Supporting Information

Advances in Siloxane-Based Coupling Reactions: Application of Palladium-Catalyzed Allyl-Aryl Coupling to the Synthesis of Pancratistatin Derivatives. The Formal Total Synthesis of (±)-7-Deoxypancratistatin

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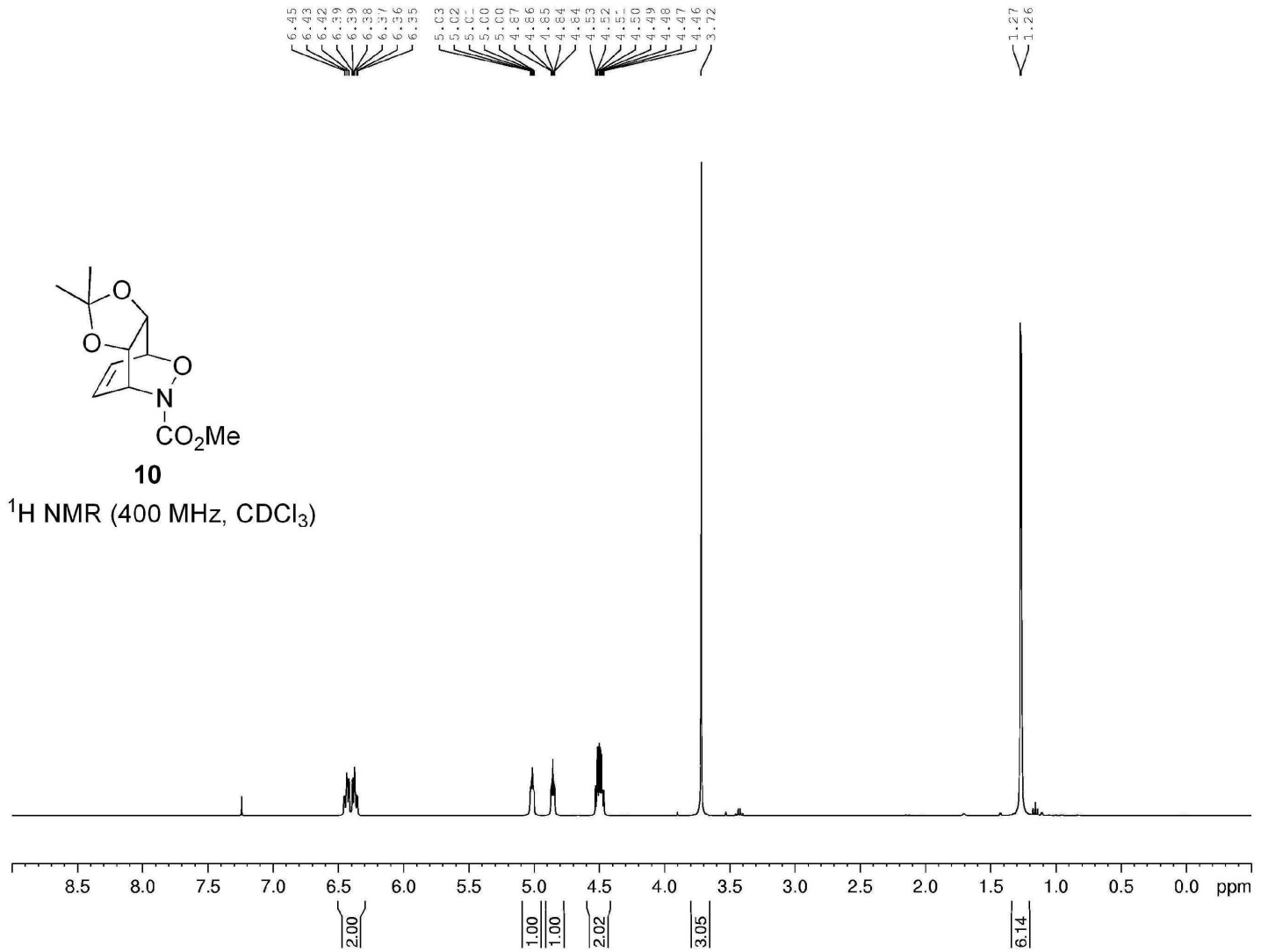
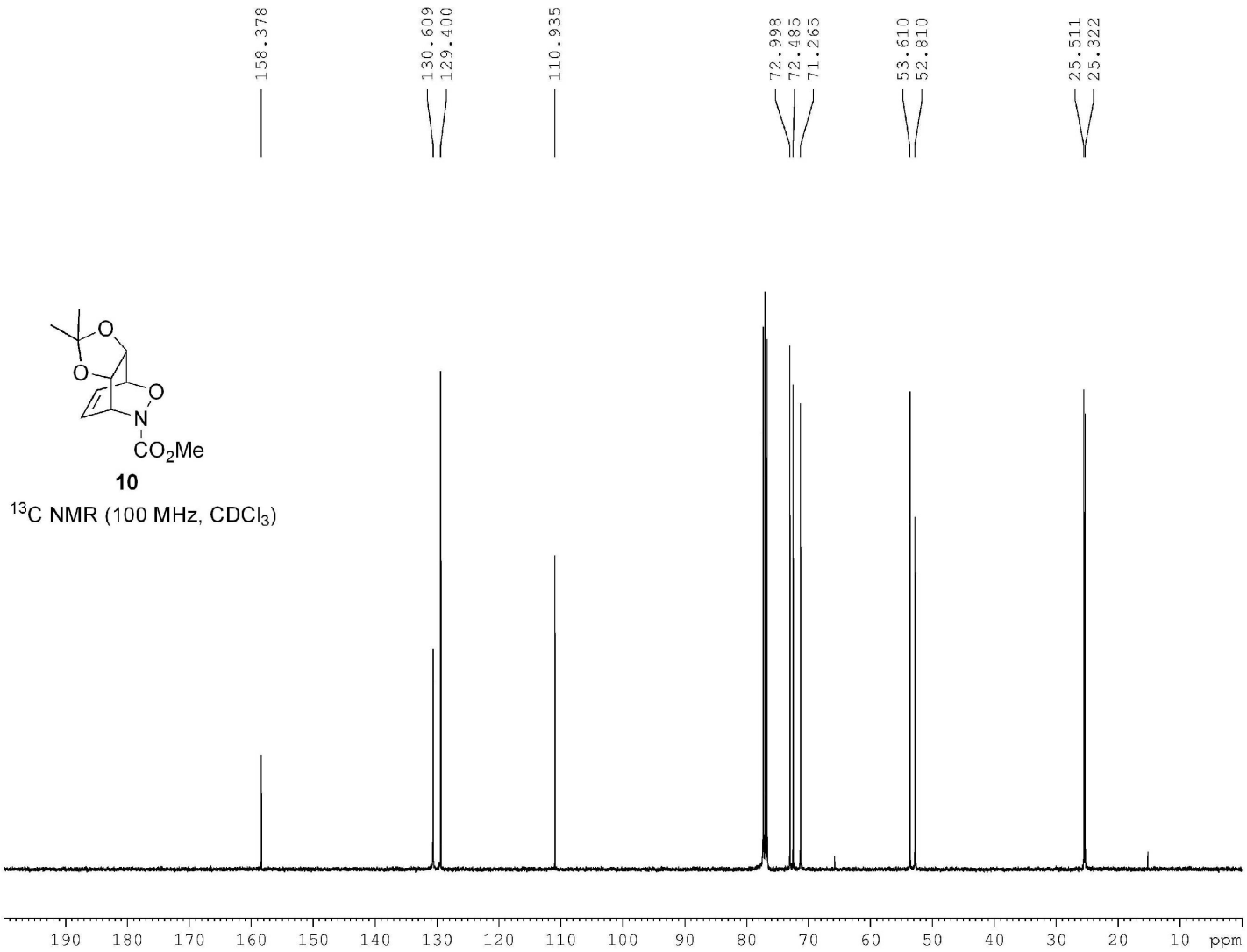
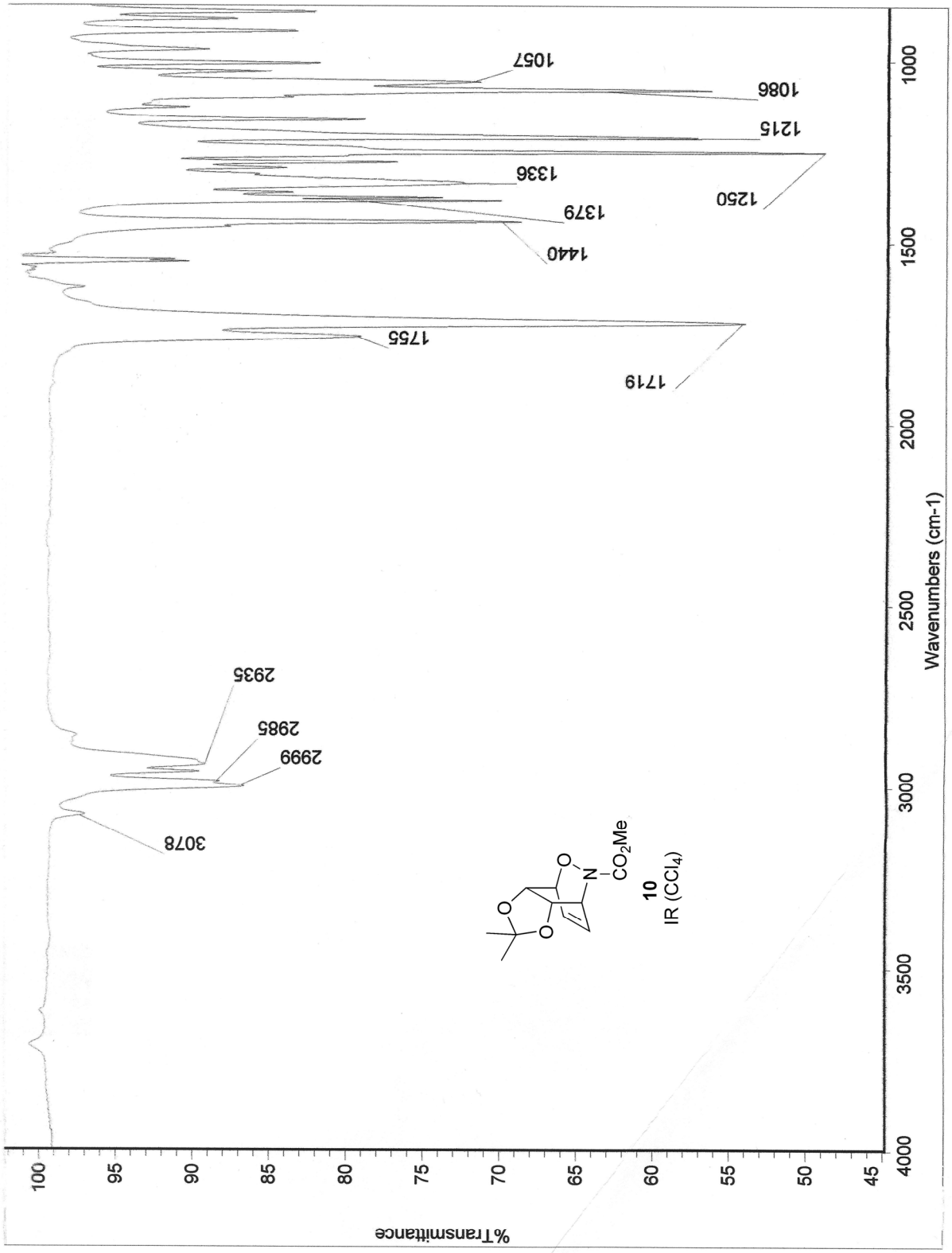
Contents

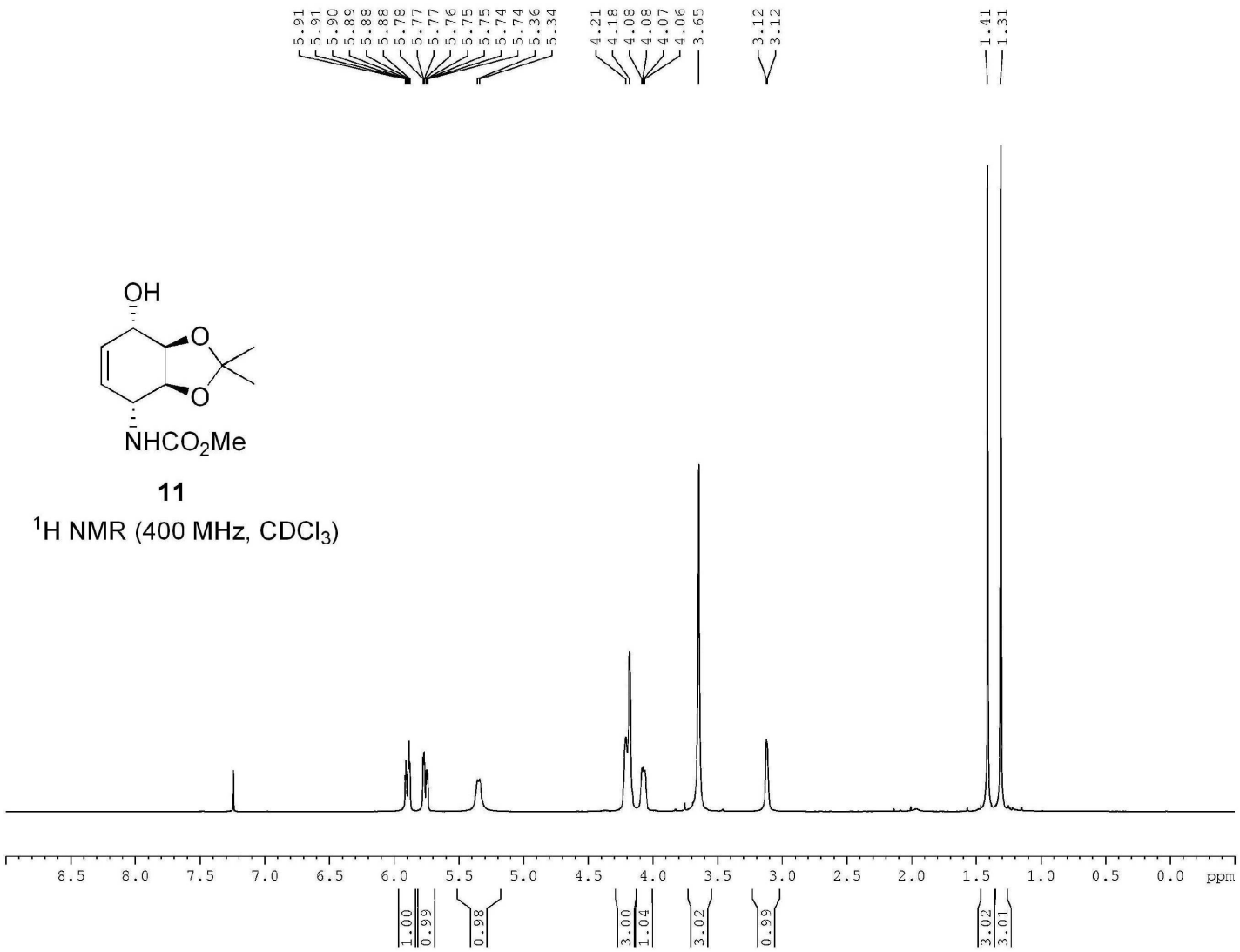


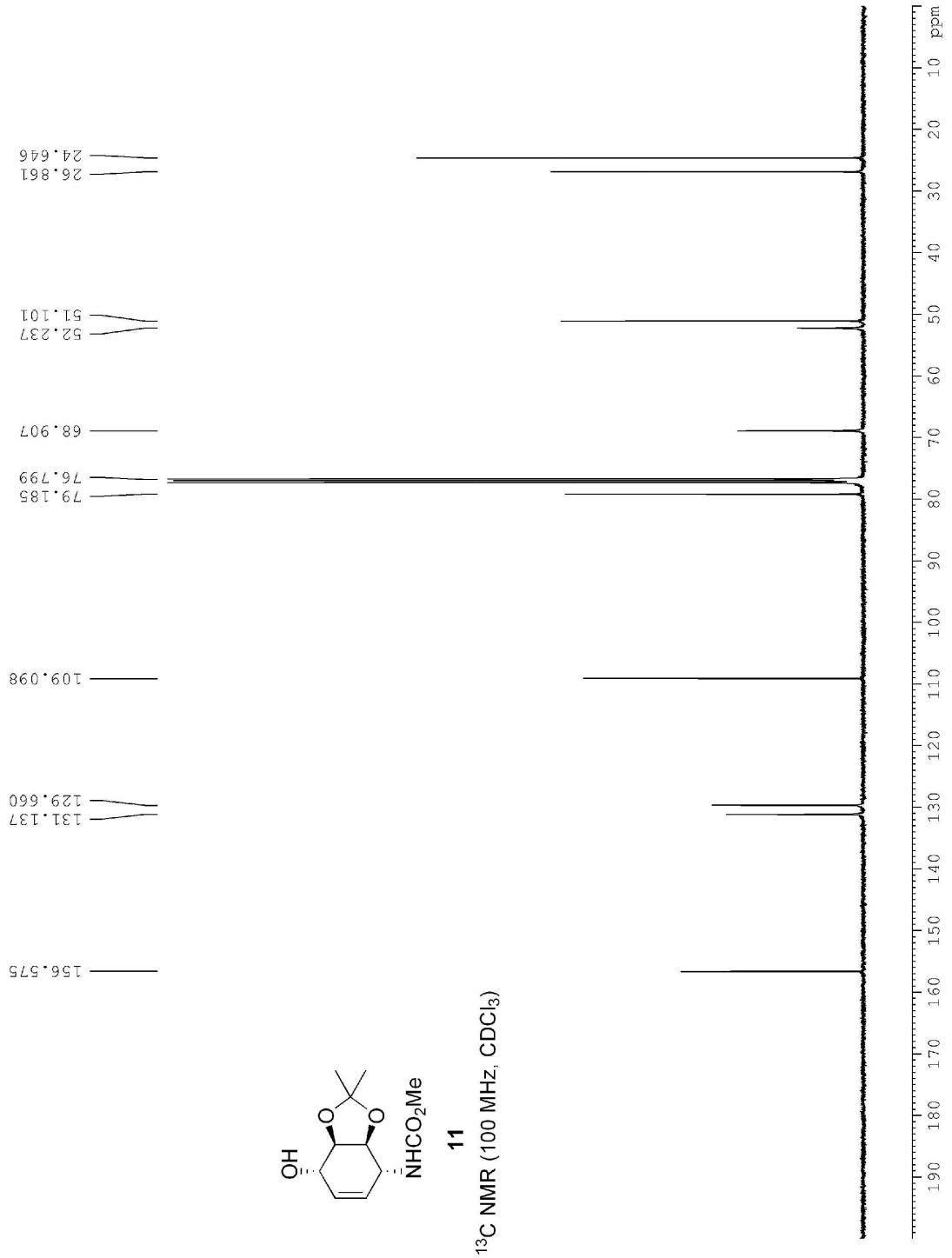
10

^{1}H NMR (400 MHz, $CDCl_3$)


158.378
130.609
129.400
110.935
72.998
72.485
71.265
53.610
52.810
25.511
25.322
O
O
O
N
CO2Me
10
13C NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

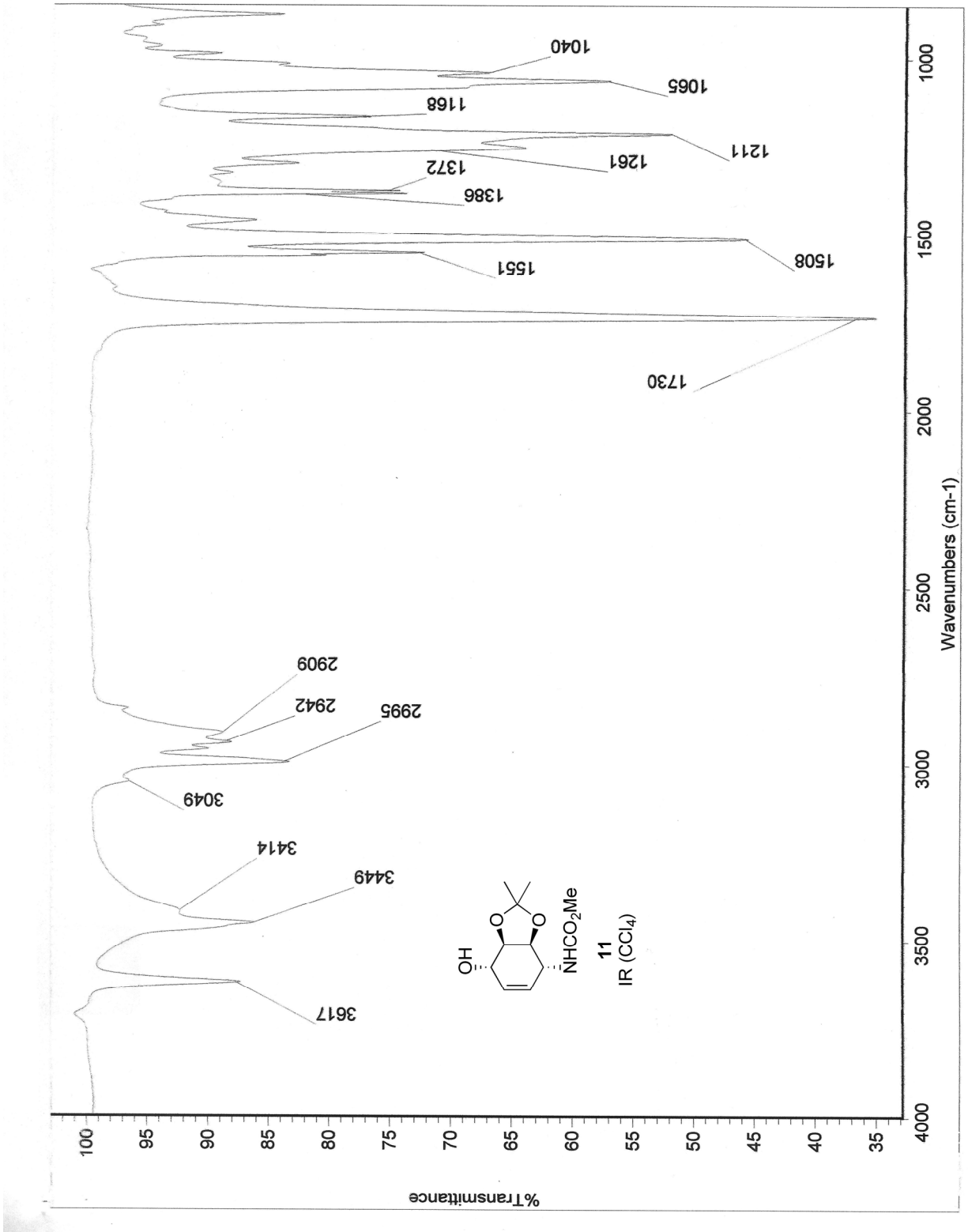

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)
3078
2999
2985
2935
1755
1719
1440
1379
1336
1250
1215
1086
1057
O
O
O
N
CO2Me
10
IR (CCl4)


OH
O
O
NHCO2Me
11
1H NMR (400 MHz, CDCl3)
5.91
5.91
5.90
5.89
5.88
5.88
5.78
5.77
5.77
5.76
5.75
5.75
5.74
5.74
5.36
5.34
4.21
4.18
4.08
4.08
4.07
4.06
3.65
3.12
3.12
1.41
1.31
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
0.98
3.00
1.04
3.02
0.99
3.02
3.01

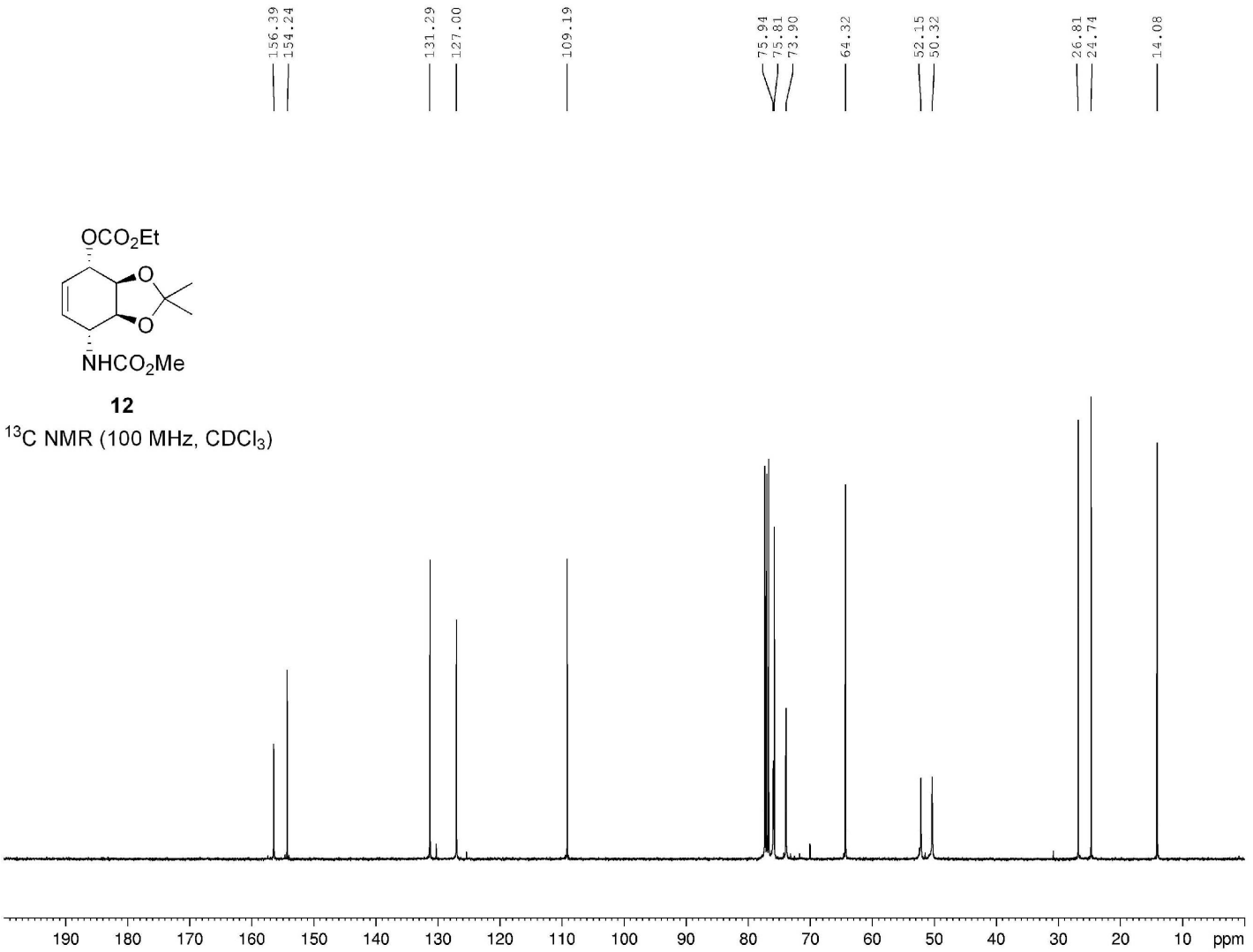


11

^{13}C NMR (100 MHz, $CDCl_3$)

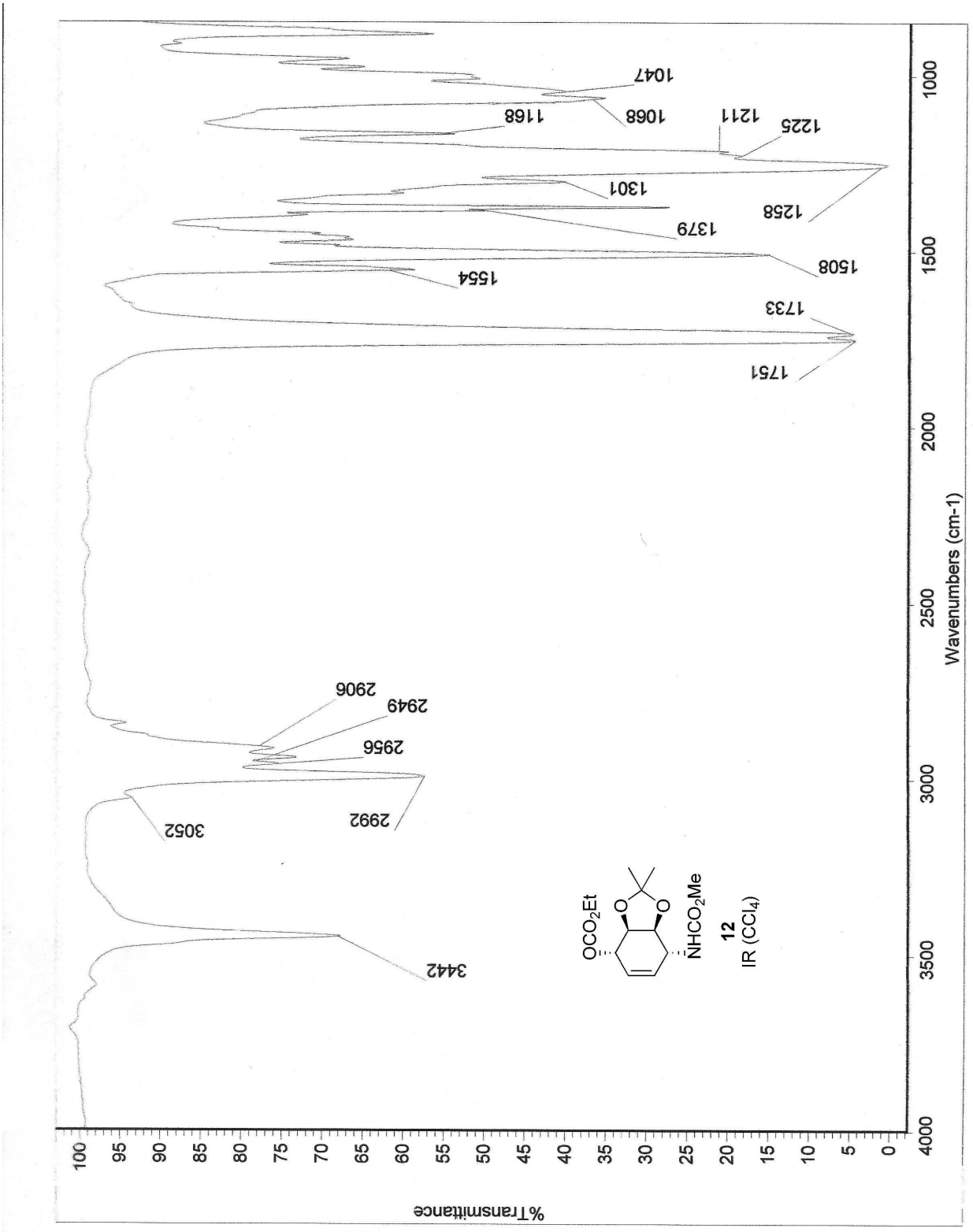

%Transmittance
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
100
95
90
85
80
75
70
65
60
55
50
45
40
35
3617
3449
3414
3049
2995
2942
2909
1730
1551
1508
1386
1372
1261
1211
1168
1065
1040
OH
NHCO2Me
11
IR (CCl4)

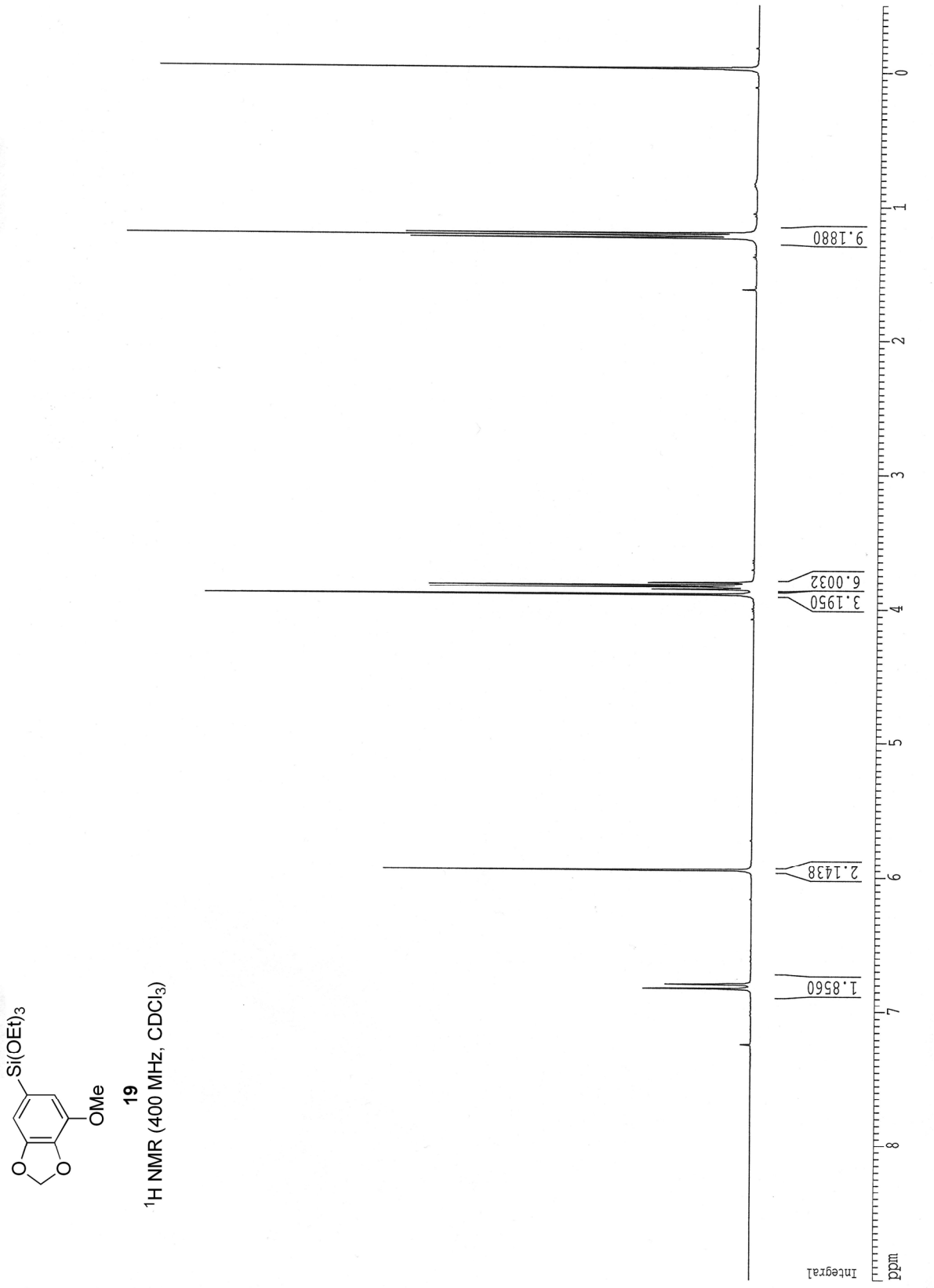
OCO2Et
NHCO2Me
12
1H NMR (400 MHz, CDCl3)
5.859
5.823
5.796
5.214
5.066
4.298
4.284
4.273
4.189
4.172
4.154
4.137
3.624
1.398
1.280
1.257
1.240
ppm
2.000
0.915
1.080
1.089
4.079
3.134
2.980
6.141



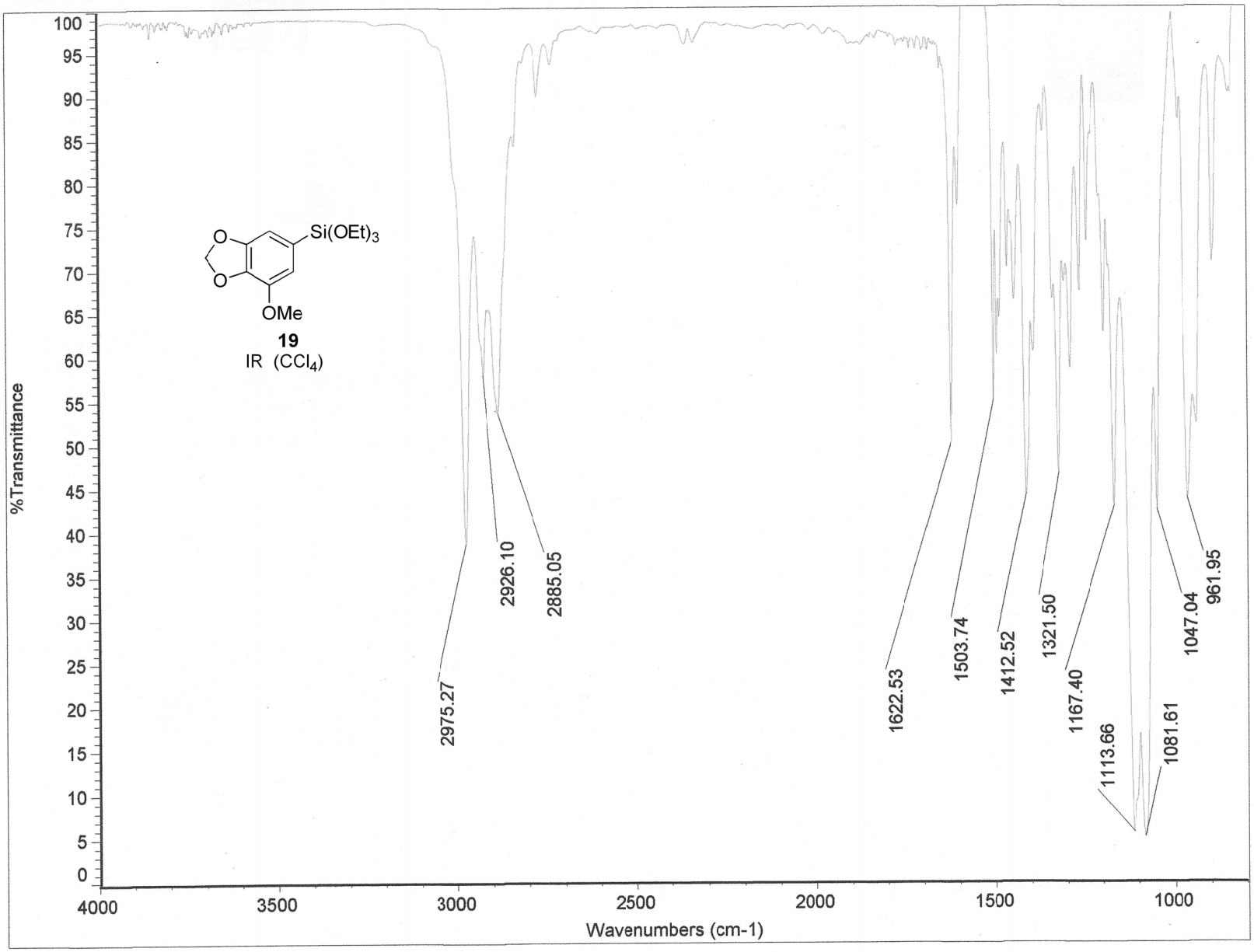
12

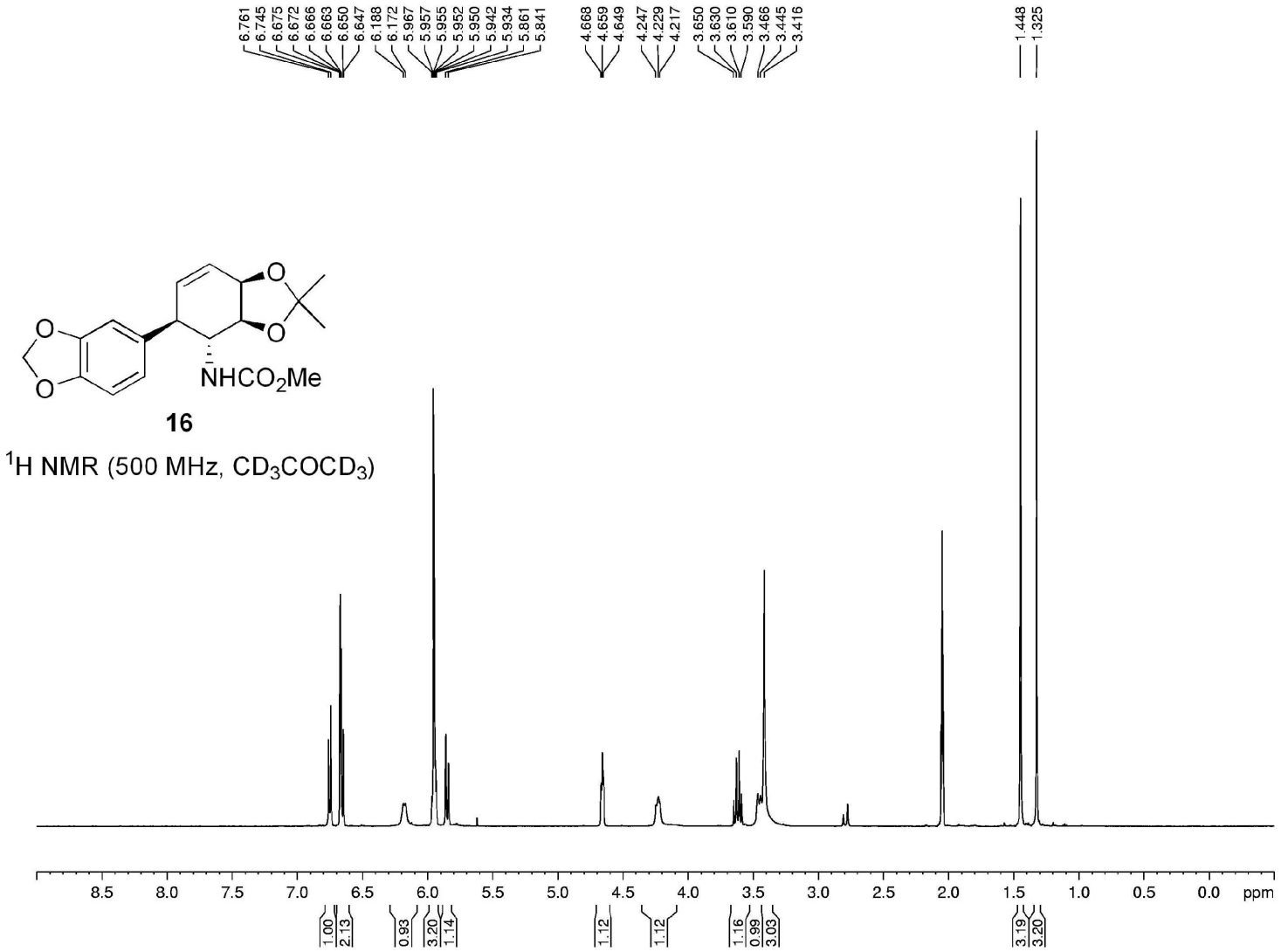
^{13}C NMR (100 MHz, $CDCl_3$)


%Transmittance
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
3442
3052
2992
2956
2949
2906
1751
1733
1554
1508
1379
1301
1258
1225
1211
1168
1068
1047
OCO2Et
NHCO2Me
12
IR (CCl4)


Si(OEt)3
OMe
O
O
19
1H NMR (400 MHz, CDCl3)
Integral
1.8560
2.1438
3.1950
6.0032
9.1880
ppm
0
1
2
3
4
5
6
7
8

-0.1
18.2
56.5
58.7
76.7
77.0
77.3
101.3
108.0
114.1
124.4
137.3
143.9
148.8
ppm
0
20
40
60
80
100
120
140
160
180
ppm
Si(OEt)3
OMe
O
O
O
19
13C NMR (100 MHz, CDCl3)


Si(OEt)3
OMe
19
IR (CCl4)
%Transmittance
Wavenumbers (cm-1)
2975.27
2926.10
2885.05
1622.53
1503.74
1412.52
1321.50
1167.40
1113.66
1081.61
1047.04
961.95

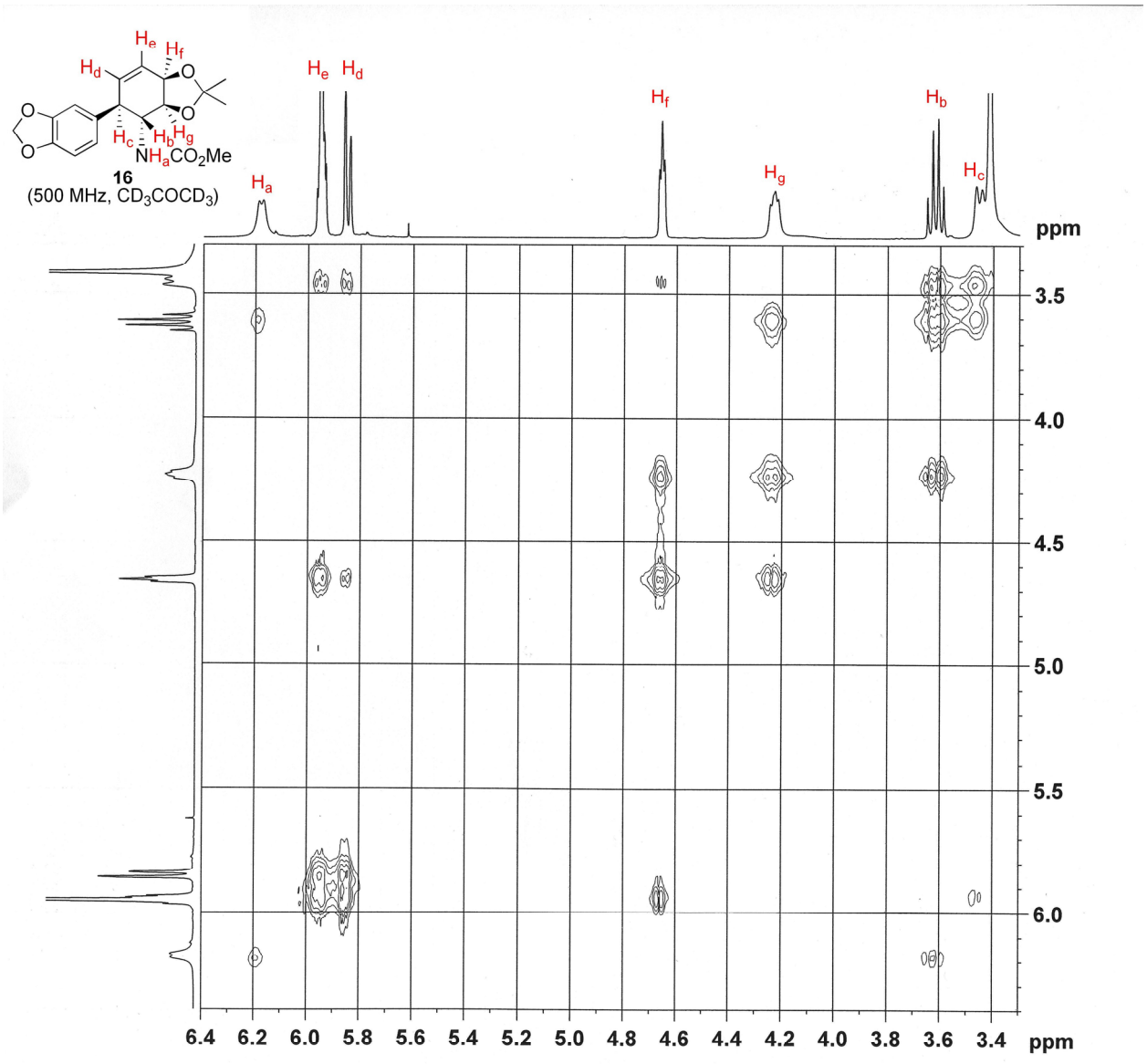


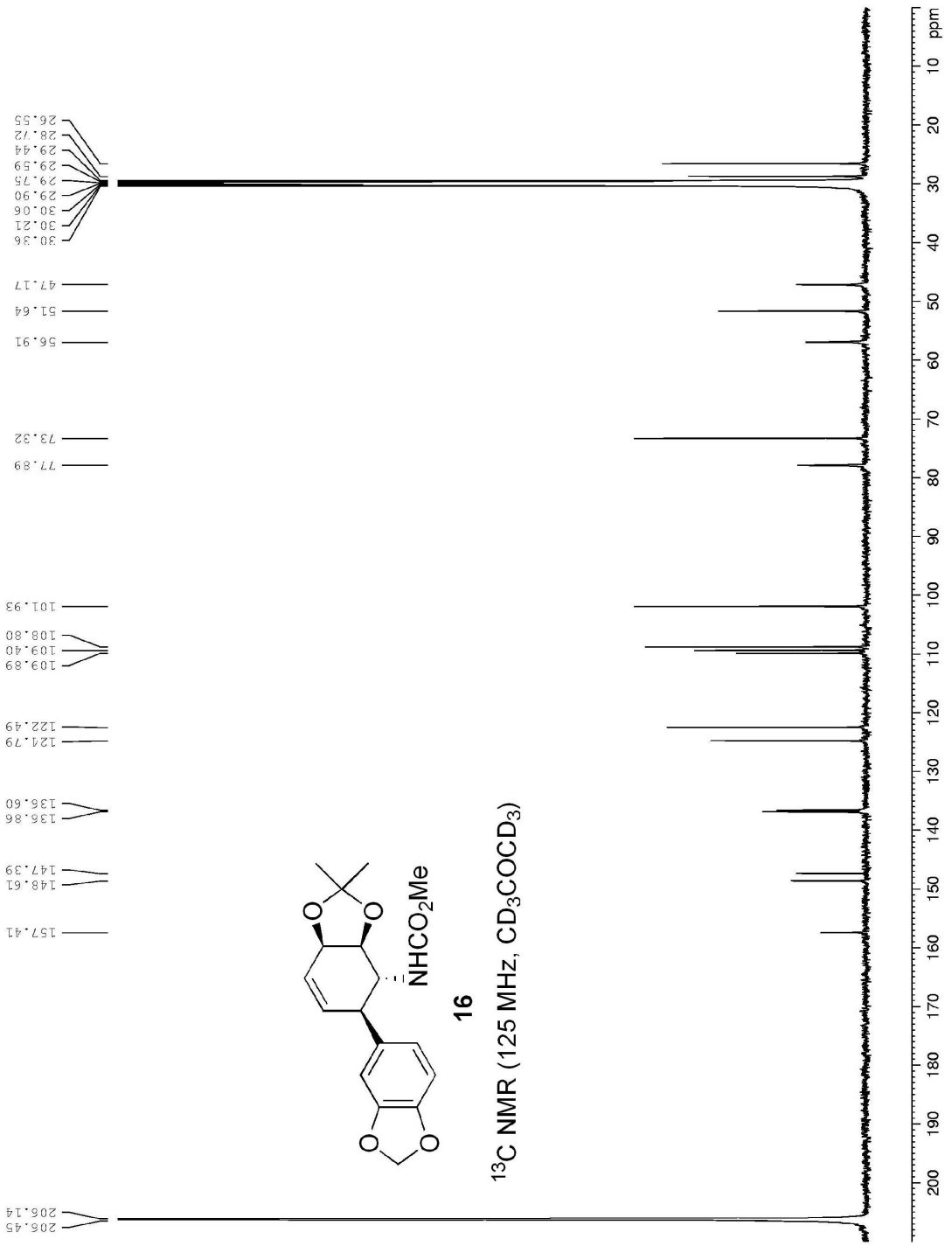
16

^{1}H NMR (500 MHz, CD_3COCD_3)

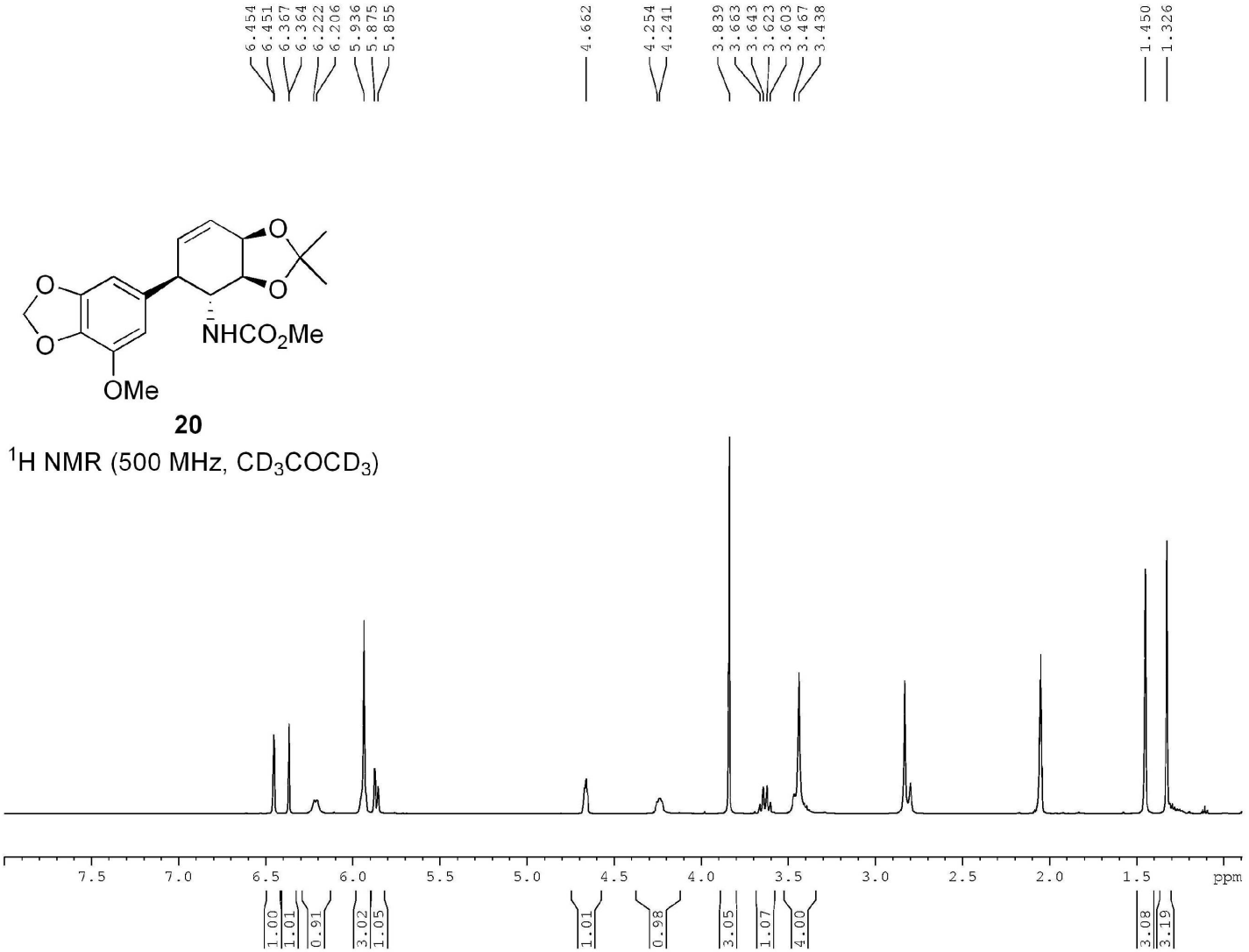
COSY analysis of Hudlicky's intermediate **16**

The regiochemistry of Hudlicky's intermediate **16** was established using ^{1}H-^{1}H COSY analysis. H_a proton (N-H proton identified using HSQC) is coupled only to H_b proton. Since H_b proton is not coupled to the vinyl proton H_d, the regioisomer was determined to be **16**. (If the other regioisomer had formed, H_b would couple to vinyl proton). The regiochemistry of carbamates **20**, **22**, **24** and **26** was confirmed using ^{1}H-^{1}H COSY in a similar manner.



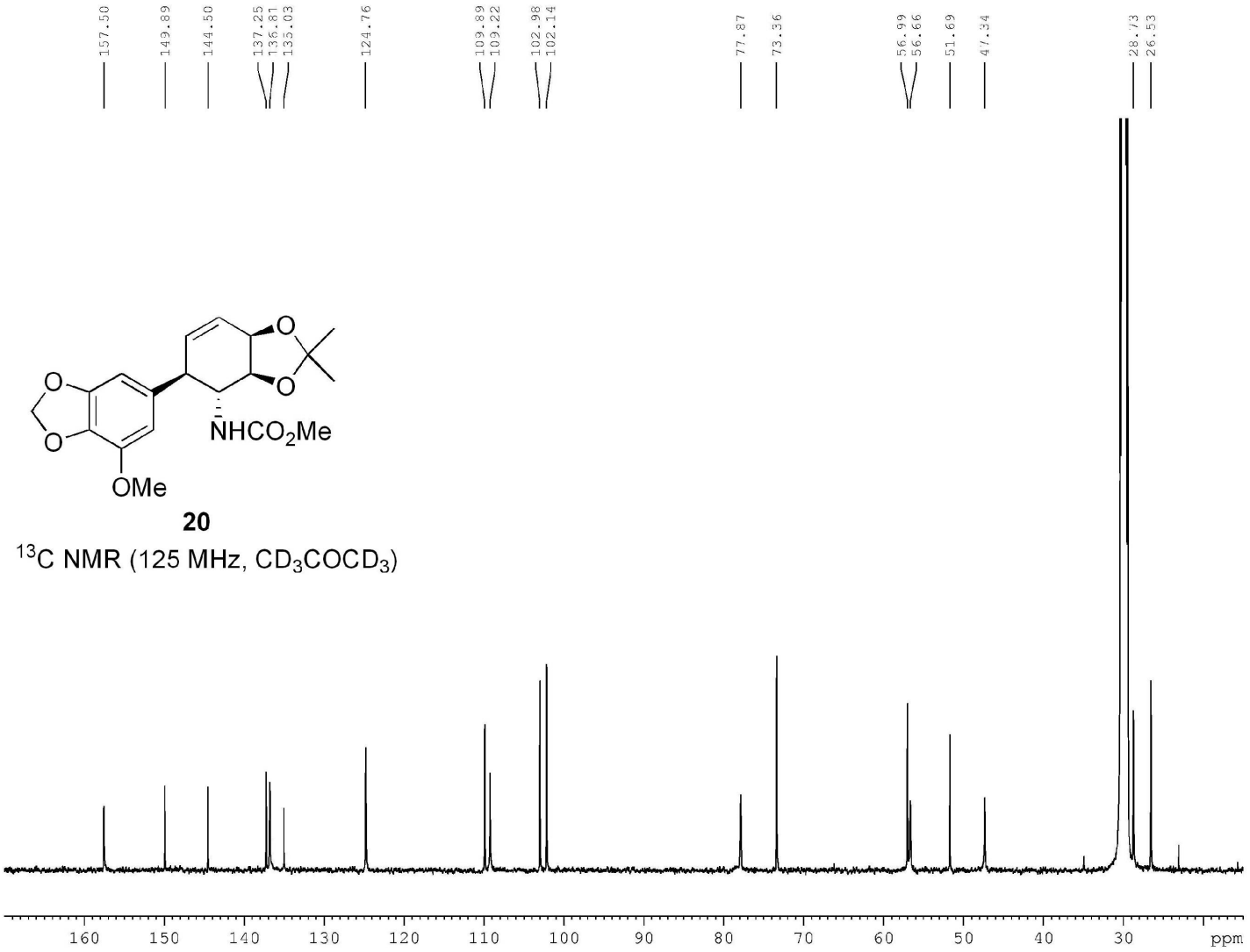

26.55
28.72
29.44
29.59
29.75
29.90
30.06
30.21
30.36
47.17
51.64
56.91
73.32
77.89
101.93
108.80
109.40
109.89
122.49
124.79
136.60
136.86
147.39
148.61
157.41
206.14
206.45
NHCO2Me
16
13C NMR (125 MHz, CD3COCD3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

%Transmittance
Wavenumbers (cm-1)
NHCO2Me
16
IR (CCl4)
3467
3442
3042
2995
2956
2938
2881
1730
1504
1486
1250
1215
1047



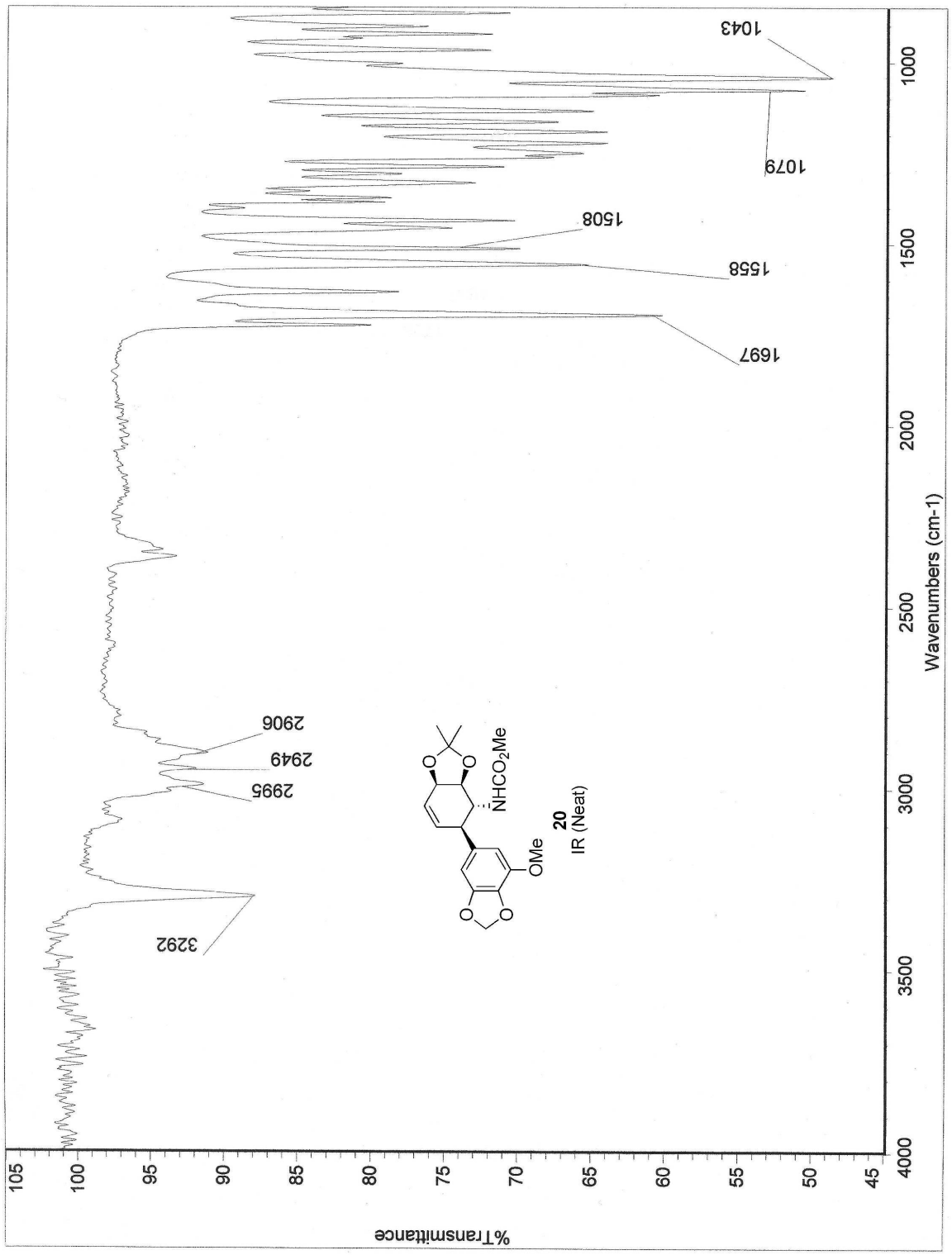
20

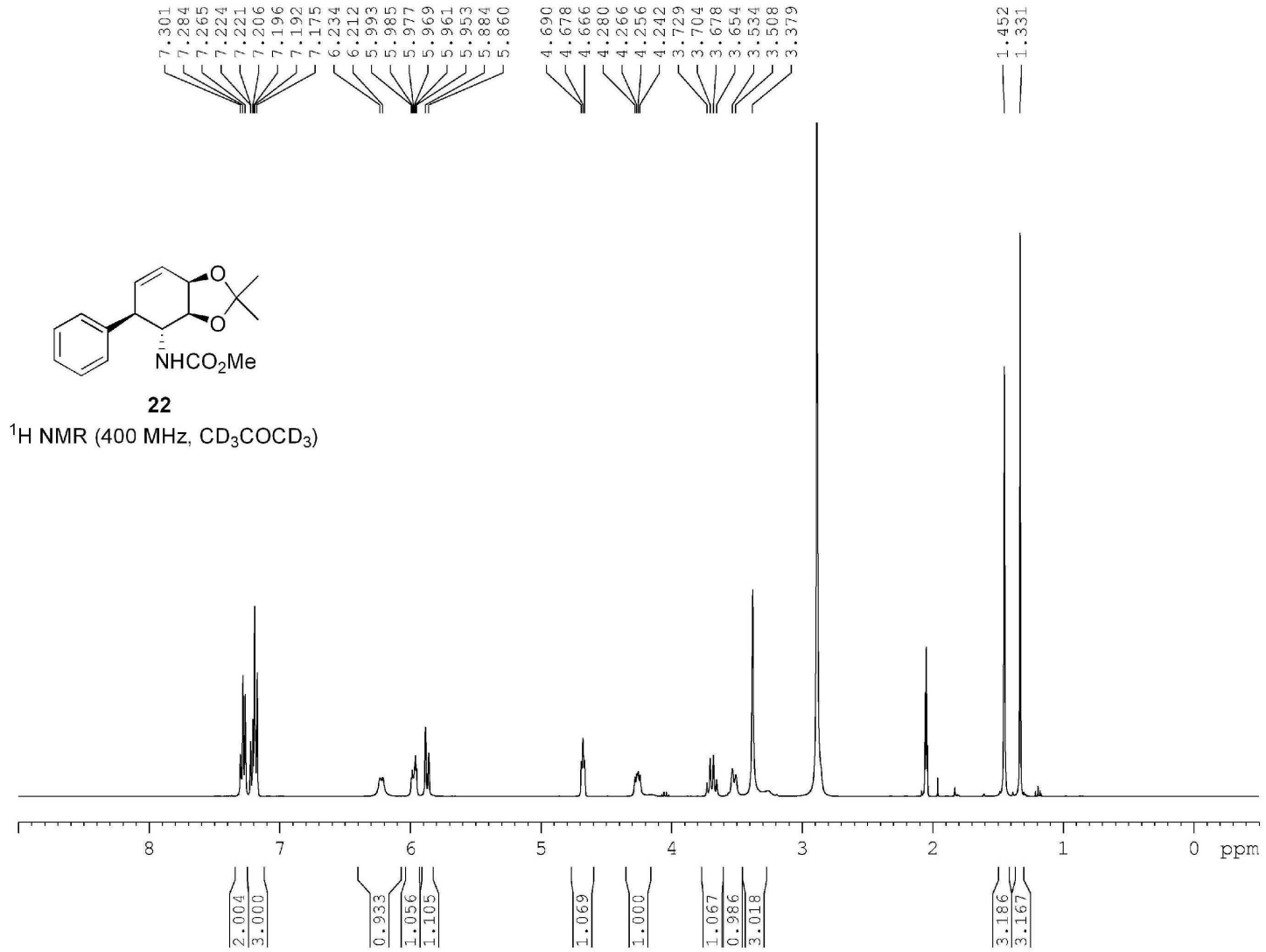
^{1}H NMR (500 MHz, CD_3COCD_3)



20

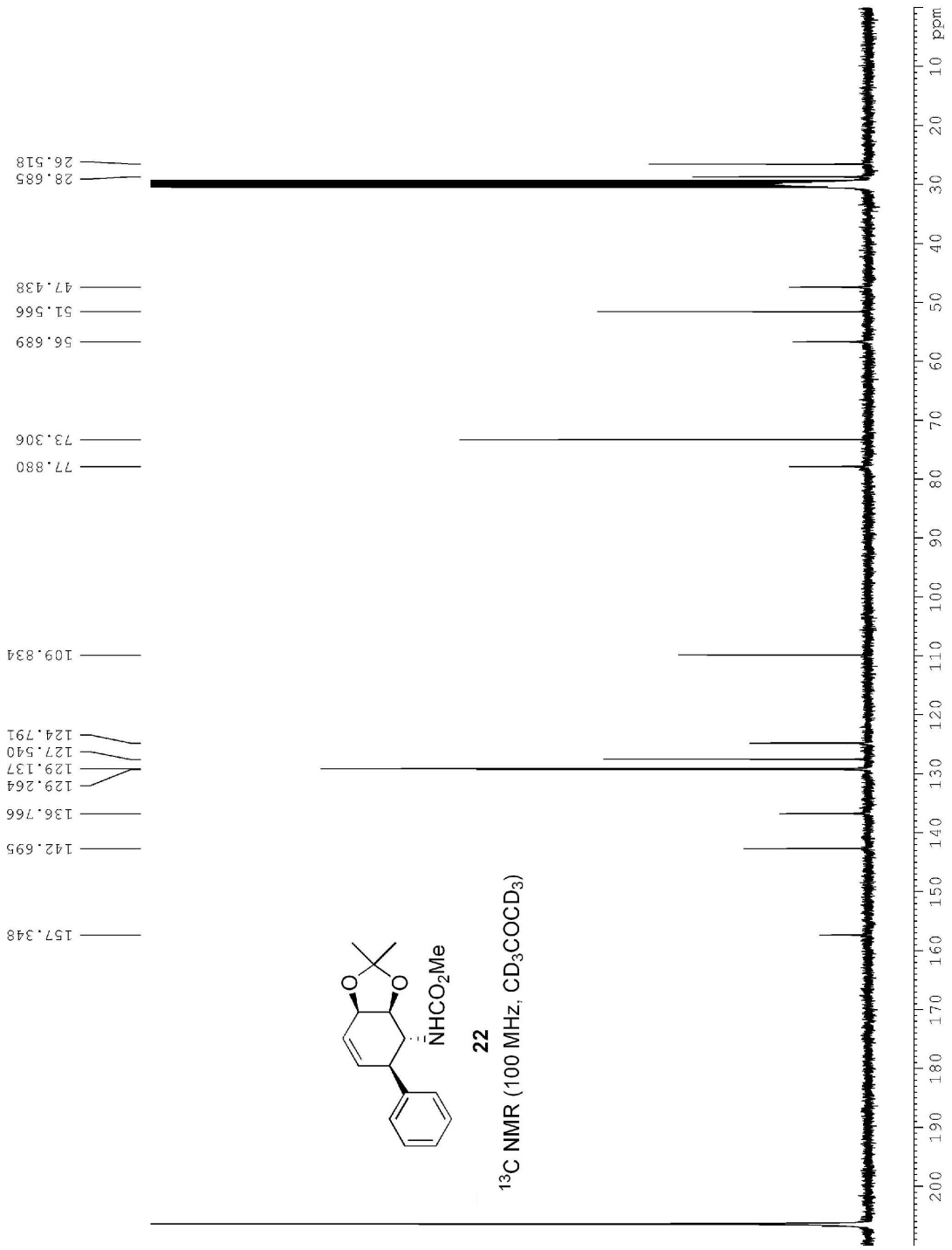
^{13}C NMR (125 MHz, CD_3COCD_3)

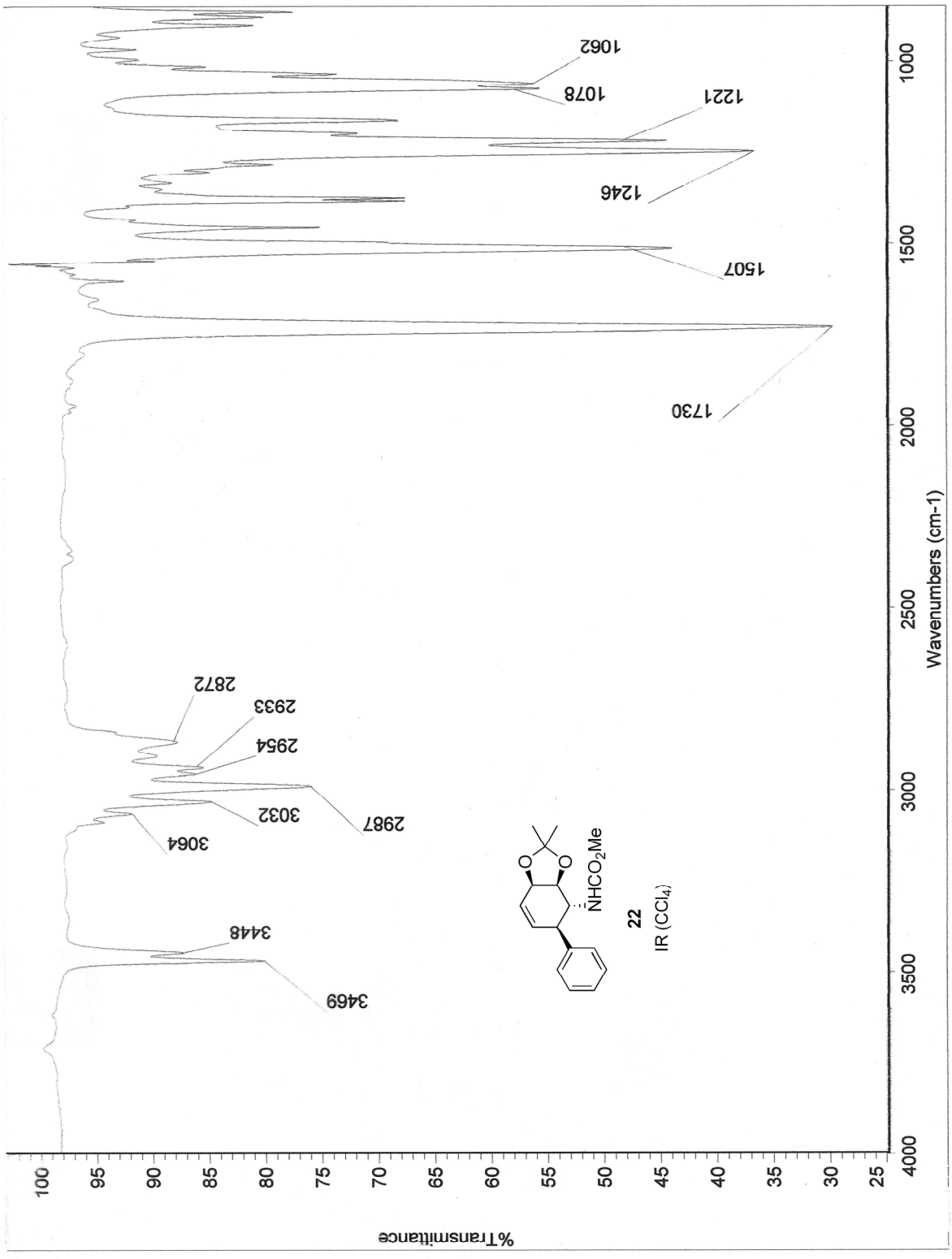

%Transmittance
Wavenumbers (cm-1)
3292
2995
2949
2906
1697
1558
1508
1079
1043
NHCO2Me
OMe
20
IR (Neat)

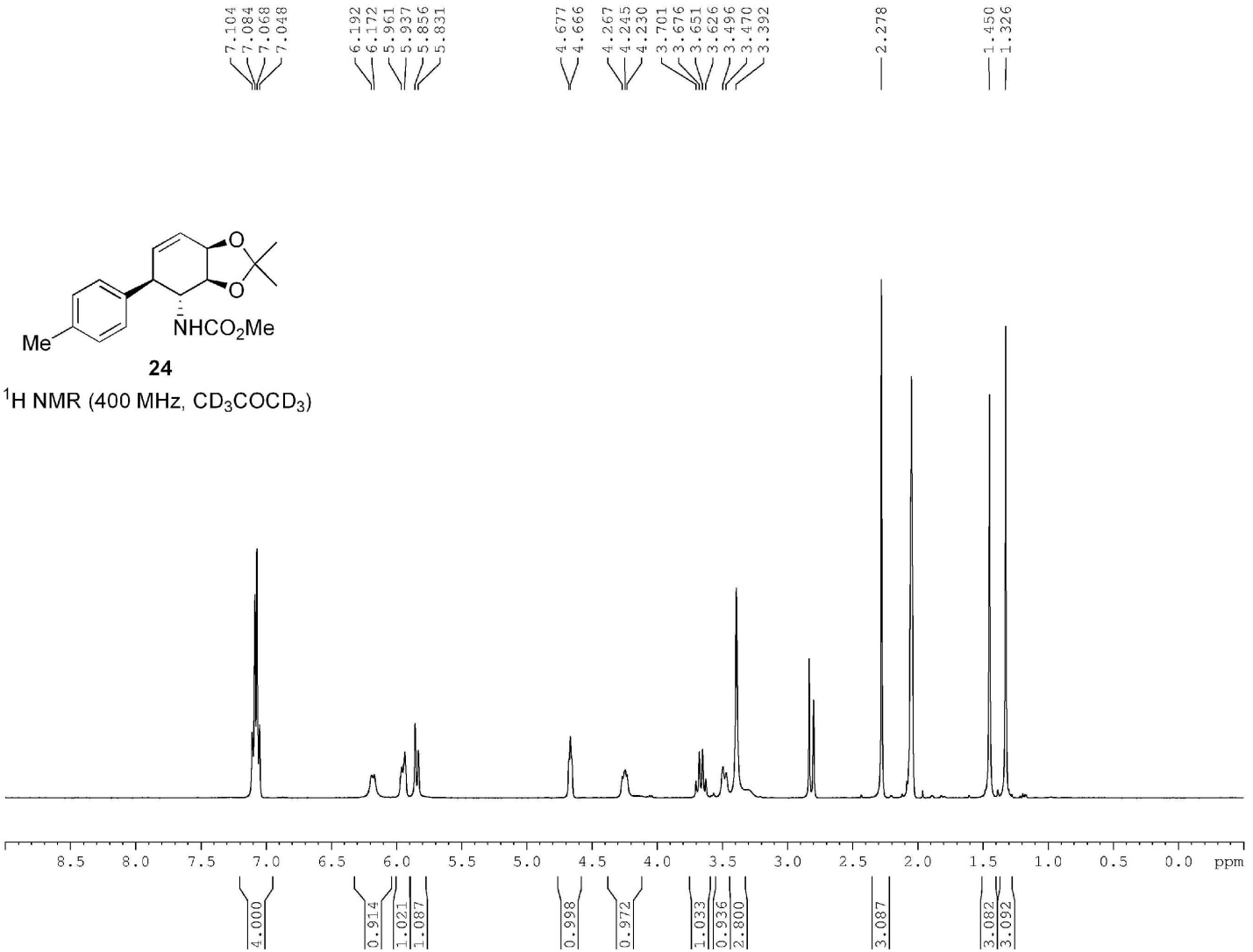


22

^{1}H NMR (400 MHz, CD_3COCD_3)

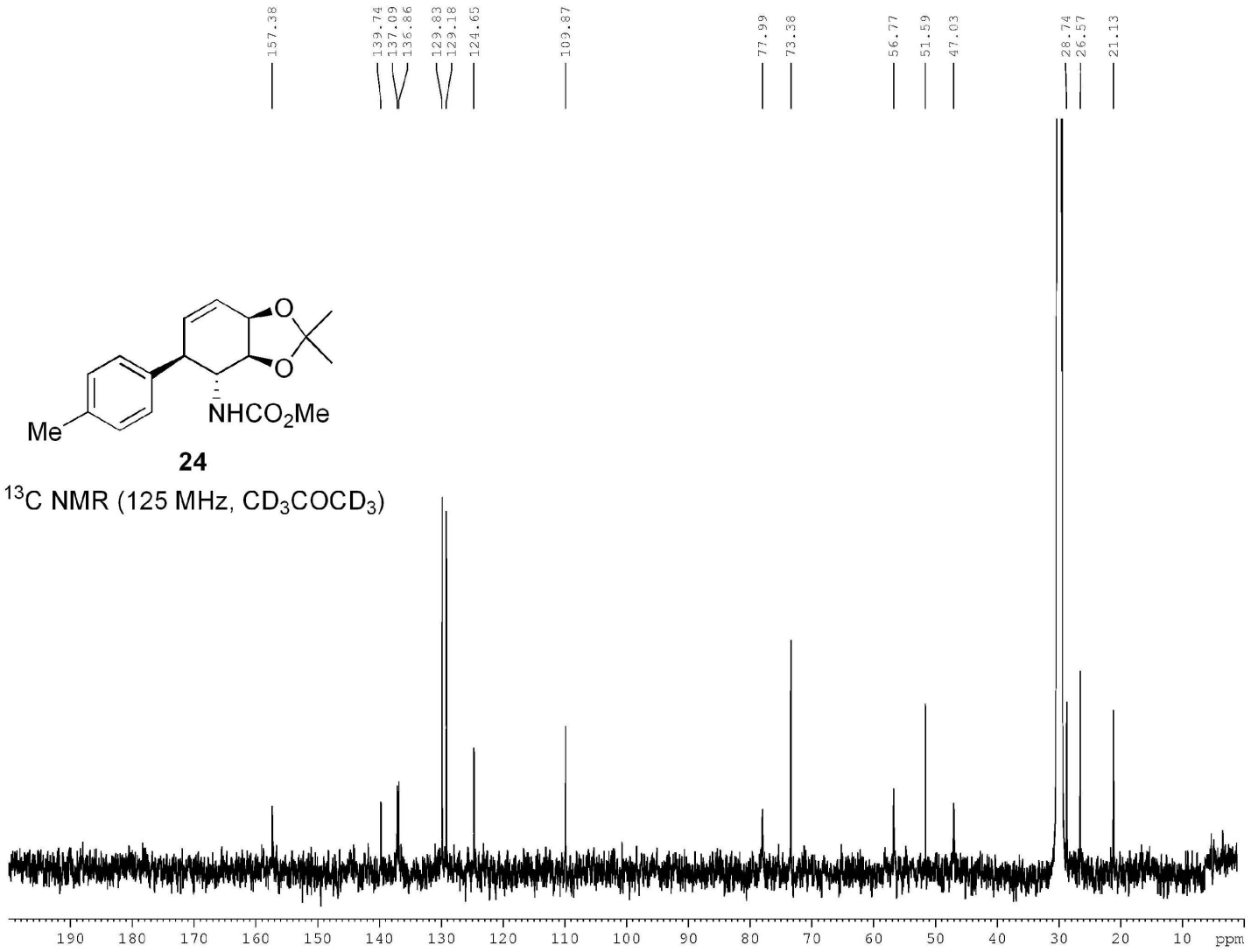

157.348
142.695
136.766
129.264
129.137
127.540
124.791
109.834
77.880
73.306
56.689
51.566
47.438
28.685
26.518
NHCO2Me
22
13C NMR (100 MHz, CD3COCD3)
ppm

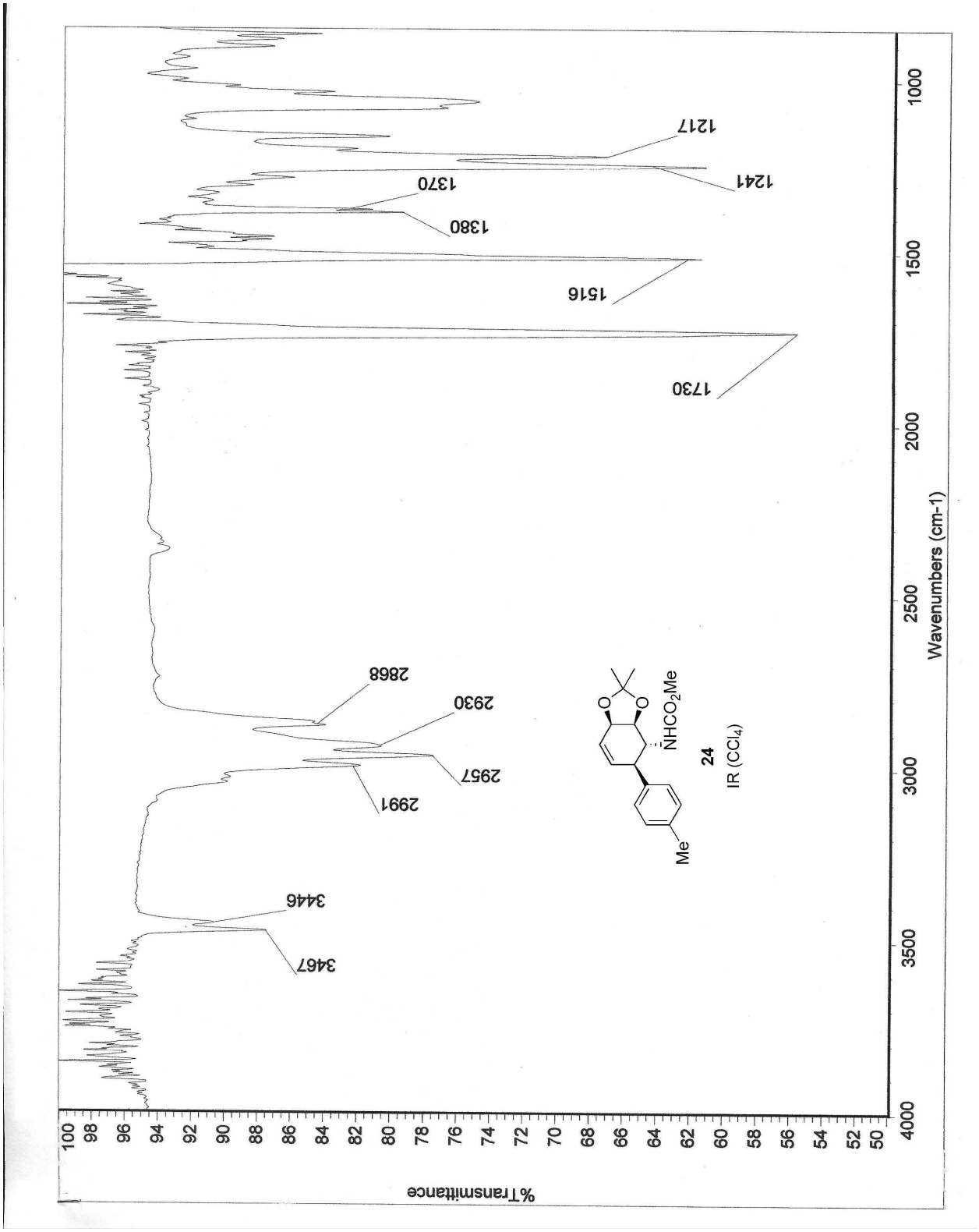

%Transmittance
Wavenumbers (cm-1)
NHCO2Me
22
IR (CCl4)
3469
3448
3064
3032
2987
2954
2933
2872
1730
1507
1246
1221
1078
1062

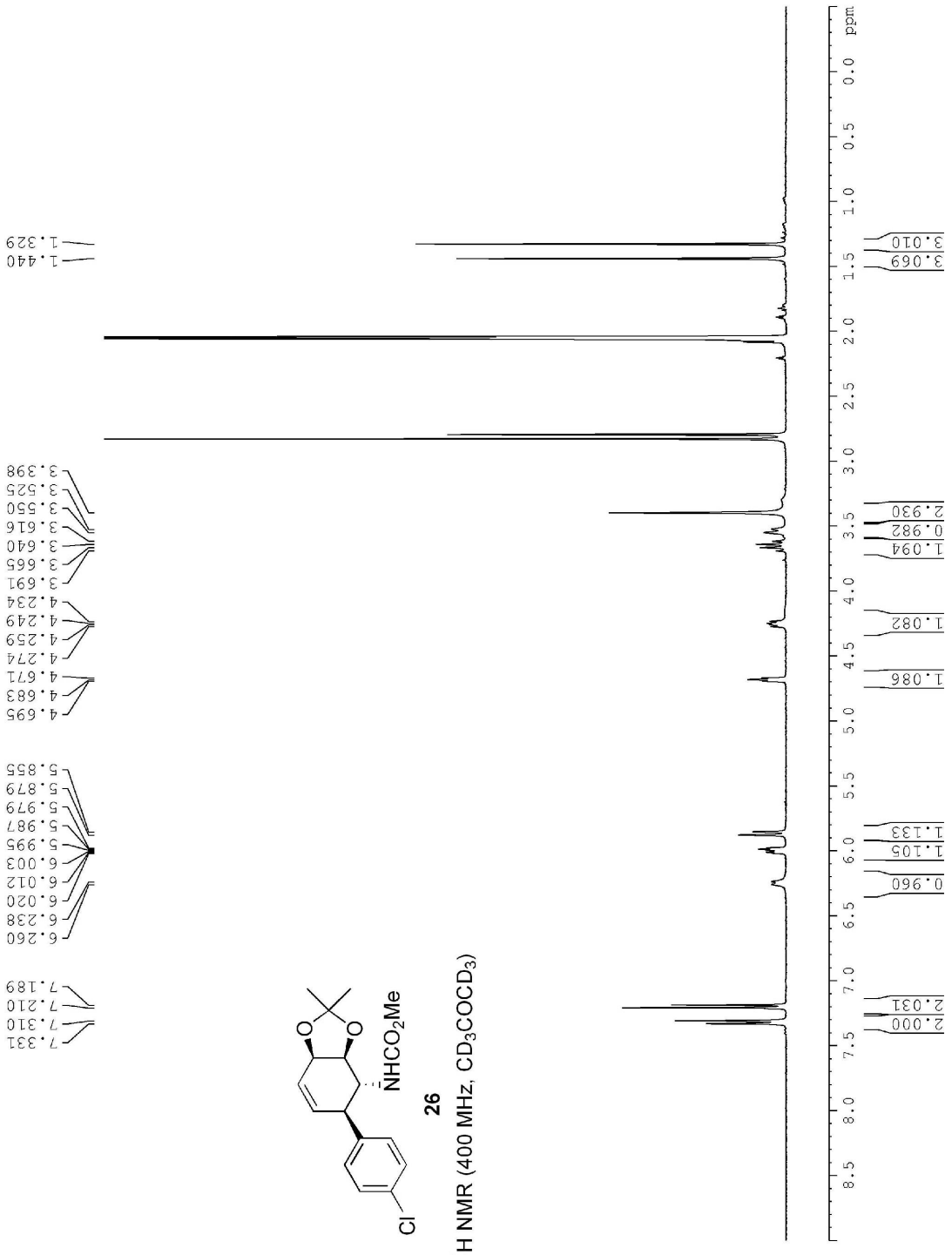


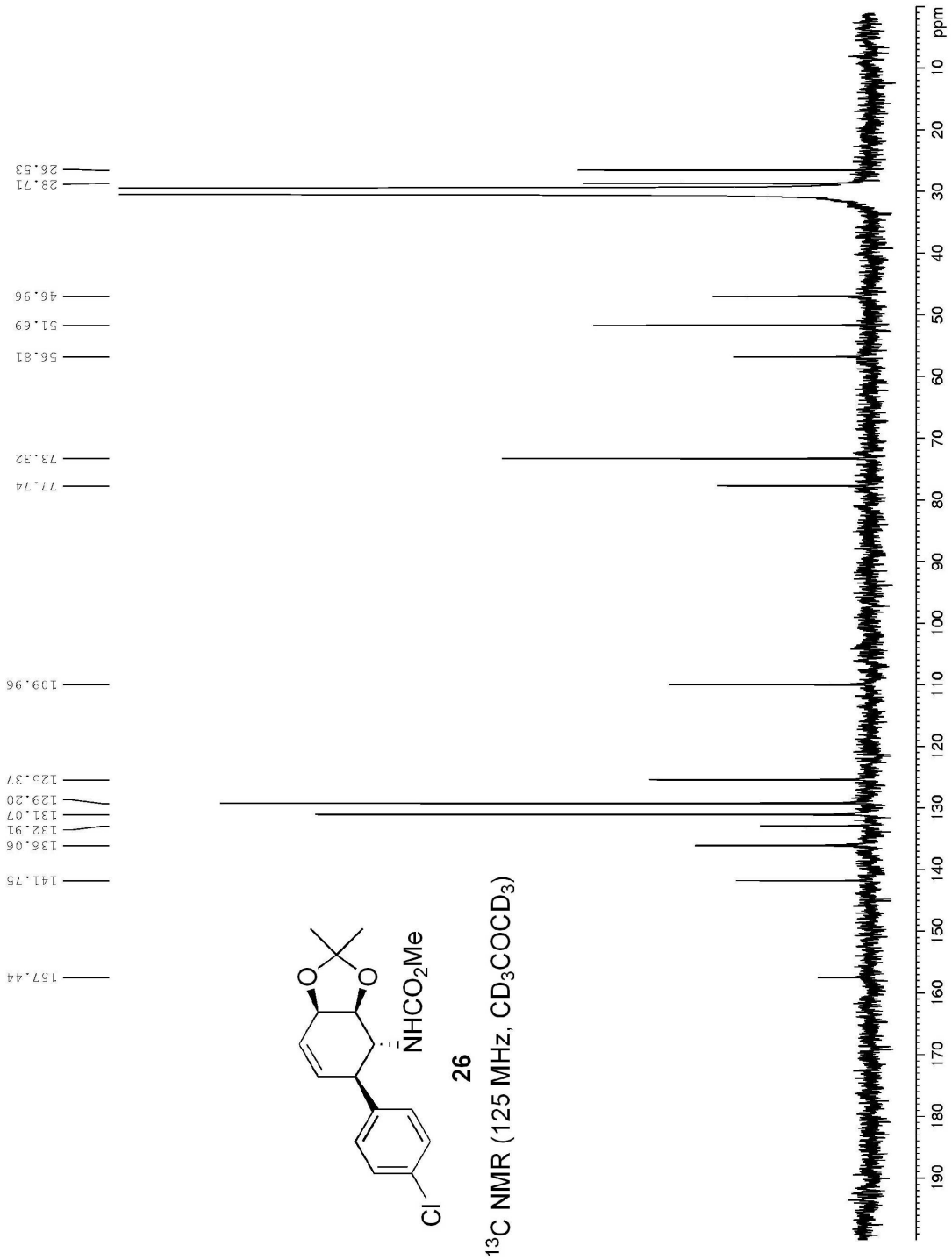
24

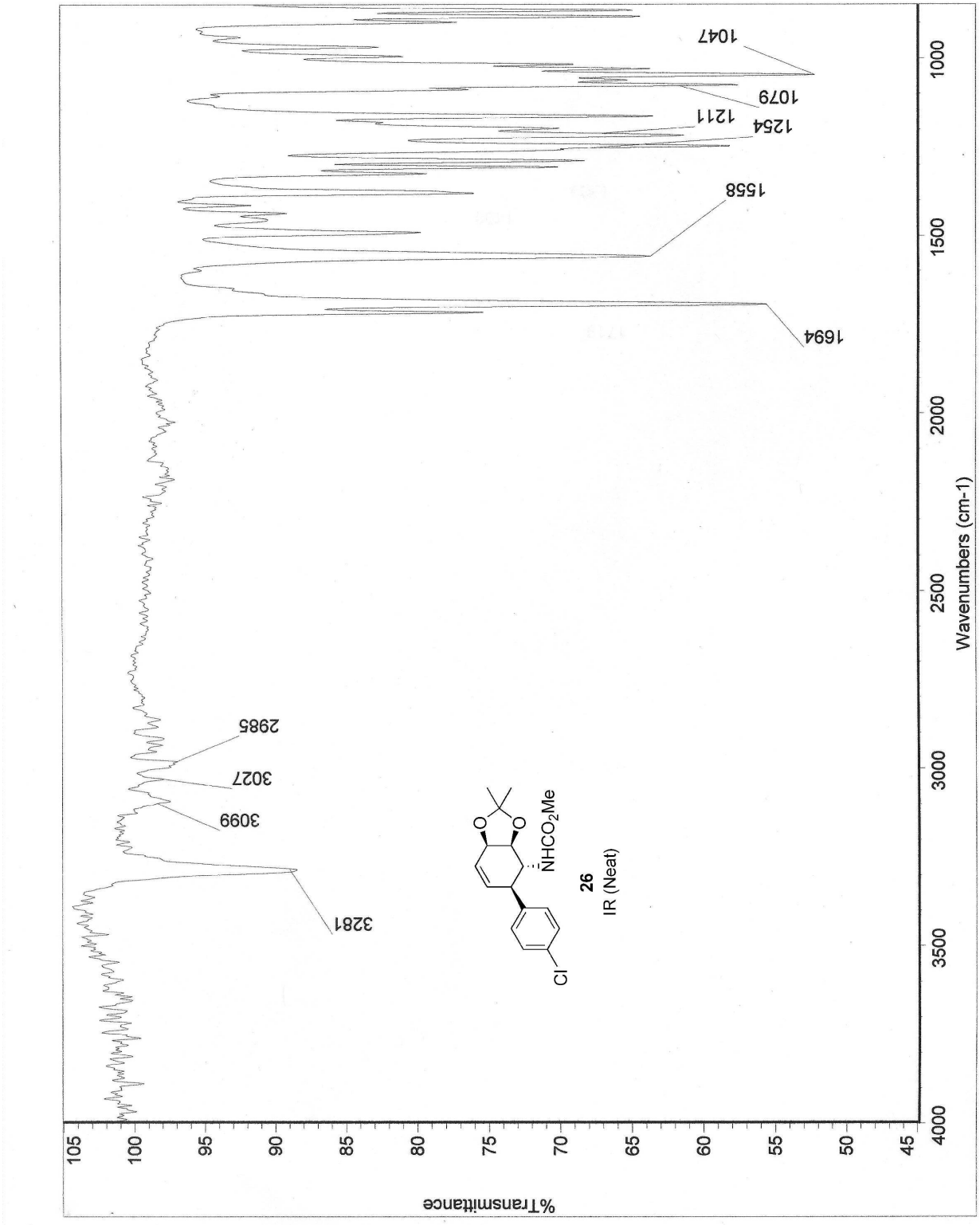
^{1}H NMR (400 MHz, CD_3COCD_3)


157.38
139.74
137.09
136.86
129.83
129.18
124.65
109.87
77.99
73.38
56.77
51.59
47.03
28.74
26.57
21.13
O
O
NHCO2Me
Me
24
13C NMR (125 MHz, CD3COCD3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


%Transmittance
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
3467
3446
2991
2957
2930
2868
1730
1516
1380
1370
1241
1217
NHCO2Me
Me
24
IR (CCl4)


1.329
1.440
3.010
3.069
2.930
0.982
1.094
1.082
1.086
1.133
1.105
0.960
2.031
2.000
3.398
3.525
3.550
3.616
3.640
3.665
3.691
4.234
4.249
4.259
4.274
4.671
4.683
4.695
5.855
5.879
5.979
5.987
5.995
6.003
6.012
6.020
6.238
6.260
7.189
7.210
7.310
7.331
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
NHCO2Me
Cl
O
O
26
1H NMR (400 MHz, CD3COCD3)


26.53
28.71
46.96
51.69
56.81
73.32
77.74
109.96
125.37
129.20
131.07
132.91
136.06
141.75
157.44
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
NHCO2Me
Cl
26
13C NMR (125 MHz, CD3COCD3)


%Transmittance
Wavenumbers (cm-1)
3281
3099
3027
2985
1694
1558
1254
1211
1079
1047
NHCO2Me
Cl
26
IR (Neat)