Gold-Catalyzed Synthesis of Alkylidene 2-Oxazolidinones and 1,3-Oxazin-2-ones

Supporting Information

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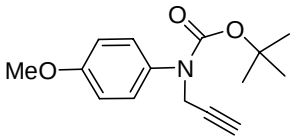
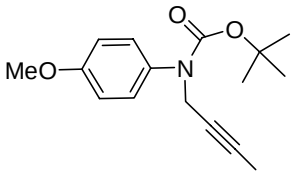
General: All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen. Dichloromethane, benzene, THF and DMF were dried and stored over microwave-activated 4Å molecular sieves. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm silica gel plates (230-400 mesh). 230-400 mesh silica gel was used for flash column chromatography. Products **1**,[1] **9**,[2] **10**,[3] **12**,[3] **13**,[4] **23**,[5] **25**,[5a] **27**,[5a] **35**[6] have been previously reported. The ^{1}H-NMR of these products matched the published spectra.

Typical procedure for the synthesis of N-*tert*-butoxycarbonyl propargylamines: N-tert-Butoxycarbonyl-N-(4-methoxyphenyl)-3-amino-1-propyne[1] (1): A solution of N- Boc-*p*-anisidine (670 mg, 3.0 mmol) in DMF (10 mL) at 0 ^{o}C was treated with NaH (132 mg, 3.30 mmol) and the mixture was stirred 30 min at room temperature. Propargyl bromide (374 μL, 3.30 mmol) was added and stirring was continued for another 7 h. The reaction was quenched with water, the mixture was extracted with diethyl ether (2 x 25 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by silica gel flash chromatography (Hex/AcOEt, 10/1) to afford **1** (715 mg, 91%, colourless oil).



^{1}H NMR (200 MHz, $CDCl_3$): 7.21 (d, *J*=8.1 Hz, 2H), 6.85 (d, *J*=8.8 Hz, 2H), 4.27 (d, *J*=1.9 Hz, 2H), 3.80 (s, 3H), 2.22 (t, *J*=1.9 Hz, 1H), 1.44 (s, 9H).

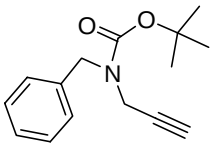
N-*tert*-Butoxycarbonyl-N-(4-methoxyphenyl)-4-amino-2-butyne (3): Following the typical procedure, the reaction of N-Boc-*p*-anisidine (300 mg, 1.34 mmol) in DMF (11 mL) with NaH (59 mg, 1.47 mmol) and 1-bromo-2-butyne (129 μL, 1.47 mmol) afforded after flash chromatography (Hex/AcOEt, 10/1) **3** (340 mg, 92 %, pale yellow oil).



^{1}H NMR (300 MHz, $CDCl_3$): 7.21 (d, *J*=8.1 Hz, 2H), 6.86 (d, *J*=8.8 Hz, 2H), 4.27 (s, 2H), 3.80 (s, 3H), 1.80 (s, 3H), 1.44 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 157.7, 154.5, 135.2, 127.8, 113.7, 80.3, 79.2, 75.2, 55.3, 31.5, 28.2, 3.5.

N-*tert*-Butoxycarbonyl-N-benzyl-3-amino-1-propyne (11): Following the typical procedure, the reaction of N-Boc-benzylamine (900 mg, 4.34 mmol) in DMF (15 mL) with NaH (191 mg, 4.78 mmol) and propargyl bromide (530 μL, 4.78 mmol) afforded after flash chromatography (Hex/AcOEt, 9/1) **11** (998 mg, 93%, pale yellow oil).



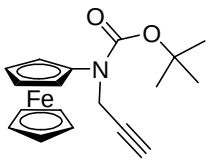
^{1}H NMR (300 MHz, $CDCl_3$): 7.26-7.17 (m, 5H), 4.47 (s, 2H), 3.94-3.84 (m, 2H), 2.12 (s, 1H), 1.40 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 155.0, 137.4, 128.4, 127.7, 127.3, 80.5, 79.3, 71.7, 49.1, 35.2, 28.3.

MS (ESI+): 268 (MNa^+, 100%).

HRMS (ESI+): calcd for ($C_{15}H_{19}NO_2Na$) [MNa^+] 268.1298, found 268.1308.

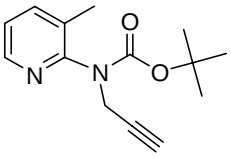
N-*tert*-Butoxycarbonyl-N-ferrocenyl-3-amino-1-propyne (19): Following the typical procedure, the reaction of N-Boc-ferrocenylamine (71 mg, 0.23 mmol) in DMF (5 mL) with NaH (10.1 mg, 0.25 mmol) and propargyl bromide (27 μL, 0.25 mmol) afforded after flash chromatography (Hex/AcOEt, 10/1) **19** (39 mg, 49 %, orange oil).



^{1}H NMR (200 MHz, $CDCl_3$): 4.53 (m, 2H), 4.40 (m, 2H), 4.21 (s, 5H), 4.02 (m, 2H), 2.31 (t, J= 2.1 Hz, 1H), 1.56 (s, 9H),

^{13}C NMR (75 MHz, $CDCl_3$): 153.2, 101.0, 81.3, 80.6, 71.5, 69.1, 64.5, 62.4, 39.4, 28.3.

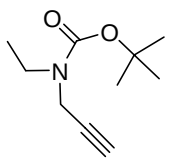
N-*tert*-Butoxycarbonyl-N-[2-(3-methylpyridyl)]-3-amino-1-propyne (21): Following the typical procedure, the reaction of N-Boc-3-methyl-2-aminopyridine (700 mg, 3.36 mmol) in DMF (11 mL) with NaH (148 mg, 3.70 mmol) and propargyl bromide (410 μL, 3.70 mmol) afforded after flash chromatography (Hex/AcOEt, 6/1) **21** (703 mg, 85%, pale yellow oil).



^{1}H NMR (300 MHz, $CDCl_3$): 8.28 (d, *J*= 4.7 Hz, 1H), 7.52 (d, *J*= 7.6 Hz, 1H), 7.08 (dd, *J*= 4.7 Hz, *J*= 7.6 Hz, 1H), 4.51 (bd, 2H), 2.27 (s, 3H), 2.08 (s, 1H), 1.40 (bs, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 152.7, 146.3, 139.2, 131.8, 122.5, 81.0, 79.4, 71.1, 37.6, 28.1, 27.3, 17.4.

N-*tert*-Butoxycarbonyl-N-ethyl-3-amino-1-propyne (15): A solution of N-Boc propargylamine **9** (200 mg, 1.29 mmol) in DMF (5 mL) was treated with NaH (57 mg, 1.42 mmol) and the mixture was stirred 30 min at room temperature. Ethyl bromide (115 μL, 1.42 mmol) was added and stirring was continued for another 14 h. The reaction was quenched with water and the mixture was extracted with diethyl ether (2x20 mL), the combined organic layers where washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by silica gel flash chromatography (Hex/AcOEt, 9/1) to afford **15** (224 mg, 95%, colourless oil).



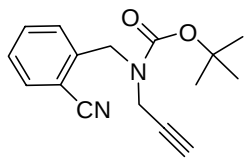
^{1}H NMR (300 MHz, $CDCl_3$): 3.96 (bs, 2H), 3.29 (q, *J*=7.1 Hz, 2H), 2.13 (t, *J*=2.4 Hz, 1H), 1.40 (s, 9H), 1.07 (t, *J*=7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 79.8, 79.7, 70.9, 41.1, 35.5, 35.4, 28.2, 13.0

MS (ESI+): 206 (MNa^+, 35%).

HRMS (ESI+): calcd for ($C_{10}H_{17}NO_2Na$) [MNa^+] 206.1141, found 206.1151.

N-*tert*-Butoxycarbonyl-N-2-cyanobenzyl-3-amino-1-propyne (17): Following the above procedure, the reaction of N-Boc propargylamine **9** (200 mg, 1.29 mmol) in DMF (5 mL) with NaH (57 mg, 1.42 mmol) and 2-cyanobenzylbromide (277 mg, 1.42 mmol) afforded after flash chromatography (Hex/AcOEt, 9/1) **17** (291 mg, 89%, pale yellow oil). **^{1}H NMR** (200 MHz, $CDCl_3$):



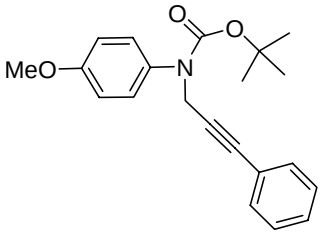
^{1}H NMR (300 MHz, $CDCl_3$): 7.62 (d, *J*=7.7 Hz, 1H), 7.56 (t, *J*=7.7 Hz, 1H), 7.41 (d, *J*=7.7 Hz, 1H), 7.35 (t, *J*=7.7 Hz, 1H), 4.74 (s, 2H), 4.13 (bs, 1H), 4.01 (bs, 1H), 2.21 (bs, 1H), 1.44 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 154.9, 141.9, 132.9, 127.7, 117.2, 111.4, 81.2, 78.6, 72.5, 48.1, 36.5, 28.1.

MS (ESI+): 271 (MH^+, 4%), 293 (MNa^+, 89%).

HRMS (ESI+): calcd for ($C_{16}H_{19}N_2O_2$) [MH^+] 271.1450, found 271.1441 and for ($C_{16}H_{18}N_2O_2Na$) [MNa^+] 293.1274, found 293.1260.

N-*tert*-Butoxycarbonyl-N-(4-methoxyphenyl)-3-amino-1-phenyl-1-propyne (5): A round bottomed flask was charged with $Pd(OAc)_2$ (5.0 mg, 0.019 mmol), CuI (4.0 mg, 0.019 mmol) and PPh_3 (10.0 mg, 0.038 mmol), capped with a rubber septum, evacuated, and backfilled with nitrogen. Anhydrous benzene (3 mL), propargyl amine **1** (50 mg, 0.19 mmol), Et_3N (55 μL, 0.38 mmol) and iodobenzene (24 μL, 0.21 mmol) were added



and the reaction mixture was stirred for 18 h at room temperature. The crude reaction mixture was filtered through a plug of Celite with the aid of CH_2Cl_2 and the solvent was removed under reduced pressure. The residue was purified by silica gel flash chromatography (Hex/AcOEt, 10:1) to afford **5** (51 mg, 79 %, pale yellow oil).

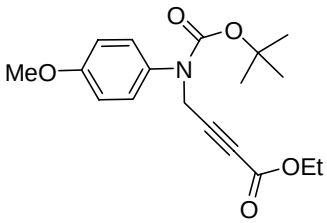
^{1}H NMR (300 MHz, $CDCl_3$): 7.42-7.27 (m, 7H), 6.92-6.81 (m, 2H), 4.54 (s, 2H), 3.80 (s, 3H), 1.50 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 157.9, 154.6, 135.1, 131.6, 128.2, 128.1, 123.0, 114.1, 113.9, 85.6, 83.6, 80.6, 55.4, 40.8, 28.3.

MS (ESI+): 338 (MH^+, 20%), 360 (MNa^+, 40%).

HRMS (ESI+): calcd for ($C_{21}H_{24}NO_3$) [MH^+] 338.1762, found 338.1750 and for ($C_{21}H_{23}NO_3Na$) [MNa^+] 360.1597, found 360.1570.

N-*tert*-Butoxycarbonyl-N-(4-methoxyphenyl)-4-amino-1-but-2-ynoic ethyl esther (7): To a solution of amine **1** (50 mg, 0.19 mmol) in THF (3 mL), cooled to 0 ^oC, *n*-

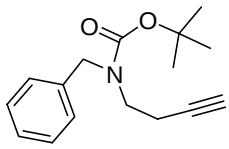


BuLi 2.5 M in hexane (75 μL, 0.19 mmol) was added under N_2 atmosphere. The resulting mixture was stirred 1h at -78 ^oC, ethyl chloroformiate **(**17 μL, 0.19 mmol) was added and the reaction mixture was stirred at room temperature for another 1h. The reaction was quenched with saturated NH_4Cl solution and the mixture was extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by silica gel flash chromatography (Hex/AcOEt, 8/1) to afford **7** (37 mg, 58 %, colourless oil).

^{1}H NMR (300 MHz, $CDCl_3$): 7.18 (d, *J*=8.9 Hz, 2H), 6.86 (d, *J*=8.9 Hz, 2H), 4.45 (s, 2H), 4.21 (q, *J*=7.1 Hz, 2H), 3.8 (s, 3H), 1.43 (bs, 9H), 1.29 (t, *J*=7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 158.2, 154.3, 153.8, 134.6, 127.9, 114.1, 83.8, 81.2, 75.6, 61.9, 55.4, 31.5, 28.2, 13.9.

N-*tert*-Butoxycarbonyl-N-benzyl-4-amino-1-butyne (29): To a solution of 3-butynyl methanesulfonate (150 mg, 1.01 mmol) in DMF (6 mL), benzylamine (109 μL, 1.01 mmol) and Et_3N (196 μL, 1.51 mmol) were added. The resulting solution was refluxed



for 15 h, the precipitate was dissolved by addition of water and the mixture was extracted with Et_2O (2 x 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated. The residue was dissolved in CH_2Cl_2 (5 mL), $(Boc)_2O$ (109 mg, 0.92 mmol) was added and the mixture was stirred for 2 h. The reaction was extracted with CH_2Cl_2 and water. The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by silica gel flash chromatography (Hex/AcOEt, 9/1) to afford **29** (218 mg, 83%, colourless oil).

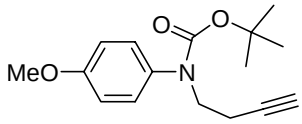
^{1}H NMR (300 MHz, $CDCl_3$): 7.30-7.20 (m, 5H), 4.47 (s, 2H), 3.31 (bd, 2H), 2.31 (bs, 2H), 1.92 (bs, 1H), 1.41 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 155.2, 138.0, 128.3, 127.5, 127.0, 84.8, 79.7, 69.4, 51.1, 50.3, 28.2, 27.1.

MS (ESI+): 282 (MNa^+, 100%).

HRMS (ESI+): calcd for ($C_{16}H_{21}NO_2Na$) [MNa^+] 282.1458, found 282.1464.

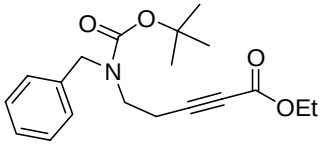
N-*tert*-Butoxycarbonyl-N-(4-methoxyphenyl)-4-amino-1-butyne (33): Following the above procedure, the reaction 3-butynyl methanesulfonate (150 mg, 1.01 mmol) in DMF (5 mL), with *p*-anisidine (123 mg, 1.01 mmol), Et_3N (196 μL, 1.51 mmol) and $(Boc)_2O$ (79 mg, 0.67 mmol) afforded after flash chromatography (Hex/AcOEt, 9/1) **33** (184 mg, 67 %, pale yellow oil).



^{1}H NMR (300 MHz, $CDCl_3$): 7.10 (d, *J*=7.7 Hz, 2H), 6.85 (d, *J*=7.7 Hz, 2H), 3.80 (s, 3H), 3.75 (t, *J*=7.3 Hz, 2H), 2.41 (dt, *J*=7.3 Hz, *J*=2.7 Hz, 2H), 1.95 (t, *J*=2.7 Hz, 1H), 1.42 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 157.8, 154.7, 134.7, 128.4, 114.0, 81.4, 79.9, 69.6, 55.2, 48.8, 28.2, 22.5

N-*tert*-Butoxycarbonyl-N-benzyl-5-aminopent-2-ynoic ethyl esther (31): To a solution of amine **29** (50 mg, 0.19 mmol) in THF (3 mL), cooled to 0 ^oC, *n*-BuLi 2.5 M in hexane (75 μL, 0.19 mmol) was added under N_2 atmosphere. The resulting mixture was stirred 1h at -78 ^oC, ethyl chloroformiate **(**17 μL, 0.19 mmol) was added and the reaction mixture was stirred at room temperature for another 1h. The

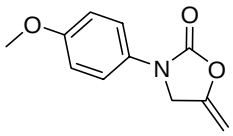


reaction was quenched with saturated NH_4Cl solution and the mixture was extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by silica gel flash chromatography (Hex/AcOEt, 8/1) to afford **31** (42 mg, 66 %, colourless oil).

^{1}H NMR (300 MHz, $CDCl_3$): 7.35-7.23 (m, 5H), 4.50 (s, 2H), 4.21 (q, *J*=7.1 Hz, 2H), 3.35 (bs, 2H), 2.51 (bd, 2H), 1.46 (bs, 9H), 1.30 (t, *J*=7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 155.4, 153.5, 138.1, 128.6, 127.8, 127.4, 80.3, 74.1, 61.9, 51.5, 50.5, 44.6, 28.4, 18.4, 14.0.

Typical procedure for the Au(I)-catalyzed synthesis of oxazolidinones: N-(4-methoxyphenyl)-5-methylidene-2-oxazolidinone (2): A round bottomed flask was charged with $AuClPPh_3$ (7.6 mg, 0.015 mmol) and $AgSbF_6$ (5.3 mg, 0.015 mmol), capped with a rubber septum, evacuated, and backfilled with nitrogen. Anhydrous CH_2Cl_2 (3 mL) was added and the resulting reaction mixture was stirred at room temperature for 1 h. A solution of **1** (80 mg, 0.30 mmol) in CH_2Cl_2 (3 mL) was added via syringe to the catalyst solution and the reaction mixture was stirred at room temperature for 5 minutes. The crude reaction mixture was filtered through a plug of Celite with the aid of CH_2Cl_2 and the solvent was removed under reduced pressure. The residue was purified by silica gel flash chromatography (Hex/AcOEt, 10/1) to afford the oxazolidinone **2** (48.3 mg, 77%, white solid).



M.p. 138-139 ºC.

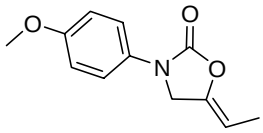
^{1}H NMR (200 MHz, $CDCl_3$): 7.44 (d, *J*=9.3 Hz, 2H), 6.91 (d, *J*=9.3 Hz, 2H), 4.84 (q, *J*=3.0 Hz, 1H), 4.61 (t, *J* = 2.5 Hz, 2H), 4.40 (q, *J*=3.0 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 156.7, 152.6, 147.9, 130.3, 120.2, 114.4, 86.9, 55.5, 48.9.

MS (ESI+): 206 (MH^+, 100%), 228 (MNa^+, 58%).

HRMS (ESI+): calcd for $(C_{11}H_{12}NO_3)[MH^+]$ 206.0810, found 208.0811, and for $(C_{11}H_{11}NO_3Na)[MNa^+]$ 228.0631, found 228.0631.

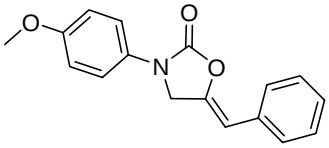
(*Z*)-N-(4-methoxyphenyl)-5-ethylidene-2-oxazolidinone (4): Following the typical procedure, the reaction of **3** (33 mg, 0.12 mmol) with $AuClPPh_3$ (3.0 mg, 0.006 mmol) and $AgSbF_6$ (2.0 mg, 0.006 mmol) in CH_2Cl_2 (1.5 mL), afforded after flash chromatography (Hex/AcOEt, 5/1) the oxazolidinone **4** (21 mg, 75%, yellow oil).



^{1}H NMR (300 MHz, $CDCl_3$): 7.25 (d, *J*=9.05 Hz, 2H), 6.93 (d, *J*=9.05 Hz, 2H), 4.93 (m, 1H), 4.13 (m, 2H), 3.80 (s, 3H), 1.92 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 158.5, 155.5, 148.5, 131.8, 126.9, 114.7, 95.0, 55.5, 49.2, 18.4.

(*Z*)-N-(4-methoxyphenyl)-5-benzylidene-2-oxazolidinone (6): Following the typical procedure, the reaction of **5** (80 mg, 0.24 mmol) with $AuClPPh_3$ (6.0 mg, 0.012 mmol) and $AgSbF_6$ (4.0 mg, 0.012 mmol) in CH_2Cl_2 (2.4 mL) afforded after flash chromatography (Hex/AcOEt, 10/1) the oxazolidinone **6** (49 mg, 74%, pale yellow oil).



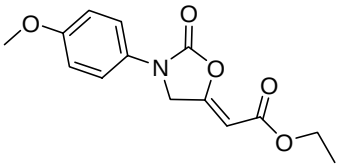
^{1}H NMR (300 MHz, $CDCl_3$): 7.60 (d, *J*=7.5 Hz, 2H), 7.47 (d, *J*=9.0 Hz, 2H), 7.35 (t, *J*=7.5 Hz, 2H), 7.23 (t, *J*=7.5 Hz, 1H), 6.93 (d, *J*=9.0 Hz, 2H), 5.62 (d, *J*=2.0 Hz, 1H), 4.76 (d, *J*=2.0 Hz, 2H), 3.82 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 156.9, 152.6, 140.6, 133.2, 130.1, 128.5, 128.3, 127.0, 120.5, 114.5, 103.3, 55.5, 50.0.

MS (ESI+): 282 (MH^+, 100%), 304 (MNa^+, 56%).

HRMS (ESI+): calcd for ($C_{17}H_{16}NO_3$)[MH^+] 282.1122, found 282.1124; and for ($C_{17}H_{15}NO_3Na$) [MNa^+] 304.0946, found 304.0944.

(*Z*)-N-(4-methoxyphenyl)-5-ethoxycarbonylmethylidene-2-oxazolidinone (8): Following the typical procedure, the reaction of **7** (40 mg, 0.12 mmol) with $AuClPPh_3$ (3.0 mg, 0.006 mmol) and $AgSbF_6$ (2.0 mg, 0.006 mmol) in CH_2Cl_2 (1.5 mL) afforded after flash chromatography (Hex/AcOEt, 3/1) the oxazolidinone **8** (31 mg, 95%, colourless oil).



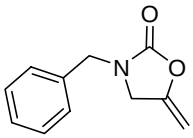
^{1}H NMR (300 MHz, $CDCl_3$): 7.42 (d, *J*=9.2 Hz, 2H), 6.92 (d, *J*=9.2 Hz, 2H), 5.23 (t, *J*=2.0 Hz, 1H), 4.68 (d, *J*=2.0 Hz, 2H), 4.24 (q, *J*=7.1 Hz, 2H), 3.81 (s, 3H), 1.31 (t, *J*=7.1 Hz, 3H) .

^{13}C NMR (75 MHz, $CDCl_3$): 182.4, 163.5, 157.2, 153.9, 127.4, 120.5, 114.6, 111.7, 60.5, 55.2, 50.0, 14.3.

MS (ESI+): 278 (MH^+, 34%), 300 ($M+Na^+$, 100%).

HRMS (ESI+): calcd for ($C_{14}H_{16}NO_5$)[MH^+] 278.1022, found 278.1028, and for ($C_{14}H_{15}NO_5Na$) [MNa^+] 300.0840, found 300.0847.

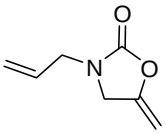
N-Benzyl-5-methylidene-2-oxazolidinone (12): Following the typical procedure, the reaction of **11** (4.95 g, 20.2 mmol) with $AuClPPh_3$ (100 mg, 0.20 mmol) and $AgSbF_6$ (70.1 mg, 0.20 mmol) in CH_2Cl_2 (200 mL) afforded after flash chromatography (Hex/AcOEt, 9/1) the oxazolidinone **12** (3.25 g, 85%, white solid).



M.p. 48.8-49.9 ºC.

^{1}H NMR (300 MHz, $CDCl_3$): 7.20-7.40 (m, 5H), 4.72-4.75 (m, 1H), 4.50 (s, 2H), 4.22-4.25 (m, 1H), 4.02 (t, J=2.4 Hz, 2H).

N-Allyl-5-methylidene-2-oxazolidinone (14): Following the typical procedure, the reaction of **13** (40 mg, 0.20 mmol) with $AuClPPh_3$ (5.1 mg, 0.01 mmol) and $AgSbF_6$ (3.5 mg, 0.01 mmol) in CH_2Cl_2 (2 mL) afforded after flash chromatography (Hex/AcOEt, 10/1) the oxazolidinone **14** (22.8 mg, 80%, brown oil).



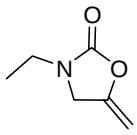
^{1}H NMR (300 MHz, $CDCl_3$): 5.83-5.7 (m, 1H), 5.28 (s, 1H), 5.24 (dd, *J*=6.3 Hz, *J*=1.0 Hz, 1H), 4.75 (q, *J*=3.0 Hz, 1H), 4.29 (q, *J*=3.0 Hz, 1H), 4.12 (t, *J*=2.4 Hz, 2H), 3.9 (dt, *J*=6.3 Hz, *J*=1.0, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 155.3, 149.0, 131.3, 119.2, 86.7, 47.4, 46.4

MS (ESI+): 140 (MH^+), 162 (MNa^+).

HRMS (ESI+): calcd for ($C_7H_{10}NO_2$)[MH^+] 140.0711, found 140.0711; and for ($C_7H_9NO_2Na$) [MNa^+] 162.0547, found 162.0530.

N-Ethyl-5-methylidene-2-oxazolidinone (16): Following the typical procedure, the reaction of **15** (40 mg, 0.22 mmol) with $AuClPPh_3$ (5.4 mg, 0.011 mmol) and $AgSbF_6$ (3.8 mg, 0.011 mmol), in CH_2Cl_2 (2.2 mL) afforded after flash chromatography (Hex/AcOEt, 4:1) the oxazolidinone **16** (19.3mg, 69%, colourless oil).



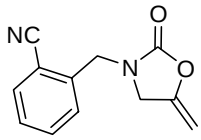
^{1}H NMR (300 MHz, $CDCl_3$): 4.74 (q, *J*=3.0 Hz, 1H), 4.28 (q, *J*=3.0 Hz, 1H), 4.16 (t, *J*=2.4 Hz, 2H), 3.36 (c, *J*=7.3 Hz, 2H), 1.18 (t, *J*=7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 152.0, 149.1, 86.5, 47.2, 38.5, 12.5.

MS (ESI+): 128 (MH^+, 100%).

HRMS (ESI+): calcd for ($C_6H_{10}NO_2$)[MH^+] 128.0702, found 128.0706.

N-2-Cyanobenzyl-5-methylidene-2-oxazolidinone (18): Following the typical procedure, the reaction of **17** (40 mg, 0.15 mmol) with $AuClPPh_3$ (3.6 mg, 0.007 mmol) and $AgSbF_6$ (2.6 mg, 0.007 mmol) in CH_2Cl_2 (1.5 mL) afforded after flash chromatography (Hex/AcOEt, 5:1) the oxazolidinone **18** (27.6 mg, 87%, colourless oil).



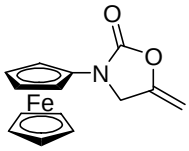
^{1}H NMR (300 MHz, $CDCl_3$): 7.70 (d, *J*=8.0 Hz, 1H), 7.64 (dt, *J*=7.6 Hz, *J*=1.0 Hz, 1H), 7.54 (d, *J*=7.4 Hz, 1H), 7.45 (dt, *J*=7.6 Hz, *J*=1.0 Hz, 1H), 4.77 (q, *J*=3.0 Hz, 1H), 4.69 (s, 2H), 4.30 (q, *J*=3.0 Hz, 1H), 4.17 (t, *J*=2.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 155.6, 148.4, 138.8, 133.7, 132.9, 129.6, 128.9, 117.1, 112.2, 87.3, 47.8, 45.7.

MS (ESI+): 215 (MH^+, 31%), 237 (MNa^+, 100%).

HRMS (ESI+): calcd for ($C_{12}H_{11}N_2O_2$)[MH^+] 215.0826, found 215.0815; and for ($C_{12}H_{10}N_2O_2Na$) [MNa^+] 237.0640, found 237.0634.

N-2-Ferrocenyl-5-methylidene-2-oxazolidinone (20): Following the typical procedure, the reaction of **19** (40 mg, 0.12 mmol) with $AuClPPh_3$ (3.0 mg, 0.006 mmol) and $AgSbF_6$ (2.0 mg, 0.006 mmol) in CH_2Cl_2 (1.2mL) afforded after flash chromatography (Hex/AcOEt, 5:1) the oxazolidinone **20** (26.7 mg, 80%, yellow solid).



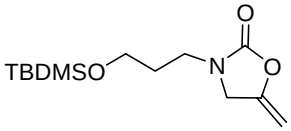
M.p. 78-79 ºC.

^{1}H NMR (300 MHz, $CDCl_3$): 4.82 (q, *J*=2.7 Hz, 1H), 4.58 (t, *J*=2.0 Hz, 2H), 4.43 (t, *J*=2.3 Hz, 2H), 4.40 (m, 1H), 4.21 (s, 5H), 4.06 (t, *J*=2.0 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 152.3, 148.3, 95.4, 87.0, 68.9, 64.9, 59.5, 49.0.

MS (FAB+): 283 (MH^+, 100%).

N-3-*tert*-Butyldimethylsilanoxipropyl-5-methylidene-2-oxazolidinone (24): Following the typical procedure, the reaction of **23** (60 mg, 0.18 mmol) with $AuClPPh_3$ (4.4 mg, 0.009 mmol) and $AgSbF_6$ (3.0 mg, 0.009 mmol) in CH_2Cl_2 (2 mL) afforded after flash chromatography (Hex/AcOEt, 5/1) the oxazolidinone **24** (22 mg, 90%, colourless oil).



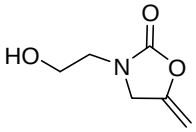
^{1}H NMR (300 MHz, $CDCl_3$): 4.73 (q, *J*=2.7 Hz, 1H), 4.27 (q, *J*=2.7 Hz, 1H), 4.19 (t, *J*=2.4 Hz, 2H), 3.67 (t, *J*=5.9 Hz, 2H), 3.40 (t, *J*=7.0 Hz, 2H), 1.78 (m, 2H), 0.9 (s, 9H), 0.05 (s, 6H) .

^{13}C NMR (75 MHz, $CDCl_3$): 155.5, 149.2, 86.3, 60.3, 48.2, 41.2, 30.3, 25.8, 18.2, -5.4

IR: 2957.41, 2929.77, 1794.77, 1694.30, 1473.43, 1283.81, 1112.38, 835.02.

MS (FAB+): 272 (MH^+, 51%).

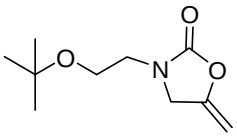
N-2-Hydroxyethyl-5-methylidene-2-oxazolidinone (26): Following the typical procedure, the reaction of **25** (50 mg, 0.25 mmol) with $AuClPPh_3$ (6.0 mg, 0.012 mmol) and $AgSbF_6$ (4.0 mg, 0.012 mmol) in CH_2Cl_2 (3 mL) and MeOH (50 μL) afforded after flash chromatography (Hex/AcOEt, 1/2) the oxazolidinone **26** (31 mg, 88%, colourless oil).



^{1}H NMR (300 MHz, $CDCl_3$): 4.75 (q, *J*=2.8 Hz, 1H), 4.31 (t, *J*=4.6 Hz, 2H), 4.29 (m, 1H), 3.84 (t, *J*=4.9 Hz, 2H), 3.45 (t, *J*=4.9 Hz, 2H), 2.1 (bs, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): 156.2, 149.3, 86.6, 60.8, 49.4, 46.3.

N-2-*tert*-Butoxyethyl-5-methylidene-2-oxazolidinone: Following the typical procedure, the reaction of **25** (25 mg, 0.13 mmol) with $AuClPPh_3$ (3.0 mg, 0.006 mmol) and $AgSbF_6$ (2.0 mg, 0.006 mmol) in CH_2Cl_2 (3.0 mL) afforded after flash chromatography (Hex/AcOEt, 1/2) the above mentioned oxazolidinone (12 mg, 59%, yellow oil).

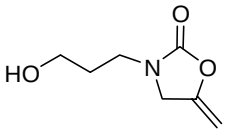


^{1}H NMR (300 MHz, $CDCl_3$): 4.71 (q, *J*=2.8 Hz, 1H), 4.32 (t, *J*=2.4 Hz, 2H), 4.25 (q, *J*=2.3 Hz , 1H), 3.53 (t, *J*=4.8 Hz, 2H), 3.42 (t, *J*=4.8 Hz, 2H), 1.17 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 155.7, 149.7, 86.0, 73.0, 60.5, 49.9, 44.7, 21.4.

MS (FAB+): 200 (MH^+, 9%).

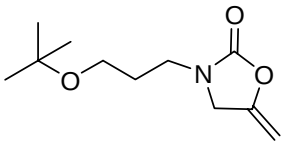
N-3-Hydroxypropyl-5-methylidene-2-oxazolidinone (28): Following the typical procedure, the reaction of **27** (20 mg, 0.09 mmol) with $AuClPPh_3$ (2.0 mg, 0.005 mmol) and $AgSbF_6$ (1.5 mg, 0.005 mmol) in CH_2Cl_2 (1.5 mL) and MeOH (25 μL) afforded after flash chromatography (Hex/AcOEt, 1/2) the oxazolidinone **28** (12 mg, 85%, yellow oil).



^{1}H NMR (300 MHz, $CDCl_3$): 4.76 (q, *J*=2.7 Hz, 1H), 4.30 (q, *J*=2.3 Hz, 1H), 4.20 (t, *J*=2.4 Hz, 2H), 3.66 (bs, 2H), 3.45 (t, *J*=5.9 Hz, 2H), 2.48 (bs, 1H), 1.77 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 156.3, 148.9, 86.8, 58.9, 48.1, 40.3, 29.7.

N-3-*tert*-Butoxypropyl-5-methylidene-2-oxazolidinone: Following the typical procedure, the reaction of **27** (19 mg, 0.09 mmol) with $AuClPPh_3$ (2.2 mg, 0.0045 mmol) and $AgSbF_6$ (1.6 mg, 0.0045 mmol) in CH_2Cl_2 (1.5 mL) afforded after flash



chromatography (Hex/AcOEt, 5/1) the above mentioned oxazolidinone (15.6 mg, 82%, colourless oil).

^{1}H NMR (300 MHz, $CDCl_3$): 4.71 (q, *J*=2.7 Hz, 1H), 4.26 (q, *J*=2.9 Hz, 1H), 4.18 (t, *J*=2.4 Hz, 2H), 3.40 (t, *J*=6.2 Hz, 4H), 1.78 (m, 2H), 1.16 (s, 9H).

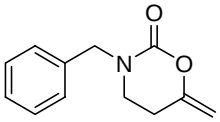
^{13}C NMR (75 MHz, $CDCl_3$): 155.6, 149.3, 86.2, 72.8, 58.8, 47.9, 41.7, 28.1, 27.4.

MS (ESI+): 214 (MH^+, 6%), 236 (MNa^+, 100%).

HRMS (ESI+): calcd for ($C_{11}H_{19}NO_3Na$) [MNa^+] 236.1261, found 236.1262.

IR: 2974.78, 1790.0, 1692.7, 1387.69, 1093.98.

N-Benzyl-6-methylidene-1,3-oxazin-2-one (30): Following the typical procedure, the reaction of **29** (40 mg, 0.15 mmol) with $AuClPPh_3$ (3.8 mg, 0.0075 mmol) and $AgSbF_6$ (2.6 mg, 0.0075 mmol) in CH_2Cl_2 (1.5 mL) afforded after flash chromatography (Hex/AcOEt, 4:1) **30** (28 mg, 90%, colourless oil).



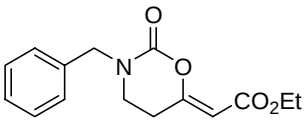
^{1}H NMR (300 MHz, $CDCl_3$): 7.38-7.28 (m, 5H), 4.60 (d, *J*=1.0 Hz, 1H), 4.58 (s, 2H), 4.23 (d, *J*=1.0 Hz, 1H), 3.21 (t, *J*=6.2 Hz, 2H), 2.54 (t, *J*=6.2 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 152.7, 151.2, 136.1, 128.8, 128.1, 127.9, 92.8, 52.7, 43.1, 26.2.

MS (ESI+): 204 (MH^+, 100%), 226 (MNa^+, 53%).

HRMS (ESI+): calcd for ($C_{12}H_{14}NO_2$)[MH^+] 204.1013, found 204.1019, and for ($C_{12}H_{13}NO_2Na$) [MNa^+] 226.0849, found 226.0838.

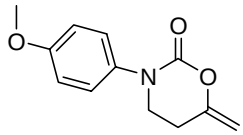
(*Z*)-N-Benzyl-6-ethoxycarbonylmethylidene-1,3-oxazin-2-one (32): Following the typical procedure, the reaction of **31** (40 mg, 0.12 mmol) with $AuClPPh_3$ (3.0 mg, 0.006 mmol) and $AgSbF_6$ (2.1 mg, 0.006 mmol) in CH_2Cl_2 (1.2 mL) afforded after flash chromatography (Hex/AcOEt, 4:1) **32** (30.2 mg, 91%, colourless oil).



^{1}H NMR (300 MHz, $CDCl_3$): 7.36-7.30 (m, 5H), 5.02 (s, 1H), 4.60 (s, 2H), 4.20 (q, *J*=7.1 Hz, 2H), 3.25 (t, *J*=6.1 Hz, 2H), 2.60 (t, *J*=6.0 Hz, 2H), 1.29 (t, J=7.1, Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 163.6, 157.6, 149.1, 135.6, 128.9, 128.3, 128.1, 99.1, 60.3, 53.0, 41.9, 27.5, 14.3.

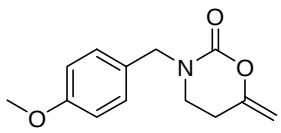
N-(4-methoxyphenyl)-6-methylidene-1,3-oxazin-2-one (34): Following the typical procedure, the reaction of **33** (40 mg, 0.145 mmol) with $AuClPPh_3$ (3.6 mg, 0.007 mmol) and $AgSbF_6$ (2.5 mg, 0.007 mmol) in CH_2Cl_2 (1.5 mL) afforded after flash chromatography (Hex/AcOEt, 8:1) **34** (30.2 mg, 81%, pale yellow oil).



^{1}H NMR (300 MHz, $CDCl_3$): 7.22 (d, *J*=9.0 Hz, 2H), 6.91 (d, *J*=9.0 Hz, 2H), 4.73 (d, *J*=1.6 Hz, 1H), 4.31 (d, *J*=1.6 Hz, 1H), 3.80 (s, 3H), 3.67 (t, *J*=6.0 Hz, 2H), 2.75 (t, *J*=6.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 158.3, 152.7, 150.2, 135.2, 126.8, 114.5, 92.9, 55.5, 47.7, 26.5.

N-(4-methoxybenzyl)-6-methylidene-1,3-oxazin-2-one (36): Following the typical procedure, the reaction of **35** (40 mg, 0.138 mmol) with $AuClPPh_3$ (3.4 mg, 0.007 mmol) and $AgSbF_6$ (2.4 mg, 0.007 mmol) in CH_2Cl_2 (1.5 mL) afforded after flash chromatography (Hex/AcOEt, 4:1) **36** (24.2 mg, 75%, colourless oil).

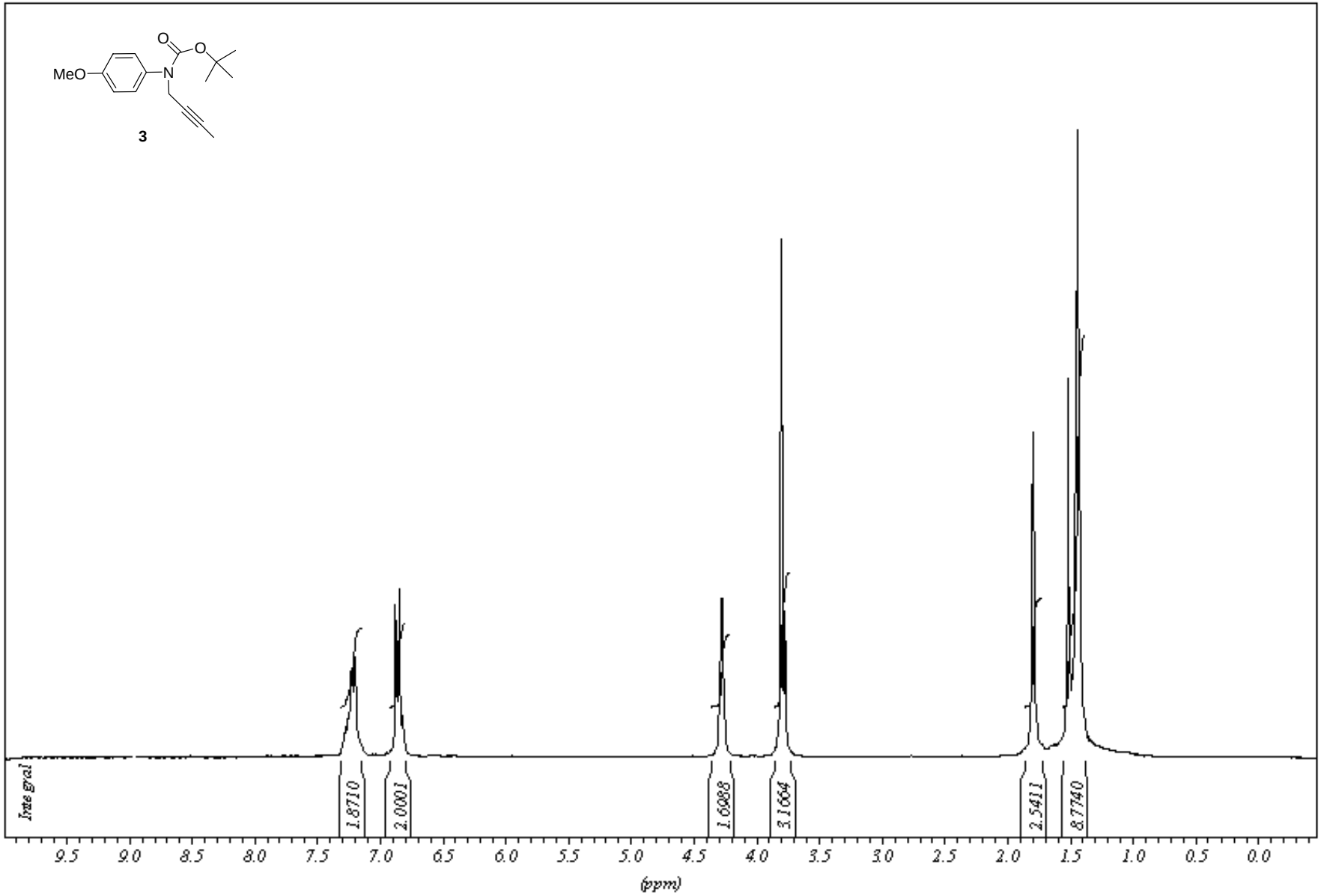


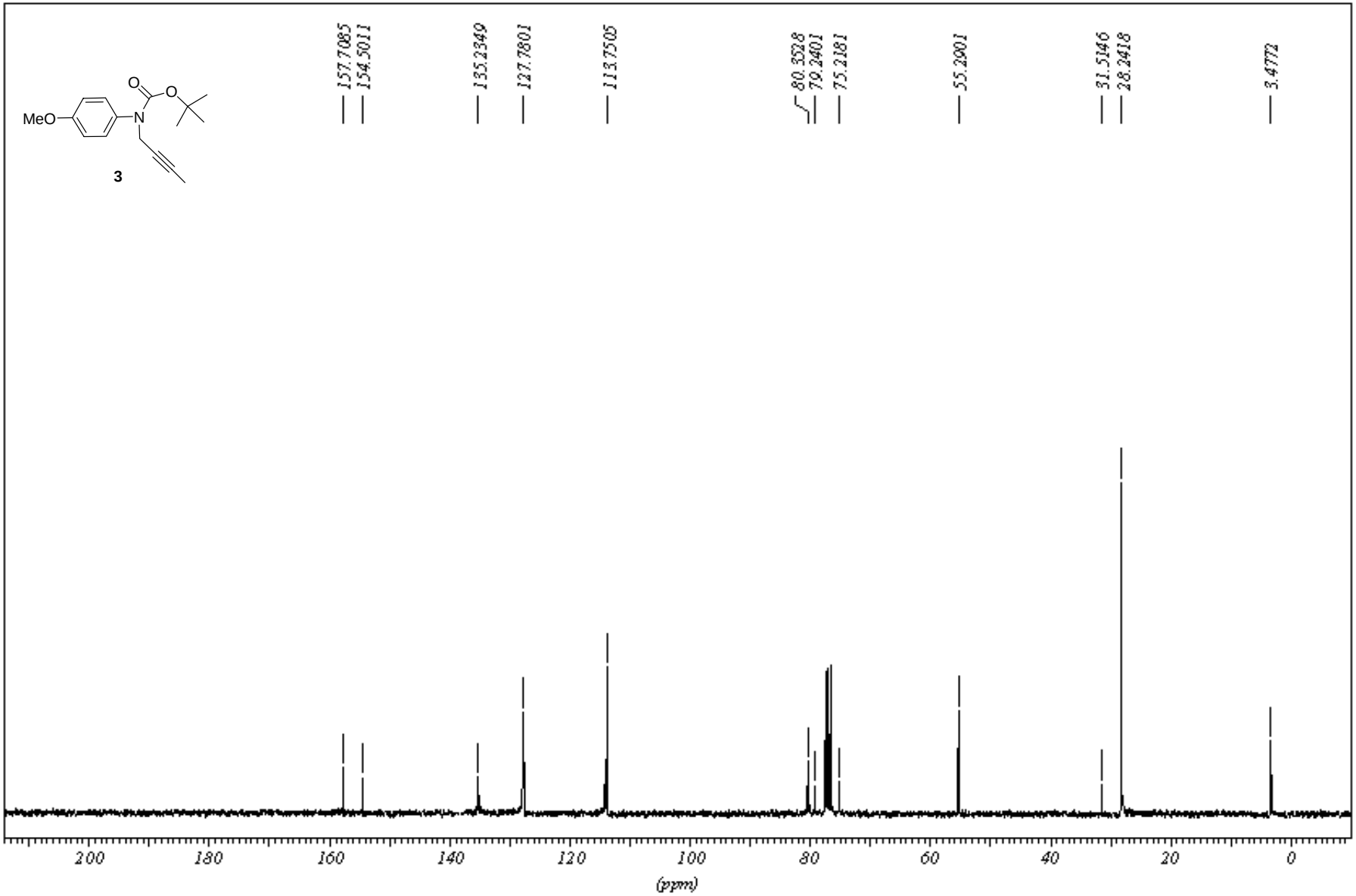
^{1}H NMR (300 MHz, $CDCl_3$): 7.22 (d, *J*=8.4 Hz, 2H), 6.86 (d, *J*=8.4 Hz, 2H), 4.65 (d, *J*=1.0 Hz, 1H), 4.51 (s, 2H), 4.22 (d, *J*=1.0 Hz, 1H), 3.80 (s, 3H), 3.19 (t, *J*=6.3 Hz, 2H), 2.52 (t, *J*=6.3 Hz, 2H) .

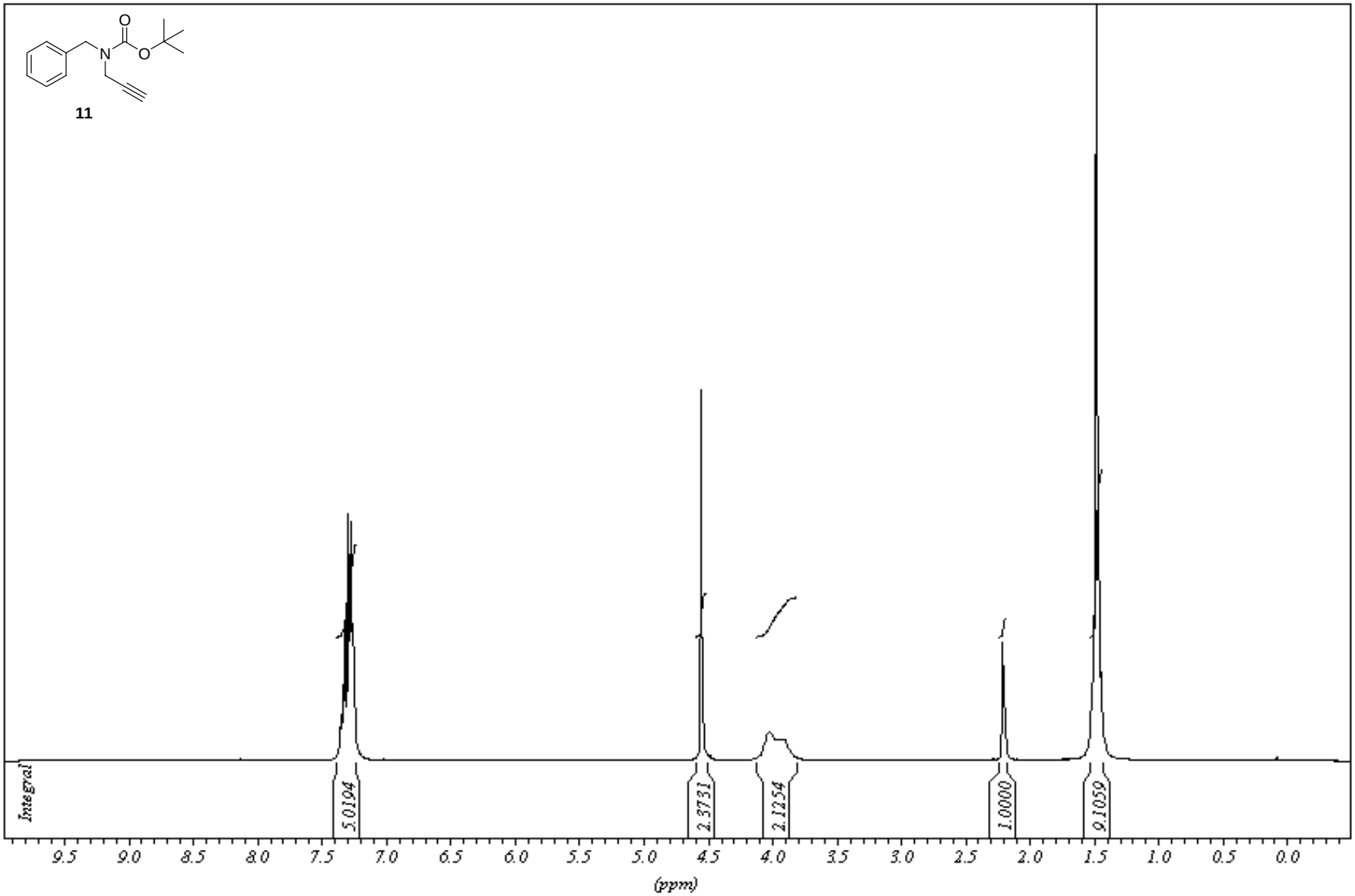
^{13}C NMR (75 MHz, $CDCl_3$): 159.3, 152.7, 151.1, 129.5, 128.2, 114.1, 92.7, 55.3, 52.1, 42.8, 26.2.

MS (ESI+): 234 (MH^+, 15%), 256 (MNa^+, 100%).

HRMS (ESI+): calcd for ($C_{13}H_{16}NO_3$)[MH^+] 234.1137, found 234.1130, and for ($C_{13}H_{15}NO_3Na$) [MNa^+] 256.0942, found 256.0949.


MeO
N
O
O
3
Integral
1.8710
2.0001
1.6088
3.1664
2.5411
8.7740
9.5
9.0
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)


MeO
N
O
O
3
157.7085
154.5011
135.2349
127.7801
113.7505
80.3528
79.2401
75.2181
55.2901
31.5146
28.2418
3.4772
200
180
160
140
120
100
80
60
40
20
0
(ppm)


O
N
O
11
Integral
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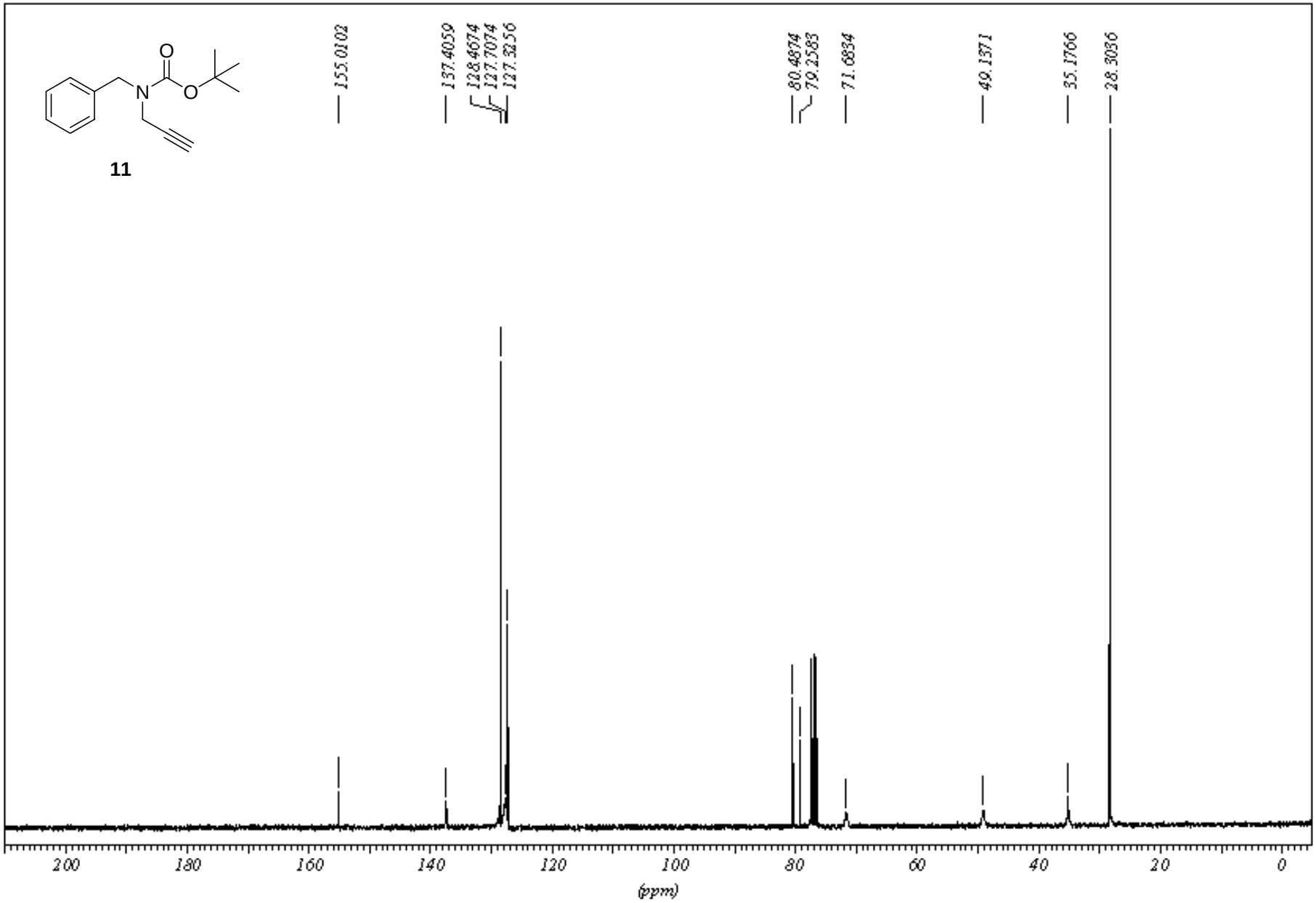
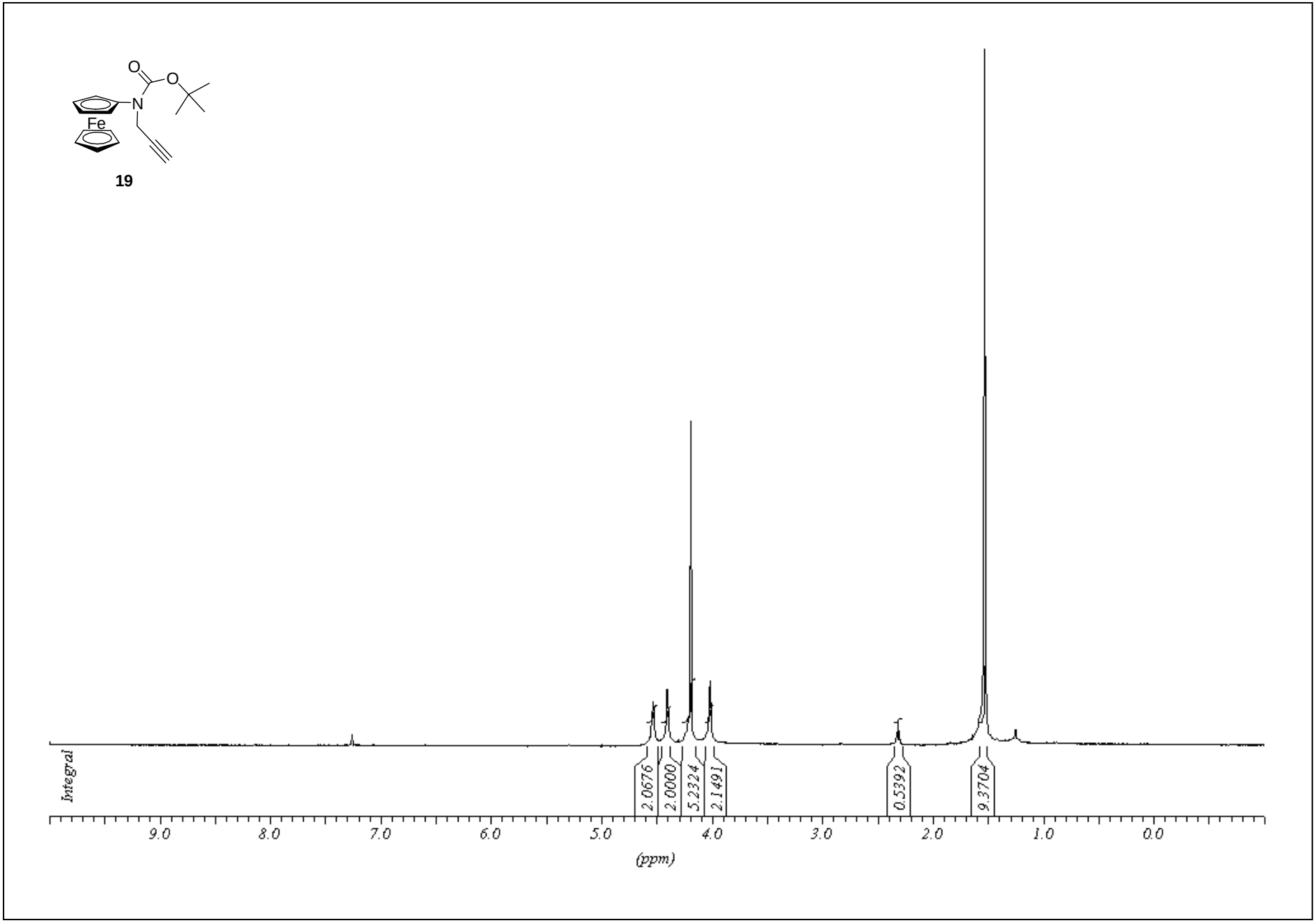
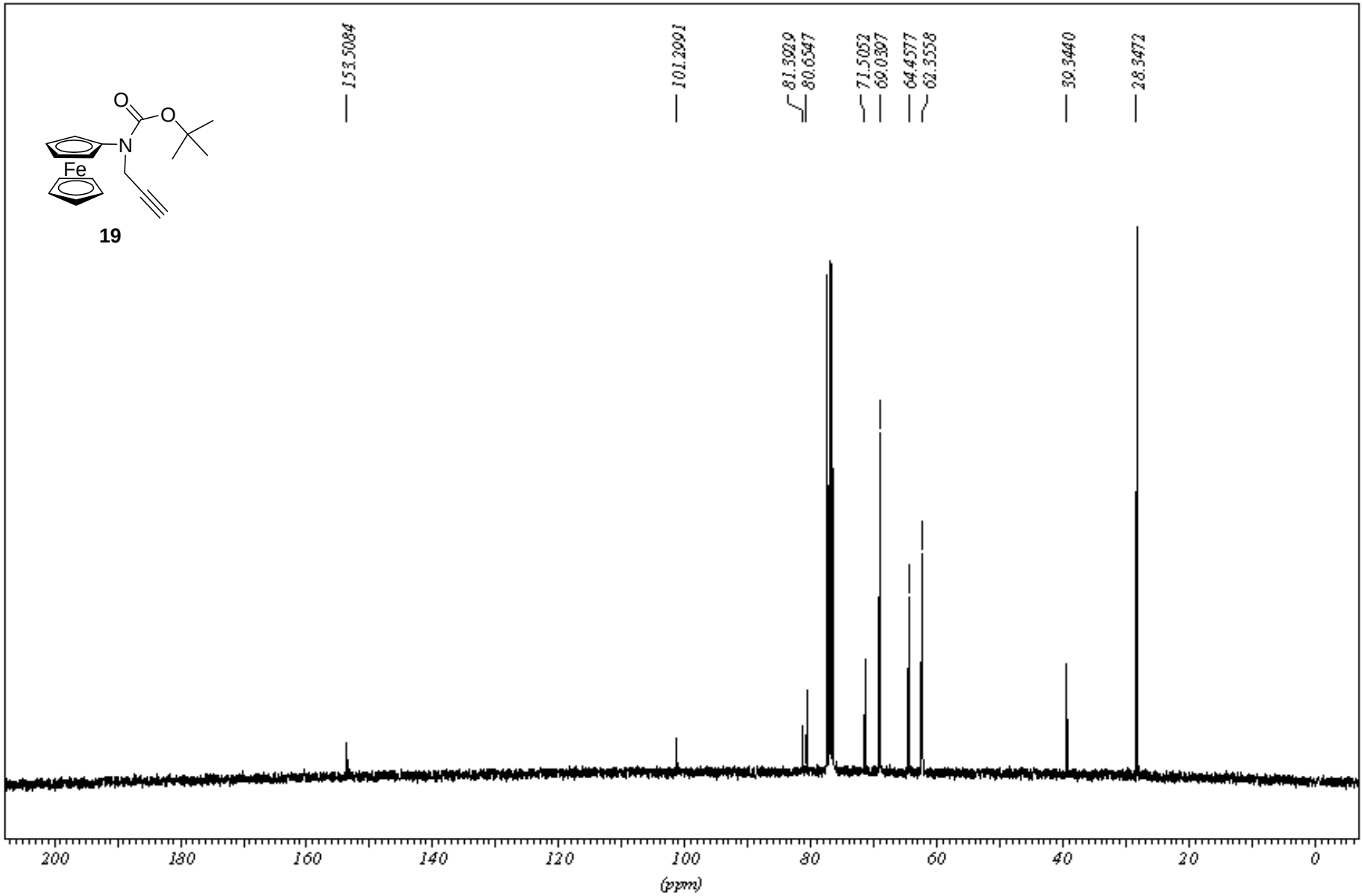
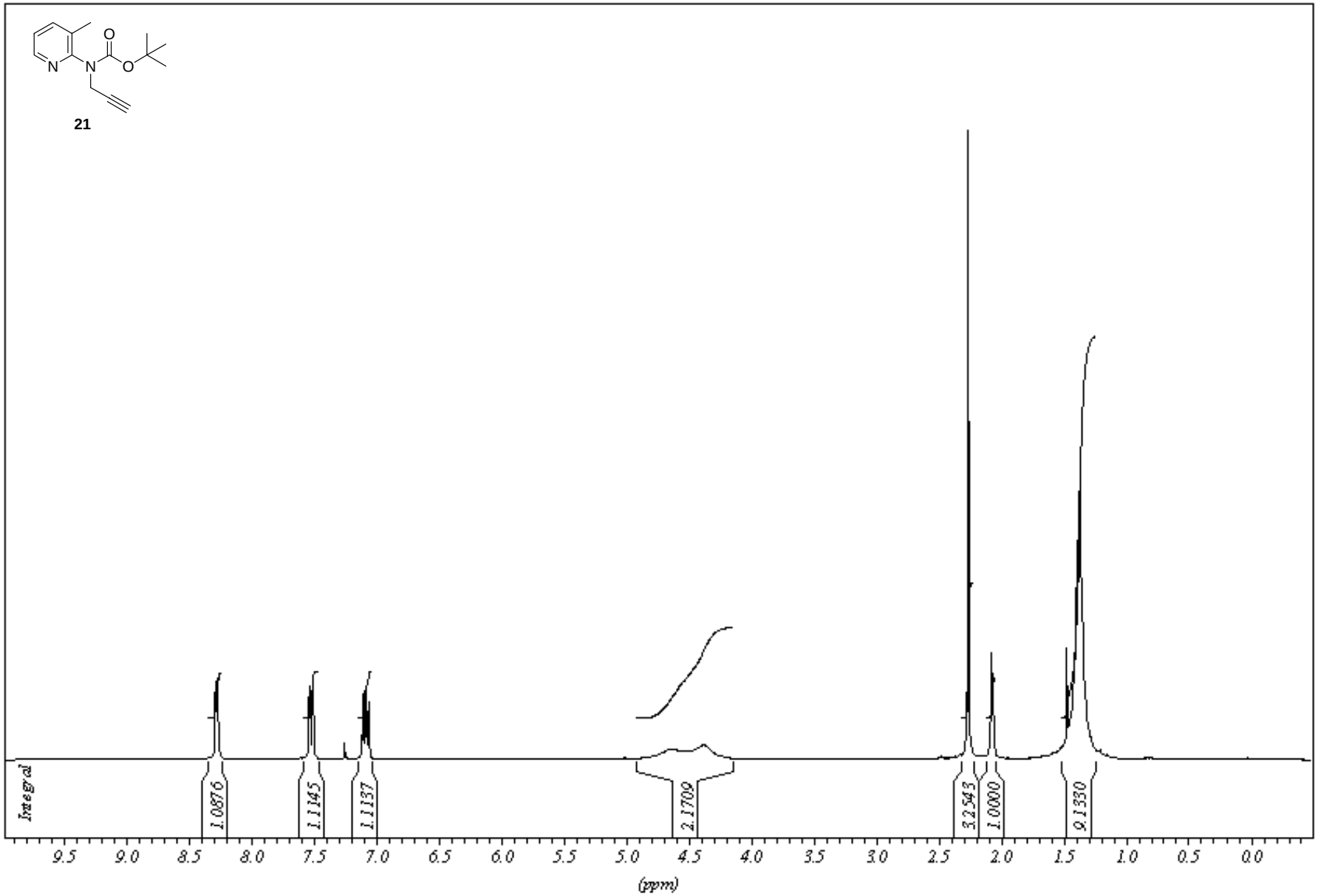
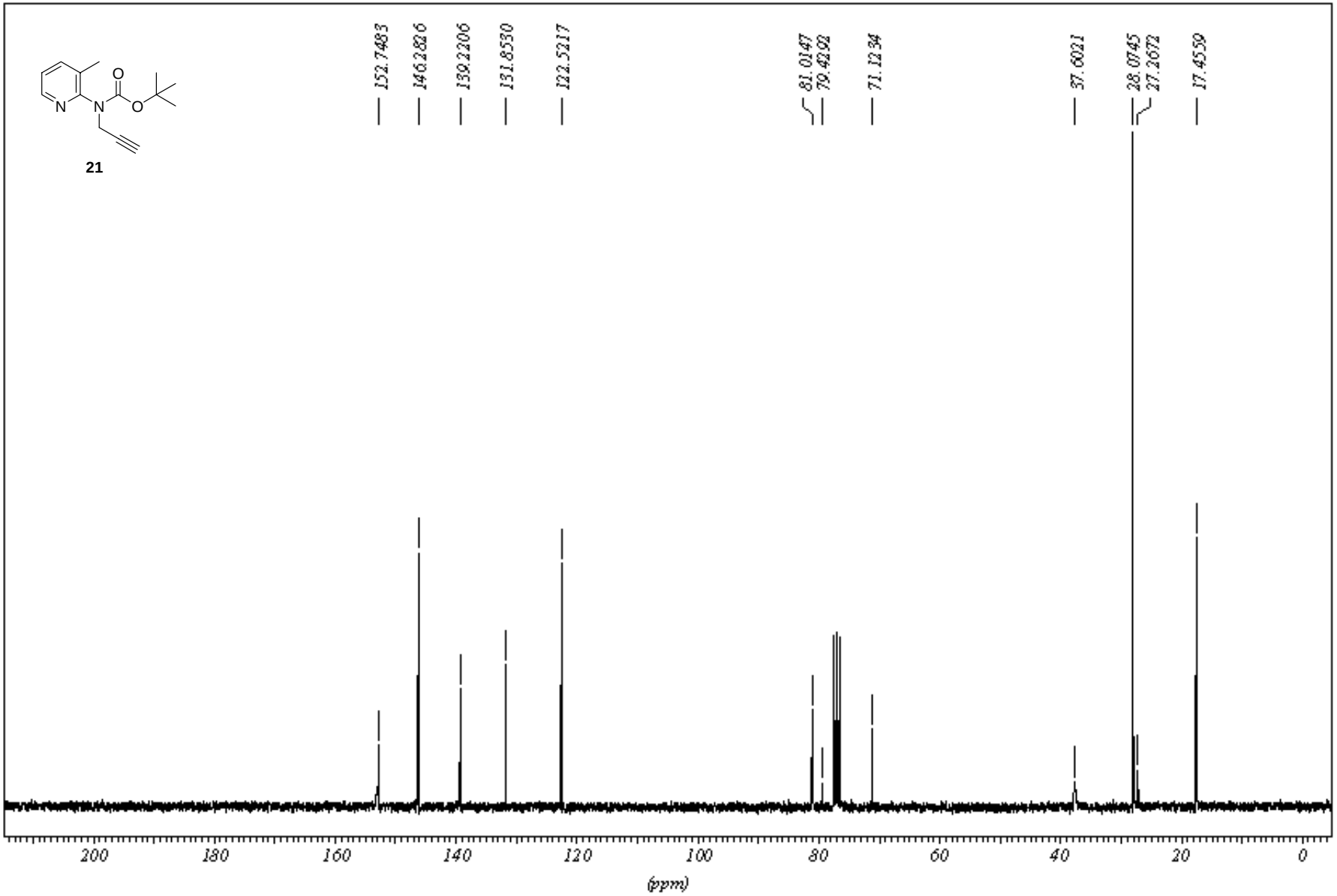
2.3731
2.1254
1.0000
9.1059
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

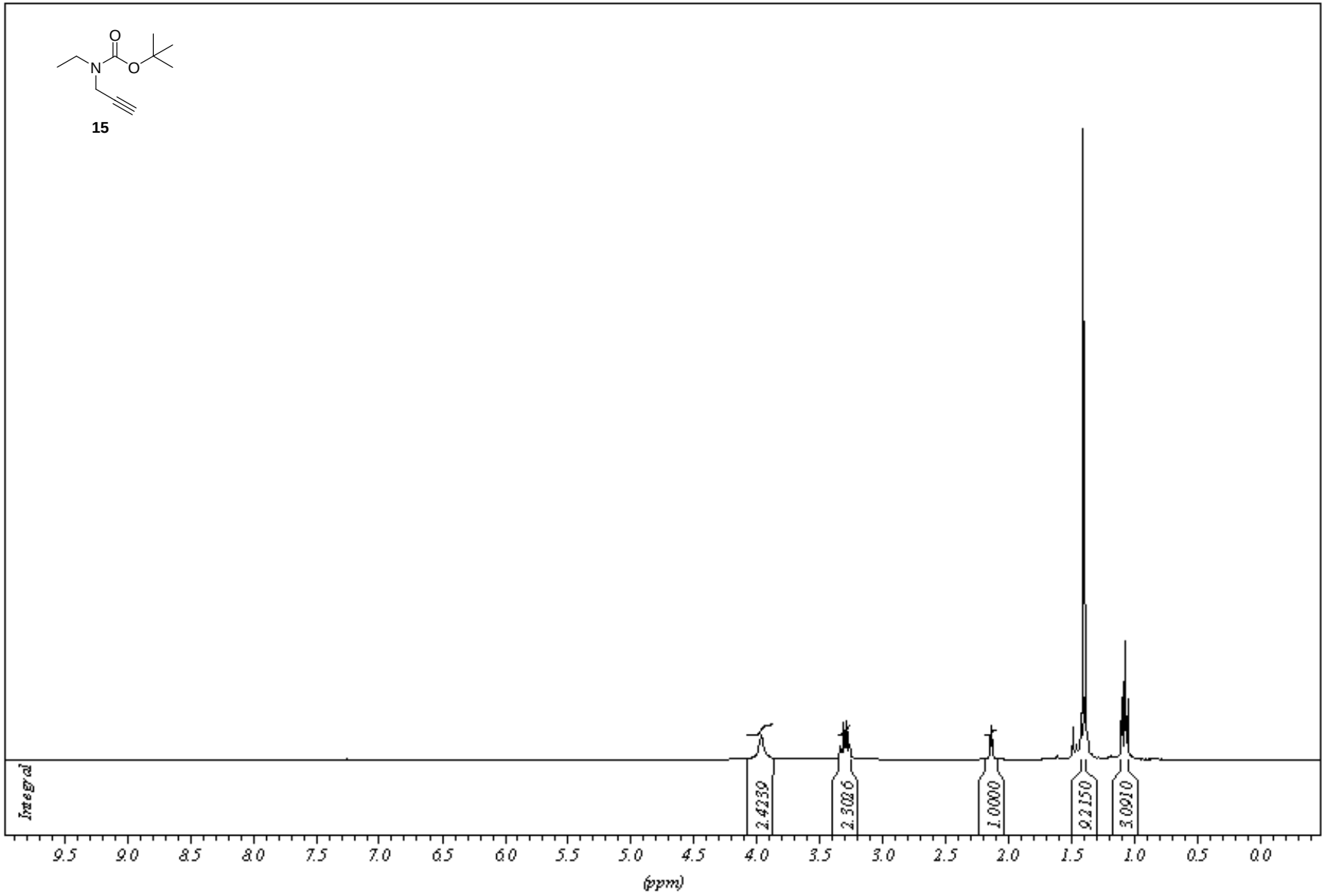

11
155.0102
137.4059
128.4674
127.7074
127.3256
80.4874
79.2583
71.6834
49.1371
35.1766
28.3036
200
180
160
140
120
100
80
60
40
20
0
(ppm)

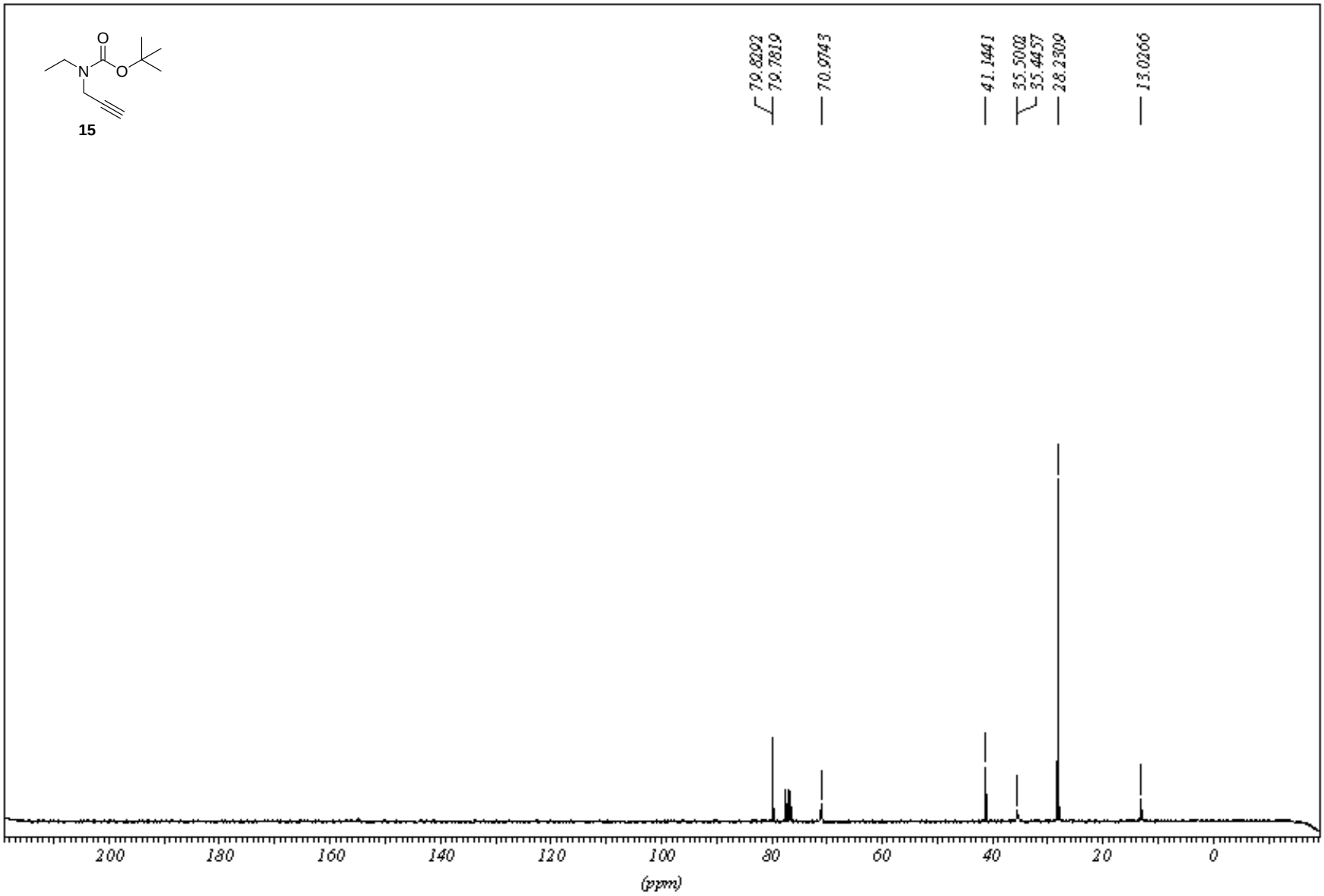

O
O
N
Fe
19
Integral
2.0676
2.0000
5.2324
2.1491
0.5392
9.3704
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

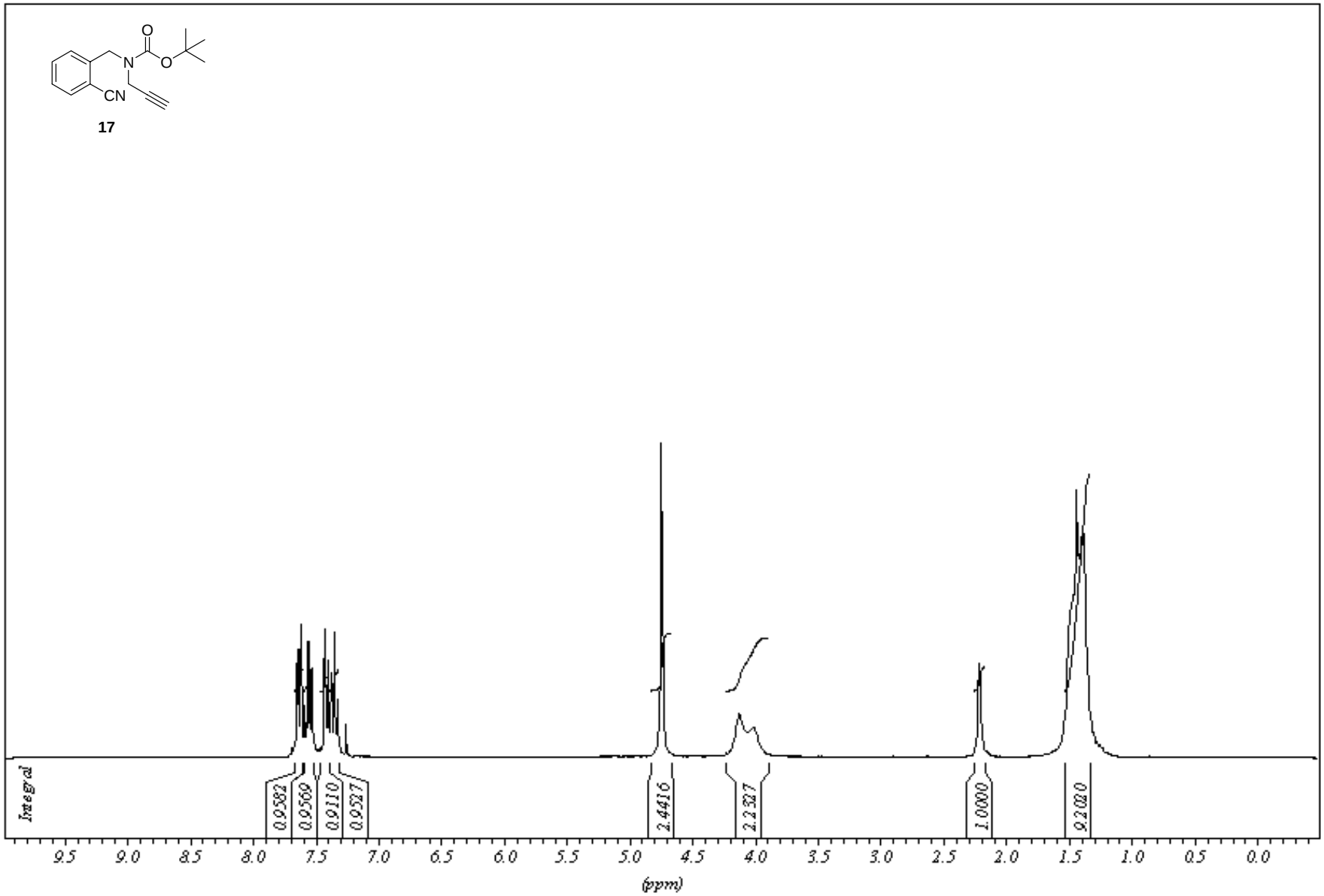

153.5084
101.2991
81.3929
80.6547
71.5052
69.0397
64.4577
62.3558
39.3440
28.3472
O
O
N
Fe
19
200
180
160
140
120
100
80
60
40
20
0
(ppm)

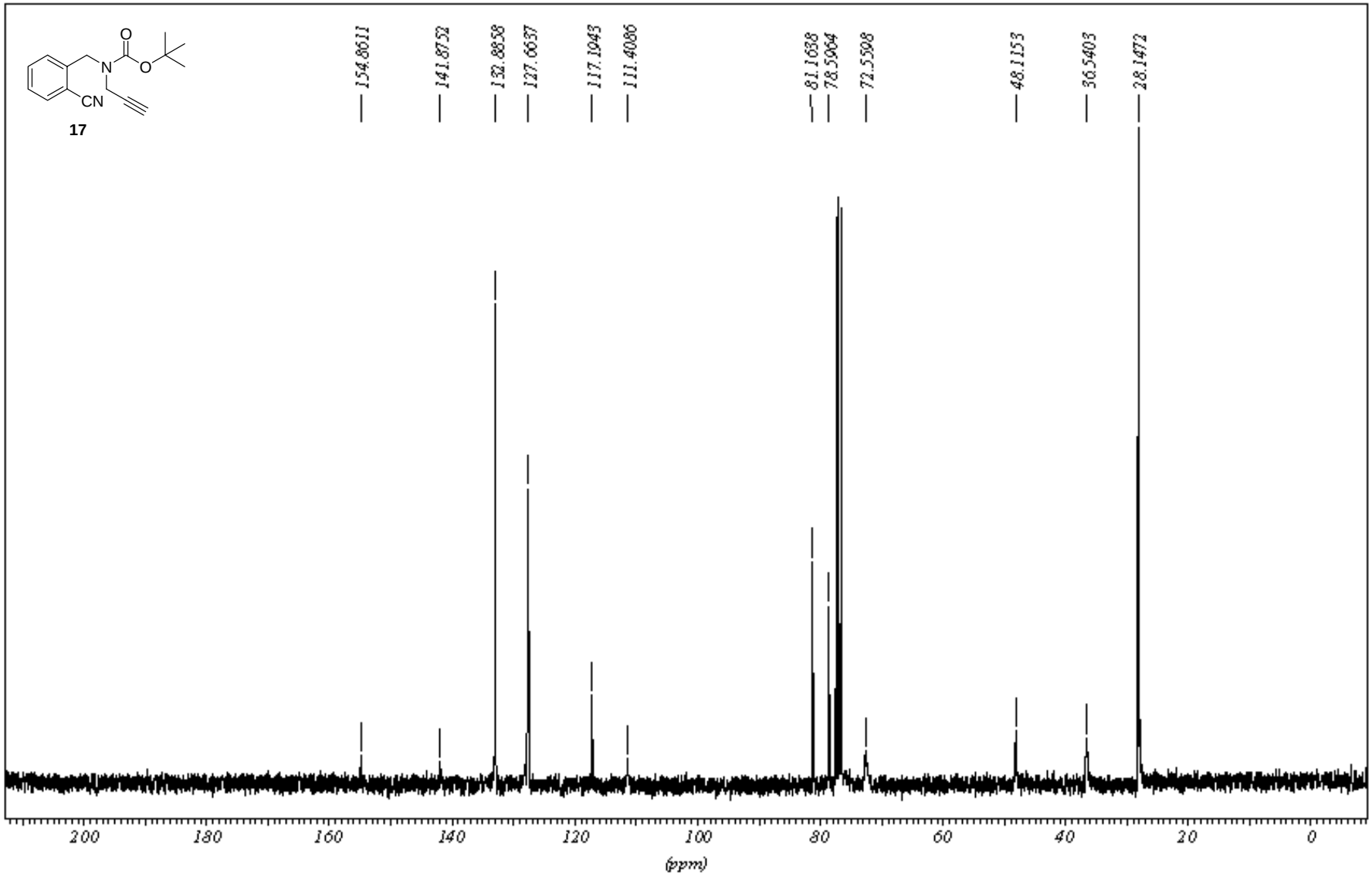

21
Integral
1.0876
1.1145
1.1137
2.1709
3.2543
1.0000
9.1330
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

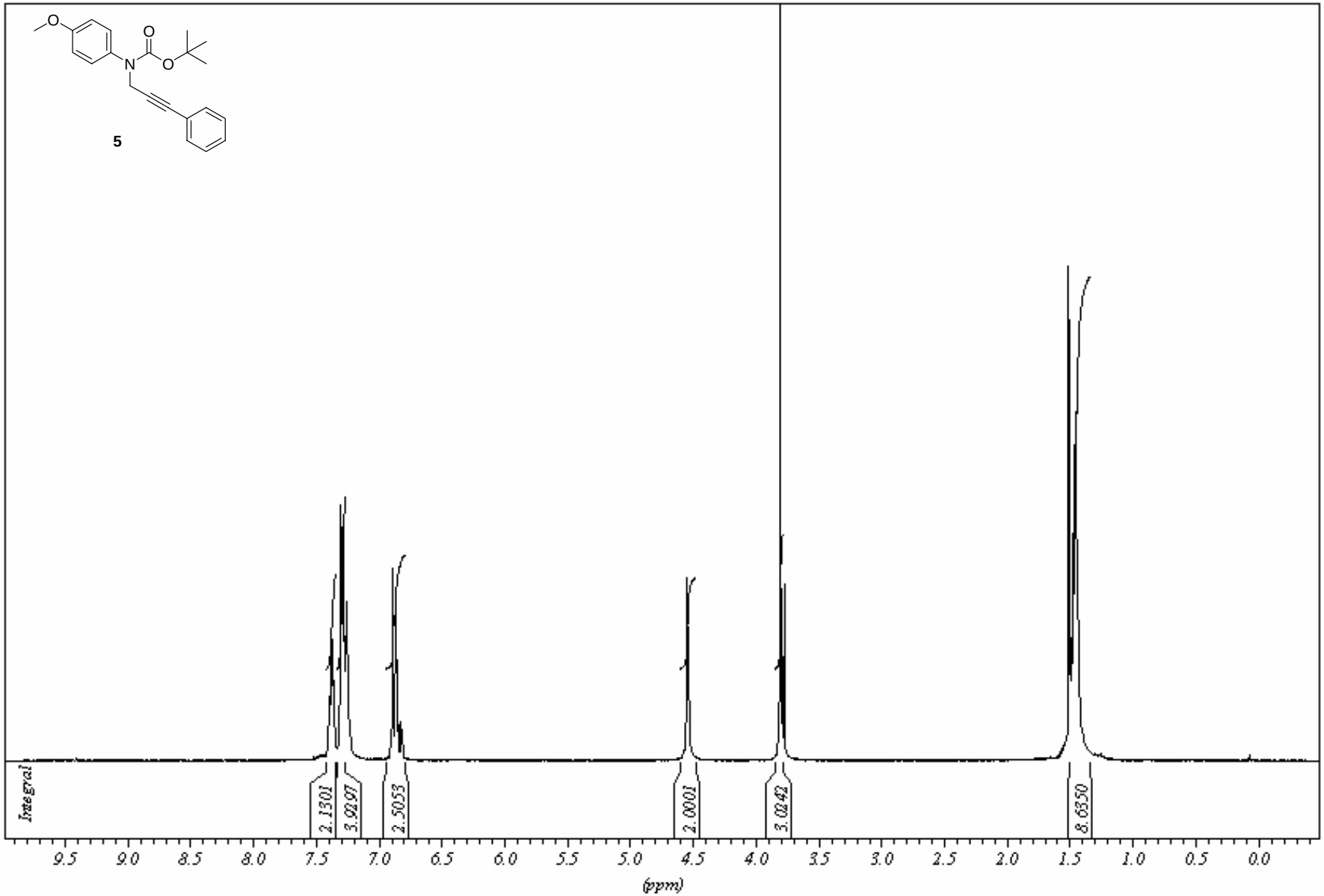

21
152.7483
146.2826
139.2206
131.8530
122.5217
81.0147
79.4292
71.1234
37.6021
28.0745
27.2672
17.4559
200
180
160
140
120
100
80
60
40
20
0
(ppm)

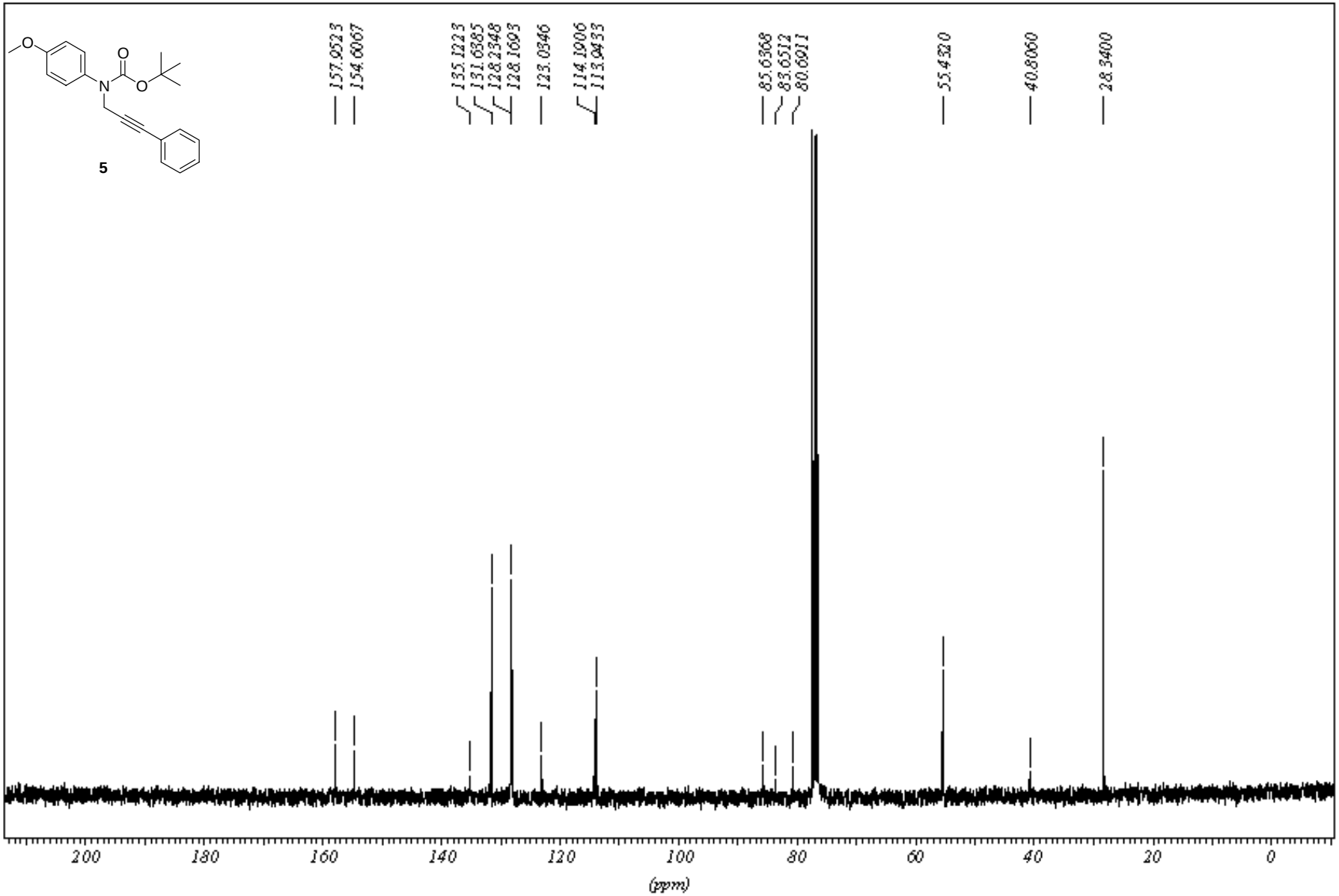

O
N
O
15
Integral
2.4239
2.3026
1.0000
9.2150
3.0910
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

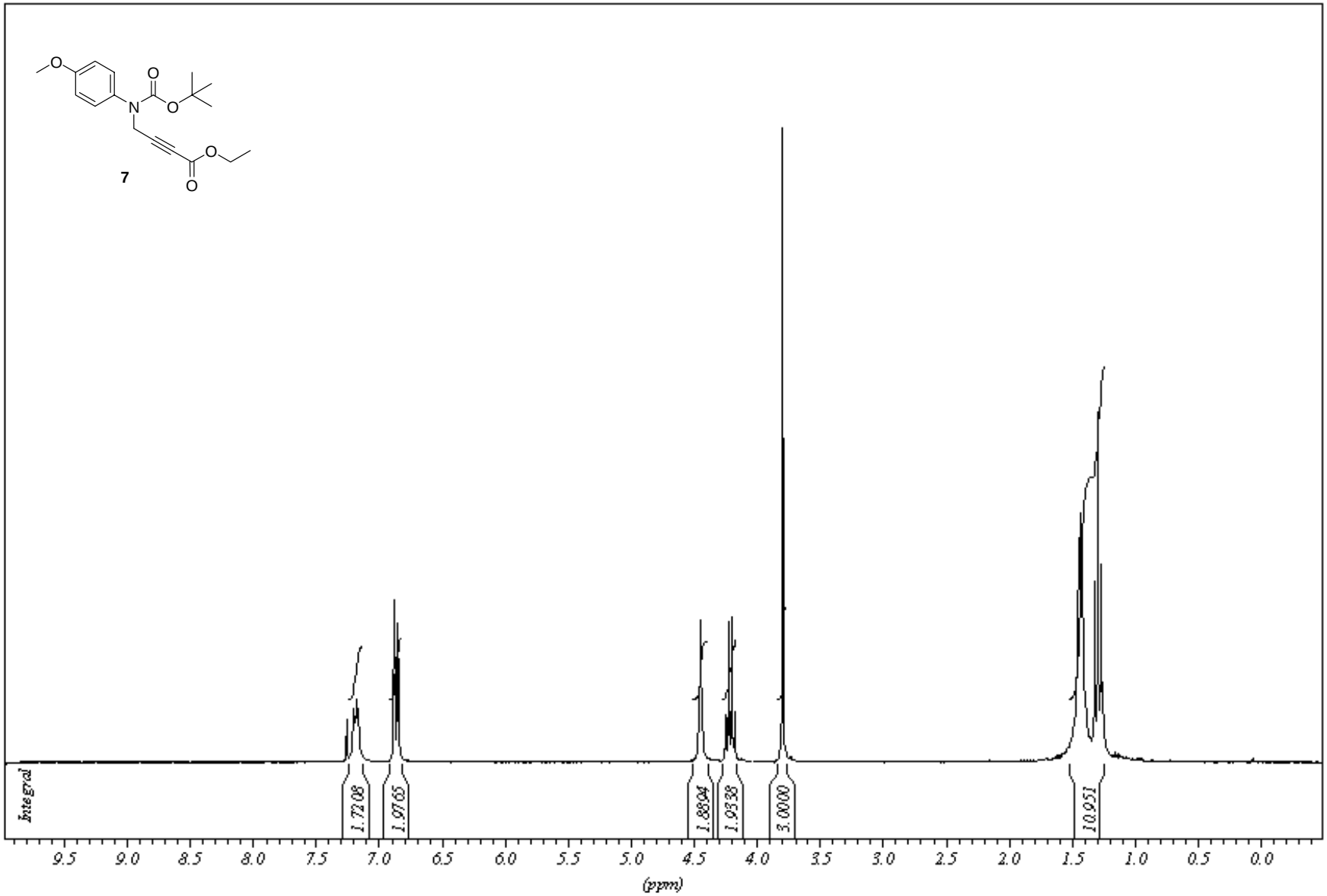

15
79.8292
79.7819
70.9743
41.1441
35.5002
35.4457
28.2309
13.0266
200
180
160
140
120
100
80
60
40
20
0
(ppm)

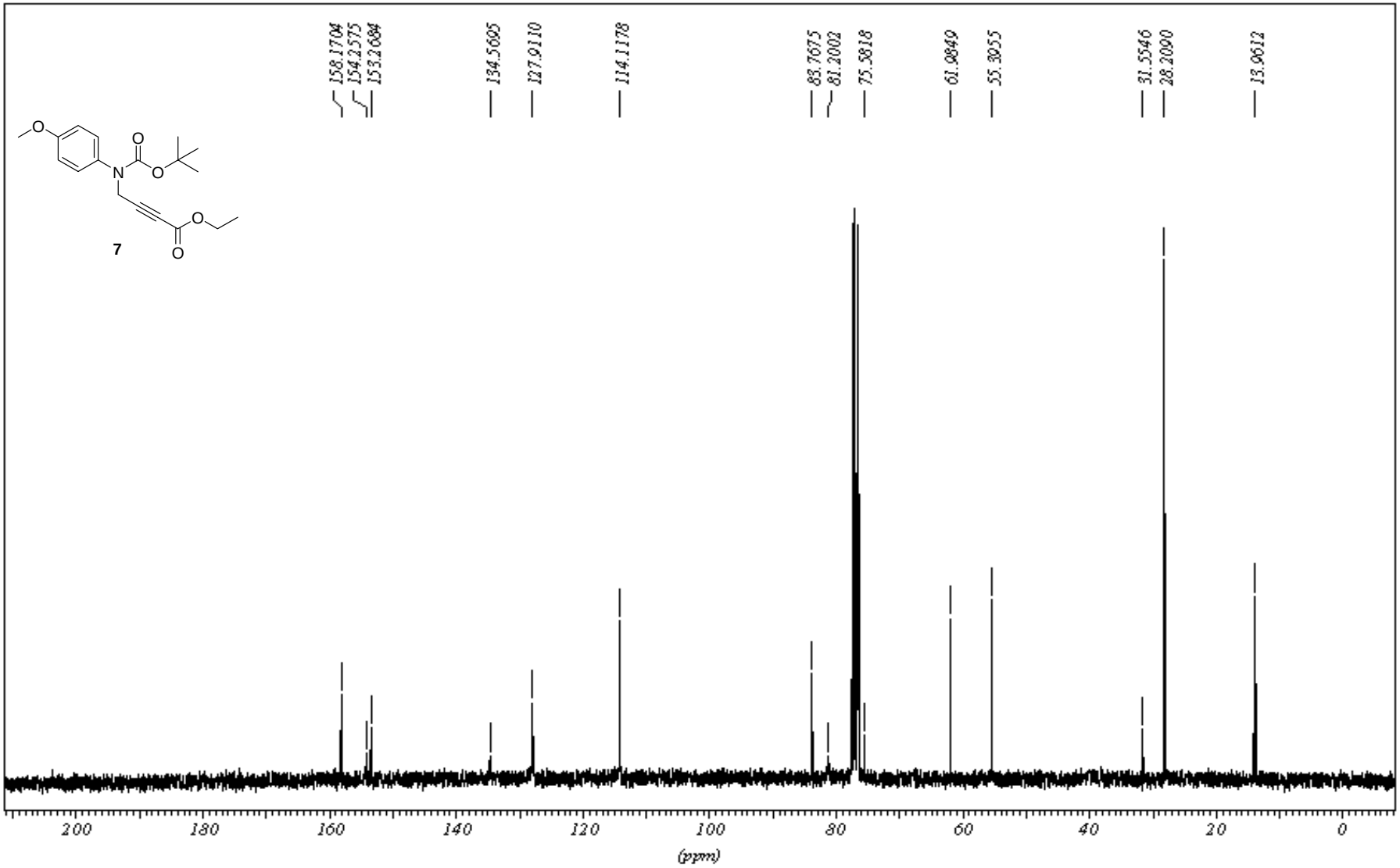

O
N
O
CN
17
Integral
0.9582
0.9569
0.9110
0.9527
2.4416
2.2327
1.0000
9.2020
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

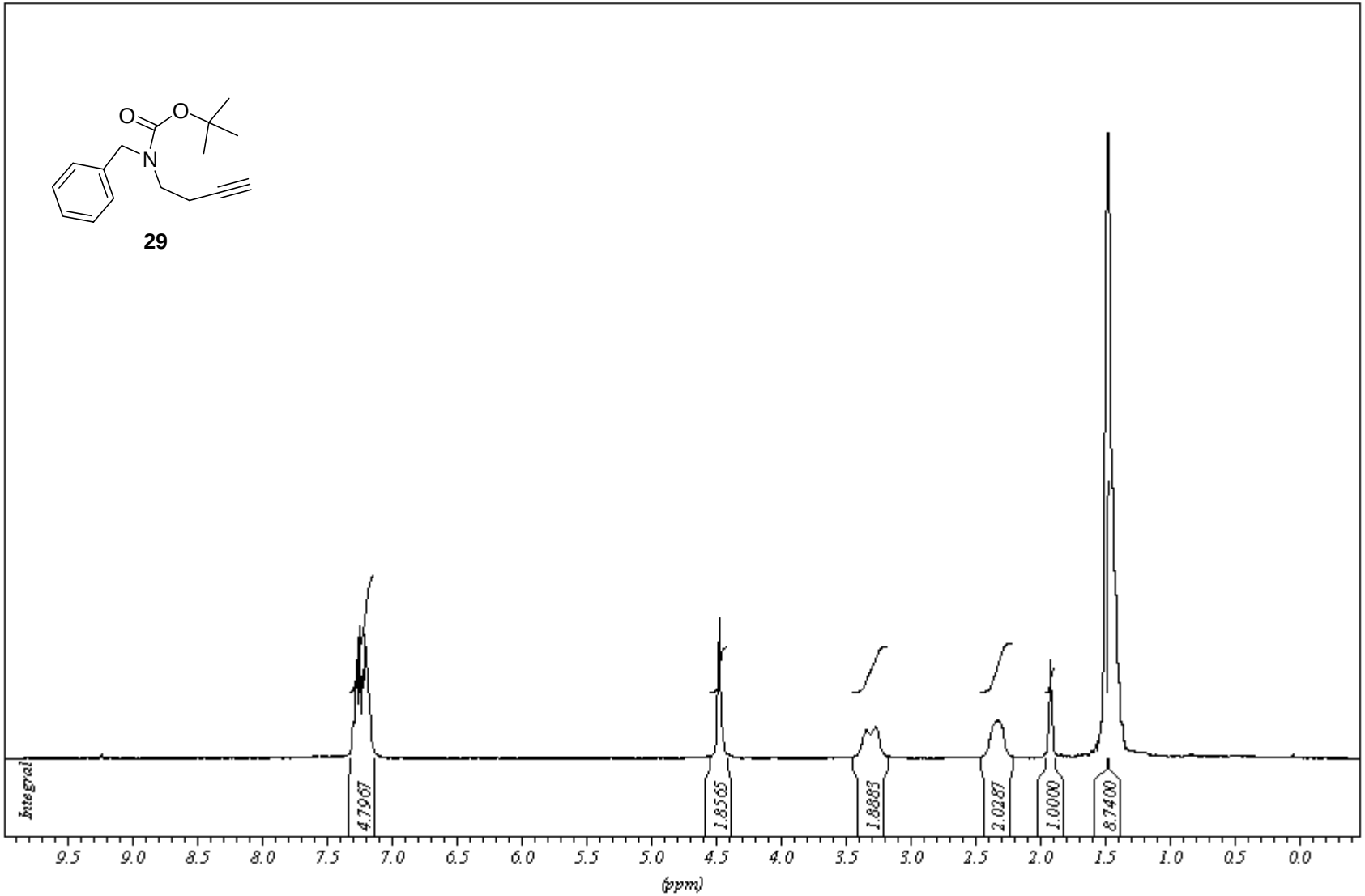

17
154.8611
141.8752
132.8858
127.6637
117.1943
111.4086
81.1638
78.5964
72.5598
48.1153
36.5403
28.1472
200
180
160
140
120
100
80
60
40
20
0
(ppm)

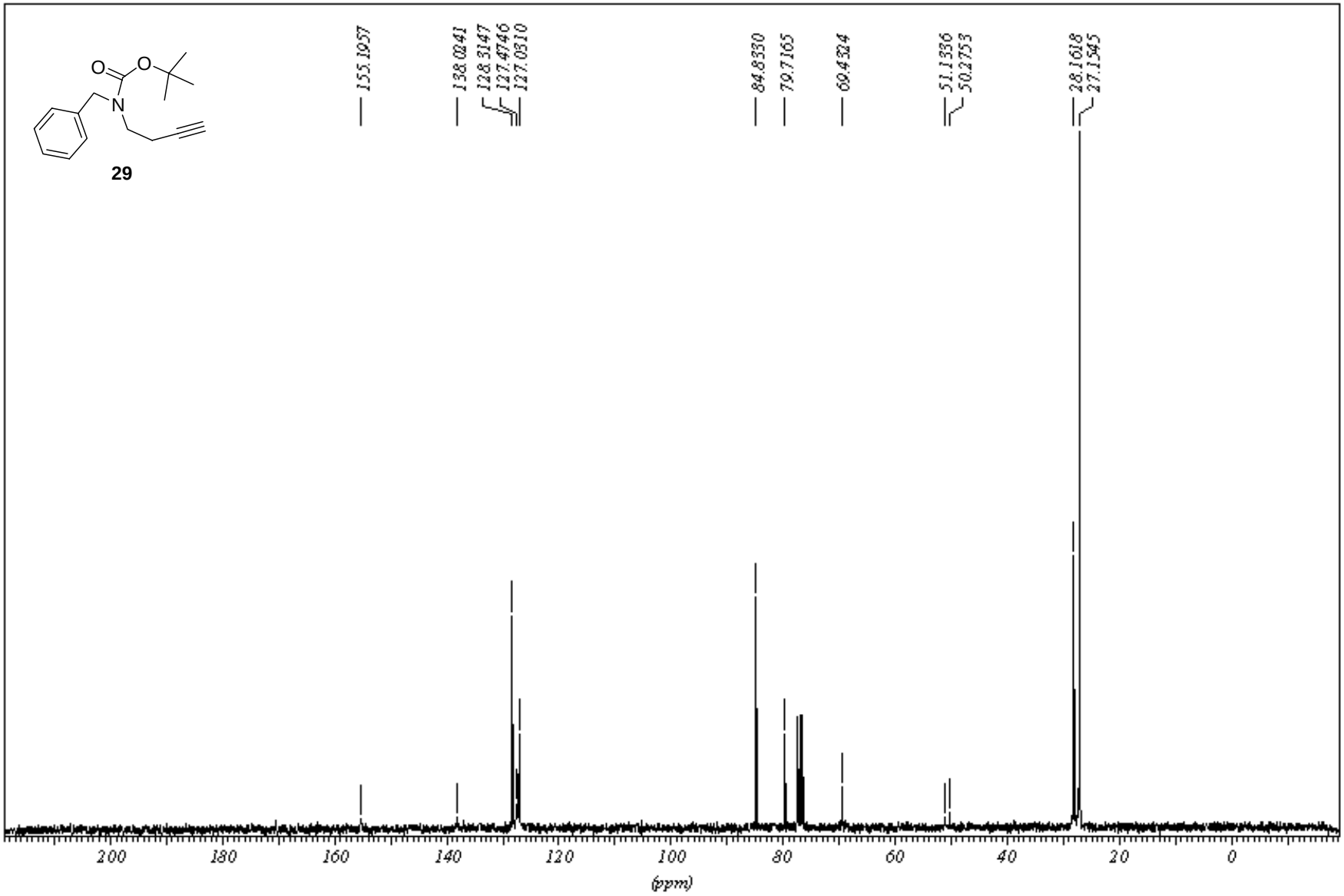

O
O
N
O
5
Integral
2.1301
3.9297
2.5053
2.0001
3.0242
8.6350
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

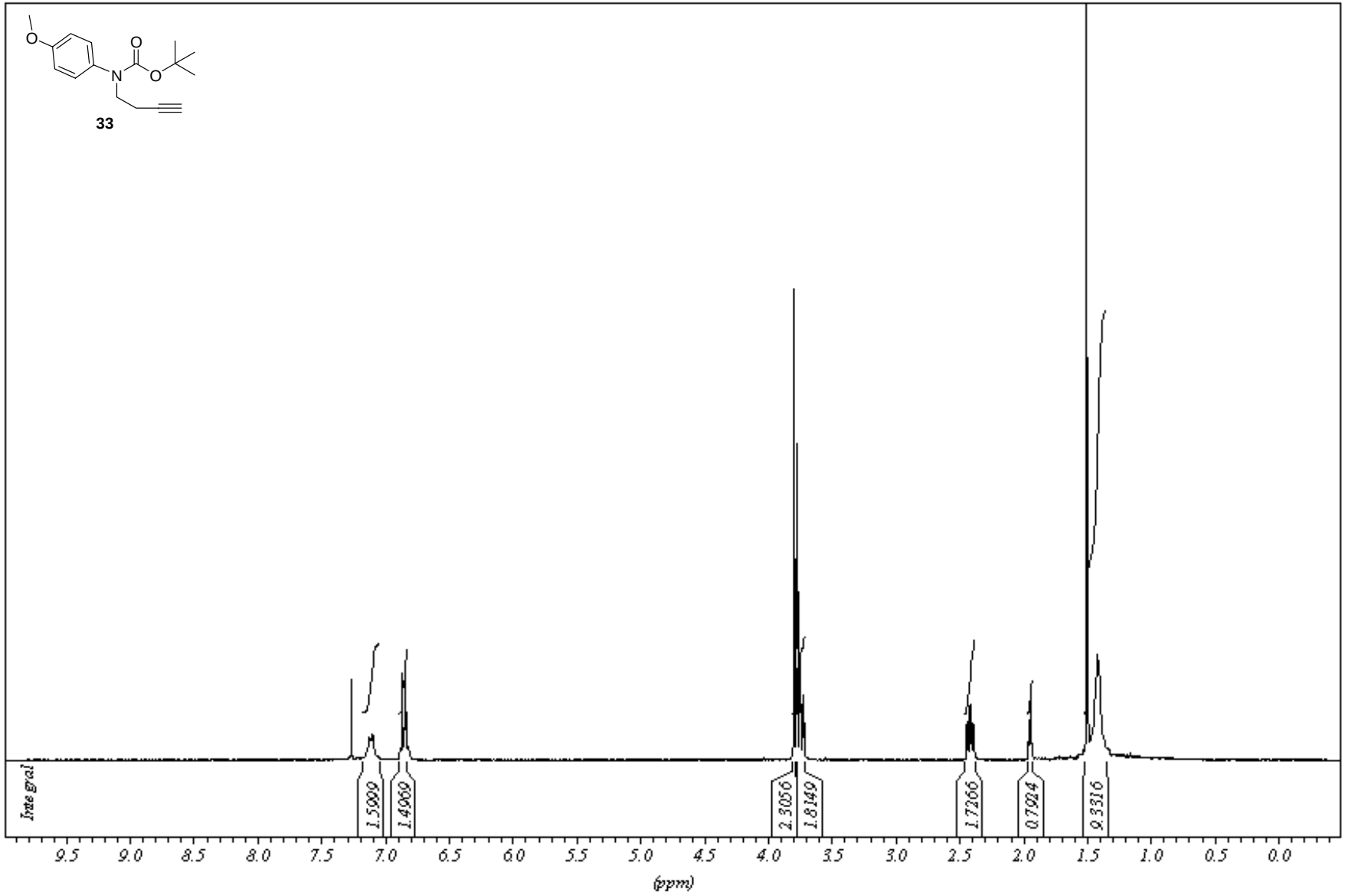

5
157.9523
154.6067
135.1223
131.6385
128.2348
128.1693
123.0346
114.1906
113.0433
85.6368
83.6512
80.6911
55.4320
40.8060
28.3400
200
180
160
140
120
100
80
60
40
20
0
(ppm)

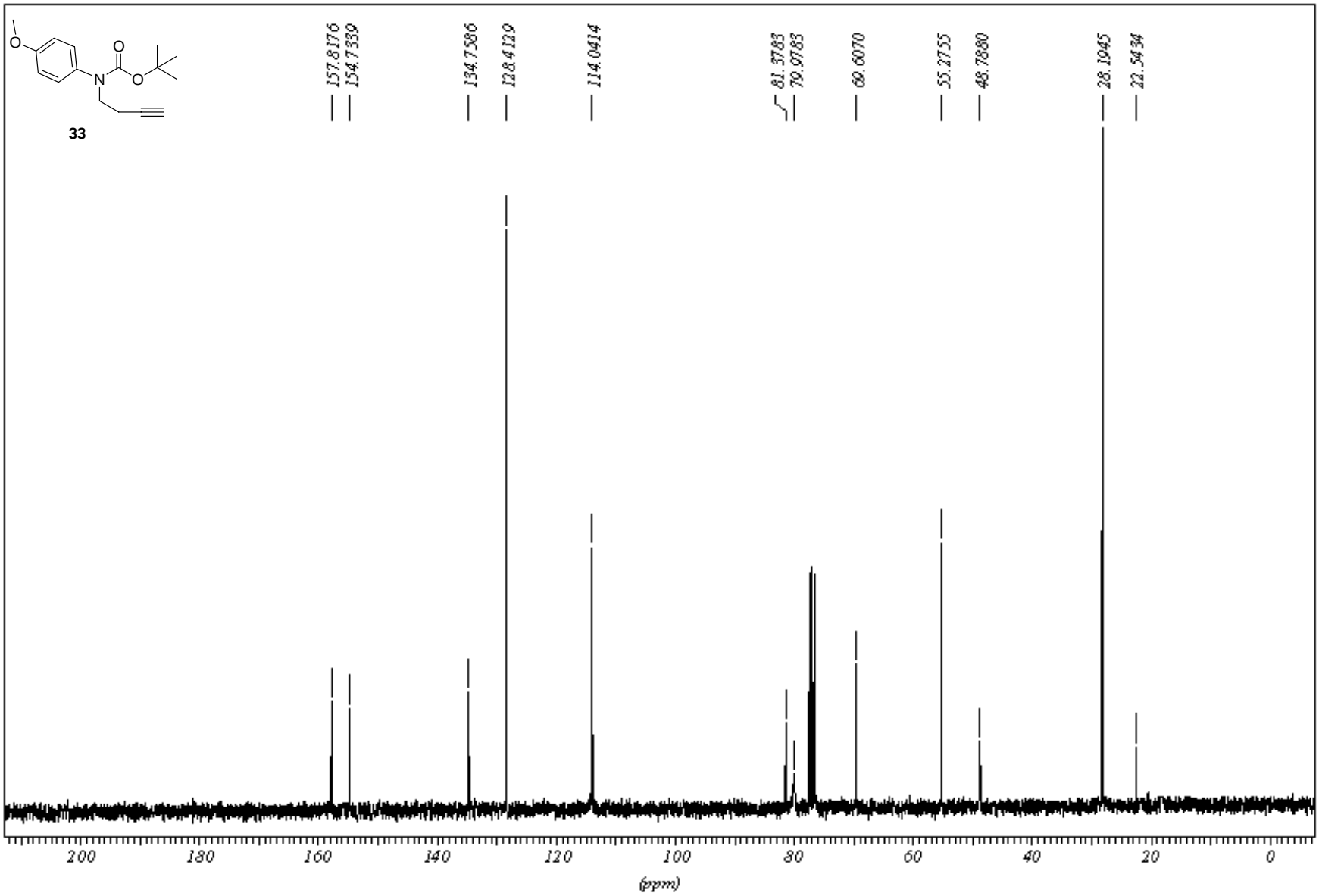

7
Integral
1.7208
1.9765
1.8894
1.9338
3.0000
10.951
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

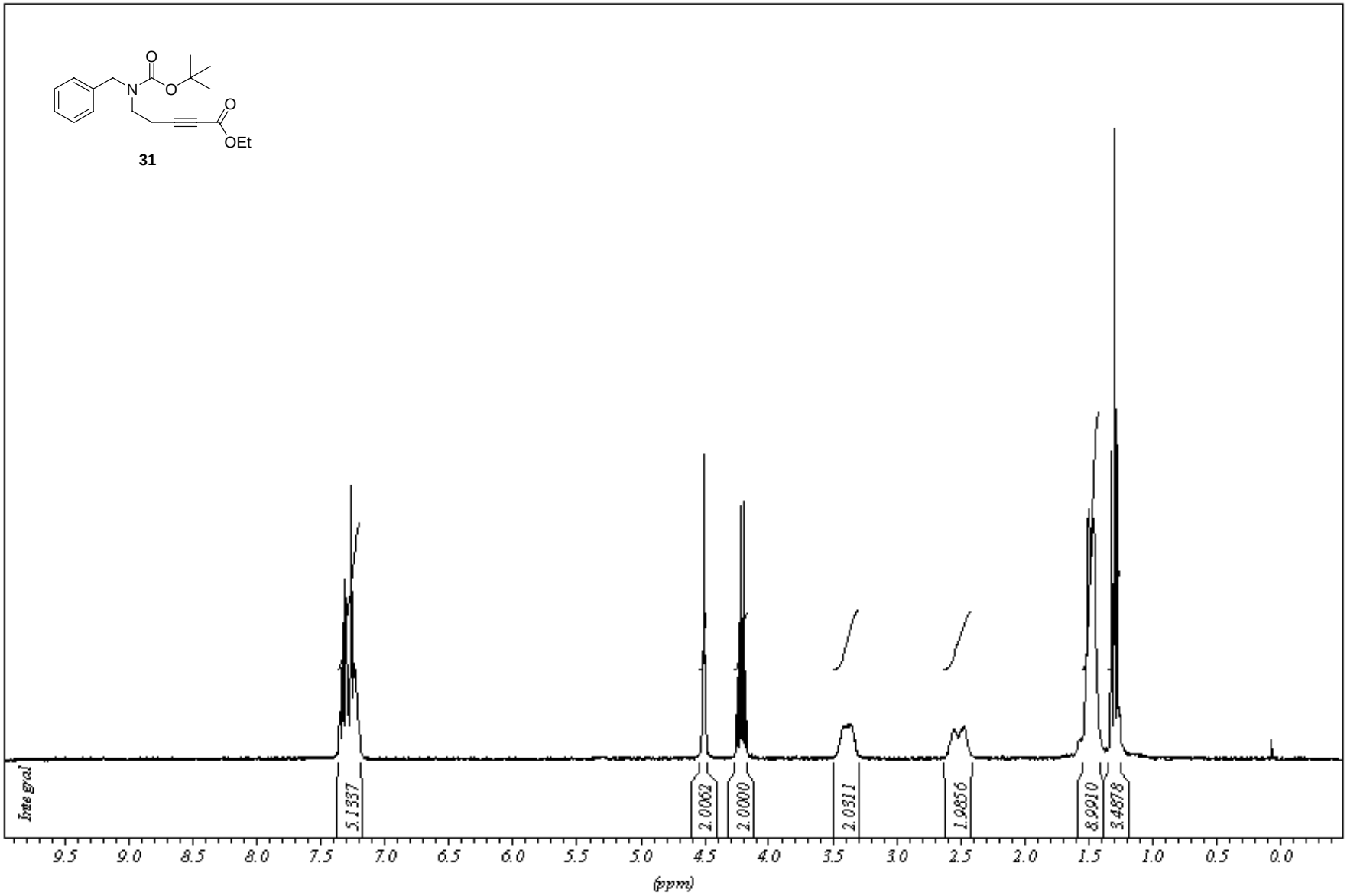

158.1704
154.2575
153.2684
134.5695
127.9110
114.1178
83.7675
81.2002
75.3818
61.9849
55.3955
31.5546
28.2090
13.9612
7
200
180
160
140
120
100
80
60
40
20
0
(ppm)

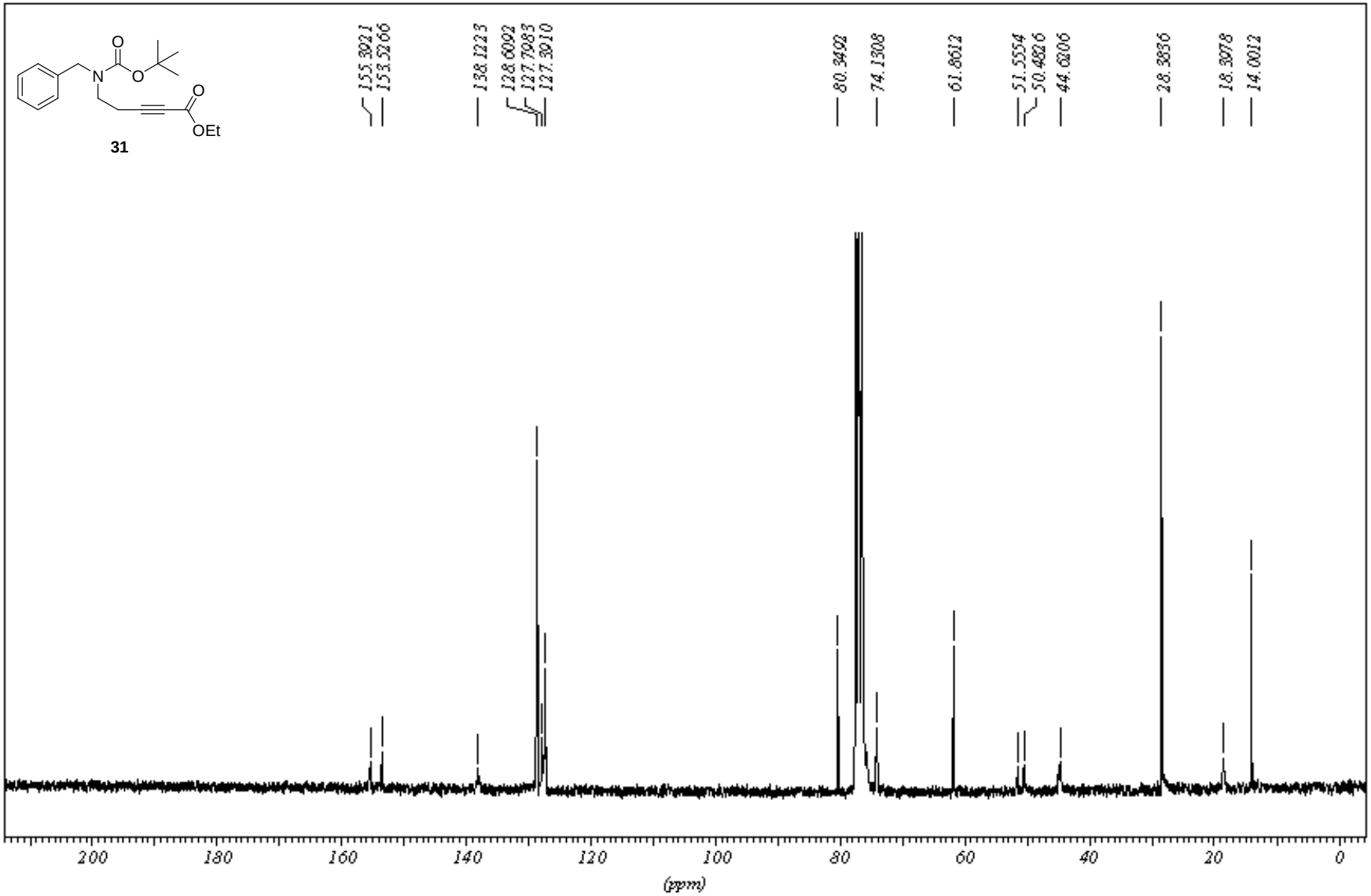

O
O
N
29
Integral
4.7967
1.8565
1.8883
2.0287
1.0000
8.7400
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


29
155.1957
138.0241
128.3147
127.4746
127.0310
84.8330
79.7165
69.4324
51.1336
50.2753
28.1618
27.1545
200
180
160
140
120
100
80
60
40
20
0
(ppm)


O
O
N
O
33
Integral
1.5099
1.4069
2.3056
1.8149
1.7266
0.7924
9.3316
9.5
9.0
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)


33
157.8176
154.7339
134.7586
128.4129
114.0414
81.3783
79.9783
69.6070
55.2755
48.7880
28.1945
22.5434
200
180
160
140
120
100
80
60
40
20
0
(ppm)


O
N
O
O
OEt
31
Integral
5.1337
2.0062
2.0000
2.0311
1.9856
8.9910
3.4878
9.5 9.0 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)


31
155.3921
153.5266
138.1223
128.6092
127.7983
127.3910
80.3492
74.1308
61.8612
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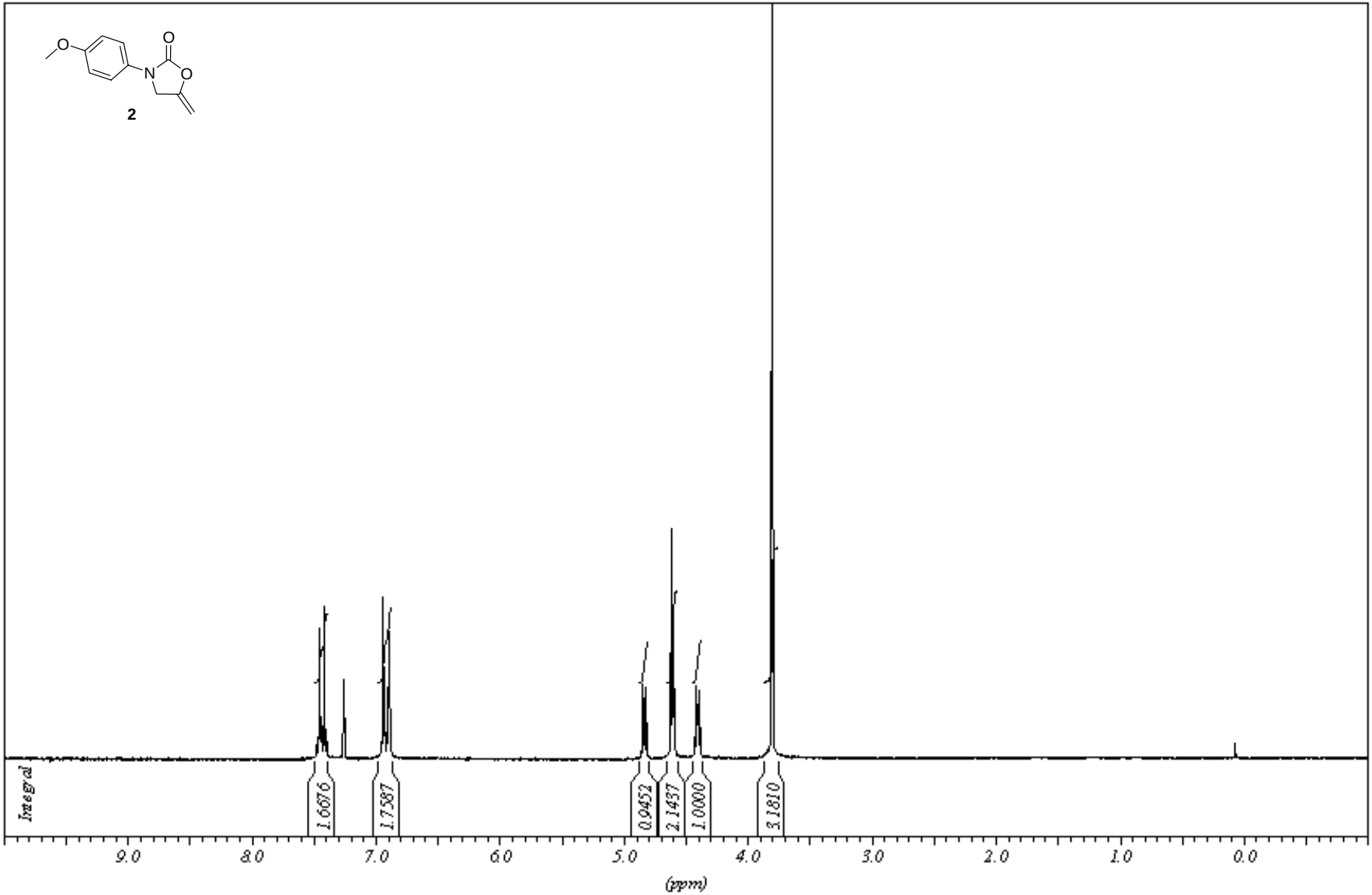
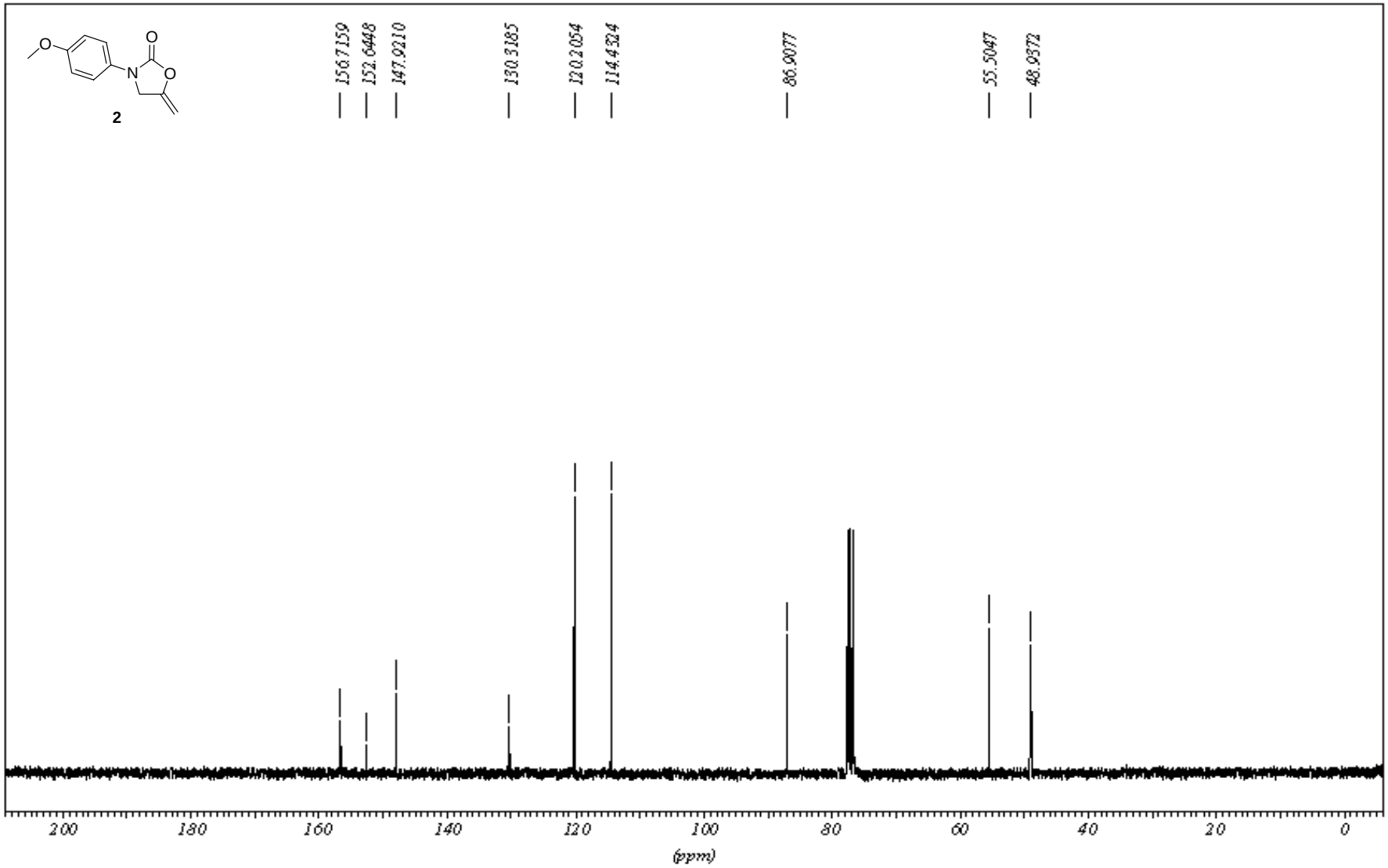
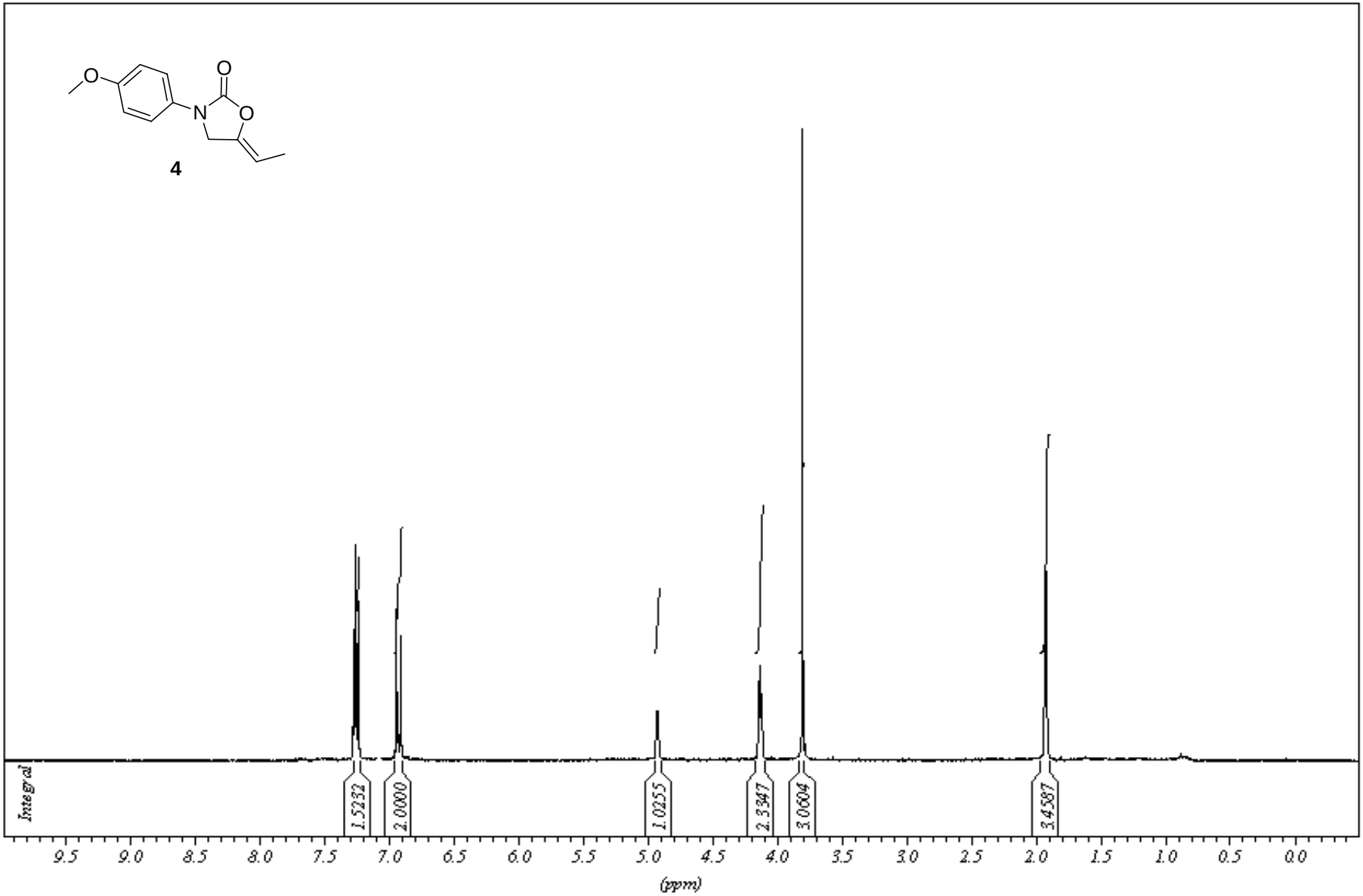
50.4826
44.6206
28.3836
18.3978
14.0012
200
180
160
140
120
100
80
60
40
20
0
(ppm)


O
O
N
O
2
Integral
1.6676
1.7587
0.9452
2.1437
1.0000
3.1810
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


2
156.7159
152.6448
147.9210
130.3185
120.2054
114.4324
86.9077
55.5047
48.9372
200
180
160
140
120
100
80
60
40
20
0
(ppm)


O
O
N
O
4
Integral
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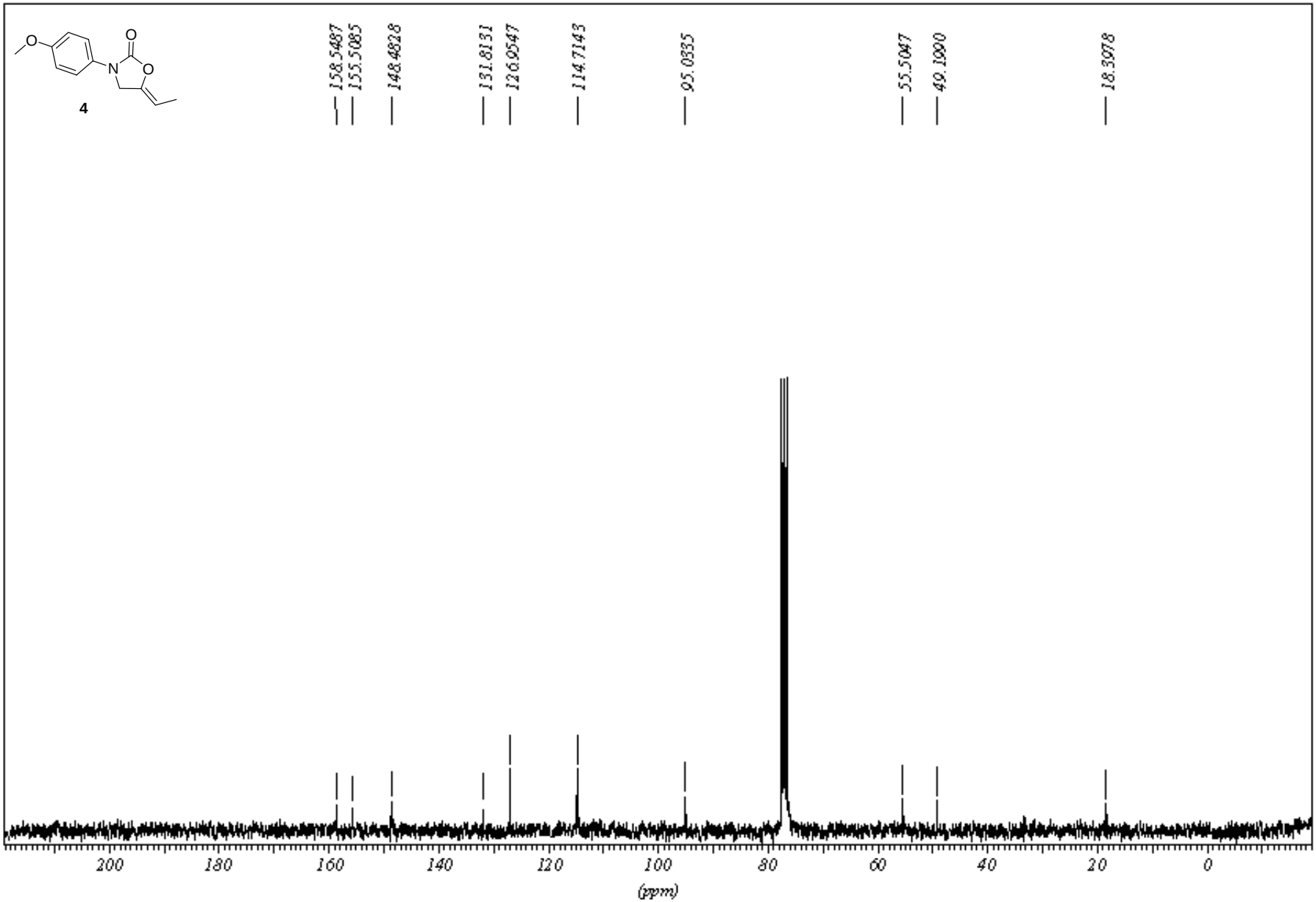
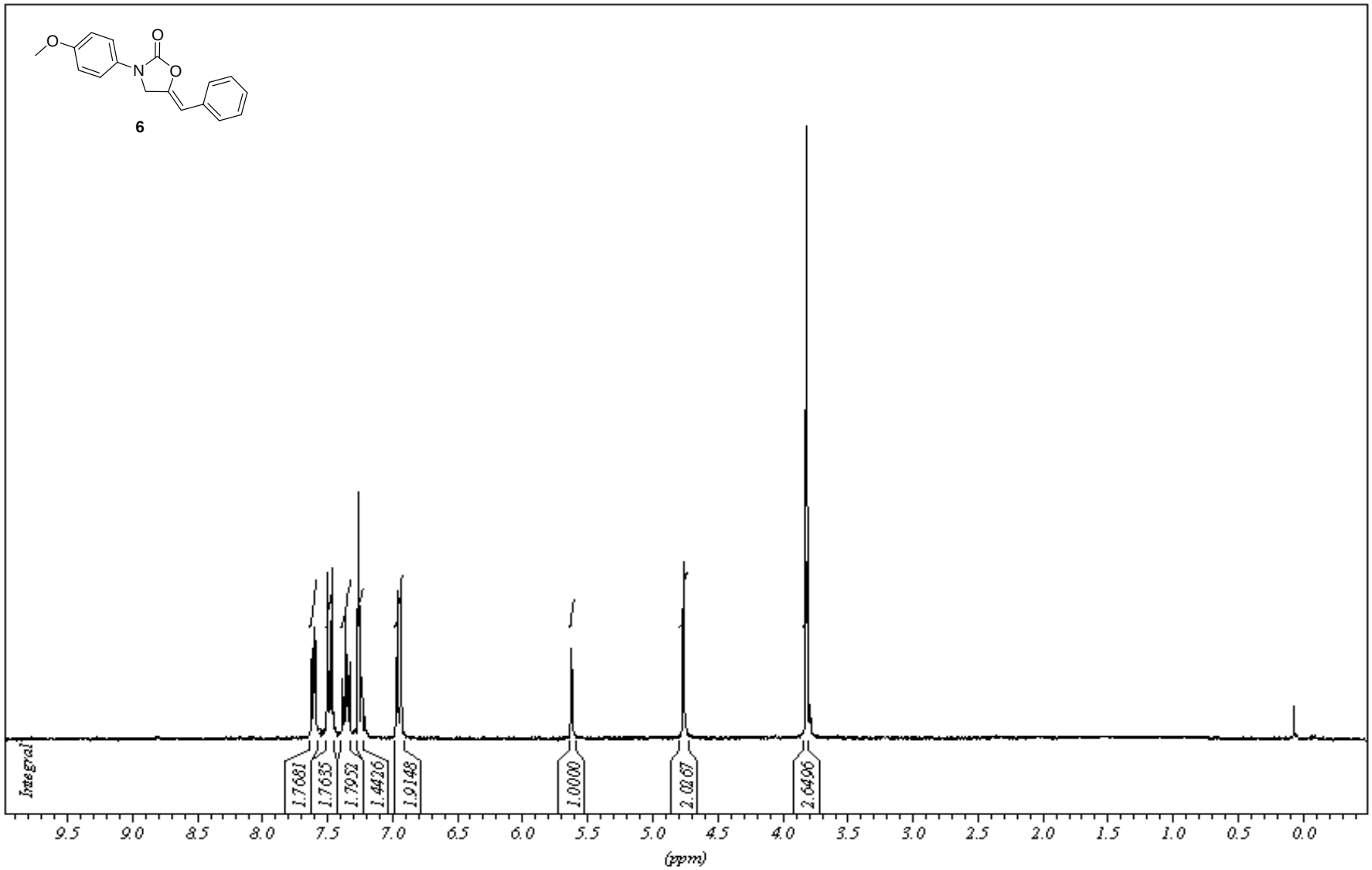
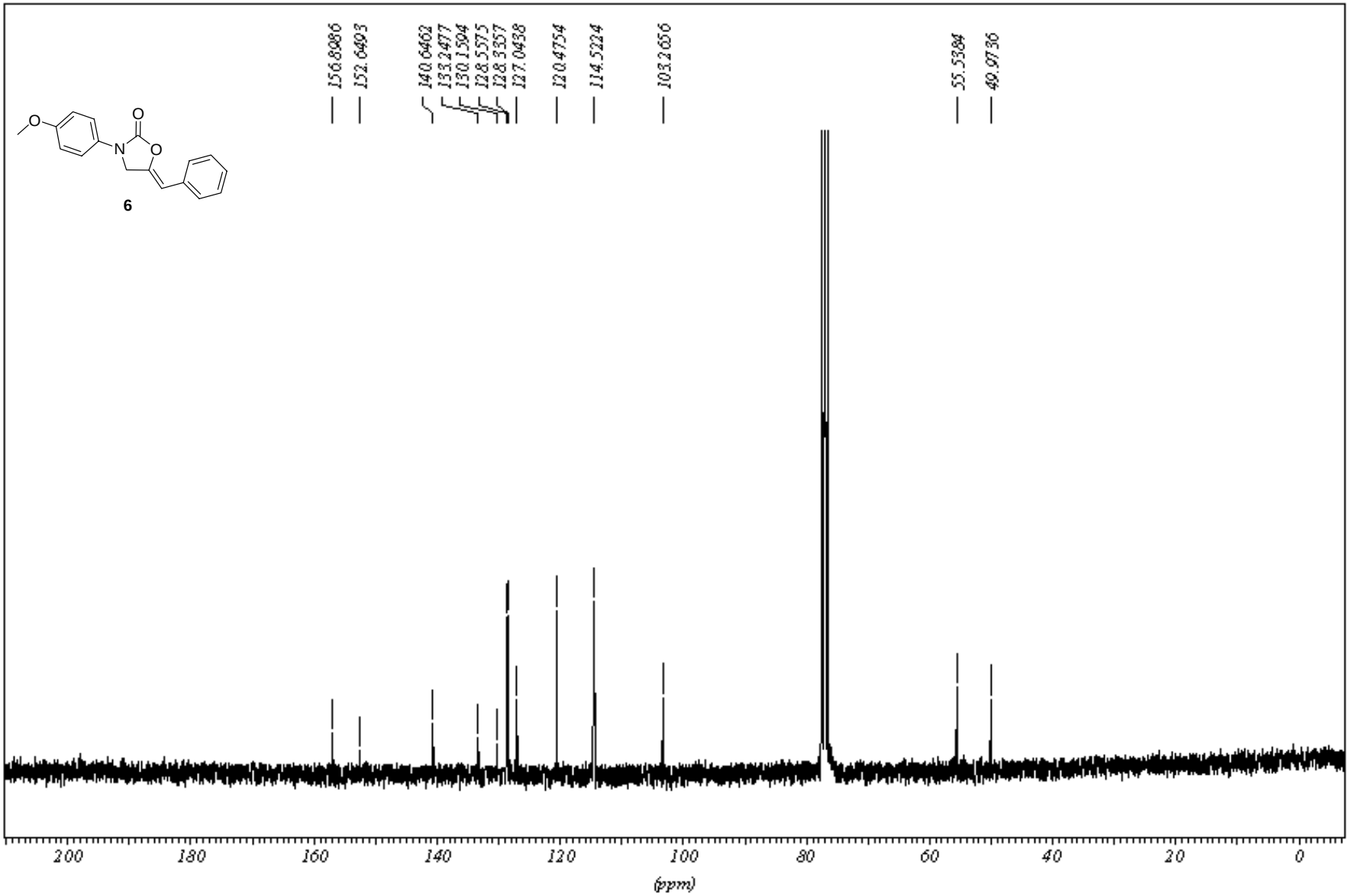
2.0000
1.0255
2.3347
3.0604
3.4587
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


4
158.5487
155.5085
148.4828
131.8131
126.9547
114.7143
95.0335
55.5047
49.1990
18.3978
200
180
160
140
120
100
80
60
40
20
0
(ppm)


O
O
N
O
6
Integral
1.7681
1.7635
1.7952
1.4426
1.9148
1.0000
2.0267
2.6496
9.5
9.0
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)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140.6462
133.2477
130.1594
128.5575
128.3357
127.0438
120.4754
114.5224
103.2656
55.5384
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O
O
6
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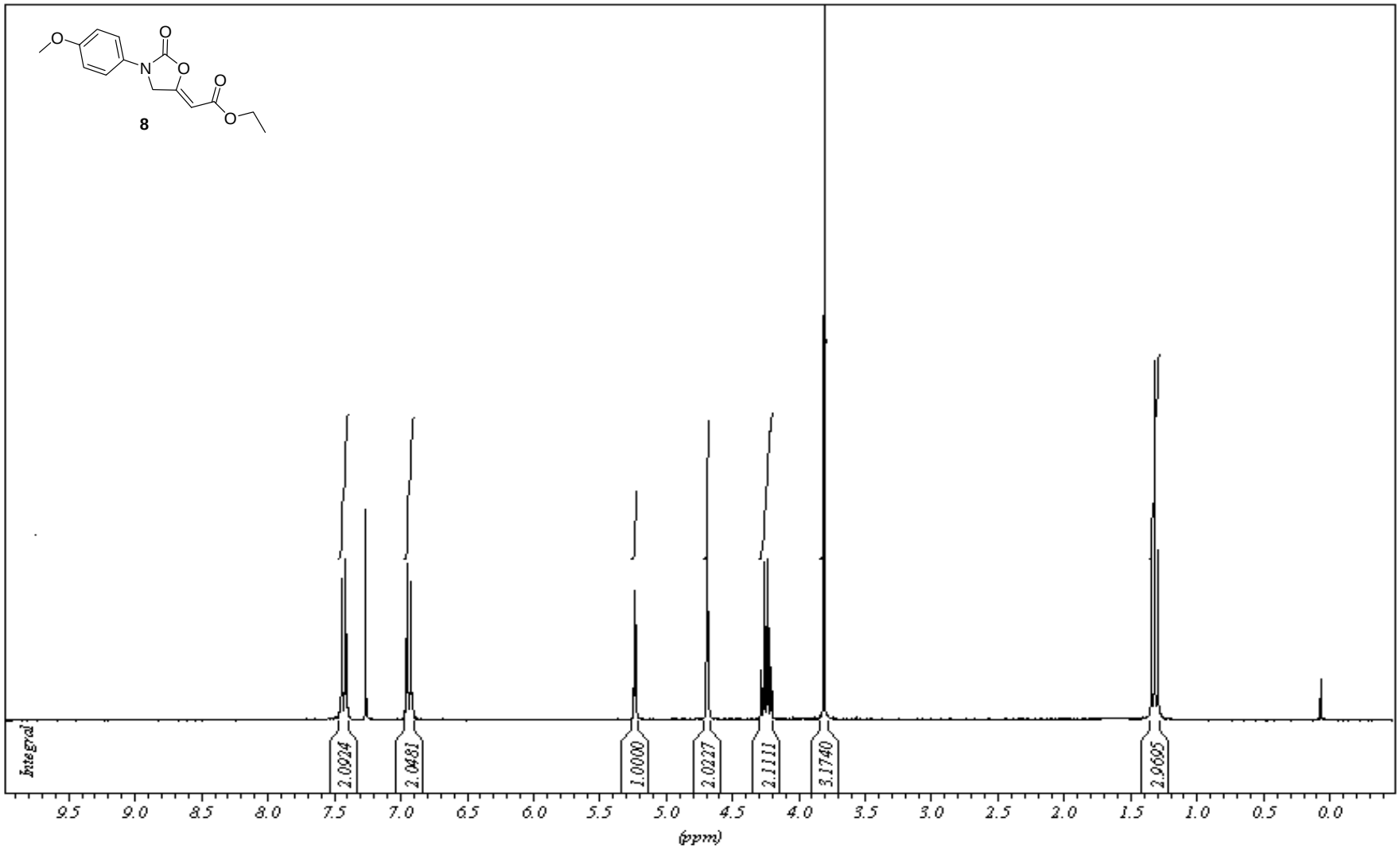
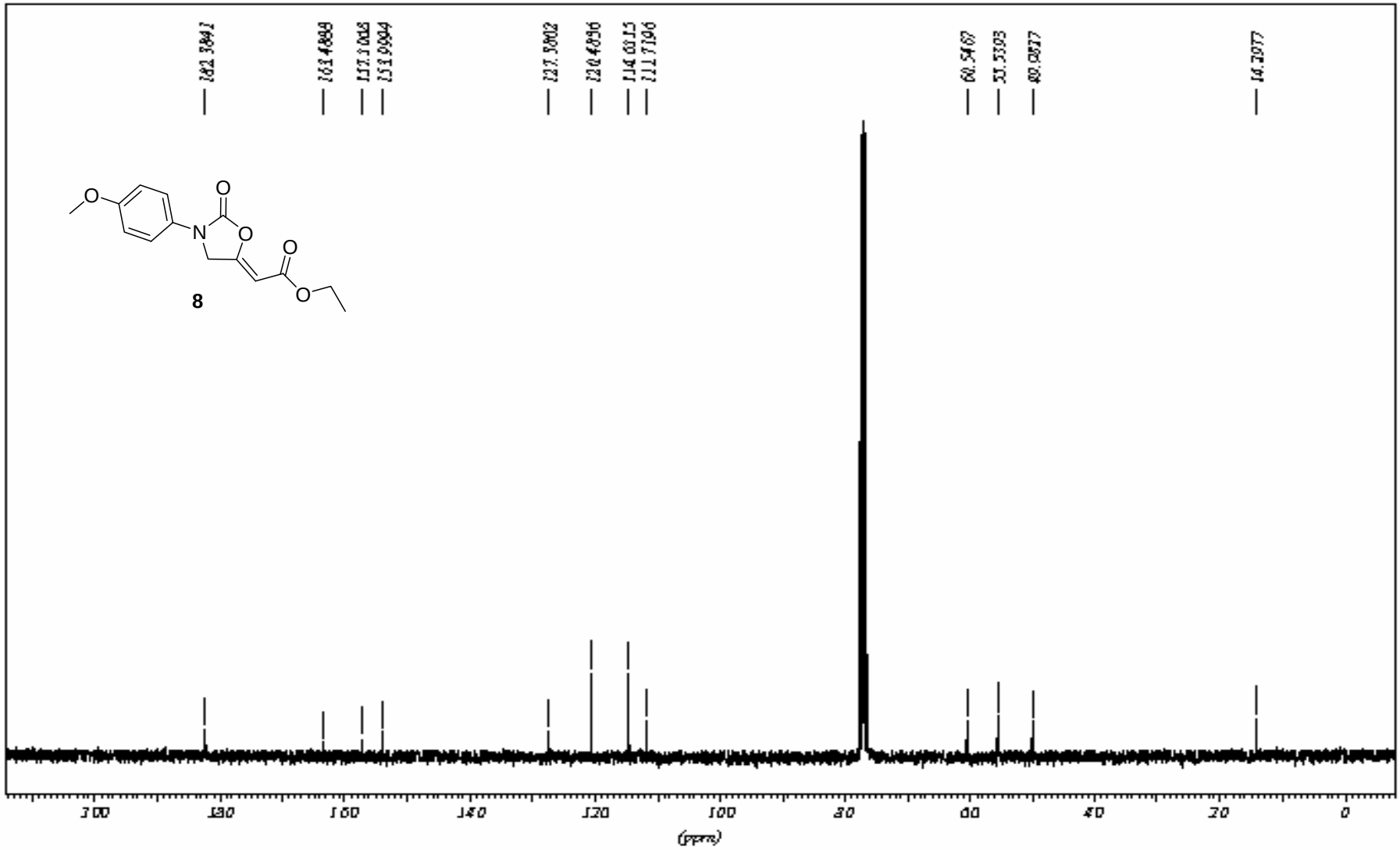
180
160
140
120
100
80
60
40
20
0
(ppm)


8
Integral
2.0924
2.0481
1.0000
2.0227
2.1111
3.1740
2.9605
9.5 9.0 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)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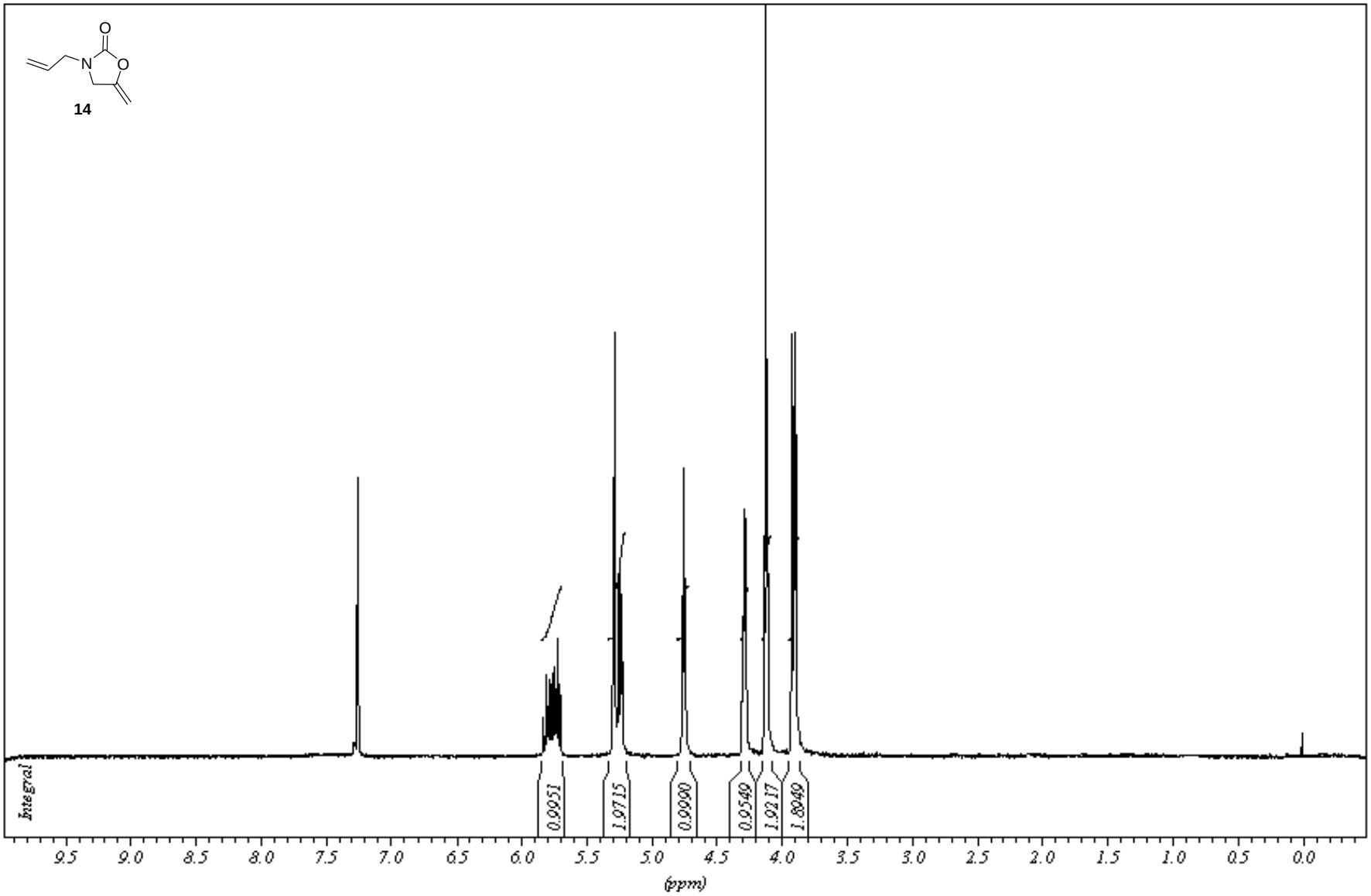
163.4888
157.5068
151.9994
127.3002
120.4096
114.0315
111.7196
60.5467
53.5393
42.0577
14.2077
O
O
N
O
O
O
8
180
160
140
120
100
80
60
40
20
0
(ppm)


O
N
O
14
Integral
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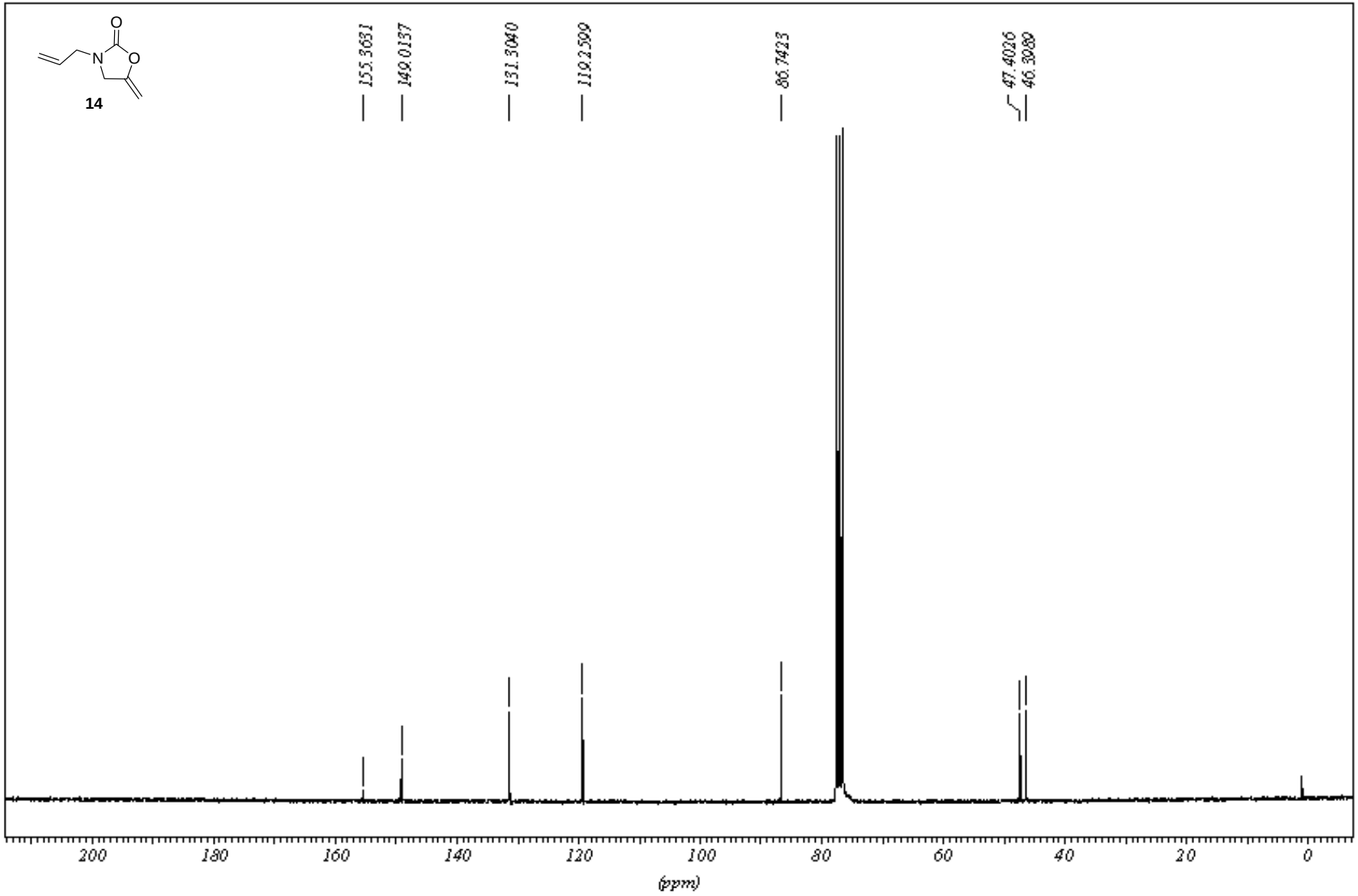
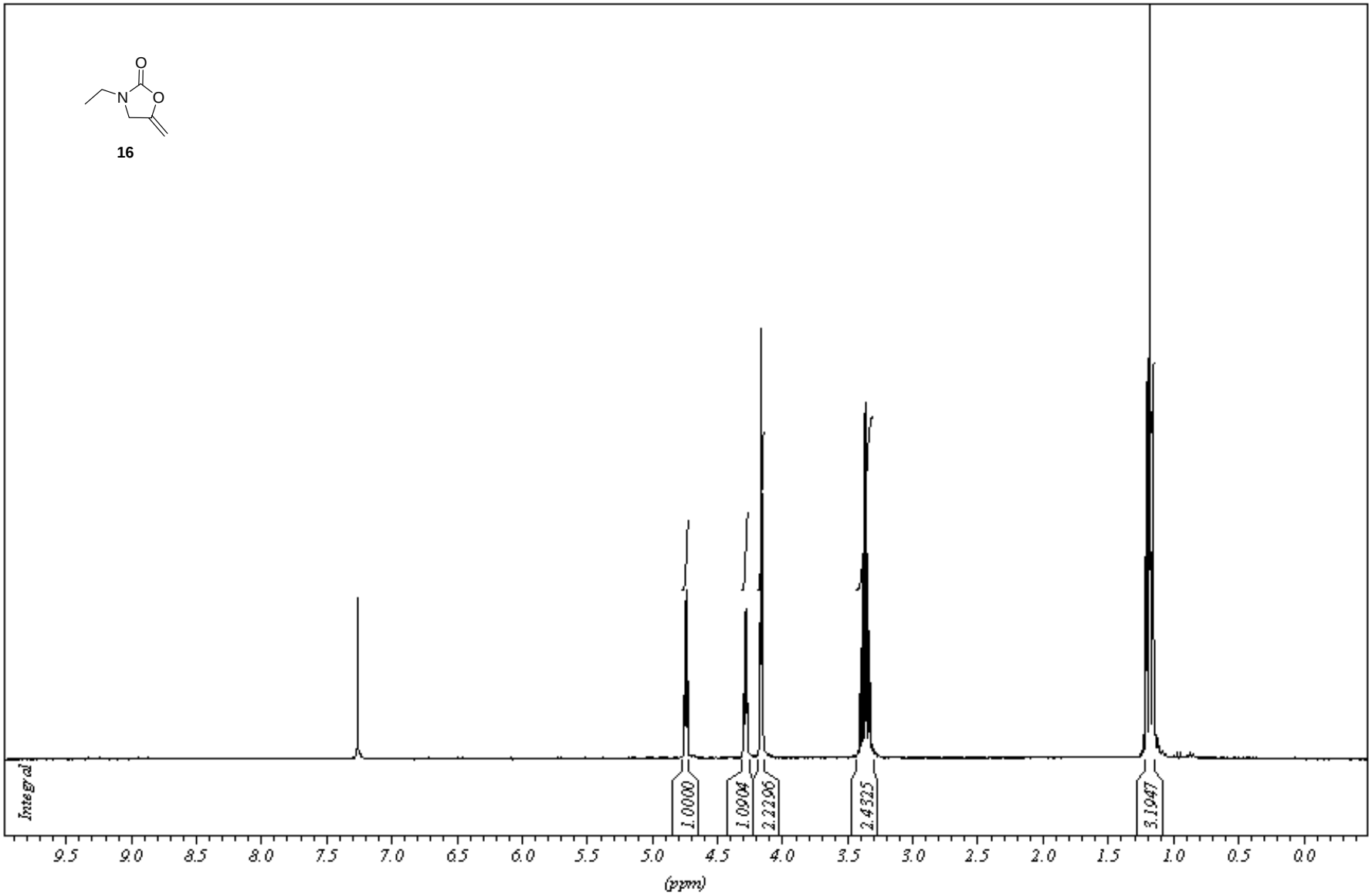
1.9715
0.9990
0.9549
1.9217
1.8949
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


14
155.3631
149.0137
131.3040
119.2599
86.7423
47.4026
46.3989
200
180
160
140
120
100
80
60
40
20
0
(ppm)


O
N
O
16
Integral
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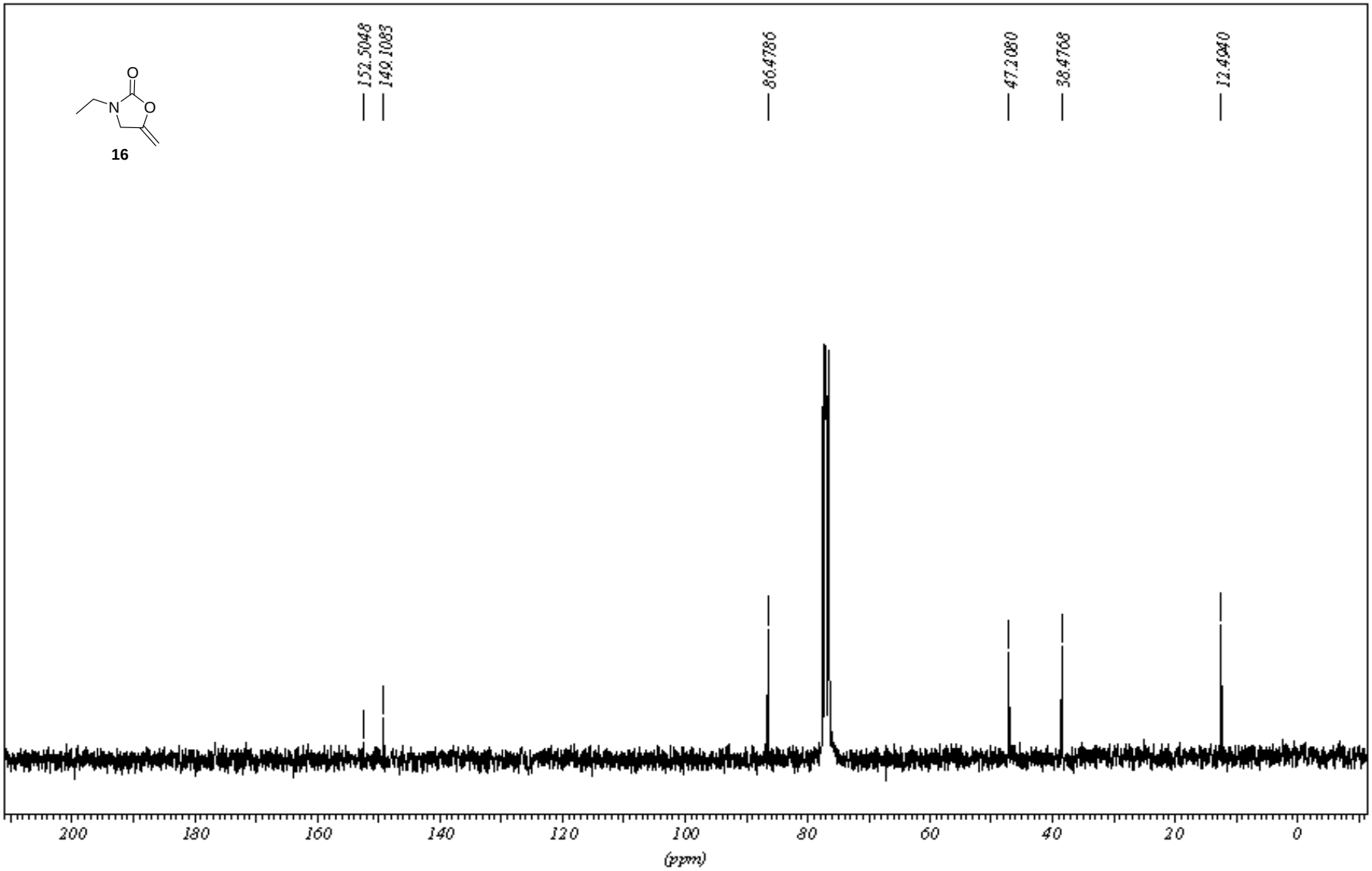
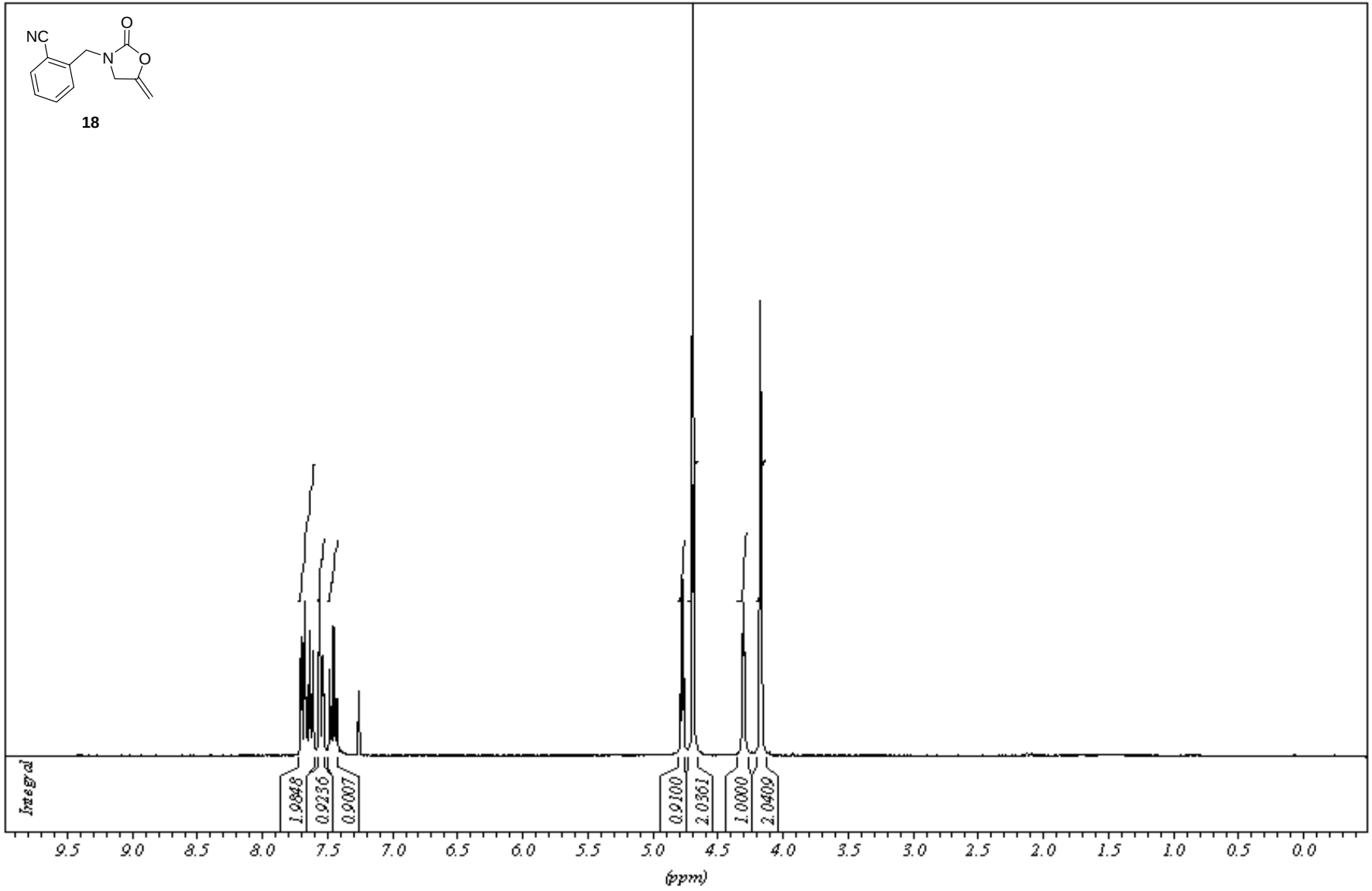
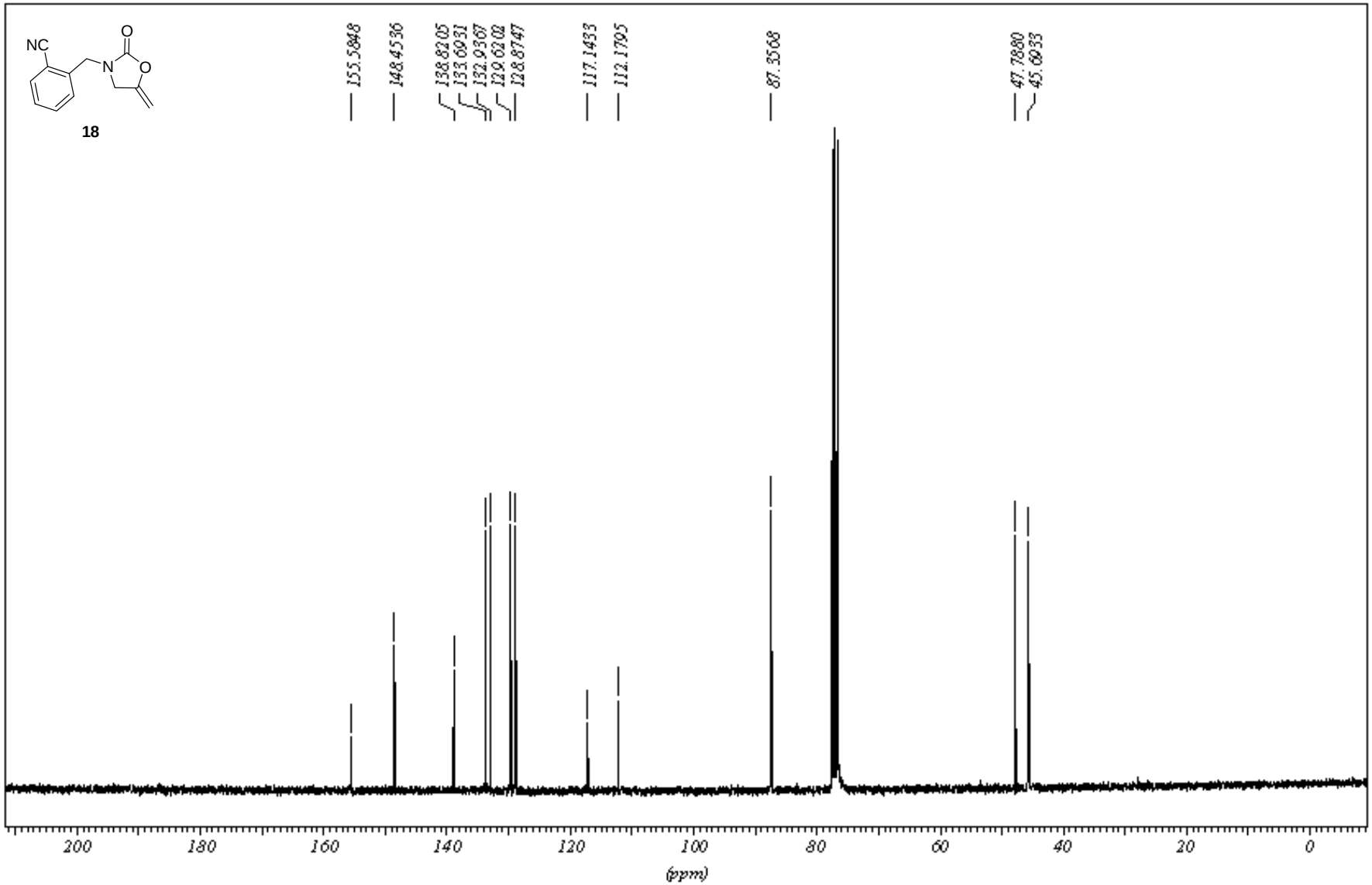
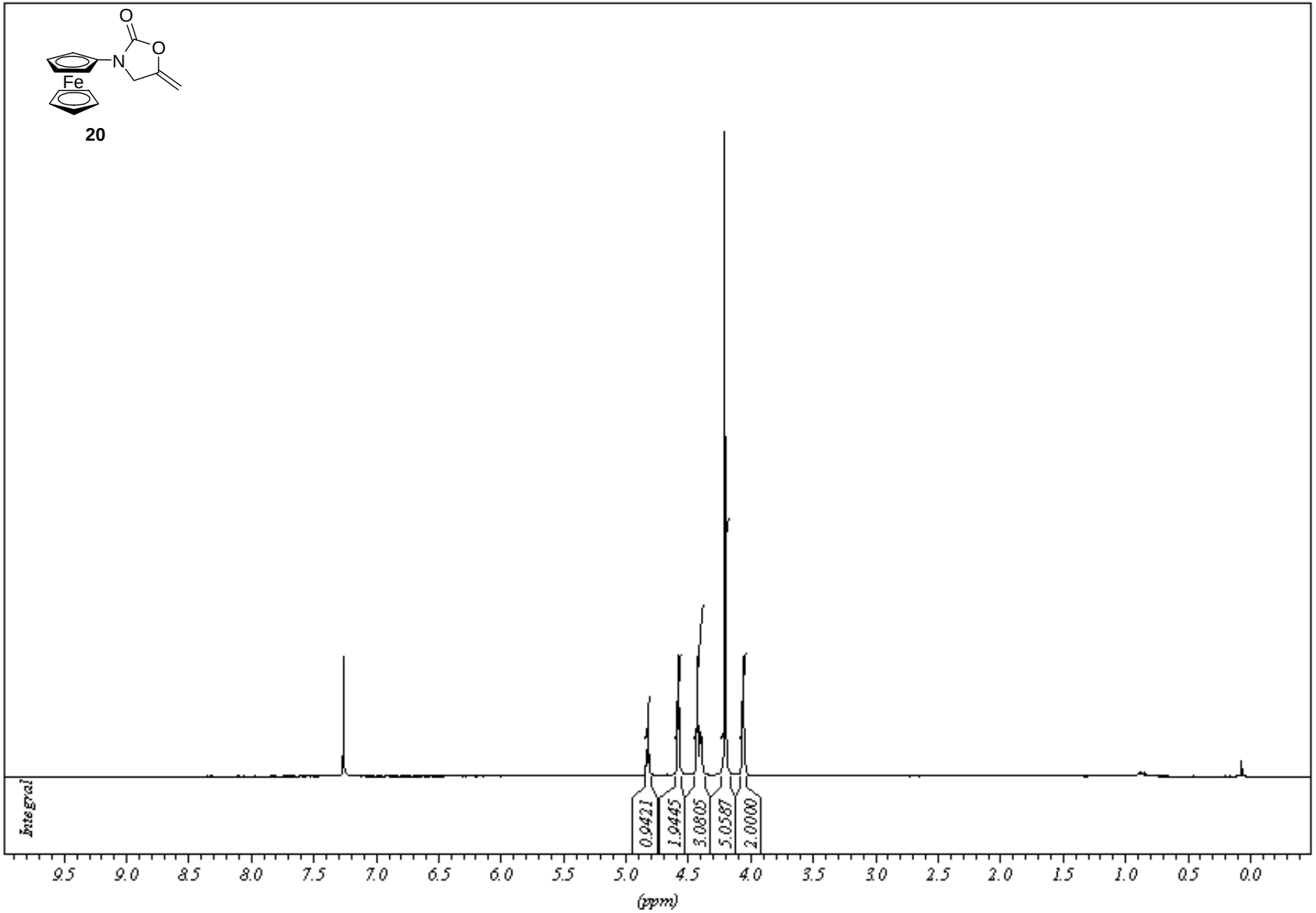
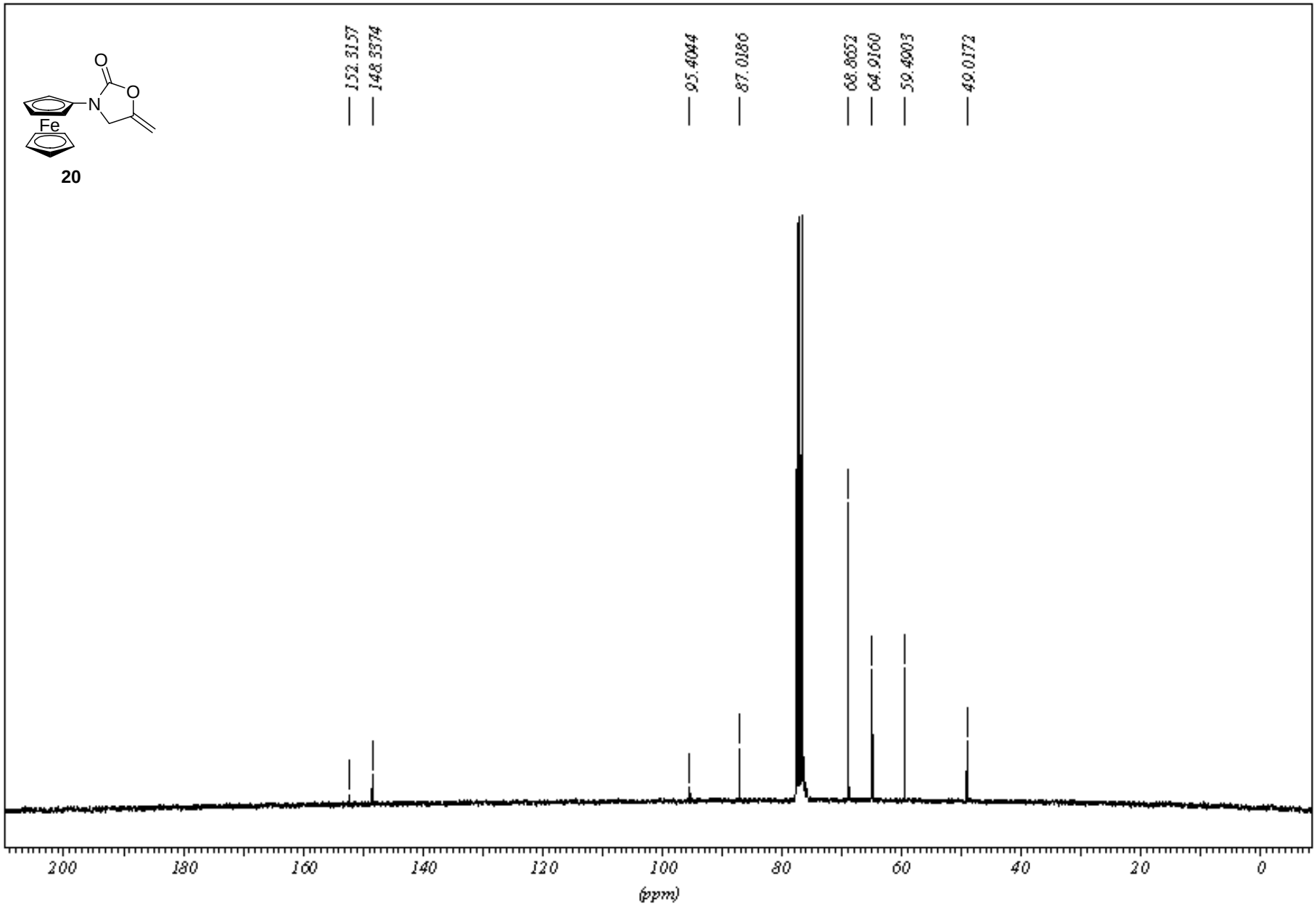
1.0904
2.2296
2.4325
3.1947
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

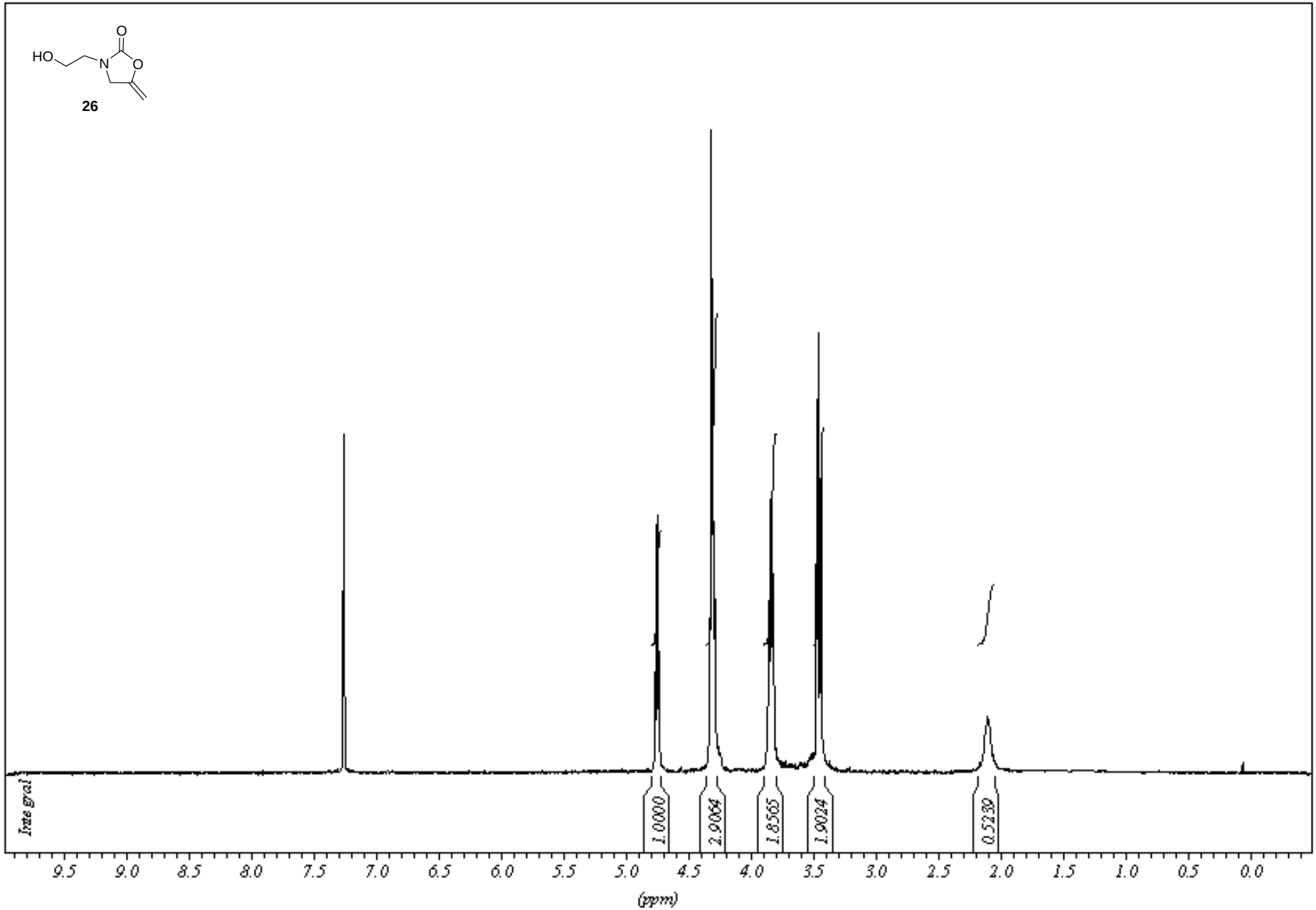

16
152.5048
149.1083
86.4786
47.2080
38.4768
12.4940
200
180
160
140
120
100
80
60
40
20
0
(ppm)

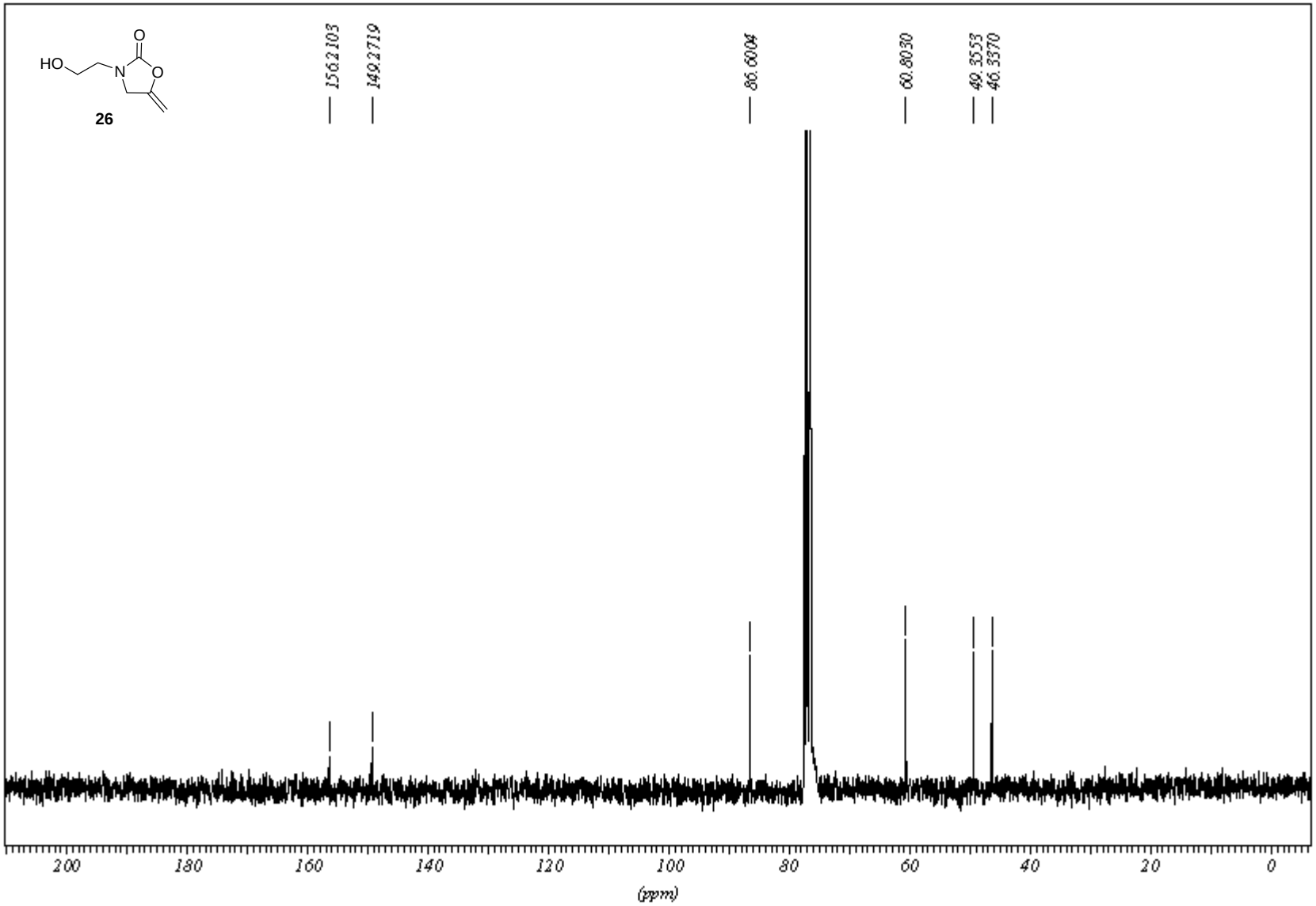

NC
O
N
O
18
Integral
1.9848
0.9236
0.9007
0.9100
2.0361
1.0000
2.0409
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

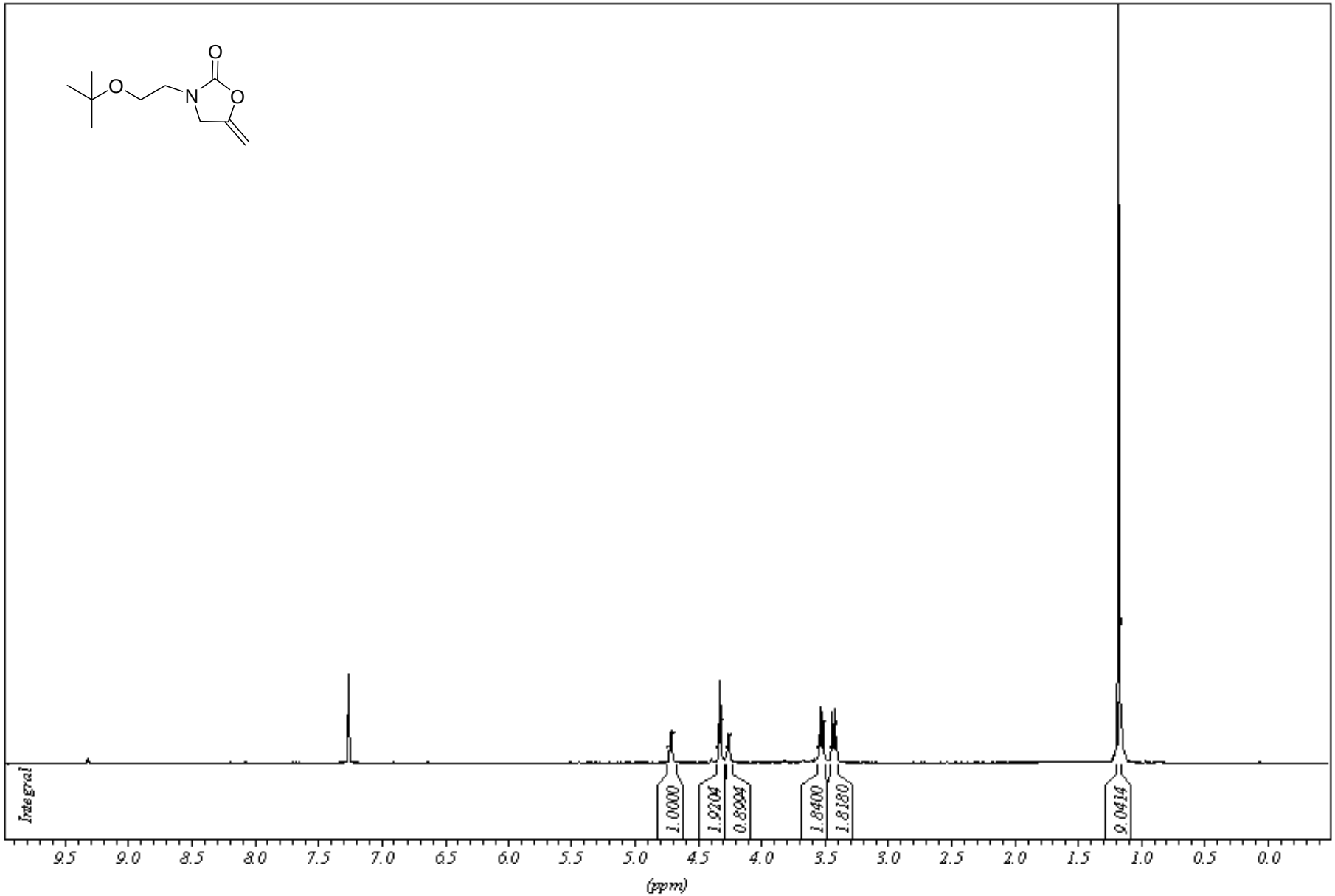

NC
O
N
O
18
155.5848
148.4536
138.8205
133.6931
132.9367
129.6202
128.8747
117.1433
112.1795
87.3568
47.7880
45.6933
200
180
160
140
120
100
80
60
40
20
0
(ppm)

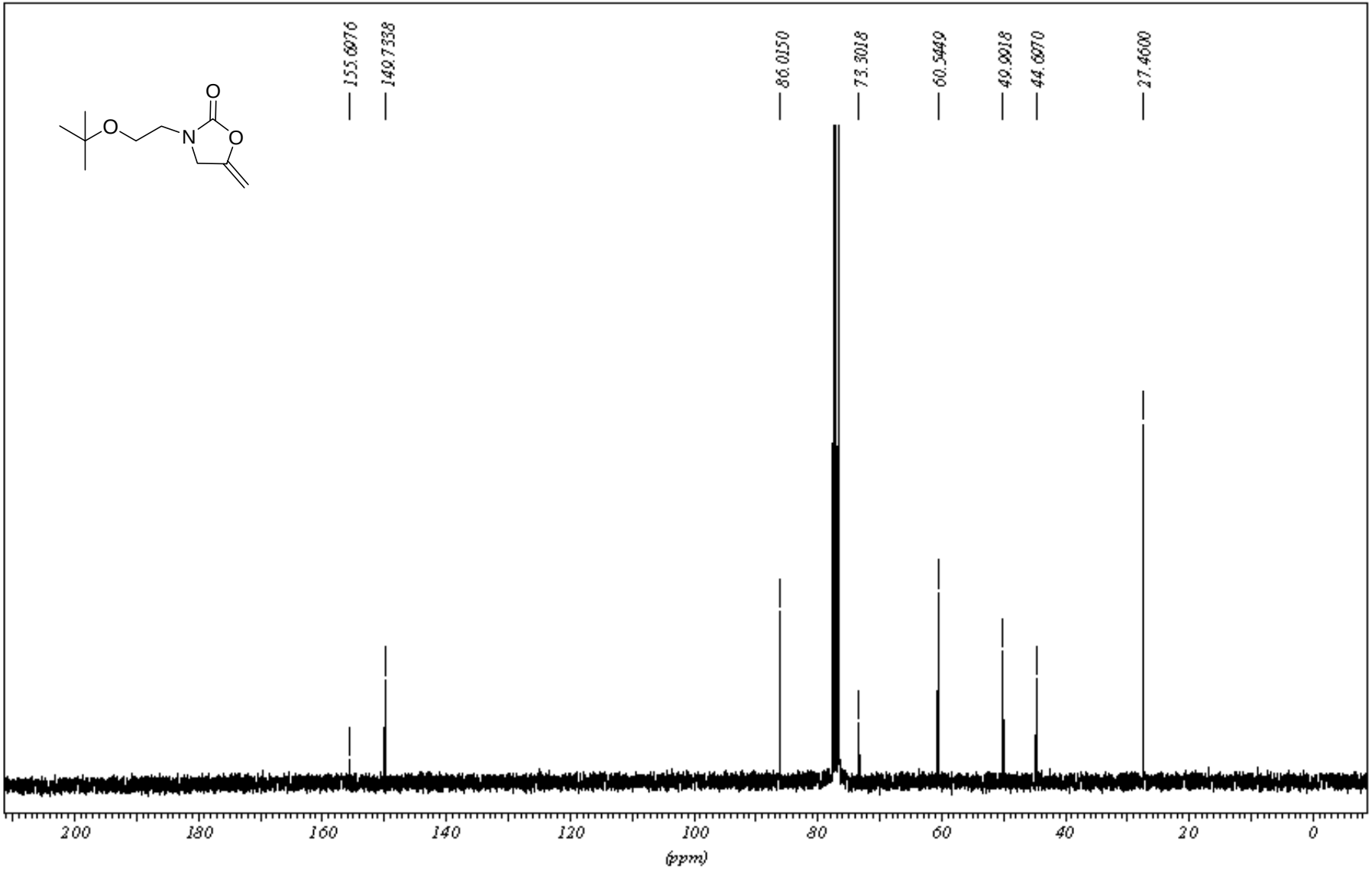

O
O
N
Fe
20
Integral
0.9421
1.9445
3.0805
5.0587
2.0000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

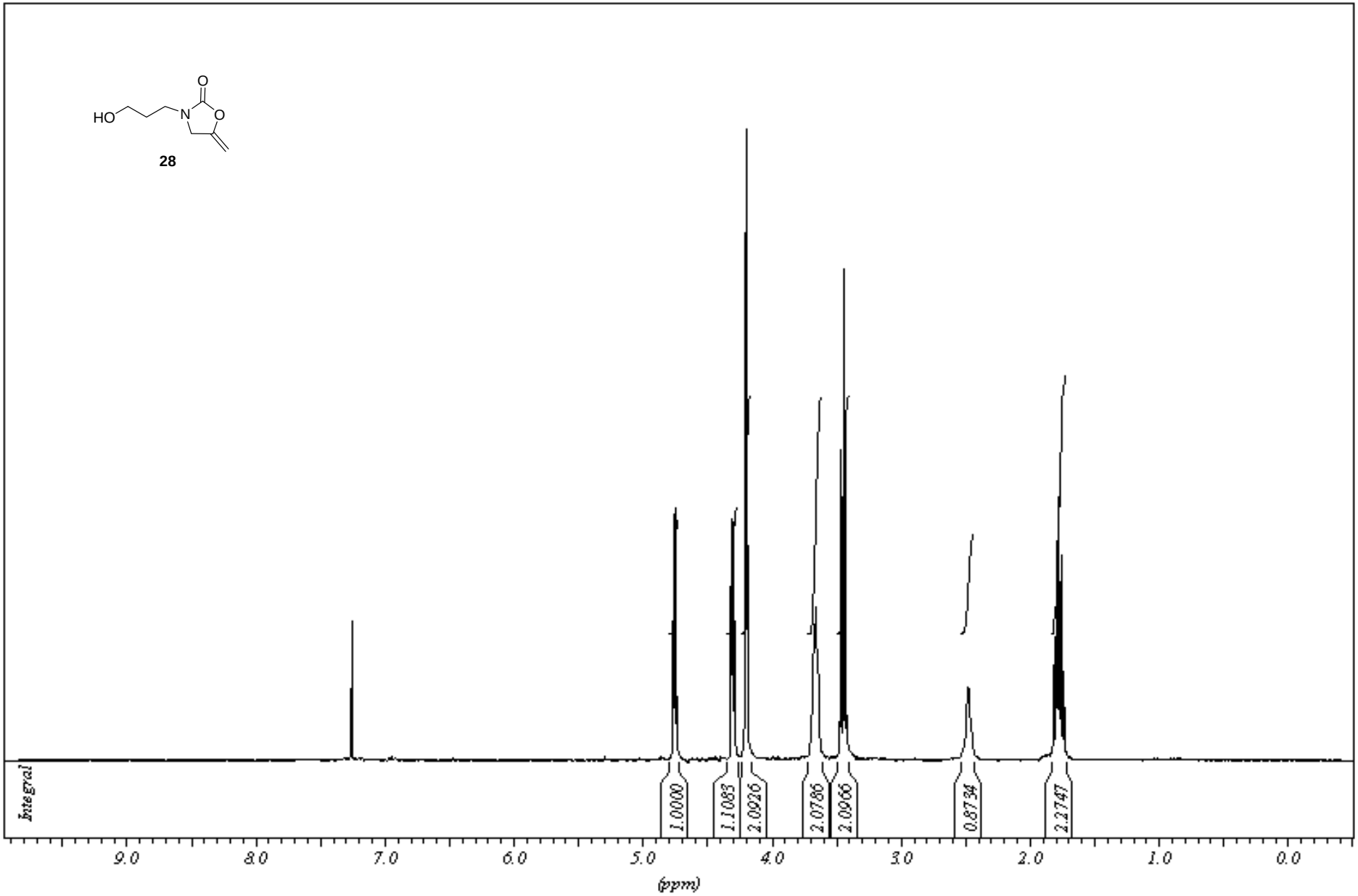

O
O
N
Fe
20
152.3157
148.3374
95.4044
87.0186
68.8652
64.9160
59.4903
49.0172
200
180
160
140
120
100
80
60
40
20
0
(ppm)

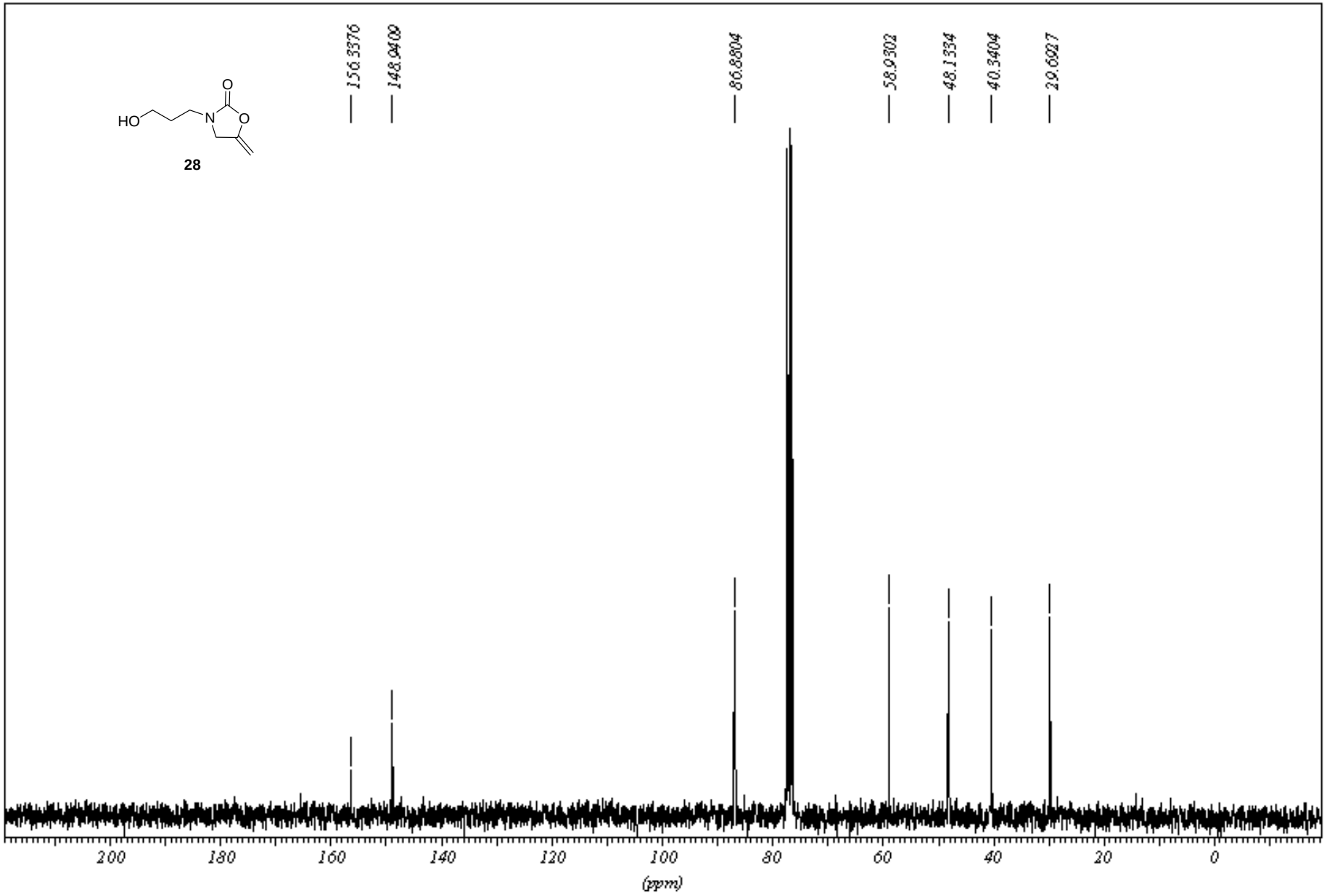

HO
N
O
O
26
Integral
1.0000
2.9064
1.8565
1.9024
0.5230
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

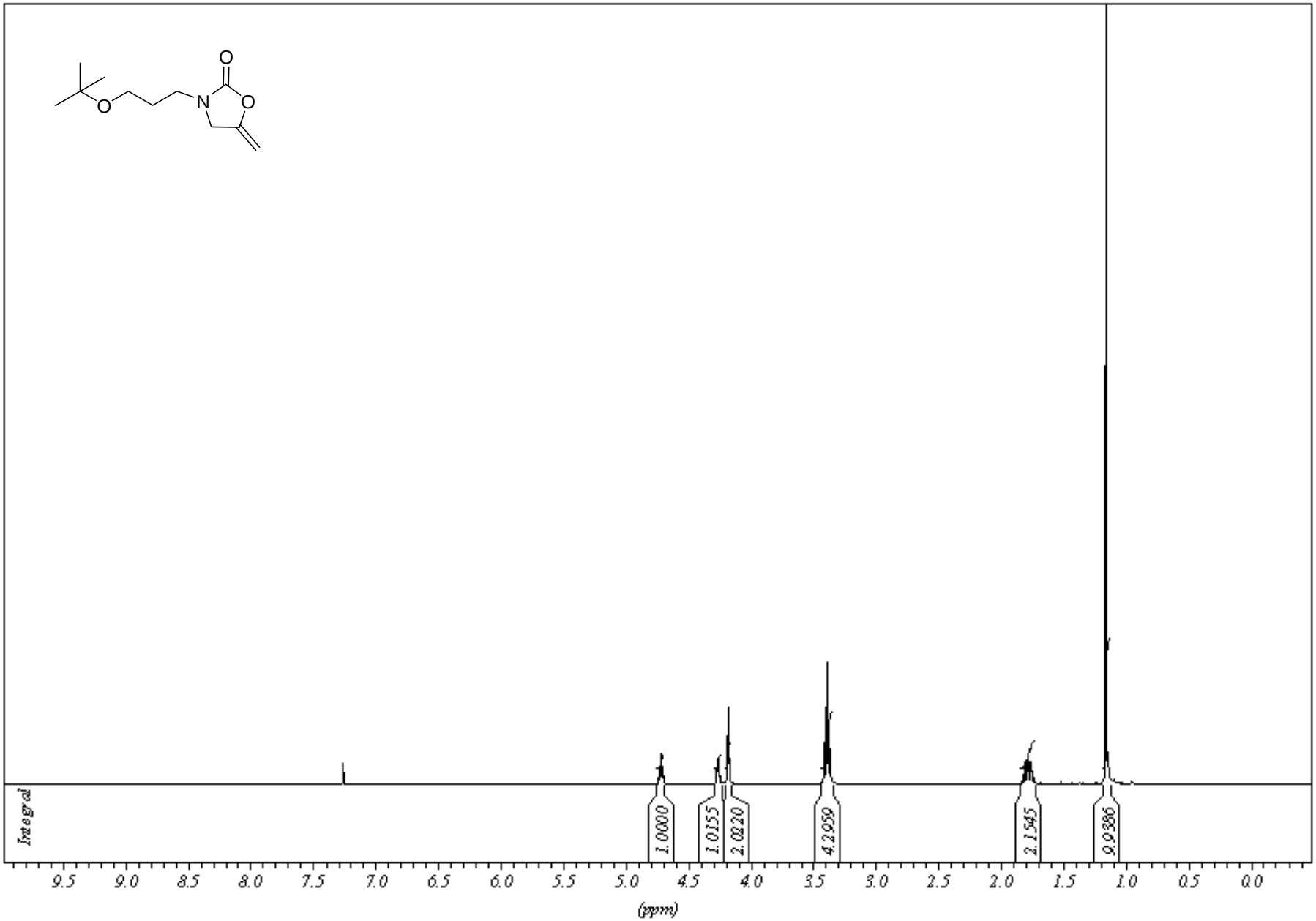

HO
N
O
O
26
156.2103
149.2719
86.6004
60.8030
49.3553
46.3370
200
180
160
140
120
100
80
60
40
20
0
(ppm)

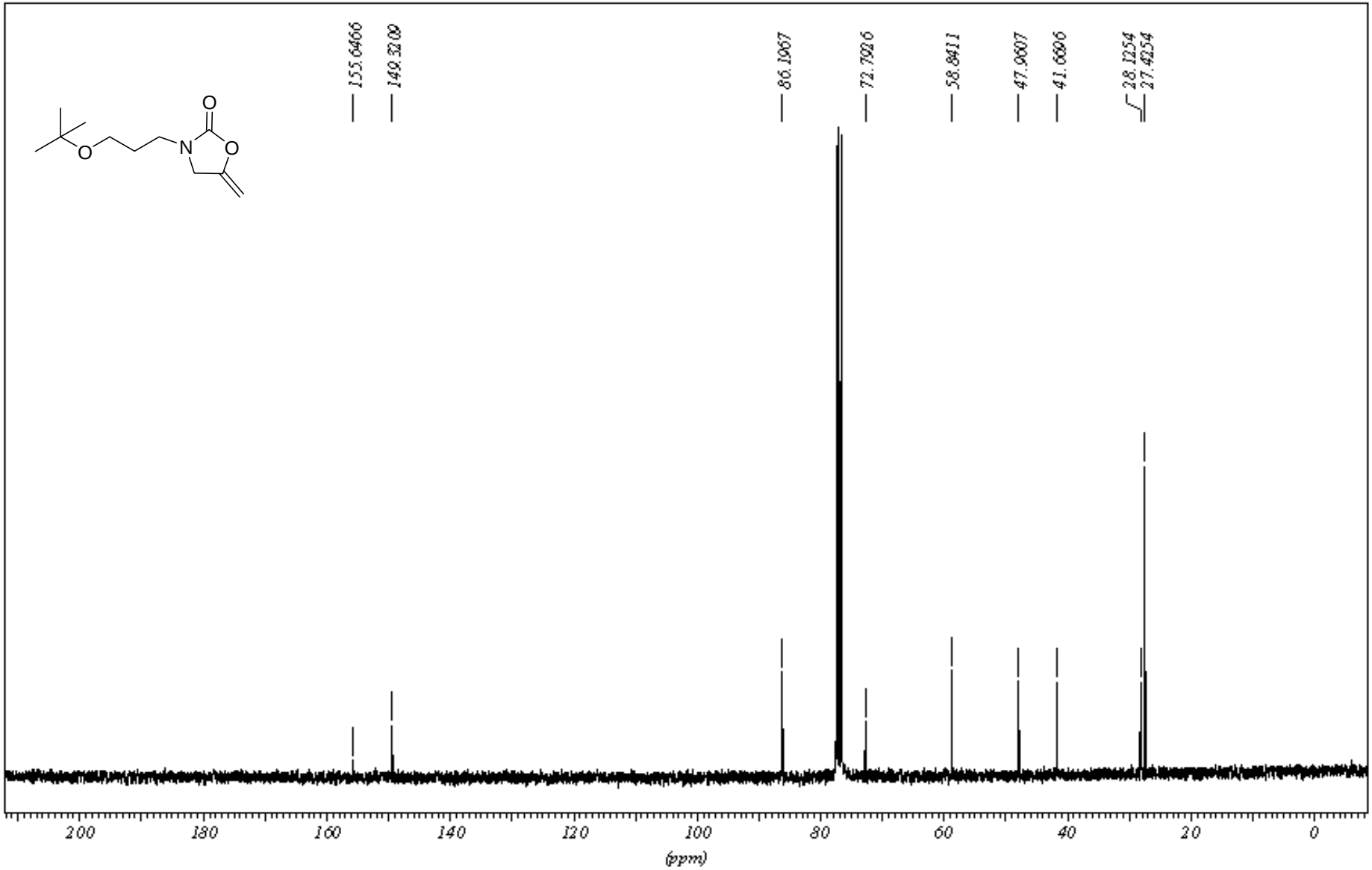

O
O
N
O
Integral
1.0000
1.9204
0.8904
1.8400
1.8180
9.0414
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

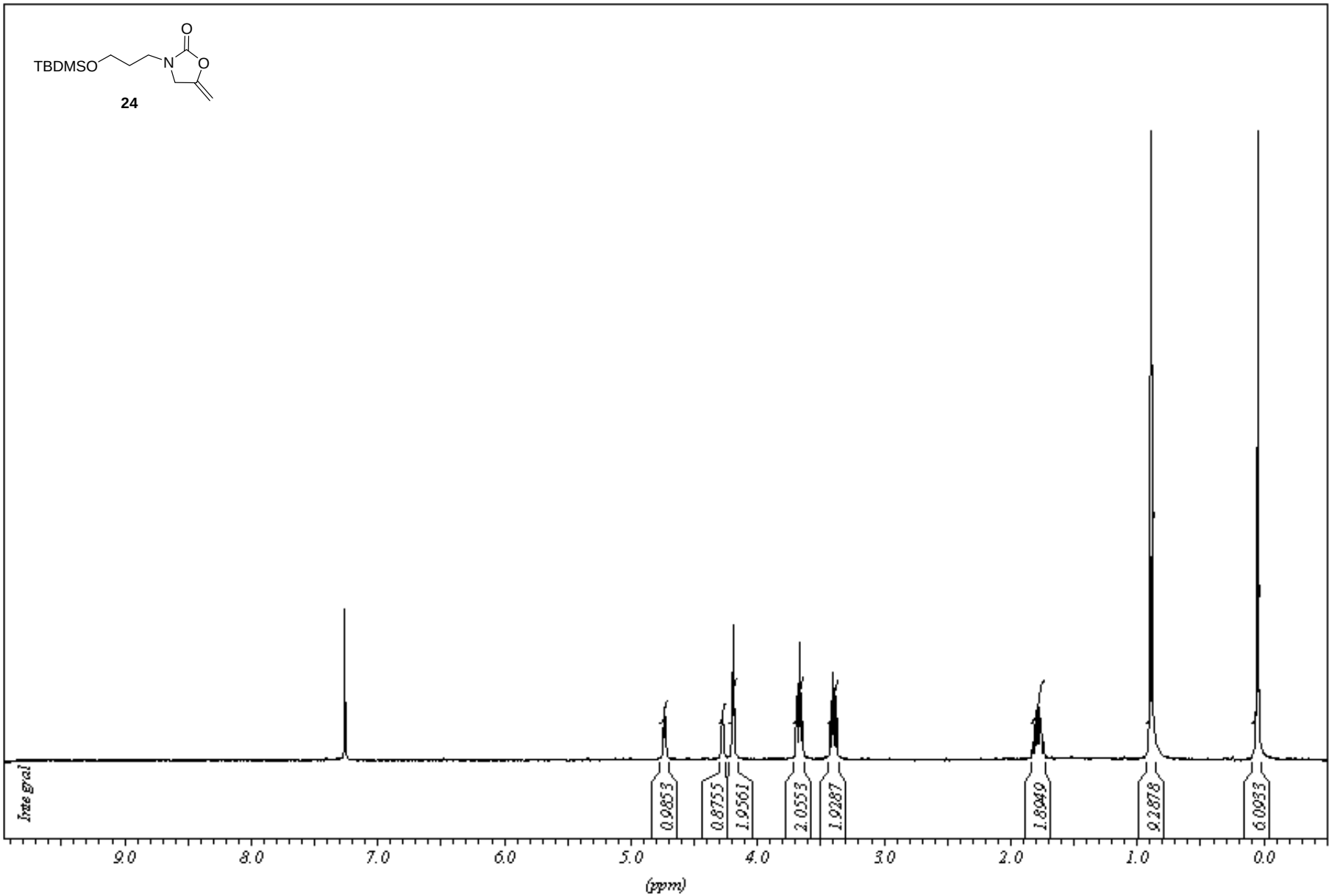

155.6976
149.7338
86.0150
73.3018
60.5449
49.9918
44.6970
27.4600
O
O
N
O
200
180
160
140
120
100
80
60
40
20
0
(ppm)

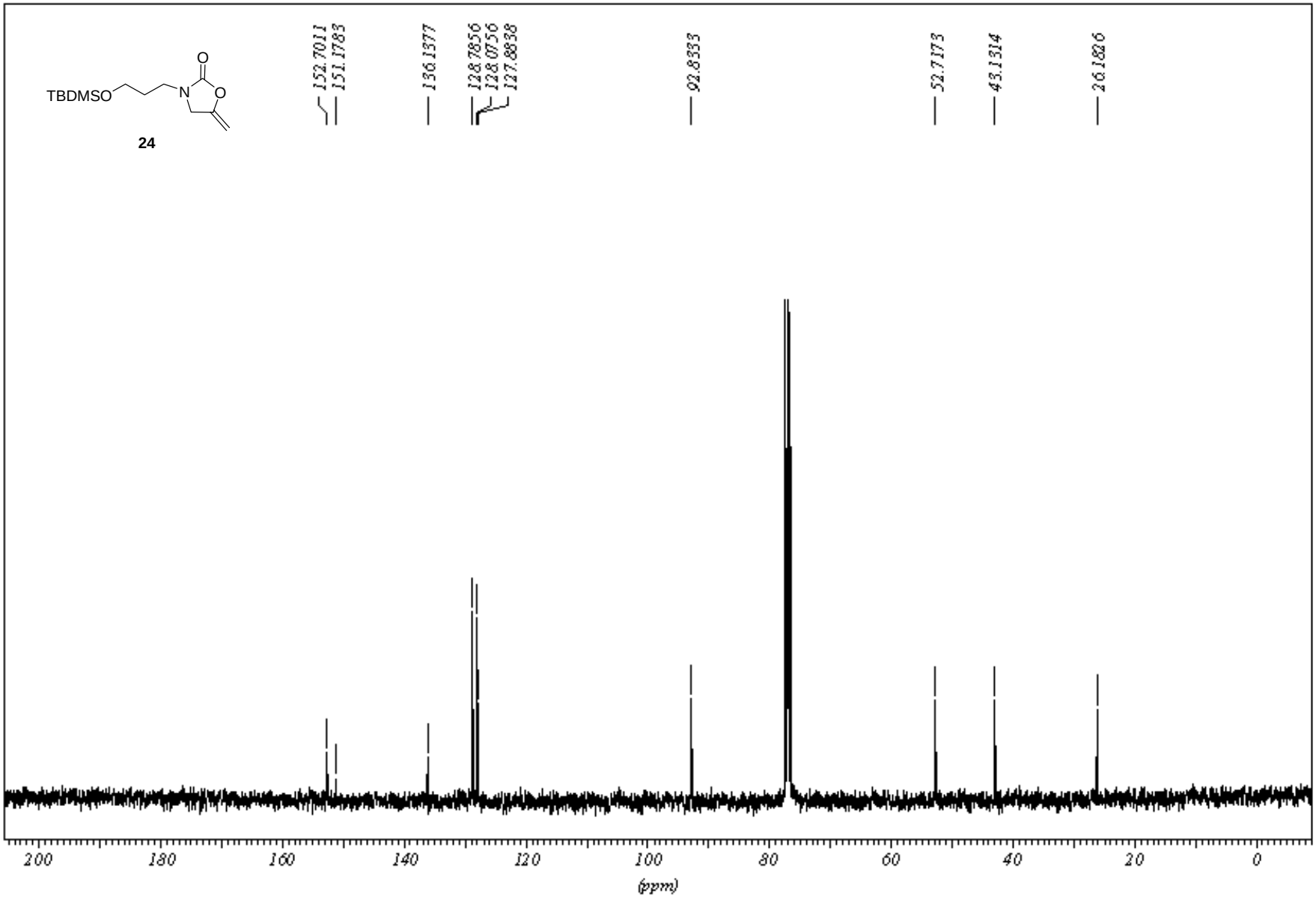

HO
N
O
O
28
Integral
1.0000
1.1083
2.0926
2.0786
2.0966
0.8734
2.2747
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

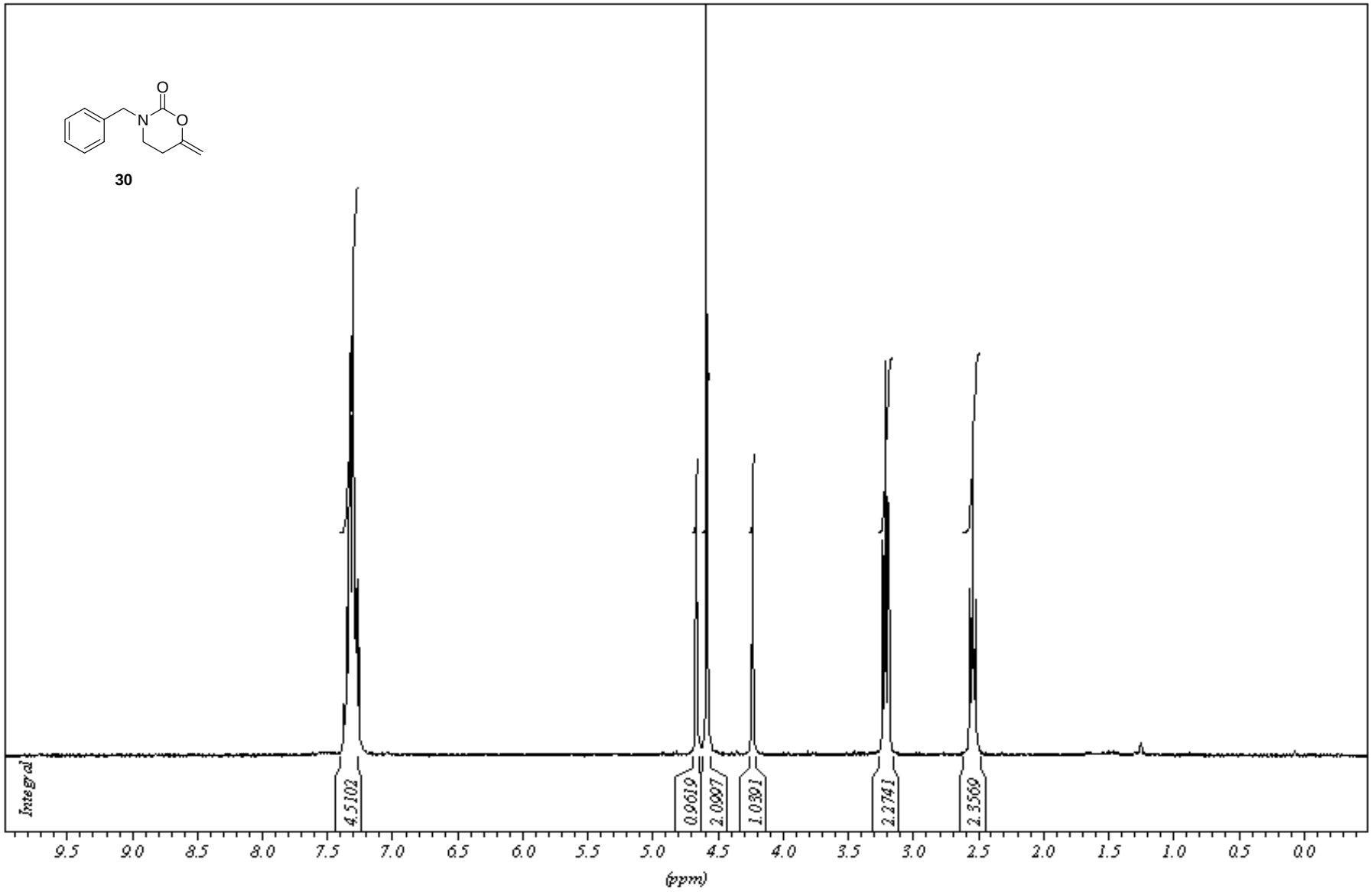

156.3376
148.9409
86.8804
58.9302
48.1334
40.3404
29.6927
HO
N
O
O
28
200
180
160
140
120
100
80
60
40
20
0
(ppm)

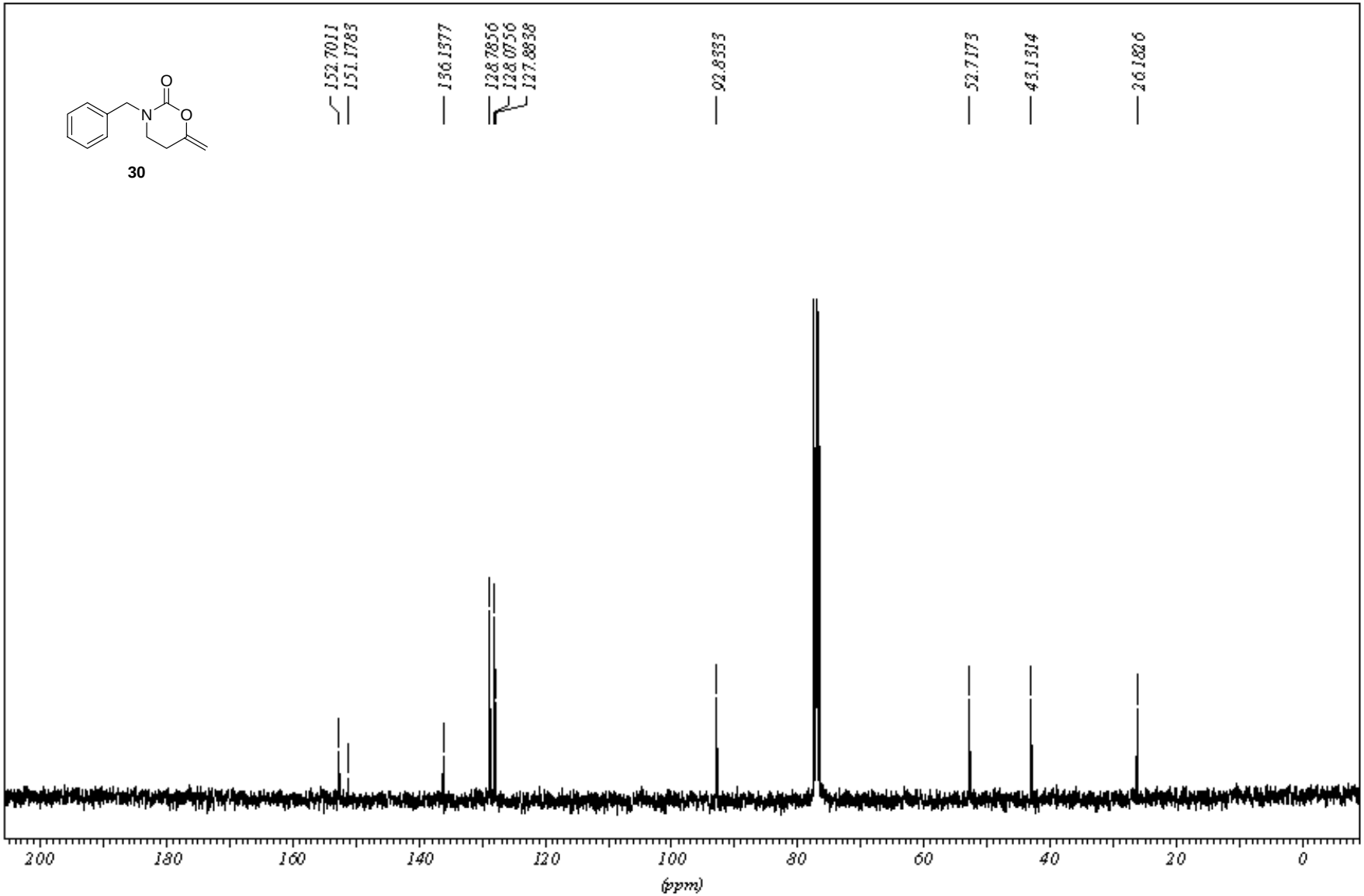

O
O
N
O
Integral
1.0000
1.0155
2.0820
4.2959
2.1545
9.9386
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

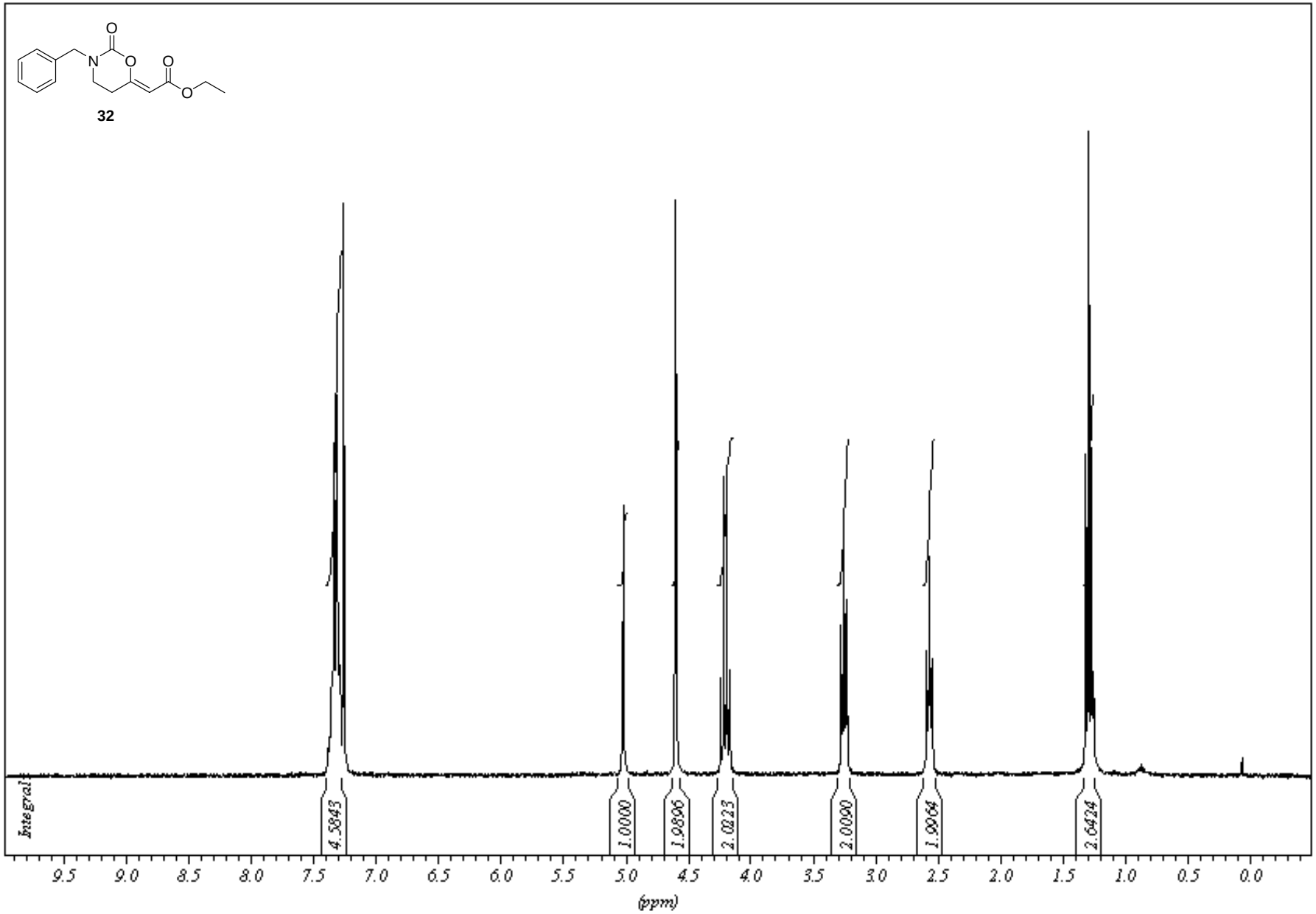

155.6466
149.3209
86.1967
72.7926
58.8411
47.9607
41.6696
28.1254
27.4254
O
O
N
O
200
180
160
140
120
100
80
60
40
20
0
(ppm)

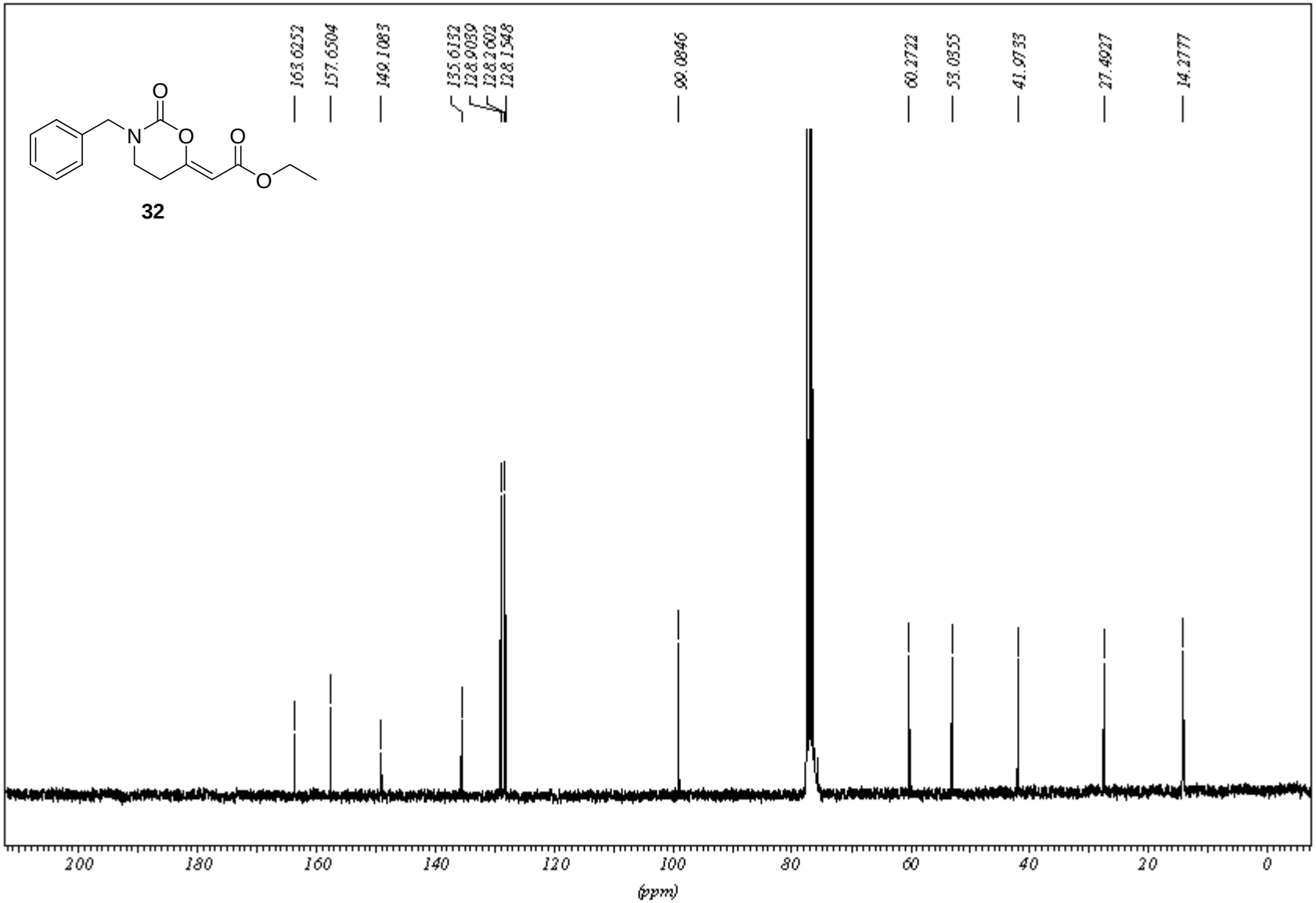

TBDMSO
N
O
O
24
Integral
0.9853
0.8755
1.9561
2.0553
1.9287
1.8949
9.2878
6.0933
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

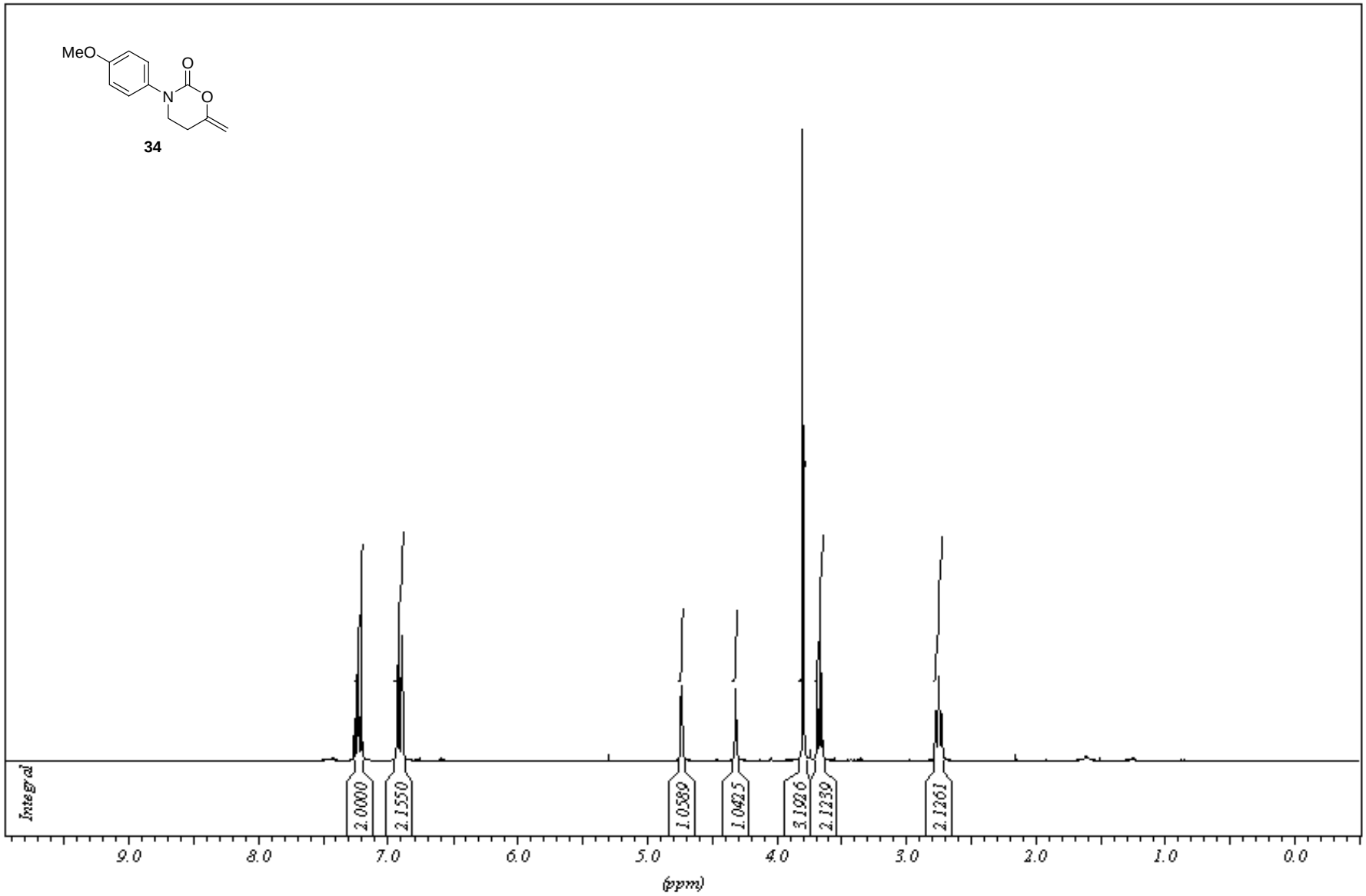

TBDMSO
N
O
O
O
24
152.7011
151.1783
136.1377
128.7856
128.0756
127.8838
92.8333
52.7173
43.1314
26.1826
200
180
160
140
120
100
80
60
40
20
0
(ppm)

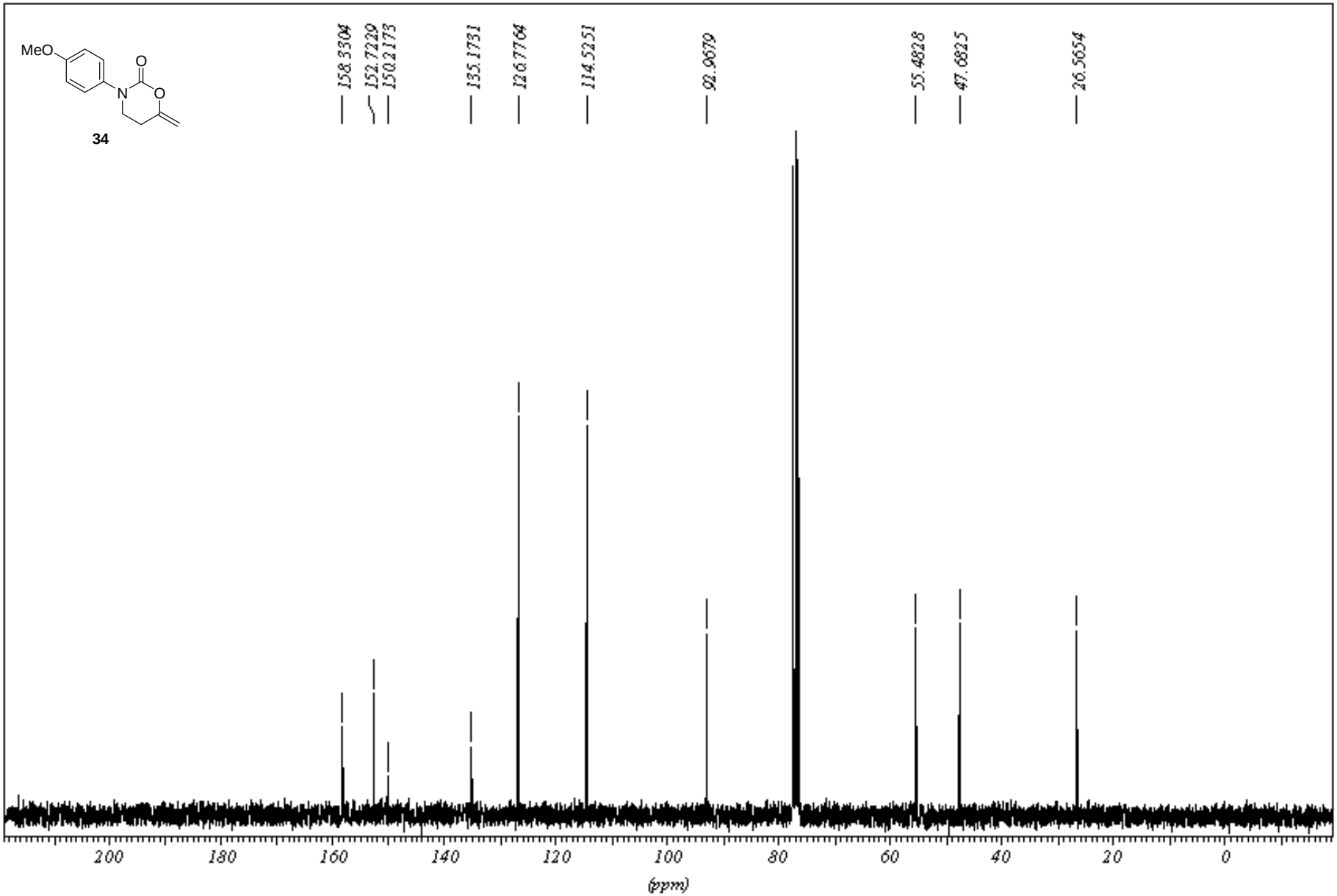

O
N
O
30
Integral
4.5102
0.9619
2.0097
1.0391
2.2741
2.3569
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

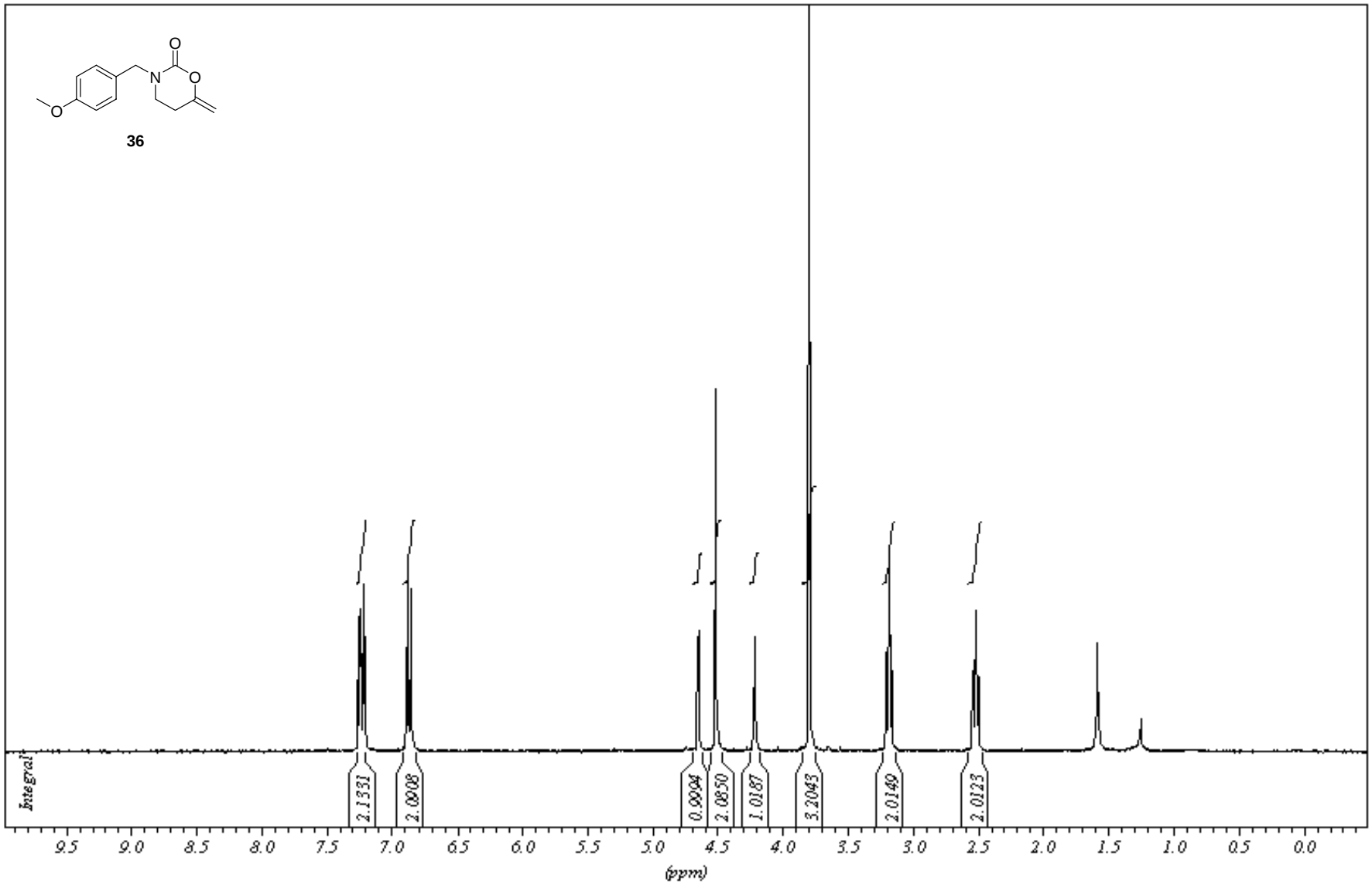

30
152.7011
151.1783
136.1377
128.7856
128.0756
127.8838
92.8333
52.7173
43.1314
26.1826
200
180
160
140
120
100
80
60
40
20
0
(ppm)

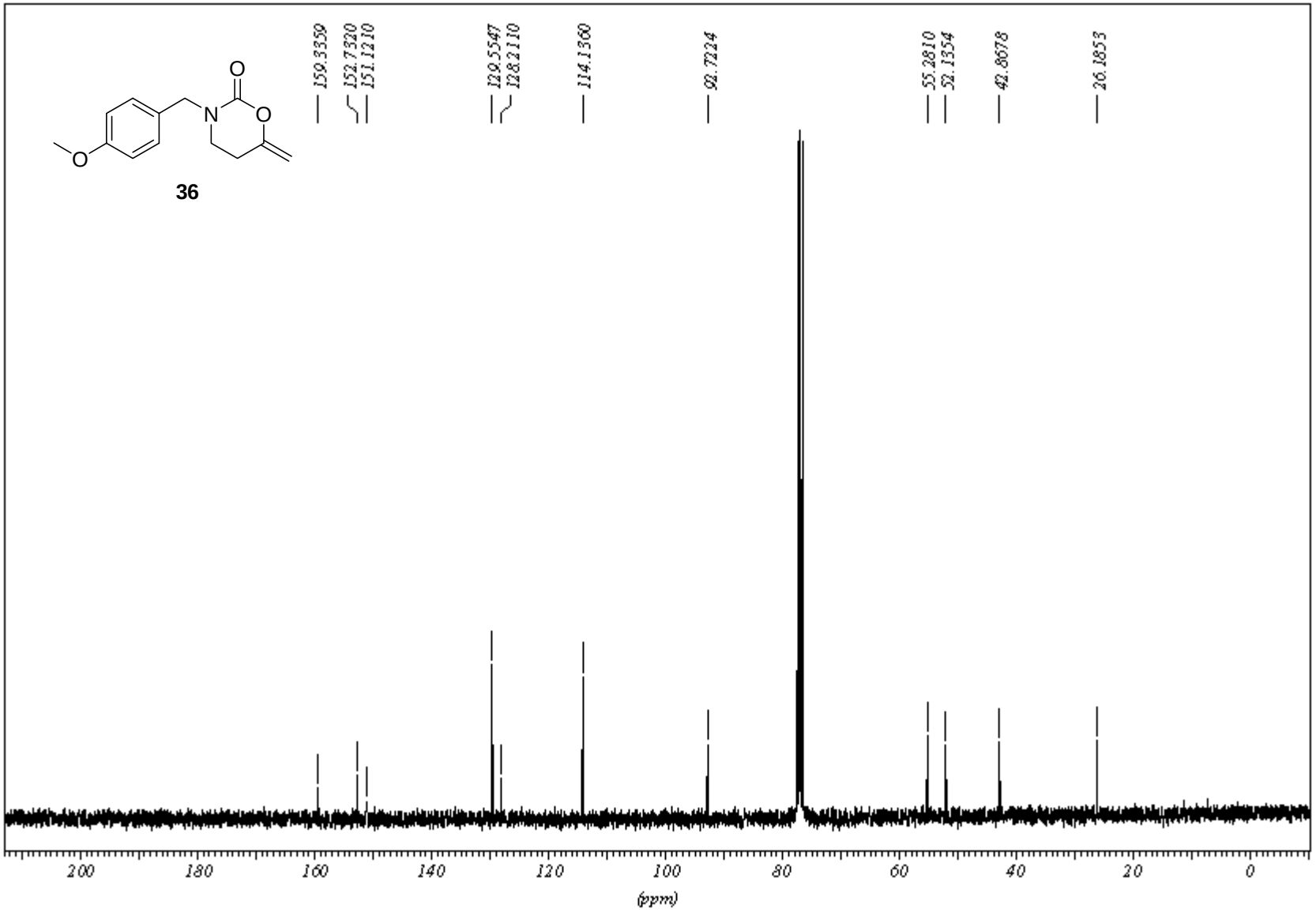

32
Integral
4.5843
1.0000
1.9896
2.0223
2.0090
1.9964
2.6424
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


163.6252
157.6504
149.1083
135.6132
128.9039
128.2602
128.1548
99.0846
60.2722
53.0355
41.9733
27.4927
14.2777
32
200
180
160
140
120
100
80
60
40
20
0
(ppm)


MeO
O
N
O
34
Integral
2.0000
2.1550
1.0589
1.0425
3.1926
2.1239
2.1261
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


MeO
N
O
O
34
158.3304
152.7229
150.2173
135.1731
126.7764
114.5251
92.9679
55.4828
47.6825
26.5654
200
180
160
140
120
100
80
60
40
20
0
(ppm)


O
N
O
O
36
Integral
2.1331
2.0908
0.9904
2.0850
1.0187
3.2043
2.0149
2.0123
9.5
9.0
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)


159.3359
152.7320
151.1210
129.5547
128.2110
114.1360
92.7224
55.2810
52.1354
42.8678
26.1853
O
N
O
O
36
200
180
160
140
120
100
80
60
40
20
0
(ppm)

(1) Wee, A. G. H.; Liu, B.; Zhang, L. *Journal of Organic Chemistry* **1992**, 57, 4404.
(2) Denton, T. T.; Zhang, X.; Cashman J. R. *J. Med. Chem.* **2005,** 48, 224.
(3) Shi, M.; Shen, Y.-M. *J. Org. Chem.* **2002**, *67*, 16.
(4) Boger, D. L.; Tarby, C. M.; Myers, P. L.; Caporale, L. H. *J. Am. Chem. Soc.* **1996**, *118*, 2109.
(5) (a) Molander, G. A.; Cormier, E. P. *J. Org. Chem.* **2005**, *70*, 2622. (b) Carretero, J. C.; Adrio, J. *Synthesis* **2001**, 1888.
(6) Fürstner, A.; Guth, O.; Düffels, A.; Seidel, G.; Liebl, M.; Gabor, B.; Mynott, R. *Chem. Eur. J.* **2001**, *7*, 4811.