Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Enantioselective Palladium Catalyzed Conjugate Additions of *Ortho*-Substituted Arylboronic Acids to β,β-Disubstituted Cyclic Enones; Total Synthesis of Herbertenediol, Enokipodin A and Enokipodin B

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General remarks

All reactions were performed using oven-dried glassware (except the screw cap vials) under an atmosphere of nitrogen (unless otherwise specified) by standard Schlenk techniques, using dry solvents. Reaction temperature refers to the temperature of the oil bath.

Solvents were taken from a MBraun solvent purification system (SPS-800). All other reagents were purchased from Sigma Aldrich, Acros, TCI Europe, Combi-Blocks, Strem or Fluorochem and used without further purification unless noted otherwise. Silver hexafluoroantimonate ($AgSbF_6$), silver hexafluorophosphate ($AgPF_6$), and silver trifluoroacetate (AgO_2CCF_3) were stored in a nitrogen dry-box in the absence of light. The bisoxazoline ligand used was stored at -20 °C. $_{PdCl2-(R,R-PhBOX)}$ catalyst was prepared as described and stored in the fridge at 4 °C.

TLC analysis was performed on Merck silica gel 60/Kieselguhr F254, 0.25 mm. Compounds were visualized using either Seebach's reagent (a mixture of phosphomolybdic acid (25 g),cerium (IV) sulfate (7.5 g), H_2O (500 mL) and H_2SO_4 (25 mL)), a $KMnO_4$ stain (K_2CO_3 (40 g), $KMnO_4$ (6 g), H_2O (600 mL) and 10% NaOH (5 mL)), an Alizarin stain[1] or elemental iodine.

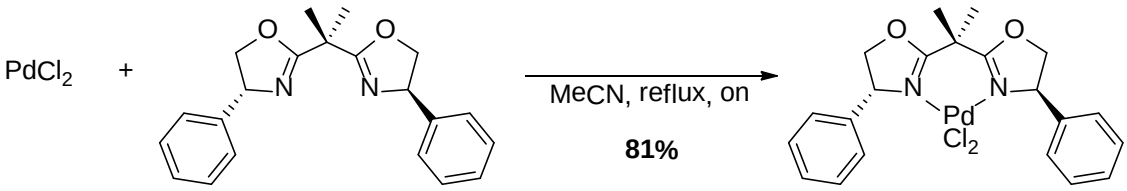
Flash chromatography was performed using SiliCycle silica gel type SiliaFlash P60 (230 – 400 mesh) as obtained from Screening Devices or with automated column chromatography using a Reveleris flash purification system purchased from Grace Davison Discovery Sciences.

^{1}H- and ^{13}C-NMR spectra were recorded on a Varian AMX400 or a Varian 400-MR (400 and 100.59 MHz, respectively) using $CDCl_3$ or DMSO-*d*6 as solvent, unless stated otherwise. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 for ^{1}H, δ 77.06 for ^{13}C, DMSO-*d*6 δ 2.50 for ^{1}H). Data are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, dd = double doublet, ddd = double double doublet, td = triple doublet, t = triplet, q = quartet, b = broad, m = multiplet), coupling constants *J* (Hz), and integration.

GC-MS measurements were performed with an HP 6890 series gas chromatography system equipped with a HP 5973 mass sensitive detector. GC measurements were made using a Shimadzu GC 2014 gas chromatograph system bearing a AT5 column (Grace Alltech) and FID detection

Enantiomeric excesses were determined by chiral HPLC analysis using a Shimadzu LC-10ADVP HPLC instrument equipped with a Shimadzu SPD-M10AVP diode-array detector. Integration at three different wavelengths (254, 225, 190 nm) was performed and the reported enantiomeric excess is an average of the three integrations. Retention times (t_R) are given in min.

High resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL.Optical rotations were measured on a Schmidt+Haensch polarimeter (Polartronic MH8) with a 10 cm cell (c given in g/mL) at ambient temperature (±20 °C).



$PdCl_2$-(*R*,*R*-PhBOX) catalyst

To an oven-dried Schlenk flask charged with palladium(II) chloride (520 mg, 2.93 mmol) was added a solution of (4*R*,4'*R*)-2,2'-(propane-2,2-diyl)bis(4-phenyl-4,5-dihydrooxazole) (1.00 g, 2.99 mmol, 1.02 eq) in dry MeCN (15 mL). An additional 10 mL of dry MeCN was used to rinse the walls of the flask. The Schlenk flask was equipped with a reflux condenser and the reaction was refluxed for 3.5 h. Over time an orange-red suspension formed which after the reaction was cooled to 0 °C with an ice-bath and filtered through a glass-filter (pore-size 4). The residue was washed twice with pentane and dried under an N_2 atmosphere. $PdCl_2$-(*R,R*-BOX) catalyst (1.22 g, 2.38 mmol, 81% yield) was isolated as an orange solid.

^{1}H NMR (400 MHz, [D_6]DMSO): d = 7.54–7.40 (m, 10H), 5.81 (d, *J*=8.6 Hz, 2H), 4.96 (t, *J*=9.1 Hz, 2H), 4.55 (d, *J*=8.2 Hz, 2 H), 1.96 ppm (s,6H)

Characterization matched the previously reported data.[2]

General procedure for the non-enantioselective conjugate additions:

To a 4 mL vial with Teflon-coated screw cap was added 2,2'-bipyridine (0.05 mmol, 7.5 mol%) and palladium trifluoroacetate (0.033 mmol, 5 mol%). The solids were dissolved in a pre-mixed MeOH/H_2O (9:1) solution (2 mL) and the vial was placed in a pre-heated oil bath at 60 °C and stirred for 15 min. The solution was cooled to rt and the α,β-unsaturated ketone (3.33 mmol, 5 eq) and the boronic acid (0.66 mmol, 1 eq), dissolved in a solution of MeOH/H_2O (9:1, 1 mL) were added. The reaction was stirred at 60 °C for 48 h. The crude mixture was flushed over a short silica plug and the elute was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Then the mixture was purified by flash chromatography with pentane:ether as the eluent.

General Prodedure for the enantioselective conjugate additions:

A 4 mL vial with Teflon-coated screw-cap was charged with Pd-Catalyst (0.021 mmol, 4 mol%), the *ortho*-substituted arylboronic acid (0.52 mmol), silver trifluoroacetate (0.052 mmol, 10 mol%), and ammonium hexafluorophosphate (0.052 mmol, 10 mol%). To the solids was added dichloroethane (0.75 mL) and the mixture was stirred at rt for 5 min. *Not all solids dissolved.* To the reaction mixture was subsequently added the β,β-disubstituted enone (3.64 mmol, 7 eq) in dichloroethane (0.75 mL). Demineralized water (4.16 mmol, 8 eq) was added. The vial was sealed and placed in a pre-heated oil bath at 60 °C. Within 30 min a black precipitate (AgCl) was formed. The reaction was allowed to stir for 48 h. The reaction mixture was cooled to rt where after it was filtered through a small silica plug, and flushed with ether (2-3 column volumes). The elute was concentrated under reduced pressure and the resulting oil was purified using flash chromatography employing a mixture of pentane : ether as the eluent.

General procedure for the preparation of Raney nickel:

An aqueous solution of NaOH (6.4 M, 500 mL) was cooled with an ice/salt bath. To the cooled solution a nickel/aluminum alloy (Ni : Al = 50 : 50, 100 g) was added in small portions over two h. The temperature was never allowed to rise above 15 °C. After addition, the ice/salt bath was removed and the suspension was allowed to warm to rt. The water was decanted and an aqueous solution of NaOH (2.5 M, 200 mL) was added to the residue. Stirring was applied for 15 min where after the suspension was allowed to settle. Decantation of the alkali solution was performed and the residue was washed with water. Washing and decantation was repeated until the washings were pH-neutral. The Raney nickel residue was washed with three portions of EtOH (95%, 600 mL) and three times with absolute EtOH (600 mL). The Raney Nickel was stored under absolute ethanol.

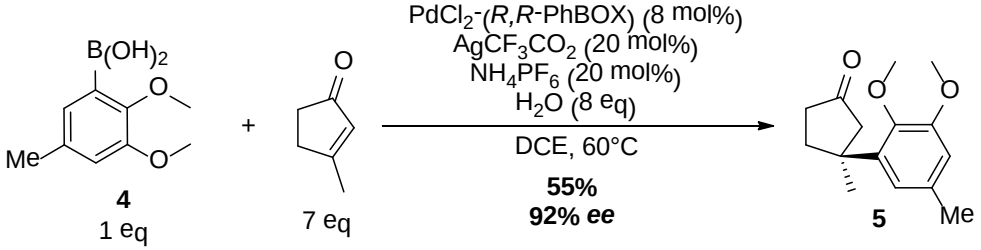
Important notes for the preparation and use of Raney nickel:

- During preparation of the Raney nickel significant quantities of hydrogen gas evolved

- The Raney nickel as prepared contains adsorbed hydrogen (sponge catalyst) and is therefore highly flammable!

- Raney nickel is pyrophoric when dry!

- Storage of the Raney Nickel can lead to pressure build-up in the storage container!



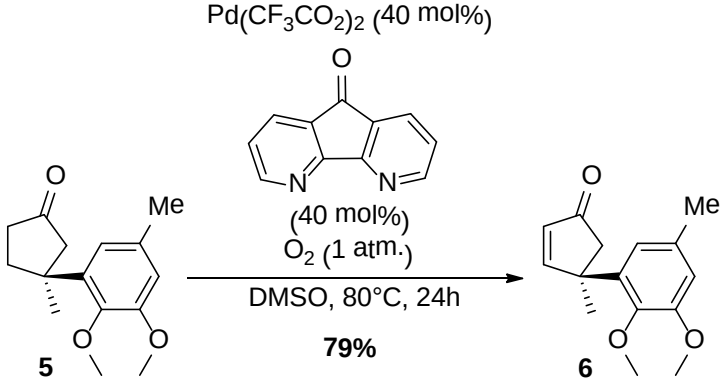
(*S*)-3-(2,3-dimethoxy-5-methylphenyl)-3-methylcyclopentanone (5)

An oven-dried Schlenk tube was charged with $PdCl_2$-(*R,R*-PhBOX) (83 mg, 0.163 mmol, 8 mol%), (2,3-dimethoxy-5-methylphenyl)boronic acid **4** (800 mg, 4.08 mmol, 1 eq), silver trifluoroacetate (90 mg, 0.408 mmol, 20 mol%), and ammonium hexafluorophosphate (66.5 mg, 0.408 mmol, 20 mol%). Three vacuum-nitrogen cycles were applied. To the solids was added dichloroethane (4 mL) and the mixture was stirred at rt for 5 min. Not all solids dissolved. To the mixture was added 3-methyl cyclopent-2-enone (2.8 ml, 28.5 mmol, 7 eq) in dichloroethane (4 mL). Demineralized water (8 eq) was added. The Schlenk tube was sealed and the reaction was heated to 60 °C in a pre-heated oil bath. Within 30 min the precipitate (Ag salt) turned black. The reaction was allowed to react for 48 h.

The reaction mixture was cooled to rt where after it was filtered through a small silica plug, an flushed with ether (2-3 column volumes). The elute was concentrated under reduced pressure and the resulting oil was purified using flash column chromatography employing a mixture of pentane : ether (5 : 1) as the eluent. (*S*)-3-(2,3-dimethoxy-5-methylphenyl)-3-methylcyclopentanone (367 mg, 36% yield, 92% *ee*) **5** was isolated as a colorless oil which solidified overnight.

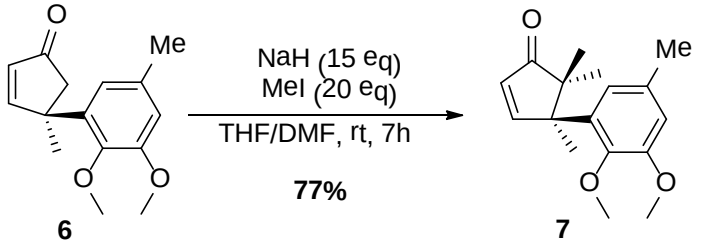
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.67 (d, *J*=1.7, 1H), 6.60 (d, *J*=1.3, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 2.66 (dd, *J*=63.9, 10.0, 2H), 2.44 – 2.25 (m, 4H), 2.31 (s, 3H), 1.36 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 219.30, 152.77, 145.17, 141.03, 132.79, 118.69, 111.80, 60.26, 55.52, 52.56, 42.77, 36.00, 35.16, 27.01, 21.38.
HRMS: (ESI^+) Calculated mass $[M+H]^+$ $C_{15}H_{21}O_3$ = 249.1485, found: 249.1486
Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 15.1 (minor) and 16.0 (major)
$[\alpha]_D^{20}$ = -47.2 ($CHCl_3$, *c* = 0.0041 for a 92% *ee* sample
Melting point = 76.2 °C

Note: The boronic acid required for the Michael addition was prepared according to a literature procedure. See: A. Abad; C. Agullo; A.C Cunat; D. Jimenez; R.H. Perni, *Tetrahedron*, **2001**, *57*, 9727.

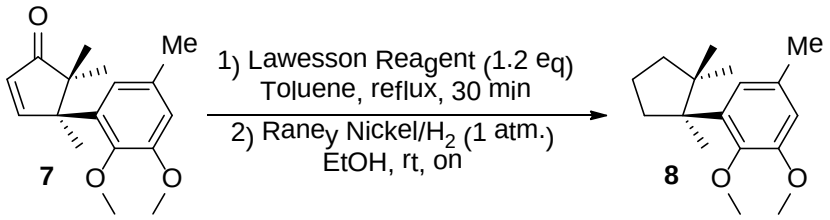


(*R*)-4-(2,3-dimethoxy-5-methylphenyl)-4-methylcyclopent-2-enone (6)
This reaction was performed, based on the procedure by Stahl *et al.*.[3] To an oven-dried Schlenk tube were added palladium trifluoroacetate (82 mg, 0.248 mmol, 40 mol%), and 5H-cyclopenta[1,2-b:5,4-b']dipyridin-5-one (45.1 mg, 0.248 mmol, 40 mol%). To the mixture was added a solution of (*S*)-3-(2,3-dimethoxy-5-methylphenyl)-3-methylcyclopentanone **5** (150 mg, 0.604 mmol) in DMSO (2 mL). An oxygen filled balloon (1 atm) was attached to the reaction set up. While vigorously stirring, the Schlenk tube was purged with three vacuum/O_2 cycles. The reaction mixture was allowed to stir at 80 °C for 24 h. GC/MS showed complete conversion of the starting material.
The reaction was cooled to rt and diluted with water. The aqueous layer was extracted five times with CH_2Cl_2 and the combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Flash column chromatography employing pentane : ether (3:2) furnished pure (*R*)-4-(2,3-dimethoxy-5-methylphenyl)-4-methylcyclopent-2-enone (117 mg, 79% yield) **6** as a colorless oil, which solidified overnight.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (d, *J*=5.6, 1H), 6.66 (d, *J*=1.6, 1H), 6.57 (d, *J*=1.3, 1H), 6.13 (d, *J*=5.6, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 2.64 (dd, *J*=49.8, 18.6, 2H), 2.28 (s, 3H), 1.55 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 209.78, 171.37, 152.96, 145.14, 137.98, 132.96, 130.55, 119.17, 112.45, 60.45, 55.71, 51.07, 47.33, 28.26, 21.44.

HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{15}H_{19}O_3$ = 247.13287, found: 247.13301; (ESI$^+$) Calculated mass $[M+Na]^+$ $C_{15}H_{19}O_3Na$ = 269.1148 found: 269.1150.
$[\alpha]_D^{20}$ = -31.2 ($CHCl_3$, *c* = 0.006) for a 92% *ee* sample.



(*R*)-4-(2,3-dimethoxy-5-methylphenyl)-4,5,5-trimethylcyclopent-2-enone (7)
The dimethylation was based on a procedure by Srikrishna *et al*..[4] To a suspension of NaH (341 mg, 60% dispersion in oil, 8.53 mmol, washed with pentane, 15 eq) in dry THF (4 mL) was added a solution of (*R*)-4-(2,3-dimethoxy-5-methylphenyl)-4-methyl cyclopent-2-enone (140 mg, 0.568 mmol) **6** in dry THF (3 mL) and DMF (0.35 mL). The resulting suspension was stirred for 15 min where after iodomethane (708 µl, 11.4 mmol, 20 eq) was added. The reaction was stirred for 7 h after which GC/MS and TLC indicated complete conversion of the starting material. The reaction was carefully quenched with water (5 mL) where after the phases were separated. The aqueous phase was extracted with ether (3 x 5 mL) and the combined organic layers were treated once with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. Flash column chromatography employing pentane : ether (4 : 1) afforded (*R*)-4-(2,3-dimethoxy-5-methylphenyl)-4,5,5-trimethyl cyclopent-2-enone (120 mg, 77% yield) **7** as a colorless oil. The oil crystallized quickly giving transparent (white appearing!) crystals.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (d, *J*=5.6, 1H), 6.66 (d, *J*=1.7, 1H), 6.49 (s, 1H), 6.07 (d, *J*=5.8, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 2.30 (s, 3H), 1.48 (s, 3H), 1.25 (s, 3H), 0.66 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 214.55, 171.22, 152.68, 145.27, 135.91, 132.72, 125.63, 120.57, 112.05, 60.24, 55.53, 50.80, 26.00, 22.20, 21.34, 19.62, 13.95.
HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{17}H_{23}O_3$ = 275.1641, found: 275.1642.
$[\alpha]_D^{20}$ = -58.5 ($CHCl_3$, *c* = 0.004) for a 92% *ee* sample.



(*S*)-1,2-dimethoxy-5-methyl-3-(1,2,2-trimethylcyclopentyl)benzene (8)
The procedure was based on a publication by Myers.[5] To a solution of (*R*)-4-(2,3-dimethoxy-5-methylphenyl)-4,5,5-trimethyl cyclopent-2-enone (100 mg, 0.364 mmol) **7** in dry toluene (5 mL) was added Lawesson's reagent (177 mg, 0.437 mmol, 1.2 eq). The suspension was heated to reflux for 45 min. The suspension turned into a clear bright pink solution over time. TLC using pentane : ether (4 : 1) indicated complete conversion of the enone into the thioenone.
The reaction mixture was cooled to rt, filtered over a small fluorosil column and flushed with CH_2Cl_2. The elute was concentrated under reduced pressure and purified using flash column

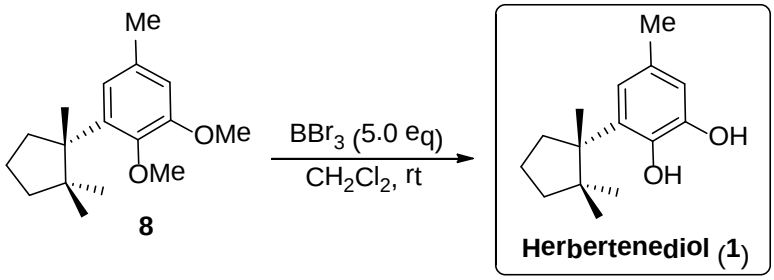
chromatography (5% EtOAc in hexane) only isolating the pink fractions. The fractions were concentrated to a bright pink oil which was dissolved in EtOH (8 mL). To the solution freshly prepared Raney nickel was added. A hydrogen balloon was fixed to the flask and the reaction mixture was purged with three vacuum/H_2 cycles. The reaction was stirred overnight where after the reaction was filtered over a silica plug and flushed with pentane : ether (1 : 1). Evaporation of the solvent under reduced pressure gave a slight yellow oil. Flash chromatography using 4% ether in pentane afforded (*S*)-1,2-dimethoxy-5-methyl-3-(1,2,2-trimethyl cyclopentyl)benzene (62 mg, 0.236 mmol, 65% yield) **8** as a colorless oil. The oil crystallized overnight producing transparent (white appearing!) crystals.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.82 (s, 1H), 6.67 (s, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 2.76 – 2.63 (m, 1H), 2.36 (s, 3H), 1.92 – 1.74 (m, 3H), 1.74 – 1.64 (m, 1H), 1.63 – 1.51 (m, 1H), 1.43 (s, 3H), 1.20 (s, 3H), 0.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) 153.10, 146.76, 140.17, 131.60, 121.69, 111.11, 60.39, 55.64, 51.62, 45.03, 40.98, 39.02, 26.92, 25.30, 24.25, 21.76, 20.44.

HRMS: (ESI^+) Calculated mass $[M+H]^+$ $C_{17}H_{27}O_2$ = 263.2005 found: 263.2007

$[\alpha]_D^{20}$ = -26.1 ($CHCl_3$, *c* = 0.00115) for a 92% *ee* sample.



(*S*)-5-methyl-3-(1,2,2-trimethylcyclopentyl)benzene-1,2-diol (herbertenediol, 1)

The procedure was based on a publication by Myers.[5] To a solution of (*S*)-1,2-dimethoxy-5-methyl-3-(1,2,2-trimethylcyclopentyl)benzene (15 mg, 0.057 mmol, 1 eq) **8** in dry CH_2Cl_2 (1 mL) at 0 °C was added BBr_3 (285 µL, 0.285 mmol, 5 eq, 1 M in CH_2Cl_2). The reaction mixture was allowed to warm to rt and was stirred for 1 h. TLC using 5% ether in pentane indicated complete conversion of the starting material. The reaction mixture was added to a 2% aqueous solution of $NaHCO_3$. The phases were separated and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure affording a white solid. Flash column chromatography using pentane : ether (7 : 3) afforded (*S*)-5-methyl-3-(1,2,2-trimethylcyclopentyl)benzene-1,2-diol (11 mg, 0,047 mmol, 82 % yield) **1** as a white solid.

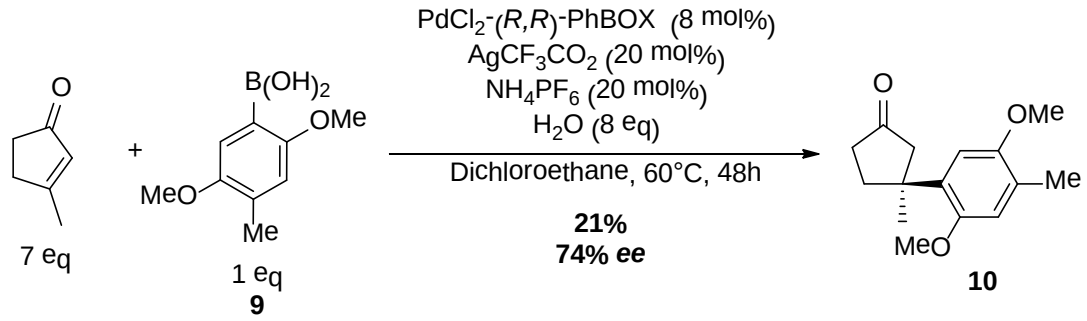
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.69 (s, 1H), 6.58 – 6.54 (m, 1H), 5.35 (s, 1H), 4.98 (s, 1H), 2.68 – 2.54 (m, 1H), 2.23 (s, 3H), 1.82 – 1.70 (m, 3H), 1.70 – 1.62 (m, 1H), 1.61 – 1.50 (m, 0H), 1.42 (s, 3H), 1.19 (s, 3H), 0.77 (s, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.48, 141.03, 133.63, 128.48, 122.06, 113.58, 51.26, 44.99, 41.08, 39.37, 26.98, 25.56, 22.98, 21.30, 20.41

HRMS: (ESI^-) Calculated mass $[M-H]^-$ $C_{15}H_{21}O_2$ = 233.1536, found: 233.1544

$[\alpha]_D^{20}$ = -52.3 ($CHCl_3$, *c* = 0.0047) for a 92% *ee* sample

The analytical data matches with that of the natural product.



(*S*)-3-(2,5-dimethoxy-4-methylphenyl)-3-methylcyclopentanone (10)

To an oven dried Schlenk tube were added palladium catalyst (42 mg, 0.143 mmol, 8 mol%), (2,5-dimethoxy-4-methylphenyl)boronic acid (350 mg, 1.79 mmol) **9**, silver trifluoroacetate (44 mg, 0.358 mmol, 20 mol%) and ammonium hexafluorophosphate (32 mg, 0.358 mmol, 20 mol%) and the Schlenk tube was alternated through three vacuum/nitrogen cycles. Dichloroethane (2.5 mL) was added to the solids and the mixture was stirred for 10 min at rt. Not all the solids dissolved. Then, 3-methyl cyclopent-2-enone (1.2 g, 12.5 mmol, 7 eq) in dichloroethane (2.5 mL) was added. Demineralized water (260 µL, 14.3 mmol, 8 eq) was added and the reaction was stirred at 60 °C. After 48 h, the mixture was cooled to rt, filtered over a silica plug and flushed with ether. The elute was concentrated and purified by flash column chromatography using pentane : ether (4 : 1). (*S*)-3-(2,5-dimethoxy-4-methylphenyl)-3-methylcyclopentanone **10** was obtained as a colorless oil (93 mg, 21% yield, 74% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.71 (s, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 2.63 (dd, *J*=18.1, 6.5, 2H), 2.44 – 2.26 (m, 4H), 2.21 (s, 3H), 1.38 (s, 3H).

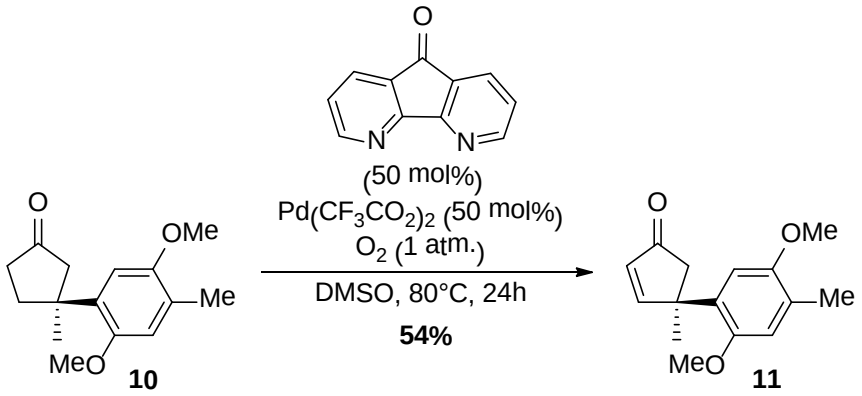
^{13}C NMR (101 MHz, $CDCl_3$) δ = 219.63, 151.34, 151.33, 134.04, 125.33, 114.67, 109.75, 56.16, 55.53, 52.35, 42.58, 36.33, 34.94, 26.28, 15.87.

HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{15}H_{21}O_3$ = 249.1485, found: 249.1474

$[\alpha]_D^{20}$ = -15.6 ($CHCl_3$, *c* = 0.002) for a 74% *ee* sample

Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 97 : 3, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 15.0 (minor) and 16.0 (major) .

Note: The boronic acid required for the Michael addition was prepared according to a literature procedure. See: K. Shishido; Y. Shoji; M. Yoshida; *Org. Lett.* **2009**, *11*, 1441.



(*R*)-4-(2,5-dimethoxy-4-methylphenyl)-4-methylcyclopent-2-enone (11)

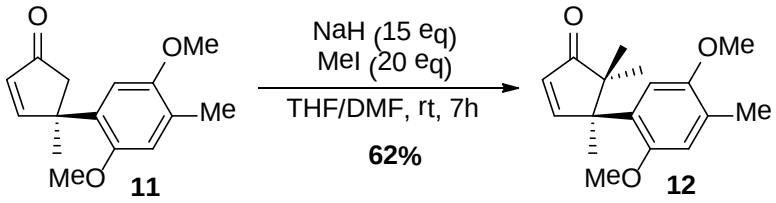
This reaction was performed based on the procedure by Stahl *et al.*.[3] To an oven-dried Schlenk tube was added palladium trifluoroacetate (150 mg, 0.47 mmol, 50 mol%) and diazafluorenone (85 mg, 0.47 mmol, 50 mol%). Compound **10** (293 mg, 1.18 mmol) was disolved in DMSO (4 mL) and added to the mixture. The Schlenk was purged with three vacuum/oxygen cycles, and the reaction was allowed to stir for 24 h at rt. Water (12 mL) was added and the reaction mixture was extracted with DCM (3 x 30 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography with pentane : ether (4 : 1) to yield (*R*)-4-(2,5-dimethoxy-4-methylphenyl)-4-methyl cyclopent-2-enone **11** as a colorless oil (157 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d, *J*=5.7, 1H), 6.71 (s, 1H), 6.66 (s, 1H), 6.16 (d, *J*=5.6, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.67 (dd, *J*=83.9, 18.7, 2H), 2.21 (s, 3H), 1.57 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 210.02, 170.73, 151.23, 151.17, 131.15, 130.88, 126.02, 114.83, 110.00, 56.21, 55.60, 50.36, 47.13, 27.36, 15.98.

HRMS: (ESI^+) Calculated mass $[M+H]^+$ $C_{15}H_{19}O_3$ = 247.13287, found: 247.13284; (ESI^+) Calculated mass $[M+Na]^+$ $C_{15}H_{18}O_3Na$ = 269.1148, found: 269.1148

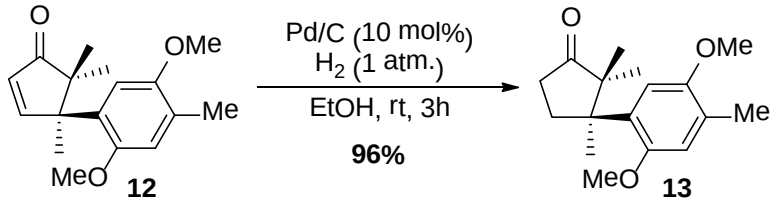
$[\alpha]_D^{20}$ = -55.2 ($CHCl_3$, *c* = 0.006) for a 74% *ee* sample



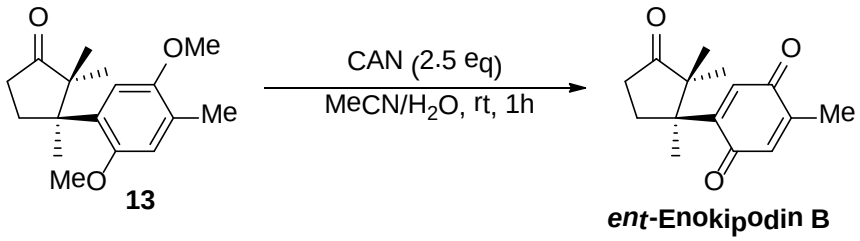
(*R*)-4-(2,5-dimethoxy-4-methylphenyl)-4,5,5-trimethylcyclopent-2-enone (12)

The dimethylation was based on a procedure by Srikrishna *et al.*.[4] NaH (222 mg, 5.55 mmol, 15 eq, 60% suspension in oil) was washed with pentane and suspended in dry THF (3 mL). Compound **11** (92 mg, 0.37 mmol) was added in dry THF (2 mL) and dry DMF (0.23 mL) and stirred for 15 min. MeI (0.46 mL, 7.4 mmol, 20 eq) was added and the reaction was stirred at rt. After 7 h, the reaction was carefully quenched with H_2O (5 mL) at 0 °C and extracted with ether (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography with pentane : ether (4 : 1) to yield **12** as a colorless oil (64 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, *J*=5.9, 1H), 6.71 (s, 1H), 6.53 (s, 1H), 6.12 (d, *J*=5.7, 1H), 3.77 (s, 6H), 2.21 (s, 3H), 1.49 (s, 3H), 1.26 (s, 3H), 0.67 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 214.85, 170.68, 151.56, 151.36, 129.60, 126.68, 125.78, 114.59, 111.27, 56.09, 55.30, 54.73, 50.78, 25.65, 24.89, 19.99, 15.97.
HRMS: (ESI^+) Calculated mass $[M+H]^+$ $C_{17}H_{23}O_3$ = 275.1641, found: 275.1641; (ESI^+) Calculated mass $[M+Na]^+$ $C_{17}H_{22}O_3Na$ = 297.1461, found: 297.1461

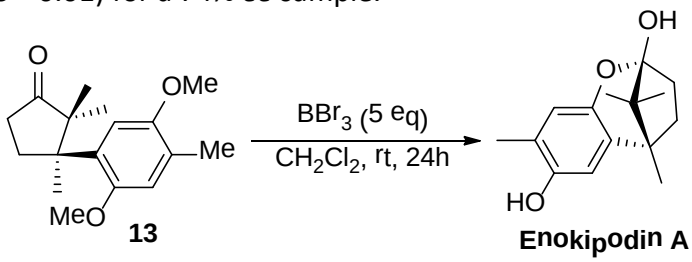


(*R*)-3-(2,5-dimethoxy-4-methylphenyl)-2,2,3-trimethylcyclopentanone (13)
Pd/C (20 mg, 10% activated Pd on charcoal) was added to an oven-dried Schlenk tube. Compound **12** (47 mg, 0.17 mmol) was disolved in ethanol (1 mL) and added to the tube. which was subsequently equipped with a hydrogen balloon and subjected to three vacuum/hydrogen cycles. After stirring for 3.5 h at rt, the mixture was flushed over a silica plug and concentrated under reduced pressure to give **13** as a colorless oil (45 mg, 96% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.85 (s, 1H), 6.68 (s, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 2.49 (ddd, *J*=20.2, 17.1, 10.2, 3H), 2.21 (s, 3H), 2.10 – 1.98 (m, 1H), 1.38 (s, 3H), 1.23 (s, 3H), 0.70 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 222.80, 151.85, 151.23, 132.44, 125.25, 114.29, 111.47, 56.19, 54.76, 52.67, 48.82, 34.42, 32.56, 23.47, 21.74, 21.57, 15.76.
HRMS: (ESI^+) Calculated mass $[M+H]^+$ $C_{17}H_{25}O_3$ = 277.1798, found: 277.1798
$[\alpha]_D^{20}$ = -13.2 ($CHCl_3$, *c* = 0.005) for a 75% *ee* sample.



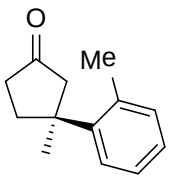
(*S*)-2-methyl-5-(1,2,2-trimethyl-3-oxocyclopentyl)cyclohexa-2,5-diene-1,4-dione (enokipodin B)
This reaction was performed according to the procedure of Srikrishna *et al*..[7] **13** (44 mg, 0.16 mmol) was dissolved in CH_3CN (3 mL) and water (3 mL) and added to an oven-dried Schlenk tube. CAN (219 mg, 0.4 mmol, 2.5 eq) was added and the reaction was stirred at rt for 1 h. The reaction mixture was extracted with DCM (3 x 5 mL) and the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The purification was performed using flash chromatography with pentane : ether (4 : 1) to yield enokipodin B as a yellow solid (33 mg, 84% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.69 (s, 1H), 6.56 (s, 1H), 2.54 – 2.35 (m, 2H), 2.27 (dd, *J*=21.7, 10.9, 1H), 2.04 (s, 3H), 1.91 – 1.83 (m, 1H), 1.32 (s, 3H), 1.22 (s, 3H), 0.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 221.00, 188.30, 187.89, 153.58, 144.57, 135.42, 134.25, 52.47, 49.07, 33.88, 31.19, 23.21, 22.27, 20.75, 15.04.
HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{15}H_{19}O_3$ = 247.1328, found: 247.1328
$[\alpha]_D^{20}$ = -24.8 ($CHCl_3$, *c* = 0.01) for a 74% *ee* sample.



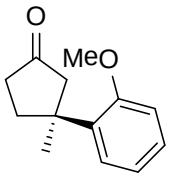
13 **Enokipodin A**

(2*R*,5*R*)-5,8,10,10-tetramethyl-2,3,4,5-tetrahydro-2,5-methanobenzo[b]oxepine-2,7-diol (*ent*-enokipodin A)
Compound **13** (50 mg, 0.18 mmol, was dissolved in DCM (10 mL) and cooled to 0 °C. BBr_3 (0.9 mL, 0.9 mmol, 5 eq) was added dropwise. The light brown solution was stirred for 24 h at rt. The reaction was quenched with a saturated aquatious solution of $NaHCO_3$ (10 mL) and extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated. The crude mixture was purified by flash chromatography with pentane : ether (3 : 1) to yield pure enokipodin A as transparent (*white appearing!*) crystals (25 mg, 57% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.55 (s, 1H), 6.50 (s, 1H), 4.25 (s, 1H), 2.69 (s, 1H), 2.17 (s, 3H), 2.14 – 2.03 (m, 2H), 1.90 (td, *J*=12.1, 6.5, 1H), 1.82 – 1.73 (m, 1H), 1.24 (s, 3H), 1.09 (s, 3H), 0.80 (s, 3H).
^{13}C NMR (101 MHz, DMSO-*d*6) δ = 148.34, 145.05, 130.24, 122.06, 115.91, 110.41, 109.01, 46.73, 42.82, 38.34, 35.20, 18.44, 15.96, 15.79, 15.64.
HRMS: (APCI$^+$) Calculated mass $[M+H]^+$ $C_{15}H_{21}O_3$ = 249.1485, found: 249.1482
$[\alpha]_D^{20}$ = +77.0 ($CHCl_3$, *c* = 0.006) for a 74% *ee* sample.



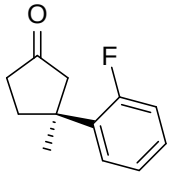
3-methyl-3-(o-tolyl)cyclopentenone
This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 82% yield, enantioselective synthesis 23% yield, 90% *ee.*
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 – 7.12 (m, 4H), 2.67 (dd, *J*=55.6, 17.5, 2H), 2.45 (s, 3H), 2.53 – 2.35 (m, 4H), 1.38 (s, 3H)
^{13}C NMR (101 MHz, $CDCl_3$) δ = 218.32, 146.40, 135.37, 132.40, 126.34, 126.07, 125.92, 52.72, 44.31, 35.85, 35.77, 26.40, 22.44
HRMS: (ESI$^+$) Calculated mass $[M+Na]^+$ $C_{13}H_{16}ONa$ = 211.1093, found: 211.1084
$[\alpha]_D^{20}$ = -35.9 ($CHCl_3$, *c* = 0.01) for a 90% *ee* sample.
Chiral HPLC analysis on a Chiracel OB-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 25.8 (minor) and 28.5 (major).

Chiral HPLC analysis on a Chiracel AS-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 13.0 (minor) and 14.0 (major) .
Chiral HPLC analysis Phenomenex LUX 5µ Cellulose-3 column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 9.5 (minor) and 10.5 (major).



3-(2-methoxyphenyl)-3-methylcyclopentanone
This compound was prepared according to the general procedure and purified employing flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 69% yield, enantioselective synthesis 45% yield, 80% *ee*

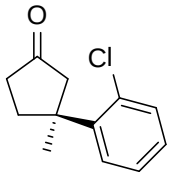
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 – 7.10 (m, 2H), 6.95 – 6.82 (m, 2H), 3.79 (s, 3H), 2.59 (dd, *J*=18.1, 18,1 2H), 2.41 – 2.23 (m, 4H), 1.36 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 219.93, 157.66, 136.14, 127.72, 126.29, 120.52, 111.39, 54.97, 52.31, 42.66, 36.41, 34.90, 26.21.
HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{13}H_{17}O_2$ = 205.1223, found: 205.1214
$[\alpha]_D^{20}$ = -21.0 ($CHCl_3$, *c* = 0.01) for a 80% *ee* sample.
Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 19.0 (minor) and 20.9 (major).
Chiral HPLC analysis on a Phenomenex LUX 5µ Cellulose-3 column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 9.8 (minor) and 11.5 (major)
Chiral HPLC analysis on a Chiracel OB-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 24.8 (minor) and 29.3 (major).



3-(2-fluorophenyl)-3-methylcyclopentanone
This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 20% yield (51% with double catalyst loading), enantioselective synthesis 20% yield, 95% *ee.*

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.23 (m, 2H), 7.19 – 7.03 (m, 2H), 2.71 – 2.59 (m, 2H), 2.54 – 2.34 (m, 4H), 1.44 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 218.50, 218.48, 162.57, 160.11, 134.99, 134.87, 128.45, 128.37, 127.11, 127.05, 124.28, 124.25, 116.62, 116.39, 52.09, 52.06, 42.29, 42.27, 36.26, 36.25, 34.81, 34.78, 26.96, 26.94. (*Spectrum contains the double amount of peaks due to carbon-fluorine coupling*).
HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{12}H_{14}OF$ = 193.1023 found: 193.1014
$[\alpha]_D^{20}$ = -23.8 ($CHCl_3$, *c* = 0.01) for a 95% *ee* sample.
Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 20.4 (major) and 21.7 (minor).

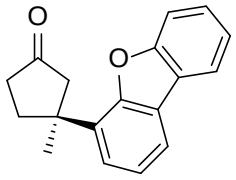
Chiral HPLC analysis on a Chiracel AS-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 12.1 (major) and 13.2 (minor).



3-(2-chlorophenyl)-3-methylcyclopentanone

This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 12% yield (31% with double catalyst loading), enantioselective synthesis 8% yield (12% with double catalyst loading), 94% *ee.*

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (dd, *J*=7.8, 1.5, 1H), 7.32 (dd, *J*=7.8, 1.8, 1H), 7.25 (td, *J*=7.6, 1.6, 1H), 7.18 (td, *J*=7.6, 1.7, 1H), 2.78 (dd, *J*=101.0, 17.9, 2H), 2.55 – 2.34 (m, 4H), 1.48 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 218.51, 144.94, 133.48, 131.83, 128.02, 127.73, 127.12, 52.23, 44.49, 36.28, 35.22, 25.68.
HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{12}H_{14}OCl$ = 209.07277 found: 209.07185; (ESI$^+$) Calculated mass $[M+Na]^+$ $C_{12}H_{13}OClNa$ = 231.0547 found: 231.0537.
$[\alpha]_D^{20}$ = -22.4 ($CHCl_3$, *c* = 0.01) for a 94% *ee* sample.
Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 23.9 (minor) and 29.2 (major).
Chiral HPLC analysis on a Phenomenex LUX 5µ Cellulose-3 column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 1.0 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 9.5 (major) and 10.4 (minor).

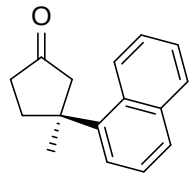


3-(dibenzo[b,d]furan-4-yl)-3-methylcyclopentanone

This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 69% yield, enantioselective synthesis 51% yield, 93% *ee.*

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J*=7.7, 1H), 7.82 (dd, *J*=6.1, 2.8, 1H), 7.56 (d, *J*=8.2, 1H), 7.47 – 7.40 (m, 1H), 7.34 – 7.29 (m, 1H), 7.27 (d, *J*=3.6, 2H), 2.83 (dd, *J*=49.5, 17.8, 2H), 2.60 – 2.30 (m, 4H), 1.56 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 218.76, 155.77, 153.87, 132.25, 127.22, 124.85, 124.06, 123.75, 122.92, 122.80, 120.65, 119.19, 111.70, 51.94, 42.56, 36.48, 34.74, 26.77.
HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{18}H_{17}O_2$ = 265.1223 found: 265.1212
$[\alpha]_D^{20}$ = -15.8 ($CHCl_3$, *c* = 0.01) for a 93% *ee* sample.
Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 25.9 (major) and 29.5 (minor).
Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 37.0 (major) and 44.3 (minor).

Chiral HPLC analysis on a Phenomenex LUX 5µ Cellulose-3 column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 1.0 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 16.7 (minor) and 23.8 (major).



3-methyl-3-(naphthalen-1-yl)cyclopentenone

This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 73% yield, enantioselective synthesis 20% yield (38% with double catalyst loading), 85% *ee.*

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (d, *J*=8.1, 1H), 7.93 – 7.86 (m, 1H), 7.82 – 7.72 (m, 1H), 7.54 – 7.45 (m, 2H), 7.45 – 7.39 (m, 2H), 2.89 (dd, *J*=18.1, 7.6, 2H), 2.72 – 2.34 (m, 4H), 1.70 (s, 3H).

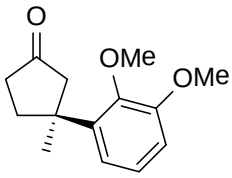
^{13}C NMR (101 MHz, $CDCl_3$) δ = 218.50, 143.75, 135.07, 131.22, 129.78, 128.11, 125.79, 125.43, 125.30, 125.21, 123.46, 53.90, 44.62, 36.67, 36.38, 27.91.

HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{16}H_{17}O$ = 225.1273 found: 225.1264

$[\alpha]_D^{20}$ = -23.2 ($CHCl_3$, *c* = 0.01) for a 85% *ee* sample.

Chiral HPLC analysis on a Chiracel AS-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 1.0 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 24.4 (major) and 27.5 (minor).

Chiral HPLC analysis on a Phenomenex LUX 5µ Cellulose-3 column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 1.0 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 19.8 and 37.3.



3-(2,3-dimethoxyphenyl)-3-methylcyclopentanone

This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 65% yield, enantioselective synthesis 25% yield, 94% *ee.*

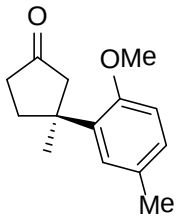
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.01 (t, *J*=8.0, 1H), 6.84 (dd, *J*=15.7, 7.7, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 2.64 (dd, *J*=64.4, 17.9, 2H), 2.45 – 2.26 (m, 4H), 1.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 219.53, 153.22, 147.58, 141.62, 123.44, 118.36, 111.15, 60.41, 55.70, 52.68, 42.96, 36.14, 35.27, 27.11.

HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{14}H_{19}O_3$ = 235.1328 found: 235.1327.

$[\alpha]_D^{20}$ = -30.2 ($CHCl_3$, *c* = 0.01) for a 94% *ee* sample.

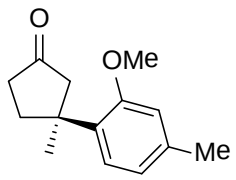
Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 31.3 (minor) and 34.2 (major).



3-(2-methoxy-5-methylphenyl)-3-methylcyclopentanone

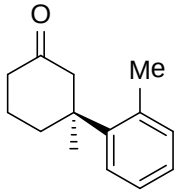
This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 78% yield, enantioselective synthesis 19% yield (32% with double catalyst loading), 80% *ee.*

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05 – 6.98 (m, 2H), 6.80 (d, *J*=8.2, 1H), 3.80 (s, 3H), 2.62 (dd, *J*=18.2, 11.5, 2H), 2.47 – 2.31 (m, 4H), 2.30 (s, 3H), 1.38 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 219.92, 155.55, 135.88, 129.46, 127.80, 127.09, 111.37, 55.06, 52.30, 42.53, 36.38, 34.89, 26.23, 20.70.
HRMS: (ESI^+) Calculated mass $[M+H]^+$ $C_{14}H_{19}O_2$ = 219.13796 found: 219.13786; (ESI^+) Calculated mass $[M+Na]^+$ $C_{14}H_{18}O_2Na$ = 241.1199 found: 241.1197
$[\alpha]_D^{20}$ = -132.3 ($CHCl_3$, *c* 0.01) for a 80% *ee* sample.
Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 15.2 (minor) and 16.8 (major).
Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 15.9 (major) and 23.8 (minor).



3-(2-methoxy-4-methylphenyl)-3-methylcyclopentanone
This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 78% yield, enantioselective synthesis 19% yield (32% with double catalyst loading), 80% *ee.*
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.08 (d, *J*=7.8, 1H), 6.74 (d, *J*=7.8, 1H), 6.72 (s, 1H), 3.81 (d, *J*=4.5, 3H), 2.61 (q, 2H), 2.44 – 2.27 (m, 7H), 1.37 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 219.98, 157.51, 137.57, 133.16, 126.10, 120.97, 112.35, 54.89, 52.38, 42.35, 36.40, 34.94, 26.29, 21.22.
HRMS: (ESI^+) Calculated mass $[M+H]^+$ $C_{14}H_{19}O_2$ = 219.13796 found: 219.13799; (ESI^+) Calculated mass $[M+Na]^+$ $C_{14}H_{18}O_2Na$ = 241.11990 found: 241.11995
$[\alpha]_D^{20}$ = -29.8 ($CHCl_3$, *c* = 0.01) for a 80% *ee* sample.
Chiral HPLC analysis on a Phenomenex LUX 5µ Cellulose-3 column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 1.0 mL/min, UV detection at 190 nm and 225 nm, retention times (min): 35.0 (major) and 37.4 (minor).
Chiral HPLC analysis on a Chiracel AS-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 20.7 and 22.6.
Chiral HPLC analysis on Chiracel OB-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 35.7 and 39.9.
Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 32.6 and 37.5.

Note: The boronic acid required for the Michael addition was prepared according to the literature procedures: P. Wucher; V. Goldbach; S. Mecking, *Organometallics* **2013**, *32*, 4516 and J.A. Lowe III, J.P. Whittle, (Pfizer Inc.) US6235747 B1, **2001.**



3-methyl-3-(o-tolyl)cyclohexanone

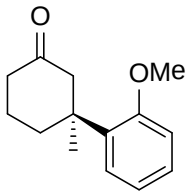
This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 41% yield, enantioselective synthesis 16% yield, 98% *ee.*

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 – 7.21 (m, *J*=4.3, 1H), 7.17 – 7.10 (m, 3H), 3.00 (d, *J*=14.2, 1H), 2.54 (s, 3H), 2.47 (d, *J*=14.4, 2H), 2.31 (t, *J*=6.8, 2H), 1.99 – 1.82 (m, 2H), 1.67 – 1.57 (m, 1H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.86, 144.31, 135.70, 133.49, 127.14, 126.59, 126.24, 55.11, 44.22, 40.84, 36.02, 27.41, 23.43, 21.91.

HRMS: (ESI^+) Calculated mass $[M+H]^+$ $C_{14}H_{19}O$ = 203.1430 found: 203.1430

Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99.5 : 0.5, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 23.9 (minor) and 26.9 (major).



3-(2-methoxyphenyl)-3-methylcyclohexanone

This compound was prepared according to the general procedure and purified with flash column chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 55% yield, enantioselective synthesis 20% yield (42% with double catalyst loading), 96% *ee.*

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (t, *J*=7.6, 2H), 6.91 (t, *J*=8.1, 2H), 3.84 (s, 3H), 3.00 (d, *J*=14.1, 1H), 2.63 – 2.52 (m, 1H), 2.45 (d, *J*=14.9, 1H), 2.31 (t, *J*=6.9, 2H), 1.93 – 1.77 (m, 2H), 1.71 – 1.61 (m, 1H), 1.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 212.36, 157.84, 134.79, 127.78, 127.40, 120.61, 111.80, 54.92, 53.41, 42.83, 40.97, 35.02, 26.37, 22.18.

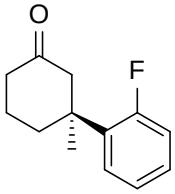
HRMS: (ESI^+) Calculated mass $[M+H]^+$ $C_{14}H_{19}O_2$ = 219.1379 found: 219.1371.

$[\alpha]_D^{20}$ = +52.5 ($CHCl_3$, *c* = 0.01) for a 96% *ee* sample.

Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 17.9 (major) and 19.2 (minor).

Chiral HPLC analysis on a Phenomenex LUX 5µ Cellulose-3 column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 1.0 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 9.3 (major) and 9.9 (minor).

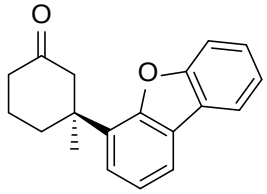
Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 19.4 and 21.1 .



3-(2-fluorophenyl)-3-methylcyclohexanone

This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 10% yield (with double catalyst loading), enantioselective synthesis 13% yield (23% with double catalyst loading), 95% *ee.*

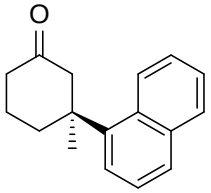
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 – 7.18 (m, 2H), 7.10 – 6.98 (m, 2H), 2.94 (d, *J*=14.7, 1H), 2.50 – 2.41 (m, 2H), 2.33 (t, *J*=6.7, 2H), 1.97 – 1.86 (m, 2H), 1.68 – 1.58 (m, 1H), 1.41 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 218.55, 218.53, 162.59, 160.13, 135.00, 134.88, 128.47, 128.38, 127.12, 127.07, 124.29, 124.26, 116.64, 116.40, 52.11, 52.08, 42.31, 42.28, 36.28, 36.27, 34.83, 34.80, 26.98, 26.96. (*Spectrum contains double amount of peaks due to the carbon-fluorine coupling*)
HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{13}H_{16}OF$ = 207.1179 found: 207.1170
$[\alpha]_D^{20}$ = +46.1 ($CHCl_3$, *c* = 0.01) for a 95% *ee* sample.
Chiral HPLC analysis on a Phenomenex LUX 5µ Cellulose-3 column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 14.0 (minor) and 15.0 (major).



3-(dibenzo[b,d]furan-4-yl)-3-methylcyclohexanone

This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 14% yield (20% with double catalyst loading), enantioselective synthesis 36% yield, 93% *ee.*

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, *J*=7.7, 1H), 7.85 (d, *J*=6.0, 1H), 7.61 (d, *J*=7.7, 1H), 7.47 (t, *J*=7.8, 1H), 7.38 – 7.27 (m, 3H), 3.15 (d, *J*=14.3, 1H), 2.85 – 2.77 (m, 1H), 2.64 (d, *J*=14.4, 1H), 2.39 (t, *J*=6.8, 2H), 2.12 – 1.88 (m, 3H), 1.61 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.78, 155.67, 153.77, 131.93, 127.23, 125.10, 124.87, 124.13, 123.08, 122.87, 120.68, 119.38, 111.76, 53.09, 42.75, 41.17, 35.69, 27.06, 22.39.
HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{19}H_{19}O_2$ = 279. 1379 found: 279.1367
$[\alpha]_D^{20}$ = +77.1 ($CHCl_3$, *c* = 0.01) for a 93% *ee* sample.
Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 25.5 (major) and 27.9 (minor)
Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 18.4 and 45.6.



3-methyl-3-(naphthalen-1-yl)cyclohexanone

This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 20% yield (34% with double catalyst loading), enantioselective synthesis 26% yield, 95% *ee.*

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41 (d, *J*=8.4, 1H), 7.88 (d, *J*=7.5, 1H), 7.74 (dd, *J*=6.9, 2.4, 1H), 7.53 – 7.43 (m, 2H), 7.42 – 7.34 (m, 2H), 3.10 (d, *J*=13.1, 1H), 2.89 – 2.80 (m, 1H), 2.64 (d, *J*=14.6, 1H), 2.36 (t, *J*=6.8, 2H), 2.17 (ddd, *J*=13.6, 9.8, 3.6, 1H), 1.94 – 1.82 (m, 1H), 1.71 (s, 3H), 1.52 – 1.43 (m, 1H)
^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.99, 142.28, 135.42, 130.86, 130.05, 128.35, 126.19, 125.31, 125.17, 125.03, 56.15, 44.58, 40.95, 37.23, 28.52, 22.07 (*one carbon signal missing due to overlap of two carbon signals*)

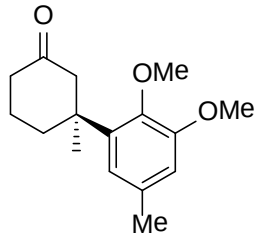
HRMS: (ESI^+) Calculated mass $[M+H]^+$ $C_{17}H_{19}O$ = 239.14304 found: 239.14196; (ESI^+) Calculated mass $[M+Na]^+$ $C_{17}H_{18}ONa$ = 261.1249 found: 261.1239

$[\alpha]_D^{20}$ = +98.5 ($CHCl_3$, *c* = 0.01) for a 95% *ee* sample.

Chiral HPLC analysis on a Phenomenex LUX 5µ Cellulose-3 column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 1.0 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 13.1 (minor) and 15.5 (major).

Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 27.2 and 41.1.

Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 18.2 and 26.0.



3-(2,3-dimethoxy-5-methylphenyl)-3-methylcyclohexanone

This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 44% yield, enantioselective synthesis 19% yield, 94% *ee.*

^1H NMR (400 MHz, $CDCl_3$) δ = 6.66 (s, 1H), 6.61 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.96 (d, *J*=14.5, 1H), 2.54 – 2.44 (m, 1H), 2.40 (d, *J*=14.3, 1H), 2.34 – 2.30 (m, 2H), 2.28 (s, 3H), 1.92 – 1.80 (m, 2H), 1.71 – 1.58 (m, 2H), 1.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 212.15, 153.13, 145.69, 139.34, 132.86, 120.05, 112.19, 60.38, 55.76, 54.04, 43.10, 40.99, 36.07, 27.61, 22.22, 21.66.

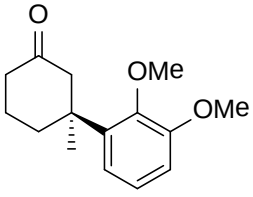
HRMS: (ESI^+) Calculated mass $[M+H]^+$ $C_{16}H_{23}O_3$ = 263.1641 found: 263.1642; (ESI^+) Calculated mass $[M+Na]^+$ $C_{16}H_{22}O_3Na$ = 285.1461 found: 285.1462.

$[\alpha]_D^{20}$ = +29.7 ($CHCl_3$, *c* = 0.01) for a 94% *ee* sample.

Chiral HPLC analysis on a Chiracel AS-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 18.3 (minor) and 25.5 (major).

Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 24.2 and 25.5.

Note: The boronic acid required for the Michael addition was prepared according to a literature procedure. See: A. Abad; C. Agullo; A.C Cunat; D. Jimenez; R.H. Perni, *Tetrahedron*, **2001**, *57*, 9727.

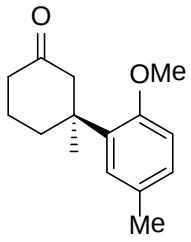


3-(2,3-dimethoxyphenyl)-3-methylcyclohexanone

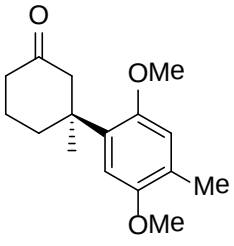
This compound was prepared according to the general procedure and purified with flash chromatography using pentane:ether (4 : 1) as the eluent. Racemic synthesis = 17% yield (28% with double catalyst loading), enantioselective synthesis 44% yield, 99% *ee.*

^1H NMR (400 MHz, $CDCl_3$) δ = 6.97 (t, *J*=8.1, 1H), 6.85 (d, *J*=7.1, 1H), 6.82

(d, *J*=8.0, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.97 (d, *J*=14.3, 1H), 2.51 (t, *J*=9.5, 1H), 2.42 (d, *J*=14.4, 1H), 2.35 – 2.25 (m, 2H), 1.94 – 1.80 (m, 2H), 1.71 – 1.58 (m, 1H), 1.41 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 212.04, 153.43, 147.98, 139.74, 123.34, 119.56, 111.41, 60.35, 55.75, 54.06, 43.20, 40.94, 36.02, 27.62, 22.19.
HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{15}H_{21}O_3$ = 249.1485 found: 249.1484.
Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 25.1 (minor) and 28.3 (major).
Chiral HPLC analysis on a Phenomenex LUX 5µ Cellulose-3 column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 1.0 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 12.4 and 14.7.
Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 23.1 and 28.7.
Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 99.5 : 0.5, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 16.5 and 17.9.

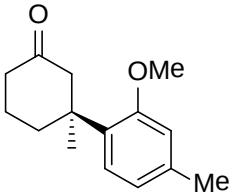


3-(2-methoxy-5-methylphenyl)-3-methylcyclohexanone
This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 63% yield, enantioselective synthesis 28% yield, 91% *ee.*
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 (s, 2H), 6.79 (d, *J*=8.9, 1H), 3.80 (s, 3H), 2.99 (d, *J*=14.2, 1H), 2.63 – 2.50 (m, 1H), 2.44 (d, *J*=13.6, 1H), 2.31 (t, *J*=6.8, 2H), 2.27 (s, 3H), 1.93 – 1.77 (m, 2H), 1.74 – 1.62 (m, 1H), 1.39 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = δ = 212.53, 155.83, 134.69, 129.68, 128.28, 127.95, 111.90, 55.13, 53.40, 42.73, 41.06, 35.12, 26.39, 22.25, 20.86.
HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{15}H_{21}O_2$ = 233.1536 found: 233.1377.
$[\alpha]_D^{20}$ = +44.1 ($CHCl_3$, *c* = 0.01) for a 91% *ee* sample.
Chiral HPLC analysis on a Chiracel AD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 13.5 (minor) and 15.4 (major).
Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 14.2 (major) and 16.0 (minor).



3-(2,5-dimethoxy-4-methylphenyl)-3-methylcyclohexanone
This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 73% yield, enantioselective synthesis <10% yield using double catalyst loading 84% *ee*
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.73 (s, 1H), 6.70 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 2.98 (d, *J*=14.4, 1H), 2.68 – 2.57 (m, 1H), 2.41 (d, *J*=14.4, 1H), 2.29

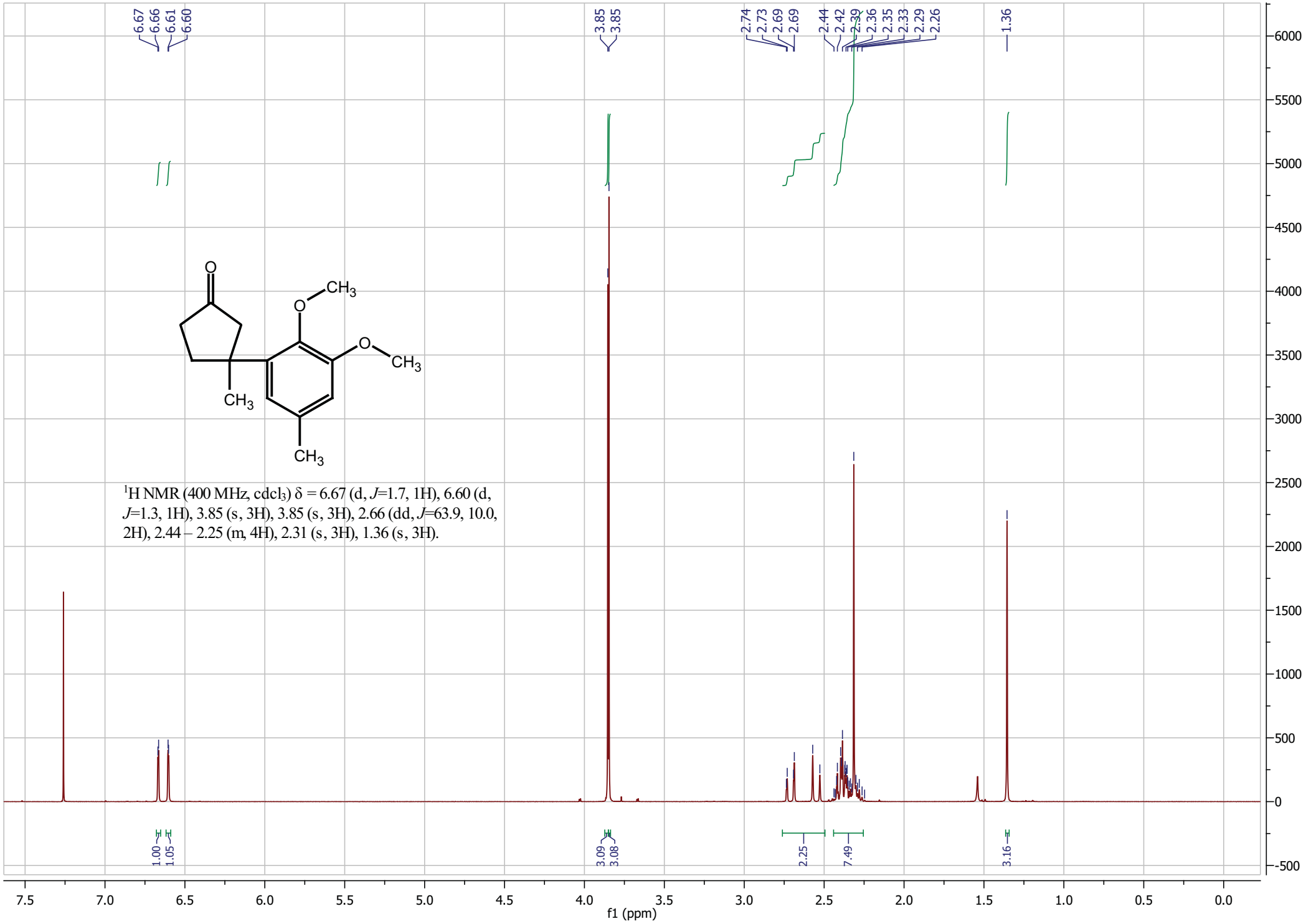
(t, *J*=7.0, 2H), 2.19 (s, 3H), 1.91 – 1.81 (m, 1H), 1.81 – 1.73 (m, 1H), 1.65 – 1.55 (m, 1H), 1.40 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 212.48, 151.39, 151.32, 132.40, 125.20, 115.22, 111.14, 56.04, 55.63, 53.97, 43.29, 41.05, 35.25, 27.07, 22.34, 15.85.
HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{16}H_{23}O_2$ = 263.16417 found: 263.16436; (ESI$^+$) Calculated mass $[M+Na]^+$ $C_{16}H_{22}O_3Na$ = 285.1461 found: 285.1463
$[\alpha]_D^{20}$ = +18.7 ($CHCl_3$, *c* = 0.003) for a 84% *ee* sample.
Chiral HPLC analysis on a Phenomenex LUX 5µ Cellulose-3 column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 1.0 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 26.3 (minor) and 26.8 (major).
Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times for racemate (min): 21.4 22.3.

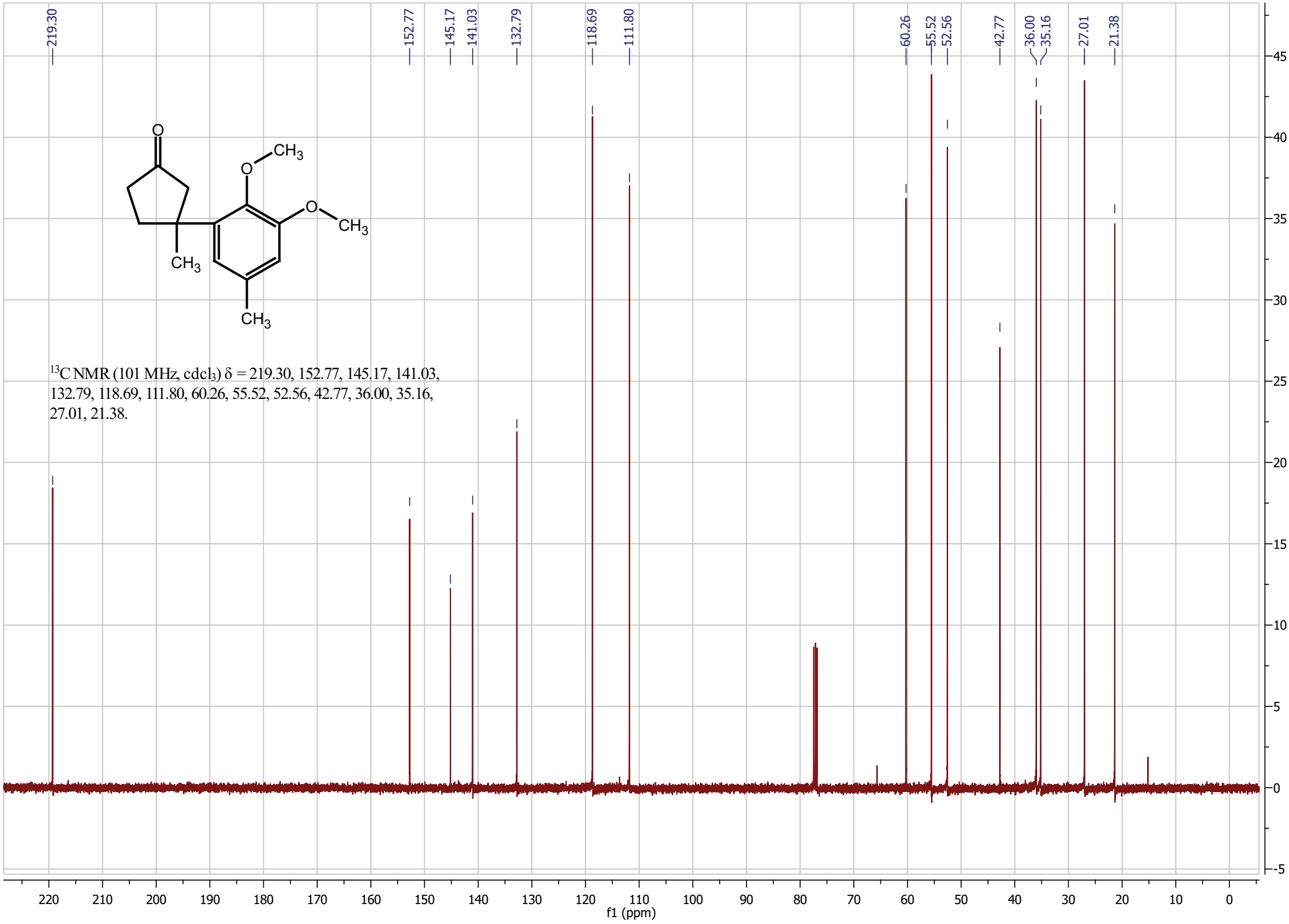


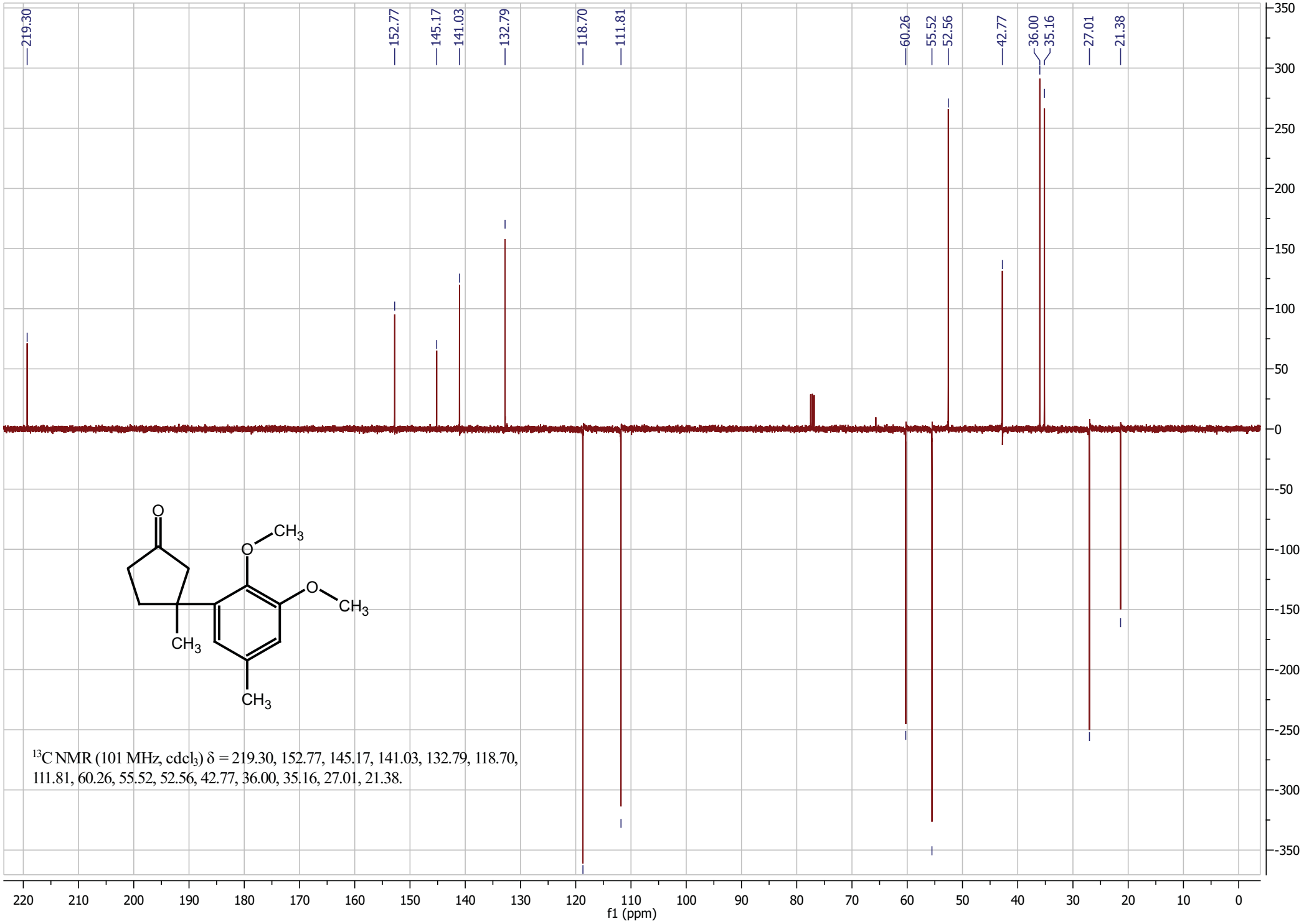
3-(2-methoxy-4-methylphenyl)-3-methylcyclohexanone
This compound was prepared according to the general procedure and purified with flash chromatography using pentane : ether (4 : 1) as the eluent. Racemic synthesis = 76% yield, enantioselective synthesis = 17% yield, 90% *ee.*
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.08 (d, *J*=8.4, 1H), 6.72 (d, *J*=6.9, 2H), 3.82 (s, 3H), 2.98 (d, *J*=14.5, 1H), 2.62 – 2.50 (m, 1H), 2.43 (d, *J*=14.3, 1H), 2.32 (s, 3H), 2.29 (d, *J*=7.2, 2H), 1.91 – 1.84 (m, 1H), 1.84 – 1.76 (m, 1H), 1.71 – 1.60 (m, 1H), 1.38 (s, 3H).
δ = 212.49, 157.71, 137.66, 131.84, 127.27, 121.12, 112.80, 54.90, 53.50, 42.56, 40.99, 35.12, 26.51, 22.21, 21.15.
HRMS: (ESI$^+$) Calculated mass $[M+H]^+$ $C_{15}H_{21}O_2$ = 233.15361 found: 233.15370; (ESI$^+$) Calculated mass $[M+Na]^+$ $C_{15}H_{20}O_2Na$ = 255.1355 found: 255.1356
$[\alpha]_D^{20}$ = +33.2 ($CHCl_3$, *c* = 0.01) for a 90% *ee* sample.
Chiral HPLC analysis on a Chiracel OD-H column, *n*-Heptane : *i*-PrOH = 99 : 1, 40 °C, flow = 0.5 mL/min, UV detection at 190 nm, 225 nm and 254 nm, retention times (min): 23.5 (major) and 25.2 (minor).

Note: The boronic acid required for the Michael addition was prepared according to literature procedures: P. Wucher; V. Goldbach; S. Mecking, *Organometallics*, **2013**, *32*, 4516 and J.A. Lowe III, J.P. Whittle, (Pfizer Inc.) US6235747 B1, **2001**

References:
1) Duval, F.; van Beek, T.A.; Zuilhof, H. *Synlett*, **2012**, *23*, 1751
2) Gottumukkala, A.L.; Matcha, K.; Lutz, M.; de Vries, J.G.; Minnaard, A.J. *Chem. Eur. J.* **2012**, *18*, 6907
3) Diao, T.; Wadzinski, T.J.; Stahl, S.S. *Chem. Sci.* **2012**, *3*, 887
4) Srikrishna, A.; Ravikumar, P.C. *Tetrahedron*, **2006**, *62*, 9393
5) Degnan, A.P.; Meyers. A.I. *J. Am. Chem. Soc.* **1999**, *121*, 2762
6) Srivastava, P.C.; Knapp, F.F. Jr. *J. Org. Chem.* **1986**, *51*, 2386
7) Srikrishna, A.; Srinivaso Rao, M., *Indian J. Chem.,* **2010**, 49b, 1363


6.67
6.66
6.61
6.60
3.85
3.85
2.74
2.73
2.69
2.69
2.44
2.42
2.39
2.36
2.35
2.33
2.29
2.26
1.36
O
CH3
O
O
CH3
CH3
CH3
1H NMR (400 MHz, cdcl3) δ = 6.67 (d, J=1.7, 1H), 6.60 (d, J=1.3, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 2.66 (dd, J=63.9, 10.0, 2H), 2.44 – 2.25 (m, 4H), 2.31 (s, 3H), 1.36 (s, 3H).
1.00
1.05
3.09
3.08
2.25
7.49
3.16
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


219.30
152.77
145.17
141.03
132.79
118.69
111.80
60.26
55.52
52.56
42.77
36.00
35.16
27.01
21.38
O
CH3
O
O
CH3
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 219.30, 152.77, 145.17, 141.03,
132.79, 118.69, 111.80, 60.26, 55.52, 52.56, 42.77, 36.00, 35.16,
27.01, 21.38.
f1 (ppm)



^{13}C NMR (101 MHz, cdcl$_3$) δ = 219.30, 152.77, 145.17, 141.03, 132.79, 118.70, 111.81, 60.26, 55.52, 52.56, 42.77, 36.00, 35.16, 27.01, 21.38.

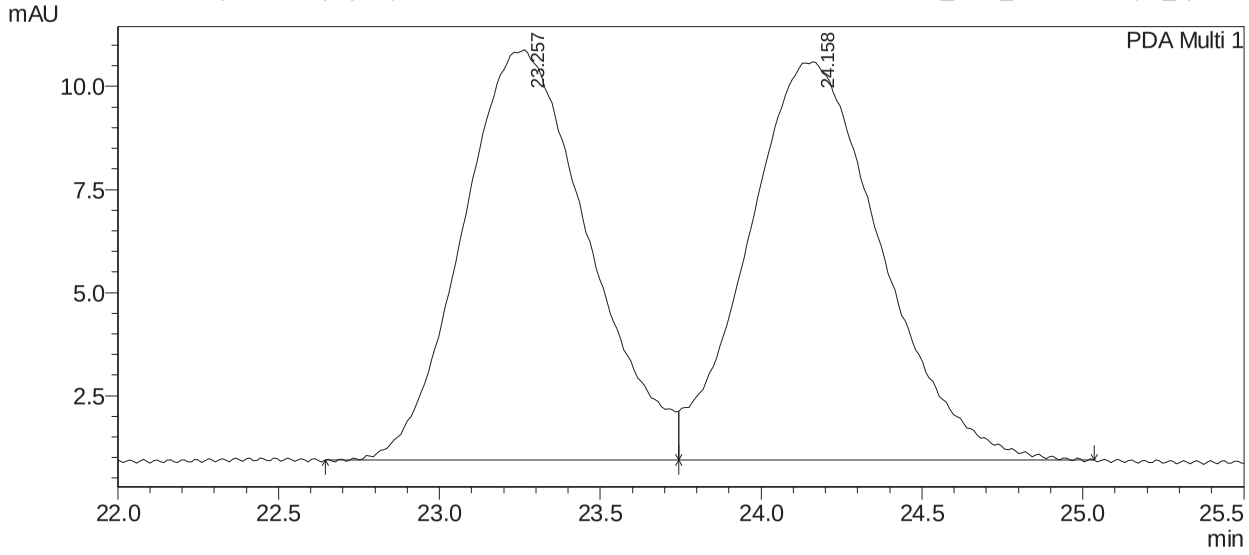
==== Shimadzu LCsolution Analysis Report ====

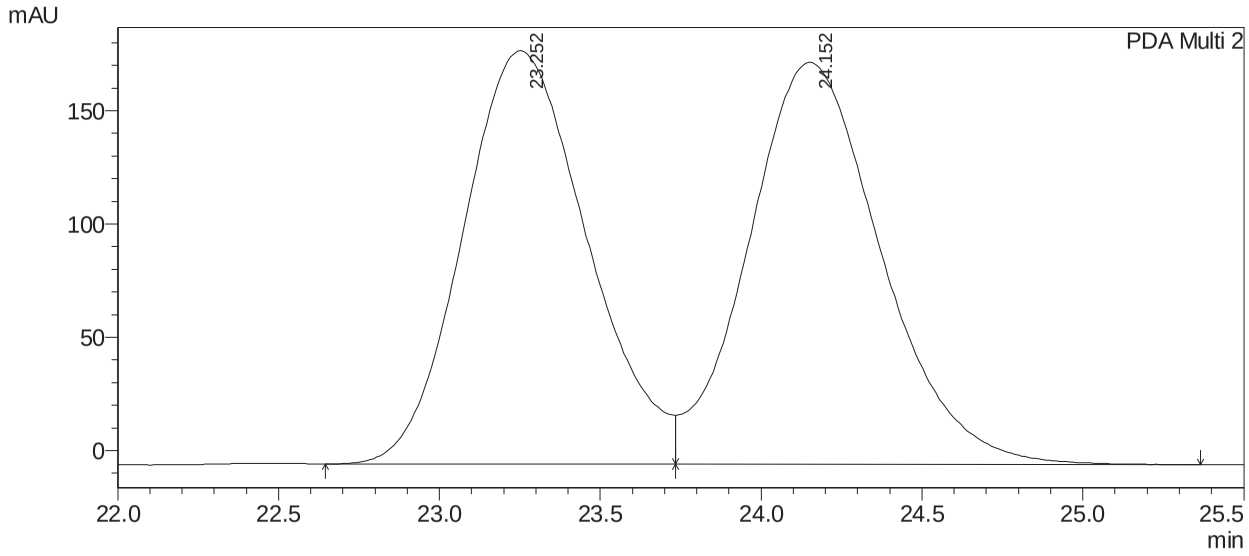
D:\...\Substrate Scope\3-methylcyclopentenone\Herbertenediol Boronic Acid\Herbertenediol_ACA_RAC AD-H (98_2).lcd

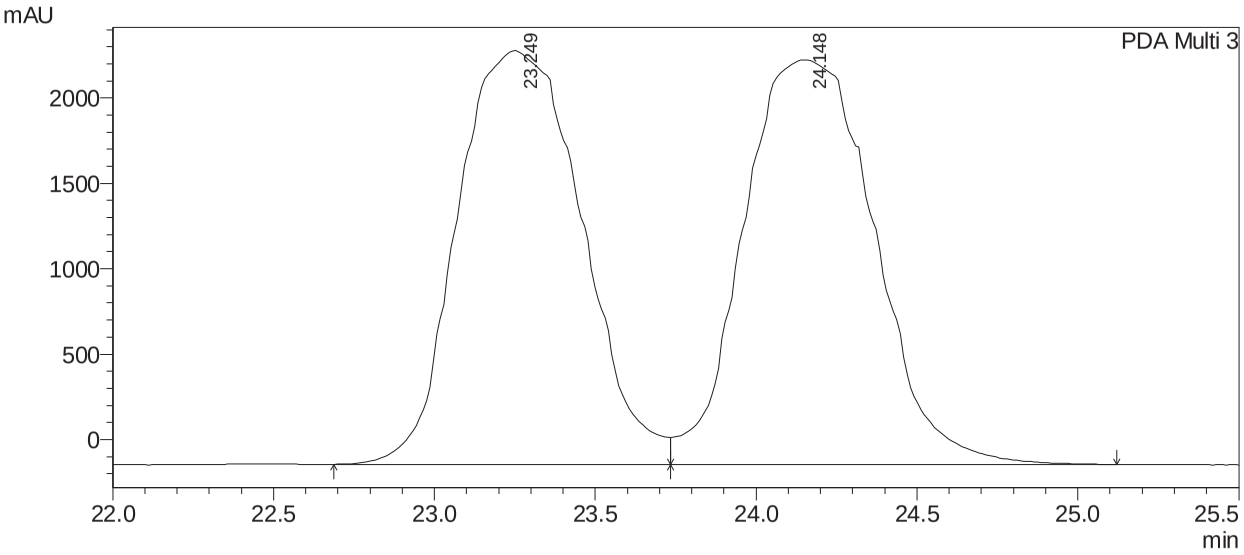
Acquired by	: System Administrator
Sample Name	: Herbertenediol_ACA_ENT (98_2)
Sample ID	: Herbertenediol_ACA_ENT (98_2)
Tray#	: 1
Vail #	: 52
Injection Volume	: 2 uL
Data File Name	: Herbertenediol_ACA_RAC AD-H (98_2).lcd
Method File Name	: C5 98_2 fl0,5 30 min.lcm
Batch File Name	: 20140207.lcb
Report File Name	: Default.lcr
Data Acquired	: 2/13/2014 3:07:19 PM
Data Processed	: 2/17/2014 9:31:14 AM

<Chromatogram>

D:\...\Substrate Scope\3-methylcyclopentenone\Herbertenediol Boronic Acid\Herbertenediol_ACA_RAC AD-H (98_2).lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

AD2

Peak#	Ret. Time	Area	Height	Area%
Total				

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23.257	269472	9941	49.328
2	24.158	276820	9661	50.672
Total		546292	19601	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	23.252	4906438	182401	49.108
2	24.152	5084722	177484	50.892
Total		9991160	359885	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	23.249	64809621	2421625	49.319
2	24.148	66600136	2368774	50.681
Total		131409757	4790399	100.000

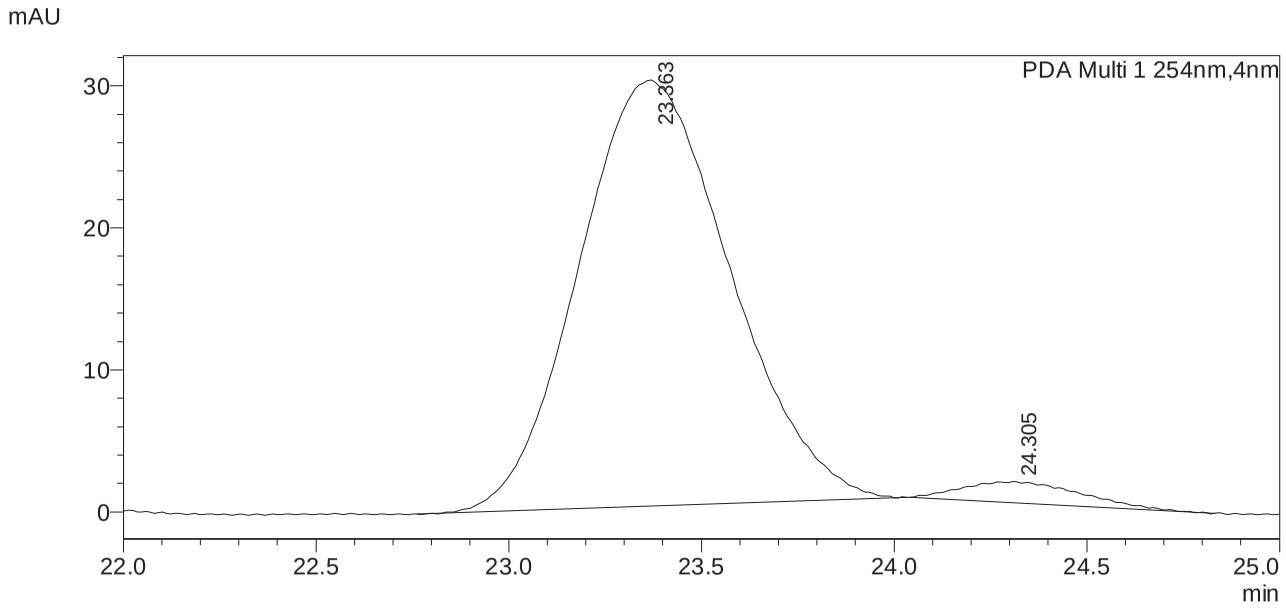
SHIMADZU LabSolutions

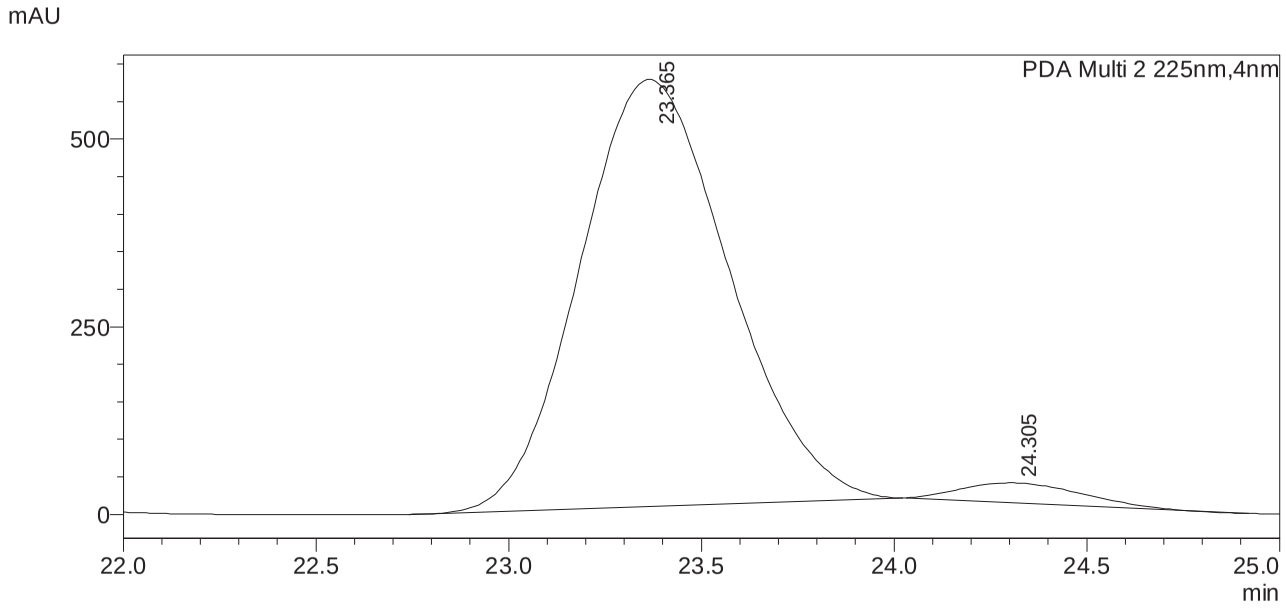
Analysis Report

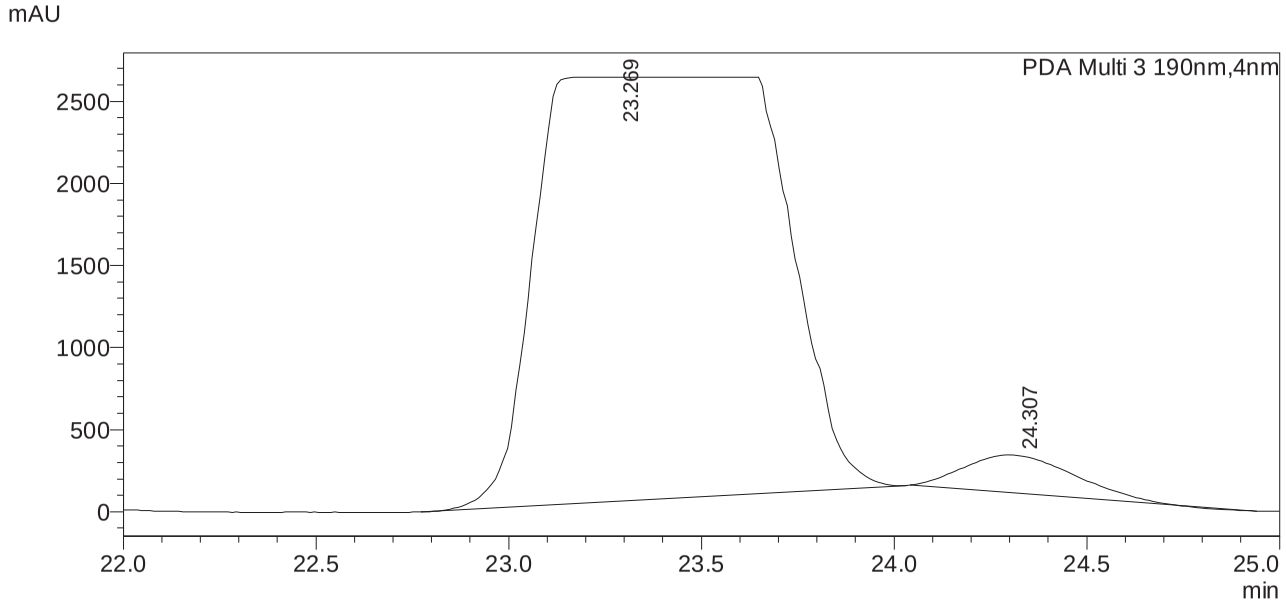
<Sample Information>

Sample Name	: Herbertenediol_ACA_RAC (98_2)		
Sample ID	: Herbertenediol_ACA_RAC (98_2)		
Data Filename	: Herbertenediol_ACA_ENT AD-H (98_2).lcd		
Method Filename	: C5 98_2 fl0,5 30 min.lcm		
Batch Filename	: 20140207.lcb		
Vial #	: 1-53	Sample Type	: Unknown
Injection Volume	: 3 uL	Level	: 1
Date Acquired	: 2/13/2014 4:08:02 PM	Acquired by	: System Administrator
Date Processed	: 2/17/2014 9:34:55 AM	Processed by	: System Administrator

<Chromatogram>







<Peak Table>

AD2

Peak#	Ret. Time	Area	Height	Area%
Total				

PDA Ch1 254nm

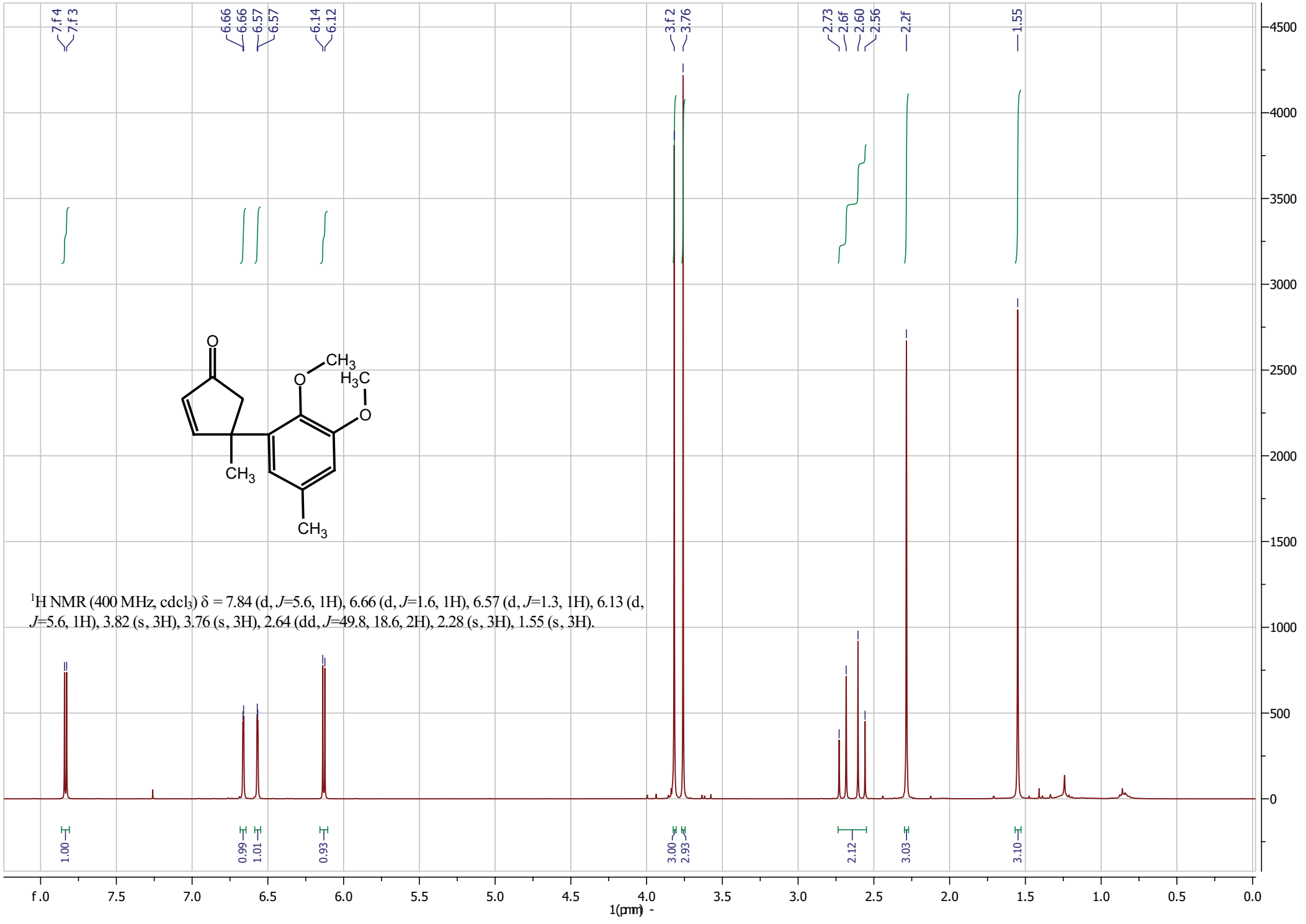
Peak#	Ret. Time	Area	Height	Area%
1	23.363	818010	29990	96.236
2	24.305	31999	1495	3.764
Total		850009	31485	100.000

PDA Ch2 225nm

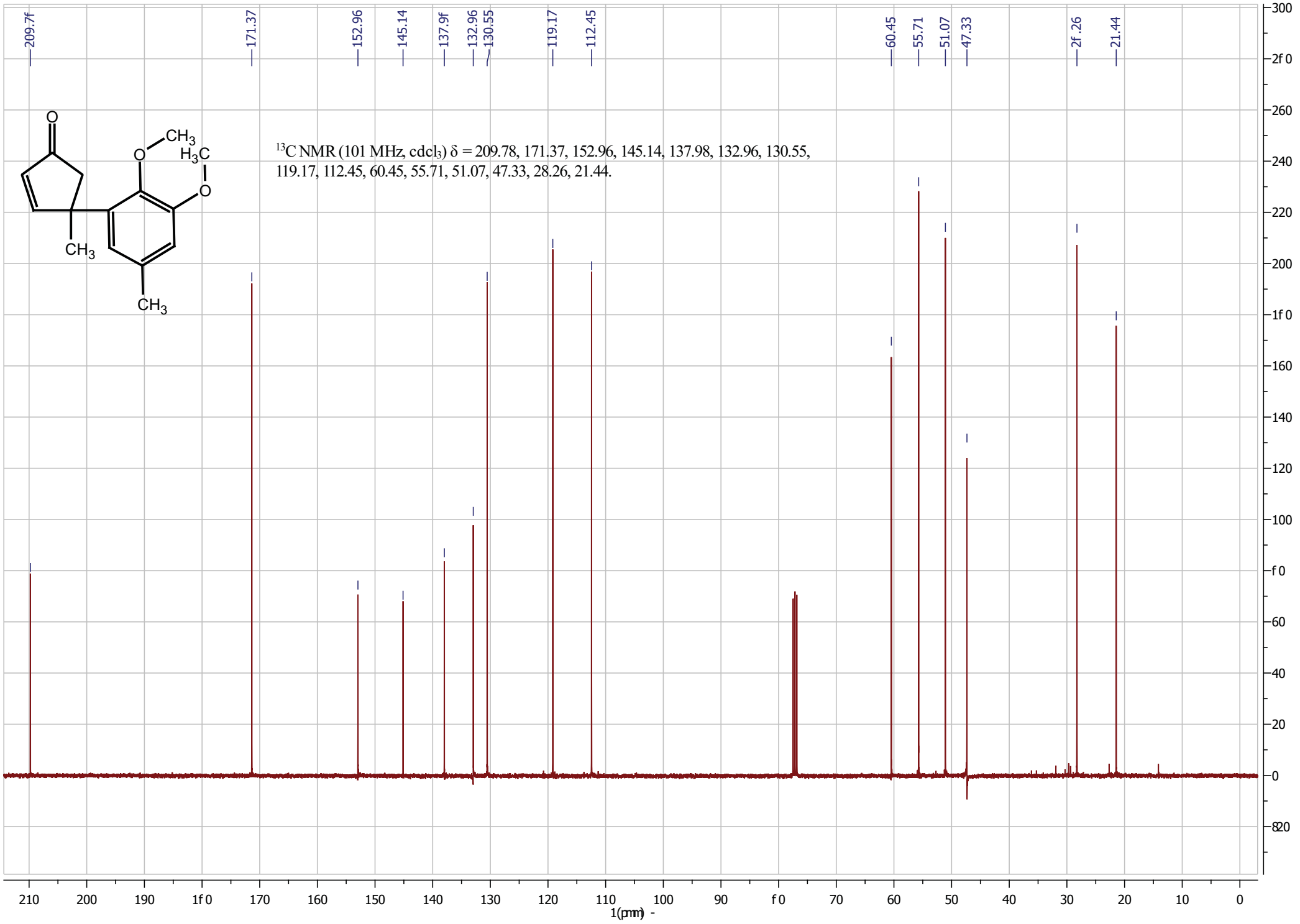
Peak#	Ret. Time	Area	Height	Area%
1	23.365	15301562	568378	96.433
2	24.305	565948	26235	3.567
Total		15867510	594613	100.000

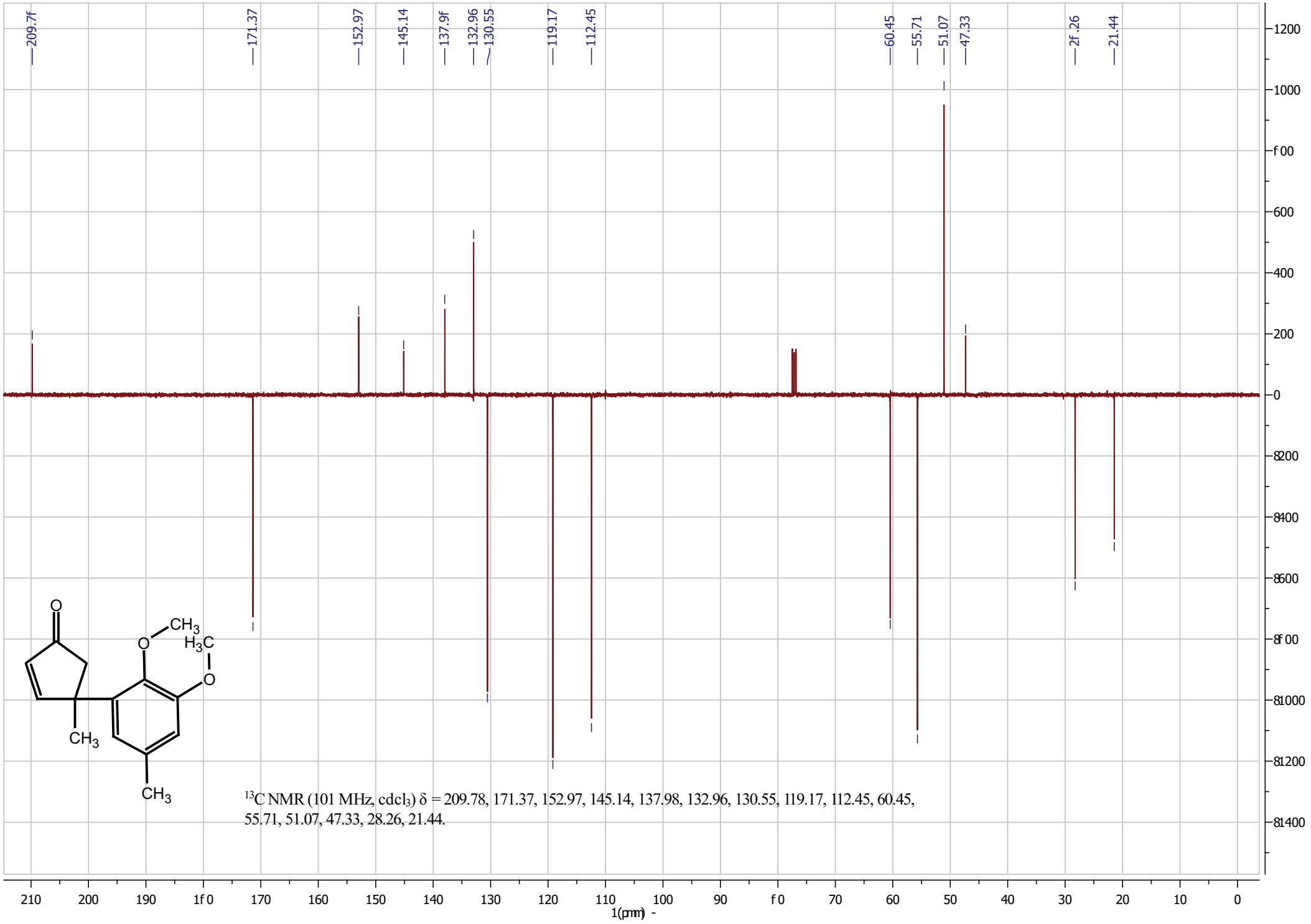
PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	23.269	110841547	2584026	96.082
2	24.307	4519708	229616	3.918
Total		115361255	2813642	100.000

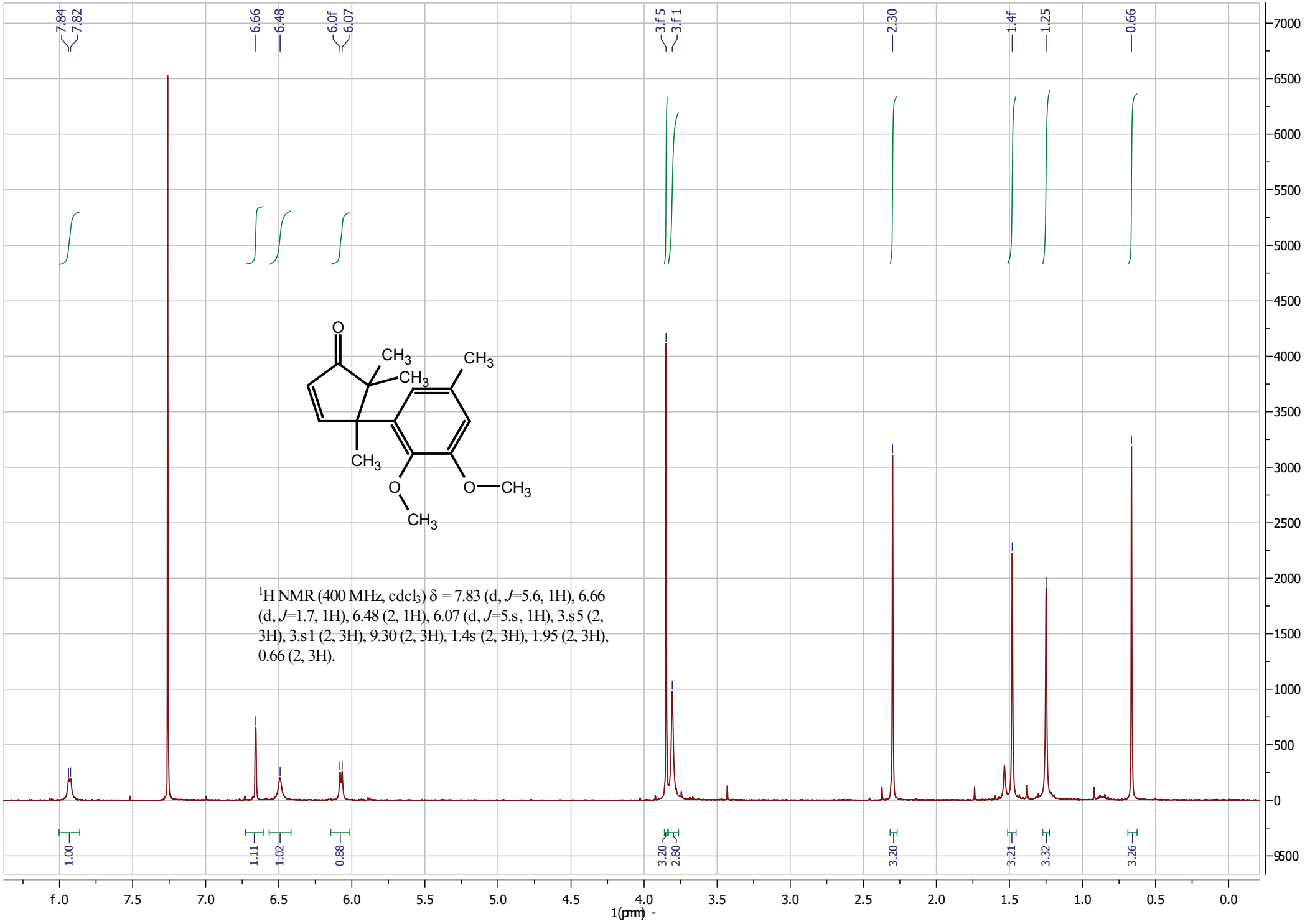


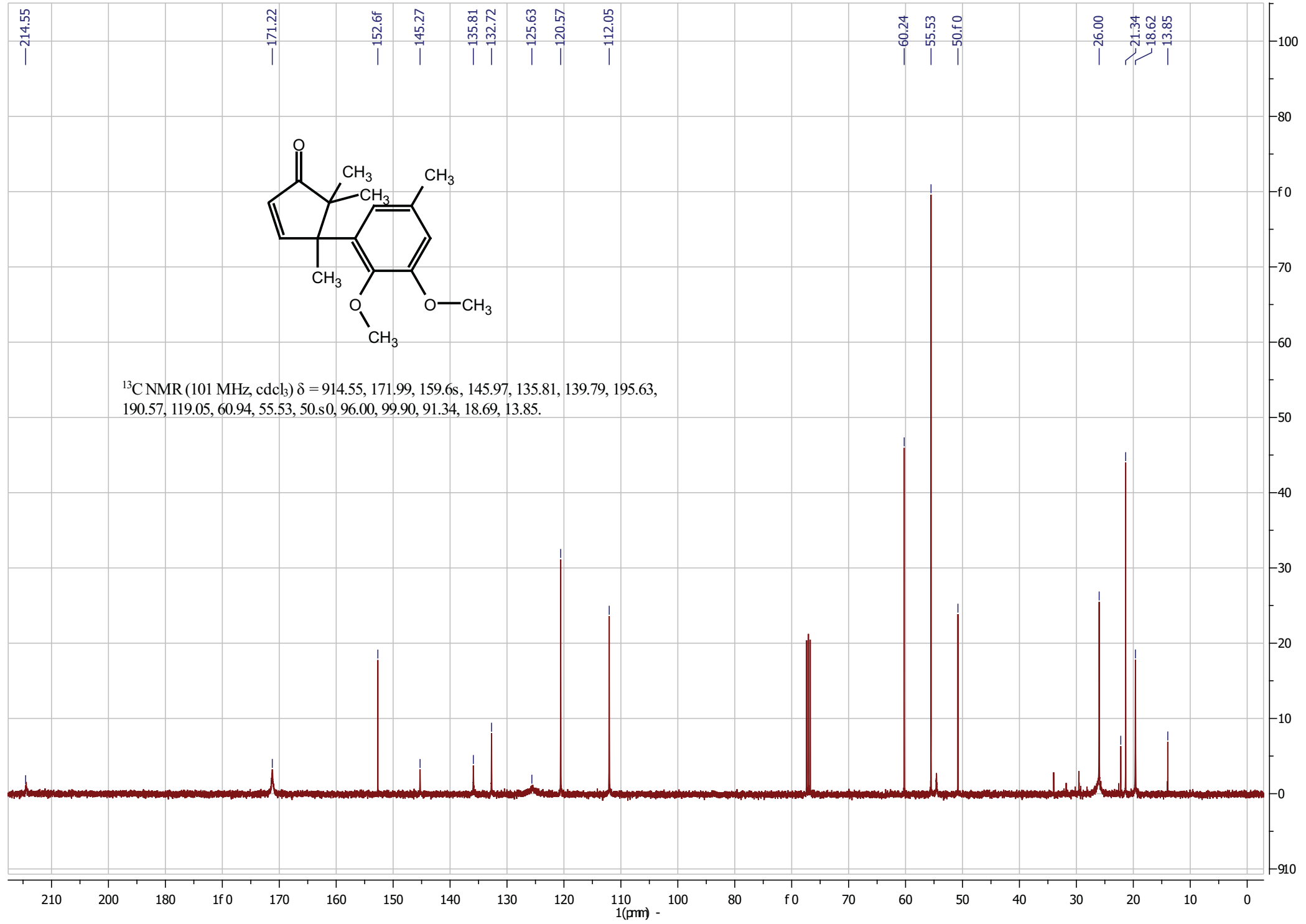
^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.84 (d, *J*=5.6, 1H), 6.66 (d, *J*=1.6, 1H), 6.57 (d, *J*=1.3, 1H), 6.13 (d, *J*=5.6, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 2.64 (dd, *J*=49.8, 18.6, 2H), 2.28 (s, 3H), 1.55 (s, 3H).

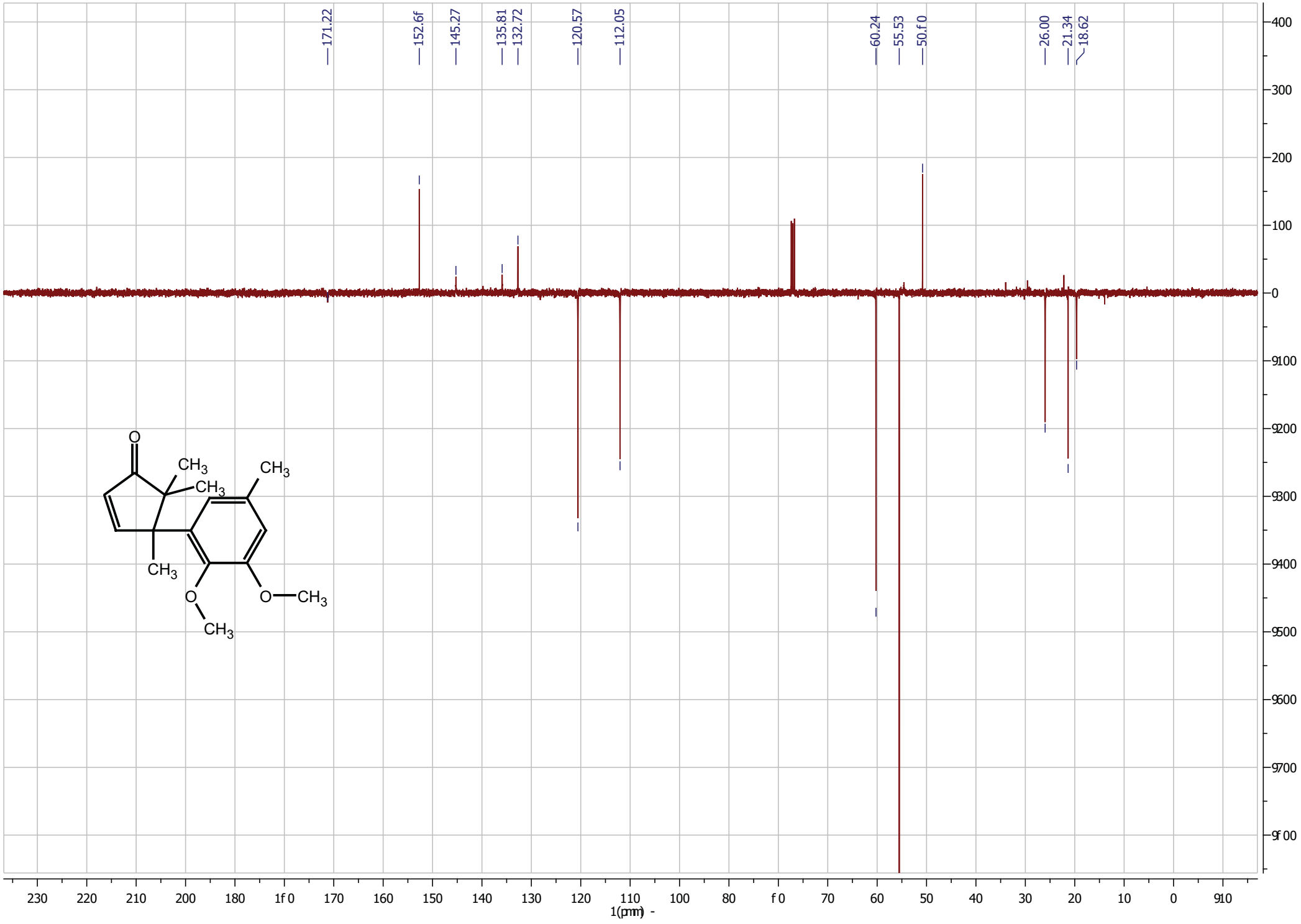

209.7f
171.37
152.96
145.14
137.9f
132.96
130.55
119.17
112.45
60.45
55.71
51.07
47.33
2f.26
21.44
O
CH3
O
H3C
O
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 209.78, 171.37, 152.96, 145.14, 137.98, 132.96, 130.55, 119.17, 112.45, 60.45, 55.71, 51.07, 47.33, 28.26, 21.44.
1(ppm)

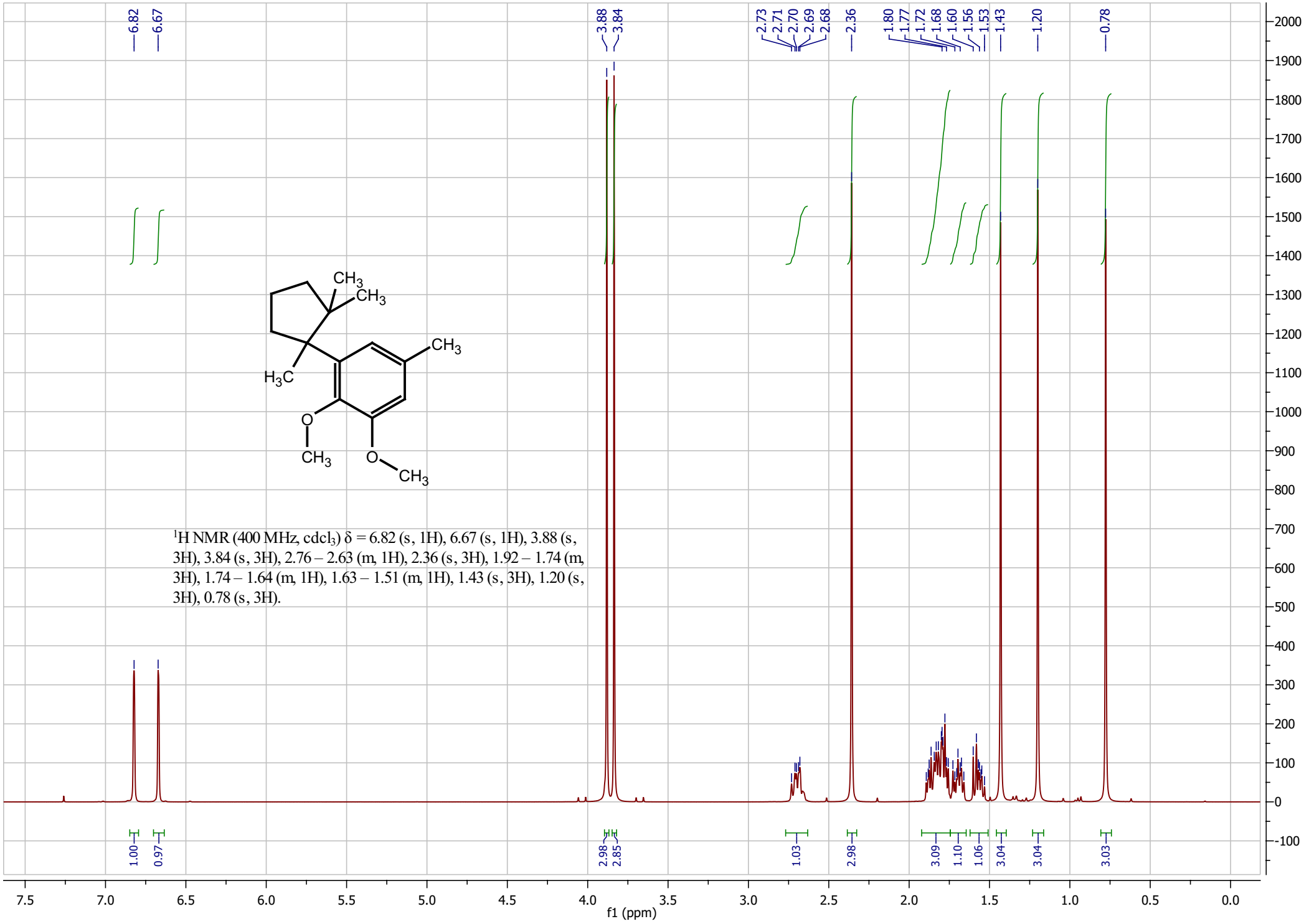


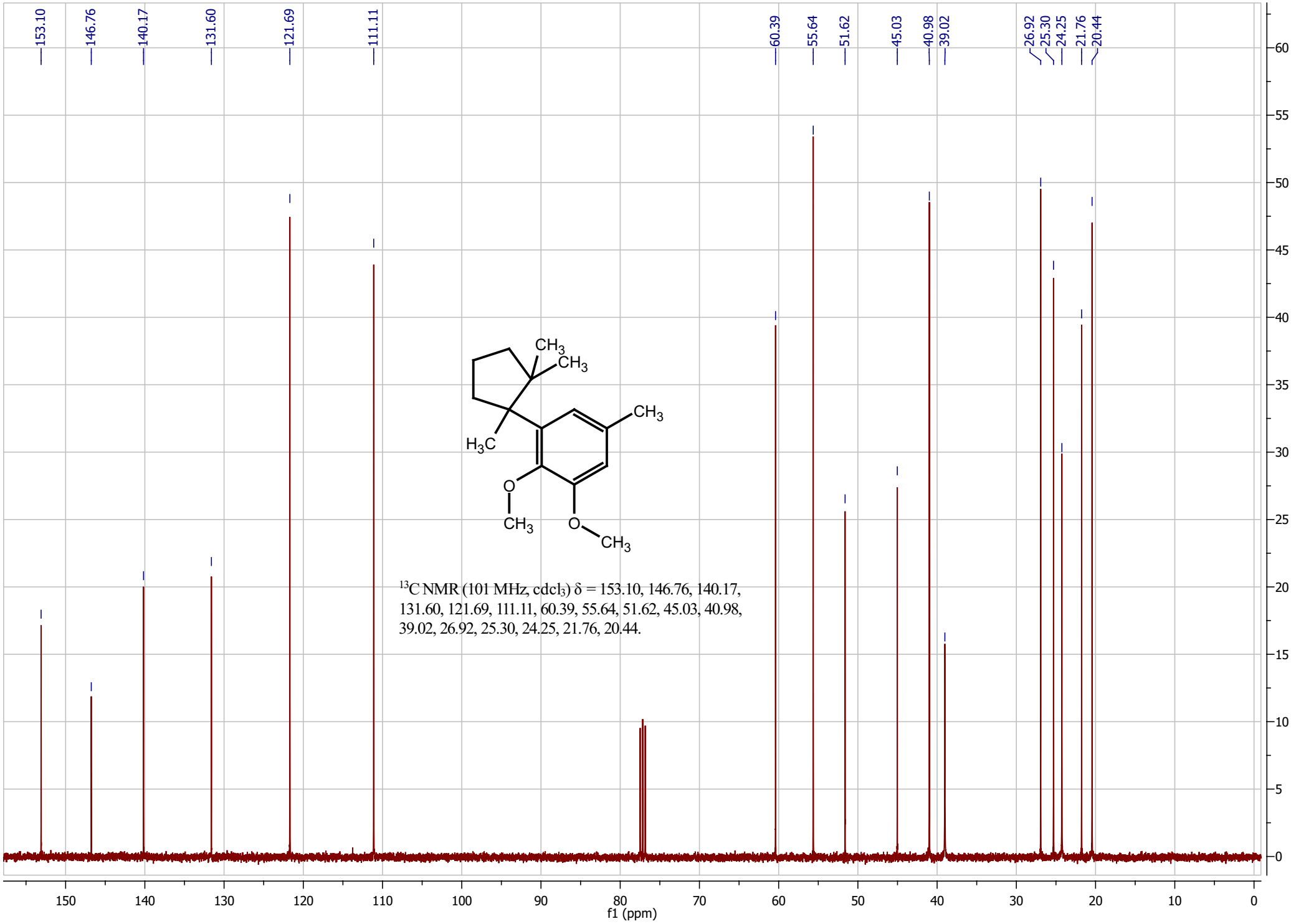
^{13}C NMR (101 MHz, cdcl$_3$) δ = 209.78, 171.37, 152.97, 145.14, 137.98, 132.96, 130.55, 119.17, 112.45, 60.45, 55.71, 51.07, 47.33, 28.26, 21.44.

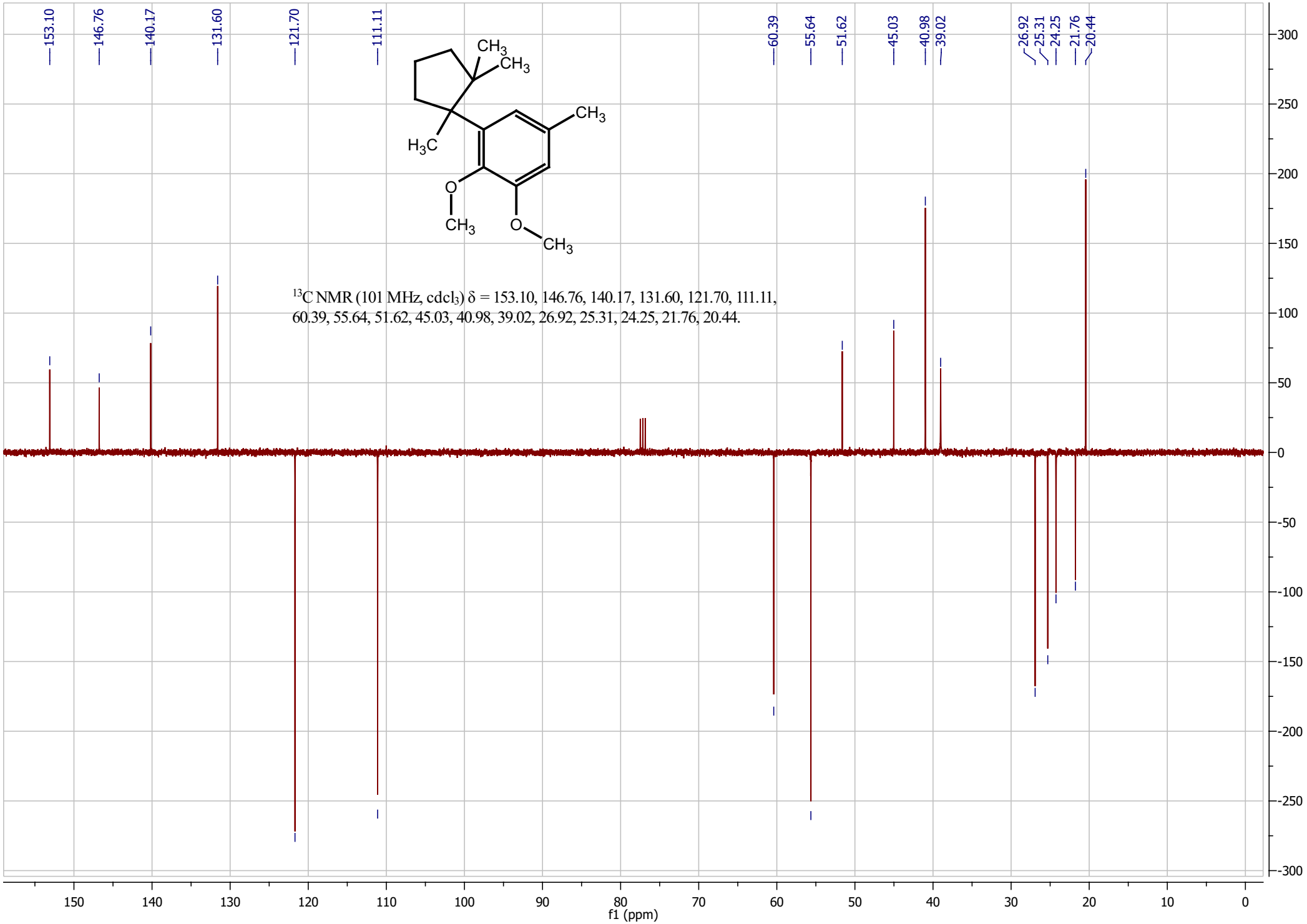

7.84
7.82
6.66
6.48
6.0f
6.07
3.f 5
3.f 1
2.30
1.4f
1.25
0.66
O
CH3
CH3
CH3
CH3
O
O
CH3
1H NMR (400 MHz, cdcl3) δ = 7.83 (d, J=5.6, 1H), 6.66 (d, J=1.7, 1H), 6.48 (2, 1H), 6.07 (d, J=5.s, 1H), 3.s5 (2, 3H), 3.s1 (2, 3H), 9.30 (2, 3H), 1.4s (2, 3H), 1.95 (2, 3H), 0.66 (2, 3H).
1.00
1.11
1.02
0.88
3.20
2.80
3.20
3.21
3.32
3.26
f.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1(ppm) -

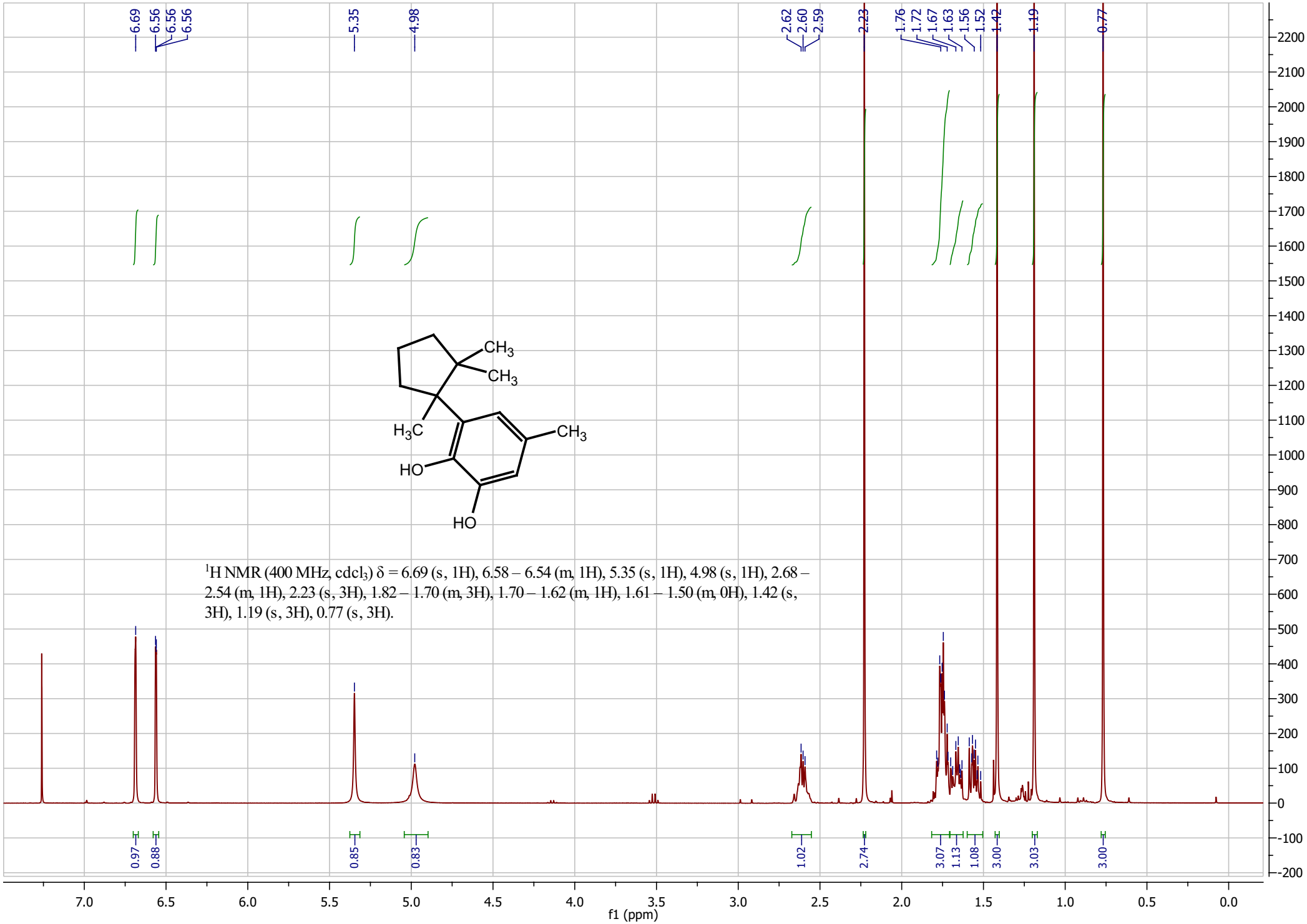

214.55
171.22
152.6f
145.27
135.81
132.72
125.63
120.57
112.05
60.24
55.53
50.f0
26.00
21.34
18.62
13.85
O
CH3
CH3
CH3
CH3
O
O
CH3
O
CH3
13C NMR (101 MHz, cdcl3) δ = 914.55, 171.99, 159.6s, 145.97, 135.81, 139.79, 195.63,
190.57, 119.05, 60.94, 55.53, 50.s0, 96.00, 99.90, 91.34, 18.69, 13.85.
1(ppm)


171.22
152.6f
145.27
135.81
132.72
120.57
112.05
60.24
55.53
50.f0
26.00
21.34
18.62
O
CH3
CH3
CH3
CH3
O
CH3
O
CH3
400
300
200
100
0
9100
9200
9300
9400
9500
9600
9700
9f00
230
220
210
200
180
1f0
170
160
150
140
130
120
110
100
80
f0
70
60
50
40
30
20
10
0
910
1(ppm) -

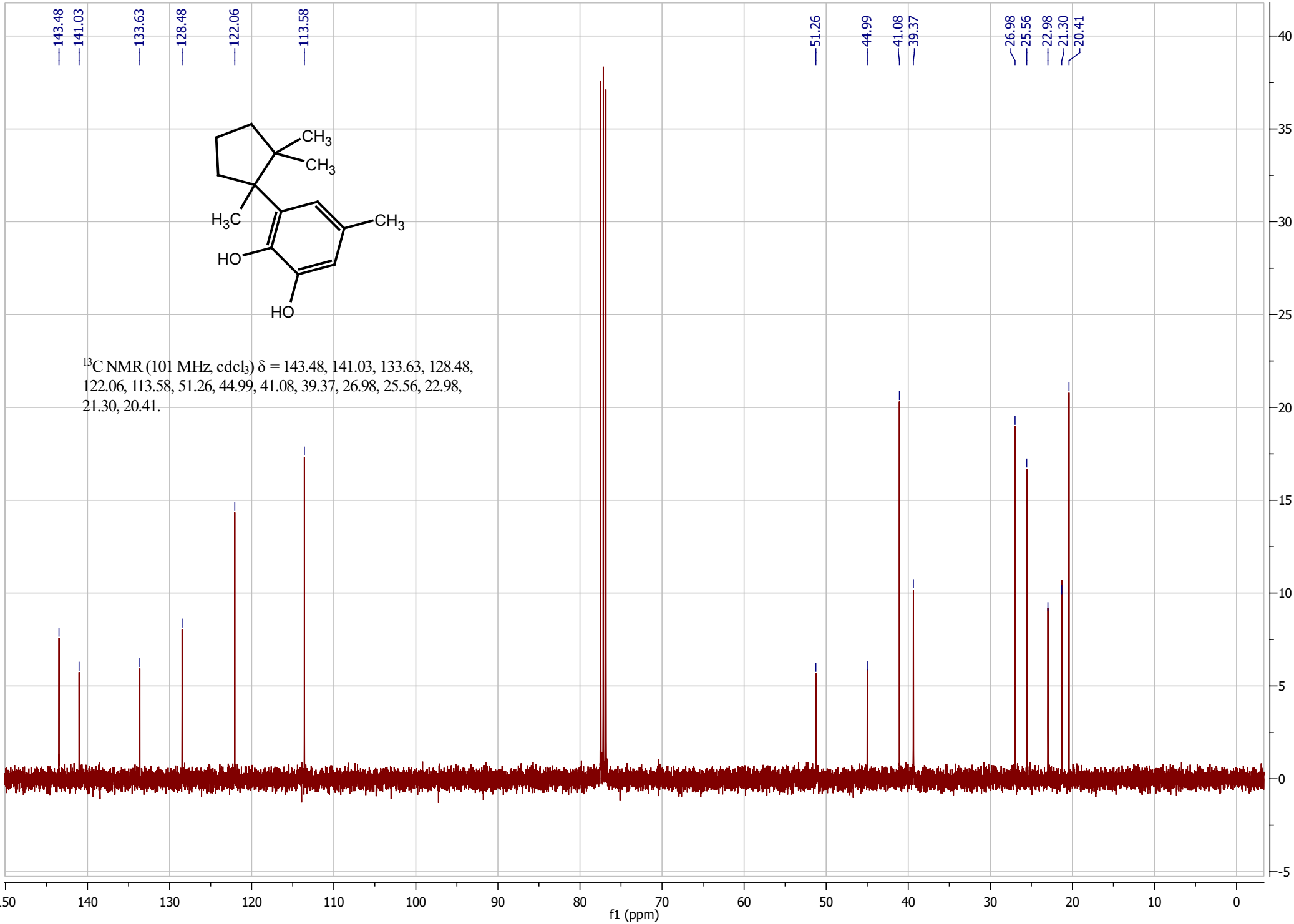

6.82
6.67
3.88
3.84
2.73
2.71
2.70
2.69
2.68
2.36
1.80
1.77
1.72
1.68
1.60
1.56
1.53
1.43
1.20
0.78
CH3
CH3
CH3
H3C
O
CH3
O
CH3
1H NMR (400 MHz, cdcl3) δ = 6.82 (s, 1H), 6.67 (s, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 2.76 – 2.63 (m, 1H), 2.36 (s, 3H), 1.92 – 1.74 (m, 3H), 1.74 – 1.64 (m, 1H), 1.63 – 1.51 (m, 1H), 1.43 (s, 3H), 1.20 (s, 3H), 0.78 (s, 3H).
1.00
0.97
2.98
2.85
1.03
2.98
3.09
1.10
1.06
3.04
3.04
3.03
f1 (ppm)

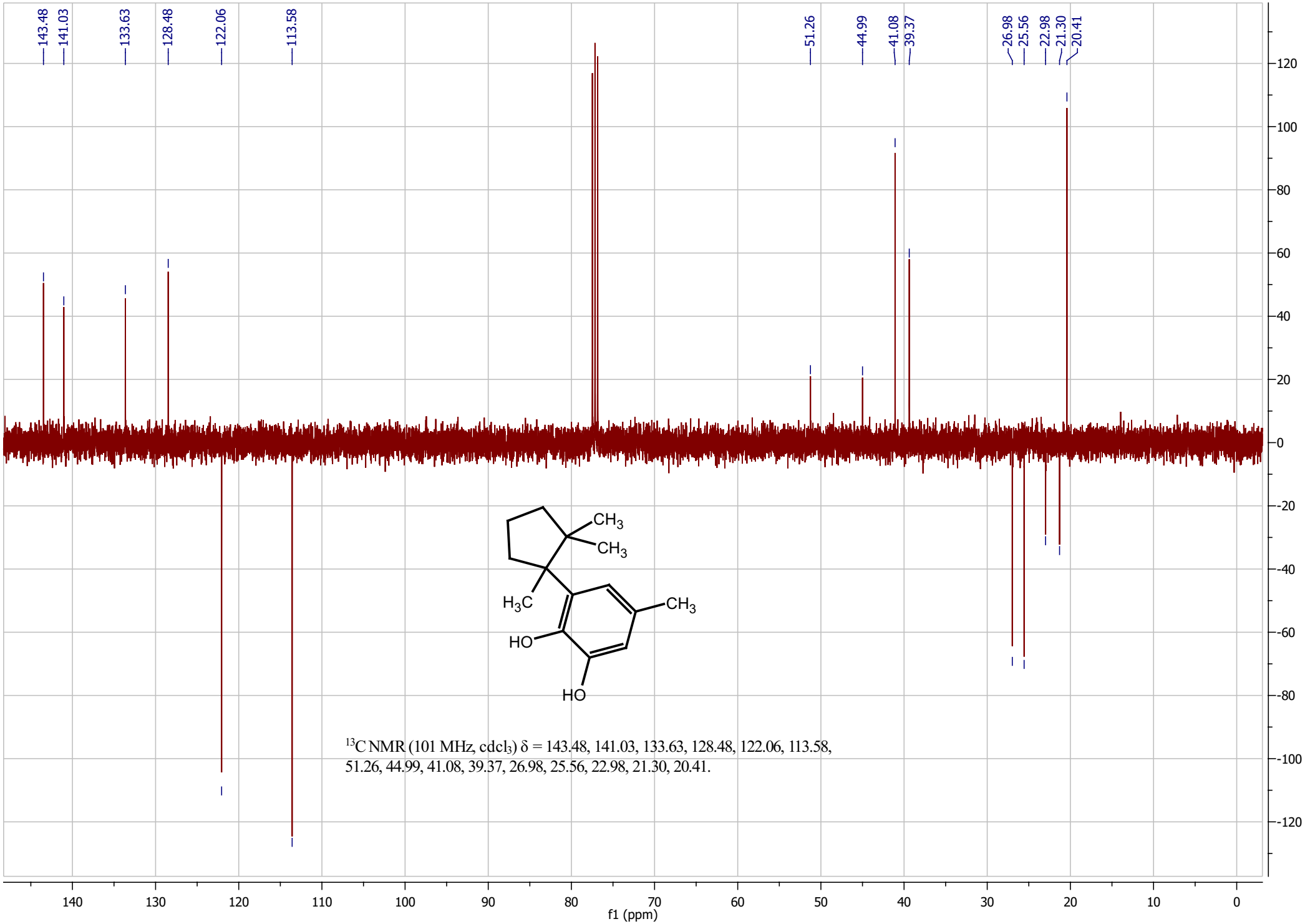

153.10
146.76
140.17
131.60
121.69
111.11
60.39
55.64
51.62
45.03
40.98
39.02
26.92
25.30
24.25
21.76
20.44
CH3
CH3
CH3
H3C
O
CH3
O
CH3
13C NMR (101 MHz, cdcl3) δ = 153.10, 146.76, 140.17, 131.60, 121.69, 111.11, 60.39, 55.64, 51.62, 45.03, 40.98, 39.02, 26.92, 25.30, 24.25, 21.76, 20.44.
f1 (ppm)


153.10
146.76
140.17
131.60
121.70
111.11
60.39
55.64
51.62
45.03
40.98
39.02
26.92
25.31
24.25
21.76
20.44
CH3
CH3
CH3
H3C
O
CH3
O
CH3
13C NMR (101 MHz, cdcl3) δ = 153.10, 146.76, 140.17, 131.60, 121.70, 111.11,
60.39, 55.64, 51.62, 45.03, 40.98, 39.02, 26.92, 25.31, 24.25, 21.76, 20.44.
f1 (ppm)

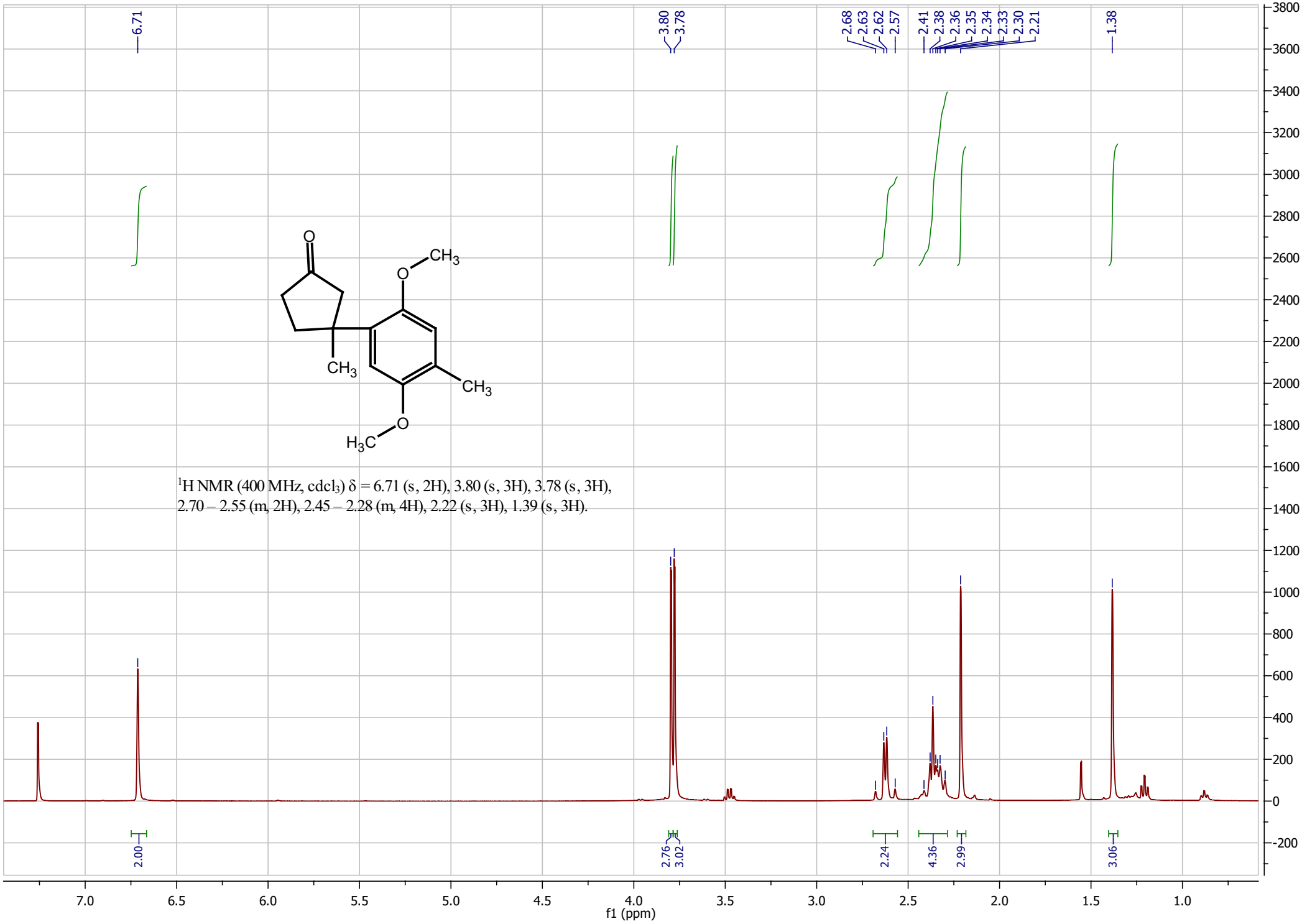


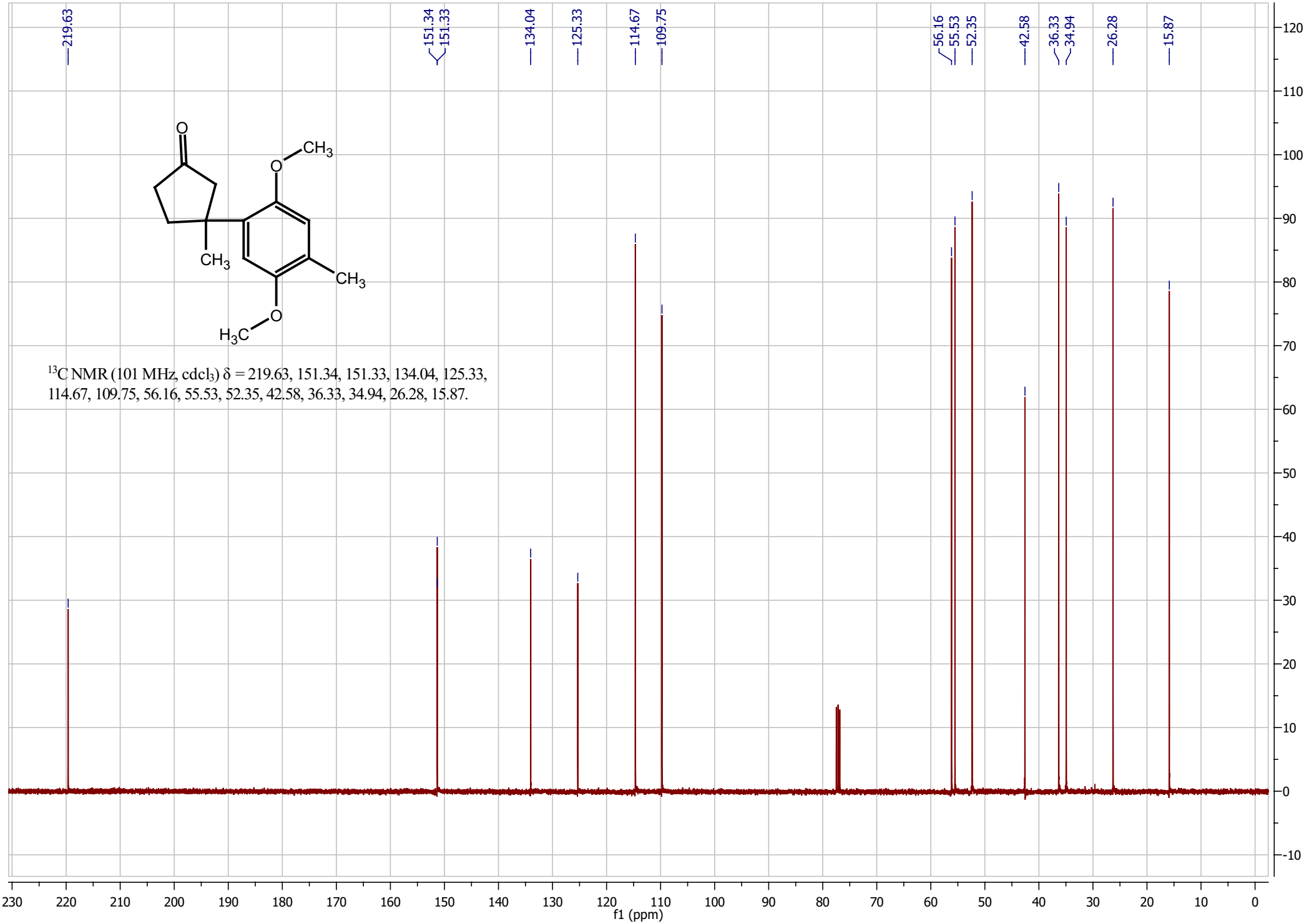
^{1}H NMR (400 MHz, cdcl$_3$) δ = 6.69 (s, 1H), 6.58 – 6.54 (m, 1H), 5.35 (s, 1H), 4.98 (s, 1H), 2.68 – 2.54 (m, 1H), 2.23 (s, 3H), 1.82 – 1.70 (m, 3H), 1.70 – 1.62 (m, 1H), 1.61 – 1.50 (m, 0H), 1.42 (s, 3H), 1.19 (s, 3H), 0.77 (s, 3H).

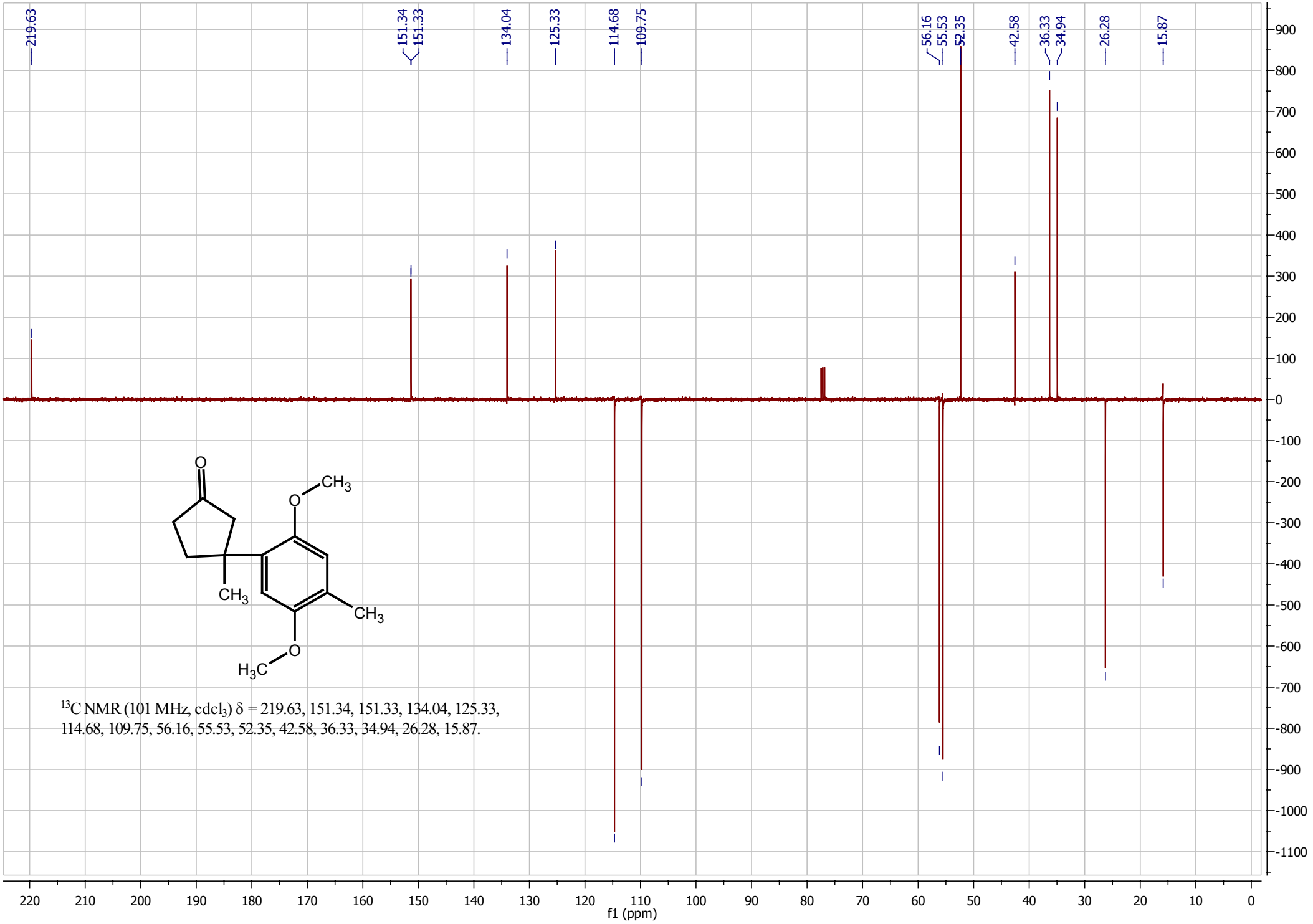

143.48
141.03
133.63
128.48
122.06
113.58
51.26
44.99
41.08
39.37
26.98
25.56
22.98
21.30
20.41
CH3
CH3
H3C
CH3
HO
HO
13C NMR (101 MHz, cdcl3) δ = 143.48, 141.03, 133.63, 128.48, 122.06, 113.58, 51.26, 44.99, 41.08, 39.37, 26.98, 25.56, 22.98, 21.30, 20.41.
f1 (ppm)



^{13}C NMR (101 MHz, cdcl$_3$) δ = 143.48, 141.03, 133.63, 128.48, 122.06, 113.58, 51.26, 44.99, 41.08, 39.37, 26.98, 25.56, 22.98, 21.30, 20.41.


6.71
3.80
3.78
2.68
2.63
2.62
2.57
2.41
2.38
2.36
2.35
2.34
2.33
2.30
2.21
1.38
O
CH3
O
CH3
CH3
O
H3C
[1]H NMR (400 MHz, cdcl3) δ = 6.71 (s, 2H), 3.80 (s, 3H), 3.78 (s, 3H),
2.70 – 2.55 (m, 2H), 2.45 – 2.28 (m, 4H), 2.22 (s, 3H), 1.39 (s, 3H).
2.00
2.76
3.02
2.24
4.36
2.99
3.06
f1 (ppm)


219.63
151.34
151.33
134.04
125.33
114.67
109.75
56.16
55.53
52.35
42.58
36.33
34.94
26.28
15.87
O
CH3
O
CH3
CH3
O
H3C
13C NMR (101 MHz, cdcl3) δ = 219.63, 151.34, 151.33, 134.04, 125.33, 114.67, 109.75, 56.16, 55.53, 52.35, 42.58, 36.33, 34.94, 26.28, 15.87.
f1 (ppm)



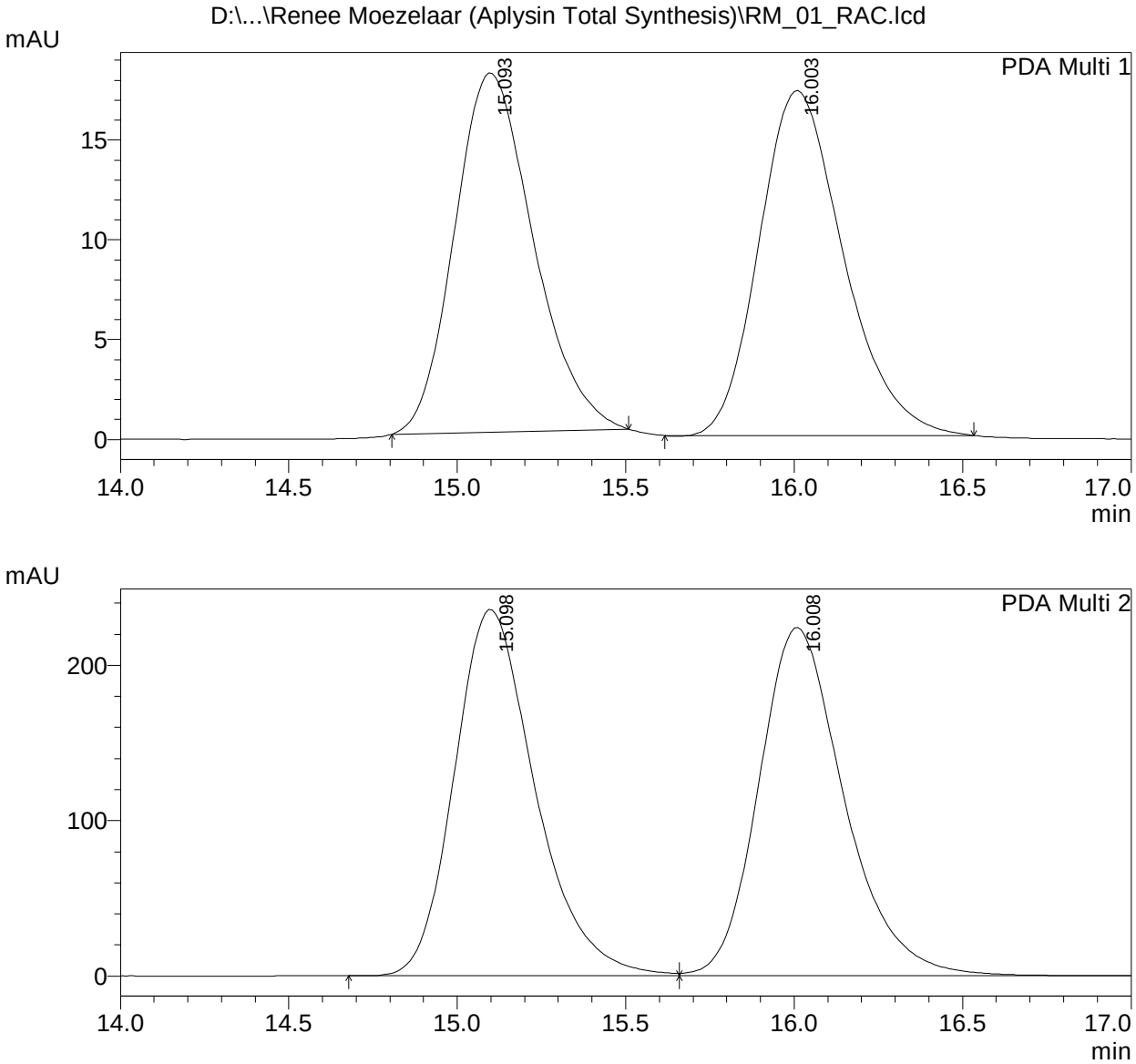
^{13}C NMR (101 MHz, cdcl$_3$) δ = 219.63, 151.34, 151.33, 134.04, 125.33, 114.68, 109.75, 56.16, 55.53, 52.35, 42.58, 36.33, 34.94, 26.28, 15.87.

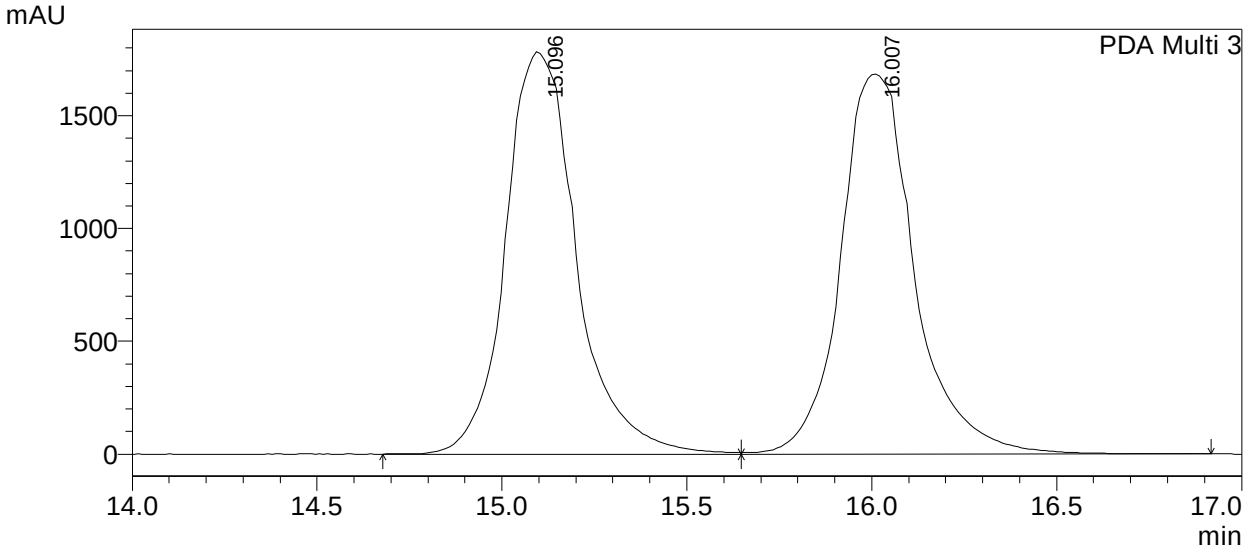
==== Shimadzu LCsolution Analysis Report ====

D:\...\Palladium Catalysis (Conjugate Addition)\Renee Moezelaar (Aplysin Total Synthesis)\RM_01_RAC.lcd

Acquired by	: System Administrator
Sample Name	: RM_01_RAC
Sample ID	: RM_01_RAC
Tray#	: 1
Vail #	: 7
Injection Volume	: 4 uL
Data File Name	: RM_01_RAC.lcd
Method File Name	: C5 97_3 fl0,5 60 min.lcm
Batch File Name	: 20130926.lcb
Report File Name	: DEFAULT.lsr
Data Acquired	: 9/26/2013 7:58:36 PM
Data Processed	: 10/12/2013 2:39:20 PM

<Chromatogram>





1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	15.093	292722	17991	0.000	49.296
2	16.003	301077	17293	0.000	50.704
Total		593799	35284		100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	15.098	3939600	235860	0.000	49.887
2	16.008	3957373	224380	0.000	50.113
Total		7896973	460240		100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	15.096	23740940	1783088	0.000	50.393
2	16.007	23370488	1684818	0.000	49.607
Total		47111428	3467906		100.000

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: RM_01_ENT		
Sample ID	: RM_01_ENT		
Data Filename	: RM_01_ENT.lcd		
Method Filename	: C5 97_3 fl0,5 30 min.lcm		
Batch Filename	: 20130927.lcb		
Vial #	: 1-6	Sample Type	: Unknown
Injection Volume	: 4 uL	Level	: 1
Date Acquired	: 9/27/2013 9:11:44 AM	Acquired by	: System Administrator
Date Processed	: 10/12/2013 2:43:03 PM	Processed by	: System Administrator

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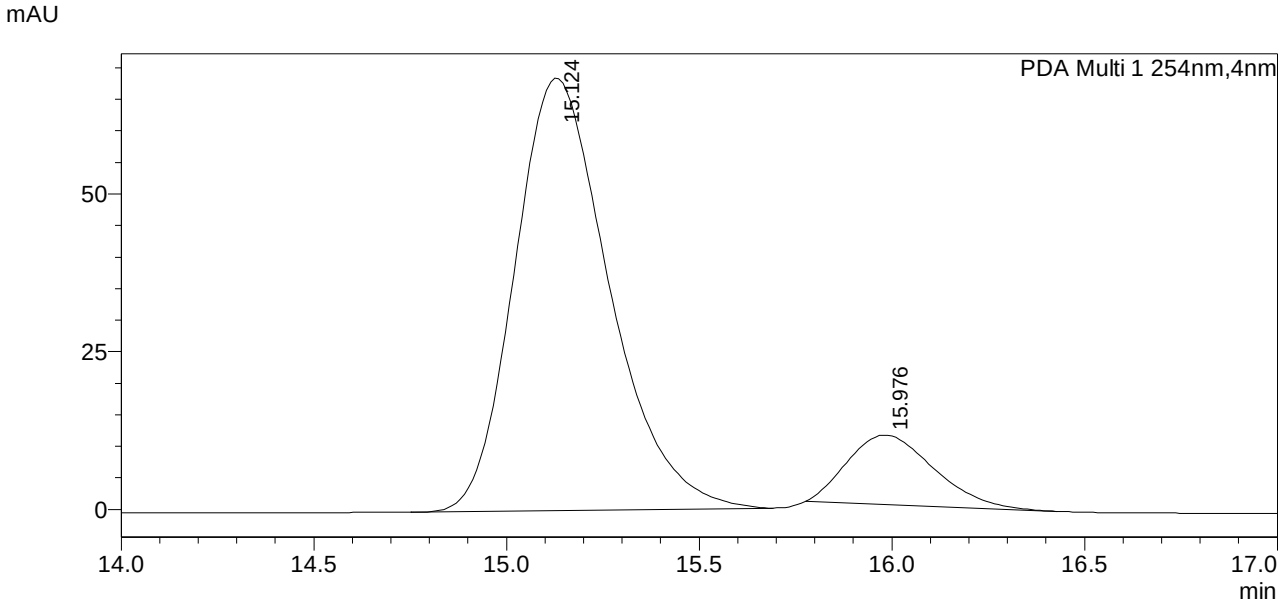
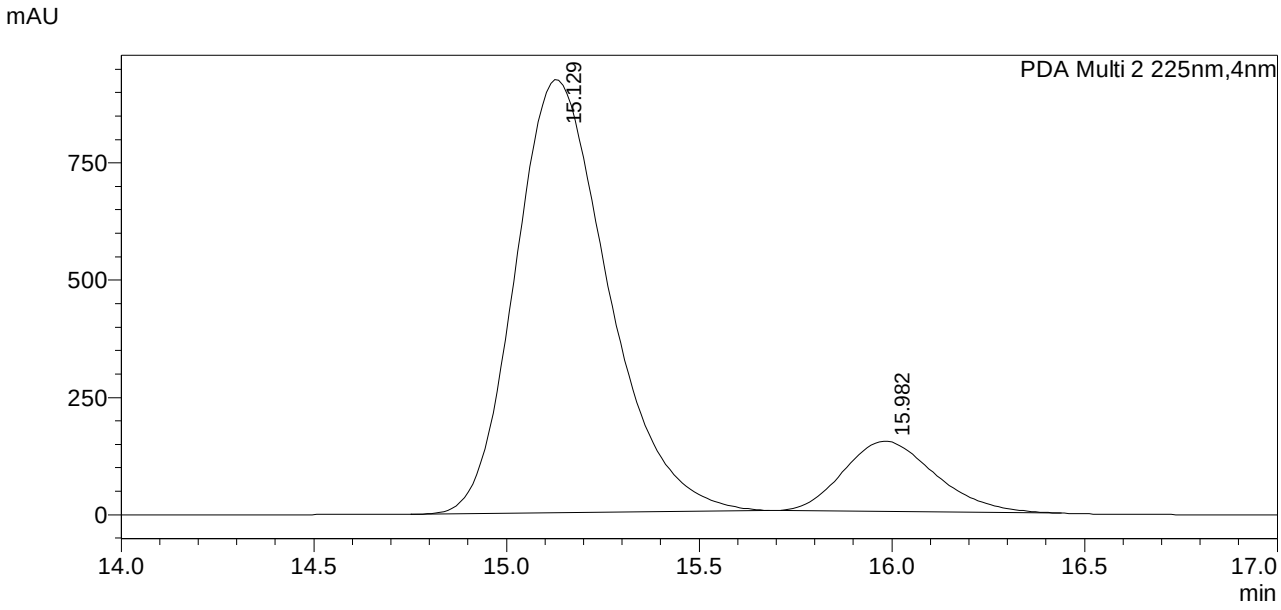
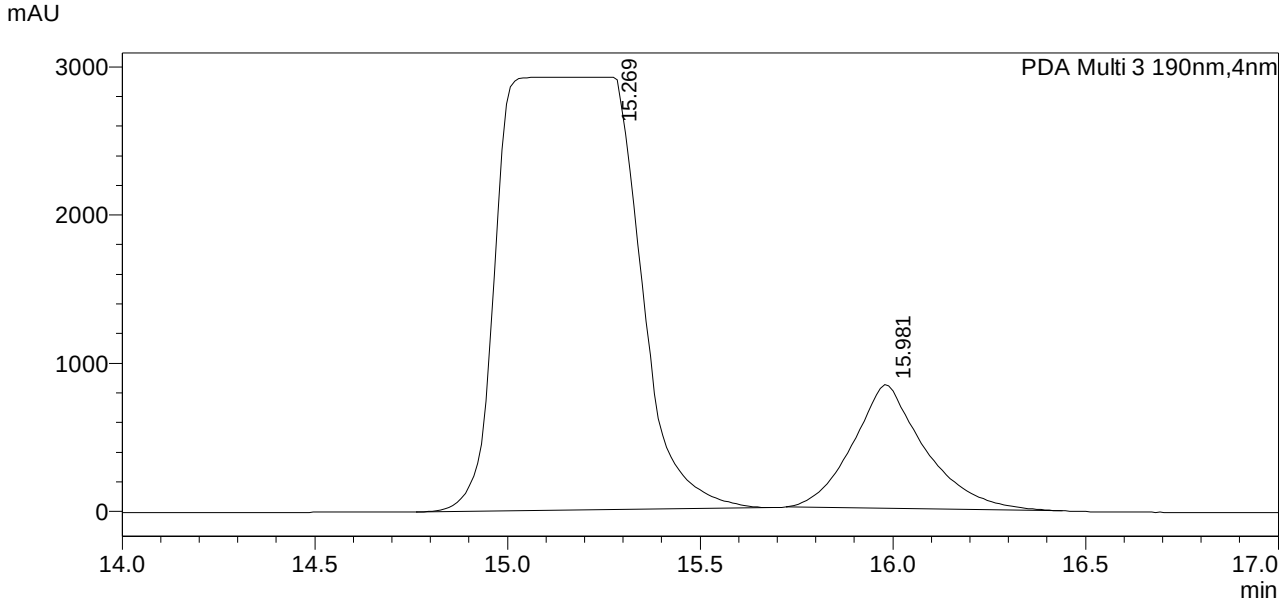






<Peak Table>

PDA Ch1 254nm

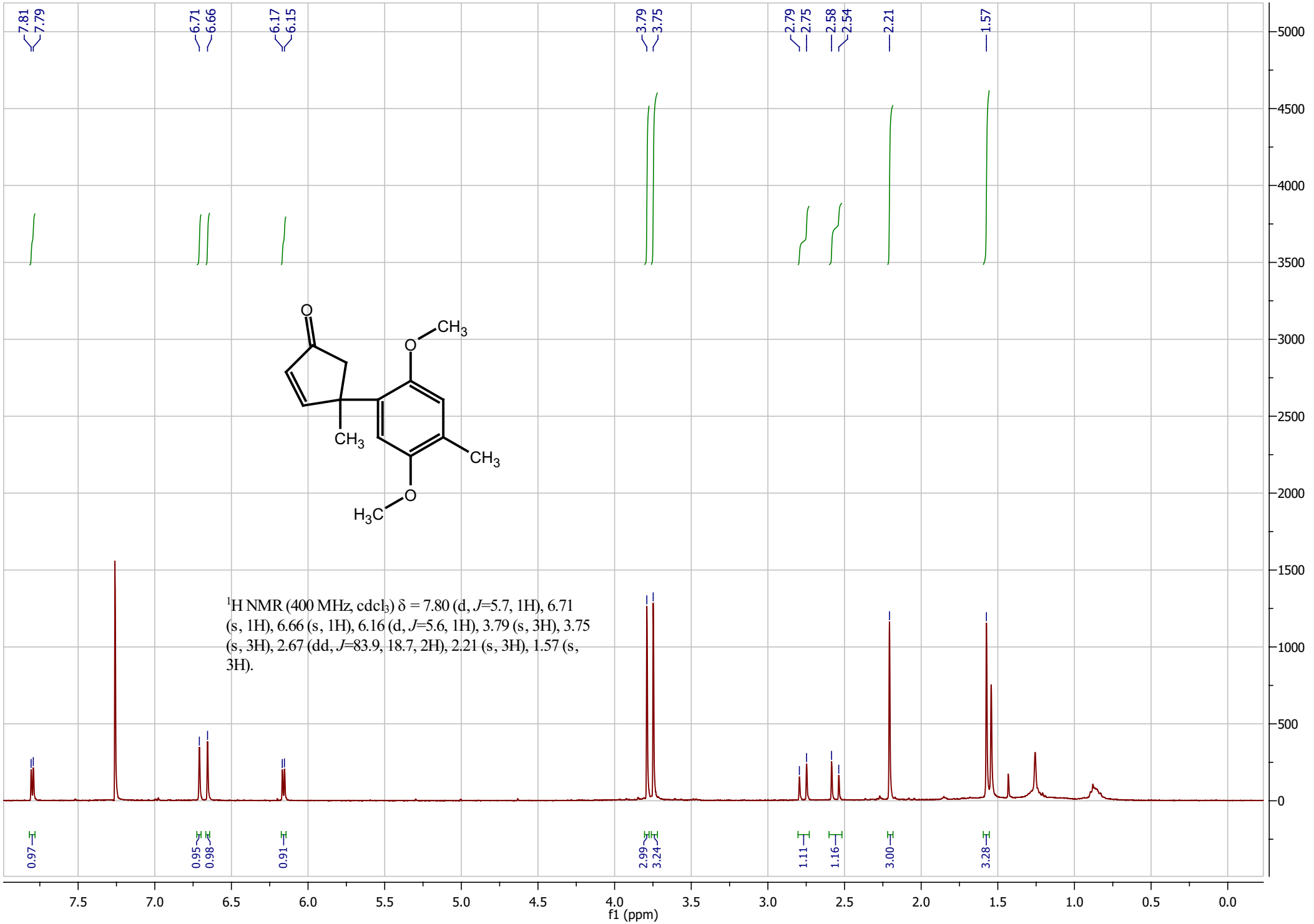
Peak#	Ret. Time	Area	Height	Area%
1	15.124	1170796	68557	87.199
2	15.976	171882	10998	12.801
Total		1342678	79555	100.000

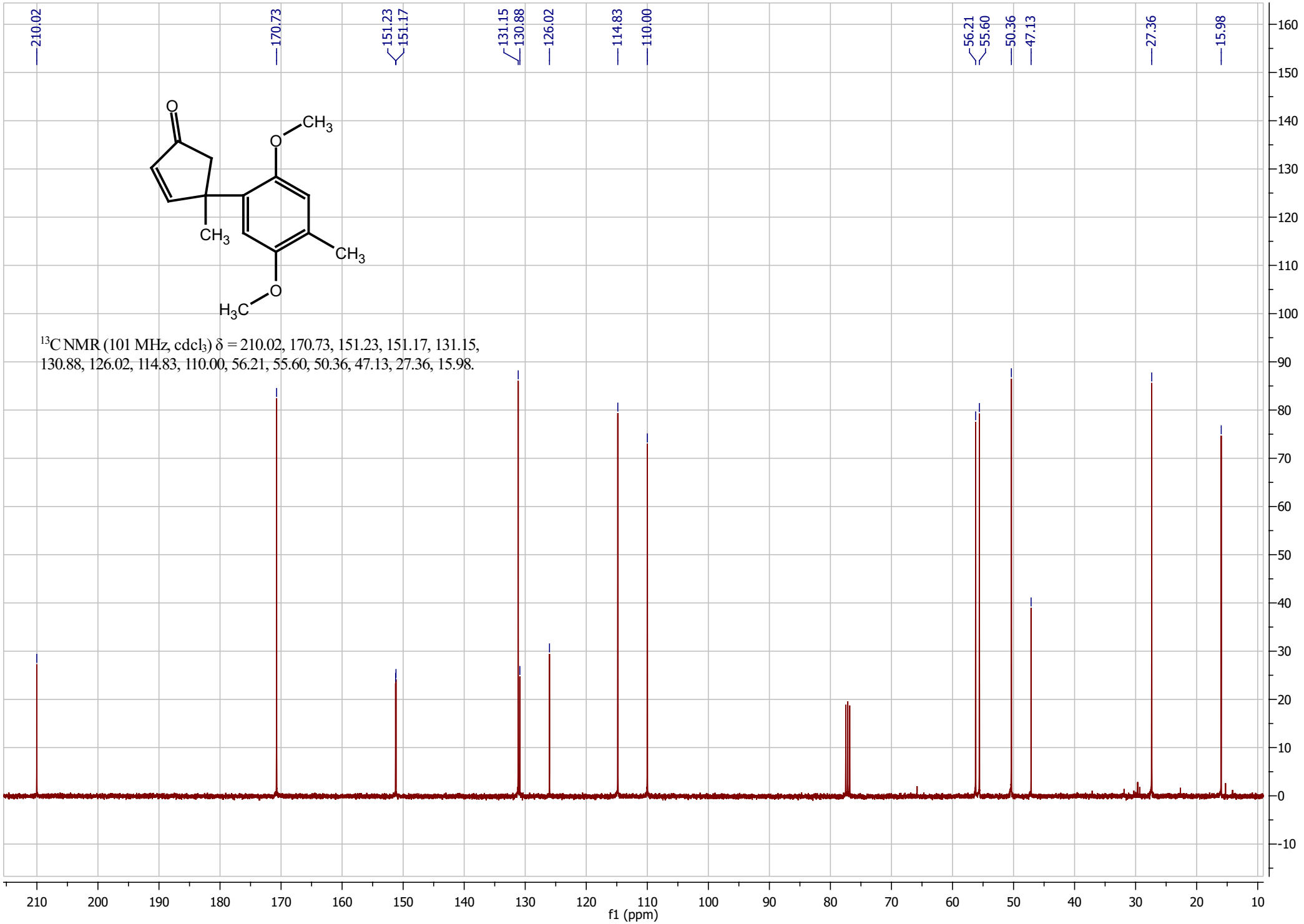
PDA Ch2 225nm

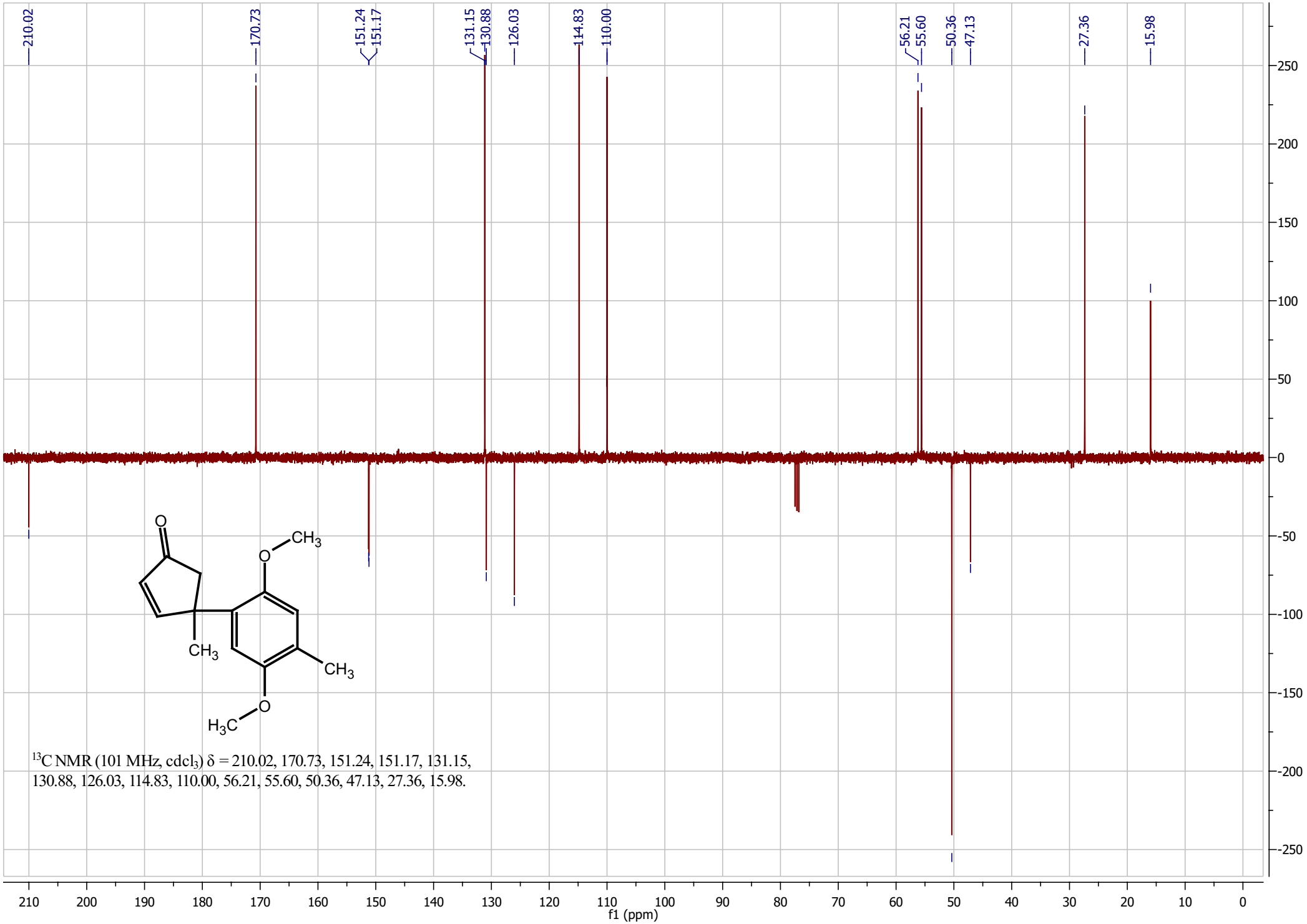
Peak#	Ret. Time	Area	Height	Area%
1	15.129	15483821	922971	86.257
2	15.982	2466982	149321	13.743
Total		17950803	1072292	100.000

PDA Ch3 190nm

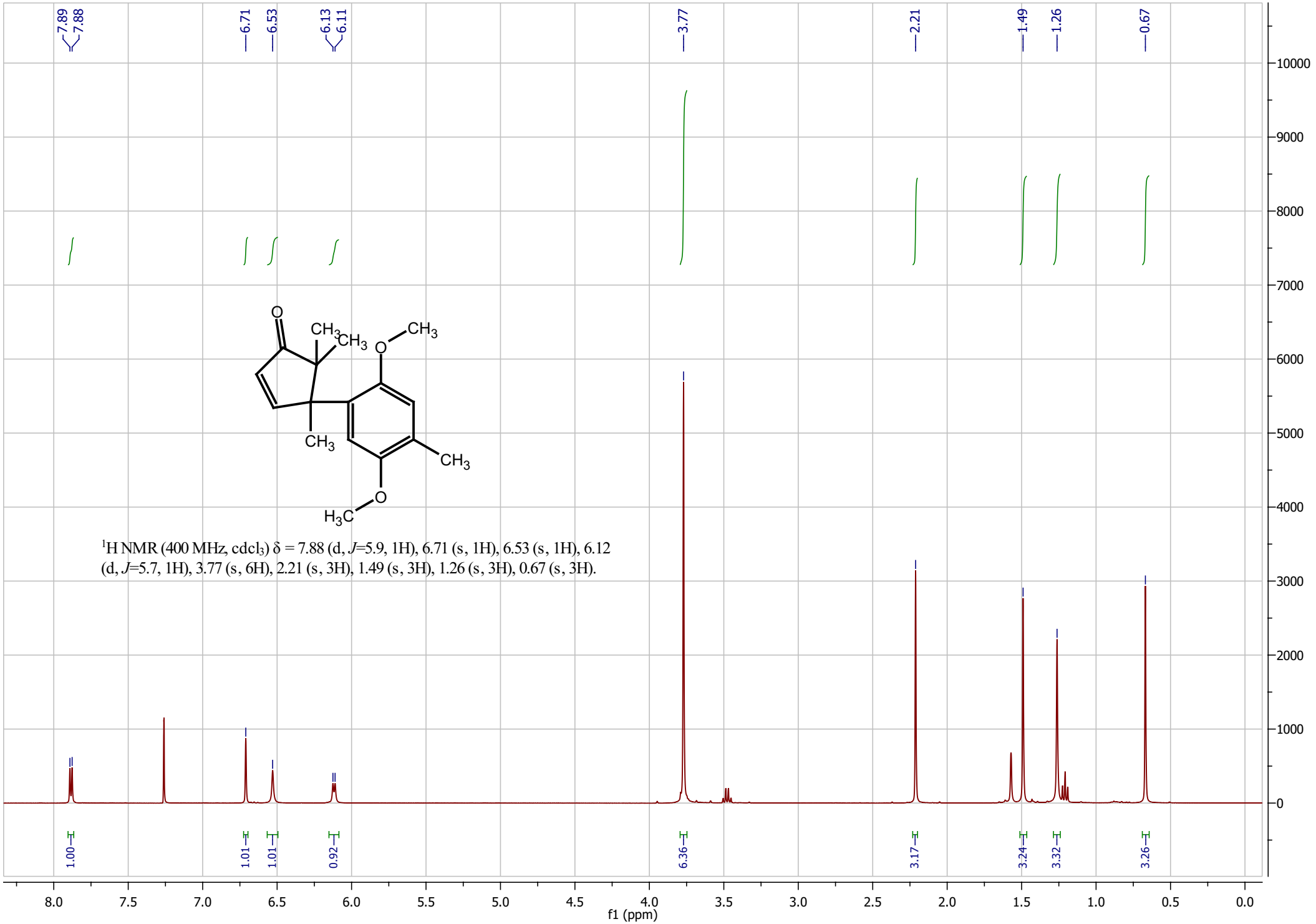
Peak#	Ret. Time	Area	Height	Area%
1	15.269	70952873	2915338	86.713
2	15.981	10872021	837011	13.287
Total		81824894	3752348	100.000

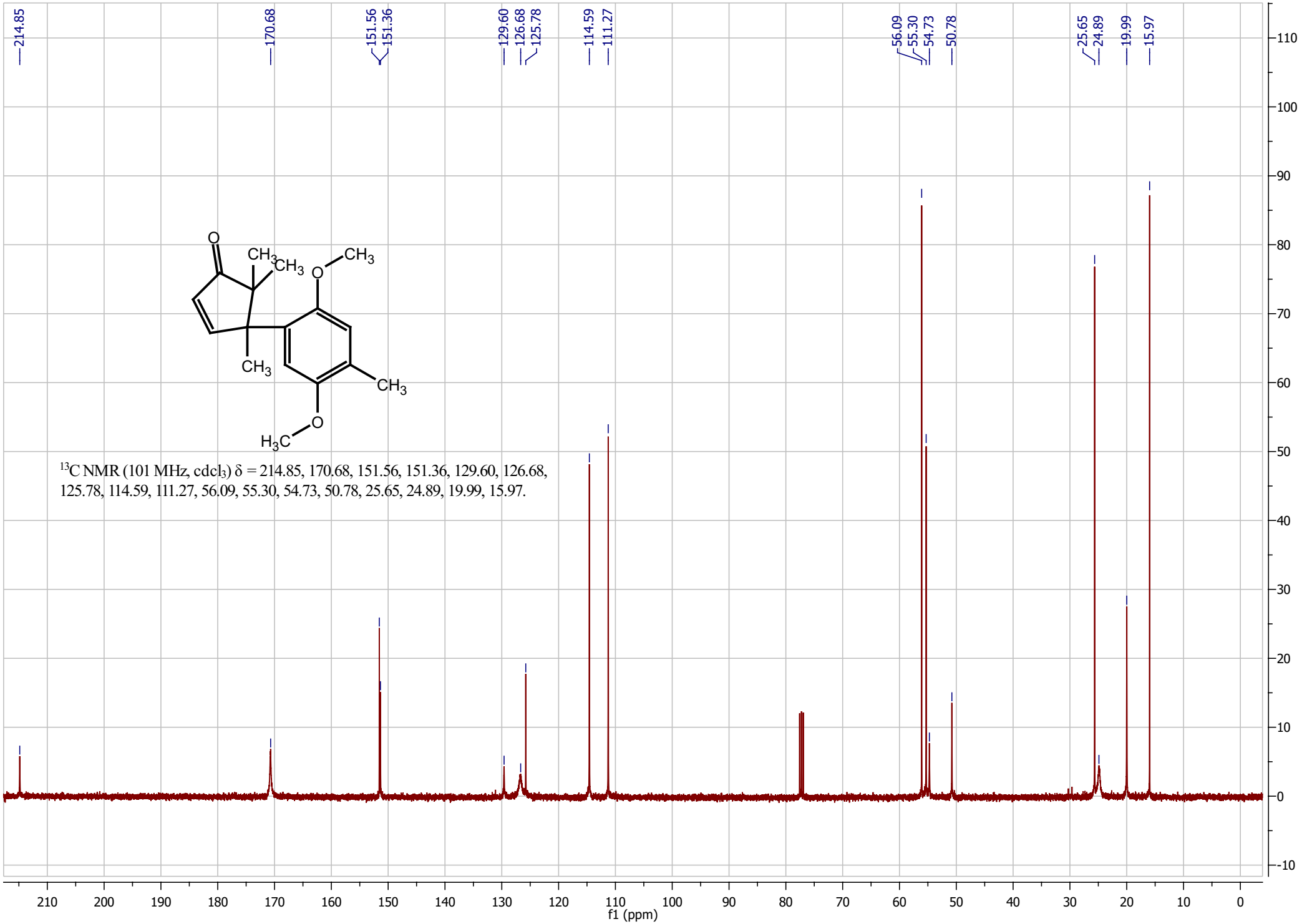

7.81
7.79
6.71
6.66
6.17
6.15
3.79
3.75
2.79
2.75
2.58
2.54
2.21
1.57
O
O
CH3
CH3
CH3
O
H3C
[1]H NMR (400 MHz, cdcl3) δ = 7.80 (d, J=5.7, 1H), 6.71 (s, 1H), 6.66 (s, 1H), 6.16 (d, J=5.6, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.67 (dd, J=83.9, 18.7, 2H), 2.21 (s, 3H), 1.57 (s, 3H).
0.97
0.95
0.98
0.91
2.99
3.24
1.11
1.16
3.00
3.28
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

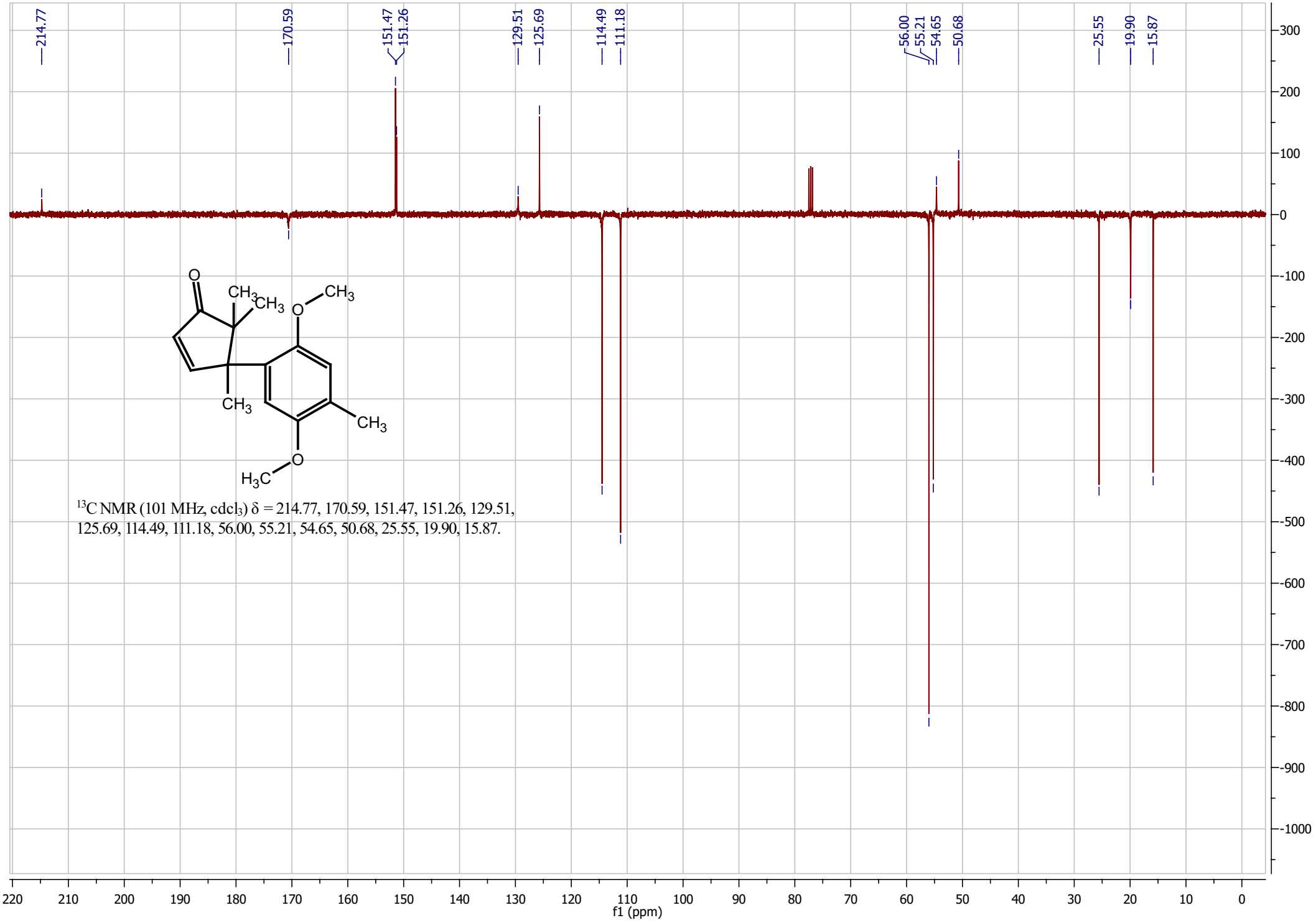

210.02
170.73
151.23
151.17
131.15
130.88
126.02
114.83
110.00
56.21
55.60
50.36
47.13
27.36
15.98
O
CH3
O
CH3
CH3
O
H3C
13C NMR (101 MHz, cdcl3) δ = 210.02, 170.73, 151.23, 151.17, 131.15,
130.88, 126.02, 114.83, 110.00, 56.21, 55.60, 50.36, 47.13, 27.36, 15.98.
f1 (ppm)



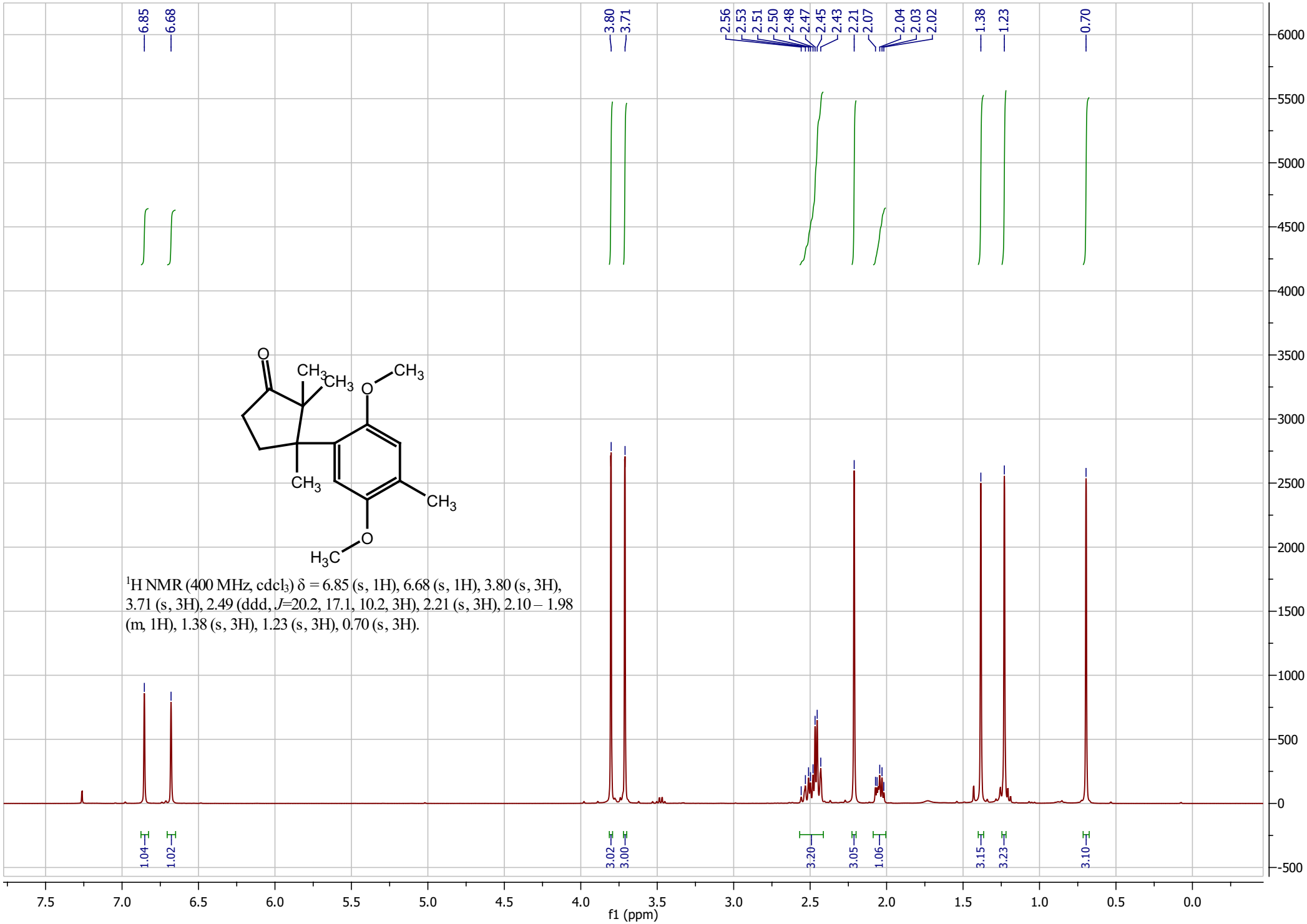
^{13}C NMR (101 MHz, cdcl$_3$) δ = 210.02, 170.73, 151.24, 151.17, 131.15, 130.88, 126.03, 114.83, 110.00, 56.21, 55.60, 50.36, 47.13, 27.36, 15.98.


7.89
7.88
6.71
6.53
6.13
6.11
3.77
2.21
1.49
1.26
0.67
O
CH3
CH3
O
CH3
CH3
CH3
O
H3C
1H NMR (400 MHz, cdcl3) δ = 7.88 (d, J=5.9, 1H), 6.71 (s, 1H), 6.53 (s, 1H), 6.12 (d, J=5.7, 1H), 3.77 (s, 6H), 2.21 (s, 3H), 1.49 (s, 3H), 1.26 (s, 3H), 0.67 (s, 3H).
1.00
1.01
1.01
0.92
6.36
3.17
3.24
3.32
3.26
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

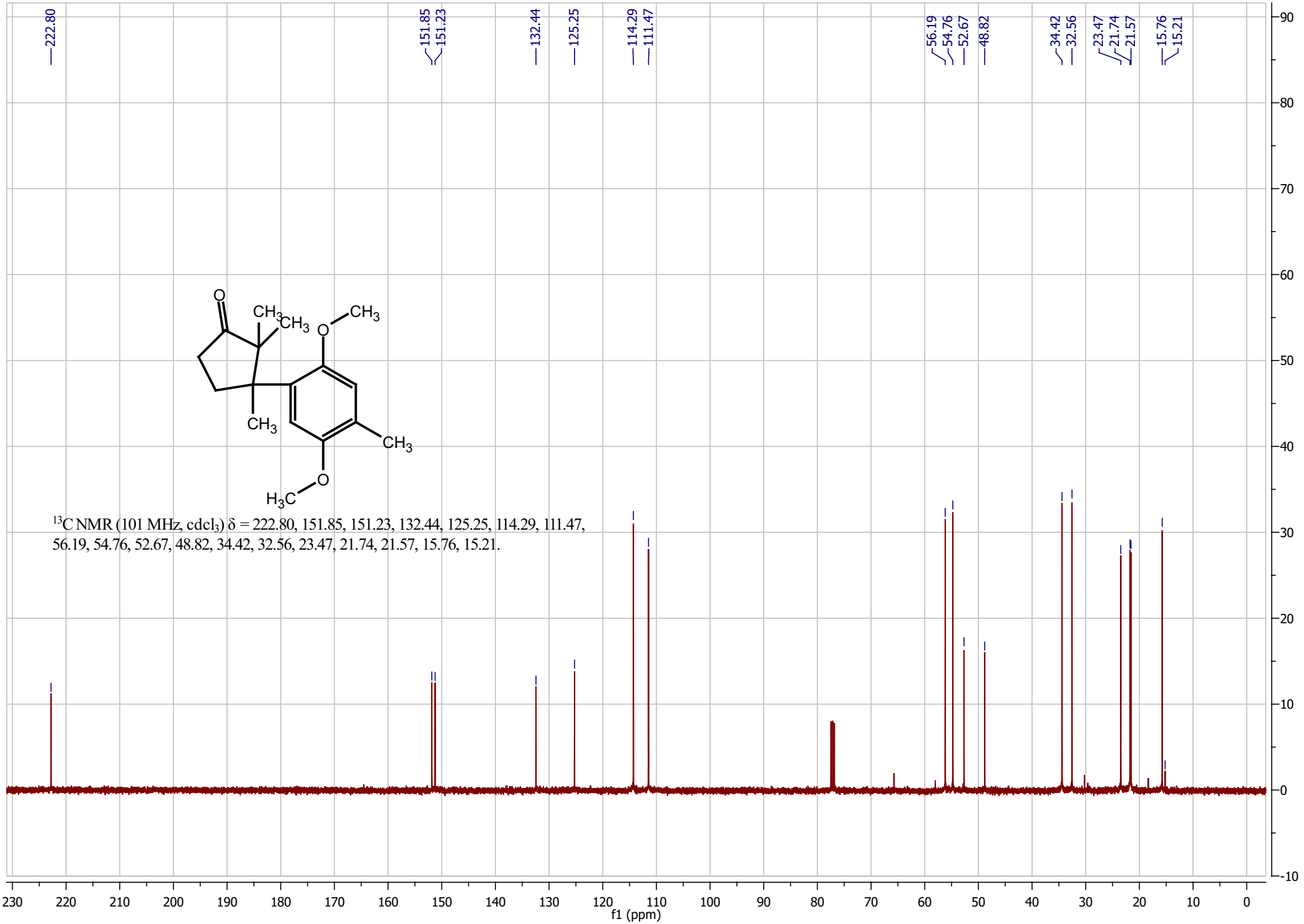

214.85
170.68
151.56
151.36
129.60
126.68
125.78
114.59
111.27
56.09
55.30
54.73
50.78
25.65
24.89
19.99
15.97
O
CH3
CH3
O
CH3
CH3
CH3
O
H3C
13C NMR (101 MHz, cdcl3) δ = 214.85, 170.68, 151.56, 151.36, 129.60, 126.68, 125.78, 114.59, 111.27, 56.09, 55.30, 54.73, 50.78, 25.65, 24.89, 19.99, 15.97.
f1 (ppm)

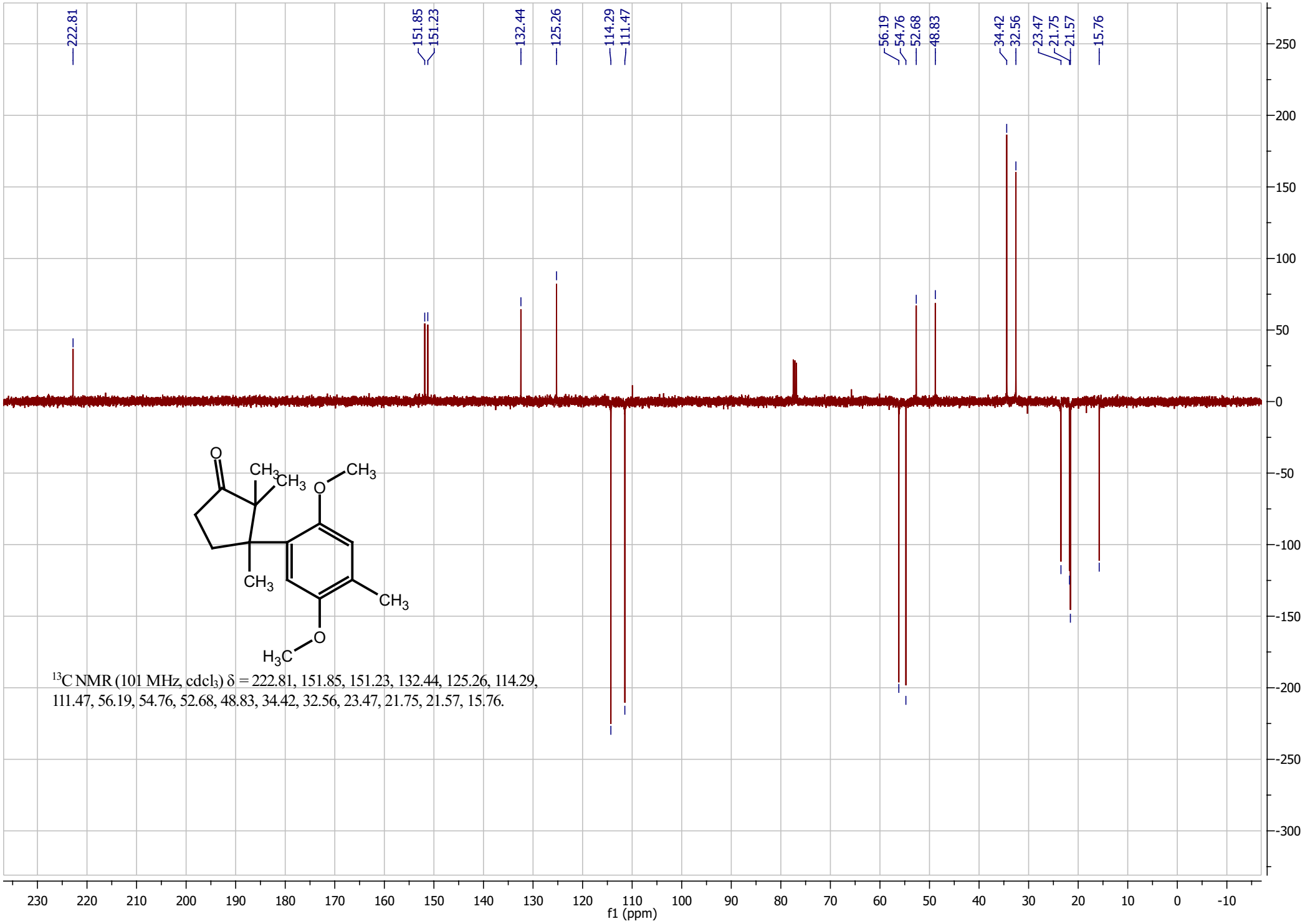


^{13}C NMR (101 MHz, cdcl$_3$) δ = 214.77, 170.59, 151.47, 151.26, 129.51, 125.69, 114.49, 111.18, 56.00, 55.21, 54.65, 50.68, 25.55, 19.90, 15.87.

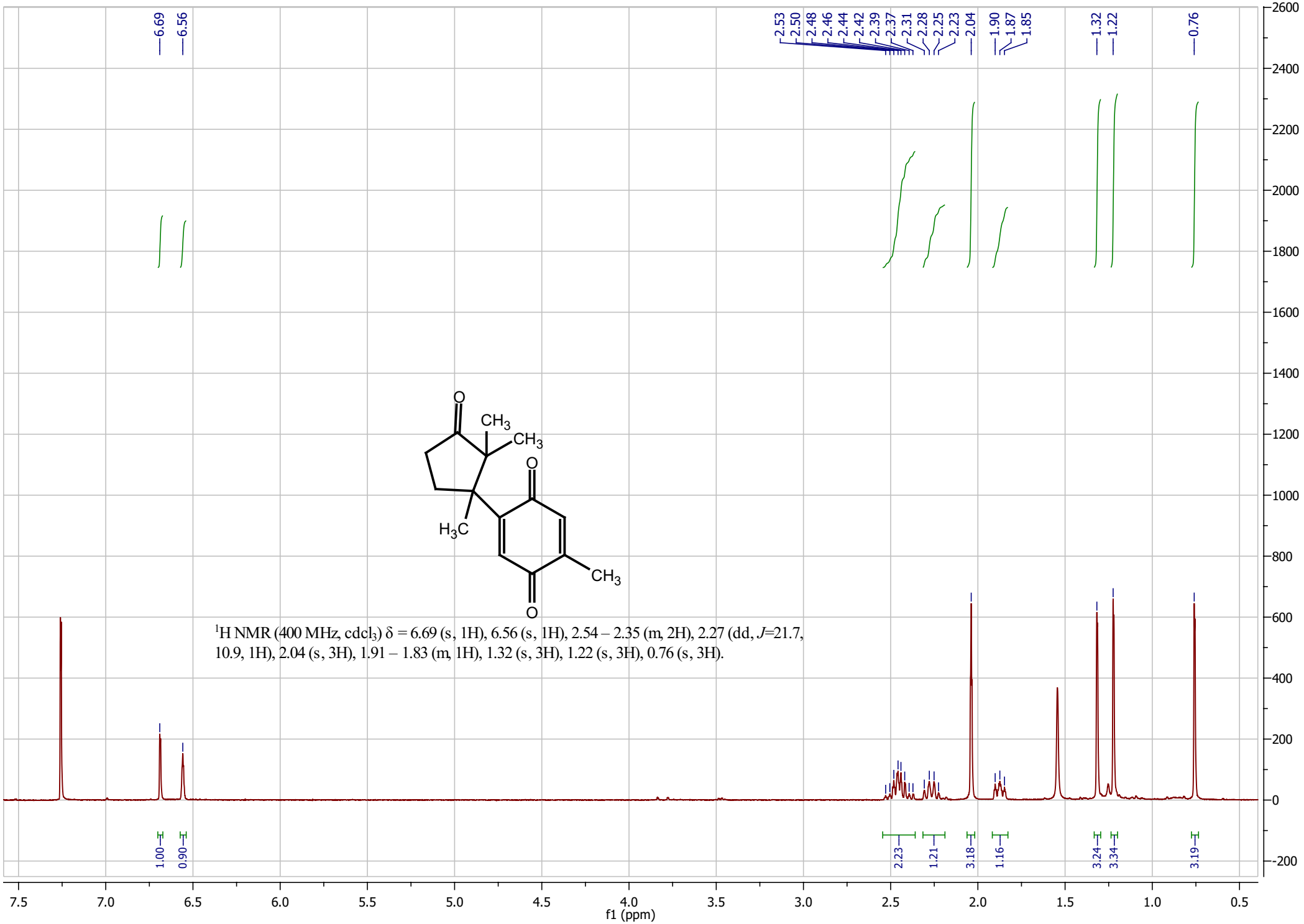


^{1}H NMR (400 MHz, cdcl$_3$) δ = 6.85 (s, 1H), 6.68 (s, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 2.49 (ddd, *J*=20.2, 17.1, 10.2, 3H), 2.21 (s, 3H), 2.10 – 1.98 (m, 1H), 1.38 (s, 3H), 1.23 (s, 3H), 0.70 (s, 3H).

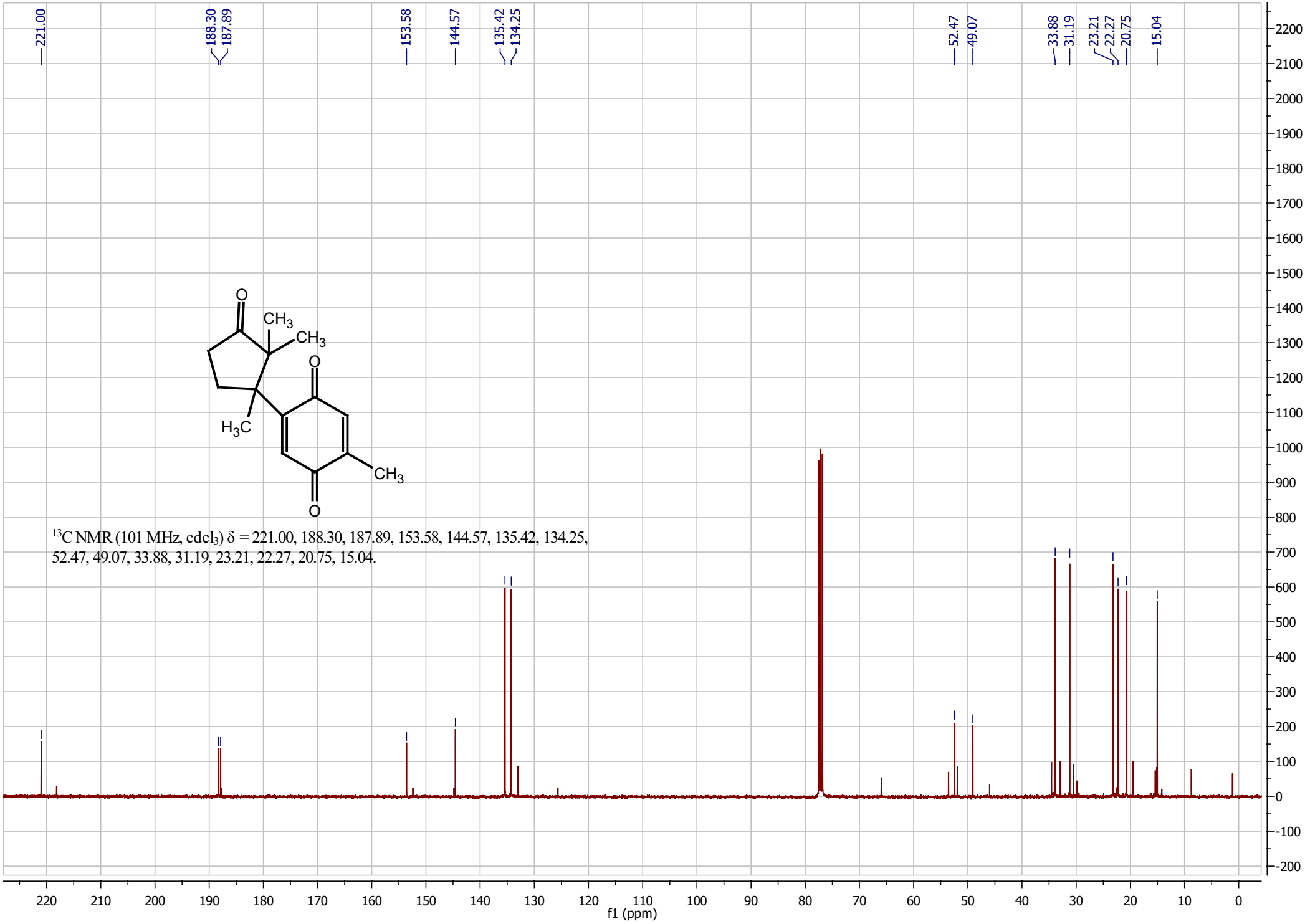

222.80
151.85
151.23
132.44
125.25
114.29
111.47
56.19
54.76
52.67
48.82
34.42
32.56
23.47
21.74
21.57
15.76
15.21
O
CH3
CH3
O
CH3
CH3
CH3
O
H3C
13C NMR (101 MHz, cdcl3) δ = 222.80, 151.85, 151.23, 132.44, 125.25, 114.29, 111.47, 56.19, 54.76, 52.67, 48.82, 34.42, 32.56, 23.47, 21.74, 21.57, 15.76, 15.21.
f1 (ppm)



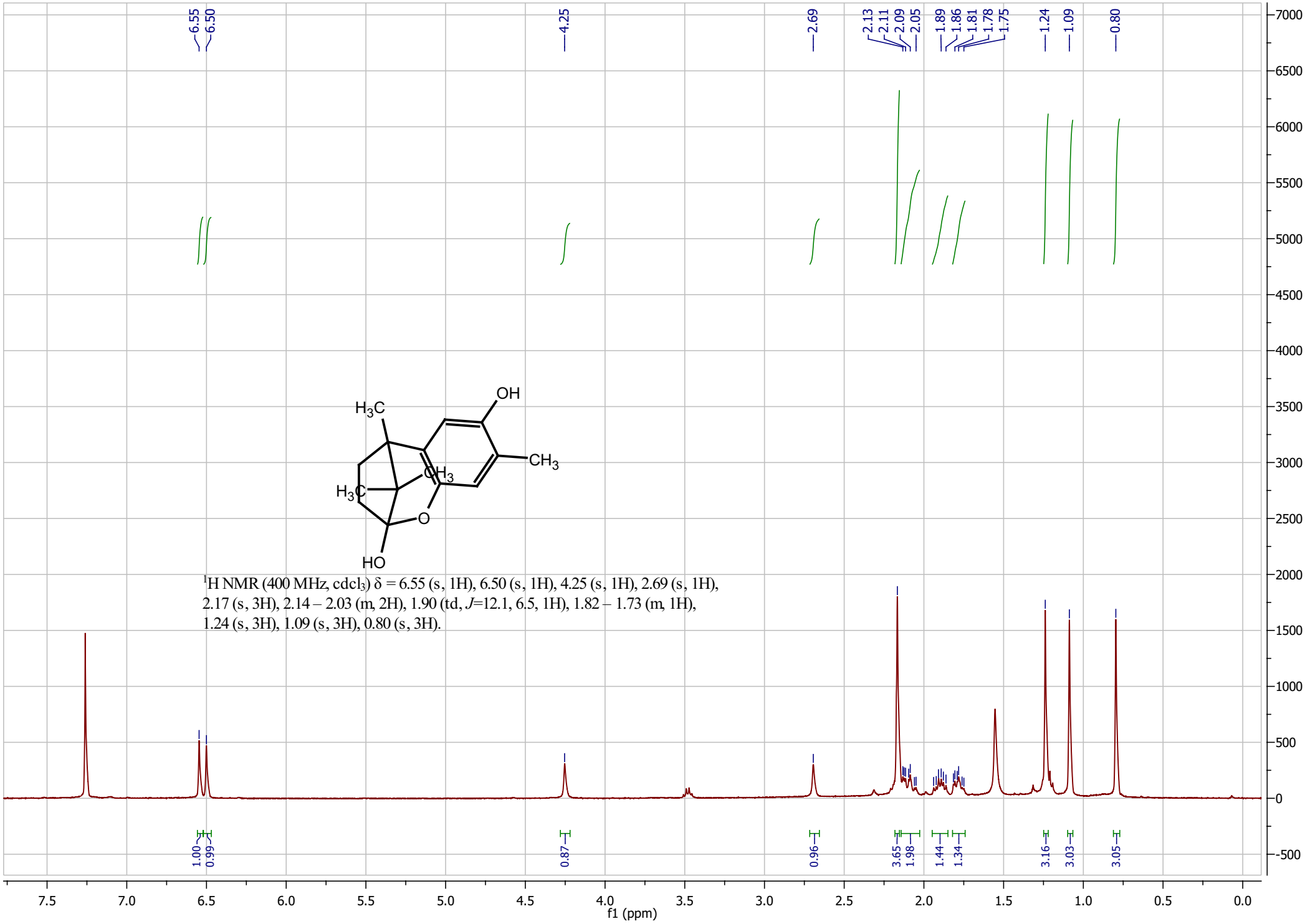
^{13}C NMR (101 MHz, cdcl$_3$) δ = 222.81, 151.85, 151.23, 132.44, 125.26, 114.29, 111.47, 56.19, 54.76, 52.68, 48.83, 34.42, 32.56, 23.47, 21.75, 21.57, 15.76.

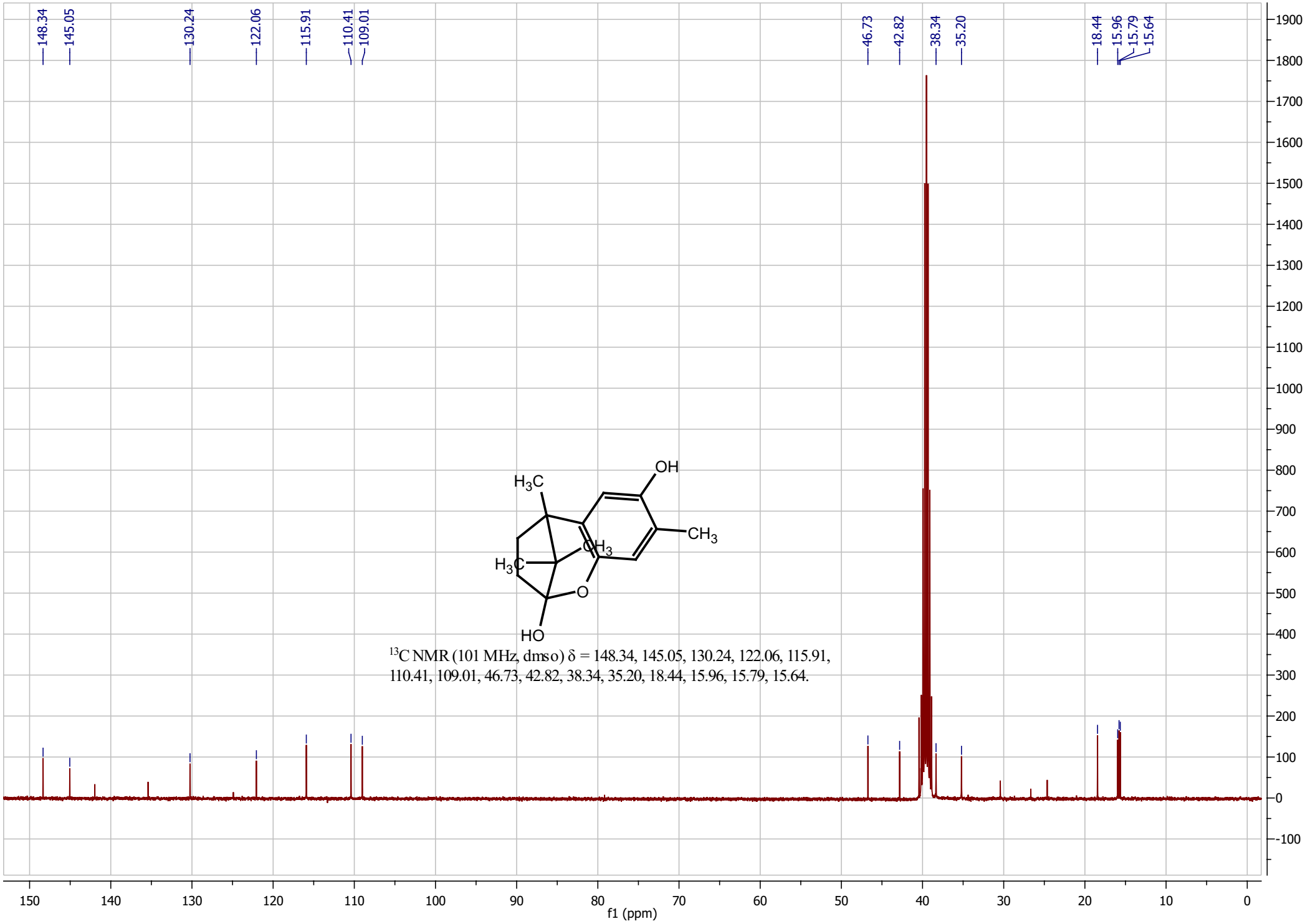


^{1}H NMR (400 MHz, cdcl$_3$) δ = 6.69 (s, 1H), 6.56 (s, 1H), 2.54 – 2.35 (m, 2H), 2.27 (dd, *J*=21.7, 10.9, 1H), 2.04 (s, 3H), 1.91 – 1.83 (m, 1H), 1.32 (s, 3H), 1.22 (s, 3H), 0.76 (s, 3H).

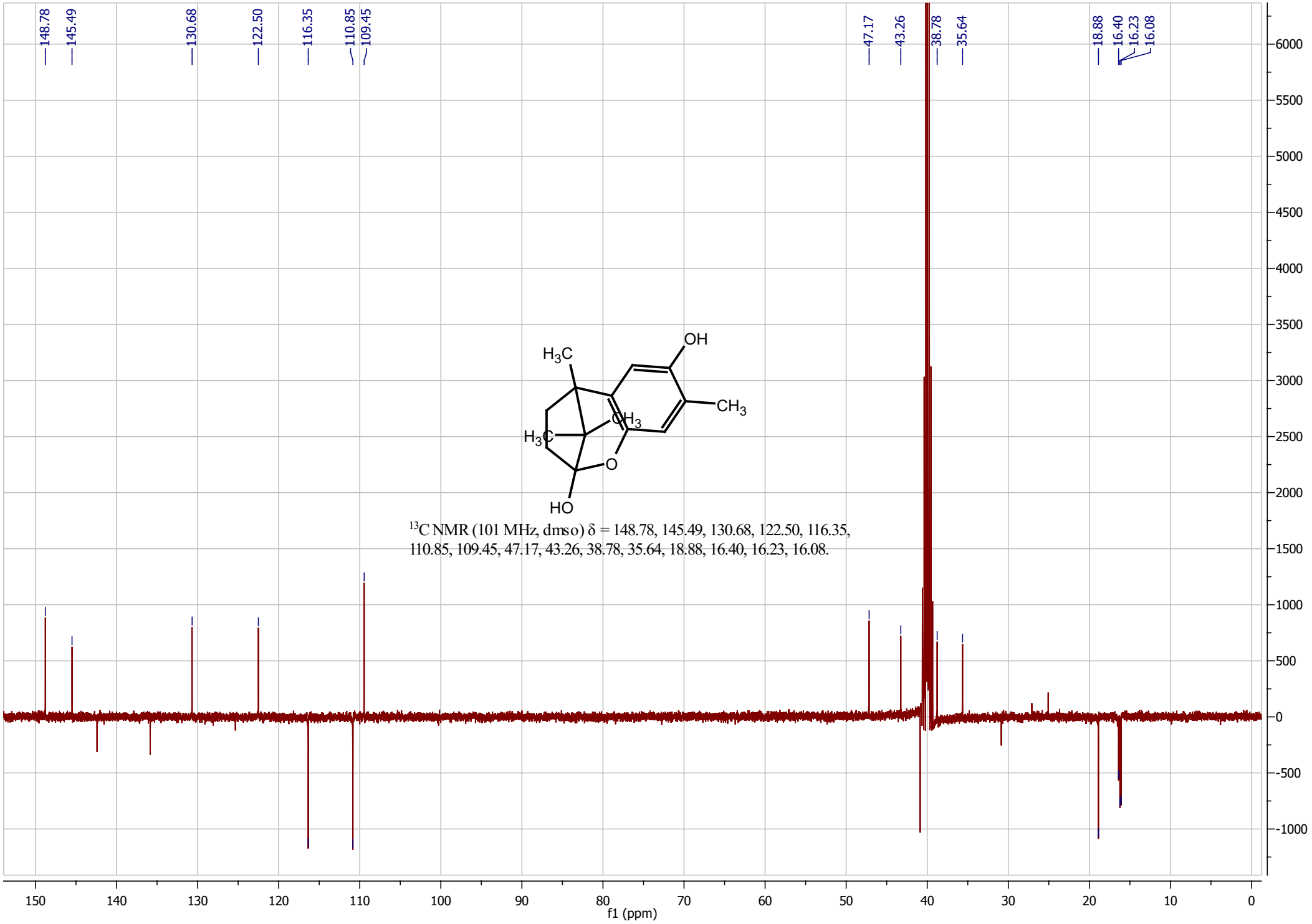

221.00
188.30
187.89
153.58
144.57
135.42
134.25
52.47
49.07
33.88
31.19
23.21
22.27
20.75
15.04
O
CH3
CH3
O
H3C
CH3
O
13C NMR (101 MHz, cdcl3) δ = 221.00, 188.30, 187.89, 153.58, 144.57, 135.42, 134.25, 52.47, 49.07, 33.88, 31.19, 23.21, 22.27, 20.75, 15.04.
f1 (ppm)

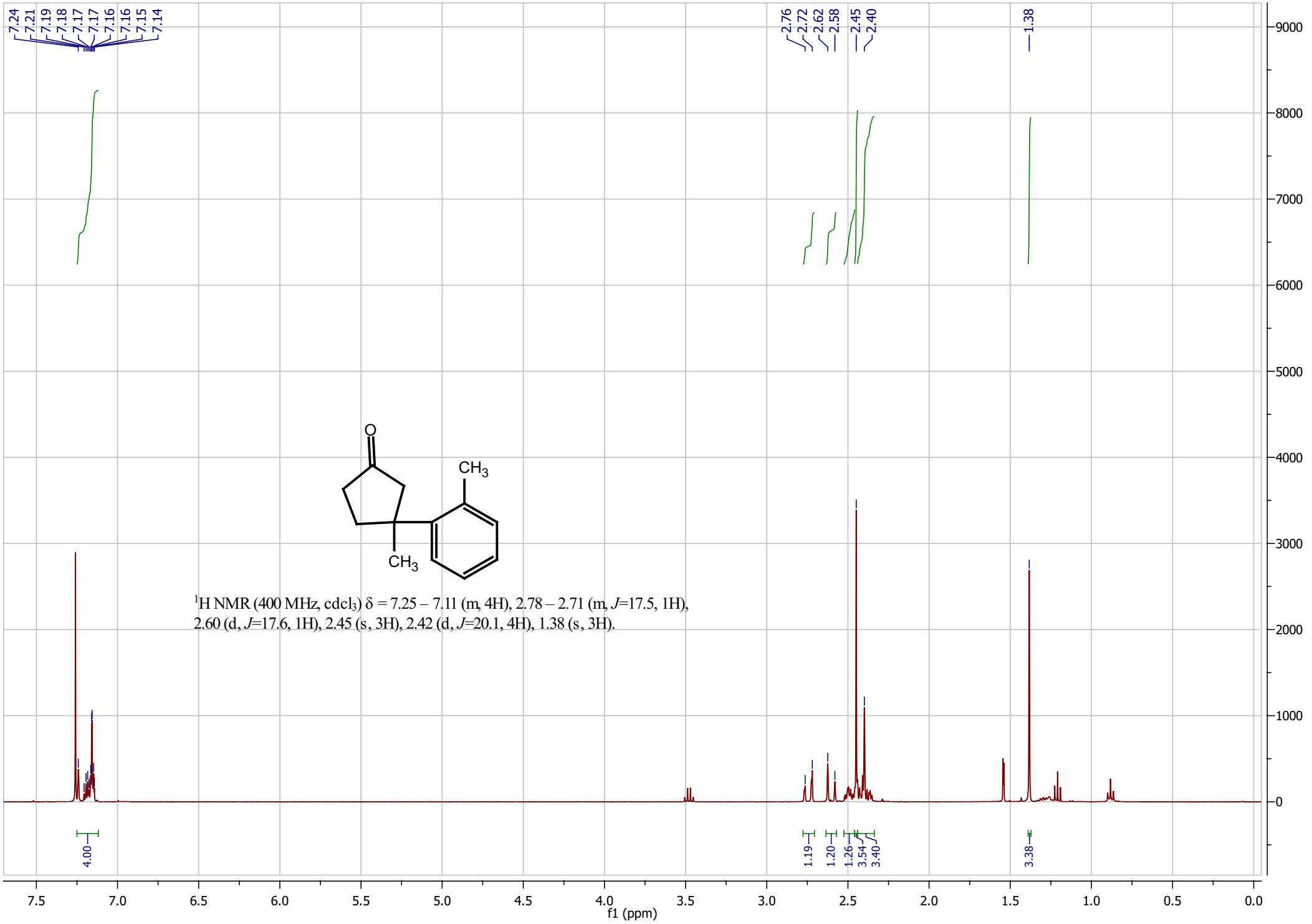
^{13}C NMR (101 MHz, cdcl$_3$) δ = 221.00, 188.31, 187.90, 153.58, 144.57, 135.42, 134.26, 52.48, 49.08, 33.88, 31.20, 23.21, 22.27, 20.75, 15.04.


6.55
6.50
4.25
2.69
2.13
2.11
2.09
2.05
1.89
1.86
1.81
1.78
1.75
1.24
1.09
0.80
OH
H3C
CH3
CH3
H3C
O
HO
1H NMR (400 MHz, cdcl3) δ = 6.55 (s, 1H), 6.50 (s, 1H), 4.25 (s, 1H), 2.69 (s, 1H),
2.17 (s, 3H), 2.14 – 2.03 (m, 2H), 1.90 (td, J=12.1, 6.5, 1H), 1.82 – 1.73 (m, 1H),
1.24 (s, 3H), 1.09 (s, 3H), 0.80 (s, 3H).
1.00
0.99
0.87
0.96
3.65
1.98
1.44
1.34
3.16
3.03
3.05
f1 (ppm)

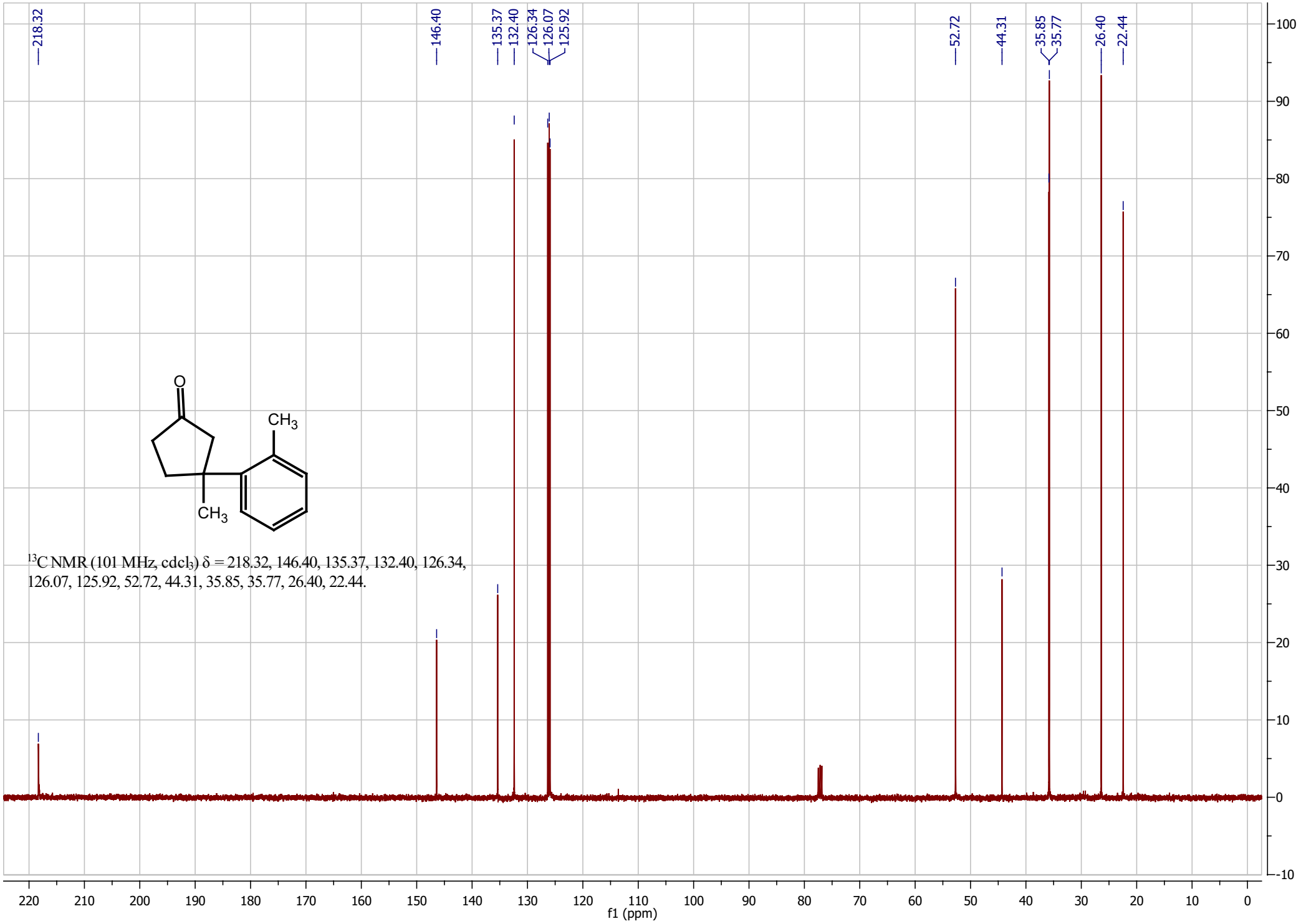


^{13}C NMR (101 MHz, dmso) δ = 148.34, 145.05, 130.24, 122.06, 115.91, 110.41, 109.01, 46.73, 42.82, 38.34, 35.20, 18.44, 15.96, 15.79, 15.64.

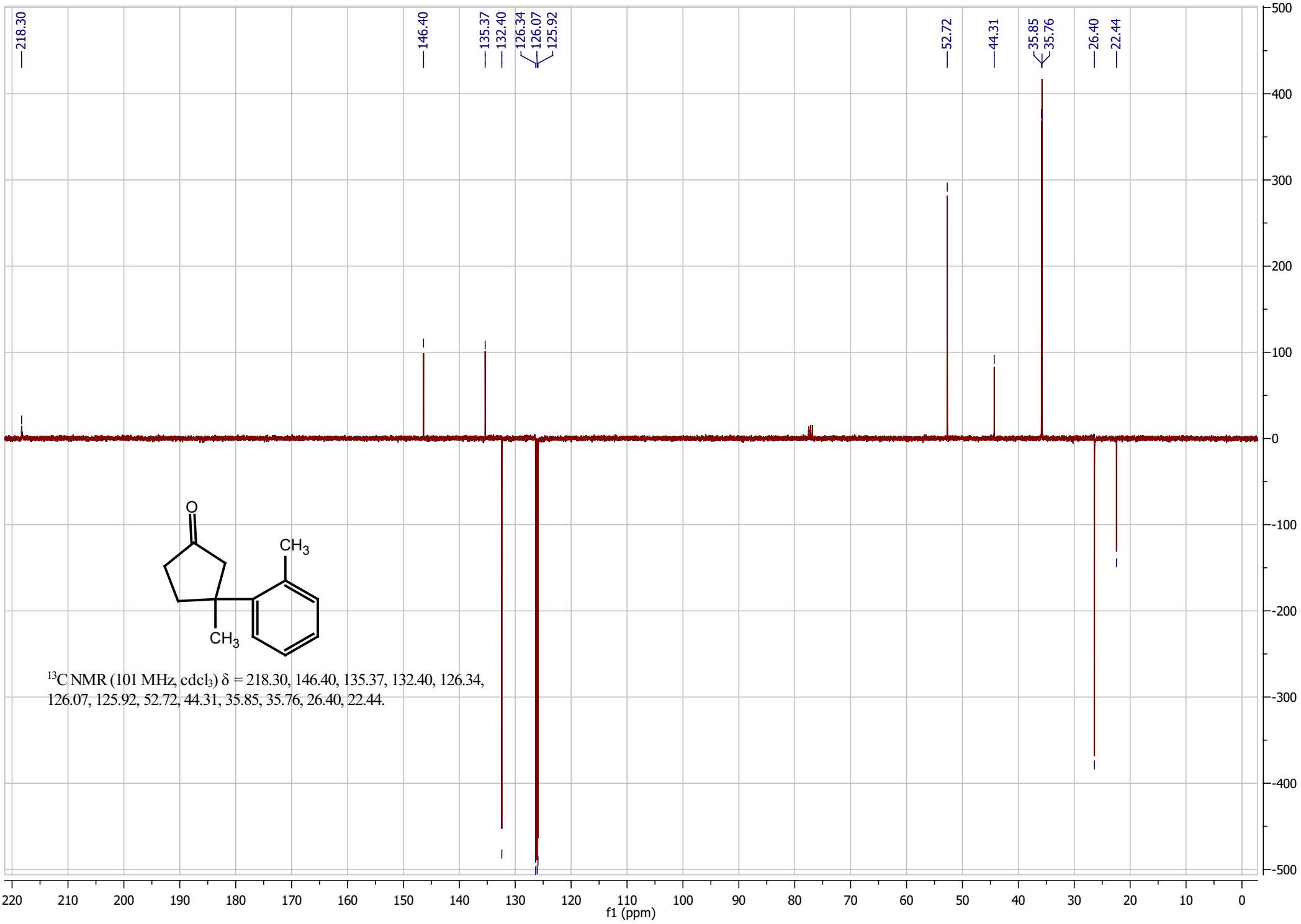

148.78
145.49
130.68
122.50
116.35
110.85
109.45
47.17
43.26
38.78
35.64
18.88
16.40
16.23
16.08
OH
H3C
CH3
CH3
H3C
O
HO
13C NMR (101 MHz, dmso) δ = 148.78, 145.49, 130.68, 122.50, 116.35, 110.85, 109.45, 47.17, 43.26, 38.78, 35.64, 18.88, 16.40, 16.23, 16.08.
f1 (ppm)



^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.25 – 7.11 (m, 4H), 2.78 – 2.71 (m, *J*=17.5, 1H), 2.60 (d, *J*=17.6, 1H), 2.45 (s, 3H), 2.42 (d, *J*=20.1, 4H), 1.38 (s, 3H).



^{13}C NMR (101 MHz, cdcl$_3$) δ = 218.32, 146.40, 135.37, 132.40, 126.34, 126.07, 125.92, 52.72, 44.31, 35.85, 35.77, 26.40, 22.44.



^{13}C NMR (101 MHz, cdcl$_3$) δ = 218.30, 146.40, 135.37, 132.40, 126.34, 126.07, 125.92, 52.72, 44.31, 35.85, 35.76, 26.40, 22.44.

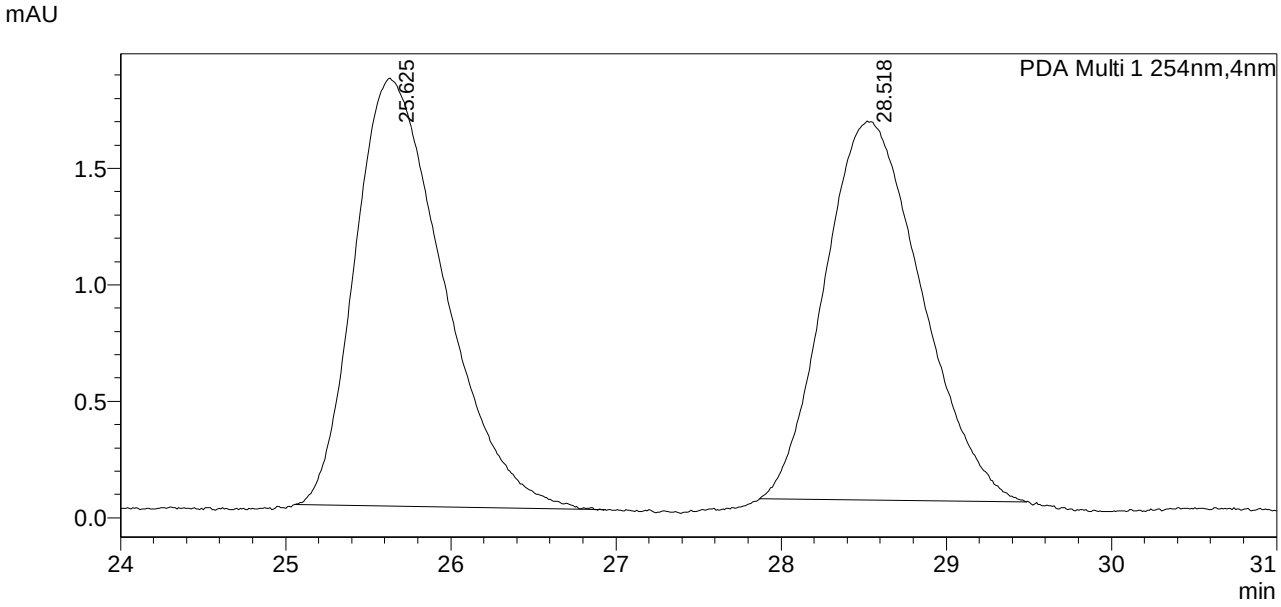
SHIMADZU LabSolutions

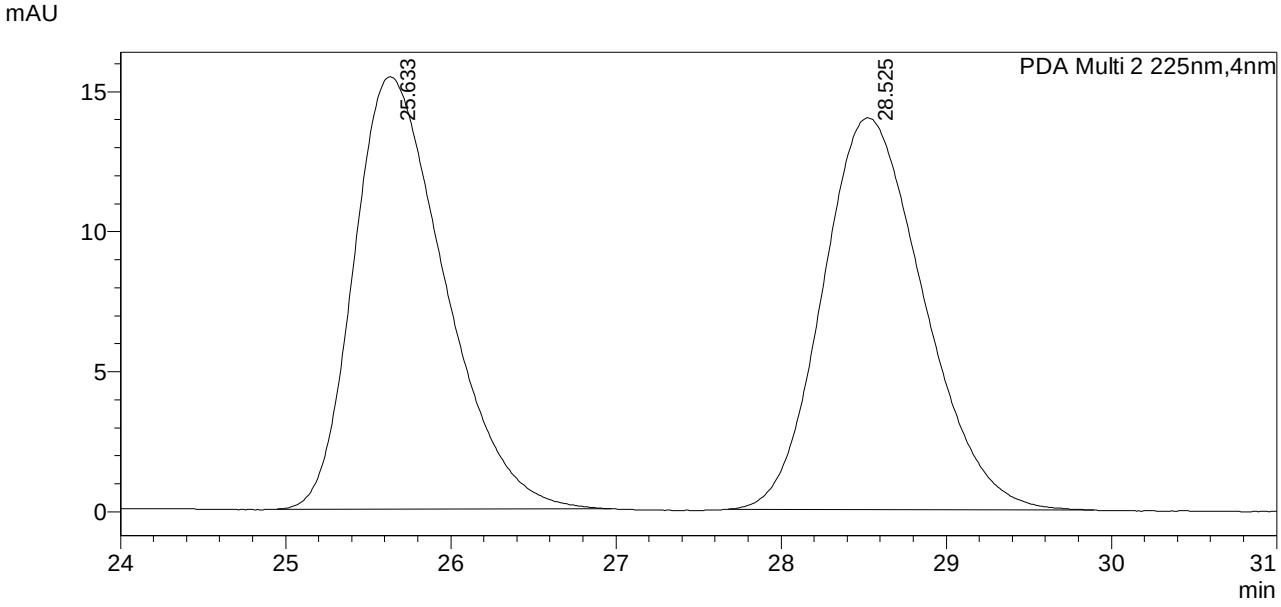
Analysis Report

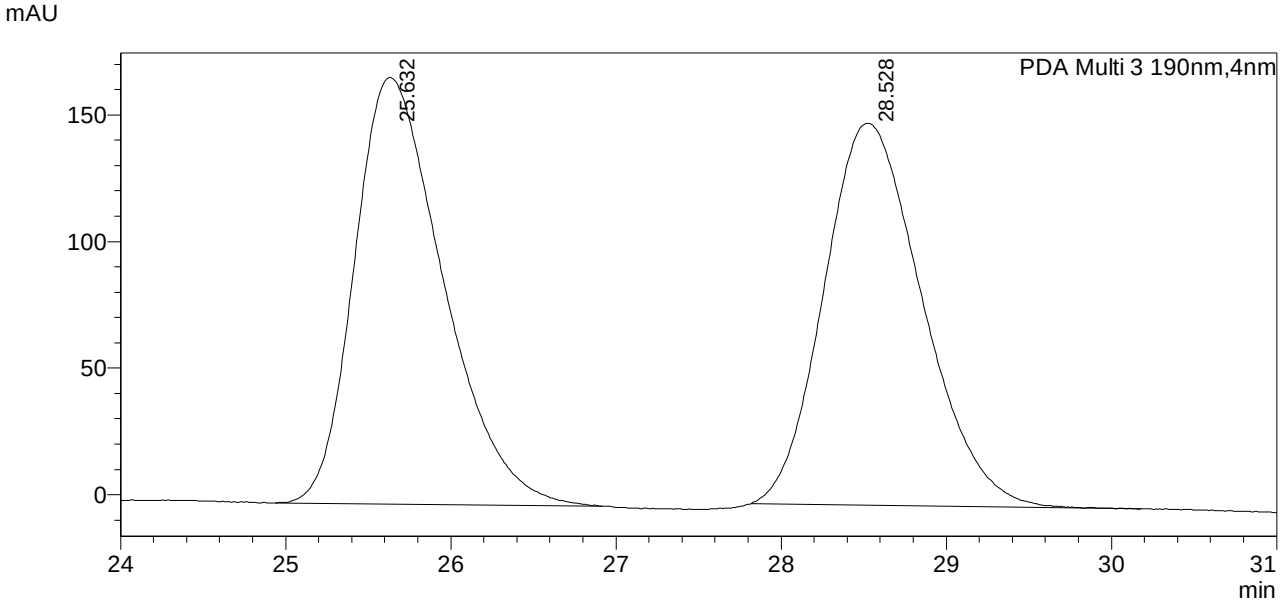
<Sample Information>

Sample Name	: o-methylboronic acid RAC OB-H-column		
Sample ID	: o-methylboronic acid RAC ODB-H		
Data Filename	: o-methylboronic acid RAC OB-H-column.lcd		
Method Filename	: C3 99_1 fl0,5 60 min.lcm		
Batch Filename	: 20131004 (99_1 all column screening).lcb		
Vial #	: 1-80	Sample Type	: Unknown
Injection Volume	: 5 uL	Level	: 1
Date Acquired	: 10/4/2013 8:16:48 PM	Acquired by	: System Administrator
Date Processed	: 10/12/2013 2:27:58 PM	Processed by	: System Administrator

<Chromatogram>







<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	25.625	68878	1836	50.894
2	28.518	66458	1624	49.106
Total		135336	3460	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	25.633	592057	15434	49.841
2	28.525	595846	13991	50.159
Total		1187903	29426	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	25.632	6321931	168504	50.350
2	28.528	6233962	150795	49.650
Total		12555892	319299	100.000

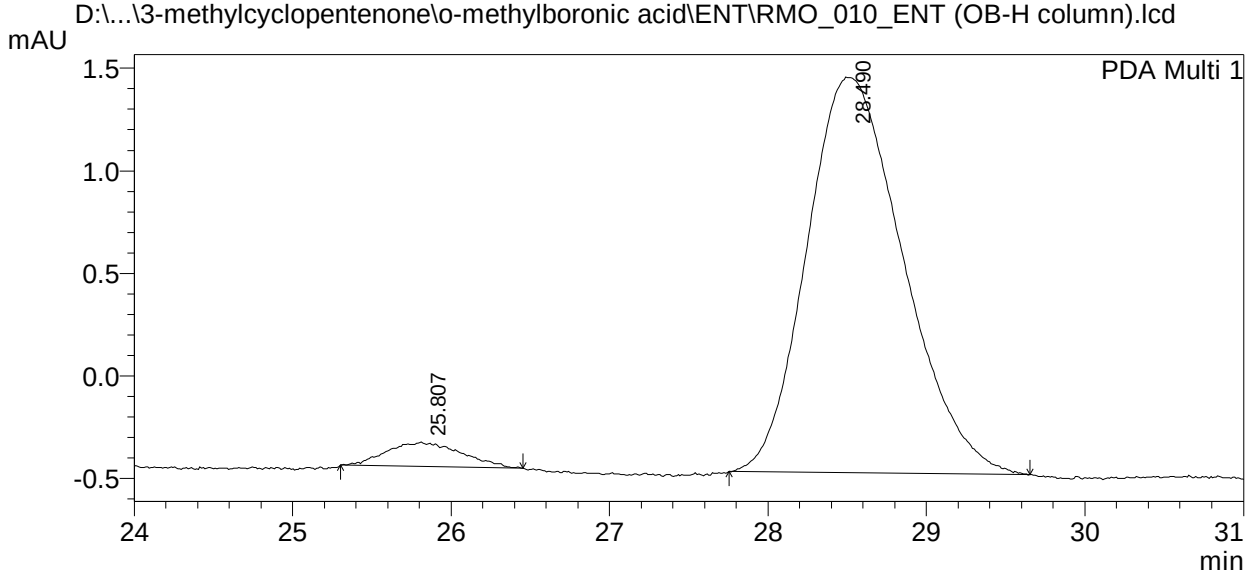
==== Shimadzu LCsolution Analysis Report ====

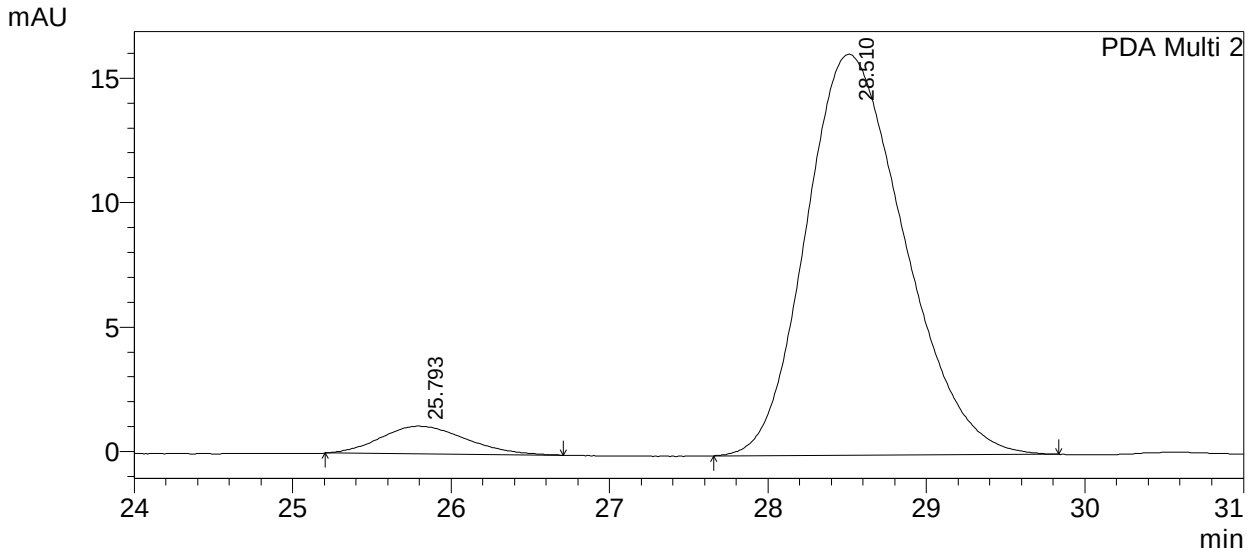
D:\...\3-methylcyclopentenone\o-methylboronic acid\ENT\RMO_010_ENT (OB-H column).lcd

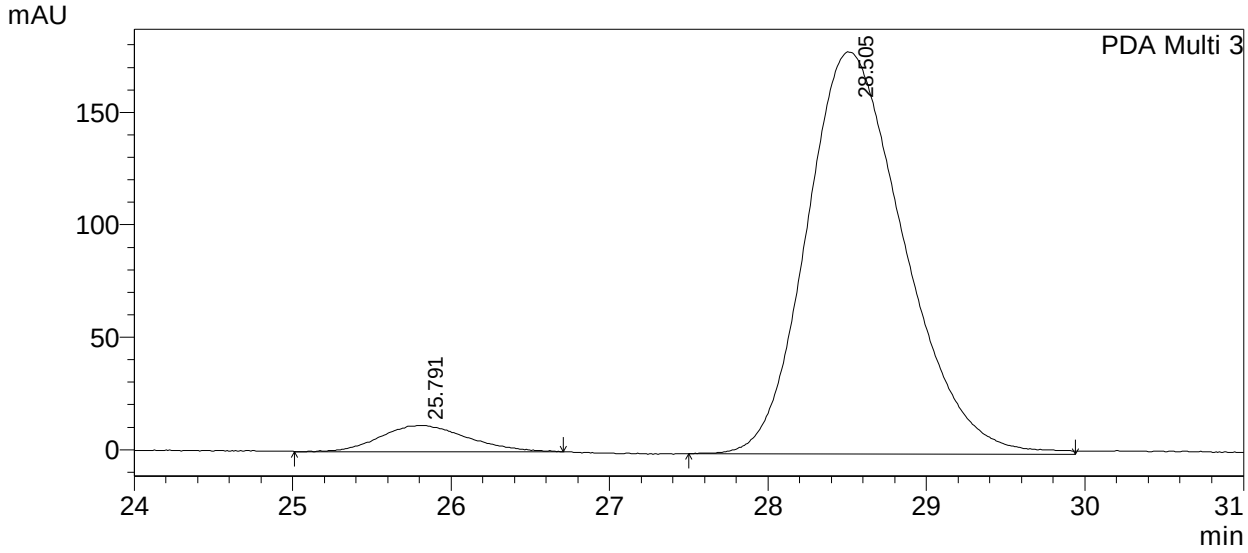
Acquired by	: System Administrator
Sample Name	: RMO_010_ENTa
Sample ID	: RMO_010_ENTa
Tray#	: 1
Vail #	: 79
Injection Volume	: 2 uL
Data File Name	: RMO_010_ENT (OB-H column).lcd
Method File Name	: C3 99_1 fl0,5 40 min.lcm
Batch File Name	: 20131007.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 10/7/2013 4:05:15 PM
Data Processed	: 10/12/2013 2:35:32 PM

<Chromatogram>

D:\...\3-methylcyclopentenone\o-methylboronic acid\ENT\RMO_010_ENT (OB-H column).lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

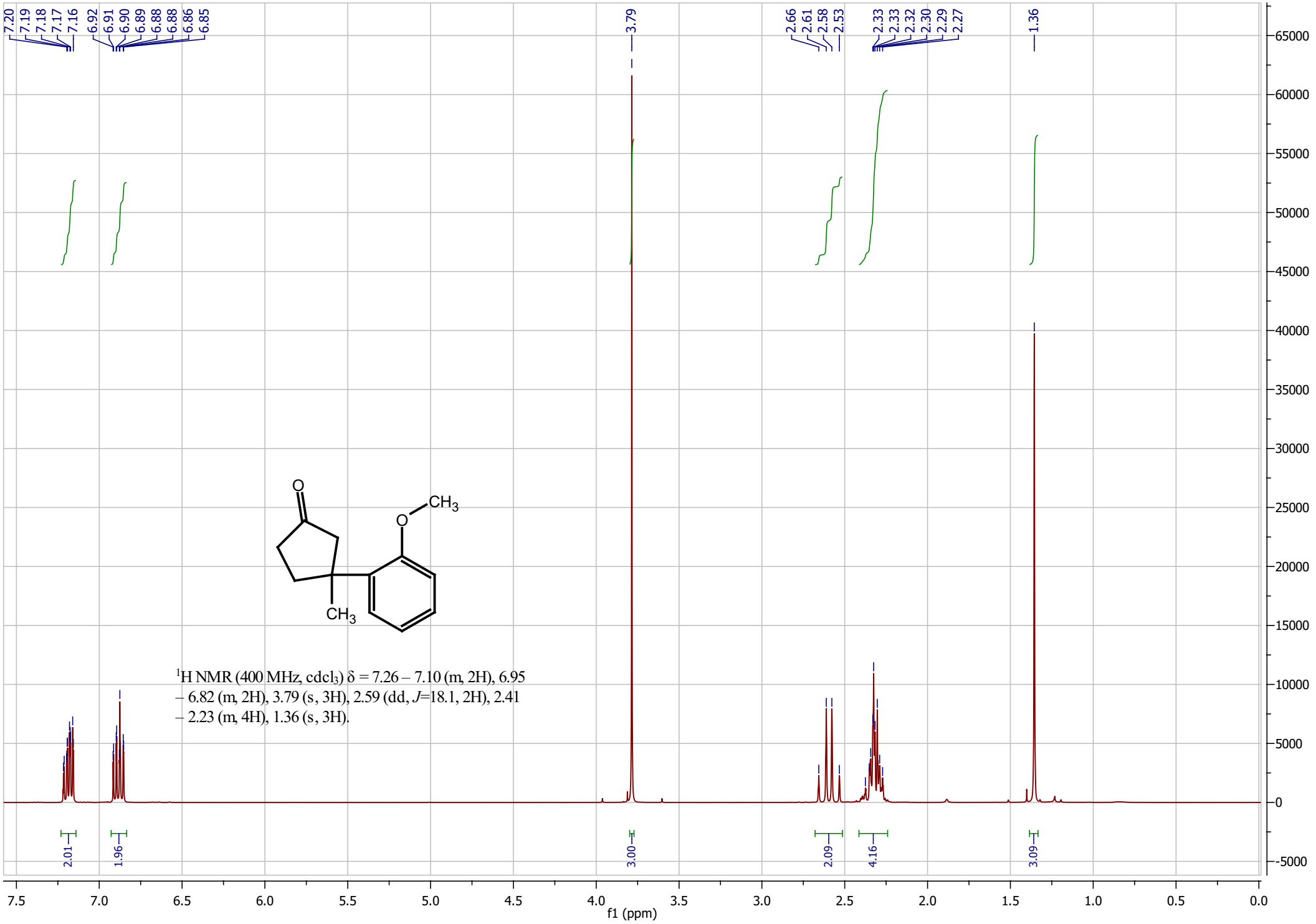
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	25.807	3916	120	0.000	4.579
2	28.490	81605	1929	0.000	95.421
Total		85521	2049		100.000

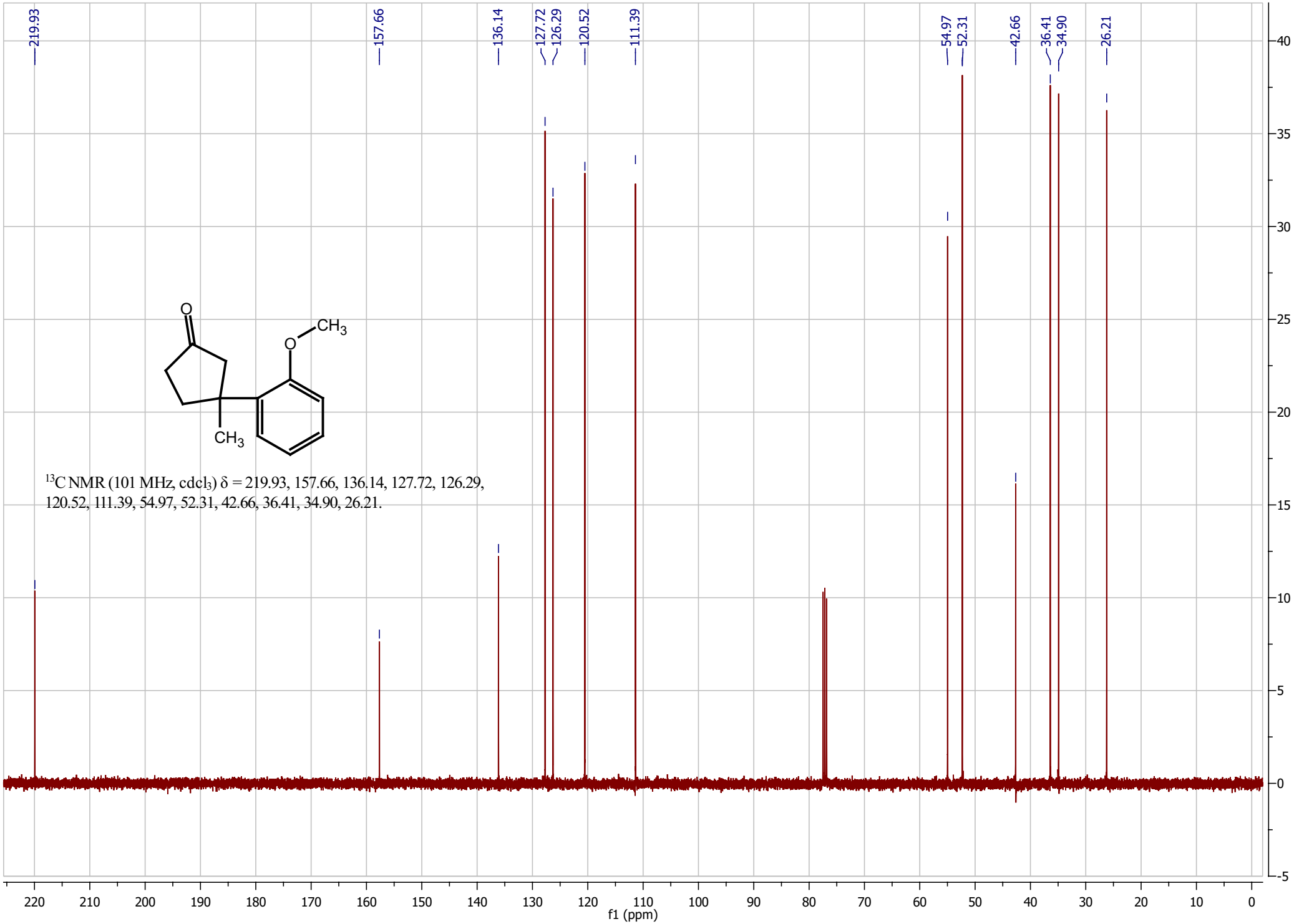
PDA Ch2 225nm

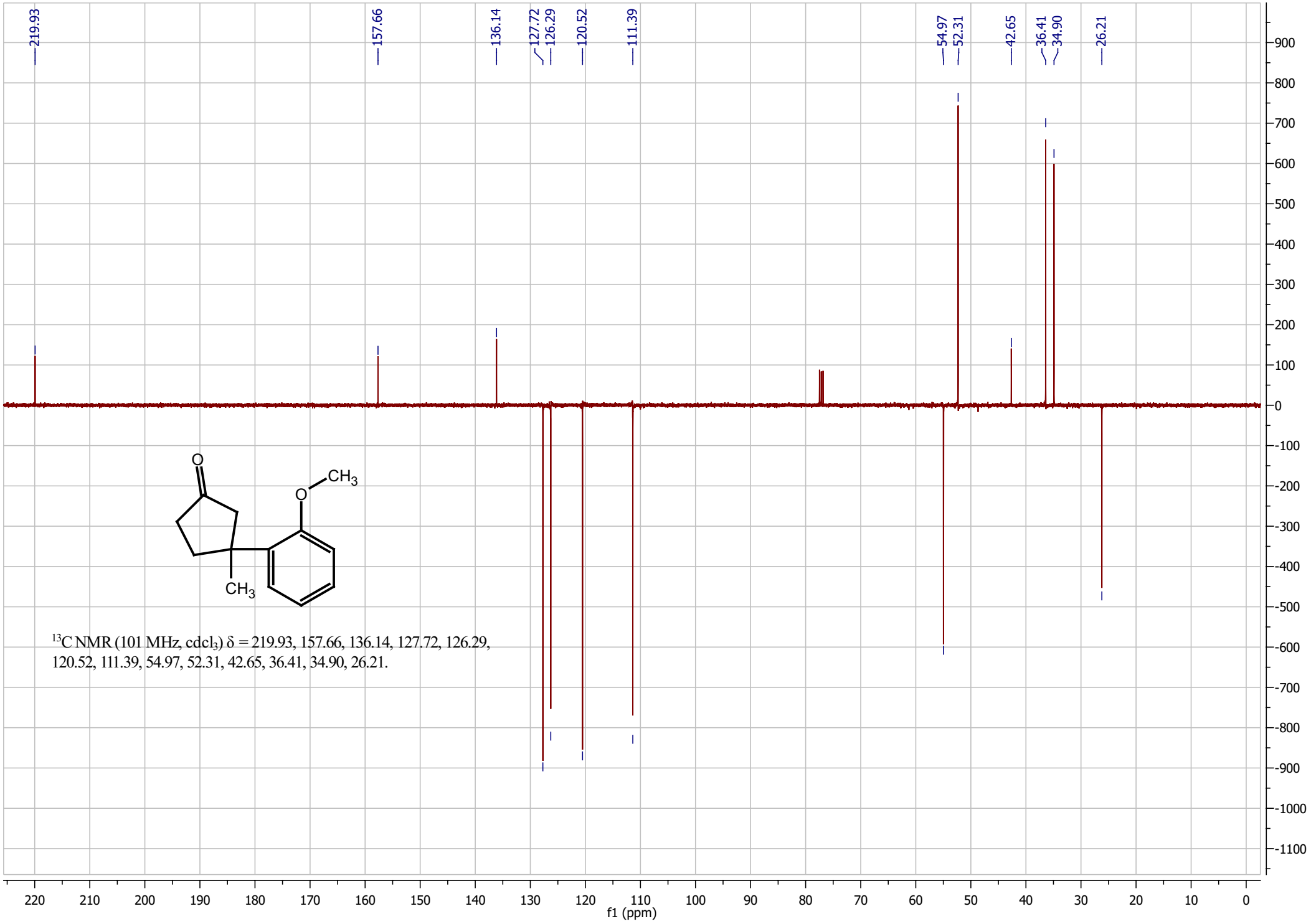
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	25.793	41548	1110	0.000	5.647
2	28.510	694242	16104	0.000	94.353
Total		735790	17214		100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	25.791	455115	11798	0.000	5.612
2	28.505	7654197	178844	0.000	94.388
Total		8109312	190643		100.000


7.20
7.19
7.18
7.17
7.16
6.92
6.91
6.90
6.89
6.88
6.88
6.86
6.85
3.79
2.66
2.61
2.58
2.53
2.33
2.33
2.32
2.30
2.29
2.27
1.36
O
CH3
O
CH3
[1]H NMR (400 MHz, cdcl3) δ = 7.26 – 7.10 (m, 2H), 6.95 – 6.82 (m, 2H), 3.79 (s, 3H), 2.59 (dd, J=18.1, 2H), 2.41 – 2.23 (m, 4H), 1.36 (s, 3H).
2.01
1.96
3.00
2.09
4.16
3.09
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


219.93
157.66
136.14
127.72
126.29
120.52
111.39
54.97
52.31
42.66
36.41
34.90
26.21
O
O
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 219.93, 157.66, 136.14, 127.72, 126.29,
120.52, 111.39, 54.97, 52.31, 42.66, 36.41, 34.90, 26.21.
f1 (ppm)



^{13}C NMR (101 MHz, cdcl$_3$) δ = 219.93, 157.66, 136.14, 127.72, 126.29, 120.52, 111.39, 54.97, 52.31, 42.65, 36.41, 34.90, 26.21.

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: o-methoxyphenyl boronic acid RAC		
Sample ID	: o-methoxyphenyl boronic acid RA		
Data Filename	: o-methoxyphenyl boronic acid RAC (AD-H column).lcd		
Method Filename	: C5 99_1 fl0,5 60 min.lcm		
Batch Filename	: 20131010.lcb		
Vial #	: 1-80	Sample Type	: Unknown
Injection Volume	: 3 uL	Level	: 1
Date Acquired	: 10/10/2013 7:15:43 PM	Acquired by	: System Administrator
Date Processed	: 10/11/2013 8:10:55 AM	Processed by	: System Administrator

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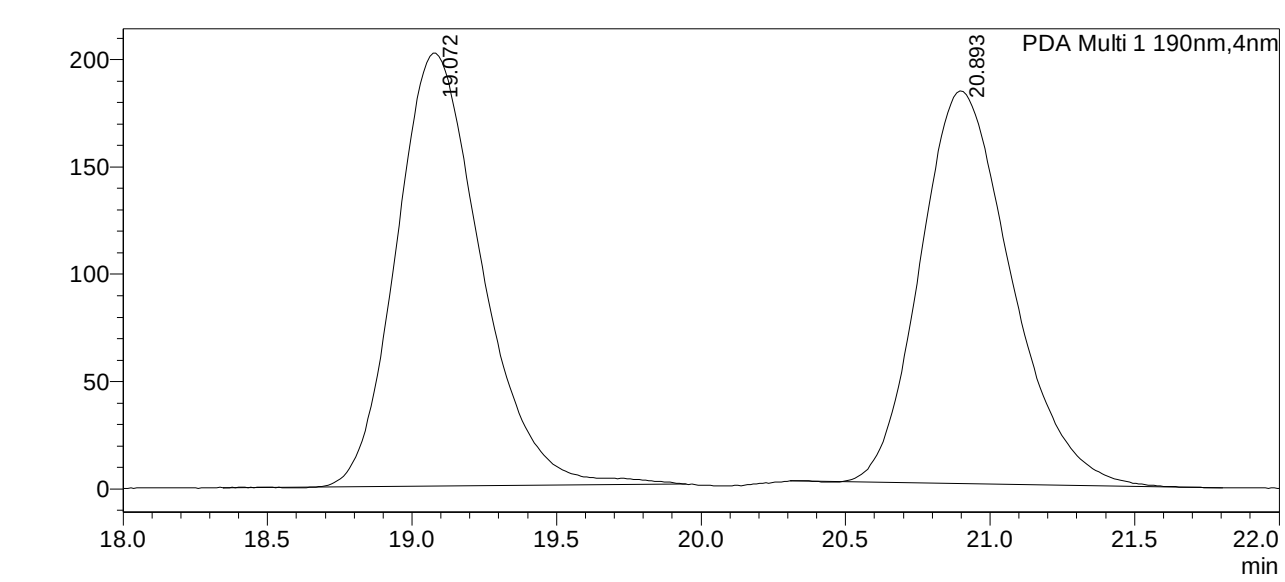

<Peak Table>

PDA Ch1 190nm

Peak#	Ret. Time	Area	Height	Area%
1	19.072	4134151	201685	50.653
2	20.893	4027507	182855	49.347
Total		8161658	384540	100.000

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: o-methoxyboronic acid ENT AD-H-column		
Sample ID	: o-methoxyboronic acid ENT AD-H-		
Data Filename	: o-methoxyboronic acid ENT AD-H-column.lcd		
Method Filename	: C5 99_1 fl0,5 60 min.lcm		
Batch Filename	: 20131015_JBR.lcb		
Vial #	: 1-82	Sample Type	: Unknown
Injection Volume	: 3 uL	Level	: 1
Date Acquired	: 10/15/2013 8:50:11 PM	Acquired by	: System Administrator
Date Processed	: 10/16/2013 8:44:29 AM	Processed by	: System Administrator

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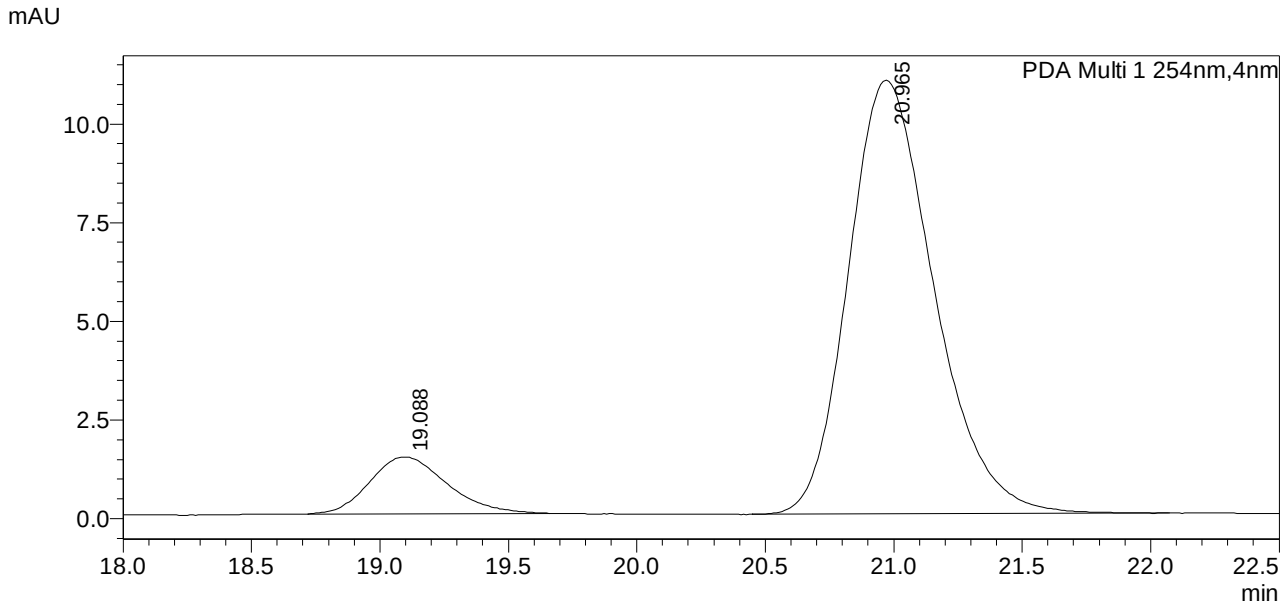
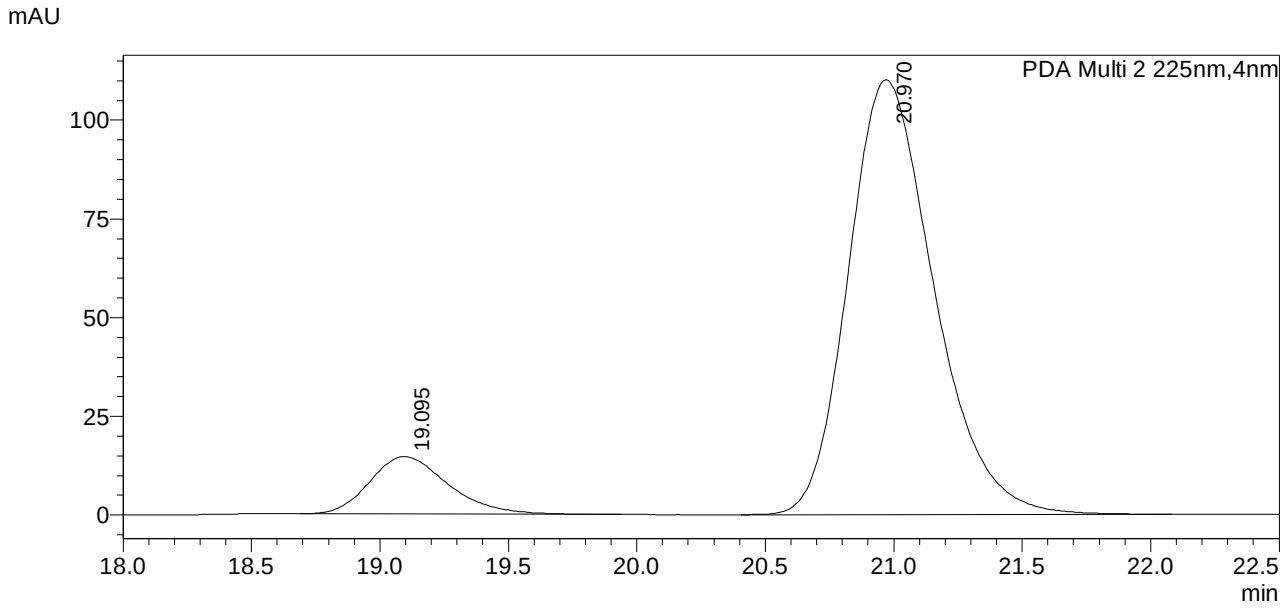
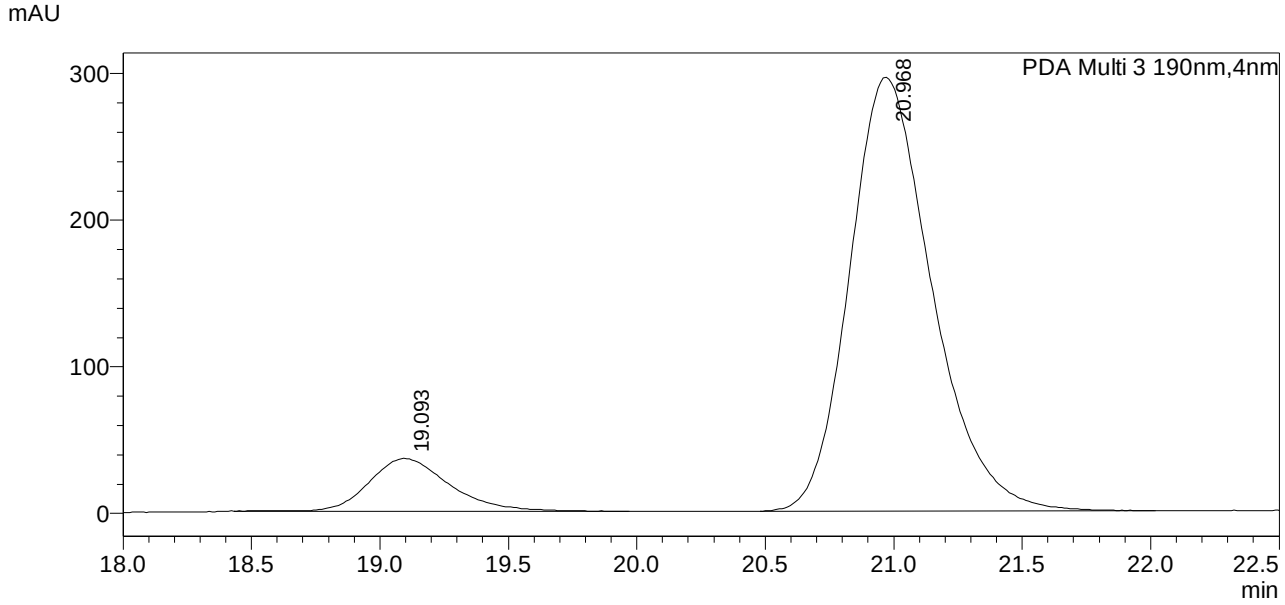






<Peak Table>

PDA Ch1 254nm

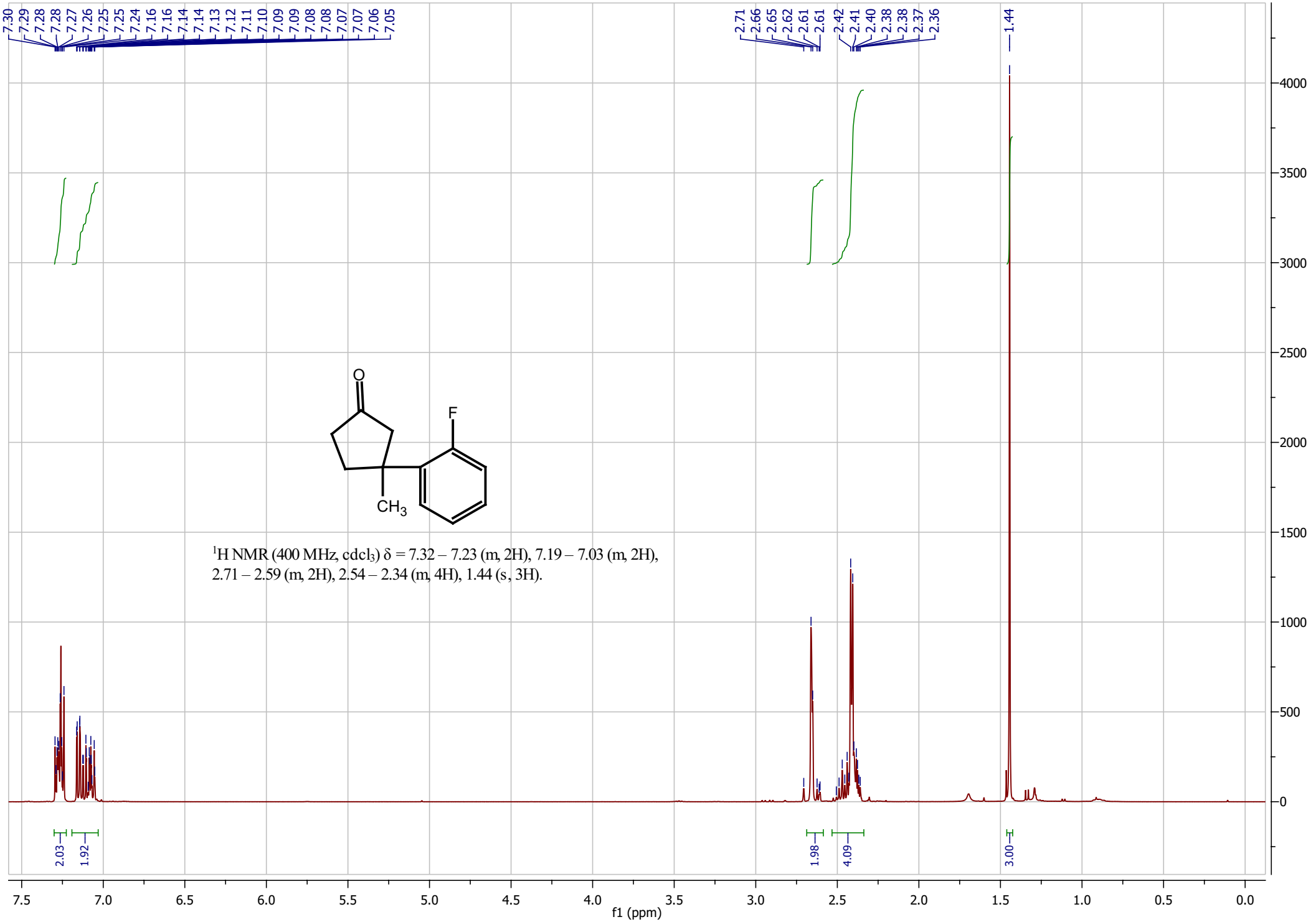
Peak#	Ret. Time	Area	Height	Area%
1	19.088	29962	1437	10.534
2	20.965	254468	10987	89.466
Total		284430	12424	100.000

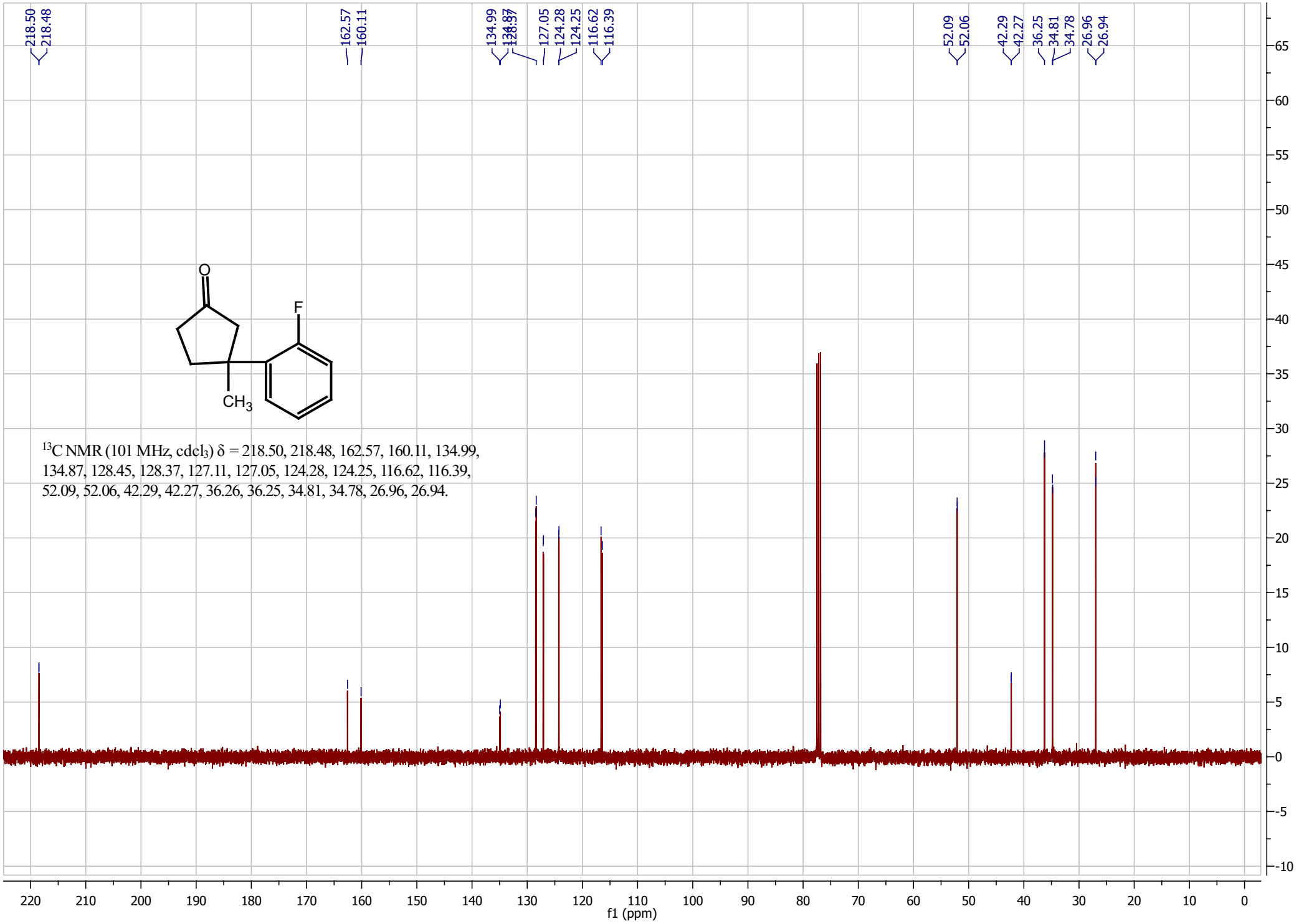
PDA Ch2 225nm

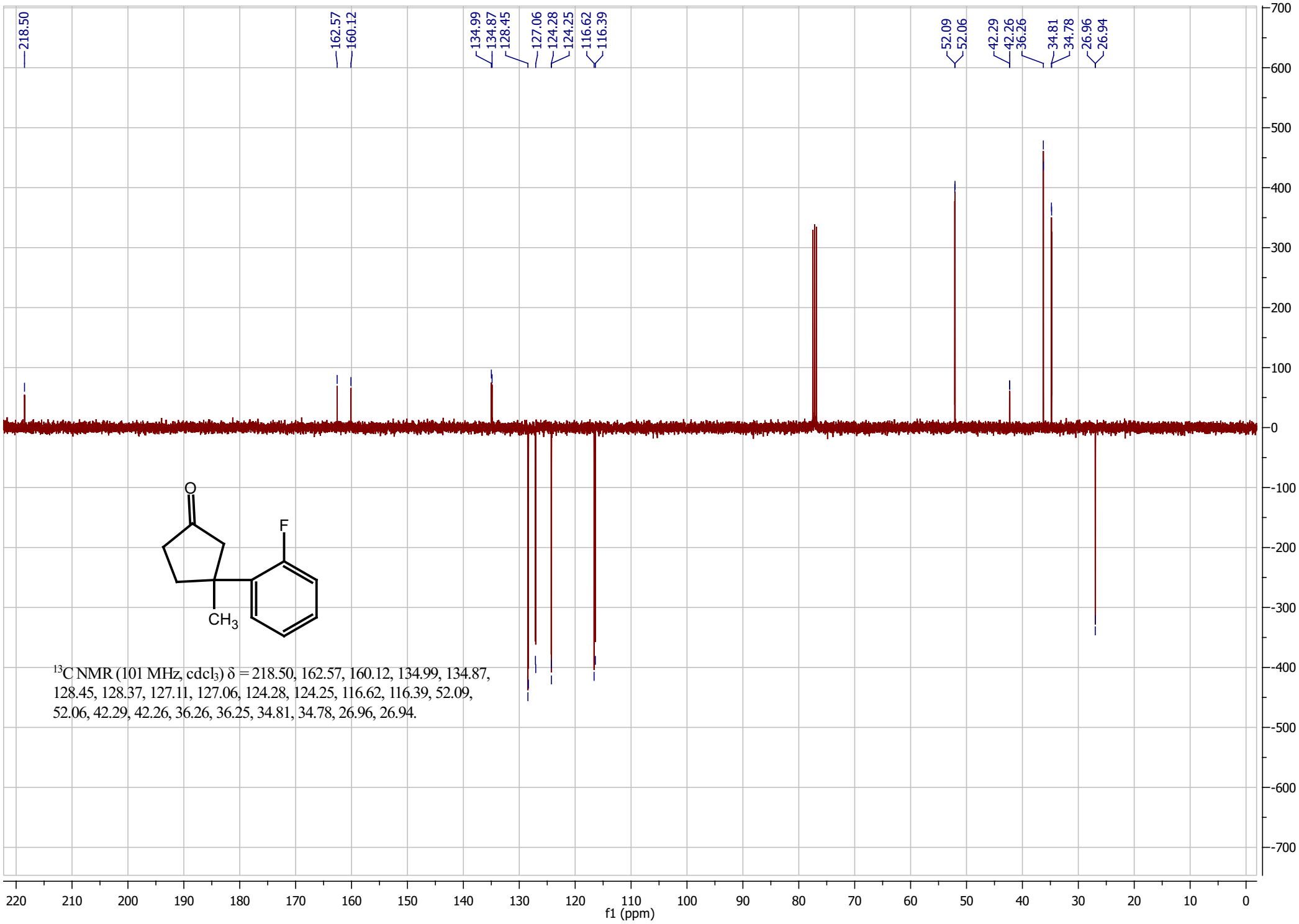
Peak#	Ret. Time	Area	Height	Area%
1	19.095	310700	14575	10.848
2	20.970	2553501	110092	89.152
Total		2864201	124667	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	19.093	787868	36115	10.671
2	20.968	6595612	295730	89.329
Total		7383480	331845	100.000


7.30 7.29 7.28 7.28 7.27 7.26 7.25 7.25 7.24 7.16 7.16 7.14 7.14 7.13 7.12 7.11 7.10 7.09 7.09 7.08 7.08 7.07 7.07 7.06 7.05
2.71 2.66 2.65 2.62 2.61 2.61 2.42 2.41 2.40 2.38 2.38 2.37 2.36
1.44
O
F
CH3
1H NMR (400 MHz, cdcl3) δ = 7.32 – 7.23 (m, 2H), 7.19 – 7.03 (m, 2H), 2.71 – 2.59 (m, 2H), 2.54 – 2.34 (m, 4H), 1.44 (s, 3H).
2.03
1.92
1.98
4.09
3.00
4000
3500
3000
2500
2000
1500
1000
500
0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


218.50
218.48
162.57
160.11
134.99
134.87
128.45
128.37
127.11
127.05
124.28
124.25
116.62
116.39
52.09
52.06
42.29
42.27
36.25
34.81
34.78
26.96
26.94
O
F
CH3
13C NMR (101 MHz, cdcl3) δ = 218.50, 218.48, 162.57, 160.11, 134.99, 134.87, 128.45, 128.37, 127.11, 127.05, 124.28, 124.25, 116.62, 116.39, 52.09, 52.06, 42.29, 42.27, 36.26, 36.25, 34.81, 34.78, 26.96, 26.94.
f1 (ppm)


218.50
162.57
160.12
134.99
134.87
128.45
127.06
124.28
124.25
116.62
116.39
52.09
52.06
42.29
42.26
36.26
34.81
34.78
26.96
26.94
O
F
CH3
13C NMR (101 MHz, cdcl3) δ = 218.50, 162.57, 160.12, 134.99, 134.87, 128.45, 128.37, 127.11, 127.06, 124.28, 124.25, 116.62, 116.39, 52.09, 52.06, 42.29, 42.26, 36.26, 36.25, 34.81, 34.78, 26.96, 26.94.
f1 (ppm)

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: o-fluoro boronic acid RAC AD-H-column		
Sample ID	: o-fluoro boronic acid RAC AD-H-		
Data Filename	: o-fluoro boronic acid RAC AD-H-column.lcd		
Method Filename	: C5 99_1 fl0,5 60 min.lcm		
Batch Filename	: 20131004 (99_1 all column screening).lcb		
Vial #	: 1-81	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 10/11/2013 5:26:44 PM	Acquired by	: System Administrator
Date Processed	: 10/12/2013 1:08:16 PM	Processed by	: System Administrator

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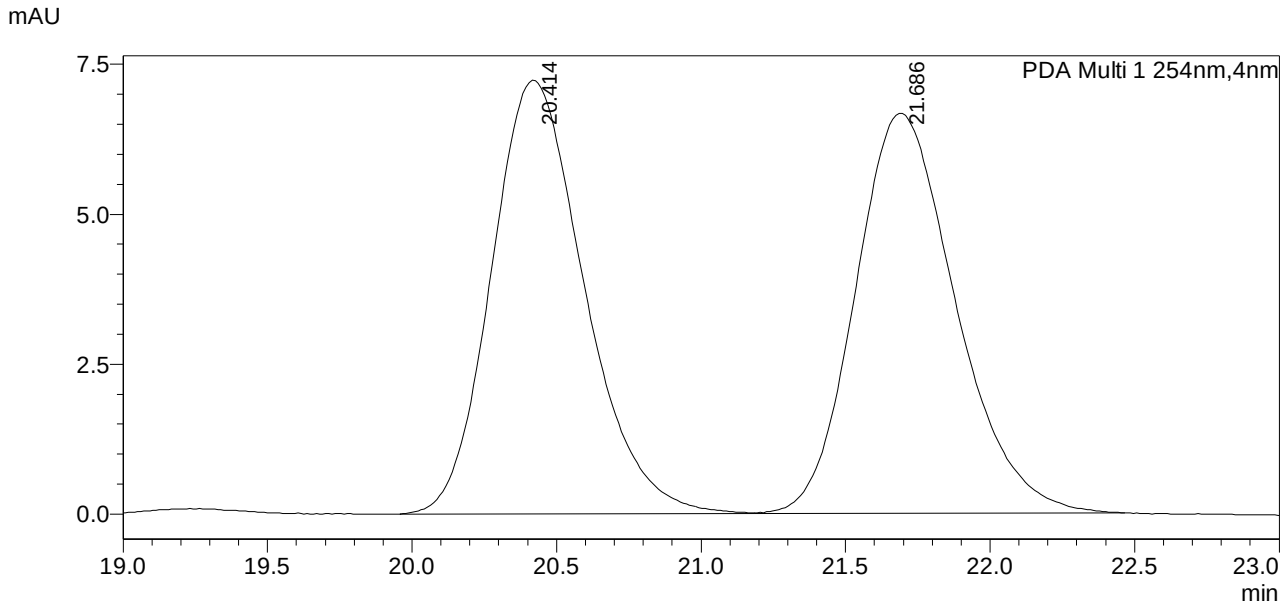

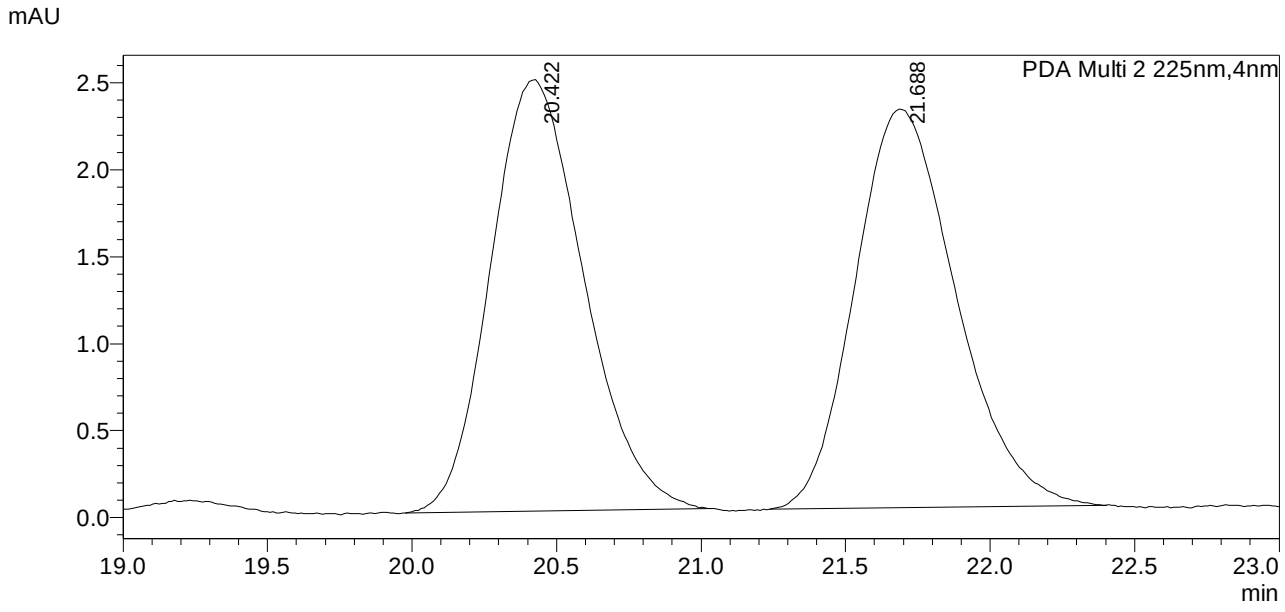

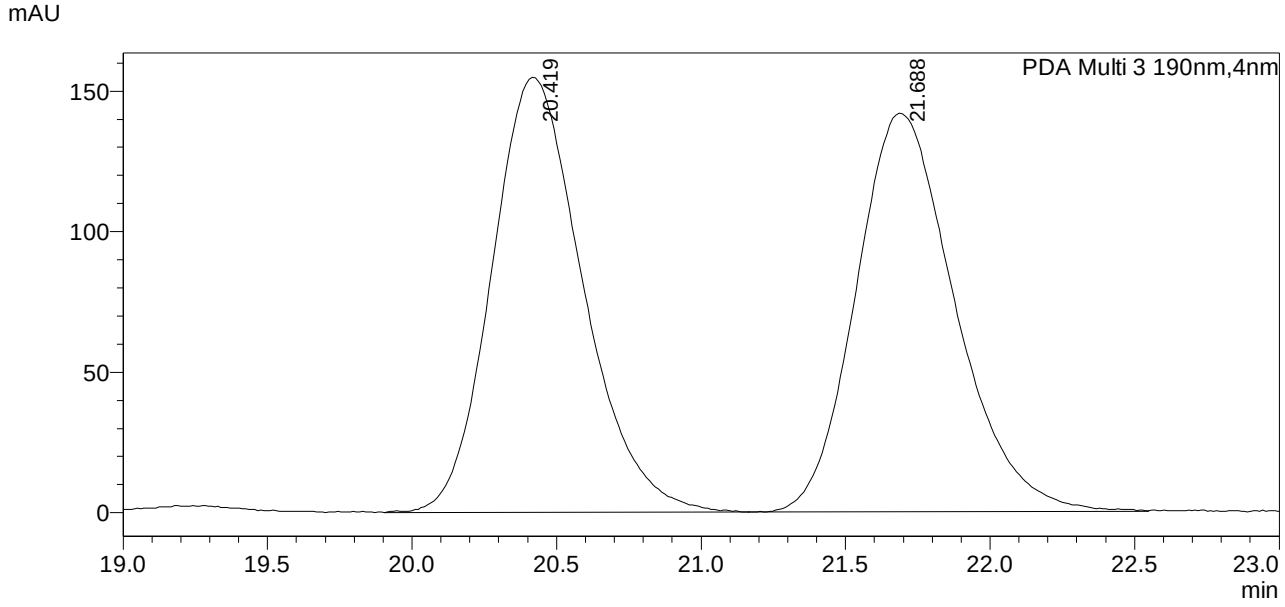

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.414	161608	7228	50.155
2	21.686	160609	6667	49.845
Total		322217	13894	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	20.422	55829	2480	49.958
2	21.688	55923	2293	50.042
Total		111752	4773	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	20.419	3401763	154693	50.156
2	21.688	3380624	141861	49.844
Total		6782386	296554	100.000

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: o-fluoro boronic acid ENT AD-H-column		
Sample ID	: o-fluoro boronic acid RAC AD-H		
Data Filename	: o-fluoro boronic acid ENT AD-H-column.lcd		
Method Filename	: C5 99_1 fl0,5 60 min.lcm		
Batch Filename	: 20131014_JBR.lcb		
Vial #	: 1-82	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
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Date Processed	: 10/15/2013 8:32:01 AM	Processed by	: System Administrator

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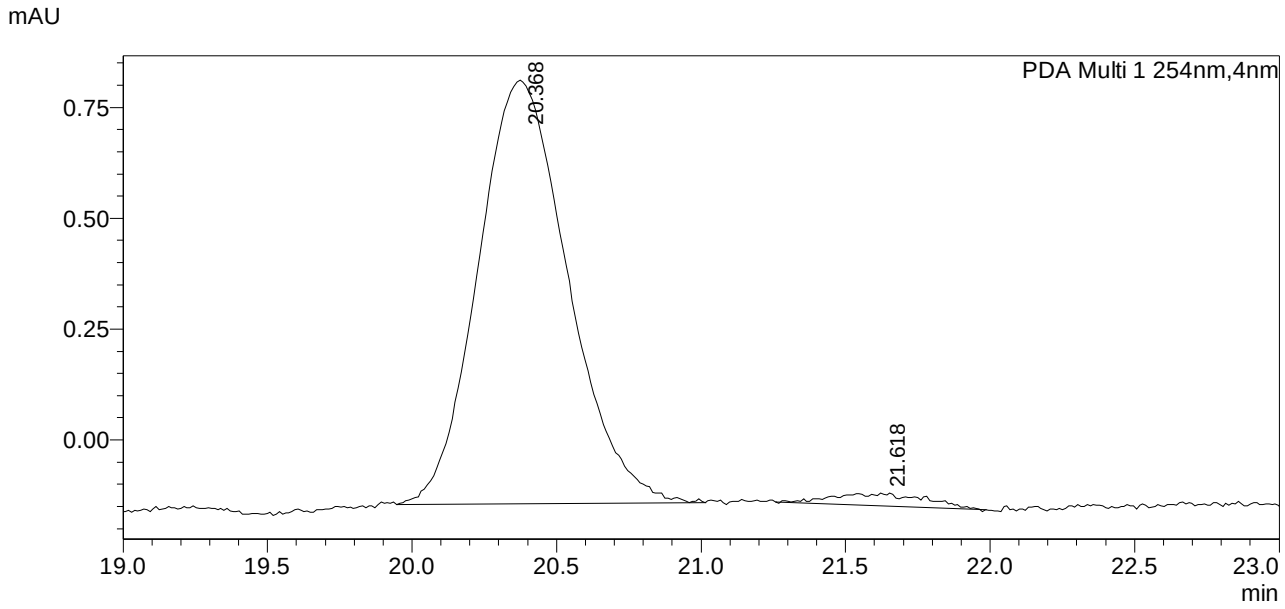
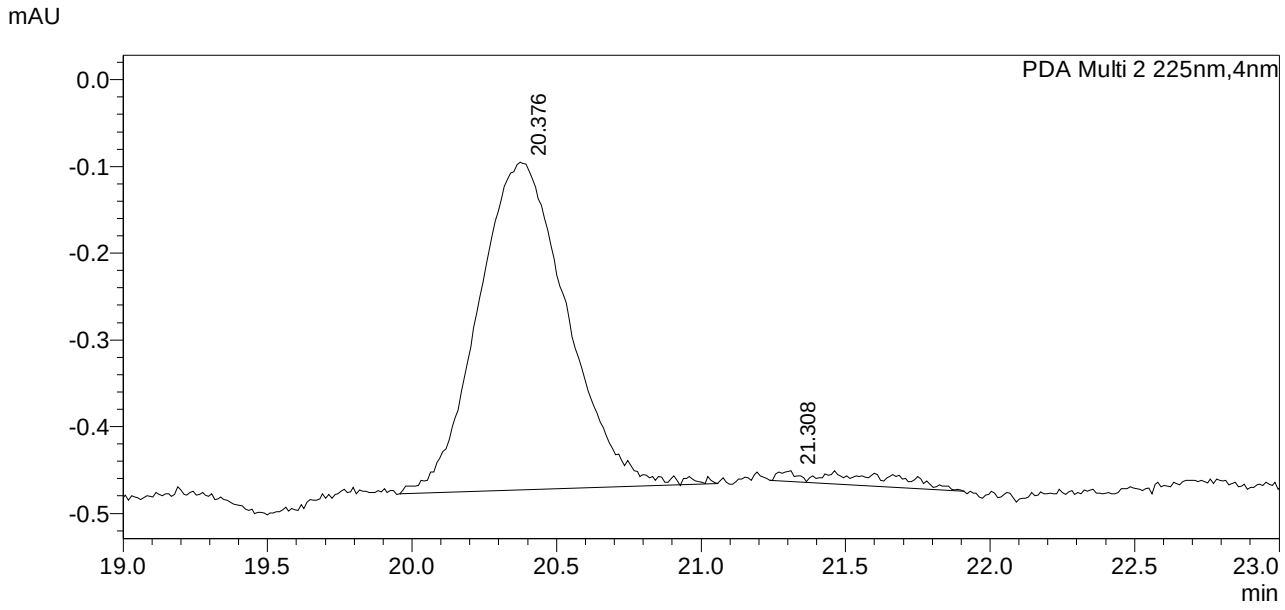
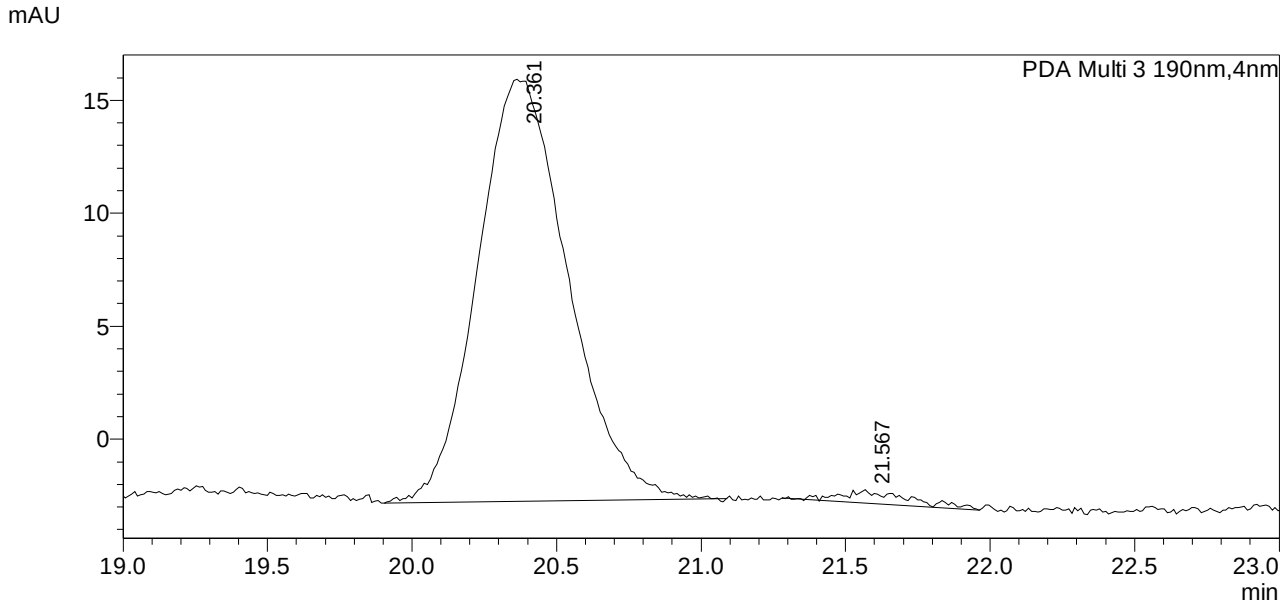






<Peak Table>

PDA Ch1 254nm

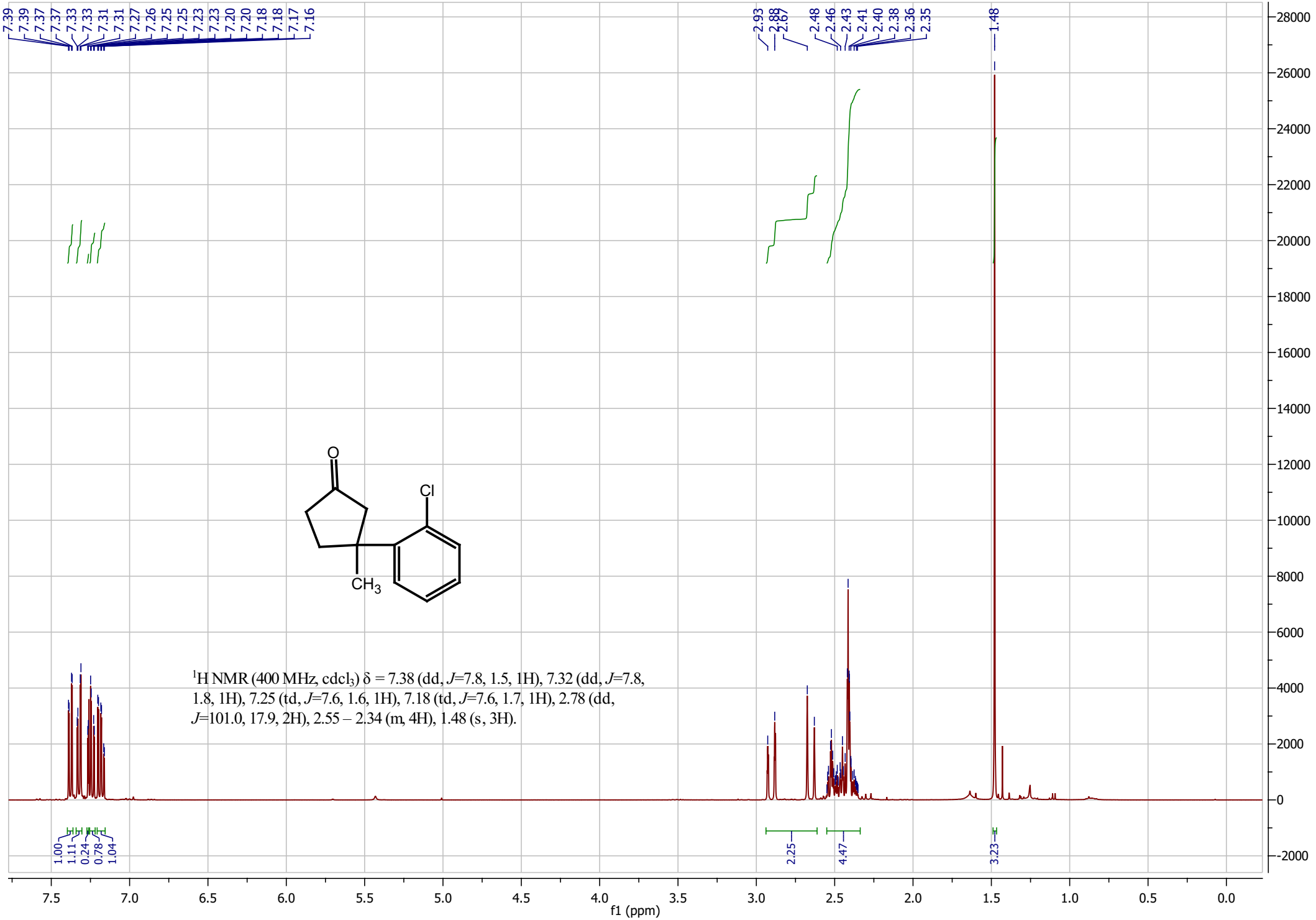
Peak#	Ret. Time	Area	Height	Area%
1	20.368	20685	956	97.199
2	21.618	596	29	2.801
Total		21281	984	100.000

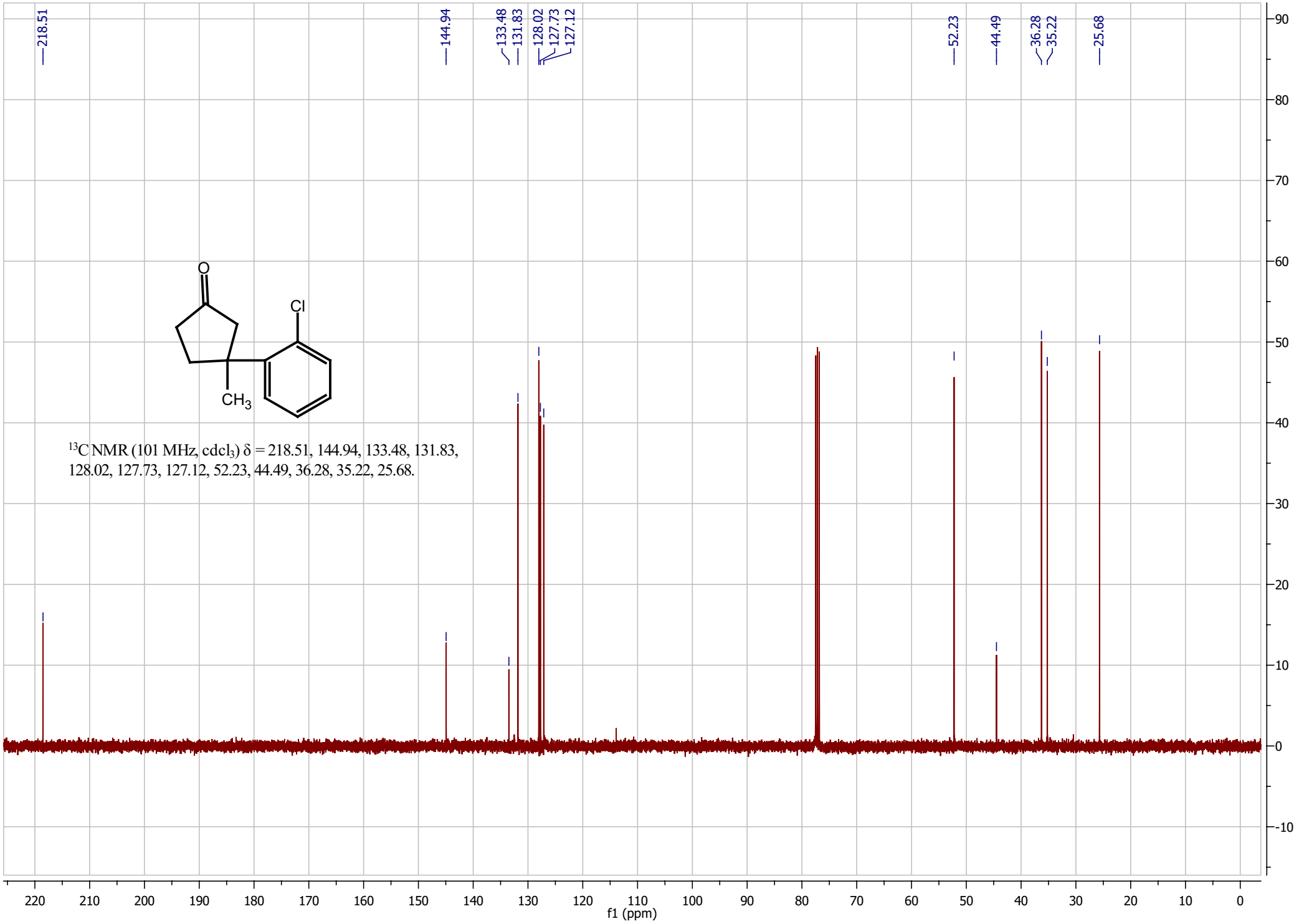
PDA Ch2 225nm

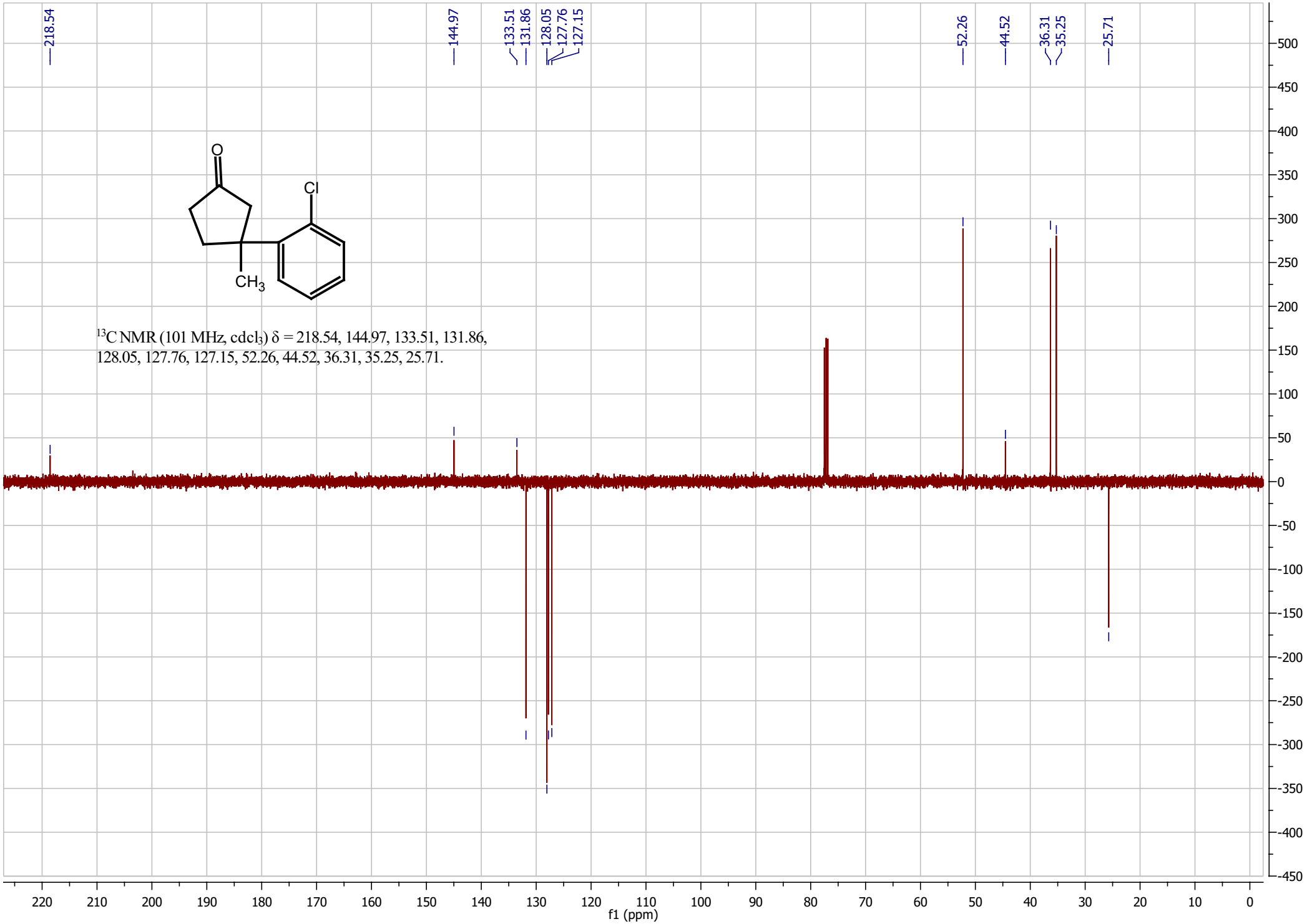
Peak#	Ret. Time	Area	Height	Area%
1	20.376	8098	378	96.296
2	21.308	311	12	3.704
Total		8410	390	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	20.361	407154	18675	97.715
2	21.567	9519	595	2.285
Total		416674	19270	100.000


7.39
7.39
7.37
7.37
7.33
7.33
7.31
7.31
7.27
7.26
7.25
7.25
7.23
7.23
7.20
7.20
7.18
7.18
7.17
7.16
2.93
2.88
2.87
2.48
2.46
2.43
2.41
2.40
2.38
2.36
2.35
1.48
O
Cl
CH3
1H NMR (400 MHz, cdcl3) δ = 7.38 (dd, J=7.8, 1.5, 1H), 7.32 (dd, J=7.8, 1.8, 1H), 7.25 (td, J=7.6, 1.6, 1H), 7.18 (td, J=7.6, 1.7, 1H), 2.78 (dd, J=101.0, 17.9, 2H), 2.55 – 2.34 (m, 4H), 1.48 (s, 3H).
1.00
1.11
0.24
0.78
1.04
2.25
4.47
3.23
f1 (ppm)


218.51
144.94
133.48
131.83
128.02
127.73
127.12
52.23
44.49
36.28
35.22
25.68
O
Cl
CH3
13C NMR (101 MHz, cdcl3) δ = 218.51, 144.94, 133.48, 131.83,
128.02, 127.73, 127.12, 52.23, 44.49, 36.28, 35.22, 25.68.
f1 (ppm)


218.54
144.97
133.51
131.86
128.05
127.76
127.15
52.26
44.52
36.31
35.25
25.71
O
Cl
CH3
13C NMR (101 MHz, cdcl3) δ = 218.54, 144.97, 133.51, 131.86,
128.05, 127.76, 127.15, 52.26, 44.52, 36.31, 35.25, 25.71.
f1 (ppm)

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: o-chloro boronic acid RAC OD-H-column		
Sample ID	: o-chloro boronic acid RAC OD-H-		
Data Filename	: o-chloro boronic acid RAC OD-H-column.lcd		
Method Filename	: C2 99_1fl0,5 60 min.lcm		
Batch Filename	: 20131004 (99_1 all column screening).lcb		
Vial #	: 1-79	Sample Type	: Unknown
Injection Volume	: 3 uL	Level	: 1
Date Acquired	: 10/12/2013 5:09:39 PM	Acquired by	: System Administrator
Date Processed	: 10/13/2013 12:54:32 PM	Processed by	: System Administrator

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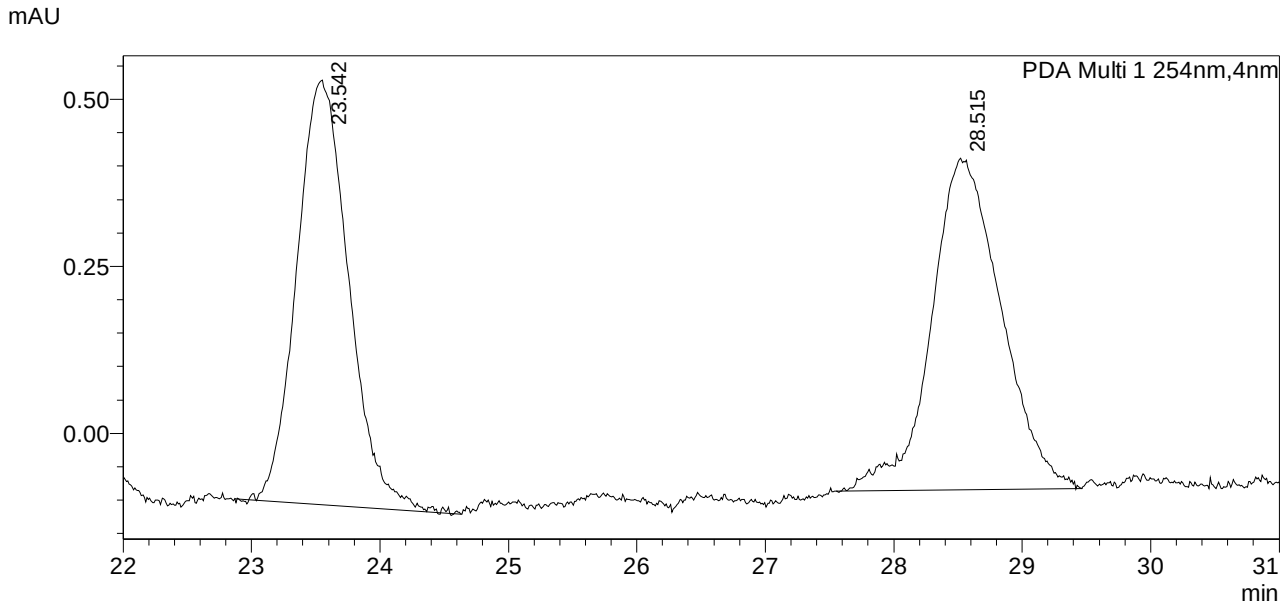

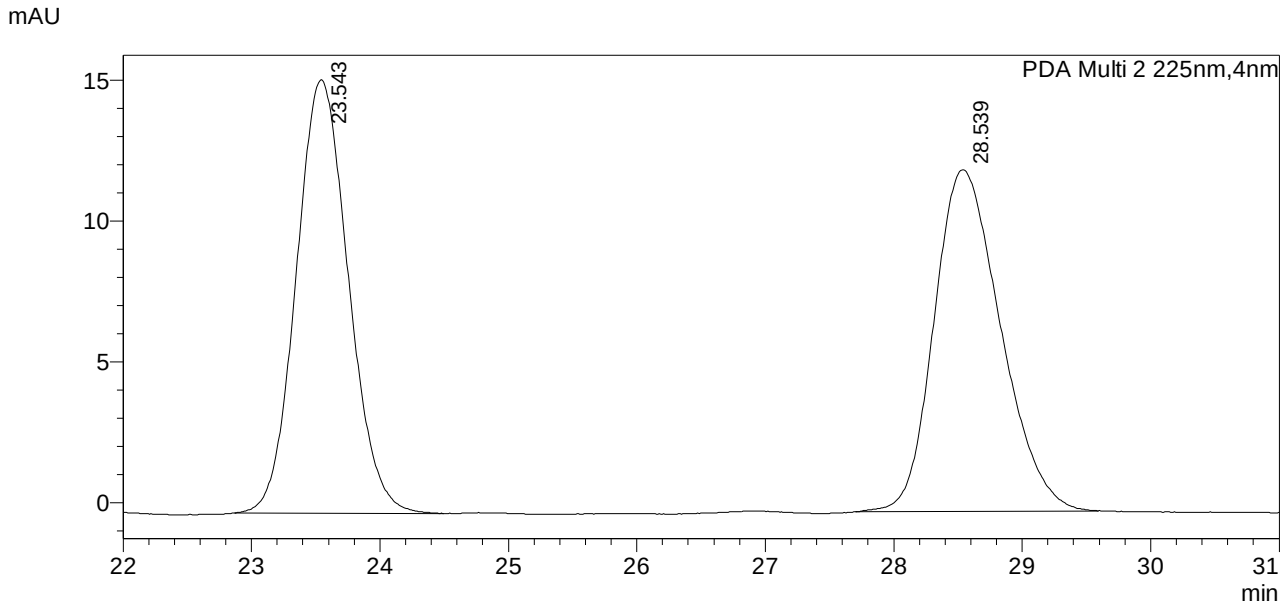

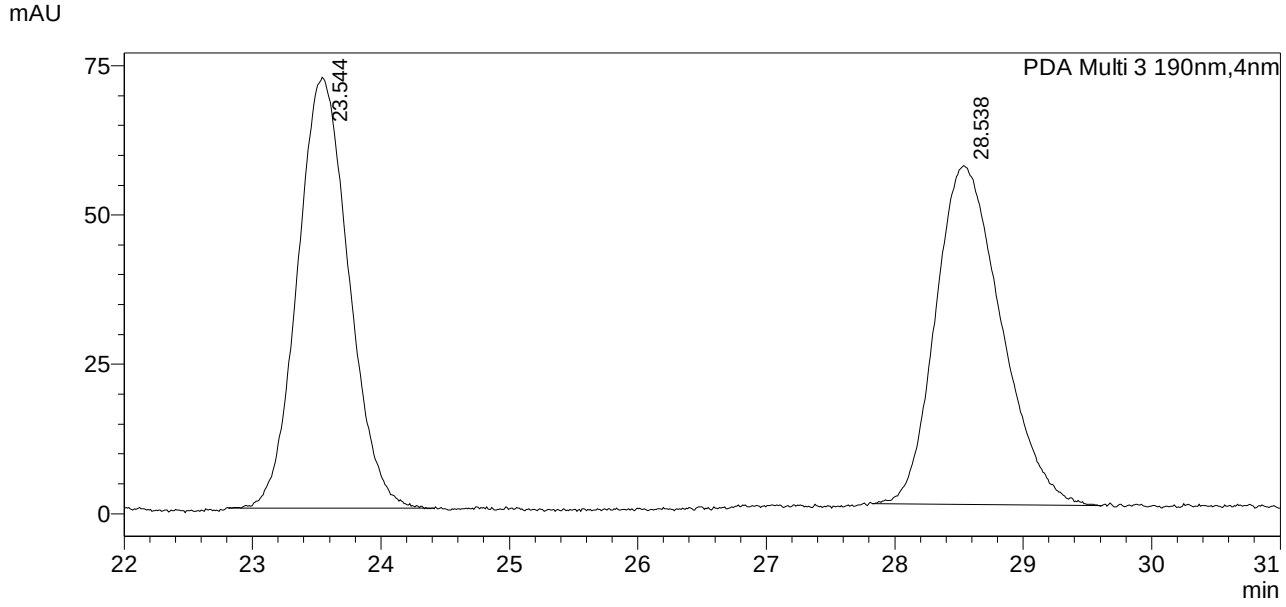

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23.542	17959	636	48.885
2	28.515	18778	496	51.115
Total		36738	1132	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	23.543	433955	15388	49.869
2	28.539	436239	12133	50.131
Total		870194	27521	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	23.544	2003295	72121	49.823
2	28.538	2017552	56701	50.177
Total		4020847	128822	100.000

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: o-chloro boronic acid ENT OD-H-column		
Sample ID	: o-chloro boronic acid ENT OD-H-		
Data Filename	: o-chloro boronic acid ENT OD-H-column.lcd		
Method Filename	: C2 99_1fl0,5 60 min.lcm		
Batch Filename	: 20131014_JBR.lcb		
Vial #	: 1-83	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 10/14/2013 6:20:46 PM	Acquired by	: System Administrator
Date Processed	: 11/7/2013 6:12:52 PM	Processed by	: System Administrator

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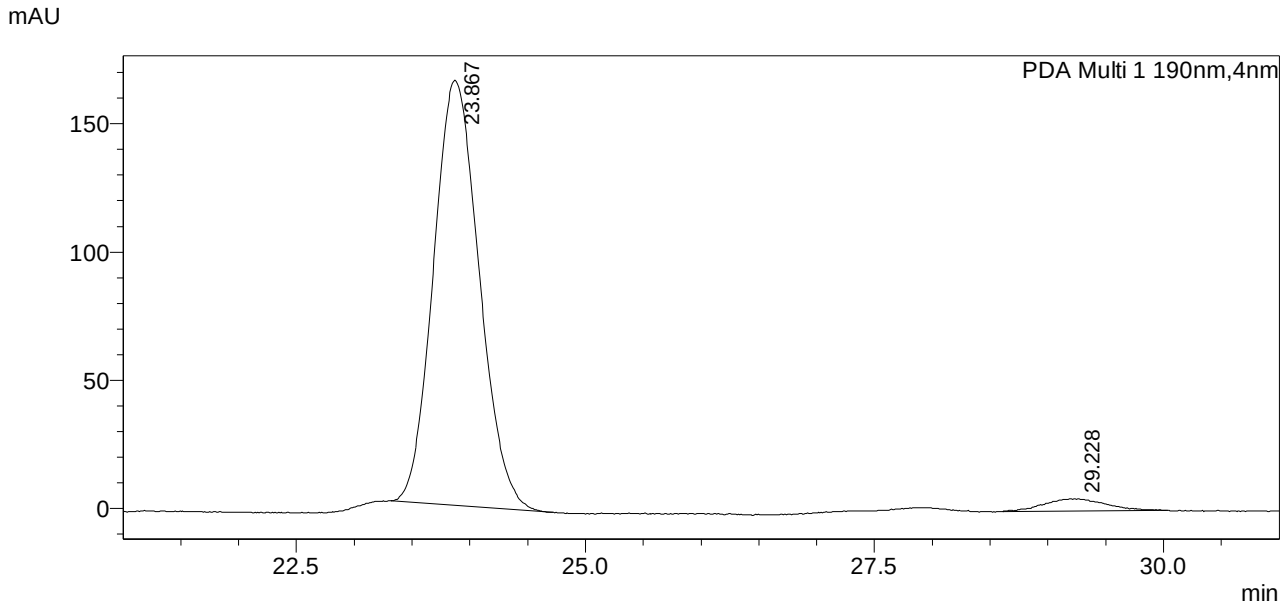
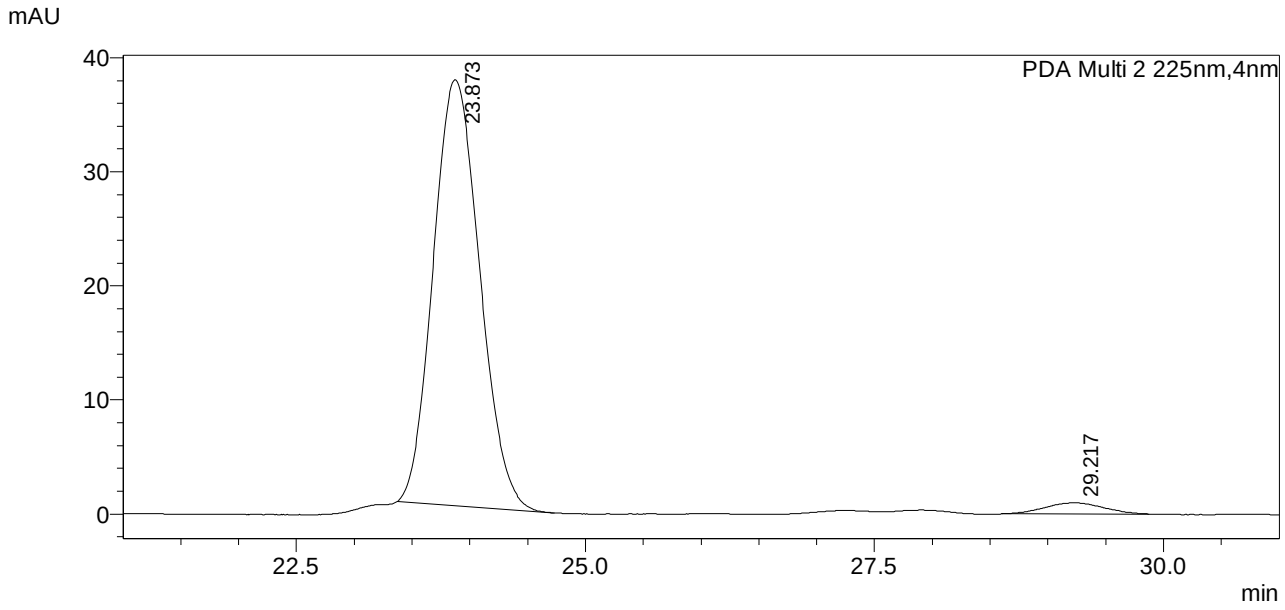
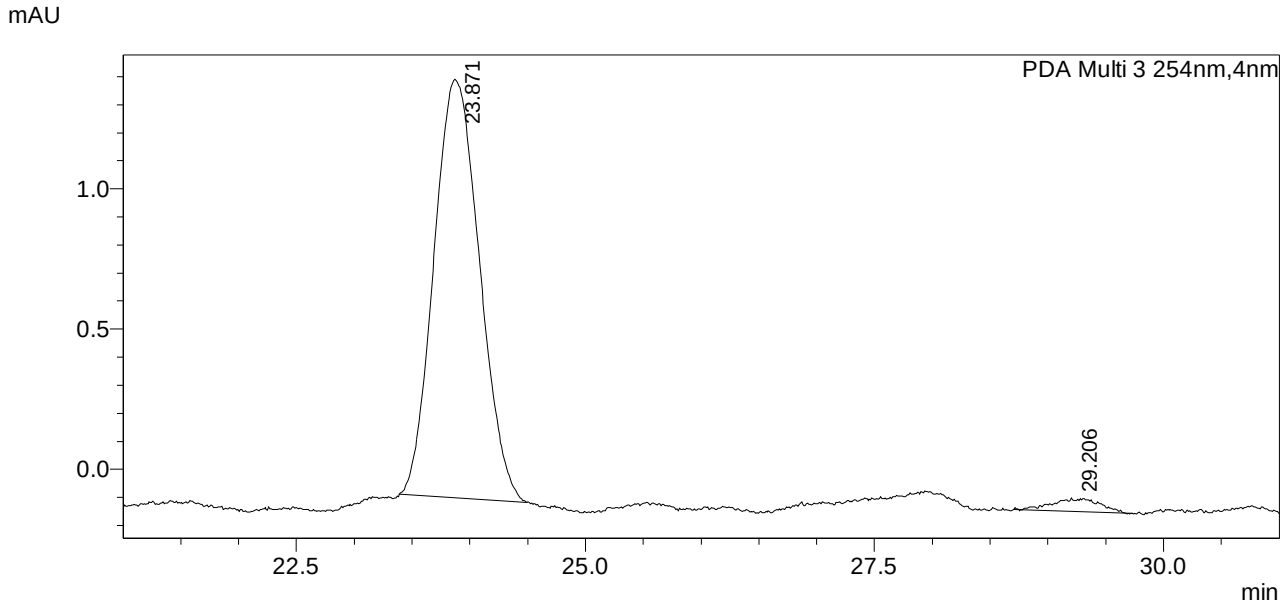






<Peak Table>

PDA Ch1 190nm

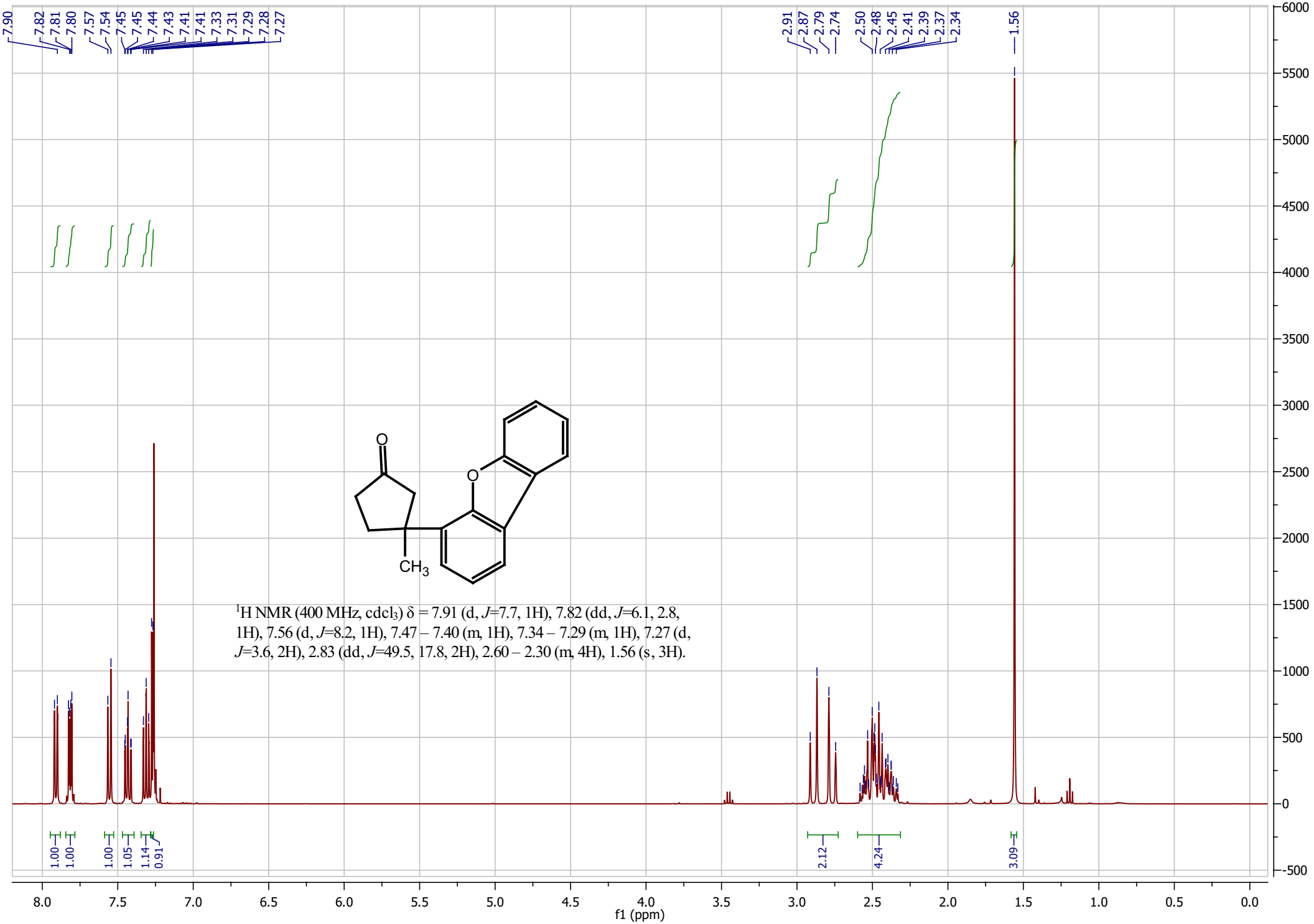
Peak#	Ret. Time	Area	Height	Area%
1	23.867	4567881	165837	96.262
2	29.228	177373	4788	3.738
Total		4745254	170625	100.000

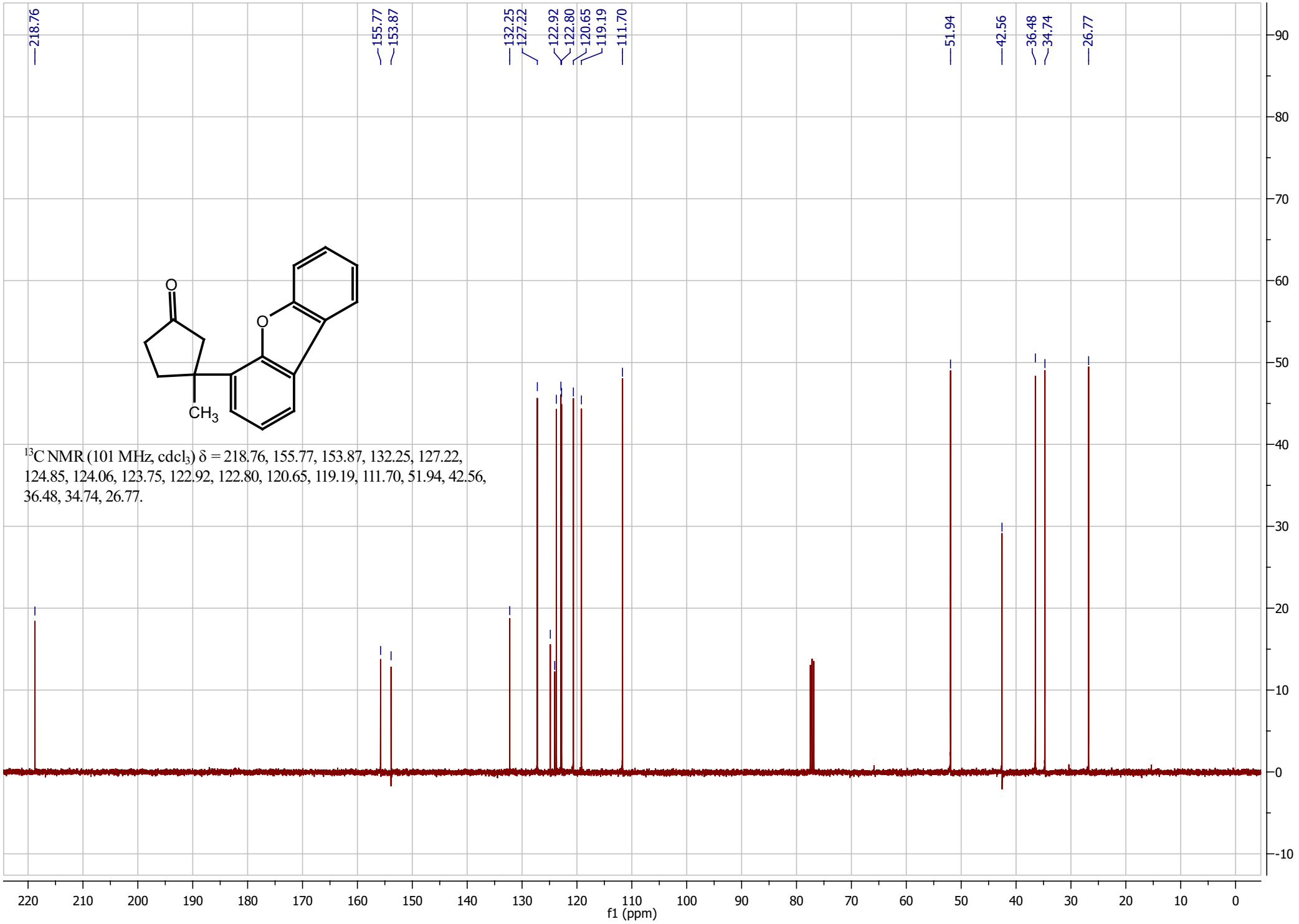
PDA Ch2 225nm

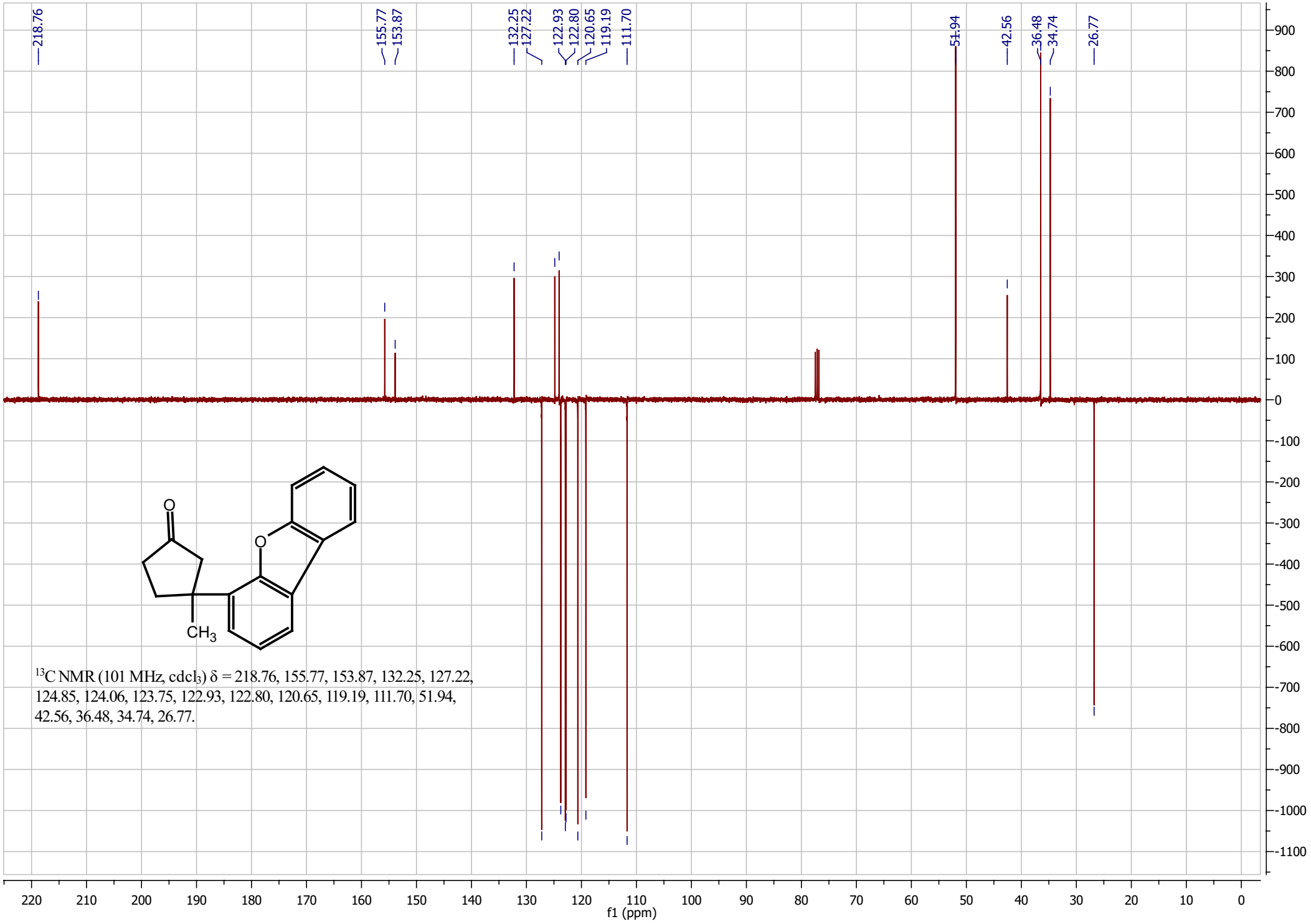
Peak#	Ret. Time	Area	Height	Area%
1	23.873	1046863	37353	96.830
2	29.217	34270	974	3.170
Total		1081132	38327	100.000

PDA Ch3 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23.871	40910	1491	96.989
2	29.206	1270	47	3.011
Total		42181	1538	100.000


7.90
7.82
7.81
7.80
7.57
7.54
7.45
7.45
7.44
7.43
7.41
7.41
7.33
7.31
7.29
7.28
7.27
2.91
2.87
2.79
2.74
2.50
2.48
2.45
2.41
2.39
2.37
2.34
1.56
O
O
CH3
1H NMR (400 MHz, cdcl3) δ = 7.91 (d, J=7.7, 1H), 7.82 (dd, J=6.1, 2.8, 1H), 7.56 (d, J=8.2, 1H), 7.47 – 7.40 (m, 1H), 7.34 – 7.29 (m, 1H), 7.27 (d, J=3.6, 2H), 2.83 (dd, J=49.5, 17.8, 2H), 2.60 – 2.30 (m, 4H), 1.56 (s, 3H).
1.00
1.00
1.00
1.05
1.14
0.91
2.12
4.24
3.09
f1 (ppm)


218.76
155.77
153.87
132.25
127.22
122.92
122.80
120.65
119.19
111.70
51.94
42.56
36.48
34.74
26.77
O
O
CH3
13C NMR (101 MHz, cdcl3) δ = 218.76, 155.77, 153.87, 132.25, 127.22, 124.85, 124.06, 123.75, 122.92, 122.80, 120.65, 119.19, 111.70, 51.94, 42.56, 36.48, 34.74, 26.77.
f1 (ppm)



^{13}C NMR (101 MHz, cdcl$_3$) δ = 218.76, 155.77, 153.87, 132.25, 127.22, 124.85, 124.06, 123.75, 122.93, 122.80, 120.65, 119.19, 111.70, 51.94, 42.56, 36.48, 34.74, 26.77.

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: benzofuranboronic acid RAC AD-H-column		
Sample ID	: benzofuranboronic acid RAC AD-H		
Data Filename	: benzofuranboronic acid RAC AD-H-column.lcd		
Method Filename	: C5 99_1 fl0,5 60 min.lcm		
Batch Filename	: 20131004 (99_1 all column screening).lcb		
Vial #	: 1-80	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 10/11/2013 11:50:17 PM	Acquired by	: System Administrator
Date Processed	: 10/12/2013 1:04:34 PM	Processed by	: System Administrator

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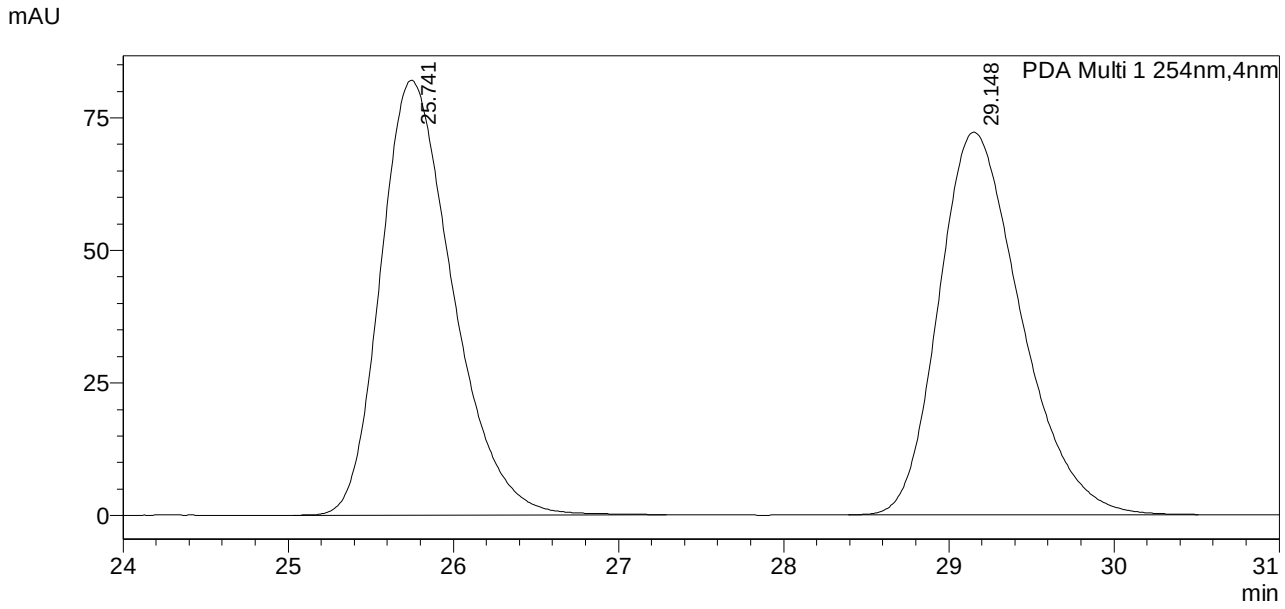
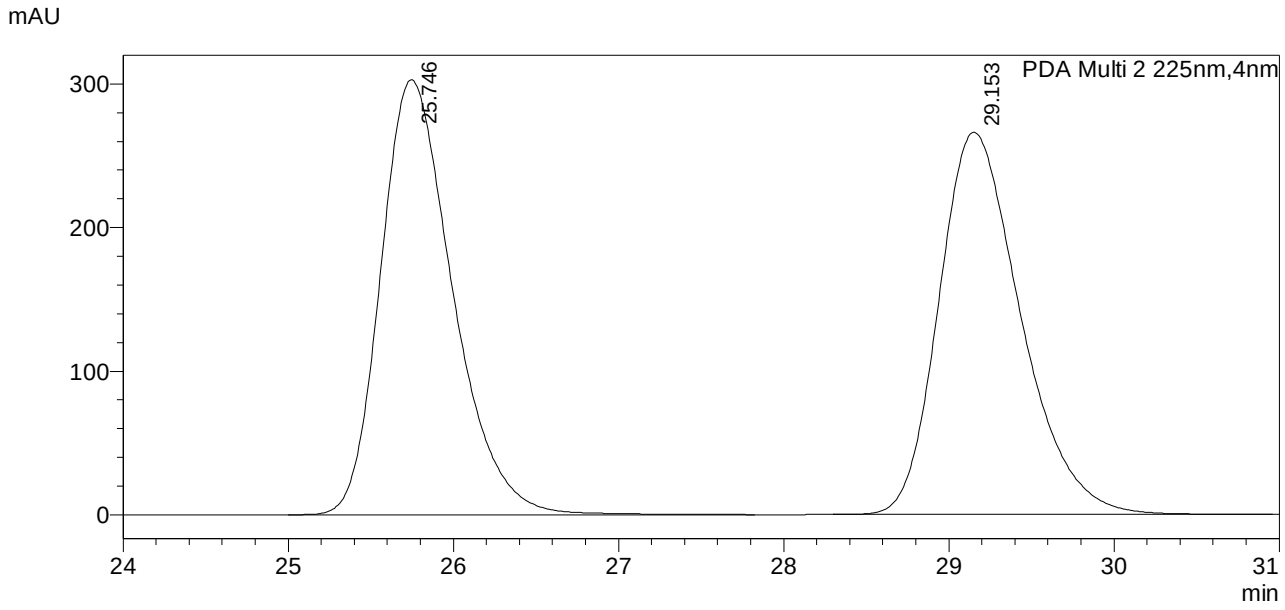
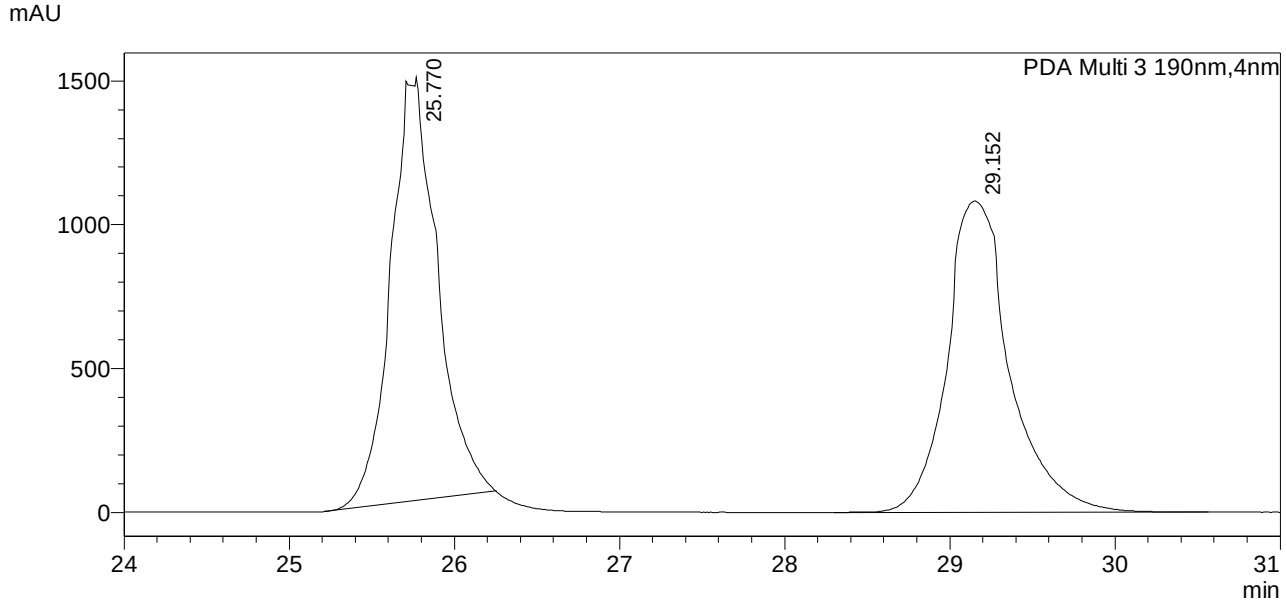






<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	25.741	2492075	81990	50.010
2	29.148	2491069	72140	49.990
Total		4983144	154130	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	25.746	9166376	302832	50.037
2	29.153	9152681	266119	49.963
Total		18319057	568952	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	25.770	29079918	1470811	50.420
2	29.152	28595726	1083412	49.580
Total		57675645	2554222	100.000

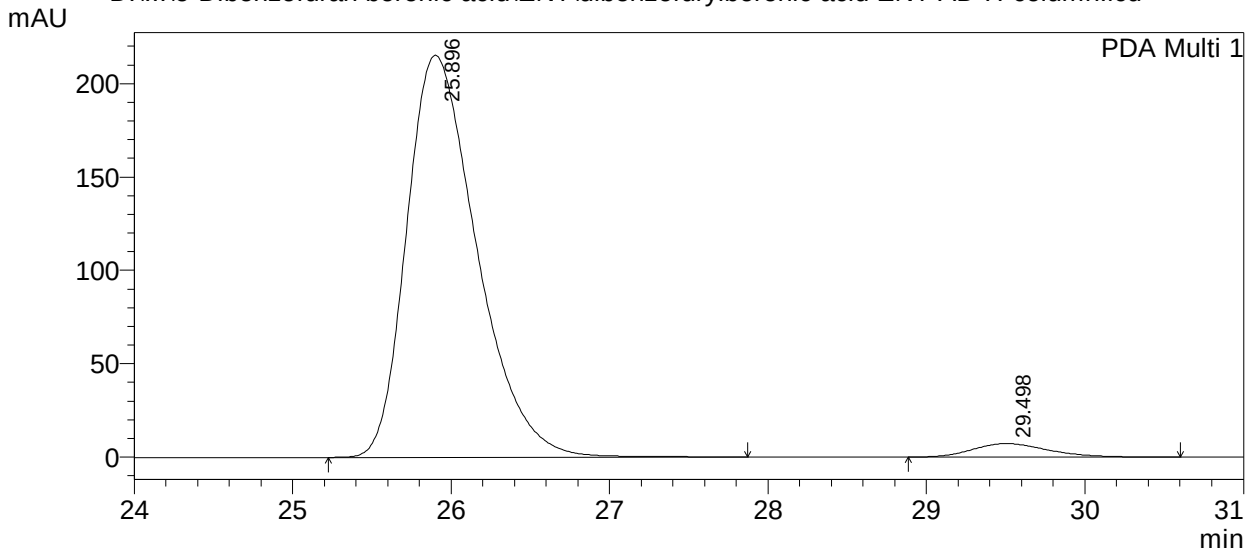
==== Shimadzu LCsolution Analysis Report ====

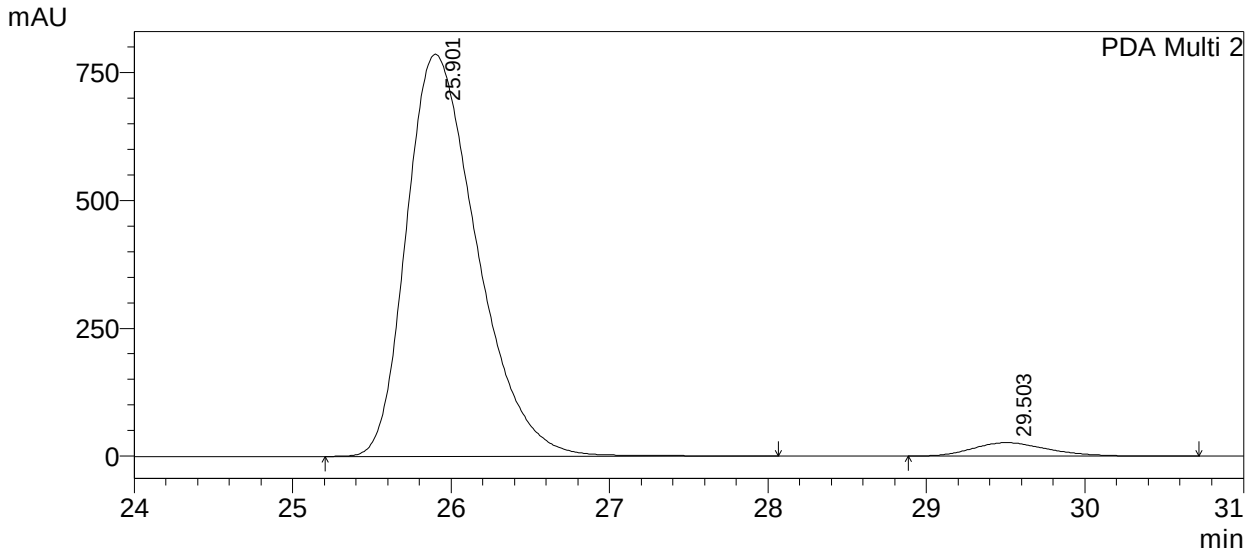
D:\...\o-Dibenzofuran boronic acid\ENT\dibenzofurylboronic acid ENT AD-H-column.lcd

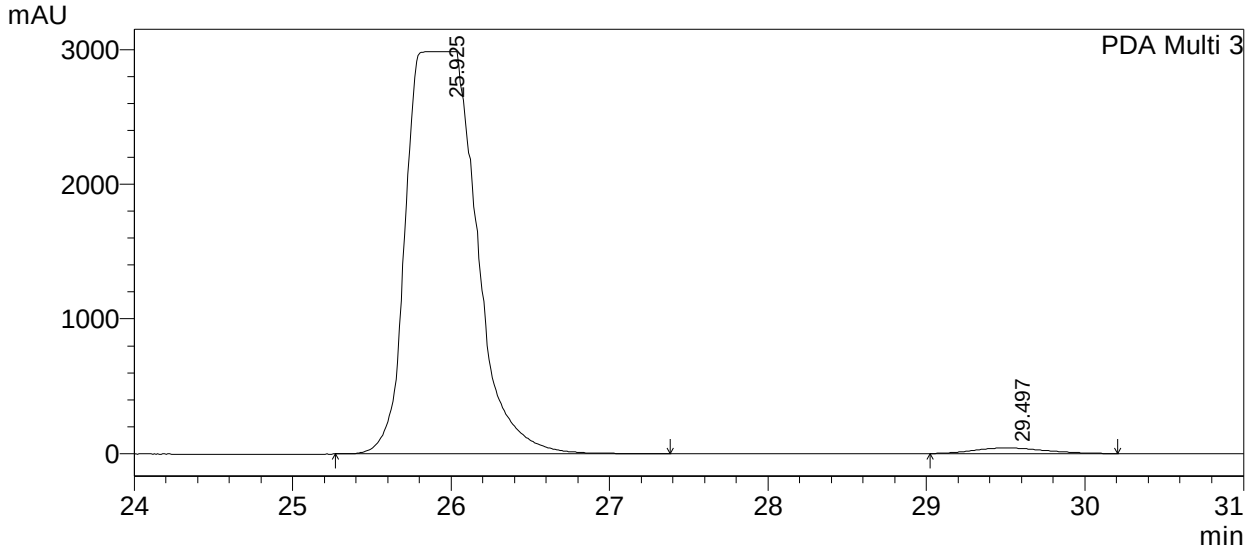
Acquired by	: System Administrator
Sample Name	: dibenzofurylboronic acid ENT AD-H-column
Sample ID	: dibenzofurylboronic acid ENT AD
Tray#	: 1
Vail #	: 83
Injection Volume	: 3 uL
Data File Name	: dibenzofurylboronic acid ENT AD-H-column.lcd
Method File Name	: C5 99_1 fl0,5 60 min.lcm
Batch File Name	: 20131015_JBR.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 10/15/2013 7:19:28 PM
Data Processed	: 10/16/2013 8:38:45 AM

<Chromatogram>

D:\...\o-Dibenzofuran boronic acid\ENT\dibenzofurylboronic acid ENT AD-H-column.lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

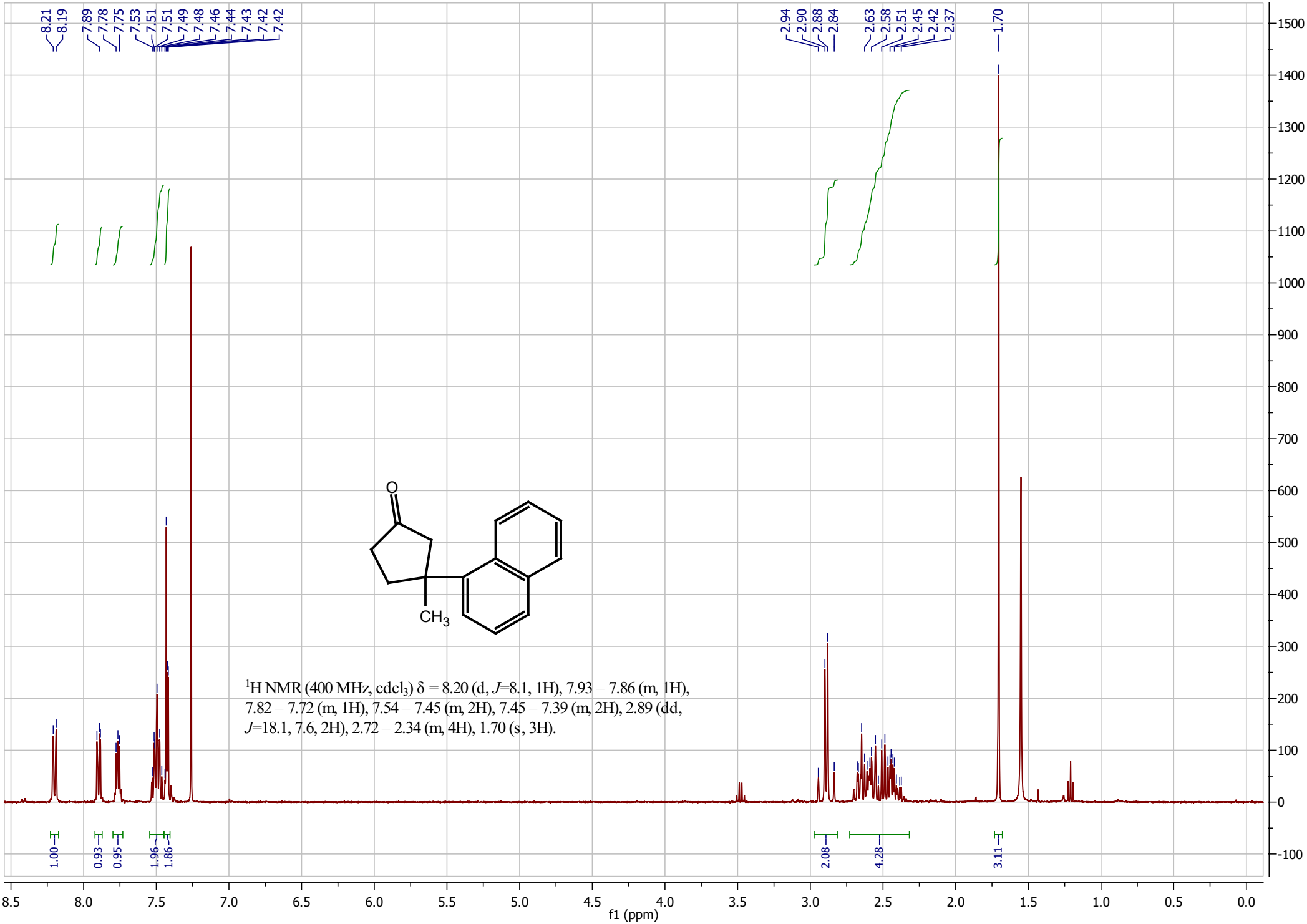
Peak#	Ret. Time	Area	Height	Area%
1	25.896	6632826	215336	96.497
2	29.498	240759	7259	3.503
Total		6873586	222595	100.000

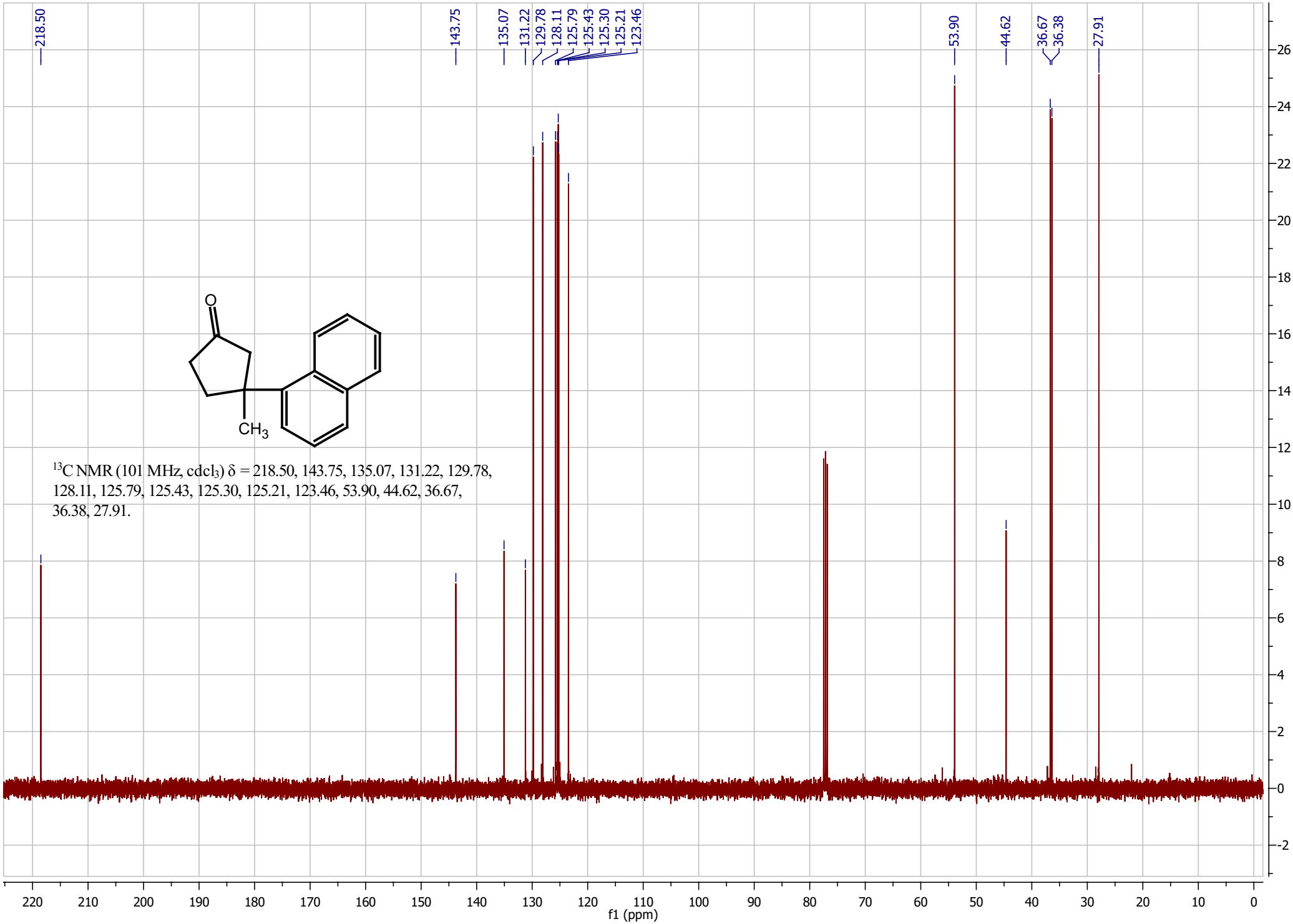
PDA Ch2 225nm

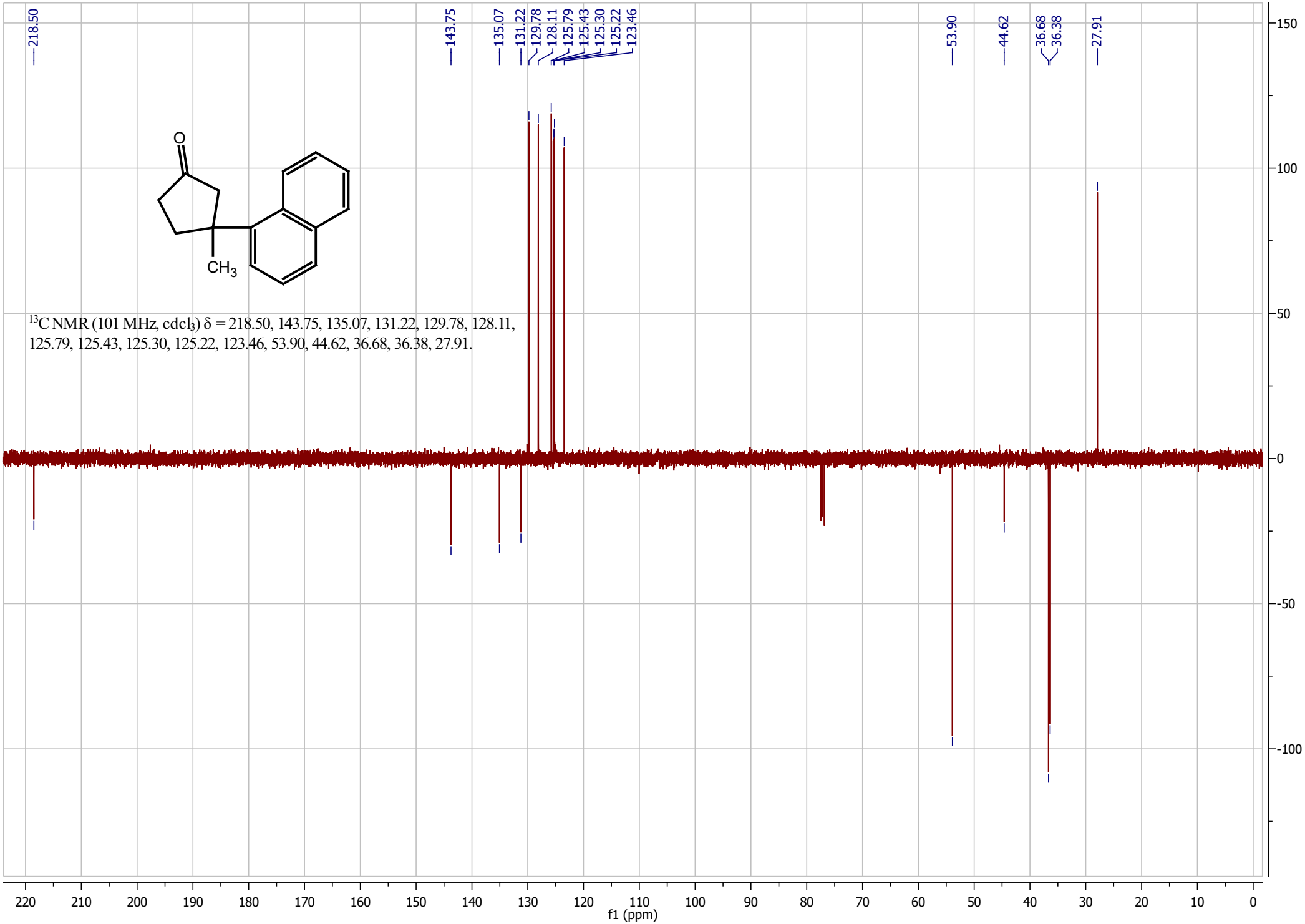
Peak#	Ret. Time	Area	Height	Area%
1	25.901	24320592	786683	96.545
2	29.503	870301	26219	3.455
Total		25190893	812903	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	25.925	90084457	2983522	98.578
2	29.497	1299118	41876	1.422
Total		91383575	3025398	100.000


8.21
8.19
7.89
7.78
7.75
7.53
7.51
7.51
7.49
7.48
7.46
7.44
7.43
7.42
7.42
2.94
2.90
2.88
2.84
2.63
2.58
2.51
2.45
2.42
2.37
1.70
O
CH3
1H NMR (400 MHz, cdcl3) δ = 8.20 (d, J=8.1, 1H), 7.93 – 7.86 (m, 1H), 7.82 – 7.72 (m, 1H), 7.54 – 7.45 (m, 2H), 7.45 – 7.39 (m, 2H), 2.89 (dd, J=18.1, 7.6, 2H), 2.72 – 2.34 (m, 4H), 1.70 (s, 3H).
1.00
0.93
0.95
1.96
1.86
2.08
4.28
3.11
f1 (ppm)


218.50
143.75
135.07
131.22
129.78
128.11
125.79
125.43
125.30
125.21
123.46
53.90
44.62
36.67
36.38
27.91
O
CH3
13C NMR (101 MHz, cdcl3) δ = 218.50, 143.75, 135.07, 131.22, 129.78, 128.11, 125.79, 125.43, 125.30, 125.21, 123.46, 53.90, 44.62, 36.67, 36.38, 27.91.
f1 (ppm)


218.50
143.75
135.07
131.22
129.78
128.11
125.79
125.43
125.30
125.22
123.46
53.90
44.62
36.68
36.38
27.91
O
CH3
13C NMR (101 MHz, cdcl3) δ = 218.50, 143.75, 135.07, 131.22, 129.78, 128.11,
125.79, 125.43, 125.30, 125.22, 123.46, 53.90, 44.62, 36.68, 36.38, 27.91.
150
100
50
0
-50
-100
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

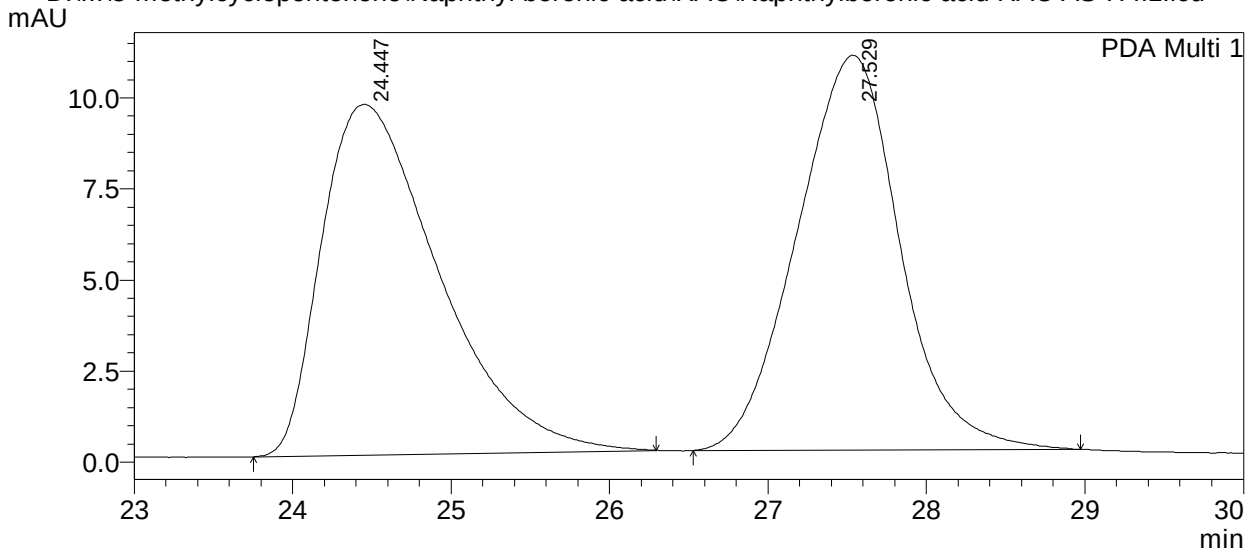
==== Shimadzu LCsolution Analysis Report ====

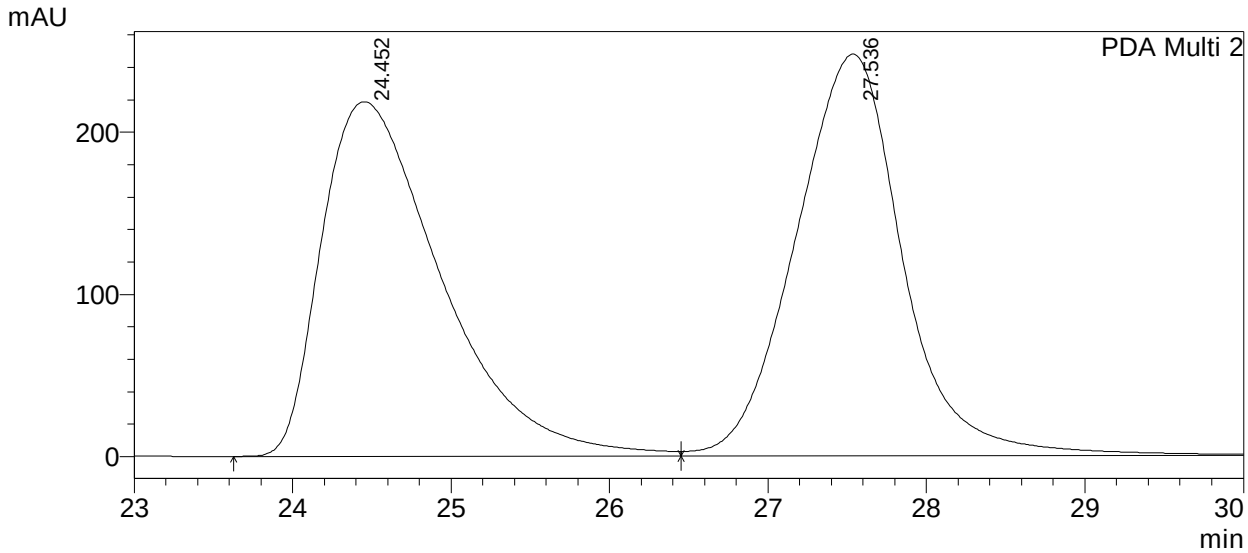
D:\...\3-methylcyclopentenone\Naphthyl boronic acid\RAC\Naphthylboronic acid RAC AS-H fl1.lcd

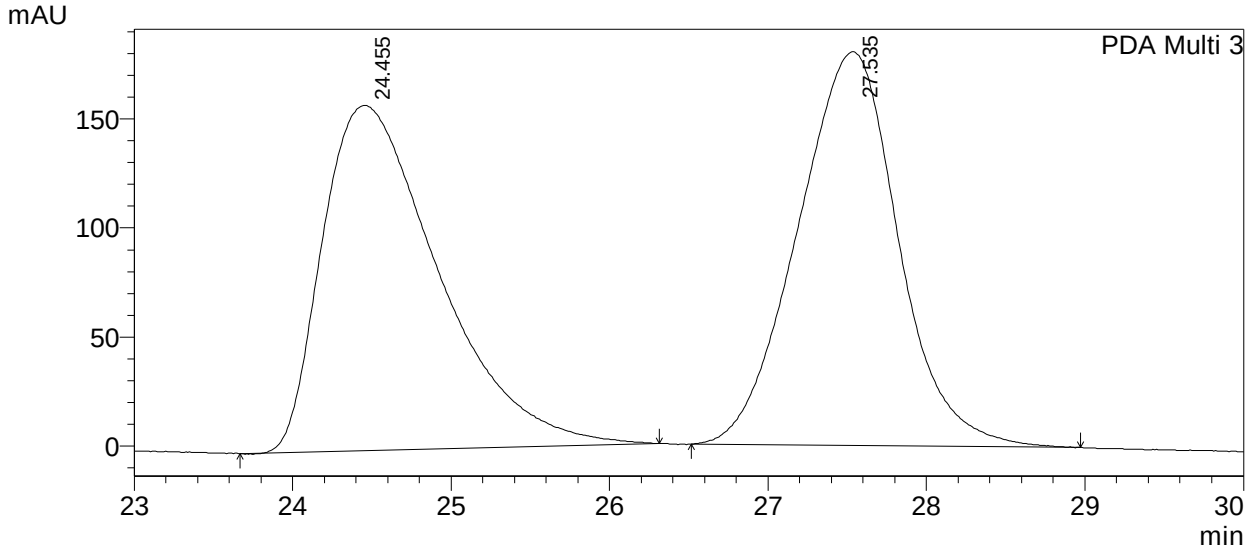
Acquired by	: System Administrator
Sample Name	: Naphthylboronic acid RAC
Sample ID	: Naphthylboronic acid RAC
Tray#	: 1
Vail #	: 79
Injection Volume	: 2 uL
Data File Name	: Naphthylboronic acid RAC AS-H fl1.lcd
Method File Name	: C4 99.5_0.5 fl0,5 70 min.lcm
Batch File Name	: 20131019_JBR.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 10/22/2013 5:24:57 PM
Data Processed	: 10/23/2013 10:20:21 AM

<Chromatogram>

D:\...\3-methylcyclopentenone\Naphthyl boronic acid\RAC\Naphthylboronic acid RAC AS-H fl1.lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	24.447	495868	9628	50.343
2	27.529	489120	10836	49.657
Total		984989	20463	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	24.452	11514522	218710	49.612
2	27.536	11694668	247814	50.388
Total		23209190	466524	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	24.455	8075682	158290	50.362
2	27.535	7959575	180345	49.638
Total		16035257	338636	100.000

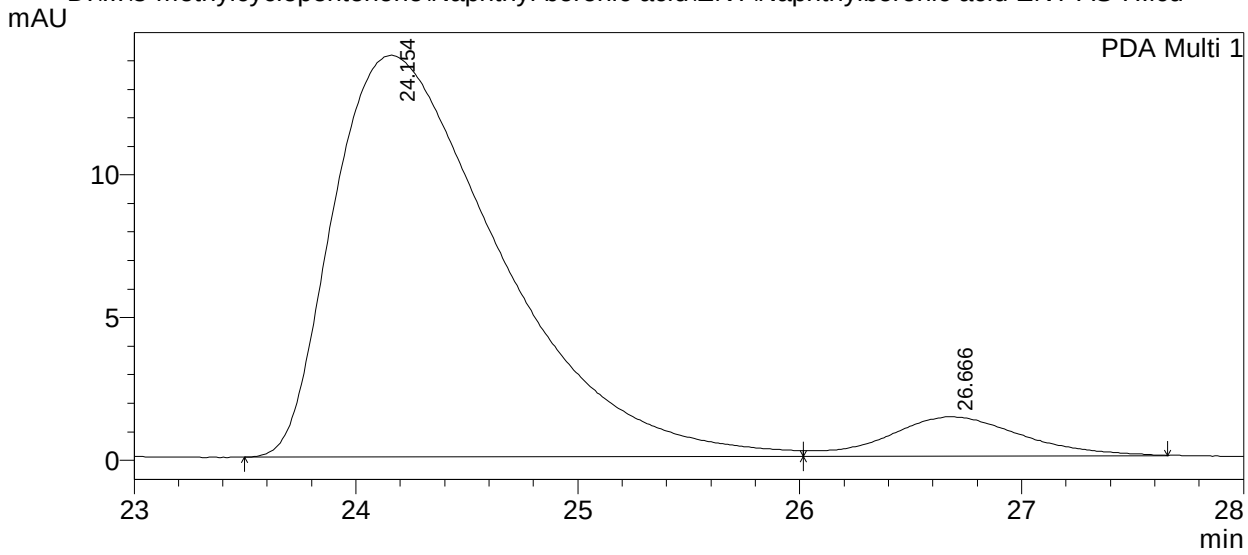
==== Shimadzu LCsolution Analysis Report ====

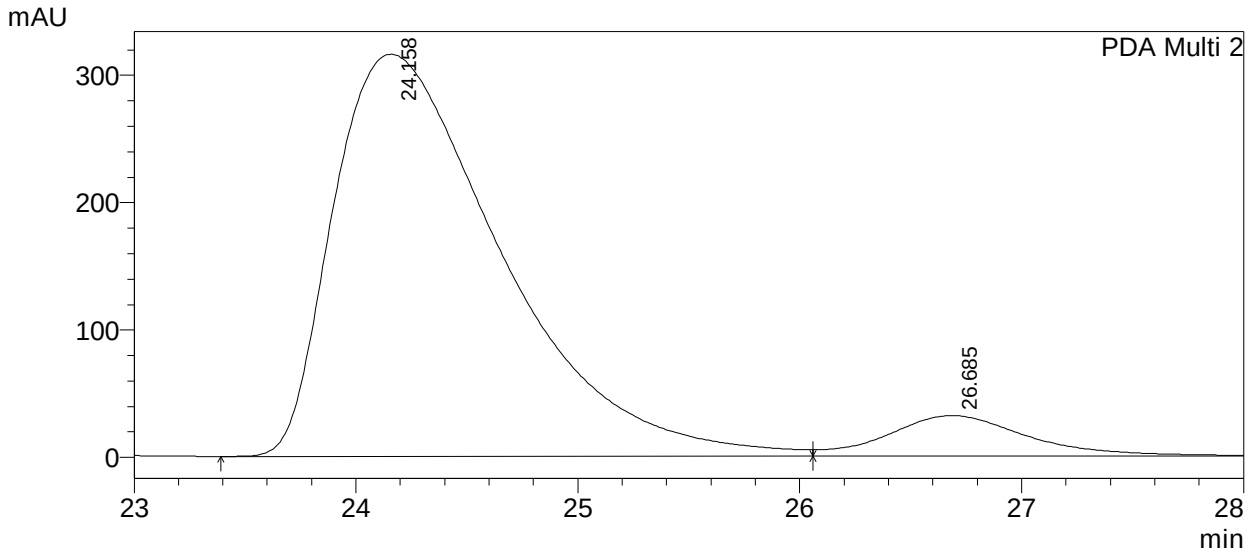
D:\...\3-methylcyclopentenone\Naphthyl boronic acid\ENT\Naphthylboronic acid ENT AS-H.lcd

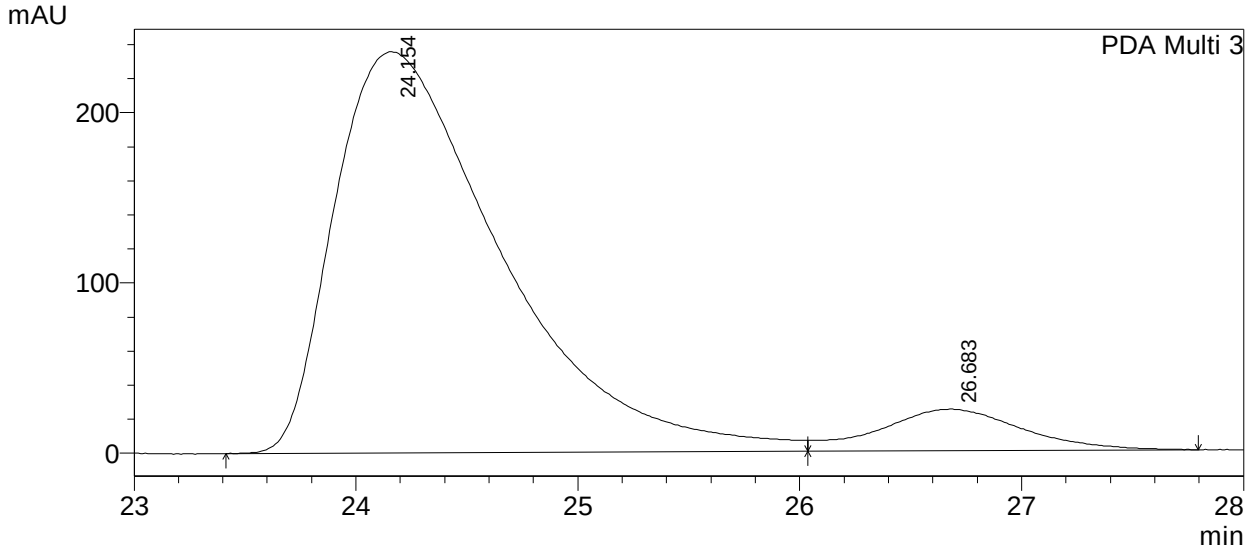
Acquired by	: System Administrator
Sample Name	: Naphthylboronic acid ENT
Sample ID	: Naphthylboronic acid ENT
Tray#	: 1
Vail #	: 84
Injection Volume	: 2 uL
Data File Name	: Naphthylboronic acid ENT AS-H.lcd
Method File Name	: C4 99.5_0.5 fl0,5 70 min.lcm
Batch File Name	: 20131019_JBR.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 10/23/2013 6:02:27 PM
Data Processed	: 10/24/2013 9:25:16 AM

<Chromatogram>

D:\...\3-methylcyclopentenone\Naphthyl boronic acid\ENT\Naphthylboronic acid ENT AS-H.lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

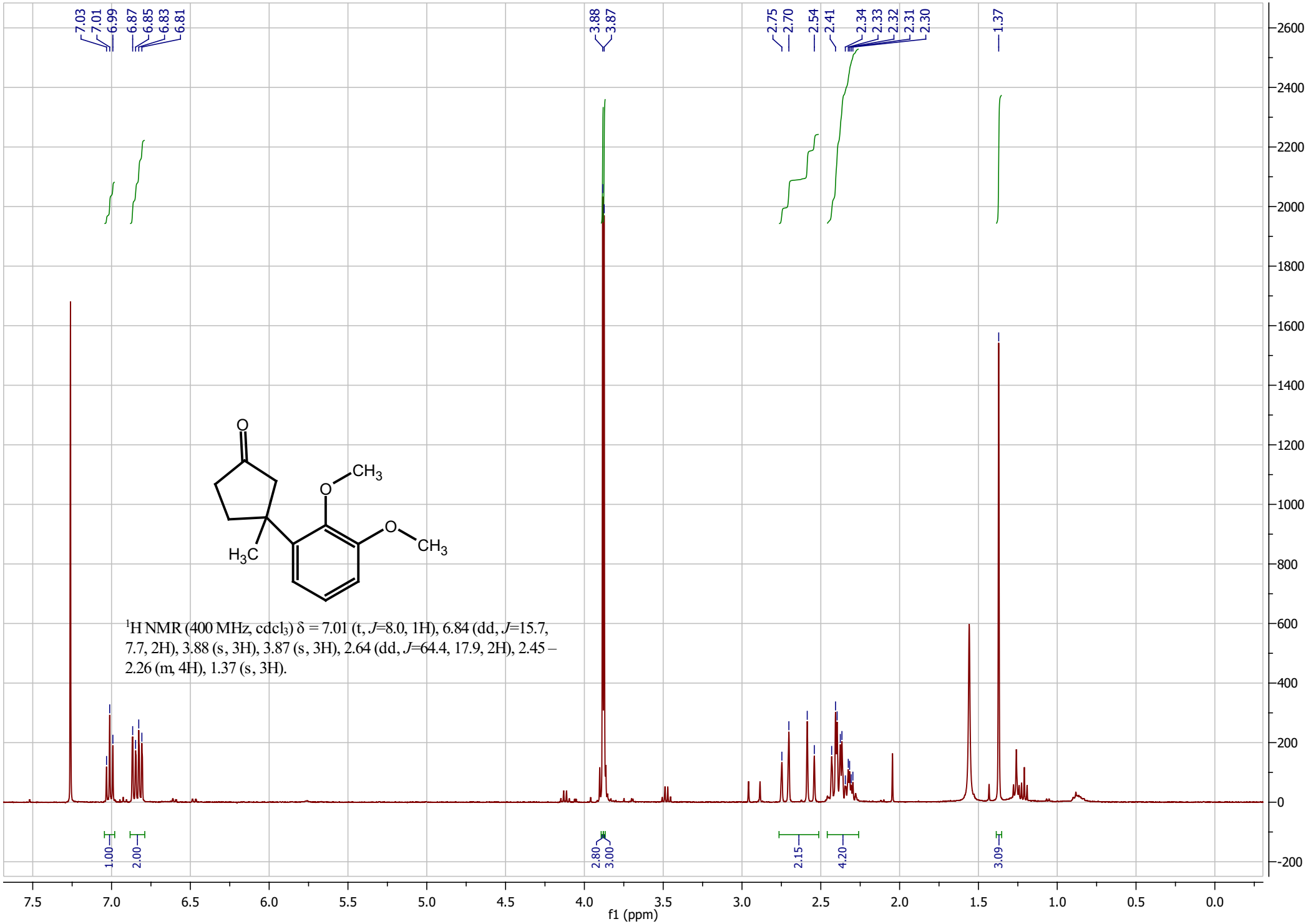
Peak#	Ret. Time	Area	Height	Area%
1	24.154	735773	14072	92.819
2	26.666	56925	1366	7.181
Total		792698	15438	100.000

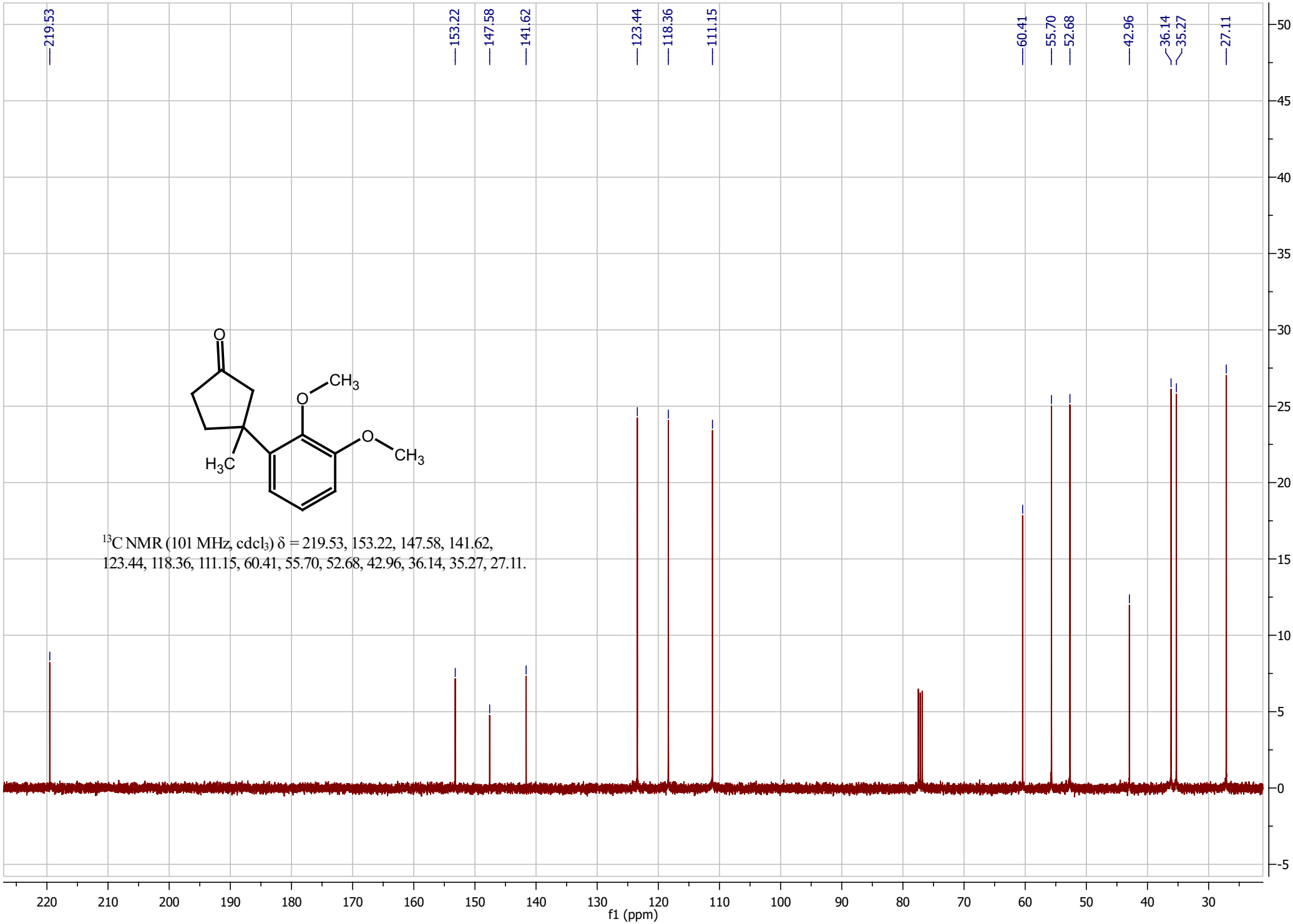
PDA Ch2 225nm

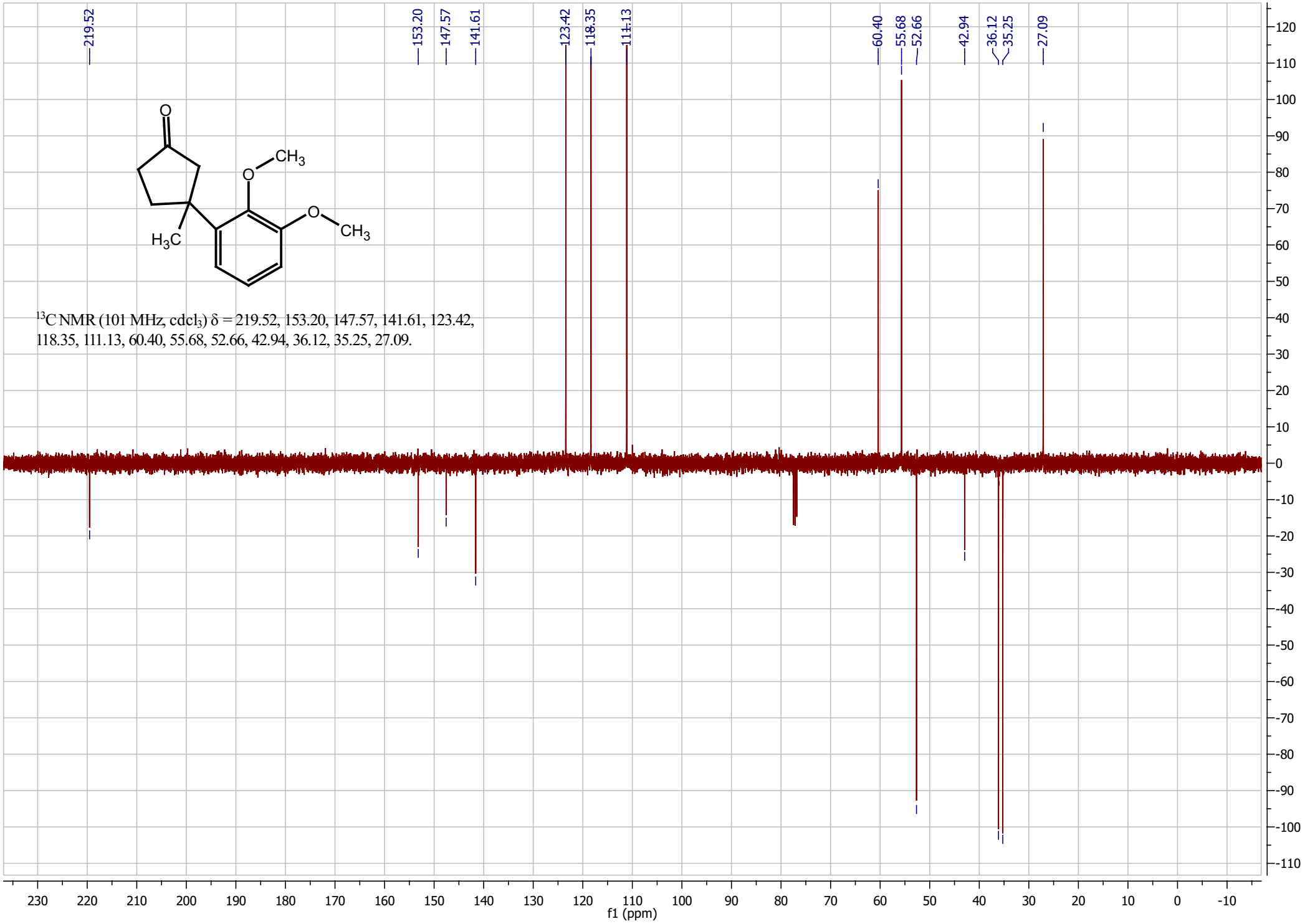
Peak#	Ret. Time	Area	Height	Area%
1	24.158	16652915	315750	92.203
2	26.685	1408229	31888	7.797
Total		18061143	347638	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	24.154	12400265	235522	91.929
2	26.683	1088743	24419	8.071
Total		13489009	259940	100.000


7.03
7.01
6.99
6.87
6.85
6.83
6.81
3.88
3.87
2.75
2.70
2.54
2.41
2.34
2.33
2.32
2.31
2.30
1.37
O
CH3
O
O
CH3
H3C
1H NMR (400 MHz, cdcl3) δ = 7.01 (t, J=8.0, 1H), 6.84 (dd, J=15.7, 7.7, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 2.64 (dd, J=64.4, 17.9, 2H), 2.45 – 2.26 (m, 4H), 1.37 (s, 3H).
1.00
2.00
2.80
3.00
2.15
4.20
3.09
f1 (ppm)


219.53
153.22
147.58
141.62
123.44
118.36
111.15
60.41
55.70
52.68
42.96
36.14
35.27
27.11
O
CH3
O
O
CH3
H3C
13C NMR (101 MHz, cdcl3) δ = 219.53, 153.22, 147.58, 141.62,
123.44, 118.36, 111.15, 60.41, 55.70, 52.68, 42.96, 36.14, 35.27, 27.11.
f1 (ppm)


219.52
153.20
147.57
141.61
123.42
118.35
111.13
60.40
55.68
52.66
42.94
36.12
35.25
27.09
O
CH3
O
O
CH3
H3C
13C NMR (101 MHz, cdcl3) δ = 219.52, 153.20, 147.57, 141.61, 123.42, 118.35, 111.13, 60.40, 55.68, 52.66, 42.94, 36.12, 35.25, 27.09.
f1 (ppm)

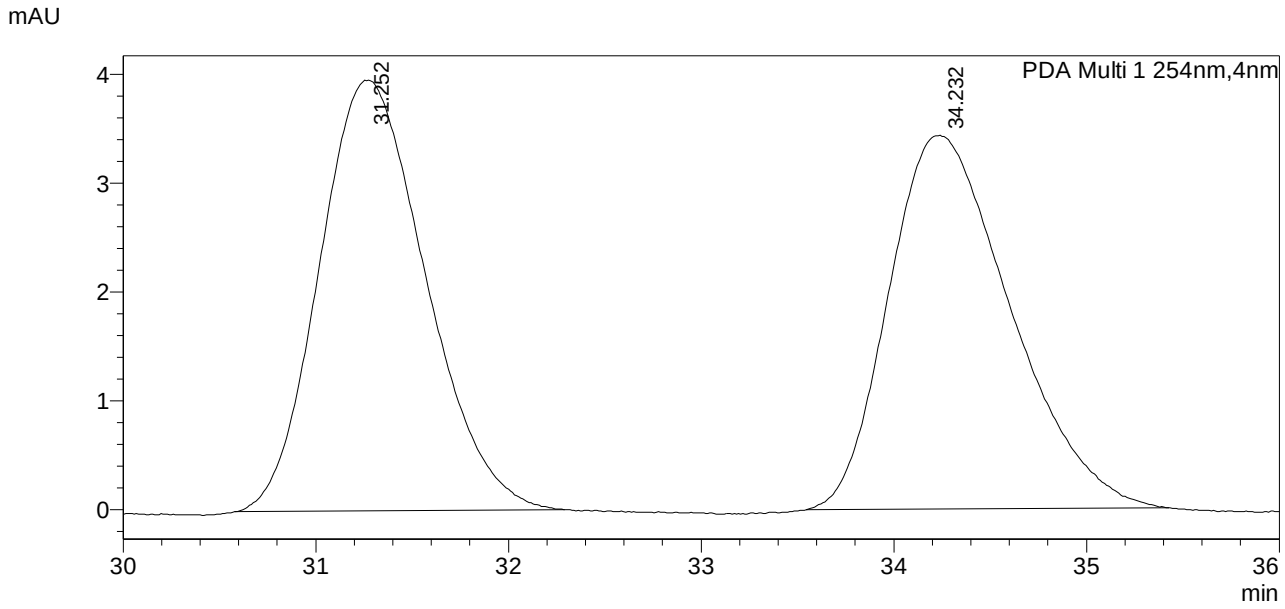
SHIMADZU LabSolutions

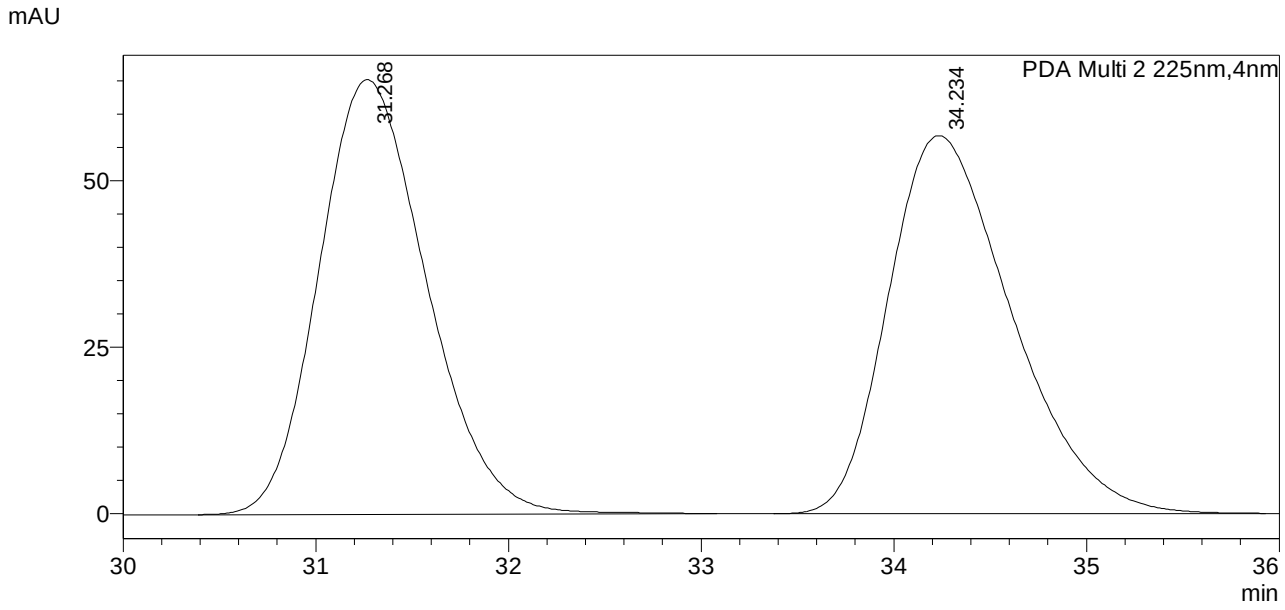
Analysis Report

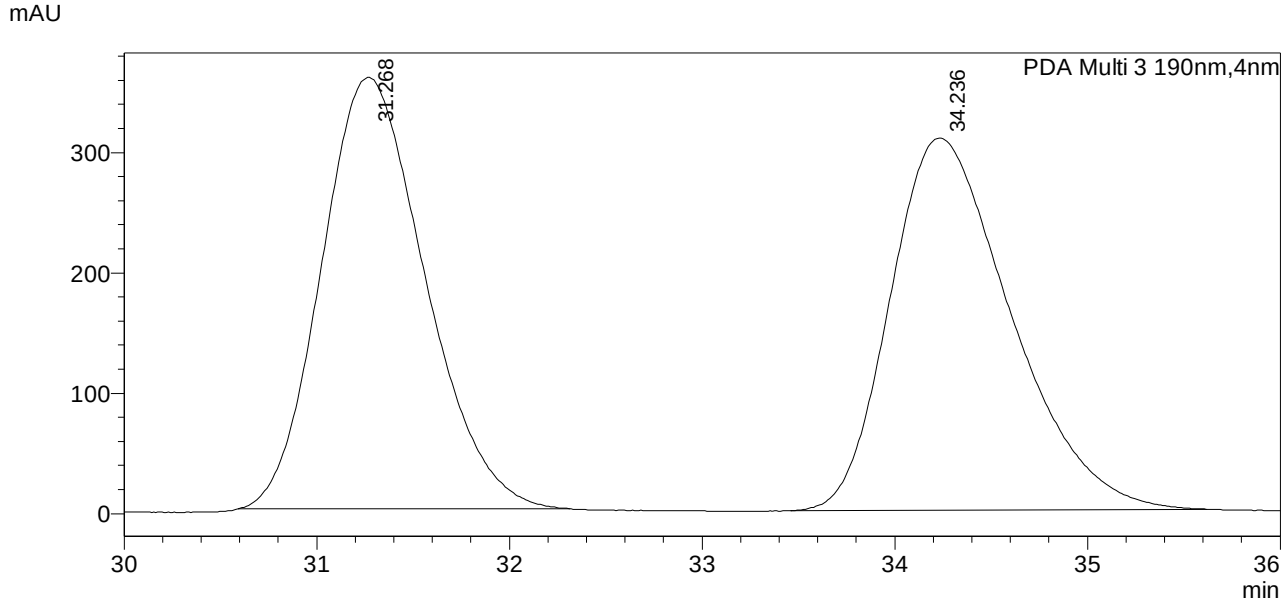
<Sample Information>

Sample Name	: 2,3-dimethyoxy boronic acid OD-H-column		
Sample ID	: 2,3-dimethyoxy boronic acid OD-		
Data Filename	: 2,3-dimethyoxy boronic acid OD-H.lcd		
Method Filename	: C2 99_1fl0,5 60 min.lcm		
Batch Filename	: 20131029_all column screening.lcb		
Vial #	: 1-31	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 10/29/2013 8:41:02 PM	Acquired by	: System Administrator
Date Processed	: 10/30/2013 9:28:46 AM	Processed by	: System Administrator

<Chromatogram>







<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	31.252	151681	3959	50.150
2	34.232	150774	3436	49.850
Total		302455	7396	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	31.268	2532855	65230	50.073
2	34.234	2525476	56744	49.927
Total		5058331	121974	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	31.268	13370650	358358	49.896
2	34.236	13426182	309219	50.104
Total		26796832	667577	100.000

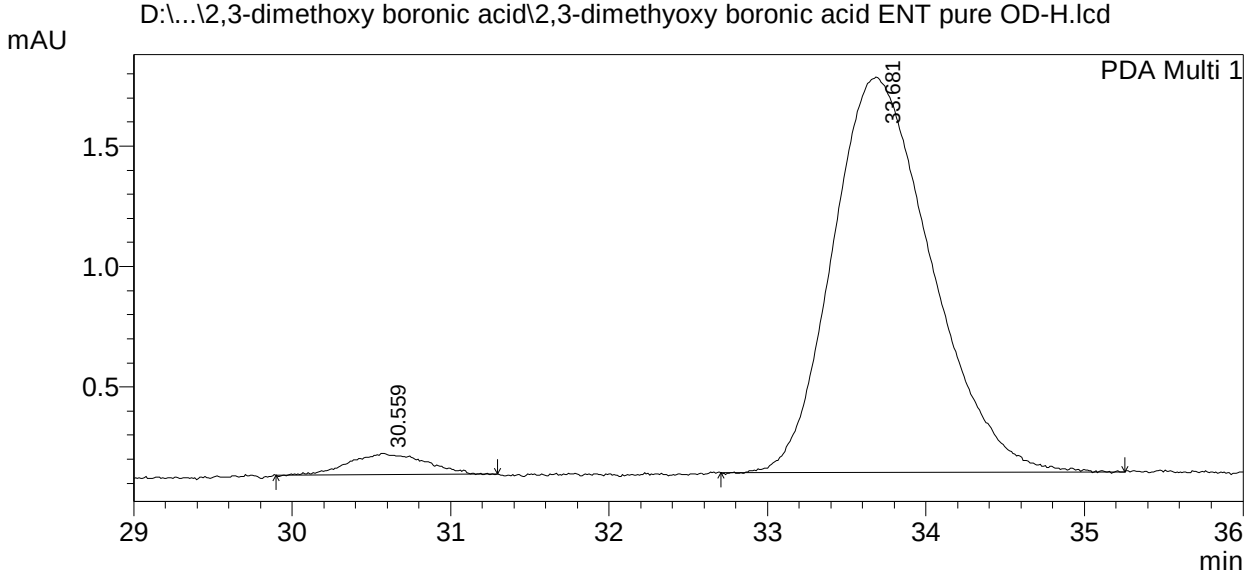
==== Shimadzu LCsolution Analysis Report ====

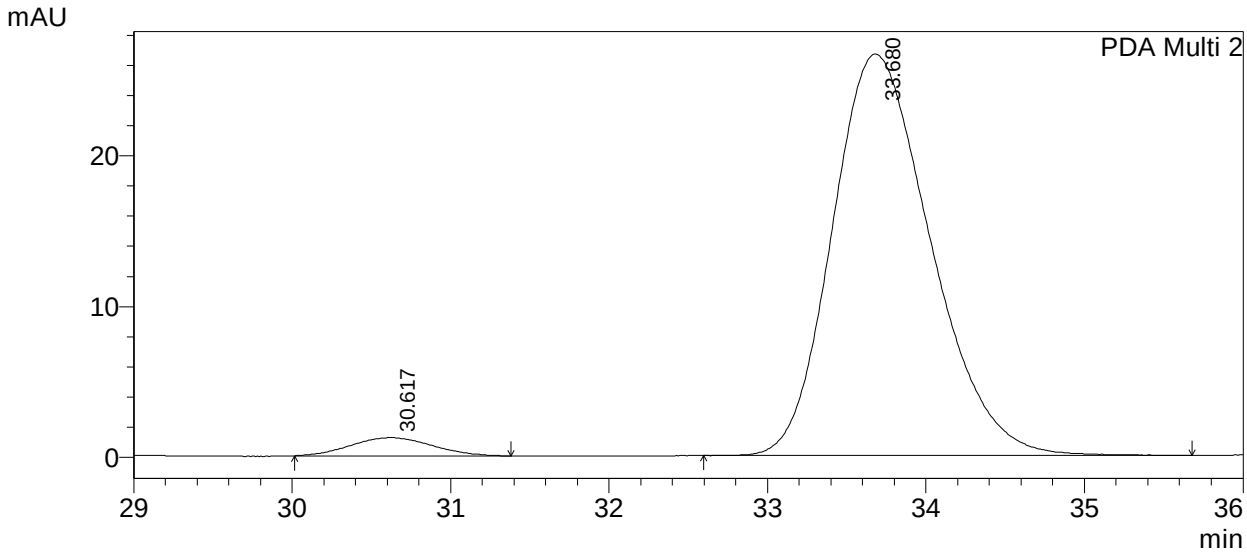
D:\...\3-methylcyclopentenone\2,3-dimethoxy boronic acid\2,3-dimethyoxy boronic acid ENT pure OD-H.lcd

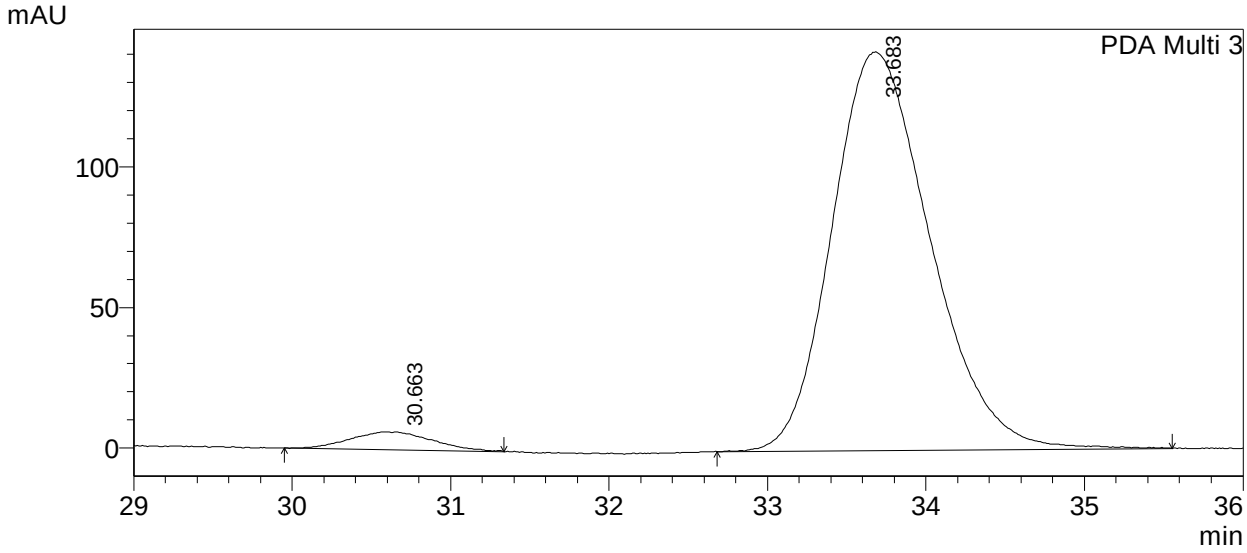
Acquired by	: System Administrator
Sample Name	: 2,3-dimethyoxy boronic acid OD-H-column
Sample ID	: 2,3-dimethyoxy boronic acid OD-
Tray#	: 1
Vail #	: 2
Injection Volume	: 2 uL
Data File Name	: 2,3-dimethyoxy boronic acid ENT pure OD-H.lcd
Method File Name	: C2 99_1fl0,5 40 min.lcm
Batch File Name	: 20131030.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 10/30/2013 12:22:12 PM
Data Processed	: 10/30/2013 1:14:04 PM

<Chromatogram>

D:\...\2,3-dimethoxy boronic acid\2,3-dimethyoxy boronic acid ENT pure OD-H.lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

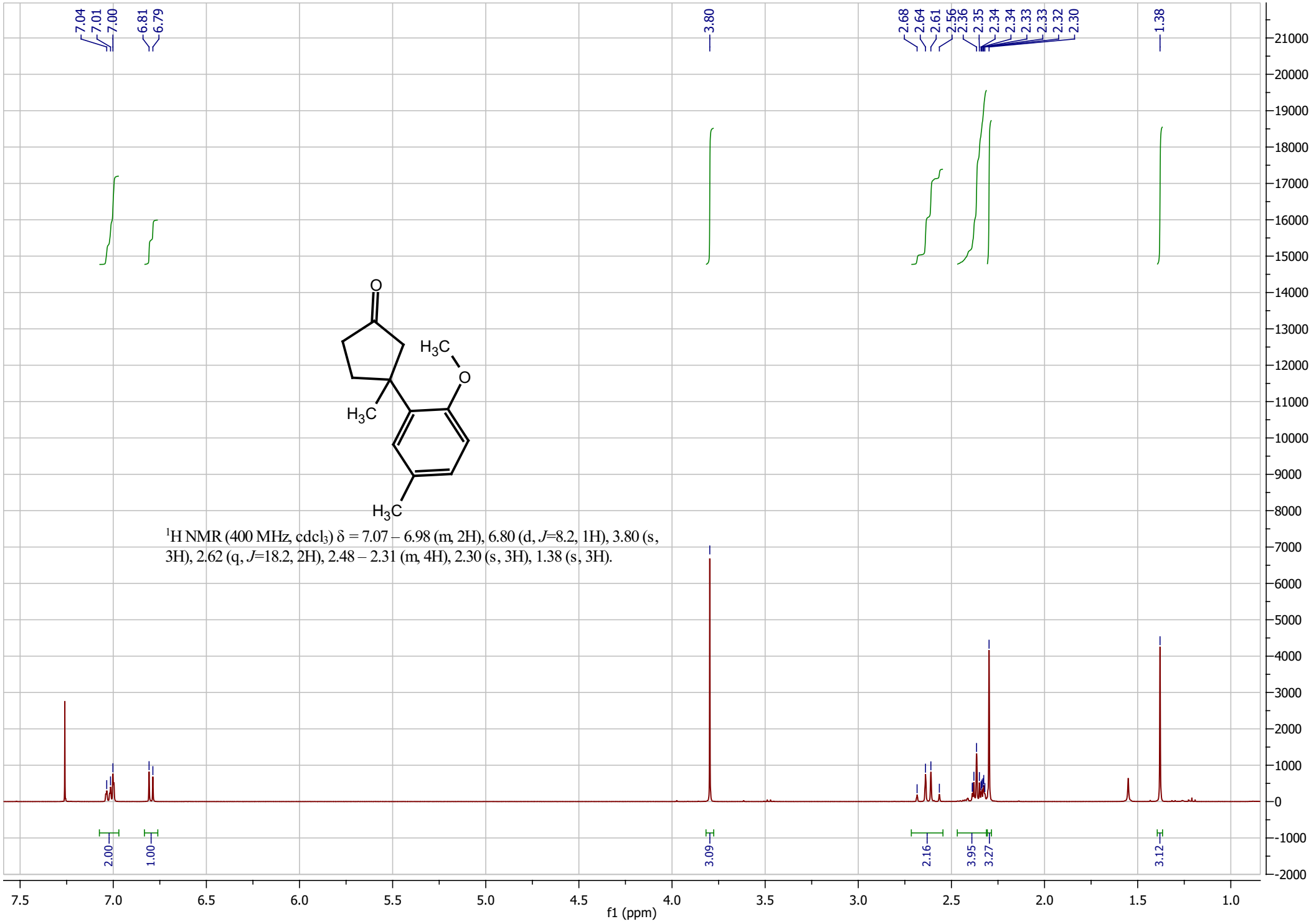
Peak#	Ret. Time	Area	Height	Area%
1	30.559	2889	87	3.906
2	33.681	71093	1642	96.094
Total		73983	1729	100.000

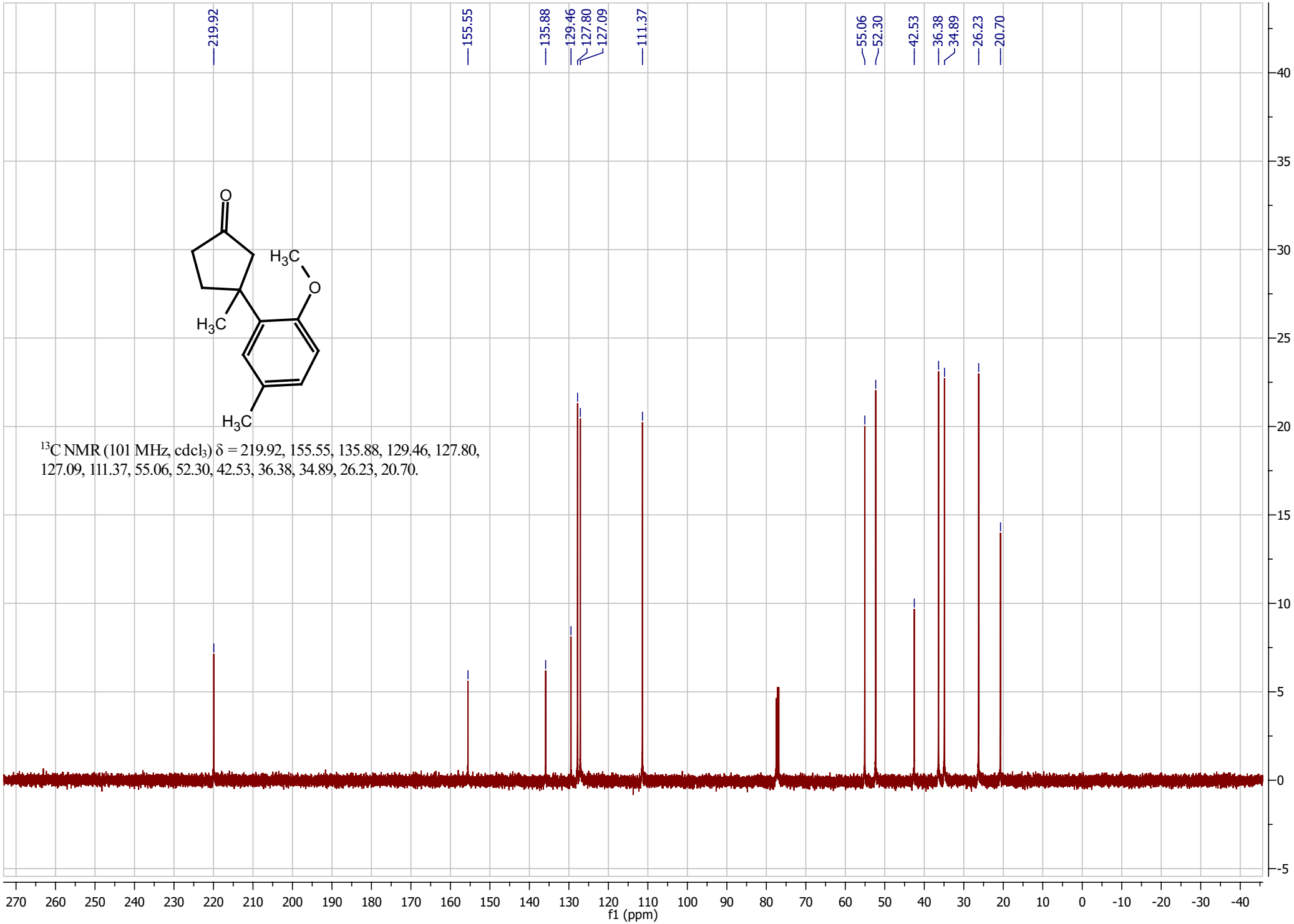
PDA Ch2 225nm

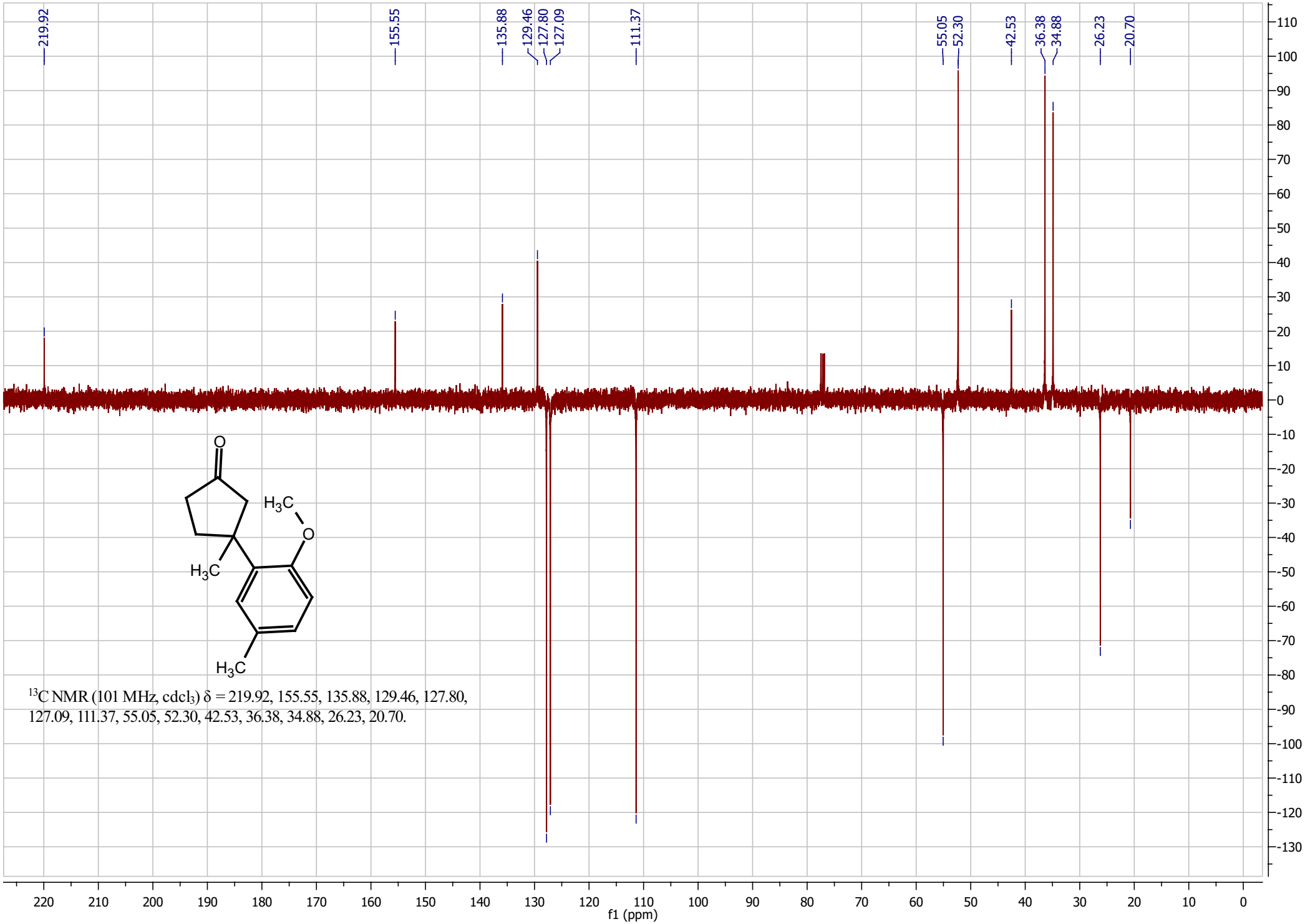
Peak#	Ret. Time	Area	Height	Area%
1	30.617	43275	1213	3.636
2	33.680	1147055	26604	96.364
Total		1190330	27818	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	30.663	230661	6420	3.635
2	33.683	6114168	141826	96.365
Total		6344829	148245	100.000


7.04
7.01
7.00
6.81
6.79
3.80
2.68
2.64
2.61
2.56
2.36
2.35
2.34
2.34
2.33
2.33
2.32
2.30
1.38
O
H3C
O
H3C
H3C
1H NMR (400 MHz, cdcl3) δ = 7.07 – 6.98 (m, 2H), 6.80 (d, J=8.2, 1H), 3.80 (s, 3H), 2.62 (q, J=18.2, 2H), 2.48 – 2.31 (m, 4H), 2.30 (s, 3H), 1.38 (s, 3H).
2.00
1.00
3.09
2.16
3.95
3.27
3.12
f1 (ppm)


219.92
155.55
135.88
129.46
127.80
127.09
111.37
55.06
52.30
42.53
36.38
34.89
26.23
20.70
O
H3C
O
H3C
H3C
13C NMR (101 MHz, cdcl3) δ = 219.92, 155.55, 135.88, 129.46, 127.80,
127.09, 111.37, 55.06, 52.30, 42.53, 36.38, 34.89, 26.23, 20.70.
f1 (ppm)



^{13}C NMR (101 MHz, cdcl$_3$) δ = 219.92, 155.55, 135.88, 129.46, 127.80, 127.09, 111.37, 55.05, 52.30, 42.53, 36.38, 34.88, 26.23, 20.70.

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: 2-OMe-5Me-boronic acid RAC AD-H		
Sample ID	: 2-OMe-5Me-boronic acid RAC AD-H		
Data Filename	: 2-OMe-5Me-boronic acid RAC AD-H.lcd		
Method Filename	: C5 99_1 fl0,5 60 min.lcm		
Batch Filename	: 20131031_all column screening.lcb		
Vial #	: 1-31	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 10/30/2013 1:50:47 PM	Acquired by	: System Administrator
Date Processed	: 10/30/2013 2:58:19 PM	Processed by	: System Administrator

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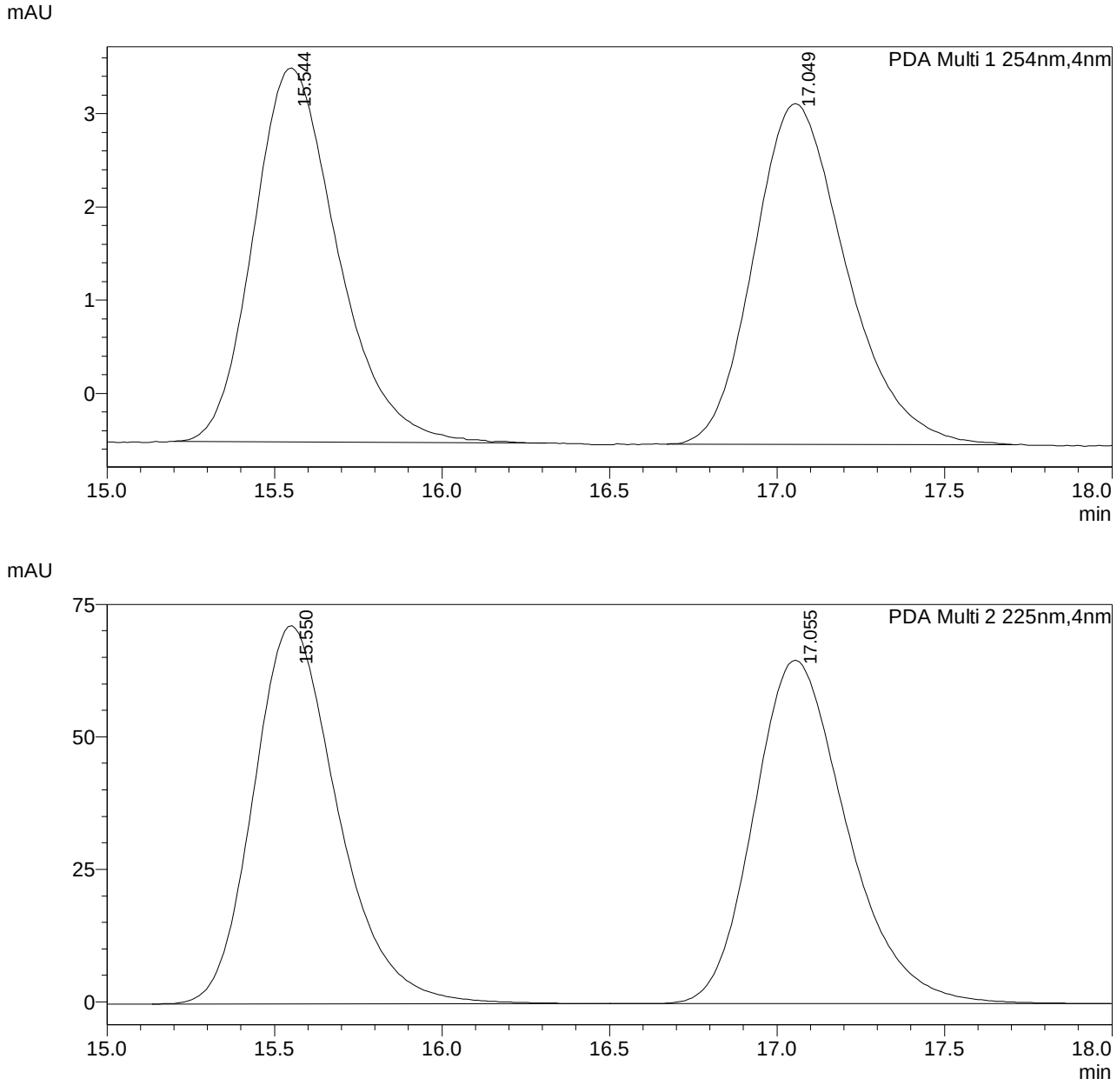

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	15.544	70138	4012	50.033
2	17.049	70046	3651	49.967
Total		140184	7663	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	15.550	1254992	71322	50.071
2	17.055	1251428	64813	49.929
Total		2506420	136135	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	15.548	3296661	191526	50.333
2	17.053	3252976	172614	49.667
Total		6549637	364139	100.000

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: 2-OMe-5-Me boronic acid ENT AD-H-column		
Sample ID	: 2-OMe-5-Me boronic acid AD-H		
Data Filename	: 2-OMe-5-Me boronic acid ENT AD-H column.lcd		
Method Filename	: C5 99_1 fl0,5 30 min.lcm		
Batch Filename	: 20131029_all column screening.lcb		
Vial #	: 1-20	Sample Type	: Unknown
Injection Volume	: 3 uL	Level	: 1
Date Acquired	: 11/1/2013 7:02:36 AM	Acquired by	: System Administrator
Date Processed	: 11/1/2013 9:57:53 AM	Processed by	: System Administrator

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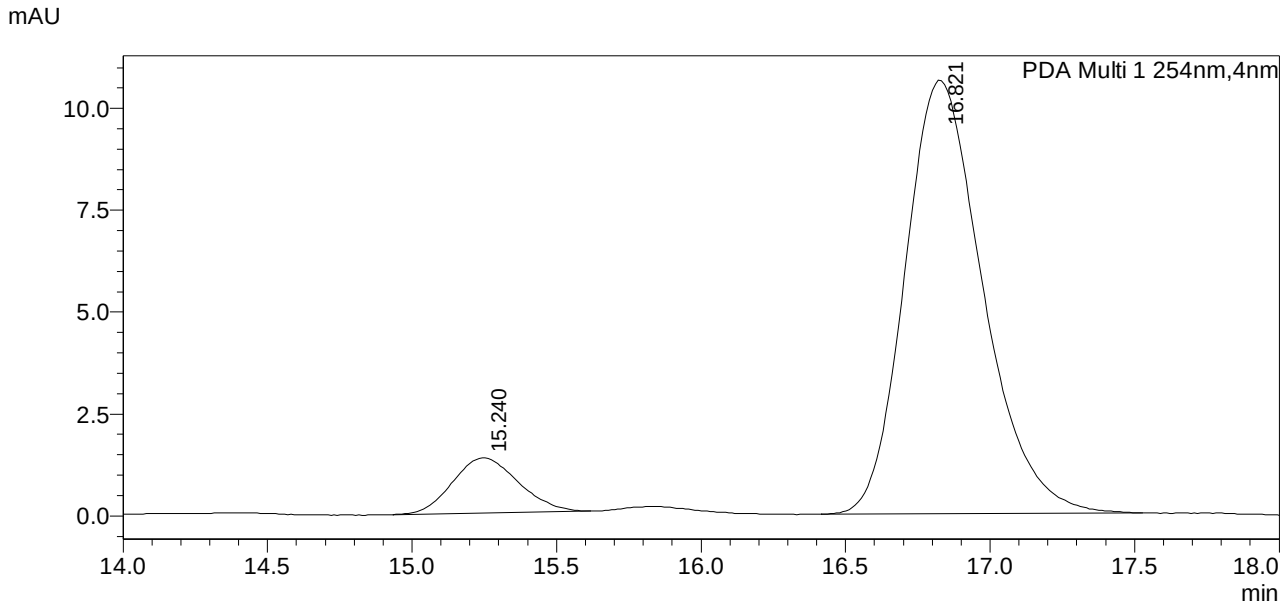
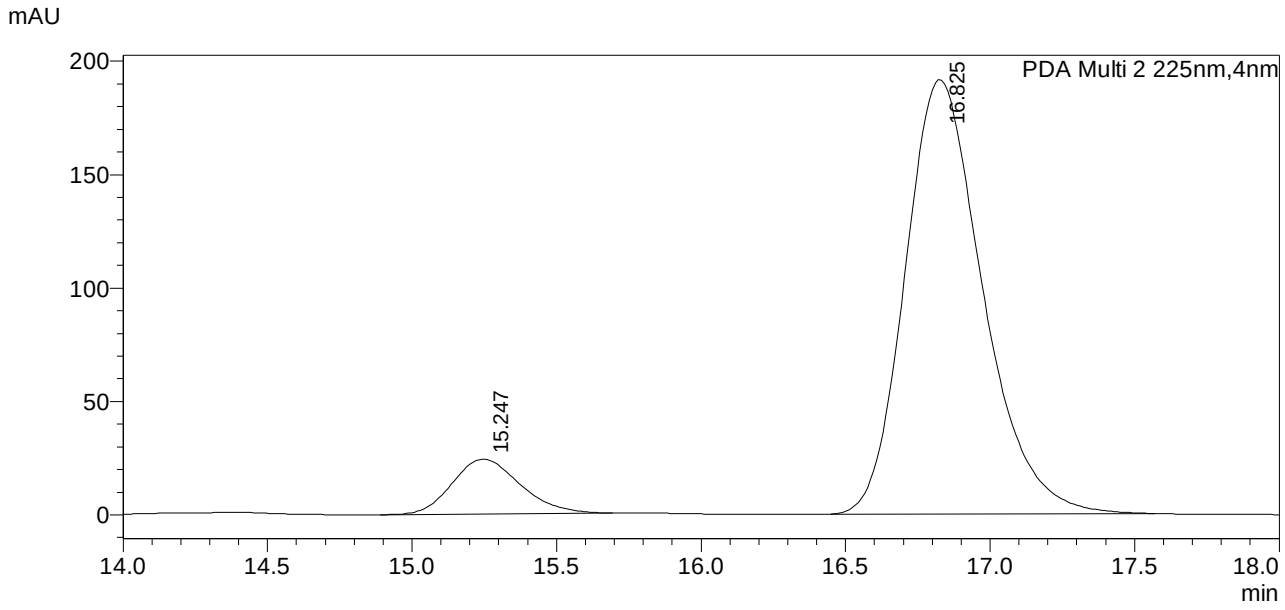
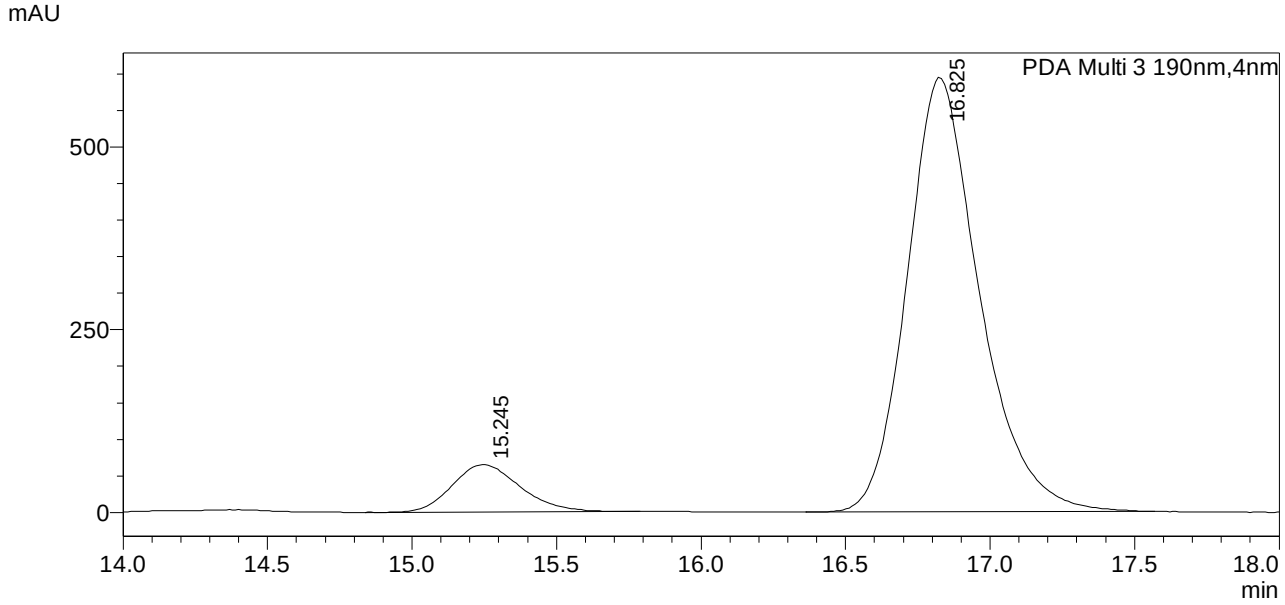






<Peak Table>

PDA Ch1 254nm

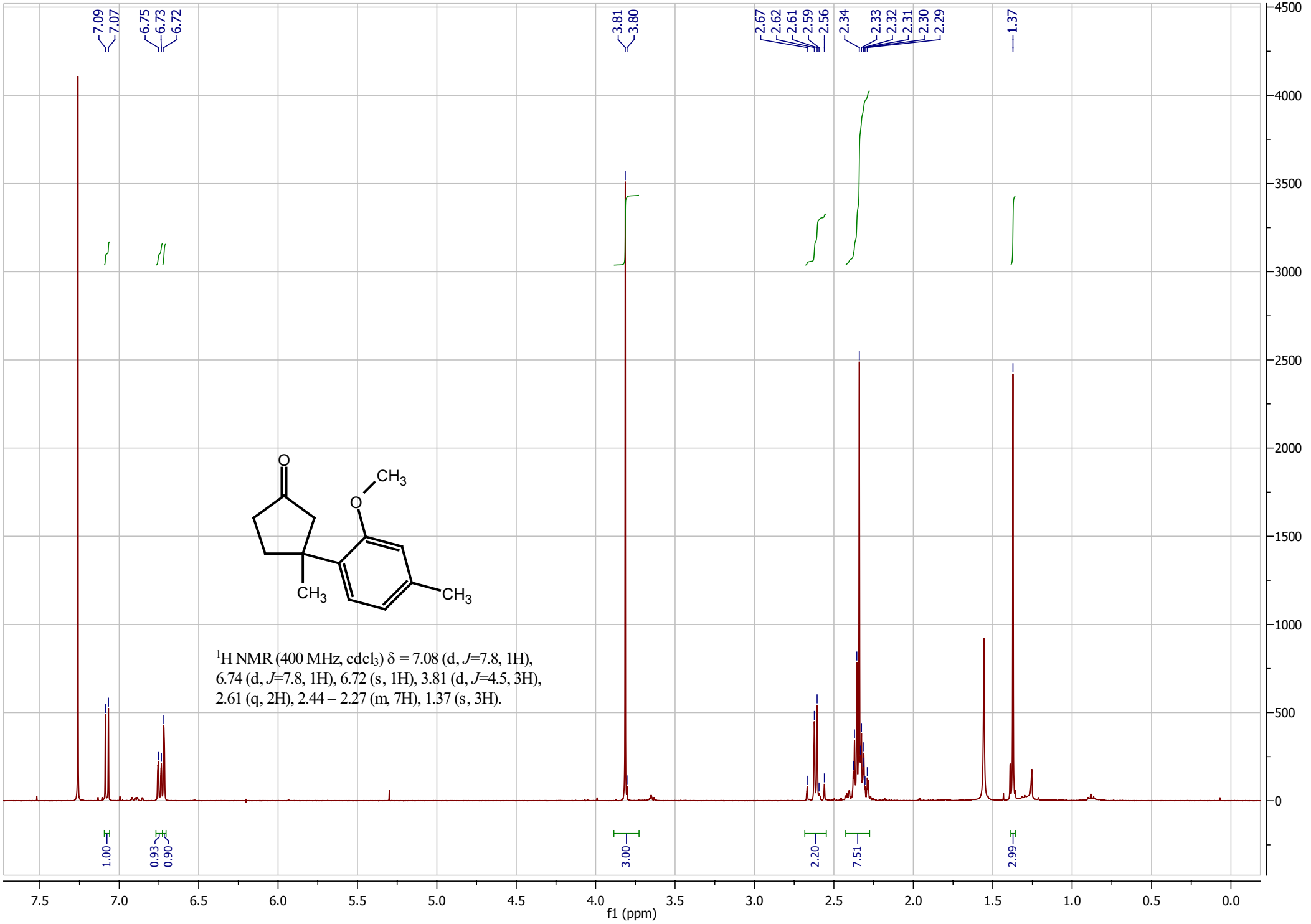
Peak#	Ret. Time	Area	Height	Area%
1	15.240	21508	1358	9.713
2	16.821	199927	10640	90.287
Total		221435	11998	100.000

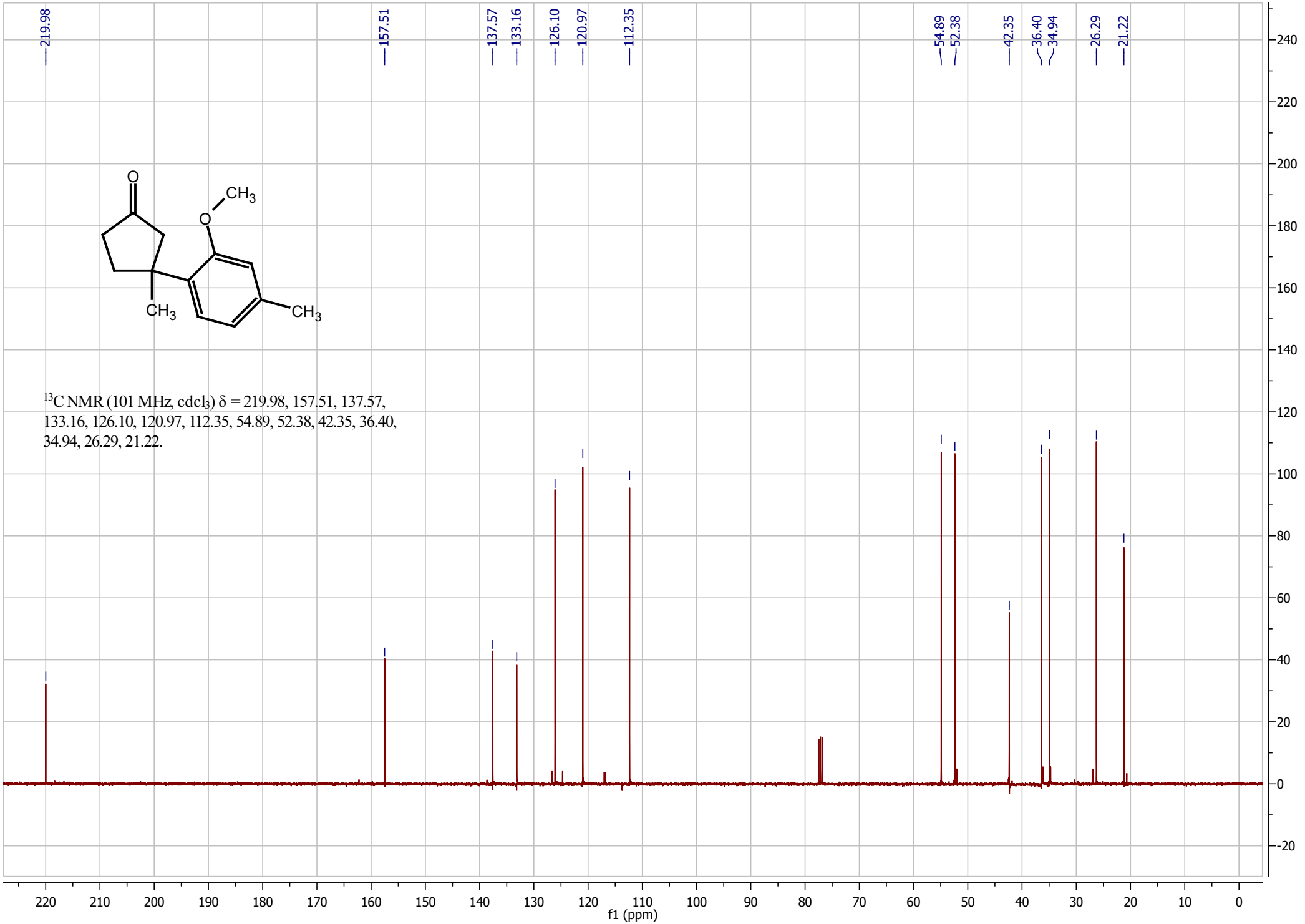
PDA Ch2 225nm

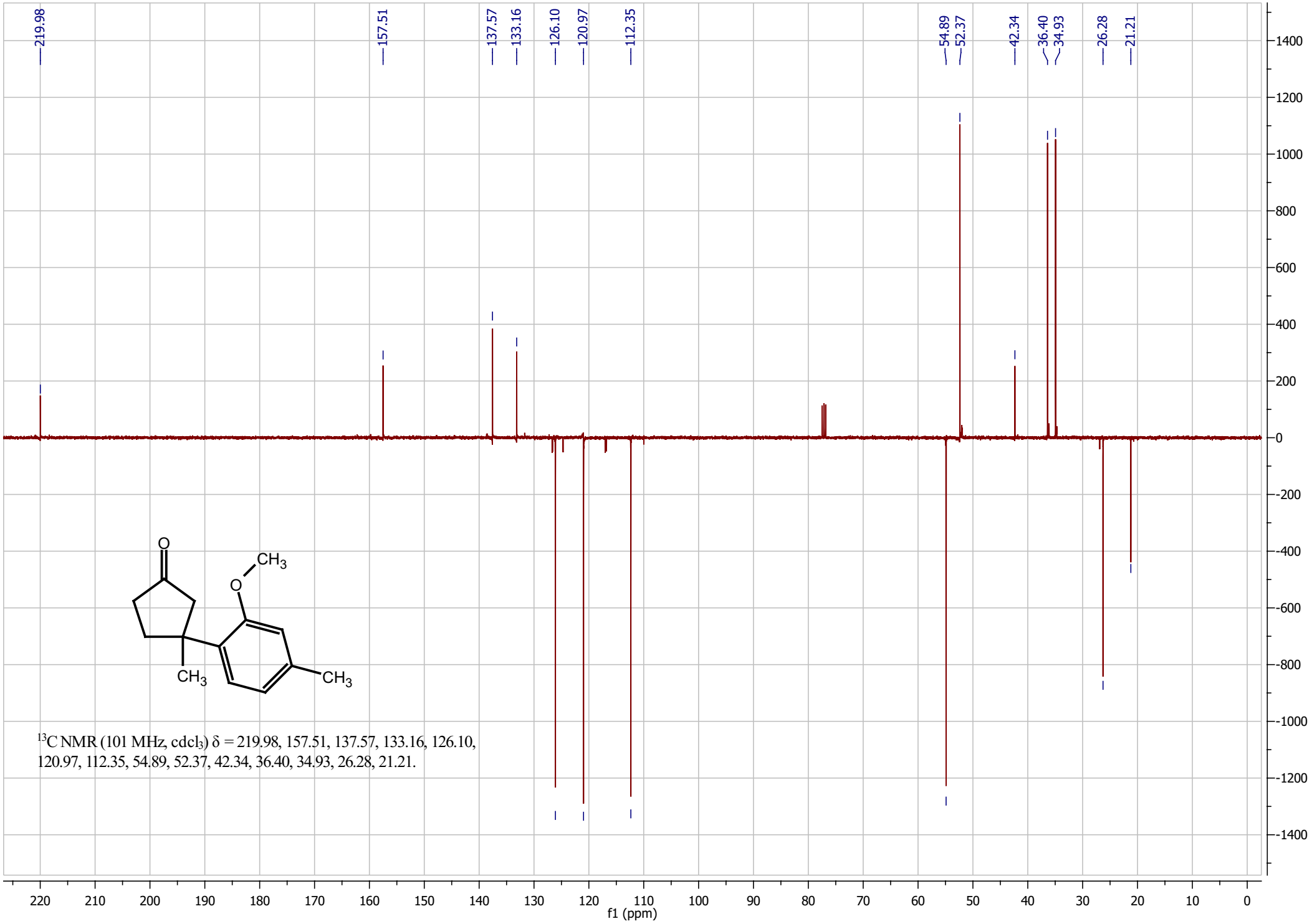
Peak#	Ret. Time	Area	Height	Area%
1	15.247	395311	24133	9.967
2	16.825	3571071	191355	90.033
Total		3966382	215488	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	15.245	1059381	64891	9.299
2	16.825	10333052	593911	90.701
Total		11392433	658802	100.000


7.09
7.07
6.75
6.73
6.72
3.81
3.80
2.67
2.62
2.61
2.59
2.56
2.34
2.33
2.32
2.31
2.30
2.29
1.37
O
CH3
O
CH3
CH3
1H NMR (400 MHz, cdcl3) δ = 7.08 (d, J=7.8, 1H),
6.74 (d, J=7.8, 1H), 6.72 (s, 1H), 3.81 (d, J=4.5, 3H),
2.61 (q, 2H), 2.44 – 2.27 (m, 7H), 1.37 (s, 3H).
1.00
0.93
0.90
3.00
2.20
7.51
2.99
f1 (ppm)


219.98
157.51
137.57
133.16
126.10
120.97
112.35
54.89
52.38
42.35
36.40
34.94
26.29
21.22
O
CH3
O
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 219.98, 157.51, 137.57, 133.16, 126.10, 120.97, 112.35, 54.89, 52.38, 42.35, 36.40, 34.94, 26.29, 21.22.
f1 (ppm)



^{13}C NMR (101 MHz, cdcl$_3$) δ = 219.98, 157.51, 137.57, 133.16, 126.10, 120.97, 112.35, 54.89, 52.37, 42.34, 36.40, 34.93, 26.28, 21.21.

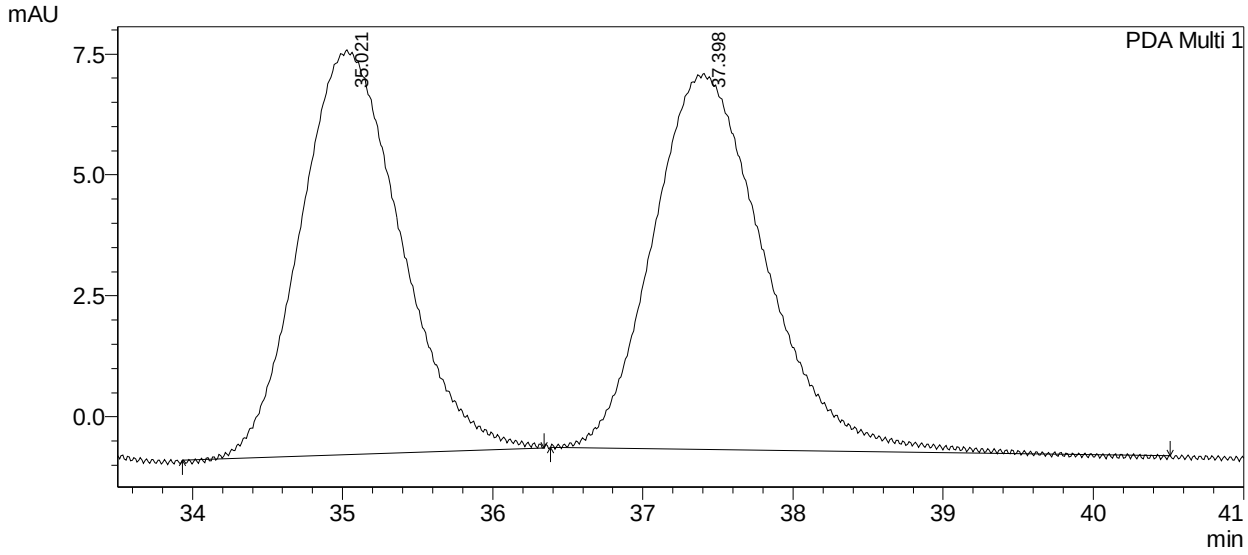
==== Shimadzu LCsolution Analysis Report ====

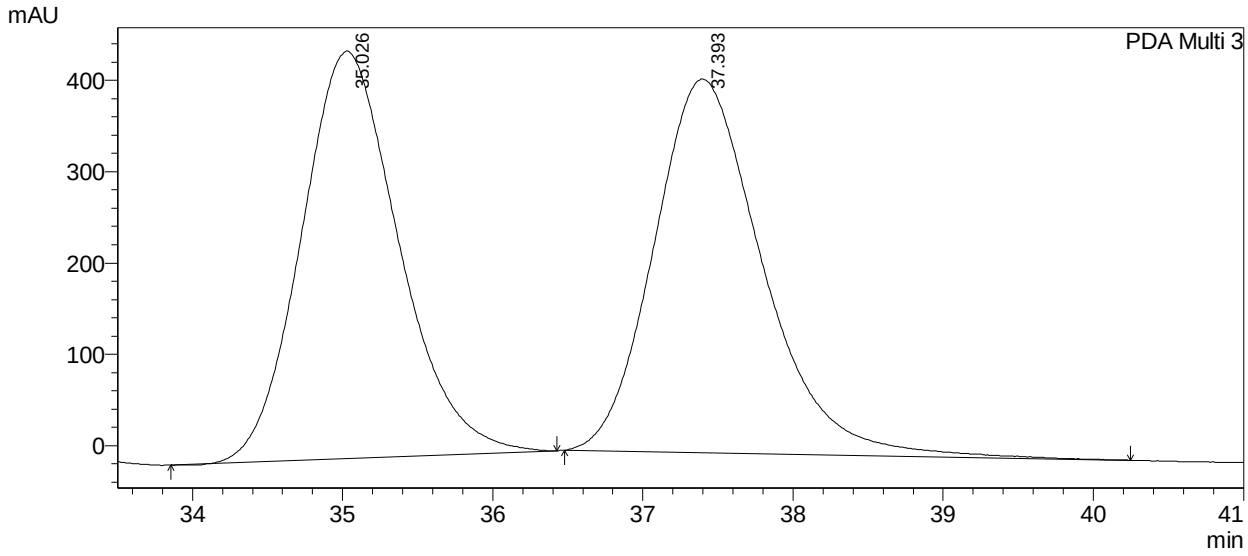
D:\...\Substrate Scope\3-methylcyclopentenone\2-methoxy-4-methyl\2-OMe-4Me boronic acid RAC Cell.lcd

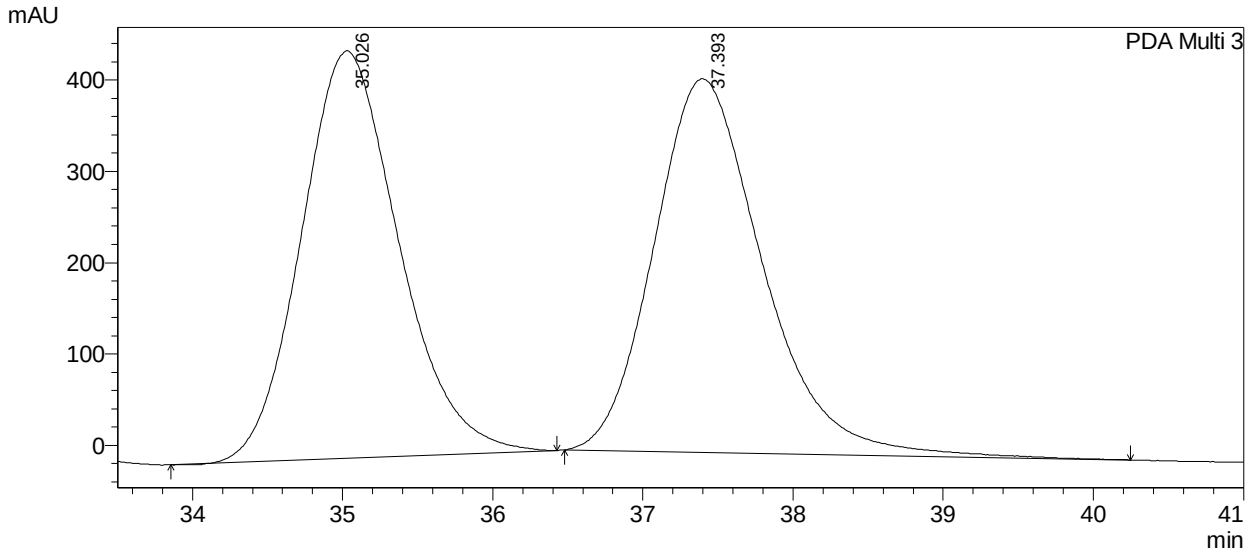
Acquired by	: System Administrator
Sample Name	: 2-OMe-4Me boronic acid RAC Cellulose-column
Sample ID	: 2-OMe-4Me boronic acid RAC Cell
Tray#	: 1
Vail #	: 5
Injection Volume	: 1 uL
Data File Name	: 2-OMe-4Me boronic acid RAC Cell.lcd
Method File Name	: C6 99.5_0.5 fl0,5 60 min.lcm
Batch File Name	: 20140120_all column screening - 2014.lcb
Report File Name	: DEFAULT.lsr
Data Acquired	: 1/21/2014 12:23:03 PM
Data Processed	: 1/21/2014 1:23:07 PM

<Chromatogram>

D:\...\Substrate Scope\3-methylcyclopentenone\2-methoxy-4-methyl\2-OMe-4Me boronic acid RAC Cell.lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 3/190nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	35.021	389314	8358	49.315
2	37.398	400136	7764	50.685
Total		789450	16122	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	35.026	5582641	119994	49.273
2	37.399	5747363	111048	50.727
Total		11330005	231042	100.000

PDA Ch3 190nm

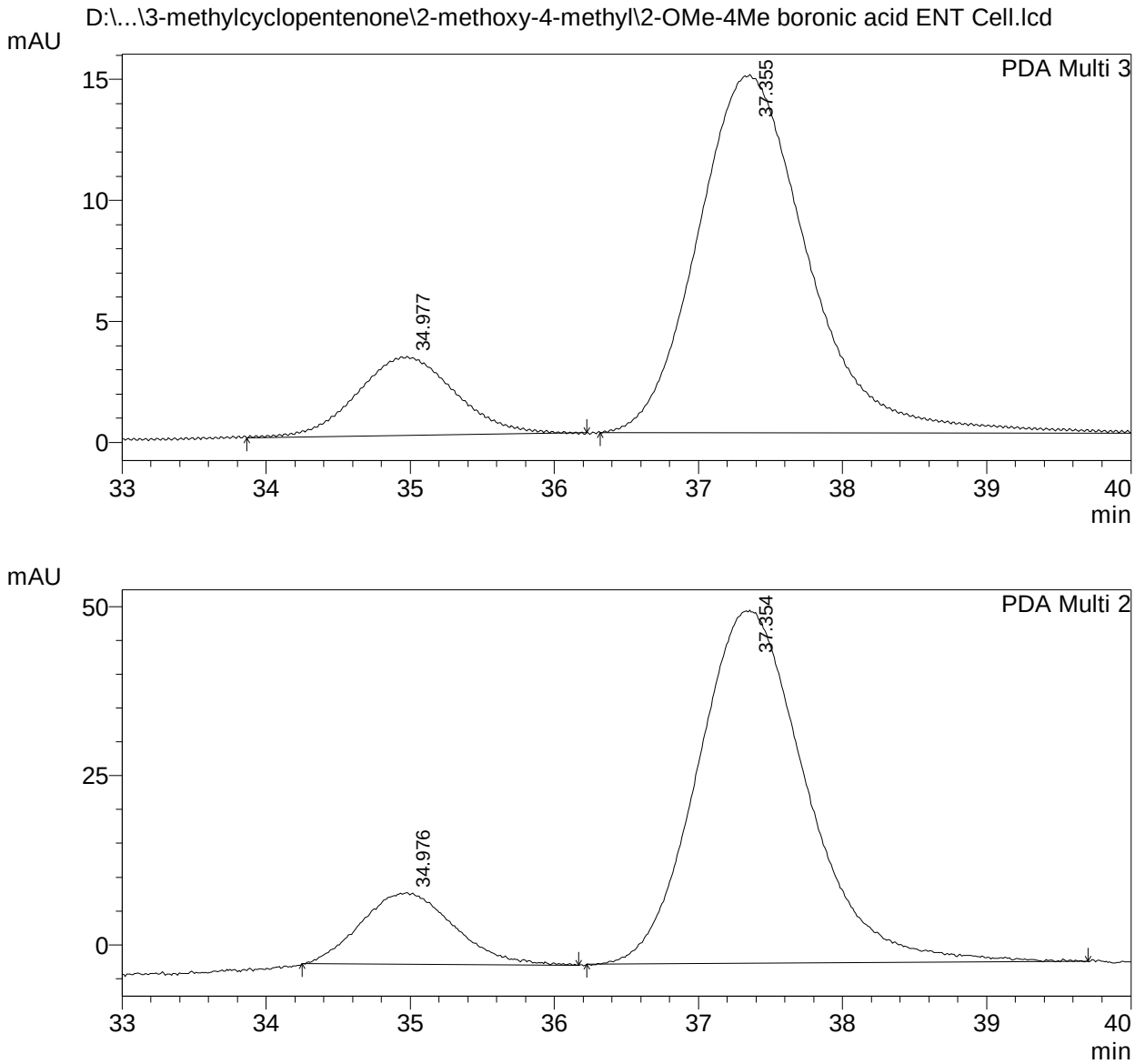
Peak#	Ret. Time	Area	Height	Area%
1	35.026	20145494	446526	49.497
2	37.393	20554782	409235	50.503
Total		40700276	855762	100.000

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

D:\...\Substrate Scope\3-methylcyclopentenone\2-methoxy-4-methyl\2-OMe-4Me boronic acid ENT Cell.lcd

Acquired by	: System Administrator
Sample Name	: 2-OMe-4Me boronic acid ENTCellulose-column
Sample ID	: 2-OMe-4Me boronic acid ENT Cell
Tray#	: 1
Vail #	: 46
Injection Volume	: 2 uL
Data File Name	: 2-OMe-4Me boronic acid ENT Cell.lcd
Method File Name	: C6 99.5_0.5 fl0,5 60 min.lcm
Batch File Name	: 20140120_all column screening - 2014.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 1/21/2014 3:24:28 PM
Data Processed	: 1/21/2014 5:42:18 PM

<Chromatogram>

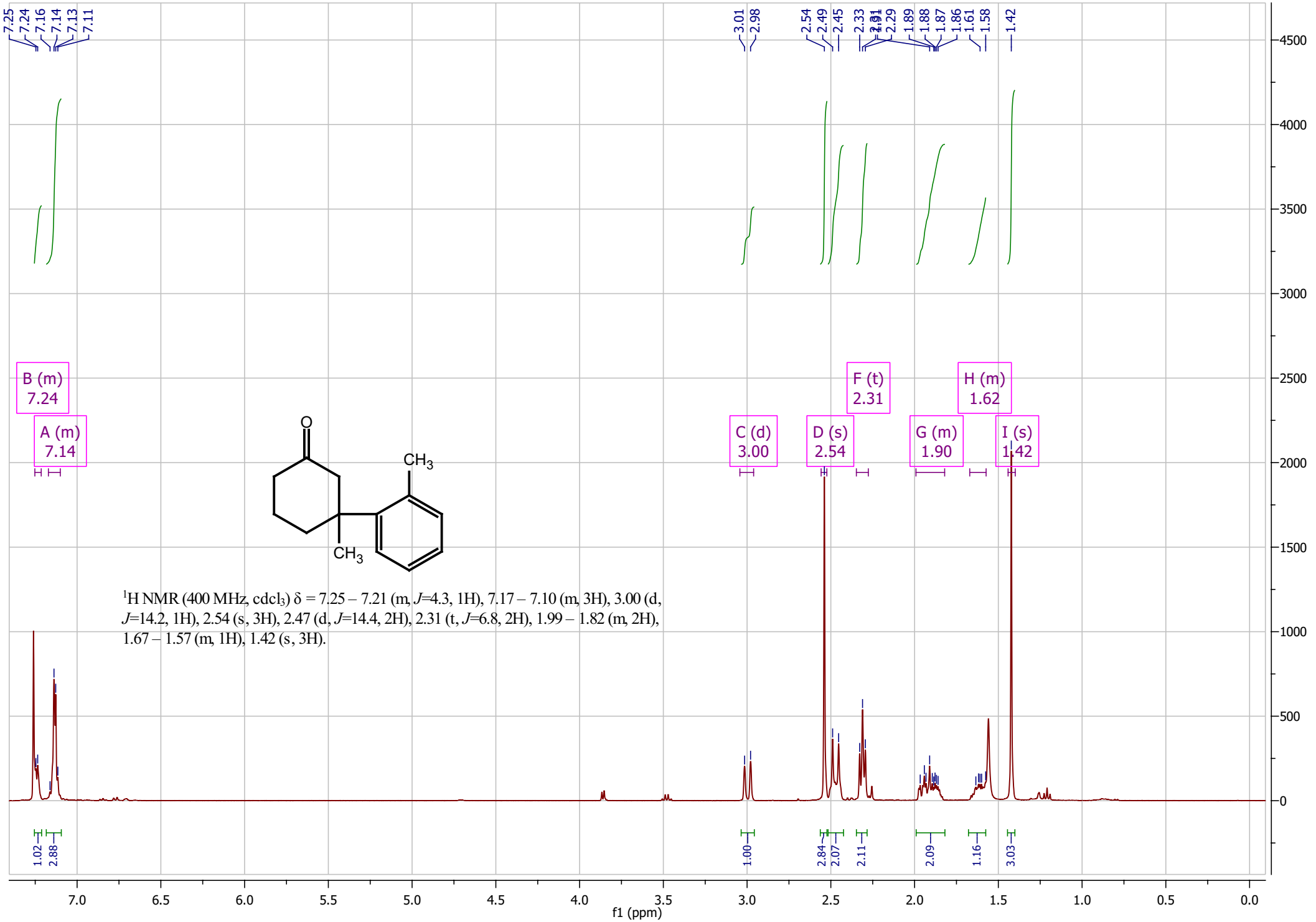


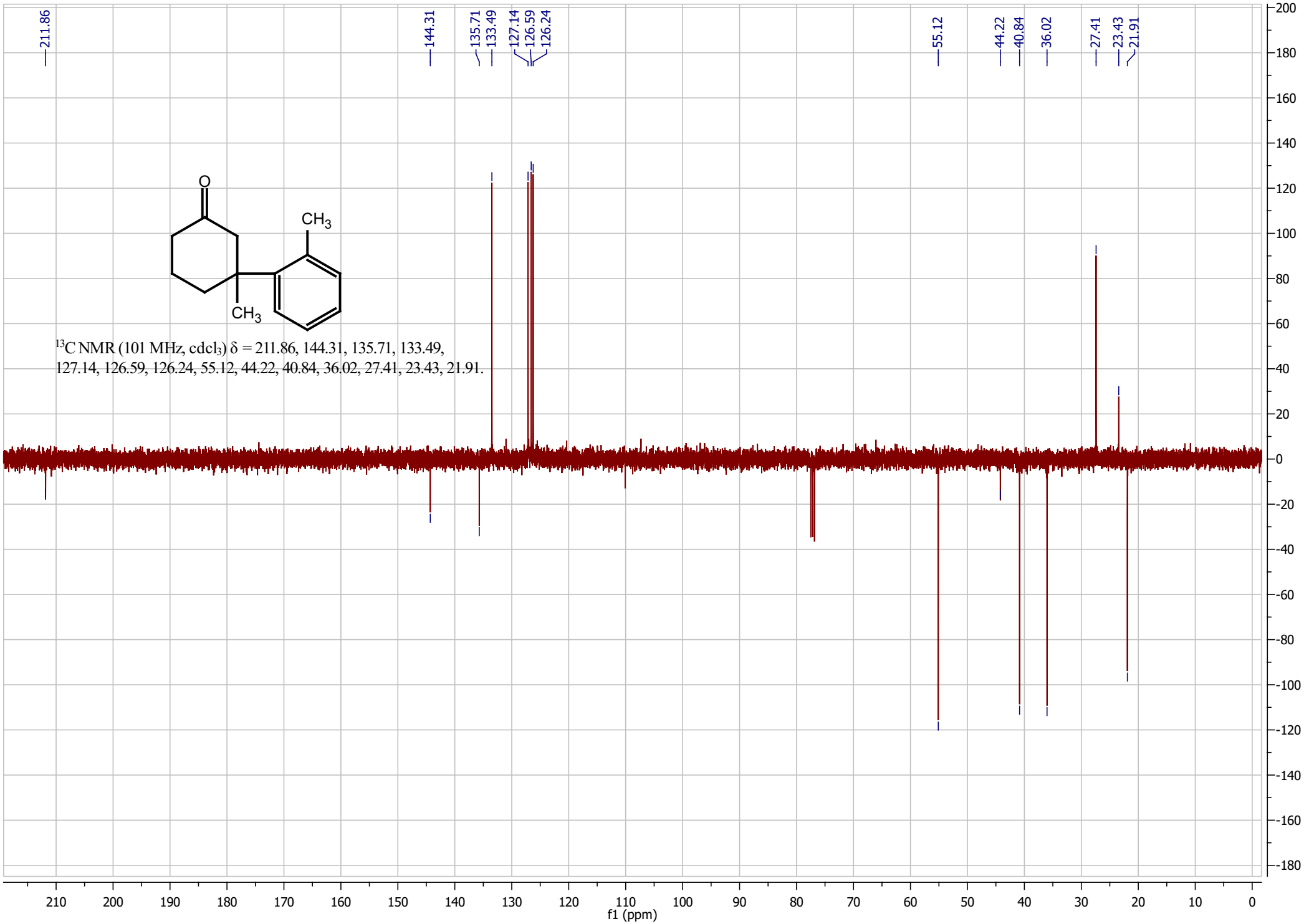
1 PDA Multi 3/225nm,4nm
2 PDA Multi 2/190nm,4nm

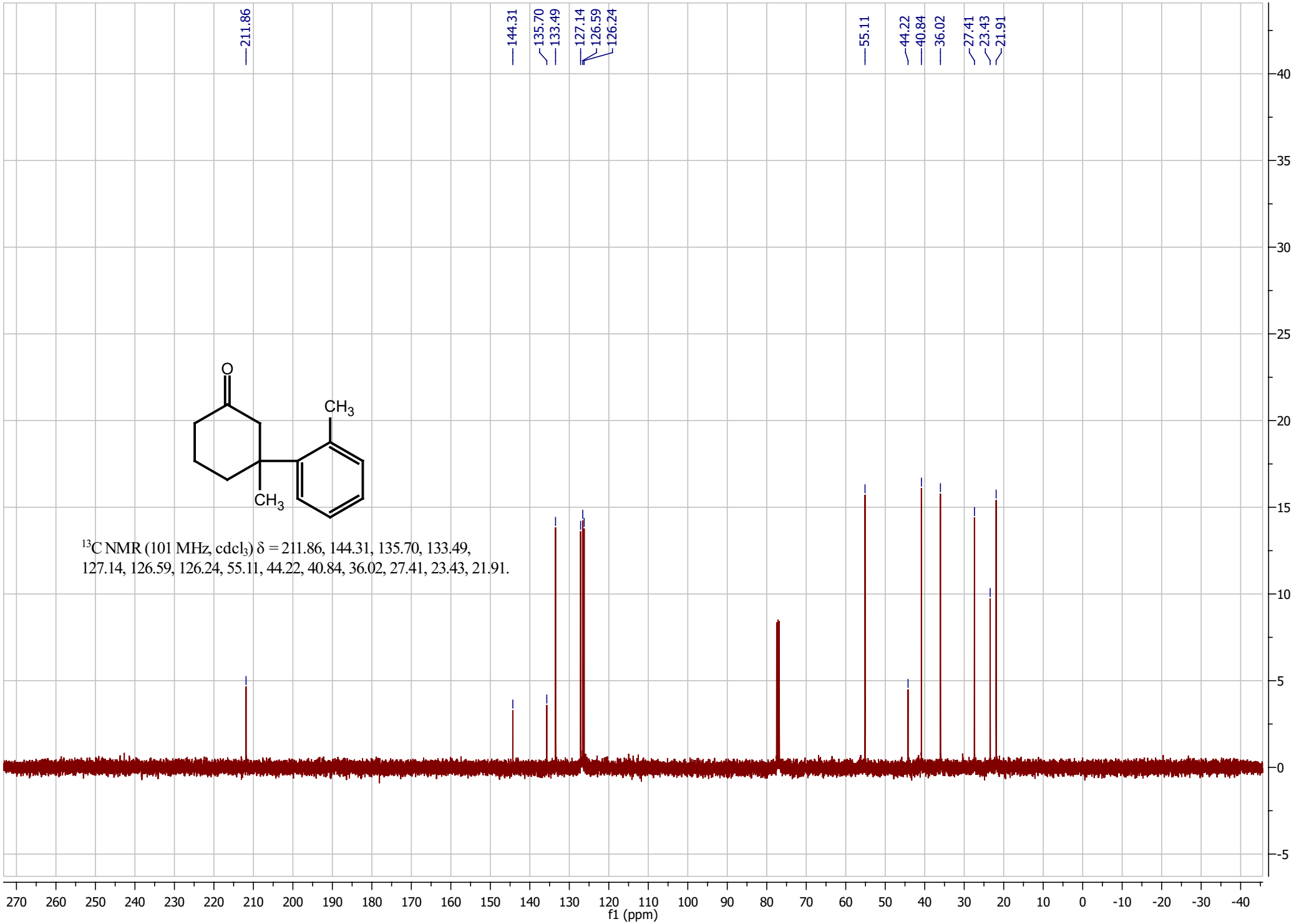
Peak Table

PDA Ch3 225nm

Peak#	Ret. Time	Area	Height	Area%
1	34.977	151690	3261	16.225
2	37.355	783217	14790	83.775
Total		934907	18051	100.000


7.25
7.24
7.16
7.14
7.13
7.11
3.01
2.98
2.54
2.49
2.45
2.33
2.31
2.29
1.89
1.88
1.87
1.86
1.61
1.58
1.42
B (m)
7.24
A (m)
7.14
C (d)
3.00
D (s)
2.54
F (t)
2.31
G (m)
1.90
H (m)
1.62
I (s)
1.42
O
CH3
CH3
1H NMR (400 MHz, cdcl3) δ = 7.25 – 7.21 (m, J=4.3, 1H), 7.17 – 7.10 (m, 3H), 3.00 (d, J=14.2, 1H), 2.54 (s, 3H), 2.47 (d, J=14.4, 2H), 2.31 (t, J=6.8, 2H), 1.99 – 1.82 (m, 2H), 1.67 – 1.57 (m, 1H), 1.42 (s, 3H).
1.02
2.88
1.00
2.84
2.07
2.11
2.09
1.16
3.03
f1 (ppm)


211.86
144.31
135.71
133.49
127.14
126.59
126.24
55.12
44.22
40.84
36.02
27.41
23.43
21.91
O
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 211.86, 144.31, 135.71, 133.49,
127.14, 126.59, 126.24, 55.12, 44.22, 40.84, 36.02, 27.41, 23.43, 21.91.
f1 (ppm)


211.86
144.31
135.70
133.49
127.14
126.59
126.24
55.11
44.22
40.84
36.02
27.41
23.43
21.91
O
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 211.86, 144.31, 135.70, 133.49,
127.14, 126.59, 126.24, 55.11, 44.22, 40.84, 36.02, 27.41, 23.43, 21.91.
f1 (ppm)

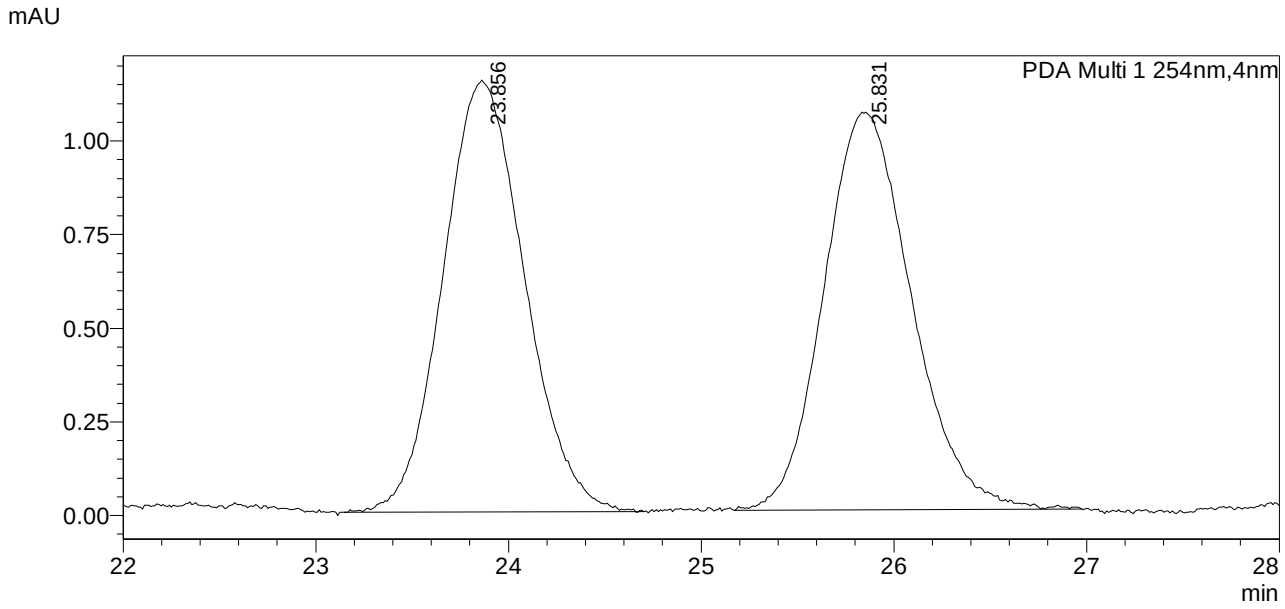
SHIMADZU LabSolutions

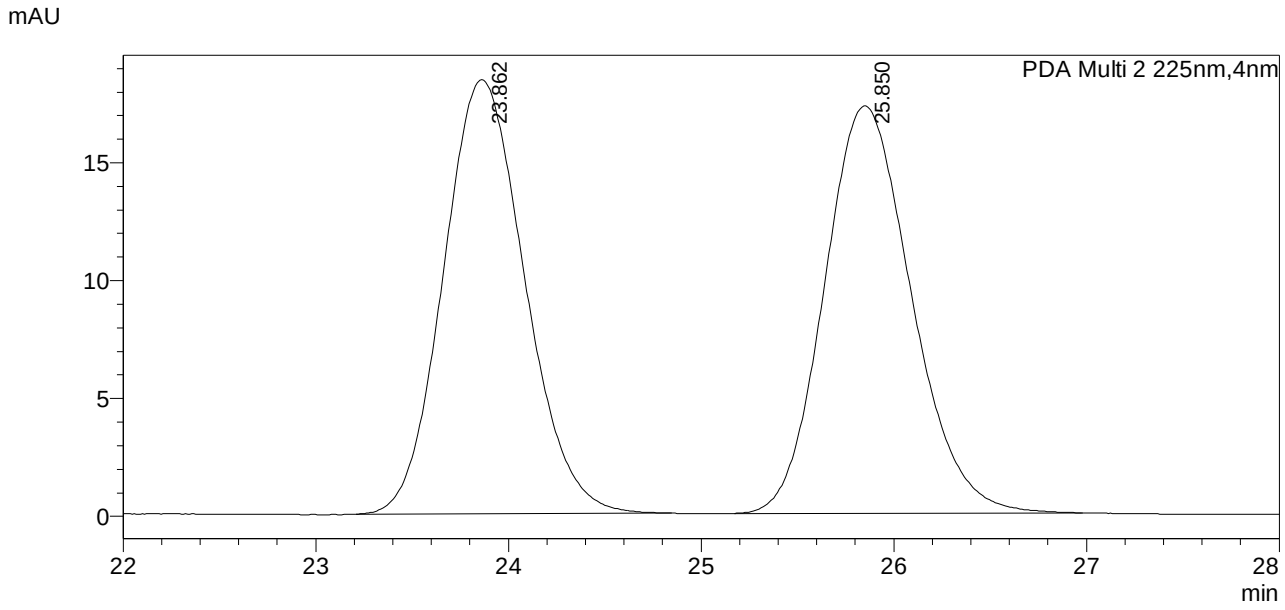
Analysis Report

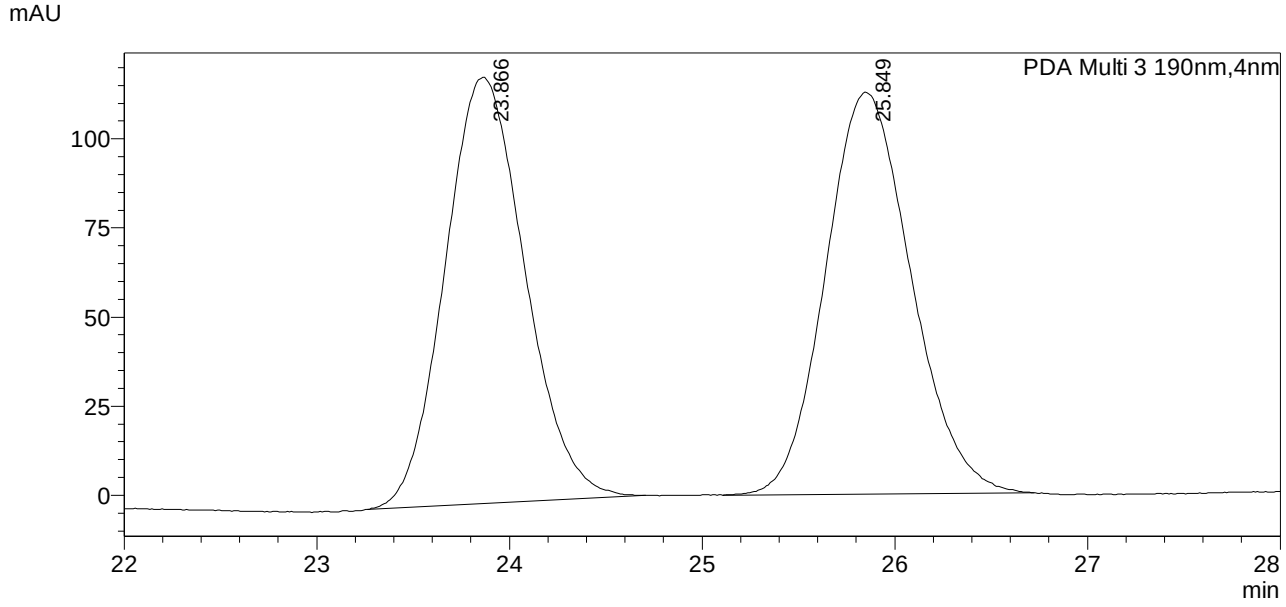
<Sample Information>

Sample Name	: o-methyl boronic acid RAC OD-H-column		
Sample ID	: o-methyl boronic acid RAC OD-H		
Data Filename	: o-methyl boronic acid RAC OD-H-column 99.5_0.5.lcd		
Method Filename	: C2 99.5_0.5 fl0,5 60 min.lcm		
Batch Filename	: 20131015_all column screening.lcb		
Vial #	: 1-78	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 10/26/2013 2:29:23 AM	Acquired by	: System Administrator
Date Processed	: 10/26/2013 4:09:10 PM	Processed by	: System Administrator

<Chromatogram>







<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23.856	33878	1153	50.137
2	25.831	33694	1063	49.863
Total		67572	2215	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	23.862	540284	18411	49.902
2	25.850	542415	17277	50.098
Total		1082698	35687	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	23.866	3459932	119599	49.811
2	25.849	3486143	112746	50.189
Total		6946076	232345	100.000

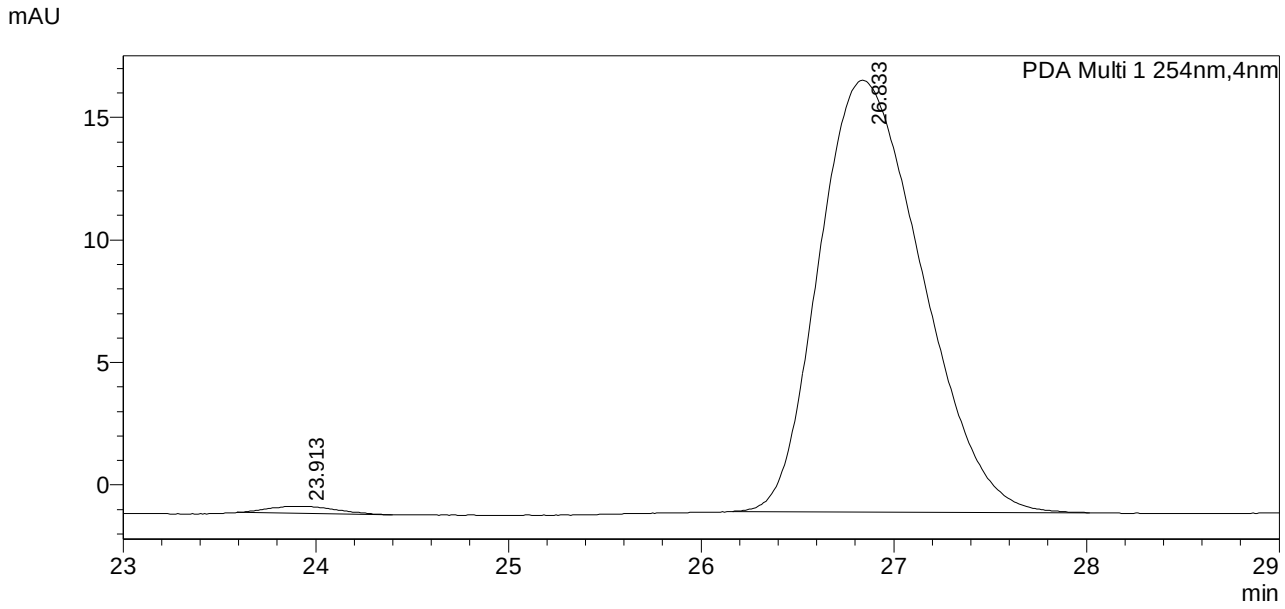
SHIMADZU LabSolutions

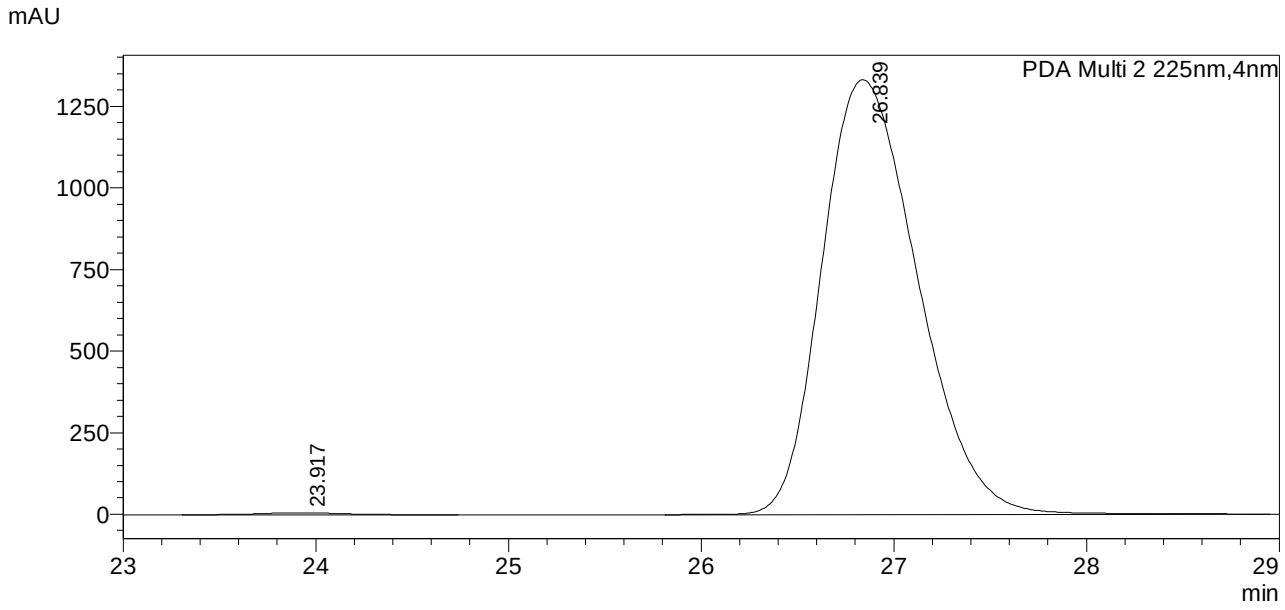
Analysis Report

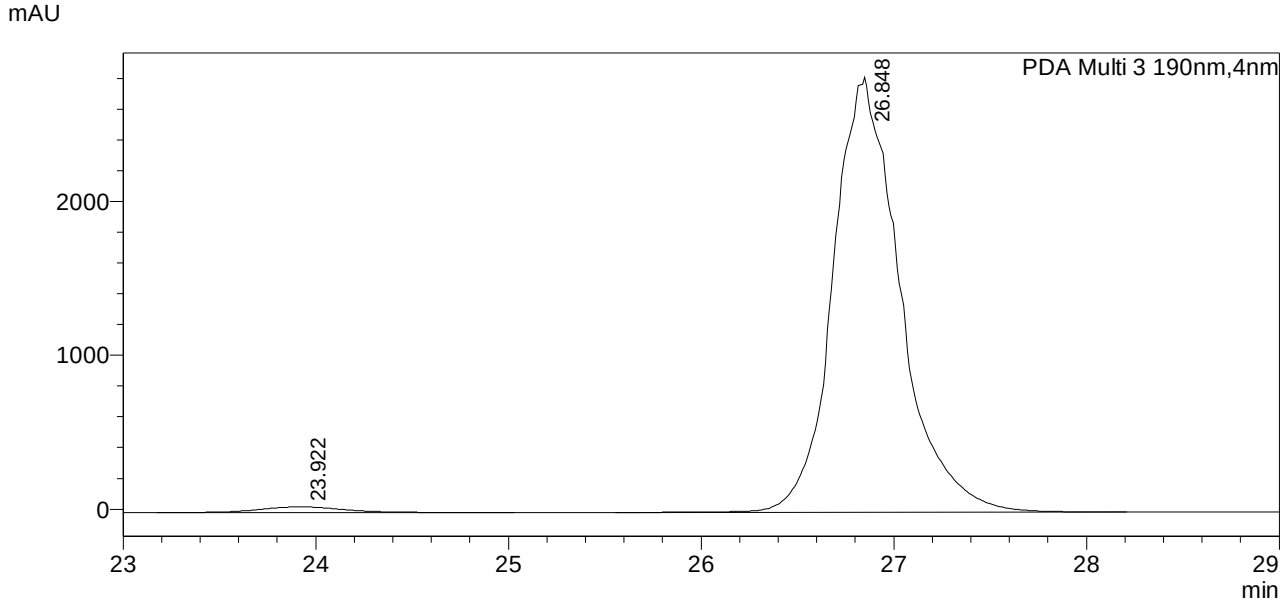
<Sample Information>

Sample Name	: o-methyl boronic acid ENT OD-H-column		
Sample ID	: o-methyl boronic acid RAC OD-H		
Data Filename	: o-methyl boronic acid ENT OD-H-column 99.5_0.5.lcd		
Method Filename	: C2 99.5_0.5 fl0,5 30 min.lcm		
Batch Filename	: 20131025.lcb		
Vial #	: 1-47	Sample Type	: Unknown
Injection Volume	: 3 uL	Level	: 1
Date Acquired	: 10/26/2013 4:46:18 PM	Acquired by	: System Administrator
Date Processed	: 10/26/2013 5:43:04 PM	Processed by	: System Administrator

<Chromatogram>







<Peak Table>

PDA Ch1 254nm

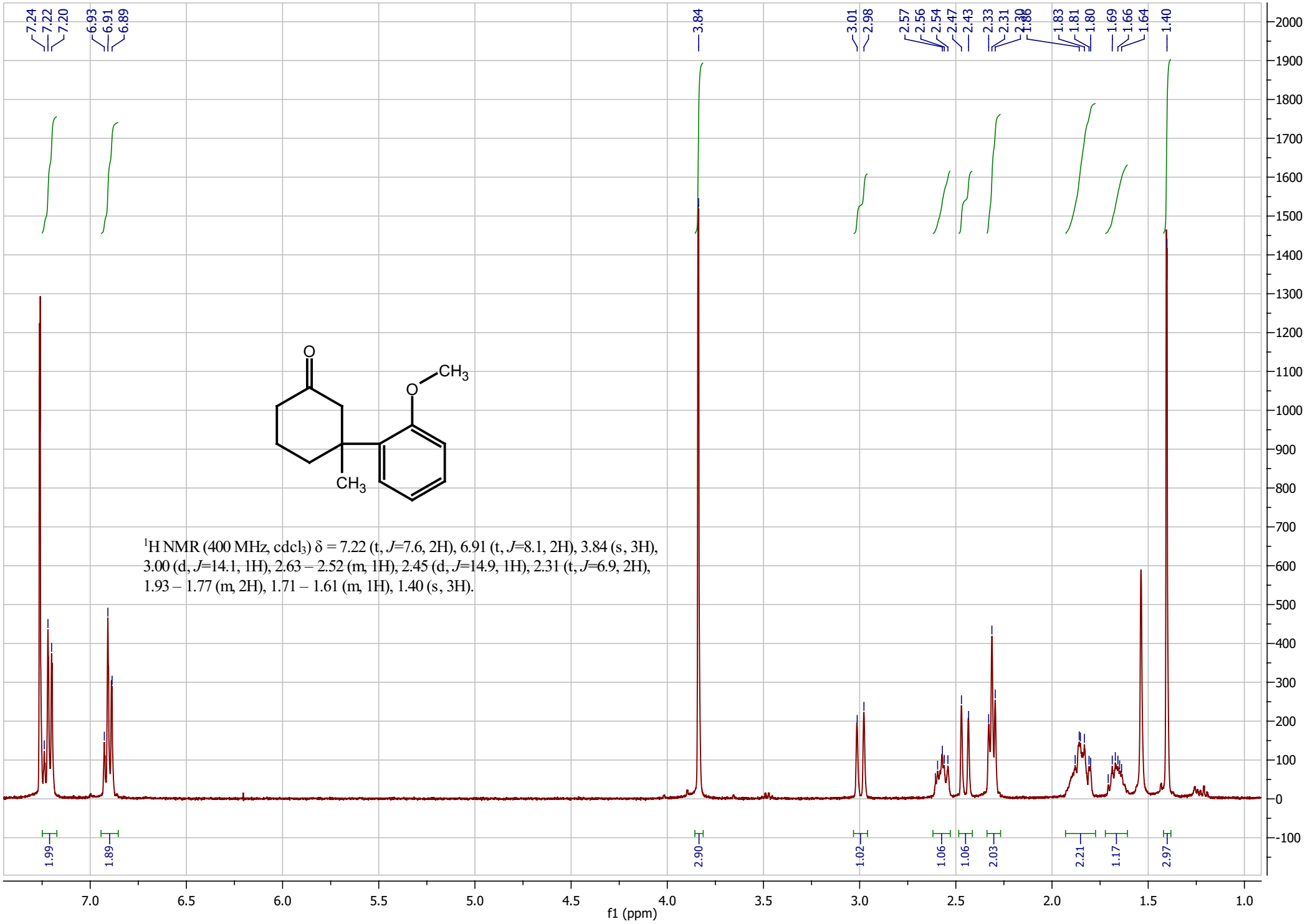
Peak#	Ret. Time	Area	Height	Area%
1	23.913	7229	297	1.097
2	26.833	651761	17612	98.903
Total		658990	17908	100.000

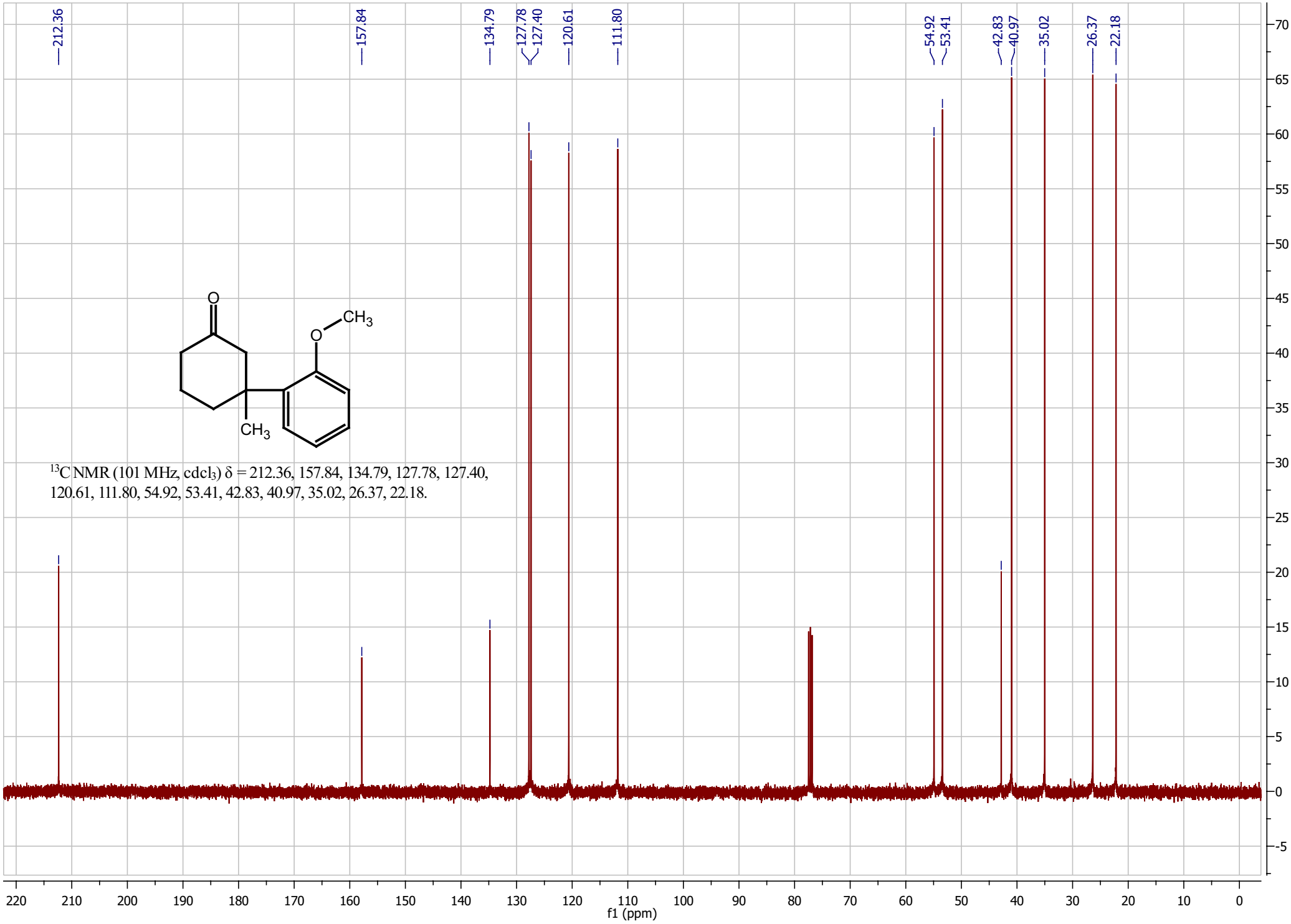
PDA Ch2 225nm

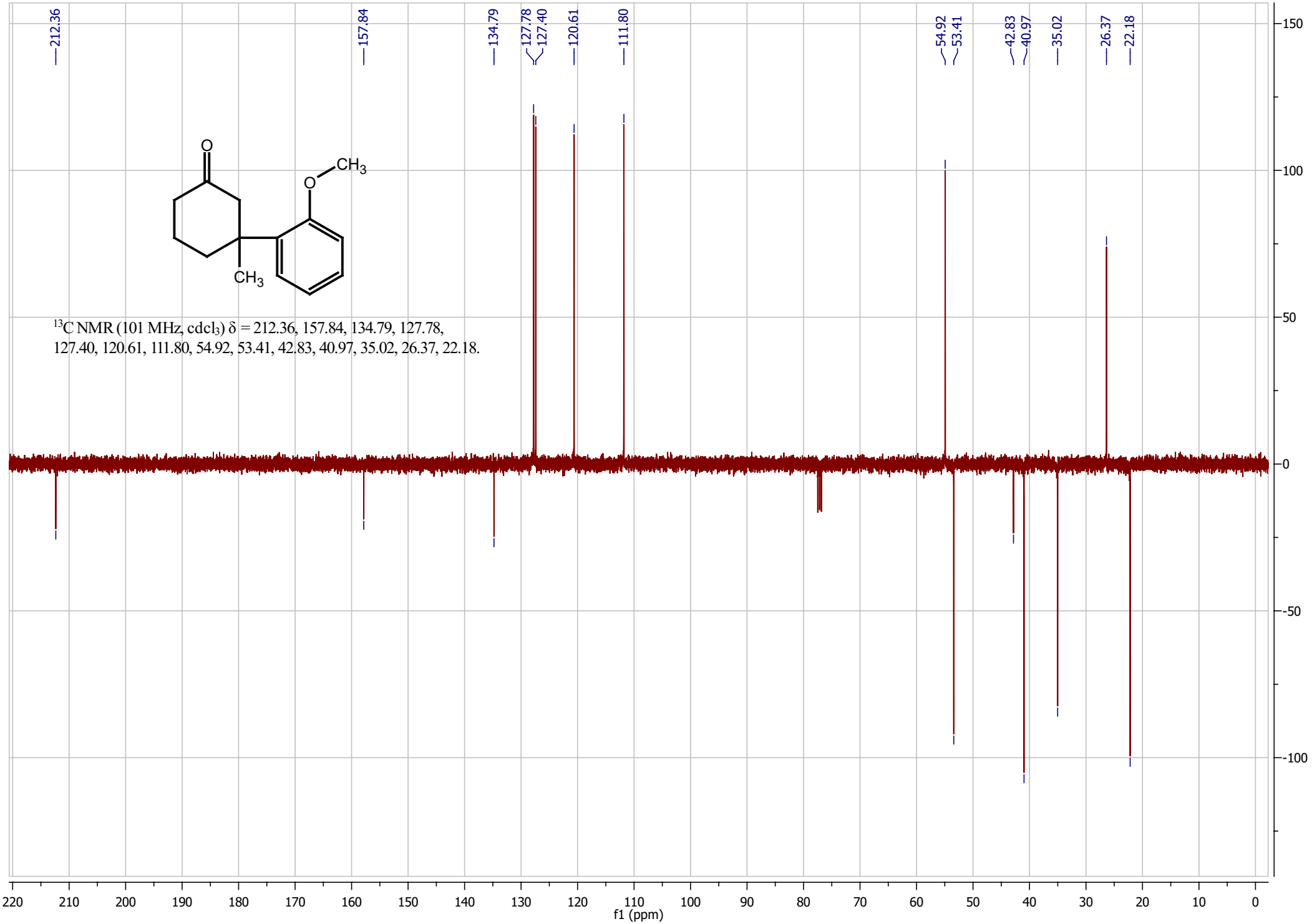
Peak#	Ret. Time	Area	Height	Area%
1	23.917	167142	5798	0.362
2	26.839	45975434	1331899	99.638
Total		46142576	1337698	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	23.922	1061063	36042	1.534
2	26.848	68103744	2825777	98.466
Total		69164807	2861819	100.000


7.24
7.22
7.20
6.93
6.91
6.89
3.84
3.01
2.98
2.57
2.56
2.54
2.47
2.43
2.33
2.31
1.83
1.81
1.80
1.69
1.66
1.64
1.40
O
O
CH3
CH3
1H NMR (400 MHz, cdcl3) δ = 7.22 (t, J=7.6, 2H), 6.91 (t, J=8.1, 2H), 3.84 (s, 3H), 3.00 (d, J=14.1, 1H), 2.63 – 2.52 (m, 1H), 2.45 (d, J=14.9, 1H), 2.31 (t, J=6.9, 2H), 1.93 – 1.77 (m, 2H), 1.71 – 1.61 (m, 1H), 1.40 (s, 3H).
1.99
1.89
2.90
1.02
1.06
1.06
2.03
2.21
1.17
2.97
f1 (ppm)


212.36
157.84
134.79
127.78
127.40
120.61
111.80
54.92
53.41
42.83
40.97
35.02
26.37
22.18
O
O
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 212.36, 157.84, 134.79, 127.78, 127.40,
120.61, 111.80, 54.92, 53.41, 42.83, 40.97, 35.02, 26.37, 22.18.
f1 (ppm)


212.36
157.84
134.79
127.78
127.40
120.61
111.80
54.92
53.41
42.83
40.97
35.02
26.37
22.18
O
CH3
O
CH3
13C NMR (101 MHz, cdcl3) δ = 212.36, 157.84, 134.79, 127.78,
127.40, 120.61, 111.80, 54.92, 53.41, 42.83, 40.97, 35.02, 26.37, 22.18.
150
100
50
0
-50
-100
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

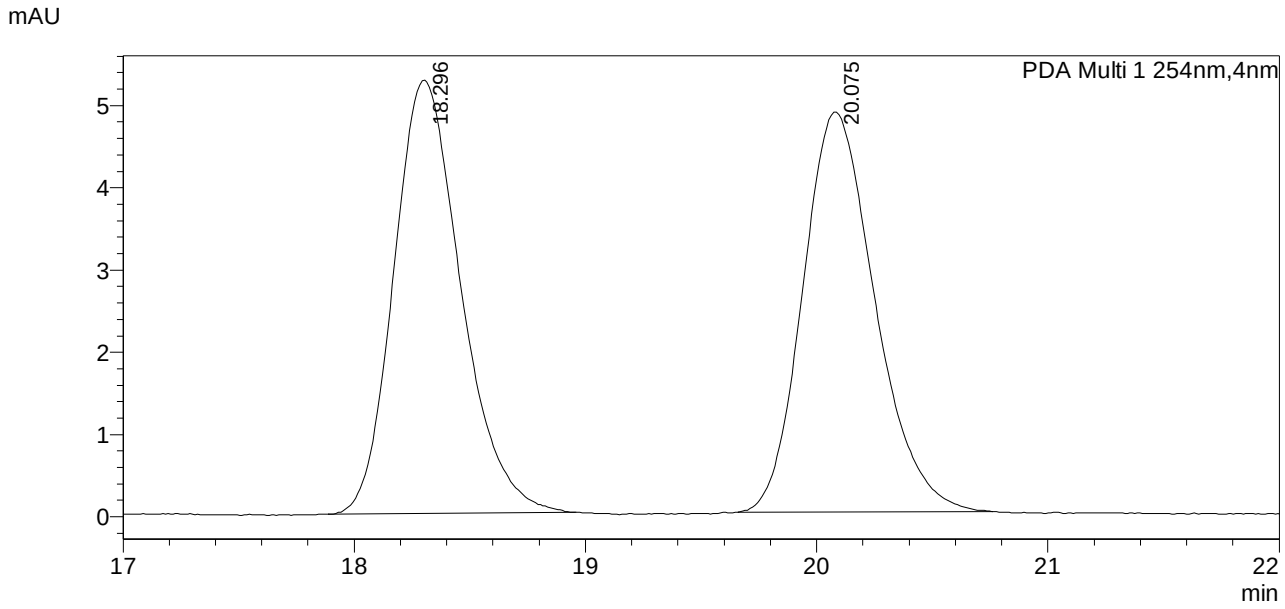
SHIMADZU LabSolutions

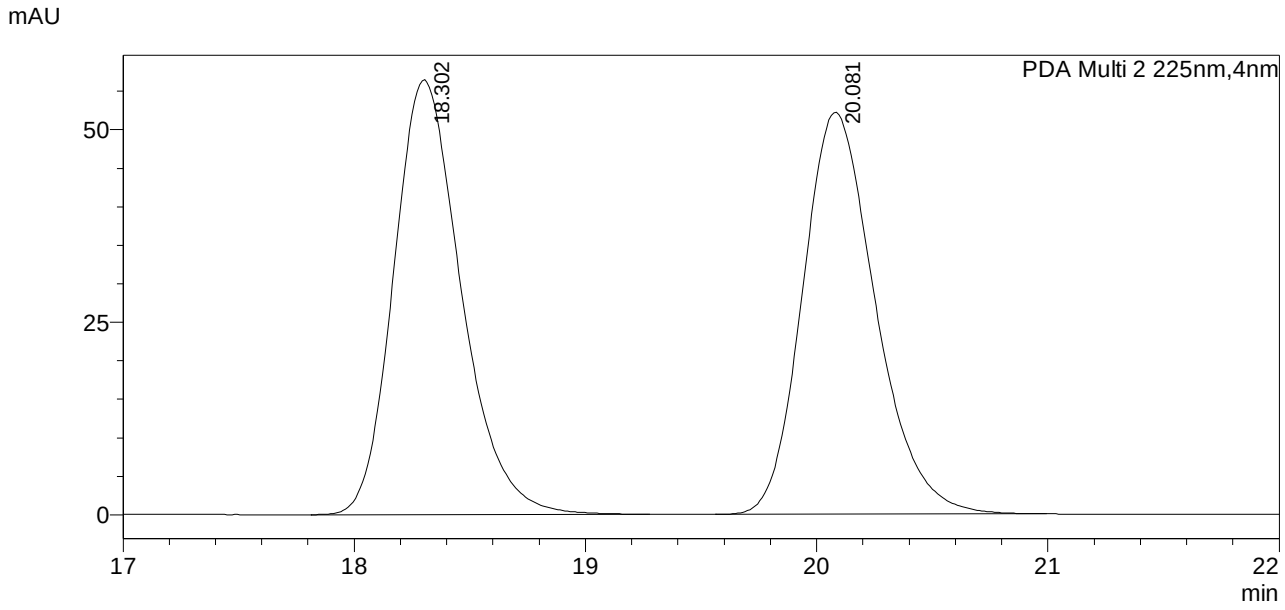
Analysis Report

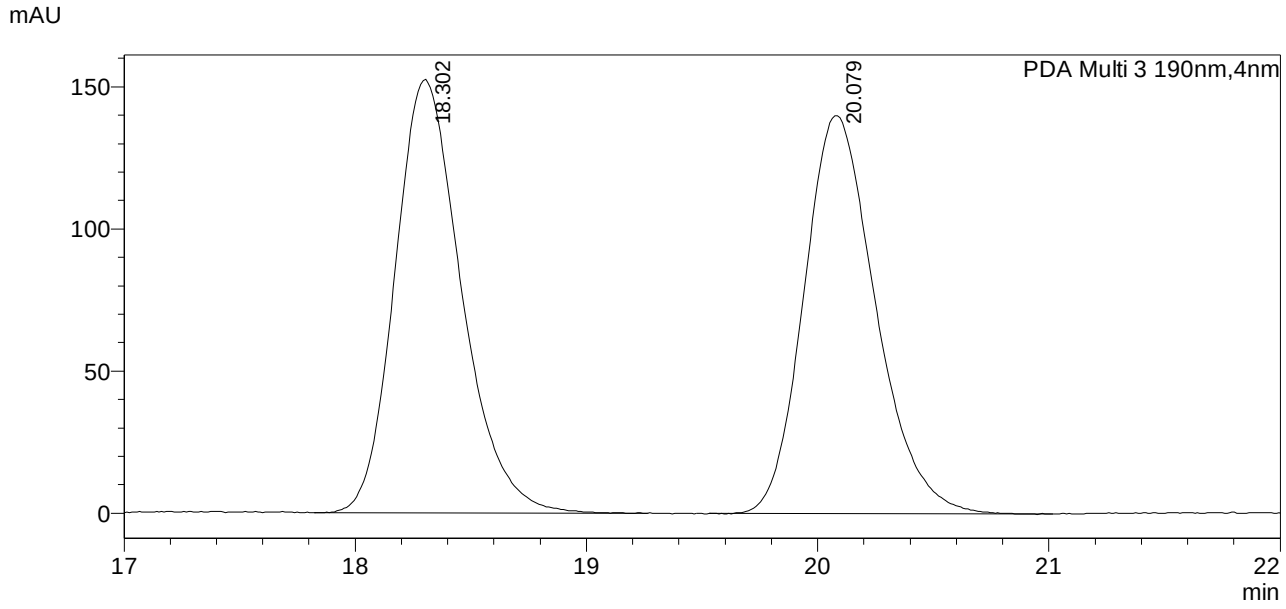
<Sample Information>

Sample Name	: o-methyl boronic acid RAC AD-H-column		
Sample ID	: o-methyl boronic acid RAC AD-H-		
Data Filename	: o-methoxy boronic acid RAC AD-H.lcd		
Method Filename	: C5 99_1 fl0,5 60 min.lcm		
Batch Filename	: 20131004 (99_1 all column screening).lcb		
Vial #	: 1-80	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 10/18/2013 12:17:39 AM	Acquired by	: System Administrator
Date Processed	: 10/19/2013 2:43:15 PM	Processed by	: System Administrator

<Chromatogram>







<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	18.296	106427	5268	50.204
2	20.075	105560	4860	49.796
Total		211987	10128	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	18.302	1148156	56451	50.072
2	20.081	1144872	52158	49.928
Total		2293028	108609	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	18.302	3058116	152561	50.358
2	20.079	3014580	139968	49.642
Total		6072697	292529	100.000

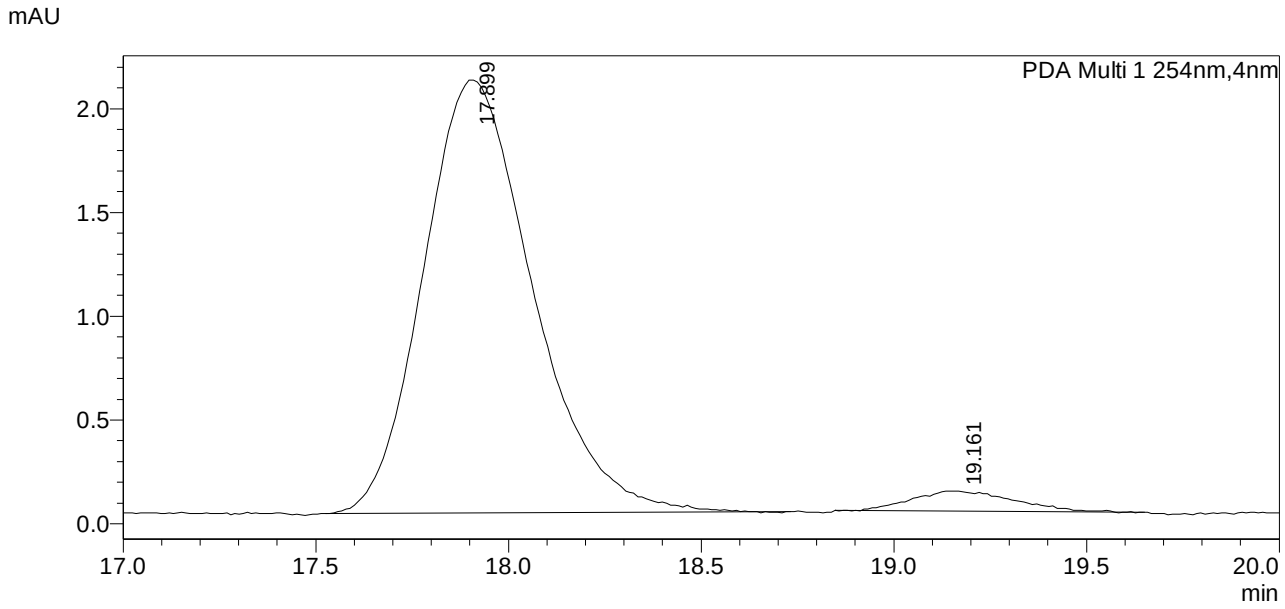
SHIMADZU LabSolutions

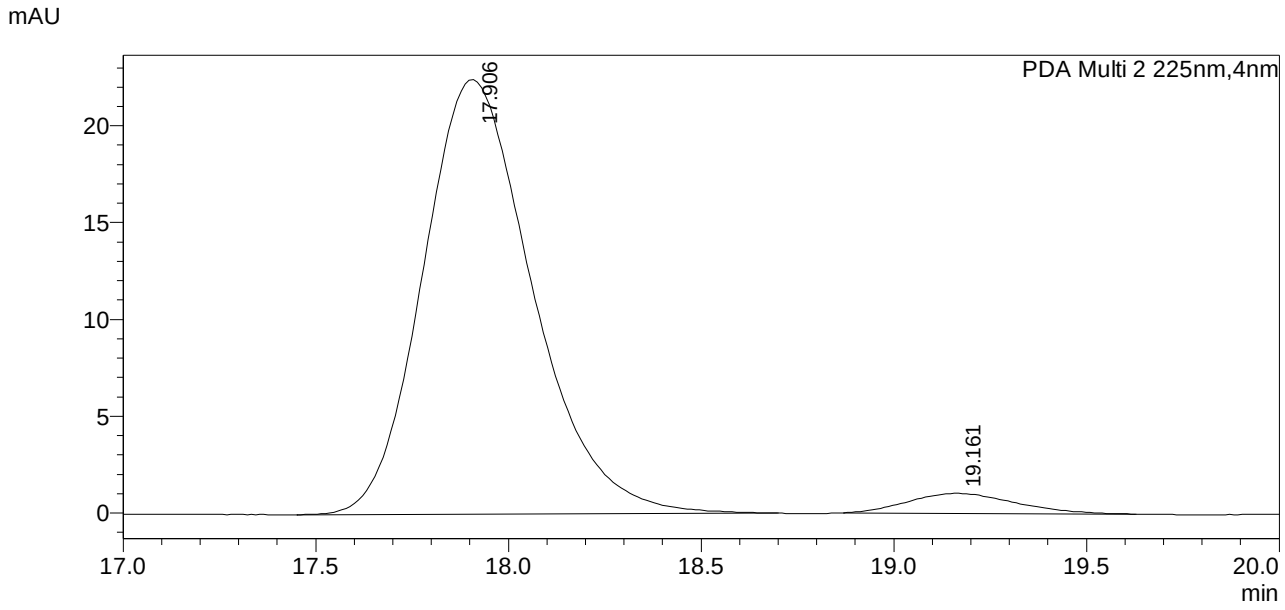
Analysis Report

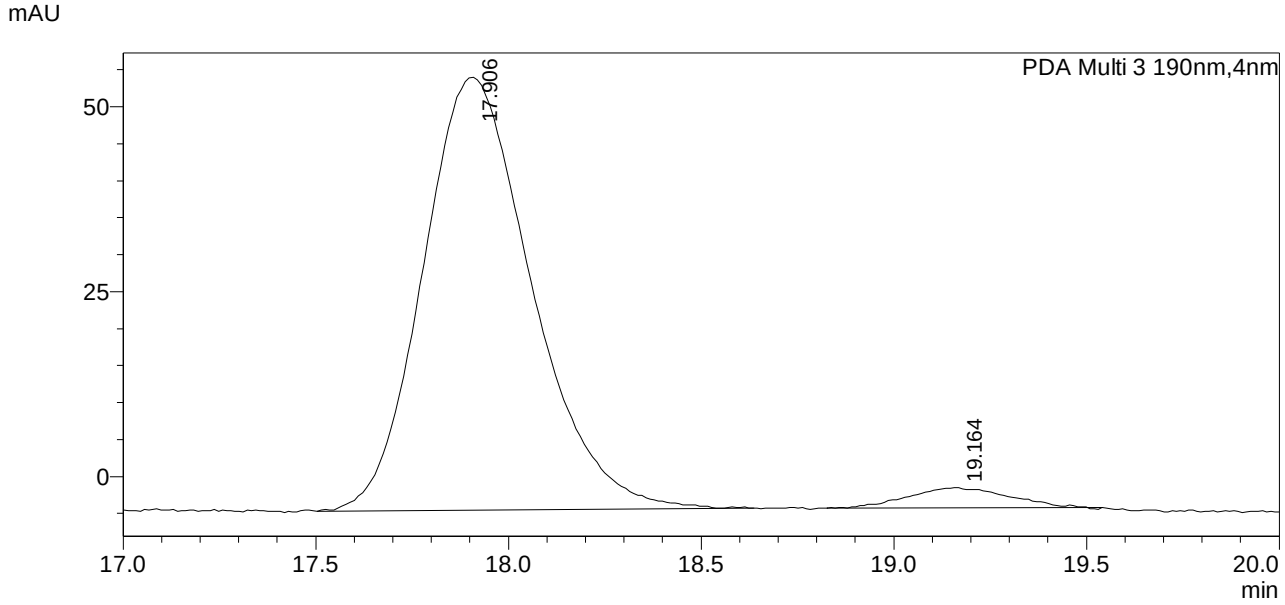
<Sample Information>

Sample Name	: o-methoxy boronic acid ENT AD-H-column		
Sample ID	: o-methoxy boronic acid ENT AD-H		
Data Filename	: o-methoxy boronic acid ENT AD-H-column.lcd		
Method Filename	: C5 99_1 fl0,5 30 min.lcm		
Batch Filename	: 20131026.lcb		
Vial #	: 1-48	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 10/27/2013 2:15:03 PM	Acquired by	: System Administrator
Date Processed	: 10/27/2013 2:59:00 PM	Processed by	: System Administrator

<Chromatogram>







<Peak Table>

PDA Ch1 254nm

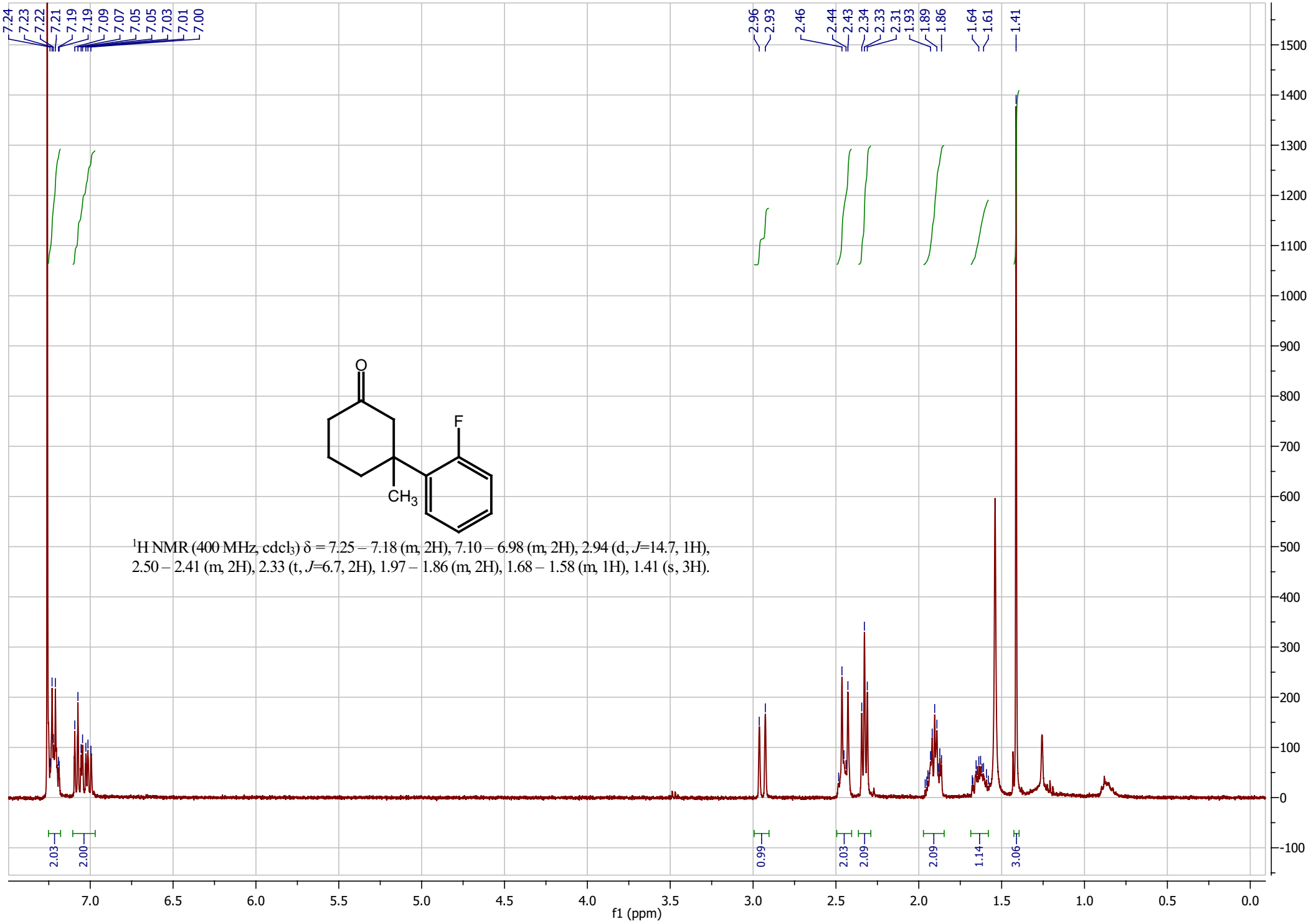
Peak#	Ret. Time	Area	Height	Area%
1	17.899	41144	2085	95.826
2	19.161	1792	97	4.174
Total		42936	2182	100.000

PDA Ch2 225nm

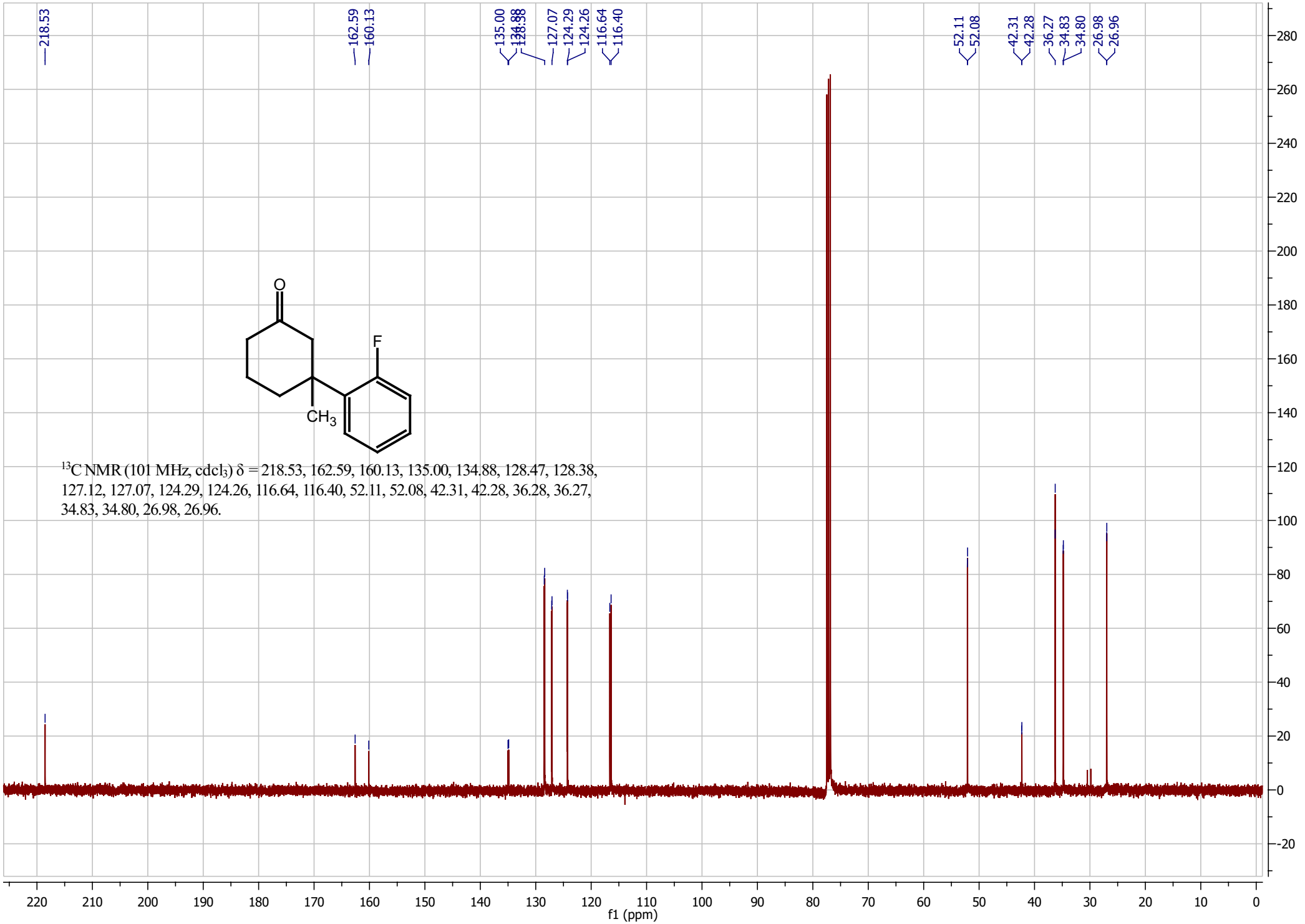
Peak#	Ret. Time	Area	Height	Area%
1	17.906	444494	22438	95.699
2	19.161	19975	1029	4.301
Total		464469	23467	100.000

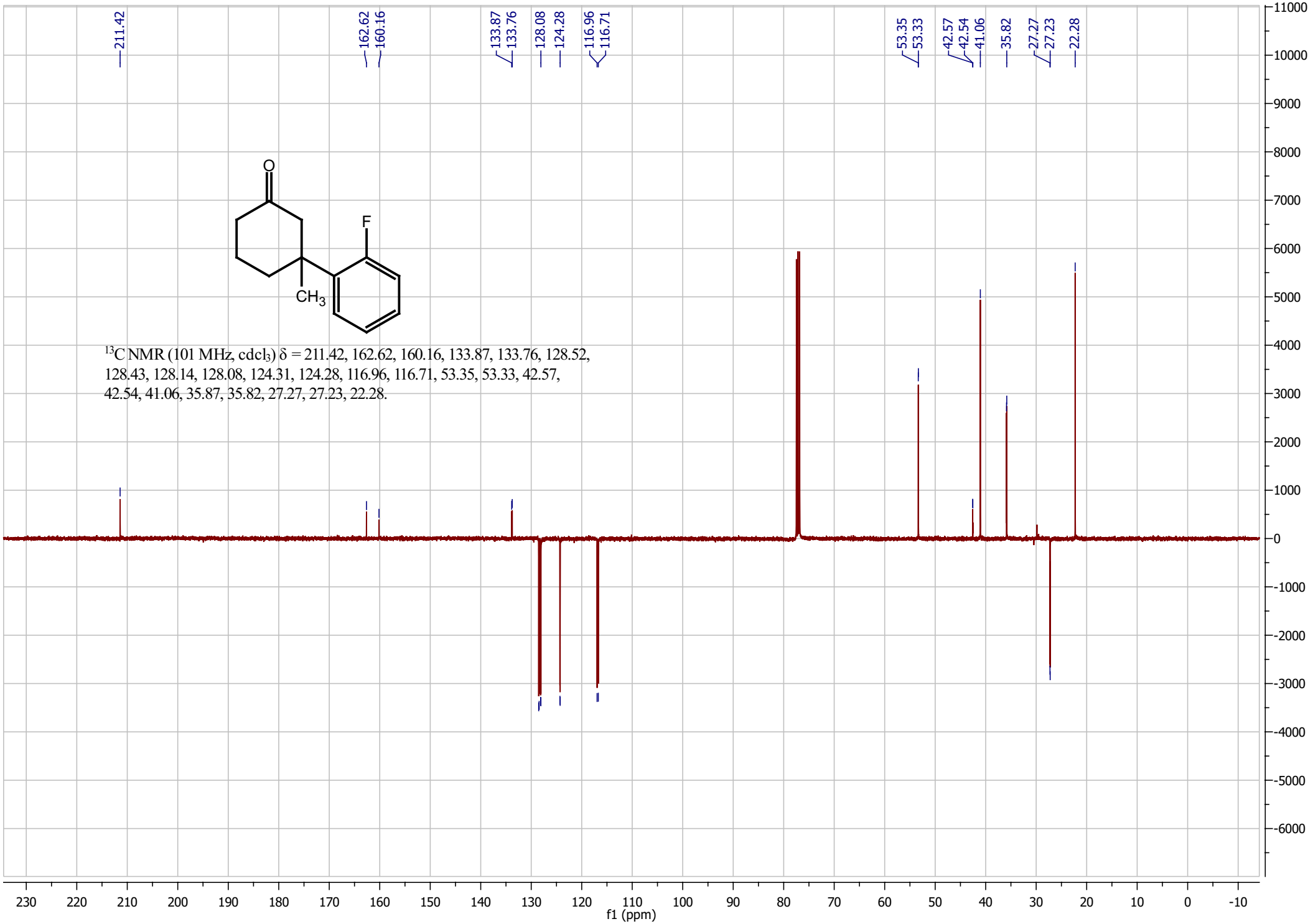
PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	17.906	1145378	58491	95.931
2	19.164	48588	2707	4.069
Total		1193965	61198	100.000



^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.25 – 7.18 (m, 2H), 7.10 – 6.98 (m, 2H), 2.94 (d, *J*=14.7, 1H), 2.50 – 2.41 (m, 2H), 2.33 (t, *J*=6.7, 2H), 1.97 – 1.86 (m, 2H), 1.68 – 1.58 (m, 1H), 1.41 (s, 3H).


218.53
162.59
160.13
135.00
134.88
128.47
128.38
127.07
124.29
124.26
116.64
116.40
52.11
52.08
42.31
42.28
36.27
34.83
34.80
26.98
26.96
O
F
CH3
13C NMR (101 MHz, cdcl3) δ = 218.53, 162.59, 160.13, 135.00, 134.88, 128.47, 128.38, 127.12, 127.07, 124.29, 124.26, 116.64, 116.40, 52.11, 52.08, 42.31, 42.28, 36.28, 36.27, 34.83, 34.80, 26.98, 26.96.
f1 (ppm)

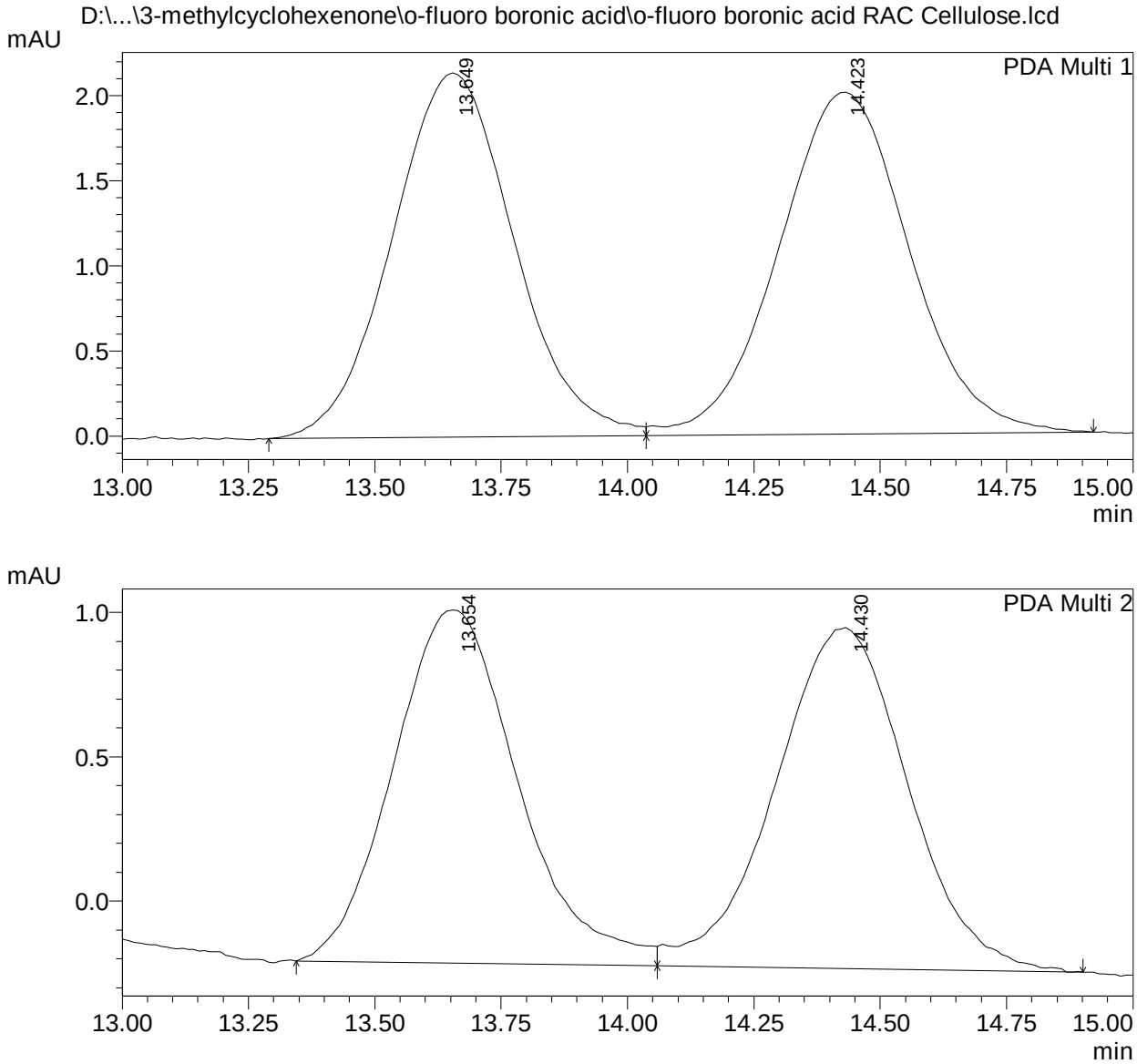

211.42
162.62
160.16
133.87
133.76
128.08
124.28
116.96
116.71
53.35
53.33
42.57
42.54
41.06
35.82
27.27
27.23
22.28
O
F
CH3
13C NMR (101 MHz, cdcl3) δ = 211.42, 162.62, 160.16, 133.87, 133.76, 128.52, 128.43, 128.14, 128.08, 124.31, 124.28, 116.96, 116.71, 53.35, 53.33, 42.57, 42.54, 41.06, 35.87, 35.82, 27.27, 27.23, 22.28.
f1 (ppm)

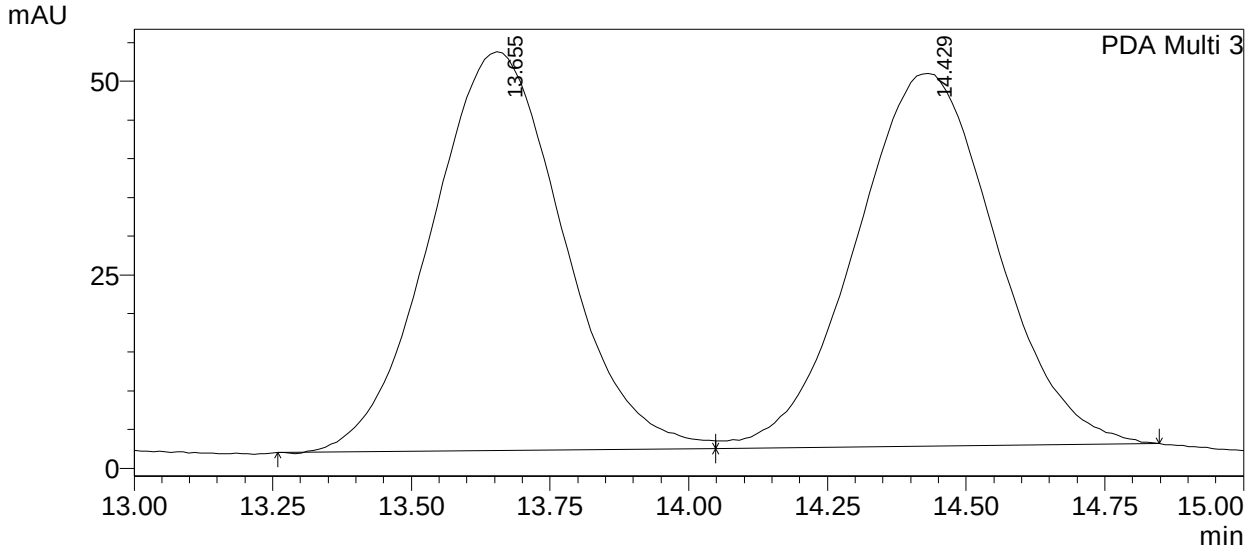
==== Shimadzu LCsolution Analysis Report ====

D:\...\Substrate Scope\3-methylcyclohexenone\o-fluoro boronic acid\o-fluoro boronic acid RAC Cellulose.lcd

Acquired by	: System Administrator
Sample Name	: o-fluoro boronic acid RAC Cellulose
Sample ID	: o-fluoro boronic acid RAC Cellu
Tray#	: 1
Vail #	: 3
Injection Volume	: 2 uL
Data File Name	: o-fluoro boronic acid RAC Cellulose.lcd
Method File Name	: C6 99_1 fl0,5 60 min.lcm
Batch File Name	: 20131031_all column screening.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 10/30/2013 7:23:55 PM
Data Processed	: 10/31/2013 10:27:53 AM

<Chromatogram>





1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	13.649	35734	2138	49.816
2	14.423	35997	2007	50.184
Total		71731	4145	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	13.654	20976	1224	49.344
2	14.430	21533	1181	50.656
Total		42509	2405	100.000

PDA Ch3 190nm

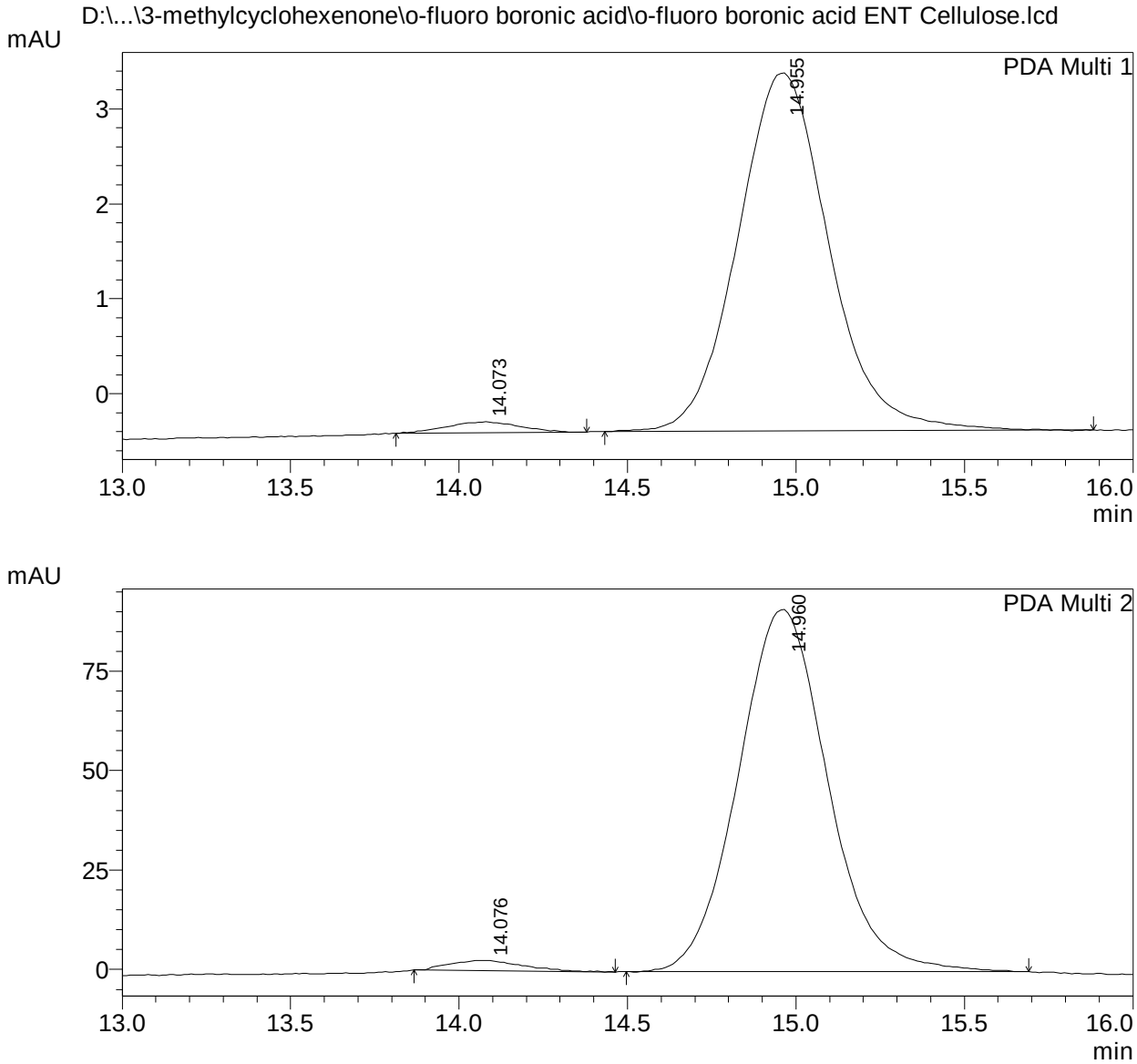
Peak#	Ret. Time	Area	Height	Area%
1	13.655	853468	51465	50.134
2	14.429	848907	48154	49.866
Total		1702374	99619	100.000

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

D:\...\Substrate Scope\3-methylcyclohexenone\o-fluoro boronic acid\o-fluoro boronic acid ENT Cellulose.lcd

Acquired by	: System Administrator
Sample Name	: o-fluoro boronic acid ENT Cellulose
Sample ID	: o-fluoro boronic acid ENT Cellu
Tray#	: 1
Vail #	: 1
Injection Volume	: 2 uL
Data File Name	: o-fluoro boronic acid ENT Cellulose.lcd
Method File Name	: C6 99_1 fl0,5 20 min.lcm
Batch File Name	: 20131031.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 10/31/2013 10:42:40 AM
Data Processed	: 10/31/2013 11:26:58 AM

<Chromatogram>



1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/190nm,4nm

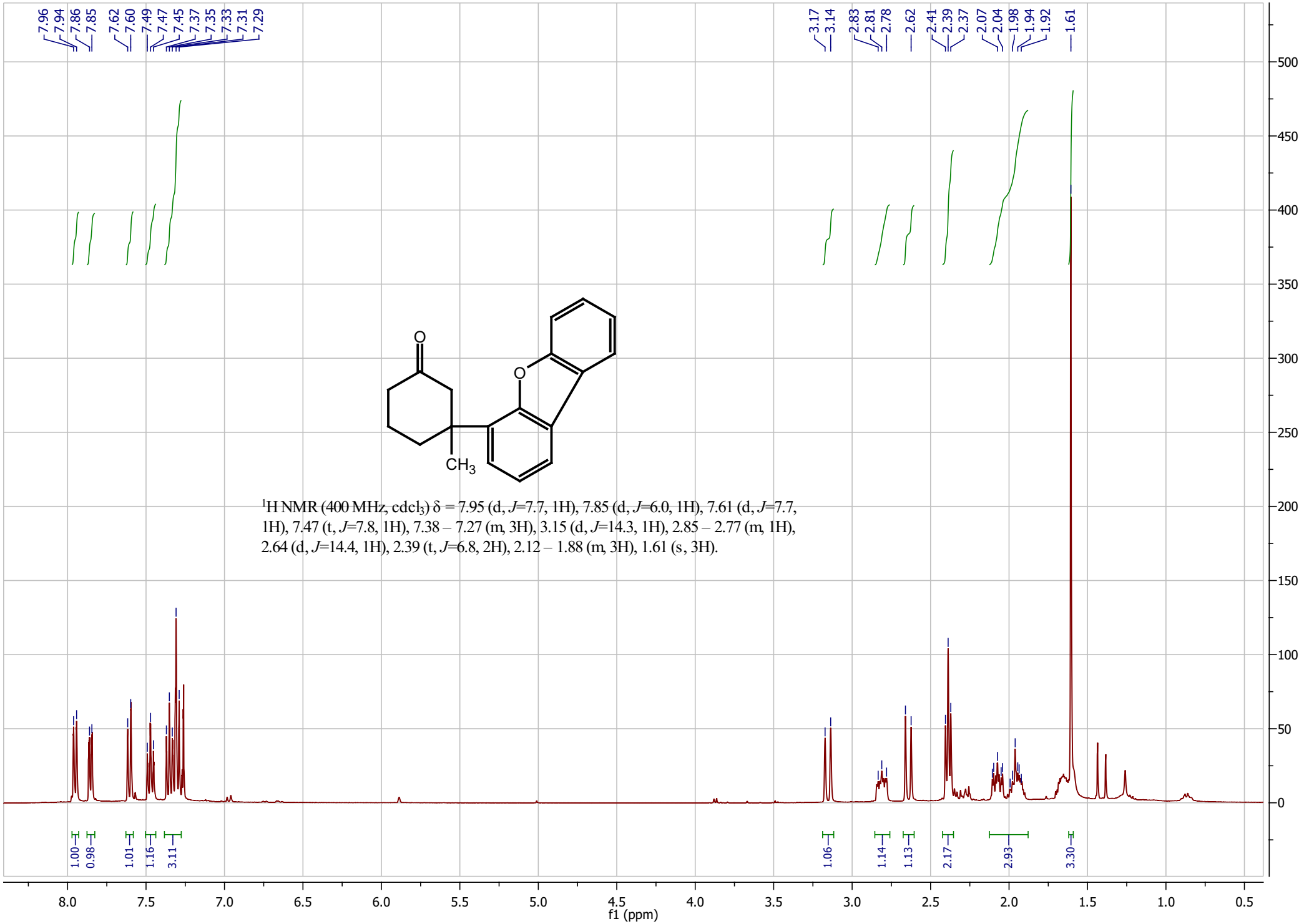
Peak Table

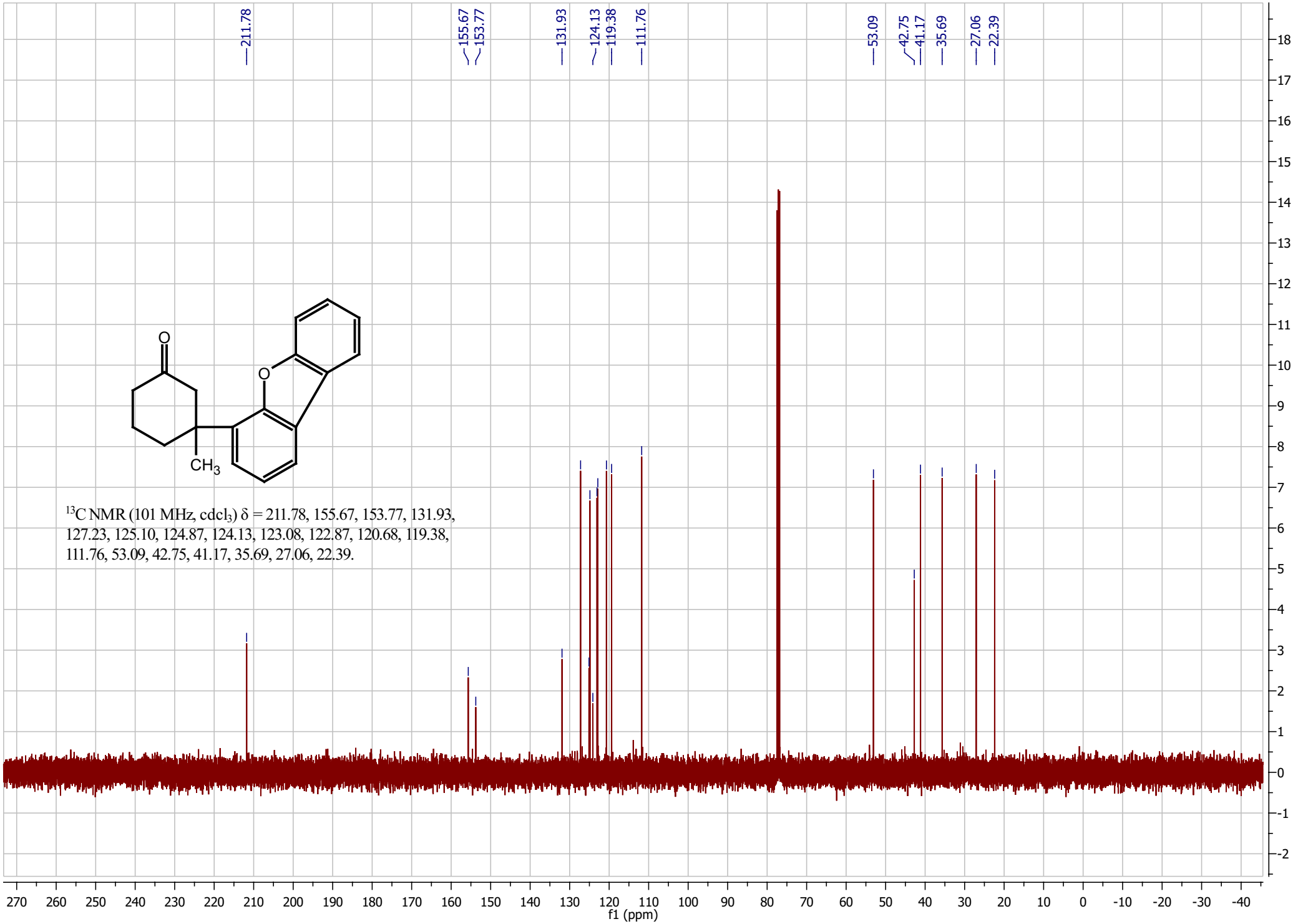
PDA Ch1 254nm

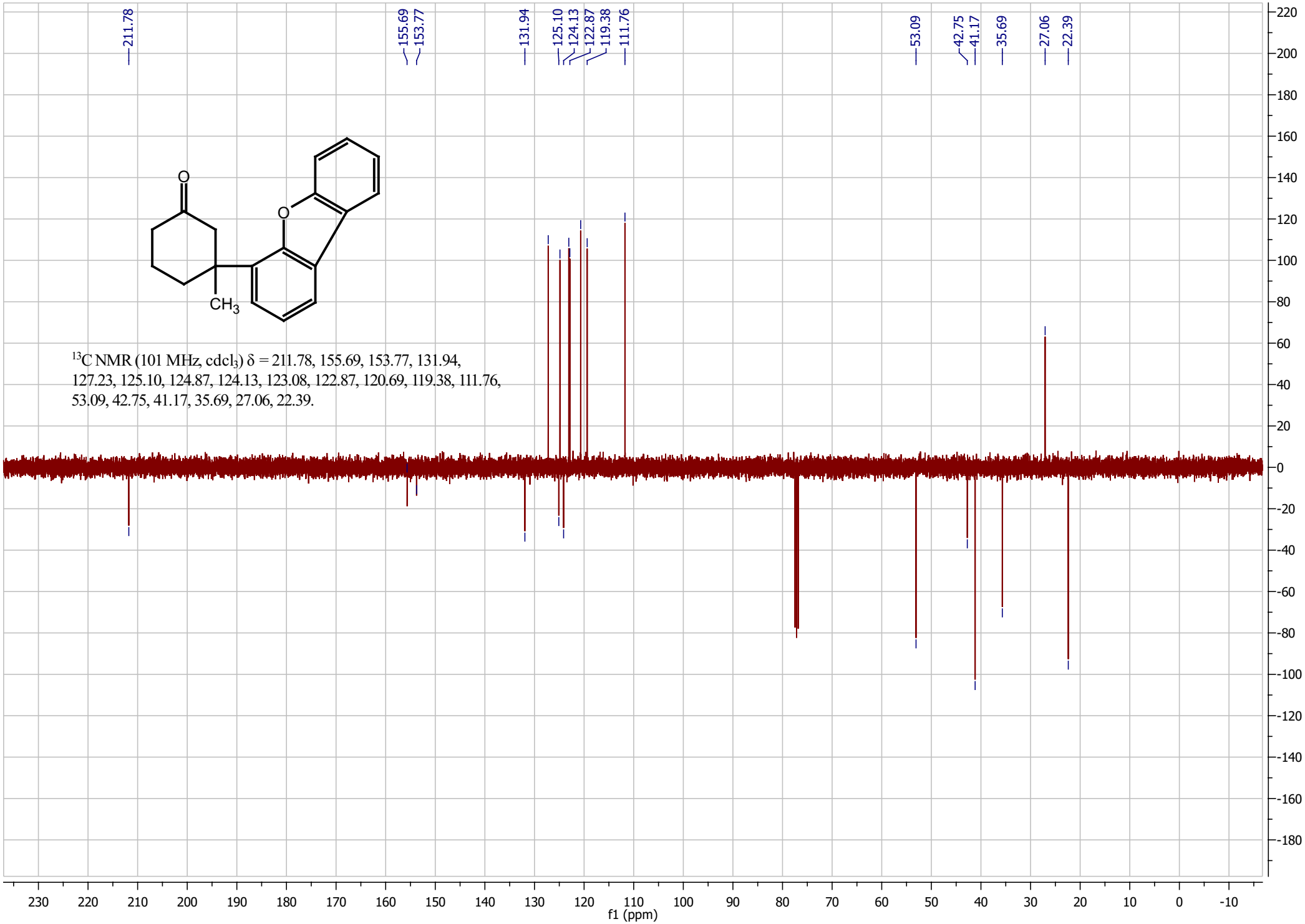
Peak#	Ret. Time	Area	Height	Area%
1	14.073	1710	114	2.355
2	14.955	70885	3769	97.645
Total		72594	3883	100.000

PDA Ch2 190nm

Peak#	Ret. Time	Area	Height	Area%
1	14.076	39568	2636	2.292
2	14.960	1686933	91076	97.708
Total		1726500	93712	100.000


7.96
7.94
7.86
7.85
7.62
7.60
7.49
7.47
7.45
7.37
7.35
7.33
7.31
7.29
3.17
3.14
2.83
2.81
2.78
2.62
2.41
2.39
2.37
2.07
2.04
1.98
1.94
1.92
1.61
O
O
CH3
[1]H NMR (400 MHz, cdcl3) δ = 7.95 (d, J=7.7, 1H), 7.85 (d, J=6.0, 1H), 7.61 (d, J=7.7, 1H), 7.47 (t, J=7.8, 1H), 7.38 – 7.27 (m, 3H), 3.15 (d, J=14.3, 1H), 2.85 – 2.77 (m, 1H), 2.64 (d, J=14.4, 1H), 2.39 (t, J=6.8, 2H), 2.12 – 1.88 (m, 3H), 1.61 (s, 3H).
1.00
0.98
1.01
1.16
3.11
1.06
1.14
1.13
2.17
2.93
3.30
f1 (ppm)


211.78
155.67
153.77
131.93
124.13
119.38
111.76
53.09
42.75
41.17
35.69
27.06
22.39
O
O
CH3
13C NMR (101 MHz, cdcl3) δ = 211.78, 155.67, 153.77, 131.93,
127.23, 125.10, 124.87, 124.13, 123.08, 122.87, 120.68, 119.38,
111.76, 53.09, 42.75, 41.17, 35.69, 27.06, 22.39.
f1 (ppm)


211.78
155.69
153.77
131.94
125.10
124.13
122.87
119.38
111.76
53.09
42.75
41.17
35.69
27.06
22.39
O
O
CH3
13C NMR (101 MHz, cdcl3) δ = 211.78, 155.69, 153.77, 131.94,
127.23, 125.10, 124.87, 124.13, 123.08, 122.87, 120.69, 119.38, 111.76,
53.09, 42.75, 41.17, 35.69, 27.06, 22.39.
f1 (ppm)

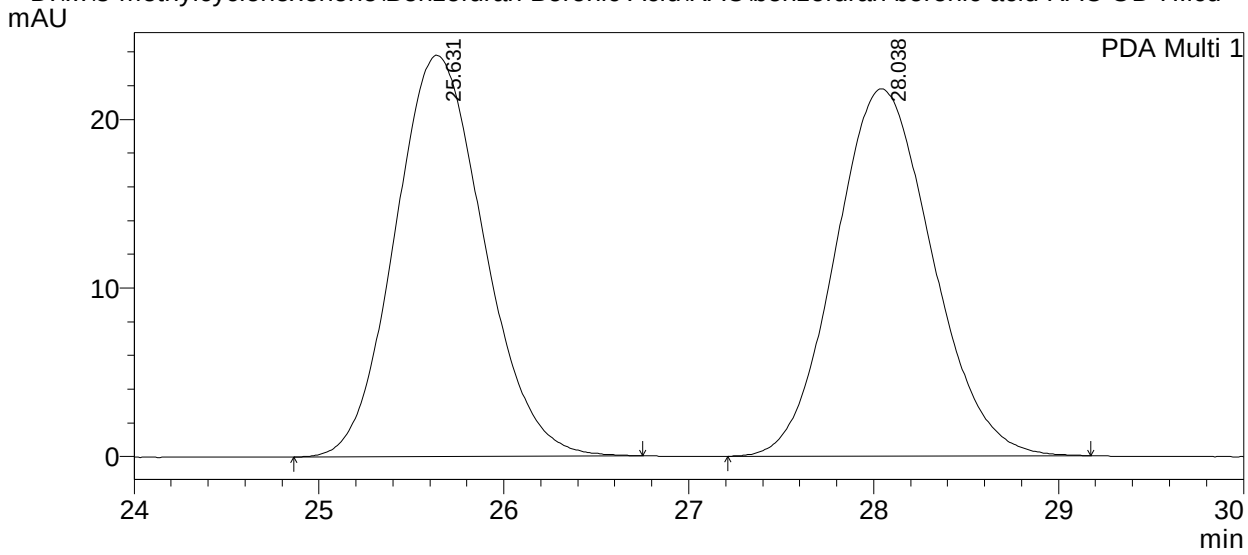
==== Shimadzu LCsolution Analysis Report ====

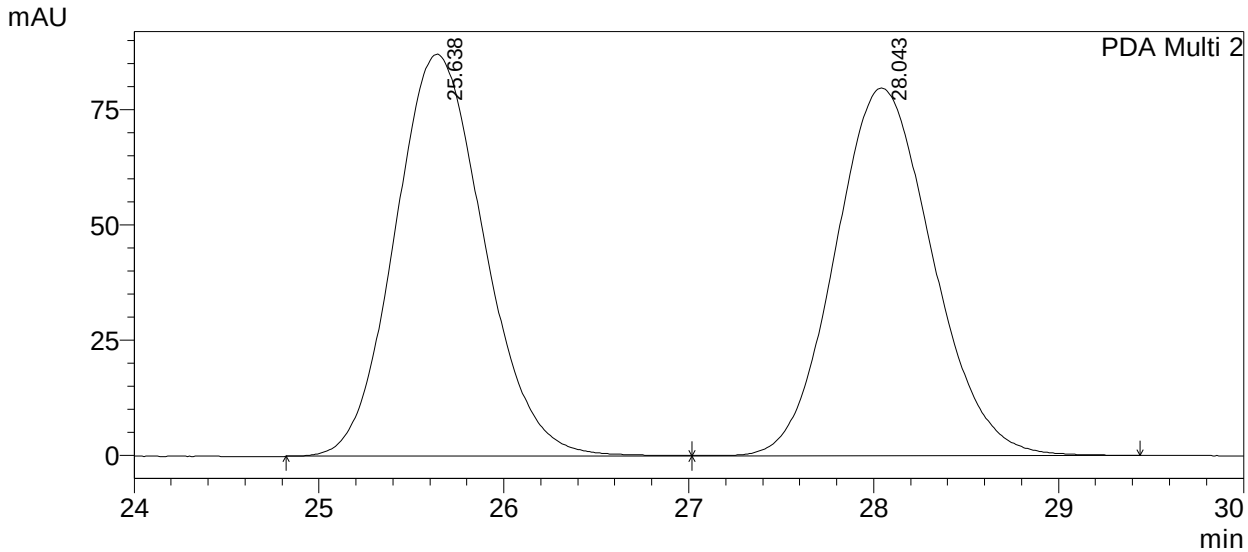
D:\...\3-methylcyclohexenone\Benzofuran Boronic Acid\RAC\benzofuran boronic acid RAC OD-H.lcd

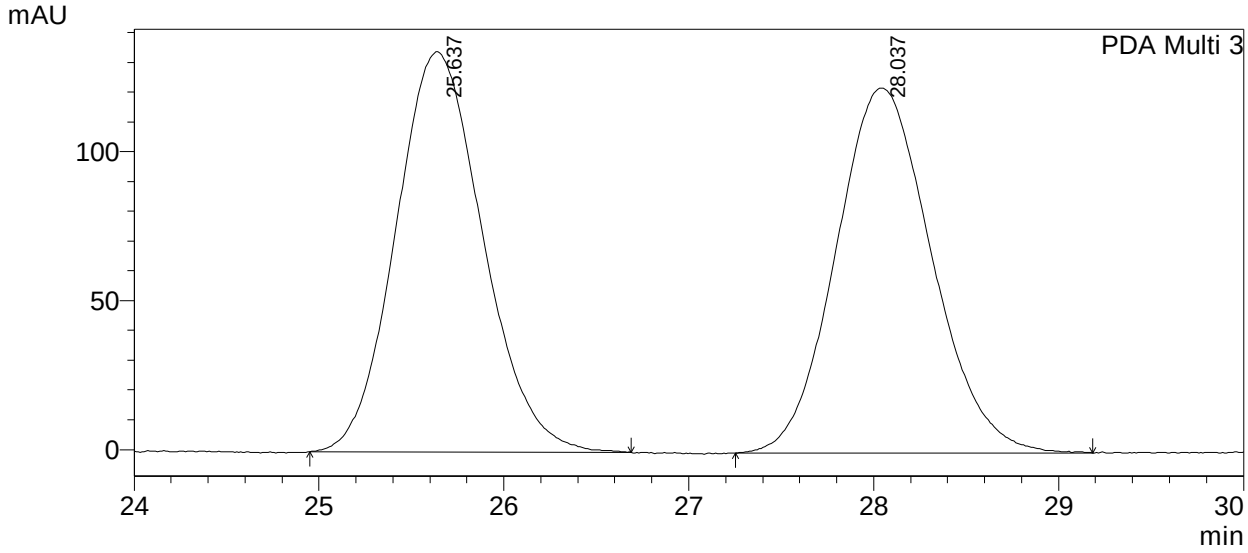
Acquired by	: System Administrator
Sample Name	: benzofuran boronic acid RAC OD-H-column
Sample ID	: benzofuran boronic acid RAC OD-
Tray#	: 1
Vail #	: 81
Injection Volume	: 2 uL
Data File Name	: benzofuran boronic acid RAC OD-H.lcd
Method File Name	: C2 99_1fl0,5 60 min.lcm
Batch File Name	: 20131004 (99_1 all column screening).lcb
Report File Name	: example PDA.lsr
Data Acquired	: 10/18/2013 5:40:20 AM
Data Processed	: 10/19/2013 2:31:27 PM

<Chromatogram>

D:\...\3-methylcyclohexenone\Benzofuran Boronic Acid\RAC\benzofuran boronic acid RAC OD-H.lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	25.631	796395	23805	50.013
2	28.038	795970	21785	49.987
Total		1592366	45590	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	25.638	2923707	87136	50.021
2	28.043	2921290	79742	49.979
Total		5844997	166878	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	25.637	4400082	134235	49.936
2	28.037	4411413	122456	50.064
Total		8811495	256691	100.000

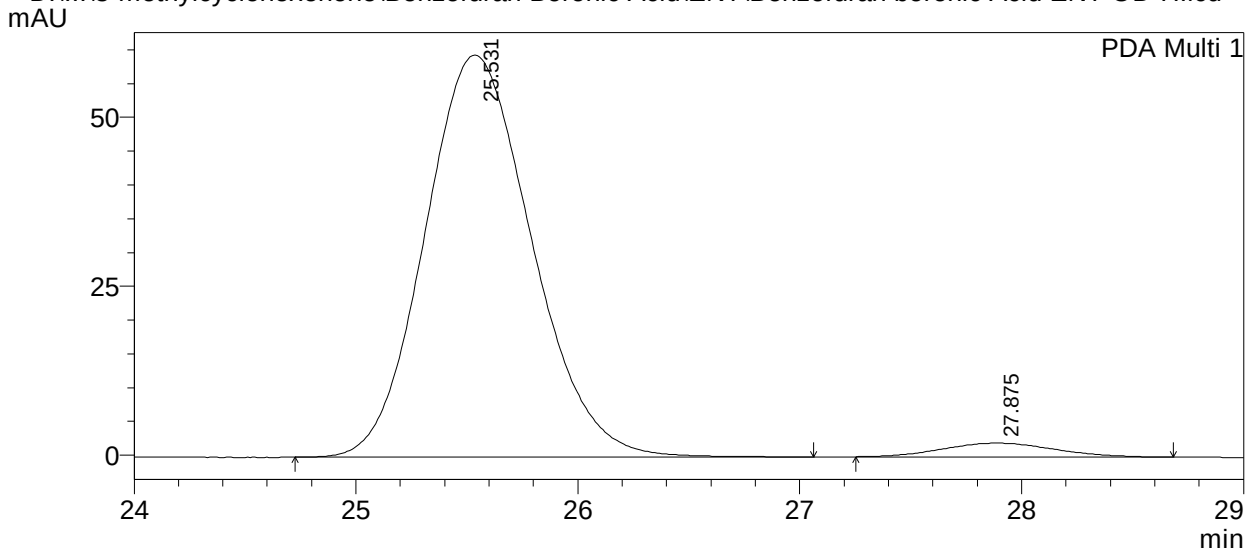
==== Shimadzu LCsolution Analysis Report ====

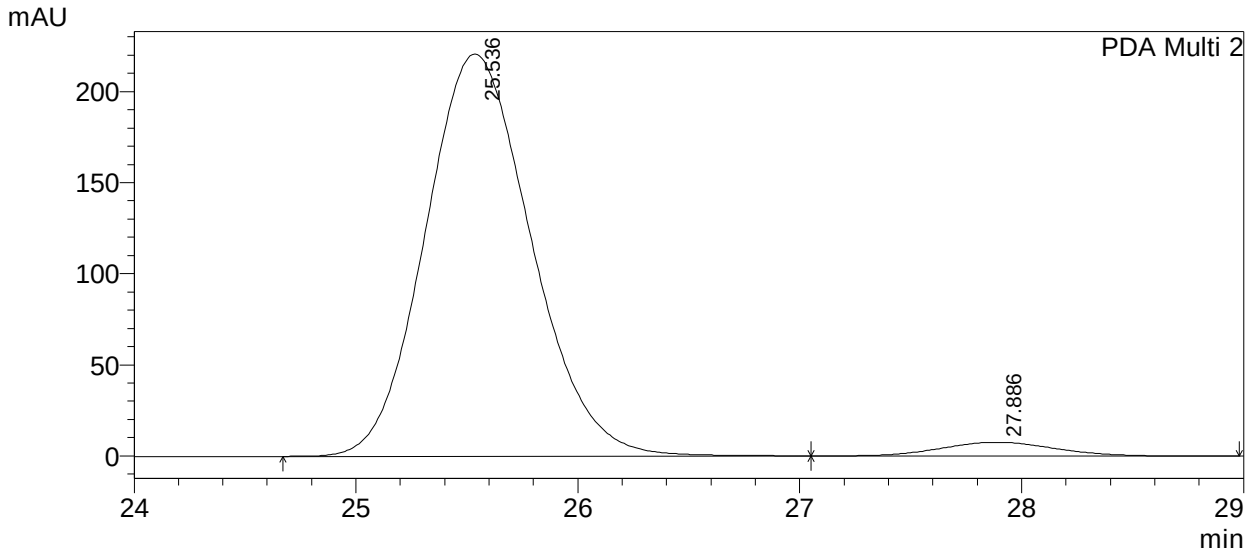
D:\...\3-methylcyclohexenone\Benzofuran Boronic Acid\ENT\Benzofuran boronic Acid ENT OD-H.lcd

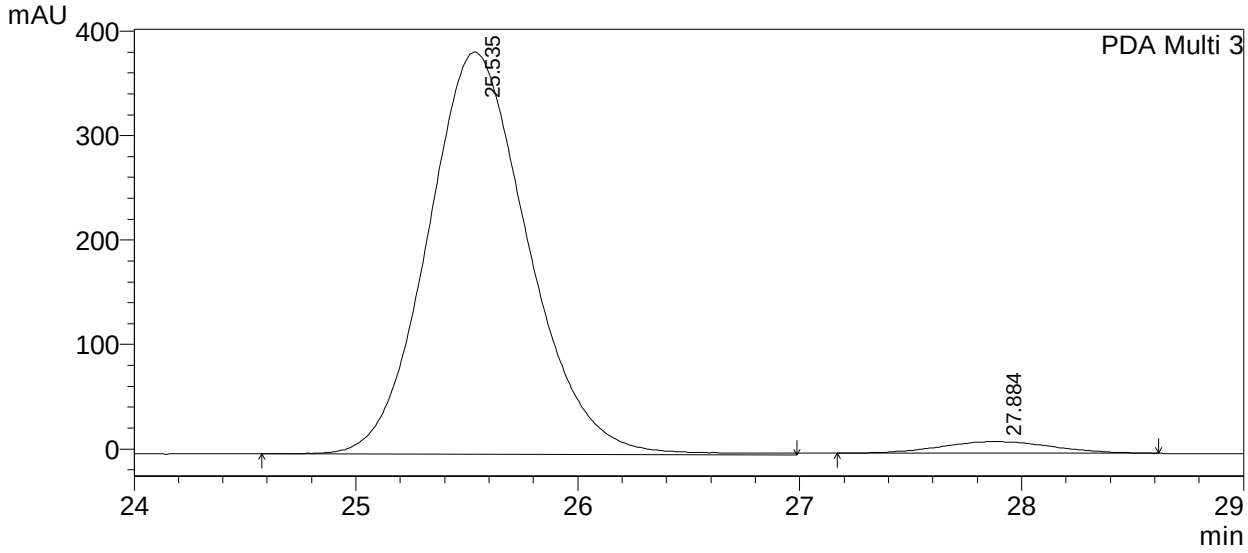
Acquired by	: System Administrator
Sample Name	: Benzofuran boronic Acid ENT OD-H
Sample ID	: Benzofuran boronic Acid ENT OD-
Tray#	: 1
Vail #	: 50
Injection Volume	: 2 uL
Data File Name	: Benzofuran boronic Acid ENT OD-H.lcd
Method File Name	: C2 99_1fl0,5 40 min.lcm
Batch File Name	: 20131015_all column screening.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 10/25/2013 2:48:26 PM
Data Processed	: 10/25/2013 4:20:57 PM

<Chromatogram>

D:\...\3-methylcyclohexenone\Benzofuran Boronic Acid\ENT\Benzofuran boronic Acid ENT OD-H.lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

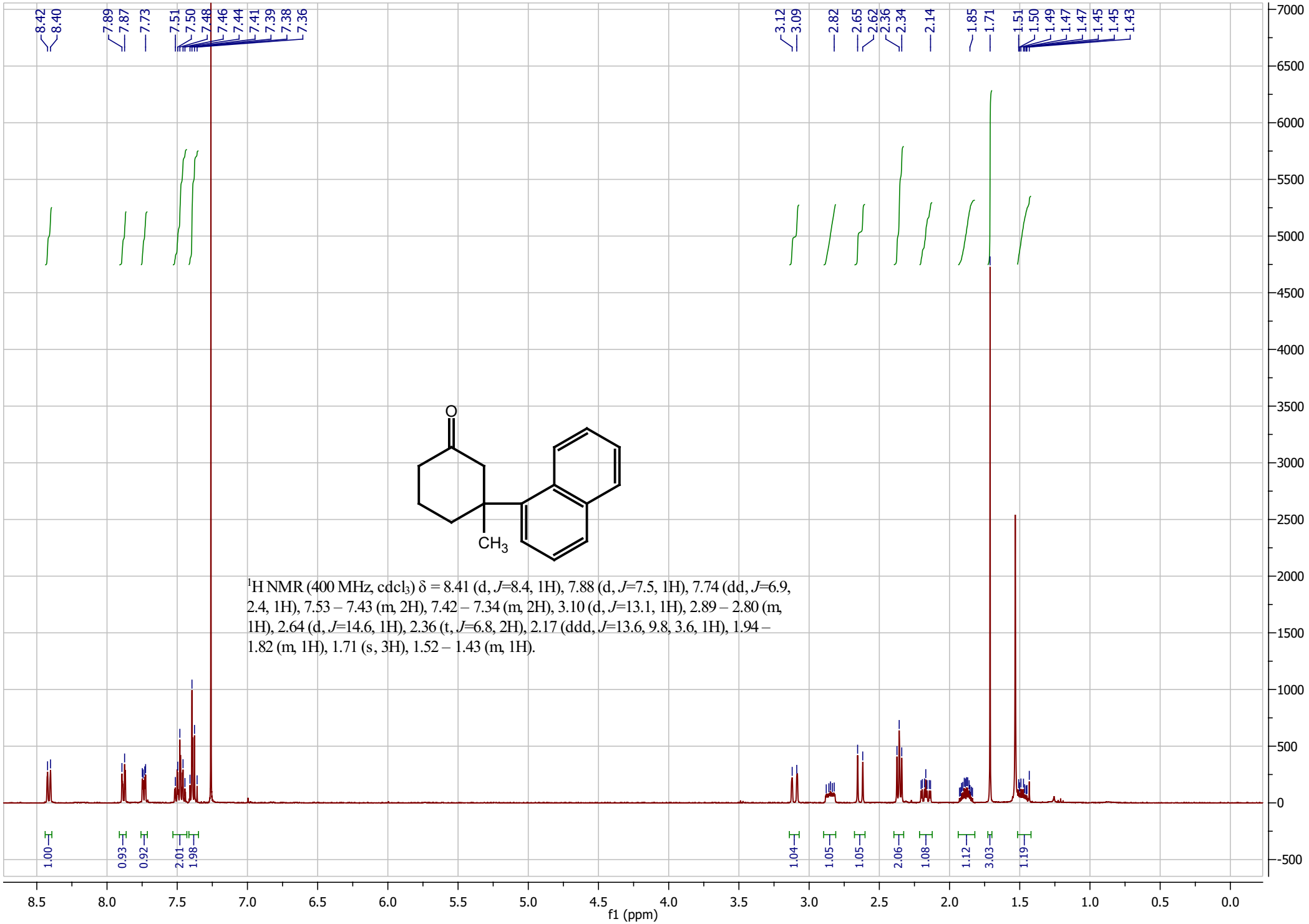
Peak#	Ret. Time	Area	Height	Area%
1	25.531	1986438	59495	96.515
2	27.875	71724	2047	3.485
Total		2058162	61542	100.000

PDA Ch2 225nm

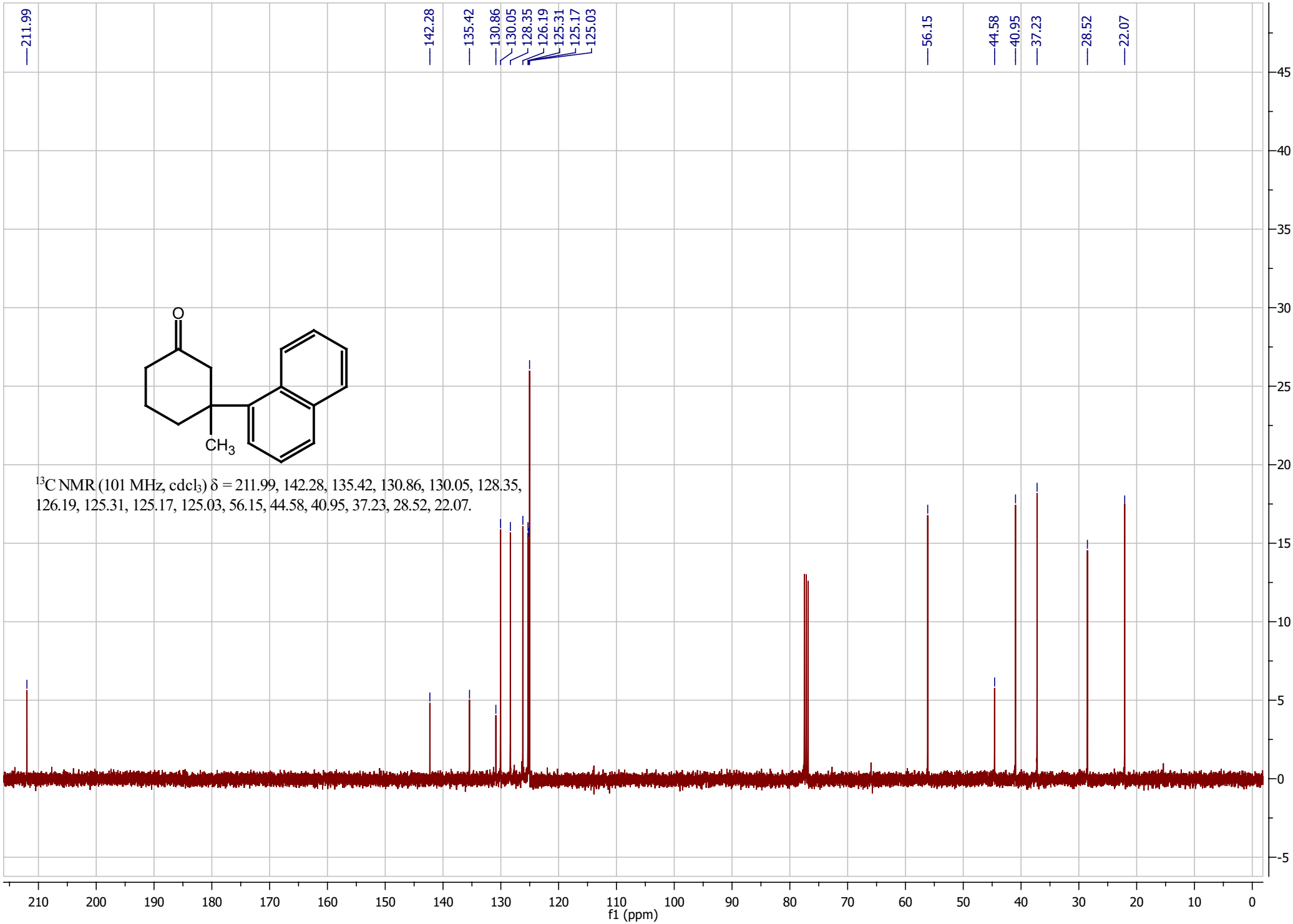
Peak#	Ret. Time	Area	Height	Area%
1	25.536	7340867	220755	96.253
2	27.886	285762	7694	3.747
Total		7626629	228449	100.000

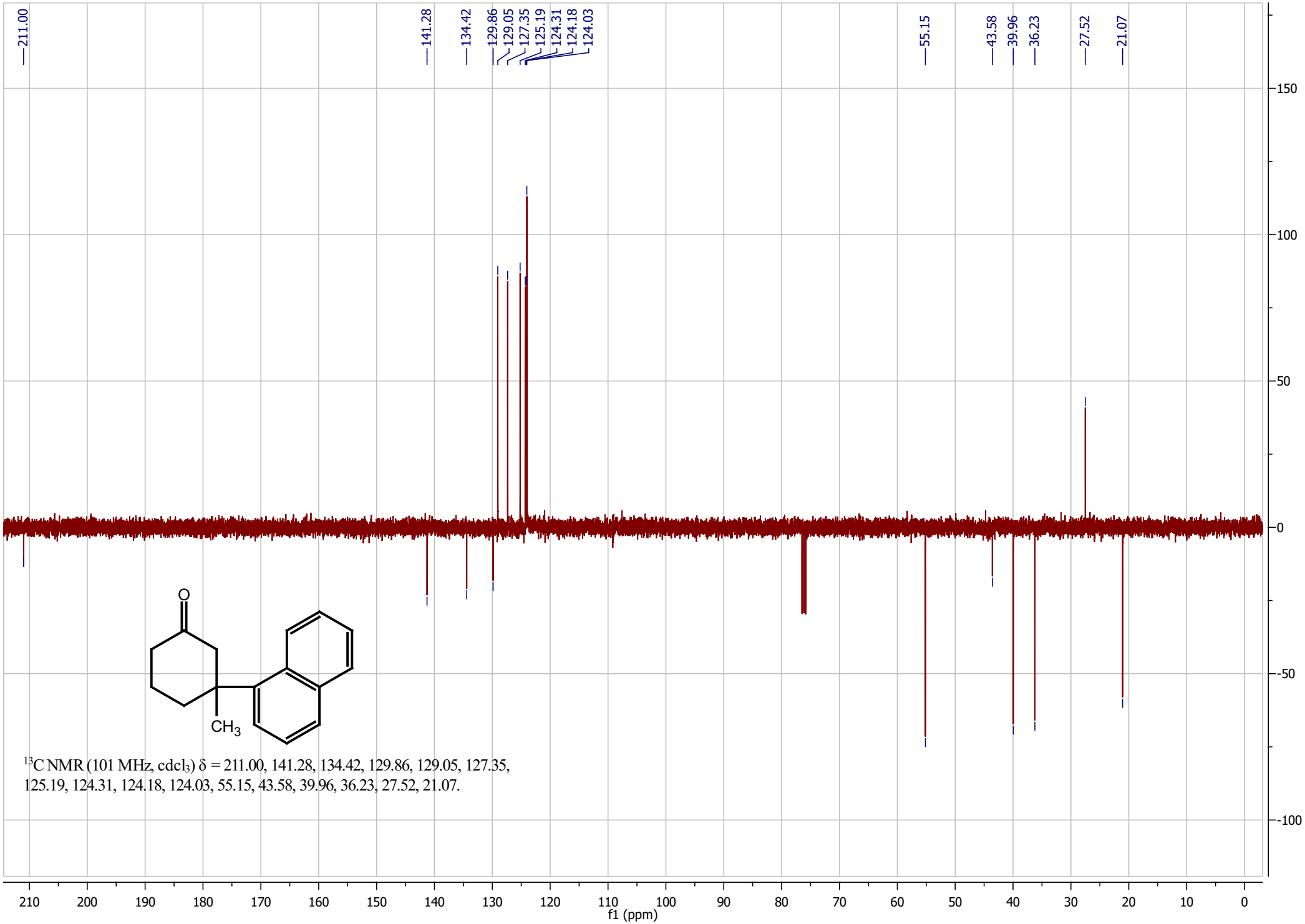
PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	25.535	12135431	385272	96.880
2	27.884	390844	11143	3.120
Total		12526275	396415	100.000



^{1}H NMR (400 MHz, cdcl$_3$) δ = 8.41 (d, *J*=8.4, 1H), 7.88 (d, *J*=7.5, 1H), 7.74 (dd, *J*=6.9, 2.4, 1H), 7.53 – 7.43 (m, 2H), 7.42 – 7.34 (m, 2H), 3.10 (d, *J*=13.1, 1H), 2.89 – 2.80 (m, 1H), 2.64 (d, *J*=14.6, 1H), 2.36 (t, *J*=6.8, 2H), 2.17 (ddd, *J*=13.6, 9.8, 3.6, 1H), 1.94 – 1.82 (m, 1H), 1.71 (s, 3H), 1.52 – 1.43 (m, 1H).


211.99
142.28
135.42
130.86
130.05
128.35
126.19
125.31
125.17
125.03
56.15
44.58
40.95
37.23
28.52
22.07
O
CH3
13C NMR (101 MHz, cdcl3) δ = 211.99, 142.28, 135.42, 130.86, 130.05, 128.35, 126.19, 125.31, 125.17, 125.03, 56.15, 44.58, 40.95, 37.23, 28.52, 22.07.
f1 (ppm)



^{13}C NMR (101 MHz, cdcl$_3$) δ = 211.00, 141.28, 134.42, 129.86, 129.05, 127.35, 125.19, 124.31, 124.18, 124.03, 55.15, 43.58, 39.96, 36.23, 27.52, 21.07.

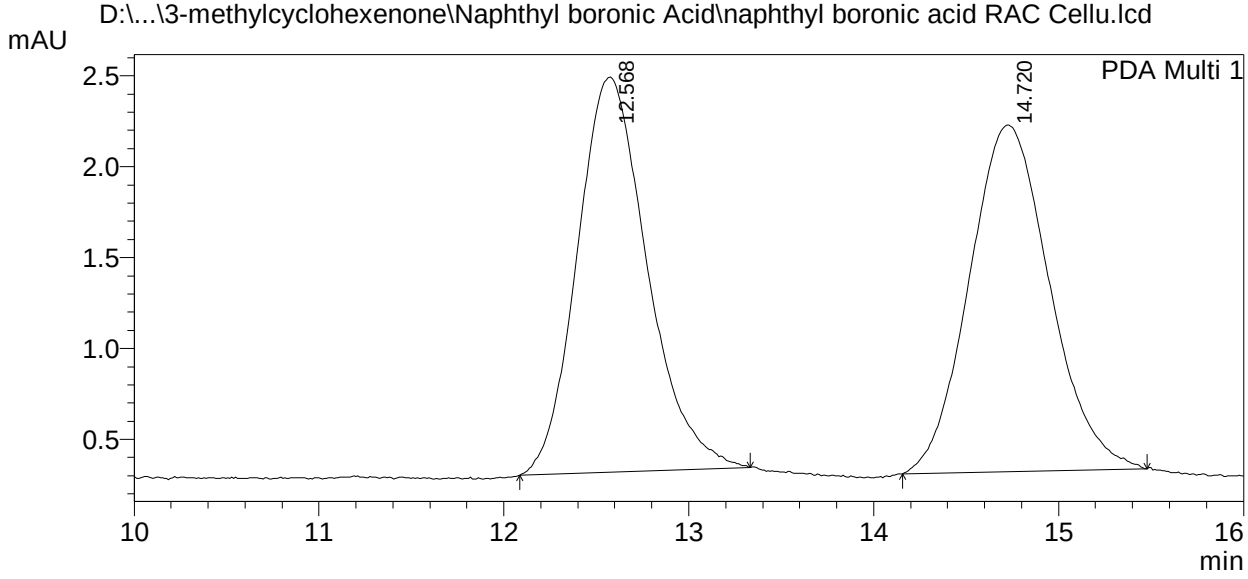
==== Shimadzu LCsolution Analysis Report ====

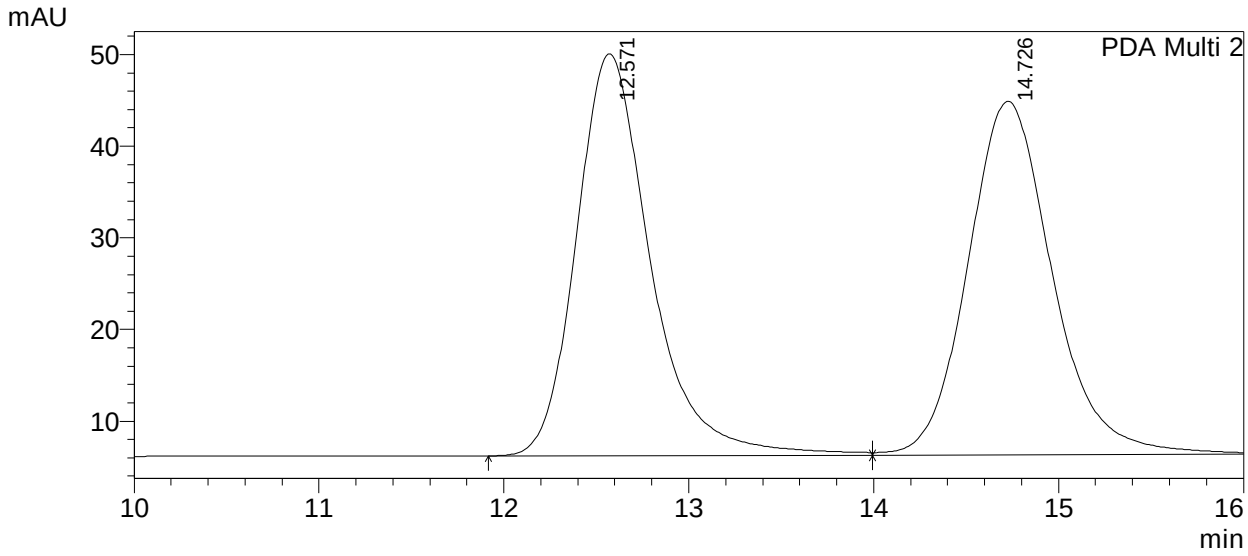
D:\...\Substrate Scope\3-methylcyclohexenone\Naphthyl boronic Acid\naphthyl boronic acid RAC Cellu.lcd

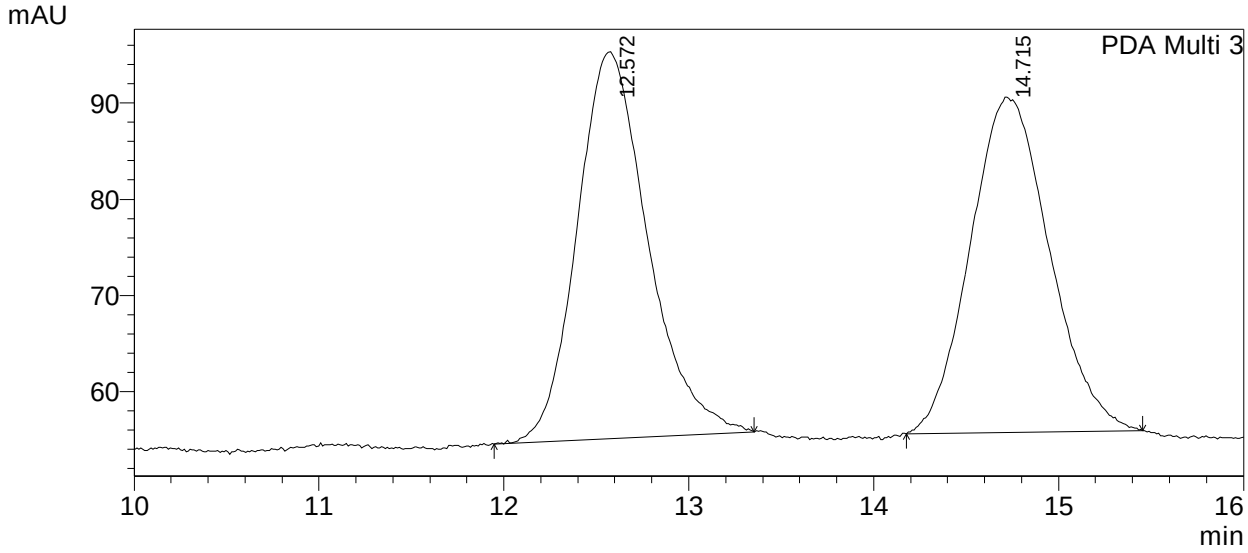
Acquired by	: System Administrator
Sample Name	: naphthyl boronic acid RAC Cellulose-column
Sample ID	: naphthyl boronic acid RAC Cellu
Tray#	: 1
Vail #	: 77
Injection Volume	: 2 uL
Data File Name	: naphthyl boronic acid RAC Cellu.lcd
Method File Name	: C6 99_1 fl1,0 60 min.lcm
Batch File Name	: 20131015_all column screening.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 10/24/2013 7:44:45 PM
Data Processed	: 10/25/2013 9:06:32 AM

<Chromatogram>

D:\...\3-methylcyclohexenone\Naphthyl boronic Acid\naphthyl boronic acid RAC Cellu.lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.568	57209	2172	49.788
2	14.720	57695	1907	50.212
Total		114903	4080	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	12.571	1222021	43799	49.884
2	14.726	1227714	38592	50.116
Total		2449734	82391	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	12.572	1069247	40211	50.652
2	14.715	1041720	34912	49.348
Total		2110967	75123	100.000

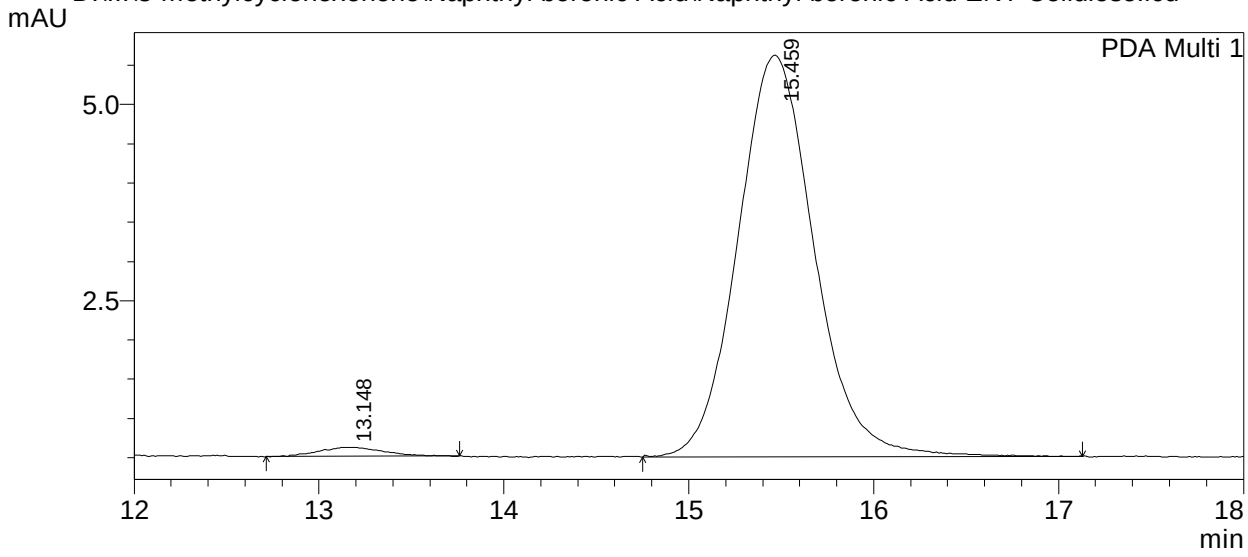
==== Shimadzu LCsolution Analysis Report ====

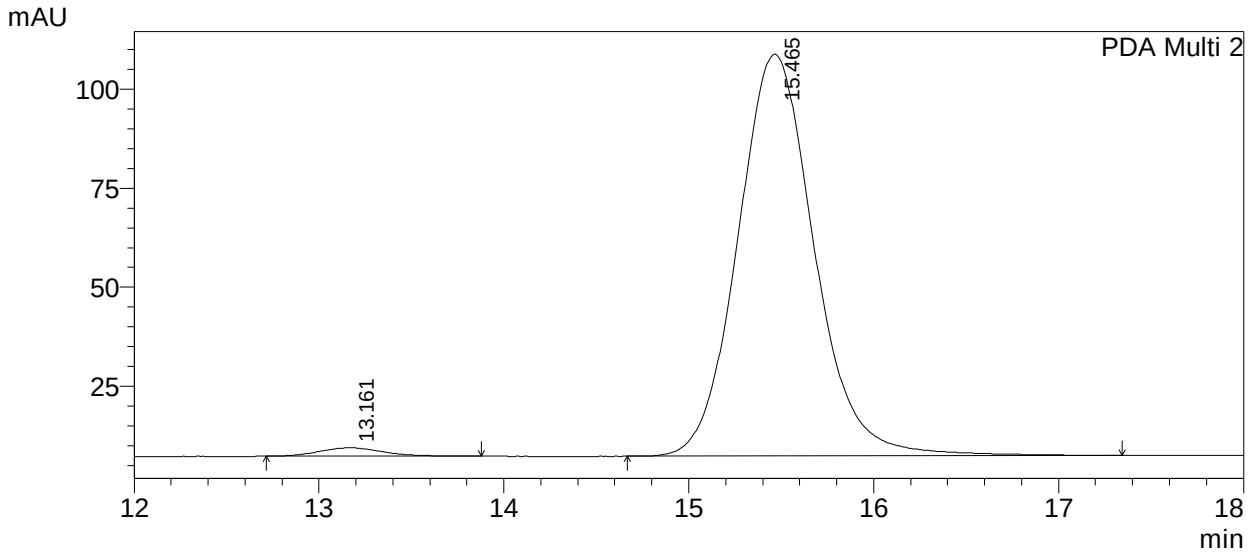
D:\...\3-methylcyclohexenone\Naphthyl boronic Acid\Naphthyl boronic Acid ENT Cellulose.lcd

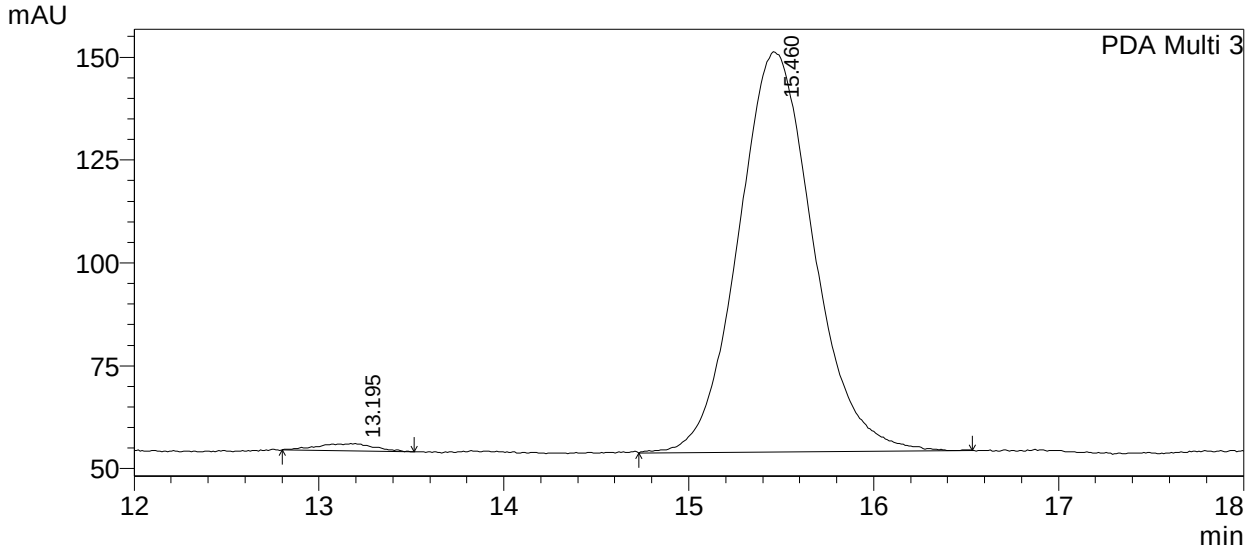
Acquired by	: System Administrator
Sample Name	: Naphthyl boronic Acid ENT Cellulose
Sample ID	: Naphthyl boronic Acid ENT Cellu
Tray#	: 1
Vail #	: 49
Injection Volume	: 5 uL
Data File Name	: Naphthyl boronic Acid ENT Cellulose.lcd
Method File Name	: C6 99_1 fl1,0 40 min.lcm
Batch File Name	: 20131015_all column screening.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 10/25/2013 4:59:36 PM
Data Processed	: 10/25/2013 6:25:57 PM

<Chromatogram>

D:\...\3-methylcyclohexenone\Naphthyl boronic Acid\Naphthyl boronic Acid ENT Cellulose.lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

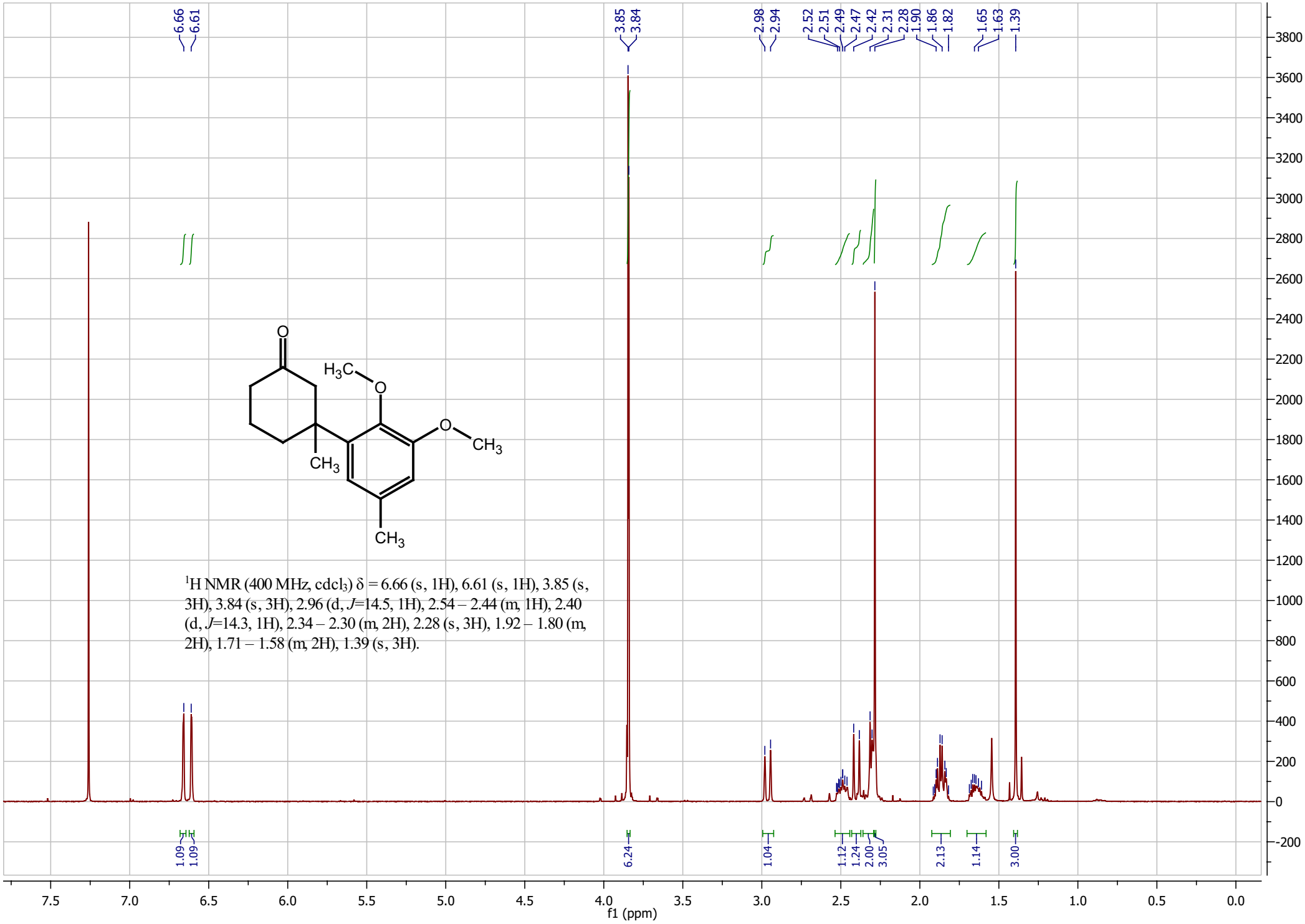
Peak#	Ret. Time	Area	Height	Area%
1	13.148	2758	114	1.840
2	15.459	147121	5119	98.160
Total		149879	5234	100.000

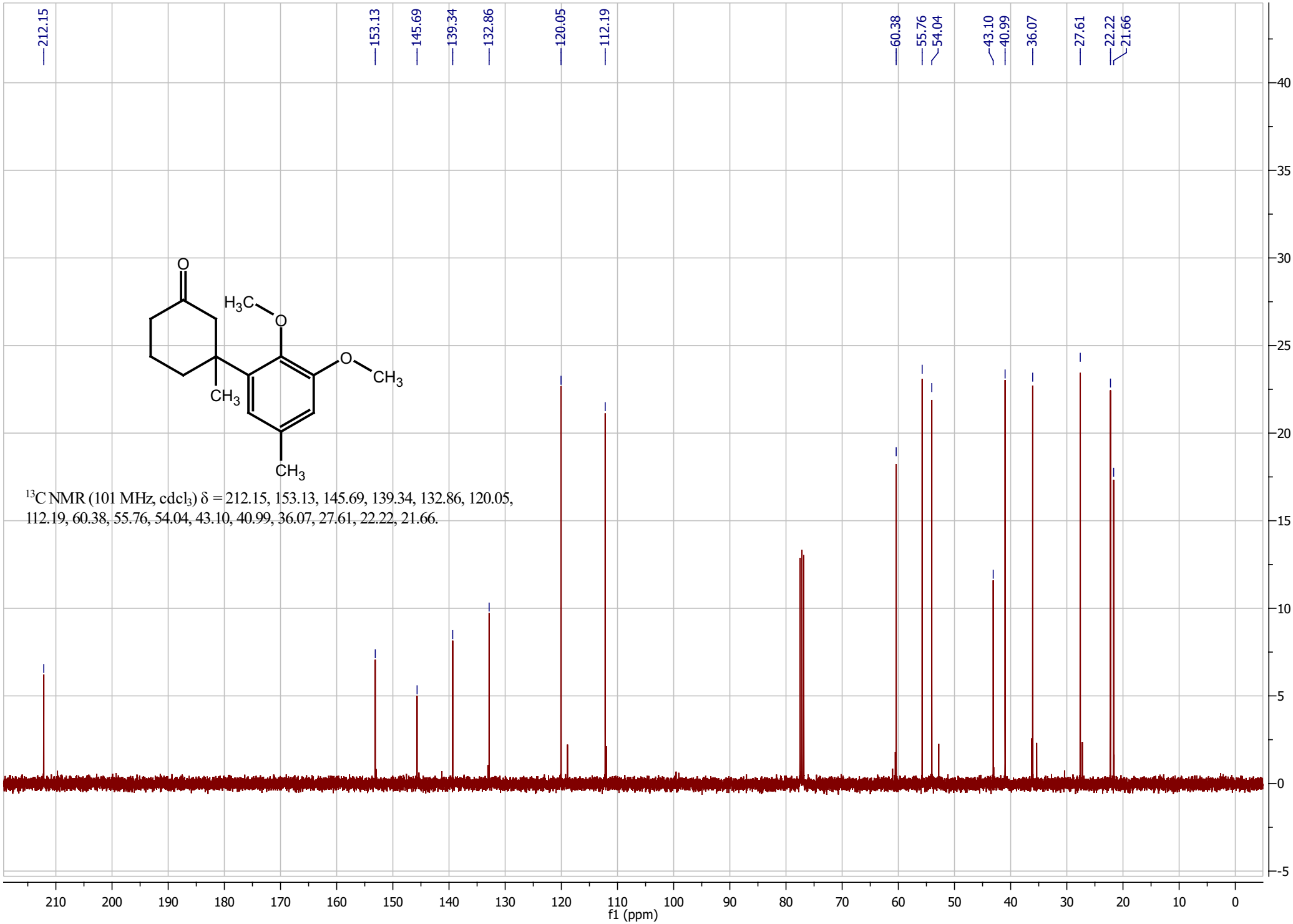
PDA Ch2 225nm

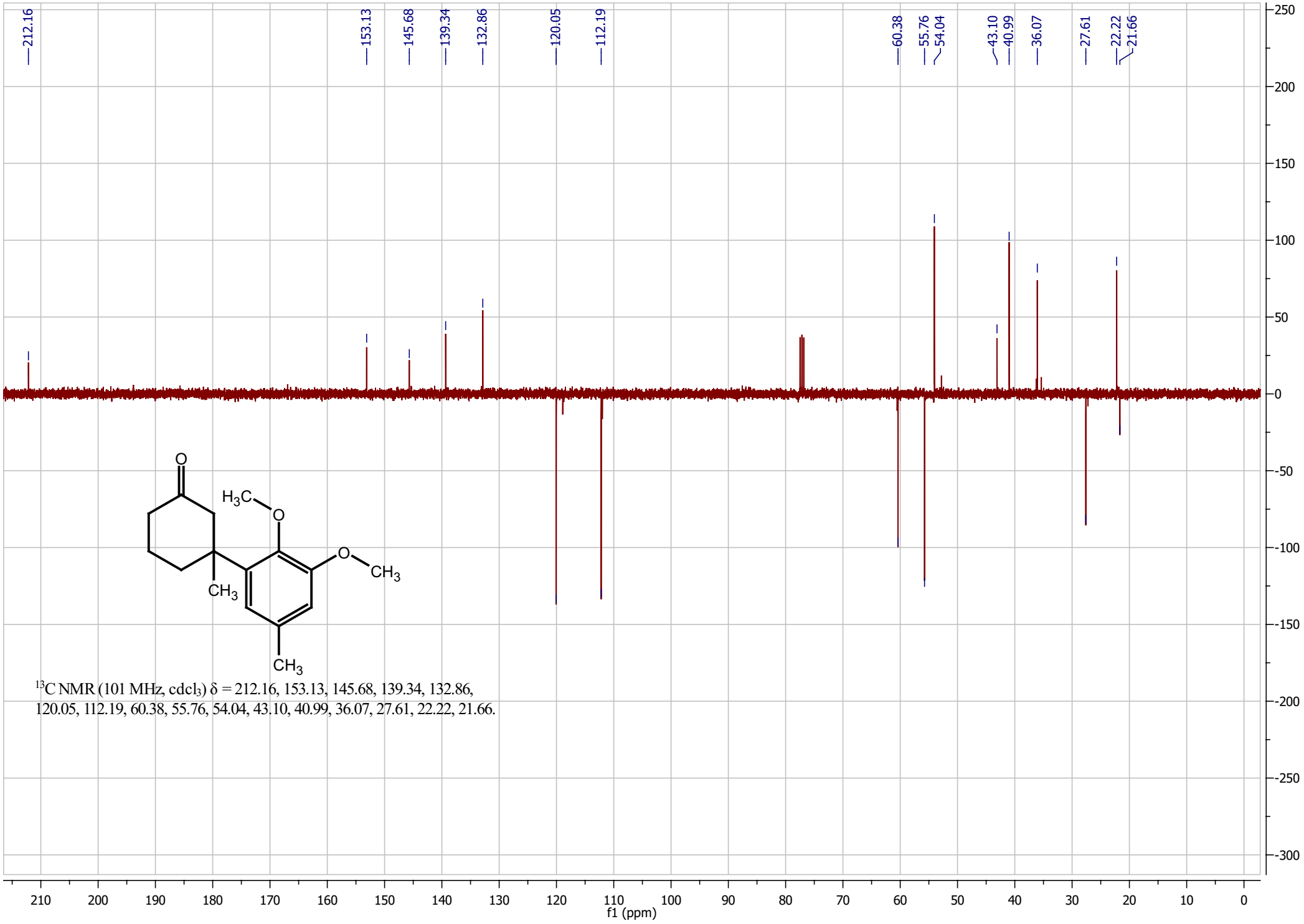
Peak#	Ret. Time	Area	Height	Area%
1	13.161	51494	2132	1.732
2	15.465	2921563	101520	98.268
Total		2973057	103652	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	13.195	36313	1811	1.308
2	15.460	2739979	97191	98.692
Total		2776293	99003	100.000


6.66
6.61
3.85
3.84
2.98
2.94
2.52
2.51
2.49
2.47
2.42
2.31
2.28
1.90
1.86
1.82
1.65
1.63
1.39
O
H3C
O
O
CH3
CH3
CH3
1H NMR (400 MHz, cdcl3) δ = 6.66 (s, 1H), 6.61 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.96 (d, J=14.5, 1H), 2.54 – 2.44 (m, 1H), 2.40 (d, J=14.3, 1H), 2.34 – 2.30 (m, 2H), 2.28 (s, 3H), 1.92 – 1.80 (m, 2H), 1.71 – 1.58 (m, 2H), 1.39 (s, 3H).
1.09
1.09
6.24
1.04
1.12
1.24
2.00
3.05
2.13
1.14
3.00
f1 (ppm)


212.15
153.13
145.69
139.34
132.86
120.05
112.19
60.38
55.76
54.04
43.10
40.99
36.07
27.61
22.22
21.66
O
H3C
O
O
CH3
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 212.15, 153.13, 145.69, 139.34, 132.86, 120.05,
112.19, 60.38, 55.76, 54.04, 43.10, 40.99, 36.07, 27.61, 22.22, 21.66.
f1 (ppm)



^{13}C NMR (101 MHz, cdcl$_3$) δ = 212.16, 153.13, 145.68, 139.34, 132.86, 120.05, 112.19, 60.38, 55.76, 54.04, 43.10, 40.99, 36.07, 27.61, 22.22, 21.66.

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: 2,3-OMe-5Me boronic acid RAC AS-H-column		
Sample ID	: 2,3-OMe-5Me boronic acid RAC		
Data Filename	: 2,3-OMe-5Me boronic acid RAC AS-H.lcd		
Method Filename	: C4 99_1 fl0,5 60 min.lcm		
Batch Filename	: 20131112_all column screening - 2014.lcb		
Vial #	: 1-6	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 1/18/2014 3:00:35 AM	Acquired by	: System Administrator
Date Processed	: 1/18/2014 3:30:40 AM	Processed by	: System Administrator

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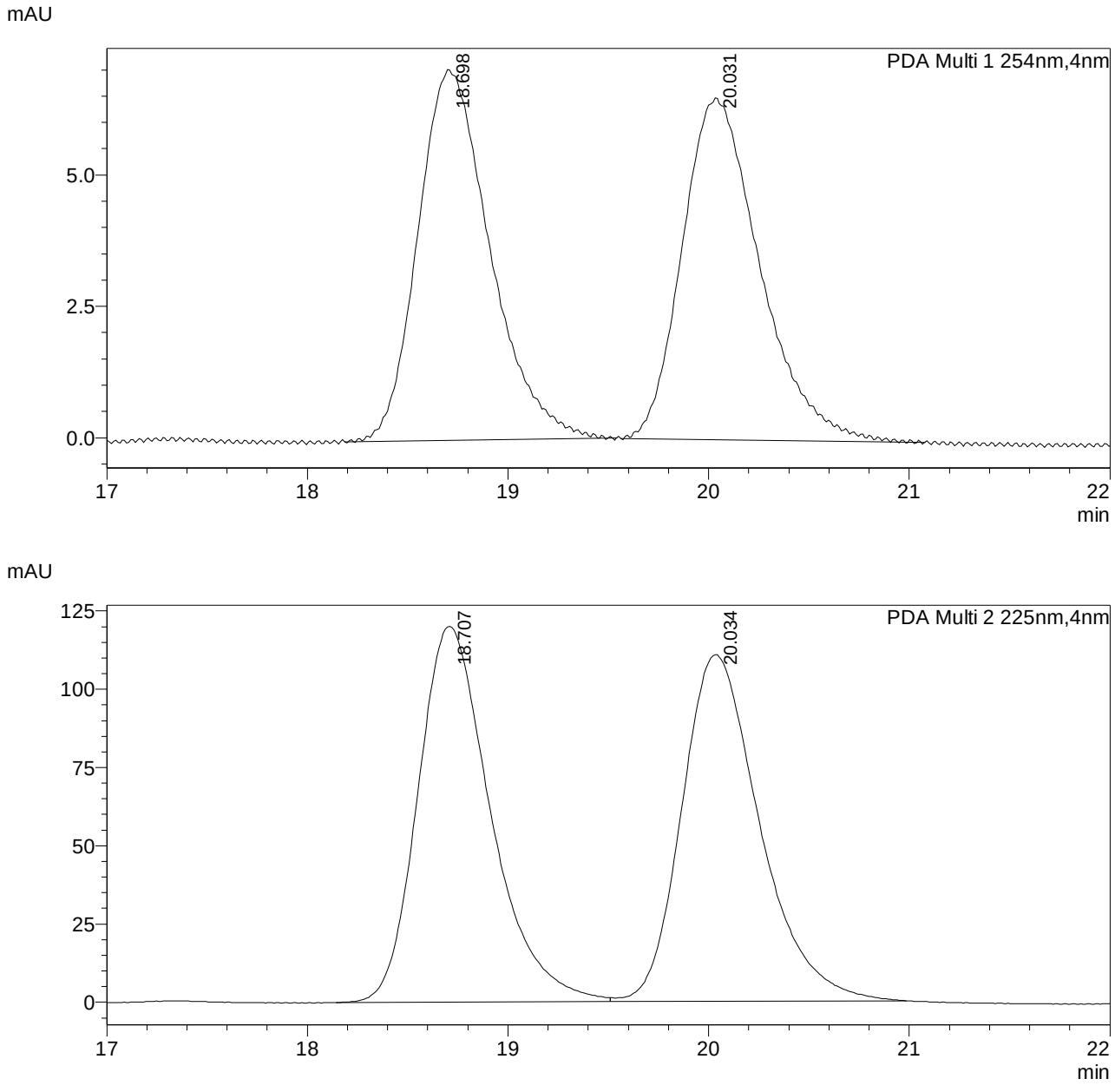
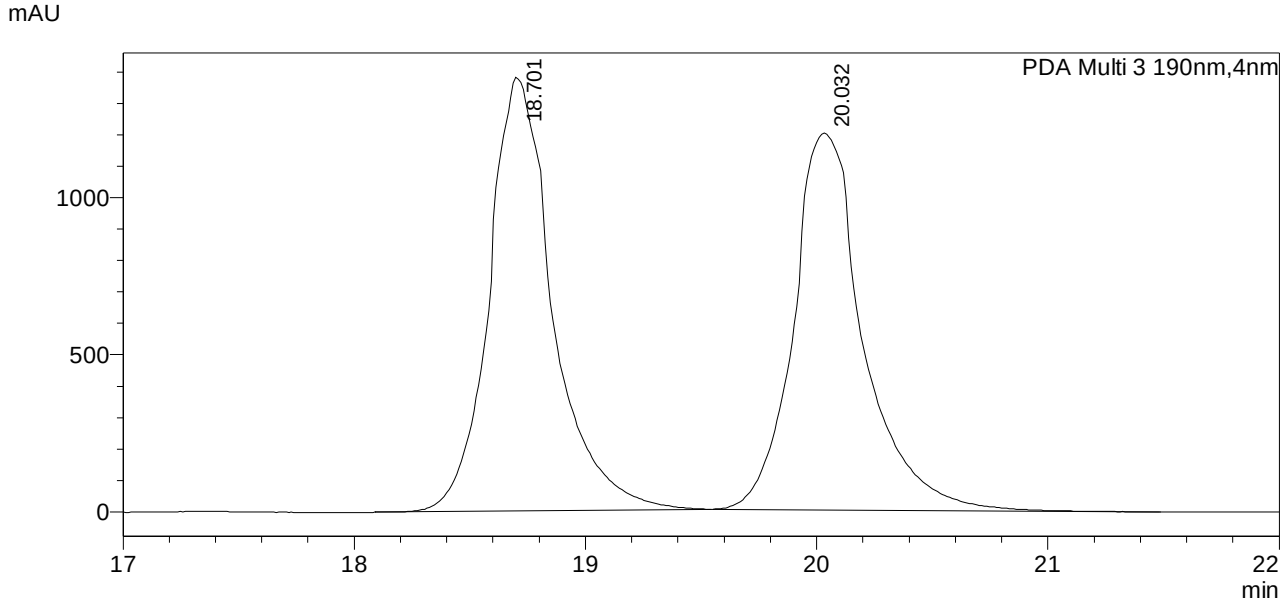




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	18.698	175839	7051	50.139
2	20.031	174867	6509	49.861
Total		350706	13560	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	18.707	3024337	120022	50.281
2	20.034	2990483	110791	49.719
Total		6014820	230813	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	18.701	26381906	1379653	51.179
2	20.032	25166795	1198797	48.821
Total		51548700	2578451	100.000

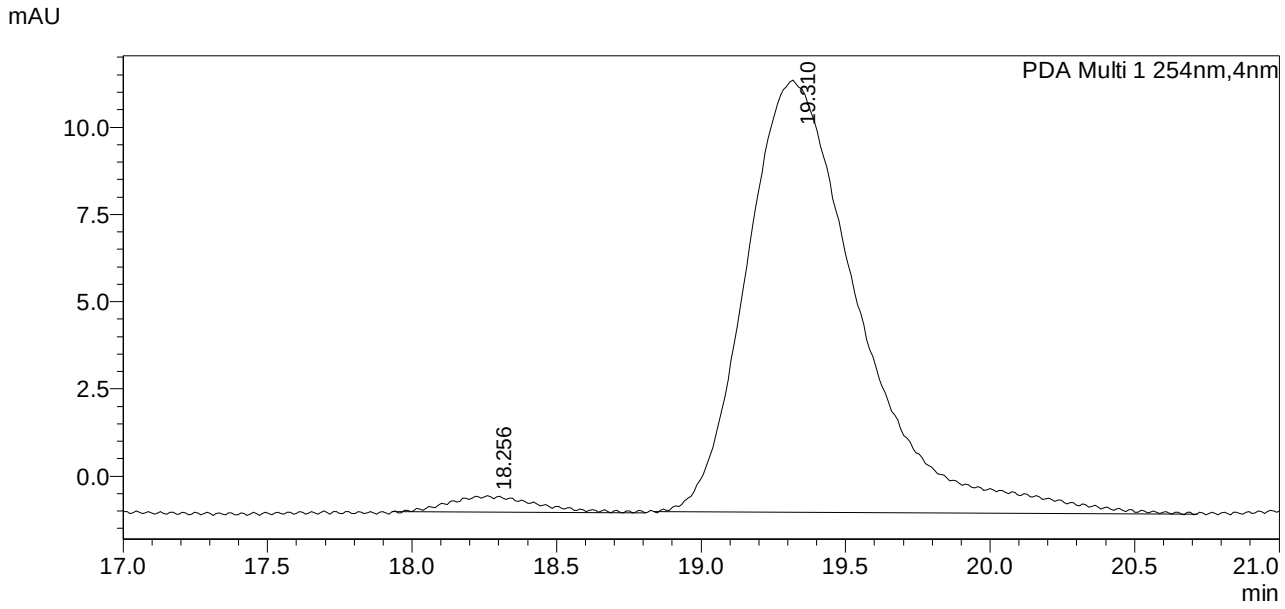
SHIMADZU LabSolutions

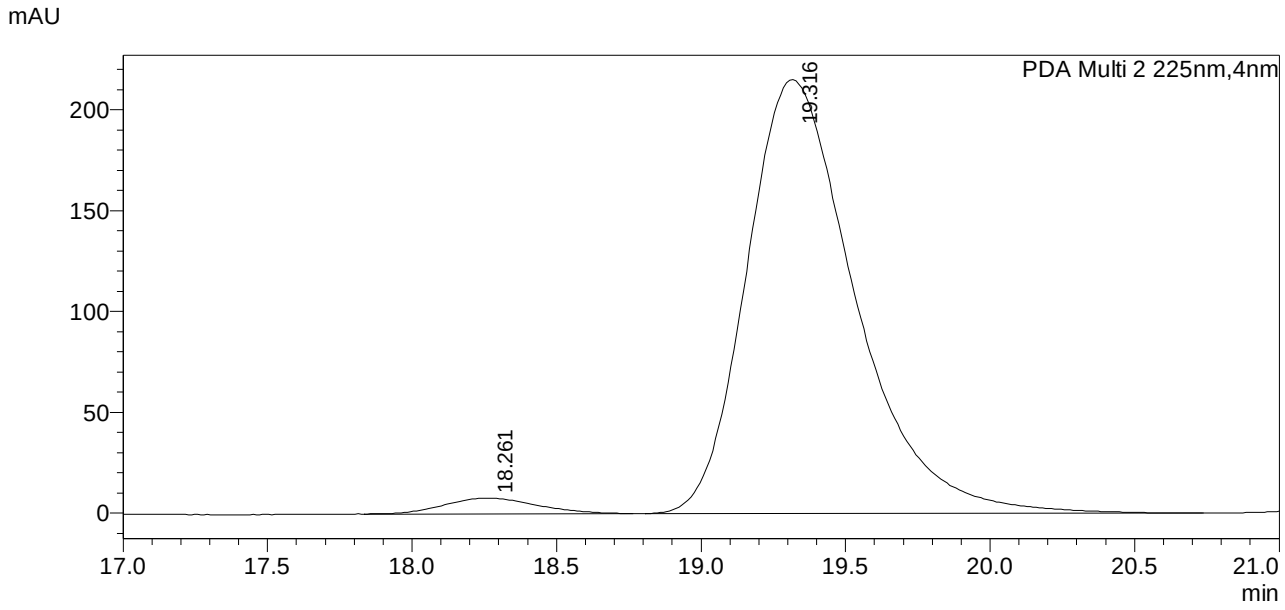
Analysis Report

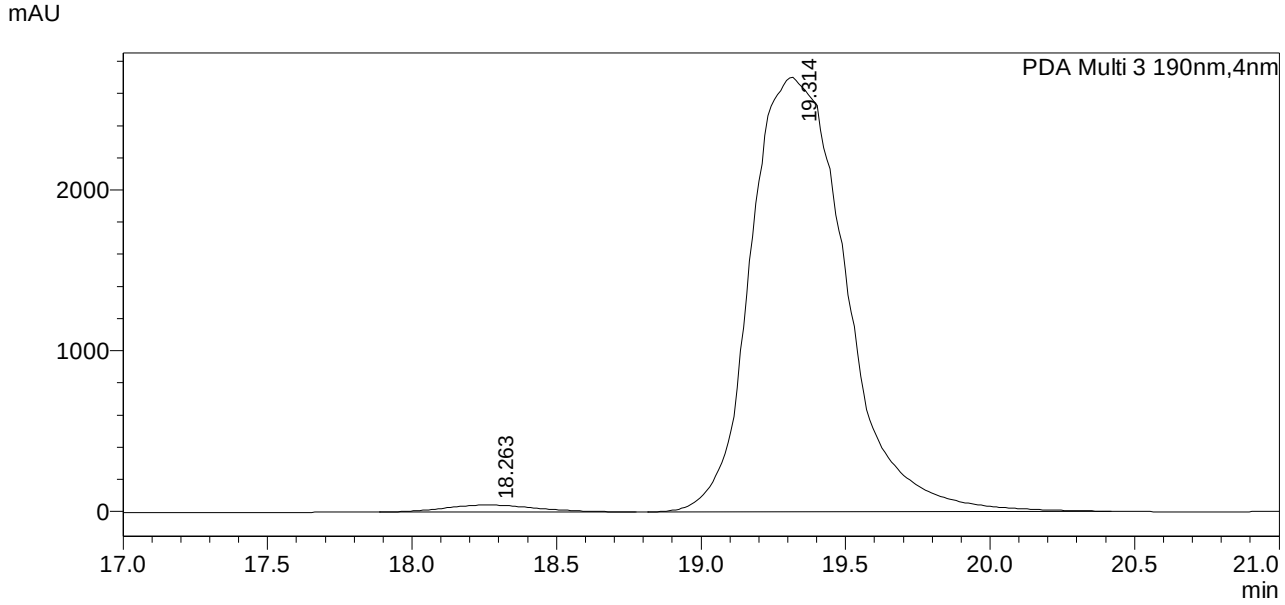
<Sample Information>

Sample Name	: 2,3-dimethoxy-5-methyl boronic acid ENT ASH-column		
Sample ID	: 2,3-dimethoxy-5-methyl boronic		
Data Filename	: 2,3-dimethoxy-5-methyl boronic acid ENT ASH-column.lcd		
Method Filename	: C4 99_1 fl0,5 30 min.lcm		
Batch Filename	: 20142001.lcb		
Vial #	: 1-5	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 1/22/2014 11:09:08 AM	Acquired by	: System Administrator
Date Processed	: 1/22/2014 11:39:12 AM	Processed by	: System Administrator

<Chromatogram>







<Peak Table>

PDA Ch1 254nm

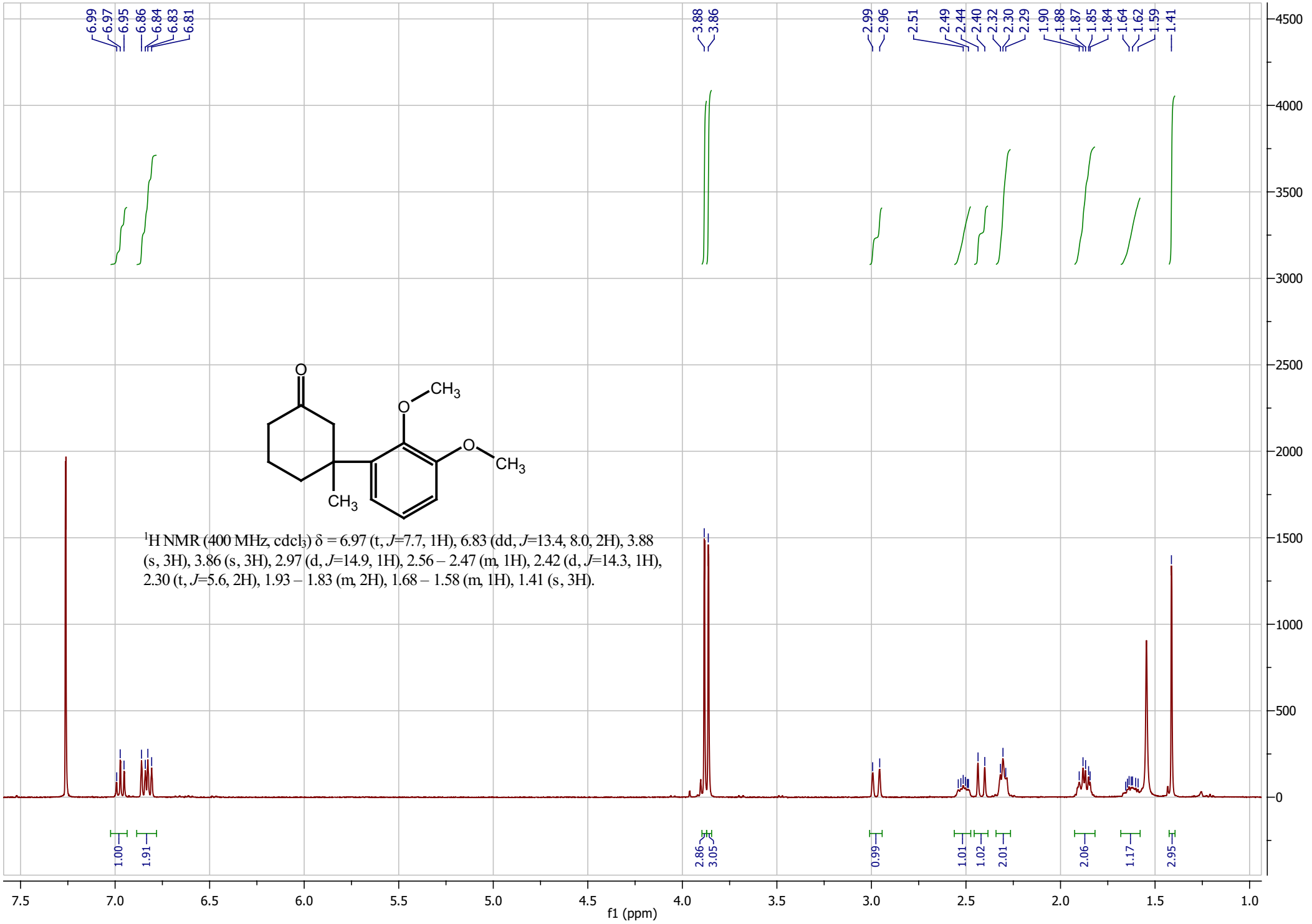
Peak#	Ret. Time	Area	Height	Area%
1	18.256	9695	472	2.804
2	19.310	336036	12379	97.196
Total		345731	12851	100.000

PDA Ch2 225nm

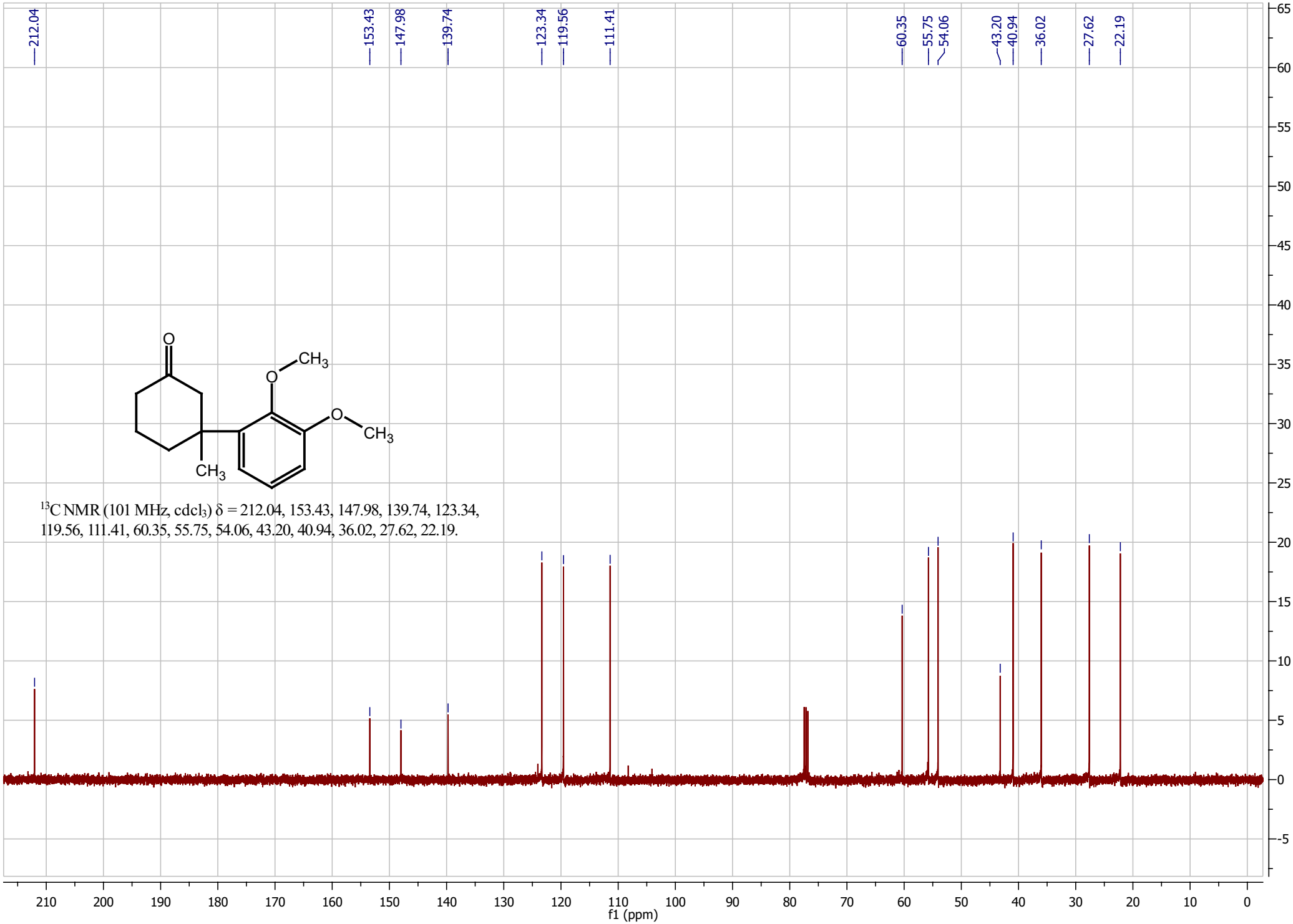
Peak#	Ret. Time	Area	Height	Area%
1	18.261	175487	7865	3.017
2	19.316	5640967	215192	96.983
Total		5816454	223057	100.000

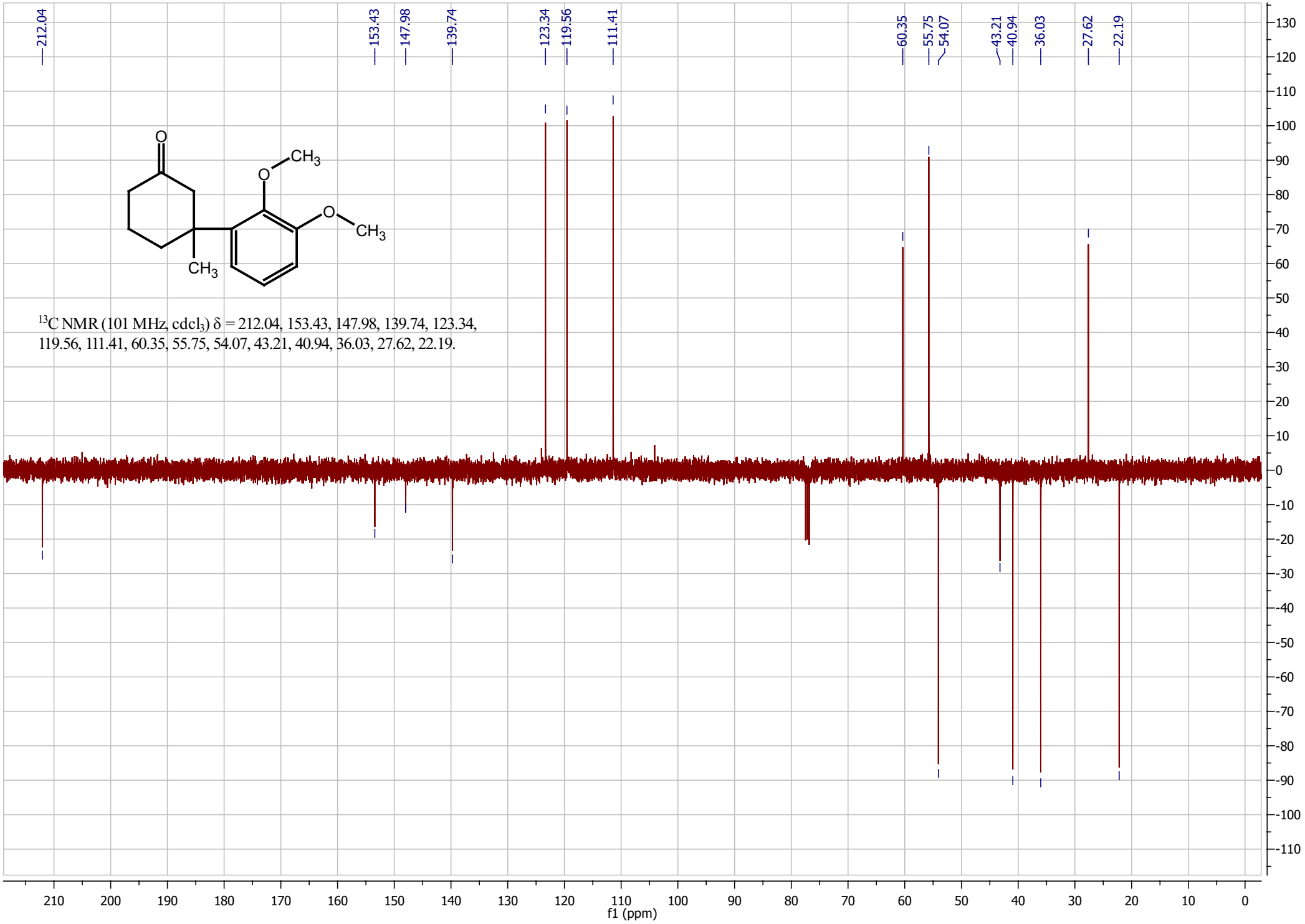
PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	18.263	968981	43804	1.550
2	19.314	61540911	2701754	98.450
Total		62509893	2745559	100.000



^{1}H NMR (400 MHz, cdcl$_3$) δ = 6.97 (t, *J*=7.7, 1H), 6.83 (dd, *J*=13.4, 8.0, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 2.97 (d, *J*=14.9, 1H), 2.56 – 2.47 (m, 1H), 2.42 (d, *J*=14.3, 1H), 2.30 (t, *J*=5.6, 2H), 1.93 – 1.83 (m, 2H), 1.68 – 1.58 (m, 1H), 1.41 (s, 3H).


212.04
153.43
147.98
139.74
123.34
119.56
111.41
60.35
55.75
54.06
43.20
40.94
36.02
27.62
22.19
O
CH3
O
O
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 212.04, 153.43, 147.98, 139.74, 123.34,
119.56, 111.41, 60.35, 55.75, 54.06, 43.20, 40.94, 36.02, 27.62, 22.19.
f1 (ppm)


212.04
153.43
147.98
139.74
123.34
119.56
111.41
60.35
55.75
54.07
43.21
40.94
36.03
27.62
22.19
O
O
CH3
O
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 212.04, 153.43, 147.98, 139.74, 123.34,
119.56, 111.41, 60.35, 55.75, 54.07, 43.21, 40.94, 36.03, 27.62, 22.19.
f1 (ppm)

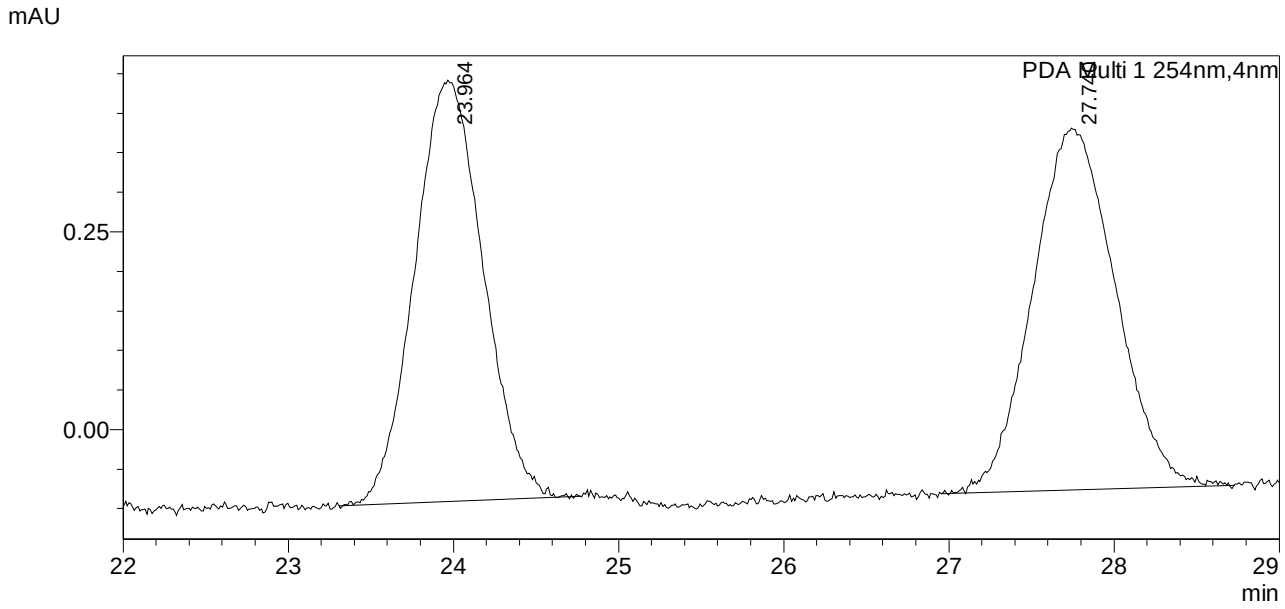
SHIMADZU LabSolutions

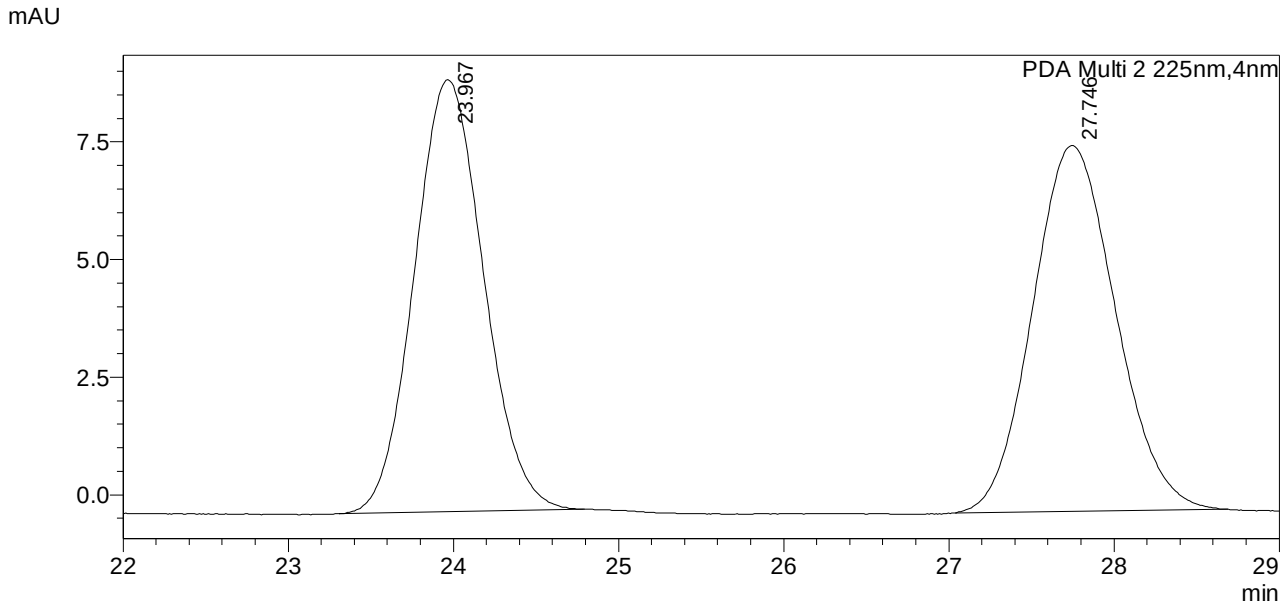
Analysis Report

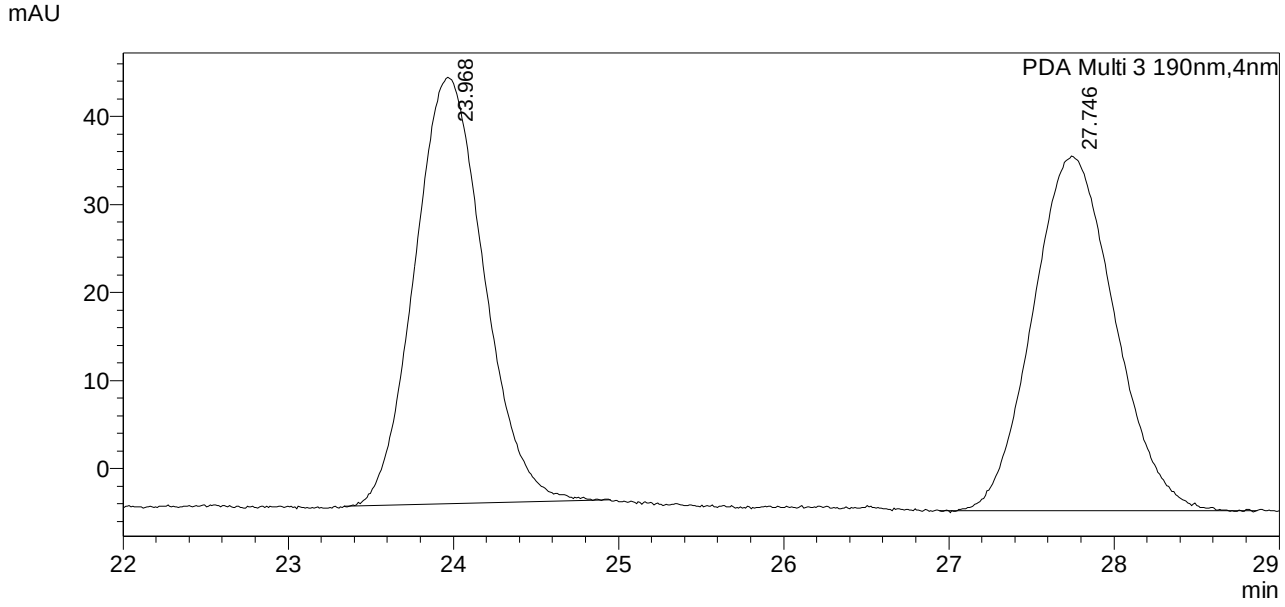
<Sample Information>

Sample Name	: 2,3-dimethyoxy boronic acid RAC OD-H-column		
Sample ID	: 2,3-dimethyoxy boronic acid OD-		
Data Filename	: 2,3-dimethyoxy boronic acid RAC OD-H-column.lcd		
Method Filename	: C2 99_1fl0,5 60 min.lcm		
Batch Filename	: 20131029_all column screening.lcb		
Vial #	: 1-17	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 10/31/2013 5:25:01 PM	Acquired by	: System Administrator
Date Processed	: 10/31/2013 7:10:56 PM	Processed by	: System Administrator

<Chromatogram>







<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23.964	15374	532	49.035
2	27.740	15979	457	50.965
Total		31353	989	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	23.967	267682	9182	49.665
2	27.746	271288	7774	50.335
Total		538970	16956	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	23.968	1413379	48425	50.428
2	27.746	1389388	40323	49.572
Total		2802766	88748	100.000

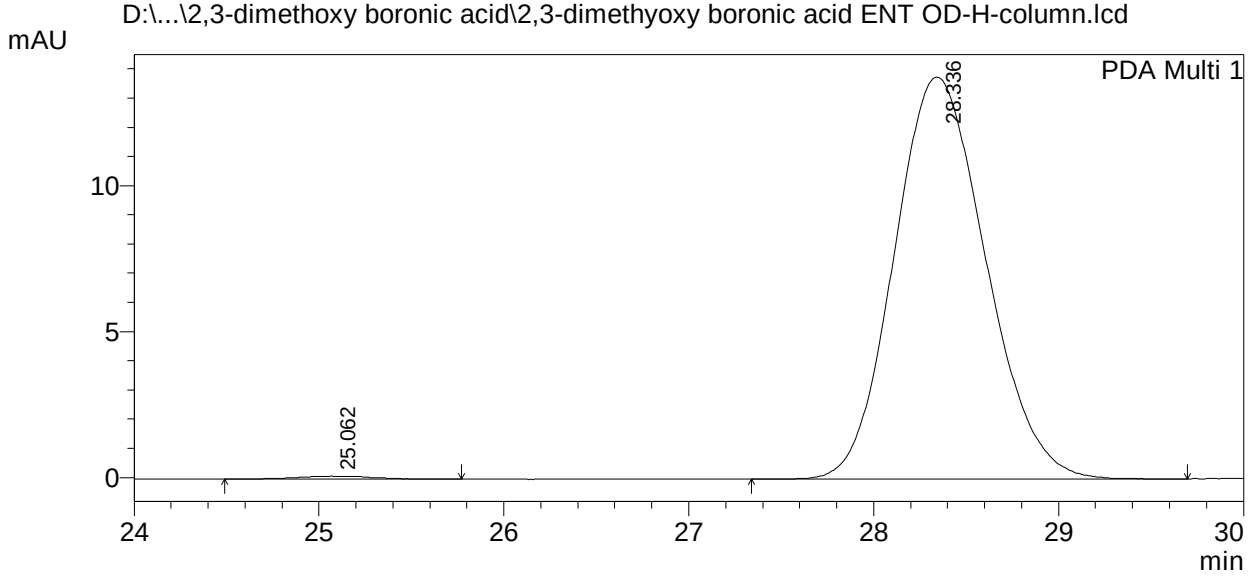
==== Shimadzu LCsolution Analysis Report ====

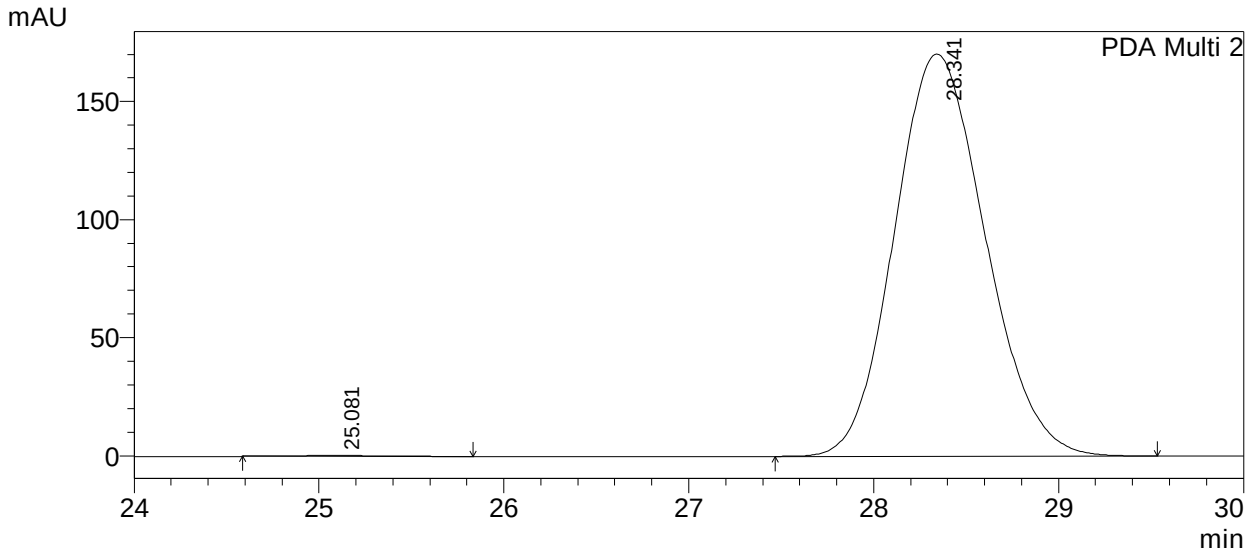
D:\...\2,3-dimethoxy boronic acid\2,3-dimethyoxy boronic acid ENT OD-H-column.lcd

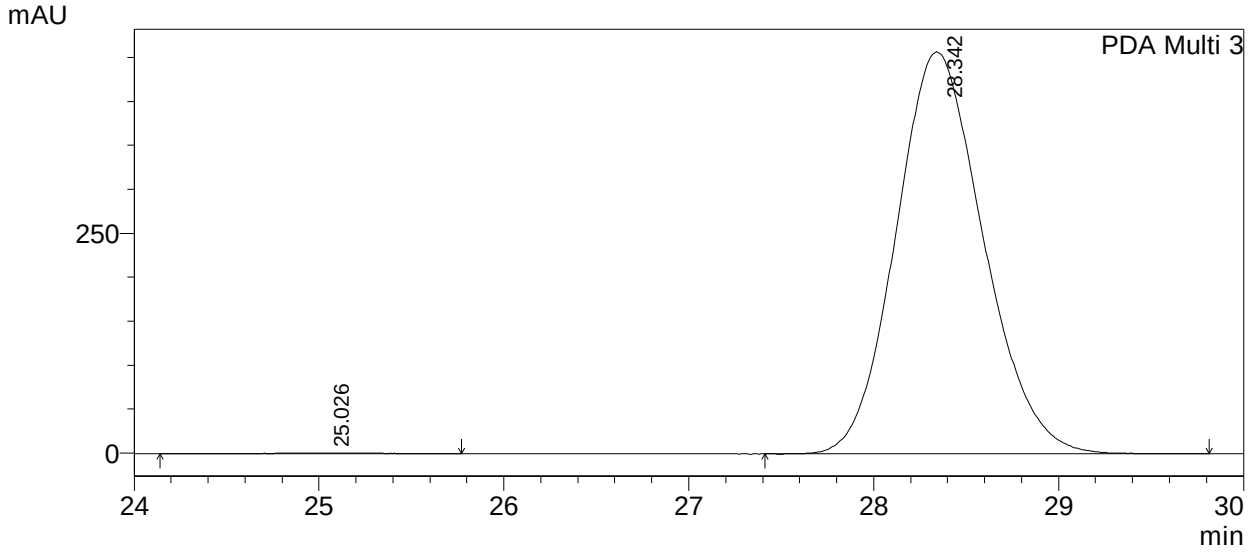
Acquired by	: System Administrator
Sample Name	: 2,3-dimethyoxy boronic acid ENT OD-H-column
Sample ID	: 2,3-dimethyoxy boronic acid OD-
Tray#	: 1
Vail #	: 18
Injection Volume	: 2 uL
Data File Name	: 2,3-dimethyoxy boronic acid ENT OD-H-column.lcd
Method File Name	: C2 99_1fl0,5 40 min.lcm
Batch File Name	: 20131029_all column screening.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 11/1/2013 4:00:41 AM
Data Processed	: 11/1/2013 9:46:38 AM

<Chromatogram>

D:\...\2,3-dimethoxy boronic acid\2,3-dimethyoxy boronic acid ENT OD-H-column.lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

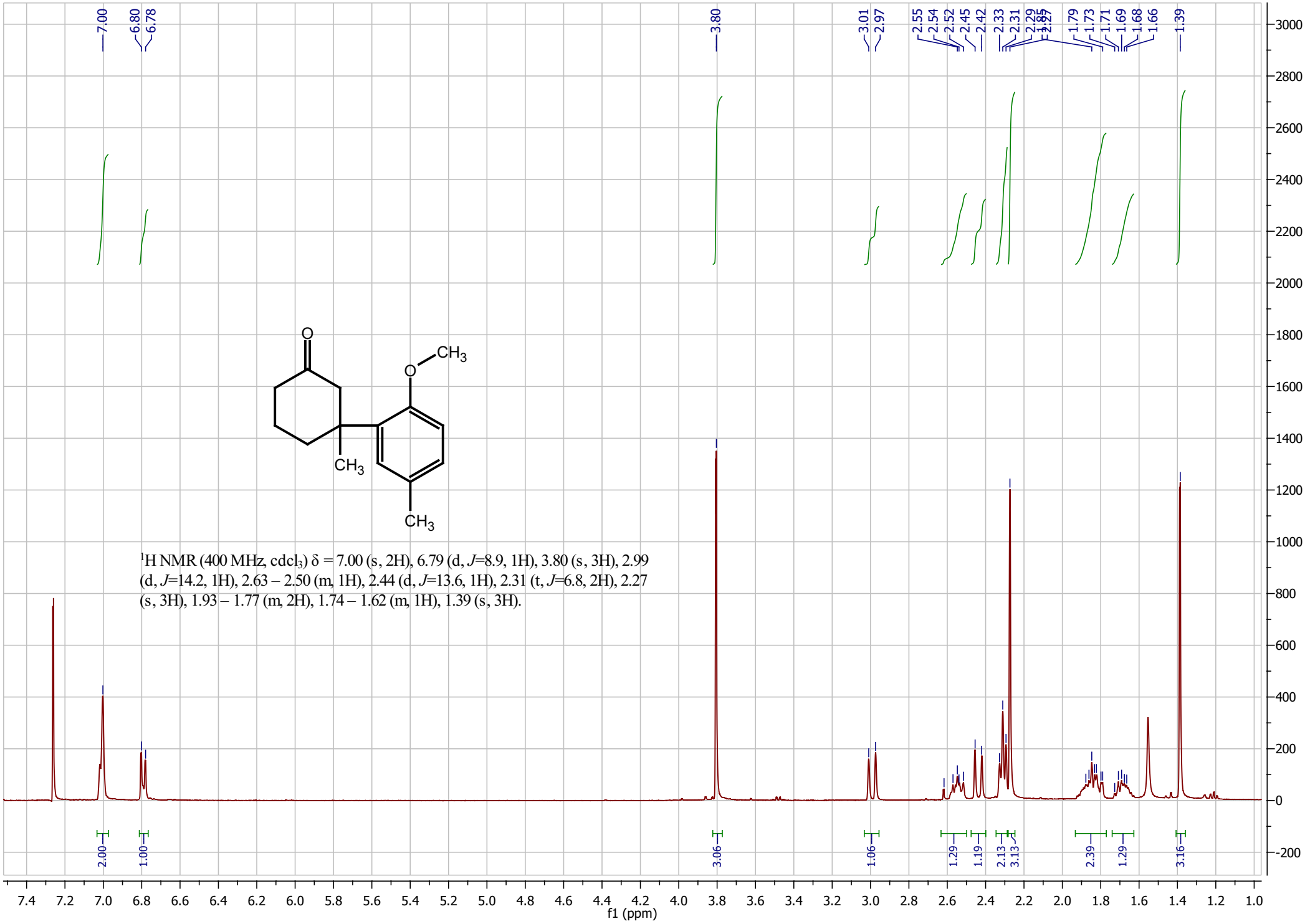
Peak#	Ret. Time	Area	Height	Area%
1	25.062	2954	104	0.621
2	28.336	473001	13764	99.379
Total		475955	13868	100.000

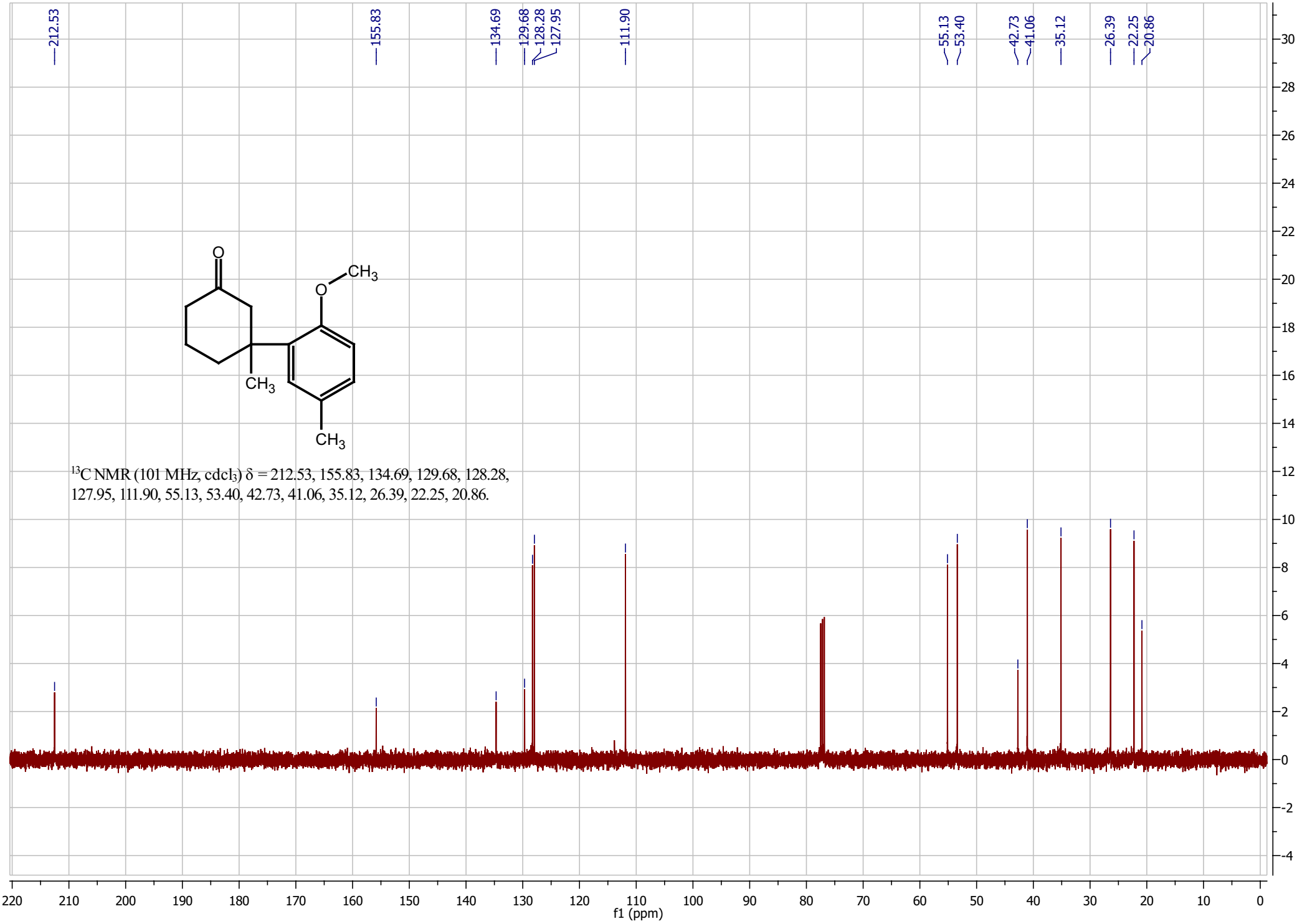
PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	25.081	11091	379	0.190
2	28.341	5820777	170263	99.810
Total		5831868	170642	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	25.026	42174	1135	0.280
2	28.342	15030142	457197	99.720
Total		15072315	458332	100.000


7.00
6.80
6.78
3.80
3.01
2.97
2.55
2.54
2.52
2.45
2.42
2.33
2.31
2.29
1.79
1.73
1.71
1.69
1.68
1.66
1.39
O
O
CH3
CH3
CH3
[1]H NMR (400 MHz, cdcl3) δ = 7.00 (s, 2H), 6.79 (d, J=8.9, 1H), 3.80 (s, 3H), 2.99 (d, J=14.2, 1H), 2.63 – 2.50 (m, 1H), 2.44 (d, J=13.6, 1H), 2.31 (t, J=6.8, 2H), 2.27 (s, 3H), 1.93 – 1.77 (m, 2H), 1.74 – 1.62 (m, 1H), 1.39 (s, 3H).
2.00
1.00
3.06
1.06
1.29
1.19
2.13
3.13
2.39
1.29
3.16
f1 (ppm)


212.53
155.83
134.69
129.68
128.28
127.95
111.90
55.13
53.40
42.73
41.06
35.12
26.39
22.25
20.86
O
O
CH3
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 212.53, 155.83, 134.69, 129.68, 128.28,
127.95, 111.90, 55.13, 53.40, 42.73, 41.06, 35.12, 26.39, 22.25, 20.86.
f1 (ppm)


212.42
155.72
134.59
129.57
128.18
127.84
111.79
55.03
53.29
42.62
40.95
35.02
26.29
22.15
20.75
O
O
CH3
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 212.42, 155.72, 134.59, 129.57, 128.18,
127.84, 111.79, 55.03, 53.29, 42.62, 40.95, 35.02, 26.29, 22.15, 20.75.
f1 (ppm)

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: 2-OMe-5-Me boronic acid RAC AD-H-column		
Sample ID	: 2-OMe-5-Me boronic acid AD-H		
Data Filename	: 2-OMe-5-Me boronic acid RAC AD-H.lcd		
Method Filename	: C5 99_1 fl0,5 60 min.lcm		
Batch Filename	: 20131029_all column screening.lcb		
Vial #	: 1-19	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 10/31/2013 7:56:25 PM	Acquired by	: System Administrator
Date Processed	: 11/1/2013 9:37:25 AM	Processed by	: System Administrator

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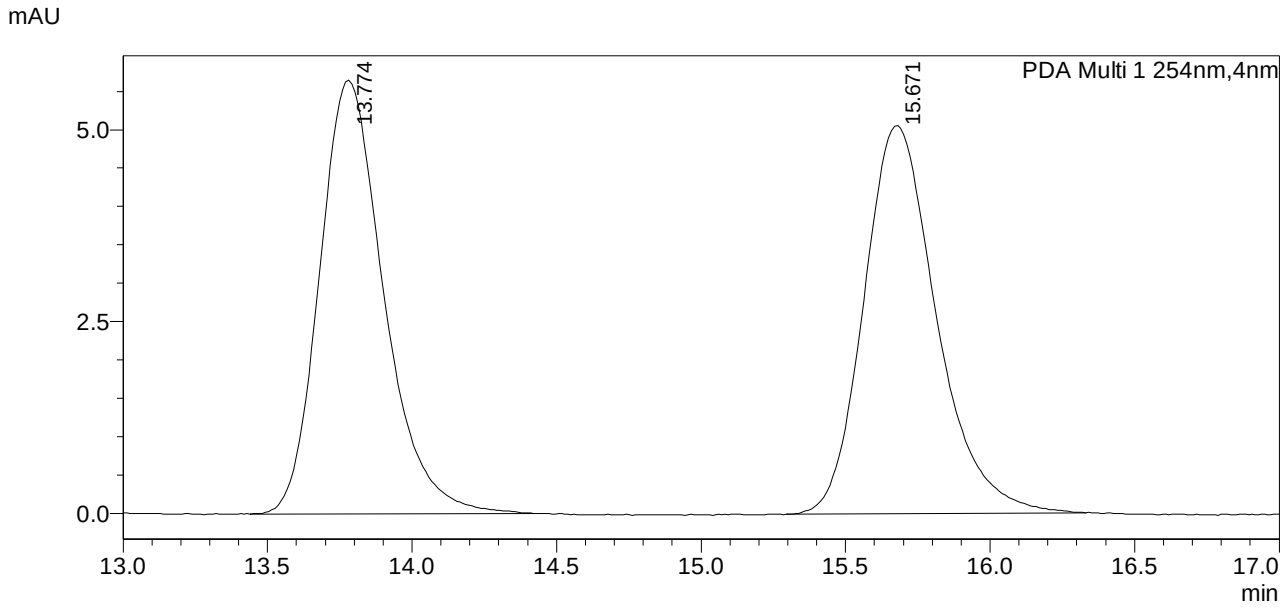
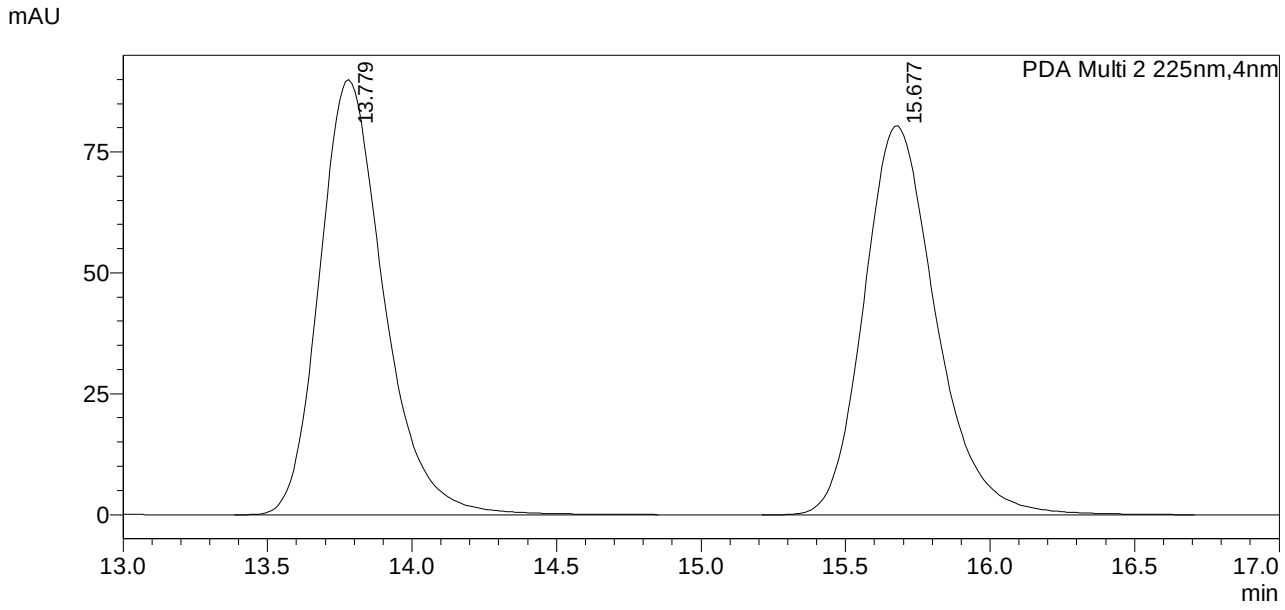
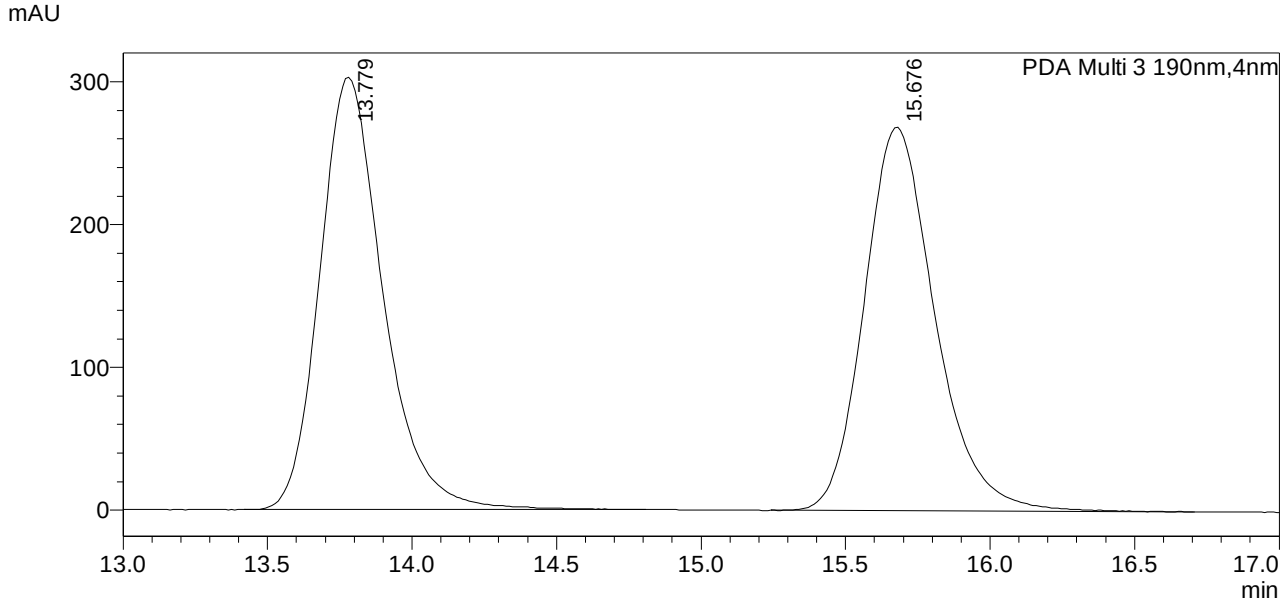






<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	13.774	87235	5650	49.670
2	15.671	88394	5063	50.330
Total		175629	10713	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	13.779	1393323	89954	49.936
2	15.677	1396879	80455	50.064
Total		2790202	170409	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	13.779	4612912	302694	50.214
2	15.676	4573610	268391	49.786
Total		9186522	571086	100.000

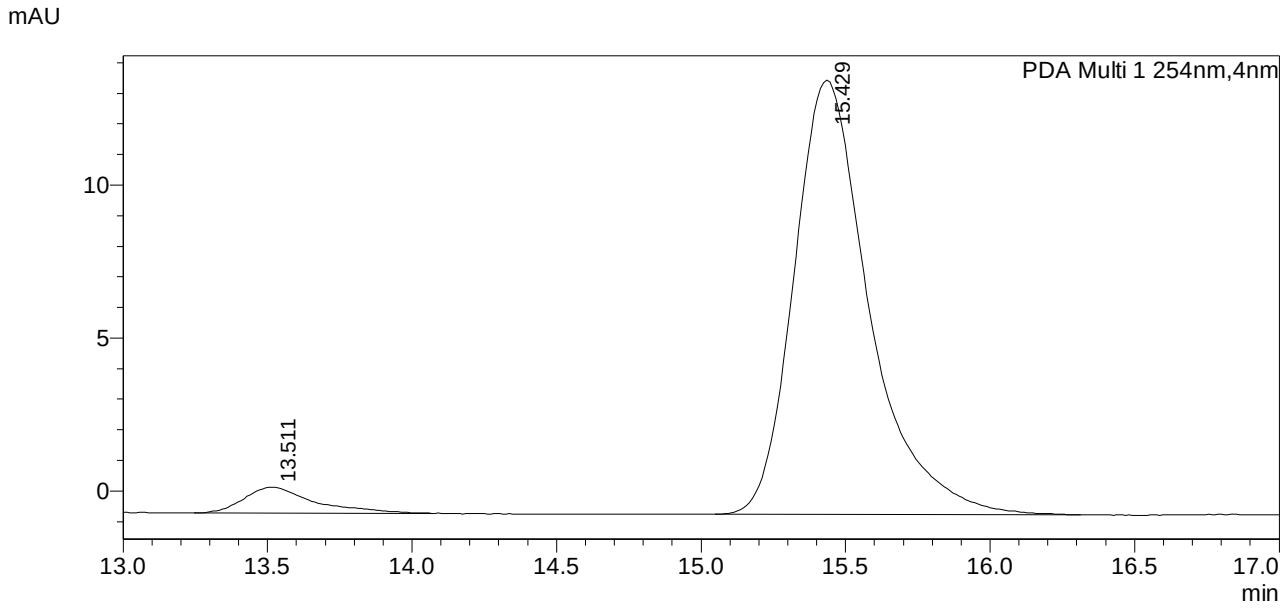
SHIMADZU LabSolutions

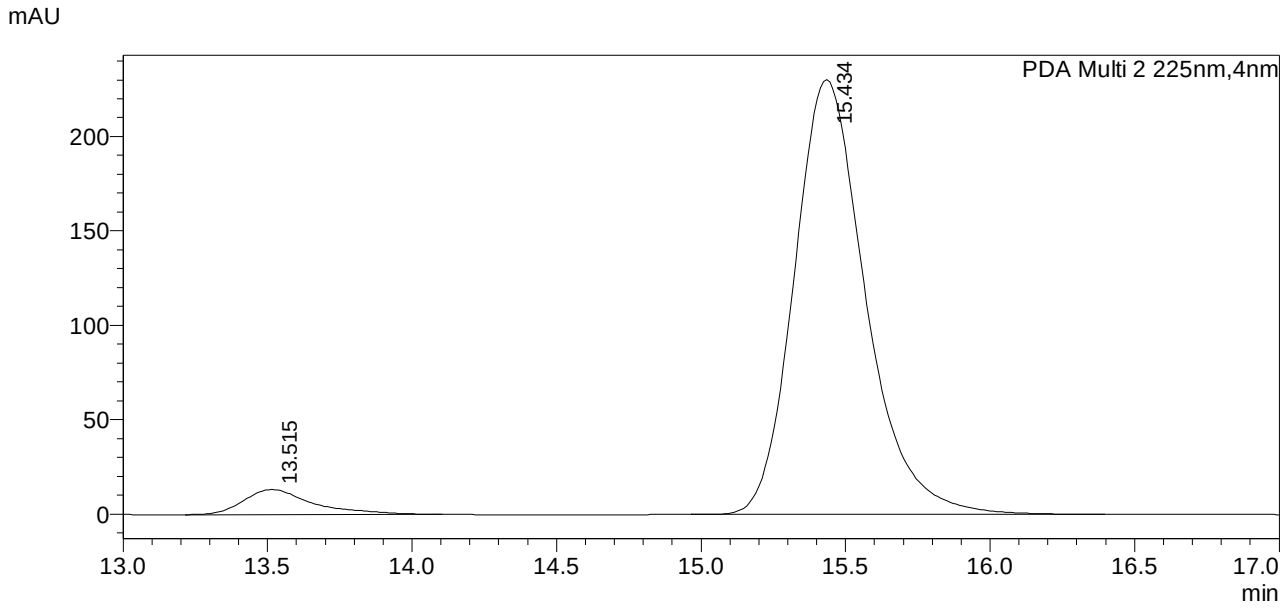
Analysis Report

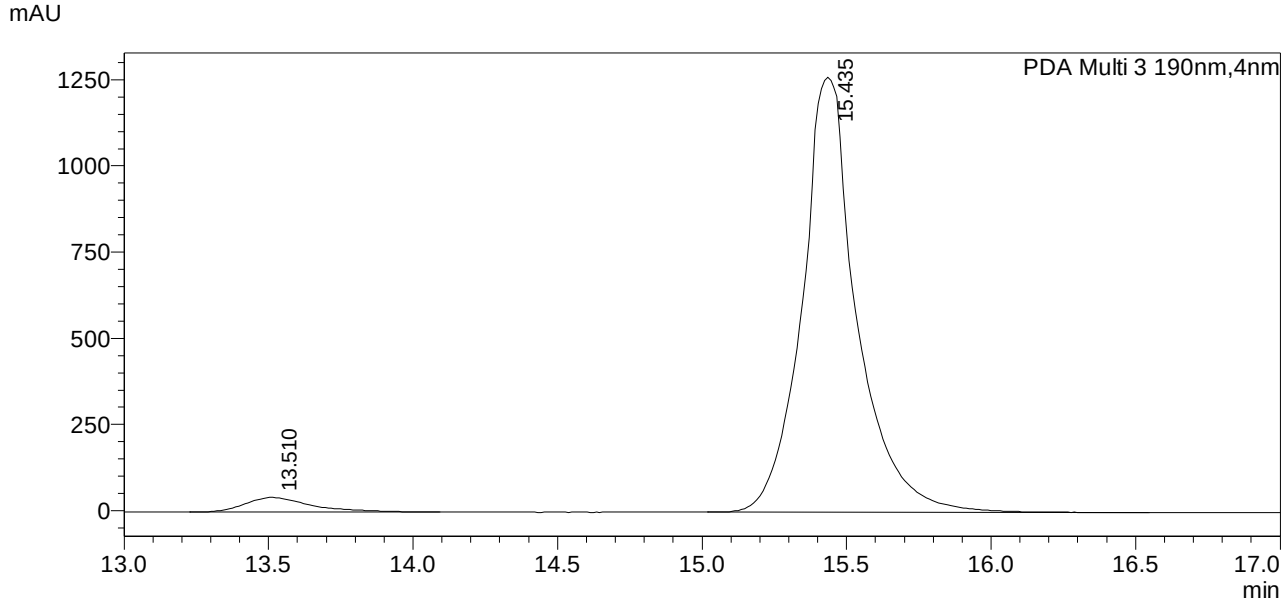
<Sample Information>

Sample Name	: 2-OMe-5-Me boronic acid ENT AD-H-column		
Sample ID	: 2-OMe-5-Me boronic acid AD-H		
Data Filename	: 2-OMe-5-Me boronic acid ENT AD-H.lcd		
Method Filename	: C5 99_1 fl0,5 30 min.lcm		
Batch Filename	: 20131101.lcb		
Vial #	: 1-61	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 11/1/2013 11:37:27 AM	Acquired by	: System Administrator
Date Processed	: 11/1/2013 12:11:23 PM	Processed by	: System Administrator

<Chromatogram>







<Peak Table>

PDA Ch1 254nm

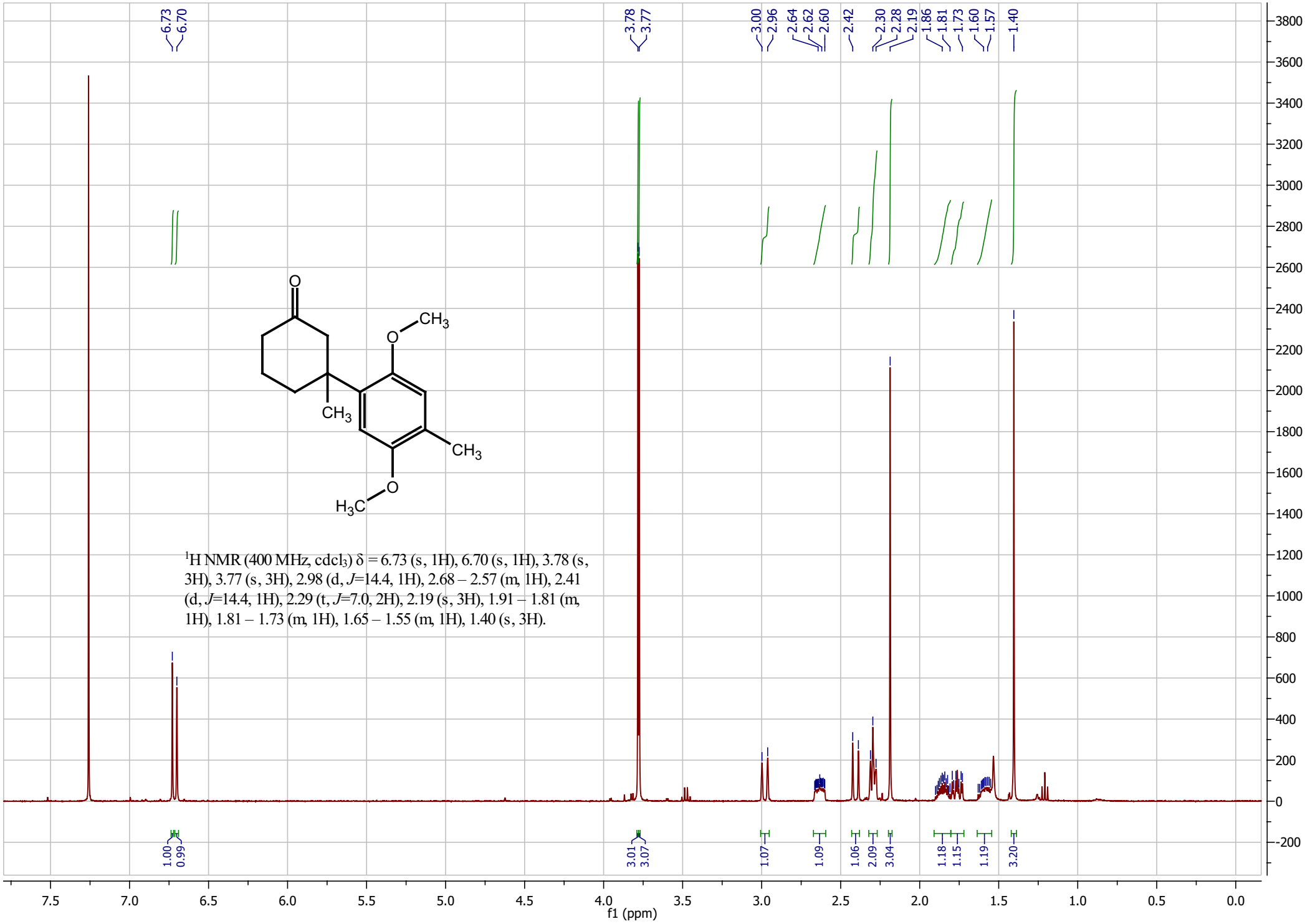
Peak#	Ret. Time	Area	Height	Area%
1	13.511	14211	837	5.232
2	15.429	257415	14193	94.768
Total		271626	15030	100.000

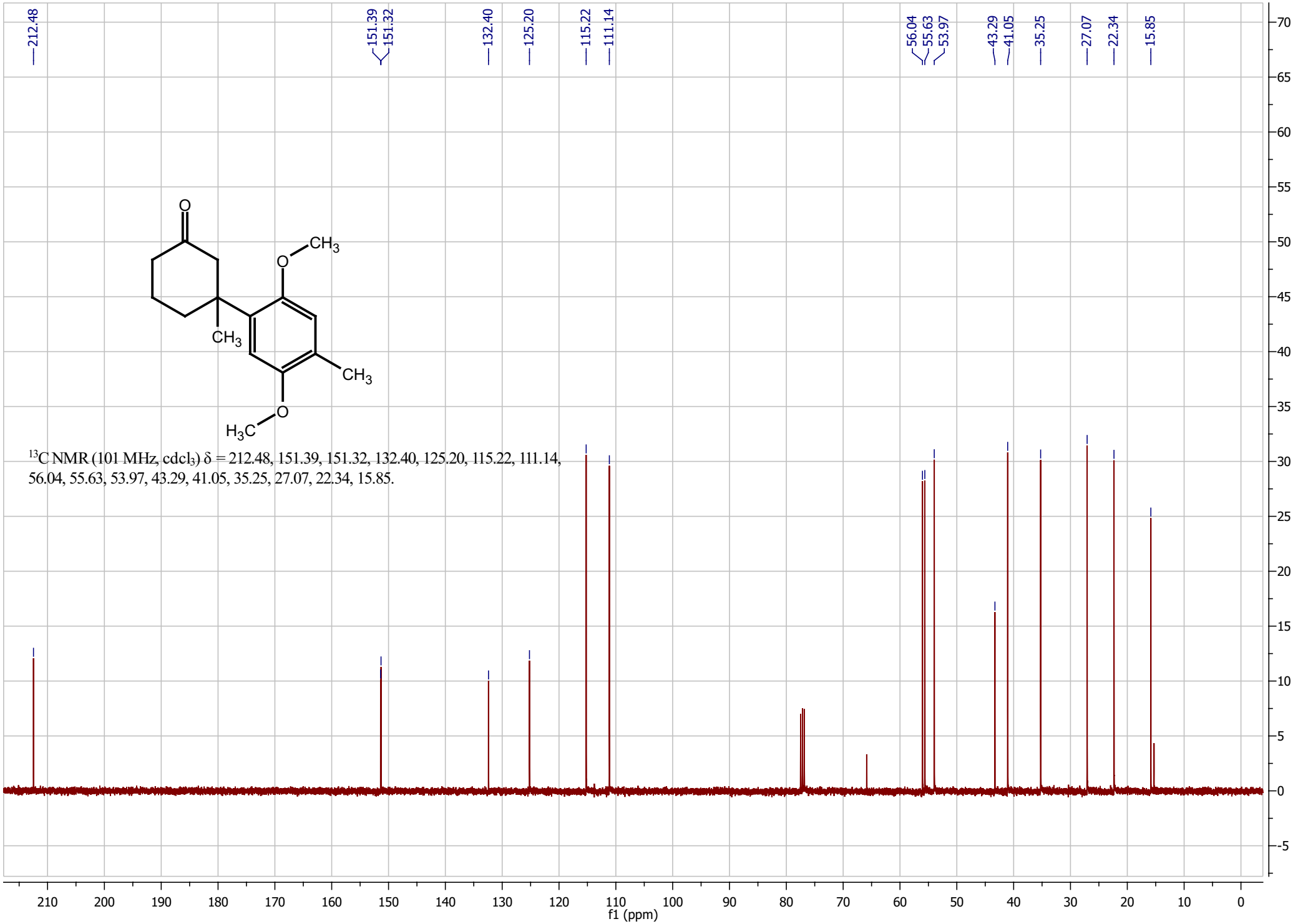
PDA Ch2 225nm

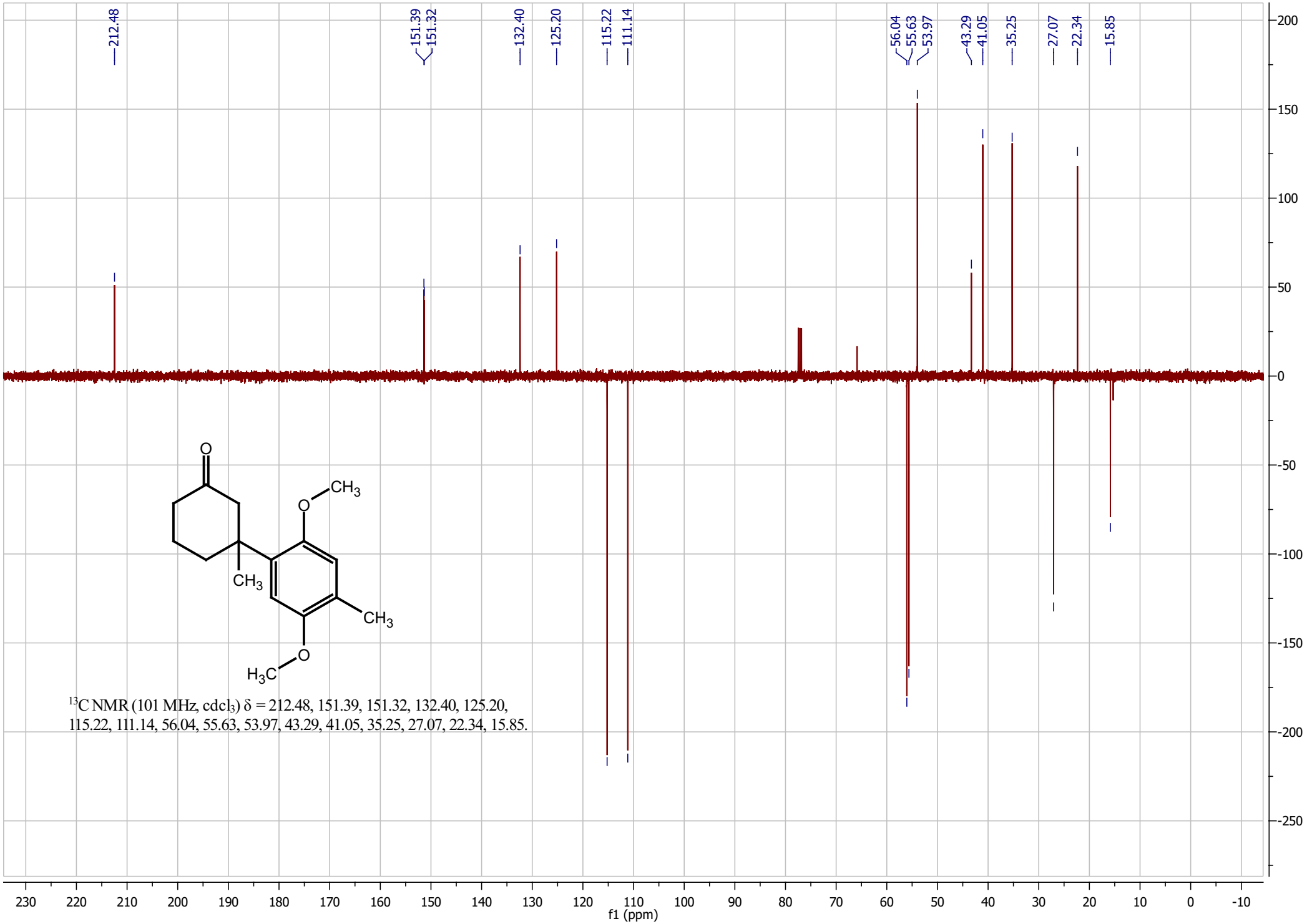
Peak#	Ret. Time	Area	Height	Area%
1	13.515	221100	13274	5.295
2	15.434	3954772	230315	94.705
Total		4175872	243589	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	13.510	684588	42320	3.951
2	15.435	16641352	1261054	96.049
Total		17325939	1303374	100.000


6.73
6.70
3.78
3.77
3.00
2.96
2.64
2.62
2.60
2.42
2.30
2.28
2.19
1.86
1.81
1.73
1.60
1.57
1.40
O
CH3
O
CH3
CH3
O
H3C
1H NMR (400 MHz, cdcl3) δ = 6.73 (s, 1H), 6.70 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 2.98 (d, J=14.4, 1H), 2.68 – 2.57 (m, 1H), 2.41 (d, J=14.4, 1H), 2.29 (t, J=7.0, 2H), 2.19 (s, 3H), 1.91 – 1.81 (m, 1H), 1.81 – 1.73 (m, 1H), 1.65 – 1.55 (m, 1H), 1.40 (s, 3H).
1.00
0.99
3.01
3.07
1.07
1.09
1.06
2.09
3.04
1.18
1.15
1.19
3.20
f1 (ppm)


212.48
151.39
151.32
132.40
125.20
115.22
111.14
56.04
55.63
53.97
43.29
41.05
35.25
27.07
22.34
15.85
O
CH3
O
CH3
CH3
O
H3C
13C NMR (101 MHz, cdcl3) δ = 212.48, 151.39, 151.32, 132.40, 125.20, 115.22, 111.14, 56.04, 55.63, 53.97, 43.29, 41.05, 35.25, 27.07, 22.34, 15.85.
f1 (ppm)



^{13}C NMR (101 MHz, cdcl$_3$) δ = 212.48, 151.39, 151.32, 132.40, 125.20, 115.22, 111.14, 56.04, 55.63, 53.97, 43.29, 41.05, 35.25, 27.07, 22.34, 15.85.

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

D:\...\Substrate Scope\3-methylcyclohexenone\2,5-DiOMe-4-Me Boronic Acid\2,5-DiOMe-4Me Boronic acid RAC Cellulose.lcd

Acquired by	: System Administrator
Sample Name	: 2,5-DiOMe-4Me Boronic acid RAC Cellulose-column
Sample ID	: 2,5-DiOMe-4Me Boronic acid RAC
Tray#	: 1
Vail #	: 54
Injection Volume	: 1 uL
Data File Name	: 2,5-DiOMe-4Me Boronic acid RAC Cellulose.lcd
Method File Name	: C6 99_1 fl0,5 60 min.lcm
Batch File Name	: 20140120_all column screening - 2014.lcb
Report File Name	: DEFAULT.lsr
Data Acquired	: 1/27/2014 5:06:18 PM
Data Processed	: 1/27/2014 6:06:26 PM

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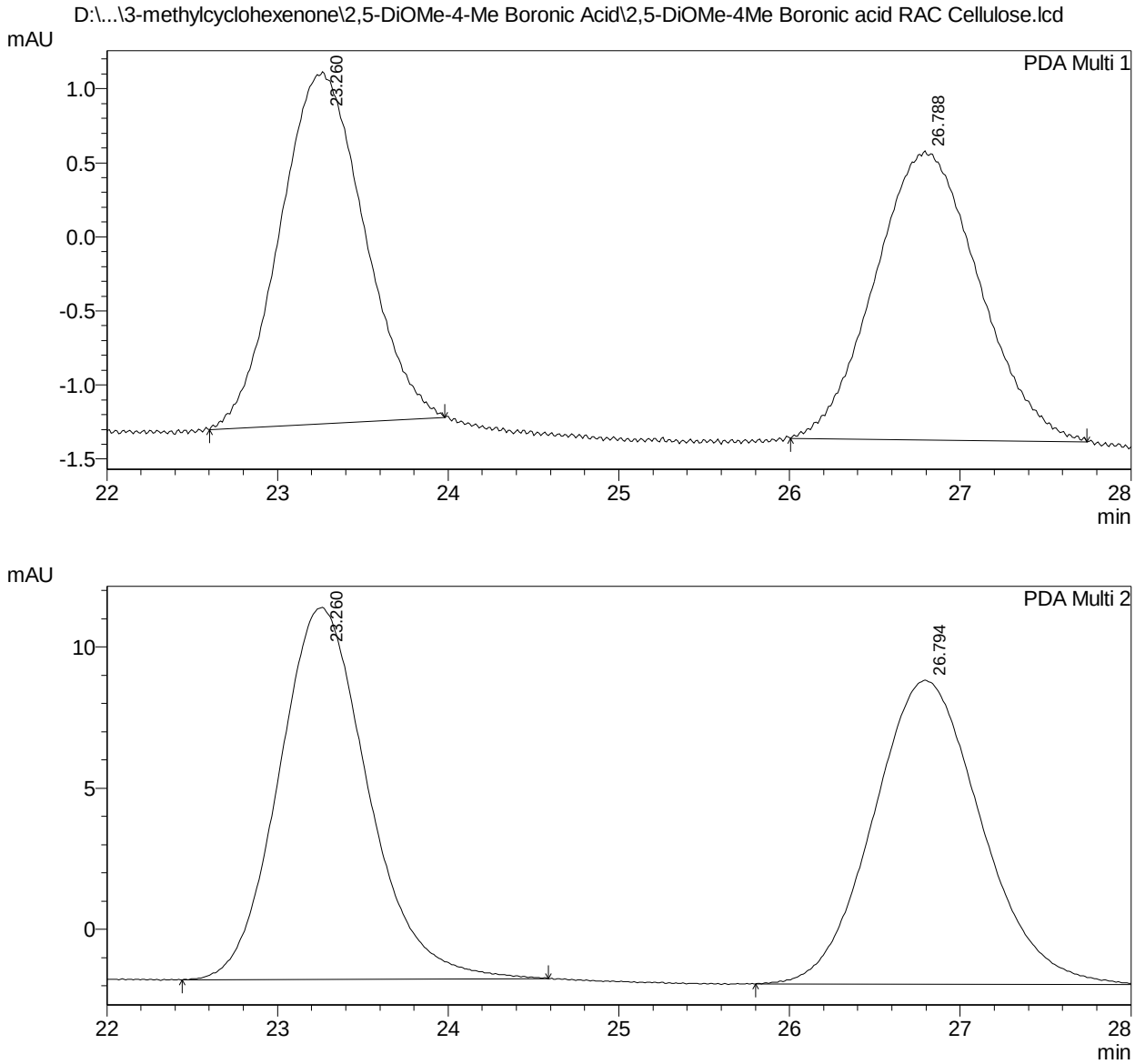
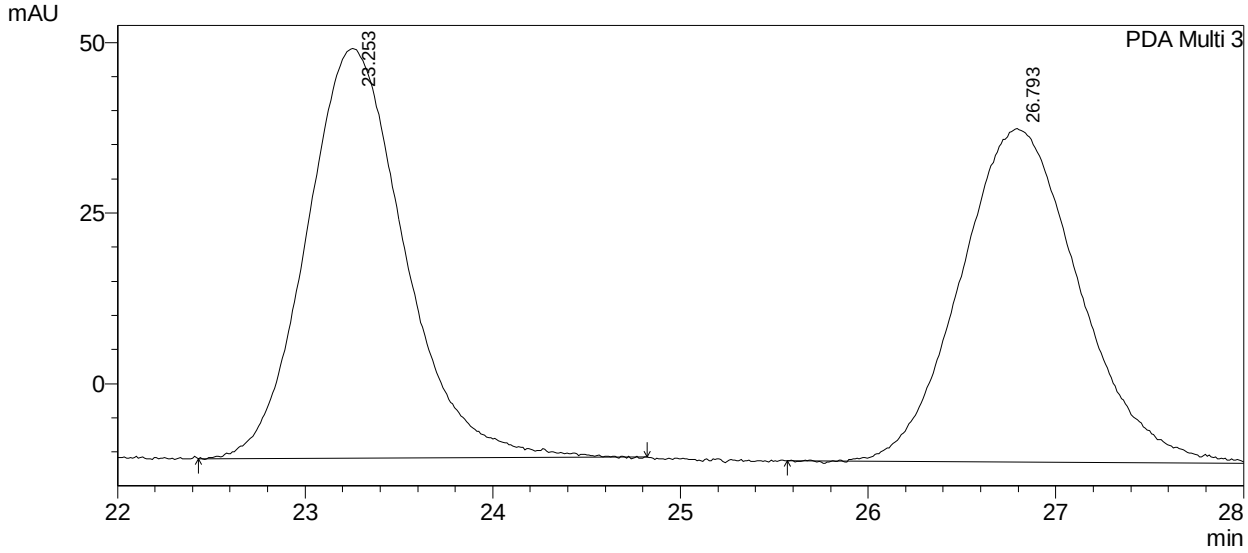




1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23.260	81636	2376	49.722
2	26.788	82550	1951	50.278
Total		164186	4327	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	23.260	478323	13169	50.297
2	26.794	472675	10764	49.703
Total		950997	23933	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	23.253	2174249	59991	50.323
2	26.793	2146296	48842	49.677
Total		4320545	108833	100.000

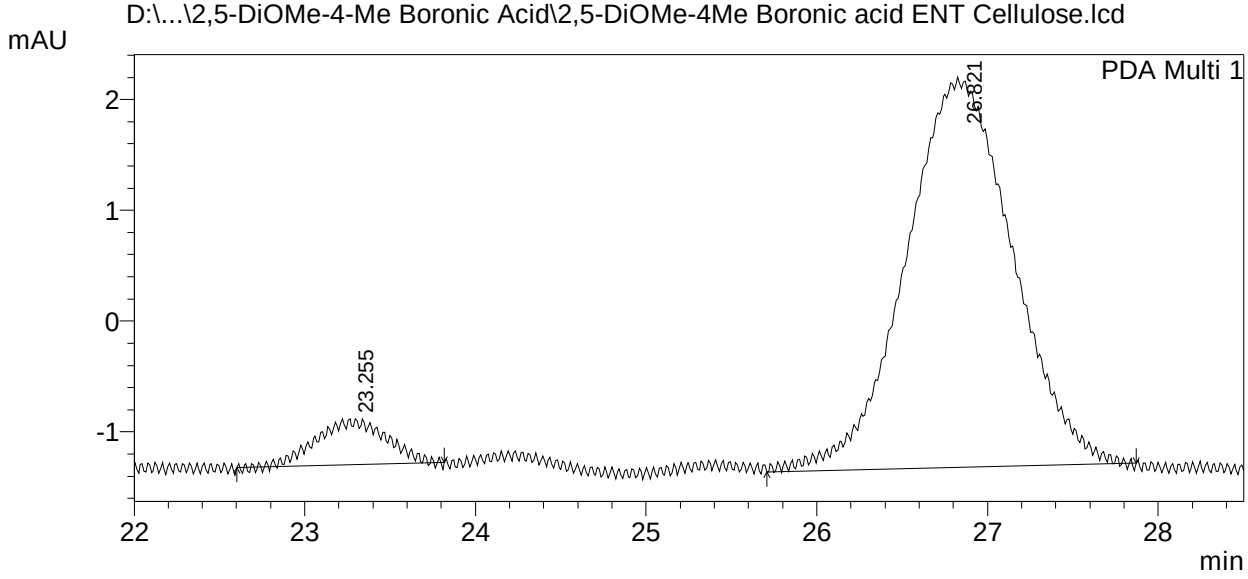
==== Shimadzu LCsolution Analysis Report ====

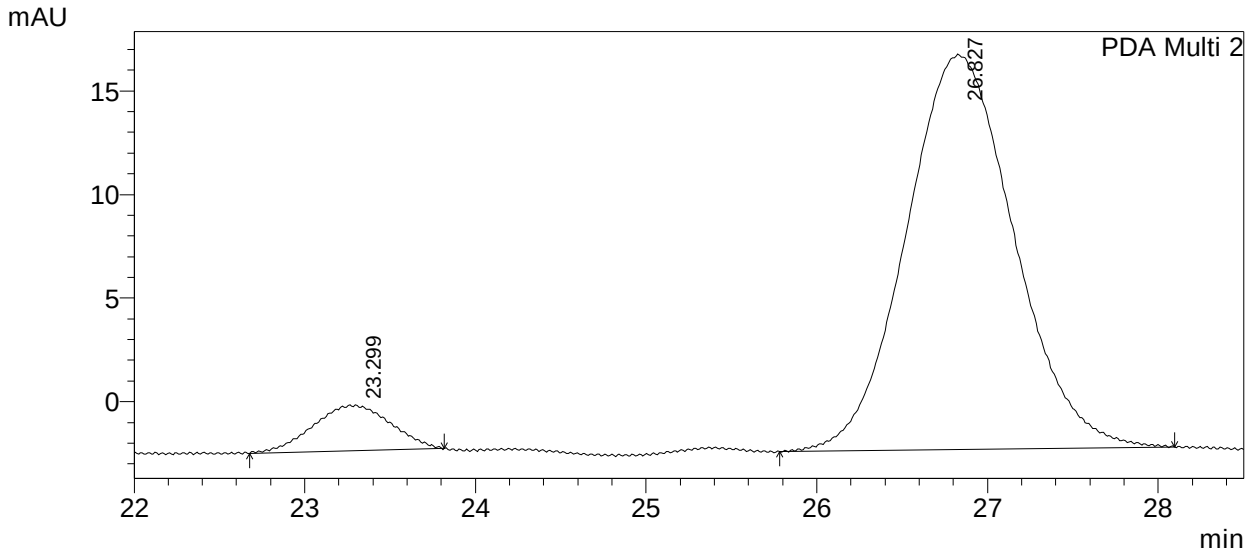
D:\...\2,5-DiOMe-4-Me Boronic Acid\2,5-DiOMe-4Me Boronic acid ENT Cellulose.lcd

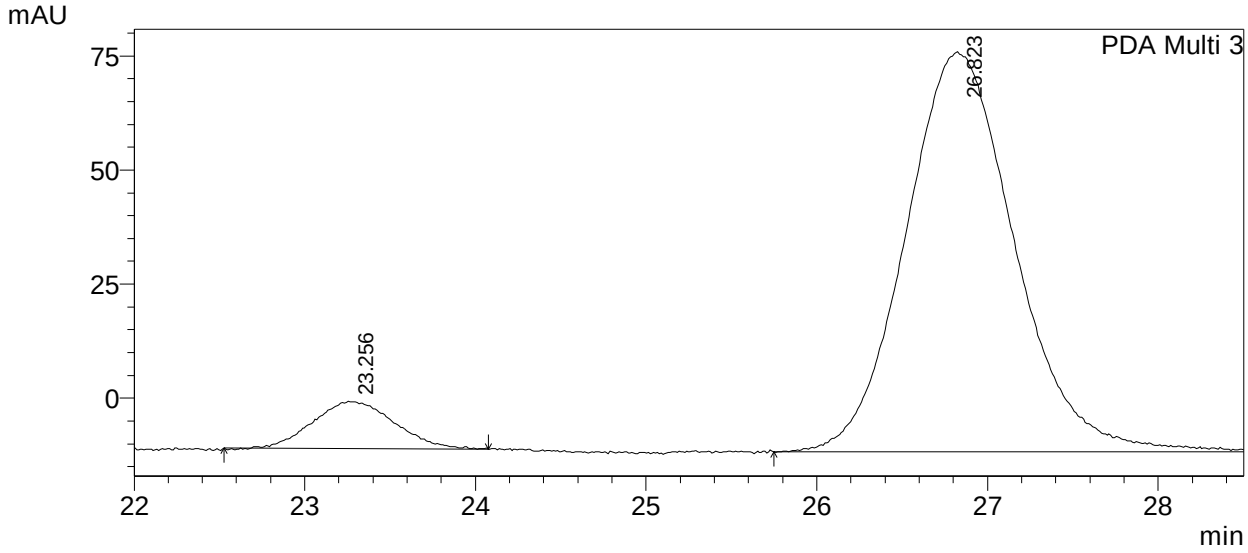
Acquired by	: System Administrator
Sample Name	: 2,5-DiOMe-4Me Boronic acid ENTCellulose-column
Sample ID	: 2,5-DiOMe-4Me Boronic acid ENT
Tray#	: 1
Vail #	: 54
Injection Volume	: 2 uL
Data File Name	: 2,5-DiOMe-4Me Boronic acid ENT Cellulose.lcd
Method File Name	: C6 99_1 fl0,5 60 min.lcm
Batch File Name	: 20140120_all column screening - 2014.lcb
Report File Name	: example PDA.lsr
Data Acquired	: 1/28/2014 9:26:02 AM
Data Processed	: 1/28/2014 11:36:25 AM

<Chromatogram>

D:\...\2,5-DiOMe-4-Me Boronic Acid\2,5-DiOMe-4Me Boronic acid ENT Cellulose.lcd







1 PDA Multi 1/254nm,4nm
2 PDA Multi 2/225nm,4nm
3 PDA Multi 3/190nm,4nm

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23.255	11318	416	6.893
2	26.821	152876	3520	93.107
Total		164194	3936	100.000

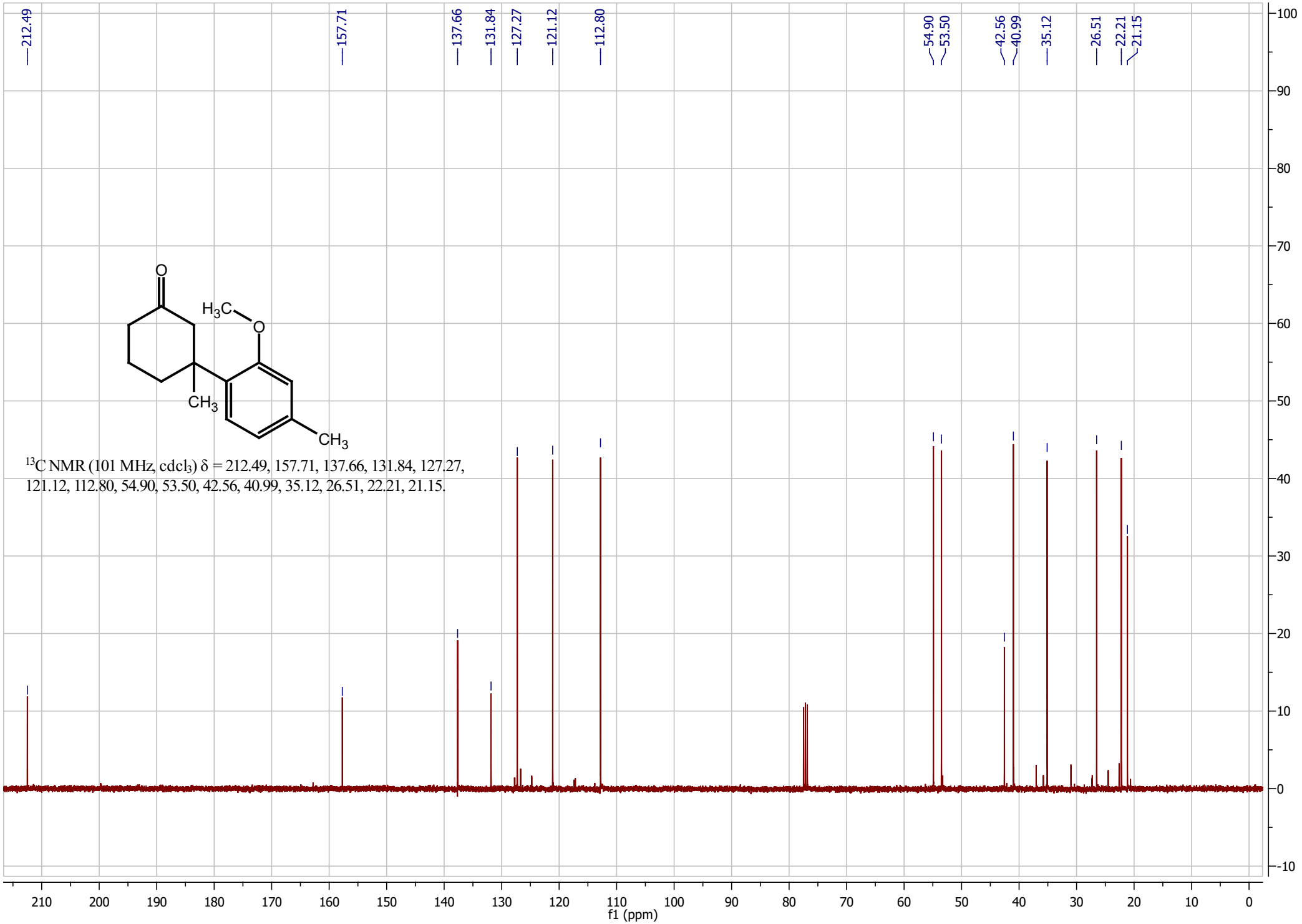
PDA Ch2 225nm

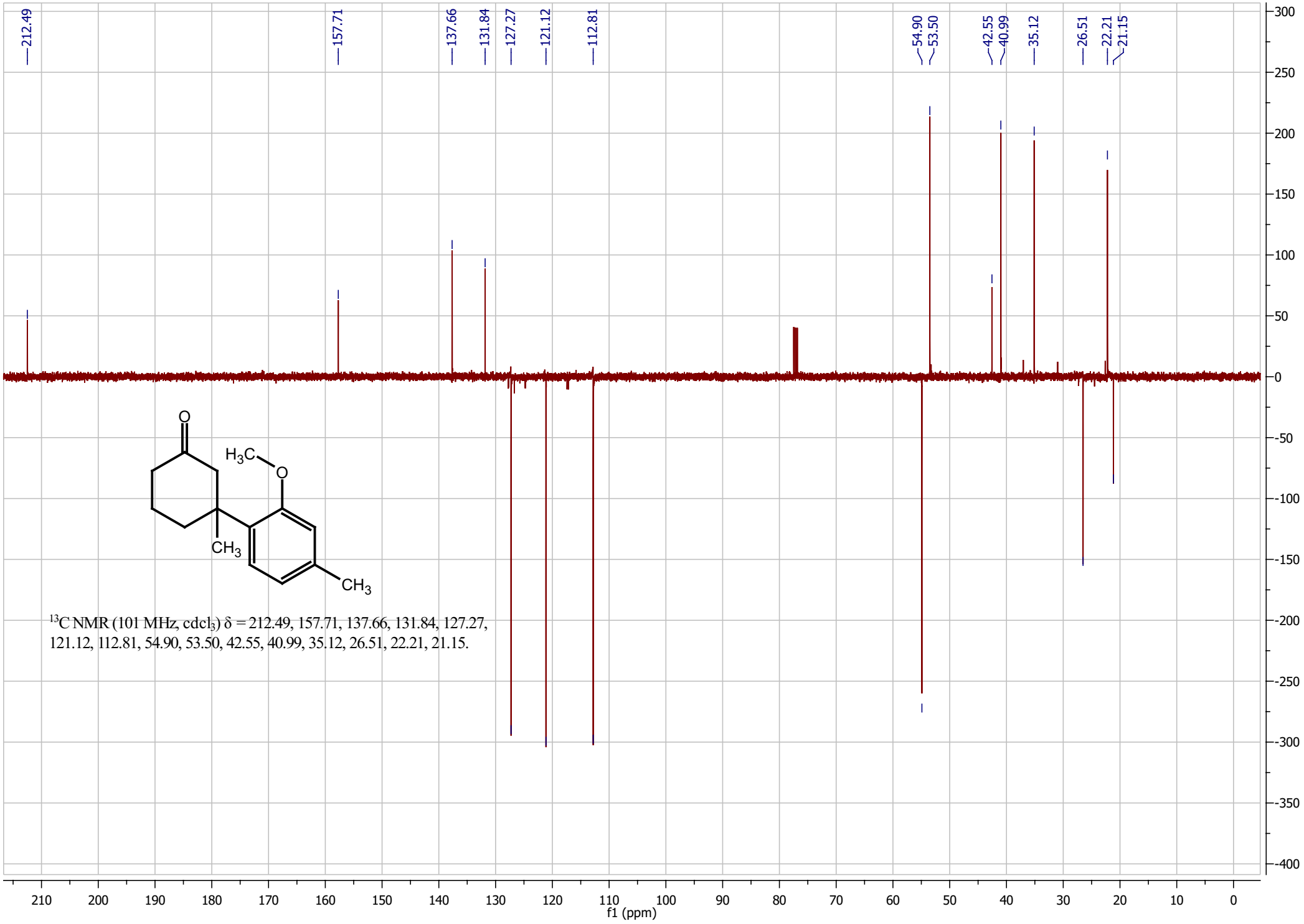
Peak#	Ret. Time	Area	Height	Area%
1	23.299	69281	2208	7.639
2	26.827	837697	19080	92.361
Total		906978	21288	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	23.256	342273	10329	8.111
2	26.823	3877691	87591	91.889
Total		4219964	97919	100.000


7.09
7.07
6.72
6.71
3.82
2.99
2.96
2.55
2.51
2.44
2.41
2.32
2.28
1.79
1.70
1.67
1.66
1.63
1.62
1.38
O
H3C
O
CH3
CH3
1H NMR (400 MHz, cdcl3) δ = 7.08 (d, J=8.4, 1H), 6.72 (d, J=6.9, 2H), 3.82 (s, 3H), 2.98 (d, J=14.5, 1H), 2.62 – 2.50 (m, 1H), 2.43 (d, J=14.3, 1H), 2.32 (s, 3H), 2.29 (d, J=7.2, 2H), 1.91 – 1.84 (m, 1H), 1.84 – 1.76 (m, 1H), 1.71 – 1.60 (m, 1H), 1.38 (s, 3H).
1.00
1.89
2.92
0.98
0.99
1.14
3.28
1.97
0.89
1.33
1.16
3.11
f1 (ppm)


212.49
157.71
137.66
131.84
127.27
121.12
112.80
54.90
53.50
42.56
40.99
35.12
26.51
22.21
21.15
O
H3C
O
CH3
CH3
13C NMR (101 MHz, cdcl3) δ = 212.49, 157.71, 137.66, 131.84, 127.27, 121.12, 112.80, 54.90, 53.50, 42.56, 40.99, 35.12, 26.51, 22.21, 21.15.
f1 (ppm)



^{13}C NMR (101 MHz, cdcl$_3$) δ = 212.49, 157.71, 137.66, 131.84, 127.27, 121.12, 112.81, 54.90, 53.50, 42.55, 40.99, 35.12, 26.51, 22.21, 21.15.

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: 2-OMe-4Me boronic acid RAC OD-H-column		
Sample ID	: 2-OMe-4Me boronic acid RAC OD-		
Data Filename	: 2-OMe-4Me boronic acid RAC OD-H.lcd		
Method Filename	: C2 99_1fl0,5 60 min.lcm		
Batch Filename	: 20131112_all column screening - 2014.lcb		
Vial #	: 1-5	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
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Date Processed	: 1/17/2014 4:34:53 PM	Processed by	: System Administrator

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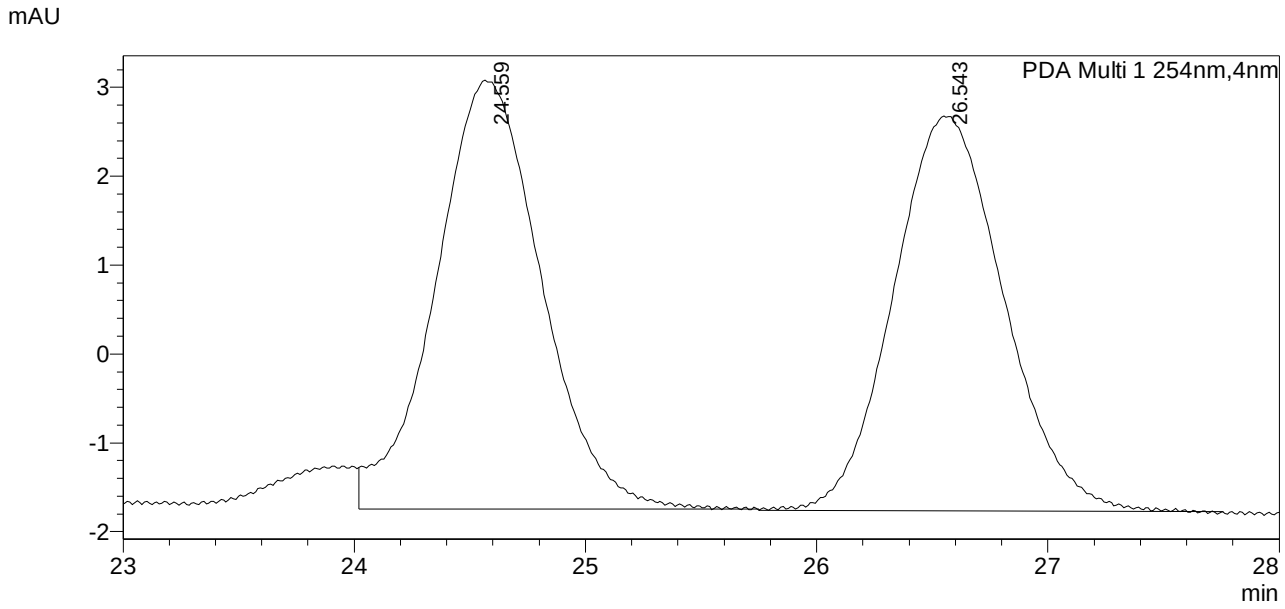

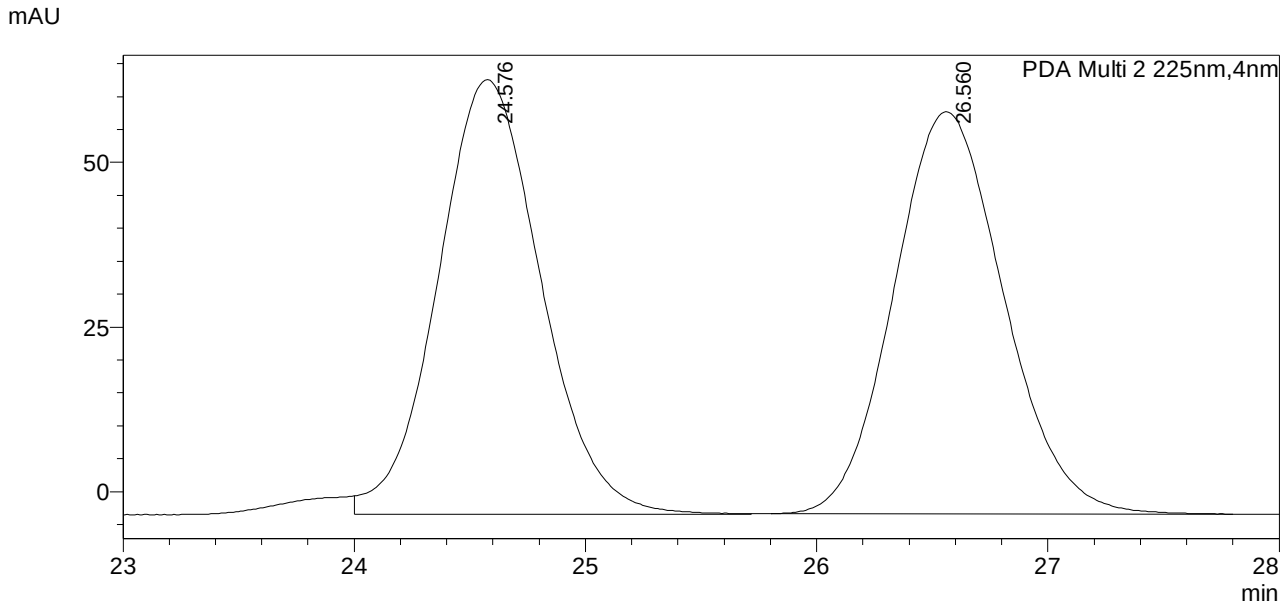

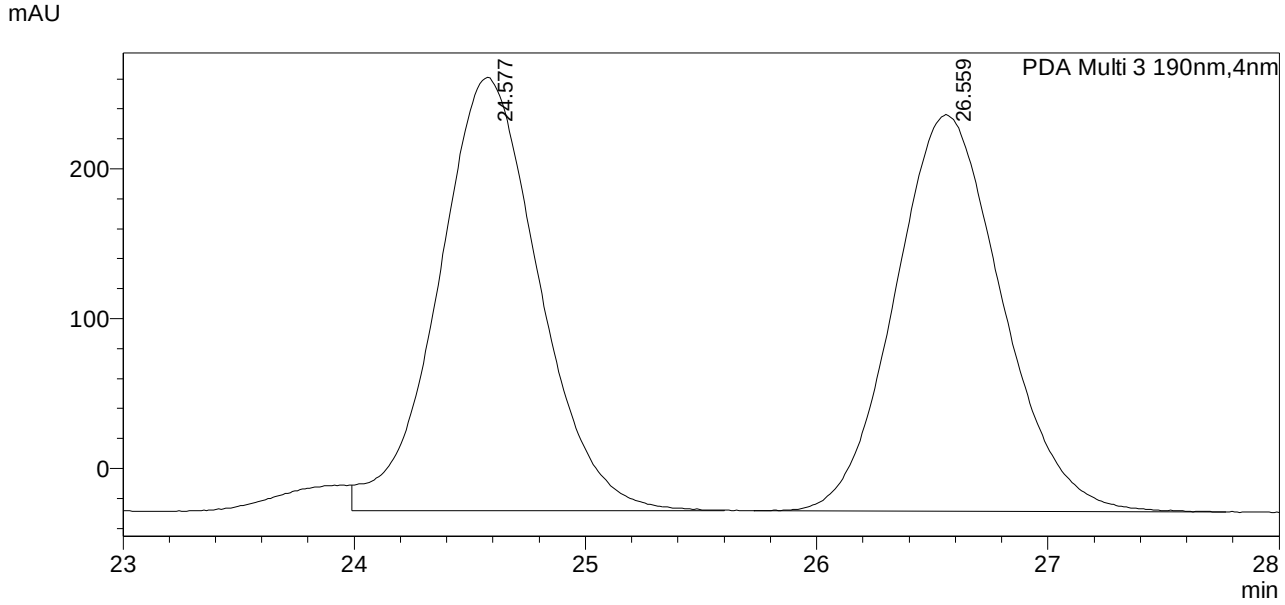

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	24.559	153331	4823	50.942
2	26.543	147661	4443	49.058
Total		300992	9267	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	24.576	2046871	66002	50.352
2	26.560	2018241	61070	49.648
Total		4065112	127072	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	24.577	8752521	289335	50.776
2	26.559	8484894	264570	49.224
Total		17237416	553905	100.000

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: 2-OMe-4Me boronic acid ENT OD-H-column		
Sample ID	: 2-OMe-4Me boronic acid ENT OD-H		
Data Filename	: 2-OMe-4Me boronic acid ENT OD-H.lcd		
Method Filename	: C2 99_1fl0,5 60 min.lcm		
Batch Filename	: 20142001.lcb		
Vial #	: 1-5	Sample Type	: Unknown
Injection Volume	: 2 uL	Level	: 1
Date Acquired	: 1/20/2014 4:13:20 PM	Acquired by	: System Administrator
Date Processed	: 1/20/2014 5:13:24 PM	Processed by	: System Administrator

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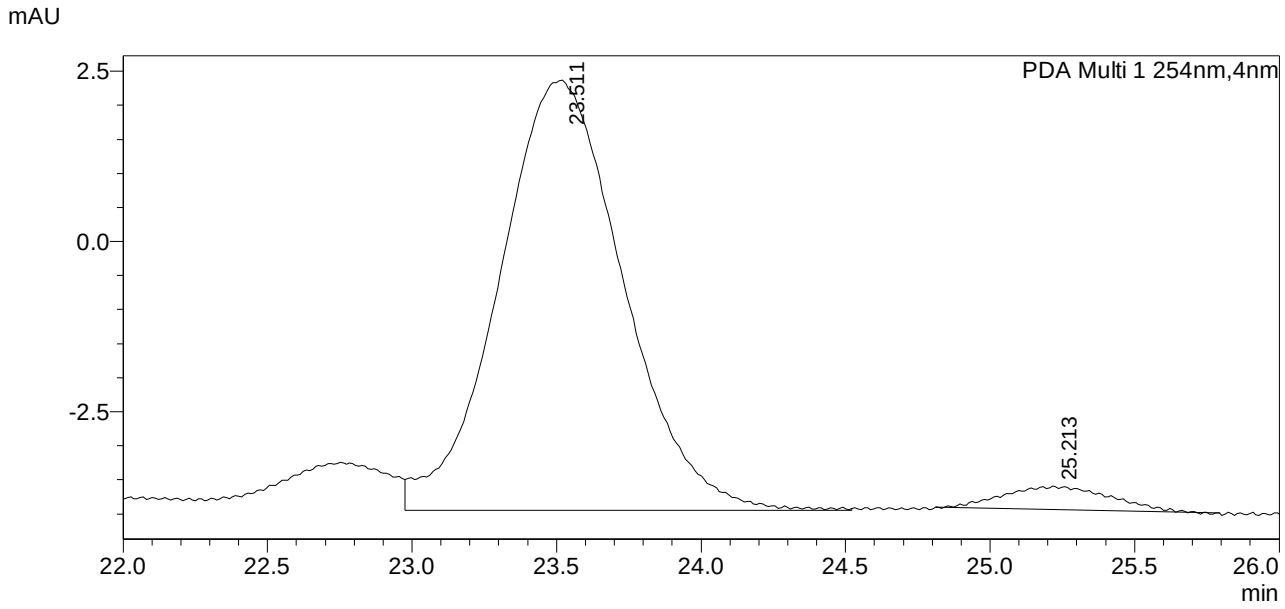

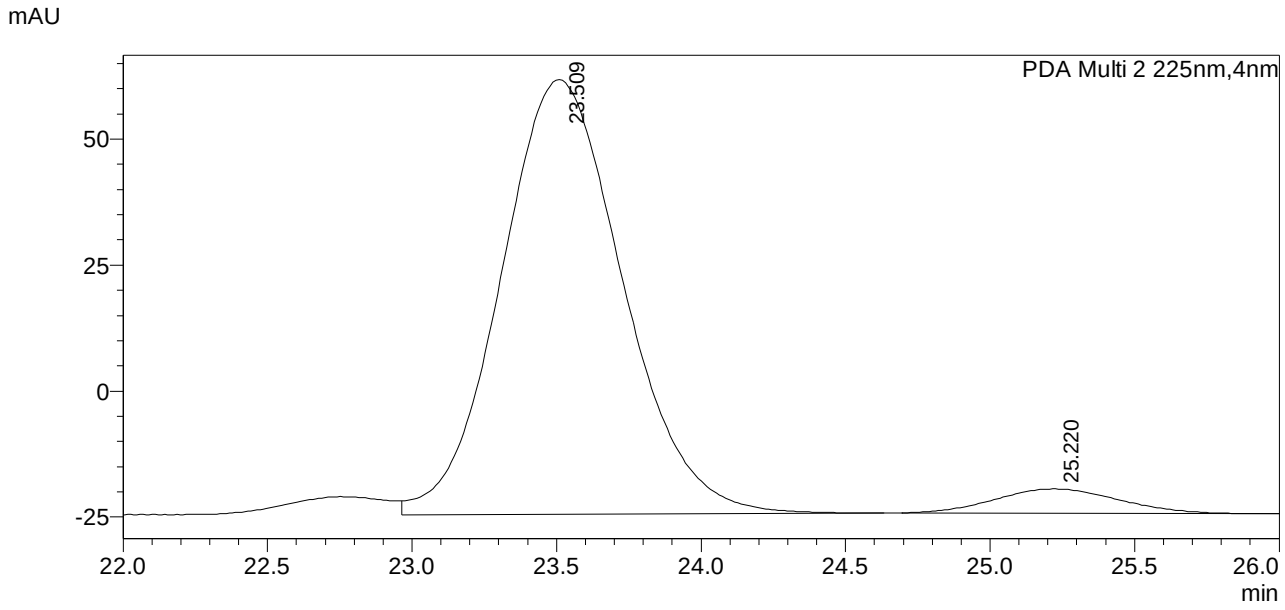

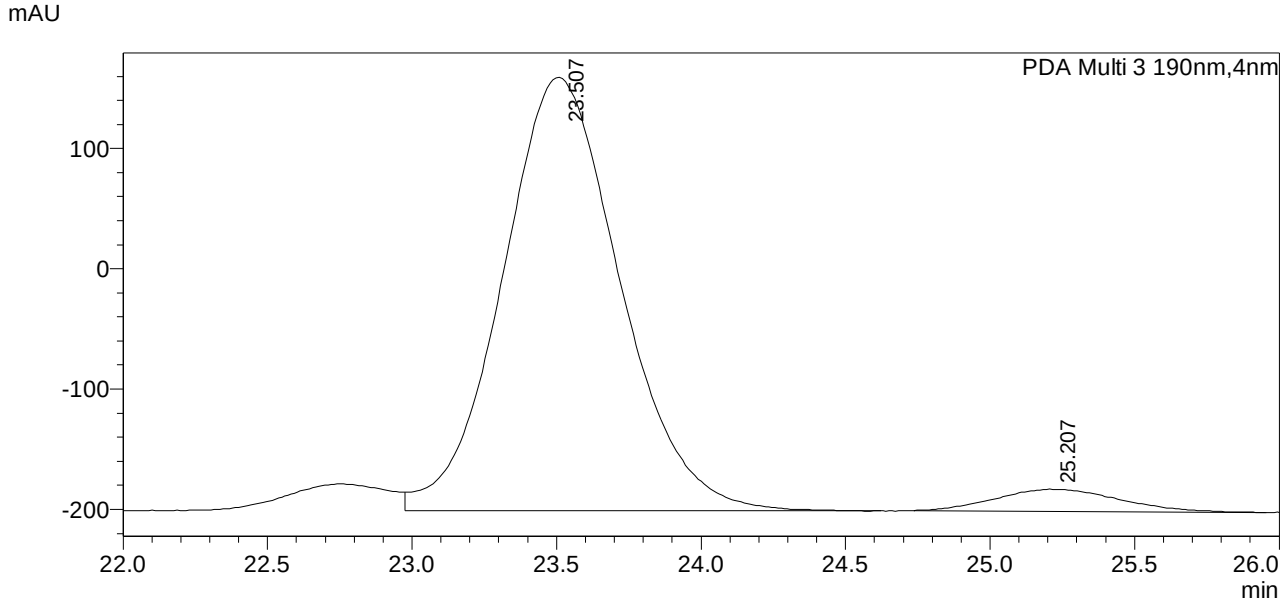

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23.511	188550	6316	95.561
2	25.213	8758	347	4.439
Total		197308	6663	100.000

PDA Ch2 225nm

Peak#	Ret. Time	Area	Height	Area%
1	23.509	2521234	86213	94.632
2	25.220	143010	4816	5.368
Total		2664244	91030	100.000

PDA Ch3 190nm

Peak#	Ret. Time	Area	Height	Area%
1	23.507	10172183	360168	94.939
2	25.207	542206	18282	5.061
Total		10714389	378450	100.000