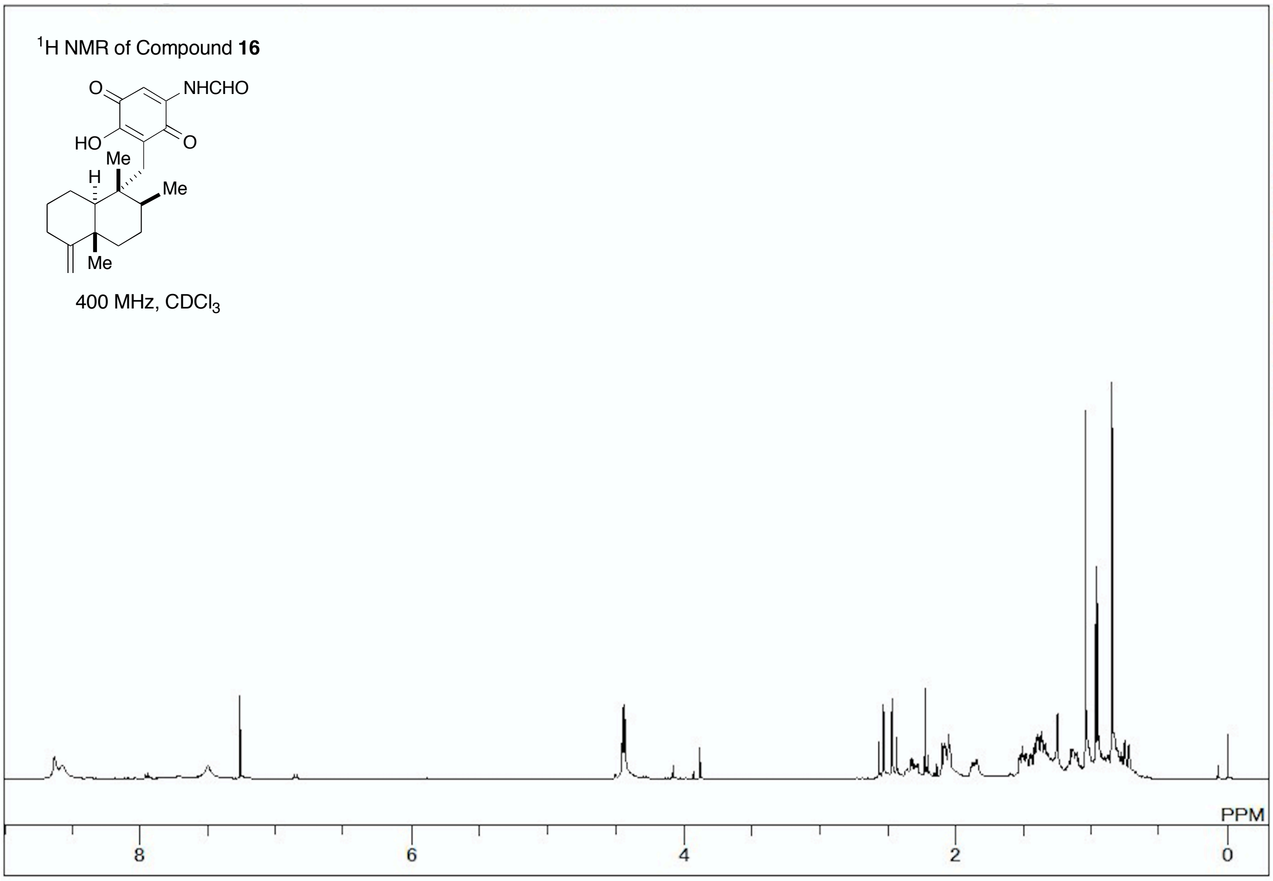
Electronic Supplementary Information

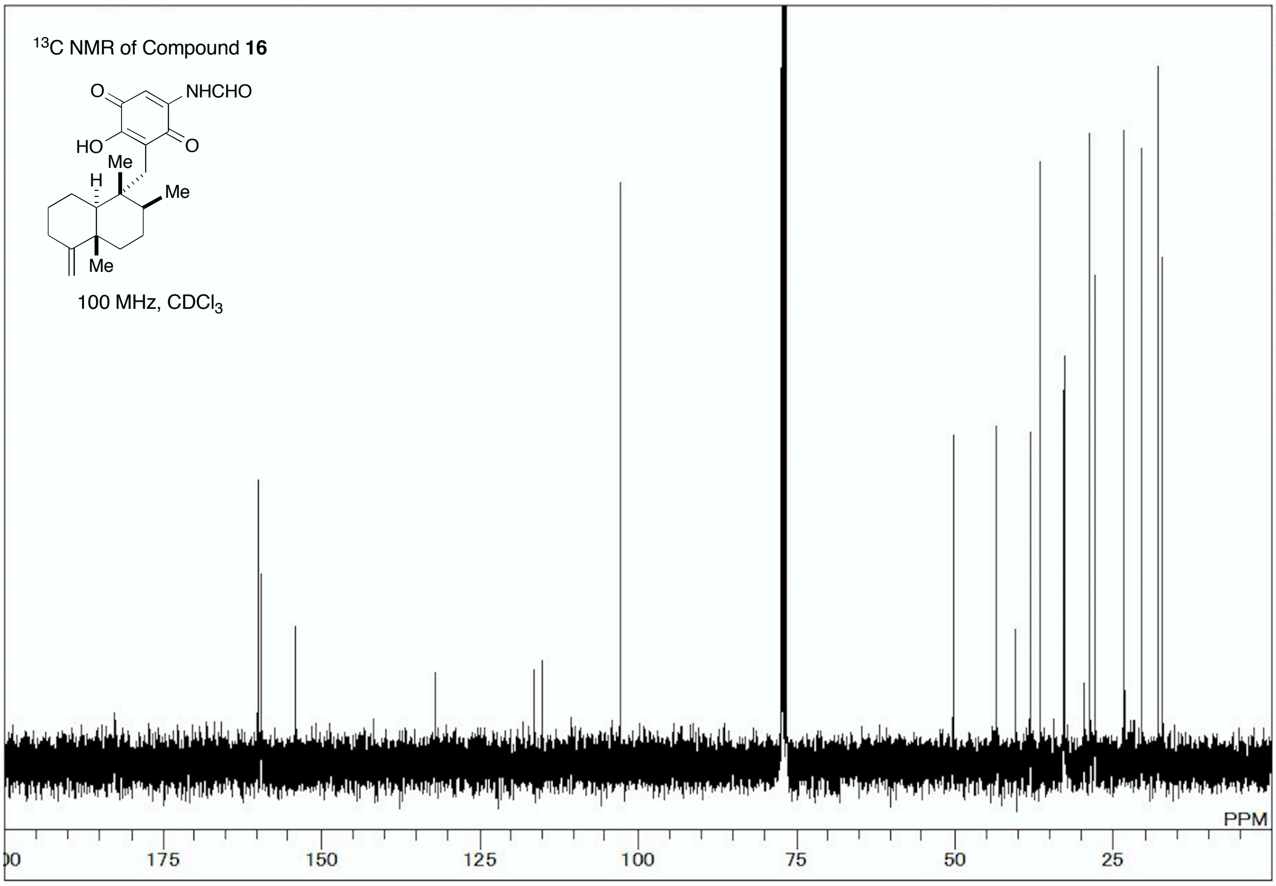
A Novel Approach to Sesquiterpenoid Benzoxazole Synthesis from Marine Sponges: Nakijinols A, B and E–G

*Yuki Takeda, Keiyo Nakai, Koichi Narita and Tadashi Katoh**

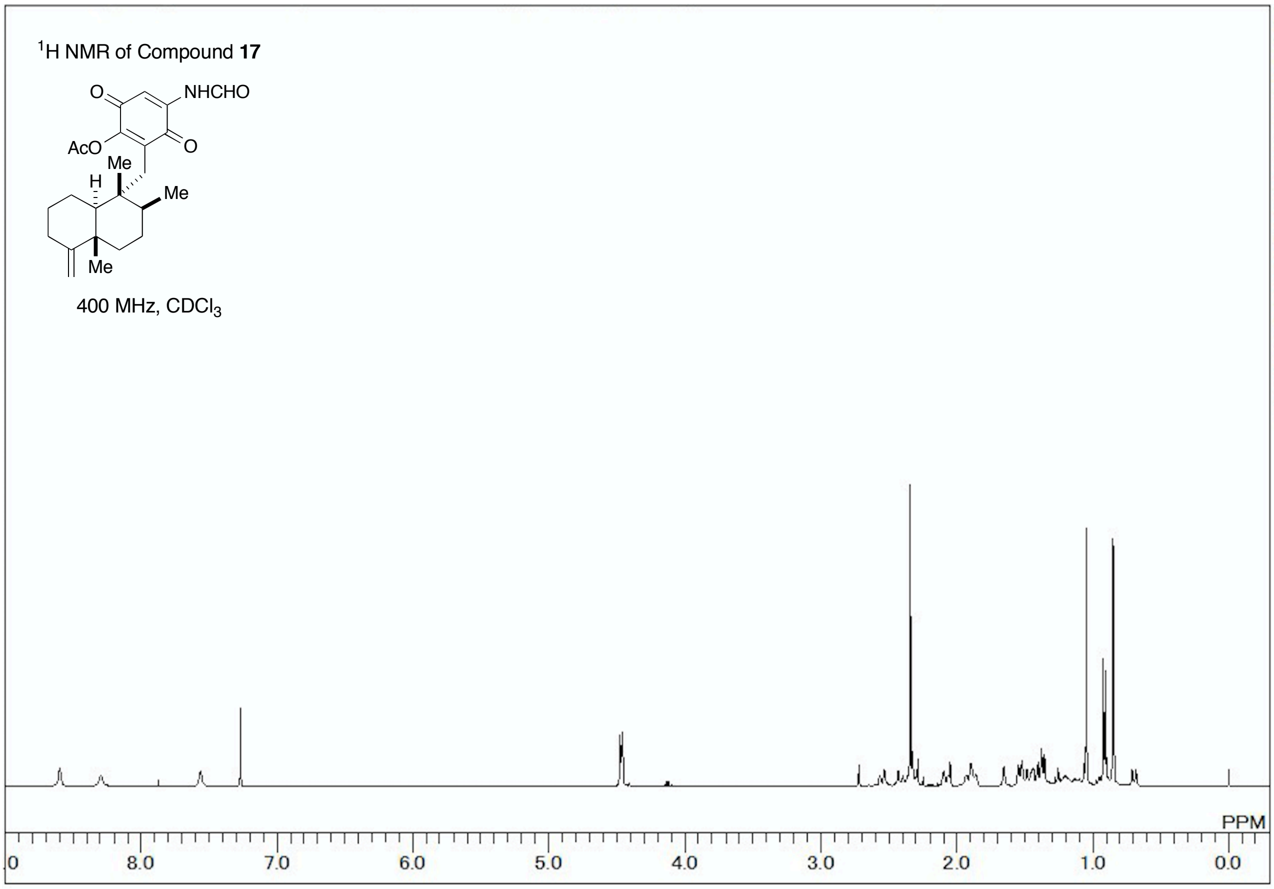
Table of Contents



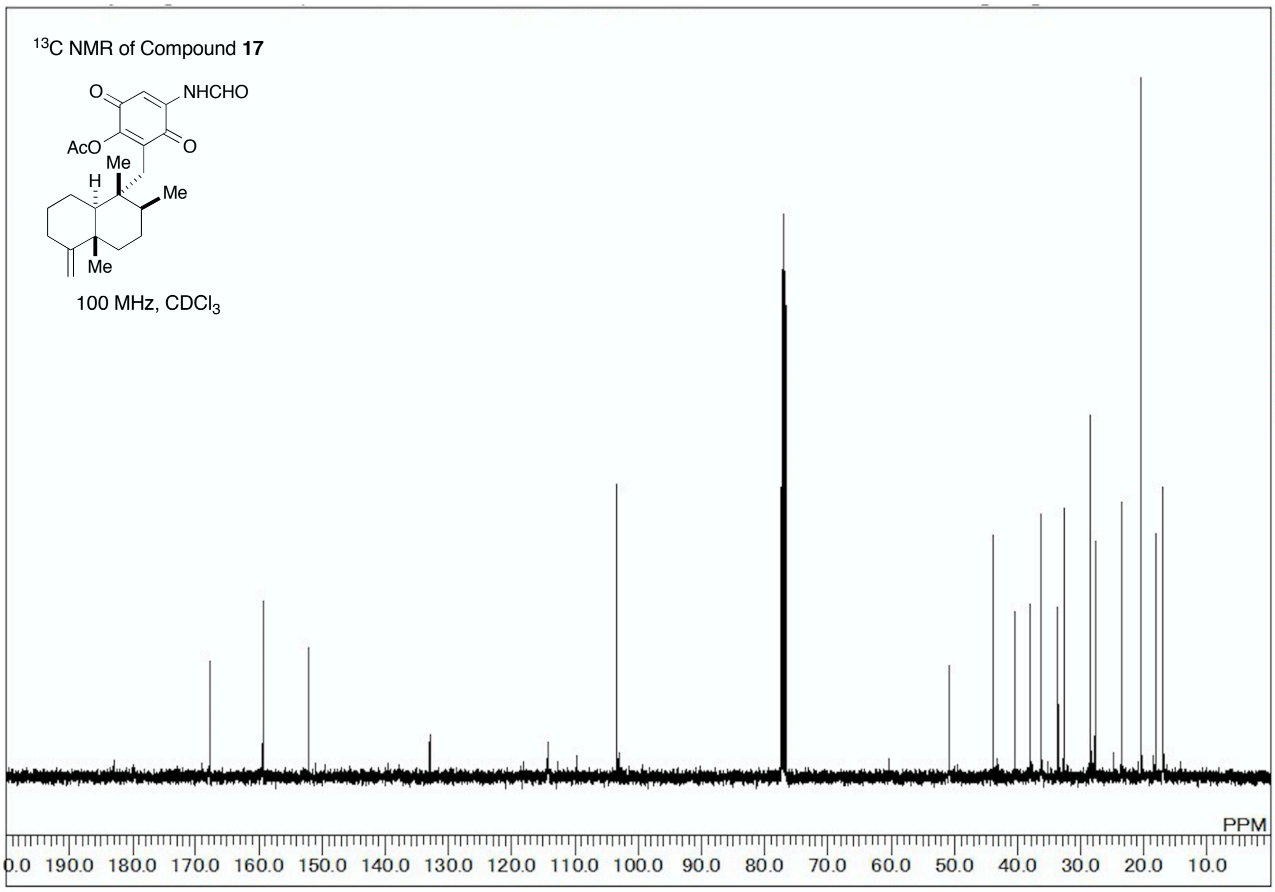
^{1}H NMR of Compound **16**
O
NHCHO
HO
O
Me
H
Me
Me
400 MHz, $CDCl_3$
PPM
8
6
4
2
0



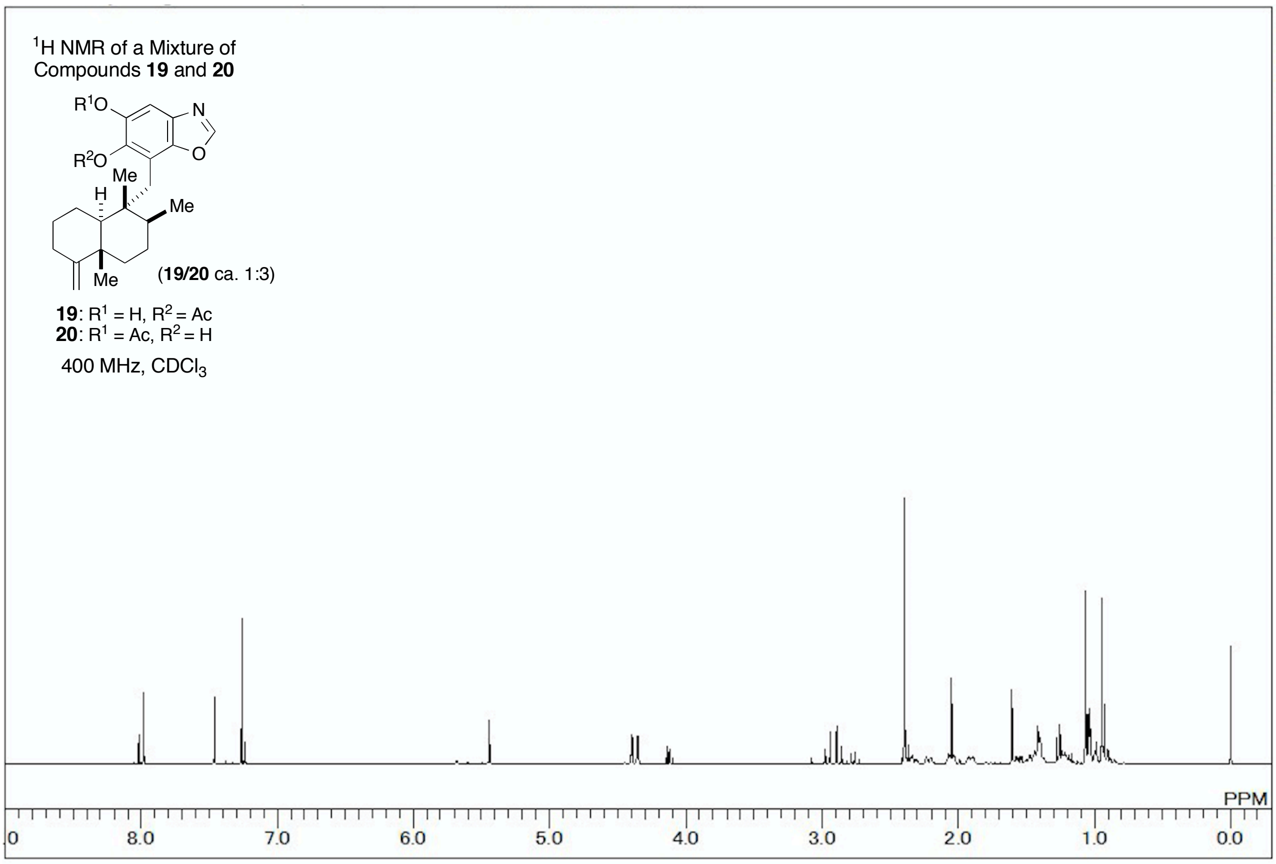
^{13}C NMR of Compound **16**
O
NHCHO
HO
O
Me
H
Me
Me
100 MHz, $CDCl_3$
PPM
175
150
125
100
75
50
25



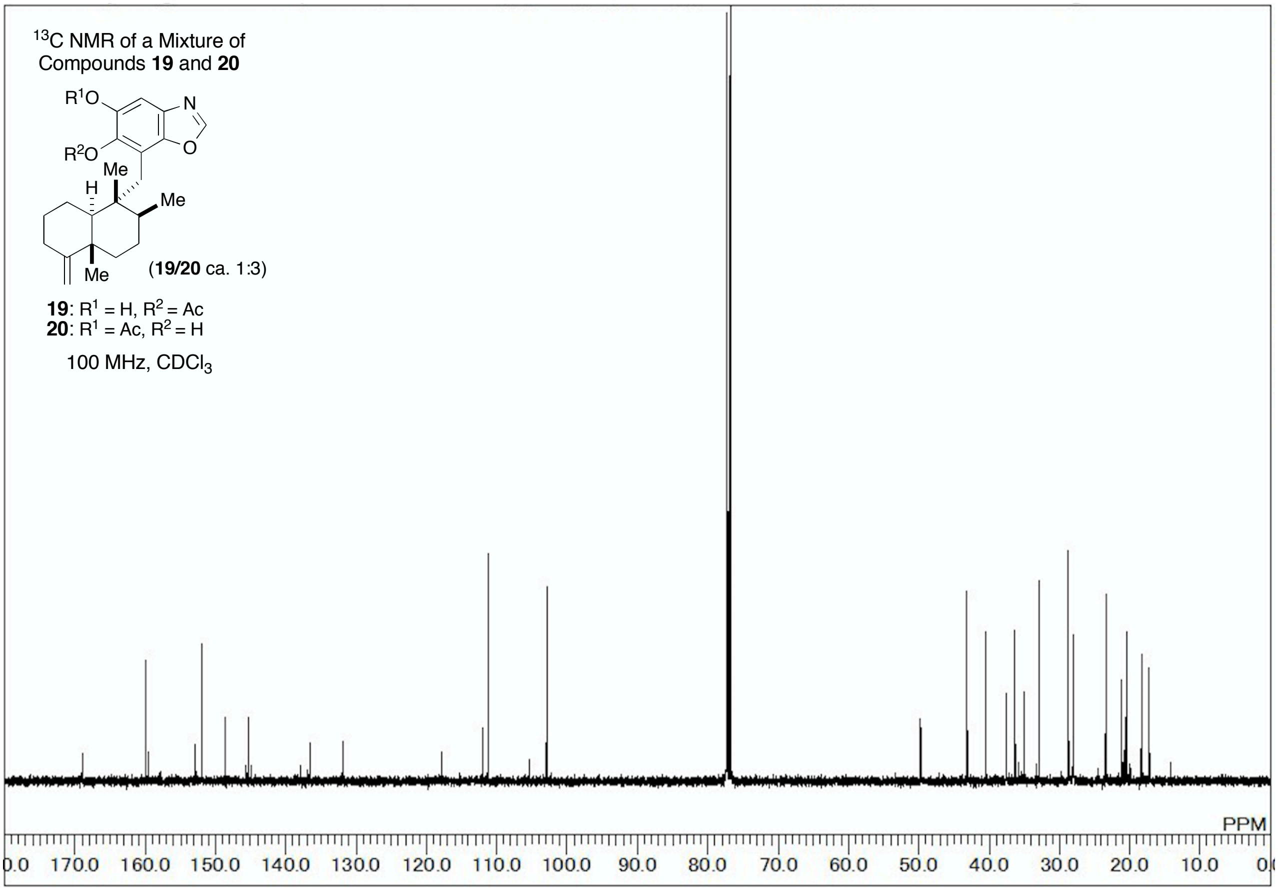
^{1}H NMR of Compound **17**
NHCHO
AcO
Me
H
Me
Me
400 MHz, $CDCl_3$
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



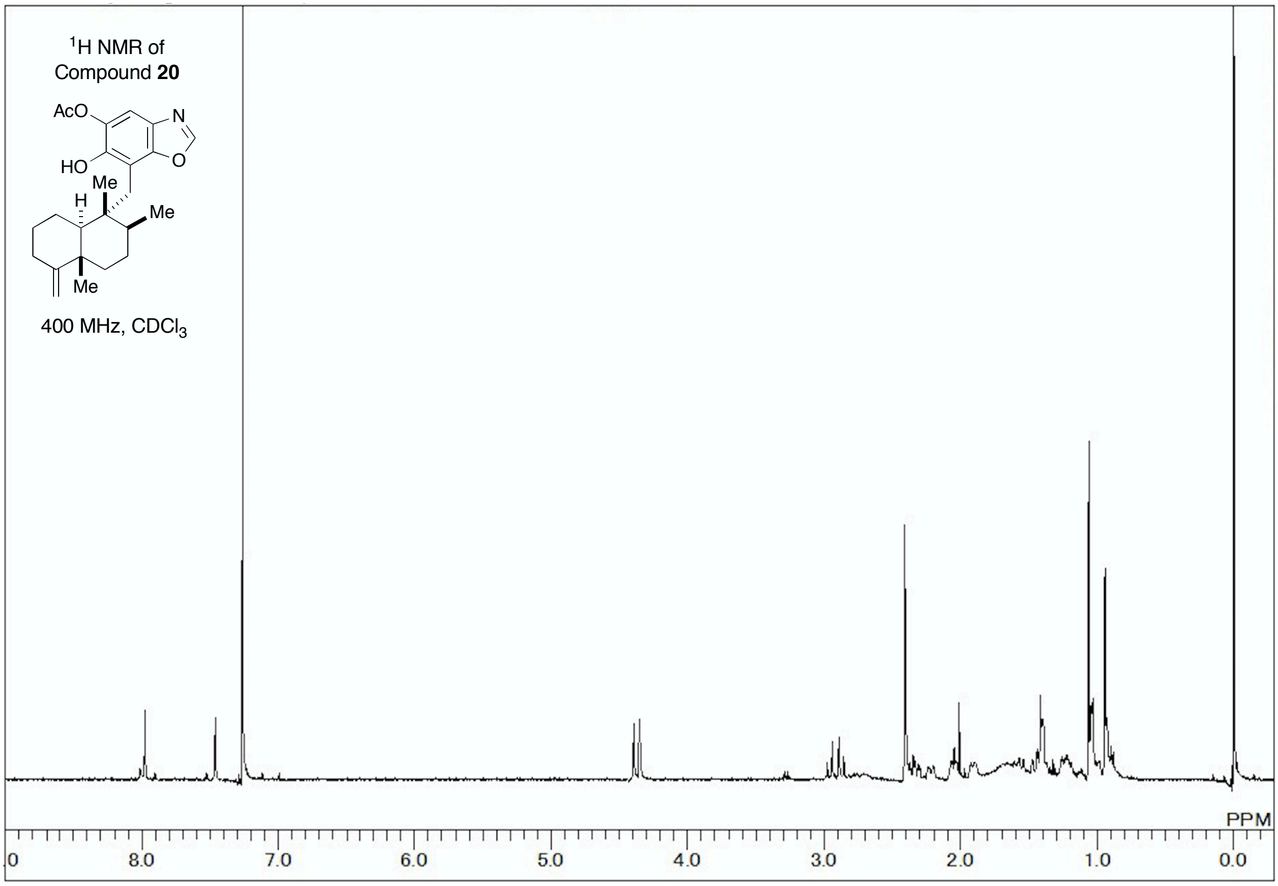
^{13}C NMR of Compound **17**
NHCHO
AcO
Me
H
Me
Me
100 MHz, $CDCl_3$
PPM
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0



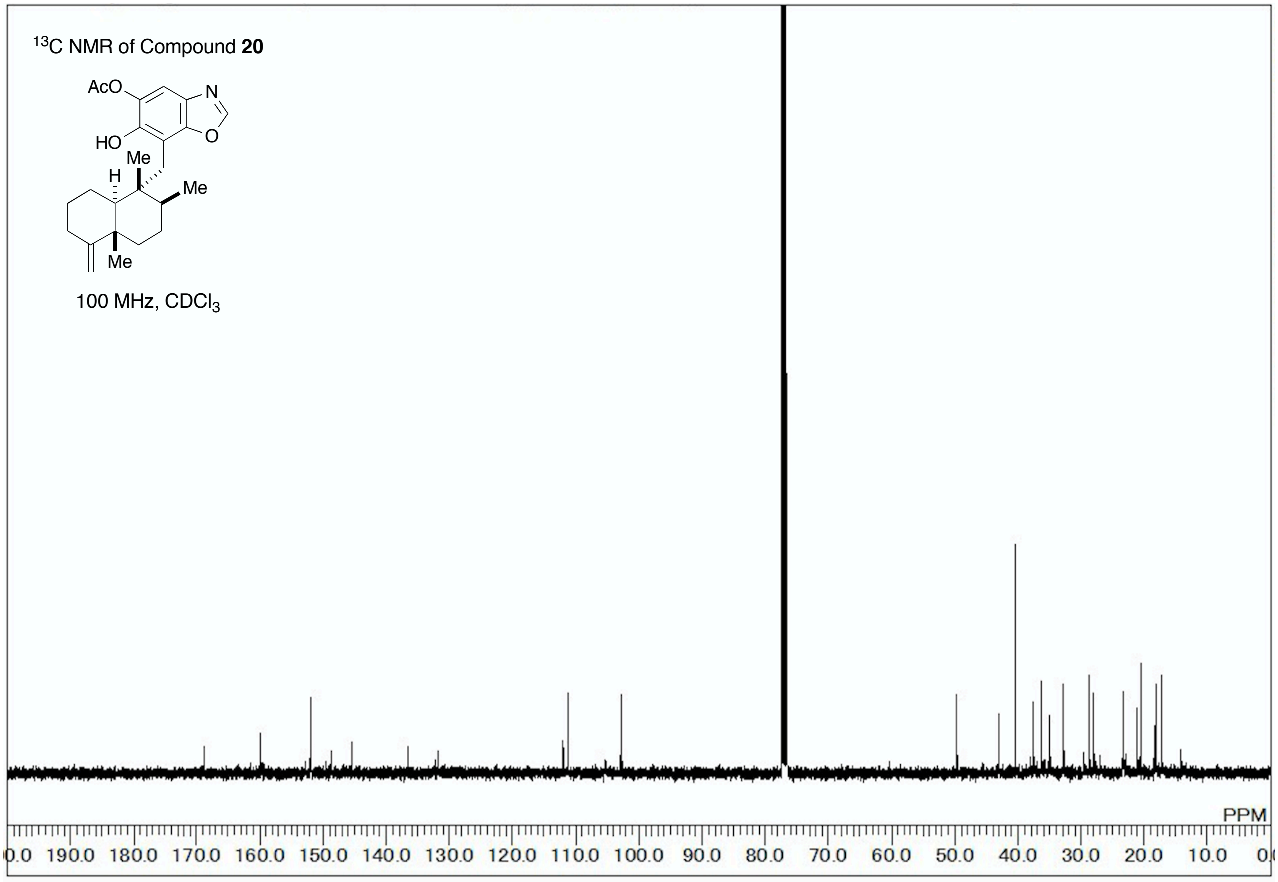
1H NMR of a Mixture of
Compounds 19 and 20
R1O
R2O
N
O
Me
H
Me
Me
(19/20 ca. 1:3)
19: R1 = H, R2 = Ac
20: R1 = Ac, R2 = H
400 MHz, CDCl3
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



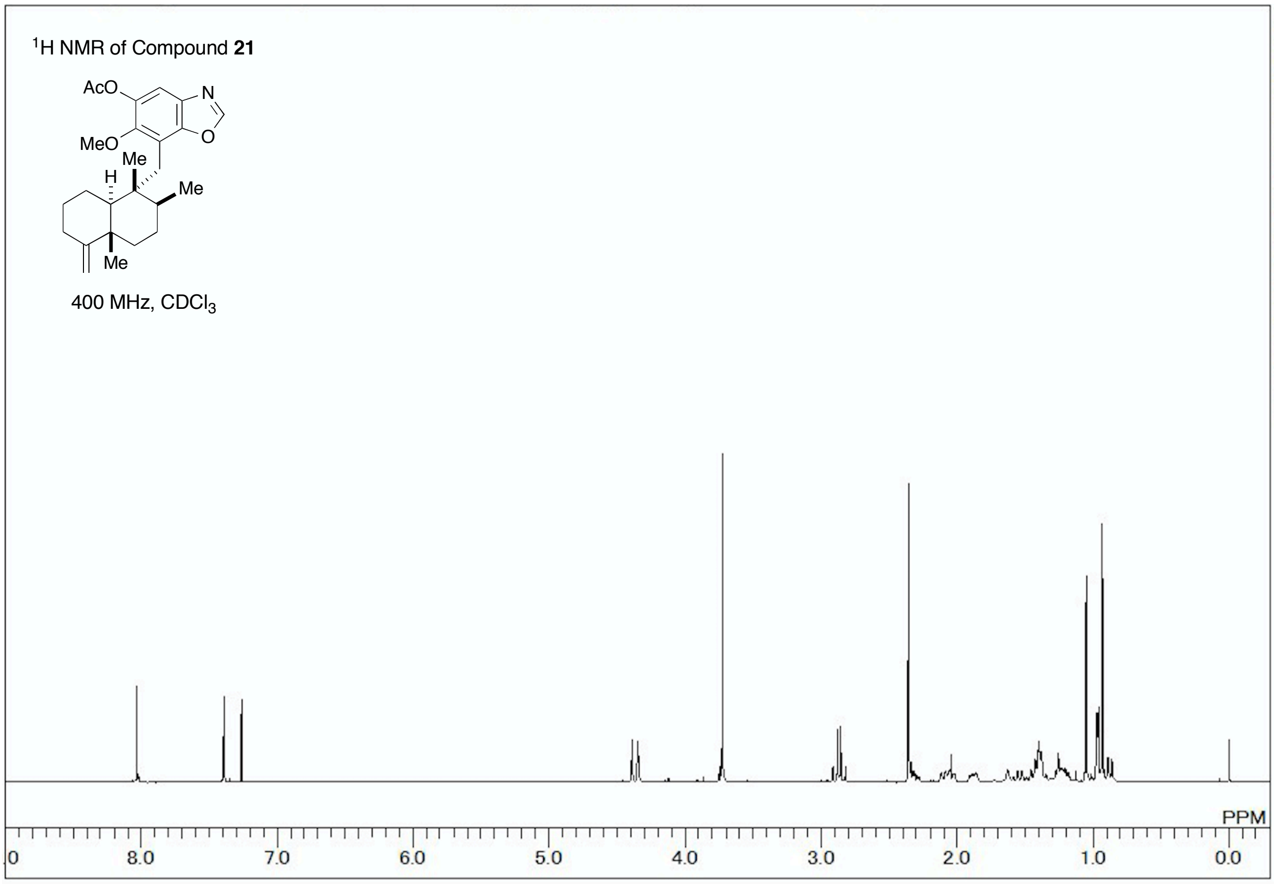
13C NMR of a Mixture of
Compounds 19 and 20
R1O
R2O
N
O
Me
H
Me
Me
(19/20 ca. 1:3)
19: R1 = H, R2 = Ac
20: R1 = Ac, R2 = H
100 MHz, CDCl3
PPM
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0



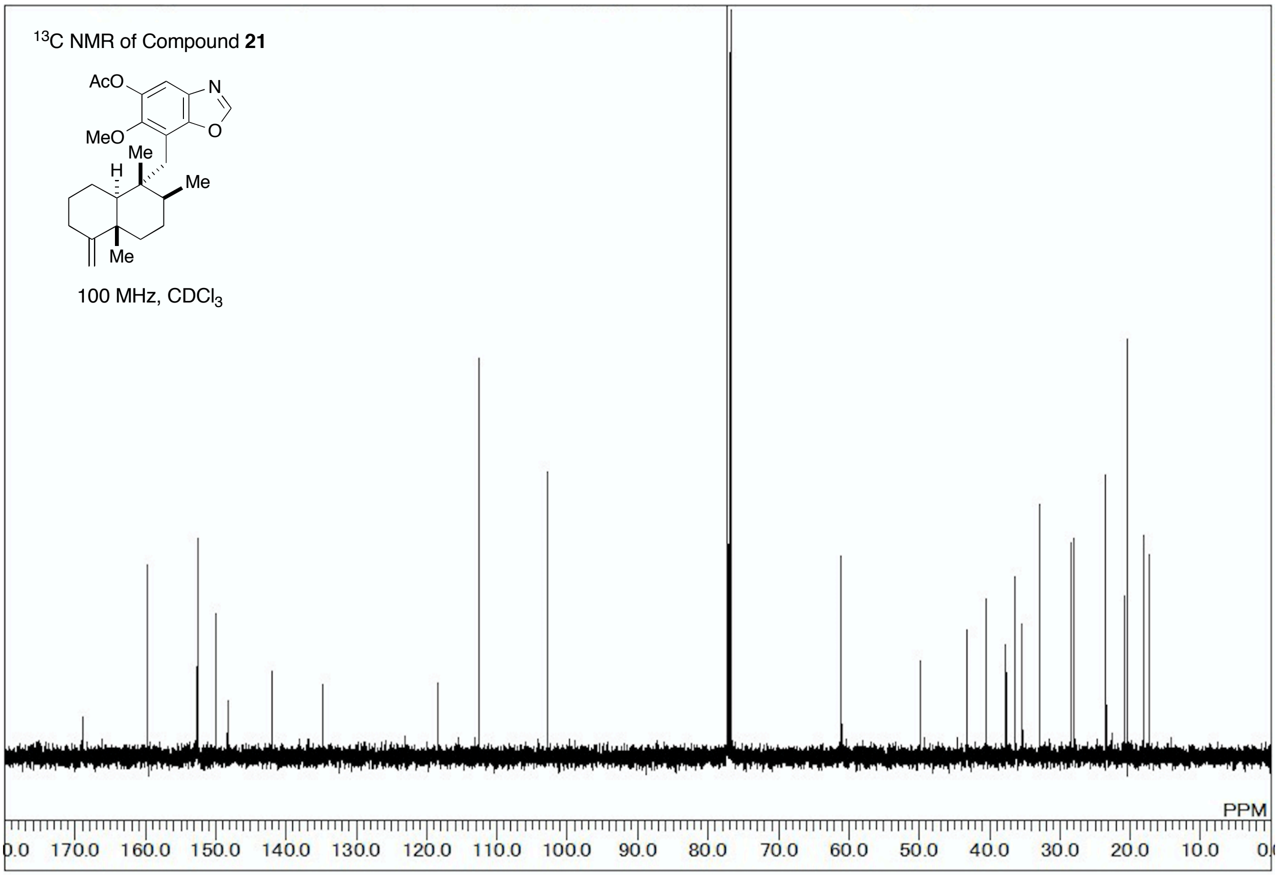
1H NMR of
Compound 20
AcO
N
O
HO
Me
H
Me
Me
400 MHz, CDCl3
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



13C NMR of Compound 20
AcO
N
O
HO
Me
H
Me
Me
100 MHz, CDCl3
PPM
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0



^{1}H NMR of Compound **21**
AcO
N
O
MeO
Me
H
Me
Me
400 MHz, $CDCl_3$
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



^{13}C NMR of Compound **21**
AcO
N
O
MeO
Me
H
Me
Me
100 MHz, $CDCl_3$
PPM
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0

HMBC of Compound **21**

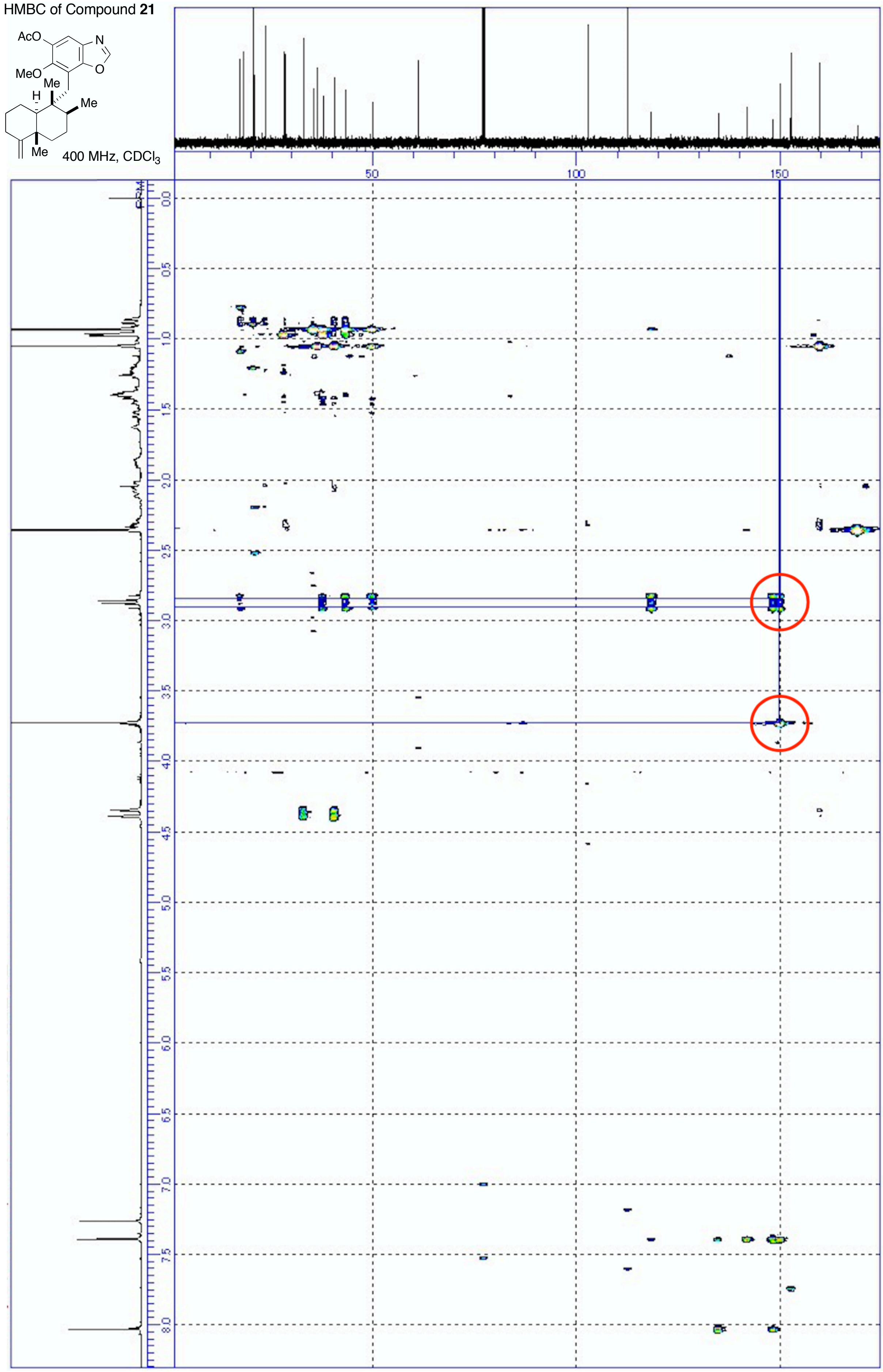
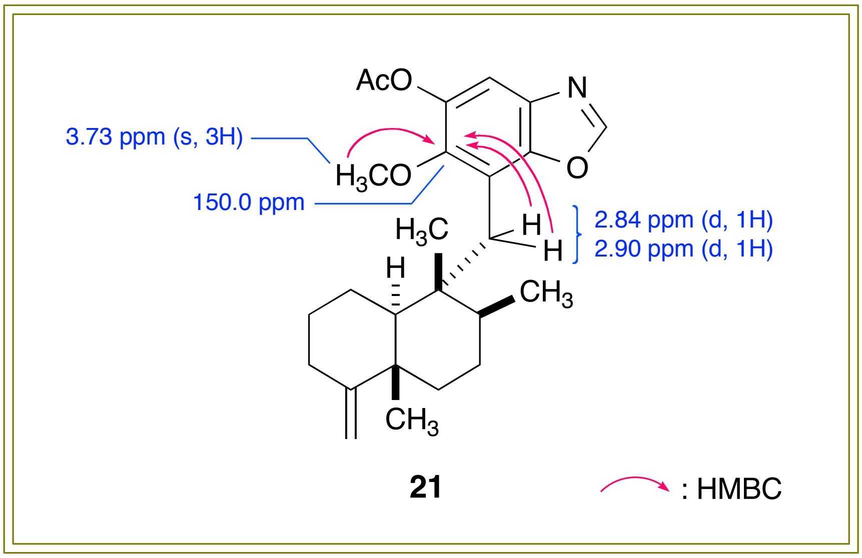
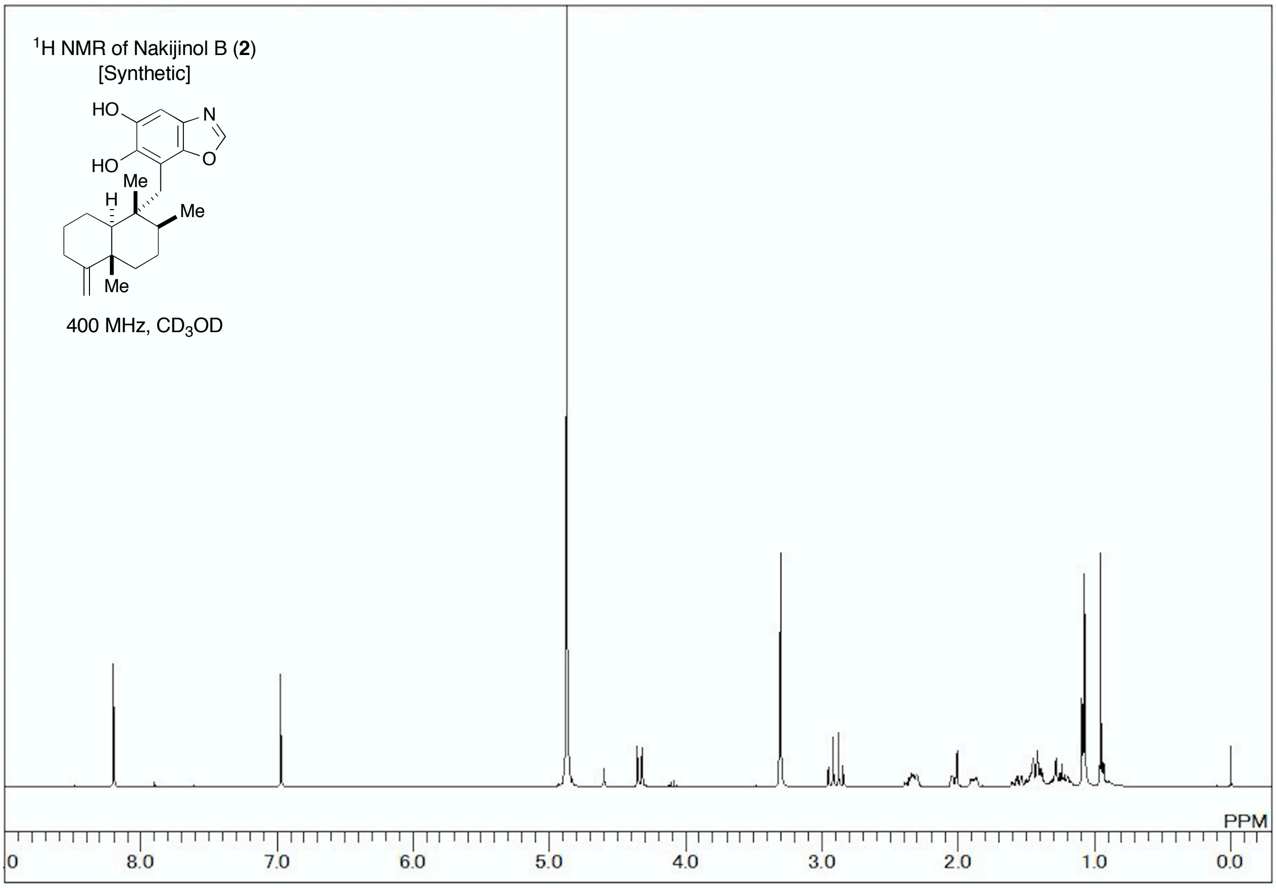
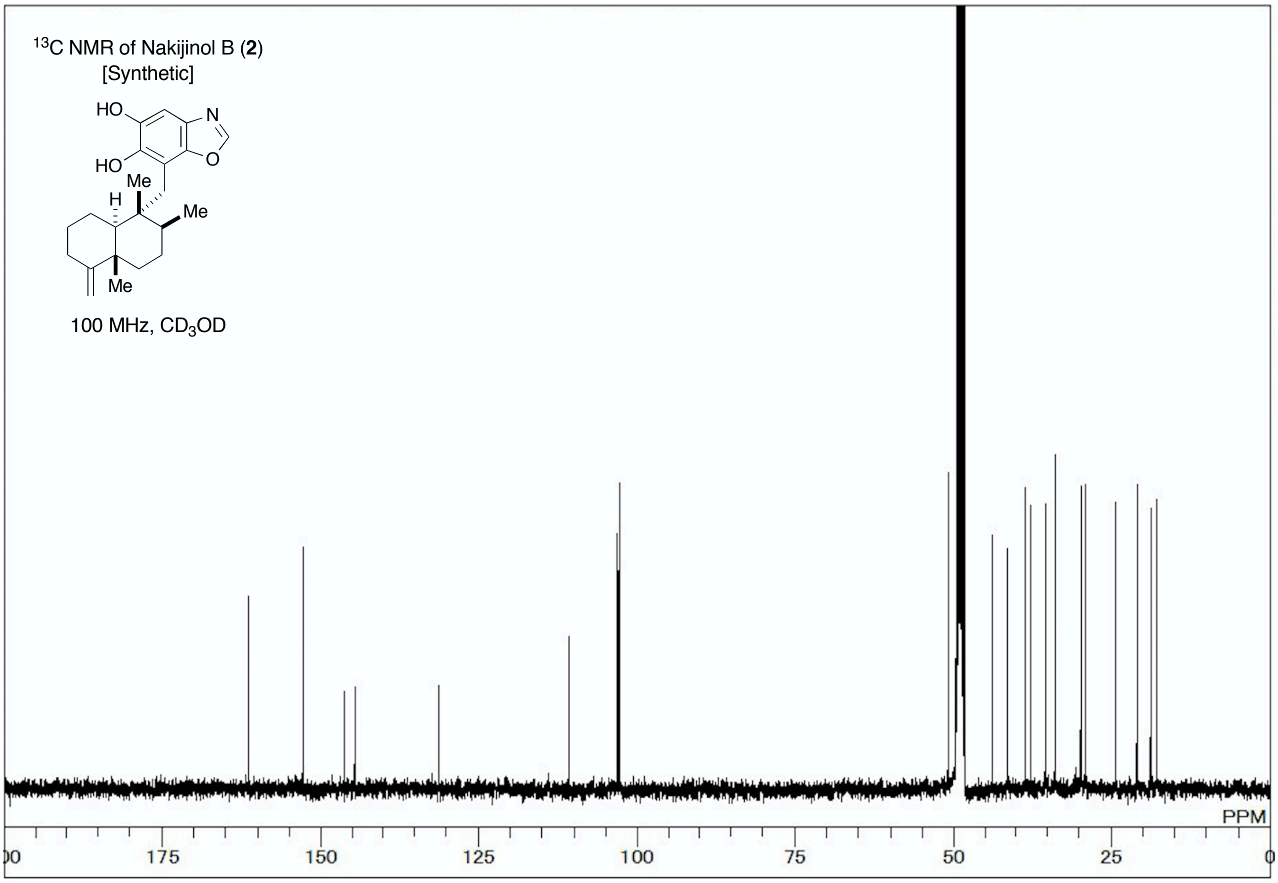


Fig. 1 Selected HMBC Correlations for Compound **21**

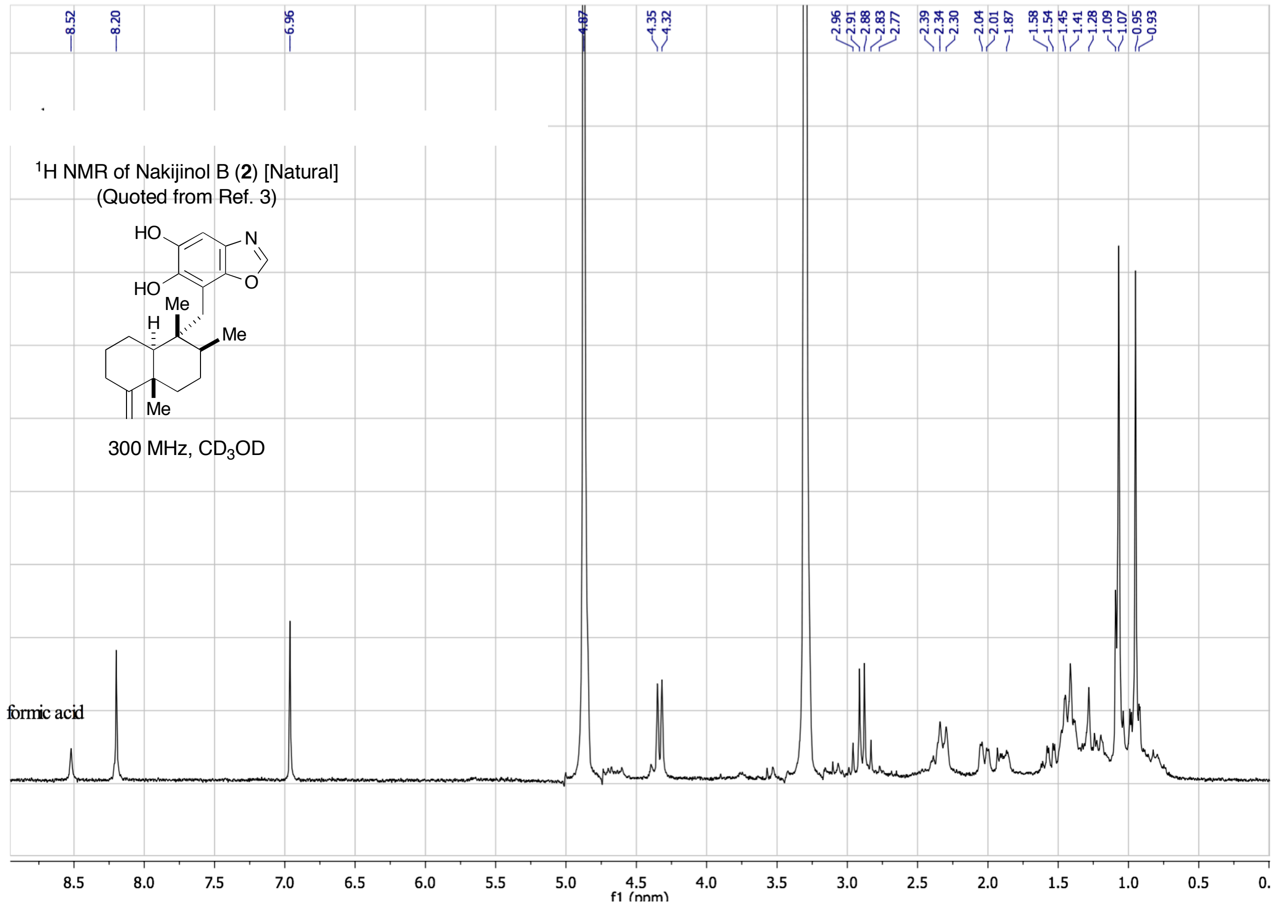




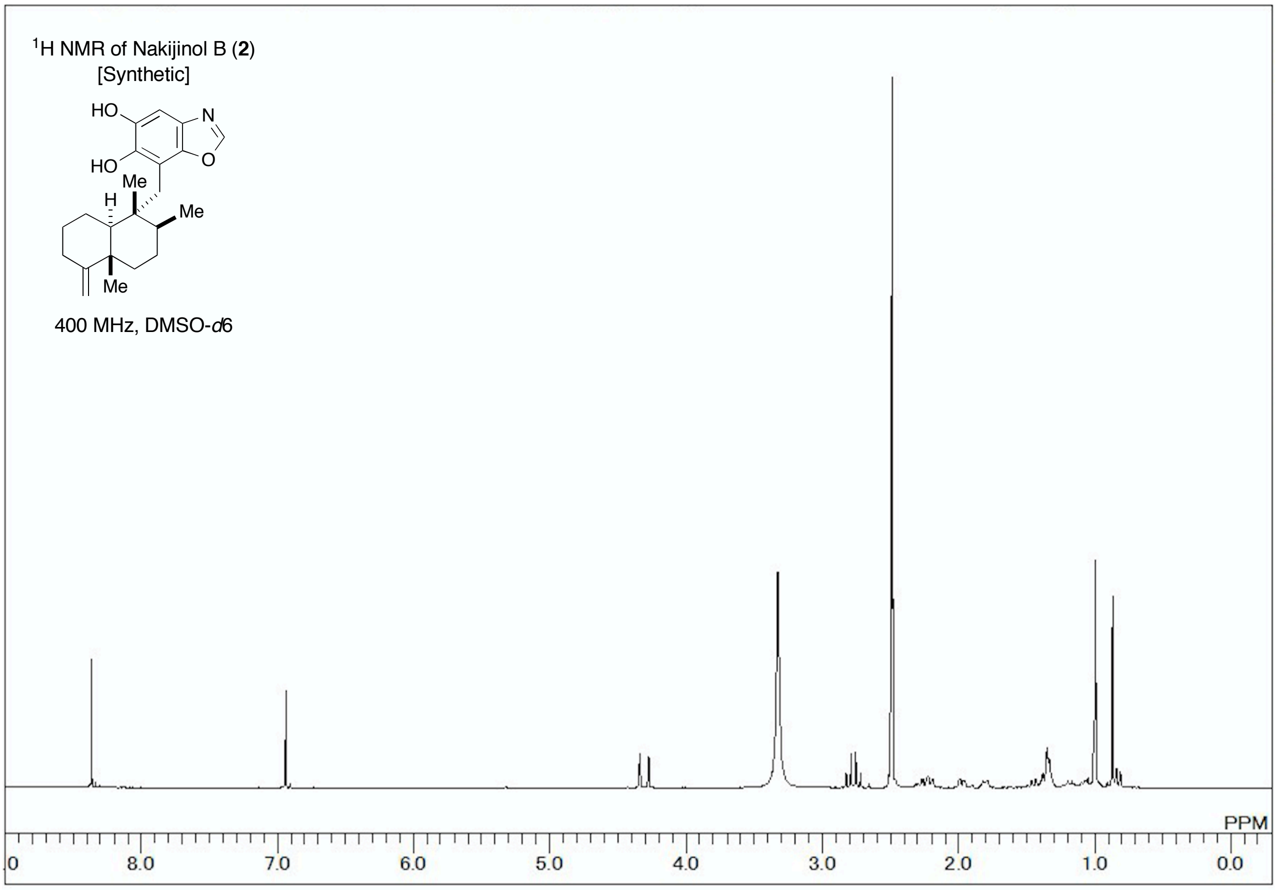
^{1}H NMR of Nakijinol B (**2**)
[Synthetic]
HO
HO
N
O
Me
H
Me
Me
400 MHz, CD_3OD
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



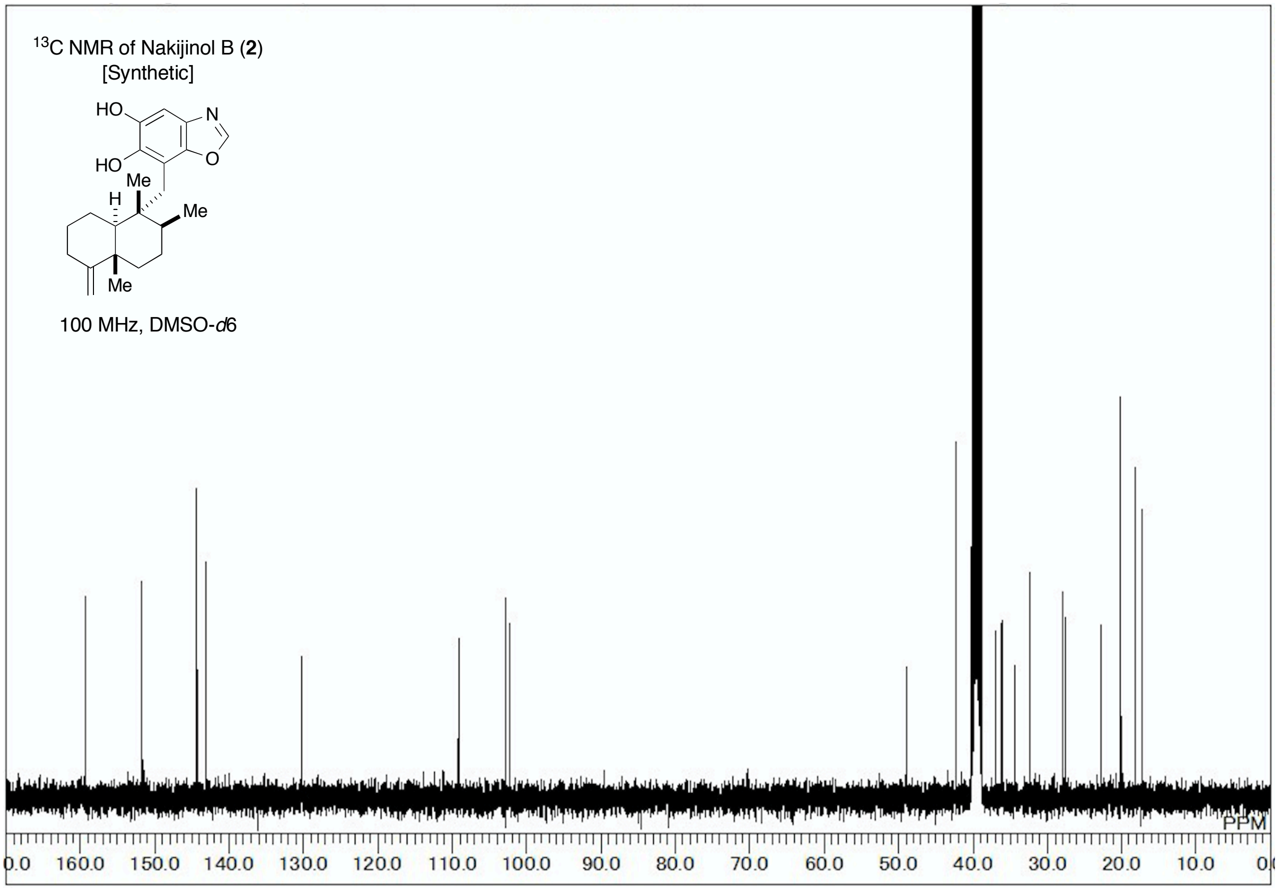
^{13}C NMR of Nakijinol B (**2**)
[Synthetic]
HO
HO
N
O
Me
H
Me
Me
100 MHz, CD_3OD
PPM
175
150
125
100
75
50
25



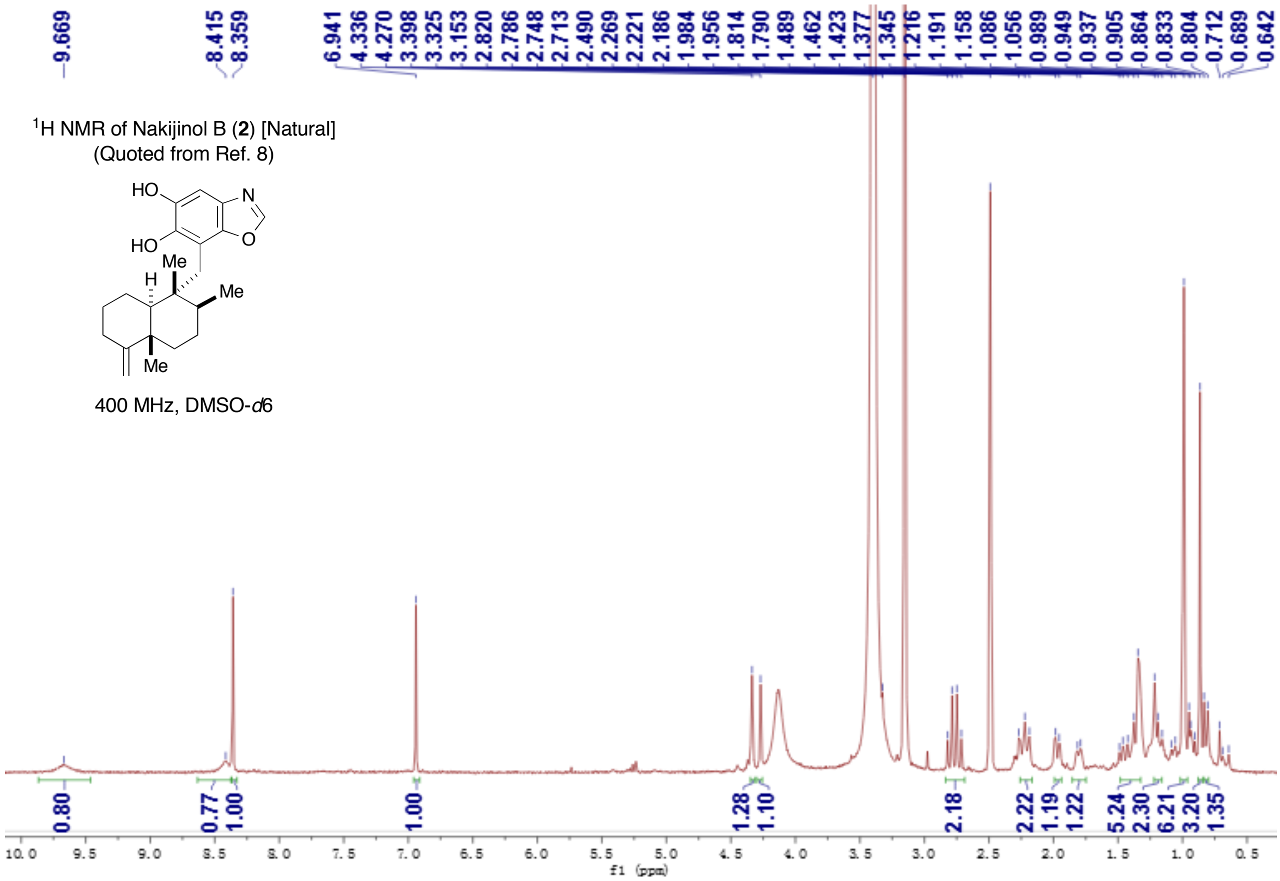
Note: ^{13}C NMR Chart of Nakijinol B (**2**) [Natural] was not given in Ref. 3.



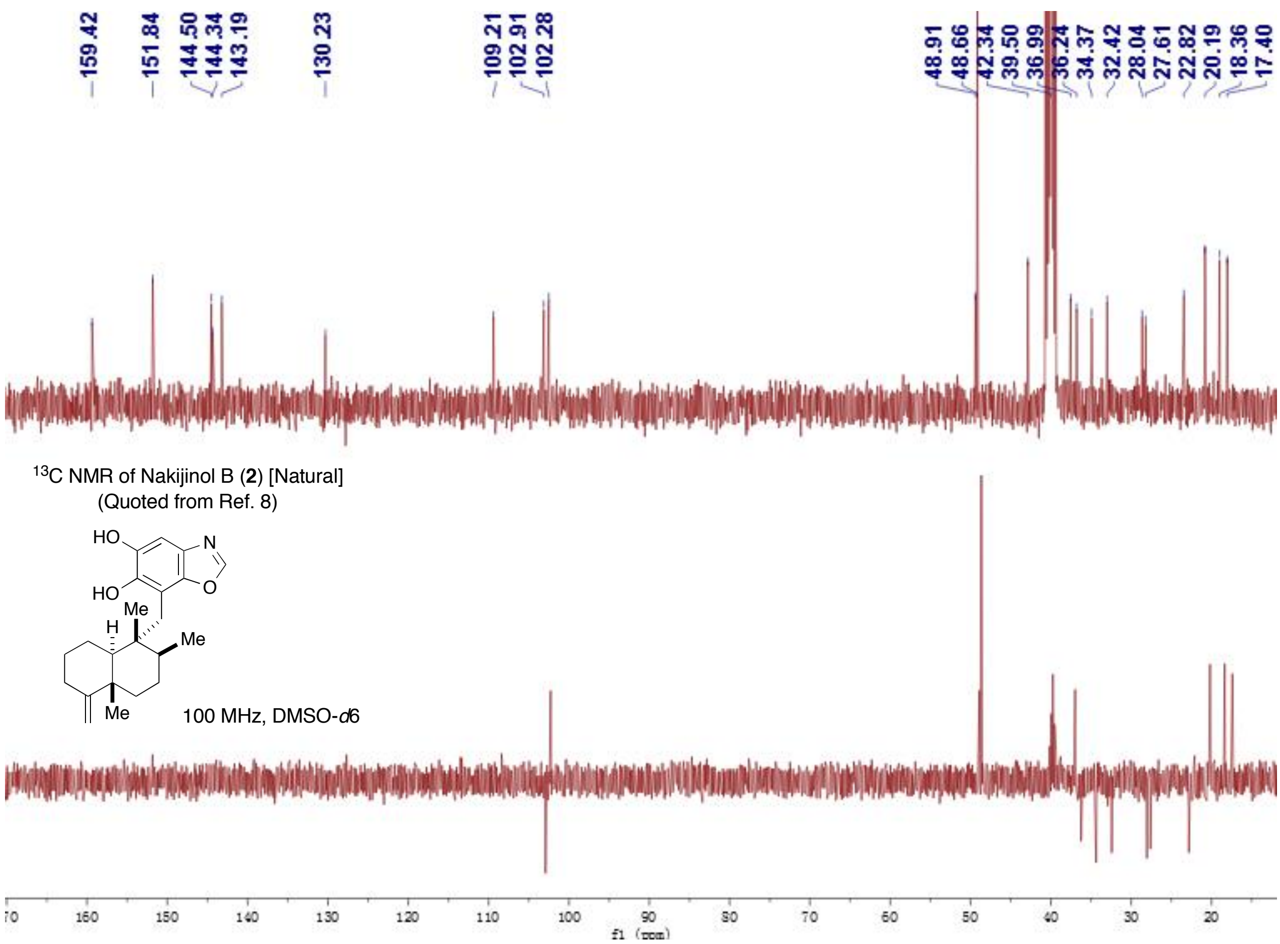
^{1}H NMR of Nakijinol B (**2**)
[Synthetic]
HO
HO
N
O
Me
H
Me
Me
400 MHz, DMSO-*d*6
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



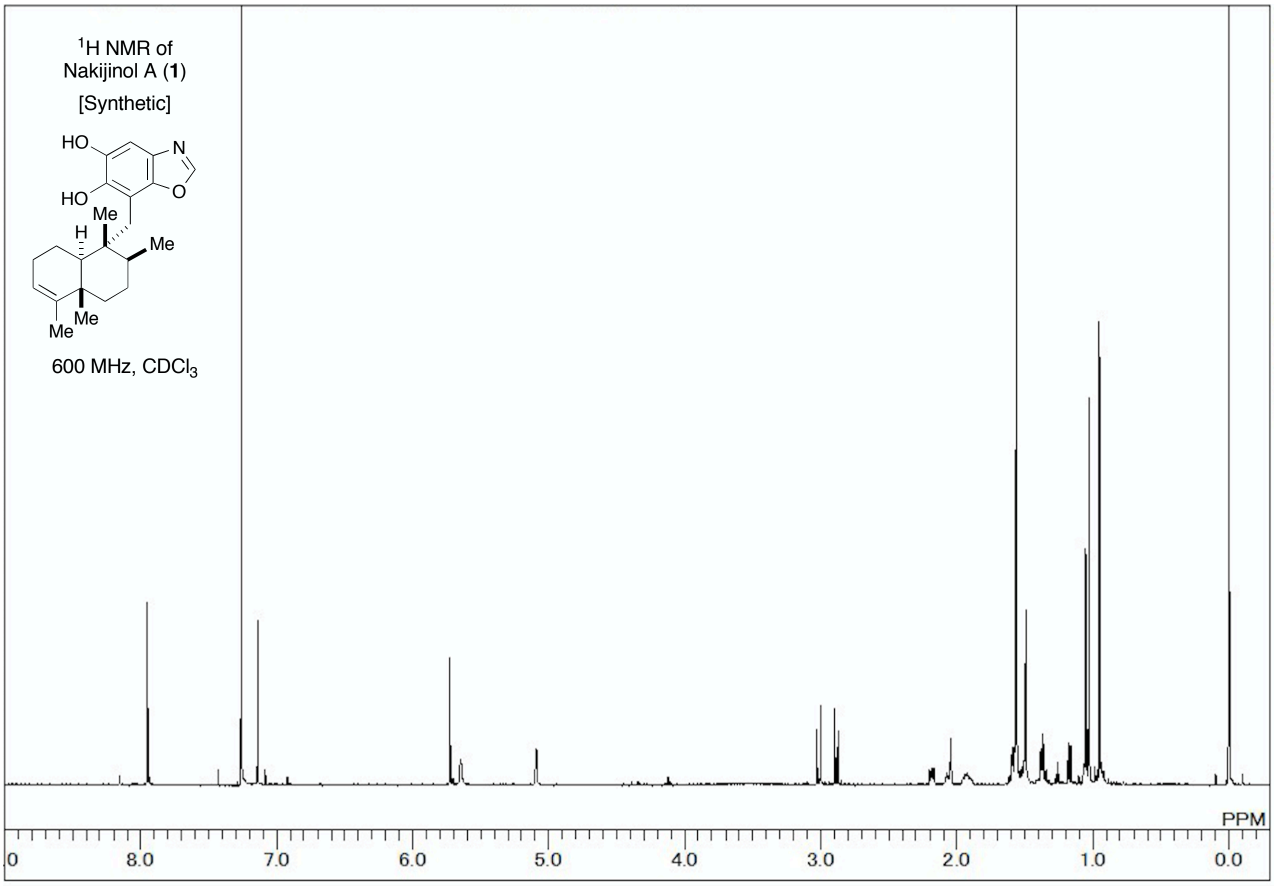
^{13}C NMR of Nakijinol B (**2**)
[Synthetic]
HO
HO
N
O
Me
H
Me
Me
100 MHz, DMSO-*d*6
PPM
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0



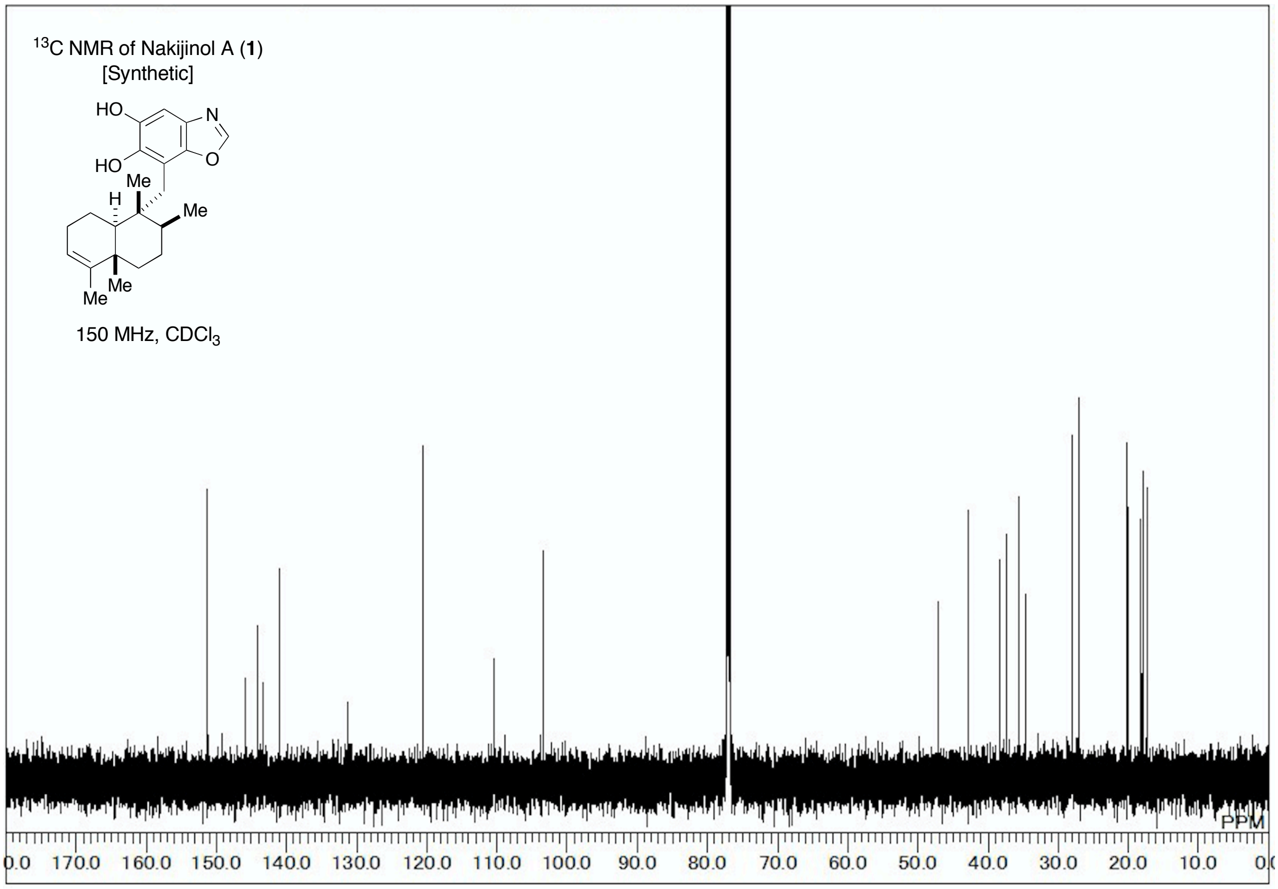
^{1}H NMR of Nakijinol B (**2**) [Natural]
(Quoted from Ref. 8)
HO
HO
N
O
Me
H
Me
Me
400 MHz, DMSO-*d*6
9.669
8.415
8.359
6.941
4.336
4.270
3.398
3.325
3.153
2.820
2.786
2.748
2.713
2.490
2.269
2.221
2.186
1.984
1.956
1.814
1.790
1.489
1.462
1.423
1.377
1.345
1.216
1.191
1.158
1.086
1.056
0.989
0.949
0.937
0.905
0.864
0.833
0.804
0.712
0.689
0.642
0.80
0.77
1.00
1.00
1.28
1.10
2.18
2.22
1.19
1.22
5.24
2.30
6.21
3.20
1.35
f1 (ppm)



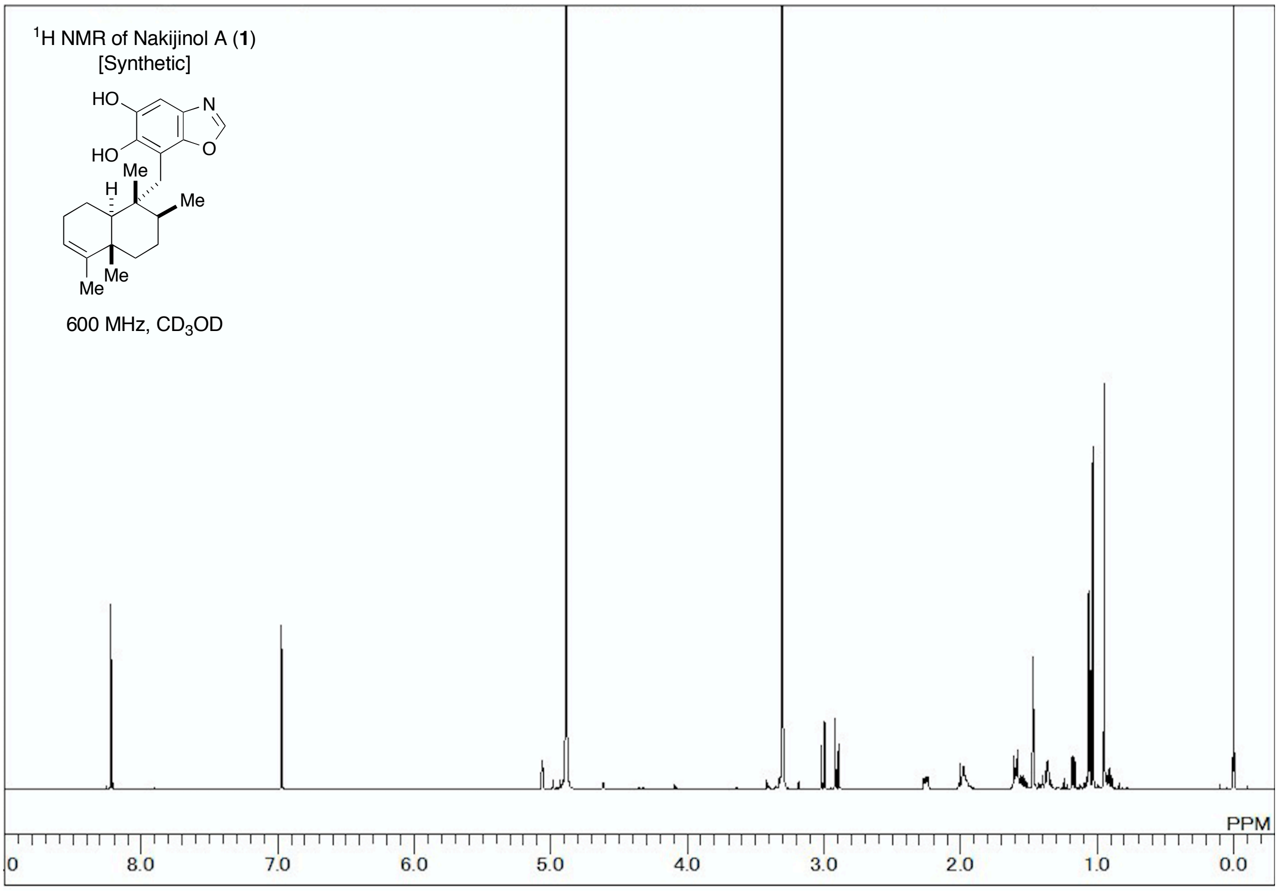
159.42
151.84
144.50
144.34
143.19
130.23
109.21
102.91
102.28
48.91
48.66
42.34
39.50
36.99
36.24
34.37
32.42
28.04
27.61
22.82
20.19
18.36
17.40
^{13}C NMR of Nakijinol B (**2**) [Natural]
(Quoted from Ref. 8)
HO
HO
N
O
Me
H
Me
Me
100 MHz, DMSO-*d*6
f1 (ppm)

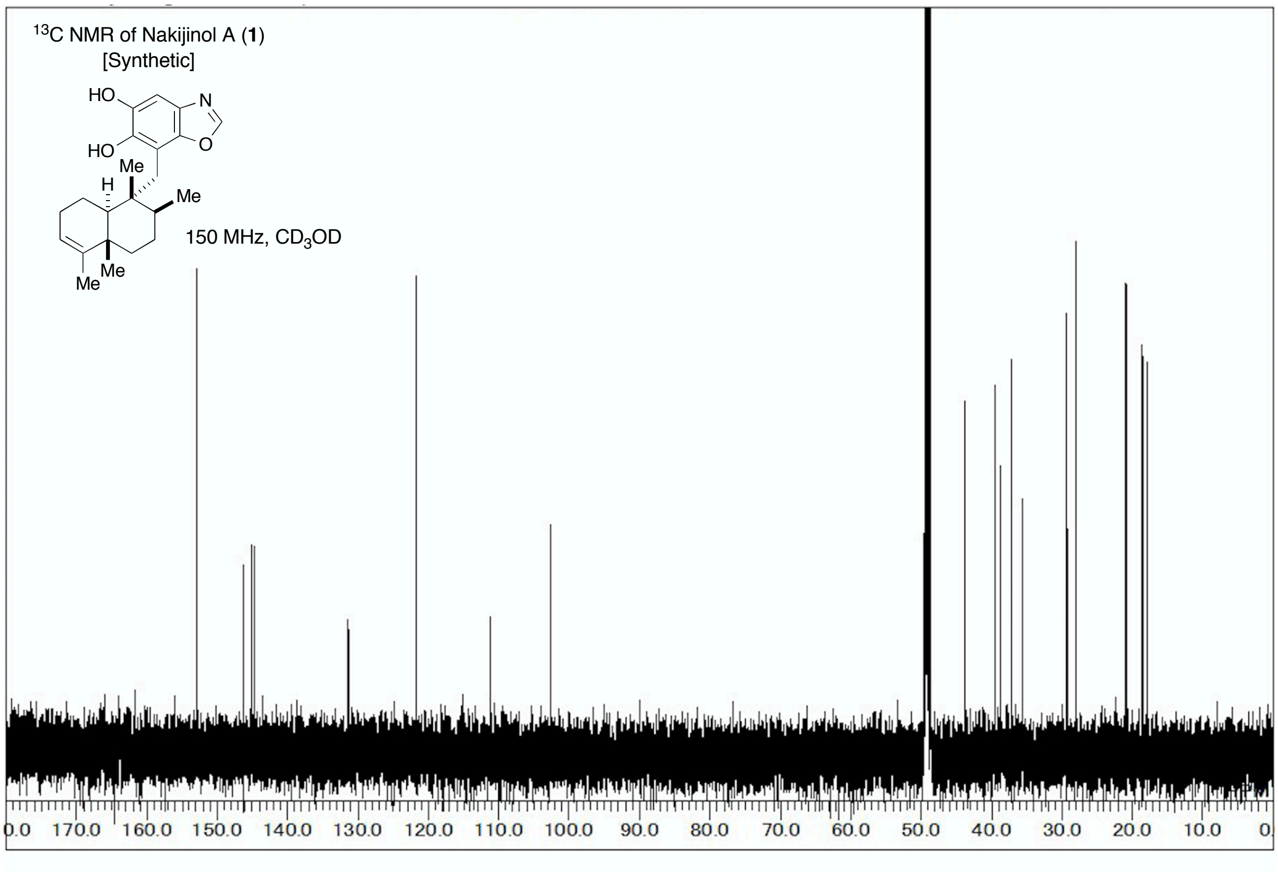


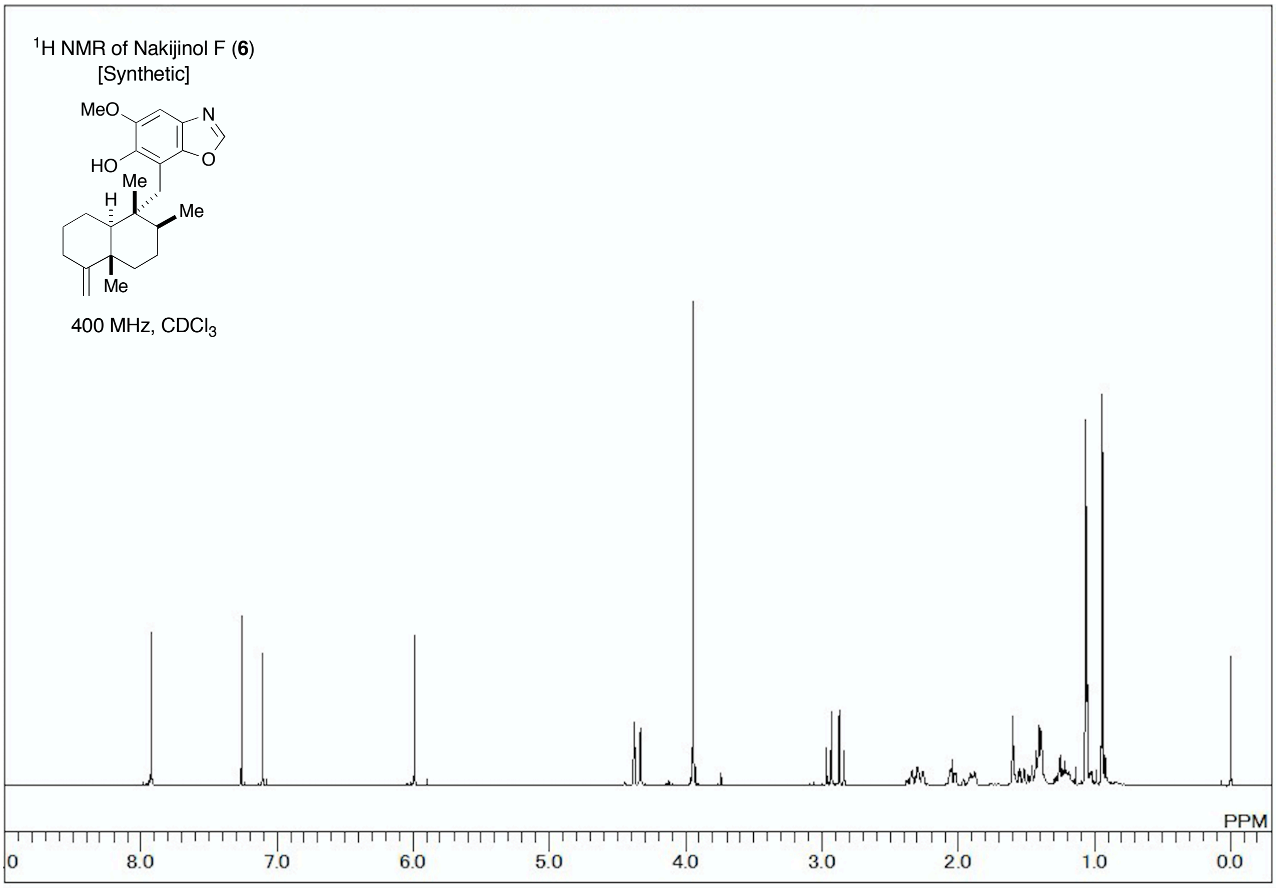
^{1}H NMR of
Nakijinol A (**1**)
[Synthetic]
HO
HO
N
O
Me
H
Me
Me
Me
600 MHz, CDCl$_3$
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

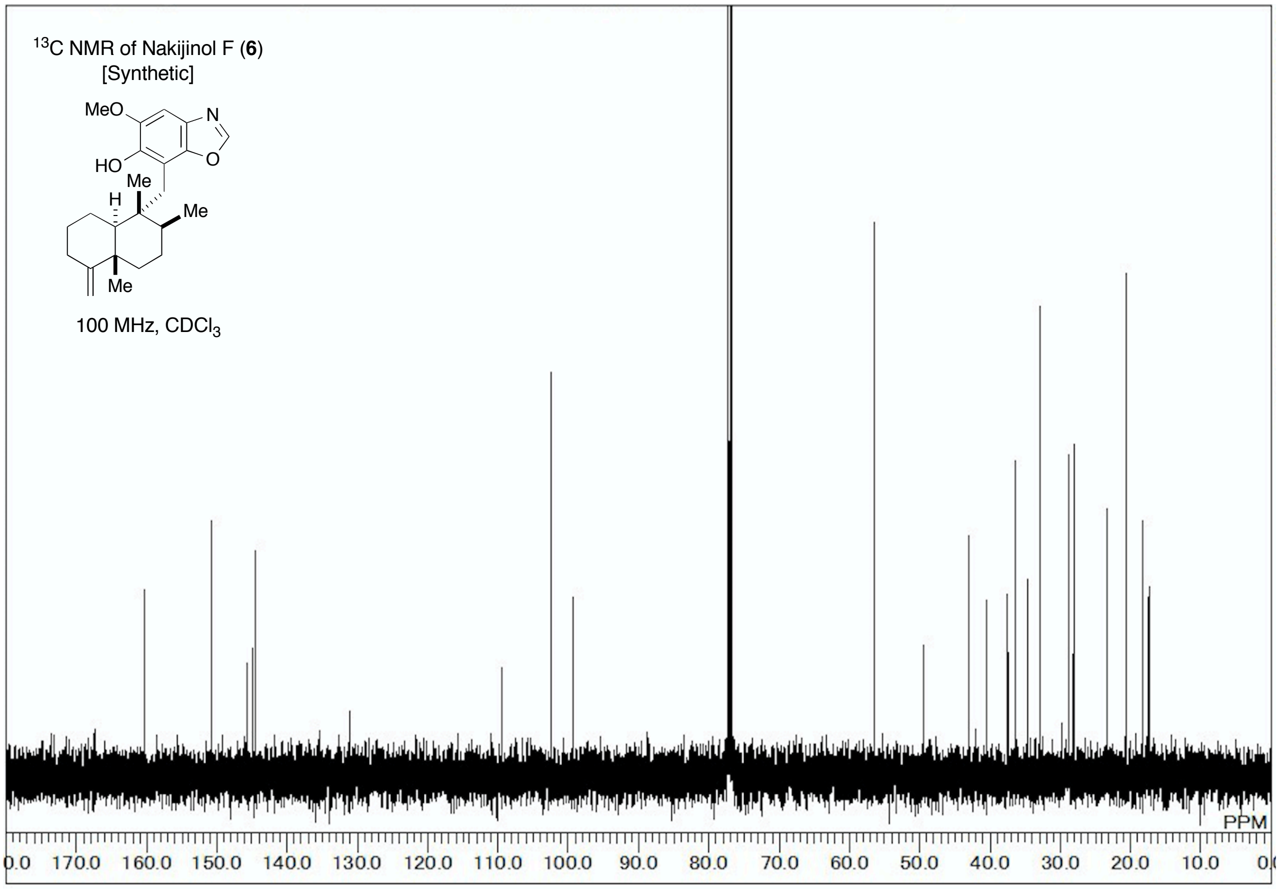


^{13}C NMR of Nakijinol A (**1**)
[Synthetic]
HO
HO
N
O
Me
H
Me
Me
Me
150 MHz, CDCl$_3$
PPM
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0


1H NMR of Nakijinol A (1)
[Synthetic]
HO
HO
N
O
Me
H
Me
Me
Me
600 MHz, CD3OD
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

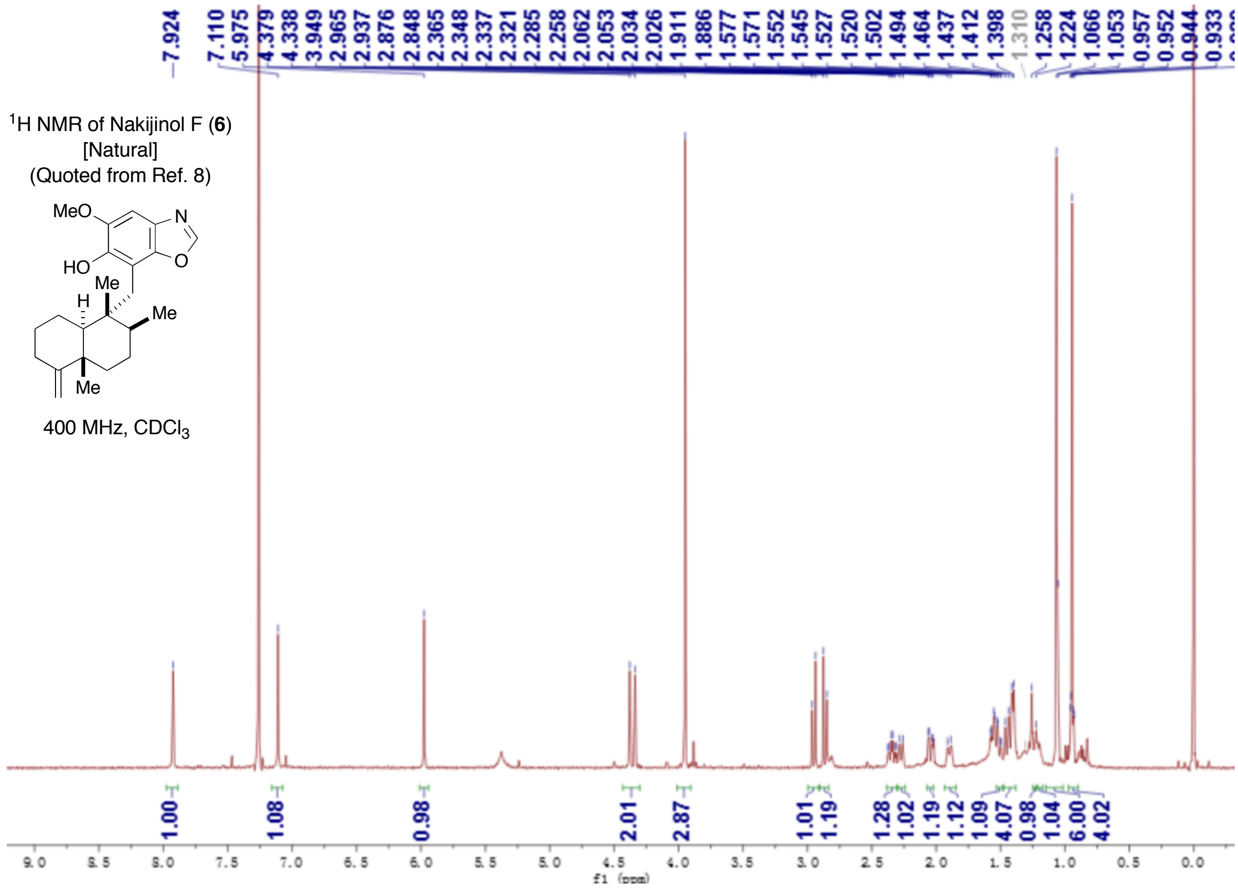

13C NMR of Nakijinol A (1)
[Synthetic]
HO
HO
N
O
Me
H
Me
Me
Me
150 MHz, CD3OD
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0


1H NMR of Nakijinol F (6)
[Synthetic]
MeO
N
O
HO
Me
H
Me
Me
400 MHz, CDCl3
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

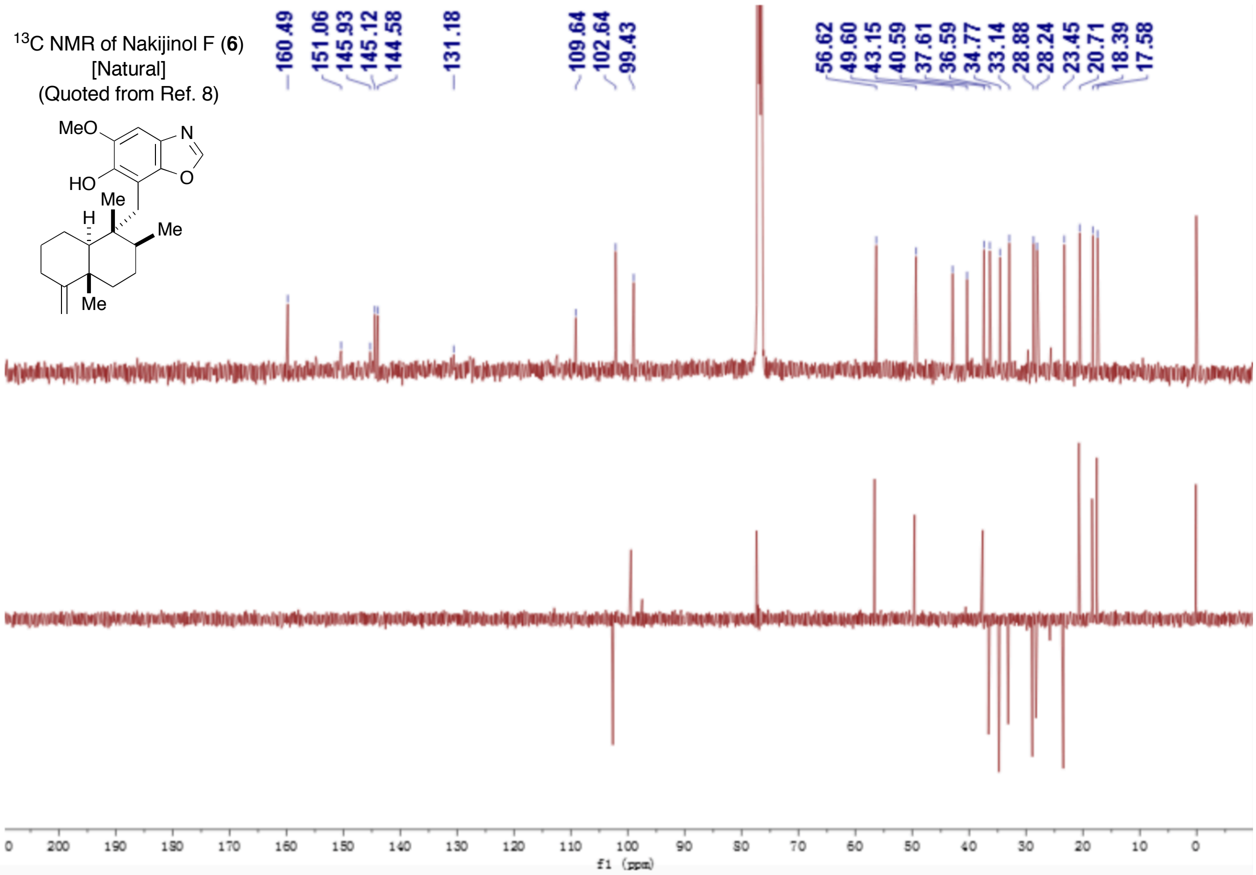

13C NMR of Nakijinol F (6)
[Synthetic]
MeO
N
O
HO
Me
H
Me
Me
100 MHz, CDCl3
PPM
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0

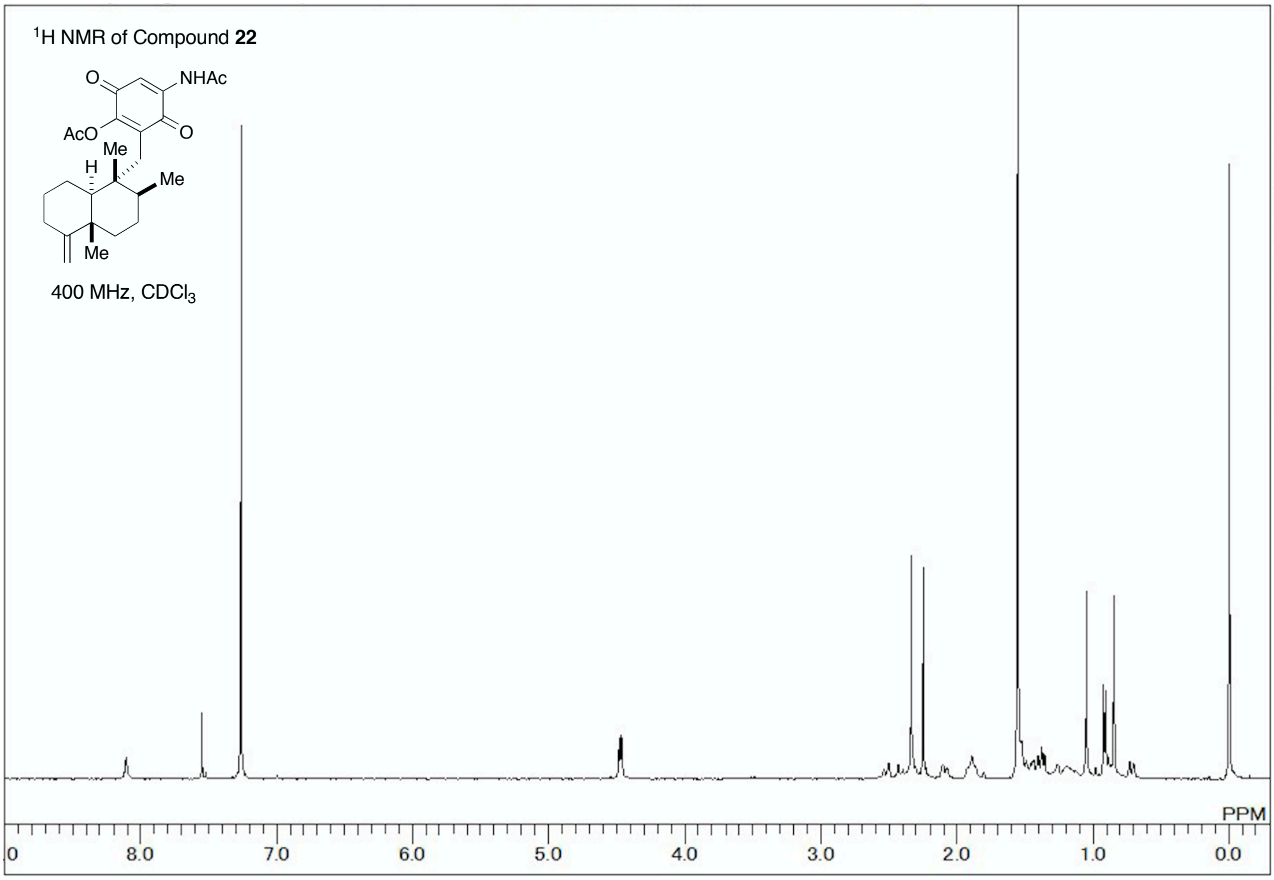
^{1}H NMR of Nakijinol F (**6**)
[Natural]
(Quoted from Ref. 8)

400 MHz, $CDCl_3$

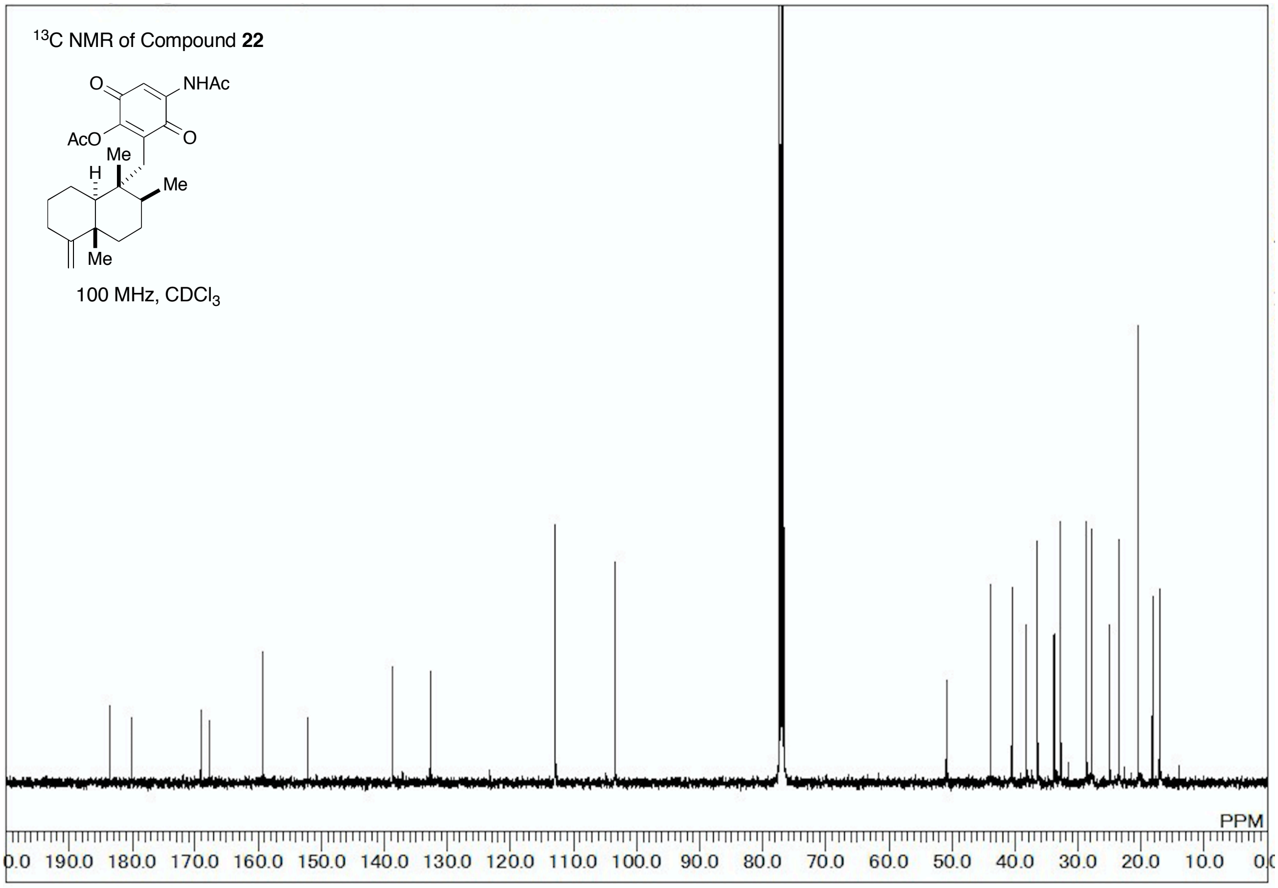


^{13}C NMR of Nakijinol F (**6**)
[Natural]
(Quoted from Ref. 8)

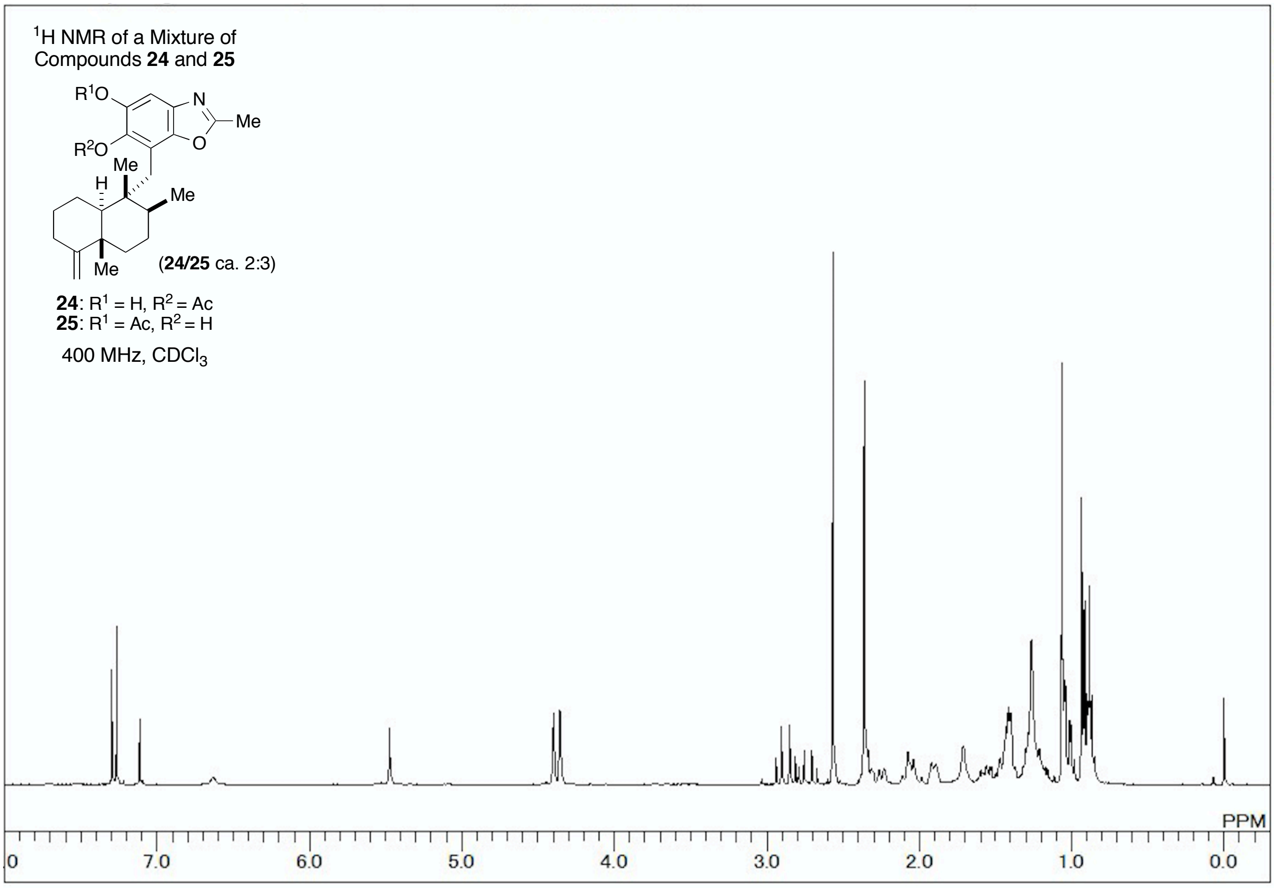


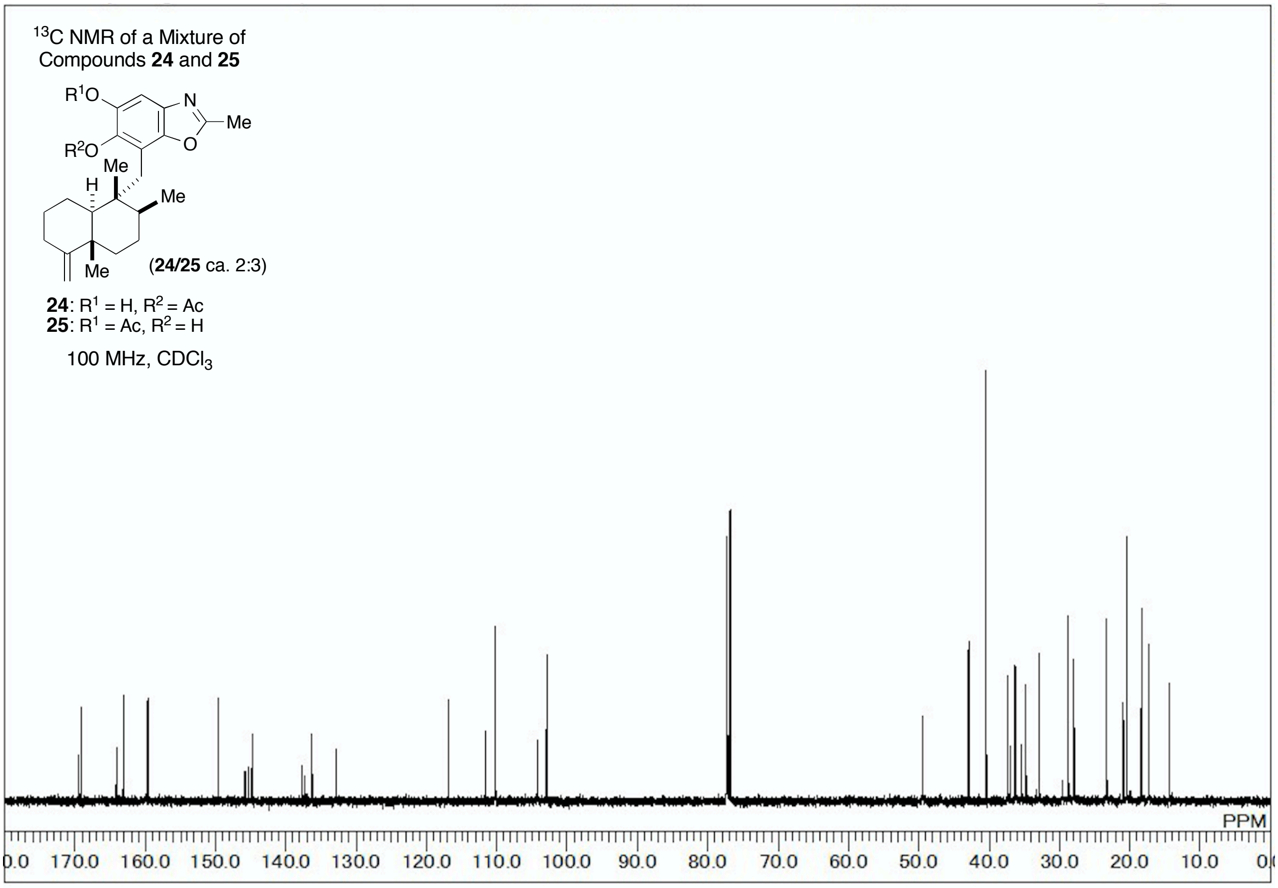


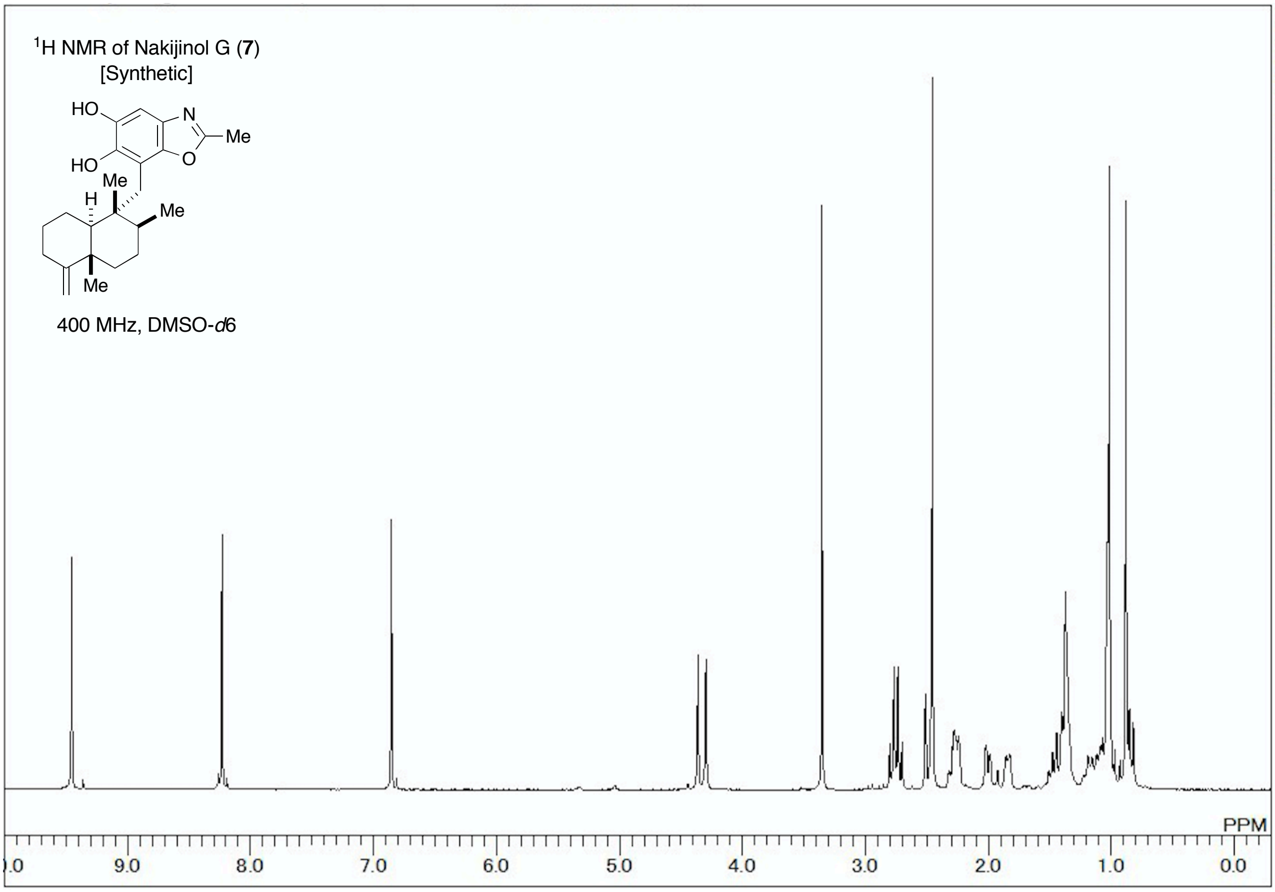
1H NMR of Compound 22
O
NHAc
AcO
O
Me
H
Me
Me
400 MHz, CDCl3
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



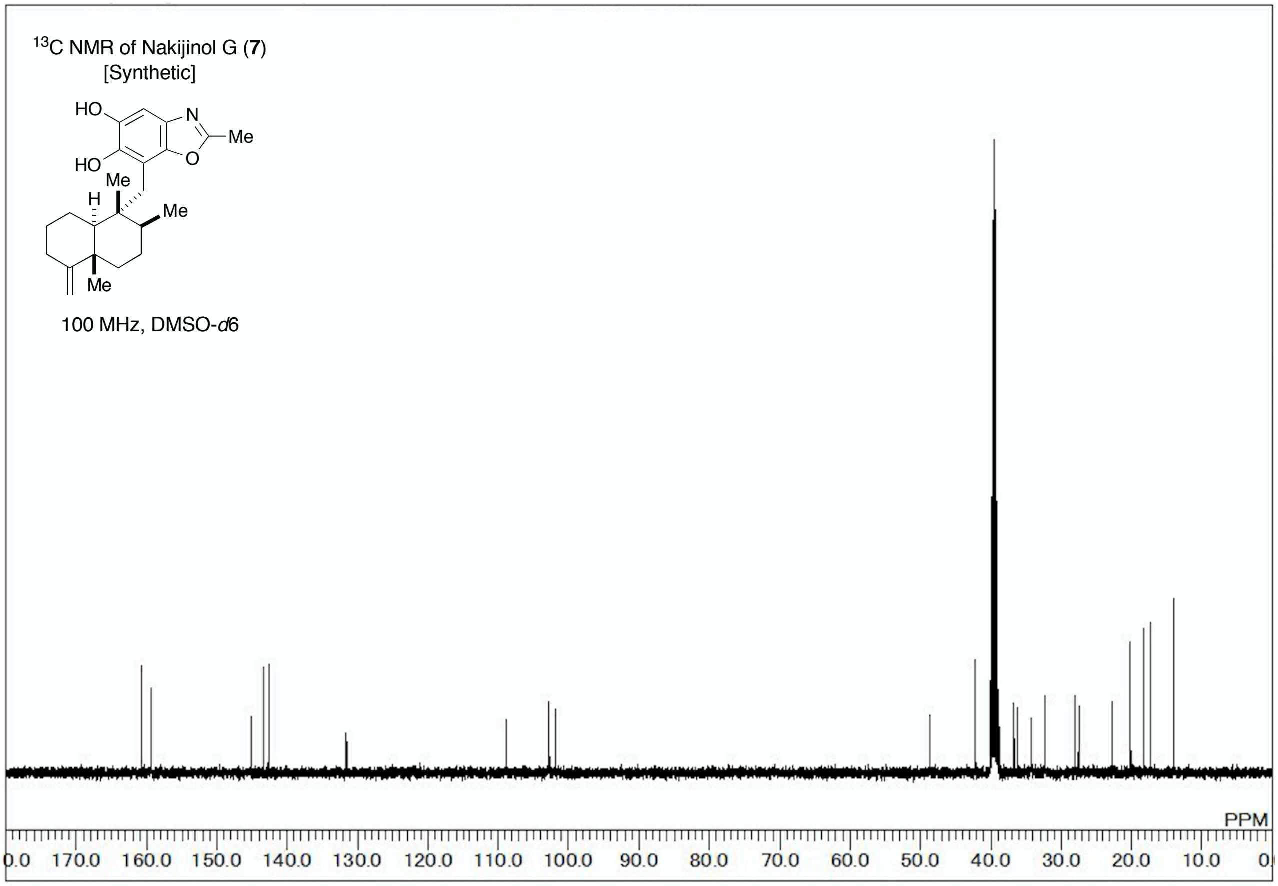
13C NMR of Compound 22
O
NHAc
AcO
O
Me
H
Me
Me
100 MHz, CDCl3
PPM
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0


1H NMR of a Mixture of
Compounds 24 and 25
R1O
R2O
N
O
Me
H
(24/25 ca. 2:3)
24: R1 = H, R2 = Ac
25: R1 = Ac, R2 = H
400 MHz, CDCl3
PPM
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

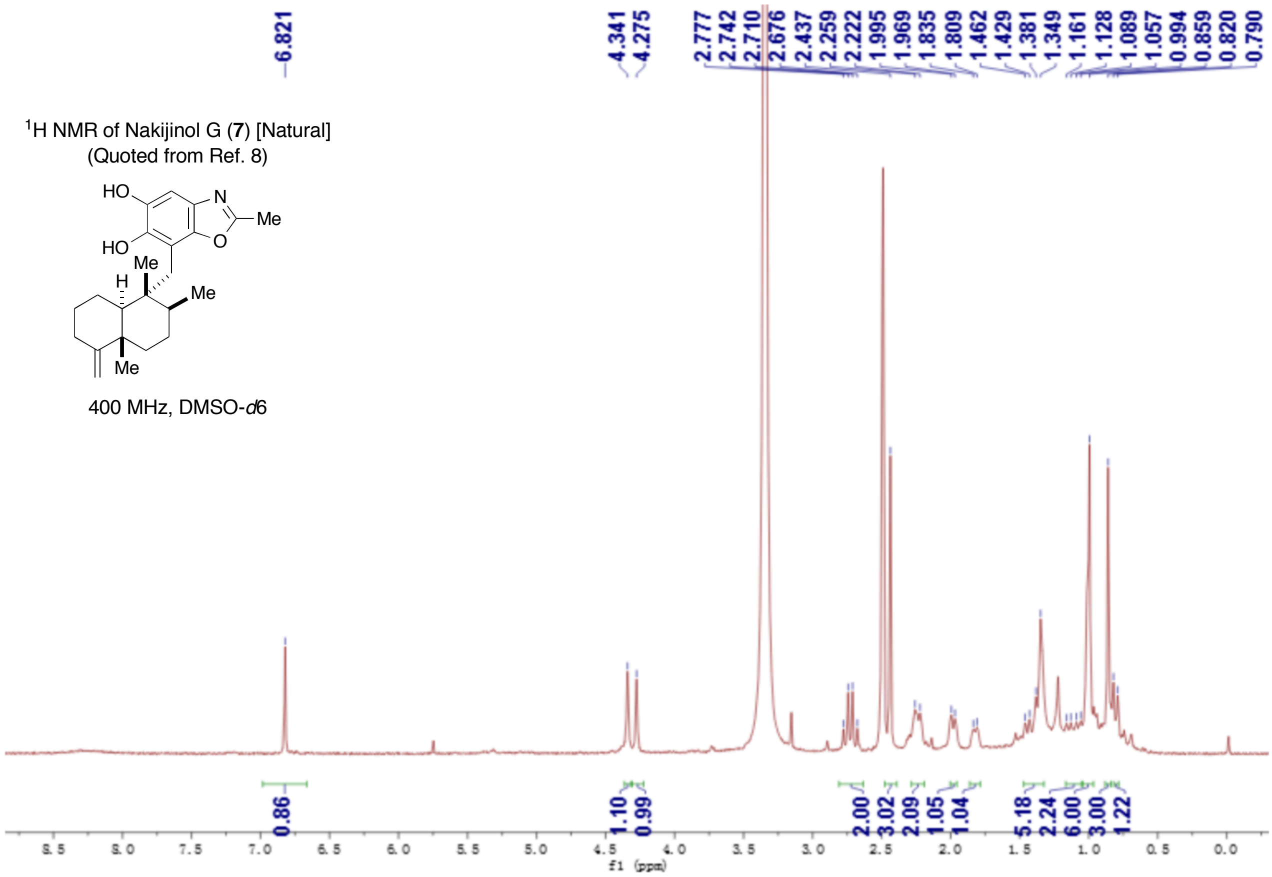

13C NMR of a Mixture of
Compounds 24 and 25
R1O
R2O
N
O
Me
H
(24/25 ca. 2:3)
24: R1 = H, R2 = Ac
25: R1 = Ac, R2 = H
100 MHz, CDCl3
PPM
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0



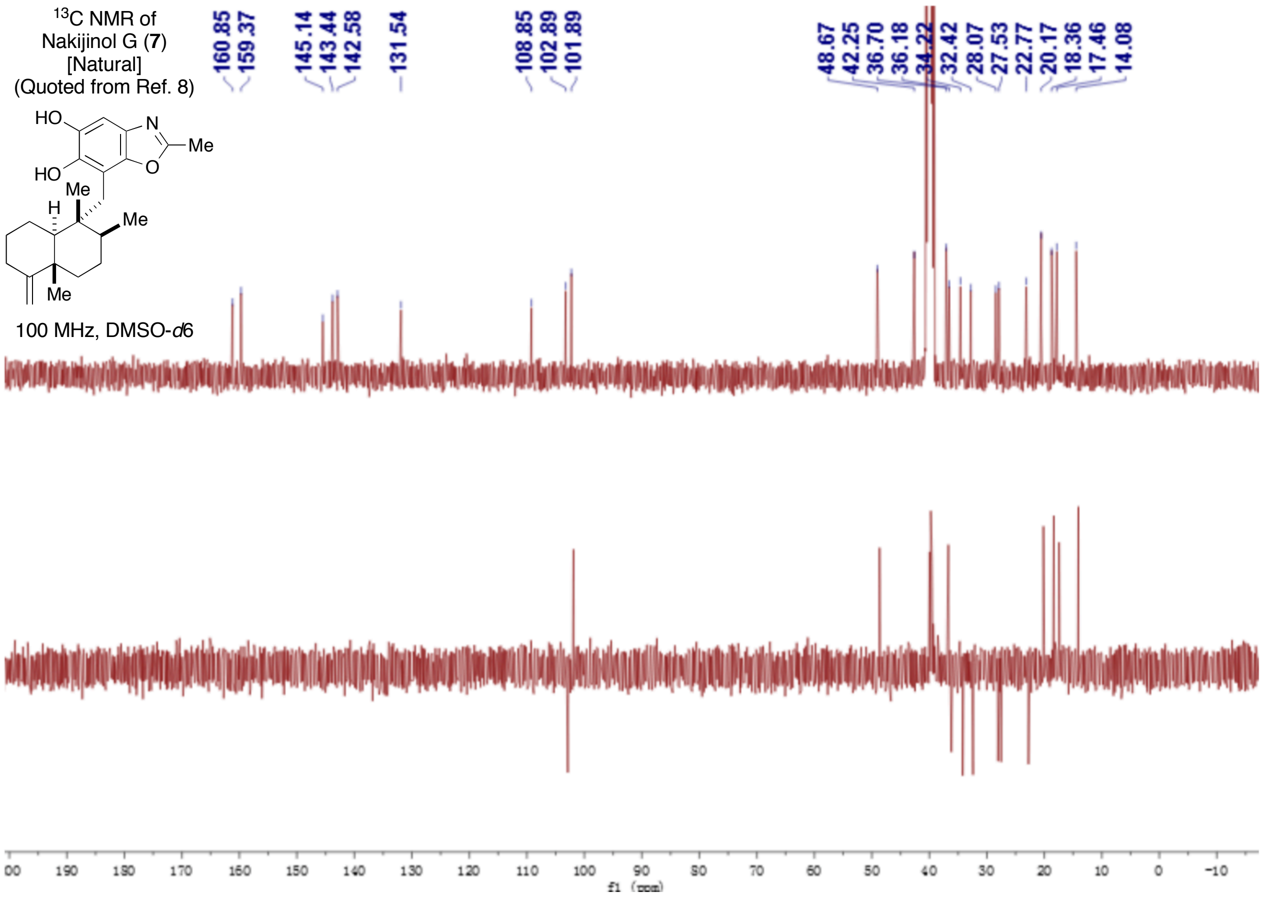
1H NMR of Nakijinol G (7)
[Synthetic]
HO
N
Me
HO
O
Me
H
Me
Me
400 MHz, DMSO-d6
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



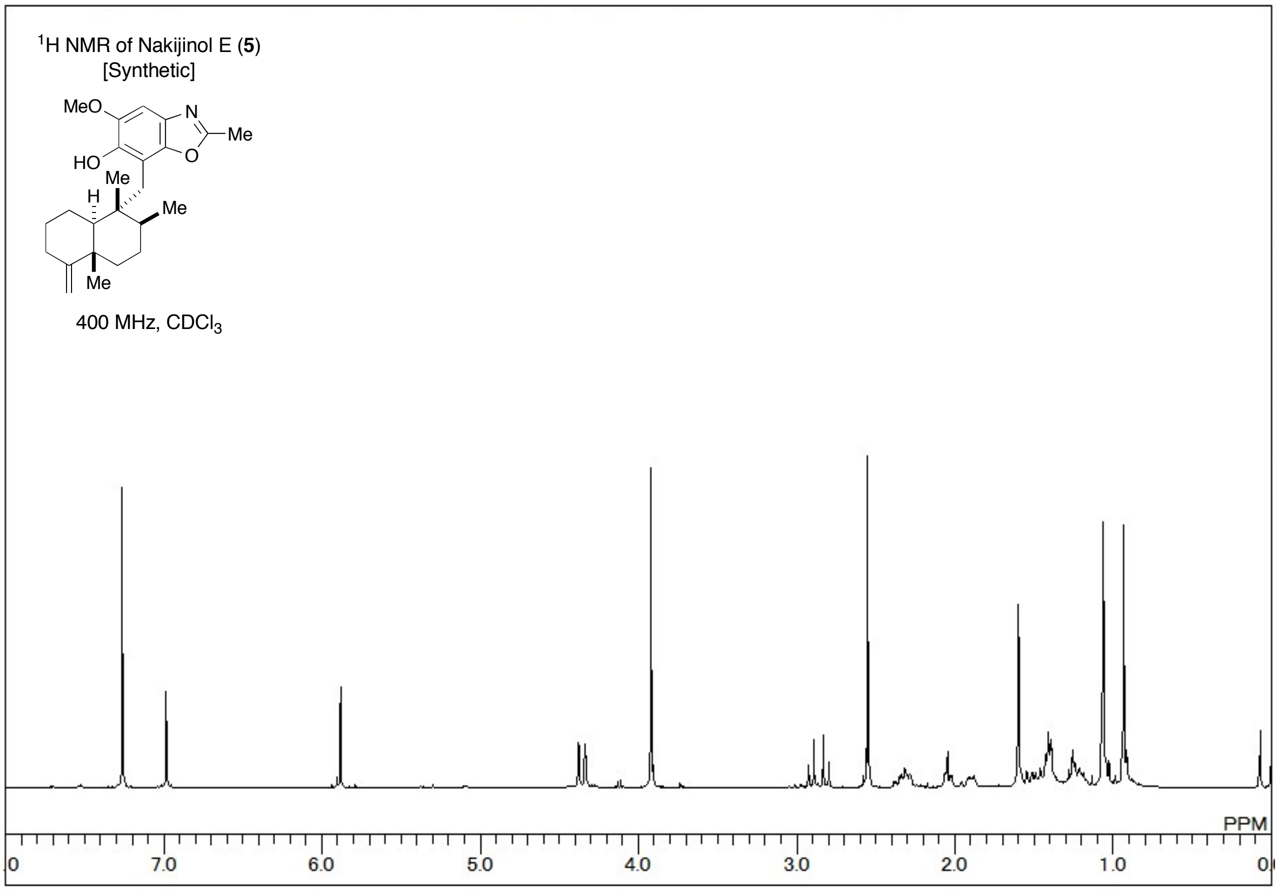
13C NMR of Nakijinol G (7)
[Synthetic]
HO
N
Me
HO
O
Me
H
Me
Me
100 MHz, DMSO-d6
PPM
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0



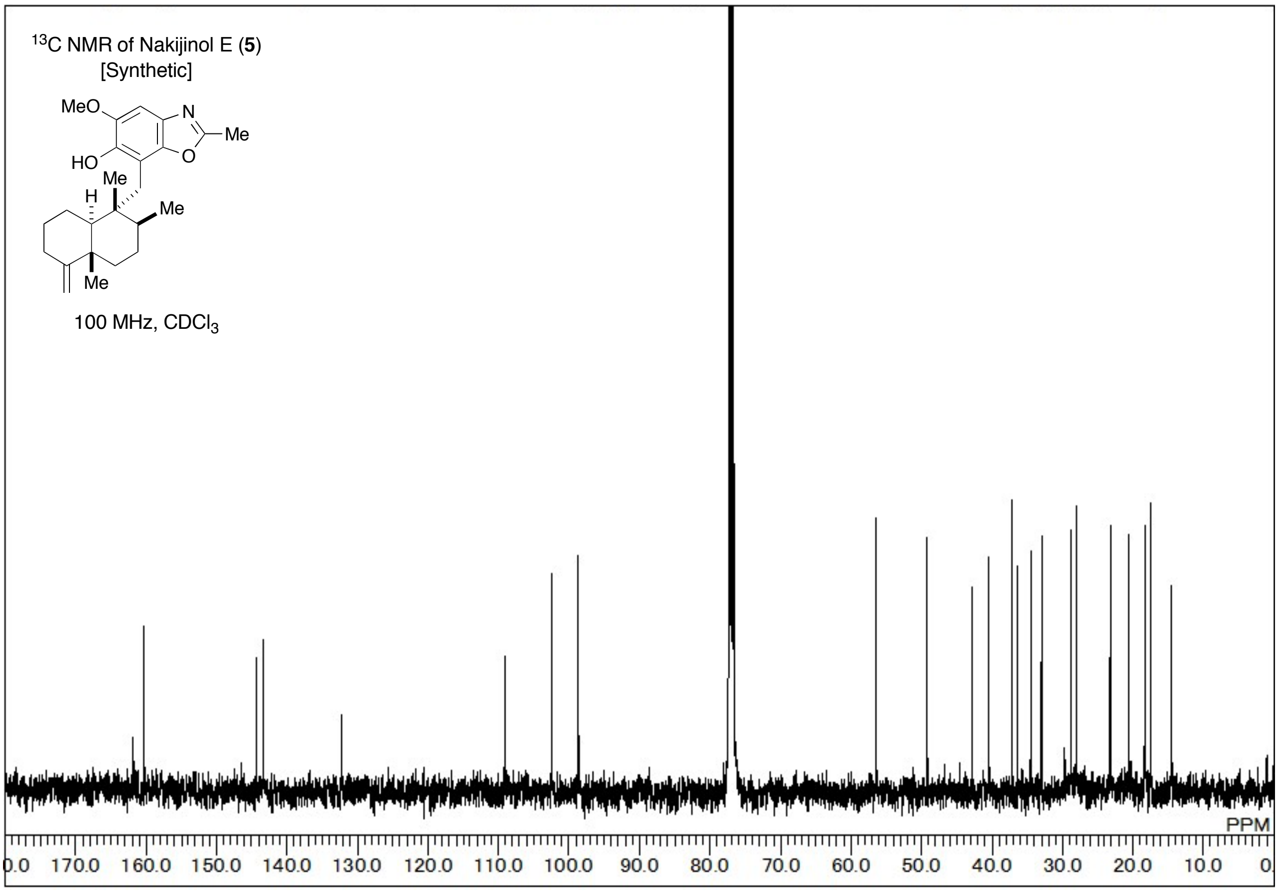
1H NMR of Nakijinol G (7) [Natural]
(Quoted from Ref. 8)
HO
N
Me
HO
O
Me
H
Me
Me
400 MHz, DMSO-d6
6.821
4.341
4.275
2.777
2.742
2.710
2.676
2.437
2.259
2.222
1.995
1.969
1.835
1.809
1.462
1.429
1.381
1.349
1.161
1.128
1.089
1.057
0.994
0.859
0.820
0.790
0.86
1.10
0.99
2.00
3.02
2.09
1.05
1.04
5.18
2.24
6.00
3.00
1.22
f1 (ppm)



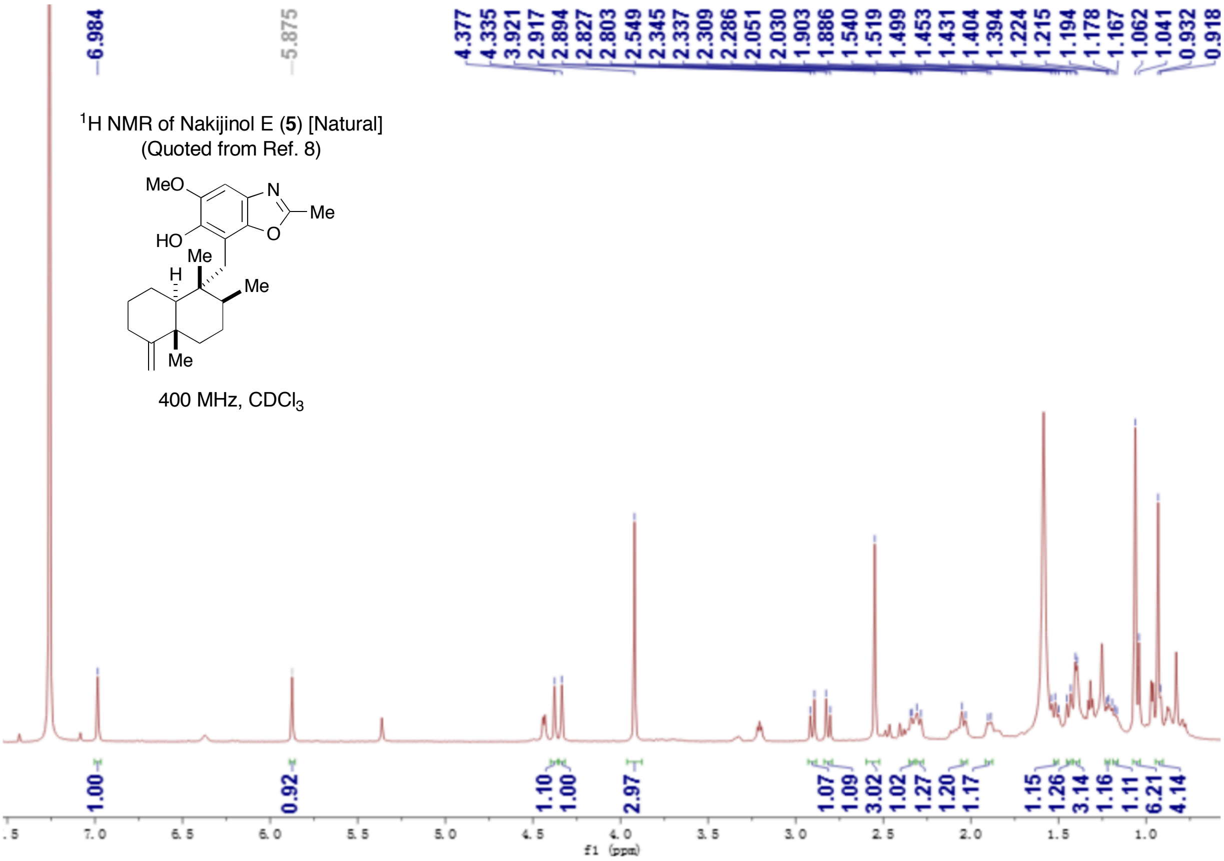
13C NMR of Nakijinol G (7) [Natural]
(Quoted from Ref. 8)
HO
N
Me
HO
O
Me
H
Me
Me
100 MHz, DMSO-d6
160.85
159.37
145.14
143.44
142.58
131.54
108.85
102.89
101.89
48.67
42.25
36.70
36.18
34.22
32.42
28.07
27.53
22.77
20.17
18.36
17.46
14.08
f1 (ppm)

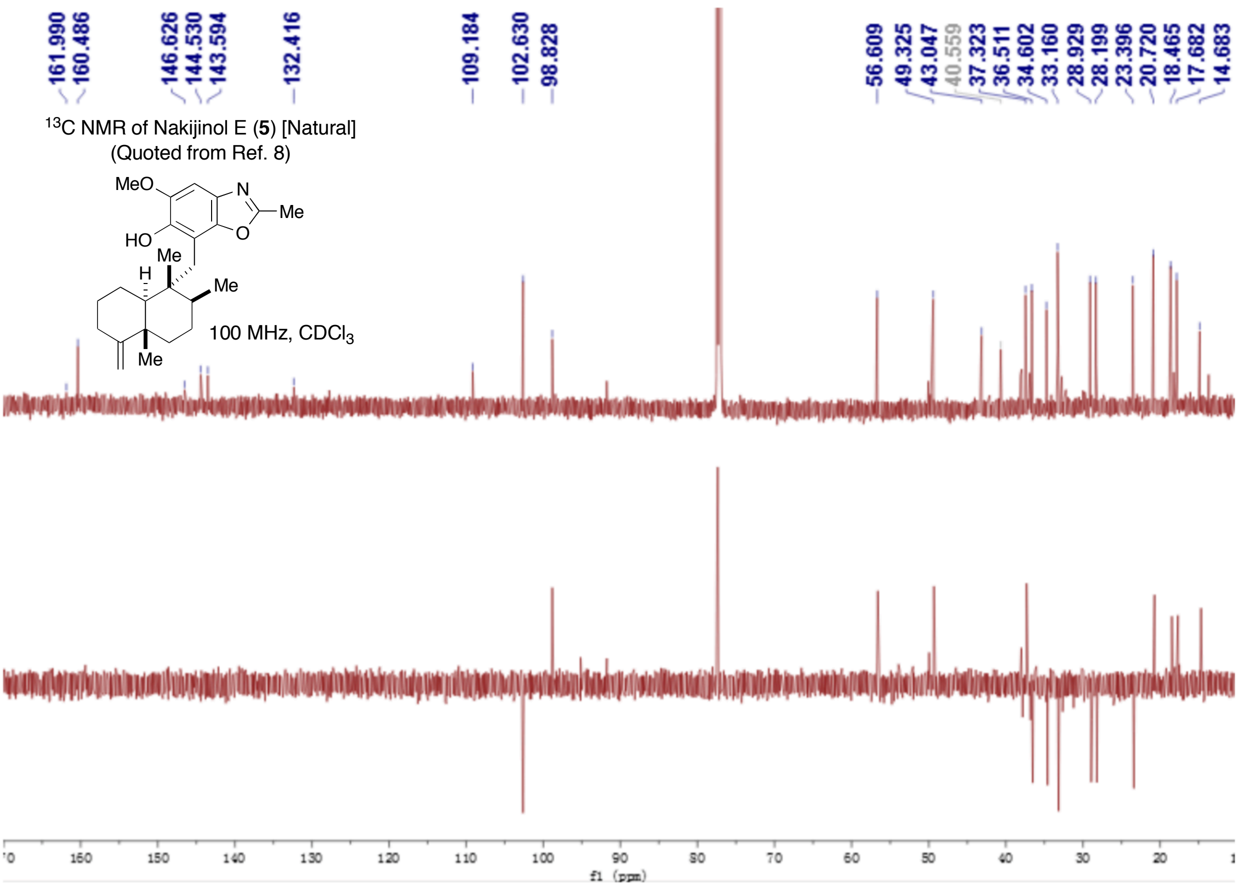


¹H NMR of Nakijinol E (5)
[Synthetic]
MeO
N
Me
HO
O
Me
H
Me
Me
400 MHz, CDCl₃
PPM
7.0
6.0
5.0
4.0
3.0
2.0
1.0



¹³C NMR of Nakijinol E (5)
[Synthetic]
MeO
N
Me
HO
O
Me
H
Me
Me
100 MHz, CDCl₃
PPM
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0


6.984
5.875
4.377 4.335 3.921 2.917 2.894 2.827 2.803 2.549 2.345 2.337 2.309 2.286 2.051 2.030 1.903 1.886 1.540 1.519 1.499 1.453 1.431 1.404 1.394 1.224 1.215 1.194 1.178 1.167 1.062 1.041 0.932 0.918
1H NMR of Nakijinol E (5) [Natural]
(Quoted from Ref. 8)
MeO
N
Me
HO
O
Me
H
Me
Me
400 MHz, CDCl3
1.00 0.92 1.10 1.00 2.97 1.07 1.09 3.02 1.02 1.27 1.20 1.17 1.15 1.26 3.14 1.16 1.11 6.21 4.14
f1 (ppm)


161.990 160.486 146.626 144.530 143.594 132.416 109.184 102.630 98.828
56.609 49.325 43.047 40.559 37.323 36.511 34.602 33.160 28.929 28.199 23.396 20.720 18.465 17.682 14.683
13C NMR of Nakijinol E (5) [Natural]
(Quoted from Ref. 8)
MeO
N
Me
HO
O
Me
H
Me
Me
100 MHz, CDCl3
f1 (ppm)

Comparison of ^{1}H and ^{13}C NMR Data for Natural and Synthetic Nakijinol B (**2**) in CD_3OD

	^{1}H NMR (Hz)		^{13}C NMR (Hz)	
position	Natural (300 MHz)[3]	Synthetic (400 MHz)	Natural (75 MHz)[3]	Synthetic (100 MHz)
1	1.55 (m, 1H) 2.37 (m, 1H)	1.55 (m, 1H) 2.35–2.39 (m, 1H)	24.8 (t)	24.4 (t)
2	1.28 (m, 1H) 1.87 (m, 1H)	1.28 (m, 1H) 1.86–1.91 (m, 1H)	30.2 (t)	29.9 (t)
3	2.03 (m, 1H) 2.32 (m, 1H)	2.01–2.05 (m, 1H) 2.31–2.35 (m, 1H)	34.4 (t)	34.0 (t)
4	———	———	161.8 (s)	161.4 (s)
5	———	———	41.8 (s)	41.6 (s)
6	1.45 (m, 2H)	1.45–1.47 (m, 2H)	38.3 (t)	37.8 (t)
7	1.41 (m, 2H)	1.38–1.43 (m, 2H)	29.5 (t)	29.2 (t)
8	1.41 (m, 1H)	1.38–1.43 (m, 1H)	38.7 (d)	38.7 (d)
9	———	———	44.2 (s)	44.0 (s)
10	0.94 (m, 1H)	0.93–0.96 (m, 1H)	51.1 (d)	50.8 (d)
11	4.32 (s, 1H) 4.35 (s, 1H)	4.32 (s, 1H) 4.35 (s, 1H)	103.4 (t)	103.1 (t)
12	1.07 (s, 3H)	1.07 (s, 3H)	20.7 (q)	21.0 (q)
13	1.08 (d, J = 6.8 Hz, 3H)	1.08 (d, J = 5.9 Hz, 3H)	19.2 (q)	18.9 (q)
14	0.95 (s, 3H)	0.95 (s, 3H)	18.3 (q)	17.9 (q)
15	2.86 (d, J = 13.9 Hz, 1H) 2.94 (d, J = 13.9 Hz, 1H)	2.86 (d, J = 14.1 Hz, 1H) 2.94 (d, J = 14.1 Hz, 1H)	35.8 (t)	35.5 (t)
16	———	———	111.0 (s)	110.8 (s)
17	———	———	146.7 (s)	146.4 (s)
18	———	———	145.2 (s)	144.6 (s)
19	6.96 (s, 1H)	6.97 (s, 1H)	102.6 (d)	102.2 (d)
20	———	———	131.7 (s)	131.3 (s)
21	———	———	146.7 (s)	146.3 (s)
22	8.20 (s, 1H)	8.20 (s, 1H)	153.2 (d)	152.8 (d)

Comparison of ^{1}H and ^{13}C NMR Data for Natural and Synthetic Nakijinol A (**1**) in $CDCl_3$

	^{1}H NMR (Hz)		^{13}C NMR (Hz)	
position	Natural (400 MHz)[1]	Synthetic (600 MHz)	Natural (100 MHz)[1]	Synthetic (125 MHz)
1	1.45 (m, 1H) 2.19 (m, 1H)	1.45–1.50 (m, 1H) 2.17–2.21 (m, 1H)	19.9 (t)	20.0 (t)
2	2.05 (m, 2H)	1.95–1.99 (m, 1H) 1.99–2.08 (m, 1H)	26.9 (t)	27.0 (t)
3	5.12 (br s, 1H)	5.10 (br s, 1H)	120.8 (d)	120.6 (d)
4	———	———	142.0 (s)	141.0 (s)
5	———	———	37.8 (s)	38.4 (s)
6	0.95 (m, 1H) 1.67 (m, 1H)	0.94–0.96 (m, 1H) 1.56–1.62 (m, 1H)	36.2 (t)	35.7 (t)
7	1.41 (m, 2H)	1.39–1.42 (m, 2H)	28.1 (t)	28.0 (t)
8	1.61 (m, 1H)	1.59–1.63 (m, 1H)	37.2 (d)	37.4 (d)
9	———	———	42.9 (s)	42.8 (s)
10	1.20 (m, 1H)	1.18 (dd, *J* = 12.3, 1.6 Hz, 1H)	47.1 (d)	47.1 (d)
11	1.51 (s, 3H)	1.51 (br s, 3H)	18.2 (q)	18.2 (q)
12	1.08 (s, 3H)	1.05 (s, 3H)	20.2 (q)	20.2 (q)
13	1.11 (d, *J* = 7.0 Hz, 3H)	1.08 (d, *J* = 6.6 Hz, 3H)	18.0 (q)	18.0 (q)
14	0.89 (s, 3H)	0.95 (s, 3H)	17.2 (q)	17.3 (q)
15	3.01 (d, *J* = 13.7 Hz, 1H) 2.89 (d, *J* = 13.7 Hz, 1H)	3.01 (d, *J* = 14.3 Hz, 1H) 2.89 (d, *J* = 14.3 Hz, 1H)	33.4 (t)	34.7 (t)
16	———	———	111.1 (s)	110.4 (s)
17	———	———	143.7 (s)	143.4 (s)
18	———	———	143.9 (s)	144.1 (s)
19	7.15 (s, 1H)	7.14 (s, 1H)	111.2 (d)*	103.4 (d)
20	———	———	141.2 (s)*	131.3 (s)
21	———	———	151.5 (s)*	145.8 (s)
22	8.02 (s, 1H)	7.97 (s, 1H)	153.1 (d)*	151.3 (d)

* We believe that the reported data for the natural product was a misassignment or a typing error.

Comparison of ^1H and ^{13}C NMR Data for Natural and Synthetic Nakijinol F (**6**) in $CDCl_3$

	^1H NMR (Hz)		^{13}C NMR (Hz)	
position	Natural (500 MHz)[8]	Synthetic (400 MHz)	Natural (125 MHz)[8]	Synthetic (100 MHz)
1	1.54 (qd, *J* = 12.5, 3.5 Hz, 1H) 2.27 (br d, *J* = 12.0 Hz, 1H)	1.46–1.58 (m, 1H) 2.26–2.30 (m, 1H)	23.5 (t)	23.3 (t)
2	1.26 (m, 1H) 1.96 (m, 1H)	1.24–1.28 (m, 1H) 1.93–1.99 (m, 1H)	28.9 (t)	28.7 (t)
3	2.04 (dd, *J* = 14.0, 4.5 Hz, 1H) 2.34 (ddd, *J* = 14.0, 5.5 Hz, 1H)	2.03–2.06 (m, 1H) 2.30–2.35 (m, 1H)	33.1 (t)	33.0 (t)
4	———	———	160.5 (s)	160.3 (s)
5	———	———	40.6 (s)	40.4 (s)
6	1.22 (m, 1H) 1.45 (m, 1H)	1.19–1.24 (m, 1H) 1.43–1.47 (m, 1H)	36.6 (t)	36.4 (t)
7	1.41 (m, 2H)	1.37–1.43 (m, 2H)	28.2 (t)	28.1 (t)
8	1.41 (m, 1H)	1.37–1.43 (m, 1H)	37.6 (d)	37.5 (d)
9	———	———	43.2 (s)	43.0 (s)
10	0.94 (dd, *J* = 12.0, 2.0 Hz, 1H)	0.94 (dd, *J* = 11.7, 2.0 Hz, 1H)	49.6 (d)	49.5 (d)
11	4.34 (t, *J* = 1.5 Hz, 1H) 4.38 (t, *J* = 1.5 Hz, 1H)	4.33 (br s, 1H) 4.37 (br s, 1H)	102.6 (t)	102.5 (t)
12	1.07 (s, 3H)	1.06 (s, 3H)	20.7 (q)	20.5 (q)
13	1.06 (d, *J* = 6.5 Hz, 3H)	1.06 (d, *J* = 6.0 Hz, 3H)	18.4 (q)	18.2 (q)
14	0.94 (s, 3H)	0.94 (s, 3H)	17.6 (q)	17.4 (q)
15	2.86 (d, *J* = 14.0 Hz, 1H) 2.95 (d, *J* = 14.0 Hz, 1H)	2.85 (d, *J* = 13.6 Hz, 1H) 2.95 (d, *J* = 13.6 Hz, 1H)	34.8 (t)	34.6 (t)
16	———	———	109.6 (s)	109.5 (s)
17	———	———	144.6 (s)	144.4 (s)
18	———	———	145.1 (s)	145.0 (s)
19	7.11 (s, 1H)	7.11 (s, 1H)	99.4 (d)	99.3 (d)
20	———	———	131.1 (s)	131.1 (s)
21	———	———	145.9 (s)	145.7 (s)
22	7.92 (s, 1H)	7.92 (s, 1H)	151.1 (d)	151.9 (d)
17-OH	5.98 (s, 1H)	5.99 (s, 1H)	———	———
18-OMe	3.95 (s, 3H)	3.95 (s, 3H)	56.6 (q)	56.5 (q)

Comparison of ^{1}H and ^{13}C NMR Data for Natural and Synthetic Nakijinol G (**7**) in DMSO-d_6

	^{1}H NMR (Hz)		^{13}C NMR (Hz)	
position	Natural (400 MHz)[8]	Synthetic (400 MHz)	Natural (100 MHz)[8]	Synthetic (100 MHz)
1	1.42 (m, 1H) 2.22 (m, 1H)	1.40–1.44 (m, 1H) 2.22–2.26 (m, 1H)	22.8 (t)	22.8 (t)
2	1.16 (m, 1H) 1.83 (m, 1H)	1.14–1.17 (m, 1H) 1.79–1.88 (m, 1H)	28.1 (t)	28.1 (t)
3	1.99 (m, 1H) 2.26 (m, 1H)	1.98–2.00 (m, 1H) 2.25–2.28 (m, 1H)	32.4 (t)	32.4 (t)
4	———	———	159.4 (s)	159.3 (s)
5	———	———	39.5 (s)	39.5 (s)
6	1.10 (m, 1H) 1.33 (m, 1H)	1.08–1.12 (m, 1H) 1.30–1.38 (m, 1H)	36.2 (t)	36.2 (t)
7	1.35 (m, 2H)	1.30–1.38 (m, 2H)	27.5 (t)	27.5 (t)
8	1.35 (m, 1H)	1.30–1.38 (m, 1H)	36.7 (d)	36.7 (d)
9	———	———	42.2 (s)	42.2 (s)
10	0.82 (d, J = 11.6 Hz, 1H)	0.82 (d, J = 10.0 Hz, 1H)	48.7 (d)	48.7 (d)
11	4.29 (s, 1H) 4.35 (s, 1H)	4.29 (s, 1H) 4.35 (s, 1H)	102.9 (t)	102.8 (t)
12	1.01 (s, 3H)	1.01 (s, 3H)	20.2 (q)	20.2 (q)
13	1.02 (s, 3H)	1.02 (d, J = 4.9 Hz, 3H)	18.4 (q)	18.3 (q)
14	0.87 (s, 3H)	0.87 (s, 3H)	17.5 (q)	17.4 (q)
15	2.70 (d, J = 14.0 Hz, 1H) 2.77 (d, J = 14.0 Hz, 1H)	2.71 (d, J = 14.4 Hz, 1H) 2.78 (d, J = 14.4 Hz, 1H)	34.2 (t)	34.2 (t)
16	———	———	108.8 (s)	108.8 (s)
17	———	———	145.1 (s)	145.1 (s)
18	———	———	142.6 (s)	142.5 (s)
19	6.83 (s, 1H)	6.83 (s, 1H)	101.9 (d)	101.9 (d)
20	———	———	131.5 (s)	131.5 (s)
21	———	———	143.4 (s)	143.4 (s)
22	———	———	160.8 (s)	160.8 (s)
23	2.45 (s, 3H)	2.45 (s, 3H)	14.1 (q)	14.0 (q)

Comparison of ^{1}H and ^{13}C NMR Data for Natural and Synthetic Nakijinol E (**5**) in $CDCl_3$

	^{1}H NMR (Hz)		^{13}C NMR (Hz)	
position	Natural (400 MHz)[7]	Synthetic (400 MHz)	Natural (100 MHz)[7]	Synthetic (100 MHz)
1	1.51 (m, 1H) 2.27 (m, 1H)	1.50–1.53 (m, 1H) 2.26–2.30 (m, 1H)	23.4 (t)	23.2 (t)
2	1.22 (m, 1H) 1.87 (m, 1H)	1.21–1.24 (m, 1H) 1.86–1.90 (m, 1H)	28.9 (t)	28.7 (t)
3	2.02 (m, 1H) 2.33 (t, *J* = 7.5 Hz, 1H)	2.00–2.03 (m, 1H) 2.28–2.38 (m, 1H)	33.2 (t)	33.0 (t)
4	———	———	160.5 (s)	160.3 (s)
5	———	———	40.6 (s)	40.4 (s)
6	1.19 (m, 1H) 1.43 (m, 1H)	1.15–1.23 (m, 1H) 1.38–1.46 (m, 1H)	36.5 (t)	36.3 (t)
7	1.39 (m, 2H)	1.38–1.46 (m, 2H)	28.2 (t)	28.0 (t)
8	1.40 (m, 1H)	1.38–1.46 (m, 1H)	37.4 (d)	37.1 (d)
9	———	———	43.1 (s)	42.8 (s)
10	0.92 (m, 1H)	0.93 (dd, *J* = 11.9, 2.3 Hz, 1H)	49.4 (d)	49.1 (d)
11	4.32 (br s, 1H) 4.36 (br s, 1H)	4.34 (s, 1H) 4.38 (s, 1H)	102.7 (t)	102.4 (t)
12	1.04 (s, 3H)	1.05 (s, 3H)	20.7 (q)	20.5 (q)
13	1.04 (d, 3H)*	1.07 (d, *J* = 5.9 Hz, 3H)	18.5 (q)	18.3 (q)
14	0.91 (s, 3H)	0.93 (s, 3H)	17.7 (q)	17.5 (q)
15	2.80 (d, *J* = 14.0 Hz, 1H) 2.89 (d, *J* = 14.0 Hz, 1H)	2.82 (d, *J* = 14.2 Hz, 1H) 2.91 (d, *J* = 14.2 Hz, 1H)	34.6 (t)	34.4 (t)
16	———	———	109.2 (s)	109.0 (s)
17	———	———	143.7 (s)	143.4 (s)
18	———	———	144.6 (s)	144.3 (s)
19	6.98 (s, 1H)	6.98 (s, 1H)	98.8 (d)	98.7 (d)
20	———	———	132.3 (s)	132.3 (s)
21	———	———	146.6 (s)	146.3 (s)
22	———	———	162.0 (s)	161.8 (s)
23	2.54 (s, 3H)	2.55 (s, 3H)	14.6 (q)	14.5 (q)
17-OH	5.87 (s, 1H)	5.91 (s, 1H)	———	———
18-OMe	3.90 (s, 3H)	3.92 (s, 3H)	56.6 (q)	56.4 (q)

* The *J* value was not recorded in Ref. 7.