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Supporting Information

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Mining the Tetraene Manifold: Total Synthesis of Complex Pyrones From *Placobranchus ocellatus*

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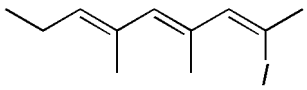
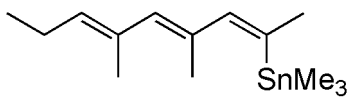
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Melting points were measured on a Büchi melting point apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DRX 500 or AVB-400 spectrometer in $CDCl_3$ with spectra calibrated to C*H*Cl_3 (δ 7.26) and C*D*Cl_3 (δ 77.23). Infrared spectra (IR) were obtained on NaCl plates with an ATI Mattson Gemini FTIR spectrometer. High-resolution mass spectra (HRMS) were obtained on a VG ProSpec Mass Spectrometer using electron impact (EI) at 70 eV.

Unless otherwise noted, all reaction mixtures were magnetically stirred in oven-dried glassware under a blanket of argon. External bath temperatures were used to record all reaction mixture temperatures. Analytical thin layer chromatography (TLC) was carried out on Merck silica gel 60 F_{254} TLC plates. TLC visualization was accomplished using 254 nm UV light or charring solutions of $KMnO_4$ and cerric ammonium molybdenate. Flash chromatography was performed on ICN siliTech 32-63 D 60 Å silica gel according to the procedure of Still.[1]

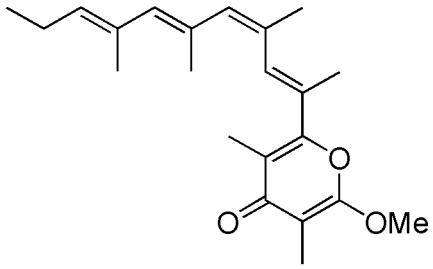
Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were dried according to the procedure described by Bergman.[2] *n*-Butyl lithium was titrated using diphenylacetic acid in THF. CuI was purified by precipitation from hot aqueous NaI. Extracts were dried over anhydrous $MgSO_4$ and solvents were removed with a rotary evaporator at aspirator pressure.



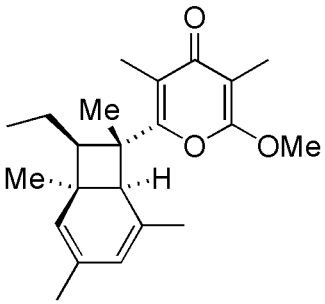
(2*Z*, 4*E*, 6*E*)-2-Iodo-4,6-dimethyl-nona-2,4,6-triene (**11**): To a suspension of ethyl triphenylphosphonium iodide (3.019 g, 7.218 mmol) in THF (72 mL) was added a solution of *n*-BuLi (2.9 mL, 7.25 mmol, 2.5 M in hexanes) at room temperature (rt) under argon. The resulting orange solution was added, via cannula, to a solution of I_2 (1.83 g, 7.21 mmol) in THF (36 mL) at –78 °C to make a thick brown mixture. After 10 min, a solution of NaHMDS (6.50 mL, 6.50 mmol, 1.0 M in THF) was added to make a slightly less thick tan mixture. After 10 min, (2*E*, 4*E*)-2,4-dimethyl-hepta-2,4-dienal (506 mg, 3.66 mmol) was added, via canulla, (neat + 3 x 1 mL THF rinses). After 30 min, the reaction mixture was diluted with pentane (400 mL) and filtered through a pad of celite. The filtrate was concentrated, taken up in pentane (50 mL) and filtered through celite. This was repeated two more times to provide 595 mg (59%) of **11** as a yellow oil. In some instances, significant amounts of triphenylphosphine contaminated the crude product. This could be removed by dissolving the crude sample in THF with an excess of MeI at rt. After 20 min, dilution with pentane and filtration through celite would provide material pure enough for further use. Due to the instability of this compound it was taken on immediately without full characterization: R_f 0.66 (hexanes); ^{1}H NMR (400 MHz, 25 °C): δ = 6.01 (s, 1 H), 5.92 (s, 1 H), 5.40 (t, *J* = 7.2 Hz, 1 H), 2.57 (s, 3 H), 2.12 (app quint, *J* = 7.4 Hz, 2 H), 1.91 (s, 3 H), 1.77 (s, 3 H), 1.01 (t, *J* = 7.6 Hz, 3 H).



Trimethyl-((1*Z*, 3*E*, 5*E*)-1,3,5-trimethyl-octa-1,3,5-trienyl)-stannane (**12**): To a solution of **11** (589 mg, 2.21 mmol) in THF (25 mL) was added a solution of *n*-BuLi (1.35 mL, 3.37 mmol, 2.5 M in hexanes) at –78 °C under argon. After 5 min, a solution of Me_3SnCl (3.90 mL, 3.90 mmol, 1.0 M in THF) was added. After 5 min, the reaction mixture was concentrated in vacuo, and purified by column chromatography. The column was prepared with 5% Et_3N in hexanes and then flushed with ~2 column volumes of 0.5% Et_3N in hexanes. The crude product was then loaded and run with 0.5% Et_3N in hexanes to provide 465 mg (69%) of **12** as a colorless oil that was used without complete characterization: R_f 0.80 (hexanes); ^{1}H NMR (500 MHz, 25 °C): δ = 6.55 (t, ^3J(Sn, H) = 69 Hz, 1 H), 5.74 (s, 1 H), 5.32 (t, J = 7.2 Hz, 1 H), 2.11 (app quint, J = 7.3 Hz, 2 H), 1.96 (t, ^3J(Sn, H) = 24 Hz, 3 H), 1.82 (s, 3 H), 1.74 (s, 3 H), 0.99 (t, J = 7.5 Hz, 3 H), 0.12 (t, ^3J(Sn, H) = 26 Hz, 9 H).



2-methoxy-3,5-dimethyl-6-((2*E*, 4*Z*, 6*E*, 8*E*)-4,6,8-trimethylundeca-2,4,6,8-tetraen-2-yl)-4H-pyran-4-one (**14**): An oven dried vial was charged with **13** (66.8 mg, 0.21 mmol), **12** (130 mg, 0.41 mmol), $Pd(PPh_3)_4$ (12.6 mg, 11 μmol), CuI (4.2 mg, 22 μmol), CsF (110.7 mg, 0.73 mmol) and DMF (0.5 mL). This mixture was then heated to 45 °C under argon. After 1.5 h, the solvent was removed with a high-vac pump. The product was purified by column chromatography (25% EtOAc in hexanes) to provide 62 mg (87%) of **14** as a yellow oil. Due to the instability of this compound, it was taken on immediately without complete characterization: R_f 0.40 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, 25 °C): δ = 6.41 (s, 1 H), 5.98 (s, 1 H), 5.83 (s, 1 H), 5.33 (t, J = 7 Hz, 1 H), 3.94 (s, 3 H), 2.09 (app quint, J = 7 Hz, 2 H), 2.02 (s, 3 H), 1.98 (s, 3 H), 1.96 (s, 3 H), 1.86 (s, 6 H), 1.73 (s, 3 H), 0.98 (t, J = 7.5 Hz, 3 H); ^{13}C (100 MHz, 25 °C): δ = 181.1, 162.1, 158.7, 136.6, 136.5, 135.7, 133.8, 132.2, 132.1, 130.8, 127.6, 117.9, 99.4, 55.3, 24.8, 21.8, 18.6, 17.0, 16.7, 14.3, 11.9, 7.1.



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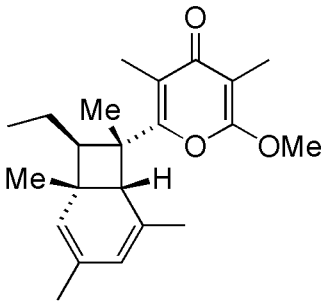


6

(±)-ocellapyrone A (**5**) and **bicyclooctadiene** (**6**): A solution of **14** (62 mg, 0.18 mmol) in $CDCl_3$ (6 mL) was made in a scintillation vial. A portion of this solution was transferred into an NMR tube and both vessels were capped under N_2 and heated to 45 °C. The reaction was monitored by ^1H NMR and was deemed complete after 5 d. The reaction mixtures were combined, concentrated, purified by column chromatography (25% EtOAc in hexanes), and then separated by reverse phase HPLC (80 to 100% CH_3CN in H_2O linear gradient over 40 minutes, Alltech Econosil C18 10μ column) to provide 8.1 mg (13%) of ocellapyrone A (**5**) and 40.9 mg (66%) of **6** as white solids. A diastereomeric bicyclo[4.2.0]octadiene of undetermined relative stereochemistry (6 mg, 10%) was also obtained from the reaction mixture. (See experimental for 9,10-deoxytridachione (**1**) for isolation of this same material under different conditions).

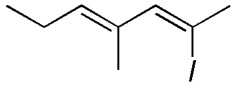
Data for ocellapyrone A (**5**): R_f 0.28 (30% EtOAc in hexanes); IR (thin film): $\tilde{\nu}$ = 2955, 2926, 1661, 1616 cm^{-1}; HRMS calcd for $C_{22}H_{30}O_3$ (M^+): 342.2195; found: 342.2189.

Table S1: Comparison of NMR data for ocellapyrone A[3]

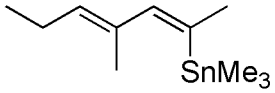
^1H (lit.)	^1H (current 500 MHz)	^{13}C (lit.)[a]	^{13}C (current 125 MHz)
0.89	0.89	7.4	7.4
1.14	1.15	10.0	10.0
1.25	1.25	13.3	13.5
1.60	1.58	15.7	15.7
1.72 (m)	1.73 (s)	19.1	19.1
1.75 (s)	1.75 (m)	22.7	22.3
1.78 (s)	1.76 (s)	23.6	23.7
1.88	1.88	32.7	32.7
1.98	1.97	38.6	38.4
2.42	2.41	47.6	47.5
3.12	3.11	49.6	49.5
4.01	4.01	56.6	57.4
5.07	5.07	57.5	57.5
5.62	5.61	101.1	100.8
		116.7	117.0
		123.1	123.1
		125.6	125.6
		130.0	130.1
		130.3	130.4
		162.7	162.4
		164.8	165.1
		182.2	182.2

[a] Literature ^{13}C data adjusted so C*H*Cl_3 is referenced to 77.2 ppm.

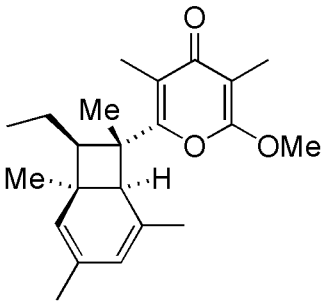
Data for **6**: R_f 0.28 (30% EtOAc in hexanes); IR (thin film): $\tilde{\nu}$ = 2957, 2926, 1658, 1611 cm^{-1}; ^1H NMR (500 MHz, 25 °C): δ = 5.39 (s, 1 H), 5.02 (s, 1 H), 3.95 (s, 3 H), 3.22 (dd, *J* = 8.4 Hz, 6.7 Hz, 1 H), 2.58 (s, 1 H), 2.05 (s, 3 H), 1.84 (s, 3 H), 1.63 (s, 3 H), 1.59 (d, *J* = 1.4 Hz, 3 H), 1.57 (m, 1 H), 1.53 (s, 3 H), 1.43 (app quint, *J* = 7 Hz, 1 H), 1.15 (s, 3 H), 0.85 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (125 MHz, 25 °C): δ = 182.0, 162.0, 161.2, 132.2, 127.8, 127.0, 124.6, 119.4, 99.2, 56.8, 55.9, 54.1, 52.1, 36.8, 23.8, 23.7, 23.1, 21.8, 19.4, 13.5, 12.3, 7.2; HRMS calcd for $C_{22}H_{30}O_3$ (M^+): 342.2195; found: 342.9194.



(2*Z*, 4*E*)-2-iodo-4-methylhepta-2,4-diene (**S1**): To a suspension of (1-iodo-ethyl)-triphenyl-phosphonium iodide[4] (3.026 g, 5.56 mmol) in THF (40 mL) was added a freshly made solution of NaHMDS (1.05 g, 5.76 mmol) in THF (5 mL) dropwise *via* cannula at rt under argon. After the addition was complete, the mixture was cooled to –78 °C and a solution of (*E*)-2-methylpent-2-enal (490 mg, 4.99 mmol) in THF (3 mL + 2 x 1 mL rinses) was added dropwise *via* cannula. After 45 min, the reaction mixture was diluted with pentane (400 mL) and filtered through celite to provide a clear, colorless solution which was concentrated. The product was purified by kugelrohr distillation (60 °C, 700 mTorr) to provide 140 mg (12%) of **S1** as a colorless oil. Due to the instability of this compound, it was taken on immediately without full characterization: R_f 0.76 (hexanes); ^1H NMR (500 MHz, 25 °C): δ = 5.96 (s, 1 H), 5.50 (t, *J* = 7.0 Hz, 1 H), 2.56 (s, 3 H), 2.09 (app quint, *J* = 7.3 Hz, 2 H), 1.76 (s, 3 H), 1.01 (t, *J* = 7.5 Hz, 3 H).



trimethyl((2*Z*, 4*E*)-4-methylhepta-2,4-dien-2-yl)stannane (**18**): To a solution of **S1** (140 mg, 0.59 mmol) in THF (10 mL) was added a solution of *n*-BuLi (0.30 mL, 0.67 mmol, 2.25 M in hexanes) at –78 °C under argon. After 5 min, a solution of Me_3SnCl (0.72 mL, 0.72 mmol, 1.0 M in THF) was added. After 5 min, the reaction mixture was quenched at –78 °C with H_2O (20 mL) and diluted with pentane (20 mL). The two layers were separated and the organic layer was dried and concentrated to afford 140 mg (86%) of **18** as a colorless oil that was used without full characterization: R_f 0.80 (hexanes); ^1H NMR (500 MHz, 25 °C): δ = 6.51 (t, ^3J(Sn, H) = 70 Hz, 1 H), 5.25 (t, *J* = 7 Hz, 1 H), 2.03 (app quint, *J* = 7 Hz, 2 H), 1.93 (t, ^3J(Sn, H) = 25 Hz, 3 H), 1.66 (s, 3 H), 0.99 (t, *J* = 8 Hz, 3 H), 0.11 (t, ^3J(Sn, H) = 26 Hz, 9 H).



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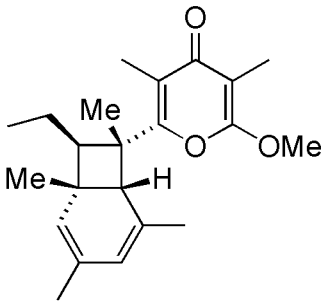
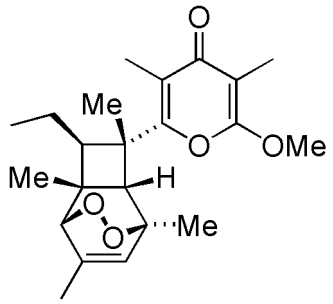


6

(±)-ocellapyrone A (**5**) and **bicyclooctadiene** (**6**): An oven dried vial was charged with **19** (50.2 mg, 0.14 mmol), **18** (55.9 mg, 0.21 mmol), $Pd(PPh_3)_4$ (10.3 mg, 8.9 μmol), CuI (4.6 mg, 24 μmol), CsF (38.0 mg, 0.25 mmol) and DMF (0.5 mL). This mixture was then heated to 45 °C under argon. After 1 h, the reaction mixture was diluted with H_2O (20 mL) and Et_2O (4 mL). The two layers were separated and the aqueous layer was extracted with Et_2O (3 x 3 mL). The combined organics were washed with H_2O (15 mL), dried, and concentrated. The products were purified by column chromatography (25 % EtOAc in hexanes) to provide 47 mg of a "pure" mixture of the two compounds. The two compounds were purified by reverse phase HPLC (80 to 100% CH_3CN in H_2O linear gradient over 40 minutes, Alltech Econosil C18 10μ column) to provide 4 mg (8%) of ocellapyrone A (**5**) and 37 mg (78%) of **6** as white solids.

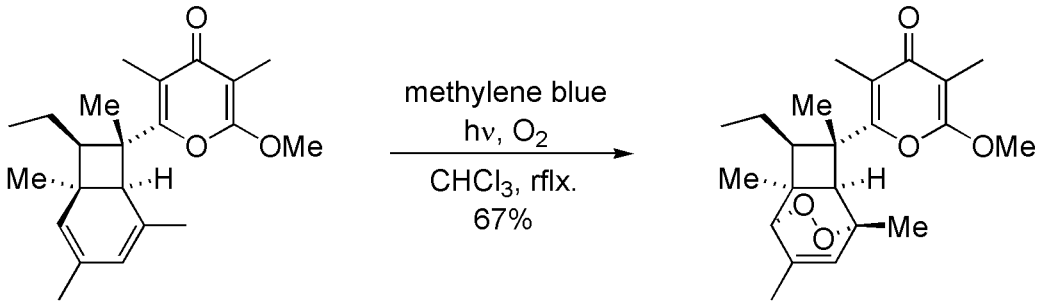


(±)-ocellapyrone B (**7**): To a solution of **6** (11.6 mg, 34 μmol) in $CHCl_3$ (20 mL) was added a spatula tip of methylene blue. This solution was irradiated with a 300 W halogen lamp while bubbling O_2 through the solution at reflux. After 30 min the reaction mixture was concentrated, dissolved in Et_2O (5 mL) and filtered through celite. The resulting colorless solution was purified by column chromatography (50% EtOAc in hexanes) to provide 11.0 mg (89%) of ocellapyrone B (**7**) as a while solid: R_f 0.34 (50% EtOAc in hexanes); IR (thin film): $\tilde{\nu}$ = 2957, 2924, 1657, 1613 cm^{-1}; HRMS calcd for $C_{22}H_{30}O_5$ (M^+): 374.2093; found: 374.2090.

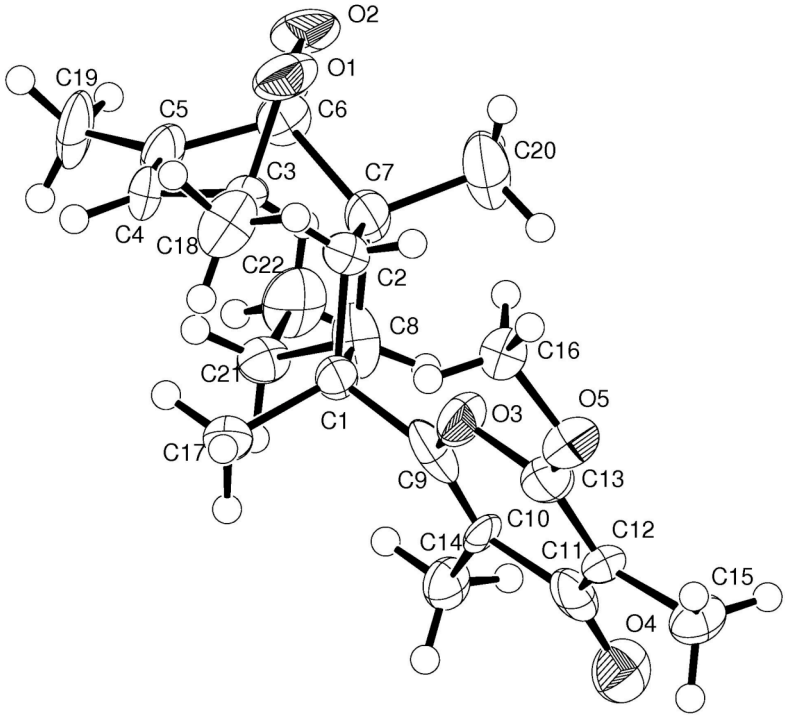
Table S2: Comparison of NMR data for ocellapyrone B[3]

^{1}H (lit.)	^{1}H (current 500 MHz)	^{13}C (lit.)[a]	^{13}C (current 125 MHz)
0.87	0.86	7.2	7.1
1.20	1.19	13.1	13.4
1.34	1.34	13.1	13.4
1.51	1.51	19.1	18.8
1.54	1.53	20.5	19.1
1.60	1.60	20.8	20.8
1.84	1.85	21.8	21.9
1.94	1.94	23.5	23.6
2.03	2.03	36.9	37.2
2.19	2.19	42.1	43.8
2.68	2.67	43.8	45.0
3.93	3.92	55.5	55.5
3.95	3.95	57.7	57.7
5.70	5.70	78.3	77.8
		83.6	84.0
		100.2	99.8
		119.5	118.8
		126.3	126.3
		143.8	143.0
		160.4	159.8
		161.5	161.9
		181.9	181.5

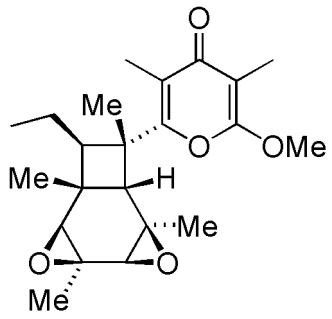
[a] Literature ^{13}C data has been adjusted so C*H*Cl_3 is referenced to 77.2 ppm.



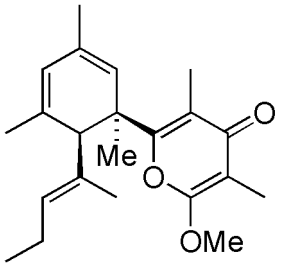
endoperoxide (**S2**): To a solution of ocellapyrone A (**5**) (8.4 mg, 25 μmol) in $CHCl_3$ (20 mL) was added a spatula tip of methylene blue. This solution was irradiated with a 300 W halogen lamp while bubbling O_2 through the solution at reflux. After 1 h the reaction mixture was concentrated, dissolved in Et_2O (5 mL) and filtered through celite. The resulting colorless solution was purified by column chromatography (50% EtOAc in hexanes) to provide 6.2 mg (67%) of **S2** as a white solid. X-ray quality crystals[5] were obtained by crystallization from CH_2Cl_2 / pentane (vapor diffusion): R_f 0.37 (50% EtOAc in hexanes); IR (thin film): $\tilde{\nu}$ = 2957, 2928, 1659, 1614, 1594 cm^{-1}; ^1H NMR (500 MHz, 25 °C): δ = 6.09 (s, 1 H), 4.13 (d, *J* = 1.5 Hz, 1 H), 3.98 (s, 3 H), 2.77 (s, 1 H), 2.57 (dd, *J* = 12.4 Hz, 4.6 Hz, 1 H), 2.10 (d, *J* = 1.3 Hz, 3 H), 1.86 (s, 6 H), 1.48-1.65 (m, 2 H), 1.46 (s, 3 H), 1.44 (s, 3 H), 1.15 (s, 3 H), 0.88 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (125 MHz, 25 °C): δ = 181.7, 164.7, 161.9, 141.3, 129.2, 117.0, 99.4, 81.2, 77.4, 56.0, 53.5, 51.4, 42.8, 39.1, 29.0, 22.6, 19.5, 19.3, 16.6, 13.0, 9.8, 7.2; HRMS calcd for $C_{22}H_{30}O_5$ (M^+): 374.2093; found: 374.2088.



ORTEP diagram of endoperoxide **S2**



***bis*-epoxide** (**20**): To a solution of ocellapyrone B (**7**) (3.5 mg, 9.3 μmol) in CH_2Cl_2 (0.5 mL) was added $RuCl_2(PPh_3)_3$ (0.9 mg, 0.94 μmol) at 0 °C under argon. After addition the reaction mixture was allowed to warm to rt. After 2 h, the reaction mixture was concentrated and the product was purified by column chromatography (50% EtOAc in hexanes) to provide 3.0 mg (86%) of **20** as a white solid. X-ray quality crystals were obtained by crystallization from CH_2Cl_2 / pentane (vapor diffusion): R_f 0.28 (50% EtOAc in hexanes); IR (thin film): $\tilde{\nu}$ = 2971, 2923, 1658, 1614 cm^{-1}; ^1H NMR (500 MHz, 25 °C): δ = 3.98 (s, 3 H), 3.16 (s, 1 H), 2.48 (s, 1 H), 2.29 (t, *J* = 7.4 Hz, 1 H), 2.22 (s, 1 H), 1.95 (s, 3 H), 1.92 (s, 3 H), 1.66 (app quint, *J* = 7.3 Hz, 2 H), 1.45 (s, 3 H), 1.44 (s, 3 H), 1.28 (s, 3 H), 1.13 (s, 3 H), 0.97 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (125 MHz, 25 °C): δ = 182.6, 165.0, 163.2, 119.4, 104.8, 62.7, 61.4, 60.1, 59.1, 56.7, 54.2, 50.2, 44.8, 36.0, 24.3, 22.0, 20.8, 19.5, 19.3, 13.6, 11.4, 7.6; HRMS calcd for $C_{22}H_{30}O_5$ (M^+): 374.2093; found: 374.2088.



(±)-9,10-deoxytridachione (**1**): A solution of **14** (10.0 mg, 0.029 mmol) in toluene (1.0 mL) was heated to 150 °C in a microwave reactor for 20 min. The reaction mixture was concentrated and the products were purified by column chromatography (25% EtOAc in hexanes) and then reverse phase HPLC (80-100% CH_3CN in H_2O linear gradient over 40 min, Alltech Econosil C18 10μ column) to provide 3.8 mg (38%) of ocellapyrone A (**5**) and 3.2 mg (32%) of 9,10-deoxytridachione (**1**). A diastereomeric bicyclo[4.2.0]octadiene of undetermined relative stereochemistry (0.4 mg, 4%) was also obtained from the reaction mixture (This is the same compound that was obtained upon heating **14** in $CDCl_3$ at 45 °C).

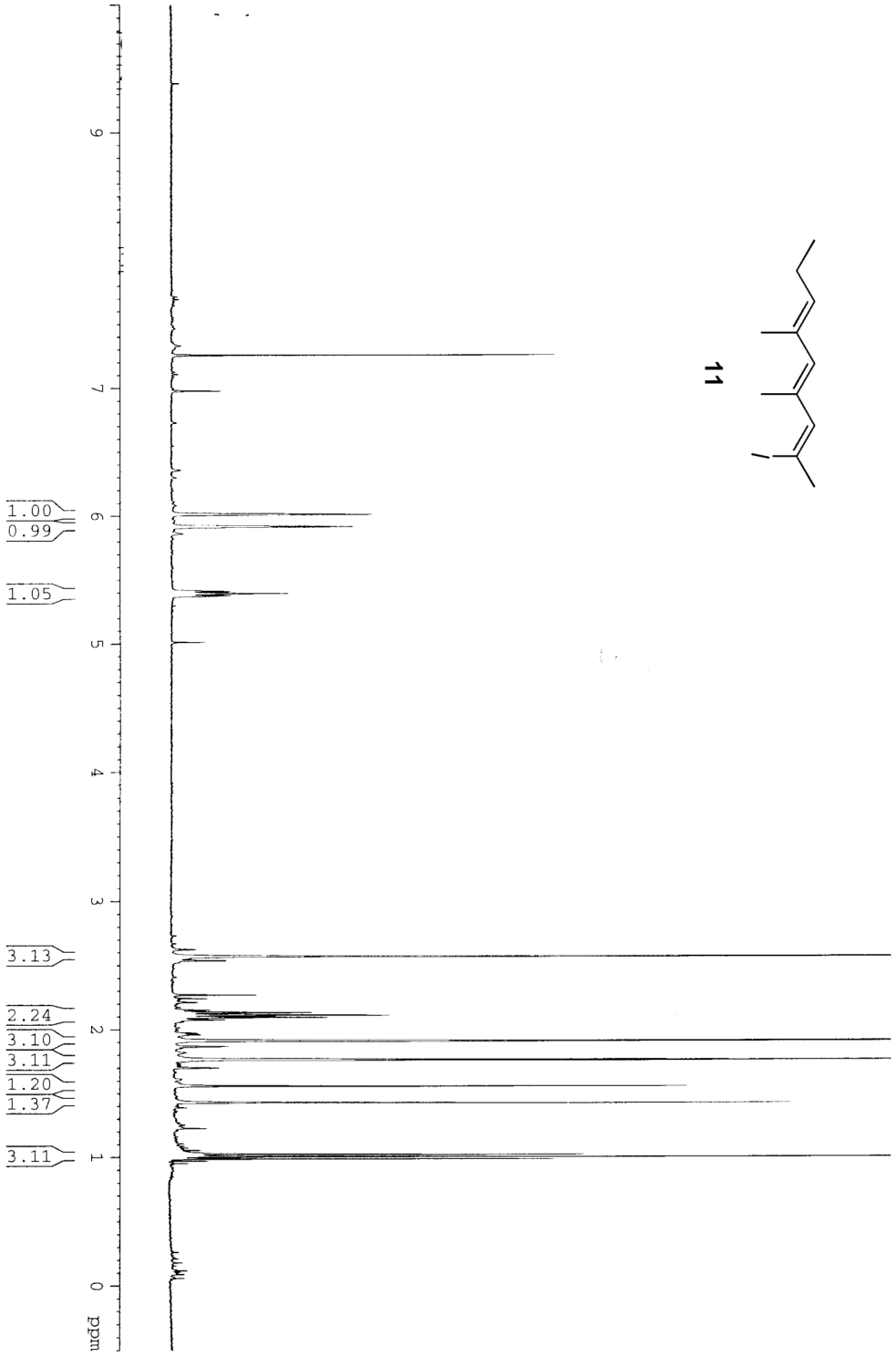
Data for 9,10-deoxytridachione (**1**): R_f 0.28 (30% EtOAc in hexanes); IR (thin film): $\tilde{\nu}$ = 2961, 2928, 1661, 1613, 1596 cm^{-1}; HRMS calcd for $C_{22}H_{30}O_3$ (M^+): 342.2195; found: 342.2195.

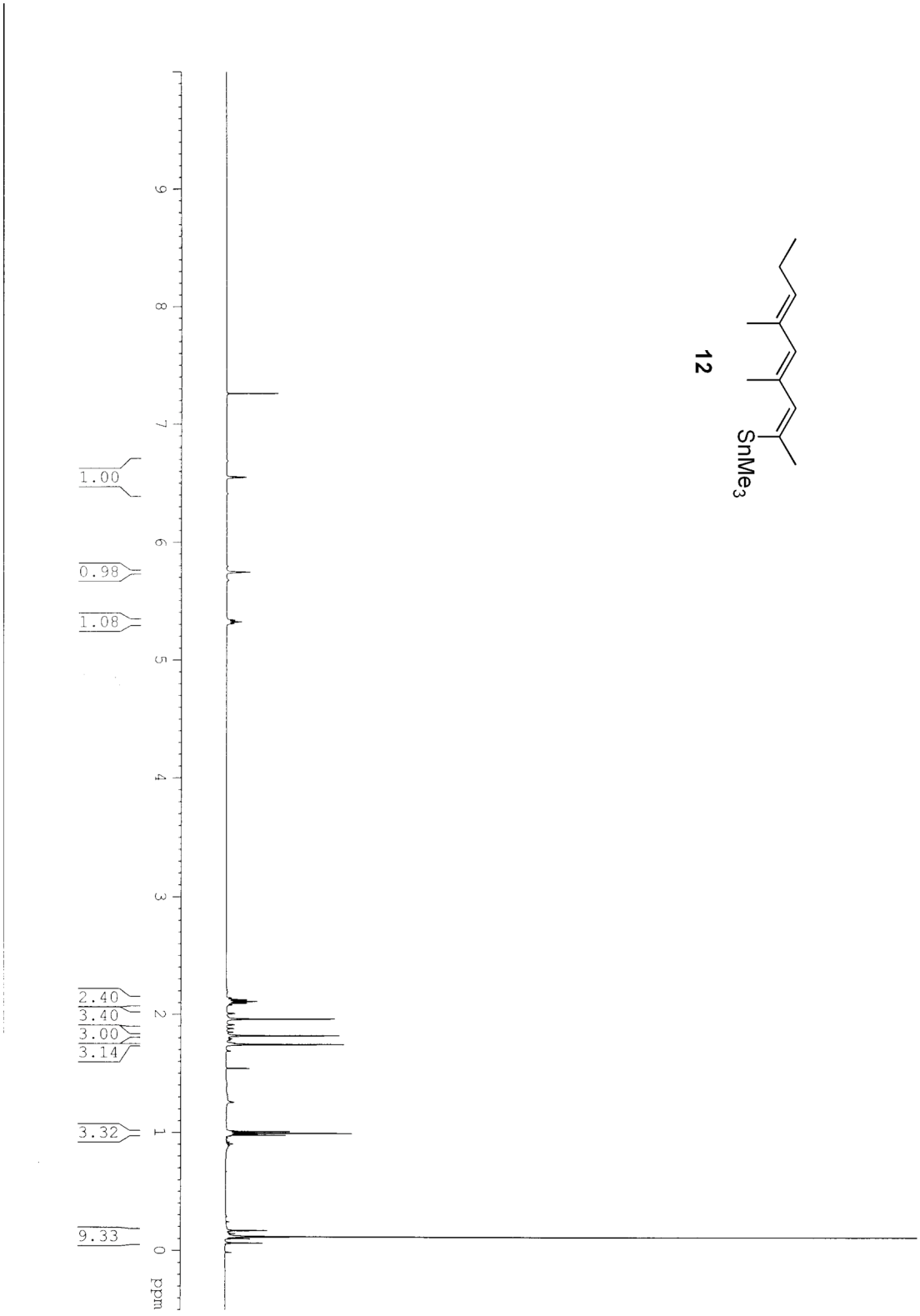
Table S3: Comparison of NMR data for 9,10-deoxytridachione

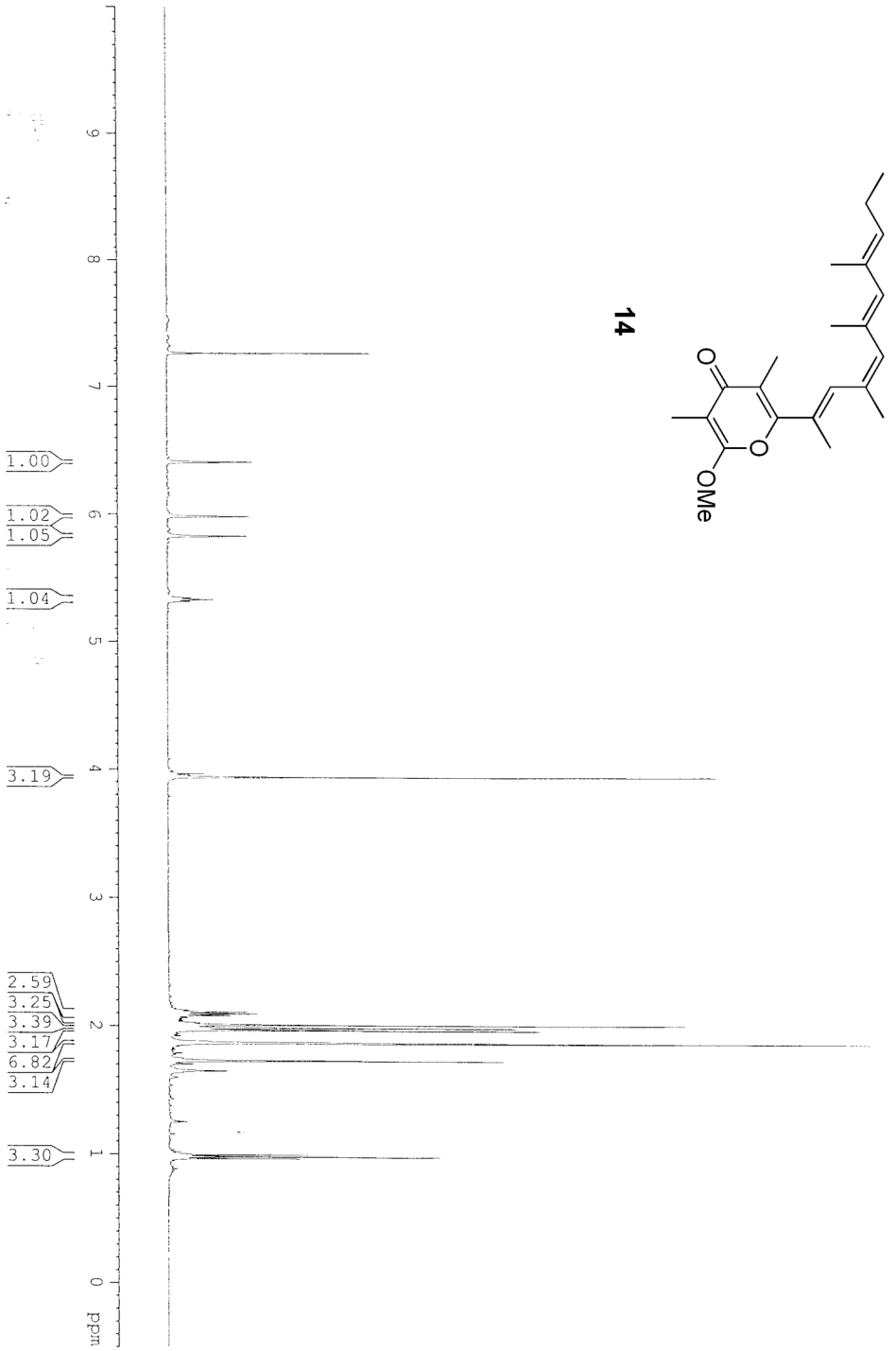
^{1}H (lit.)[6]	^{1}H (lit.)[7]	^{1}H (current 500 MHz)	^{13}C (lit.)[6]	^{13}C (lit.)[7]	^{13}C (current 125 MHz)
0.69	0.70	0.70	6.8	6.80	7.0
1.32	1.32	1.32	12.2	12.19	12.4
1.42	1.43	1.43	13.7	13.67	13.8
1.69	1.72	1.71	13.8	13.78	13.9
Not reported	1.76 (m)	1.77 (m)	21.1	21.08	21.3
1.76	1.78	1.78	21.5	21.49	21.7
1.81	1.83	1.82	22.3	22.27	22.5
2.03	2.03	2.05	26.9	26.85	27.0
2.71	2.71	2.71	47.6	47.58	47.7
3.95	3.99	3.98	55.4	55.34	55.5
5.09	5.05	5.05	59.6	59.51	59.6
5.56	5.58	5.57	98.8	98.78	98.9
5.65	5.67	5.67	120.0	120.02	120.1
			122.4	122.4	122.6
			124.3	124.27	124.4
			127.8	127.8	127.9
			131.0	130.94	131.1
			132.2	132.13	132.3
			134.9	134.86	135.0
			161.1	161.04	161.2
			161.7	161.64	161.8
			181.8	181.84	182.0

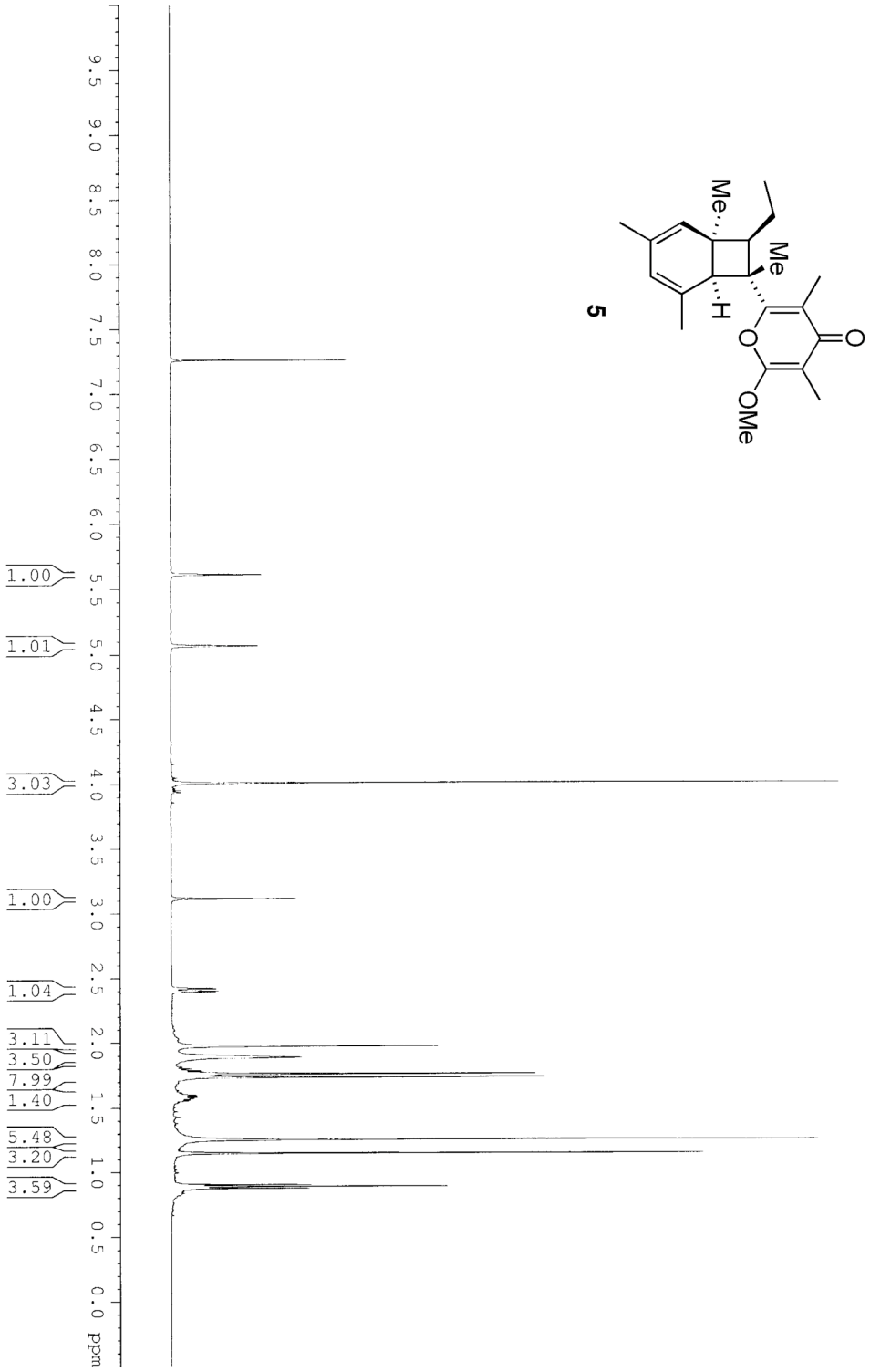
[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

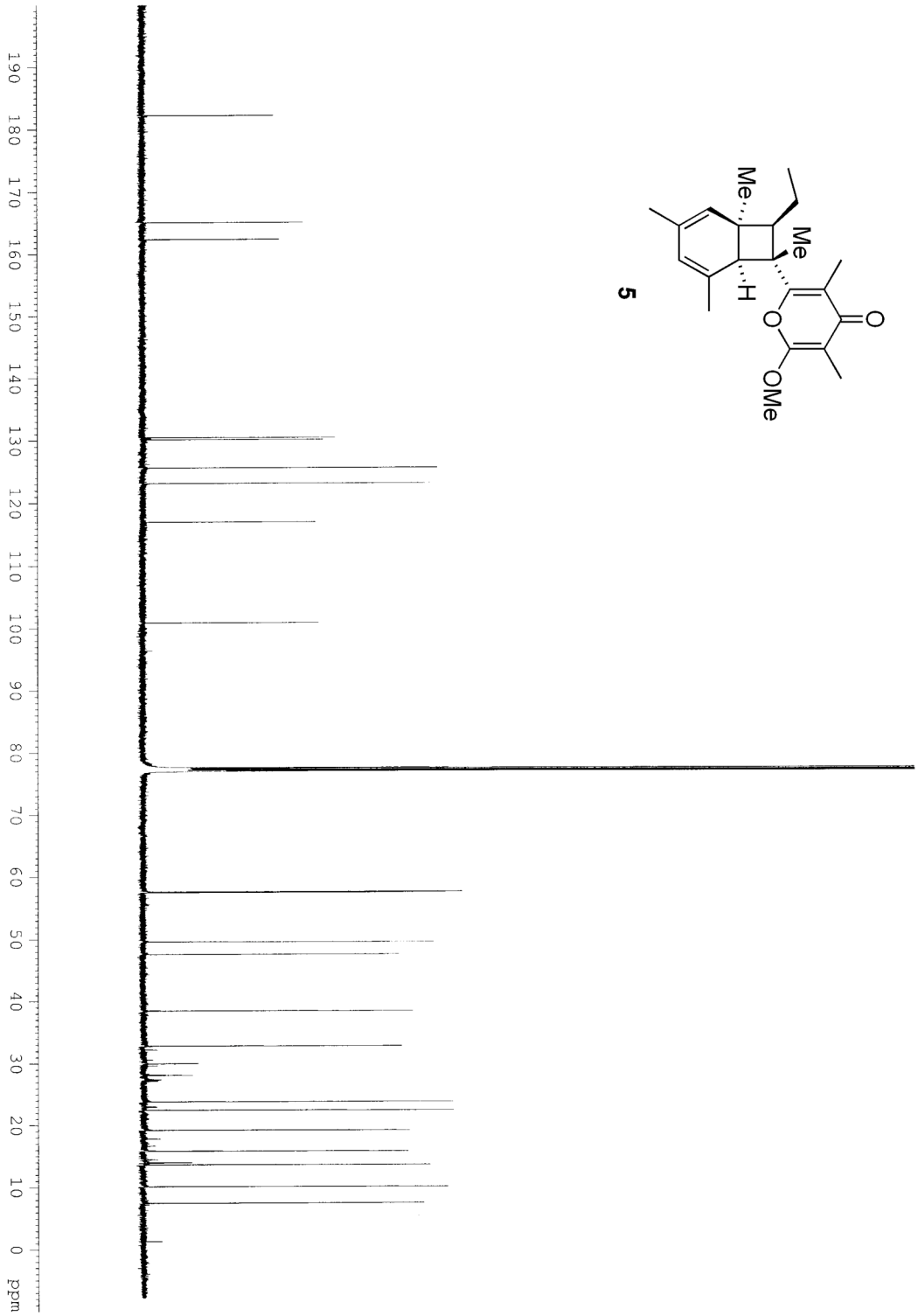
[2] Alaimo, P. J.; Peters, D. W.;Arnold, J.; Bergman, R. G. *J. Chem. Ed.* **2001**, *78*, 64.
[3] Manzo, E.; Ciavatta, M. L.; Gavagnin, M.; Mollo, E.; Wahidulla, S.; Cimino, G. *Tetrahedron Lett*. **2005**, *46*, 465.
[4] Chen, J.; Wang, T.; Zhao, K. *Tet. Lett.* **1984**, *35*, 2827.
[5] The ORTEP diagram shown is a simplified version of the actual data set. The compound partially resolved upon crystallization with the minor enantiomer appearing as disorder in the crystal. Inspection of the difference Fourier map showed a number of relatively strong peaks in positions suggestive of a superposition of a disordered molecule representing the other enantiomer of the compound, related to the first by a very approximate mirror plane normal to the cyclobutane ring and the pyran-4-one ring. Peaks were found for all atoms, which were not approximately related by the mirror plane to an already-present atom. All of these atoms were included with fixed parameters in least squares and their occupancy (and the corresponding occupancy of the majority component) was refined with a single parameter. With this in mind, the chemical identity of the compound is well determined as is the configuration and connectivity.
[6] Ireland, C.; Faulkner, J. *Tetrahedron*, **1981**, *37*, 233 (Supplement 1).
[7] Dawe, R. D.; Wright, J. L. C. *Tetrahedron Lett.* **1986**, *27*, 2559.

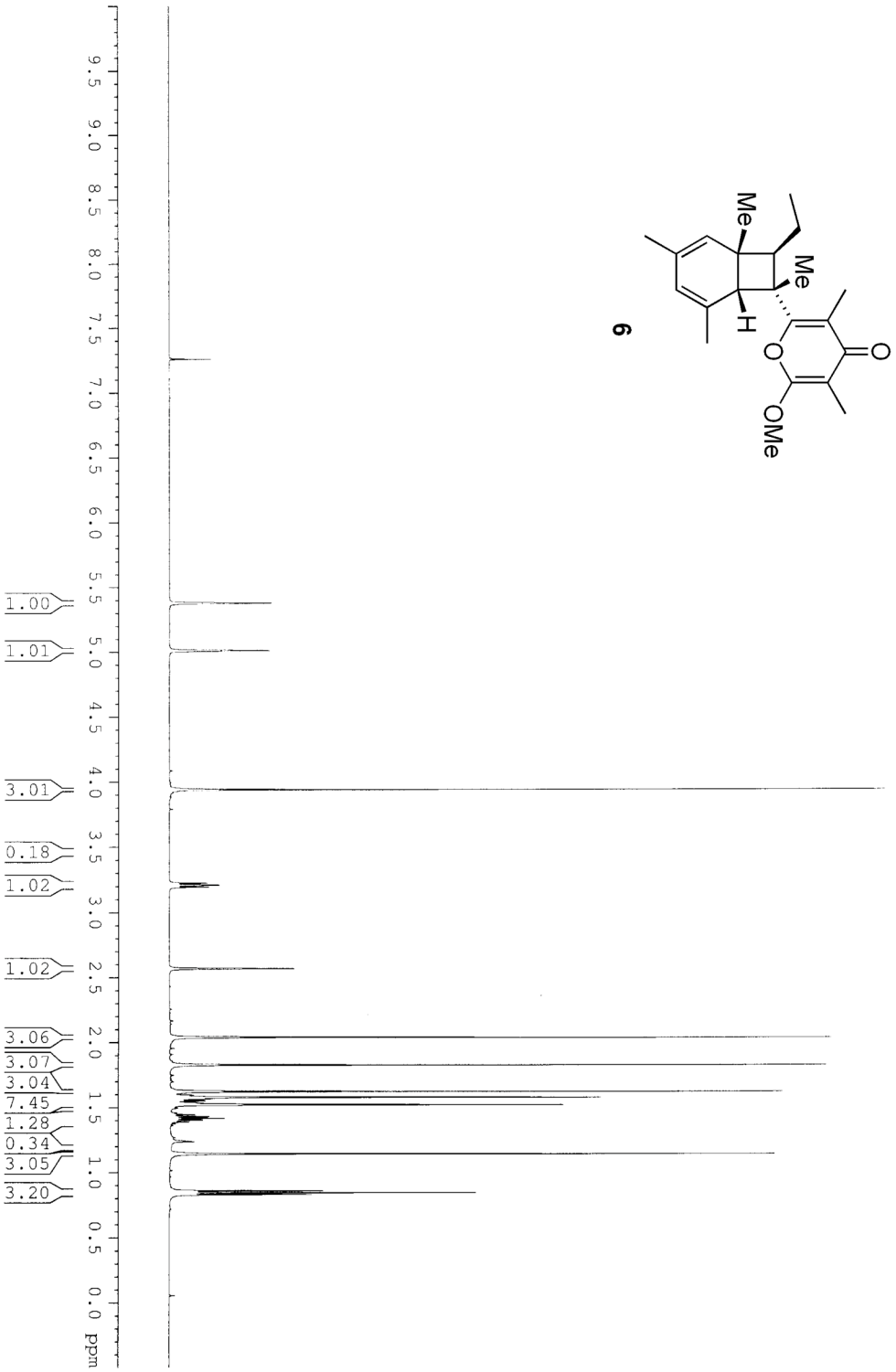

11
1.00
0.99
1.05
3.13
2.24
3.10
3.11
1.20
1.37
3.11
9
7
6
5
4
3
2
1
0
ppm

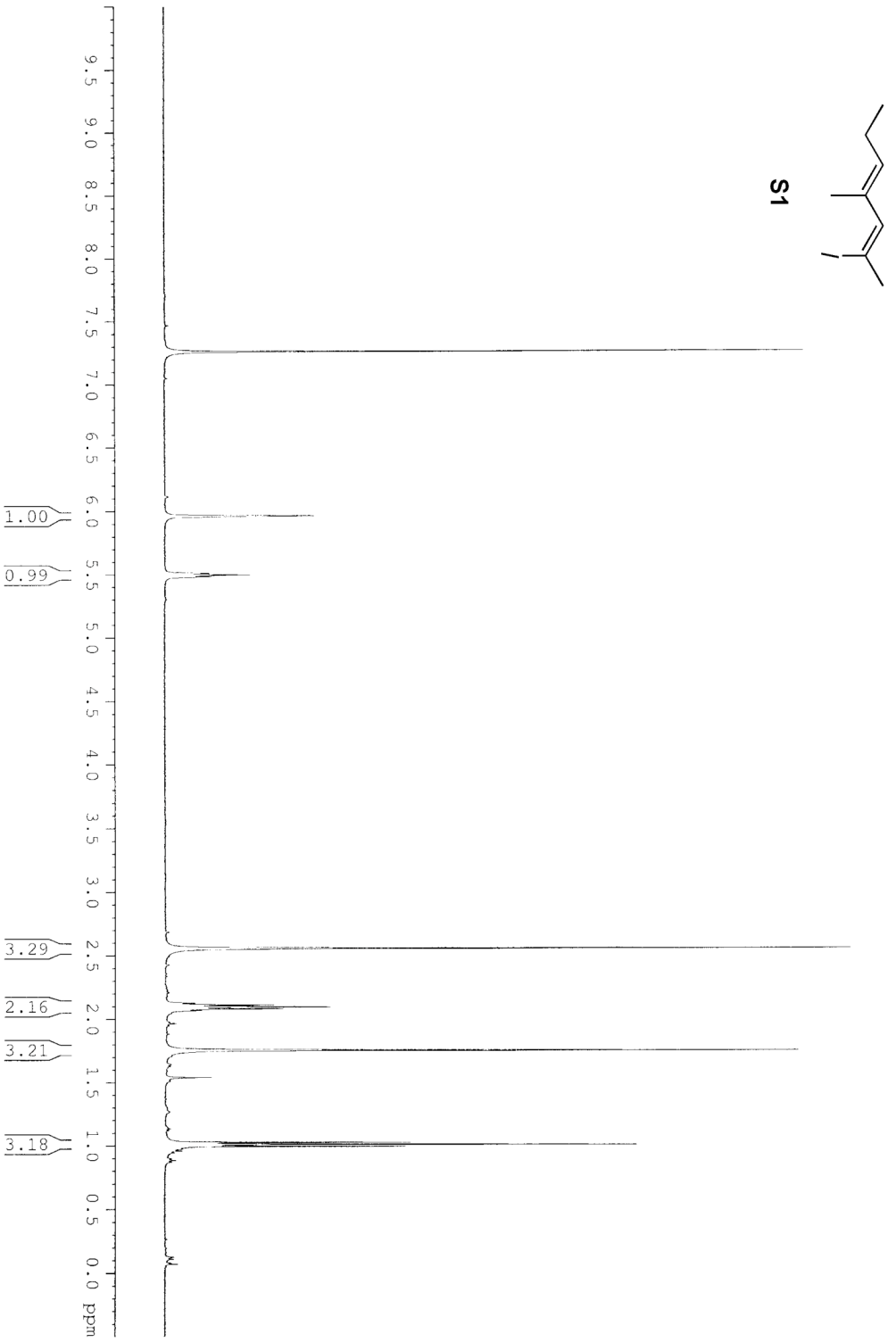

SnMe3
12
1.00
0.98
1.08
2.40
3.40
3.00
3.14
3.32
9.33
ppm

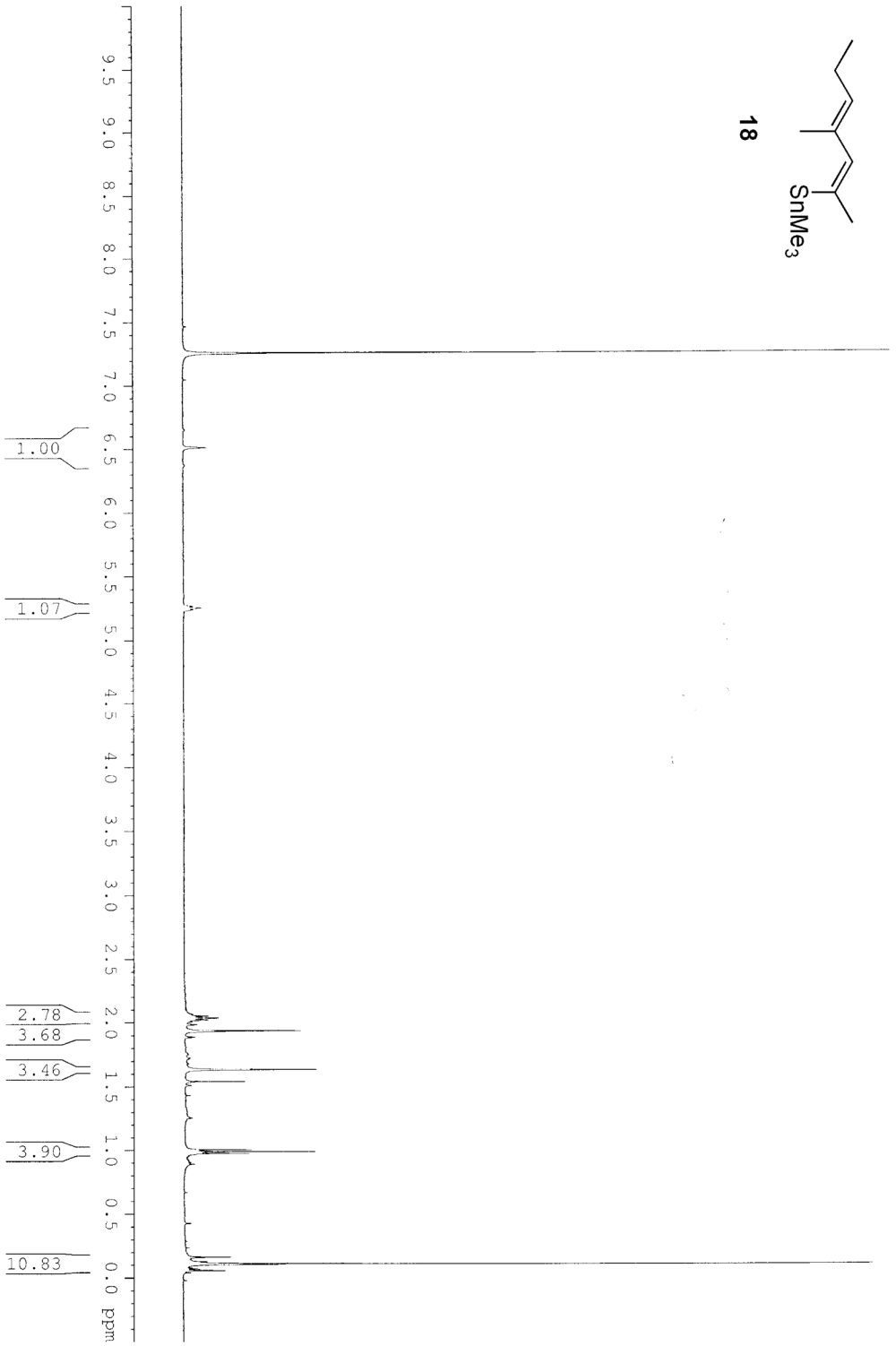

1.00
1.02
1.05
1.04
3.19
2.59
3.25
3.39
3.17
6.82
3.14
3.30
ppm
14
OMe

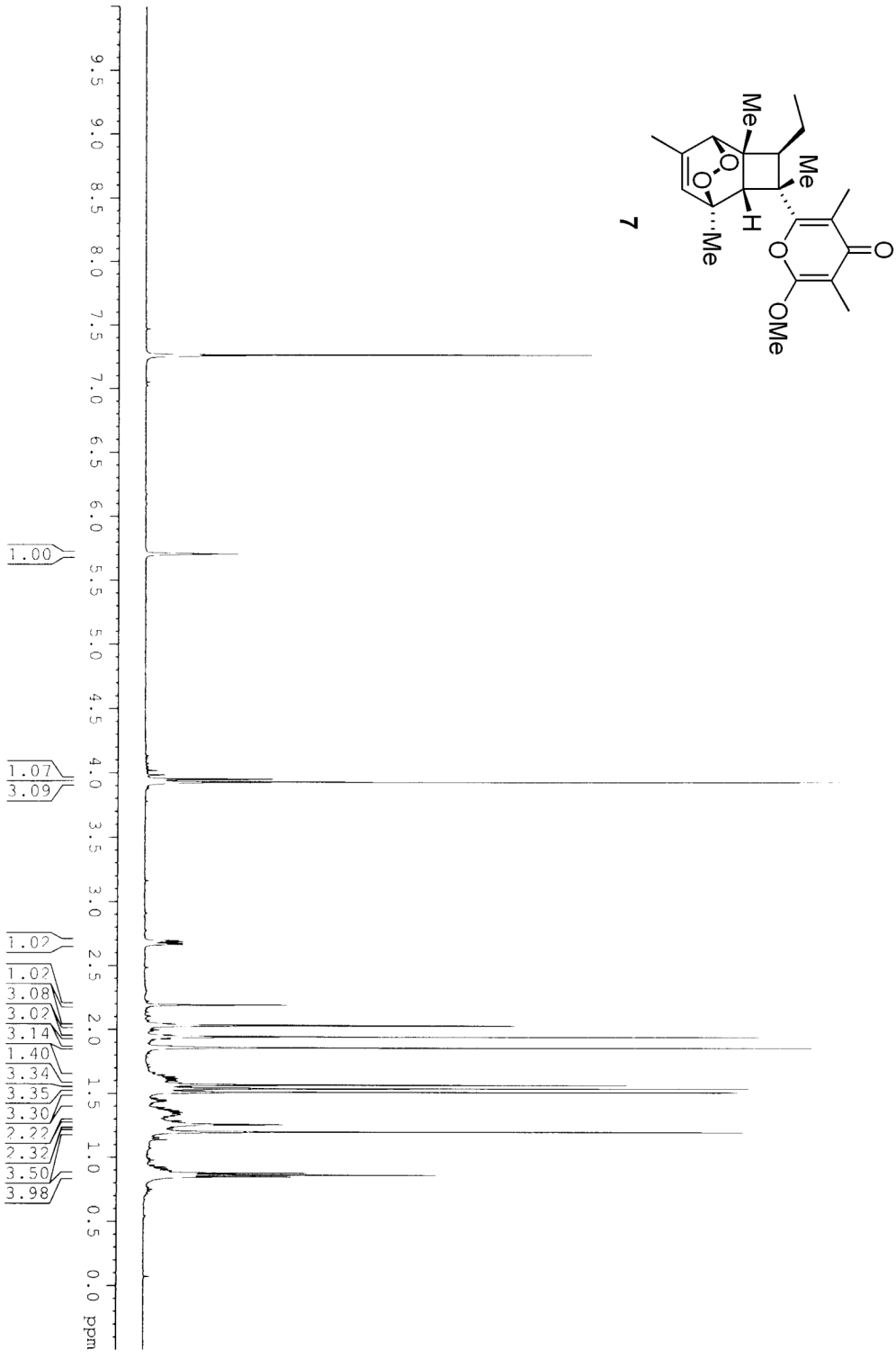

Me
Me
H
O
O
OMe
5
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.01
3.03
1.00
1.04
3.11
3.50
7.99
1.40
5.48
3.20
3.59


Me
Me
H
O
O
OMe
5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

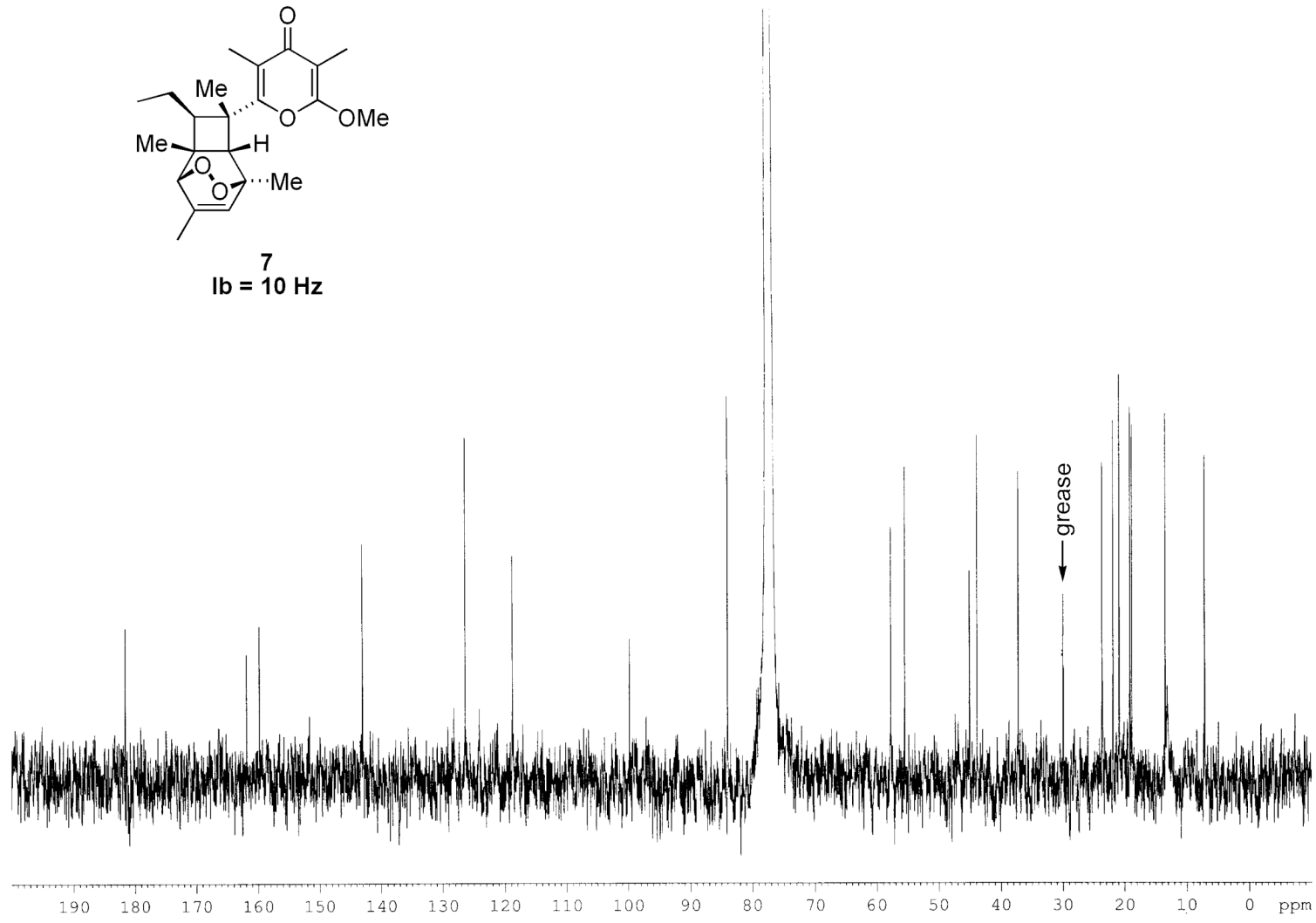

Me
Me
H
O
O
OMe
6
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.01
3.01
0.18
1.02
1.02
3.06
3.07
3.04
7.45
1.28
0.34
3.05
3.20

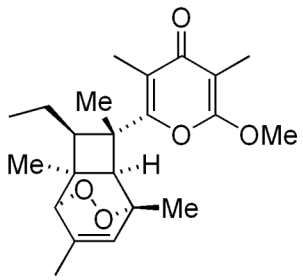

S1
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
0.99
3.29
2.16
3.21
3.18


SnMe3
18
1.00
1.07
2.78
3.68
3.46
3.90
10.83
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


Me
Me
O
O
H
Me
O
O
OMe
7
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
1.07
3.09
1.02
1.02
3.08
3.02
3.14
1.40
3.34
3.35
3.30
2.22
2.32
3.50
3.98

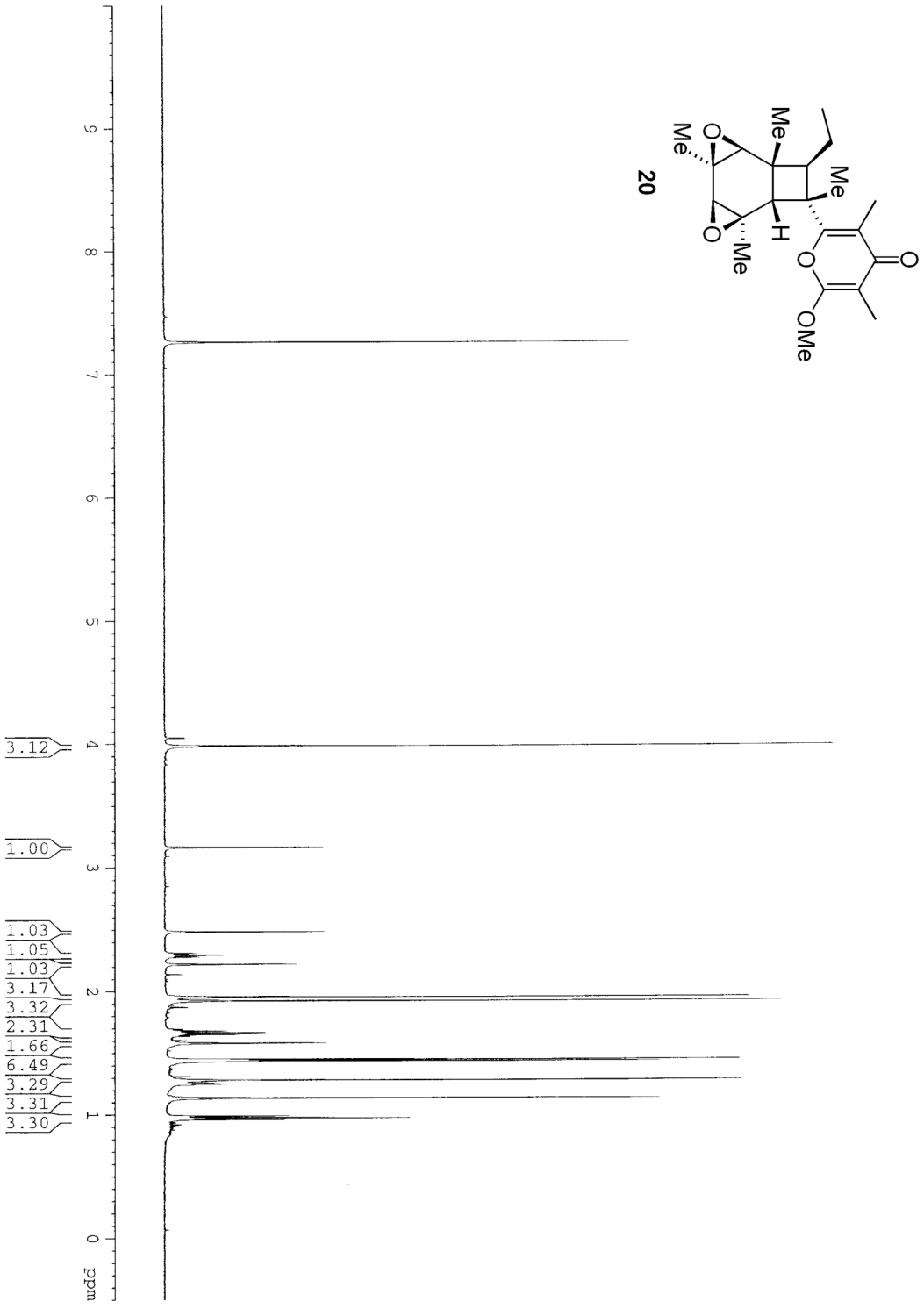
Me
Me
H
Me
O
O
O
OMe
7
lb = 2 Hz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
Me
O
OMe
Me
H
O
O
Me
7
Ib = 10 Hz
grease
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

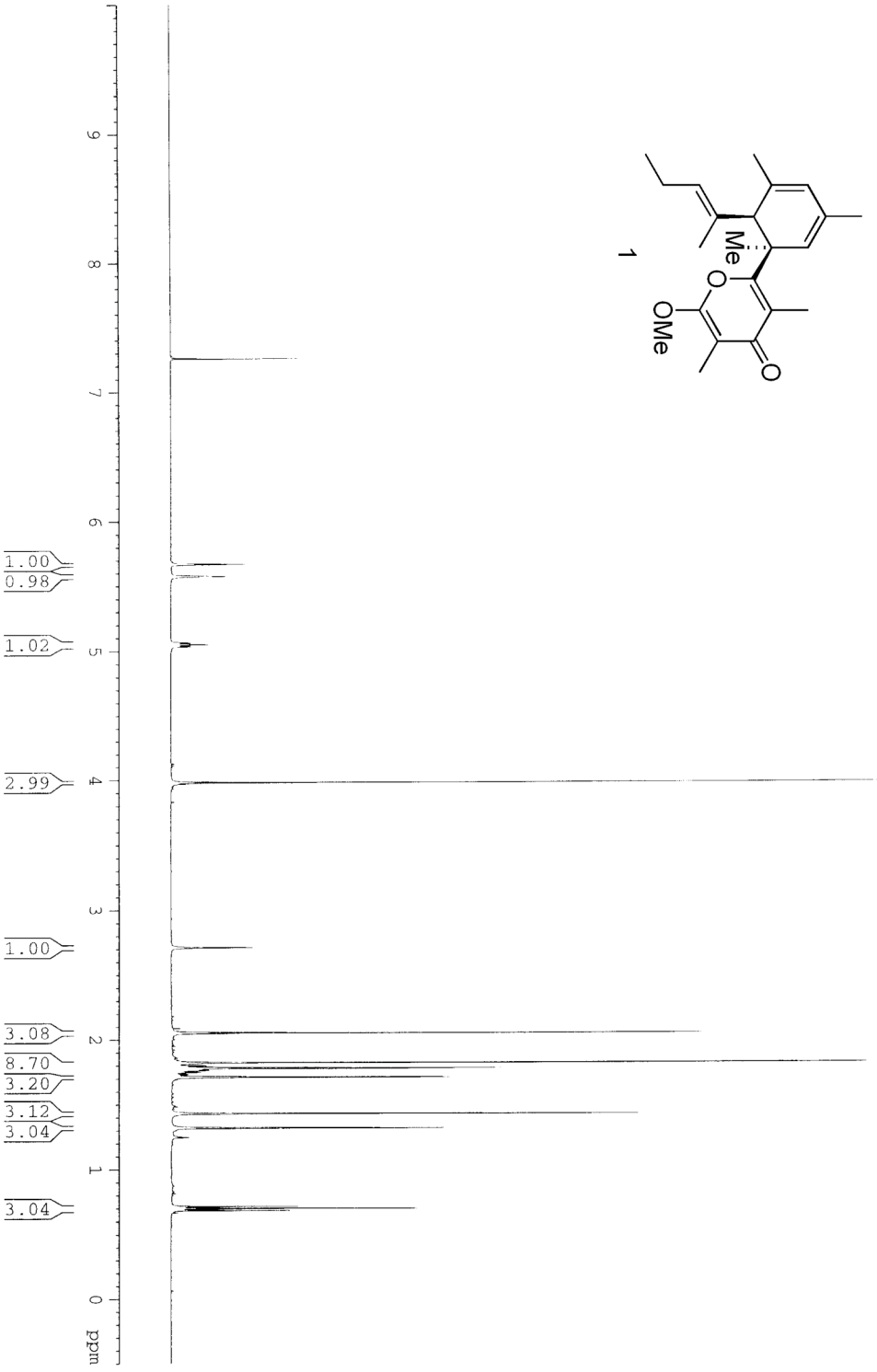

O
Me
O
OMe
Me
H
O
O
Me

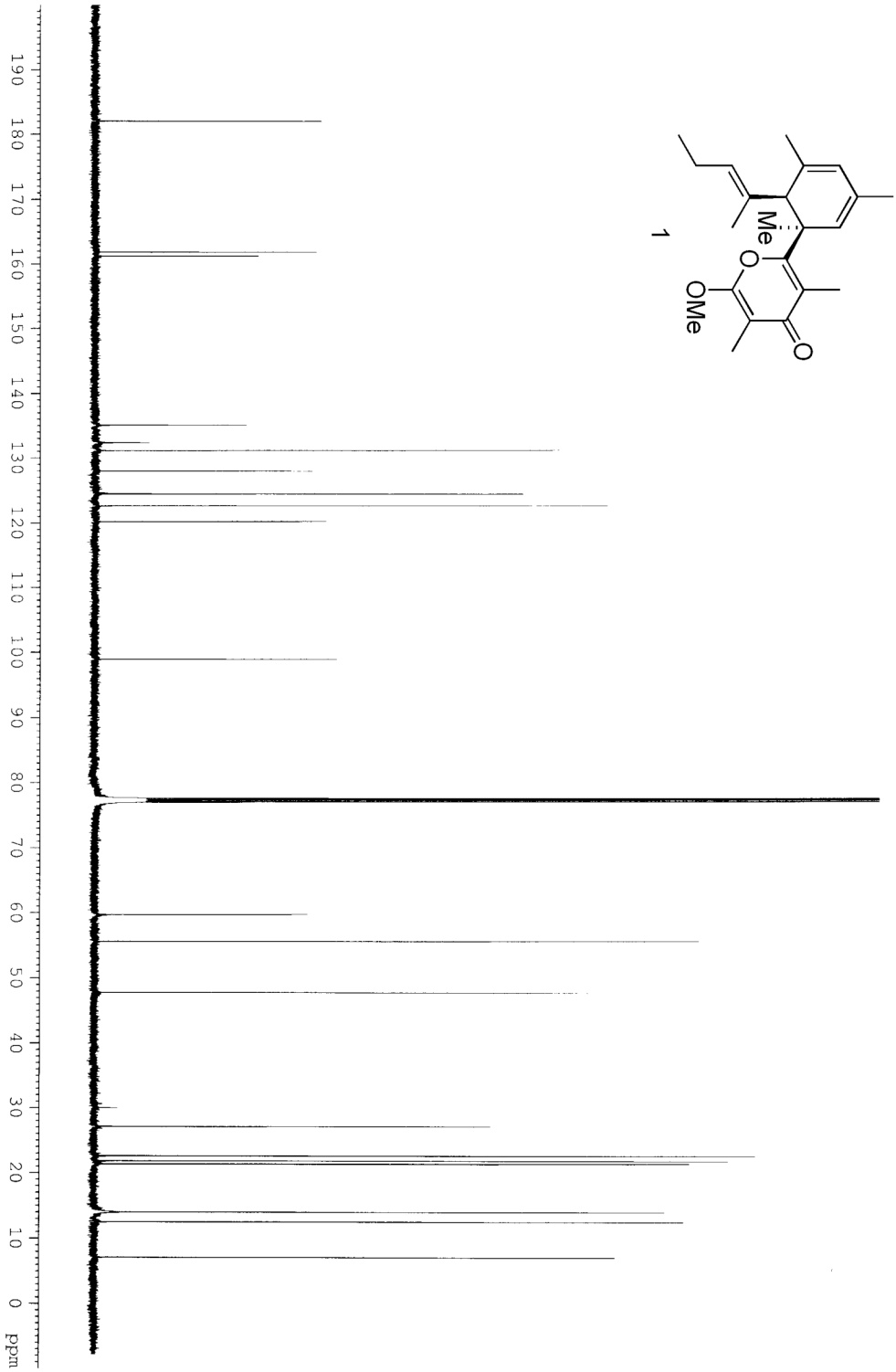
S2

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
1.03
3.05
0.99
1.02
3.02
6.41
1.89
3.43
3.39
3.08
3.39


3.12
1.00
1.03
1.05
1.03
3.17
3.32
2.31
1.66
6.49
3.29
3.31
3.30
ppm
Me
Me
Me
Me
H
O
O
O
O
OMe

20


1.00
0.98
1.02
2.99
1.00
3.08
8.70
3.20
3.12
3.04
3.04
ppm
Me
O
OMe
O
1


Me
O
OMe
O
1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm