Electronic Supplementary Information

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Formal Synthesis of (±)-Platensimycin

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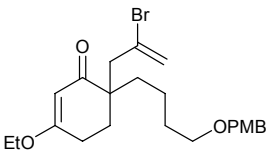
Experimental Methods

General Procedures. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), toluene, benzene, diethyl ether (Et_2O), *N*,*N*-dimethylformamide (DMF), and methylene chloride (CH_2Cl_2) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker DRX-600, DRX-500, AMX-400, or Varian MER-400 instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintuplet, sext = sextet, sep = septet, br = broad. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a VG ZAB-ZSE mass spectrometer using MALDI (matrix-assisted laser-desorption ionization) or ESI (electrospray ionization).

Compound **8**: R_f = 0.38 (silica gel, EtOAc/hexanes 30:70); IR (film) ν_{max} 2938w, 2860w, 1649m, 1607s, 1512m, 1245m, 1186s, 1097m, 1034m, 820m cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23 (d, *J* = 8.5 Hz, 2 H), 6.86 (d, *J* = 8.5 Hz, 2 H), 5.57 (s, 1 H), 5.51 (s, 1 H), 5.25 (s, 1 H), 4.38 (s, 2 H), 3.87 (m, 2 H), 3.78 (s, 3 H), 3.39 (t, *J* = 6.0 Hz, 2 H), 3.06 (d, *J* = 14.5 Hz, 1 H), 2.57 (d, *J* = 14.5 Hz, 1 H), 2.44 (m, 2 H), 1.92 (m, 1 H), 1.55 (m, 4 H), 1.35 (m, 1 H), 1.34 (t, *J* = 7.0 Hz, 3 H), 1.27 (m, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.2, 175.4, 158.9, 130.5, 129.2, 129.0, 121.0, 113.5, 101.5, 72.3, 69.5, 64.0, 55.0, 47.0, 44.9, 34.8, 30.0, 28.4, 25.7, 20.5, 14.0 ppm; HRMS (ESI TOF) calcd for $C_{23}H_{32}BrO_4^+$ [M+H$^+$] 451.1478, found 451.1472.



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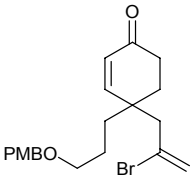
Compound **9**: R_f = 0.35 (silica gel, EtOAc/hexanes 30:70); IR (film) ν_{max} 2937w, 2860w, 1674s, 1612s, 1511s, 1244m, 1172s, 1094m, 1033m, 809s cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.31 (d, *J* = 8.5 Hz, 2 H), 6.94 (d, *J* = 8.5 Hz, 2 H), 6.80 (d, *J* = 10.0 Hz, 1 H), 6.01 (d, *J* = 10.0 Hz, 1 H), 5.66 (m, 2 H), 4.47 (s, 2 H), 3.85 (m, 3 H), 3.50 (t, *J* = 6.0 Hz, 2 H), 2.74 (s, 2 H), 2.54 (m, 2 H), 2.10 (m, 1 H), 1.95 (m, 1 H), 1.66 (m, 3 H), 1.61 (m, 1 H), 1.55 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.8, 158.9, 157.0, 130.3, 129.0, 128.2, 128.0, 121.5, 113.5, 72.4, 69.3, 55.0, 48.8, 38.9, 37.9, 33.7, 30.0, 20.6 ppm; HRMS (ESI TOF) calcd for $C_{21}H_{27}BrO_3Na^+$ [M+Na^+] 429.1036, found 429.1043.



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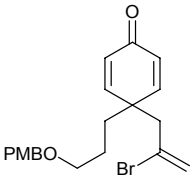
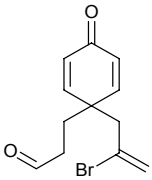
Compound **10**: R_f = 0.30 (silica gel, EtOAc/hexanes 30:70); IR (film) ν_{max} 2937w, 2861w, 1664s, 1623s, 1512m, 1247m, 1097m, 1033m, 861s cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ (500 MHz) 7.23 (d, *J* = 8.5 Hz, 2 H), 6.88 (d, *J* = 8.5 Hz, 2 H), 6.79 (d, *J* = 10.0 Hz, 1 H), 6.35 (d, *J* = 10.0 Hz, 1 H), 5.50 (d, *J* = 2.0 Hz, 1 H), 5.48 (s, 1 H), 4.42 (s, 2 H), 3.80 (s, 3 H), 3.36 (t, *J* = 6.5 Hz, 2 H), 2.80 (s, 2 H), 1.66 (m, 2 H), 1.52 (m, 2 H), 1.21 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 186.2, 159.1, 153.1, 130.4, 129.3, 129.2, 126.7, 121.3, 113.7, 72.5, 69.3, 55.2, 51.1, 46.1, 39.0, 29.7, 21.23 ppm; HRMS (ESI TOF) calcd for $C_{21}H_{25}BrO_3Na^+$ [M+Na^+] 427.0879, found 427.0868



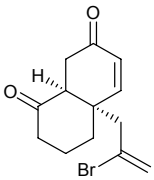
10

Compound **11**: R_f = 0.6 (silica gel, EtOAc/hexanes 70:30); IR (film) ν_{max} 2937w, 1721s, 1662s, 1624w, 1405w, 1260w, 861w cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.82 (d, *J* = 10.0 Hz, 2 H), 6.38 (d, *J* = 10.0 Hz, 2 H), 5.52 (d, *J* = 2.0 Hz, 1 H), 5.50 (s, 1 H), 2.81 (s, 2 H), 2.42 (t, *J* = 6.5 Hz, 2 H), 1.71 (m, 2 H), 1.46 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 201.2, 186.0, 152.5, 130.7, 126.3, 121.6, 51.1, 46.0, 43.4, 38.2, 16.9 ppm; HRMS (ESI TOF) calcd for $C_{13}H_{16}BrO_2^+$ [M+H^+] 283.0328, found 283.0337



11

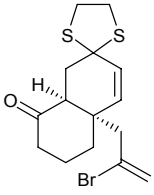
Compound **13**: R_f = 0.65 (silica gel, EtOAc/hexanes 70:30); IR (film) ν_{max} 2938w, 1706s, 1678s, 1622w, 1240w, 903w, 798s cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.60 (dd, *J* =



13

10.0, 1.5 Hz, 1 H), 5.98 (d, *J* = 10.0 Hz, 1 H), 5.71 (d, *J* = 2.0 Hz, 1 H), 5.70 (s, 1 H), 3.05 (m, 1H), 2.97 (dd, *J* = 17.5, 3.0 Hz, 1 H), 2.83 (dd, *J* = 15.0 Hz, 2 H), 2.57 (dd, *J* = 17.5, 5.0 Hz, 1 H), 2.48 (m, 1H), 2.34 (m,1H), 2.07 (m, 3 H), 1.70 (m, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 208.6, 196.5, 152.7, 130.3, 126.7, 122.8, 52.2, 50.8, 44.2, 40.4, 34.6, 34.0, 22.1 ppm; HRMS (ESI TOF) calcd for $C_{13}H_{16}BrO_2^+$ [M+H$^+$] 283.0328, found 283.0321

Compound **14**: R_f = 0.3 (silica gel, EtOAc/hexanes 20:80); IR (film) ν_{max} 2923w, 1702s, 1621w, 1504w, 1236w, 894w, 733s cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.85 (dd, *J* = 10.0, 1.2 Hz, 1 H), 5.75 (d, *J* = 10.0 Hz, 1 H), 5.64 (d, *J* = 1.6 Hz, 1 H), 5.58 (d, *J* = 0.8



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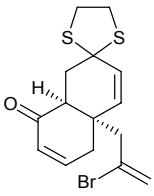
Hz, 1 H), 3.40 - 3.17 (m, 4 H), 2.83 (dd, *J* = 12.6, 3.2 Hz, 1 H), 2.54 (d, *J* = 11.2 Hz, 1 H), 2.51 (d, *J* = 11.2 Hz, 1 H), 2.40 (m, 1H), 2.32 (m,1 H), 2.19 (ddd, *J* = 13.6, 3.2, 1.6 Hz, 1 H), 1.93 (m, 1 H), 1.81 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.6, 133.9, 130.5, 127.2, 122.4, 63.6, 53.5, 48.3, 41.3, 41.2, 40.4, 39.7, 38.0, 31.2, 21.0 ppm; HRMS (ESI TOF) calcd for $C_{15}H_{20}BrOS_2^+$ [M+H$^+$] 359.0133, found 359.0132.

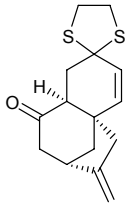
Compound **15**: R_f = 0.25 (silica gel, EtOAc/hexanes 20:80); IR (film) ν_{max} 2921w, 1665s, 1622w, 1423w, 1387w, 1256w, 1151w, 825w cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 6.86 (ddd, *J* = 10.2, 5.4, 3.0 Hz, 1 H), 6.11 (d, *J* = 10.2 Hz, 1 H), 5.87 (dd, *J* = 10.2, 1.2Hz, 1



15

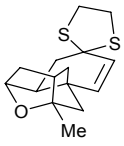
H), 5.80 (d, *J* = 10.2 Hz, 1 H), 5.61 (d, *J* = 1.8 Hz,,1 H), 5.52 (s, 1H), 3.43 - 3.25 (m, 4 H), 2.82 (dd, *J* = 12.6, 3.6 Hz, 1 H), 2.67 (d, *J* = 15.0 Hz, 1 H), 2.61 (d, *J* = 15.0 Hz, 1 H), 2.44 (m, 1 H), 2.33 – 2.27 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz) δ 199.8, 146.8, 133.5, 130.9, 128.9, 127.5, 122.2, 63.9, 50.0, 48.4, 41.0, 40.6, 39.7, 33.8 ppm; HRMS (ESI TOF) calcd for $C_{15}H_{18}BrOS_2^+$ [M+H$^+$] 356.9977, found 356.9977.

Compound **16**: R_f = 0.7 (silica gel, EtOAc/hexanes 30:70); IR (film) ν_{max} 2925s, 1704s, 1433w, 1228w, 1200w, 884w, 829w cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 5.87 (d, *J* = 10.2 Hz, 1 H), 5.51 (d, *J* = 10.2 Hz, 1 H), 5.00 (s, 1 H), 4.95 (s, 1 H), 3.42 - 3.24 (m, 4 H), 2.93 (br, 1 H), 2.60 – 2.57 (ddd, *J* = 12.6, 1.8, 1.8 Hz, 1 H), 2.47 (m, 2 H), 2.41 (d, *J* = 16.8 Hz, 1 H), 2.35 (d, *J* = 16.8 Hz, 1 H), 2.31 – 2.23 (m, 2 H), 1.83 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz) δ 212.7, 152.1, 134.2, 131.8, 108.8, 64.7, 56.3, 50.0, 46.9, 43.5, 43.1, 40.5, 40.2, 39.8, 39.7 ppm; HRMS (ESI TOF) calcd for $C_{15}H_{19}OS_2^+$ [M+H^+] 279.0872, found 279.0879.



16

Compound **19**: R_f = 0.7 (silica gel, EtOAc/hexanes 30:70); IR (film) ν_{max} 2945s, 1446w, 1377w, 1165w, 993w, 816s cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 5.73 (d, *J* = 9.6 Hz, 1 H), 5.35 (d, *J* = 9.6 Hz, 1 H), 4.16 (br, 1 H), 3.42 - 3.24 (m, 4 H), 2.18 (m, 2 H), 2.11 (d, *J* = 7.2 Hz, 1 H), 1.88 (m, 1 H), 1.80 (dd, *J* = 10.8, 1.8 Hz, 1 H), 1.76 (d, *J* = 10.8 Hz, 1 H), 1.58 – 1.54 (m, 2 H), 1.49 (d, *J* = 10.8 Hz, 1 H), 1.39 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz) δ 133.1, 131.6, 86.8, 79.7, 65.8, 52.0, 44.9, 44.4, 43.9, 43.5, 41.6, 40.2, 39.7, 38.3, 23.2 ppm; HRMS (ESI TOF) calcd for $C_{15}H_{21}OS_2^+$ [M+H^+] 281.1028, found 281.1030.



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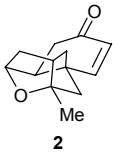
Compound **2**: R_f = 0.25 (silica gel, EtOAc/hexanes 30:70); IR (film) ν_{max} 2949w, 2871w, 1675s, 1448w, 1082w, 993w, 819w cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 6.62 (d, *J* = 11.2 Hz, 1 H), 5.94 (d, *J* = 11.2 Hz, 1 H), 4.15 (dd, *J* = 3.6, 3.6 Hz, 1 H), 2.41 (m, 4 H), 1.95 – 1.93 (m, 2 H), 1.89 (d, *J* = 11.4, 1.8 Hz, 1 H), 1.78 – 1.74 (m, 2 H), 1.66 (d, *J* = 10.8 Hz, 1 H), 1.44 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz) δ 199.0, 155.2, 128.8, 87.0, 78.9, 51.6, 46.2, 44.1, 42.7, 37.9, 37.4, 23.1 ppm; HRMS (ESI TOF) calcd for $C_{13}H_{17}O_2^+$ [M+H^+] 205.1223, found 205.1215.



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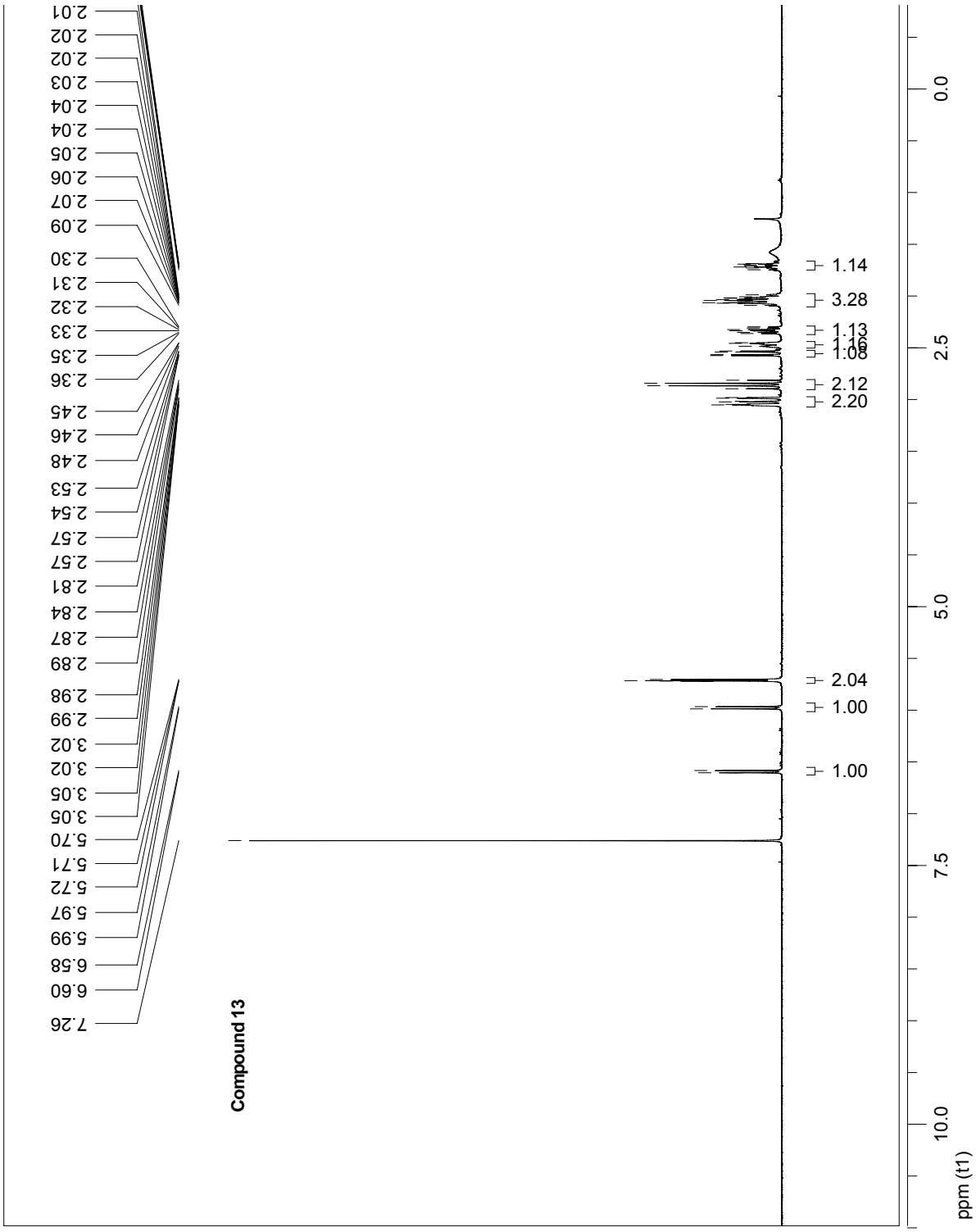
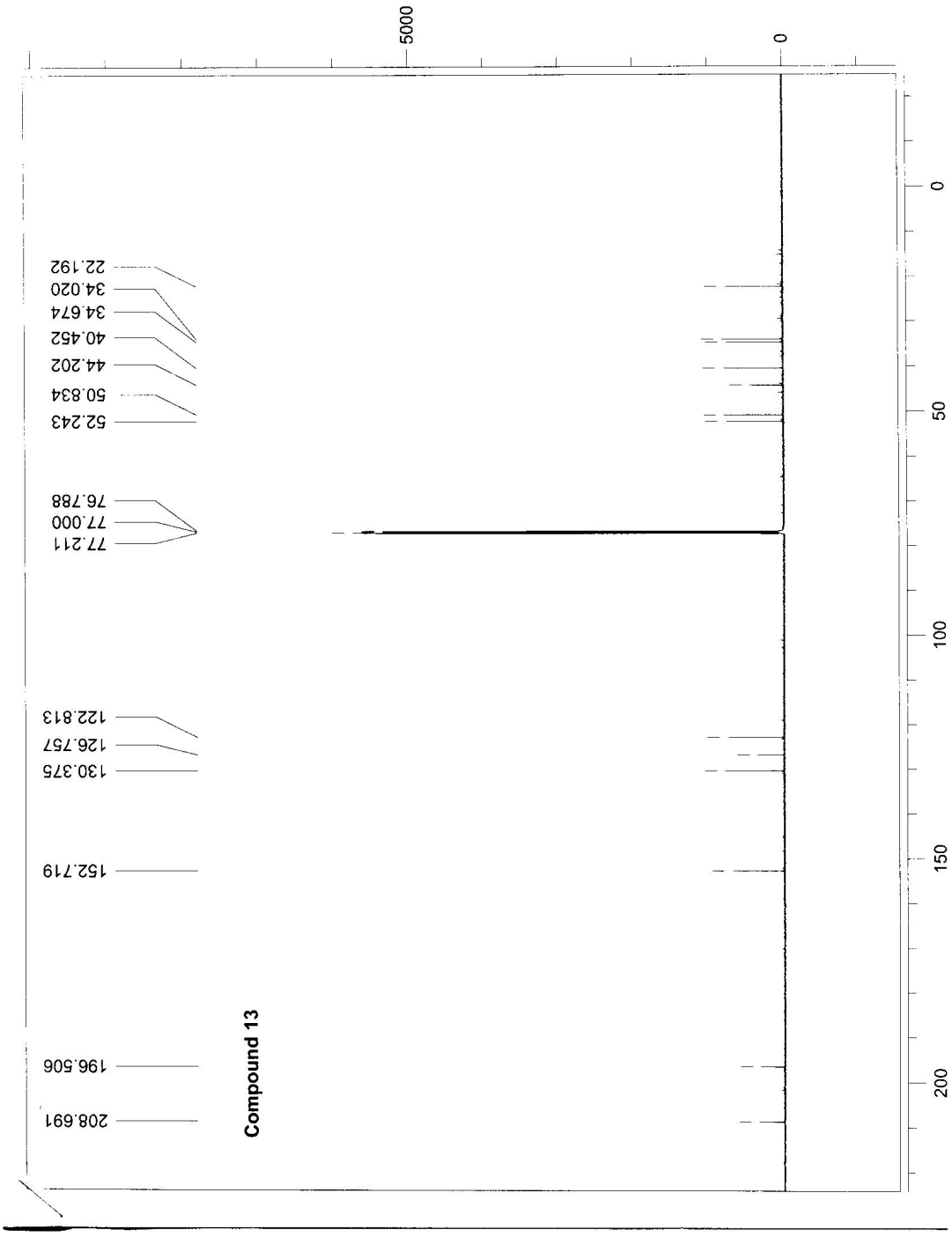
Selected NMR spectra.

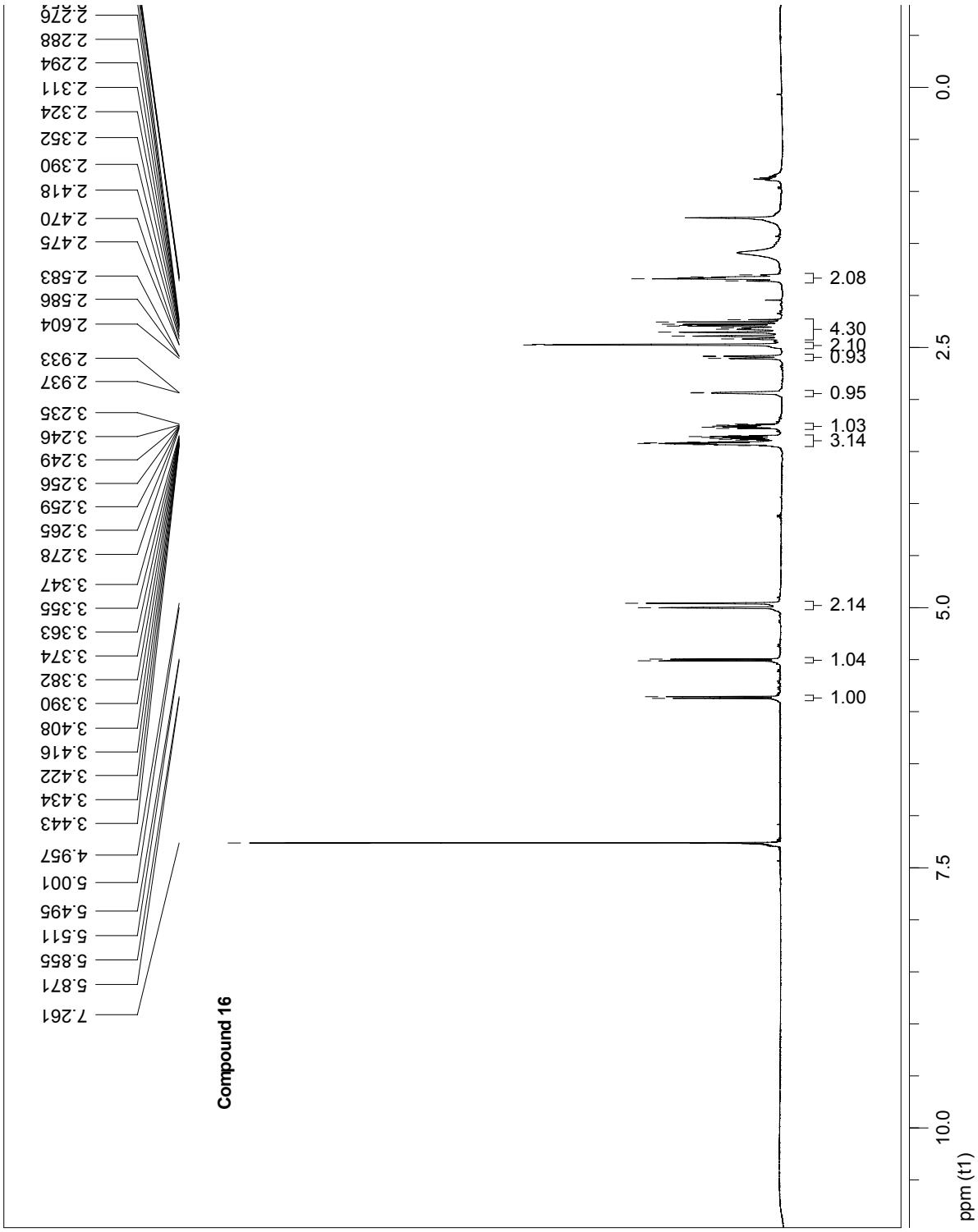
Compound **13**: ^{1}H NMR spectrum ($CDCl_3$, 600 MHz).



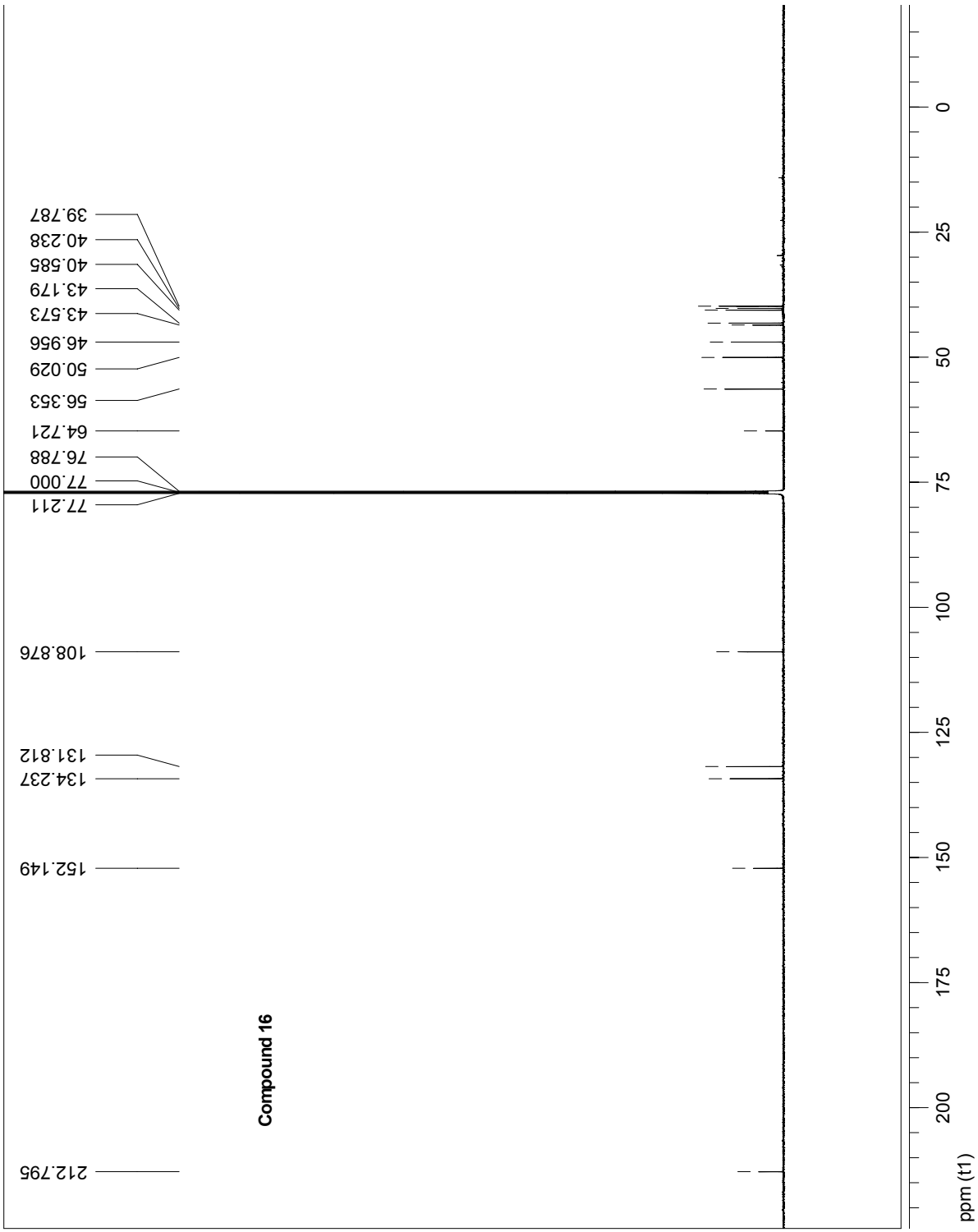
Compound **13**: ^{13}C NMR spectrum ($CDCl_3$, 125 MHz).



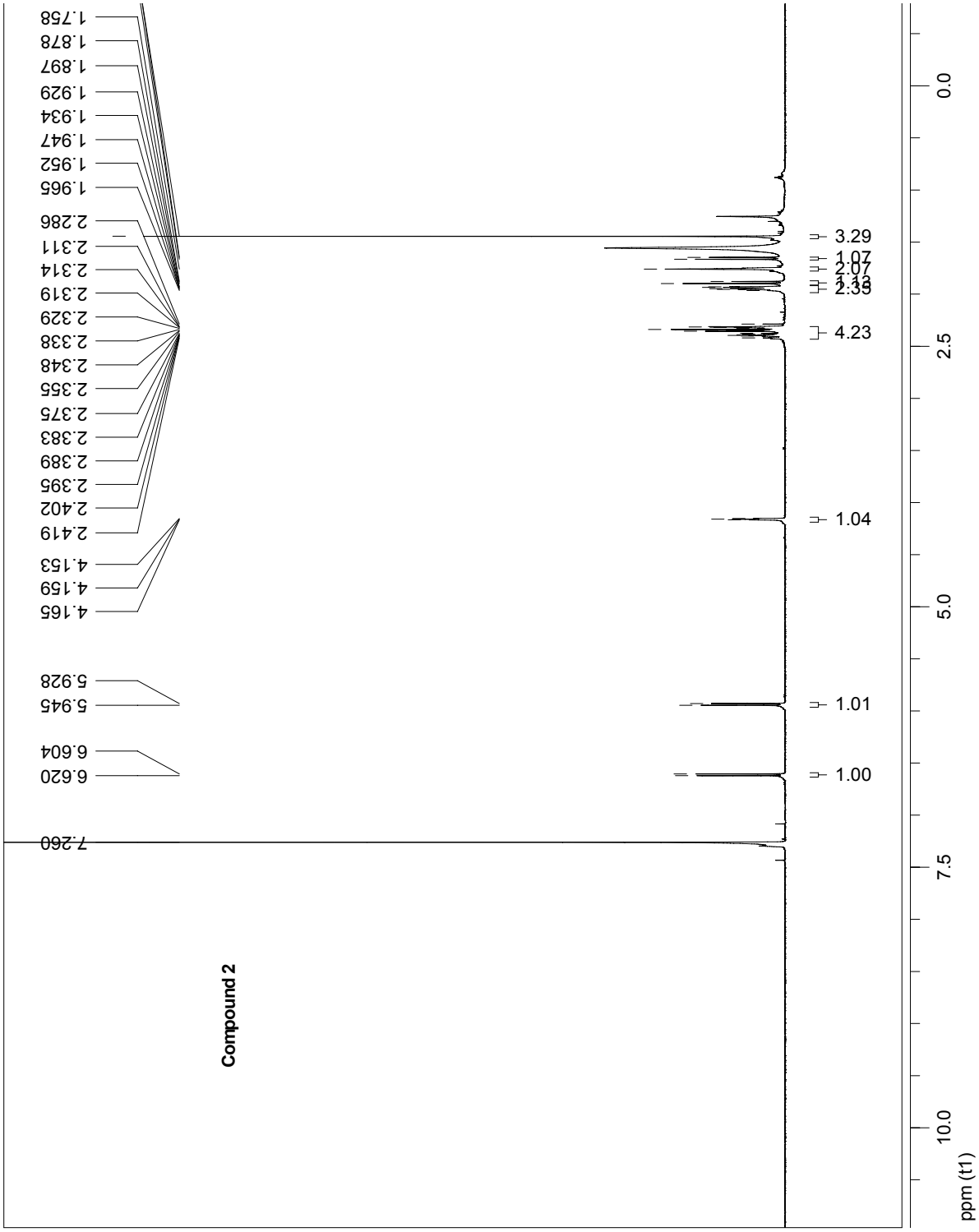
Compound **16**: ^{1}H NMR spectrum ($CDCl_3$, 600 MHz).



Compound **16**: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz).



Compound **2**: ^{1}H NMR spectrum ($CDCl_3$, 600 MHz).



Compound **2**: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz).