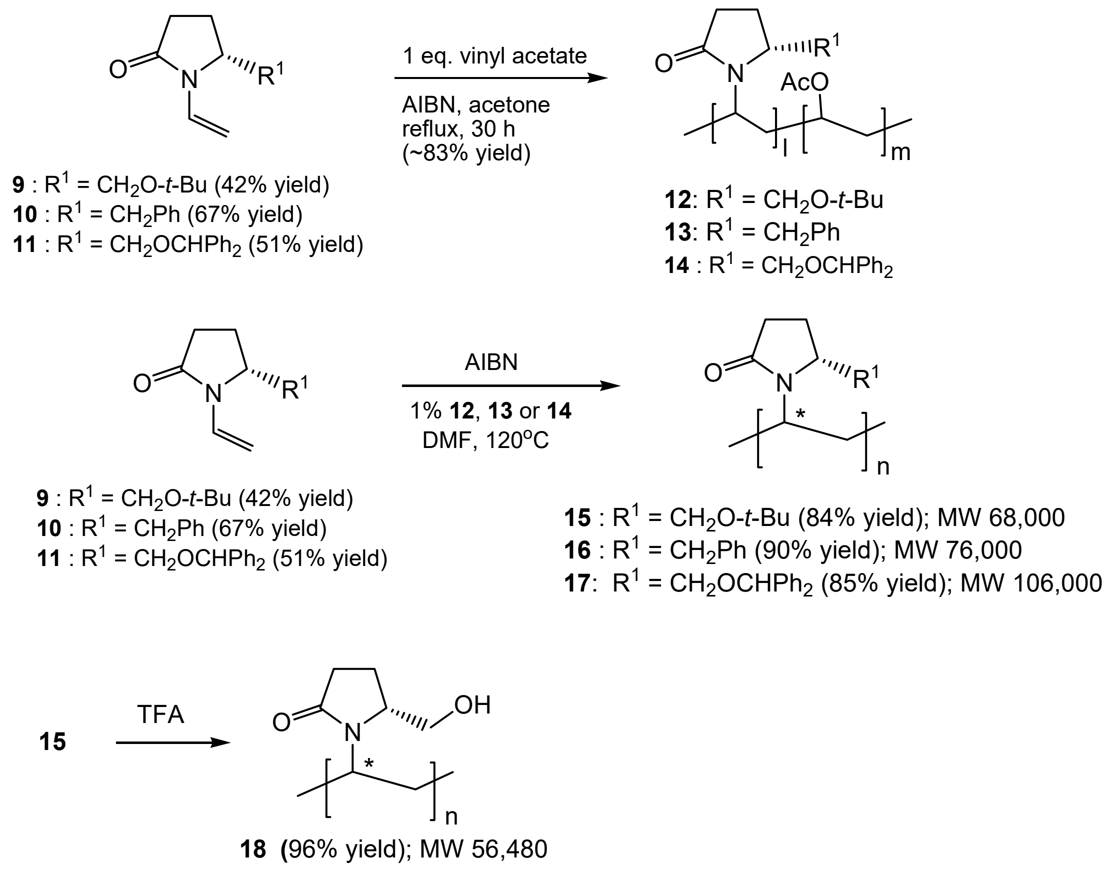
The material was used in the subsequent step without purification. $[\alpha]_D^{22}$ = +48.7 (c 1.5, $CHCl_3$); Lit.[9] +48.5 (c 1.50, $CHCl_3$). ^1H NMR δ 7.34 – 7.29 (m, 2 H), 7.28 – 7.24 (m, 1 H), 7.20 – 7.17 (m, 2 H), 4.39 – 4.34 (m, 1 H, CHN), 3.13 (dd, J = 13.5, 4 Hz, 1 H), 2.73 (dd, J = 13.5, 9.6 Hz, 1 H), 2.35 – 2.27 (m, 2 H), 2.20 – 1.90 (m, 1 H), 1.85 – 1.76 (m, 1 H), 1.57 (s, 9 H); ^{13}C NMR δ 174.8, 150.1, 137.3, 129.6 (2 C), 129.0 (2 C), 127.1, 83.3, 59.3, 39.7, 31.3, 28.4 (3 C), 21.8. MS (ESI, MeOH): *m/z* = 298.1 ($[M + Na]^+$).

(*R*)-5-Benzylpyrrolidin-2-one (7).[5] A solution of 1.0 g (12.9 mmol) of compound **4** in 5 mL of 10% trifluoroacetic acid in dichloromethane was stirred at 25°C for 2 hours, diluted with dichloromethane, and washed with an 10% aqueous solution of $NaHCO_3$, then water and brine, dried ($MgSO_4$), concentrated to give 0.61 g (96% yield) of compound **7**[5] as a brown oil. This material was used in the subsequent step without further purification. $[\alpha]_D^{22}$ = +39.7 (c 1.19, EtOH); Lit.[9] +39.6 (c 1.19, EtOH). ^1H NMR δ 7.33 – 7.12 (m, 5 H), 5.95 - 5.90 (bs, 1 H, NH), 3.92 – 3.83 (m, 1 H, CHN), 2.83 (dd, J = 13.4, 5.6 Hz, 1 H), 2.72 (dd, J = 13.4, 7.6 Hz, 1 H), 2.34 – 2.20 (m, 3 H), 1.89 – 1.80 (m, 1 H); ^{13}C NMR δ 178.1, 137.8, 129.3 (2 C), 129.2 (2 C), 127.1, 55.9, 43.2, 30.3, 27.2; MS (ESI, MeOH): *m/z* = 198.1 ($[M + Na]^+$).

(*R*)-5-(Benzyl)-1-vinylpyrrolidin-2-one (10). To a solution of 0.60 g (3.42 mmol) of compound **7** in 30 mL of vinyl acetate under argon, were added 2.0 g of 3 Å molecular sieves, 88 mg (0.30 mmol) of Na_2PdCl_4, and 0.86 g (6.2 mmol) of K_2CO_3. The mixture was stirred at 50°C under argon for 28 hours, cooled to 25°C, filtered, concentrated under vacuum, and column chromatographed on silica gel using a mixture of hexane and diethyl ether (1:1) as an eluent to give 0.46 g (67% yield) of pure compound **10** as a yellow oil. $[\alpha]_D^{22}$ = +38.3 (c 1.0, $CHCl_3$); ^1H NMR δ 7.34 – 7.23 (m, 3 H), 7.18 – 7.14 (m, 2 H), 7.08 (dd, J = 16.4, 9.6 Hz, 1 H,

=CH), 4.63 (d, J = 16.4 Hz, 1 H, =CH_2), 4.60 (d, J = 9.6 Hz, 1 H, =CH_2), 4.22- 4.17 (m, 1 H, CHN), 3.00 (dd, J = 14, 3 Hz, 1 H), 2.81 (dd, J = 14, 8 Hz, 1 H), 2.24 – 2.17 (m, 1 H), 2.10 – 1.91 (m, 3 H); ^{13}C NMR δ 173.7, 137.1, 129.7, 128.9 (2 C), 128.4, 127.1 (2 C), 95.3, 57.0, 36.6, 30.1, 22.8; MS (ESI, MeOH): *m/z* = 224.1 ($[M + Na]^+$), 202.0 ($M+H^+$; 100%). HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_{13}H_{15}NONa$: 224.1051; found: 224.1076.

Scheme S3. Synthesis of CSPVPs.



Representative syntheses of copolymers, poly(5-substituted *N*-vinyl pyrrolidinone-co-vinyl acetate) [P(SVP-co-VAc)] 12 - 14.[10,11]

Copolymer 14 from (*R*)-5-(benzhydryloxymethyl)-1-vinylpyrrolidin-2-one (11) and vinylacetate. To a solution of 93 mg (0.33 mmol) of compound **11** and 28 mg (0.33 mmol) of vinyl acetate in 0.15 mL of acetone under argon, was added 10 mg (0.066 mmol) of AIBN, and the solution was stirred under reflux for 30 h. The solution was cooled to 25°C, diluted with hexane, and stirred for 10 min. The white precipitate was collected by filtration, dried under vacuum to give 0.106 g (88% yield) of copolymer **14** as a white solid. ^{1}H NMR δ 7.50 – 6.3 (m, 11 H, Ph & CH), 3.6 – 1.0 (m, 16 H).

Copolymer 12 from (*R*)-5-(*tert*-butoxymethyl)-1-vinylpyrrolidin-2-one (9) and vinylacetate. From 30 mg (0.15 mmol) of **9**, 13 mg (0.15 mmol) of vinyl acetate and 0.25 mg of AIBN, copolymer **12**, 39 mg (90% yield), was obtained. ^{1}H NMR δ 4.90 – 2.75 (m, 5 H), 2.70 – 0.80 (m, 20 H).

Copolymer 13 from (*R*)-5-benzyl-1-vinylpyrrolidin-2-one (10) and vinylacetate. From 50 mg (0.25 mmol) of monomer **10**, 21.4 mg (0.25 mmol) of vinyl acetate and 0.7 mg of AIBN, copolymer **13**, 65 mg (91% yield), was obtained. ^{1}H NMR δ 7.20 – 6.80 (m, 3 H), 6.75 – 6.30 (m, 2 H), 3.50 – 3.00 (m, 3 H), 2.5 – 1.1 (m, 13 H).

Poly[(5*R*)-5-(benzhydryloxymethyl)-1-vinylpyrrolidin-2-one] (17). To a hot (120°C) solution of 1.2 mg (1% by weight) of copolymer **14** in 0.5 mL of DMF under argon, were added 120 mg (0.43 mmol) of compound **11** and 0.28 mg (1.7 μmol) of AIBN. The solution was stirred for 6 days at 120°C (until no monomer **11** was found by NMR spectrum of an aliquot from the reaction solution), cooled to 25°C, and diluted with hexane. The precipitate was collected by filtration, dried under vacuum to give 102 mg (84% yield) of polymer **17** as a white solid. The average molecular weight of polymer **17**, 106,000, was determined by gel permeation chromatography using TSKgel GMHxl column and THF as solvent with a flow rate of 1 mL/min. ^{1}H NMR δ 7.3 – 6.8 (m, 6 H, Ph), 6.6 – 6.3 (m, 4 H, Ph), 3.8 – 3.76 (m, 1

H), 3.4 – 3.0 (m, 3 H), 2.45 – 1.0 (m, 7 H). IR (neat) ν 3050, 2954, 2890, 1650 (s), 1462, 1441, 1423, 1290. The polymer was used in the subsequent catalytic asymmetric oxidation reactions without further purification. AFM images of the polymer were taken and a representative graph is shown in Figure S2. A diluted solution of polymer **17** in water was added onto a mica chip and the water was slowly evaporated by a slow stream of argon. AFM images were obtained using the resulting polymer deposited on the mica from a Nanoscope IIIa SPM atomic force microscope (Digital Instrument).

Poly[(5*R*)-5-(*tert*-butoxymethyl)-1-vinylpyrrolidin-2-one] (15). To a solution of 90 mg (0.45 mmol) of monomer **9** and 2 mg of copolymer **12** in 0.2 mL of ethyl acetate under argon was added a solution of 0.3 mg of AIBN in 0.1 mL of ethyl acetate. The solution was heated to reflux for 14 h, cooled to 25°C, diluted with hexane, and filtered to collect the white solid. The solid was dried under vacuum to give 76 mg (83% yield) of polymer **15**. The average molecular weight of polymer **15** was 68,000, which was determined by gel permeation chromatography using TSKgel GMHxl column and THF as solvent with a flow rate of 1 mL/min. ^{1}H NMR δ 4.0 – 3.0 (m, 4 H), 2.5 – 1.4 (bm, 6 H), 1.71 (bs, 9 H, *t*-Bu). The polymer was used in the subsequent catalytic asymmetric oxidation reactions without further purification.

Poly[(5*R*)-5-(benzyl)-1-vinylpyrrolidin-2-one] (16). To a solution of 0.30 g (1.5 mmol) of monomer **10** and 3 mg of copolymer **13** in 0.6 mL of ethyl acetate under argon was added a solution of 1 mg of AIBN in 0.1 mL of ethyl acetate. The solution was heated to reflux for 6 h, cooled to 25°C, diluted with hexane, and filtered to collect the white solid. The solid was dried under vacuum to give 0.27 g (89% yield) of polymer **16**. The average molecular weight of polymer **16** was 76,000, which was determined by gel permeation chromatography using TSKgel GMHxl column and THF as solvent with a flow rate of 1 mL/min. ^{1}H NMR δ 7.25 – 6.25 (m, 5 H, Ph), 4.0 – 3.0 (m, 4 H), 2.5 – 1.2 (m, 6 H). The polymer was used in the subsequent catalytic asymmetric oxidation reactions without further purification.

Poly[(5*R*)-5-(hydroxymethyl)-1-vinylpyrrolidin-2-one] (18). A solution of 0.20 g (3 μmol) of polymer **15** and 34 mg (0.3 mmol) of trifluoroacetic acid in 0.2 mL of CH_2Cl_2 was stirred at 25°C for 2 h, and concentrated to dryness to give 0.14 g (96% yield) of polymer **18**. The average molecular weight of polymer **18** was 56,480, which was determined by gel permeation chromatography using TSKgel GMHxl column and THF as solvent with a flow rate of 1 mL/min. ^{1}H NMR δ 4.1 – 2.8 (m, 4 H), 2.5 – 1.25 (m, 7 H). The polymer was used in the subsequent catalytic asymmetric oxidation reactions without further purification.

General procedure for the preparation of Pd/Au (3:1)-chiral substituted PVP 17.

To a solution of 88 μL (0.88 μmol) of a 10 mM aqueous solution of Na_2PdCl_4 and 29 μL (0.29 μmol) of a 10 mM aqueous solution of $HAuCl_4 \cdot 3H_2O$ in 2 mL of deionized H_2O was added 3.4 mg (0.032 μmol; 0.027 equiv based on total Pd and Au moles of atoms) of **17** and the solution was stirred at 0°C for 0.5 h. To it, was added 0.44 mg (0.012 mmol) of $NaBH_4$ and the resulting light black solution was stirred at 25°C for 0.5 h to give the bimetallic nanoclusters Pd/Au (3:1)-**17** in aqueous solution (see Figure S1 for the appearance of the solution). The solution was used in subsequent catalytic asymmetric oxidation without further manipulation.

Characterization of Pd/Au (3:1)-17 (representative example). A solution of Pd/Au (3:1)-**17** was prepared by following the above mentioned procedure. It was filtered through a Vivaspin 20 (Sartorius Inc.) centrifugal filter device (with a 3,000 MWCO) using a centrifugation instrument (Eppendorf Centrifuge model 5430) at 3,000 rpm for 1 – 3 min, and washed with deionized water twice to remove low molecular weight inorganic materials. The resulting nanocluster was dissolved in water, lyophilized to give Pd/Au (3:1)-**17** as light brown solids, which was subjected to analyses including atomic force microscopy (AFM), dynamic light scattering (DLS), TEM, XPS, and ICP-MS. IR (neat) ν 3050, 2950, 2924, 1641 (s), 1425, 1441, 1420, 1292.

General procedure for the catalytic asymmetric oxidation of *trans*-diols.

Oxidation of a mixture of (*R,R*)- and (*S,S*)-*trans*-1,3-cyclohexanediol (20). **Formation of (*S*)-3-hydroxycyclohexanone (23)**. To a solution of 4.8 mL of Pd/Au (3:1)-**17** (2.1 μmol of Pd/0.7 μmol of Au-0.08 μmol of **17**) in H_2O, were added 0.16 g (1.39 mmol) of racemic *trans*-1,3-cyclohexanediol (**20**) and 68 mg (0.42 mmol) K_2CO_3 under 1 atmospheric pressure of O_2 (a balloon was used). The solution was stirred at 60 °C for 7 days and the reaction progress was monitored by ^{1}H NMR until about a half of the diol was consumed. The reaction solution was cooled to 25°C, diluted with water, and extracted three times with dichloromethane (20 mL each). The combined extracts were dried (anhydrous Na_2SO_4), concentrated, and column chromatographed on silica gel using a mixture of ethyl acetate and diethyl ether (3:7) as an eluent to give 78 mg [97.5% yield based on reacted (*S,S*)-**20**] of (*S*)-3-hydroxycyclohexanone (**23**) in 99% ee and 81 mg (50% recovery based on racemic diol) of (*R,R*)-**20** in 92% ee. (*S*)-**23**: $[\alpha]_D^{22}$ = +45.2 (c 0.8, $CHCl_3$); Lit.[12] +37.3 (c 0.80, $CHCl_3$; 82% ee). ^{1}H NMR[8] δ 4.13 – 4.07 (m, 1 H, CHO), 3.30 (bs, 1 H, OH), 2.56 (dd, J = 14, 4.4 Hz, 1 H, $CH_2C{=}O$), 2.33 (dd, J = 14, 8 Hz, 1 H, $CH_2C{=}O$), 2.24 (t, J = 7 Hz, 2 H, $CH_2C{=}O$), 2.05 – 1.87 (m, 2 H), 1.75 – 1.56 (m, 2 H); ^{13}C NMR δ 210.9, 69.8, 50.6, 41.1, 32.9, 20.9. MS (ESI, MeOH): *m/z* = 137.1 ([M +

Na]$^+$). The % ee's of the hydroxyketones and diols were determined by subjecting the benzoate derivatives to HPLC using chiral column [Chiralpak AD(-H) column, size: 0.46 cm x 25 cm] (*vide infra*).

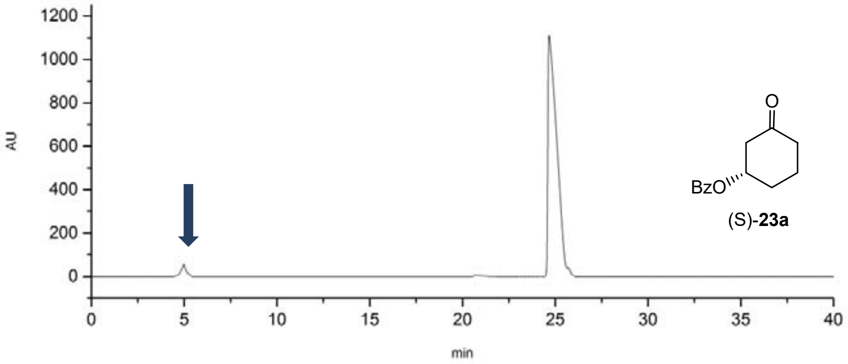
(*R,R*)-**20**: NMR spectra were identical to the authentic *trans*-1,3-cyclohexanediol. $[\alpha]_D^{22}$ = +3.18 (c 2.0, CH_2Cl_2); Lit.[13] -3.5 (c 2.0, CH_2Cl_2).

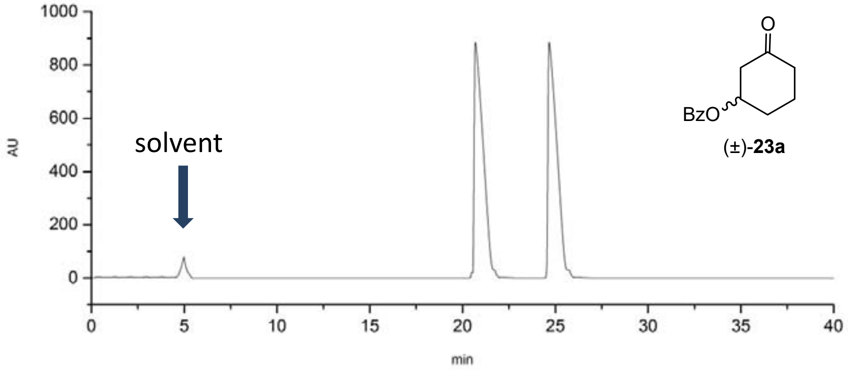
Other Pd/Au (3:1)-**15**, Pd/Au (3:1)-**16**, and Pd/Au (3:1)-**20** were also used in the oxidation of diol (±)-**20**, and results were described in Table 1.

In all cases, PVP was used in place of CSPVP to produce the racemic mixture of products for HPLC/chiral column analyses.

Representative preparation of benzoate derivative and dibenzoate derivative for determination of optical purity.

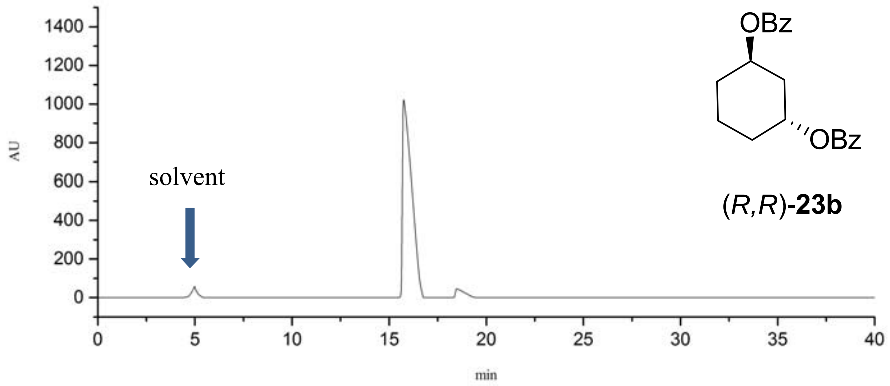
(*S*)-3-Oxocyclohexyl benzoate (23a). To a solution of 50 mg (0.44 mmol) of (*S*)-**23** in 1.5 mL of dichloromethane under argon at 0°C, was added 0.1 mL of pyridine and 0.12 g (0.85 mmol) of benzoyl chloride. The reaction solution was stirred at 0°C for 1 h, diluted with water, and extracted with CH_2Cl_2 twice. The combined extracts were washed with brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a mixture of ethyl acetate and hexane (1:2) as an eluent to give 88 mg (92% yield) of (*S*)-**23a** in 99% ee. ^{1}H NMR[11] δ 8.00 (d, J = 7.6 Hz, 2 H), 7.56 (t, J = 7.6 Hz 1 H), 7.43 (t, J = 7.6 Hz, 2 H), 5.55 – 5.50 (m, 1 H, CHO), 2.75 (dd, J = 14.8, 4 Hz, 1 H), 2.66 (dd, J = 14.8, 5.6 Hz, 1 H), 2.50 – 2.40 (m, 2 H), 2.17 – 2.2.0 (m, 3 H), 1.97 – 1.85 (m, 1 H); ^{13}C NMR δ 208.4, 165.7, 133.4, 129.8, 128.7, 128.6, 72.4, 46.8, 41.3, 29.6, 21.1. MS (ESI, MeOH): *m/z* = 241.1 ([M + Na]$^+$). The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, n-hexane-i-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 21 min (*R* enantiomer, minor), t_R = 25 min (*S* enantiomer, major).

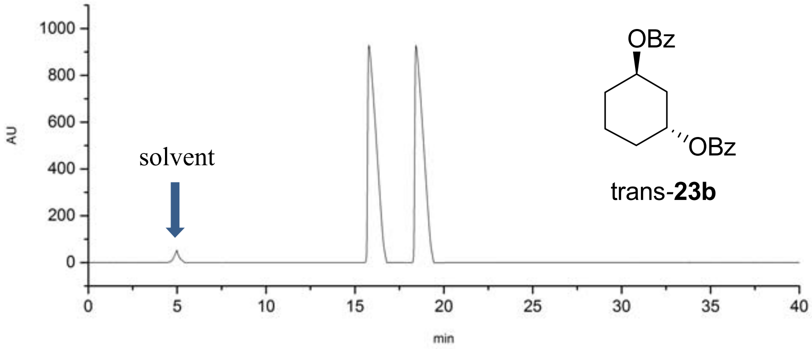




(*R*,*R*)-1,3-Di(phenylcarbonyloxy)cyclohexane (23b). A solution of 10 mg (86 μmol) of (*R*,*R*)-**20**, 24 mg (0.17 mmol) of benzoyl chloride in 0.1 mL of pyridine and 0.3 mL of dichloromethane was stirred at 25°C for 8 h under argon. The solution was diluted with 1 mL of water, concentrated to dryness, and column chromatographed on silica gel using a gradient mixture of hexane and ethyl acetate as eluents to give 17 mg (61% yield) of (*R*,*R*)-**23b** in 92% ee. ^{1}H NMR δ 8.06 (d, J = 8 Hz, 4 H), 7.56 (t, J = 8 Hz, 2 H), 7.45 (t, J = 8 Hz, 4 H), 5.47 – 5.45 (m, 2 H), 2.15 – 2.12 (m, 2 H), 1.94 – 1.91 (m, 2 H), 1.90 – 1.60 (m, 4 H); ^{13}C NMR δ 166.0 (2 C), 133.1 (2 C), 130.8 (2 C), 129.8 (4 C), 128.6 (4 C), 70.8 (2 C), 36.1, 30.6 (2 C), 19.7. MS (ESI, MeOH): *m/z* = 347.2 ([M + Na]$^+$), 203.2, 107.1. The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane:*i*-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 15.7 min (*R*,*R* enantiomer, major), t_R = 18.6 min (*S*,*S* enantiomer, minor).

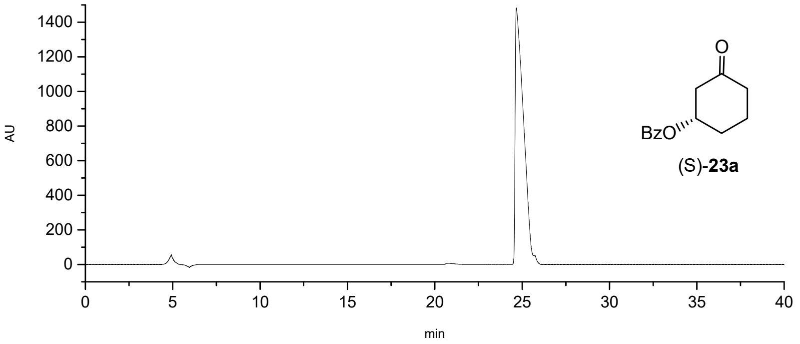
The racemic *trans*-dibenzoate **23b** were similarly prepared for HPLC/chiral column study from the corresponding racemic *trans*-diols.

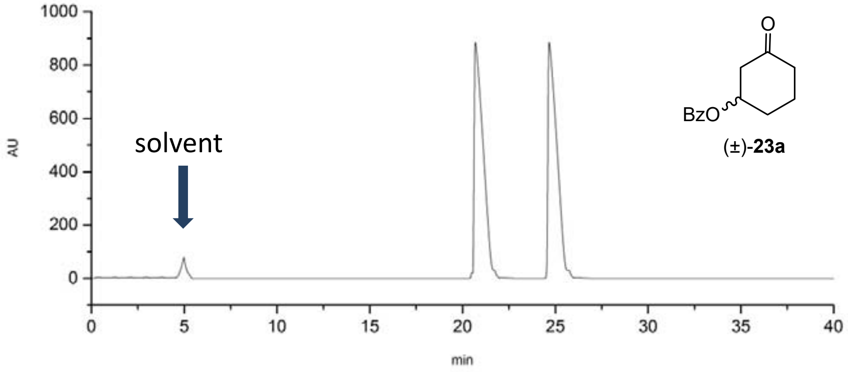




Oxidation of a mixture of (*R,R*)- and (*S,S*)-*trans*-1,3-cyclohexanediol (20) using <u>double amounts</u> of Pd/Au-17 catalyst for 6 days at 60ºC. Formation of (*S*)-3-hydroxycyclohexanone (23). Following the general procedure described above, 80 mg (0.70 mmol) of racemic *trans*-1,3-cyclohexanediol (**20**) was treated with of 4.8 mL of Pd/Au (3:1)-**17** (2.1 μmol of Pd/0.7 μmol of Au-0.08 μmol of **17**) in H_2O and 34 mg (0.21 mmol) K_2CO_3 under 1 atmospheric pressure of O_2. The reaction progress was monitored by ^{1}H NMR and after

6 days about a half of the diol was consumed. After aqueous work-up and silica gel column chromatography, 37 mg (47% yield) of (*S*)-**23** along with 40 mg (50% recovery) of (*R,R*)-**20**. The % ee of (*S*)-**23** was found to be 99% from HPLC/chiral column (Chiralpak AD(-H) column) analysis of the benzoate derivative as described above, using *n*-hexane-*i*-PrOH = 90:10 as eluent and with a flow rate of 0.5 mL/min; t_R = 21 min (*R* enantiomer, minor), t_R = 25 min (*S* enantiomer, major).

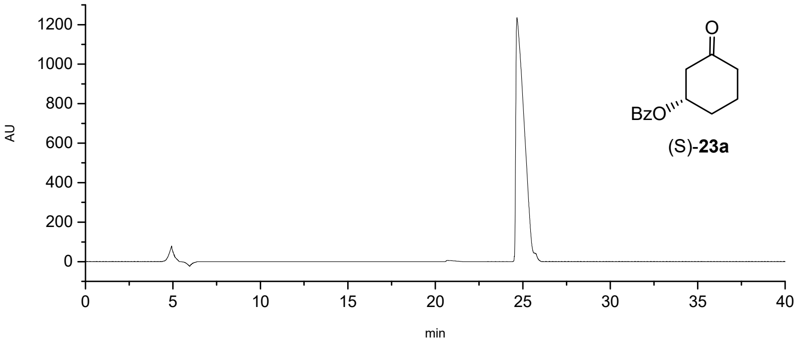


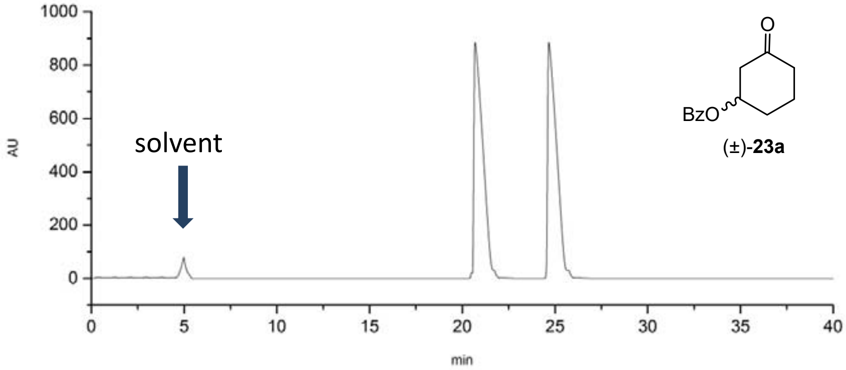


Oxidation of a mixture of (*R,R*)- and (*S,S*)-*trans*-1,3-cyclohexanediol (20) using <u>quadruple amounts</u> of Pd/Au-17 catalyst for 5 days at 60°C. **Formation of (*S*)-3-hydroxycyclohexanone (23)**. Following the general procedure described above, 80 mg (0.70 mmol) of racemic *trans*-1,3-cyclohexanediol (**20**) was treated with of 9.6 mL of Pd/Au (3:1)-**17** (4.2 μmol of Pd/1.4 μmol of Au-0.16 μmol of **17**) in H_2O and 34 mg (0.21 mmol) K_2CO_3

under 1 atmospheric pressure of O_2. The reaction progress was monitored by ^{1}H NMR and after 5 days about a half of the diol was consumed. Aqueous work-up of the reaction mixture followed by silica gel column chromatography gave 38 mg (49% yield) of (*S*)-**23** along with 40 mg (50% recovery) of (*R*,*R*)-**20** in 93% ee.

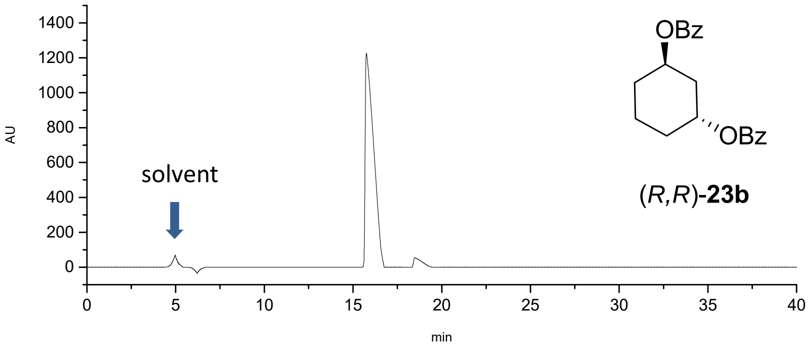
The % ee of (*S*)-**23** was found to be 99% from HPLC/chiral column (Chiralpak AD(-H) column) analysis of the benzoate derivative as described above, using *n*-hexane-*i*-PrOH = 90:10 as eluent and with a flow rate of 0.5 mL/min; t_R = 21 min (*R* enantiomer, minor), t_R = 25 min (*S* enantiomer, major).

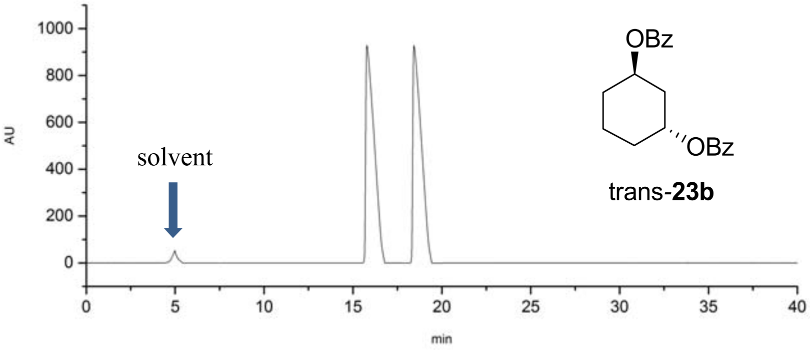




Recover diol from quadruple amounts catalyst oxidation

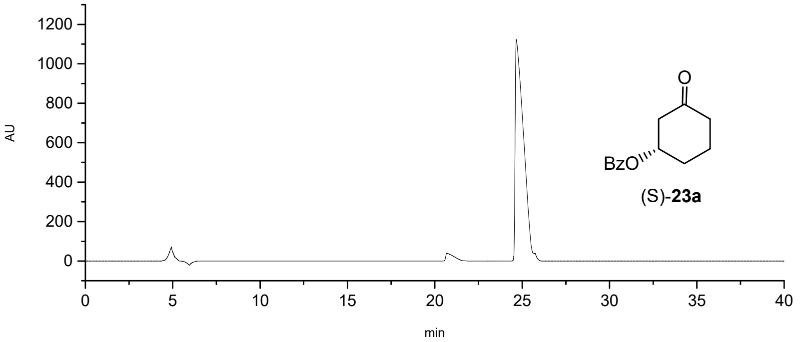
The % ee of (*R*,*R*)-**20** was found to be 93% determined by HPLC/chiral column (Chiralpak AD(-H) column), eluent of *n*-hexane:*i*-PrOH = 90:10, and a flow rate of 0.5 mL/min; t_R = 15.7 min (*R*,*R* enantiomer, major), t_R = 18.6 min (*S*,*S* enantiomer, minor).

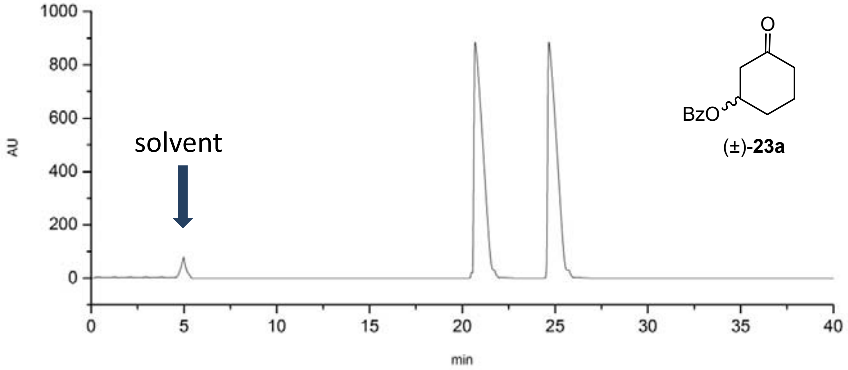




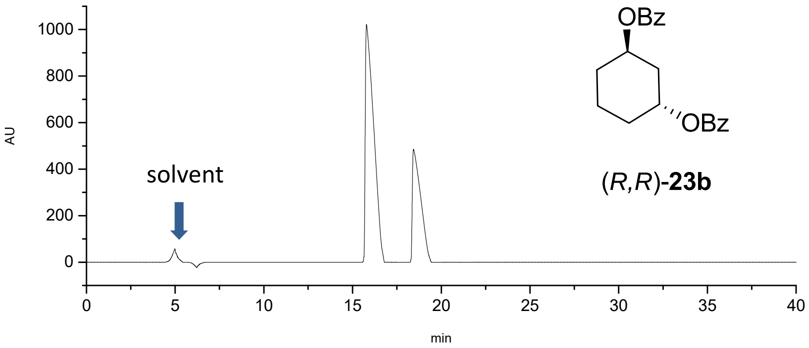
Oxidation of a mixture of (*R,R*)- and (*S,S*)-*trans*-1,3-cyclohexanediol (20) using 0.15 mol% Pd-17 catalyst for 7 days at 60°C. **Formation of (*S*)-3-hydroxycyclohexanone (23)**. To a solution of 4.8 mL of Pd-**17** (2.8 μmol of Pd-0.08 μmol of **17**) in H_2O, were added 0.16 g (1.39 mmol) of racemic *trans*-1,3-cyclohexanediol (**20**) and 68 mg (0.42 mmol) K_2CO_3 under 1 atmospheric pressure of O_2 (a balloon was used). The solution was stirred at 60 °C for 7 days and the reaction progress was monitored by ^{1}H NMR until about a half of the diol was consumed. The reaction solution was cooled to 25°C, diluted with water, and extracted three times with dichloromethane (20 mL each). The combined extracts were dried (anhydrous Na_2SO_4), concentrated, and column chromatographed on silica gel using a mixture of ethyl acetate and diethyl ether (3:7) as an eluent to give 46 mg (29% yield) of (*S*)-3-hydroxycyclohexanone (**23**) in 95% ee along with 107 mg (68% recovery based on racemic diol) of (*R*,*R*)-**20** in 35% ee.

The % ee of (*S*)-**23** was found to be 95% from HPLC/chiral column (Chiralpak AD(-H) column) analysis of the benzoate derivative as described above, using *n*-hexane-*i*-PrOH = 90:10 as eluent and a flow rate of 0.5 mL/min; t_R = 21 min (*R* enantiomer, minor), t_R = 25 min (*S* enantiomer, major).

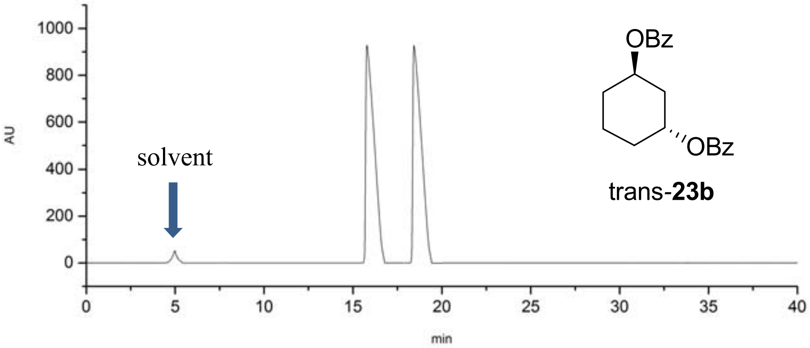




The % ee of recovered (*R*,*R*)-**20** was found to be 35% from HPLC/chiral column analysis of its dibenzoate **23b**. Chiralpak AD(-H) column and eluent of *n*-hexane:*i*-PrOH = 90:10 with a flow rate of 0.5 mL/min were used for the analysis. Retention times for t_R (*R*,*R* enantiomer, major) and (*S*,*S* enantiomer, minor) are 15.7 and 18.6 min, respectively.



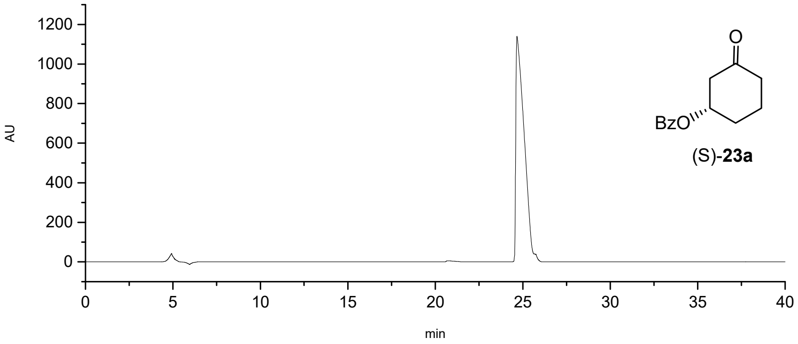
(*R*,*R*)-**23b**

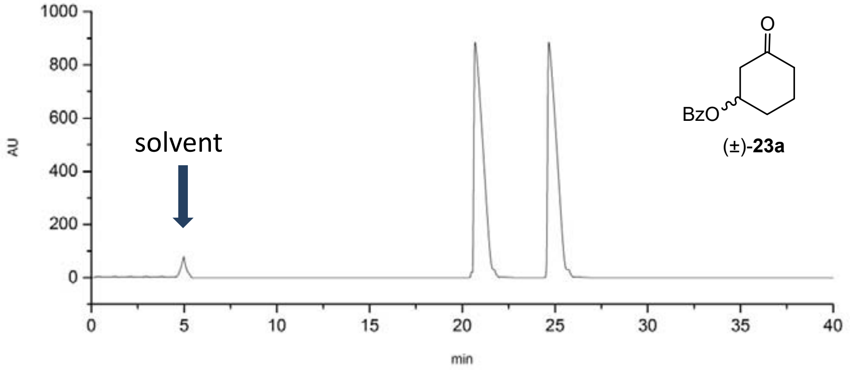


trans-**23b**

Oxidation of a mixture of (*R,R*)- and (*S,S*)-*trans*-1,3-cyclohexanediol (20) using 0.15 mol% of <u>first recovered</u> Pd/Au (3:1)-17 catalyst for 7 days at 60°C. **Formation of (*S*)-3-hydroxycyclohexanone (23)**. Following the above general procedure for the oxidation of *trans* diol, a solution of racemic **20** (80 mg; 0.70 mmol) and 34 mg (0.21 mmol) K_2CO_3 in 2.4 mL of aqueous solution of Pd/Au (3:1)-**17** (1.05 µmol of Pd/0.35 µmol of Au-0.04 µmol of **17**) was stirred under 1 atmospheric pressure of O_2. The reaction progress was followed by ^{1}H NMR, and after stirring at 60°C for 7 days, the crude reaction mixture was diluted with deionized water and extracted with dichloromethane twice. The aqueous layer was filtered through a Vivaspin 20 (Sartorius Inc.) centrifugal filter device (with a 3,000 MWCO) using a centrifugation instrument (Eppendorf Centrifuge model 5430) at 4,000 rpm for 10 min, and washed with deionized water twice to remove low molecular weight inorganic materials. The resulting nanocluster was diluted with 5 mL of water and added 80 mg (0.70 mmol) of racemic diol-**20** and 34 mg (0.2 mmol) of K_2CO_3, and stirred at 60°C for 7 days. After aqueous work-up, extraction of dichloromethane, and silica gel column chromatography, 31 mg (39% yield) of (*S*)-**23** in 99% ee and 46 mg (58% recovery) of (*R*,*R*)-diol **20** were isolated.

The % ee of (*S*)-**23** was 99% determined by HPLC/chiral column (Chiralpak AD(-H) column) analysis of the benzoate derivative as described above, using *n*-hexane-*i*-PrOH = 90:10 as eluent and a flow rate of 0.5 mL/min; t_R = 21 min (*R* enantiomer, minor), t_R = 25 min (*S* enantiomer, major).

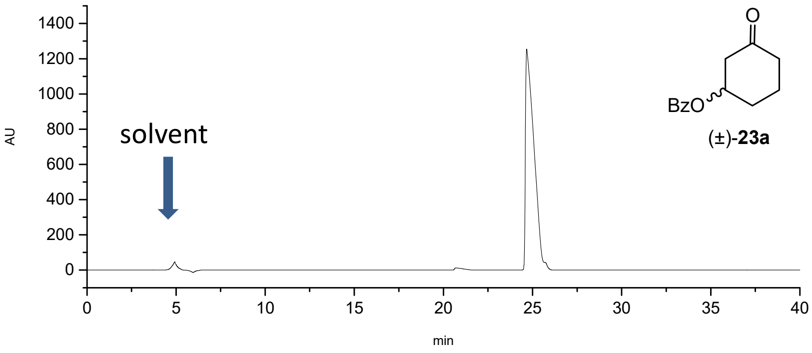


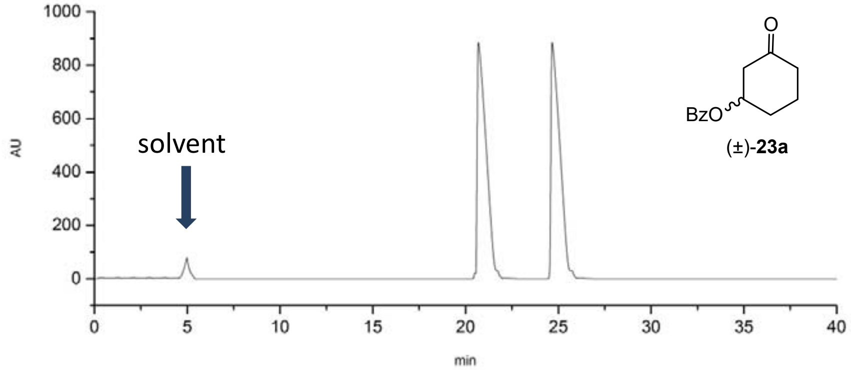


Oxidation of a mixture of (*R,R*)- and (*S,S*)-*trans*-1,3-cyclohexanediol (20) using 0.15 mol% of <u>second recovered</u> Pd/Au (3:1)-17 catalyst for 7 days at 60°C. **Formation of (*S*)-3-hydroxycyclohexanone (23)**. The aforementioned aqueous layer was filtered through a

Vivaspin 20 (Sartorius Inc.) centrifugal filter device (with a 3,000 MWCO) using a centrifugation instrument (Eppendorf Centrifuge model 5430) at 4,000 rpm for 10 min, and washed with deionized water twice to remove low molecular weight inorganic materials. The resulting nanocluster was diluted with 4 mL of water and added 80 mg (0.70 mmol) of racemic diol-**20** and 34 mg (0.2 mmol) of K_2CO_3, and stirred at 60°C for 7 days. After aqueous work-up, extraction of dichloromethane, and silica gel column chromatography, 14 mg (18% yield) of (*S*)-**23** in 99% ee and 61 mg (77% recovery) of (*R*,*R*)-diol **20** were isolated.

The % ee of (*S*)-**23** was 98% determined by HPLC/chiral column (Chiralpak AD(-H) column) analysis of the benzoate derivative as described above, using *n*-hexane-*i*-PrOH = 90:10 as eluent and a flow rate of 0.5 mL/min; t_R = 21 min (*R* enantiomer, minor), t_R = 25 min (*S* enantiomer, major).

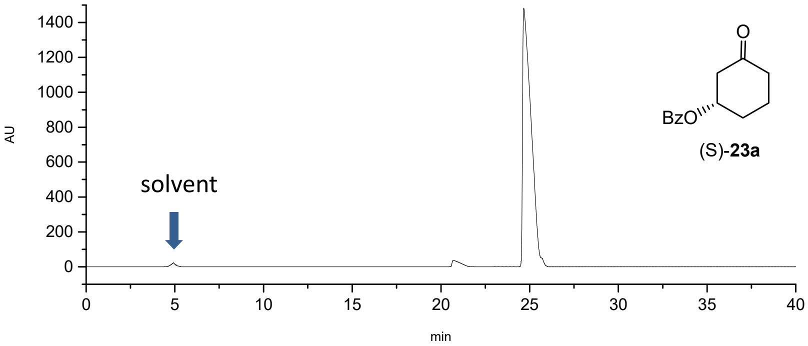


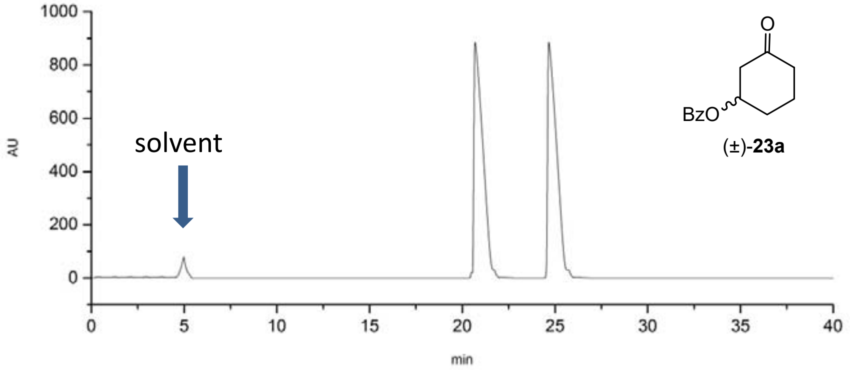


Oxidation of a mixture of racemic *trans*-1,3-cyclohexanediol (20) using 0.15 mol% of

Pd/Au (3:1)-17 catalyst for 7 days at <u>80ºC</u>. Formation of (*S*)-3-hydroxycyclohexanone (23). Following the above general procedure for the oxidation of *trans* diol, a solution of racemic **20** (80 mg; 0.70 mmol) and 34 mg (0.21 mmol) K_2CO_3 in 2.4 mL of Pd/Au (3:1)-**17** (1.05 µmol of Pd/0.35 µmol of Au-0.04 µmol of **17**) in H_2O was stirred under 1 atmospheric pressure of O_2 at 80ºC. The reaction progress was monitored by TLC and ^{1}H NMR. After stirring at 80ºC for 7 days, ^{1}H NMR spectrum of an aliquot of the reaction solution showed 50% of the starting material was converted to product. The reaction solution was worked up as mentioned above and 37.1 mg (47% yield) of (*S*)-**23** in 94% ee along with 40.2 mg of (*R*,*R*)-**20** was isolated after silica gel column chromatography.

The % ee of (*S*)-**23** was determined through its benzyoate derivative and then HPLC/chiral column to be 94%. Chiralpak AD(-H) column and an eluent of *n*-hexane/*i*-PrOH = 90:10 with a flow rate of 0.5 mL/min were used for the HPLC analysis; t_R = 21 min (*R* enantiomer, minor), t_R = 25 min (*S* enantiomer, major).



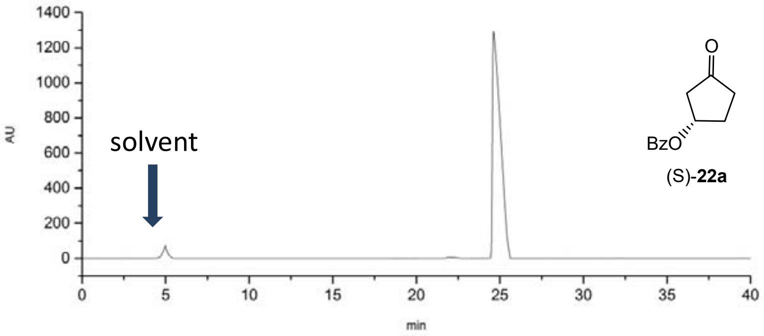


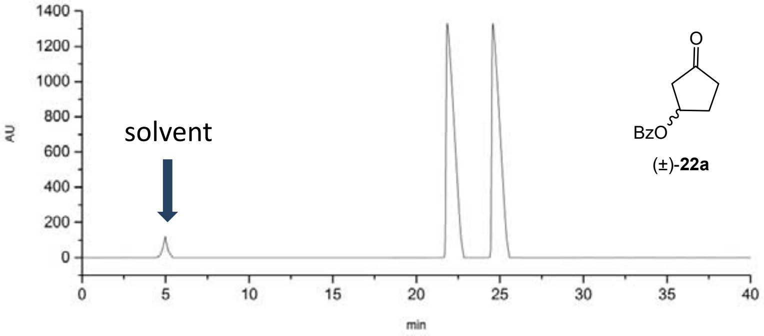
(*S*)-3-Hydroxycyclopentanone (22). From 15 mg (0.147 mmol) of (±)-cyclopentanediol (**19**), 0.48 mL of Pd/Au (3:1)-**17** (0.22 μmol of Pd/0.07 μmol of Au-0.008 μmol of **17**) in H_2O, 6.8 mg (96% yield based on reacted diols **19**; 99% ee) of (*S*)-**22** and 8.0 mg (53% recovery of (*R,R*)-**19** in 91% ee. Compound (*S*)-**22**: $[\alpha]_D^{22}$ = -33.8 (c 0.6, CH_2Cl_2); Lit.[14] -18.3 (c 0.50, CH_2Cl_2; for S-configuration, 83% ee). ^{1}H NMR δ 4.63 – 4.60 (m, 1 H, CHO), 2.52 – 2.36 (m, 2 H), 2.28 – 2.12 (m, 3 H), 2.10 – 2.00 (m, 1 H), 1.85 – 1.87 (bs, 1 H, OH); ^{13}C NMR δ 218.0, 69.9, 47.9, 35.8, 32.3. MS (ESI, MeOH): *m/z* = 123.0 ($[M + Na]^+$).

(*R,R*)-**19**: The NMR spectra were identical to those of the authentic 1,3-*trans*-cyclopentanediol. $[\alpha]_D^{22}$ = +17.3 (c 1.0, $CHCl_3$).

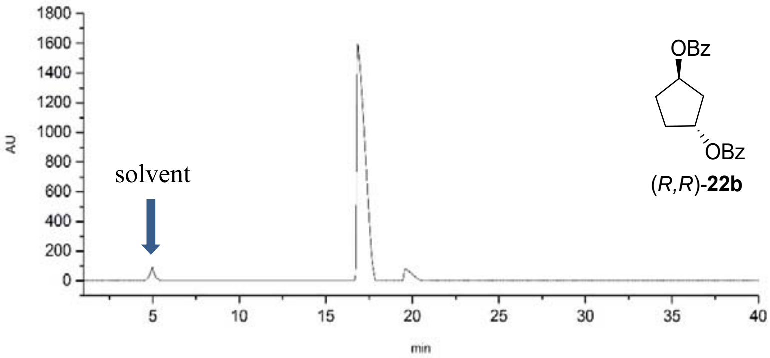
(*S*)-3-Oxocyclopentyl benzoate (22a). From 6.8 mg (68 μmol) of (*S*)-**22** and 19 mg (0.14 mmol) of benzoyl chloride and 0.1 mL of pyridine in 1 mL of dichloromethane, 13 mg (94% yield) of (*S*)-**22a** in 99% ee. ^{1}H NMR[15] δ 8.09 – 8.07 (m, 2 H), 7.59 – 7.46 (m, 1 H), 7.45 – 7.42 (m, 2 H), 5.49 – 5.44 (m, 1 H), 2.73 – 2.68 (m, 1 H), 2.55 – 2.51 (m, 1 H), 2.37 – 2.25 (m, 4 H); ^{13}C NMR δ 215.8, 165.7, 133.4, 129.8, 128.7, 128.6, 72.5, 44.4, 35.6, 29.2. MS (ESI, MeOH): *m/z* = 227.2 ($[M + Na]^+$), 177.0. The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, n-hexane/i-PrOH = 90:10, flow rate:

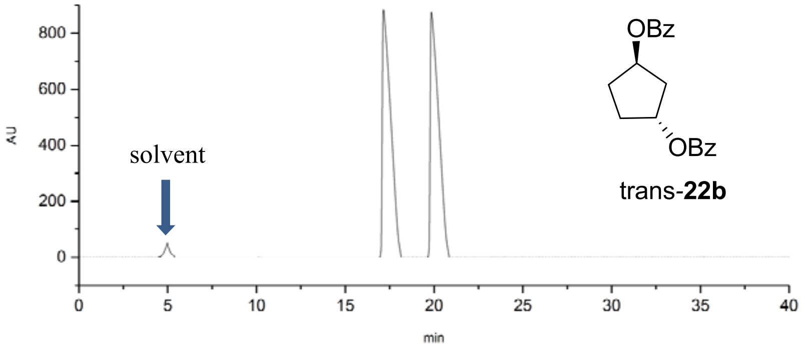
0.5 mL/min; t_R = 22 min (*R* enantiomer, minor), t_R = 24.5 min (*S* enantiomer, major).





(*R,R*)-1,3-Diphenylcarbonyloxycyclopentane (22b). From 15 mg (0.147 mmol) of (R,R)-19 and 82 mg (0.59 mmol) of benzoyl chloride in 0.2 mL of pyridine and 0.5 mL of dichloromethane, 26 mg (57% yield) of (*R,R*)-**22b** in 91% ee. ^{1}H NMR δ 8.06 (d, J = 8.5 Hz, 4 H), 7.56 (t, J = 8.5 Hz, 2 H), 7.45 (t, J = 8.5 Hz, 4 H), 5.49 – 5.44 (m, 2 H), 2.16 – 2.13 (m, 2 H), 1.94 – 1.86 (m, 4 H); ^{13}C NMR δ 166.6 (2 C), 133.1 (2 C), 130.8 (2 C), 129.8 (4 C), 128.6 (4 C), 71.5 (2 C), 39.7, 24.5 (2 C). MS (ESI, MeOH): *m/z* = 332.8 ([M + Na]$^+$), 188.8. The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane:*i*-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 16.8 min (*R,R* enantiomer, major), t_R = 19.6 min (*S,S* enantiomer, minor). The racemic *trans*-dibenzoate **22b** were similarly prepared for HPLC/chiral column study from the corresponding racemic *trans*-diols.

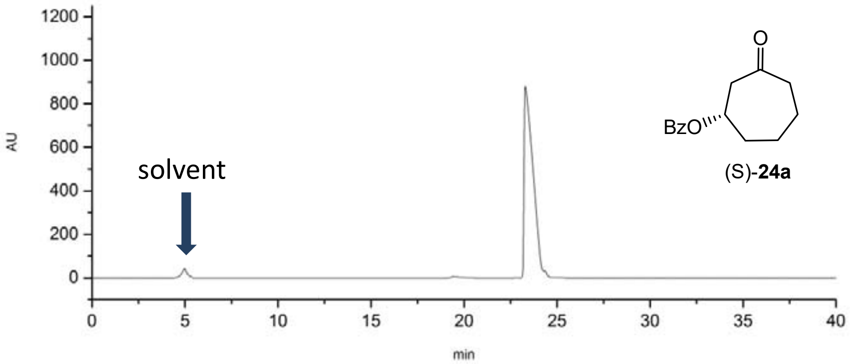


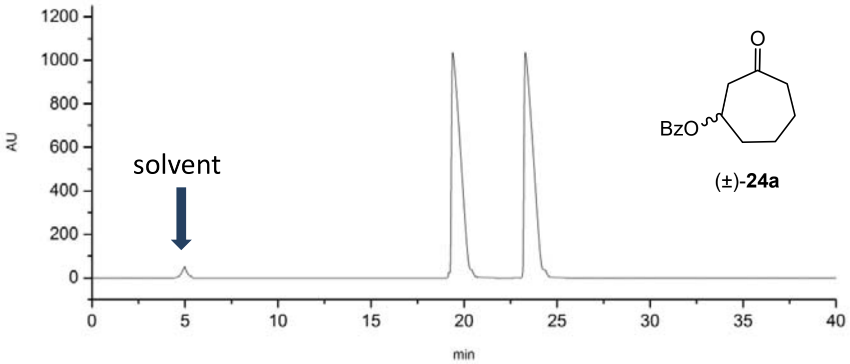


(*S*)-3-Hydroxycycloheptanone (24). From 30 mg (0.23 mmol) of (±)-cycloheptanediol (**21**), 0.8 mL of Pd/Au (3:1)-**17** (0.35 μmol of Pd/0.12 μmol of Au-0.013 μmol of **17**) in H_2O, 13.4 mg (92% yield based on reacted diols **21**; 99% ee) of (*S*)-**24** and 15.8 mg (53% recovery of (*R,R*)-**21**. Compound (*S*)-**24**: $[\alpha]_D^{22} = +16.4$ (c 0.8, CH_2Cl_2). ^1H NMR[16] δ 4.13 – 4.06 (m, 1 H, CHO), 2.84 – 2.74 (m, 2 H), 2.54 – 2.40 (m, 2 H), 1.94 – 1.70 (m, 6 H), 1.65 – 1.55 (m, 1 H); ^{13}C NMR δ 212.4, 67.7, 51.8, 44.5, 39.0, 24.5, 23.9. MS (ESI, MeOH): *m/z* = 151.1 ([M + Na]$^+$). The % ee was determined from the HPLC/chiral column of the benzoate derivative (*S*)-**24a**.

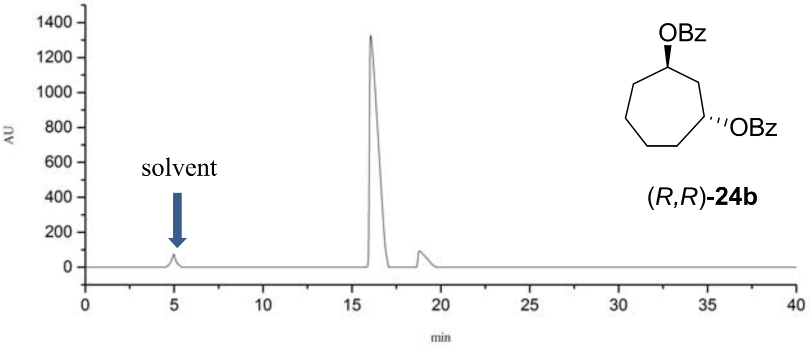
(*R,R*)-**21**: The NMR spectra were identical to those of authentic 1,3-*trans*-cycloheptanediol. $[\alpha]_D^{22} = +16.9$ (c 1.0, $CHCl_3$).

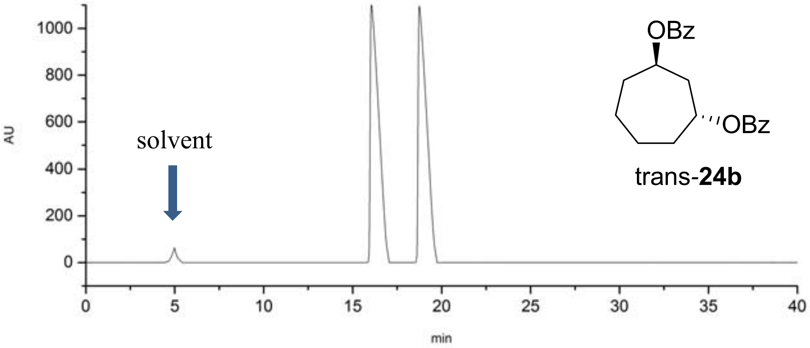
(*S*)-3-Oxocycloheptyl benzoate (24a). From 10 mg (0.078 mmol) of (*S*)-**24**, 22 mg (0.16 mmol) of benzoyl chloride and 0.1 mL of pyridine in 0.5 mL of dichloromethane, 18 mg (98% yield) of (*S*)-**24a** (99% ee) was obtained. ^{1}H NMR δ 8.00 (d J = 7.6 Hz, 2 H), 7.56 (t, J = 7.6 Hz, 1 H), 7.43 (t, J = 7.6 Hz, 2 H), 5.54 – 5.50 (m, 1 H), 2.86 (dd, J = 12, 4.4 Hz, 1 H), 2.81 (dd, J = 12, 8 Hz, 1 H), 2.47 – 2.40 (m, 2 H), 2.32 – 2.25 (m, 2 H), 2.15 – 2.05 (m, 3 H), 1.96 – 1.86 (m, 1 H); ^{13}C NMR δ 208.2, 165.7, 133.7, 129.8 (2 C), 129.0, 128.6 (2 C), 72.4, 46.8, 40.8, 29.1, 21.8, 21.0. MS (ESI, MeOH): *m/z* = 255.1 ([M + Na]$^+$). The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, n-hexane/i-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 19 min (*R* enantiomer, minor), t_R = 23 min (*S* enantiomer, major).





(*R*,*R*)-1,3-(Diphenylcarbonyloxy)cycloheptane (24b). From 15 mg (0.12 mmol) of (*R*,*R*)-**21** and 64 mg (0.46 mmol) of benzoyl chloride in 0.2 mL of pyridine and 0.5 mL of dichloromethane, 22 mg (56% yield) of (*R,R*)-**24b** in 85% ee. ^{1}H NMR δ 8.06 (d, J = 8 Hz, 4 H), 7.56 (t, J = 8 Hz, 2 H), 7.45 (t, J = 8 Hz, 4 H), 5.49 – 5.44 (m, 2 H), 2.13 (t, J = 6 Hz, 2 H), 2.02 – 1.88 (m, 4 H), 1.87 – 1.74 (m, 4 H); ^{13}C NMR δ 166.5 (2 C), 133.1 (2 C), 130.8 (2 C), 129.8 (4 C), 128.6 (4 C), 70.9 (2 C), 36.3, 29.1 (2 C), 24.1 (2 C). MS (ESI, MeOH): *m/z* = 361.4 ([M + Na]$^+$), 249.1, 217.3, 123.1, 102.2. The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane:*i*-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 16.1 min (*R,R* enantiomer, major), t_R = 18.8 min (*S,S* enantiomer, minor). The racemic *trans*-dibenzoate **24b** were similarly prepared for HPLC/chiral column study from the corresponding racemic *trans*-diols.

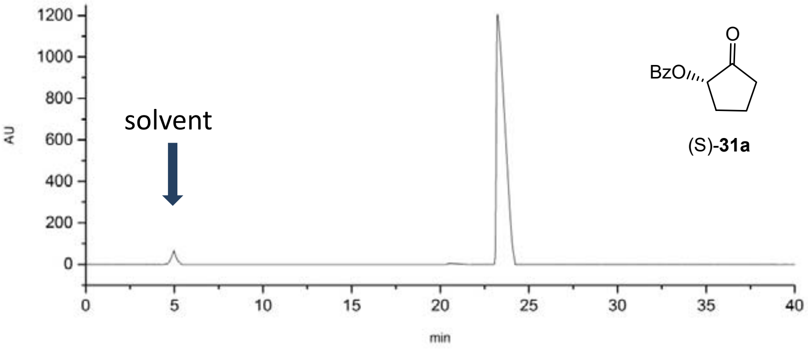


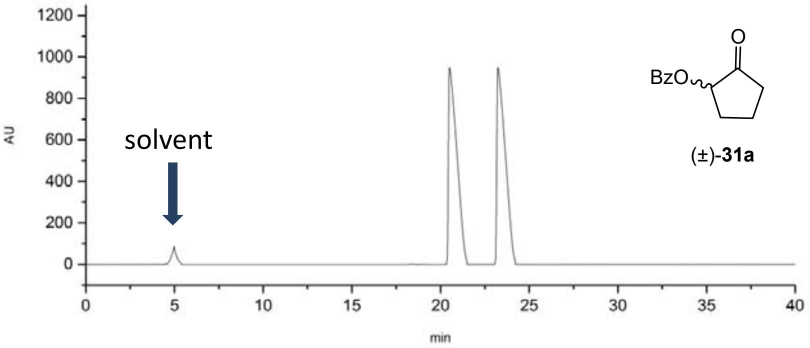


Oxidation of a mixture of (*R,R*)- and (*S,S*)-*trans*-1,2-cyclopentanediol (28). Formation of (*S*)-2-hydroxycyclopentanone (31) and recovered (*R,R*)-28. From 30 mg (0.29 mmol) of (±)-**28**, 1.0 mL of Pd/Au (3:1)-**17** (0.438 μmol of Pd/0.146 μmol of Au-0.017 μmol of **17**) in H_2O, 14 mg (94% yield; based on reacted (*S,S*)-**28**) of (*S*)-**31** (99% ee) and 15 mg (50% recovery) of (*R,R*)-**28**. The % ee of (*S*)-**31** was determined by HPLC/chiral of benzoate derivative (*S*)-**31a**. Compound (*S*)-**31**: $[\alpha]_D^{22}$ = +40.6 (c 1.0, $CHCl_3$); Lit.[17] -37.4 (c 1.0, $CHCl_3$) for (*R*)-configuration (>99% ee). ^1H NMR[17] δ 4.10 (dd, J = 12, 5 Hz, 1 H, CHO), 3.65 – 3.55 (bs, 1 H, OH), 2.50 – 2.34 (m, 2 H), 2.27 – 2.10 (m, 2 H), 1.86 – 1.60 (m, 2 H); ^{13}C NMR δ 211.9, 75.1, 40.5, 37.6, 26.3. MS (ESI, MeOH): *m/z* = 123.0 ($M+Na^+$).

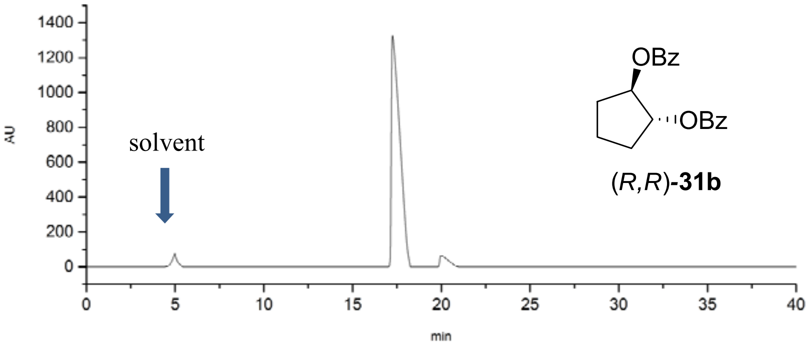
(*R,R*)-**28**: The NMR spectra were identical to those of the authentic 1,2-*trans*-cyclopentanediol. $[\alpha]_D^{22}$ = -19.9 (c 1.1, $CHCl_3$); Lit.[18] -21.3 (c 1.1, $CHCl_3$) for (*R,R*)-configuration (>99% ee).

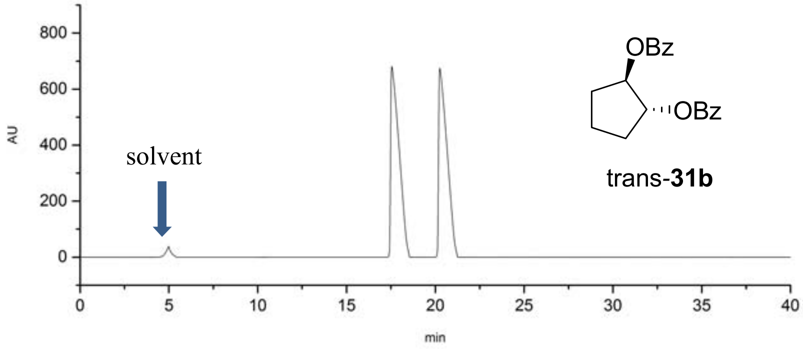
(*S*)-2-Oxocyclopentyl benzoate (31a). From 10 mg (0.1 mmol) of (*S*)-**31** and 28 mg (0.2 mmol) of benzoyl chloride in 0.1 mL of pyridine and 0.5 mL of dichloromethane, 16.8 mg (82% yield) of (*S*)-**31a** in 99% ee was obtained. ^1H NMR[19] δ 8.08 (d, J = 7.6 Hz, 2 H), 7.57 (t, J = 7.6 Hz, 1 H), 7.45 (t, J = 7.6 Hz, 2 H), 5.46 (dd, J = 9, 3 Hz, 1 H), 2.75 – 2.65 (m, 1 H), 2.55 – 2.45 (m, 1 H), 2.17 – 2.08 (m, 1), 1.95 – 1.85 (m, 3 H); ^{13}C NMR δ 204.6, 169.2, 133.4, 130.1 (2 C), 129.9, 128.6 (2 C), 77.2, 39.9, 31.2, 21.4. MS (ESI, MeOH): *m/z* = 227.2 ($M+Na^+$), 177.2, 123.0. The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, n-hexane/i-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 20.5 min (*R* enantiomer, minor), t_R = 23.3 min (*S* enantiomer, major).





(*R,R*)-1,2-(Diphenylcarbonyloxy)cyclopentane (31b). From 14 mg (0.14 mmol) of (*R,R*)-**28**, 58 mg (0.41 mmol) of benzoyl chloride in 0.1 mL of pyridine and 2 mL of dichloromethane, gave 29 mg (67% yield) of (*R,R*)-**31b**. ^{1}H NMR δ 8.04 – 8.00 (m, 4 H), 7.58 – 7.53 (m, 2 H), 7.46 – 7.38 (m, 4 H), 5.50 (t, J = 4 Hz, 2 H, CHO), 2.36 – 2.29 (m, 2 H), 2.00 – 1.80 (m, 4 H); ^{13}C NMR δ 166.2, 133.3, 130.3, 129.9 (4 C), 128.6 (4 C), 79.7, 30.8, 21.9. MS (ESI, MeOH): *m/z* = 333.0 (M+Na$^+$), 265.3, 189.1, 105.2. The % ee (88%) of (*R,R*)-**31b** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 17.3 min (*R*,*R* enantiomer, major), t_R = 20.0 min (*S*,*S* enantiomer, minor). The racemic *trans*-dibenzoate **31b** were similarly prepared for HPLC/chiral column study from the corresponding racemic *trans*-diols.

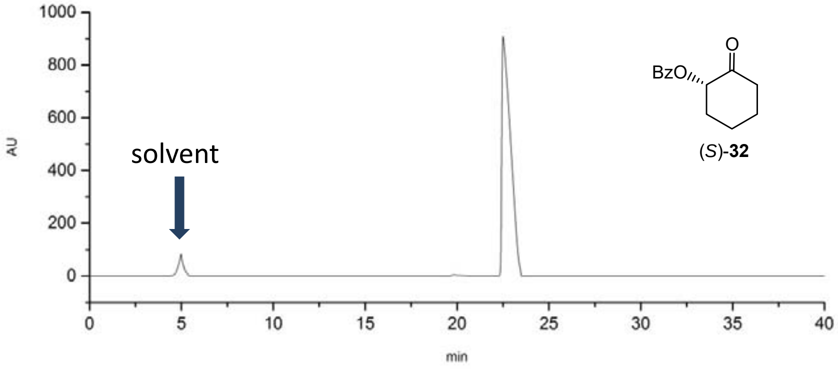


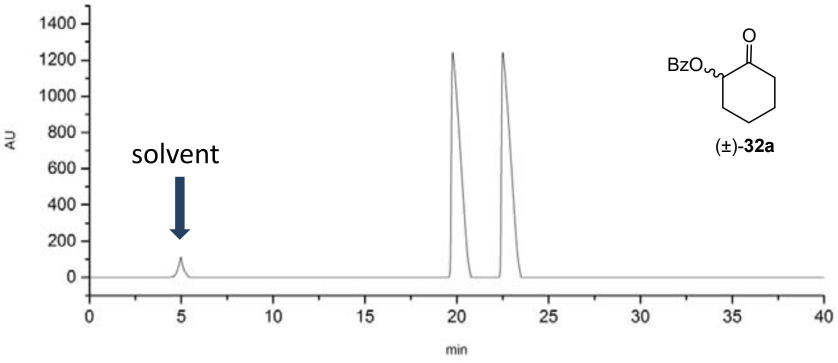


Oxidation of a mixture of (*R,R*)- and (*S,S*)-*trans*-1,2-cyclohexanediol (29). **Formation of (*S*)-2-hydroxycyclohexanone (32) and recovered (*R,R*)-29**. From 161 mg (1.39 mmol) of (±)-**29**, 4.8 mL of Pd/Au (3:1)-**17** (2.1 µmol of Pd/0.7 µmol of Au-0.08 µmol of **17**) in H_2O, 72 mg (89% yield; based on reacted (*S,S*)-**29**) of (*S*)-**32** (99% ee) and 80 mg (50% recovery) of (*R,R*)-**29**. Compound (*S*)-**32**: $[\alpha]_D^{22}$ = -20.7 (c 0.65, $CHCl_3$); Lit.[20] +20.6 (c 1.0, $CHCl_3$) for (*R*)-**32** (>99.0% ee). ^{1}H NMR δ 4.11 (dd, J = 12, 7 Hz, 1 H, CHO), 3.70 – 3.55 (bs, 1 H, OH), 2.60 – 2.30 (m, 3 H), 2.15 – 1.45 (m, 5 H); ^{13}C NMR δ 211.7, 75.6, 39.7, 36.9, 27.8, 23.6. MS (ESI, MeOH): *m/z* = 115.1 ($M+H^+$), 97.2, 74.1.

(*R,R*)-**29**: $[\alpha]_D^{22}$ = -34.7 (c 1.0, H_2O); Lit.[17] +37.1 (c 1.0, H_2O) for (*S,S*)-**29** (>99.0% ee).

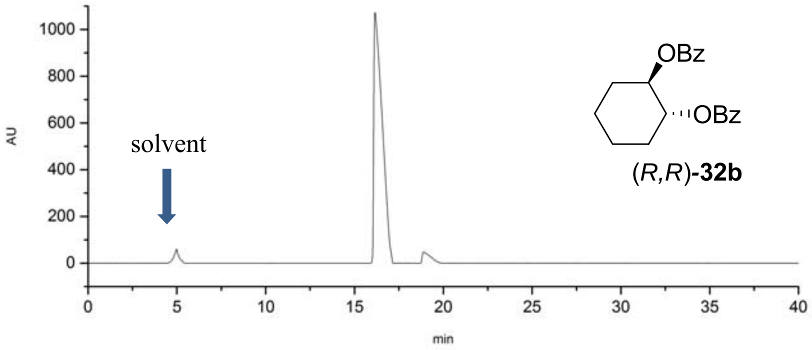
(S)-2-Oxocyclohexyl benzoate (32a). From 50 mg (0.44 mmol) of (*S*)-**32** and 0.122 mg (0.87 mmol) of benzoyl chloride in 0.1 mL of pyridine and 1.5 mL of dichloromethane, 66 mg (69% yield) of (*S*)-**32a** (99% ee). ^{1}H NMR[20] δ 8.08 (d, J = 8 Hz, 2 H), 7.56 (t, J = 8 Hz, 1 H), 7.45 (t, J = 8 Hz, 2 H), 5.41 (dd, J = 12, 7 Hz, 1 H), 2.60 – 2.40 (m, 3 H), 2.18 – 1.64 (m, 5 H); ^{13}C NMR δ 204.7, 169.2, 133.3, 130.1 (2 C), 129.9, 128.6 (2 C), 77.2, 40.7, 33.4, 27.4, 24.0. MS (ESI, MeOH): *m/z* = 241.4 ($M+Na^+$), 219.1 (M+1), 203.2. The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 20 min (*R* enantiomer, minor), t_R = 22.5 min (*S* enantiomer, major).

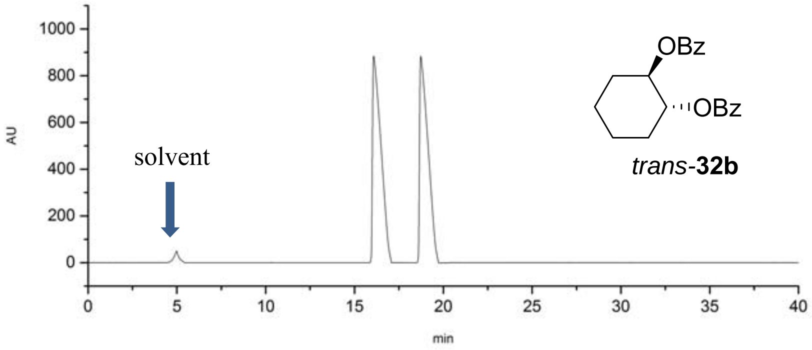




***(R,R)*-1,2-Di(phenylcarbonyloxy)cyclohexane (32b)**. From 20 mg (0.17 mmol) of (*R*,*R*)-**29** and 49 mg (0.34 mmol) of benzoyl chloride in 0.2 mL of pyridine and 0.6 mL of dichloromethane, 51 mg (85% yield) of (*R*,*R*)-**32b** was isolated after silica gel column chromatography. ^{1}H NMR δ 7.94 (d, J = 7.5 Hz, 4 H), 7.46 (t, J = 7.5 Hz, 2 H), 7.33 (t, J = 7.5 Hz, 4 H), 5.41 – 5.35 (m, 2 H), 2.27 – 2.23 (m, 1 H), 2.12 – 2.06 (m, 1 H), 1.90 – 1.77 (m, 3 H), 1.63 – 1.49 (m, 3 H); ^{13}C NMR δ 166.2 (2 C), 133.1 (2 C), 129.9 (2 C), 129.1 (4 C), 128.6 (4 C), 74.5 (2 C), 30.4 (2 C), 23.6 (2 C). MS (ESI, MeOH): *m/z* = 347.2 (M+Na$^+$), 243.2, 123.1, 102.1. The % ee (87%) of (*R*,*R*)-**32b** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 16.2 min (*R*,*R* enantiomer, major), t_R = 18.9 min (*S*,*S* enantiomer, minor).

The racemic *trans*-dibenzoate **32b** were similarly prepared for HPLC/chiral column study from the corresponding racemic *trans*-diols.

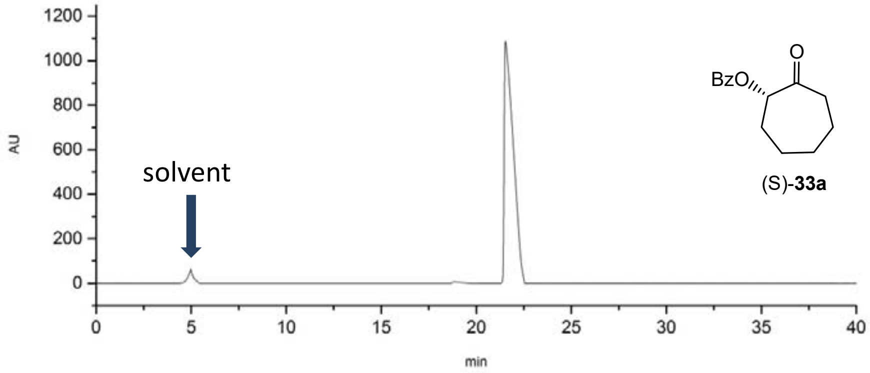


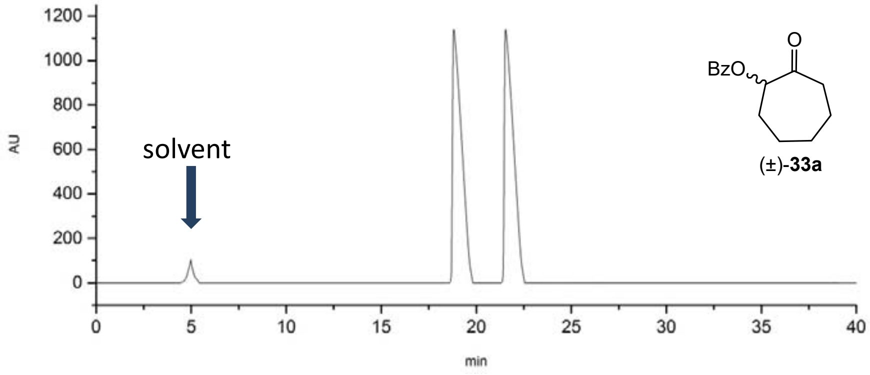


Oxidation of a mixture of (*R,R*)- and (*S,S*)-*trans*-1,2-cycloheptanediol (30). **Formation of (*S*)-2-hydroxycycloheptanone (33) and recovered (*R,R*)-30**. From 30 mg (0.23 mmol) of (±)-cycloheptanediol (**30**), 0.8 mL of Pd/Au (3:1)-**17** (0.35 µmol of Pd/0.12 µmol of Au-0.013 µmol of **17**) in H_2O, 13.5 mg (93% yield based on reacted diols (*S,S*)-**30**; 99% ee) of (*S*)-**33** and 16.3 mg (54% recovery) of (*R,R*)-**30**. The % ee was determined by HPLC/chiral column of benzoate derivative (*S*)-**33a**. Compound (*S*)-**33**: $[\alpha]_D^{22}$ = -143.9 (c 0.8, $CHCl_3$); Lit.[17] -86.4 (c 1.0, $CHCl_3$) for (*R*)-**33** (>99.0% ee). ^{1}H NMR δ 4.31 – 4.26 (m, 1 H), 3.83 – 3.75 (bs, 1 H, OH), 2.71 – 2.61 (m, 1 H), 2.46 (ddd, J = 17, 11, 4 Hz, 1 H), 2.08 – 1.55 (m, 7 H), 1.40 – 1.30 (m, 1 H); ^{13}C NMR δ 213.3, 77.20, 39.9, 33.5, 29.4, 26.5, 23.6. MS (ESI, MeOH): *m/z* = 129.2 ($M+H^+$), 107.1.

(*R*,*R*)-**30**: The NMR spectra were identical to those of the authentic 1,2-*trans*-cycloheptanediol. $[\alpha]_D^{22}$ = -4.9 (c 0.7, $CHCl_3$); Lit.[17] +10.7 (c 1.0, $CHCl_3$) for (*S*,*S*)-**30** (>99.0% ee).

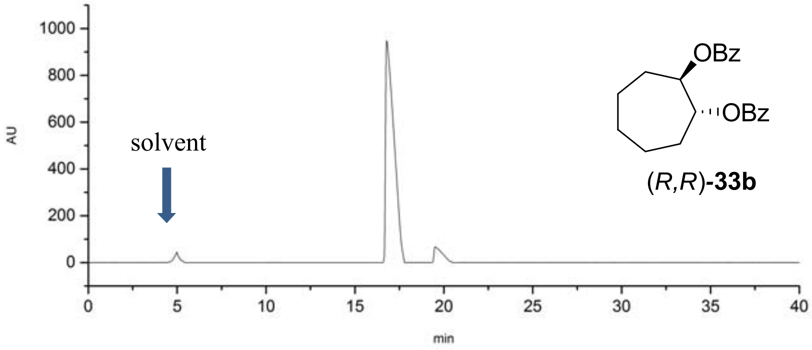
(S)-2-Oxocycloheptyl benzoate (33a). From 10 mg (78 μmol) of (*S*)-**33** and 22 mg (0.16 mmol) of benzoyl chloride in 0.1 mL of pyridine and 0.5 mL of dichloromethane, 17.6 mg (97% yield) of (*S*)-**33a** (99% ee) was obtained. ^1H NMR[19] δ 8.08 (d, J = 8 Hz, 2 H), 7.57 (d, J = 8 Hz, 1 H), 7.45 (t, J = 8 Hz, 2 H), 2.75 – 2.65 (m, 1 H), 2.55 – 2.45 (m, 1 H), 2.16 – 2.10 (m, 1 H), 2.0 – 1.65 (m, 6 H), 1.51 – 1.40 (m, 1 H); ^{13}C NMR δ 207.4, 165.1, 133.4, 130.1 (2 C), 129.9, 128.6 (2 C), 79.9, 40.8, 30.8, 27.3, 26.1, 22.0. MS (ESI, MeOH): *m/z* = 255.1 ($[M + Na]^+$). The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 19 min (*R* enantiomer, minor), t_R = 21.5 min (*S* enantiomer, major).

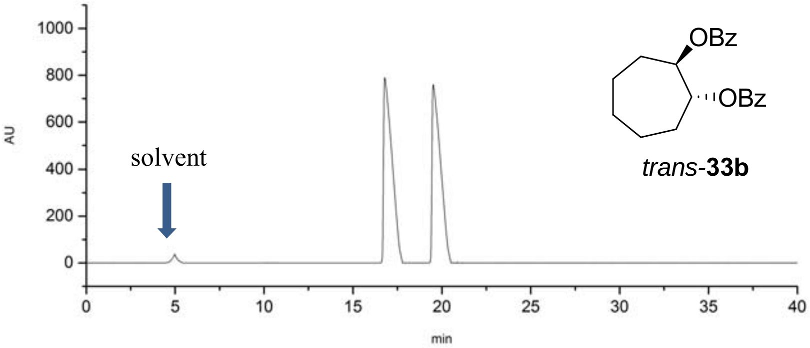




***(R,R)*-1,2-Di(phenylcarbonyloxy)cycloheptane (33b)**. From 10 mg (0.077 mmol) of (*R*,*R*)-**30** and 32 mg (0.23 mmol) of benzoyl chloride in 61 μL of pyridine and 2 mL of dichloromethane, 23 mg (90% yield) of (*R*,*R*)-**33b** was isolated after silica gel column chromatography. ^{1}H NMR δ 7.97 (d, J = 7 Hz, 4 H), 7.49 (t, J = 7 Hz, 2 H), 7.38 – 7.34 (m, 4 H), 5.42 – 5.40 (m, 2 H, CHO), 2.20 – 2.00 (m, 2 H), 1.88 – 1.75 (m, 4 H), 1.75 – 1.60 (m, 4 H); ^{13}C NMR δ 166.3, 133.1, 130.5, 129.8 (4 C), 128.5 (4 C), 77.6, 30.7, 28.5, 23.1. MS (ESI, MeOH): *m/z* = 361.3 ([M + Na]$^+$), 217.5, 194.3, 105.2. The % ee (88%) of (*R*,*R*)-**33b** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 16.8 min (*R*,*R* enantiomer, major), t_R = 19.5 min (*S*,*S* enantiomer, minor).

The racemic *trans*-dibenzoate **33b** were similarly prepared for HPLC/chiral column study from the corresponding racemic *trans*-diols.



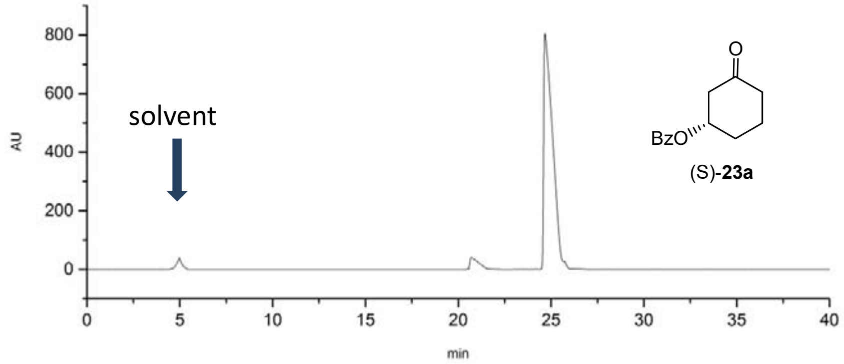


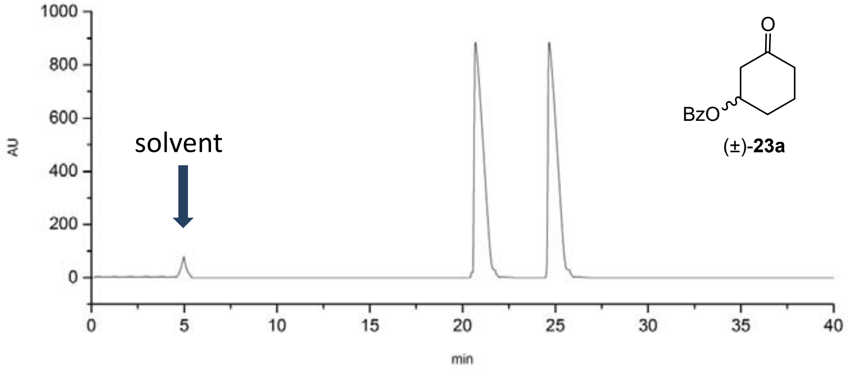
General procedure for the catalytic asymmetric oxidation of *cis*-diols.

Oxidation of meso-*cis*-1,3-cyclohexanediol (26). Formation of (*S*)-3-hydroxycyclohexanone (23). (The preparation of Pd/Au (3:1)-CSPVP **17** was similar to that described in the General Procedure). To a solution of 4.8 mL of Pd/Au (3:1)-**17** (2.1 µmol of Pd/0.7 µmol of Au-0.08 µmol of **17**) in H_2O, were added 16 mL of deionized H_2O, 0.16 g (1.39 mmol; 662 equivalents based on Pd mole atoms) of racemic meso-*cis*-1,3-cyclohexanediol (**26**) and 68 mg (0.42 mmol) K_2CO_3. The solution was transferred into a high pressure apparatus (Parr Pressure Reactor), stirred at 120°C under 30 psi O_2 for 3 days. The stirring was stopped and reactor was cooled to 25°C. The solution was extracted three times with dichloromethane (20 mL each) and the combined extracts were washed with water and brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a mixture of ethyl acetate and hexane (1:1) as an eluent to give 0.141 g (89% yield) of (*S*)-**23** in 91% ee (determined by HPLC/chiral column of the benzoate derivative (*S*)-**23a**). (*S*)-**23**: $[\alpha]_D^{22}$ = +40.1 (c 0.8, $CHCl_3$).; Lit.[12] for (*S*)-**23**: +37.3 (c 0.80, $CHCl_3$; 82% ee). ^1H and ^{13}C NMR spectra were identical to those of (*S*)-**23** obtained from the oxidation of *trans*-1,3-cyclohexanediol.

(*S*)-3-Oxocyclohexyl benzoate (23a) obtained from the benzoylation of (*S*)-23 of the above reaction. From 0.1 g (0.87 mmol) of (*S*)-**23** and 0.24 g (1.74 mmol) of benzoyl chloride in 0.2

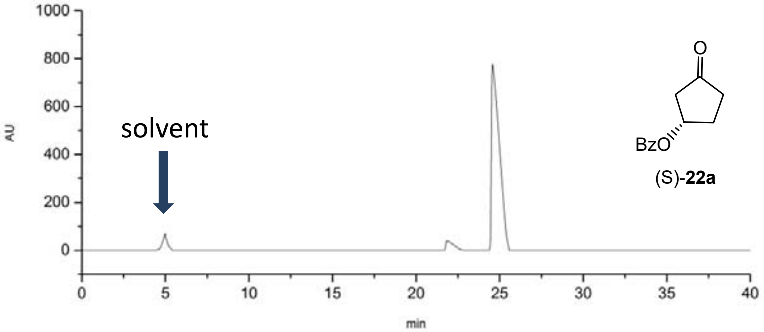
mL of pyridine and 3 mL of dichloromethane, 0.174 g (92% yield) of (*S*)-**23a** (91% ee) was obtained. The % ee of (*S*)-**23a** was determined by HPLC using chiral column, Chiralpak AD(-H) column, n-hexane/i-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 21 min (*R* enantiomer, minor), t_R = 25 min (*S* enantiomer, major).

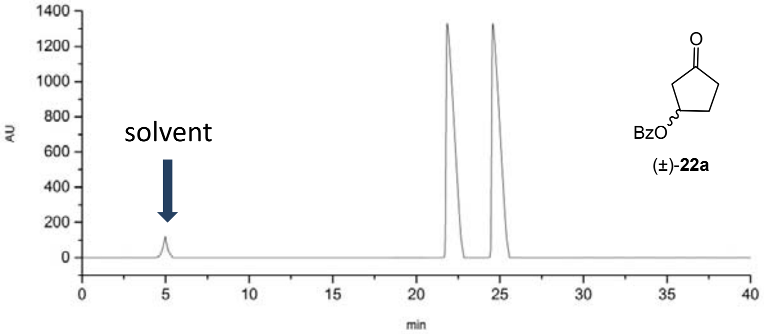




(S)-3-Hydroxycyclopentanone (22) obtained from the oxidation of meso-*cis*-1,3-cyclopentanediol (25). From 30 mg (0.29 mmol) of **25**, 1.0 mL of Pd/Au (3:1)-**17** (0.438 μmol of Pd/0.146 μmol of Au-0.017 μmol of **17**) in H_2O at 120°C and 30 psi of O_2 for 3 days, 28.3 mg (97% yield) of (*S*)-**22** in 90% ee (determined by HPLC/chiral column of the benzoate derivative (*S*)-**22a**). (*S*)-**22**: $[\alpha]_D^{22}$ = -29.9 (c 0.6, CH_2Cl_2), Lit.[14] -18.3 (c 0.50, CH_2Cl_2; for S-configuration, 83% ee). ^1H and ^{13}C NMR spectra were identical to those of (*S*)-**22** obtained from the oxidation of *trans*-1,3-cyclopentanediol.

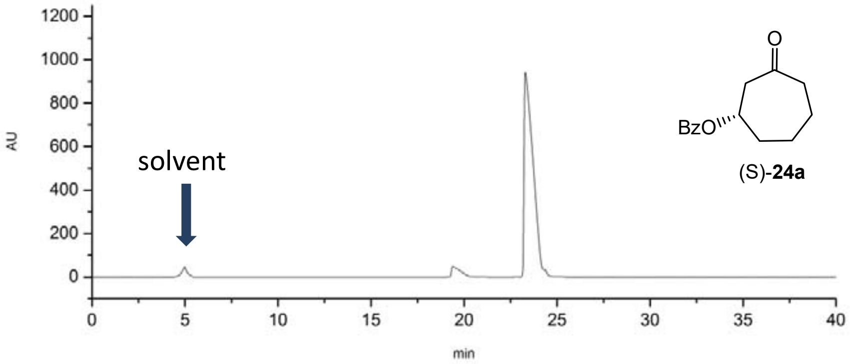
(*S*)-3-Oxocyclopentyl benzoate (22a) obtained from the benzoylation of (*S*)-22 of the above reaction. From 20 mg (0.20 mmol) of (*S*)-**22** and 56 mg (0.40 mmol) of benzoyl chloride in 0.1 mL of pyridine and 1 mL of dichloromethane, 29 mg (71% yield) of (*S*)-**22a** (90% ee) was obtained. The % ee (90%) of compound (*S*)-**22a** was determined by HPLC using chiral column, Chiralpak AD(-H) column, n-hexane/i-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 21.8 min (*R* enantiomer, minor), t_R = 24.5 min (*S* enantiomer, major).

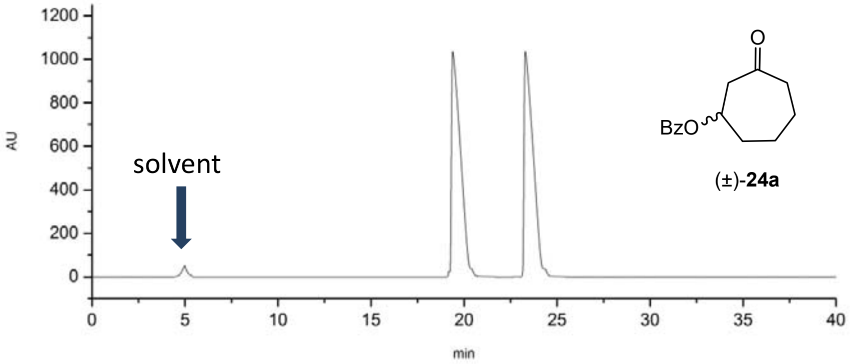




(S)-3-Hydroxycycloheptanone (24) obtained from the oxidation of meso-*cis*-1,3-cycloheptanediol (27). From 30 mg (0.23 mmol) of **27**, 0.79 mL of Pd/Au (3:1)-**17** (0.347 μmol of Pd/0.116 μmol of Au-0.013 μmol of **17**) in H_2O at 120°C and 30 psi of O_2 for 3 days, 28 mg (94.5% yield) of (*S*)-**24** in 92% ee (determined by HPLC/chiral column of the benzoate derivative (*S*)-**24a**). $[\alpha]_D^{22}$ = +15.2 (c 0.8, $CHCl_3$). ^{1}H and ^{13}C NMR spectra were identical to those of (*S*)-**24** obtained from the oxidation of *trans*-1,3-cycloheptanediol.

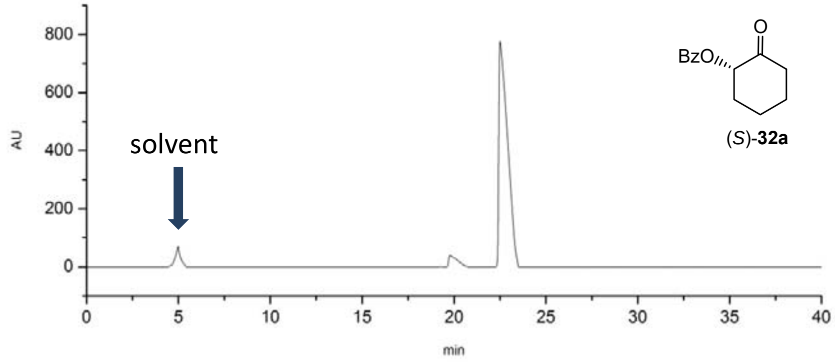
(*S*)-3-Oxocycloheptyl benzoate (24a) obtained from the benzoylation of (*S*)-24 of the above reaction. From 25 mg (0.20 mmol) of (*S*)-**24** and 55 g (0.39 mmol) of benzoyl chloride in 0.1 mL of pyridine and 1 mL of dichloromethane, 44 mg (97% yield) of (*S*)-**24a** (92% ee) was obtained. ^{1}H and ^{13}C NMR spectra were identical to those of (*S*)-**24a** as described above. The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, n-hexane/i-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 19 min (*R* enantiomer, minor), t_R = 23 min (*S* enantiomer, major).

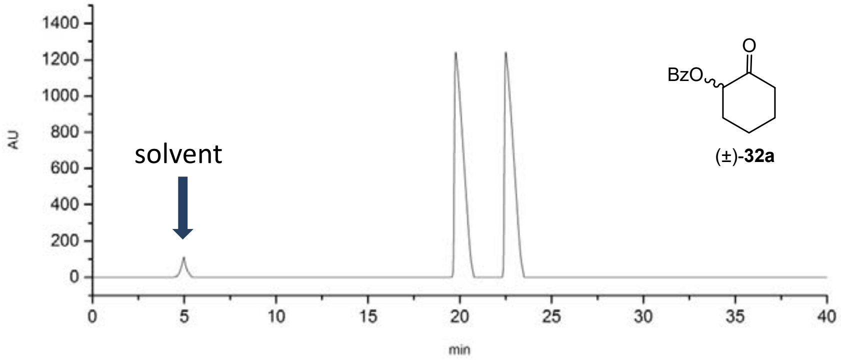




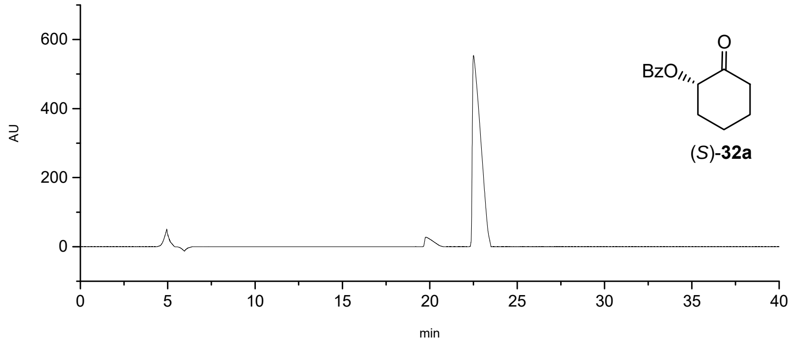
Oxidation of meso-*cis*-1,2-cyclohexanediol (35). Formation of (*S*)-2-hydroxycyclohexanone (32). From 0.161 g (1.39 mmol; 662 equivalents based on Pd mole atoms) of **35**, 4.8 mL of Pd/Au (3:1)-**17** (2.1 µmol of Pd/0.7 µmol of Au-0.08 µmol of **17**) in H_2O at 120°C and 30 psi of O_2 for 4 days, 0.142 g (96.5% yield) of (*S*)-**32** in 92% ee [determined by HPLC/chiral column of the benzoate derivative (*S*)-**32a**]. (*S*)-**32**: $[\alpha]_D^{22}$ = -18.8 (c 0.65, $CHCl_3$); Lit.[20] +20.6 (c 1.0, $CHCl_3$) for (*R*)-**32** (>99.0% ee). ^{1}H and ^{13}C NMR spectra were identical to those of (*S*)-**32** obtained from the oxidation of *trans*-1,2-cyclohexanediol.

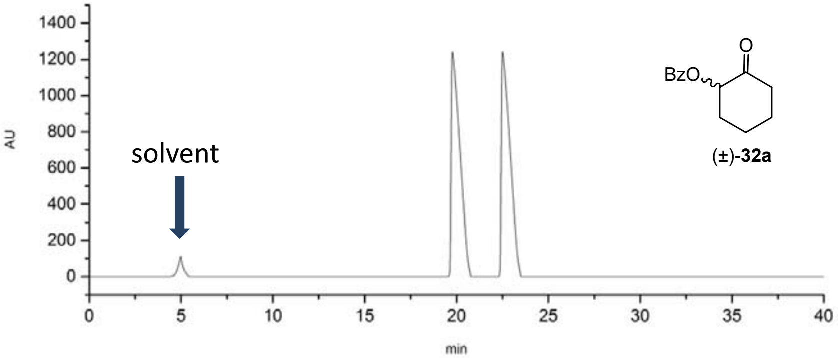
(*S*)-3-Oxocyclohexyl benzoate (32a) obtained from the benzoylation of (*S*)-32 of the above reaction. From 0.10 g (0.87 mmol) of (*S*)-**32** and 0.245 g (1.74 mmol) of benzoyl chloride in 0.2 mL of pyridine and 3 mL of dichloromethane, 0.169 g (89% yield) of (*S*)-**32a** (92% ee) was obtained. ^{1}H and ^{13}C NMR spectra were identical to those of (*S*)-**32a** as described above. The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, n-hexane/i-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 20 min (*R* enantiomer, minor), t_R = 22.5 min (*S* enantiomer, major).





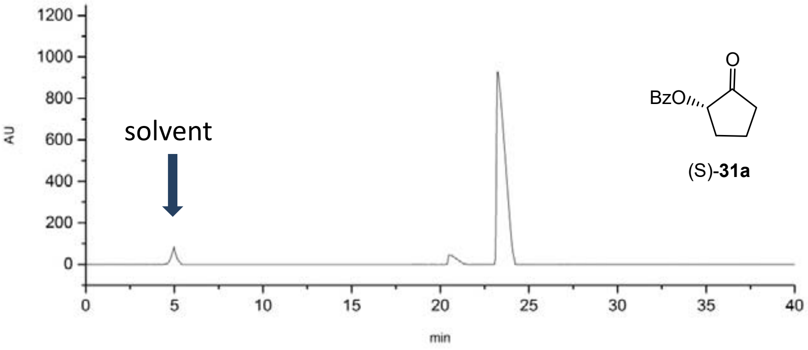
Oxidation of meso-*cis*-1,2-cyclohexanediol (35) using 0.15 mol% of Pd/Au (3:1) and <u>double amounts of 17</u>. To a solution of 104 µL (1.04 µmol) of a 10 mM aqueous solution of Na_2PdCl_4 and 34 µL (0.34 µmol) of a 10 mM aqueous solution of $HAuCl_4{\cdot}3H_2O$ in 2.4 mL of deionized H_2O was added 8.0 mg (0.07 µmol; 0.054 equiv based on total Pd and Au moles of atoms) of **17** and the solution was stirred at 0°C for 0.5 h. To it, was added 0.50 mg (0.012 mmol) of $NaBH_4$ and the resulting light black solution was stirred at 25°C for 0.5 h to give the bimetallic nanoclusters Pd/Au (3:1)-**17** in aqueous solution. To it, was added 80 mg (0.70 mmol) of meso diol **35** and 34 mg (0.2 mmol) of K_2CO_3. The solution was stirred under 30 psi of O_2 and at 120°C for 3 days. After aqueous work-up, extraction with dichloromethane, and silica gel column chromatography, 74 mg (94% yield) of (*S*)-**32** in 91% ee was isolated. The % ee was determined by HPLC/chiral column (Chiralpak AD(-H) column) analysis of the benzoate derivative, using *n*-hexane-*i*-PrOH = 90:10 as eluent and a flow rate of 0.5 mL/min; t_R = 21 min (*R* enantiomer, minor), t_R = 25 min (*S* enantiomer, major).

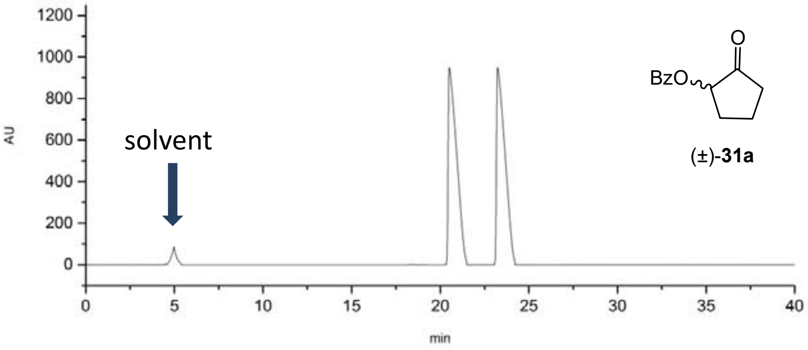




Oxidation of meso-*cis*-1,2-cyclopentanediol (34). Formation of (S)-2-hydroxycyclopentanone (31). From 60 mg (0.588 mmol) of **34**, 2 mL of Pd/Au (3:1)-**17** (0.89 μmol of Pd/0.296 μmol of Au-0.034 μmol of **17**) in H_2O at 120°C and 30 psi of O_2 for 3 days, 55.4 mg (94.2% yield) of (*S*)-**31** in 91% ee (determined by HPLC/chiral column of the benzoate derivative (*S*)-**31a**). $[\alpha]_D^{22}$ = +38.4 (c 1.0, $CHCl_3$); Lit.[17] -37.4 (c 1.0, $CHCl_3$) for (*R*)-configuration (>99% ee). ^{1}H and ^{13}C NMR spectra were identical to those of (*S*)-**31** obtained from the oxidation of *trans*-1,2-cyclopentanediol.

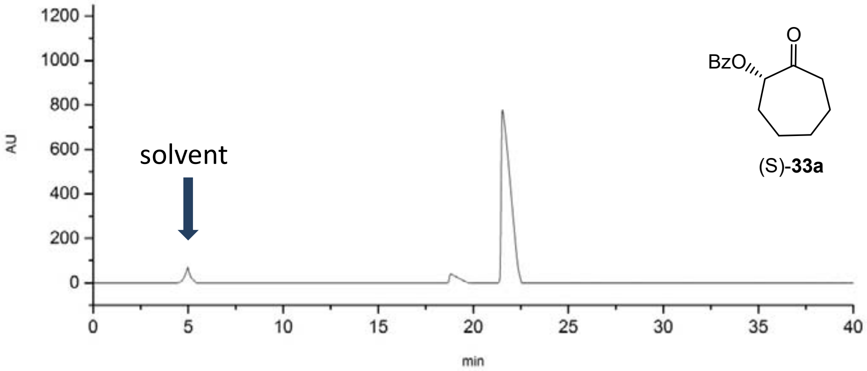
(*S*)-2-Oxocyclopentyl benzoate (31a) obtained from the benzoylation of (*S*)-31 of the above reaction. From 40 mg (0.40 mmol) of (*S*)-**31** and 0.112 g (0.80 mmol) of benzoyl chloride in 0.3 mL of pyridine and 1.5 mL of dichloromethane, 80 mg (98% yield) of (*S*)-**31a** (91% ee) was obtained. ^{1}H and ^{13}C NMR spectra were identical to those of (*S*)-**31a** as described above. The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, n-hexane/i-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 20.5 min (*R* enantiomer, minor), t_R = 23.3 min (*S* enantiomer, major).

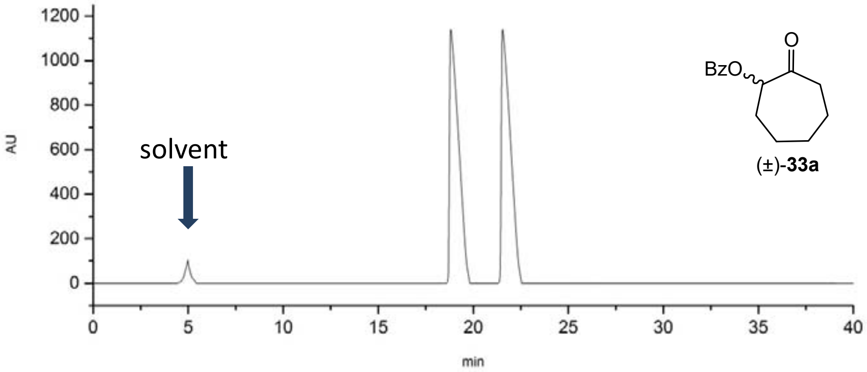




Oxidation of meso-*cis*-1,2-cycloheptanediol (36). Formation of (*S*)-2-hydroxycycloheptanone (33). From 30 mg (0.23 mmol) of **36**, 0.79 mL of Pd/Au (3:1)-**17** (0.347 μmol of Pd/0.116 μmol of Au-0.013 μmol of **17**) in H_2O at 120°C and 30 psi of O_2 for 3 days, 27.6 mg (94% yield) of (*S*)-**33** in 91% ee (determined by HPLC/chiral column of the benzoate derivative (*S*)-**33a**). (*S*)-**33**: $[\alpha]_D^{22}$ = -130.6 (c 1.0, $CHCl_3$). Lit.[17] -86.4 (c 1.0, $CHCl_3$) for (*R*)-**33** (>99.0% ee). ^1H and ^{13}C NMR spectra were identical to those of (*S*)-**33** obtained from the oxidation of *trans*-1,2-cycloheptanediol.

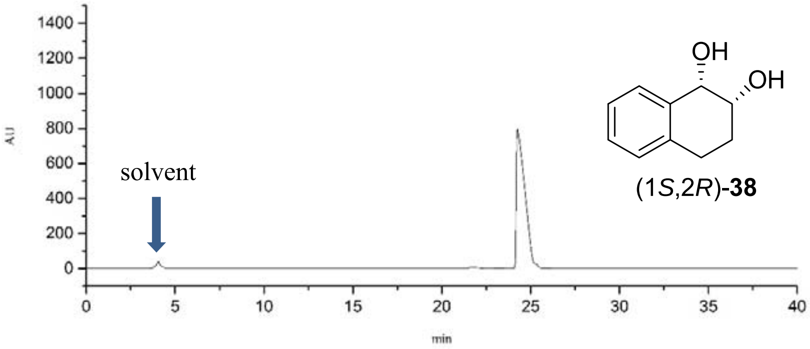
(*S*)-2-Oxocycloheptyl benzoate (33a) obtained from the benzoylation of (*S*)-33 of the above reaction. From 20 mg (0.156 mmol) of (*S*)-**33** and 44 mg (0.31 mmol) of benzoyl chloride in 0.2 mL of pyridine and 1 mL of dichloromethane, 35 mg (97% yield) of (*S*)-**33a** (91% ee) was obtained. ^1H and ^{13}C NMR spectra were identical to those of (*S*)-**33a** as described above. The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, n-hexane/i-PrOH = 90:10, flow rate: 0.5 mL/min; t_R = 19 min (*R* enantiomer, minor), t_R = 21.5 min (*S* enantiomer, major).

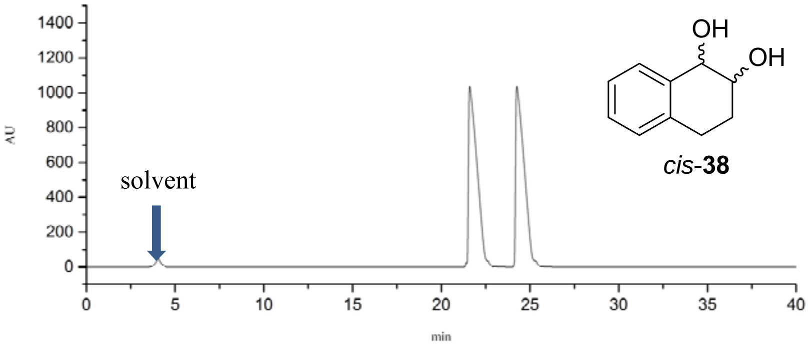




General procedure for the catalytic asymmetric oxidation of alkenes. The procedure for the preparation of Pd/Au (3:1)-**17** was the same as that described above for the oxidation of diols. For the catalytic asymmetric oxidation of alkenes, 0.5 mol% of the Pd/Au (3:1)-**17** (based on the alkenes) was used.

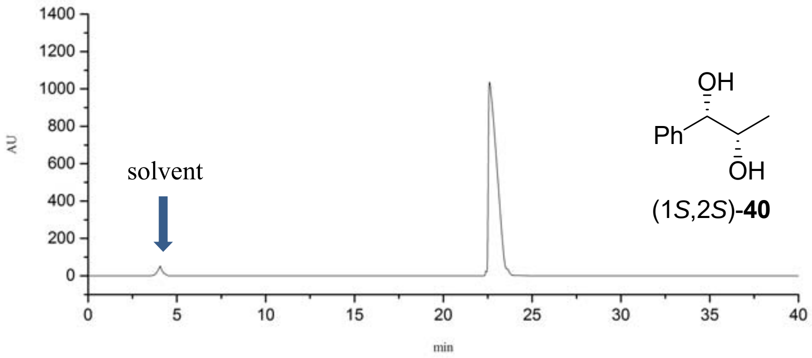
(1*S*,2*R*)-1,2,3,4-Tetrahydronaphthalene-1,2-diol (38). To an aqueous solution of 6.6 mL of Pd/Au (3:1)-**17** (2.9 μmol of Pd/0.96 μmol of Au-0.10 μmol of **17**) in a Parr pressure reactor, were added 14 mL of deionized H_2O and 0.10 g (0.77 mmol) of 1,2-dihydronaphthalene (**37**). The apparatus was charged at 30 psi of O_2 and stirred at 25°C for 3 days. The solution was then maintained under normal atmosphere, extracted with ethyl acetate three times (20 mL each), and the combined extracts were washed with water, and brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane and ethyl acetate as eluents to give 89 mg (86% yield) of (1*S*,2*R*)-**38**[20] in 99% ee. The optical purity was determined using HPLC-chiral column. $[\alpha]_D^{22}$ = +35.0 (c 0.74, $CHCl_3$). Lit.[20] +35 (c 0.74, $CHCl_3$; >98% ee). ^{1}H NMR[20] δ 7.44 – 7.41 (m, 1 H), 7.26 – 7.20 (m, 2 H), 7.13 – 7.11 (m, 1 H), 4.68 (d, J = 3.6 Hz, 1 H), 4.02 – 3.98 (m, 1 H), 3.00 – 2.92 (m, 1 H), 2.82 – 2.78 (m, 1 H), 2.53 – 2.45 (bs, 2 H, OH), 2.07 – 2.00 (m, 1 H), 2.00 – 1.87 (m, 1 H); ^{13}C NMR δ 136.6, 136.4, 130.1, 128.8, 128.4, 126.7, 70.2, 69.8, 27.1, 26.5. MS (ESI, MeOH): *m/z* = 165.1 ($[M + H]^+$), 116.2. The % ee of this compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 85:15, flow rate: 0.5 mL/min; t_R = 21.6 min (1*S*,2*R* enantiomer, minor), t_R = 24.2 min (1*R*,2*S* enantiomer, major).

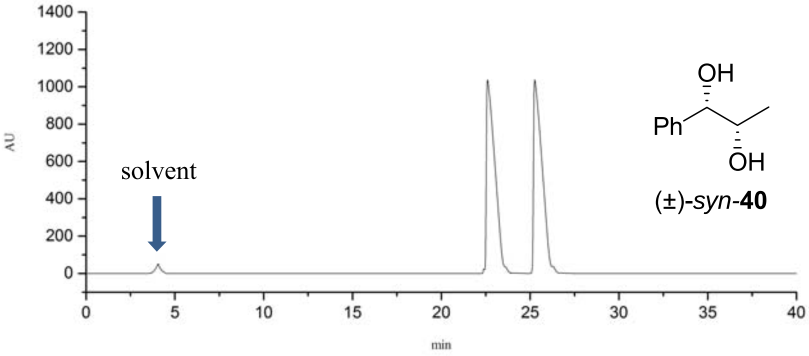




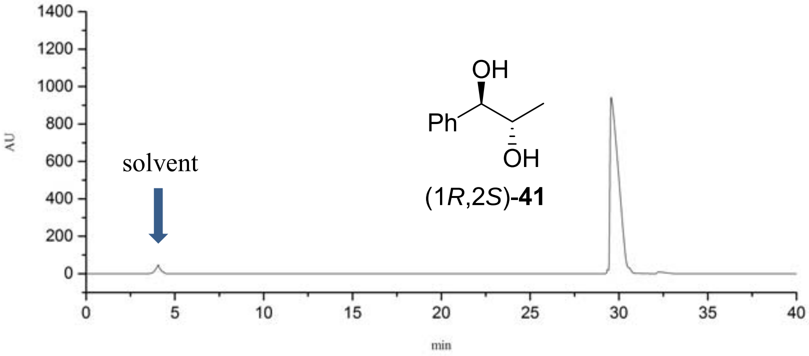
(1*S*,2*S*)-1-Phenylpropane-1,2-diol (40) and (1*R*,2*S*)-1-phenylpropane-1,2-diol (41). From

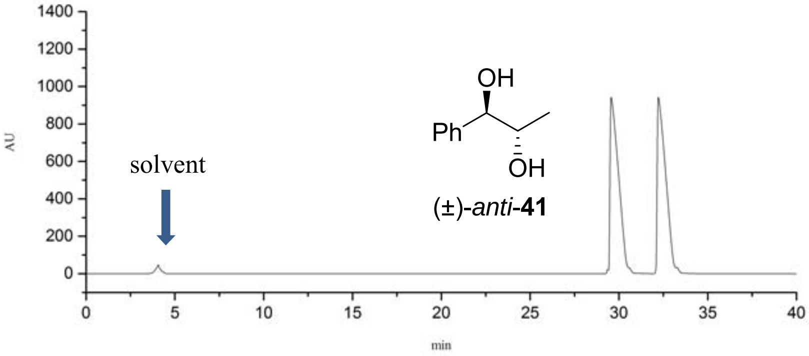
Pd/Au (3:1)-**17** (7.9 μmol of Pd/2.65 μmol of Au-0.29 μmol of **17**) and 0.25 g (2.1 mmol) of *trans*-β-methylstyrene (**39**) in 30 mL of deionized water, after stirring at 25°C under 30 psi of O_2 in a Parr pressure reactor for 3 days, 0.281 g (87% yield) of (1*S*,2*S*)-**40** (99% ee) and 19 mg (6% yield) of (1*R*,2*S*)-**41** (97% ee) along with 13 mg of **39** (5% recovery) were obtained after column chromatography. The optical purity was determined using HPLC/chiral column as described above. (1*S*,2*S*)-**40**: $[\alpha]_D^{22}$ = +51.7 (c 1.9, $CHCl_3$). Lit.[21] +54.3 (c 1.9, $CHCl_3$). ^{1}H NMR δ 7.45 – 7.24 (m, 5 H), 4.37 (d, J = 8 Hz, 1 H), 3.86 (pent, J = 6.5 Hz, 1 H), 2.30 – 2.15 (bs, 1 H, OH), 1.75 – 1.60 (bs, 1 H, OH), 1.07 (d, J = 6.5 Hz, 3 H, Me); ^{13}C NMR δ 142.3, 129.9 (2 C), 128.6, 126.7 (2 C), 79.9, 72.4, 18.1. MS (ESI, MeOH): *m/z* = 175.1 ($[M + Na]^+$), 139.1. (1*R*,2*S*)-**41**: $[\alpha]_D^{22}$ = -37.3 (c 2.52, $CHCl_3$). Lit.[21] -29.9 (c 2.52, $CHCl_3$). ^{1}H NMR δ 7.36 – 7.27 (m, 5 H), 4.68 (d, J = 4.4 Hz, 1 H), 4.03 – 4.00 (m, 1 H), 2.15 – 1.80 (bs, 1 H, OH), 1.75 – 1.50 (bs, 1 H, OH), 1.05 (d, J = 6 Hz, 3 H, Me); ^{13}C NMR δ 140.4, 128.2 (2 C), 127.9, 126.7 (2 C), 77.5, 71.4, 17.5. MS (ESI, MeOH): *m/z* = 174.9 ($[M + Na]^+$). The % ee (99%) of (1*S*,2*S*)-**40** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 85:15, flow rate: 0.5 mL/min; t_R = 22.6 min (1*S*,2*S* enantiomer, major), t_R = 25.8 min (1*R*,2*R* enantiomer, minor).



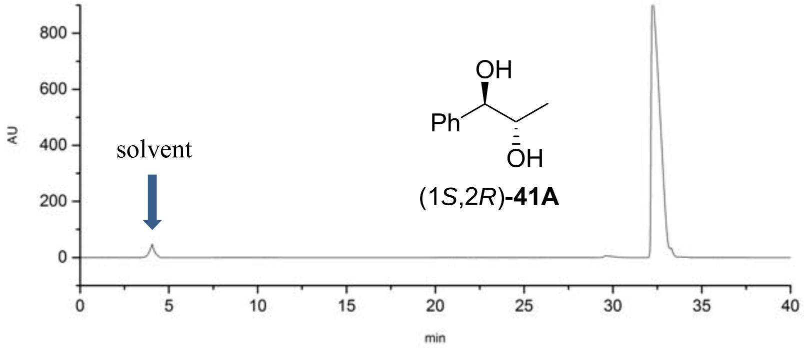


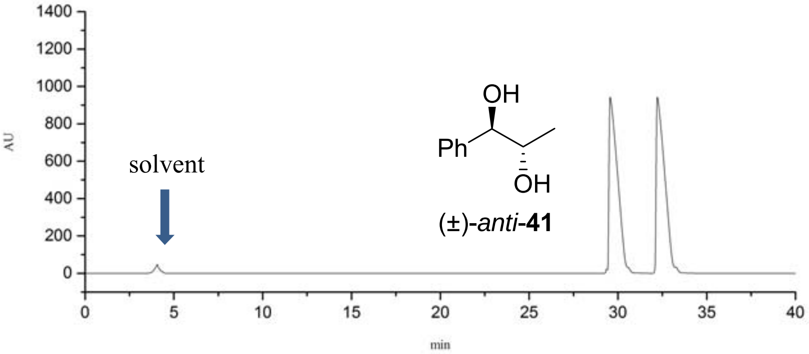
The % ee (97%) of (1*R*,2*S*)-**41** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 85:15, flow rate: 0.5 mL/min; t_R = 29.6 min (1*R*,2*S* enantiomer, major), t_R = 32.2 min (1*S*,2*R* enantiomer, minor).



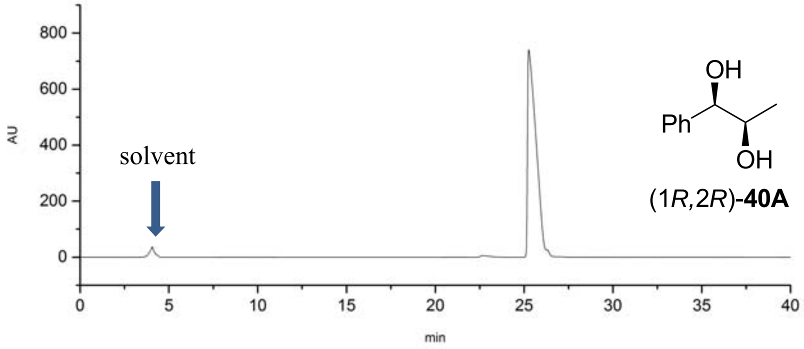


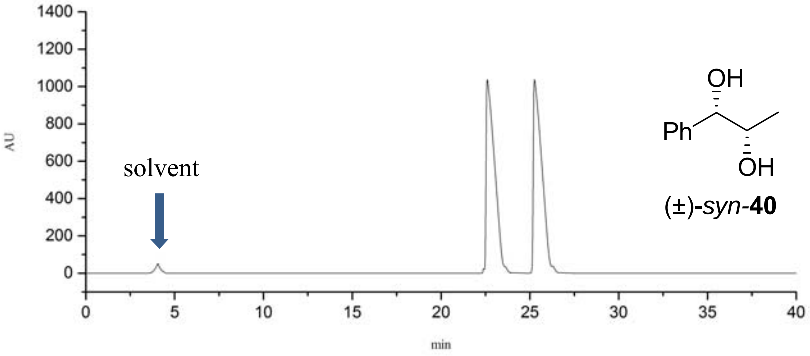
(1*S*,2*R*)-1-Phenylpropane-1,2-diol (41A) and (1*R*,2*R*)-1-phenylpropane-1,2-diol (40A). From Pd/Au (3:1)-**17** (7.94 µmol of Pd/2.65 µmol of Au-0.29 µmol of **17**) and 0.25 g (2.1 mmol) of *cis*-β-methylstyrene (**39A**) in 30 mL of deionized water, after stirring at 25°C under 30 psi of O_2 in a Parr pressure reactor for 3 days, 0.291 g (90% yield) of (1*S*,2*R*)-**41A** (98% ee) and 26 mg (8% yield) of (1*R*,2*R*)-**40A** (98% ee) were obtained after column chromatography. (1*S*,2*R*)-**41A**: $[\alpha]_D^{22}$ = +37.1 (c 2.52, $CHCl_3$). Lit.[21] +36.1 (c 2.52, $CHCl_3$). ^1H and ^{13}C NMR spectra were identical to those of compound (1*R*,2*S*)-**41**. The % ee (98%) of (1*S*,2*R*)-**41A** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 85:15, flow rate: 0.5 mL/min; t_R = 29.6 min (1*R*,2*R* enantiomer, minor), t_R = 32.2 min (1*S*,2*R* enantiomer, major).





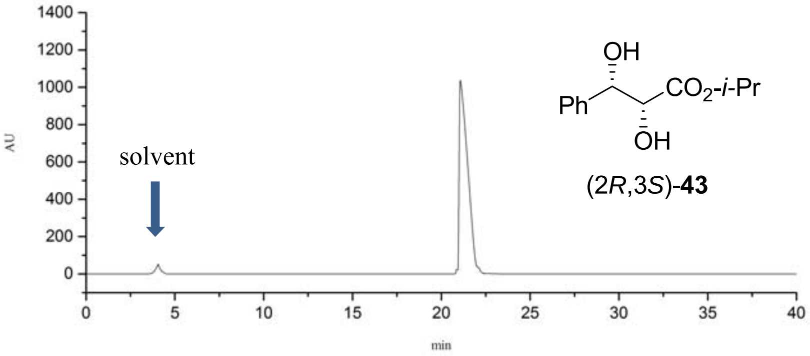
(1*R*,2*R*)-**40A**: $[\alpha]_D^{22}$ = -51.8 (c 1.9, $CHCl_3$). Lit.[21] -51.3 (c 3.5, $CHCl_3$). ^1H and ^{13}C NMR spectra were identical to those of (1*S*,2*S*)-**40**. The % ee (98%) of (1*R*,2*R*)-**40A** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 85:15, flow rate: 0.5 mL/min; t_R = 22.6 min (1*S*,2*S* enantiomer, minor), t_R = 25.8 min (1*R*,2*R* enantiomer, major).

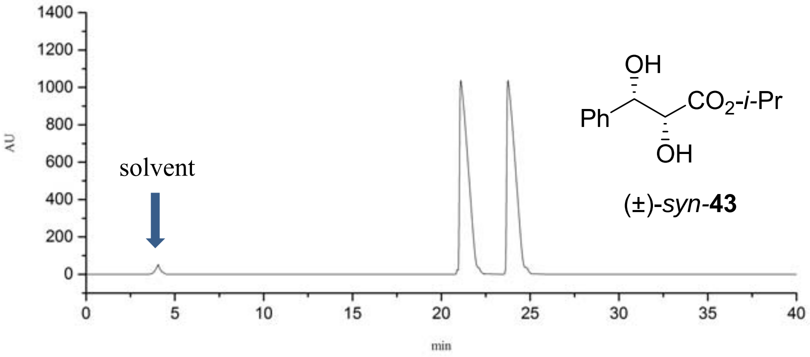




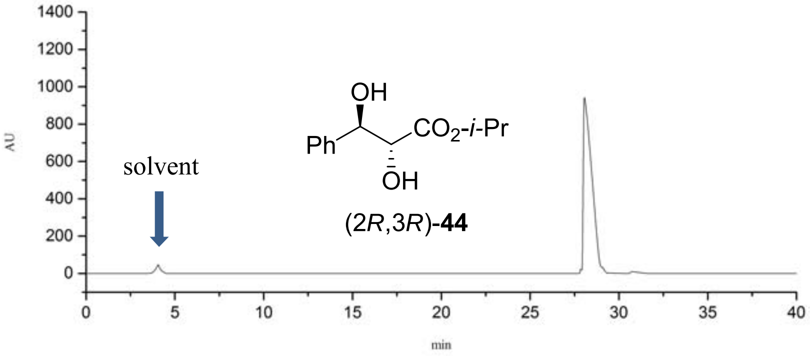
(2*R*,3*S*)-Isopropyl 2,3-dihydroxy-3-phenylpropanoate (43) and (2*R*,3*R*)-isopropyl 2,3-dihydroxy-3-phenylpropanoate (44). From Pd/Au (3:1)-**17** (1.97 μmol of Pd/0.66 μmol of Au-0.073 μmol of **17**) and 0.10 g (0.52 mmol) of *trans*-isoproyl 3-phenylpropenoate (**42**) in 20 mL of deionized water, after stirring at 50°C under 30 psi of O_2 in a Parr pressure reactor for 3 days, 96 mg (82% yield) of (2*R*,3*S*)-**43** (99% ee) and 3.7 mg (3% yield) of (2*R*,3*R*)-**44** (97% ee) were obtained after column chromatography. The optical purity was determined using HPLC/chiral column as described above. (2*R*,3*S*)**-43**: $[\alpha]_D^{22}$ = +9.7 (c 0.15, $CHCl_3$). Lit.[22] +10.6 (c 1.02, $CHCl_3$; >99%). ^1H NMR[18] δ 7.40 – 7.36 (m, 3 H), 7.34 – 7.32 (m, 2 H), 5.16 (hept, J = 6 Hz, 1 H), 5.01 (d, J = 6 Hz, 1H), 4.36 (d, J = 6 Hz, 1 H), 2.70 – 2.48 (bs, 2 H, OH), 1.31 (d, J = 6 Hz, 3 H); ^{13}C NMR δ 166.8, 144.6, 130.3, 129.1 (2 C), 128.2 (2 C), 86.1, 74.2, 67.9, 22.2. MS (ESI, MeOH): *m/z* = 225.0 ($[M + H]^+$), 120.0. The % ee (99%) of (2*R*,3*S*)-**43** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH =

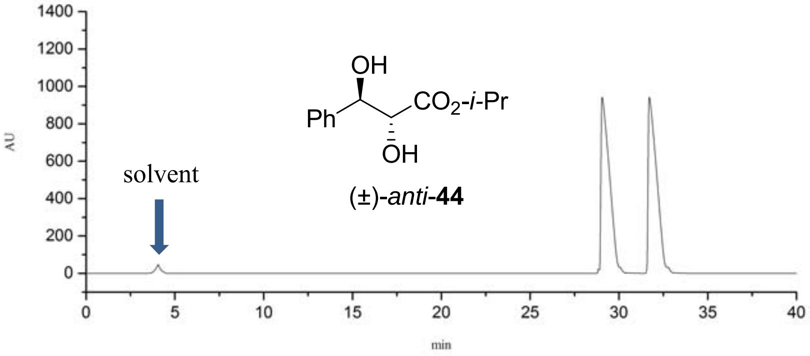
85:15, flow rate: 0.5 mL/min; t_R = 21.1 min (2*R*,3*S* enantiomer, major), t_R = 25.8 min (2*S*,3*R* enantiomer, minor).





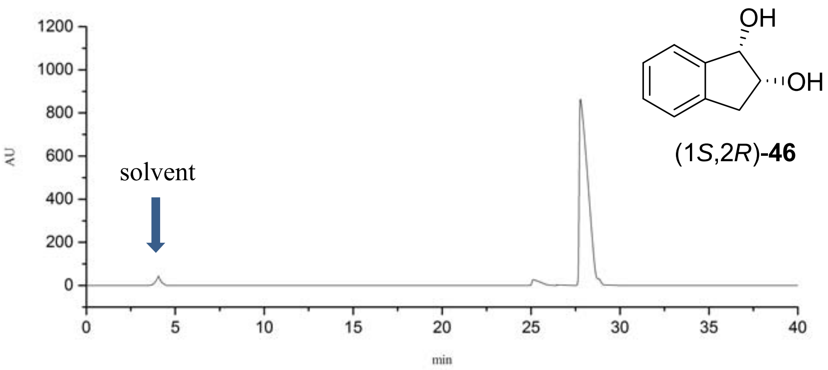
(2*R*,3*R*)-**44**: $[\alpha]_D^{22}$ = +7.3 (c 0.15, $CHCl_3$). ^{1}H NMR δ 7.40 – 7.35 (m, 3 H), 7.34 – 7.31 (m, 2 H), 5.14 (hept, J = 6 Hz, 1 H), 5.06 (d, J = 6.8 Hz, 1H), 4.38 (d, J = 5.2 Hz, 1 H), 2.25 – 2.00 (bs, 2 H, OH), 1.31 (d, J = 6 Hz, 3 H); ^{13}C NMR δ 169.4, 145.4, 131.3, 130.0 (2 C), 129.2 (2 C), 87.4, 75.1, 69.1, 23.1. MS (ESI, MeOH): *m/z* = 225.0 ($[M + H]^+$, 100%), 141.4. The % ee (97%) of (2*R*,3*R*)-**44** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 85:15, flow rate: 0.5 mL/min; t_R = 28.1 min (2*R*,3*R* enantiomer, major), t_R = 32.0 min (2*S*,3*S* enantiomer, minor).

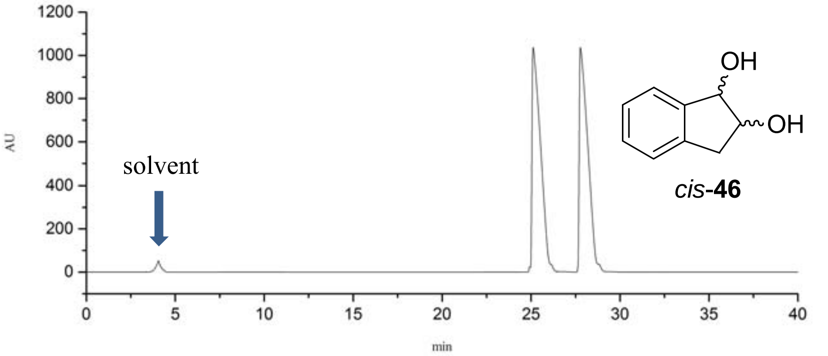




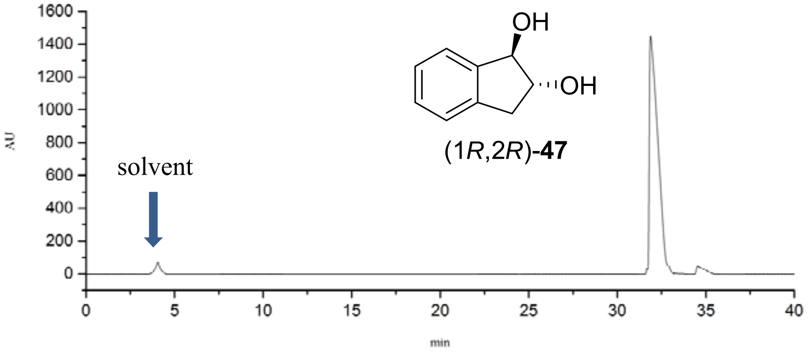
(1*S*,2*R*)-2,3-Dihydro-1H-indene-1,2-diol (46) and (1*R*,2*R*)-2,3-dihydro-1H-indene-1,2-diol (47). (Without additive) From Pd/Au (3:1)-**17** (19.3 μmol of Pd/6.7 μmol of Au-0.74 μmol of **17**) and 0.30 g (2.59 mmol) of indene (**45**) in 20 mL of deionized water, after stirring at 50°C under 30 psi of O_2 in a Parr pressure reactor for 2 days, 0.261 g (67% yield) of (1*S*,2*R*)-**46** (93% ee) and 44 mg (11% yield) of (1*R*,2*R*)-**47** (94% ee) were obtained after column chromatography. The optical purity was determined using HPLC/chiral column. Compound (1*S*,2*R*)-**46**: $[\alpha]_D^{22}$ = -46.9 (c 1.14, $CHCl_3$). Lit.[20] -48.0 (c 1.14, $CHCl_3$). ^1H NMR[16] δ 7.45 – 7.42 (m, 1 H), 7.31 – 7.20 (m, 3 H), 5.03 – 5.02 (m, 1 H, CH-O), 4.54 – 4.52 (m, 1 H, CH-O), 3.14 (dd, J = 16, 6 Hz, 1 H), 2.96 (dd, J = 16, 4 Hz, 1 H), 2.50 – 2.25 (bs, 2 H, OH); ^{13}C NMR δ 142.2, 140.2, 129.0, 127.4, 125.6, 125.3, 76.2, 73.7, 38.9. MS (ESI, MeOH): *m/z* = 173.1 ($[M + Na]^+$), 122.2. Compound (1*R*,2*R*)-**47**: $[\alpha]_D^{22}$ = -28.8 (c 0.675, EtOH). Lit.[23] +30.5 (c 0.675, EtOH). ^1H NMR[23] δ 7.40 – 7.36 (m, 1 H), 7.28 – 7.18 (m, 3 H), 5.02 – 5.01 (m, 1 H), 4.40 – 4.38 (m, 1

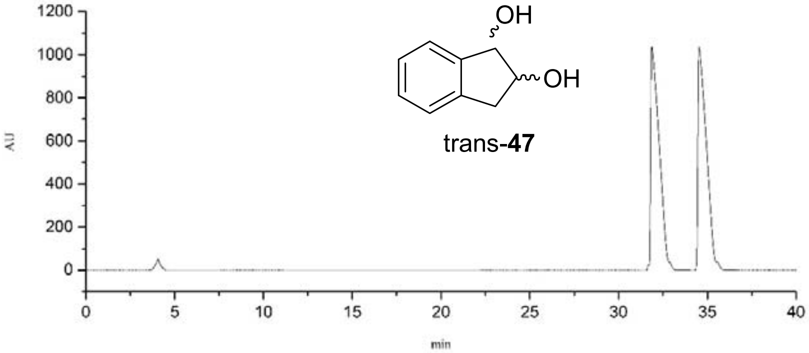
H), 3.28 (dd, J = 16, 7.6 Hz, 1 H), 2.83 (dd, J = 16, 8 Hz, 1 H), 2.10 – 2.09 (m, 1 H, OH), 2.05 - 2.02 (m, 1 H, OH); ^{13}C NMR δ 141.8, 141.3, 130.1, 128.9, 128.3, 126.6, 73.0, 72.4, 37.5 MS (ESI, MeOH): *m/z* = 151.1 ([M + H]$^+$), 122.2. The % ee (93%) of (1*S*,2*R*)-**46** compound was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 85:15, flow rate: 0.5 mL/min; t_R = 25.0 min (1*R*,2*S* enantiomer, minor), t_R = 27.8 min (1*S*,2*R* enantiomer, major).



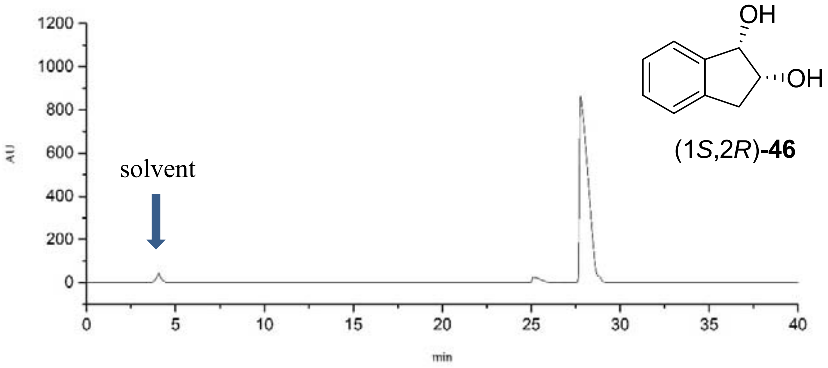


The % ee (94%) of compound (1*R*,2*R*)-**47** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 85:15, flow rate: 0.5 mL/min; t_R = 31.5 min (1*R*,2*R* enantiomer, major), t_R = 35 min (1*S*,2*S* enantiomer, minor).

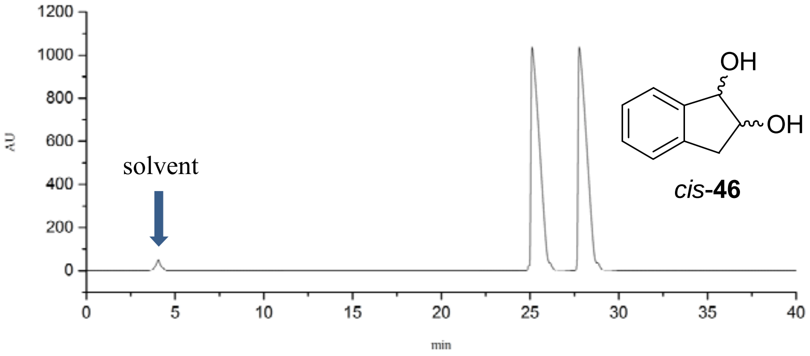




(1*S*,2*R*)-2,3-Dihydro-1H-indene-1,2-diol (46) and (1*R*,2*R*)-2,3-dihydro-1H-indene-1,2-diol (47). (With K_2CO_3 additive) To an aqueous solution of 15 mL of Pd/Au (3:1)-**17** (6.5 μmol of Pd/2.2 μmol of Au-0.24 μmol of **17**) in a Parr pressure reactor, were added 5 mL of deionized H_2O, 77 mg (0.56 mmol) of K_2CO_3, and 0.20 g (1.75 mmol) of indene (**45**). The apparatus was charged at 30 psi of O_2 and stirred at 70°C for 5 hours. The solution was then maintained under normal atmosphere, extracted with ethyl acetate three times (20 mL each), and the combined extracts were washed with water, and brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane and ethyl acetate as eluents to give 0.117 g (59% yield based on recovered **45**) of (1*R*,2*R*)-**47**[23] in 91% ee and 10 mg (5% yield based on recovered **45**) of (1*S*,2*R*)-**46** in 89% ee, along with 47 mg (23.5% recovery) of **45**. (1*R*,2*R*)-**47**: $[\alpha]_D^{22}$ = -27.7 (c 1.14, $CHCl_3$). Lit.[23] +30.5 (c 0.675, EtOH). (1*S*,2*R*)-**46**: $[\alpha]_D^{22}$ = -44.9 (c 1.14, $CHCl_3$). Lit.[22] -48.0 (c 1.14, $CHCl_3$). ^1H NMR and ^{13}C NMR spectra of **46** and **47** were identical to those described above. No hydroxyindanones were detected. The % ee (89%) of (1*S*,2*R*)-**46** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 85:15, flow rate: 0.5 mL/min; t_R = 25.0 min (1*R*,2*S* enantiomer, minor), t_R = 27.8 min (1*S*,2*R* enantiomer, major).

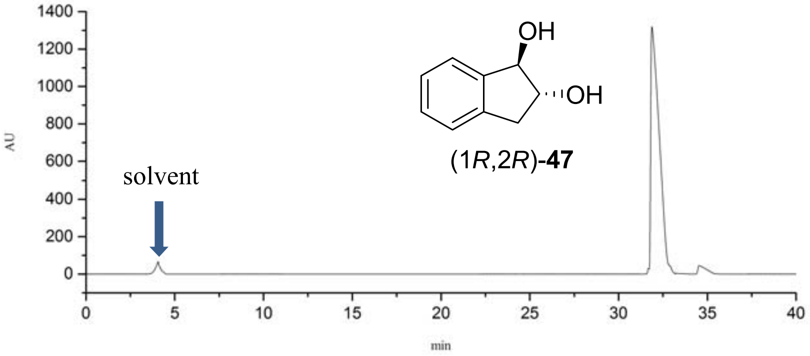


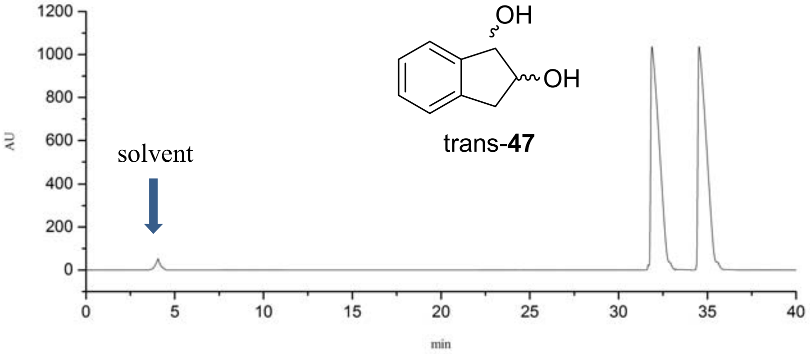
(1*S*,2*R*)-**46**



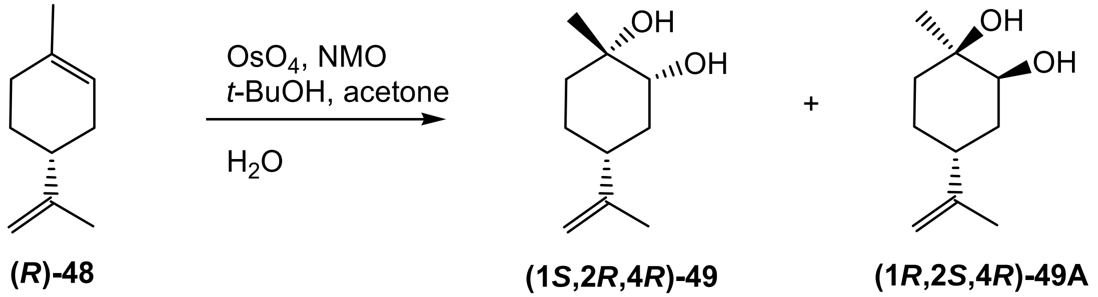
cis-**46**

The % ee (91%) of (1*R*,2*R*)-**47** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 85:15, flow rate: 0.5 mL/min; t_R = 31.5 min (1*R*,2*R* enantiomer, major), t_R = 34.6 min (1*S*,2*S* enantiomer, minor).





(1*S*,2*R*,4*R*)-1-Methyl-4-(prop-1-en-2-yl)cyclohexane-1,2-diol (49). From Pd/Au (3:1)-**17** (2.86 μmol of Pd/0.99 μmol of Au-0.11 μmol of **17**) and 52 mg (0.39 mmol) of (*R*)-(+)-limonene (**48**) in 20 mL of deionized water, after stirring at 25°C under 30 psi of O_2 in a Parr pressure reactor for 3 days, 61 mg (92% yield) of (1*S*,2*R*,4*R*)-**49** was obtained as a single stereoisomer after column chromatography. No other stereoisomers were detected. $[\alpha]_D^{22}$ = +22.6 (c 0.5, $CHCl_3$). ^{1}H NMR δ 4.74 (s, 2 H), 3.92 (s, 1 H), 2.32 – 2.23 (m, 1 H), 2.18 – 2.09 (m, 1 H), 2.03 – 1.94 (m, 1 H), 1.88 – 1.64 (m, 4 H), 1.73 (s, 3 H), 1.63 (s, 3 H), 1.64 – 1.58 (bs, 2 H, OH); ^{13}C NMR δ 149.3, 109.3, 74.4, 71.7, 37.5, 35.6, 33.9, 29.4, 27.0, 21.1. MS (ESI, MeOH): *m/z* = 171.0 ([M + H]$^+$). HRMS-ESI: *m/z* [M + Na]$^+$ calcd for $C_{10}H_{18}NO_2Na^+$: 193.1199; found: 193.1197.



Scheme S4. Alternative synthesis of (*1S,2R,4R*)-**49** and (*1R,2S,4R*)-**49A**.

Alternative synthesis of (1*S*,2*R*,4*R*)-49 from OsO_4 oxidation[24] of (*R*)-(+)-limonene (48).

A solution of 0.20 g (1.47 mmol) of (*R*)-(+)-limonene (**48**), 7.5 mg (29 µmol) of OsO_4, and 0.21 g (1.76 mmol) of *N*-methylmorpholine *N*-oxide (NMO) in 2 mL of *t*-BuOH, 7 mL of acetone and 2.5 mL of water was stirred 0°C for 30 min and 25°C for 14 h. The reaction mixture was filtered through Celite and concentrated on a rotary evaporator to remove acetone and t-BuOH, diluted with water (20 mL), and extracted three times with dichloromethane (20 mL each). The combined extract was washed with brine, dried (anhydrous Na_2SO_4), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane and ether as eluent to give 27 mg (11% yield) of (1*S*,2*R*,4*R*)-**49** and 0.118 g (47% yield) of (1*R*,2*S*,4*R*)-**49A**[25] along with 46 mg (23% recovery) of (*R*)-limonene.

(1*S*,2*R*,4*R*)-**49**: $[\alpha]_D^{22}$ = +22.6 (c 0.5, $CHCl_3$). ^1H and ^{13}C NMR spectra were identical to those of compound **49** obtained from the catalytic asymmetric dihydroxylation reaction described above.

(1*R*,2*S*,4*R*)-**49A**:[25] $[\alpha]_D^{22}$ = +41.8 (c 1.0, MeOH); Lit.[21] +42 (c 1.0, MeOH). ^1H NMR[25] δ 4.72 – 4.69 (m, 2 H), 3.67 – 3.64 (m, 1 H), 2.38 – 2.30 (bs, 1 H, OH), 1.93 – 1.78 (m, 3 H), 1.74 – 1.67 (m, 1 H), 1.71 (s, 3 H, Me), 1.55 – 1.50 (m, 1 H), 1.42 (s, 1 H, OH), 1.34 – 1.25 (m, 2 H), 1.25 (s, 3 H, Me); ^{13}C NMR[25] δ 148.9, 108.7, 73.5, 71.2, 37.2, 33.6, 33.3, 26.1, 25.7, 20.6.

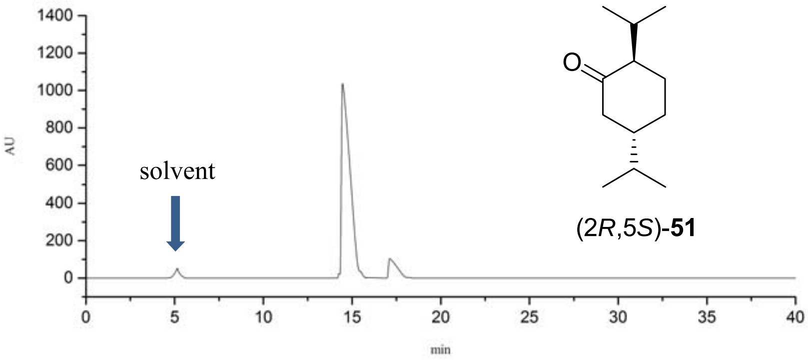
General procedure for the catalytic asymmetric C-H oxidation. For the asymmetric C-H oxidation, 1 mol% of the Cu/Au (3:1)-**17** was used in all reactions.

Preparation of the catalyst. To a cold (0°C) solution of 3.75 mL of 2 mmol/L of CuCl (0.0075 mmol) in deionized water, 0.25 mL of 10 mmol/L of $HAuCl_4 \cdot 3H_2O$ (0.0025 mmol) in deionized water, and 29.1 mg (0.000275 mmol) of CSPVP **17**, was added 1.89 mg (0.05 mmol) of $NaBH_4$. The color of the solution changed to brown and stirred for 30 minutes at 25°C to give the Cu/Au (3:1)-**17** nanoclusters in aqueous solution. This solution was used in catalytic asymmetric C-H oxidation reactions without further purification.

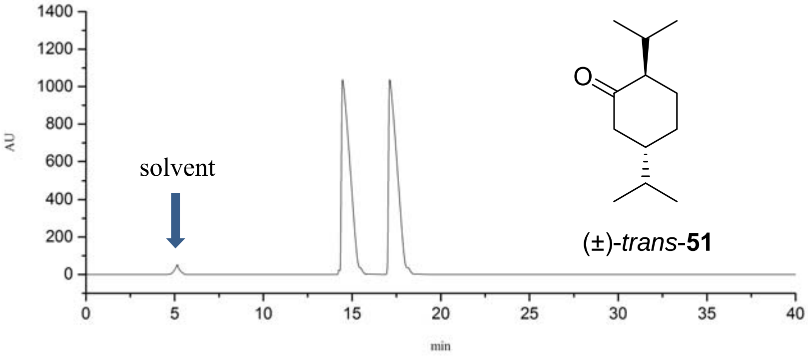
***trans*-1,4-Diisopropylcyclohexane (50)**. To a cold (-78°C) solution of 40 mL of liquid NH_3 under argon was added 0.86 g (0.12 mol) of lithium wire, and the resulting blue solution was stirred at -35°C for 1 h. To it, a solution of 4.0 g (24.7 mmol) of 1,4-diisopropylbenzene (from Sigma Aldrich Co.) in 5.4 g of *t*-BuOH was added, and the solution was stirred for 6 h at -35°C under argon. The reaction solution was diluted with aqueous NH_4Cl (10 mL), extracted twice with diethyl ether, and the combined extract was washed with water, brine, and dried ($MgSO_4$). The solvents were removed by distillation under normal pressure, and residue was column chromatographed on silica gel using hexane as eluent to give 2.81 g (70% yield) of 1,4-diisopropyl-1,4-cyclohexadiene along with 0.96 g (24% recovery) of 1,4-diisopropylbenzene. ^{1}H NMR δ 5.46 (s, 2 H, =CH), 2.64 (s, 4 H, CH_2), 2.19 (hept, J = 7 Hz, 2 H), 1.01 (d, J = 7 Hz, 12 H); ^{13}C NMR δ 140.9, 116.4, 34.7, 27.8, 21.5. MS (ESI, MeOH): *m/z* = 165.0 ($[M + H]^+$), 122.9. A mixture of 2.0 g (12.2 mmol) of 1,4-diisopropyl-1,4-cyclohexadiene and 0.14 g of 10% Pd/C in 30 mL of ethyl acetate in a bottle was shaken under 30 psi of H_2 on a Parr hydrogenator for 16 h and then maintained under normal pressure. The mixture was filtered through Celite, and the filtrate was concentrated by distillation under normal pressure and column chromatographed on silica gel using pentane as solvent to give 1.3 g (65% yield) of pure **50** along with 0.50 g of **50** and 1,4-diisopropyl-1,4-cyclohexadiene (2:1). Compound **50**: ^{1}H NMR δ 1.73 – 1.68 (m, 2 H), 1.59 – 1.05 (m, 7 H), 0.95 – 0.90 (m, 3 H), 0.84 (d, J = 7.2 Hz, 12 H); ^{13}C NMR δ 42.6, 30.2, 26.7, 20.1. MS (ESI, MeOH): *m/z* = 207.0 ($[M + K]^+$).

(2*R*,5*S*)-2,5-diisopropylcyclohexanone (51). To a solution of 2 mL of Cu/Au (3:1)-**17** (4.46 μmol of Cu/1.49 μmol of Au-0.16 μmol of **17**) were added 3 mL of acetonitrile, 0.10 g (0.60 mmol) of **50** and 3 mL of 30% H_2O_2, and the resulting solution was stirred at 50°C for 7 days. The solution was cooled to 25°C and extracted three times with diethyl ether (15 mL each). The combined extracts were washed with water and then brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane and diethyl ether as eluents to give 94 mg (87% yield) of (2*R*,5*S*)-**51** in 81% ee along with 7 mg (7% recovery) of **50**. The optical purity was determined using HPLC/chiral column. Compound (2*R*,5*S*)-**51**: $[\alpha]_D^{22}$ = +12.1 (c 1.5, $CHCl_3$). Lit.[26] +14 (c 1.51, $CHCl_3$). ^{1}H NMR[26] δ 2.38 (ddd, J = 12, 3.4, 2.2 Hz, 1 H), 2.13 - 2.05 (m, 1 H), 1.83 – 1.52 (m, 3 H), 1.43 – 0.85 (m, 5 H), 1.01 (d, J = 7 Hz, 6 H), 0.84 (d, J = 7 Hz, 6 H); ^{13}C NMR δ 213.0, 56.2, 46.5, 32.6, 28.8, 27.9, 25.9, 21.2, 19.6 (2 C), 18.6 (2 C). MS (ESI, MeOH): *m/z* = 205.1 ($[M + Na]^+$; 100%), 139.0.

The % ee (81%) of (1*R*,5*S*)-**51** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, detected at 220 nm wavelength; t_R = 14.5 min (2*R*,5*S* enantiomer, major), t_R = 17.2 min (2*S*,5*R* enantiomer, minor).



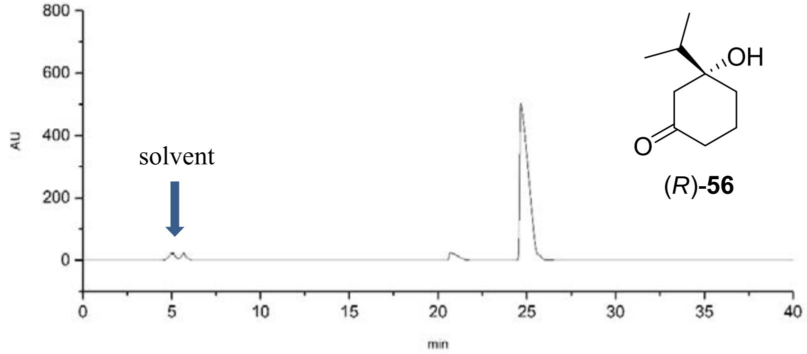
(2*R*,5*S*)-**51**

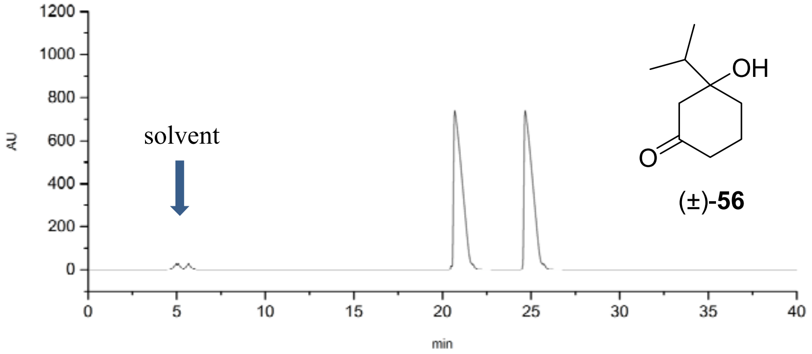


(±)-*trans*-**51**

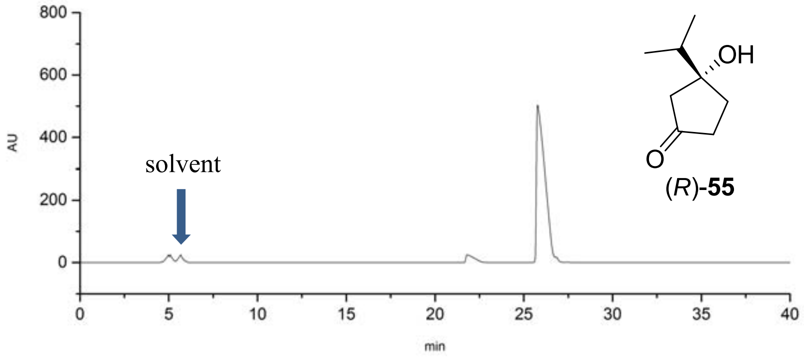
(*R*)-3-Hydroxy-3-isopropylcyclohexanone (56). From 0.10 g (0.70 mmol) of 1-isopropylcyclohexanol (**53**), 2.4 mL of Cu/Au (3:1)-**17** (5.27 μmol of Cu/1.75 μmol of Au-0.19 μmol of **17**), 2 mL of H_2O_2, and 1 mL of CH_3CN stirring at 50°C for 7 days, 0.107 g (98% yield) of (*R*)-**56** in 91.4% ee. $[\alpha]_D^{22} = +6.1$ (c 0.20, $CHCl_3$). ^1H NMR δ 2.45 – 2.40 (m, 2 H), 2.15 – 2.10 (m, 2 H), 1.96 – 1.88 (m, 2 H), 1.77 – 1.60 (m, 4 H), 0.88 (d, J = 6.8 Hz, 6 H). The proton NMR assignments were derived from 2D COSY spectrum. ^{13}C NMR δ 205.1, 73.2, 54.2, 42.4, 34.3, 29.3, 23.7, 17.5. MS (ESI, MeOH): *m/z* = 157.3 ($[M + H]^+$), 119.0, 116.2, 104.9. HRMS-Hexane Atmospheric Pressure Chemical Ionization (HAPCI): *m/z* $[M+H]^+$ calcd for $C_9H_{17}O_2$: 157.1229; found: 157.1221. The % ee (91.4%) of (*R*)-**56** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, detected at 220 nm wavelength; t_R = 20.8 min (*S* enantiomer, minor), t_R = 24.7

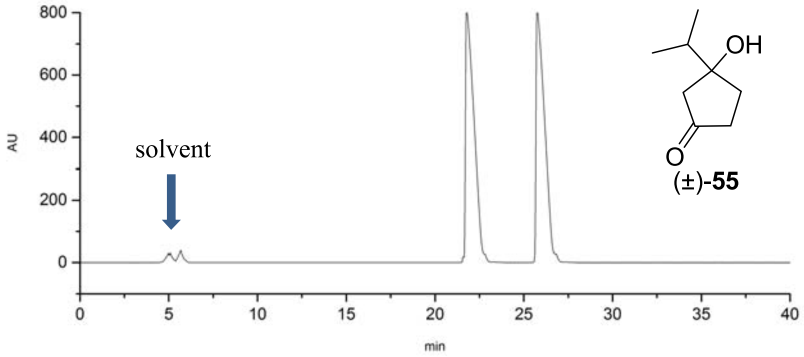
min (*R* enantiomer, major).





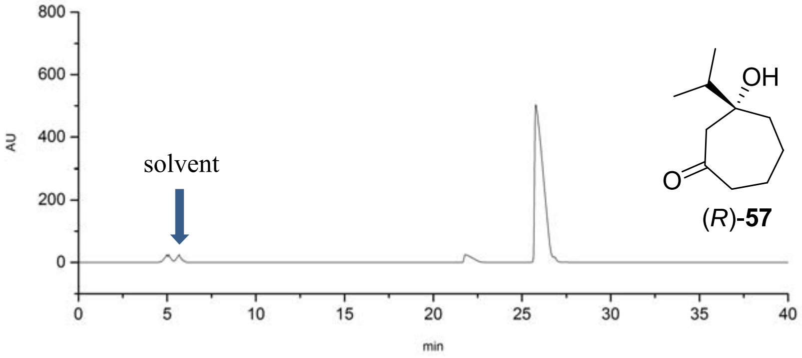
***(R)*-3-Hydroxy-3-isopropylcyclopentanone (55)**. From 90 mg (0.70 mmol) of 1-isopropylcyclopentanol (**52**), 2.4 mL of Cu/Au (3:1)-**17** (5.27 μmol of Cu/1.75 μmol of Au-0.19 μmol of **17**), 2 mL of H_2O_2, and 1 mL of CH_3CN stirring at 50°C for 7 days, 91 mg (91% yield) of (*R*)-**55** in 92% ee. $[\alpha]_D^{22}$ = +13.7 (c 0.20, $CHCl_3$). ^{1}H NMR δ 2.41 – 2.30 (m, 2 H, C2 Hs), 2.30 - 2.17 (m, 1 H, C5 H), 2.07 – 1.80 (m, 4 H, C5 H, C4 Hs, & $C\underline{H}Me_2$), 1.72 – 1.60 (m, 2 H, C4 H & OH), 1.02 (d, J = 7 Hz, 6 H). The proton NMR assignments were derived from 2D COSY spectrum. ^{13}C NMR δ 205.9, 73.3, 53.6, 42.4, 32.5, 22.0, 16.7. MS (ESI, MeOH): *m/z* = 143.0 ($[M + H]^+$), 129.0, 123.0, 115.2. HRMS-Hexane Atmospheric Pressure Chemical Ionization (HAPCI): *m/z* $[M]^+$ calcd for $C_8H_{14}O_2$: 142.0994; found: 142.0049. The % ee (92%) of (*R*)-**55** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, detected at 220 nm wavelength; t_R = 23.5 min (*S* enantiomer, minor), t_R = 27.5 min (*R* enantiomer, major).

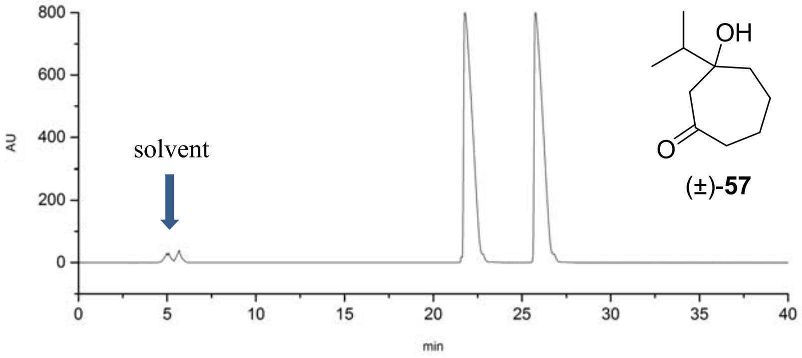




(*R*)-3-Hydroxy-3-isopropylcycloheptanone (57). From 42 mg (0.27 mmol) of 1-isopropylcycloheptanol (**54**), 0.92 mL of Cu/Au (3:1)-**17** (2.0 µmol of Cu/0.65 µmol of Au-0.074 µmol of **17**), 1 mL of H_2O_2, and 1 mL of CH_3CN stirring at 50°C for 7 days, 41 mg (89% yield) of (*R*)-**57** in 93% ee. $[\alpha]_D^{22}$ = +23.8 (c 0.20, $CHCl_3$). ^1H NMR δ 2.35 (d, J = 2 Hz, 2 H, C2 Hs), 2.16 – 2.18 (m, 2 H, C7 Hs), 1.97 - 1.93 (m, 2 H, C6 Hs), 1.90 – 1.83 (m, 1 H, C<u>H</u>Me_2), 1.75 – 1.70 (m, 1 H, C4 H), 1.67 – 1.58 (m, 3 H, C5 Hs & C4 H), 1.30 – 1.20 (bs, 1 H, OH), 0.86 (d, J = 8 Hz, 6 H). The proton NMR assignments were derived from 2D COSY spectrum. ^{13}C NMR δ 206.1, 74.4, 52.8, 41.6, 37.4, 33.9, 27.0, 21.0, 17.1 (2 C). MS (ESI, MeOH): *m/z* = 171.1 ($[M + H]^+$), 142.1, 123.1, 107.0. HRMS-Hexane Atmospheric Pressure

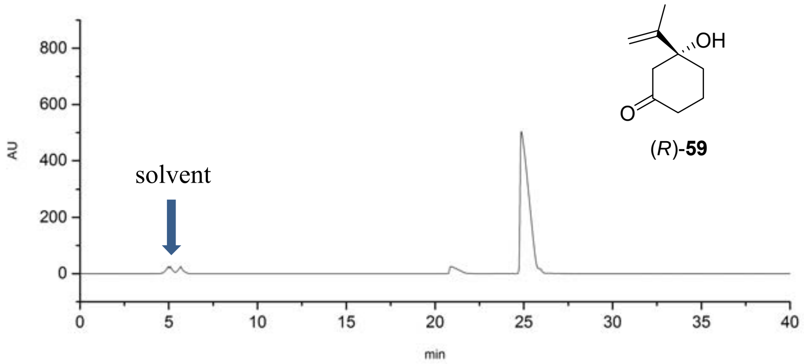
Chemical Ionization (HAPCI): *m/z* $[M+H]^+$ calcd for $C_{10}H_{19}O_2$: 171.1385; found: 171.1381. The % ee (93%) of (*R*)-**57** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, detected at 220 nm wavelength; t_R = 21.7 min (*S* enantiomer, minor), t_R = 25.8 min (*R* enantiomer, major).

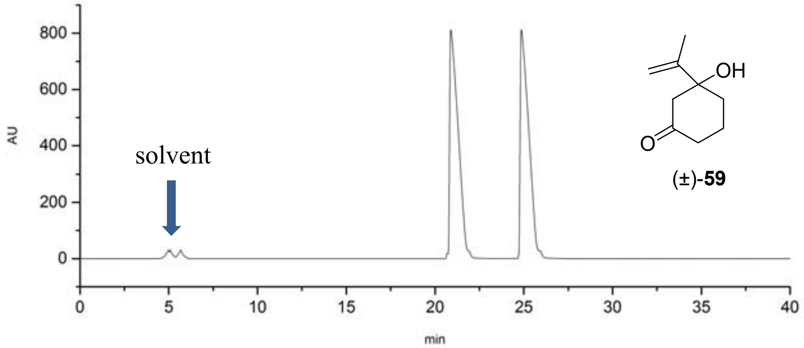




(*R*)-Hydroxy-3-(isopropenyl)cyclohexanone (59). From 70 mg (0.50 mmol) of 1-isopropenylcyclohexanol (**58**), 1.7 mL of Cu/Au (3:1)-**17** (3.75 µmol of Cu/1.25 µmol of Au-0.13 µmol of **17**), 1.5 mL of H_2O_2, and 1.5 mL of CH_3CN stirring at 50°C for 8 days, 76 mg (98% yield) of (*R*)-**59** in 93% ee. $[\alpha]_D^{22}$ = +17.3 (c 1.0, $CHCl_3$). ^1H NMR δ 5.07 (d, J = 0.8 Hz, 1 H, =CH), 4.95 (d, J = 0.8 Hz, 1 H, =CH), 2.35 – 2.32 (m, 2 H, C2 Hs), 2.16 – 2.15 (m, 2 H, C6 Hs), 2.00 – 1.95 (m, 2 H, C4 Hs), 1.85 (s, 3 H), 1.85 – 1.7 (m, 2 H, C5 Hs), 1.7 – 1.55 (bs, 1 H, OH). The proton NMR assignments were derived from 2D COSY spectrum. ^{13}C

NMR δ 209.5, 152.2, 109.2, 76.1, 52.9, 40.8, 38.8, 23.0, 17.8. MS (ESI, MeOH): *m/z* = 177.1 ([M + Na]$^+$), 142.2, 130.1. HRMS-Hexane Atmospheric Pressure Chemical Ionization (HAPCI): *m/z* [M+H]$^+$ calcd for $C_9H_{15}O_2$: 155.1072; found: 155.1088. The % ee (93%) of (*R*)-**59** was determined by HPLC using chiral column, Chiralpak AD(-H) column, *n*-hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, detected at 220 nm wavelength; t_R = 20.8 min (*S* enantiomer, minor), t_R = 24.9 min (*R* enantiomer, major).





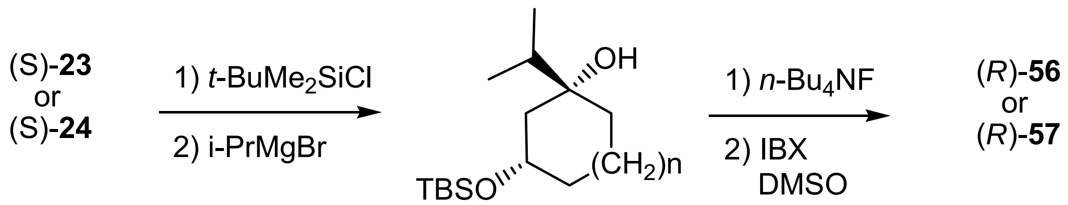
(+)-2*S*-2-Hydroxysclareolide (61). To a solution of 12 mL of Cu/Au (3:1)-**17** (24 μmol of Cu/8.0 μmol of Au-0.88 μmol of **17**) in H_2O (as described above) were added 12 mL of acetonitrile, 100 mg (0.40 mmol) of (+)-sclareolide (**60**) and 1.5 mL of 30% H_2O_2, and the resulting solution was stirred at 60°C for 6 days. The solution was cooled to 25°C, diluted with water, and extracted three times with diethyl ether (20 mL each). The combined extracts were washed with water and then brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane and ethyl acetate, followed by dichloromethane and methanol as eluents to give 40 mg (37.5% yield) of (2*S*)-**61**[27] and 3.3 mg (3% yield) of 1-oxosclareolide[27] along with 46 mg (46% recovery) of **60** and 10 mg of unidenficable polymers.

Compound (2*S*)-**61**: $[\alpha]_D^{22}$ = +78 (c 0.1, MeOH). Lit.[27] -100 (c 0.006, MeOH). ^{1}H NMR[27] δ 4.03 – 3.94 (m, 1 H), 2.42 (t, J = 14.4 Hz, 1 H), 2.27 (dd, J = 16.4, 6.4 Hz, 1 H), 2.10 (dt, J = 12, 3.2 Hz, 1 H), 2.01 (dd, J = 14.4, 6.4 Hz, 1 H), 1.94 – 1.80 (m, 3 H), 1.74 – 1.66 (m, 1 H), 1.40 – 1.35 (m, 1 H), 1.33 (s, 3 H), 1.28 – 1.25 (m, 1 H), 1.17 (t, J = 11.6 Hz, 1 H), 1.08 (dd, J = 13, 3 Hz, 1 H), 0.96 (s, 3 H), 0.95 (s, 3 H), 0.89 (s, 3 H); ^{13}C NMR[27] δ 176.0, 86.0, 64.4, 58.9, 56.3, 51.6, 48.4, 38.5, 37.5, 34.7, 33.2, 28.7, 21.9, 21.7, 20.1, 16.2; MS (ESI, MeOH): *m/z* = 289.4 ($[M + Na]^+$), 267.3 ($M+H^+$), 134.1.

1-Oxosclareolide: ^{1}H NMR δ 2.96 (dd, J = 17, 7 Hz, 1 H), 2.68 (ddd, J = 16, 8.8, 6.4 Hz, 1 H), 2.53 (dd, J = 16.8, 14.4 Hz, 1 H), 2.29 (ddd, J = 15.6, 8.8, 5.2 Hz, 1 H), 2.15 (dd, J = 14.4, 6.4 Hz, 1 H), 2.10 – 2.05 (m, 1 H), 1.94 – 1.80 (m, 2 H), 1.70 – 1.60 (m, 2 H), 1.35 (s, 3 H), 1.19 (s, 3 H), 1.05 (s, 3 H), 1.04 – 0.96 (m, 1 H), 1.02 (s, 3 H), 0.91 – 0.86 (m, 1 H). MS (ESI, MeOH): *m/z* = 287.3 ($[M + Na]^+$), 250.2, 122.9.

Alternative syntheses of (*R*)-56 and (*R*)-57.

Scheme S5. Alternative syntheses of (*R*)-**56** and (*R*)-**57**.



62 : n = 1, TBS = *t*-BuMe$_2$Si
63 : n = 2, TBS = *t*-BuMe$_2$Si

Synthesis of (*R*)-56 from (*S*)-23. To a solution of 40 mg (0.35 mmol) of (*S*)-3-hydroxycyclohexanone (**23**), 4 mg (0.036 mmol) of 4-dimethylaminopyridine, and 0.10 g (1.0 mmol) of trimethylamine in 3 mL of dichloromethane at 0ºC under argon, was added 77 mg (0.51 mmol) of *t*-butyldimethylsilyl chloride. The solution was stirred for 4 h, diluted with 10 mL of water, and extracted three times with ethyl acetate (10 mL each). The combined extract was washed with brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel to give 28 mg (35% yield) of (*S*)-3-(*t*-butyldimethylsilyloxy)cyclohexanone and 17 mg (49% yield) of 2-cyclohexenone along with 4 mg (10% recovery) of starting 3-hydroxyketone **23**. The silyloxycyclohexanone was used in the following step without purification. (*S*)-3-(*t*-Butyldimethylsilyloxy)cyclohexanone: ^{1}H NMR δ 4.17 – 4.12 (m, 1 H), 2.62 (dd, J = 14, 4 Hz, 1 H), 2.36 (dd, J = 14, 7.5 Hz, 1 H), 2.28 (t, J = 6.5 Hz, 2 H), 2.15 – 2.00 (m, 2 H), 1.82 – 1.65 (m, 2 H), 1.00 (s, 9 H), 0.38 (s, 6 H). To a mixture of 1.7 mg (13 μmol) of anhydrous $ZnCl_2$ in 2 mL of dry THF under argon at 25ºC, was added a solution of 0.18 mmol of isopropylmagnesium bromide in 1 mL of THF, and the solution was stirred for 1 h and then cooled to 0ºC. To it, was added a solution of 28 mg (0.12 mmol) of (*S*)-3-(*t*-butyldimethylsilyloxy)cyclohexanone in 0.5 mL of THF via cannula under argon and the resulting solution was stirred at 0ºC for 4 h. The solution was diluted with aqueous NH_4Cl and water (10 mL), extracted three times with ethyl acetate (20 mL each), and the combined extract was washed with brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane and ethyl acetate as eluent to give 23 mg (70% yield) of (1*R*,3*S*)-3-(*t*-butyldimethylsilyloxy)-1-isopropylcyclohexanone (**62**). No other stereoisomer was found. Compound **62**: ^{1}H NMR δ 4.37 (m, 1 H), 1.96 – 1.50 (m, 8 H), 1.32 – 1.24 (m, 2 H), 0.97 (s, 9 H), 0.91 (d, J = 7 Hz, 6 H), 0.36 (s, 6 H); ^{13}C NMR δ 73.3, 66.2, 37.5, 35.6, 33.1, 26.2, 23.9 (3 C), 20.9, 18.6, 16.9 (2 C), -1.15 (2 C).

A solution of 14 mg (52 μmol) of the above (1*R*,3*S*)-**62** and 0.10 mL (0.10 mmol) of *n*-Bu_4NF (1 M in THF) in 0.5 mL of THF was stirred under argon at 0°C for 1 h and then at 25°C for 1.5 h. The solution was diluted with water (10 mL), and extracted three times with diethyl ether (10 mL each). The combined extract was washed with brine, dried ($MgSO_4$), and concentrated under vacuum to give 8.7 mg of (1*R*,3*S*)-1-isopropyl-1,3-cyclohexanediol, which was used immediately in the following reaction without further purification. To a solution of the above diol in 0.5 mL of DMSO was added 16 mg (57 μmol) of IBX under argon at 25°C. The resulting mixture was stirred for 14 h, filtered to remove white solid, and rinsed with 20 mL of diethyl ether. The ether filtrate was washed three times with water (10 mL each), dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a mixture of hexane and ethyl acetate (1:2) as eluent to give 7.6 mg (95% yield) of (*R*)-3-hydroxy-3-isopropylcyclohexanone (**56**). $[\alpha]_D^{22}$ = +6.4 (c 0.20, $CHCl_3$). ^{1}H and ^{13}C NMR spectra were identical those of **56** synthesized from the Pd/Au-**17** catalytic oxidation reaction.

Synthesis of (*R*)-57 from (*S*)-24. To a solution of 15 mg (0.12 mmol) of (*S*)-3-hydroxycycloheptanone (**24**), 1.5 mg (0.012 mmol) of 4-dimethylaminopyridine, and 35 mg (0.35 mmol) of trimethylamine in 1 mL of dichloromethane at 0°C under argon, was added 25 mg (0.17 mmol) of *t*-butyldimethylsilyl chloride. The solution was stirred for 8 h, diluted with 10 mL of water, and extracted three times with ethyl acetate (10 mL each). The combined extract was washed with brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel to give 19 mg (76% yield) of (*S*)-3-(*t*-butyldimethylsilyloxy)cycloheptanone and 3.2 mg (25% yield) of 2-cycloheptenone. The silyloxycycloheptanone was used in the following step without purification. (*S*)-3-(*t*-Butyldimethylsilyloxy)cycloheptanone: ^{1}H NMR δ 4.12 – 4.10 (m, 1 H), 2.85 – 2.75 (m, 2 H), 2.55 – 2.40 (m, 2 H), 1.95 – 1.55 (m, 6 H), 0.98 (s, 9 H), 0.37 (s, 6 H). To a mixture of 1.1 mg (8 μmol) of anhydrous $ZnCl_2$ in 0.5 mL of dry THF under argon at 25°C, was added a solution of 0.12 mmol of isopropylmagnesium bromide in 0.2 mL of THF, and the solution was stirred for 1 h and then cooled to 0°C. To it, was added a solution of 19 mg (0.078 mmol) of (*S*)-3-(*t*-butyldimethylsilyloxy)cycloheptanone in 0.2 mL of THF via cannula under argon and the resulting solution was stirred at 0°C for 3 h. The solution was diluted with aqueous NH_4Cl and water (10 mL), extracted three times with ethyl acetate (10 mL each), and the combined extract was washed with brine, dried (anh. Na_2SO_4), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane and ethyl acetate as eluent to give 14 mg (62% yield) of (1*R*,3*S*)-3-(*t*-butyldimethylsilyloxy)-1-isopropylcycloheptanone (**63**). No other stereoisomer was found. Compound **63**: ^{1}H NMR δ 4.42 – 4.35 (m, 1 H), 2.02 – 1.50 (m, 9 H), 1.35 – 1.20 (m, 3 H), 0.97 (s, 9 H), 0.91 (d, J = 7 Hz, 6 H), 0.36 (s, 6 H); ^{13}C NMR δ 75.6, 70.9, 35.0, 33.1, 30.6, 29.6, 25.8 (3 C), 25.5, 24.3, 20.0, 17.2 (2 C), -1.6 (2 C).

A solution of 7 mg (24 μmol) of the above (1*R*,3*S*)-**63** and 48 μL (48 μmol) of *n*-Bu_4NF (1 M in THF) in 0.5 mL of THF was stirred under argon at 25°C for 2 h. The solution was diluted with water (10 mL), and extracted three times with diethyl ether (10 mL each). The combined extract was washed with brine, dried ($MgSO_4$), and concentrated under vacuum to give 4.2 mg of (1*R*,3*S*)-1-isopropyl-1,3-cycloheptanediol, which was used immediately in the following reaction without further purification. To a solution of the above diol in 0.5 mL of DMSO was added 8 mg (26 μmol) of IBX under argon at 25°C. The resulting mixture was stirred for 14 h, filtered to remove white solid, and rinsed with 10 mL of diethyl ether. The ether filtrate was washed three times with water (10 mL each), dried (anh. Na_2SO_4), concentrated, and column chromatographed on silica gel using a mixture of hexane and ethyl acetate (1:2) as eluent to give 4.0 mg (96% yield) of (*R*)-3-hydroxy-3-isopropylcycloheptanone (**57**). $[\alpha]_D^{22} = +25.9$ (c 0.20, $CHCl_3$). ^1H and ^{13}C NMR spectra were identical those of **57** synthesized from the Pd/Au-**17** catalytic oxidation reaction.

10. **Table S1.** Selectivity factors for all HPLC/chiral column analyses.

Compounds	**Selectivity factors**
22a	1.15
22b	1.24
23a	1.25
23b	1.27
24a	1.28
24b	1.24
31a	1.18
31b	1.22
32a	1.17
32b	1.24
33a	1.18
33b	1.23
cis-**38**	1.15
syn-**40**	1.17
anti-**41**	1.10
syn-**43**	1.27
anti-**44**	1.16
cis-**46**	1.13

trans-**47**	1.13
trans-**51**	1.28
56	1.25
55	1.22
57	1.24
58	1.26

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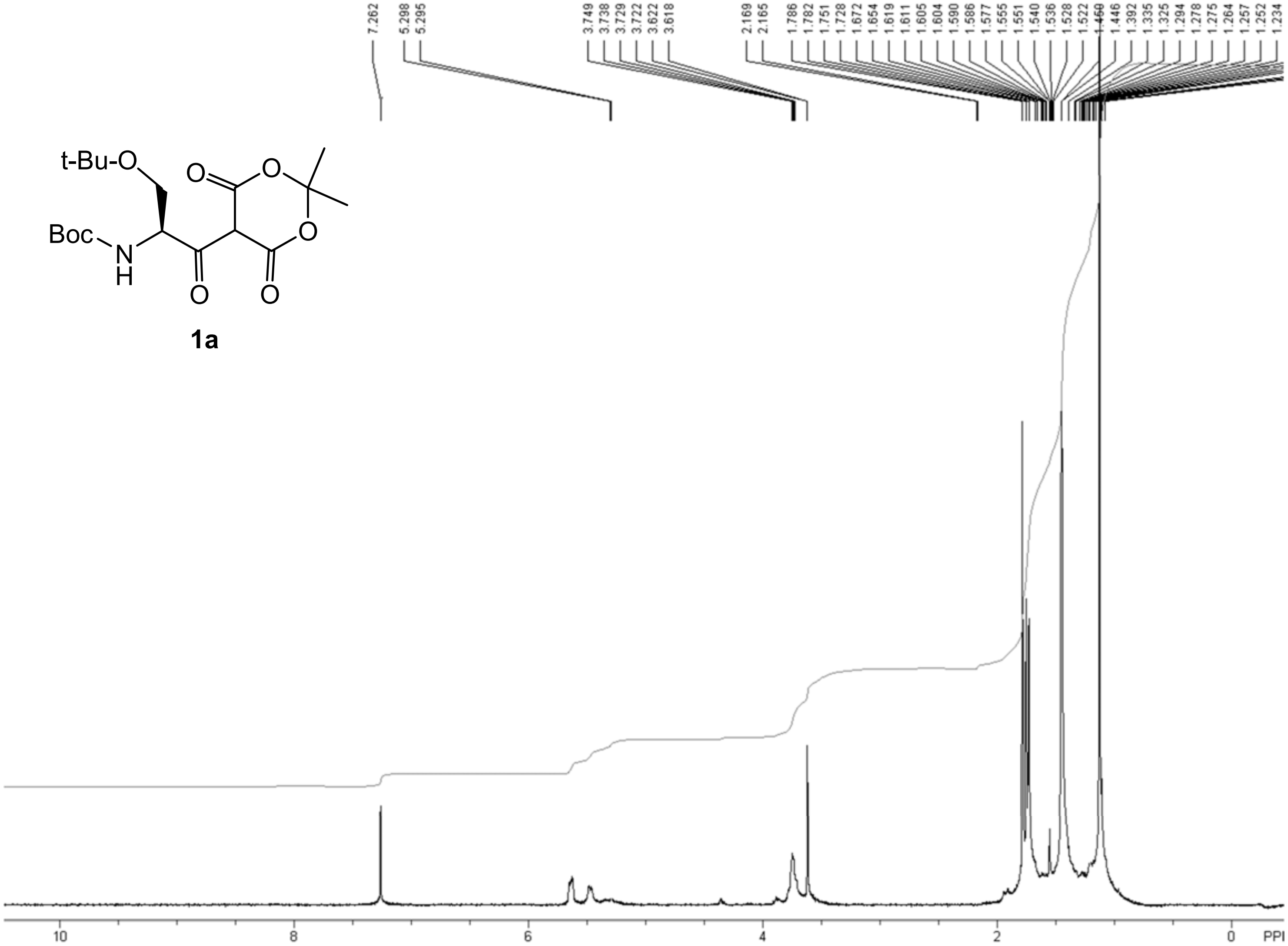
12. ^{1}H and ^{13}C NMR spectra of compounds **1 – 18, 22 – 24, 31 – 33, 38, 40, 41, 43, 44, 46, 47, 49 – 51**, and **55 – 59**, **61 - 63** including 2D COSY spectra of compounds **56** – **58**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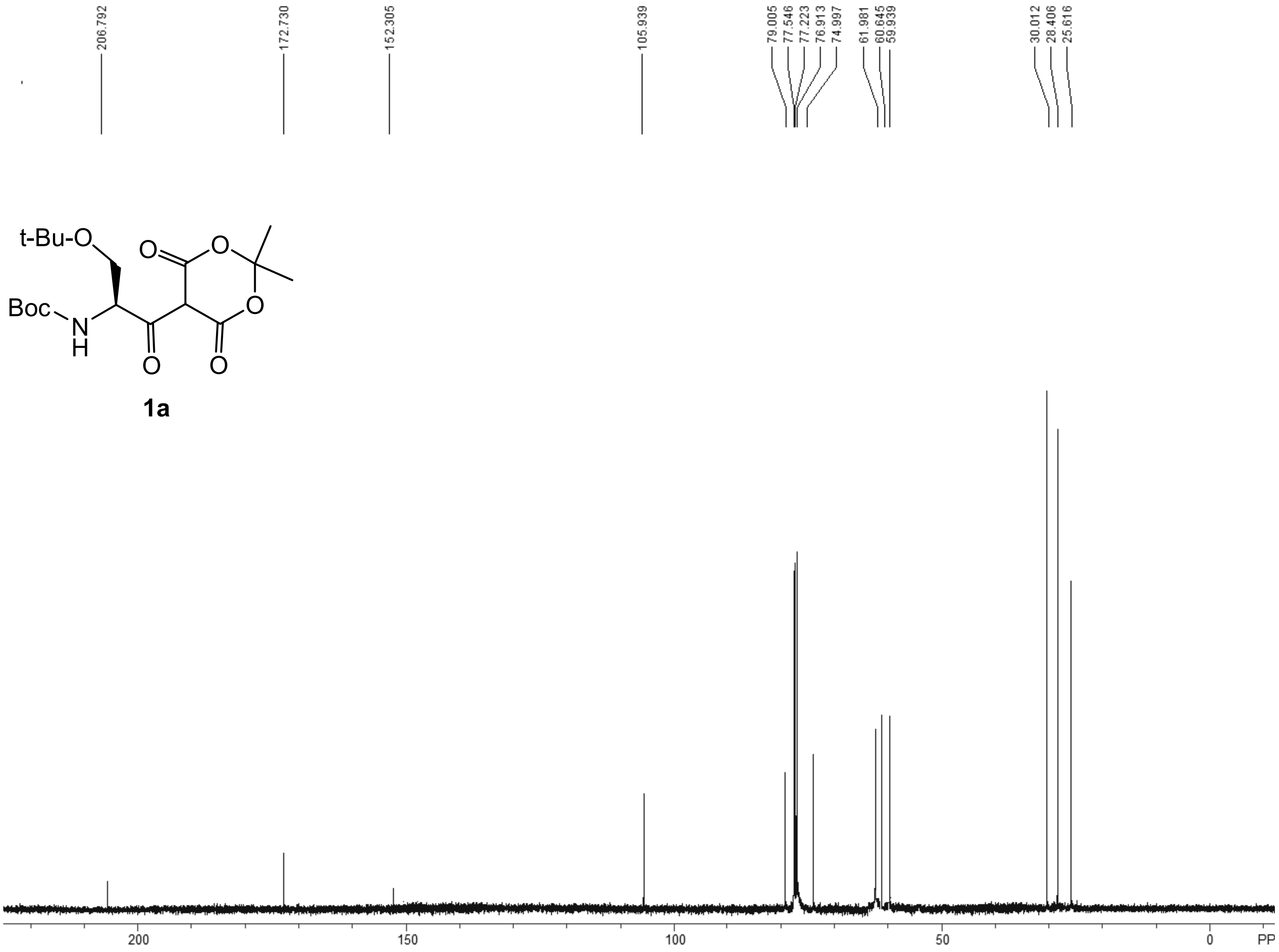
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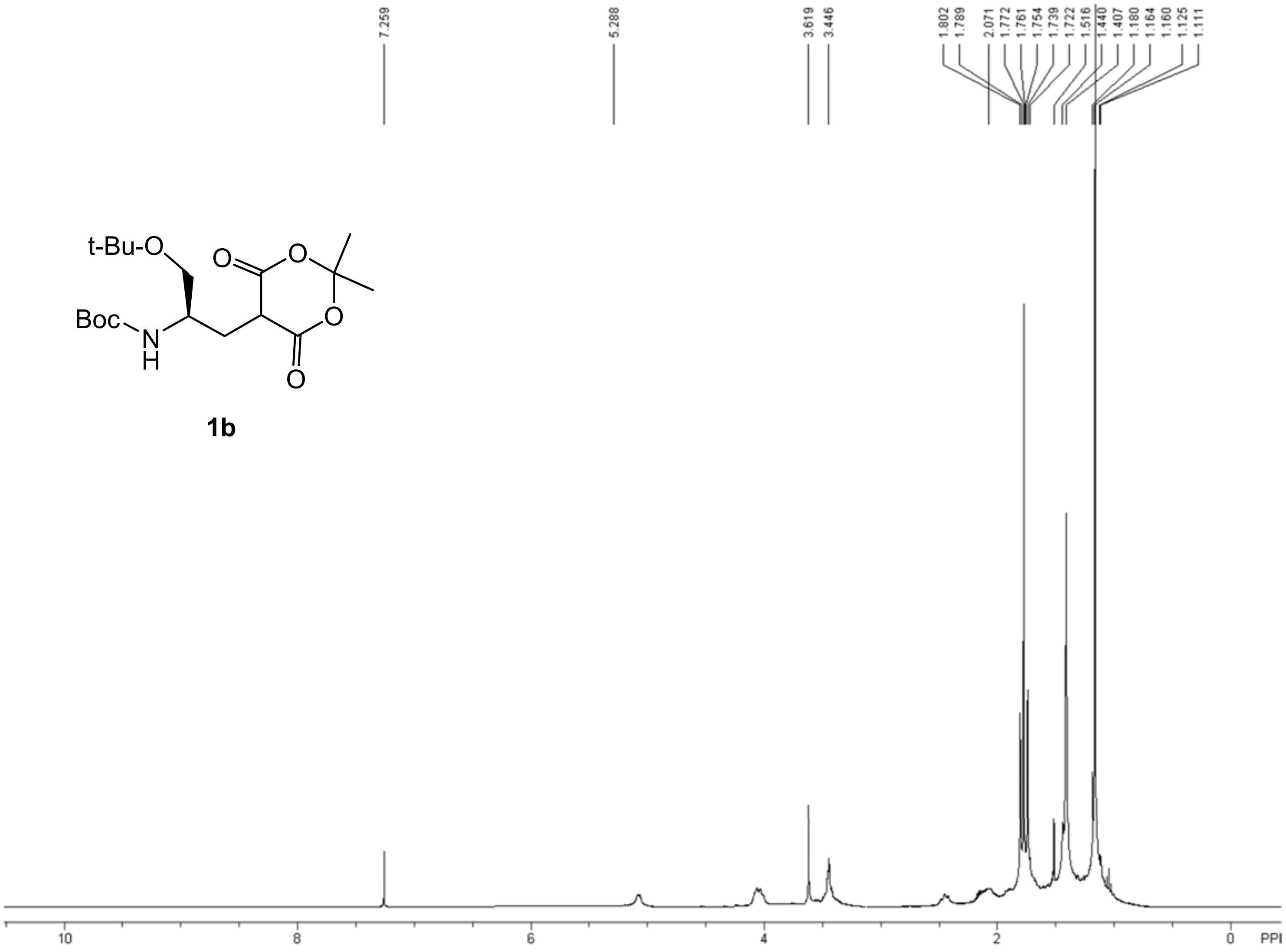

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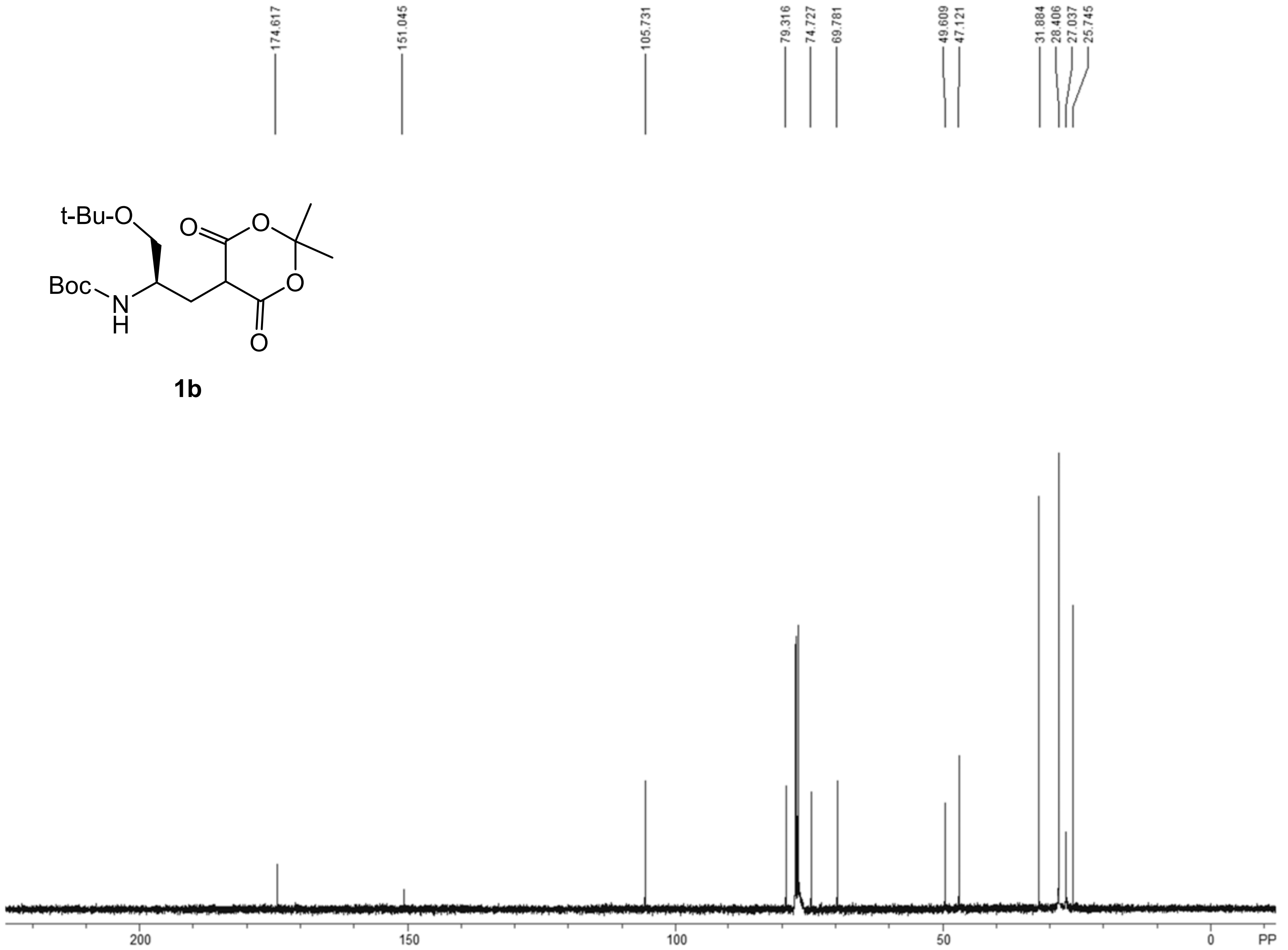
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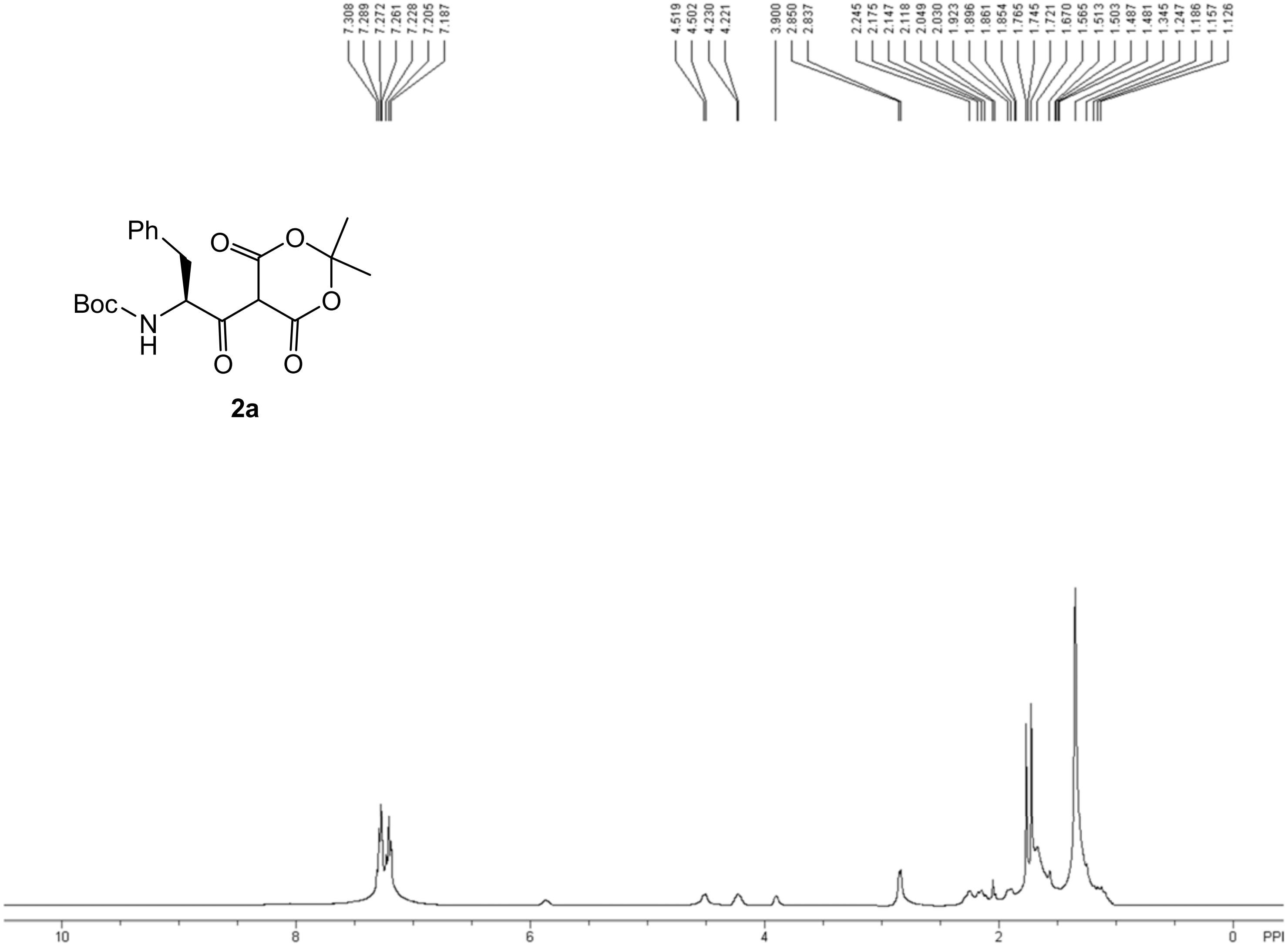
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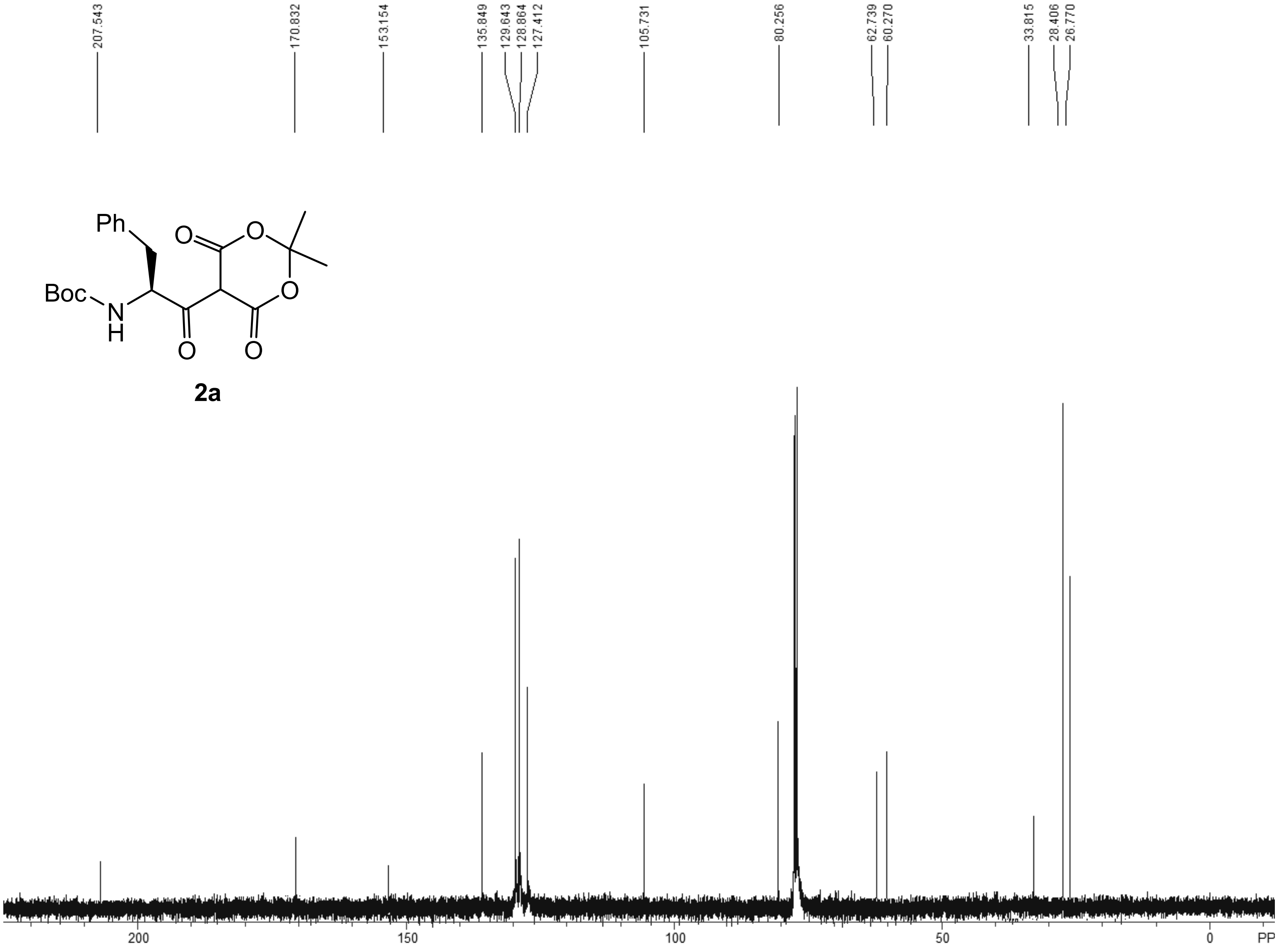
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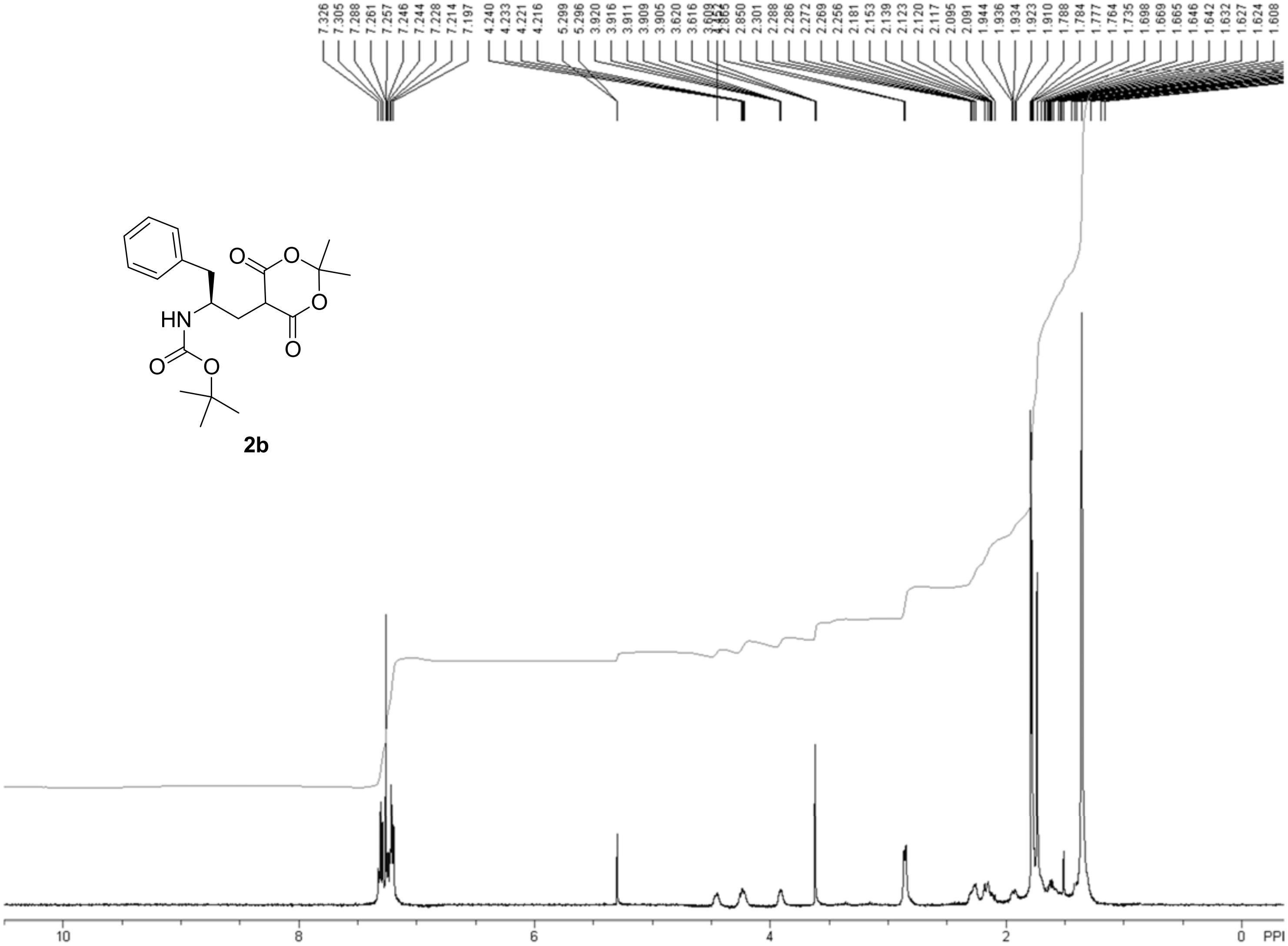

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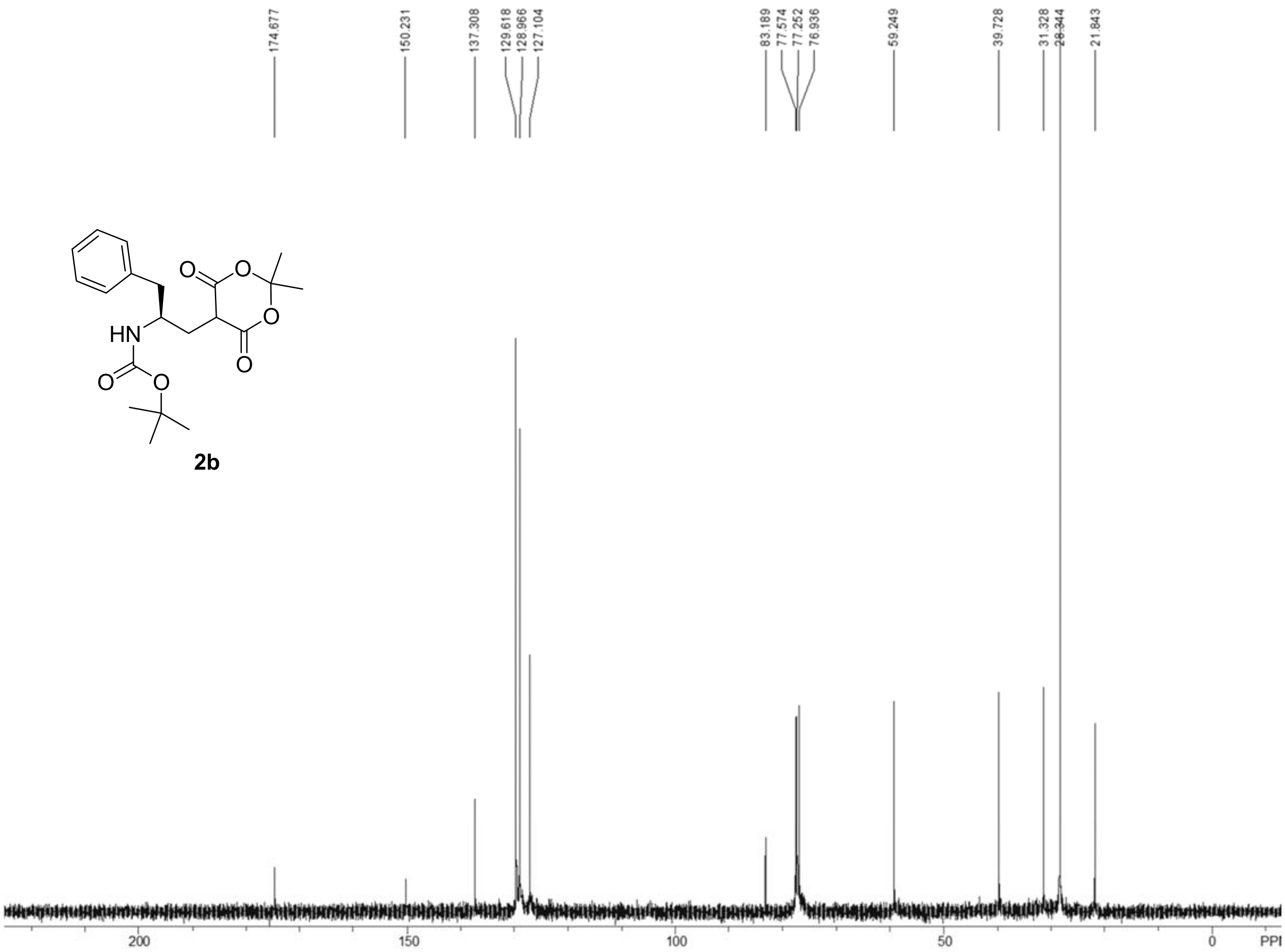

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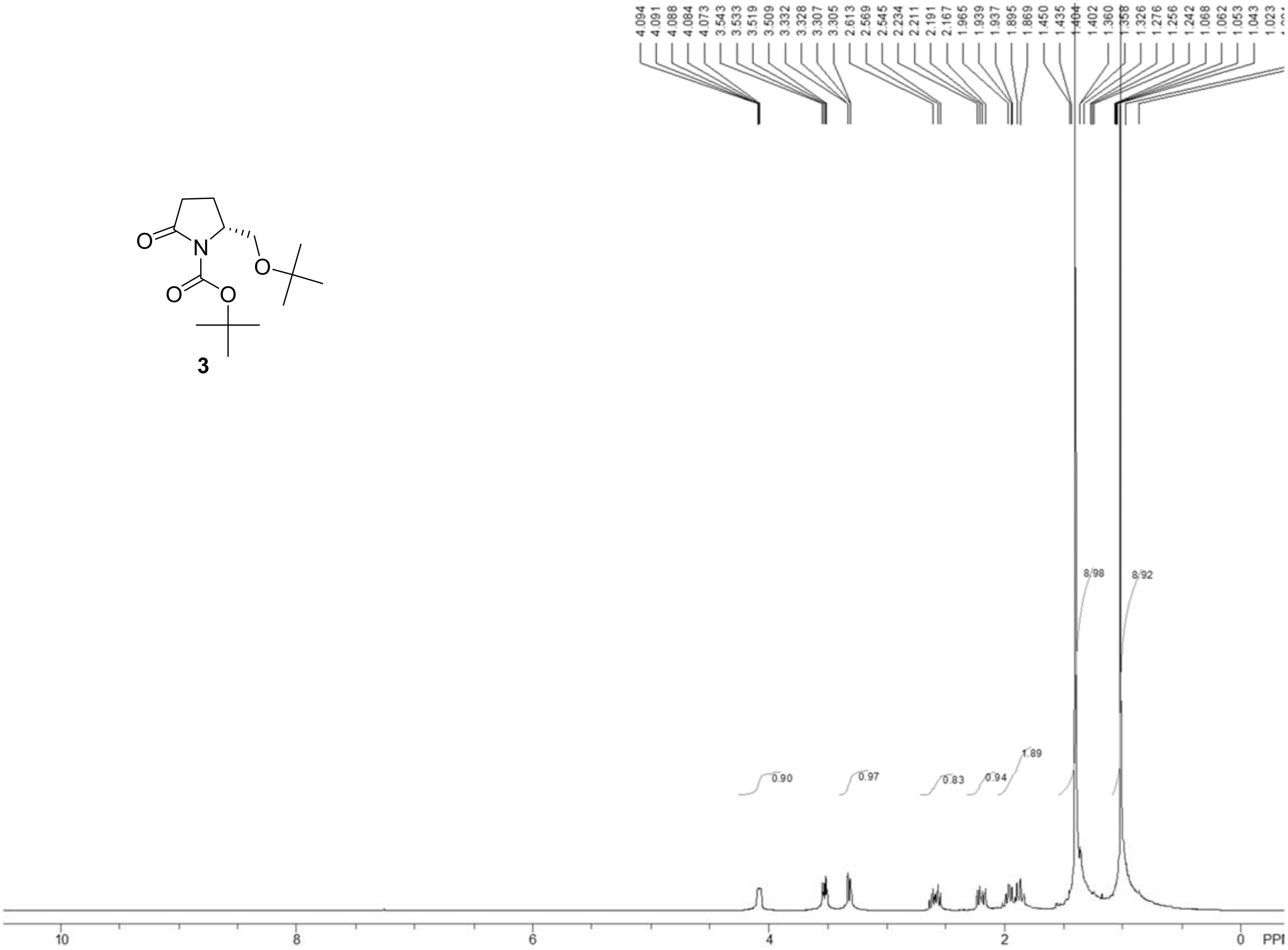
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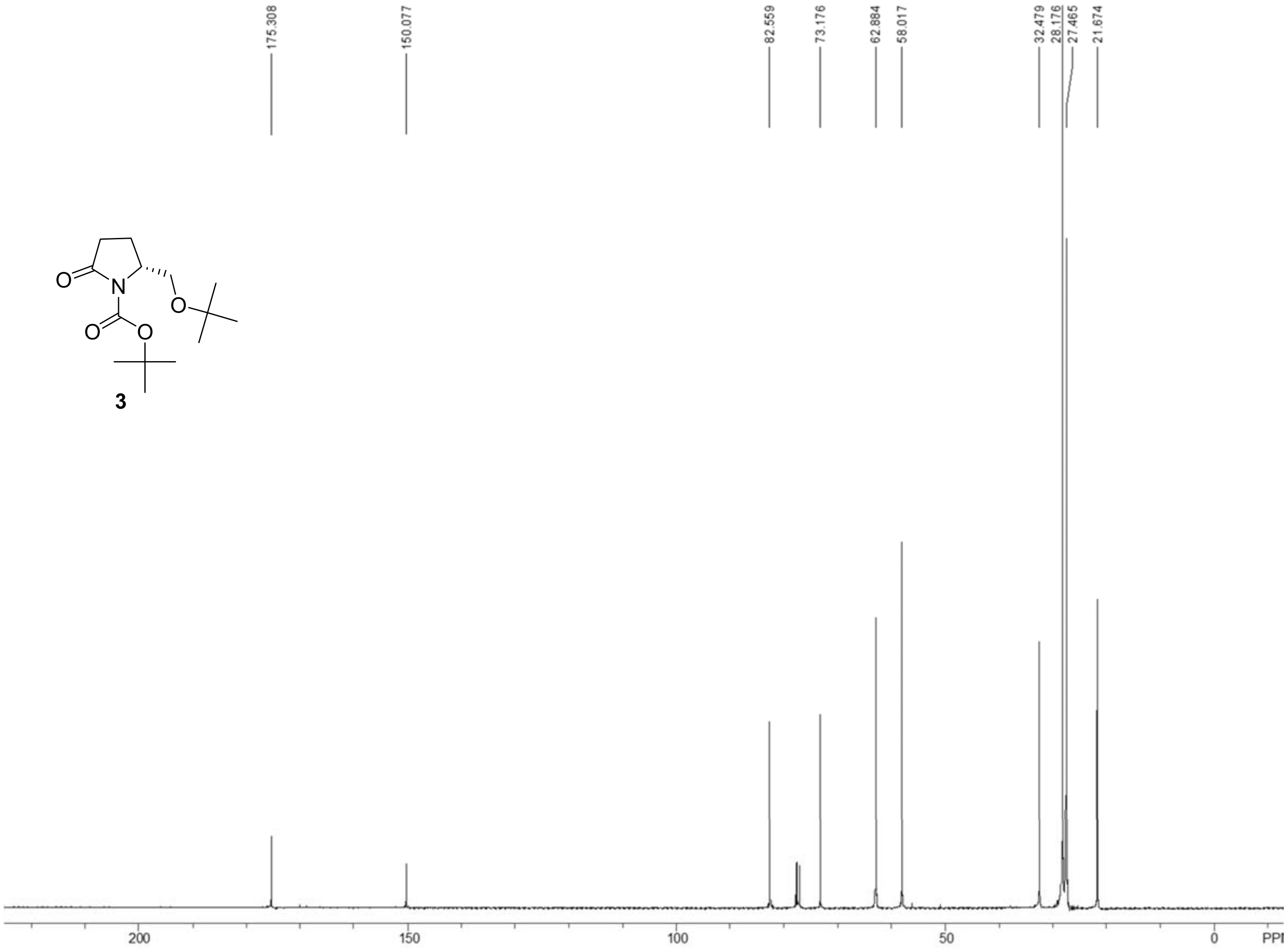

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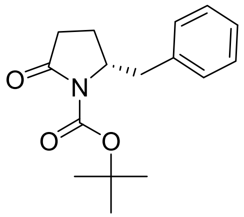
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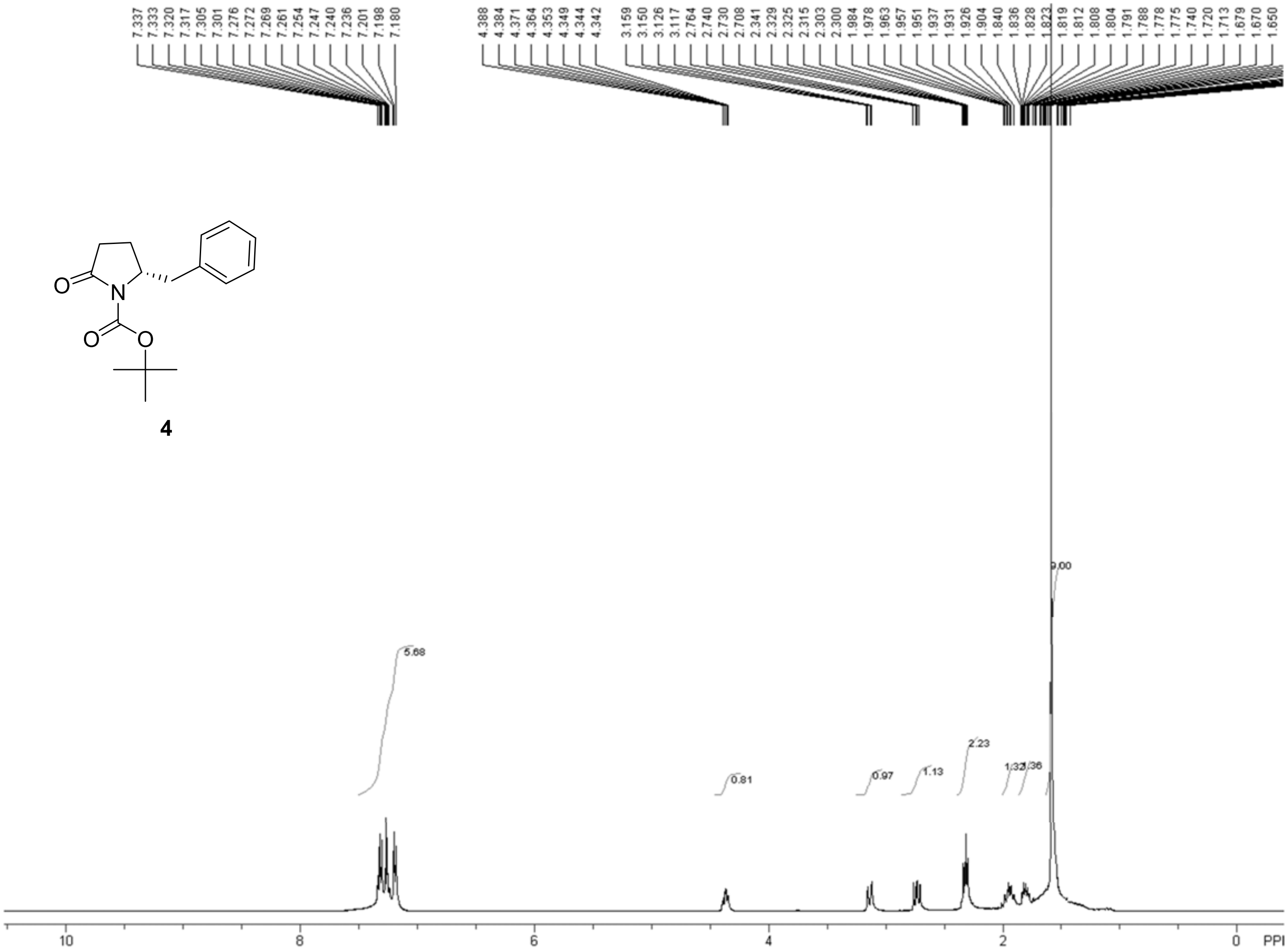
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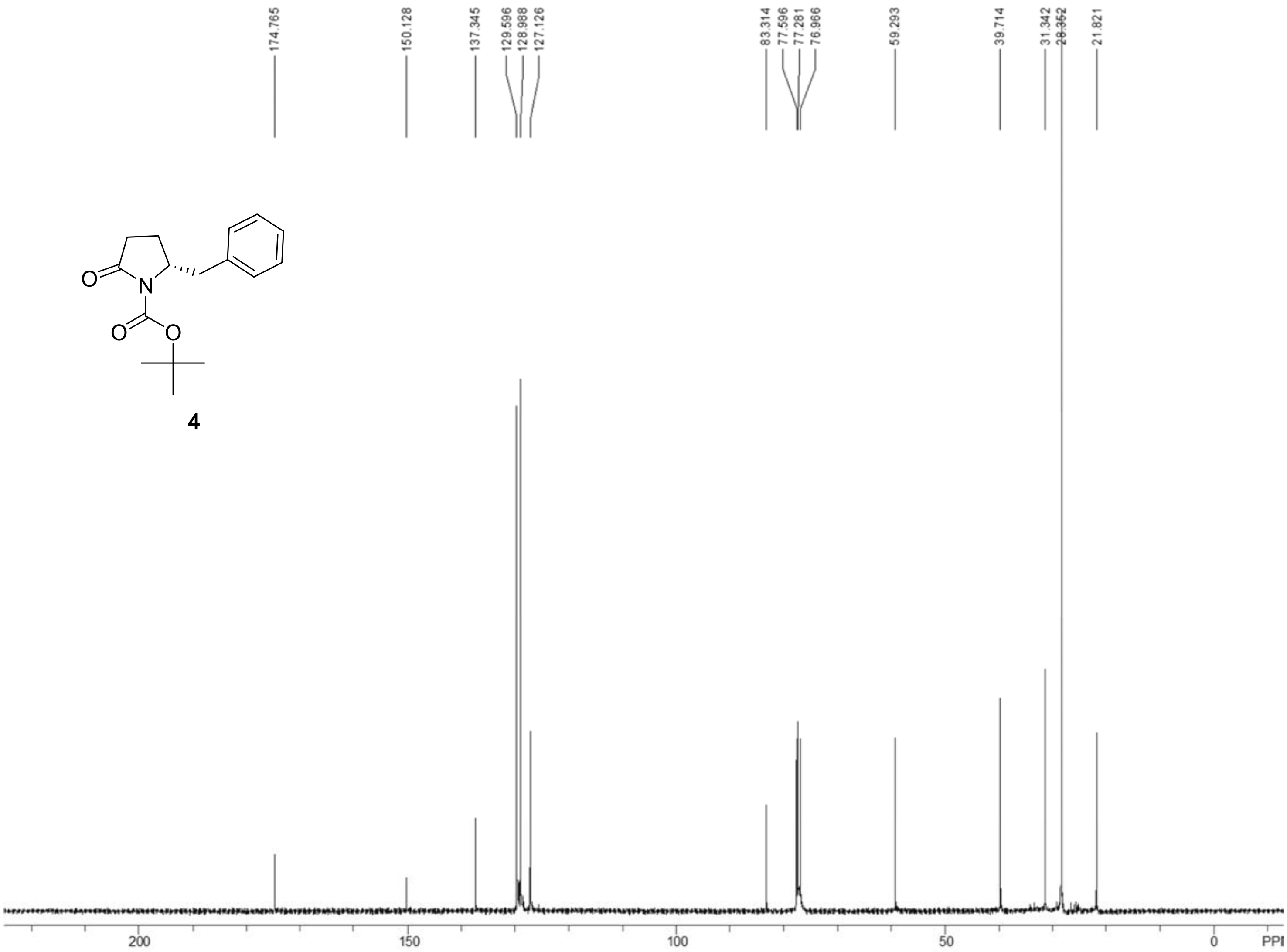

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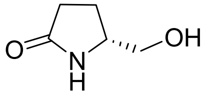
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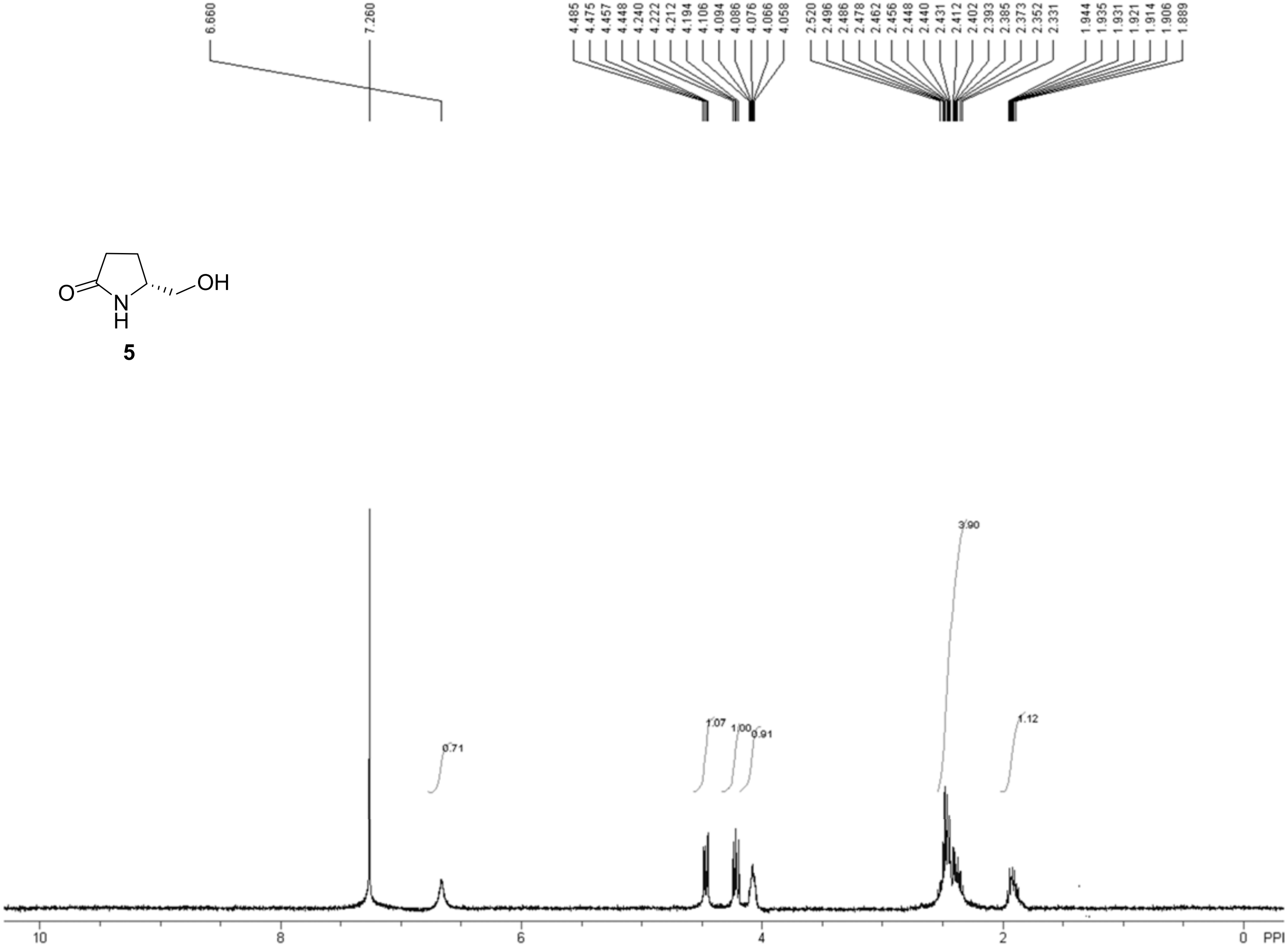
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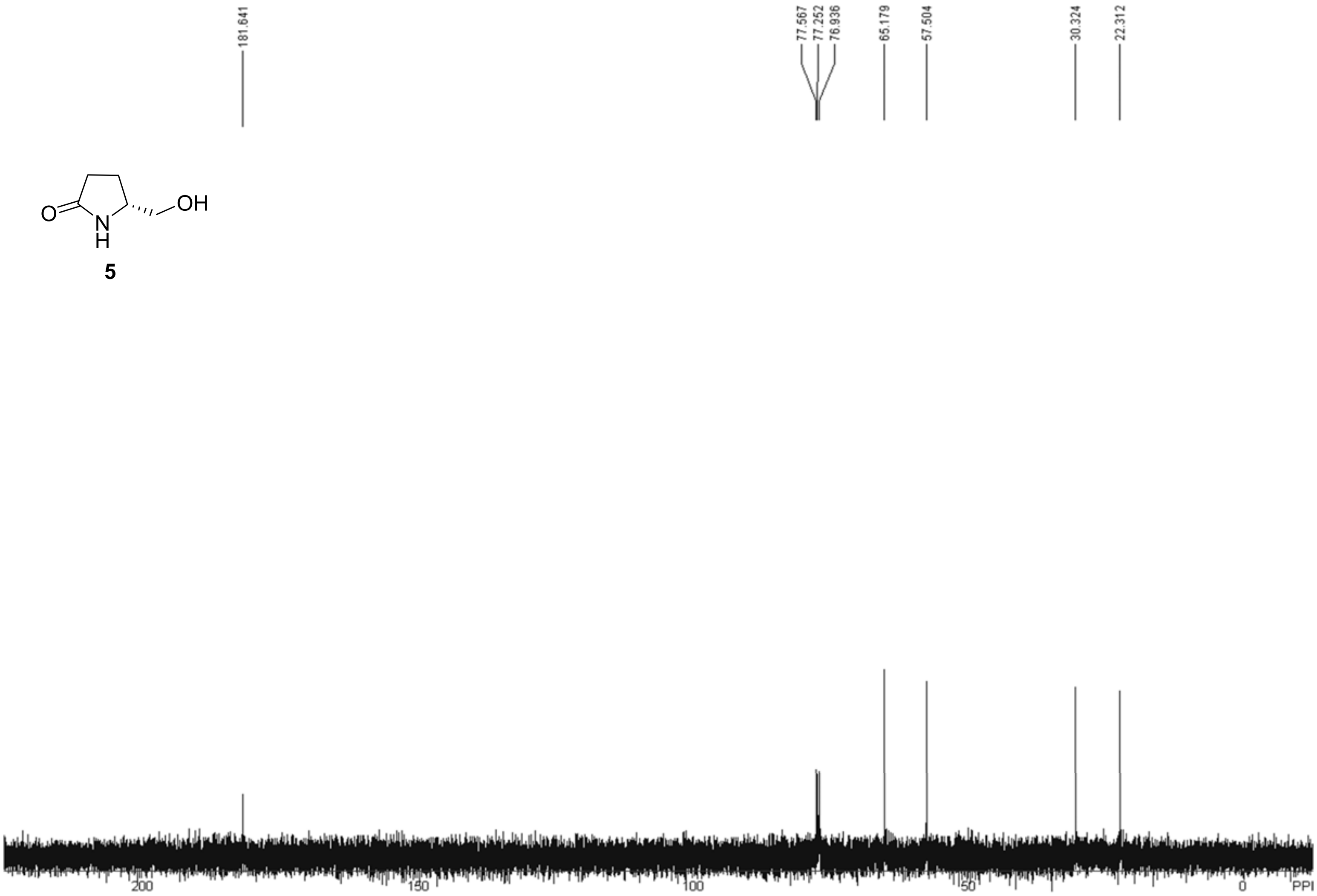
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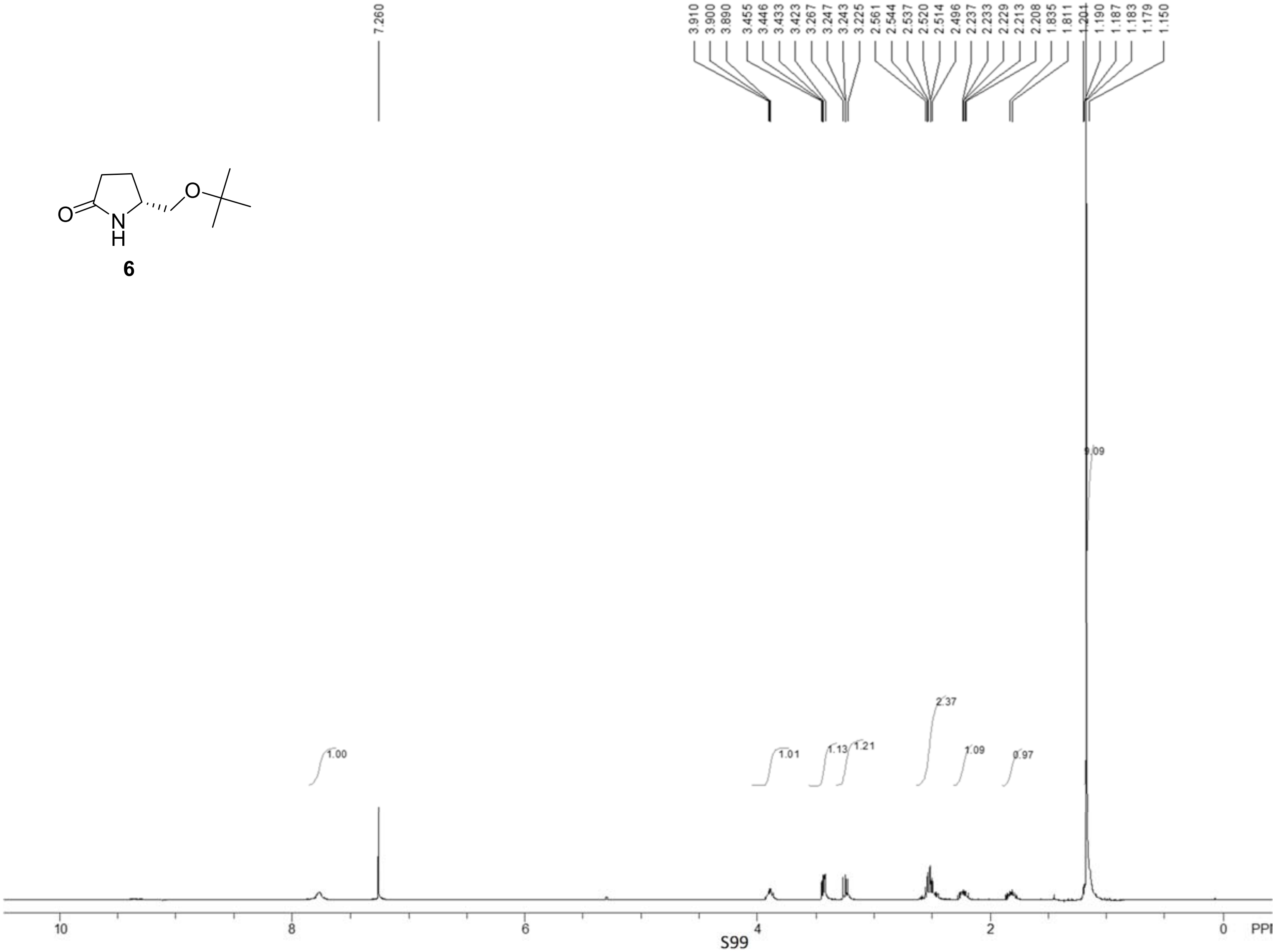
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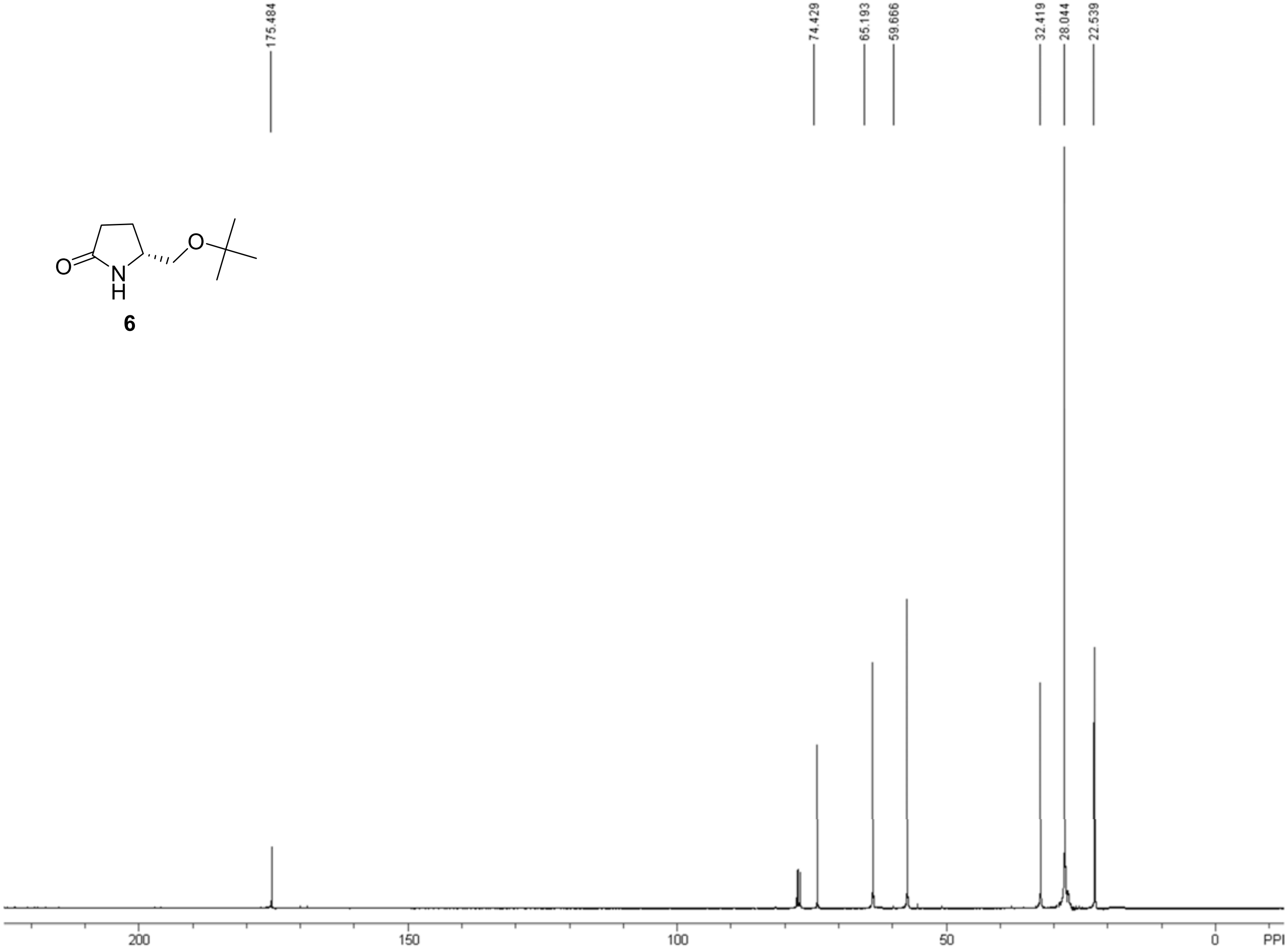
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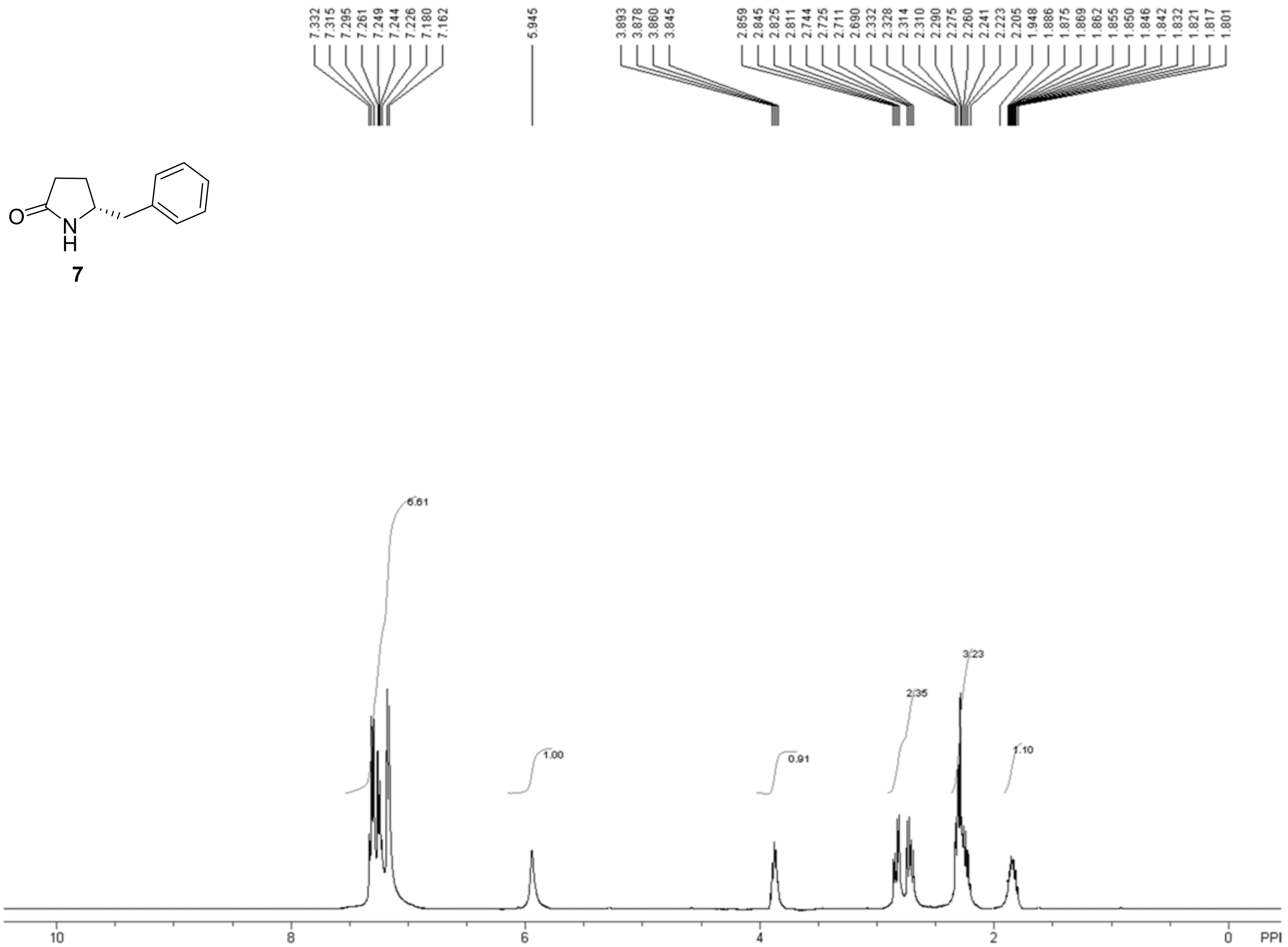
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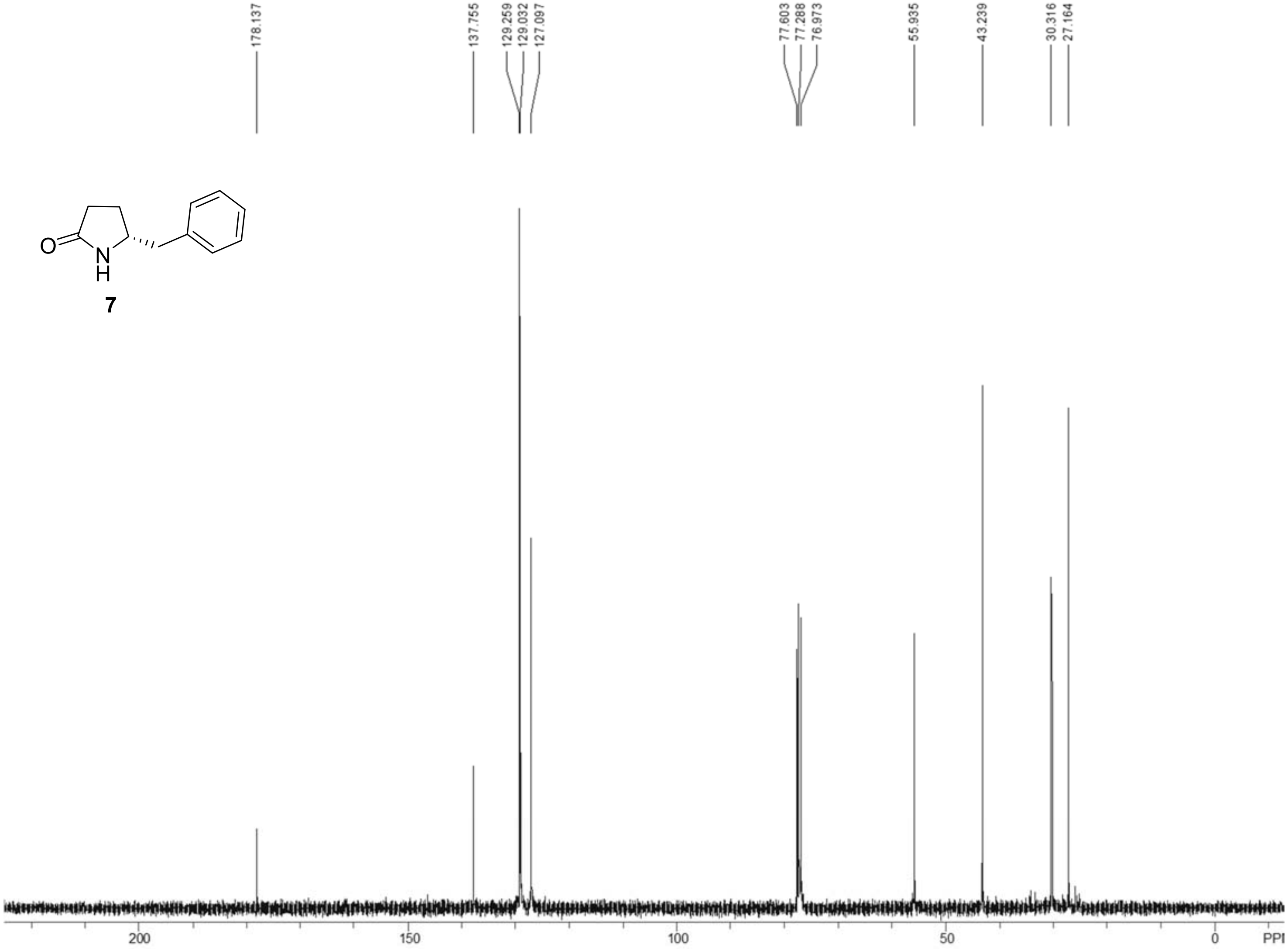
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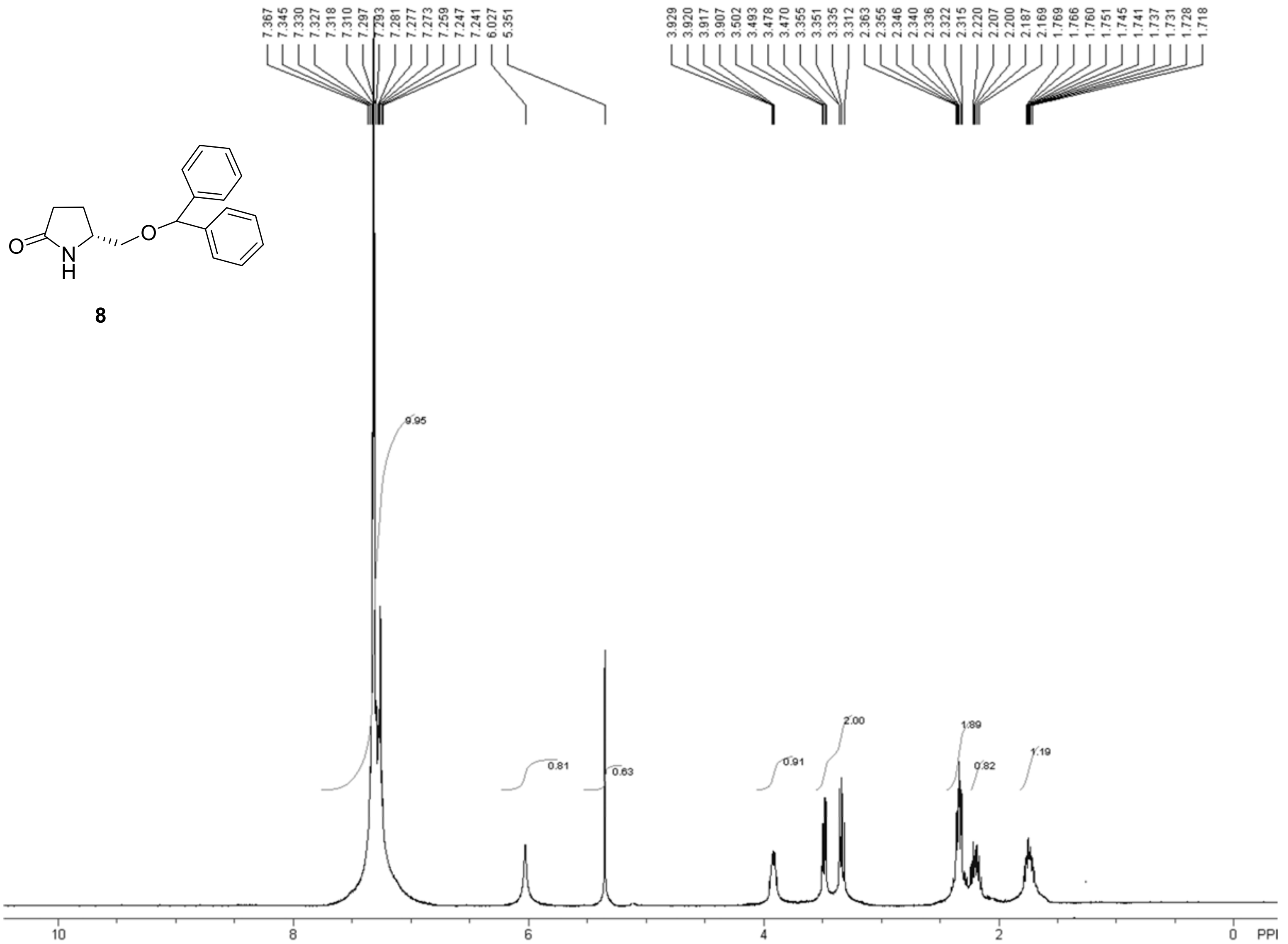
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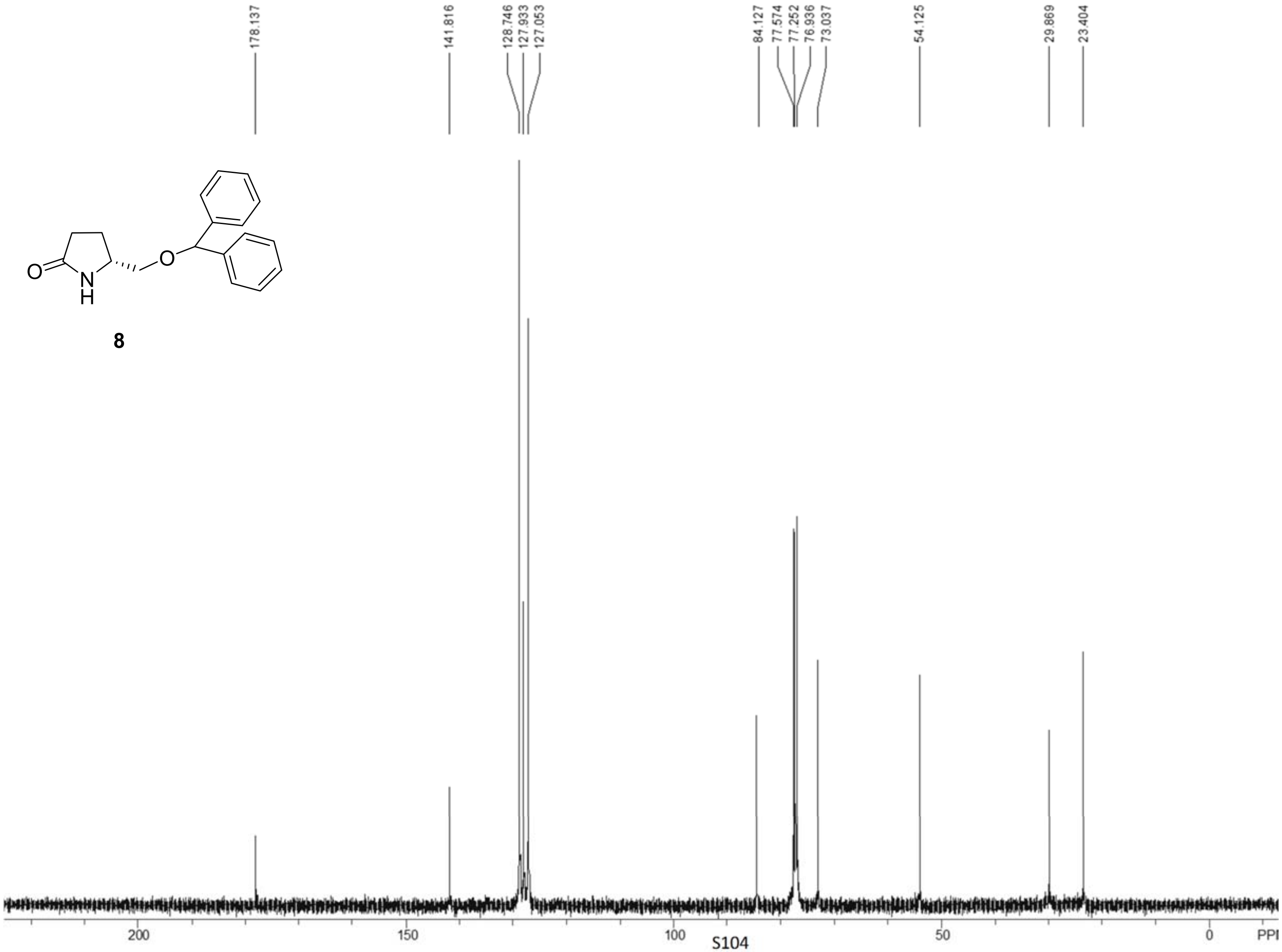

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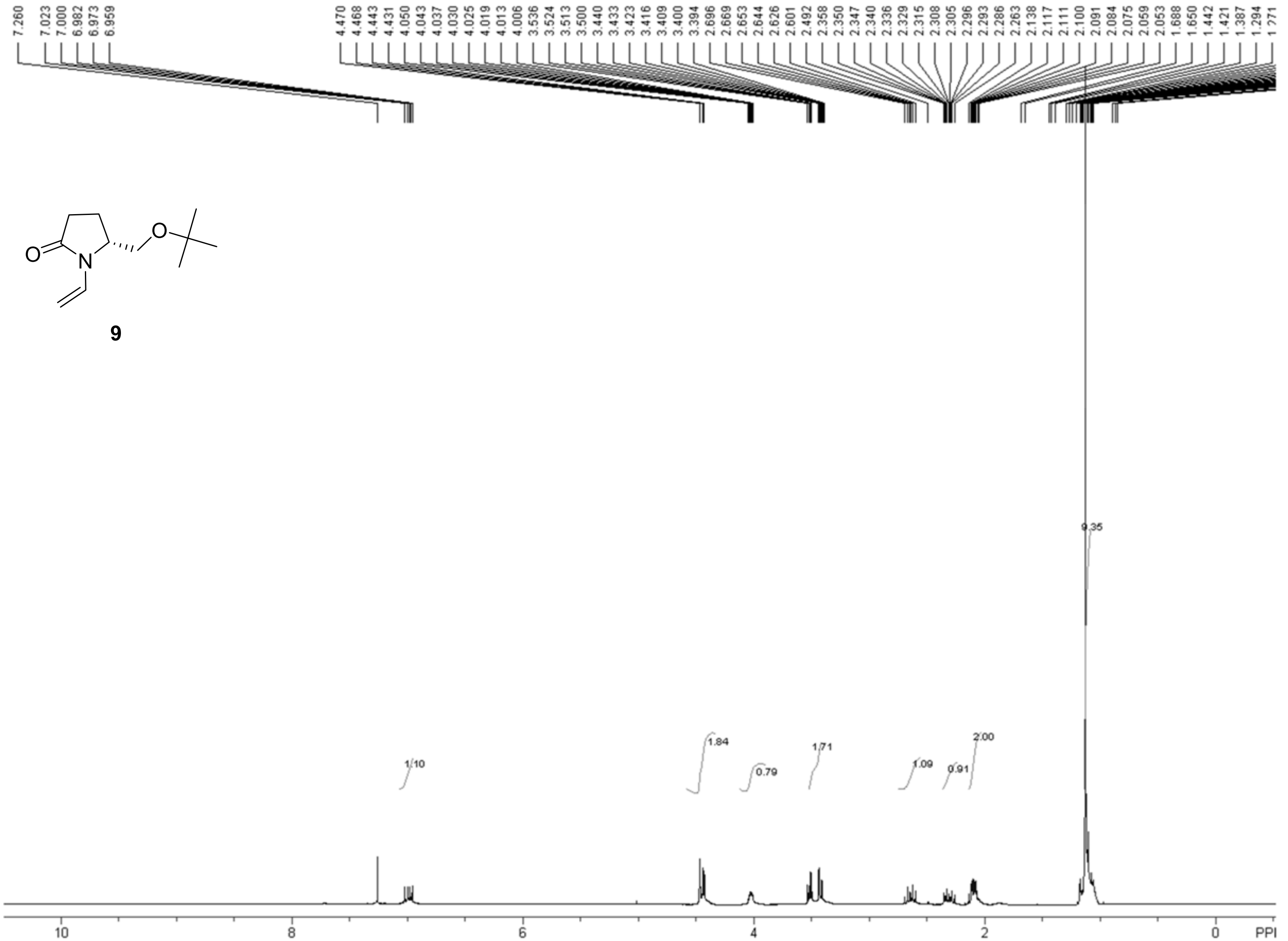
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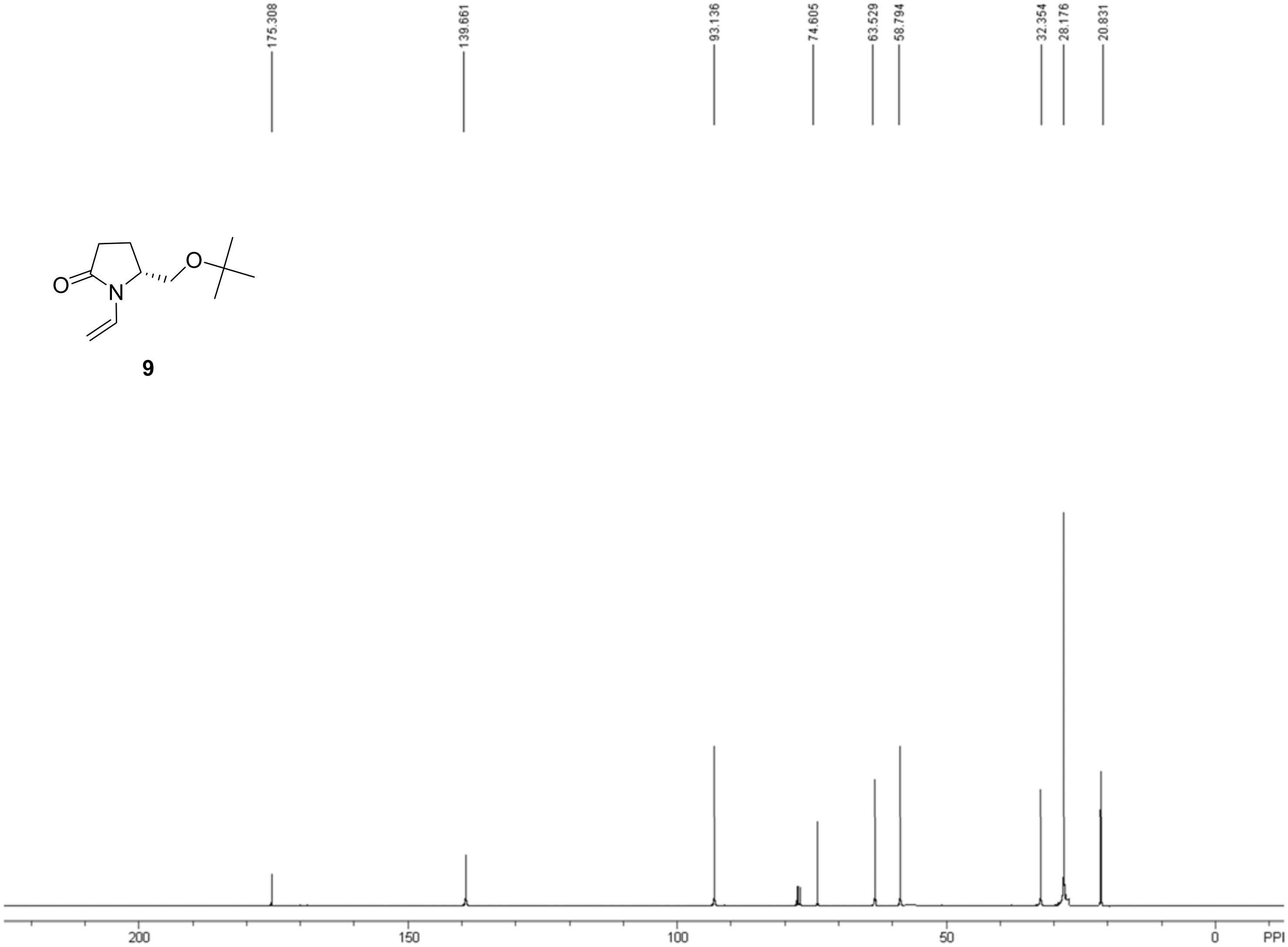

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PPI

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N

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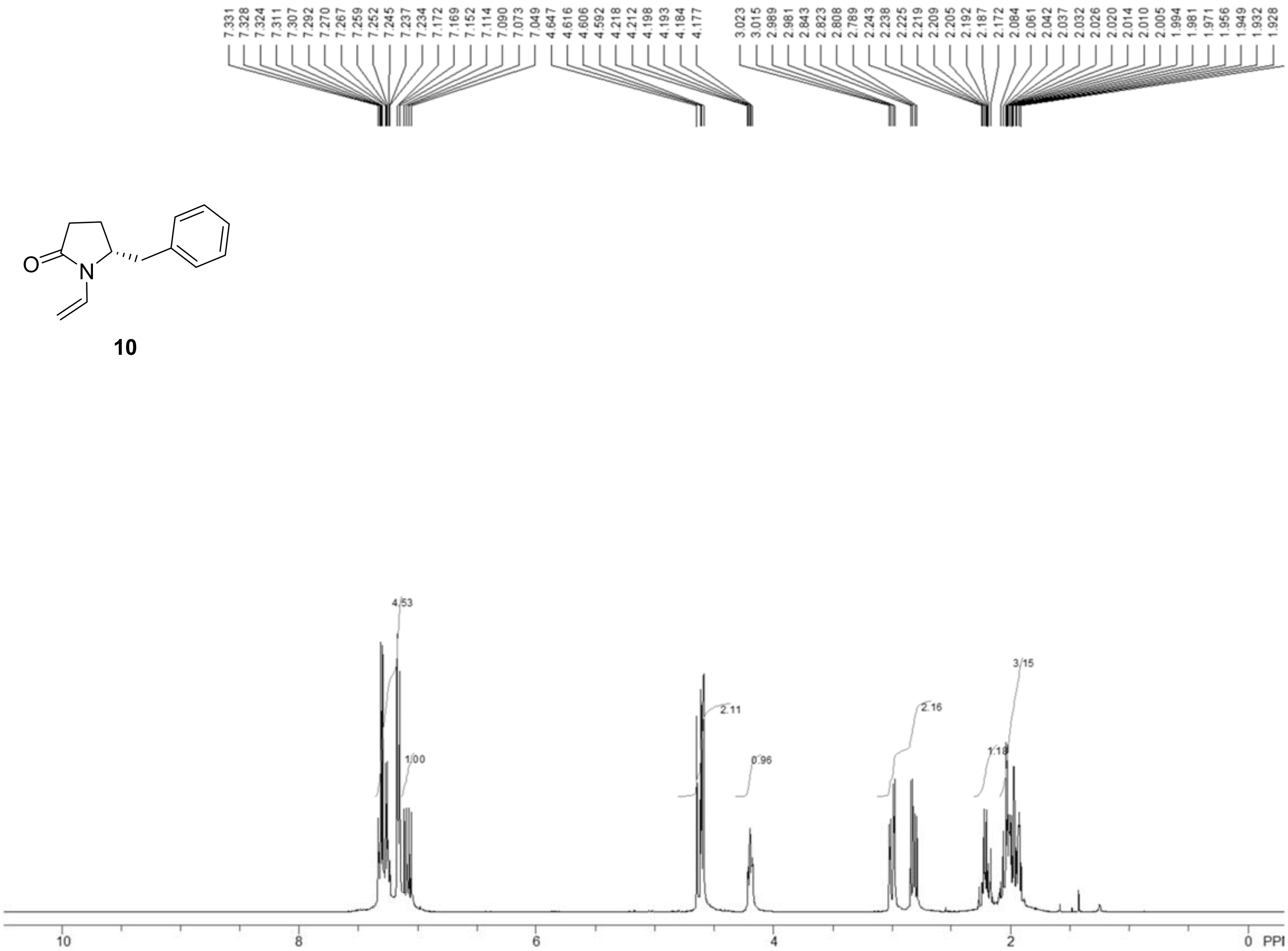
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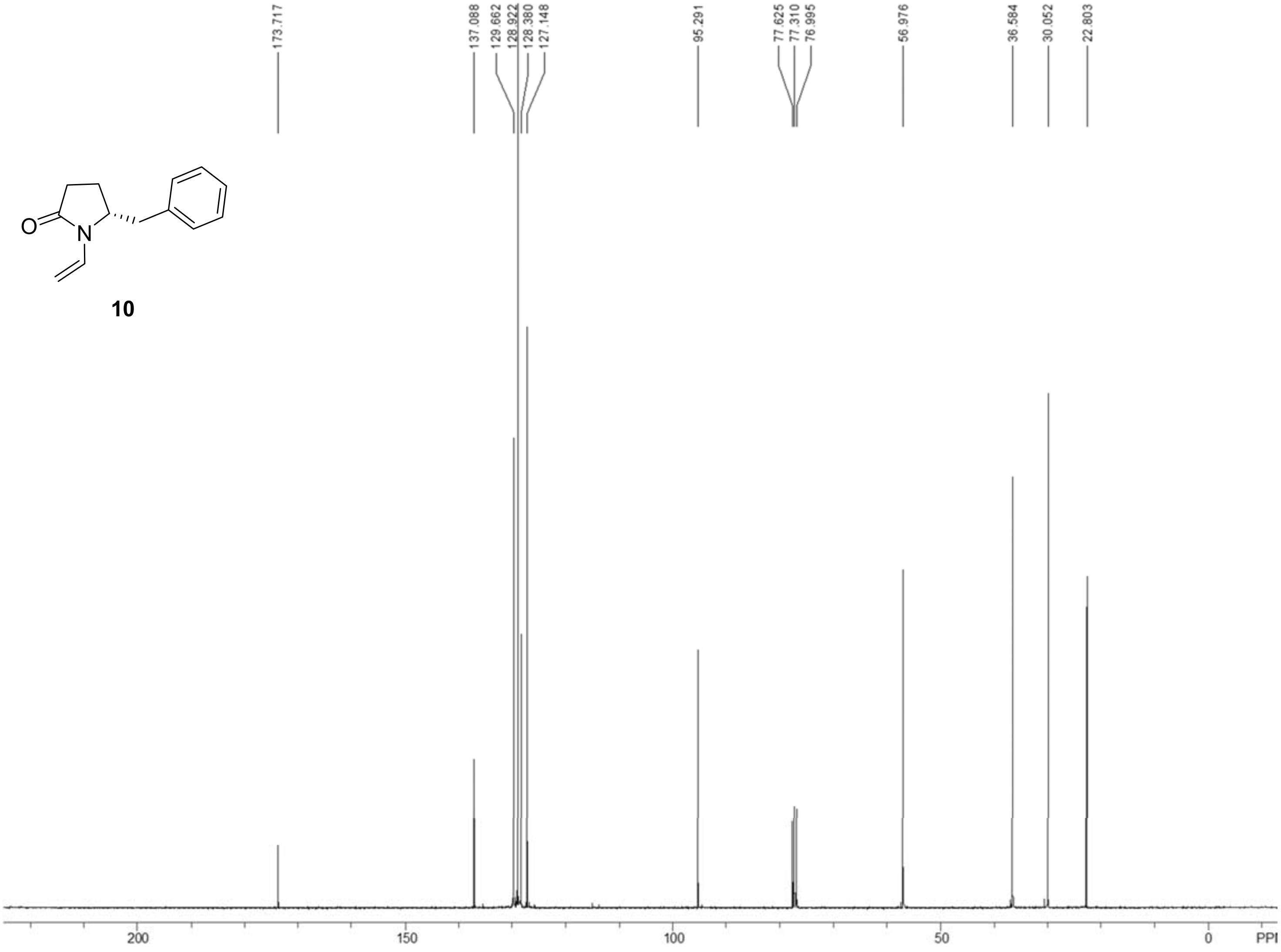
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PPM
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N

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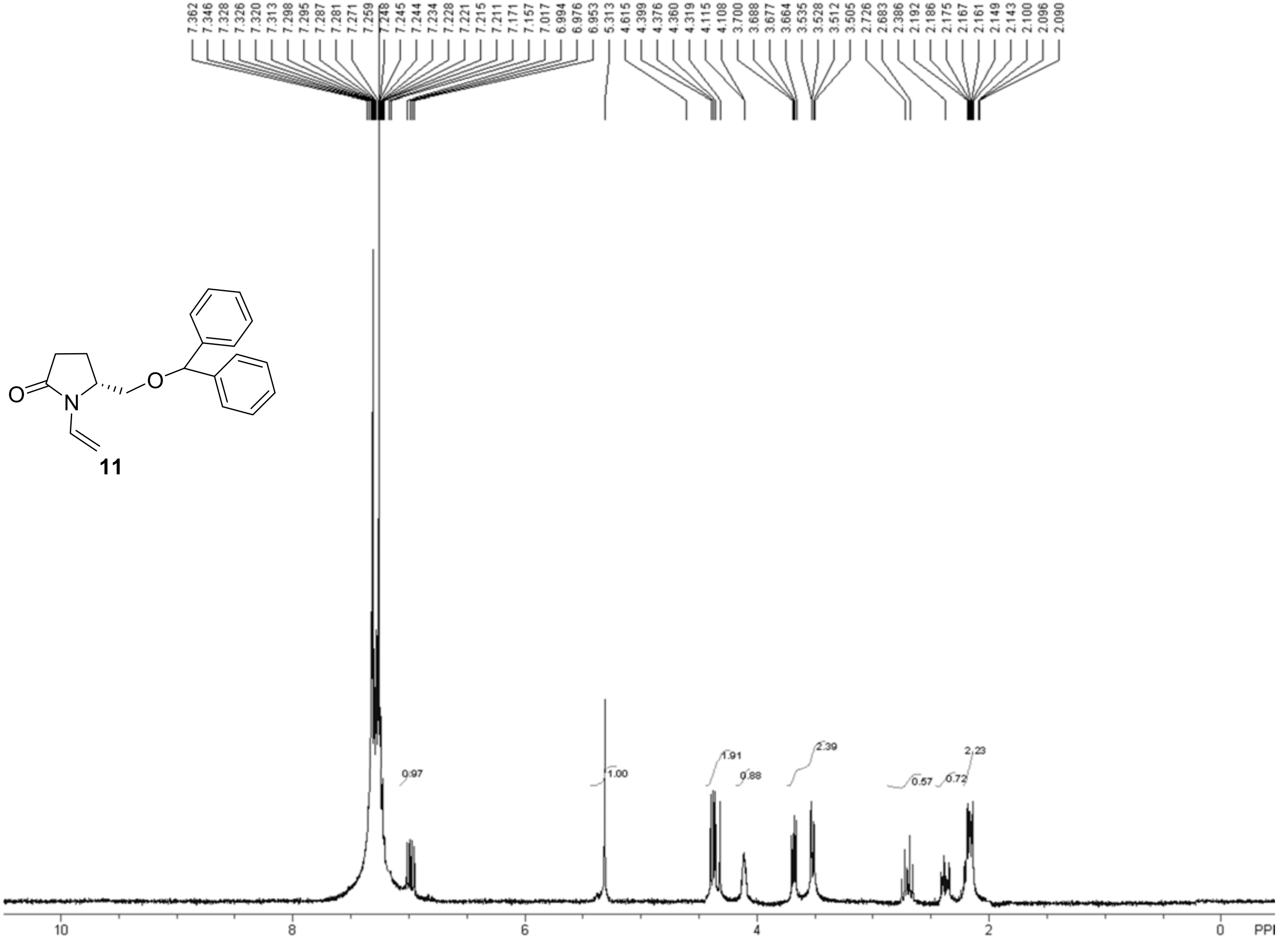

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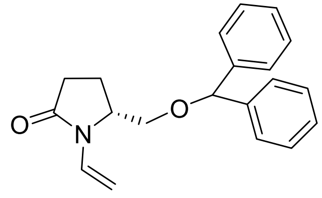
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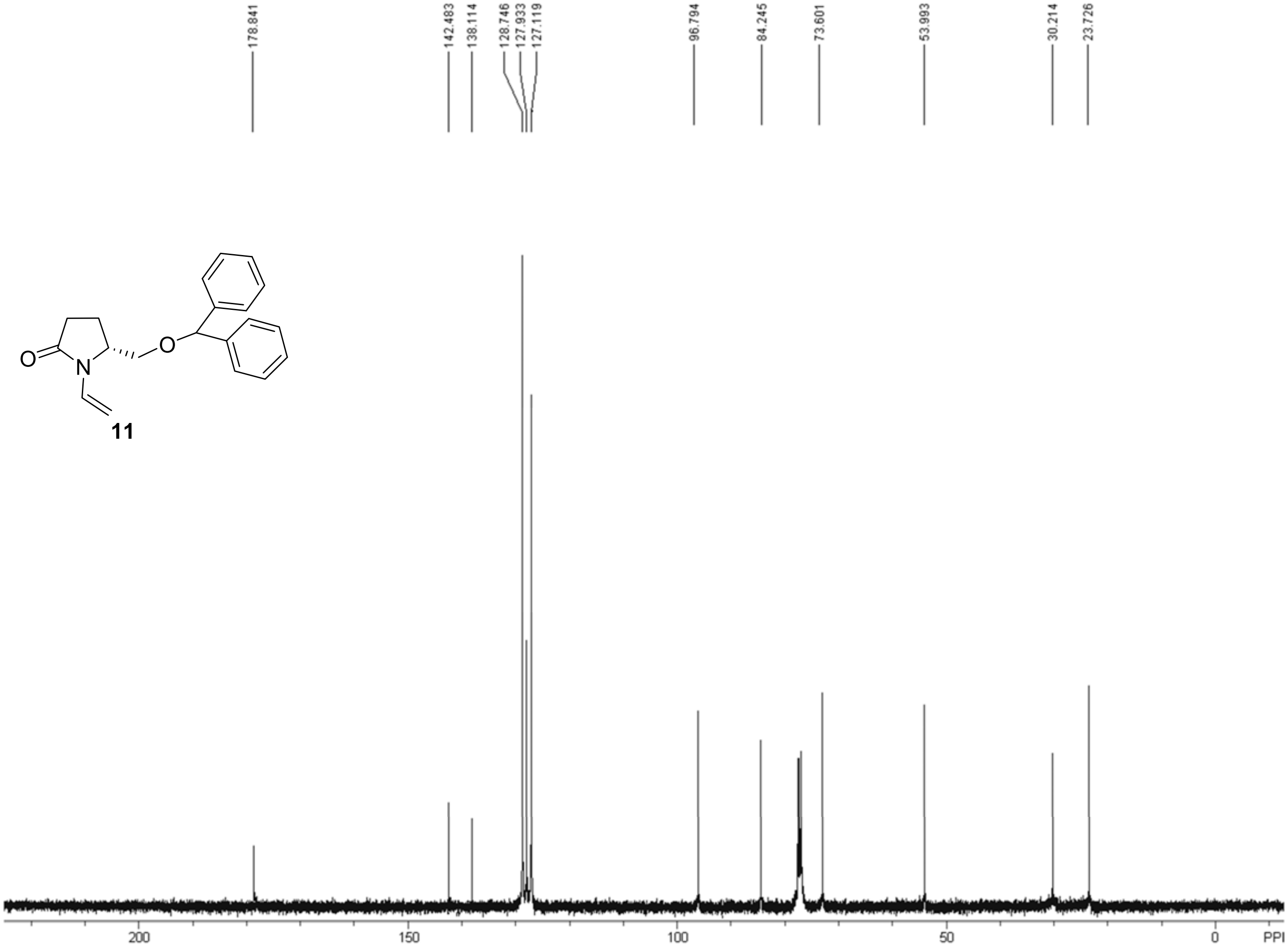
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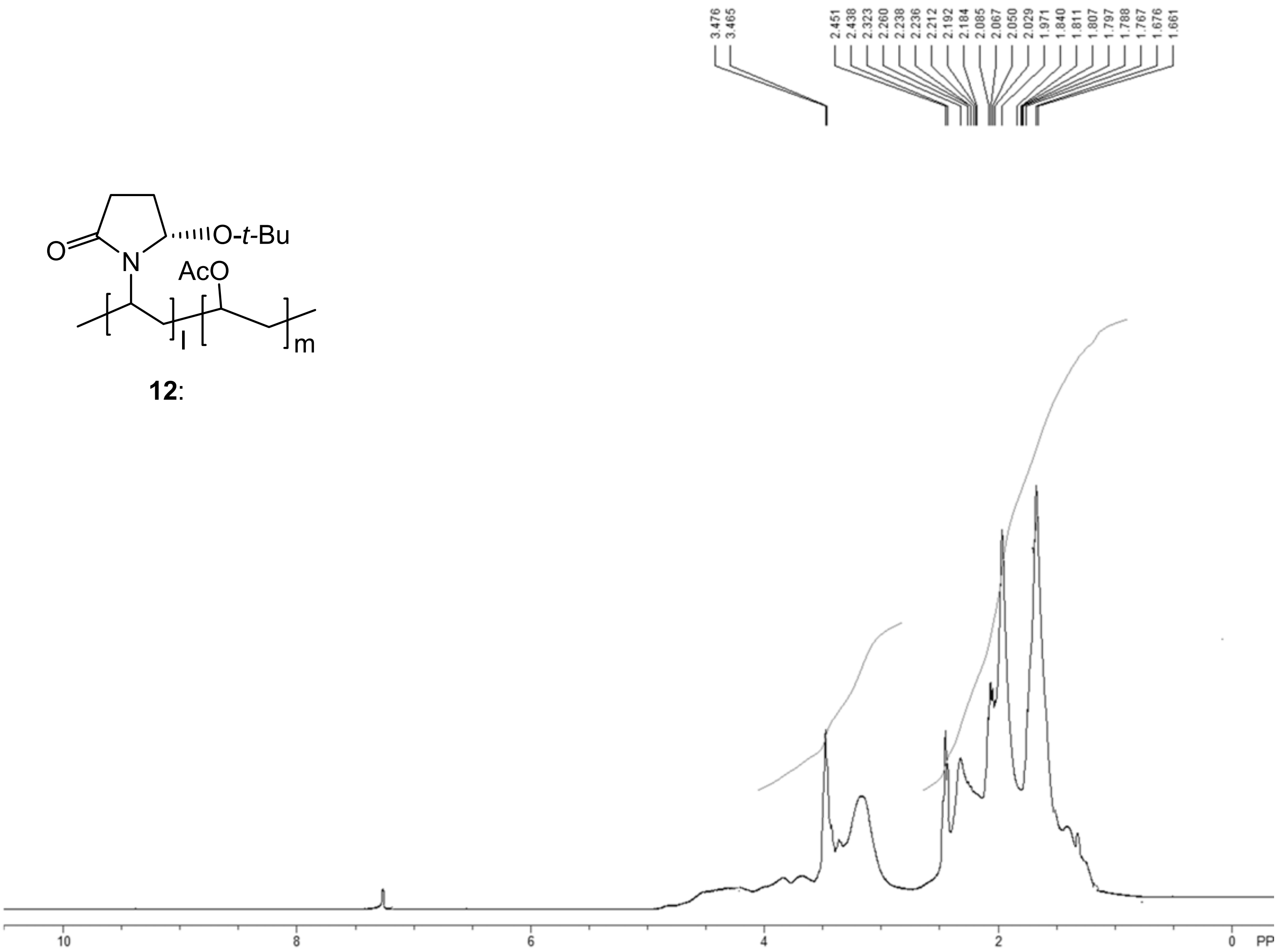
PPI


O-t-Bu
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AcO
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m

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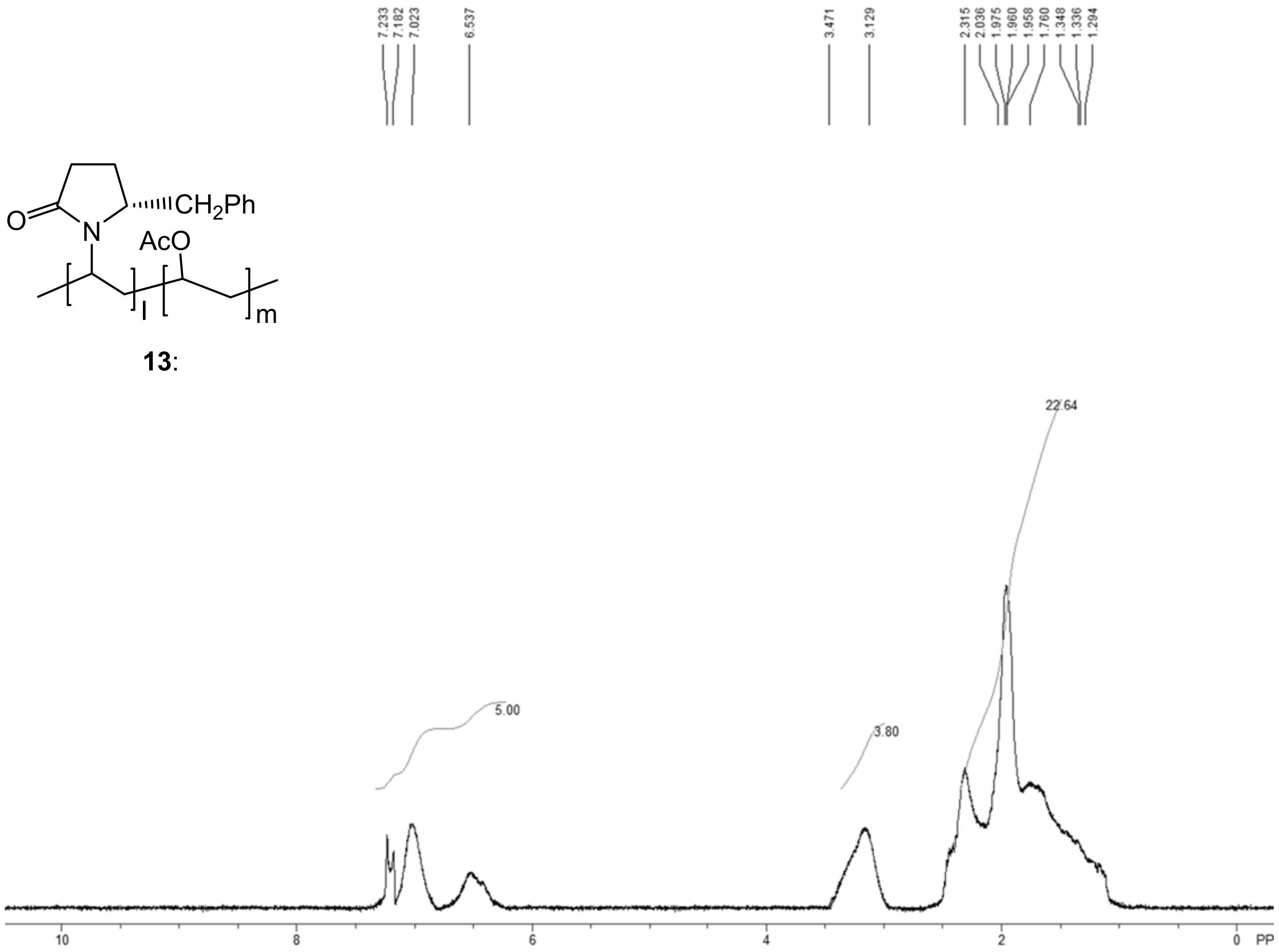
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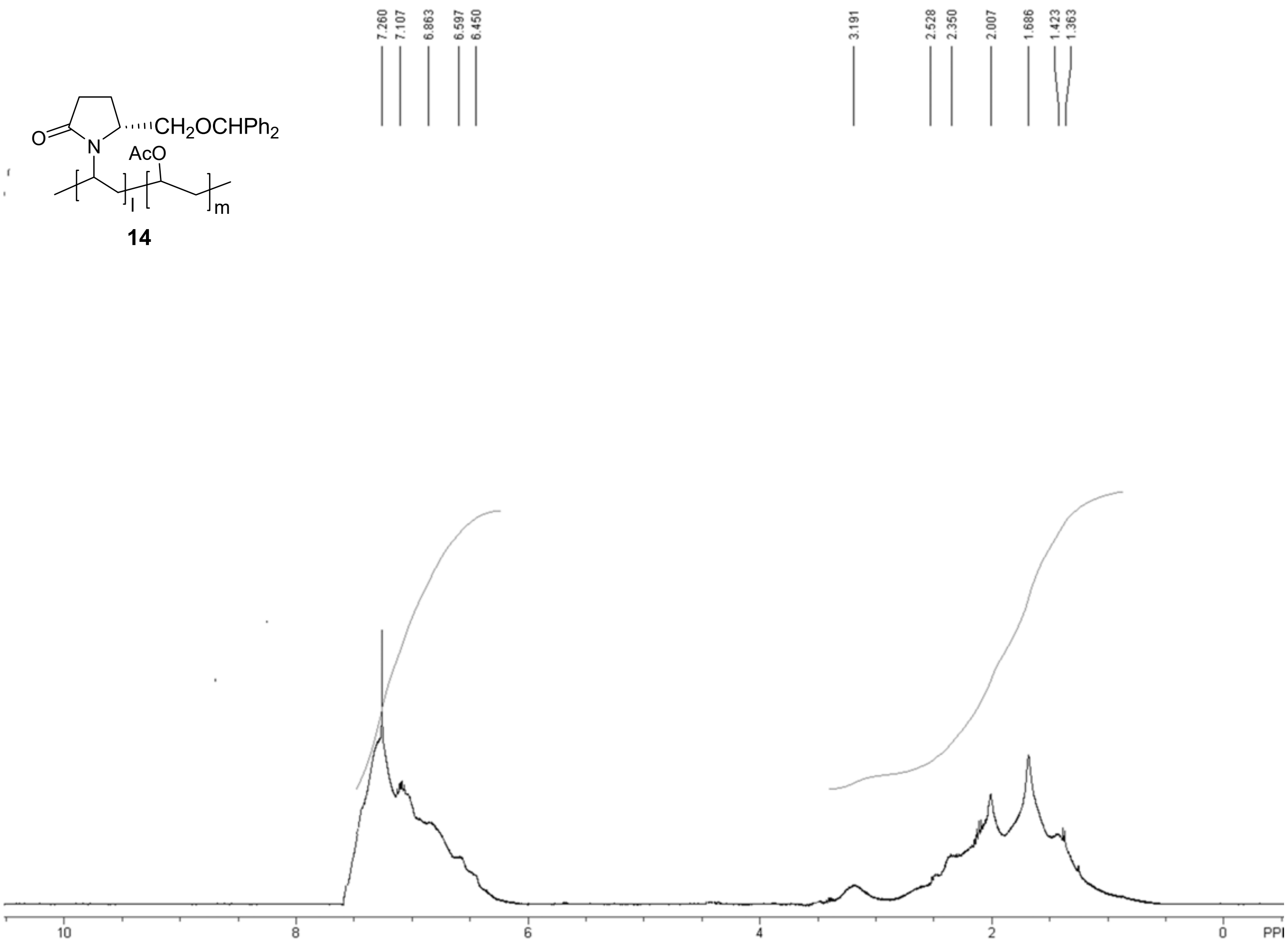
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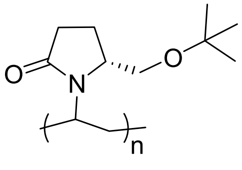
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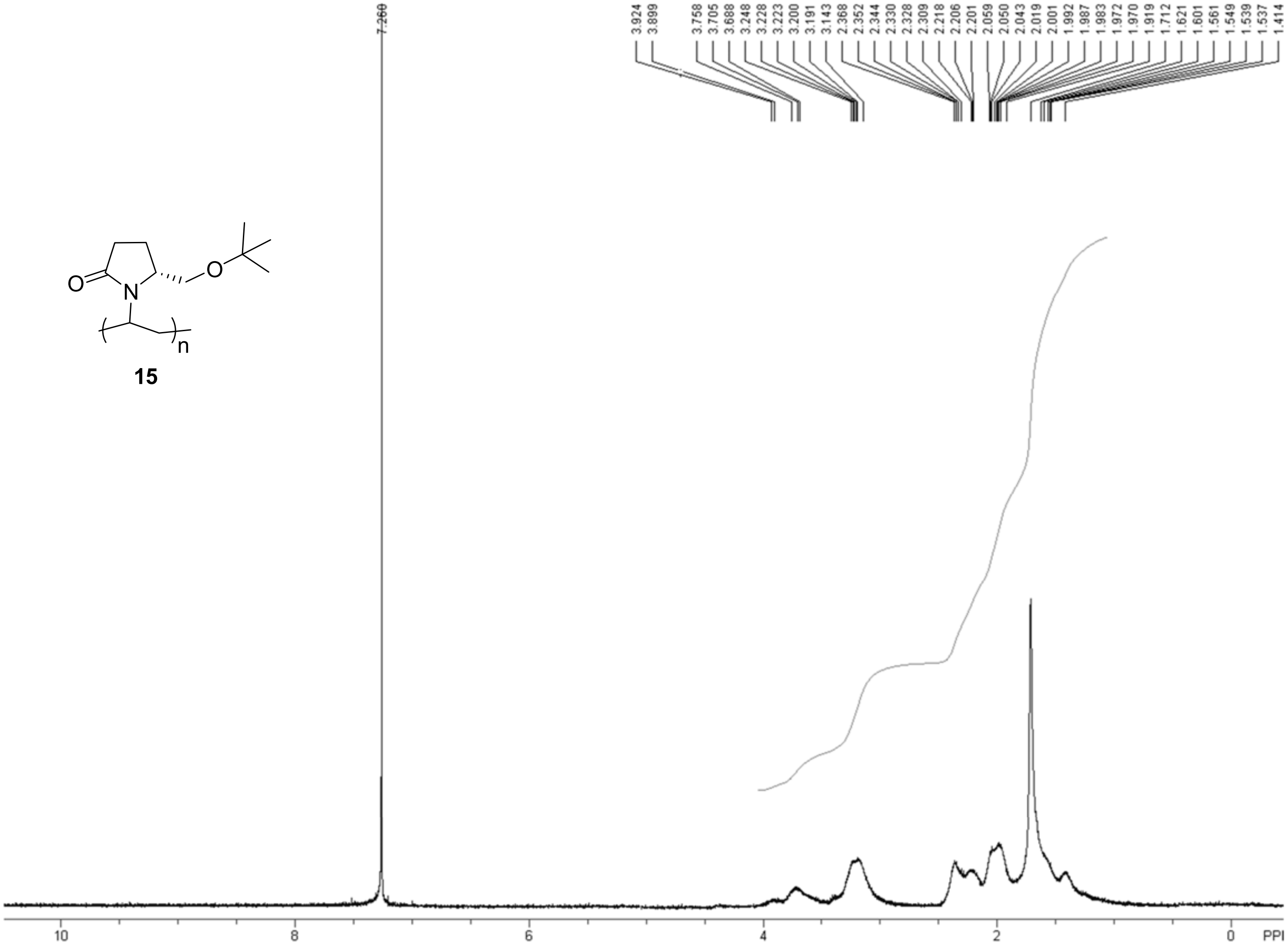
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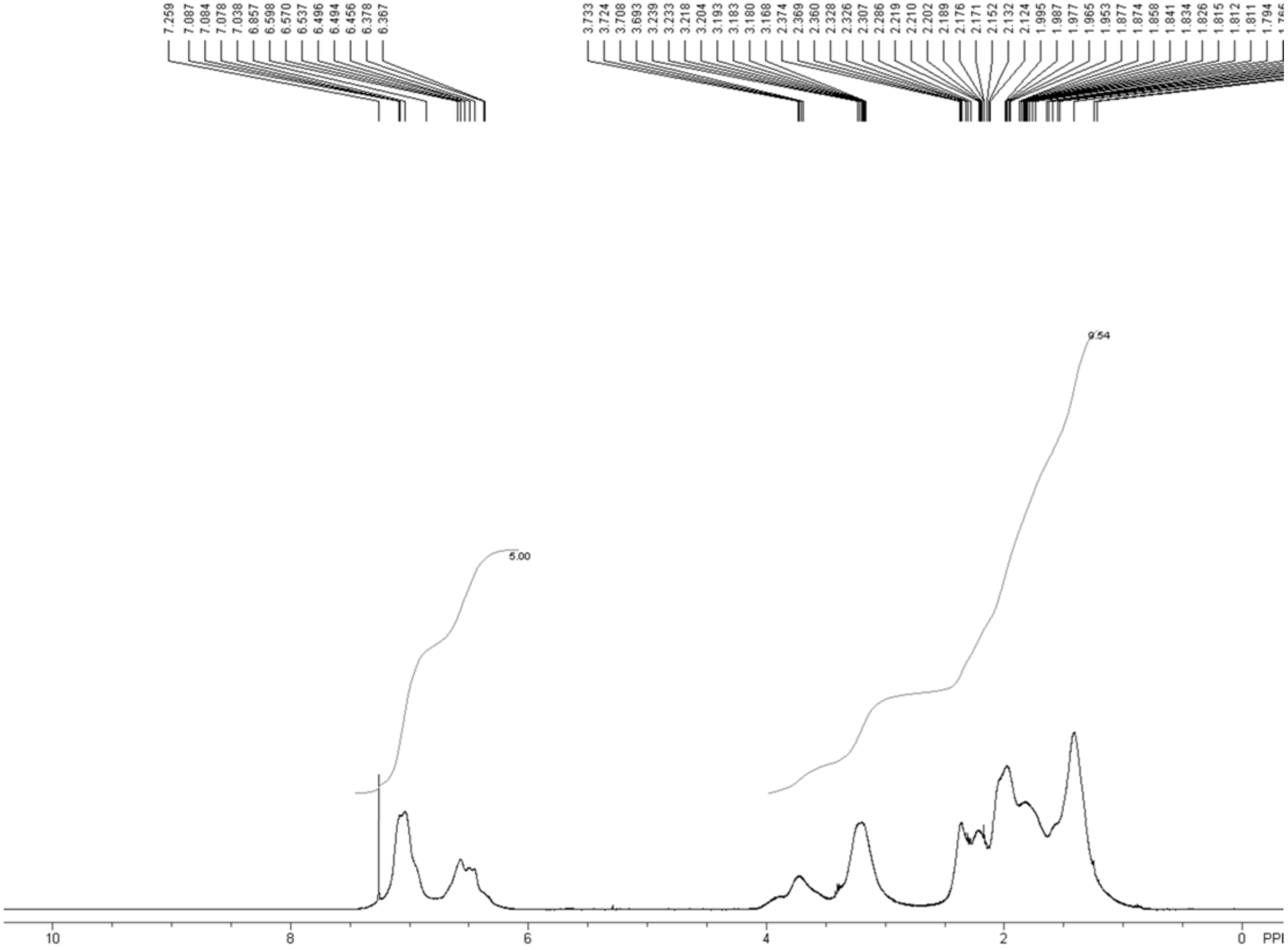
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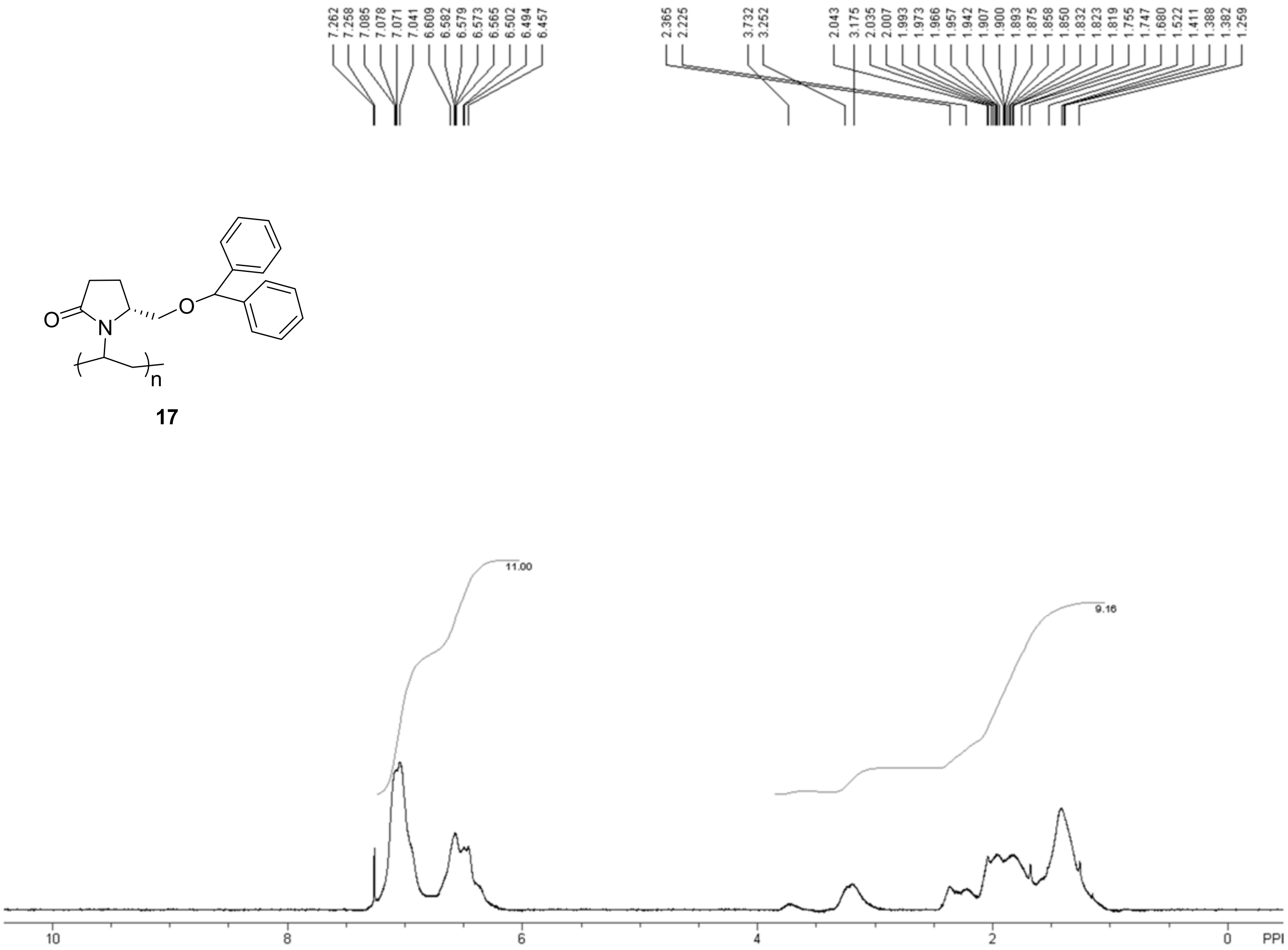
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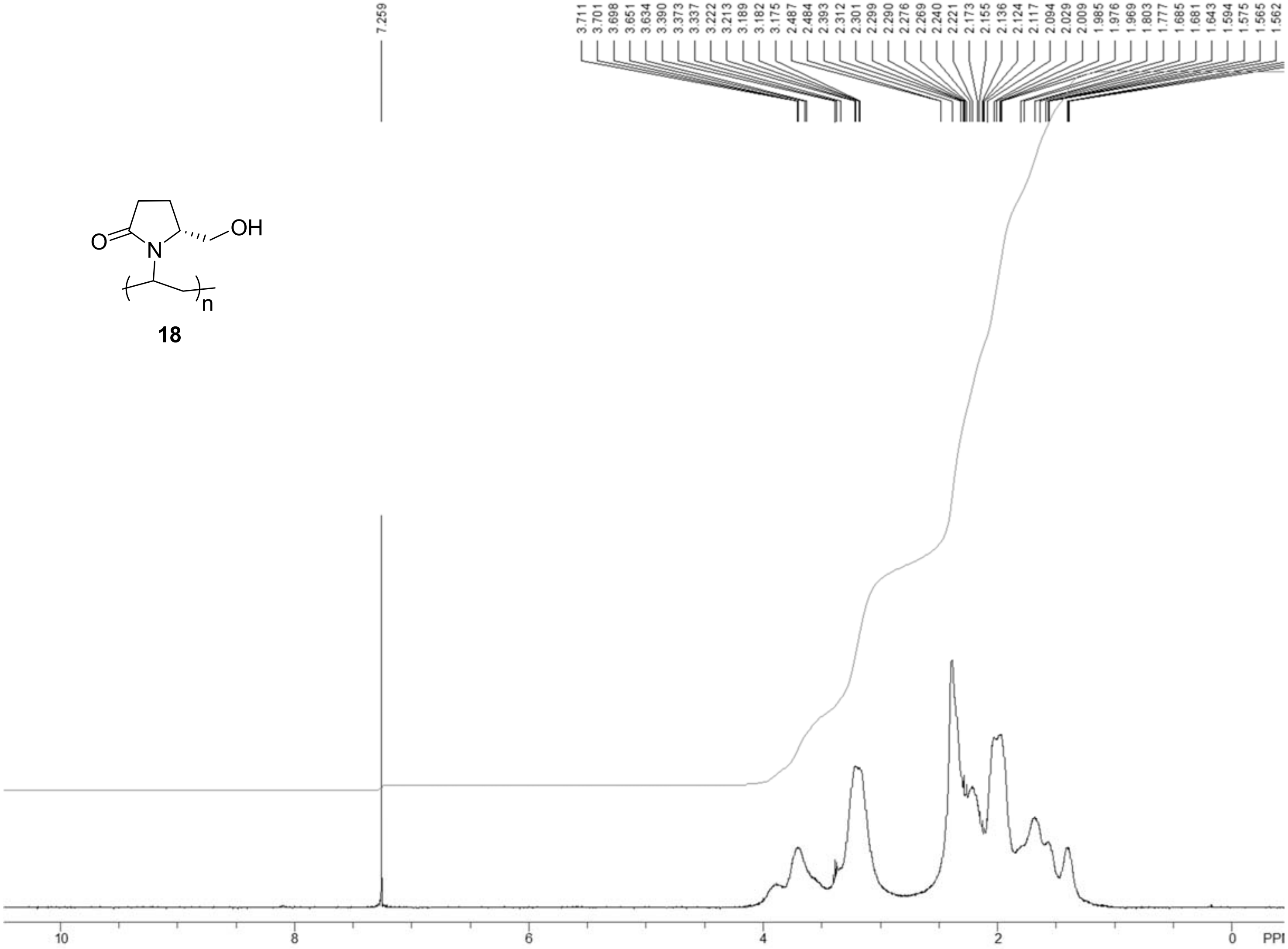

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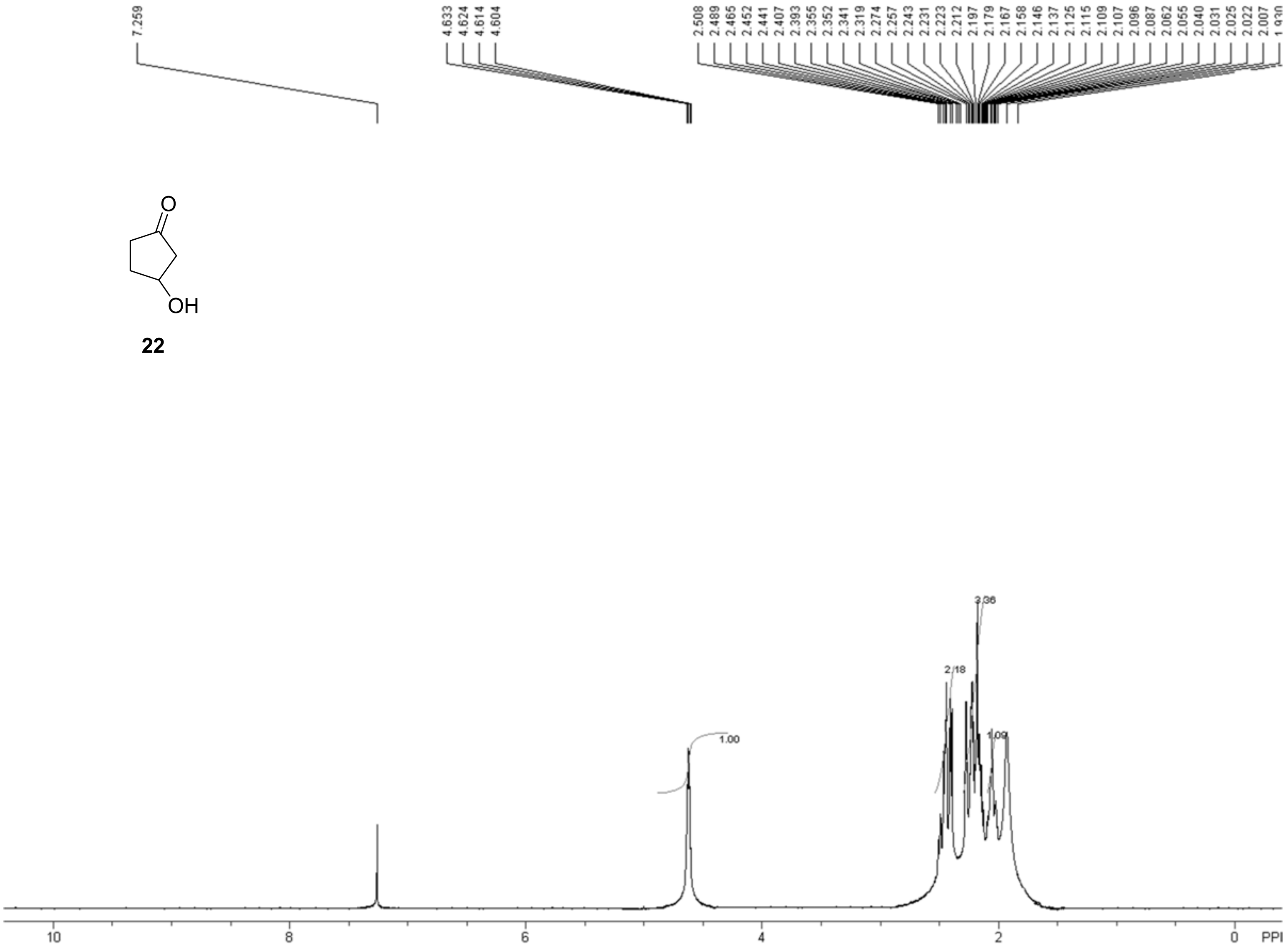
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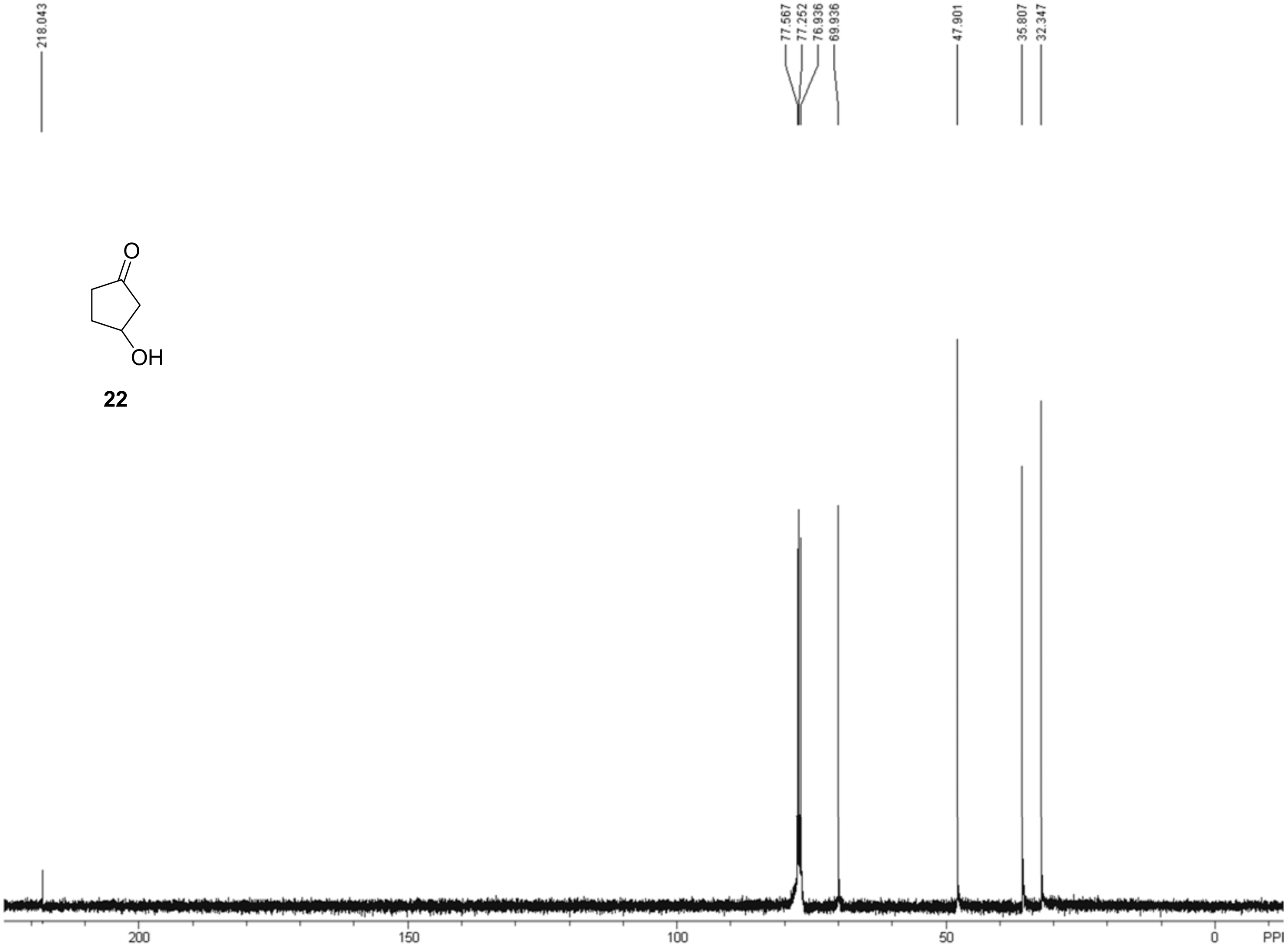
22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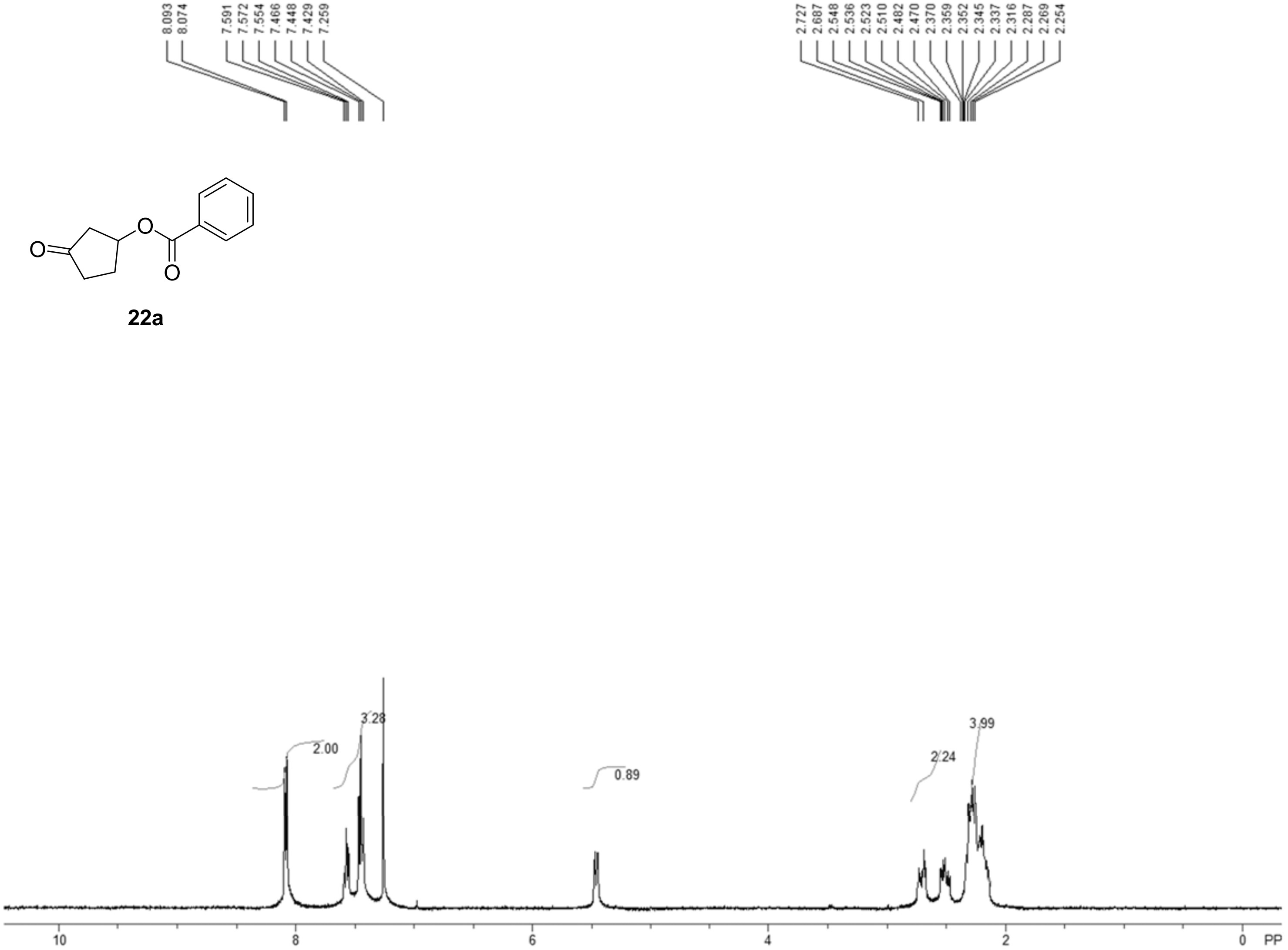
PPM

22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8.074
7.591
7.572
7.554
7.466
7.448
7.429
7.259
2.727
2.687
2.548
2.536
2.523
2.510
2.482
2.470
2.370
2.359
2.352
2.345
2.337
2.316
2.287
2.269
2.254
O
O
O
2.00
3.28
0.89
2.24
3.99
10
8
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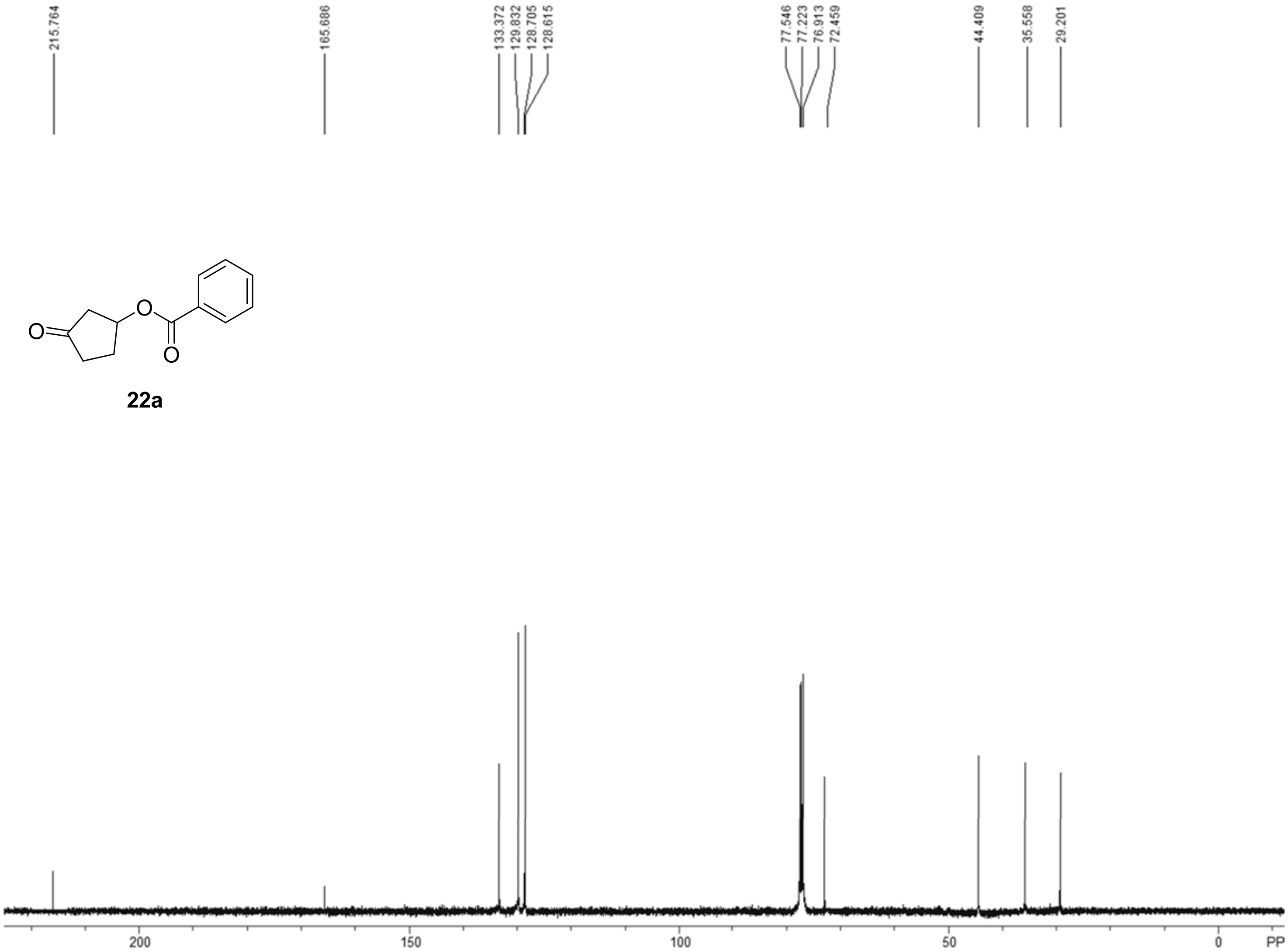
4
2
0
PP

22a



22a

215.764
165.686
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129.832
128.705
128.615
77.546
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72.459
44.409
35.558
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O
O
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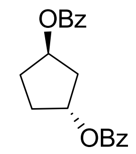
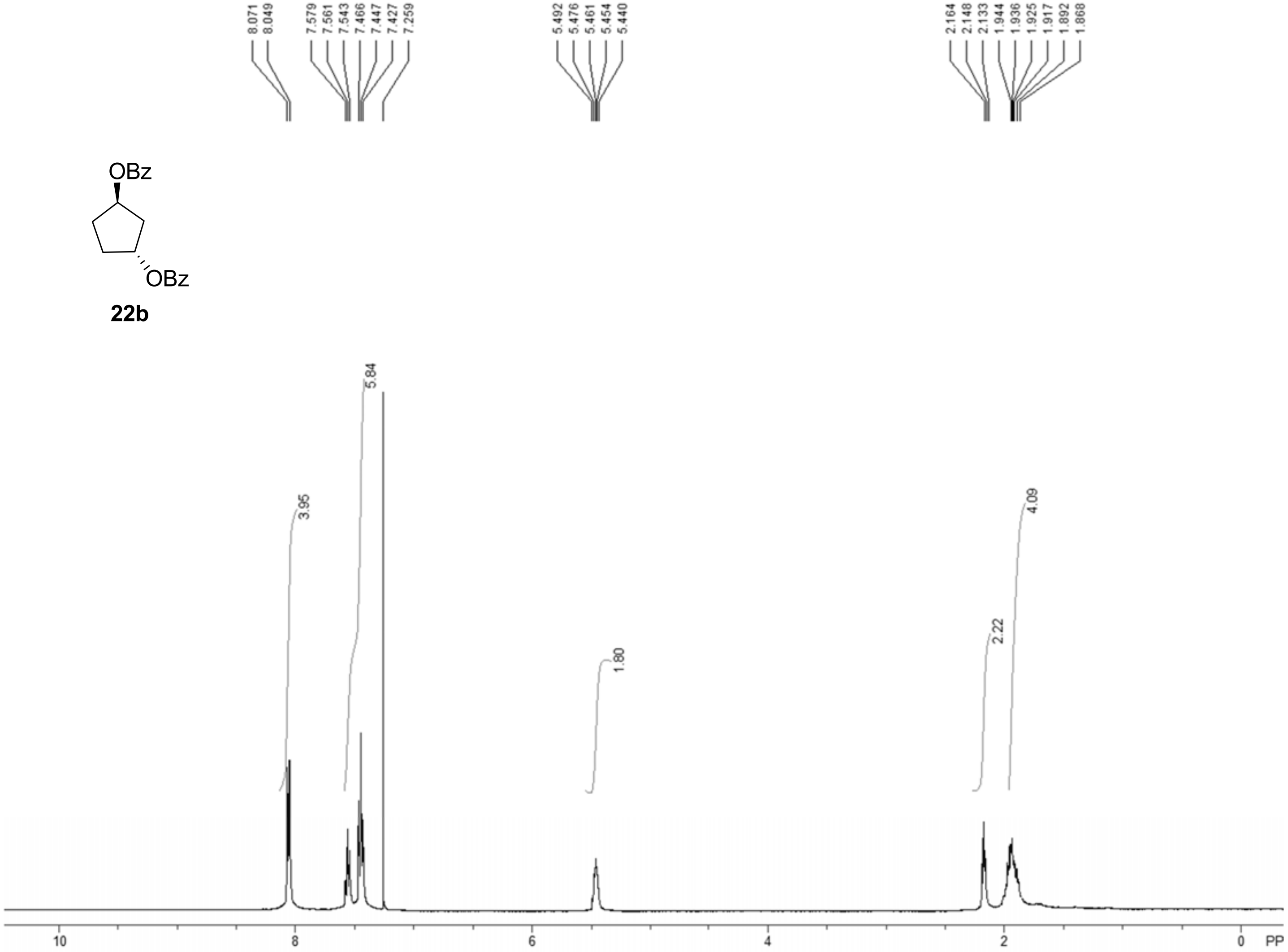
PP


OBz
OBz

22b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7.561
7.543
7.466
7.447
7.427
7.259
5.492
5.476
5.461
5.454
5.440
2.164
2.148
2.133
1.944
1.936
1.925
1.917
1.892
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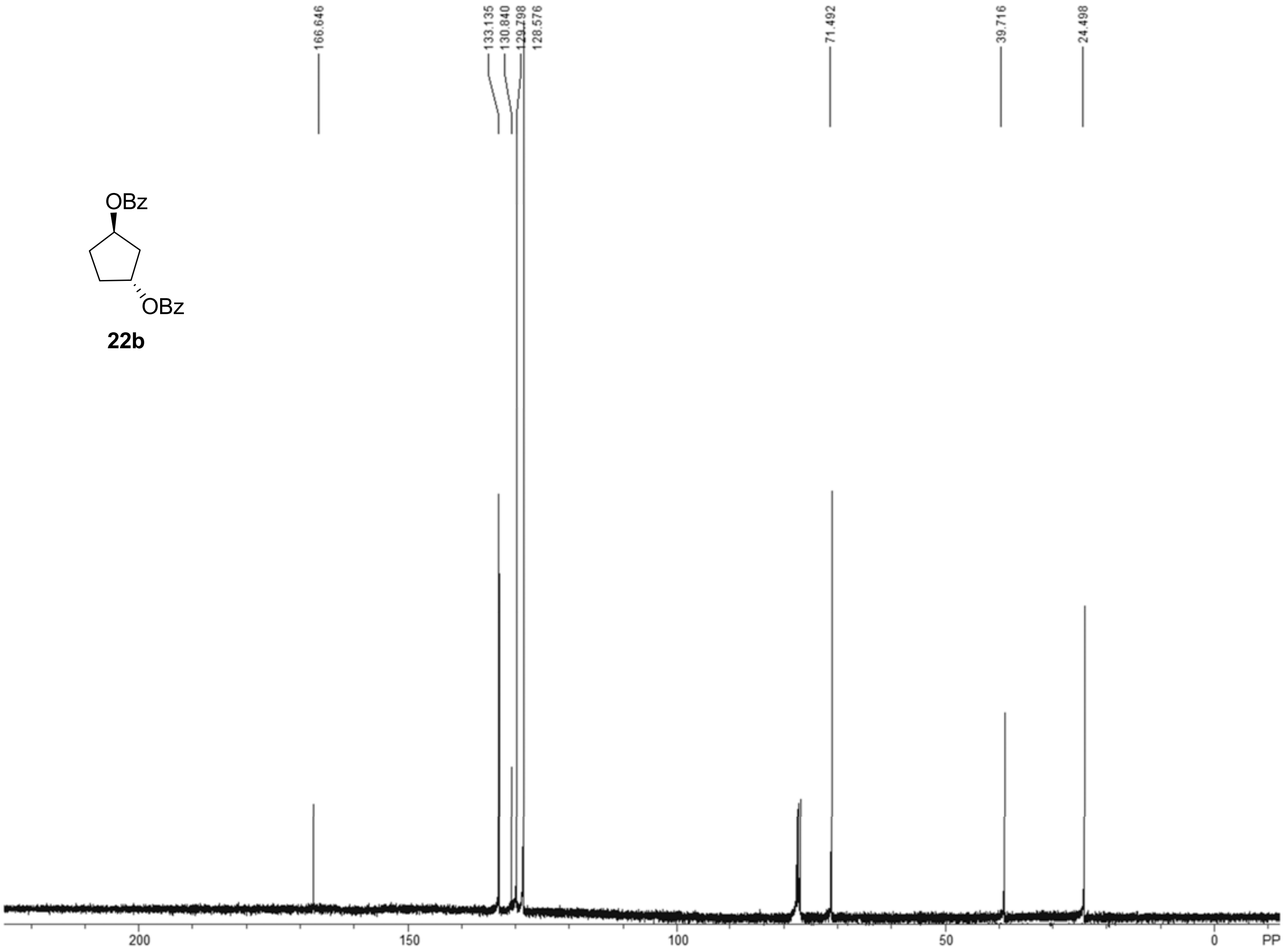
5.84
1.80
2.22
4.09
10
8
6
4
2
0
PP


OBz
OBz

22b

166.646
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71.492
39.716
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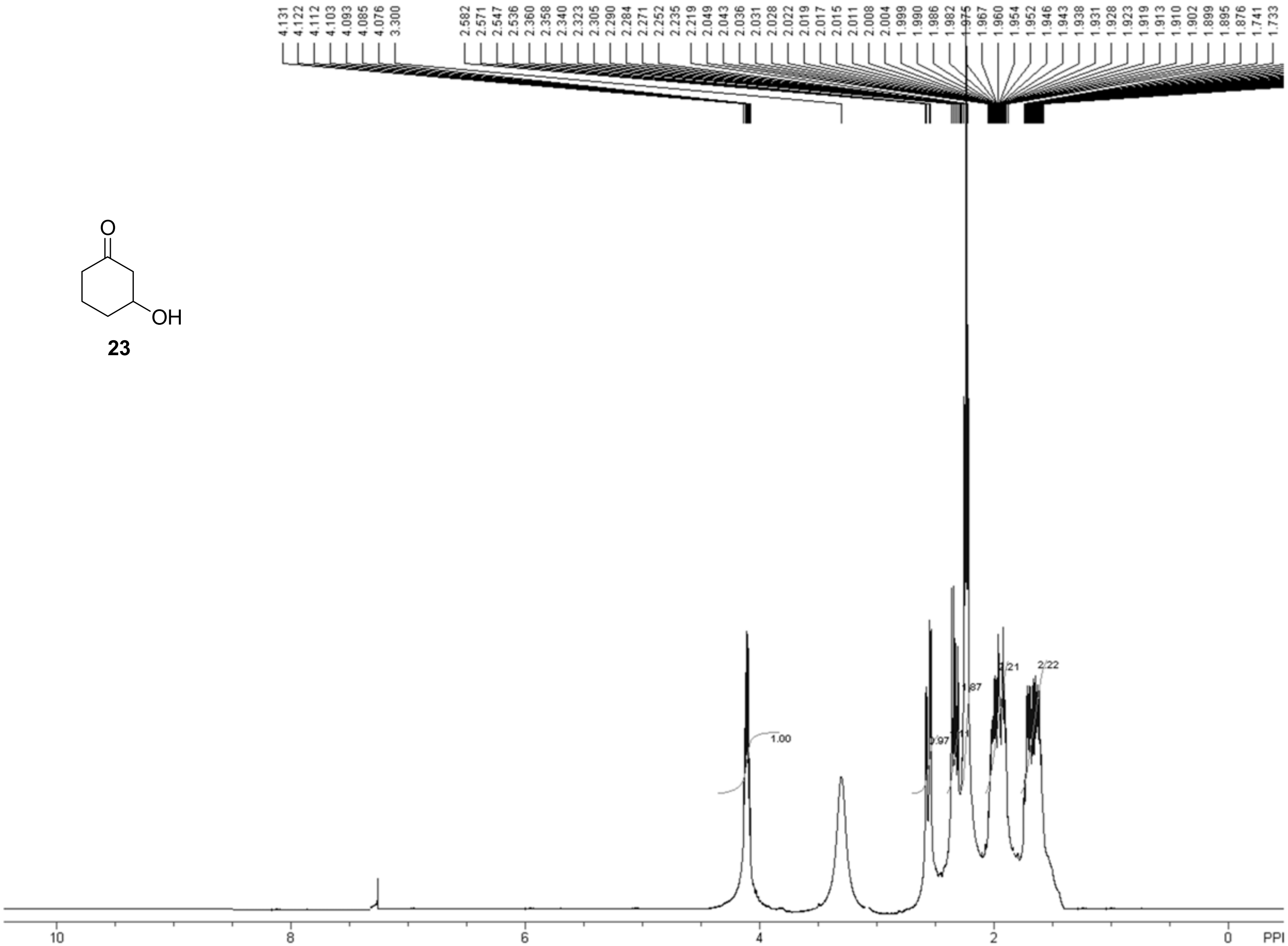
150
100
50
0
PP

O
OH

23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4.112
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4.085
4.076
3.300
2.582
2.571
2.547
2.536
2.360
2.358
2.340
2.323
2.305
2.290
2.284
2.271
2.252
2.235
2.219
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2.043
2.036
2.031
2.028
2.022
2.019
2.017
2.015
2.011
2.008
2.004
1.999
1.990
1.986
1.982
1.975
1.967
1.960
1.954
1.952
1.946
1.943
1.938
1.931
1.928
1.923
1.919
1.913
1.910
1.902
1.899
1.895
1.876
1.741
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0.97
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4
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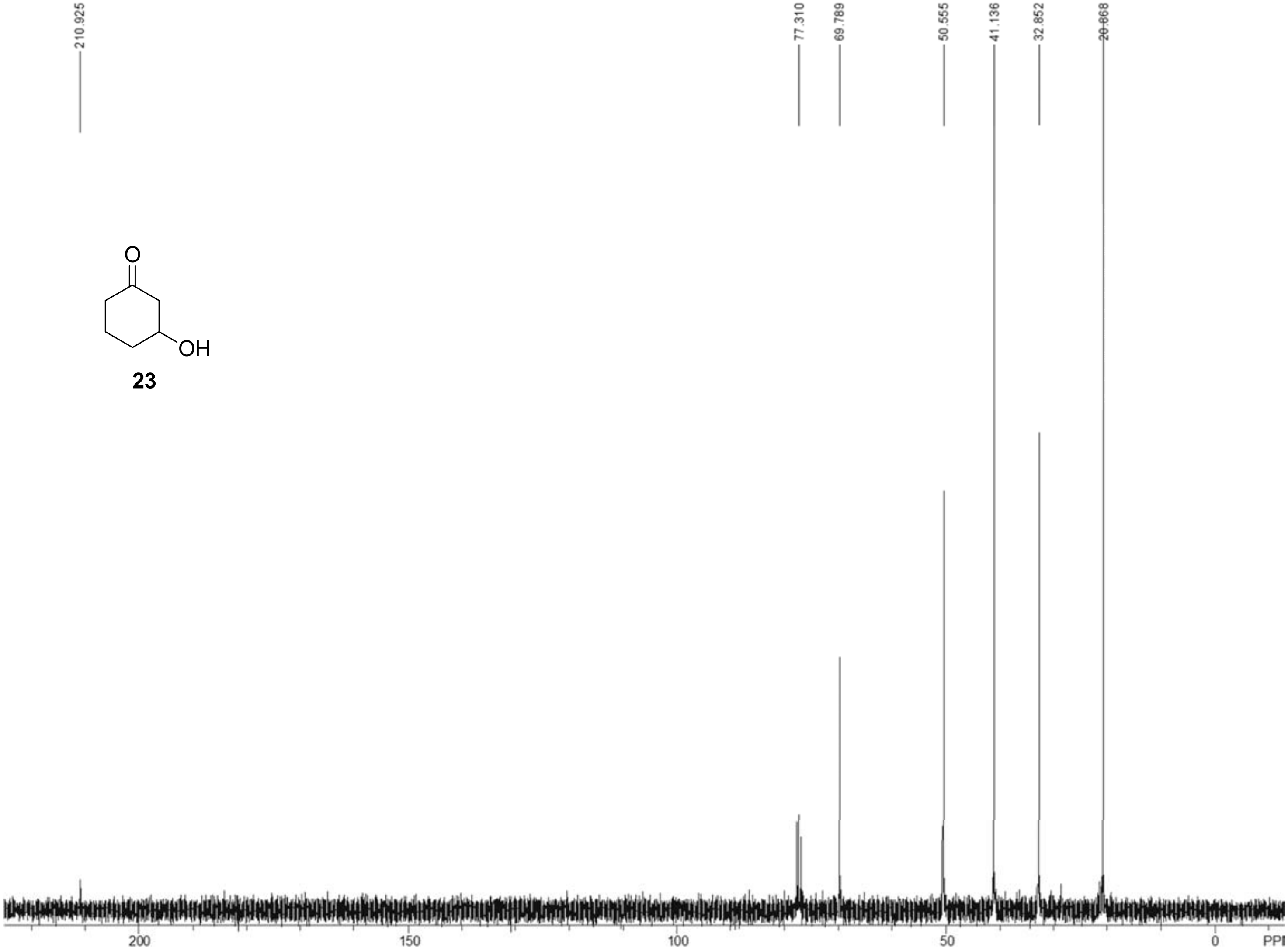
PPM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69.789
50.555
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100
50
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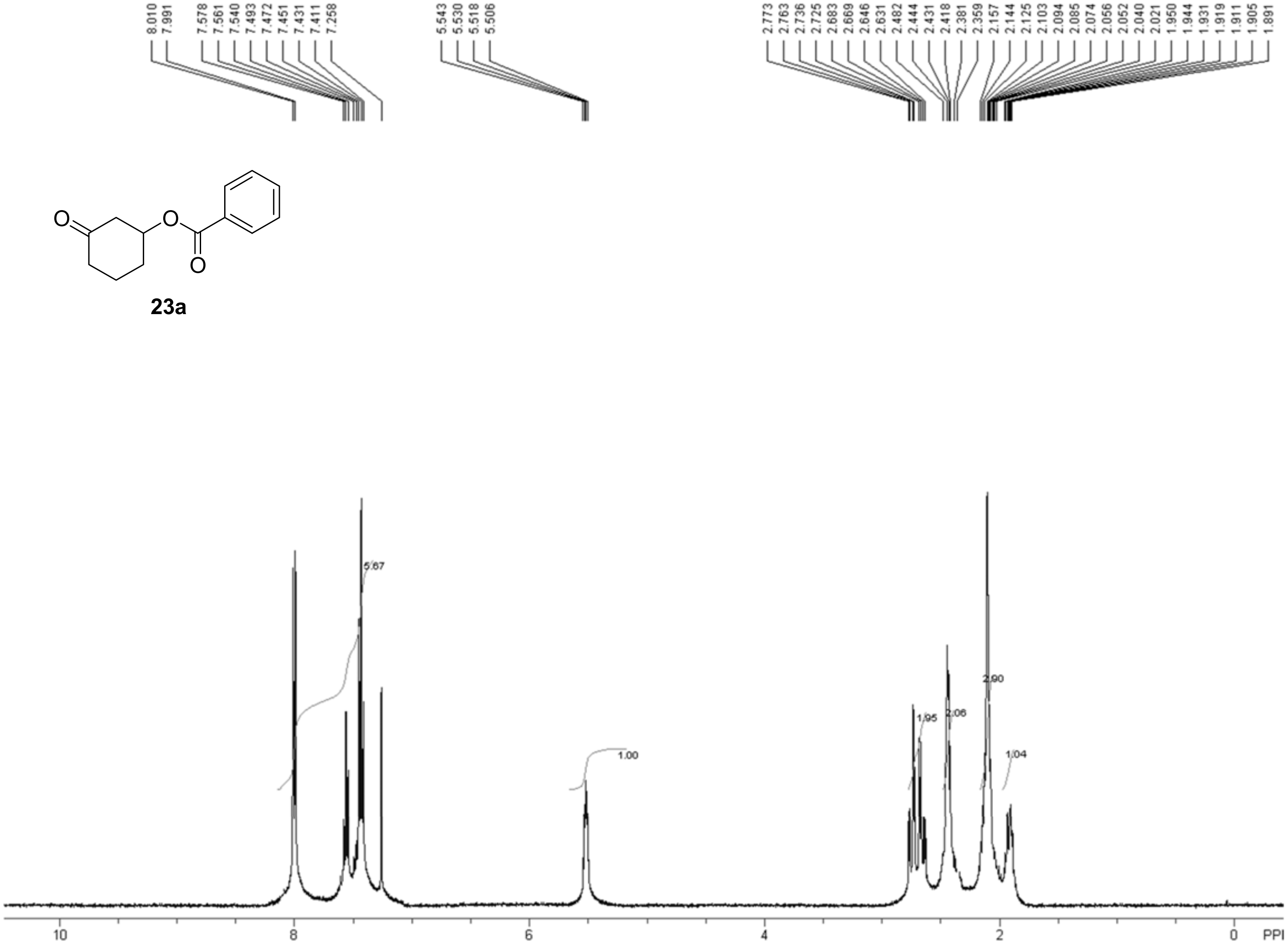
PPI

23



23a

8.010
7.991
7.578
7.561
7.540
7.493
7.472
7.451
7.431
7.411
7.258
5.543
5.530
5.518
5.506
2.773
2.763
2.736
2.725
2.683
2.669
2.646
2.631
2.482
2.444
2.431
2.418
2.381
2.359
2.157
2.144
2.125
2.103
2.094
2.085
2.074
2.056
2.052
2.040
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1.911
1.905
1.891
O
O
O
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1.00
1.95
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1.04
10
8
6
4
2
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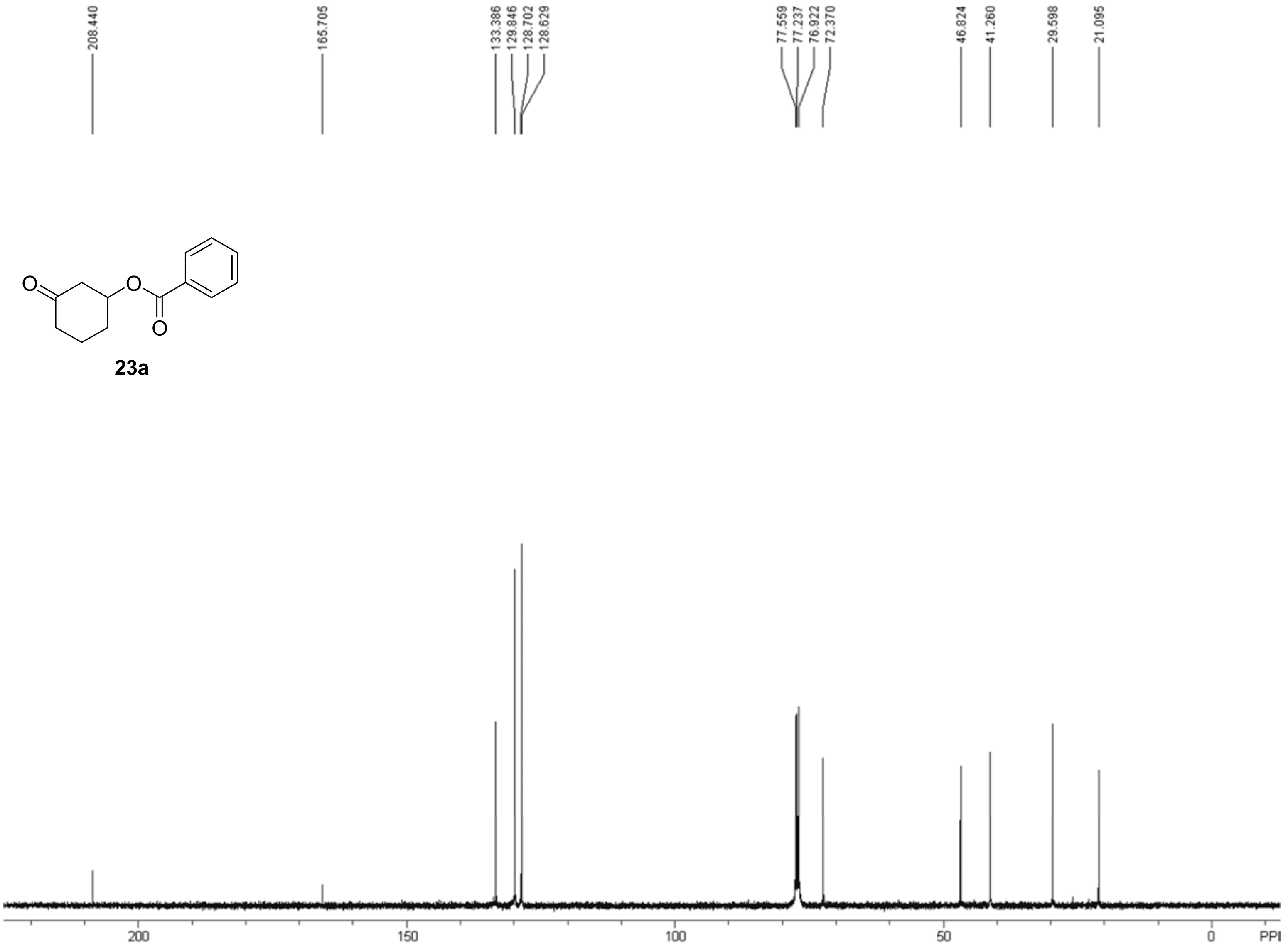
PPI



23a

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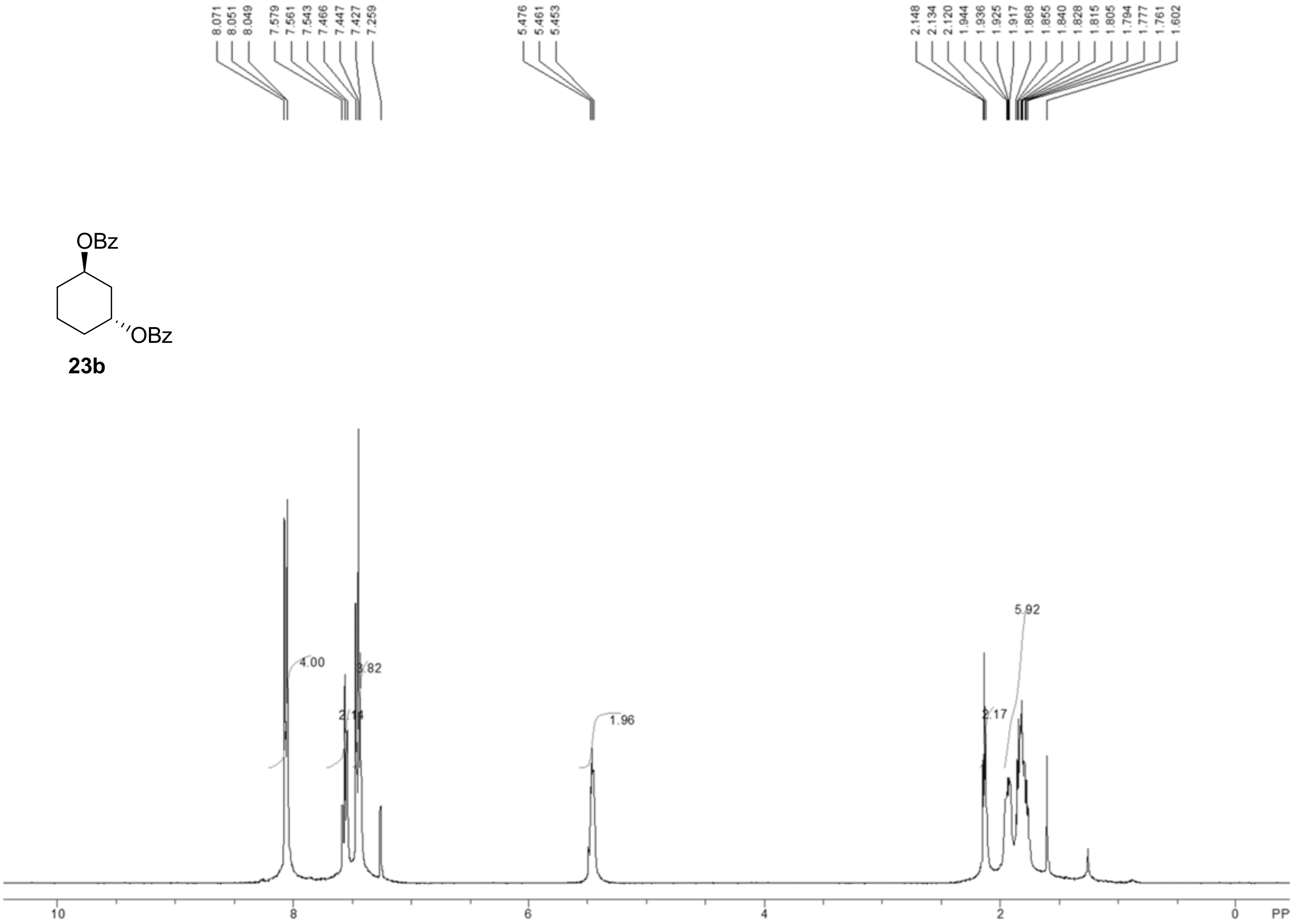
128.702
128.629
77.559
77.237
76.922
72.370
46.824
41.260
29.598
21.095
O
O
O
200
150
100
50
0
PPI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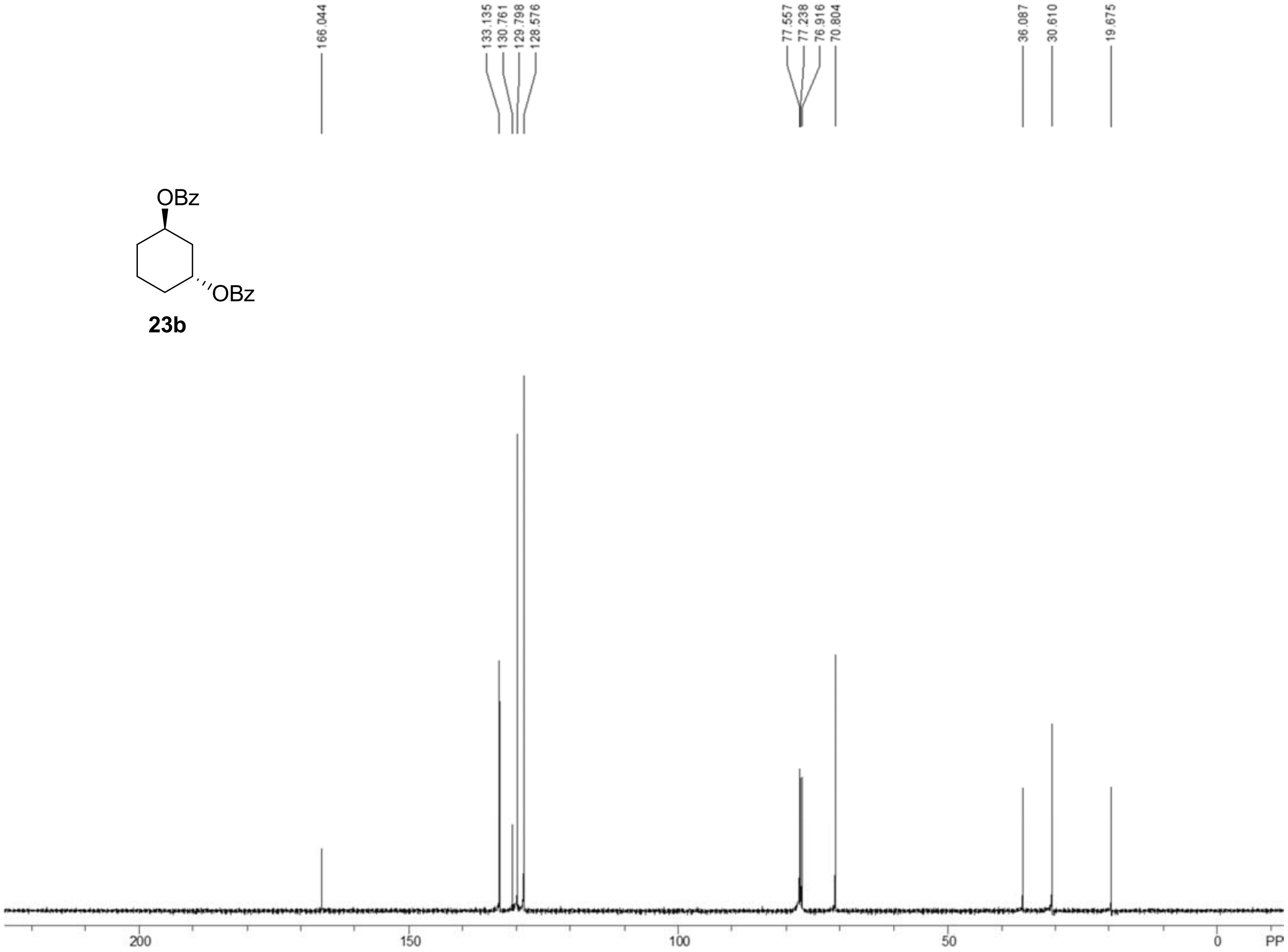
8.051
8.049
7.579
7.561
7.543
7.466
7.447
7.427
7.259
5.476
5.461
5.453
2.148
2.134
2.120
1.944
1.936
1.925
1.917
1.868
1.855
1.840
1.828
1.815
1.805
1.794
1.777
1.761
1.602
OBz
OBz
23b
4.00
3.82
2.14
1.96
2.17
5.92
10
8
6
4
2
0
PP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130.761
129.798
128.576
77.557
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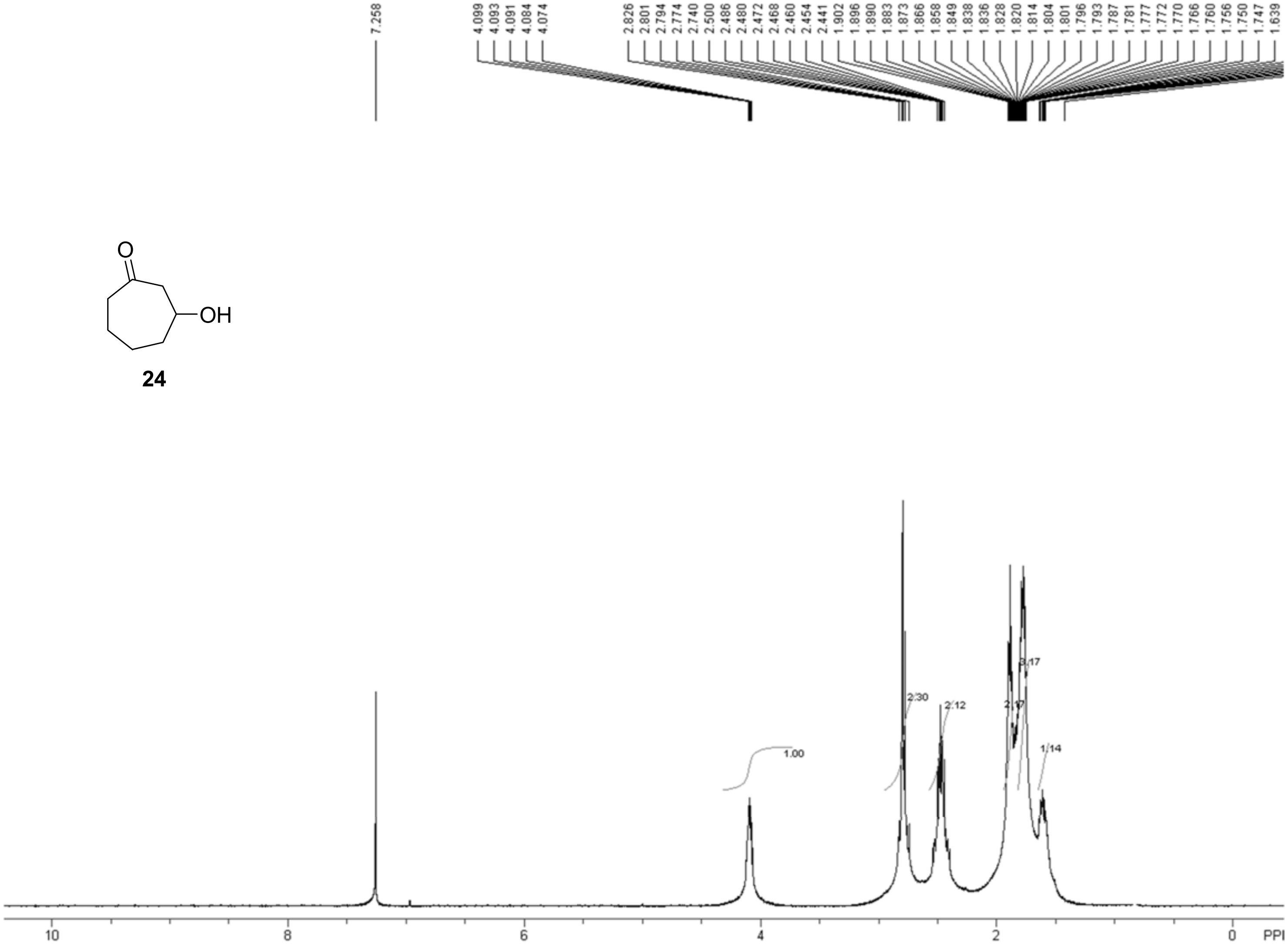
76.916
70.804
36.087
30.610
19.675
OBz
OBz
200
150
100
50
0
PP

23b



24

7.258
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4.091
4.084
4.074
2.826
2.801
2.794
2.774
2.740
2.500
2.486
2.480
2.472
2.468
2.460
2.454
2.441
1.902
1.896
1.890
1.883
1.873
1.866
1.858
1.849
1.838
1.836
1.828
1.820
1.814
1.804
1.801
1.796
1.793
1.787
1.781
1.777
1.772
1.770
1.766
1.760
1.756
1.750
1.747
1.639
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2.12
2.17
3.17
1.14
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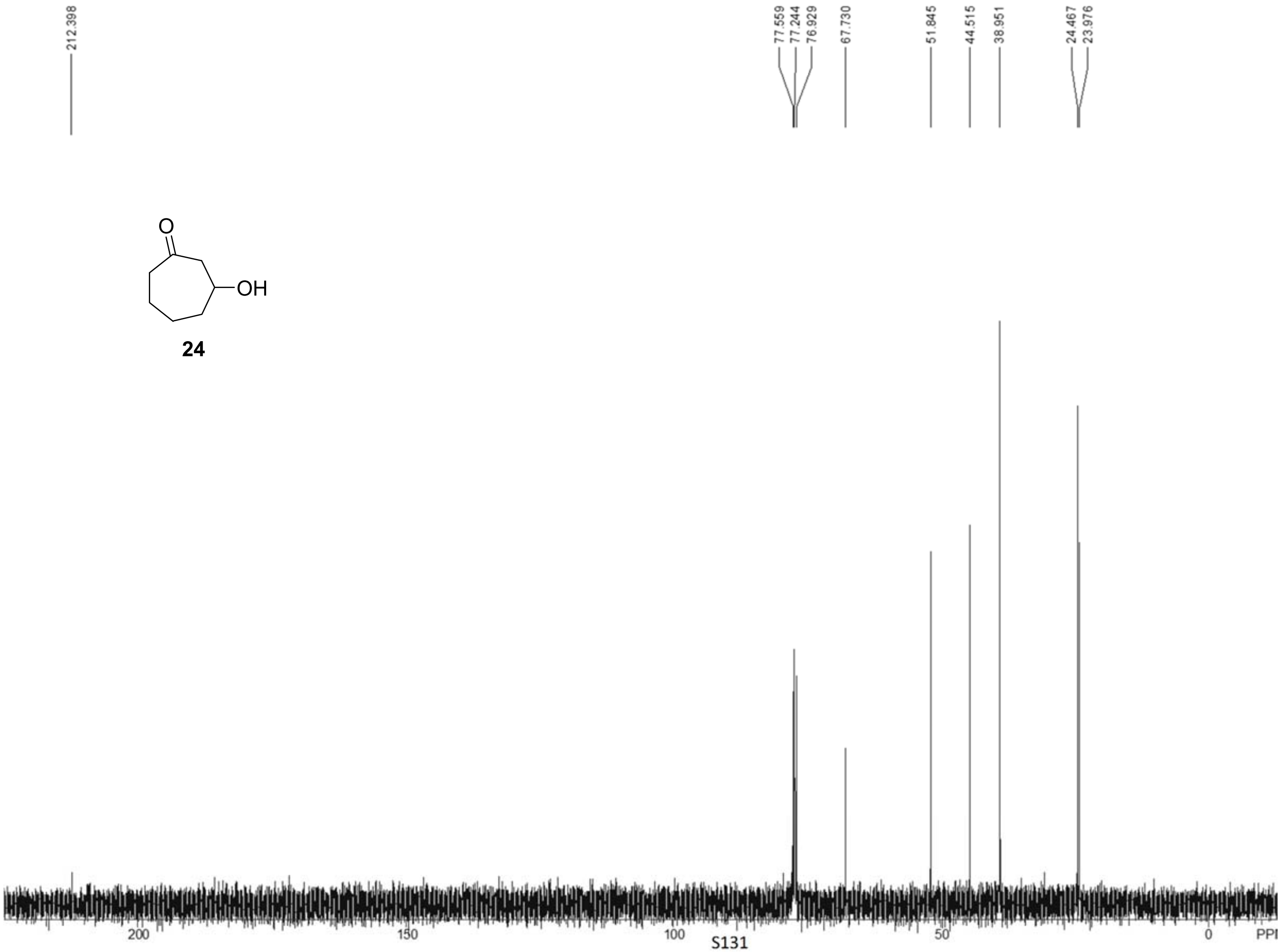
8
6
4
2
0
PPI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77.244
76.929
67.730
51.845
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38.951
24.467
23.976
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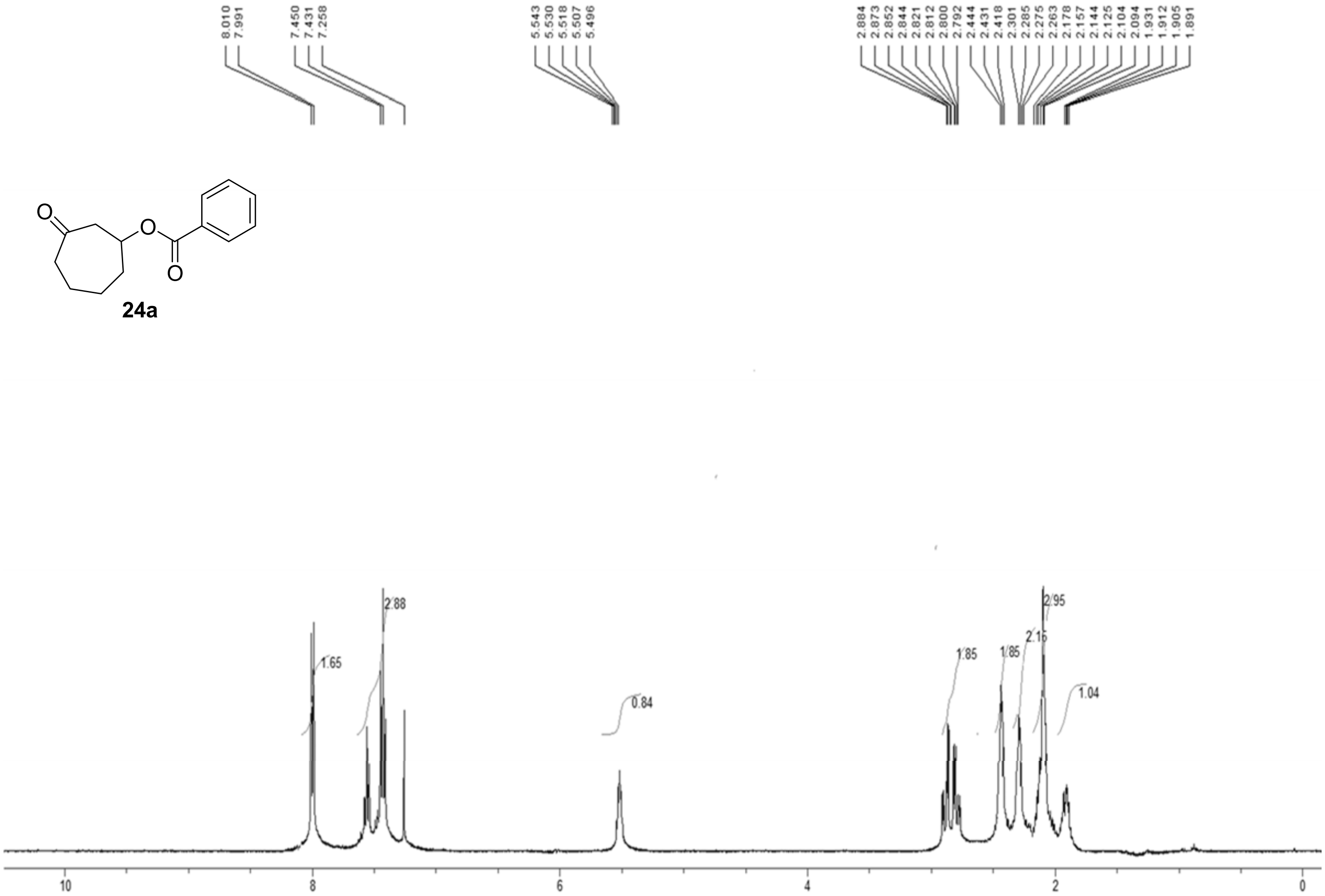
OH
24
200
150
100
50
0
PP

O
O
O

24a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7.450
7.431
7.258
5.543
5.530
5.518
5.507
5.496
2.884
2.873
2.852
2.844
2.821
2.812
2.800
2.792
2.444
2.431
2.418
2.301
2.285
2.275
2.263
2.178
2.157
2.144
2.125
2.104
2.094
1.931
1.912
1.905
1.891
1.65
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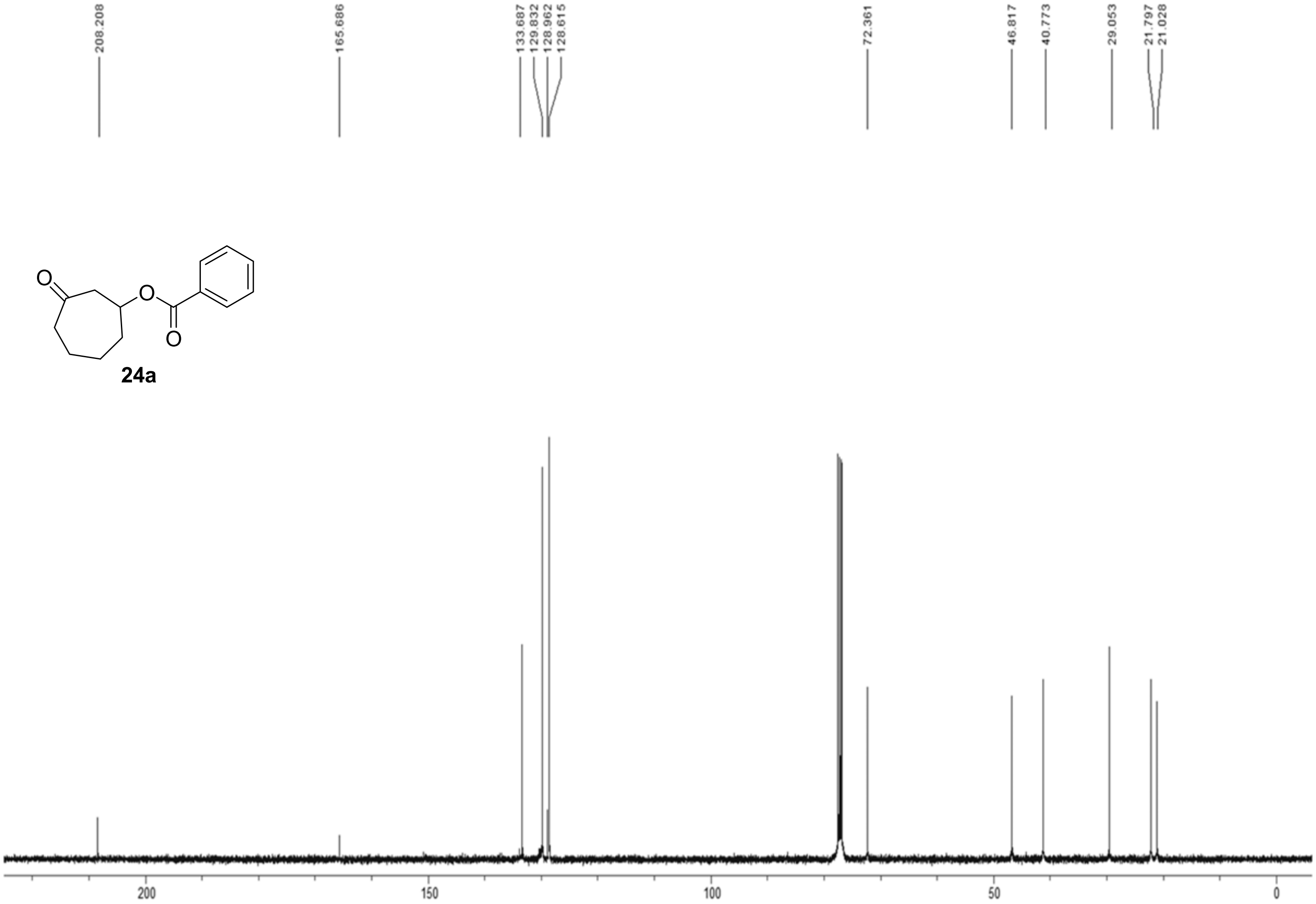
0.84
1.85
1.85
2.16
2.95
1.04
10
8
6
4
2
0



24a

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133.687
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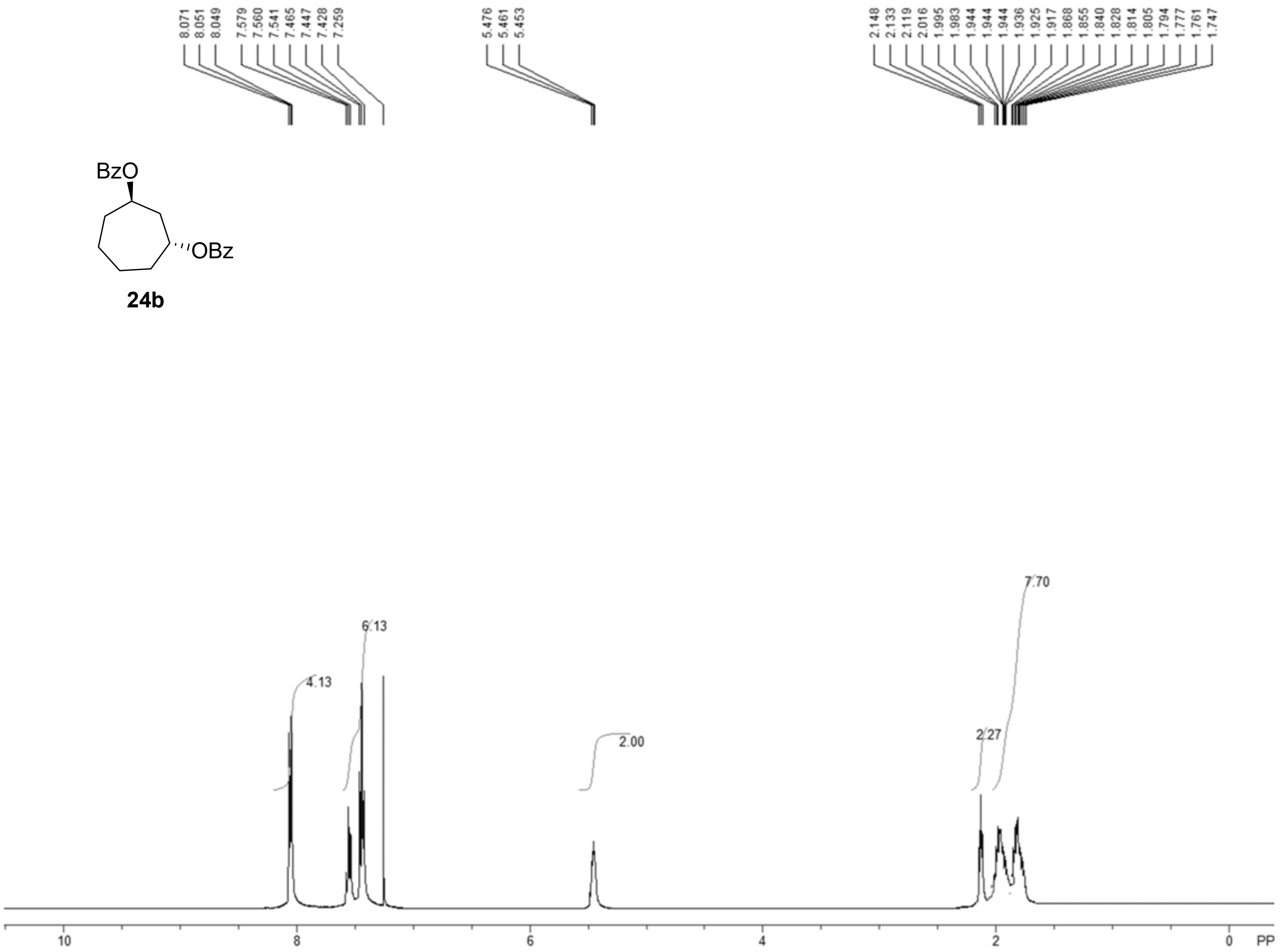
128.962
128.615
72.361
46.817
40.773
29.053
21.797
21.028
200
150
100
50
0
O
O
O

BzO
OBz

24b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8.049
7.579
7.560
7.541
7.465
7.447
7.428
7.259
5.476
5.461
5.453
2.148
2.133
2.119
2.016
1.995
1.983
1.944
1.944
1.944
1.936
1.925
1.917
1.868
1.855
1.840
1.828
1.814
1.805
1.794
1.777
1.761
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6.13
2.00
2.27
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10
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4
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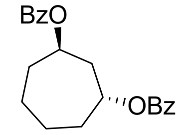
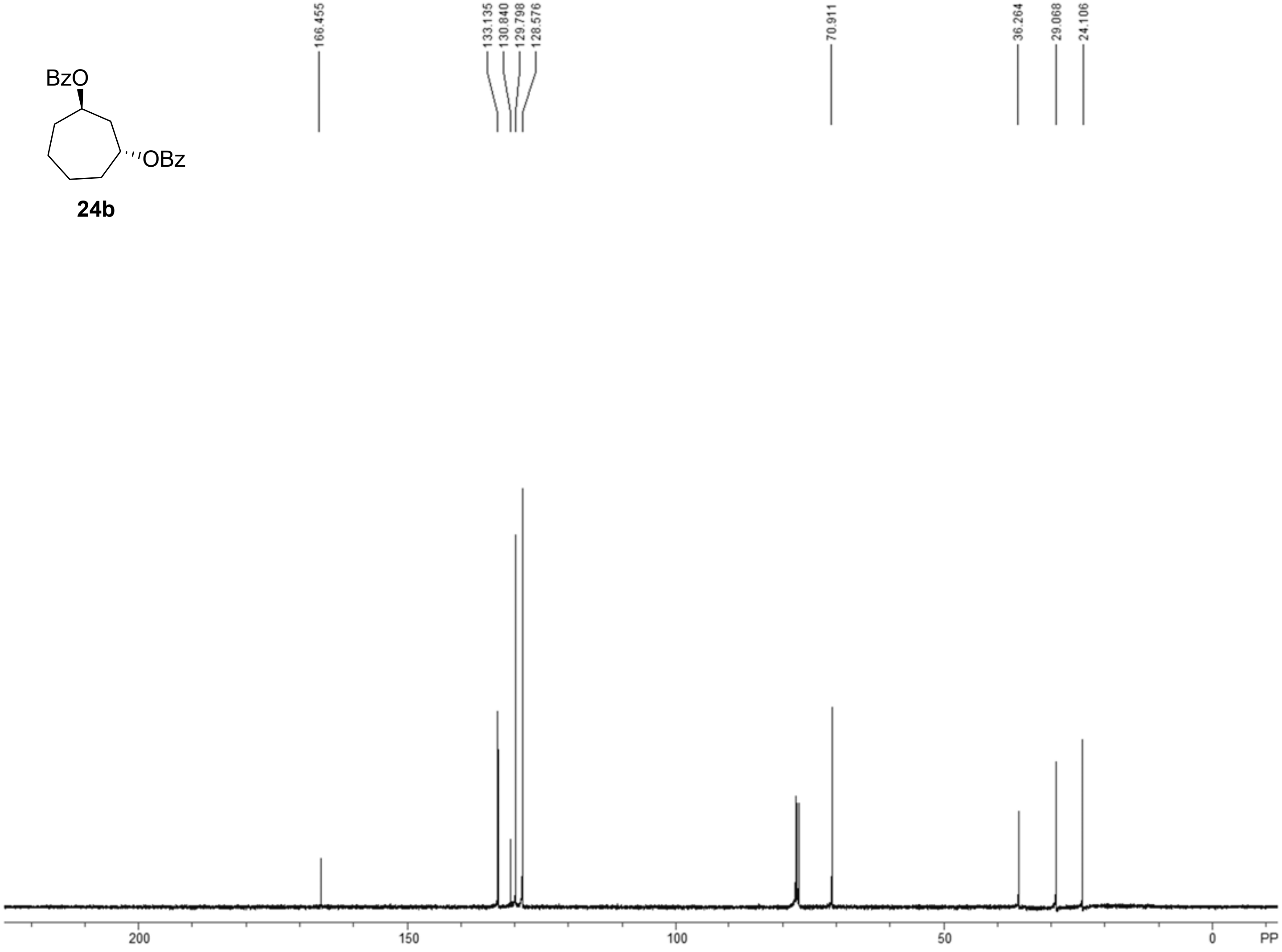
0
PP


BzO
OBz

24b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70.911
36.264
29.068
24.106
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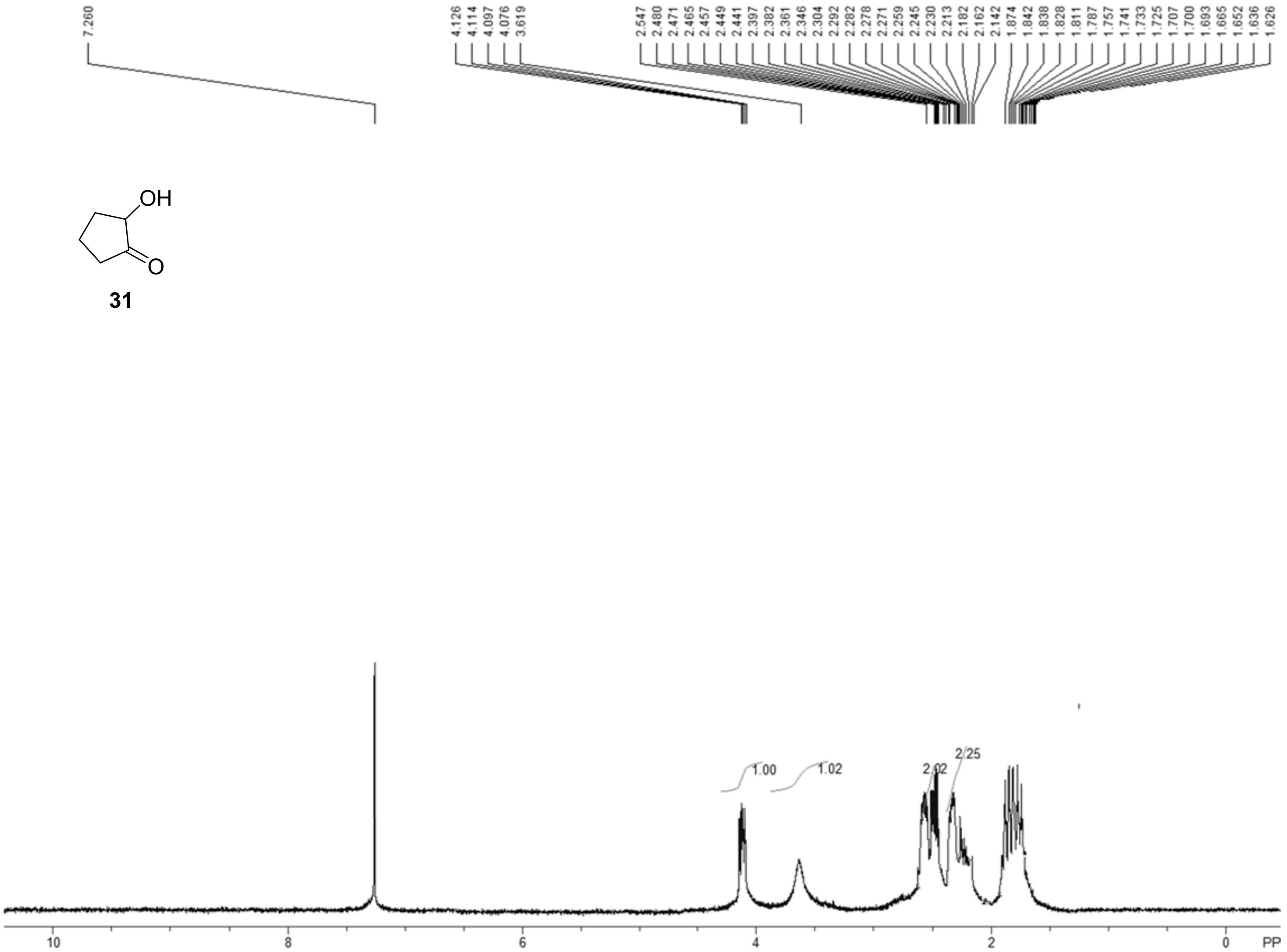
150
100
50
0
PP



31
7.260
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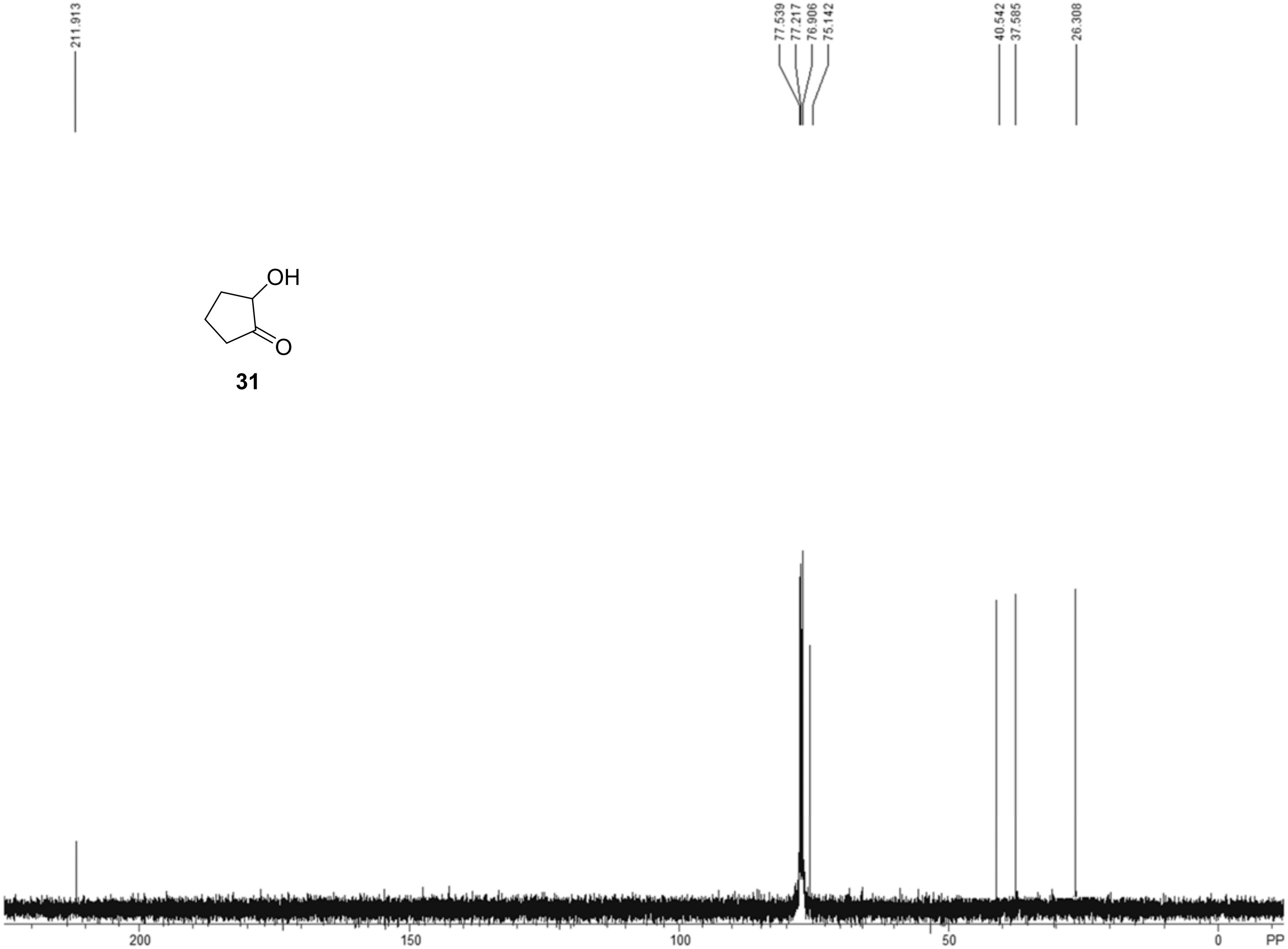
4.114
4.097
4.076
3.619
2.547
2.480
2.471
2.465
2.457
2.449
2.441
2.397
2.382
2.361
2.346
2.304
2.292
2.282
2.278
2.271
2.259
2.245
2.230
2.213
2.182
2.162
2.142
1.874
1.842
1.838
1.828
1.811
1.787
1.757
1.741
1.733
1.725
1.707
1.700
1.693
1.665
1.652
1.636
1.626
1.00
1.02
2.02
2.25
10
8
6
4
2
0
PP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75.142
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26.308
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O
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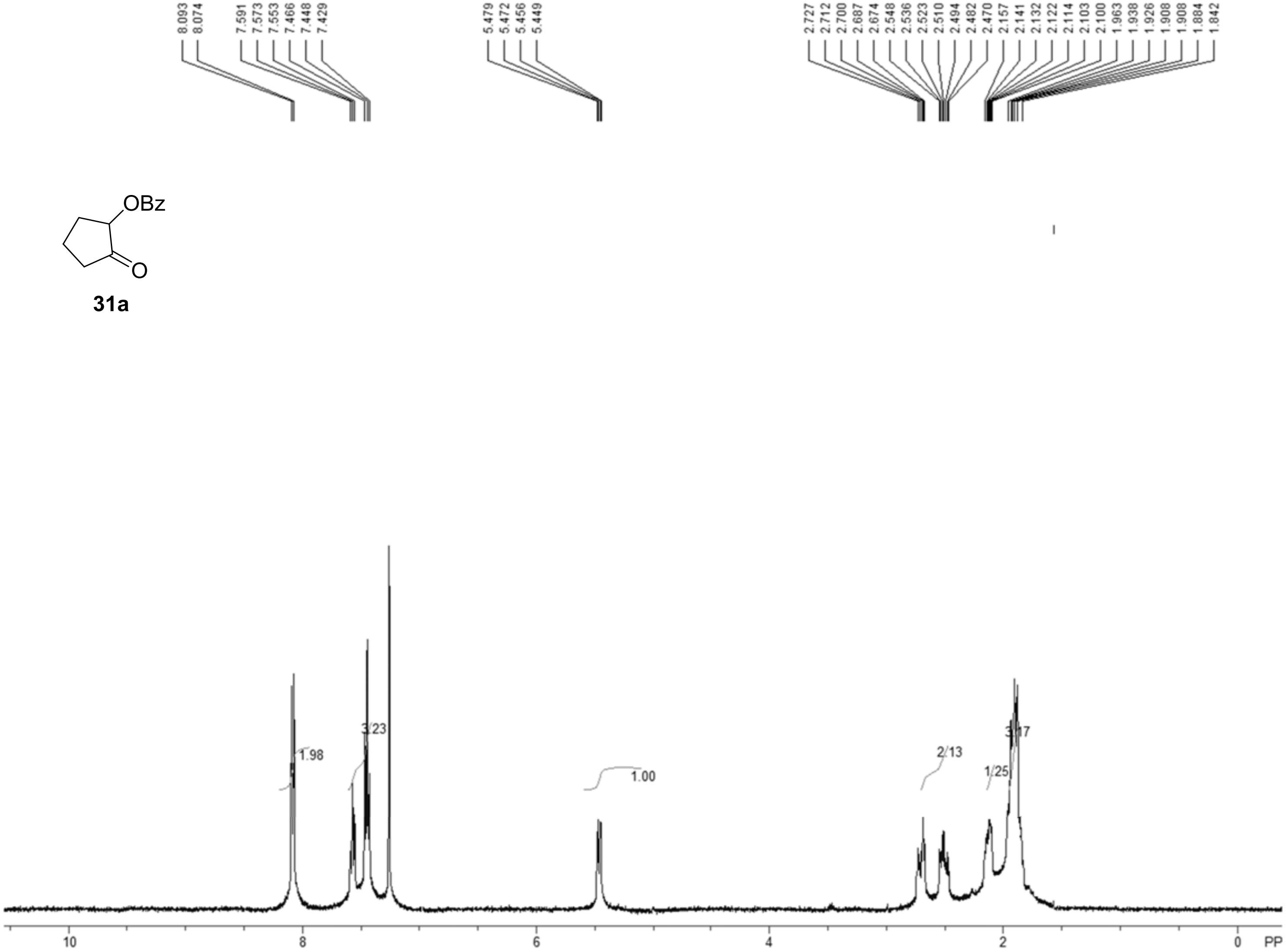
150
100
50
0
PP

31



31a

8.093
8.074
7.591
7.573
7.553
7.466
7.448
7.429
5.479
5.472
5.456
5.449
2.727
2.712
2.700
2.687
2.674
2.548
2.536
2.523
2.510
2.494
2.482
2.470
2.157
2.141
2.132
2.122
2.114
2.103
2.100
1.963
1.938
1.926
1.908
1.908
1.884
1.842
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2.13
1.25
3.17
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4
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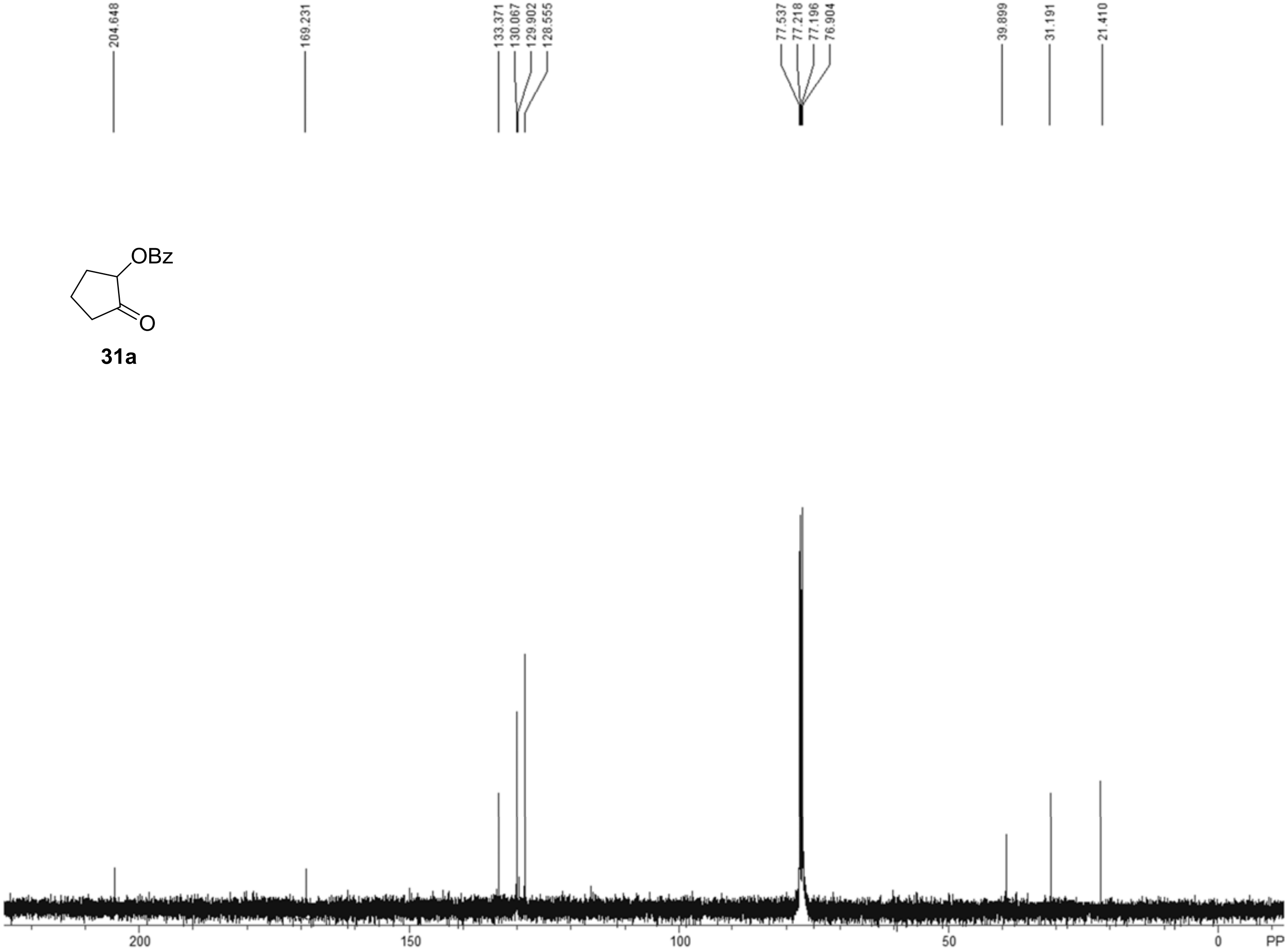
0
PP



31a

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76.904
39.899
31.191
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OBz
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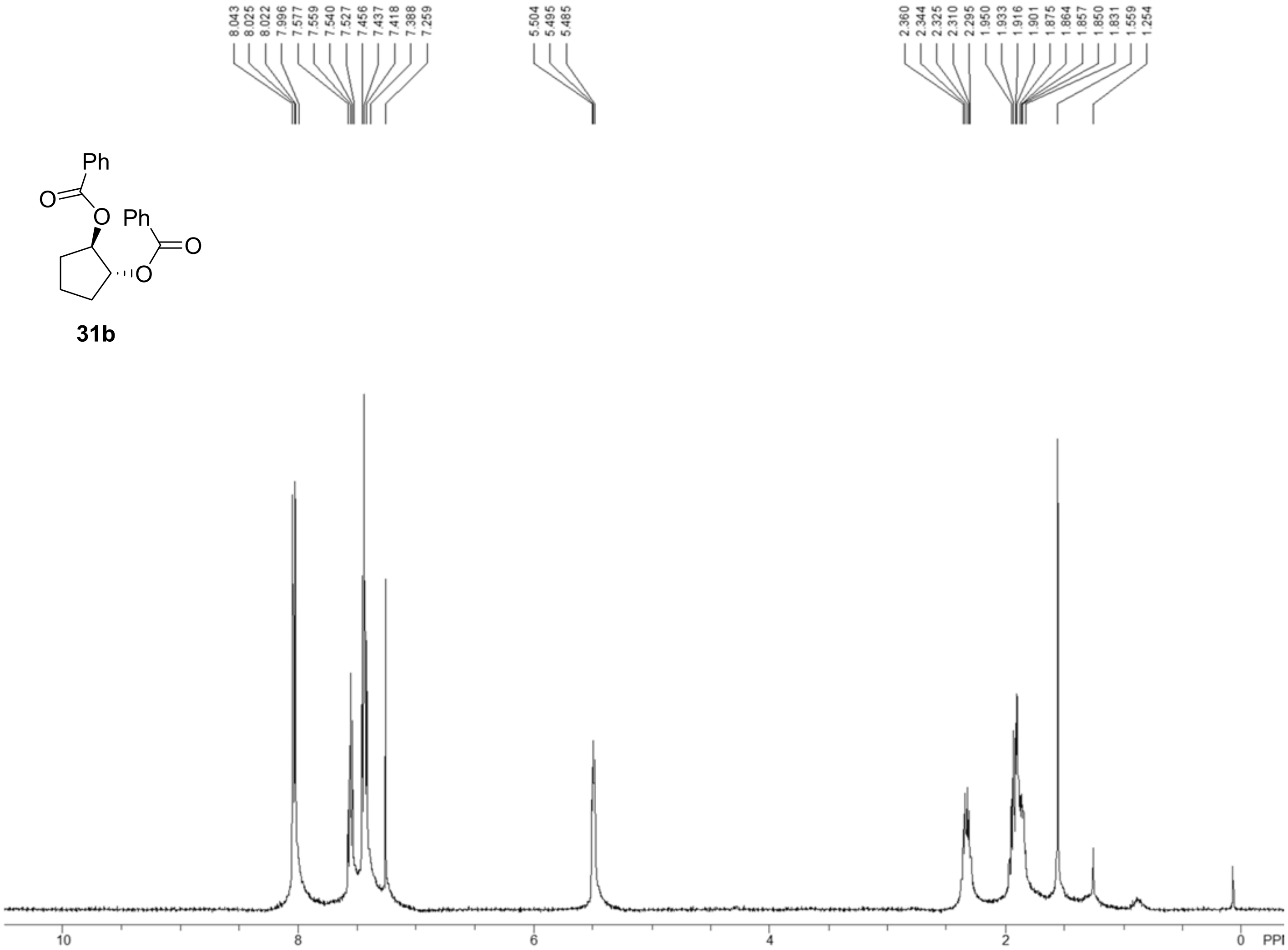
150
100
50
0
PP



31b

8.043
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7.559
7.540
7.527
7.456
7.437
7.418
7.388
7.259
5.504
5.495
5.485
2.360
2.344
2.325
2.310
2.295
1.950
1.933
1.916
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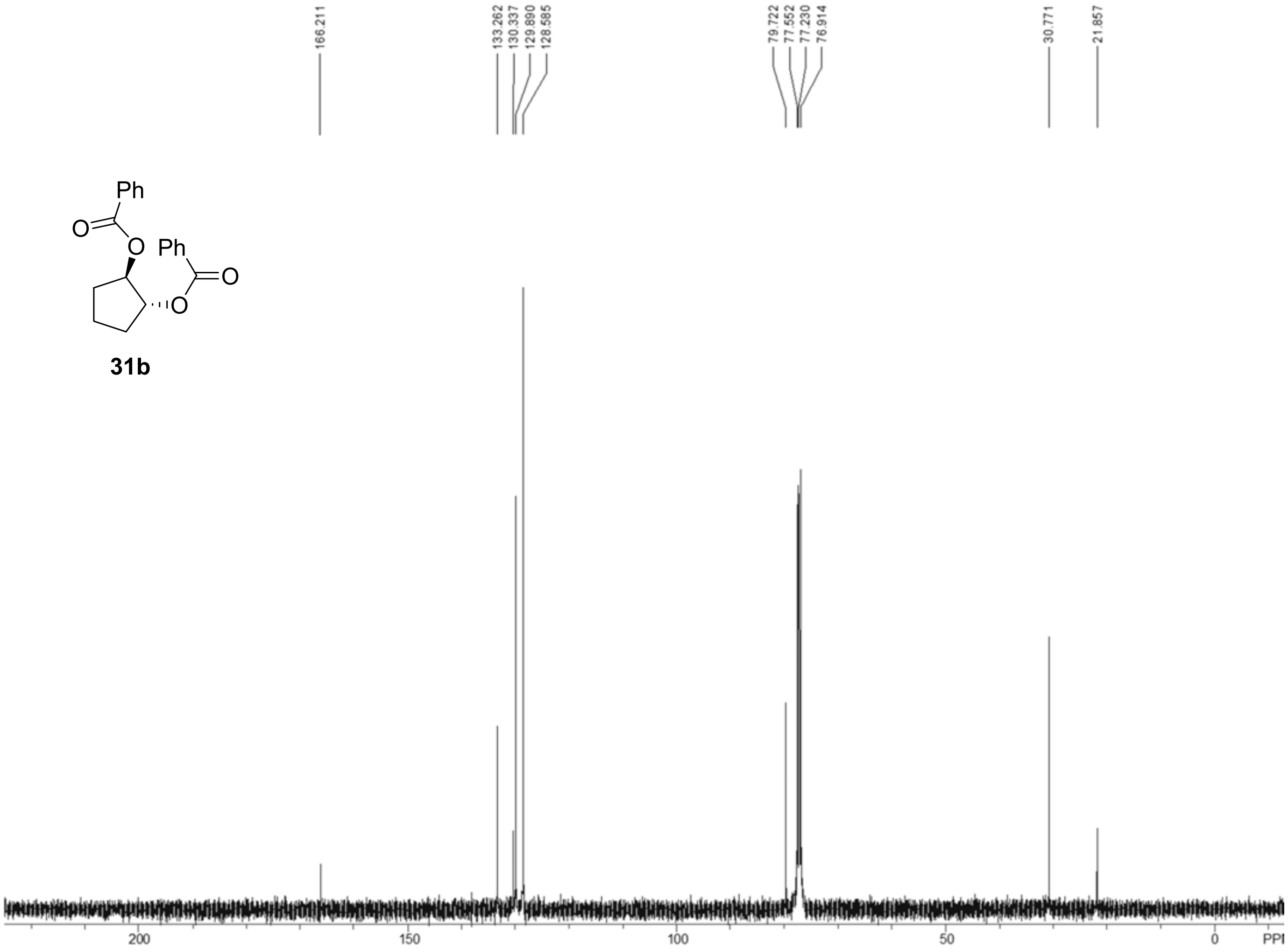
1.857
1.850
1.831
1.559
1.254
10
8
6
4
2
0
PPM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79.722
77.552
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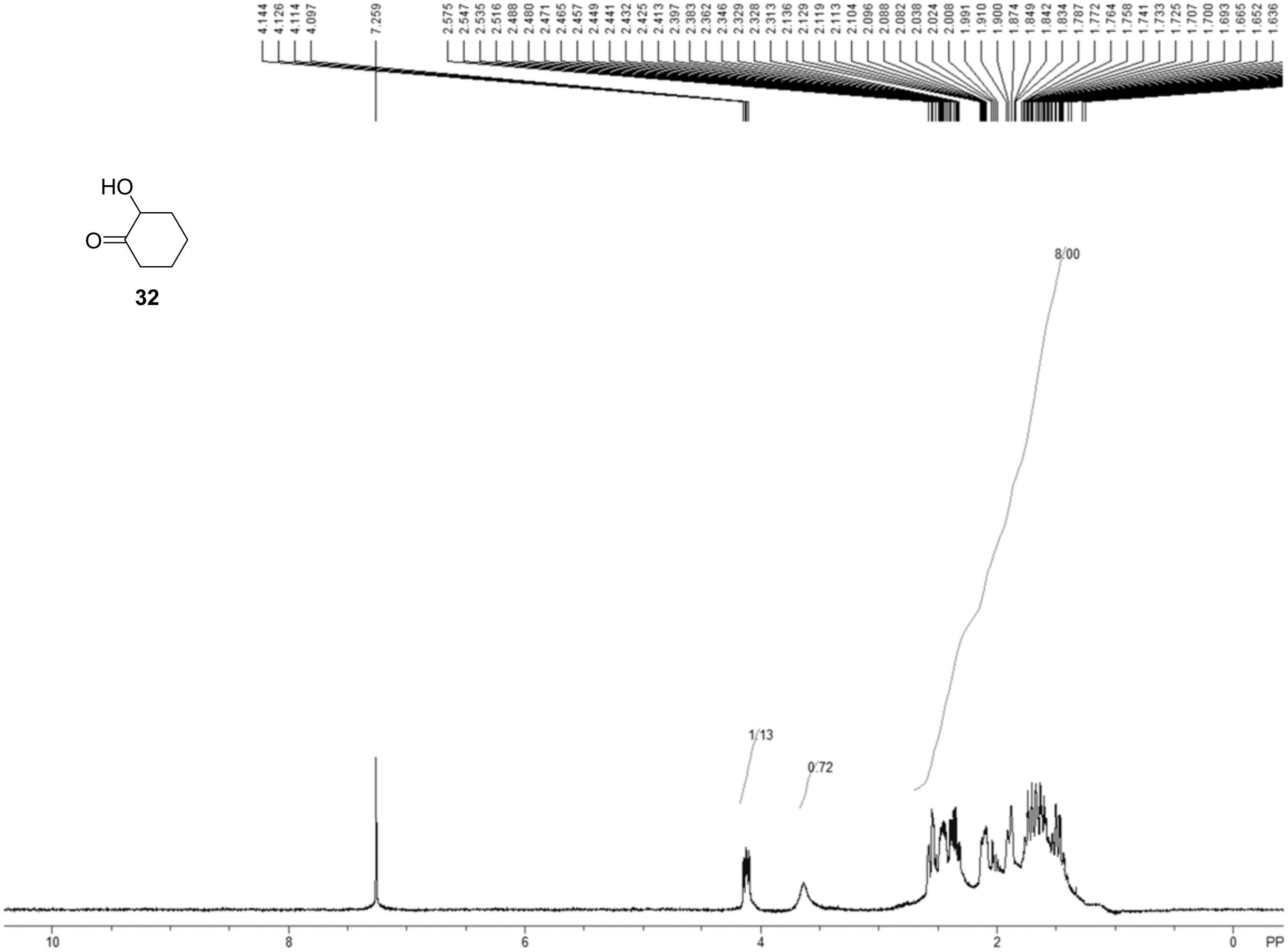
76.914
30.771
21.857
Ph
O
O
Ph
O
O
200
150
100
50
0
PPI

31b


HO
O
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4.114
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7.259
2.575
2.547
2.535
2.516
2.488
2.480
2.471
2.465
2.457
2.449
2.441
2.432
2.425
2.413
2.397
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2.362
2.346
2.329
2.328
2.313
2.136
2.129
2.119
2.113
2.104
2.096
2.088
2.082
2.038
2.024
2.008
1.991
1.910
1.900
1.874
1.849
1.842
1.834
1.787
1.772
1.764
1.758
1.741
1.733
1.725
1.707
1.700
1.693
1.665
1.652
1.636
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10
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6
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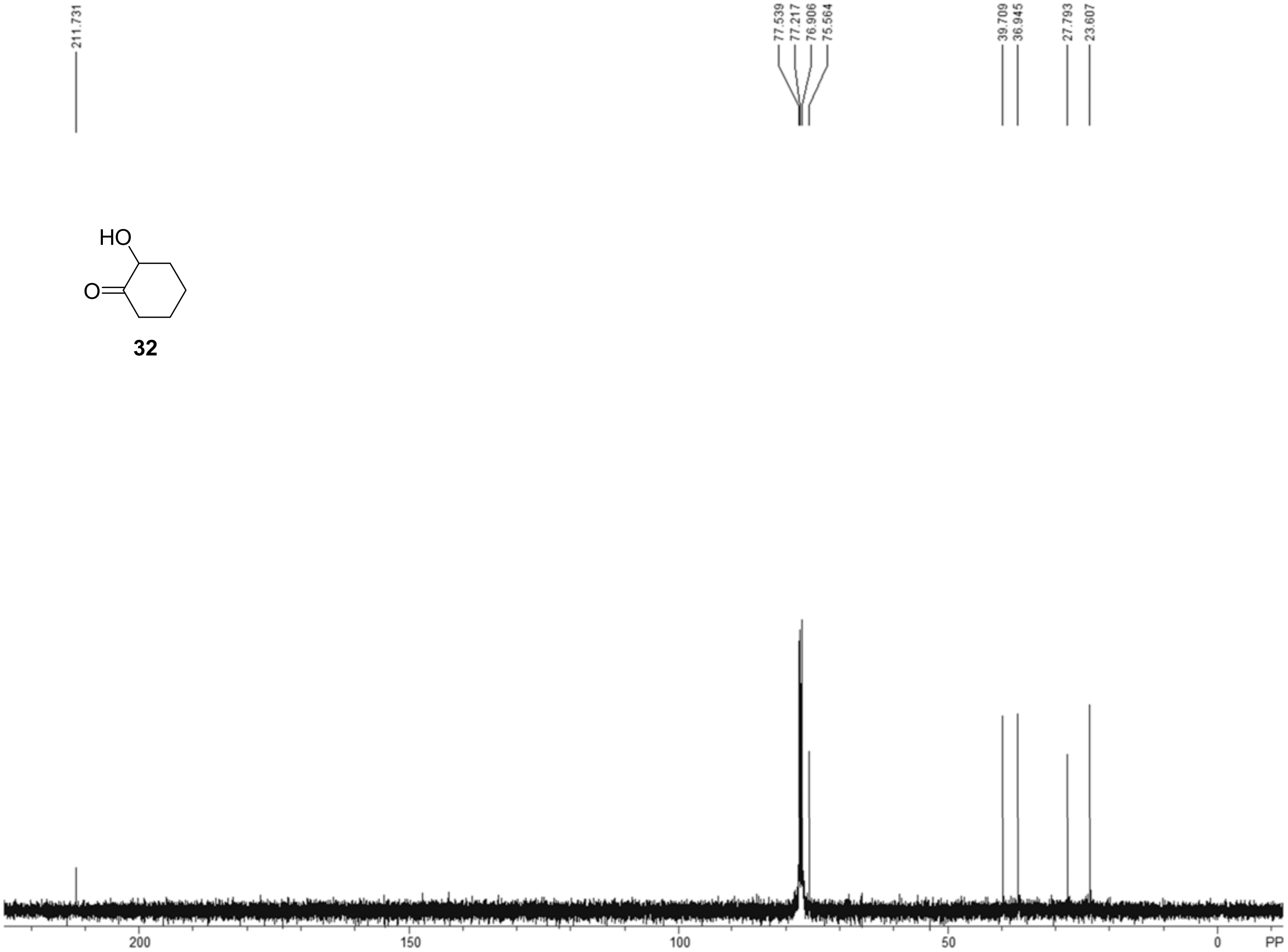
PP

32


211.731
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39.709
36.945
27.793
23.607
HO
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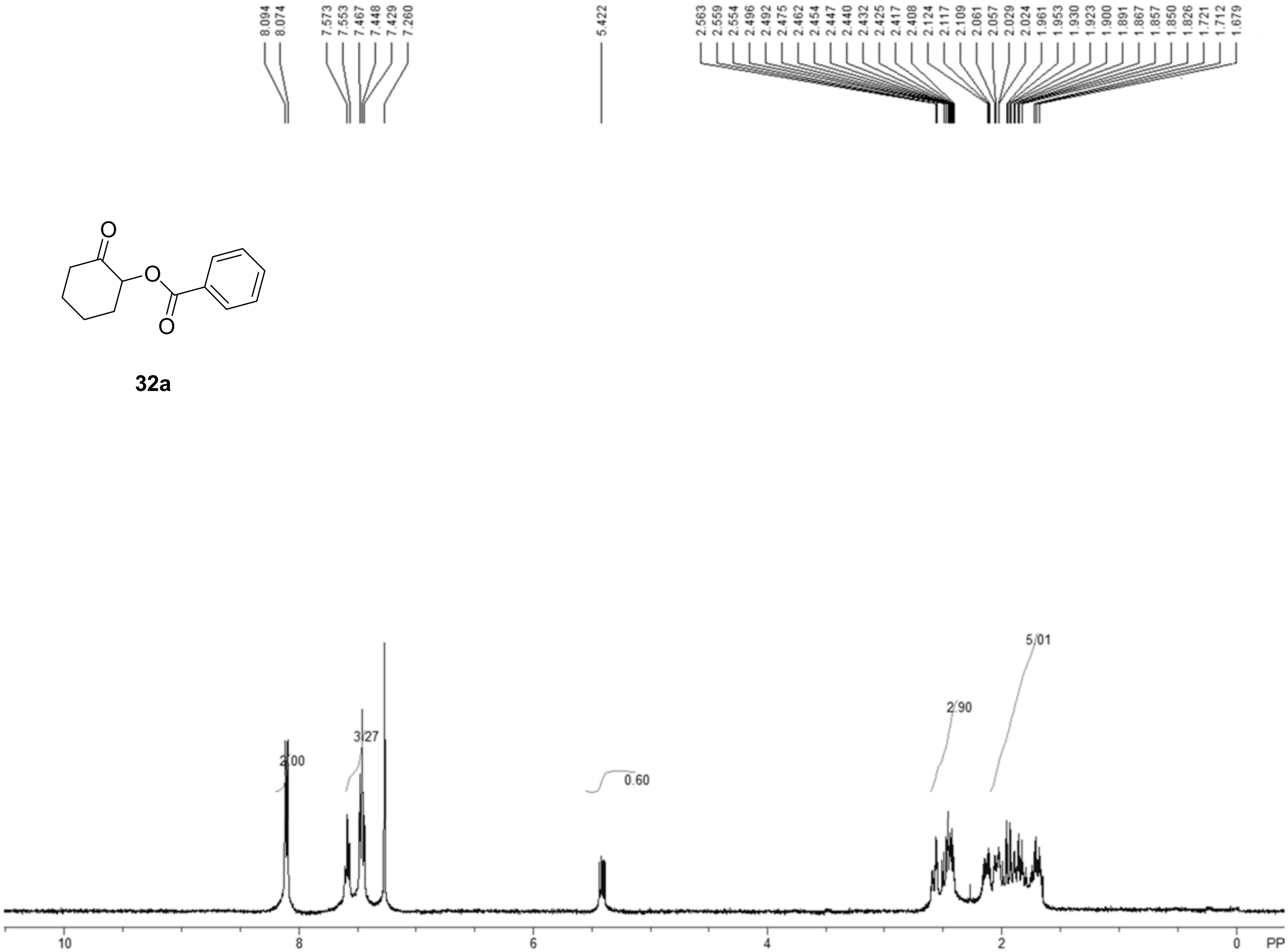
150
100
50
0
PP

32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7.429
7.260
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2.559
2.554
2.496
2.492
2.475
2.462
2.454
2.447
2.440
2.432
2.425
2.417
2.408
2.124
2.117
2.109
2.061
2.057
2.029
2.024
1.961
1.953
1.930
1.923
1.900
1.891
1.867
1.857
1.850
1.826
1.721
1.712
1.679
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10
8
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4
2
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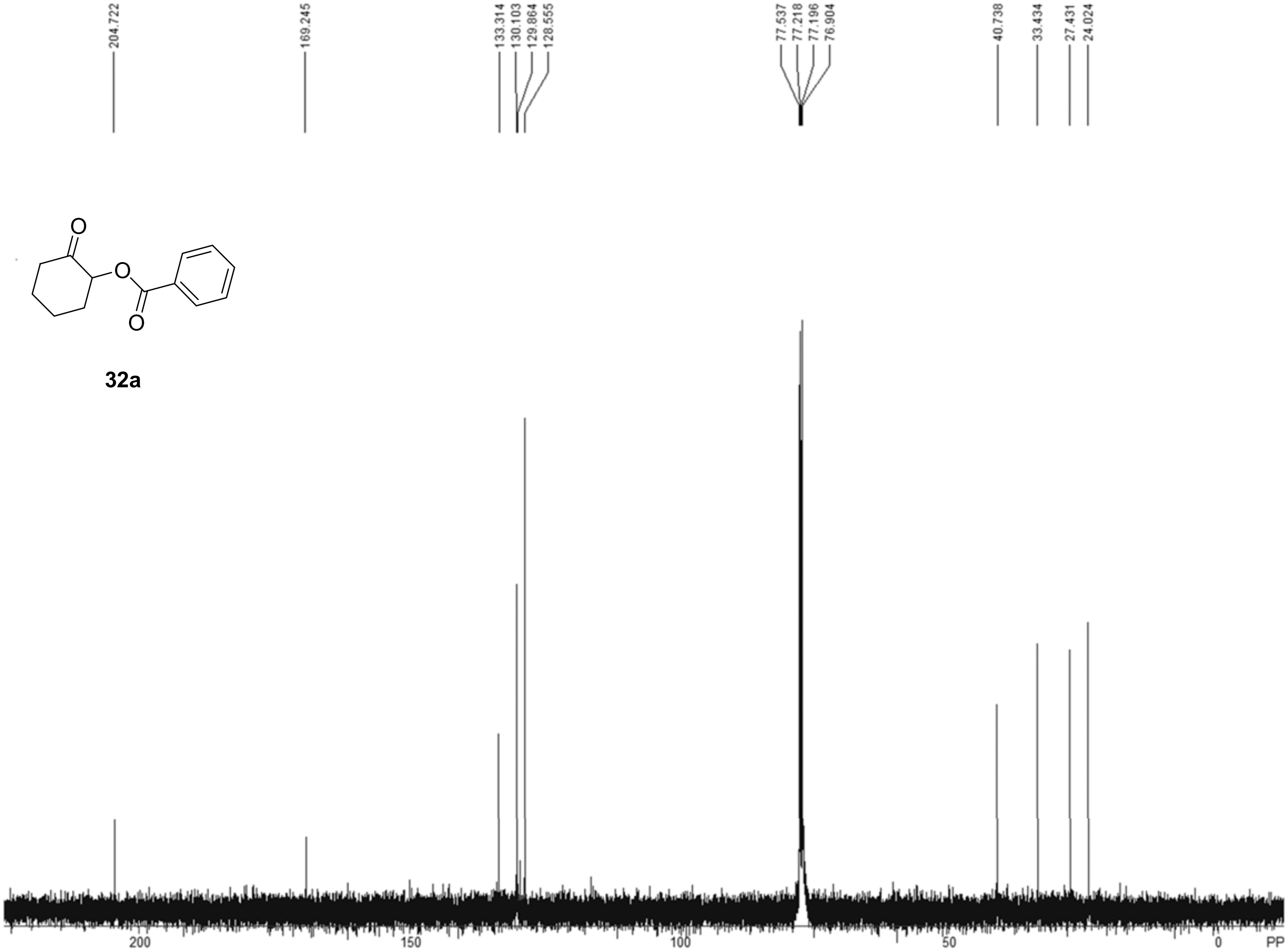
PP

32a



32a

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77.537
77.218
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40.738
33.434
27.431
24.024
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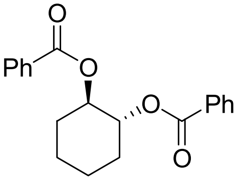
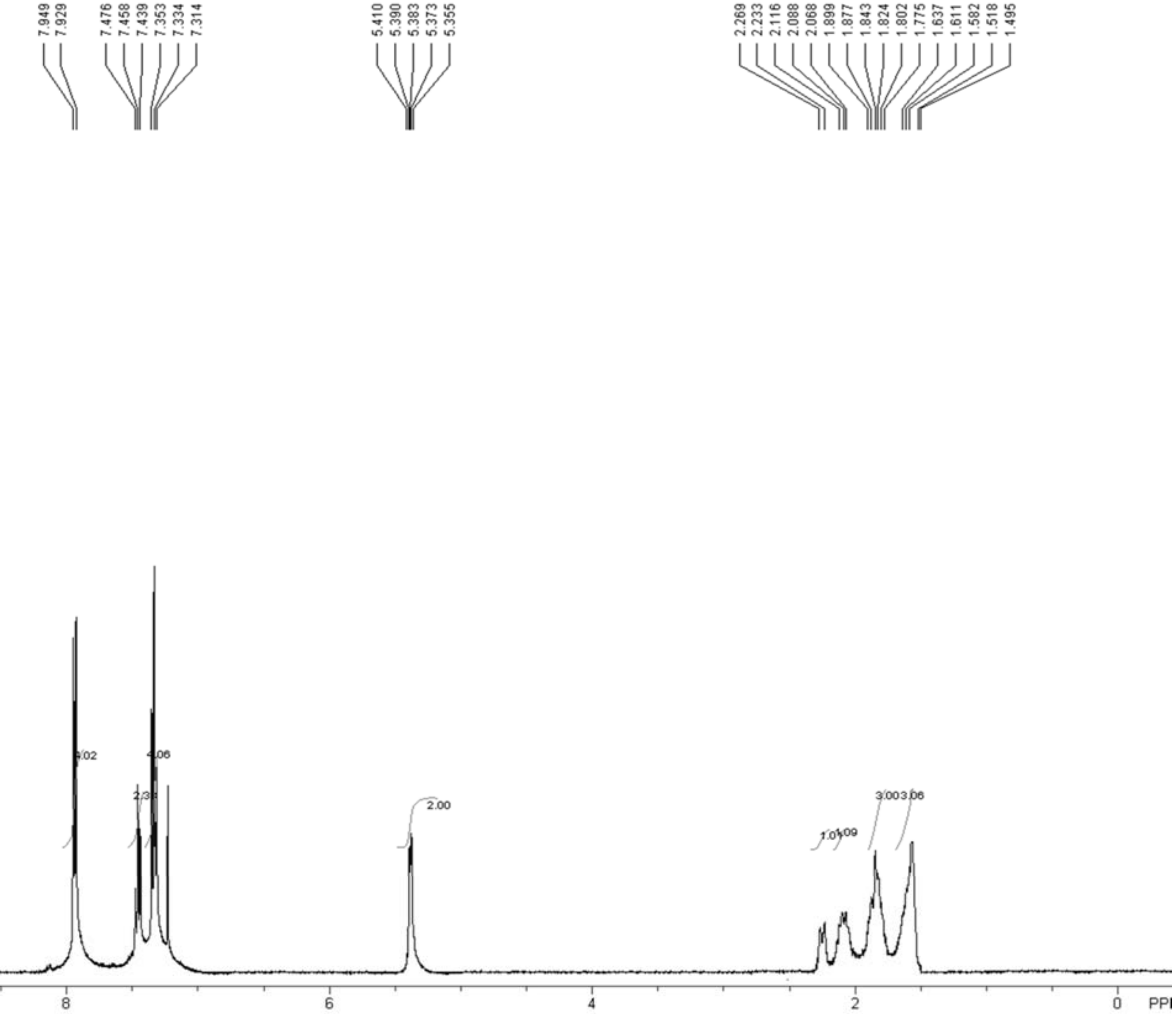
150
100
50
0
PP
O
O
O


O
Ph
O
O
Ph
O

32b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5.383
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5.355
2.269
2.233
2.116
2.088
2.068
1.899
1.877
1.843
1.824
1.802
1.775
1.637
1.611
1.582
1.518
1.495
4.02
2.3
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1.01
1.09
3.00
3.06
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4
2
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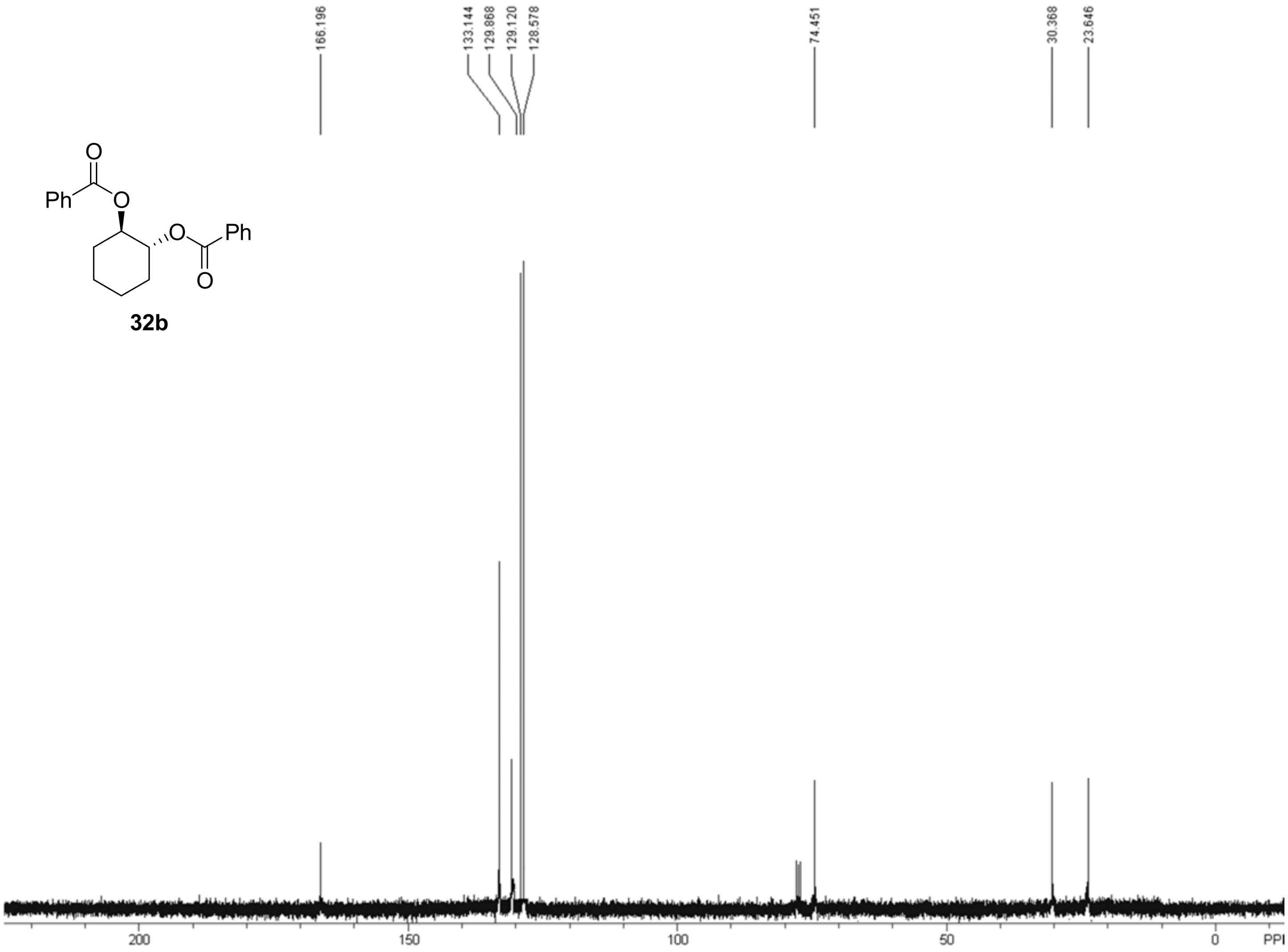
PPM



32b

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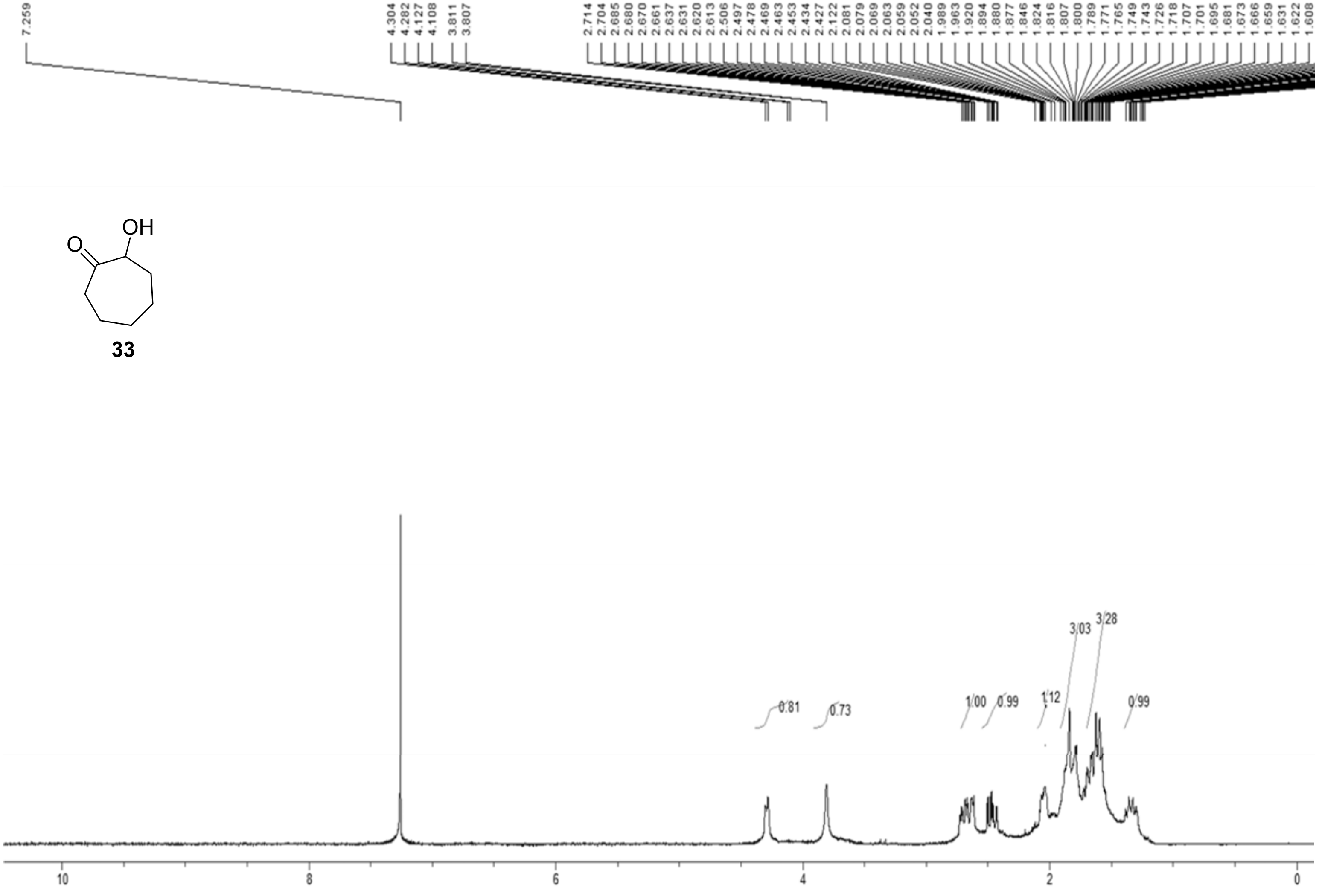
23.646
200
150
100
50
0
PPI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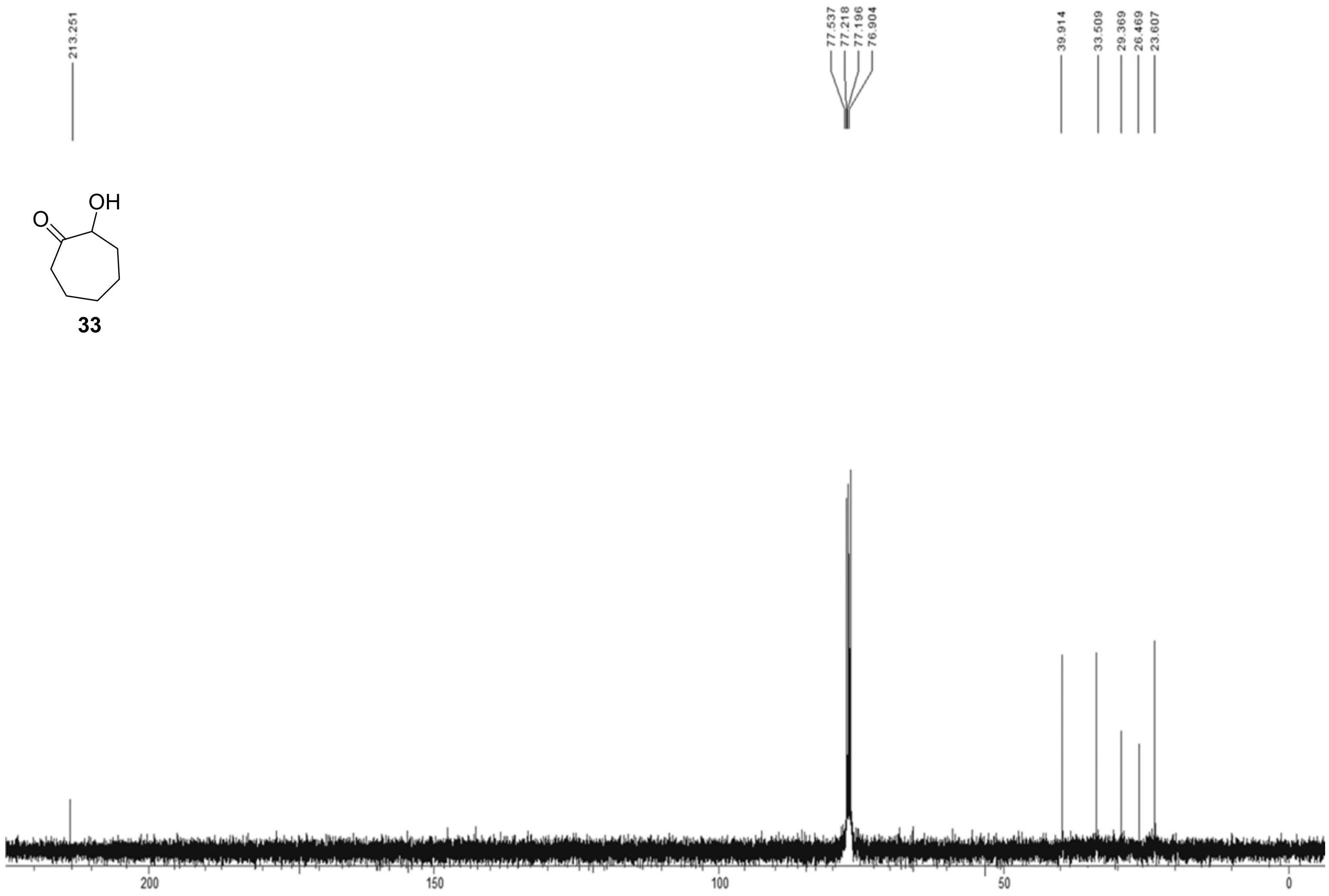
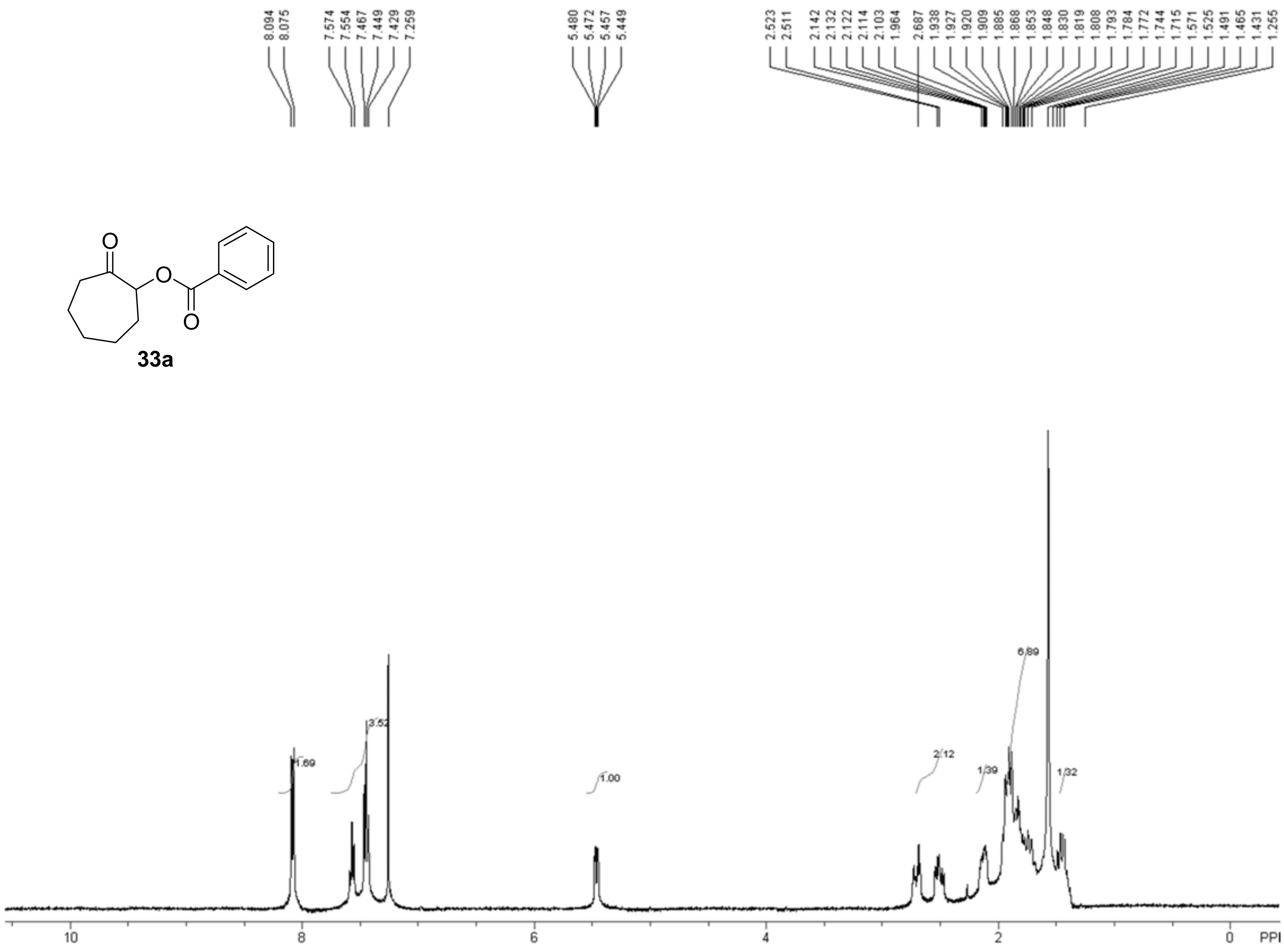
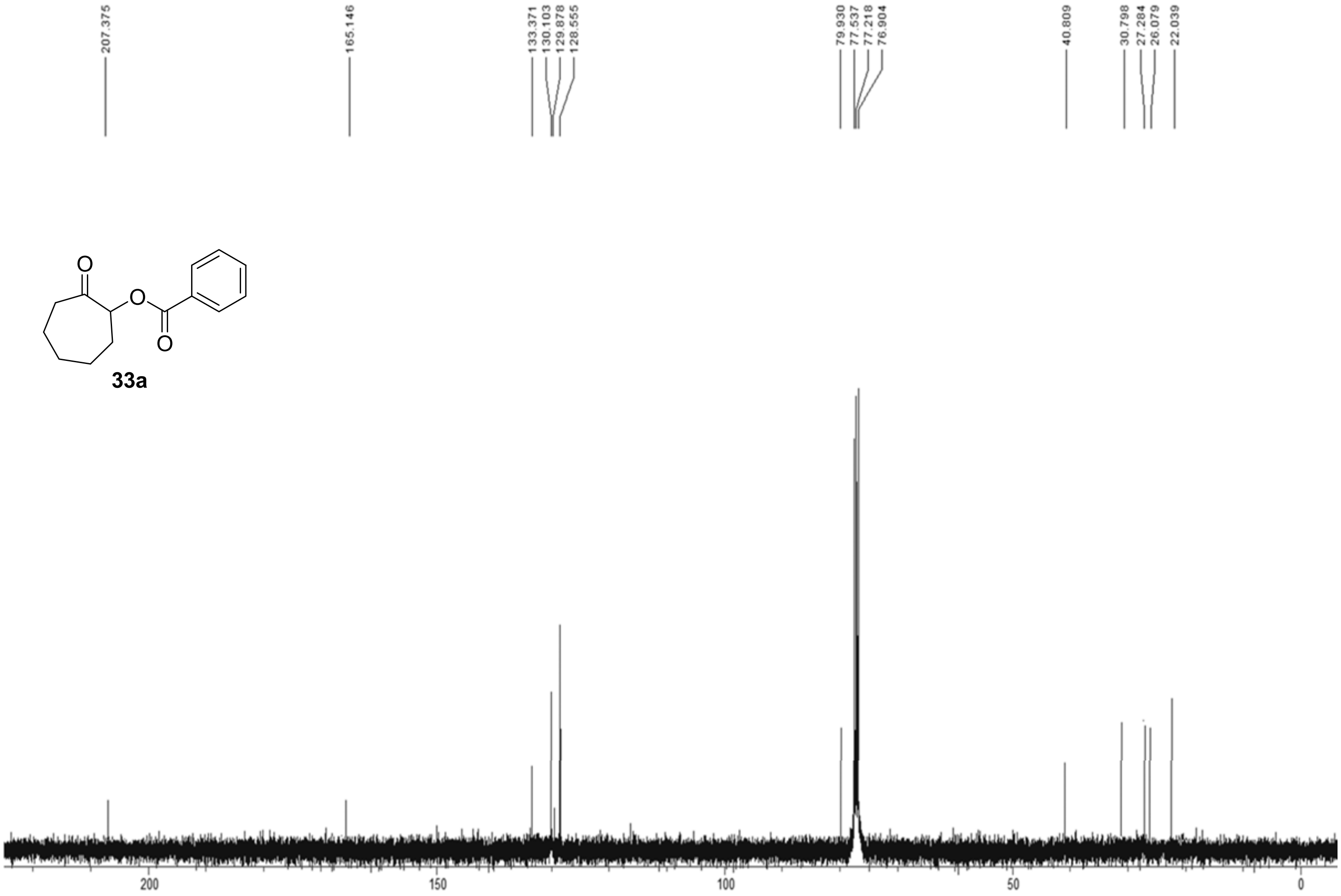
4.282
4.127
4.108
3.811
3.807
2.714
2.704
2.685
2.680
2.670
2.661
2.637
2.631
2.620
2.613
2.506
2.497
2.478
2.469
2.463
2.453
2.434
2.427
2.122
2.081
2.079
2.069
2.063
2.059
2.052
2.040
1.989
1.963
1.920
1.894
1.880
1.877
1.846
1.824
1.816
1.807
1.800
1.789
1.771
1.765
1.749
1.743
1.726
1.718
1.707
1.701
1.695
1.681
1.673
1.666
1.659
1.631
1.622
1.608
OH
O
0.81
0.73
1.00
0.99
1.12
3.03
3.28
0.99
10
8
6
4
2
0

33


213.251
77.537
77.218
77.196
76.904
39.914
33.509
29.369
26.469
23.607
O
OH
33
200
150
100
50
0


33a

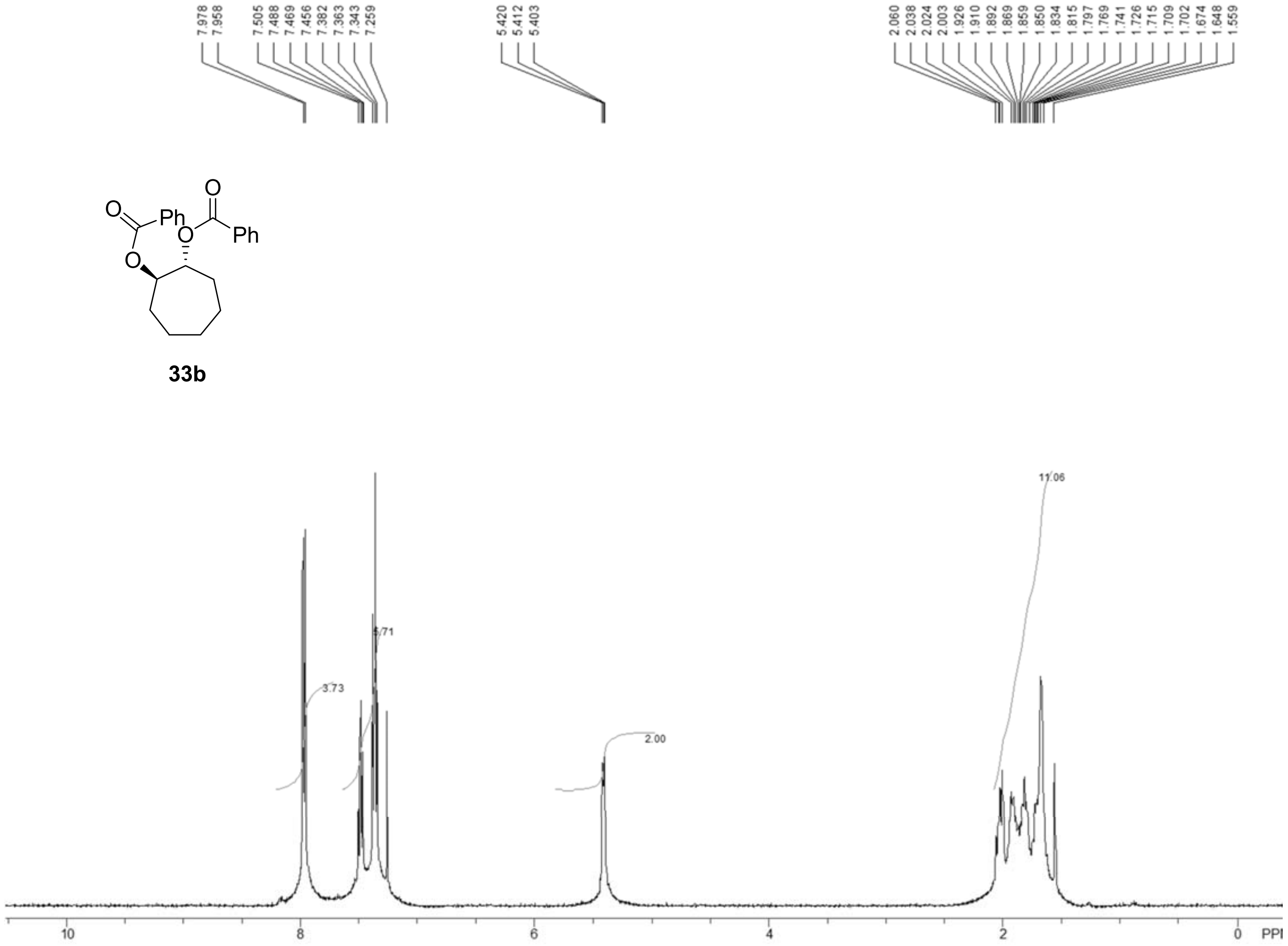
8.094
8.075
7.574
7.554
7.467
7.449
7.429
7.259
5.480
5.472
5.457
5.449
2.523
2.511
2.142
2.132
2.122
2.114
2.103
1.964
2.687
1.938
1.927
1.920
1.909
1.885
1.868
1.853
1.848
1.830
1.819
1.808
1.793
1.784
1.772
1.744
1.715
1.571
1.525
1.491
1.465
1.431
1.255
O
O
O
1.69
3.52
1.00
2.12
1.39
6.89
1.32
10
8
6
4
2
0
PP


207.375
165.146
133.371
130.103
129.878
128.555
79.930
77.537
77.218
76.904
40.809
30.798
27.284
26.079
22.039
O
O
O
200
150
100
50
0

33a

O
Ph
O
O
Ph
O

33b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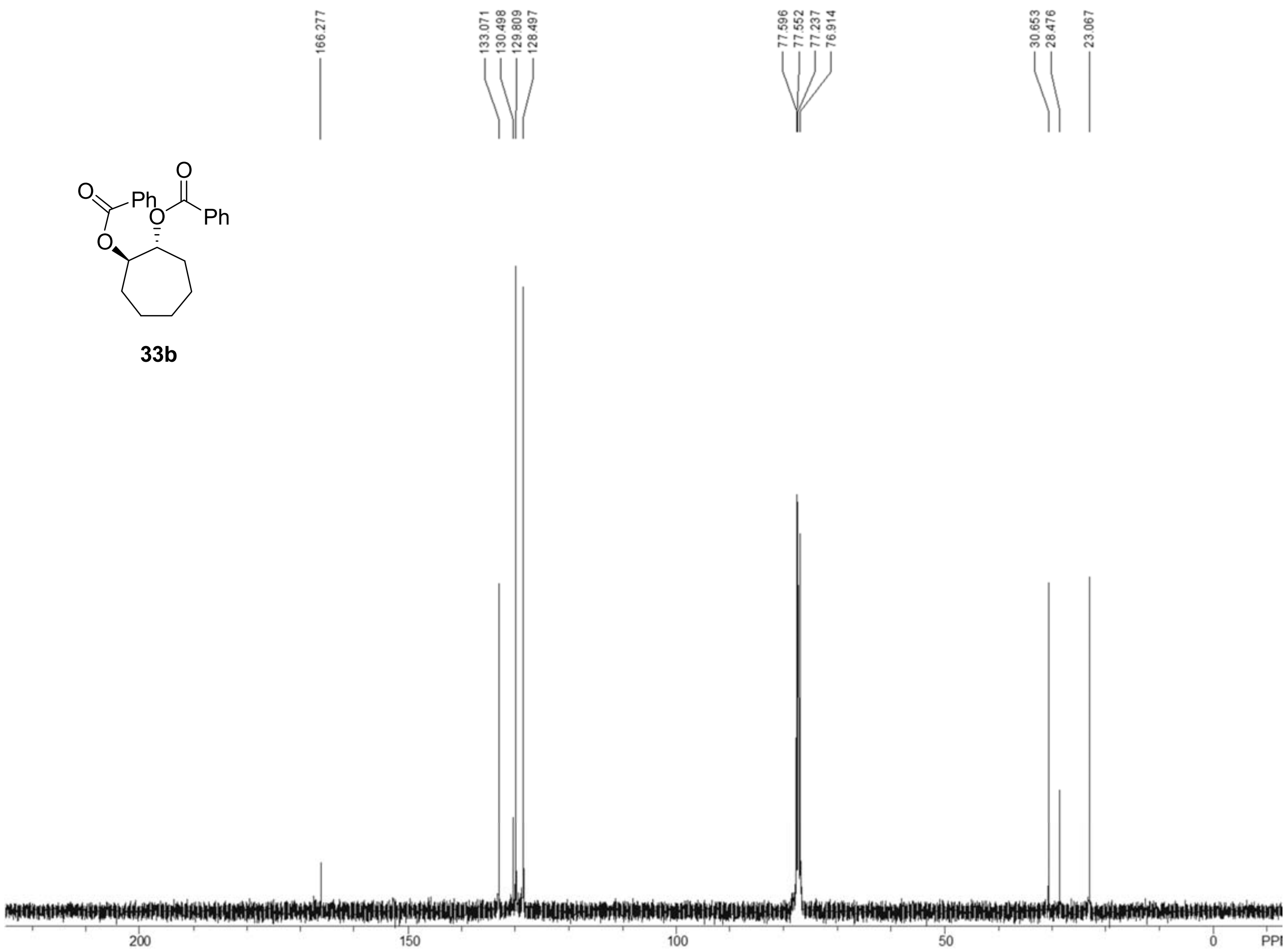
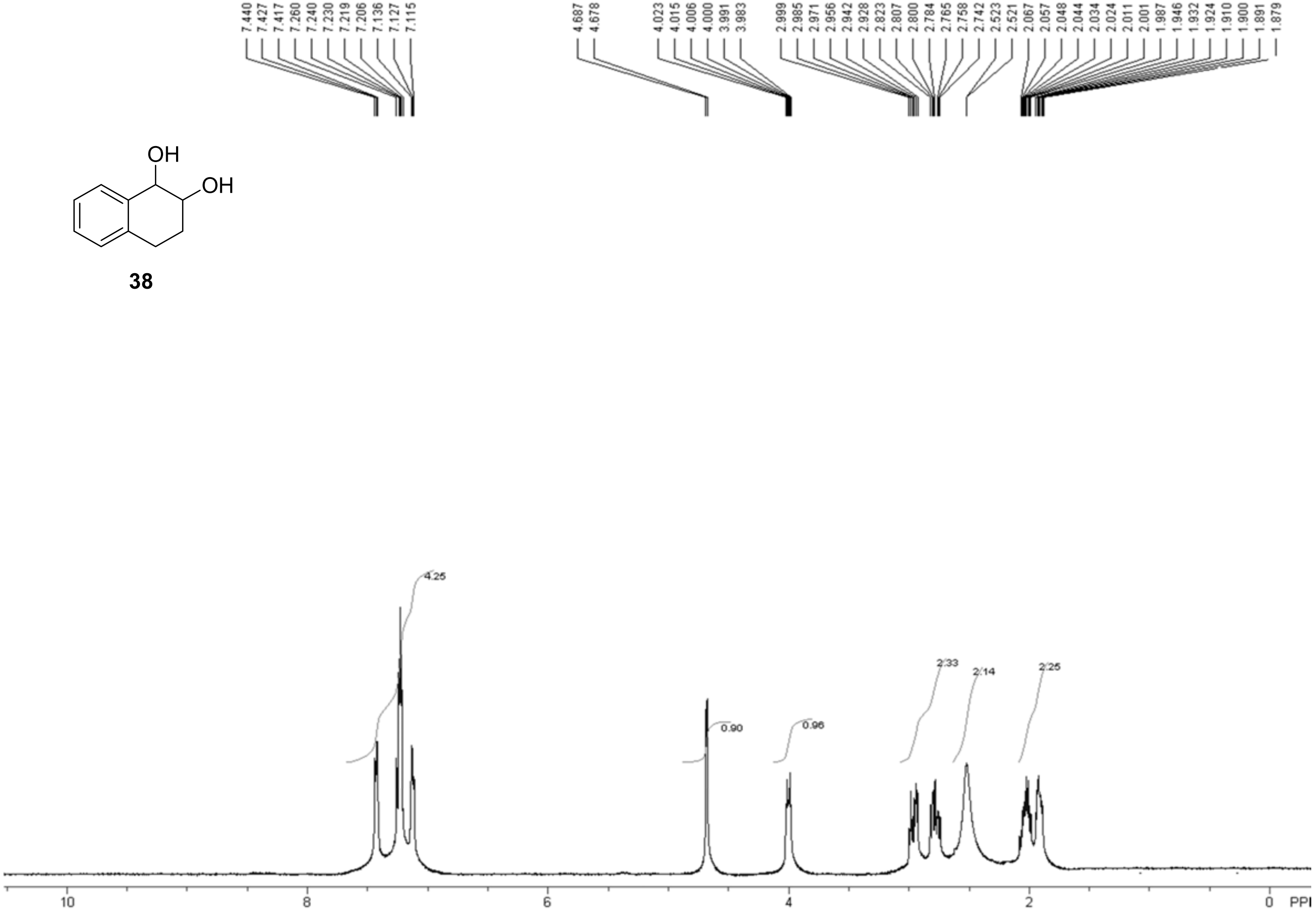
7.958
7.505
7.488
7.469
7.456
7.382
7.363
7.343
7.259
5.420
5.412
5.403
2.060
2.038
2.024
2.003
1.926
1.910
1.892
1.869
1.859
1.850
1.834
1.815
1.797
1.769
1.741
1.726
1.715
1.709
1.702
1.674
1.648
1.559
3.73
5.71
2.00
11.06
10
8
6
4
2
0
PPI



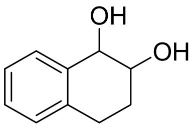
33b

166.277
133.071
130.498
129.809
128.497
77.596
77.552
77.237
76.914
30.653
28.476
23.067
O
Ph
O
O
Ph
O
200
150
100
50
0
PPI

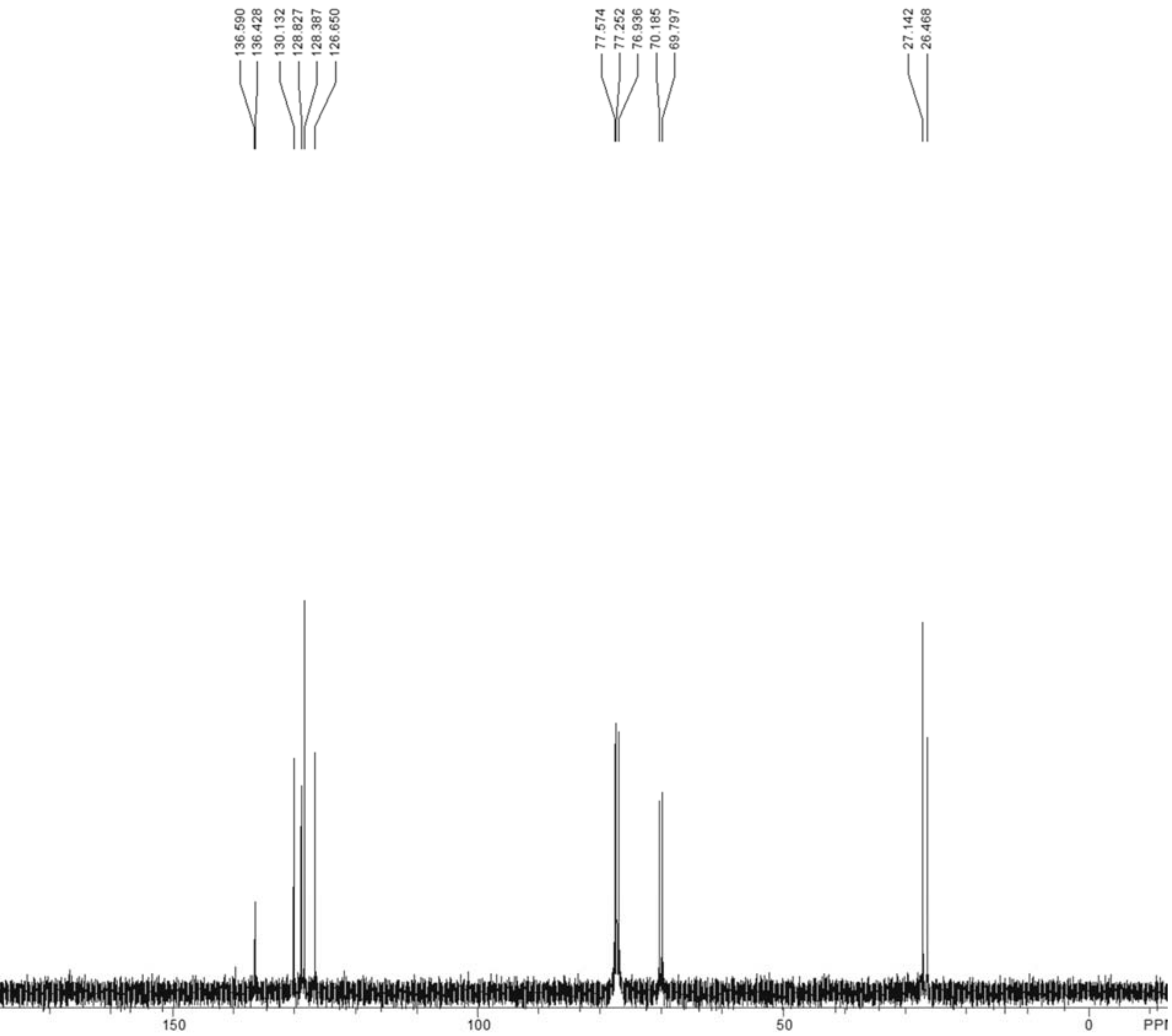


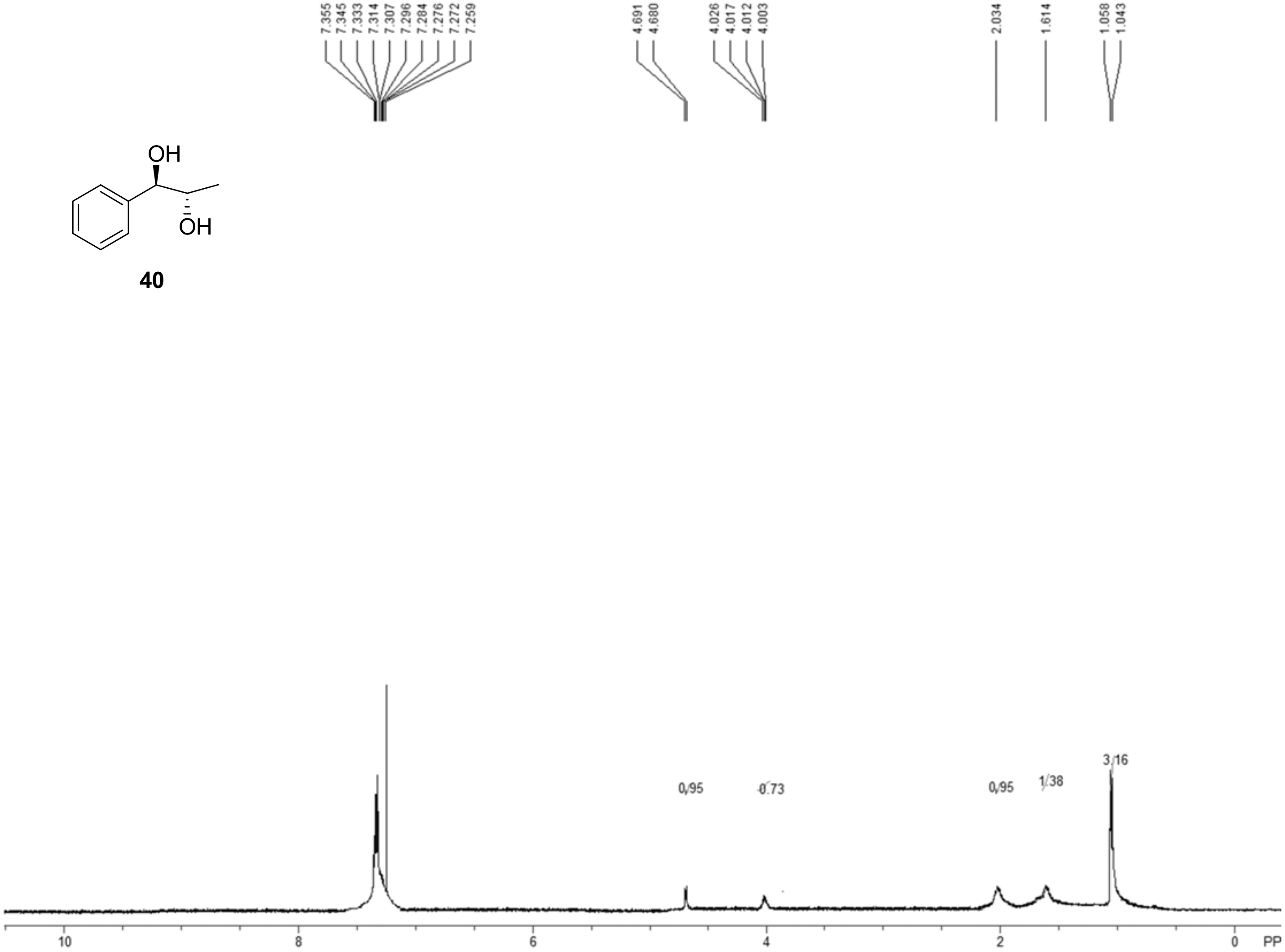
38

7.440
7.427
7.417
7.260
7.240
7.230
7.219
7.206
7.136
7.127
7.115
4.687
4.678
4.023
4.015
4.006
4.000
3.991
3.983
2.999
2.985
2.971
2.956
2.942
2.928
2.823
2.807
2.800
2.784
2.765
2.758
2.742
2.523
2.521
2.067
2.057
2.048
2.044
2.034
2.024
2.011
2.001
1.987
1.946
1.932
1.924
1.910
1.900
1.891
1.879
4.25
0.90
0.96
2.33
2.14
2.25
10
8
6
4
2
0
PPI

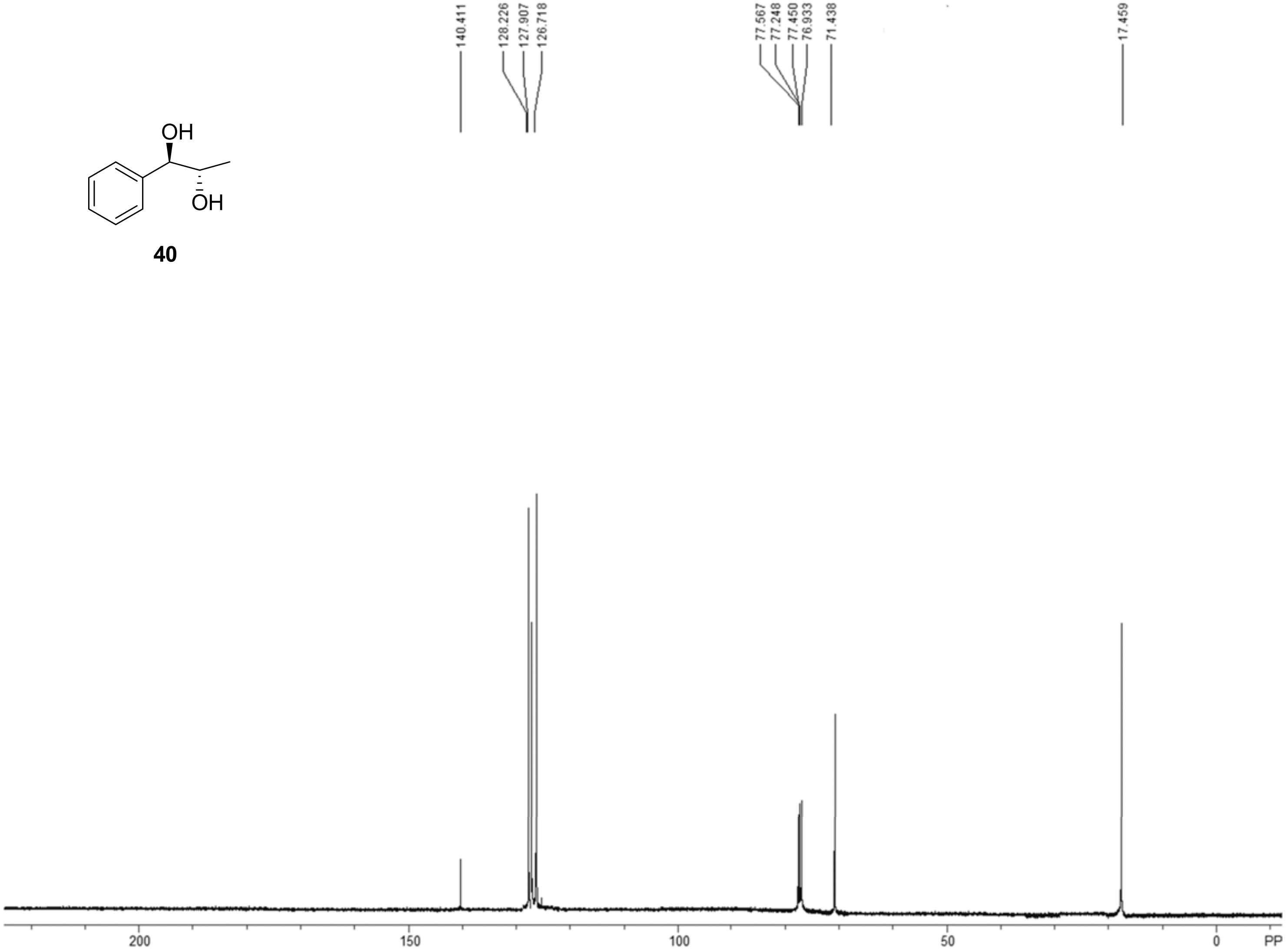

OH
OH

38


136.590
136.428
130.132
128.827
128.387
126.650
77.574
77.252
76.936
70.185
69.797
27.142
26.468
200
150
100
50
0
PPI

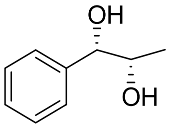

7.355
7.345
7.333
7.314
7.307
7.296
7.284
7.276
7.272
7.259
4.691
4.680
4.026
4.017
4.012
4.003
2.034
1.614
1.058
1.043
OH
OH
0,95
0.73
0,95
1,38
3,16
10
8
6
4
2
0
PP

40

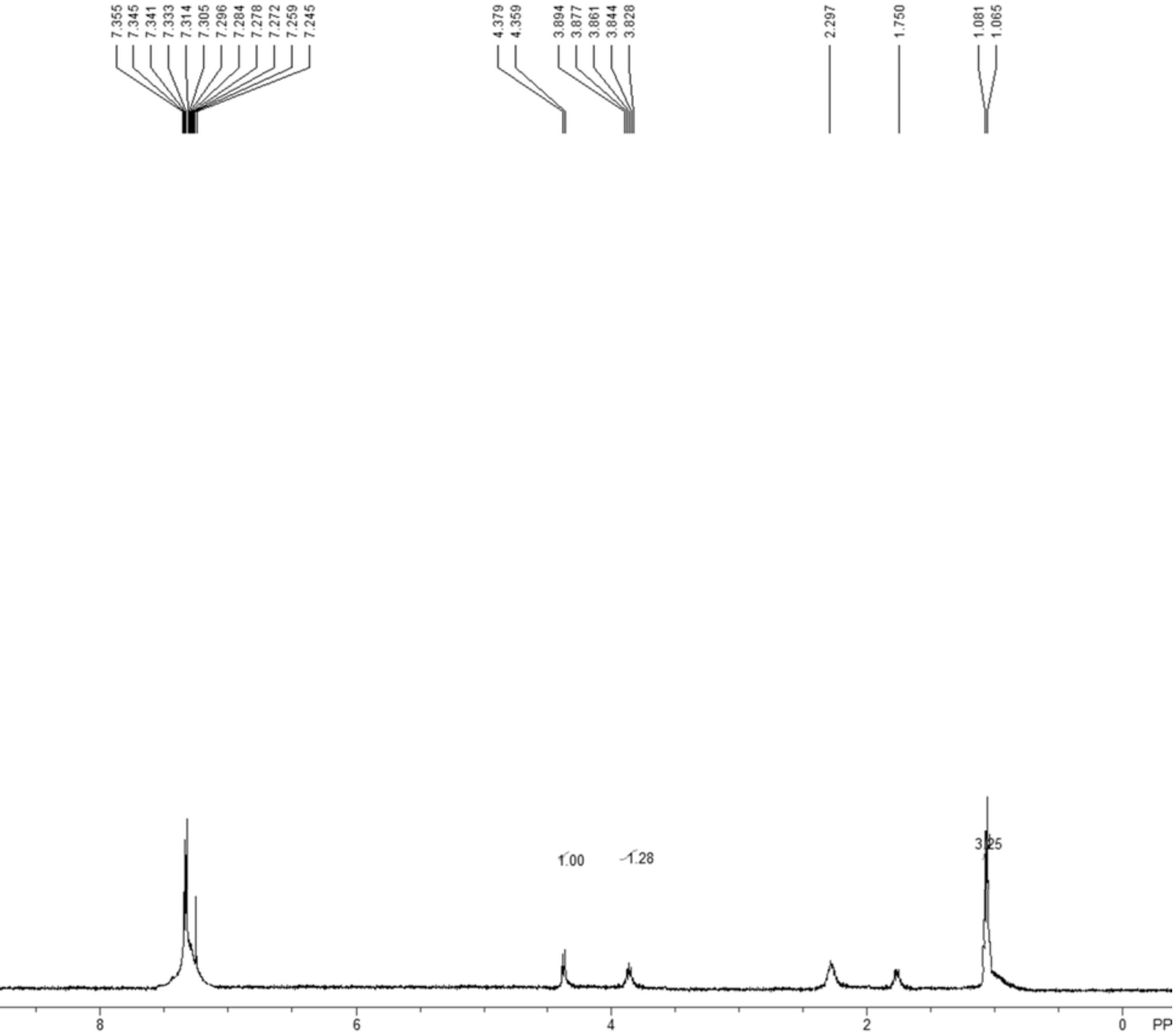


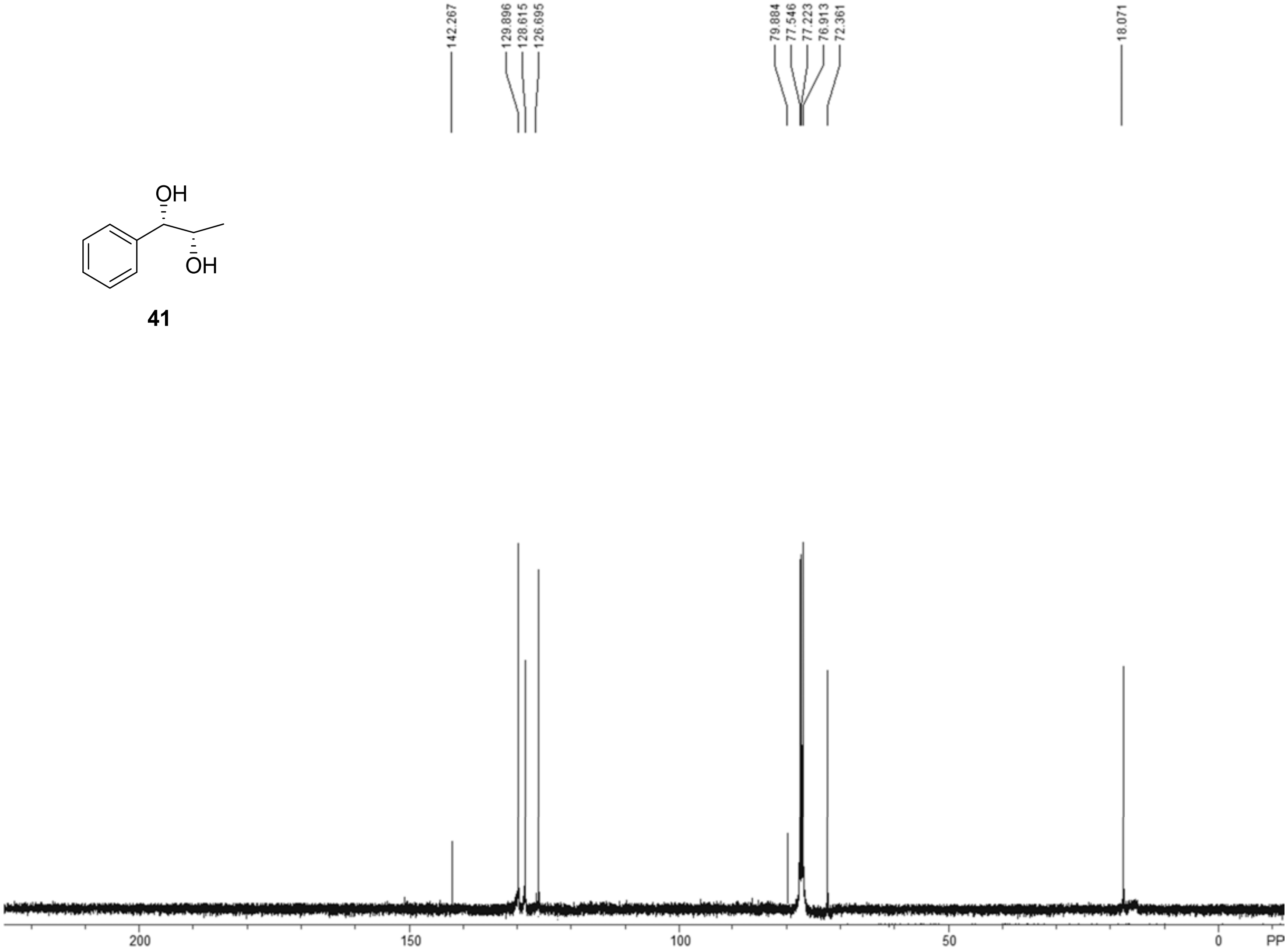
40

140.411
128.226
127.907
126.718
77.567
77.248
77.450
76.933
71.438
17.459
OH
OH
200
150
100
50
0
PP



41

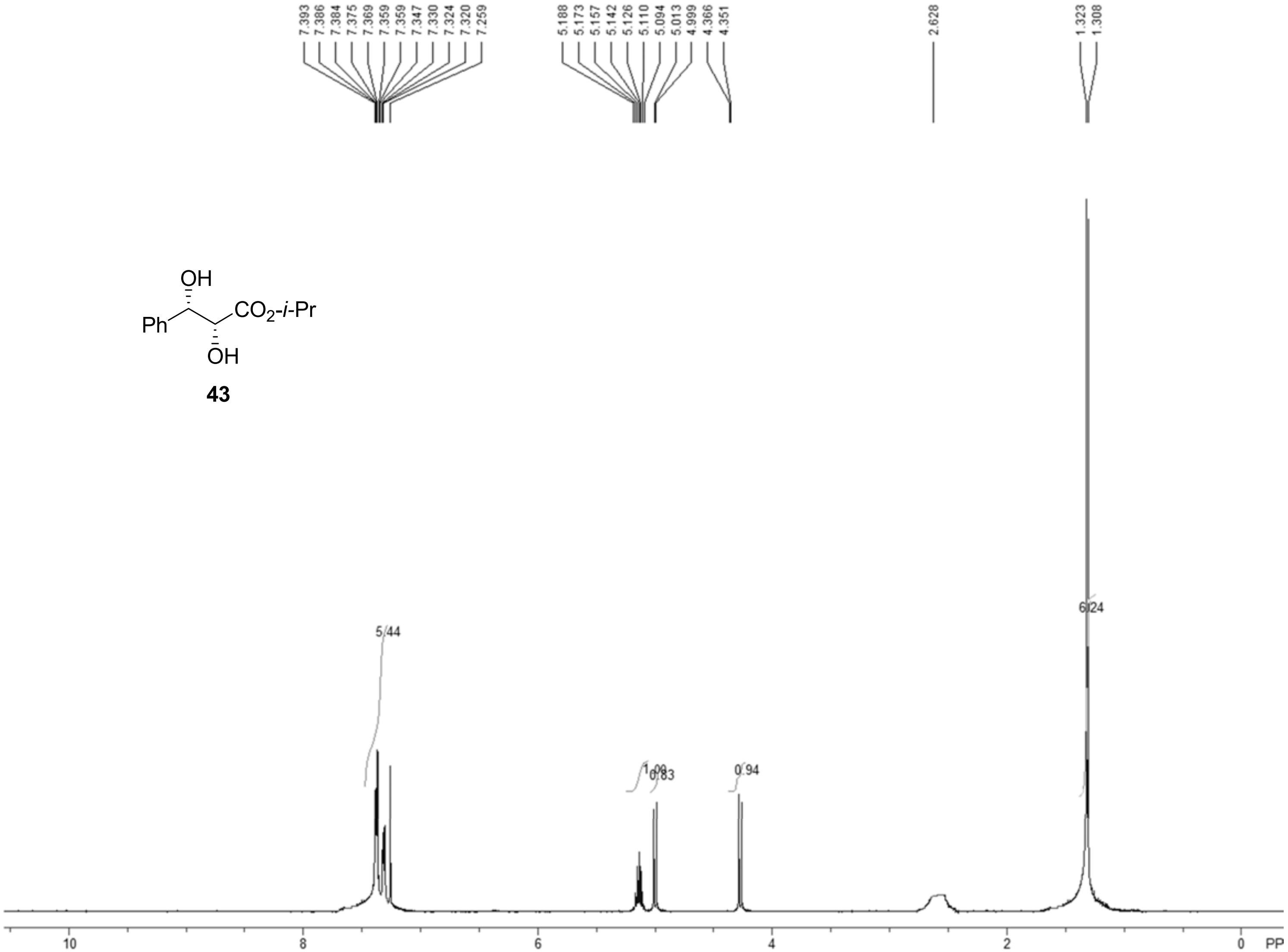

7.355
7.345
7.341
7.333
7.314
7.305
7.296
7.284
7.278
7.272
7.259
7.245
4.379
4.359
3.894
3.877
3.861
3.844
3.828
2.297
1.750
1.081
1.065
1.00
1.28
3.25
10
8
6
4
2
0
PP

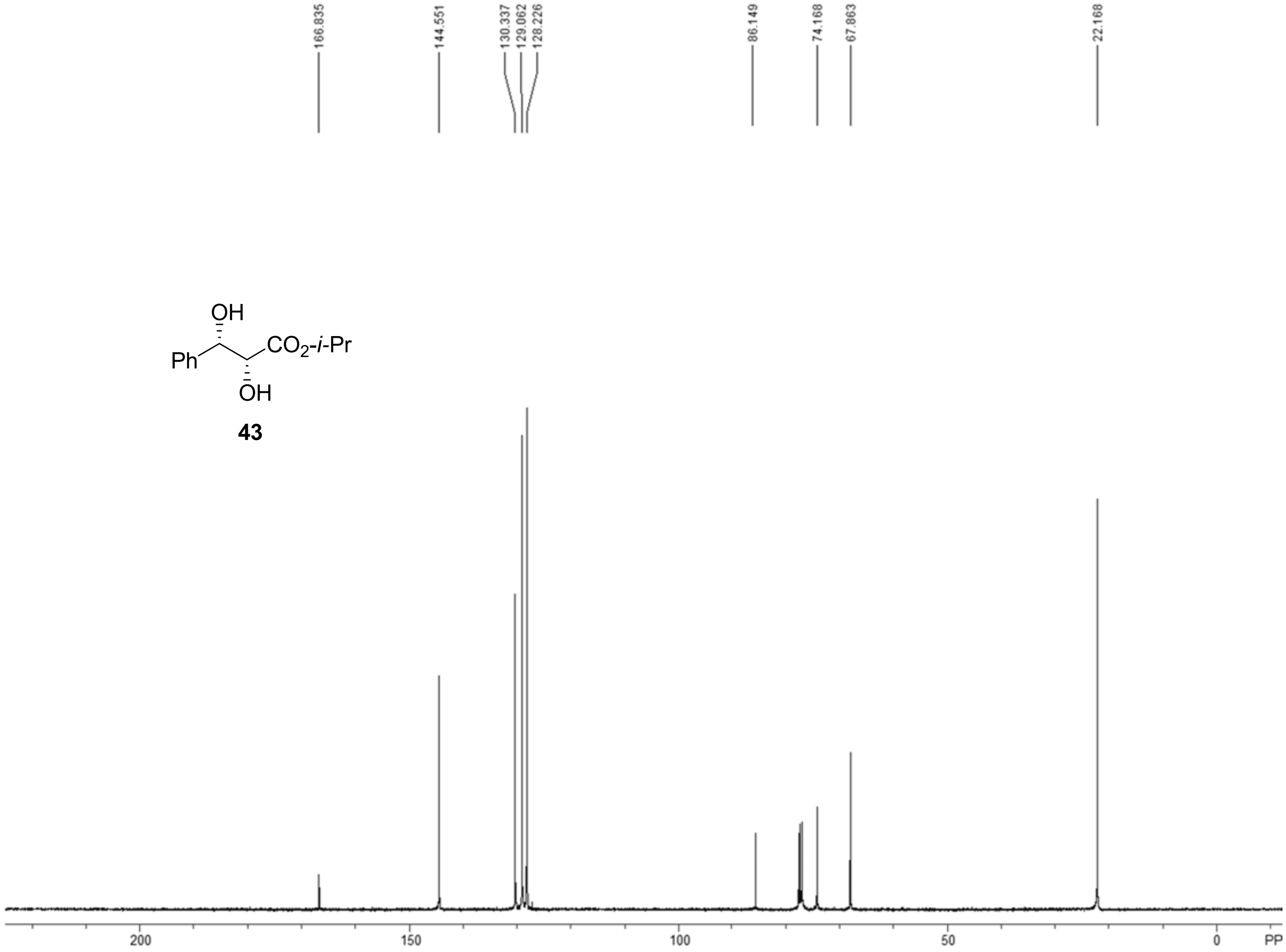


41
142.267
129.896
128.615
126.695
79.884
77.546
77.223
76.913
72.361
18.071
200
150
100
50
0
PP

OH
Ph
CO2-i-Pr
OH

43

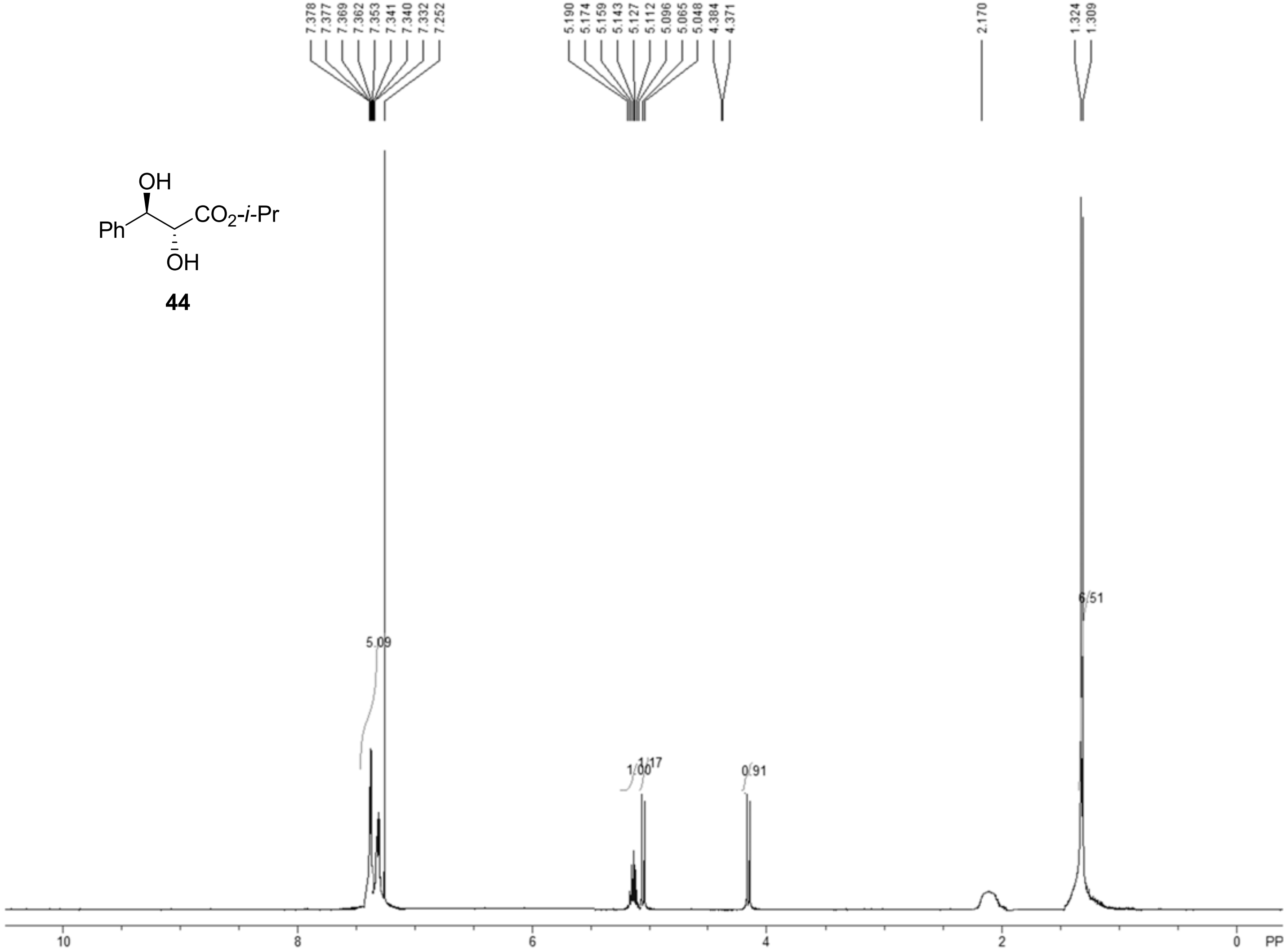

7.393
7.386
7.384
7.375
7.369
7.359
7.359
7.347
7.330
7.324
7.320
7.259
5.188
5.173
5.157
5.142
5.126
5.110
5.094
5.013
4.999
4.366
4.351
2.628
1.323
1.308
5.44
1.00
0.83
0.94
6.24
10
8
6
4
2
0
PP

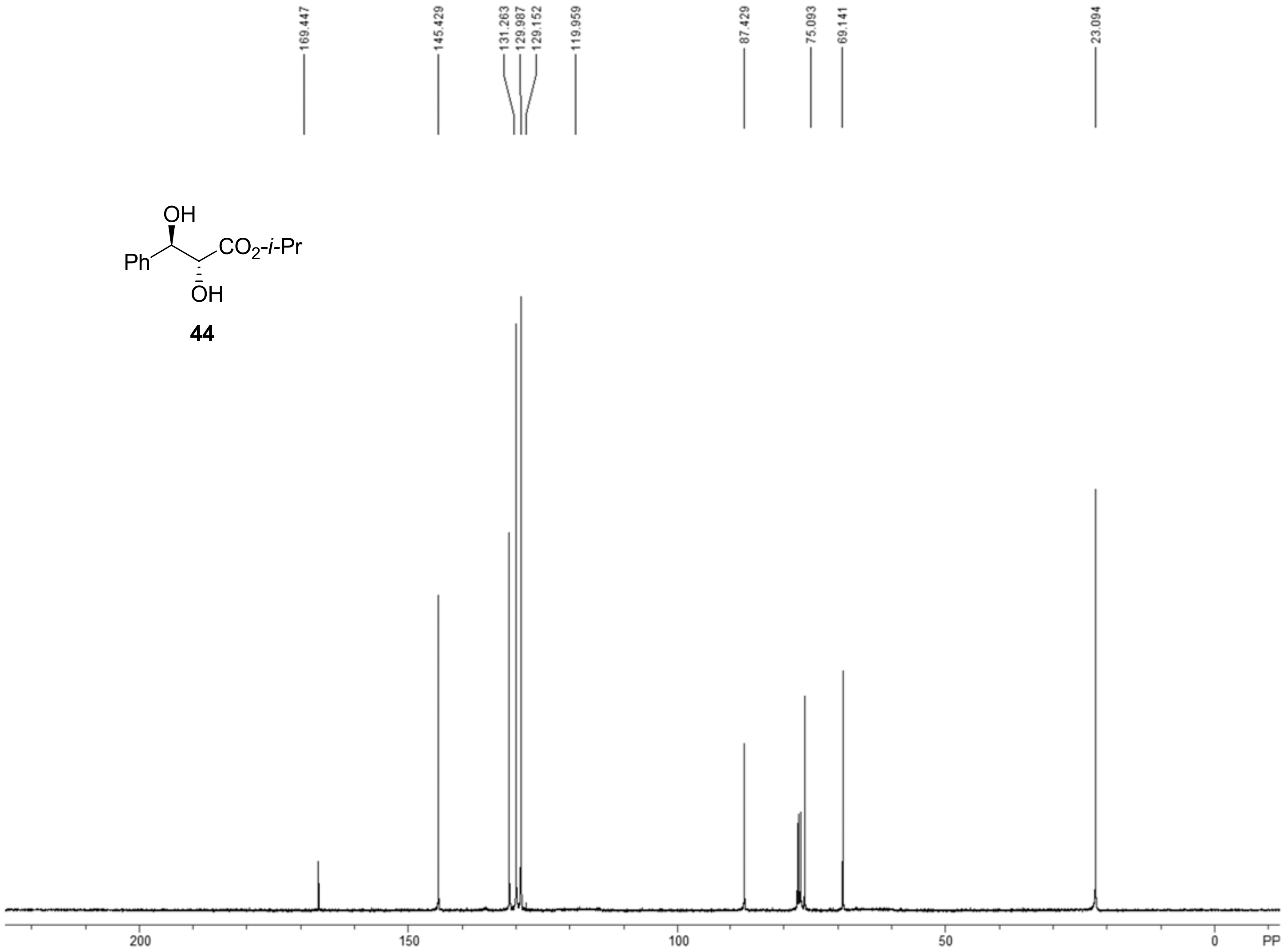

166.835
144.551
130.337
129.062
128.226
86.149
74.168
67.863
22.168
OH
Ph
CO2-i-Pr
OH
200
150
100
50
0
PP

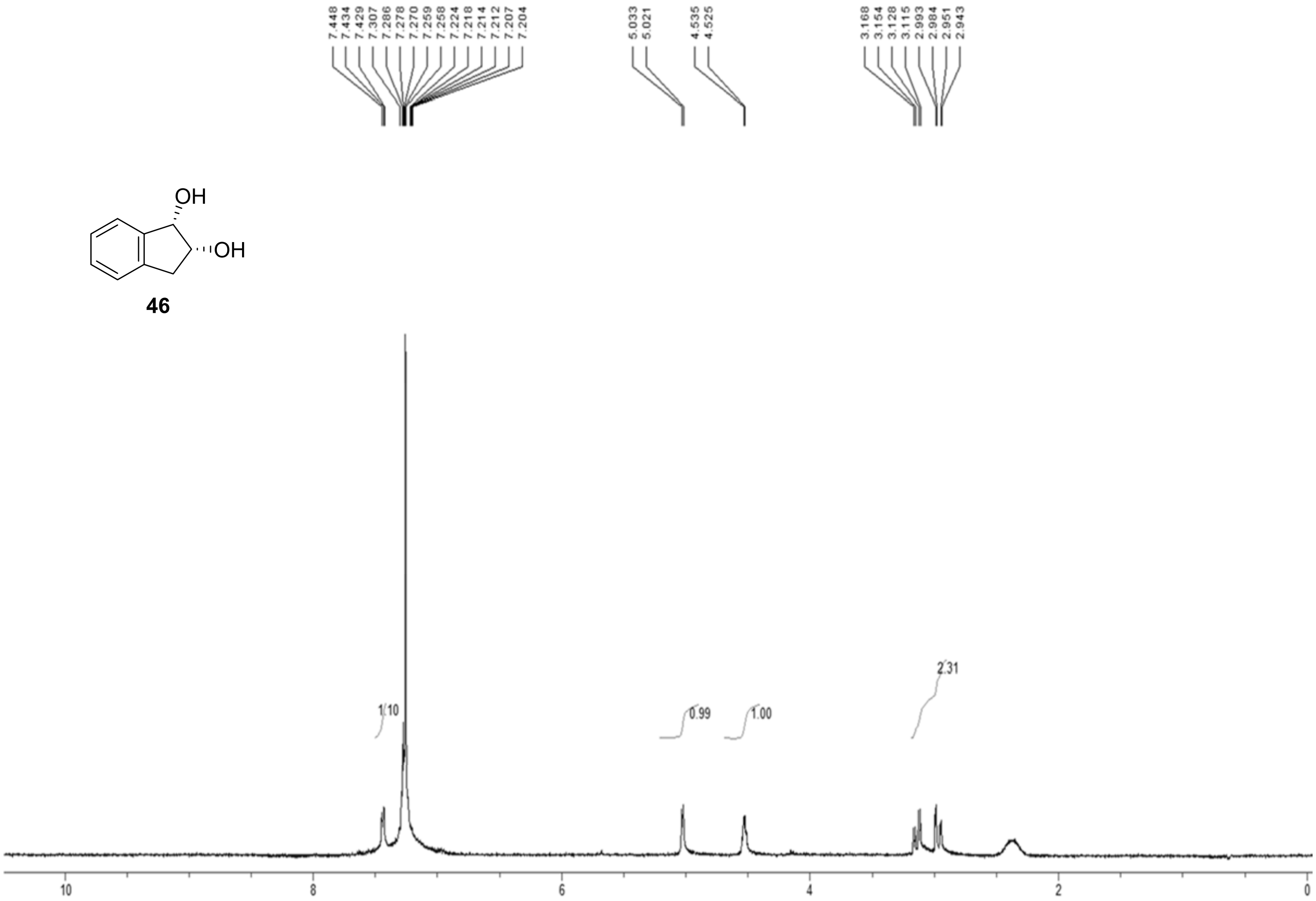
43

OH
Ph
CO_2-*i*-Pr
OH

44


7.378
7.377
7.369
7.362
7.353
7.341
7.340
7.332
7.252
5.190
5.174
5.159
5.143
5.127
5.112
5.096
5.065
5.048
4.384
4.371
2.170
1.324
1.309
5.09
1.00
1.17
0.91
6.51
10
8
6
4
2
0
PP


169.447
145.429
131.263
129.987
129.152
119.959
87.429
75.093
69.141
23.094
OH
Ph
CO2-i-Pr
OH
44
200
150
100
50
0
PP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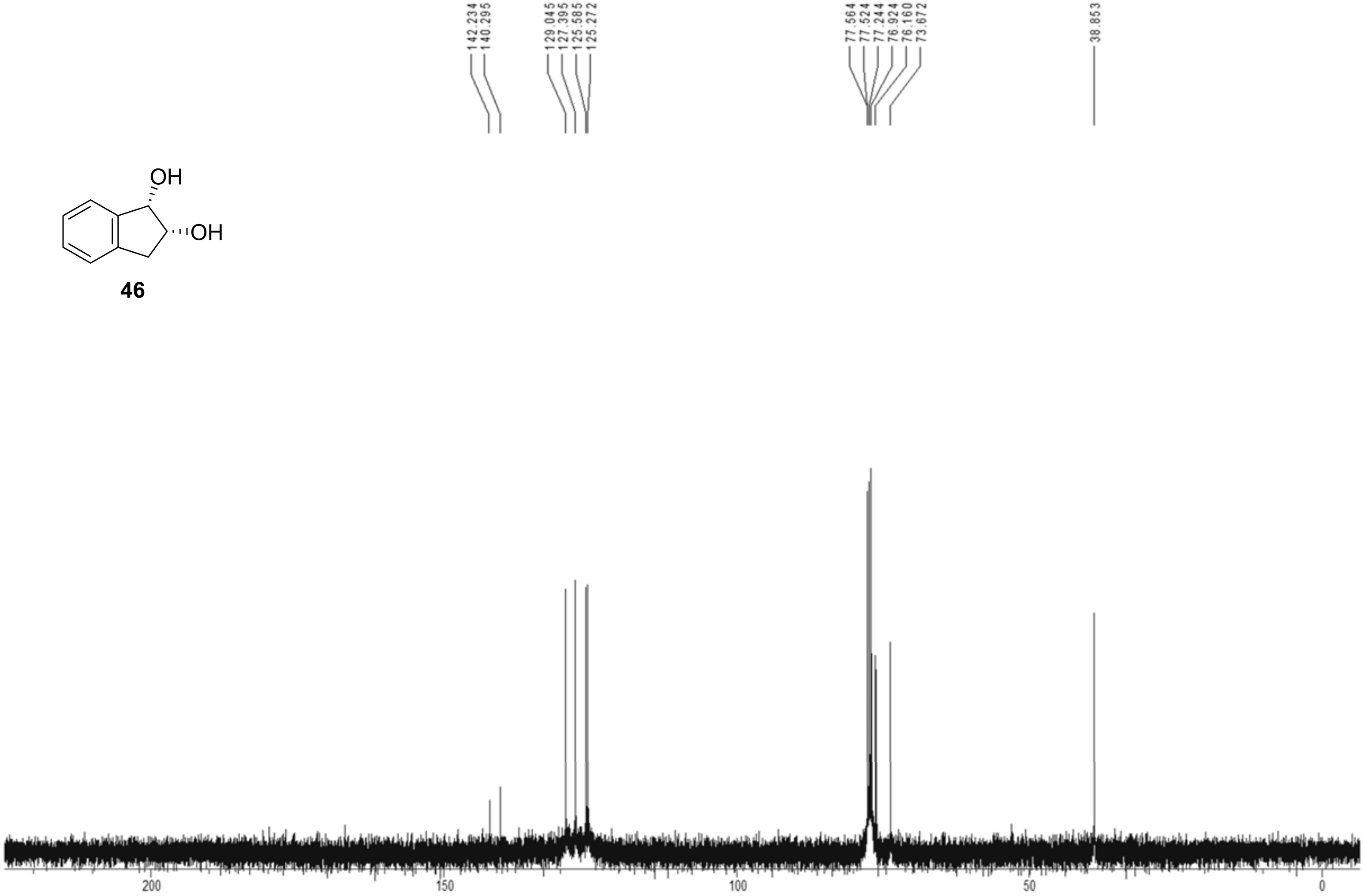
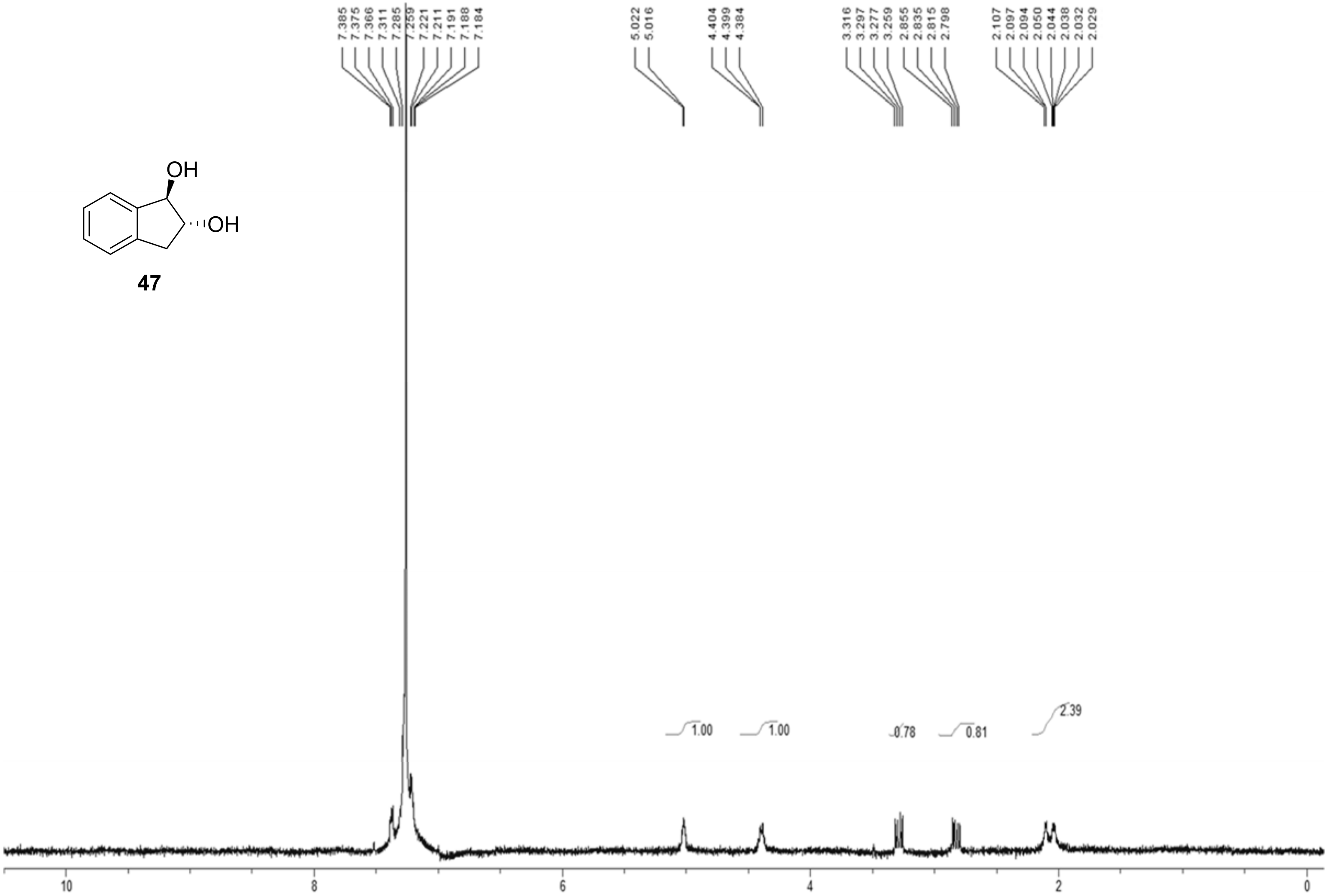
7.434
7.429
7.307
7.286
7.278
7.270
7.259
7.258
7.224
7.218
7.214
7.212
7.207
7.204
5.033
5.021
4.535
4.525
3.168
3.154
3.128
3.115
2.993
2.984
2.951
2.943
OH
OH
46
1.10
0.99
1.00
2.31
10
8
6
4
2
0


OH
OH

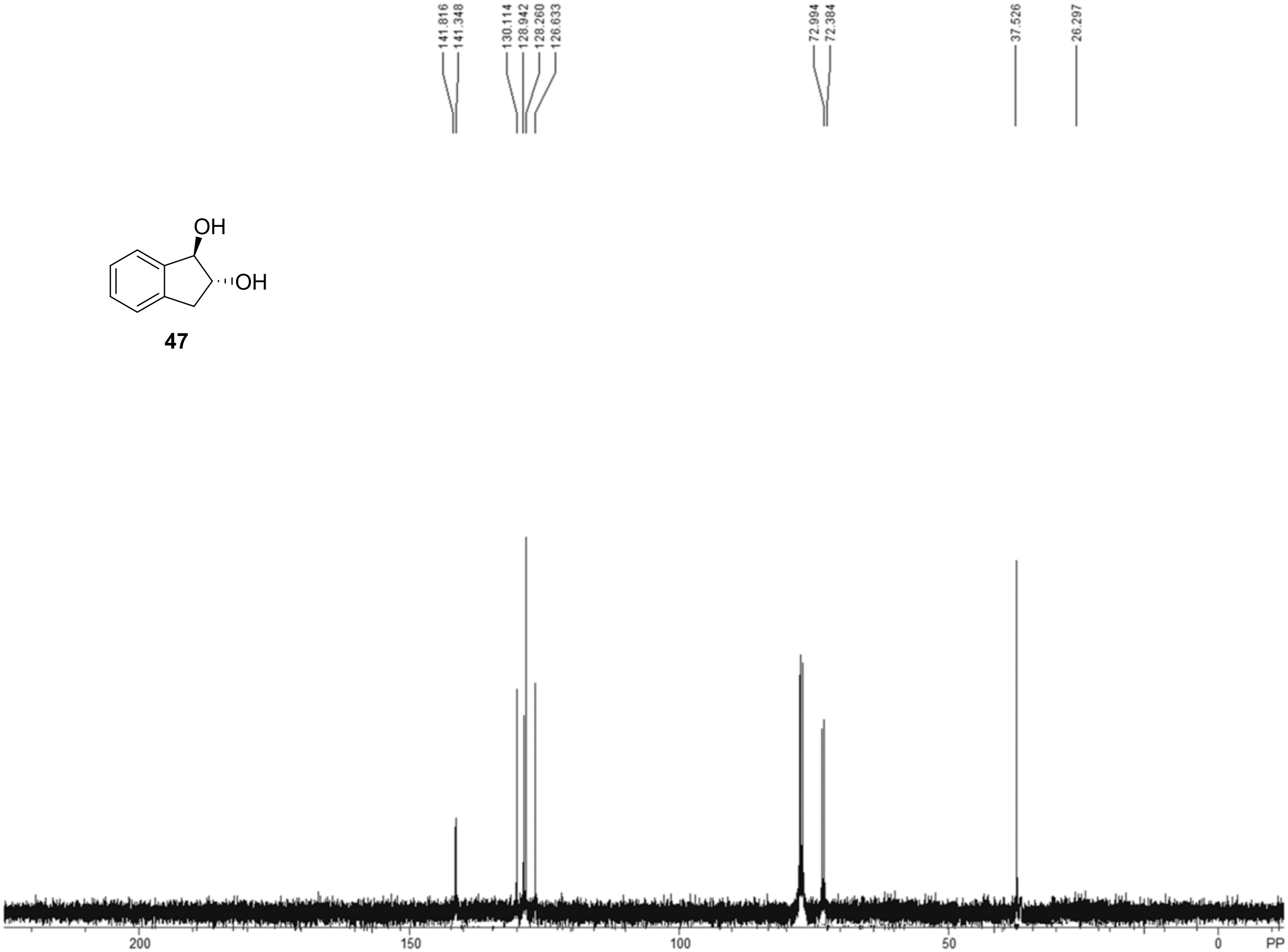
46

142.234
140.295
129.045
127.395
125.585
125.272
77.564
77.524
77.244
76.924
76.160
73.672
38.853
200
150
100
50
0



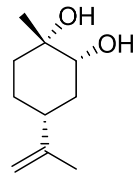
7.385
7.375
7.366
7.311
7.285
7.259
7.221
7.211
7.191
7.188
7.184
5.022
5.016
4.404
4.399
4.384
3.316
3.297
3.277
3.259
2.855
2.835
2.815
2.798
2.107
2.097
2.094
2.050
2.044
2.038
2.032
2.029
OH
OH
1.00
1.00
0.78
0.81
2.39
10
8
6
4
2
0

47

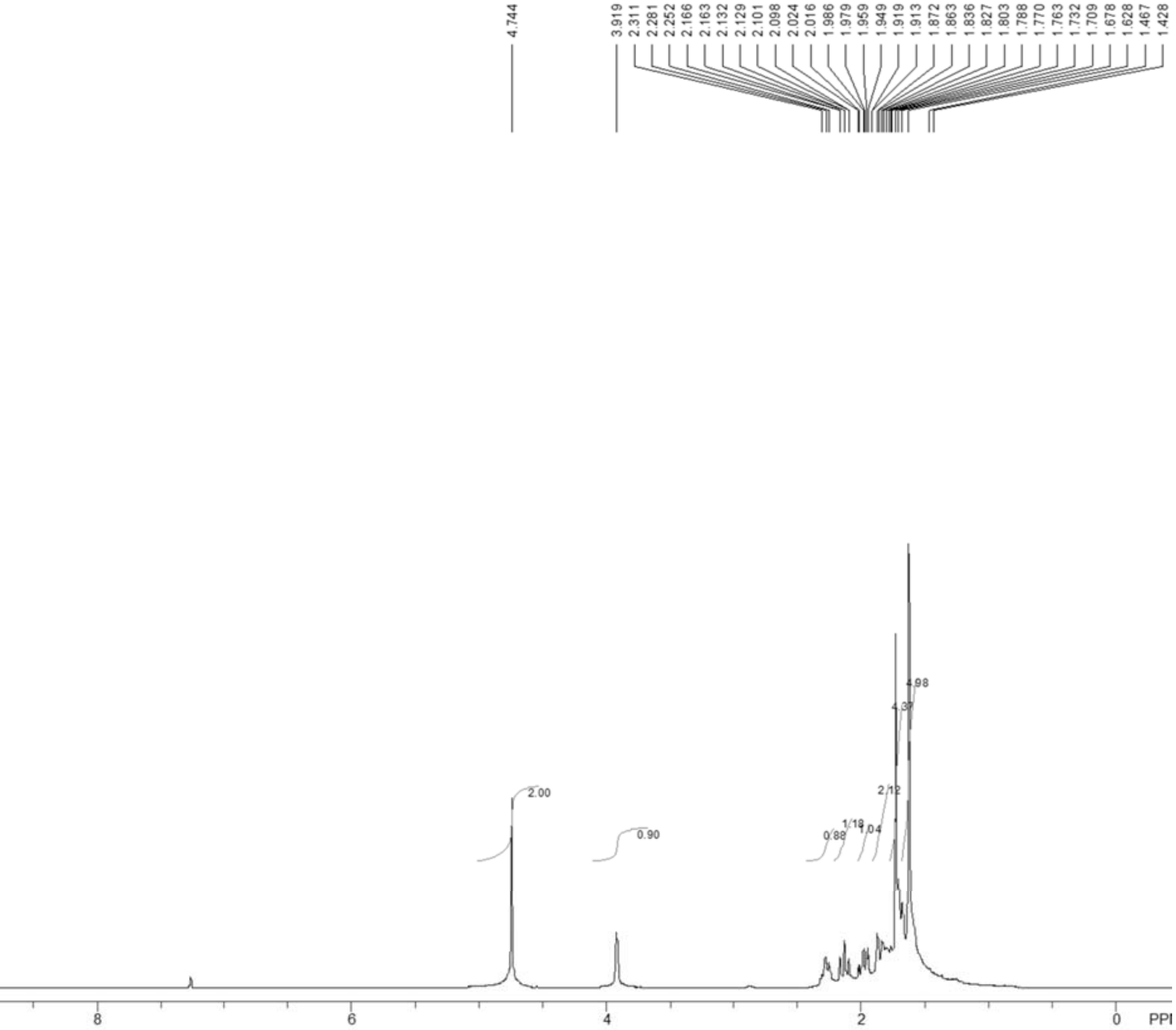


47

141.816
141.348
130.114
128.942
128.260
126.633
72.994
72.384
37.526
26.297
OH
OH
200
150
100
50
0
PP


OH
OH

49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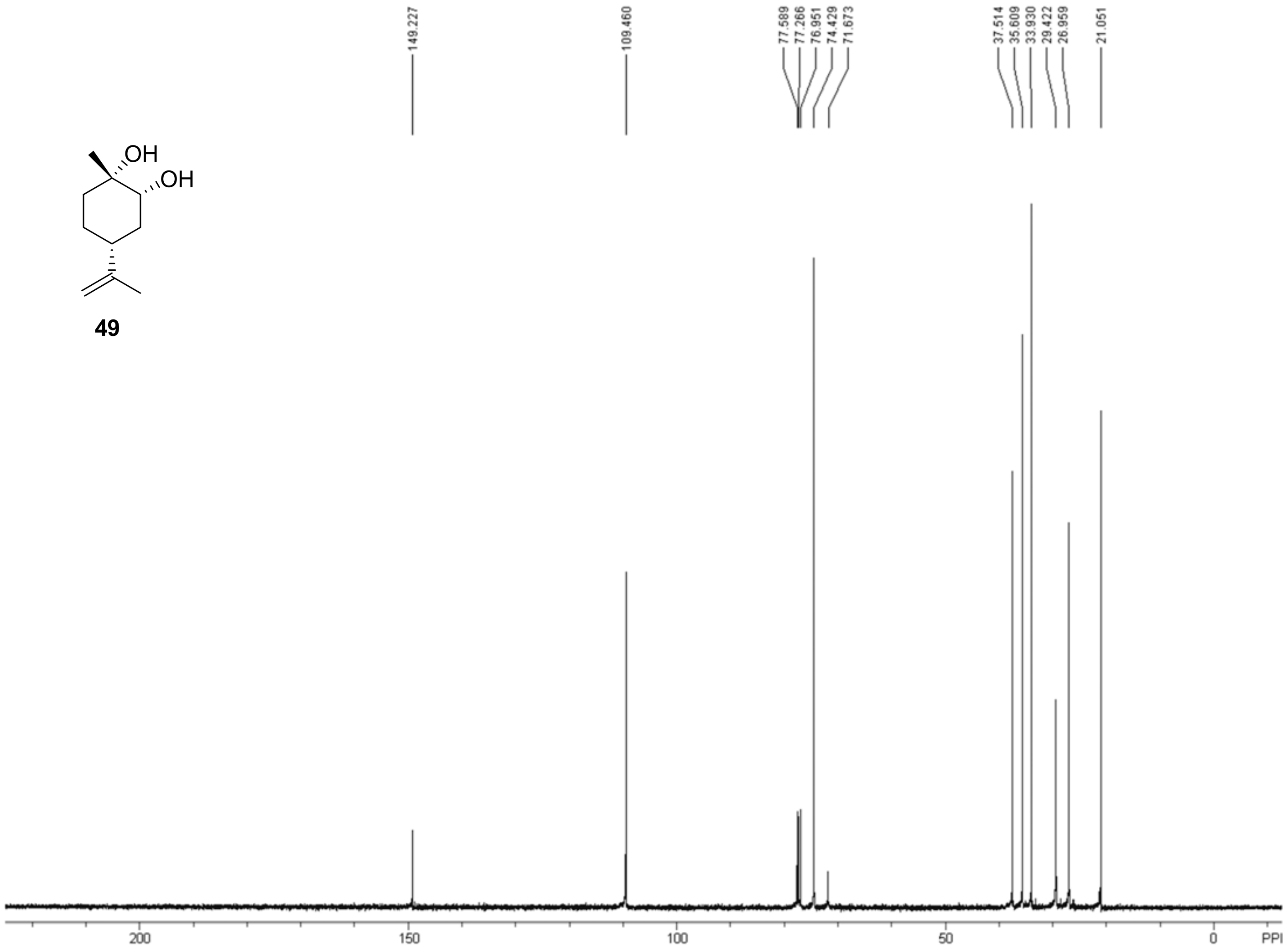
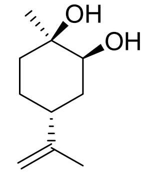
3.919
2.311
2.281
2.252
2.166
2.163
2.132
2.129
2.101
2.098
2.024
2.016
1.986
1.979
1.959
1.949
1.919
1.913
1.872
1.863
1.836
1.827
1.803
1.788
1.770
1.763
1.732
1.709
1.678
1.628
1.467
1.428
2.00
0.90
0.88
1.18
1.04
2.12
4.37
4.98
10
8
6
4
2
0
PPI



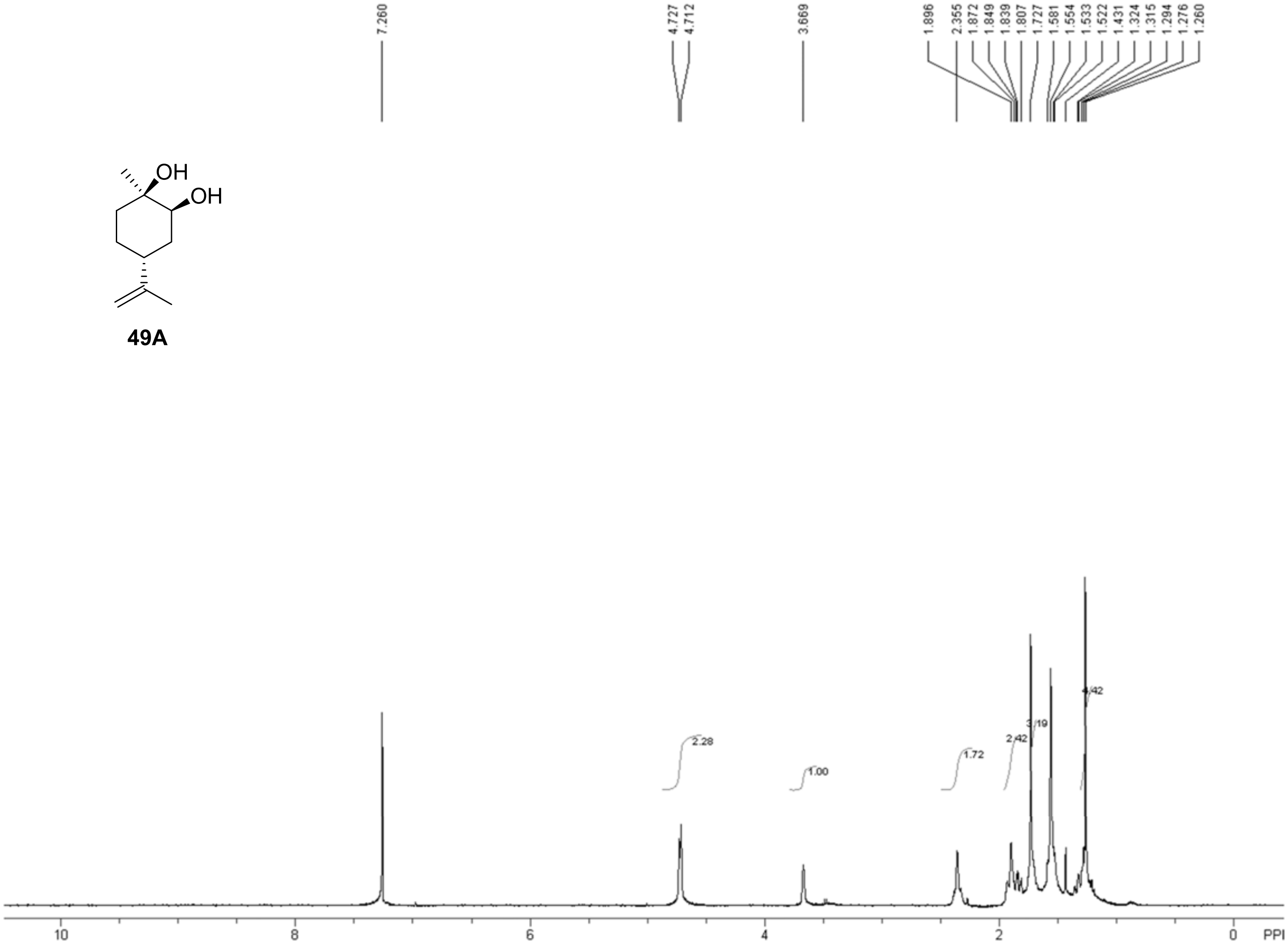
OH
OH

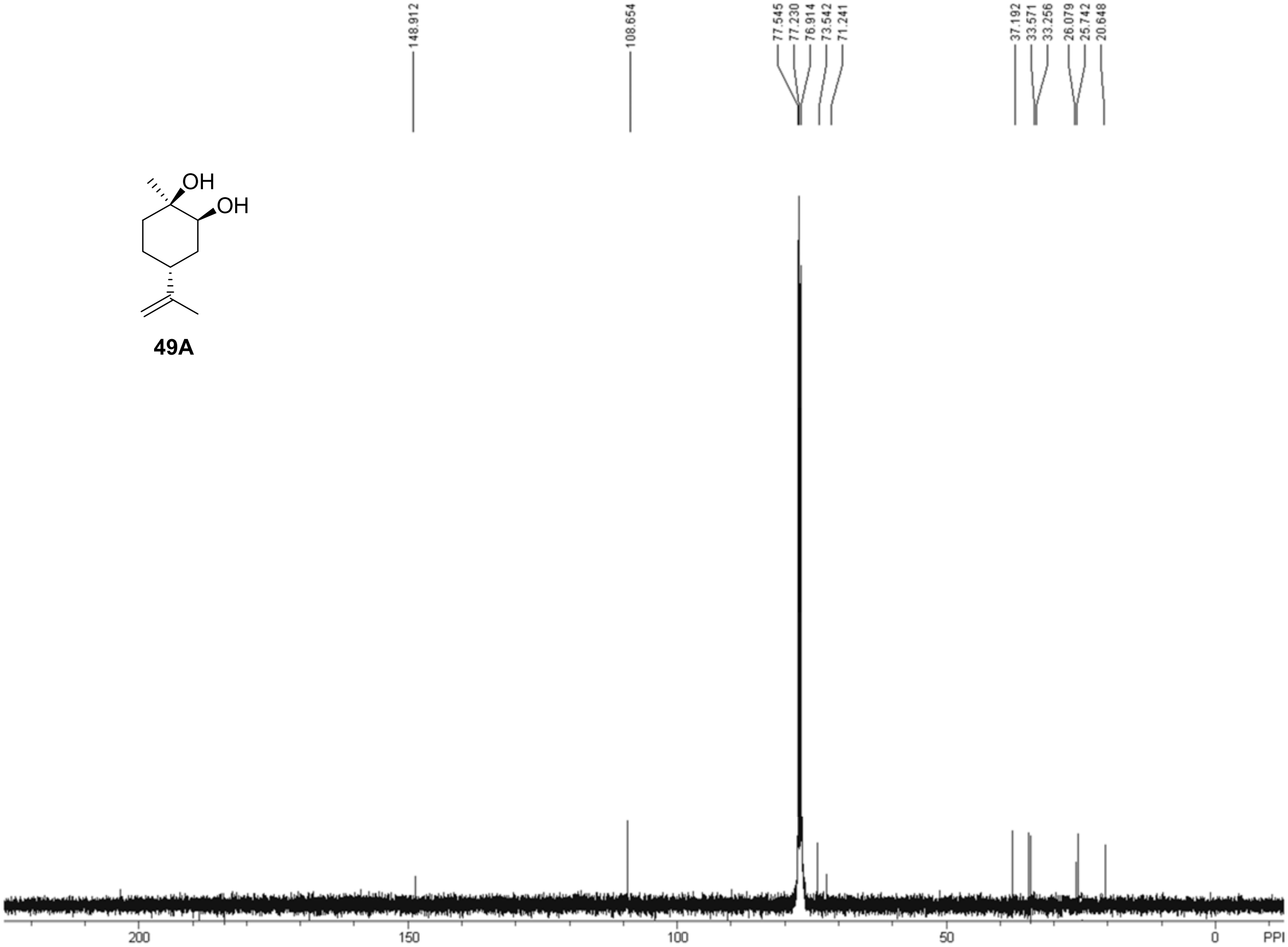
49

149.227
109.460
77.589
77.266
76.951
74.429
71.673
37.514
35.609
33.930
29.422
26.959
21.051
200
150
100
50
0
PP


OH
OH

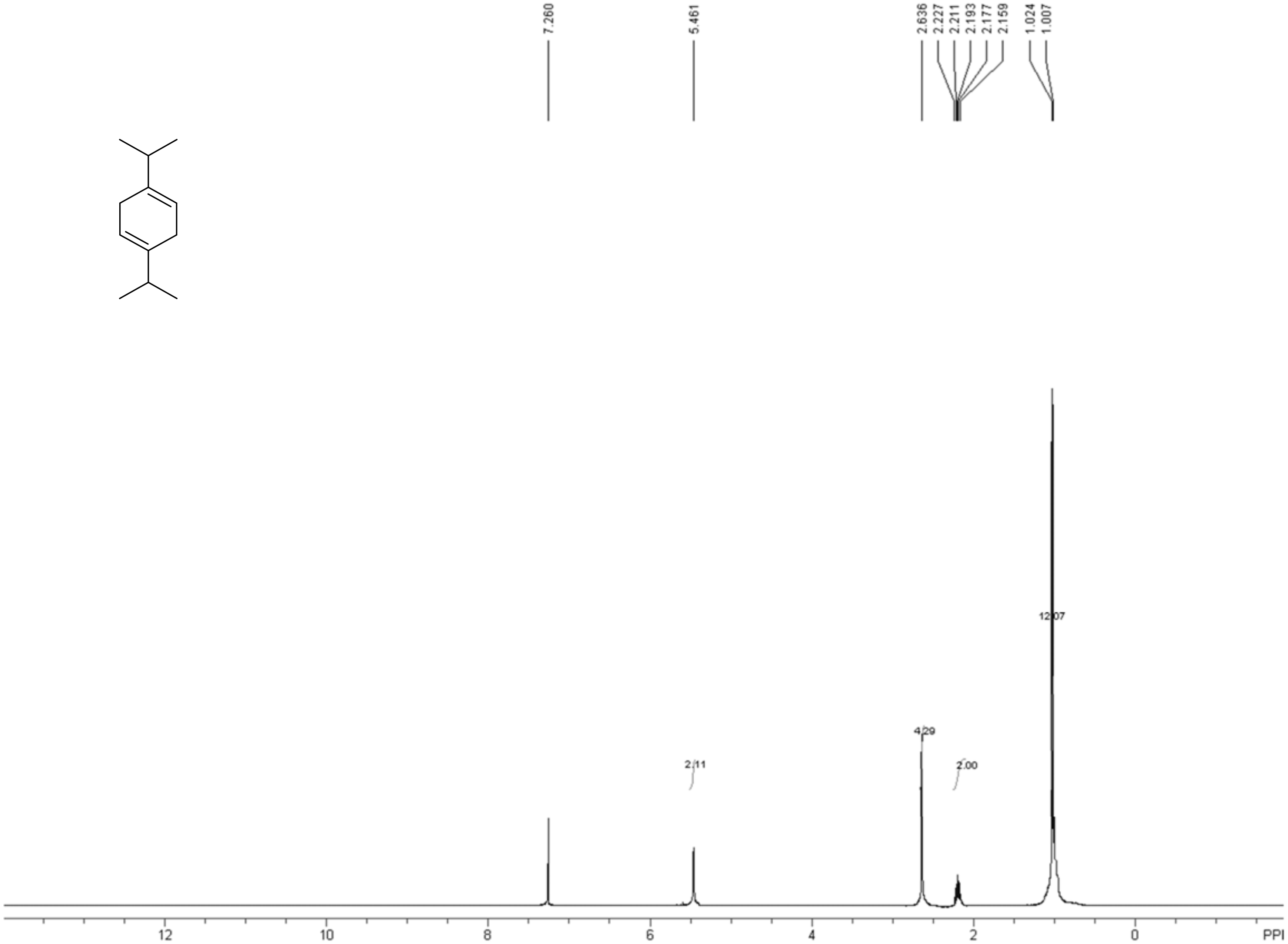
49A


7.260
4.727
4.712
3.669
1.896
2.355
1.872
1.849
1.839
1.807
1.727
1.581
1.554
1.533
1.522
1.431
1.324
1.315
1.294
1.276
1.260
2.28
1.00
1.72
2.42
3.19
4.42
10
8
6
4
2
0
PP

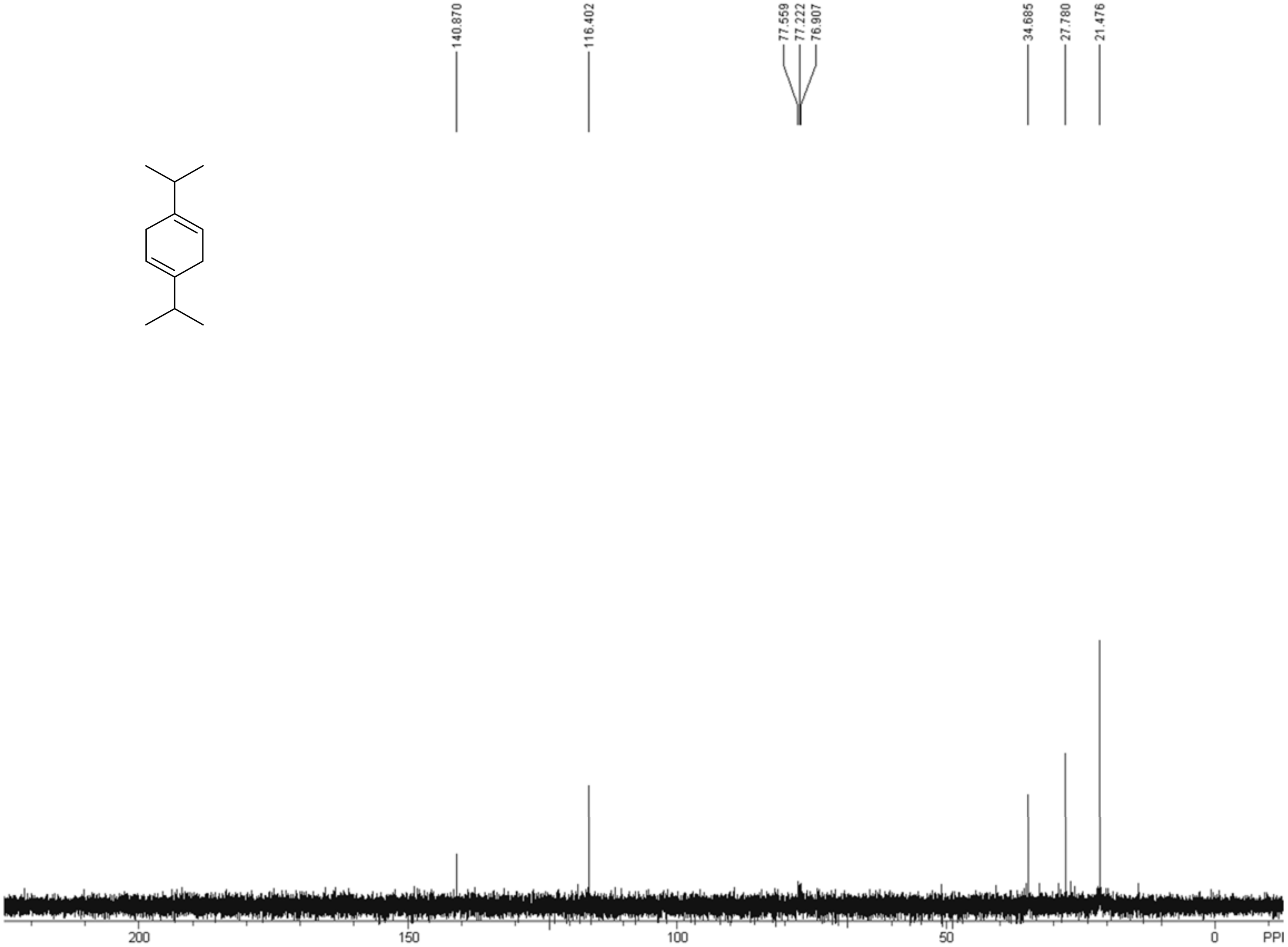


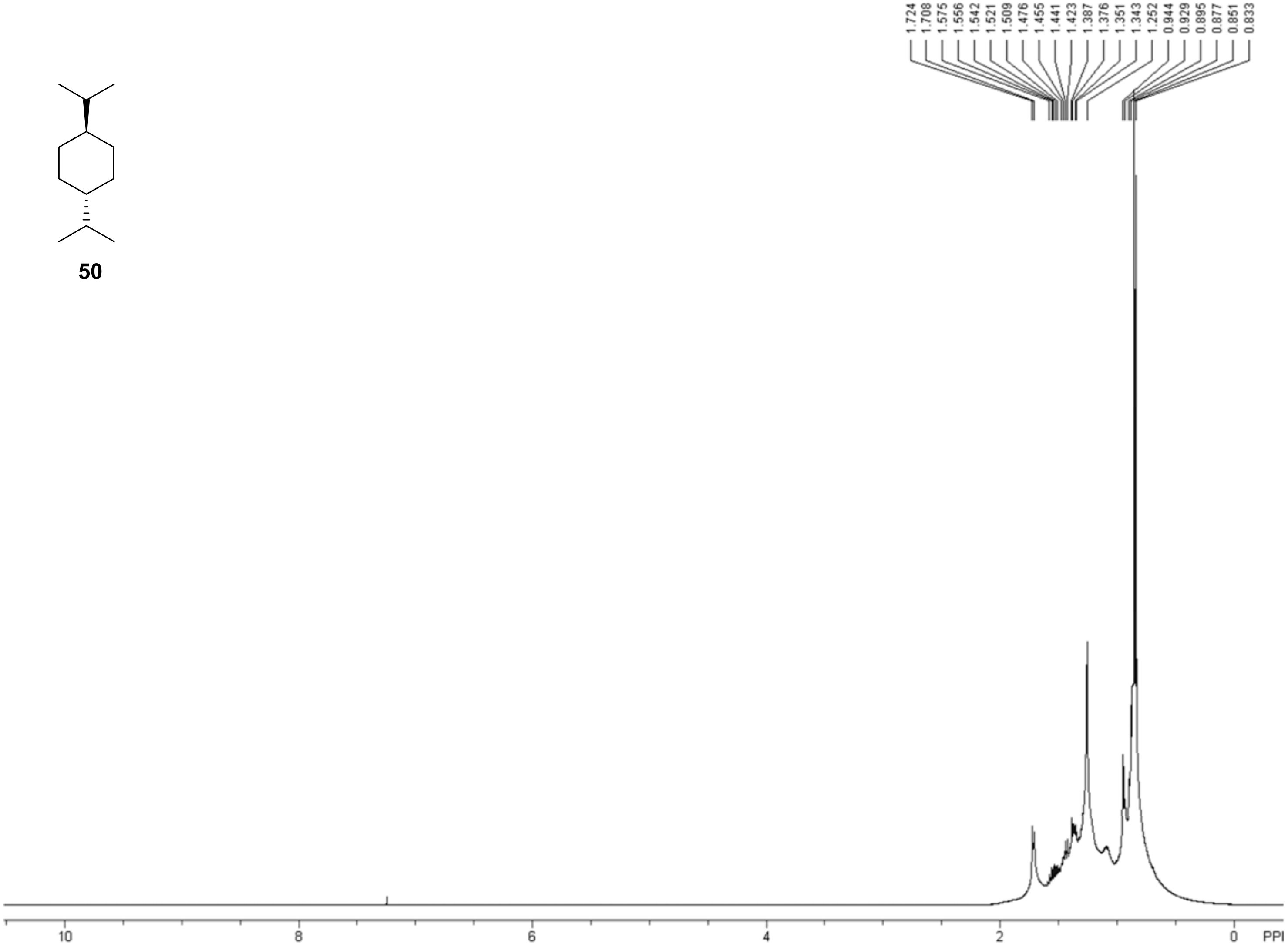
49A

148.912
108.654
77.545
77.230
76.914
73.542
71.241
37.192
33.571
33.256
26.079
25.742
20.648
200
150
100
50
0
PP

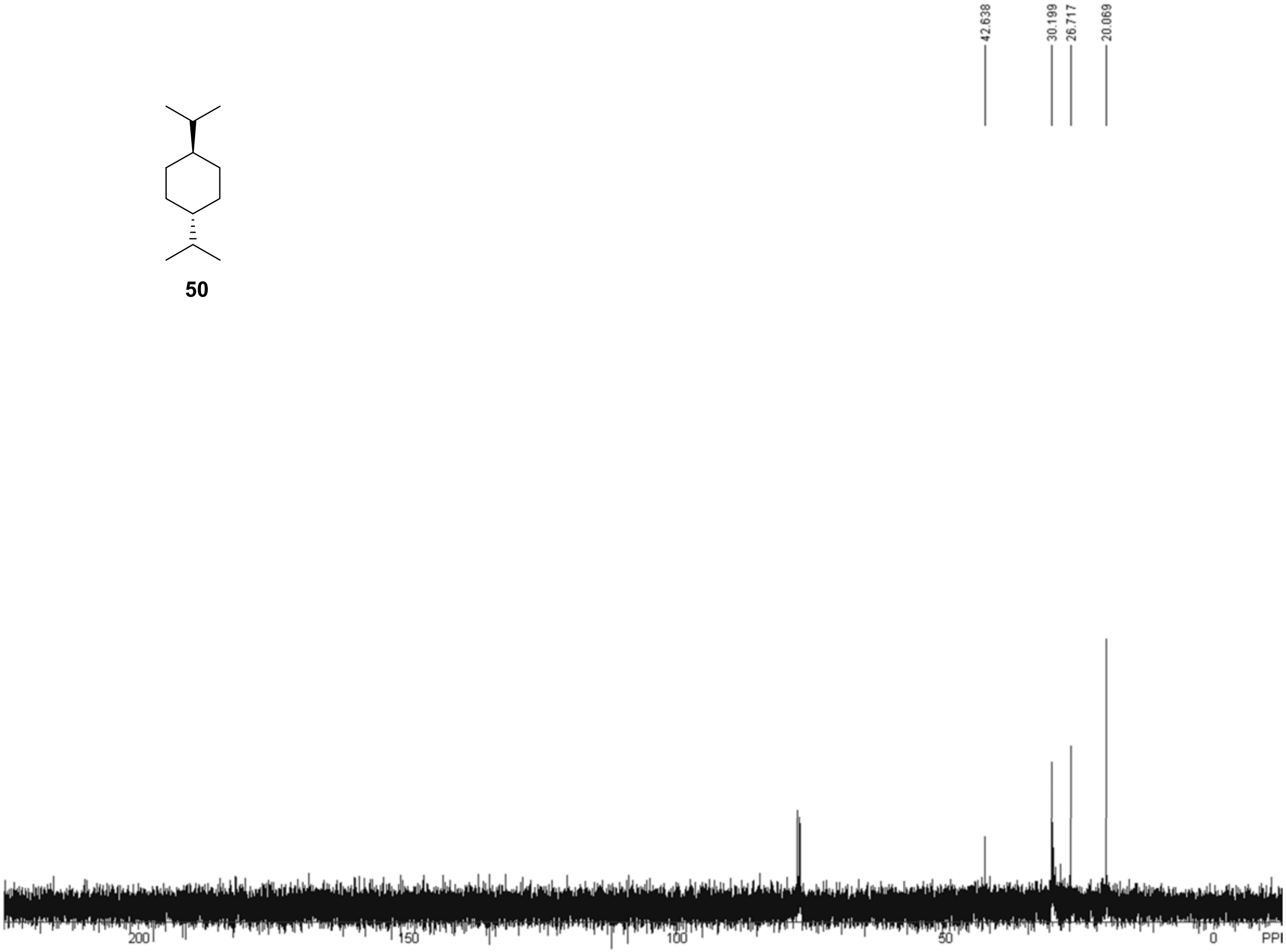


7.260
5.461
2.636
2.227
2.211
2.193
2.177
2.159
1.024
1.007
2.11
4.29
2.00
12.07
12
10
8
6
4
2
0
PPI

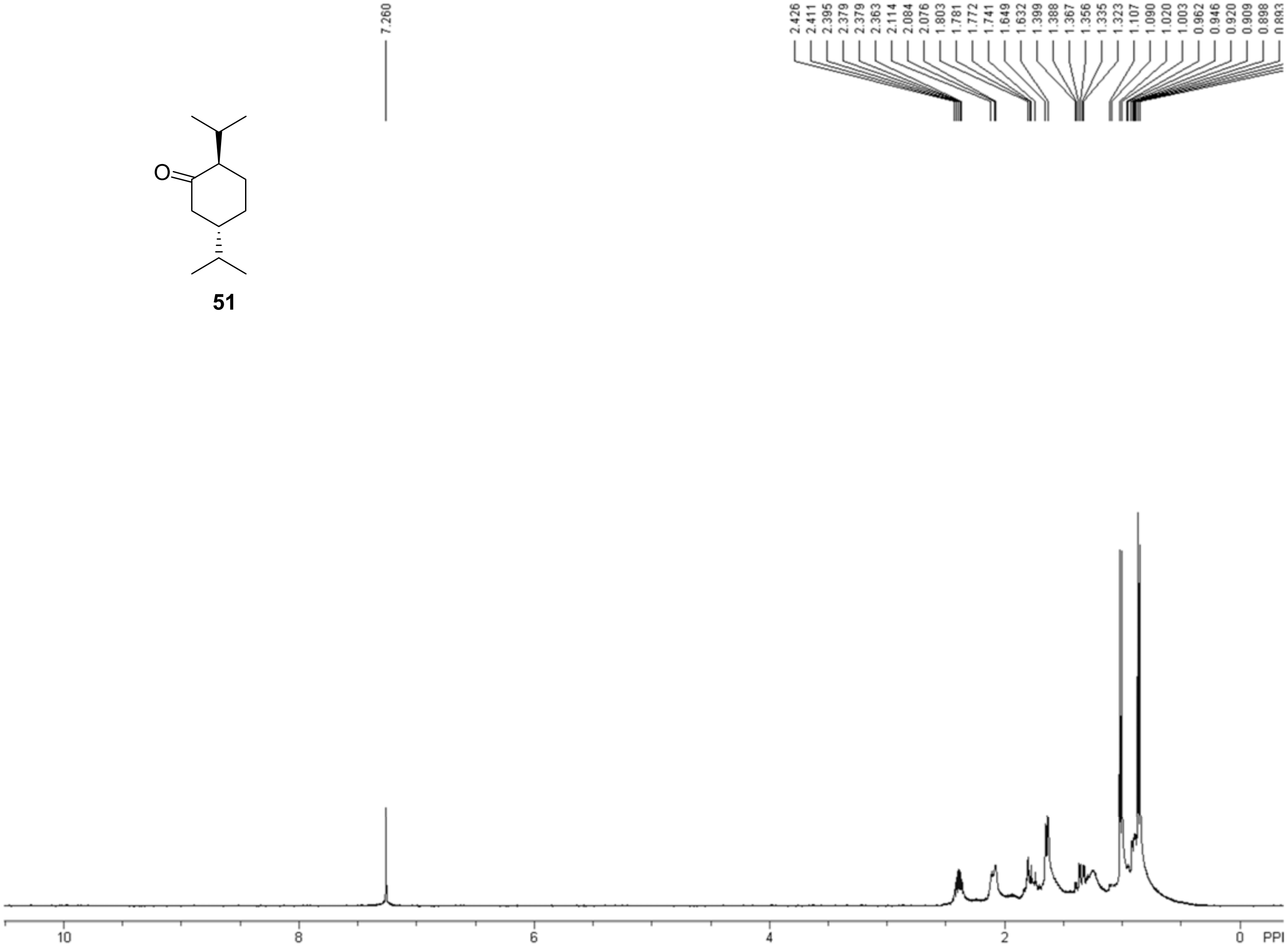

140.870
116.402
77.559
77.222
76.907
34.685
27.780
21.476
200
150
100
50
0
PPI



50
1.724
1.708
1.575
1.556
1.542
1.521
1.509
1.476
1.455
1.441
1.423
1.387
1.376
1.351
1.343
1.252
0.944
0.929
0.895
0.877
0.851
0.833
10
8
6
4
2
0
PP

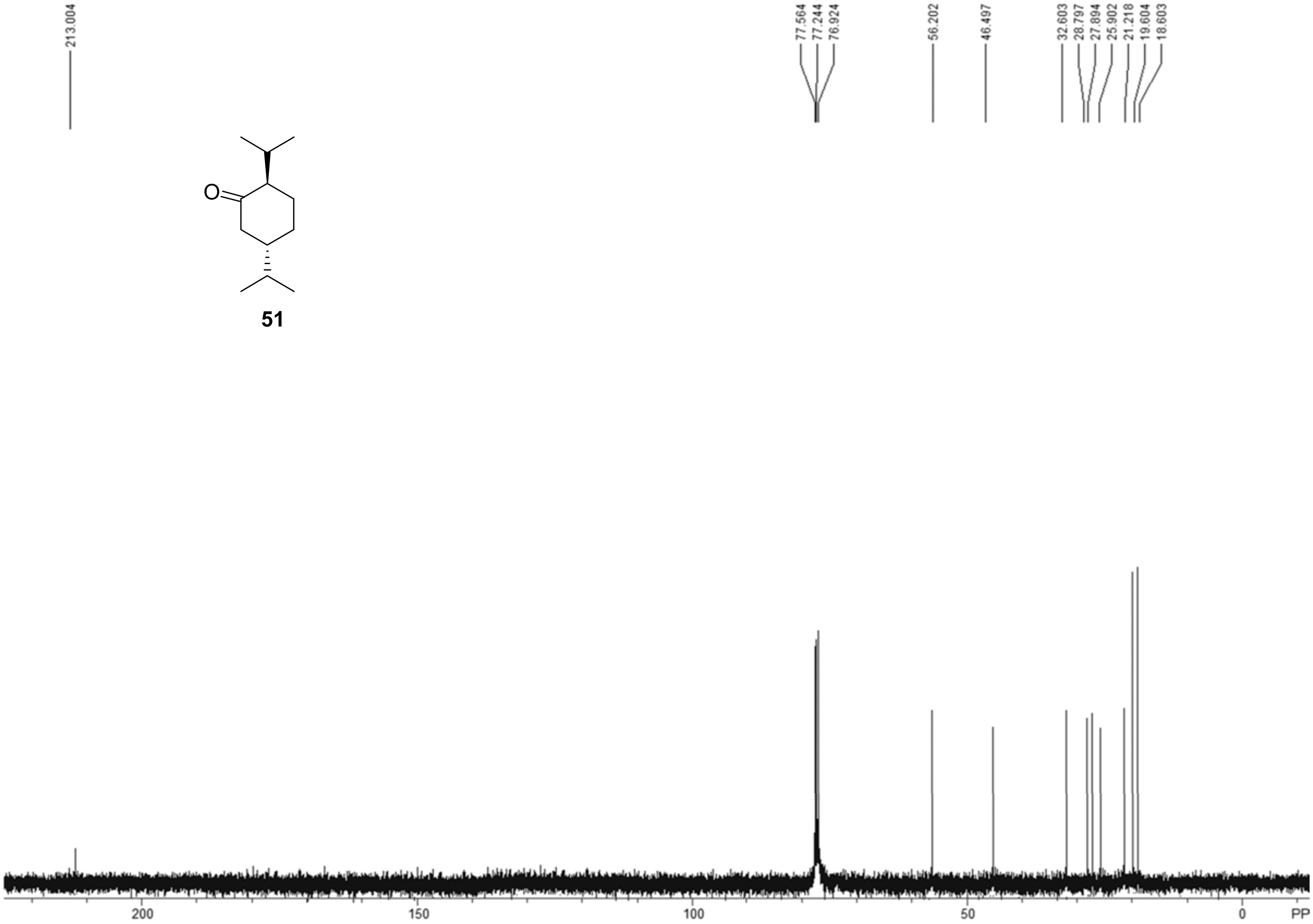


50

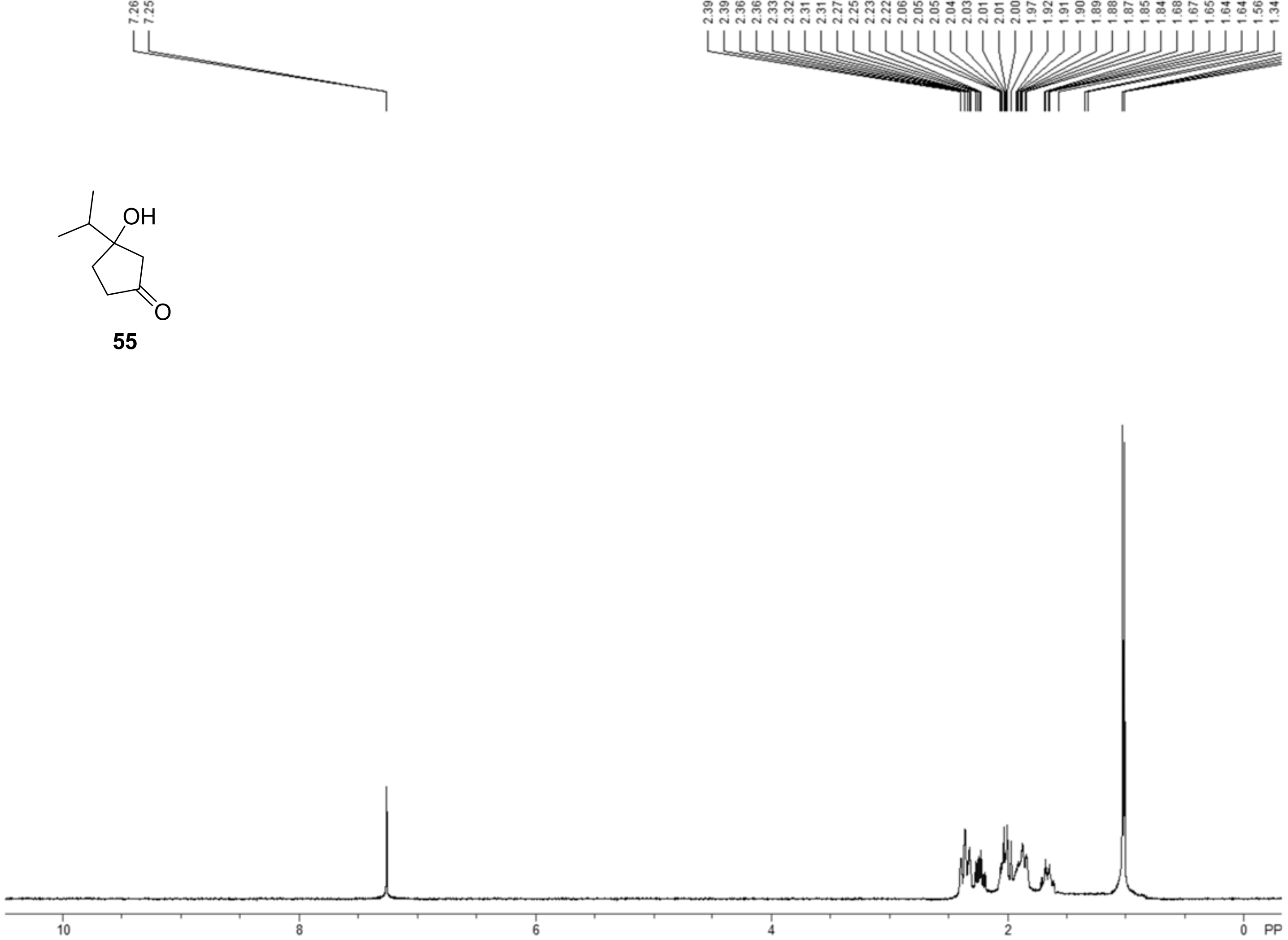


51

7.260
2.426
2.411
2.395
2.379
2.379
2.363
2.114
2.084
2.076
1.803
1.781
1.772
1.741
1.649
1.632
1.399
1.388
1.367
1.356
1.335
1.323
1.107
1.090
1.020
1.003
0.962
0.946
0.920
0.909
0.898
0.893
10
8
6
4
2
0
PPM

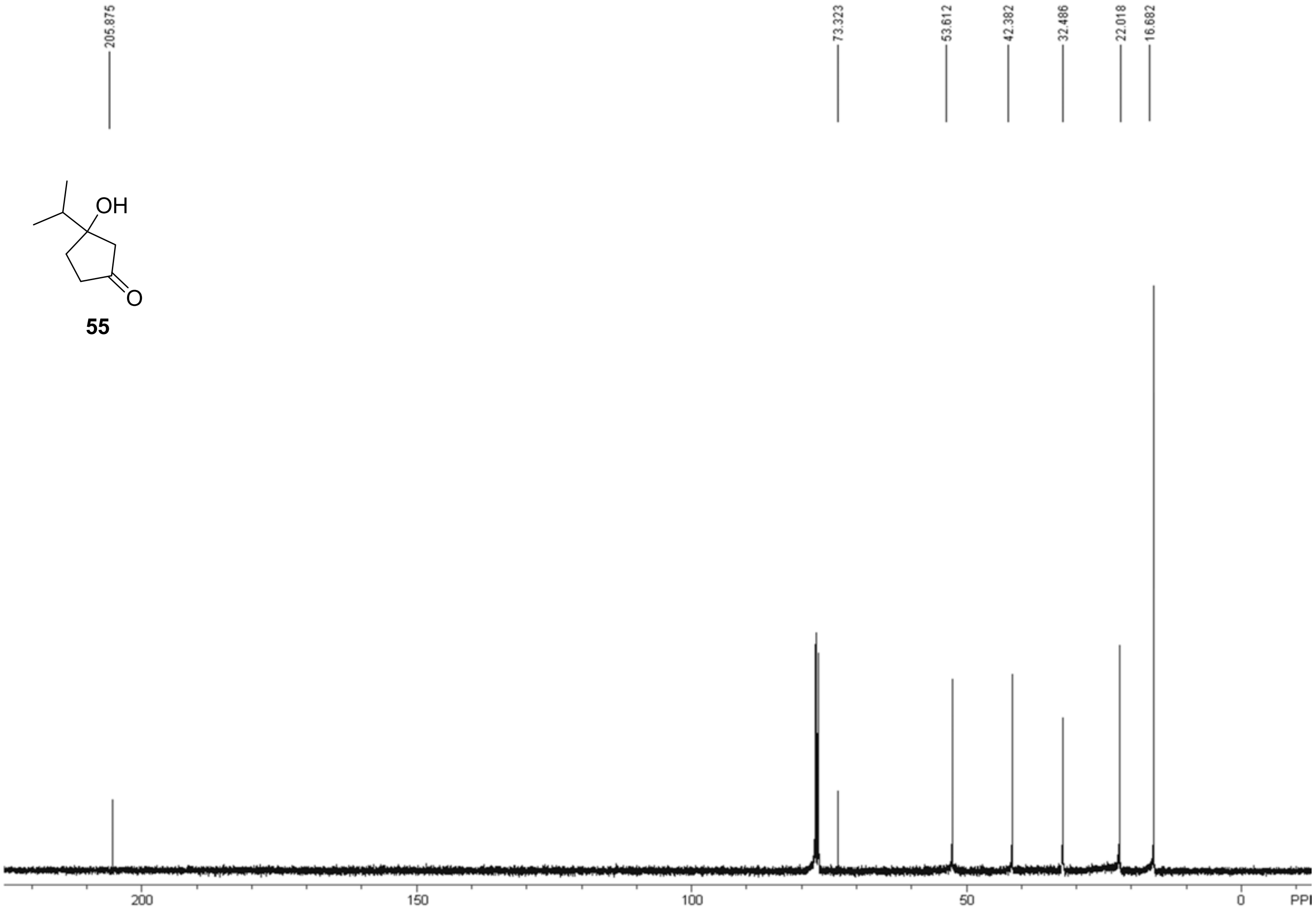

213.004
77.564
77.244
76.924
56.202
46.497
32.603
28.797
27.894
25.902
21.218
19.604
18.603
O
200
150
100
50
0
PP

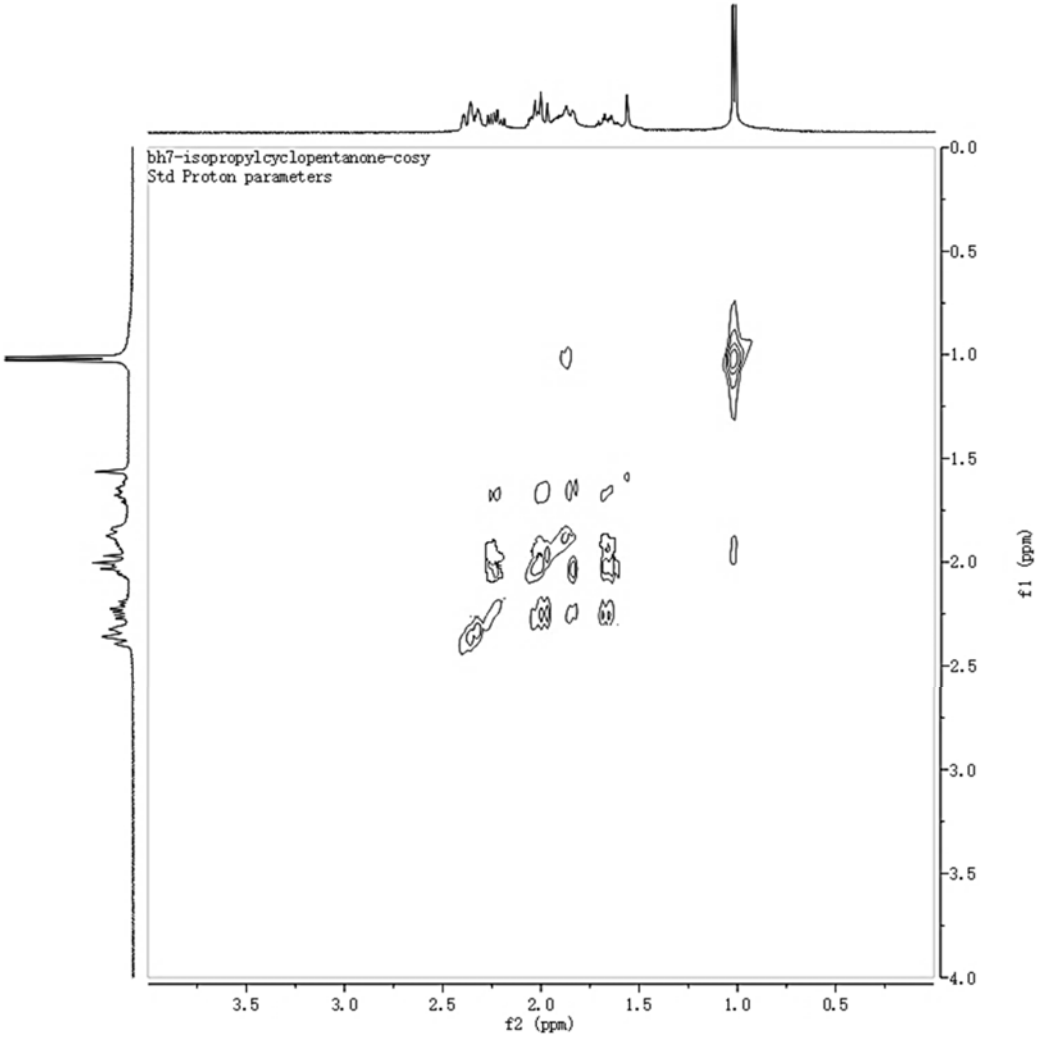
51

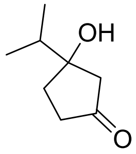


55

7.260
7.259
2.398
2.393
2.364
2.360
2.334
2.322
2.317
2.314
2.270
2.255
2.239
2.224
2.062
2.055
2.052
2.046
2.030
2.018
2.012
2.003
1.970
1.928
1.919
1.909
1.893
1.880
1.873
1.854
1.840
1.686
1.678
1.656
1.647
1.644
1.564
1.345
OH
O
10
8
6
4
2
0
PP


205.875
73.323
53.612
42.382
32.486
22.018
16.682
OH
O
55
200
150
100
50
0
PPI

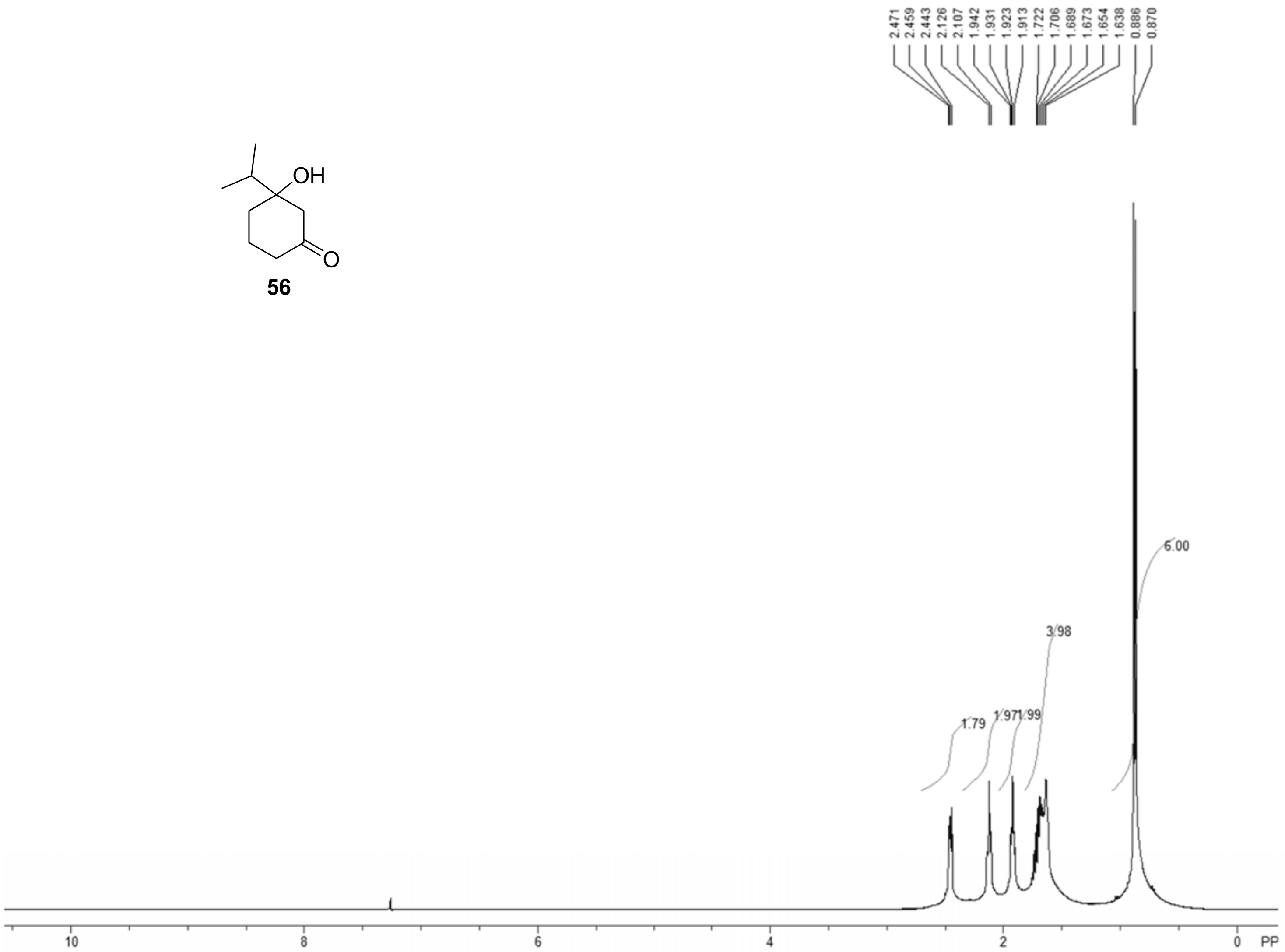

bh7-isopropylcyclopentanone-cosy
Std Proton parameters
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
f1 (ppm)

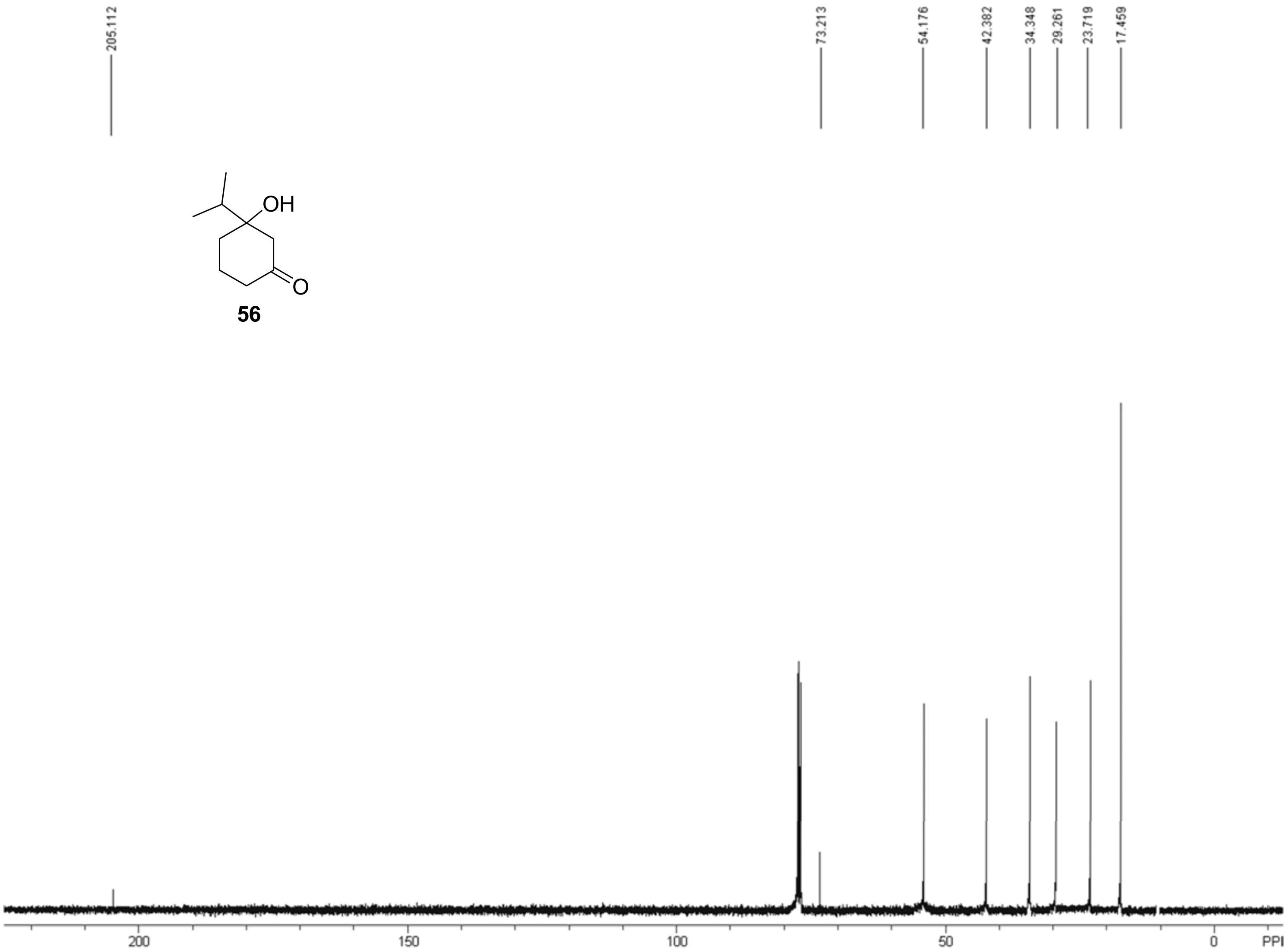

OH
O

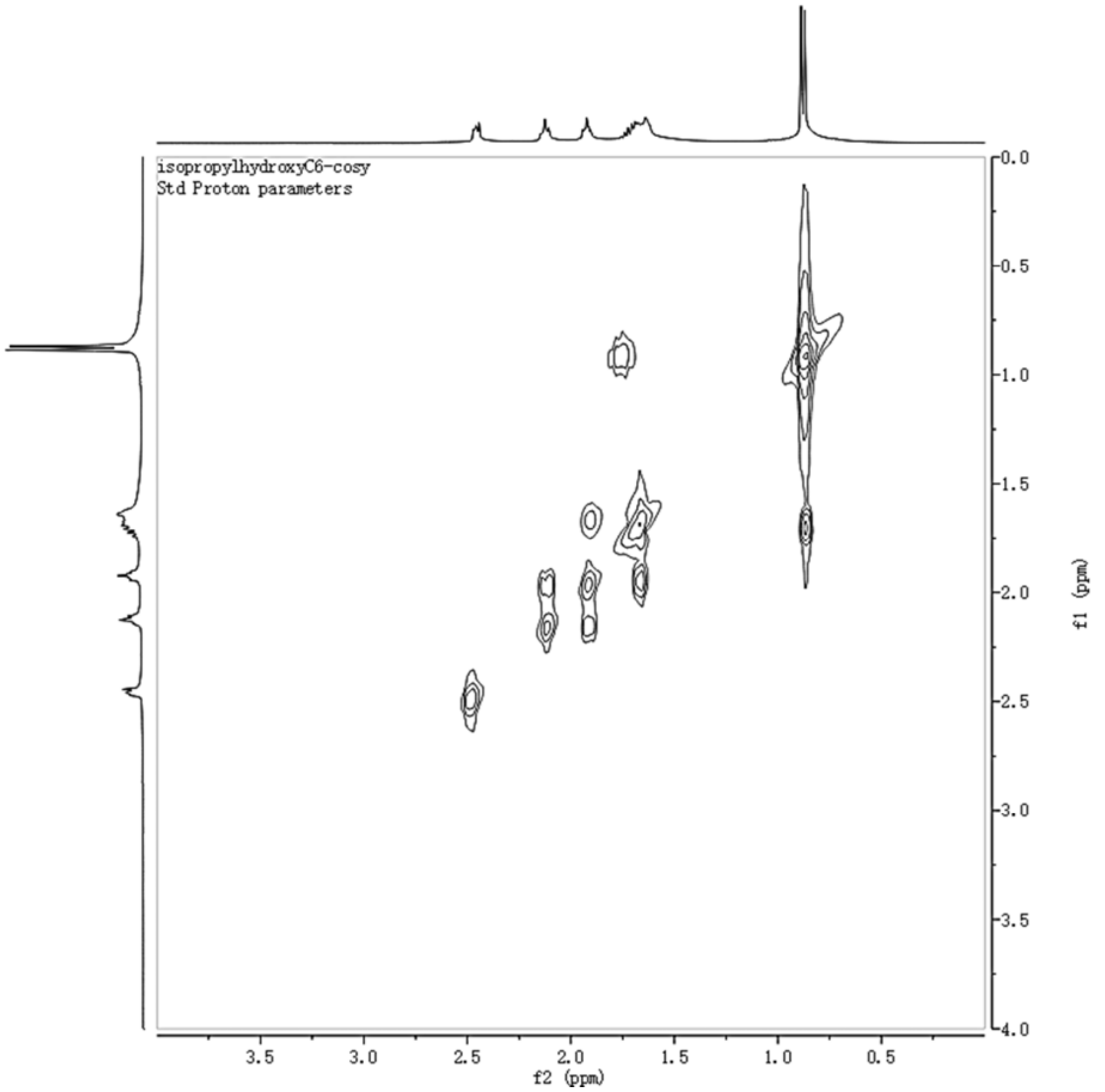
55

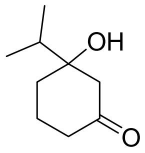
OH
O

56

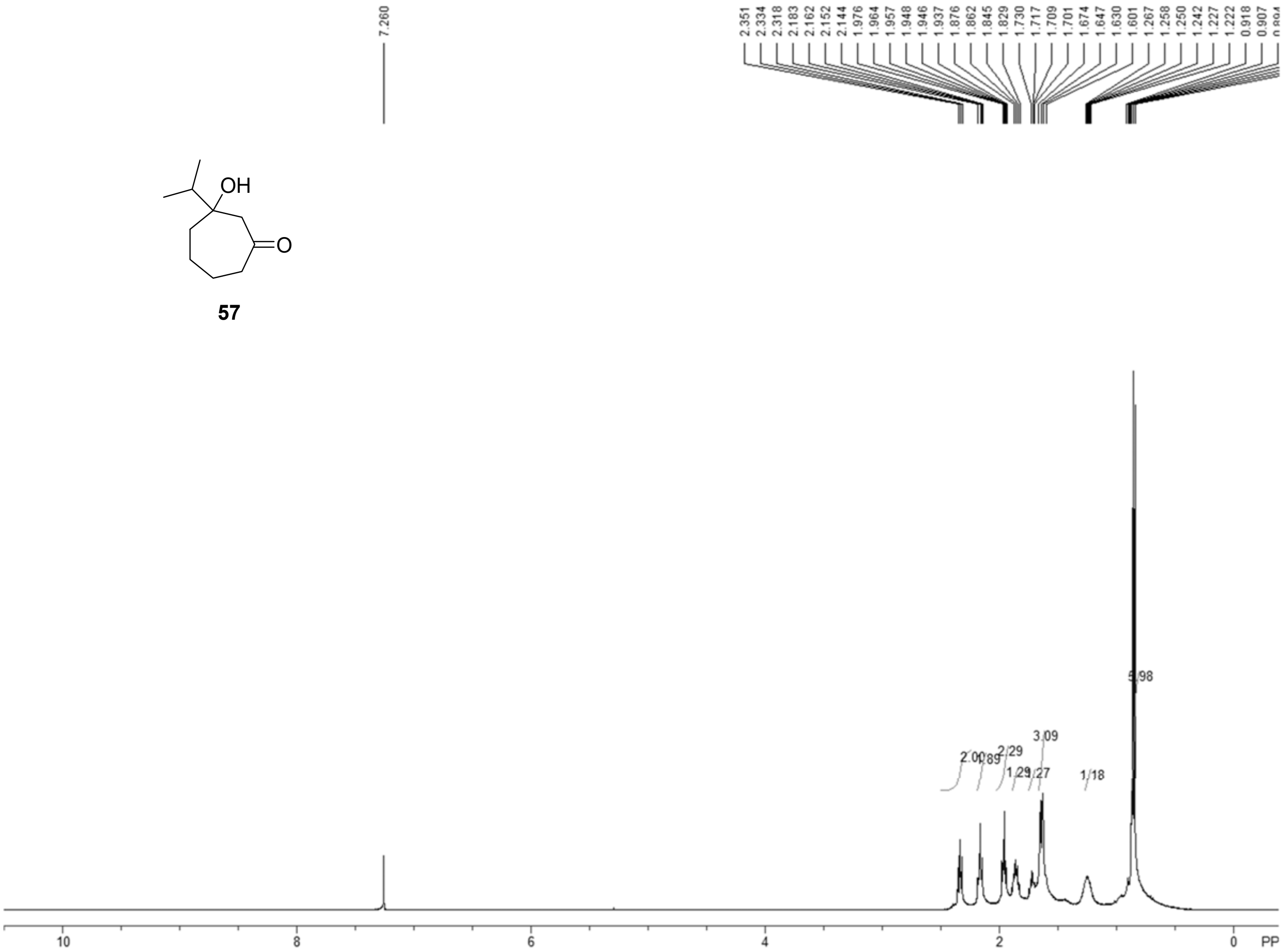

2.471
2.459
2.443
2.126
2.107
1.942
1.931
1.923
1.913
1.722
1.706
1.689
1.673
1.654
1.638
0.886
0.870
1.79
1.97
1.99
3.98
6.00
10
8
6
4
2
0
PP


205.112
73.213
54.176
42.382
34.348
29.261
23.719
17.459
OH
O
56
200
150
100
50
0
PP


isopropylhydroxyC6-cosy
Std Proton parameters
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
f1 (ppm)

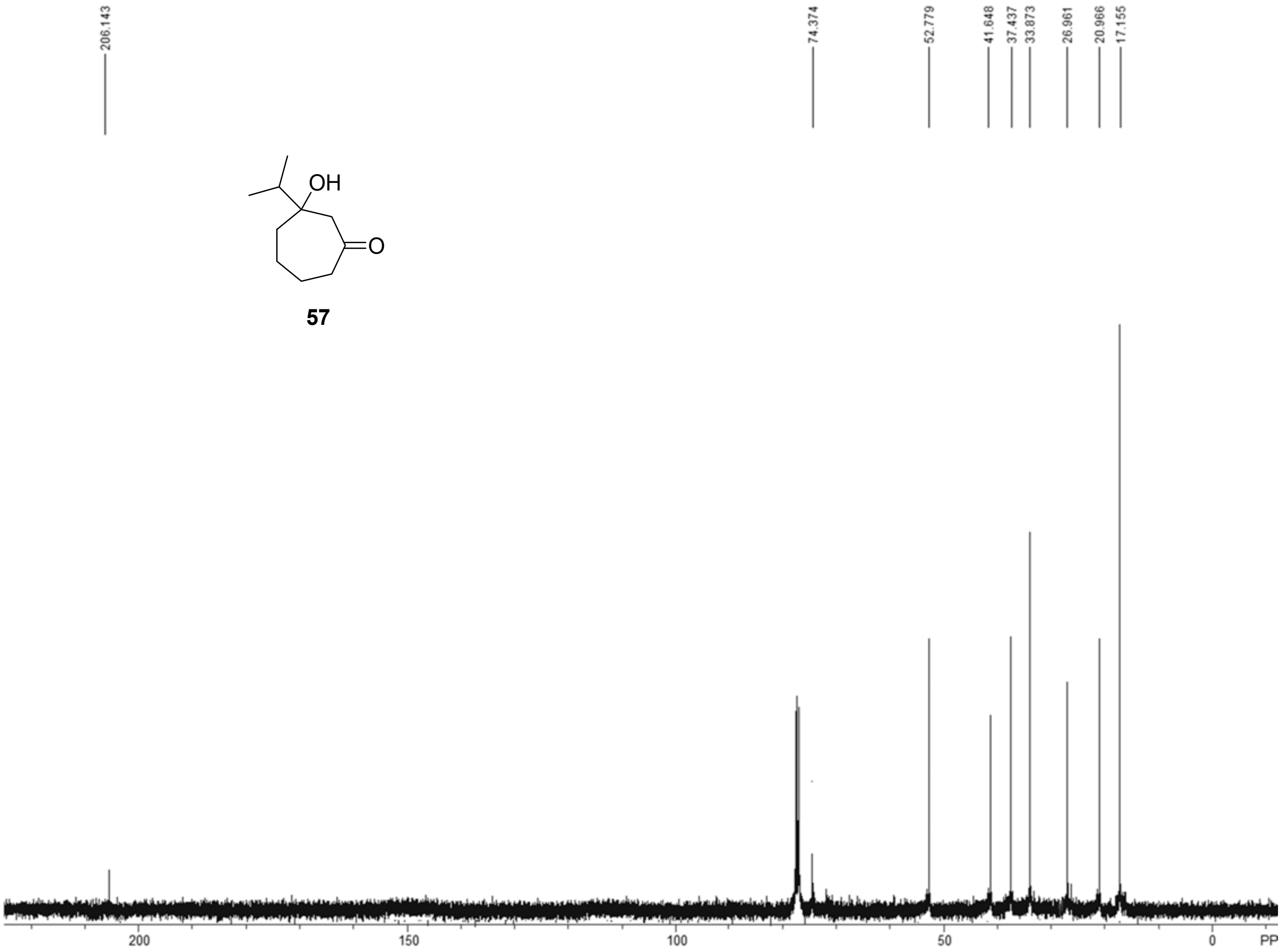

OH
O

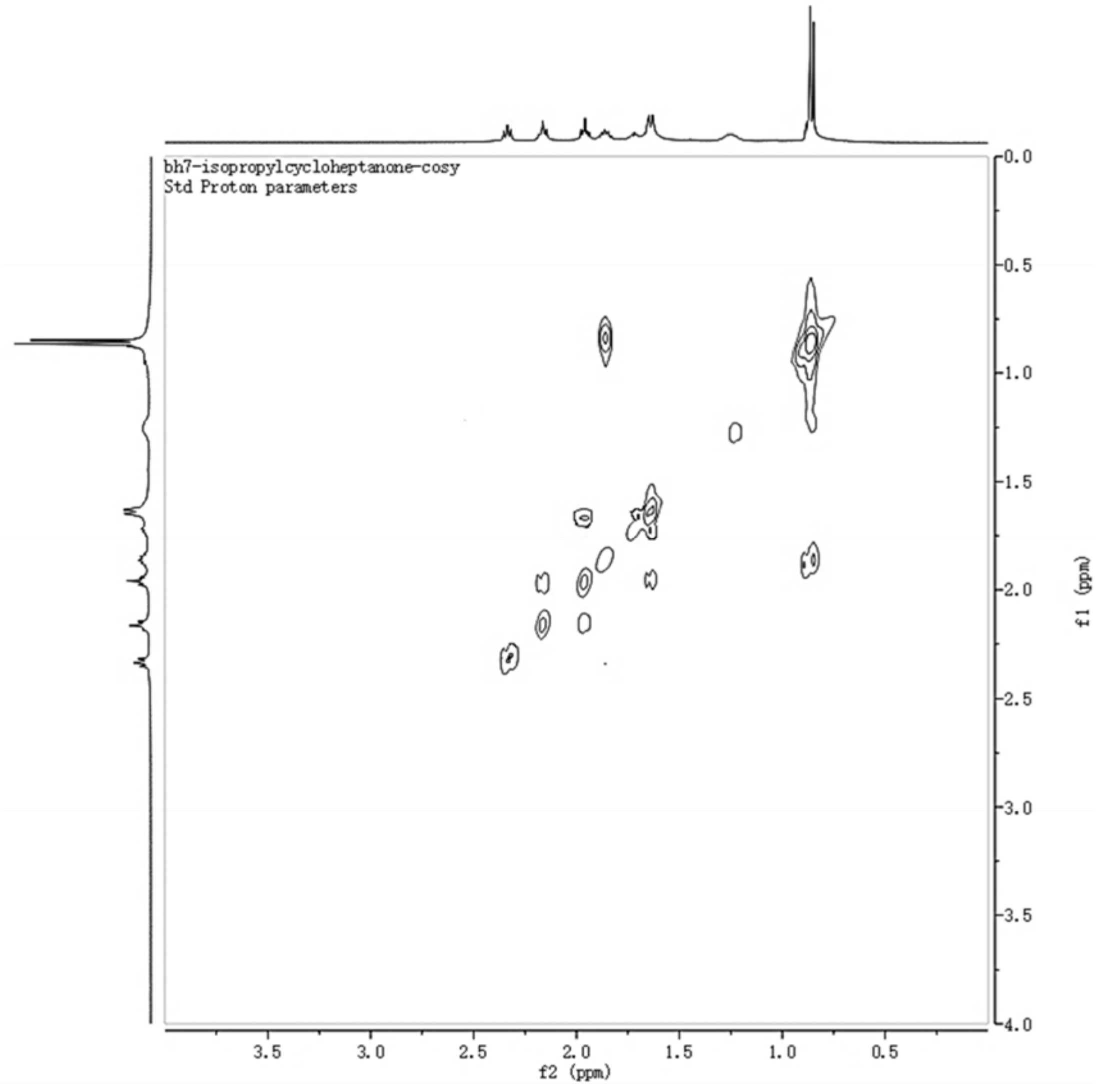
56

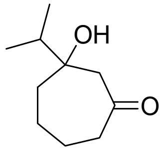


57

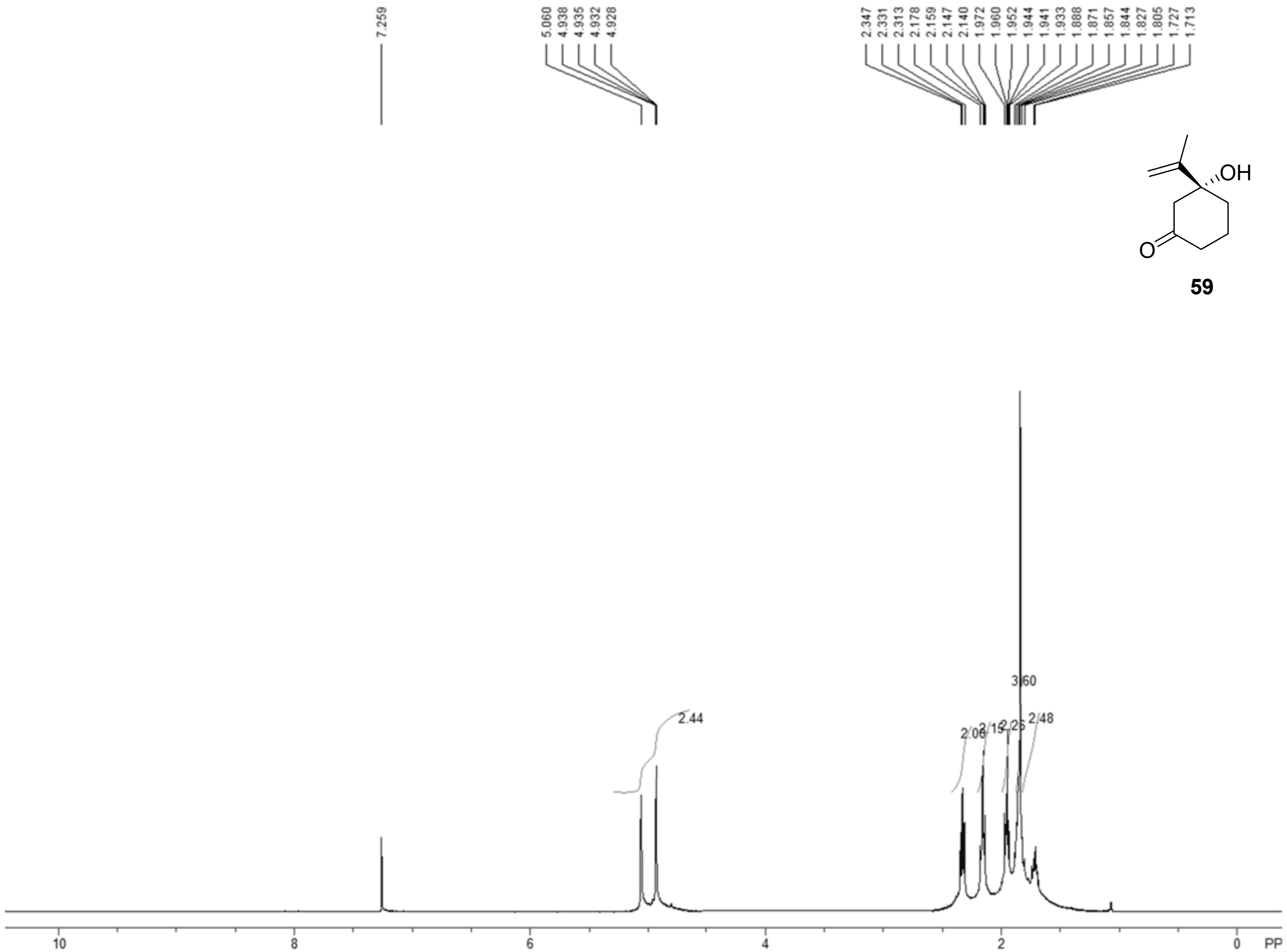
OH
O
7.260
2.351
2.334
2.318
2.183
2.162
2.152
2.144
1.976
1.964
1.957
1.948
1.946
1.937
1.876
1.862
1.845
1.829
1.730
1.717
1.709
1.701
1.674
1.647
1.630
1.601
1.267
1.258
1.250
1.242
1.227
1.222
0.918
0.907
0.89
2.00
1.89
2.29
1.29
1.27
3.09
1.18
5.98
10
8
6
4
2
0
PP


57
206.143
74.374
52.779
41.648
37.437
33.873
26.961
20.966
17.155
OH
O
200
150
100
50
0
PP

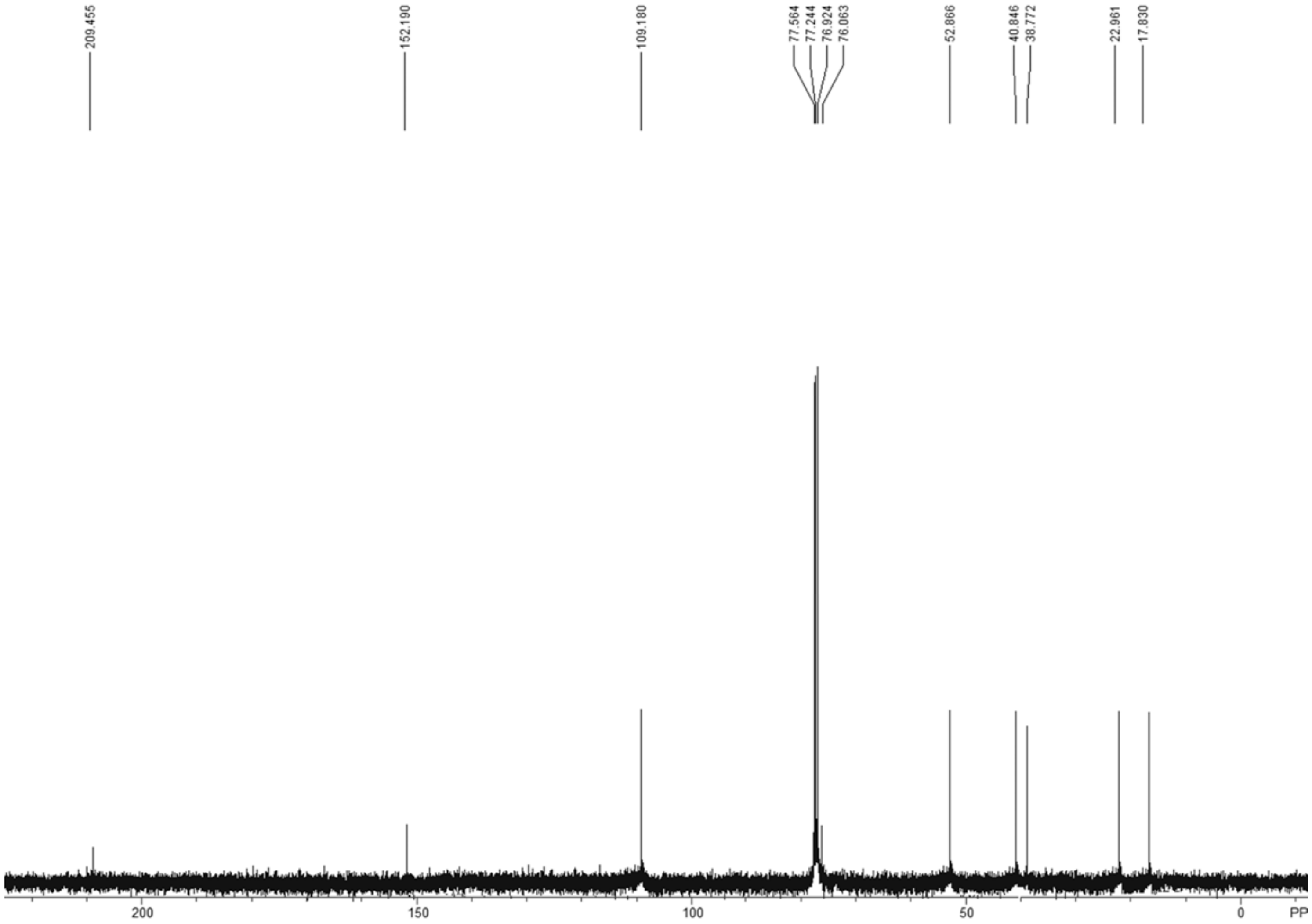

bh7-isopropylcycloheptanone-cosy
Std Proton parameters
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
f1 (ppm)

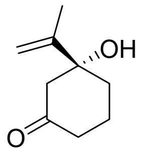

OH
O

57

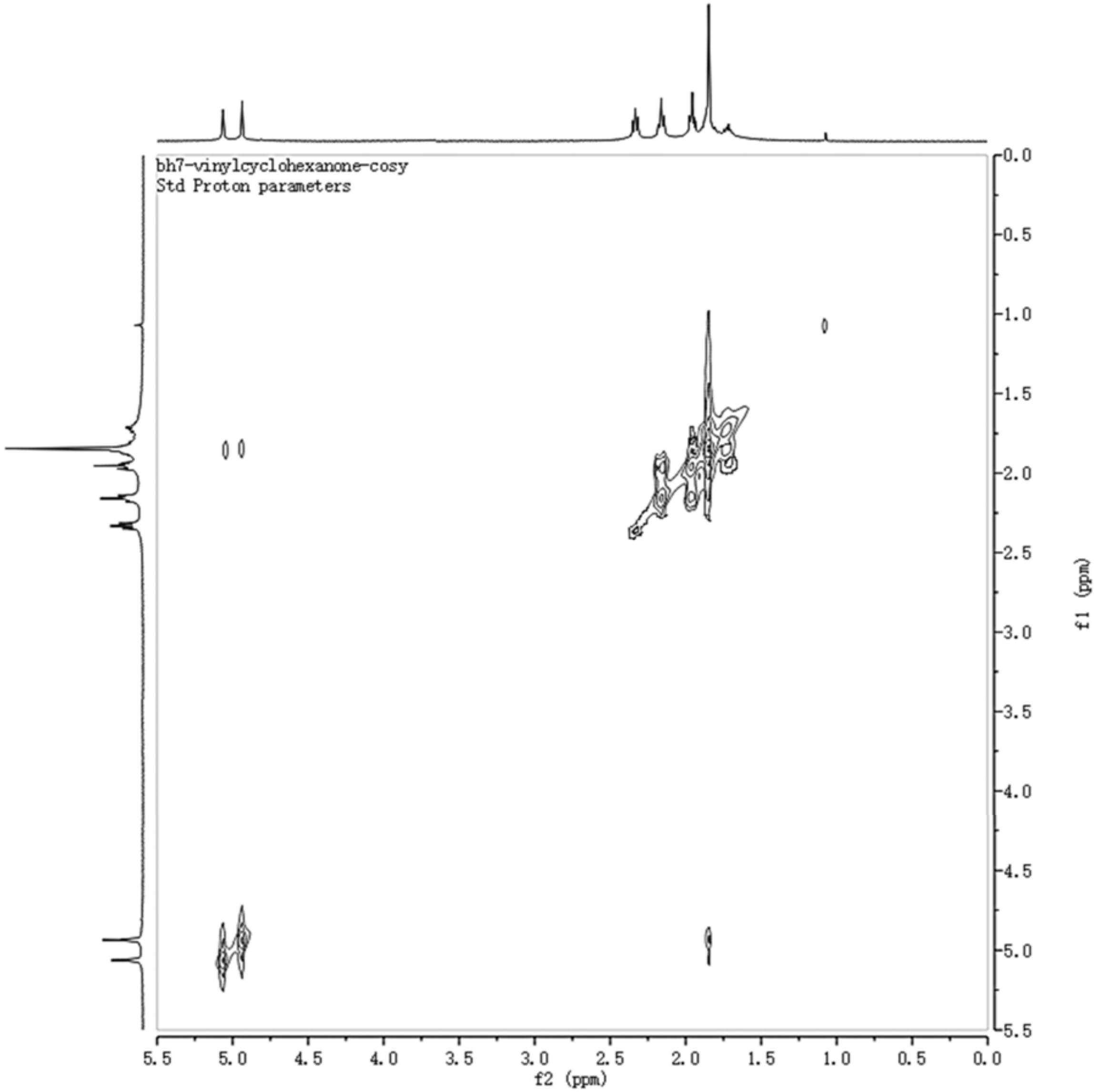

7.259
5.060
4.938
4.935
4.932
4.928
2.347
2.331
2.313
2.178
2.159
2.147
2.140
1.972
1.960
1.952
1.944
1.941
1.933
1.888
1.871
1.857
1.844
1.827
1.805
1.727
1.713
OH
O
2.44
2.06
2.15
2.26
3.60
2.48
10
8
6
4
2
0
PP

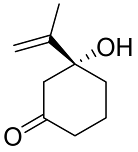
59


209.455
152.190
109.180
77.564
77.244
76.924
76.063
52.866
40.846
38.772
22.961
17.830
200
150
100
50
0
PP

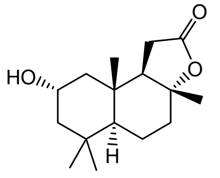

OH
O

59

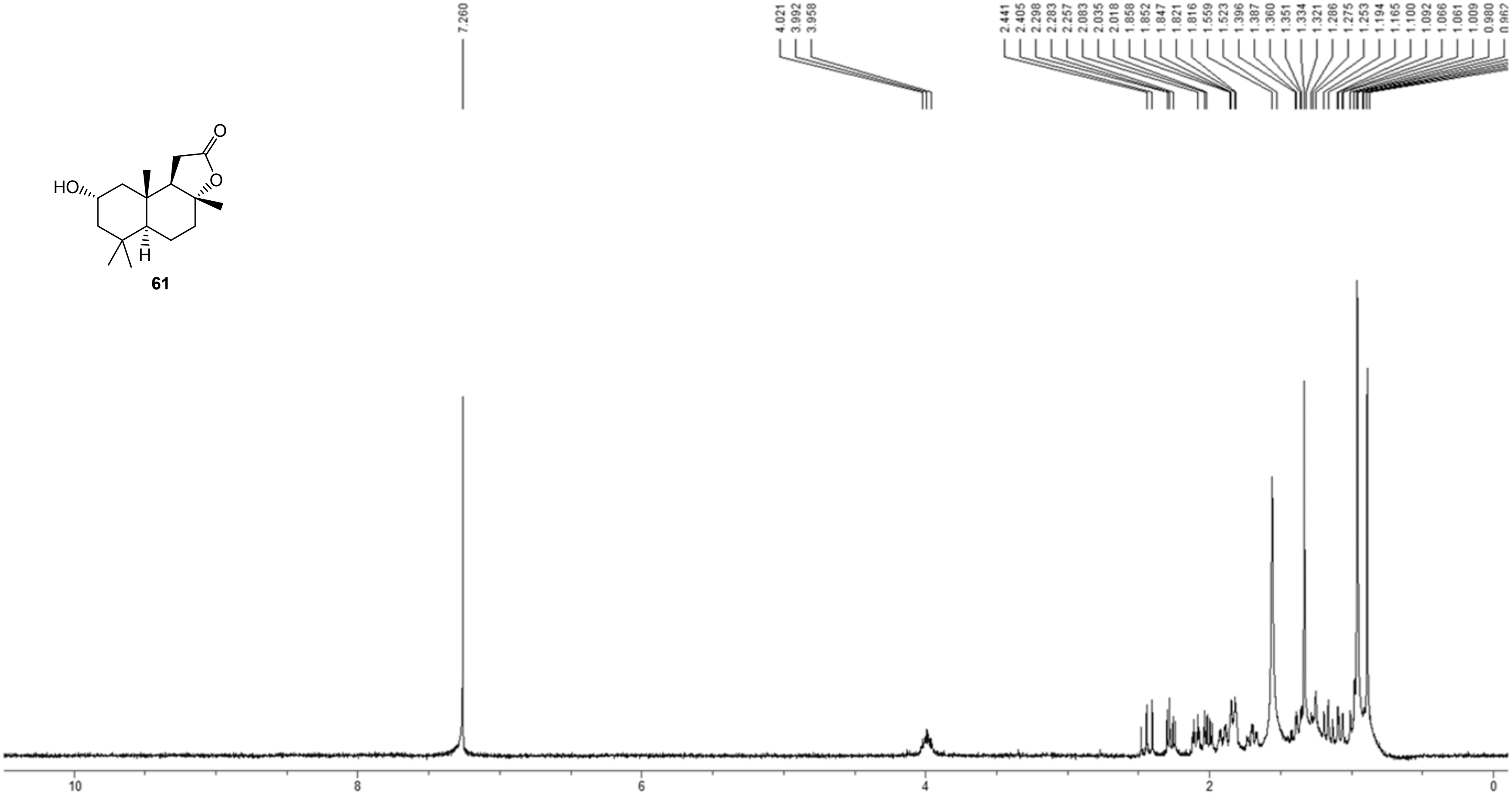

bh7-vinylcyclohexanone-cosy
Std Proton parameters
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
-0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
f1 (ppm)

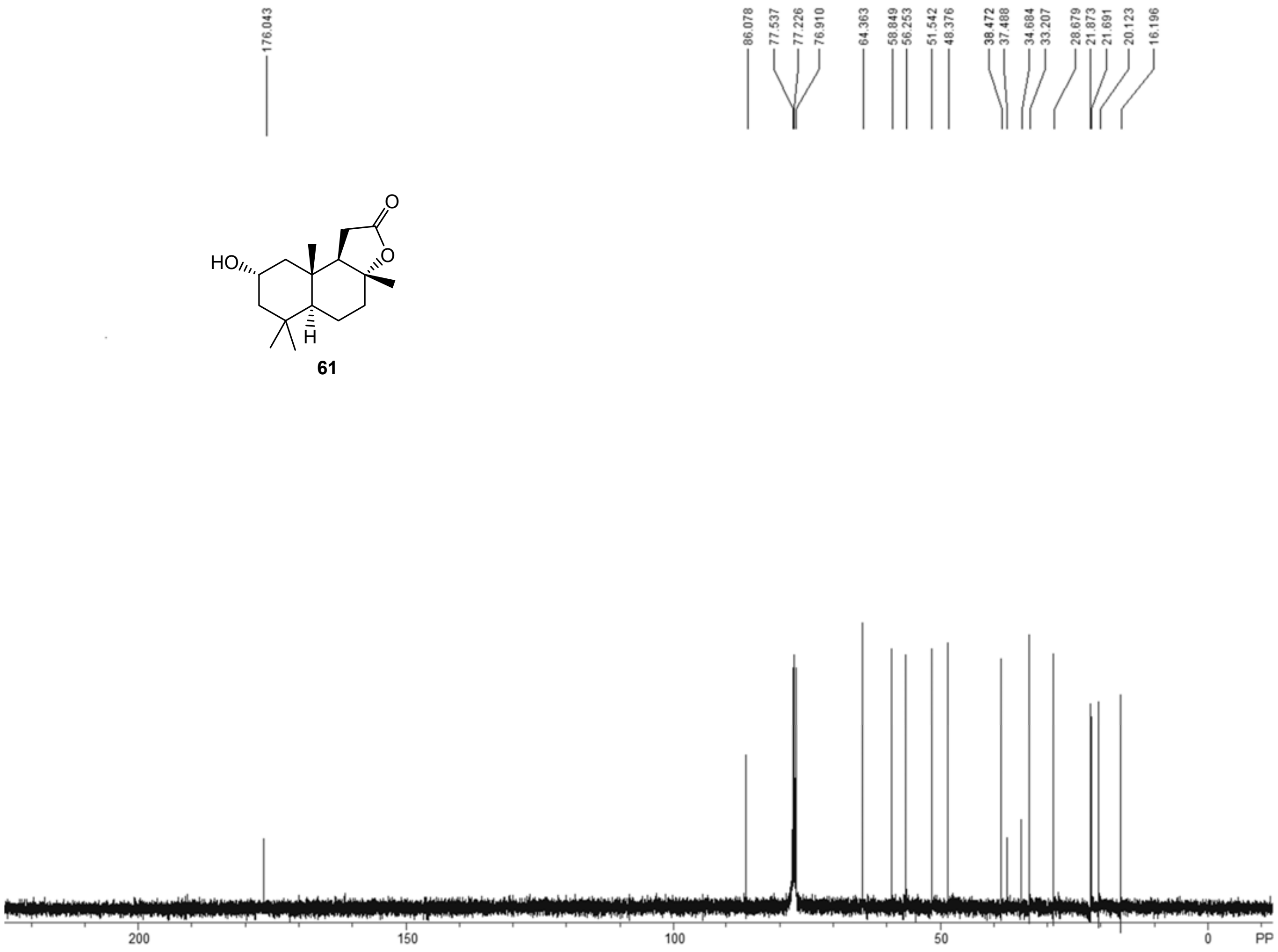

OH
O

59

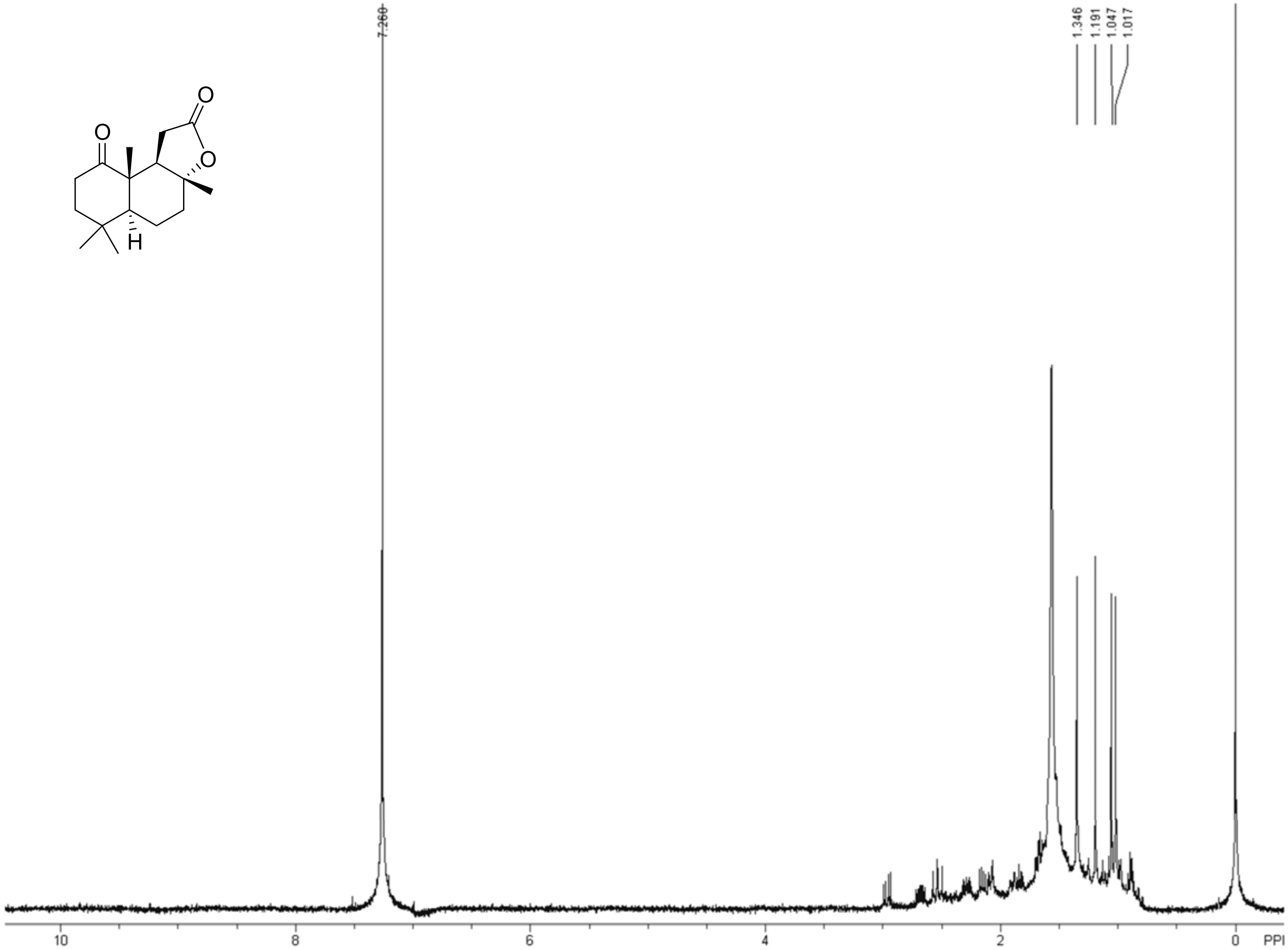


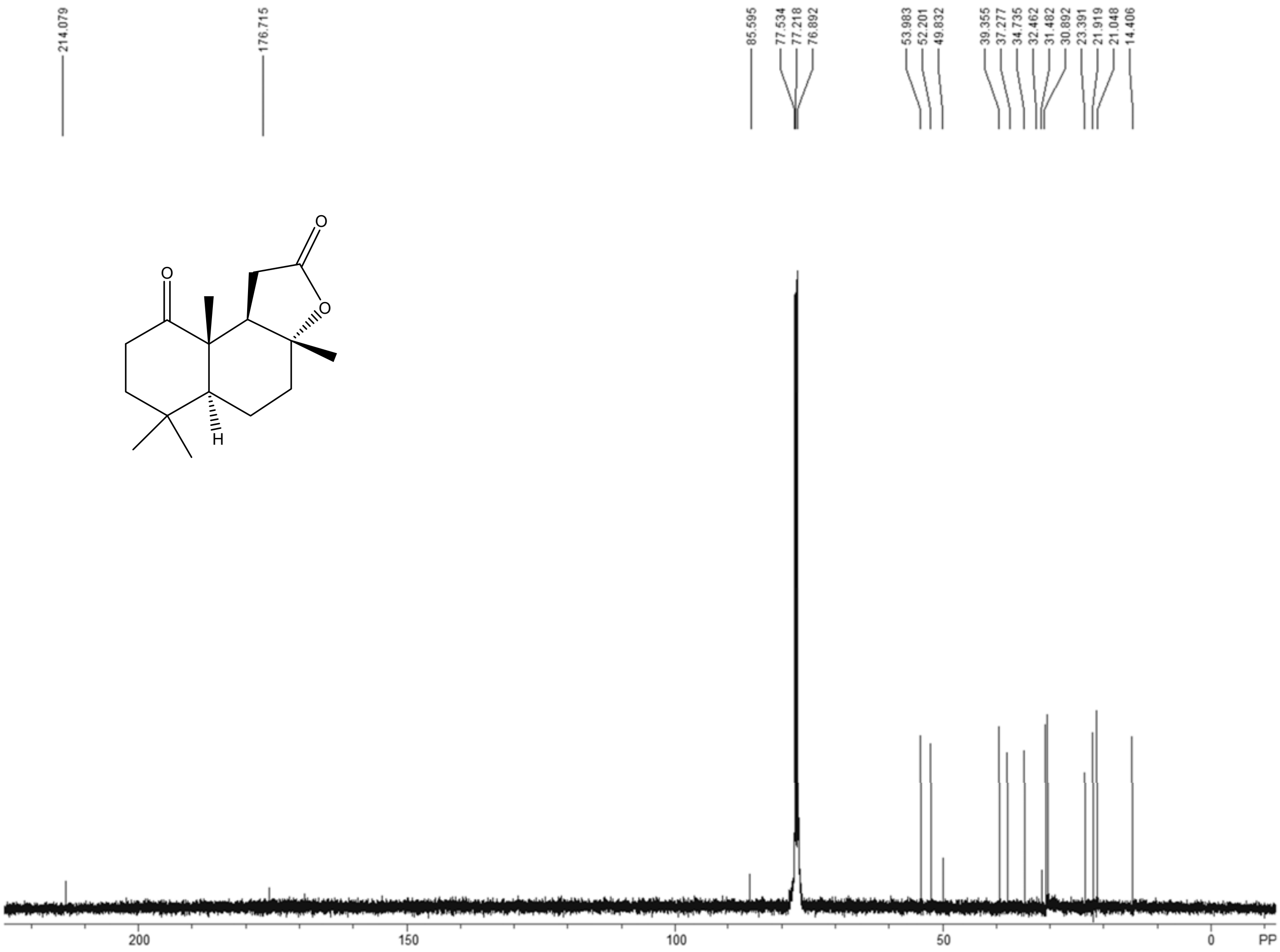
61

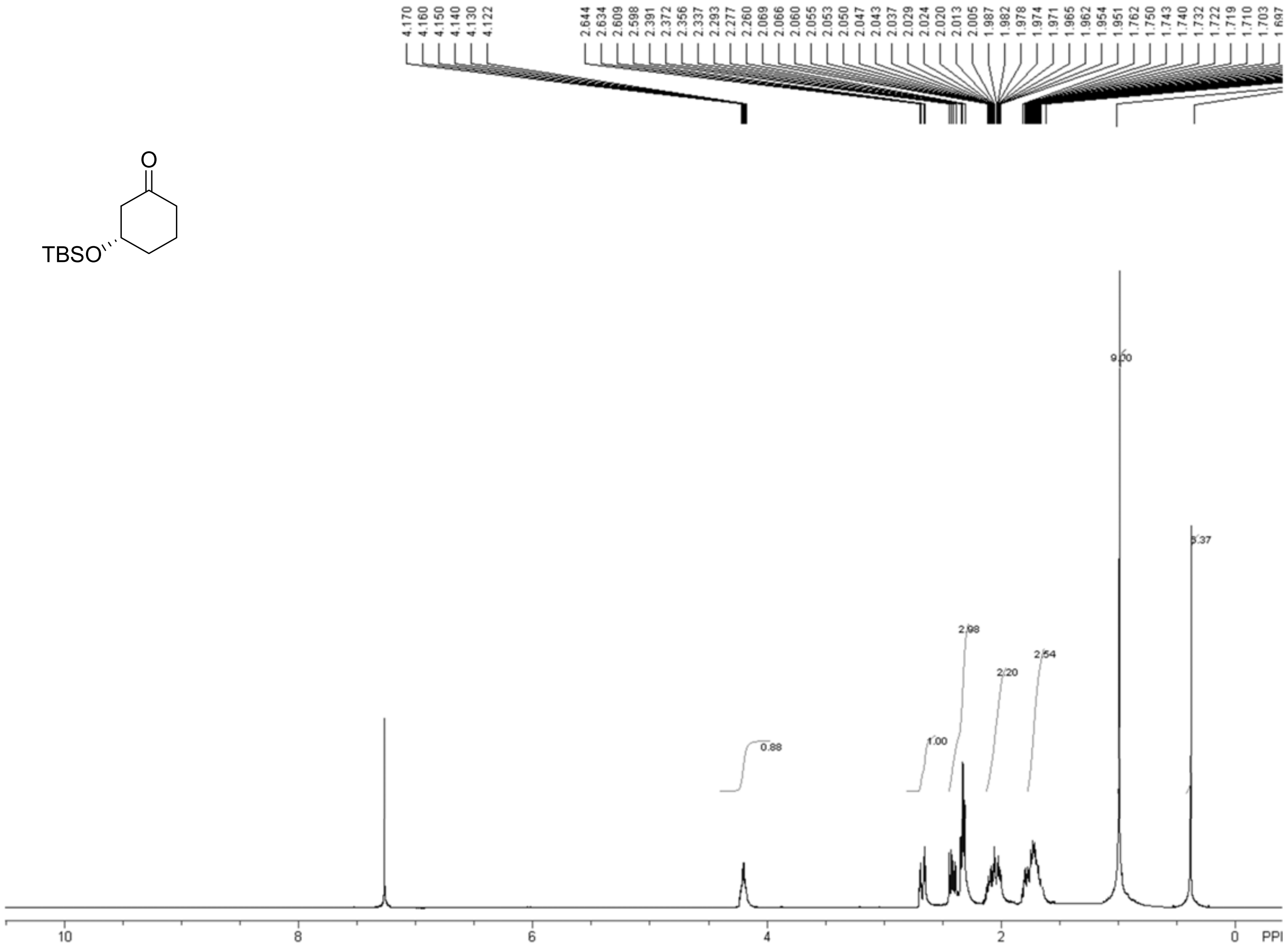

7.260
4.021
3.992
3.958
2.441
2.405
2.298
2.283
2.257
2.083
2.035
2.018
1.858
1.852
1.847
1.821
1.816
1.559
1.523
1.396
1.387
1.360
1.351
1.334
1.321
1.286
1.275
1.253
1.194
1.165
1.100
1.092
1.066
1.061
1.009
0.980
0.962
10
8
6
4
2
0

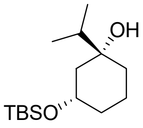

176.043
86.078
77.537
77.226
76.910
64.363
58.849
56.253
51.542
48.376
38.472
37.488
34.684
33.207
28.679
21.873
21.691
20.123
16.196
HO
O
O
H
200
150
100
50
0
PP

61

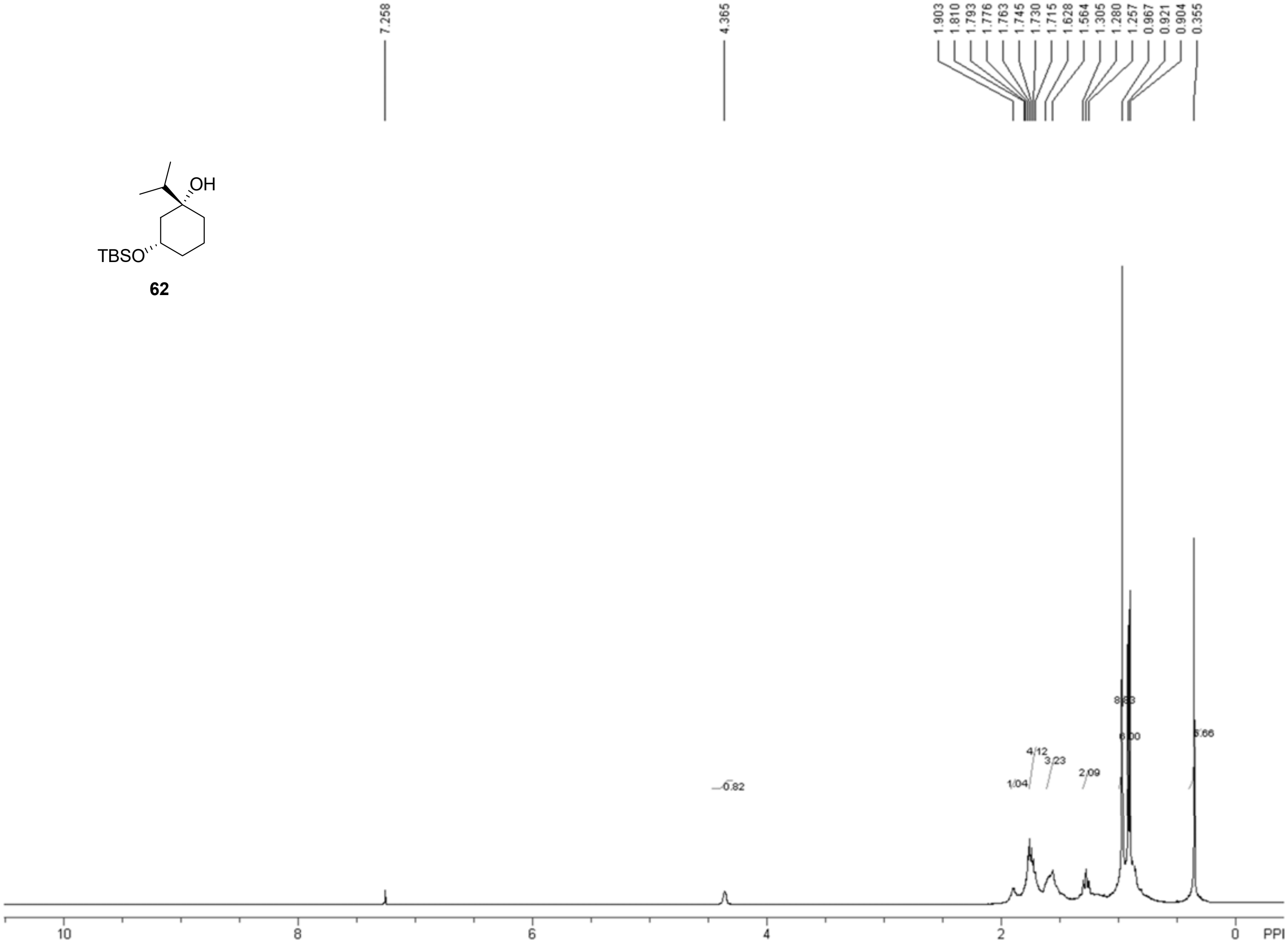

7.260
1.346
1.191
1.047
1.017
O
O
O
H
10
8
6
4
2
0
PPI


214.079
176.715
85.595
77.534
77.218
76.892
53.983
52.201
49.832
39.355
37.277
34.735
32.462
31.482
30.892
23.391
21.919
21.048
14.406
O
O
O
H
200
150
100
50
0
PP


O
TBSO
4.170
4.160
4.150
4.140
4.130
4.122
2.644
2.634
2.609
2.598
2.391
2.372
2.356
2.337
2.293
2.277
2.260
2.069
2.066
2.060
2.055
2.053
2.050
2.047
2.043
2.037
2.029
2.024
2.020
2.013
2.005
1.987
1.982
1.978
1.974
1.971
1.965
1.962
1.954
1.951
1.762
1.750
1.743
1.740
1.732
1.722
1.719
1.710
1.703
1.697
9.00
6.37
2.98
2.54
2.20
1.00
0.88
10
8
6
4
2
0
PPI

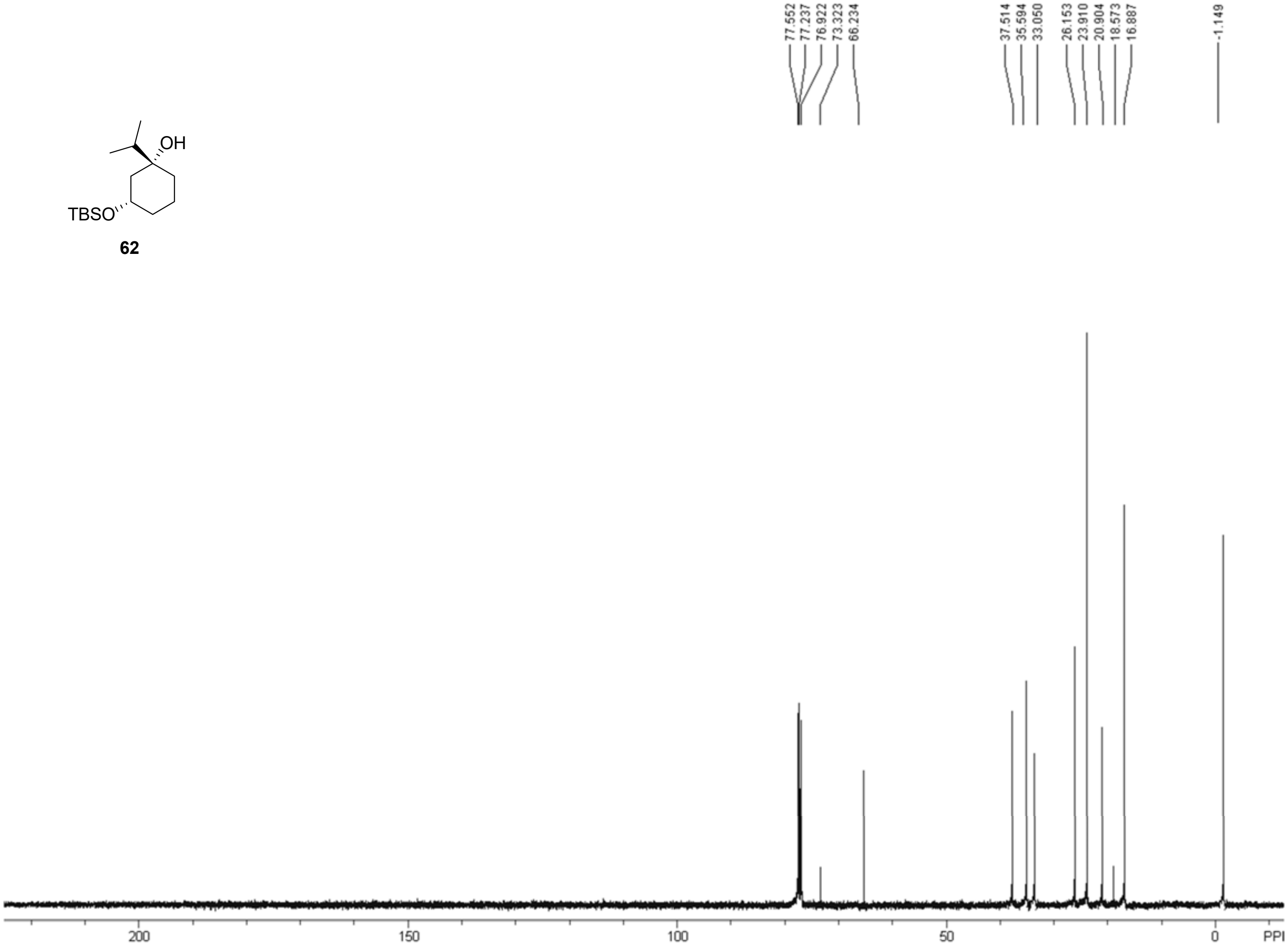

OH
TBSO

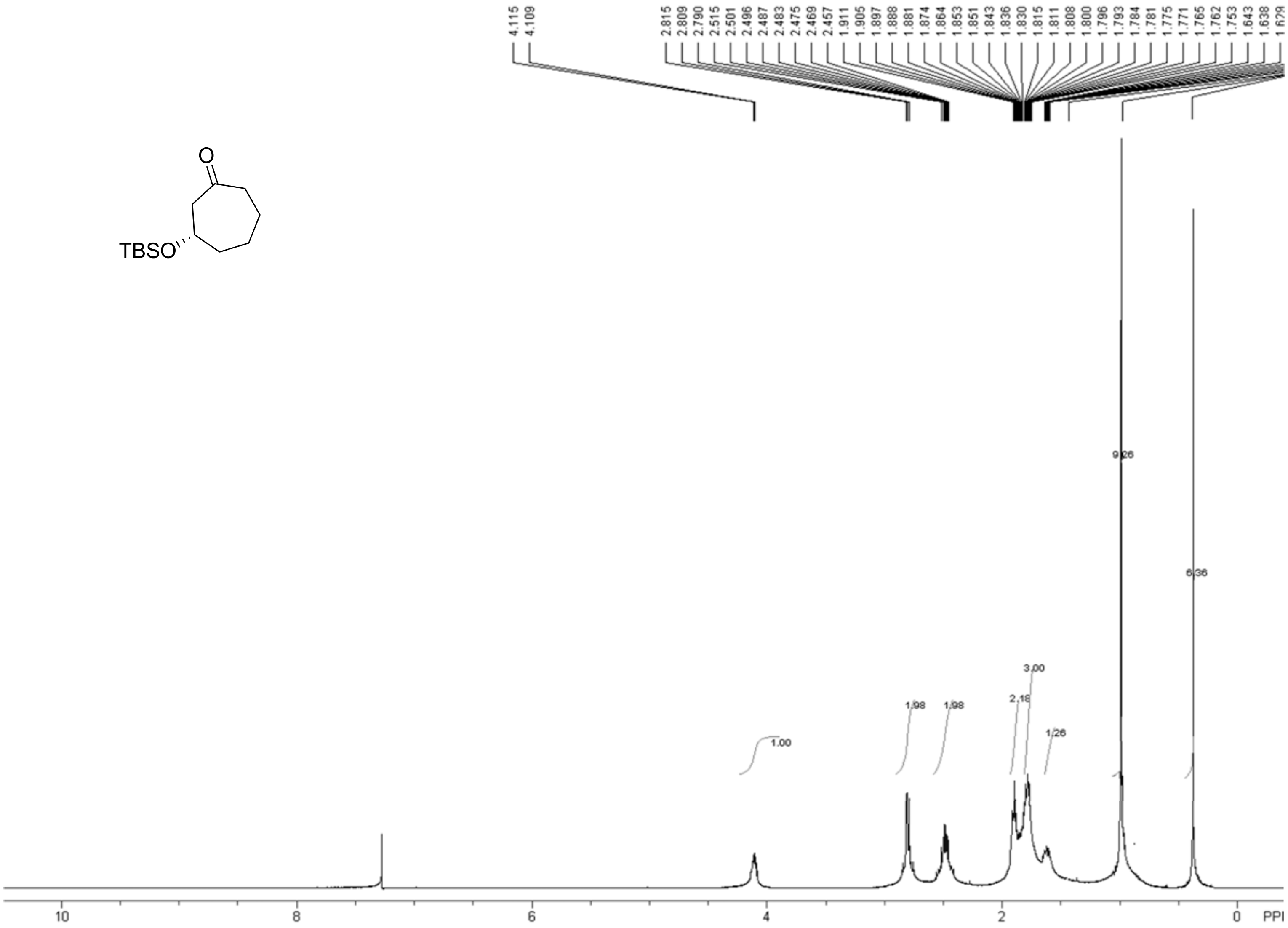
62


7.258
4.365
1.903
1.810
1.793
1.776
1.763
1.745
1.730
1.715
1.628
1.564
1.305
1.280
1.257
0.967
0.921
0.904
0.355
0.82
1.04
4.12
3.23
2.09
8.83
6.00
5.66
10
8
6
4
2
0
PPI

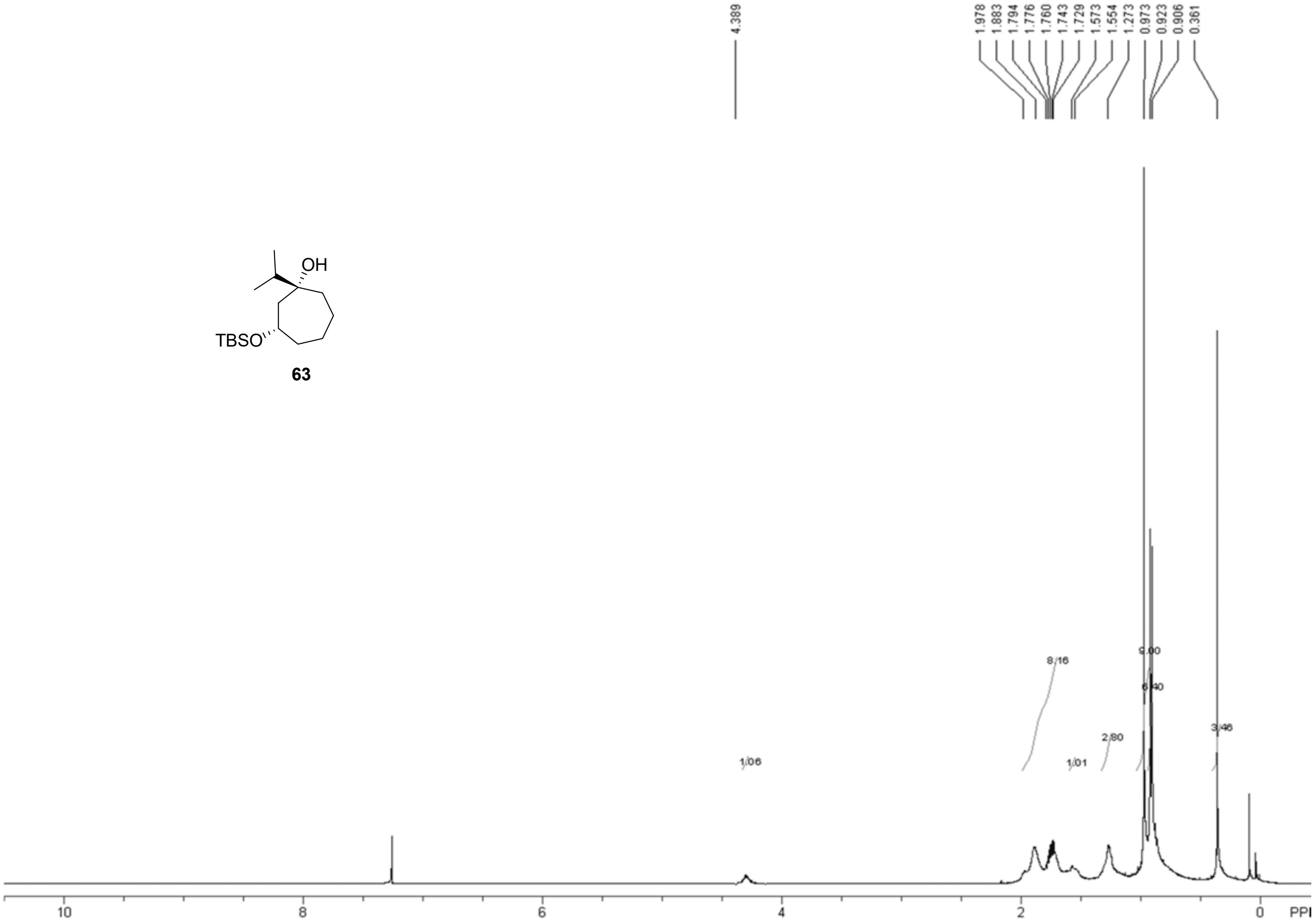
OH
TBSO

62


77.552
77.237
76.922
73.323
66.234
37.514
35.594
33.050
26.153
23.910
20.904
18.573
16.887
-1.149
200
150
100
50
0
PP


O
TBSO

4.115
4.109
2.815
2.809
2.790
2.515
2.501
2.496
2.487
2.483
2.475
2.469
2.457
1.911
1.905
1.897
1.888
1.881
1.874
1.864
1.853
1.851
1.843
1.836
1.830
1.815
1.811
1.808
1.800
1.796
1.793
1.784
1.781
1.775
1.771
1.765
1.762
1.753
1.643
1.638
1.629
1.00
1.98
1.98
2.18
3.00
1.26
9.26
6.36
10
8
6
4
2
0
PP

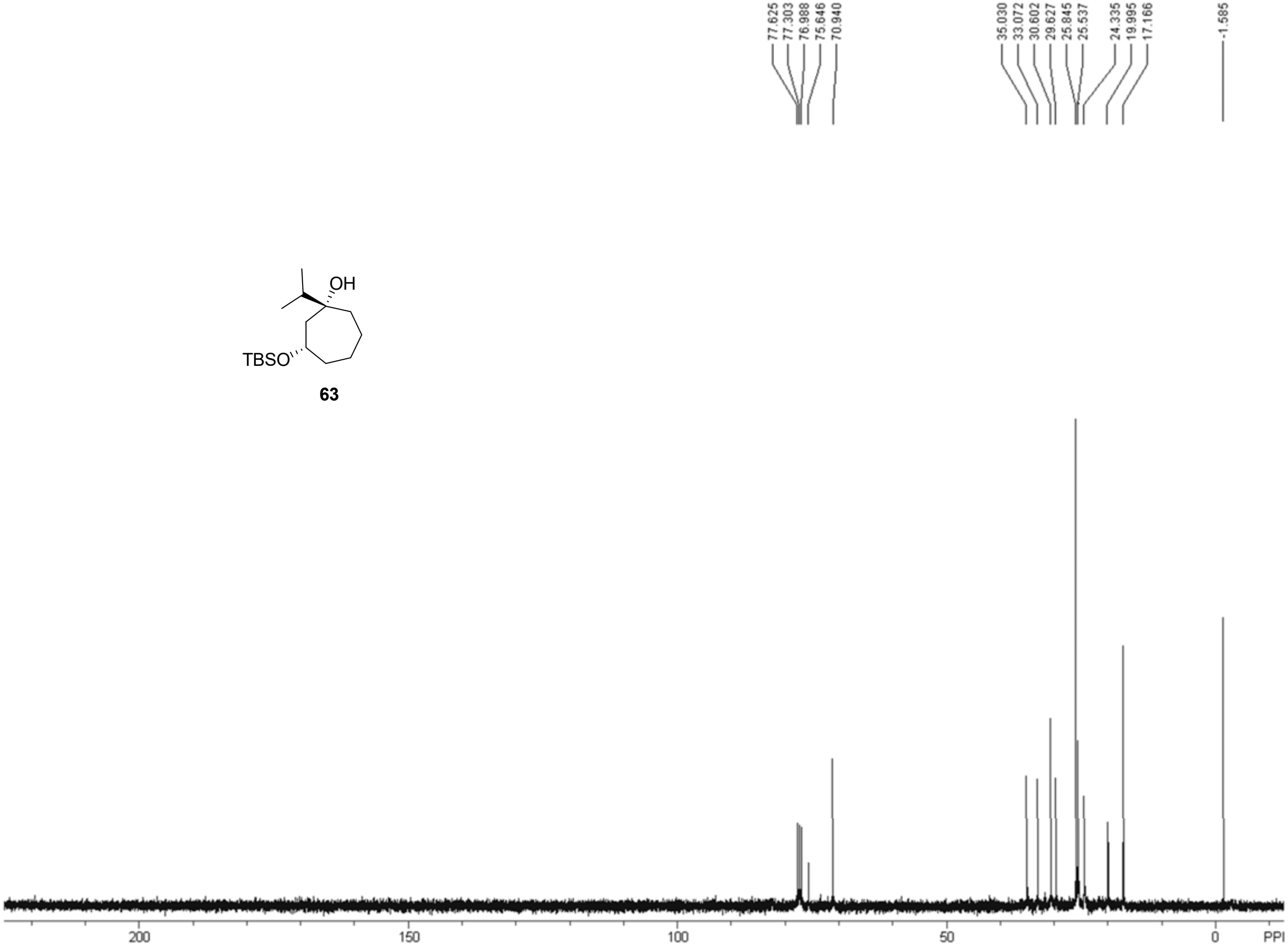

OH
TBSO

63

4.389
1.978
1.883
1.794
1.776
1.760
1.743
1.729
1.573
1.554
1.273
0.973
0.923
0.906
0.361
1.06
8.16
1.01
2.80
9.00
6.40
3.46
10
8
6
4
2
0
PP

OH
TBSO

63


77.625
77.303
76.988
75.646
70.940
35.030
33.072
30.602
29.627
25.845
25.537
24.335
19.995
17.166
-1.585
200
150
100
50
0
PPI