Nickel-Catalyzed Regiodivergent Opening of Epoxides with Aryl Halides: Co-Catalysis Controls Regioselectivity

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Supporting Information

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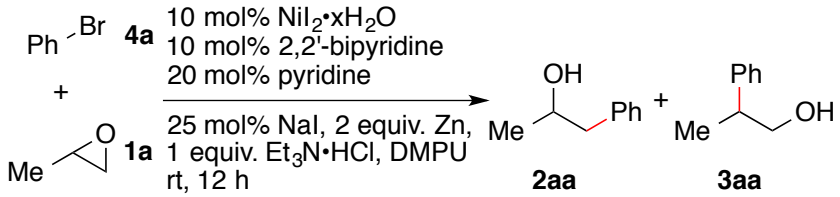
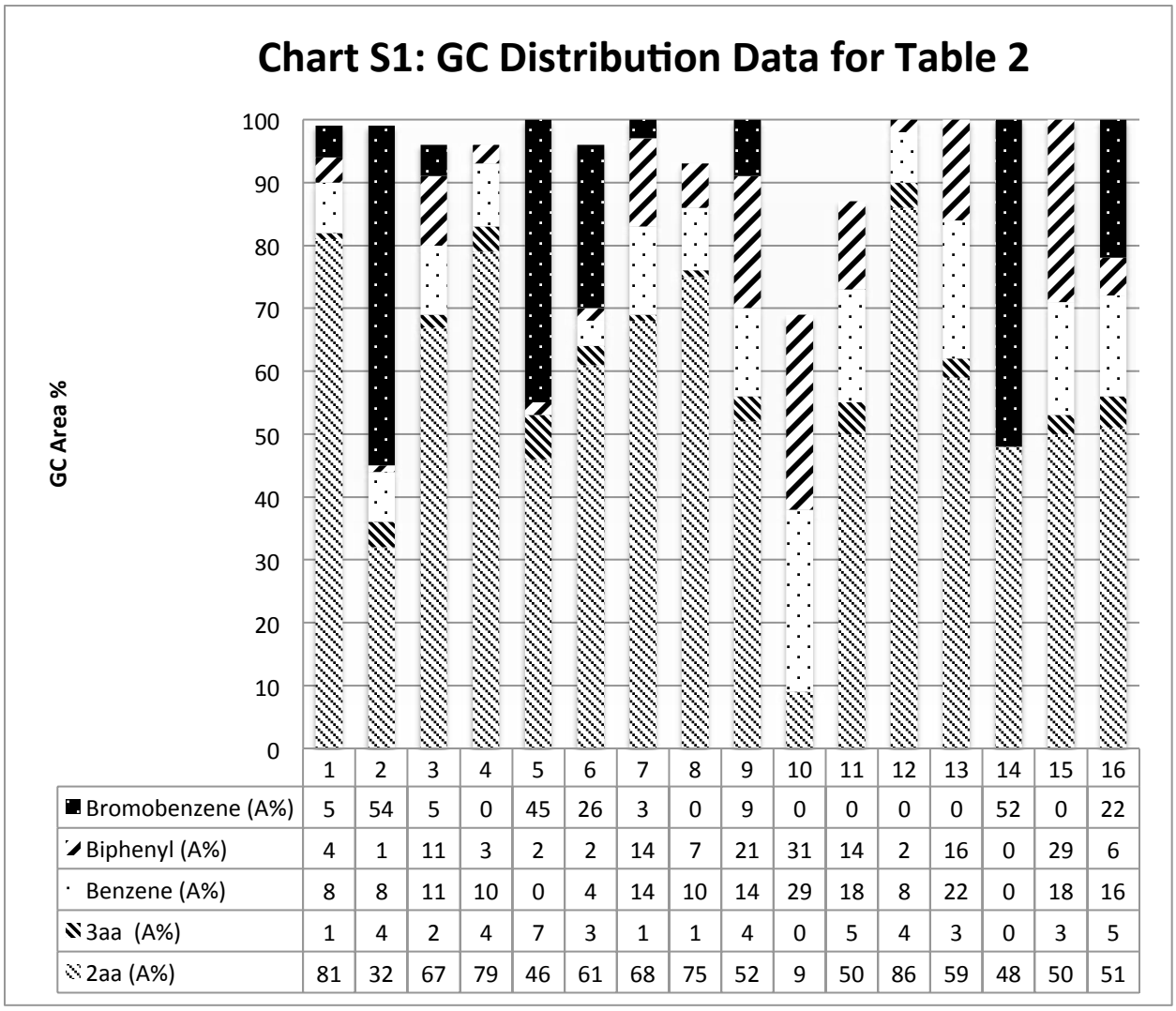
I. Supplemental Data

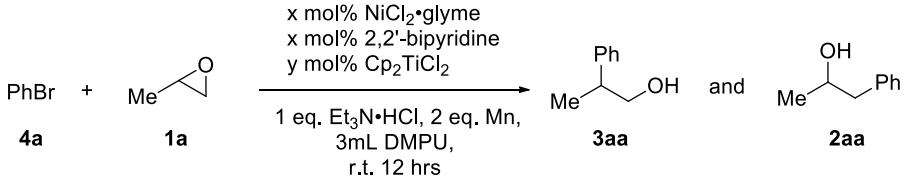
Chart S1: GC Distribution Data for Table 2





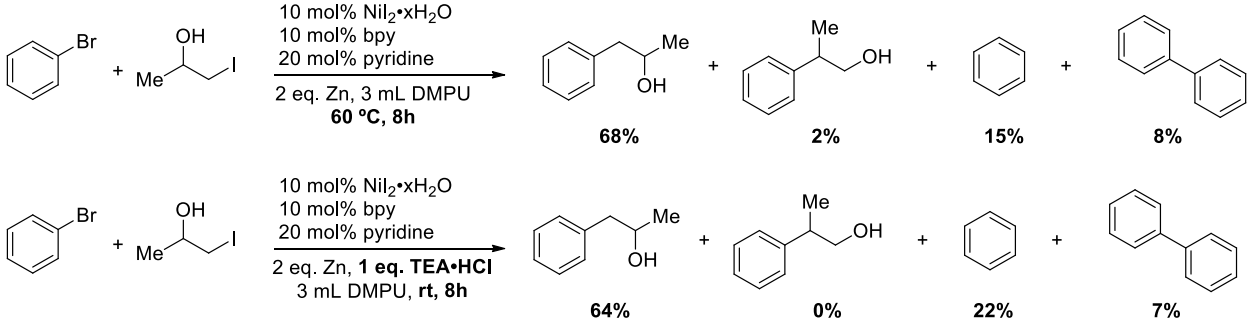
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Bromobenzene (A%)	5	54	5	0	45	26	3	0	9	0	0	0	0	52	0	22
Biphenyl (A%)	4	1	11	3	2	2	14	7	21	31	14	2	16	0	29	6
Benzene (A%)	8	8	11	10	0	4	14	10	14	29	18	8	22	0	18	16
3aa (A%)	1	4	2	4	7	3	1	1	4	0	5	4	3	0	3	5
2aa (A%)	81	32	67	79	46	61	68	75	52	9	50	86	59	48	50	51

Table S1. Catalyst Ratio Studies for Ni/Ti Co-catalysis



$NiCl_2$•glyme (mol%)	Cp_2TiCl_2 (mol%)	PhH %	2aa %	3aa %	Biphenyl %
10	2	22	6	12	30
10	5	21	7	24	24
10	**10**	**0**	**13**	**54**	**16**
10	20	4	12	51	17
10	15	3	11	43	22
5	10	7	11	45	18
2.5	10	9	11	47	17
2.5	2.5	32	4	16	18

Scheme S1. Cross-coupling Reaction of Iodohydrin[1] and Bromobenzene



[1] Iodohydrin was synthesized from propylene oxide according to published procedure: Chini, M.; Crotti, P.; Gardelli, C.; Macchia, F. *Tetrahedron* **1992**, *48*, 3805.

II. Materials

Metals. NiI_2 (anhydrous, Alfa Aesar), $NiI_2 \bullet xH_2O$ (x = 3.9, Strem Chemical), zinc powder (<10 micron, Aldrich), manganese powder (-325 mesh, Aldrich), anhydrous zinc iodide (Strem Chemical), anhydrous manganese iodide (Strem Chemical), and titanocene dichloride (Strem Chemical) were kept under N_2 in drybox and used as received. $NiCl_2$(dme) (x = 0.97) was synthesized according to the known procedure and assayed by elemental analysis.[2]

Ligands. Anhydrous pyridine was prepared from ACS grade solvent by passage through activated alumina and molecular sieves in a purification system provided by Vacuum Atmospheres. 4-4'-di-*tert*-butyl-2,2'-bipyridine and 4,4'-dimethoxy-2,2'-bipyridine were purchased from Aldrich. Neocuproine and 2,2'-bipyridine were purchased from Alfa Aesar.

Substrates. Iodobenzene (Aldrich), bromobenzene (Aldrich) (**4a**), bromotoluene (Aldrich) (**4j**), 1-bromo-4-(*tert*-butyl)benzene (Alfa Aesar) (**4d**), 1-bromo-4-methoxybenzene (Alfa Aesar) (**4b**), 4-bromobenzaldehyde (Alfa Aesar) (**4h**), 4'-bromoacetophenone (Aldrich) (**4f**), 1-bromo-4-(trifluoromethyl)benzene (Alfa Aesar) (**4e**), 4-bromobenzonitrile (Alfa Aesar) (**4g**), 4-bromophenol (Alfa Aesar) (**4i**), (±)-propylene oxide (Aldrich) (**1a**), (R)-propylene oxide (Alfa Aesar) (**1j**), cyclohexene oxide (Aldrich) (**1f**), (±)-styrene oxide (Aldrich) (**1e**), (±)-glycidol (Alfa Aesar), isobutene oxide (Alfa Aesar) (**1i**), and (±)-1,2-epoxyhexane (Aldrich) (**1b**), (±)-1,2-epoxyoctane (**1c**) were purchased and used as received. N-(4-bromophenyl)-4-methylbenzenesulfonamide (**4c**) [3], N-acetyl-5-bromoindole (**4k**) [4], cyclohex-1-en-1-yl trifluoromethanesulfonate (**4l**) [5], 1-bromocyclohex-1-ene (**4m**) [6], benzyl (oxiran-2-ylmethyl)carbamate (**2k**)[7], *tert*-butyl (oxiran-2-ylmethyl)carbamate (**2h**)[8], indene oxide (**2l**)[9], *tert*-butyldimethyl(oxiran-2-ylmethoxy)silane (**2g**)[10], and 2-((benzyloxy)methyl)oxirane (**2d**)[11] were synthesized according to literature procedures.

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[2] Ward, L. G. L.; Pipal, J. R. *Inorg. Synth*. **1971**, *13*, 154-164
[3] McKeown, S. C.; Hall, A.; Blunt, R.; Brown, S. H.; Chessell, I. P.; Chowdhury, A.; Giblin, G. M. P.; Healy, M. P.; Johnson, M. R.; Lorthioir, O.; Michel, A. D.; et al. *Bioorg. Med. Chem*. **2007**, *17*, 1750-1754
[4] Phipps, R. J.; Brimster, N. P.; Gaunt, M. J. *J. Am. Chem. Soc*. **2008**, *130*, 8172
[5] Martínez, A. G.; Herrera, A.; Martínez, R.; Teso, E.; García, A.; Osío, J.; Pargada, L.; Unanue, R.; Subramanian, L. R.; Hanack, M. *J. Heterocyclic Chem.* **1988**, 1237-1241
[6] Zhan, F.; Liang, G. *Angew. Chem. Int. Ed*. **2013**, *52*, 1266-1269
[7] Actelion Pharmaceuticals Ltd. U.S. Patent 0,039,823, 2011.
[8] Klee, N.; Wong, P. E.; Baragaña, B.; Mazouni, F. E.; Phillips, M. A.; Barrett, M. P.; Gilbert, I. H. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 4364-4366
[9] Imuta, M.; Ziffer, H. *J. Org. Chem*. **1979**, *44*, 1351-1352
[10] Swift, M. D.; Donaldson, A.; Sutherland, A. *Tetrahedron Lett.* **2009**, *50*, 3241-3244
[11] Barbe, R.; Hasserodt, J. *Tetrahedron*, **2007**, *63*, 2199-2207

Solvents. DMPU (1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone) (AK Scientific) was distilled from calcium hydride (60-61 °C, 50 mtorr) followed by drying over 10 wt% molecular sieves (4 Å). Anhydrous *N*,*N*-dimethylformamide (DMF), anhydrous N,N-dimethylacetamide (DMAc), and anhydrous tetrahydrofuran (THF) were prepared from ACS grade, inhibitor free solvents by passage through activated alumina and molecular sieves in a solvent purification system supplied by Vacuum Atmospheres. Solvent water content was routinely verified by Karl-Fisher titration.

Other Reagents. Dodecane (Aldrich), tetrabutylammonium iodide (Aldrich), anhydrous sodium iodide (Strem Chemical), and triethylamine hydrochloride (Aldrich) were used as received. Triethylamine hydrobromide and triethylamine hydroiodide were prepared according to known methods.[12]

[12] Yang, Z.; He, L.; Miao, C.; Chanfreau, S. *Adv. Synth. Catal*. **2010**, *352*, 2233-2240

III. General Methods

NMR Spectroscopy.

NMR spectra were recorded at 400.13 MHz ^{1}H NMR frequency, and data analysis was performed using the MestReNova software package (version 6.1.0) and Topspin (Bruker). NMR chemical shifts are reported in ppm and referenced to the residual solvent peak of $CDCl_3$ (7.26 ppm). Coupling constants (*J*) are reported in Hertz.

Gas Chromatography.

Instrument. GC analyses were performed on an Agilent 7890A GC equipped with dual DB-5 columns (20 m x 180 μm x 0.18 μm), dual FID detectors, and using hydrogen as the carrier gas.

Sample preparation. A 100 μL aliquot was removed from the reaction mixture using a gas-tight syringe and quenched with pH = 8 phosphate buffer[13]. This mixture was then diluted with 1 mL of diethylether and the resulting mixture was then passed through a 1-inch pipette column of celite. The filtrate is used for GC and GC-MS analysis.

Analysis Method. 1 μL inj. of sample, inj. temp of 300 °C, 100:1 split ratio, initial inlet pressure was 20.3 psi but varied as the column flow was held constant at 1.8 mL/min for the duration of the run. Initial oven temperature of 50 °C was held for 0.46 min followed by a temperature ramp up to 300 °C at 65 °C/min and finally the temperature was held at 300 °C for 0.69 min. Total run time was ~ 5 min. FID temperature was 325 °C.

Chiral-phase Gas Chromatography.

Instrument. Chiral-phase GC analyses were performed on an Hewlett Packard 5890 Series II instrument equipped with Restek RT-βDEXsm column (30 m x .32 mm x .25 μm), FID detector, and helium carrier gas.

Sample preparation. Same as for GC analysis.

Analysis Method. 1 μL inj. of sample, inj. temp of 250 °C, 50:1 split ratio, inlet pressure of 20.3 psi. Initial oven temperature of 50 °C was held for 8.0 min followed by a temperature ramp up to 135 °C at 1.2 °C/min and finally the temperature was held at 135 °C for 10.0 min. Total run time was 88.8 min. FID temperature was 250 °C.

GC/MS Analysis

GC/MS analyses were performed on a Shimadzu GCMS-QP2010 equipped with an RTX-XLB column (30 m x 0.25 mm x 0.28 μm) with a quadrupole mass analyzer using helium as the

[13] 0.1 M pH 8 phosphate buffer was prepared by dissolving 1 gram of $NaH_2PO_4 \cdot H_2O$ and 34.2 grams of $Na_2HPO_4 \cdot 12H_2O$ in 1000 mL of de-ionized water.

carrier gas. The analysis method used in all cases was 5 μL inj. of sample, inj. temp of 225 ºC, 25:1 split ratio, initial inlet pressure was 7.8 psi, but varied as the column flow was held constant at 1.0 mL/min for the duration of the run, the interface temperature was held at 250 ºC, and the ion source (EI, 30 eV) was held at 250 ºC. Initial oven temperature was held at 50 ºC for 3 min with the detector off followed by a temperature ramp, with the detector on, to 280 ºC at 40 ºC/min, and finally the temperature was held at 280 ºC for 3 min. Total run time was 11.75 min.

Chromatography was performed on silica gel (EMD, silica gel 60, particle size 0.040-0.063 mm) using standard flash techniques or on a Teledyne Isco Rf-200 (detection at 254 nm and 280 nm; or at 210 nm when ether or acetone was used as eluent.). Products were visualized by one of the following methods: UV stain, ninhydrin stain, $KMnO_4$ stain or by GC.

Elemental Analysis.

Elemental analyses were performed by CENTC Elemental Analysis Facility at University of Rochester, funded by NSF CHE-0650456.

High Resolution Mass Spectrometry.

High resolution mass spectra (HRMS) under electron spray ionization (+ ion mode) were obtained on a Micromass 70-VSE instrument at the University of Illinois Mass Spectrometry Lab.

LC/MS Analysis

LC/MS analyses were performed on a Shimadzu LCMS-2010A equipped with an ESI probe with a quadrupole mass analyzer. Direct injection analysis was employed in all cases with 5 μL of sample solution in methanol. The ion source (ESI) was held at 250 ºC, sample flow rate at 1mL/min.

IV. General Reaction Procedures

General procedure A for Ni/iodide catalyzed epoxide ring opening reactions

Glovebox procedure: To an oven-dried 1-dram vial containing a teflon-coated stir-bar was sequentially added: triethylamine hydrohalide (69 mg, 0.5 mmol), Zn^0 dust (65 mg, 1 mmol), nickel pre-catalyst (20 mg of $NiI_2 \cdot 3.9H_2O$ or 16 mg of NiI_2 0.05 mmol), bipyridine ligand (8 mg, 0.05 mmol), sodium iodide (20 mg, 0.125 mmol), DMPU (3 mL), pyridine (10 μL, 0.1 mmol), dodecane (if used, 10 μL as internal standard), organohalide (0.5 mmol), and epoxide (0.5 mmol). The reaction vials were capped with a PTFE-faced silicone septum, removed from the glove box, and stirred (800 RPM) in a reaction block on the benchtop at room temperature.

Benchtop procedure: To an oven-dried 1-dram vial containing a teflon-coated stir-bar was sequentially added: triethylamine hydrohalide (0.5 mmol), Zn^0 dust (65 mg, 1 mmol), nickel pre-catalyst (20 mg of $NiI_2 \cdot 3.9H_2O$), bipyridine ligand (8 mg, 0.05 mmol), sodium iodide (20 mg, 0.125 mmol), DMPU (3 mL), pyridine (10 μL, 0.1 mmol), organohalide (0.5 mmol), and epoxide (0.5 mmol). The reaction vials were capped with a PTFE-faced silicone septum, and the head space of the vial was purged vigorously with nitrogen gas for one minute, then stirred (800 RPM) in a reaction block on the benchtop at room temperature. Comparable yield was obtained for 1-phenylpropan-2-ol (*vide infra*).

General procedure B for Ni/Ti catalyzed epoxide ring opening reactions

Reactions were set up in a nitrogen filled glove box.[14] To an oven-dried 1-dram vial containing a teflon-coated stir-bar was added. The ingredients of the reaction were added to the vial in the following order: triethylamine hydrohalide (0.5 mmol), Mn^0 (55 mg, 1 mmol), nickel catalyst (11 mg of $NiCl_2 \cdot (DME)_{0.97}$, 0.05 mmol), bipyridine ligand (8 mg, 0.05 mmol), titanocene dichloride (13 mg, 0.05 mmol), DMPU (3 mL), dodecane (if used, 10 μL as internal standard), organohalide (0.5 mmol), and epoxide (0.5 mmol). The reaction vials were capped with a PTFE-faced silicone septum, removed from the glove box and stirred in a reaction block on the benchtop at room temperature. After 2 hours, under the protection of nitrogen, 5 mg (4 mol%) of Cp_2TiCl_2 was added. The reaction was allowed to react for another 3 to 10 hours before workup.

[14] While some success was observed in reactions set up on a vacuum line using a reaction ampule (60% yield in one case), lower yields were obtained in several cases (10-20% yield). The side-products obtained appear to indicate that the titanium catalyst is poisoned by H_2O or O_2 because we observe complete consumption of the aryl bromide but incomplete conversion of the epoxide.

GC analysis

After 12-24 h reaction time, 100 μL aliquots of the reaction mixture were removed with a 500 μL gas-tight syringe and quenched with 200 μL of 0.1 M pH 8 phosphate buffer,[13] diluted with ethyl ether (1 mL), and filtered through a short celite pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography and percent yield was calculated vs. the internal standard.

Isolation and purification

After 12-24 h reaction time, the reaction mixture was poured into 50 mL of 0.1 M pH 8 phosphate buffer.[13] This aqueous mixture was then extracted with diethyl ether (3 × 50 mL). The organic layers were combined, washed with 50 mL of brine, and dried over anhydrous Na_2SO_4. After decantation of the organic layer, volatile materials were removed on a rotary evaporator. The crude product was purified by flash chromatography on silica gel to afford the pure product.

Purification procedure for products contaminated with 1,3,5-trimethyl-1,3,5-triazine-2,4,6-(1H,3H,5H)trione

In some cases 1,3,5-trimethyl-1,3,5-triazine-2,4,6-(1H,3H,5H)trione [CAS: 827-16-7] was observed as a contaminant,[15] which proved difficult to separate by column chromatography. In these examples, acidic washes were found to be capable of removing this impurity effectively. After extraction with diethyl ether, the organic layers were combined, rinsed with 1 M $NaHSO_4$ (2 × 50 mL), phosphate buffer (20 mL of 0.1 M pH 8 phosphate buffer[16]), and dried over anhydrous Na_2SO_4. No significant loss of the product was observed with this alternative workup procedure.

Purification procedure for removal of small amounts of primary alcohol products

The secondary alcohol products of terminal attack (**2**) were sometimes difficult to separate from the primary alcohol products of internal attack (**3**) even though the amount of primary alcohol was very low. In order to obtain pure linear product, it was occasionally necessary to selectively silylate **3**. After the mixture of isomers was obtained from column chromatography, it was dissolved in 1 mL of N,N'-dimethylformamide before 10 mg of tert-butylchlorodimethylsilane, 5 mg of imidazole, and 1 mg of dimethylaminopyridine were added[17]. This mixture was stirred for 12 hours before it was purified on a column to produce the pure linear product.

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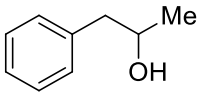
[15] Everson, D. A.; George, D. T.; Weix, D. J.; Buergler, J. F.; Wood, J. L., *Org. Synth.* **2013**, *90*, 200-214.
[16] Rinsing with buffer was necessary to prevent some products from undergoing Wagner-Meerwein rearrangement at acidic condition during subsequent rotovapping. For preparation of this buffer, see ref. 12.
[17] Aladro, F. J.; Guerra, F. M.; Moreno-Dorado, F. J.; Bustamante, J. M.; Jorge, Z. D.; Massanet, G. M. *Tetrahedron Lett.* **2000**, *41*, 3209-3214

V. Product Characterization



1-phenylpropan-2-ol (2aa) (table 3, entry 1) [CAS: 698-87-3].[18] General procedure A was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 12 hours. After removal of the triazine impurity following the general procedure, the product was isolated by flash column chromatography (5:1 hexane/diethyl ether) as colorless oil in 87% yield (60 mg) or 86% yield (59 mg) when (*R*)-(+)-propylene oxide was used. Characterization data matched those reported in the literature. The same reaction set up according to the benchtop procedure yielded 59 mg (86%) of purified product.

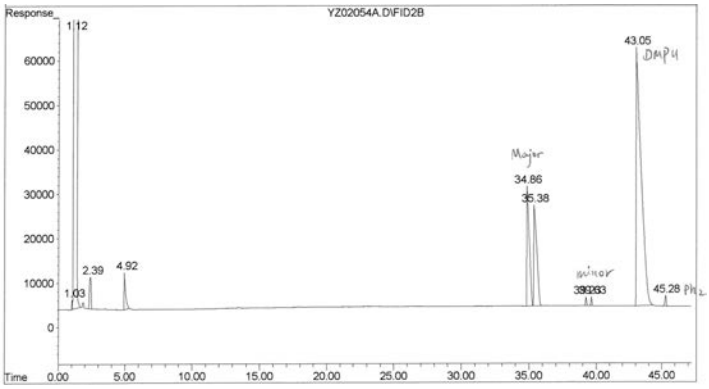
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 2H), 7.22 (m, 3H), 4.01 (sextet, J = 6.6 Hz, 1H), 2.78 (dd, J = 13.4, 4.9 Hz, 1H), 2.69 (dd, J = 13.4, 7.9 Hz, 1H), 1.71 (s, 1H), 1.24 (d, J = 6.2 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 138.6, 129.4, 128.6, 126.5, 68.9, 45.8, 22.8.

GC-MS m/z (% relative intensity, ion): 136.10 (4.89, M^+), 121.05 (5.02, M^+-CH_3), 92.00 (100.0, M^+-C_2H_4O), 91.00 (64.83, M^+-C_2H_5O), 77 (3.24, M^+-C_3H_6O).

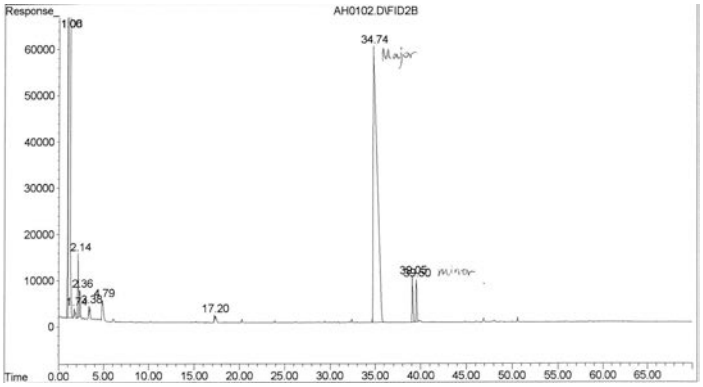
(*R*)-1-phenylpropan-2-ol (2aj) (table 3, entry 1) [CAS: 1572-95-8].

Run as above, but with (*R*)-(+)-propylene oxide (**1j**). The product **2aj** (major) was isolated in 86% yield (59 mg) and was determined to have a 99.0% *ee*, while product **3aj** (minor) had a 0.7% *ee* by chiral-phase GC analysis: $t_{2aj\text{-}R}$ = 34.9 min (99 %), $t_{2aj\text{-}S}$ = 35.4 min (ND); $t_{3aj\text{-}a}$ = 39.1 min (50.3%), $t_{3aj\text{-}b}$ = 39.5 min (49.7%). Configuration of the major product was assigned as (*R*)-1-phenylpropan-2-ol based upon the mechanism of epoxide opening.

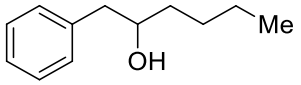


Reaction with racemic epoxide **1a** to form **2aa** (racemate of **2aj**). Major = **2aa/2aj**, Minor = **3aa/3aj**.

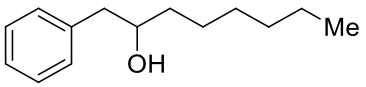
[18] Vitale, P.; Perna, F. M.; Perrone, M. G.; Scilimati, A. *Tetrahedron: Asymmetry* **2011**, *22*, 1985-1993



Reaction with enantiopure epoxide **1j** to form **2aj** and **3aj**. Major = **2aj**, Minor = **3aj**.



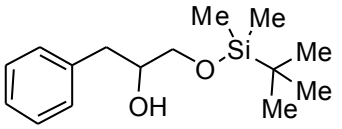
1-phenylhexan-2-ol (2ab) (scheme 2) [CAS: 25755-72-0].[19] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and 1,2-epoxyhexane (60 mg, 0.5 mmol, 1.00 equiv) at room temperature for 12 hours. After removal of the triazine impurity following the general procedure, the product was isolated by flash column chromatography (5:1 hexane/diethyl ether) as colorless oil in 76% yield (68 mg). NMR data suggested a mixture of linear (66%) and branched isomers (10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (m, 2H), 7.23 (m, 2H), 3.81 (m, 1H), 2.83 (dd, J = 13.5, 4.2 Hz, 1H), 2.64 (dd, J = 13.5, 8.4 Hz, 1H), 1.50 (m, 3H), 1.34 (m, 3H), 0.91 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz; $CDCl_3$): δ 138.7, 129.4, 128.6, 126.4, 72.7, 44.1, 36.5, 28.0, 22.7, 14.1. GC-MS m/z (% relative intensity, ion): 178.15 (0.42, M^+), 121.05 (4.66, M^+-C_4H_9), 92.00 (100.00, M^+-$C_5H_{11}O$), 77.00 (1.97, M^+-$C_6H_{13}O$).



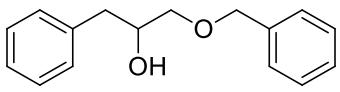
1-phenyloctan-2-ol (2ac) (scheme 2) [CAS: 19396-72-6][20]**.** General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and 1,2-epoxyhexane (64 mg, 0.5 mmol, 1.00 equiv) at room temperature for 12 hours. After removal of the triazine impurity following the general procedure, the product was isolated by flash column chromatography (5:1 hexane/diethyl ether) as colorless oil in 82% yield (85 mg). NMR data matched those reported in the literature.

[19] Blakemore, P. R.; Marsden, S. P.; Vater, H. D. *Org.Lett.* **2006**, *8*, 773-776
[20] Melhado, A. D.; Brenzovich, W. E.; Lackner, A. D.; Toste, F. D. *J. Am. Chem. Soc*. **2010**, *132*, 8885-8887

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 2H), 7.23 (m, 3H), 3.86 – 3.75 (m, 1H), 2.83 (dd, *J* = 13.5, 4.2 Hz, 2H), 2.64 (dd, *J* = 13.5, 8.4 Hz, 2H), 1.55 – 1.42 (m, 3H), 1.22 – 1.42 (m, 6H), 0.89 (t, *J* = 6.5 Hz, 3H).
^{13}C NMR (101 MHz; $CDCl_3$): δ 138.7 129.4, 128.6, 126.4, 72.7, 44.1, 36.9, 31.9, 29.3, 25.8, 22.6, 14.1.
GC-MS m/z (% relative intensity, ion): 206.05 (0.32, M^+), 176.05 (0.34, M^+-C_2H_6), 92 (100.00, $C_7H_8^+$).



1-((*tert*-butyldimethylsilyl)oxy)-3-phenylpropan-2-ol (2ag) (scheme 2) [CAS: 173917-45-8].[21] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and *tert*-butyldimethyl(oxiran-2-ylmethoxy)silane (94 mg, 0.5 mmol, 1.00 equiv) at room temperature for 12 hours. After removal of the triazine impurity following the general procedure, the product was isolated by flash column chromatography (5:1 hexane/diethyl ether) as colorless oil in 79% yield (105 mg). NMR data matched those reported in the literature.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 2H), 7.21 (m, 3H), 3.88 (m, 1H), 3.61 (dd, *J* = 10.0, 3.8 Hz, 1H), 3.48 (dd, *J* = 10.0, 6.5 Hz, 1H), 2.78 (d, *J* = 6.6 Hz, 2H), 2.46 (d, *J* = 4.0 Hz, 1H), 0.91 (s, 9H), 0.07 (s, 3H), 0.07 (s, 3H).
^{13}C NMR (101 MHz; $CDCl_3$): δ 138.3, 129.3, 128.4, 126.4, 72.8, 66.2, 39.6, 25.9, 18.3, 5.34.
LRMS (ESI+) m/z (% relative intensity, ion): 289.10 (97.23, M+Na^+), 267.15 (53.49, M+H^+).



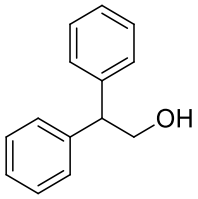
1-(benzyloxy)-3-phenylpropan-2-ol (2ad) (scheme 2) [CAS: 173917-50-5]. [22] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and *2*-((benzyloxy)methyl)oxirane (82 mg, 0.5 mmol, 1.00 equiv) at room temperature for 12 hours. After removal of the triazine impurity following the general procedure, the product was isolated by flash column chromatography (5:1 hexane/diethyl ether) as colorless oil in 64% yield (77 mg). NMR data matched those reported in the literature.

[21] Poppe, L.; Recseg, K.; Novak, L. *Synth. Commun*. **1995**, *25*, 3993-4000
[22] Fessard, T. C.; Motoyoshi, H.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2007**, *46*, 2078-2081

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 7H), 7.24 (m, 3H), 4.56 (s, 2H), 4.07 (m, 1H), 3.52 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.42 (dd, *J* = 9.4, 7.0 Hz, 1H), 2.82 (d, *J* = 6.7 Hz, 2H), 2.46 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 138.0, 137.9, 129.4, 128.5, 127.8, 126.5, 73.6, 73.4, 71.5, 39.9.

GC-MS m/z (% relative intensity, ion): 242.05 (2.08, M^+), 151.10 (5.38, M^+-C_7H_7), 121.05 (33.57, M^+-C_8H_9O), 90.95 (100.00, M^+-$C_9H_{11}O_2$).

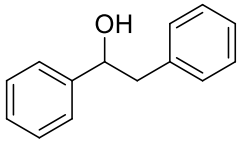


2,2-diphenylethanol (3ae) (scheme 2) [CAS: 1883-32-5].[23] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and styrene oxide (50 mg, 0.5 mmol, 1.00 equiv) at room temperature for 12 hours. After removal of the triazine impurity following the general procedure, the product was isolated by flash column chromatography (5:1 hexane/diethyl ether) as white solid in 55% yield (54 mg). NMR data matched those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.12 (m, 10H), 4.19 (m, 3H), 1.59 (s, 1H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 141.4, 128.7, 128.3 126.9, 66.2, 53.6.

GC-MS m/z (% relative intensity, ion): 198.10 (5.69, M^+), 167.15 (100.00, M^+-CH_3O), 152.10 (30.74, M^+-C_4H_4O).



1,2-diphenylethanol (2ae) (scheme 2, footnote b) [CAS: 5773-56-8].[24] The product of linear attack was also isolated from the above reaction as white solid in 14% yield (14 mg). NMR data matched those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.15 (m, 10H), 4.90 (ddd, *J* = 8.1, 4.9, 3.0 Hz, 1H), 3.05 (dd, *J* = 13.7, 5.0 Hz, 1H), 3.00 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.03 (d, *J* = 2.9 Hz, 1H).

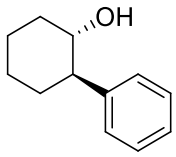
^{13}C NMR (101 MHz; $CDCl_3$): δ 143.8, 138.1, 129.6, 128.5, 128.4, 127.6, 126.7, 125.9, 75.4, 46.1.

GC-MS m/z (% relative intensity, ion): 198.10 (0.88, M^+), 107.00 (80.37, M^+-C_7H_7), 92.05 (M^+-

[23] Gomez, C.; Macia, B.; Lillo, V. J.; Yus, M. *Tetrahedron* **2006**, *62*, 9832-9839

[24] Lewis, F. W.; McCabe, T. C.; Grayson, D. H. *Tetrahedron* **2011**, *67*, 7517-7528

C_7H_6O), 79.00 (65.42, M^+-C_8H_7O), 77.00 (29.33, M^+-C_8H_9O).

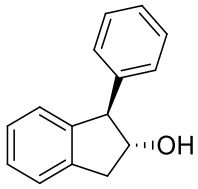


***trans*-2-phenylcyclohexanol (2af) (scheme 2, and eq. 2) [CAS: 2362-61-0].**[25] General procedure (Ni/Iodide or Ni/Titanium) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and cyclohexene oxide (60 mg, 0.5 mmol, 1.00 equiv) at room temperature for 12 hours. The product was isolated by flash column chromatography (2:1 hexane/diethyl ether) as white crystals in 61% yield (54 mg) for Ni/Iodide condition or 75% yield (66 mg) for Ni/Titanium condition. NMR data matched those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.29 (m, 2H), 7.29 – 7.13 (m, 3H), 3.70 – 3.60 (m, 1H), 2.48 – 2.35 (m, 1H), 2.17 – 2.05 (m, 1H), 1.91 – 1.79 (m, 2H), 1.79 – 1.69 (m, 1H), 1.62 – 1.23 (m, 5H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 143.27, 128.8, 127.9, 126.8, 74.5, 74.4, 53.2, 34.4, 33.3, 26.1, 25.1.

GC-MS m/z (% relative intensity, ion): 176.15 (63.36, M^+), 130.10 (100.00, M^+-C_2H_6O), 117.05 (60.70, M^+-C_3H_7O), 104.05 (50.36, M^+-C_4H_8O), 91.00 (91.89, M^+-C_5H_9O).



***trans*-2-hydroxy-1-phenylindane (3al) (scheme 2) [CAS: 81707-26-8].**[26] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and 2,3-dihydro-1H-indene 2,3-oxide (105 mg, 0.5 mmol, 1.00 equiv) at room temperature for 12 hours. The product was isolated by flash column chromatography (1:1 hexane/diethyl ether) as light yellow oil in 50% yield (53 mg). ^{1}H-NMR data matched those reported in the literature. ^{13}C-NMR was obtained for the first time.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.12 (m, 9H), 6.95 (d, J = 7.4 Hz, 1H), 4.50 (s, 1H), 4.19 (br, 1H), 3.32 (dd, J = 15.6, 6.9 Hz, 1H), 2.97 (dd, J = 15.6, 7.4 Hz, 1H), 2.02 (br, 1H).

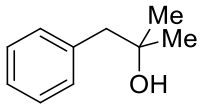
^{13}C NMR (101 MHz; $CDCl_3$): δ 143.5, 141.8, 140.4, 128.7, 128.5, 127.3, 127.1, 126.9, 125.2,

[25] Boyd, D. R.; Sharma, N. D.; Berberian, M. V.; Hardacre, C.; Kaik, M.; Malone, J. F.; McGregor, S. T.; Stevenson, P. J.; Dunne, K. S.; Kelly, B. *Adv. Synth. Catal*. **2010**, *352*, 855-868

[26] Laus, G.; Tourwe, D.; Binst, G. V. *Heterocycles*, **1984**, *22*, 311-331

124.7, 82.3, 60.3, 40.1.

GC-MS m/z (% relative intensity, ion): 210.05 (100.00, M^+), 192.10 (92.52, M^+-H_2O), 181.10 (58.27, M^+-CHO), 165.10 (63.86, M^+-C_2H_5O), 91.00 (41.32, $C_7H_7^+$).

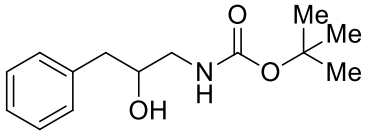


2-methyl-1-phenylpropan-2-ol (2ai) (scheme 2) [CAS: 100-86-7]. [27] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and isobutene oxide (40 mg, 0.56 mmol, 1.11 equiv) at room temperature for 12 hours. The TLC spot of this product was not visible under UV at either 254 nm or 280 nm. No suitable stain was found either. Successful isolation was achieved with a Teledyne Isco Rf-200 device when UV detection was set at 210 nm and 10/1 hexane/acetone was used as eluent. Isolated yield: 65% (49 mg). NMR data matched those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.05 (m, 5H), 2.76 (s, 2H), 1.23 (s, 6H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 137.7, 130.5, 128.2, 126.5, 70.8, 49.7, 29.2.

GC-MS m/z (% relative intensity, ion): 150.15 (1.15, M^+), 135.10 (25.86, M^+-CH_3), 92.05 (100.00, M^+-C_3H_6O), 59.00 (86.45, M^+-C_7H_7).



***tert*-butyl (2-hydroxy-3-phenylpropyl)carbamate (2ah) (scheme 2) [CAS: 162541-45-9].**[28] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and *tert*-butyl (oxiran-2-ylmethyl)carbamate (87 mg, 0.5 mmol, 1.00 equiv) at room temperature for 12 hours. The product was isolated by flash column chromatography (1:1 hexane/ethyl acetate) as colorless oil in 60% yield (75 mg). NMR data matched those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.13 (m, 5H), 5.01 (br, 1H), 3.90 (m, 1H), 3.34 (s, 2H), 3.05 (m, 1H), 2.81 – 2.64 (m, 3H), 1.43 (s, 9H).

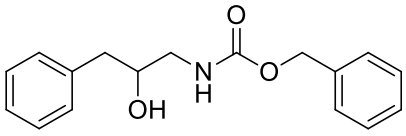
^{13}C NMR (101 MHz; $CDCl_3$): δ 156.8, 137.7, 129.4, 128.6, 126.6, 79.7, 72.4, 45.9, 41.3, 28.4.

GC-MS m/z (% relative intensity, ion): 177.10 (17.98, M^+-$OC(CH_3)_3$), 160.10 (16.74, M^+-$PhCH_2$), 116.05 (42.36, M^+-$PhCH_2CHOH$), 104.00 (71.03, $PhCHCH_2^+$), 91.00 (23.19, $C_7H_7^+$),

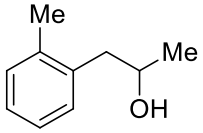
[27] Fernandez-Mateos, A.; Madrazo, S. E.; Teijon, P. H.; Gonzalez, R. R. *J. Org. Chem*. **2009**, *74*, 3913-3918

[28] Moree, W. J.; Marel, G. A.; Liskamp, R. J. *J. Org. Chem*. **1995**, *60*, 5157-5169

75.00 (41.02, $(CH_3)_3COH_2^+$), 57.00 (100.00, $(CH_3)_3C^+$).
LRMS (ESI+) m/z (% relative intensity, ion): 274.10 (56.63, M+Na^+), 196.00 (100.00, M-^{t}BuO+H_2O).



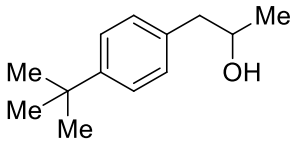
benzyl (2-hydroxy-3-phenylpropyl)carbamate (2ak) (scheme 2) [No CAS number].[29] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and benzyl (oxiran-2-ylmethyl)carbamate (104 mg, 0.5 mmol, 1.00 equiv) at room temperature for 12 hours. 60 mg of the pure product was isolated by flash column chromatography (1:1 hexane/ethyl acetate) as colorless oil in 42% yield (about 10% 5-benzyloxazolidin-2-one was also observed but not isolated). The spectra of the product matched with published ones.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.08 (m, 10H), 5.26 (s, 1H), 5.10 (s, 2H), 4.02 – 3.81 (m, 1H), 3.51 – 3.37 (m, 1H), 3.20 – 3.05 (m, 1H), 2.80 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.67 (dd, *J* = 26.8, 13.1 Hz, 1H), 2.41 (d, *J* = 3.1 Hz, 1H).
^{13}C NMR (101 MHz; $CDCl_3$): δ 157.1, 137.5, 136.4, 129.4, 128.7, 128.6, 128.2, 128.1, 126.7, 72.1, 66.9, 46.3, 41.2.
GC-MS m/z (% relative intensity, ion): 177.10 (14.53, M^+-OCH_2Ph), 108.05 (43.07, $PhCH_2OH^+$), 92.00 (100.00, $C_7H_8^+$).
LRMS (ESI+) m/z (% relative intensity, ion): 308.10 (100.00, M+Na^+), 286.10 (61.66, M+H^+).



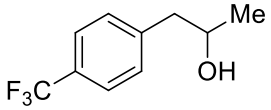
1-(o-tolyl)propan-2-ol (2ja) (table 3, entry 10) [CAS: 50354-46-6].[30] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), *ortho*-bromotoluene (86 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 12 hours. After removal of the triazine impurity following the general procedure, the product was isolated by flash column chromatography (5:1 hexane/diethyl ether) as colorless oil in 99% yield (74 mg). NMR data matched those reported in the literature.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 – 7.03 (m, 4H), 4.07 – 3.94 (m, 1H), 2.80 (dd, *J* = 13.7, 5.0 Hz, 1H), 2.73 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.33 (s, 3H), 1.65 (s, 1H), 1.27 (d, *J* = 6.1 Hz, 3H).

[29] Hirschhaeuser, C.; Haddow, M. F.; Gallagher, T.; Parker, J. S.; Perry, M. W. D. *Org. Lett*. **2012**, *14*, 4846-4849
[30] Liu, C.; Kelly, G. T.; Watanabe, C. M. H. *Org. Lett*. **2006**, *8*, 1065-1068

^{13}C NMR (101 MHz; $CDCl_3$): δ 136.8, 136.7, 130.5, 130.2, 126.6, 126.0, 67.9, 42.9, 22.9, 19.7.
GC-MS m/z (% relative intensity, ion): 150.10 (6.04, M^+), 135.10 (4.21, M^+-CH_3), 106.05 (100.00, M^+-C_2H_4O), 91.00 (74.28, $C_7H_7^+$).



1-(4-(*tert*-butyl)phenyl)propan-2-ol. (2da) (table 3, entry 4) General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), 1-bromo-4-(*tert*-butyl)benzene (107 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 12 hours. After removal of the triazine impurity following the general procedure, the product was isolated by flash column chromatography (5:1 hexane/diethyl ether) as colorless oil in 72% yield (69 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 4.01 (m, 1H), 2.77 (dd, J = 13.5, 4.6 Hz, 1H), 2.65 (dd, J = 13.5, 8.1 Hz, 1H), 1.60 (s, 1H), 1.31 (s, 9H), 1.25 (d, J = 6.2 Hz, 3H).
^{13}C NMR (101 MHz; $CDCl_3$): δ 149.3, 135.4, 129.1, 125.5, 68.9, 45.3, 34.4, 31.4, 22.8.
GC-MS m/z (% relative intensity, ion): 192.15 (5.74, M^+), 148.15 (34.76, M^+-C_2H_4O), 132.95 (100.00, M^+-C_3H_7O), 57.00 (38.72, $(CH_3)_3C^+$).
HRMS (ESI+): [M+Na^+] calcd for $C_{13}H_{20}ONa$ 215.1412, found 215.1419.
IR (cm^{-1}): 3371 (OH, strong), 2962, 2931, 2904, 2870 (CH, strong), 1512, 1458 (C=C, medium).



1-(4-(trifluoromethyl)phenyl)propan-2-ol. (2ea) (table 3, entry 5) General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), 1-bromo-4-(trifluoromethyl)benzene (113 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 12 hours. After removal of the triazine impurity following the general procedure, the product was isolated by flash column chromatography (2:1 hexane/ethyl acetate) as a mixture of regioisomers. The primary alcohol **3** was selectively silylated and the linear product was isolated by flash column chromatography (2:1 hexane/ethyl acetate) to give the title product as colorless oil in 79% yield (81 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 4.05 (m, 1H), 2.82 (t, J = 6.8 Hz, 1H), 2.76 (dd, J = 13.5, 7.7 Hz, 1H), 1.53 (s, 1H), 1.25 (d, J = 6.2 Hz, 3H).
^{13}C NMR (101 MHz; $CDCl_3$): δ 142.8, 129.7, 128.8 (q, J = 132 Hz), 125.4, 122.9, 68.7, 45.4,

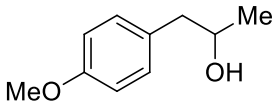
23.1

^{19}F NMR (375 MHz, $CDCl_3$, calibrated with CF_3Ph as standard): δ -0.03.

GC-MS m/z (% relative intensity, ion): 204.05 (0.12, M^+), 203.05 (0.39, M^+-H), 189.10 (1.91, M^+-CH_3), 160.10 (2.99, M^+-C_2H_4O), 140.05 (100.00, M^+-C_2H_5FO).

Anal. Calcd for $C_{10}H_{11}F_3O$: C 58.82%, H 5.43%. Found: C 58.89%, H 5.59%.

IR (cm^{-1}): 3356 (O-H, strong), 2970, 2928, 2854 (C-H, medium), 1458, 1419 (C=C, weak), 1323 (C-F, strong).

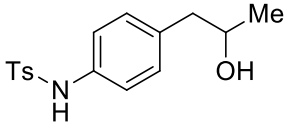


1-(4-methoxyphenyl)propan-2-ol (2ba) (table 3, entry 2) [CAS: 131029-01-1].[31] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), 1-bromo-4-methoxybenzene (94 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 12 hours. The product was isolated by flash column chromatography (3:1 hexane/ethyl acetate) as colorless oil in 83% yield (69 mg). NMR data matched those reported in the literature.

^1H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.95 (dd, *J* = 12.3, 6.2 Hz, 1H), 3.78 (s, 3H), 2.72 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.61 (dd, *J* = 13.6, 7.9 Hz, 1H), 1.68 (s, 1H), 1.22 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 158.3, 130.5, 130.4, 113.9, 68.9, 55.3, 44.8, 22.7.

GC-MS m/z (% relative intensity, ion): 166.15 (18.05, M^+), 121.05 (100.00, M^+-C_2H_5O), 107.00 (16.34, M^+-C_3H_7O).

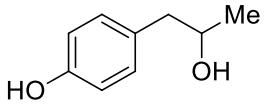


N-(4-(2-hydroxypropyl)phenyl)-4-methylbenzenesulfonamide. (2ca) (table 3, entry 3) General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), N-(4-bromophenyl)-4-methylbenzenesulfonamide (163 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 12 hours. The product was isolated by flash column chromatography (1:1 hexane/ethyl acetate) as viscous colorless oil in 84% yield (128 mg).

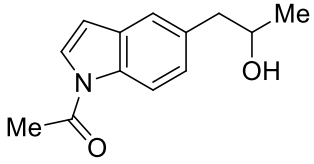
^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.55 (s, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.01 (q, *J* = 8.5 Hz, 4H), 3.93 (dd, *J* = 12.5, 6.2 Hz, 1H), 2.66 (dd, *J* = 13.6, 5.1 Hz, 1H), 2.59

[31] Tauber, K.; Fuchs, M.; Sattler, J. H.; Pitzer, J.; Pressnitz, D.; Koszelewski, D.; Faber, K.; Kroutil, W.; Pfeffer, J.; Haas, T. *Chem. Eur. J.* **2013**, *19*, 4030-4035

(dd, J = 13.6, 7.7 Hz, 1H), 2.33 (s, 3H), 1.88 (s, 1H), 1.16 (d, J = 6.2 Hz, 3H).
^{13}C NMR (101 MHz; $CDCl_3$): δ 143.8, 136.1, 135.5, 135.0, 130.2, 129.6, 127.3, 121.8, 68.8, 44.9, 22.8, 21.5.
LRMS (ESI+) m/z (% relative intensity, ion): 306.00 (13.14, $M+H^+$), 323.00 (100.00, M^++H_2O), 328.00 (59.89, $M+Na^+$).
HRMS (ESI+): [$M+H^+$] calcd for $C_{16}H_{20}NO_3S$ 306.1164, found 306.1170.
IR (cm^{-1}): 3402, 3255 (OH and NH, medium), 2966, 2924, 2870 (CH, medium), 1153 (S=O, strong), 1512, 1454 (C=C, medium).



4-(2-hydroxypropyl)phenol (2ia) (table 3, entry 9) [CAS: 22805-43-2].[32] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), 4-bromophenol (87 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 24 hours. The product was isolated by flash column chromatography (1:1 hexane/ethyl acetate) as white solid in 58% yield (44 mg). NMR data suggested a mixture of linear (53%) and branched (5%) isomers.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, J = 8.4 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 5.87 (s, 1H), 3.98 (d, J = 6.4 Hz, 1H), 2.72 (dd, J = 13.7, 4.6 Hz, 1H), 2.59 (dd, J = 13.7, 8.1 Hz, 1H), 1.81 (s, 1H), 1.24 (d, J = 6.2 Hz, 2H).
^{13}C NMR (101 MHz; $CDCl_3$): δ 154.5, 130.5, 130.1, 115.5, 6.2, 44.7, 22.6.
GC-MS m/z (% relative intensity, ion): 152.10 (18.05, M^+), 133.10 (7.64, M^+-H_2O-H), 108.00 (100.00, M^+-C_2H_4O).



1-(5-(2-hydroxypropyl)-1H-indol-1-yl)ethanone. (2ka) (table 3, entry 11) General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), 1-(5-bromo-1H-indol-1-yl)ethanone (119 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 12 hours. The product was isolated by flash column chromatography (1:1 hexane/ethyl acetate) as a mixture of regioisomers. The primary alcohol **3** was selectively silylated and the linear product was isolated by flash column

[32] Barradas, S.; Carreno, M. C.; Gonzalez-Lopez, M.; Latorre, A.; Urbano, A. *Org. Lett*. **2007**, *9*, 5019-5022

chromatography (1:1 hexane/ethyl acetate) to give the title product as slightly yellowish oil in 99% yield (107 mg).

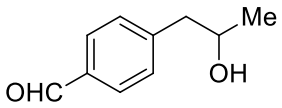
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 1.0 Hz, 2H), 7.19 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.59 (d, *J* = 3.7 Hz, 1H), 4.04 (dd, *J* = 12.7, 6.2 Hz, 1H), 2.87 (dd, *J* = 13.5, 4.8 Hz, 1H), 2.76 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.61 (s, 3H), 1.69 (s, 1H), 1.25 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 168.6, 134.4, 133.9, 130.8, 126.5, 125.6, 121.4, 116.5, 109.0, 69.1, 45.7, 23.9, 22.8.

GC-MS m/z (% relative intensity, ion): 216.95 (16.46, M^+), 173.00 (24.56, M^+-C_2H_4O), 129.95 (100.00, M^+-C_2H_4O-C_2H_3O).

HRMS (ESI+): [M+H^+] calcd for $C_{13}H_{16}NO_2$ 218.1181, found 218.1185.

IR (cm^{-1}): 3402 (OH, strong), 2966, 2928, 2874 (CH, medium), 1697 (C=O, strong), 1465, 1442 (C=C, medium).

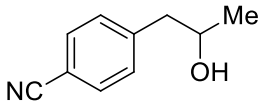


4-(2-hydroxypropyl)benzaldehyde (2ha) (table 3, entry 8) [CAS: 1357255-97-0].[33] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), 4-bromobenzaldehyde (93 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 12 hours. The product was isolated by flash column chromatography (1:1 hexane/ethyl acetate) as a mixture of regioisomers. The primary alcohol **3** was selectively silylated and the linear product was isolated by flash column chromatography (1:1 hexane/ethyl acetate) to give the title product as colorless oil in 62% yield (51 mg). NMR data suggested a mixture of linear (55%) and branched (7%) isomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.12 – 4.02 (m, 1H), 2.85 (dd, *J* = 13.5, 5.1 Hz, 1H), 2.79 (dd, *J* = 13.5, 7.6 Hz, 1H), 1.25 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 192.1, 146.1, 134.9, 68.6, 15.8, 23.2.

GC-MS m/z (% relative intensity, ion): 164.10 (0.17, M^+), 149.10 (0.53, M^+-CH_3), 120.05 (100.00, M^+-C_2H_4O).



4-(2-hydroxypropyl)benzonitrile. (2ga) (table 3, entry 7) General procedure (Ni/Iodide) was

[33] Fujioka, H.; Yahata, K.; Kubo, O.; Sawama, Y.; Hamada, T.; Maegawa, T. *Angew. Chem. Int. Ed.* **2011**, *50*, 12232-12235

followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), 4-bromobenzonitrile (91 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 12 hours. The product was isolated by flash column chromatography (1:1 hexane/ethyl acetate) as a mixture of regioisomers. The primary alcohol **3** was selectively silylated and the linear product was isolated by flash column chromatography (1:1 hexane/ethyl acetate) to give the title product as colorless oil in 55% yield (46 mg).

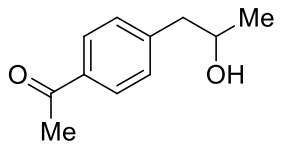
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.09 – 3.98 (m, 1H), 2.82 (dd, *J* = 13.6, 5.0 Hz, 1H), 2.76 (dd, *J* = 13.6, 7.6 Hz, 1H), 1.54 (s, 1H), 1.24 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 144.4, 132.2, 130.2, 118.9, 110.3, 68.5, 45.6, 23.3.

GC-MS m/z (% relative intensity, ion): 161.10 (0.16, M^+), 160.10 (0.31, M^+-H), 146.05 (2.38, M^+-CH_3), 117.00 (100.00, M^+-C_2H_4O).

HRMS (ESI+): [M^+] calcd for $C_{10}H_{12}NO$ 162.0919, found 162.0925.

IR (cm^{-1}): 3433 (OH, strong), 2970, 2928, 2877 (CH, medium), 2225 (CN, strong), 1504, 1453 (C=C, medium).



1-(4-(2-hydroxypropyl)phenyl)ethanone. (2fa) (table 3, entry 6) General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), 1-(4-bromophenyl)ethanone (100 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 12 hours. The product was isolated by flash column chromatography (1:1 hexane/ethyl acetate) as a mixture of regioisomers. The primary alcohol **3** was selectively silylated and the linear product was isolated by flash column chromatography (1:1 hexane/ethyl acetate) to give the title product as colorless oil in 84% yield (76 mg).

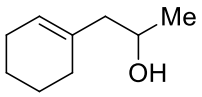
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.05 (m, 1H), 2.82 (dd, *J* = 13.5, 5.1 Hz, 1H), 2.77 (dd, *J* = 13.4, 7.6 Hz, 1H), 2.57 (s, 3H), 1.62 (d, *J* = 3.7 Hz, 1H), 1.24 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 197.8, 144.4, 135.5, 129.6, 128.6, 68.7, 45.6, 26.6.

GC-MS m/z (% relative intensity, ion): 178.10 (0.31, M^+), 163.10 (1.61, M^+-CH_3), 145.05 (0.66, M^+-CH_3OH-H), 134.05 (100.00, M^+-C_2H_4O), 119.00 (26.48, M^+-C_3H_7O).

HRMS (ESI): [M+H^+] calcd for $C_{11}H_{15}O$ 179.1072, found 179.1077.

IR (cm^{-1}): 3417 (O-H, strong), 2966, 2924, 2874 (C-H, medium), 1674 (C=O, strong), 1450, 1415 (C=C, medium).

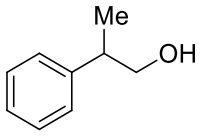


1-(cyclohex-1-en-1-yl)propan-2-ol (2la and 2ma) (table 3, entry 12 and 13) [CAS: 24826-68-4].[34] General procedure (Ni/Iodide) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), cyclohex-1-en-1-yl trifluoromethanesulfonate (115 mg, 0.5 mmol, 1.00 equiv) or 1-bromocyclohex-1-ene (80 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 12 hours. 66 mg of the pure product was isolated by flash column chromatography (5:1 hexane/diethyl ether) as colorless oil in 93% yield. (or 61 mg, 86% yield when 1-bromocyclohex-1-ene was used.). NMR data mostly matched those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.50 (s, 1H), 3.91 – 3.78 (m, 1H), 2.11 – 1.92 (m, 5H), 1.92 – 1.71 (m, 2H), 1.66 – 1.48 (m, 4H), 1.16 (d, J = 6.1 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 134.8, 124.9, 64.9, 48.4, 28.4, 25.3, 22.9, 22.8, 22.3.

GC-MS m/z (% relative intensity, ion): 140.15 (7.10, M^+), 122.10 (27.70, M^+-H_2O), 107.05 (18.56, M^+-CH_3-H_2O), 96.05 (28.01, M^+-C_2H_4O), 81.05 (100.00, M^+-C_3H_6O).



2-phenylpropan-1-ol (3aa) (table 4, entry 1) [CAS: 1123-85-9].[35] General procedure (Ni/Titanium) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 12 hours. A mixture of inseparable linear and branched products (branched/linear = 77:23) was isolated by flash column chromatography (2:1 hexane/diethyl ether) as colorless oil in 70% yield (48 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.07 (m, 5H), 3.70 (d, J = 6.7 Hz, 2H), 2.95 (dd, J = 13.9, 6.9 Hz, 1H), 1.68 (br, 1H), 1.28 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz; CDCl3): δ 143.7, 128.7, 127.5, 126.7, 68.7, 42.4, 17.6.

GC-MS m/z (% relative intensity, ion): 136.10 (23.52, M^+), 105.00 (100.00, M^+-CH_3O), 91.00 (9.91, M^+-C_2H_6O).

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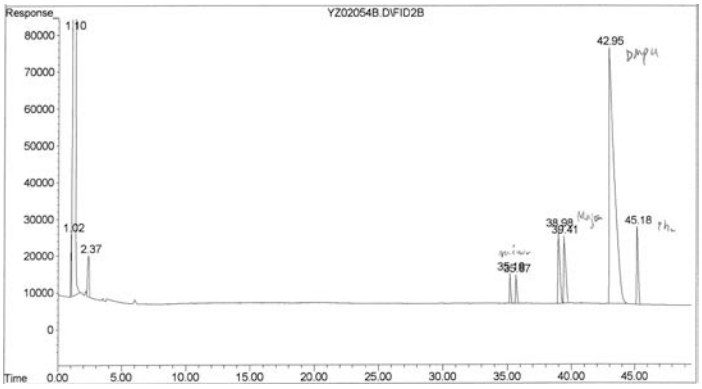
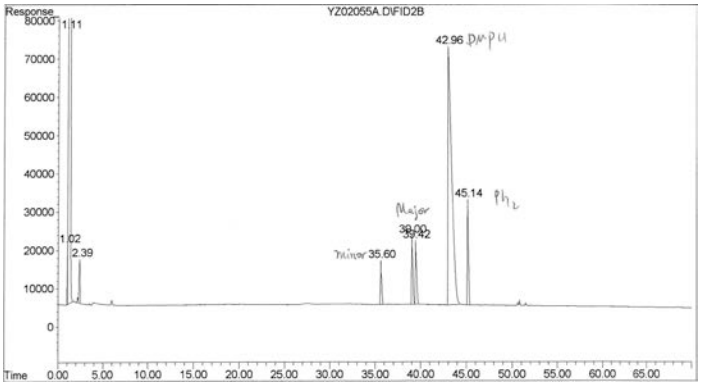
[34] Barluenga, J.; Alvarez, F.; Concellon, J. M.; Bernad, P.; Yus, M. *Synthesis* **1987**, 318-320. ^{1}H-NMR for compound 3e in this paper was taken in CCl_4, while ^{13}C-NMR was taken with neat sample.

[35] Cheung, L. L. W.; Vasapollo, G.; Alper, H. *Adv. Synth. Catal*. **2012**, *354*, 2019-2022

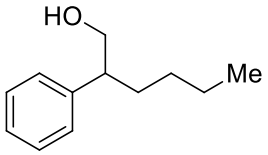
Run as above, but with (*R*)-(+)-propylene oxide (**1j**). The product **3aj** (major) was determined to have a 0.2% *ee*, while product **2aj** (minor) had a 99.0% *ee* by chiral-phase GC analysis: $t_{3aj\text{-}a}$ = 39.0 min (50.1%), $t_{3aj\text{-}b}$ = 39.4 min (49.9%); $t_{2aj\text{-}R}$ = 35.6 min (99%), $t_{2aj\text{-}S}$ = 35.2 min (ND). Configuration of the minor product **2aj** was assigned as (*R*)-1-phenylpropan-2-ol based upon the mechanism of epoxide opening



Reaction with racemic epoxide **1a** to form **3aa** (racemate of **3aj**). Major = **3aa/3aj**, Minor = **2aa/2aj**.



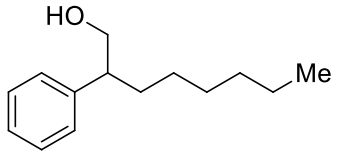
Reaction with enantiopure epoxide **1j** to form **3aj** and **2aj**. Major = **3aj**, Minor = **2aj**.



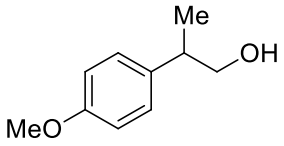
2-phenylhexan-1-ol (3ba) (table 4, entry 2) [CAS: 25755-73-1].[36] General procedure (Ni/Titanium) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and (±)-1,2-epoxyhexane (50 mg, 0.5 mmol, 1 equiv) at room temperature for 12 hours. A mixture of inseparable linear and branched products

[36] Balamurugan, R.; Gudla, V. *Org. Lett.* **2009**, *11*, 3116-3119

(branched/linear = 86:14) was isolated by flash column chromatography (2:1 hexane/diethyl ether) as colorless oil in 54% yield (48 mg). ^{13}C-NMR was obtained for the first time.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 2H), 7.23 (m, 3H), 3.73 (m, 2H), 2.76 (m, 1H), 1.75 – 1.17 (m, approx. 6H), 0.84 (t, J = 6.9 Hz, 3H).
^{13}C NMR (101 MHz; CDCl3): δ 142.6, 128.6, 128.1, 126.7, 67.6, 48.7, 31.8, 29.6, 22.8, 13.9.
GC-MS m/z (% relative intensity, ion): 194.10 (33.40, M^+), 162.95 (100.00, M^+-CH_3), 149.05 (31.13, M^+-C_2H_5), 131.05 (65.48, M^+-C_2H_5-H_2O), 117.05 (17.90, M^+-C_3H_7-H_2O), 105.05 (43.65, M^+-C_4H_9-H_2O), 91.00 (44.06, $C_7H_7^+$).



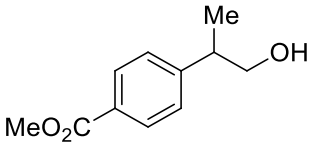
2-phenyloctan-1-ol (3ca) (table 4, entry 3) [CAS: 21078-90-0]. [37] General procedure (Ni/Titanium) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), bromobenzene (80 mg, 0.5 mmol, 1.00 equiv), and (±)-1,2-epoxyoctane (64 mg, 0.5 mmol, 1 equiv) at room temperature for 12 hours. The pure branched product was isolated by flash column chromatography (2:1 hexane/diethyl ether) as colorless oil in 41% yield (42 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J = 7.4 Hz, 2H), 7.27 – 7.13 (m, 3H), 3.73 (qd, J = 10.7, 7.1 Hz, 2H), 2.76 (s, 1H), 1.75 – 1.45 (m, 2H), 1.36 – 1.02 (m, 8H), 0.84 (t, J = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 142.5, 128.6, 128.1, 126.7, 67.7, 48.7, 32.1, 31.7, 29.4, 27.3, 22.6, 14.1.
GC-MS m/z (% relative intensity, ion): 206.10 (8.93, M^+), 175.15 (27.85, M^+-CH_3O), 133.10 (16.19, M^+-C_4H_9O), 119.10 (30.91, M^+-$C_5H_{11}O$), 105.05 (36.04, M^+-$C_6H_{13}O$), 90.95 (100.00, $C_7H_7^+$)



2-(4-methoxyphenyl)propan-1-ol (3ab) (table 4, entry 4) [CAS: 93397-63-8]. [32] General procedure (Ni/Titanium) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), 4-bromoanisole (94 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 5 hours. A mixture of inseparable linear and branched products (branched/linear = 80:20) was isolated by flash column chromatography (3:1 hexane/acetone) as colorless oil in 63% yield (53 mg).

[37] No reliable published NMR spectrum for this compound was found.

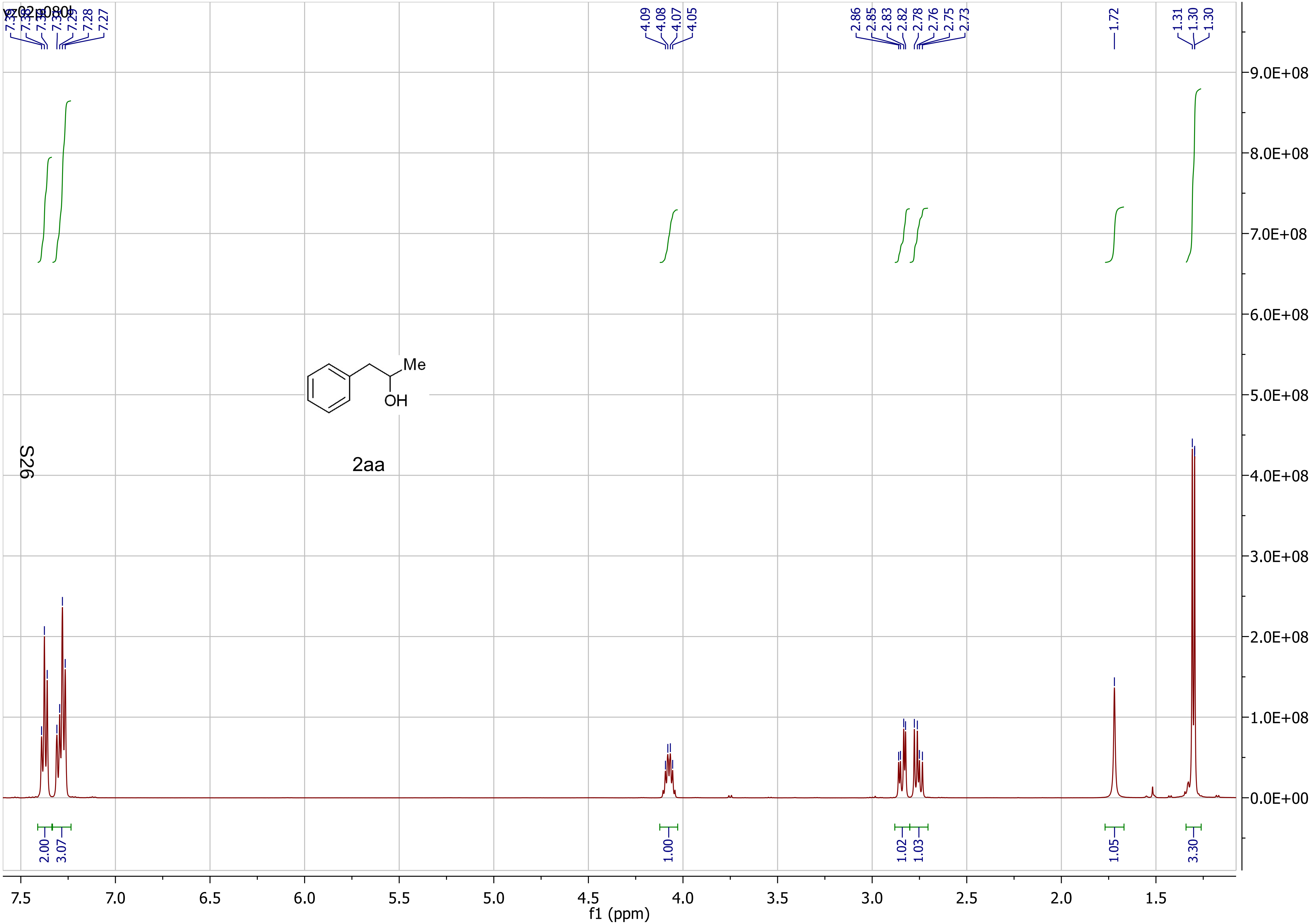
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 3.70 – 3.59 (m, 2H), 2.95 – 2.83 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ158.3, 135.6, 128.4, 114.0, 68.8, 55.27, 41.58, 17.75.
GC-MS m/z (% relative intensity, ion): 166.15 (10.47, M^+), 135.05 (100.00, M^+-CH_3O).

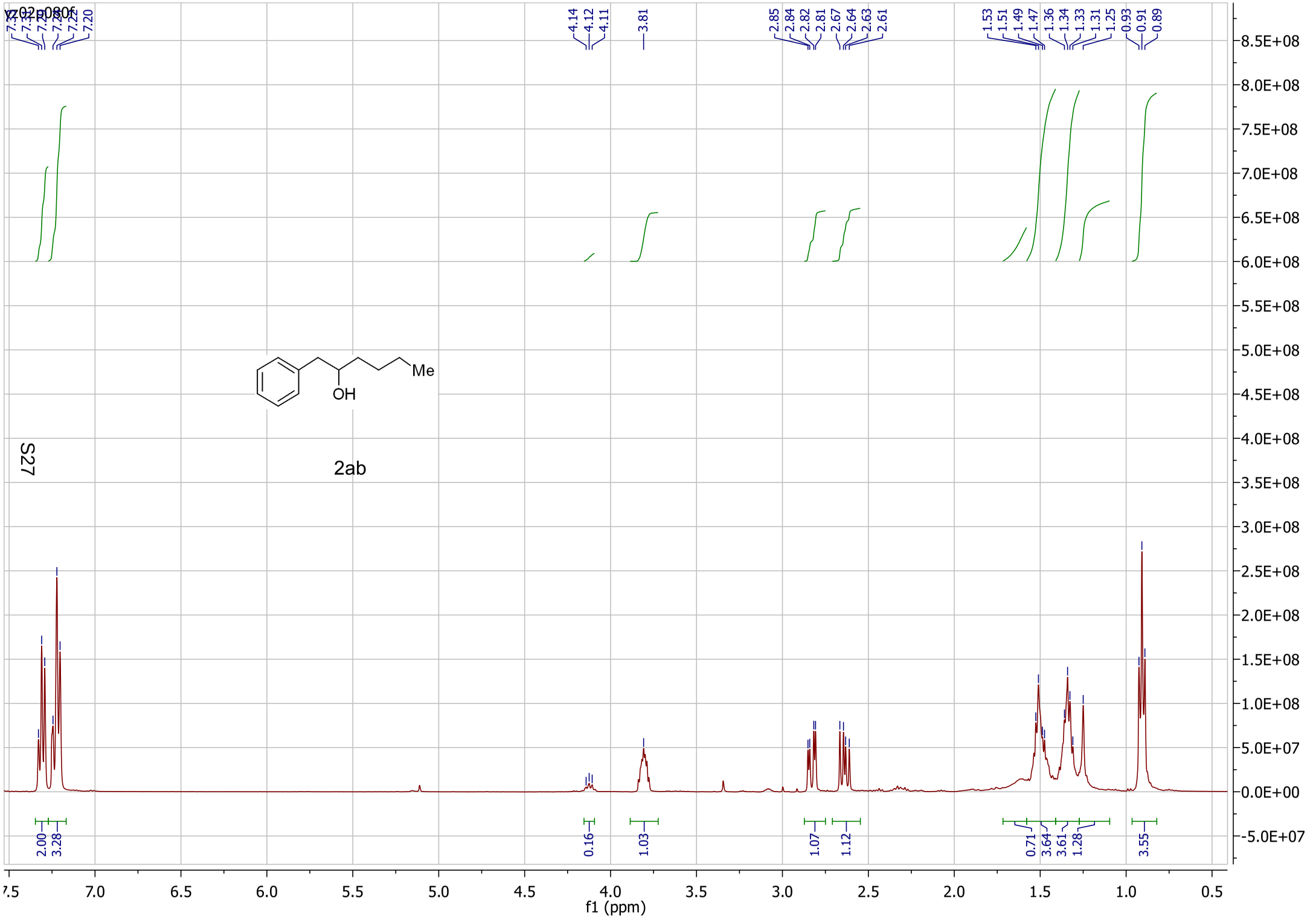


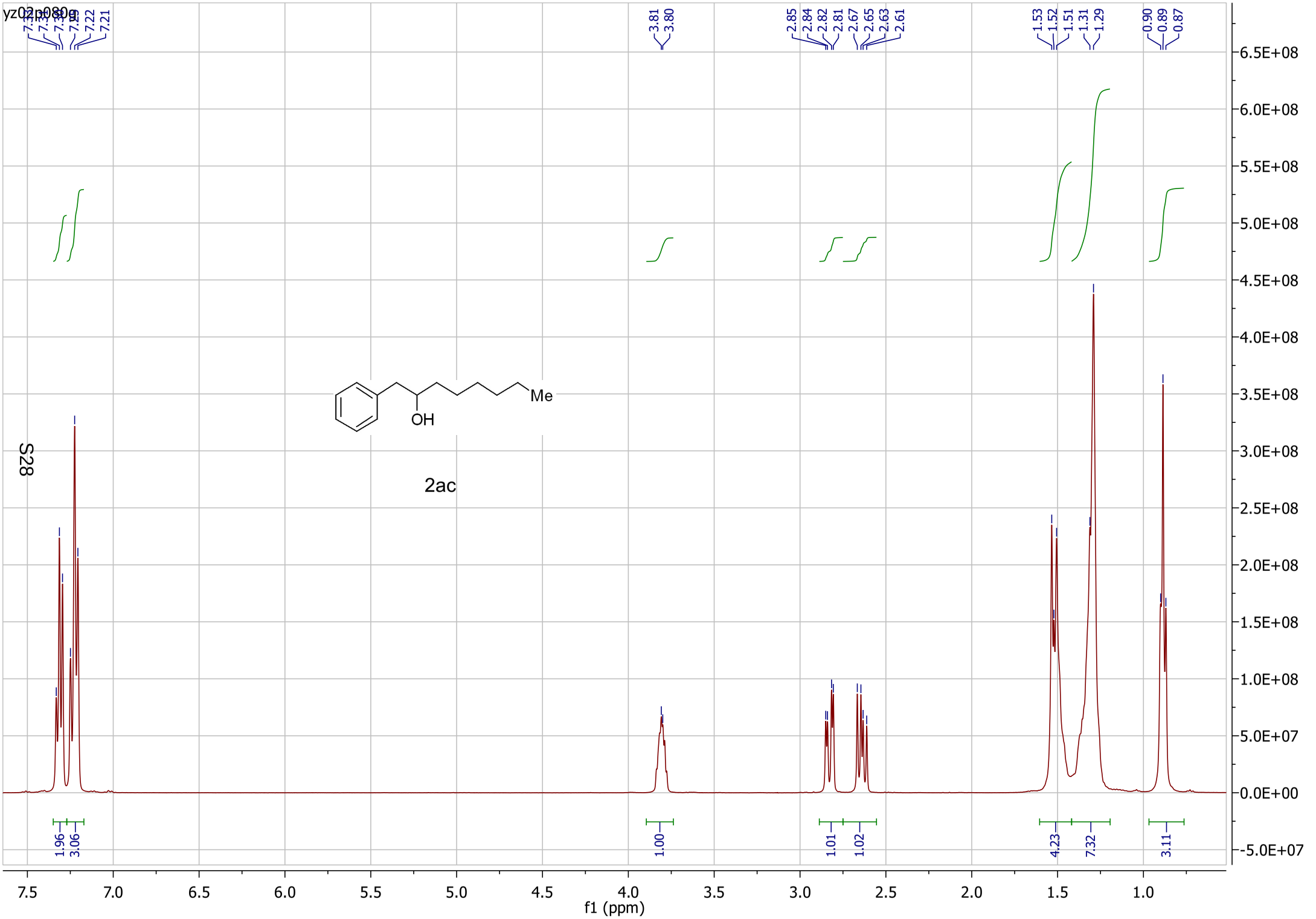
methyl (±)-p-(2-hydroxy-1-methylethyl)benzoate (3an) (table 4, entry 5) [CAS: 145621-80-3 for S-(-) enantiomer].[38] General procedure (Ni/Titanium) was followed with triethylamine hydrochloride (69 mg, 0.5 mmol, 1 equiv), methyl 4-bromobenzoate (107 mg, 0.5 mmol, 1.00 equiv), and (±)-propylene oxide (40 mg, 0.67 mmol, 1.33 equiv) at room temperature for 5 hours. A mixture of inseparable linear and branched products (branched/linear = 78:22) was isolated by flash column chromatography (3:1 hexane/acetone) as colorless oil in 62% yield (60 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 3.89 (s, 3H), 3.71 (d, *J* = 6.7 Hz, 2H), 3.10 – 2.92 (m, 1H), 1.63 (br s, 1H), 1.28 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 167.1, 149.4, 129.9, 129.5, 128.5, 127.5, 68.3, 52.1, 42.5, 17.4.
GC-MS m/z (% relative intensity, ion): 194.15 (33.40, M^+), 162.95 (100.00, M^+-CH_3O), 149.05 (31.13, M^+-C_2H_5O).

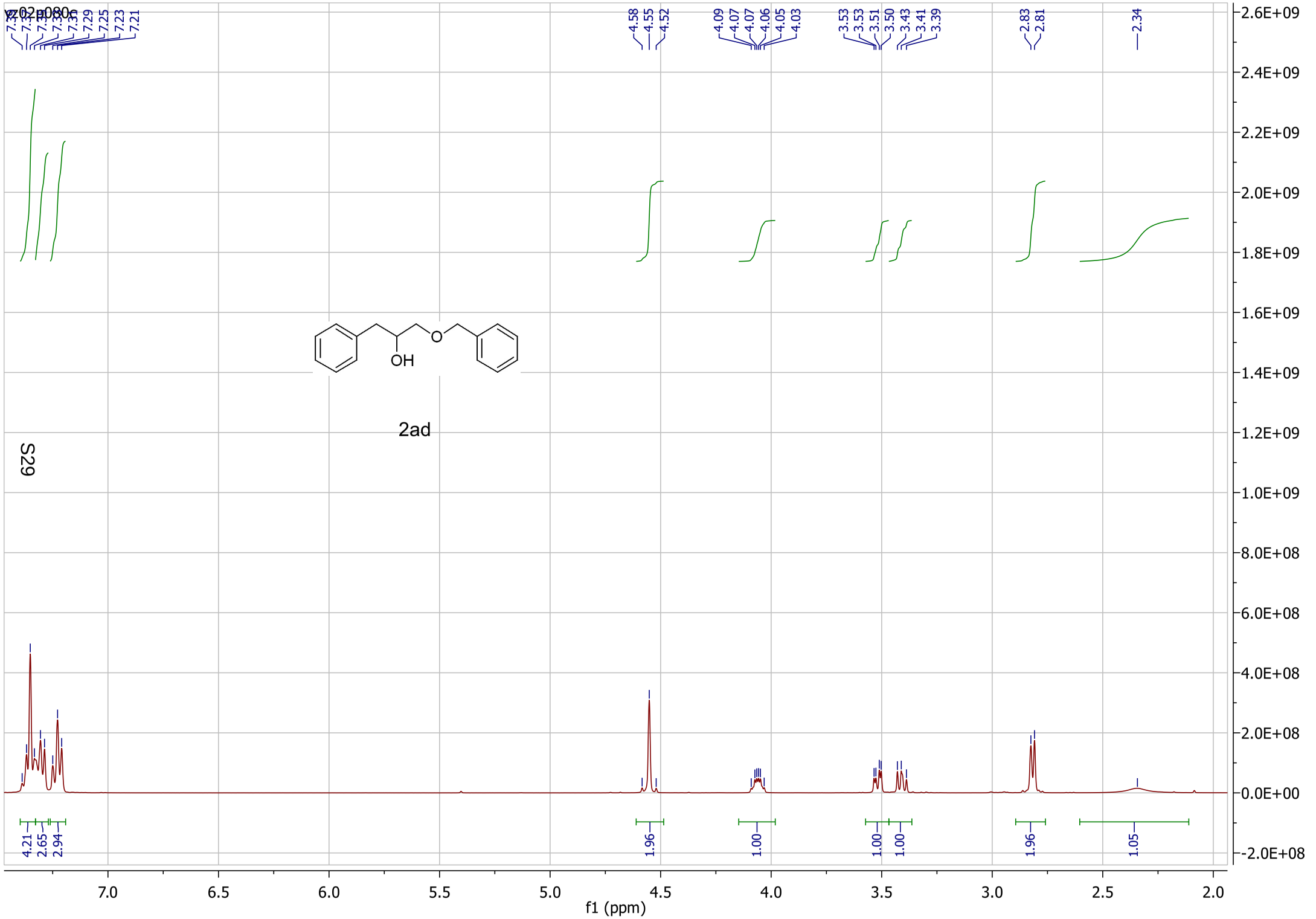
VI. NMR Spectra

[38] Matsumoto, T.; Ishida, T.; Yoshida, T.; Terao, H.; Takeda, Y.; Asakawa, Y. *Chem. Pharm. Bull*. **1992**, *40*, 1721-1726

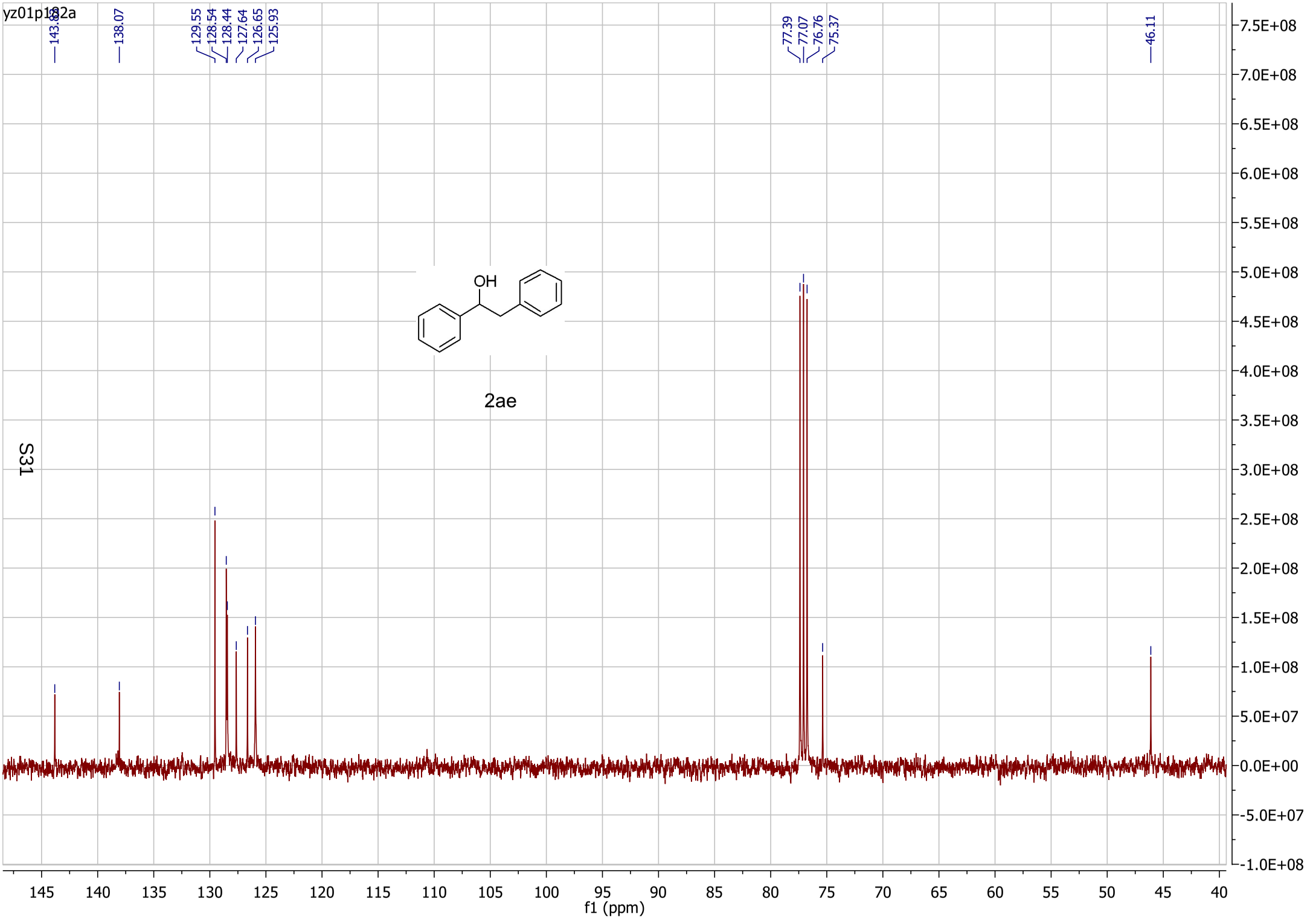

yz02p080
7.27
7.28
7.29
7.30
4.09
4.08
4.07
4.05
2.86
2.85
2.83
2.82
2.78
2.76
2.75
2.73
1.72
1.31
1.30
1.30
Me
OH
2aa
2.00
3.07
1.00
1.02
1.03
1.05
3.30
f1 (ppm)
9.0E+08
8.0E+08
7.0E+08
6.0E+08
5.0E+08
4.0E+08
3.0E+08
2.0E+08
1.0E+08
0.0E+00

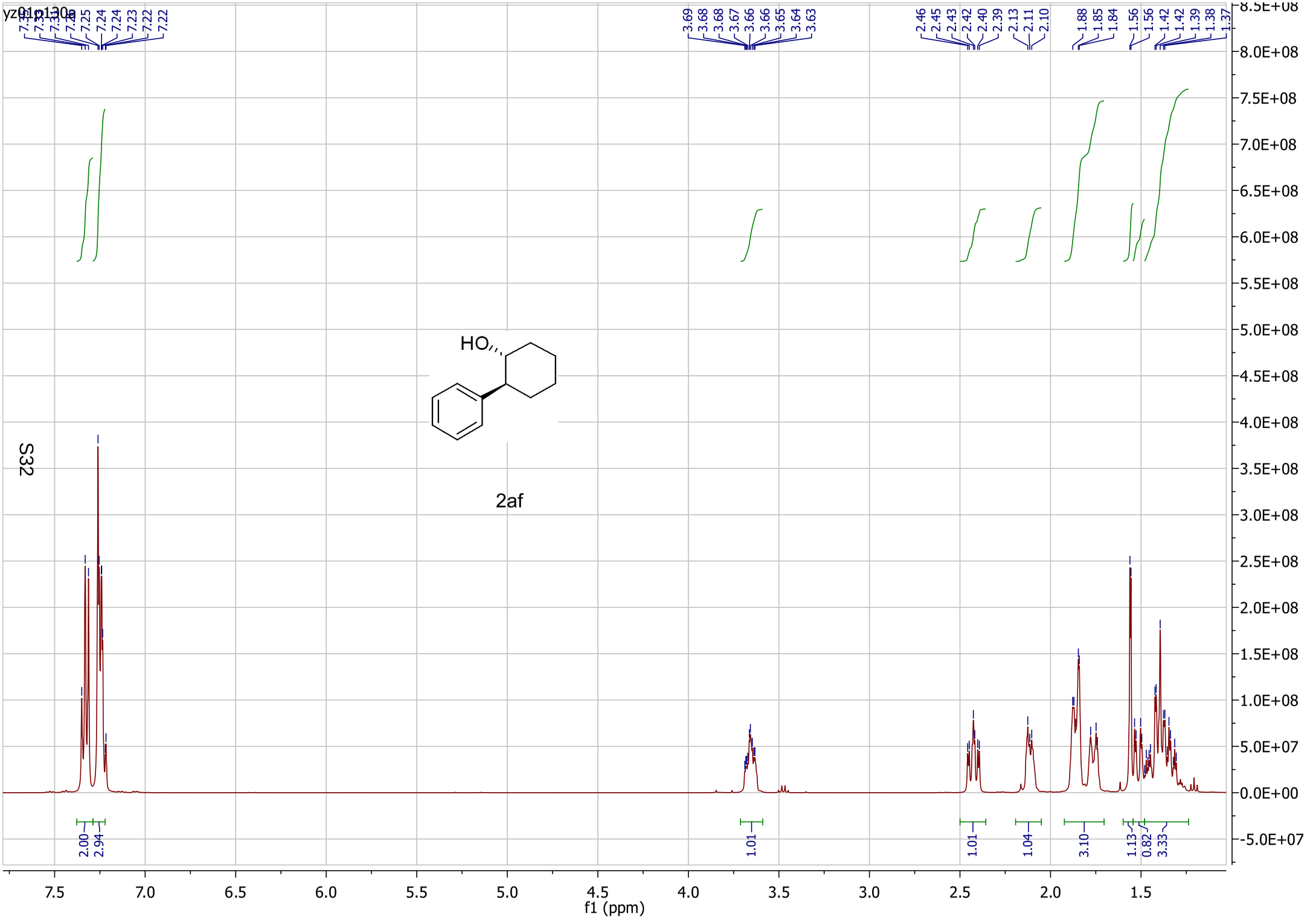

7.31
7.30
7.28
7.22
7.20
4.14
4.12
4.11
3.81
2.85
2.84
2.82
2.81
2.67
2.64
2.63
2.61
1.53
1.51
1.49
1.47
1.36
1.34
1.33
1.31
1.25
0.93
0.91
0.89
Me
OH
S27
2ab
2.00
3.28
0.16
1.03
1.07
1.12
0.71
3.64
3.61
1.28
3.55
f1 (ppm)

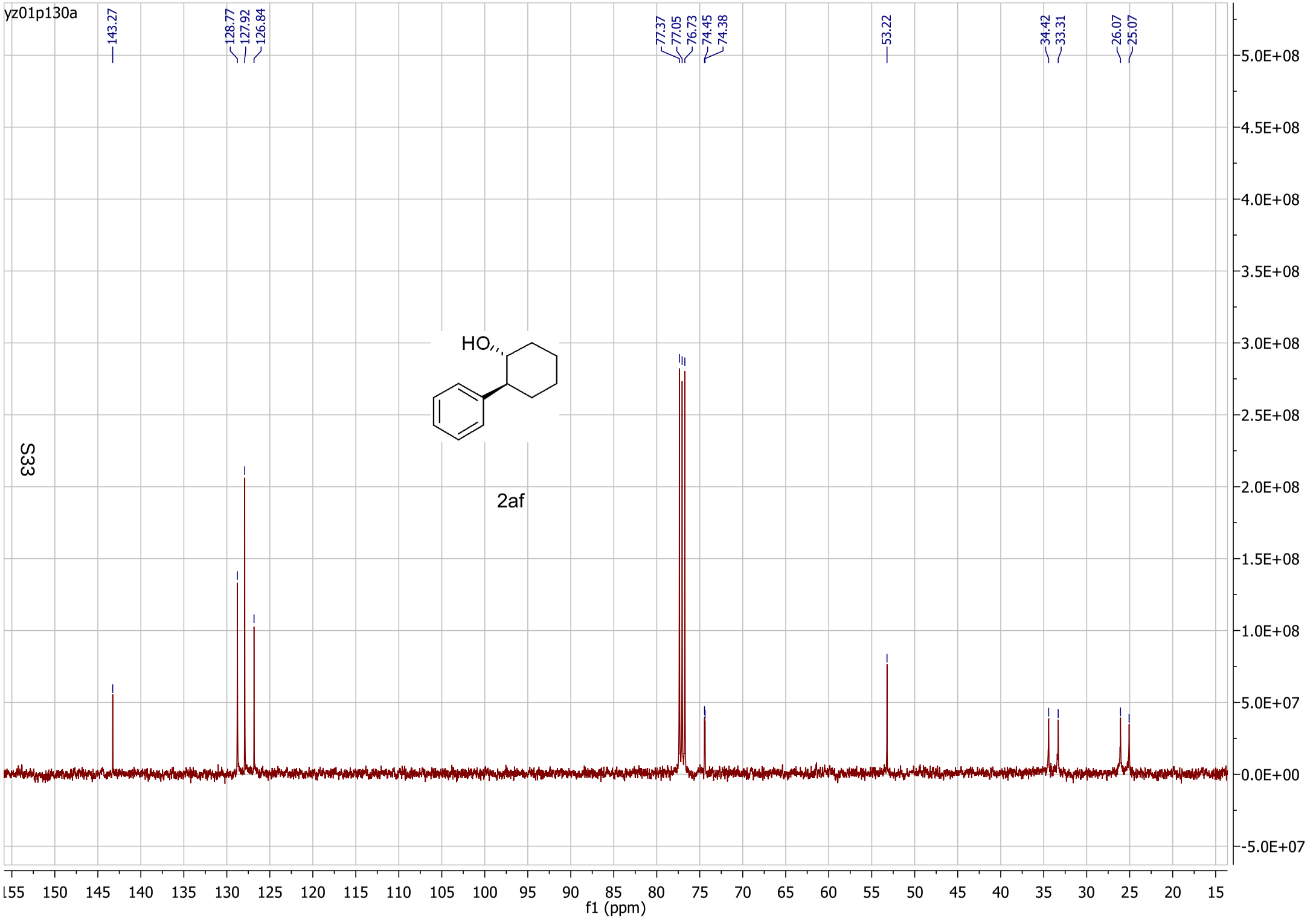

yz02p080g
7.25
7.24
7.23
7.22
7.21
3.81
3.80
2.85
2.84
2.82
2.81
2.67
2.65
2.63
2.61
1.53
1.52
1.51
1.31
1.29
0.90
0.89
0.87
Me
OH
2ac
S28
1.96
3.06
1.00
1.01
1.02
4.23
7.32
3.11
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
7.5
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
f1 (ppm)

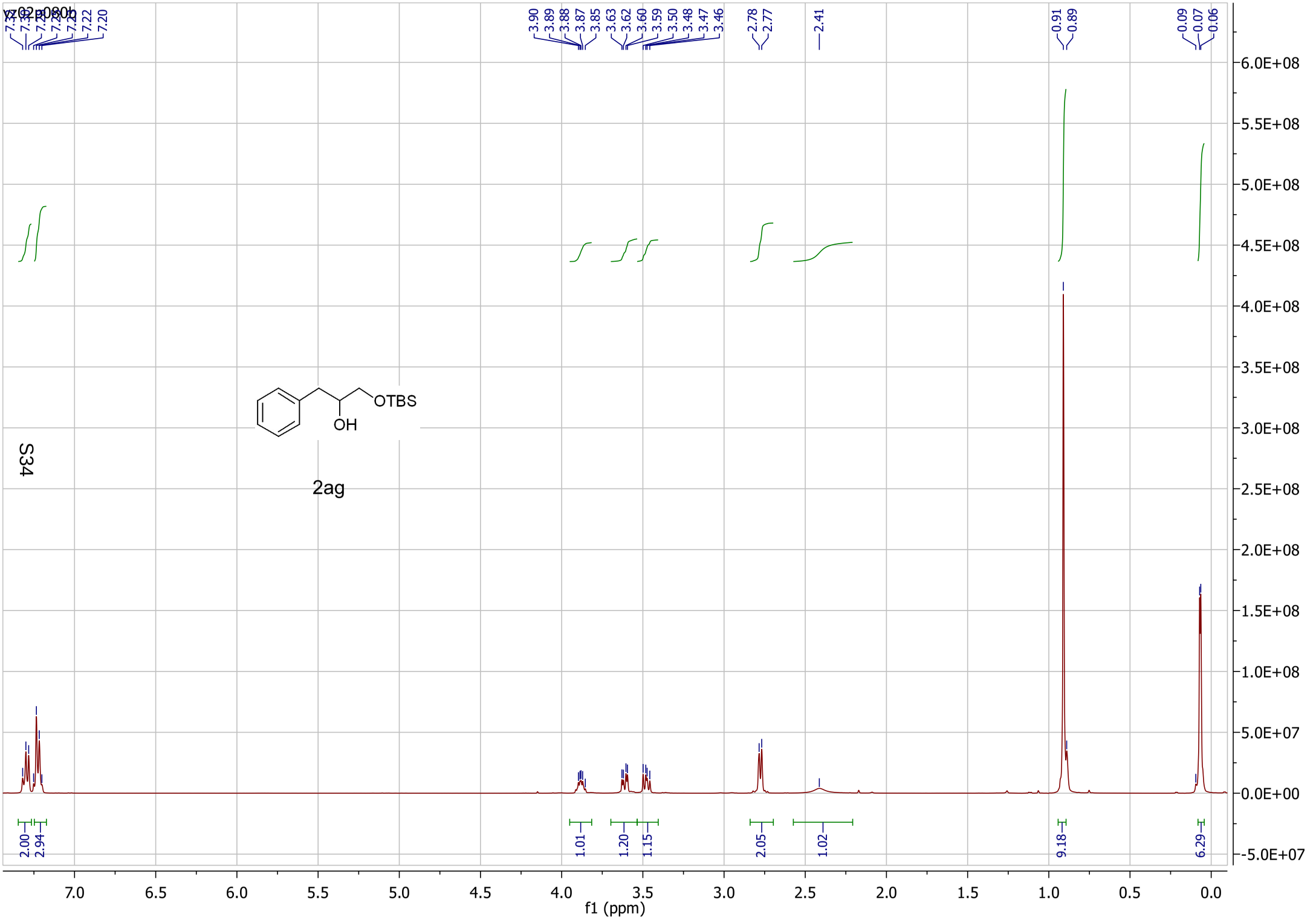

yz02p080c
7.31
7.29
7.25
7.23
7.21
4.58
4.55
4.52
4.09
4.07
4.07
4.06
4.05
4.03
3.53
3.53
3.51
3.50
3.43
3.41
3.39
2.83
2.81
2.34
OH
O
2ad
S29
4.21
2.65
2.94
1.96
1.00
1.00
1.00
1.96
1.05
2.6E+09
2.4E+09
2.2E+09
2.0E+09
1.8E+09
1.6E+09
1.4E+09
1.2E+09
1.0E+09
8.0E+08
6.0E+08
4.0E+08
2.0E+08
0.0E+00
-2.0E+08
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

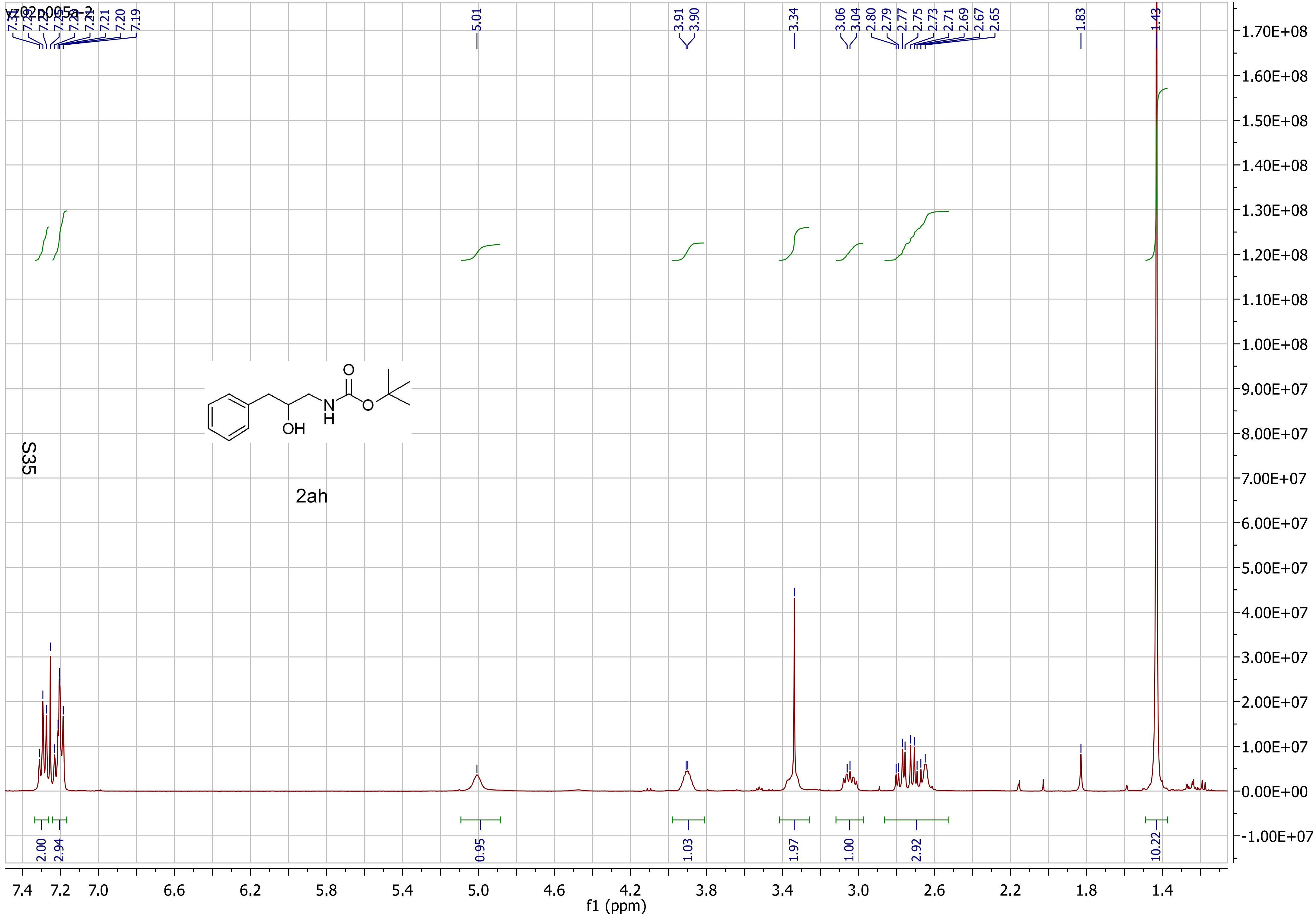

yz01p182a
7.33
7.32
7.30
7.27
7.25
7.23
7.21
7.20
4.92
4.91
4.90
4.90
4.89
4.88
4.88
3.08
3.06
3.04
3.03
3.02
3.00
2.99
2.97
2.04
2.03
OH
2ae
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)


yz01p1_2a
143.88
138.07
129.55
128.54
128.44
127.64
126.65
125.93
77.39
77.07
76.76
75.37
46.11
OH
2ae
S31
f1 (ppm)

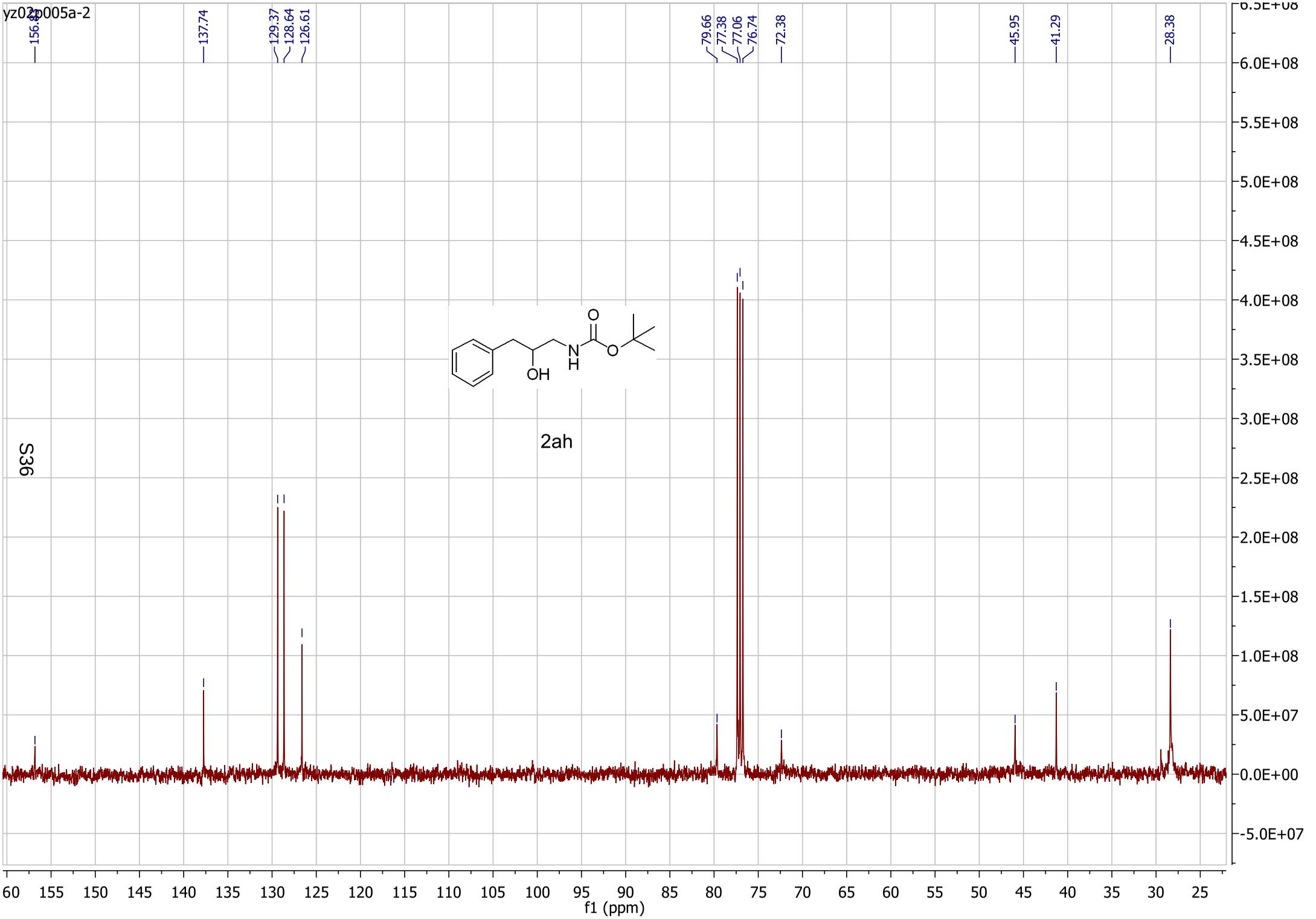

yz01m130a
7.31
7.30
7.28
7.25
7.24
7.24
7.23
7.22
7.22
3.69
3.68
3.68
3.67
3.66
3.66
3.65
3.64
3.63
2.46
2.45
2.43
2.42
2.40
2.39
2.13
2.11
2.10
1.88
1.85
1.84
1.56
1.56
1.42
1.42
1.39
1.38
1.37
HO
S32
2af
2.00
2.94
1.01
1.01
1.04
3.10
1.13
0.82
3.33
f1 (ppm)

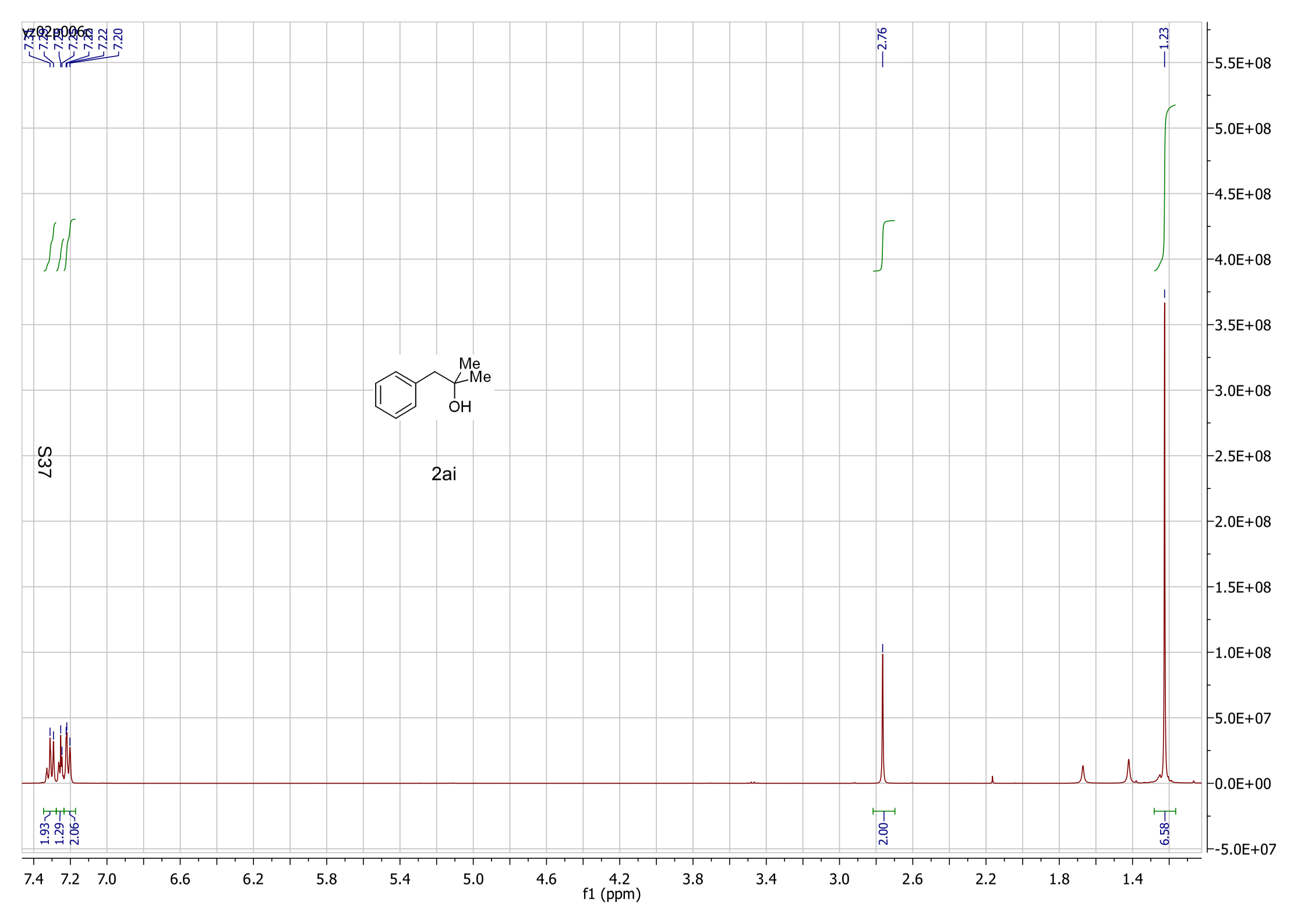

yz01p130a
143.27
128.77
127.92
126.84
77.37
77.05
76.73
74.45
74.38
53.22
34.42
33.31
26.07
25.07
HO
2af
S33
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

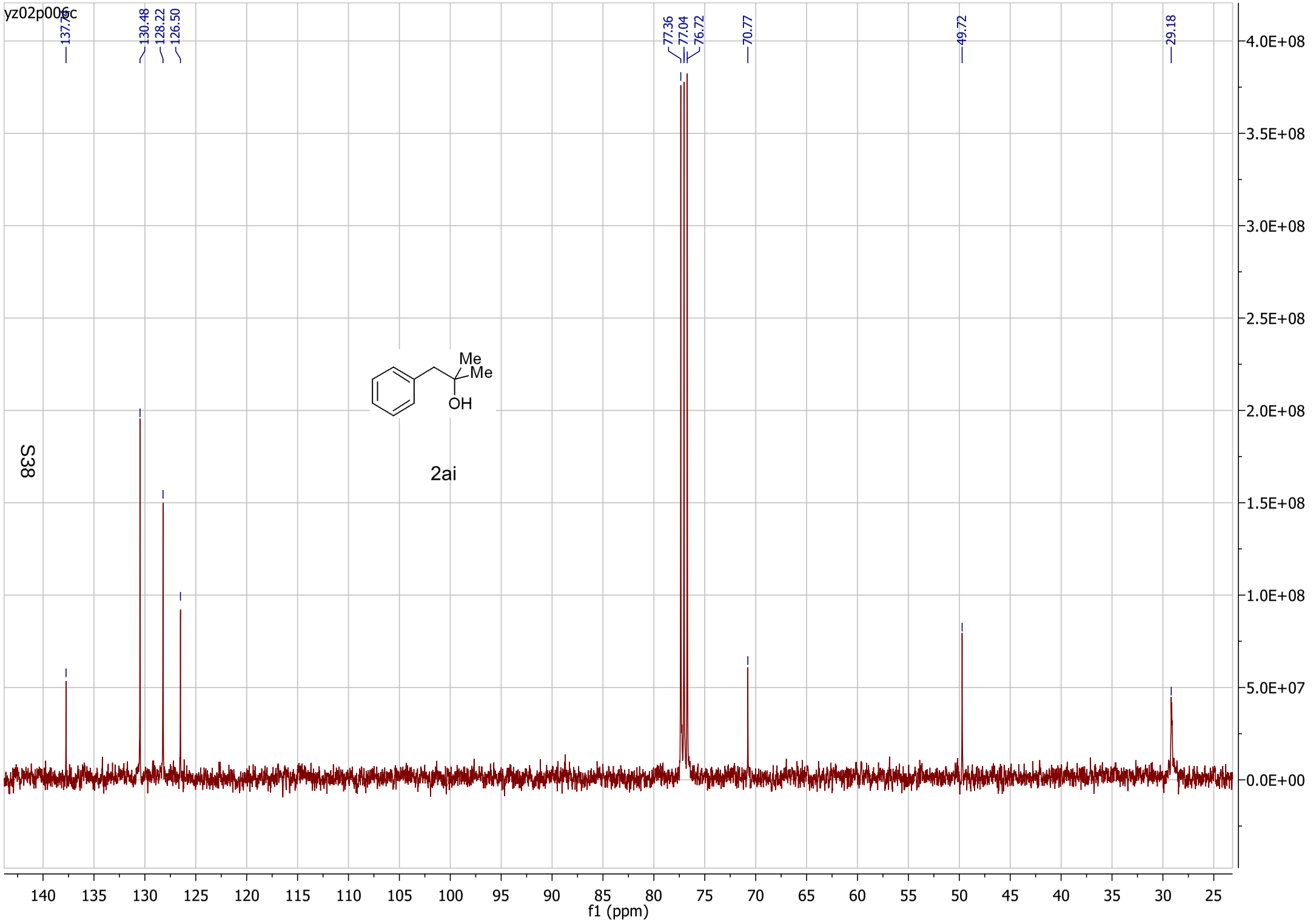

7.26
7.24
7.22
7.20
3.90
3.89
3.88
3.87
3.85
3.63
3.62
3.60
3.59
3.50
3.48
3.47
3.46
2.78
2.77
2.41
0.91
0.89
0.09
0.07
0.06
OTBS
OH
2ag
S34
2.00
2.94
1.01
1.20
1.15
2.05
1.02
9.18
6.29
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
7.0
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)

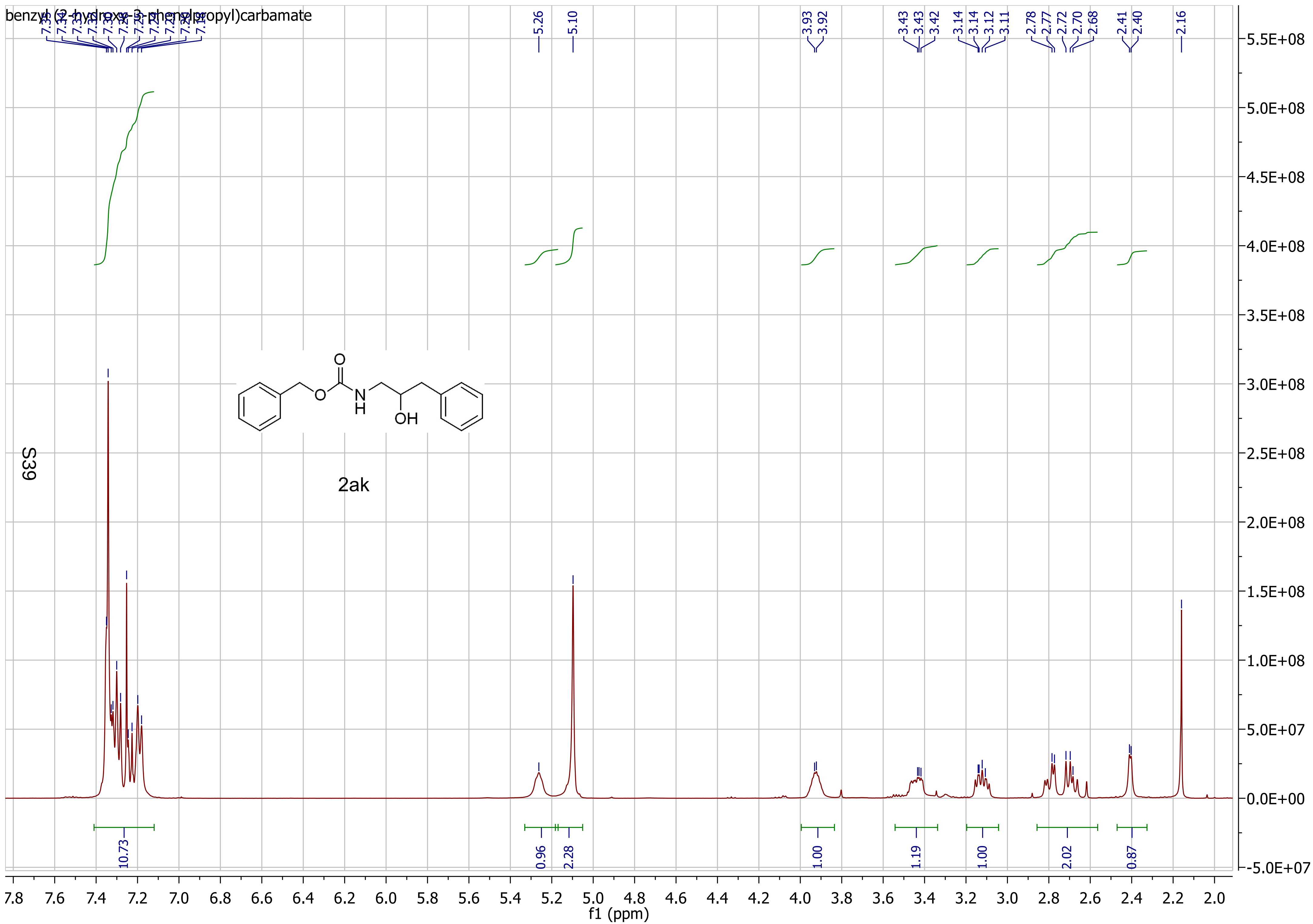

yz02p005a-2
7.19 7.20 7.21
5.01
3.91 3.90
3.34
3.06 3.04
2.80 2.79 2.77 2.75 2.73 2.71 2.69 2.67 2.65
1.83
1.43
2.00 2.94 0.95 1.03 1.97 1.00 2.92 10.22
OH
N
H
O
f1 (ppm)

2ah

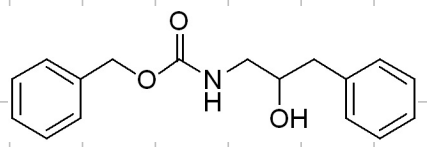

yz02p005a-2
156.40
137.74
129.37
128.64
126.61
79.66
77.38
77.06
76.74
72.38
45.95
41.29
28.38
O
N
H
O
OH
2ah
S36
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
60 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)


Me
Me
OH
2ai
S37
f1 (ppm)

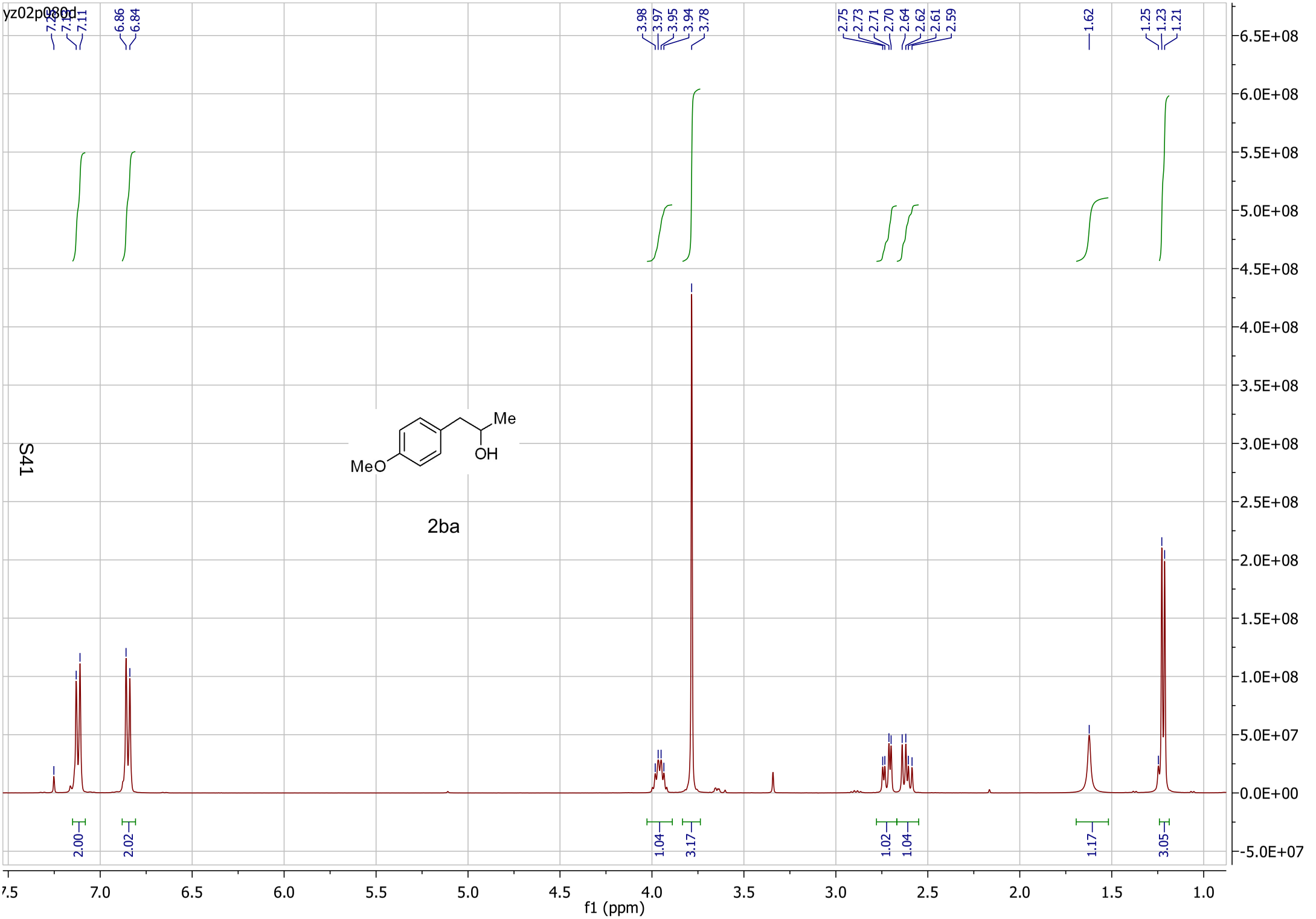

yz02p006c
137.76
130.48
128.22
126.50
77.36
77.04
76.72
70.77
49.72
29.18
Me
Me
OH
2ai
S38
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

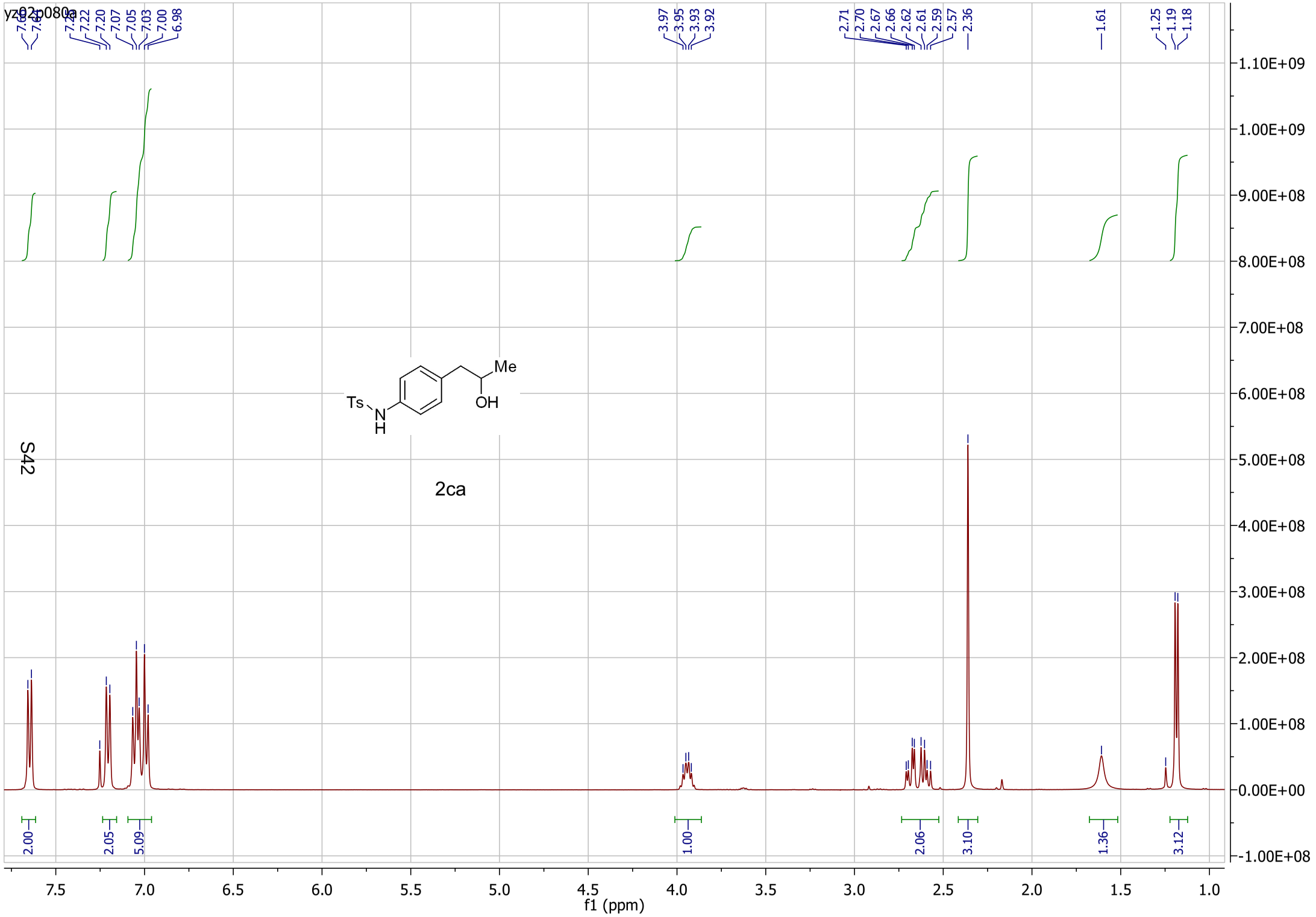

benzyl (2-hydroxy-3-phenylpropyl)carbamate
5.26
5.10
3.93
3.92
3.43
3.43
3.42
3.14
3.14
3.12
3.11
2.78
2.77
2.72
2.70
2.68
2.41
2.40
2.16
2ak
O
N
H
OH
10.73
0.96
2.28
1.00
1.19
1.00
2.02
0.87
f1 (ppm)

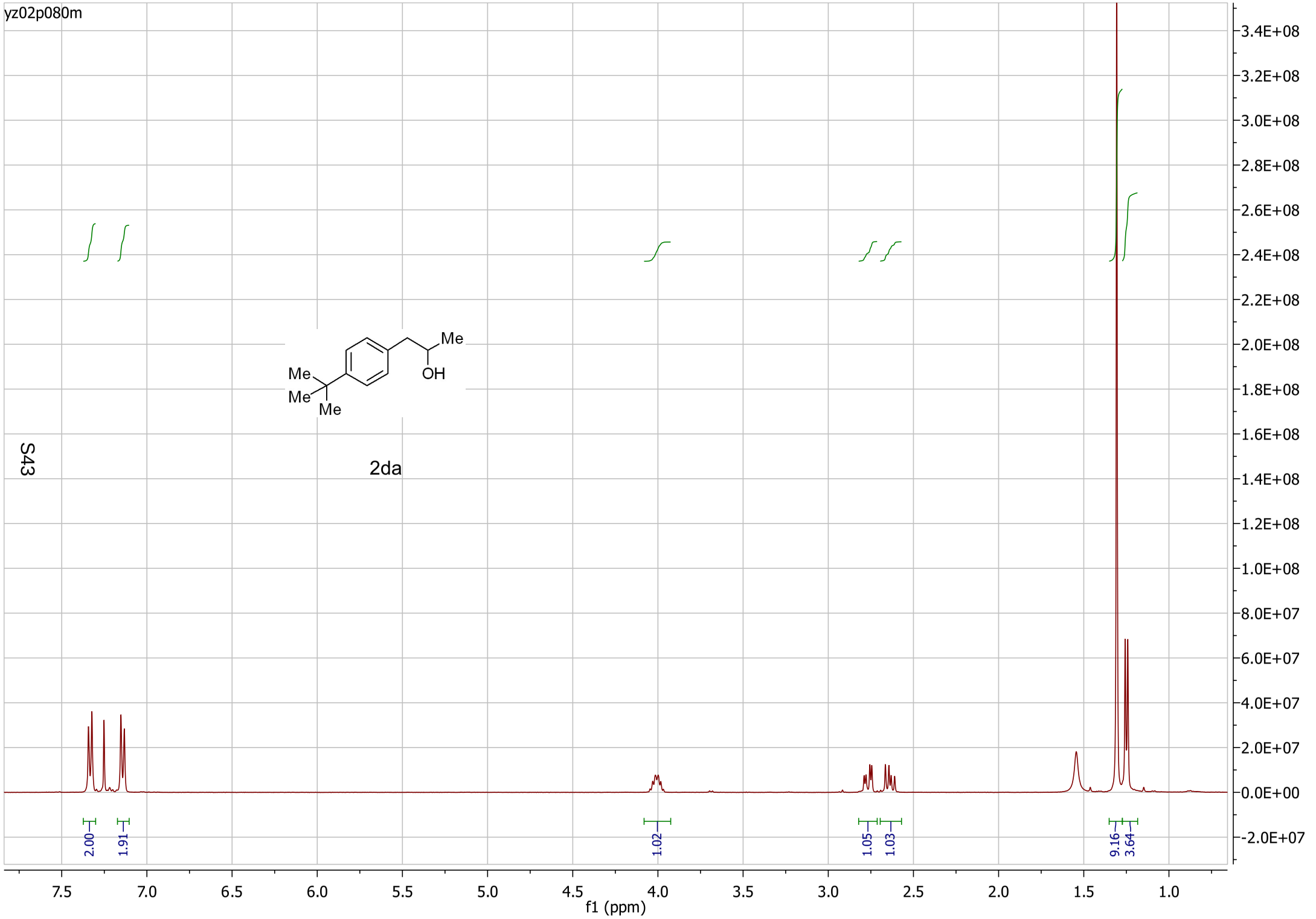
benzyl (2-hydroxy-3-phenylpropyl)carbamate

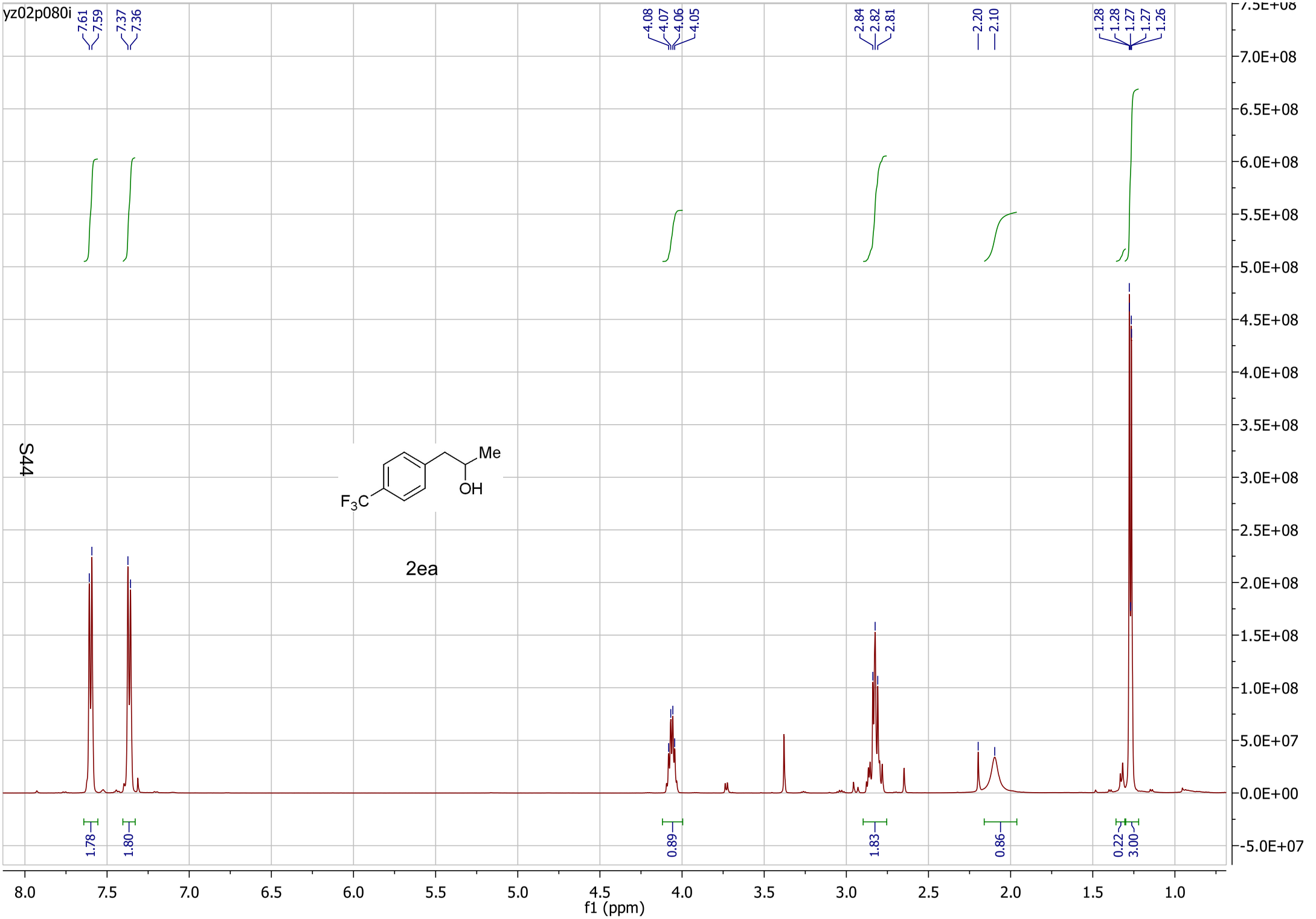


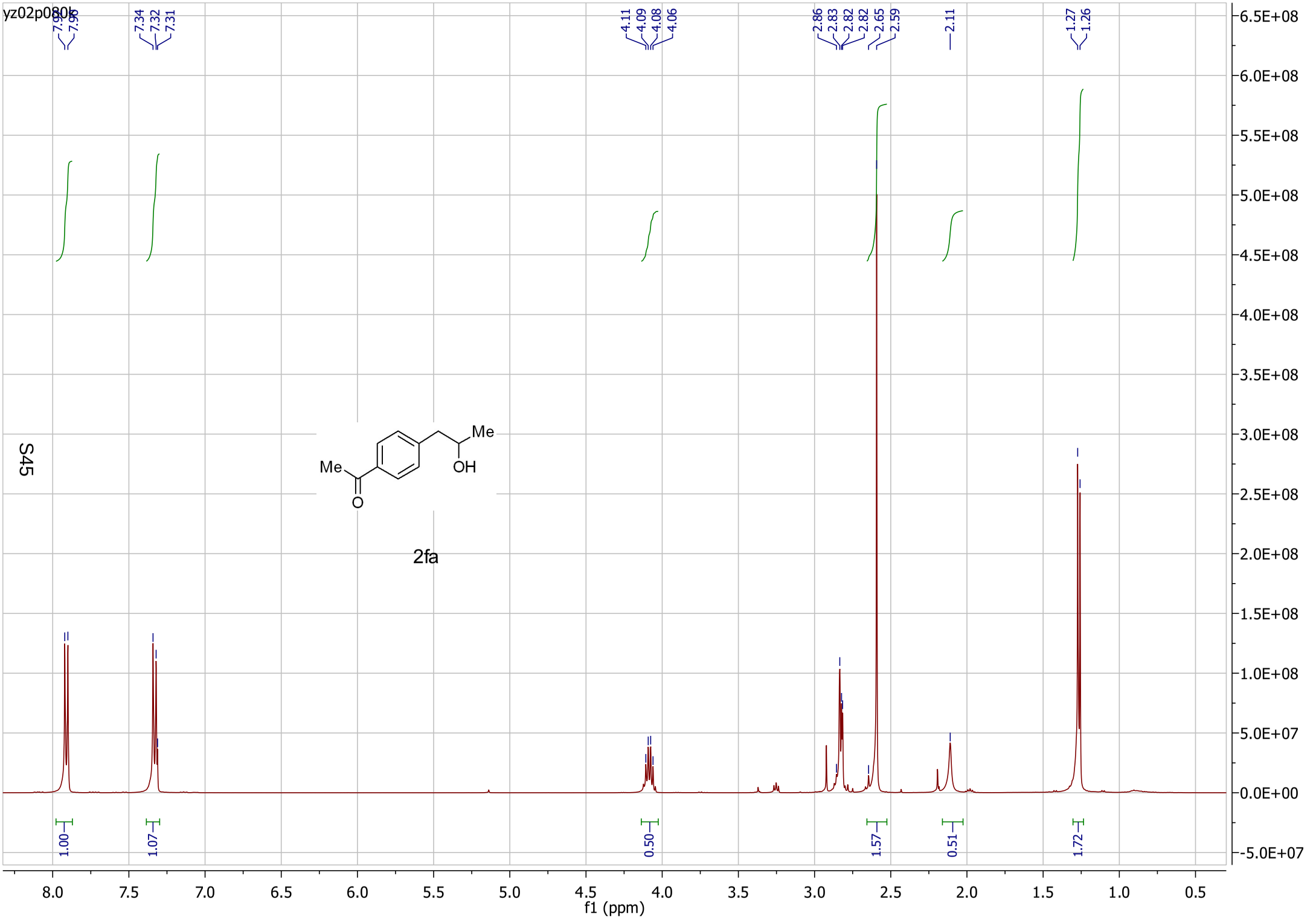
2ak

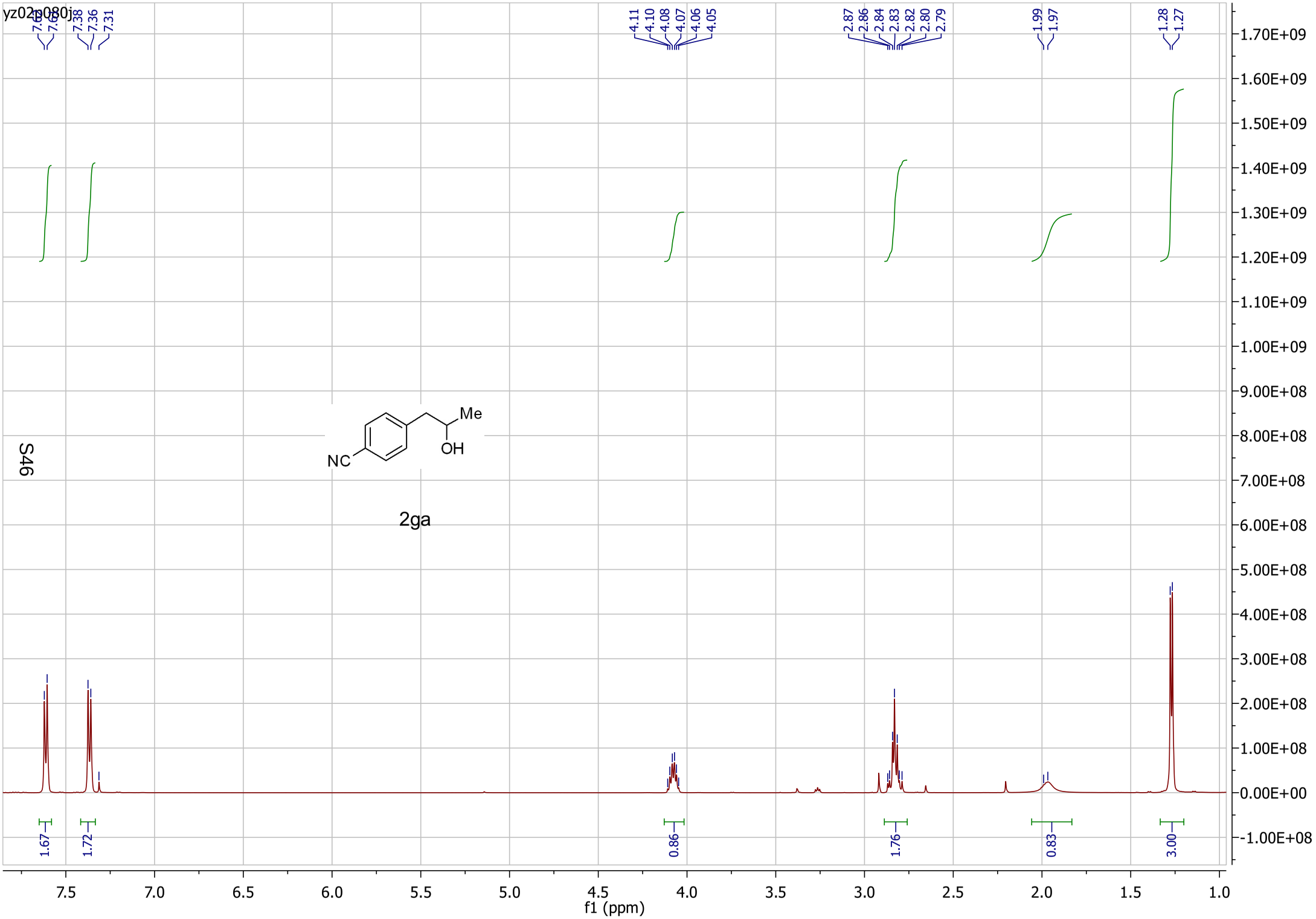

yz02p080d
7.26
7.13
7.11
6.86
6.84
3.98
3.97
3.95
3.94
3.78
2.75
2.73
2.71
2.70
2.64
2.62
2.61
2.59
1.62
1.25
1.23
1.21
S41
Me
OH
MeO
2ba
2.00
2.02
1.04
3.17
1.02
1.04
1.17
3.05
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
7.5
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
f1 (ppm)

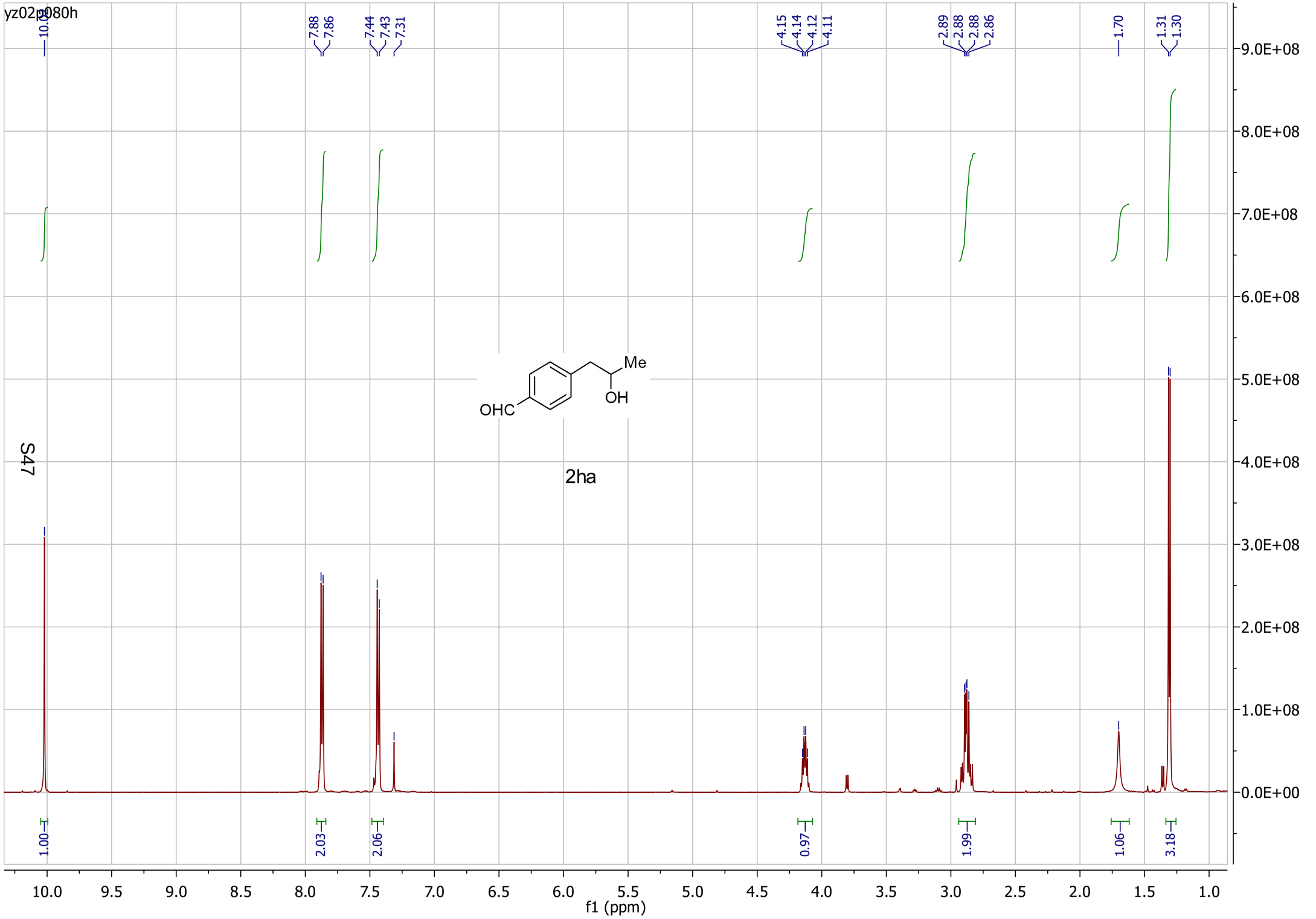

yz02p080a
7.68
7.66
7.24
7.22
7.20
7.07
7.05
7.03
7.00
6.98
3.97
3.95
3.93
3.92
2.71
2.70
2.67
2.66
2.62
2.61
2.59
2.57
2.36
1.61
1.25
1.19
1.18
Me
OH
Ts
N
H
2ca
S42
2.00
2.05
5.09
1.00
2.06
3.10
1.36
3.12
1.10E+09
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
-1.00E+08
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
f1 (ppm)

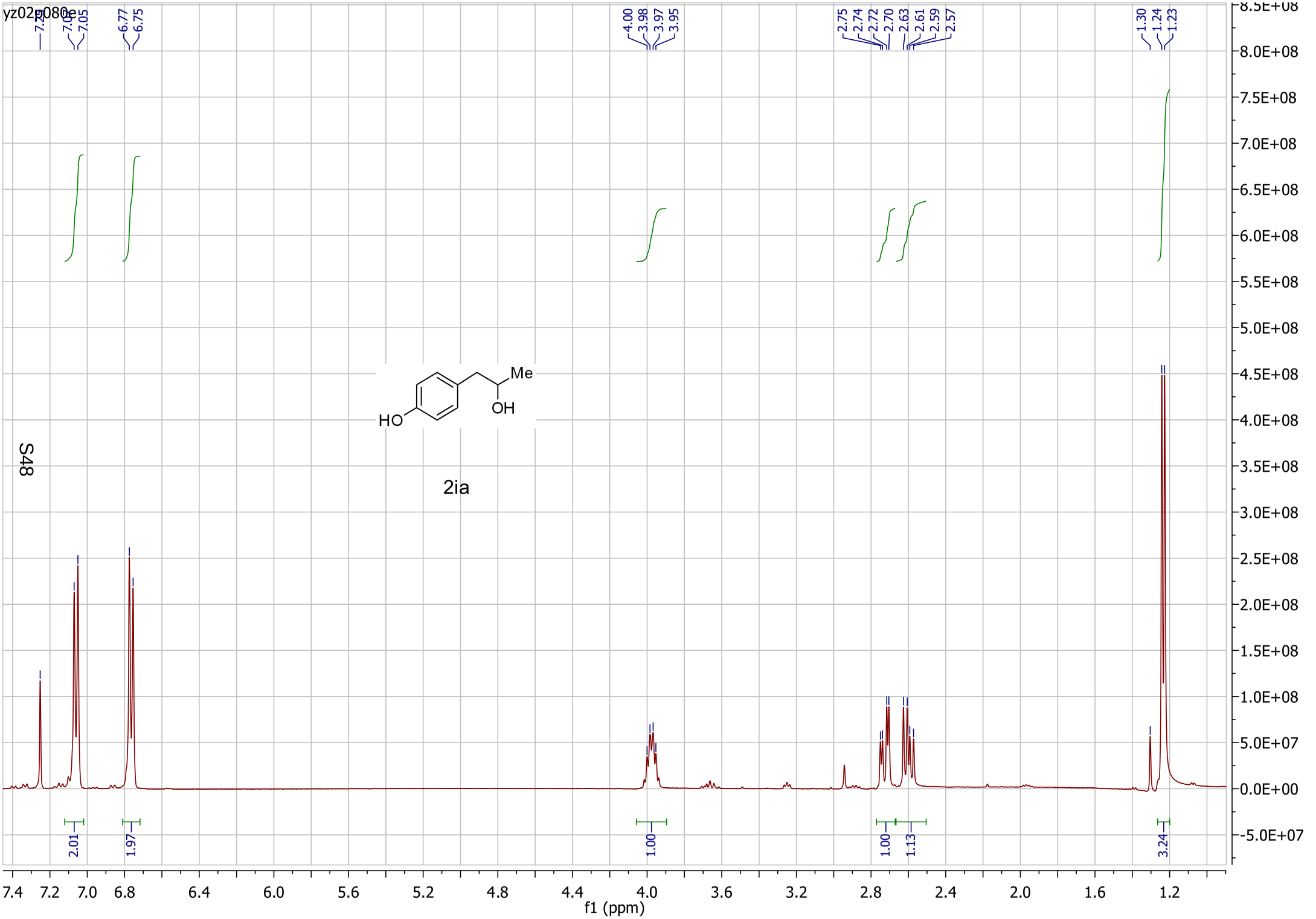

yz02p080m
Me
Me
Me
OH
2da
S43
2.00
1.91
1.02
1.05
1.03
9.16
3.64
f1 (ppm)

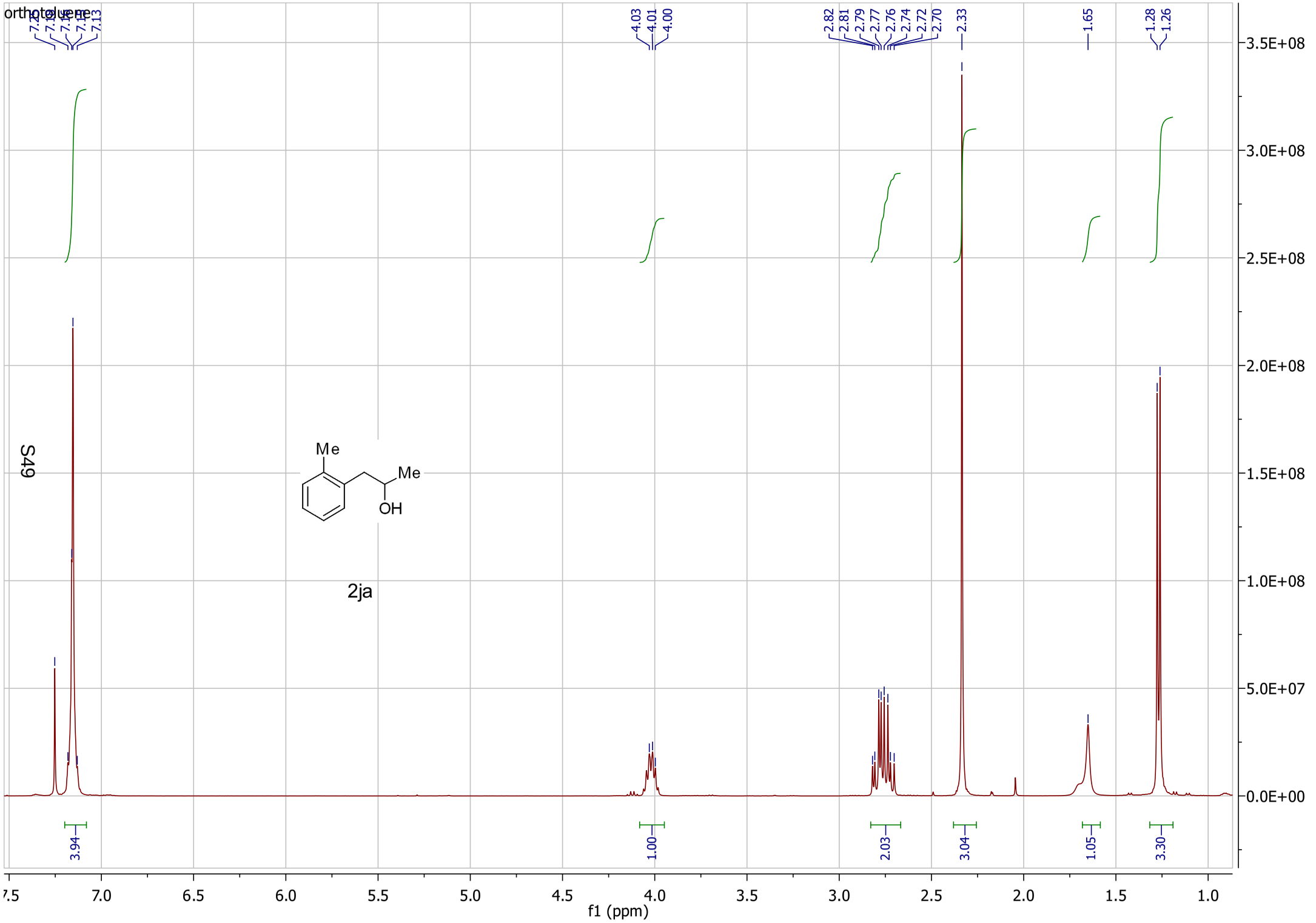

yz02p080i
7.61
7.59
7.37
7.36
4.08
4.07
4.06
4.05
2.84
2.82
2.81
2.20
2.10
1.28
1.28
1.27
1.27
1.26
S44
Me
OH
F3C
2ea
1.78
1.80
0.89
1.83
0.86
0.22
3.00
f1 (ppm)

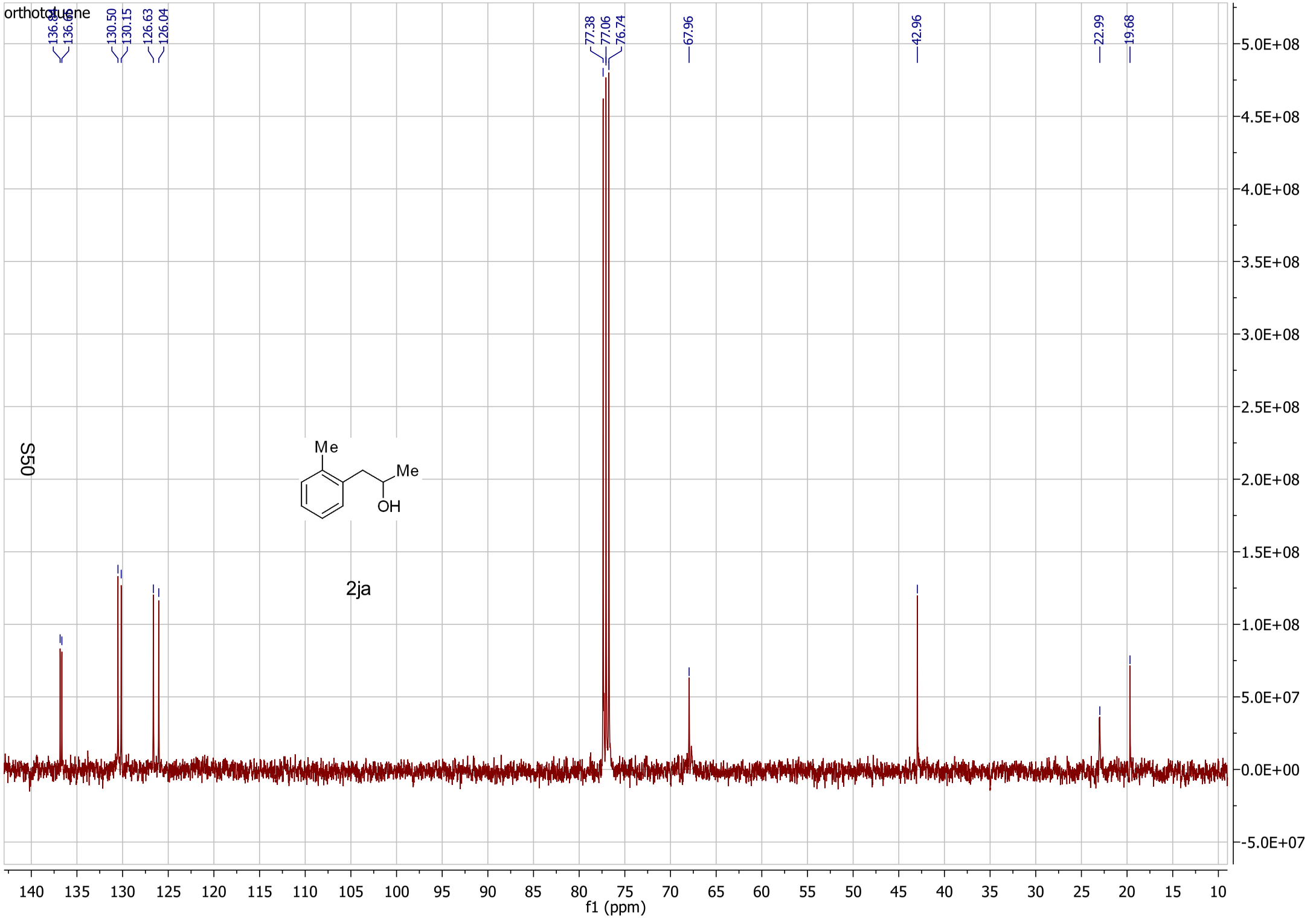

yz02p080b
7.96
7.95
7.34
7.32
7.31
4.11
4.09
4.08
4.06
2.86
2.83
2.82
2.82
2.65
2.59
2.11
1.27
1.26
S45
Me
Me
OH
O
2fa
1.00
1.07
0.50
1.57
0.51
1.72
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

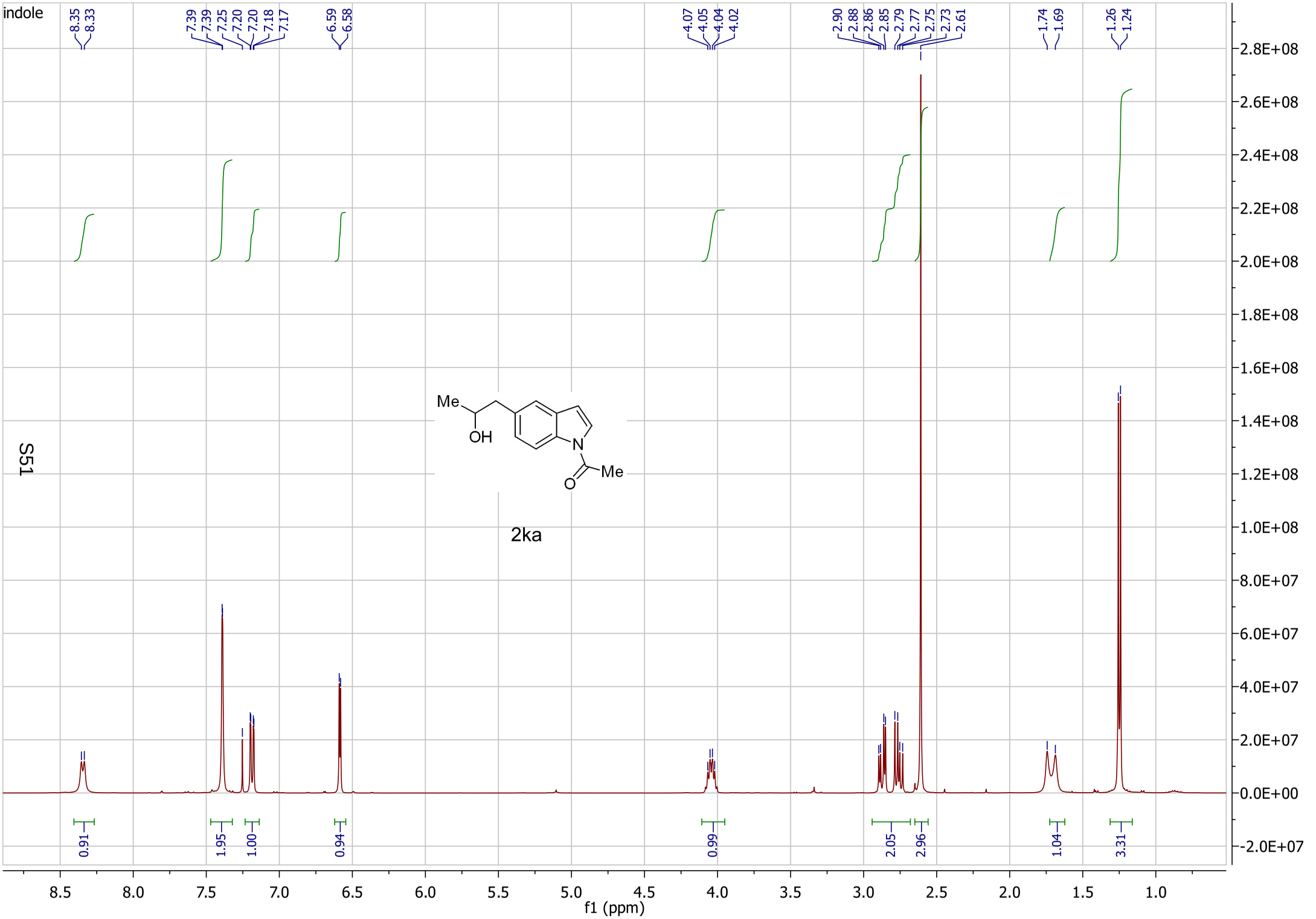

yz02p080j
7.68
7.66
7.38
7.36
7.31
4.11
4.10
4.08
4.07
4.06
4.05
2.87
2.86
2.84
2.83
2.82
2.80
2.79
1.99
1.97
1.28
1.27
S46
Me
OH
NC
2ga
1.67
1.72
0.86
1.76
0.83
3.00
f1 (ppm)

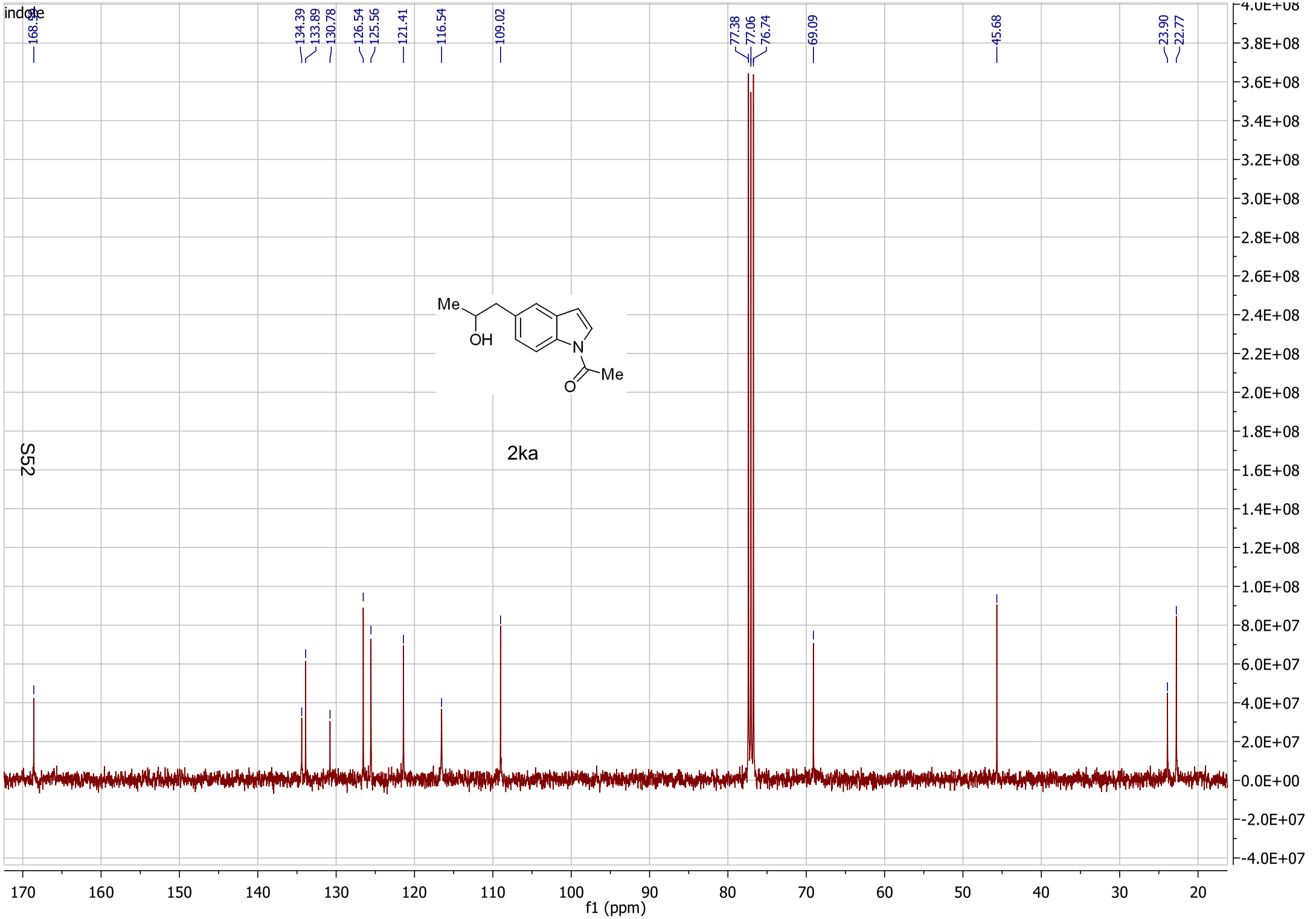

yz02p080h
10.02
7.88
7.86
7.44
7.43
7.31
4.15
4.14
4.12
4.11
2.89
2.88
2.88
2.86
1.70
1.31
1.30
Me
OH
OHC
2ha
S47
1.00
2.03
2.06
0.97
1.99
1.06
3.18
9.0E+08
8.0E+08
7.0E+08
6.0E+08
5.0E+08
4.0E+08
3.0E+08
2.0E+08
1.0E+08
0.0E+00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

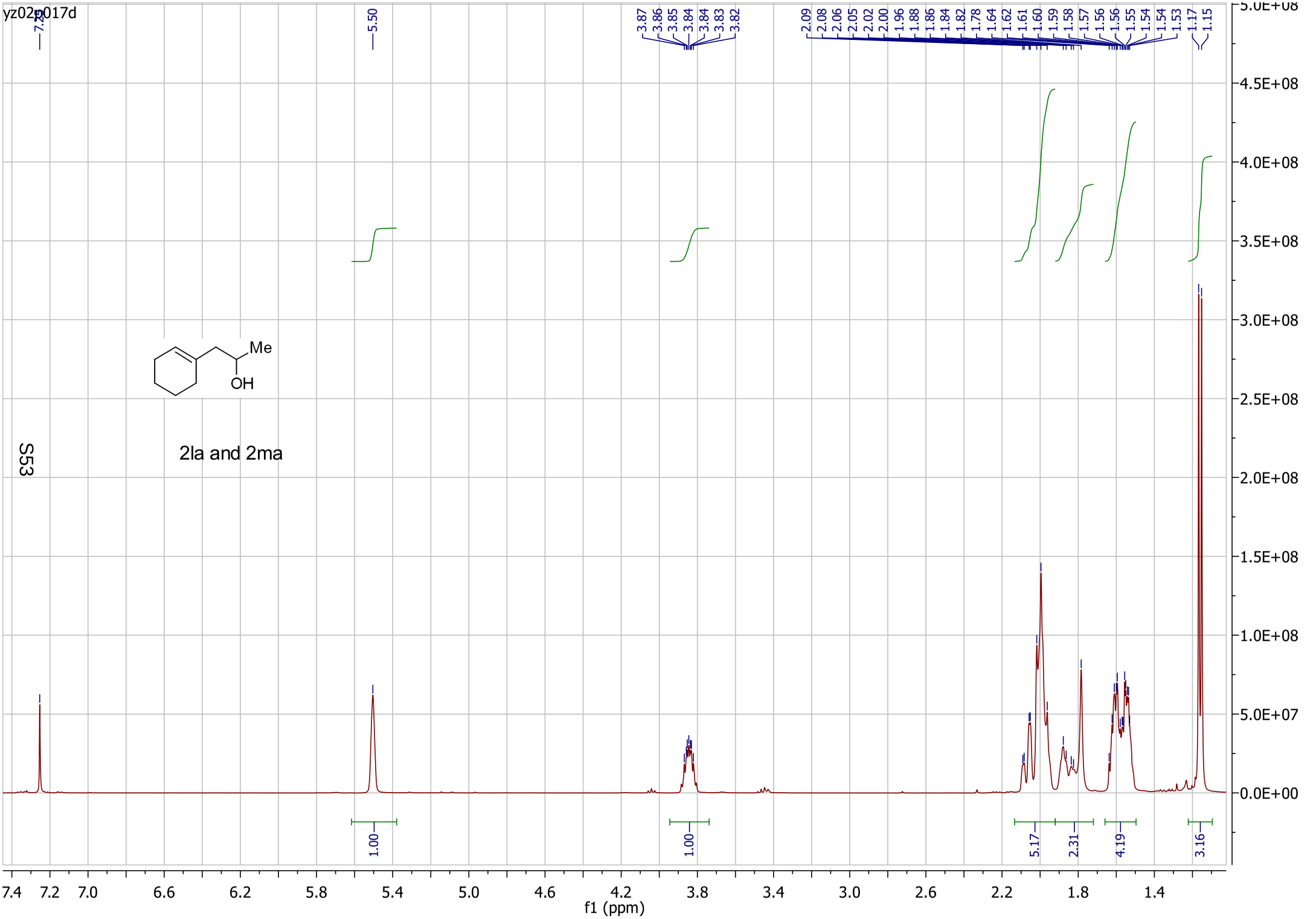

yz02p080e
7.22
7.06
7.05
6.77
6.75
4.00
3.98
3.97
3.95
2.75
2.74
2.72
2.70
2.63
2.61
2.59
2.57
1.30
1.24
1.23
Me
OH
HO
2ia
S48
2.01
1.97
1.00
1.00
1.13
3.24
f1 (ppm)

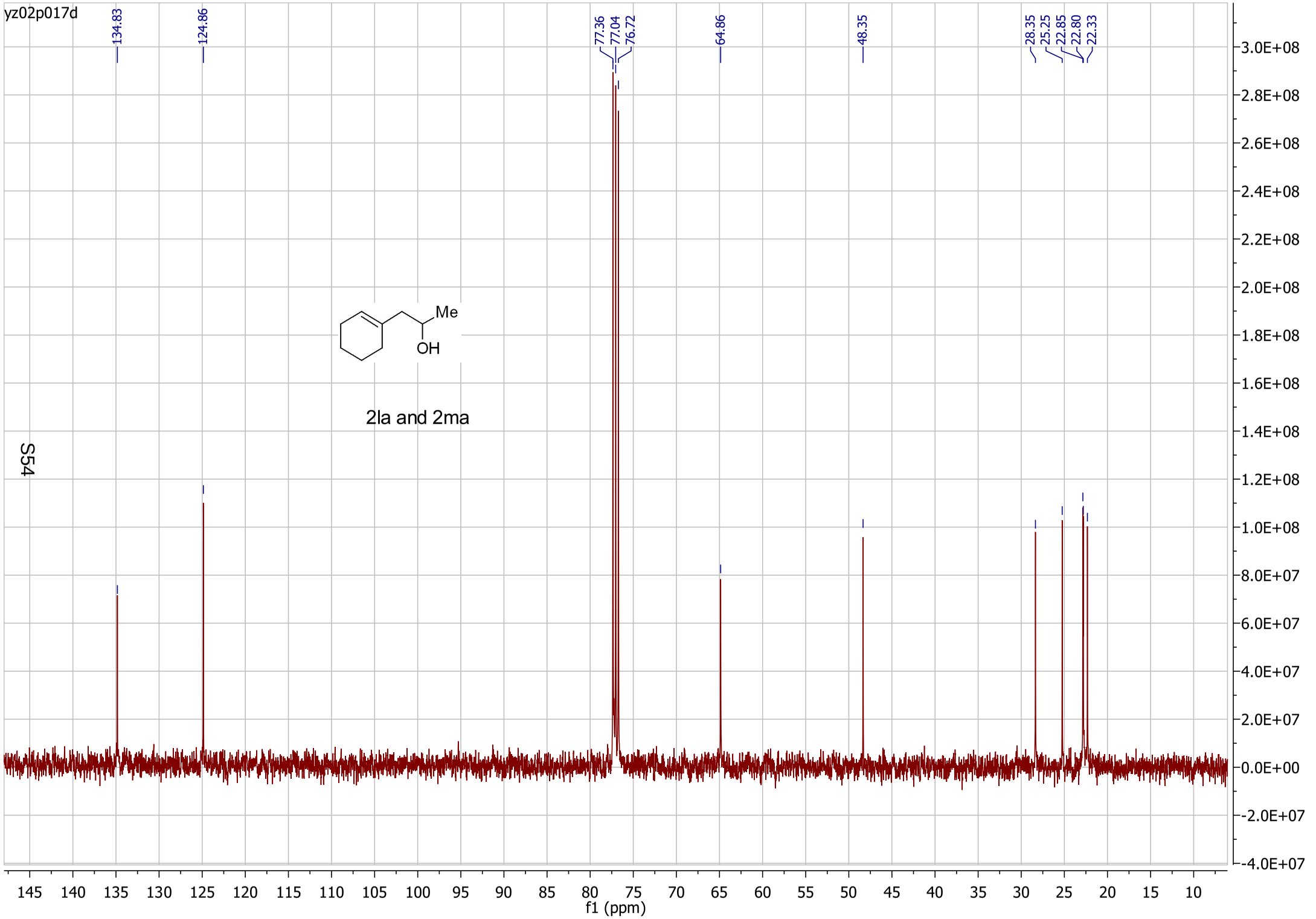

orthotoluene
7.22
7.15
7.14
7.13
7.13
4.03
4.01
4.00
2.82
2.81
2.79
2.77
2.76
2.74
2.72
2.70
2.33
1.65
1.28
1.26
S49
Me
Me
OH
2ja
3.94
1.00
2.03
3.04
1.05
3.30
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

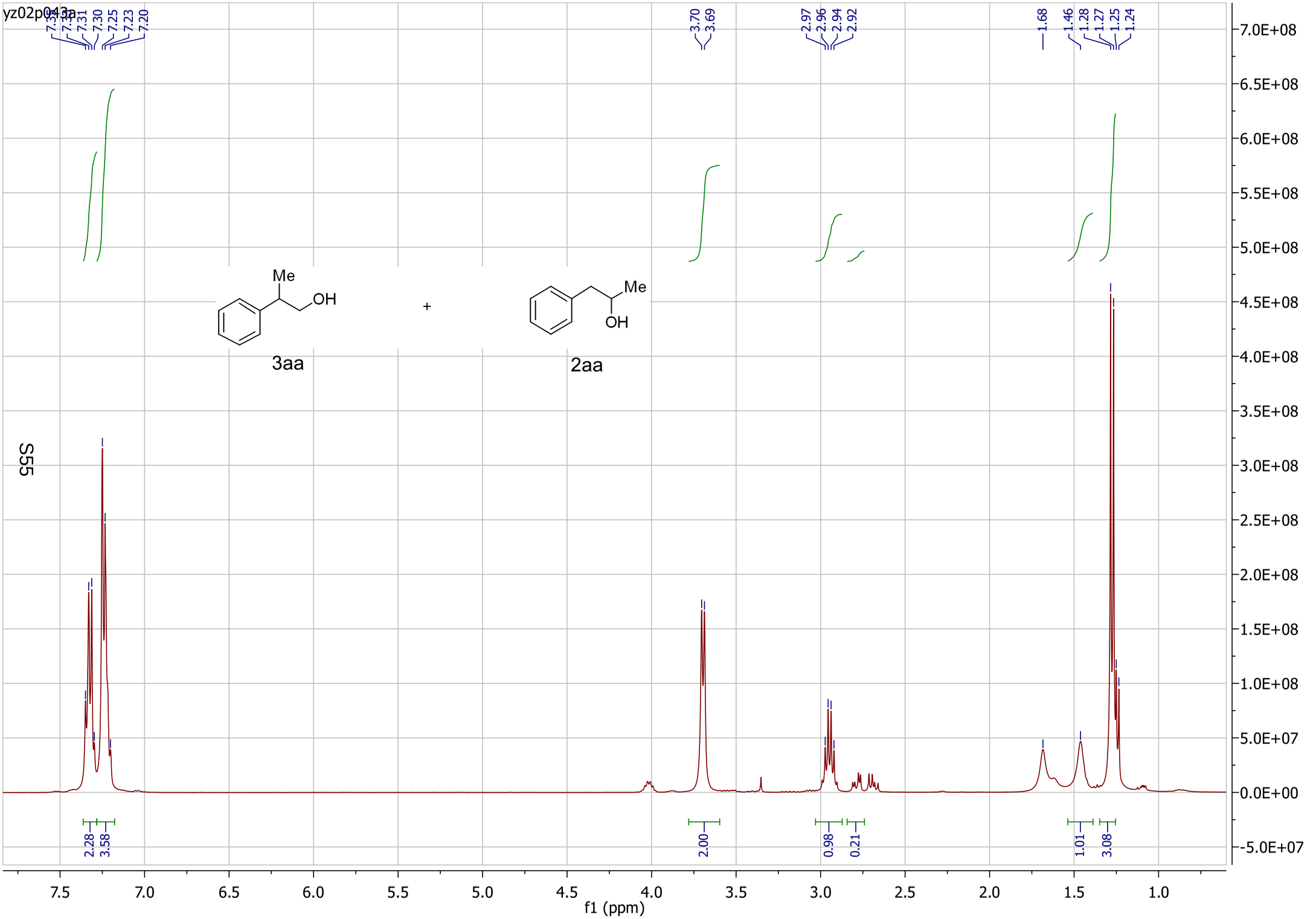

orthotoluene
136.83
136.65
130.50
130.15
126.63
126.04
77.38
77.06
76.74
67.96
42.96
22.99
19.68
S50
Me
Me
OH
2ja
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

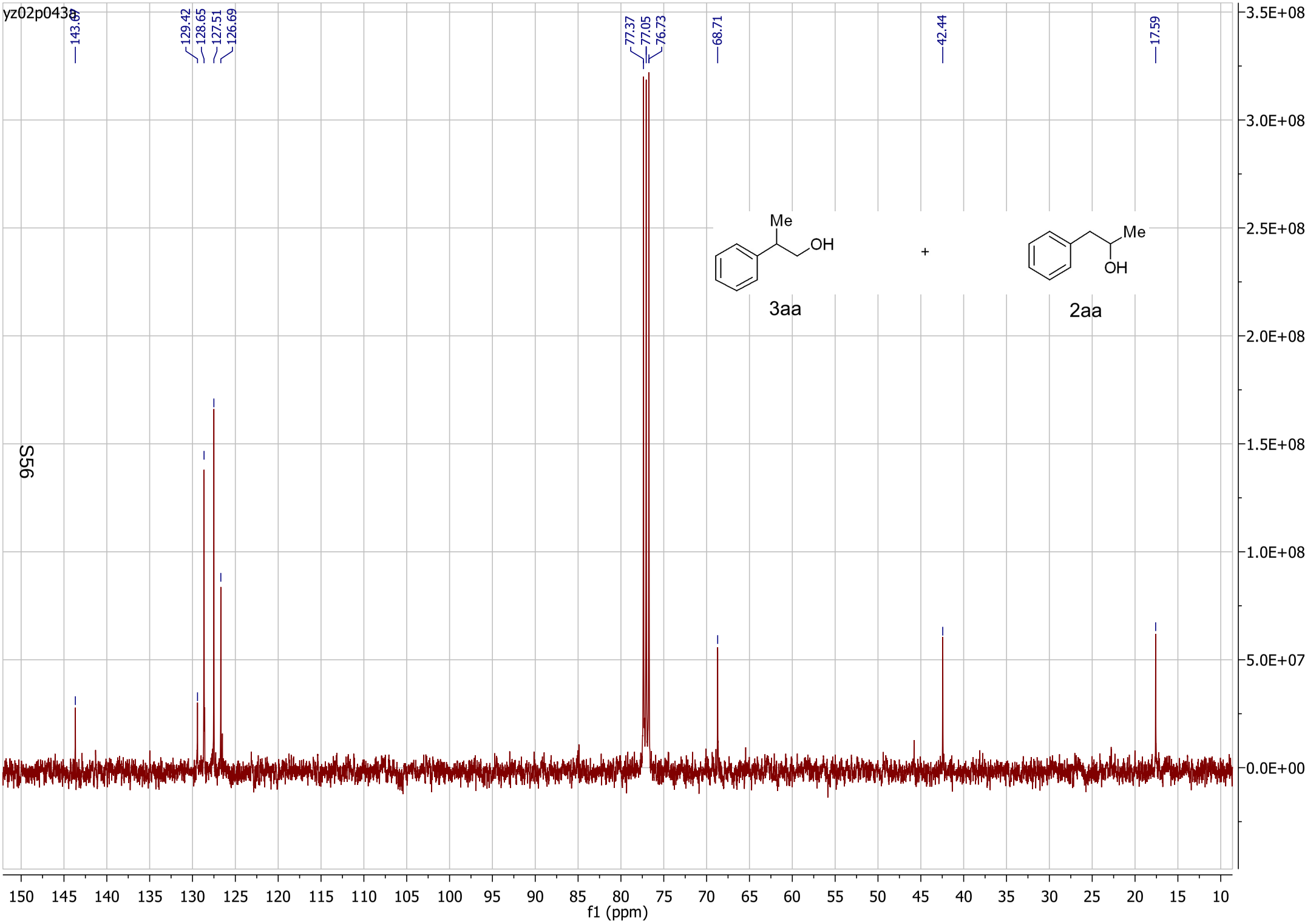

indole
8.35
8.33
7.39
7.39
7.25
7.20
7.20
7.18
7.17
6.59
6.58
4.07
4.05
4.04
4.02
2.90
2.88
2.86
2.85
2.79
2.77
2.75
2.73
2.61
1.74
1.69
1.26
1.24
Me
OH
N
O
Me
2ka
S51
0.91
1.95
1.00
0.94
0.99
2.05
2.96
1.04
3.31
f1 (ppm)

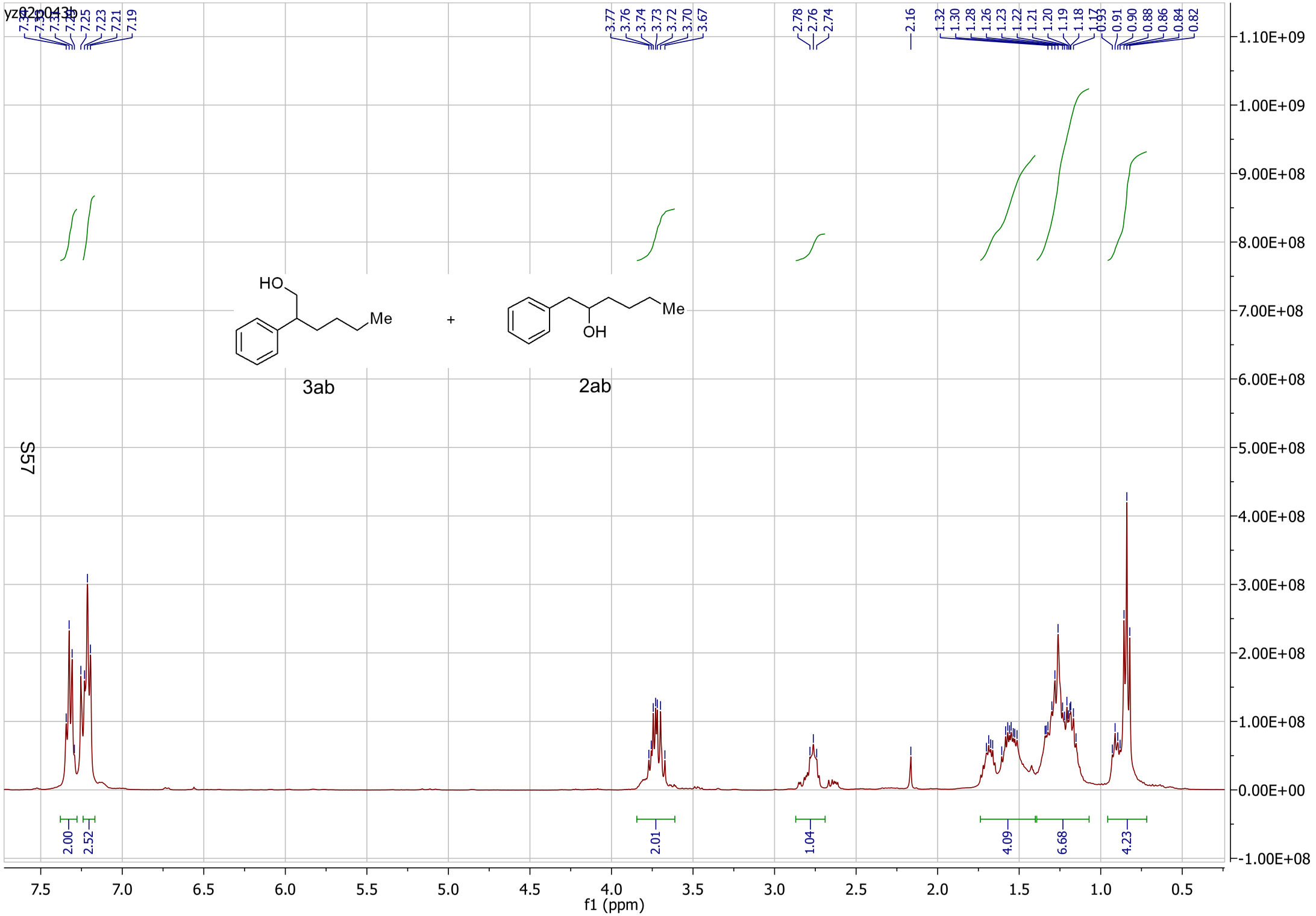

indole
168.45
134.39
133.89
130.78
126.54
125.56
121.41
116.54
109.02
77.38
77.06
76.74
69.09
45.68
23.90
22.77
Me
OH
N
O
Me
2ka
S52
4.0E+08
3.8E+08
3.6E+08
3.4E+08
3.2E+08
3.0E+08
2.8E+08
2.6E+08
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
-4.0E+07
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

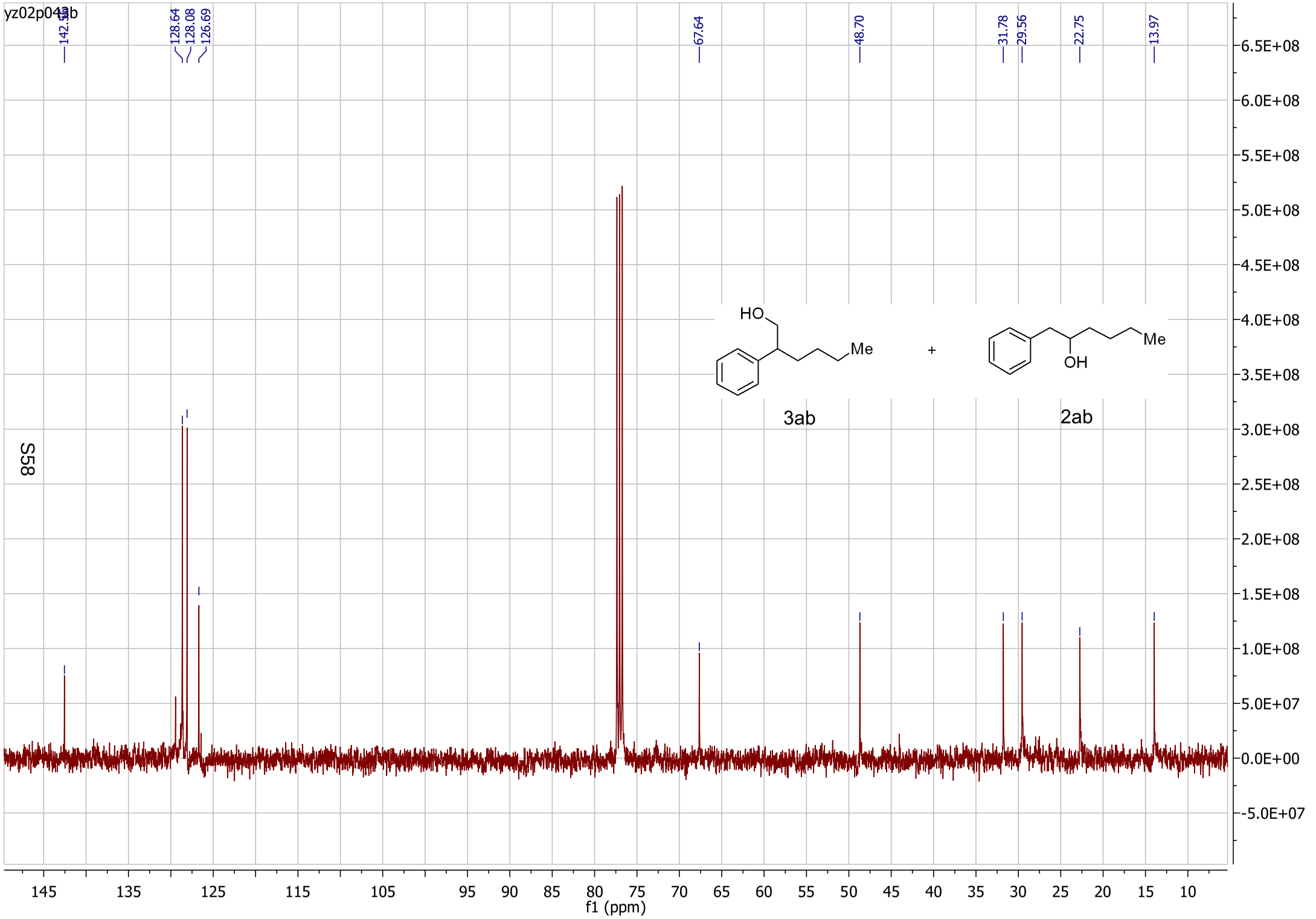

yz02p017d
7.25
5.50
3.87
3.86
3.85
3.84
3.84
3.83
3.82
2.09
2.08
2.06
2.05
2.02
2.00
1.96
1.88
1.86
1.84
1.82
1.78
1.64
1.62
1.61
1.60
1.59
1.58
1.57
1.56
1.56
1.55
1.54
1.54
1.53
1.17
1.15
Me
OH
2la and 2ma
S53
1.00
1.00
5.17
2.31
4.19
3.16
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
7.4
7.2
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
f1 (ppm)

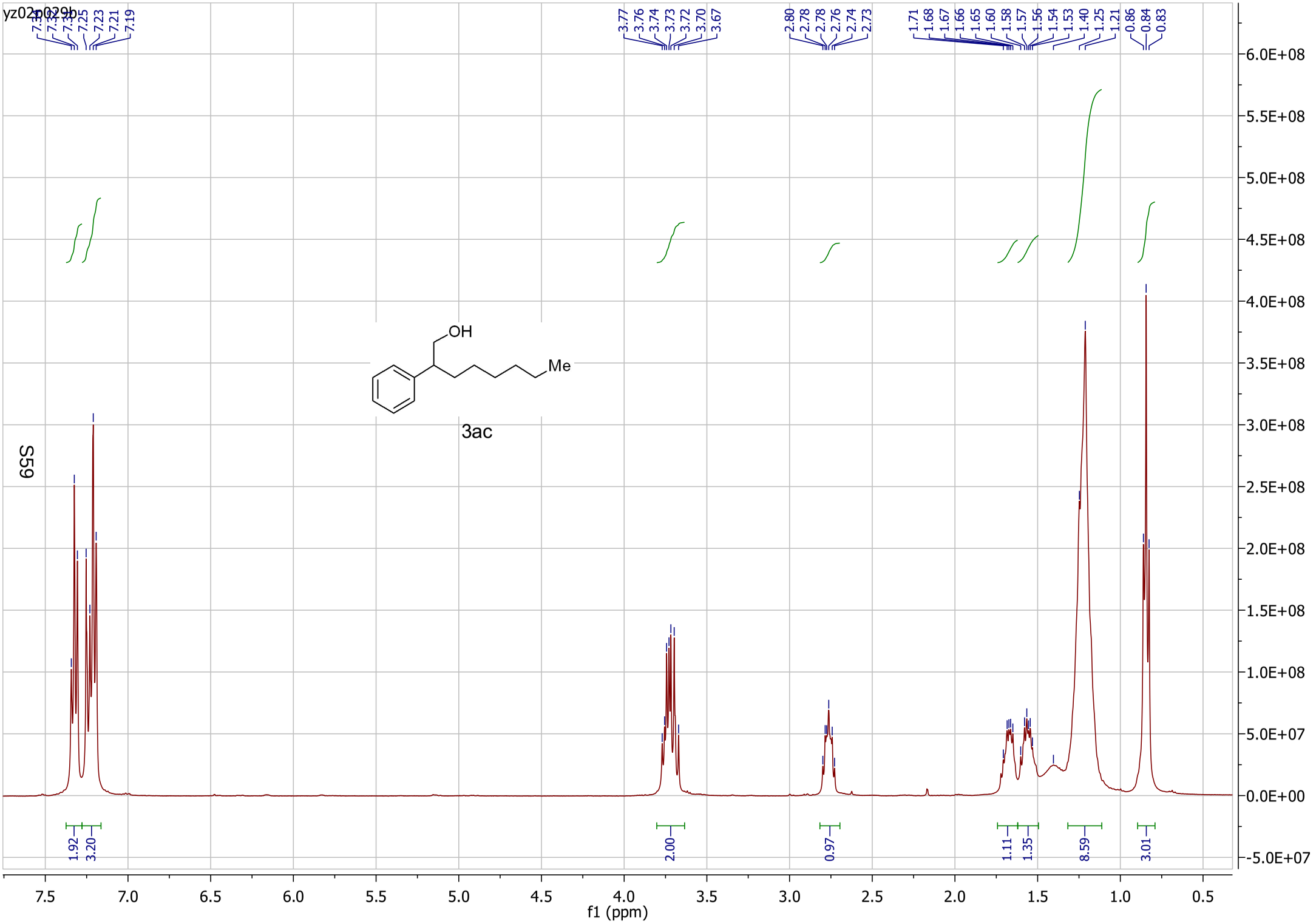

yz02p017d
134.83
124.86
77.36
77.04
76.72
64.86
48.35
28.35
25.25
22.85
22.80
22.33
Me
OH
2la and 2ma
S54
3.0E+08
2.8E+08
2.6E+08
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
-4.0E+07
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

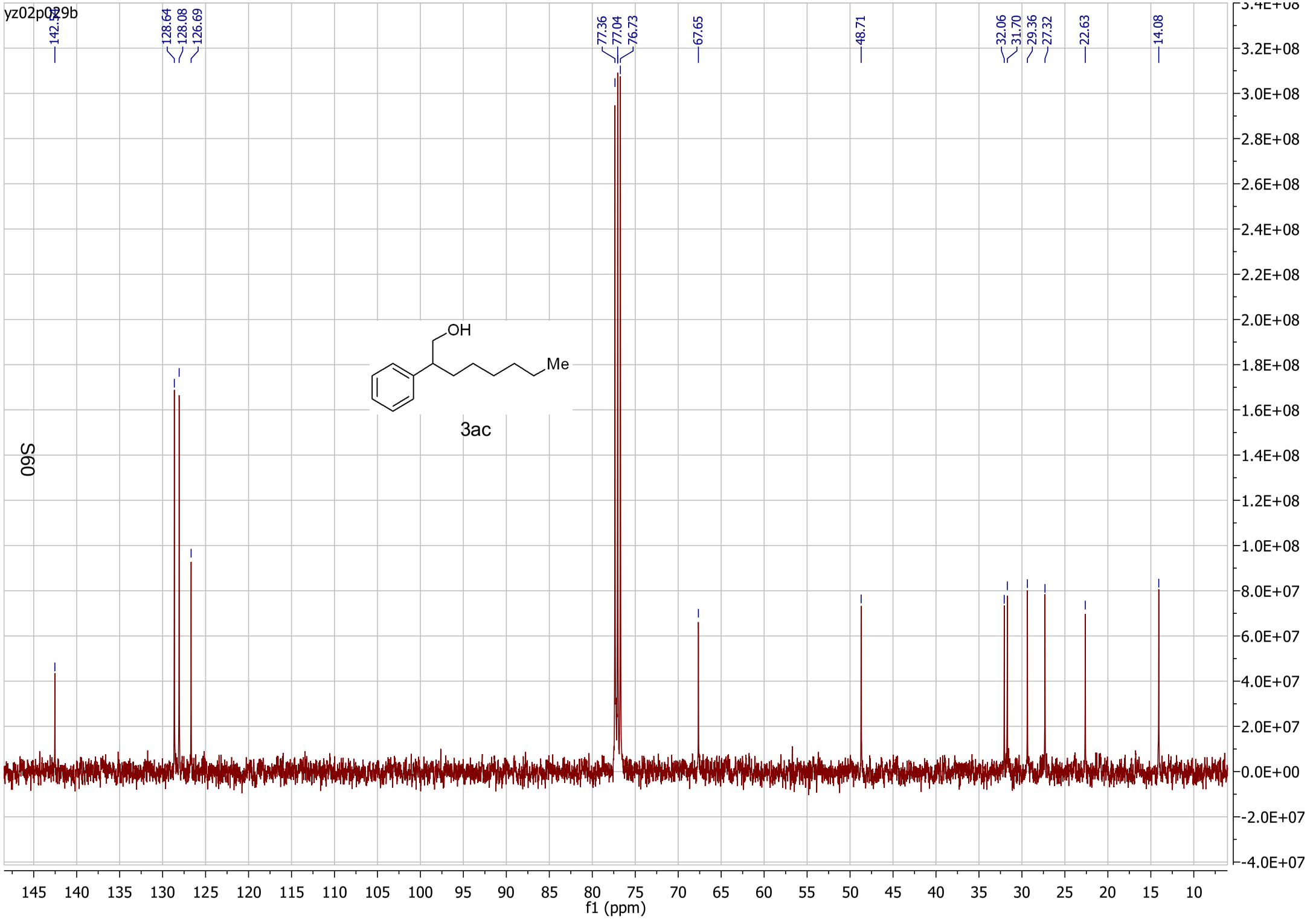

yz02p043a
7.35
7.33
7.31
7.30
7.25
7.23
7.20
3.70
3.69
2.97
2.96
2.94
2.92
1.68
1.46
1.28
1.27
1.25
1.24
Me
OH
3aa
+
Me
OH
2aa
S55
2.28
3.58
2.00
0.98
0.21
1.01
3.08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

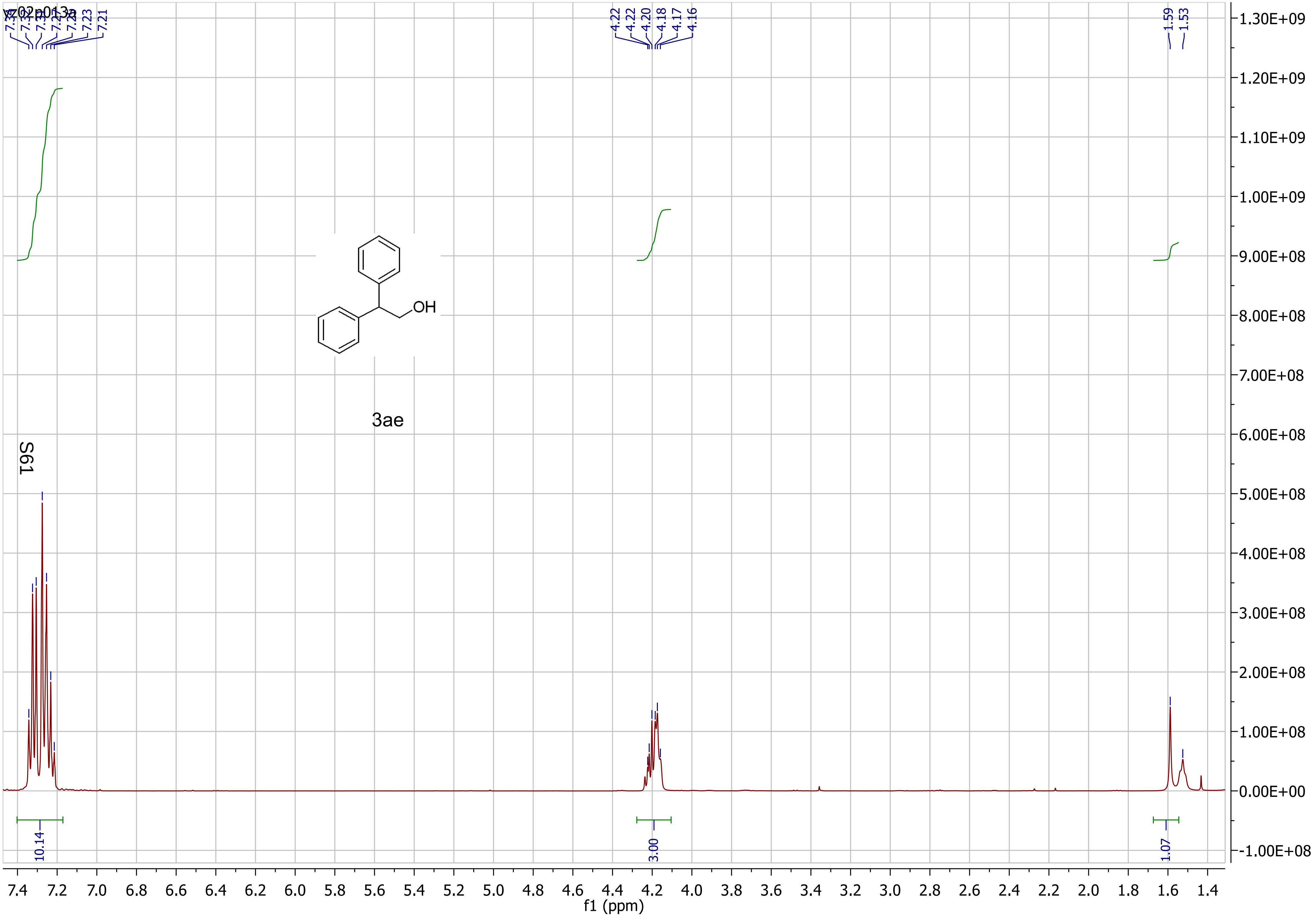

yz02p043a
143.87
129.42
128.65
127.51
126.69
77.37
77.05
76.73
68.71
42.44
17.59
Me
OH
3aa
+
Me
OH
2aa
S56
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)


yz82n043b
7.27
7.25
7.23
7.21
7.19
3.77
3.76
3.74
3.73
3.72
3.70
3.67
2.78
2.76
2.74
2.16
1.32
1.30
1.28
1.26
1.23
1.22
1.21
1.20
1.19
1.18
1.17
0.93
0.91
0.90
0.88
0.86
0.84
0.82
HO
Me
+
OH
Me
3ab
2ab
S57
2.00
2.52
2.01
1.04
4.09
6.68
4.23
1.10E+09
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
-1.00E+08
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
f1 (ppm)

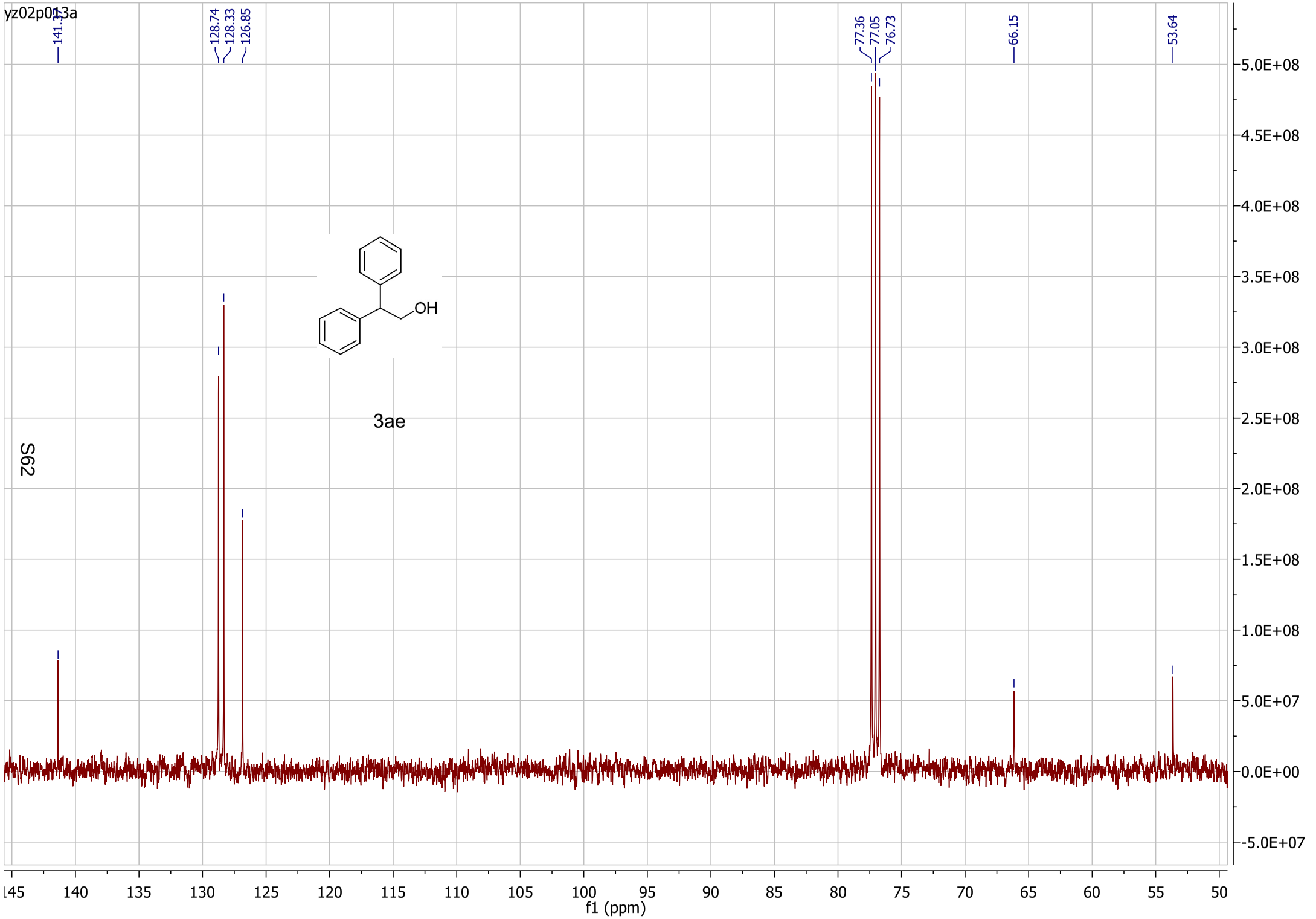

yz02p043b
142.53
128.64
128.08
126.69
67.64
48.70
31.78
29.56
22.75
13.97
HO
Me
3ab
+
Me
OH
2ab
S58
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

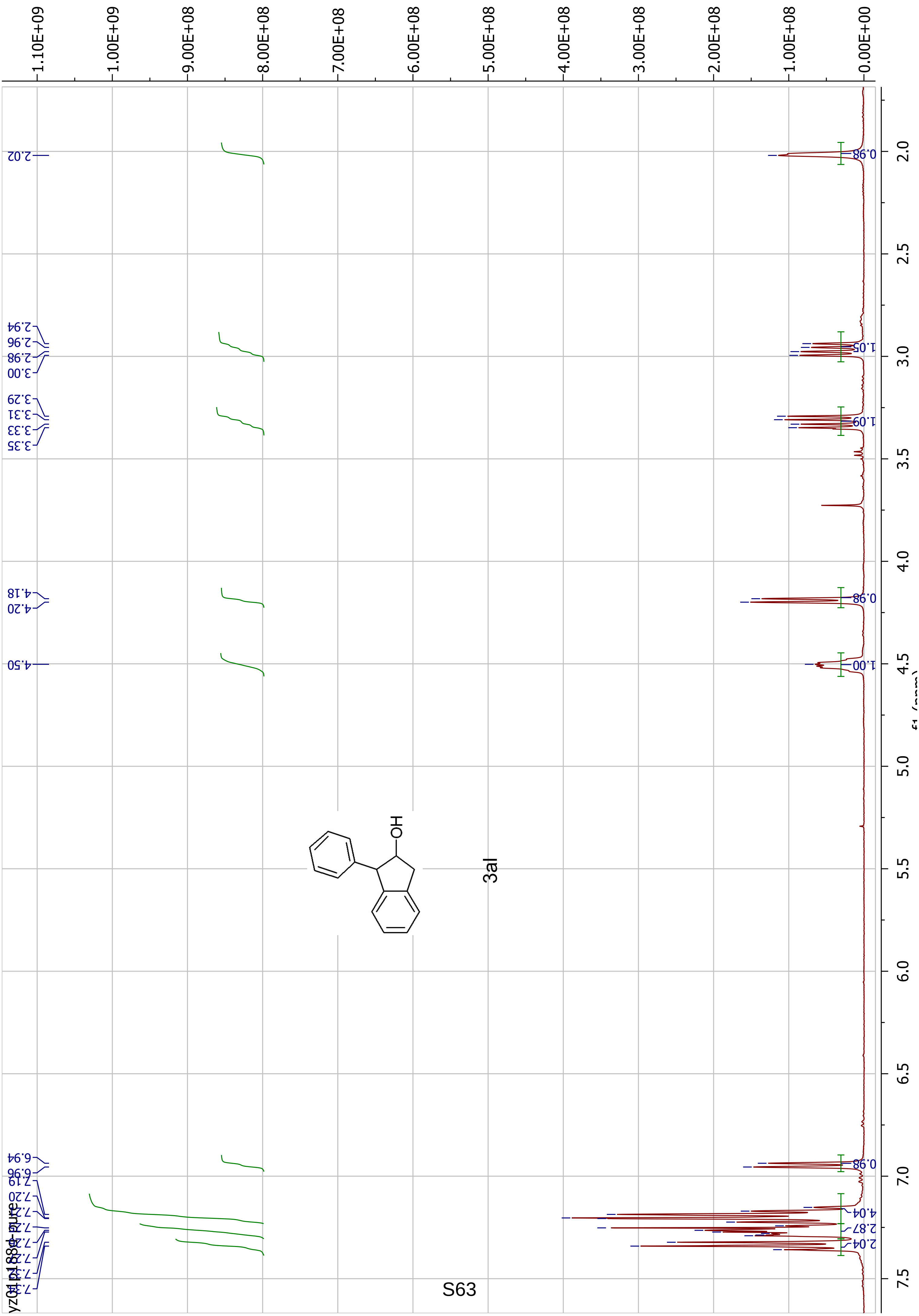

yz02p029b
7.25
7.23
7.21
7.19
3.77
3.76
3.74
3.73
3.72
3.70
3.67
2.80
2.78
2.78
2.76
2.74
2.73
1.71
1.68
1.67
1.66
1.65
1.60
1.58
1.57
1.56
1.54
1.53
1.40
1.25
1.21
0.86
0.84
0.83
OH
Me
3ac
S59
1.92
3.20
2.00
0.97
1.11
1.35
8.59
3.01
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
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
f1 (ppm)

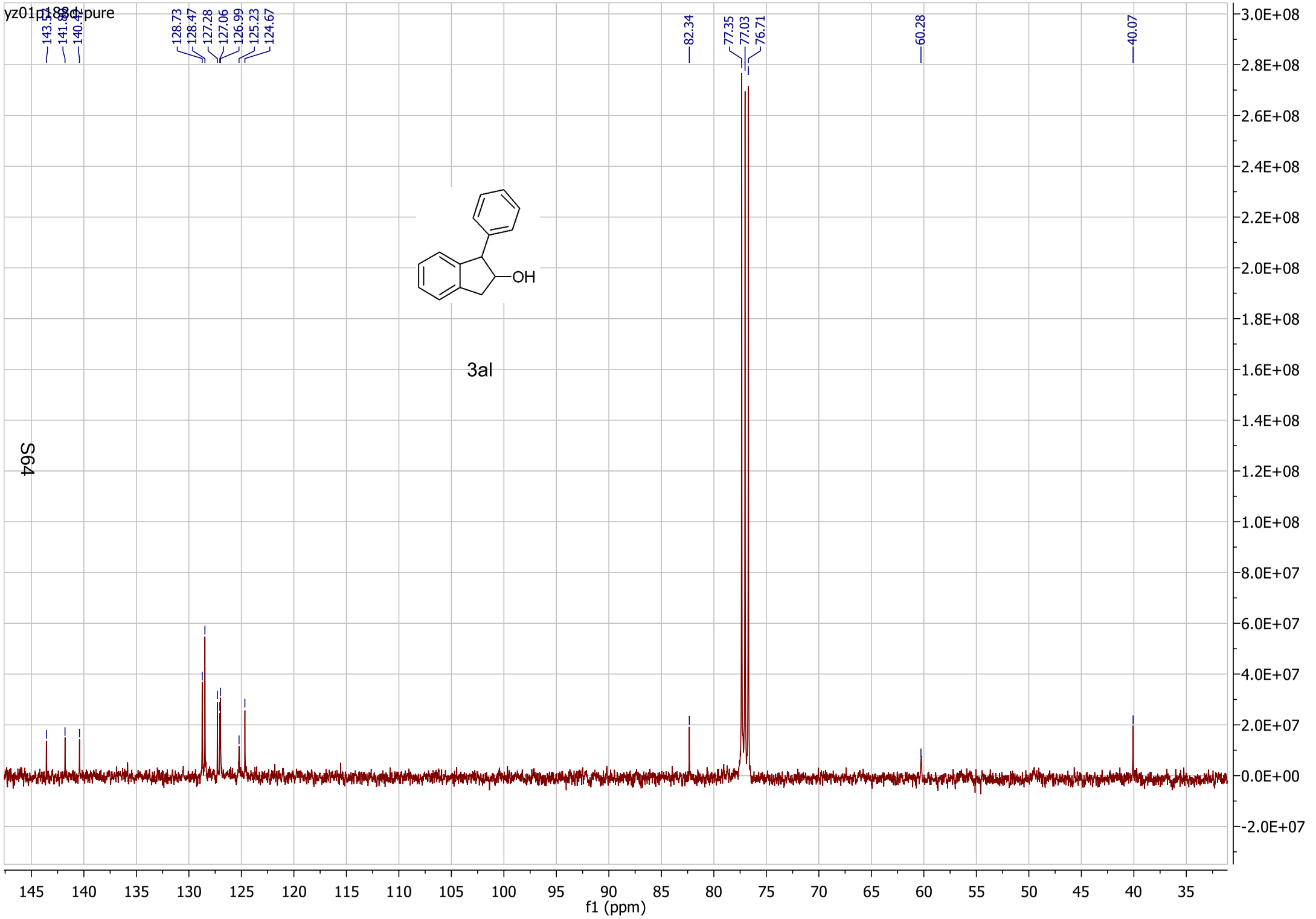

yz02p029b
142.47
128.64
128.08
126.69
77.36
77.04
76.73
67.65
48.71
32.06
31.70
29.36
27.32
22.63
14.08
OH
Me
3ac
S60
f1 (ppm)

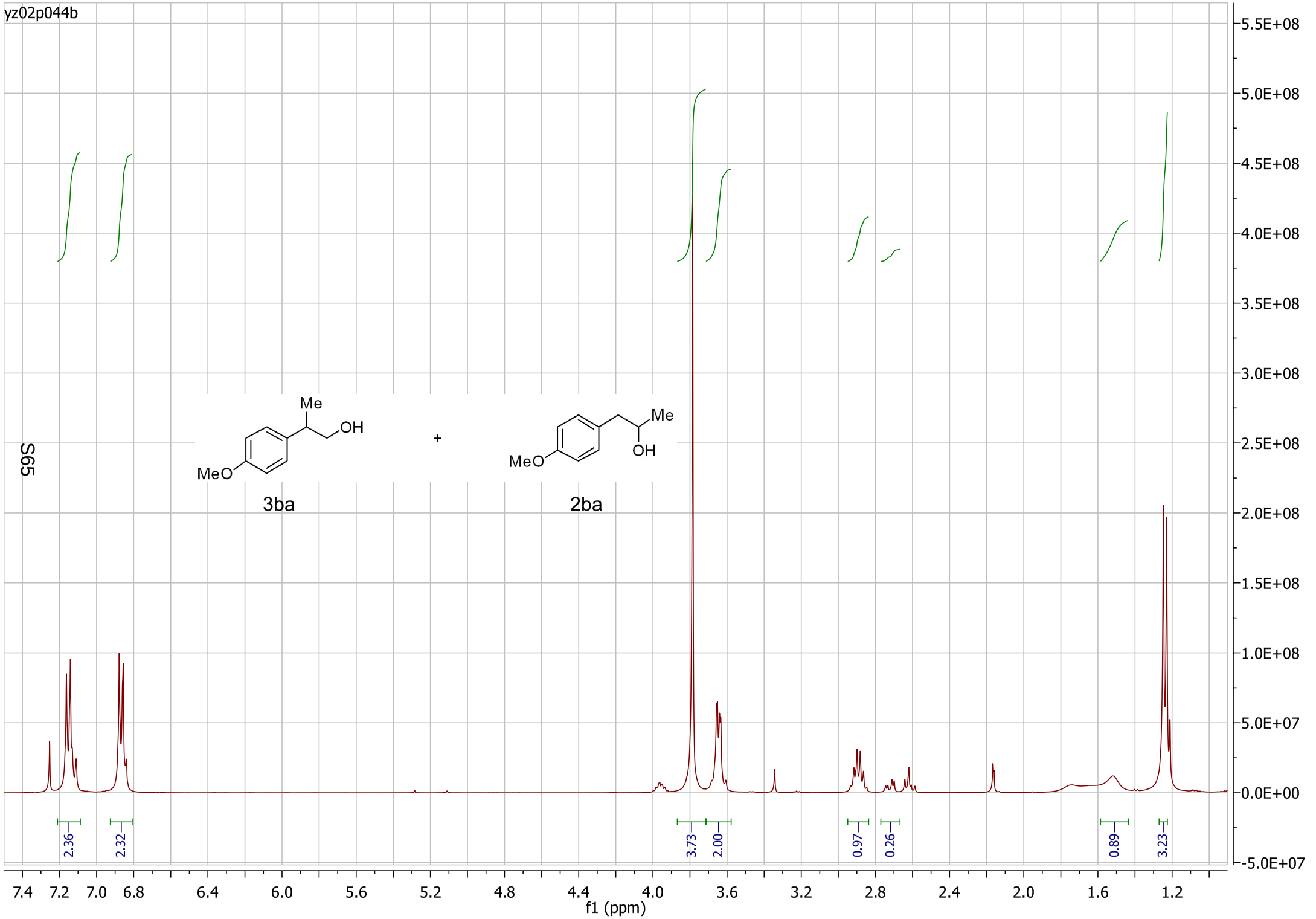


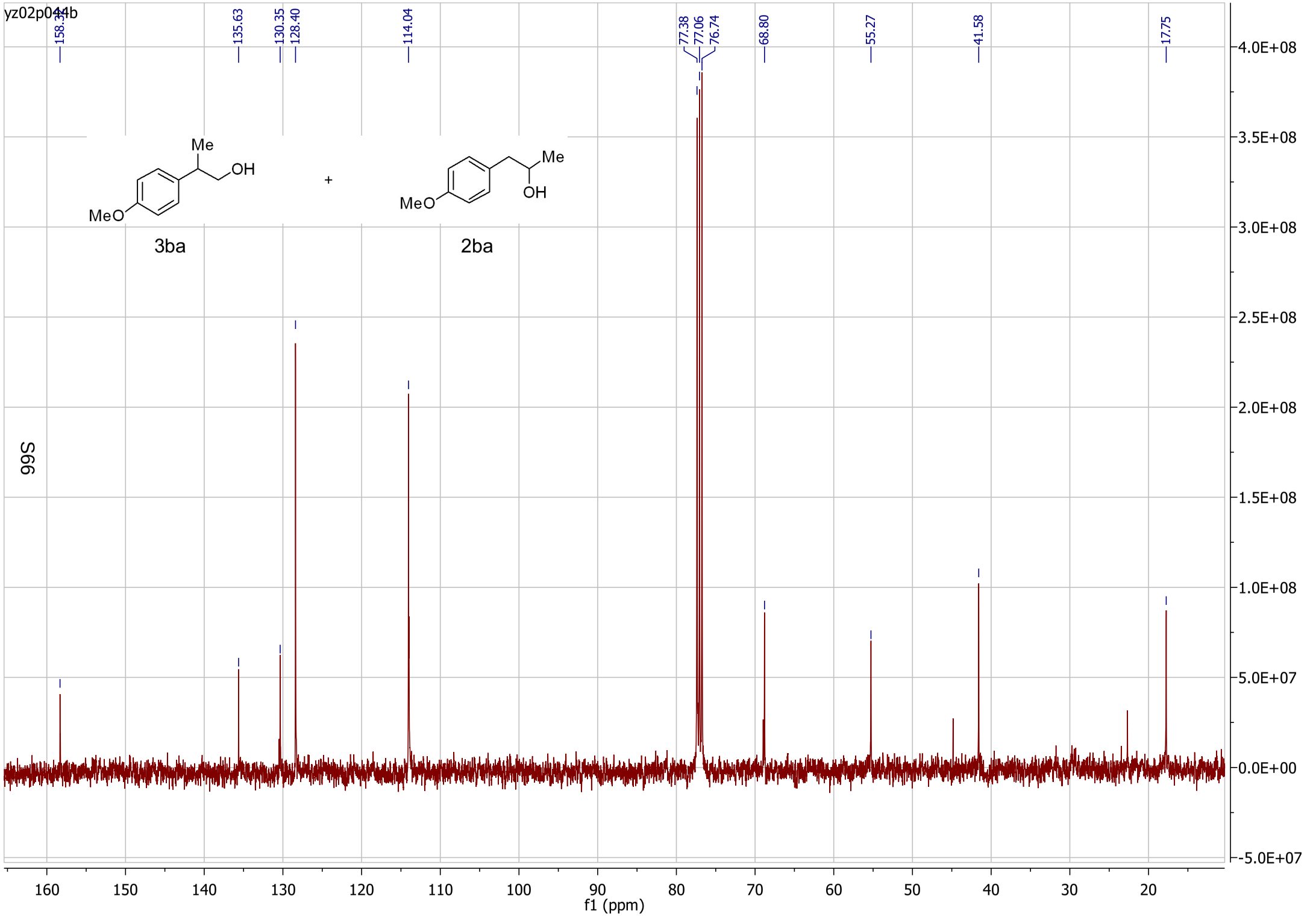
7.23
7.21
4.22
4.22
4.20
4.18
4.17
4.16
1.59
1.53
OH
3ae
10.14
3.00
1.07
f1 (ppm)

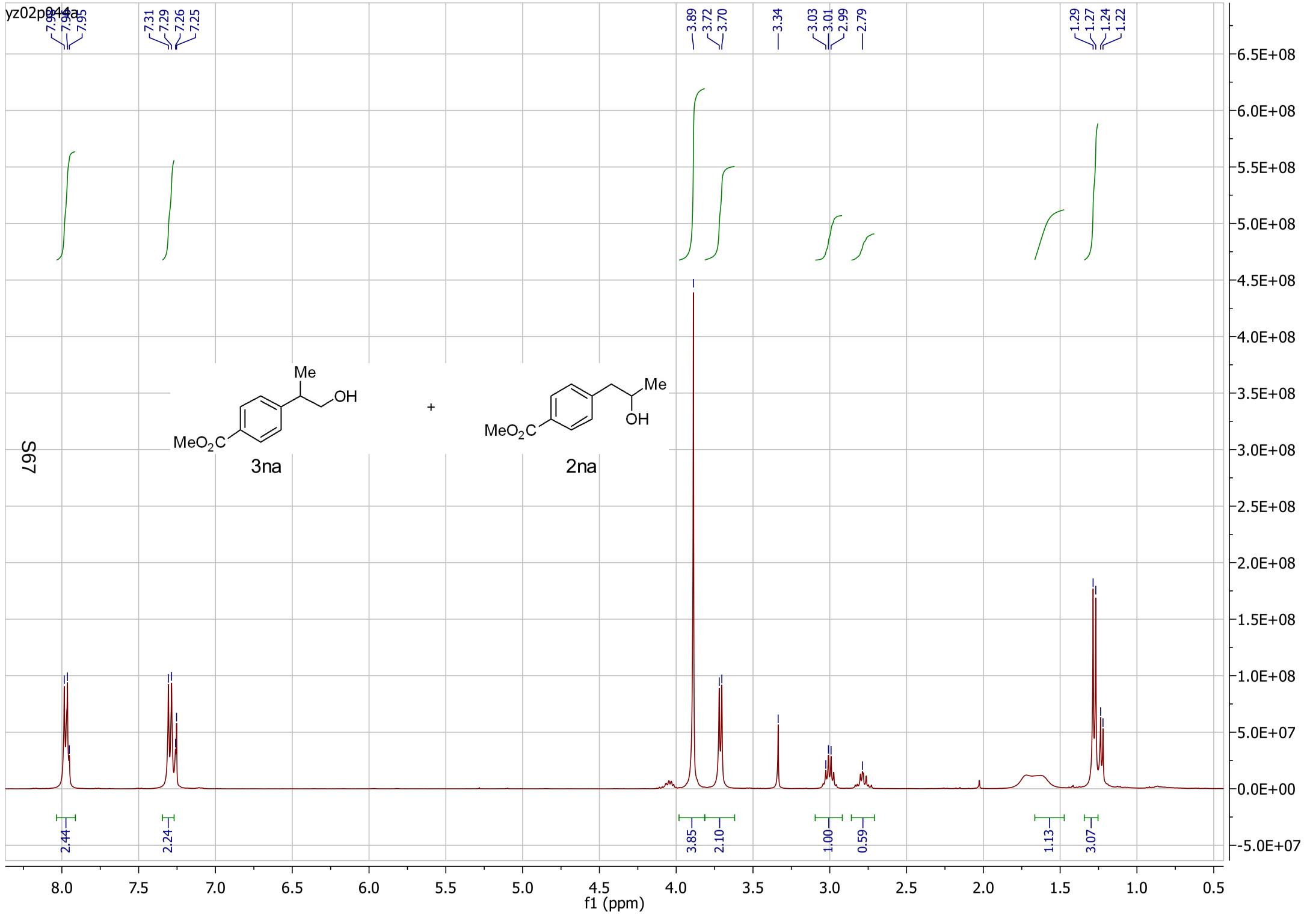

yz02p013a
141.37
128.74
128.33
126.85
77.36
77.05
76.73
66.15
53.64
OH
3ae
S62
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
f1 (ppm)

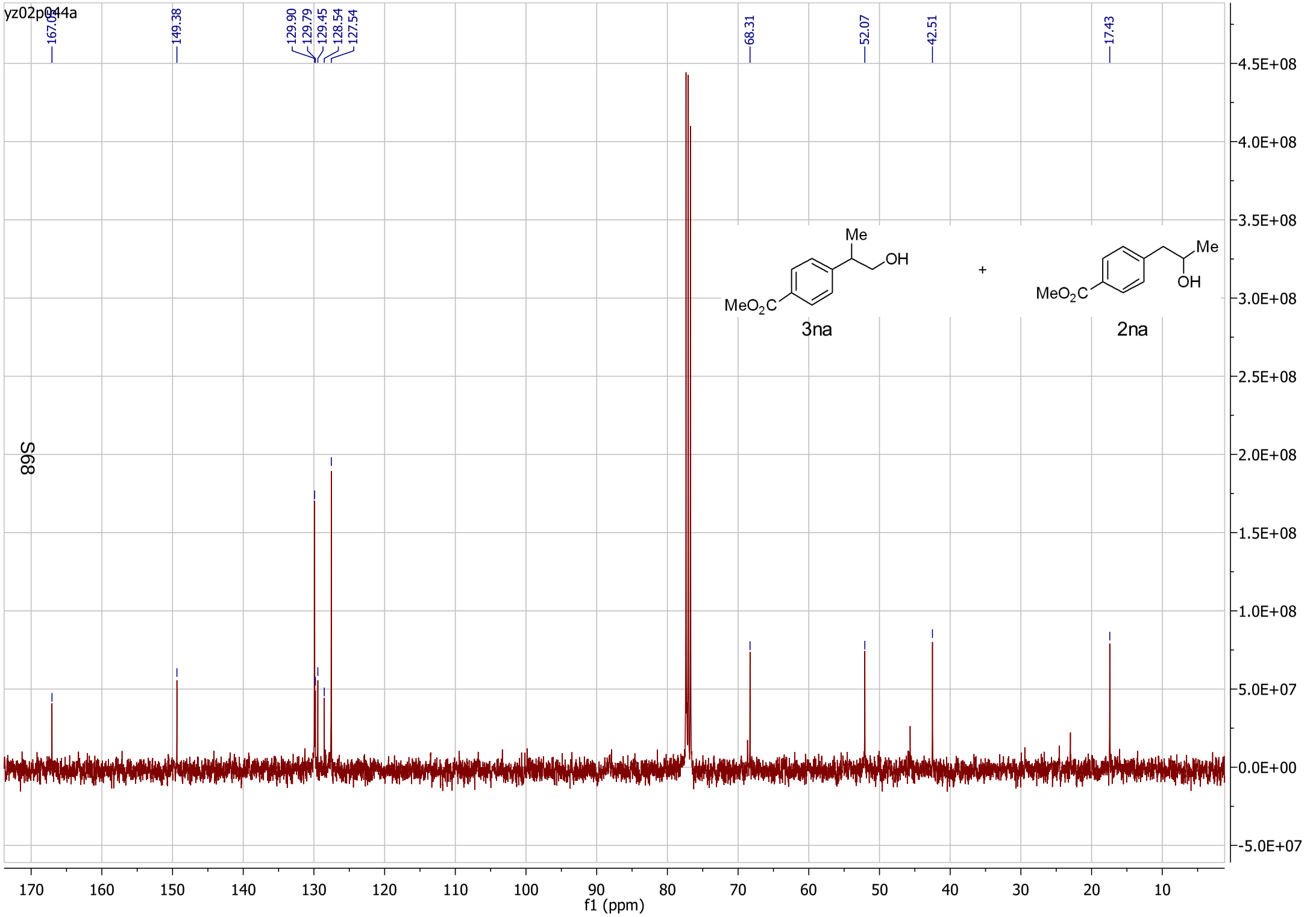

3al
OH
f1 (ppm)
2.02
2.94
2.96
2.98
3.00
3.29
3.31
3.33
3.35
4.18
4.20
4.50
6.94
6.96
7.19
7.20
0.98
1.05
1.09
0.98
1.00
0.98
4.04
2.87
2.04


yz01p188c1pure
143.73
141.89
140.42
128.73
128.47
127.28
127.06
126.99
125.23
124.67
82.34
77.35
77.03
76.71
60.28
40.07
OH
3al
S64
f1 (ppm)


yz02p044b
S65
Me
OH
MeO
3ba
+
Me
OH
MeO
2ba
2.36
2.32
3.73
2.00
0.97
0.26
0.89
3.23
7.4
7.2
7.0
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
f1 (ppm)
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07


yz02p044b
158.34
135.63
130.35
128.40
114.04
77.38
77.06
76.74
68.80
55.27
41.58
17.75
Me
OH
MeO
3ba
+
Me
OH
MeO
2ba
S66
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


yz02p044a
7.96
7.95
7.31
7.29
7.26
7.25
3.89
3.72
3.70
3.34
3.03
3.01
2.99
2.79
1.29
1.27
1.24
1.22
Me
OH
MeO2C
3na
+
Me
OH
MeO2C
2na
S67
2.44
2.24
3.85
2.10
1.00
0.59
1.13
3.07
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
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
f1 (ppm)


yz02p044a
167.05
149.38
129.90
129.79
129.45
128.54
127.54
68.31
52.07
42.51
17.43
Me
OH
MeO2C
3na
+
Me
OH
MeO2C
2na
S68
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)