Supporting Information

1-Bromo-1-lithioethene: a Practical Reagent for the Efficient Preparation of 2-Bromo-1-alken-3-ols.

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General. All manipulations were conducted under a dry argon atmosphere. All glassware used dried in vacuum (0.5 – 0.1 mmHg) for at least 1 h at rt. THF and ether were distilled from sodium/benzophenone immediately prior to use. LiBr was heated in a short test tube until it started to melt and then was cooled under a flow of argon. The same test tube fitted with a septum was used to prepare the LiBr solution. Bromoethene (Aldrich) was dried by passing it through a tube (200 mm length, 16 mm outer diameter) filled with $CaCl_2$ granules and was condensed in a small graduated test tube (cooled in an ice bath) fitted with a septum. The remaining solvents and reagents, including $CeBr_3$ (ultra dry, Alfa Aesar) and pentane (anhydrous, Acros), were used as supplied. Thin layer chromatography was performed using Whatman silica gel F-254 aluminium backed plates. Flash chromatographic separations were carried out on Fisher 170 – 400 mesh silica gel 60. Gas chromatography was performed on an HP 5890 Gas Chromatograph using an HP-1 capillary column (15 m × 0.53 mm, 1.5μm film). Melting point determinations were conducted on a Mettler FP52 hotstage. Unless otherwise stated, NMR spectra were recorded on a Bruker AMX 300 spectrometer in $CDCl_3$ as follows: ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz). Chemical shifts are reported relative to Me_4Si (δ 0.0) for ^1H NMR and chloroform (δ 77.0) for ^{13}C NMR spectra.

Low temperature reactor design.

A low temperature glass reactor was constructed to allow easy addition of cold solutions and slurries to a reaction mixture at uniform (± 5 °C) temperatures as low as –127 °C (see Figure 1). All parts of the reactor contacting with all solutions during an experiment were beneath the level of the stirred coolant. The entire setup, which includes the reactor equipped with a mechanical stirrer (450 rpm) and a thermometer, a coolant bath stirrer (450 rpm) and a heat exchanger,[1] was inserted in a standard Dewar flask (120 mm inner diameter, 190 mm inside depth, 1.9 L volume) filled with methylcyclohexane. The reactor was cooled by addition of liquid nitrogen into the heat exchanger.

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[1] A large glass test tube (30 mm outer diameter, 200 mm length) inserted into the coolant and filled with liquid nitrogen was used as a heat exchanger. It is much safer to pour liquid nitrogen into the heat exchanger than directly into the methylcyclohexane coolant. This completely removes the dangerous freezing of the top layer of the coolant which otherwise becomes a problem below –95 °C. This freezing blocks the rotation of the coolant bath stirrer, isolates the coolant from the next portion of the liquid nitrogen and creates unsafe stresses within the entire setup. The typical cooling time with the heat exchanger was 30-45 min.

A photograph of the entire setup is presented in Figure 2.

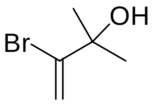
Operating the unit requires two argon lines from a standard manifold. A mercury manometer in the argon line is highly desirable. The usual working argon pressure was 10-30 mmHg above atmospheric pressure. One argon line was attached directly to the *main argon inlet* of the unit. The second argon line was attached through a flow regulator[2] to the *auxiliary argon inlet* of the unit.

There are three modes for operation of the reactor:

1. Waiting – both bubblers are open;
2. Addition – the *auxiliary bubbler* is stopped and the *main bubbler* is open; the rate of addition of the *side tube* contents can be regulated by the auxiliary argon flow regulator;
3. *Side tube* content stirring – the *main bubbler* is stopped and the *auxiliary bubbler* is open. In this mode argon bubbling through the side tube prevents particulate material from sedimentation and clogging the *capillary tube* of the unit.

It is important to use a mechanical stirrer inside of the main flask because of the considerable viscosity of the reaction mixture at the low reaction temperature employed.

The maximum capacity of the *side tube* of the reactor is 30 mL while the total useful volume of the reactor is 100 mL. Thus, the molar amount of *n*-BuLi that can be added in one pass is limited to ca 14 mmol (2.0 M solution of *n*-BuLi in pentane was typically used). This allows for the preparation of up to maximum 12 mmol (for method A; 6 mmol for method B) of the final addition product.



1a

General Procedure A: Reaction of 1-bromo-1-lithioethene (2) with acetone – preparation of 3-bromo-2-methylbut-3-en-2-ol (**1a**).

A solution of bromoethene (3.0 mL, 42.5 mmol), lithium bromide (0.23 g, 3.2 mmol) and the Trapp mixture (THF : ether : pentane, 4 : 1 : 1 by volume) (20 mL) was placed into the central flask of the low temperature reactor described above. A mixture of anhydrous THF (21 mL) and anhydrous ether (7 mL) was placed into the side tube. The reactor was cooled down to –70 ^{o}C (methylcyclohexane / liquid N_2) and *n*-butyllithium (8.1 mL, 16.1 mmol, 2M in pentane, Aldrich) was added to the side tube. The main bubbler was temporarily stopped for *ca.* 10 sec (argon started to bubble through the side tube mixing the contents of the side tube) and then the unit was further cooled down with liquid nitrogen to –110 ^{o}C. At this point the

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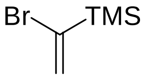
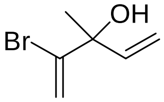
[2] A piece of a capillary tube from a laboratory thermometer with an attached bypass stopcock was actually used: see bottom of Figure 1.

auxiliary bubbler was stopped and the contents of the side tube were slowly transferred to the main flask with argon pressure. (To achieve good yields this addition should be done over 15 - 45 min.) The side tube was washed with the Trapp mixture (2 x 1.5 mL). The white viscous reaction mixture was stirred for 45 min at –110 to –108 ^{o}C and a solution of acetone (1.0 mL, 14 mmol) in the Trapp mixture (10 mL) was placed into the side tube. After thermal equilibration (usually 5-10 min), the contents of the side tube were transferred as described above to the central flask over 2-15 min. (The time for this addition was not so critical). The reaction mixture was stirred at –100 to –105 ^{o}C for 1 h. A solution of acetic acid (1.05 mL, 1.25 mmol) in the Trapp mixture (15 mL) was placed into the side tube and, five minutes later, it was transferred into the central flask. The cooling bath was removed and the contents were transferred to a separatory funnel. The organic layer was washed with 4% aq $NaHCO_3$ (10 mL), brine (10 mL), dried ($MgSO_4$) and concentrated at atmospheric pressure. Vacuum distillation gave 3-bromo-2-methylbut-3-en-2-ol (**1a**) (1.79 g, 77%) as a colorless liquid which was 99.5% pure by GC, b.p. 53 ^{o}C at 17mmHg. ^{1}H NMR δ 1.49 (s, 6H), 2.10 (br s, 1H, OH), 5.49 (d, J=2.3 Hz, 1H), 5.89 (d, J=2.3 Hz, 1H); ^{13}C NMR δ 28.7, 74.1, 115.2, 142.7.

Each of the following compounds was prepared from the indicated electrophile following General Procedure A and was purified by vacuum distillation to afford a colorless oil. The purity of the distilled materials were determined by GC analysis.



(1-Bromoethenyl)trimethylsilane: prepared from chlorotrimethylsilane (no acetic acid quench was performed) in 64% yield, bp 54-57 ^{o}C at 70 mmHg. The product was contaminated by 11% THF and 3.8% bis-trimethylsylylethyne (by ^{1}H NMR analysis). ^{1}H and ^{13}C NMR spectra were closely similar to the published data.[3]



1b

2-Bromo-3-methylpenta-1,4-dien-3-ol (**1b**): prepared from 3-buten-2-one in 78% yield, bp 63 ^{o}C at 14 mmHg, GC purity was 98%. ^{1}H NMR δ 1.55 (s, 3H), 2.36 (s, 1H, OH), 5.22 (dd, J=10.6, 0.9 Hz, 1H), 5.39 (dd, J=17.3, 0.9 Hz, 1H), 5.57 (d, J=2.3 Hz, 1H), 5.94 (d, J=2.3 Hz, 1H), 6.01 (dd, J=17.3, 10.6 Hz, 1H); ^{13}C NMR δ 26.8, 76.2, 114.6, 116.8, 140.3, 141.6.

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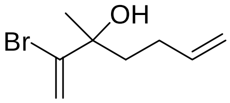
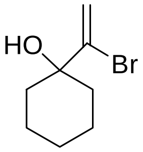
[3] Dawson, I. M.; Gregory, J. A.; Herbert, R. B.; Sammes, P. G. *J. Chem. Soc. Perkin Trans. 1* **1988**, 2585-2594; Kamienska, T. K.; Biedrzycka, Z.; Dabrowski, A. *Magn. Reson. Chem.* 1991, *29*, 1216-1220.



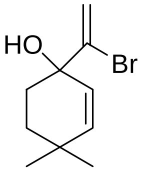
1c

2-Bromo-3-methylhepta-1,6-dien-3-ol (**1c**): prepared from 5-hexen-2-one in 84% yield, bp 89-91°C at 14 mmHg, a single peak by GC analysis. ^{1}H NMR δ 1.46 (s, 3H), 1.73 (ddd, J=13.8, 9.6, 7.1 Hz, 1H), 1.89 (ddd, J=13.8, 9.5, 6.2 Hz, 1H), 2.03-2.15 (m, 2H), 2.30 (br s, 1H, OH), 4.98 (dm, J=10.1 Hz, 1H), 5.05 (ddd, 17.2, 3.2, 1.6 Hz, 1H), 5.56 (d, J=2.1 Hz, 1H), 5.83 (ddt, J=16.9, 10.3, 6.7 Hz, 1H), 5.92 (dd, J=2.1, 0.36 Hz, 1H); ^{13}C NMR δ 27.2, 28.5, 39.4, 76.8, 115.2, 116.5, 138.5, 140.6.



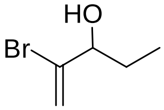
1d

1-(1-Bromoethenyl)cyclohexanol (**1d**): prepared from cyclohexanone in 85% yield, bp 62°C at 1 mmHg, GC purity was 98.8%. ^{1}H NMR δ 1.18-1.30 (m, 1H), 1.53-1.79 (m, 9H), 1.94 (s, 1H, OH), 5.55 (d, J=2.3 Hz, 1 H), 5.90 (d, J=2.3 Hz, 1H); ^{13}C NMR δ 22.0, 25.6, 36.1, 74.6, 115.6, 143.7.



1e

1-(1-Bromoethenyl)-4,4-dimethylcyclohex-2-enol (**1e**): prepared from 4,4-dimethylcyclohex-2-enone in 80% yield, bp 64-65°C at 1 mmHg, GC purity was 96%. ^{1}H NMR δ 0.99 (s, 3H), 1.03 (s, 3H), 1.44 (ddd, J=13.2, 9.7, 3.3 Hz, 1H), 1.59 (dddd, J=13.6, 8.5, 3.1, 0.5 Hz, 1H), 1.73 (ddd, J=13.2, 9.6, 3.2 Hz, 1H), 2.11 (dddd, J=13.4, 8.5, 3.3, 0.8 Hz), 2.49 (s, OH, 1H), 5.50 (d, J=10.0 Hz, 1H), 5.59 (d, J=2.0 Hz, 1H), 5.67 (d, J=10.0 Hz, 1H), 5.90 (d, J=2.0 Hz, 1H); ^{13}C NMR δ 27.8, 28.7, 28.9, 32.2, 33.4, 74.3, 118.0, 126.7, 140.7, 142.2.



1f

2-Bromopent-1-en-3-ol (**1f**)[4]: prepared from propanal in 46% yield, bp 67-69°C at 14 mmHg, GC purity was 99%. ^{1}H NMR δ 0.92 (t, J=7.5 Hz, 3H), 1.62-1.75 (m, 2H), 2.41 (s, 1H, OH), 4.02 (td, J=6.5, 0.7 Hz, 1H), 5.57 (d, J=1.9 Hz, 1H), 5.87 (dd, J=1.9, 0.8 Hz, 1H); ^{13}C NMR δ 9.6, 28.3, 77.5, 117.3, 137.3.

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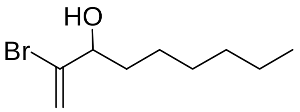
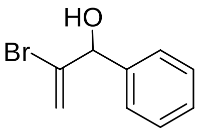
[4] Marshall, J. A.; DuBay, W. J. *J. Org. Chem.* **1993**, *58*, 3435-3443.



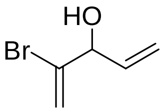
1g

2-Bromonon-1-en-3-ol (**1g**): prepared from heptanal in 50% yield, bp 78-80^{o}C at 0.6 mmHg, a single peak by GC analysis. ^{1}H NMR δ 0.88 (t, J=6.2 Hz, 3H), 1.20-1.45 (m, 8H), 1.55-1.75 (m, 2H), 2.50 (br s, 1H, OH), 4.07 (t, J=6.2 Hz, 1H), 5.54 (dd, J=1.8, 0.9 Hz, 1H), 5.86 (dd, J=1.9, 0.8 Hz, 1H); ^{13}C NMR δ 14.2, 22.7, 25.3, 29.1, 31.9, 35.4, 76.2, 117.0, 137.8.



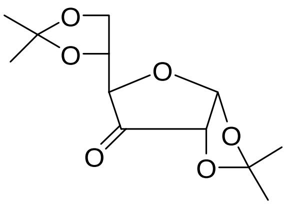
1h

2-Bromo-1-phenylprop-2-en-1-ol (**1h**)[5]: prepared from benzaldehyde in 81% yield, bp 87-88^{o}C at 0.6 mmHg, GC purity was 99.5%. ^{1}H NMR δ 2.74 (br s, OH, 1H), 5.20 (s, 1H), 5.64 (d, J=2.0 Hz, 1H), 6.00 (ddd, J=1.9, 1.1, 0.2 Hz, 1H), 7.30-7.38 (m, 5H); ^{13}C NMR: 78.0, 117.9, 126.9, 128.6, 128.7, 135.8, 139.9.



1i

2-Bromo-penta-1,4-dien-3-ol (**1i**): prepared from acrolein in 74% yield, bp 67^{o}C at 14 mmHg, GC purity was 98.6%. ^{1}H NMR δ 2.64 (br s, OH, 1H), 4.67 (br d, J=5.5 Hz, 1H), 5.30 (dt, J=10.4, 1.3 Hz, 1H), 5.42 (dt, J=17.2, 1.3 Hz, 1H), 5.60 (dd, J=2.0, 0.3 Hz, 1H), 5.90 (ddd, J=17.2, 10.3, 5.6 Hz, 1H), 5.96 (dd, J=2.0, 1.0 Hz, 1H); ^{13}C NMR δ 76.7, 117.6, 117.8, 135.3, 136.9.



3

1,2:5,6-Di-O-(1-methylethylidene)-α-D-ribo-3-hexulofuranose (**3**)[6]**:** 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (5.10 g, 20 mmol), 3Å powdered molecular sieves (18 g, Alfa Aesar brand; activated at 350 ^{o}C for 12 h) and PCC (10.6 g, 48.9 mmol) was stirred in dichloromethane (50mL) for 17 h at rt. Most of the

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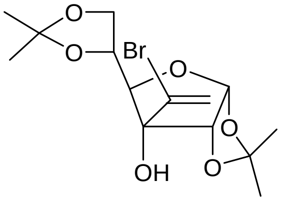
[5] Mori, M.; Chiba, K.; Okita, M.; Kayo, I.; Ban, Y. *Tetrahedron* **1985**, *41*, 375-385.

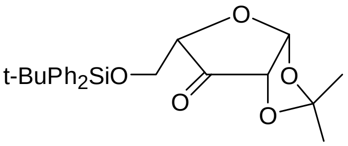
[6] The title compound was described in the literature many times. Nevertheless, in our hands, most known methods gave the product contaminated with pyridine, acetic acid and other polar admixtures. The present method is a modification of the procedure described by Herscovici and Antonakis: Herscovici, J.; Antonakis, K. *J. Chem. Soc. Chem. Commun.* **1980**, 561-562.

dichloromethane was removed under vacuum (100 mmHg) and anhydrous ether (100 mL) was added to the brown residue. The mixture was stirred 2 h at rt (no large pieces of solid should remain at this point) and petroleum ether (100 mL) was added. The slurry was promptly filtered through a short pad of silica (predried at 150°C for 12 h because **3** is extremely hygroscopic) and the solid was washed with 1:1 petroleum ether : anhydrous ether (2 x 50 mL). Concentration *in vacuo* gave 4.02 g (79%) of **3** as a clear oil which was sufficiently clean by ^{1}H NMR analysis to be used directly in the next step. ^{1}H NMR δ 1.34 (s, 6H), 1.44 (br d, J=0.5 Hz, 3H), 1.46 (s, 3H), 4.00-4.05 (m, 2H), 4.33-4.43 (m, 3H), 6.15 (d, J=4.5 Hz, 1H, H-1); ^{13}C NMR δ 25.4, 26.1, 27.3, 27.7, 64.4, 76.5, 77.4, 79.1, 103.2, 110.4, 114.3, 209.0.



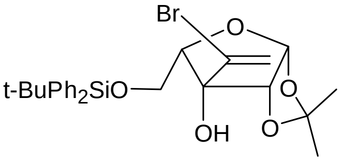
4

General Procedure B: reaction of 1-bromo-1-lithioethene with (3) – preparation of 3-C-(1-bromoethenyl)-1,2:5,6-bis-O-(1-methylethylidene)-α-D-allofuranose (4): Anhydrous $CeBr_3$ (0.588 g, 1.55 mmol) was stirred in the Trapp mixture (14 mL) for 4 h at rt. Bromoethene (5.45 ml, 77.4 mmol), lithium bromide (0.35 g, 4.2 mmol) and the Trapp mixture (18 mL) were placed into the central flask of the low temperature reactor (described above). Anhydrous ether (10 mL) and anhydrous THF (10 mL) were placed into the side tube. The low temperature reactor was cooled down to –60 °C (methylcyclohexane was used as coolant) and the first half of *n*-butyllithium (9.7 mL, 19.4 mmol, 2.0 M in pentane, Aldrich) was added into the side tube. The reactor was further cooled down with liquid nitrogen to –110 °C and the contents of the side tube were displaced into the central flask over 25 min. Then anhydrous ether (10 mL), anhydrous THF (10 mL) and the second half of *n*-butyllithium (9.7 mL, 19.4 mmol, 2.0M in pentane, Aldrich) were placed into the side tube. After thermal equilibration (5 min) the contents of the side tube were again displaced into the central flask. The side tube was washed with the Trapp mixture (4 mL). The whole process of addition took 1 h 30 min. (The addition of *n*-BuLi was done in two steps because of the insufficient volume of the side tube). The mixture was stirred at –110 °C for 20 min and the slurry of $CeBr_3$ in the Trapp mixture (prepared as described earlier) was added to the side tube. The main bubbler of the unit was stopped for 3 min which allowed gentle bubbling of argon through the contents of the side tube (this was necessary to prevent the precipitation of cerium(III) bromide). Then the stopper was removed from the main bubbler and was placed on the auxiliary bubbler. The argon pressure developed in the side tube (10-20 mmHg) transferred its contents to the central flask in *ca* 10 sec. This addition should be done fast to avoid clogging of the capillary tube of the reactor. No rise in temperature was observed. The yellowish mixture was stirred for 5 min and a solution of the starting ketone **3** (4.02 g, 15.5 mmol) in the Trapp mixture (20 mL) was placed into the side tube. After thermal equilibration (5 min) the contents of the side tube were slowly added over *ca* 5 min to the central flask at –110 °C. The side tube was washed with the Trapp mixture (4 mL). The slurry was stirred for 45 min at –110 to –108 °C and then quenched by addition of a solution of acetic acid (3.5 mL, 62 mmol) in the Trapp mixture (25 mL). The cooling bath was removed and sat. aq $NaHCO_3$ (25 mL) was added at –20 °C to the flask. The mixture was stirred overnight, then the organic layer was separated, dried over anhydrous sodium sulfate (5 g) and evaporated. Column chromatography (40 g silica, petroleum ether : ethylacetate, 6:1) gave 4.76 g (84%) of the title compound **4** as a white solid, mp 113-115 °C. ^{1}H NMR δ 1.34 (s, 3H), 1.40 (s, 3H), 1.44 (s, 3H), 1.62 (s, 3H), 3.28 (s, 1H, OH), 3.95 (d, J=7.5 Hz, 1H, H-4), 3.98 (dd, J=8.6, 5.8 Hz, 1H, H-6), 4.08 (dd, J=8.6, 6.0 Hz, 1H, H-6), 4.25 (dt, J=7.5, 5.9 Hz, 1H, H-5), 4.54 (d, J=3.9 Hz, 1H, H-2), 5.85 (d, J=1.8 Hz, 1H), 5.96 (d, J=3.9 Hz, 1H, H-1), 6.33 (d, J=1.8 Hz, 1H); ^{13}C NMR δ 25.6, 26.8 (2C), 26.9, 67.3, 73.8, 81.6, 83.2, 84.1, 105.6, 109.7, 113.1, 120.8, 128.0.



6

5-O-tert-Butyldiphenylsilyl-1,2-O-(1-methylethylidene)-β-L-threo-pentofuranose-3-ulose (6): Compound **6** was prepared in 60% yield as a colorless oil from 5-O-tert-butyldiphenylsilyl-L-1,2-O-1-methylethylidene arabinofuranose[7] by the same procedure as for the preparation of **3**. ^{1}H NMR δ 1.07 (s, 9H), 1.37 (s, 3H), 1.39 (s, 3H), 3.93 (dd, J=11.2, 6.2 Hz, 1H, H-5), 3.98 (dd, J=11.2, 4.3 Hz, 1H, H-5), 4.30 (dd, J=6.2, 4.3 Hz, 1H, H-4), 4.40 (dd, J=4.3, 0.7 Hz, 1H, H-2), 6.04 (d, J=4.3 Hz, 1H, H-1), 7.35-7.45 (m, 6H), 7.66-7.74 (m, 4H); ^{13}C NMR δ 19.4, 26.9, 27.6, 64.6, 76.9, 82.5, 102.8, 116.0, 127.9, 129.9, 133.0, 133.3, 135.8, 135.9, 206.9.



7

3-C-(1-Bromoethenyl)-5-O-tert-butyldiphenylsilyl-1,2-O-(1-methylethylidene)-β-L-lyxofuranose (7): The title product **7** was obtained from **6** using General Procedure B with the exception that the addition of *n*-butyllithium was done in a single step due to smaller loading. Column chromatography (silica, petroleum ether : diethyl ether, 6:1) gave 67% of **7** as a colorless oil. ^{1}H NMR δ 1.06 (s, 9H), 1.45 (s, 3H), 1.58 (s, 3H), 3.63 (d, J=0.5 Hz, 1H, OH), 3.87 (dd, J=11.0, 6.0 Hz, 1H, H-5), 4.00 (dd, J=11.0, 5.0 Hz, 1H, H-5), 4.39 (t, J=5.5 Hz, 1H, H-4), 4.81 (d, J=4.2 Hz, 1H, H-2), 5.62 (d, J=1.9 Hz, 1H), 5.80 (d, J=4.2 Hz, 1H, H-

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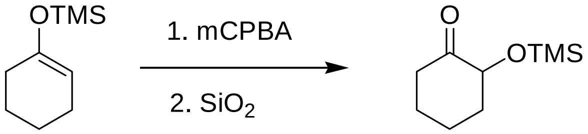
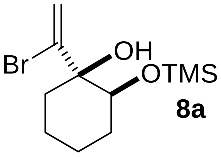
[7] Chamberlain, S.D.; Biron, K.K.; Dornsife, R.E.; Averett, D.R.; Beauchamp, L.; Koszalka, G.W. *J. Med. Chem.* **1994**, *37*, 1371-1377.

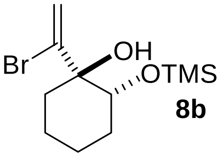
1), 6.19 (d, J=1.9 Hz, 1H), 7.30-7.50 (m, 6H), 7.70-7.85 (m, 4H); ^{13}C NMR δ 19.4, 27.0, 27.8, 28.0, 62.7, 79.5, 83.6, 85.4, 105.0, 116.3, 118.6, 127.9, 129.9, 133.4, 133.7, 133.9, 135.9, 136.0.



2-Trimethylsiloxycyclohexanone. Although the title compound is well known,[8] our attempts to reproduce literature methods for its preparation were not successful. The product was always severely contaminated with 2-hydroxycyclohexanone which was slowly dimerizing. (The limited commercial availability of adipoine, the dimer of 2-hydroxycyclohexanone, prevented the effective use of another approach.[9]) The origin of the failure was in the acidic admixtures which were still present in the crude 2-trimethylsiloxycyclohexanone and which caused its decomposition during distillation. The following modification of the known procedure[8] allowed successful isolation of the title compound, albeit in mediocre yield: 1-trimethylsiloxy-1-cyclohexene (8.1 g, 48 mmol) was dissolved in dichloromethane (100 mL) and a solution of potassium carbonate (5.3 g, 38 mmol) in water (50 mL) was added. The mixture was cooled down to 0 °C (NaCl/ice bath) and mCPBA (11g (75% assay), 48 mmol) was added over 30 min so that the temperature did not rise above 0 °C. The mixture was stirred for 1 h at 0 °C, then filtered and the organic layer was dried over Na_2SO_4. Concentration *in vacuo* (100 mmHg) at rt afforded a colorless oil which was dissolved in petroleum ether (100 mL). Oven-dried (24 h at 130 °C) silica (10 g) was added to the solution. The slurry was stirred for 6 h at rt. During this time a significant amount of *m*-chlorobenzoic acid was precipitated. The solution was filtered, the precipitate was washed with petroleum ether (2x30 mL) and the combined organic layers were filtered again through a small pad of dried silica. Vacuum distillation gave 4.4 g (50%) of 2-trimethylsiloxycyclohexanone as a clear liquid, bp 95-100°C at 17 mmHg, which was 95% pure by GC and ^{1}H NMR analysis. ^{1}H NMR (C_6D_6) δ 0.18 (s, 9H), 1.05-1.27 (m, 2H), 1.35-1.60 (m, 3H), 1.72-1.93 (m, 2H), 2.28 (dtd J=13.4, 4.4, 1.9 Hz, 1H), 3.91 (ddd, J=10.1, 5.6, 1.2 Hz, 1H); ^{13}C NMR (C_6D_6) δ 0.9, 23.5, 27.6, 37.6, 40.3, 77.2, 208.2.



8a



8b

1-(1-Bromoethenyl)-2-trimethylsiloxy-cyclohexanols (8a, 8b): the title compounds were prepared from 2-trimethylsiloxycyclohexanone following General Procedure B. ^{1}H NMR analysis of the crude reaction

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[8] Brook, A.G.; Macrae, D.M. J. *Organomet. Chem* **1974**, *77*, C19-C21; Pennanen, S.I. *Tetrahedron Lett*. **1980**, *21*, 657-658.

[9] Minor, K.P.; Overman, L.E. *Tetrahedron* **1997**, *53*, 8927-8940.

mixture showed an 88:12 ratio of diastereomeric **8a** and **8b.** Column chromatography (silica, petroleum ether : ether, 8:1) afforded 61% yield of the major diastereomer **8a** as a white solid, mp 73-74 ^{o}C, and 9% yield of the minor diastereomer **8b** as a colorless oil.

Spectral data for **8a:** ^{1}H NMR δ 0.10 (s, 9H), 1.33-1.40 (m, 1H), 1.50-1.65 (m, 5H), 1.80-1.95 (m, 1H), 1.97 (d, J=1.2 Hz, 1H, OH), 2.03-2.15 (m, 1H), 3.84 (br t, J=3.6 Hz, 1H, H-2), 5.63 (d, J=2.5 Hz, 1H), 5.82 (d, J=2.5 Hz, 1H); ^{13}C NMR δ 0.5, 19.5, 21.7, 29.5, 30.5, 71.6, 76.2, 118.6, 142.2.

Spectral data for **8b:** ^{1}H NMR δ 0.11 (s, 9H), 1.10-1.30 (m, 1H), 1.40-1.60 (m, 3H), 1.62-1.75 (m, 3H), 1.92 (dddd, J=14.4, 11.8, 5.4, 2.6 Hz, 1H), 2.90 (d, J=2.6 Hz, 1H, OH), 4.05 (dd, J=10.7, 4.9 Hz, 1H, H-2), 5.56 (d, J=1.6 Hz, 1H), 6.09 (d, J=1.6 Hz, 1H); ^{13}C NMR δ 0.6, 20.7, 24.1, 31.4, 34.1, 71.6, 78.2, 117.2, 140.2.

Figure 1 Schematic Representation of Low Temperature Reactor
(all dimensions are in mm)

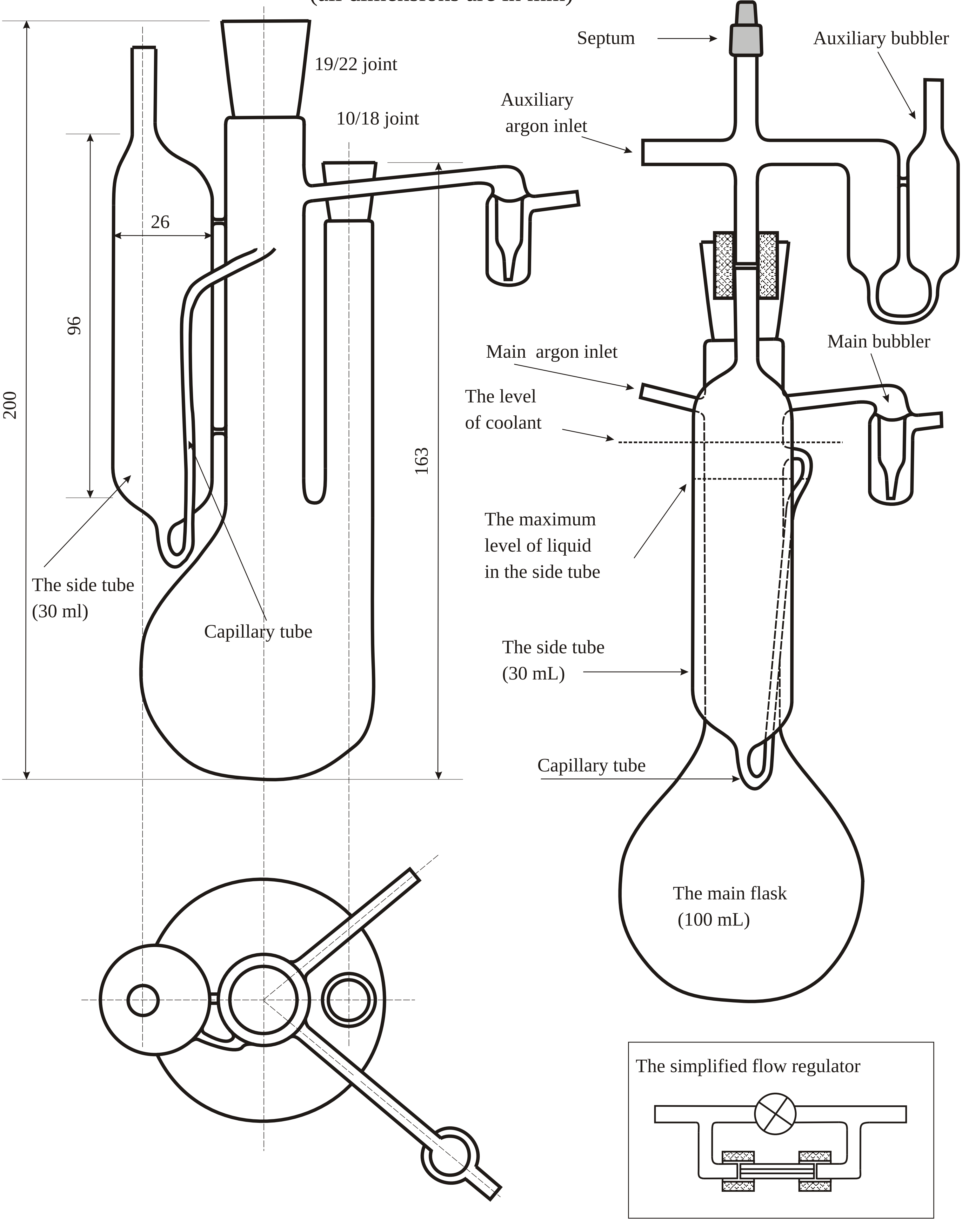
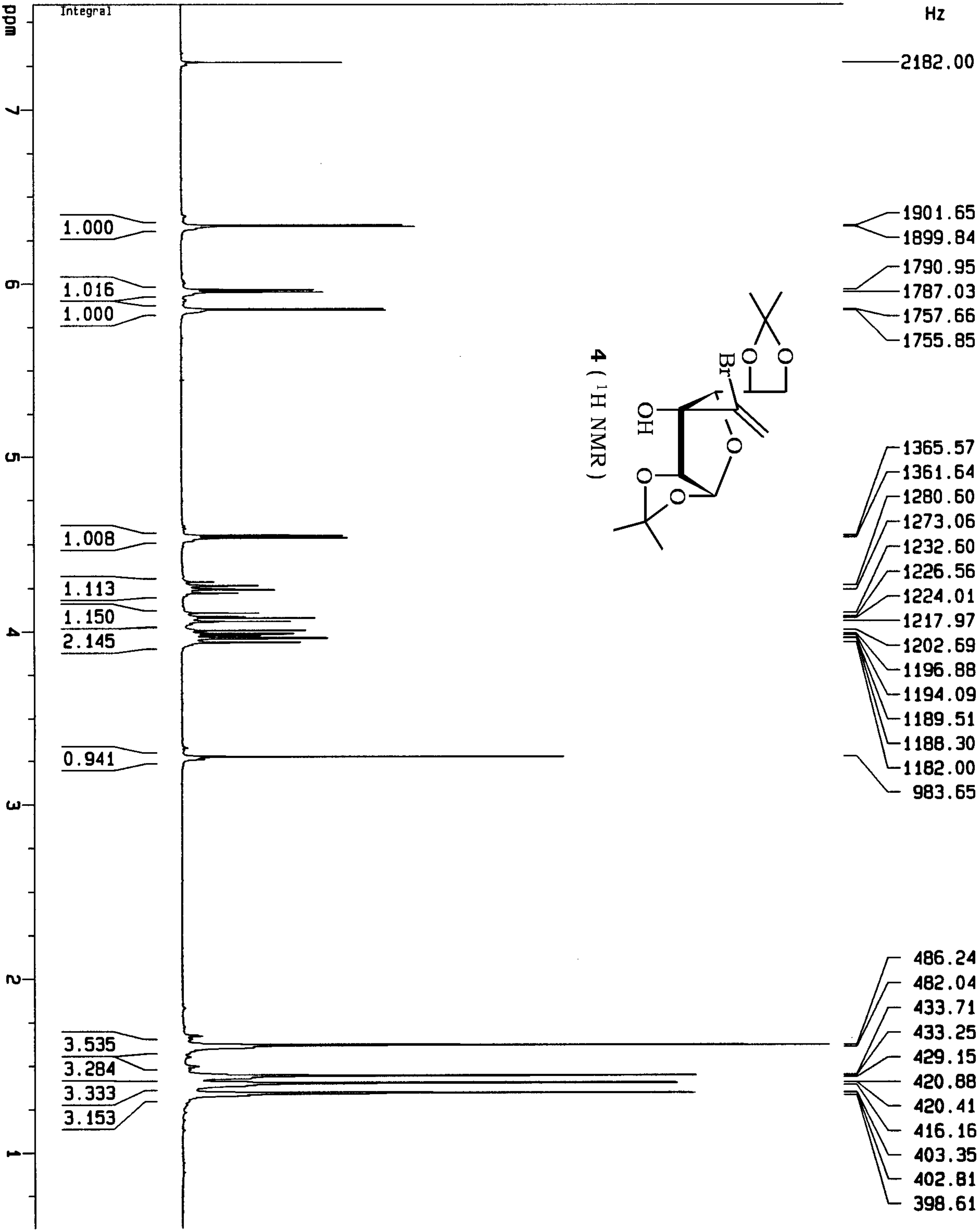


Figure 2. Photograph of Low Temperature reactor

ppm
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Hz
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5
4
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2
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1.000
1.008
1.113
1.150
2.145
0.941
3.535
3.284
3.333
3.153
2182.00
1901.65
1899.84
1790.95
1787.03
1757.66
1755.85
1365.57
1361.64
1280.60
1273.06
1232.60
1226.56
1224.01
1217.97
1202.69
1196.88
1194.09
1189.51
1188.30
1182.00
983.65
486.24
482.04
433.71
433.25
429.15
420.88
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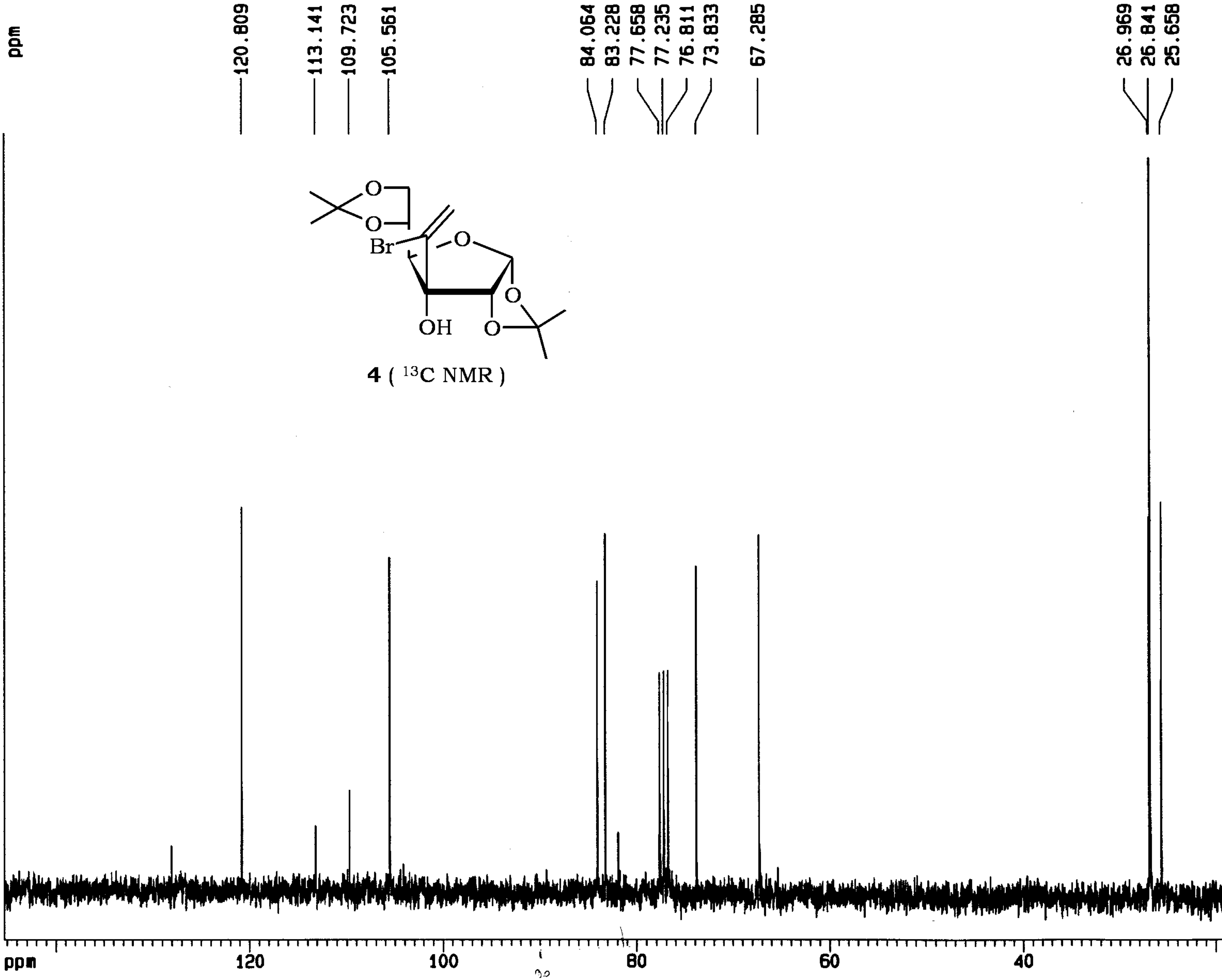
402.81
398.61
Br
OH
O
O
O
O
O

4 (^{1}H NMR)



4 (^{13}C NMR)

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83.228
77.658
77.235
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67.285
26.969
26.841
25.658
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OH
O
ppm
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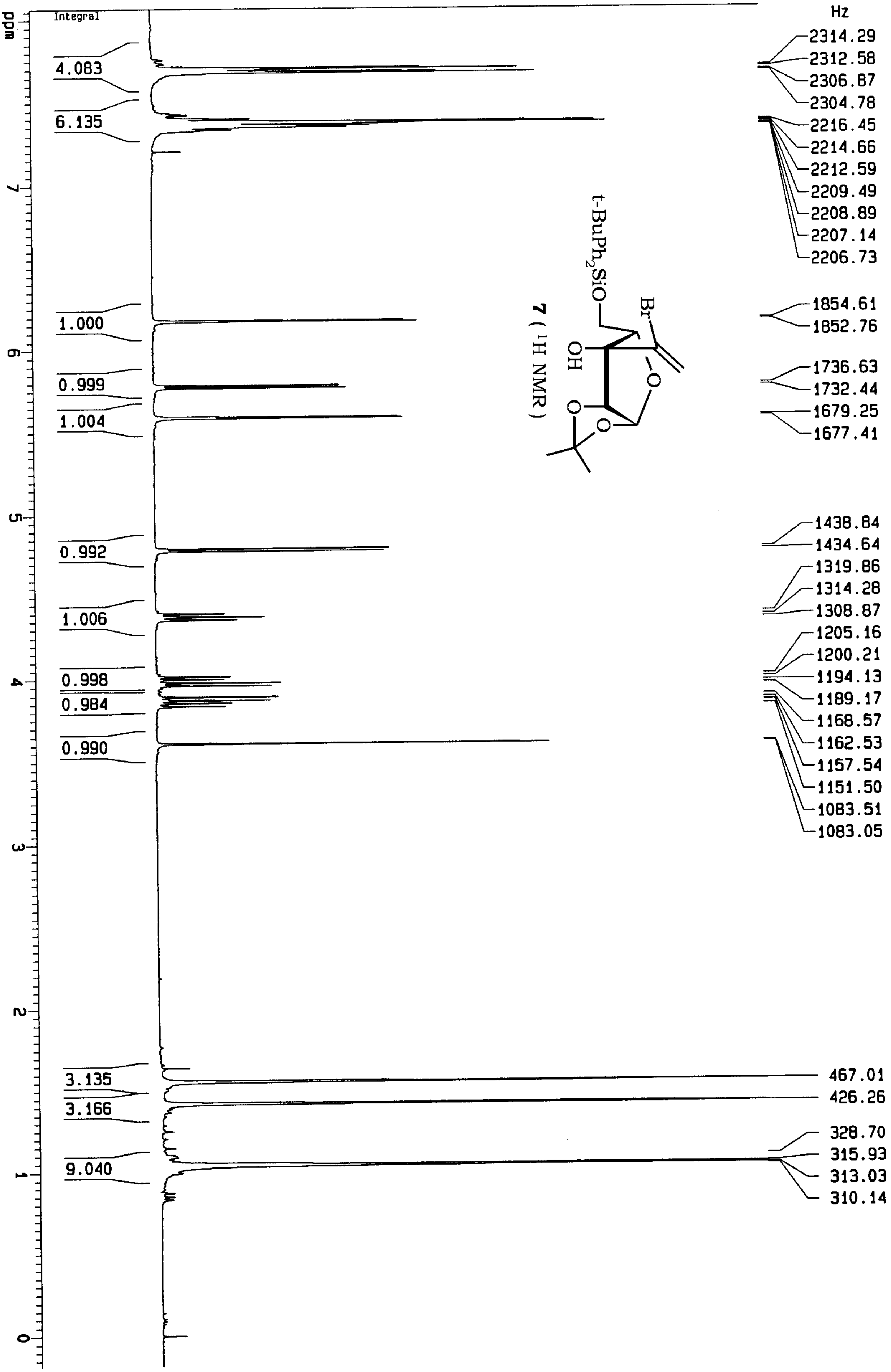
100
80
60
40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3.166
9.040
7
6
5
4
3
2
1
0
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2312.58
2306.87
2304.78
2216.45
2214.66
2212.59
2209.49
2208.89
2207.14
2206.73
1854.61
1852.76
1736.63
1732.44
1679.25
1677.41
1438.84
1434.64
1319.86
1314.28
1308.87
1205.16
1200.21
1194.13
1189.17
1168.57
1162.53
1157.54
1151.50
1083.51
1083.05
467.01
426.26
328.70
315.93
313.03
310.14
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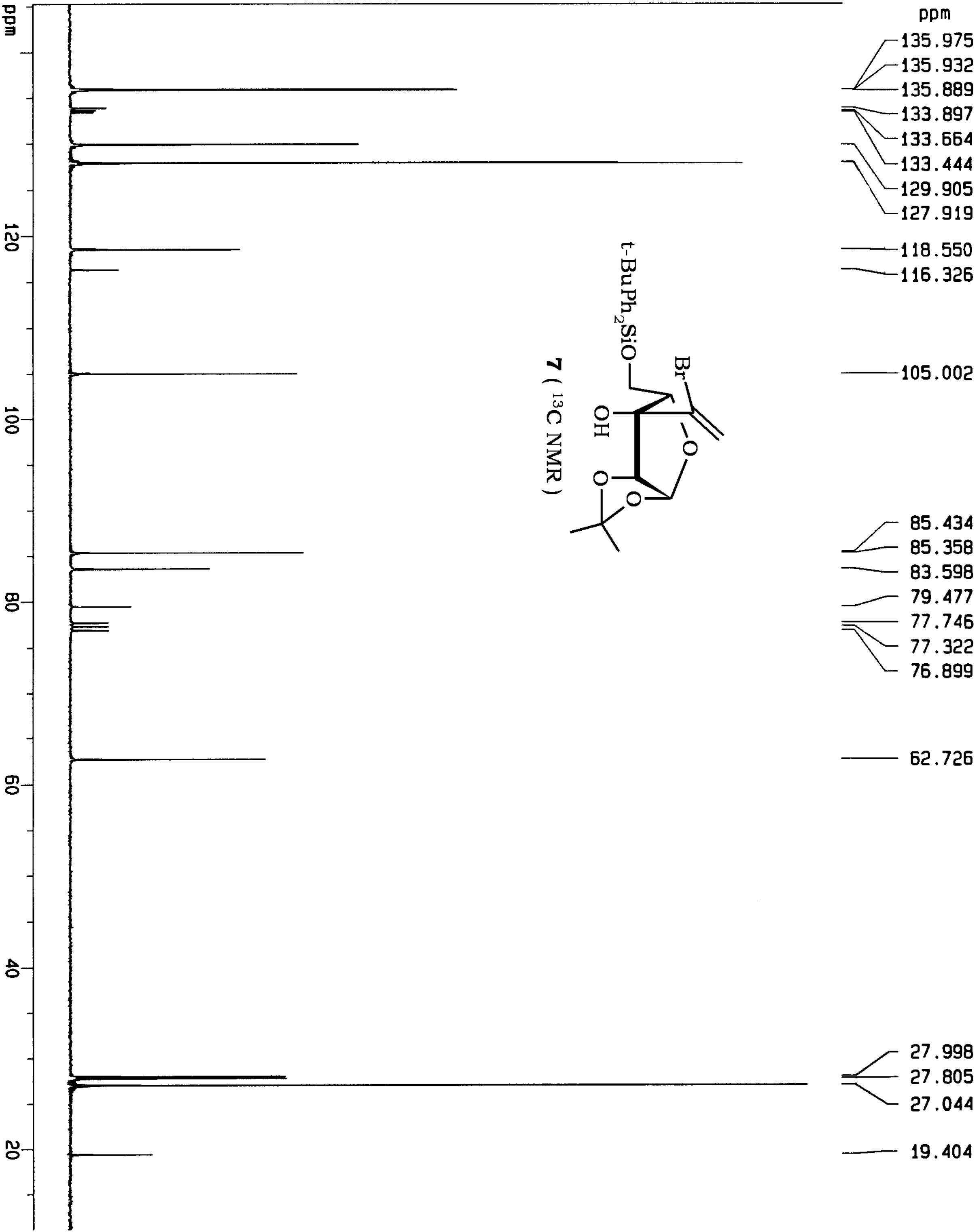
Br
OH
O
O
O

7 (^{1}H NMR)

ppm
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133.664
133.444
129.905
127.919
118.550
116.326
105.002
85.434
85.358
83.598
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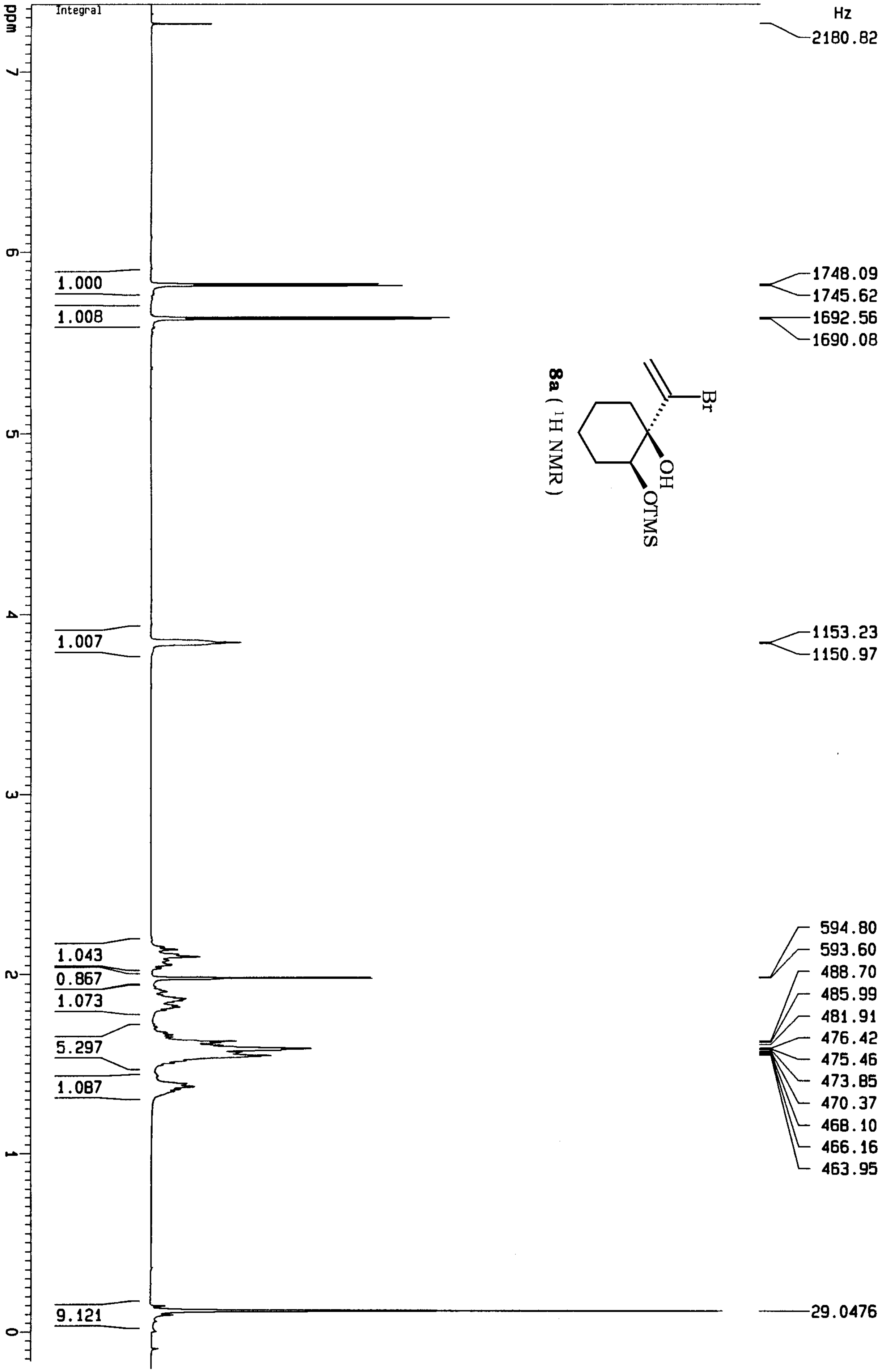
27.998
27.805
27.044
19.404

7 (^{13}C NMR)



8a (^{1}H NMR)

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6
5
4
3
2
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0
Integral
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1.007
1.043
0.867
1.073
5.297
1.087
9.121
Hz
2180.82
1748.09
1745.62
1692.56
1690.08
1153.23
1150.97
594.80
593.60
488.70
485.99
481.91
476.42
475.46
473.85
470.37
468.10
466.16
463.95
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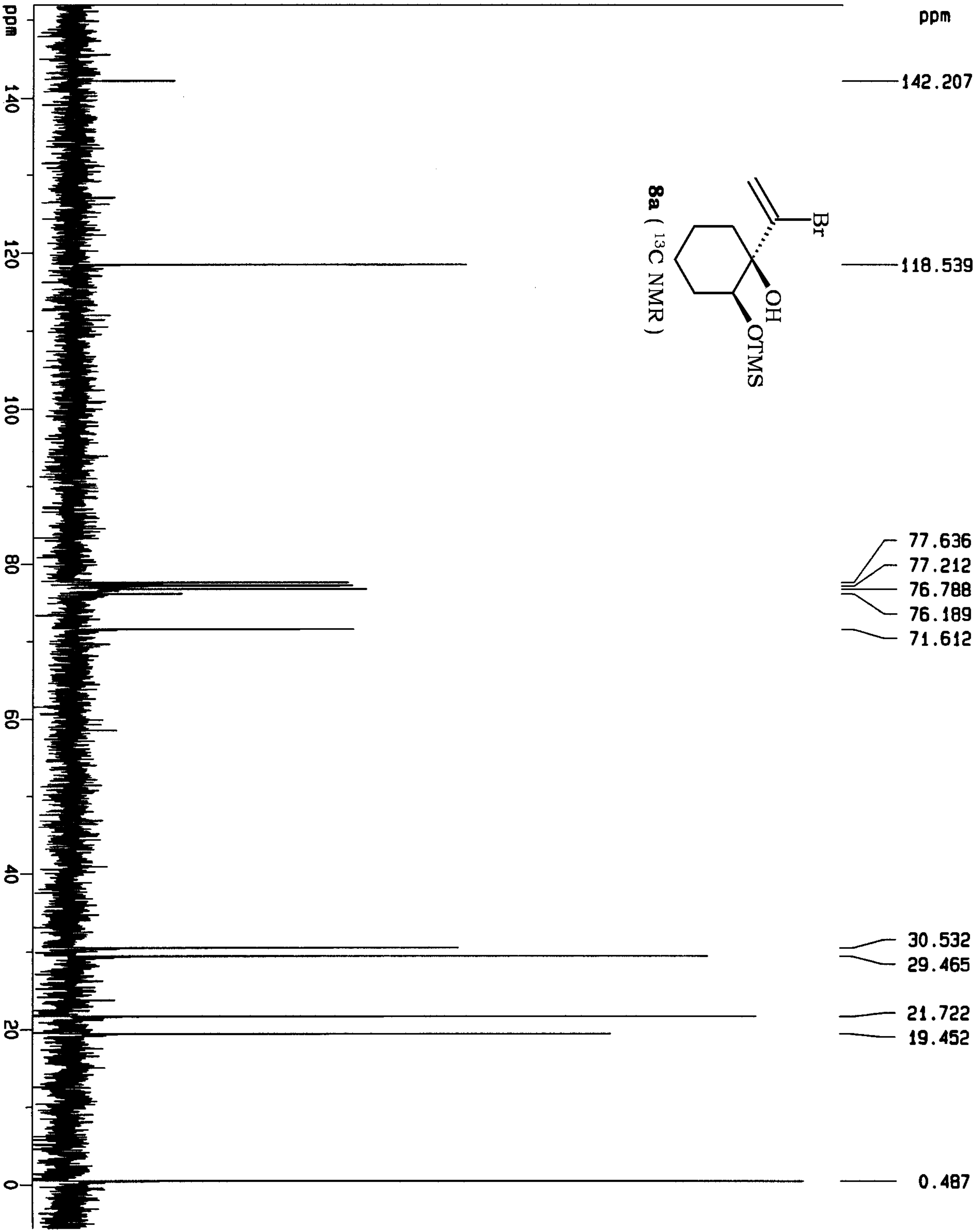
Br
OH
OTMS


8a (^{13}C NMR)

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OH
OTMS
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19.452
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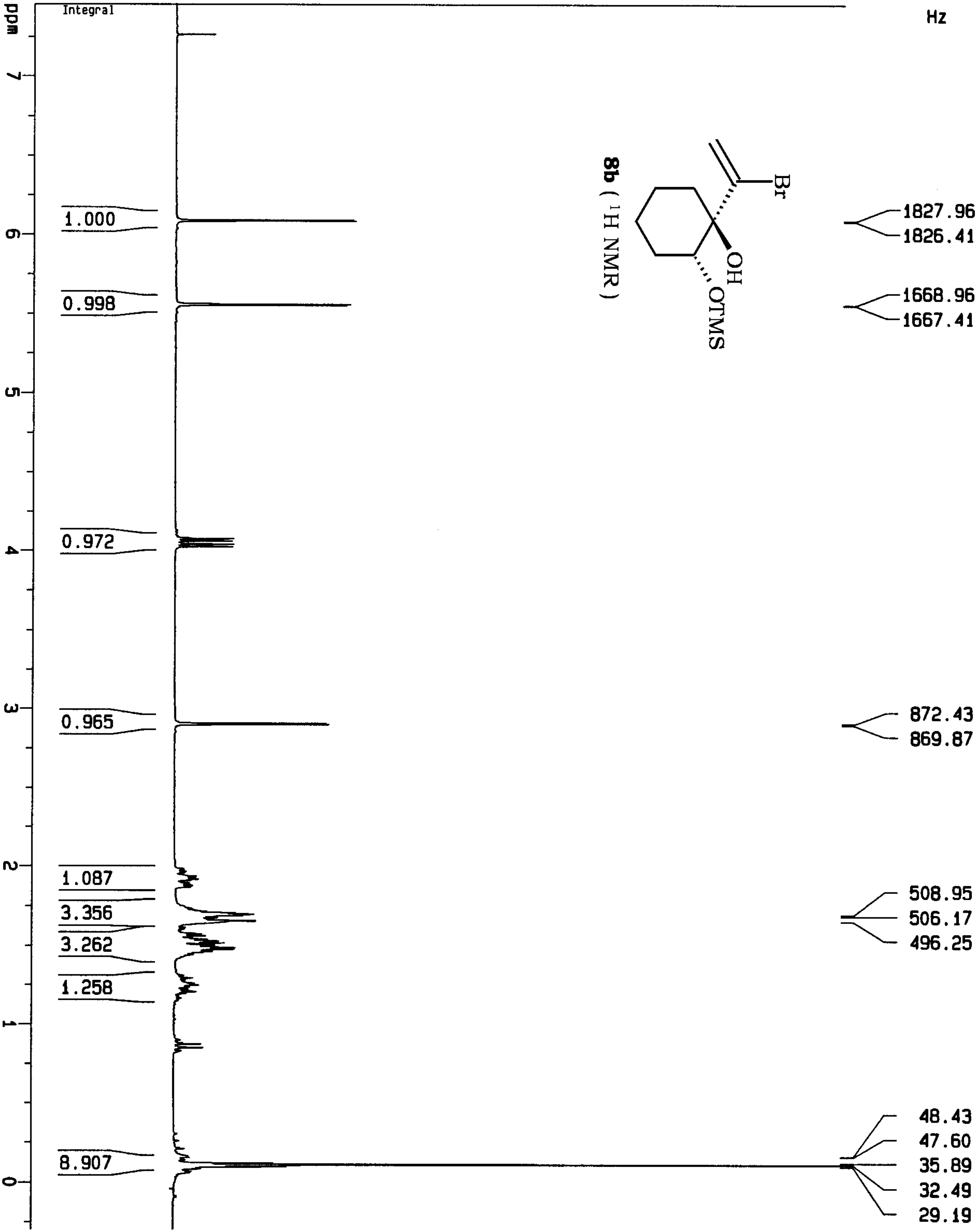
80
60
40
20
0



8b (^{1}H NMR)

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5
4
3
2
1
0
Integral
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1.087
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3.262
1.258
8.907
Hz
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1667.41
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47.60
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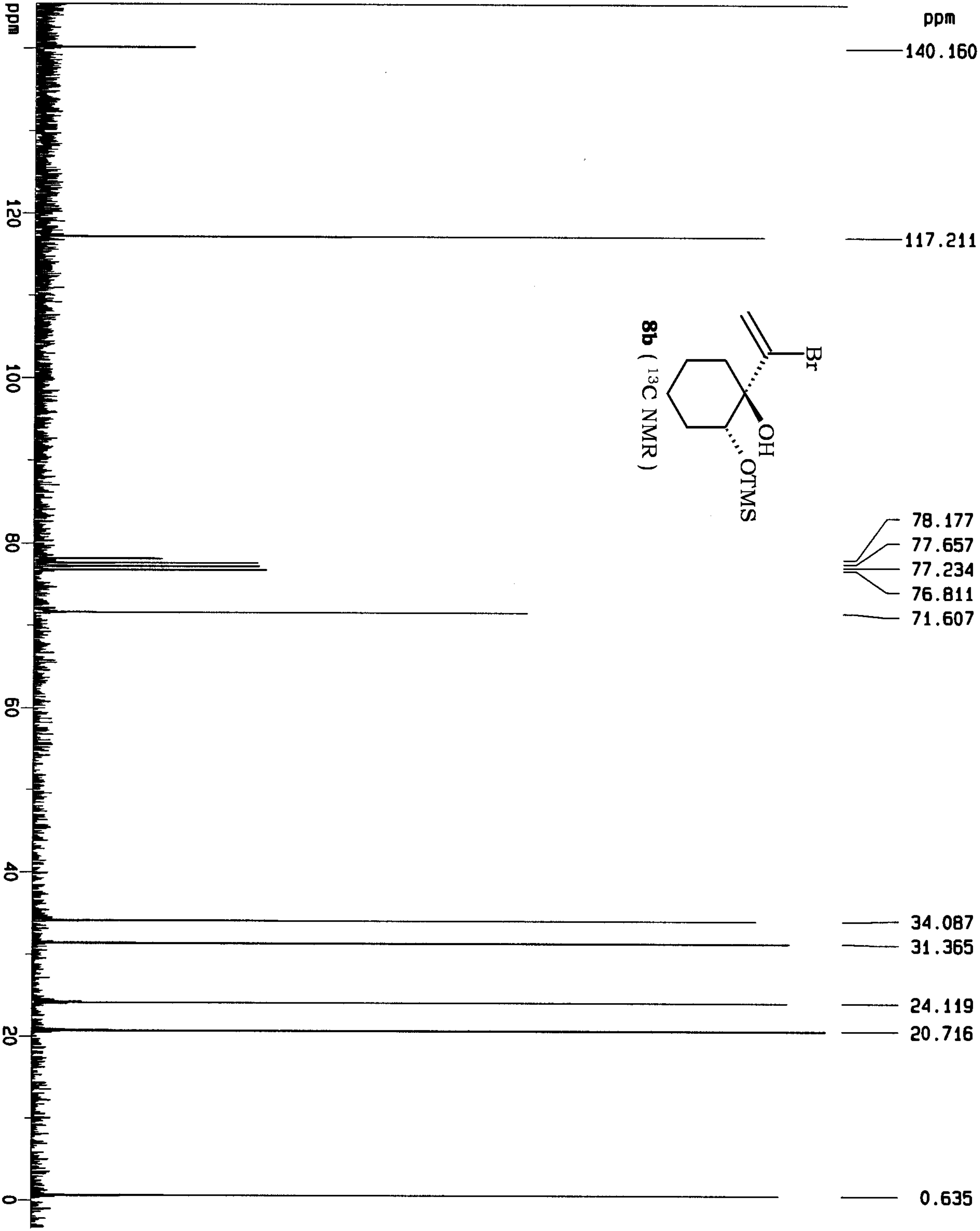
29.19
Br
OH
OTMS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24.119
20.716
0.635
ppm
120
100
80
60
40
20
0
Br
OH
OTMS