# Supporting Information

# for

# A new phenylethyl alkyl amide from the *Ambrostoma quadriimpressum* Motschulsky

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**Detailed experimental procedures for the synthesis of compound 1**

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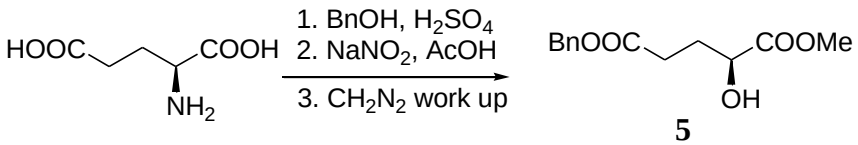
## Experimental details

General Methods: Commercial spectral grade solvents were used for experiments unless otherwise stated. Infrared spectra were recorded on a Perkin–Elmer 1710 Fourier transform spectrometer. Low-resolution mass spectra were obtained from Agilent 7890A-5975C GC–MS by means of electron impact (EI) ionization at 70 eV. $^{1}$H NMR spectra were obtained at 400 MHz on Bruker AV-400 instrument. $^{13}$C NMR spectra were recorded at 100 MHz. High-resolution mass spectra were recorded on an Agilent 1200-6520 Q-TOF electrospray mass spectrometer.

## Synthesis of (*S*)-5-benzyl 1-methyl 2-hydroxypentanedioate (**5**)

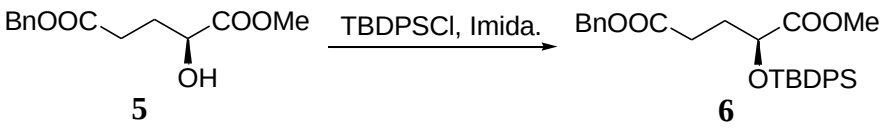



**5**

The γ-benzyl ester of glutamic acid (**5**) was prepared according to Rapoport et al. [1-3]. Benzyl alcohol (200 mL, 1.9 mol) was added slowly to a solution of conc. $H_2SO_4$ (20 mL, 375 mmol) in dry $Et_2O$ (200 mL). The solution was concentrated in vacuo, and glutamic acid (29.6 g, 201 mmol) was added sequentially. The reaction mixture was stirred overnight at r.t., then 95% EtOH (400 mL) and pyridine (100 mL) were added. The mixture was stirred for 1 h in an ice bath. The white precipitate γ-benzylglutamic acid was obtained by filtration, washed with $Et_2O$, dried at 60 °C for 24 h in vacuo, and was used for next step without further purification (yield 28.6 g, 60%). To a solution of γ-benzylglutamic acid (23.8 g, 100 mmol) in $H_2O$ (150 mL) and AcOH (50 mL), a solution of $NaNO_2$ (10.3 g, 149 mmol) in $H_2O$ (100 mL) was added slowly over 4 h. After stirring for 2 h at rt, the reaction mixture was extracted with $CHCl_3$ and isopropanol (v/v = 3:1). The extracts were washed with brine, dried with $Na_2SO_4$, and concentrated in vacuo to give a colorless oil. The crude product was immediately

esterified with $CH_2N_2$ in $Et_2O$, and then concentrated in vacuo. Column chromatography ($SiO_2$, AcOEt/PE 1:1) of the residue afforded compound **5** (12.4 g, 70%) as a colorless oil. $[\alpha]_D^{20}$ −13.8 (*c* 0.52, $CHCl_3$); IR (film, KBr) $\nu_{max}$: 3487, 2944, 1738, 1455, 1162 cm $^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.38–7.31 (m, 5H), 5.12 (s, 2H), 4.27–4.22 (m, 1H), 3.77 (s, 3H), 2.98 (t, *J* = 6.4 Hz, 1H), 2.59–2.47 (m, 2H), 2.23–2.16 (m, 1H), 1.99–1.93 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 175.0, 173.0, 135.9, 128.6, 128.3, 128.2, 69.5, 66.4, 52.7, 29.7, 29.3; EIMS (*m/z*): 252, 234, 145, 108, 91(base), 85; HRMS–ESI: Calcd. for $C_{13}H_{16}O_5$: 253.1076 $[M + H]^+$. Found: 253.1080.

## Synthesis of (*S*)-5-benzyl 1-methyl 2-(*tert*-butyldiphenylsilyloxy)-pentanedioate **(6)**

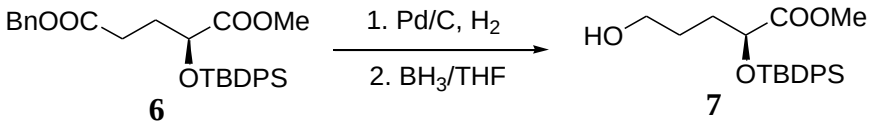



**5** **6**

Imidazole (1.36 g, 20 mm) was added sequentially to a solution of **5** (2.52 g, 10 mmol) in dry $CH_2Cl_2$ (150 mL) at 0 °C. The mixture was stirred for 15 min, and then TBDPSCl (4.12 g, 15 mmol) was added and stirred at rt for 3 h. The reaction mixture was quenched with $H_2O$ and extracted with $CH_2Cl_2$. The combined extracts were washed with brine, dried ($Na_2SO_4$) and concentrated in vacuo. Column chromatography ($SiO_2$, 10% AcOEt in PE) of the residue afforded TBDPS ether (4.9 g, 100%) as a colorless oil. $[\alpha]_D^{20}$ −12.8 (*c* 1.0, $CHCl_3$); IR (film, KBr) $\nu_{max}$: 2945, 2831, 1740, 1455, 1109, 751, 699 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.76–7.71 (m, 4H), 7.69–7.58 (m, 11H), 5.09 (s, 2H), 4.32 (t, *J* = 5.2 Hz, 1H), 3.77 (s, 3H), 2.58 (m, 1H), 2.46 (m, 1H), 2.08 (m, 2H), 1.09 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 172.9, 172.9, 136.0, 135.8, 135.2, 133.1, 132.9, 129.9, 129.8, 128.6, 127.7, 127.6, 71.4, 66.3, 51.5, 30.0, 29.2, 26.9, 19.4.

EIMS (*m/z*): 433, 373, 289, 265, 237, 213, 183, 153, 135, 91(base). HRMS (ESI): Calcd. for $C_{29}H_{34}O_5Si$: 508.2519 $[M + NH_4]^+$. Found: 508.2530.

## Synthesis of (*S*)-methyl 2-(*tert*-butyldiphenylsilyloxy)-5-hydroxy pentanoate (**7**)

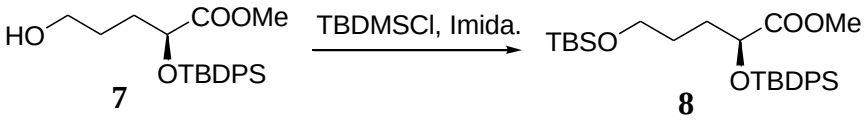



**6** **7**

To a solution of **6** (4.9 g, 10 mmol) in MeOH (30 mL), 10% Pd/C (447 mg) was added and the mixture was hydrogenated for 12 h. It was then filtered through a short pad of Celite and the filter cake was washed with MeOH. The filtrate was concentrated in vacuo to give the acid as a colorless oil, which was used without further purification.

To a solution of the above acid in dried THF (30 mL) at −5 °C, $BH_3$·THF (1.0 M in THF, 11 mL) was added over 10 min. After addition, the reaction mixture was allowed to warm to rt for 3 h. Then it was carefully quenched with MeOH at 0 °C and concentrated in vacuo. Purification of the residue by flash chromatography ($SiO_2$, AcOEt/PE 1:1) provided the alcohol **7** (3.67 g, 95%) as a colorless oil. $[\alpha]_D^{20}$ −33.2 (*c* 0.93, $CHCl_3$); IR (film, KBr) $\nu_{max}$: 3434, 2952, 1755, 1427, 1111 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.68–7.63 (m, 4H), 7.44–7.34 (m, 6H), 4.29 (t, *J* = 5.6 Hz, 1H), 3.59 (t, *J* = 6.4 Hz, 2H), 3.49 (s, 3H), 1.84–1.77 (m, 2H), 1.66–1.59 (m, 2H), 1.10 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 173.4, 136.0, 13.8, 133.3, 133.0, 129.9, 129.8, 127.7, 127.5, 72.3, 62.5, 51.5, 31.5, 27.8, 26.9, 19.4; EIMS (*m/z*): 297 (base), 277, 253, 227, 199, 183, 165, 135, 105, 77. HRMS–ESI: Calcd for $C_{22}H_{30}O_4Si$: 387.1992 $[M + H]^+$. Found: 387.1991.

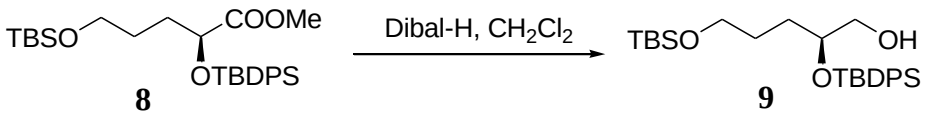
## Synthesis of (*S*)-methyl 5-(*tert*-butyldimethylsilyloxy)-2-(*tert*-butyl-diphenylsilyloxy)pentanoate (**8**)




**7** **8**

To a solution of **7** in anhydrous $CH_2Cl_2$ (40 mL) were added imidazole (1.29 g, 19 mmol) and TBSCl (2.15 g, 14.3 mm). After stirring for 5 h at rt, the reaction mixture was quenched with $H_2O$ and extracted with $CH_2Cl_2$. The extracts were washed with brine, dried ($Na_2SO_4$), and concentrated in vacuo. Column chromatography (5% EtOAc in PE) of the residue afforded the TBS ether **8** (4.75 g, 100 %) as a colorless oil. $[\alpha]_D^{20}$ −18.3 (*c* 0.52, $CHCl_3$); IR (film, KBr) $\nu_{max}$: 2948, 1757, 1473, 1427, 1257, 1192, 1107 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.70–7.64 (m, 4H), 7.45–7.36 (m, 6H), 4.27 (t, *J* = 5.6 Hz, 2H), 3.60–3.55 (m, 2H), 3.50 (s, 3H), 1.80–1.76 (m, 2H), 1.65–1.56 (m, 2H), 1.12 (s, 9H), 0.90 (s, 9H), 0.04 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 173.6, 136.0, 135.8, 133.4, 133.2, 129.8, 129.7, 127.6, 127.5, 72.5, 62.8, 51.4, 31.6, 27.9, 26.9, 25.9, 19.4, 18.3, −5.3; EIMS (*m/z*): 485, 443, 415, 355, 309, 283, 213, 183, 135, 91, 75. HRMS–ESI: Calcd for $C_{28}H_{44}O_4Si_2$: 501.2856 $[M + H]^+$. Found: 501.2859.

## Synthesis of (*S*)-5-(*tert*-butyldimethylsilyloxy)-2-(*tert*-butyldiphenylsilyloxy) pentan-1-ol **(9)**

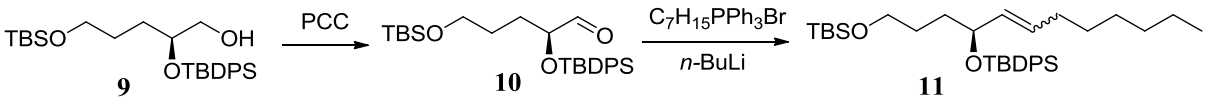



**8** **9**

To a solution of **8** (1.1 g, 2.1 mmol) in $CH_2Cl_2$ at −78 °C Dibal-H (3.0 mL, 1.487 mol/L in toluene, 4.4 mmol) was added. After stirring for 30 min at this temperature, the reaction mixture was then stirred at rt for 2 h. The reaction mixture was then carefully quenched with saturated aqueous $NH_4Cl$, and diluted with AcOEt, filtered, washed

with brine, dried ($Na_2SO_4$) and concentrated in vacuo. Purification by flash chromatography (10% AcOEt in PE) gave the product (854 mg, 86%) as a colorless oil. $[\alpha]_D^{20}$ +26.6 (*c* 0.83, $CHCl_3$); IR (film, KBr) $\nu_{max}$: 3452, 2931, 1428, 1111, 702 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.71–7.67 (m, 4H), 7.46–7.37 (m, 6H), 3.82–3.81 (m, 1H), 3.55–3.40 (m, 4H), 1.87 (t, *J* = 6.4 Hz,1H), 1.65–1.40 (m, 4H), 1.09 (s, 9H), 0.87 (s, 9H), −0.01 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 135.9, 135.7, 134.0, 133.8, 129.8, 127.8, 127.7, 73.9, 65.9, 63.1, 30.0, 28.3, 27.1, 26.0, 19.4, 18.3, −5.3; EIMS (*m/z*): 415, 309, 283, 253, 199, 181, 159, 135. HRMS–ESI: Calcd for $C_{27}H_{45}O_3Si_2$: 473.2907, $[M + H]^+$. Found: 473.2911.

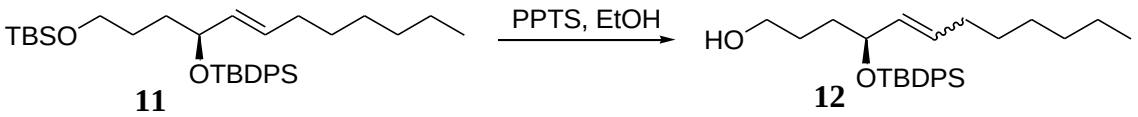
## Synthesis of (*S*)-1-(*tert*-butyl(1-(*tert*-butyldimethylsilyloxy)dodec-5-en-4-yloxy)(phenyl)silyl)benzene **(11)**




To a solution of PCC (630 mg, 3 mmol) in dry $CH_2Cl_2$ (30 mL), **9** (709 mg, 1.5 mmol) in $CH_2Cl_2$ (10 mL) was added slowly and stirred at rt for 2 h. Purification by FC (1% AcOEt in PE) afforded the aldehyde (664 mg, 94%), which was directly used for the next reaction step. To a solution of *n*-heptylidenetriphenylphosphonium bromide (950 mg, 2.1 mmol) in THF (20 mL) at −40 °C, *n*-BuLi (1.0 mL, 2.2 M in hexane, 2.2 mm) was slowly added. The orange colored solution was stirred for 1 h, then aldehyde **10** in THF (5 mL) was added. The mixture was allowed to stir at rt for 12 h and quenched with aqueous $NH_4Cl$. Ether was added, and the mixture was washed with brine, dried with $Na_2SO_4$ and concentrated in vacuo. Chromatography of the residue (1% AcOEt in PE) afforded **11** (585 mg, 75%) as a colorless oil. $[\alpha]_D^{20}$ +10.8 (c 1.1, $CHCl_3$); IR (film, KBr) $\nu_{max}$: 2952, 1461, 1427, 1253, 1105, 836 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$):

$\delta$ 7.68–7.64 (m, 4H), 7.41–7.32 (m, 6H), 5.42–5.34 (m, 1H), 5.21–5.18 (m, 1H), 4.43–4.41 (m, 1H), 3.52–3.48 (m, 2H), 2.04–2.00 (m, 2H), 1.58–1.05 (m, 12H), 1.04 (s, 9H), 0.87 (s, 9H), 0.85 (t, $J$ = 7.2 Hz, 3H), 0.05 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 136.0, 135.9, 134.6, 134.5, 132.7, 129.9, 129.4, 129.3, 127.4, 127.3, 69.4, 63.3, 34.7, 31.8, 29.8, 29.0, 28.3, 27.2, 27.02, 25.98, 22.7, 19.3, 18.3, 14.0, −5.3; EIMS (*m/z*): 441, 415, 309, 283, 253, 235, 199, 181, 159, 135, 115, 91, 73; HRMS–ESI: Calcd for $C_{34}H_{56}O_2Si_2$: 575.3717 $[M + Na]^+$. Found: 575.3717.

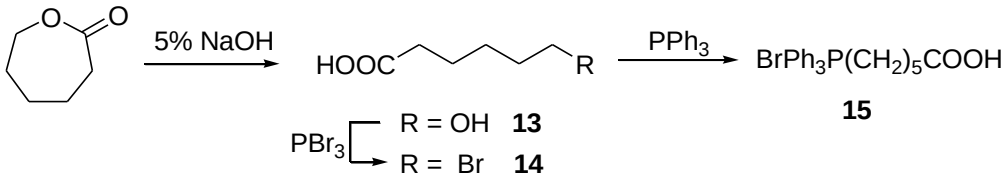
## Synthesis of (*S*)-4-(*tert*-butyldiphenylsilyloxy)dodec-5-en-1-ol (**12**)




**11** **12**

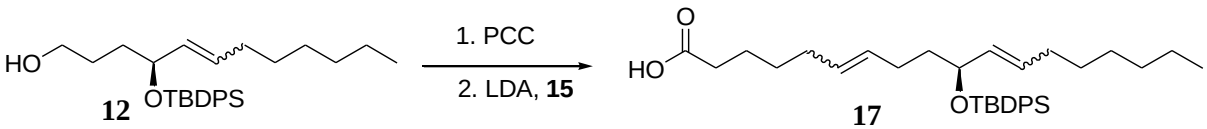
A solution of **11** (420 mg, 0.76 mmol), pyridinium *p*-toluenesulfonate (95 mg, 0.38 mmol) in absolute EtOH (10 mL) was stirred at rt for 24 h. Purification by flash chromatography ($CH_2Cl_2$) of the residue obtained after removal of the solvent afforded **12** (326 mg, 98%) as a colorless oil. $[\alpha]_D^{20}$ +10.5 (c 0.55, $CHCl_3$); IR (film, KBr) $\nu_{max}$: 3347, 2933, 1471, 1427, 1107, 1056, 821 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.67 (t, $J$ = 8.4 Hz, 4H), 7.44–7.32 (m, 6H), 5.46–5.41 (m, 1H), 5.37–5.18 (m, 1H), 4.49–4.45 (m, 1H), 3.55–3.51 (m, 2H), 1.87–1.49 (m, 6H), 1.25–1.05 (m, 8H), 1.04 (s, 9H), 0.85 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 136.1, 136.0, 134.4, 134.1, 132.3, 130.2, 129.6, 129.5, 127.5, 127.3, 69.3, 63.0, 34.7, 31.7, 29.4, 29.0, 28.1, 27.6, 27.0, 22.6, 19.3, 14.0; EIMS (*m/z*): 381, 339, 303, 269, 254, 199, 181, 165, 139, 123, 81; HRMS–ESI: Calcd for $C_{28}H_{42}O_2Si$: 461.2852 $[M + Na]^+$. Found: 461.2853.

## Synthesis of (5-carboxypentyl)triphenylphosphonium bromide (**15**)




A solution of ε-caprolactone (1.14 g, 10 mmol) in 5% NaOH (50 mL) was stirred at rt for 12 h. The solution was cooled in an ice bath and acidified with 10% HCl. The aqueous phase was extracted with $Et_2O$ three times. The extracts were washed with brine, dried ($Na_2SO_4$), concentrated in vacuo to give crude product **13** (1.34 g, 100%), which was directly used for next step. To a solution of **13** (1.34 g, 10 mmol) in $CH_2Cl_2$ (30 mL), $PBr_3$ ( 0.8 mL,8.4 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise at 0 °C. The reaction mixture was warmed to 40 °C and stirred for 5 h. The mixture was cooled to rt, then poured into ice water and extracted with $CH_2Cl_2$ (50 mL). The extracts were washed (brine), dried and concentrated in vacuo to afford crude compound **14** (1.6 g, 82%). A solution of **14** and $PPh_3$ in $CH_3CN$ was refluxed under $N_2$ for 12 h. After removal of the solvent, the residue was washed with $Et_2O$ to give **15** as a white solid (3.6 g, 98%) [4,5]. $^1$H NMR (400 MHz, $D_2O$): $\delta$ 7.71–7.53 (m, 15H), 3.18–3.10 (m, 2H), 2.17 (t, $J$ = 7.2 Hz, 3H), 1.57–1.36 (m, 6H); $^{13}$C NMR (100 MHz, $D_2O$): $\delta$ 178.5, 134.9, 133.5, 133.4, 130.0, 128.9, 118.5, 117.7, 33.3, 29.2, 29.0, 23.4, 21.4, 21.3, 20.9.

## Synthesis of (*S*)-10-(*tert*-butyldiphenylsilyloxy)octadeca-6,11-dienoic acid (**17**)

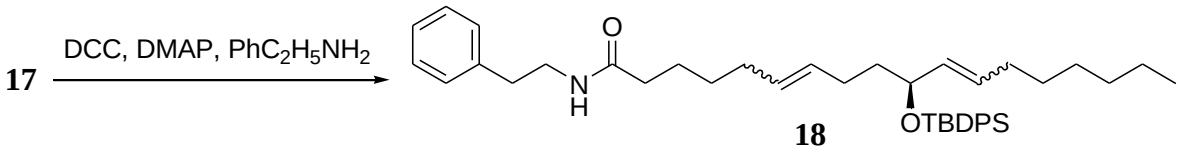



To a solution of PCC (210 mg, 1 mmol) in dry $CH_2Cl_2$ (10 mL), **12** (230 mg, 0.52 mmol) in $CH_2Cl_2$ (2 mL) was slowly added and stirred at rt for 4 h. Purification by

flash chromatography (5% AcOEt in PE) afforded the aldehyde (220 mg, 96%), which was used for the next reaction step without further purification.

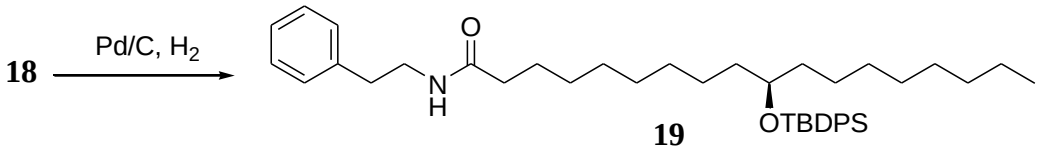
A stirred solution of diisopropylamine (0.29 mL, 2 mmol) in dry THF (2 mL) was treated under $N_2$ at −30 °C with *n*-butyllithium (0.91 mL, 2.2 M in hexane). The solution was stirred at −30 °C for 30 min and was added to a suspension of **15** (456 mg, 1 mmol) in dry THF (20 mL). The blood-red solution was stirred for 30 min at rt and treated dropwise with a solution of the above aldehyde in dry THF (2 mL). The mixture was stirred for 3 h. An ice-cold 10% solution of $NaHSO_4$ (20 mL) was added, and the aqueous phase was extracted with AcOEt. The extracts were washed with brine, dried ($Na_2SO_4$) and concentrated in vacuo. Column chromatography (50% AcOEt in PE) of the residue afforded acid **17** (192 mg, 72%) as a colorless oil. $[\alpha]_D^{20}$ +8.7 (c 0.69, $CHCl_3$); IR (film, KBr) $\nu_{max}$: 3005, 2925, 2853, 1711, 1461, 1427, 1289, 1069, 1109, 823 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.67 (t, $J$ = 8.0 Hz, 4H), 7.44–7.32 (m, 6H), 5.42–5.36 (m, 1H), 5.32–5.17 (m, 3H), 4.47–4.43 (m, 1H), 2.33 (t, $J$ = 7.6 Hz, 2H), 1.97–1.92 (m, 4H), 1.62–1.05 (m, 16H), 1.03 (s, 9H), 0.85 (t, $J$ = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 178.6, 136.1, 136.0, 134.6, 134.4, 132.6, 130.2, 130.1, 129.5, 129.5, 129.4, 127.4, 127.3, 69.4, 38.5, 33.7, 31.7, 29.4, 29.0, 29.0, 27.6, 27.1, 27.0, 24.3, 22.9, 22.6, 19.3, 14.1; HRMS–ESI: Calcd for $C_{34}H_{50}O_3Si$: 533.3451 $[M - H]^-$. Found: 533.3453.

## Synthesis of (*S*)-10-(*tert*-butyldiphenylsilyloxy)-*N*-phenethyloctadeca-6,11-dienamide (**18**)



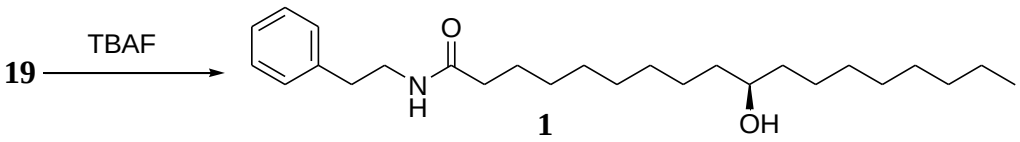

A solution of **17** (150 mg, 0.28 mmol), 2-phenylethylamine (34 mg, 0.28 mmol), DCC (58 mg, 0.28 mmol) and DMAP (20 mg) in $CH_2Cl_2$ (10mL) was stirred for 24 h. The precipitated solid was removed by filtration, the filtrate washed with aqueous HCl (2 N), water and brine, and dried ($Na_2SO_4$). Solvent removal followed by column chromatography of the residue (10% AcOEt in PE) gave the amide (143 mg, 80%) as a colorless oil. $[\alpha]_D^{20}$ +9.9 (*c* 0.39, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.67 (t, *J* = 6.4 Hz, 4H), 7.40–7.17 (m, 11H), 5.45–5.37 (m, 2H), 5.26–5.21 (m, 3H), 4.43 (m, 1H), 3.51 (q, *J* = 6.4 Hz, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.09 (t, *J* = 7.6 Hz, 2H), 1.97–1.92 (m, 4H), 1.61–1.05 (m, 16H), 1.03 (s, 9H), 0.85 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 172.9, 138.9, 136.0, 135.9, 134.6, 134.4, 132.6, 130.2, 129.9, 129.5, 129.4, 129.3, 128.8, 128.7, 127.5, 127.3, 126.5, 69.4, 40.5, 38.6, 36.7, 35.8, 31.7, 29.4, 29.3, 29.0, 27.6, 27.1, 27.0, 26.9, 25.4, 22.9, 22.6, 19.3, 14.1; HRMS–ESI: Calcd for $C_{42}H_{59}NO_2Si$: 636.4237 $[M - H]^-$. Found: 636.4208.

## Synthesis of (*R*)-10-(*tert*-butyldiphenylsilyloxy)-*N*-phenethyloctadecanamide (**19**)




To a solution of the amide **18** (50 mg, 0.078 mmol) in MeOH (20 mL), 10% Pd/C (10 mg) was added and the mixture was hydrogenated for 24 h. It was then filtered through a short pad of Celite and the filter cake was washed with MeOH. The filtrate were concentrated in vacuo to give the product (50 mg, 100%) as a colorless oil. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.67 (d, $J$ = 6.8 Hz, 4H), 7.42–7.18 (m, 11H), 5.46 (br s, 1H), 3.70 (m, 1H), 3.51 (q, $J$ = 6.4 Hz, 2H), 2.81 (t, $J$ = 7.2 Hz, 2H), 2.10 (t, $J$ = 7.6 Hz, 2H), 1.58–1.05 (m, 24H), 1.03 (s, 9H), 0.87 (t, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 173.2, 139.0, 136.0, 134.9, 129.4, 128.8, 128.6, 127.4, 126.5, 73.3, 40.5, 36.9, 36.4, 31.9, 29.7, 29.7, 29.5, 29.4, 29.3, 29.3, 27.1, 25.8, 24.9, 22.7, 19.4, 14.1; HRMS–ESI: Calcd for $C_{42}H_{63}NO_2Si$: 640.4550 $[M - H]^-$. Found: 640.4527.

## Synthesis of (*R*)-10-hydroxy-*N*-phenethyloctadecanamide (**1**)




A solution of **19** (50 mg, 0.078 mmol) and TBAF (42 mg, 0.16 mmol) in THF (10 mL) was stirred for 24 h. After removal of the solvent, the residue was purified by flash chromatography (30 % EtOAc in PE) to afford (*R*)-**1** (29 mg, 93%) as a white solid. Mp 106–107 °C; $[\alpha]_D^{20}$ +37.2 (*c* 0.85, $CHCl_3$); IR (KBr) $\nu_{max}$: 3312, 2920, 2846, 1643, 1554 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.32 (t, $J$ = 7.6 Hz, 2H), 7.22 (d, $J$ = 7.6 Hz, 1H), 7.19 (t, $J$ = 7.6 Hz, 2H), 5.39 (br s, 1H), 3.58 (br m, 1H), 3.52 (q, *J = 6.4 Hz,* 2H),

2.82 (t, *J* = 6.8 Hz, 2H), 2.11 (t, *J* = 7.2 Hz, 2H), 1.58–1.05 (m, 24H), 0.88 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 173.1, 139.0, 128.8, 128.6, 126.5, 72.0, 40.5, 37.5, 37.5, 36.8, 35.7, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 25.7, 25.6, 22.7, 14.1; EIMS (*m/z*): 403, 385, 294, 290, 265, 176, 163, 122, 104 (base), 91, 83, 69, 55, 43; HRMS–ESI: Calcd. for $C_{26}H_{45}NO_2$: 404.3529 $[M+H]^+$. Found: 404.3529.

# References


1. Civitello, E. R.; Rapoport, H. *J. Org. Chem.* **1994**, *59*, 3775–3782.

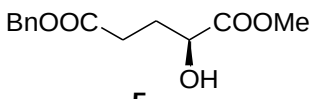
2. Liu, R.; Ma, J.; Wei, B.; Lin, G.; Huang, W. *Tetrahedron Lett.* **2009**, *50*, 4046–4049.

3. Qabar, M. N.; Kahn, M. *Tetrahedron Lett.* **1996**, *37,* 965–968.

4. Sankaranarayanan, S.; Chattopadhyay, S. *Tetrahedron: Asymmetry* **1998**, *9*, 1345–1350.

5. Nanda, S.; Yadav, J. S. *Tetrahedron: Asymmetry* **2003**, *14*, 1799–1806.

## $^{1}$H NMR and $^{13}$C NMR spectra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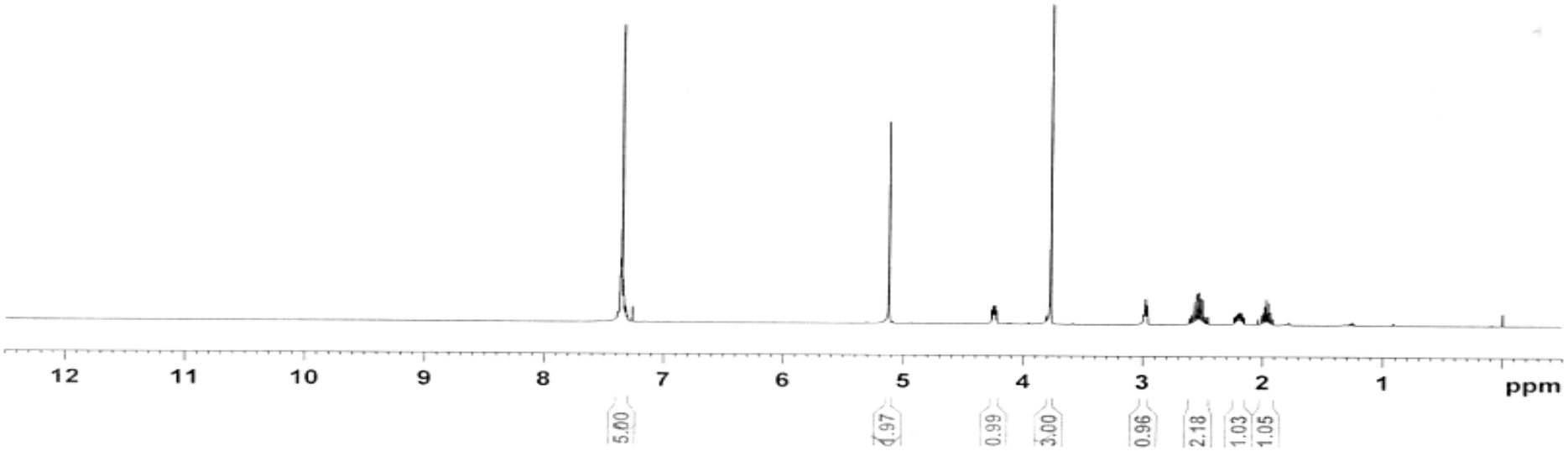


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128.23
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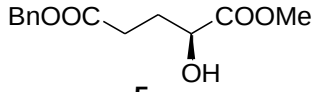
29.27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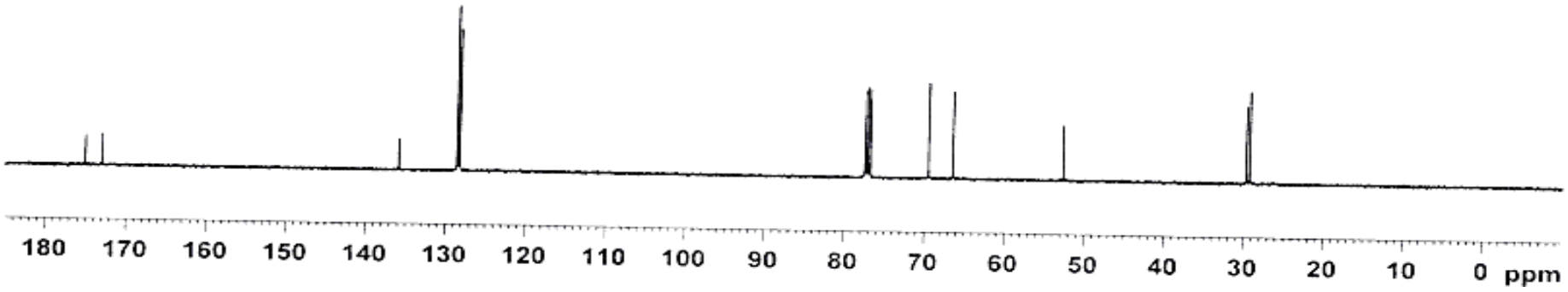
COOMe
OH

**5**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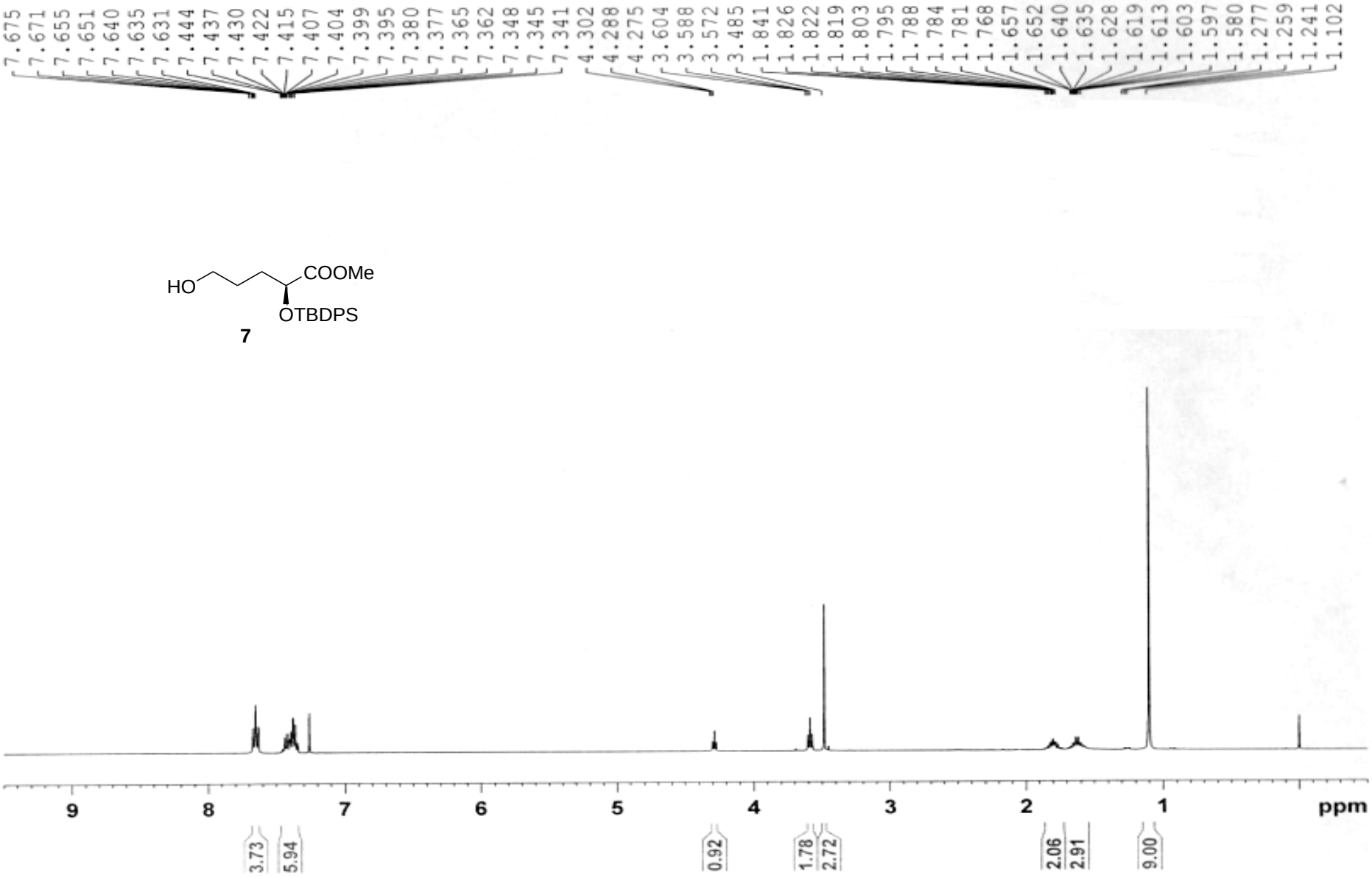
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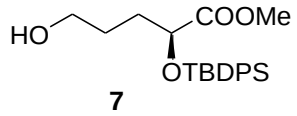
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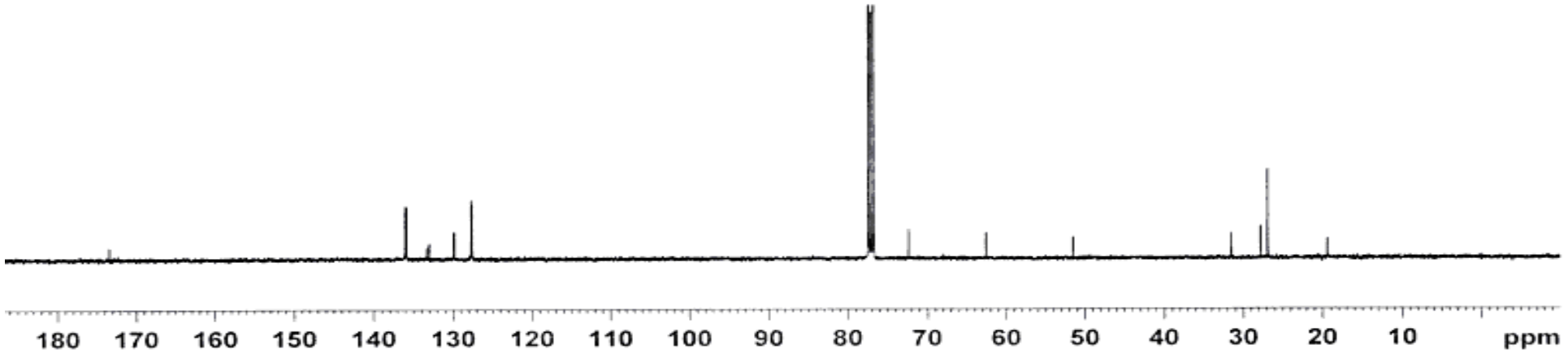
COOMe
OTBDPS

**7**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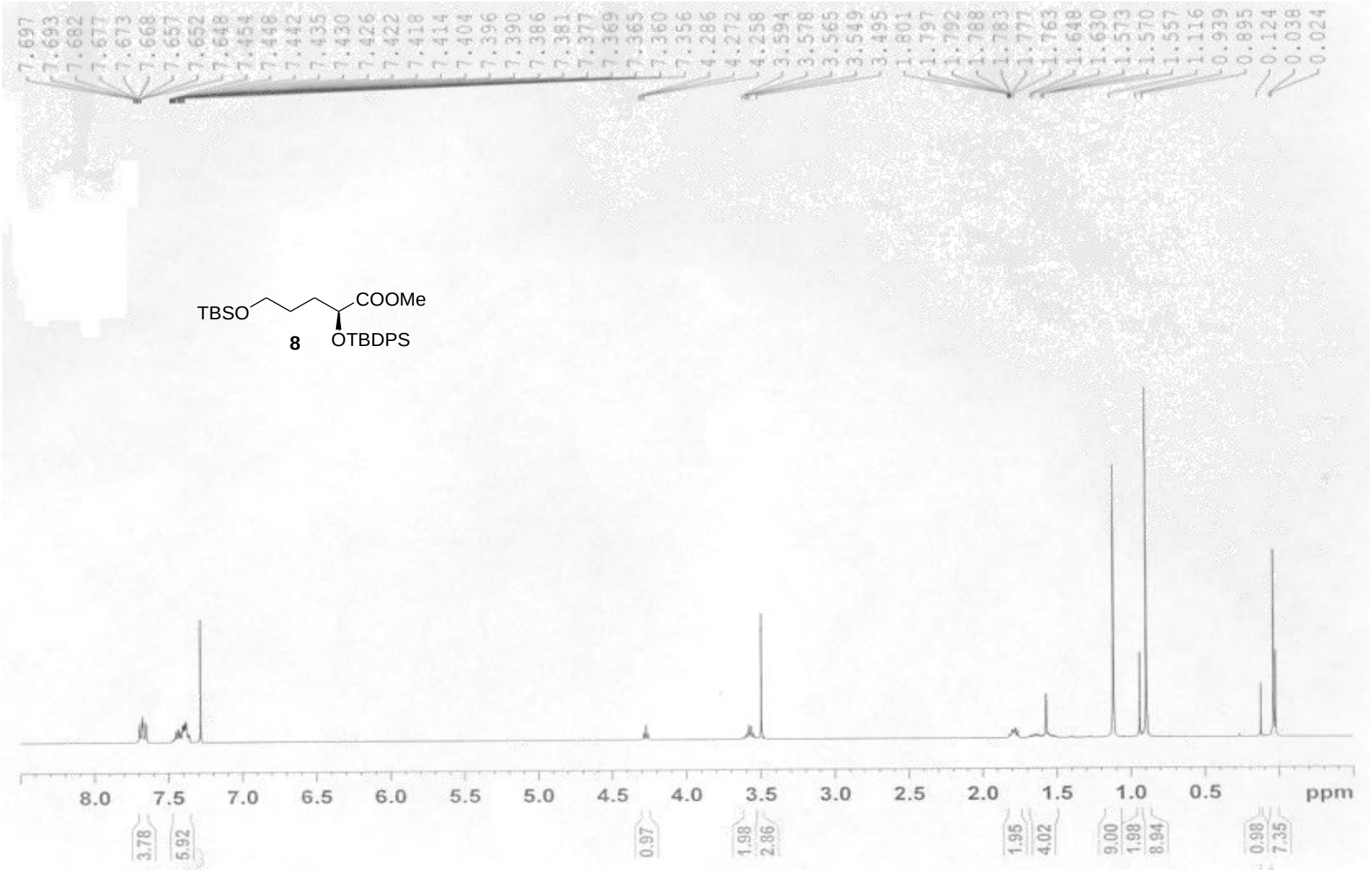
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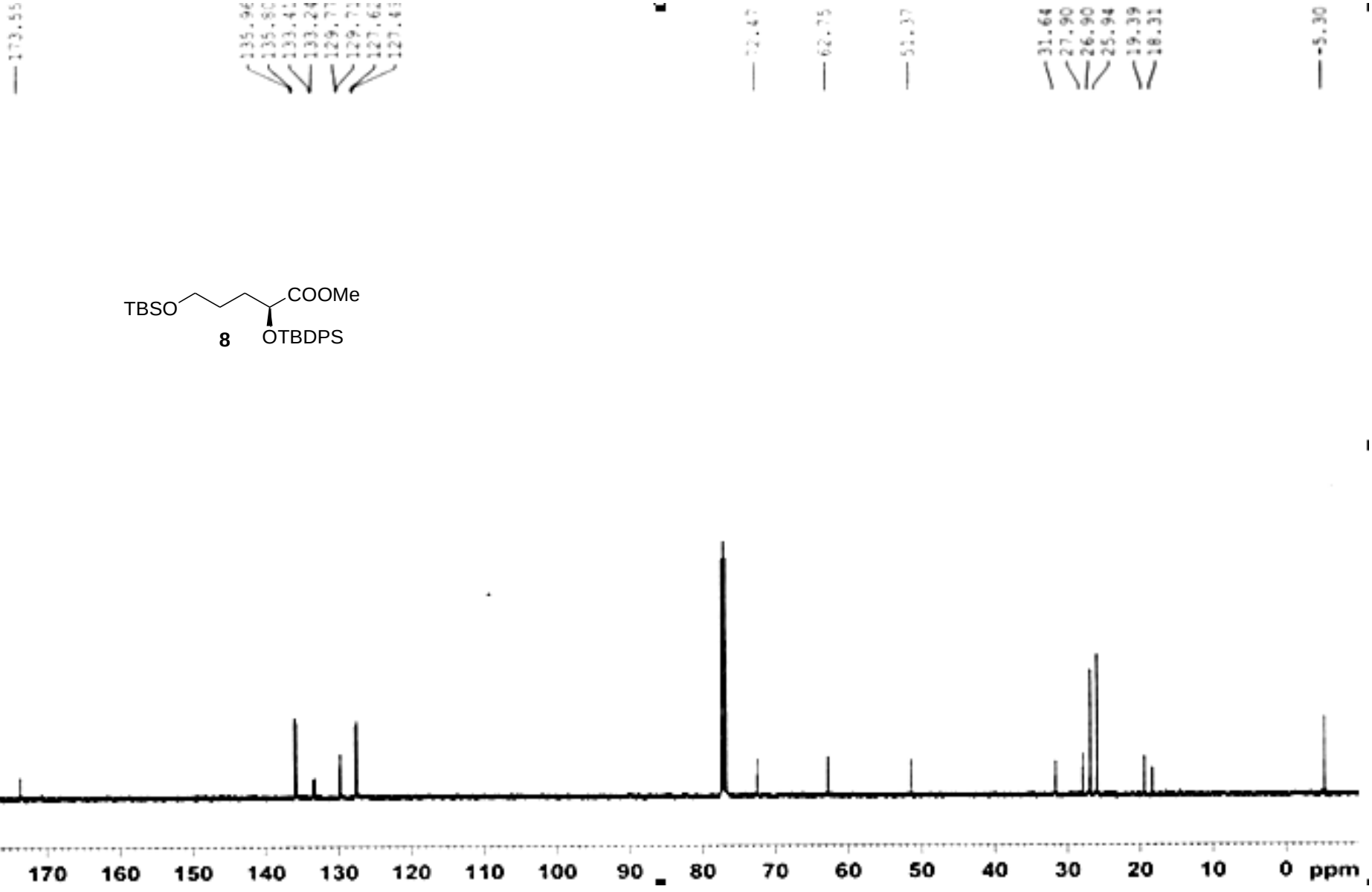
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COOMe
OTBDPS
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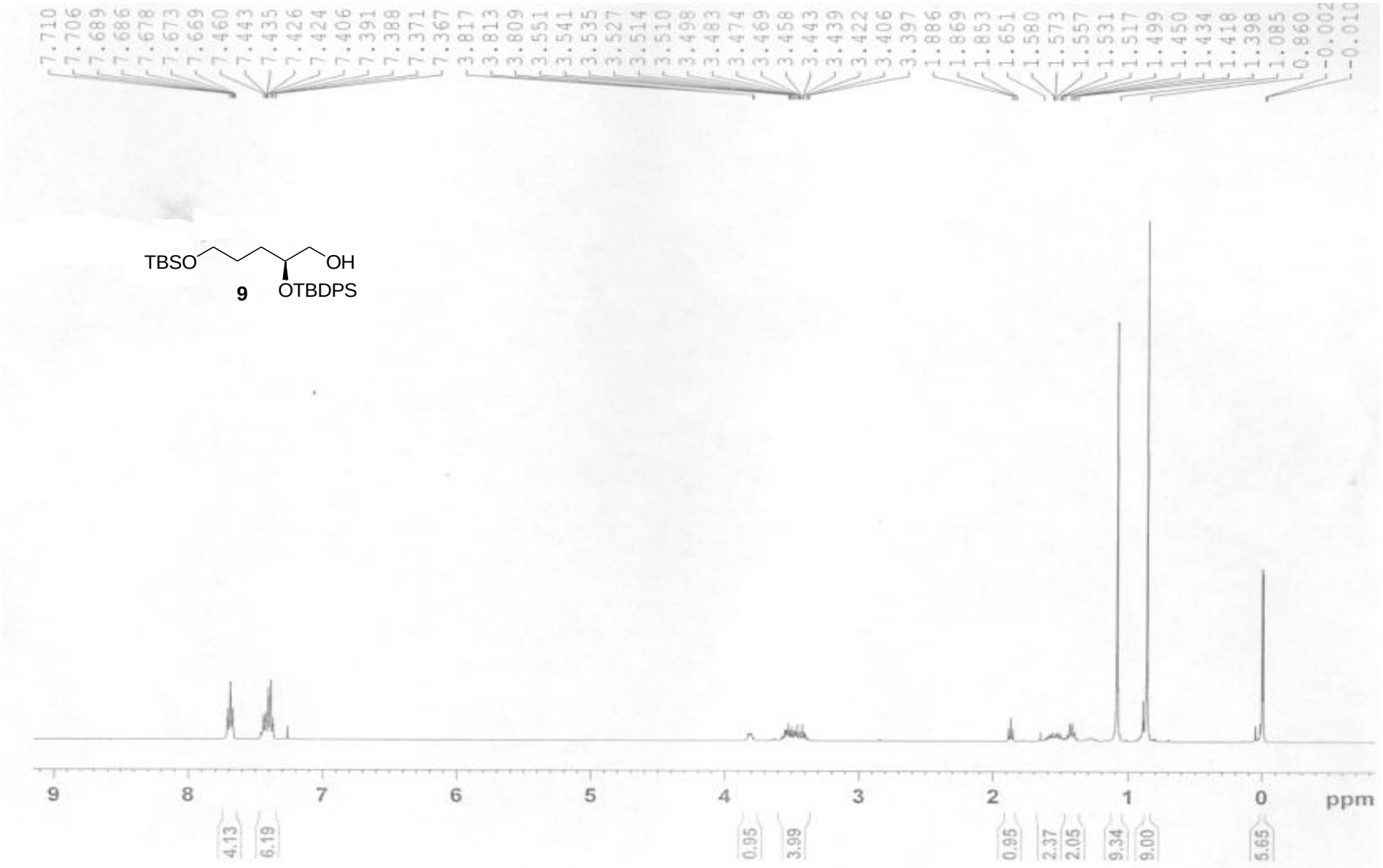
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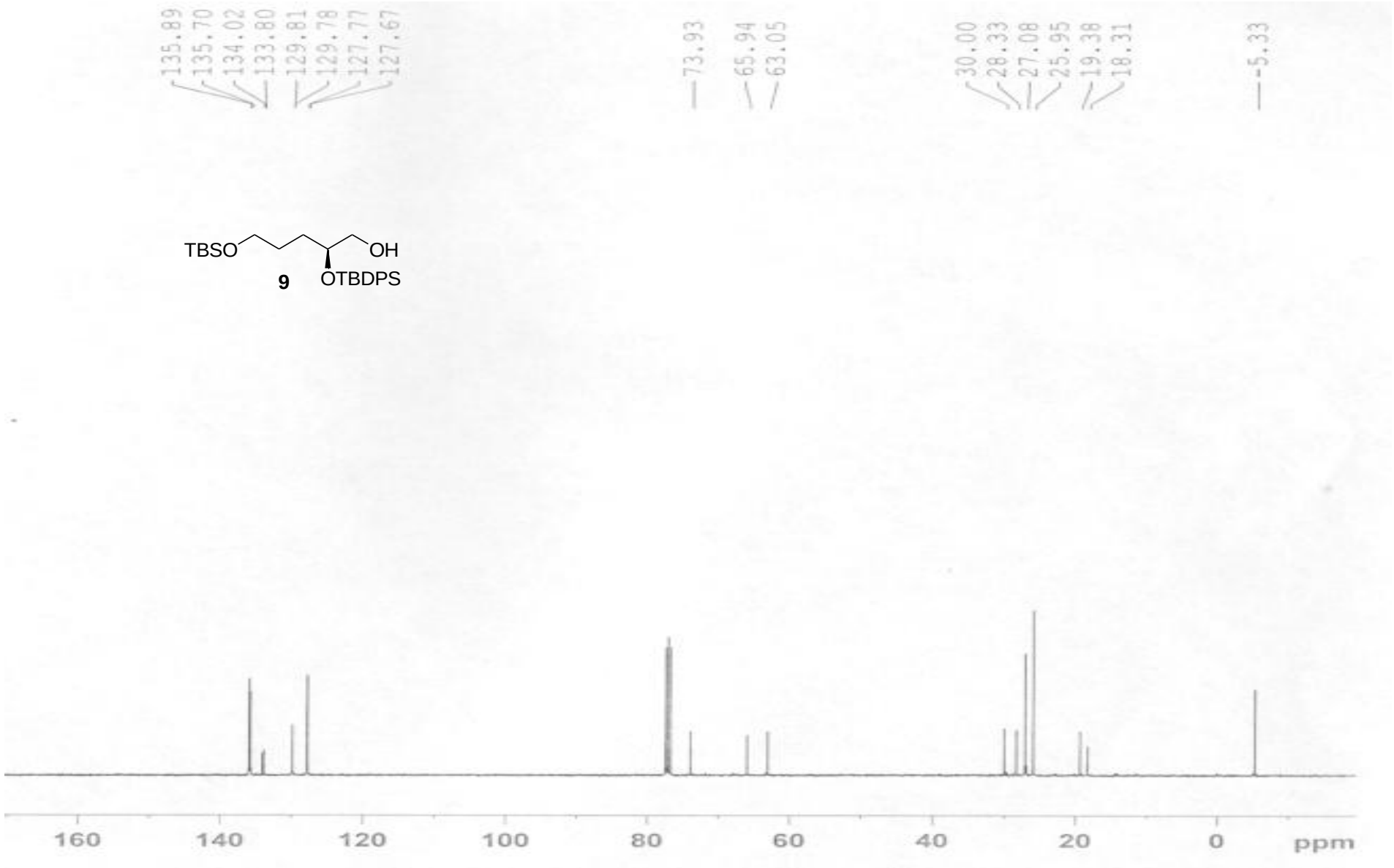
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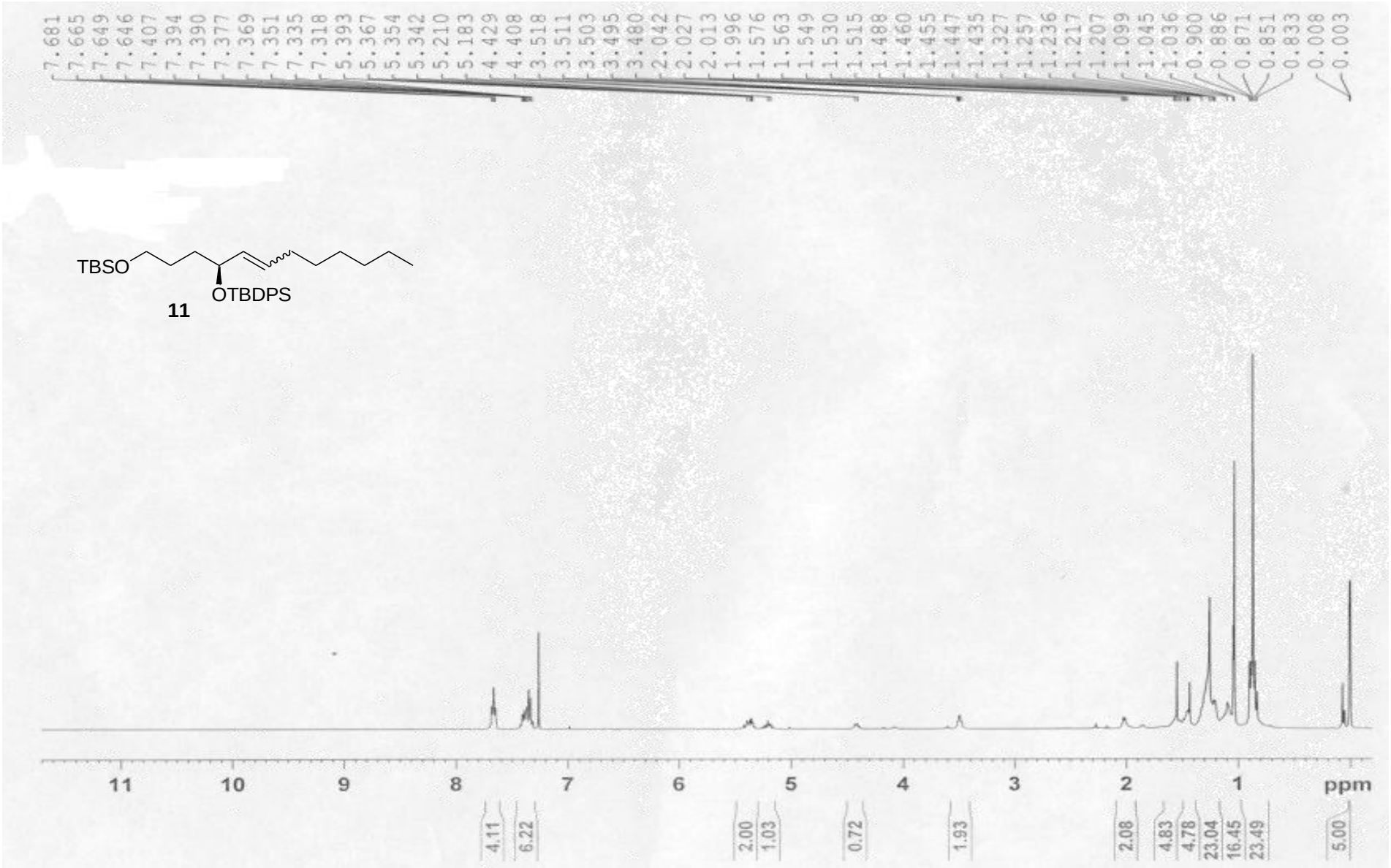
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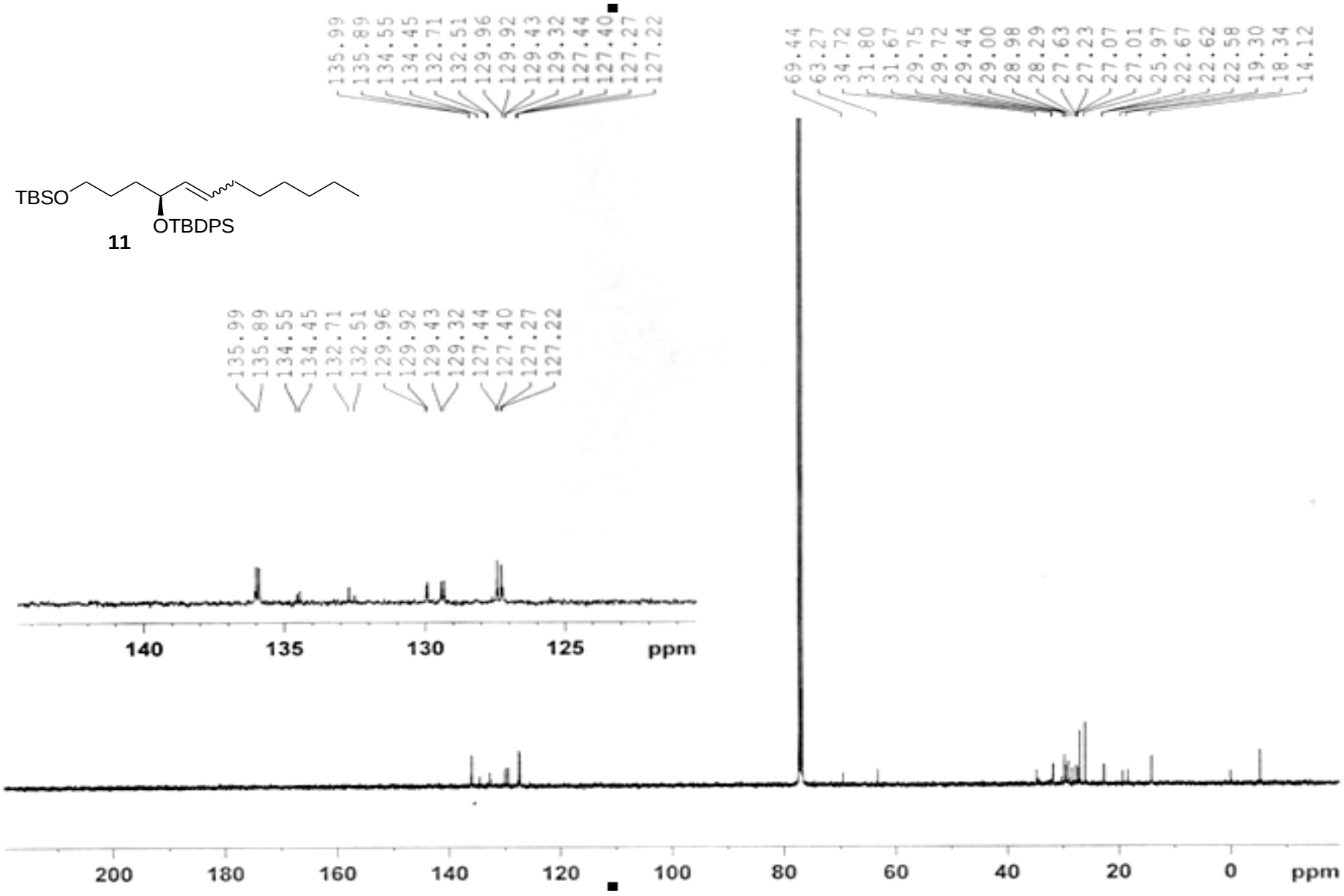
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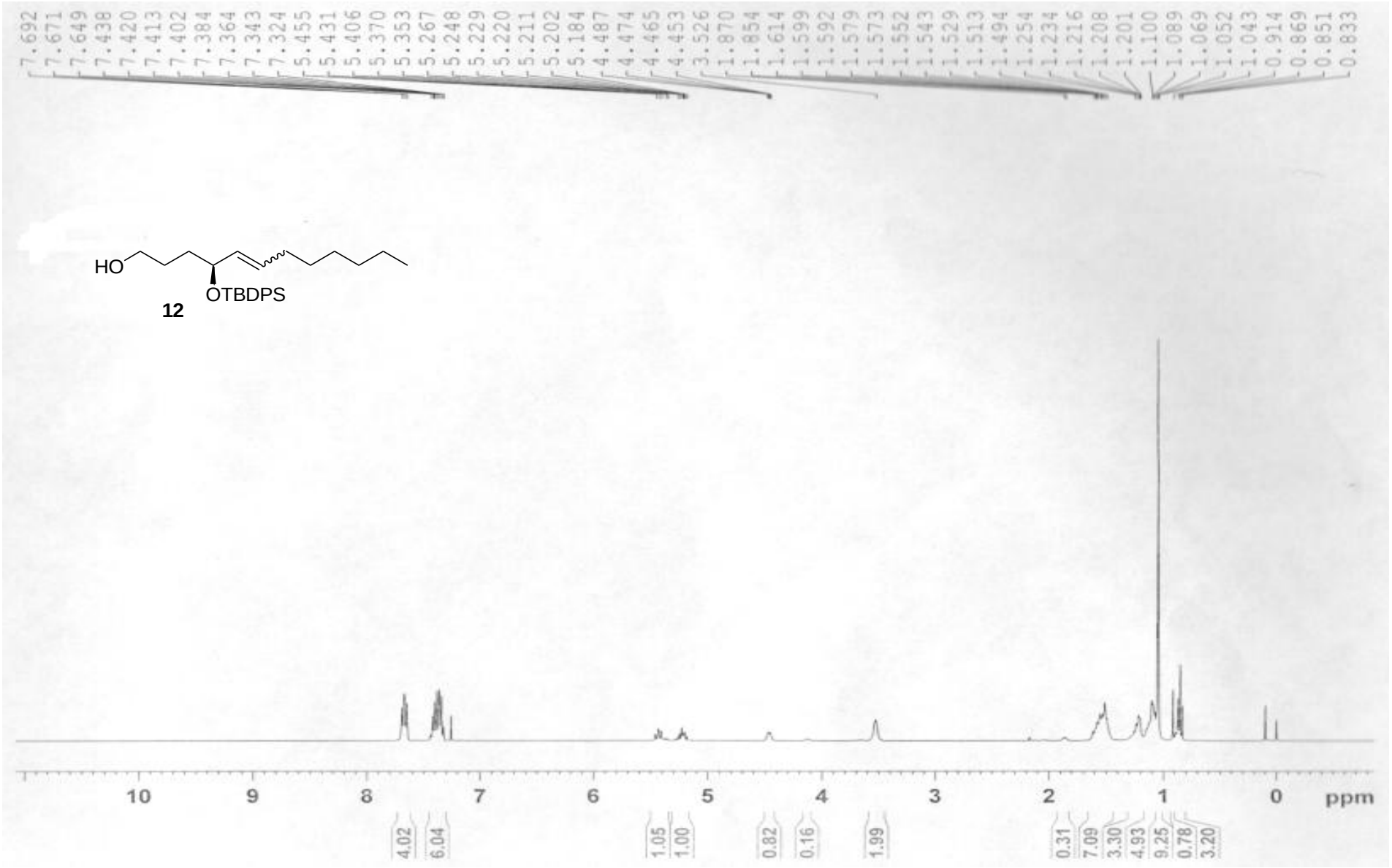
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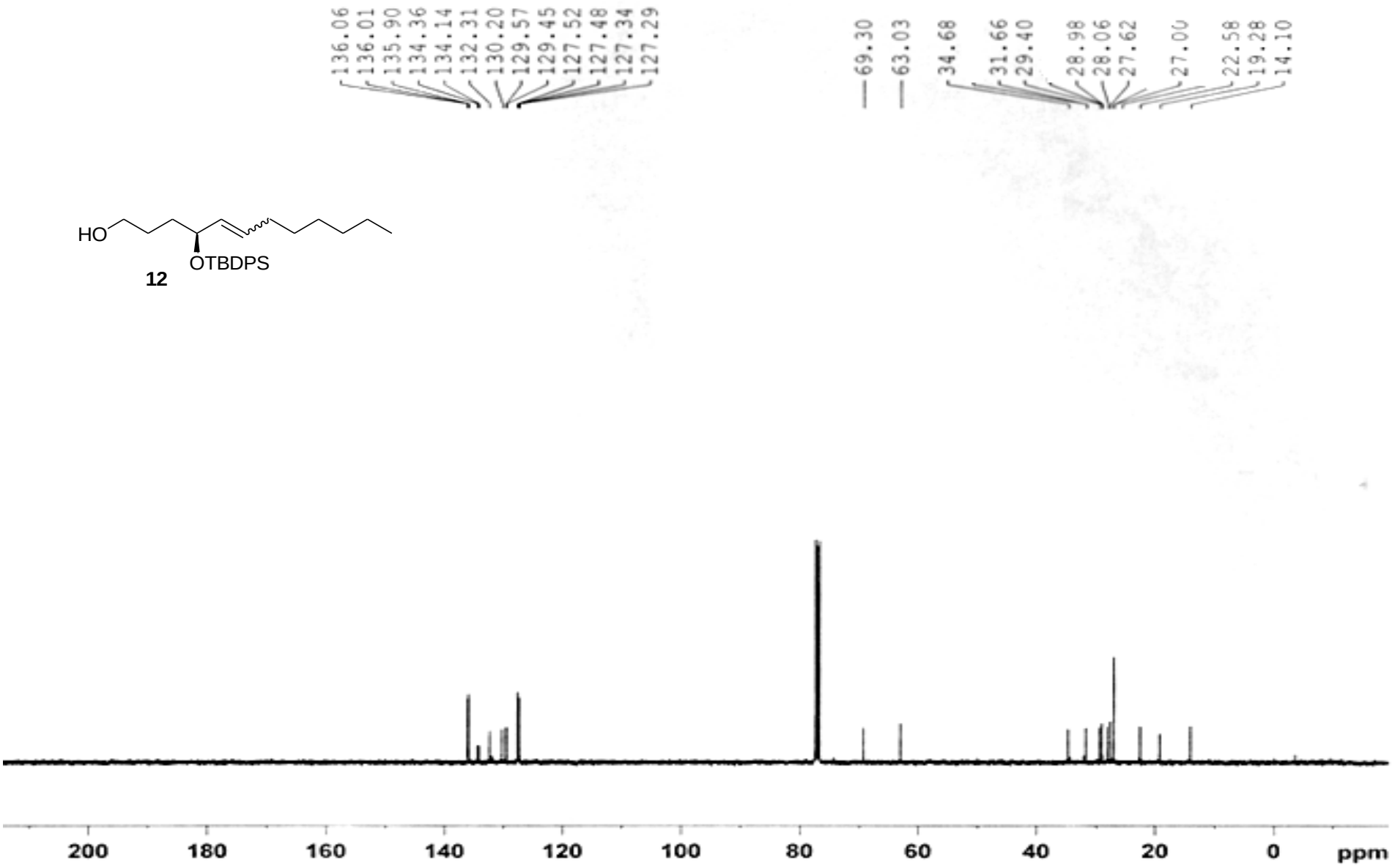
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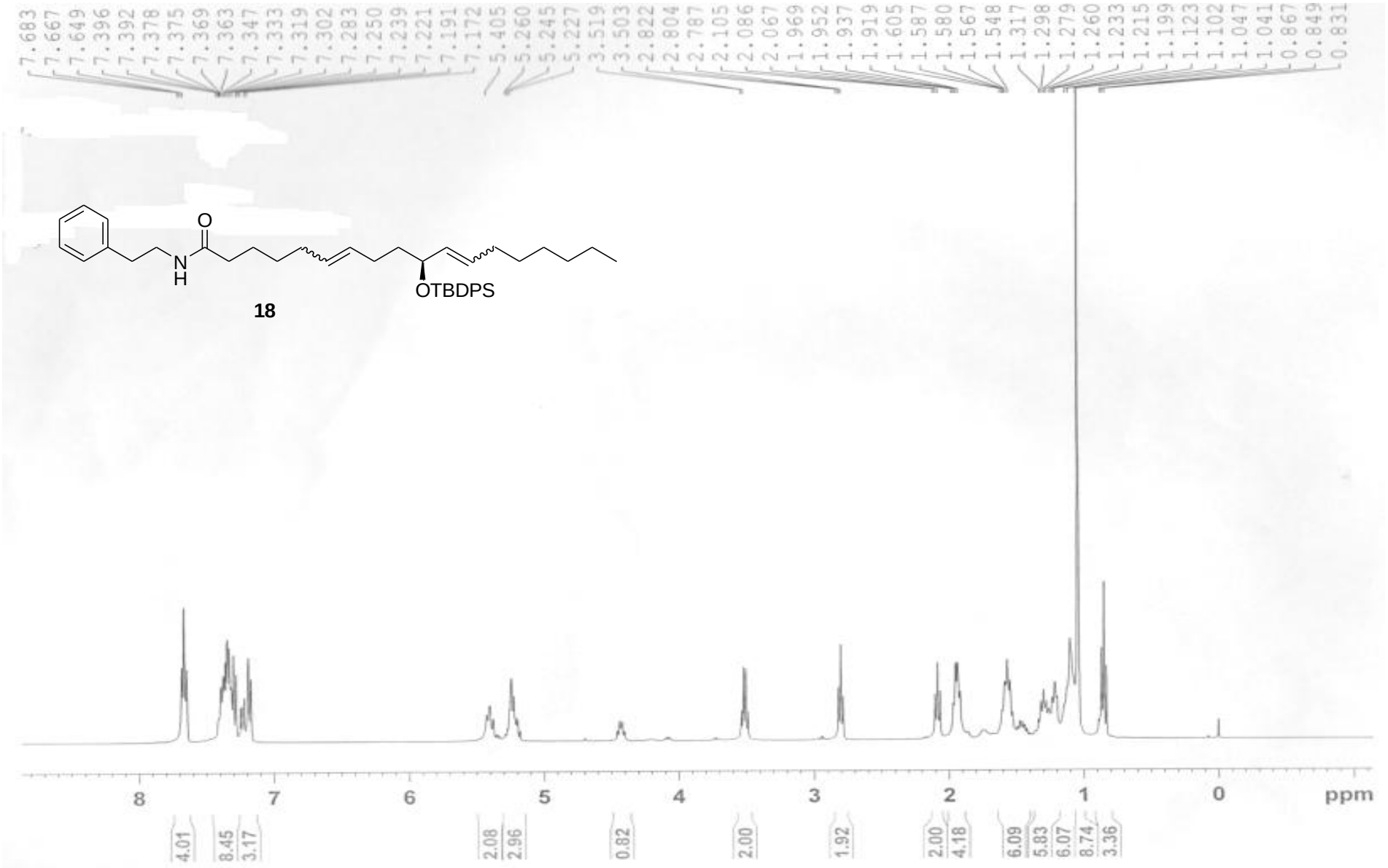
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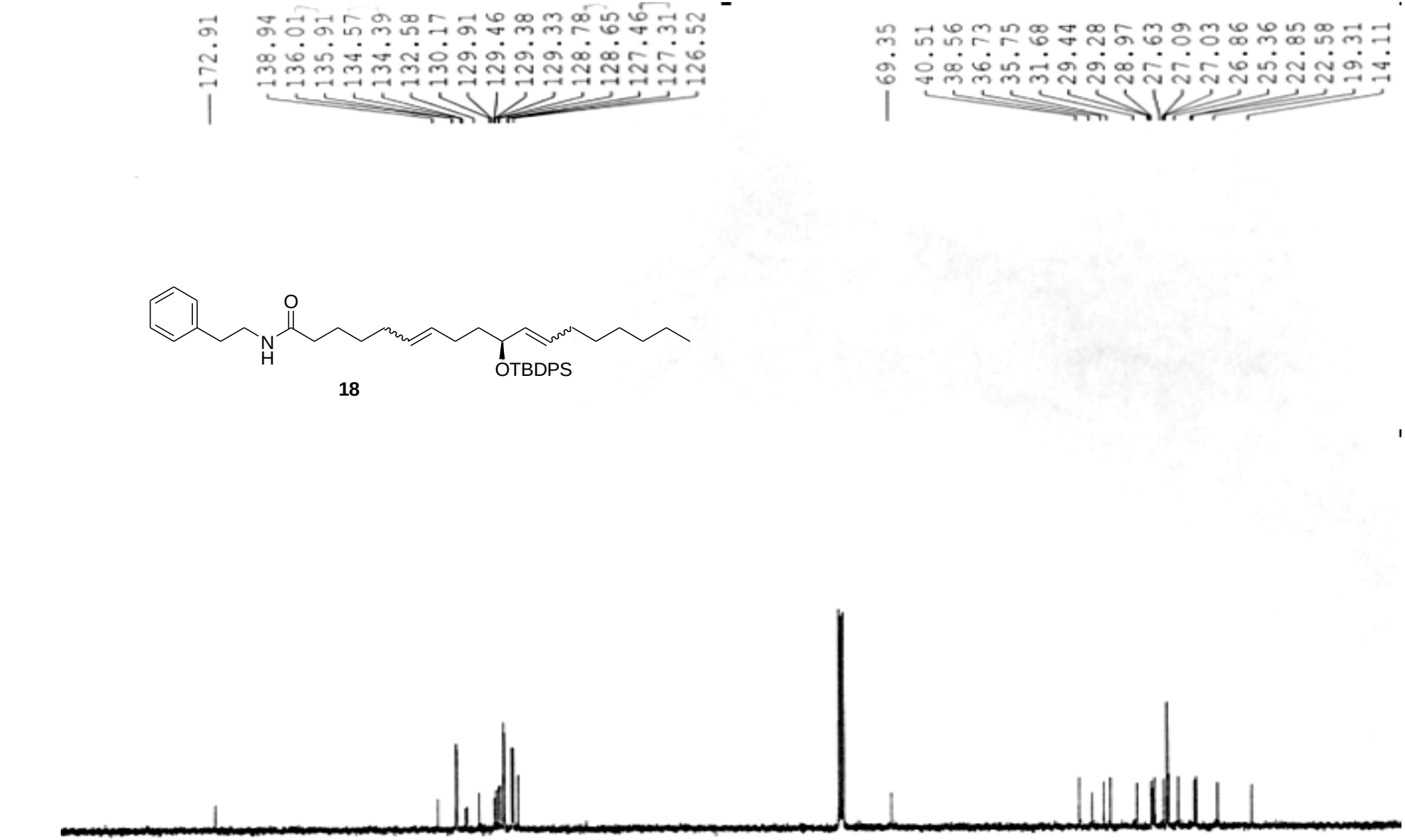
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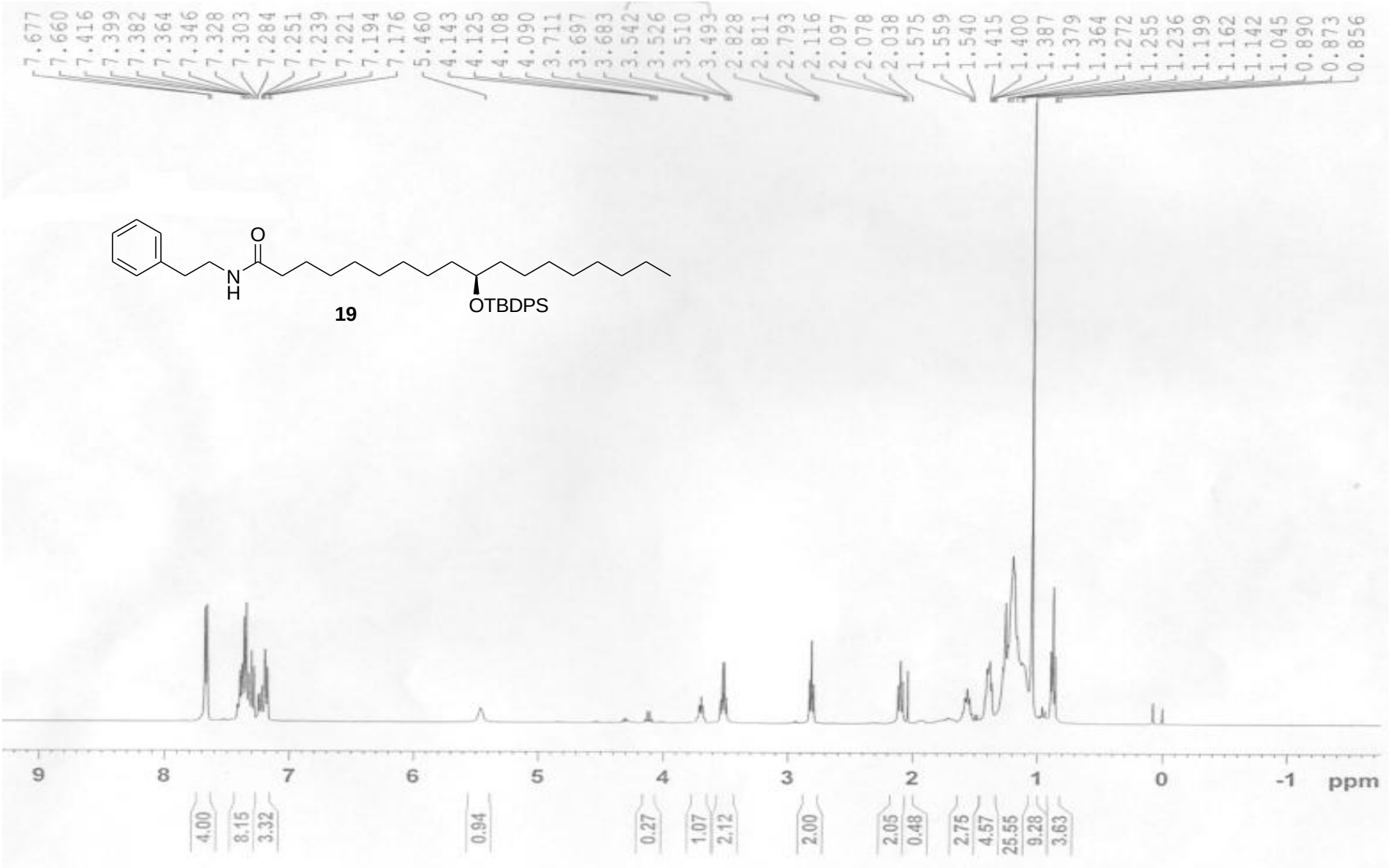
**18**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173.15
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126.51


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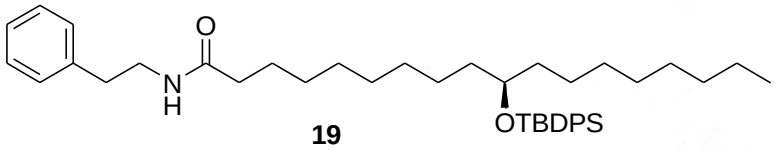
O
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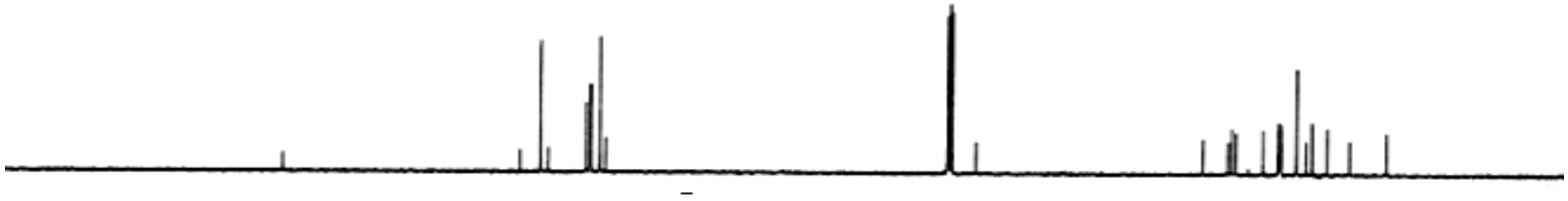
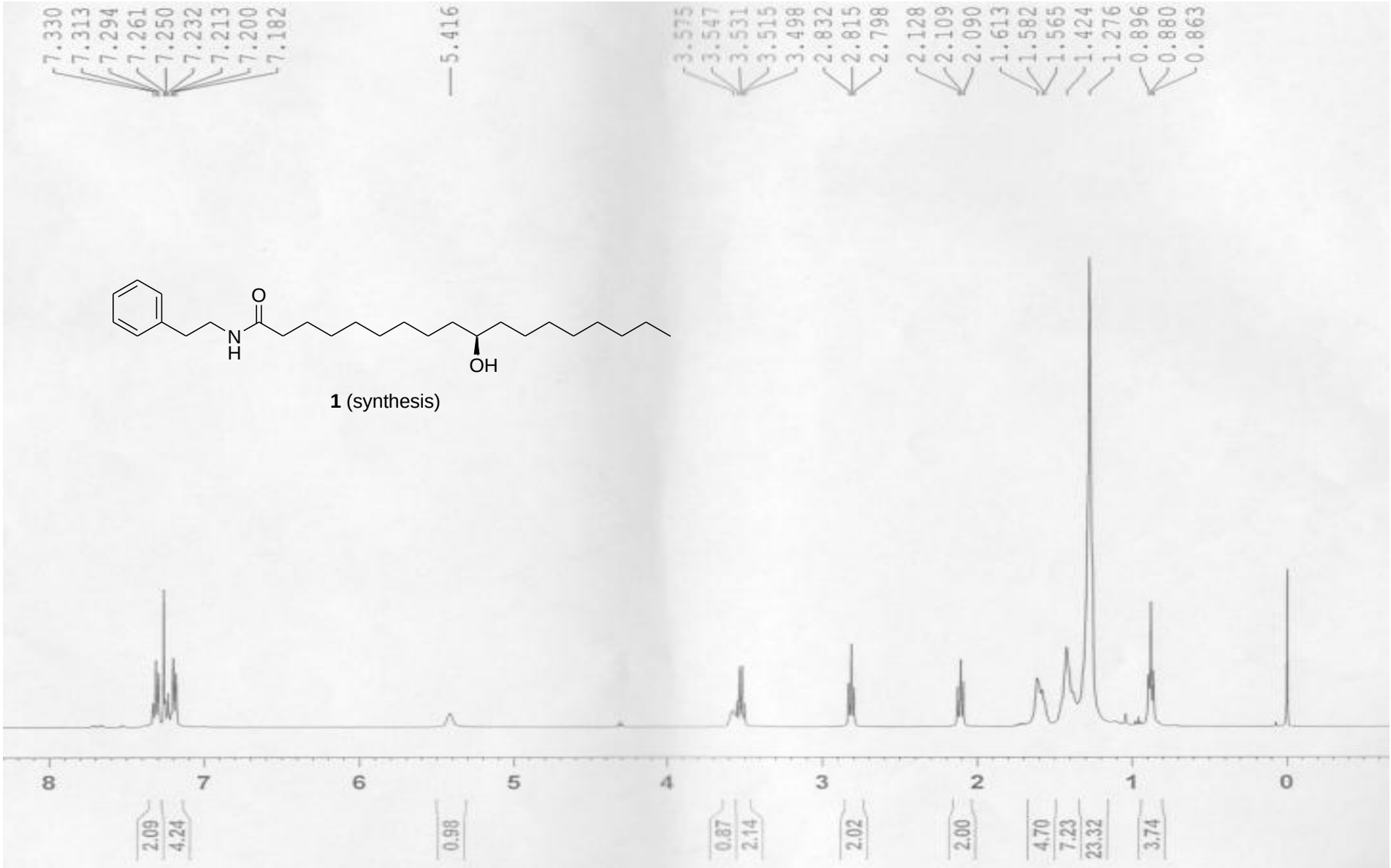
OTBDPS

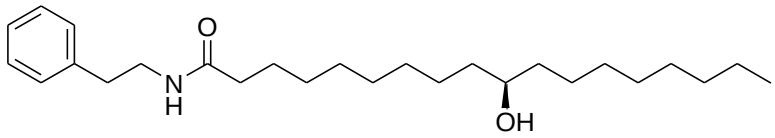
**19**



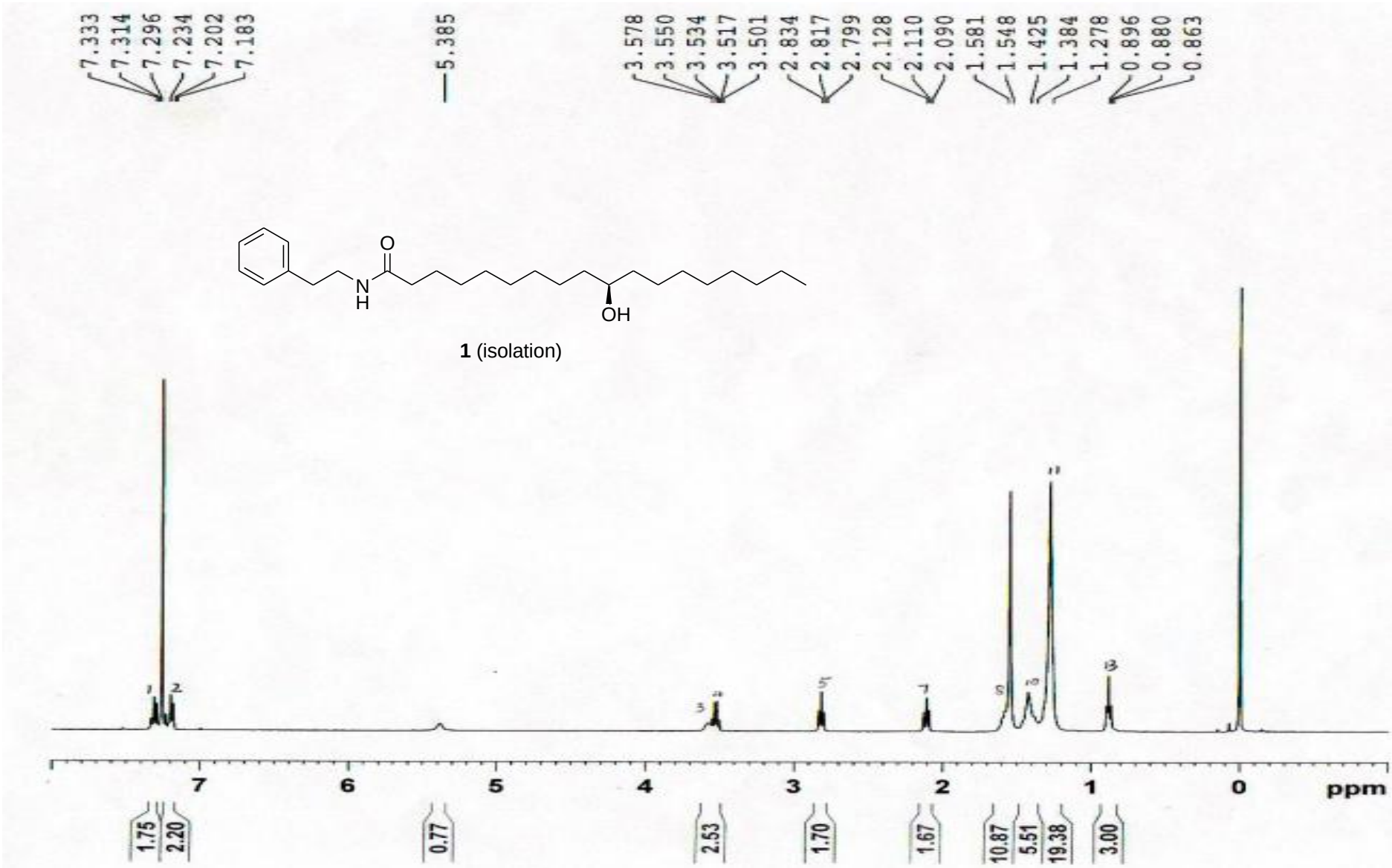

7.330
7.313
7.294
7.261
7.250
7.232
7.213
7.200
7.182
5.416
3.575
3.547
3.531
3.515
3.498
2.832
2.815
2.798
2.128
2.109
2.090
1.613
1.582
1.565
1.424
1.276
0.896
0.880
0.863
O
N
H
OH
8
7
6
5
4
3
2
1
0
2.09
4.24
0.98
0.87
2.14
2.02
2.00
4.70
7.23
23.32
3.74

**1** (synthesis)

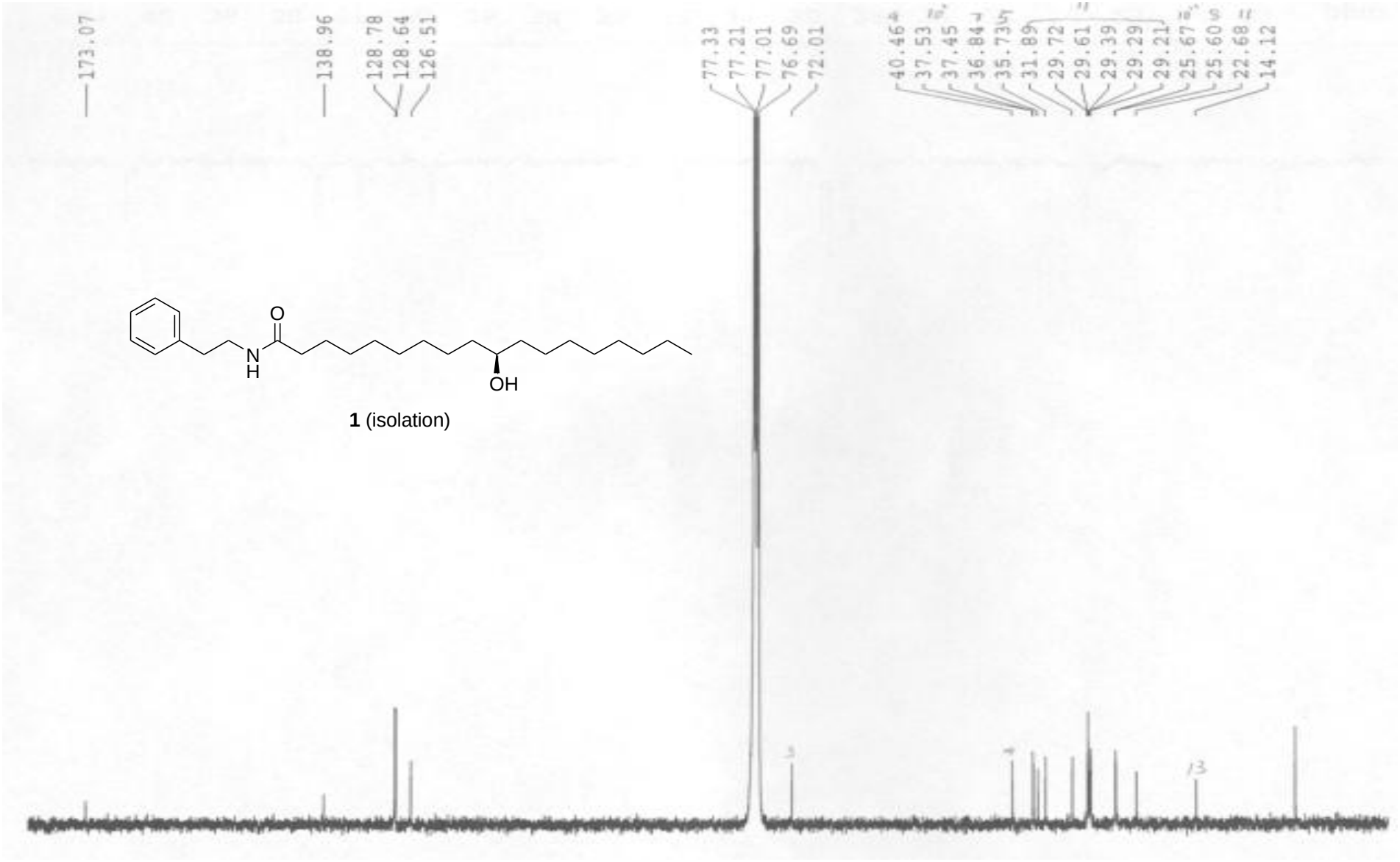

173.13
138.97
128.77
128.62
126.49
71.98
40.49
37.53
37.45
36.80
35.73
31.88
29.73
29.61
29.40
29.28
29.24
29.21
25.71
25.67
25.60
22.67
14.10


O
N
H
OH

**1** (synthesis)

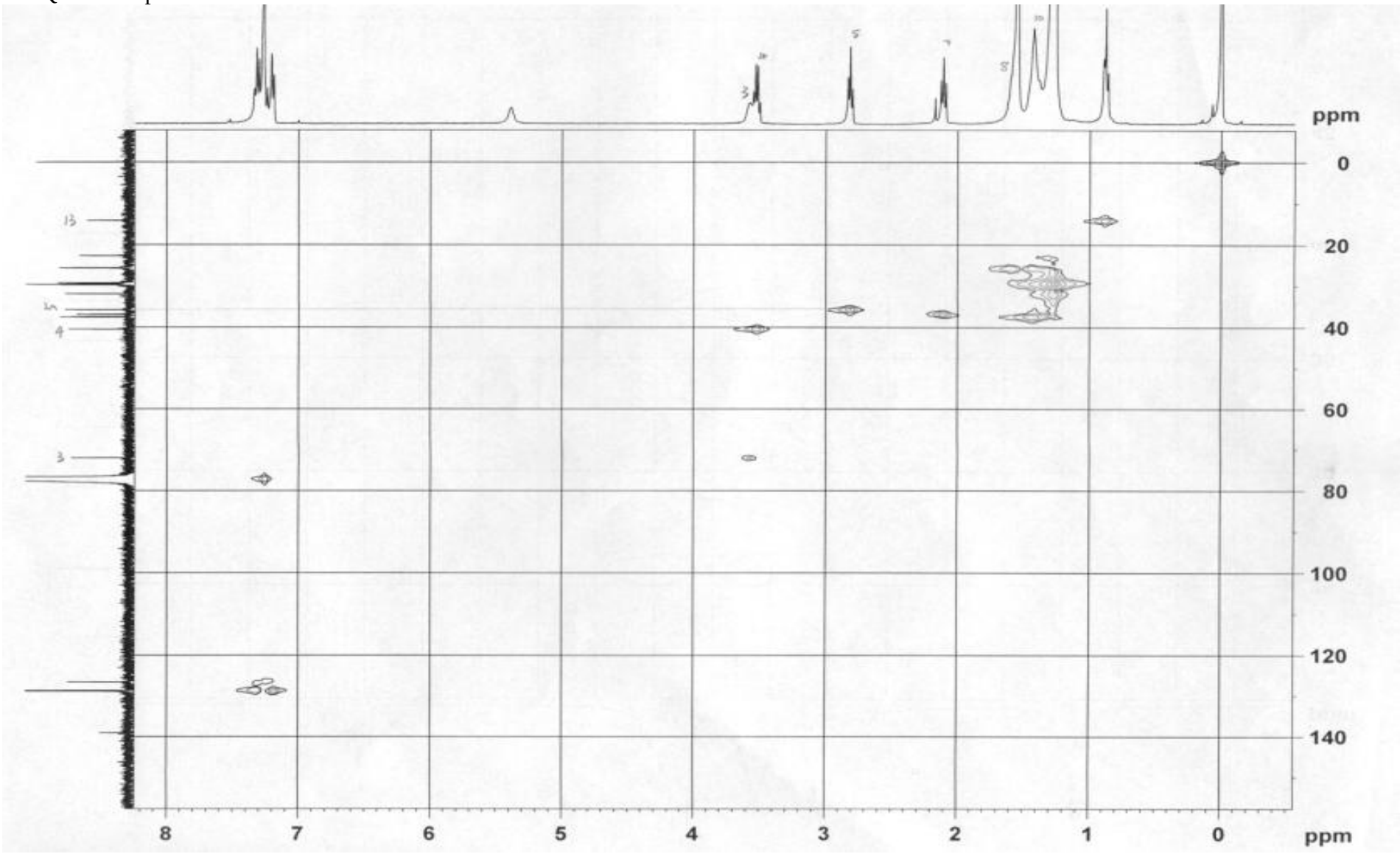

7.333
7.314
7.296
7.234
7.202
7.183
5.385
3.578
3.550
3.534
3.517
3.501
2.834
2.817
2.799
2.128
2.110
2.090
1.581
1.548
1.425
1.384
1.278
0.896
0.880
0.863
O
N
H
OH
7
6
5
4
3
2
1
0
ppm
1.75
2.20
0.77
2.53
1.70
1.67
10.87
5.51
19.38
3.00

**1** (isolation)

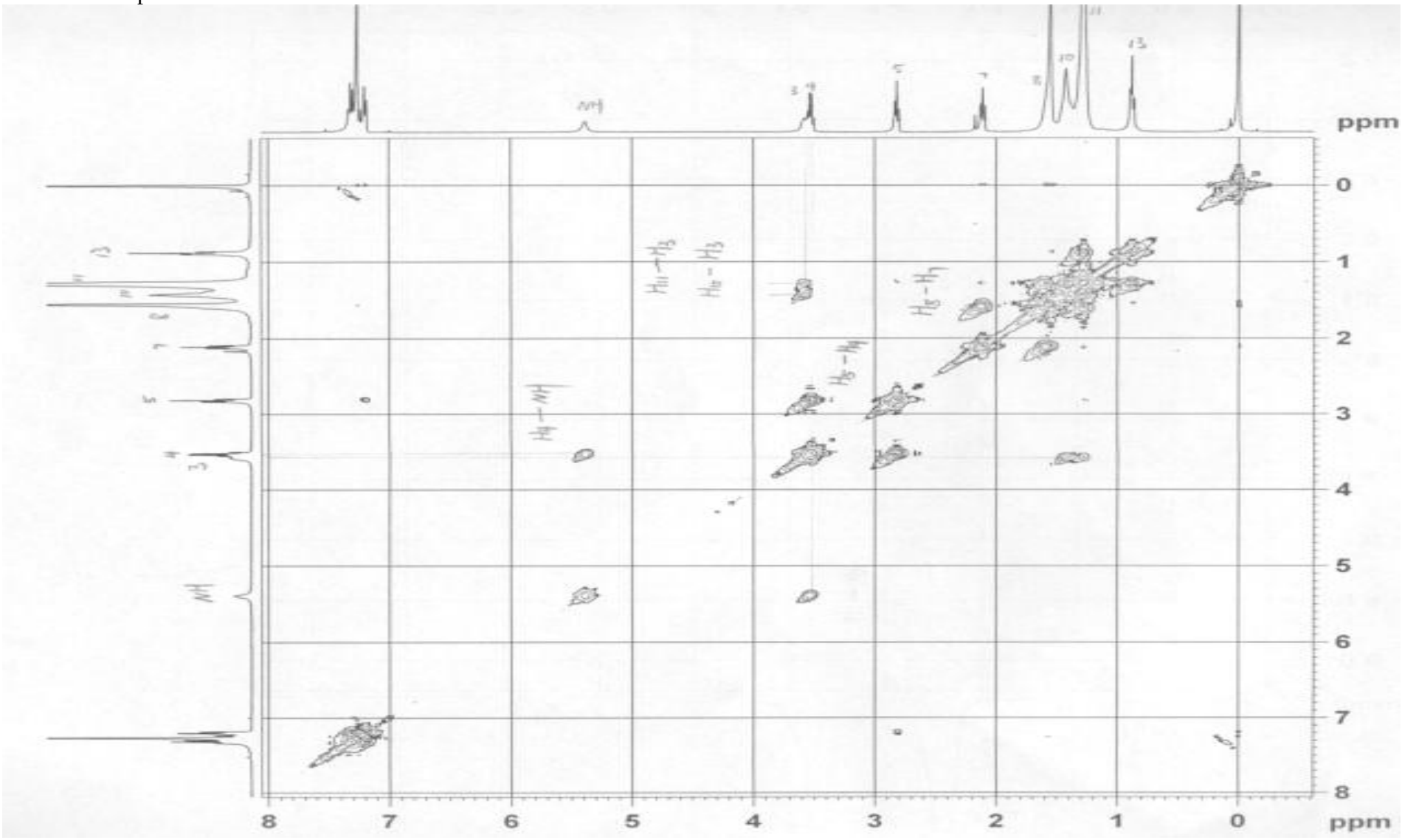

173.07
138.96
128.78
128.64
126.51
77.33
77.21
77.01
76.69
72.01
40.46
37.53
37.45
36.84
35.73
31.89
29.72
29.61
29.39
29.29
29.21
25.67
25.60
22.68
14.12
O
N
H
OH

**1** (isolation)

HMQC of compound **1**



COSY of compound **1**



HMBC of compound **1**