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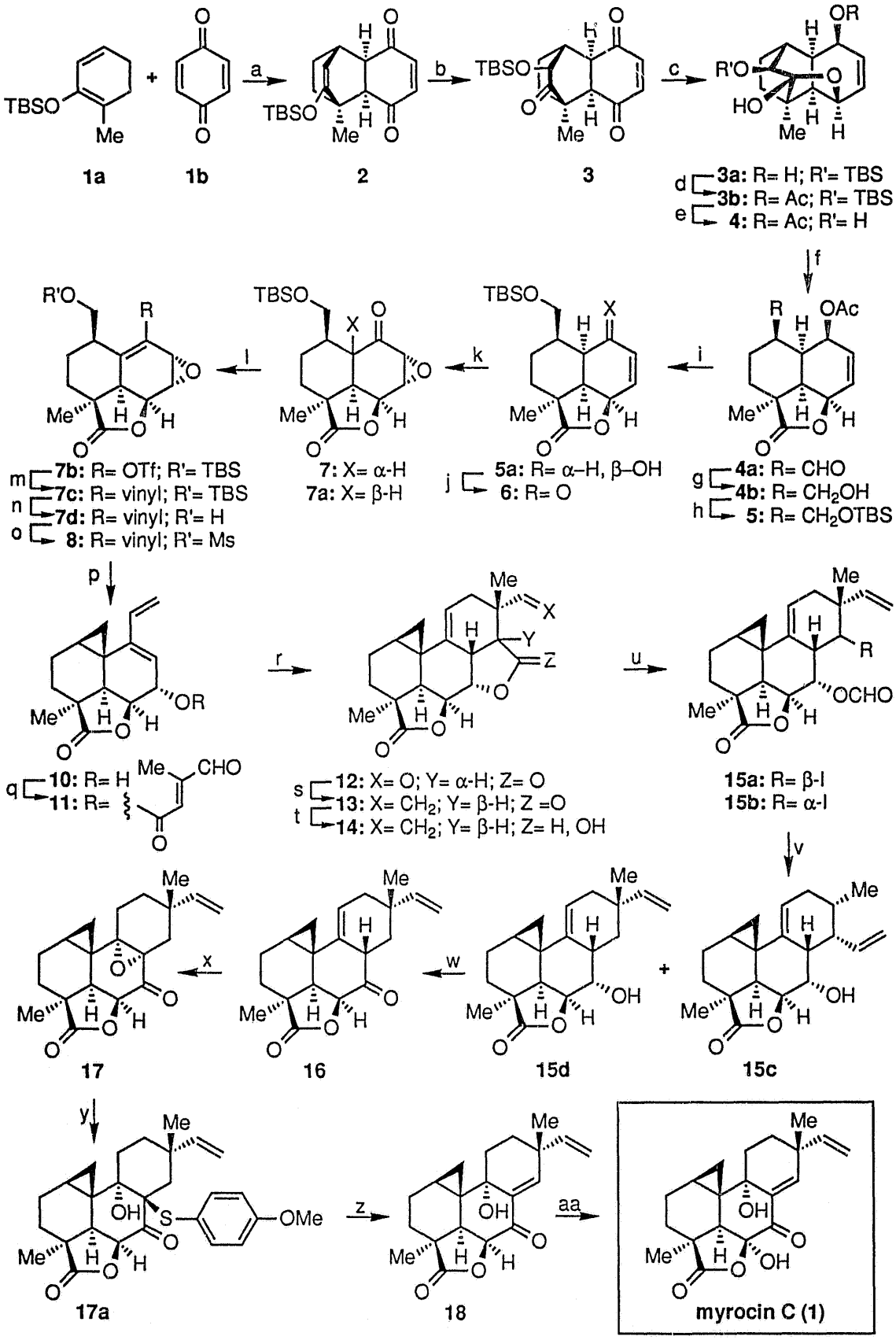
CHU-MOYER
8333-8334

J-8334-m1


1a
1b
2
3
3a: R= H; R'= TBS
3b: R= Ac; R'= TBS
4: R= Ac; R'= H
4a: R= CHO
4b: R= CH2OH
5: R= CH2OTBS
5a: R= α–H, β–OH
6: R= O
7: X= α-H
7a: X= β-H
7b: R= OTf; R'= TBS
7c: R= vinyl; R'= TBS
7d: R= vinyl; R'= H
8: R= vinyl; R'= Ms
10: R= H
11: R=
12: X= O; Y= α-H; Z= O
13: X= CH2; Y= β-H; Z =O
14: X= CH2; Y= β-H; Z= H, OH
15a: R= β-I
15b: R= α-I
15c
15d
16
17
17a
18
myrocin C (1)

J-8334-M2

(a) THF (2M), rt, 5 d, 94%

(b) 2,2-dimethyldioxirane, acetone, CH_2Cl_2, -78 °C → rt, 2.5 h

(c) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, MeOH, -78 °C, 1 h, 67% from **2**

(d) Ac_2O, Et_3N, DMAP, CH_2Cl_2, 0 °C, 30 min, 97%

(e) TBAF, AcOH, THF, 0 °C, 30 min, 91%

(f) $NaIO_4$, THF/ H_2O (2:1), rt, 1 h

(g) $NaBH_4$, MeOH, 0 °C, 30 min

(h) TBSOTf, Et_3N, CH_2Cl_2, 0 °C, 30 min, 99% from **4**

(i) NaOMe, MeOH, rt, 24 h, 96%

(j) PDC, CH_2Cl_2, Celite, rt, 20 h, 84%

(k) H_2O_2, NaOH, MeOH, -78 °C → -48 °C, 5.5 h, **7** (82%) and **7a** (8%)

(l) NaHMDS, Tf_2NPh, THF, -78 °C, 30 min, 81% from **7**

(m) $Bu_3SnCH{=}CH_2$, $PdCl_2(PPh_3)_2$, LiCl, THF, reflux, 3.5 h, 54%

(n) TBAF, AcOH, THF, 0 °C → rt, 4 h, 96%

(o) MsCl, Et_3N, DMAP, CH_2Cl_2, 0 °C, 15 min, 96%

(p) Me_3SnLi, THF, 0 °C, 5 min, 66%

(q) (*E*)-3-methyl-4-oxo-2-butenoic acid, DCC, DMAP, CH_2Cl_2, 0 °C → rt, 1 h, 93%

(r) PhH, reflux, 13 h

(s) $Ph_3P{=}CH_2$, THF, -78 °C → 0 °C, 20 min, 85% from **11**

(t) DIBAL-H, CH_2Cl_2, -48 °C, 10 min then PDC, CH_2Cl_2, Celite, rt, 5 h, 74% (14% recovered sm)

(u) I_2, $PhI(OAc)_2$, hv, cyclohexane, rt, 30 min, **15a** (84%)and**15b** (12%)

(v) Bu_3SnH, AIBN, 80 °C, 20 min, **15d** (78%) and **15c** (15%) from **15a**; Bu_3SnH, AIBN, 110 °C, 10 min, **15d** (61%) and **15c** (27%) from **15b**

(w) Dess-Martin periodinane, CH_2Cl_2, rt, 10 min

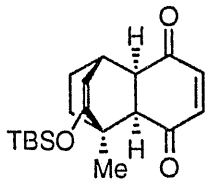
(x) H_2O_2, NaOH, MeOH, rt, 15 min, 67% from **15d**

(y) 4-OMe-PhSAlMe$_3$Li, THF, -20 °C → 0 °C, 1 h, 99%

(z) 2,2-dimethyldioxirane, acetone, CH_2Cl_2, 0 °C, 30 min, 56%

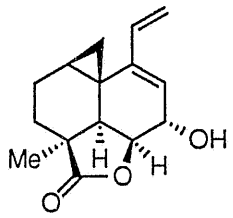
(aa) O_2, *t*-BuOK, THF/*t*-BuOH (2:1), -78 °C, 3 h then $(EtO)_3P$, THF, 0 °C, 10 min, 68%

J-8334-m3



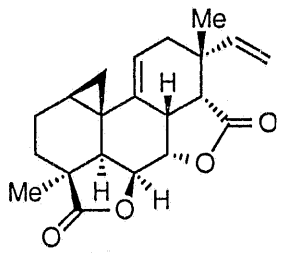
2

Diels-Alder adduct 2: mp 96-98 °C; R_f 0.17 (1:9 EtOAc/Hex); IR ($CDCl_3$) 2950, 2850, 1665, 1625, 1460 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 6.59 (d, J = 10.5 Hz, 1 H), 6.54 (d, J = 10.5 Hz, 1 H), 4.90 (d, J = 7.0 Hz, 1 H), 3.03 (m, 1 H), 2.91 (dd, J = 8.4, 3.0 Hz, 1 H), 2.69 (d, J = 8.4 Hz, 1 H), 1.74-1.57 (c, 2 H), 1.52-1.35 (c, 2 H), 1.08 (s, 3 H), 0.84 (s, 9 H), 0.09 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 199.7, 198.2, 155.8, 142.2 (2), 100.5, 54.9, 51.4, 41.3, 36.7, 36.6, 25.5, 25.4, 19.0, 17.9, -4.8, -5.0; MS (CI, methane) m/z 333 (MH^+); HRMS (CI, isobutane) exact mass calcd for $C_{19}H_{29}O_3Si$ (MH^+) 333.1887, found 333.1905. Anal. Calcd for $C_{19}H_{28}O_3Si$: C, 68.63; H, 8.49. Found: C, 68.70; H, 8.65.



10

Cyclopropyldienol 10: mp 101-103 °C; R_f 0.42 (1:1 EtOAc/Hex); IR ($CDCl_3$) 3590 (s), 3450 (br), 2960, 2930, 2860, 1760 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 6.01 (dd, J = 17.4, 10.8 Hz, 1 H), 5.84 (d, J = 2.0 Hz, 1 H), 5.34 (d, J = 17.3 Hz, 1 H), 5.02 (d, J = 10.8 Hz, 1 H), 4.63 (dd, J = 6.9, 4.6 Hz, 1 H), 4.59 (m, 1 H), 2.84 (d, J = 4.4 Hz, 1 H), 2.28 (d, J = 6.8 Hz, 1 H), 1.90-1.78 (c, 3 H), 1.72 (m, 1 H), 1.49 (m, 1 H), 1.26 (s, 3 H), 0.81 (t, J = 5.0 Hz, 1 H), 0.07 (dd, J = 8.4, 5.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 183.0, 143.3, 132.5, 127.4, 115.9, 86.7, 72.0, 44.4, 40.1, 26.5, 26.4, 20.4, 18.6, 14.4, 8.3; MS (EI) m/z 246 (M^+); HRMS (EI) exact mass calcd for $C_{15}H_{18}O_3$ (M^+) 246.1256, found 246.1252. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.96; H, 7.37.

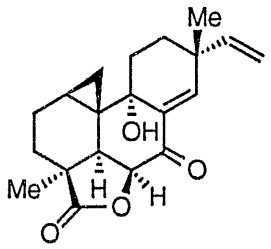


13

Wittig product 13: mp 216-217 °C; R_f 0.33 (1:3 EtOAc/Hex); IR ($CDCl_3$) 2960, 2920, 1770 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 6.38 (dd, J =17.5, 10.9 Hz, 1 H), 5.59 (m, 1 H), 5.11 (d, J = 10.9 Hz, 1 H), 5.08 (d, J = 17.5 Hz, 1 H), 4.88

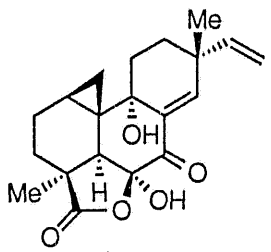
J-8334-m4

(d, J = 4.7 Hz, 1 H), 4.75 (d, J = 4.3 Hz, 1 H), 3.14 (m, 1 H), 2.68 (dd, J = 6.3, 1.1 Hz, 1 H), 2.48 (d, J = 4.5 Hz, 1 H), 2.39 (dt, J = 18.2, 2.4 Hz, 1 H), 1.96 (dd, J = 13.9, 5.7 Hz, 1 H), 1.89-1.68 (c, 3 H), 1.55-1.37 (c, 2 H), 1.23 (s, 3 H), 1.00 (s, 3 H), 0.78 (dd, J = 5.5, 4.0 Hz, 1 H), 0.03 (dd, J = 8.3, 5.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 181.5, 174.2, 144.8, 133.1, 122.4, 112.3, 77.1, 74.5, 49.7, 44.8, 43.0, 37.6, 35.0, 32.8, 27.4, 24.3, 23.6, 21.6, 19.1, 14.5, 10.2; MS (EI) m/z 340 (M^+); HRMS (EI) exact mass calcd for $C_{21}H_{24}O_4$ (M^+) 340.1675, found 340.1661.



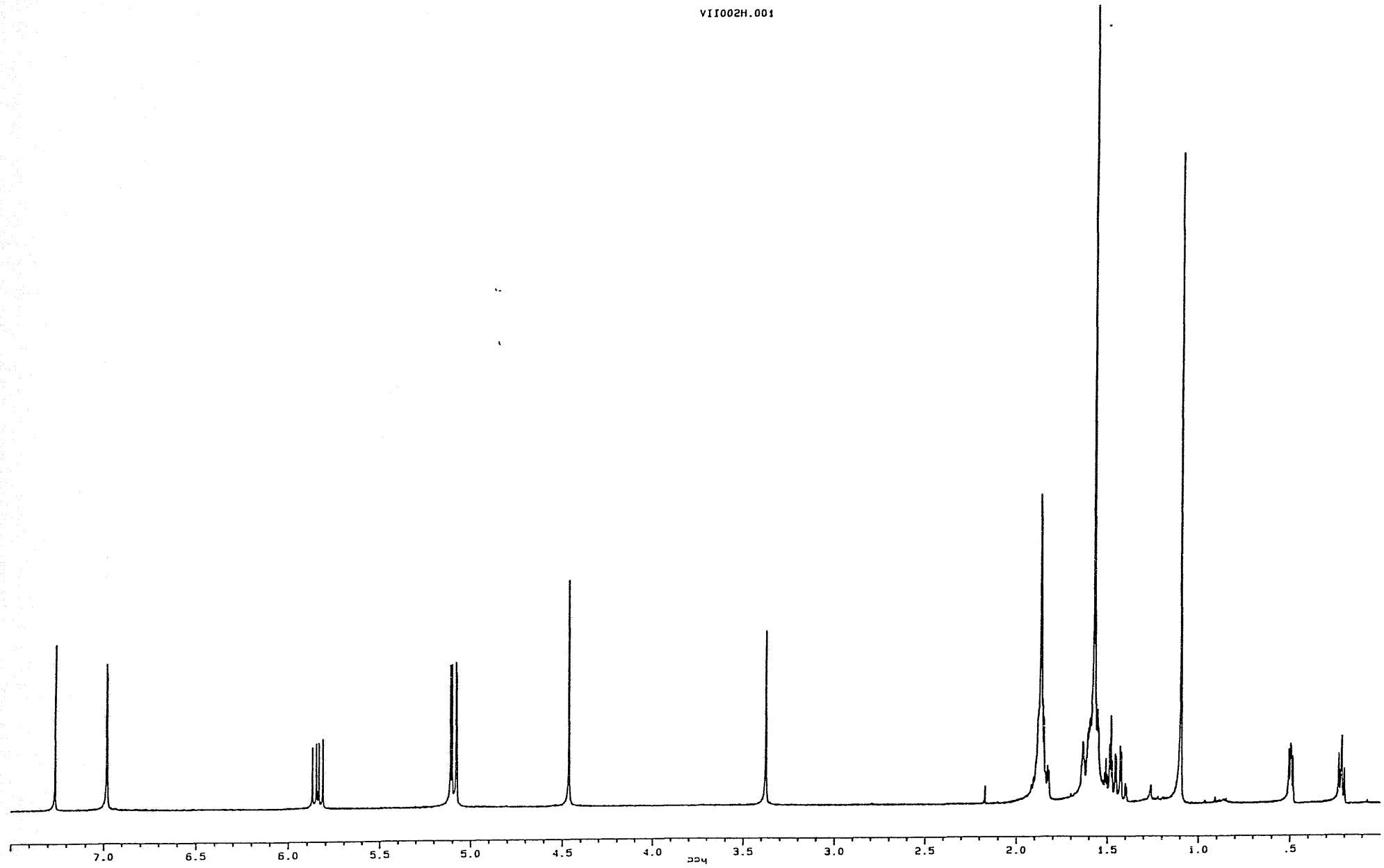
18

6-Desoxymyrocin C (18): mp 177-179 °C; R_f 0.24 (1:1 EtOAc/Hex); IR ($CDCl_3$) 3580 (s), 3470 (br), 2950, 2920, 2850, 1760, 1690, 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.90 (d, J = 1.6 Hz, 1 H), 5.81 (dd, J = 17.5, 10.7 Hz, 1 H), 5.04 (d, J = 17.4 Hz, 1 H), 5.03 (d, J = 10.7 Hz, 1 H), 4.83 (d, J = 6.8 Hz, 1 H), 3.51 (d, J = 6.8 Hz, 1 H), 1.95-1.78 (c, 5 H), 1.64-1.44 (c, 3 H), 1.40 (m, 1 H), 1.33 (s, 3 H), 1.32 (m, 1 H), 1.06 (s, 3 H), 0.48 (dd, J = 6.8, 4.6 Hz, 1 H), 0.20 (td, J = 7.2, 1.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 192.2, 181.9, 147.6, 144.9, 134.2, 112.8, 77.5, 69.9, 41.1, 39.9, 39.2, 29.1, 27.1, 26.3, 26.2, 24.0, 23.9, 18.8, 13.5, 5.9; MS (EI) m/z 328 (M^+); HRMS (EI) exact mass calcd for $C_{20}H_{24}O_4$ (M^+) 328.1675, found 328.1677.



1

Myrocin C (1): mp > 214 °C (dec); R_f 0.36 (1:1 EtOAc/Hex); IR (KBr) 3430 (s), 3290 (br), 2950, 2920, 2840, 1740, 1695, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.96 (d, J = 1.5 Hz, 1 H), 5.82 (dd, J = 17.5, 10.6 Hz, 1 H), 5.09 (d, J = 17.4 Hz, 1 H), 5.09 (d, J = 10.7 Hz, 1 H), 4.44 (s, 1 H), 3.35 (s, 1 H), 1.92-1.83 (c, 4 H), 1.65-1.54 (c, 4 H), 1.55 (s, 3 H), 1.47 (dt, J = 14.0, 3.7 Hz, 1 H), 1.42 (td, J = 13.9, 3.6 Hz, 1 H), 1.07 (s, 3 H), 0.47 (dd, J = 6.9, 4.7 Hz, 1 H), 0.19 (dd, J = 8.1, 7.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 192.8, 181.9, 149.0, 144.5, 134.2, 112.9, 99.0, 70.0, 44.8, 41.7, 39.3, 29.2, 28.8 (2), 26.5, 23.9, 23.7, 18.8, 14.0, 6.3; MS (CI, isobutane) m/z 345 (MH^+); HRMS (CI, isobutane) exact mass calcd for $C_{20}H_{25}O_5$ (MH^+) 345.1702, found 345.1717.

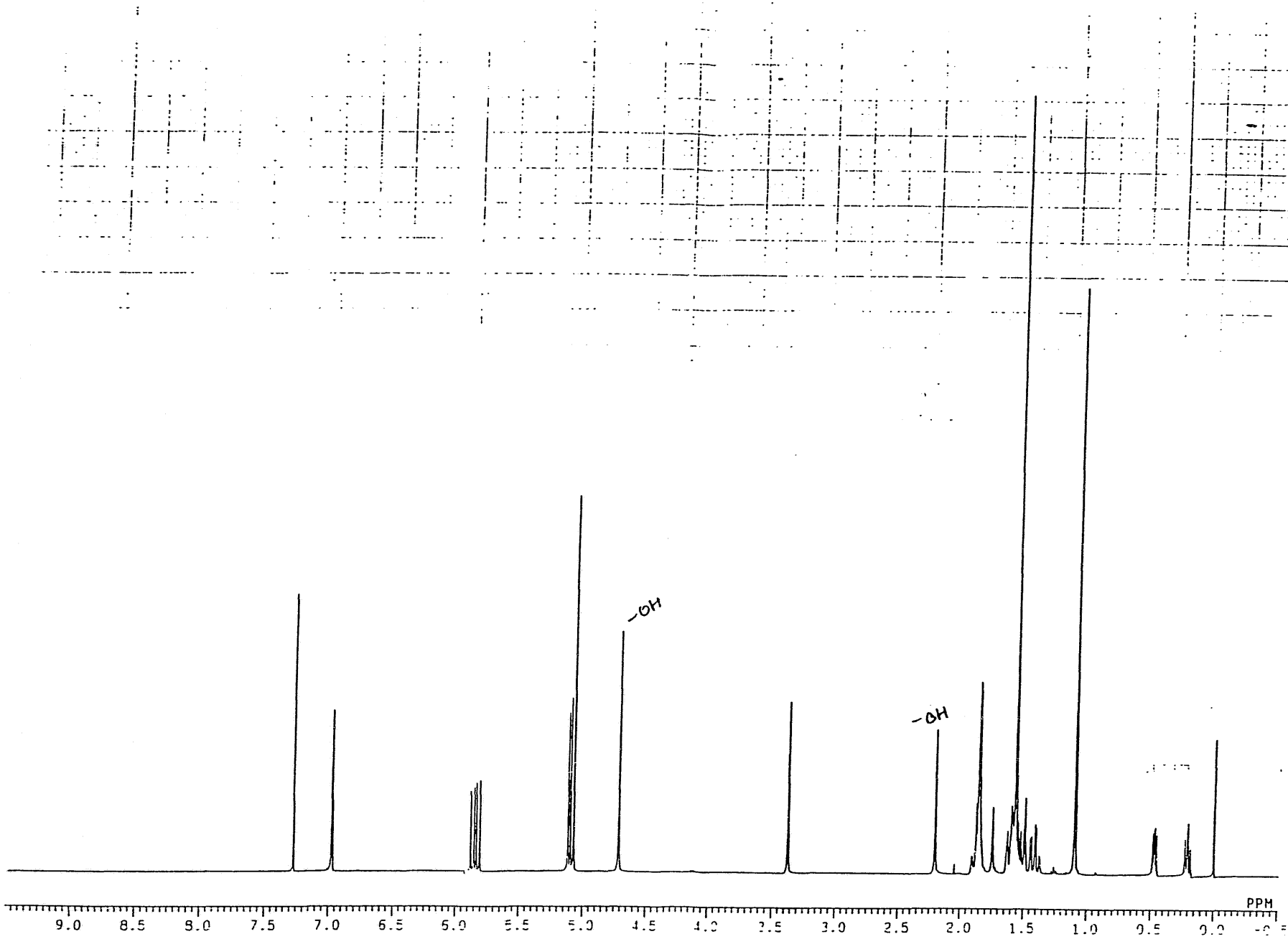


J-8337-MS

Myrocin C - synthetic

^1H NMR (500MHz) $CDCl_3$

Myroc;

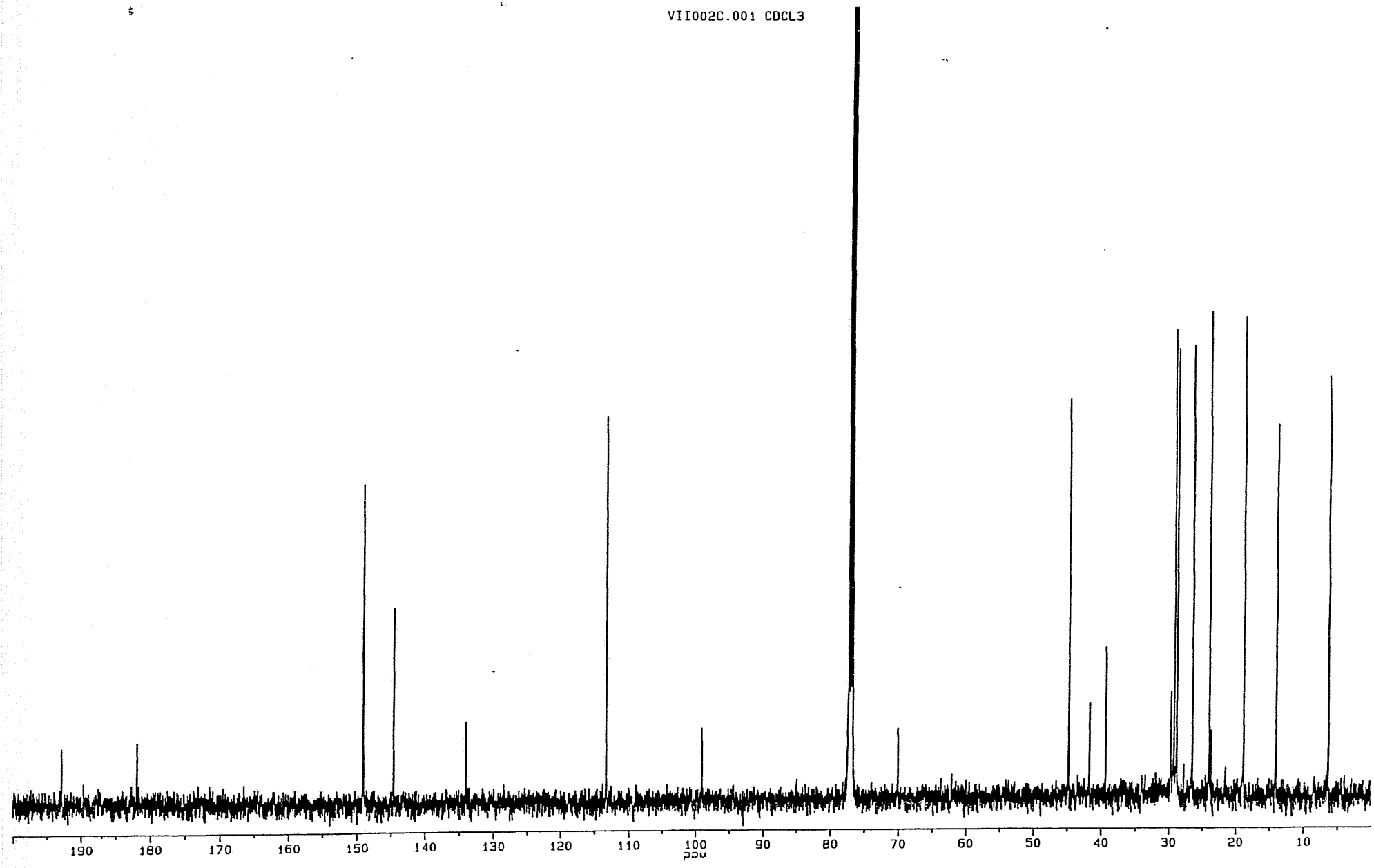


J-8334-mo

Myrocin C - natural

^1H NMR (270MHz) $CDCl_3$

-courtesy of Dr. Y.-H. Hsu



J-8334-m7

Myrocin C - synthetic

^{13}C NMR (125 MHz) $CDCl_3$ only

TOTAL 28
RESOL 7326? -4 HZ
EXREF 0.0000PPM
OBS 2313.4375 HZ
NGAIN 11

NO	FREQ(HZ)	PPM	INT%
1	4934.13	193.090	930
2	4595.28	183.464	1721
3	3725.33	148.772	5416
4	3634.75	145.116	5828
5	3361.47	134.205	2853
6	2829.82	112.939	5656
7	1973.98	-78.803	2984
8	1941.56	77.516	3128
9	1909.32	-76.229-	3873
10	1737.15	69.355	2972
11	1293.15	51.628	533
12	1271.17	50.751	1755
13	1249.92	49.902	3463
14	1229.68	49.054	3656
15	1205.70	48.177	3455
16	1185.45	47.329	1324
17	1164.20	46.433	533
18	1142.95	45.632	5231
19	1049.91	41.917	4839
20	991.23	39.577	4744
21	729.60	29.105	7873
22	722.48	28.841	5245
23	663.06	26.472	5219
24	599.32	23.927	6232
25	471.33	18.837	5243
26	356.80	14.245	5463
27	153.85	6.142	4331
28	0.00	0.000	4473

100

~~#2~~ Myrocin

^{13}C-complete deco
CDCl3 + CD3OD

TMS
RT

^{13}C ✓
^{1}H

47.50
51 40
✓
5

2.0

8K
8,0

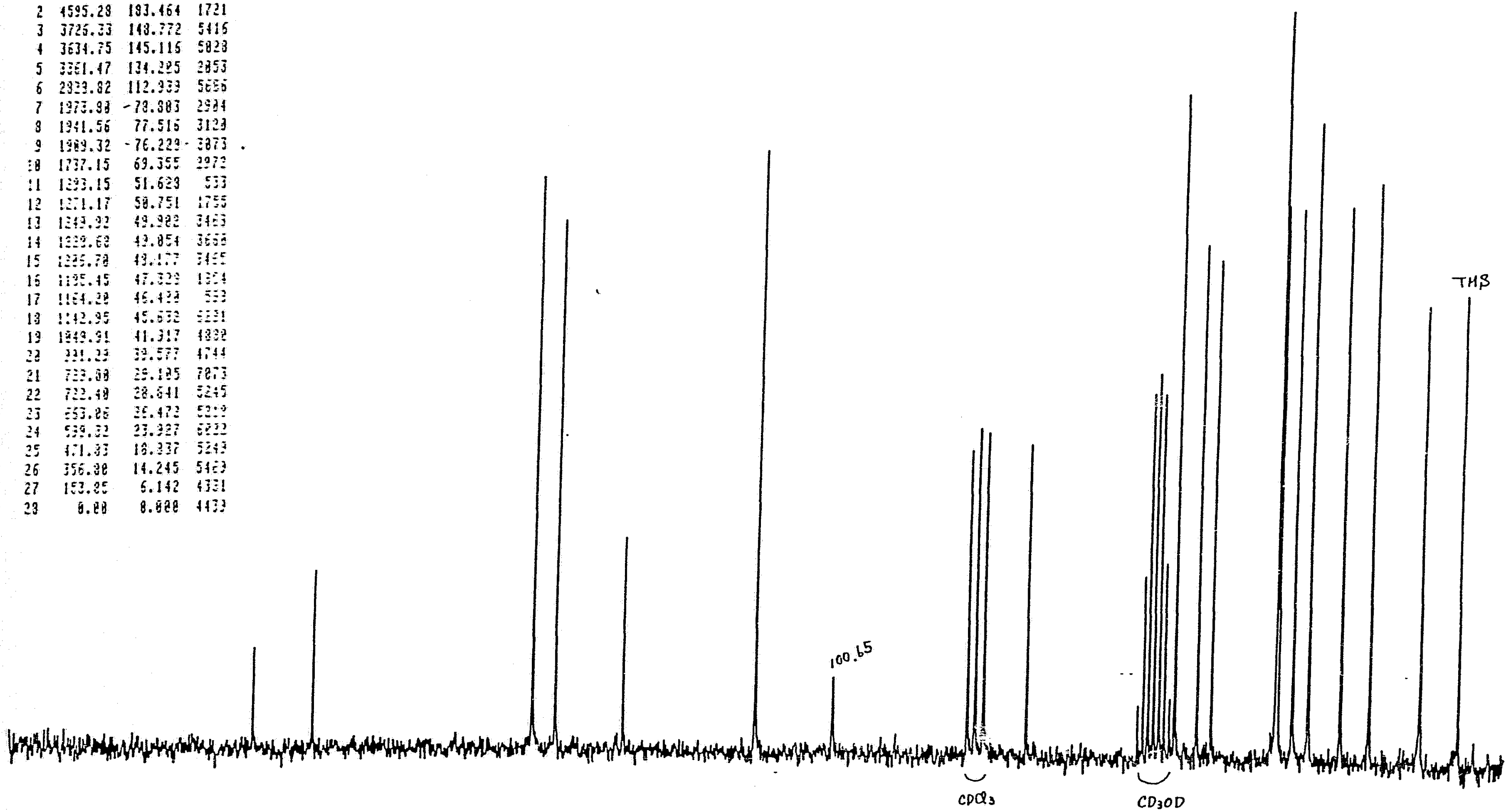
6,00
12
16

✓

COM
Low-

21

61 1 2



J-837-MB

myrocin C - natural

^{13}C NMR (25 MHz) $CDCl_3$ / CD_3OD

- courtesy of Dr. Y.-H. Hsu.