Electronic Supplementary Material (ESI) for RSC Advances.

Electronic supplementary information for:

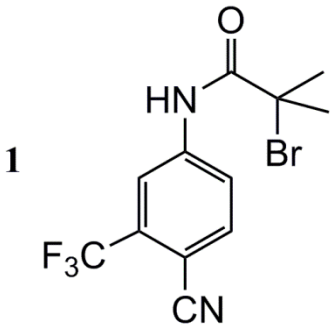
Bromo–nitro substitution on a tertiary α carbon—a previously uncharacterized facet of the Kornblum substitution

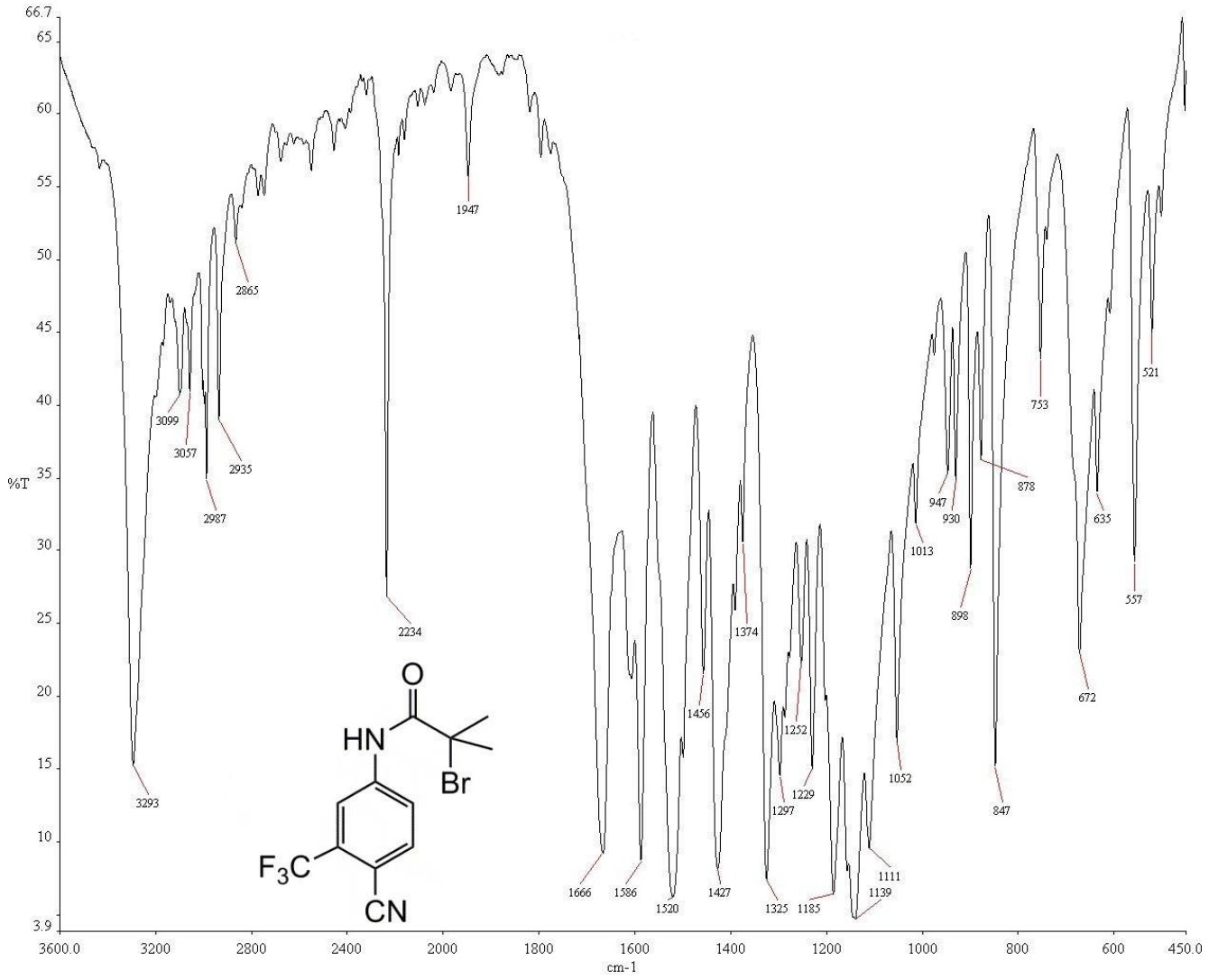
By Matthew J. Leonard, Peter G. McKay and Anthony R. Lingham.

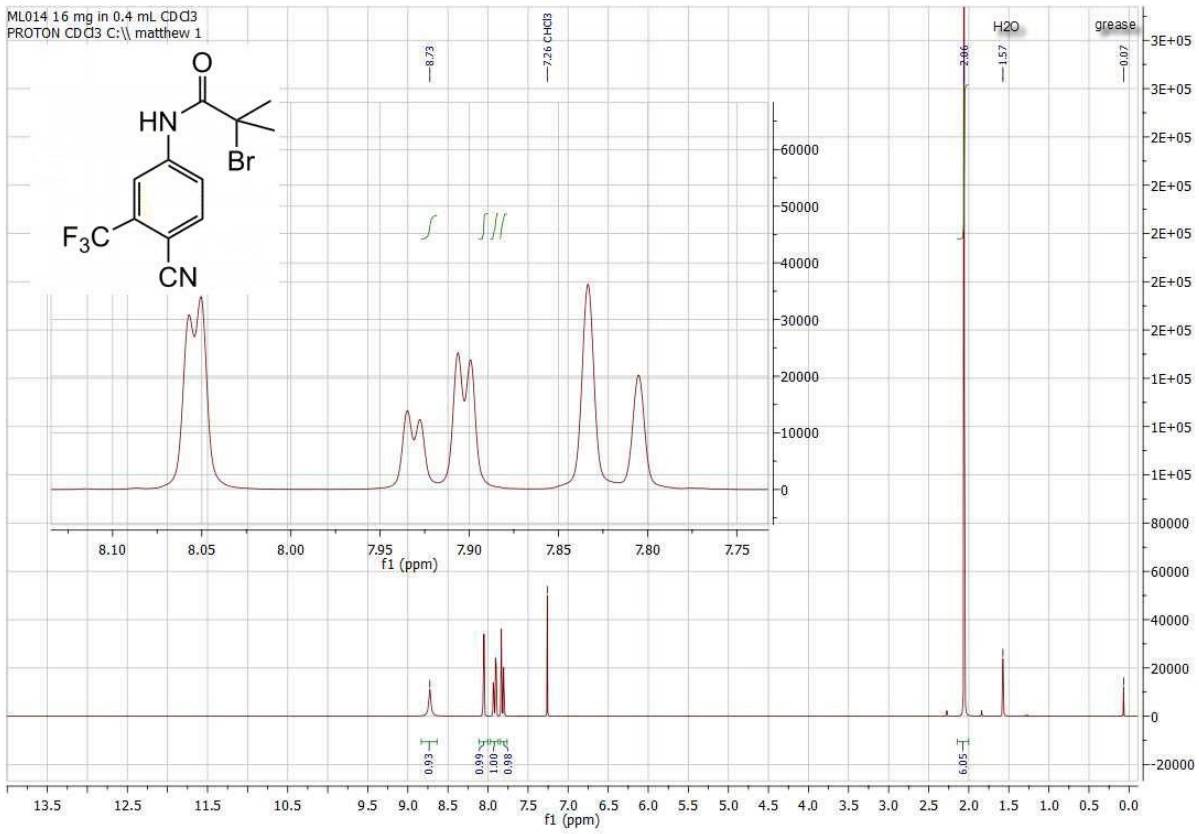
The infra red spectra of compounds **1** and **2** were taken using the KBr disc method.

NMR conditions are given below each spectrum.

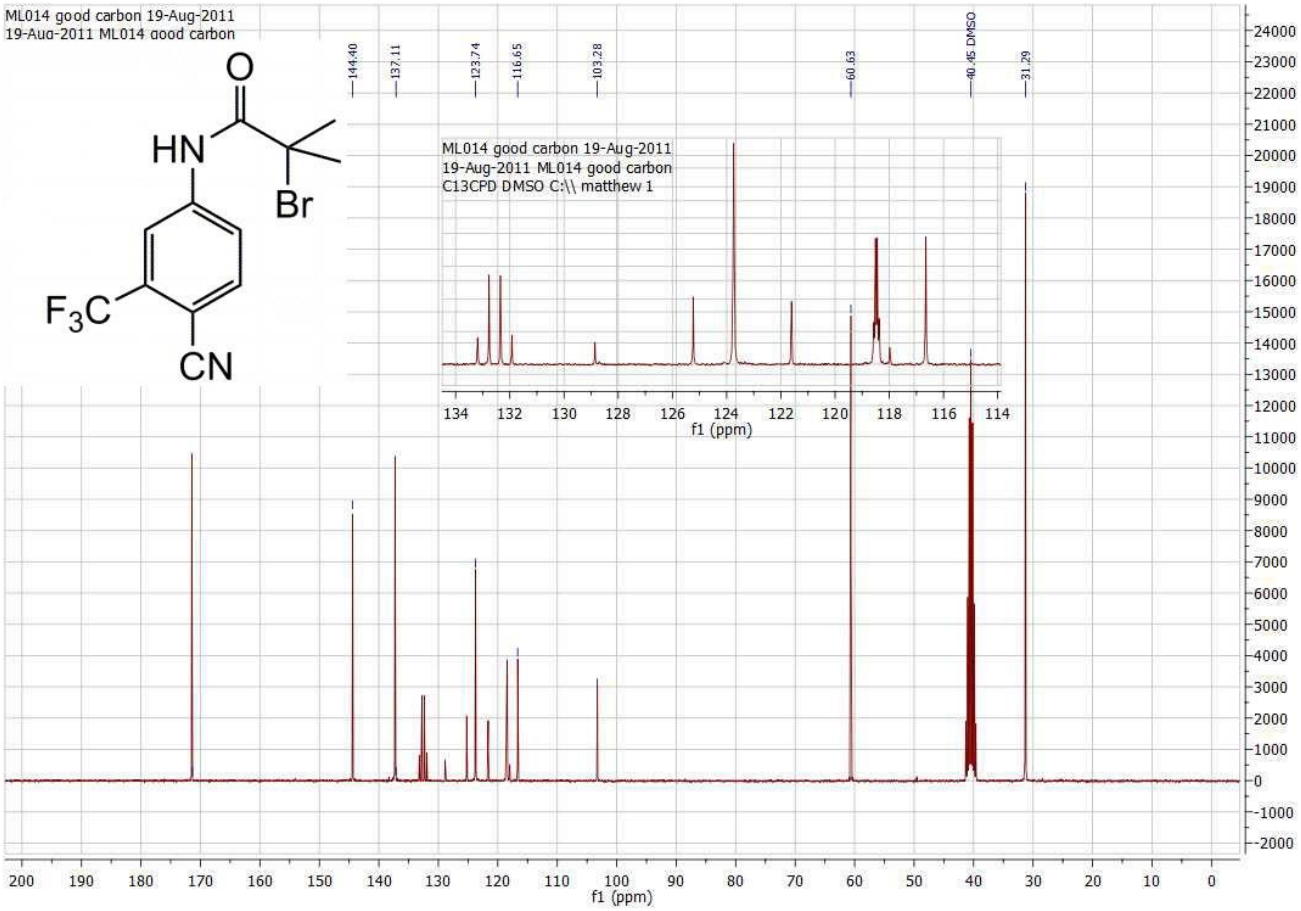
1







20 mg of **1** in 0.4 mL $CDCl_3$, 300 MHz, 256 scans

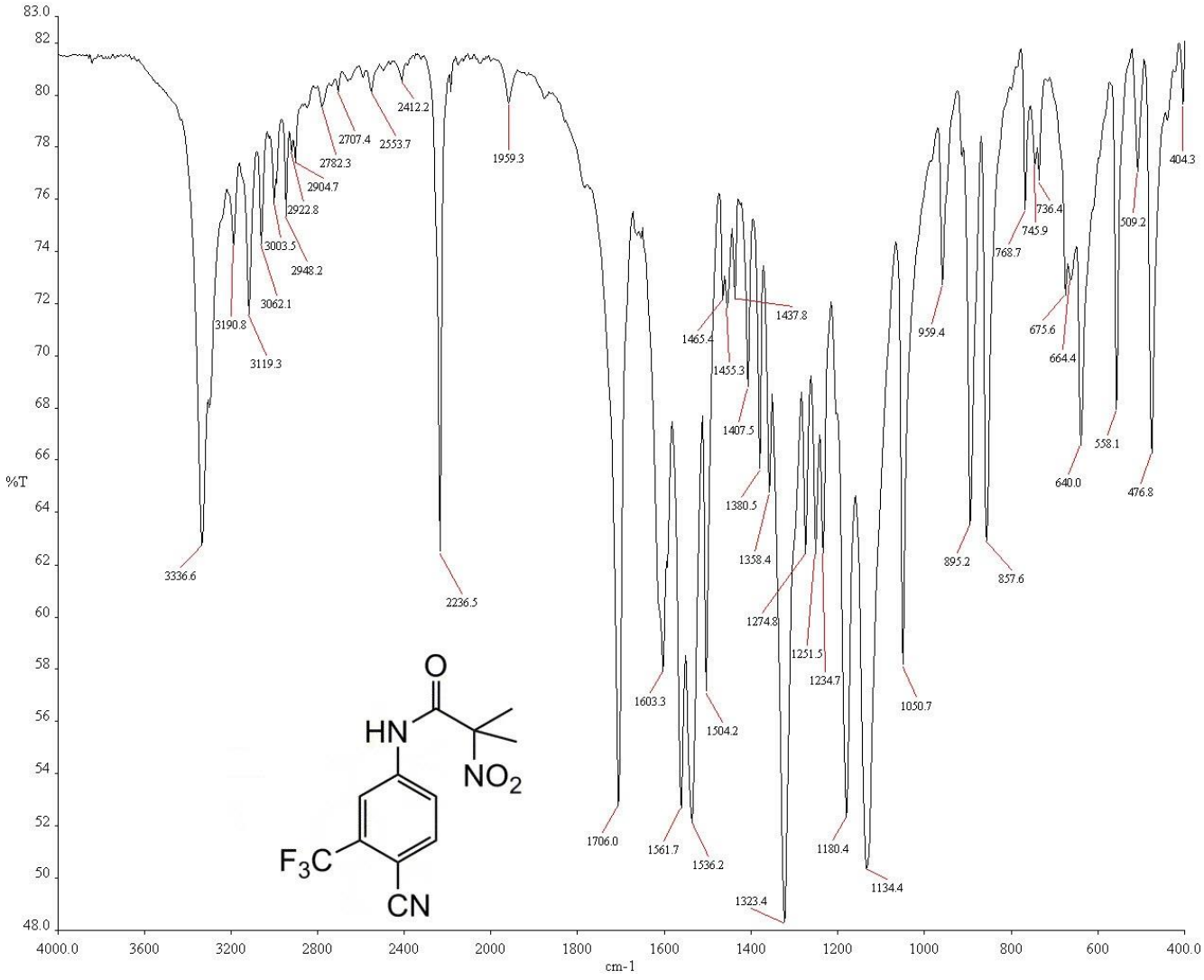


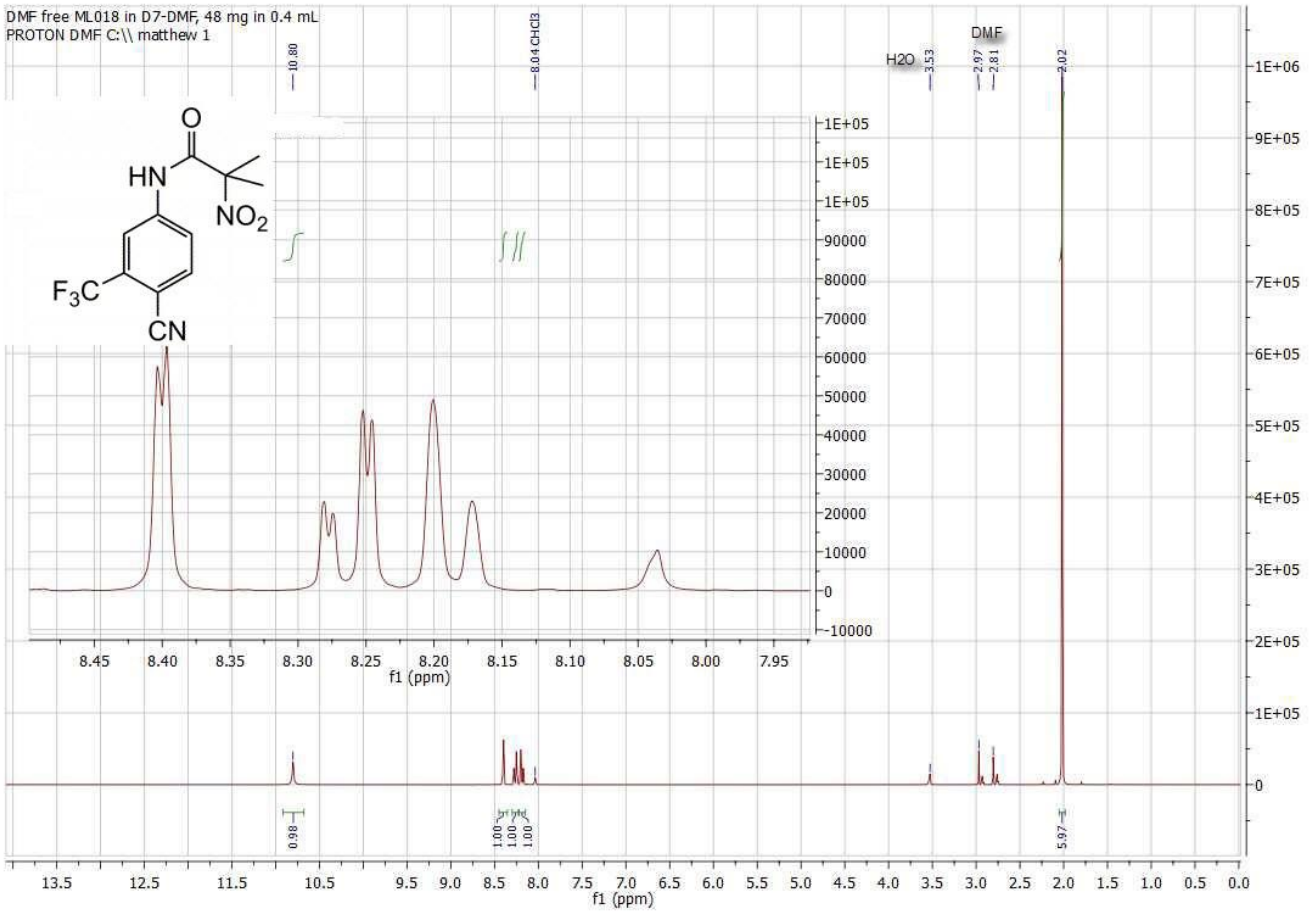
40 mg of **1** in 0.4 mL d_6-DMSO, 75 MHz, 2048 scans

ESI for:

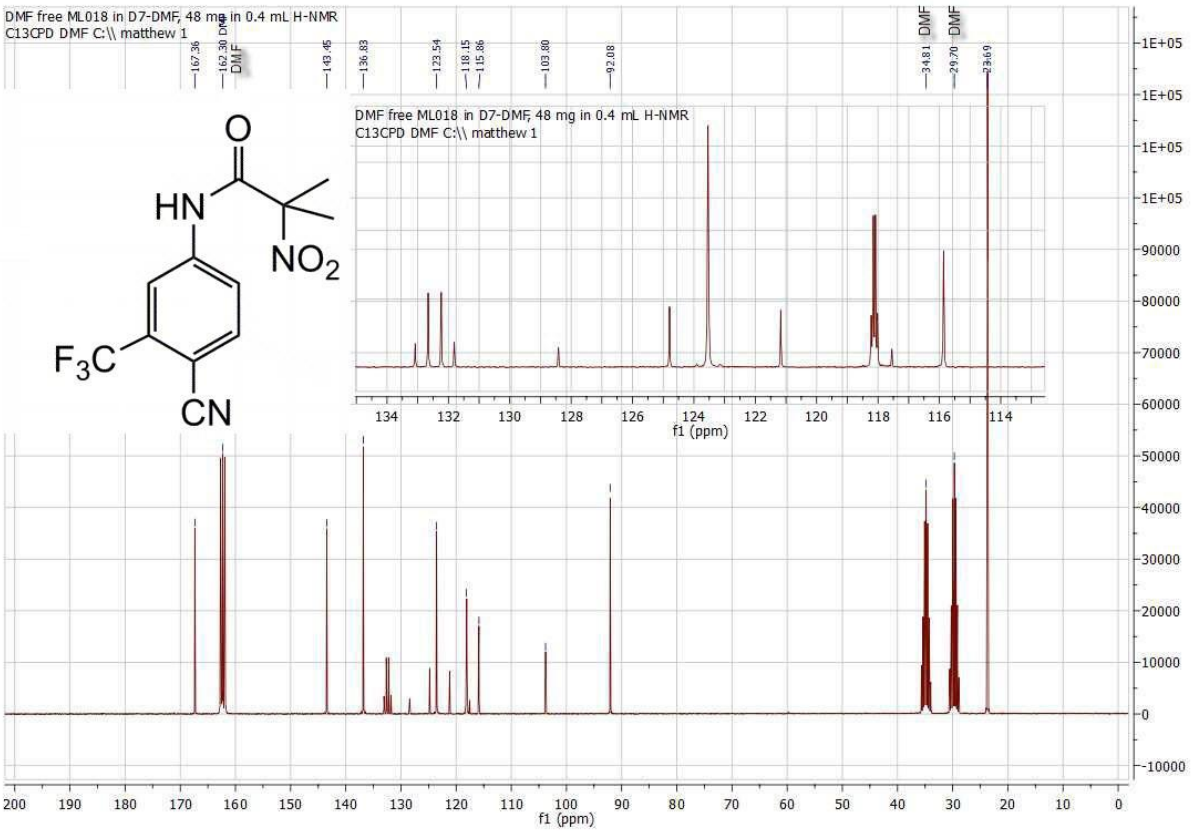
Bromo–nitro substitution on a tertiary α carbon—a previously uncharacterized facet of the Kornblum substitution

2





48 mg of **2** in 0.4 mL d_7-DMF, 300 MHz, 256 scans

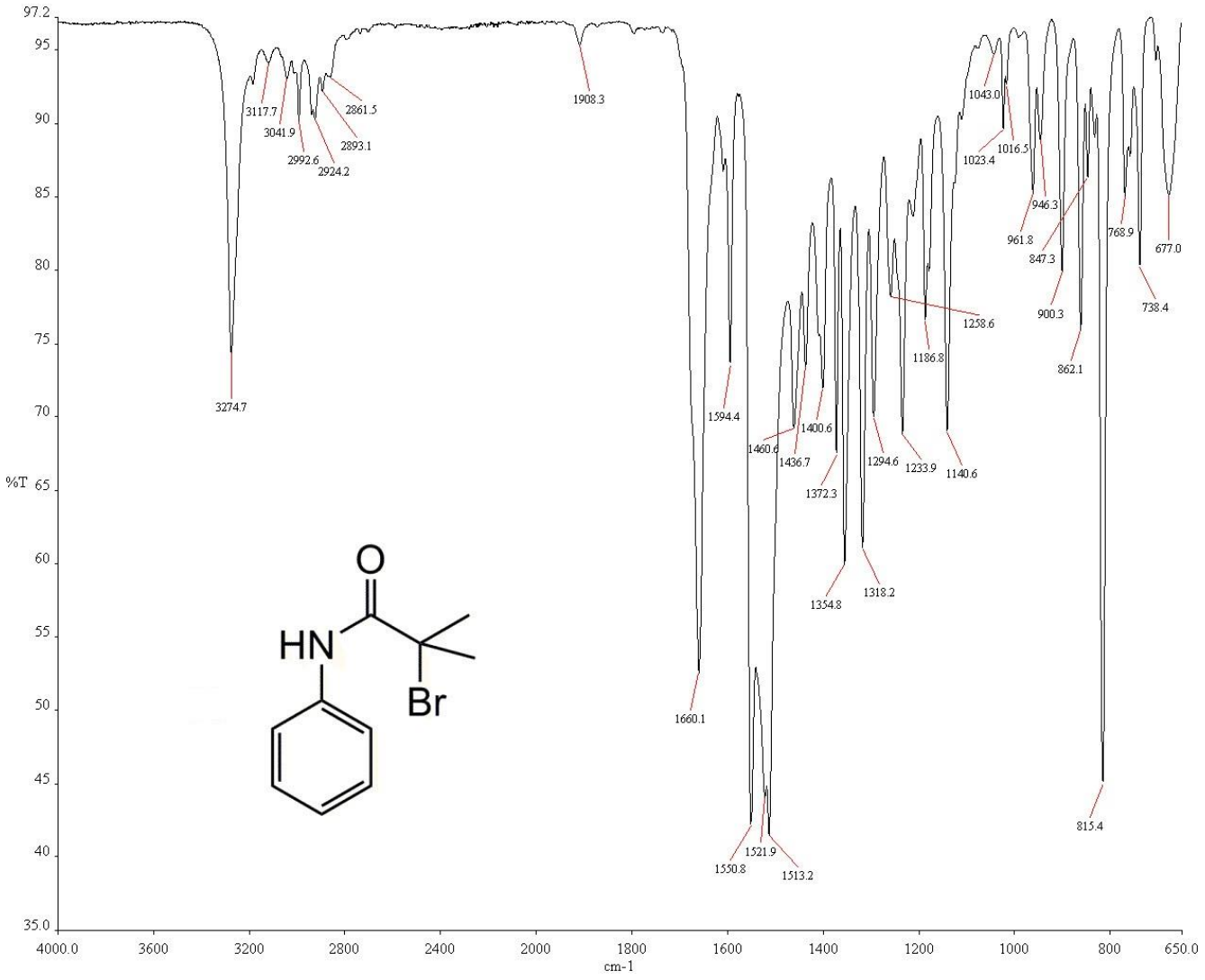


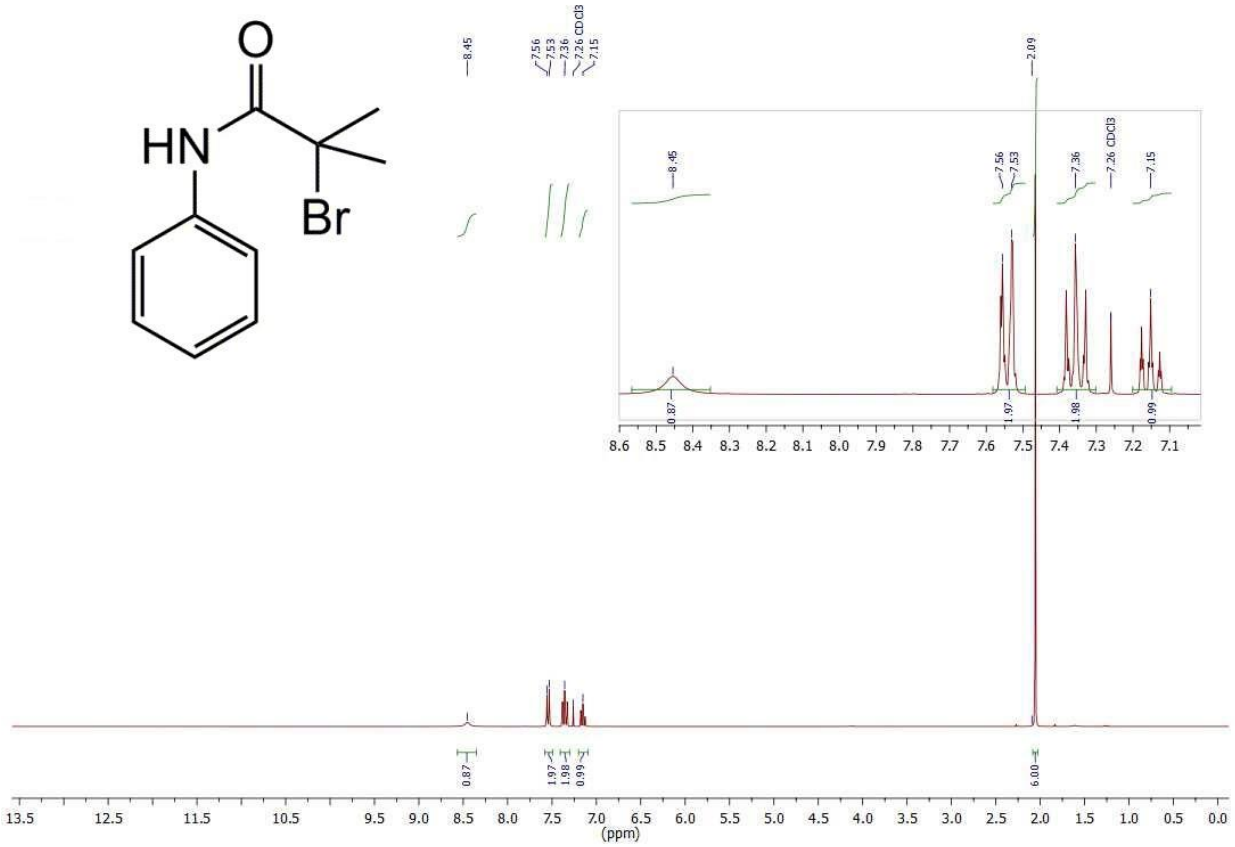
48 mg of **2** in 0.4 mL d_7-DMF, 75 MHz, 20000 scans

All infra red spectra from here on were taken using the diamond ATR method.

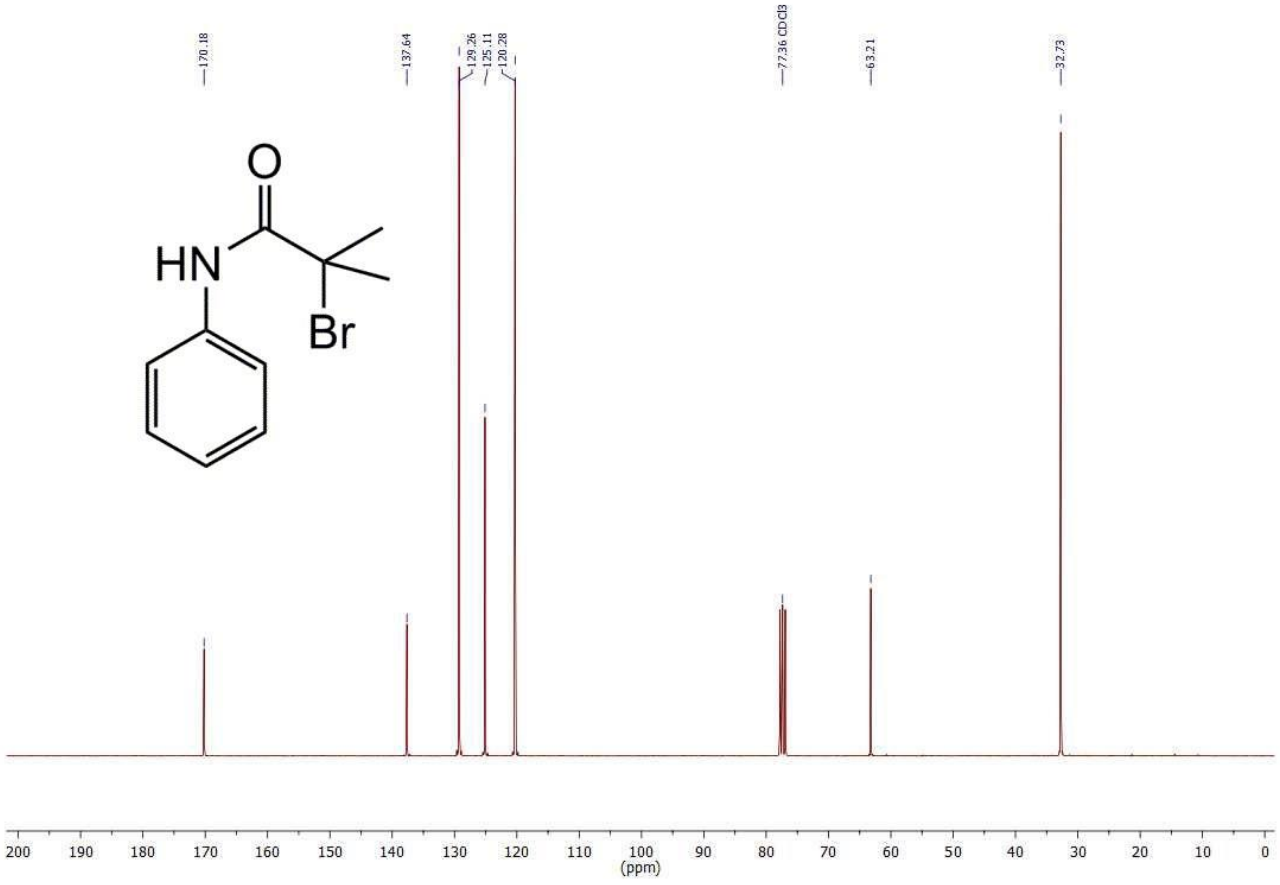
NMR conditions are given below each spectrum.

5



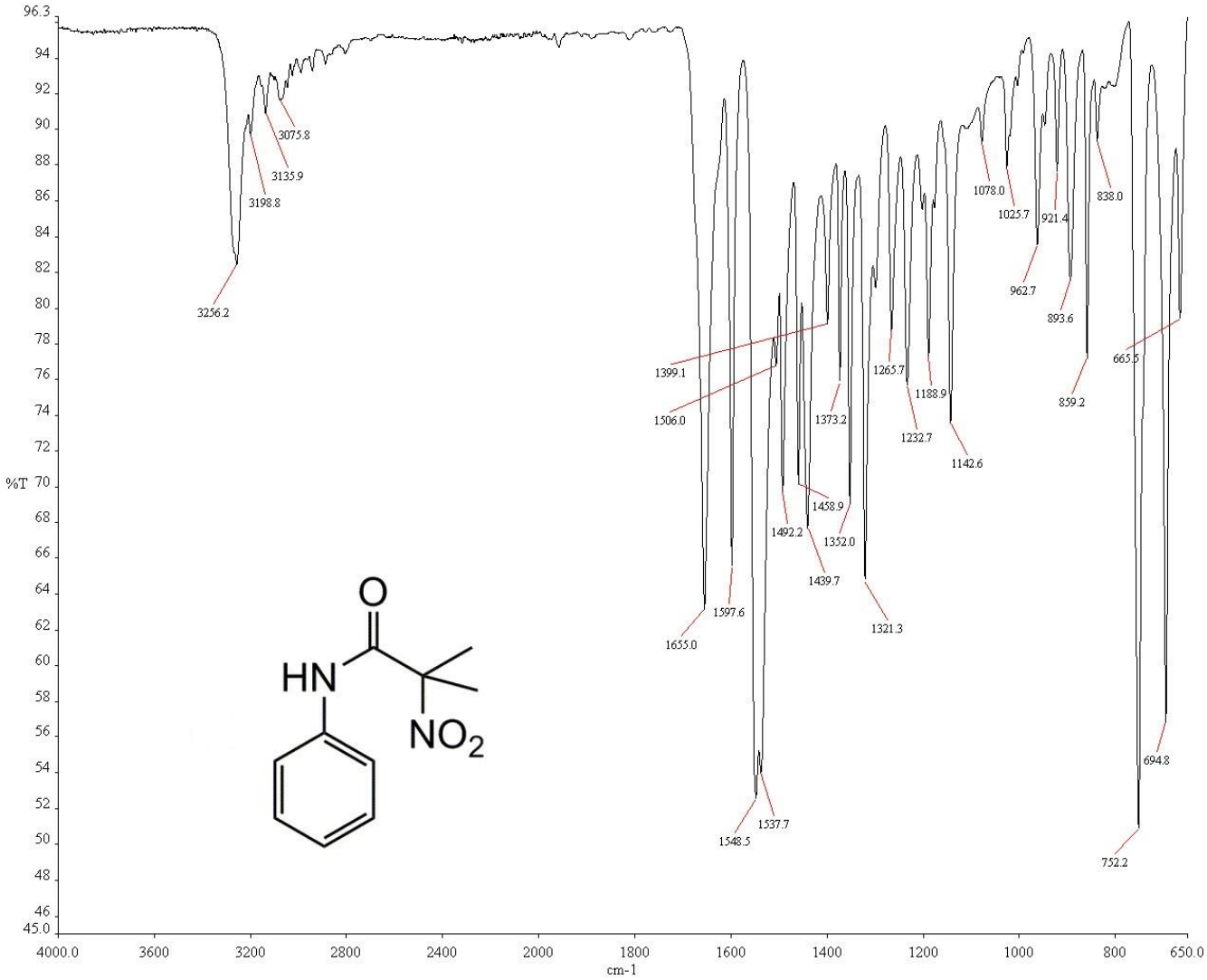


26 mg of **5** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans



137 mg of **5** in 0.4 mL $CDCl_3$, 75 MHz, 21737 scans

6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88
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84
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76
74
72
70
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64
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60
58
56
54
52
50
48
46
45.0
3256.2
3198.8
3135.9
3075.8
1655.0
1597.6
1548.5
1537.7
1506.0
1492.2
1458.9
1439.7
1399.1
1373.2
1352.0
1321.3
1265.7
1232.7
1188.9
1142.6
1078.0
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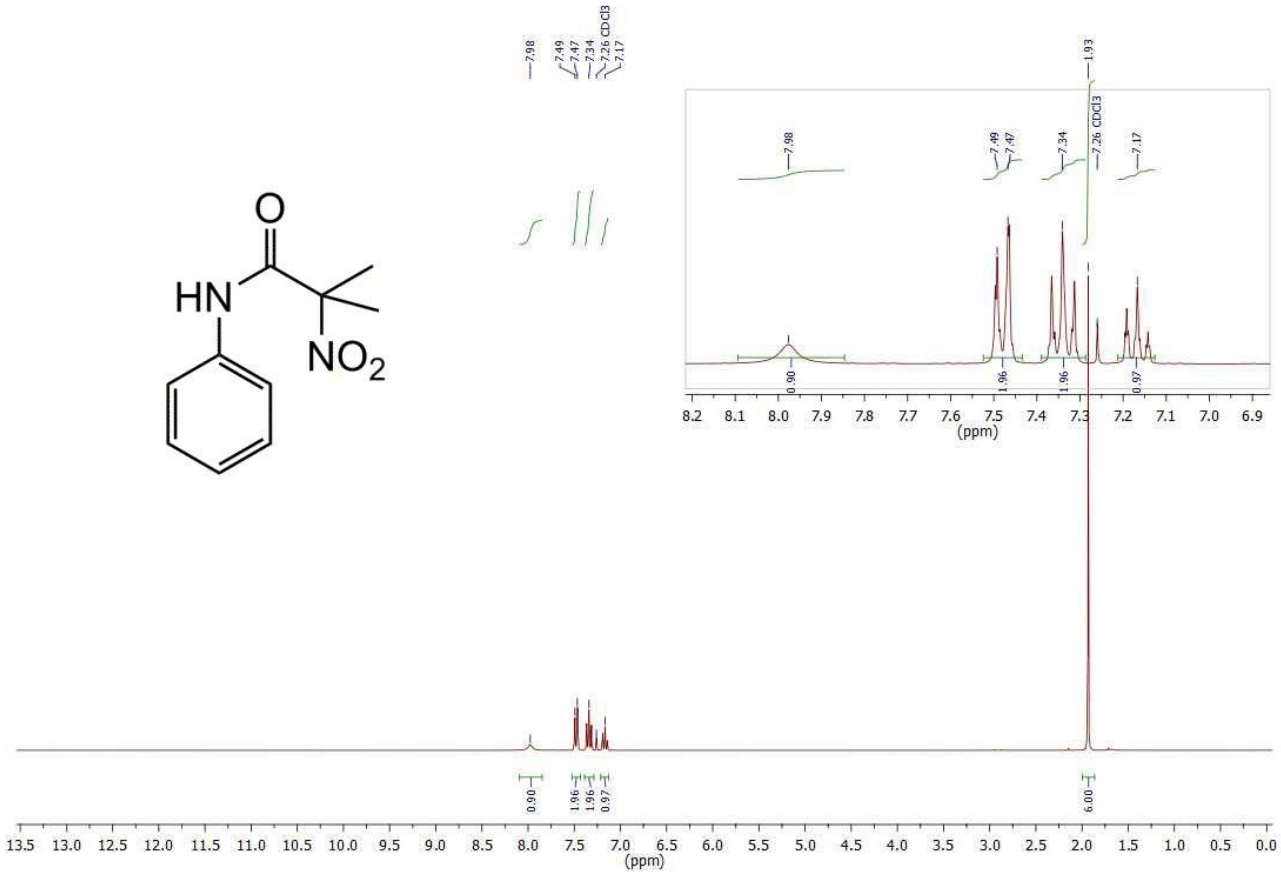
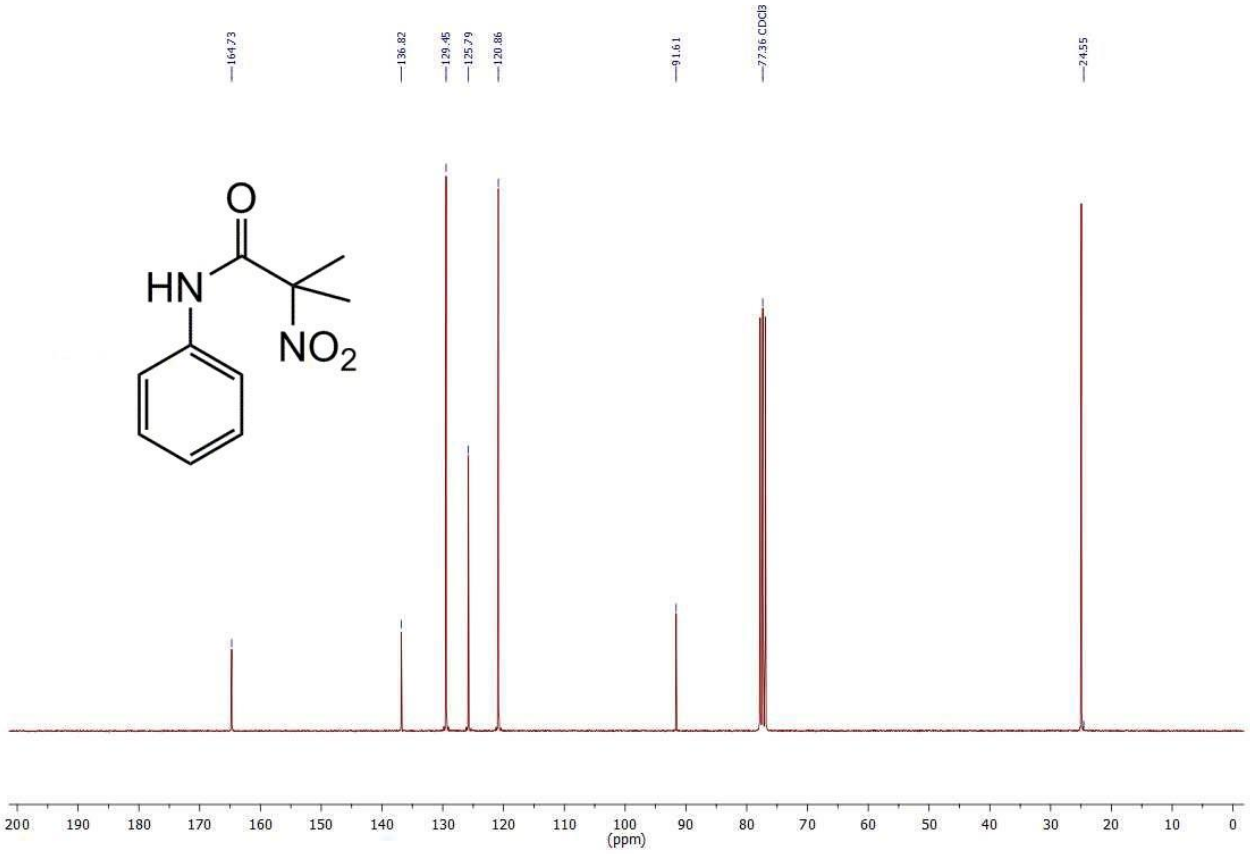
752.2
694.8
665.5
HN
O
NO2

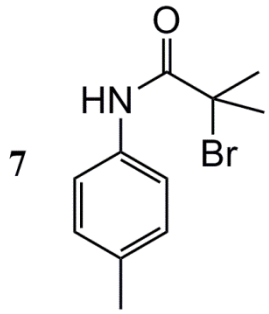


26 mg of **6** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans

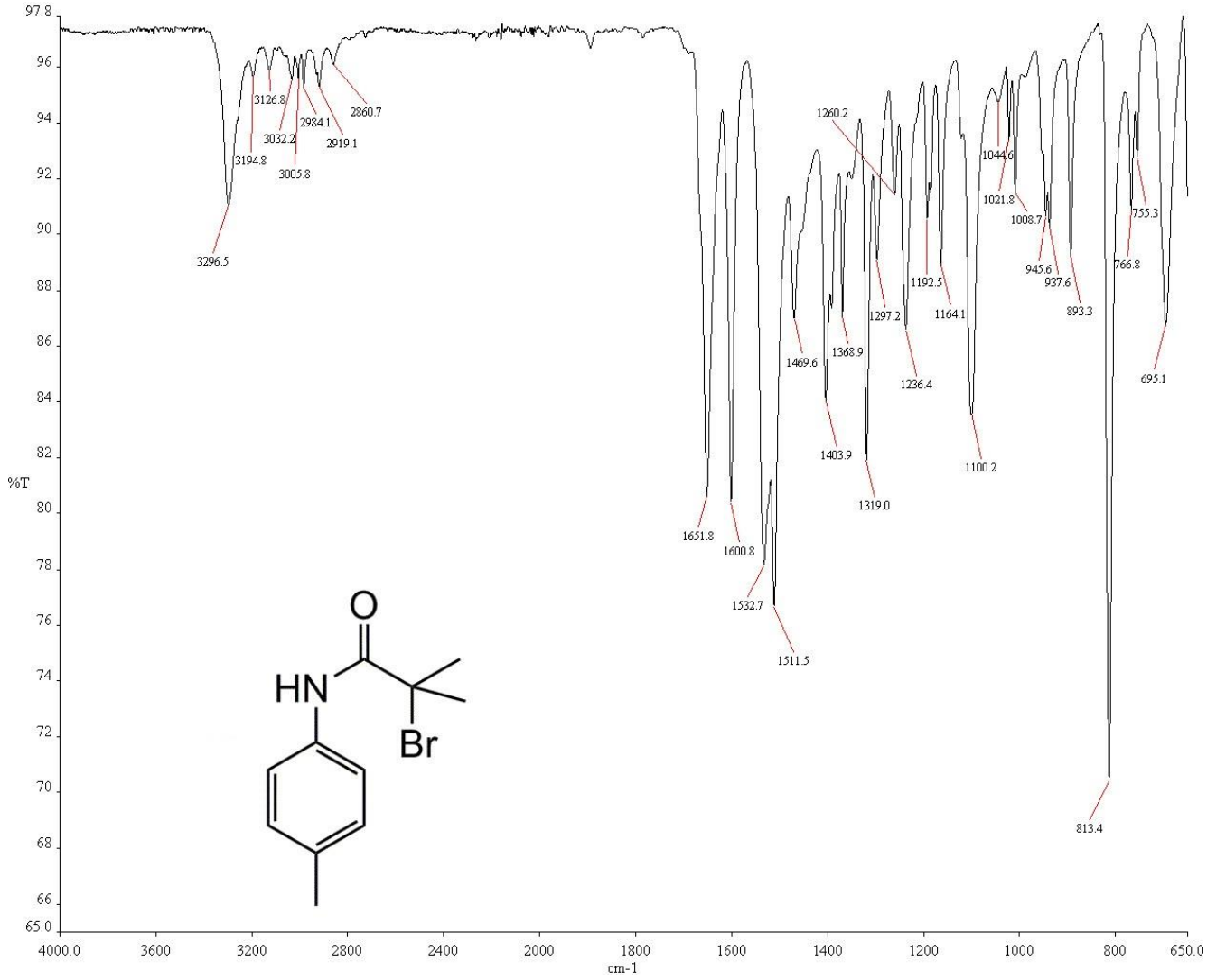


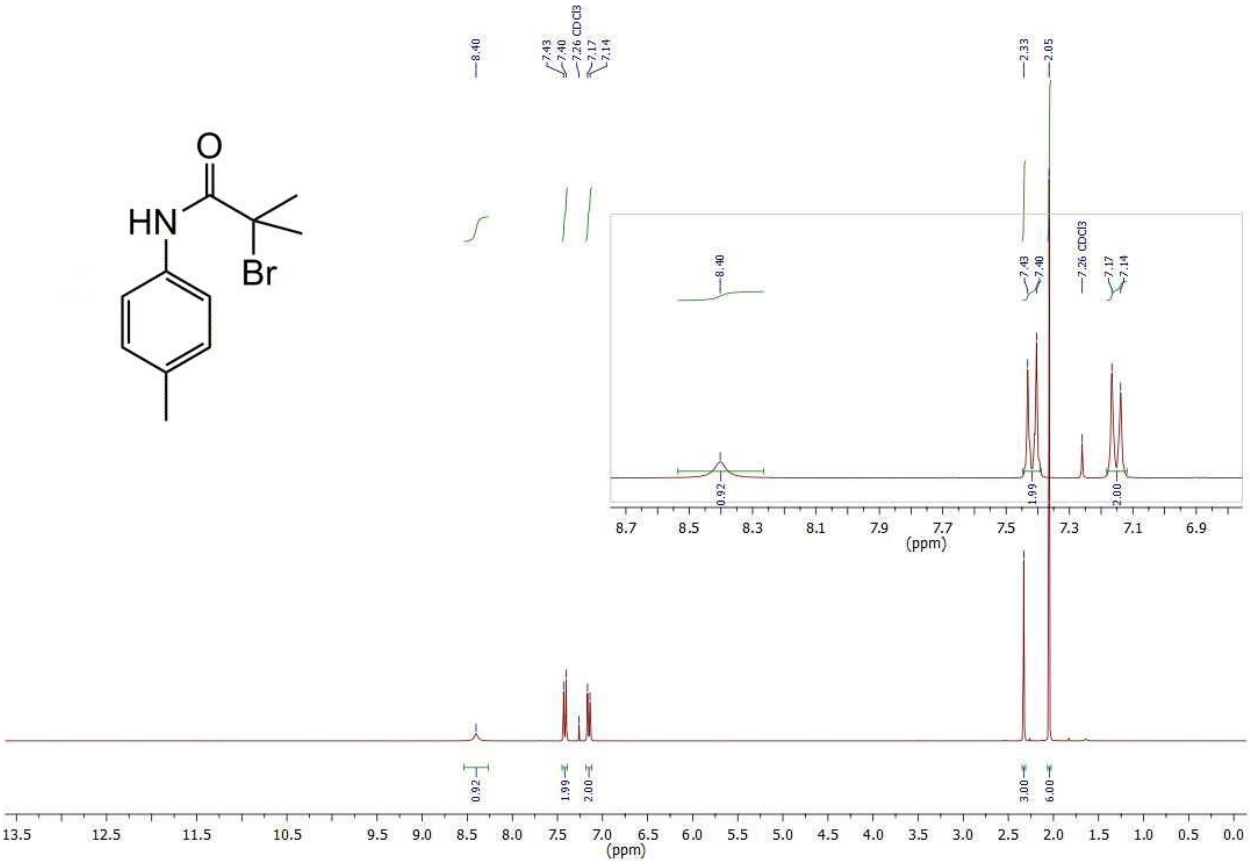
26 mg of **6** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

ESI for:
Bromo–nitro substitution on a tertiary α carbon—a previously uncharacterized facet of the Kornblum substitution

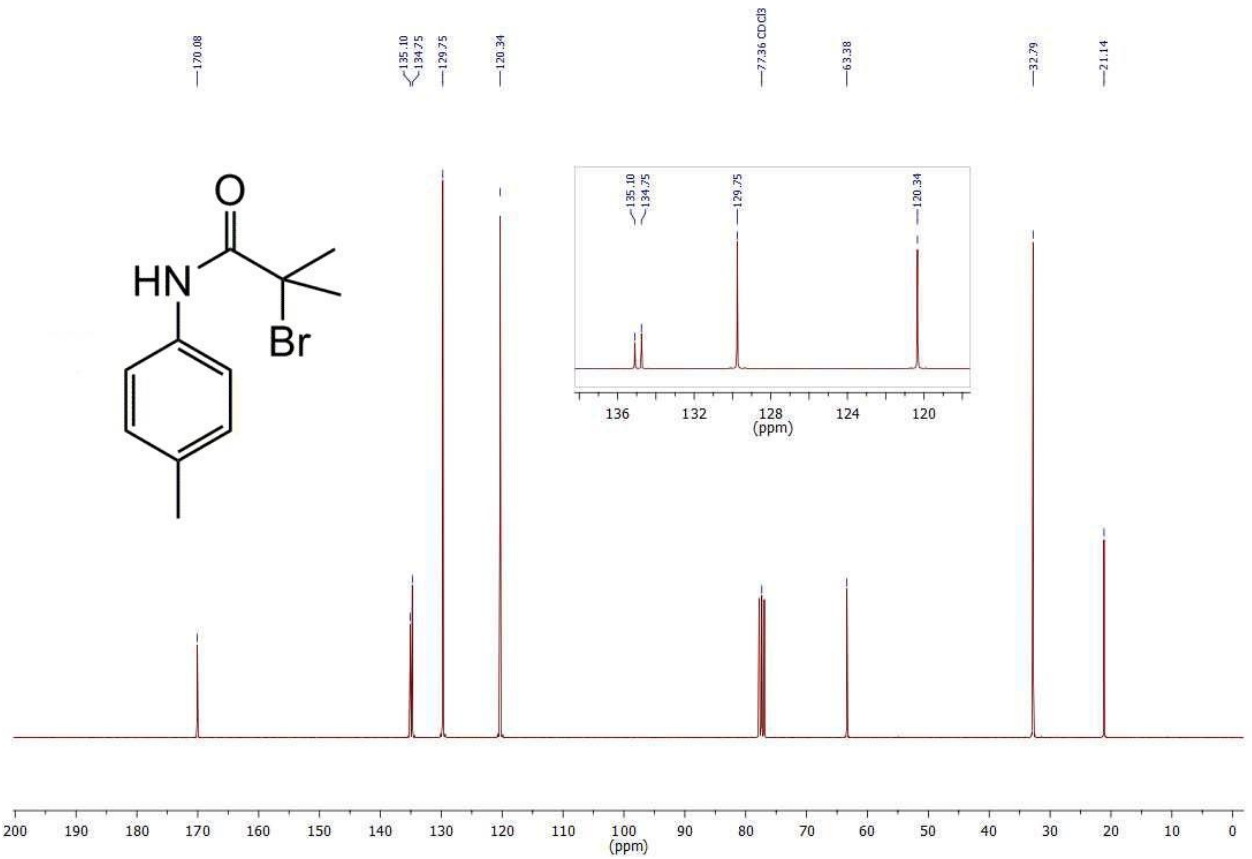


7



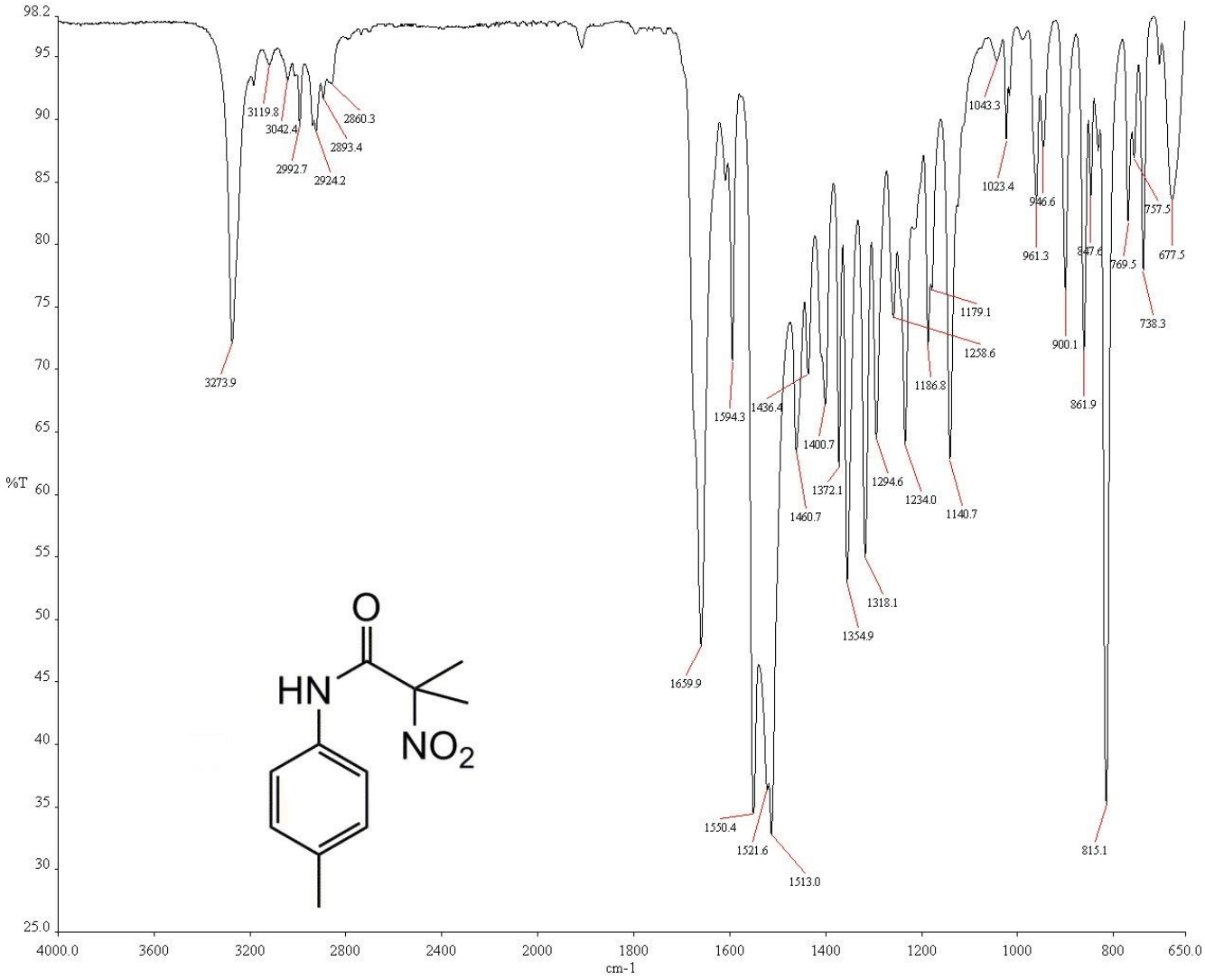


35 mg of **7** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans



135 mg of **7** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

8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1294.6
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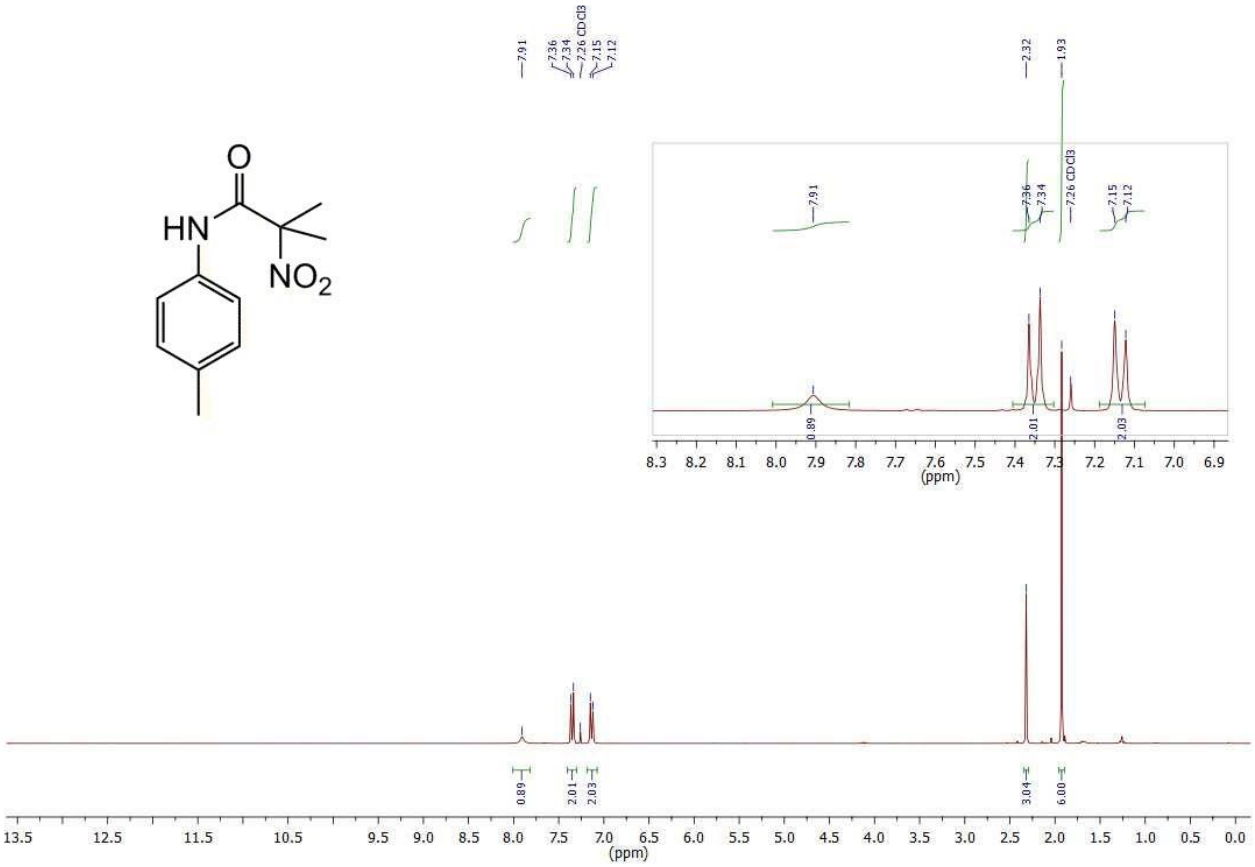
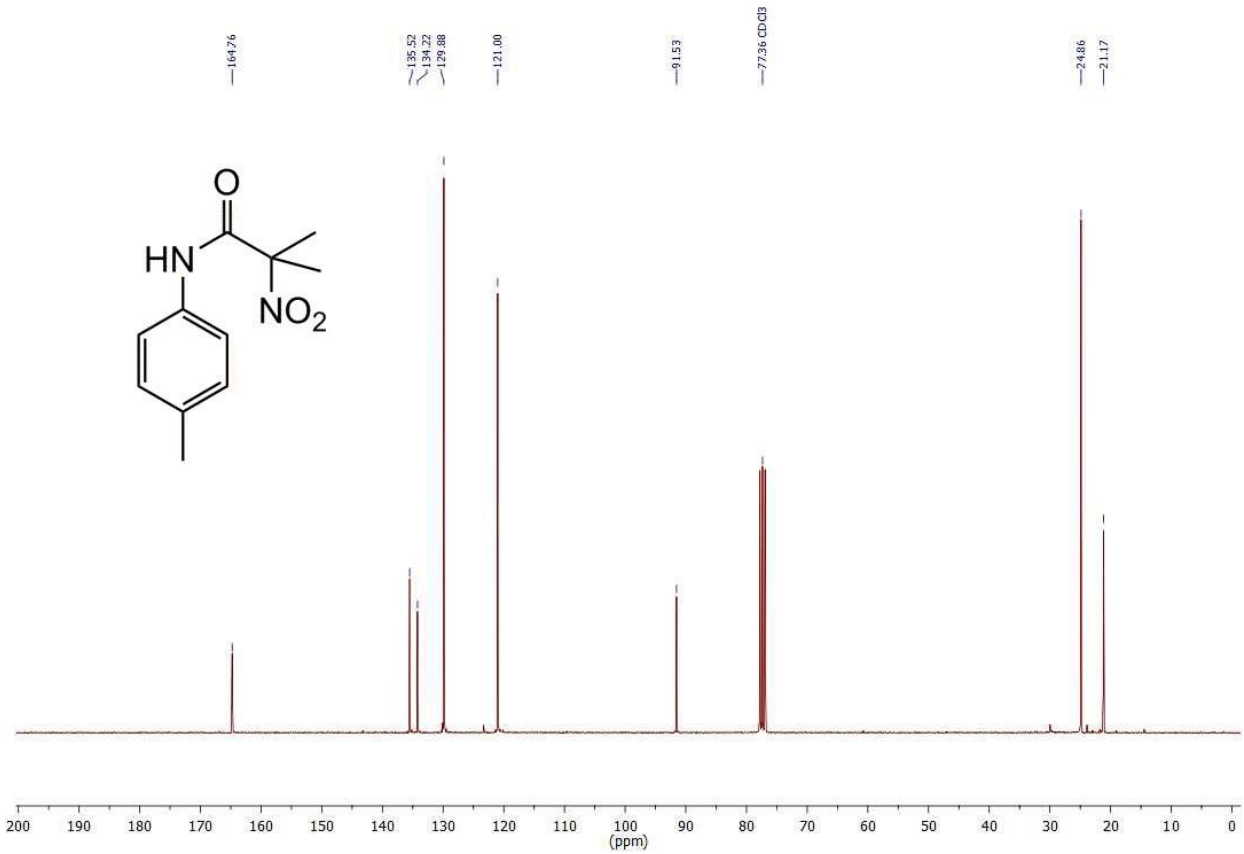
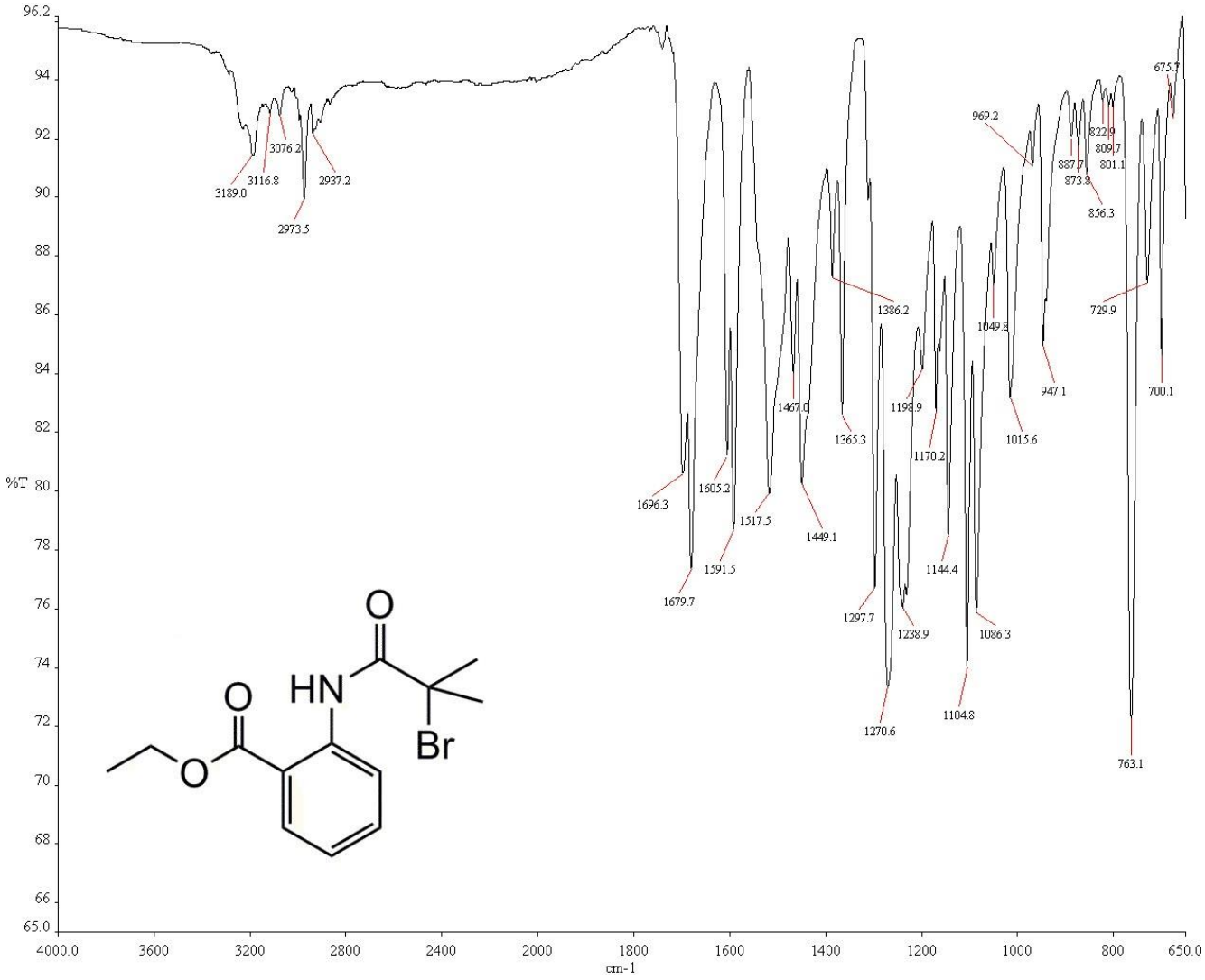


21 mg of **8** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans



42 mg of **8** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

9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90
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84
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76
74
72
70
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66
65.0
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2937.2
1696.3
1679.7
1605.2
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1467.0
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1365.3
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1270.6
1238.9
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1144.4
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1015.6
969.2
947.1
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675.7
763.1
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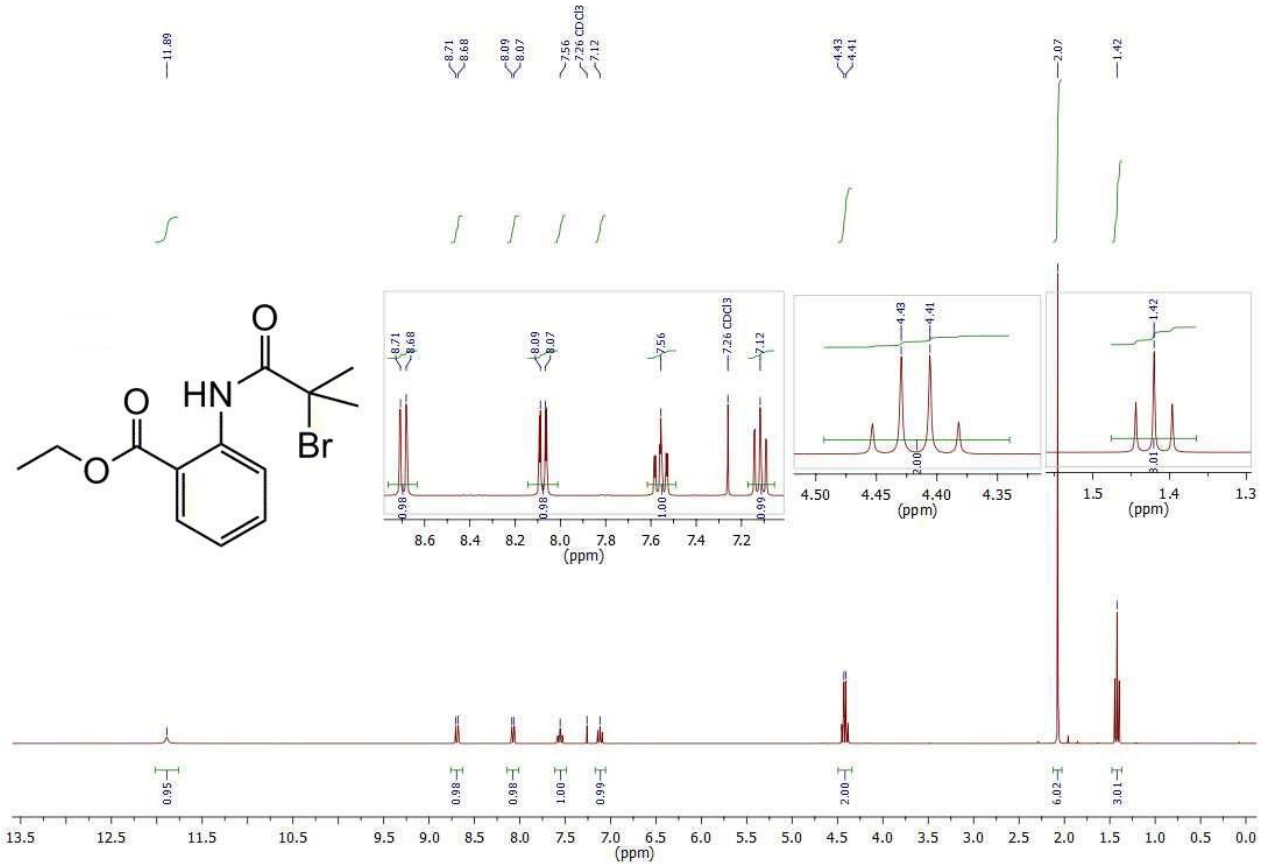
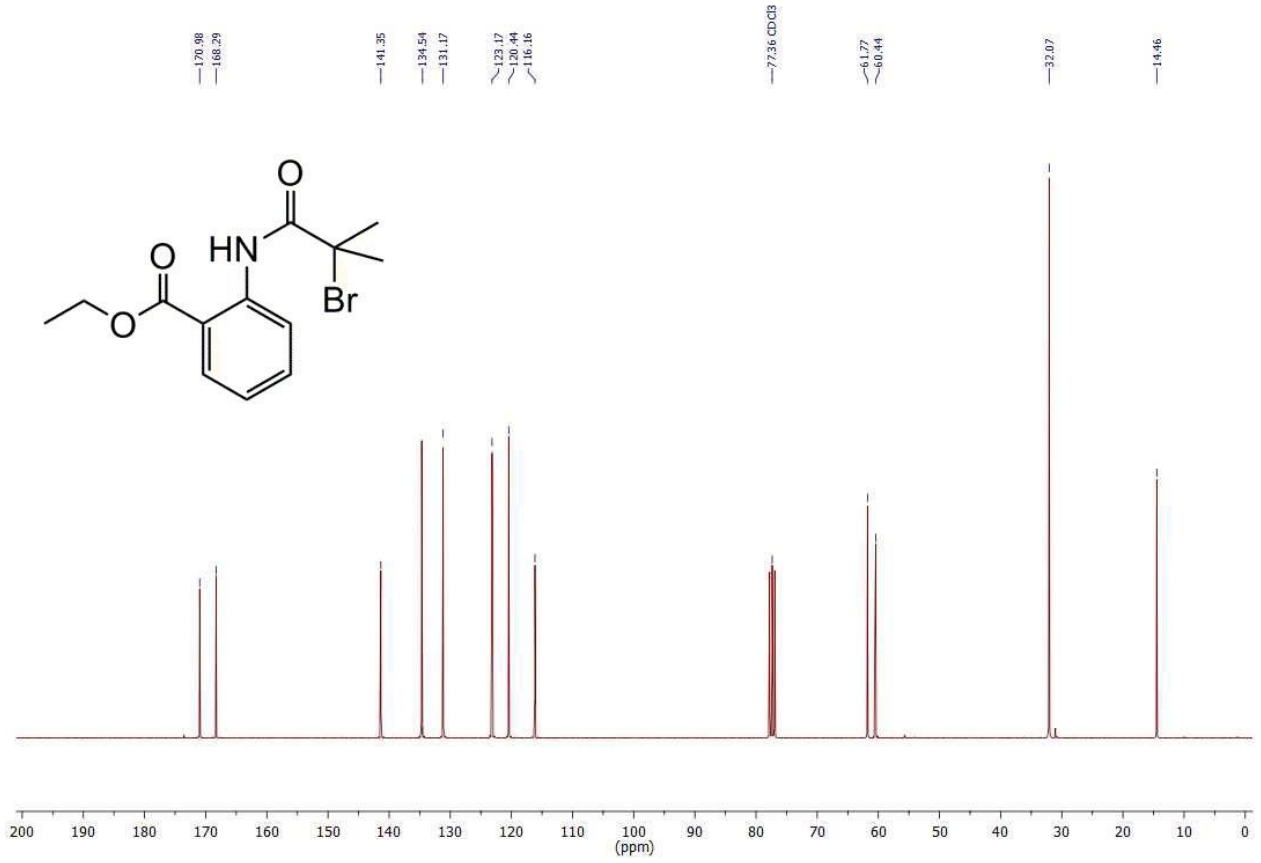
Br
O
O

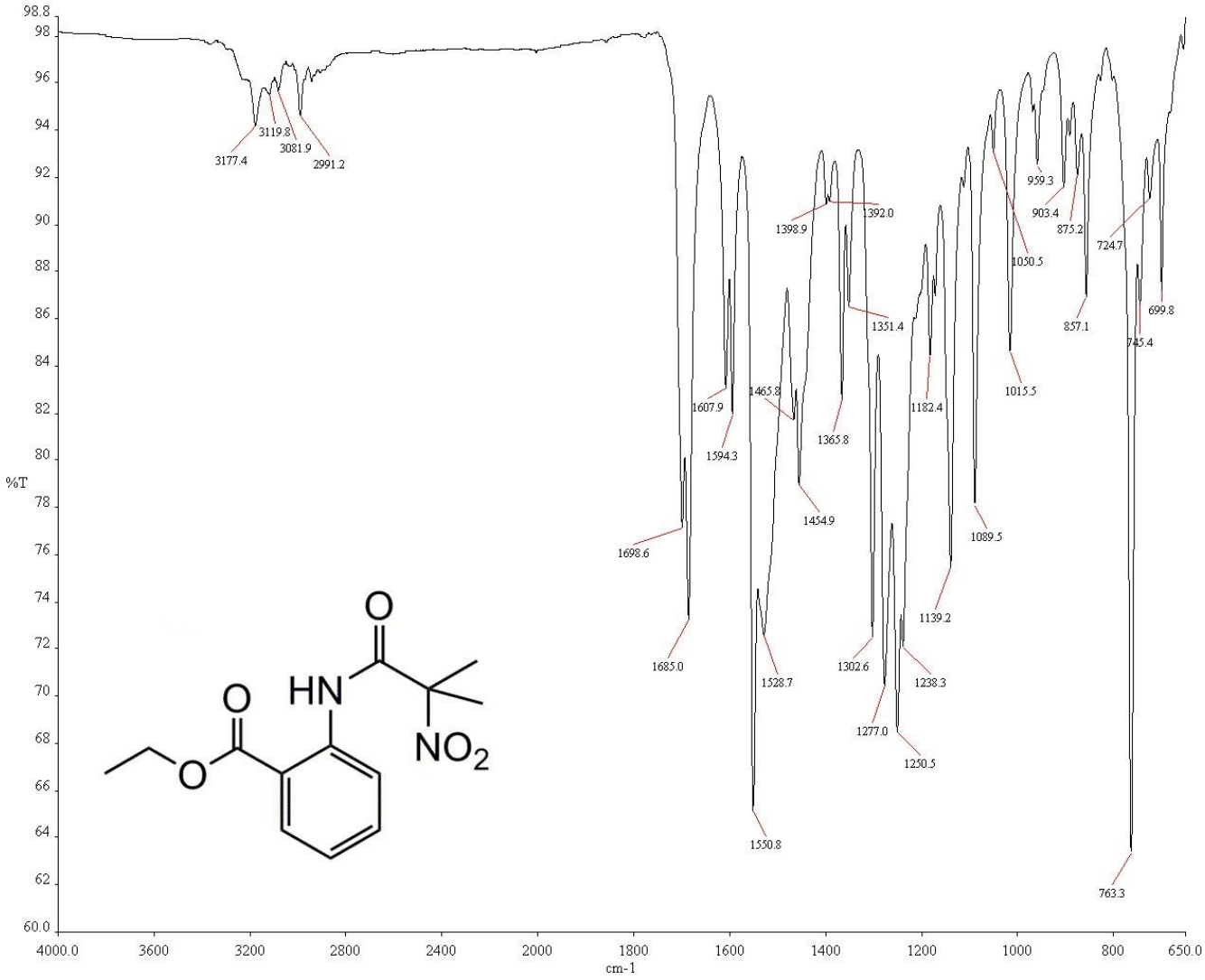


30 mg of **9** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans



1425 mg of **9** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

10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1392.0
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1250.5
1238.3
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1139.2
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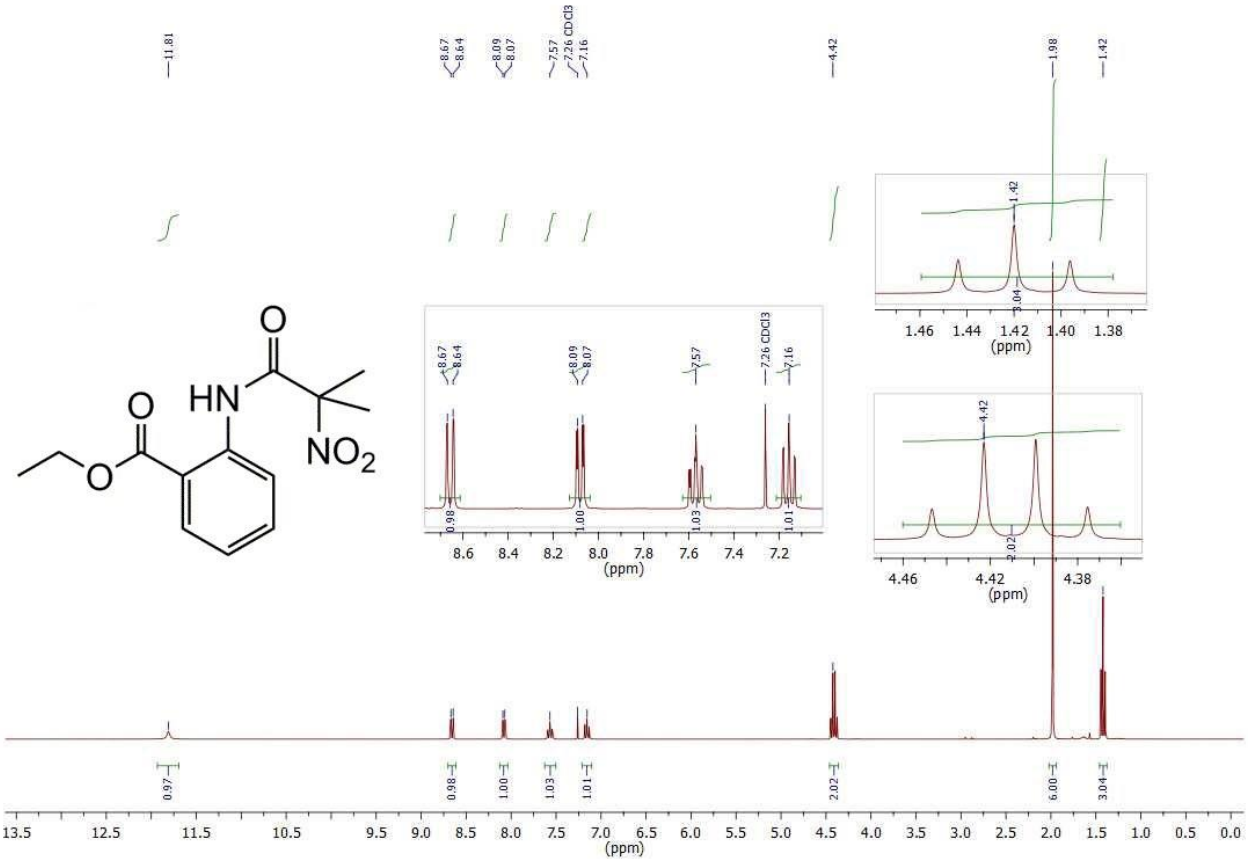
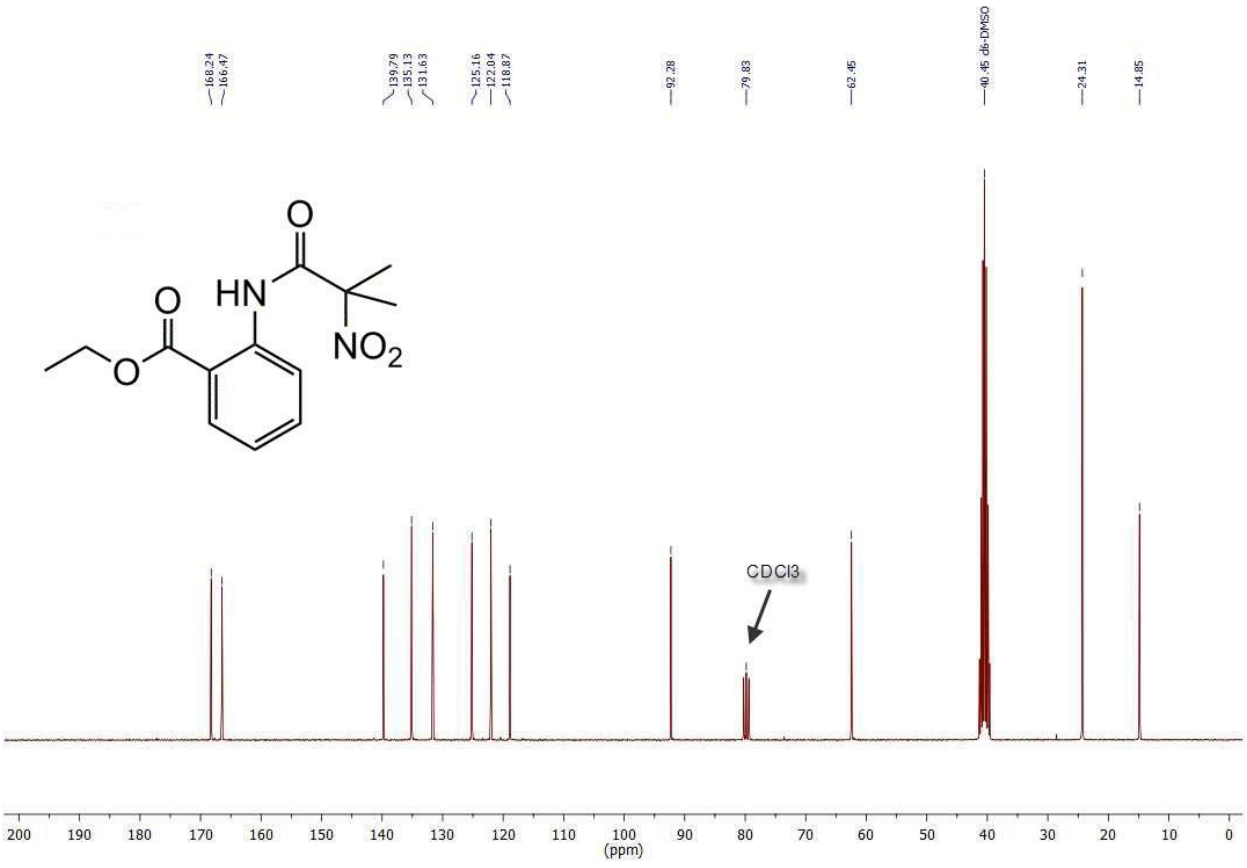
745.4
724.7
699.8



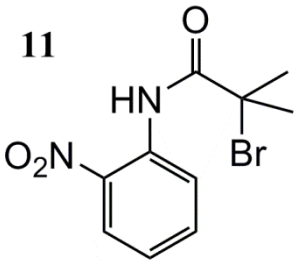
25 mg of **10** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans

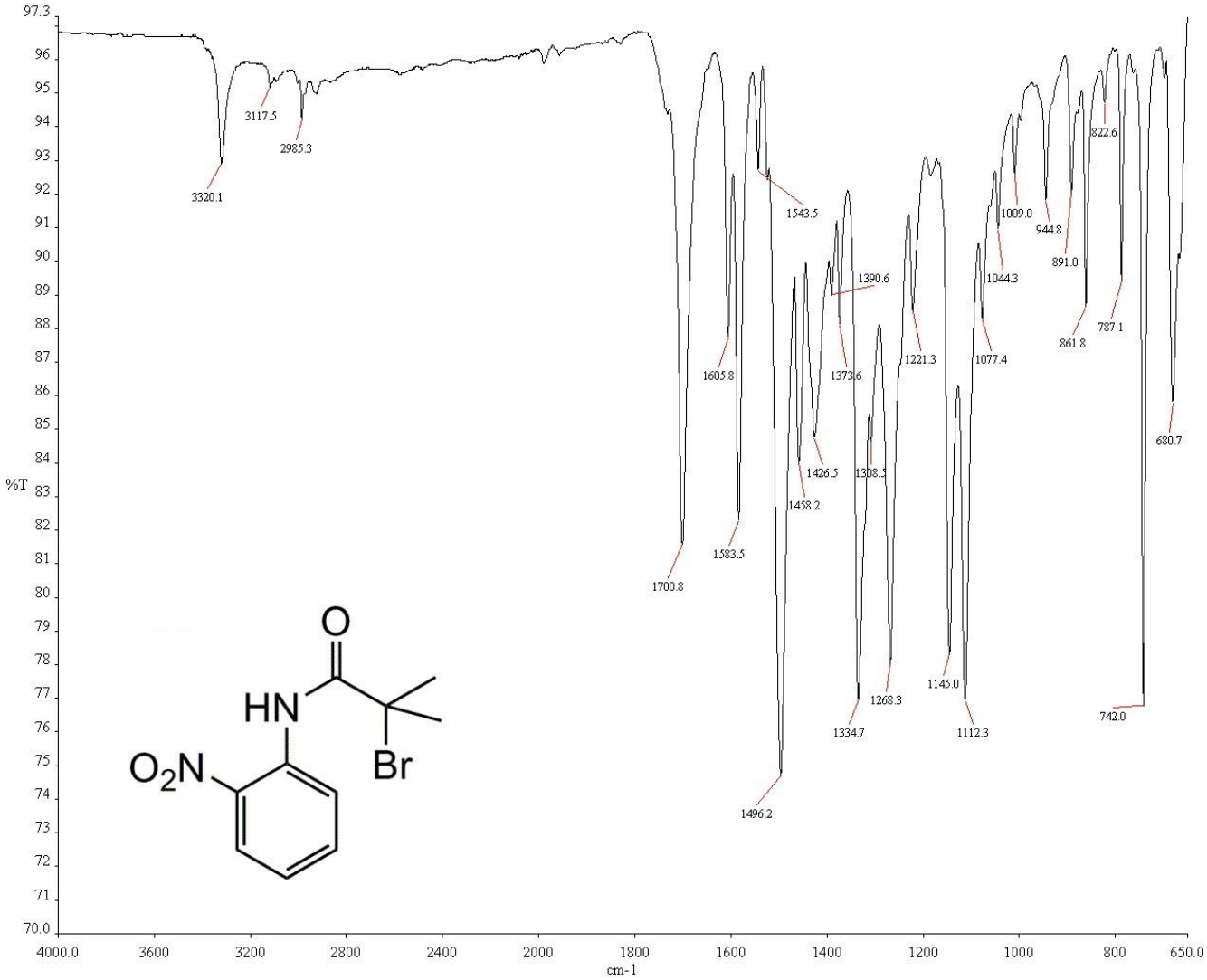


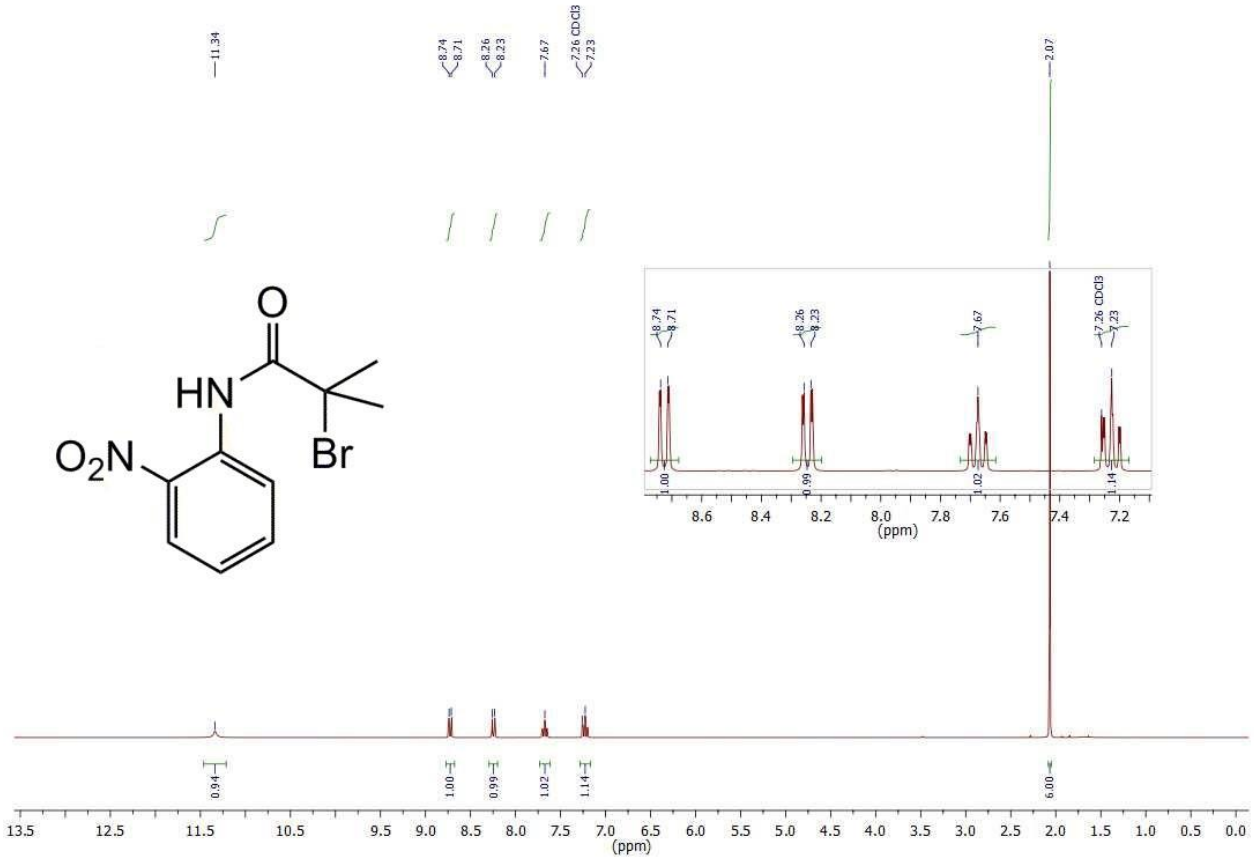
68 mg of **10** in 0.4 mL d_6-DMSO/0.1 mL $CDCl_3$, 75 MHz, 14000 scans

ESI for:
Bromo–nitro substitution on a tertiary α carbon—a previously uncharacterized facet of the Kornblum substitution

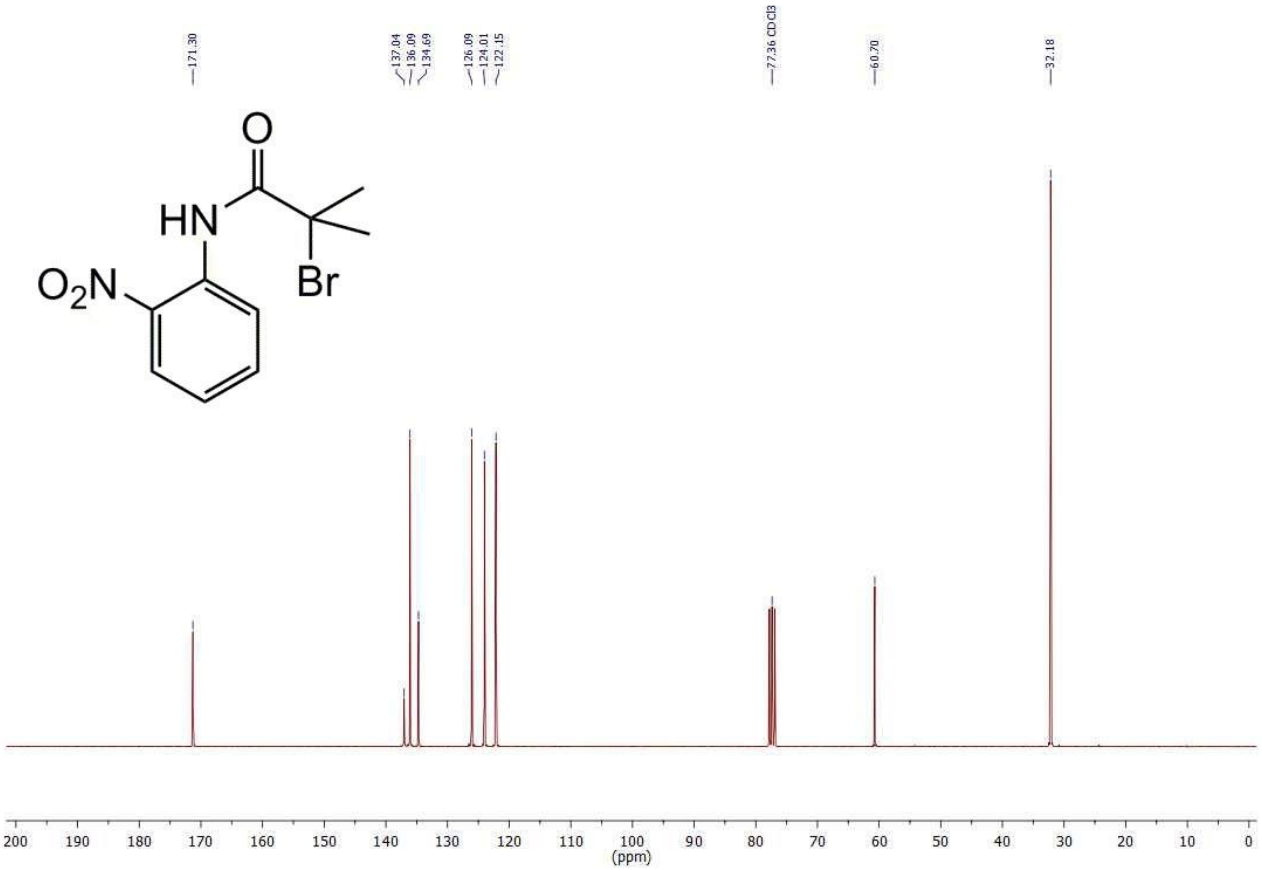
11





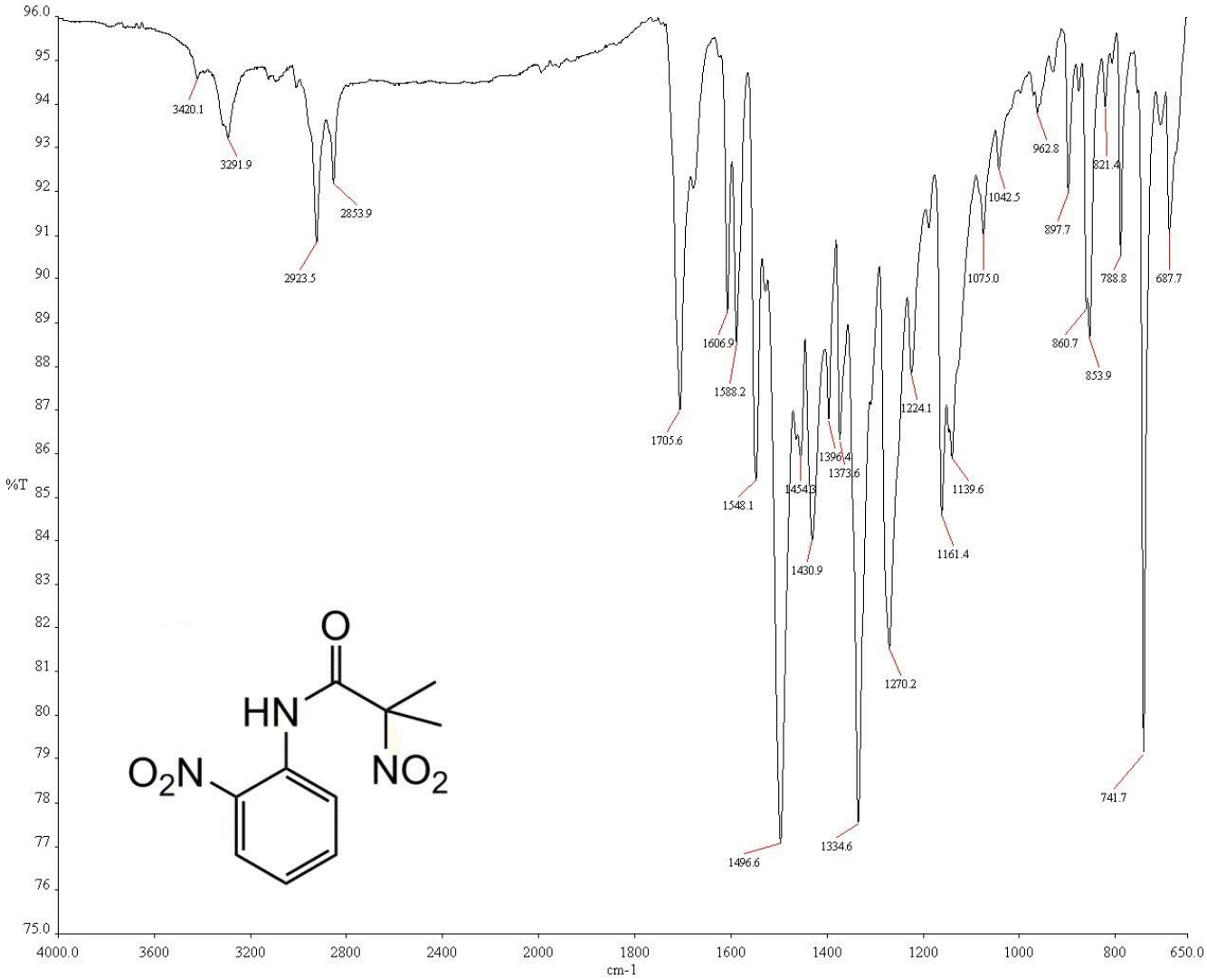


32 mg of **11** in 0.4 mL $CDCl_3$, 300 MHz, 32 scans



138 mg of **11** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

12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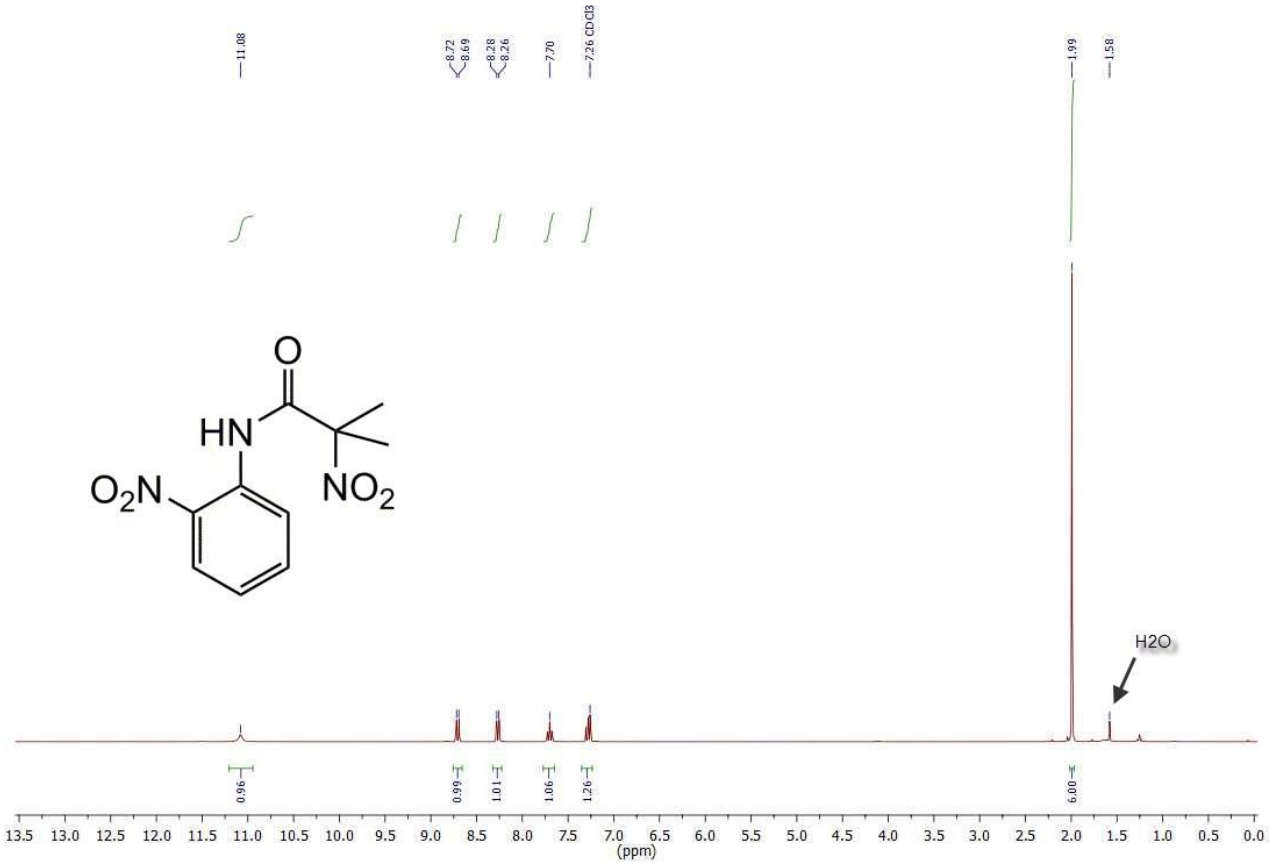
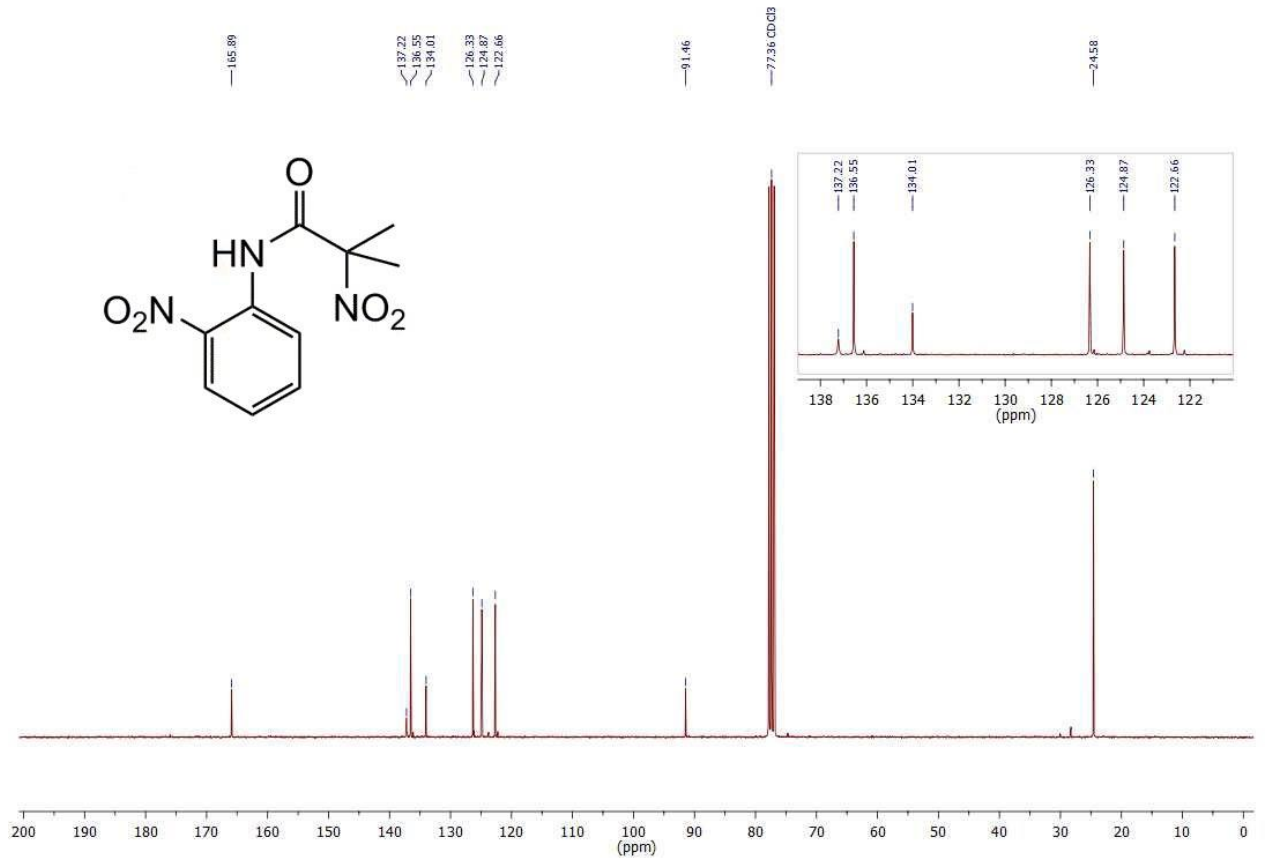
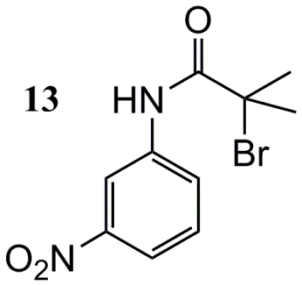


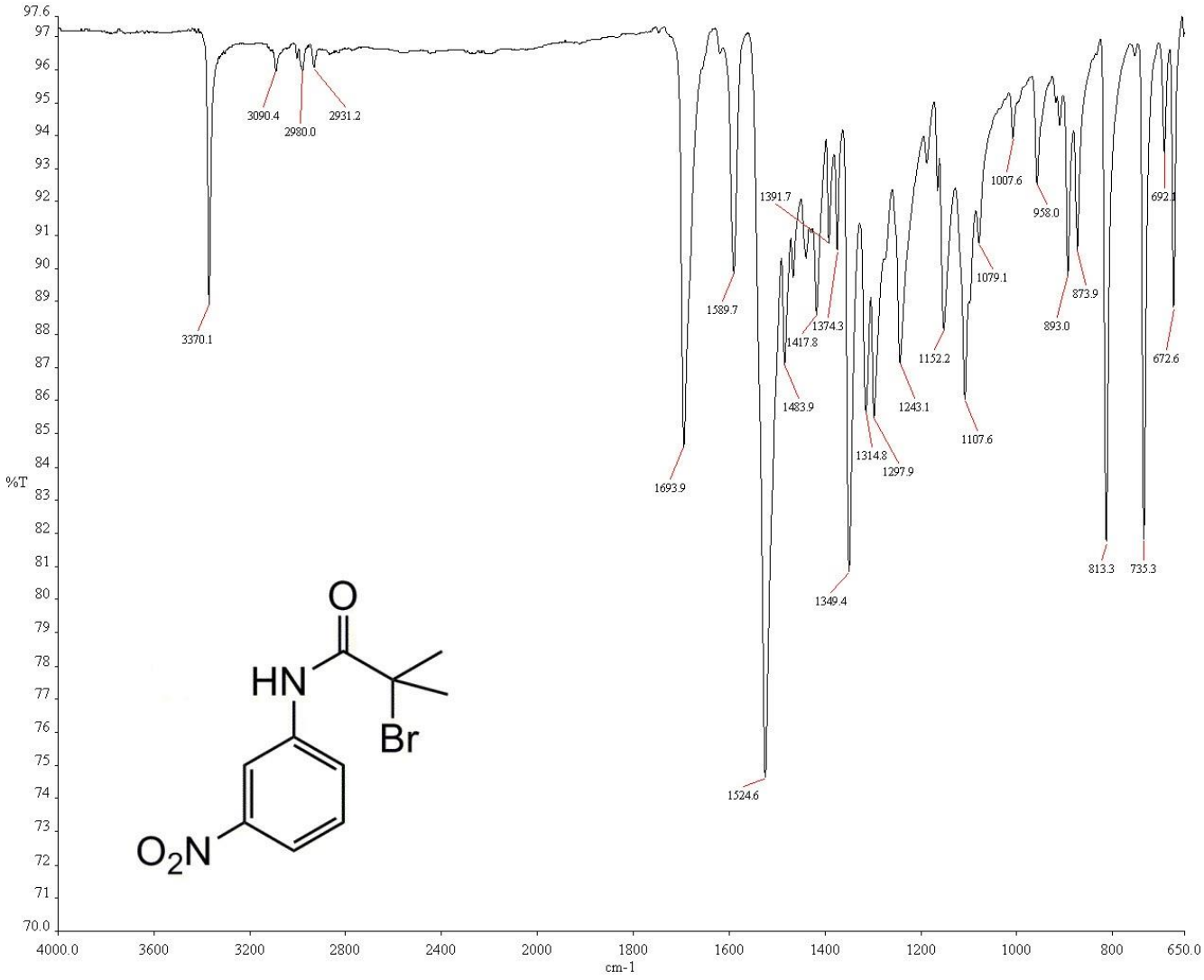
18 mg of **12** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans



18 mg of **12** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

13


O
HN
Br
O_2N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1107.6
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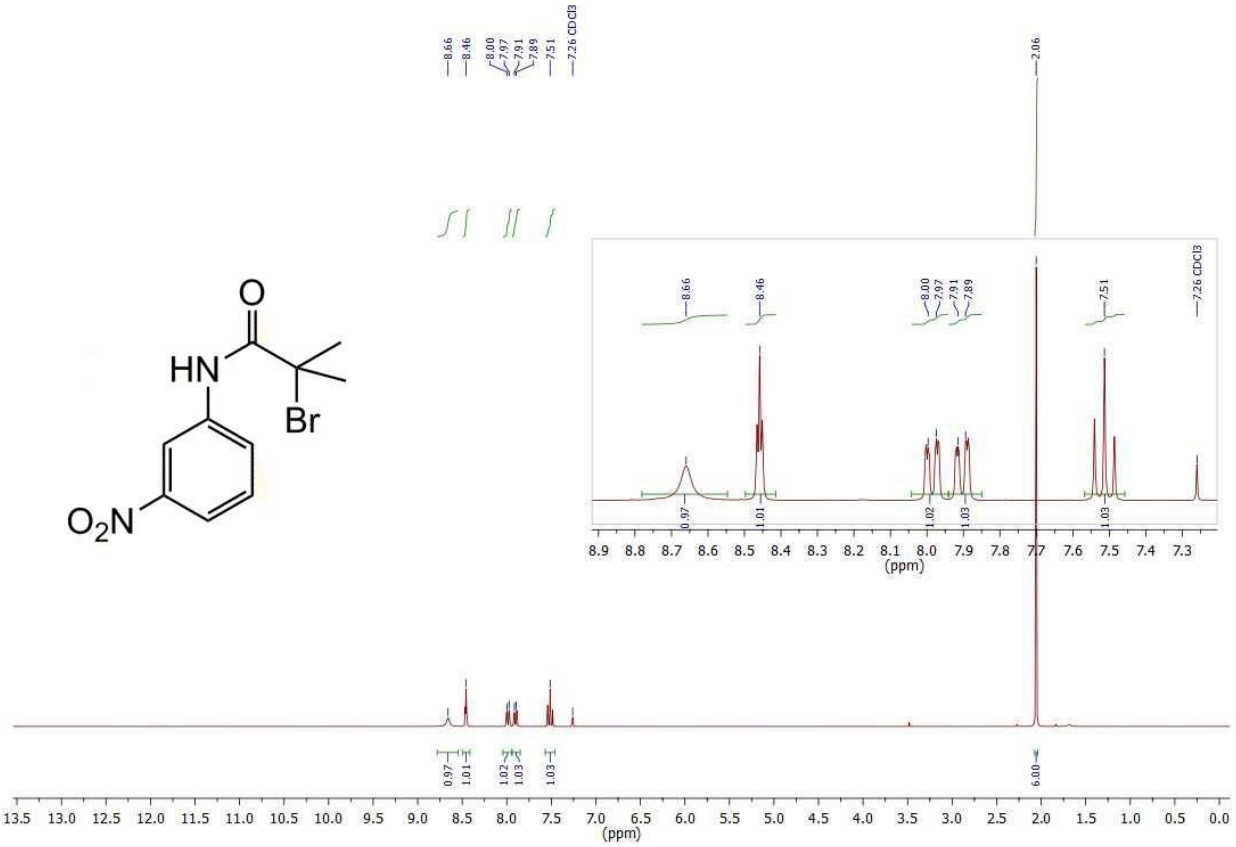
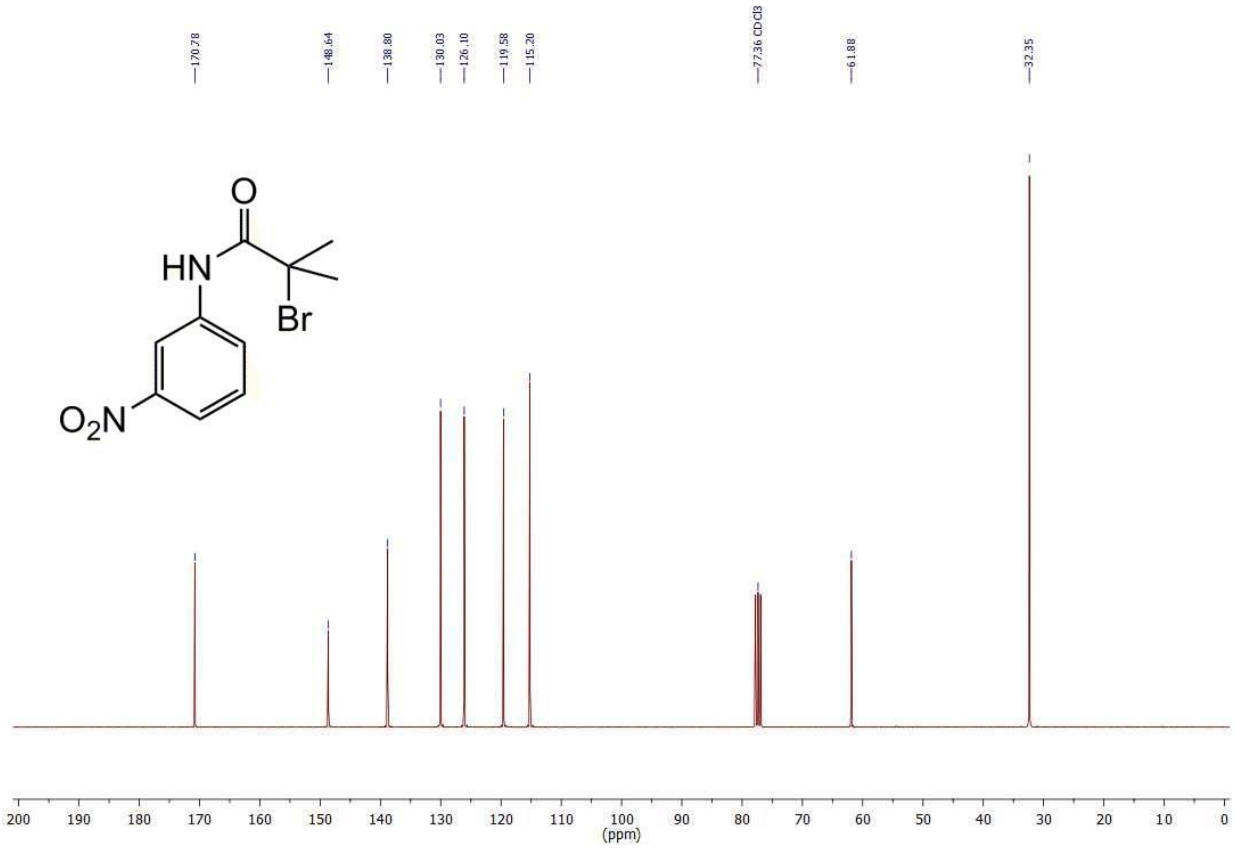
672.6
O
HN
Br
O_2N

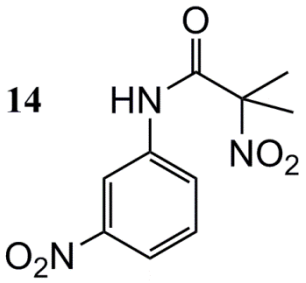


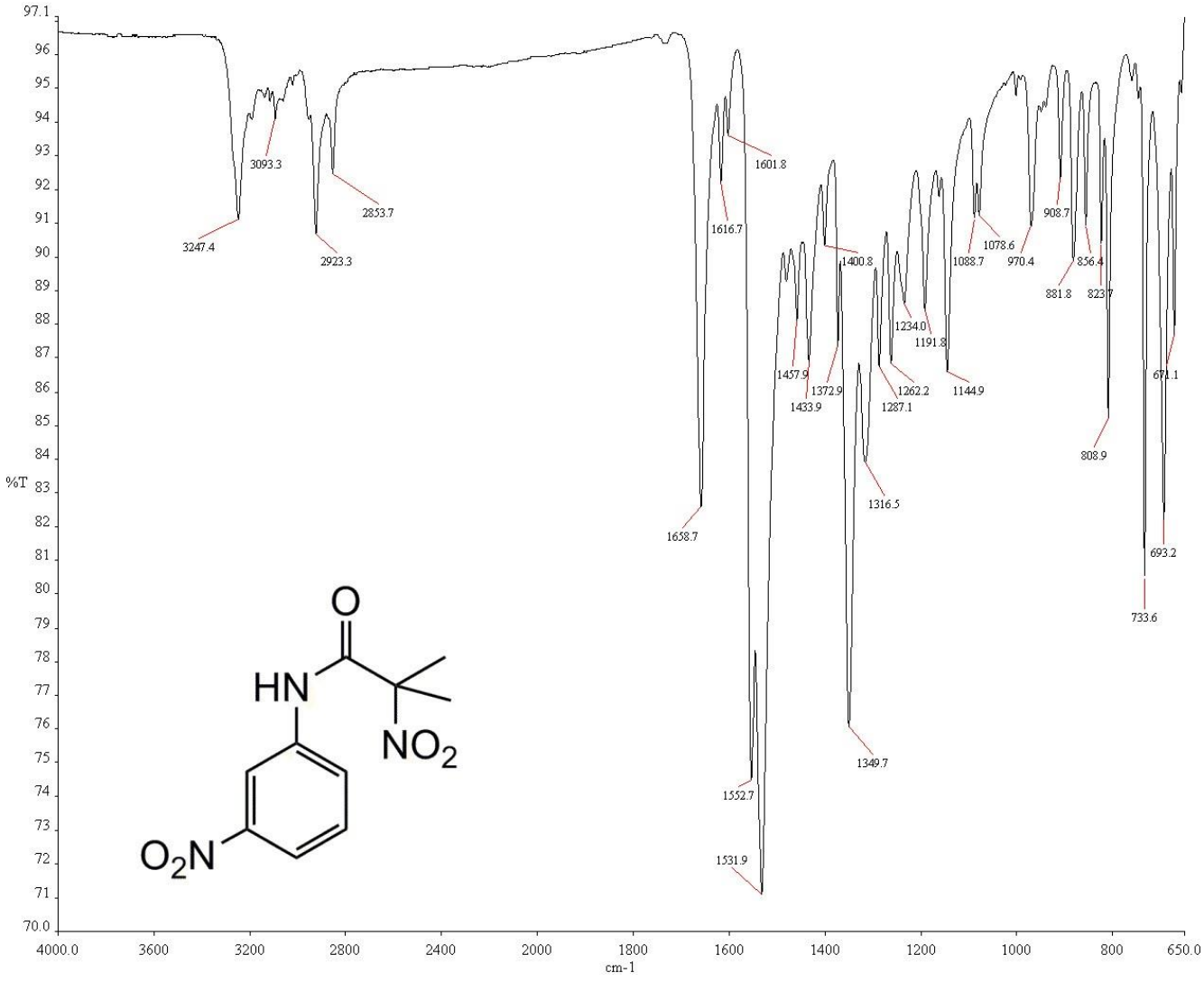
45 mg of **13** in 0.4 mL $CDCl_3$, 300 MHz, 32 scans



138 mg of **13** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

14


O
HN
NO2
O2N


%T
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1400.8
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1234.0
1191.8
1144.9
1088.7
1078.6
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856.4
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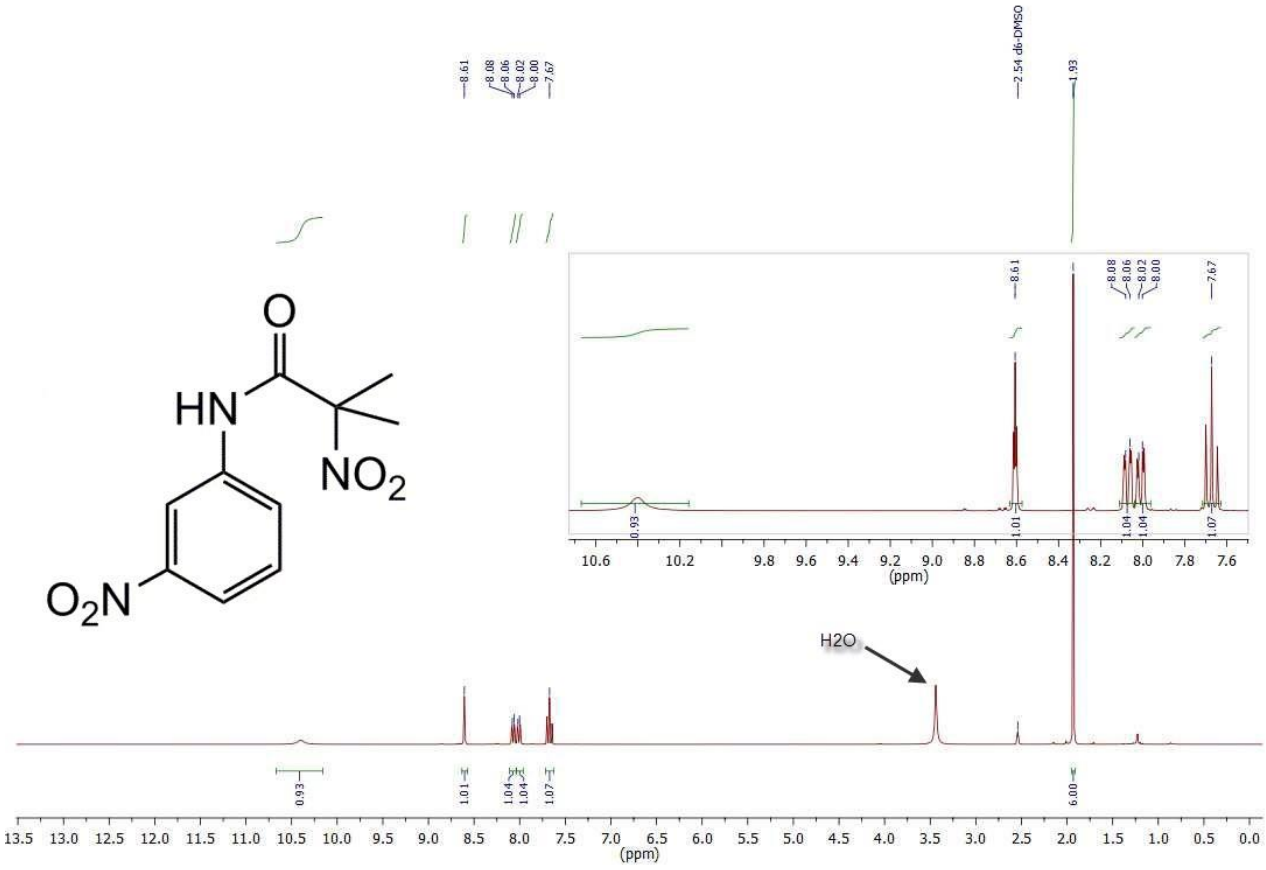
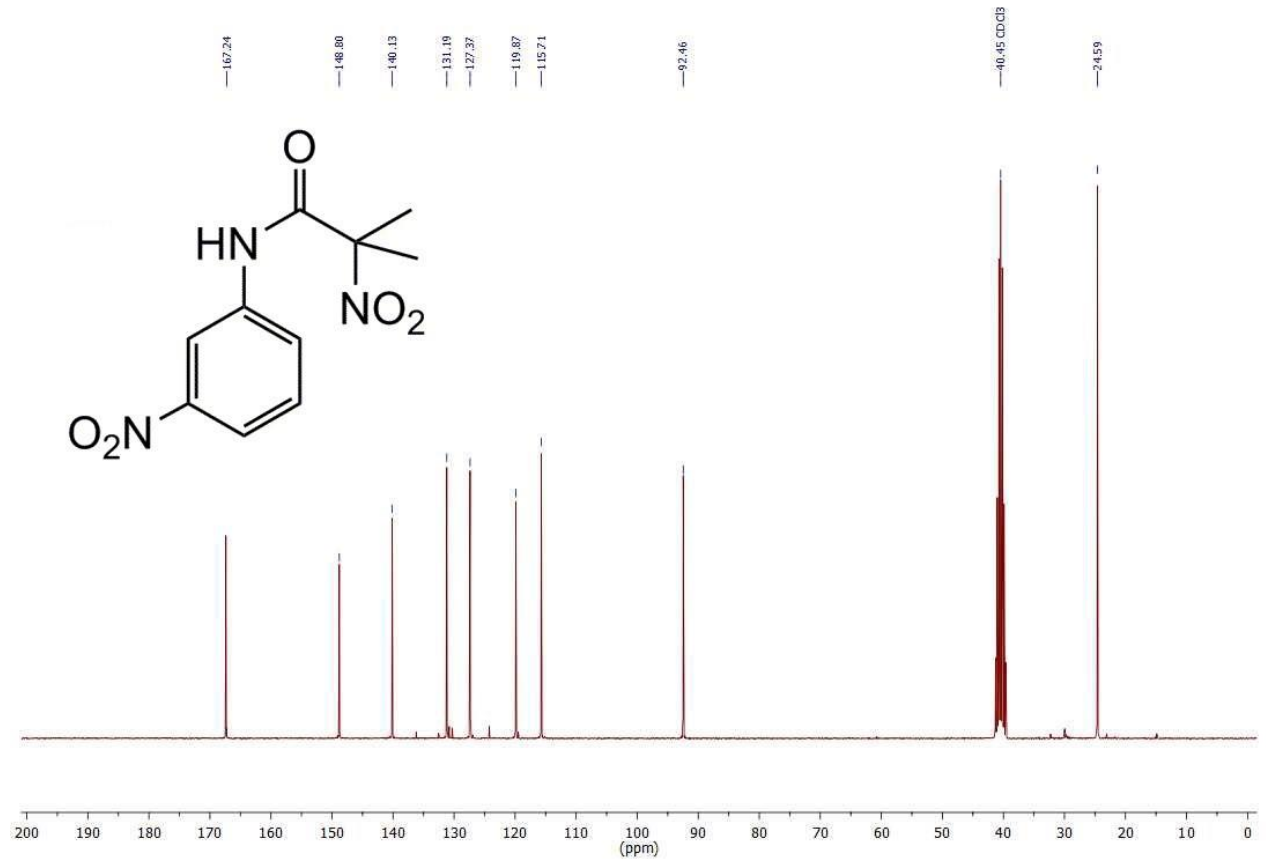
808.9
733.6
693.2
671.1
O
HN
NO2
O2N



50 mg of **14** in 0.4 mL d_6-DMSO, 300 MHz, 16 scans



50 mg of **14** in 0.4 mL d_6-DMSO, 75 MHz, 14000 scans

ESI for:
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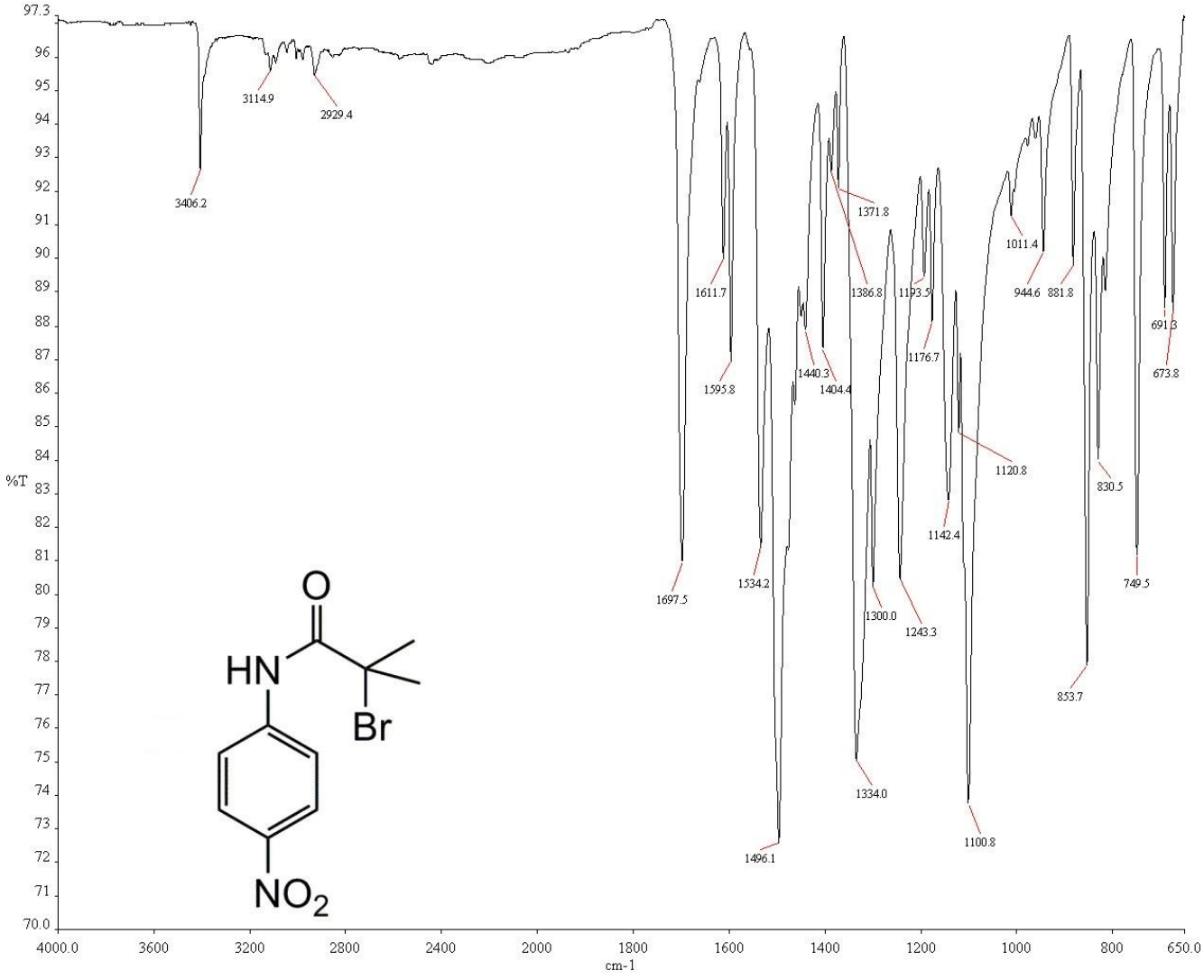
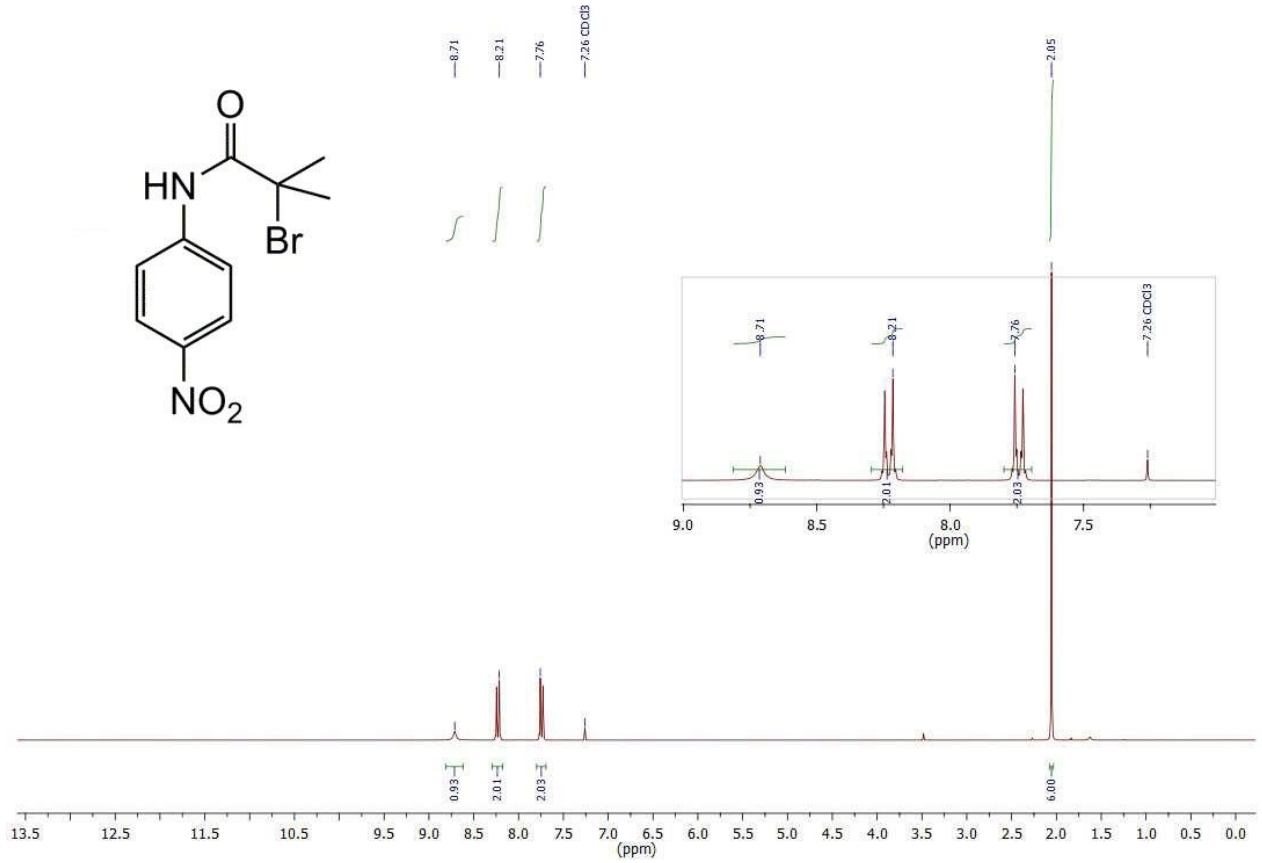
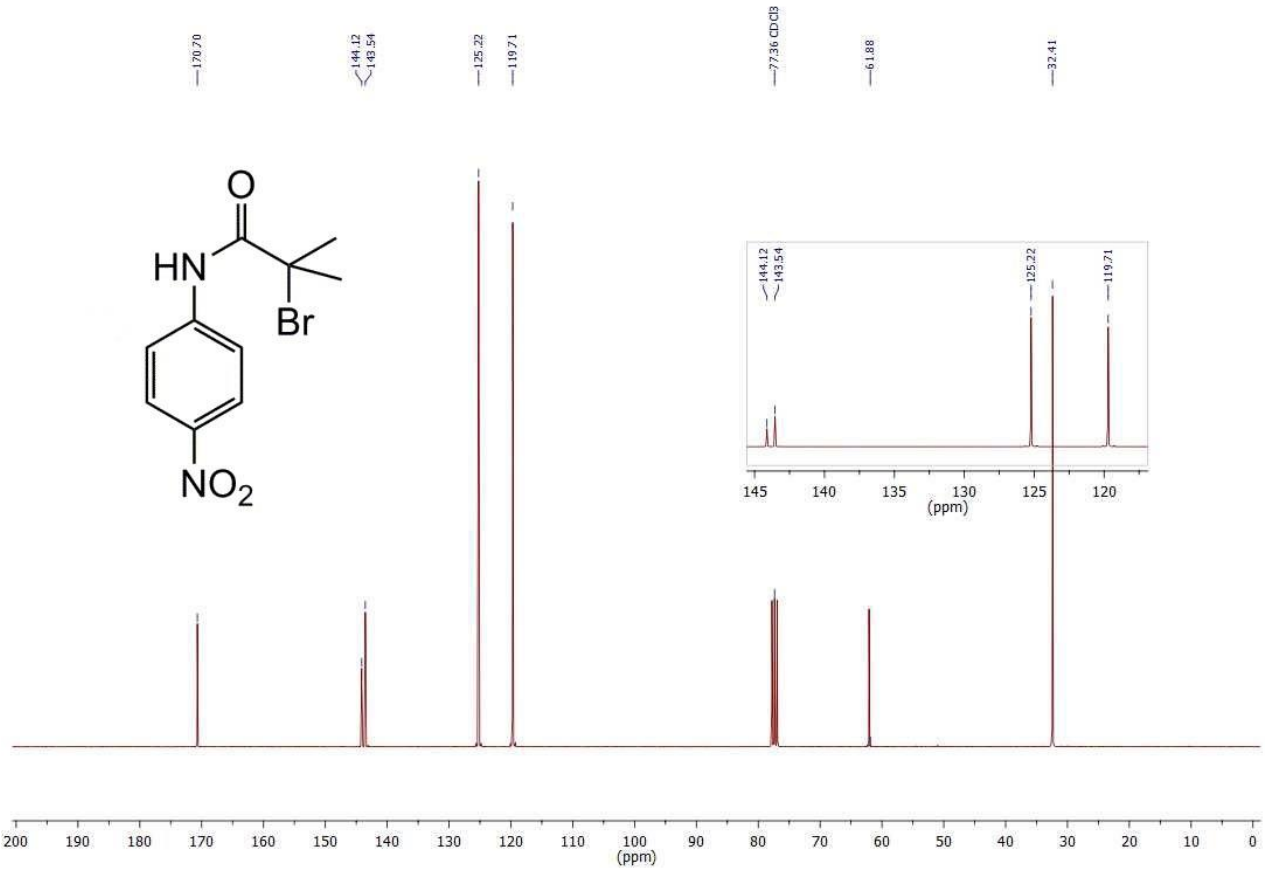
15



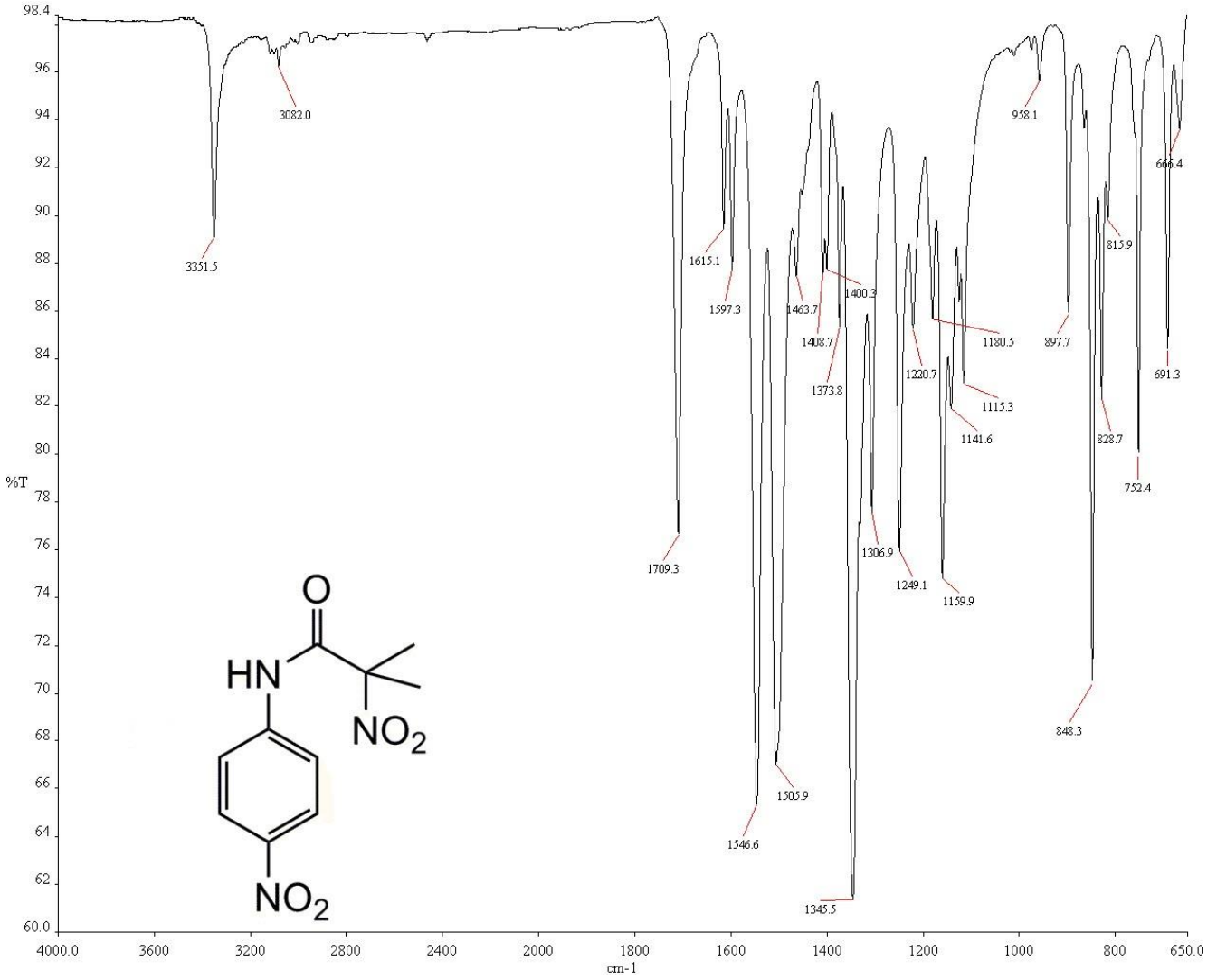


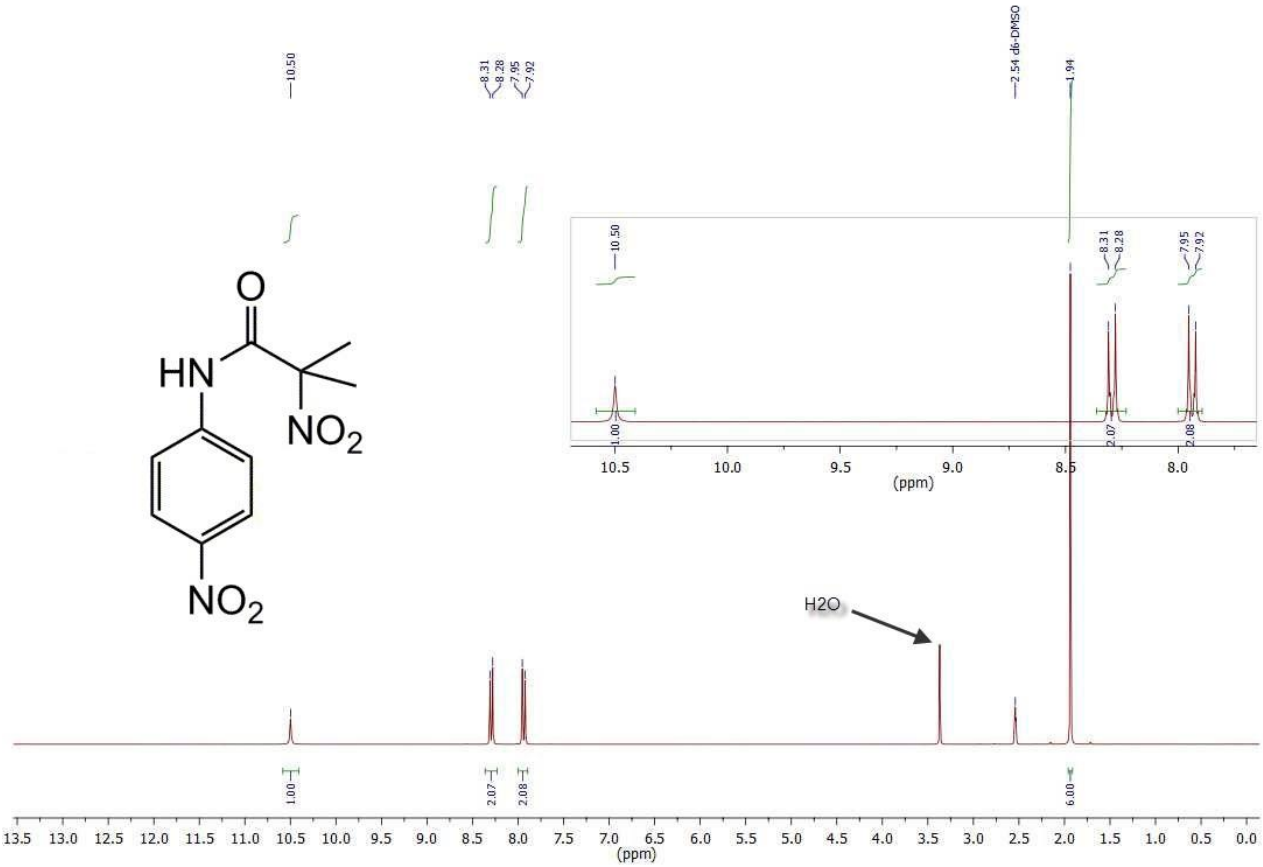
30 mg of **15** in 0.4 mL $CDCl_3$, 300 MHz, 32 scans



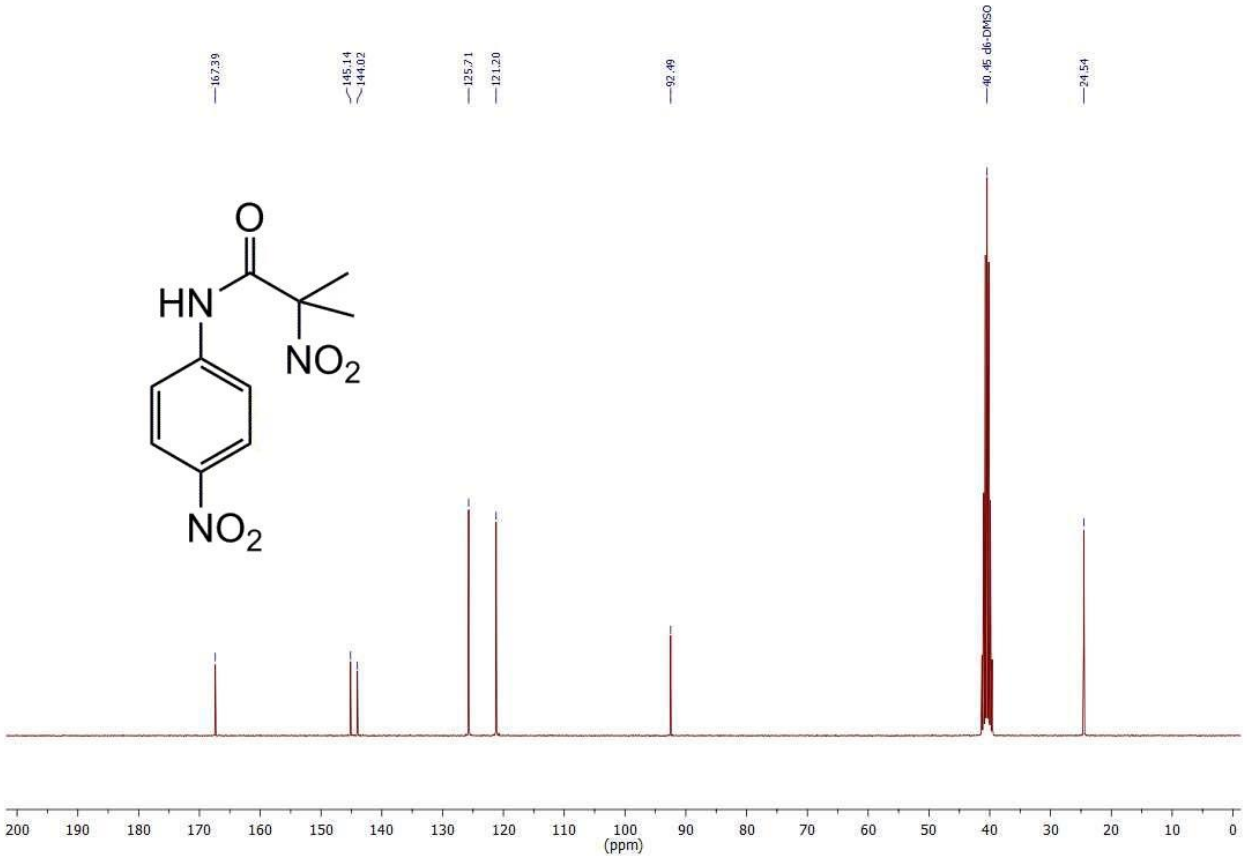
122 mg of **15** in 0.4 mL $CDCl_3$, 75 MHz, 19456 scans

16


%T
cm-1
3351.5
3082.0
1709.3
1615.1
1597.3
1546.6
1505.9
1463.7
1408.7
1400.3
1373.8
1345.5
1306.9
1249.1
1220.7
1180.5
1159.9
1141.6
1115.3
958.1
897.7
848.3
828.7
815.9
752.4
691.3
666.4

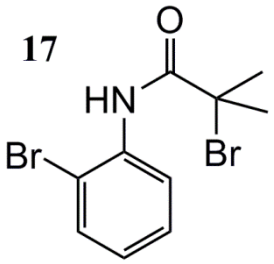


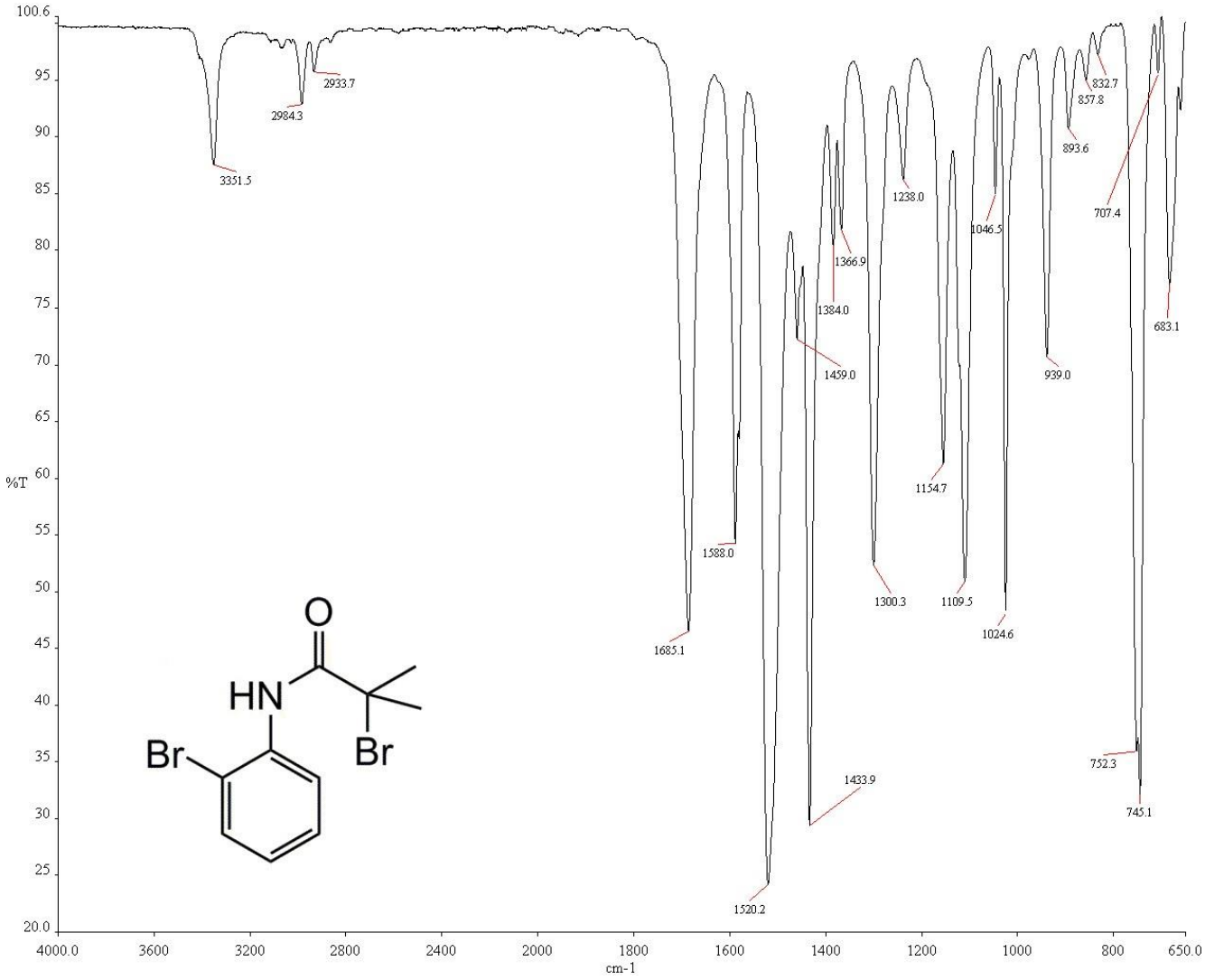
27 mg of **16** in 0.4 mL d_6-DMSO, 300 MHz, 32 scans

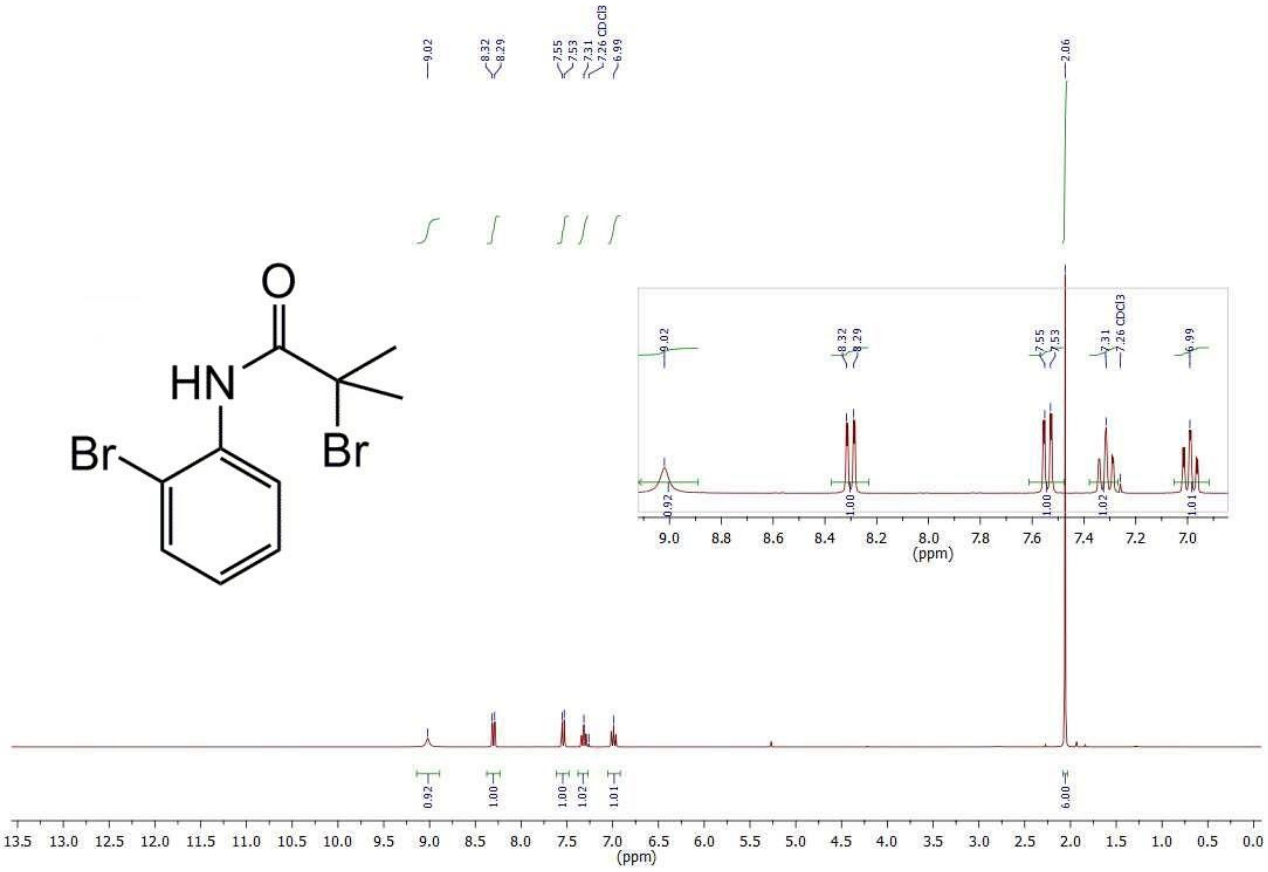


27 mg of **16** in 0.4 mL d_6-DMSO, 75 MHz, 14000 scans

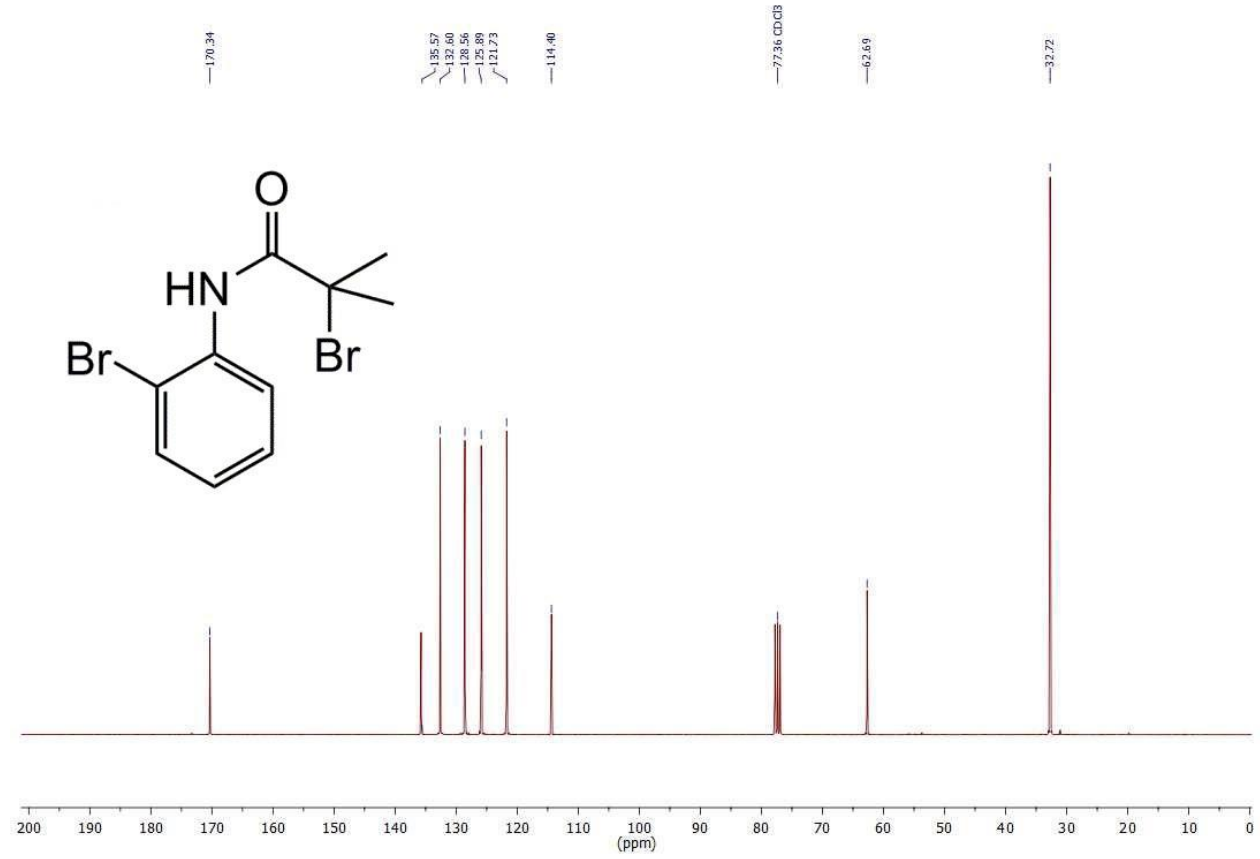
17


O
HN
Br
Br


100.6
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20.0
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
650.0
cm-1
3351.5
2984.3
2933.7
1685.1
1588.0
1520.2
1459.0
1433.9
1384.0
1366.9
1300.3
1238.0
1154.7
1109.5
1046.5
1024.6
939.0
893.6
857.8
832.7
752.3
745.1
707.4
683.1
O
HN
Br
Br

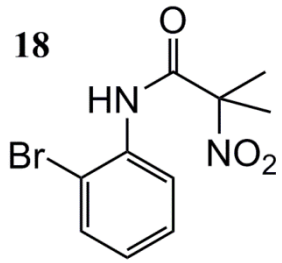


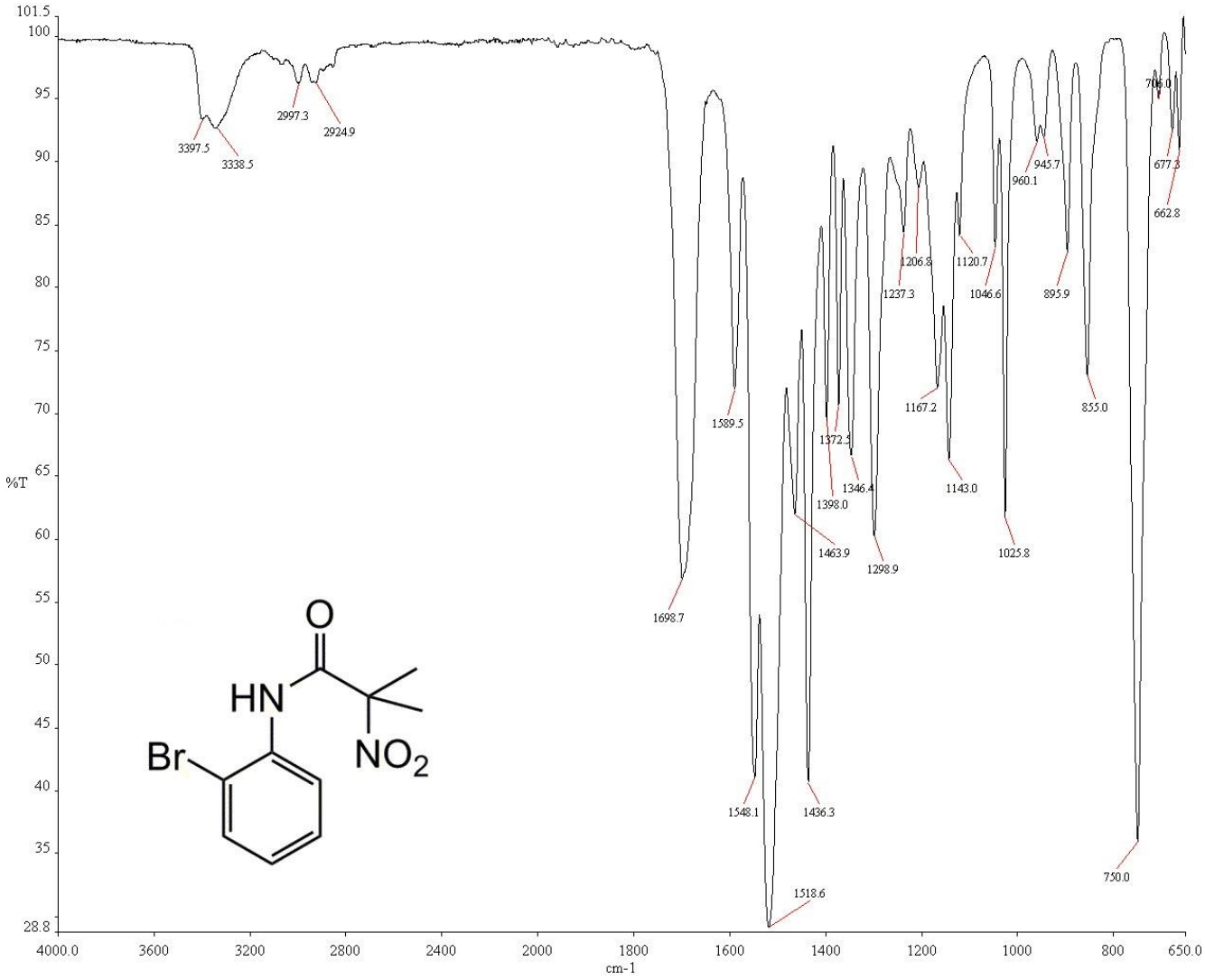
144 mg of **17** in 0.4 mL $CDCl_3$, 300 MHz, 8 scans

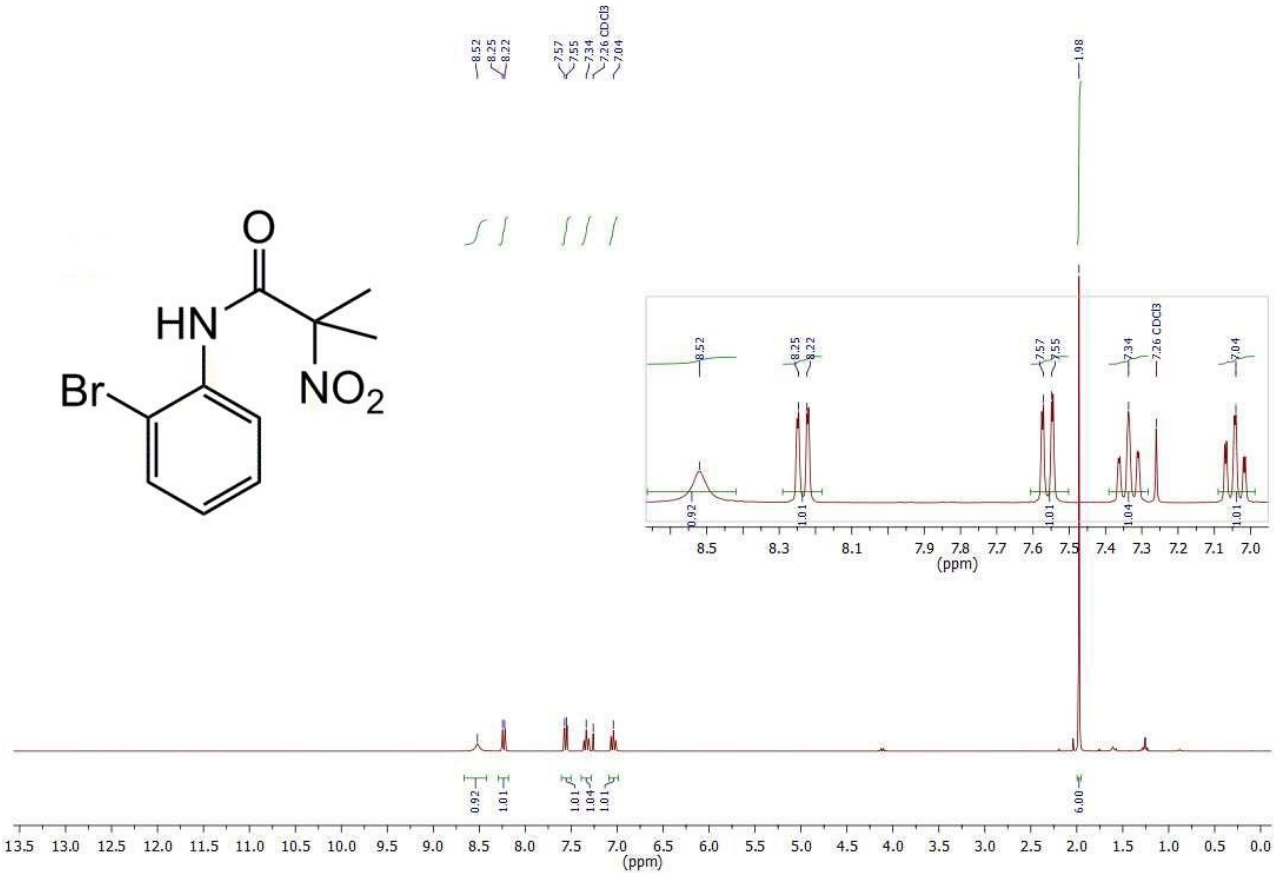


144 mg of **17** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

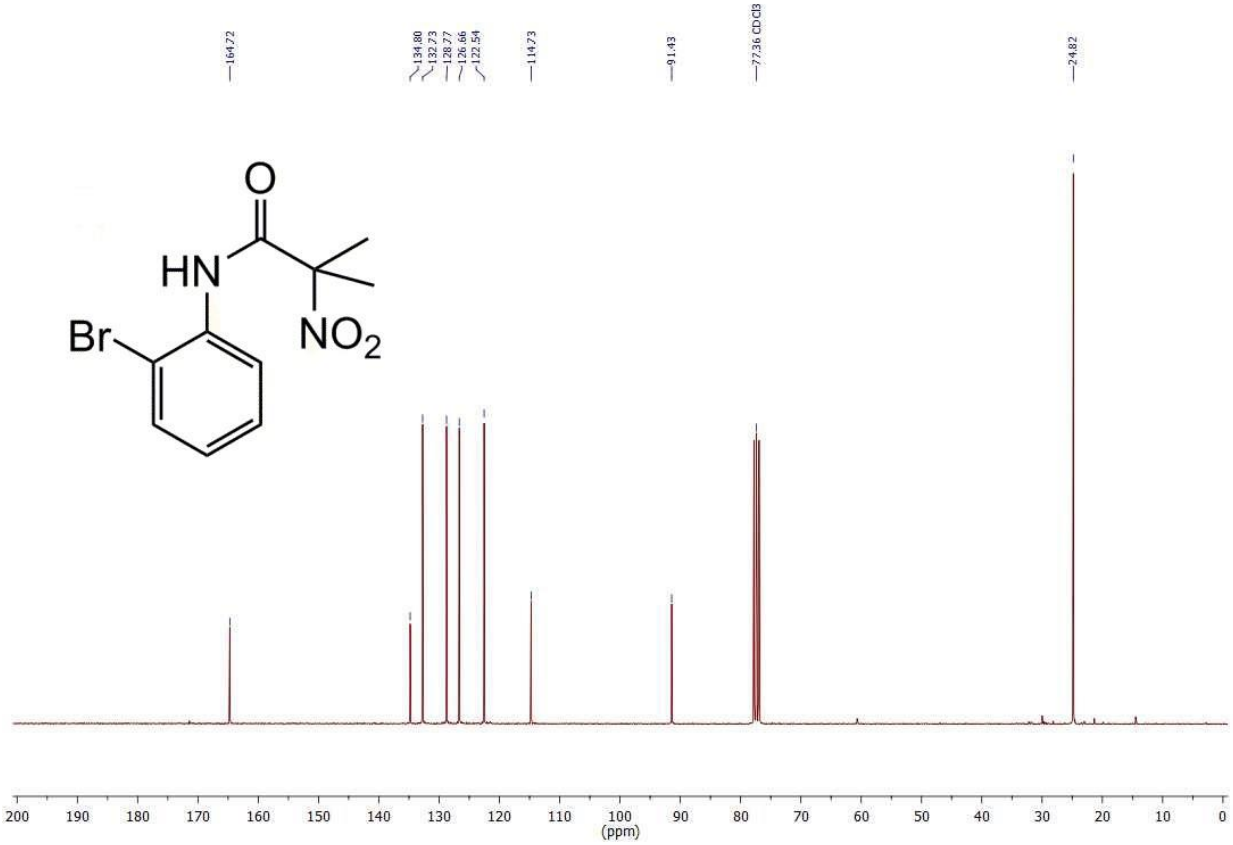
ESI for:
Bromo–nitro substitution on a tertiary α carbon—a previously uncharacterized facet of the Kornblum substitution





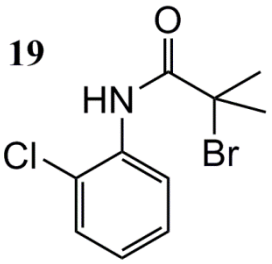


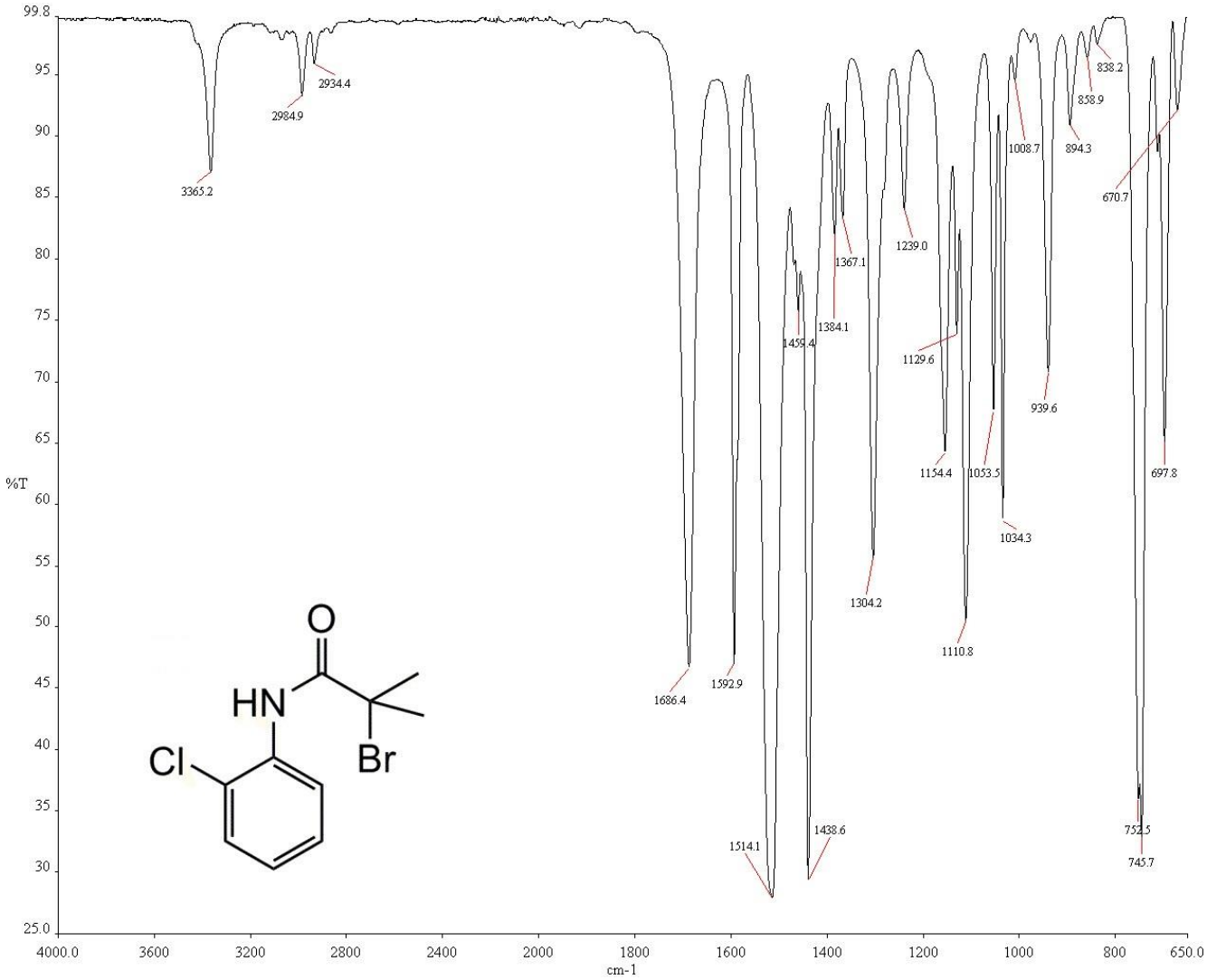
26 mg of **18** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans

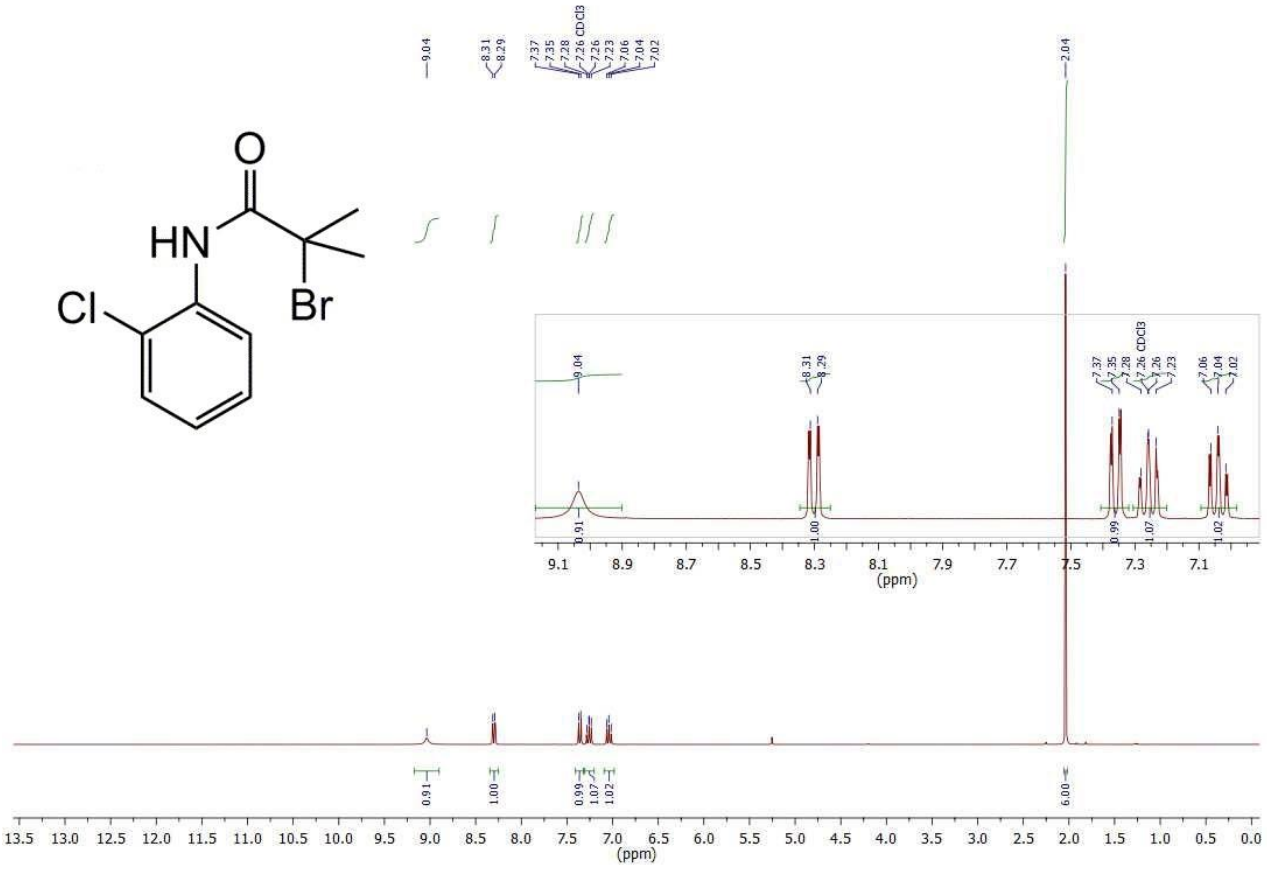


66 mg of **18** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

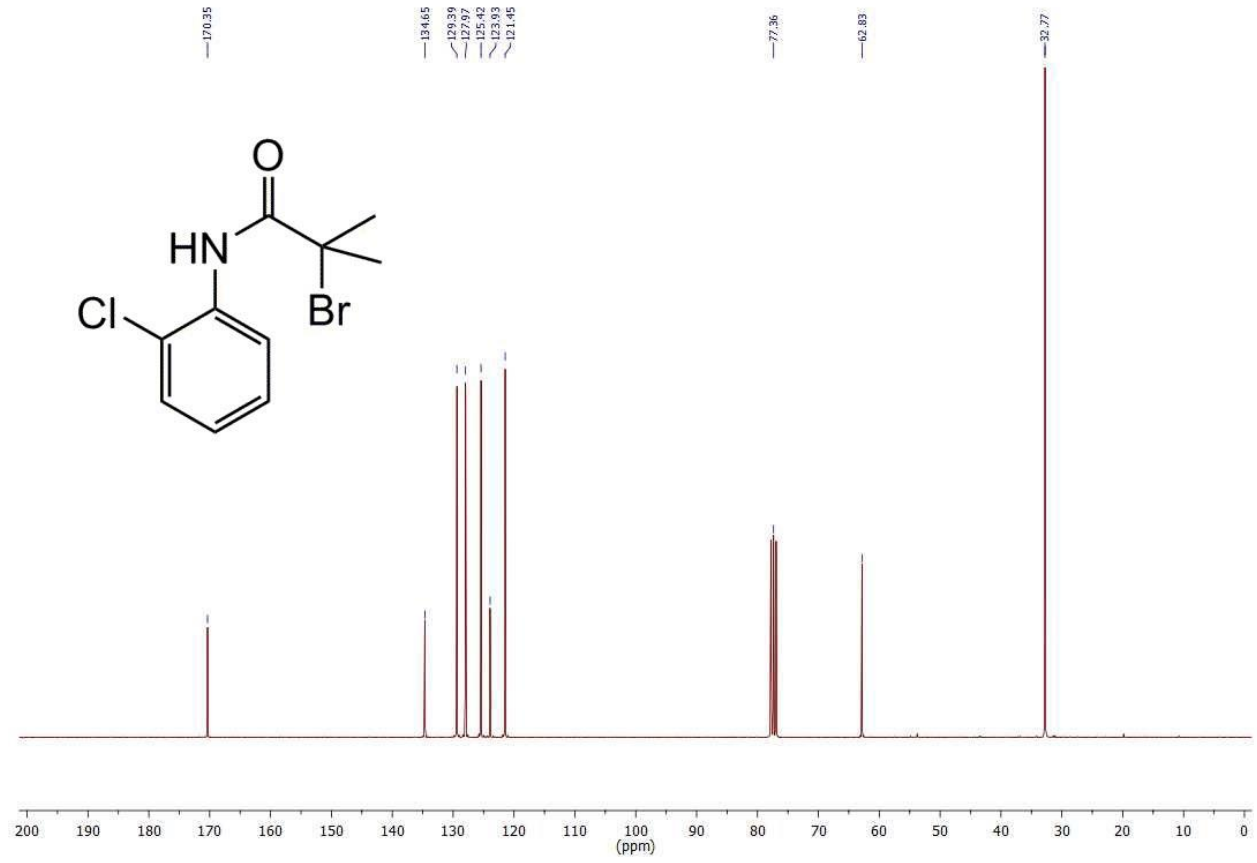
19


O
HN
Cl
Br


99.8
95
90
85
80
75
70
65
%T
60
55
50
45
40
35
30
25.0
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
650.0
cm-1
3365.2
2984.9
2934.4
1686.4
1592.9
1514.1
1459.4
1438.6
1384.1
1367.1
1304.2
1239.0
1154.4
1129.6
1110.8
1053.5
1034.3
1008.7
939.6
894.3
858.9
838.2
752.5
745.7
697.8
670.7
O
HN
Cl
Br



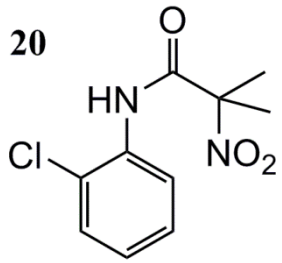
139 mg of **19** in 0.4 mL $CDCl_3$, 300 MHz, 8 scans

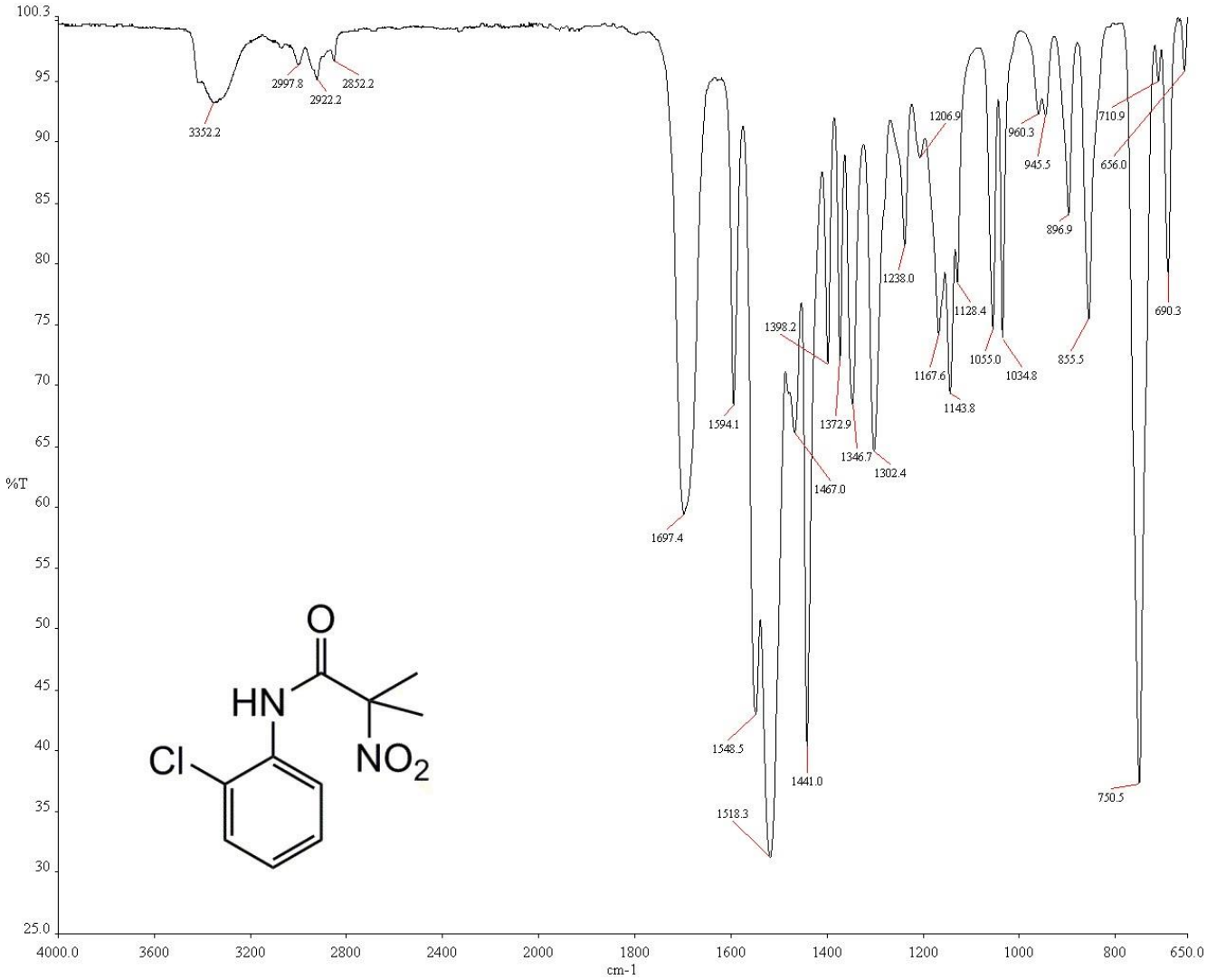


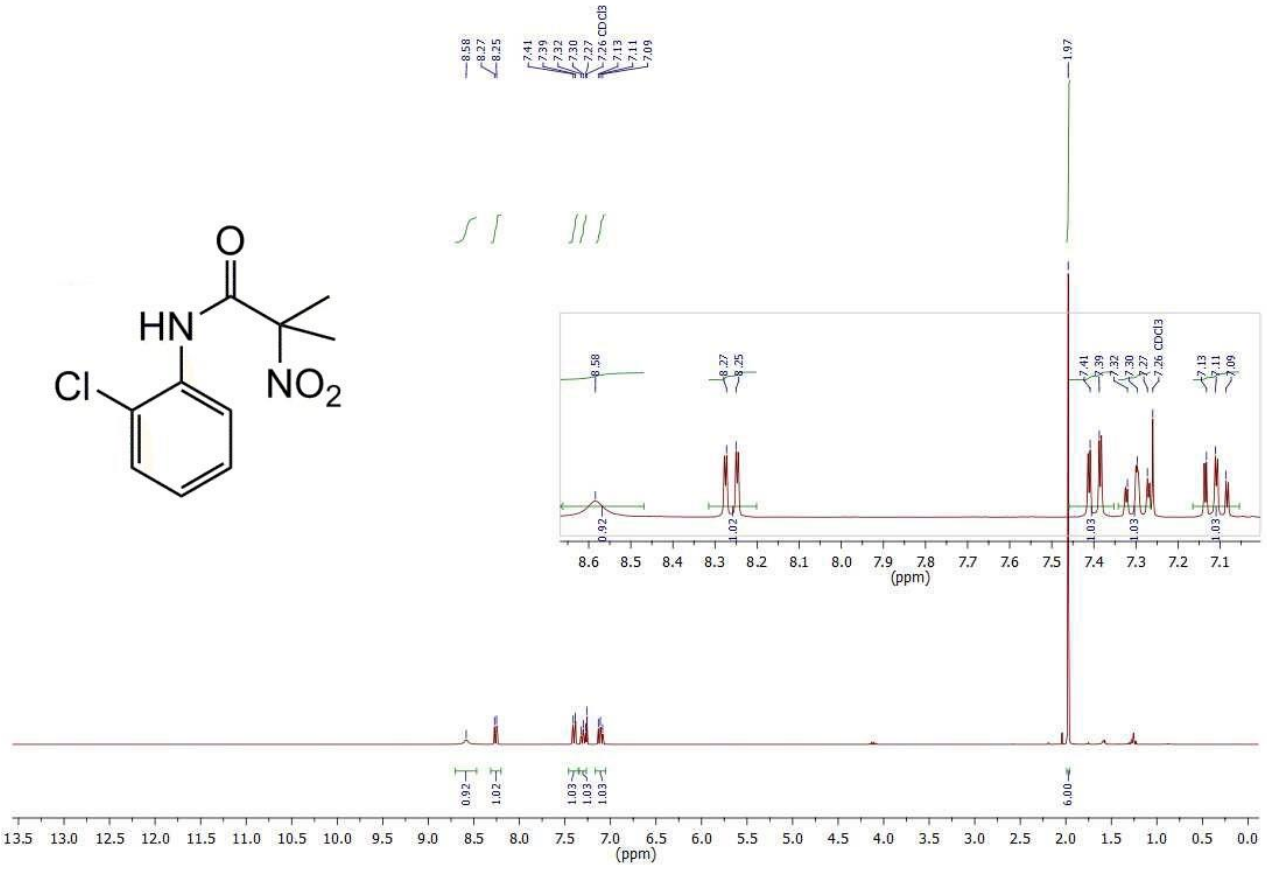
139 mg of **19** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

ESI for:
Bromo–nitro substitution on a tertiary α carbon—a previously uncharacterized facet of the Kornblum substitution

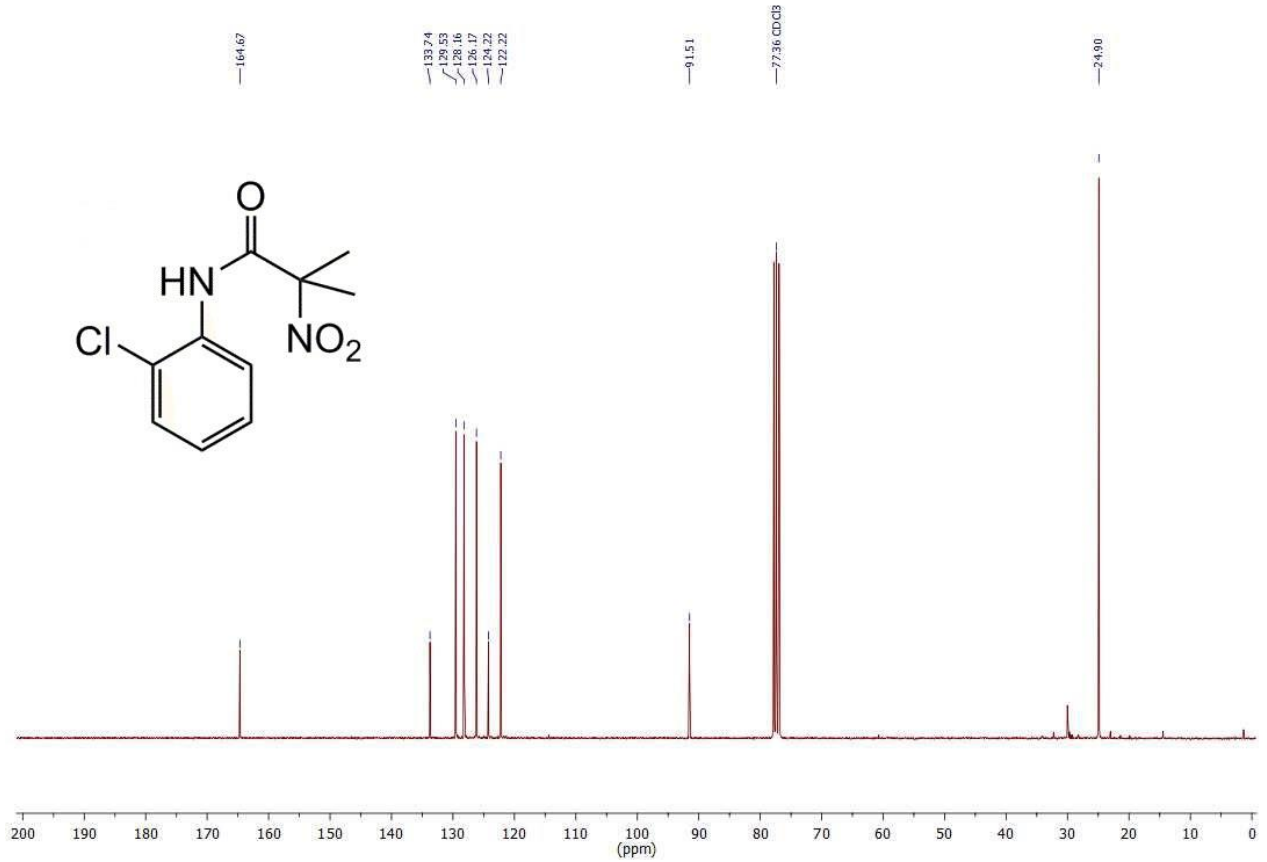
20





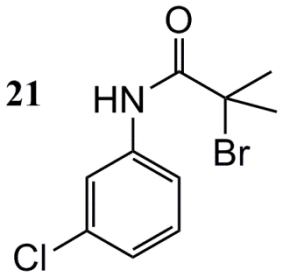


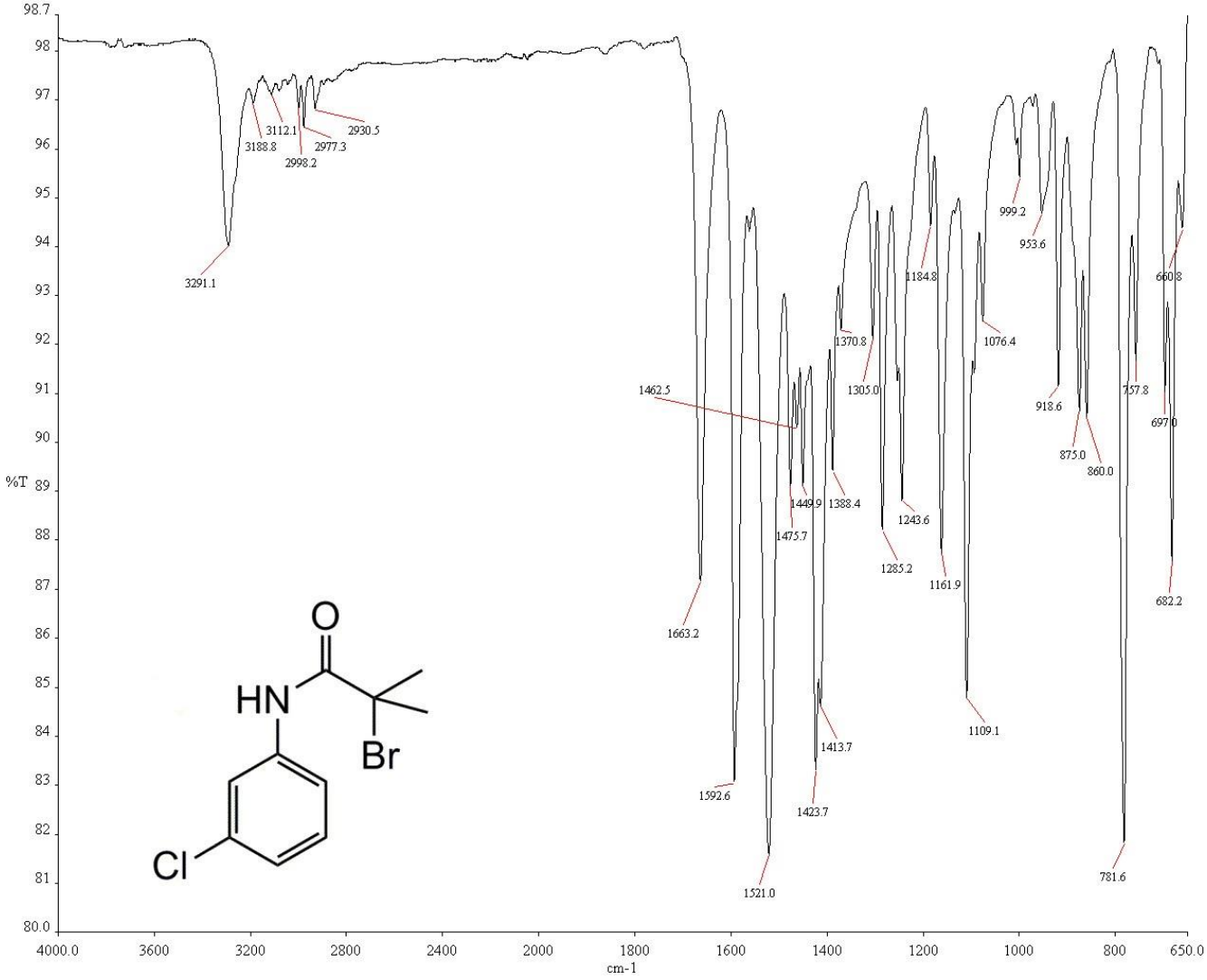
21 mg of **20** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans

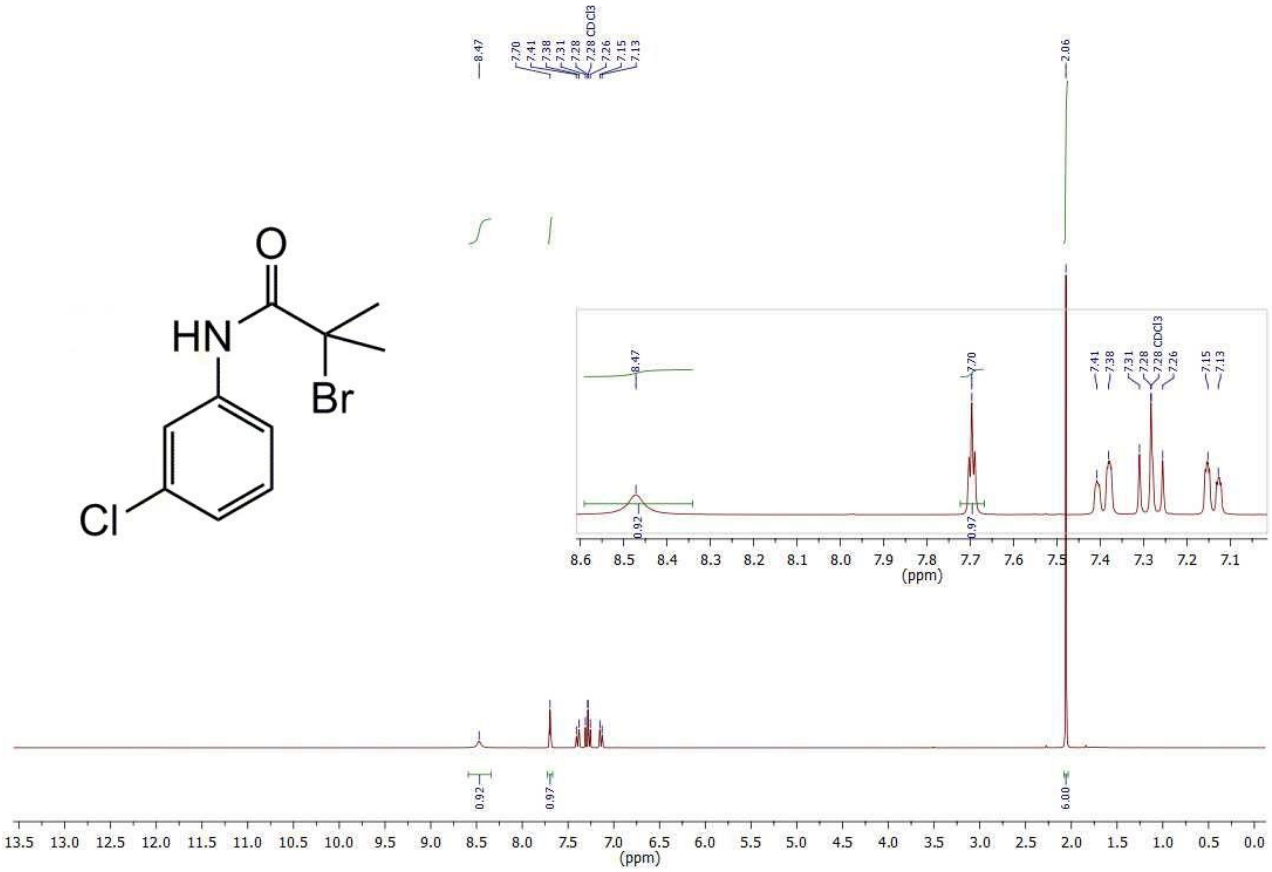


39 mg of **20** in 0.4 mL $CDCl_3$, 75 MHz, 13000 scans

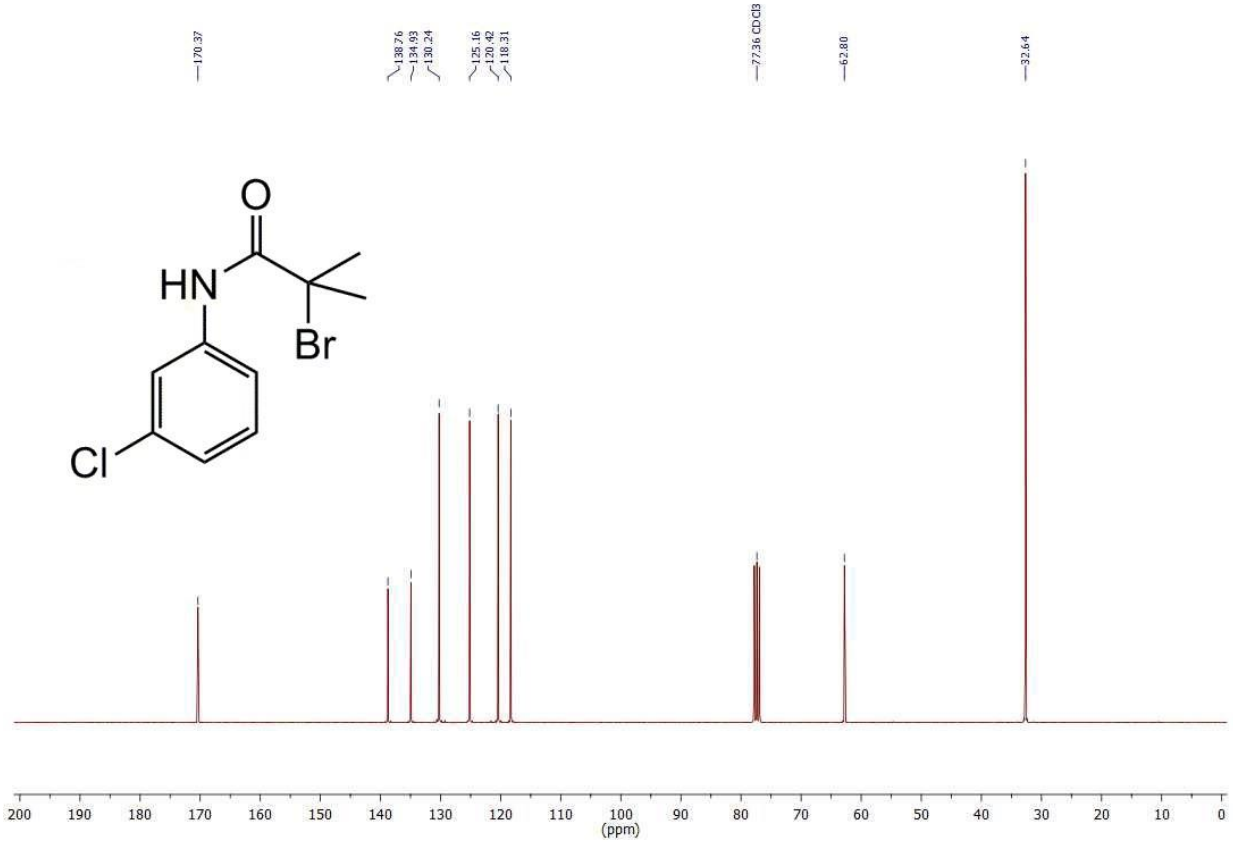
ESI for:
Bromo–nitro substitution on a tertiary α carbon—a previously uncharacterized facet of the Kornblum substitution





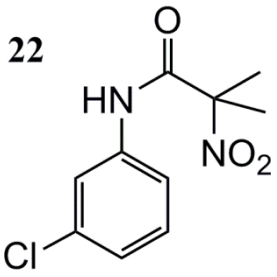


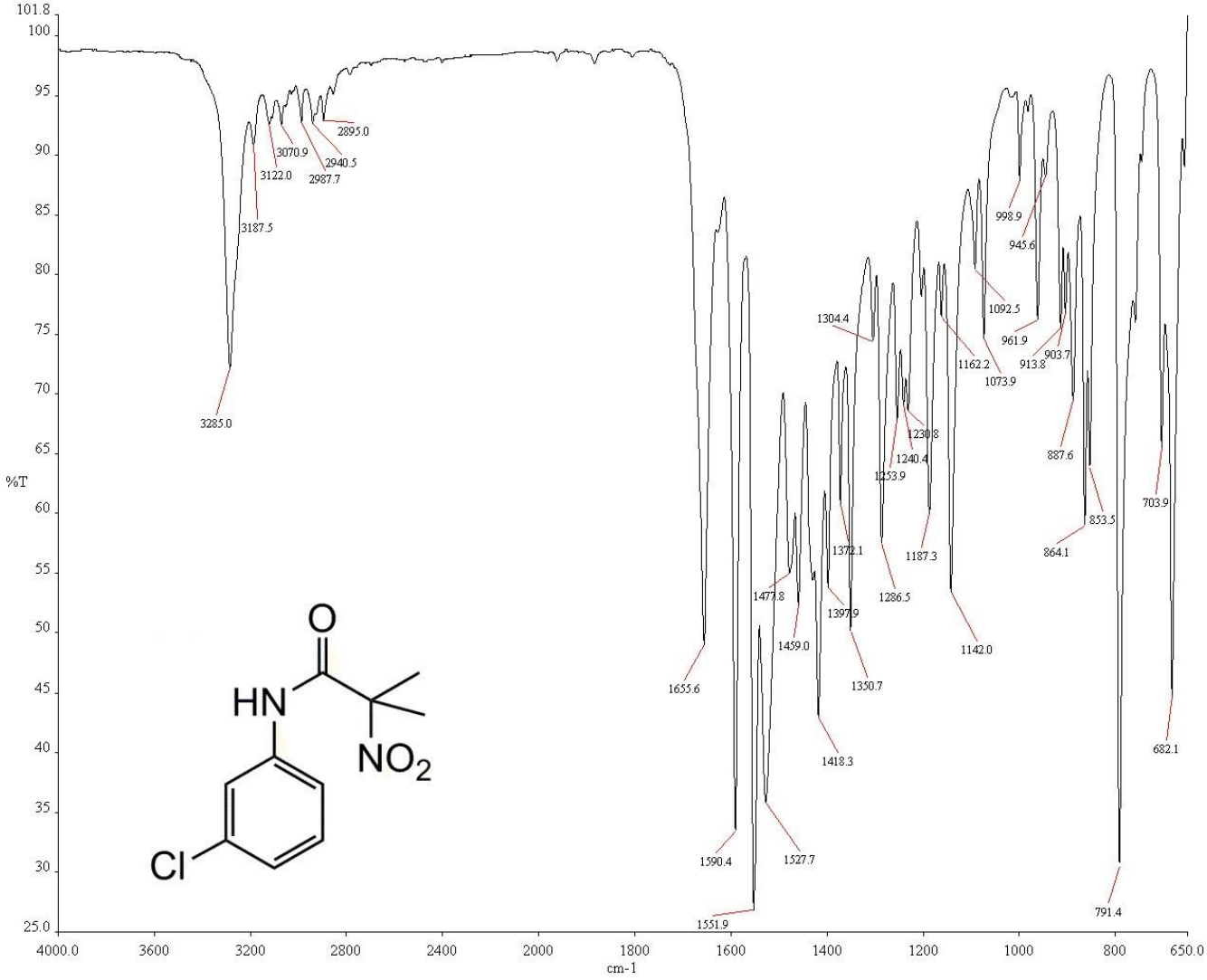
31 mg of **21** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans

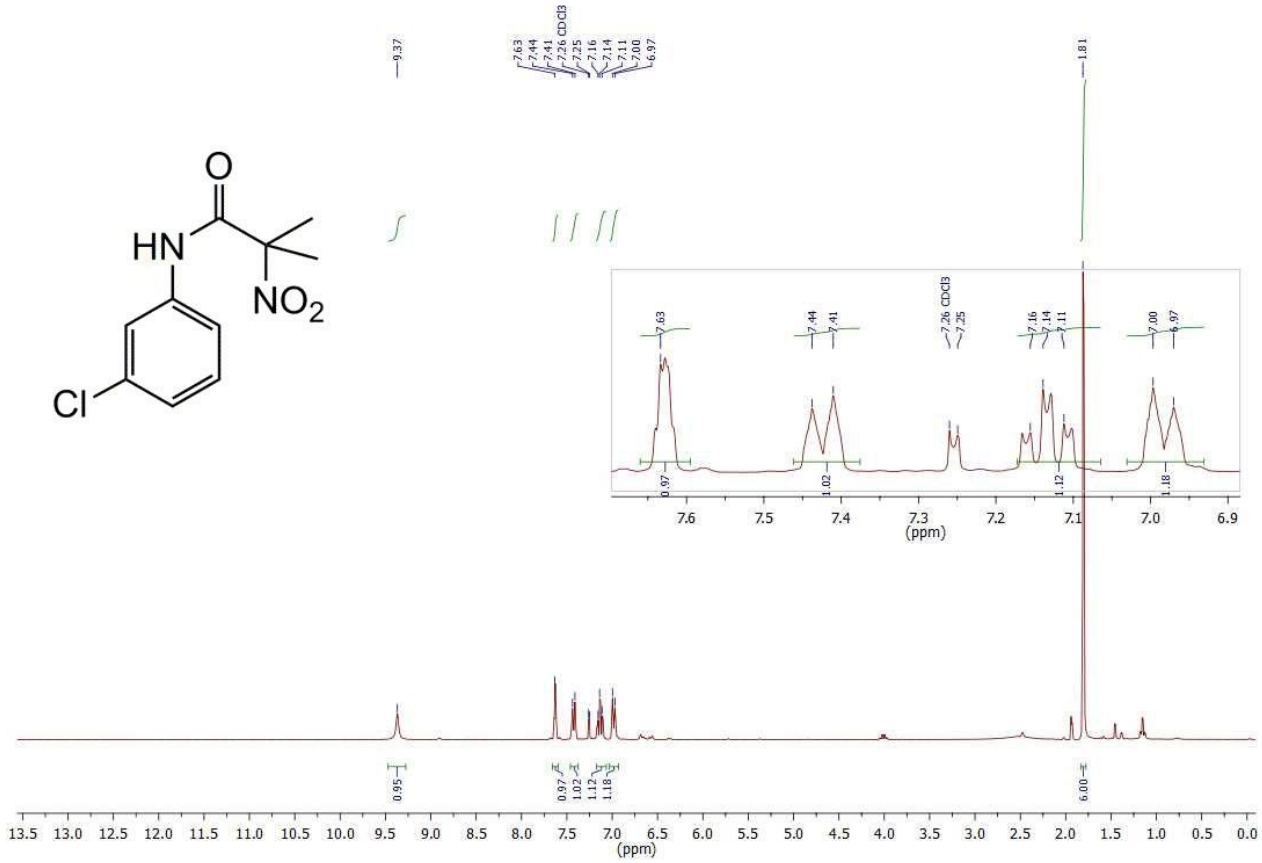


136 mg of **21** in 0.4 mL $CDCl_3$, 75 MHz, 15000 scans

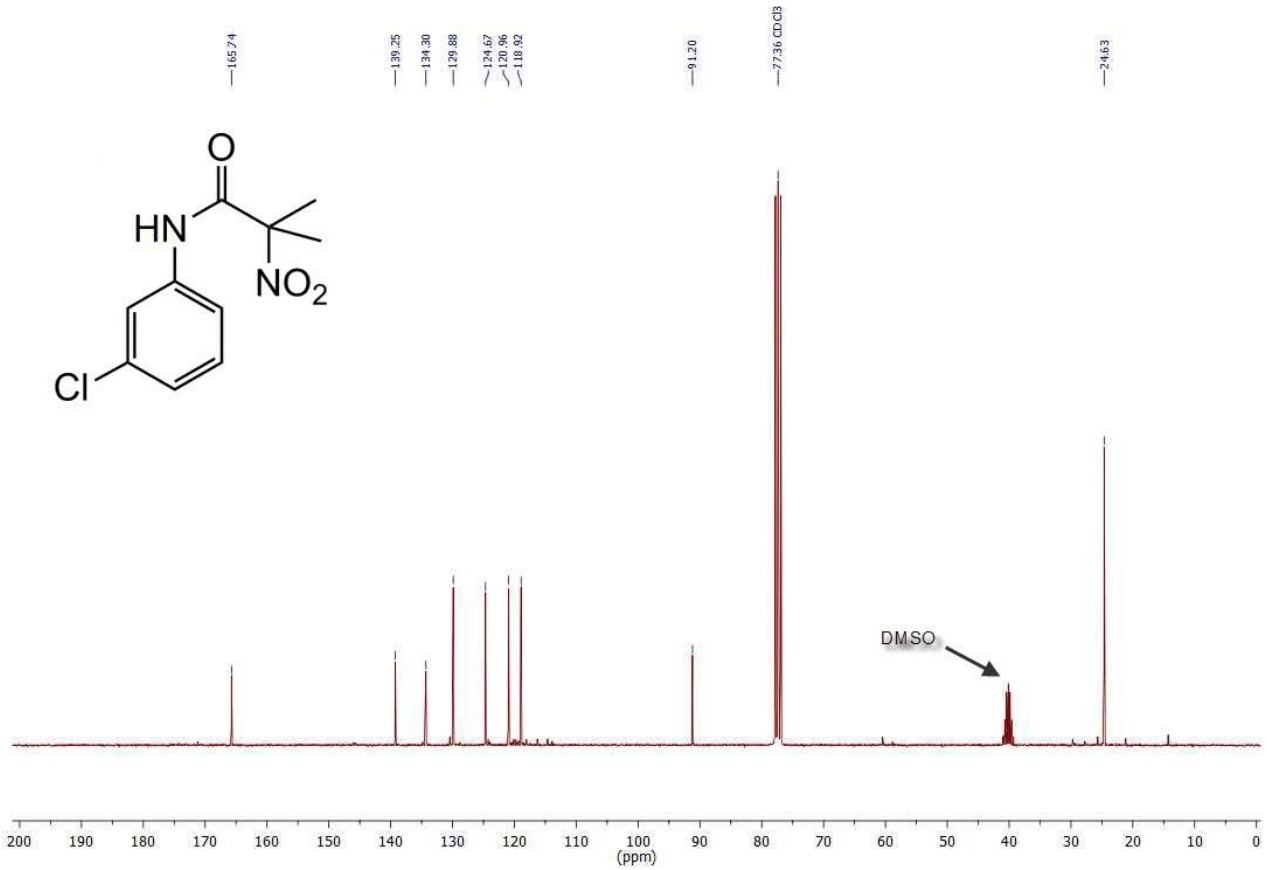
ESI for:
Bromo–nitro substitution on a tertiary α carbon—a previously uncharacterized facet of the Kornblum substitution







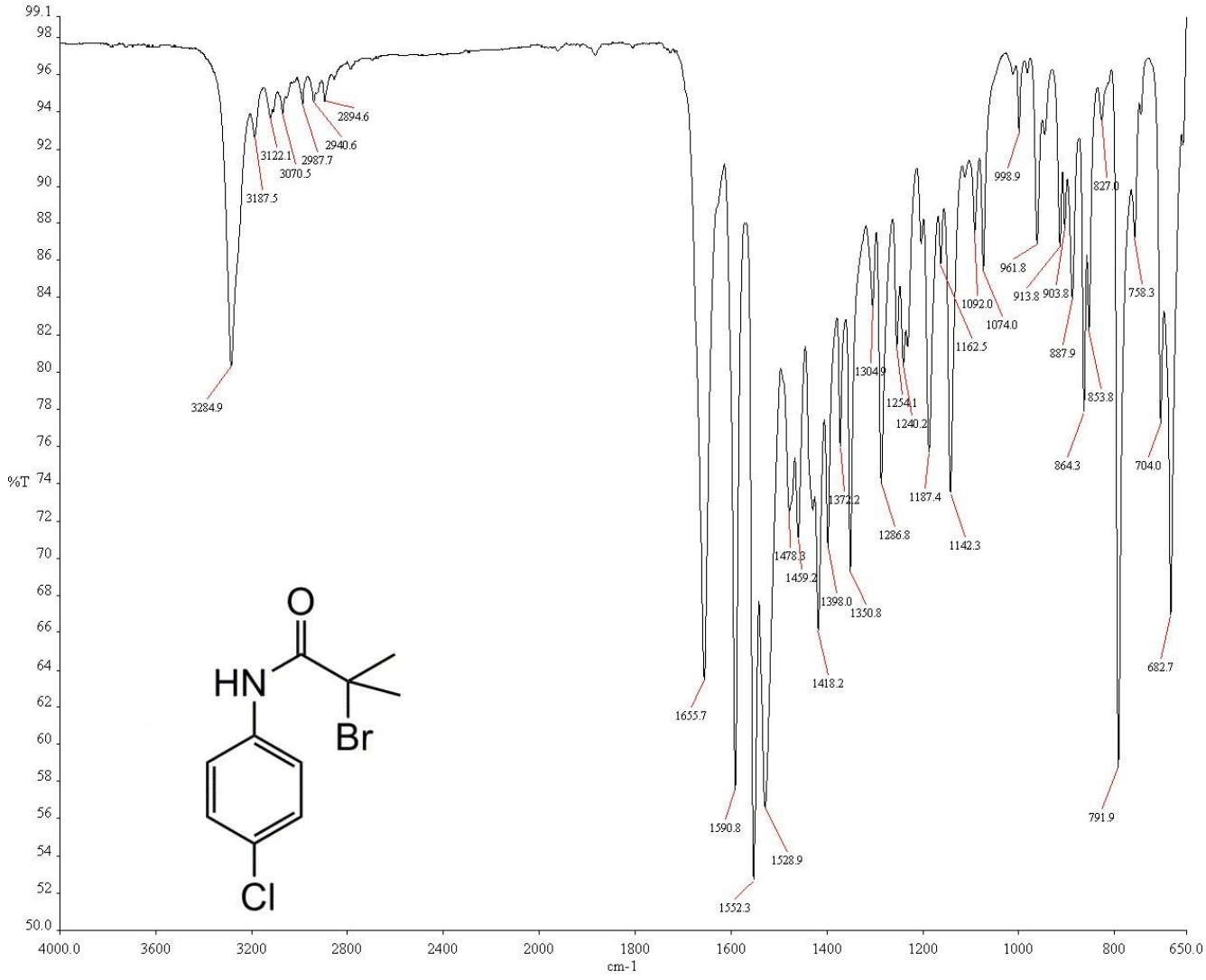
18 mg of **22** in 0.4 mL $CDCl_3$/2 drops d_6-DMSO, 300 MHz, 16 scans

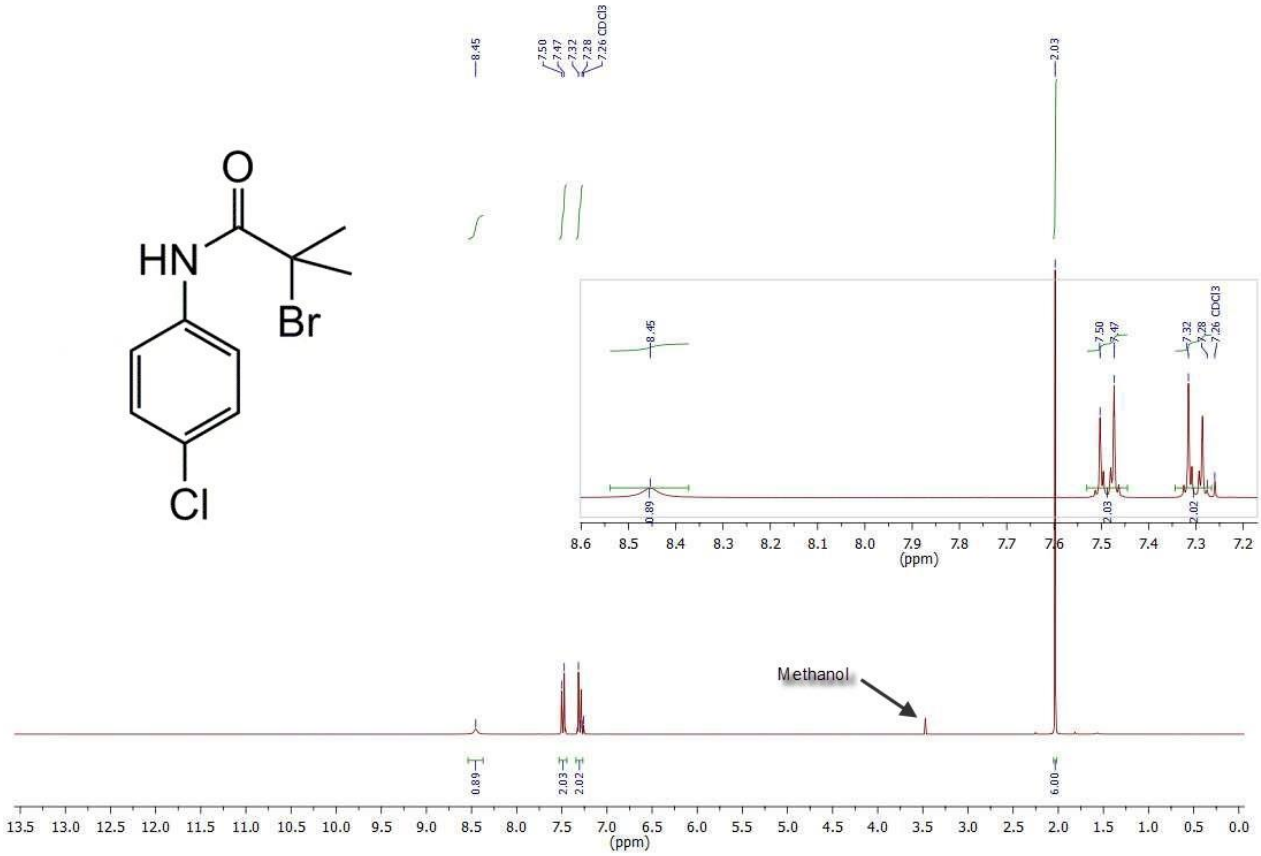


18 mg of **22** in 0.4 mL $CDCl_3$/2 drops d_6-DMSO, 75 MHz, 15000 scans

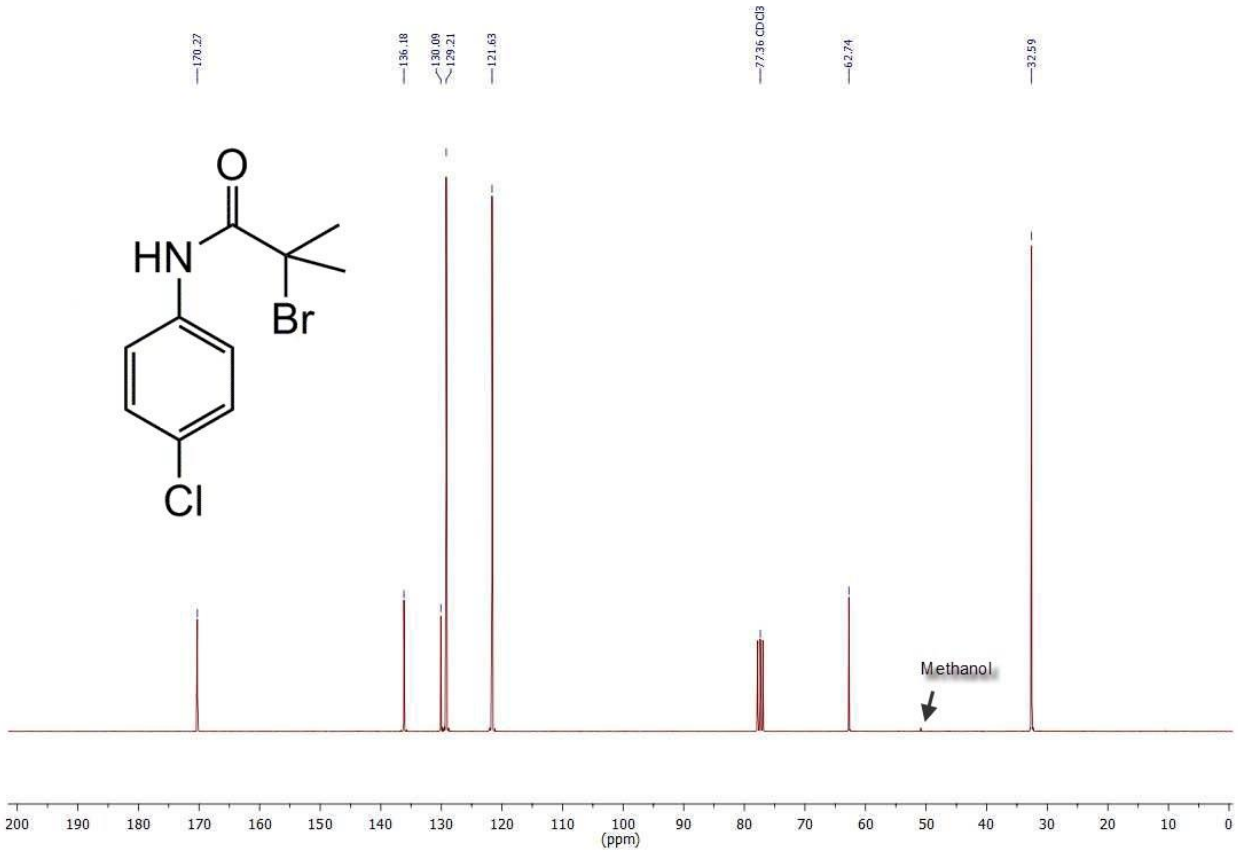
ESI for:
Bromo–nitro substitution on a tertiary α carbon—a previously uncharacterized facet of the Kornblum substitution

23



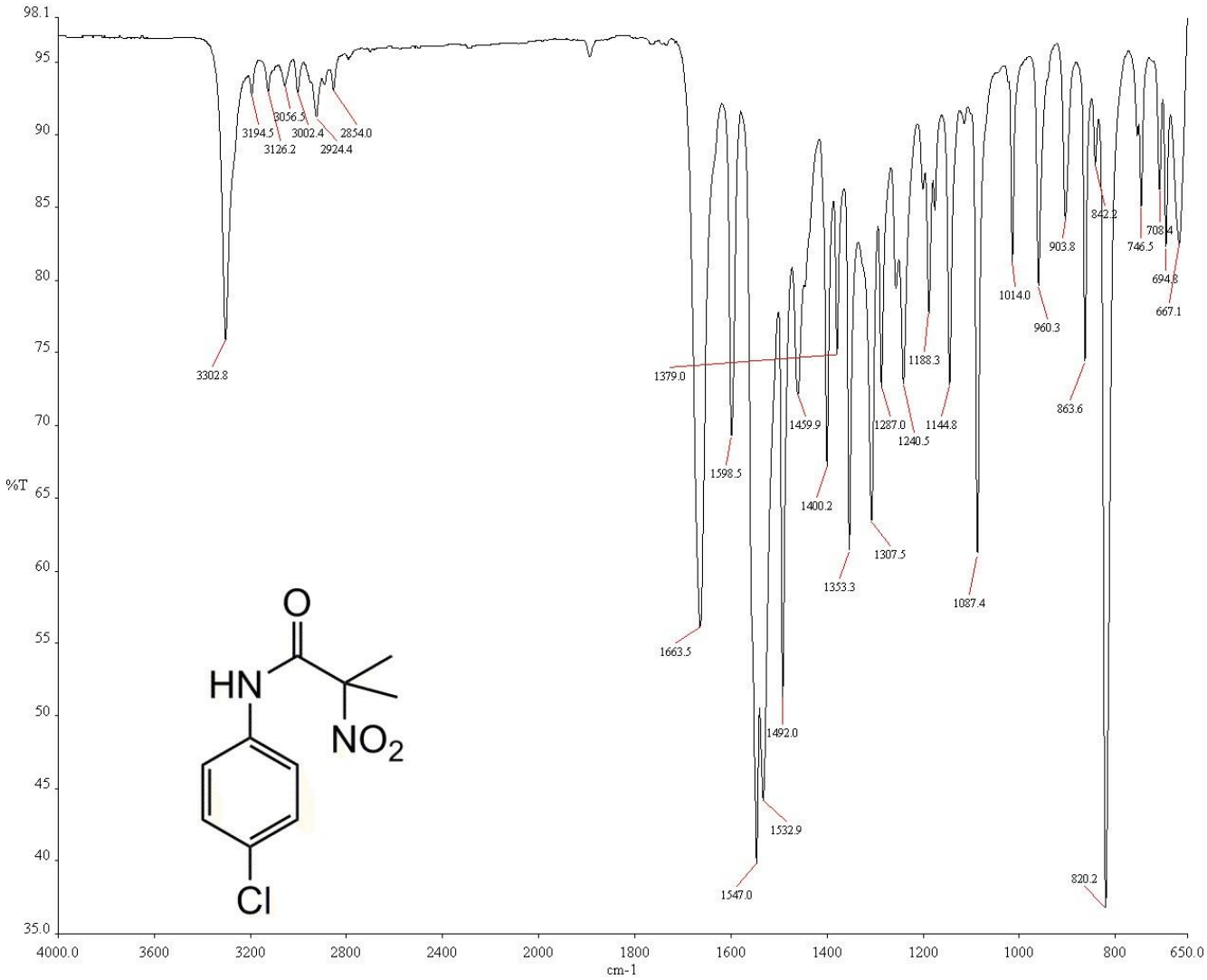


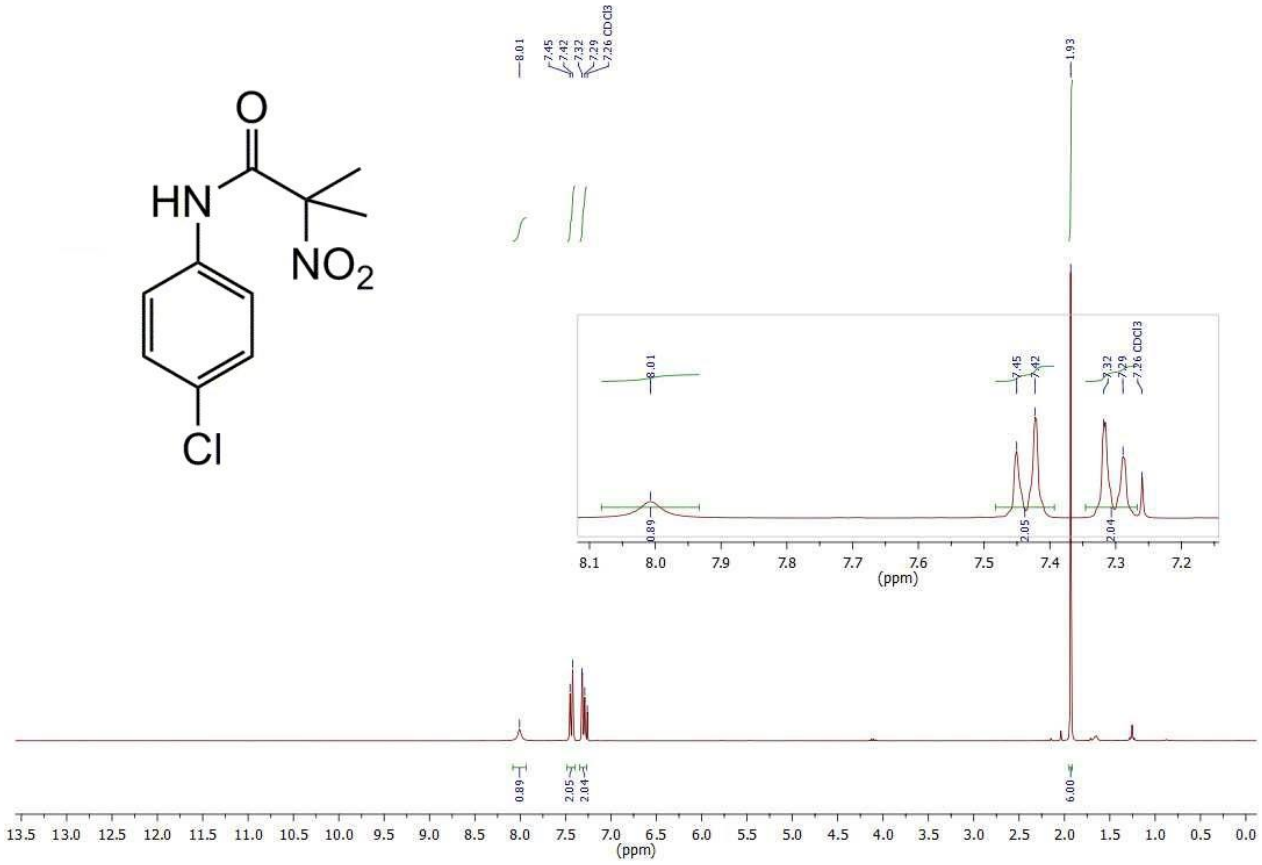
43 mg of **23** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans



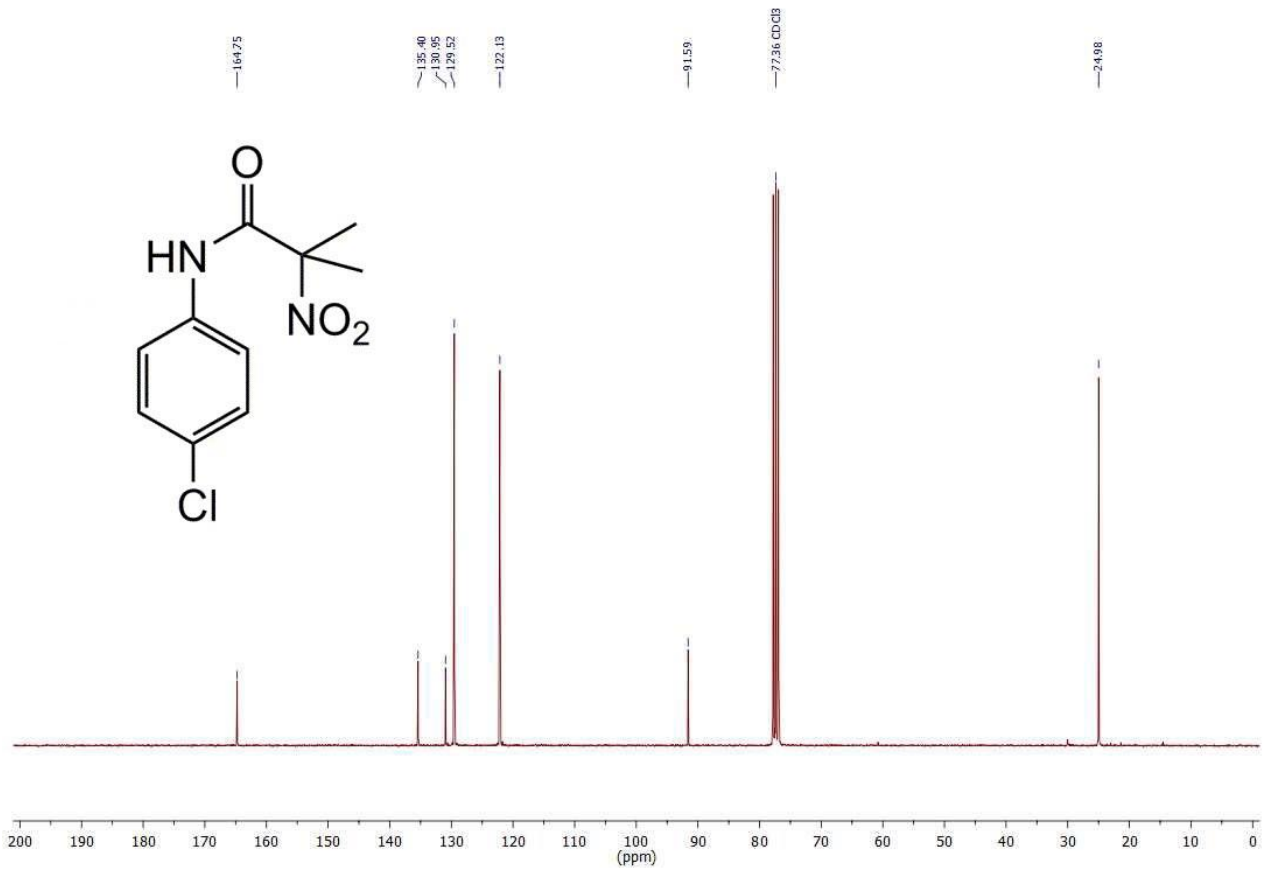
157 mg of **23** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

24


%T
cm-1
3302.8
3194.5
3126.2
3056.5
3002.4
2924.4
2854.0
1663.5
1598.5
1547.0
1532.9
1492.0
1459.9
1400.2
1379.0
1353.3
1307.5
1287.0
1240.5
1188.3
1144.8
1087.4
1014.0
960.3
903.8
863.6
842.2
820.2
746.5
708.4
694.8
667.1

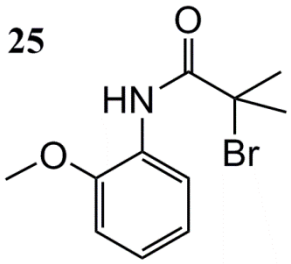


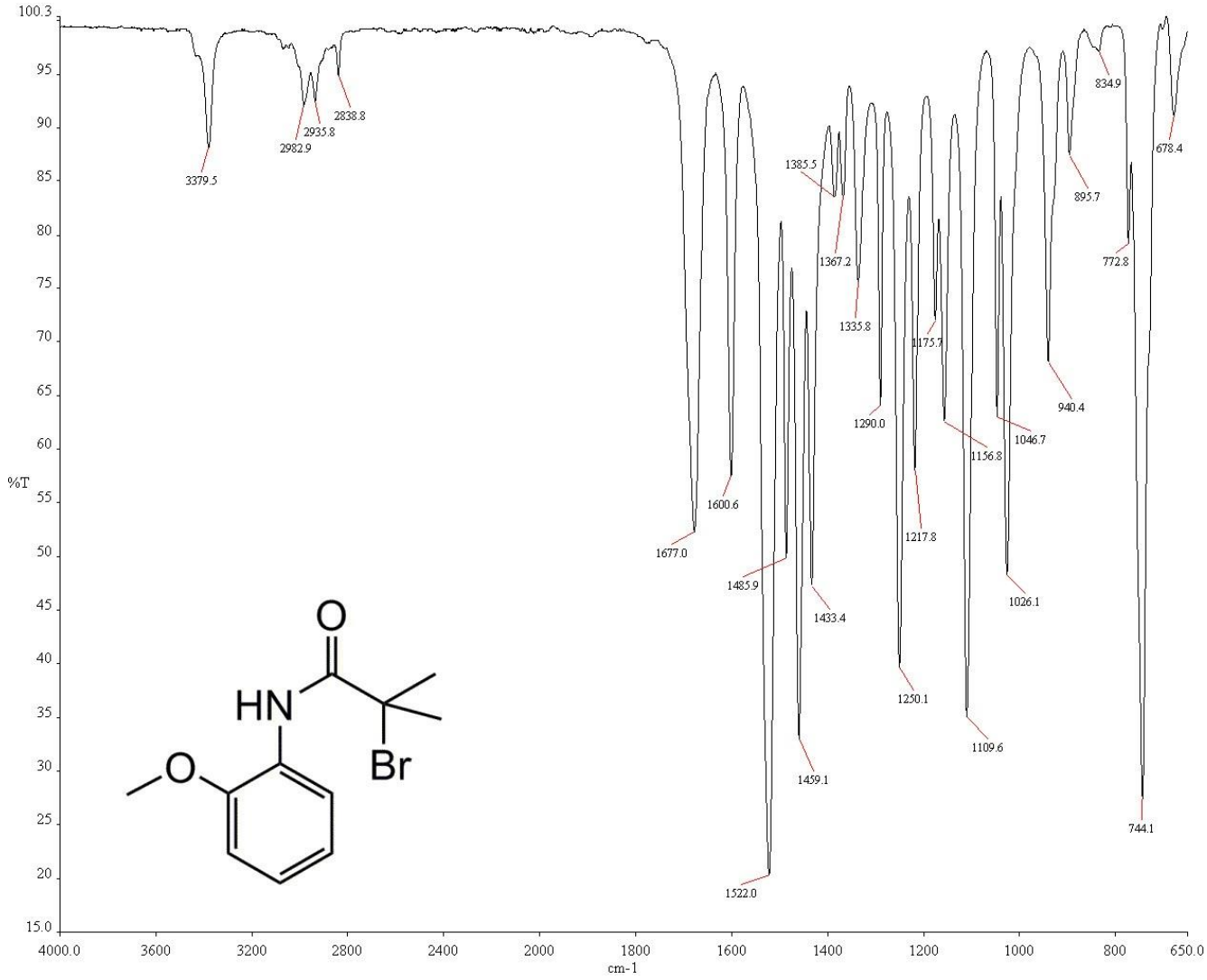
21 mg of **24** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans

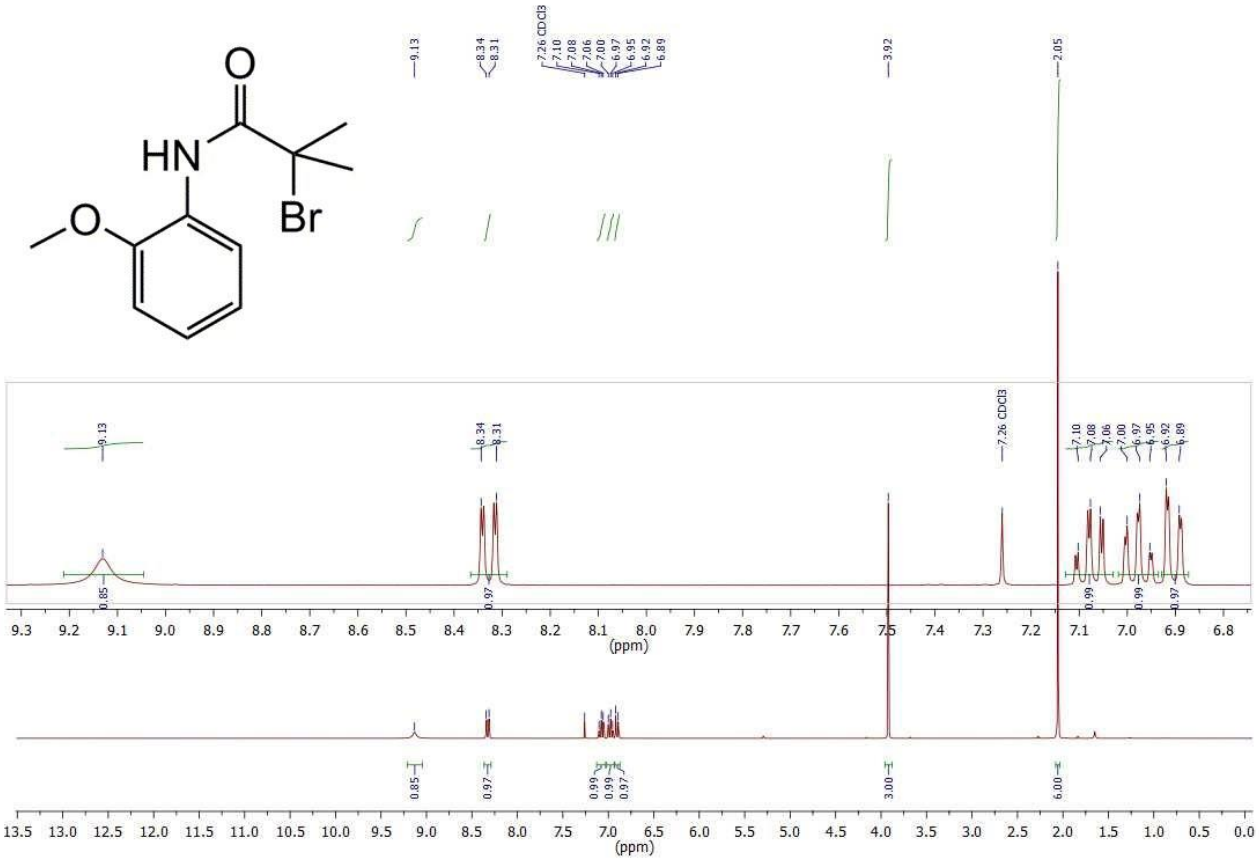


21 mg of **24** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

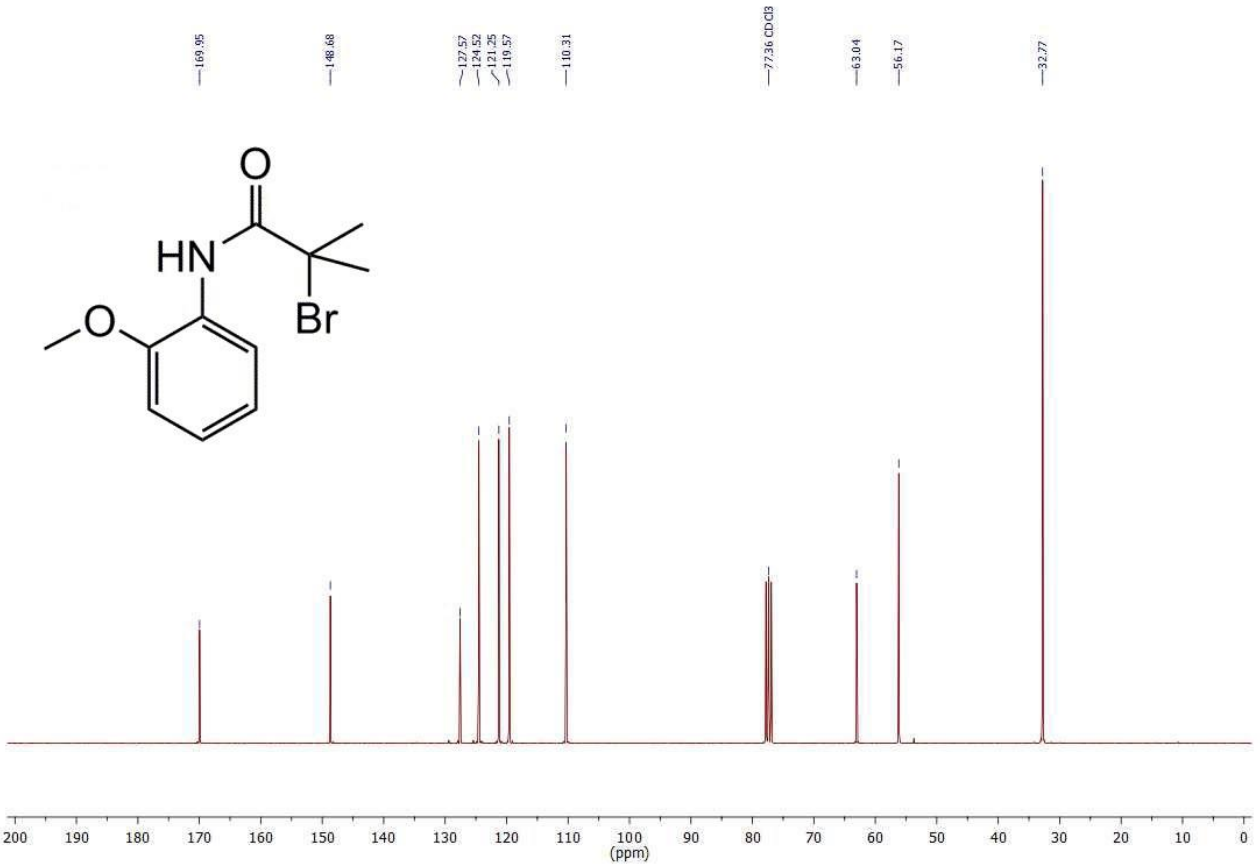
ESI for:
Bromo–nitro substitution on a tertiary α carbon—a previously uncharacterized facet of the Kornblum substitution





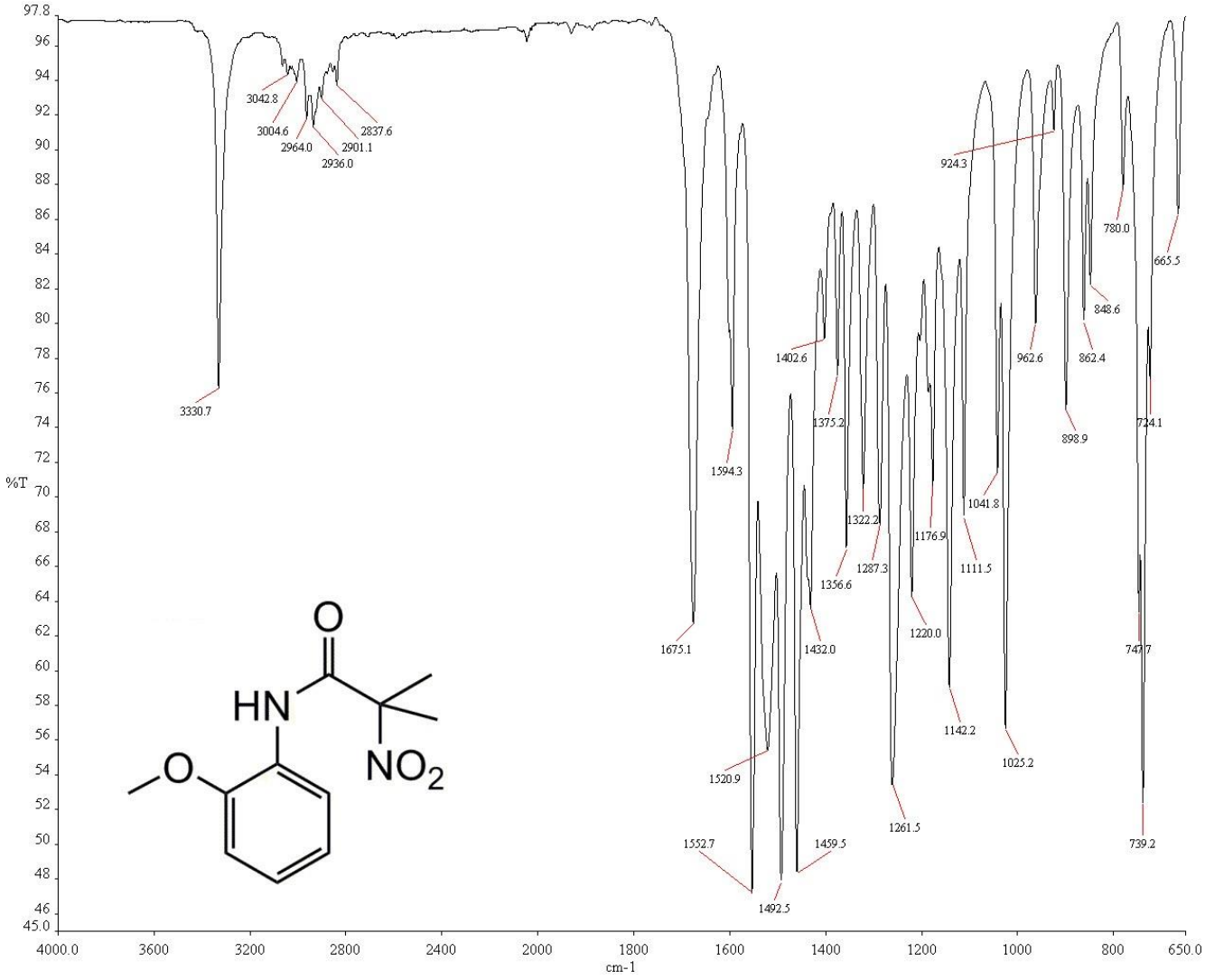


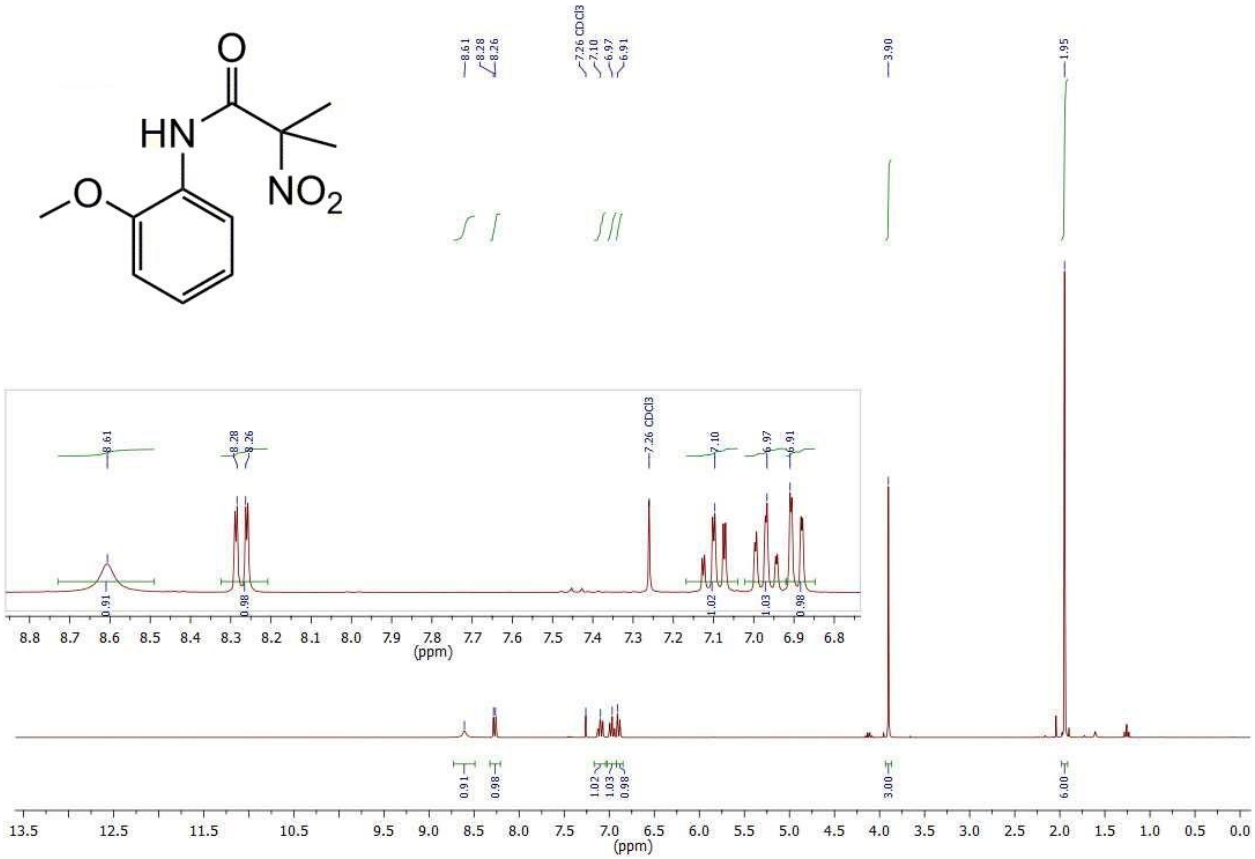
28 mg of **25** in 0.4 mL $CDCl_3$, 300 MHz, 32 scans



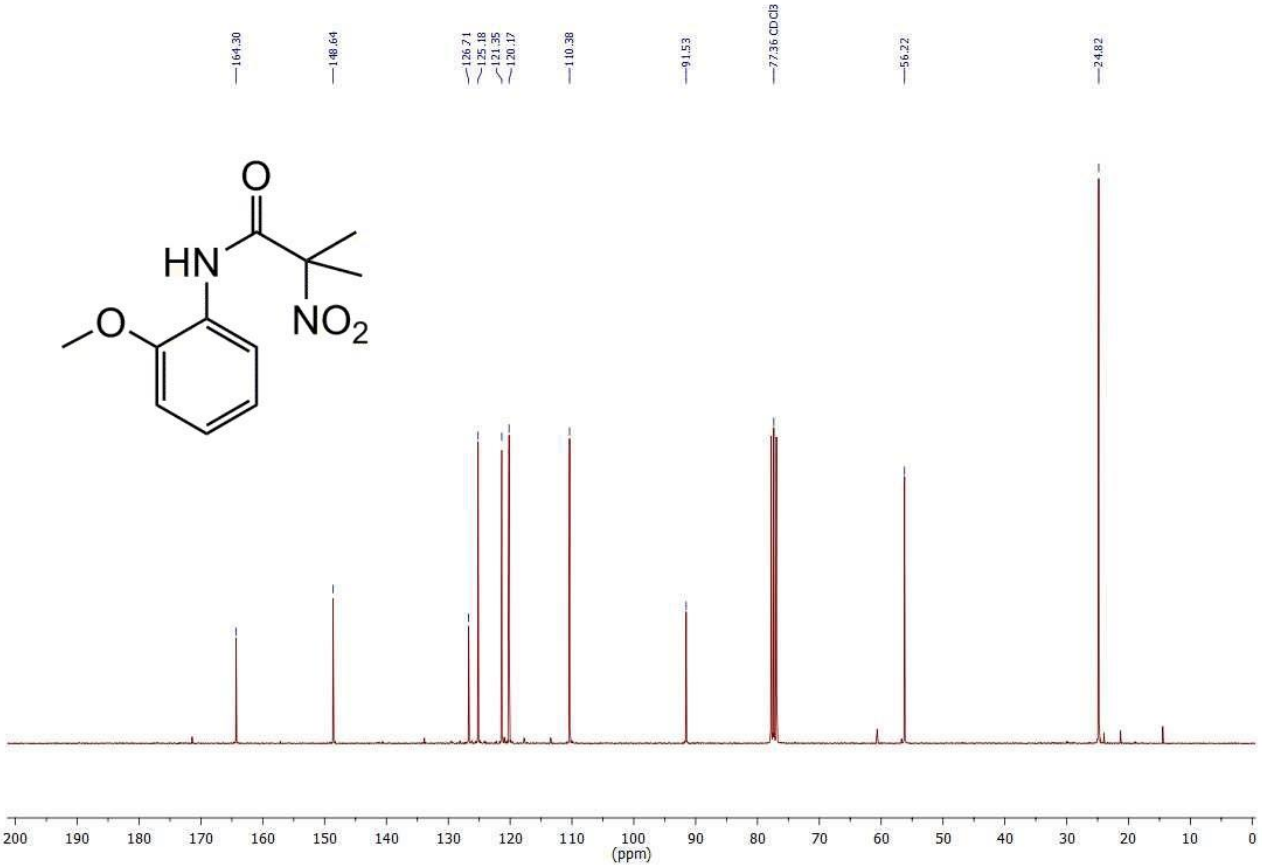
133 mg of **25** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

26

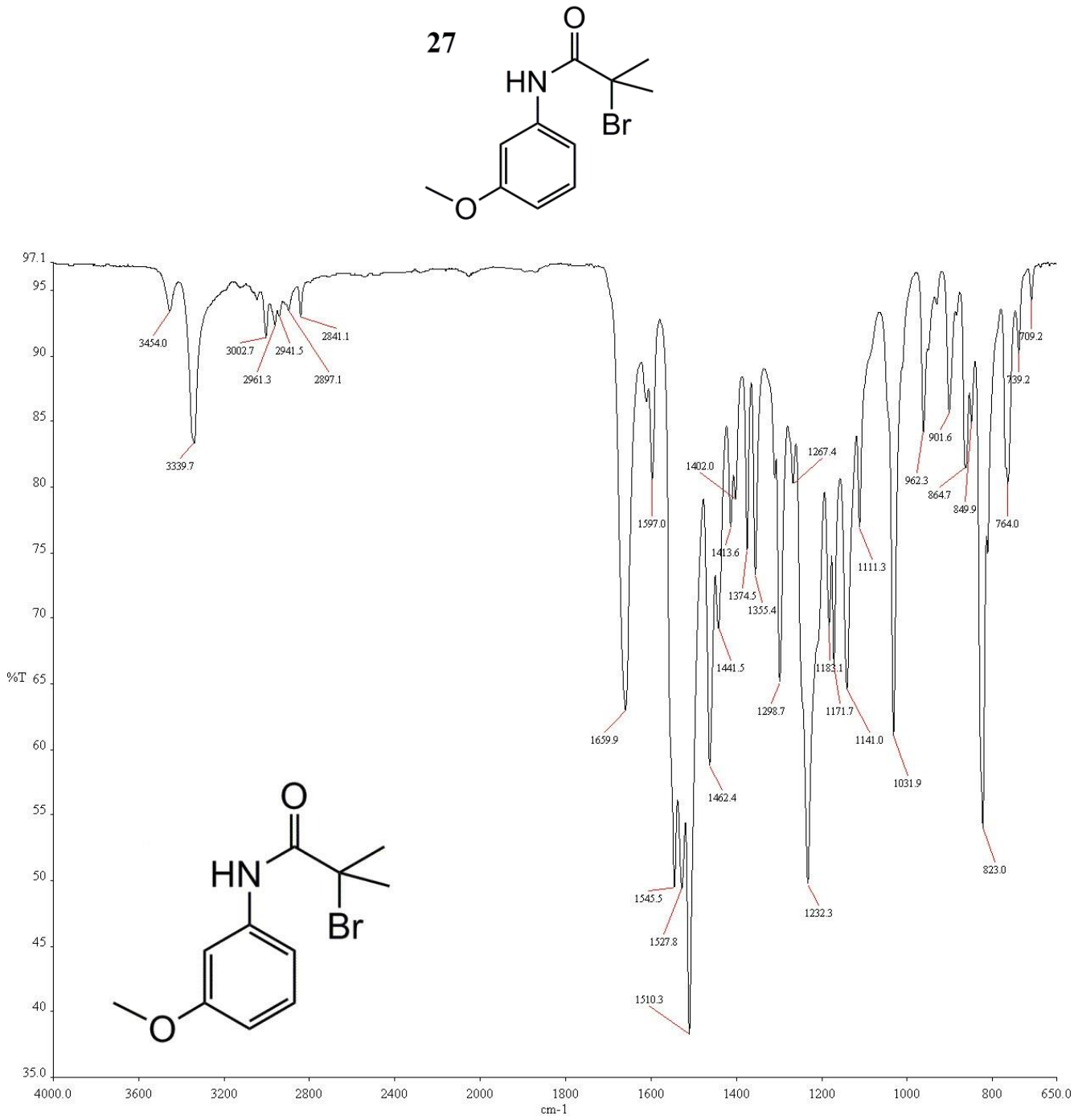

%T
cm-1
3330.7
3042.8
3004.6
2964.0
2936.0
2901.1
2837.6
1675.1
1594.3
1552.7
1520.9
1492.5
1459.5
1432.0
1402.6
1375.2
1356.6
1322.2
1287.3
1261.5
1220.0
1176.9
1142.2
1111.5
1041.8
1025.2
962.6
924.3
898.9
862.4
848.6
780.0
747.7
739.2
724.1
665.5

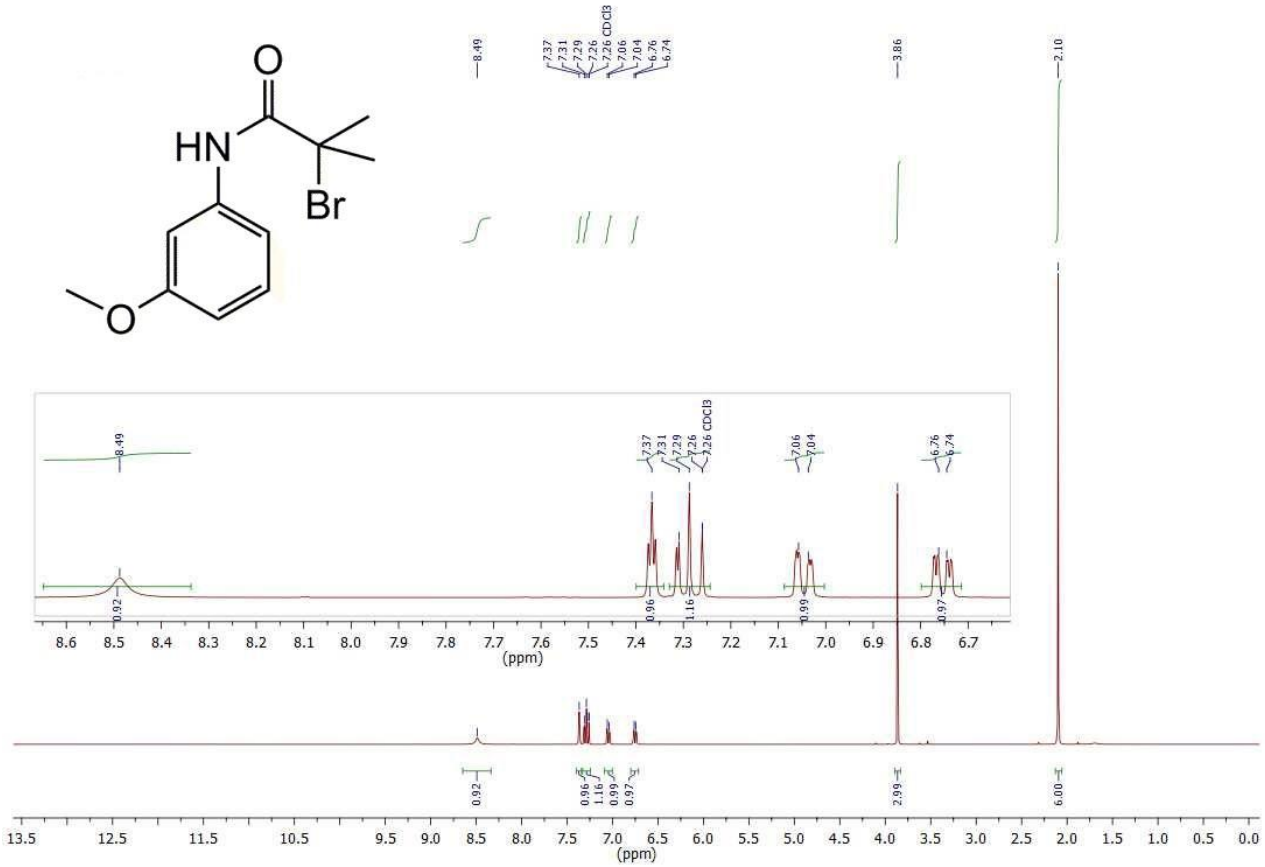


19 mg of **26** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans

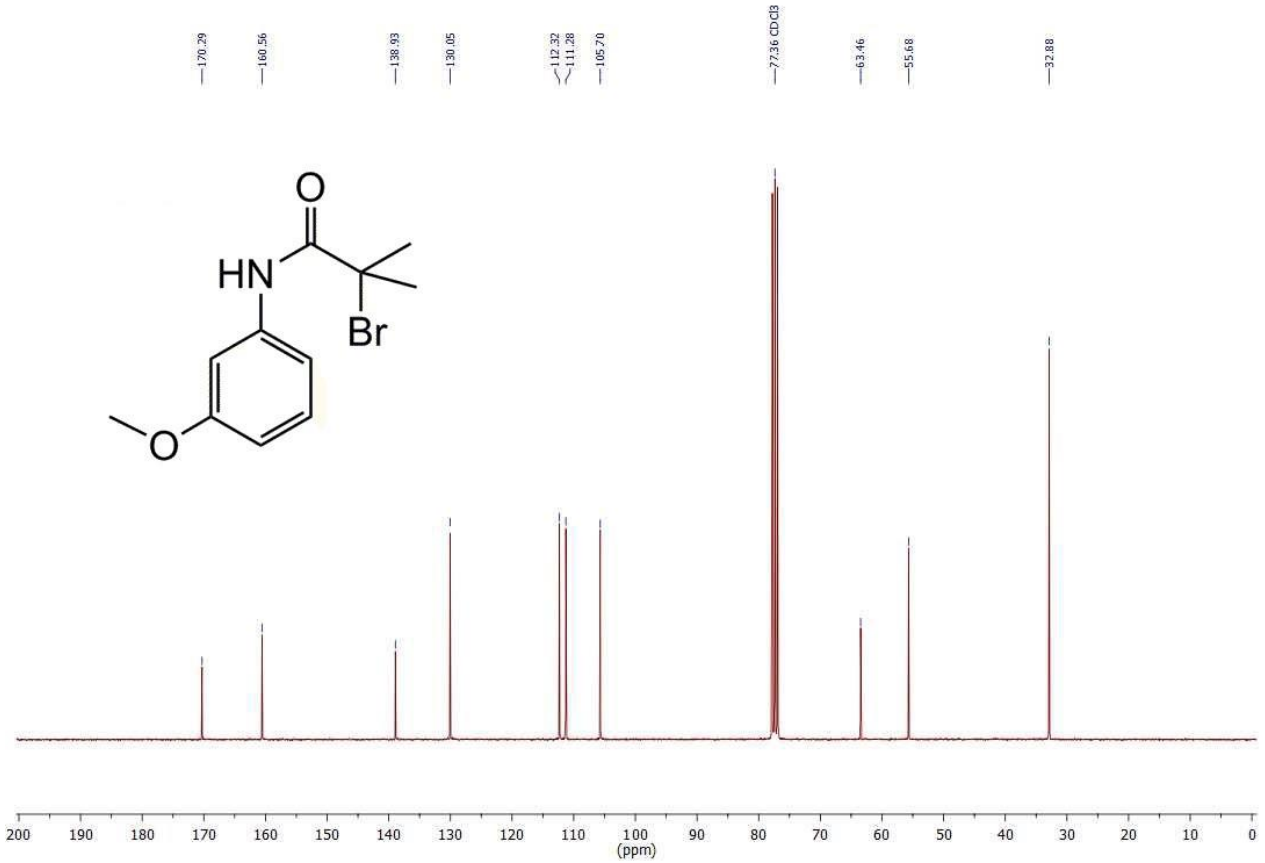


57 mg of **26** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans


27
O
HN
Br
O
97.1
95
90
85
80
75
70
%T 65
60
55
50
45
40
35.0
3454.0
3339.7
3002.7
2961.3
2941.5
2897.1
2841.1
1659.9
1597.0
1545.5
1527.8
1510.3
1462.4
1441.5
1413.6
1402.0
1374.5
1355.4
1298.7
1267.4
1232.3
1183.1
1171.7
1141.0
1111.3
1031.9
962.3
901.6
864.7
849.9
823.0
764.0
739.2
709.2
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
650.0
cm-1

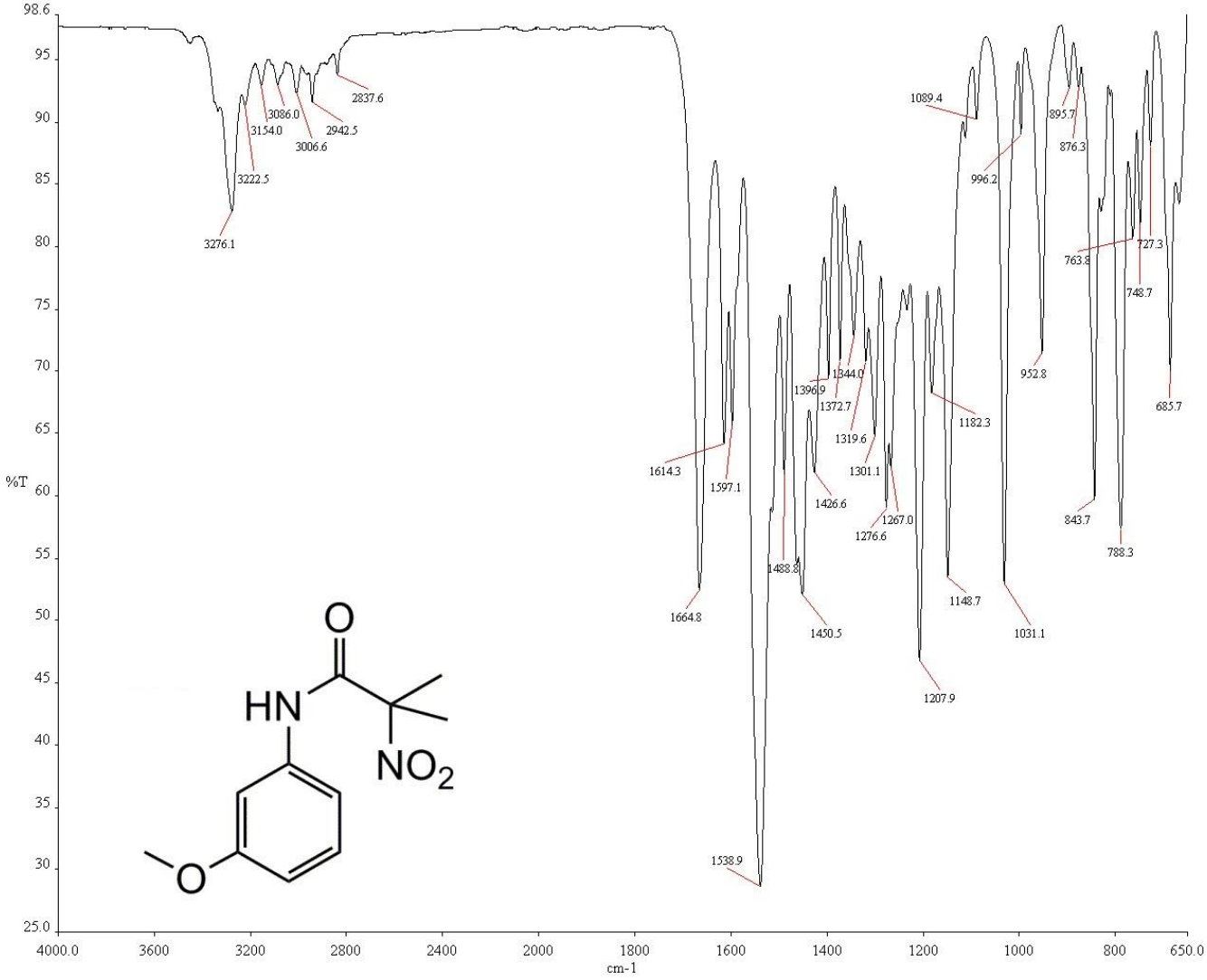


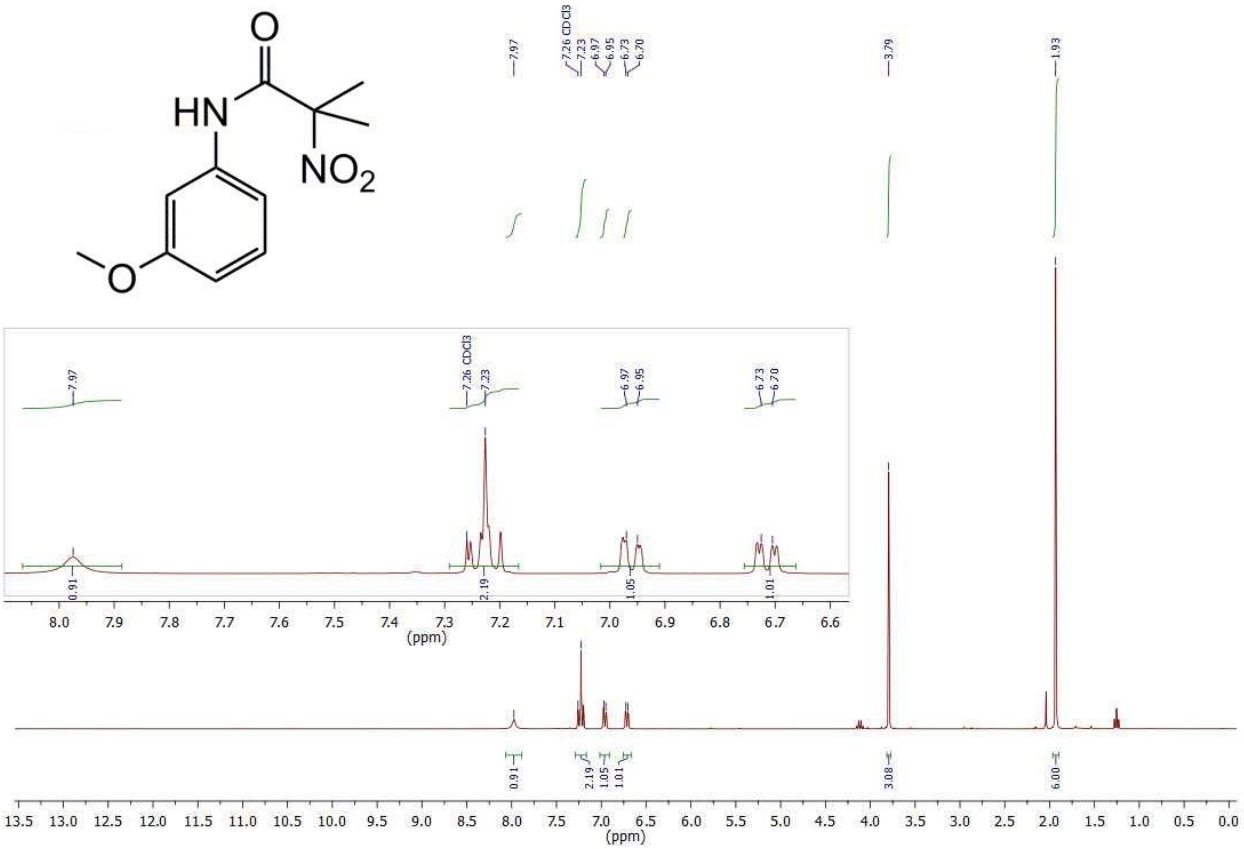
31 mg of **27** in 0.4 mL $CDCl_3$, 300 MHz, 128 scans



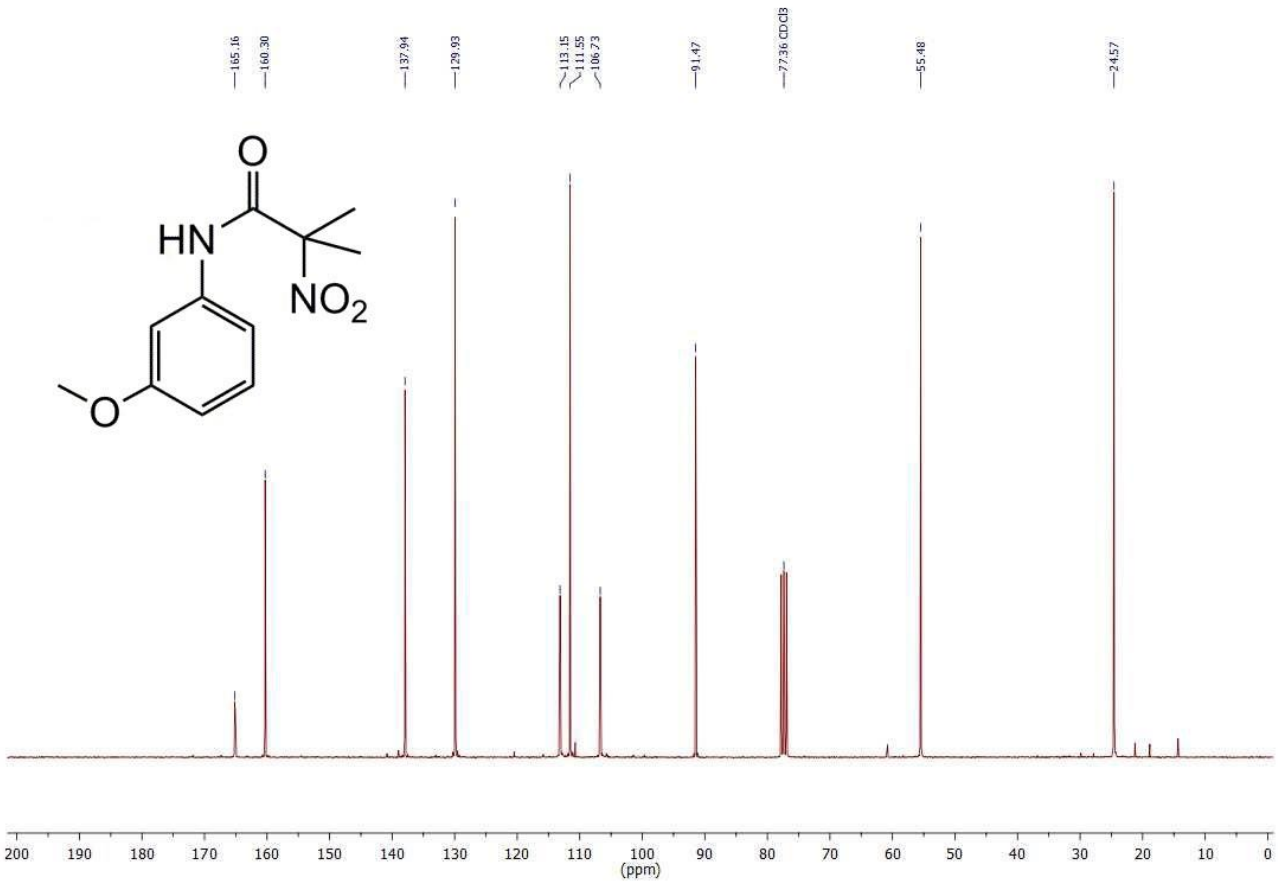
31 mg of **27** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

28


%T
cm-1
3276.1
3222.5
3154.0
3086.0
3006.6
2942.5
2837.6
1664.8
1614.3
1597.1
1538.9
1488.8
1450.5
1426.6
1396.9
1372.7
1344.0
1319.6
1301.1
1276.6
1267.0
1207.9
1182.3
1148.7
1089.4
1031.1
996.2
952.8
895.7
876.3
843.7
788.3
763.8
748.7
727.3
685.7

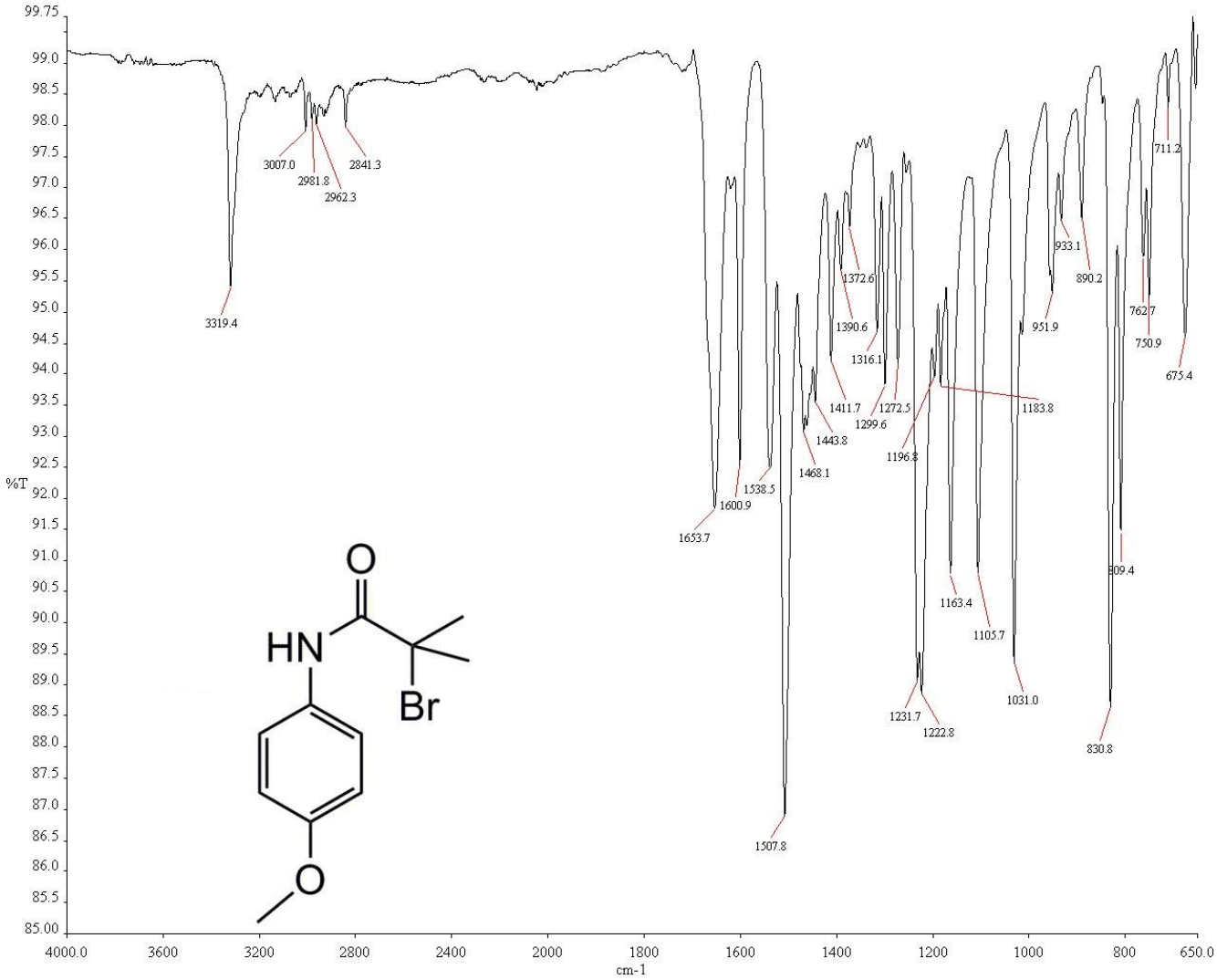


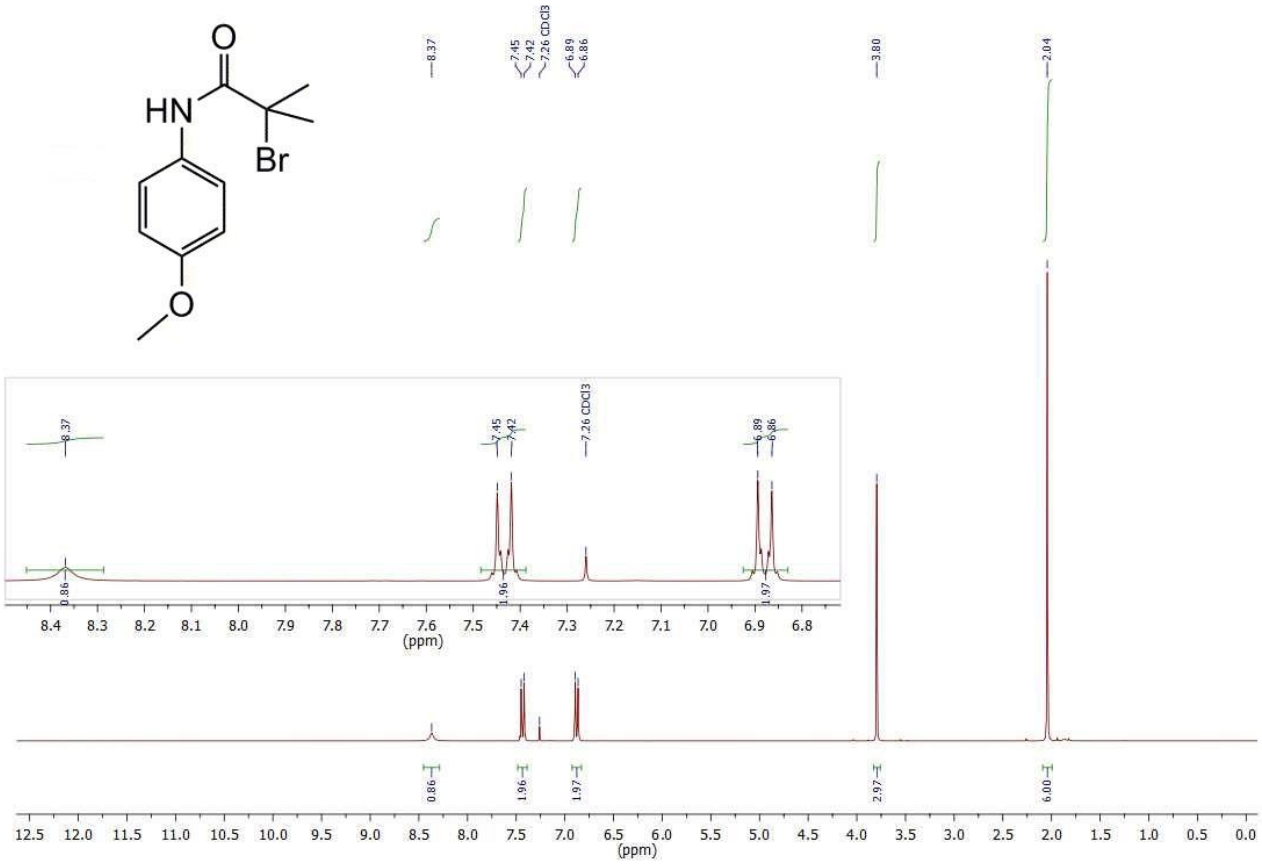
28 mg of **28** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans



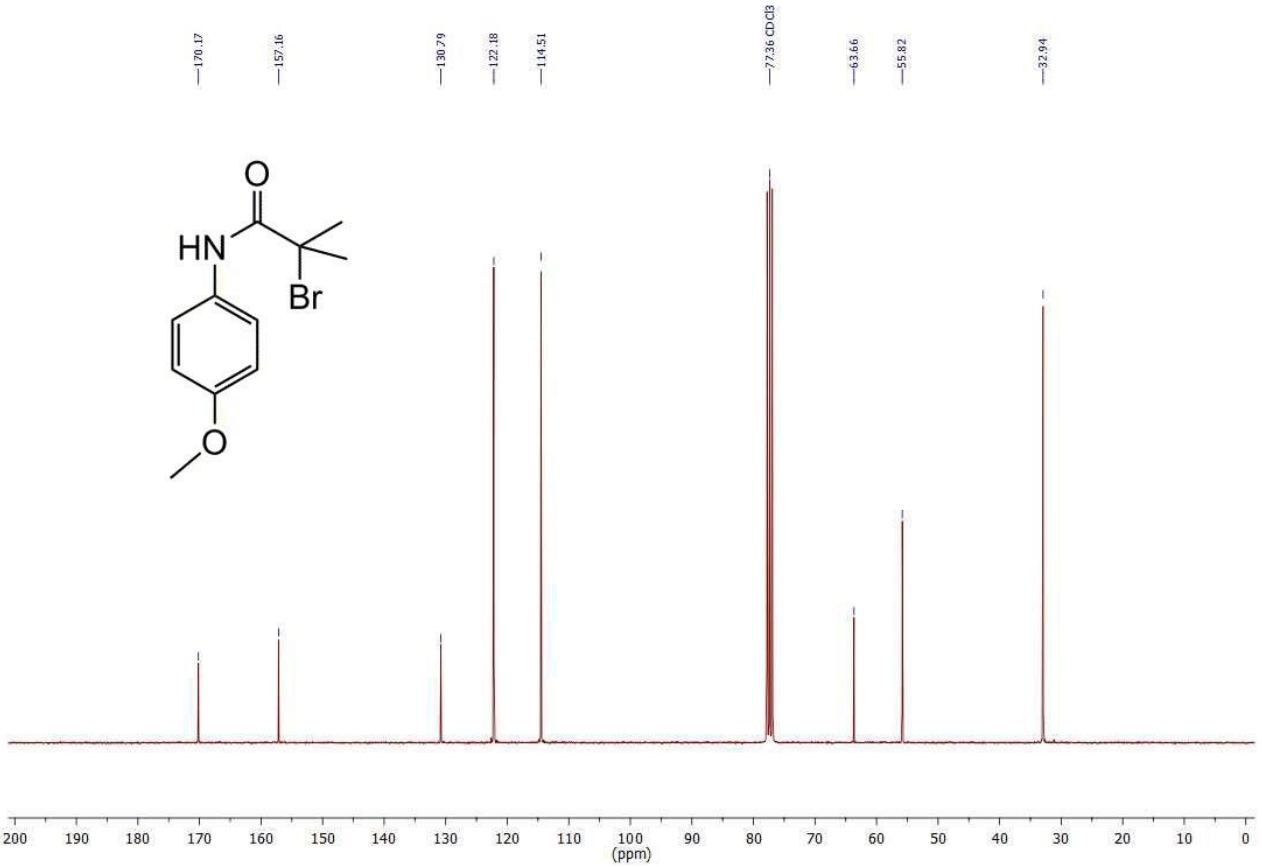
120 mg of **28** in 0.4 mL $CDCl_3$, 75 MHz, 15000 scans

29


%T
cm-1
3319.4
3007.0
2981.8
2962.3
2841.3
1653.7
1600.9
1538.5
1507.8
1468.1
1443.8
1411.7
1390.6
1372.6
1316.1
1299.6
1272.5
1231.7
1222.8
1196.3
1183.8
1163.4
1105.7
1031.0
951.9
933.1
890.2
830.8
809.4
762.7
750.9
711.2
675.4

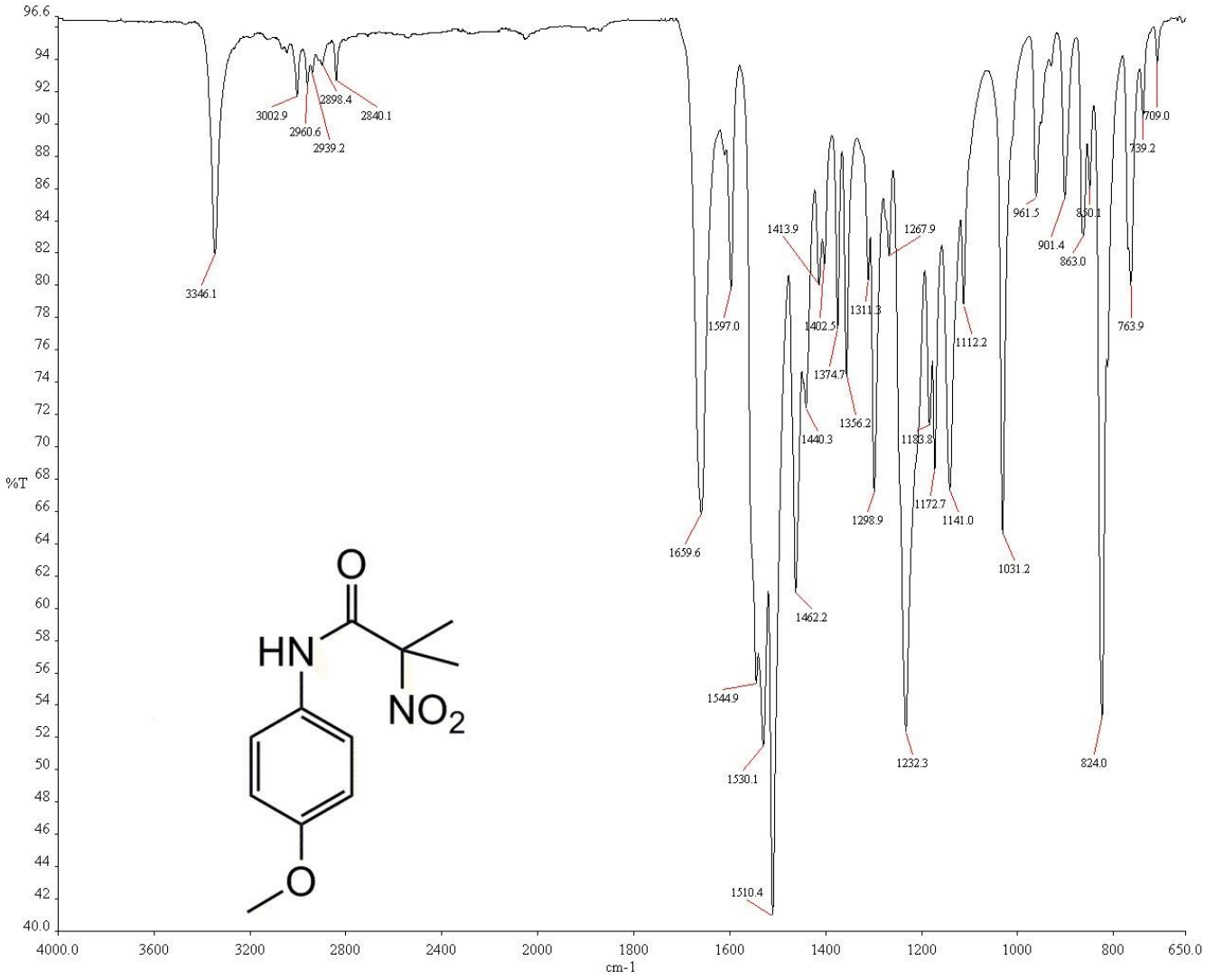


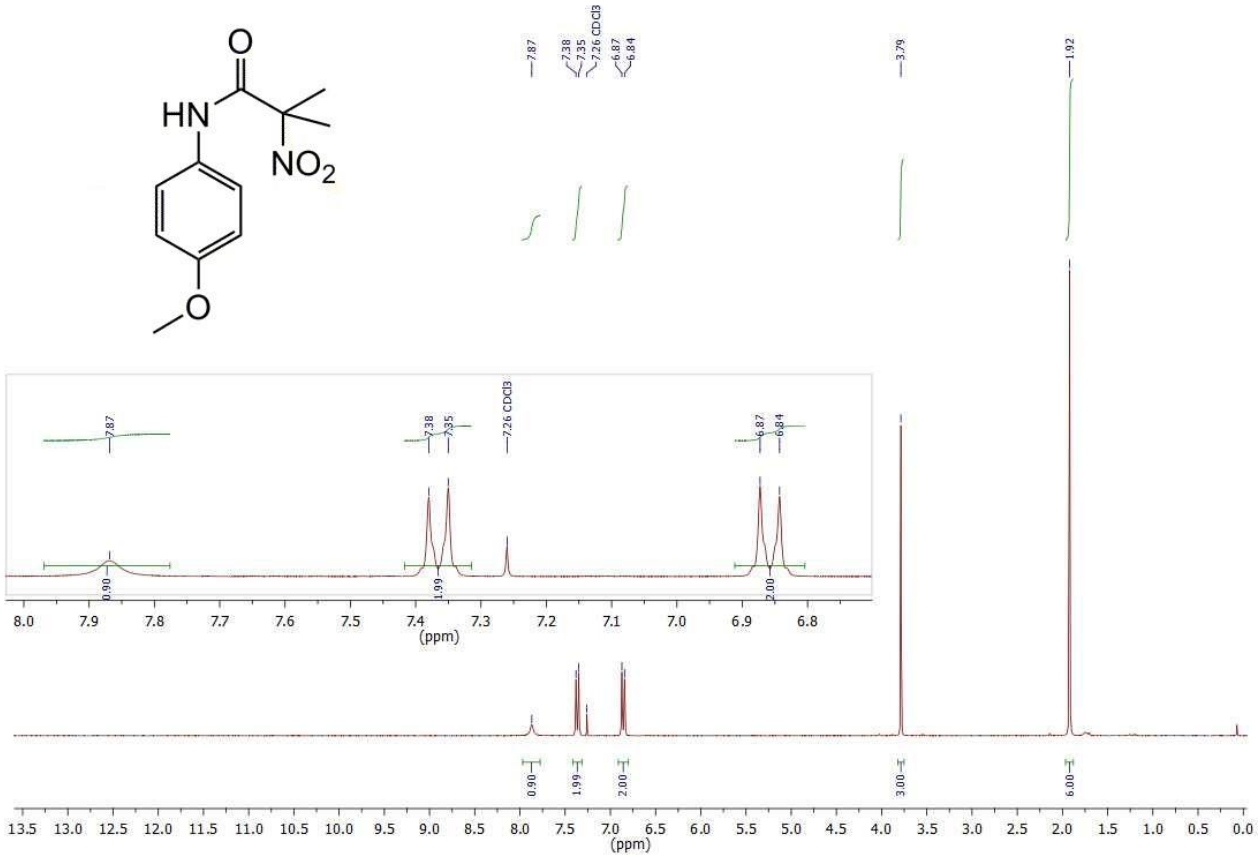
25 mg of **29** in 0.4 mL $CDCl_3$, 300 MHz, 350 scans



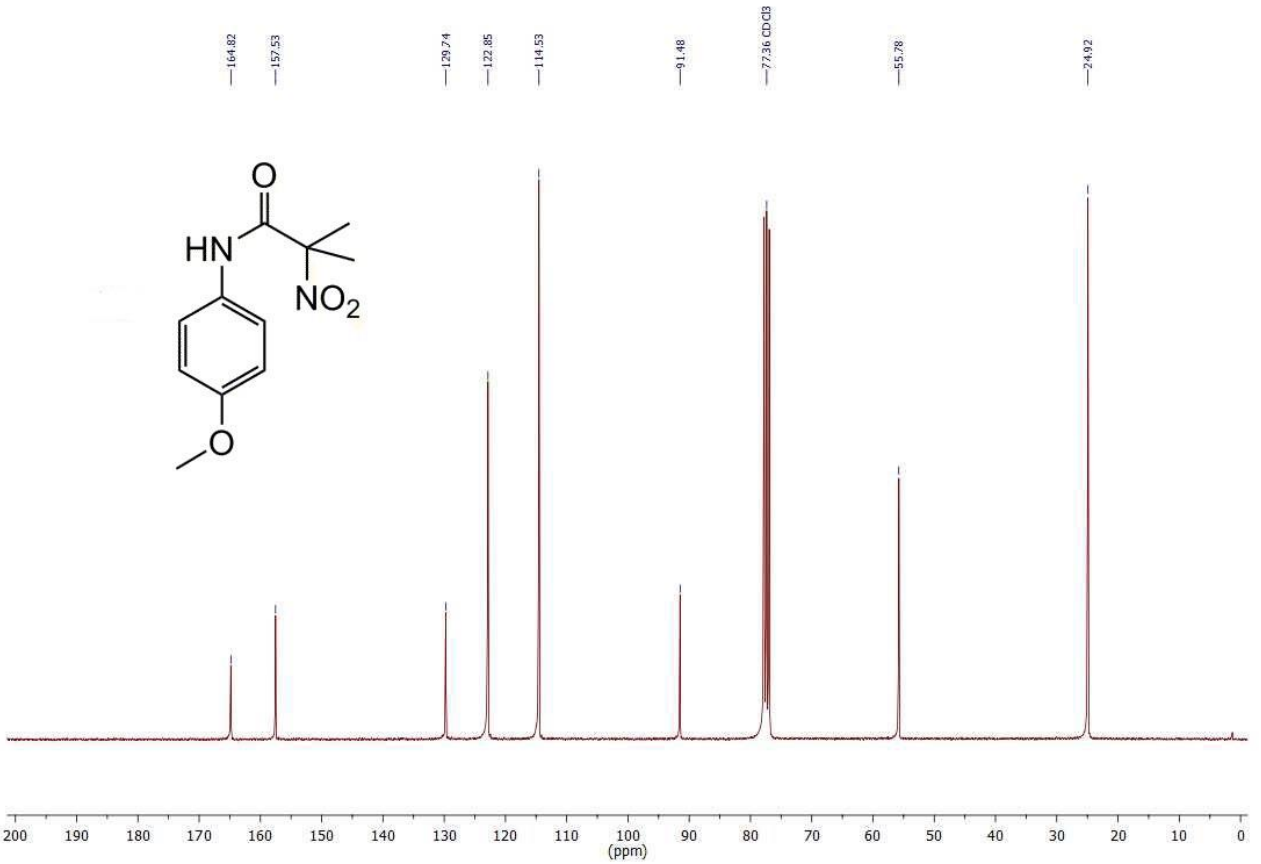
25 mg of **29** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

30


%T
cm-1
3346.1
3002.9
2960.6
2939.2
2898.4
2840.1
1659.6
1597.0
1544.9
1530.1
1510.4
1462.2
1440.3
1413.9
1402.5
1374.7
1356.2
1311.3
1298.9
1267.9
1232.3
1183.8
1172.7
1141.0
1112.2
1031.2
961.5
901.4
863.0
830.1
824.0
763.9
739.2
709.0

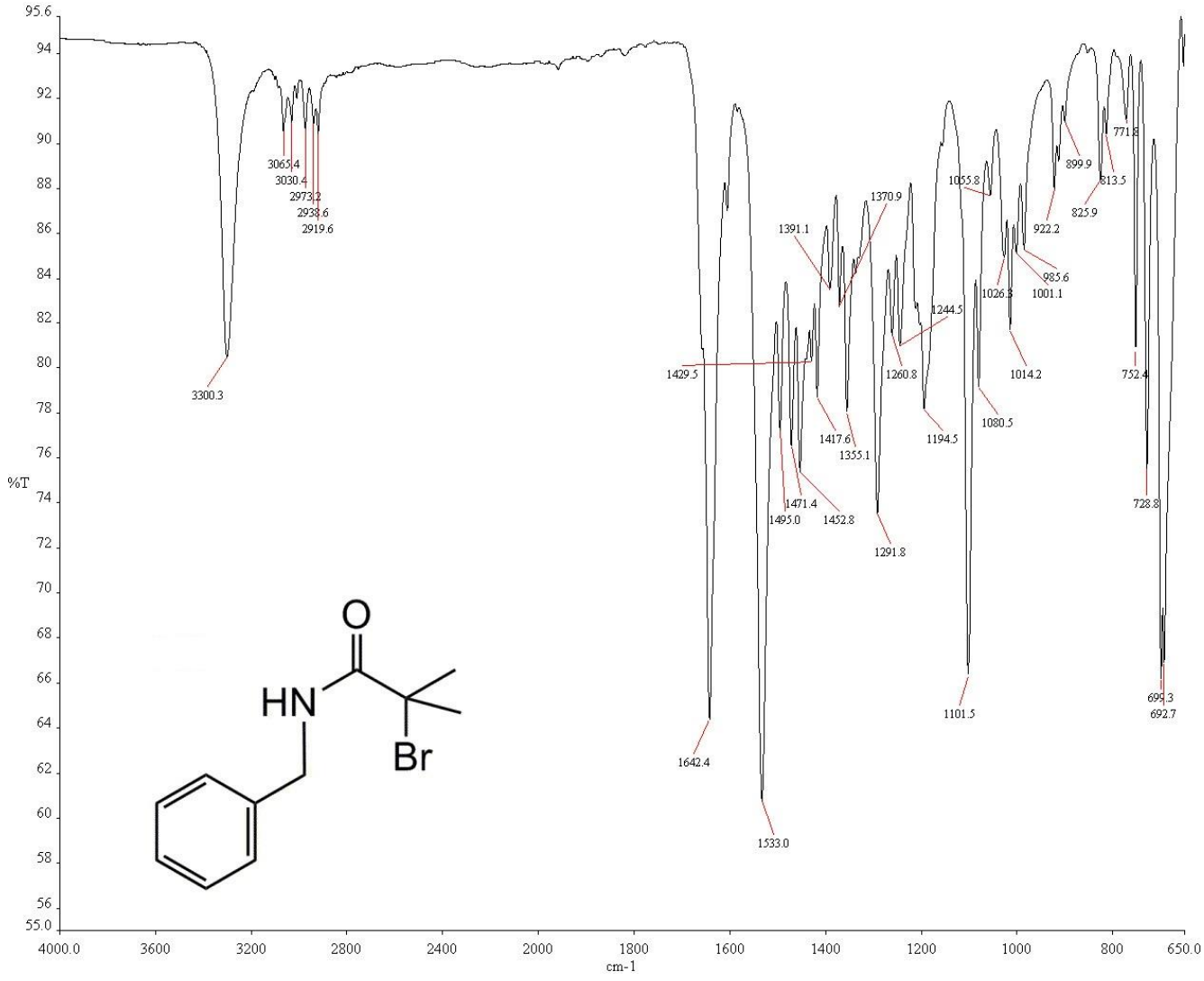


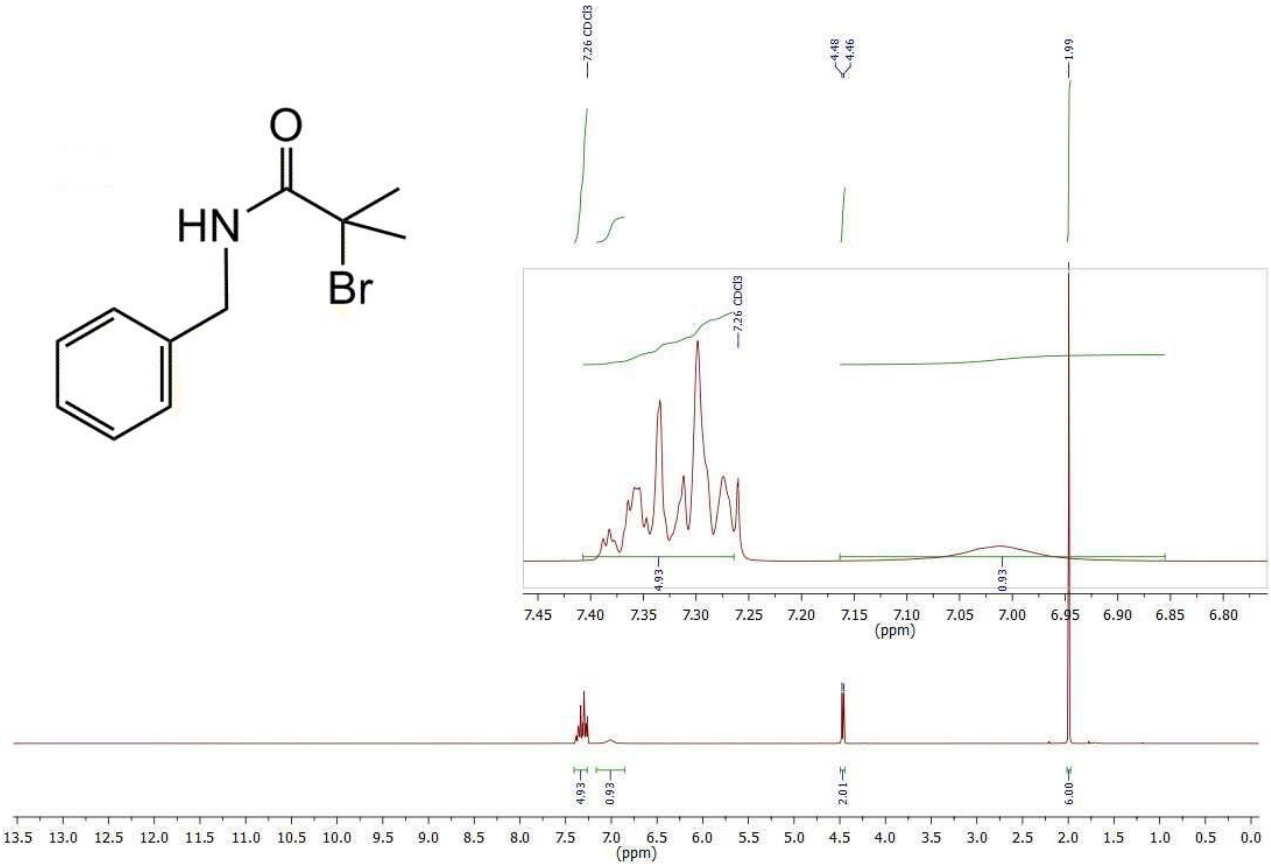
24 mg of **30** in 0.4 mL $CDCl_3$, 300 MHz, 32 scans



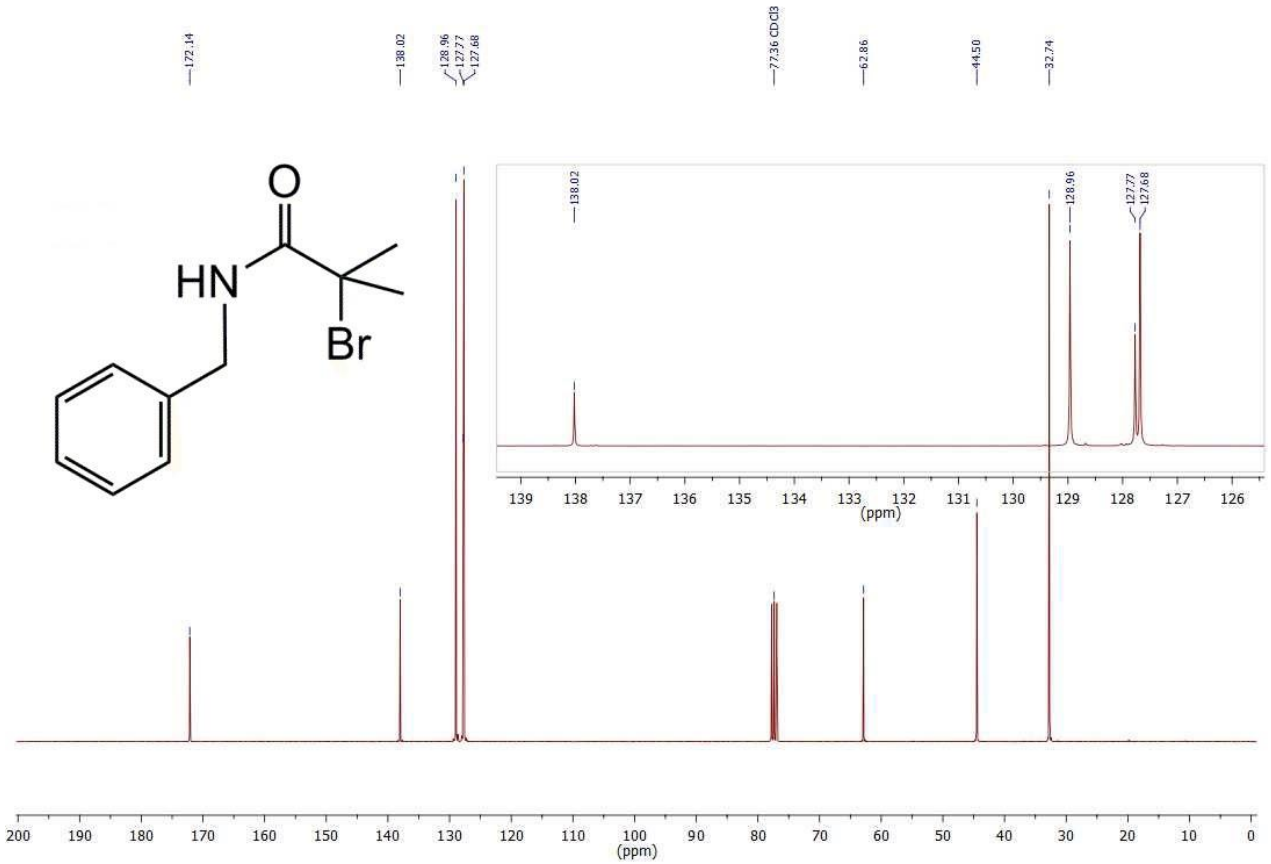
24 mg of **30** in 0.4 mL $CDCl_3$, 75 MHz, 36302 scans

31

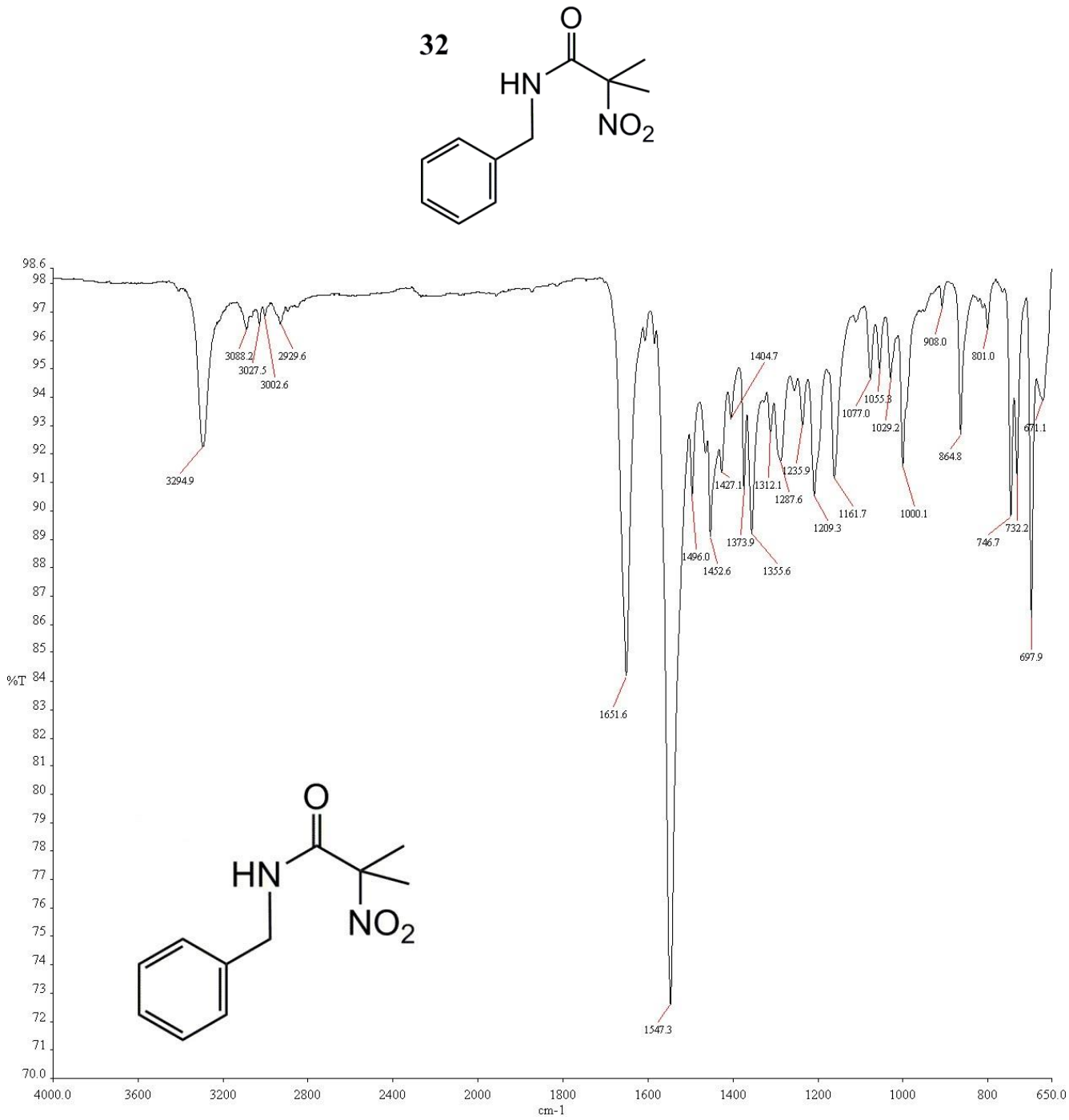

%T
cm-1
3300.3
3065.4
3030.4
2973.2
2938.6
2919.6
1642.4
1533.0
1495.0
1471.4
1452.8
1429.5
1417.6
1391.1
1370.9
1355.1
1291.8
1260.8
1244.5
1194.5
1101.5
1080.5
1055.8
1026.3
1014.2
1001.1
985.6
922.2
899.9
825.9
813.5
771.8
752.4
728.8
699.3
692.7

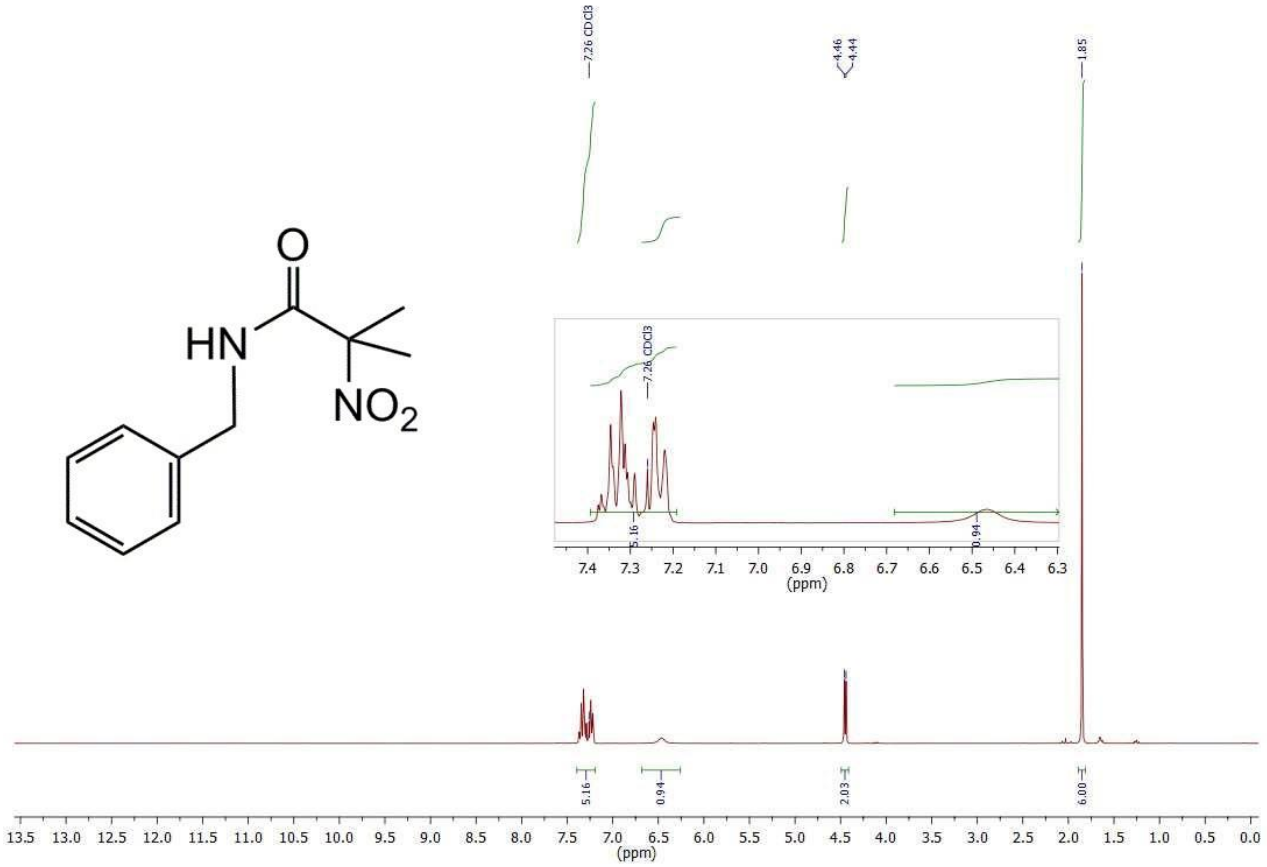


23 mg of **31** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans

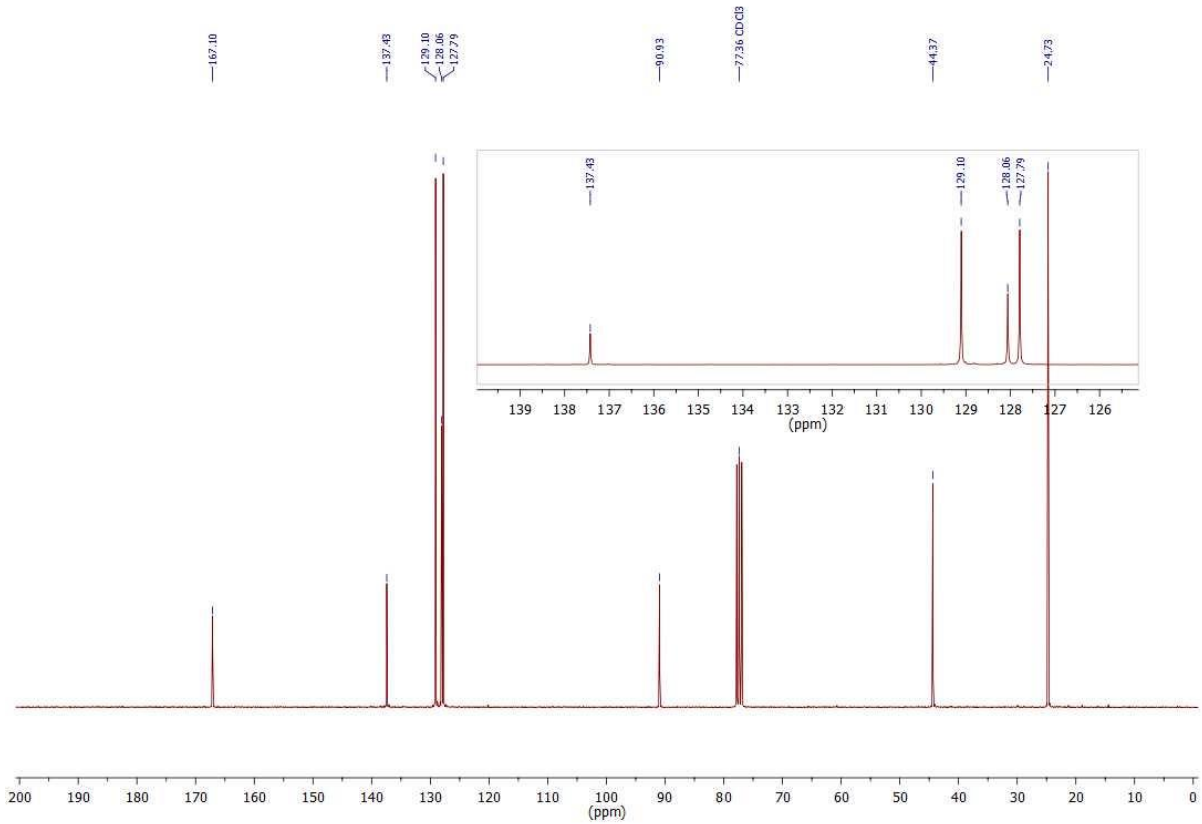


125 mg of **31** in 0.4 mL $CDCl_3$, 75 MHz, 13720 scans


32
O
HN
NO2
%T
cm-1
3294.9
3088.2
3027.5
3002.6
2929.6
1651.6
1547.3
1496.0
1452.6
1427.1
1404.7
1373.9
1355.6
1312.1
1287.6
1235.9
1209.3
1161.7
1077.0
1055.3
1029.2
1000.1
908.0
864.8
801.0
746.7
732.2
697.9
671.1

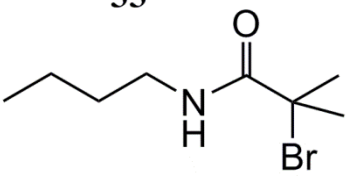


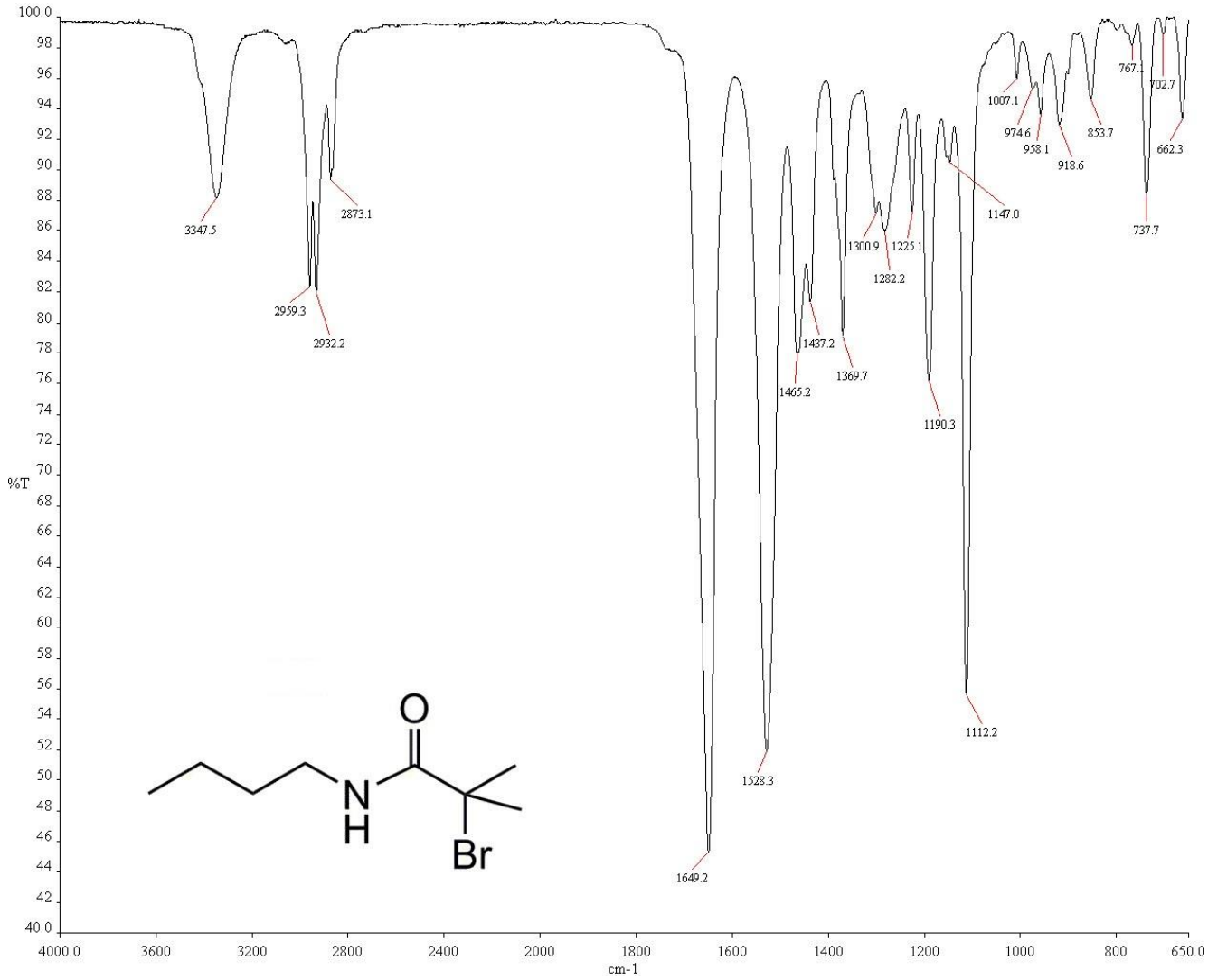
19 mg of **32** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans

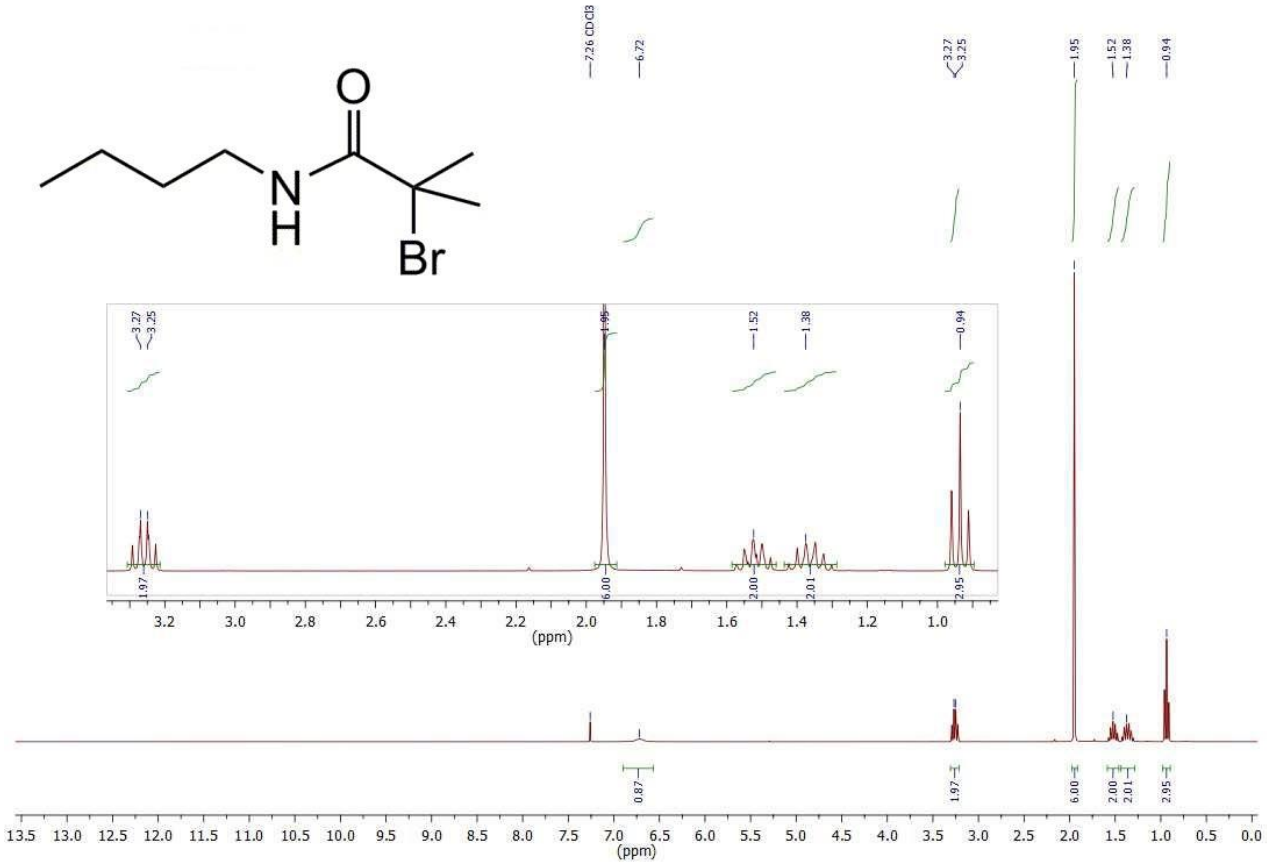


55 mg of **32** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

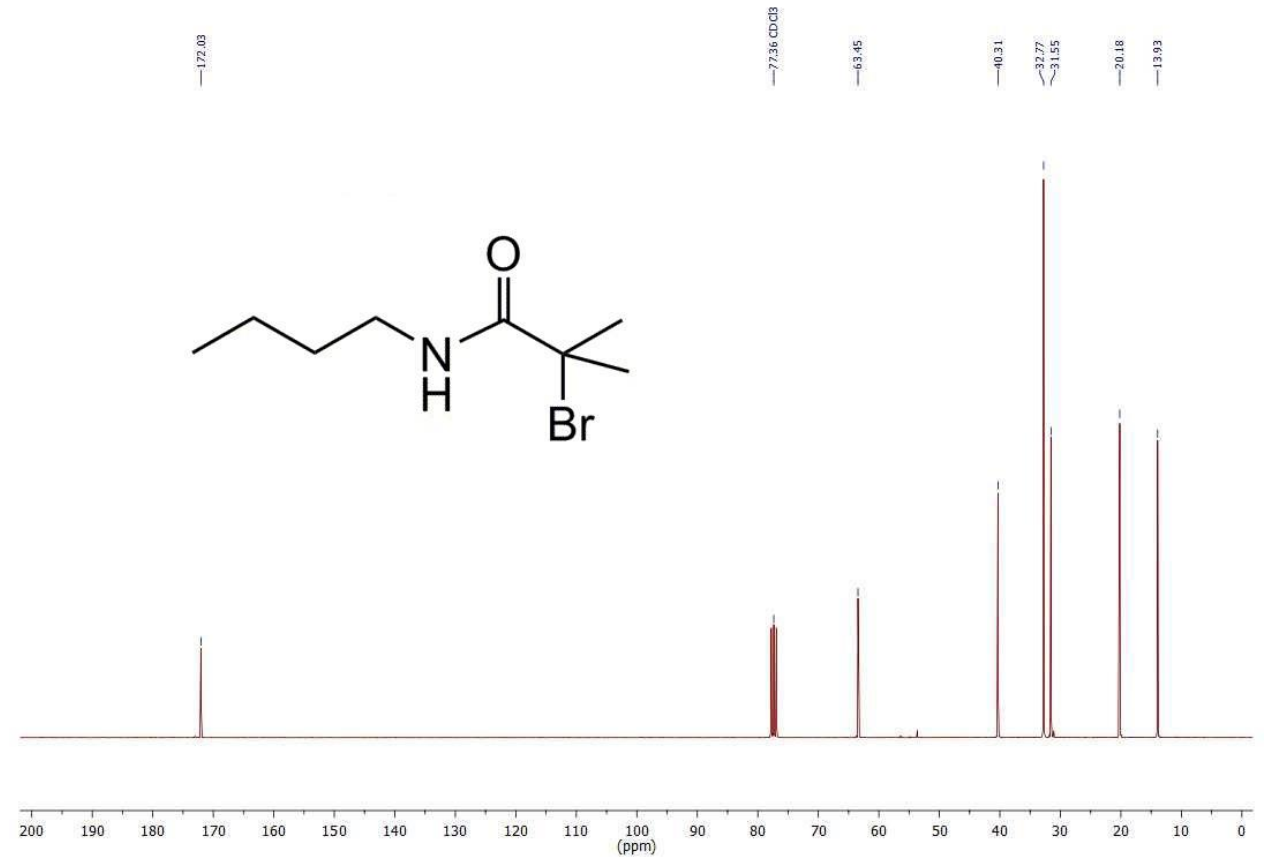
33


O
N
H
Br


%T
cm-1
3347.5
2959.3
2932.2
2873.1
1649.2
1528.3
1465.2
1437.2
1369.7
1300.9
1282.2
1225.1
1190.3
1147.0
1112.2
1007.1
974.6
958.1
918.6
853.7
767.1
737.7
702.7
662.3
O
N
H
Br

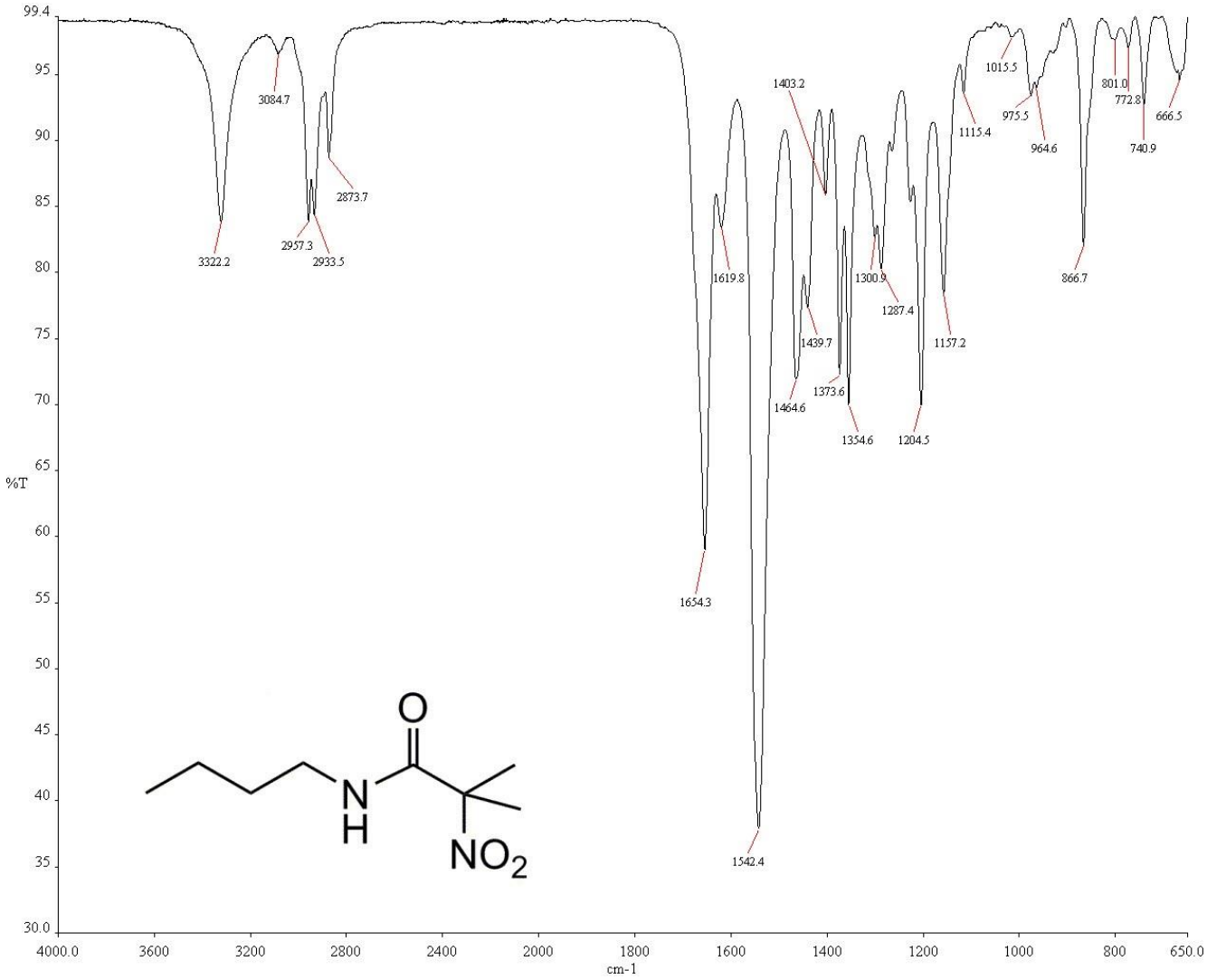


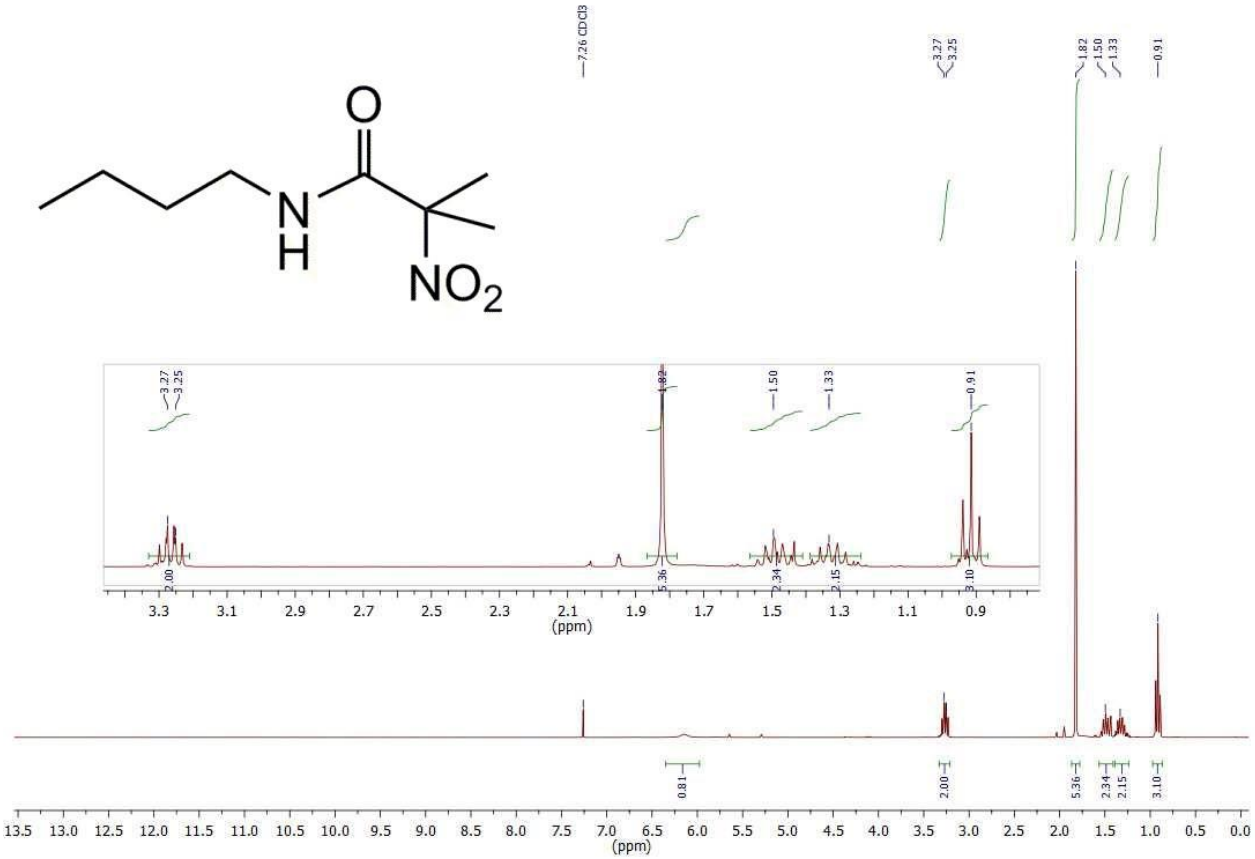
26 mg of **33** in 0.4 mL $CDCl_3$, 300 MHz, 65 scans



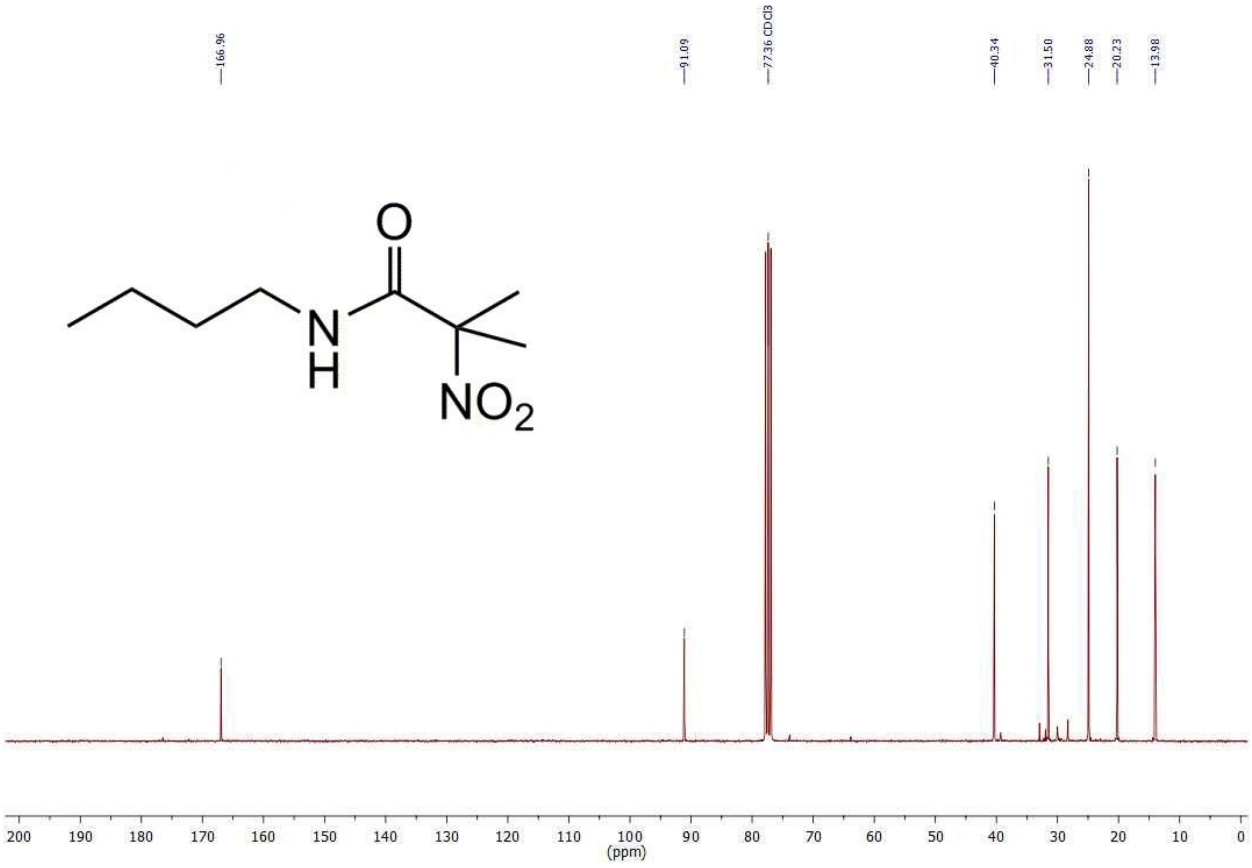
147 mg of **33** in 0.4 mL $CDCl_3$, 75 MHz, 14000 scans

34


%T
cm-1
3322.2
3084.7
2957.3
2933.5
2873.7
1654.3
1619.8
1542.4
1464.6
1439.7
1403.2
1373.6
1354.6
1300.9
1287.4
1204.5
1157.2
1115.4
1015.5
975.5
964.6
866.7
801.0
772.8
740.9
666.5



16 mg of **34** in 0.4 mL $CDCl_3$, 300 MHz, 16 scans



21 mg of **34** in 0.4 mL $CDCl_3$, 75 MHz, 17407 scans