Fully Reagent-Controlled Asymmetric Synthesis of (–)-Spongidepsin via the Zr-Catalyzed Asymmetric Carboalumination of Alkenes (ZACA Reaction)

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Supporting Information

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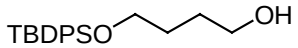
General. THF and ether were distilled from sodium and benzophenone. CH_2Cl_2 was distilled from CaH_2. Flash chromatographic separation was carried out on 230–400 mesh silica gel 60. Gas chromatography was performed on an HP 6890 Gas Chromatograph using an HP-5 capillary column (30 m × 0.32 mm, 0.5 μm film) with appropriate hydrocarbons as internal standards. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Inova-300 spectrometer. Optical rotations were measured on an Autopol III automatic polarimeter. $ZnBr_2$ and $Zn(OTf)_2$ were flame-dried under vacuum prior to use. (+)- and (–)-$(NMI)_2ZrCl_2$[a] as well as $Pd(DPEphos)Cl_2$[b] were prepared as reported in the literature.

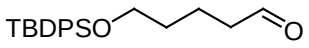
5-*tert*-Butyldiphenylsilyloxy-1-pentanol. Representative Procedure A

This compound was prepared by a literature method[c] with a modification involving the use of ten-fold excess of inexpensive 1,5-pentanediol rather than one equivalent leading to higher product yield. To a solution of 43 mL (500 mmol) of 1,5-pentanediol and 4.1 g (60 mmol) of imidazole in 200 mL of DMF was added dropwise 13 mL (50 mmol) of *tert*-butyldiphenylchlorosilane over 2 h at 0 ^{o}C. After stirring for 3 h at 23 ^{o}C, the reaction mixture was quenched with 200 mL of water, extracted with ether, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 70/30 hexanes-EtOAc) afforded 15.7 g (92%) of the title compound as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (s, 9 H), 1,4-1.75 (m, 6 H), 1.95-2.15 (m, 1 H), 3.65 (t, *J* = 6.6 Hz, 2 H), 3.76 (t, *J* = 6.6 Hz, 2 H), 7.4-7.55 (m, 6 H), 7.7-7.85 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.11, 21.86, 26.78 (3 C), 32.17, 32.28, 62.63, 63.69, 127.50 (4 C), 129.44 (2 C), 133.91 (2 C), 135.45 (4 C).



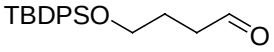
4-*tert*-Butyldiphenylsilyloxy-1-butanol.

The title compound was prepared according to Representative Procedure A except that 0.9 g (10 mmol) of 1,4-butanediol was used in place of 1,5-pentanediol to afford 3.0 g (90%) of the desired product; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (s, 9 H), 1.75-1.9 (m, 4 H), 3.0-3.15 (m, 1 H), 3.75-3.85 (m, 4 H), 7.5-7.6 (m, 6 H), 7.8-7.9 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.03, 26.72 (3 C), 29.11, 29.47, 62.37, 63.86, 127.53 (4 C), 129.53 (2 C), 133.54 (2C), 135.42 (4 C).



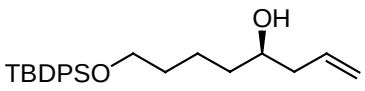
5-*tert*-Butyldiphenylsilyloxy-1-pentanal. Representative Procedure B

This compound was prepared by the Swern oxidation[d], as follows. To a solution of 5.2 mL (60 mmol) of oxalyl chloride in 100 mL of CH_2Cl_2 was added slowly a solution of 7.1 mL (100 mmol) of DMSO in 20 mL of CH_2Cl_2 at –78 °C. After stirring for 15 min, 15.6 g (46 mmol) of 5-*tert*-butyldiphenylsilyloxy-1-pentanol in 30 mL of CH_2Cl_2 was added to the above solution. After stirring at –78 °C for 1 h, 14 mL (100 mmol) of Et_3N was added at –78 °C. The reaction mixture was slowly warmed to 23 °C, quenched with saturated aqueous NH_4Cl, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 95/5 hexanes-EtOAc) afforded 14.4 g (92%) of the desired aldehyde as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (s, 9 H), 1.7-1.85 (m, 4 H), 2.52 (t, *J* = 6.6 Hz, 2 H), 3.87 (t, *J* = 6.3 Hz, 2 H), 7.5-7.6 (m, 6 H), 7.85-7.9 (m, 4 H), 9.84 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.30, 18.97, 26.66 (3 C), 31.58, 43.17, 63.05, 127.45 (4 C), 129.41 (2 C), 133.56 (2 C), 135.31 (4 C), 202.10.



4-*tert*-Butyldiphenylsilyloxy-1-butanal.

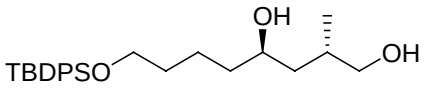
The title compound was prepared according to Representative Procedure B except that 3.0 g (9 mmol) of 4-*tert*-butyldiphenylsilyloxy-1-butanol was used in place of 5-*tert*-butyldiphenylsilyloxy-1-pentanol to afford 2.6 g (88%) of the desired product; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (s, 9 H), 1.9-2.0 (m, 2 H), 2.57 (td, *J* = 6.9, 1.5 Hz, 2 H), 3.74 (t, *J* = 6.0 Hz, 2 H), 7.4-7.5 (m, 6 H), 7.7-7.75 (m, 4 H), 9.81 (t, *J* = 1.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.06, 25.12, 26.72 (3 C), 40.62, 62.80, 127.59 (4 C), 129.58 (2 C), 133.46 (2 C), 135.42 (4 C), 202.21.



(4*R*)-8-*tert*-Butyldiphenylsilyloxy-1-octen-4-ol (8). **Representative Procedure C**

Allylboration of 5-*tert*-butyldiphenylsilyloxy-1-pentanal was carried out by the Brown

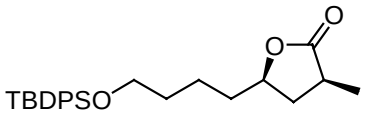
allylboration.[e] To a suspension of 9.5 g (30 mmol) of (–)-$Ipc_2B(OMe)$ in 150 mL of ether was added 30 mL (30 mmol) of 1.0 M solution of allylmagnesium bromide in ether at –78 °C. After stirring for 15 min at –78 °C, the reaction mixture was warmed to 23 °C and kept at this temperature for 1 h. A solution of 8.5 g (25 mmol) of 5-*tert*-butyldiphenylsilyloxy-1-pentanal in 30 mL of ether was added at –78 °C. After stirring for 2 h at –78 °C, the reaction mixture stirred at 23 °C for 2 h, which was followed by addition of 50 mL of 2 N NaOH and 30 mL of 50% H_2O_2. After stirring overnight at 23 °C, the reaction mixture was extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 90/10 hexanes-EtOAc) afforded 8.3 g (87%) of the title compound as a colorless oil: $[\alpha]_D^{23}$ = +2.7 (*c*, 1.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 9 H), 1.4-1.7 (m, 6 H), 2.1-2.4 (m, 2 H), 3.6-3.75 (m, 3 H), 5.1-5.2 (m, 2 H), 5.8-5.95 (m, 1 H), 7.4-7.5 (m, 6 H), 7.7-7.75 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.17, 21.86, 26.83 (3 C), 32.45, 36.43, 41.85, 63.75, 70.54, 118.02, 127.56 (4 C), 129.50 (2 C), 134.02 (2 C), 134.83, 135.53 (4 C); HRMS calcd. for $C_{24}H_{35}O_2Si$ $[M+H]^+$: 383.2401, found: 383.2409.



(2*S*,4*R*)-8-*tert*-Butyldiphenylsilyloxy-2-methyl-1,4-octanediol (9). **Representative Procedure D**

1.911 g (5 mmol) of (4*R*)-8-*tert*-butyldiphenylsilyloxy-1-octen-4-ol dissolved in 5 mL of CH_2Cl_2 was mixed with 0.5 mL (5 mmol) of Me_3Al in 5 mL of CH_2Cl_2 at –78 °C, and the mixture was warmed to 23 °C and stirred for 1 h to generate the Me_2Al-protected alkenol. In a separate reactor, 1.5 mL (15 mmol) of Me_3Al in 5 mL of CH_2Cl_2 was treated with 90 uL (5 mmol) of H_2O to partially convert Me_3Al to methylaluminoxane (MAO).[f] To this was added 167 mg (0.25 mmol) of (+)-$(NMI)_2ZrCl_2$. To a wine-red solution thus formed was added the Me_2Al-protected alkenol solution in CH_2Cl_2, and the resultant mixture was

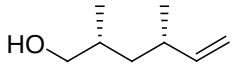
stirred overnight at 23 °C. After confirming the total consumption of the starting alkenol by GC, the mixture was treated at 0 °C with a stream of oxygen bubbled through at the rate of 5 mL per min for 1 h and further stirred at 23 °C for 6 h under O_2 atmosphere. It was quenched with 2 N NaOH, extracted with CH_2Cl_2, washed with saturated aqueous NH_4Cl and brine, dried over $MgSO_4$, and concentrated. After passing it through a short path column of silica gel using EtOAc as an eluent remove metal-containing impurities, evaporation provided 1.5 g (73%) of the crude product, which essentially consisted of the desired product and its diastereomers (dr = 3.5/1). Purification by column chromatography (silica gel, 95/5–85/15 hexanes-EtOAc) provided 872 mg (42%) of the desired product (dr = 40/1, by ^{13}C NMR); $[\alpha]_D^{23} = -7.5$ (*c*, 2.1, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (d, *J* = 6.9 Hz, 3 H), 1.07 (s, 9 H), 1.4-1.9 (m, 9 H), 3.05-3.3 (m, 2 H), 3.37 (dd, *J* = 10.5, 7.8 Hz, 1 H), 3.57 (dd, *J* = 10.5, 4.8 Hz, 1 H), 3.65-3.7 (m, 1 H), 3.69 (t, *J* = 6.3 Hz, 2 H), 7.35-7.5 (m, 6 H), 7.65-7.7 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.05, 19.14, 21.86, 26.83 (3 C), 32.39, 34.53, 38.12, 43.09, 63.75, 68.69, 70.85, 127.53 (4 C), 129.50 (2 C), 133.96 (2 C), 135.51 (4 C); HRMS (ESI) calcd. for $C_{25}H_{38}NaO_3Si$ $[M+Na]^+$: 437.2482, found: 437.2489.



(2*S*,4*R*)-4-[4'-(*tert*-Butyldiphenylsilyloxy)butyl]-2-methyl-γ-butylrolactone (10).

A solution of 830 mg (2 mmol) of (2*S*,4*R*)-8-*tert*-butyldiphenylsilyloxy-2-methyl-1,4-oct anediol in 10 mL of CH_2Cl_2 and 3 mL of H_2O was added 31 mg (0.2 mmol) of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and 1.4 g (4.4 mmol) of $PhI(OAc)_2$. After stirring for 2 h at 23 °C, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, extracted with CH_2Cl_2, washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 80/20 hexanes-EtOAc) afforded 722 mg (88%) of the desired product as a colorless oil; $[\alpha]_D^{23} = +5.9$ (*c*, 1.0, $CHCl_3$); ^1H NMR

(300 MHz, $CDCl_3$) δ 1.05 (s, 9 H), 1.26 (d, *J* = 6.3 Hz, 3 H), 1.4-1.8 (m, 7 H), 2.4-2.7 (m, 2 H), 3.67 (t, *J* = 6.0 Hz, 2 H), 4.25-4.35 (m, 1 H), 7.35-7.45 (m, 6 H), 7.6-7.7 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14,68, 18,75, 21.22, 26.41 (3 C), 31.69, 34.75, 35.45, 36.88, 63.05, 78.15, 127.17 (4 C), 129.13 (2 C), 133.46 (2 C), 135.08 (4 C), 179.13; HRMS calcd. for $C_{25}H_{35}O_3Si$ $[M+H]^+$: 411.2350, found: 411.2354.



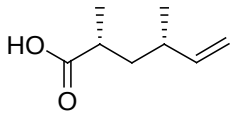
(2*R*,4*S*)-2,4-Dimethyl-5-hexen-1-ol

To a solution of 1.1 mL (13 mmol) of oxalyl chloride in 20 mL of CH_2Cl_2 was added dropwise a solution of 1.4 mL (20 mmol) of DMSO in 5 mL of CH_2Cl_2 at –78 °C. After stirring for 15 min at –78 °C, 2.5 g (10 mmol) of (*2R,4S*)-5-*tert*-butyldimethylsilyloxy-2,4-dimethyl-1-pentanol[g] in 10 mL of CH_2Cl_2 was added. After stirring at –78 °C for 1 h, 3.5 mL (25 mmol) of Et_3N was added at –78 °C. Then the reaction mixture stirred at 23 °C for 3 h and quenched with 30 mL of water, extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 95/5 hexanes-EtOAc) afforded 2.0 g (89%) of the desired aldehyde as a colorless oil.

To a solution of 7.1 g (20 mmol) of methyl triphenyl phosphonium bromide in 40 mL of THF under argon was added 8 mL (20 mmol) of 2.5 M n-BuLi solution in hexanes at 0 °C. After stirring at 0 °C for 30 min, the above aldehyde in 10 mL of THF was added. The reaction mixture was warmed to at 23 °C over 3 h then quenched with saturated aqueous NH_4Cl, extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated. The residue mixture was filtered on a plug of silica gel (5 cm), washed with ether, and concentrated to afford the crude alkenes product.

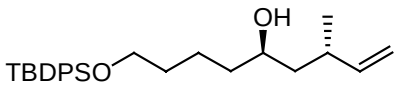
To a solution of the crude alkenes in 10 mL of THF was added 6 mL (6 mmol) of 1.0 M solution of TBAF in THF. After stirring for 3 h at 23 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl, extracted with ether, washed with brine, dried

over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 67/33 hexanes-EtOAc) afforded 360 mg (84%, 2 steps) of the desired alcohol[h] as a colorless oil; $[\alpha]_D^{23}$ = +35.7 (*c*, 2.0, $CHCl_3$);[h] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (d, *J* = 6.9 Hz, 3 H), 1.00 (d, *J* = 7.2 Hz, 3 H), 1.0-1.1 (m, 1 H), 1.3-1.45 (m, 1 H), 1.5-1.7 (m, 1 H), 2.2-2.3 (m, 1 H), 3.2-3.45 (m, 3 H), 4.85-5.0 (m, 2 H), 5.61 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.19, 21.30, 33.15, 35.34, 40.20, 68.10, 112.65, 144.21.



(2*R*,4*S*)-2,4-Dimethyl-5-hexenoic acid (2)

To a solution of 350 mg (2.7 mmol) of (*2R,4S*)-2,4-dimethyl-5-hexen-1-ol in 10 mL of DMF was added 4.1 g (10.8 mmol) of pyridinium dichromate at 0 °C. After stirring overnight at 23 °C, the reaction mixture was quenched with 2 mL of saturated aqueous $Na_2S_2O_3$ and 20 mL of brine, extracted with EtOAc, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 80/20 hexanes-EtOAc) afforded 301 mg (77%) of the desired acid[h] as a colorless oil; $[\alpha]_D^{23}$ = –6.2 (*c*, 1.1, $CHCl_3$);[h] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 (d, *J* = 6.6 Hz, 3 H), 1.16 (d, *J* = 6.3 Hz, 3 H), 1.3-1.45 (m, 1 H), 1.7-1.85 (m, 1 H), 2.15-2.3 (m, 1 H), 2.45-2.55 (m, 1 H), 4.9-5.05 (m, 2 H), 5.55-5.7 (m, 1 H), 11.3-11.7 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.61, 20.57, 35.79, 37.22, 39.92, 113.55, 143.37, 183.74.

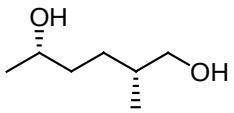


(3*S*,5*R*)-9-*tert*-Butyldiphenylsilyloxy-3-methyl-1-nonen-5-ol (3)

To a solution of 718 mg (1.75 mmol) of (*2S,4R*)-4-[4'-(*tert*-butyldiphenylsiloxy)butyl]-2-methyl-γ-butylrolactone in 20 mL of CH_2Cl_2 under argon was added dropwise 3.5 mL (3.5 mmol) of 1.0 M solution of

DIBAL-H in CH_2Cl_2 at –78 ^oC. After stirring for 30 min at –78 ^oC, the reaction mixture was quenched with 10 mL of MeOH. The resultant mixture was allowed to warm to 23 ^oC over 1 h until a white precipitate appeared. The residue was filtered on a pad of celite, washed with ether, and concentrated to give the crude lactol, which was directly used in the next step.

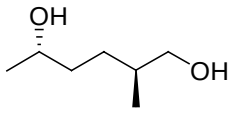
To a solution of 2.8 g (8 mmol) of methyl triphenyl phosphonium bromide in 30 mL of THF under argon was added 3.2 mL (8 mmol) of 2.5 M solution of n-BuLi in hexanes at 0 ^oC. After stirring at 0 ^oC for 30 min, the crude lactol in 10 mL of THF was added. After stirring further 3 h at 23 ^oC, the reaction mixture was quenched with saturated aqueous NH_4Cl, extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 80/20 hexanes-EtOAc) gave 524 mg (73%) of alcohol as a colorless oil; $[\alpha]_D^{23}$ = –2.8 (*c*, 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.07 (d, *J* = 6.9 Hz, 3 H), 1.12 (s, 9 H), 1.4-1.7 (m, 8 H), 2.3-2.5 (m, 1 H), 3.6-3.7 (m, 1 H), 3.73 (t, *J* = 6.6 Hz, 2 H), 4.95-5.1 (m, 2 H), 5.73 (ddd, *J* = 17.1, 10.2, 8.4 Hz, 1 H), 7.35-7.5 (m, 6 H), 7.7-7.8 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.14, 21.16, 21.81, 26.83 (3 C), 32.45, 34.67, 37.56, 44.15, 63.72, 69.53, 113.36, 127.53 (4 C), 129.44 (2 C), 133.96 (2 C), 135.51 (4 C), 144.10; HRMS calcd. for $C_{26}H_{39}O_2Si$ $[M+H]^+$: 411.2714, found: 411.2709.



(2*R*,5*S*)-2-Methyl-1,5-hexanediol (17a).

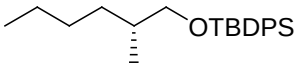
The title compound was prepared according Representative Procedure D except that 200 mg (2 mmol) of (*S*)-(+)-hexen-2-ol (>98% *ee*, commercial available from Aldrich) and 67 mg (0.1 mmol) of (–)-$(NMI)_2ZrCl_2$ was used to afford 206 mg (78%) of the desired product **17a** (dr = 7.7/1, by ^{13}C NMR); ^1H NMR (300 MHz, $CDCl_3$) δ 0.81 (d, *J* = 6.3 Hz, 3 H), 1.11 (d, *J* = 6.3 Hz, 3 H), 1.15-1.6 (m, 5 H), 3.25-3.4 (m, 4 H), 3.65-3.75 (m, 1 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 16.33 (16.67), 23.21, 28.52 (29.02), 34.97, 35.62 (36.29), 67.26, 67.40, (68.05).



(2*S*,5*S*)-2-Methyl-1,5-hexanediol (17b).

The title compound was prepared according Representative Procedure D except that 200 mg (2 mmol) of (*S*)-(+)-hexen-2-ol (>98% *ee*, commercial available from Aldrich) and 67 mg (0.1 mmol) of (+)-$(NMI)_2ZrCl_2$ was used to afford 208 mg (79%) of the desired product **17b** (dr = 4.5/1, by ^{13}C NMR); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (d, *J* = 6.6 Hz, 3 H), 1.11 (d, *J* = 6.3 Hz, 3 H), 1.0-1.6 (m, 5 H), 3.3-3.4 (m, 2 H), 3.5-3.9 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.67 (16.36), 23.27, 29.02 (28.55), 35.56 (35.00), 36.32, 67.14, 68.05 (67.43).



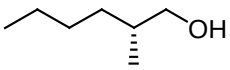
(2*R*)-1-*tert*-Butyldiphenylsilyloxy-2-methyl-hexane

To a solution of 530 mg (4.0 mmol) of (*2R,5S*)-2-methyl-1,5-hexanediol and 408 mg (6.0 mmol) of imidazole in 20 mL of DMF was added dropwise 1.0 mL (4.0 mmol) of TBDPSCl. After stirring for 3 h at 23 ^{o}C, the reaction mixture was quenched with 20 mL of H_2O, extracted with ether, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 80/20 hexanes-EtOAc) afforded 1.3 g (91%) of the desired secondary alcohol as a colorless oil.

To a solution of 1.2 g (3.2 mmol) of the alcohol prepared above, 40 mg (0.3 mmol) of DMAP (4-dimethylaminopyridine), and 0.9 mL (6 mmol) of Et_3N in 10 mL of CH_2Cl_2 was added 0.4 mL (5 mmol) of MsCl at 0 ^{o}C. After stirring at 23 ^{o}C for 3 h, the reaction mixture was quenched with water, extracted with ether, dried over $MgSO_4$, filtered on a plug of silica gel (3 cm), washed with ether, and concentrated to afford the crude

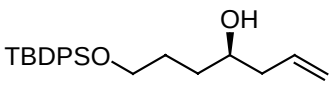
mesylate.

To a solution of the mesylate prepared above in 30 mL of dry ether was added 400 mg (10.5 mmol) of lithium aluminium hydride at 0 ^{o}C. After stirring overnight at 23 ^{o}C, the reaction mixture was quenched with 2 mL of water, then acidified with 5% HCl, extracted with ether, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 97/3 hexanes-EtOAc) afforded 259 mg (70%) of the desired product as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.9-1.1 (m, 6 H), 1.18 (s, 9 H), 1.3-1.8 (m, 7 H), 3.5-3.7 (m, 2 H), 7.45-7.55 (m, 6 H), 7.75-8.05 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.12, 16.95, 19.34, 22.99, 26.89 (3 C), 29.22, 32.84, 35.70, 68.94, 127.56 (4 C), 129.47 (2 C), 134.13 (2 C), 135.65(4 C).



(2*R*)-2-Methyl-1-hexanol

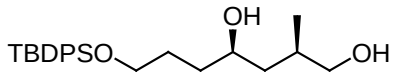
To a solution of 555 mg (1.5 mmol) of (*2R*)-1-*tert*-butyldiphenylsilyloxy-2-methyl-hexane in 3 mL of THF was added 2 mL (2 mmol) of 1.0 M solution of TBAF in THF. After stirring at 23 ^{o}C for 3 h, the reaction mixture was quenched with saturated aqueous NH_4Cl, extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 70/30 hexanes-EtOAc) afforded 134 mg (78%) of the desired alcohol[i] as a colorless oil; optical purity by Mosher ester analysis, 77% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.8-0.95 (m, 6 H), 1.0-1.6 (m, 7 H), 2.65-3.05 (m, 1 H), 3.25-3.5 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.95, 16.47, 22.90, 29.14, 32.81, 35.59, 67.99.



(4*R*)-7-*tert*-Butyldiphenylsilyloxy-1-hepten-4-ol (15)

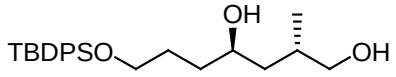
The title compound was prepared according to Representative Procedure C except that

2.5 g (7.5 mmol) of 4-*tert*-butyldiphenylsilyloxy-1-butanal was used to afford 2.3 g (83%) of desired product (**15**); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (s, 9 H), 1.45-1.65 (m, 4 H), 2.05-2.25 (m, 3 H), 3.6-3.65 (m, 3 H), 5.0-5.1 (m, 2 H), 5.7-5.85 (m, 1 H), 7.3-7.4 (m, 6 H), 7.55-7.65 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.06, 26.75 (3 C), 28.66, 33.37, 41.82, 63.97, 70.38, 117.59, 127.53 (4 C), 129.50 (2 C), 133.57 (2 C), 134.89, 135.45 (4 C); MS (CI): 369 (1.5), 351 (3.4), 327 (5.0), 179 (100).



(2*R*,4*R*)-7-*tert*-Butyldiphenylsilyloxy-2-methyl-1,4-heptanediol (18a).

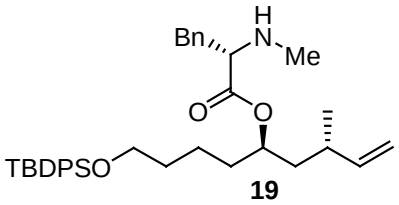
The title compound was prepared according Representative Procedure D except that 1.8 g (5 mmol) of **15** and 168 mg (0.25 mmol) of (–)-$(NMI)_2ZrCl_2$ was used to afford 1.3 g (67%) of **18a** (dr = 5.5/1, by ^{13}C NMR); the product was further purified by column chromatography (silica gel, 85/15 hexanes-EtOAc) to give 782 mg (40%) of **18a** (dr = 40/1, by ^{13}C NMR); $[\alpha]_D^{23}$ = +1.2 (*c*, 1.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (d, *J* = 6.9 Hz, 3 H), 1.09 (s, 9 H), 1.5-2.0 (m, 7 H), 3.45-3.6 (m, 2 H), 3.73 (t, *J* = 5.7 Hz, 2 H), 3.8-3.95 (m, 2 H), 7.35-7.5 (m, 6 H), 7.65-7.75 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.37, 19.09, 26.75 (3 C), 29.02, 32.14, 34.61, 41.88, 64.31, 67.82, 68.75, 127.64 (4 C), 129.64 (2 C), 133.43 (2 C), 135.51 (4 C); HRMS (ESI) calcd. for $C_{24}H_{36}NaO_3Si$ $[M+Na]^+$: 423.2326, found: 423.2335.



(2*S*,4*R*)-7-*tert*-Butyldiphenylsilyloxy-2-methyl-1,4-heptanediol (18b).

The title compound was prepared according Representative Procedure D except that 1.8 g (5 mmol) of **15** and 168 mg (0.25 mmol) of (–)-$(NMI)_2ZrCl_2$ was used to afford 1.4 g (69%) of **18b** (dr = 3.5/1, by ^{13}C NMR); the product was further purified by column chromatography (silica gel, 85/15 hexanes-EtOAc) to give 700 mg (35%) of **18b** (dr = 40/1, by ^{13}C NMR); $[\alpha]_D^{23}$ = –6.9 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (d,

J = 6.9 Hz, 3 H), 1.03 (s, 9 H), 1.4-1.9 (m, 7 H), 3.38 (dd, *J* = 7.5 Hz, 1 H), 3.3-3.4 (m, 1 H), 3.56 (dd, *J* = 7.5 Hz, 1 H), 3.68 (t, *J* = 5.4 Hz, 2 H), 3.7-3.8 (m, 1 H), 7.3-7.45 (m, 6 H), 7.4-7.5 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.21, 19.09, 26.78 (3 C), 28.85, 34.81, 35.68, 43.42, 64.34, 68.80, 70.74, 127.67 (4 C), 129.67 (2 C), 133.40 (2 C), 135.51 (4 C).

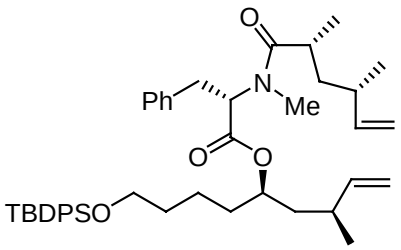


19

Compound 19

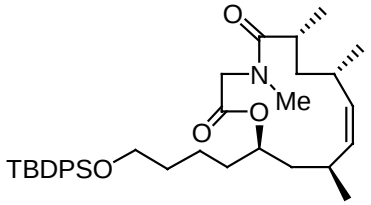
To a solution of 420 mg (1.5 mmol) of (*S*)-*N*-Boc-methylphenylalanine, 411 mg (1.0 mmol) of **3** and 24 mg (0.2 mmol) of DMAP (4-dimethylaminopyridine) in 5 mL of CH_2Cl_2 was added a solution of 4.2 g (2.0 mmol) of DCC in 5 mL of CH_2Cl_2. After stirring overnight, the reaction mixture was filtered on a pad of celite, washed with ether. The residue was concentrated and purified by column chromatography (silica gel, 95/5 hexanes-EtOAc) to give 597 mg (89%) of the coupled product as a colorless oil.

To a solution of 503 mg (0.75 mmol) of the above amide in 2 mL of dry CH_2Cl_2 under argon was added 0.6 mL (7.5 mmol) of CF_3CO_2H at 0 ^{o}C. After stirring for 3 h at 23 ^{o}C, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, extracted with EtOAc, washed with brine, dried over Na_2SO_4, and concentrated. Purification by column chromatography (silica gel, 60/40 hexanes-EtOAc) gave 590 mg of the desired product[h] (87%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (d, *J* = 6.6 Hz, 3 H), 1.18 (s, 9 H), 1.2-1.8 (m, 8 H), 2.2-2.3 (m, 1 H), 2.48 (s, 3 H), 3.0-3.15 (m, 2 H), 3.5-3.6 (m, 1 H), 3.7-3.8 (m, 2 H), 5.0-5.25 (m, 3 H), 5.75-5.9 (m, 1 H), 7.25-7.35 (m, 5 H), 7.45-7.55 (m, 6 H), 7.75-7.85 (m, 4 H).



Compound 21

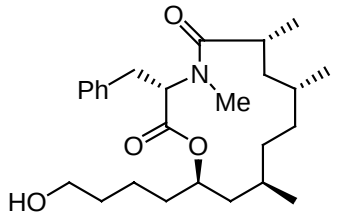
To a solution of 372 mg (0.65 mmol) of **19** and 128 mg (0.90 mmol) of **2** in 5 mL of CH_2Cl_2 was added 45 mg (0.30 mmol) of HOBt (1-hydroxybenzotriazole), 550 mg (3.0 mmol) of EDCI (*N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide). After stirring 24 h at 23 ^oC, the reaction was quenched with 1 N HCl, extracted with ether, washed with brine, dried over Na_2SO_4, and concentrated. Purification by column chromatography (silica gel, 95/5 hexanes-EtOAc) afforded 384 mg (85%) of diene (**21**) as a colorless oil; $[\alpha]_D^{23}$ = –18.4 (*c*, 1.0, $CHCl_3$);[h] ^1H NMR (300 MHz, $CDCl_3$) δ 0.54 (d, *J* = 6.6 Hz, 0.6 H), 0.68 (d, *J* = 6.6 Hz, 2.4 H), 0.8-1.0 (m, 16 H), 1.1-1.65 (m, 9 H), 1.7-1.9 (m, 1 H), 2.0-2.2 (m, 1 H), 2.4-2.55 (m, 1 H), 2.72 (s, 2.4 H), 2.73 (s, 0.6 H), 2.8-3.0 (m, 1 H), 3.1-3.35 (m, 1 H), 3.5-3.6 (m, 2 H), 4.5-4.55 (m, 0.2 H), 4.7-4.95 (m, 5 H), 5.3-5.7 (m, 2.8 H), 7.0-7.2 (m, 5 H), 7.25-7.4 (m, 6 H), 7.58 (dd, *J* = 13.5, 4.5 Hz, 4 H).



Compound 22

To a solution of 200 mg (0.29 mmol) of **21** in 500 mL of dry CH_2Cl_2 under argon was added 25 mg (0.028 mmol) of 2nd generation Grubbs catalyst. After stirring overnight at reflux, 13 mg (0.014 mmol) of 2nd generation Grubbs catalyst was added. After stirring further 8 h at reflux, the reaction mixture was concentrated and purified by column chromatography (silica gel, 90/10 hexanes-EtOAc) to afford 174 mg (92%) of **22** as a

colorless oil; $[\alpha]_D^{23} = -89.2$ (*c*, 1.0, $CHCl_3$);[h] ^1H NMR (300 MHz, $CDCl_3$) δ 0.7-0.8 (m, 1 H), 1.00 (t, *J* = 6.3 Hz, 6 H), 1.06 (s, 9 H), 1.10 (d, *J* = 7.2 Hz, 3 H), 1.25-1.8 (m, 8 H), 1.90 (t, *J* = 12.6 Hz, 1 H), 2.05-2.2 (m, 1 H), 2.4-2.55 (m, 1 H), 2.61 (s, 3 H), 3.33 (dd, *J* = 12.3, 3.0 Hz, 1 H), 3.49 (t, *J* = 12.0 Hz, 1 H), 3.57 (dd, *J* = 10.8, 3.9 Hz, 1 H), 3.66 (t, *J* = 6.3 Hz, 1 H), 5.0-5.25 (m, 3 H), 7.1-7.3 (m, 5 H), 7.35-7.45 (m, 6 H), 7.6-7.7 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.50, 19.11, 19.31, 19.84, 21.44, 26.78 (3 C), 30.09, 32.34, 33.57, 34.36, 35.06, 39.27, 43.00, 44.07, 63.41, 66.78, 73.07, 126.38, 127.50 (4 C), 128.29, 129.33, 129.44, 133.82, 135.39 (4 C), 135.53, 135.95, 138.54, 169.90, 176.44.

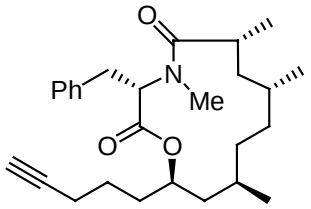


Compund 23

To a solution of 170 mg (0.26 mmol) of **22** in 5 mL of THF was added 0.75 mL (0.75 mmol) of 1.0 M solution of TBAF in THF. After stirring for 3 h at 23 ^oC, the reaction mixture was quenched with saturated aqueous NH_4Cl, extracted with ether, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 70/30 hexanes-EtOAc) afforded 106 mg (95%) of the corresponding alcohol as a white solid.

To a solution of 105 mg (0.24 mmol) of the macrocyclic olefin prepared above and 80 mg (0.03 mmol) of 5% Pd/C in 8 mL of EtOAc was bubbled with H_2 overnight. The mixture was filtered on a plug of silica gel (5 cm), washed with EtOAc, and concentrated to give 99 mg (94%) of the title compound as a colorless oil; $[\alpha]_D^{23} = -175.6$ (*c*, 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.66 (ddd, *J* = 13.5, 11.1, 3.0 Hz, 1 H), 0.82 (d, *J* = 6.3 Hz, 6 H), 1.04 (d, *J* = 7.2 Hz, 3 H), 1.1-1.7 (m, 16 H), 1.91 (t, *J* = 12.6 Hz, 1 H), 2.57 (s, 3 H), 2.65-2.8 (m, 1 H), 3.22 (dd, *J* = 12.9, 3.6 Hz, 1 H), 3.42 (t, *J* = 13.5 Hz, 1 H), 3.51 (dd, *J* = 11.4, 7.2 Hz, 1 H), 3.58 (t, *J* = 6.9 Hz, 2 H), 5.05-5.1 (m, 1 H), 7.05-7.25 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.72, 21.33, 21.64, 22.23, 24.00, 27.20, 31.38, 32.25, 32.53,

33.26, 34.33, 35.54, 36.94, 39.10, 39.58, 62.60, 66.84, 73.15, 126.41, 128.35 (2 C), 129.39 (2 C), 138.68, 170.15, 176.80; MS (EI): 432 (4.3), 431 (9.2), 296 (6.7), 284 (7.4), 134 (55); HRMS calcd. for $C_{26}H_{41}NO_4$ $[M]^+$: 431.3036, 431.3001.



(-)-spongidepsin (1)

To a solution of 45.1 mg (0.1 mmol) of **23** in 3 mL of CH_2Cl_2 was added 85 mg (0.2 mmol) of Dess-Martin periodinane at 0 °C. After stirring for 1 h at 23 °C, the reaction mixture was quenched with 0.3 mL of saturated aqueous Na_2SO_3 and 0.3 mL of saturated aqueous $NaHCO_3$. After stirring for 30 min at 23 °C, the resultant mixture was filtered on a plug of silica gel (5 cm), washed with ether, and concentrated to give the crude aldehyde, which was directly used in the next step.

To a solution of the aldehyde prepared above and 110 mg (0.5 mmol) of Ohira-Bestmann's reagent[j] in 10 mL of MeOH was added 56 mg (0.45 mmol) of K_2CO_3 under argon. After stirring for 2 h at 35 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl, extracted with ether, dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, 95/5 hexanes-EtOAc) gave 35.2 mg (79%, 2 steps) of (–)-spongidepsin (**1**) as a crystalline solid; $[\alpha]_D^{23}$ = –211.8 (*c*, 1.0, CH_3OH); $[\alpha]_D^{23}$ = –203.2 (*c*, 0.4, CH_3OH)[h]; ^1H NMR (300 MHz, $CDCl_3$) δ 0.7-0.85 (ddd, *J* = 13.5, 11.2, 3.0 Hz, 1 H), 0.89 (d, *J* = 6.0 Hz, 3 H), 0.92 (d, *J* = 6.3 Hz, 3 H), 1.07 (d, *J* = 6.9 Hz, 3 H), 1.2-1.8 (m, 10 H), 1.91 (t, *J* = 12.6 Hz, 1 H), 2.2-2.3 (m, 3 H), 2.71 (s, 3 H), 2.85-3.0 (m, 1 H), 3.24 (dd, *J* = 14.1, 5.1 Hz, 1 H), 3.40 (dd, *J* = 14.1, 11.1 Hz, 1 H), 3.98 (dd, *J* = 11.1, 4.5 Hz, 1 H), 5.1-5.25 (m, 1 H), 7.15-7.35 (m, 5 H); ^{13}C NMR (75 MHz, CD_3OD) δ 18.93 (2 C), 21.63, 22.47, 25.19, 25.47, 28.31, 32.49, 33.36, 34.46, 35.27, 35.75, 37.97, 40.30, 40.38, 67.56, 69.97, 73.90, 84.63, 127.66, 129.49 (2 C),

130.55 (2 C), 139.51, 171.82, 179.35; MS (CI): 427 (23), 426 (79), 275 (11), 180 (100); HRMS calcd. for $C_{27}H_{39}NO_3$ $[M+H]^+$: 426.3003, found: 426.3009.

References:

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INDEX	FREQUENCY	PPM	HEIGHT
1	2332.445	7.776	47.0
2	2330.687	7.770	54.8
3	2328.930	7.764	31.0
4	2325.415	7.752	46.4
5	2323.071	7.745	48.3
6	2244.567	7.483	23.7
7	2239.294	7.465	90.6
8	2232.850	7.444	48.3
9	2226.405	7.422	18.2
10	1133.199	3.778	22.7
11	1126.754	3.756	45.3
12	1120.310	3.735	23.7
13	1102.148	3.674	17.5
14	1095.704	3.653	32.7
15	1089.260	3.631	18.6
16	501.061	1.670	20.5
17	494.030	1.647	19.7
18	488.758	1.629	17.0
19	482.313	1.608	19.1
20	475.283	1.584	19.2
21	453.606	1.512	17.2
22	447.162	1.491	16.4
23	350.496	1.168	39.7
24	342.880	1.143	386.6
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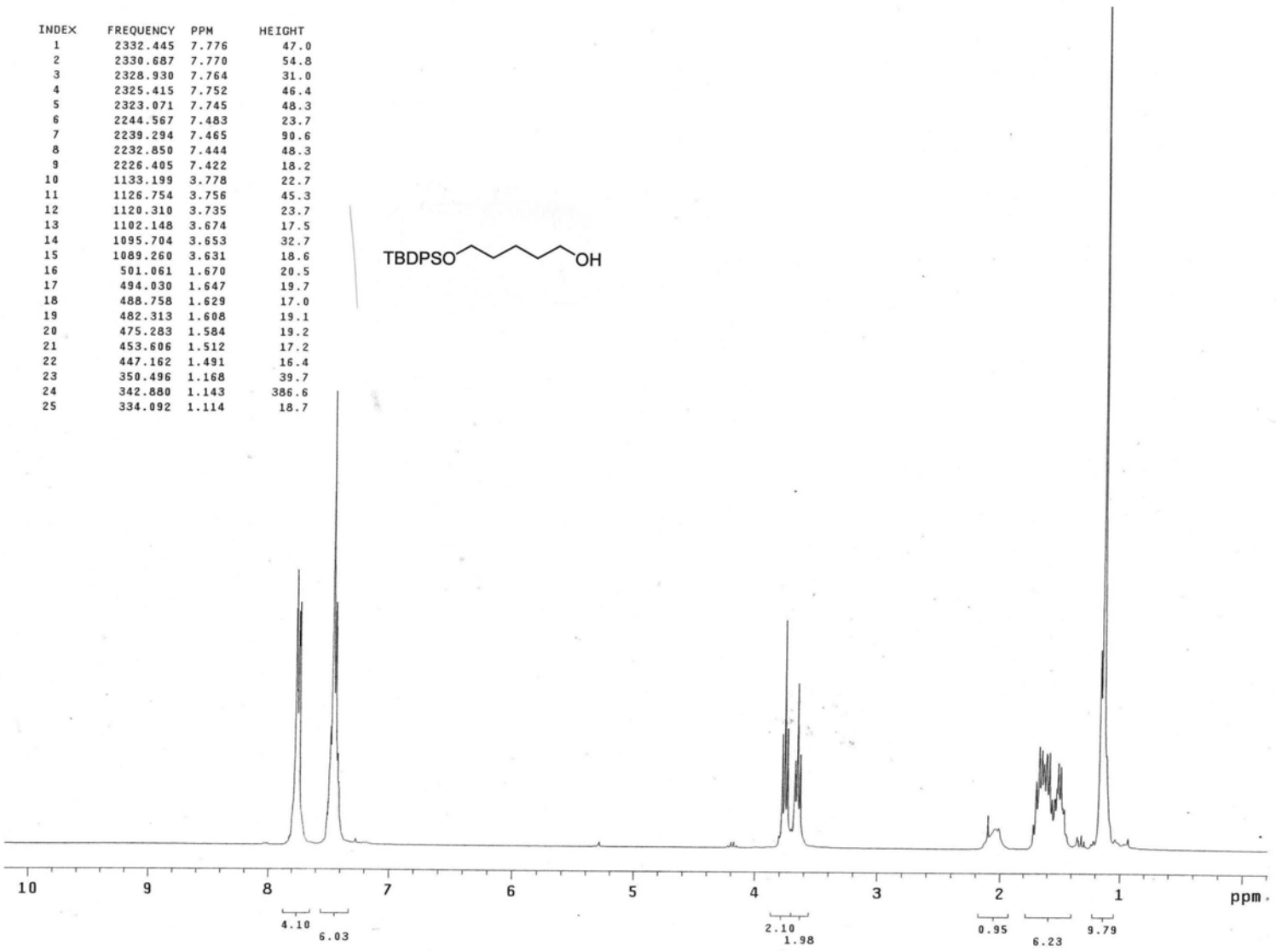

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4	9616.995	127.504	87.2
5	5839.486	77.421	6.9
6	5807.724	77.000	6.3
7	5773.845	76.551	6.3
8	4804.058	63.693	19.2
9	4723.596	62.626	17.2
10	2434.645	32.279	22.3
11	2426.175	32.167	22.6
12	2019.627	26.777	66.3
13	1649.076	21.864	19.5
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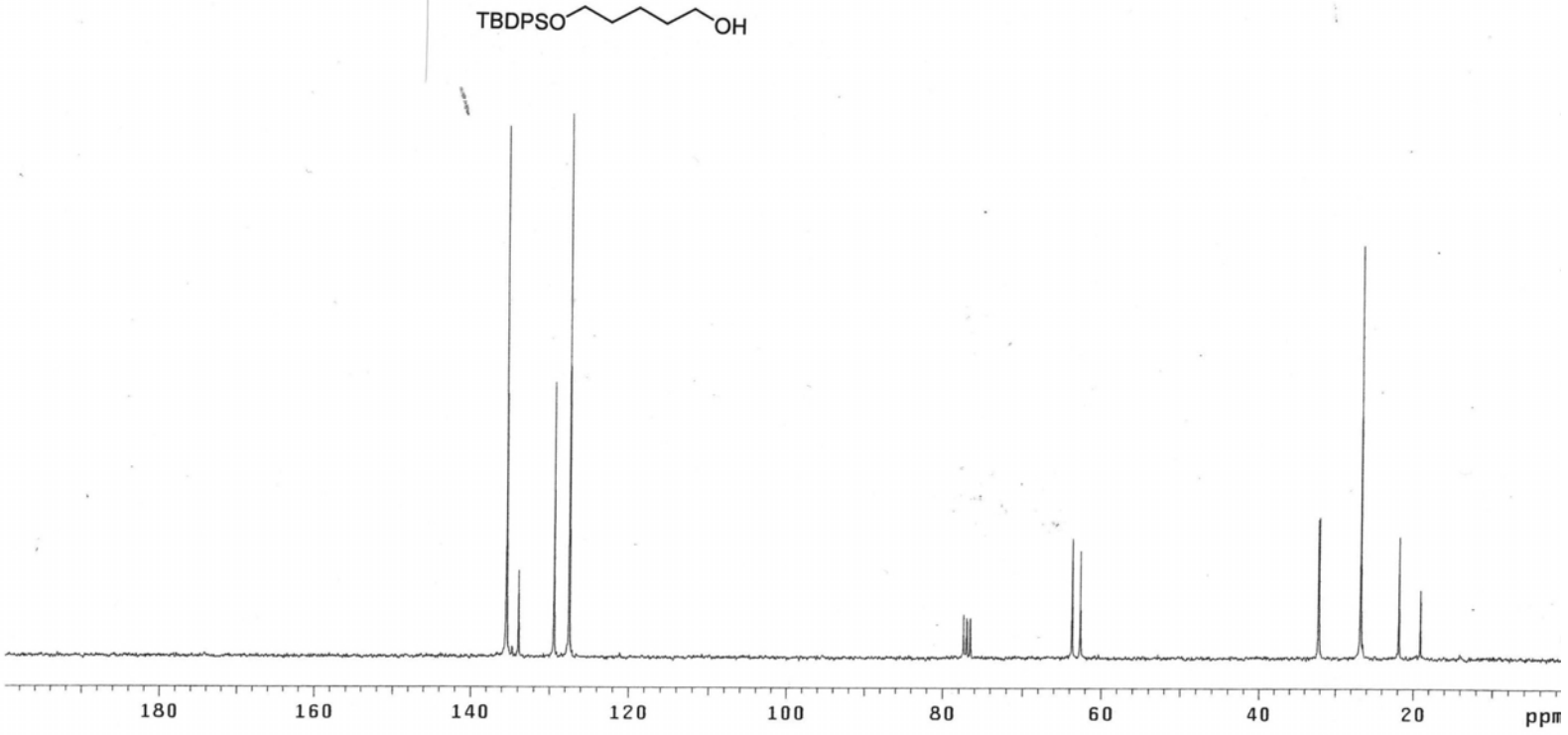

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4	2356.805	7.857	30.3
5	2354.462	7.849	35.8
6	2264.826	7.550	58.6
7	2258.967	7.531	34.6
8	1162.246	3.875	21.1
9	1135.882	3.787	21.0
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11	547.097	1.824	27.7
12	544.168	1.814	27.9
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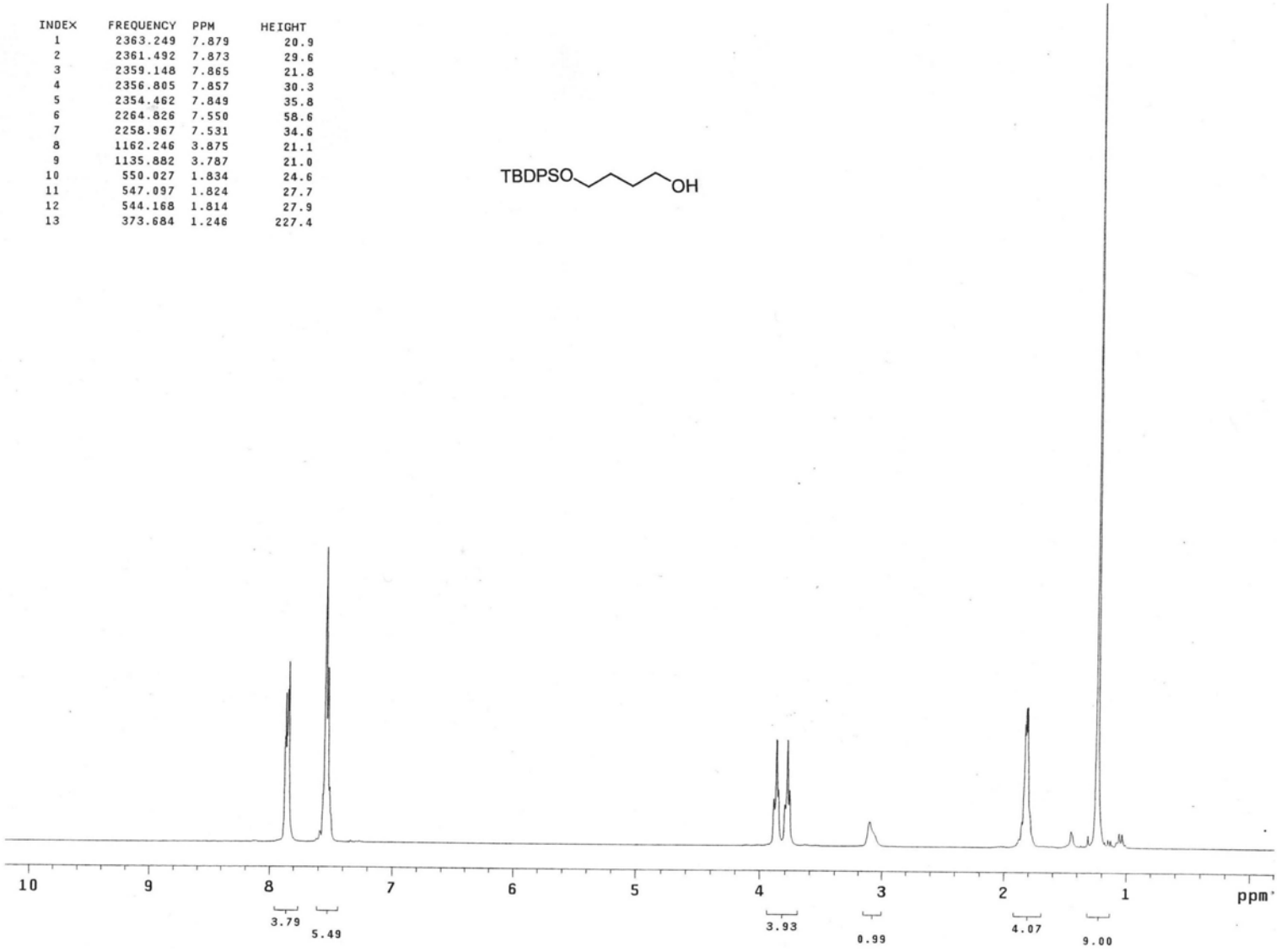

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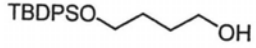
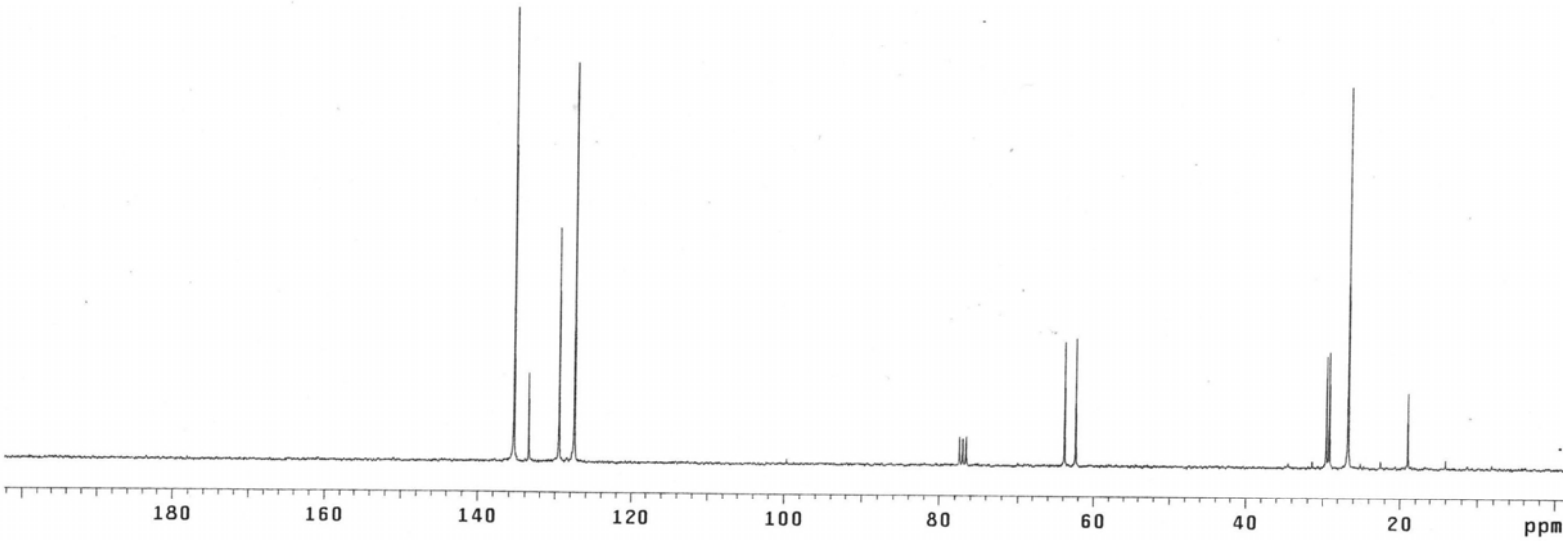
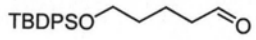
7	5775.963	76.579	4.5
8	4816.763	63.862	19.9
9	4704.539	62.374	20.5
10	2222.902	29.472	18.0
11	2195.375	29.107	18.6
12	2015.393	26.720	61.3
13	1435.215	19.028	12.2

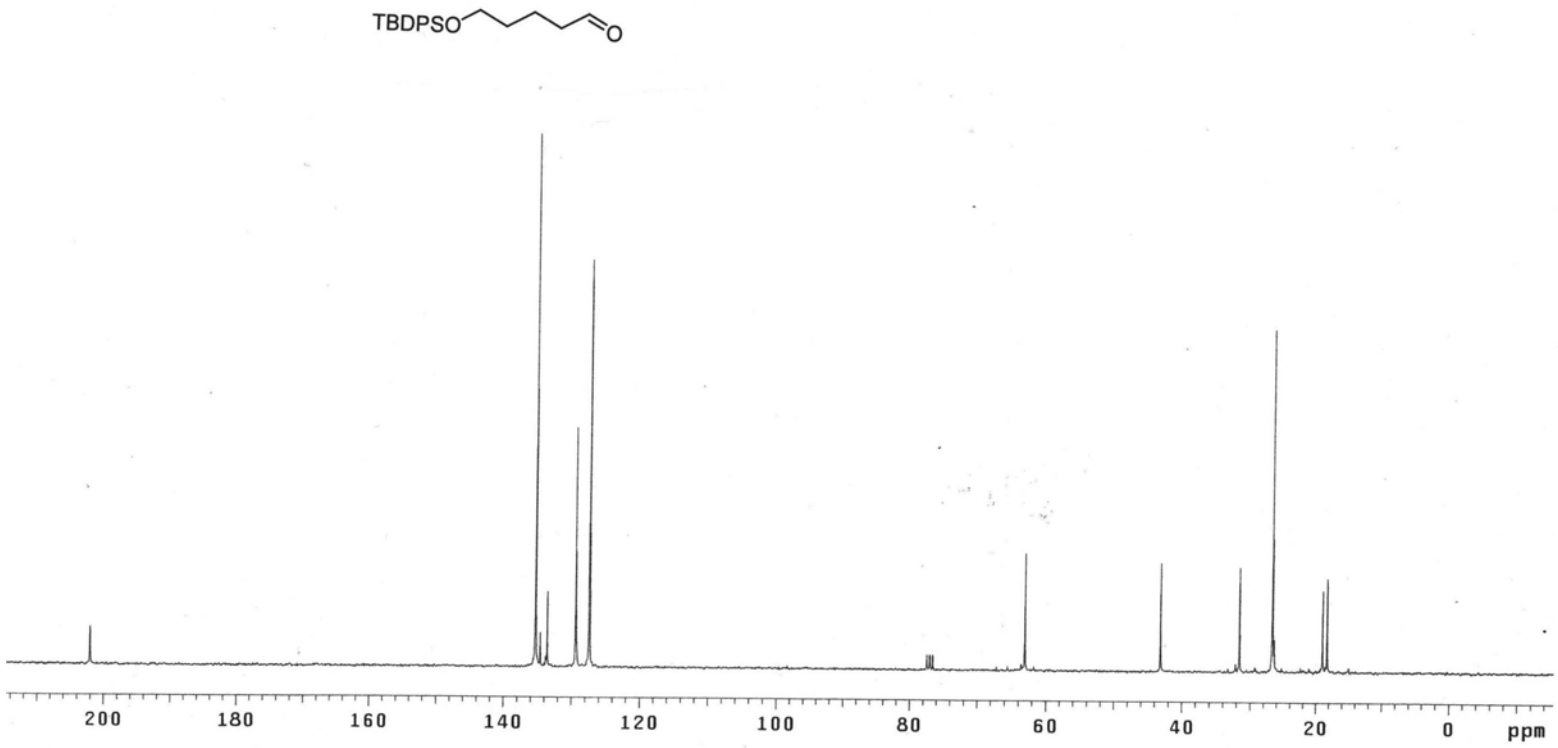




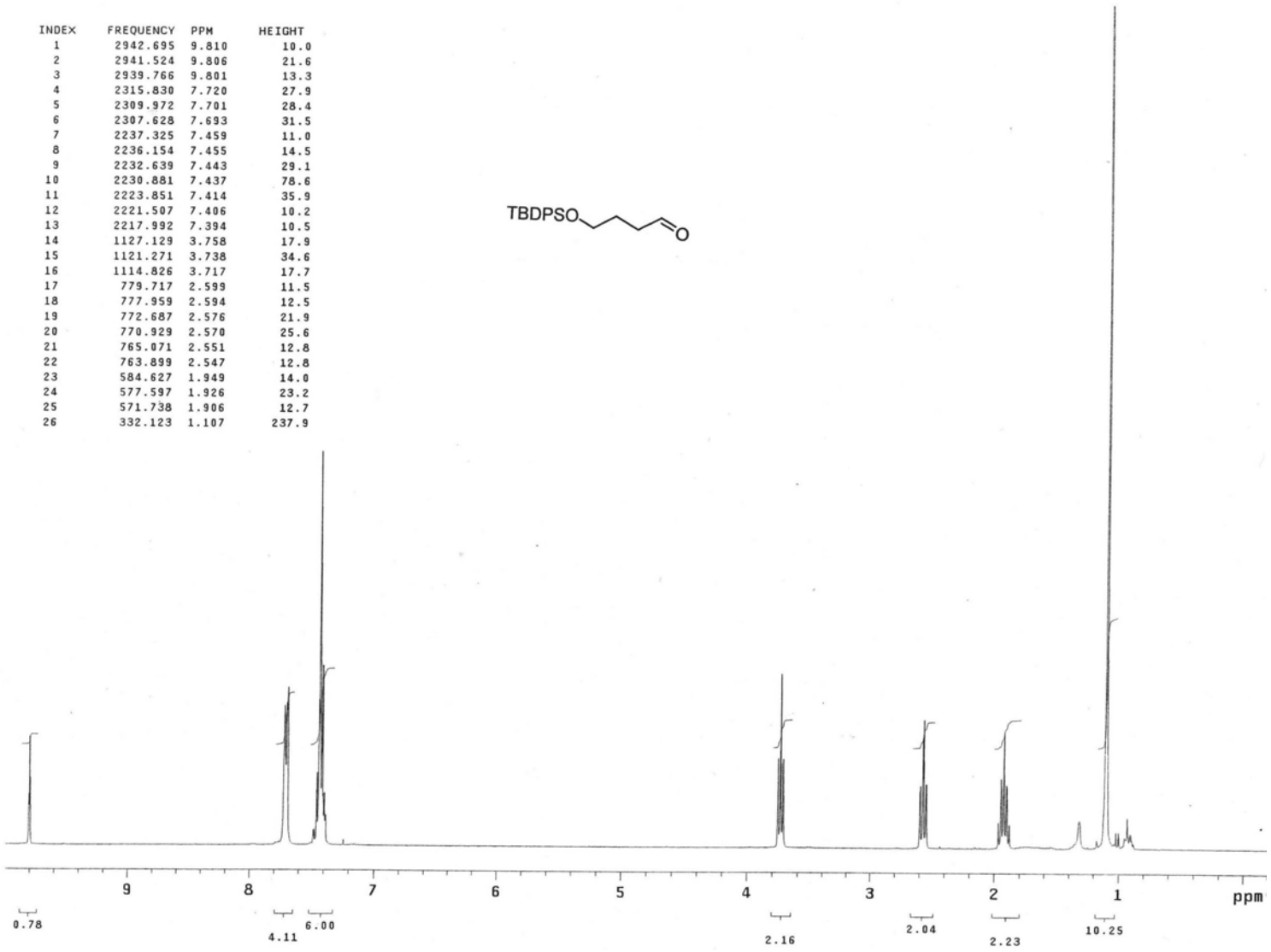
INDEX	FREQUENCY	PPM	HEIGHT
1	2952.034	9.841	12.7
2	2366.764	7.890	35.7
3	2364.421	7.882	35.8
4	2362.078	7.875	35.6
5	2359.734	7.867	36.4
6	2267.755	7.560	71.1
7	2266.583	7.556	71.5
8	2261.896	7.541	43.9
9	2256.038	7.521	17.7
10	2253.694	7.513	11.0
11	1167.518	3.892	15.4
12	1161.074	3.871	28.5
13	1155.215	3.851	14.8
14	762.106	2.541	9.8
15	755.662	2.519	19.9
16	748.632	2.496	11.3
17	576.976	1.924	11.2
18	569.946	1.900	15.6
19	561.744	1.873	14.2
20	534.209	1.781	15.3
21	528.936	1.763	13.6
22	526.007	1.754	14.7
23	520.148	1.734	10.5
24	381.886	1.273	200.0



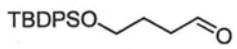
INDEX	FREQUENCY	PPM	HEIGHT
1	15243.030	202.095	6.2
2	10205.644	135.309	86.5
3	10074.363	133.568	12.2
4	9760.982	129.413	38.8
5	9612.762	127.448	66.1
6	4755.358	63.048	19.0
7	3256.212	43.172	17.6
8	2381.710	31.577	16.9
9	2011.158	26.664	55.4
10	1430.980	18.972	13.2
11	1380.162	18.298	15.2

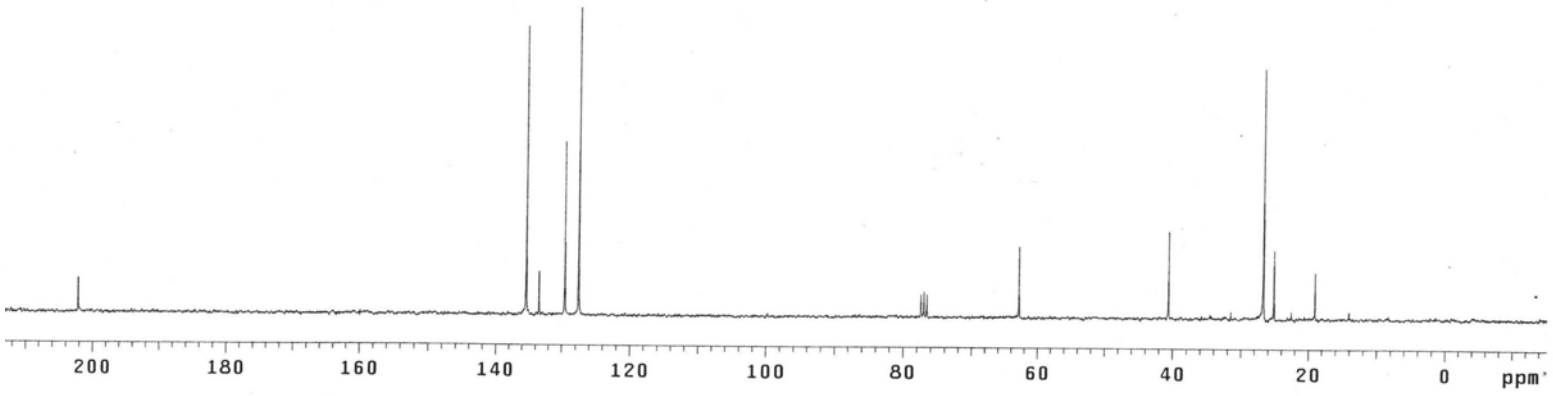


INDEX	FREQUENCY	PPM	HEIGHT
1	2942.695	9.810	10.0
2	2941.524	9.806	21.6
3	2939.766	9.801	13.3
4	2315.830	7.720	27.9
5	2309.972	7.701	28.4
6	2307.628	7.693	31.5
7	2237.325	7.459	11.0
8	2236.154	7.455	14.5
9	2232.639	7.443	29.1
10	2230.881	7.437	78.6
11	2223.851	7.414	35.9
12	2221.507	7.406	10.2
13	2217.992	7.394	10.5
14	1127.129	3.758	17.9
15	1121.271	3.738	34.6
16	1114.826	3.717	17.7
17	779.717	2.599	11.5
18	777.959	2.594	12.5
19	772.687	2.576	21.9
20	770.929	2.570	25.6
21	765.071	2.551	12.8
22	763.899	2.547	12.8
23	584.627	1.949	14.0
24	577.597	1.926	23.2
25	571.738	1.906	12.7
26	332.123	1.107	237.9

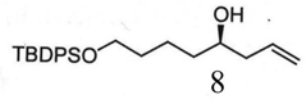


INDEX	FREQUENCY	PPM	HEIGHT
1	15251.499	202.208	5.6
2	10214.113	135.421	46.7
3	10065.892	133.456	7.1
4	9773.686	129.582	28.1
5	9623.348	127.588	49.8
6	5839.486	77.421	3.6
7	5807.724	77.000	4.1
8	5775.963	76.579	3.7
9	4736.300	62.795	11.5
10	3063.524	40.617	14.2
11	2015.392	26.720	40.5
12	1894.698	25.120	11.2
13	1437.332	19.056	7.5





INDEX	FREQUENCY	PPM	HEIGHT
1	2317.799	7.727	26.4
2	2316.041	7.721	24.2
3	2314.869	7.717	17.9
4	2312.526	7.709	24.1
5	2310.182	7.702	26.6
6	2236.951	7.457	12.0
7	2230.506	7.436	46.3
8	2223.476	7.413	25.9
9	1589.580	5.299	10.3
10	1556.186	5.188	10.5
11	1555.015	5.184	12.0
12	1543.298	5.145	12.3
13	1542.126	5.141	13.1
14	1120.310	3.735	9.4
15	1115.623	3.719	16.2
16	1113.866	3.713	16.8
17	1109.179	3.698	9.5
18	1108.007	3.694	9.7
19	488.172	1.627	8.3
20	454.192	1.514	9.5
21	448.334	1.495	15.1
22	446.576	1.489	14.2
23	444.819	1.483	13.9
24	329.405	1.098	133.3
25	327.648	1.092	165.4



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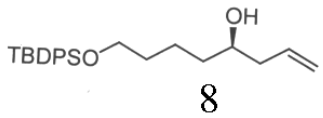
INDEX	FREQUENCY	PPM	HEIGHT
1	10222.582	135.533	70.8
2	10169.646	134.831	15.3
3	10108.240	134.017	11.3
4	9767.333	129.497	35.1
5	9621.230	127.560	69.3
6	8901.301	118.015	17.7
7	5839.485	77.421	9.8
8	5807.723	77.000	10.6
9	5775.962	76.579	11.5
10	5320.713	70.543	16.4
11	4808.293	63.749	16.0
12	3156.691	41.852	17.3
13	2748.025	36.434	14.6
14	2447.349	32.447	15.1
15	2023.861	26.833	48.8
16	1649.075	21.864	16.6
17	1445.801	19.169	10.6



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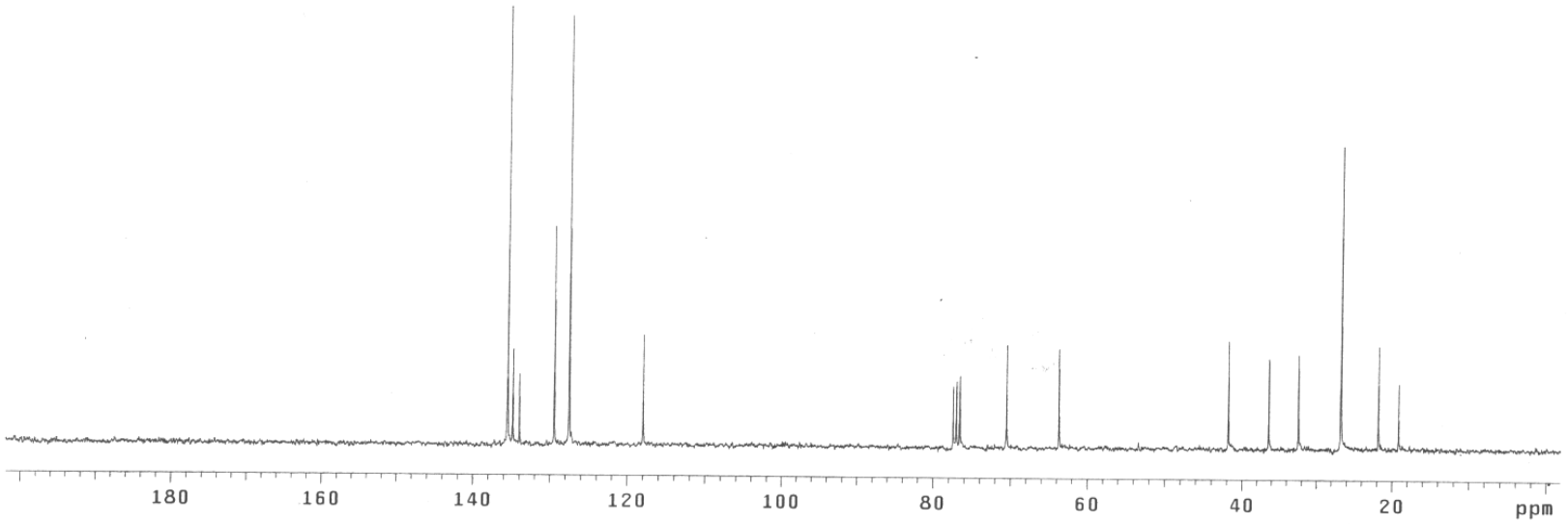
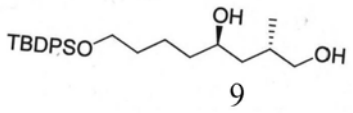


INDEX	FREQUENCY	PPM	HEIGHT
1	2310.182	7.702	34.5
2	2309.011	7.698	47.3
3	2307.253	7.692	27.2
4	2304.910	7.684	20.0
5	2303.152	7.678	48.3
6	2300.809	7.670	50.9
7	2231.092	7.438	22.4
8	2228.163	7.428	13.9
9	2226.991	7.424	27.9
10	2224.648	7.416	72.2
11	2222.890	7.411	56.5
12	2219.961	7.401	15.6
13	2217.031	7.391	48.3
14	2214.688	7.383	12.5
15	2211.173	7.372	14.1
16	2208.244	7.362	9.6
17	2180.708	7.270	9.1
18	1112.694	3.709	22.5
19	1106.249	3.688	46.5
20	1100.391	3.668	27.0
21	1079.886	3.600	10.6
22	1075.199	3.584	9.9
23	1069.341	3.565	14.5
24	1064.654	3.549	13.6
25	1020.129	3.401	11.3
26	1012.513	3.375	11.5
27	1009.583	3.366	9.2
28	478.798	1.596	11.2
29	477.627	1.592	11.7
30	472.354	1.575	10.4
31	437.202	1.458	25.0
32	431.344	1.438	39.8
33	425.485	1.418	43.4
34	419.041	1.397	19.0
35	321.203	1.071	449.1
36	277.264	0.924	80.1
37	270.234	0.901	85.1



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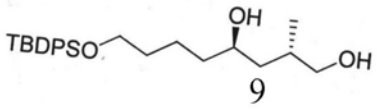
INDEX	FREQUENCY	PPM	HEIGHT
1	10220.465	135.505	66.7
2	10104.006	133.961	11.8
3	9767.333	129.497	26.2
4	9619.112	127.532	51.6
5	5839.485	77.421	16.5
6	5807.723	77.000	16.4
7	5775.962	76.579	15.3
8	5344.005	70.852	15.2
9	5180.962	68.690	13.0
10	4808.293	63.749	16.0
11	3249.858	43.087	13.6
12	2875.072	38.118	14.5
13	2604.039	34.525	16.3
14	2443.114	32.391	15.5
15	2023.861	26.833	47.7
16	1649.075	21.864	15.7
17	1443.683	19.141	8.9
18	1361.103	18.046	15



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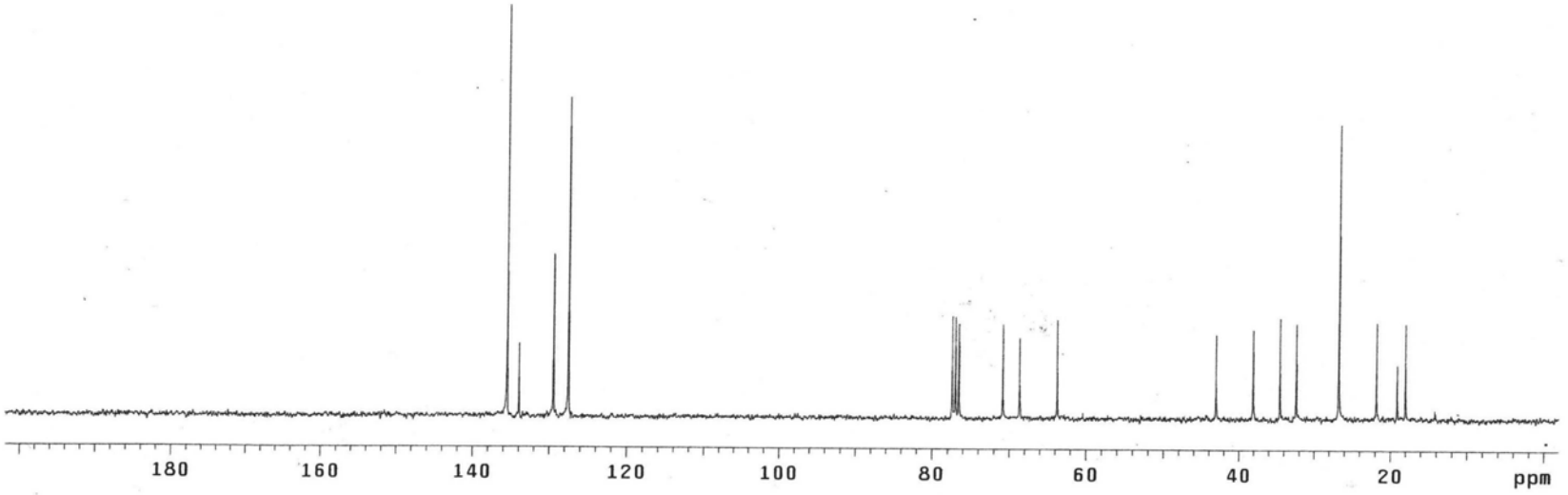
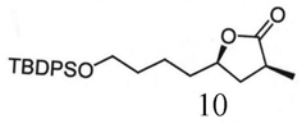


INDEX	FREQUENCY	PPM	HEIGHT
1	2300.654	7.670	40.5
2	2294.796	7.650	40.6
3	2293.624	7.646	38.2
4	2227.423	7.426	19.6
5	2220.392	7.402	59.5
6	2212.776	7.377	38.8
7	2206.918	7.357	11.4
8	1106.095	3.687	13.3
9	1100.237	3.668	26.0
10	1094.378	3.648	12.9
11	479.230	1.598	18.3
12	473.371	1.578	22.6
13	462.826	1.543	13.3
14	456.381	1.521	13.4
15	445.836	1.486	14.5
16	444.664	1.482	14.6
17	434.119	1.447	12.3
18	381.978	1.273	64.8
19	375.533	1.252	53.3
20	314.604	1.049	296.0
21	265.393	0.885	16.4



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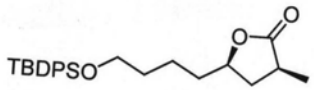
INDEX	FREQUENCY	PPM	HEIGHT
1	13510.966	179.131	4.4
2	10188.706	135.084	55.2
3	10065.894	133.456	9.5
4	9739.809	129.132	36.8
5	9591.588	127.167	59.3
6	5894.541	78.151	13.7
7	5839.488	77.421	90.1
8	5807.726	77.000	91.9
9	5775.964	76.579	90.5
10	4755.359	63.048	16.5
11	2781.907	36.883	16.2
12	2673.917	35.451	13.8
13	2620.981	34.749	17.4
14	2390.181	31.689	17.4
15	1992.102	26.412	53.1
16	1600.376	21.218	16.0
17	1414.042	18.748	10.6
18	1107.013	14.677	13.2



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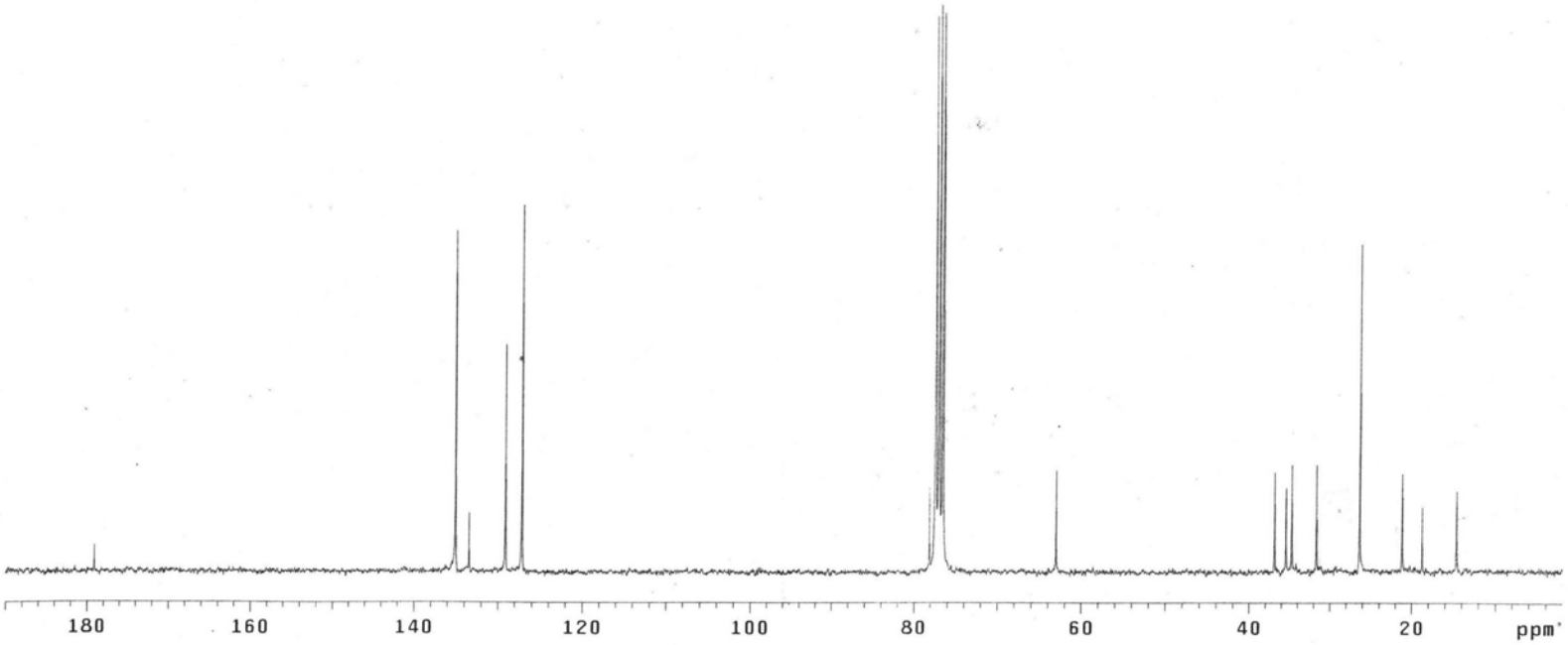
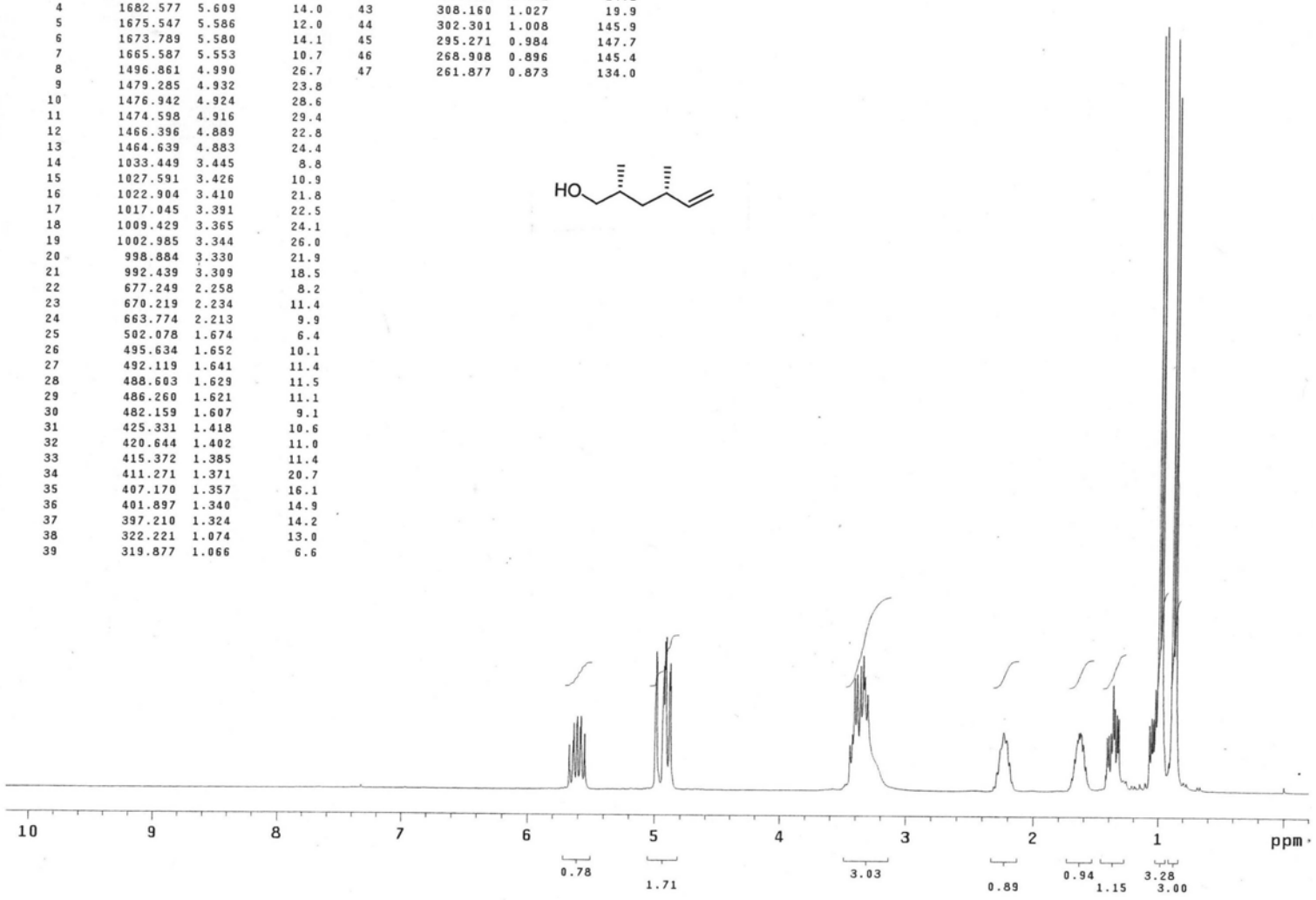
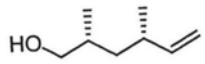
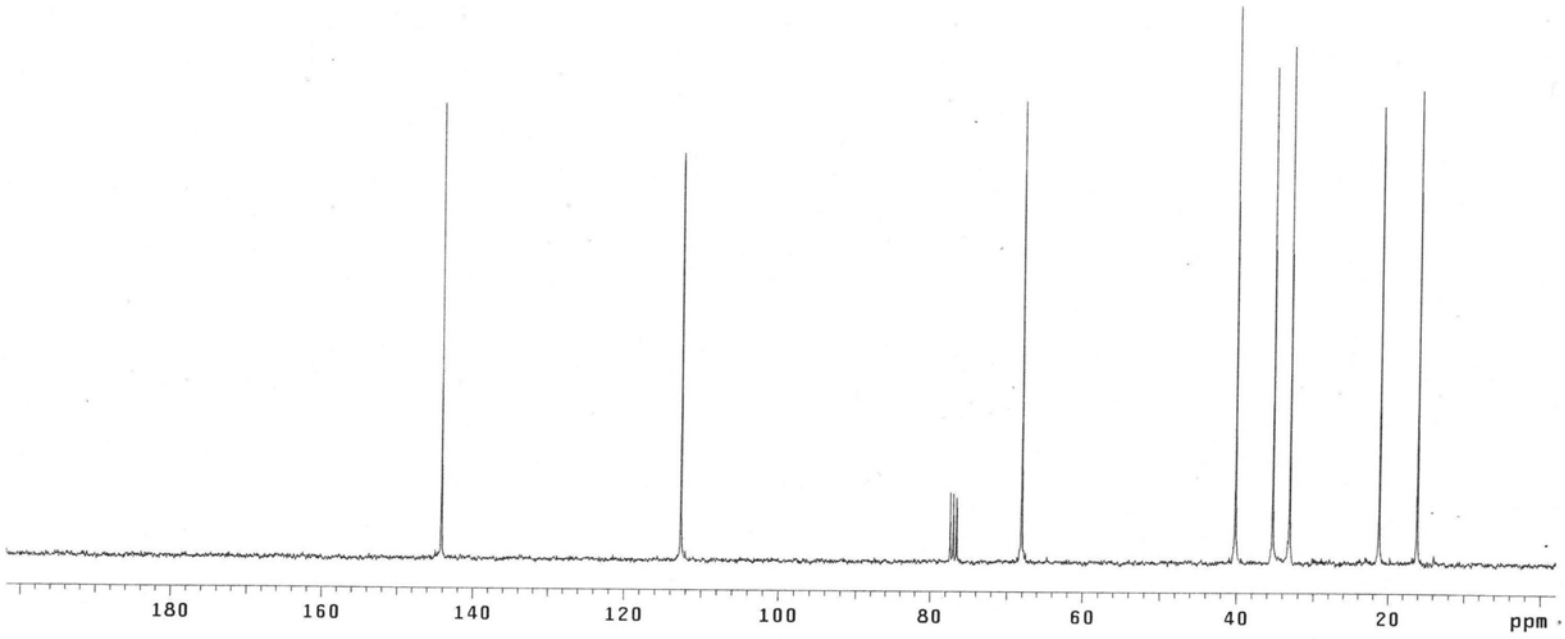


INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	1700.738	5.670	8.6	40	316.948	1.057	14.4
2	1692.536	5.643	9.4	41	315.190	1.051	8.0
3	1690.779	5.637	12.8	42	312.261	1.041	14.2
4	1682.577	5.609	14.0	43	308.160	1.027	19.9
5	1675.547	5.586	12.0	44	302.301	1.008	145.9
6	1673.789	5.580	14.1	45	295.271	0.984	147.7
7	1665.587	5.553	10.7	46	268.908	0.896	145.4
8	1496.861	4.990	26.7	47	261.877	0.873	134.0
9	1479.285	4.932	23.8				
10	1476.942	4.924	28.6				
11	1474.598	4.916	29.4				
12	1466.396	4.889	22.8				
13	1464.639	4.883	24.4				
14	1033.449	3.445	8.8				
15	1027.591	3.426	10.9				
16	1022.904	3.410	21.8				
17	1017.045	3.391	22.5				
18	1009.429	3.365	24.1				
19	1002.985	3.344	26.0				
20	998.884	3.330	21.9				
21	992.439	3.309	18.5				
22	677.249	2.258	8.2				
23	670.219	2.234	11.4				
24	663.774	2.213	9.9				
25	502.078	1.674	6.4				
26	495.634	1.652	10.1				
27	492.119	1.641	11.4				
28	488.603	1.629	11.5				
29	486.260	1.621	11.1				
30	482.159	1.607	9.1				
31	425.331	1.418	10.6				
32	420.644	1.402	11.0				
33	415.372	1.385	11.4				
34	411.271	1.371	20.7				
35	407.170	1.357	16.1				
36	401.897	1.340	14.9				
37	397.210	1.324	14.2				
38	322.221	1.074	13.0				
39	319.877	1.066	6.6				

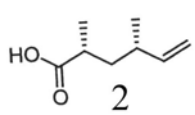


INDEX	FREQUENCY	PPM	HEIGHT
1	10876.871	144.208	73.9
2	8496.870	112.653	66.0
3	5136.496	68.101	74.8
4	3031.762	40.196	90.5
5	2665.445	35.339	80.5
6	2500.285	33.149	84.0
7	1606.726	21.302	74.2
8	1221.353	16.193	76.9



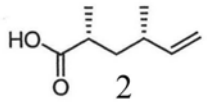


INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	1703.752	5.680	9.7	40	301.800	1.006	167.1
2	1695.550	5.653	11.7				
3	1693.792	5.647	11.3				
4	1686.176	5.621	16.0				
5	1678.560	5.596	14.4				
6	1676.217	5.588	13.8				
7	1668.600	5.563	11.5				
8	1505.147	5.018	30.9				
9	1486.985	4.957	50.4				
10	1476.440	4.922	27.7				
11	1475.268	4.918	23.8				
12	758.767	2.530	11.3				
13	751.737	2.506	20.6				
14	744.706	2.483	20.9				
15	737.676	2.459	12.2				
16	670.889	2.237	11.1				
17	663.858	2.213	15.4				
18	656.828	2.190	12.4				
19	649.798	2.166	8.2				
20	536.728	1.789	12.8				
21	530.283	1.768	14.9				
22	527.940	1.760	13.9				
23	523.253	1.744	20.2				
24	521.495	1.739	15.4				
25	516.809	1.723	19.3				
26	514.465	1.715	17.7				
27	508.021	1.694	14.3				
28	427.759	1.426	10.2				
29	418.385	1.395	16.3				
30	412.526	1.375	18.6				
31	410.183	1.367	18.4				
32	404.324	1.348	24.8				
33	398.466	1.328	15.3				
34	396.708	1.323	15.1				
35	390.850	1.303	12.3				
36	375.032	1.250	8.2				
37	352.183	1.174	156.0				
38	345.739	1.153	151.3				
39	308.244	1.028	162.0				

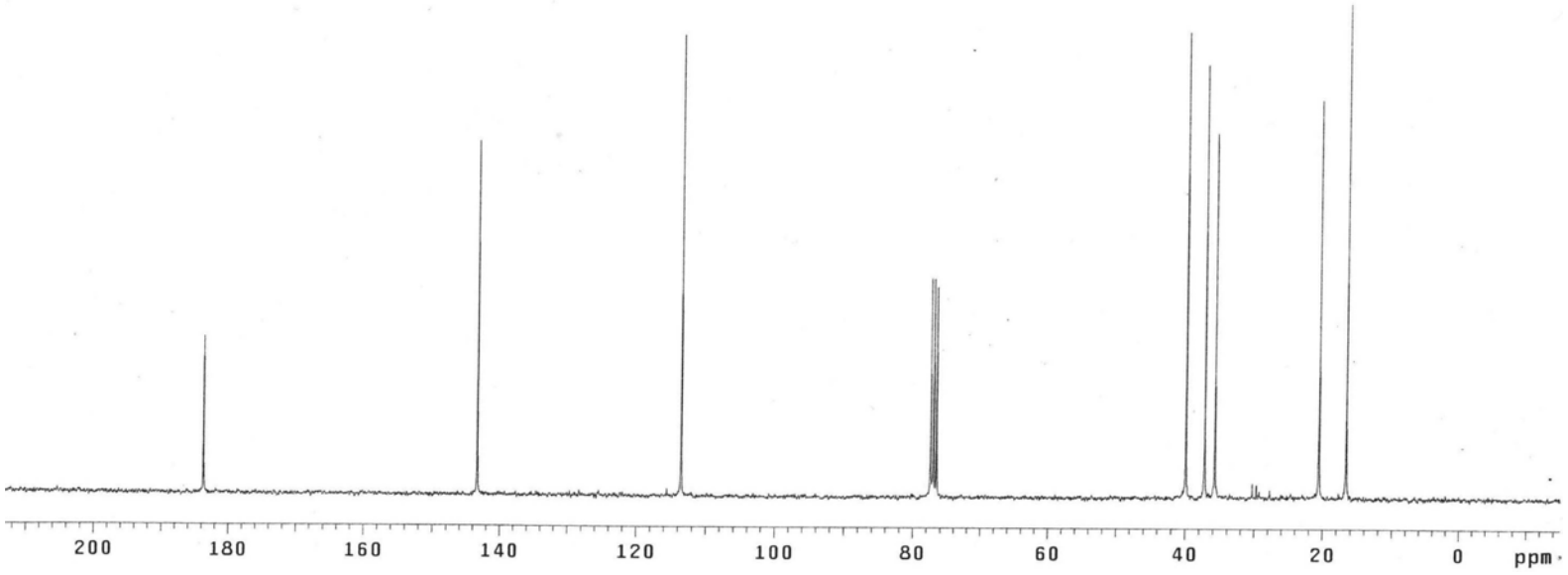


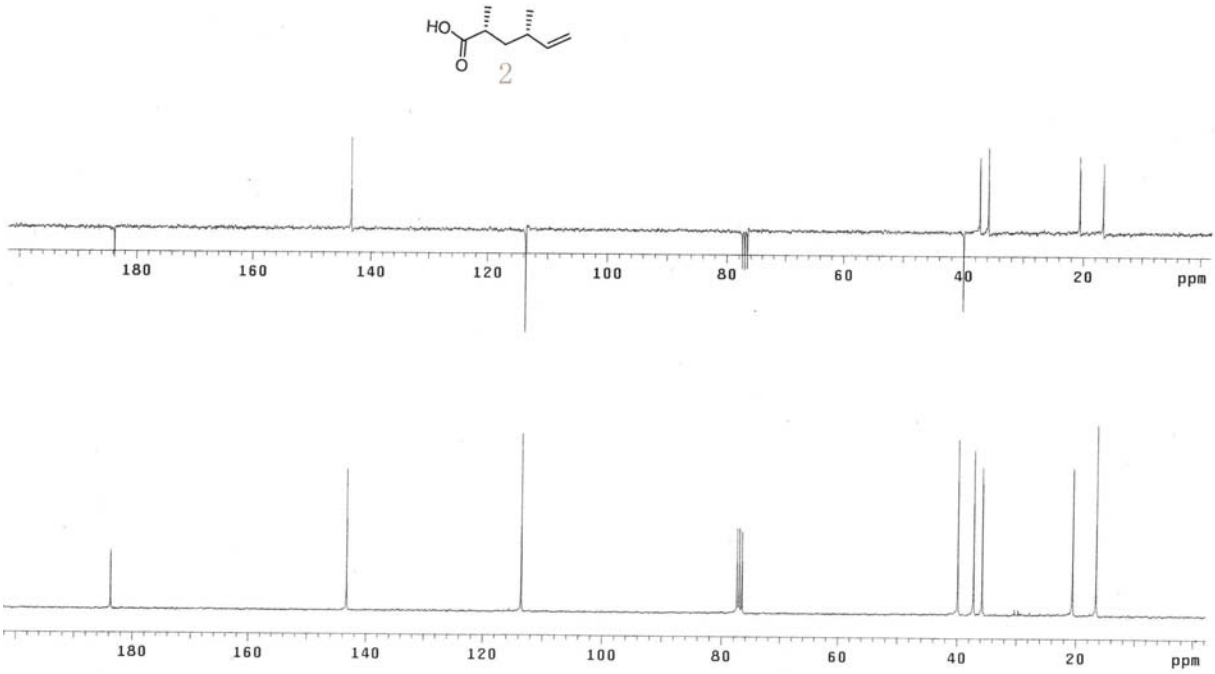
2

INDEX	FREQUENCY	PPM	HEIGHT
1	13858.223	183.735	25.3
2	10813.347	143.366	56.8
3	8564.628	113.552	74.1
4	5839.485	77.421	35.0
5	5807.723	77.000	35.0
6	5775.962	76.579	33.6
7	3010.587	39.915	74.8
8	2807.313	37.220	69.6
9	2699.324	35.788	58.5
10	1551.672	20.572	63.9
11	1253.114	16.614	79.4



2

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160
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120
100
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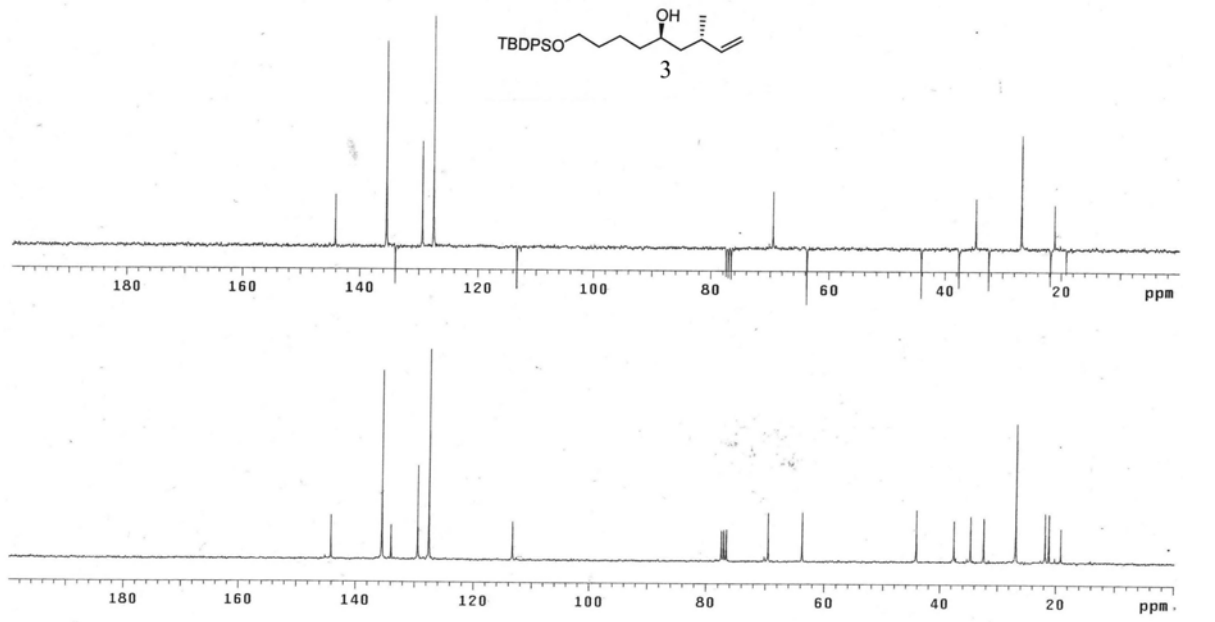
20
ppm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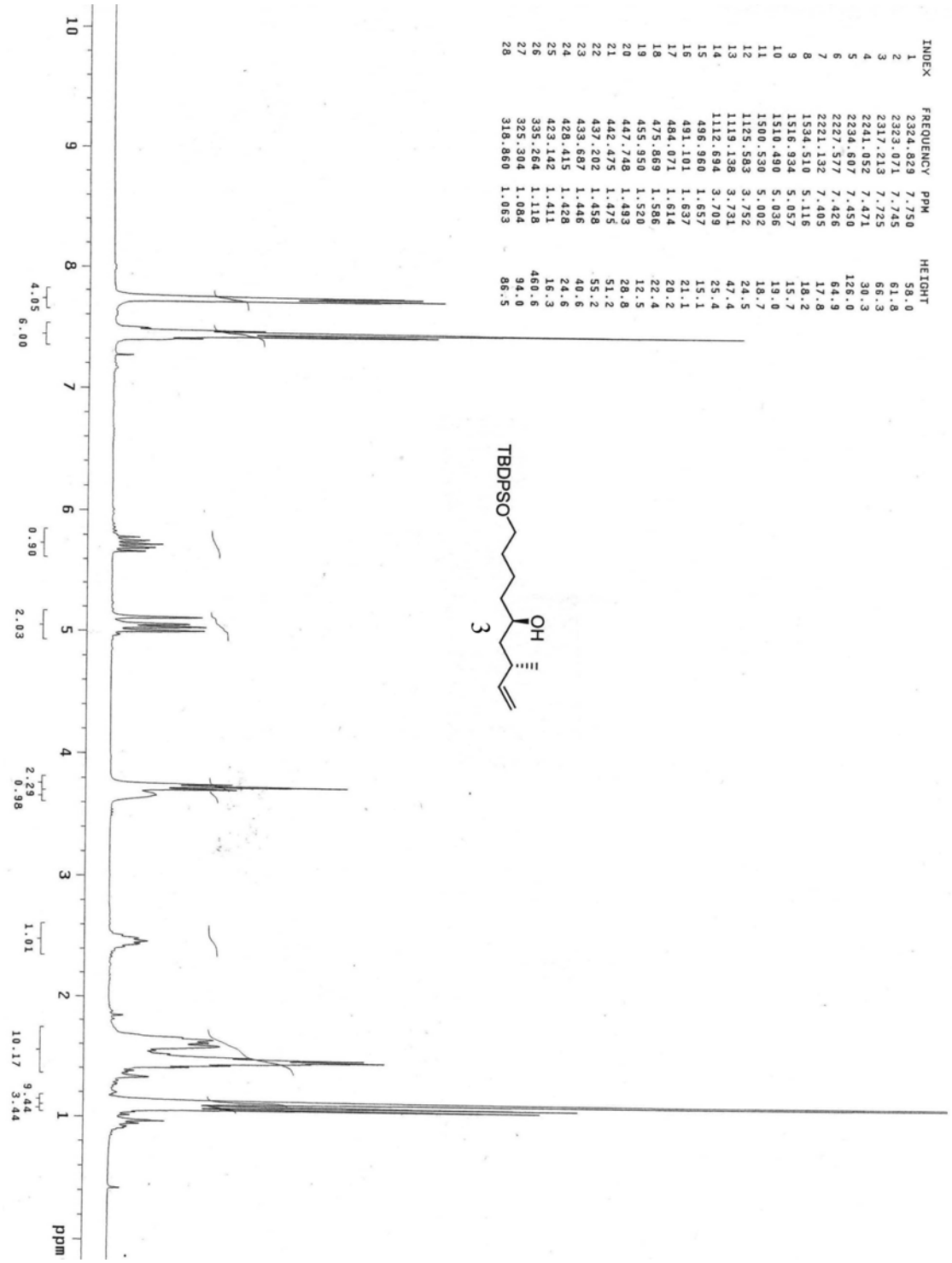
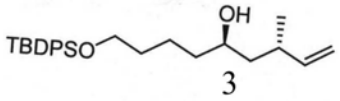
20
ppm


INDEX FREQUENCY PPM HEIGHT
1 2324.829 7.750 58.0
2 2323.071 7.745 61.8
3 2317.213 7.725 66.3
4 2241.052 7.471 30.3
5 2234.607 7.450 126.0
6 2227.577 7.426 64.9
7 2221.132 7.405 17.8
8 1534.510 5.116 18.2
9 1516.934 5.057 15.7
10 1510.490 5.036 19.0
11 1500.530 5.002 18.7
12 1125.583 3.752 24.5
13 1119.138 3.731 47.4
14 1112.694 3.709 25.4
15 496.960 1.657 15.1
16 491.101 1.637 21.1
17 484.071 1.614 20.2
18 475.869 1.586 22.4
19 455.950 1.520 12.5
20 447.748 1.493 28.8
21 442.475 1.475 51.2
22 437.202 1.458 55.2
23 433.687 1.446 40.6
24 428.415 1.428 24.6
25 423.142 1.411 16.3
26 335.264 1.118 460.6
27 325.304 1.084 94.0
28 318.860 1.063 86.5
TBDPSO
OH
3
4.05
6.00
0.90
2.03
2.29
0.98
1.01
10.17
9.44
3.44
10
9
8
7
6
5
4
3
2
1
ppm

INDEX	FREQUENCY	PPM	HEIGHT
1	10868.401	144.096	15.0
2	10220.465	135.505	58.2
3	10104.006	133.961	12.2
4	9763.098	129.441	33.3
5	9619.113	127.532	66.5
6	8547.689	113.327	12.3
7	5839.485	77.421	10.4
8	5807.724	77.000	11.0
9	5775.962	76.579	11.4
10	5244.485	69.532	15.7
11	4806.176	63.721	17.7
12	3330.321	44.154	17.7
13	2832.723	37.557	15.4
14	2614.627	34.665	16.4
15	2445.232	32.419	16.4
16	2021.744	26.805	48.1
17	1644.840	21.808	14.5
18	1596.139	21.162	16.8
19	1443.684	19.141	11.5



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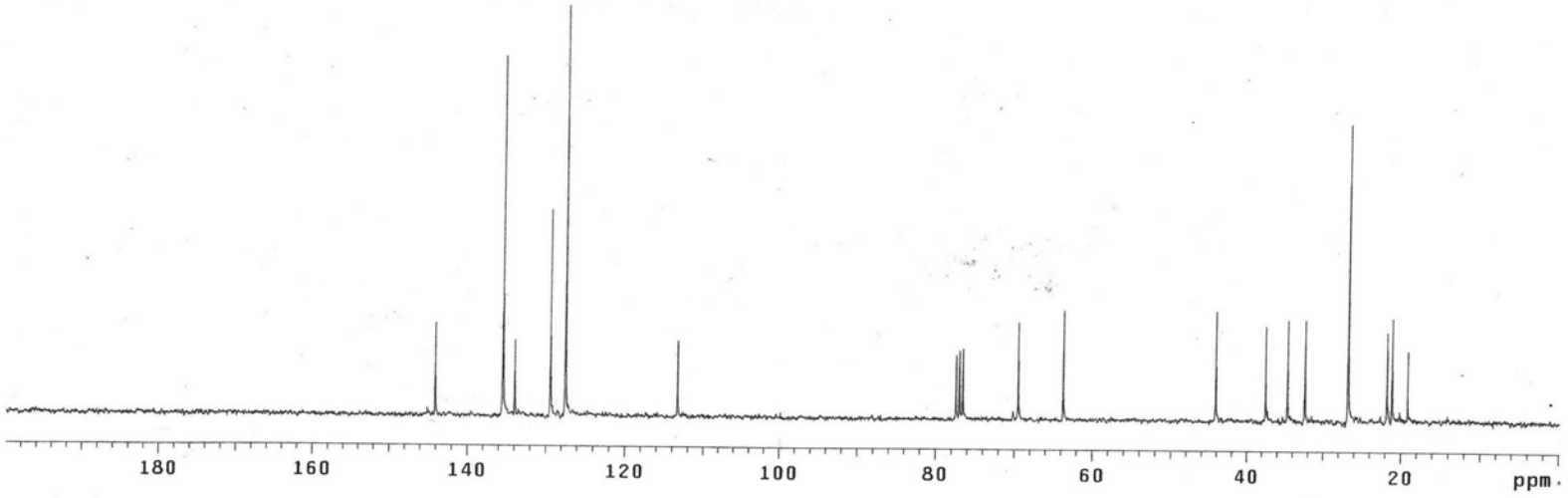
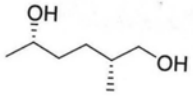
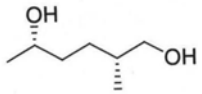


INDEX	FREQUENCY	PPM	HEIGHT
1	1114.297	3.715	13.8
2	1109.024	3.697	15.2
3	1009.429	3.365	74.1
4	1004.156	3.348	64.7
5	991.853	3.307	15.7
6	434.119	1.447	16.1
7	430.604	1.436	22.5
8	425.331	1.418	25.6
9	422.988	1.410	28.2
10	418.887	1.396	35.1
11	416.543	1.389	32.8
12	408.927	1.363	14.4
13	402.483	1.342	16.9
14	354.443	1.182	15.5
15	336.281	1.121	143.0
16	329.837	1.100	133.6
17	253.675	0.846	17.1
18	247.231	0.824	136.4
19	240.787	0.803	121.0



17a

INDEX	FREQUENCY	PPM	HEIGHT
1	5839.485	77.421	8.5
2	5807.724	77.000	8.7
3	5775.962	76.579	8.1
4	5132.261	68.045	6.1
5	5083.560	67.399	49.4
6	5072.973	67.259	45.6
7	2737.438	36.294	5.5
8	2686.620	35.620	39.9
9	2637.919	34.974	40.4
10	2189.022	29.023	5.0
11	2150.908	28.517	35.6
12	1750.712	23.211	51.6
13	1257.349	16.670	4.8
14	1231.940	16.333	40.8



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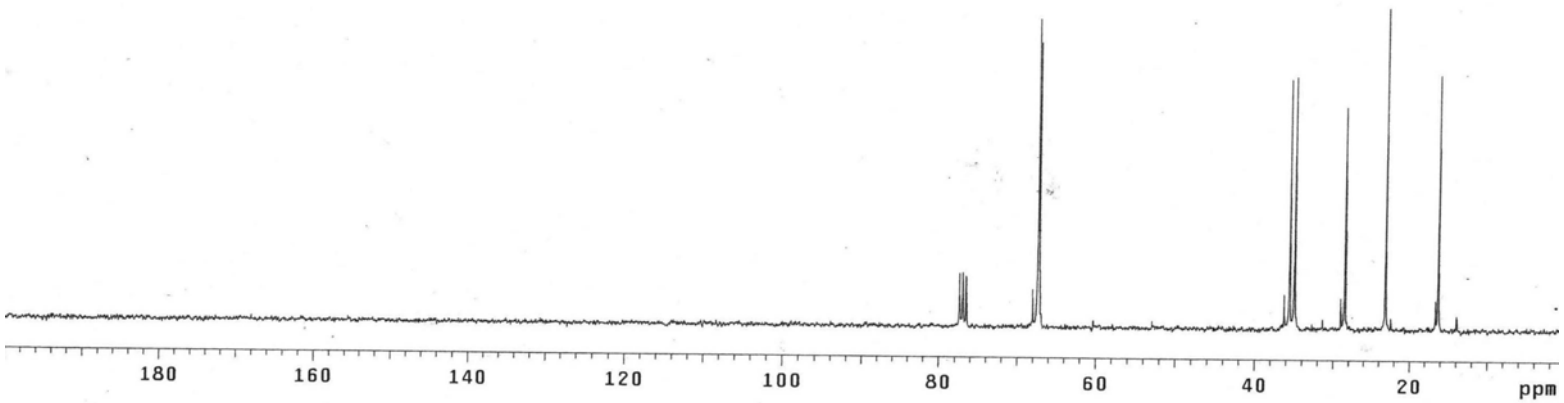
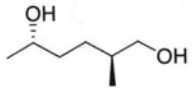
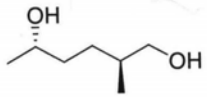


INDEX	FREQUENCY	PPM	HEIGHT
1	1108.007	3.694	24.0
2	1103.906	3.680	32.4
3	1097.462	3.659	32.2
4	1006.068	3.354	74.6
5	1003.725	3.346	70.4
6	454.192	1.514	34.8
7	451.849	1.506	34.3
8	443.061	1.477	26.4
9	440.132	1.467	25.4
10	437.788	1.459	24.3
11	420.213	1.401	32.7
12	413.768	1.379	32.1
13	409.081	1.364	30.5
14	403.809	1.346	21.0
15	336.435	1.122	132.0
16	334.092	1.114	135.1
17	330.577	1.102	142.9
18	327.648	1.092	134.3
19	255.001	0.850	94.3
20	253.244	0.844	108.1
21	248.557	0.829	138.4
22	246.799	0.823	133.2
23	242.113	0.807	50.4



17b

INDEX	FREQUENCY	PPM	HEIGHT
1	5839.485	77.421	11.8
2	5807.724	77.000	11.5
3	5775.962	76.579	10.9
4	5132.261	68.045	29.3
5	5085.677	67.427	9.5
6	5066.620	67.174	33.7
7	2739.556	36.322	40.0
8	2682.385	35.564	45.8
9	2640.036	35.002	12.0
10	2189.022	29.023	38.0
11	2153.025	28.545	9.7
12	1754.947	23.267	38.8
13	1257.349	16.670	46.6
14	1234.057	16.361	9.7



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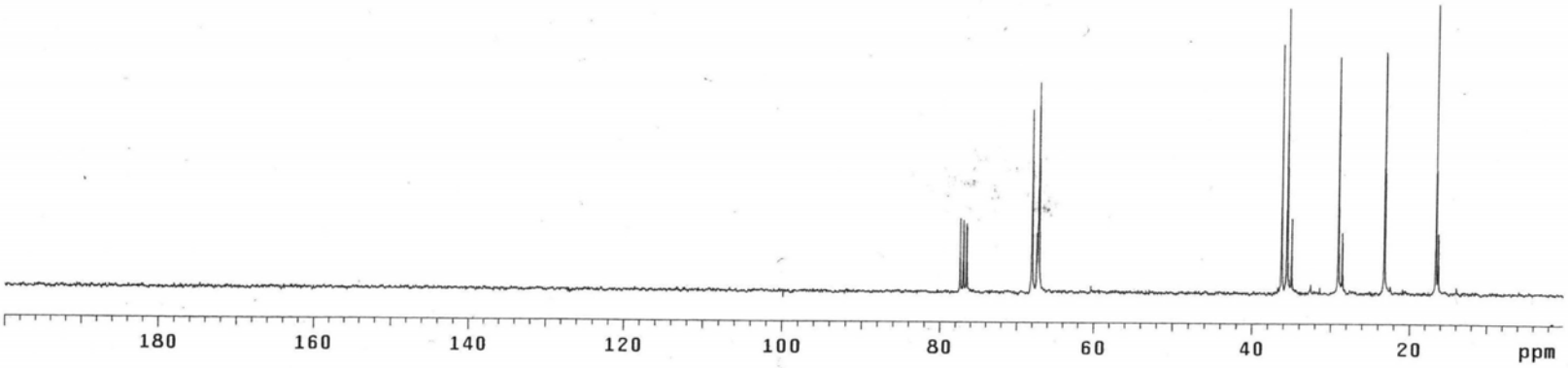
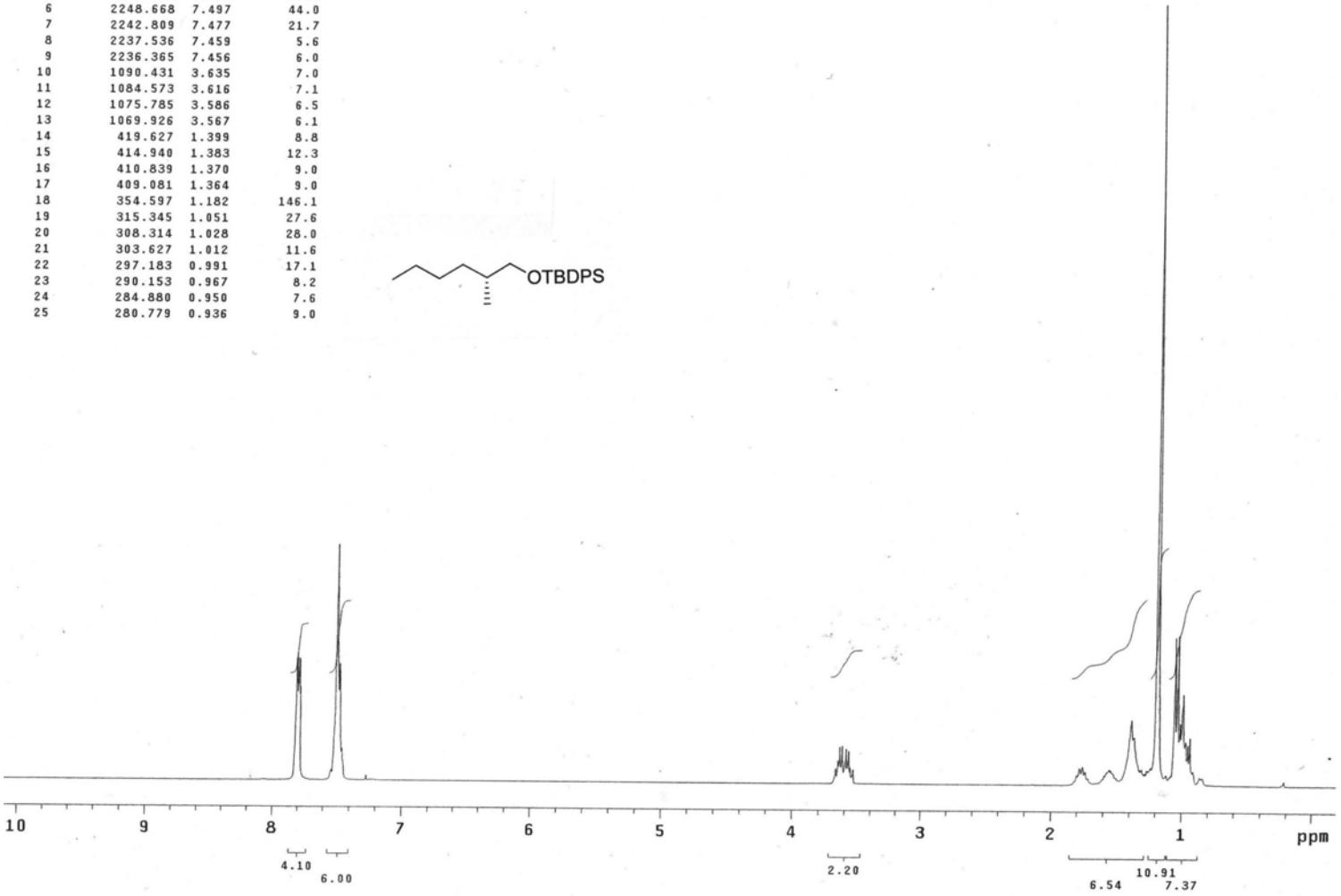
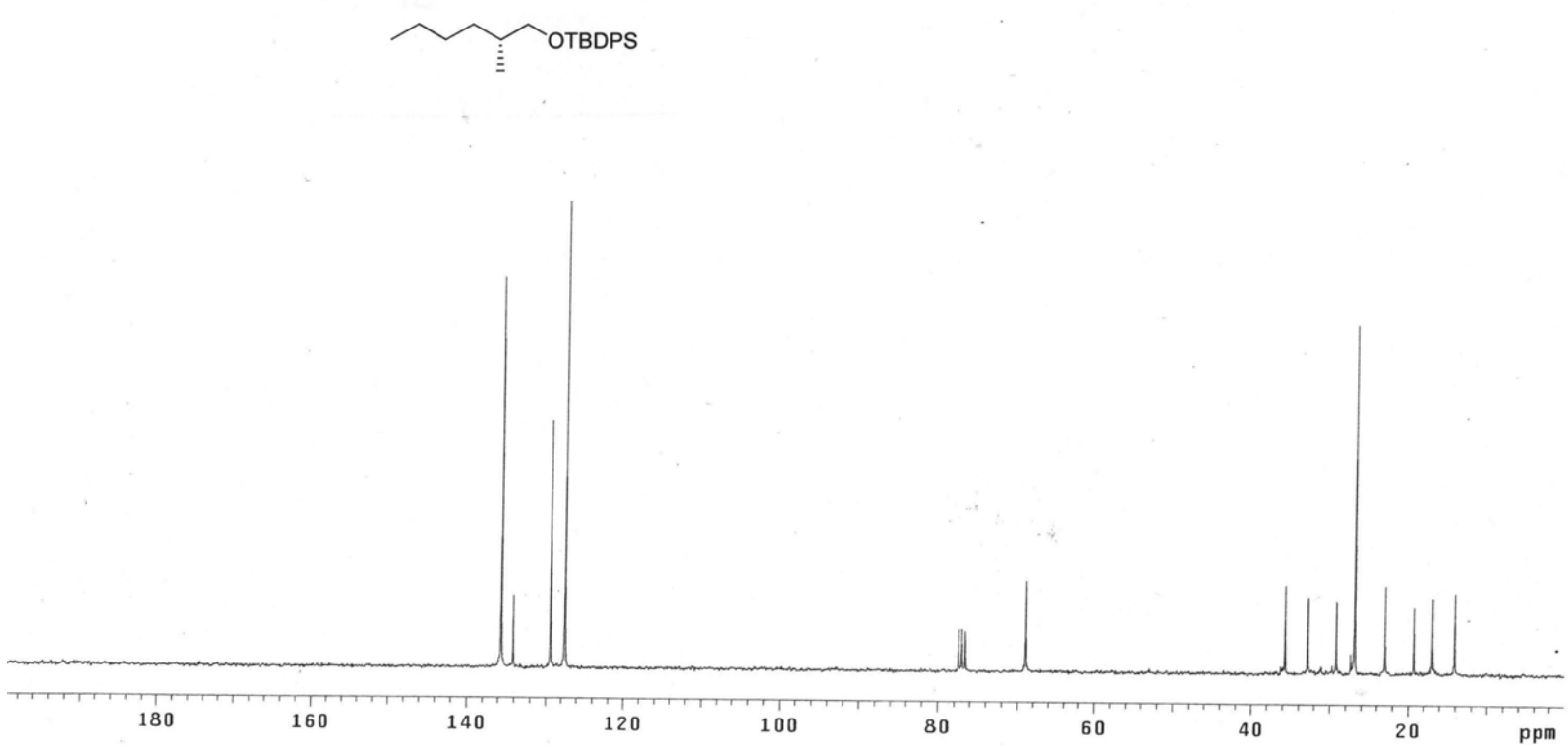


INDEX	FREQUENCY	PPM	HEIGHT
1	2343.576	7.813	22.7
2	2341.819	7.807	23.6
3	2339.475	7.799	18.1
4	2336.546	7.790	22.8
5	2334.203	7.782	17.4
6	2248.668	7.497	44.0
7	2242.809	7.477	21.7
8	2237.536	7.459	5.6
9	2236.365	7.456	6.0
10	1090.431	3.635	7.0
11	1084.573	3.616	7.1
12	1075.785	3.586	6.5
13	1069.926	3.567	6.1
14	419.627	1.399	8.8
15	414.940	1.383	12.3
16	410.839	1.370	9.0
17	409.081	1.364	9.0
18	354.597	1.182	146.1
19	315.345	1.051	27.6
20	308.314	1.028	28.0
21	303.627	1.012	11.6
22	297.183	0.991	17.1
23	290.153	0.967	8.2
24	284.880	0.950	7.6
25	280.779	0.936	9.0

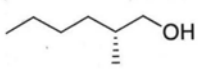


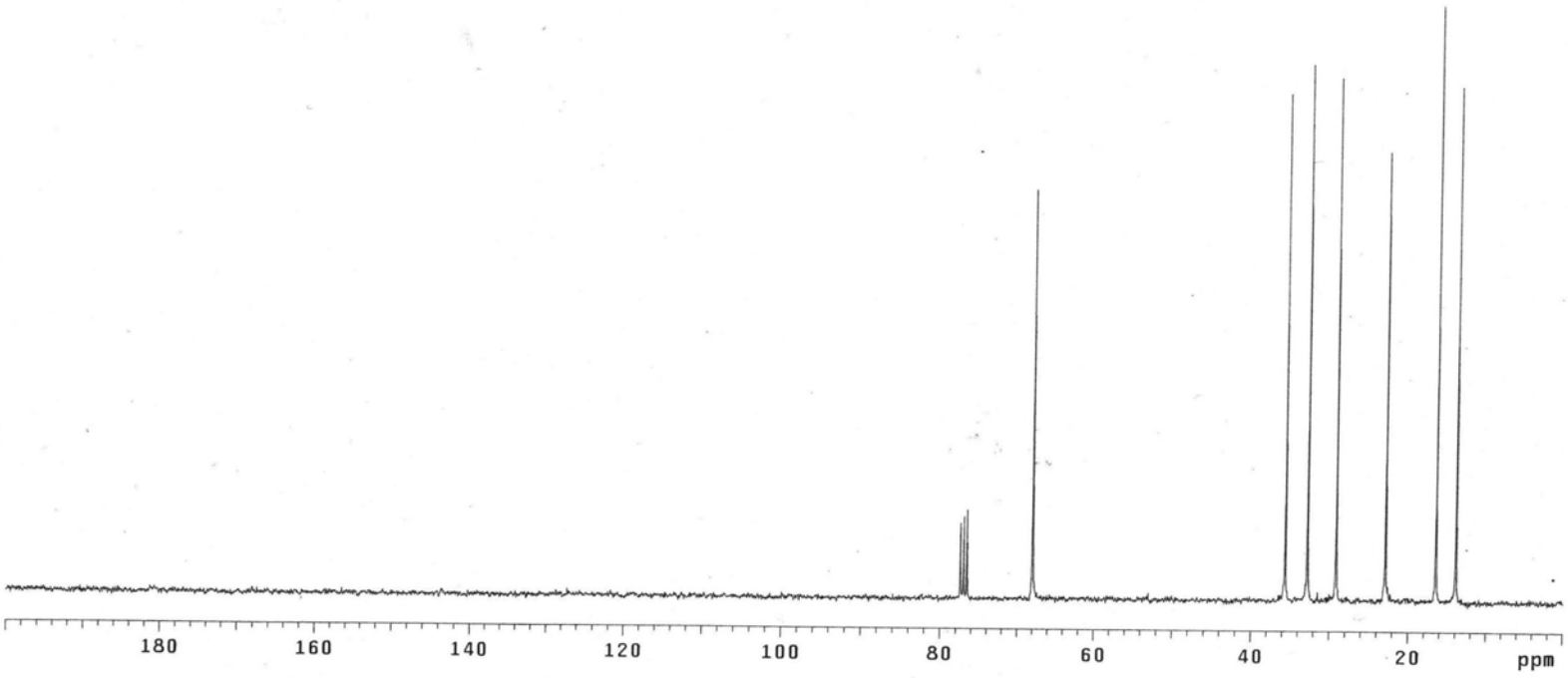
INDEX	FREQUENCY	PPM	HEIGHT
1	10231.052	135.645	62.8
2	10116.710	134.129	11.6
3	9765.216	129.469	39.8
4	9621.230	127.560	75.2
5	5200.019	68.943	14.5
6	2692.972	35.704	14.2
7	2476.993	32.840	12.3
8	2203.844	29.219	11.8
9	2028.096	26.889	56.0
10	1733.773	22.987	14.2
11	1458.506	19.337	10.7
12	1278.523	16.951	12.3
13	1064.662	14.116	13.1



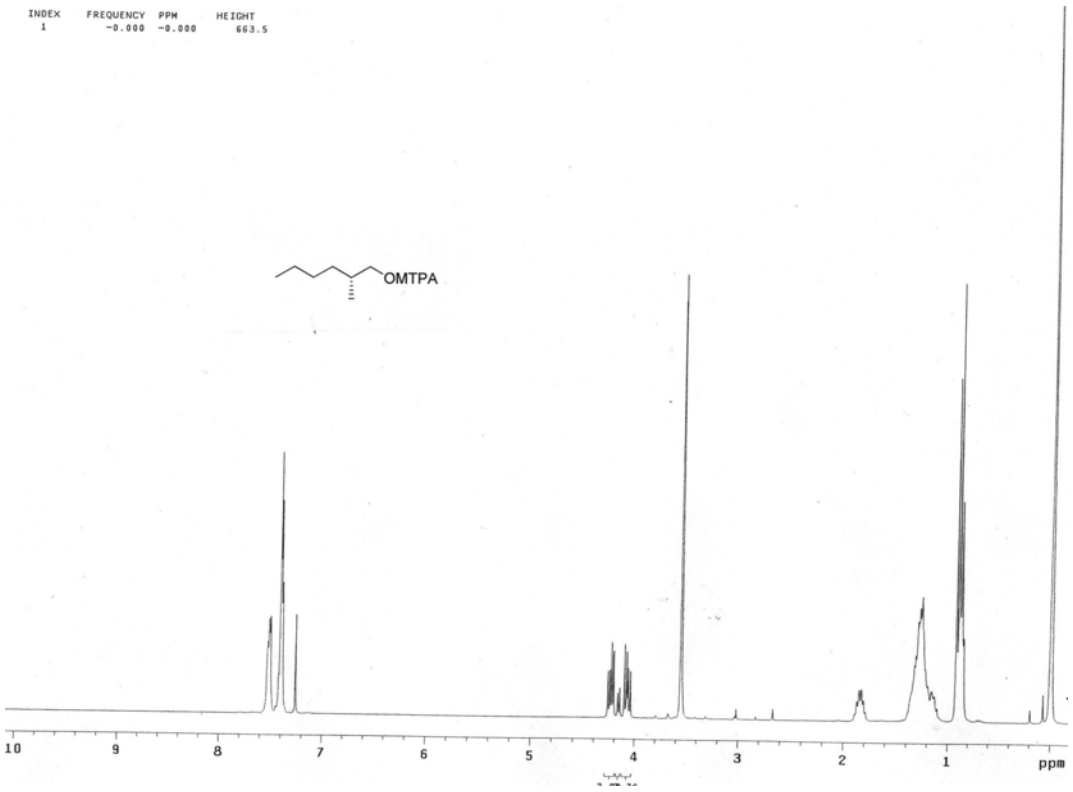
INDEX	FREQUENCY	PPM	HEIGHT
1	1025.987	3.420	36.1
2	1022.472	3.409	35.2
3	1019.543	3.399	33.5
4	1003.725	3.346	28.1
5	1000.210	3.334	31.3
6	996.694	3.323	32.9
7	993.765	3.313	35.5
8	465.909	1.553	25.5
9	462.394	1.542	22.6
10	460.051	1.534	27.4
11	408.496	1.362	23.0
12	406.738	1.356	23.5
13	403.223	1.344	25.0
14	396.193	1.321	40.7
15	392.677	1.309	51.5
16	388.576	1.295	40.1
17	383.304	1.278	74.4
18	382.132	1.274	75.8
19	378.617	1.262	82.8
20	375.688	1.252	93.0
21	373.930	1.247	95.3
22	369.243	1.231	82.4
23	356.354	1.188	26.5
24	314.759	1.049	29.5
25	313.001	1.043	30.1
26	304.799	1.016	27.0
27	260.860	0.870	323.0
28	258.517	0.862	280.0
29	253.830	0.846	386.9
30	252.072	0.840	277.8

INDEX	FREQUENCY	PPM	HEIGHT
1	5839.485	77.421	12.1
2	5807.723	77.000	13.1
3	5775.962	76.579	14.2
4	5128.026	67.988	65.8
5	2684.502	35.592	81.6
6	2474.876	32.812	86.4
7	2197.491	29.135	84.2
8	1727.420	22.902	72.3
9	1242.527	16.474	95.9
10	1051.957	13.947	82.8

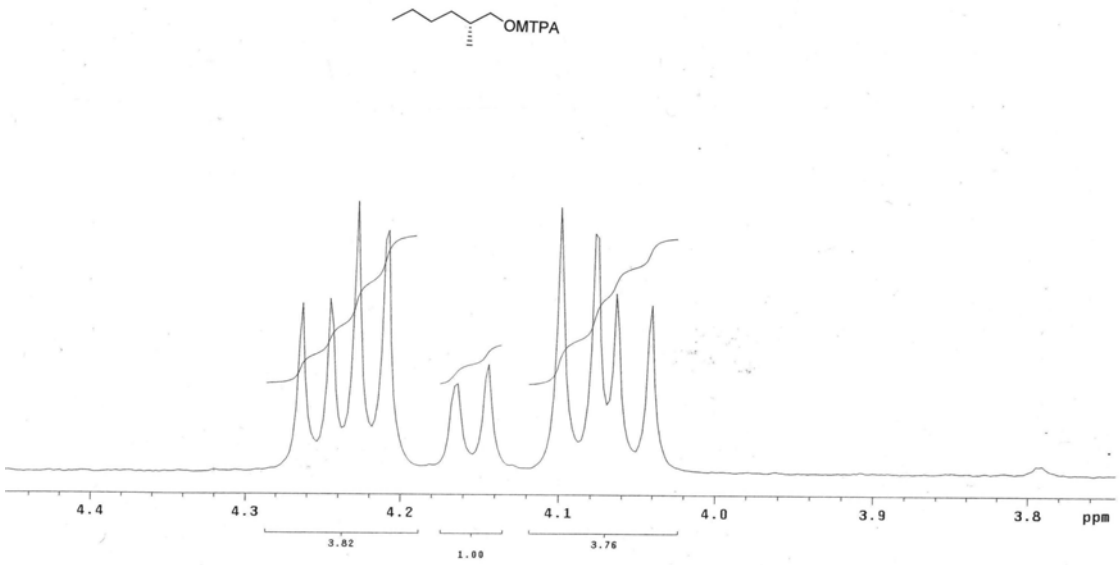




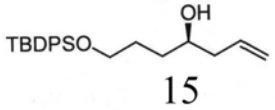
INDEX	FREQUENCY	PPM	HEIGHT
1	-0.000	-0.000	663.5



INDEX	FREQUENCY	PPM	HEIGHT
1	1278.923	4.264	38.0
2	1273.650	4.246	39.1
3	1268.377	4.228	61.1
4	1262.519	4.209	54.5
5	1249.044	4.164	20.1
6	1243.185	4.145	24.4
7	1229.711	4.100	59.9
8	1223.266	4.078	54.0
9	1219.165	4.064	40.5
10	1212.135	4.041	37.8

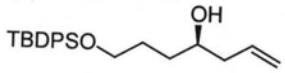


INDEX	FREQUENCY	PPM	HEIGHT
1	2283.665	7.613	21.6
2	2281.907	7.607	31.7
3	2276.049	7.588	31.3
4	2274.291	7.582	32.6
5	2206.918	7.357	16.2
6	2203.988	7.348	8.2
7	2202.231	7.342	16.5
8	2199.301	7.332	46.5
9	2194.615	7.316	12.5
10	2191.685	7.307	35.6
11	2185.827	7.287	10.4
12	2183.483	7.279	6.9
13	2154.776	7.184	15.6
14	1524.982	5.084	6.5
15	1523.810	5.080	10.2
16	1519.709	5.066	10.2
17	1507.992	5.027	20.8
18	1092.035	3.641	12.0
19	1090.277	3.635	8.9
20	1086.176	3.621	29.6
21	1080.318	3.602	18.4
22	639.168	2.131	8.8
23	625.694	2.086	17.0
24	621.593	2.072	15.7
25	485.088	1.617	6.6
26	483.331	1.611	8.0
27	479.816	1.600	10.7
28	477.472	1.592	11.8
29	473.957	1.580	7.8
30	472.200	1.574	7.8
31	468.099	1.561	7.7
32	462.826	1.543	6.3
33	432.361	1.441	6.0
34	299.372	0.998	13.3
35	296.443	0.988	20.4
36	293.514	0.979	377.9



15

INDEX	FREQUENCY	PPM	HEIGHT
1	10216.231	135.449	50.3
2	10173.882	134.887	11.6
3	10074.362	133.568	9.7
4	9767.334	129.497	25.1
5	9619.113	127.532	50.7
6	8869.540	117.594	14.3
7	5839.486	77.421	5.6
8	5807.724	77.000	5.5
9	5773.845	76.551	5.3
10	5308.009	70.375	13.0
11	4825.233	63.974	13.2
12	3154.574	41.824	14.0
13	2517.225	33.374	14.4
14	2161.496	28.658	12.9
15	2017.510	26.749	41.0
16	1437.332	19.056	8.7



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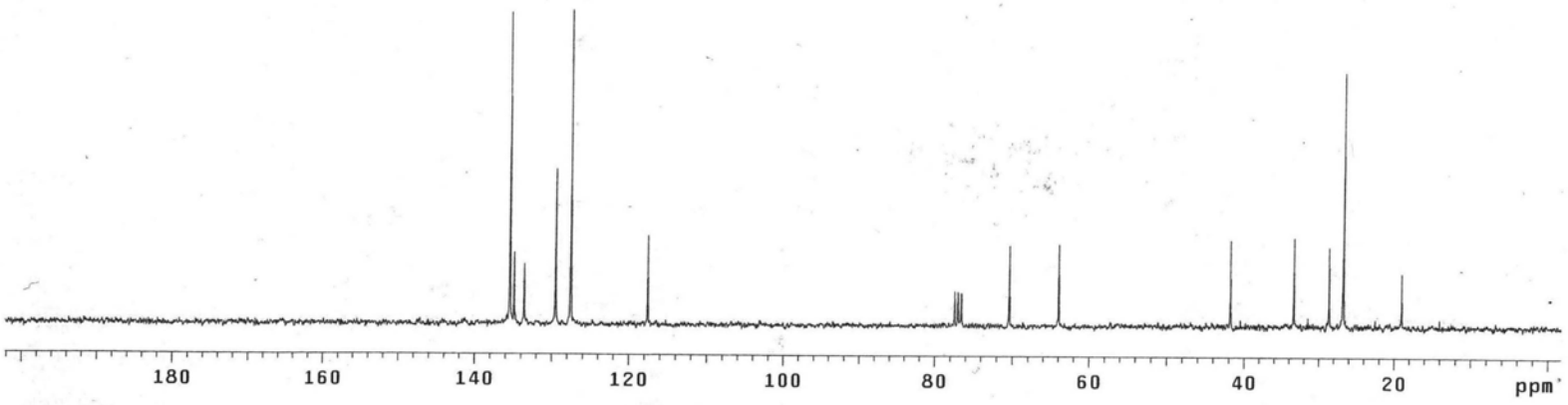
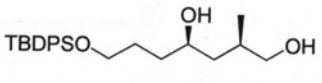
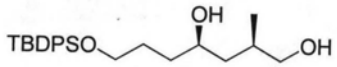


INDEX	FREQUENCY	PPM	HEIGHT
1	2316.041	7.721	27.8
2	2309.011	7.698	31.5
3	2235.779	7.454	13.0
4	2229.920	7.434	64.6
5	2225.819	7.420	15.0
6	2222.304	7.409	33.9
7	1124.411	3.749	12.1
8	1119.138	3.731	23.2
9	1113.280	3.711	13.3
10	506.333	1.688	10.2
11	503.404	1.678	10.4
12	470.010	1.567	12.9
13	465.909	1.553	12.9
14	462.980	1.543	10.6
15	328.233	1.094	217.3
16	291.910	0.973	42.0
17	284.880	0.950	44.4

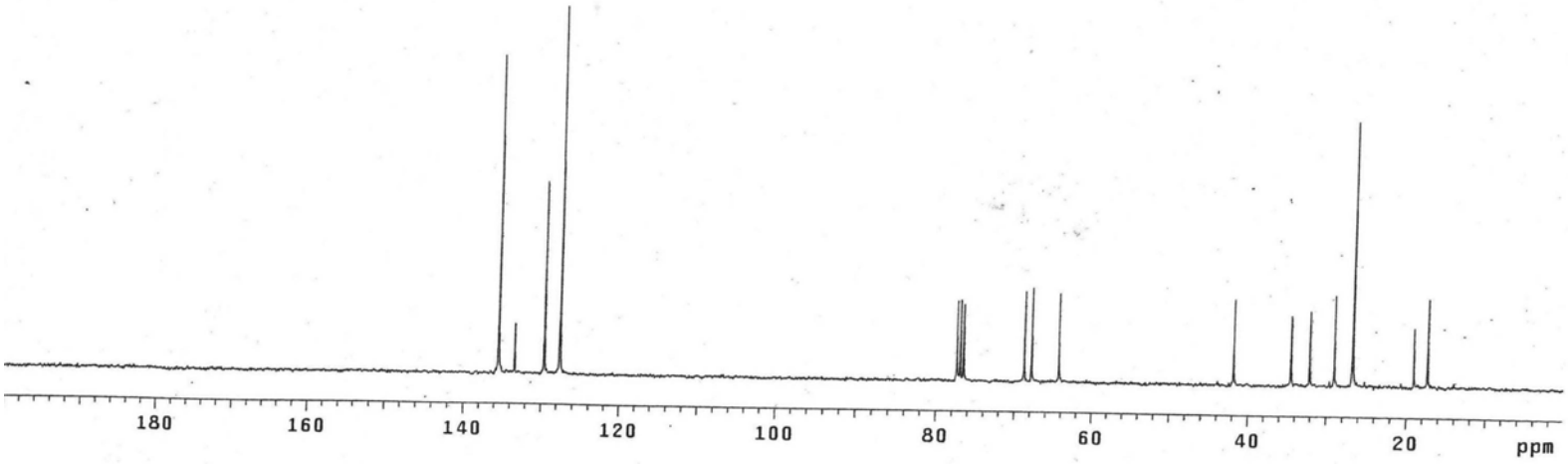


18a

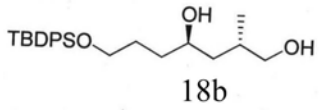
INDEX	FREQUENCY	PPM	HEIGHT
1	10220.465	135.505	51.3
2	10063.774	133.428	8.2
3	9777.920	129.638	31.0
4	9627.582	127.644	59.4
5	5839.485	77.421	13.1
6	5807.723	77.000	13.2
7	5775.962	76.579	12.5
8	5185.197	68.746	14.7
9	5115.321	67.820	15.3
10	4850.641	64.311	14.5
11	3158.808	41.880	13.9
12	2610.392	34.609	11.4
13	2424.057	32.139	12.1
14	2189.022	29.023	14.7
15	2017.509	26.749	42.7
16	1439.448	19.085	9.6
17	1310.285	17.372	14.4



18a

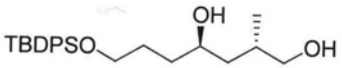


INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2304.113	7.681	28.5	40	292.871	0.976	6.5
2	2300.598	7.670	15.3	41	285.841	0.953	5.5
3	2296.497	7.656	30.6	42	281.154	0.937	9.7
4	2225.608	7.420	13.5	43	274.124	0.914	12.5
5	2219.164	7.398	60.7	44	271.194	0.904	49.7
6	2217.406	7.392	36.8	45	264.750	0.883	50.3
7	2214.477	7.383	12.9	46	257.720	0.859	7.4
8	2211.548	7.373	33.5				
9	2205.689	7.353	9.4				
10	2202.760	7.344	5.4				
11	1111.897	3.707	14.3				
12	1106.624	3.689	25.0				
13	1100.766	3.670	14.0				
14	1068.544	3.562	5.3				
15	1062.099	3.541	7.4				
16	1057.998	3.527	6.9				
17	1014.645	3.383	5.8				
18	1006.443	3.355	6.2				
19	507.294	1.691	6.2				
20	500.850	1.670	9.6				
21	494.991	1.650	13.3				
22	485.032	1.617	6.0				
23	479.759	1.599	7.5				
24	477.416	1.592	5.8				
25	475.072	1.584	6.5				
26	473.315	1.578	6.4				
27	467.456	1.558	6.9				
28	459.840	1.533	7.7				
29	455.153	1.517	5.6				
30	441.093	1.471	5.4				
31	433.476	1.445	6.0				
32	431.719	1.439	6.5				
33	429.961	1.433	6.6				
34	427.032	1.424	7.6				
35	424.689	1.416	8.8				
36	421.173	1.404	5.8				
37	412.386	1.375	5.8				
38	378.992	1.263	12.6				
39	315.720	1.053	250.8				



18b

INDEX	FREQUENCY	PPM	HEIGHT
1	10220.465	135.505	32.1
2	10061.657	133.400	6.3
3	9780.037	129.666	18.3
4	9629.699	127.673	33.3
5	5839.485	77.421	12.4
6	5807.723	77.000	12.9
7	5775.962	76.579	12.6
8	5335.535	70.740	7.9
9	5189.431	68.803	7.1
10	4852.759	64.339	8.6
11	3275.267	43.424	7.4
12	2690.854	35.676	7.7
13	2625.214	34.806	8.3
14	2176.317	28.854	8.4
15	2019.626	26.777	30.5
16	1439.448	19.085	5.7
17	1373.808	18.214	7.6



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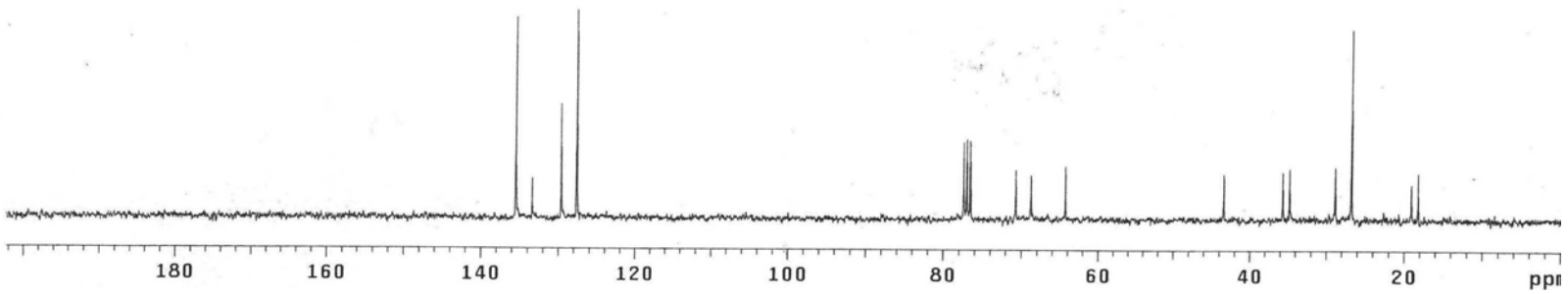
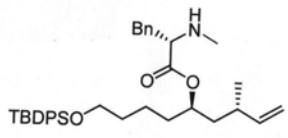
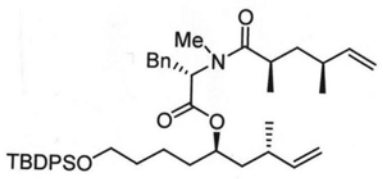


INDEX	FREQUENCY	PPM	HEIGHT
1	2339.229	7.798	17.3
2	2335.714	7.787	19.1
3	2333.371	7.779	21.4
4	2258.381	7.529	8.2
5	2253.109	7.511	40.2
6	2251.351	7.506	40.0
7	2245.492	7.486	23.0
8	2243.735	7.480	16.7
9	2199.210	7.332	11.6
10	2192.765	7.310	25.2
11	2190.422	7.302	24.0
12	1600.466	5.336	6.6
13	1514.345	5.048	11.6
14	1506.143	5.021	6.7
15	1118.892	3.730	10.5
16	1115.963	3.720	7.5
17	915.015	3.050	11.9
18	907.984	3.027	10.1
19	743.359	2.478	42.1
20	741.016	2.470	25.9
21	640.834	2.136	6.5
22	489.684	1.632	7.1
23	484.411	1.615	8.4
24	478.552	1.595	6.7
25	457.461	1.525	7.8
26	451.603	1.506	9.8
27	446.916	1.490	7.8
28	444.573	1.482	7.4
29	353.179	1.177	108.3
30	349.664	1.166	81.4
31	335.604	1.119	17.9
32	332.674	1.109	13.2
33	329.159	1.097	17.9
34	326.230	1.088	11.0



INDEX	FREQUENCY	PPM	HEIGHT
1	2276.634	7.590	26.3
2	2270.776	7.570	27.8
3	2269.604	7.566	27.6
4	2197.544	7.326	11.4
5	2191.685	7.307	53.9
6	2184.655	7.283	26.3
7	2146.574	7.156	10.1
8	2144.231	7.148	10.9
9	2142.473	7.143	11.0
10	2137.201	7.125	16.0
11	2128.413	7.096	20.9
12	2124.312	7.082	9.4
13	2121.383	7.072	10.5
14	1472.841	4.910	9.4
15	1457.023	4.857	13.6
16	1447.649	4.826	14.6
17	1430.073	4.768	10.2
18	1068.600	3.562	13.5
19	840.703	2.803	8.6
20	819.612	2.732	10.3
21	814.339	2.715	42.1
22	439.977	1.467	16.3
23	434.705	1.449	15.9
24	391.937	1.307	9.5
25	289.413	0.965	154.1
26	278.281	0.928	35.1
27	271.251	0.904	25.7
28	265.978	0.887	9.6
29	257.191	0.857	8.9
30	253.675	0.846	8.6
31	250.746	0.836	8.8
32	207.393	0.691	20.2
33	200.948	0.670	19.2



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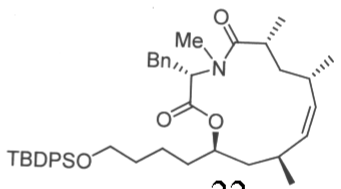
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2304.873	7.684	44.6	40	481.105	1.604	10.3
2	2302.529	7.676	34.3	41	474.074	1.580	17.1
3	2299.600	7.666	42.9	42	468.216	1.561	18.3
4	2297.257	7.659	46.7	43	463.529	1.545	15.2
5	2217.580	7.393	84.0	44	455.913	1.520	14.6
6	2211.136	7.371	44.6	45	449.469	1.498	13.4
7	2206.449	7.356	14.0	46	435.994	1.454	13.9
8	2204.692	7.350	11.1	47	428.964	1.430	20.6
9	2202.934	7.344	8.0	48	422.519	1.409	12.8
10	2184.772	7.284	8.4	49	412.560	1.375	12.6
11	2178.328	7.262	25.0	50	400.257	1.334	9.9
12	2170.712	7.237	27.5	51	379.752	1.266	6.4
13	2167.783	7.227	14.6	52	342.843	1.143	10.8
14	2165.439	7.219	18.2	53	333.469	1.112	46.1
15	2158.995	7.198	16.0	54	326.439	1.088	48.6
16	2154.894	7.184	7.8	55	318.237	1.061	314.9
17	2152.550	7.176	7.2	56	304.176	1.014	51.0
18	2151.379	7.172	7.3	57	298.318	0.995	85.6
19	2141.419	7.139	26.3	58	291.873	0.973	52.4
20	2139.662	7.133	28.1	59	282.500	0.942	7.0
21	2133.217	7.112	22.0	60	275.469	0.918	6.8
22	1567.867	5.227	12.9				
23	1561.422	5.205	12.4				
24	1553.806	5.180	19.5				
25	1545.018	5.151	11.3				
26	1534.473	5.116	7.4				
27	1105.627	3.686	13.6				
28	1099.182	3.664	28.8				
29	1093.324	3.645	16.2				
30	1068.132	3.561	12.2				
31	1064.617	3.549	13.7				
32	1058.758	3.530	10.6				
33	1045.869	3.487	11.6				
34	1034.738	3.450	6.4				
35	1007.203	3.358	9.7				
36	1004.274	3.348	9.5				
37	840.234	2.801	9.7				
38	783.992	2.614	107.5				
39	570.155	1.901	10.4				



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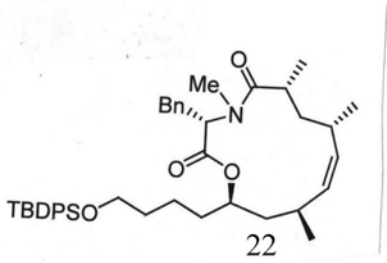
INDEX	FREQUENCY	PPM	HEIGHT
1	13307.690	176.436	9.9
2	12814.327	169.895	10.0
3	10449.149	138.537	10.4
4	10256.462	135.982	12.0
5	10222.583	135.533	14.9
6	10211.996	135.393	81.9
7	10093.419	133.821	14.4
8	9763.099	129.441	38.7
9	9754.629	129.329	28.4
10	9676.284	128.290	29.9
11	9616.995	127.504	76.8
12	9532.298	126.381	13.2
13	5839.486	77.421	11.7
14	5807.724	77.000	12.6
15	5775.963	76.579	12.6
16	5511.283	73.070	12.9
17	5036.977	66.781	13.4
18	4782.884	63.412	15.0
19	3323.969	44.070	12.2
20	3245.624	43.031	10.4
21	2961.887	39.269	11.6
22	2644.271	35.058	13.4
23	2591.336	34.356	13.2
24	2532.047	33.570	12.9
25	2438.880	32.335	15.2
26	2269.485	30.089	13.5
27	2019.627	26.777	57.8
28	1617.314	21.443	14.2
29	1496.620	19.842	15.5
30	1456.389	19.309	12.8
31	1441.567	19.113	12.5
32	1394.983	18.495	14.1



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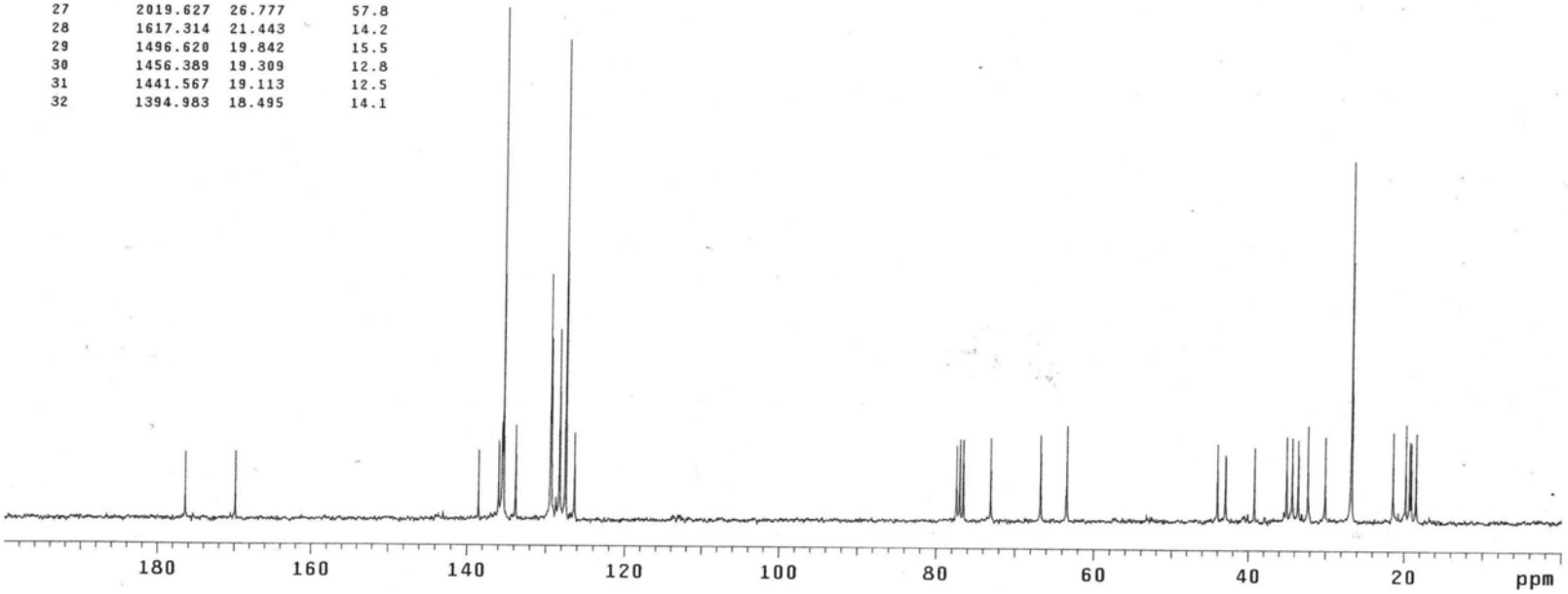
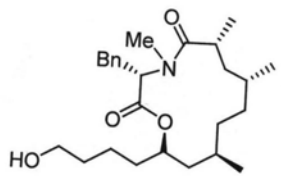


INDEX	FREQUENCY	PPM	HEIGHT
1	2162.978	7.211	38.4
2	2160.635	7.203	31.6
3	2155.362	7.186	43.8
4	2148.918	7.164	22.8
5	2141.888	7.141	21.9
6	2128.999	7.098	39.4
7	2127.241	7.092	44.8
8	2120.797	7.070	32.7
9	1079.146	3.598	21.6
10	1072.701	3.576	42.8
11	1066.257	3.555	22.2
12	1048.681	3.496	24.7
13	1044.580	3.482	27.8
14	1037.550	3.459	22.4
15	1024.661	3.416	24.5
16	770.986	2.570	198.7
17	469.270	1.564	22.5
18	465.755	1.553	21.0
19	463.412	1.545	21.3
20	459.311	1.531	32.2
21	455.210	1.518	38.7
22	453.452	1.512	38.2
23	448.765	1.496	28.6
24	446.422	1.488	31.9
25	443.493	1.479	32.1
26	440.563	1.469	28.0
27	434.119	1.447	20.0
28	408.341	1.361	21.9
29	400.725	1.336	24.0
30	397.796	1.326	28.8
31	393.109	1.311	25.9
32	315.776	1.053	84.1
33	308.746	1.029	86.8
34	248.403	0.828	170.3
35	241.958	0.807	159.8



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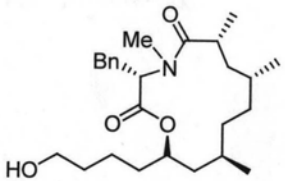
INDEX	FREQUENCY	PPM	HEIGHT
1	13335.216	176.801	15.0
2	12833.383	170.148	14.0
3	10459.735	138.677	14.1
4	9758.863	129.385	43.2
5	9680.518	128.346	50.9
6	9534.415	126.409	28.3
7	5839.485	77.421	50.8
8	5807.723	77.000	52.5
9	5775.962	76.579	53.0
10	5517.634	73.154	22.0
11	5041.211	66.837	29.2
12	4721.478	62.598	26.9
13	2985.178	39.578	19.8
14	2949.182	39.101	24.1
15	2786.139	36.939	23.1
16	2680.267	35.536	23.7
17	2589.217	34.328	25.9
18	2508.755	33.262	25.2
19	2453.701	32.532	22.1
20	2432.527	32.251	22.6
21	2366.886	31.381	24.7
22	2051.388	27.198	24.3
23	1810.000	23.997	25.6
24	1676.601	22.229	21.6
25	1632.135	21.639	23.8
26	1608.843	21.330	27.7
27	1411.922	18.720	24.3



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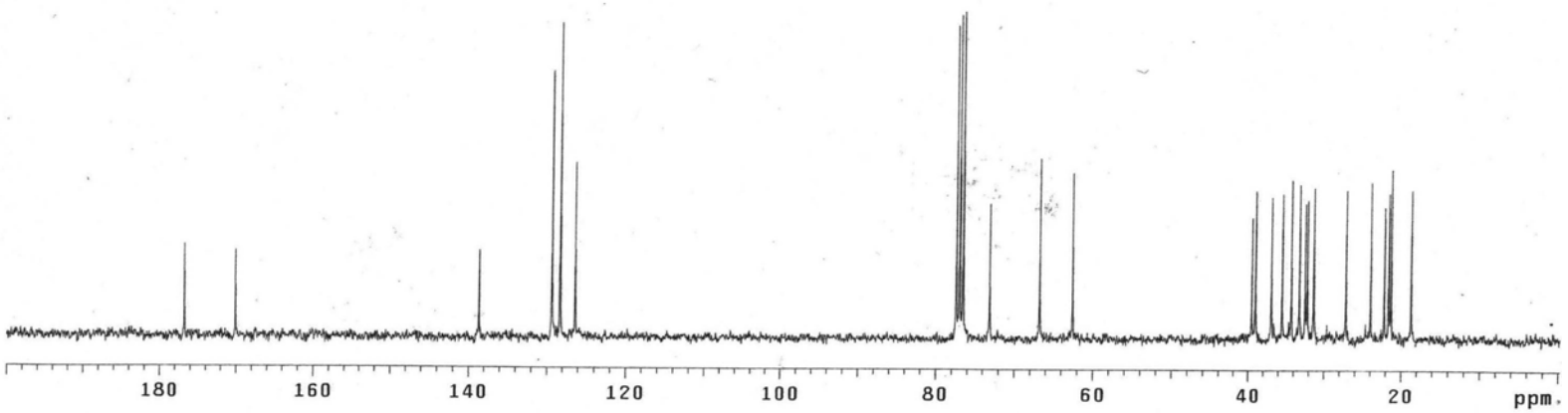

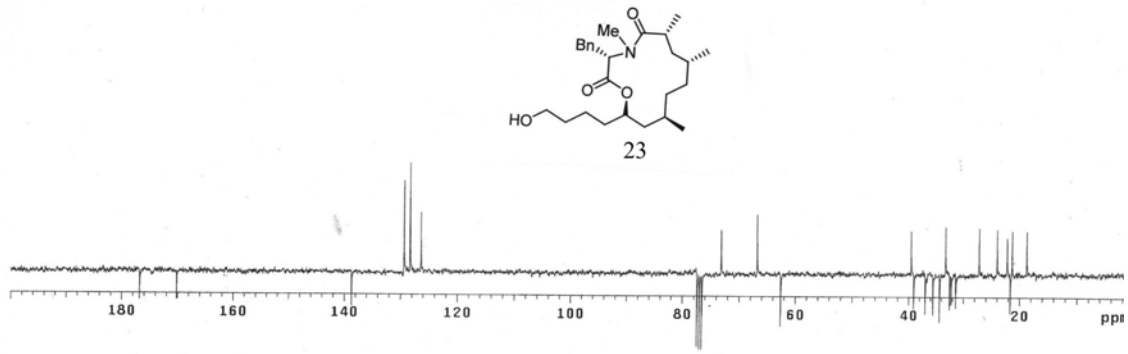

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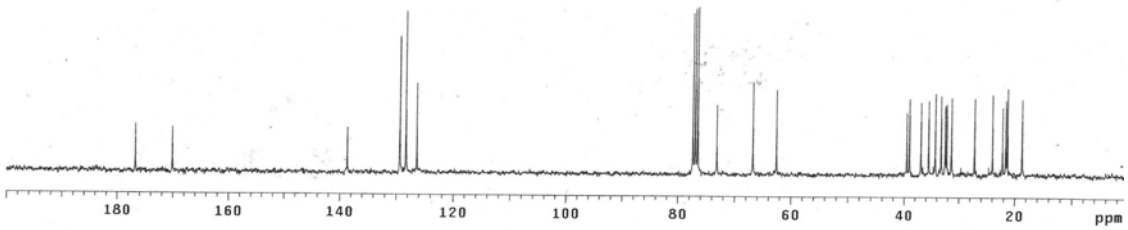
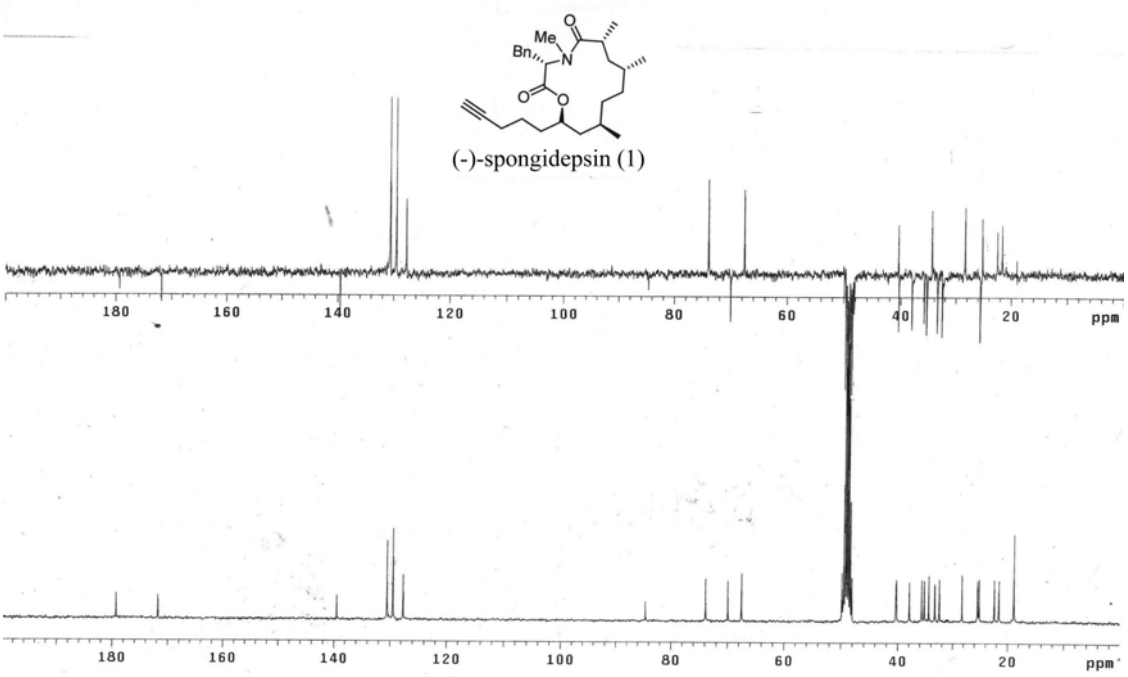
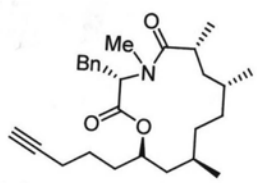




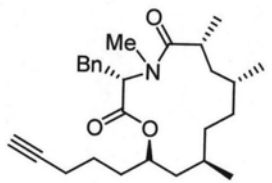
(-)-spongidepsin (1)

INDEX	FREQUENCY	PPM	HEIGHT
1	2163.564	7.213	26.2
2	2161.807	7.207	17.2
3	2159.463	7.199	14.1
4	2156.534	7.189	27.0
5	2150.090	7.168	15.3
6	2143.059	7.144	15.5
7	2128.999	7.098	25.3
8	2127.241	7.092	30.1
9	2120.797	7.070	21.3
10	1048.095	3.494	16.6
11	1044.580	3.482	20.9
12	1039.893	3.467	16.3
13	1027.005	3.424	17.2
14	770.986	2.570	184.8
15	646.784	2.156	21.3
16	644.441	2.148	20.9
17	568.866	1.896	27.4
18	476.301	1.588	20.6
19	469.856	1.566	23.3
20	463.998	1.547	25.0
21	451.695	1.506	22.3
22	445.250	1.484	20.5
23	438.220	1.461	14.2
24	408.341	1.361	17.5
25	398.382	1.328	31.9
26	316.948	1.057	57.1
27	309.918	1.033	64.1
28	249.574	0.832	93.4
29	243.716	0.812	98.2
30	236.100	0.787	18.1
31	234.342	0.781	16.5
32	-0.000	-0.000	13.5



(−)-spongidepsin (1)

INDEX	FREQUENCY	PPM	HEIGHT
1	13527.099	179.345	10.5
2	12959.625	171.821	9.7
3	10522.454	139.509	9.9
4	9846.991	130.553	33.3
5	9766.529	129.486	38.3
6	9628.895	127.662	18.8
7	6382.862	84.625	7.9
8	5574.001	73.901	17.6
9	5277.560	69.971	16.8
10	5095.460	67.556	19.9
11	3759.356	49.842	20.4
12	3738.182	49.561	57.6
13	3717.008	49.281	107.7
14	3695.833	49.000	117.4
15	3672.541	48.691	94.3
16	3651.367	48.410	50.4
17	3630.193	48.130	18.4
18	3045.780	40.381	15.6
19	3039.427	40.297	17.6
20	2863.680	37.967	16.6
21	2696.402	35.749	17.6
22	2660.406	35.272	17.1
23	2599.000	34.458	19.3
24	2516.420	33.363	15.8
25	2450.780	32.493	17.8
26	2135.281	28.310	19.7
27	1921.420	25.475	17.3
28	1900.246	25.194	18.1
29	1694.854	22.471	17.5
30	1631.331	21.628	17.2
31	1428.057	18.933	36.9



(-)-spongidepsin (1)