Total Synthesis of (–)-Archazolid B.

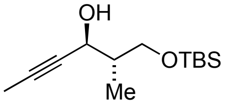
Paul A. Roethle, Ingrid T. Chen, and Dirk Trauner*

Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720-1460.

Supporting Information

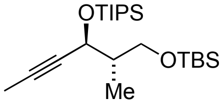
General Experimental Details: All reactions were carried out under an inert N_2 atmosphere in oven-dried glassware. Flash column chromatography was carried out with EcoChrom ICN SiliTech 32-63 D 60 Å silica gel. Reactions and chromatography fractions were monitored with Merck silica gel 60 F_{254} plates and visualized with potassium permanganate, ceric ammonium molybdate, and anisaldehyde. Tetrahydrofuran (THF), toluene ($PhCH_3$), diethyl ether (Et_2O), and methylene chloride (CH_2Cl_2) were dried by passage through activated alumina columns. *N*-Butyllithium (*n*BuLi) was titrated with diphenylacetic acid prior to use. All other reagents and solvents were used without further purification from commercial sources. Organic extracts were dried over $MgSO_4$ unless otherwise noted.

Instrumentation: FT-IR spectra were obtained on NaCl plates with an ATI Mattson Gemini spectrometer. Proton and carbon NMR spectra (^1H NMR and ^{13}C NMR) were recorded in deuterated chloroform ($CDCl_3$) on a Bruker DRX-500 spectrometer and calibrated to residual solvent peaks. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet. Melting points were determined with an electrothermal apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 241 Polarimeter.



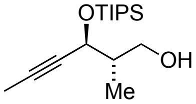
(2S,3S)-1-(*tert*-Butyl-dimethyl-silanyloxy)-2-methyl-hex-4-yn-3-ol (S1). To neat **9** (16.2 g, 67.4 mmol) was added a solution of (*S*)-Alpine Borane (0.5 M in THF, 270 mL, 135 mmol). The solution was concentrated to make the reaction mixture approximately 1 M in THF. The reaction was stirred at 40 ºC for 42 h. The reaction was cooled to rt and propionaldehyde (10 mL) was added. After 30 min, the reaction was cooled to 0 ºC, diluted with Et_2O (135 mL) and a 3:2 mixture of 3 M NaOH and 30% aqueous H_2O_2 (70 mL) was added slowly. After stirring at rt for 18 h, the reaction mixture was poured onto a saturated K_2CO_3 solution (100 mL). The layers were separated, and the aqueous was extracted 1 x Et_2O (100 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography twice (7-9% EtOAc/Hex) to give 14.5 g (89%) of **S1** as a colorless oil.

R_f 0.42, 20% EtOAc/Hexanes. ^1H NMR (500 MHz): δ 4.35 (m, 1 H), 3.89 (dd, 1 H, *J* = 10, 4 Hz), 3.56 (dd, 1 H, *J* = 10, 6.5 Hz), 3.46 (br d, 1 H, *J* = 5 Hz), 1.88 (m, 1 H), 1.86 (s, 3 H), 0.99 (d, 3 H, *J* = 7 Hz), 0.90 (s, 9 H), 0.76 (s, 6 H). ^{13}C (125 MHz): δ 81.3, 79.2, 67.1, 66.9, 40.8, 25.7, 18.1, 13.0, 3.5, –5.6, –5.7. IR: 3417, 2956, 2929, 2858.



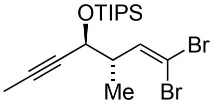
(4S,5S)-6-(*tert*-Butyl-dimethyl-silanyloxy)-5-methyl-4-triisopropylsilanyloxy-hex-2-yne (S2). To a solution of **S1** (9.70 g, 40.0 mmol) in CH_2Cl_2 was added imidazole (3.27 g, 48.0 mmol), triisopropylsilyl chloride (9.42 mL, 44.0 mmol), and DMAP (49 mg, 0.40 mmol). After stirring at rt for 18 h, filtered through celite with CH_2Cl_2. The solution was concentrated *in vacuo*. The crude oil was purified by flash column chromatography (1% EtOAc/Hex) to give 14.8 g (93%) of **S2** as a colorless oil.

R_f 0.48, 100% Hexanes. ^{1}H NMR (500 MHz): δ 4.64 (m, 1 H), 3.52 (m, 2 H), 1.94 (m, 1 H), 1.81 (m, 3 H), 1.11 (m, 21 H), 0.93 (d, 3 H, J = 7 Hz), 0.89 (s, 9 H), 0.04 (s, 3 H), 0.03 (s, 3 H). ^{13}C (125 MHz): δ 80.8, 78.9, 65.0, 64.5, 43.2, 25.8, 18.2, 18.0, 12.3, 11.2, 3.4, –5.5, –5.6. IR: 2944, 2893, 2866, 1464, 1255 1084 cm^{-1}. $[\alpha]^{25}_D$ +3.1° (c = 0.97, $CHCl_3$). HRMS (EI+) calcd for $C_{21}H_{43}O_2Si_2$ $[(M – Me)^+]$ 383.2802, found 383.2807.



(2S,3S)-2-Methyl-3-triisopropylsilanyloxy-hex-4-yn-1-ol (10). A solution of **S2** (11.3 g, 28.3 mmol) in 2:1:1 acetic acid/THF/H_2O (160 mL total) was stirred at rt 16 h. The reaction mixture was then poured onto H_2O (200 mL) and Et_2O (150 mL). The layers were separated. The organics were washed 2 x H_2O (200 mL) and 1 x saturated $NaHCO_3$ solution (200 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (10% EtOAc/Hexanes) to give 7.77 g (97%) of **10** as a colorless oil.

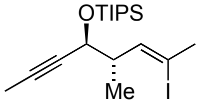
R_f 0.31, 10% EtOAc/Hexanes. ^{1}H NMR (500 MHz): δ 4.49 (m, 1 H), 3.77 (dd, 1 H, J = 11, 4 Hz), 3.62 (dd, 1 H, J = 11, 7 Hz), 2.48 (br s, 1 H), 1.92 (m, 1 H), 1.82 (s, 3 H), 1.15 (m, 3 H), 1.10, (m, 18 H), 1.01 (d, 3 H, J = 7 Hz). ^{13}C (125 MHz): δ 81.7, 79.6, 67.4, 65.9, 42.4, 18.0, 13.0, 12.3, 3.4. IR: 3385, 2943, 2866, 1462 cm^{-1}. $[\alpha]^{25}_D$ –34.0° (c = 0.77, $CHCl_3$). HRMS (EI+) calcd for $C_{13}H_{25}O_2Si$ $[(M – C_3H_7)^+]$ 241.1624, found 241.1625.



((1S,2S)-4,4-Dibromo-2-methyl-1-prop-1-ynyl-but-3-enyloxy)-triisopropyl-silane (11). To a solution of **S2** (10.2 g, 36.0 mmol) in CH_2Cl_2 (144 mL) was added $NaHCO_3$ (15.1 g, 180 mmol) followed by Dess-Martin periodinane (16.0 g, 37.8 mmol). After 20 min, a 1:1:1 solution of saturated $NaHCO_3$, saturated $Na_2S_2O_3$, and H_2O (150 mL total) was added. The resulting biphasic mixture was stirred vigorously for 30 min. The layers were separated, and the aqueous was extracted 1 x CH_2Cl_2 (75 mL). The organics were dried, filtered, and concentrated *in vacuo*. Meanwhile, to a solution of PPh_3 (49.1 g, 187 mmol) and K_2CO_3 (6.47 g, 46.8 mmol) in CH_2Cl_2

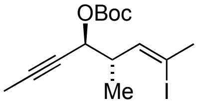
(187 mL) at 0 ºC was added CBr_4 (31.0 g, 93.6 mmol) in CH_2Cl_2 (94 mL) via cannula over 30 min. After 40 min, the aldehyde in CH_2Cl_2 (36 mL) was added over 5-10 min. After 1 h, the reaction mixture was poured onto a saturated $NaHCO_3$ solution (200 mL). The layers were separated, and the aqueous was extracted 1 x CH_2Cl_2 (100 mL). The organics were dried, filtered, and concentrated *in vacuo*. A 1:1 solution of Et_2O and hexanes was added. The suspension was filtered and washed with Et_2O. The solution was concentrated and this was repeated three times. The resulting oil was purified by flash column chromatography (100 % Hexanes) to give 11.8 g (75%) of **11** as a colorless oil.

R_f 0.53, 100% Hexanes. ^{1}H NMR (500 MHz): δ 6.34 (d, 1 H, J = 9.5 Hz), 4.38 (m, 1 H), 2.71 (m, 1 H), 1.83 (s, 3 H), 1.51-1.07 (m, 24 H). ^{13}C (125 MHz): δ 140.4, 88.7, 81.5, 78.7, 65.1, 45.7, 18.0, 13.7, 12.2, 3.5. IR: 3423, 2943, 2866, 1463, 1095, 1066 cm^{-1}. $[\alpha]^{25}_D$ +38.5° (c = 1.11, $CHCl_3$). HRMS (EI+) calcd for $C_{14}H_{23}OSiBr_2$ $[(M - C_3H_7)^+]$ 396.9844, found 396.9845.



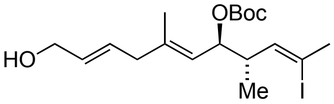
((Z)-(1S,2S)-4-Iodo-2-methyl-1-prop-1-ynyl-pent-3-enyloxy)-triisopropyl-silane (S3). To a suspension of CuI (14.3 g, 75.0 mmol) in Et_2O (214 mL) at 0 ºC was added MeLi (1.60 M in Et_2O, 93.8 mL, 150 mmol) over 30 min via syringe pump. After 5 min, cooled to –78 ºC. A solution of **11** (11.0 g, 25.0 mmol) in Et_2O (100 mL) was added via syringe pump with the needle wrapped in dry ice over 1 h. After 30 min, I_2 (38.0 g, 150 mmol) in Et_2O (150 mL) was added via cannula over 20 min. The reaction mixture had difficulty stirring after addition of the I_2 solution. After 10 min, the reaction was warmed to 0 ºC upon which stirring resumed. The reaction was poured onto a saturated NH_4Cl solution (400 mL). The layers were separated, and the aqueous was extracted 1 x Et_2O (200 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (100% hexanes) to give 8.91 g (72%) of **S3**. (77% on 2.7 g scale). The product was often contaminated with dimethyl adduct and/or vinyl bromide as noted by Tanino and Miyashita. Analytically pure material could be obtained by flash column chromatography with 6% by weight $AgNO_3$ on SiO_2 and eluted with 100% hexanes.

R_f 0.46, 100% Hexanes. ^{1}H NMR (500 MHz): δ 5.32 (dd, 1 H, J = 9, 1.5 Hz), 4.39 (m, 1 H), 2.61 (m, 1 H), 2.50 (s, 3 H), 1.83 (s, 3 H), 1.17-1.04 (m, 24 H). ^{13}C (125 MHz): δ 137.3, 100.5, 80.9, 79.2, 65.5, 48.7, 33.8, 18.0, 13.7, 12.3, 3.5. IR: 2943, 2891, 2866, 1462, 1085, 1065 cm^{-1}. $[\alpha]^{25}_D$ +80.0° (c = 1.03, $CHCl_3$). HRMS (EI+) calcd for $C_{15}H_{26}OSiI$ $[(M - C_3H_7)^+]$ 377.0798, found 377.0787.



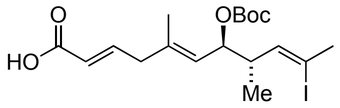
Carbonic acid *tert*-butyl ester (Z)-(1S,2S)-4-iodo-2-methyl-1-prop-1-ynyl-pent-3-enyl ester (12). To a solution of **S3** (7.50 g, 17.8 mmol) in THF (49 mL) at 0 ºC was added tetrabutylammonium fluoride (1.0 M in THF, 22.3 mL, 22.3 mmol) over 5 min. After 20 min at 0 ºC, the reaction was warmed to rt. Then after 15 min, the mixture was poured onto a saturated $NaHCO_3$ solution (75 mL). The layers were separated, and the aqueous was extracted 1 x Et_2O (50 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was dissolved in CH_2Cl_2 (59 mL) and pyridine (4.33 mL, 53.5 mmol), di-*tert*-butyl dicarbonate (Boc_2O) (8.55 g, 39.2 mmol), and DMAP (218 mg, 1.78 mmol) were added sequentially. After 1.5 h, the reaction mixture was poured onto 0.5 M citric acid solution (75 mL). The layers were separated, and the aqueous was extracted 1 x CH_2Cl_2 (50 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (3% EtOAc/Hexanes) to give 6.45 g (99%) of **12** as a colorless oil.

R_f 0.42, 5% EtOAc/Hexanes. ^{1}H NMR (500 MHz): δ 5.35 (dd, 1 H, J = 9, 1.5 Hz), 5.11 (m, 1 H), 2.78 (m, 1 H), 2.50 (s, 3 H), 1.86 (s, 3 H), 1.49 (s, 9 H), 1.11 (d, 3 H, J = 6.5 Hz). ^{13}C (125 MHz): δ 152.7, 135.6, 101.9, 83.3, 82.4, 74.8, 69.5, 46.0, 33.8, 27.7, 14.8, 3.7. IR: 2978, 1743, 1275, 1254 cm^{-1}. $[\alpha]^{25}_D$ +49.2° (c = 0.65, $CHCl_3$). HRMS (FAB+) calcd for $C_{14}H_{22}O_3I$ [$(M + H)^+$] 365.0614, found 365.0610.



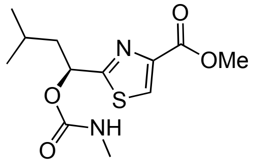
Carbonic acid *tert*-butyl ester (2E,5E)-(S)-7-hydroxy-1-((Z)-(S)-3-iodo-1-methyl-but-2-enyl)-3-methyl-hepta-2,5-dienyl ester (13). To a solution of **12** (1.00 g, 2.75 mmol) in acetone (5.5 mL) was added 3-buten-1-ol (709 µL, 8.24 mmol) followed by $RuCp(MeCN)_3PF_6$ (60 mg, 0.14 mmol). After 25 min, the reaction mixture was concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (25% EtOAc/Hexanes) to give 1.05 g (88%) of **13** as a light yellow oil.

R_f 0.33, 25% EtOAc/Hexanes. ^{1}H NMR (500 MHz): δ 5.66 (m, 2 H), 5.33 (d, 1 H, J = 8 Hz), 5.29 (m, 1 H), 5.18 (m, 1 H), 4.09 (m, 2 H), 2.74 (m, 2 H), 2.61 (m, 1 H), 2.49 (s, 3 H), 1.72 (s, 3 H), 1.46 (s, 9 H), 0.97 (d, 3 H, J = 7 Hz). ^{13}C (125 MHz): δ 153.2, 139.7, 136.4, 131.1, 129.8, 122.6, 101.5, 81.7, 76.4, 63.5, 46.3, 42.1, 33.7, 27.8, 17.1, 15.6. IR: 3385, 2977, 2931, 2872, 1736, 1276, 1254, 1159 cm^{-1}. $[\alpha]^{25}_D$ +44.4° (c = 0.50, $CHCl_3$). HRMS (FAB+) calcd for $C_{18}H_{29}O_4ILi$ [$(M + Li)^+$] 443.1271, found 443.1273.



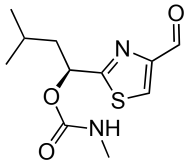
(2E,5E,9Z)-(7S,8S)-7-*tert*-Butoxycarbonyloxy-10-iodo-5,8-dimethyl-undeca-2,5,9-trienoic acid (6). To a solution of **13** (2.32 g, 5.32 mmol) in CH_2Cl_2 (27 mL) was added $NaHCO_3$ (2.23 g, 26.6 mmol) followed by Dess-Martin periodinane (2.37 g, 5.58 mmol). After 20 min, a 1:1:1 solution of saturated $NaHCO_3$, saturated $Na_2S_2O_3$, and H_2O (30 mL total) was added. The resulting biphasic mixture was stirred vigorously for 30 min. The layers were separated, and the aqueous was extracted 1 x CH_2Cl_2 (25 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was dissolved in *t*BuOH (20.2 mL) and 2-methyl-2-butene (1.06 mL). To the solution was added a solution of $NaClO_2$ (80% purity, 5.41 g, 47.9 mmol) and NaH_2PO_4 in H_2O (21.3 mL). After 45 min, the yellow, biphasic reaction mixture was poured onto H_2O (30 mL) and Et_2O (60 mL). The mixture was acidified using a 1 M HCl solution (~5 mL). The layers were separated. The organics were dried, filtered, and concentrated *in vacuo*. This gave 2.38 g (99%) of **6** as a light yellow oil and was taken on without further purification.

R_f 0.48, 40% EtOAc/Hexanes. ^1H NMR (500 MHz): δ 7.03 (dt, 1 H, *J* = 15.5, 7 Hz), 5.85 (d, 1 H, *J* = 15.5 Hz), 5.34 (d, 1 H, *J* = 9 Hz), 5.28 (m, 1 H), 5.24 (m, 1 H), 2.92 (d, 2 H, *J* = 7 Hz), 2.63 (m, 1 H), 2.49 (s, 3 H), 1.75 (s, 3 H), 1.48 (s, 9 H), 0.95 (d, 3 H, *J* = 7 Hz). ^{13}C (125 MHz): δ 171.2, 153.1, 148.7, 137.2, 136.0, 124.5, 122.1, 101.8, 81.9, 76.1, 46.1, 42.0, 33.7, 27.8, 17.3, 15.6. IR: 2977, 1736, 1698, 1276, 1254, 1157 cm^{-1}. $[\alpha]^{25}_D$ +46.5° (*c* = 1.26, $CHCl_3$). HRMS (FAB+) calcd for $C_{18}H_{27}O_5ILi$ [$(M + Li)^+$] 457.1063, found 457.1069.



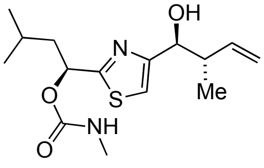
2-((S)-3-Methyl-1-methylcarbamoyloxy-butyl)-thiazole-4-carboxylic acid methyl ester (S4). To a solution of **14** (17.2 g, 75.0 mmol) in CH_2Cl_2 (150 mL) was added carbonyldiimidazole (CDI) (24.3 g, 150 mmol) in portions over 1.5 h. The reaction was cooled to 0 ºC and a solution of $MeNH_2$ (2.0 M in THF, 46.9 mL, 93.8 mmol) was added. The reaction was warmed to rt and after 10 min, a saturated $NaHCO_3$ solution (200 mL) was added. The layers were separated, and the aqueous was extracted 1 x CH_2Cl_2 (100 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (40-45% EtOAc/Hexanes) to give 16.9 g (79%) of **S4** as a white solid. (88% on 2.3 g scale)

mp 77-79 ºC. R_f 0.45, 50% EtOAc/Hexanes. ^1H NMR (500 MHz): δ 8.11 (s, 1 H) 6.08 (m, 1 H), 4.89 (br s, 1 H) 3.92 (s, 3 H), 2.80 (d, 3 H, *J* = 4.5 Hz) 1.87 (m, 2 H), 1.74 (m, 1 H), 0.95 (d, 3 H, *J* = 6.5 Hz), 0.92 (d, 3 H, *J* = 6.5 Hz). ^{13}C (125 MHz): δ 172.7, 161.8, 155.8, 146.7, 127.5, 72.1, 52.4, 44.2, 27.6, 24.6, 23.1, 21.7. IR: 3358, 2957, 1724, 1533, 1244 cm^{-1}. $[\alpha]^{25}_D$ –36.7° (*c* = 1.01, $CHCl_3$). HRMS (EI+) calcd for $C_{12}H_{19}N_2O_4S$ [$(M + H)^+$] 287.1066, found 287.1076.



Methyl-carbamic acid (S)-1-(4-formyl-thiazol-2-yl)-3-methyl-butyl ester (S5). To a solution of **S4** (9.70 g, 33.9 mmol) in THF (68 mL) at –78 ºC was added a solution of DIBAL-H (1.0 M in $PhCH_3$, 81.3 mL, 81.3 mmol) via cannula over 45 min. After 1.5 h, a ½ saturated Rochelle's salt solution (150 mL) was added. The reaction mixture was stirred vigorously for 2 h at rt. The layers were separated, and the aqueous was extracted 1 x Et_2O (100 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (40% EtOAc/Hexanes) to give 6.92 g (80%) of **S5** as a white solid.

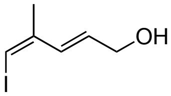
mp 57-59 ºC. R_f 0.47, 40% EtOAc/Hexanes. ^{1}H NMR (500 MHz): δ 10.0 (s, 1 H), 8.13 (s, 1 H), 6.07 (m, 1 H), 4.87 (br s, 1 H), 2.82 (d, 3 H, $J = 5$ Hz), 1.93 (m, 1 H), 1.86 (m, 1 H), 1.74 (m, 1 H), 0.99 (m, 6 H). ^{13}C (125 MHz): δ 184.7, 173.0, 155.8, 154.7, 127.4, 71.9, 44.1, 27.6, 24.5, 23.0, 21.8. IR: 3355, 2958, 1701, 1539, 1253, 1132 cm^{-1}. $[\alpha]^{25}_{D}$ –32.1° (c = 0.93, $CHCl_3$). HRMS (EI+) calcd for $C_{11}H_{17}N_2O_3S$ [$(M + H)^+$] 257.0960, found 257.0967.



Methyl-carbamic acid (S)-1-[4-((1S,2S)-1-hydroxy-2-methyl-but-3-enyl)-thiazol-2-yl]-3-methyl-butyl ester (7). To a solution of trans-2-butene (condensed) in THF (26 mL) at –78 ºC was added a solution of KO*t*Bu (3.37 g, 30.0 mmol) in THF (30 mL) via cannula over 15 min. A solution of *n*BuLi (2.50 M in hexanes, 12.0 mL, 30.0 mmol) was then added dropwise to give a bright yellow solution. After warming to –45 ºC and stirring for 45 min, the mixture was cooled to –78 º C. A solution of (–)-MeOB(Ipc)$_2$ (10.3 g, 32.5 mmol) in THF (33 mL) was added over 5 min. The reaction mixture became clear upon this addition. After 1 h at –78 ºC, a solution of **S5** (6.41 g, 25.0 mmol) in THF (25 mL) was added dropwise. The reaction was warmed to –30 ºC over 3 h. A 3:2 mixture of 3 M NaOH/30% aqueous H_2O_2 (50 mL total) was added slowly. The reaction mixture was stirred at rt for 18 h. The layers were separated, and the aqueous was extracted 1 x Et_2O (150 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (40% EtOAc/Hexanes) to give 7.01 g (90%) of **7** as a clear, viscous oil.

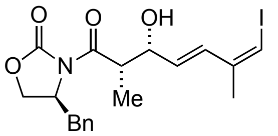
R_f 0.36, 40% EtOAc/Hexanes. ^{1}H NMR (500 MHz): δ 7.07 (s, 1 H), 6.01 (m, 1 H), 5.76 (m, 1 H), 5.11 (s, 1 H), 5.09 (s, 1 H), 4.86 (br s, 1 H), 4.60 (d, 1 H, $J = 6$ Hz), 2.79 (d, 3 H, $J = 5$ Hz), 2.73 (m, 1 H), 2.63 (br s, 1 H), 1.88 (m, 1 H), 1.81 (m, 1 H), 1.68 (m, 1 H), 0.98 (d, 3 H, $J = 6.5$ Hz), 0.94 (m, 6 H). ^{13}C (125 MHz): δ 170.8, 158.0, 156.0, 139.5, 116.5, 114.2, 74.0, 72.0, 44.3, 44.1, 27.6, 24.5, 22.9, 22.0, 16.0. IR: 3346, 2959, 2871, 1709, 1527, 1258, 1131 cm^{-1}. $[\alpha]^{25}_{D}$ –

79.6° (*c* = 2.00, $CHCl_3$). HRMS (EI+) calcd for $C_{15}H_{25}N_2O_3S$ [(M+H)+] 313.1586, found 313.1583.



(2E,4Z)-5-Iodo-4-methyl-penta-2,4-dien-1-ol (S6). To a solution of **15** (16.8 g, 66.7 mmol) in CH_2Cl_2 (500 mL) at –78 °C was added DIBAL-H (1.5 M in $PhCH_3$, 161 mL, 241 mmol) via cannula. The reaction was stirred at –78 °C for 15 min then diluted with CH_2Cl_2 (500 mL), and a ½ saturated Rochelle's salt solution (1200 mL) was added. The biphasic mixture was vigorously stirred at rt for 2 h. The layers were separated, and the aqueous was extracted 1 x Et_2O (200 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (25% EtOAc/Hexanes) to give 14.3 g (96%) of **S6** as a yellow oil.

R_f 0.28, 25 % EtOAc/Hexanes. ^{1}H NMR (500 MHz): δ 6.61 (d, 1 H, *J* = 15.5 Hz), 6.32 (s, 1 H), 6.02 (dt, 1 H, *J* = 16.0, 5.5 Hz), 4.26 (dd, 1 H, *J* = 5.5, 1.0 Hz), 2.15 (s, 1 H), 1.95 (s, 3 H). ^{13}C NMR (125 MHz): δ 141.3, 133.4, 132.1, 79.8, 63.1, 21.2. IR: 3331, 3120, 2914, 2852, 1675, 1439, 1295, 1156, 1096, 1025, 1005, 966 cm^{-1}. HRMS (FAB+) calcd for C_6H_9IO (M^+) 223.9698, found 223.9697. Anal. Calcd for C_6H_9IO: C, 32.17; H, 4.05. Found: C, 32.34; H, 4.01.

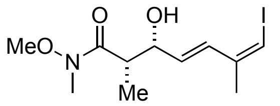


(S)-4-Benzyl-3-((4E,6Z)-(2S,3R)-3-hydroxy-7-iodo-2,6-dimethyl-hepta-4,6-dienoyl)-oxazolidin-2-one (17). To a solution of **S6** (14.4 g, 64.1 mmol) in CH_2Cl_2 (500 mL) was added $NaHCO_3$ (18.8 g, 224 mmol). The reaction was cooled to 0 °C, covered in foil to protect from light, and then added Dess-Martin periodinane (25.8 g, 160 mmol). After 20 min, a 1:1:1 solution of saturated $NaHCO_3$, saturated $Na_2S_2O_3$, and H_2O (600 mL total) was added. The resulting biphasic mixture was stirred vigorously for 30 min. The layers were separated, and the aqueous was extracted 1 x Et_2O (200 mL). The organics were dried, filtered, and concentrated *in vacuo*. The crude material was filtered through a pad of silica to give 14.2 g (>99%) of an unstable aldehyde as white solid, (note that product was generally taken on crude and that isomerization and polymerization were observed on exposure to light).

R_f 0.50, 25 % EtOAc/Hexanes. ^{1}H NMR (400MHz): δ 9.73 (d, 1 H, *J* = 7.6 Hz), 7.48 (d, 1 H, *J* = 15.6 Hz), 6.78 (s, 1 H), 6.29 (dd, 1 H, *J* = 15.6, 7.6 Hz), 2.03 (s, 3 H). ^{13}C NMR (100 MHz): δ 193.9, 152.1, 141.1, 132.1, 90.8, 21.0. IR: 3055.5, 2980, 2820, 2720, 1681, 1608, 1441, 1304, 1265, 1165, 1122, 970, 742, 705 cm^{-1}. HRMS (FAB+) calcd for C_6H_7IO (M^+) 221.9542, found 221.9537.

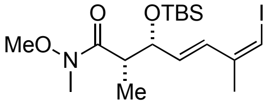
To a solution of **16** (5.92 g, 25.4 mmol) in CH_2Cl_2 (60 mL) at 0 °C was added freshly distilled Bu_2BOTf (6.73 mL, 26.9 mmol) dropwise, followed by Et_3N (4.70 mL, 34.0 mmol). The light orange solution was stirred at 0 °C for 40 min, then cooled to –78 °C and covered flask in foil to protect from light. A solution of the crude aldehyde (6.21 g, 29.0 mmol) in CH_2Cl_2 (15 mL) was added dropwise over 15 min. The reaction was stirred at –78°C for 10 min, then a 1:3 solution of pH 7 phosphate buffer (20 mL) and MeOH (60 mL) was added. The mixture was warmed to 0 °C, stirred for 10 min. Then a 1:2 solution of 30 % H_2O_2 (25 mL) and MeOH (50 mL) was added. After 30 min, the mixture was warmed to rt and stirred for an additional 90 min. The solution was diluted with EtOAc (200 mL), washed with a saturated $NaHCO_3$ solution (2 x 200 mL), then brine (100 mL). The organics were dried, filtered, and concentrated *in vacuo*. The crude product was recrystallized from ether and hexanes (1:20**)**. The condensed mother liquor was purified by flash column chromatography (25% EtOAc/Hexanes) to afford 8.12 g (70%) of **17** as a white crystalline solid and a single diastereomer. (76% on 1.0 g scale)

mp 92-93 °C. R_f 0.49, 5 % EtOAc/CH_2Cl_2. ^{1}H NMR (500 MHz): δ 7.32 (m, 1 H), 7.26 (m, 1 H), 7.19 (d, 1 H, *J* = 7.5 Hz), 6.65 (d, 1 H, *J* = 15.5 Hz), 6.14 (s, 1 H), 5.89 (dd, 1 H, *J* = 15.5, 6.0 Hz), 4.71 (m, 1 H), 4.60 (s, 1 H), 4.18 (m, 2 H), 3.93 (m, 1 H), 3.22 (dd, 1 H, *J* = 13.5, 3.0 Hz), 3.13 (s, 1 H), 2.79 (dd, 1 H, *J* = 12.5, 9.5 Hz), 2.07 (s, 3 H), 1.24 (d, 3 H, J = 7.0 Hz). ^{13}C NMR (125 MHz): δ 176.0, 153.2, 141.3, 135.1, 134.0, 132.6, 129.5, 128.9, 127.4, 80.3, 72.6, 66.3, 55.1, 42.9, 37.7, 21.2, 11.7. IR: 3691, 3054, 2987, 2685, 2305, 1782, 1551, 1422, 1263, 1157, 896, 750 cm^{-1}. $[\alpha]^{25}_D$ +38.0° (*c* = 1.00, $CHCl_3$). HRMS (FAB+) calcd for $C_{19}H_{22}INO_4Li$ $[(M + Li)^+]$ 462.0754, found 462.0745. Anal. Calcd for $C_{19}H_{22}INO_4$: C, 50.12; H, 4.87; N, 3.08. Found: C, 50.28; H, 4.77; N, 3.00.



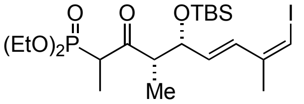
(4E,6Z)-(2S,3R)-3-Hydroxy-7-iodo-2,6-dimethyl-hepta-4,6-dienoic acid methoxy-methyl-amide (S7). To a solution of N,O-dimethylhydroxylamine hydrochloride (6.87 g, 70.4 mmol) in THF (30 mL) at 0 °C was added a solution of Me_3Al (2.0 M in toluene, 35.2 mL, 70.4 mmol) dropwise. Methane gas evolved. The reaction mixture was warmed to rt for 15 min, then cooled to –20 °C. A solution of **17** (8.02 g, 17.6 mmol) in THF (30 mL) was added. A white precipitate formed in the reaction. The mixture was warmed to 0 °C and stirred for 1 h. A solution of 0.5 N HCl (100 mL) in CH_2Cl_2 (100 mL) at 0 ºC was added via cannula. Vigorous gas evolution was observed. The layers were separated, and the aqueous was extracted 1 x CH_2Cl_2 (100 mL). The combined organic layers were washed with a saturated $NaHCO_3$ solution (2 x 100mL), and brine (50 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (50% EtOAc/Hexanes) to give 4.80 g (80%) of **S7** as a light yellow solid.

mp 70-71 °C. R_f 0.42, 55 % EtOAc/Hexanes. ^{1}H NMR (500 MHz): δ 6.67 (d, 1 H, *J* = 15.5 Hz), 6.14 (s, 1 H), 5.88 (dd, 1 H, *J* = 15.5, 5.5 Hz), 4.56 (s, 1 H), 3.94 (s, 1 H), 3.66 (s, 3 H), 3.20 (s, 3 H), 3.00 (br s, 1 H), 1.95 (s, 3 H), 1.18 (d, 3 H, *J* = 7.0 Hz). ^{13}C NMR (125 MHz): δ 177.4, 141.3, 134.1, 132.4, 79.7, 72.2, 61.6, 39.6, 31.9, 21.1, 10.8. IR: 3451, 3054, 2984, 2940, 2305, 1658, 1641, 1631, 1422, 1390, 1265, 1179, 1158, 995, 969, 896, 822, 738 cm^{-1}. $[\alpha]^{25}_{D}$ –1.4° (*c* = 1.00, $CHCl_3$). HRMS (FAB+) calcd for $C_{11}H_{19}INO_3$ [$(M + H)^+$] 340.0410, found 340.0420. Anal. Calcd for $C_{11}H_{18}INO_3$: C, 38.95; H, 5.35; N, 4.13. Found: C, 39.06; H, 5.40; N, 4.01.



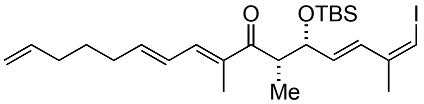
(4E,6Z)-(2S,3R)-3-(*tert*-Butyl-dimethyl-silanyloxy)-7-iodo-2,6-dimethyl-hepta-4,6-dienoic acid methoxy-methyl-amide (S8). To a solution of **S7** (4.70g, 13.9 mmol) in CH_2Cl_2 (70 mL) was added imidazole (2.08 g, 30.5 mmol) followed by TBSCl (4.18 g, 27.7 mmol). The reaction mixture was stirred at rt for 16 h. It was then diluted with Et_2O (50 mL). The organics were washed with a saturated $NaHCO_3$ solution (2 x 40 mL) and brine (30 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (12 % EtOAc/Hexanes) to give 5.58 g (89%) of **S8** as yellow oil.

R_f 0.48, 25 % EtOAc/Hexanes. ^{1}H NMR (500 MHz): δ 6.55 (d, 1 H, *J* = 16.0 Hz), 6.08 (s, 1 H), 5.91 (dd, 1 H, *J* = 15.5, 6.0 Hz), 4.36 (t, 1 H, *J* = 7.0 Hz), 3.77 (s, 3 H), 3.13 (s, 3 H), 3.04 (br s, 1 H), 1.90 (s, 3 H), 1.19 (d, 3 H, *J* = 7.0 Hz), 0.92 (s, 9 H), 0.20 (s, 3 H), 0.15 (s, 3 H). ^{13}C NMR (125 MHz): δ 175.5, 141.4, 136.3, 131.4, 79.0, 74.6, 61.5, 43.1, 32.1, 25.9, 21.2, 18.1, 14.4, –4.0, –4.9. IR: 3054, 2958, 2932, 2896, 2857, 2306, 1653, 1472, 1463, 1421, 1387, 1264, 1158, 1129, 1066, 1019, 995, 895, 838, 740 cm^{-1}. $[\alpha]^{25}_{D}$ –1.2° (*c* = 1.00, $CHCl_3$). HRMS (FAB+) calcd for $C_{17}H_{32}INO_3Si$ (M^+) 453.1196, found 453.1193. Anal. Calcd for $C_{17}H_{32}INO_3Si$: C, 45.03; H, 7.11; N, 3.09. Found: C, 44.73; H, 7.22; N, 3.08.



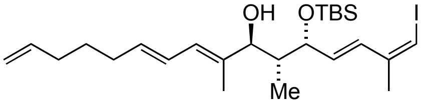
[(5E,7Z)-(3S,4R)-4-(*tert*-Butyl-dimethyl-silanyloxy)-8-iodo-1,3,7-trimethyl-2-oxo-octa-5,7-dienyl]-phosphonic acid diethyl ester (18). To a solution of diethylethylphosphonate (1.56 mL, 9.70 mmol) in THF (20 mL) at –78 °C was added *n*BuLi (2.50 M in hexanes, 3.57 mL, 8.92 mmol) dropwise. The reaction was stirred for 15 min and then a solution of **S7** (1.76 g, 3.88 mmol) in THF (20 mL) was added dropwise. The dark yellow solution was stirred at –78 °C for 15 min, then a saturated NH_4Cl solution (20 mL) was added. The mixture was warmed to rt and diluted with H_2O (20 mL). The layers were separated, and the aqueous was extracted 2 x CH_2Cl_2 (20 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (25 % to 50% EtOAc/Hexanes) to afford 2.05 g (95%) of **S8** as yellow oil and mixture of diastereomers of stereocenter alpha to phosphonate ester.

R_f 0.42, 65 % EtOAc/Hexanes. ^{1}H NMR (500 MHz) of major diastereomer: δ 6.47 (d, 1 H, *J* = 15.5 Hz), 6.12 (s, 1 H), 5.73 (dd, 1H, *J* = 15.5, 7.0 Hz), 4.25 (t, 1 H, *J* = 6.0 Hz), 4.10 (m, 4 H), 3.58 (m, 1 H), 3.38 (m, 1 H), 1.91 (s, 3 H), 1.28 (m, 10 H), 1.04 (d, 2 H, *J* = 7.0 Hz), 0.88 (s, 9 H), 0.02 (d, 6 H, *J* = 16.5 Hz). ^{13}C NMR (125 MHz), major diastereomer: δ 208.1, 141.1, 133.7, 132.5, 79.8, 76.1, 62.3, 62.3, 53.6, 48.8, 47.8, 25.8, 25.7, 21.1, 18.1, 16.4, 13.1, 11.4, –3.92, –4.23. IR: 3054, 2986, 2958, 2686, 2356, 1305, 1710, 1422, 1266, 1158, 1053, 1025, 1025, 972, 896, 838, 703 cm^{-1}. $[\alpha]^{25}_{D}$ +42.1° (c = 1.00, $CHCl_3$) for 3:1 mixture of diastereomers. HRMS (FAB+) calcd for $C_{21}H_{40}IO_5PSiLi$ [$(M + Li)^+$] 565.1587, found 565.1576. Anal. Calcd for $C_{21}H_{40}IO_5PSi$: C, 45.16; H, 7.22. Found: C, 45.57; H, 7.47.



(1Z,3E,8E,10E)-(5R,6S)-5-(*tert*-Butyl-dimethyl-silanyloxy)-1-iodo-2,6,8-trimethyl-hexadeca-1,3,8,10,15-pentaen-7-one (20). $Ba(OH)_2$ (6.59 g, 11.8 mmol) was dried *in vacuo* at 120 °C for 5 hours then cooled to rt and added to a solution of **18** (2.81 g, 5.03 mmol) in THF (35 mL). The light yellow suspension was stirred for 30 min. Then a solution of **19**[1] in wet THF (40:1 THF/H_2O, 41 mL) was added. The bright orange solution was stirred for 12 h. A saturated $NaHCO_3$ solution (50 mL) was added and followed by Et_2O (100 mL). The organics were washed with a saturated $NaHCO_3$ solution (2 x 100 mL) and brine (50 mL). The organics were dried, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (2.5 % EtOAc/Hexanes) to afford 4.95 g (79 %) of **20** as yellow oil. Product should be used promptly upon purification due to instability.

R_f 0.47, 10 % EtOAc/Hexanes. ^{1}H NMR (500 MHz): δ 6.99 (d, 1 H, J = 10.5 Hz), 6.51 (d, 1 H, J = 16.0 Hz), 6.41 (t, 1 H, J = 14.0 Hz), 6.12 (m, 1 H), 6.06 (s, 1 H), 5.80 (dd, 2 H, J = 15.5, 6.0 Hz), 5.02 (d, 1 H, J = 17.0 Hz), 4.97 (d, 1 H, J = 10.5 Hz), 4.35 (t, 1 H, J = 6.5 Hz), 3.40 (t, 1 H, J = 7.0 Hz), 2.22 (d, 1 H, J = 7.5 Hz), 2.08 (d, 1 H, J = 7.0 Hz), 1.84 (d, 6 H, J = 2.0 Hz), 1.55 (m, 2 H), 1.16 (d, 3 H, J = 6.5 Hz), 0.93 (s, 9 H), 0.07 (s, 3 H), 0.03 (s, 3 H). ^{13}C NMR (125 MHz): δ 204.2, 143.5, 141.4, 139.0, 138.2, 136.1, 134.5, 131.3, 126.9, 114.9, 79.0, 75.2, 46.7, 33.1, 32.7, 28.0, 25.9, 21.1, 18.1, 15.2, 11.7, –4.0, –4.9. IR: 3054, 2986, 2957, 2931, 2857, 2685, 2360, 2306, 1654, 1631, 1472, 1422, 1362, 1265, 1158, 1127, 1026, 971, 896, 838, 739 cm^{-1}. $[\alpha]^{25}_{D}$ –28.3° (c = 1.00, $CHCl_3$).



(1Z,3E,8E,10E)-(5R,6R,7S)-5-(*tert*-Butyl-dimethyl-silanyloxy)-1-iodo-2,6,8-trimethyl-hexadeca-1,3,8,10,15-pentaen-7-ol (S9). To a solution of **20** (4.95 g, 9.36 mmol) in methanol (120 mL) at 0 °C was added $NaBH_4$ (2.12 g, 56.2 mmol). There was vigorous evolution of gas. The reaction was stirred at 0 °C for 20 min. Then a saturated NH_4Cl solution (50 mL) was added. The mixture was extracted with 2 x Et_2O (100 mL). The organics were washed with brine (75 mL), then dried, filtered, and concentrated *in vacuo*. The crude oil was purified by flash column chromatography (10 % EtOAc/Hexanes) to give 4.55 g (92 %) of **S9** as yellow oil with > 95 : 5 diastereoselectivity.

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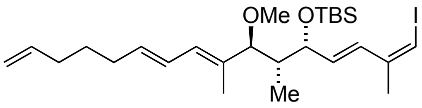
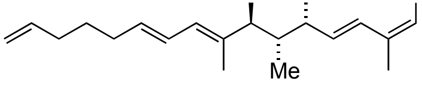
[1] Singh, O. V.; Han, H., *Org. Lett.* **2004**, *6*, 3067-3070.

R_f 0.35, 10 % EtOAc/Hexanes. ^{1}H NMR (500 MHz): δ 6.58 (d, 1 H, *J* = 15.5 Hz), 6.24 (m, 1 H), 6.13 (s, 1 H), 5.93 (m, 2 H), 5.79 (m, 1 H), 5.65 (m, 1 H), 4.99 (d, 1 H, *J* = 17.5 Hz), 4.94 (d, 1 H, *J* = 10.0 Hz), 4.55 (s, 1 H), 3.89 (d, 1 H, *J* = 9.5 Hz), 3.56 (s, 1 H), 2.11 (m, 2 H), 2.05 (m, 2 H), 1.97 (s, 1 H), 1.90 (m, 1 H), 1.71 (s, 3 H), 1.48 (dt, 2 H, *J* = 15.0, 7.5 Hz), 0.95 (s, 9 H), 0.67 (d, 3H, *J* = 7.0 Hz), 0.12 (s, 3 H), 0.08 (s, 3 H). ^{13}C NMR (125 MHz): δ 141.3, 138.6, 135.8, 134.5, 134.3, 132.4, 127.7, 126.3, 114.5, 80.4, 79.3, 75.8, 41.6, 33.2, 32.3, 28.6, 25.9, 25.9, 21.3, 18.1, 12.2, 11.2, –4.1, –5.2. IR: 3459, 3053, 2955, 2930, 2857, 2360, 1767, 1640, 1471, 1462, 1441, 1362, 1297, 1265, 1157, 1074, 1039, 1005, 970, 914, 894, 838, 811, 778, 740, 705 cm^{-1}. $[\alpha]^{25}_{D}$ +0.41° (*c* = 1.00, $CHCl_3$). HRMS (EI+) calcd for $C_{25}H_{43}IO_2Si$ (M^+) 530.2077, found.



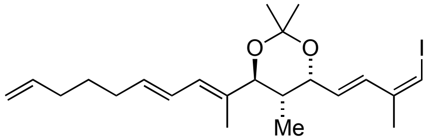
***tert*-Butyl-[(4E,6E)-(1R,2R,3S)-1-((1E,3Z)-4-iodo-3-methyl-buta-1,3-dienyl)-3-methoxy-2,4-dimethyl-dodeca-4,6,11-trienyloxy]-dimethyl-silane (S10)**. To a solution of **S9** (4.70 g, 8.85 mmol) in CH_2Cl_2 (180 mL) was added proton sponge (7.59 g, 35.4 mmol) and Me_3OBF_4 (3.93 g, 26.6 mmol). The tan solution was stirred for 2 h and then ice cold H_2O (150 mL) was added. The organics were washed with a saturated $NaHCO_3$ solution (2 x 150 mL) and brine (100 mL). The aqueous layer was extracted 1 x Et_2O (100 mL). The combined organics were dried, filtered, and concentrated *in vacuo*. The oil was purified by flash column chromatography (2.5 % to 12 % EtOAc/Hexanes) to give 4.28 g (89 %) of **S10** as yellow oil.

R_f 0.55, 10 % EtOAc / Hexanes. ^{1}H NMR (500 MHz): δ 6.57 (d, 1 H, *J* = 16.0 Hz), 6.27 (m, 1 H), 6.06 (s, 1 H), 5.90 (m, 2 H), 5.81 (m, 1 H), 5.71 (dt, 1 H, *J* = 15.0, 7.5 Hz), 5.02 (d, 1 H, *J* = 17.5 Hz), 4.96 (d, 1 H, *J* = 10.5 Hz), 4.80 (d, 1 H, *J* = 5.5 Hz), 3.77 (d, 1 H, *J* = 10.0 Hz), 3.16 (s, 3 H), 2.14 (m, 2 H), 2.08 (m, 2 H), 1.94 (s, 3 H), 1.66 (m, 1 H), 1.62 (s, 3 H), 1.52 (dt, 2 H, *J* = 15.0, 7.5 Hz), 0.98 (s, 9 H), 0.63 (d, 3 H, *J* = 7.0 Hz), 0.09 (s, 3 H), 0.05 (s, 3 H). ^{13}C NMR (125 MHz): δ 141.5, 138.5, 138.3, 134.5, 133.2, 131.8, 130.5, 129.9, 126.2, 114.7, 88.1, 78.1, 70.7, 55.6, 41.8, 33.3, 32.4, 28.7, 26.1, 21.3, 18.2, 10.6, 9.0, –3.6, –5.3. IR: 2928, 2856, 1461, 1440, 1383, 1251, 1131, 1085, 1093, 969, 912, 876, 838, 808, 775, 743 cm^{-1}. $[\alpha]^{25}_{D}$ –0.11° (*c* = 0.93, $CHCl_3$). Anal. Calcd for $C_{26}H_{45}IO_2Si$: C, 57.34; H, 8.33. Found: C, 57.36; H, 8.34.



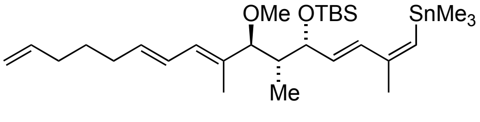
(1Z,3E,8E,10E)-(5R,6S,7S)-1-Iodo-2,6,8-trimethyl-hexadeca-1,3,8,10,15-pentaene-5,7-diol (S11). To a solution of **S9** (120 mg, 0.226 mmol) in THF (3.5 mL) at 0 °C was added tetrabutylammonium fluoride (1.0 M in THF, 0.25 mL 0.25 mmol). After 20 min, a saturated $NaHCO_3$ solution (2 mL) was added. The mixture was diluted with Et_2O (5 mL). The layers were separated. The organics were washed with brine (5 mL). The organics were dried, filtered, and concentrated *in vacuo*. The crude material was purified by flash column chromatography (65% Et_2O/Hexanes) to give 90.0 mg (96 %) of **S11** as yellow oil.

R_f 0.19, 25 % EtOAc/Hexanes. ^1H NMR (500 MHz): δ 6.63 (d, 1 H, *J* = 16.0 Hz), 6.25 (m, 1 H), 6.14 (s, 1 H), 5.98 (m, 2 H), 5.80 (m, 1 H), 5.70 (m, 1 H), 5.01 (d, 1 H, *J* = 17.0 Hz), 4.95 (d, 1 H, *J* = 10.5 Hz), 4.48 (s, 1 H), 4.01 (d, 1 H, *J* = 8.0 Hz), 3.25 (br s, 1 H), 2.45 (br s, 1 H), 2.07 (m, 2 H), 2.04 (m, 3 H), 2.00 (s, 3 H), 1.74 (s, 3 H), 1.50 (dt, 2 H, *J* = 15.0, 7.5 Hz), 0.80 (d, 3 H, *J* = 7.0 Hz). ^{13}C NMR (500 MHz): δ 141.3, 138.6, 135.4, 135.3, 134.7, 132.3, 127.5, 126.0, 114.6, 81.1, 79.4, 74.4, 40.1, 33.2, 32.3, 28.5, 21.3, 12.3, 11.8. IR: 3346, 3061, 2975, 2925, 2855, 1640, 1439, 1376, 1297, 1265, 1218, 1157, 1085, 1009, 966, 912, 756, 703, 686 cm^{-1}. $[\alpha]^{25}_D$ +0.59° (*c* = 1.0, $CHCl_3$). HRMS (FAB+) calcd for $C_{19}H_{29}IO_2$ [(M + Li^+)] 423.1372, found 423.1371.

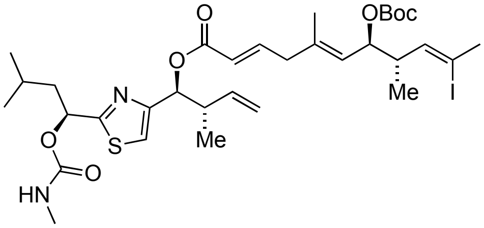


(4R,5S,6S)-4-((1E,3Z)-4-Iodo-3-methyl-buta-1,3-dienyl)-2,2,5-trimethyl-6-((1E,3E)-1-methyl-nona-1,3,8-trienyl)-[1,3]dioxane (S12). To a solution of **S11** (28 mg, 0.067 mmol) in CH_2Cl_2 (0.8 mL) was added 2-methoxypropene (0.013 mL, 0.13 mmol) and pyridinium para-toluenesulfonate (PPTS) (< 0.5 mg). After 20 min, a saturated $NaHCO_3$ solution (2 mL) and CH_2Cl_2 (5 mL) were added. The layers were separated. The organic was washed 1 x brine (5 mL). The organics were dried, filtered, and concentrated *in vacuo*. The crude material was purified by flash column chromatography (10 % EtOAc/Hexanes) to give 21 mg (67%) of **S12** as yellow oil.

R_f 0.62, 25 % EtOAc/Hexanes. ^1H NMR (500 MHz): δ 6.59 (d, 1 H, *J* = 16.0 Hz), 6.25 (m, 1 H), 6.14 (s, 1 H), 6.02 (d, 1 H, *J* = 11.0 Hz), 5.87 (dd, 1 H, *J* = 15.5, 7.0 Hz), 5.71 (m, 1 H), 5.70 (m, 1 H), 5.01 (d, 1 H, *J* = 17.0 Hz), 4.95 (d, 1 H, *J* = 10.0 Hz), 4.58 (t, 1 H, *J* = 6.0 Hz), 3.76 (d, 1 H, *J* = 8.0 Hz), 2.12 (m, 2 H), 2.07 (m, 3 H), 1.97 (s, 3 H), 1.49 (m, 2H), 1.25 (s, 6 H), 0.82 (d, 3 H, J = 7.0). ^{13}C NMR (500 MHz): δ 141.4, 138.6, 135.1, 133.2, 132.5, 132.2, 127.4, 126.2, 114.6, 100.8, 80.5, 79.5, 71.0, 38.1, 33.2, 32.3, 28.5, 25.3, 24.2, 21.1, 12.6, 12.5. IR: 2984, 2926, 2854, 1640, 1455, 1439, 1378, 1338, 1313, 1221, 1173, 1159, 1122, 1088, 1070, 1014, 992, 967, 936, 910, 753, 675 cm^{-1}. $[\alpha]^{25}_D$ –0.77° (*c* = 1.0, $CHCl_3$). Anal. Calcd for $C_{22}H_{33}IO_2$: C, 57.90; H, 7.29. Found: C, 57.89; H, 7.58.

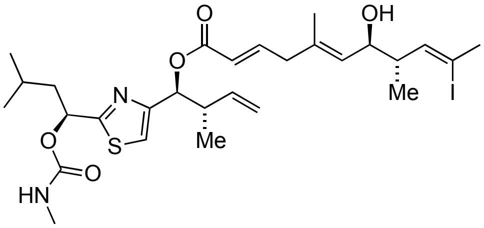


***tert*-Butyl-[(4E,6E)-(1R,2R,3S)-3-methoxy-2,4-dimethyl-1-((1E,3Z)-3-methyl-4-trimethylstannanyl-buta-1,3-dienyl)-dodeca-4,6,11-trienyloxy]-dimethyl-silane (5)**. To a solution of **S10** (1.09 g, 2.00 mmol) in THF (13 mL) at –78 ºC was added *n*BuLi (2.44 M in hexanes, 902 μL, 2.20 mmol) dropwise. After 20 min, a solution of Me_3SnCl (1.0 M in THF, 3.00 mL, 3.00 mmol) was added over 2 min. After 1.5 h at –78 ºC, the reaction was poured onto H_2O (20 mL) and Et_2O (10 mL). The layers were separated. The organics were dried, filtered, and concentrated *in vacuo* to give ~1.1 g of **5**. This material was taken on without further purification and not fully characterized due to extreme sensitivity.



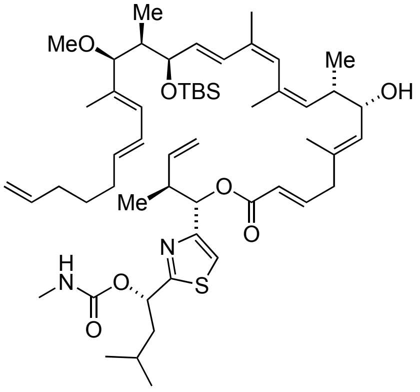
(2E,5E,9Z)-(7S,8S)-7-*tert*-Butoxycarbonyloxy-10-iodo-5,8-dimethyl-undeca-2,5,9-trienoic acid (1S,2S)-2-methyl-1-[2-((S)-3-methyl-1-methylcarbamoyloxy-butyl)-thiazol-4-yl]-but-3-enyl ester (21). To a solution a solution of **6** (2.00 g, 4.44 mmol) in $PhCH_3$ (22 mL) at 0 ºC was added $[RuCl_2(cymene)]_2$ (136 mg, 0.222 mmol) followed by ethoxyacetylene (50% w/w in hexanes, 2.60 mL, 13.3 mmol) dropwise. After 10 min, the reaction was warmed to rt. Then after 20 min, the mixture was filtered through a plug of SiO_2 (30% EtOAc/Hex). After concentration, the resulting oil was added via syringe pump in CH_2Cl_2 (6.3 mL) to a solution of **7** (1.80 g, 5.77 mmol) and dry *p*-toluenesulfonic acid (TsOH) (153 mg, 0.888 mmol) in CH_2Cl_2 (11.5 mL) over 3 h. After stirring at rt for 16 h, the mixture was concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (25% EtOAc/Hexanes) to give 1.80 g (54%) of **21** as a yellow oil. All excess **7** could be recovered and reused.

R_f 0.48, 30 % EtOAc/Hexanes. ^1H NMR (500 MHz): 7.07 (s, 1 H), 6.92 (dt, 1 H, $J = 15.5$, 7 Hz), 6.03 (m, 1 H), 5.86 (m, 2 H), 5.73 (m, 1 H), 5.31 (d, 1 H, $J = 8$ Hz), 5.18 (m, 2 H), 4.99 (m, 2 H), 4.81 (br s, 1 H), 2.99 (m, 1 H), 2.87 (m, 2 H), 2.80 (d, 3 H, $J = 5$ Hz), 2.60 (m, 1 H), 2.46 (s, 3 H), 1.85 (m, 2 H), 1.83 (s, 3 H), 1.82 (m, 1 H), 1.47 (s, 9 H), 0.96 (m, 12 H). ^{13}C NMR (500 MHz): δ 171.2, 164.4, 155.9, 154.1, 153.1, 146.5, 139.0, 137.5, 136.0, 124.2, 122.6, 116.1, 115.7, 101.8, 81.8, 76.1, 75.0, 72.1, 46.1, 44.3, 42.0, 41.6, 33.7, 27.8, 27.6, 24.5, 23.0, 22.1, 17.2, 16.3, 15.5. IR: 3388, 2967, 2933, 1737, 1728, 1716, 1272, 1255, 1158 cm^{-1}. $[\alpha]^{25}_D$ –11.2° (c = 1.51, $CHCl_3$). HRMS (FAB+) calcd for $C_{33}H_{50}IO_7N_2S$ $[(M + H)^+]$ 745.2384, found 745.2382.



(2E,5E,9Z)-(7S,8S)-7-Hydroxy-10-iodo-5,8-dimethyl-undeca-2,5,9-trienoic acid (1S,2S)-2-methyl-1-[2-((S)-3-methyl-1-methylcarbamoyloxy-butyl)-thiazol-4-yl]-but-3-enyl ester (22). To a solution of **21** (900 mg, 1.21 mmol) in Et_2O (25 mL) was added SiO_2 (14.5 g, 12 g/mmol of substrate). The slurry was concentrated *in vacuo.* The dry SiO_2 was heated under vacuum at 125 °C for 5 min. The SiO_2 was washed and filtered with Et_2O (~100 mL). The solution was concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (40% EtOAc/Hexanes) to give 335 mg (43%) of **22** as a colorless oil. (66% on 60 mg scale)

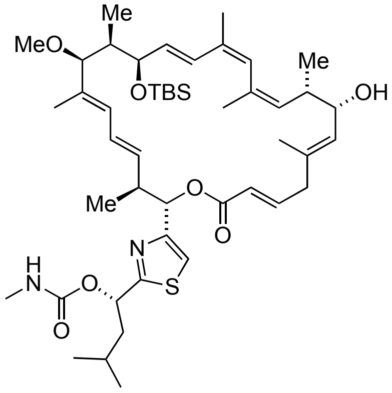
R_f 0.37, 40 % EtOAc/Hexanes. ^{1}H NMR (500 MHz): 7.08 (s, 1 H), 6.91 (dt, 1 H, J = 15.5, 7 Hz), 6.05 (m, 1 H), 5.88 (m, 2 H), 5.75 (m, 1 H), 5.33 (d, 1 H, J = 9 Hz), 5.25 (d, 1 H, J = 9 Hz), 5.00 (m, 2 H), 4.78 (br s, 1 H), 4.26 (dd, 1 H, J = 9, 6.5 Hz), 3.01 (m, 1 H), 2.89 (d, 2 H, J = 7 Hz), 2.82 (d, 3 H, J = 5 Hz), 2.51 (s, 3 H), 2.48 (m, 1 H), 1.85 (m, 2 H), 1.72 (m, 1 H), 1.69 (s, 3 H), 0.95 (m, 12 H). ^{13}C NMR (500 MHz): δ 171.3, 165.5, 155.9, 154.1, 146.8, 139.1, 137.0, 135.9, 128.2, 122.6, 116.2, 115.7, 102.0, 75.0, 72.2, 71.4, 47.9, 44.4, 42.2, 41.6, 33.8, 27.6, 24.5, 23.0, 22.1, 17.0, 16.3, 15.5. IR: 3364, 2960, 2930, 2871, 1716, 1707, 1264 cm^{-1}. $[\alpha]^{25}_D$ –40.6° (c = 0.68, $CHCl_3$). HRMS (FAB+) calcd for $C_{28}H_{42}IO_5N_2S$ [$(M + H)^+$] 645.1859, found 645.1864.



Linear RCM precursor (4b). To a solution of **22** (300 mg, 0.465 mmol) and **5** (338 mg, 0.582 mmol) in DMF (4.7 mL) was added $Pd(PPh_3)_4$ (54 mg, 0.047 mmol) and copper thiophenecarboxylate (CuTC) (133 mg, 0.698 mmol) simultaneously. After 30 min, a saturated $NaHCO_3$ solution (15 mL) and Et_2O (15 mL) added. The layers were separated, and the aqueous was extracted 1 x Et_2O (10 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (25% EtOAc/Hexanes) to give 138 mg of **4b** as a yellow oil and 203 mg of **22** was recovered (32%, 92% based on recovered starting material). No conditions attempted saw complete consumption of **22**.

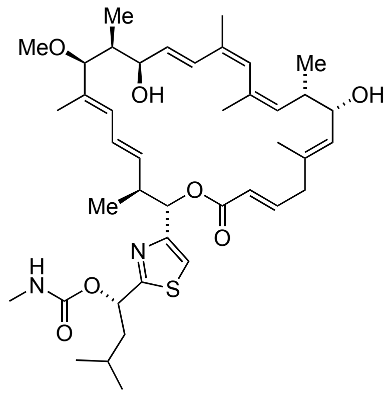
R_f 0.69, 40 % EtOAc/Hexanes. ^{1}H NMR (500 MHz): 7.07 (s, 1 H), 6.91 (dt, 1 H, J = 15.5, 7 Hz), 6.41 (d, 1 H, J = 16 Hz), 6.27 (dd, 1 H, J = 15, 11 Hz), 5.90-5.66 (m, 8 H), 5.18 (d, 1 H, J = 9 Hz), 5.12 (d, 1 H, J = 10 Hz), 4.98 (m, 4 H), 4.78 (br d, 1 H, J = 4.5 Hz), 4.69 (d, 1 H, J = 6.5 Hz), 4.01 (t, 1 H, J = 8.5 Hz), 3.35 (d, 1 H, J = 10 Hz), 3.12 (s, 3 H), 3.00 (m, 1 H), 2.87 (m, 2 H), 2.80 (d, 3 H, J = 4.5 Hz), 2.36 (m, 1 H), 2.13 (m, 2 H), 2.07 (m, 2 H), 1.85 (m, 2 H), 1.84 (s, 6 H), 1.72 (m, 2 H), 1.69 (s, 3 H), 1.61 (m, 1 H), 1.60 (s, 3 H), 1.52 (m, 2 H), 0.99 (m, 9 H), 0.91 (s, 9 H), 0.83 (d, 3 H, J = 7 Hz), 0.63 (d, 3 H, J = 7 Hz), 0.03 (s, 3 H), –0.02 (s, 3 H). ^{13}C NMR (500 MHz): δ 171.2, 165.5, 155.9, 154.2, 147.0, 146.8, 139.0, 138.6, 135.8, 135.7, 135.6, 134.4, 134.3, 133.5, 133.4, 130.6, 129.8, 128.3, 128.0, 127.3, 126.0, 122.4, 122.1, 88.2, 75.0, 72.1, 72.0, 71.9, 71.4, 55.5, 44.4, 42.3, 41.7, 40.3, 33.3, 32.3, 28.5, 27.6, 25.9, 24.9, 24.5, 23.0, 22.1, 20.4, 18.2, 17.1, 16.3, 16.2, 10.5, 9.0, –4.0, –5.1. IR: 3363, 2957, 2928, 1723, 1711, 1255 cm^{-1}. $[\alpha]^{25}_D$

–31.2° (c = 0.92, $CHCl_3$). HRMS (FAB+) calcd for $C_{54}H_{86}O_7N_2SSiNa$ [$(M + Na)^+$] 957.5823, found 957.5815.



15-O-TBS-Archazolid B (S13). To a solution of **4b** (57 mg, 0.061 mmol) in $PhCH_3$ (120 mL) at 110 °C was added Grubbs' second generation catalyst (2.6 mg, 3.0 x 10^{-3} mmol). Over the next 2 h, additional catalyst added each 30 min (3 x 5 mol%). The reaction was cooled to rt and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (30% EtOAc/Hexanes) to give 14 mg (27%) of **S13** as a yellow foam.

R_f 0.69, 40 % EtOAc/Hexanes. ^1H NMR (500 MHz): 7.05 (s, 1 H), 6.82 (dt, 1 H, J = 15.5, 7.5 Hz), 6.37 (d, 1 H, J = 16 Hz), 6.06 (m, 2 H), 5.99 (d, 1 H, J = 5.5 Hz), 5.83 (m, 2 H), 5.72 (dd, 1 H, J = 16, 6.5 Hz), 5.63 (s, 1 H), 5.55 (m, 1 H), 5.23 (d, 1 H, J = 10 Hz), 5.09 (d, 1 H, J = 9.5 Hz), 4.76 (m, 1 H), 4.62 (br s, 1 H), 3.90 (t, 1 H, J = 9.5 Hz), 3.25 (d, 1 H, J = 9.5 Hz), 3.12 (m, 1 H), 3.09 (s, 3 H), 2.85 (m, 6 H), 2.20 (m, 1 H), 1.91 (m, 2 H), 1.88 (s, 3 H), 1.78 (s, 3 H), 1.73 (m, 2 H), 1.72 (s, 3 H), 1.62 (s, 3 H), 1.56 (m, 2 H), 1.08 (d, 3 H, J = 6.5 Hz), 0.97 (m, 6 H), 0.92 (s, 9 H), 0.84 (d, 3 H, J = 7 Hz), 0.64 (d, 3 H, J = 7 Hz), 0.03 (s, 3 H), –0.01 (s, 3 H). ^{13}C NMR (500 MHz): δ 171.2, 165.2, 155.9, 154.7, 147.0, 146.9, 136.0, 135.8, 134.8, 133.3, 132.7, 130.4, 128.9, 128.4, 128.1, 127.0, 126.2, 122.5, 115.6, 86.8, 76.0, 75.7, 72.6, 72.1, 55.7, 44.4, 44.4, 43.3, 40.7, 40.0, 29.7, 27.6, 25.9, 24.6, 24.6, 23.0, 22.0, 21.0, 18.2, 16.9, 16.8, 14.2, 10.5, –4.1, –5.4. IR: 3356, 2957, 2927, 2855, 1723, 1712, 1253 cm^{-1}. $[\alpha]^{25}_D$ –91.7° (c = 0.62, $CHCl_3$). HRMS (FAB+) calcd for $C_{47}H_{74}O_7N_2SSiNa$ [$(M + Na)^+$] 861.4884, found 861.4865.



Archazolid B (2). To a solution of **S13** (22 mg, 0.026 mmol) in THF (600 μL) at 0 ºC was added H_2O (100 μL) and formic acid (300 μL). After 26 h at 0 ºC, the reaction mixture was poured onto H_2O (5 mL) and Et_2O (10 mL). A saturated $NaHCO_3$ solution (5 mL) was added. The layers were separated, and the aqueous was extracted 1 x Et_2O (10 mL). The organics were dried, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography to give 16 mg (84%) of archazolid B (**2**) as a white solid.

R_f 0.33, 40% EtOAc/Hex. $[\alpha]^{25}_{D}$ –61.9º (c = 0.52, MeOH).

^{1}H NMR isolation	^{1}H NMR current	^{13}C NMR isolation	^{13}C NMR current
7.31 (s, 1 H)	7.29 (s, 1 H)	174.2	174.4
6.94 (ddd, 1 H, *J* = 15.5, 8.4, 6.4 Hz)	6.92 (ddd, 1 H, *J* = 15, 8.5, 6.5 Hz)	166.7	166.8
6.60 (d, 1 H, *J* = 15.8 Hz)	6.59 (d, 1 H, *J* = 16 Hz)	158.3	158.4
6.28 (ddd, 1 H, *J* = 15.3, 10.7, 1.0 Hz)	6.26 (dd, 1 H, *J* = 15, 10.5 Hz)	155.7	155.9
6.03 (dd, 1 H, *J* = 8.9, 4.8 Hz)	6.01 (dd, 1 H, *J* = 9, 4.5 Hz)	149.0	149.2
5.92 (d, 1 H, *J* = 15.7 Hz)	5.92-5.88 (m, 3 H)	136.2	136.4
5.90 (d, 1 H, *J* = 4.4 Hz)		135.6	135.7
5.90 (d, 1 H, *J* = 10.2 Hz)		135.5	135.6
5.79 (d, 1 H, *J* = 0.6 Hz)	5.78-5.70 (m, 3 H)	134.6	134.7
5.77 (dd, 1 H, *J* = 16.2, 5.6 Hz)		133.5	133.6
5.75 (dd, 1 H, *J* = 15.3,		133.4	133.5
5.28 (d, 1 H, *J* = 9.7 Hz)	5.27 (d, 1 H, *J* = 9.5 Hz)	132.9	133.1
5.18 (dd, 1 H, *J* = 9.2, 1.0 Hz)	5.17 (d, 1 H, *J* = 9.5 Hz)	130.7	130.9
4.38 (dd, 1 H, *J* = 5.6, 3.2 Hz)	4.37 (br s, 1 H)	130.7	130.9
4.03 (dd, 1 H, *J* = 9.2, 9.2 Hz)	4.02 (t, 1 H, *J* = 9.5 Hz)	130.0	130.2
3.47 (d, 1 H, *J* = 9.2 Hz)	3.45 (d, 1 H, *J* = 9 Hz)	129.4	129.5

3.19 (s, 3 H)	3.18 (s, 3 H)	127.3	127.4
3.09 (ddq, 1 H, *J* = 6.6, 4.6, 6.8 Hz)	3.07 (m, 1 H)	123.3	123.5
2.96 (dd, 1 H, *J* = 14.7, 8.6 Hz)	2.97-2.88 (m, 2 H)	117.5	117.5
2.91 (dd, 1 H, *J* = 14.7, 6.6 Hz)		90.0	90.1
2.75 (s, 3 H)	2.73 (s, 3 H)	77.2	77.4
2.30 (ddq, 1 H, *J* = 9.5, 9.5, 7.0 Hz)	2.29 (m, 1 H)	74.8	74.9
1.93 (d, 3 H, *J* = 1.1 Hz)	1.92 (s, 3 H)	73.8	73.9
1.92 (m, 2 H)	1.92 (m, 1 H), 1.81 (m, 1 H)	73.4	73.5
1.79 (m, 1 H)	1.78 (m, 1 H)	56.4	56.5
1.79 (br s, 3 H)	1.78 (s, 3 H)	46.0	46.1
1.78 (m, 1 H)	1.78 (m, 1 H)	44.0	44.2
1.74 (d, 3 H, *J* = 1.0 Hz)	1.72 (s, 3 H)	44.0	44.1
1.67 (d, 3 H, *J* = 1.0 Hz)	1.65 (s, 3 H)	41.5	41.6
1.11 (d, 3 H, *J* = 6.8 Hz)	1.10 (d, 3 H, *J* = 7 Hz)	41.3	41.4
1.02 (d, 3 H, *J* = 6.1 Hz)	1.01 (d, 3 H, *J* = 6 Hz)	27.5	27.7
1.01 (d, 3 H, *J* = 6.6 Hz)	1.00 (d, 3 H, *J* = 6.5 Hz)	25.8	26.0
0.81 (d, 3 H, *J* =6.6 Hz)	0.79 (d, 3 H, *J* = 6.5 Hz)	24.7	24.9
0.72 (d, 3 H, *J* = 7.1 Hz)	0.70 (d, 3 H, *J* = 7.5 Hz)	23.4	23.5
		22.3	22.5
		19.9	20.1
		17.7	17.9
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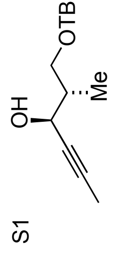
		16.9	17.1
		12.6	12.7
		12.3	12.5

S1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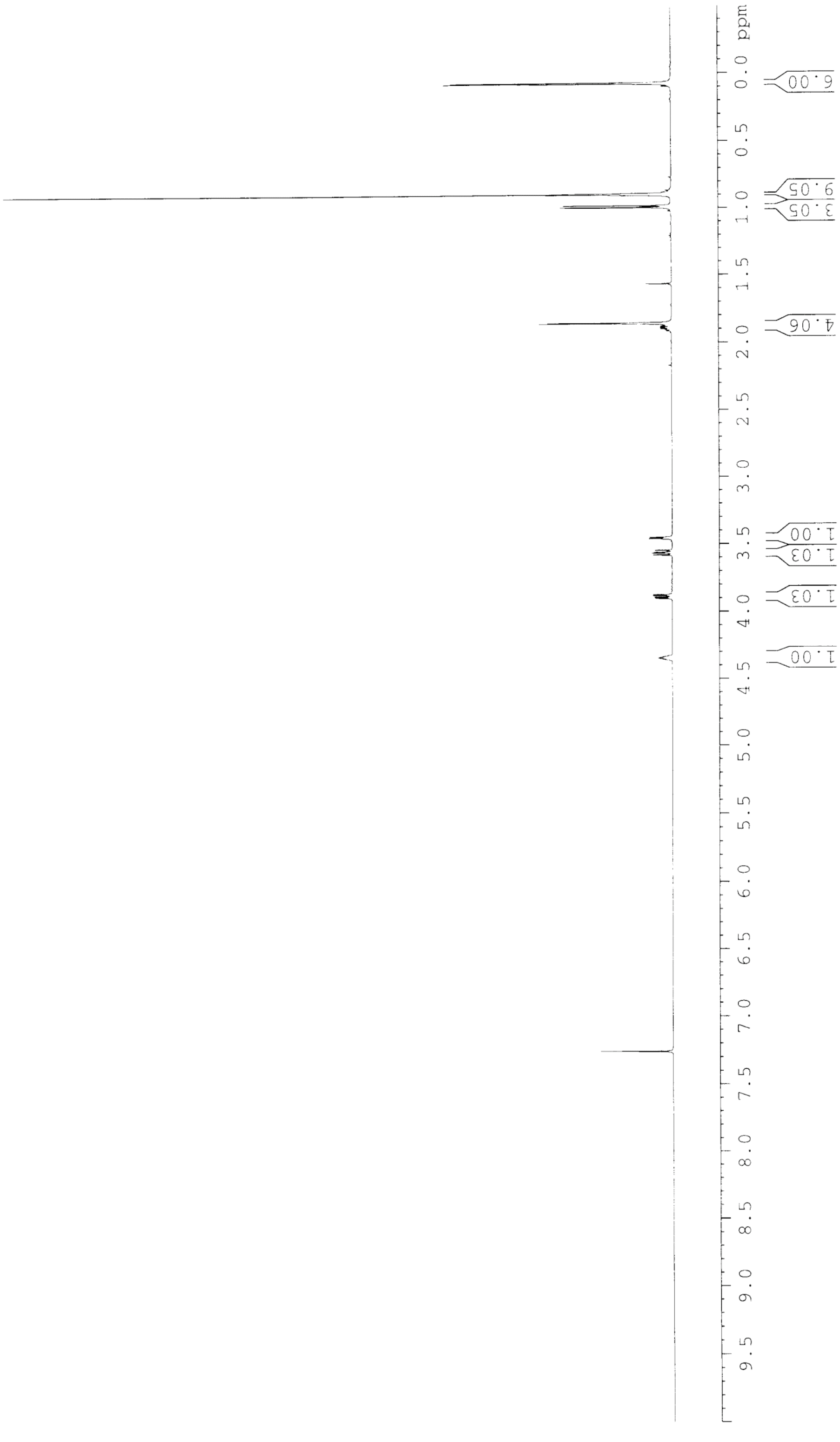
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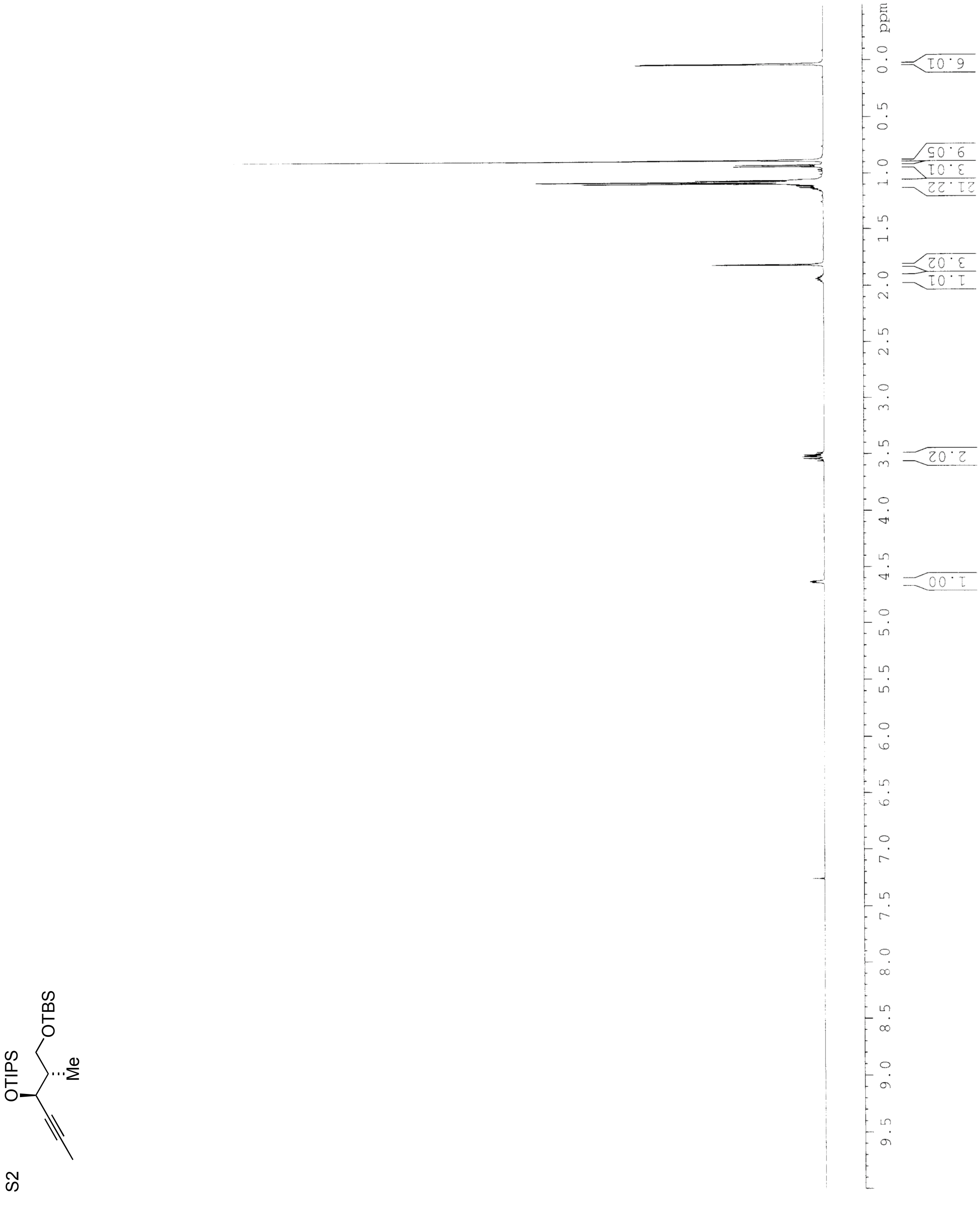
S2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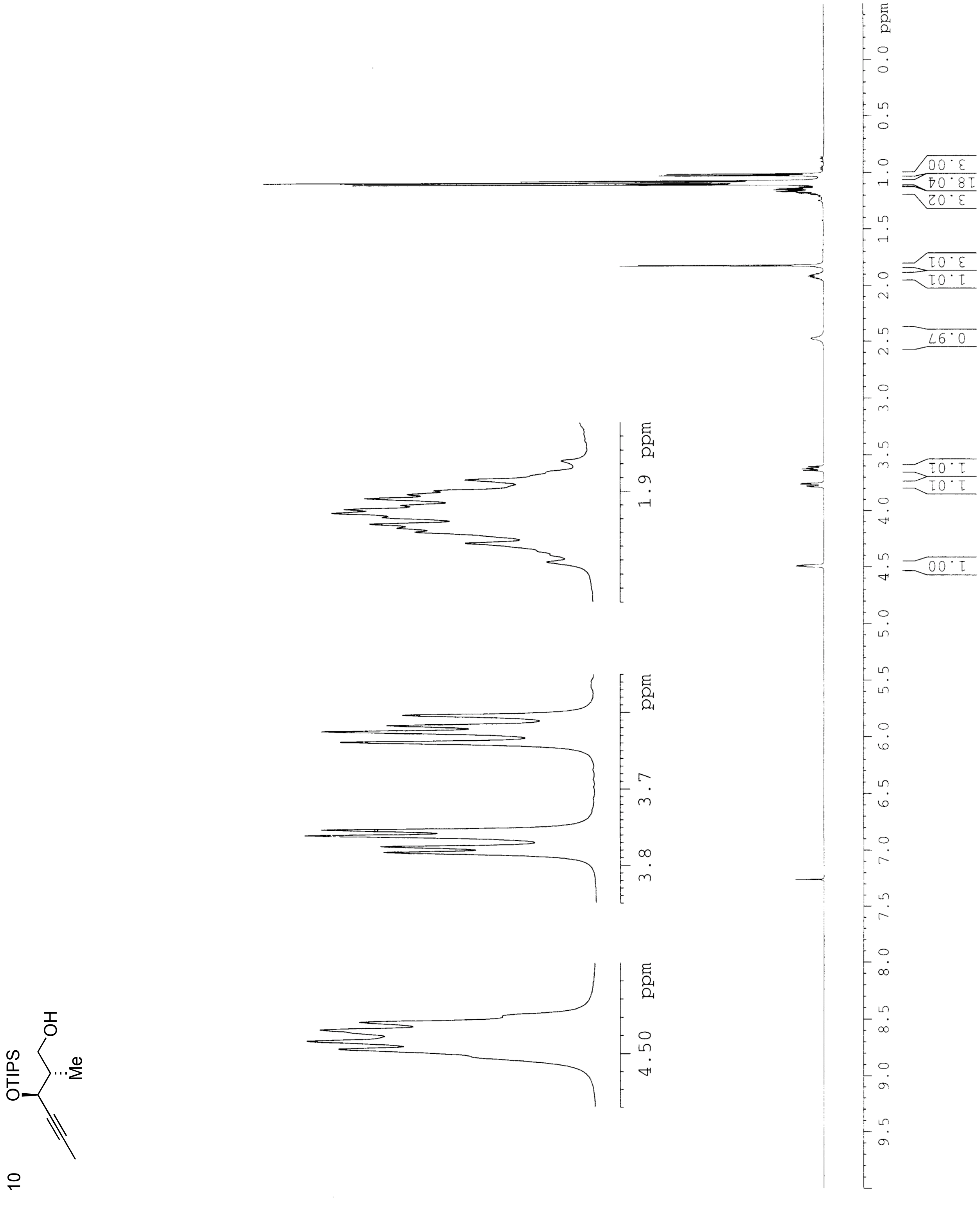
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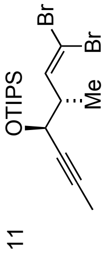
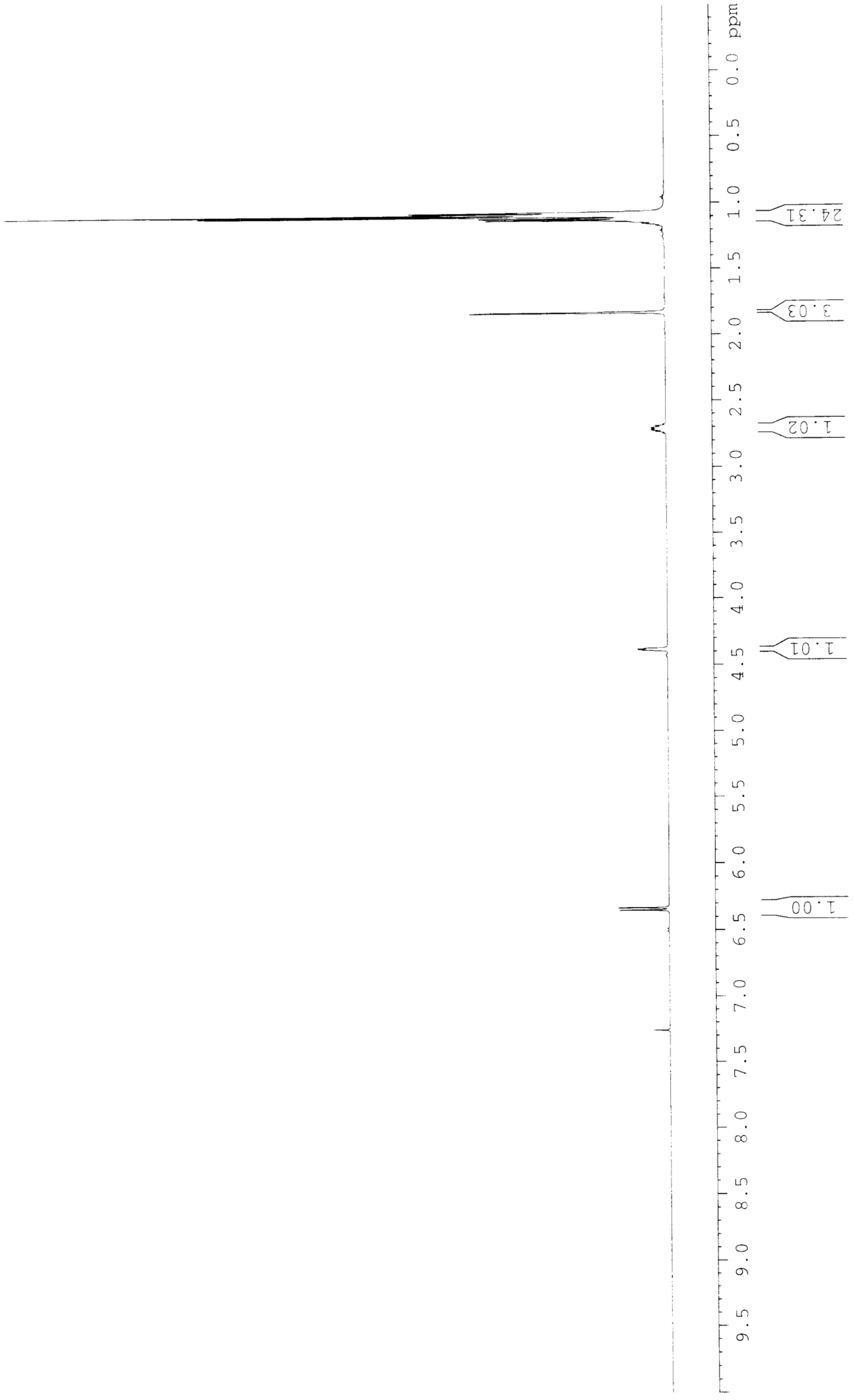


11

OTIPS
Br
Br
Me



ppm
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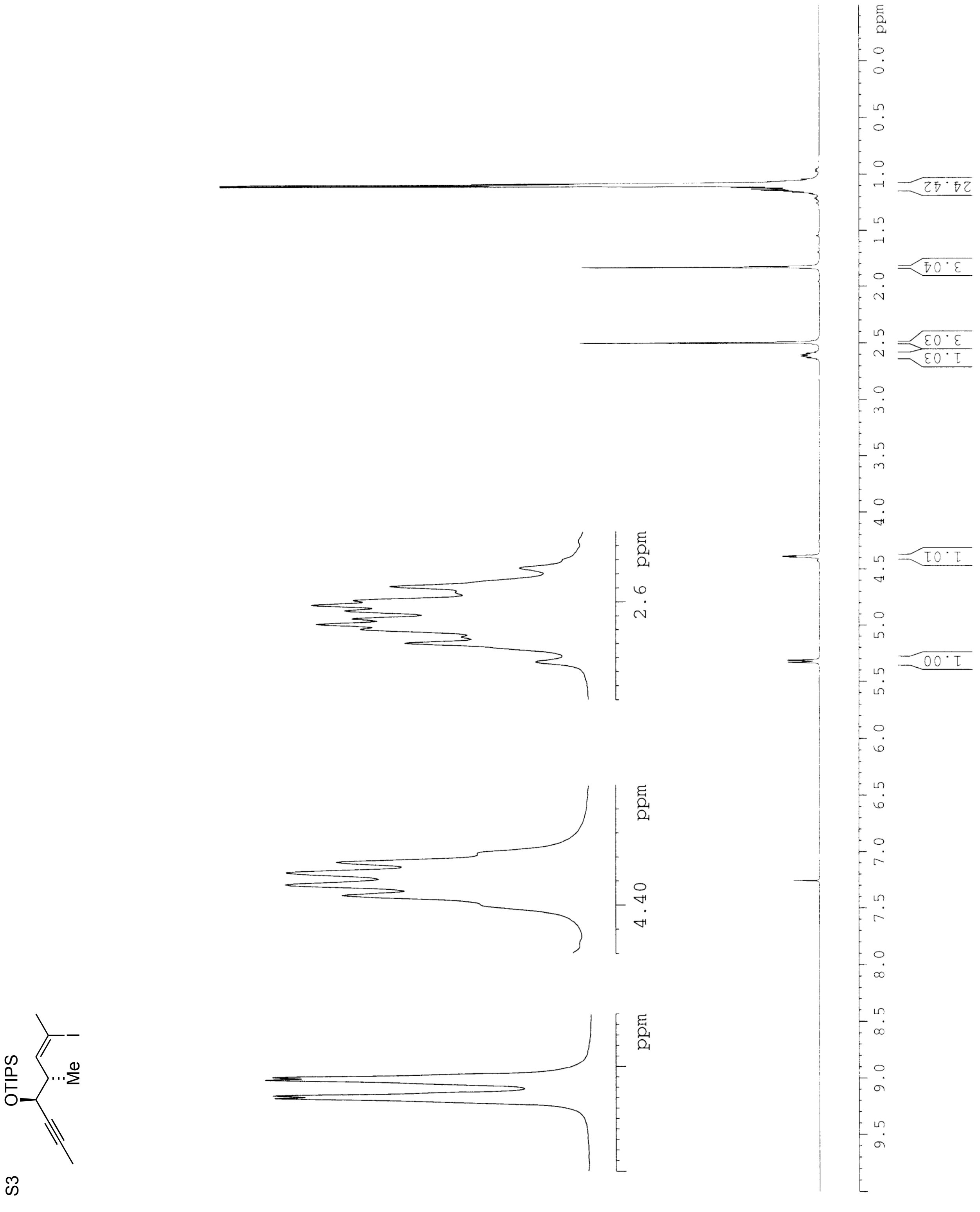
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
24.31
3.03
1.02
1.01
1.00



S3

OTIPS
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8.0
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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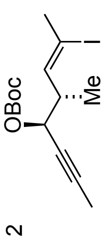
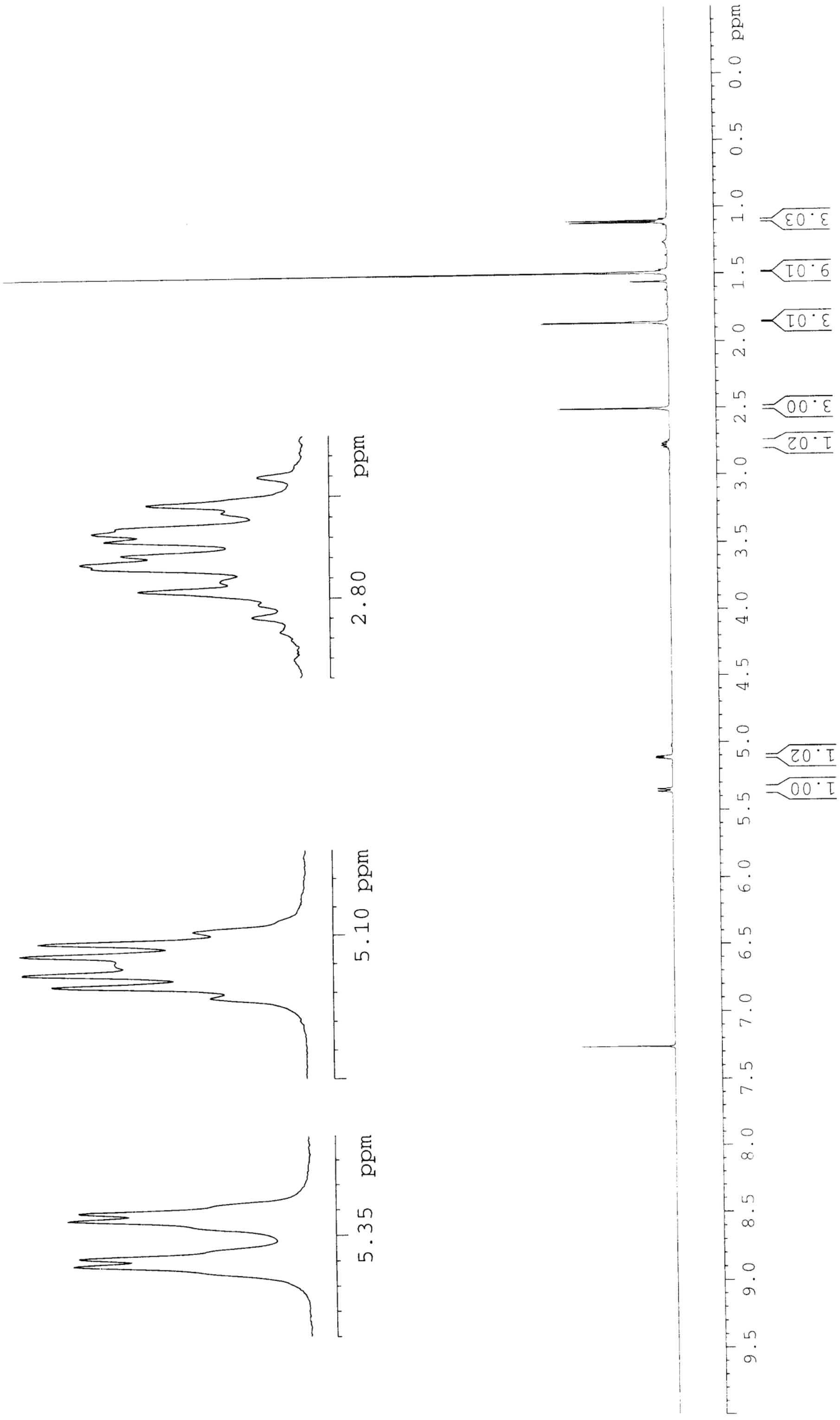
0.0
4.40
2.6
1.00
1.01
1.03
3.03
3.04
24.42

12



OBoc
Me



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8.5
8.0
7.5
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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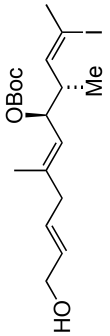
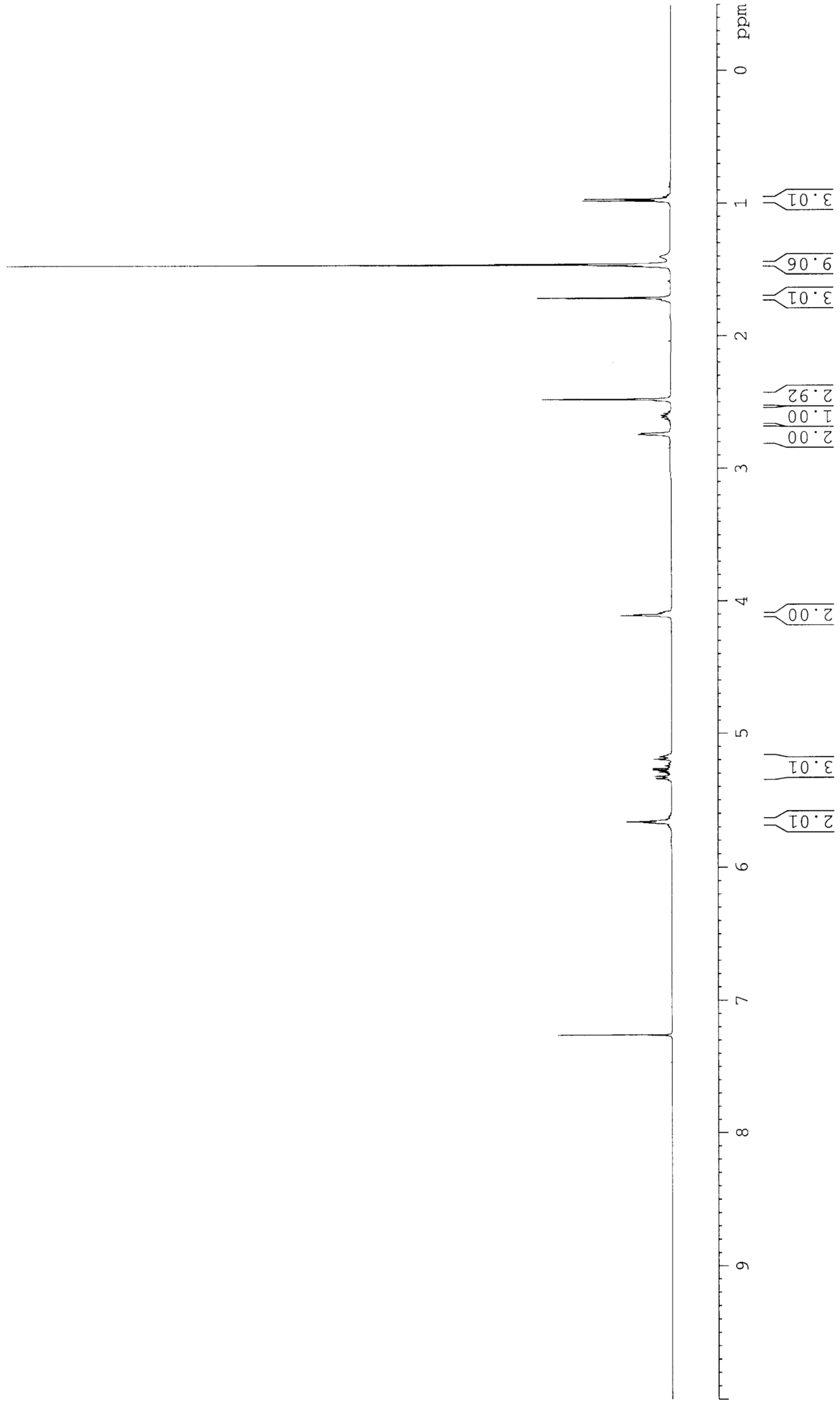
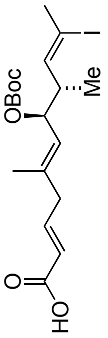
0.5
0.0 ppm
1.00
1.02
1.02
3.00
3.01
9.01
3.03

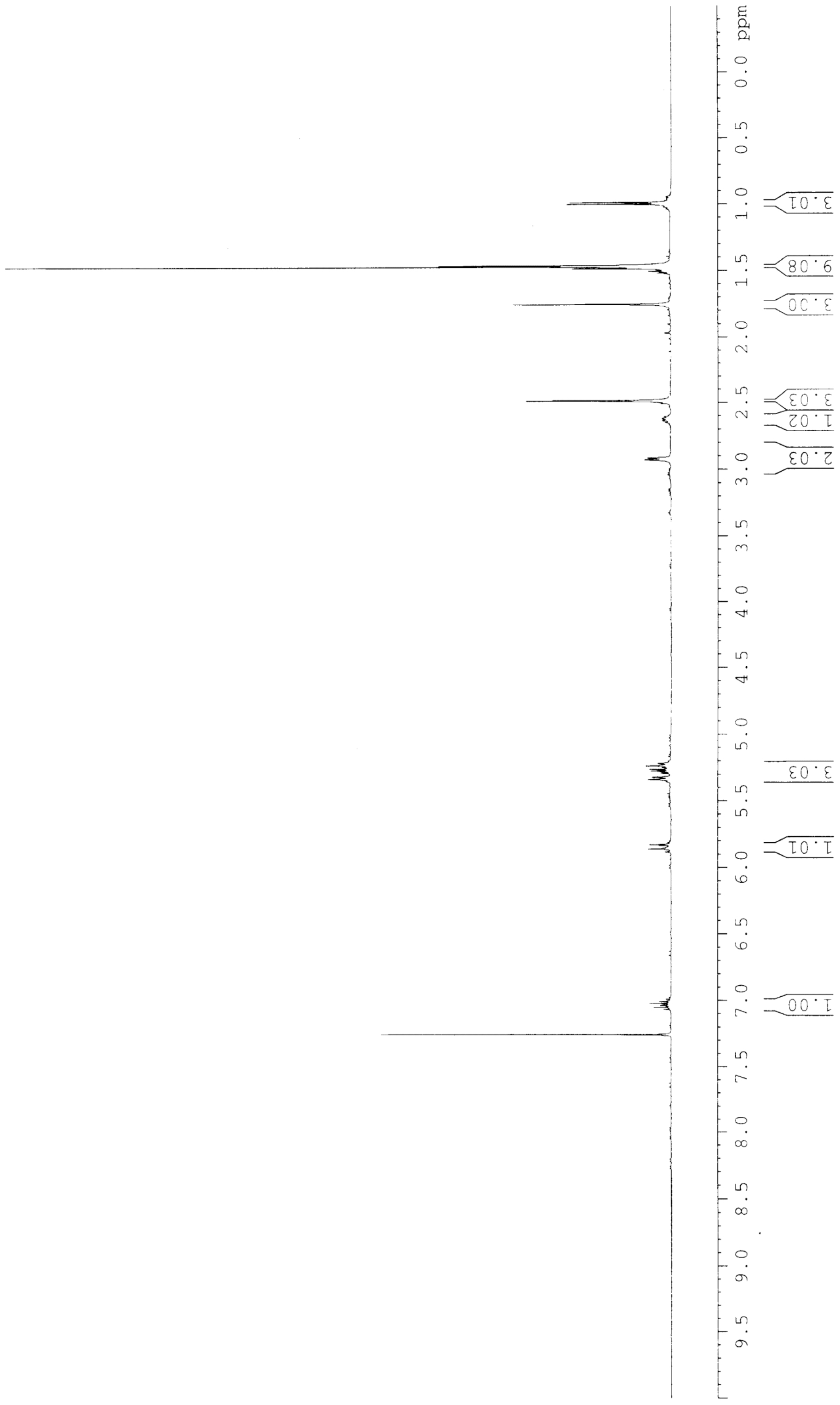
13





6


OBoc
Me
I
HO
O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2.5
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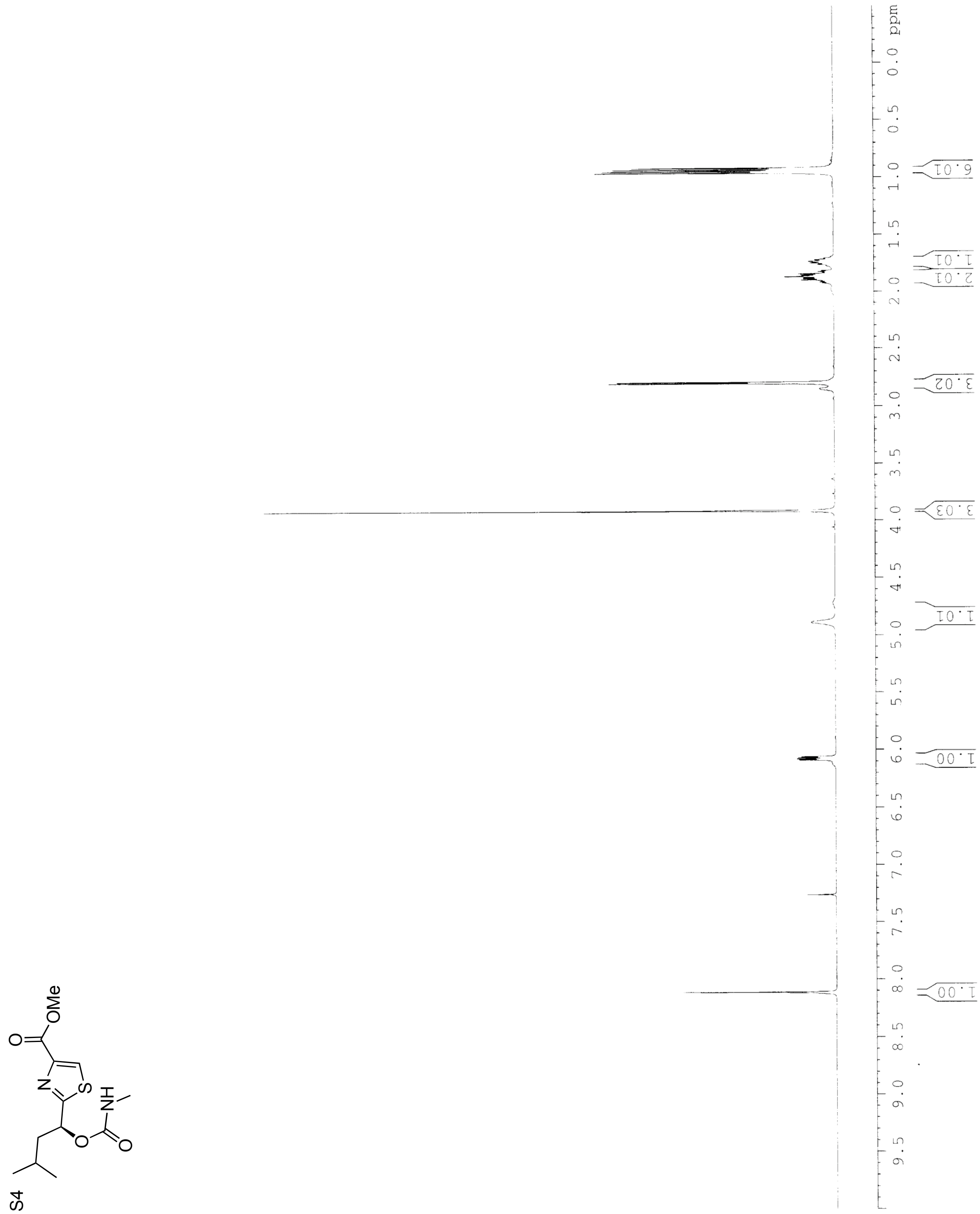
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
3.01
9.08
3.00
3.03
1.02
2.03
3.03
1.01
1.00


ppm
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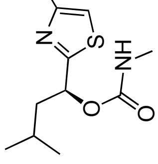
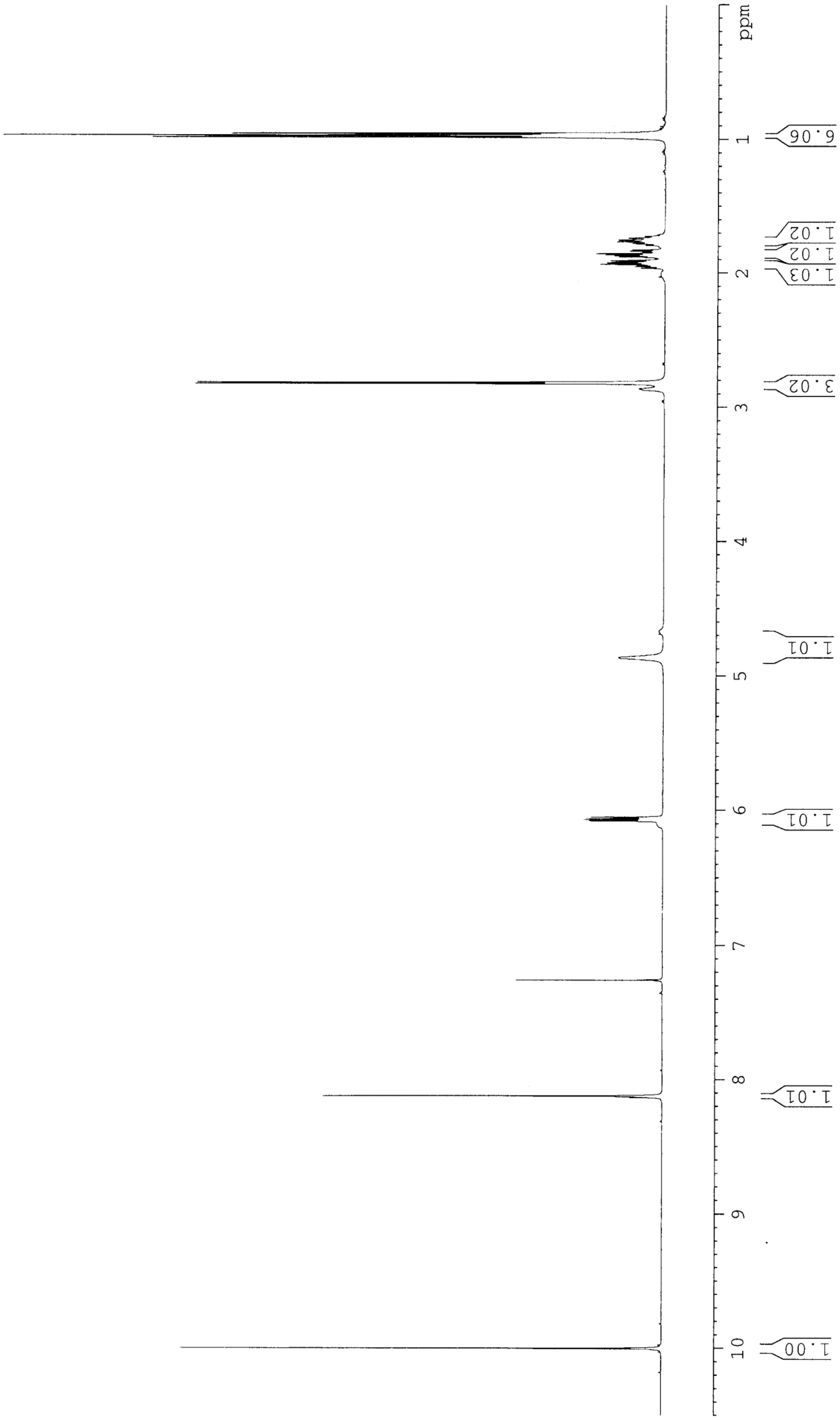
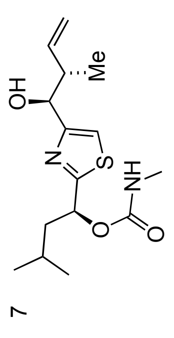
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
6.01
1.01
2.01
3.02
3.03
1.01
1.00
1.00
OMe
O
N
S
NH
O
O

S4



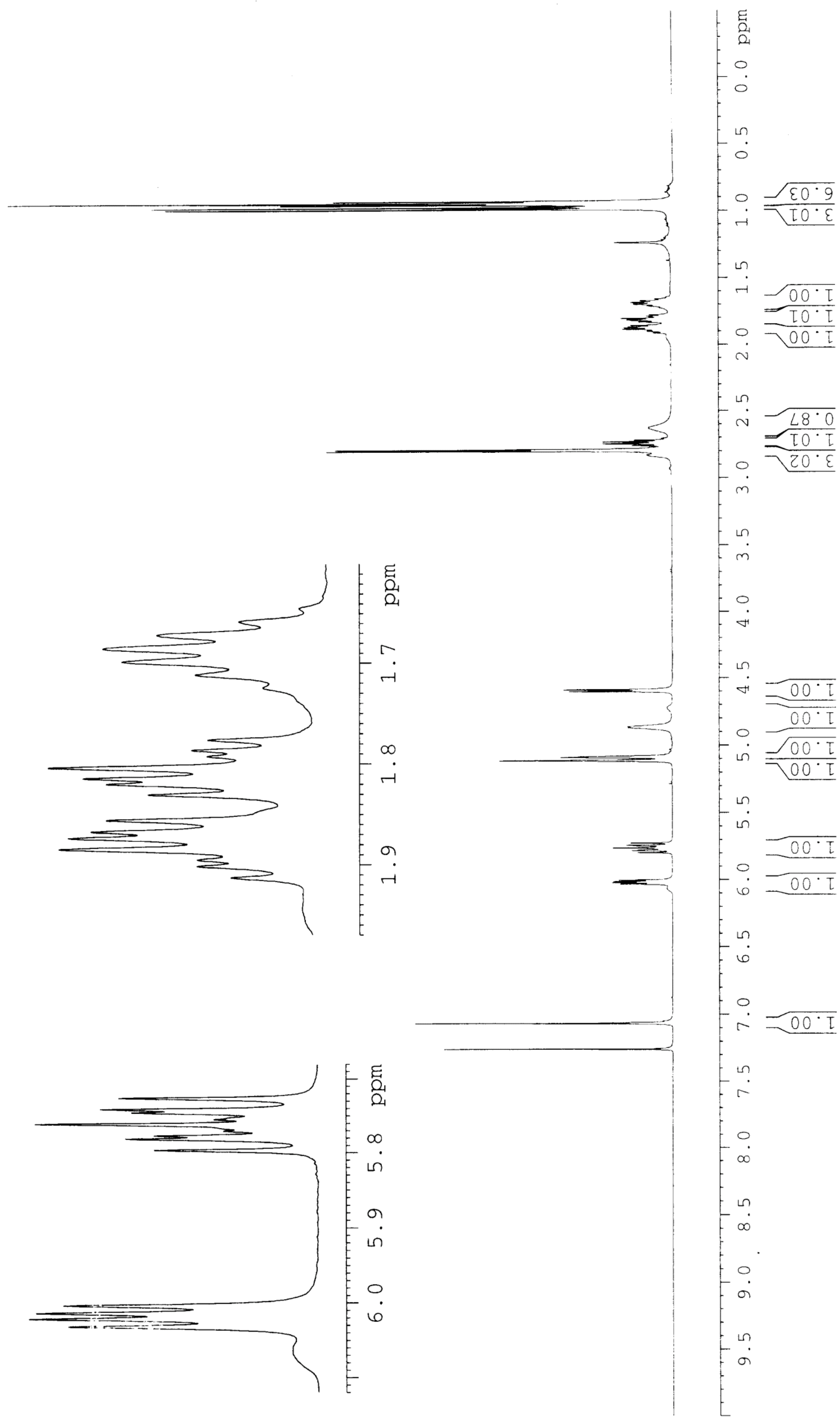
S5





OH
Me
N
S
NH
O
O

7



ppm
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2.5
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4.0
4.5
5.0
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6.5
7.0
7.5
8.0
8.5
9.0
9.5
6.03
3.01
1.00
1.01
1.00
0.87
1.01
3.02
1.00
1.00
1.00
1.00
1.00
1.00
1.00
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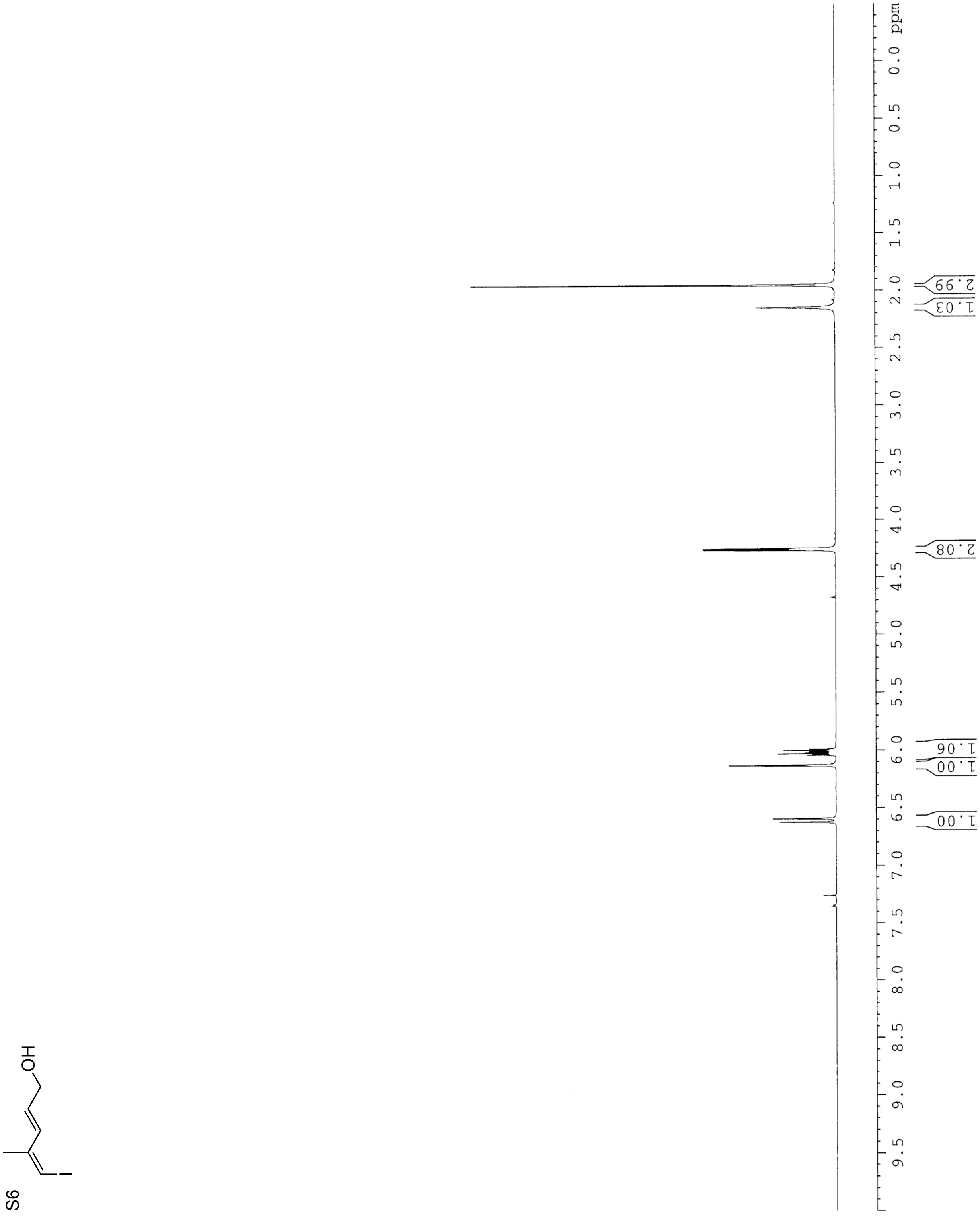
1.8
1.9
5.8
5.9
6.0


S6
OH
I
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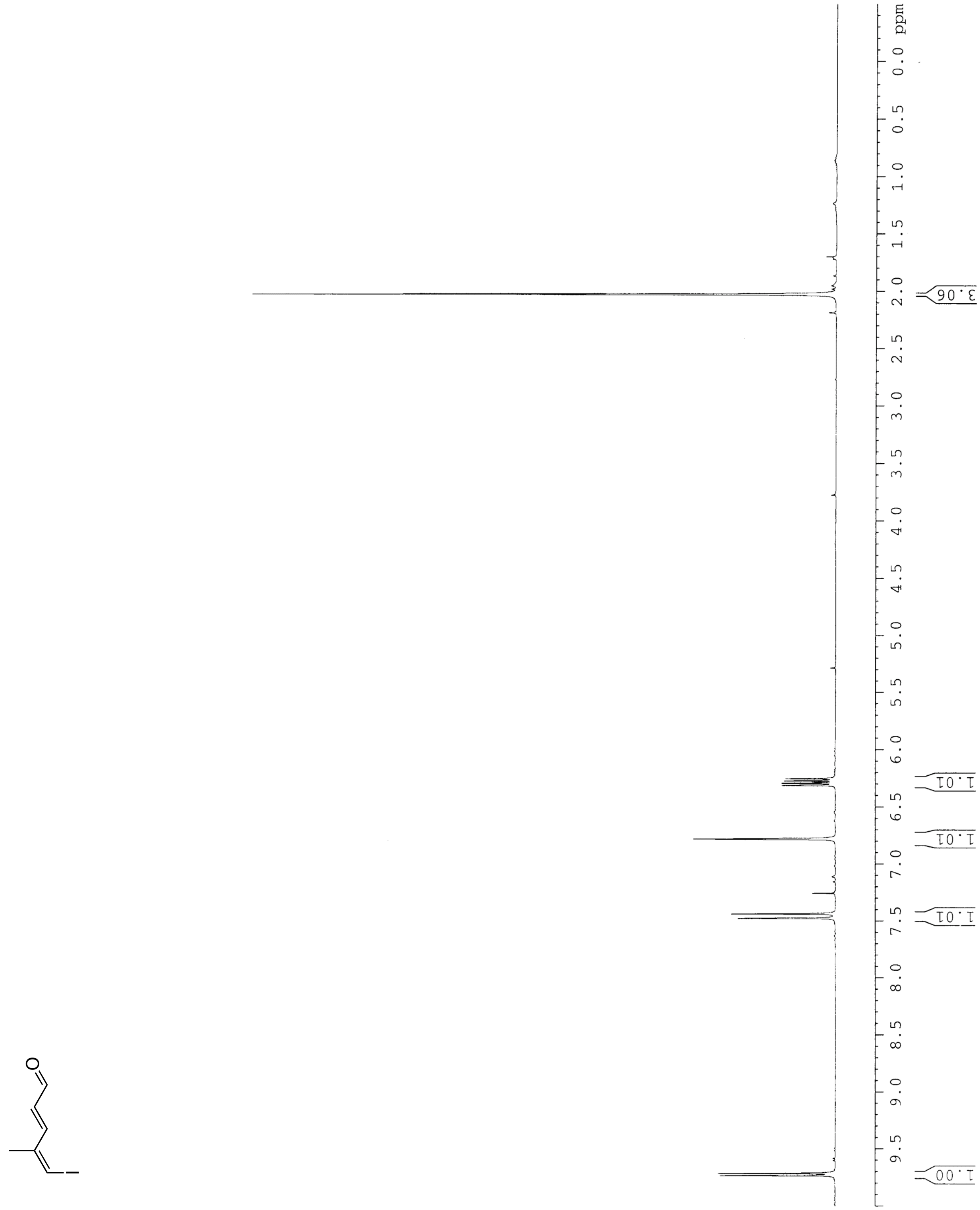
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
2.99
1.03
2.08
1.06
1.00
1.00


O
I
ppm
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1.0
1.5
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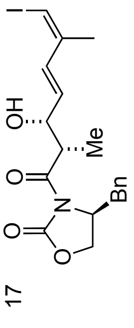
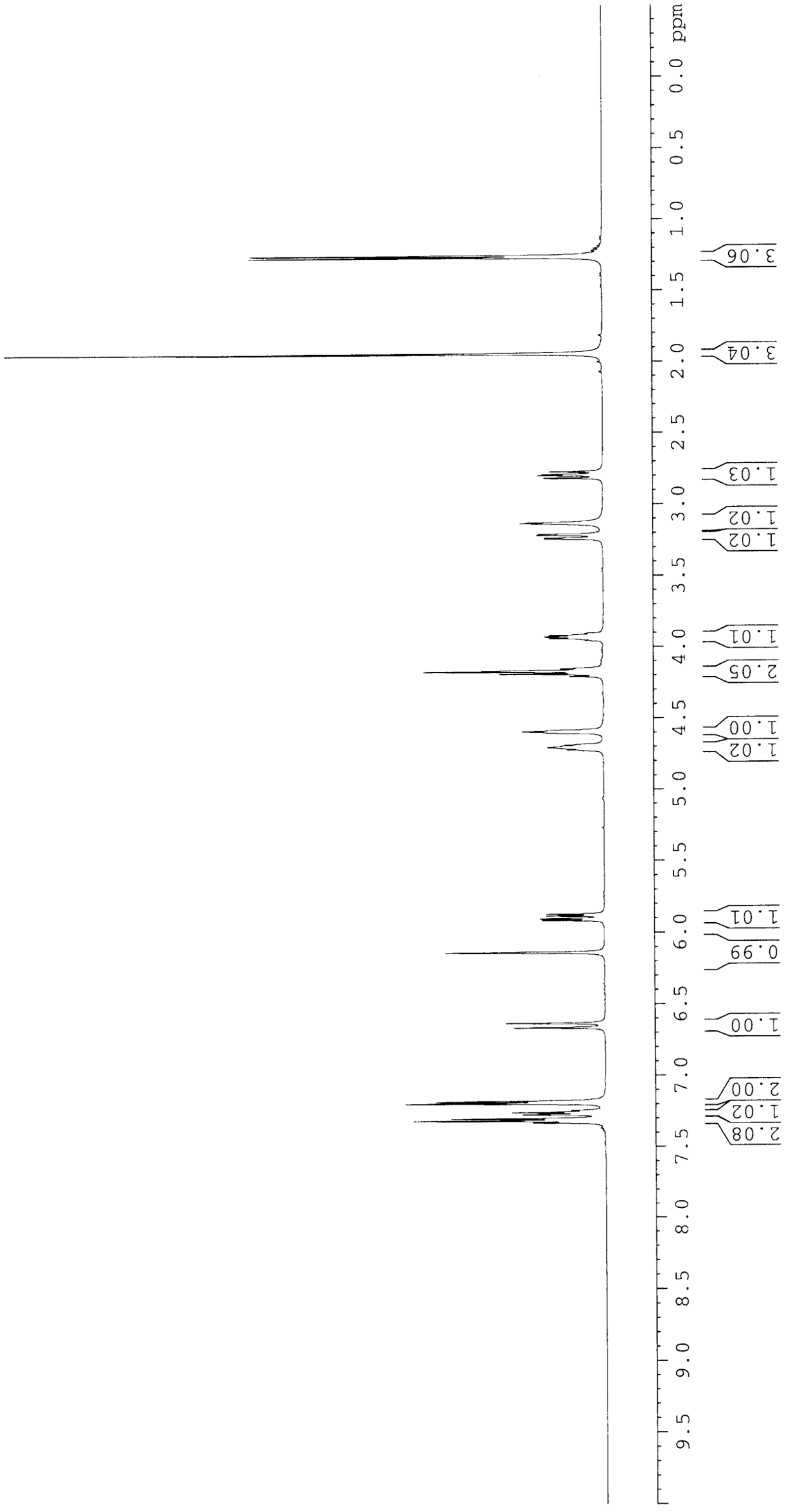
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
3.06
1.01
1.01
1.01
1.00

17



OH
O
O
O
N
Me
Bn
I



ppm
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1.5
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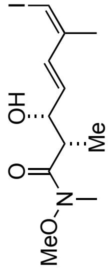
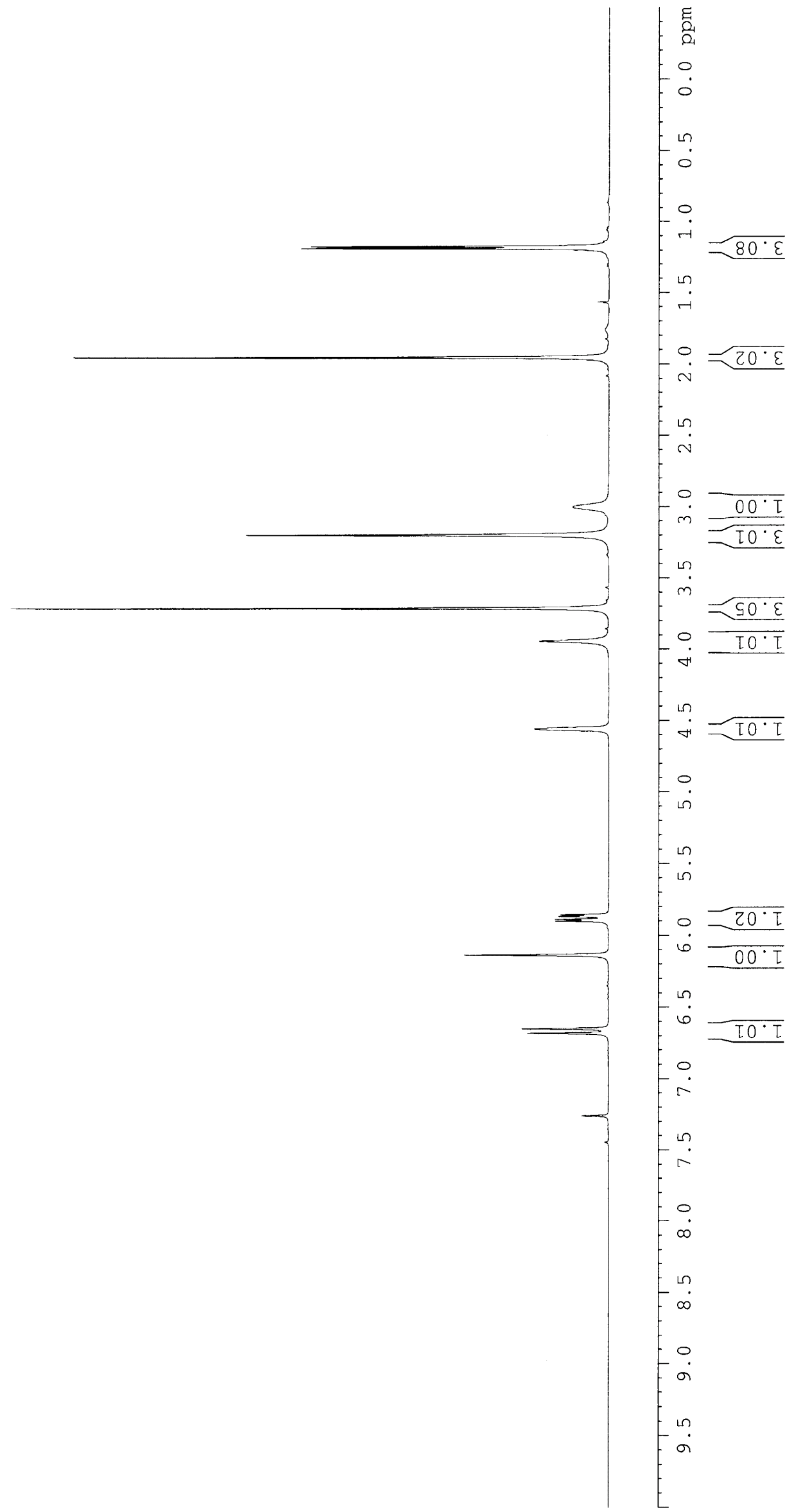
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
3.06
3.04
1.03
1.02
1.02
1.01
2.05
1.00
1.02
1.01
0.99
1.00
2.00
1.02
2.08

S7



MeO
N
O
OH
Me
I



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4.0
4.5
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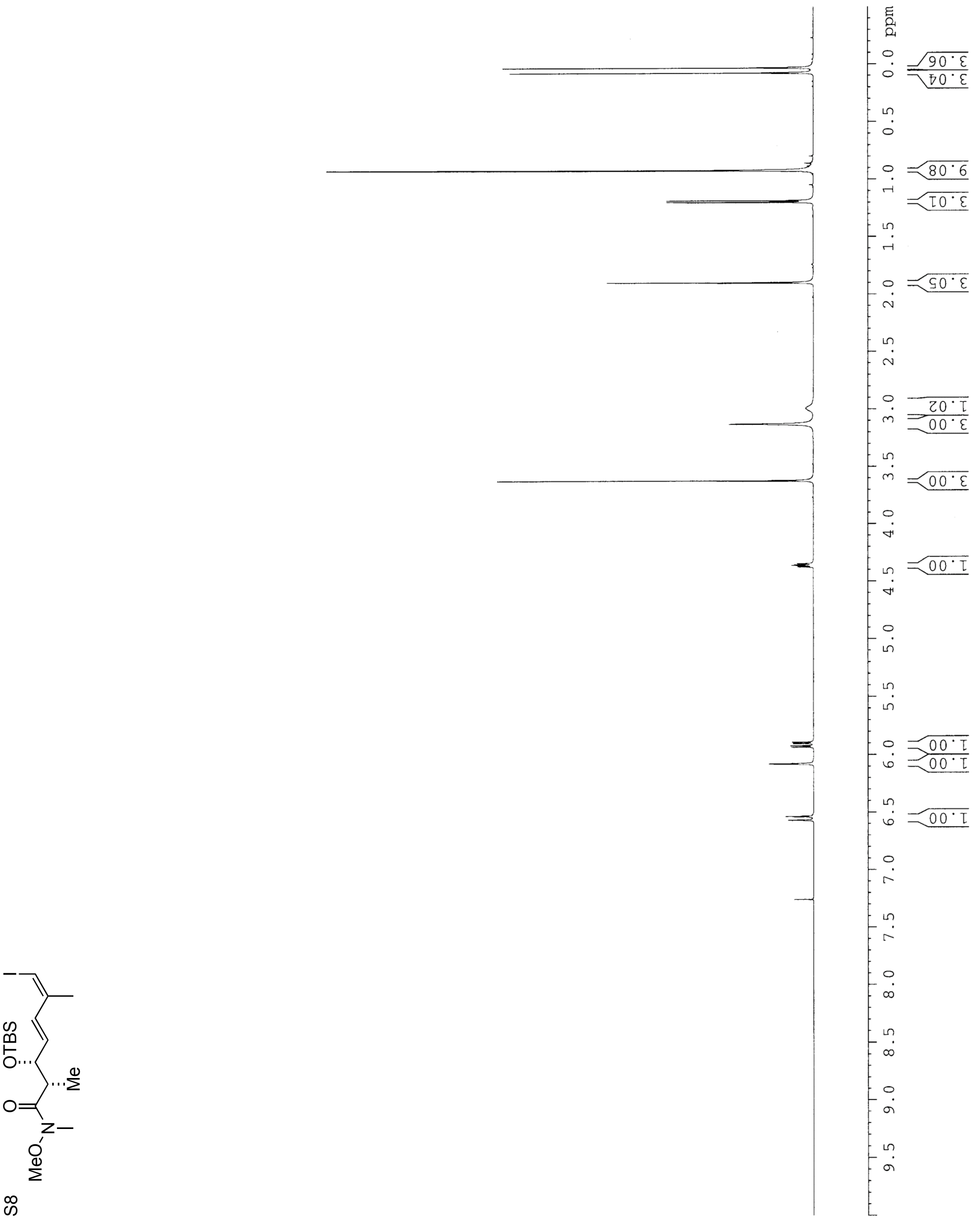
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
3.08
3.02
1.00
3.01
3.05
1.01
1.01
1.02
1.00
1.01

S8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N
O
OTBS
Me
I
ppm
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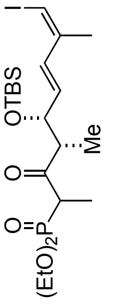
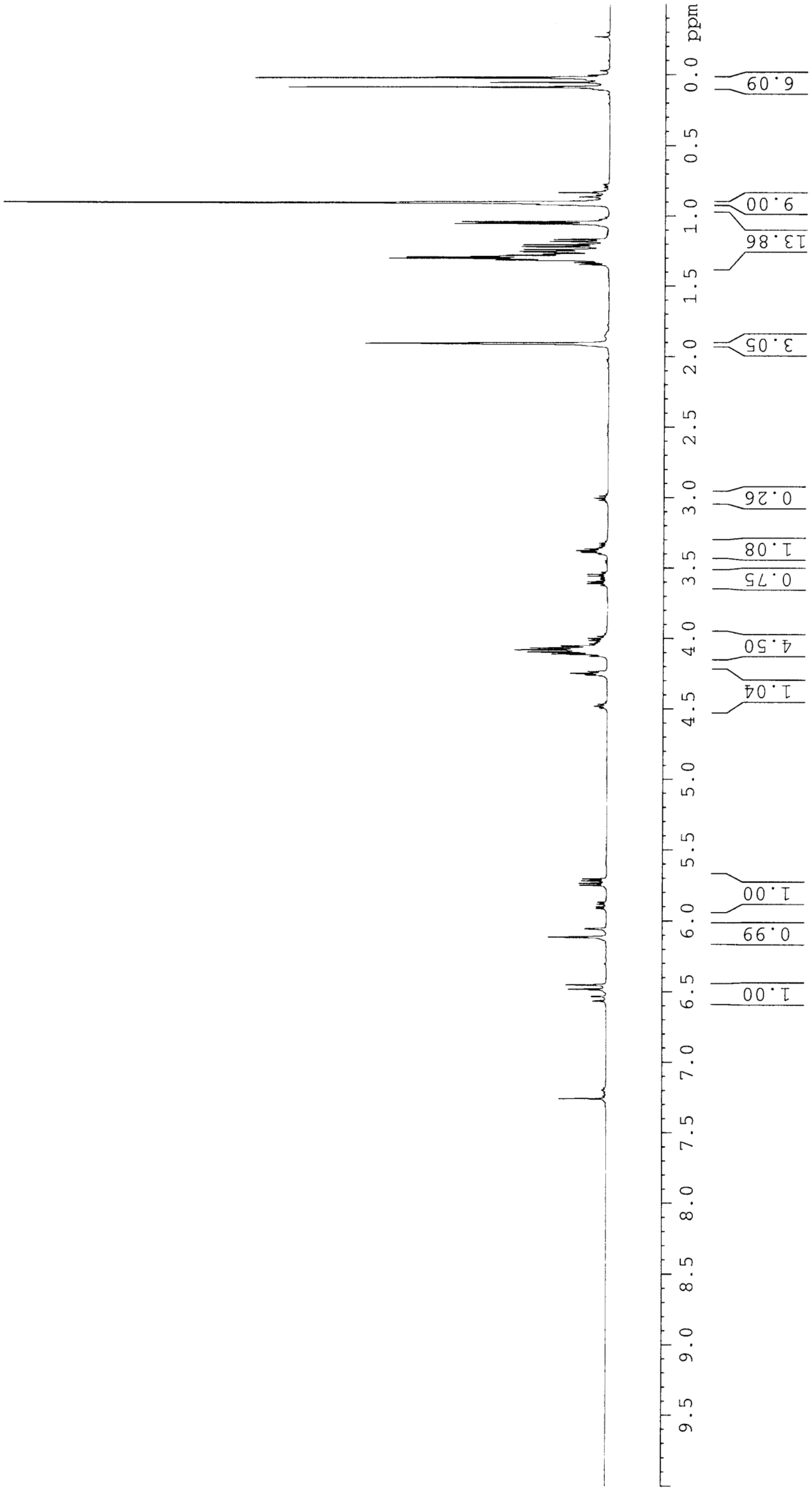
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
3.06
3.04
9.08
3.01
3.05
1.02
3.00
3.00
1.00
1.00
1.00
1.00

18


OTBS
(EtO)2P
O
O
Me
I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7.0
7.5
8.0
8.5
9.0
9.5
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4.50
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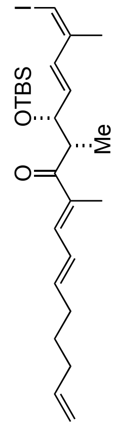
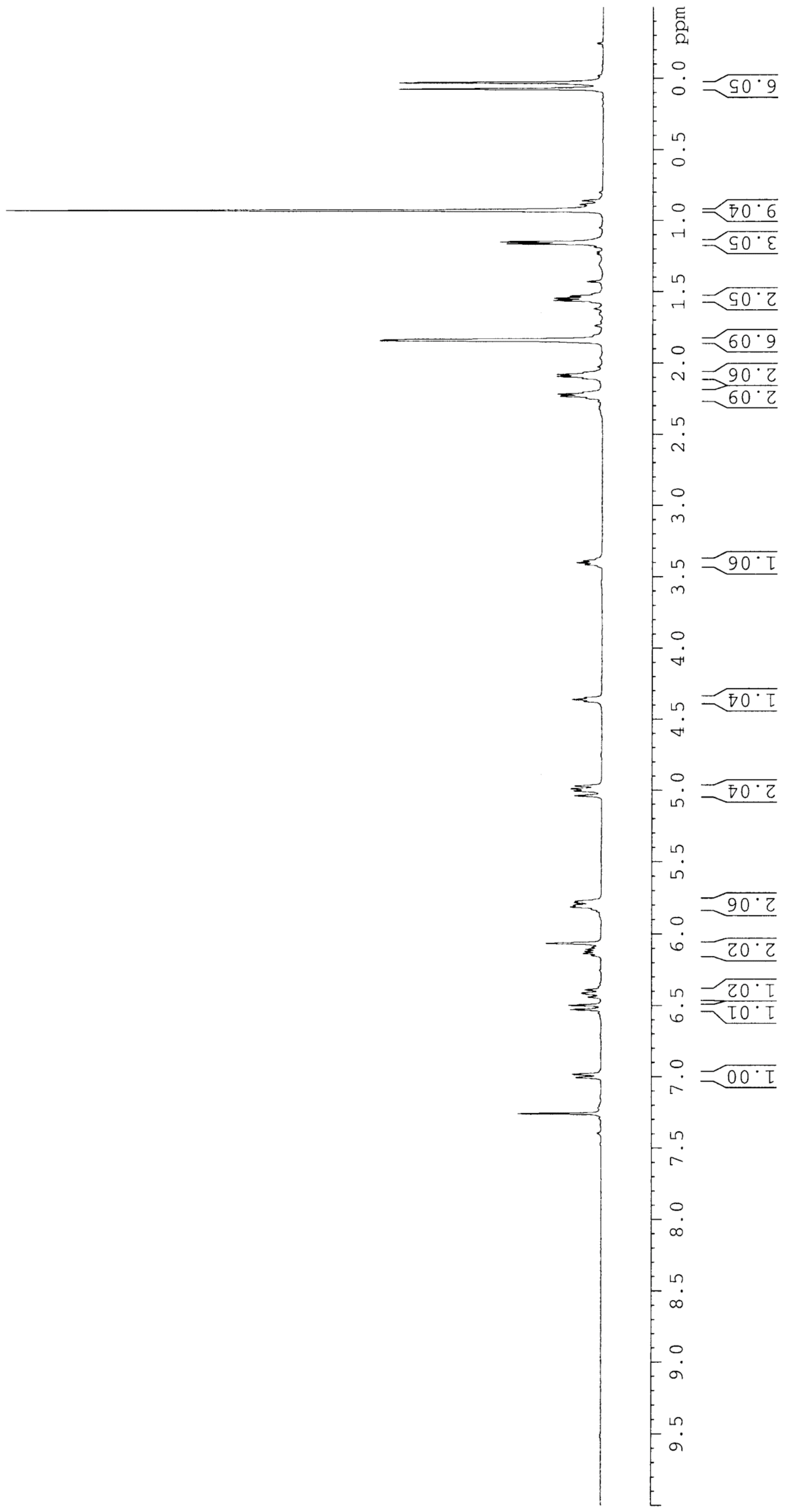
0.99
1.00


OTBS
O
Me
I

20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6.5
7.0
7.5
8.0
8.5
9.0
9.5
6.05
9.04
3.05
2.05
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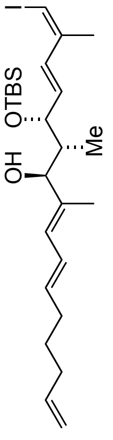
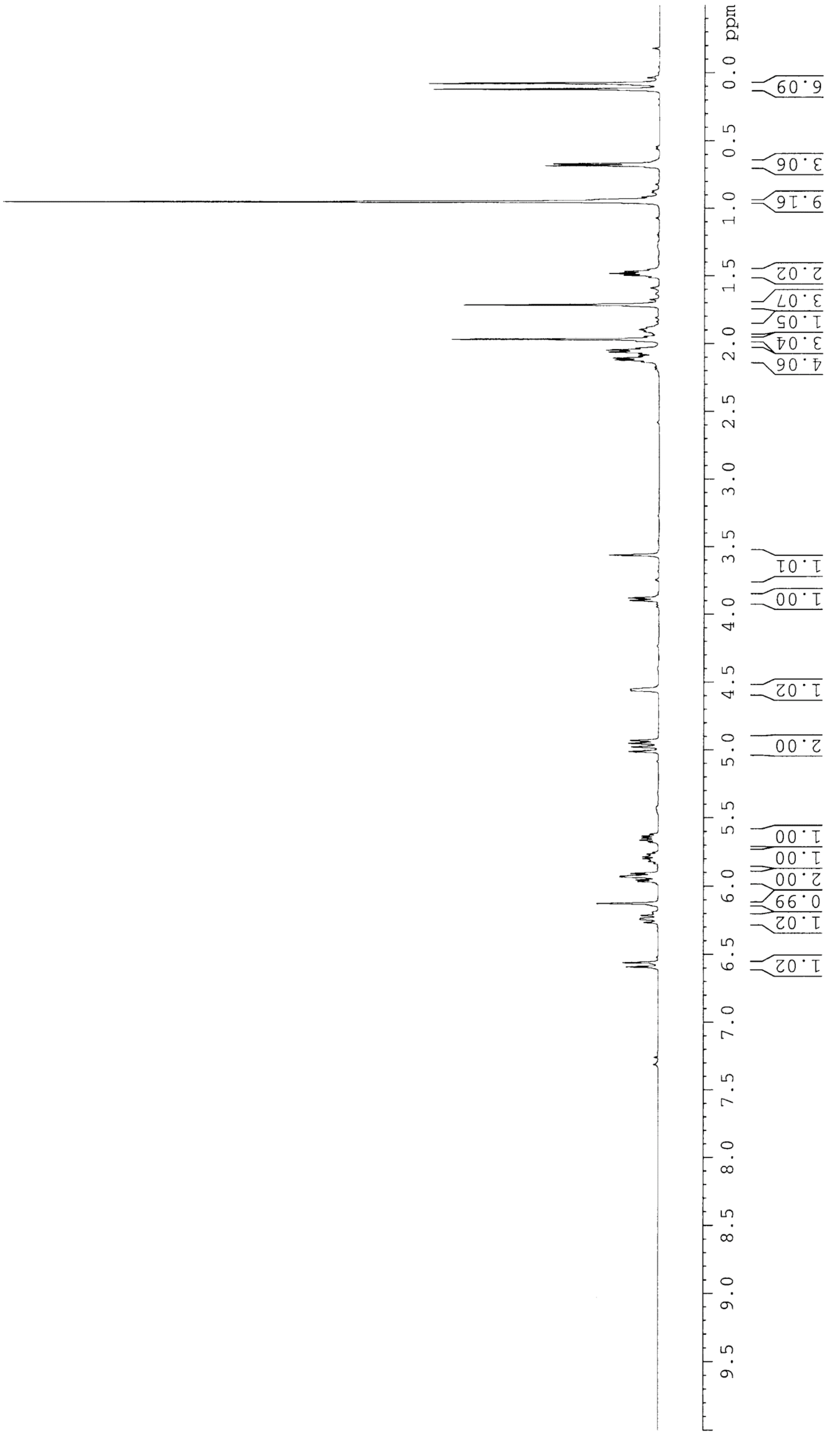
2.06
2.09
1.06
1.04
2.04
2.06
2.02
1.02
1.01
1.00

S9


OH
OTBS
Me
I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5.5
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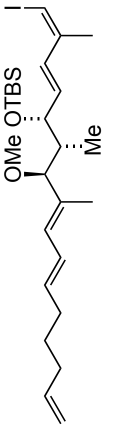
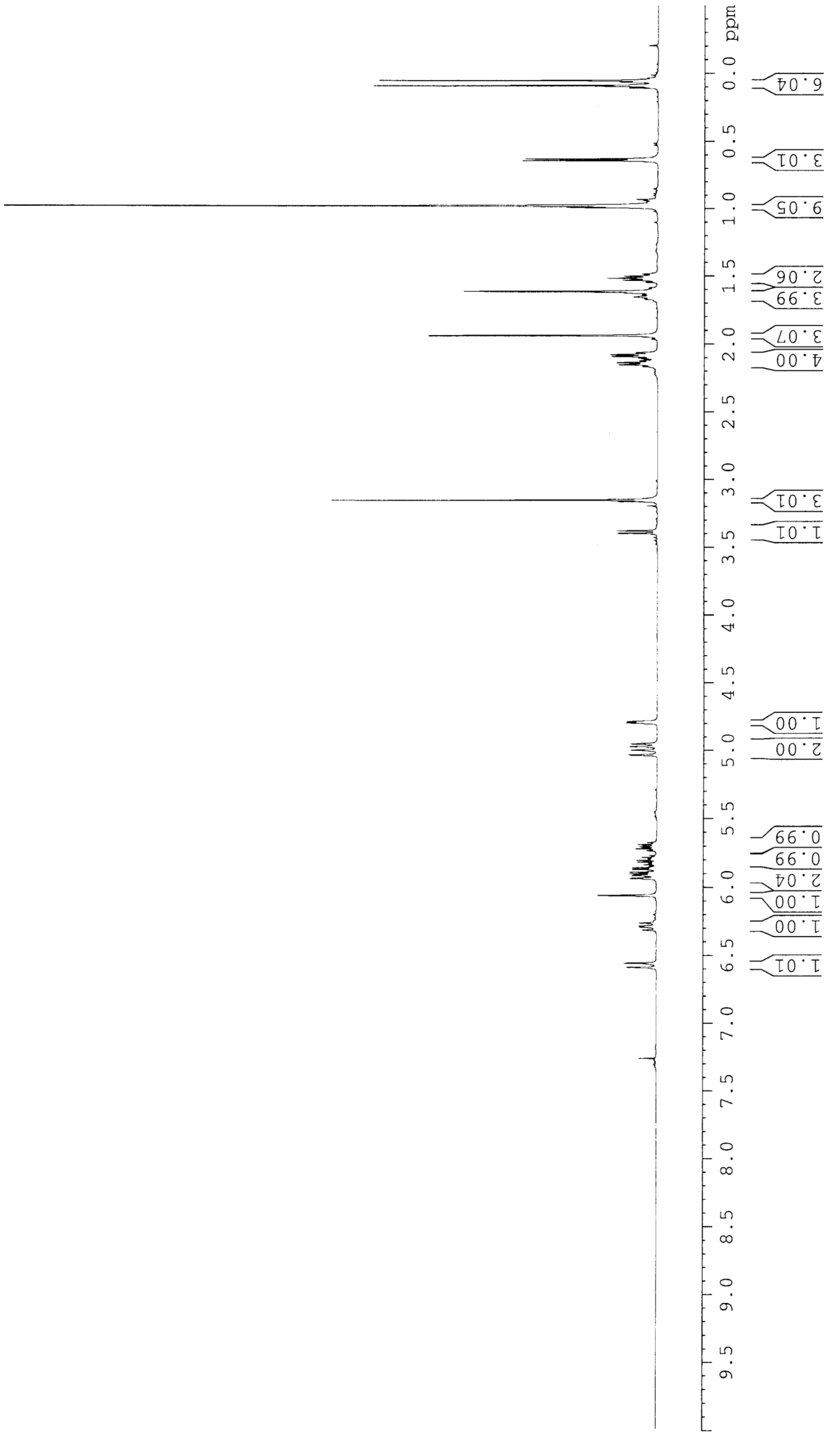
6.5
7.0
7.5
8.0
8.5
9.0
9.5
6.09
3.06
9.16
2.02
3.07
1.05
3.04
4.06
1.01
1.00
1.02
2.00
1.00
1.00
2.00
0.99
1.02
1.02

S10



OMe
OTBS
Me
I



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4.0
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5.0
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6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
6.04
3.01
9.05
2.06
3.99
3.07
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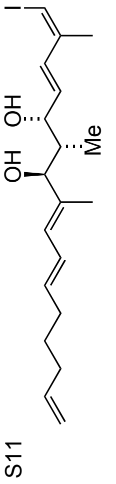
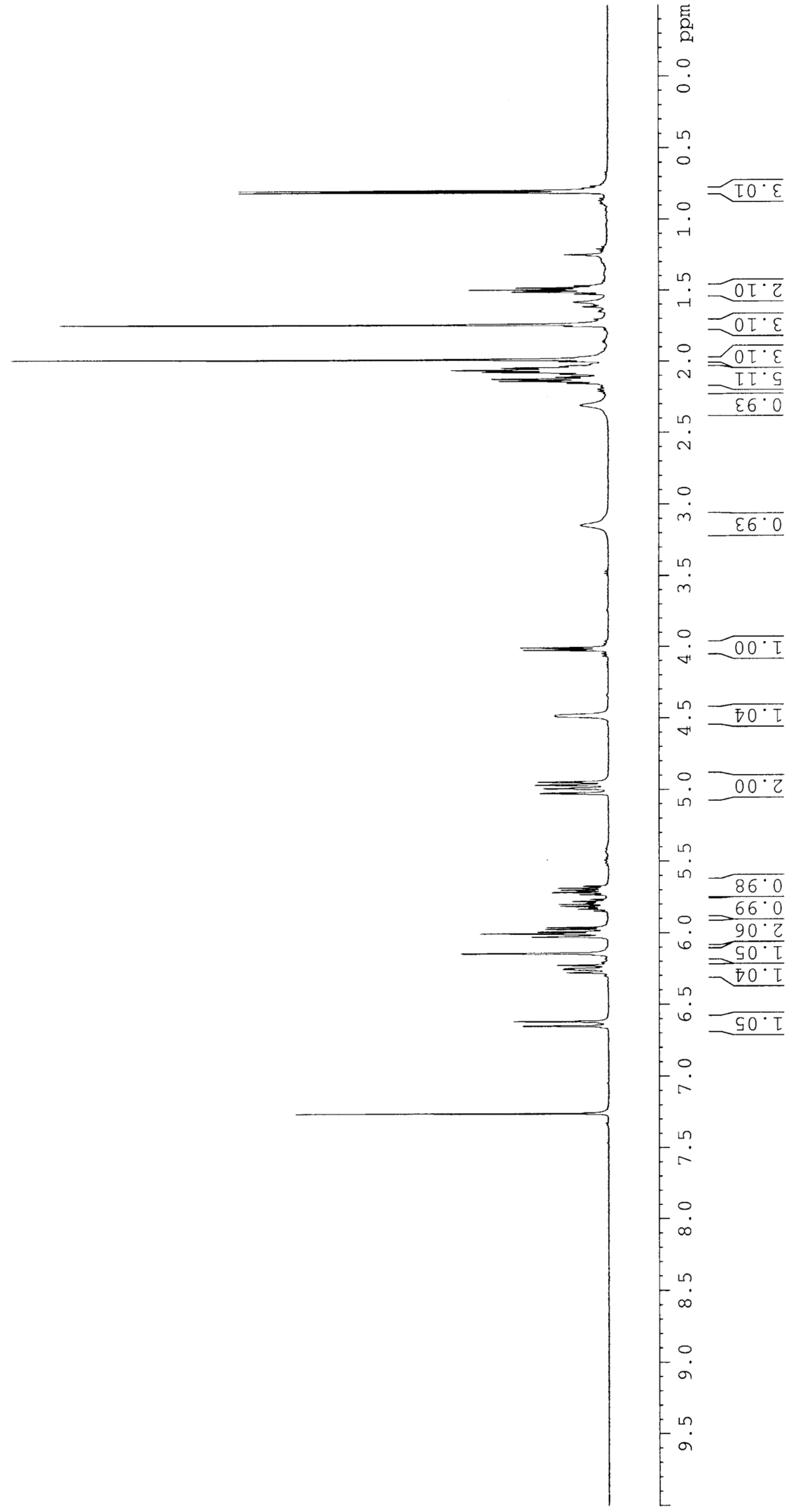
3.01
1.01
1.00
2.00
0.99
0.99
2.04
1.00
1.00
1.01

S11



OH
OH
Me
I



ppm
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4.0
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5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
3.01
2.10
3.10
3.10
5.11
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1.04
2.00
0.98
0.99
2.06
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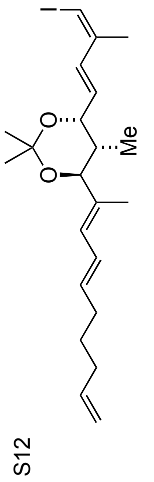
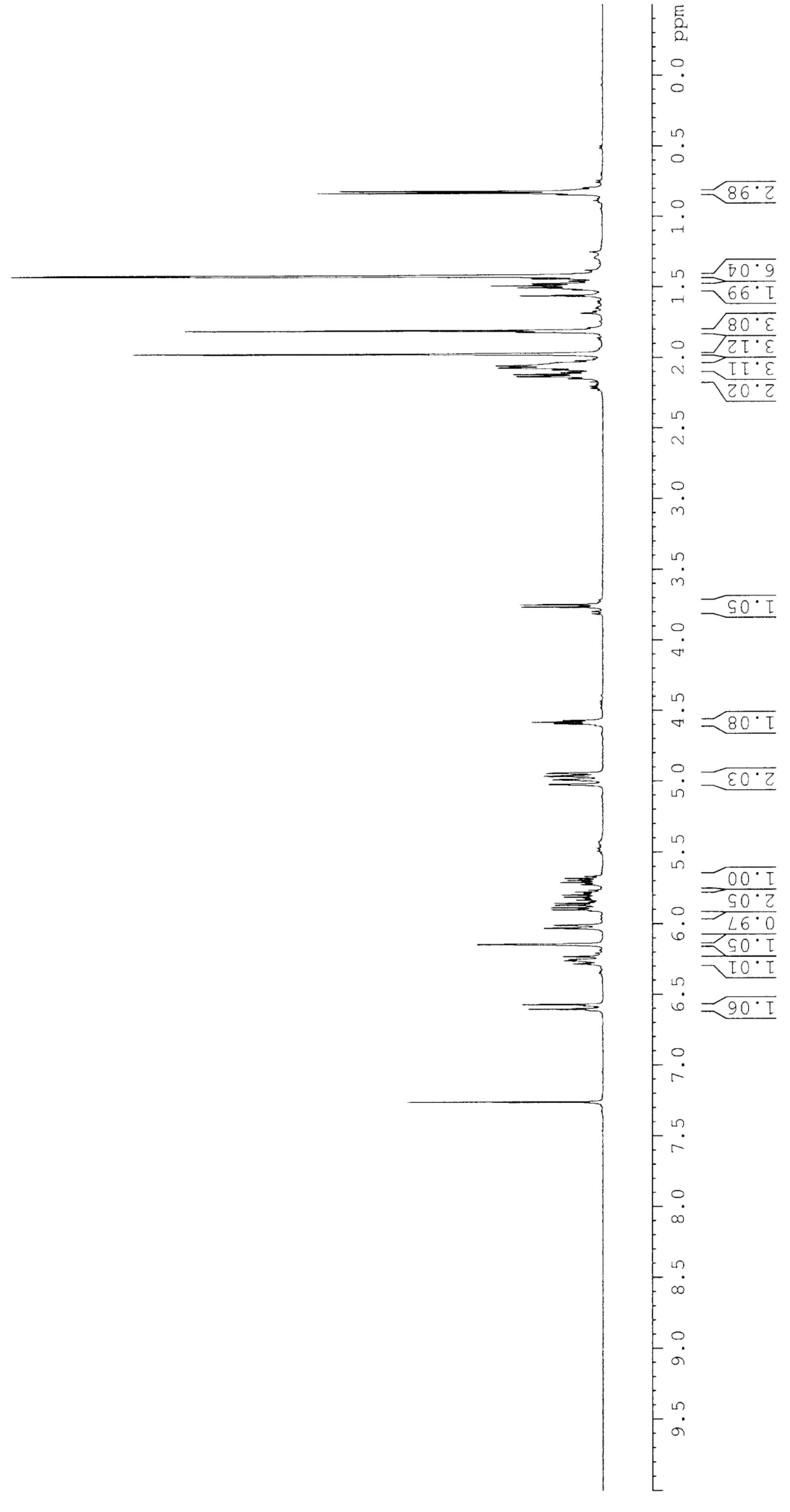
1.04
1.05

S12


O
O
Me
I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7.5
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8.5
9.0
9.5
2.98
6.04
1.99
3.08
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1.08
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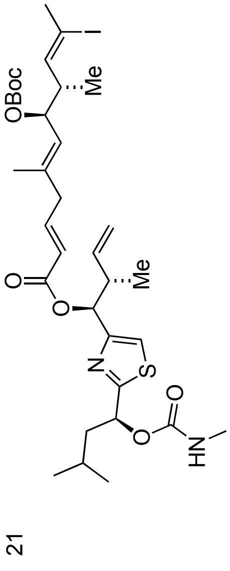
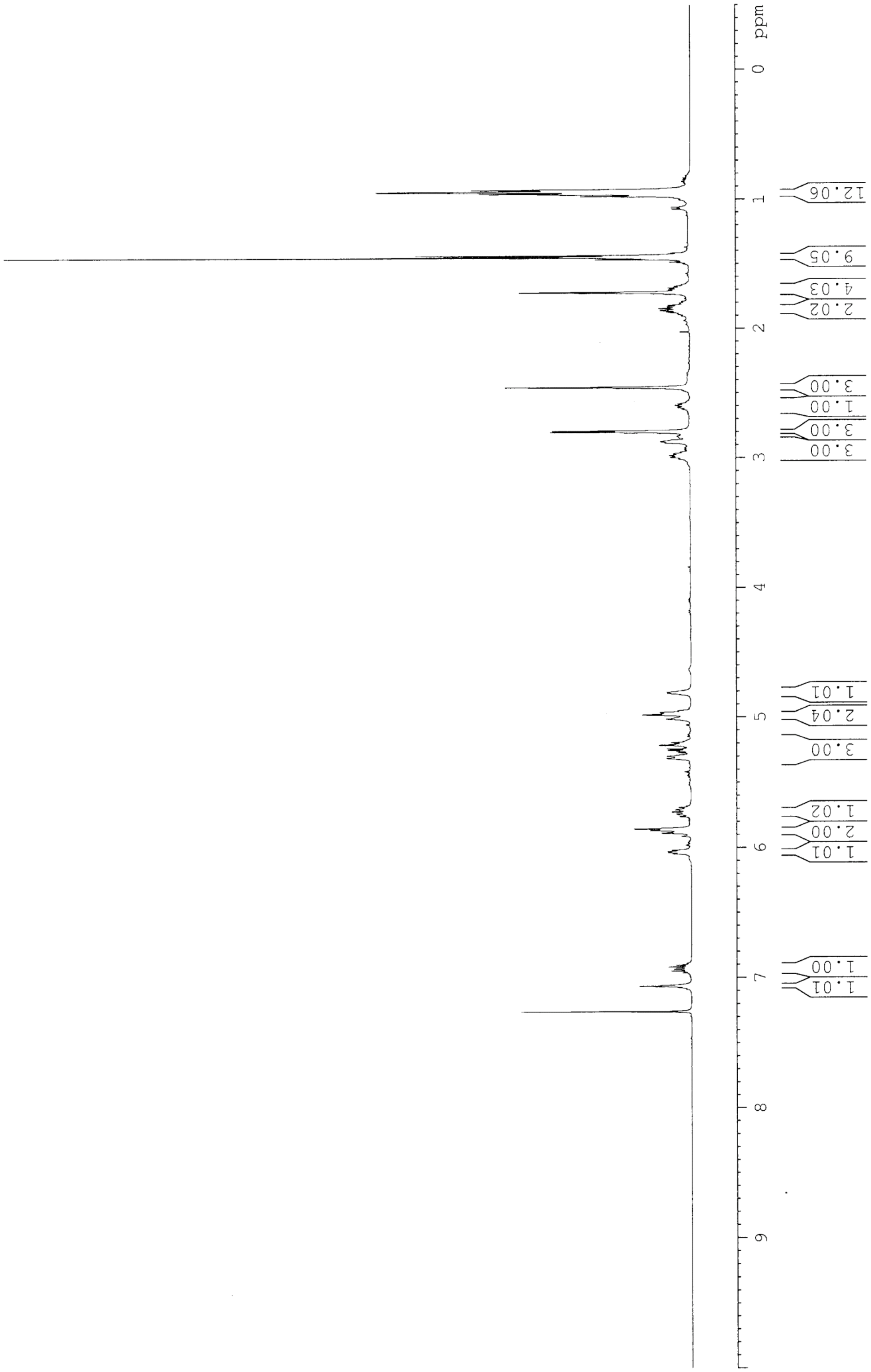
1.01
1.06

21



OBoc
Me
O
O
Me
N
S
O
O
HN



ppm
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9.05
4.03
2.02
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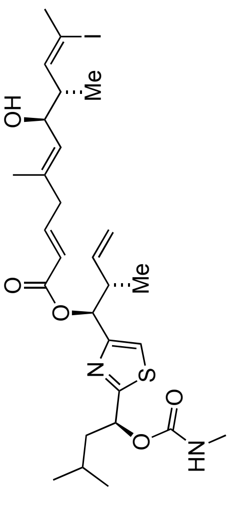
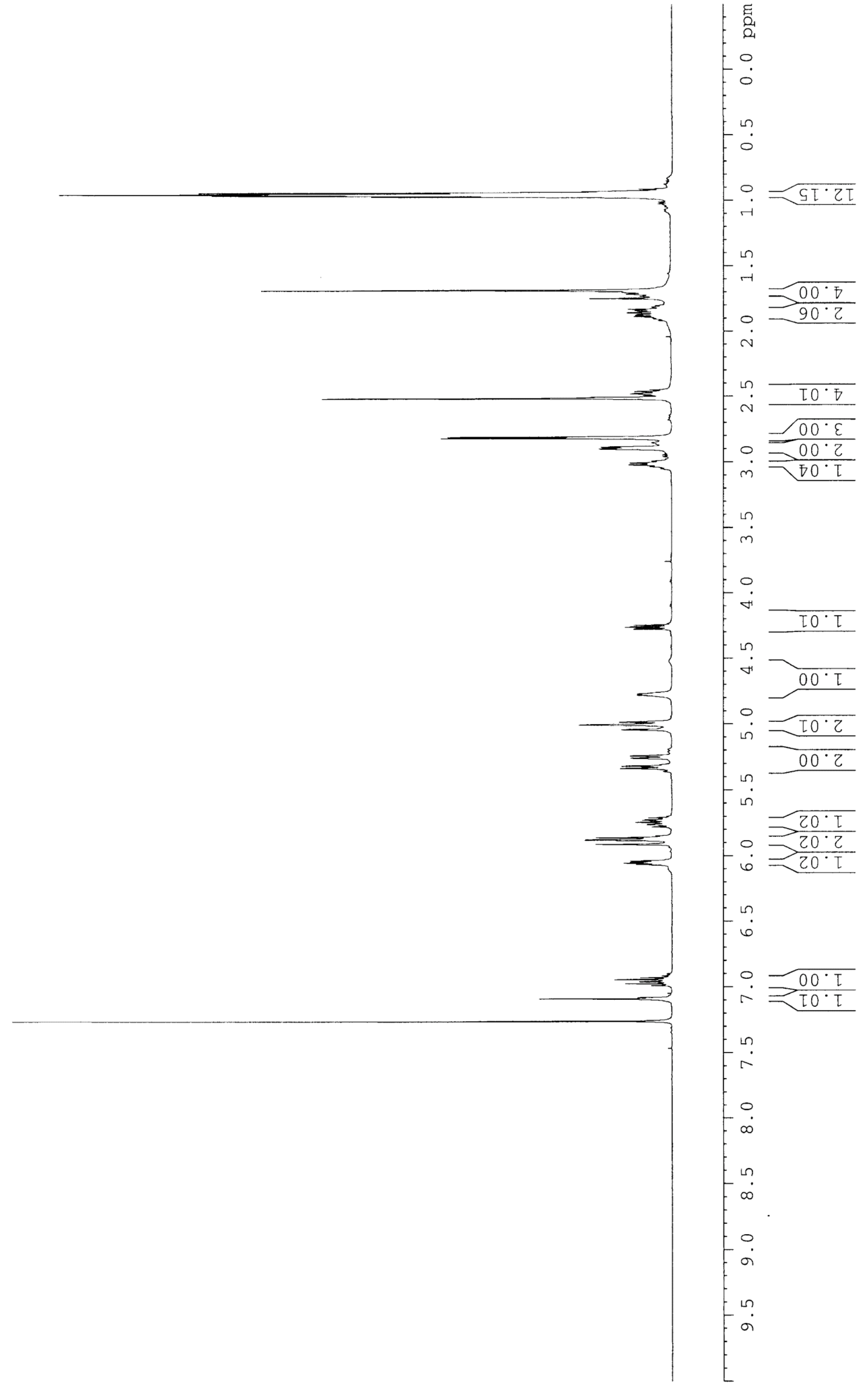
2.00
1.01
1.00
1.01


OH
Me
I
O
O
Me
N
S
O
O
HN

22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6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
12.15
4.00
2.06
4.01
3.00
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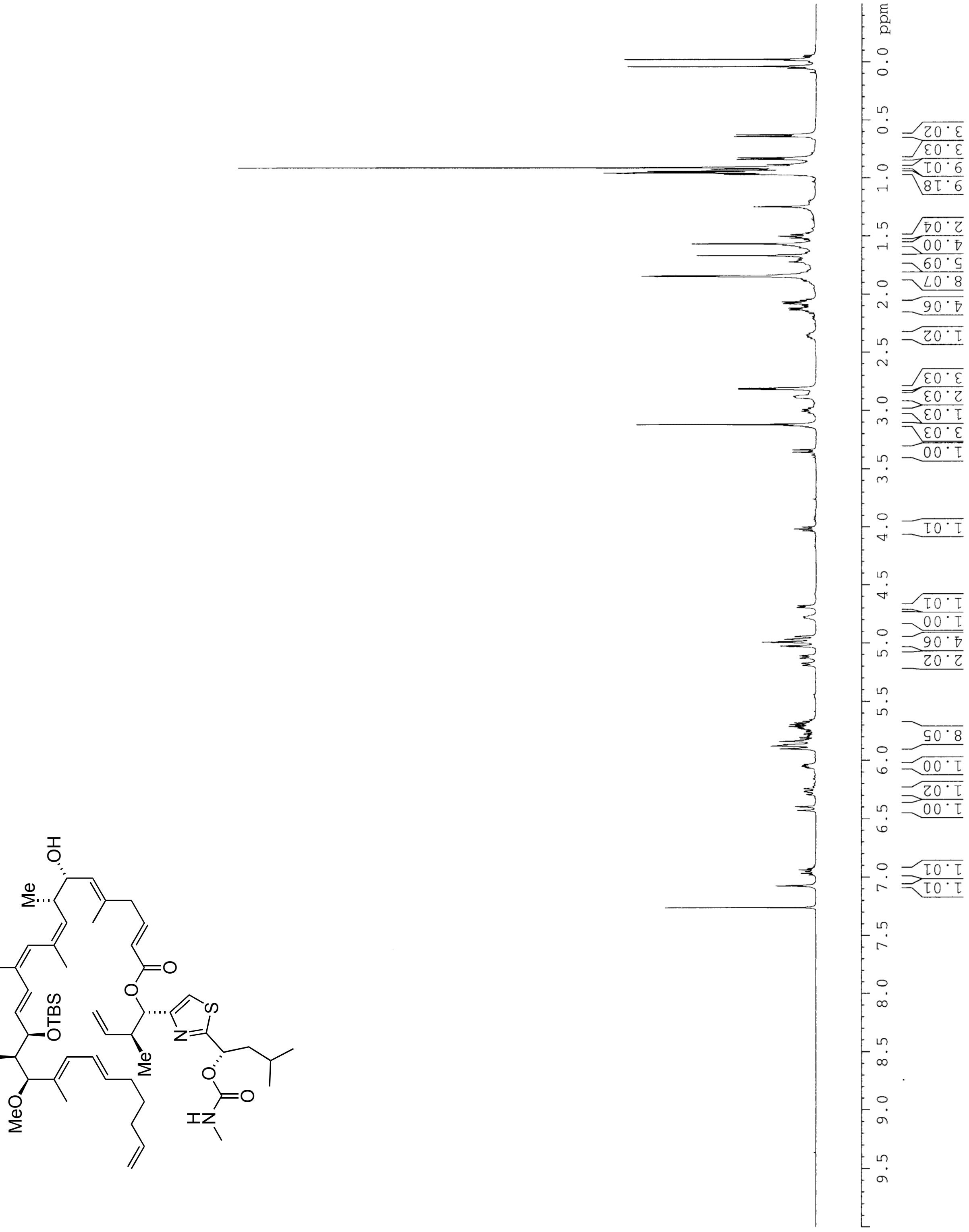
1.01
1.00
2.01
2.00
1.02
2.02
1.02
1.00
1.01

4b



OH
Me
Me
OTBS
Me
MeO
O
O
S
N
Me
O
O
H
N
ppm
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1.0
1.5
2.0
2.5
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3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
3.02
3.03
9.01
9.18
2.04
4.00
5.09
8.07
4.06
1.02
3.03
2.03
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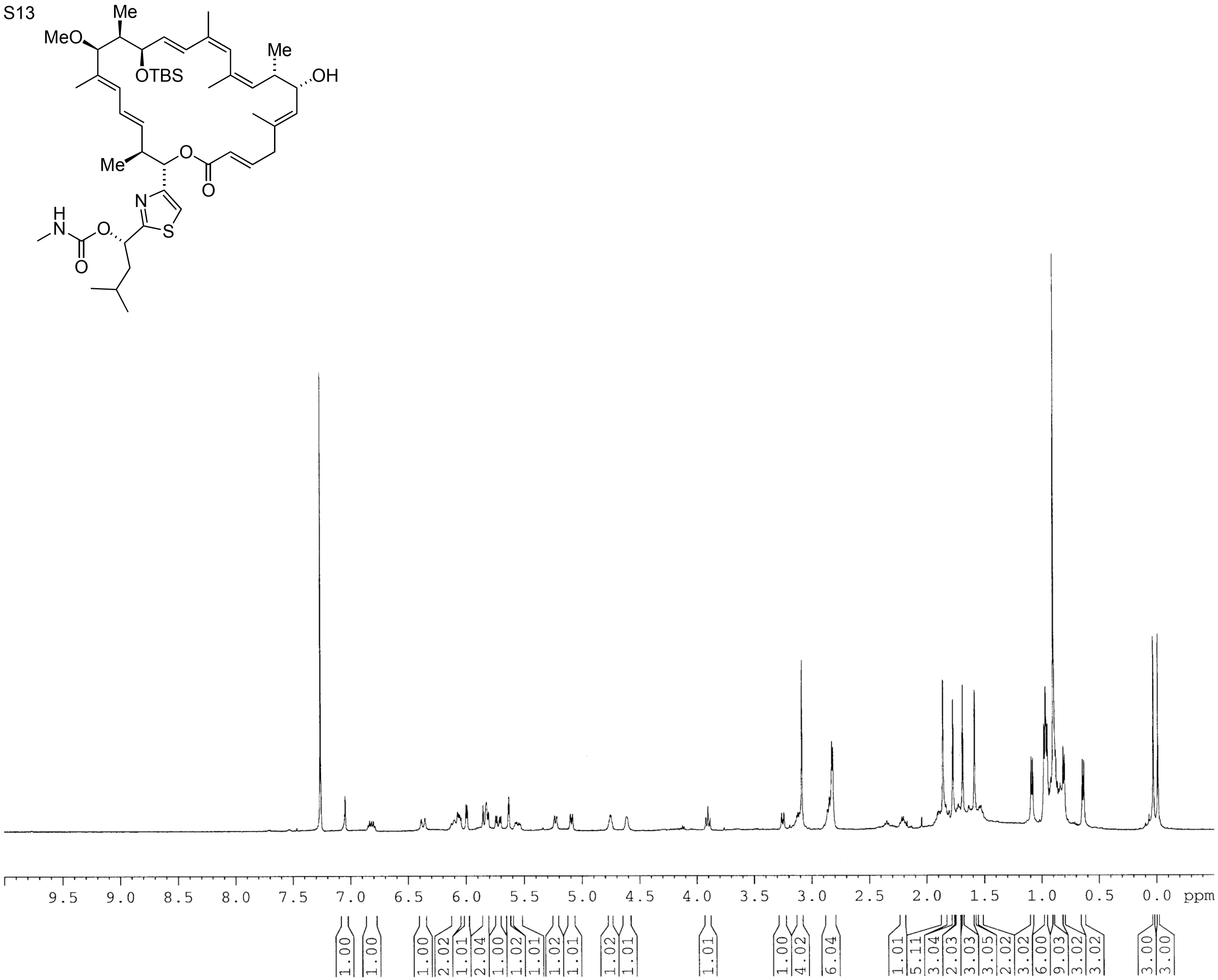
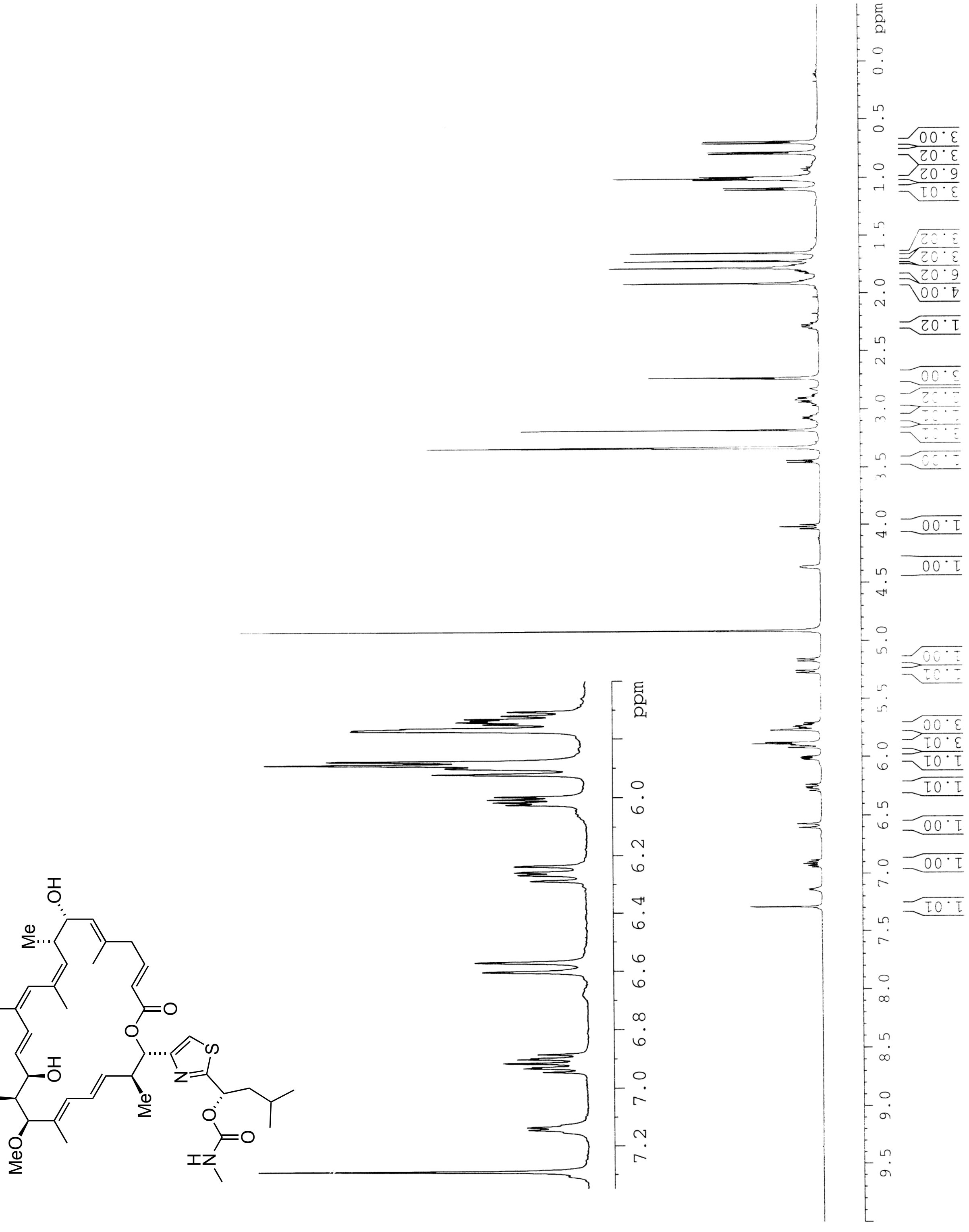
1.00
1.01
1.01

S13


MeO
Me
OTBS
Me
OH
Me
O
O
N
S
H
N
O
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.00 1.00 2.02 1.01 2.04 1.00 1.02 1.01 1.02 1.01 1.02 1.01 1.01 1.00 4.02 6.04 1.01 5.11 3.04 2.03 3.03 3.05 2.02 3.02 6.00 9.03 3.02 3.02 3.00 3.00

2



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Me
OH
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Me
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S
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O
N
H
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6.8
6.6
6.4
6.2
6.0
9.5
9.0
8.5
8.0
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7.0
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4.0
3.5
3.0
2.5
2.0
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1.0
0.5
0.0
1.01
1.00
1.00
1.01
1.01
3.01
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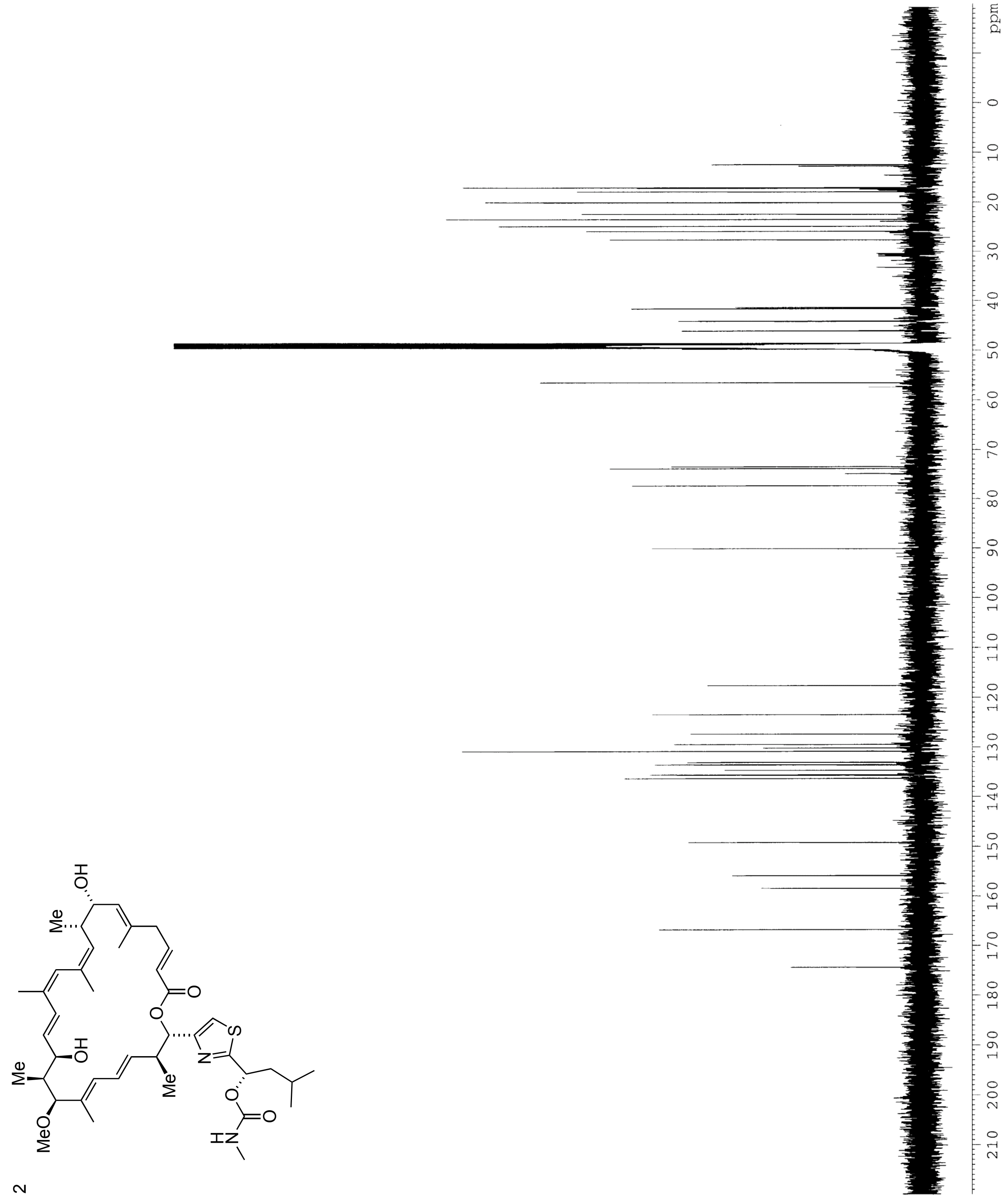
3.00

2



OH
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Me
OH
MeO
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O
S
N
Me
O
O
H
N
ppm
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40
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60
70
80
90
100
110
120
130
140
150
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170
180
190
200
210