Supporting Information

Stereocontrolled Synthesis of Oxygen-bridged Polycycles via Intermolecular [3+2] Cyclization of Platinum-bound Pyrylium with Alkenes

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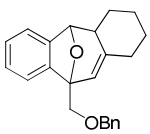
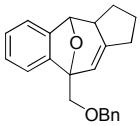
1. General experimental procedure:

Platinum chloride (II) (5 mol%) was added to a mixture of 2-alkynylbeznaldehydes **3** (or **3'**) and alkenes (**4a-e**, **6a-b**, **8a-c**, and **10**) in dry toluene under argon atmosphere. The resulting mixture was stirred for about 1 to 20 hours at the indicated temperature. Upon completion of the reaction, the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was subjected for flash column chromatography using a mixture of EtOAc and *n*-hexane to afford the corresponding products **5a-e**, **5a'**, **7a-b**, **9a-c**, and **11**.

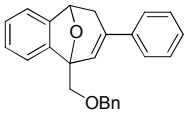
2. Spectroscopic data of compounds



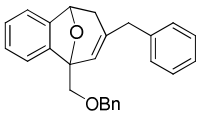
Spectroscopic data of compound 5a: IR(NaCl, cm^{-1}) 3064, 2928, 2854, 1454, 1100; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 5H), 7.19-7.12 (m, 3H), 7.05-7.03 (m, 1H), 5.77 (s, 1H), 5.17 (d, *J* = 6.0 Hz, 1H), 4.69 (s, 2H), 3.88 (ABq, Δδ = 48.0 Hz, *J* = 10.8 Hz, 2H), 2.76-2.73 (m, 1H), 2.10-1.93 (m, 2H), 1.76-1.60 (m, 3H), 1.38-1.27 (m, 1H), 1.00-0.87 (m, 1H), 0.79-0.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.92, 140.55, 138.08, 137.89, 128.35, 127.83, 127.61, 126.66, 125.88, 123.15, 123.07, 117.67, 83.28, 81.17, 73.74, 70.92, 39.72, 34.03, 27.62, 26.87, 25.26; HRMS calculated for $C_{23}H_{24}NaO_2$ 355.1674; found, 355.1684.



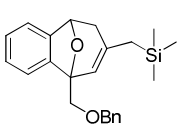
Spectroscopic data of compound 5b: IR(NaCl, cm^{-1}) 3028, 2949, 2865, 1454, 1100; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 4H), 7.31-7.28 (m, 1H), 7.20-7.12 (m, 3H), 7.03-7.01 (m, 1H), 5.69 (s, 1H), 5.53 (d, *J* = 5.6 Hz, 1H), 4.70 (s, 2H), 3.92 (ABq, Δδ = 46.2 Hz, *J* = 10.4 Hz, 2H), 3.07-3.01 (m, 1H), 2.28-2.21 (m, 1H), 1.99-1.91 (m, 1H), 1.84-1.77 (m, 1H) 1.66-1.51 (m, 2H), 0.84-0.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.39, 141.30, 139.04, 138.12, 128.37, 127.83, 127.61, 126.70, 126.03, 123.01, 121.76, 117.37, 83.25, 80.94, 73.71, 70.69, 42.33, 28.45, 25.86, 22.92; HRMS calculated for $C_{22}H_{22}NaO_2$ 341.1517; found, 341.1523.



Spectroscopic data of compound 5c: IR(NaCl, cm^{-1}) 2927, 2855, 1454, 1097; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.36 (m, 4H), 7.33-7.29 (m, 4H), 7.27-7.15 (m, 5H), 7.13-7.09 (m, 1H), 6.56 (s, 1H), 5.61 (d, *J* = 5.6 Hz, 1H), 4.74 (t, *J* = 13.2 Hz, 2H), 4.05 (ABq, Δδ = 46.2 Hz, *J* = 10.4 Hz, 2H), 3.26 (ddd, *J* = 17.4, 6.0, 1.6 Hz, 1H), 2.31 (d, *J* = 17.2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.22, 142.87, 139.58, 138.04, 132.49, 128.43, 128.25, 127.91, 127.86, 127.73, 127.52, 126.89, 124.78, 120.97, 117.89, 82.90, 77.32, 73.84, 70.96, 31.33; HRMS calculated for $C_{25}H_{22}NaO_2$ 377.1517; found, 377.1509.

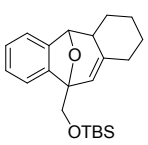


Spectroscopic data of compound 5d: IR(NaCl, cm^{-1}) 3066, 2944, 1640, 1417; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 5H), 7.24-7.14 (m, 6H), 7.05-7.03 (m, 1H), 6.93 (d, *J* = 6.4 Hz, 2H), 5.87 (s, 1H), 5.41 (d, *J* = 6.4 Hz, 1H), 4.70 (ABq, Δδ = 17.2, 12.4 Hz, 2H), 3.93 (ABq, Δδ = 45.8 Hz *J* = 10.0 Hz, 2H), 3.15 (s, 2H), 2.75 (dd, *J* = 17.8, 6.4 Hz, 1H), 1.74 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.69, 142.89, 138.66, 138.13, 133.92, 128.80, 128.38, 128.31, 128.24, 127.83, 127.64, 126.70, 126.64, 126.07, 120.90, 117.58, 82.93, 73.69, 70.79, 42.89, 32.78; HRMS calculated for $C_{26}H_{24}NaO_2$ 391.1674; found, 391.1686.

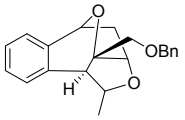


Spectroscopic data of compound 5e: IR(NaCl, cm^{-1}) 2927, 2844, 1253, 1119; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.37 (m, 4H), 7.34-7.23 (m, 2H), 7.19-7.13 (m, 2H), 7.05-7.03 (m, 1H), 5.65 (s, 1H), 5.44 (d, *J* = 6.0 Hz, 1H), 4.73 (s, 2H), 3.94 (ABq, Δδ = 17.2, 10.8 Hz, 2H), 2.82 (dd, *J* = 17.4, 4.0 Hz, 1H), 1.77 (d, *J* = 17.2 Hz, 1H),

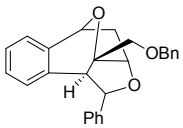
1.34 (ABq, Δδ = 40.6 Hz, *J* = 14.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.40, 142.73, 138.19, 132.90, 128.31, 127.80, 127.55, 126.61, 126.32, 123.99, 120.72, 117.20, 82.99, 77.32, 73.66, 71.00, 35.20, 26.65, -1.51; HRMS calculated for $C_{23}H_{28}NaO_2Si$ 387.1756; found, 387.1750.



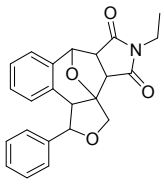
Spectroscopic data of compound 5a': IR (NaCl, cm^{-1}) 2828, 2855, 1470, 1243, 1100, 890; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.26 (m, 1H), 7.17-7.11 (m, 3H), 5.91 (s, 1H), 5.12 (d, *J* = 6.4 Hz, 1H), 4.02 (ABq, Δδ = 35.2 Hz *J* = 10.4 Hz, 2H), 2.72-2.67 (m, 1H), 2.12-1.91 (m, 2H), 1.75-1.61 (m, 3H), 1.38-1.27 (m, 1H), 1.03-0.81 (m, 1H), 0,95 (s, 9H), 0.79-0.69 (m, 1H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.01, 140.64, 137.27, 126.66, 125.69, 123.18, 122.77, 118.32, 83.28, 81.09, 65.19, 40.02, 34.10, 27.67, 26.91, 25.94, 25.33, 18.37, -5.40, -5.47; HRMS calculated for $C_{22}H_{32}NaO_2Si$ 379.2069; found, 379.2080.



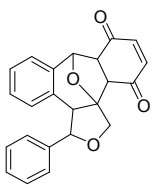
Spectroscopic data of compound 7a: IR (NaCl, cm^{-1}) 2972, 2932, 2863, 2453, 1155, 1111, 1056, 1028, 1004; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36-7.27 (m, 5H), 7.22-7.05 (m, 4H), 5.04 (d, *J* = 6.4 Hz, 1H), 4.67 (s, 2H), 4.44 (d, *J* = 7.2 Hz, 1H), 4.29-4.23 (m, 1H), 3.91 (ABq, Δ*δ* = 54.8 Hz, *J* = 10.8 Hz, 2H), 3.33 (d, *J* = 4.4 Hz, 1H), 2.34 (td, *J* = 13.6, 13.2 Hz, 1H), 2.01 (d, *J* = 12.8 Hz, 1H), 0.99 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 142.03, 137.92, 130.64, 130.08, 128.39, 127.71, 126.38, 126.03, 124.65, 92.36, 81.49, 78.15, 76.57, 73.73, 71.05, 47.86, 43.50, 17.60. HRMS calculated for $C_{21}H_{22}NaO_3$ 345.1467; found, 345.1469.



Spectroscopic data of compound 7b: IR (NaCl, cm^{-1}) 3029, 2939, 2859, 1489, 1452, 1152, 1108, 1029; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43-7.30 (m, 5H), 7.16-7.11 (m, 3H), 7.06-7.00 (m, 2H), 6.79 (d, *J* = 6.4 Hz, 2H), 6.70 (td, *J* = 7.6, 1.6 Hz, 1H), 5.97 (d, *J* = 7.6 Hz, 1H), 5.31 (d, *J* = 4.4 Hz, 1H), 5.08 (d, *J* = 6.4 Hz, 1H), 4.74 (dd, *J* = 12.4, 5.2 Hz, 2H), 4.63 (d, *J* = 7.2 Hz, 1H), 4.03 (ABq, Δ*δ* = 45.2 Hz, *J* = 10.4 Hz, 2H), 3.59 (d, *J* = 4.0 Hz, 1H), 2.50-2.44 (m, 1H), 2.23 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 141.96, 138.16, 137.93, 130.82, 129.59, 128.46, 127.78, 127.61, 127.51, 127.40, 126.68, 125.91, 125.72, 123.80, 92.24, 83.64, 82.02, 78.20, 73.76, 71.04, 50.04, 43.90. HRMS calculated for $C_{26}H_{24}NaO_3$ 407.1623; found, 407.1633.

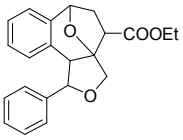


Spectroscopic data of compound 9a: IR (NaCl, cm^{-1}) 1698, 1403, 1227, 1051; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.12 (m, 2H), 7.08-7.01 (m, 5H), 6.98-6.94 (m, 2H), 6.72 (d, *J* = 8.0 Hz, 1H) 5.52 (d, *J* = 10.0 Hz, 1H), 5.33 (s, 1H) 44.2 (ABq, Δδ = 182.8 Hz, *J* = 10.8 Hz, 2H), 3.63-3.57 (m, 3H), 3.30 (ABq, Δδ = 26.8 Hz, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.26, 175.35, 138.82, 136.77, 130.81, 129.96, 128.44, 127.64, 127.04, 127.36, 126.67, 123.84, 89.65, 84.68, 78.79, 72.05, 55.17, 51.69, 48.93, 34.31, 12.96; HRMS calculated for $C_{23}H_{21}NNaO_4$ 398.1368; found, 398.1376.

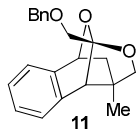


Spectroscopic data of compound 9b: IR (NaCl, cm^{-1}) 1673, 1292, 1018, 911; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.13 (m, 2H), 7.09-6.96 (m, 6H), 6.89-6.76 (m, 3H), 5.48 (d, *J* = 10H, 1H), 5.40 (s, 1H), 4.16 (ABq, Δδ = 58.2 Hz, *J* = 10.4 Hz, 2H), 3.71

(d, J = 10.0 H, 1H), 3.43 (ABq, Δδ = 30.4 Hz, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.06, 195.70, 142.15, 141.40, 138.88, 136.80, 130.83, 129.77, 128.32, 127.69, 127.39, 127.31, 126.77, 124.17, 90.72, 83.85, 81.90, 71.95, 58.69, 54.19, 52.79; HRMS calculated for $C_{23}H_{18}NaO_4$ 381.1103; found, 381.1110.



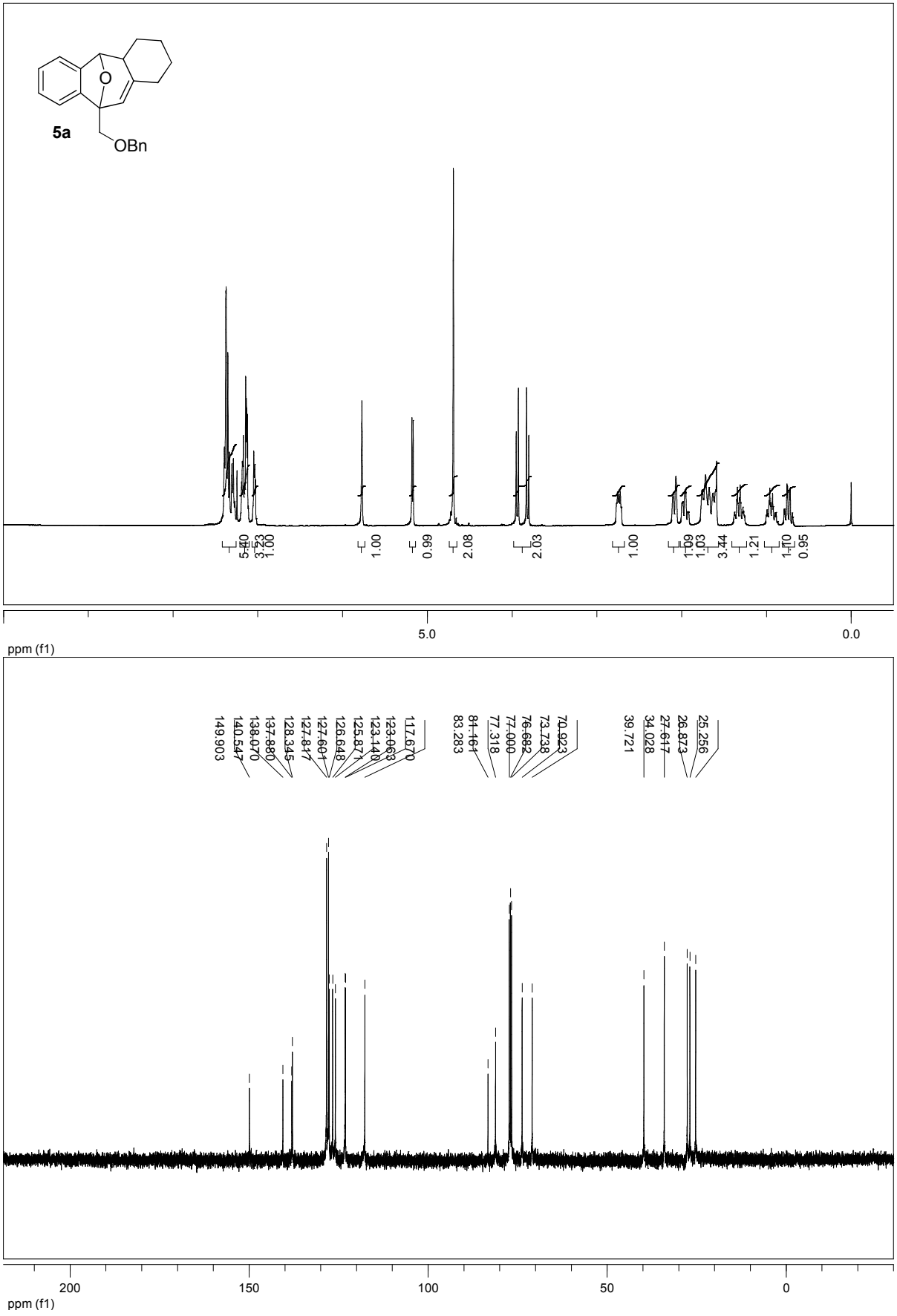
Spectroscopic data of compound 9c: IR (NaCl, cm^{-1}) 1670, 1610, 1455, 1018; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 6.8Hz, 2H), 7.06-6.93 (m, 6H), 6.78 (d, J = 7.6 Hz, 1H), 5.52 (d, J = 10.0 Hz, 1H), 5.29 (s, 1H), 4.45 (d, J = 10.0 Hz, 1H), 4.25-4.19 (m, 3H), 3.51 (d, J = 9.6 Hz, 1H), 3.04 (dd, J = 9.2 , 4.4Hz, 1H), 2.56 (dd, J = 13.2, 9.2 Hz, 1H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.15, 139.68, 139.18, 130.88, 130.82, 128.43, 127.26, 127.02, 126.99, 126.23, 123.69, 88.85, 85.27, 79.99, 74.42, 61.25, 52.20, 32.69, 14.25; HRMS calculated for $C_{22}H_{22}NaO_4$ 373.1416; found, 373.1420.

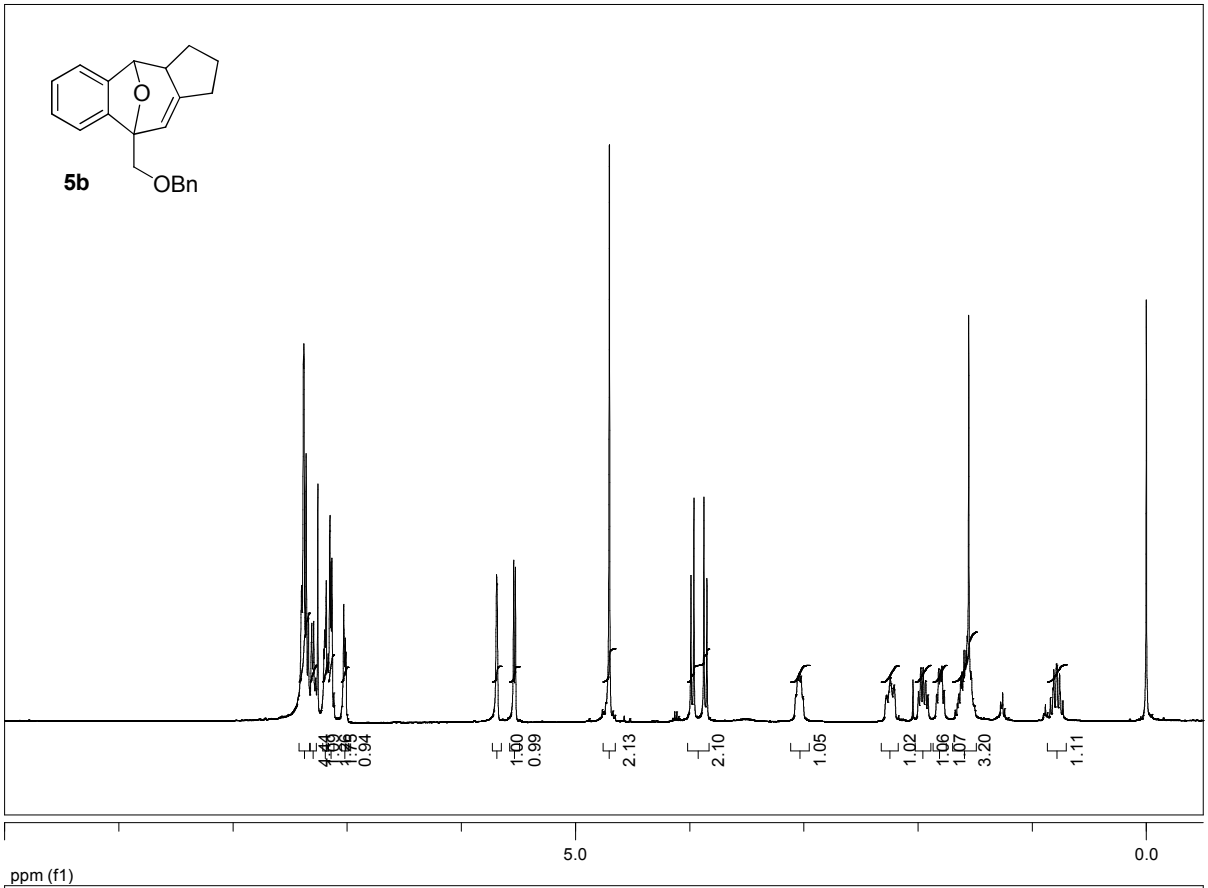


11

Spectroscopic data of compound 11: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 6H), 7.21-7.19 (m, 3H), 4.87 (d, J = 4.4 Hz, 1H), 4.59 (d, J = 12.4 Hz, 1H), 4.40 (d, J = 12.4 Hz, 1H), 3.85 (d, J = 7.2 Hz, 1H), 3.77 (d, J = 7.2 Hz, 1H), 3.44 (d, J = 10.8 Hz, 1H), 3.21 (s, 1H), 3.01 (d, J = 10.8 Hz, 1H), 2.39 (dd, J = 13.6, 4.8 Hz, 1H), 1.41 (d, J = 13.6 Hz, 1H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.95, 138.41, 133.93, 128.45, 127.83, 127.70, 127.10, 121.71, 106.67, 79.59, 73.63, 70.32, 69.10, 50.79, 43.97, 38.92, 21.33.

3. ^{1}H and ^{13}C NMR Spectra of Compounds

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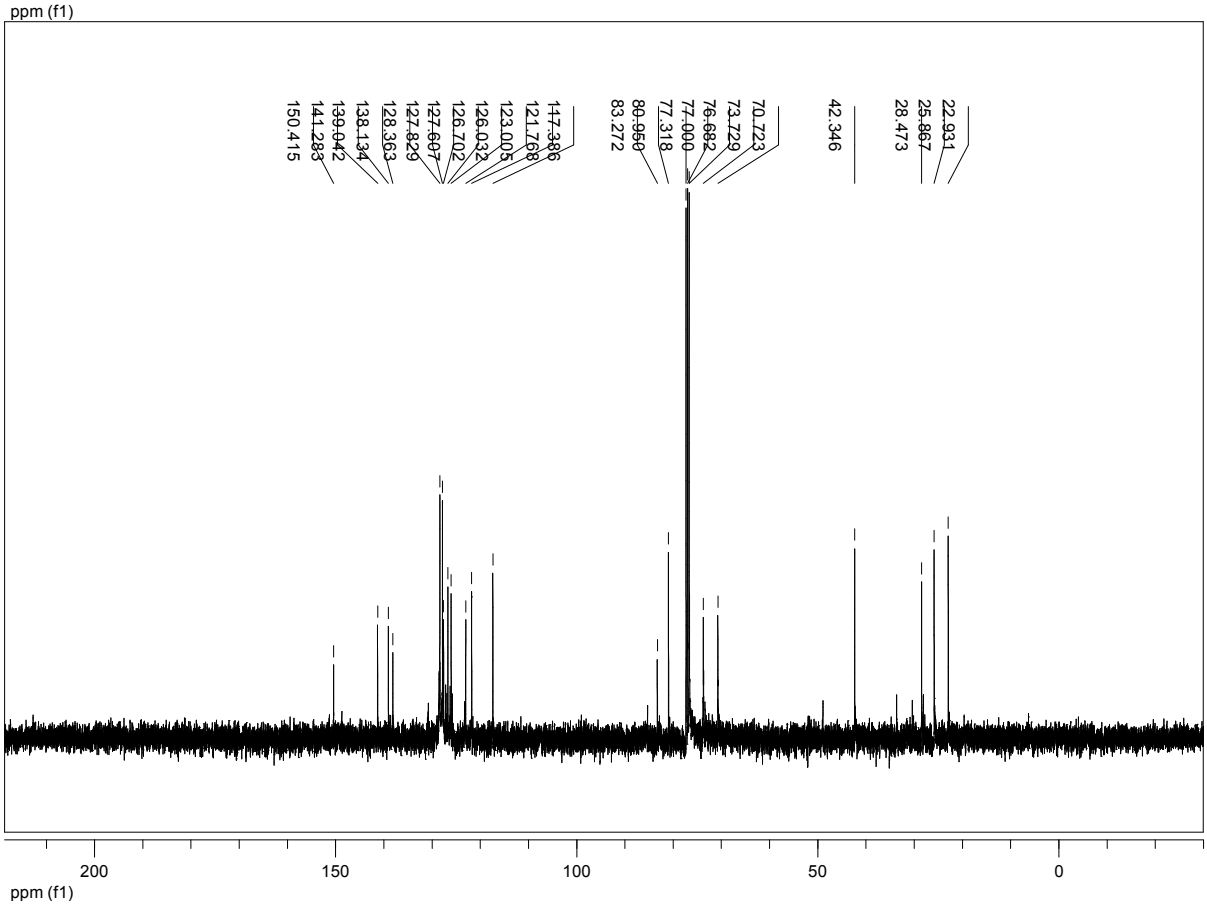
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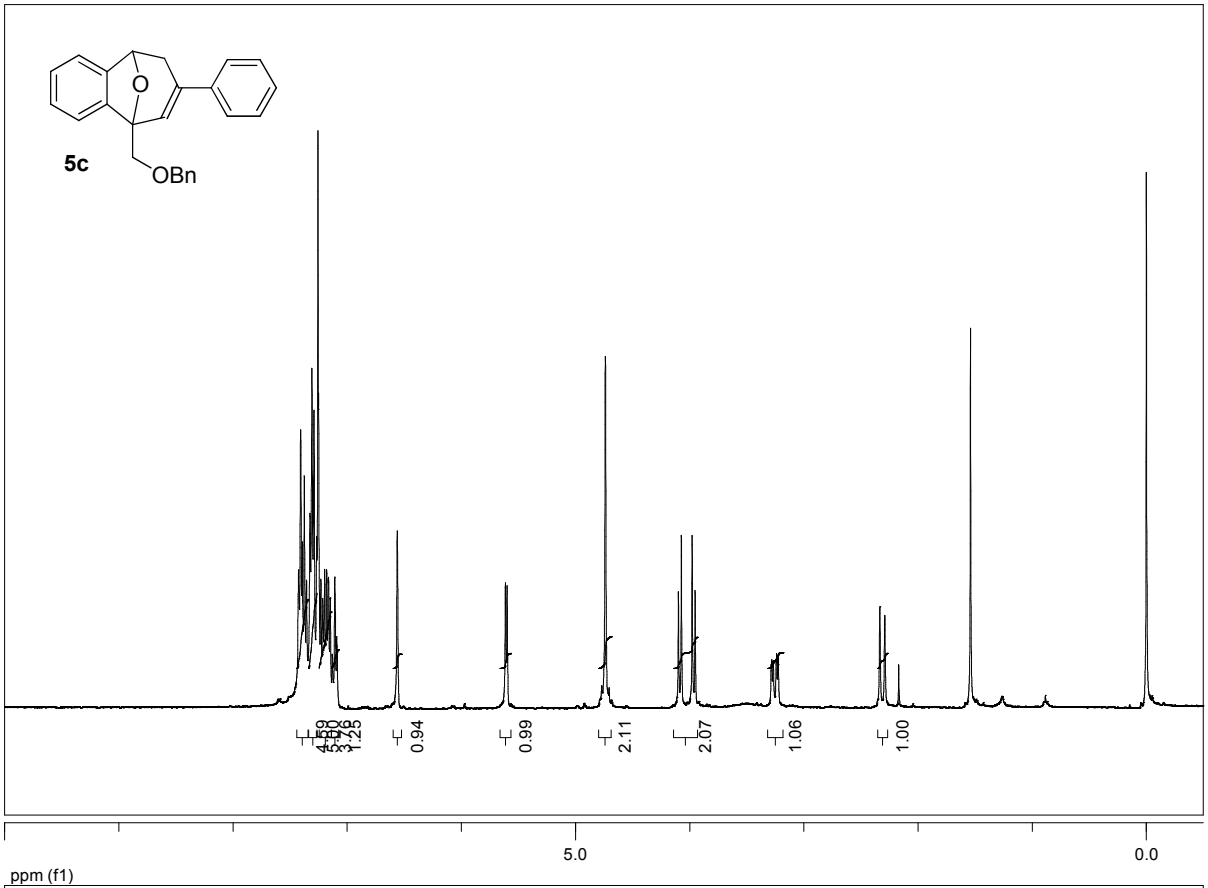
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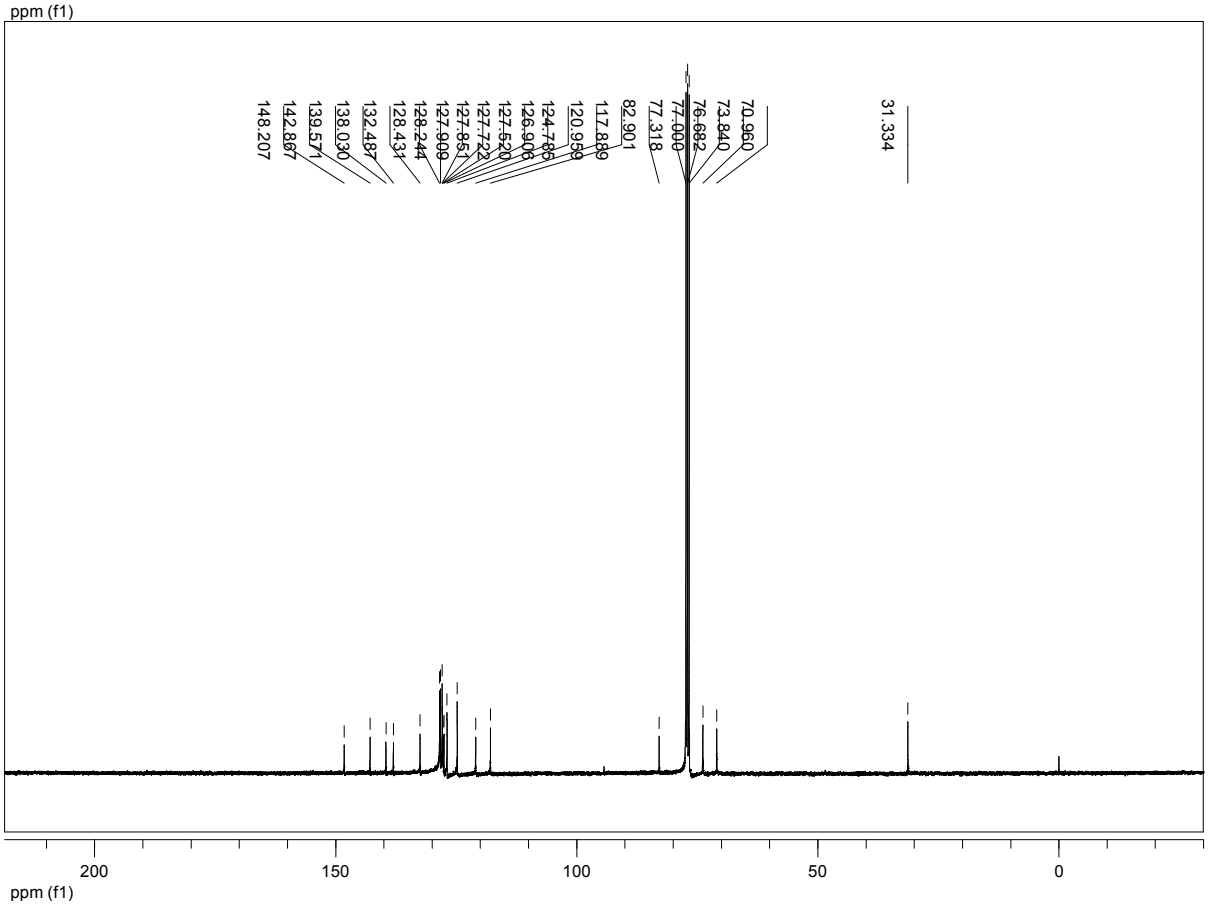
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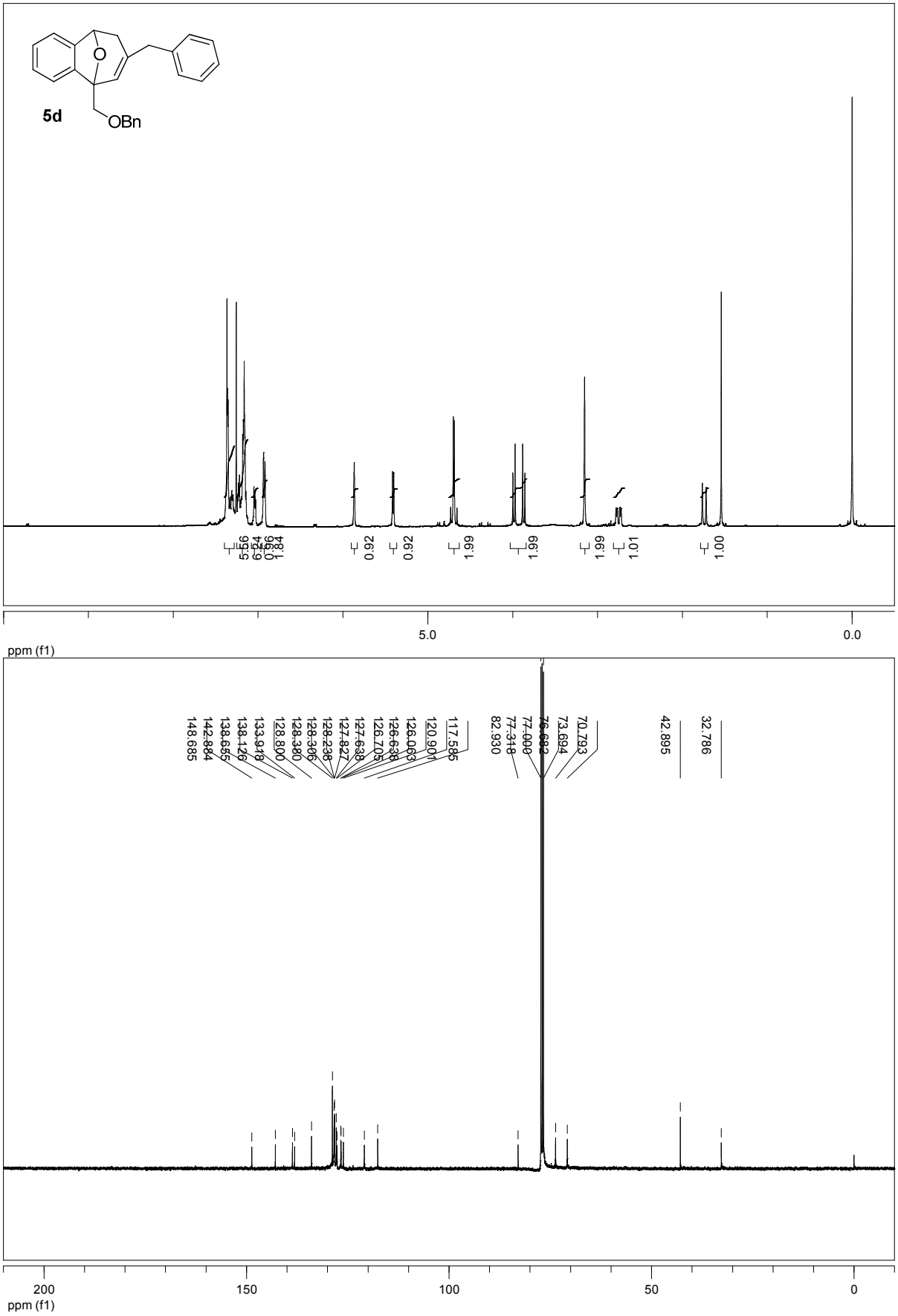
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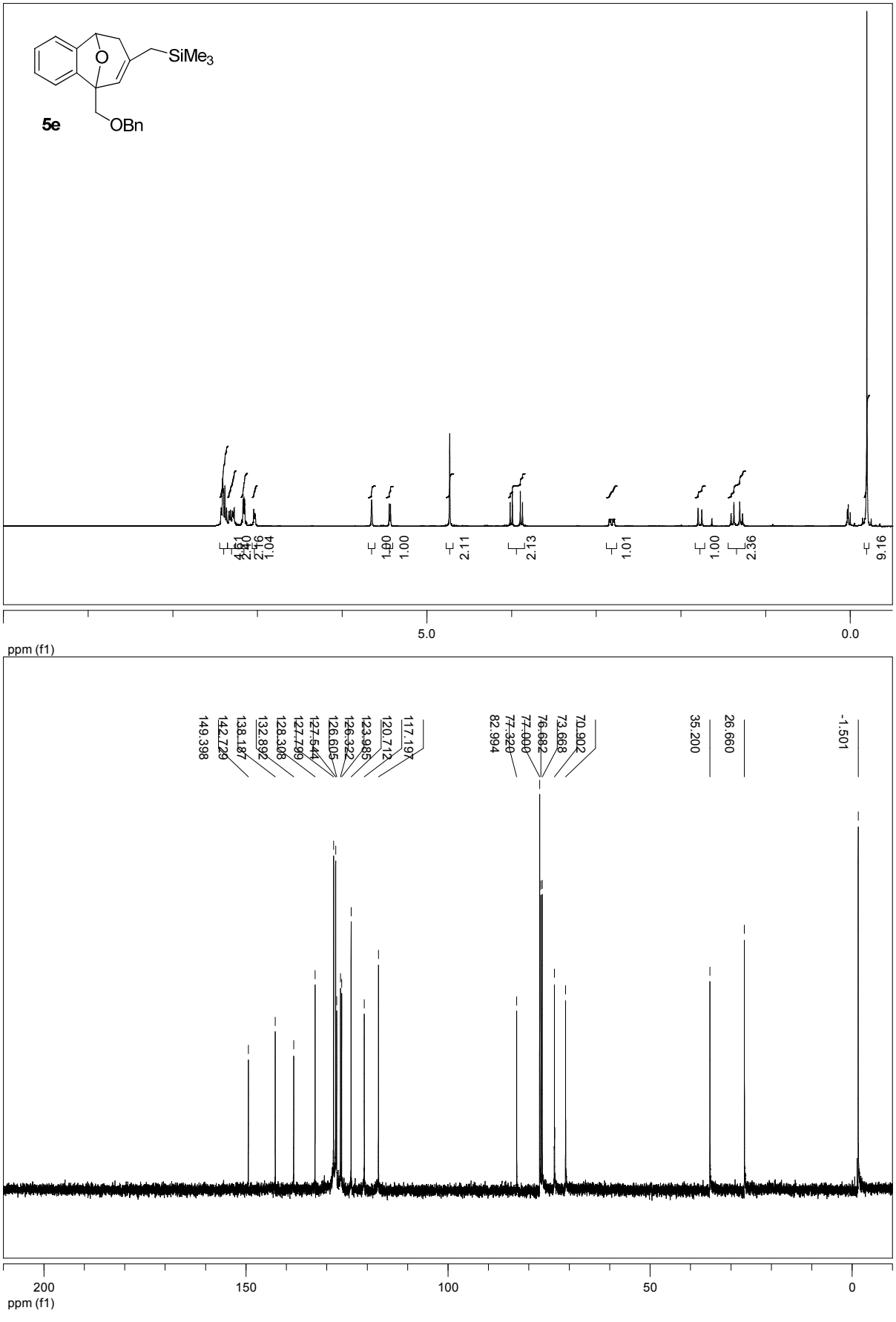
ppm (f1)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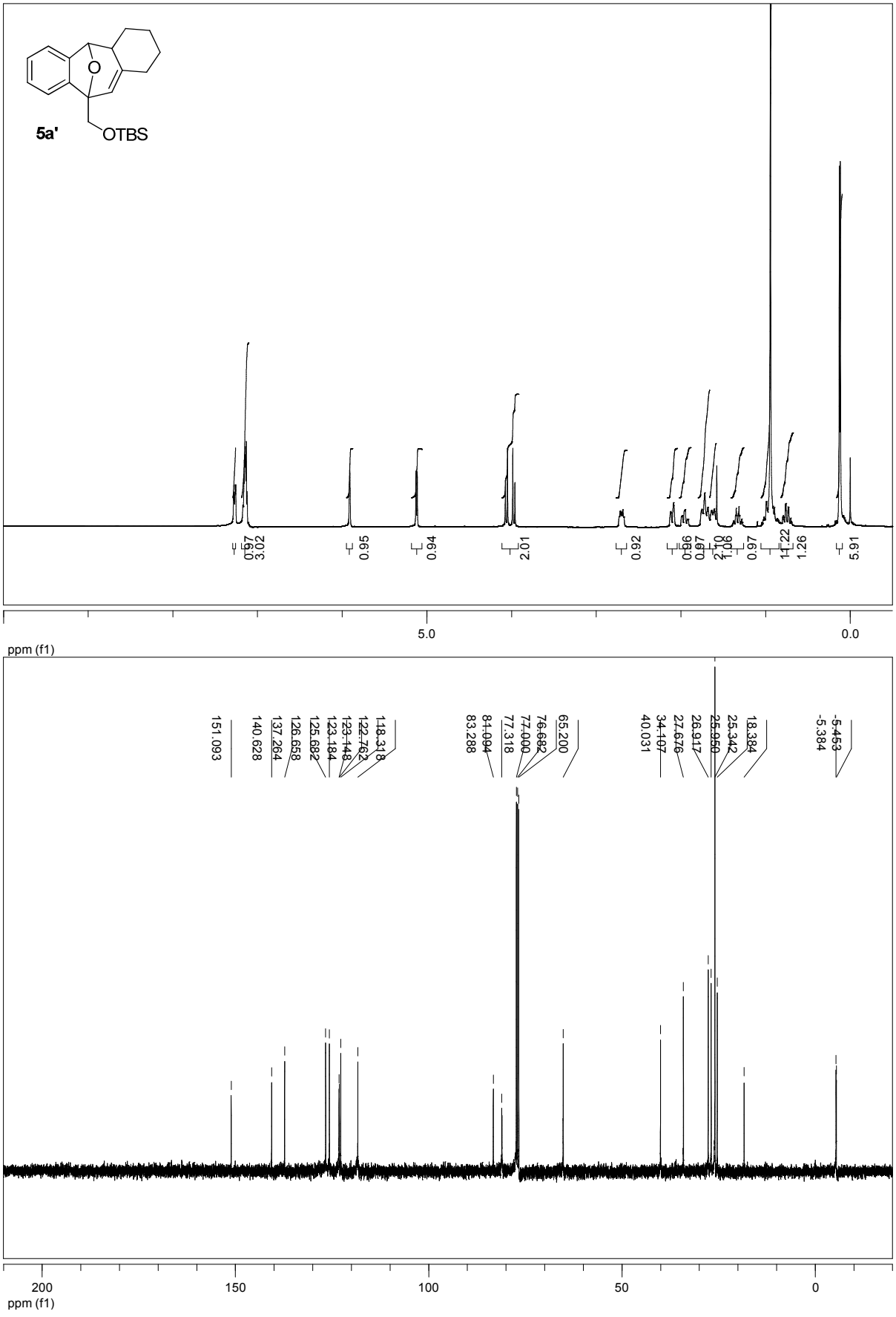
ppm (f1)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5a'
OTBS
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0.96
0.94
2.01
0.92
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0.97
2.10
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11.22
1.26
5.91
5.0
0.0
ppm (f1)
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140.628
137.264
126.658
125.682
123.184
123.148
122.762
118.318
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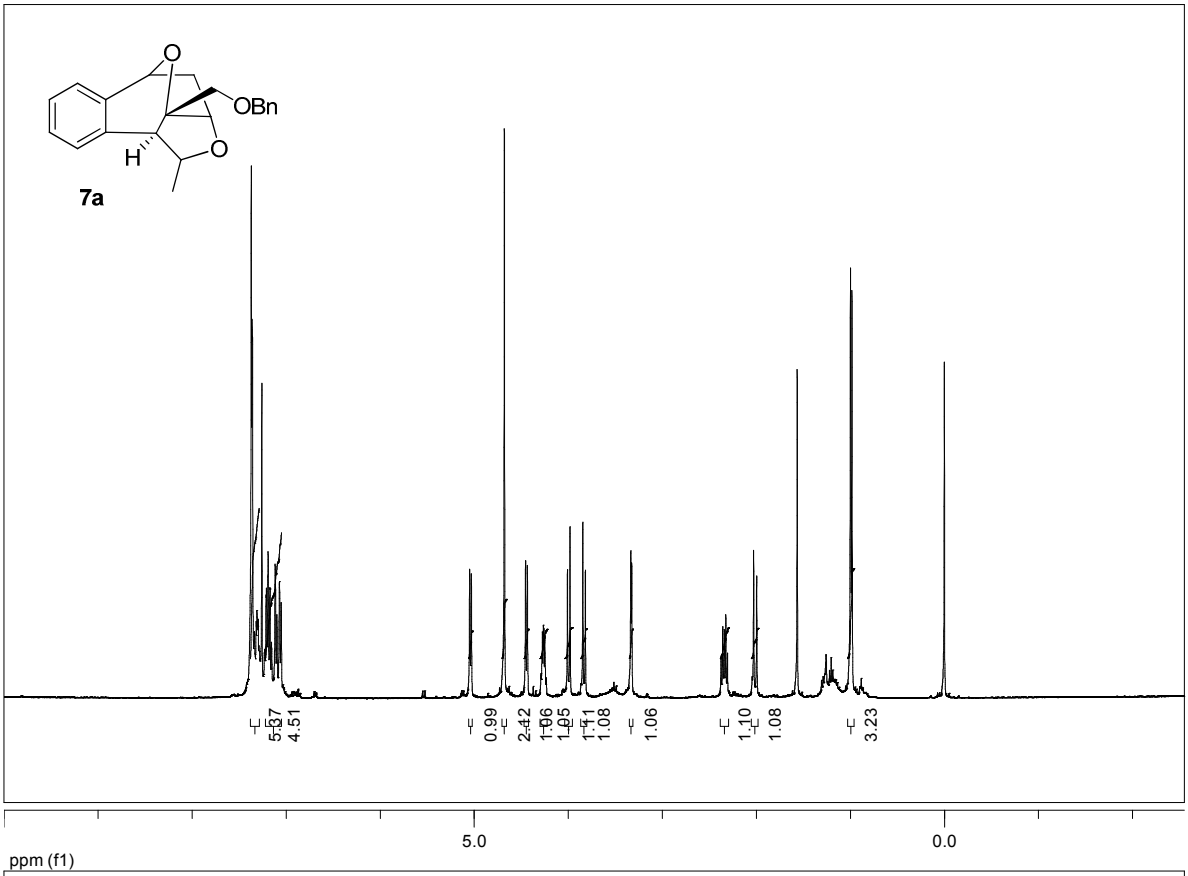
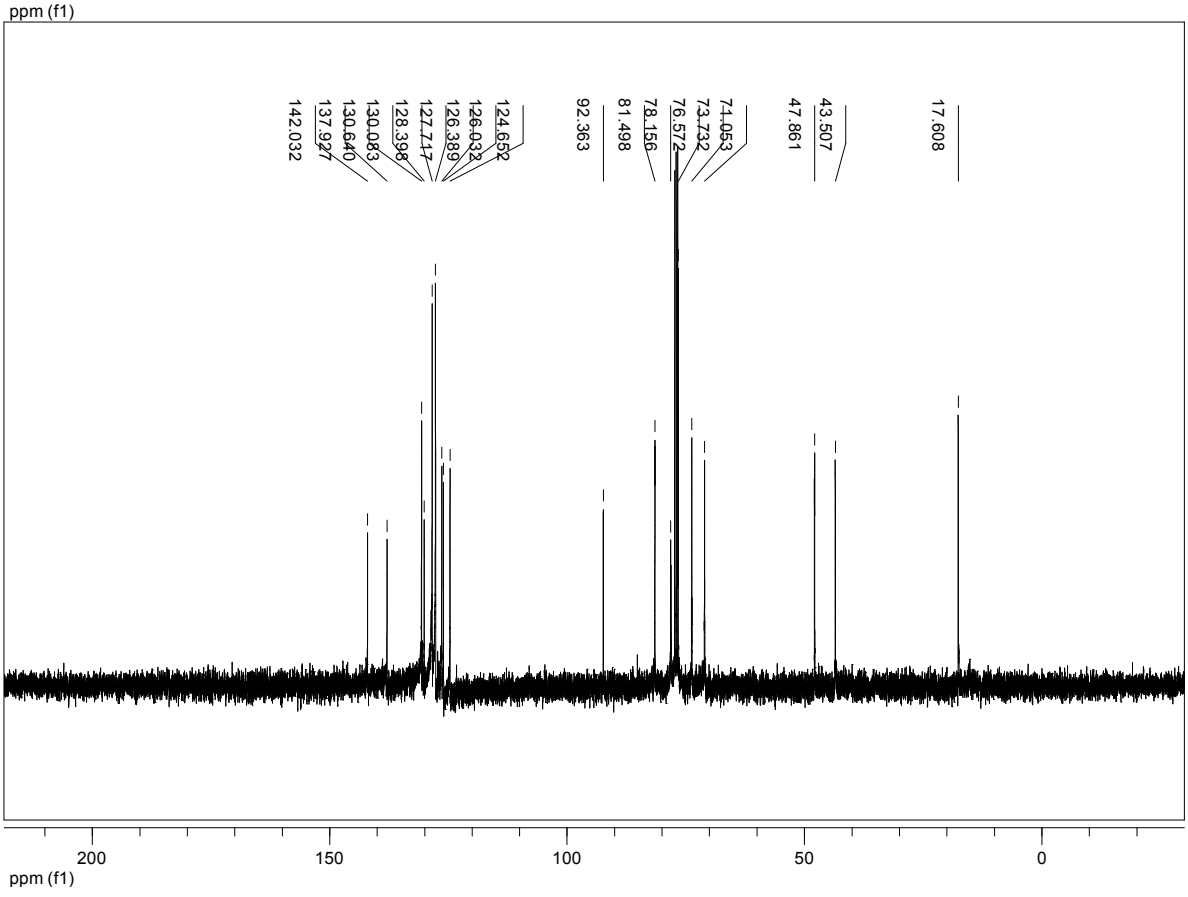
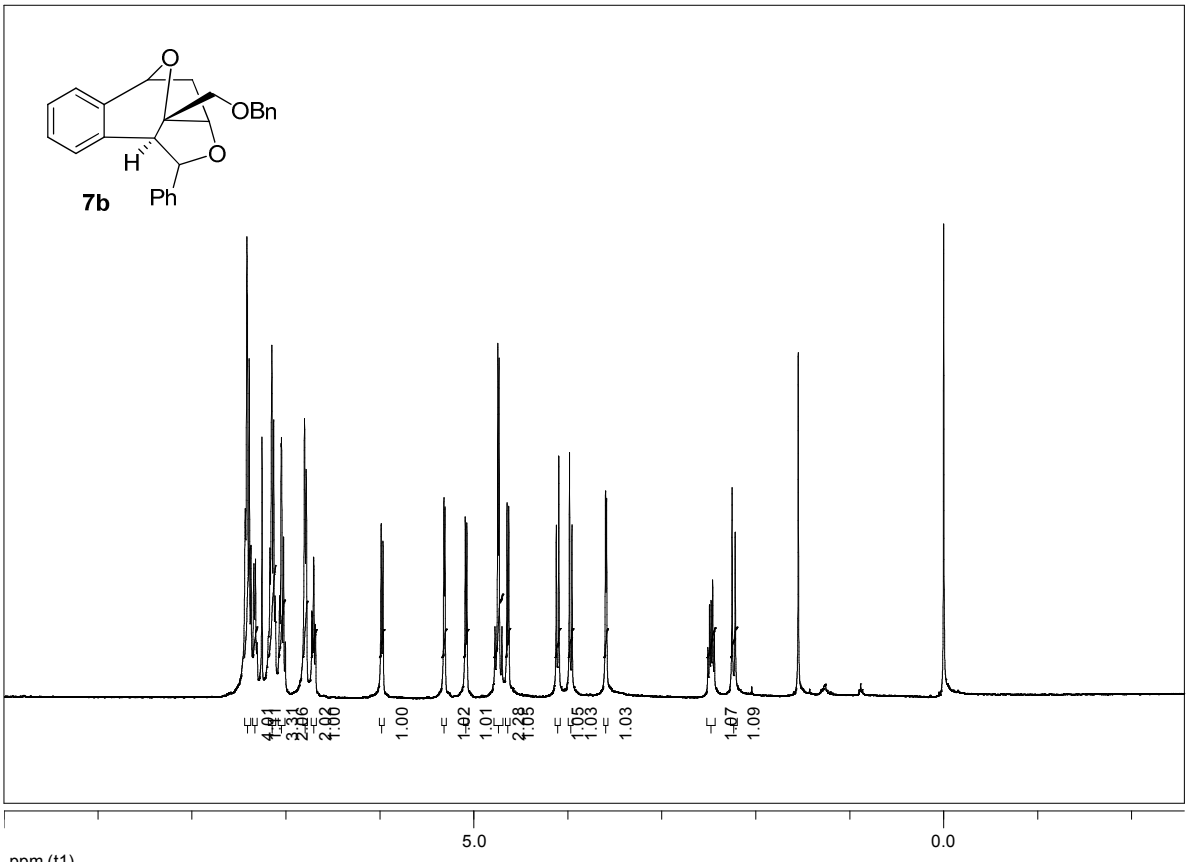
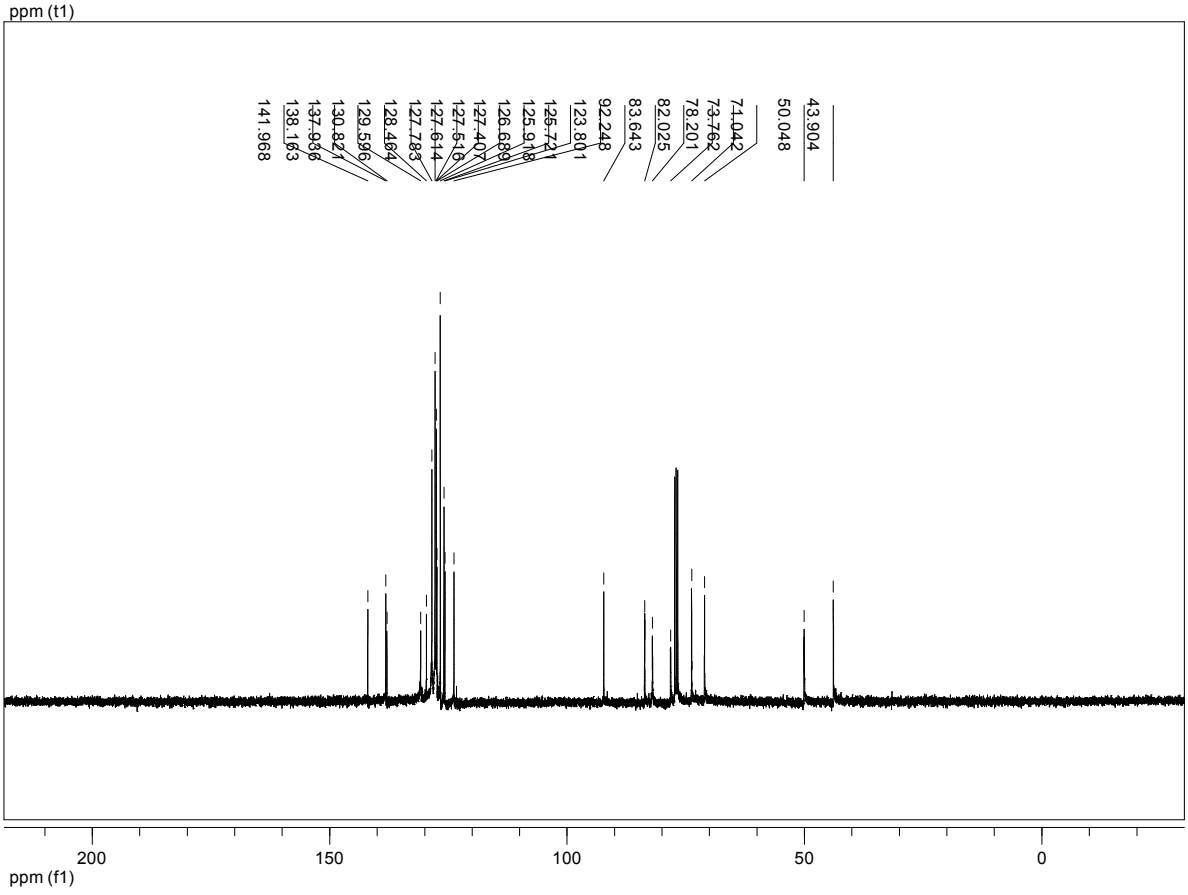
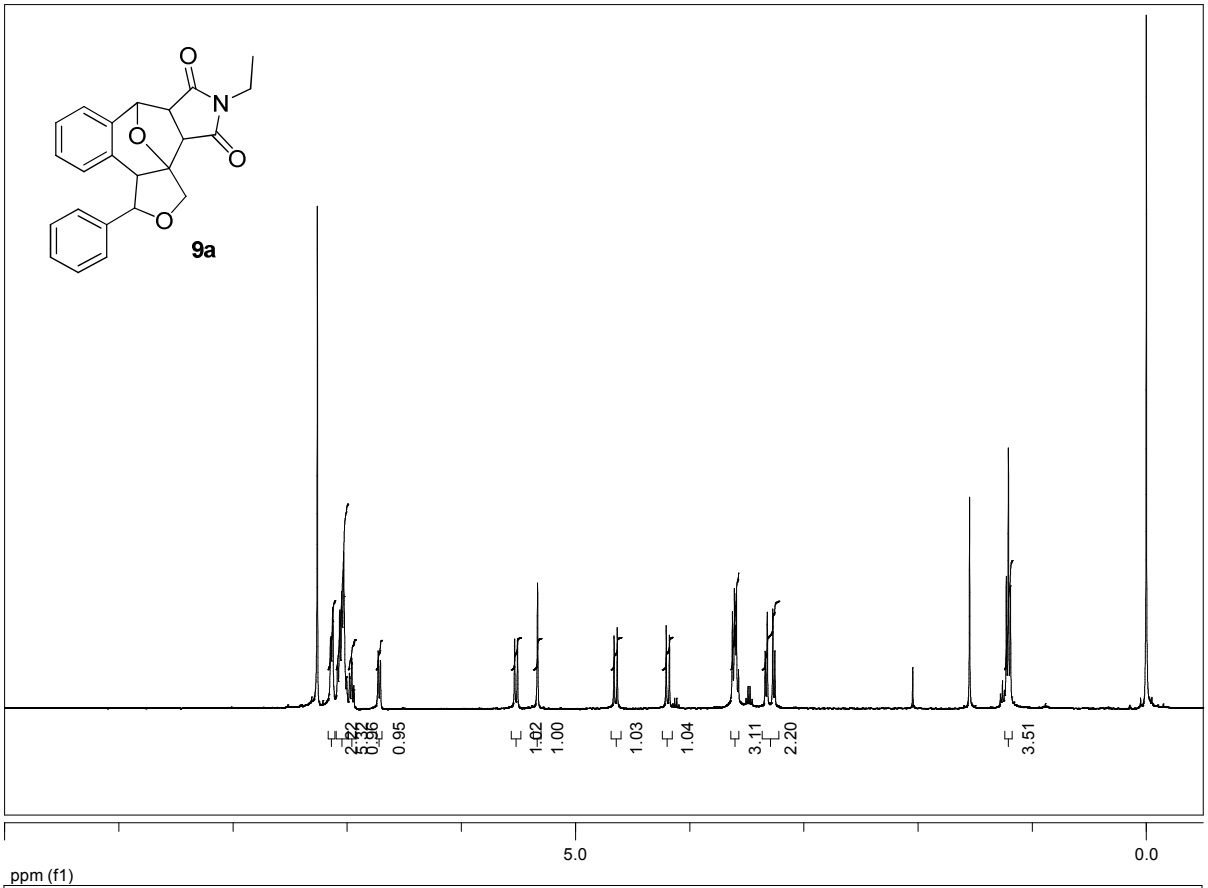
77.000
76.682
65.200
40.031
34.107
27.676
26.917
25.950
25.342
18.384
-5.384
-5.453
200
150
100
50
0
ppm (f1)

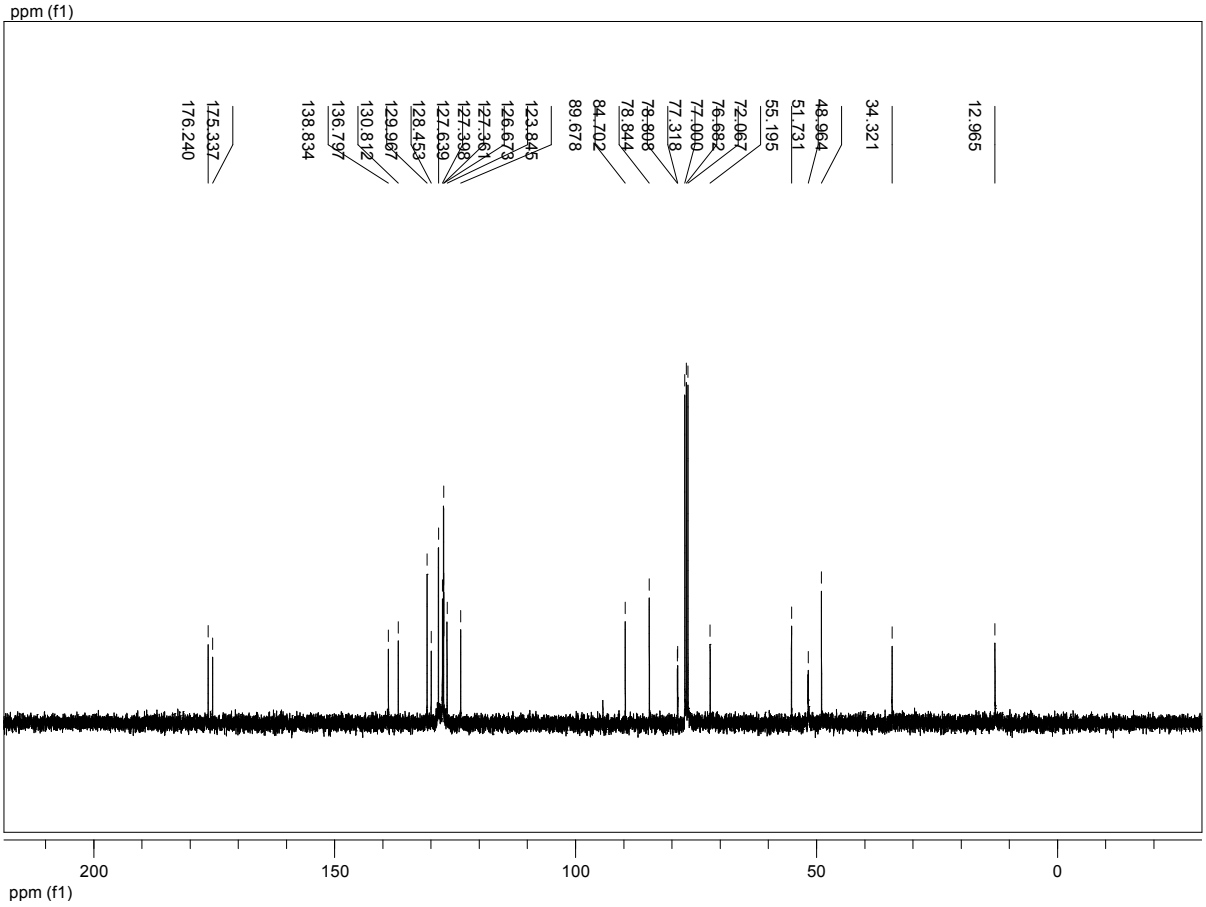

O
OBn
H
O
7a
5.97
4.51
0.99
2.42
1.06
1.05
1.11
1.08
1.06
1.10
1.08
3.23
5.0
0.0
ppm (f1)

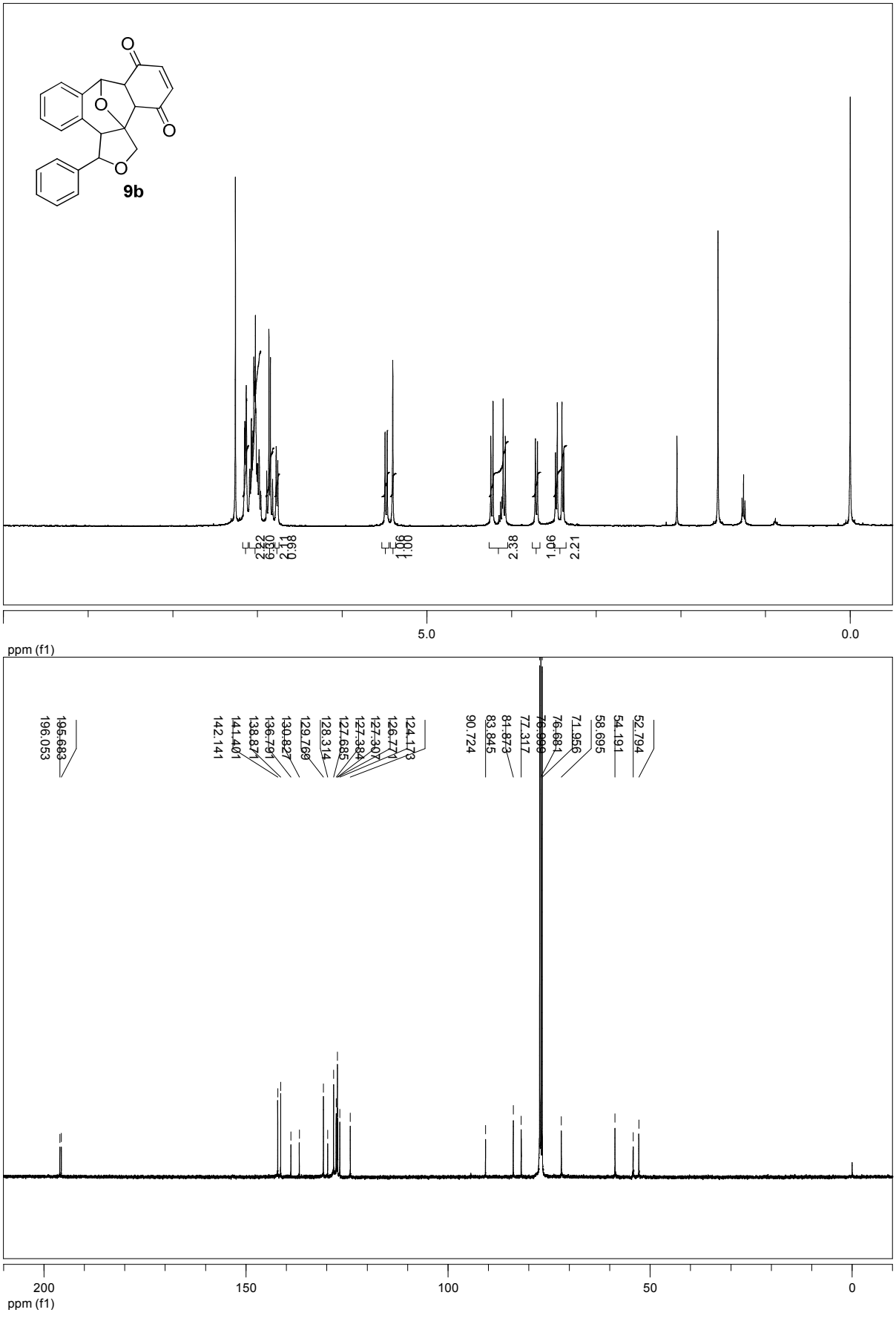

142.032
137.927
130.640
130.083
128.398
127.717
126.389
126.032
124.652
92.363
81.498
78.156
76.572
73.732
71.053
47.861
43.507
17.608
200
150
100
50
0
ppm (f1)

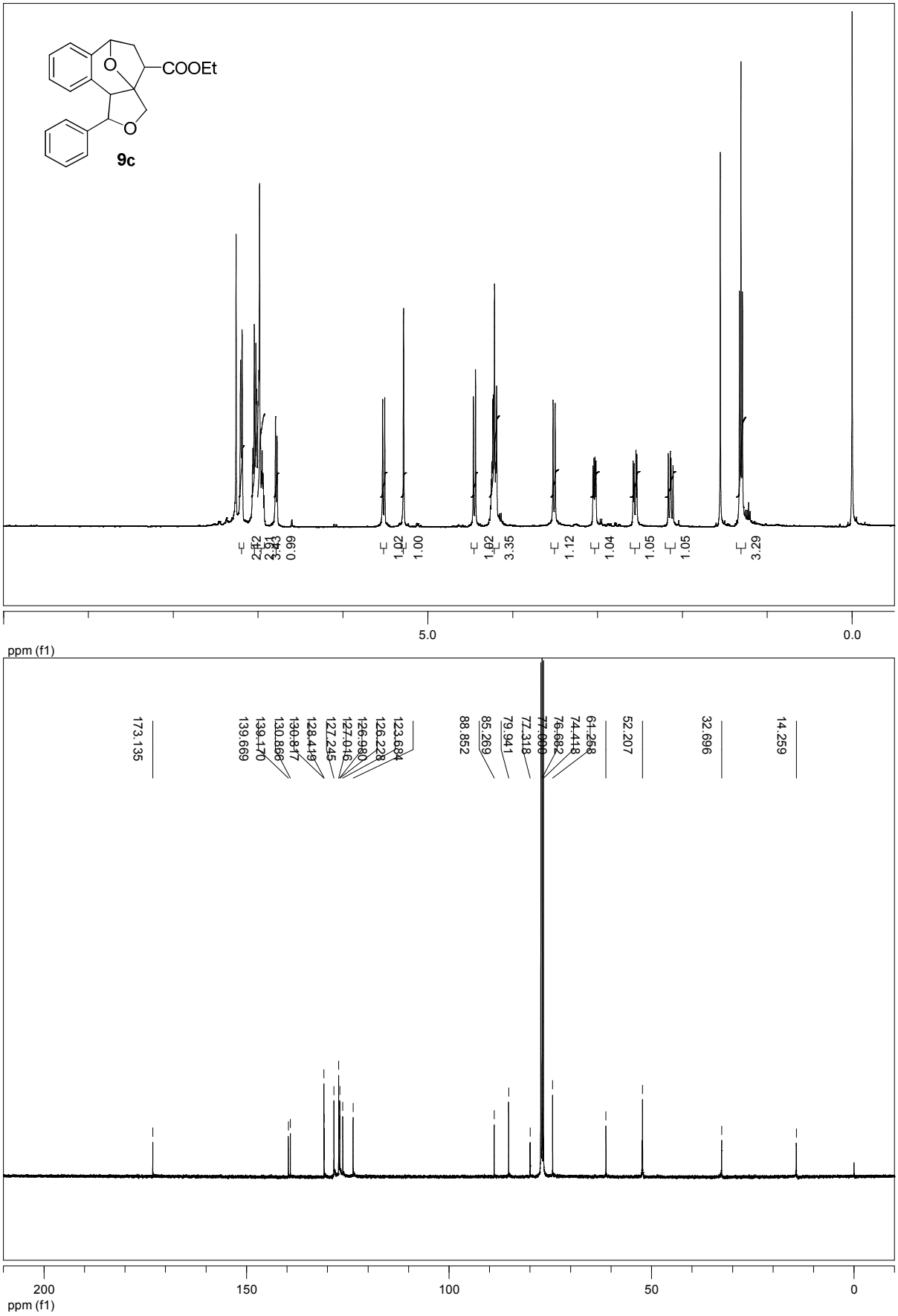

O
OBn
H
O
Ph
7b
4.01
3.31
2.16
2.02
1.00
1.02
1.01
2.28
1.05
1.03
1.03
1.07
1.09
5.0
0.0
ppm (t1)

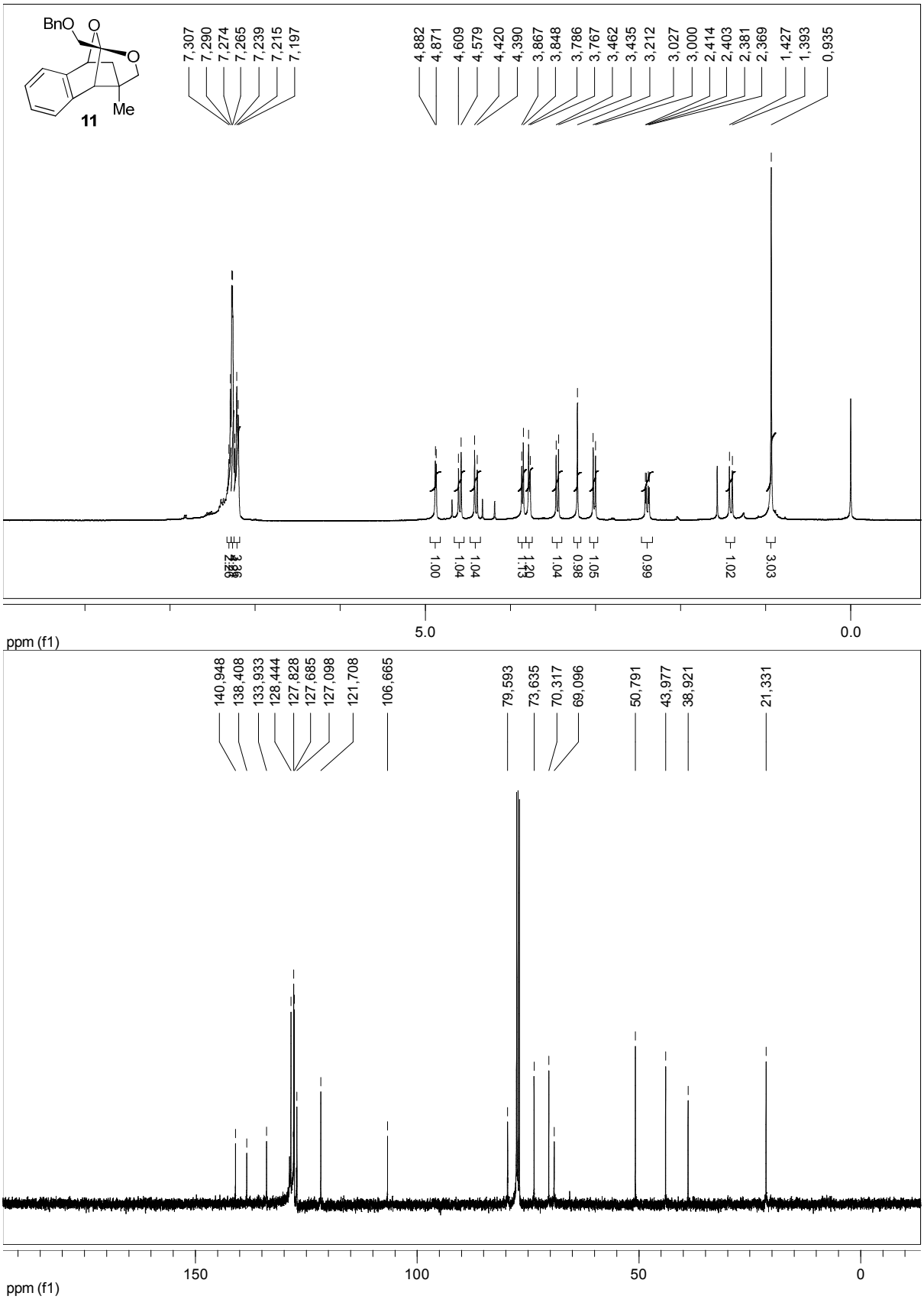

141.968
138.163
137.936
130.821
129.596
128.464
127.783
127.614
127.518
127.407
126.688
125.918
125.721
123.801
92.248
83.643
82.025
79.201
73.762
71.042
50.048
43.904
200
150
100
50
0
ppm (f1)


9a
0.95
1.02
1.00
1.03
1.04
3.11
2.20
3.51
5.0
0.0
ppm (f1)


176.240
175.337
138.834
136.797
130.812
129.967
128.453
127.639
89.678
84.702
78.844
77.318
55.195
51.731
48.964
34.321
12.965
200
150
100
50
0
ppm (f1)


9b
2.32
6.50
2.11
0.98
1.06
1.00
2.38
1.06
2.21
5.0
0.0
ppm (f1)
196.053
195.683
142.141
141.401
138.871
136.791
130.827
129.769
128.314
127.685
127.384
127.307
126.774
124.173
90.724
83.845
81.873
77.317
76.681
71.956
58.695
54.191
52.794
200
150
100
50
0
ppm (f1)


COOEt
O
O
9c
2.52
2.51
2.43
0.99
1.02
1.00
1.02
3.35
1.12
1.04
1.05
1.05
3.29
5.0
0.0
ppm (f1)
173.135
139.669
139.170
130.866
130.817
128.419
127.245
127.016
126.980
126.228
123.684
88.852
85.269
79.941
77.318
77.000
76.682
74.418
61.268
52.207
32.696
14.259
200
150
100
50
0
ppm (f1)


BnO
O
O
Me
11
7,307
7,290
7,274
7,265
7,239
7,215
7,197
4,882
4,871
4,609
4,579
4,420
4,390
3,867
3,848
3,786
3,767
3,462
3,435
3,212
3,027
3,000
2,414
2,403
2,381
2,369
1,427
1,393
0,935
1,00
1,04
1,04
1,19
1,04
0,98
1,05
0,99
2,02
3,03
5.0
0.0
ppm (f1)
140,948
138,408
133,933
128,444
127,828
127,685
127,098
121,708
106,665
79,593
73,635
70,317
69,096
50,791
43,977
38,921
21,331
150
100
50
0
ppm (f1)