Supplementary Information

a biomimetic approach towards phorone sesterterpenoids

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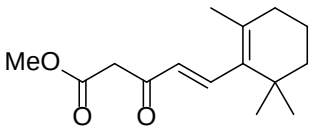
General Experimental Details

Commercially available reagents were used as received without further purification. All reactions that required anhydrous conditions were conducted in flame-dried apparatus under an atmosphere of argon. Analytical thin-layer chromatography (TLC) was performed on silica gel plates (0.25 mm) precoated with a fluorescent indicator. Visualisation of TLC plates was performed by fluorescence quenching and potassium permanganate-, *p*-anisaldehyde- or vanillin-type staining solutions. Unless specifically stated, flash chromatography procedures were performed using Kieselgel 60 (40–63 μm). 'Petrol' refers to the fraction of petroleum ether boiling between 40–60 °C. 'Brine' refers to a saturated aqueous solution of sodium chloride. Infrared spectra were recorded directly on a Bruker Tensor 37 FTIR machine fitted with a PIKE MIRacle ATR accessory as either solids or neat oils. Infrared spectra are reported as follows: wavelength (cm^{-1}) and intensity of absorbance (s = strong, m = medium, w = weak, vw = very weak, br = broad). ^{1}H and ^{13}C NMR spectra were typically recorded on Bruker AV400 machines at 400 and 101 MHz respectively. ^{1}H NMR spectroscopy chemical shift values in ppm are reported relative to the residual protonated solvent peaks: $CHCl_3$ [δ_H 7.26], C_6H_6 [δ_H 7.16], DMSO [δ_H 2.50], acetone [δ_H 2.05], CH_3OH [δ_H 3.31]. ^{13}C NMR spectroscopy chemical shift values in ppm are reported relative to the deuterated solvent peaks. ^{1}H NMR data are reported as follows: chemical shift (δ), integration, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, qn= quintet and m = multiplet,), *J* coupling constant(s) (Hz), and assignment. ^{1}H NMR peaks were assigned using chemical shift, *J* couplings and standard two-dimensional NMR experiments. ^{13}C NMR peaks were assigned using chemical shift, DEPT experiments and standard two-dimensional NMR experiments.

Experimental Details and Characterisation

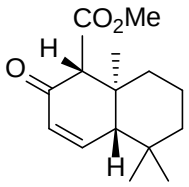


15

Methyl-5-(2',6',6'-trimethylcyclohex-1'-enyl)-3-keto-4-pentenoate 15

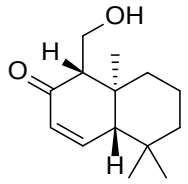
To a strongly stirred suspension of NaH (60% in mineral oil) (18.5 g, 0.46 mol) in dioxane (130 mL) was added dimethyl carbonate (42.0 g, 0.43 mol) at 23 °C. After heating to reflux, a solution of commercially purchased β-ionone (22.0 g, 0.11 mol) in dioxane (30 mL) was added over 4 h (using an automatic syringe pump), before continued stirring for 1.5 h. After this time, the mixture was cooled to 0 °C, neutralised by the *very cautious* addition of 4 M aq. HCl (until pH 7 as judged by indicator paper) and then Et_2O (200 mL) was added. The separated organic layer was repeatedly washed with water, then brine (100 mL), separated, dried over $MgSO_4$ and filtered. The solvents were removed *in vacuo* to give the title compound as golden-orange oil (23 g, 79%). Data are consistent with those previously reported in the literature.[1] The ^{1}H NMR spectrum indicated tautomerisation of enol:ketone 3:7 in $CDCl_3$, with the alkenyl proton resonating at 4.97 ppm. ν_{max}/cm^{-1} 2931w, 2866w, 1743m (C=O), 1715m (C=O), 1655m (C=O), 1590m, 1445w, 1398w, 1362w, 1236s, 1153s, 1020m. Assignments for ketone in mixture: ^{1}H NMR (400 MHz, $CDCl_3$) 7.36 (1H, d, J = 16.0 Hz, =CH), 6.19 (1H, d, J =16.0 Hz, =CH), 3.73 (3H, s, CH_3), 3.62 (2H, s, CH_2), 2.09–2.01 (2H, m, CH_2), 1.76 (3H, s, CH_3), 1.64–1.43 (4H, m, 2 × CH_2), 1.06 (6H, s, 2 × CH_3); *m/z* calculated for $[C_{15}H_{23}O_3]^+$ 251.1642 found $[M + H]^+$ 251.1638.

Methyl 5,5,8a-trimethyl-2-oxo-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxylate 16



16

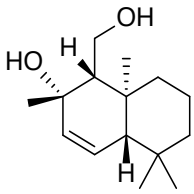
A solution of sodium methoxide (freshly prepared from 1.83 g sodium sticks added to anhydrous MeOH) in anhydrous MeOH (50 mL), was added to a solution of ester **15** (13.0 g, 52.9 mmol) in anhydrous MeOH (100 mL). The solution was degassed by bubbling through a stream of nitrogen *via* a needle, for approximately 10 min. After this, the solution was irradiated in an immersion well photochemical reactor using a high pressure 400 W mercury lamp under a slow stream of nitrogen with strong stirring for 20 h. After this time NH_4Cl (aq. sat., 100 mL) was added. The organic layer was diluted with Et_2O (200 mL), washed with NH_4Cl (aq. sat., 20 mL), separated, dried over $MgSO_4$ and filtered. After removal of the solvents *in vacuo*, purification of the residue by flash column chromatography (SiO_2; 10% Et_2O → 50% Et_2O in petrol) gave the title compound as pale yellow needles (1.90 g, 15%). Data are consistent with those previously reported in the literature.[2] mp 111–115 °C (lit[2] 111–113 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (1H, dd, J = 10.3 and 2.1 Hz, OC–CH=C*H*), 6.14 (1H, dd, J = 10.3 and 3.3 Hz, OC–C*H*=CH), 3.73 (3H, s, OCH_3), 3.26 (1H, s, MeO_2CCH), 2.19 (1H, apparent t, $J \approx 2.7$ Hz, CH=CH–C*H*), 1.57–1.09 (6H, m, 3 × CH_2), 1.06 (3H, s, CH_3), 0.89 (3H, s, CH_3), 0.80 (3H, s, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2 (O=C), 169.2 (O=C), 150.5 (=C), 130.2 (=C), 69.4 (H*C*–C=O), 56.3 (CH), 51.7 (OCH_3), 43.7 (C_q), 41.1 (CH_2), 37.9 (CH_2), 32.9 (C_q), 32.7 (CH_3), 22.6 (CH_3), 18.3 (CH_2), 14.0 (CH_3).



17

1-(Hydroxymethyl)-5,5,8a-trimethyl-4a,5,6,7,8,8a-hexahydronaphthalen-2(1H)-one 17

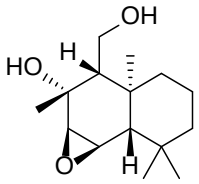
To a stirred solution of ester **16** (1.70 g, 6.79 mmol) in Et_2O (50 mL) was cautiously added $LiAlH_4$ (520 mg, 13.7 mmol) at 0 °C before continued stirring for 2 h. After this time, NH_4Cl (sat. aq., 10 mL) was added cautiously with vigorous stirring. The separated organic layer was washed with water (30 mL), brine (30 mL), dried over $MgSO_4$ and filtered through a sintered funnel under reduced pressure. The filtrate was reduced *in vacuo* to give the title compound as orange needles which were used directly. To a stirred solution of the diol (1.25 g, 5.57 mmol) in CH_2Cl_2 (20 mL) was added MnO_2 (5.80 g, 66.7 mmol), before continued stirring for 24 h or until completion by TLC analysis. After this, the mixture was filtered through a sintered funnel under reduced pressure and the solid residue was rinsed repeatedly with EtOAc. The filtrate was then dried over $MgSO_4$, filtered and the solvent was removed *in vacuo* to give the title compound as orange wax (870 mg, 67% for two steps) which was used without further purification. Data are consistent with those previously reported in the literature.[3] ν_{max}/cm^{-1} 3440br (O–H), 2926m, 2869m, 1662s (C=O), 1460w, 1385w, 1385m, 1367m, 1204m, 1033s; ^1H NMR (400 MHz, $CDCl_3$) δ 7.00 (1H, dd, J = 10.2 and 2.1 Hz, =CH), 6.07 (1H, dd, J =10.2 and 3.3 Hz, =CH), 3.92 (1H, dd, J = 11.1 and 8.7 Hz, OCH_a), 3.67 (1H, m, OCH_b), 3.25 (1H, s, OH), 2.30 (1H, dd, J = 8.7 and 3.2 Hz, $HOCH_2CH$), 2.23 (1H, apparent t, $J \approx$ 2.7 Hz, CH=CHC*H*), 1.73–1.04 (6H, m, 3 × CH_2), 1.02 (3H, s, CH_3), 0.91 (3H, s, CH_3), 0.87 (3H, s, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0 (C=O), 151.5 (=C), 130.0 (=C), 64.0 (H*C*C=O), 58.6 (OCH_2), 56.3 (H*C*C=), 43.2 (C_q), 40.9 (CH_2), 37.6 (CH_2), 32.8 (C_q), 32.7 (CH_3), 22.5 (CH_3), 18.4 (CH_2), 14.9 (CH_3); m/z calculated for $[C_{14}H_{23}O_2]^+$ 223.1693 found $[M + H]^+$ 223.1692.



18

1-(Hydroxymethyl)-2,5,5,8a-tetramethyl-1,2,4a,5,6,7,8,8a-octahydronaphthalen-2-ol 18

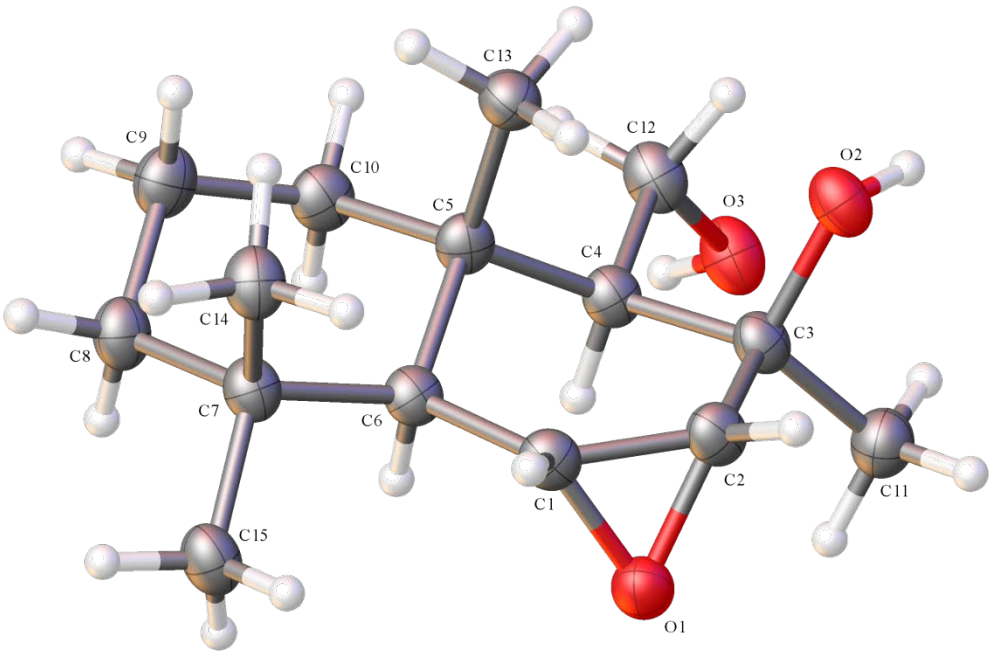
To a stirred solution of 1-(Hydroxymethyl)-5,5,8a-trimethyl-4a,5,6,7,8,8a-hexahydronaphthalen-2(1H)-one **S1** (2.05 g, 9.22 mmol) in Et_2O (20 mL) was cautiously added MeLi (29.0 mL, 1.6 M, 46.4 mmol) at –78 °C. After continued stirring for 6 h at –78 °C the reaction was allowed to warm to 23 °C, before immeadiate re-cooling to –78 °C and with the addition of NH_4Cl (sat. aq.) (10 mL). After warming to 23 °C the separated organic layer was washed with water (50 mL), dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give an orange residue which was purified by flash column chromatography (SiO_2; 20% → 50% EtOAc in petrol) to give the title compound as an off-white solid (663 mg, 31%) identified as a ≈15:1 mixture of diastereomers. Data were consistent with those previously reported in the literature.[3] mp 120–122 °C; ν_{max}/cm^{-1} 3350br (O–H), 2924s, 2869s, 1453m, 1383m, 1384s, 1131s, 1080s, 1035s; NMR assignments for major diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ 5.73 (1H, dd, J = 10.1, 2.1 Hz, =CH), 5.64 (1H, dd, J = 10.1 and 3.0 Hz, =CH), 4.05 (2H, d, J = 4.4 Hz, OCH_2), 2.51 (1H, brs, OH), 1.91–1.82 (1H, m, CH_a), 1.71–1.63 (1H, m, CH_b), 1.59 (1H, apparent t, J = 2.4 Hz, CH=CHC*H*), 1.54–1.41 (2H, m, CH_2), 1.37 (3H, s, $OCCH_3$), 1.29 (1H, t, J = 4.4 Hz, OCH_2CH), 1.19–1.15 (2H, m, CH_2), 1.08 (3H, s, CH_3), 0.91 (3H, s, CH_3), 0.88 (3H, s, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5 (=C), 128.0 (=C), 72.1 (OC_q), 60.3 (OCH_2), 58.6 (OCH_2CH), 54.8 (=C*C*H), 41.2 (CH_2), 37.6 (CH_2), 36.8 (C_q), 32.9 (CH_3), 32.8 (Me_2C_q), 30.8 (CH_3), 22.0 (CH_3), 18.4 (CH_2), 15.8 (CH_3); m/z calculated [$C_{15}H_{26}O_2$ –H_2O + NH_4] 238.2165 found [M –H_2O + NH_4] 238.2163.

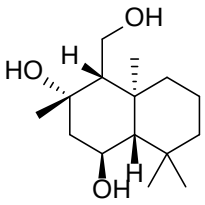


19

3-(Hydroxymethyl)-2,3a,7,7-tetramethyldecahydronaphtho[1,2-b]oxiren-2-ol 19

To a stirred solution of diol **18** (775 mg, 3.3 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (1.12 g, 6.5 mmol) before continued stirring for 25 h. After this time, the reaction mixture was vigorously washed with 1 M aq. sol. $NaHCO_3$ (2 × 5 mL). The separated organic layer was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo.* Purification of the crude residue by flash column chromatography (SiO_2; 50% EtOAc in petrol) gave the *title compound* as pale yellow crystals (475 mg, 58%). mp 66–75 °C; ν_{max}/cm^{-1} 3363br (OH), 2951m, 2925m, 2870m, 1706w, 1458m, 1392m, 1369m, 1262m, 1128m, 1070m, 1025m,; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.08 (1H, dd, *J* = 12.0 and 3.5 Hz, HOCH_a), 4.03 (1H, dd, *J* = 12.0 and 3.6 Hz, HOCH_b), 3.15 (1H, dd, *J* = 3.9 and 2.7 Hz, CHCOC*H*), 2.98 (1H, d, *J* = 3.9 Hz, OCHC$_q$), 2.96 (1H, s, OH), 2.36 (1H, s, OH), 1.76–1.63 (2H, m, CH_2), 1.54–1.46 (5H, m, CH_2, CH_3), 1.22 (3H, s, CH_3) 1.18–0.98 (8H, m, CH_2, 2 × CH_3), 0.95 (1H, d, *J* = 3.9 Hz, OCHC*H*), 0.88 (1H, t, *J* = 3.5 Hz, H_2CC*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 72.8 (OC$_q$), 60.3 (OCH_2), 59.6 (OC), 56.3 (OC), 55.0 (CH), 54.8 (CH), 41.5 (CH_2), 37.21 (C_q), 37.18 (CH_2), 33.2 (C_q), 32.8 (CH_3), 27.7 (CH_3), 22.5 (CH_3), 18.4 (CH_2), 18.2 (CH_3); *m*/*z* calculated for $[C_{15}H_{27}O_3 + NH_4]^+$ 272.2220 found $[M + NH_4]^+$ 272.2216. **X-Ray Crystallographic Data 19**: These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif CCDC 1043793 contains the supplementary crystallographic data for this compound.



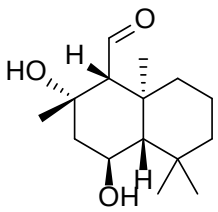


20

4-(Hydroxymethyl)-3,4a,8,8-tetramethyldecahydronaphthalene-1,3-diol 20

To a stirred solution of epoxide **19** (475 mg, 1.87 mmol) in PhMe (10 mL) was added Red-Al (2.0 mL, 65 wt% in PhMe, 5.6 mmol) at 23 °C. After 10 min the evolution of H_2 had slowed and the solution was heated to reflux with continued stirring over 24 h. After this time the mixture was cooled to rt and NH_4Cl (aq. sat., 2 mL) was added and the mixture was filtered through a 30 mm pad of $MgSO_4$ with EtOAc (30 mL). The solvent was removed *in vacuo* to give a crude residue which was purified by flash column chromatography (SiO_2; 50% EtOAc in petrol → 100% EtOAc) to give the *title compound* as pale yellow needles (475 mg, 99%). mp 190–192 °C; ν_{max}/cm^{-1} 3300br (O–H), 3004w, 2959m, 2926m, 2891m, 2872m, 2842m, 1461m, 1373s, 1190m, 1118m, 1047s; ^1H NMR (400 MHz, CD_3OD) δ 4.12 (1H, td, J = 11.0 and 4.0 Hz, OCH), 4.00 (1H, dd, J = 11.8 and 2.6 Hz, OCH_{a1}), 3.90 (1H, dd, J = 11.8 and 3.4 Hz, OCH_{b1}),

2.04 (1H, dd, *J* = 13.2 and 4.1 Hz, OC_qCHa2), 1.93–1.87 (1H, m, CH_{a3}), 1.75–1.65 (1H, m, CH_{a4}), 1.58 (1H, dd, *J* = 13.2 and 11.2 Hz, OC_qCH_{b2}), 1.50-1.38 (2H, m, CH_{b4}, CH_{a5}), 1.36 (3H, s, CH_3), 1.31-1.23 (1H, m, CH_{b5}), 1.21 (3H, s, CH_3), 1.19 (3H, s, CH_3), 1.11 (3H, s, CH_3), 1.06–0.99 (2H, m, CH_{b3}, HOCC*H*); ^{13}C NMR (101 MHz, CD_3OD) δ 75.2 (OC_q), 68.3 (OCH), 61.7 (OCCH), 60.4 (OCH_2), 59.9 (CH_2), 53.5 (CH_2), 45.1 (CH_2), 41.3 (CH_2), 41.0 (CH), 37.5 (CH_3), 34.7 (CH_3), 31.4 (CH_3), 22.8 (CH_3), 19.3 (CH_2), 18.1 (CH_3); *m*/*z* calculated for $[C_{15}H_{26}O_2 + NH_4 - H_2O]^+$ 256.2271 found $[M + NH_4 - H_2O]^+$ 256.2265

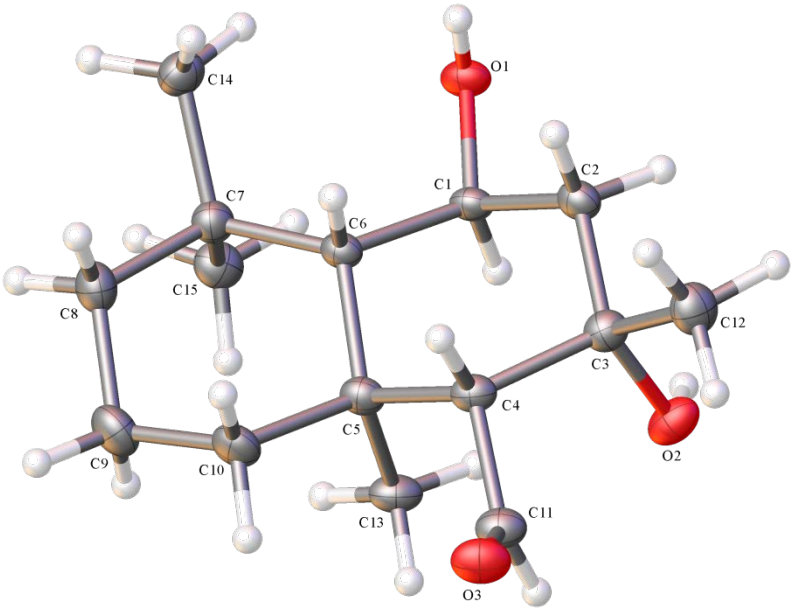


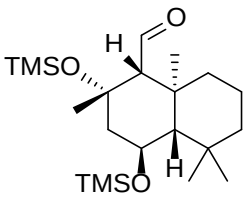
21

2,4-Dihydroxy-2,5,5,8a-tetramethyldecahydronaphthalene-1-carbaldehyde 21

To a suspension of triol **20** (475 mg, 1.85 mmol) in CH_2Cl_2 (5 mL) was added TEMPO (58 mg, 0.37 mmol) and $PhI(OAc)_2$ (715 mg, 2.2 mmol). After stirring for 5 h, $NaHCO_3$ (sat. aq., 1 mL) was added. The separated organic layer was then dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give a crude solid which was purified by flash column chromatography (SiO_2; 30% EtOAc in petrol) to give the *title compound* as colourless crystals (339 mg, 72%). mp 144–147 °C; ν_{max}/cm^{-1} 3390br (O–H), 2969w, 2923w, 2906w, 2874w, 2846w, 1698s (C=O), 1459m, 1291m, 1175m, 1040s; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.04 (1H, d, *J* = 2.6 Hz, CHO), 4.20 (1H, td, *J* = 10.8 and 4.1 Hz, OCH), 3.06 (1H, s, OH), 2.18 (1H, d, *J* = 2.6 Hz, CHOC*H*), 2.09–2.03 (1H, m, CH_{a1}), 1.70–1.56 (2H, m, CH_{a2}, CH_{a3}), 1.47–1.22 (8H, m, CH_{b3}, CH_{b2}, CH_{b1}, CH_2, CH_3), 1.26 (3H, m, CH_3), 1.20 (3H, s, CH_3), 1.18 (3H, s, CH_3), 1.08−1.04 (4H, s, CH_3, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.5 (C=O), 72.7 (OC_q), 68.6 (O=C*C*H), 67.6 (HCO), 60.1 (CH), 52.3 (CH_2), 43.5 (CH_2), 41.8 (C_q), 40.9 (CH_2), 37.1 (CH_3), 33.9 (C_q), 31.2 (CH_3), 22.3 (CH_3), 18.2 (CH_3), 18.00 (CH_2); *m*/*z*

calculated $[C_{15}H_{24}O_3]^+$ 253.1798 found $[M - H]^+$ 253.1796. **X-Ray Crystallographic Data 21**: These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif**.** CCDC 1043794 contains the supplementary crystallographic data for this compound.



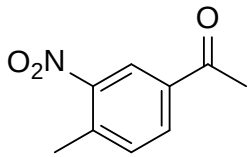


22

2,5,5,8a-Tetramethyl-2,4-bis((trimethylsilyl)oxy)decahydronaphthalene-1-carbaldehyde 22

To a stirred solution of aldehyde **21** (18 mg, 0.071 mmol) in CH_2Cl_2 (1 mL) cooled to –15 °C was added NEt_3 (200 µL, 1.4 mmol) and TMSOTf (≈30 µL, 0.17 mmol). After stirring for 30 min 1M aq. $NaHCO_3$ (5 mL) was added before allowing to warm to rt. The organic layer was separated, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give a crude residue which was purified by flash column chromatography (SiO_2; 5% Et_2O in petrol) to give the *title compound* as pale yellow wax (26 mg, 93%).

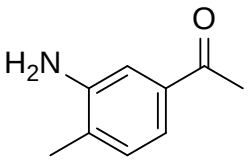
ν_{max}/cm^{-1} 2954m, 2928m, 2848m, 1715m (C=O), 1288s, 1105s, 1047m; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (1H, d, *J* = 5.3 Hz, CHO), 4.32 (1H, td, *J* = 10.5 and 4.0 Hz, TMSOC*H*), 2.08 (1H, dd, *J* = 13.6 and 4.0 Hz, C_qCH_{a1}), 1.60–1.43 (3H, m, CHOC*H*, CH_{a2}, C_qCH_{b1}), 1.40–1.31 (6H, m, CH_{b2}, CH_{a3}, CH_{a4}, CH_3), 1.23–1.01 (11H, 3 × CH_3, CH_{b4}, CH_{b3}), 0.93 (1H, d, *J* = 10.5 Hz, CH), 0.18 (9H, s, $Si(CH_3)_3$), 0.16 (9H, s, $Si(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1 (C=O), 75.8 (OC_q), 70.6 (CHOC*H*), 68.7 (TMSOC*H*), 60.0 (CH), 53.2 (CH_2), 44.1 (CH_2), 41.3 (CH_2), 39.6 (C_q), 36.9 (CH_3), 33.6 (C_q), 30.6 (CH_3), 22.6 (CH_3), 18.1 (CH_3), 17.9 (CH_2), 2.6 ($Si(CH_3)_3$), 1.2 ($Si(CH_3)_3$); *m*/*z* calculated $[C_{21}H_{40}O_3Si_2]^+$ 397.2589 found $[M - H]^+$ 397.2584.



23

3-Nitro-4-methylacetophenone 23

To a stirring solution of conc. HNO_3 (31 mL) and conc. H_2SO_4 (40 mL) cooled to 0 °C was slowly added commercially purchased 4-methylacetophenone (10.0 g, 0.075 mol) over 30 min, using a thermometer to ensure the internal reaction temp maintained <10 °C (*mitigating potentially hazardous di- or tri-nitro tolyl derivatives*). After continued stirring for 10 min, the solution was carefully poured onto crushed ice and allowed to warm to rt. The yellow precipitate was collected by filtration and washed with copious amounts of water and then *n*-hexane (300 mL). The solid was collected and dried under high vacuum to give the *title compound* as a pale yellow amorphous solid (8.1 g, 60 %) which was used without further purification. Data are consistent with those previously reported in the literature.[4] mp 60–62 °C (lit[4] 60–61 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (1H, s, ArCH), 8.07 (1H, d, *J* = 8.0 Hz, ArCH), 7.46 (1H, d, *J* = 8.0 Hz, ArCH), 2.65 (3H, s, CH_3), 2.64 (3H, s, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0 (C=O), 149.4 (ArCH), 138.8 (ArCH), 136.1 (ArCH), 133.5 (Ar_q), 132.1 (Ar_q), 124.7 (Ar_q), 26.7 (CH_3), 20.7 (CH_3).

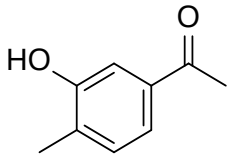


S1

3-Amino-4-methylacetophenone S1

Procedure 1: To a stirring solution of 3-nitro-4-methylacetophenone (3.1 g, 17 mmol) in MeOH (60 mL) was added 5% Pd/C (500 mg) followed by vigorous stirring under a balloon of hydrogen. After 1.5 h the mixture was filtered under vacuum. The filtrate was collected and the solvent was removed *in vacuo* to give the title compound as off-white crystals (2.40 g, 94%) which were used without further purification. Data are consistent with those previously reported in the literature.[4] mp 78–79 °C (lit[4] 80–81 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (1H, d, J = 1.7 Hz, ArCH), 7.26 (ArCH), 7.10 (1H, d, J = 7.5 Hz, ArCH), 3.75 (2H, s, NH_2), 2.53 (3H, s, CH_3), 2.20 (3H, s, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3 (C=O), 145.0 (NC_q), 136.4 (OCC_q), 130.5 (ArCH), 128.1 (MeC_q), 119.1 (ArCH), 114.0 (ArCH), 26.6 (CH_3) , 17.6 ($ArCH_3$).

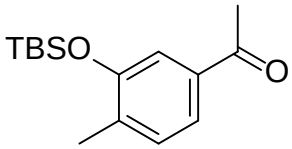
Procedure 2: (for >3 g)**:** To a stirred suspension of 3-nitro-4-methylacetophenone (14.0 g, 78 mmol) in 1.2 M HCl (100 mL) was added $SnCl_2{\cdot}2H_2O$ (53 g, 0.23 mol). The suspension was heated to 70 °C before continued stirring for 1 h. After cooling to 0 °C, $NaHCO_3$ (sat. aq.) was added until neutralisation (judged as pH 7 by indicator paper). The copious amounts of solid residues were removed by vacuum filtration and rinsed with EtOAc (3 x 50 mL) to give a biphasic filtrate. The separated organic filtrate was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give the title compound as orange crystals (7.2 g, 62%) which were used without further purification.[5] Data were in accord with those reported for procedure 1.



24

3-Hydroxy-4-methylacetophenone 24

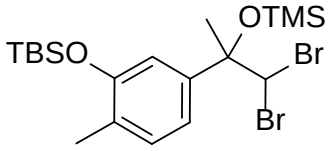
To a stirred suspension of 3-amino-4-methylacetophenone (15.8 g, 0.11 mol) in ice-cold water (200 mL) was slowly added conc. H_2SO_4 (54 mL). After 30 min a blast shield was installed (potentially explosive diazonium intermediate will be formed) and the solution was cooled to 0 °C before $NaNO_2$ (9.0 g, 0.13 mol) in water (30 mL) was added. After stirring for 10 min the solution was heated to reflux and stirring was continued for 5 h. After this time, the mixture was carefully poured onto ice-cold water (50 mL) which was then allowed to warm to 23 °C over 17 h. After this time, the solid was collected using a sintered funnel under reduced pressure, washing with copious amount of water. Dissolution of the collected solid in EtOAc (40 mL) was followed by washing with water (50 mL), $NaHCO_3$ (sat. aq., 20 mL), brine (20 mL), drying over $MgSO_4$ and filtering. The solvent was removed *in vacuo* to give the title compound as light brown crystals (16.3 g, 99%). The data are consistent with those previously reported in the literature.[4] mp 108–109 °C (lit[4] 110–111 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (1H, d, J = 1.6 Hz, ArCH), 7.45 (1H, dd, J = 7.7 and 1.6 Hz, ArCH), 7.20 (1H, d, J = 7.7 Hz, ArCH), 5.61 (1H, s, OH), 2.57 (3H, s, CH_3), 2.32 (3H, s, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4 (C=O), 154.4 (Ar_q), 136.6 (Ar_q), 131.2 (ArCH), 130.8 (Ar_q), 121.5 (ArCH), 114.1 (ArCH), 26.7 (CH_3), 16.25 (CH_3).



25

3-(*tert*-Butyldimethylsiloxy)-4-methylacetophenone 25

To a stirred solution of 3-hydroxy-4-methylacetophenone **24** (16.3 g, 0.11 mol) in CH_2Cl_2 (100 mL) was added imidazole (22.2 g, 0.33 mol) and TBSCl (24 g, 0.16 mol). After stirring for 16 h, water (100 mL) was added. The separated organic layer was washed with NH_4Cl (sat. aq., 100 mL), water (5 × 300 mL), dried over $MgSO_4$ and filtered. The volatiles were removed *in vacuo* to give *the title compound* as brown oil (18.3 g, 63%), which was used without further purification. ν_{max}/cm^{-1} 2956w, 2930w, 2858w, 1684s (C=O), 1602w, 1573w, 1500m, 1410m, 1356s, 1224s, 1193m, 1136w, 1068w; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (1H, dd, J = 7.8 and 1.6 Hz, ArCH), 7.36 (1H, d, J = 1.6 Hz, ArCH), 7.20 (1H, d, J = 7.8 Hz, ArCH), 2.55 (3H, s, CH_3), 2.26 (3H, s, CH_3), 1.03 (9H, s, $SiC(CH_3)_3$), 0.25 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7 (C=O), 154.3 (Ar_q), 136.5 (Ar_q), 135.4 (Ar_q), 131.0 (ArCH), 121.7 (ArCH), 117.7 (ArCH), 26.7 (CH_3), 25.9 ($SiC(CH_3)_3$), 18.4 (SiC), 17.3 (CH_3), –4.06 ($Si(CH_3)_2$): *m/z* calculated for $[C_{15}H_{25}O_2Si]^+$ 265.1618 found $[M + H]^+$ 265.1620.



27

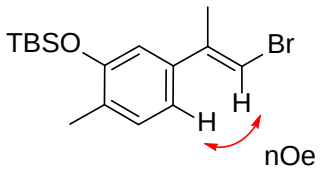
***tert*-Butyl(5-(1,1-dibromo-2-((trimethylsilyl)oxy)propan-2-yl)-2-methylphenoxy)dimethylsilane 27**

A solution of acetophenone **25** (1.0 g, 3.8 mmol) and dibromomethane (1.4 g, 7.9 mmol) in THF (10 mL) was transferred *via* cannula into an RBF containing a THF (10 mL) solution of freshly prepared lithium diisopropylamide (7.6 mmol) at –78 °C. After stirring for 4 h at –78 °C, NH_4Cl aq. (2 mL) and Et_2O (20 mL) were added. The separated organic layer was dried over $MgSO_4$, filtered and the solvent was removed *in*

vacuo. The crude residue was then dried under high vacuum over 17 h. The crude residue (1.3 g) was dissolved in CH_2Cl_2 (20 mL) before imidazole (1.0 g, 14.9 mmol) and TMSCl (1.5 mL, 11.9 mmol) were added. After stirring for 4 h, water (10 mL) was added. The separated organic layer was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give a crude residue which was purified by flash column chromatography (SiO_2; petrol → 10% Et_2O in petrol) to give the *title compound* as brown viscous oil (1.3 g, 66% for two steps). ν_{max}/cm^{-1} 2956w, 2930w, 2897w, 2858w, 1609w, 1576w, 1502m, 1463m, 1251m, 1184m, 1065m; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (1H, d, J = 8.22 Hz, ArCH), 6.93–6.90 (2H, m, 2 × ArCH), 5.65 (1H, s, Br_2CH), 2.20 (3H, s, CH_3), 1.90 (3H, s, CH_3), 1.03 (9H, s, $SiC(CH_3)_3$), 0.23 (3H, s, $SiC(CH_3)$), 0.22 (3H, s, $SiC(CH_3)$), 0.10 (9H, s, $Si(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6 (ArCO), 141.8 (Ar_q), 130.5 (ArCH), 128.9 (Ar_q), 119.24 (ArCH), 117.42 (ArCH), 79.4 (CBr_2), 58.6 (*C*–OTMS), 26.0 ($SiC(CH_3)_3$), 23.7 (CH_3), 18.4 (SiC), 16.7 (CH_3), 2.2 ($Si(CH_3)_3$), –3.89 ($Si(CH_3)$), –3.96 ($Si(CH_3)$); *m*/*z* the expected ions could not be observed.

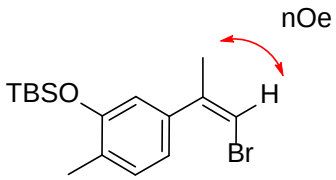
3-(*tert*-Butyldimethylsiloxy)-4-methylbromostyrene 28

To a solution of *bis*-dibromo **27** (1.3 g, 2.5 mmol) in THF (10 mL) was added *n*-BuLi (1.1 mL, 2.8 mmol) at –78 °C. After stirring for 1 h, NH_4Cl (sat. aq., 1 mL) and Et_2O (15 mL) were added before warming to room temp. The organic layer was separated, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give a crude mixture of *E*:*Z* alkenes in a 1.0:1.3 ratio respectively, as determined by ^{1}H NMR spectroscopy. The isomers were separated by flash column chromatography (SiO_2; *n*-hexane) to give (*Z*)-alkene **27** (140 mg, 16%) and (*E*)-alkene **27** (100 mg, 12%) both as colourless oils. The geometry of each alkene isomer was determined by NOESY.



(*E*)-28

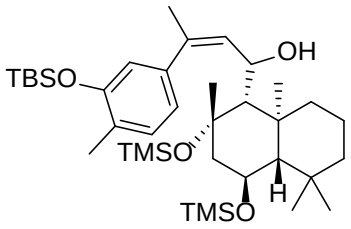
(*E*)-Alkene 28: ν_{max}/cm^{-1} 2956w, 2930w, 2887w, 2858w, 1608w, 1562w, 1510w, 1499w, 1402m, 1252s, 1180w, 1134w, 1001m; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (1H, d, J = 7.8 Hz, ArCH), 6.85 (1H, dd, J = 7.8 and 1.7 Hz, ArCH), 6.75 (1H, d, J = 1.7 Hz, ArCH), 6.40 (1H, q, J = 1.2 Hz, =CH), 2.21 (3H, s, ArCH_3), 2.20 (3H, d, J = 1.2 Hz, CH_3), 1.04 (9H, s, $SiC(CH_3)_3$), 0.24 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0 (ArCO), 141.4 (=C_q), 139.7 (Ar_q), 131.1 (ArCH), 128.9 (Ar_q), 118.8 (ArCH), 116.4 (ArCH), 104.7 (CBr), 25.9 ($SiC(CH_3)_3$), 19.8 (CH_3), 18.4 (SiC), 16.7 (CH_3), –4.0 ($Si(CH_3)_2$); *m/z* calculated for $[C_{16}H_{26}BrSi]^+$ 341.0931 found $[M + H]^+$ 341.0929. NOESY showed correlation between the alkenyl proton at 6.40 ppm and the proximal proton resonating at 6.85 ppm on the aromatic ring. There is no correlation observed between the alkenyl proton and the alkenyl methyl group.



(*Z*)-28

(*Z*)-Alkene 28: ν_{max}/cm^{-1} 2955w, 2929w, 2858w, 1607w, 1566m, 1500m, 1250s, 1130m; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (1H, d, J = 7.7 Hz, ArCH), 6.84 (1H, dd, J = 7.7 and 1.7 Hz, ArCH), 6.82 (1H, d, J = 1.7 Hz, ArCH), 6.19 (1H, q, J = 1.5 Hz, =CH), 2.24 (3H, s, ArCH_3), 2.11 (3H, d, J = 1.5 Hz, CH_3), 1.05 (9H ,s, $SiC(CH_3)_3$), 0.27 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6 (ArCO), 141.3 (=C_q), 138.7 (Ar_q),

130.8 (ArCH), 128.6 (Ar_q), 120.2 (ArCH), 118.2 (ArCH), 101.1 (CBr), 25.9 (Si*C*$(CH_3)_3$), 25.15 (CH_3), 18.4 (SiC), 16.9 (CH_3), –4.0 (Si$(CH_3)_2$); *m*/*z* calculated for $[C_{16}H_{26}BrSi]^+$ 341.0931 found $[M + H]^+$ 341.0933. NOESY showed a correlation between the alkenyl proton at 6.19 ppm and the alkenyl CH_3 group at 2.11 ppm.



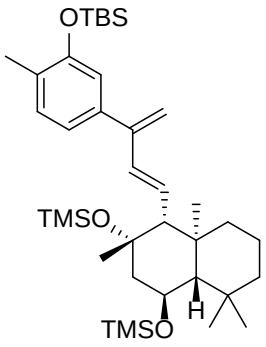
29

(*Z*)-3-(3-((*tert*-Butyldimethylsilyl)oxy)-4-methylphenyl)-1-((2,5,5,8a-tetramethyl-2,4-bis((trimethylsilyl)oxy)decahydronaphthalen-1-yl)but-2-en-1-ol 29

To a stirred solution of (*Z*)-bromoalkene **28** (174 mg, 0.51 mmol) in THF (1 mL) at –78 °C was added *t*-BuLi (0.6 mL, 1.0 mmol) dropwise over 2 min, to give a canary yellow solution. After continued stirring for 25 min a solution of aldehyde **22** (68 mg, 0.17 mmol) in THF (1 mL) was added dropwise. After continued stirring for 30 min the reaction was quenched by the addition of NH_4Cl (sat. aq., 0.1 mL), before dilution with Et_2O (5 mL). After warming to 23 °C the separated organic layer was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give a crude residue which was purified by flash column chromatography (SiO_2; petrol → 5% Et_2O in petrol) to give the *title compound* as pale yellow oil and as a single diastereomer (60 mg, 53%). The stereochemistry of the secondary alcohol was not determined. The geometry of the alkene was determined by NOESY.

ν_{max}/cm^{-1} 3518br (O–H), 2955m, 2929m, 2859m, 1503m, 1201s, 1081s; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (1H, d, *J* = 7.6 Hz, ArCH), 6.66 (1H, dd, *J* = 7.6 and 1.3 Hz, ArCH), 6.57 (1H, d, *J* = 1.3 Hz, ArCH), 5.88 (1H, d, *J* = 8.3 Hz, =CH), 4.89–4.85 (1H, apparent broad d, *J* ≈ 8.4 Hz, OHC*H*), 4.09 (1H, dt, *J* = 9.5 and 4.4 Hz, TMSOC*H*), 2.62 (1H, s, OH), 2.17 (3H, s, $ArCH_3$), 2.01 (1H, dd, *J* = 14.0 and 4.4 Hz, CH_{a1}), 1.97 (3H, s,

=CC*H*$_3$), 1.89–1.83 (1H, m, CH_{a2}), 1.55–1.26 (7H, m, CH_2, CH_3, CH_{b1}, CH_{a3}), 1.22–1.06 (2H, m, $CH_{b3,}$ CH_{b2}), 1.03 (3H, s, CH_3), 1.02 (9H, s, $SiC(CH_3)_3$)), 0.98 (3H, m, CH_3,), 0.96 (1H, d, $J \approx 1.0$ Hz, HOCC*H*), 0.92 (1H, d, $J = 9.5$ Hz, TMSOCC*H*), 0.89 (3H, s, CH_3), 0.22 (3H, s, $Si(CH_3)$), 0.20 (3H, s, $Si(CH_3)$), 0.130 (9H, s, $Si(CH_3)_3$), 0.126 (9H, s, $Si(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0 (ArCO), 140.9 (=C_q), 136.1 (Ar_q), 131.7 (=CH), 130.9 (ArCH), 127.3 (Ar_q), 120.6 (ArCH), 117.9 (ArCH), 79.7 (OC_q), 70.7 (HOCH), 68.8 (TMSOC*H*), 62.3 (HOCC*H*), 61.3 (TMSOCC*H*), 52.6 (CH_2), 43.8 (CH_2), 42.9 (CH_2), 41.3 (C_q), 36.7 ($ArCH_3$), 33.6 (C_q), 32.0 (CH_3), 26.3 (CH_3), 26.0 ($SiC(CH_3)_3$), 22.9 (CH_3), 18.9 (SiC), 18.4 (CH_2), 16.7 (CH_3), 2.8 ($Si(CH_3)_3$), 1.3 ($Si(CH_3)_3$), –3.85 ($Si(CH_3)$), –3.94 ($Si(CH_3)$); *m/z* calculated for $[C_{37}H_{68}O_4Si_3]^+$ 660.4365 found $[M]^+$ 660.4420.

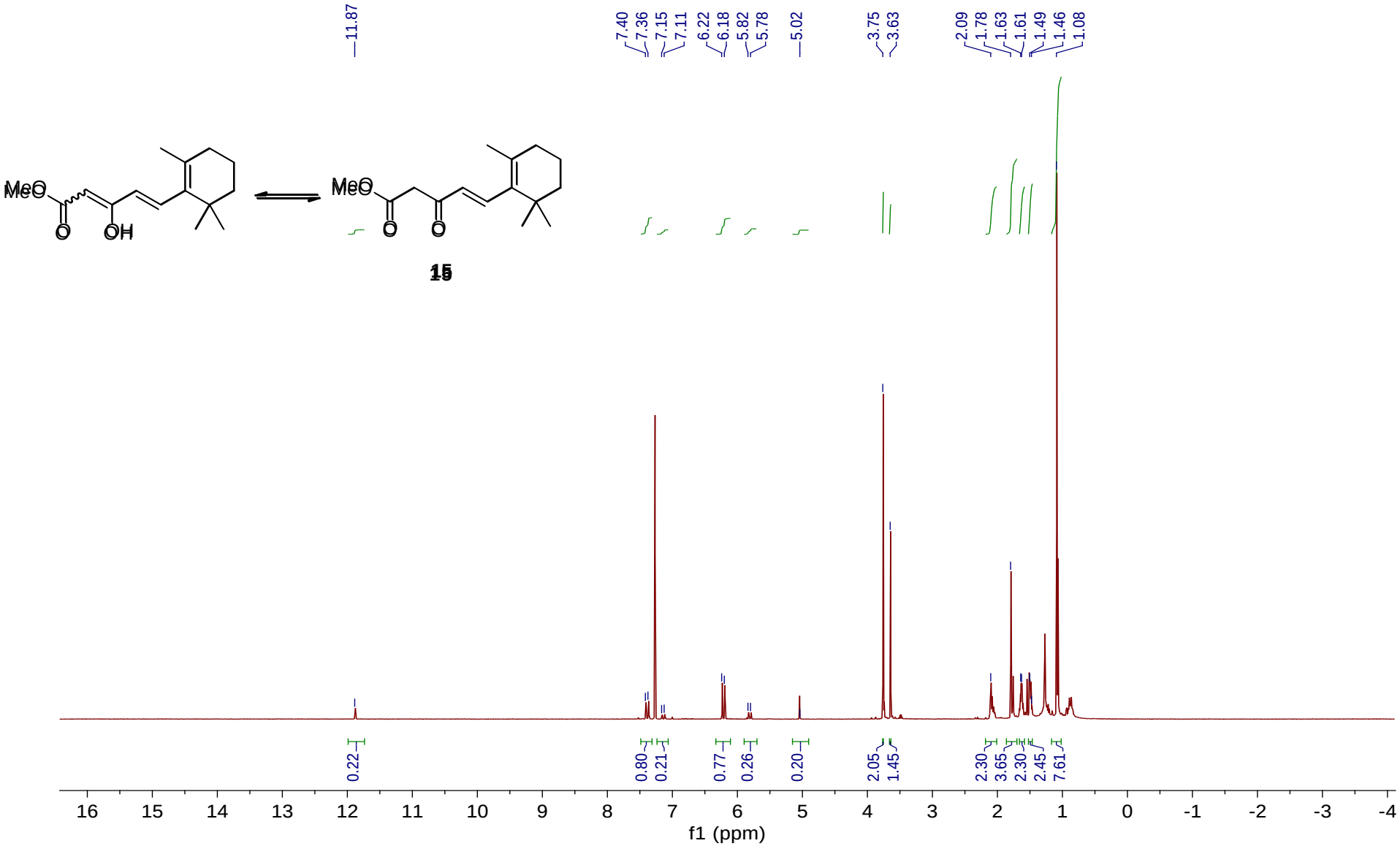


30

Ansellane diene 30

Ansellane alcohol **29** (≈60 mg) was left standing for several days in a fumehood, giving a mixture of degradation products. Purification of the oil by flash column chromatography (SiO_2; petrol) gave *the title compound* as pale yellow oil (≈10 mg). ν_{max}/cm^{-1} 2931m, 1860m, 1885m, 1836m, 1774m, 1411m, 1250m; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (1H, d, J = 7.7 Hz, ArCH), 6.83 (1H, dd, J = 7.7 and 1.6 Hz, ArCH), 6.73 (1H, d, J = 1.6 Hz, ArCH), 6.14 (1H, d, J = 15.8 Hz, HC=C*H*C_q), 5.76 (1H, dd, J = 15.8 and 10.0 Hz, *H*C=CHC_q), 5.14 (1H, d, J = 1.9 Hz, C_q=CH), 5.04 (1H, d, J = 1.9 Hz, C_q=CH), 4.21 (1H, td, J = 10.6 and 4.0 Hz, TMSOC*H*), 2.20 (3H, s, ArC*H*$_3$), 2.07–2.01 (1H, m, CH_{a1}), 1.56–1.16 (7H, m, 2 × CH_2, CH_{b1}, CH_{a2}, C_qCH), 1.13 (3H, s, CH_3), 1.11 (3H, s, CH_3), 1.01 (10H, brs, $SiC(CH_3)_3$, C_qCH), 0.99 (6H, brs, 2 × CH_3), 0.20 (6H, s,

$Si(CH_3)_2$), 0.16 (9H, s, $Si(CH_3)_3$), 0.00 (9H, s, $Si(CH_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7 (ArCO), 148.2 (Ar_q), 139.6 (=C_q), 134.9 (C=*C*HC_q), 132.8 (H*C*=CHC_q), 130.5 (ArCH), 128.1 (Ar_q), 120.9 (ArCH), 118.4 (ArCH), 113.4 (=CH_2), 76.4 (OC_q), 69.0 (TMSO*C*), 64.5 (CH), 60.7 (CH), 53.8 (CH_2), 44.6 (CH_2), 41.9 (CH_2), 40.0 (C_q), 36.9 ($ArCH_3$), 33.8 (C_q), 30.9 (CH_3), 25.9 ($Si(CH_3)_3$), 22.5 (CH_3), 18.4 (SiC), 18.3 (CH_2), 17.2 (CH_3), 16.8 (CH_3), 2.6 ($Si(CH_3)_3$), 1.2 ($Si(CH_3)_3$), –3.99 ($Si(CH_3)$), –4.01 ($Si(CH_3)$); *m/z* calculated for $[C_{37}H_{66}O_3Si_3]^+$ 642.4320 found $[M]^+$ 642.4316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1.46
1.08
MeO
O
OH
MeO
O
O
15
0.22
0.80
0.21
0.77
0.26
0.20
2.05
1.45
2.30
3.65
2.30
2.45
7.61
16
15
14
13
12
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-1
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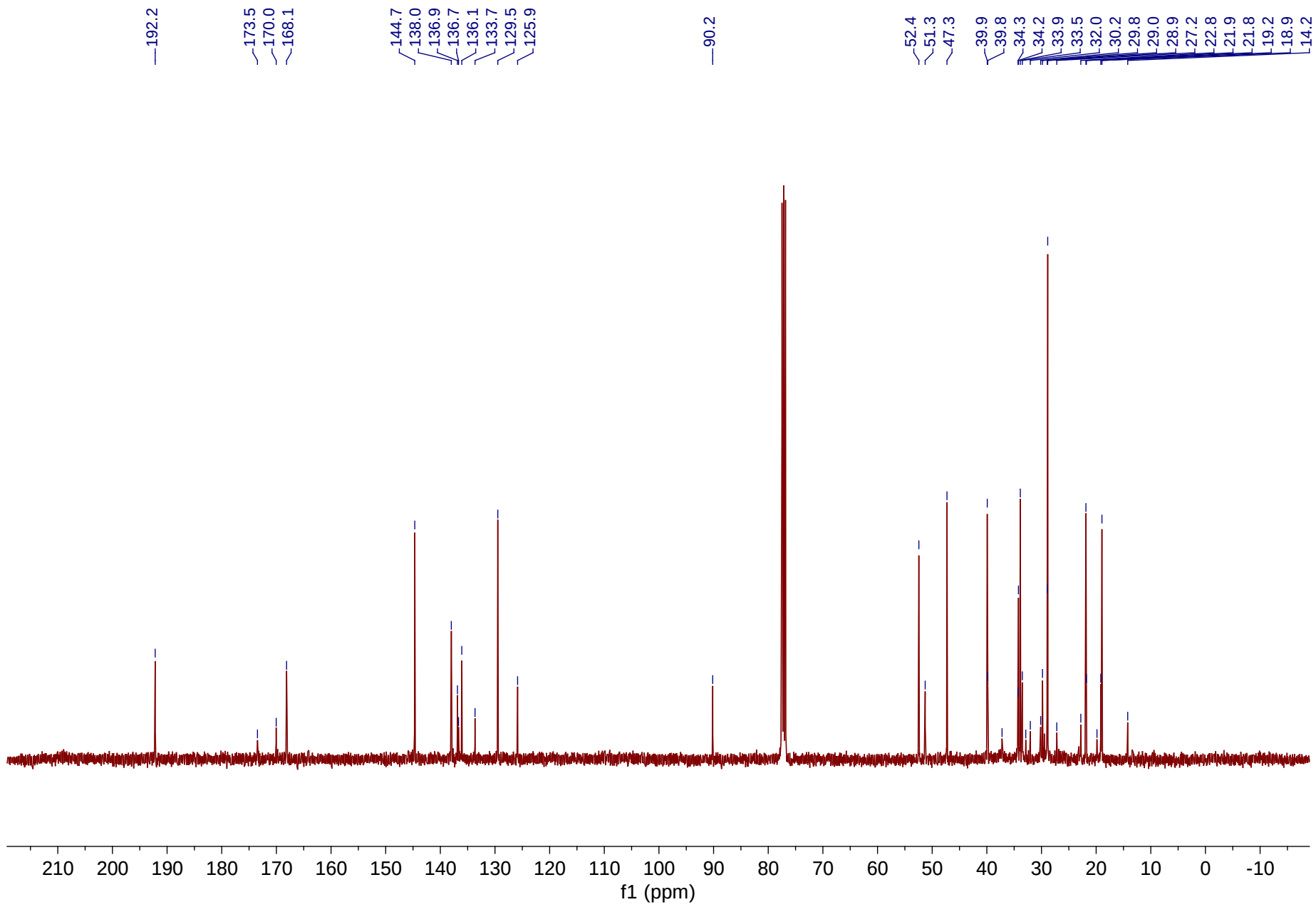
-3
-4
f1 (ppm)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52.4
51.3
47.3
39.9
39.8
34.3
34.2
33.9
33.5
32.0
30.2
29.8
29.0
28.9
27.2
22.8
21.9
21.8
19.2
18.9
14.2
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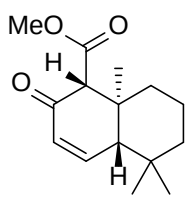
f1 (ppm)


MeO
O
H
O
H

16

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6.15
6.13
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3.26
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1.53
1.43
1.26
1.22
1.04
0.95
0.89
1.08
1.07
3.27
1.00
1.08
6.45
4.66
3.12
12.94
10.5
9.5
9.0
8.5
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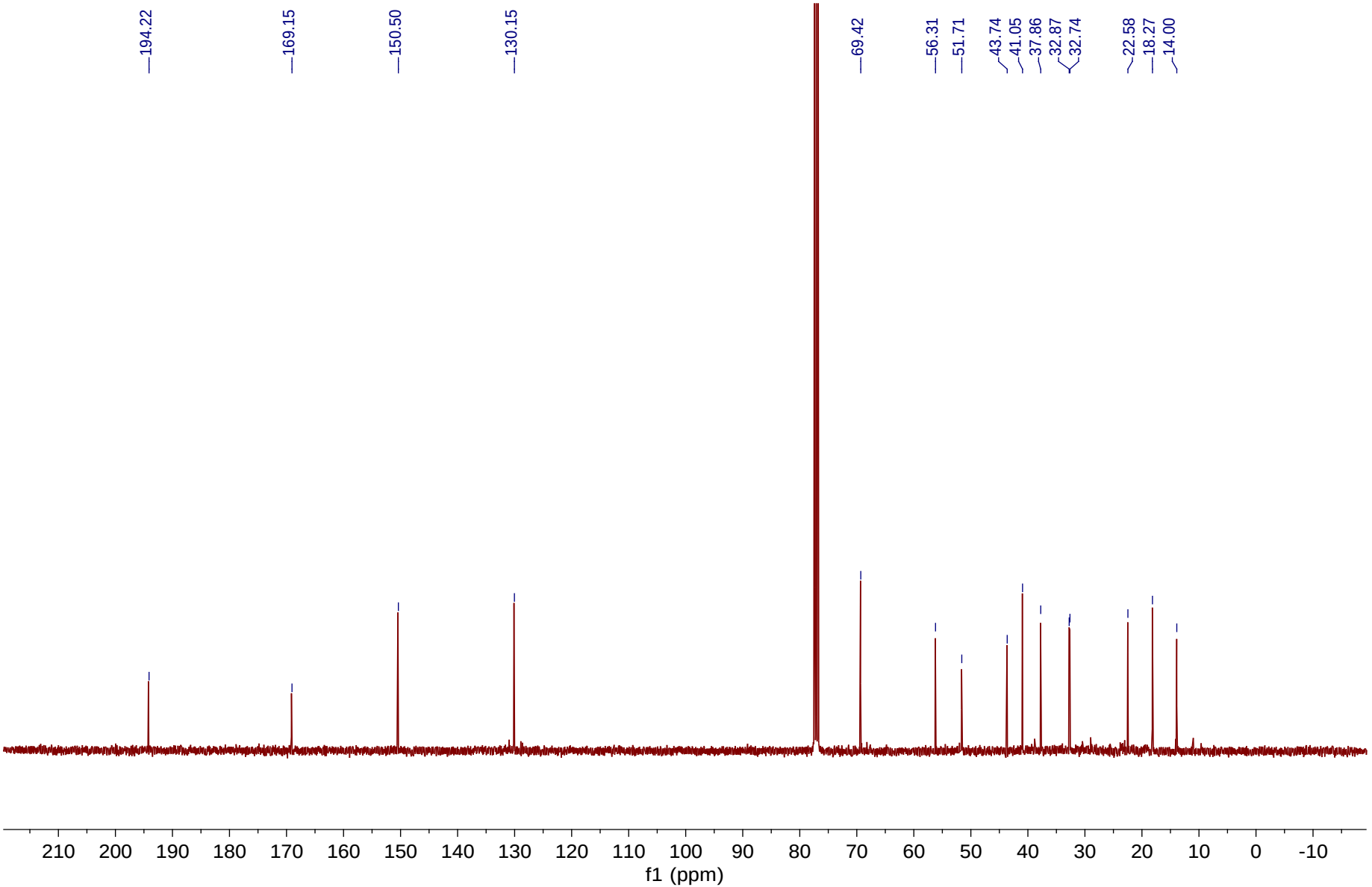
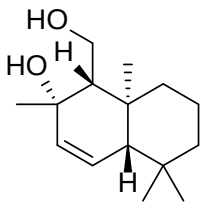
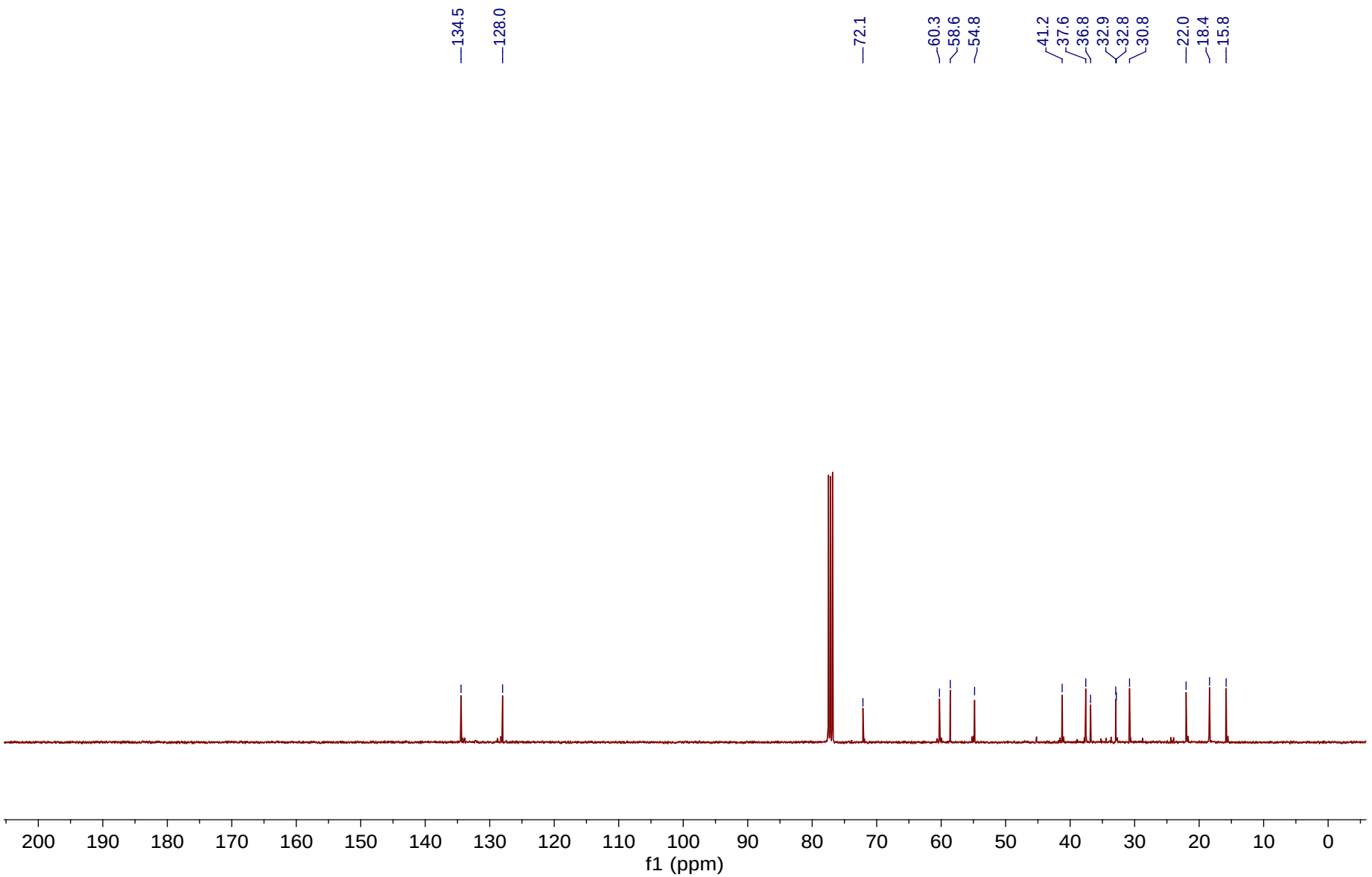
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

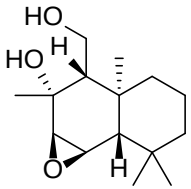

194.22
169.15
150.50
130.15
69.42
56.31
51.71
43.74
41.05
37.86
32.87
32.74
22.58
18.27
14.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


HO
H
HO
H

18

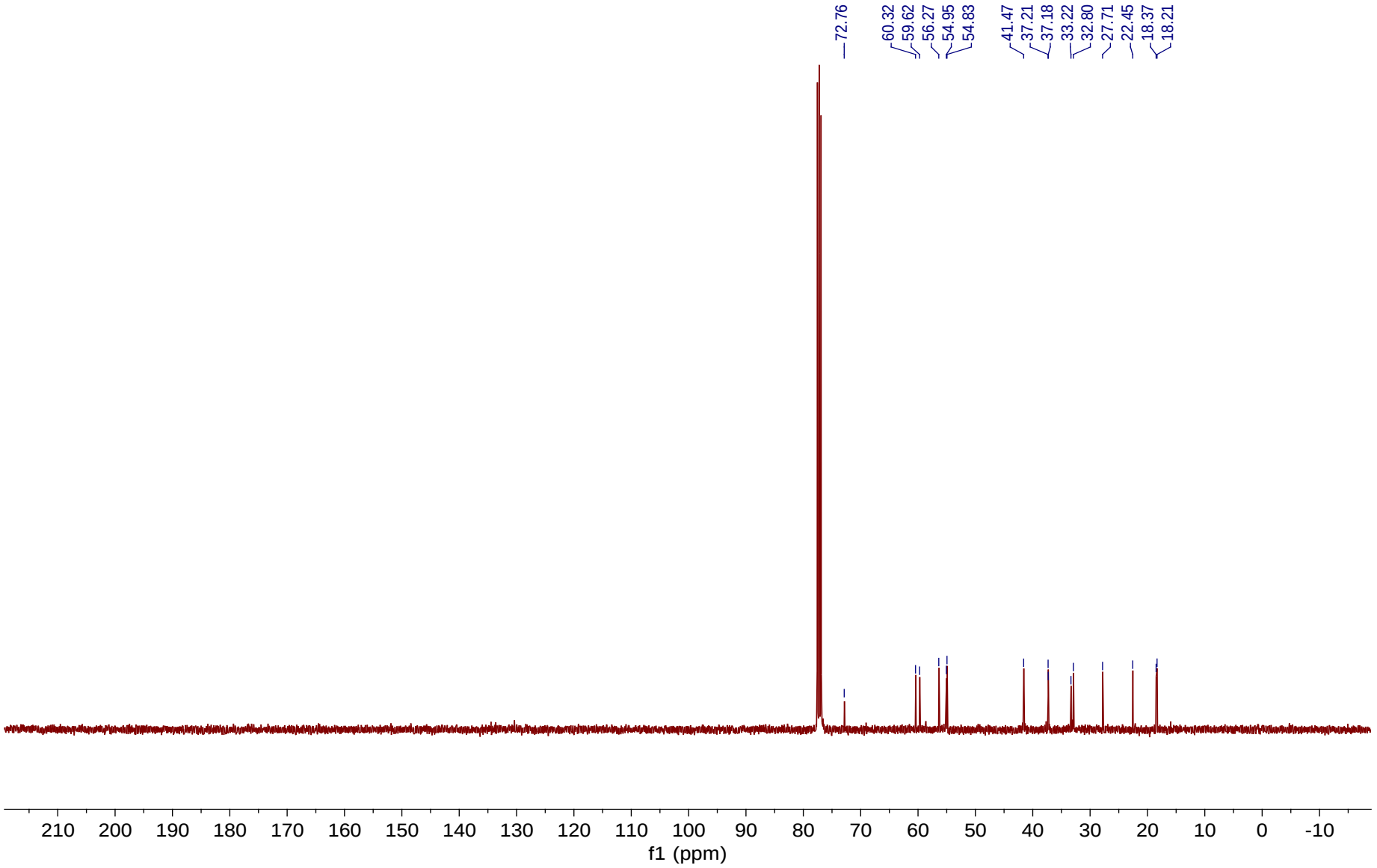
5.74
5.71
5.65
5.62
4.05
4.04
2.51
1.88
1.74
1.42
1.40
1.37
1.29
1.23
1.08
0.91
0.88
0.81
2.00
1.95
2.09
6.33
2.83
3.79
3.40
7.44
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

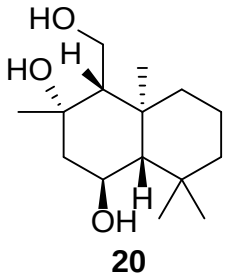

134.5
128.0
72.1
60.3
58.6
54.8
41.2
37.6
36.8
32.9
32.8
30.8
22.0
18.4
15.8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
H
HO
O
H

19

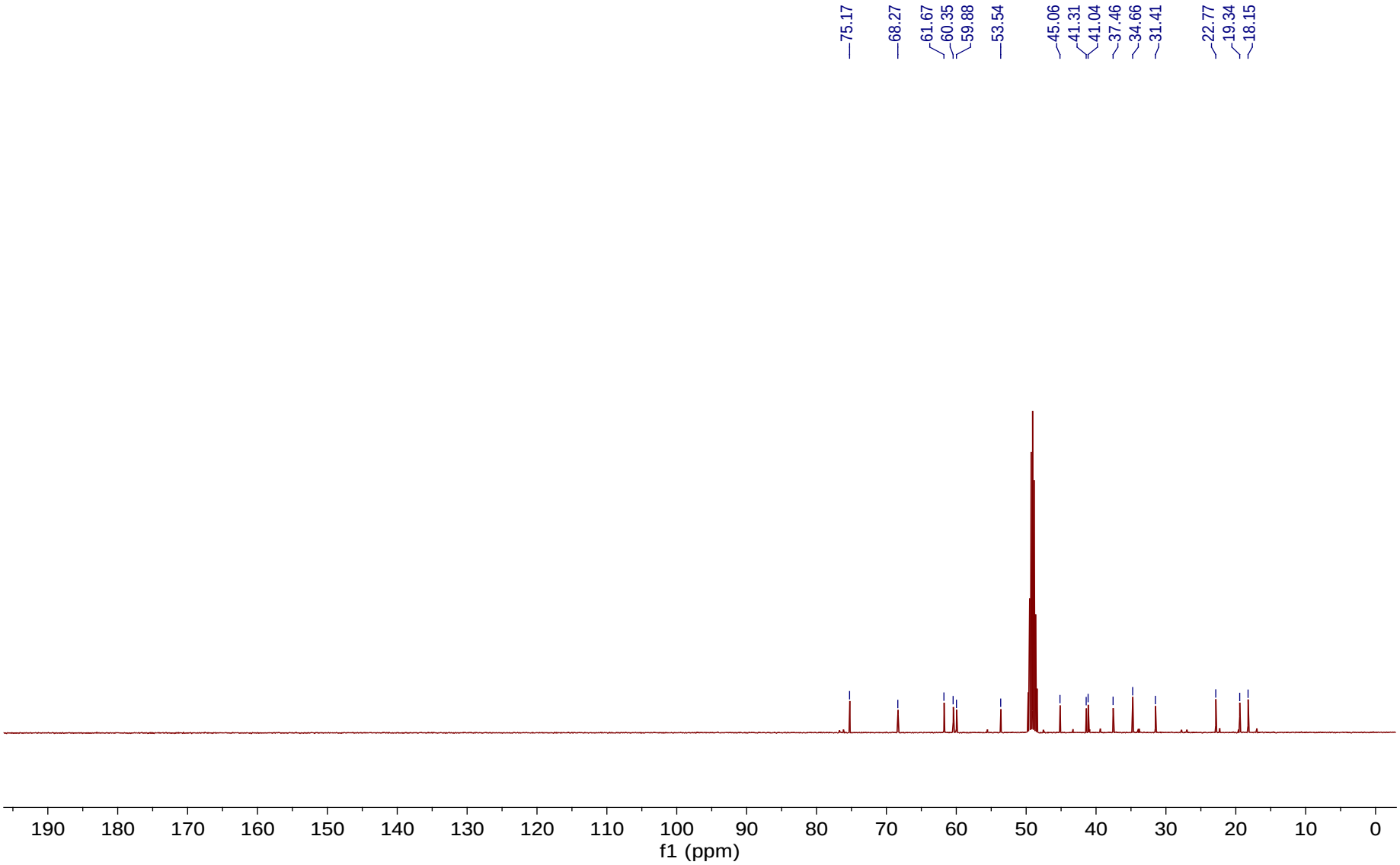
4.10
4.07
4.04
4.02
3.15
2.99
2.36
1.75
1.49
1.28
1.22
1.14
1.04
1.02
0.88
2.00
1.00
1.90
1.00
2.49
5.63
15.83
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

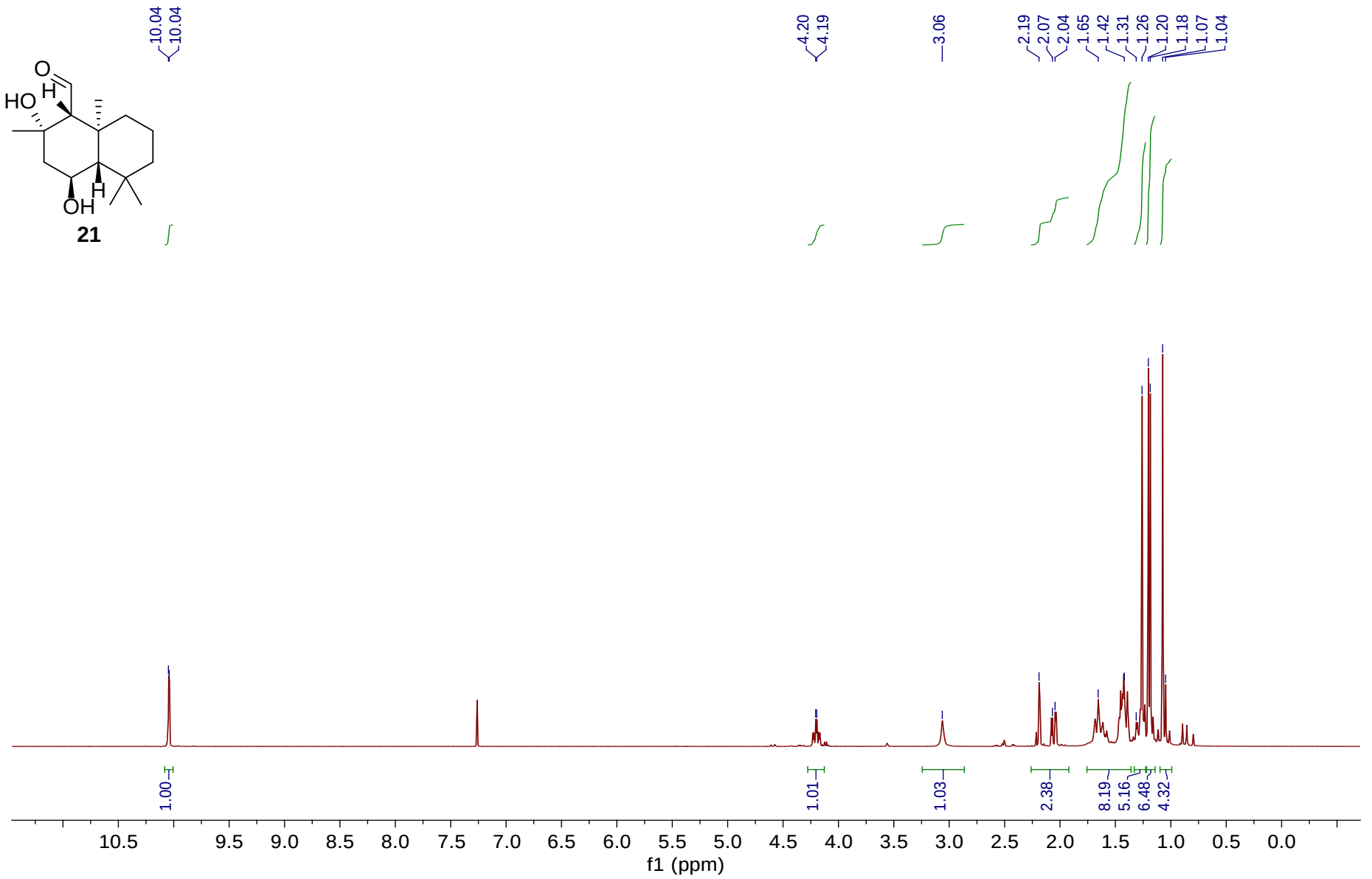

72.76
60.32
59.62
56.27
54.95
54.83
41.47
37.21
37.18
33.22
32.80
27.71
22.45
18.37
18.21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

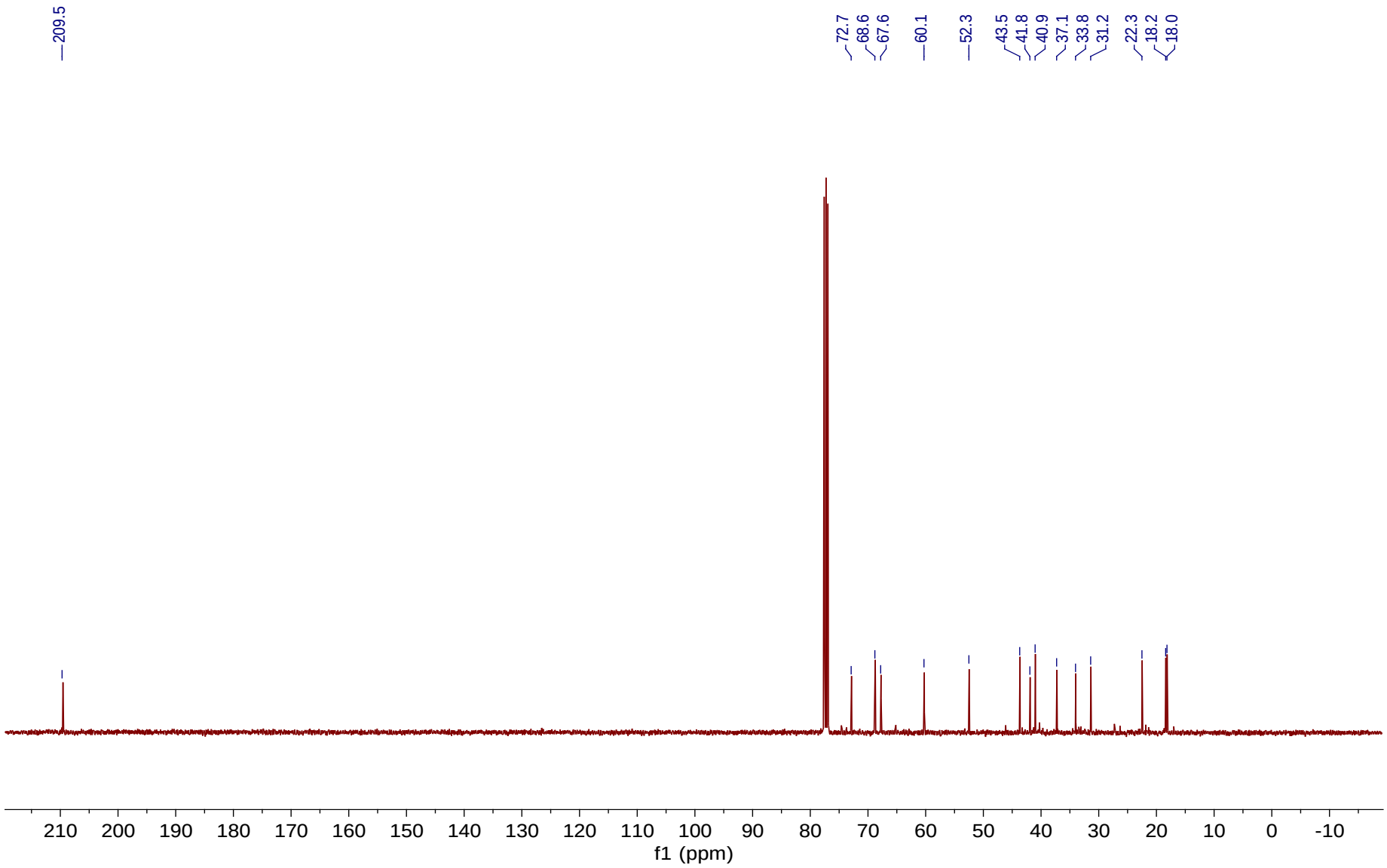

HO
H
HO
H
OH

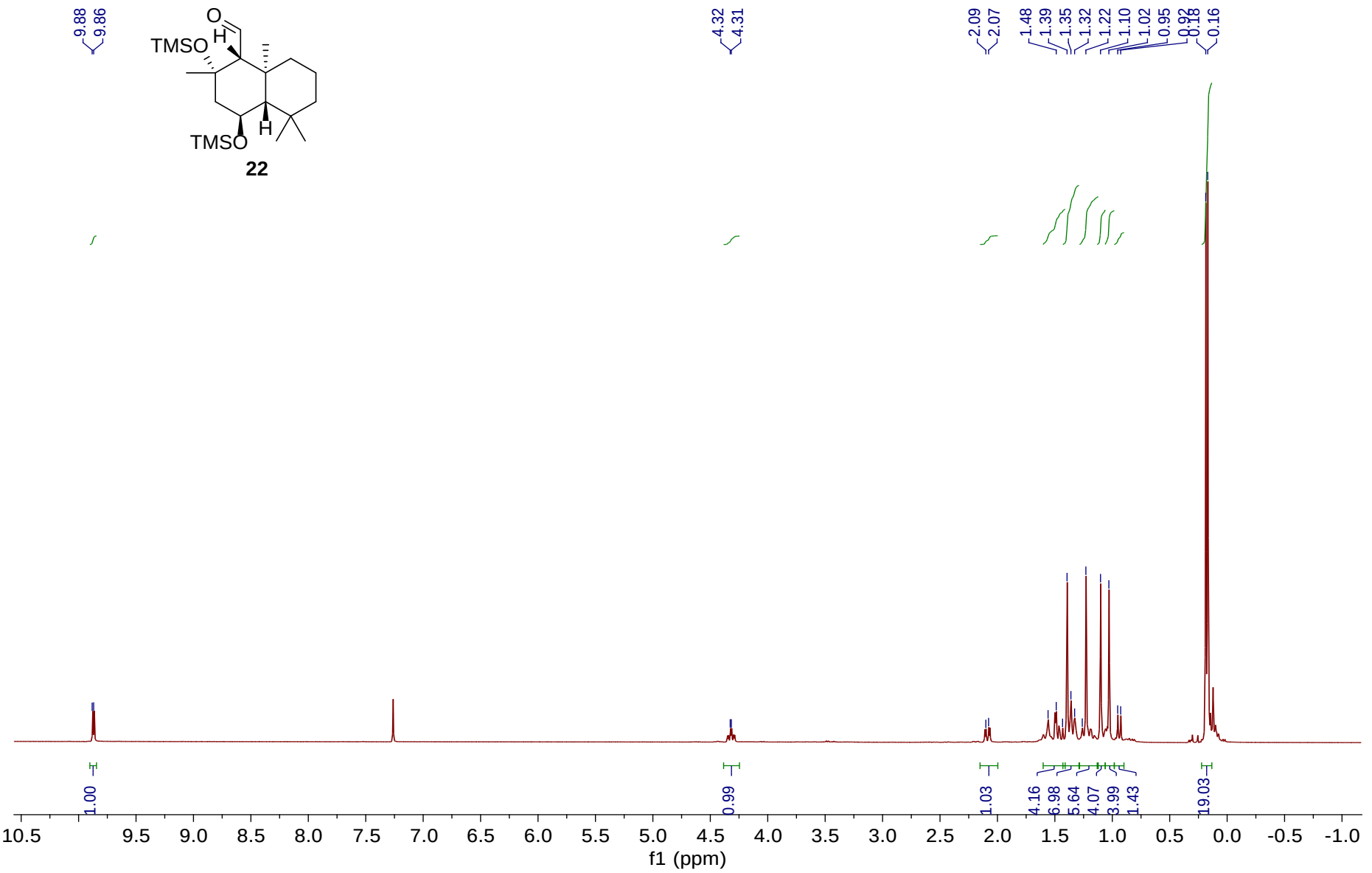
20

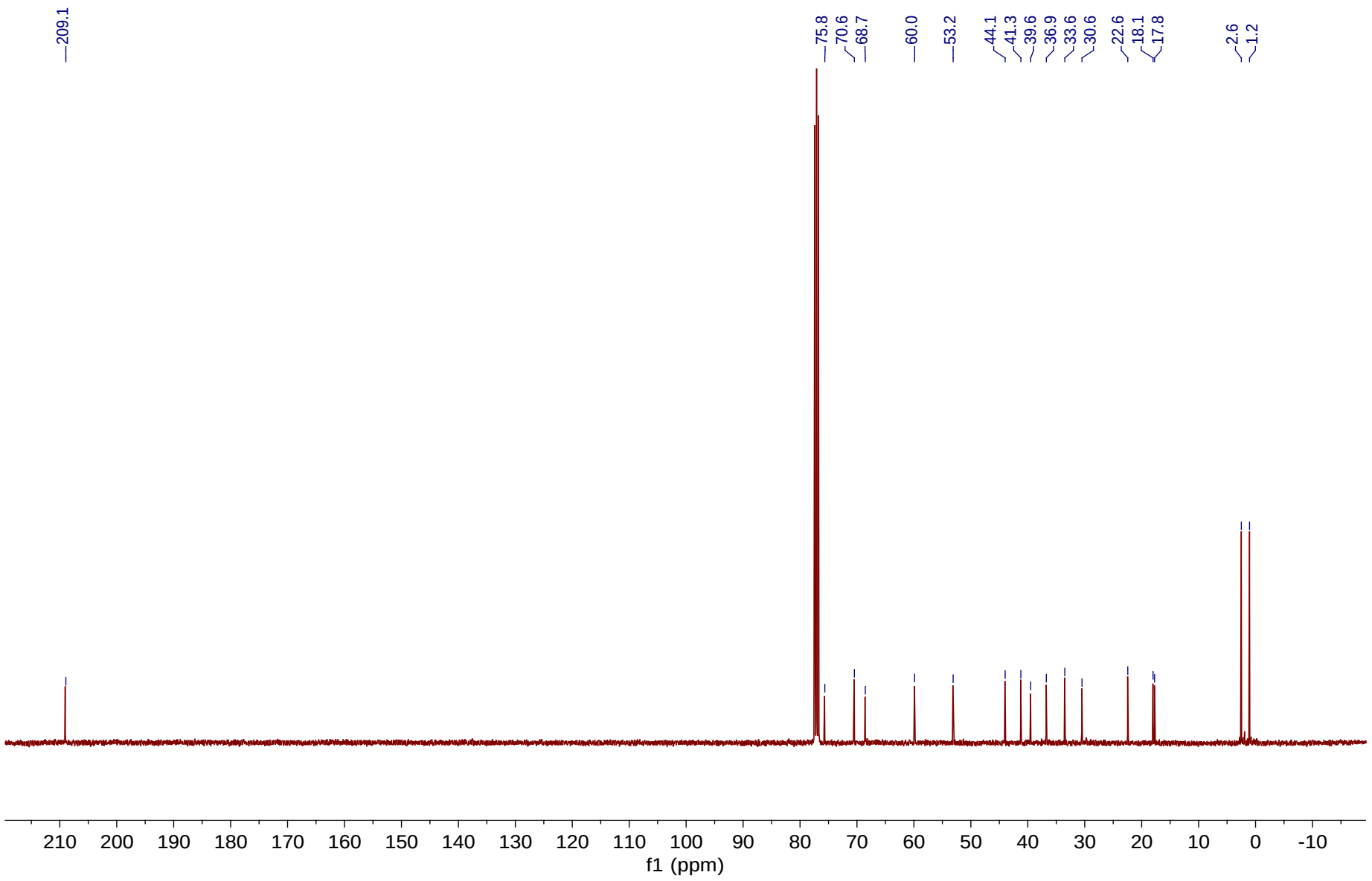
4.12
4.11
4.01
3.98
3.92
3.89
3.36
2.06
2.03
1.91
1.88
1.73
1.70
1.58
1.48
1.39
1.36
1.31
1.27
1.21
1.19
1.11
1.02
0.91
1.00
1.02
1.06
1.30
1.12
1.13
4.62
3.42
1.42
5.57
2.84
3.88
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

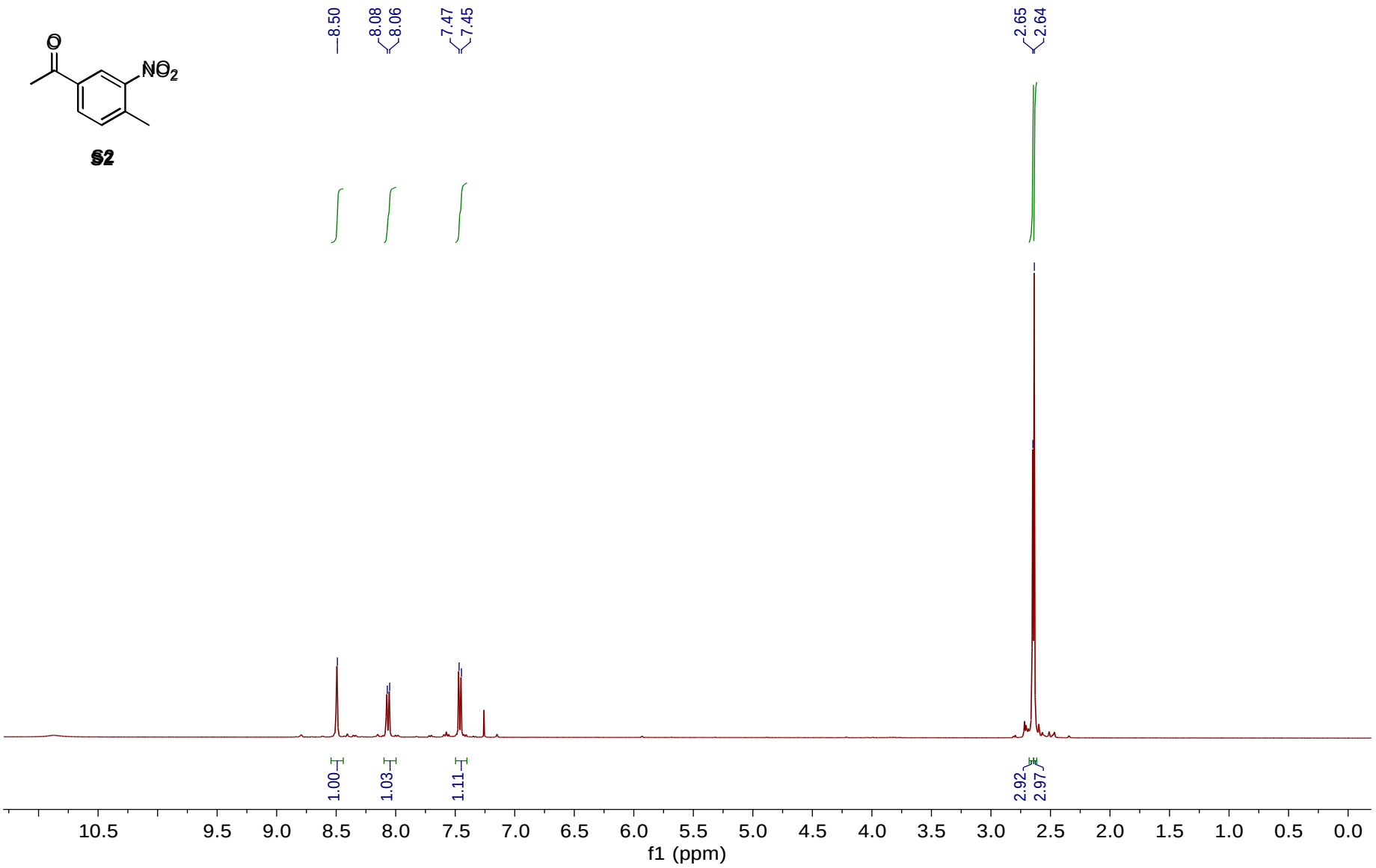

75.17
68.27
61.67
60.35
59.88
53.54
45.06
41.31
41.04
37.46
34.66
31.41
22.77
19.34
18.15
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

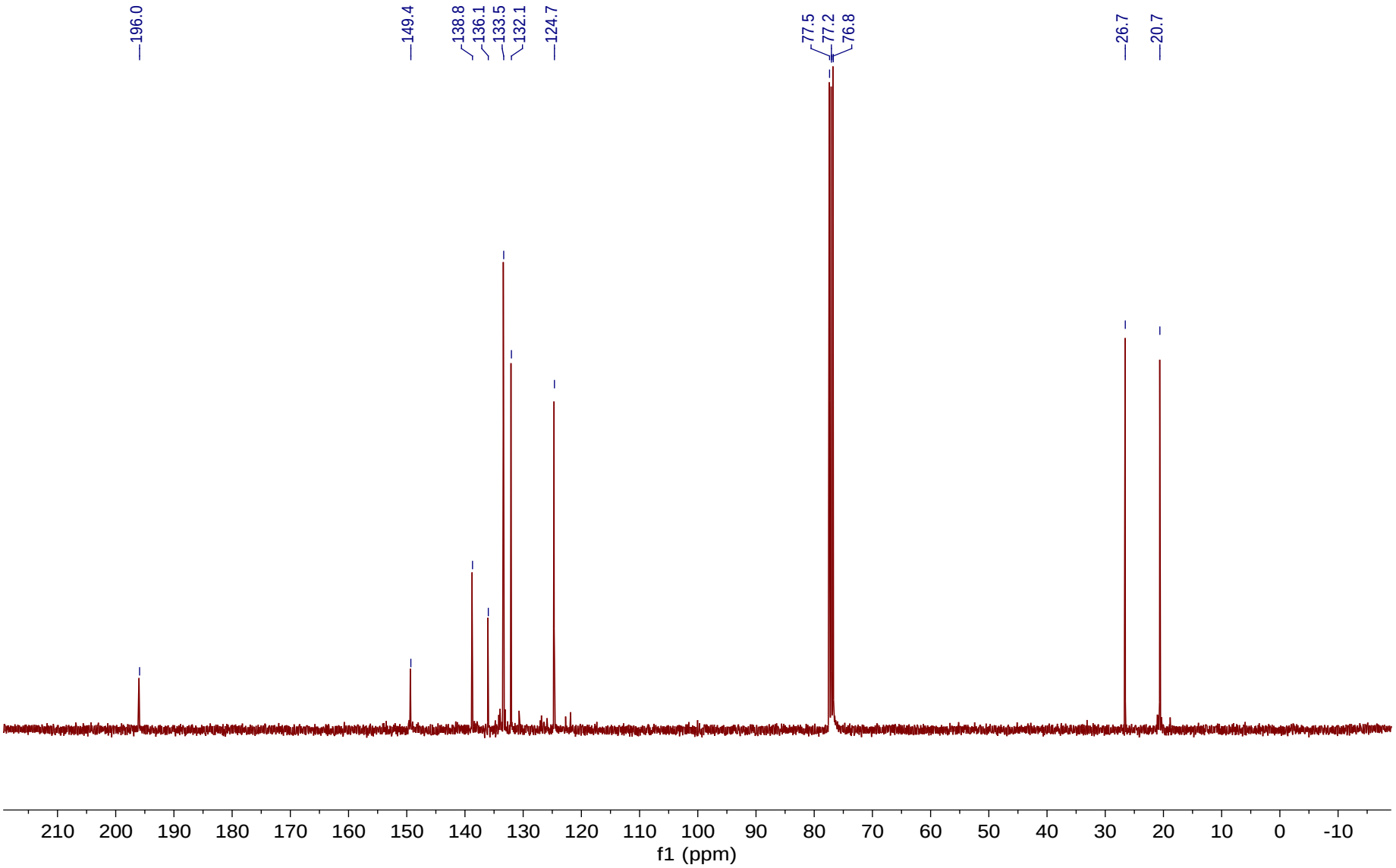

10.04
10.04
4.20
4.19
3.06
2.19
2.07
2.04
1.65
1.42
1.31
1.26
1.20
1.18
1.07
1.04
O
H
HO
H
OH
21
1.00
1.01
1.03
2.38
8.19
5.16
6.48
4.32
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

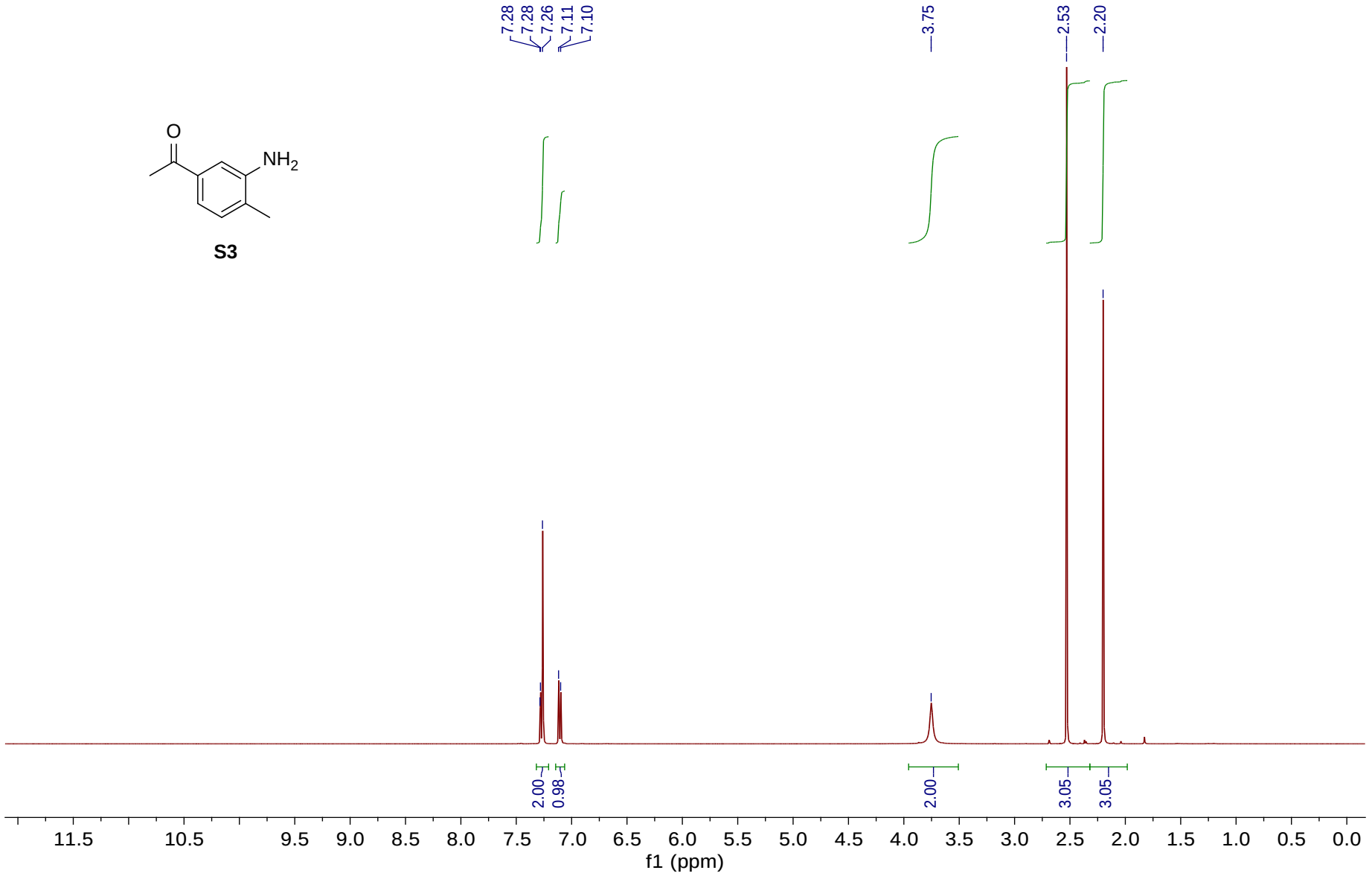

209.5
72.7
68.6
67.6
60.1
52.3
43.5
41.8
40.9
37.1
33.8
31.2
22.3
18.2
18.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

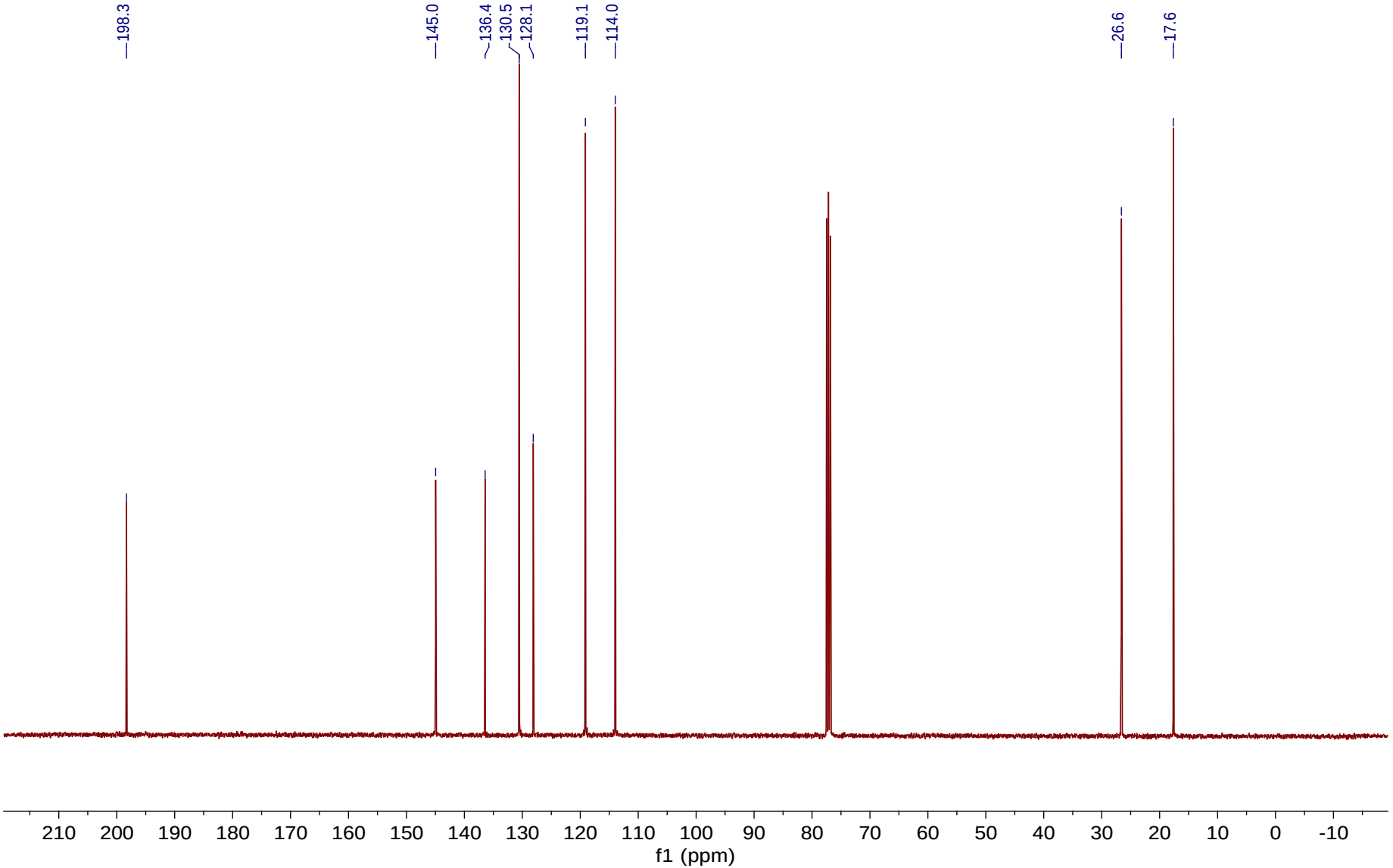

O
H
TMSO
TMSO
H
22
9.88
9.86
4.32
4.31
2.09
2.07
1.48
1.39
1.35
1.32
1.22
1.10
1.02
0.95
0.18
0.16
1.00
0.99
1.03
4.16
6.98
5.64
4.07
3.99
1.43
19.03
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

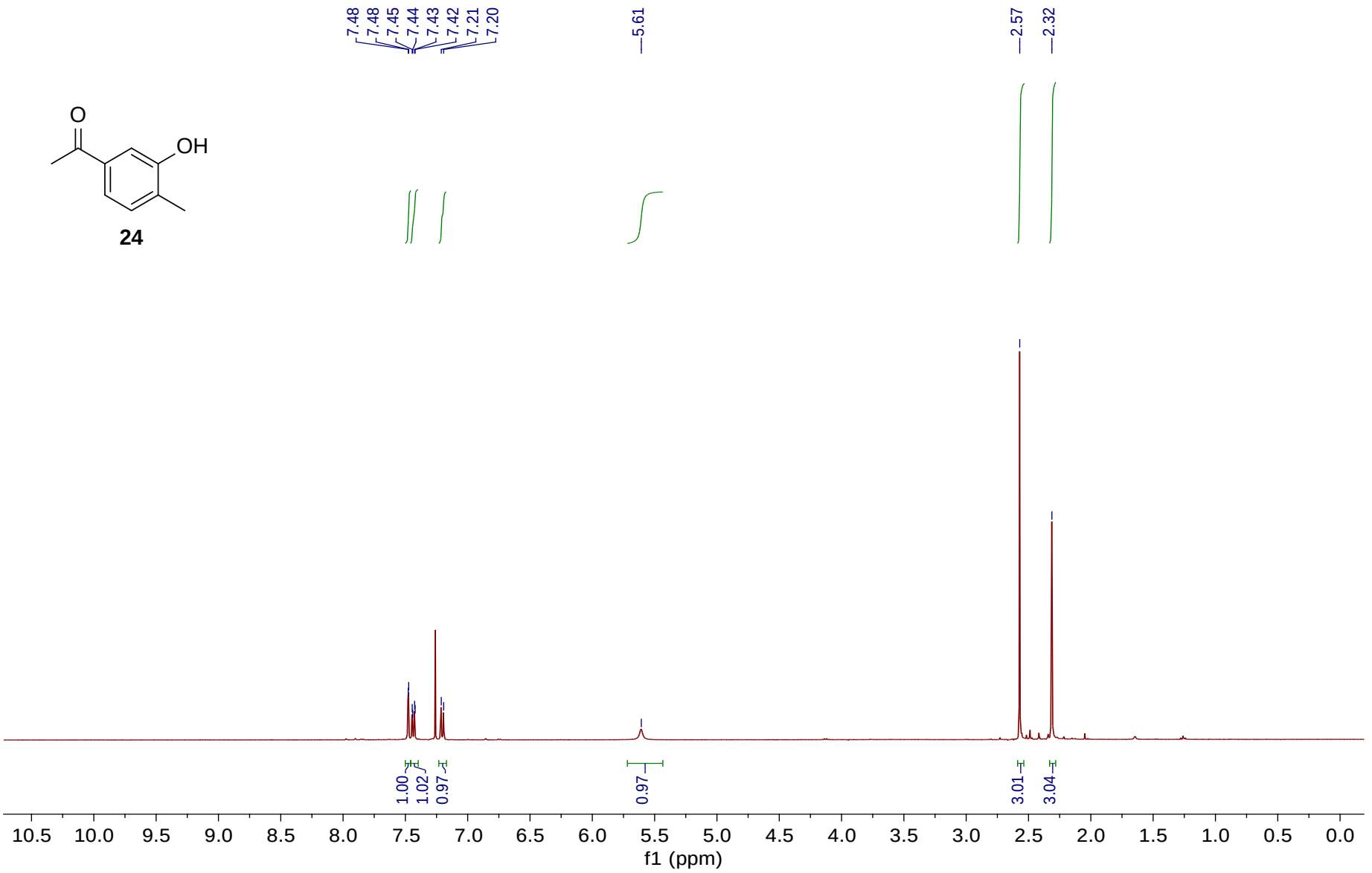

209.1
75.8
70.6
68.7
60.0
53.2
44.1
41.3
39.6
36.9
33.6
30.6
22.6
18.1
17.8
2.6
1.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

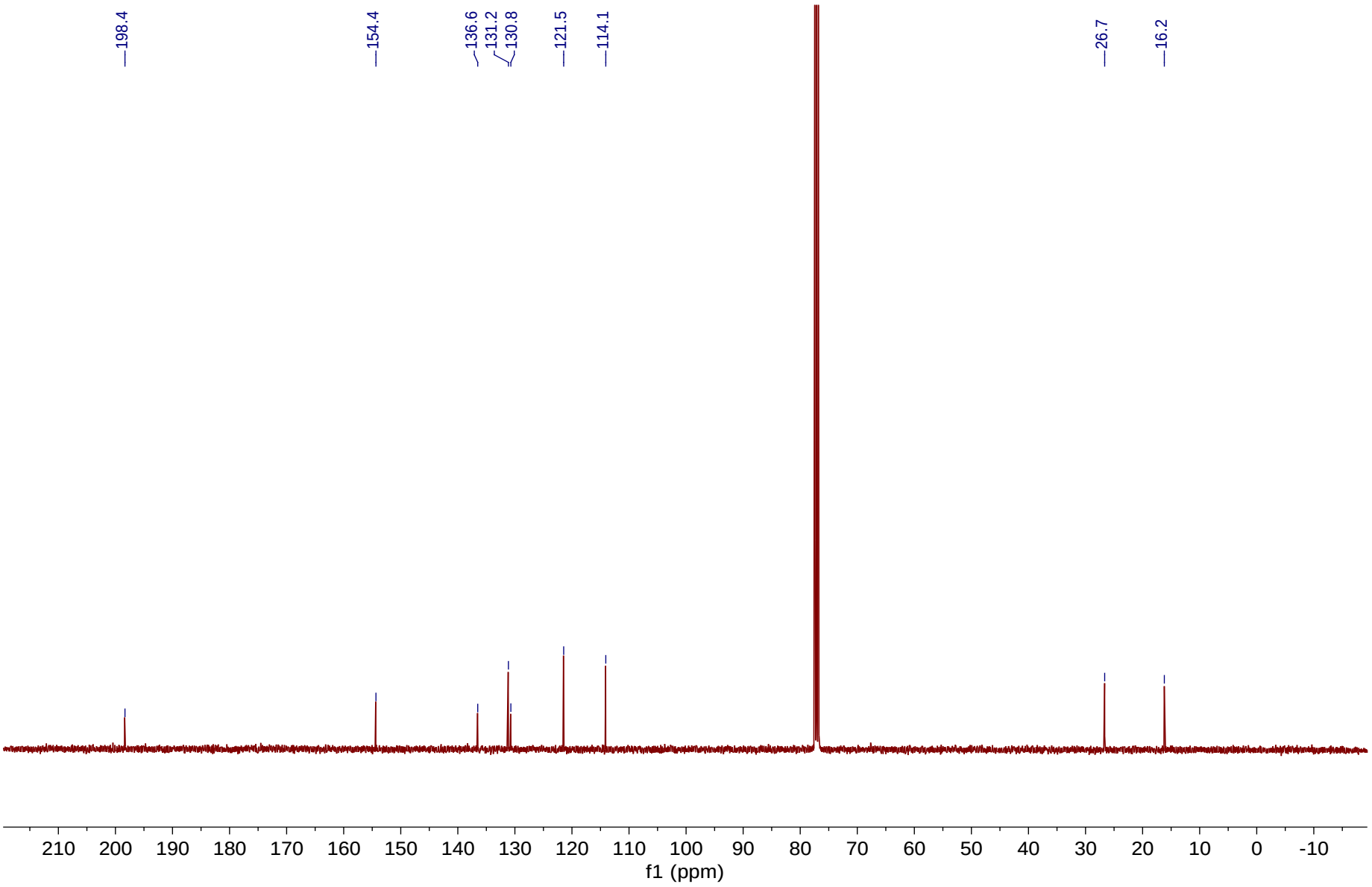

O
NO2
S2
8.50
8.08
8.06
7.47
7.45
2.65
2.64
1.00
1.03
1.11
2.92
2.97
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

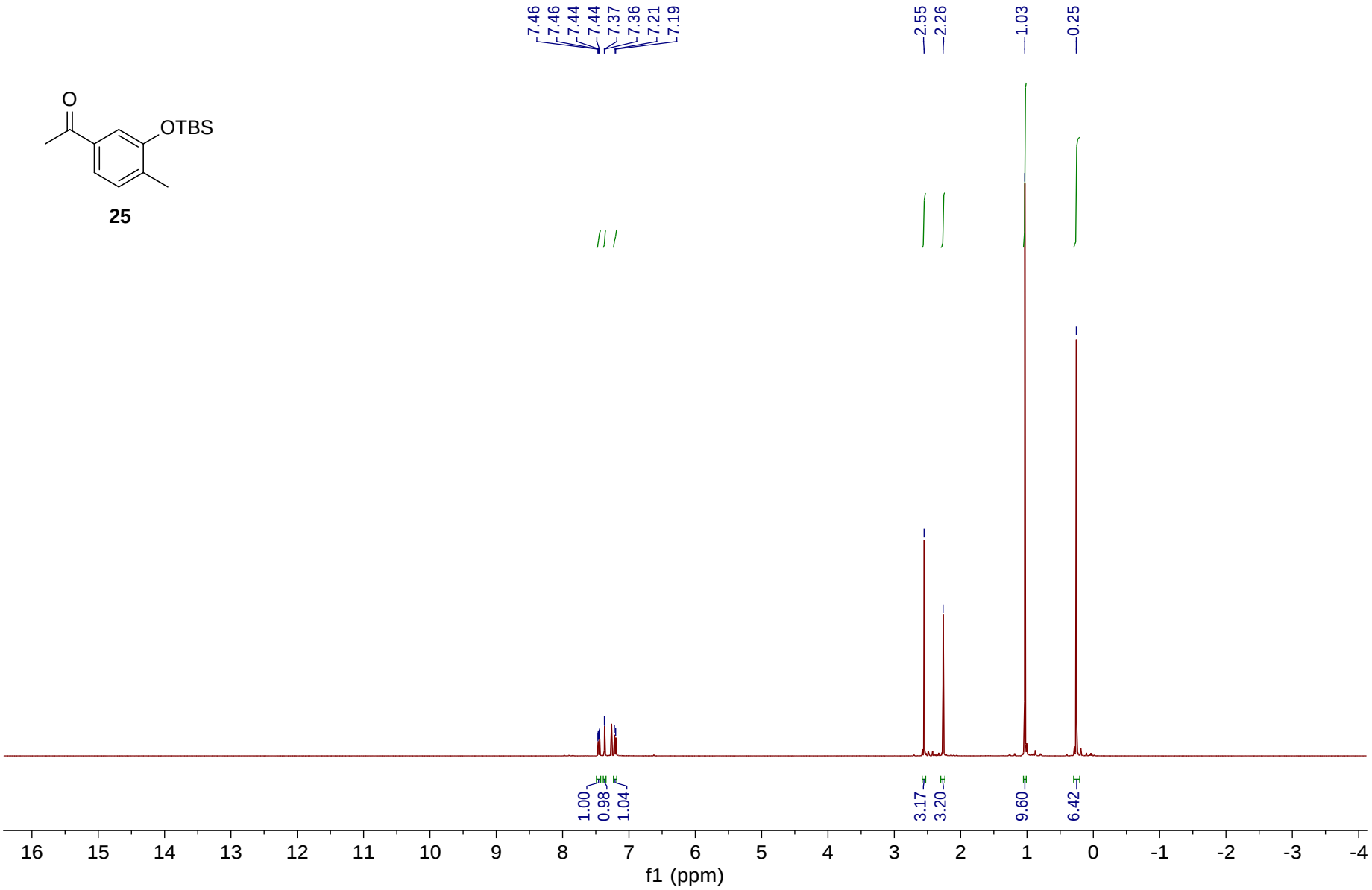

196.0
149.4
138.8
136.1
133.5
132.1
124.7
77.5
77.2
76.8
26.7
20.7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

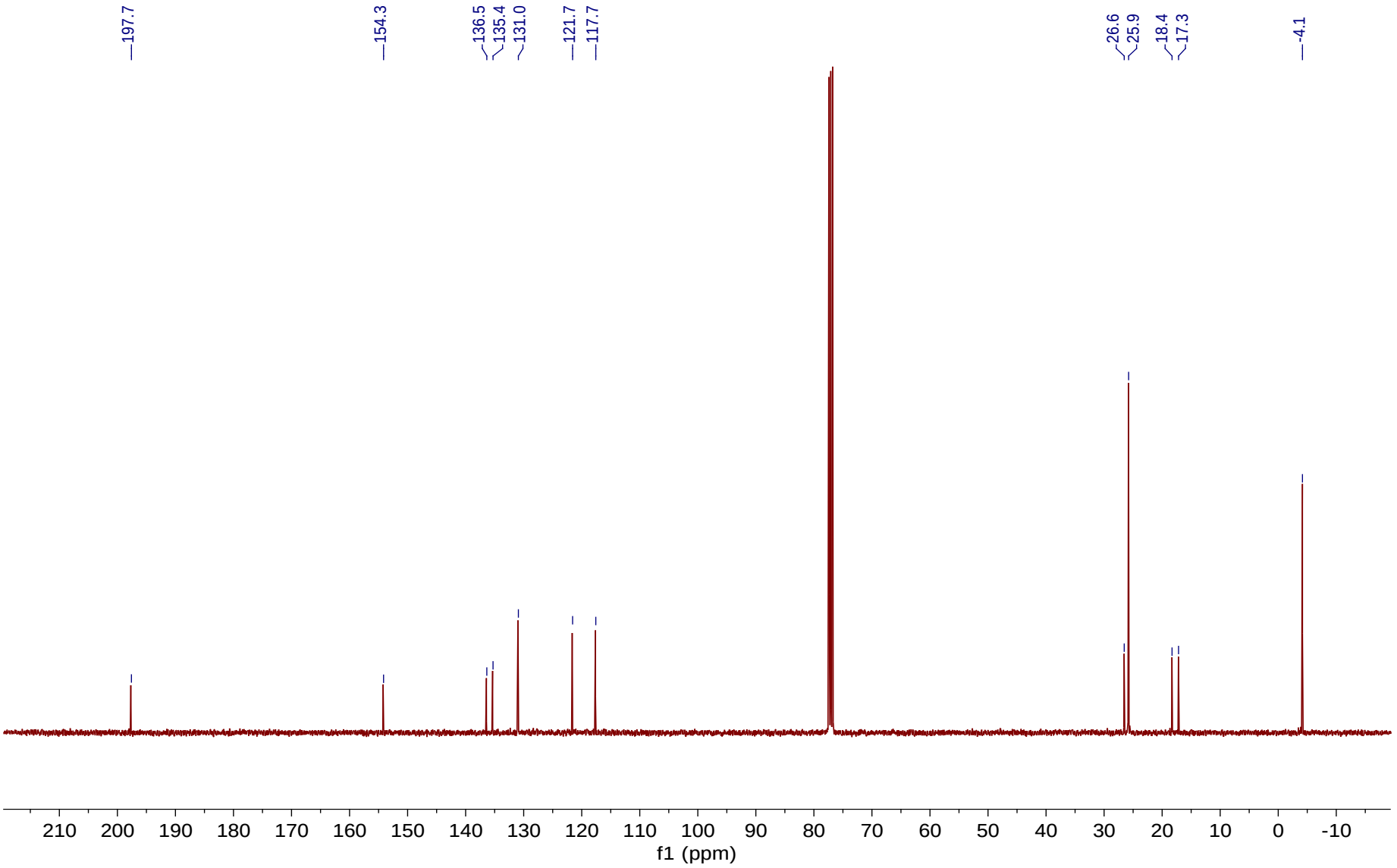

O
NH2
S3
7.28
7.28
7.26
7.11
7.10
3.75
2.53
2.20
2.00
0.98
2.00
3.05
3.05
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

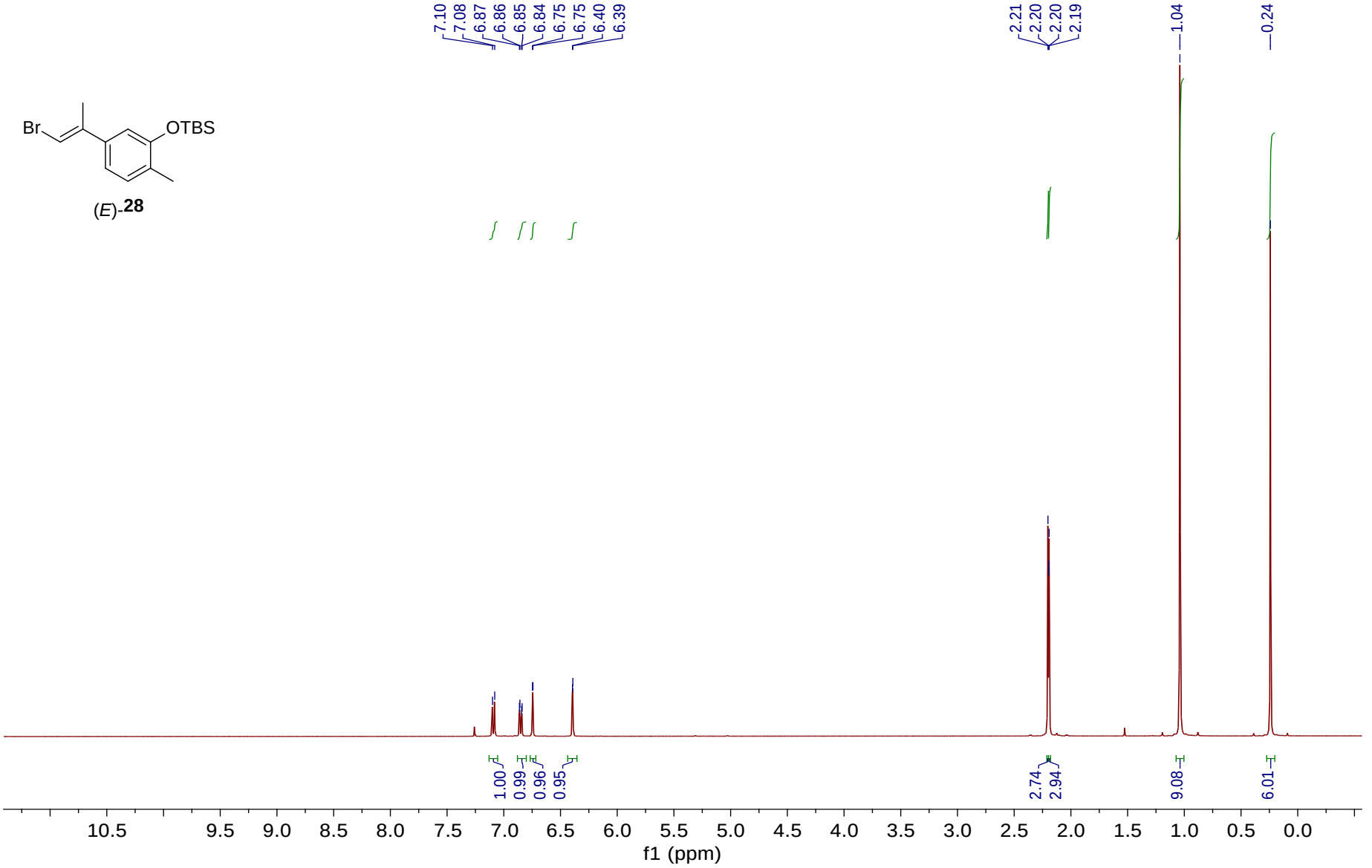

198.3
145.0
136.4
130.5
128.1
119.1
114.0
26.6
17.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

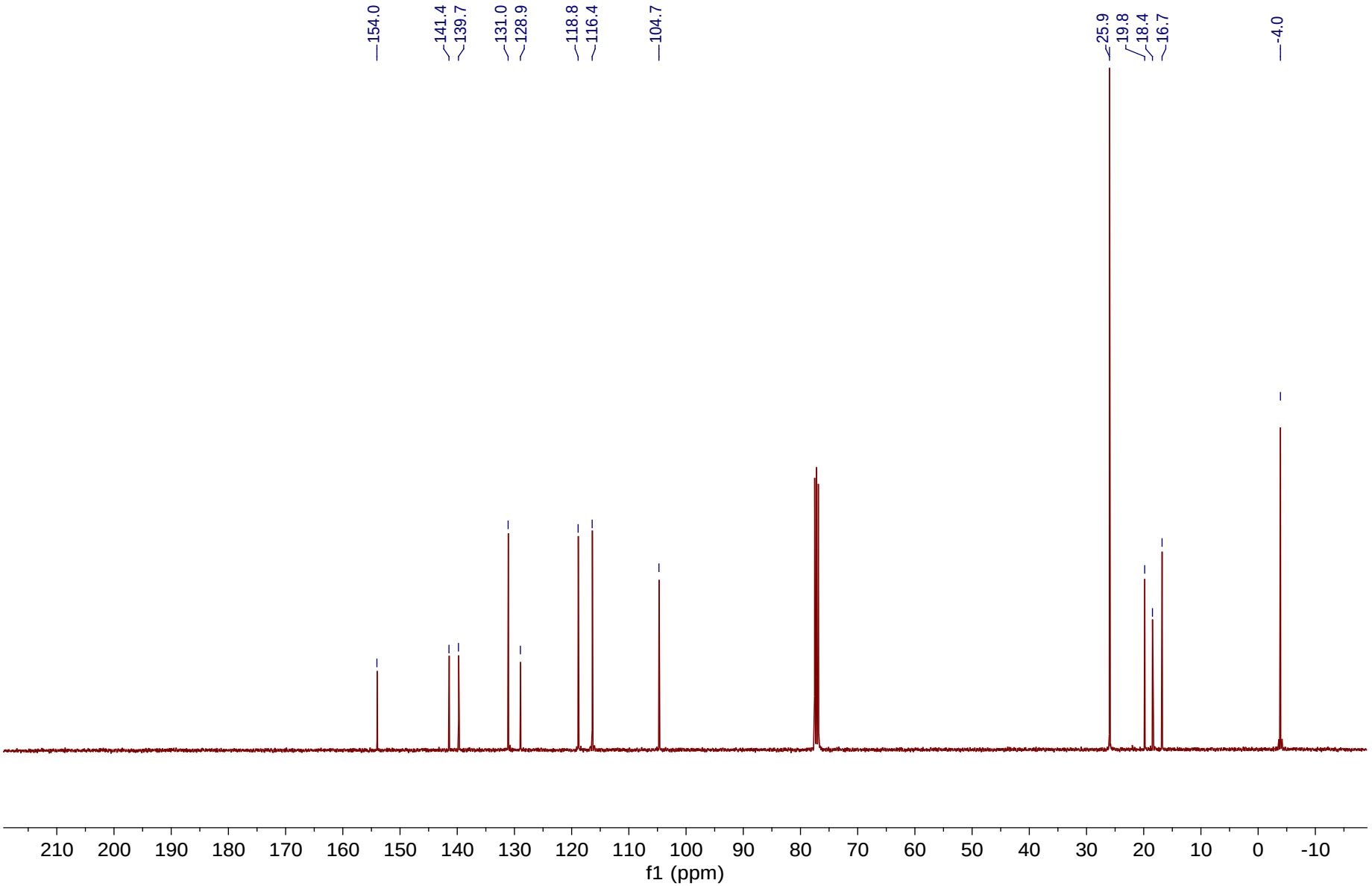

7.48
7.48
7.45
7.44
7.43
7.42
7.21
7.20
5.61
2.57
2.32
O
OH
24
1.00
1.02
0.97
0.97
3.01
3.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


198.4
154.4
136.6
131.2
130.8
121.5
114.1
26.7
16.2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

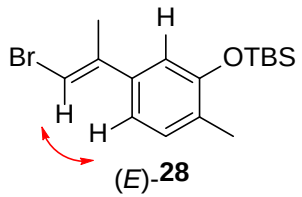

O
OTBS
25
7.46
7.46
7.44
7.44
7.37
7.36
7.21
7.19
2.55
2.26
1.03
0.25
1.00
0.98
1.04
3.17
3.20
9.60
6.42
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


197.7
154.3
136.5
135.4
131.0
121.7
117.7
26.6
25.9
18.4
17.3
-4.1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

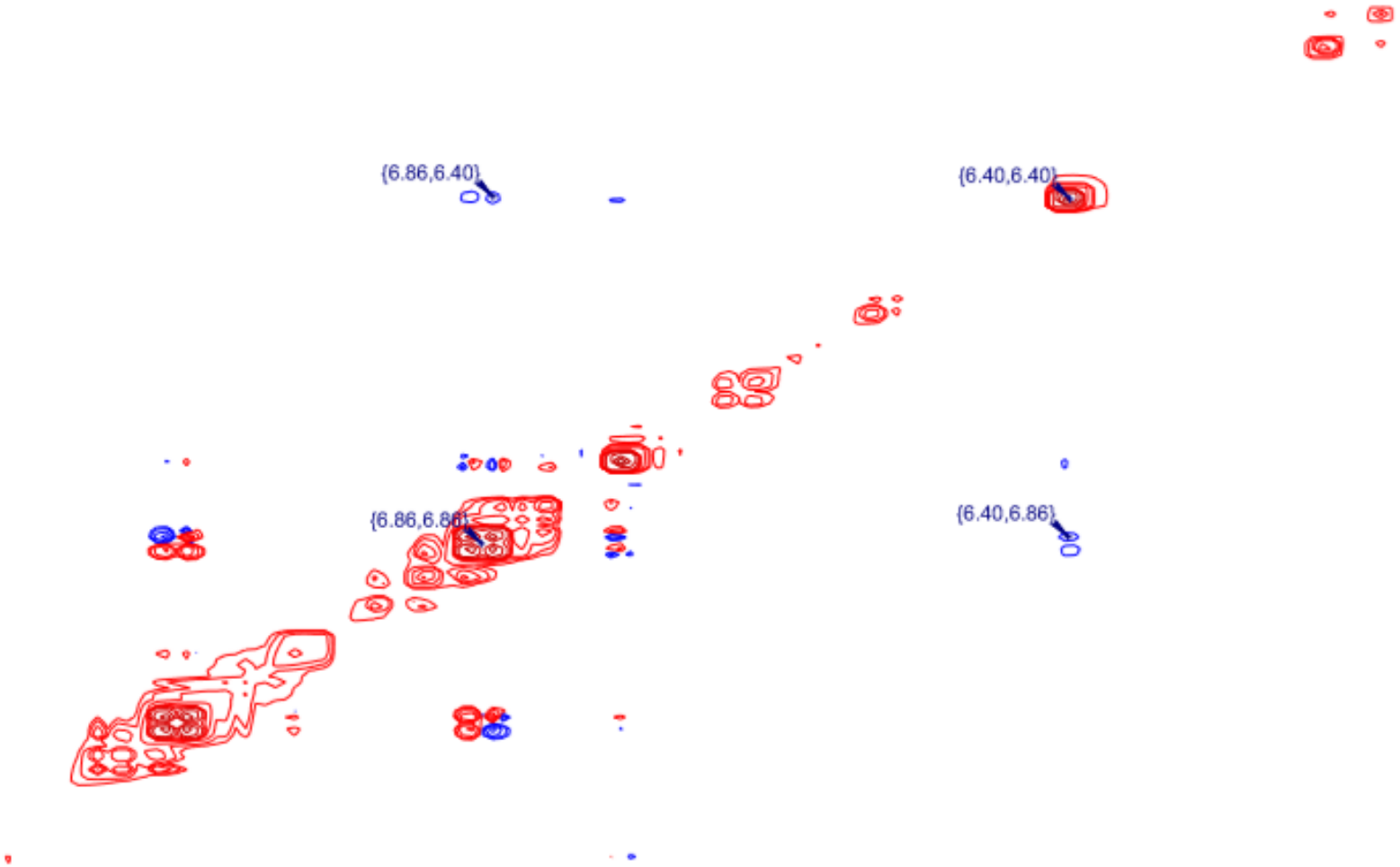

Br
OTBS
(E)-28
7.10
7.08
6.87
6.86
6.85
6.84
6.75
6.75
6.40
6.39
2.21
2.20
2.20
2.19
1.04
0.24
1.00
0.99
0.96
0.95
2.74
2.94
9.08
6.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

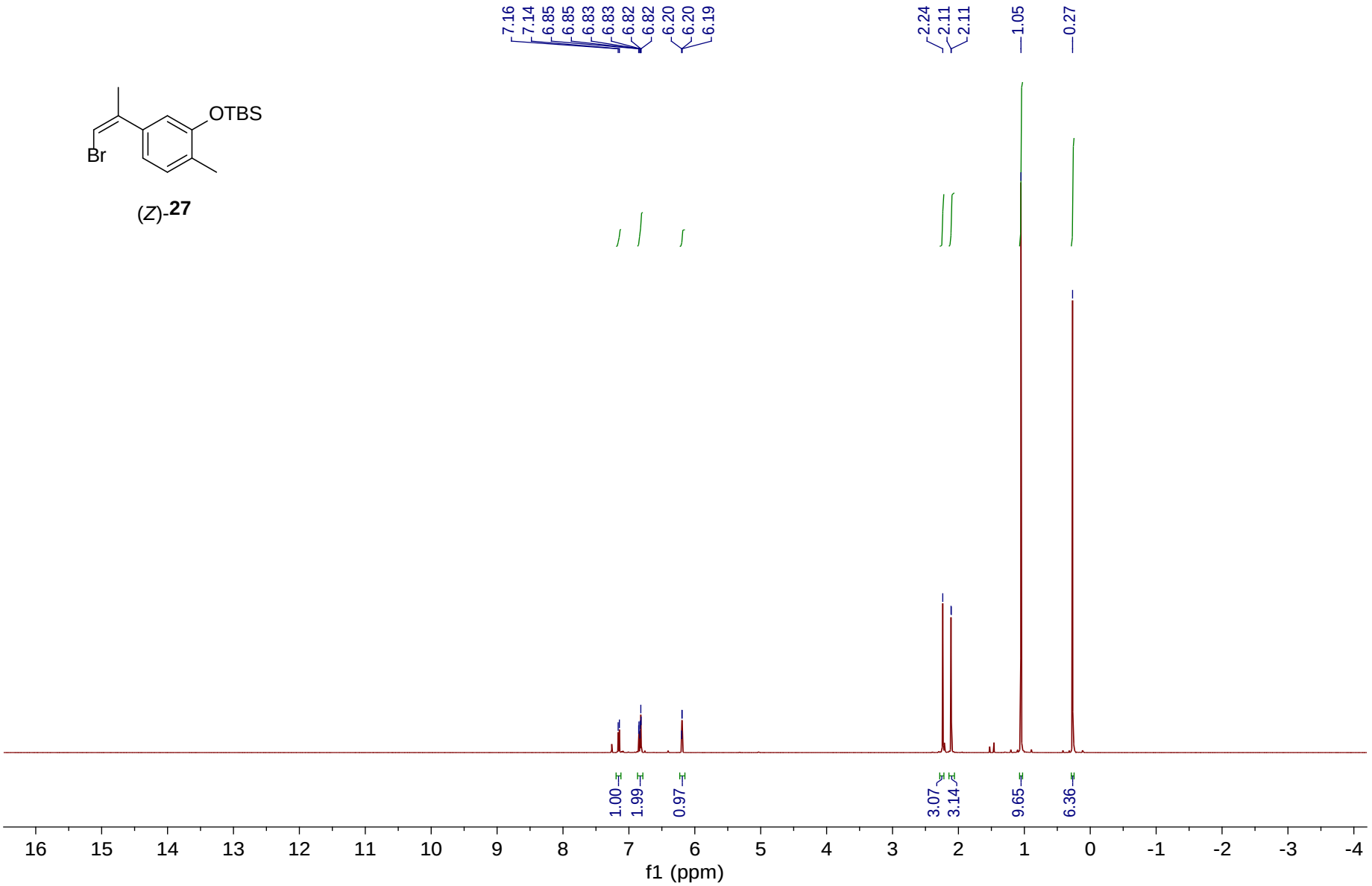

154.0
141.4
139.7
131.0
128.9
118.8
116.4
104.7
25.9
19.8
18.4
16.7
-4.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

NOESY

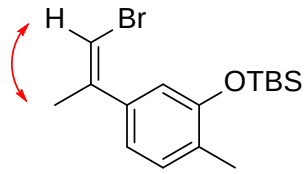


(*E*)-**28**

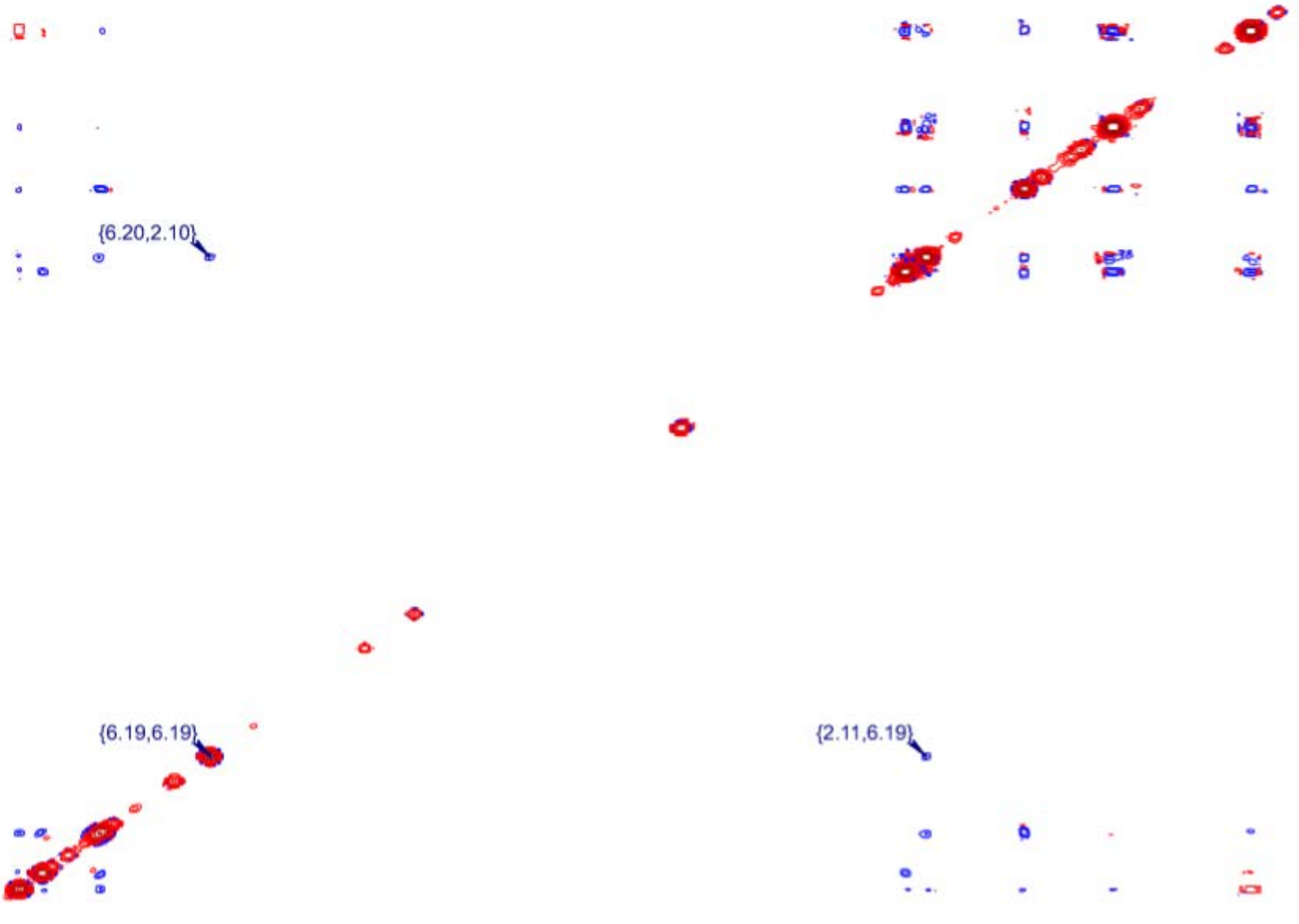


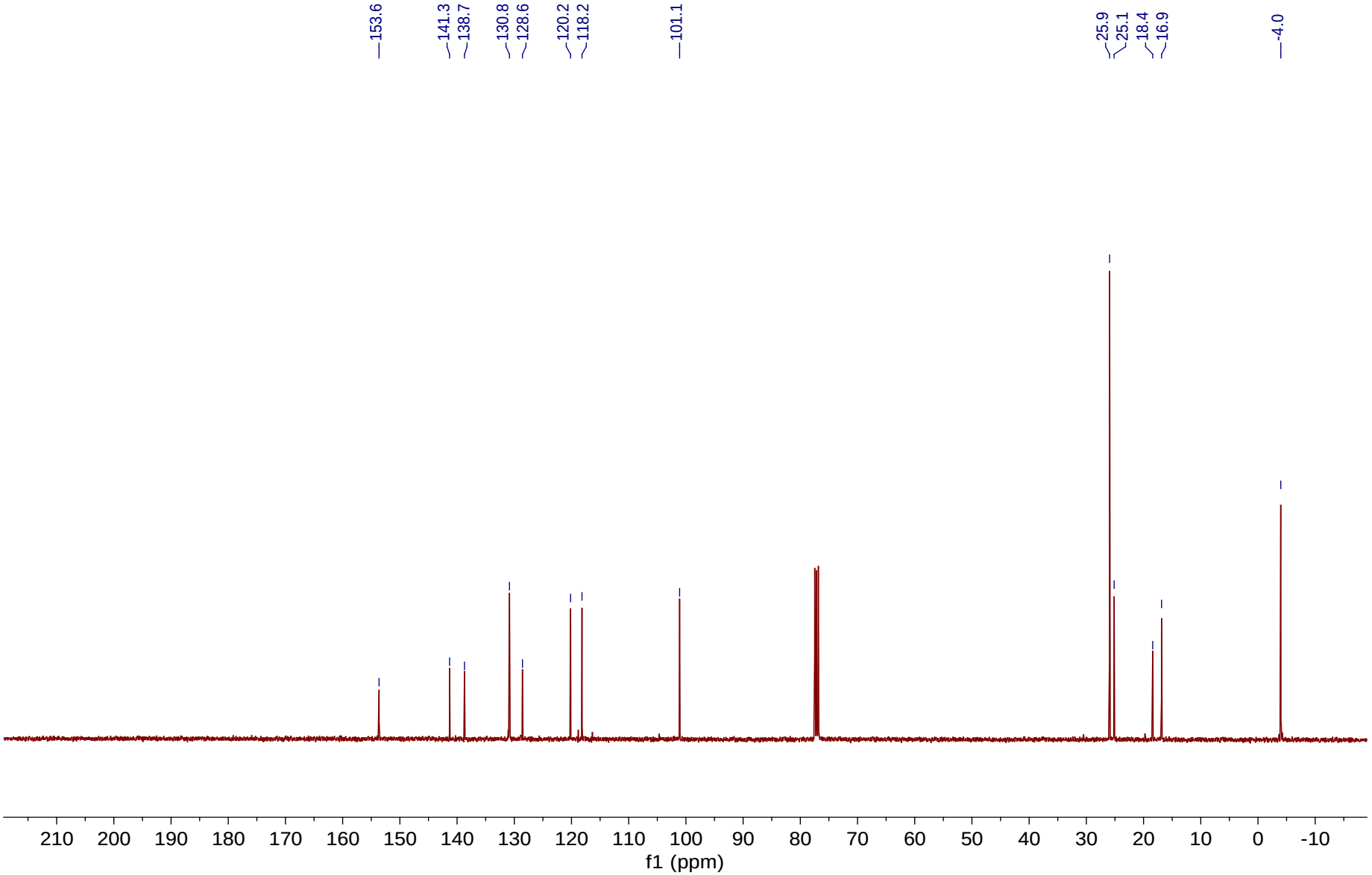

OTBS
Br
(Z)-27
7.16
7.14
6.85
6.85
6.83
6.83
6.82
6.82
6.20
6.20
6.19
2.24
2.11
2.11
1.05
0.27
1.00
1.99
0.97
3.07
3.14
9.65
6.36
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

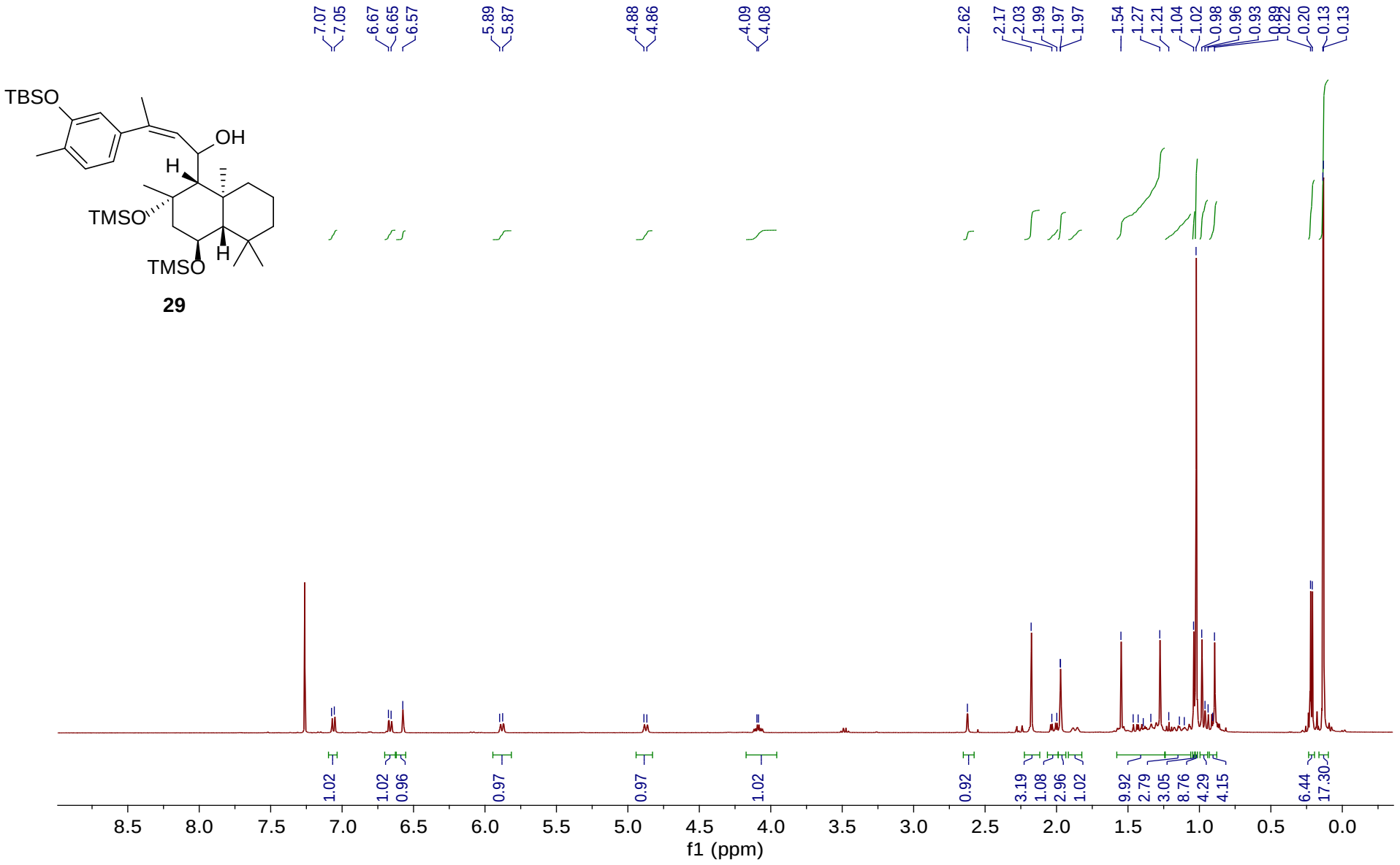
NOESY

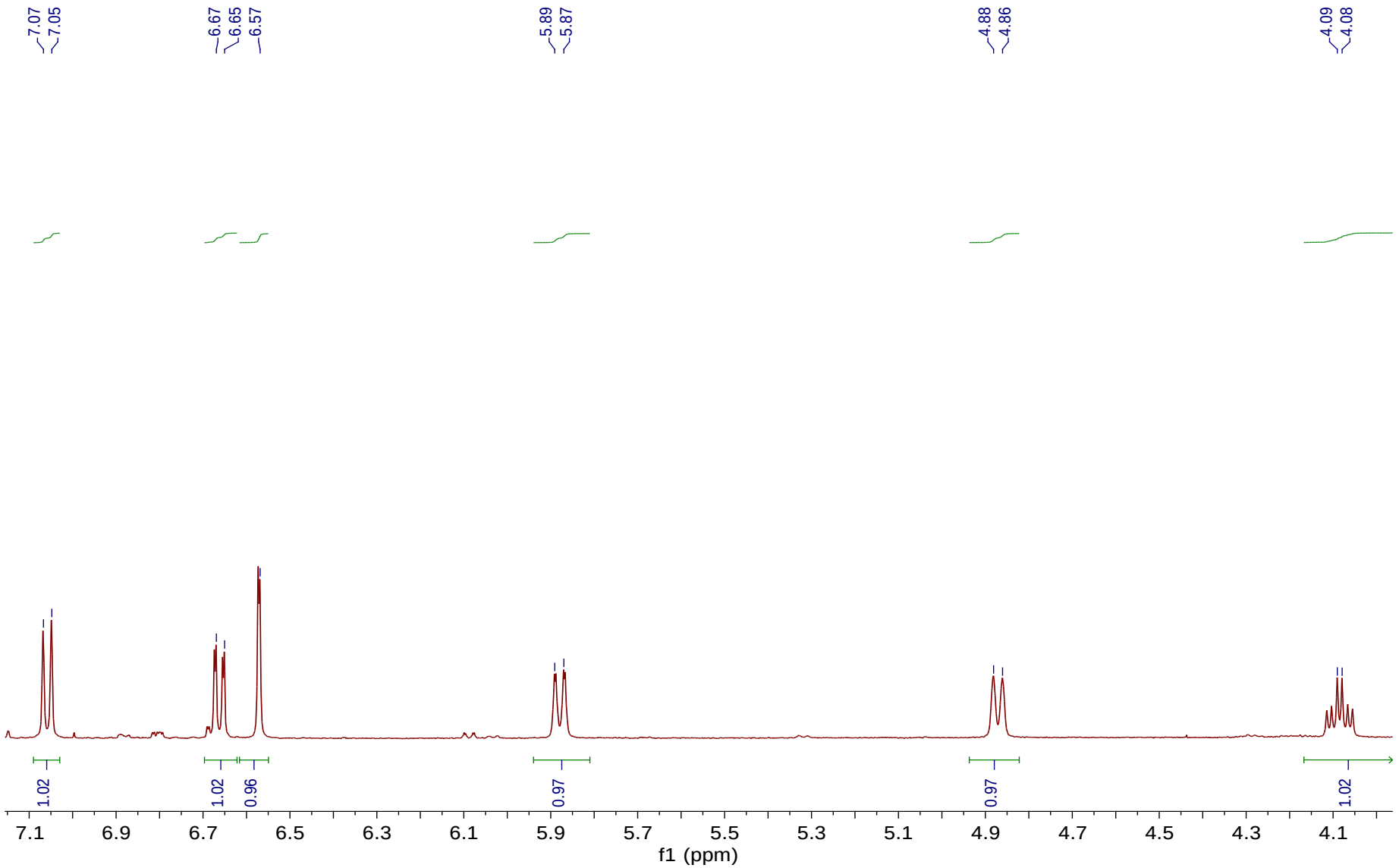


(*Z*)-**28**

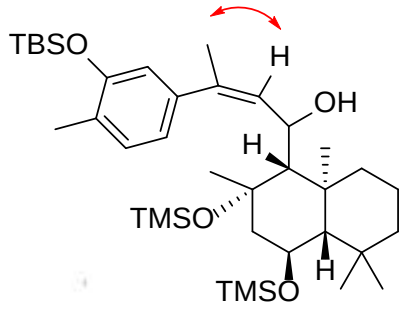



153.6
141.3
138.7
130.8
128.6
120.2
118.2
101.1
25.9
25.1
18.4
16.9
-4.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

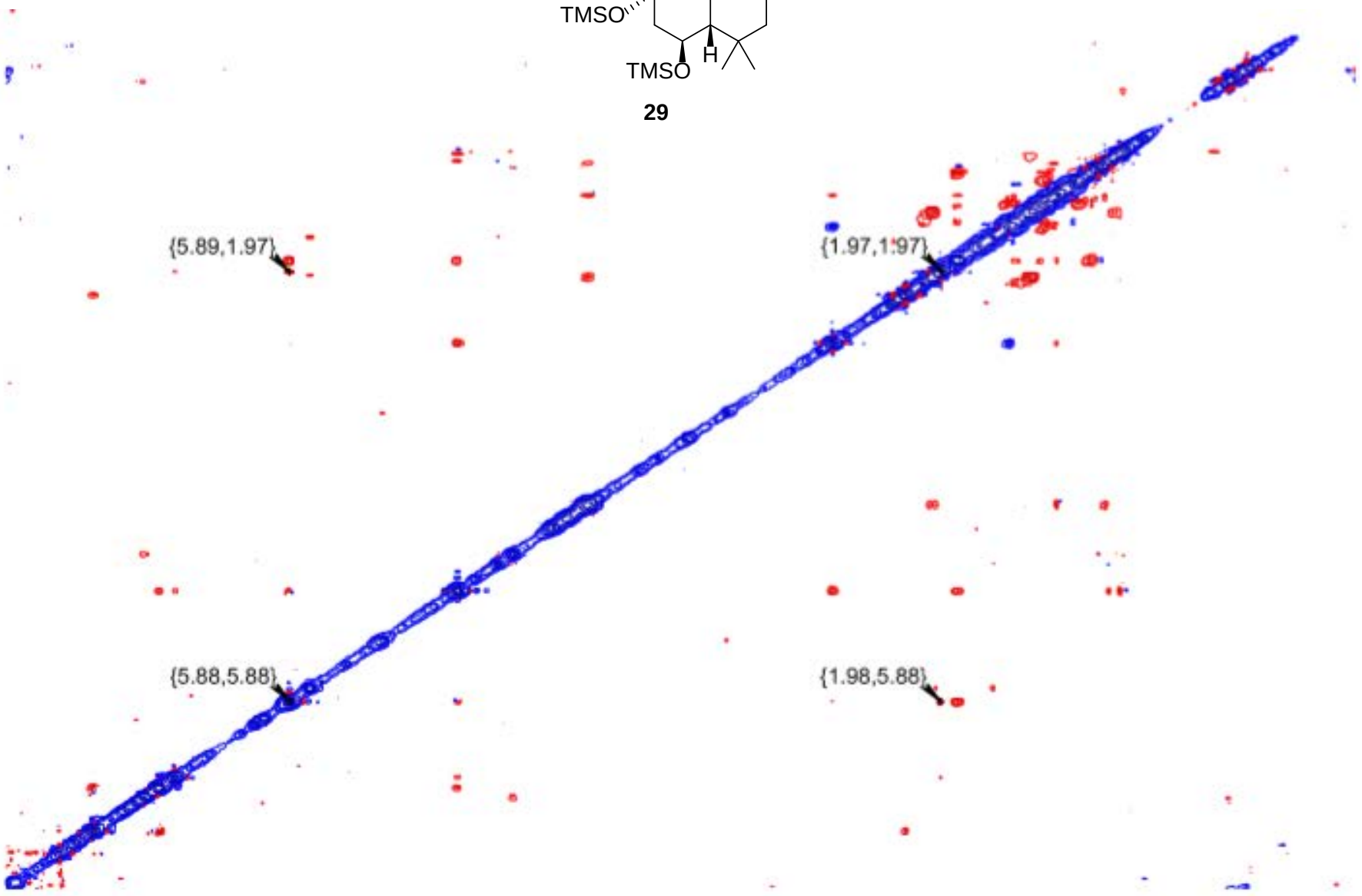

TBSO
OH
H
TMSO
H
TMSO
29
7.07
7.05
6.67
6.65
6.57
5.89
5.87
4.88
4.86
4.09
4.08
2.62
2.17
2.03
1.99
1.97
1.97
1.54
1.27
1.21
1.04
1.02
0.98
0.96
0.93
0.89
0.22
0.20
0.13
0.13
1.02
1.02
0.96
0.97
0.97
1.02
0.92
3.19
1.08
2.96
1.02
9.92
2.79
3.05
8.76
4.29
4.15
6.44
17.30
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

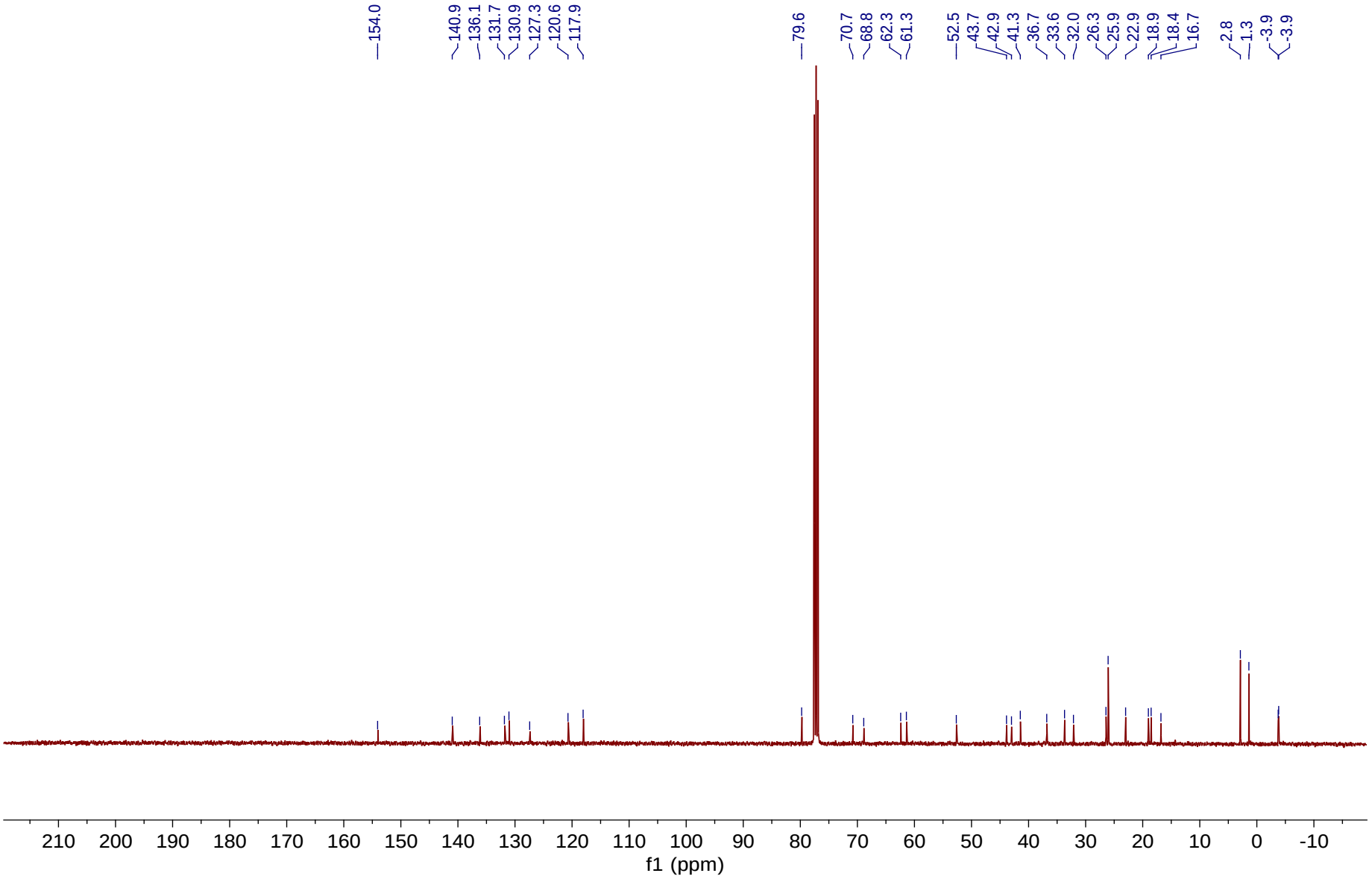

7.07
7.05
6.67
6.65
6.57
5.89
5.87
4.88
4.86
4.09
4.08
1.02
1.02
0.96
0.97
0.97
1.02
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
5.1
4.9
4.7
4.5
4.3
4.1
f1 (ppm)

NOESY



29

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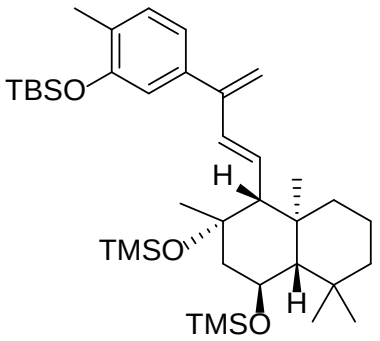
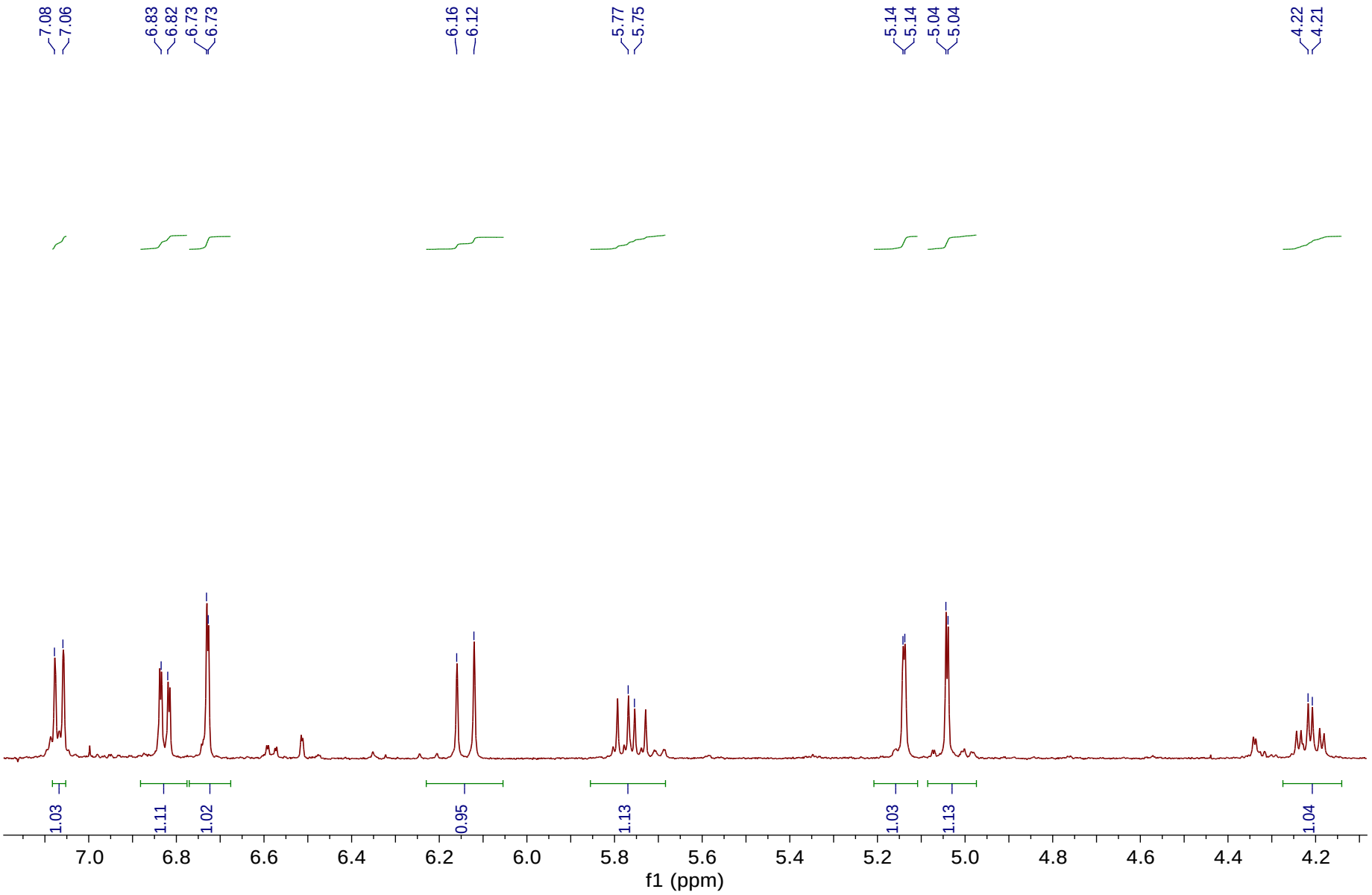
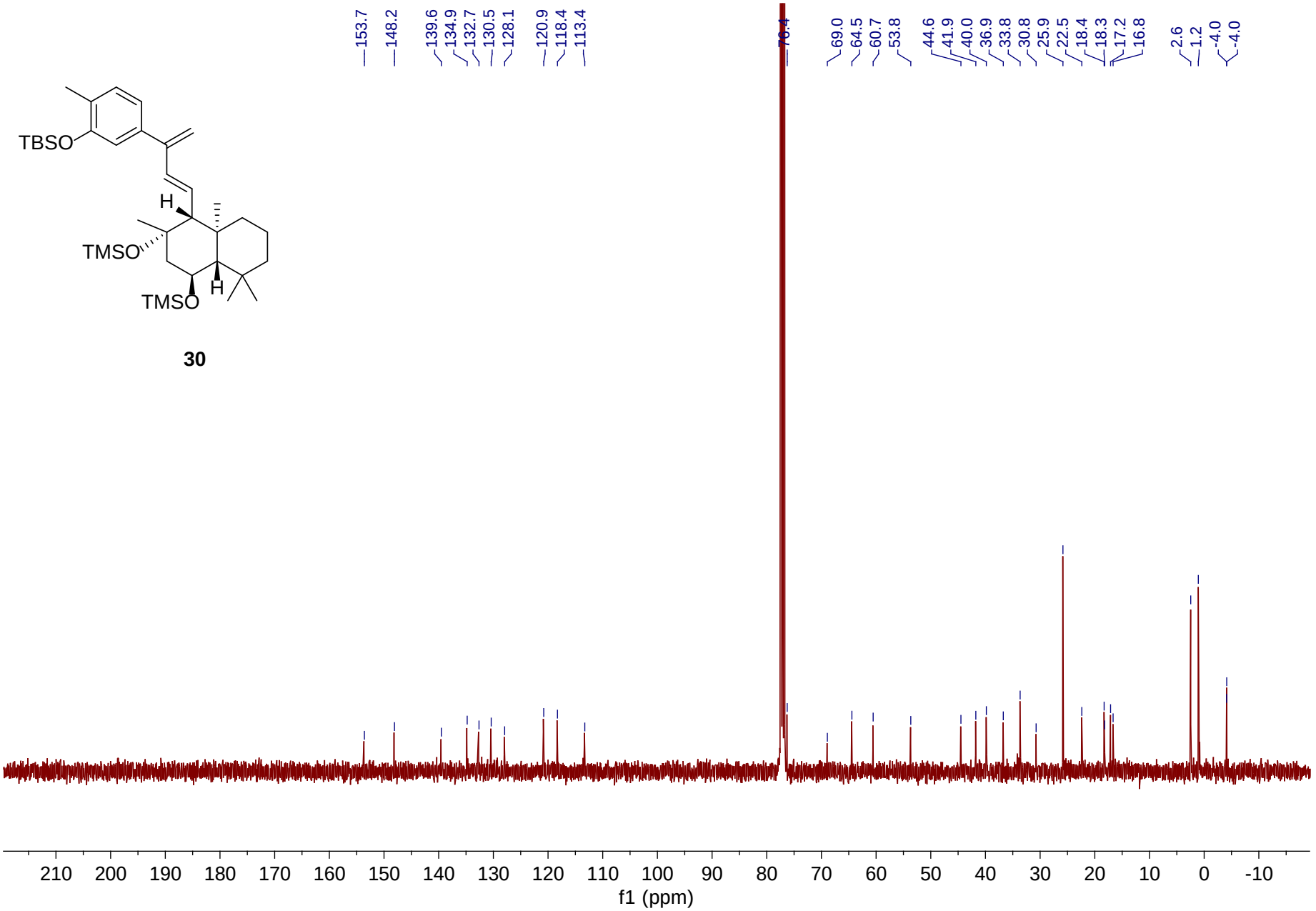
140.9
136.1
131.7
130.9
127.3
120.6
117.9
79.6
70.7
68.8
62.3
61.3
52.5
43.7
42.9
41.3
36.7
33.6
32.0
26.3
25.9
22.9
18.9
18.4
16.7
2.8
1.3
-3.9
-3.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


TBSO
H
TMSO
H
TMSO

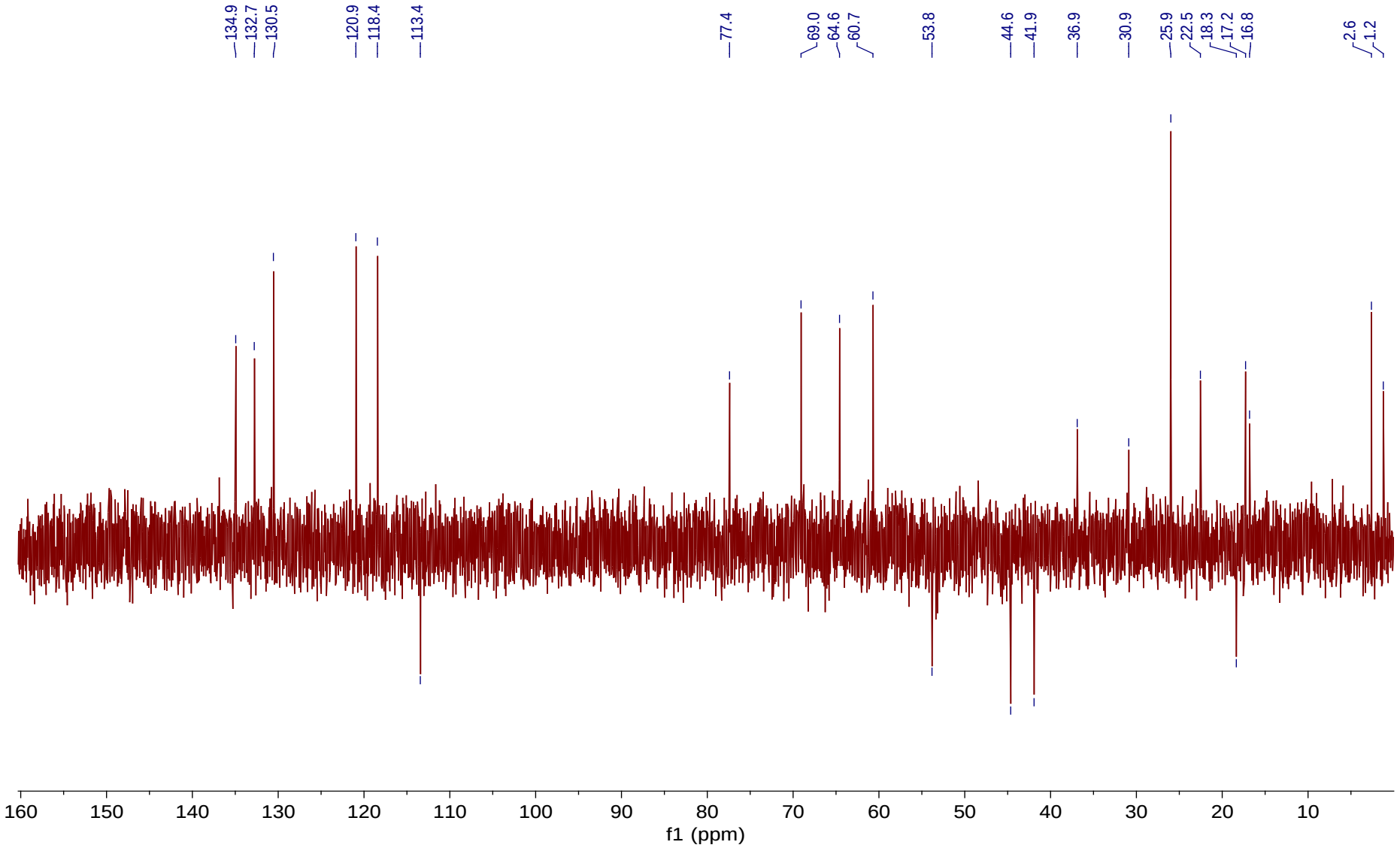
30

7.08
7.06
6.83
6.82
6.73
6.73
6.16
6.12
5.77
5.75
5.14
5.14
5.04
5.04
4.22
4.21
2.20
2.07
2.02
1.53
1.45
1.40
1.30
1.13
1.11
1.02
0.98
0.20
0.16
-0.00
1.03
1.11
1.02
0.95
1.13
1.03
1.13
1.04
2.84
1.21
13.15
6.71
9.82
6.37
6.61
8.42
8.81
10.5
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
0.5
0.0
-0.5
f1 (ppm)


7.08
7.06
6.83
6.82
6.73
6.73
6.16
6.12
5.77
5.75
5.14
5.14
5.04
5.04
4.22
4.21
1.03
1.11
1.02
0.95
1.13
1.03
1.13
1.04
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
f1 (ppm)


153.7
148.2
139.6
134.9
132.7
130.5
128.1
120.9
118.4
113.4
76.4
69.0
64.5
60.7
53.8
44.6
41.9
40.0
36.9
33.8
30.8
25.9
22.5
18.4
18.3
17.2
16.8
2.6
1.2
-4.0
-4.0
TBSO
H
TMSO
H
TMSO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

30


134.9
132.7
130.5
120.9
118.4
113.4
77.4
69.0
64.6
60.7
53.8
44.6
41.9
36.9
30.9
25.9
22.5
18.3
17.2
16.8
2.6
1.2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

References

[1] S. Katsumura. A. Kimura and S. Isoe, *Tetrahedron*, 1989, **45**, 1337–1346.
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