A new safety catch photolabile protecting group

Emmanuel Riguet and Christian G. Bochet*

Department of Chemistry, university of Fribourg, Chemin du Musée 9, CH-1700 Fribourg, Switzerland.

Christian.bochet@unifr.ch

Supplementary material

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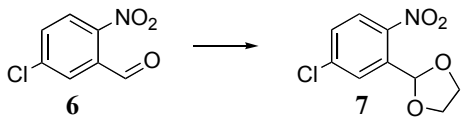
General experimental

Reactions were generally carried out under an atmosphere of nitrogen. Solvents were dried by filtration, under an argon atmosphere, through a purification system similar to the one proposed by Grubbs *et al.*[1] Thin layer chromatography (TLC) analyses were done using aluminium sheets coated with silica gel 60 F_{254}. Flash column chromatography (FC) was carried out using Brunschwig silica gel 60 Å (32-63 mesh). Commercially available products were used without further purification.
NMR spectra were recorded with a Bruker Avance DPX 360 (^{1}H: 360 and ^{13}C: 90.55 MHz) spectrometer in $CDCl_3$. Chemical shifts are given in ppm, calibrated to the residual solvent peak 7.27 ppm and 77.0 ppm for ^{1}H and ^{13}C respectively, coupling constants "*J*" are expressed in hertz (multiplicity: s = singlet, bs = broad singlet, d = doublet, dd = double doublet, t = triplet, q = quadruplet, quint = quintet, sext = sextet, m = multiplet). IR were recorded on a FTIR Unicam Mattson 5000 spectrometer. Electrospray ionization (ESI) mass spectra (MS) were obtained with a FT/ICR mass spectrometer Bruker 4.7T BioApex II, relative intensities are given in parenthesis. Photochemical irradiations were made in a Rayonet photoreactor, in a quartz vessel, with 16 300 nm lamps (spectral distribution available from www.rayonet.org). All melting points are uncorrected.

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. **Safe and Convenient Procedure for Solvent Purification**, *Organometallics* **1996**, *15*, 1518-1520.

I Experimental procedure for the synthesis of the substrates

5-Chloro-2-nitrobenzaldehyde ethylene acetal 7



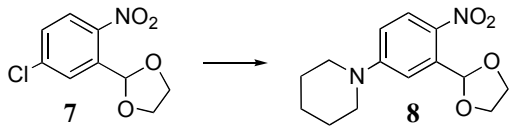
In a flask equipped with a *Dean-Stark* water separator, 5-chloro-2-nitrobenzaldehyde **6** (1g, 5.38 mmol), ethylene glycol (900 µL, 16.16 mmol) and *para*-toluenesulfonic acid (51 mg, 0.26 mmol) were dissolved in 25 mL of toluene. The mixture was stirred at reflux for 4 h. CH_2Cl_2 was then added, and the organic phase was washed once with satd $NaHCO_3$ and once with brine. The organic phase was then dried over $MgSO_4$, filtered and evaporated. The residue was purified by FC (silica gel)(hexane/CH_2Cl_2 4/6). After evaporation, compound **7** was obtained as a pale yellow oil (1.1g; 4.80 mmol, 89%).

^{1}H NMR (360 MHz, $CDCl_3$) δ 4.95-4.02 (m, 4 H), 6.44 (s, 1 H), 7.42 (dd, , *J* = 8.6 Hz, *J* = 2.3 Hz, 1 H), 7.74 (d, *J* = 2.3 Hz, 1 H), 7.85 (d, *J* = 8.6 Hz, 1 H)
^{13}C NMR (90 MHz, $CDCl_3$) δ 65.83, 99.45, 126.47, 128.34, 130.05, 135.83, 139.94, 147.33

Product described in :

Meanwell, N. A.; Dennis, R. D.; Roth, H. R.; Rosenfeld, M.J.; Smith, Edward, C. R.; Wright, J. J. Kim; Buchanan, J. O.; Brassard, C. L.; Gamberdella, M.; Gillespie, E.; Seiler, S. M.; Zavoico, G. B.; Fleming, J. S. *J. Med. Chem.* **1992**, 14, 2688-2696.

5-(*N*-piperidinyl)-2-nitrobenzaldehyde ethylene acetal 8



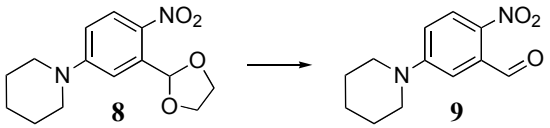
Compound **7** (650 mg, 2.83 mmol) was dissolved in 4 mL of piperidine. The mixture was then heated to reflux. After 16 hours the mixture was allowed to room temperature and CH_2Cl_2 was added. The organic phase was washed twice with water. The organic layer was dried over $MgSO_4$, filtered and evaporated. Purification by FC (silica gel) (CH_2Cl_2) gave compound **8** (695 mg, 2.49 mmol, 88 %) as a yellow oil.

^{1}H NMR (360 MHz, $CDCl_3$) δ 1.65 (s, 6 H); 3.40 (s, 4 H); 4.0 (s, 4 H); 6.58 (s, 1H); 6.75 (dd, *J* = 9.0 Hz, *J* = 2.7 Hz, 1 H); 7.17 (d, *J* = 2.7 Hz); 8.01 (d, *J* = 9.0 Hz, 1 H)
^{13}C NMR (90 MHz, $CDCl_3$) δ 24.57; 25.68; 48.95; 65.67; 100.35; 111.56; 113.06; 128.64; 136.24
TLC *Rf* = 0.21 (CH_2Cl_2)
MS (ESI) m/z : 301 ;12 $[M+Na]^+$

Product described in :

Meanwell, N. A.; Dennis, R. D.; Roth, H. R.; Rosenfeld, M.J.; Smith, Edward, C. R.; Wright, J. J. Kim; Buchanan, J. O.; Brassard, C. L.; Gamberdella, M.; Gillespie, E.; Seiler, S. M.; Zavoico, G. B.; Fleming, J. S. *J. Med. Chem.* **1992**, 14, 2688-2696.

5-(*N*-piperidinyl)-2-nitrobenzaldehyde 9



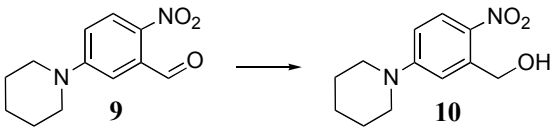
Compound **8** (675 mg, 2.43 mmol) was dissolved in acetone/water (3 mL/3 mL). Then *p*-toluenesulfonic acid was added (23 mg, 0.12 mmol) and the mixture was heated to reflux. After 4 h CH_2Cl_2 was added and the organic layer was washed once with satd $NaHCO_3$ and once with brine. The organic layer was dried over $MgSO_4$, filtered and evaporated. Compound **9** was obtained in a pure form, without further purification, as a yellow solid (555 mg, 2.37 mmol, 97 %).

^{1}H NMR (360 MHz, $CDCl_3$) δ1.66 (s, 6 H); 3.47 (s, 4 H); 6.87 (dd, *J* = 9.0 Hz, *J* = 2.7 Hz, 1 H); 7.05 (d, *J* = 2.7, 1 H); 8.04 (d, *J* = 9.0, 1 H); 10.48 (s, 1H)
^{13}C NMR (90 MHz, $CDCl_3$) δ 24.51; 25.65; 48.71; 112.55; 115.23; 128.20; 135.62; 154.36; 190.72
TLC *Rf* = 0.29 (CH_2Cl_2)
MS (ESI) m/z : 235.11 $[M+ H]^+$; 257.09 $[M+Na]^+$; 289.11 $[M + MeOH + Na]^+$

Product described in :

Meanwell, N. A.; Dennis, R. D.; Roth, H. R.; Rosenfeld, M.J.; Smith, Edward, C. R.; Wright, J. J. Kim; Buchanan, J. O.; Brassard, C. L.; Gamberdella, M.; Gillespie, E.; Seiler, S. M.; Zavoico, G. B.; Fleming, J. S. *J. Med. Chem.* **1992**, 14, 2688-2696.

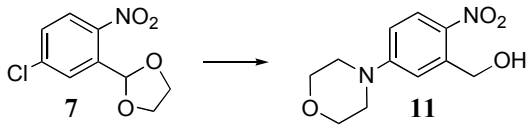
5-(*N*-piperidinyl)-2-nitrobenzyl alcohol 10



Compound **9** (540 mg, 2.30 mmol) was dissolved in 8 mL of THF and $NaBH_4$ (87 mg, 2.30 mmol) was slowly added. The mixture was stirred at room temperature. After 1h the mixture was partitioned between ether and satd NH_4Cl. After two extractions of the aqueous layer with Et_2O, the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and evaporated. The expected product **10** was isolated by FC (silica gel)(CH_2Cl_2/EtOAc 95/5) as yellow solid (520 mg, 2.20 mmol, 95 %).

^{1}H NMR (360 MHz, $CDCl_3$) δ 1.68 (s, 6 H); 3.10 (bs, 1 H); 3.46 (bs, 4 H), 4.89 (s, 2 H); 6.70 (dd, *J* = 9.0 Hz, *J* = 1.8 Hz, 1 H), 6.93 (d, *J* = 1.8 Hz, 1 H); 8.09 (d, *J* = 9.0 Hz, 1 H)
^{13}C NMR (90 MHz, $CDCl_3$) δ 24.17; 25.26; 48.18; 64.12; 111.37, 112.82; 128.70;135.89; 140.11; 154.35
TLC *Rf* = 0.76 (CH_2Cl_2/EtOAc)(60/40)
mp = 83 °C
IR (neat) 3290, 2941, 2856, 1606, 1573, 1481, 1447, 1385, 1352, 1316; 1254; 1168; 1124; 1089; 1031; 1019; 849; 801; 750 cm^{-1}
MS (ESI) m/z : 237.12 $[M+ H]^+$; 259.10 $[M+Na]^+$
HR-MS (ESI): 237.1231 (calcd for $[C_{12}H_{16}N_2O_3 + H]^+$: 237.1233)

5-(*N*-morpholin)-2-nitrobenzyl alcohol 11



Compound **7** (500 mg, 2.17 mmol) was dissolved in 5 mL of morpholine. The mixture was then heated to reflux. After 16 hours the mixture was allowed to room temperature and CH_2Cl_2 was added. The organic phase was washed twice with water. The organic layer was dried over $MgSO_4$, filtered and evaporated. Purification by FC (silica gel) (CH_2Cl_2) gave the expected acetal (450 mg, 1.60 mmol, 73 %) as a pale yellow oil.

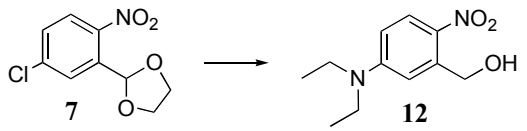
^{1}H NMR (360 MHz, $CDCl_3$) δ 3.37 (t, *J* = 5.00 Hz, 4 H); 3.85 (t, *J* = 5.00 Hz, 4 H); 4.06 (bs, 4 H); 6.58 (s, 1 H); 6.80 (dd, *J* = 9.08 Hz, *J* = 2.73 Hz, 1 H); 7.22 (d, *J* = 2.73 Hz, 1 H); 8.04 (d, *J* = 9.08 Hz, 1 H)
TLC *Rf* =0.15 (Cyclohexane/EtOAc)(95/5)

The acetal (500mg, 1.783 mmol) was dissolved in acetone/water (2 mL/2 mL). Then *p*-toluenesulfonic acid was added (17 mg, 0.089 mmol) and the mixture was heated to reflux.

After 4 h EtOAc was added and the organic layer was washed once with satd $NaHCO_3$ and once with brine. The organic layer was dried over $MgSO_4$, filtered and evaporated. The crude aldeheyde was obtained without specific purification as a yellow solid (360mg).
To a suspension of the crude aldehyde (360 mg) in THF/EtOH (2 mL/2 mL), $NaBH_4$ (51mg, 1.354 mmol) was slowly added. The mixture was stirred at room temperature. After 1h the mixture was partitioned between ether and satd NH_4Cl. After two extractions of the aqueous layer with Et_2O, the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and evaporated. The expected product was isolated by FC (silica gel)(CH_2Cl_2/EtOAc 95/5). After evaporation compound **11** (322 mg, 1.351 mmol, 76 %) was obtained as a yellow solid.

^{1}H NMR (360 MHz, $CDCl_3$) δ 2.90 (bs, 1H); 3.40 (t, *J* = 5.00 Hz, 4 H); 3.85 (t, *J* = 5.00 Hz, 4 H); 4.94 (s, 2 H); 6.75 (dd, *J* = 9.50 Hz, *J* = 2.73 Hz, 1 H); 7.03 (d, *J* = 2.73 Hz, 1 H); 8.14 (d, *J* = 9.50 Hz, 1 H)
^{13}C NMR (90 MHz, $CDCl_3$) δ 46.88; 63.73; 66.32; 111.62; 112.98; 128.28; 137.51; 139.87; 154.55
TLC *Rf* =0.33 (CH_2Cl_2/EtOAc)(60/40)
mp = 157 °C
IR (neat) 3346, 2967, 2901, 2871, 1603, 1574, 1479, 1445,1389, 1319, 1306 1242, 1181, 1120, 1092, 1050, 1021, 971, 945, 876, 851, 820, 753 cm^{-1}
HR-MS (ESI): 261.0847 (calcd for $[C_{11}H_{14}N_2O_4 + Na]^+$: 261.0845)

5-(*N*,*N*-diethyl)-2-nitrobenzyl alcohol 12



Compound **7** (1.6 g, 6.968 mmol) and diethylamine (14.5 mL, 139 mmol) were dissolved in 20 mL of DMSO. The mixture was then heated at 80 °C. After 48 hours the mixture was allowed to room temperature and CH_2Cl_2 was added. The organic phase was washed twice with water. The organic layer was dried over $MgSO_4$, filtered and evaporated. Purification by FC (silica gel) (CH_2Cl_2) gave the expected acetal (750 mg, 2.816 mmol, 40 %) as a pale yellow oil.

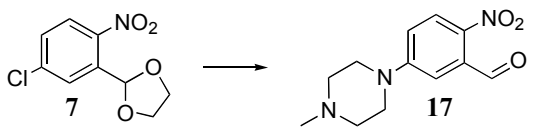
^{1}H NMR (360 MHz, $CDCl_3$) δ 1.20 (t, *J* = 7.26 Hz, 6 H); 3.45 (q, *J* = 7.26 Hz, 4 H); 4.05 (m, 4 H); 6.53 (dd, *J* = 9.5 Hz, *J* = 2.73 Hz, 1 H); 6.66 (s, 1 H); 6.97 (d, *J* = 2.73 Hz, 1 H); 8.06 (d, *J* = 9.5 Hz, 1 H)

The acetal (650 mg, 2.440 mmol) was dissolved in acetone/ water (1 mL/1 mL). *p*-Toluenesulfonic acid was then added (93 mg, 0,488 mmol) and the mixture was heated to reflux. After 4 h EtOAc was added and the organic layer was washed once with satd $NaHCO_3$ and once with brine. The organic layer was dried over $MgSO_4$, filtered and evaporated. The crude aldehyde was obtained as a yellow solid (500 mg).
To a suspension of the crude aldehyde (500 mg) in THF/EtOH (1 mL/1 mL), $NaBH_4$ (76 mg, 2.024 mmol) was slowly added. The mixture was stirred at room temperature. After 1h the mixture was partitioned between ether and satd NH_4Cl. After two extractions of the aqueous layer with Et_2O, the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and evaporated. The expected product was isolated by FC (silica gel)(CH_2Cl_2/EtOAc

95/5). After evaporation, compound **12** (430 mg, 1.917 mmol, 78 % overall yield) was obtained as a yellow solid.

^{1}H NMR (360 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.26 Hz, 6 H); 3.18 (t, *J* = 6.36 Hz, 1 H); 3.46 (q, *J* = 7.26 Hz, 4 H); 4.89 (d, *J* = 6.36 Hz, 2 H); 6.52 (dd, *J* = 9.54 Hz, *J* = 2.73 Hz, 1 H); 6.72 (d, *J* = 2.73 Hz, 1 H); 8.12 (d, *J* = 9.54 Hz, 1 H)
^{13}C NMR (90 MHz, $CDCl_3$) δ 12.38; 44.87; 64.37; 109.32; 110.72; 129.10; 134.85; 140.46; 152.05
TLC *Rf* = 0.36 (CH_2Cl_2/EtOAc)(90/10)
mp = 121 °C
IR (neat) 3276, 2974, 2926,1606, 1567, 1513, 1477, 1468, 1444, 1403, 1382, 1359, 1303, 1264, 1252, 1197, 1189, 1086, 1029, 974, 958, 845, 807, 790, 751 cm^{-1}
HR-MS (ESI): 225.1231 (calcd for $[C_{11}H_{16}N_2O_3 + H]^+$: 225.1233)

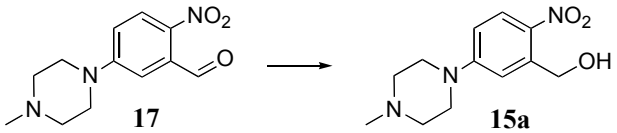
<u>5-(4-methylpiperazin-1-yl)-2-nitrobenzaldehyde</u> 17



Compound **7** (1.5 g, 6.532 mmol) was dissolved in *N*-methylpiperazine (13.085 g, 130.650 mmol). The mixture was then heated at 100 °C for 4 hours. The mixture was cooled to RT and CH_2Cl_2 was added; the organic phase was washed twice with water. The organic layer was then dried over Na_2SO_4 filtered and evaporated. The residue was dissolved in a mixture of acetone and HCl 1M (50 mL/50 mL) and heated at 60 °C for 2 hours. After cooling at RT the mixture was slowly neutralized with Na_2CO_3 and extracted with CH_2Cl_2. The organic layer over Na_2SO_4 filtered and evaporated. The crude product was purified by FC (CH_2Cl_2) (CH_2Cl_2/MeOH)(95/5) to afford compound **17** as a yellow solid (1.4 g, 5.616 mmol, 86 %).

^{1}H NMR (360 MHz, $CDCl_3$) δ 2.34 (3 H, s) 2.54 (2 H, t) 3.48 (2 H, t) 6.93 (1 H, dd, *J*=9.31, 2.95 Hz) 7.12 (1 H, d, *J*=3.18 Hz) 8.08 (1 H, d, *J*=9.08 Hz) 10.49 (1 H, s)
^{13}C NMR (90 MHz, $CDCl_3$) δ 45.87; 46.63; 54.25; 112.36; 115.17; 127.51; 134.74; 138.04; 153.94; 189.93
TLC *Rf* = 0.60 (CH_2Cl_2/MeOH)(90/10)
mp = 154 °C
IR (neat) 2943, 2862, 2852, 2803, 2776, 1687, 1592, 1575, 1488, 1458, 1439, 1431, 1397, 1323, 1294, 1256, 1234, 1151, 1146, 1093, 1076, 1044, 1004, 872, 825, 794 cm^{-1}
HR-MS (ESI): 250.1187 (calcd for $[C_{12}H_{15}N_3O_3 + H]^+$: 250.1186)

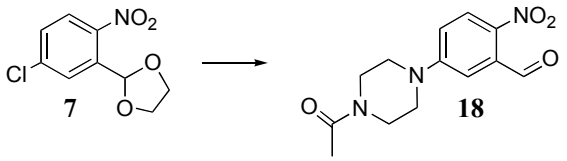
<u>5-(4-methylpiperazin-1-yl)-2-nitrobenzyl alcohol</u> 15a



Compound **17** (600 mg, 2.407 mmol) was dissolved in 20mL of isopropanol and basic aluminum oxide (2 g) was added. The mixture was heated at reflux overnight. The mixture was then filtered and the Alox was washed with (CH_2Cl_2/MeOH)(70/30). Solvents were evaporated and the residue was purified by FC (CH_2Cl_2) (CH_2Cl_2/MeOH)(90/10). Compound **15a** was obtained as a yellow solid (540 mg, 2.148 mmol, 90 %).

^{1}H NMR (360 MHz, $CDCl_3$) δ 2.34 (3 H, s) 2.53 (4 H, t) 3.43 (4 H, t) 3.64 (1 H, br. s.) 4.93 (2 H, s) 6.72 (1 H, dd, *J*=9.54, 2.72 Hz) 7.05 (1 H, d, *J*=2.72 Hz) 8.10 (1 H, d, *J*=9.08 Hz)
^{13}C NMR (90 MHz, $CDCl_3$) δ 45.96; 46.62; 54.43; 63.37; 111.63; 112.65; 128.22; 136.88; 140.34; 154.33
TLC *Rf* = 0.16 (CH_2Cl_2/MeOH)(95/5)
mp = 129 °C
IR (neat) 3110, 2954, 2900, 2834, 2816, 1607, 1578, 1488, 1442, 1382, 1320, 1303, 1256, 1213, 1166, 1141, 1098, 1069, 1039, 1002, 971, 862, 854, 834, 814, 797, 752 cm^{-1}
HR-MS (ESI): 274.1159 (calcd for $[C_{12}H_{17}N_3O_3 + Na]^+$: 274.1162)

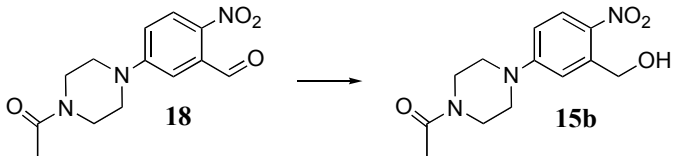
<u>5-(4-acetylpiperazin-1-yl)-2-nitrobenzaldehyde</u> 18



Compound **7** (500 mg, 2.177 mmol) was dissolved of *N*-acetylpiperazine (5.597 g, 43.666 mmol). The mixture was then heated at 100 °C. After 4 hours, the mixture was allowed to room temperature and CH_2Cl_2 was added. The organic phase was washed twice with satd NH_4Cl. The organic layer was then dried over Na_2SO_4 filtered and evaporated. The crude product was then dissolved in CH_2Cl_2 (20 mL). Amberlite-H^+ was added and the mixture was heated at reflux for 24 hours. After cooling to RT, the Amberlite-H^+ was filtered and washed three times with 50 mL of CH_2Cl_2. The solvent was evaporated. The crude product was purified by FC (silica gel) (CH_2Cl_2 and CH_2Cl_2/MeOH (90/10)) and recrystallization (Hexane/EtOAc) to afford compound **18** (230 mg, 0.829 mmol, 38 %) as a yellow solid.

^{1}H NMR (360 MHz, $CDCl_3$) δ 2.15 (3 H, s); 3.40 - 3.60 (4 H); 3.61 - 3.73 (2 H); 3.72 - 3.86 (2 H); 6.94 (1 H, dd, *J*=9.31, 2.95 Hz); 7.11 (1 H, d, *J*=2.72 Hz); 8.10 (1 H, d, *J*=9.54 Hz); 10.48 (1 H, s)
^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 21.28; 40.50; 45.20; 46.48; 46.55; 112.49; 115.40; 127.53; 134.63; 138.71; 153.54; 169.18; 189.64
TLC *Rf* = 0.13 (CH_2Cl_2/MeOH)(95/5)
mp = 147 °C
IR (neat) 3107, 3009, 2993, 2923, 2900, 2863, 1689, 1649, 1589, 1576, 1491, 1475, 1430, 1395, 1362, 1324, 1286, 1243, 1228, 1167, 1154, 1085, 1035, 1028, 995, 972, 866, 833, 828, 752 cm^{-1}
HR-MS (ESI): 300.0950 (calcd for $[C_{13}H_{15}N_3O_4 + Na]^+$: 300.0955)

<u>5-(4-acetylpiperazin-1-yl)-2-nitrobenzyl alcohol</u> 15b



Compound **18** (200 mg, 0.721 mmol) was dissolved in THF (5 mL) and $NaBH_4$ (27 mg, 0.721 mmol) was added. The mixture was stirred at room temperature for 30min. The reaction was quenched by satd NH_4Cl and the solution was then extracted with CH_2Cl_2. The organic layer

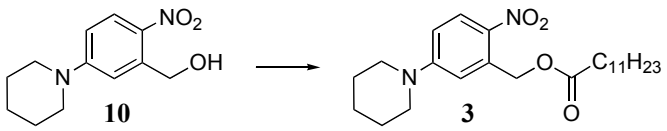
was dried over $MgSO_4$ filtered and evaporated. The crude product was purified by FC (silica gel, CH_2Cl_2 and CH_2Cl_2/MeOH (95/5)) to afford compound **15b** (190 mg, 0.680 mmol, 94%) as a yellow solid.

^{1}H NMR (360 MHz, DMSO-d_6) δ 2.04 (3 H, s) 3.42 - 3.49 (2 H, m) 3.49 - 3.56 (2 H, m) 3.56 - 3.68 (4 H, m) 4.85 (2 H, d, *J*=5.45 Hz) 5.49 (1 H, t, *J*=5.45 Hz) 6.92 (1 H, dd, *J*=9.54, 2.72 Hz) 7.24 (2 H, d, *J*=2.72 Hz) 8.05 (1 H, d, *J*=9.54 Hz)
^{13}C NMR (100 MHz, DMSO-d_6) δ 21.23; 40.29; 44.77; 45.88; 46.14; 60.88; 110.37; 111.03; 127.57; 135.48; 142.21; 153.73; 168.53
TLC *Rf* = 0.33 (CH_2Cl_2/MeOH)(95/5)
mp = 161 °C
IR (neat) 3280, 2981, 2930, 2904, 2845, 1626, 1610, 1574, 1482, 1450, 1433, 1367, 1348, 1306, 1245, 1160, 1093, 1065, 1033, 1002, 980, 976, 851, 824, 803, 754 cm^{-1}
HR-MS (ESI): 302.1113 (calcd for $[C_{13}H_{17}N_3O_4 + Na]^+$: 302.1111)

General procedure for the synthesis of the esters

Alcohols, triethylamine and DMAP were dissolved in anhydrous THF. Lauroyl chloride was then added and the mixture was stirred at room temperature for 2 h. CH_2Cl_2 was then added, the organic phase was washed once with satd NH_4Cl, once with satd $NaHCO_3$ and once with brine. The organic layer was dried over $MgSO_4$, filtered and evaporated. The residue was purified by FC (silica gel). Esters were obtained after evaporation as a yellow solid.

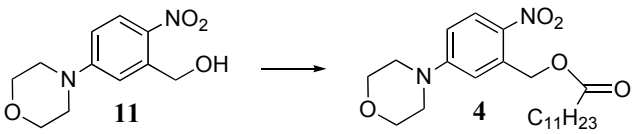
Dodecanoic acid 5-(*N*-piperidin)-2-nitrobenzyl ester 3



Compound **10** (320 mg, 1.35 mmol), lauroyl chloride (386 µL, 2.70 mmol), DMAP (16 mg, 0.13 mmol), triethylamine (380 µL, 1.62 mmol).
Compound **3** (504 mg, 1.20 mmol, 89 %) was obtained after evaporation as a yellow solid.

^{1}H NMR (360 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.81 Hz, 3H), 1.2-1.4 (16 H); 1.6-1.7 (8H); 2.42 (t, *J* = 7.49 Hz, 2 H); 3.43 (bs, 4H), 5.53 (s, 2H); 6.73 (dd, *J* = 9.31 Hz, *J* = 2.50 Hz, 1 H); 6.84 (d, *J* = 2.50 Hz, 1 H); 8.12 (d, *J* = 9.31 Hz, 1H)
^{13}C NMR (90 MHz, $CDCl_3$) δ14.08, 22.64, 24.16, 25.05, 25.23, 29.17, 29.27, 29.29, 29.41, 29.57, 31.86, 34.36, 48.29, 63.92, 111.59, 111.68, 128.34, 135.47, 136.00, 154.14, 173.06
TLC *Rf* = 0,50 (CH_2Cl_2)
mp = 49 °C
IR (neat) 2918, 2849, 1732, 1605, 1569,1505, 1483, 1468, 1449, 1381, 1359, 1314, 1238, 1163, 1083, 1023, 1005, 968, 883, 843, 803, 750 cm^{-1}
MS (ESI) m/z : 441.27 $[M+Na]^+$
HR-MS (ESI): 419.2900 (calcd for $[C_{24}H_{39}N_2O_4 + H]^+$: 419.2904)

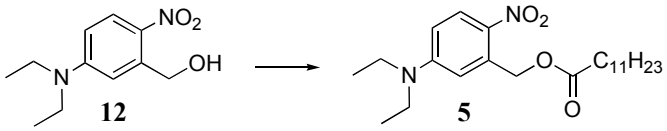
Dodecanoic acid 5-(*N*-morpholin)-2-nitrobenzyl alcohol 4



Alcohol **11** (200 mg, 0.839 mmol) ; lauroyl chloride (240 µL, 1 mmol) ; DMAP (10 mg, 0.083 mmol) ; triethylamine (235 µL, 1.678 mmol).
The product **4** was obtained after FC (328 mg, 0.780 mmol, 93 %)

^{1}H NMR (360 MHz, $CDCl_3$) δ 0,87 (t, *J* = 6.36 Hz, 3 H); 1.2-1.4 (16 H); 1.66 (2 H); 2.41 (t, *J* = 7.49 Hz, 2 H); 3.36 (q, *J* = 5 Hz, 4H) ; 3.85 (q, *J* = 5 Hz, 4H) ; 5.52 (s, 2 H); 6.77 (d, *J* = 9.5 Hz, 1 H); 6.88 (s, 1 H); 8.14 (d, *J* = 9.5 Hz, 1 H)
^{13}C NMR (90 MHz, $CDCl_3$) δ 14.10; 22.66 ; 25.03 ; 29.17 ; 29.29 ; 29.43 ; 29.57 ; 31.86 ; 34.31 ; 46.95 ; 63.69 ; 66.31 ; 112.01 ; 128.04 ; 135.25 ; 137.50 ; 154.25 ; 173.06
TLC *Rf* = 0.33 (Cyclohexane/EtOAc)(95/5)
mp = 80°C
IR (neat) 2948, 2921, 2854, 1740, 1605, 1579, 1497, 1473, 1433, 1379, 1326, 1301, 1266, 1240, 1167, 1124, 1090,1044, 1021, 995, 974, 941, 885, 843, 825, 753 cm^{-1}
HR-MS (ESI): 443.2516 (calcd for $[C_{23}H_{36}N_2O_5 + Na]^+$: 443.2516)

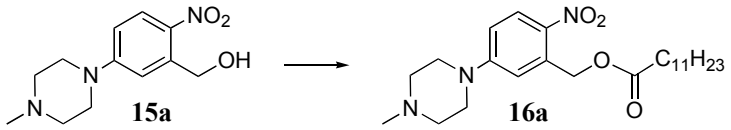
Dodecanoic acid 5-(*N,N*-diethyl)-2-nitrobenzyl alcohol 5



Alcohol **12** (150 mg, 0.669 mmol) ; lauroyl chloride (190 µL, 0.802 mmol) ; DMAP (8 mg, 0.070 mmol) ; triethylamine (188 µL, 1.337 mmol).
The product **5** was obtained after FC (250 mg, 0.615 mmol, 91 %)

^{1}H NMR (360 MHz, $CDCl_3$) δ 0,87 (t, *J* = 6.58 Hz, 3 H); 1.2-1.4 (m, 22 H); 1.6-1.7 (m, 2 H); 2.42 (t, *J* = 7.49 Hz, 2 H); 3.45 (q, *J* = 7.11 Hz, 4H); 5.56 (s, 2 H); 6.53 (dd, *J* = 9.5 Hz, *J* = 2.7 Hz, 1 H); 6.62 (d, *J* = 2.7 Hz, 1 H); 8.16 (d, *J* = 9.5 Hz, 1 H)
^{13}C NMR (90 MHz, $CDCl_3$) δ 12.38; 14.09; 22.65; 25.00; 29.19; 29.26; 29.29; 29.41; 29.56; 31.86; 34.38; 44.94; 64.10; 108.88; 109.19; 128.76; 134.69; 135.93; 151.57; 173.04
TLC *Rf* = 0.32 (CH_2Cl_2)
mp = 64 °C
IR (neat) 2916, 2849, 1728, 1603, 1569, 1510, 1482, 1465, 1450, 1417, 1403, 1377, 1355, 1299, 1259, 1197, 1187, 1168, 1081, 963, 884, 850, 832, 807, 786, 751 cm^{-1}
HR-MS (ESI): 407.2906 (calcd for $[C_{23}H_{39}N_2O_4 + H]^+$: 407.2904)

5-(4-methylpiperazin-1-yl)-2-nitrobenzyl dodecanoate 16a

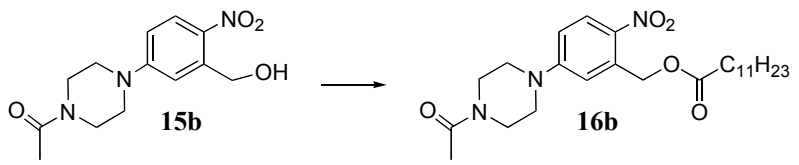


Alcohol **15a** (350 mg, 1.392 mmol) ; lauroyl chloride (364 µL, 1.532 mmol) ; DMAP (17 mg, 0.140 mmol) ; triethylamine (587 µL, 4.178 mmol).
The product **16a** was obtained after FC (580 mg, 1.337 mmol, 96 %)

^{1}H NMR (360 MHz, $CDCl_3$) 0.86 (3 H, t, *J*=6.58 Hz) 1.17 - 1.40 (16 H, m) 1.61 - 1.74 (2 H, m) 2.35 (3 H, br. s.) 2.41 (2 H, t, *J*=7.72 Hz) 2.54 (4 H, t) 3.43 (4 H, t) 5.52 (2 H, s) 6.76 (1 H, dd, *J*=9.08, 2.72 Hz) 6.87 (1 H, d, *J*=2.72 Hz) 8.13 (1 H, d, *J*=9.54 Hz)
^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 14.03; 22.58; 24.97; 29.10; 29.24; 29.35; 29.51; 31.80; 34.25; 45.95; 46.74; 54.39; 63.69; 76.64; 77.00; 77.35; 111.86; 128.03; 135.22; 136.86; 154.04; 172.96;

TLC *Rf* = 0.33 (CH_2Cl_2/MeOH)(95/5)
mp = 48 °C
IR (neat) 2938, 2918, 2802, 1731, 1605, 1575, 1498, 1472, 1439, 1417, 1387, 1316, 1296, 1250, 1161, 1091, 1051, 1006, 975, 884, 859, 835, 808, 795, 751 cm^{-1}
HR-MS (ESI): 434.3019 (calcd for $[C_{24}H_{39}N_3O_4 + H]^+$: 434.3013)

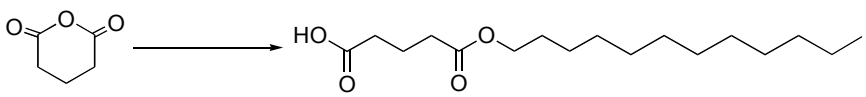
<u>5-(4-acetylpiperazin-1-yl)-2-nitrobenzyl dodecanoate</u> 16b



Alcohol **15b** (100 mg, 0.358 mmol) ; lauroyl chloride (100 µL, 0.802 mmol) ; DMAP (4.8 mg, 0.040 mmol) ; triethylamine (150 µL, 1.060 mmol).
The product **16b** was obtained after FC (135 mg, 0.292 mmol, 82 %)

^{1}H NMR (360 MHz, $CDCl_3$) δ 0.86 (3 H, t, *J*=6.58 Hz); 1.16 - 1.47 (16 H, m); 1.53 - 1.78 (2 H, m); 2.15 (3 H, s); 2.41 (2 H, t, *J*=7.49 Hz); 3.34 - 3.56 (4 H, m); 3.67 (2 H, br. s.); 3.80 (2 H, br. s.); 5.52 (2 H, s); 6.77 (1 H, d, *J*=9.08 Hz); 6.88 (1 H, br. s.); 8.14 (1 H, d, *J*=9.54 Hz)
^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 14.08; 21.28; 22.63; 24.99; 29.15; 29.28; 29.43; 29.56; 31.85; 34.27; 40.61; 45.38; 46.81; 63.61; 112.25; 112.32; 128.08; 135.33; 137.68; 153.61; 169.14; 173.04
TLC *Rf* = 0.20 (CH_2Cl_2/MeOH)(95/5)
mp = 74 °C
IR (neat) 2923, 2851, 1748, 1640, 1601, 1571, 1505, 1482, 1471; 1442, 1430, 1399, 1315, 1307, 1239, 1158, 1086, 1051, 1032, 995, 980, 845, 828, 814, 752 cm^{-1}
HR-MS (ESI): 556.3723 (calcd for $[C_{30}H_{51}N_3O_5 + Na]^+$: 556.3721)

<u>Pentanedioic acid monododecyl ester</u> 19

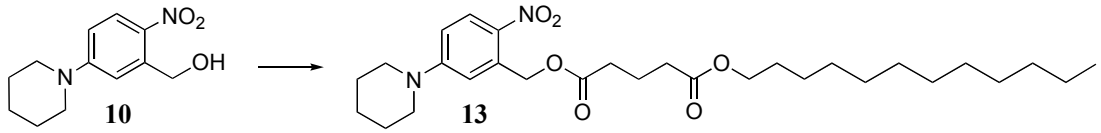


Glutaric anhydride (500 mg, 4.322 mmol) and dodecanol (1.224 g, 6.573 mmol) were dissolved in 10 mL of THF. Triethylamine (1.8 mL, 13.146 mmol) and DMAP were then added. The mixture was stirred at reflux for 4 hours. Dichloromethane was then added and the organic layer was washed once with HCl 10% and twice with water. The organic layer was

then dried over $MgSO_4$, filtered and evaporated. The expected product **19** was isolated (1 g, 3.328 mmol, 76%) as a white solid, by FC (silica gel) (CH_2Cl_2 followed by CH_2Cl_2/MeOH 95/5).

^{1}H NMR (360 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.4 Hz, 3H); 1.2-1.4 (m, 18H), 1.61 (m, 2H), 1.95 (q, *J* = 7.3 Hz, 2H); 2.41 (m, 4H); 4.06 (t, *J* = 6.8 Hz, 2H)
^{13}C NMR (90 MHz, $CDCl_3$) δ 14.25; 19.98; 22.82, 26.04, 28.73, 29.38, 29.48, 29.65, 29.70, 29.76, 29.78, 32.05, 33.11, 33.34, 64.89, 173.13, 178.99.
TLC *Rf* = 0.42 (CH_2Cl_2/MeOH)(95/5)

<u>Pentanedioic acid dodecyl ester 2-nitro-5-piperidin-1-yl-benzyl ester</u> 13



Compound **10** (350 mg, 1.165 mmol) and compound **19** (302 mg, 1.281mmol) were dissolved in 10 mL of THF. DCC (288 mg, 1.397 mmol) and DMAP (28 mg, 0.230mmol) were then added. The reaction mixture was stirred overnight. The mixture was then filtered and the filtrate was evaporated. The residue was purified by FC (silica gel)(CH_2Cl_2). After evaporation of solvent, the expected product **13** (497 mg, 0.958mmol, 82%) was obtained as a yellow oil.

^{1}H NMR (360 MHz, $CDCl_3$) δ 0.86 (t, *J* = 6.4 Hz, 3H); 1.2-1.4 (m, 18 H); 1.6-1.7 (m, 8H); 2.0 (q, *J* = 7.3 Hz, 2 H); 2.39 (t, *J* = 7.3 Hz, 2 H); 2.49 (t, *J* = 7.3 Hz, 2 H); 3.43 (bs, 4H), 4.04 (t, *J* = 6.8 Hz, 2 H); 5.52 (s, 2H); 6.73 (dd, *J* = 9.5 Hz, *J* = 2.7 Hz, 1 H); 6.83 (d, *J* = 2.7 Hz, 1 H); 8.12 (d, *J* = 9.5 Hz, 1H)
^{13}C NMR (90 MHz, $CDCl_3$) δ 14.07, 20.14, 22.63, 24.15, 25.21, 25.86, 28.56, 29.20, 29.29, 29.46, 29.52, 29.57, 29.59, 31.86, 33.23, 33.26, 48.28, 64.18, 64.63, 111.71, 128.37, 135.15, 135.95, 154.13, 172.21, 172.90
TLC *Rf* = 0.55 (CH_2Cl_2/EtOAc)(90/10)
mp = 45 °C
IR (neat) 2927, 2855, 1738, 1603, 1575, 1500, 1497, 1391, 1317, 1243, 1174, 1149, 1085, 1022, 852, 815cm^{-1}
HR-MS (ESI): 541.3242 (calcd for $[C_{29}H_{46}N_2O_6 + Na]^+$: 541.3248)

II Photolysis of compounds 3, 4, 5, 16a and 16b

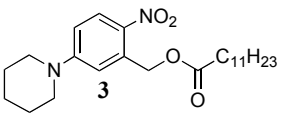
General procedure for the kinetic measurements

Esters (60 μmol) were dissolved in 10mL of acetonitrile in a quartz vessel. The solution was deaerated by a stream of argon for 10 minutes and the mixture was irradiated at 300 nm in a Rayonet apparatus equipped with 15 fluorescent tubes RPR3000. Aliquots were taken after a given time, the solvent was evaporated and the residue was analysed by ^{1}H NMR in $CDCl_3$. The percentage of the remaining starting material was evaluated by relative integration of the benzylic methylene protons and the side chain terminal methyl group (^{1}H NMR).

Compound **3** 60 μmol in 10 mL of acetonitrile

Compound **3** 60 μmol in 10 mL of acetonitrile after addition of 1 equiv of trifluoromethane sulfonic acid

Dodecanoic acid 5-(*N*-piperidin)-2-nitrobenzyl ester 3



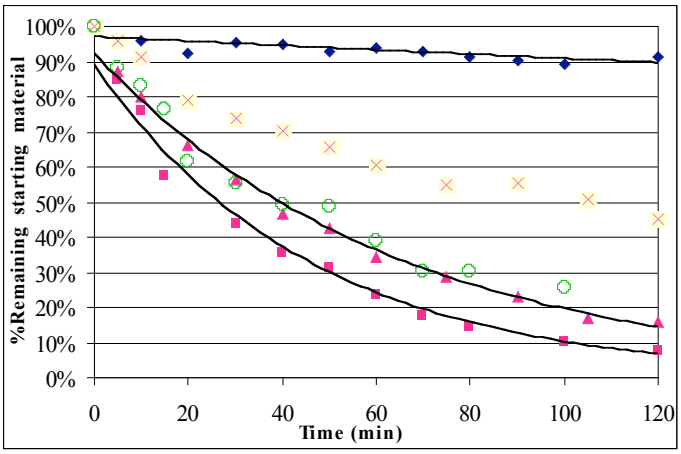
hν 300nm

hν 300nm

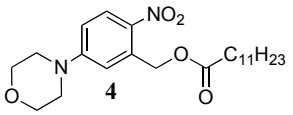
0.5 equivalent of trifluoromethanesulfonic acid (cross)
1 equivalent of trifluoromethanesulfonic acid (triangle)
2 equivalents of trifluoromethanesulfonic acid (square)

hν 300nm

1 equivalent of $Cu(ClO_4)$



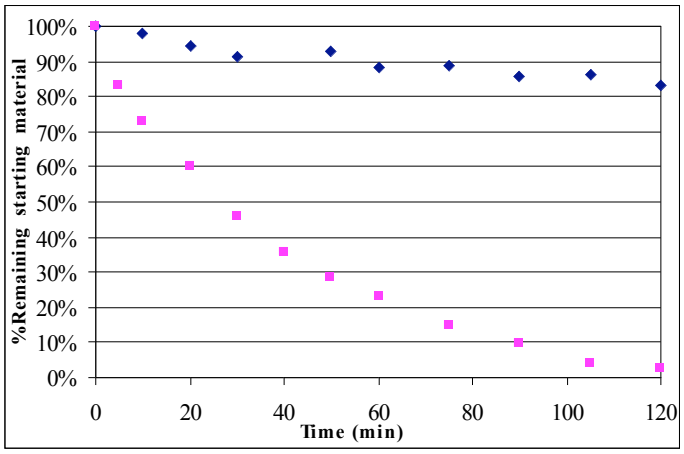
Dodecanoic acid 5-(*N*-morpholin)-2-nitrobenzyl alcohol 4



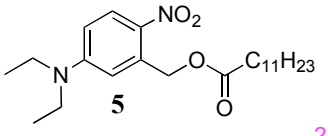
hν 300nm

hν 300nm

2 equivalents of trifluoromethanesulfonic acid



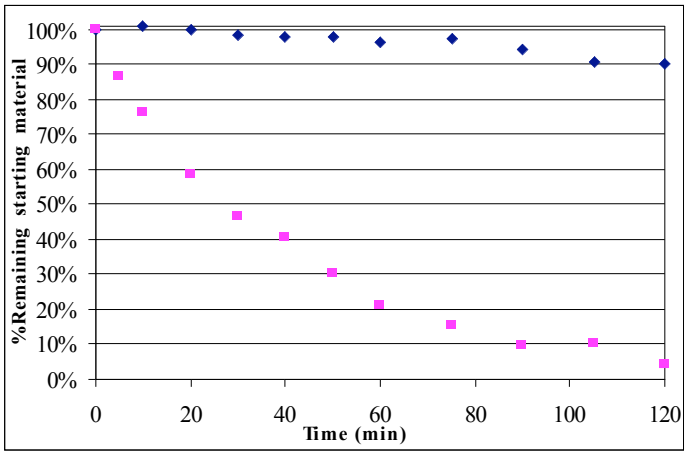
Dodecanoic acid 5-(*N*,*N*-diethyl)-2-nitrobenzyl alcohol 5



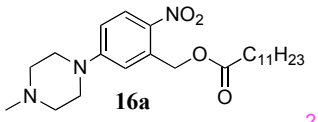
hν 300nm

hν 300nm

2 equivalents of trifluoromethanesulfonic acid



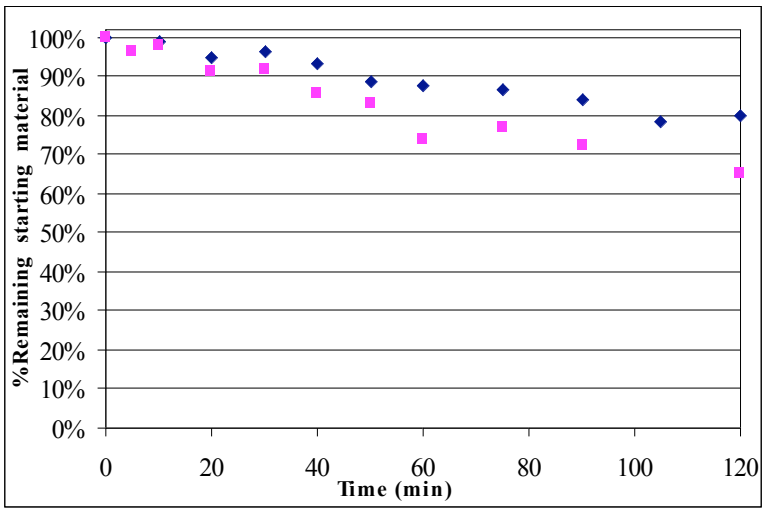
5-(4-methylpiperazin-1-yl)-2-nitrobenzyl dodecanoate 16a



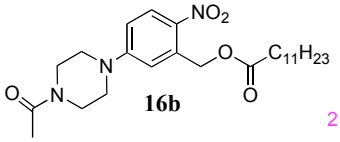
hν 300nm

hν 300nm

2 equivalents of trifluoromethanesulfonic acid



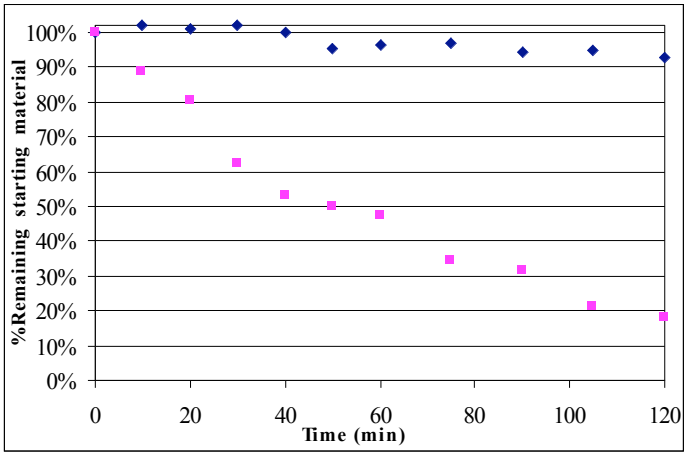
5-(4-acetylpiperazin-1-yl)-2-nitrobenzyl dodecanoate



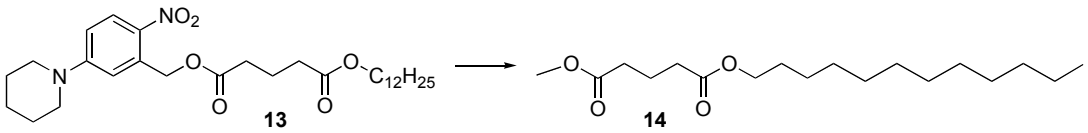
hν 300nm

hν 300nm

2 equivalents of trifluoromethanesulfonic acid



Pentanedioic acid dodecyl ester methyl ester 14



In a quartz vessel, compound **13** (78 mg, 150 μL) was dissolved in 15 mL of CH_3CN. HCl was then added (1.5 ml of 1M solution in ether, 1.5 mmol). The solution was deaereted by a stream of argon for 10 minute; the mixture was irradiated at 300 nm for 4 hours and the solvent was then evaporated. The crude product was dissolved in 4 mL of a mixture of benzene/methanol (1/1) and (trimethylsilyl)diazomethane (1.5 mmol): The solvent was evaporated and the residue was purified by FC (silica) (CH_2Cl_2/Hexane 70/30). The expected product **14** was obtained as colourless oil (33 mg, 105 μmol, 70%).

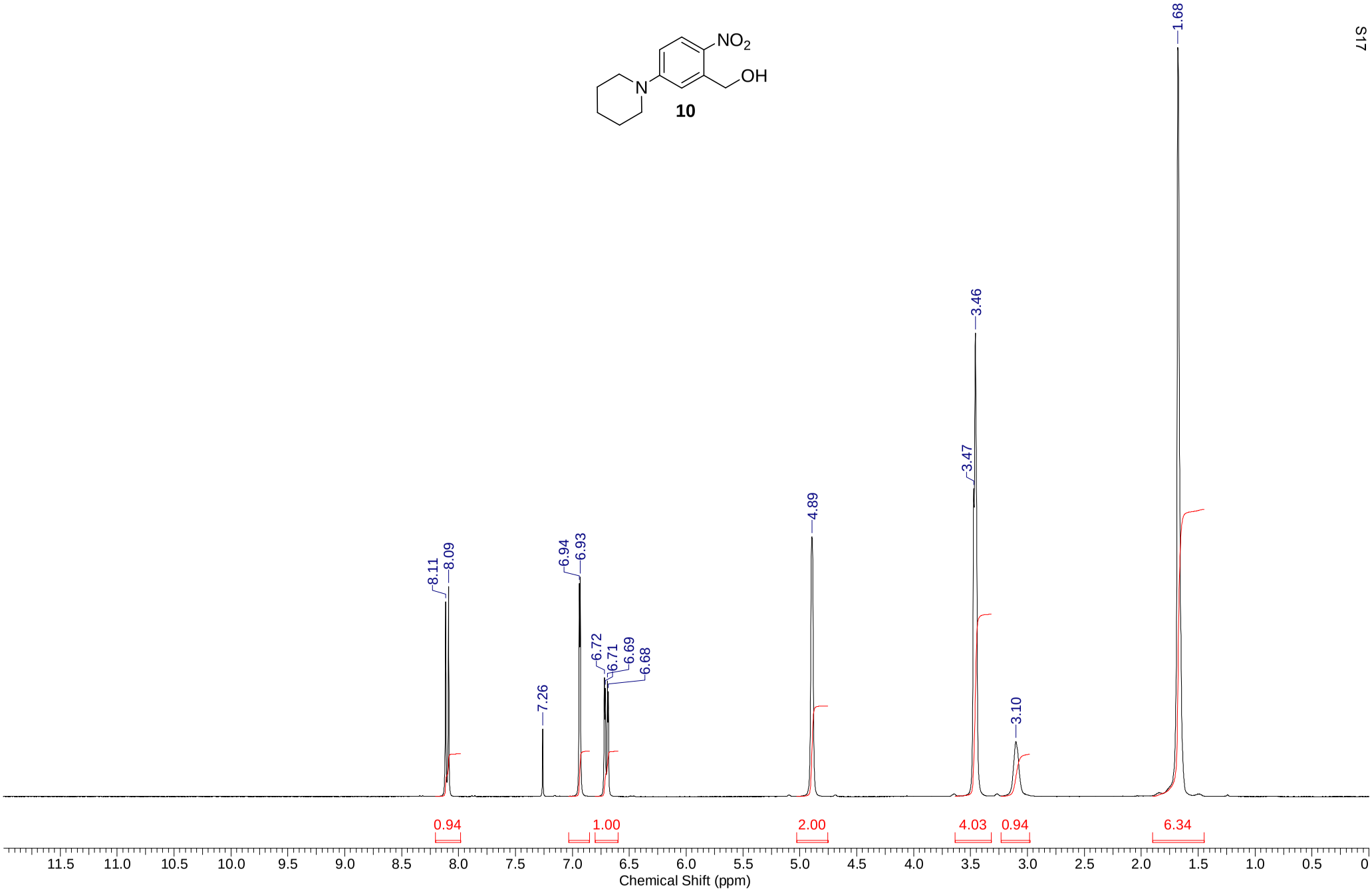
^{1}H NMR (360 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.4 Hz, 3H); 1.29 (m, 18H); 1.60 (m, 2H); 1.94 (q, *J* = 7.33 Hz, 2H) 2.37 (m, 4H); 3.66 (s, 3H); 4.06 (t, *J* = 6.8 Hz, 2H)
^{13}C NMR (90 MHz, $CDCl_3$) δ 14.09, 20.12, 22.66, 25.88, 28.58, 29.22, 29.32, 29.49, 29.54, 29.60, 29.62, 31.89, 33.05, 33.30, 51.57, 64.64, 173.01, 173.41
TLC *Rf* = 0.35 (CH_2Cl_2)
IR (neat) 2922, 2854, 1738, 1461, 1437, 1376, 1315, 1196, 1173, 1064, 1028, 998, 722 cm^{-1}
MS MS (ESI) m/z : 315.2 $[M+H]^+$

III ^{1}H and ^{13}C-NMR spectra of compounds 10, 11, 12, 17, 15a, 18, 15b, 3, 4, 5,16a 16b ,13 and 14

ER98

NO2
OH
N

10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2.00
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6.34
11.5
11.0
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9.5
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6.5
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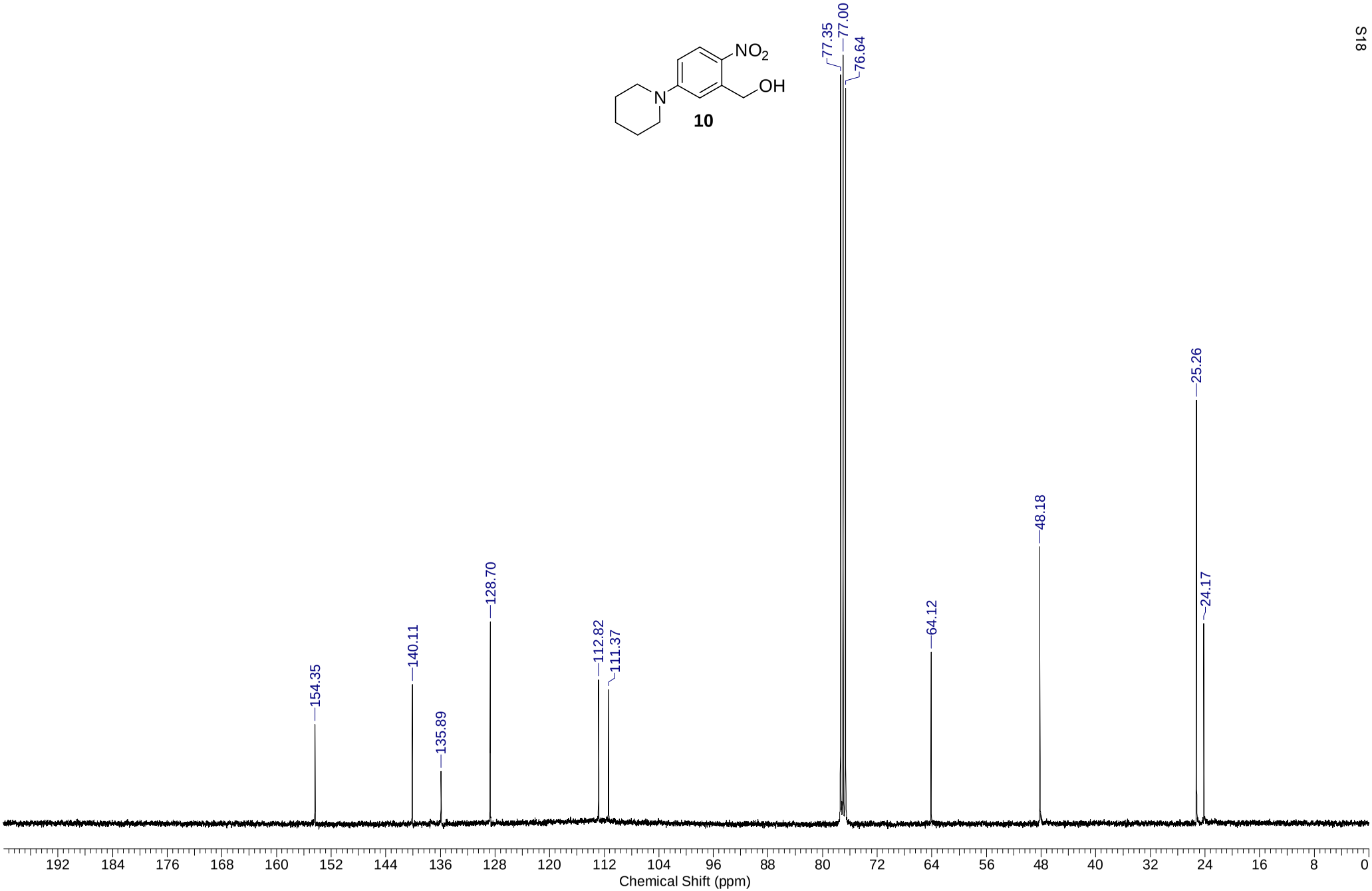
0
Chemical Shift (ppm)

ER98

NO2
OH
N

10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160
152
144
136
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24
16
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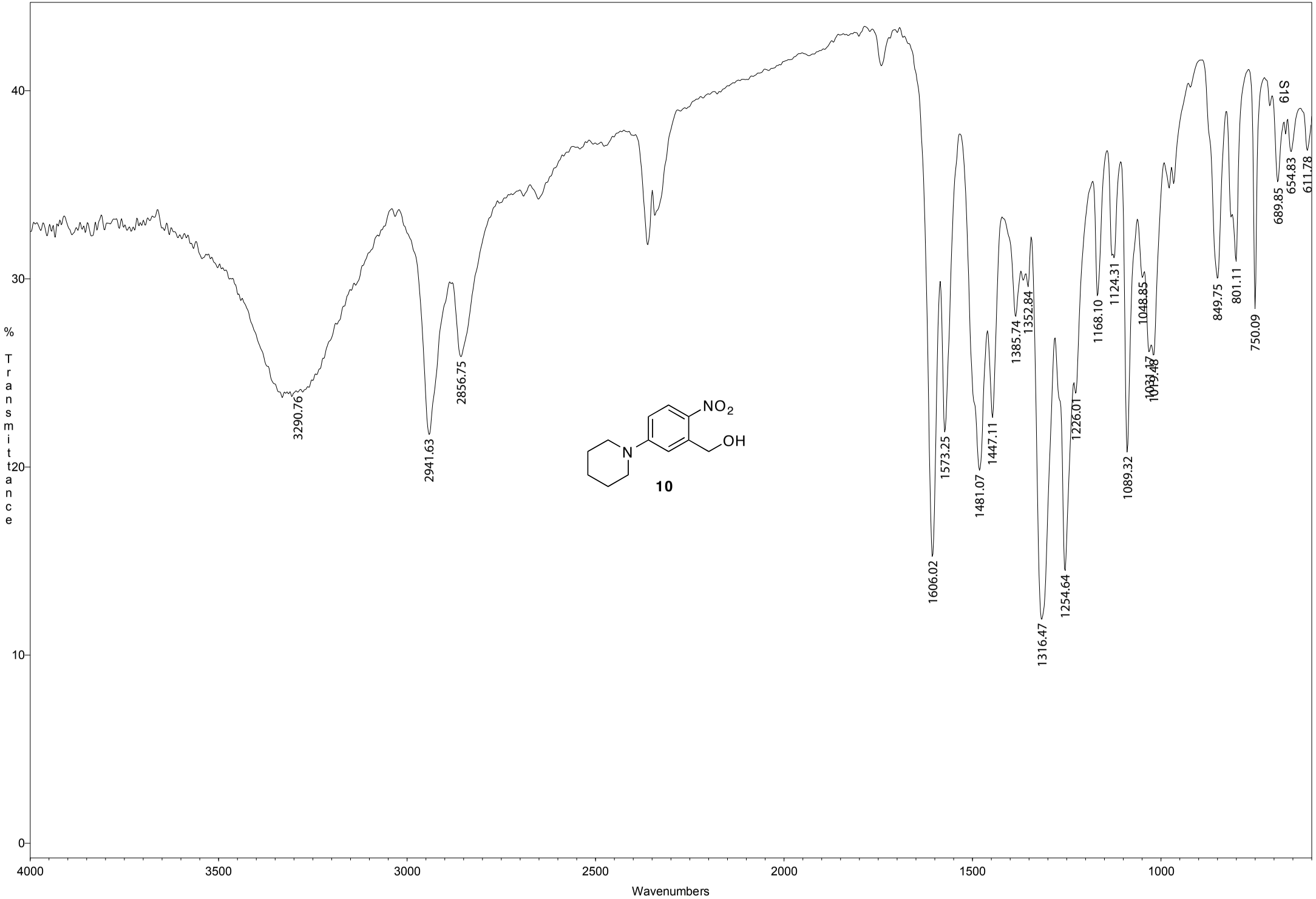
Chemical Shift (ppm)

ER98


% Transmittance
Wavenumbers
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3500
3000
2500
2000
1500
1000
0
10
20
30
40
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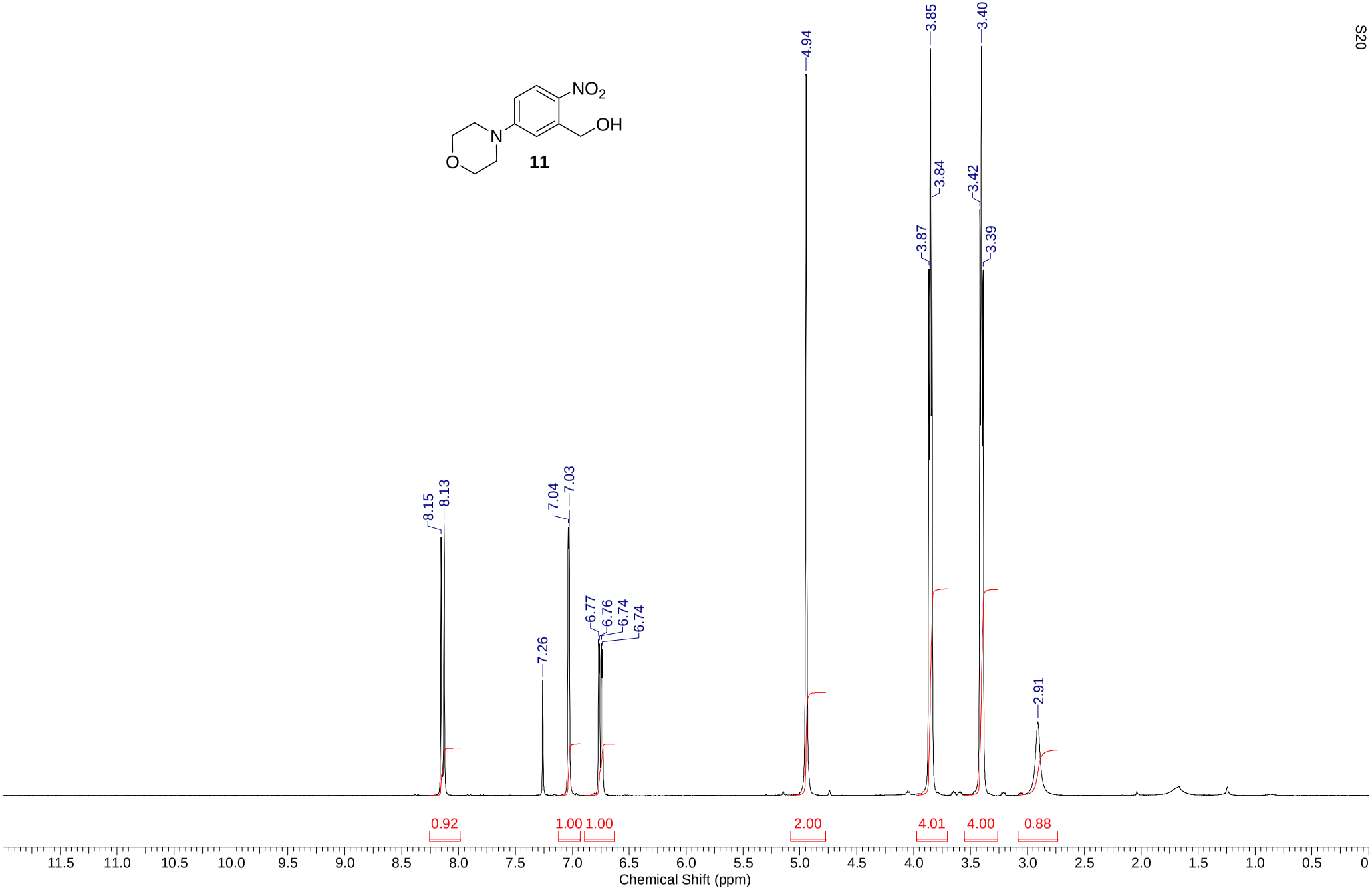
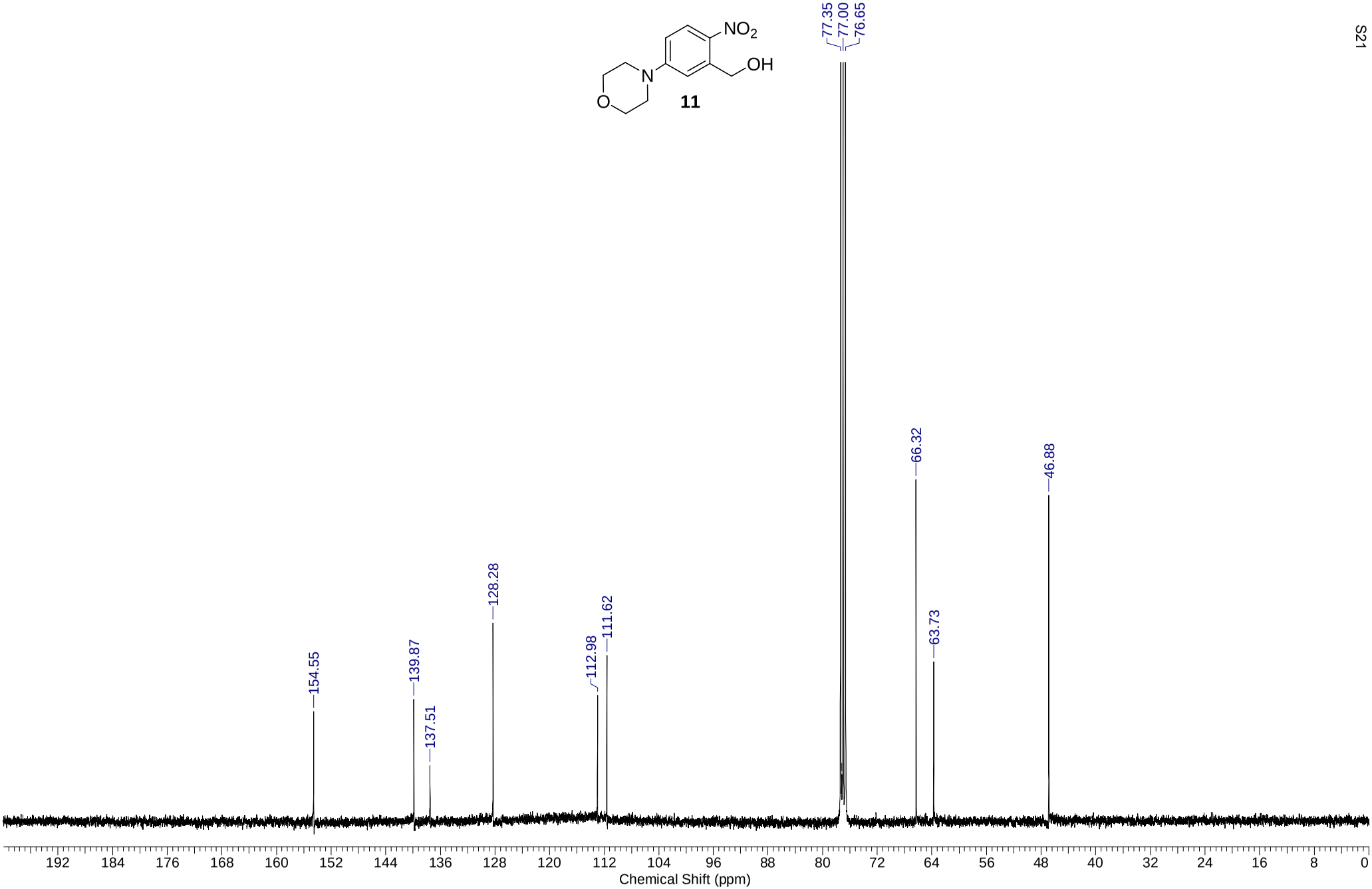
2941.63
2856.75
1606.02
1573.25
1481.07
1447.11
1385.74
1352.84
1316.47
1254.64
1226.01
1168.10
1124.31
1089.32
1048.85
1031.47
1019.48
849.75
801.11
750.09
689.85
654.83
611.78
NO2
OH
N
10
S19

ER10

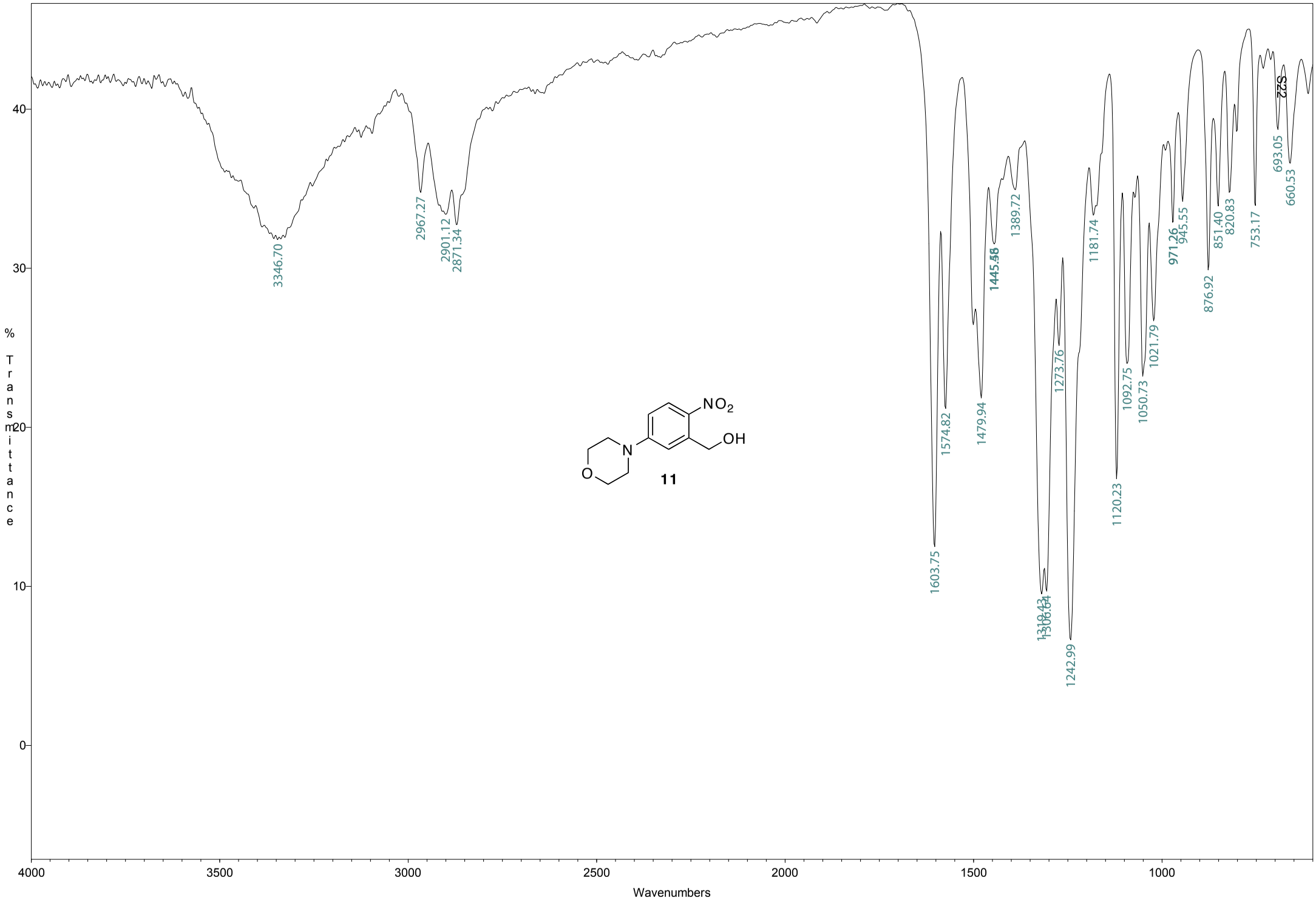

NO2
OH
N
O
11
8.15
8.13
7.26
7.04
7.03
6.77
6.76
6.74
6.74
4.94
3.87
3.85
3.84
3.42
3.40
3.39
2.91
0.92
1.00
1.00
2.00
4.01
4.00
0.88
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

ER10

NO2
OH
N
O
11


77.35
77.00
76.65
66.32
46.88
63.73
128.28
111.62
112.98
154.55
139.87
137.51
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

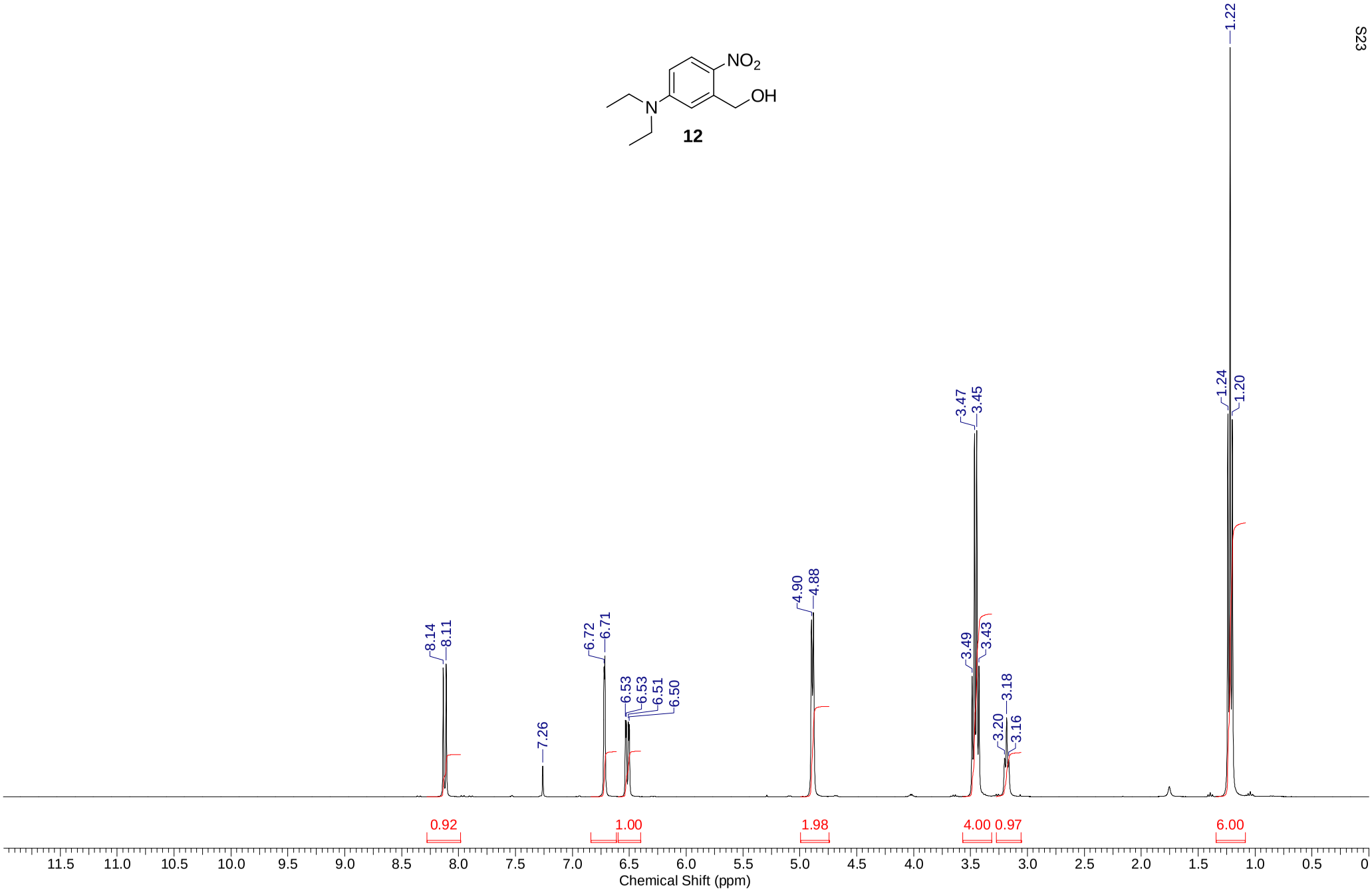
ER 10


% Transmittance
Wavenumbers
4000
3500
3000
2500
2000
1500
1000
0
10
20
30
40
3346.70
2967.27
2901.12
2871.34
1603.75
1574.82
1479.94
1445.58
1389.72
1310.43
1308.54
1273.76
1242.99
1181.74
1120.23
1092.75
1050.73
1021.79
971.26
945.55
876.92
851.40
820.83
753.17
693.05
660.53
S22
NO2
OH
N
O
11

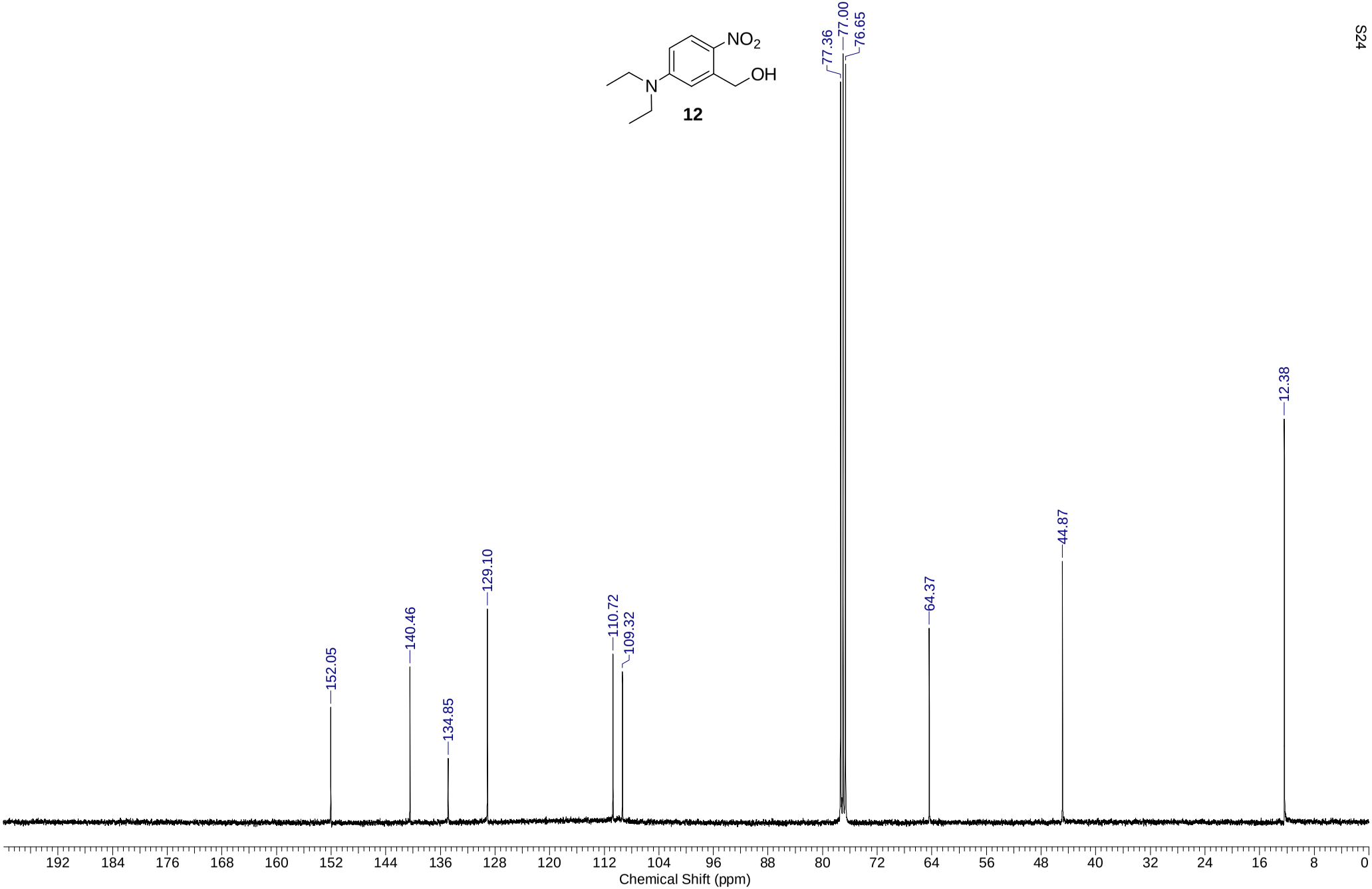
ER85

NO2
OH
N

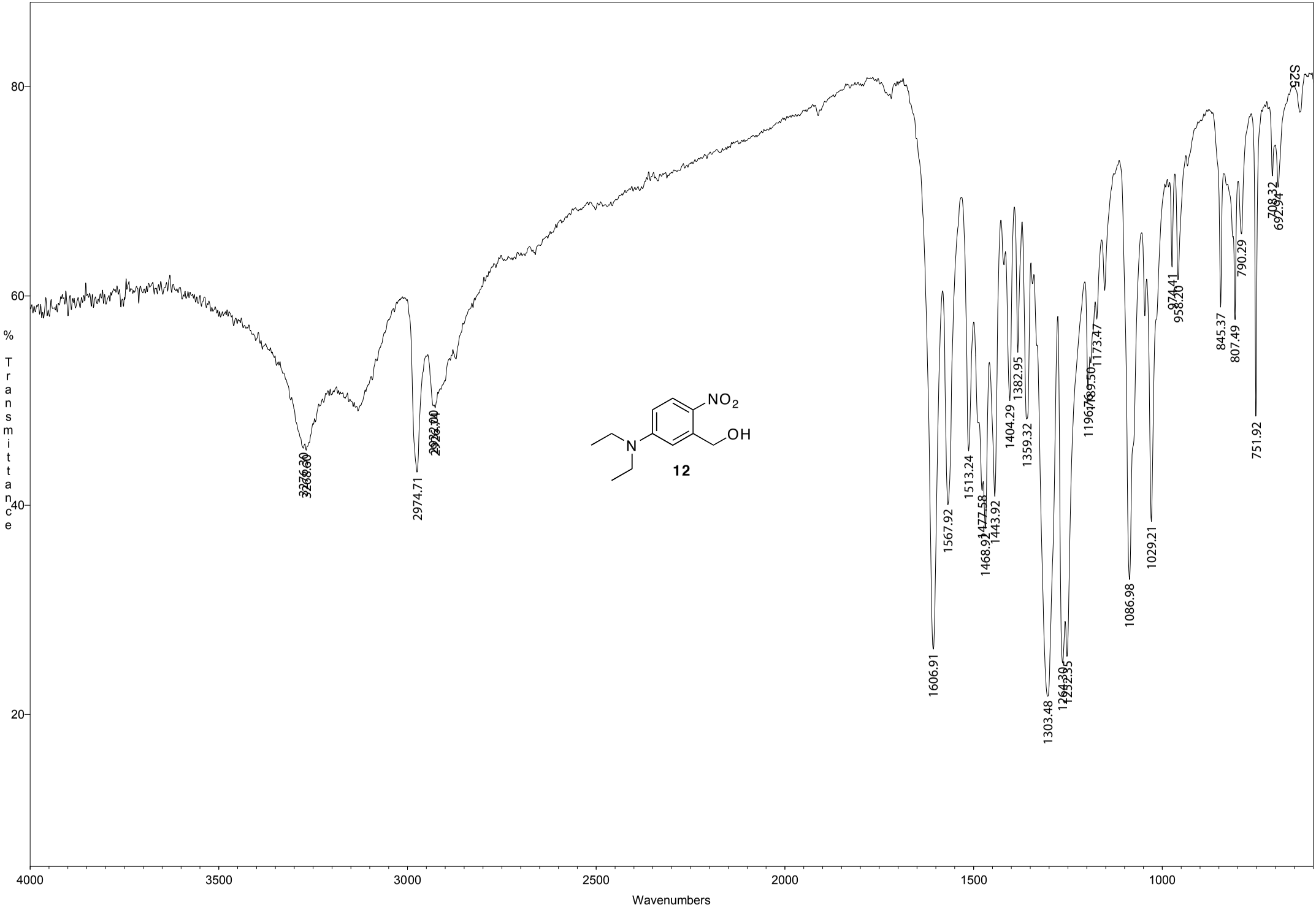
12


8.14
8.11
7.26
6.72
6.71
6.53
6.53
6.51
6.50
4.90
4.88
3.47
3.45
3.49
3.43
3.20
3.18
3.16
1.24
1.20
1.22
0.92
1.00
1.98
4.00
0.97
6.00
11.5
11.0
10.5
10.0
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
Chemical Shift (ppm)

ER85


NO2
OH
N
12
77.36
77.00
76.65
12.38
44.87
64.37
129.10
110.72
109.32
152.05
140.46
134.85
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

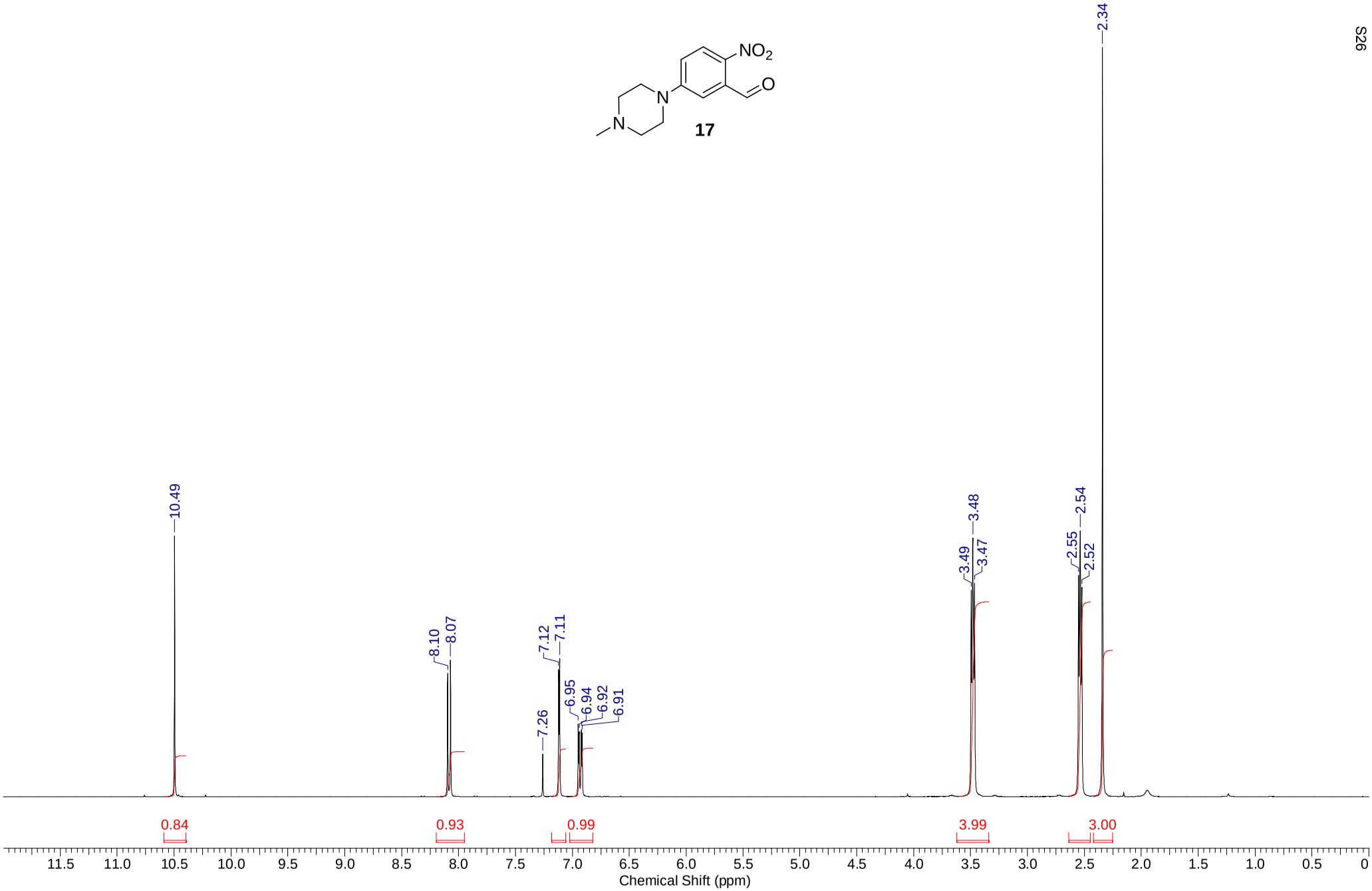
er85


% Transmittance
Wavenumbers
4000
3500
3000
2500
2000
1500
1000
80
60
40
20
3276.30
3206.60
2974.71
2932.10
2926.70
1606.91
1567.92
1513.24
1477.58
1468.91
1443.92
1404.29
1382.95
1359.32
1303.48
1264.30
1252.35
1196.17
1189.50
1173.47
1086.98
1029.21
958.20
874.41
845.37
807.49
790.29
751.92
708.32
692.94
S25
NO2
OH
N
12

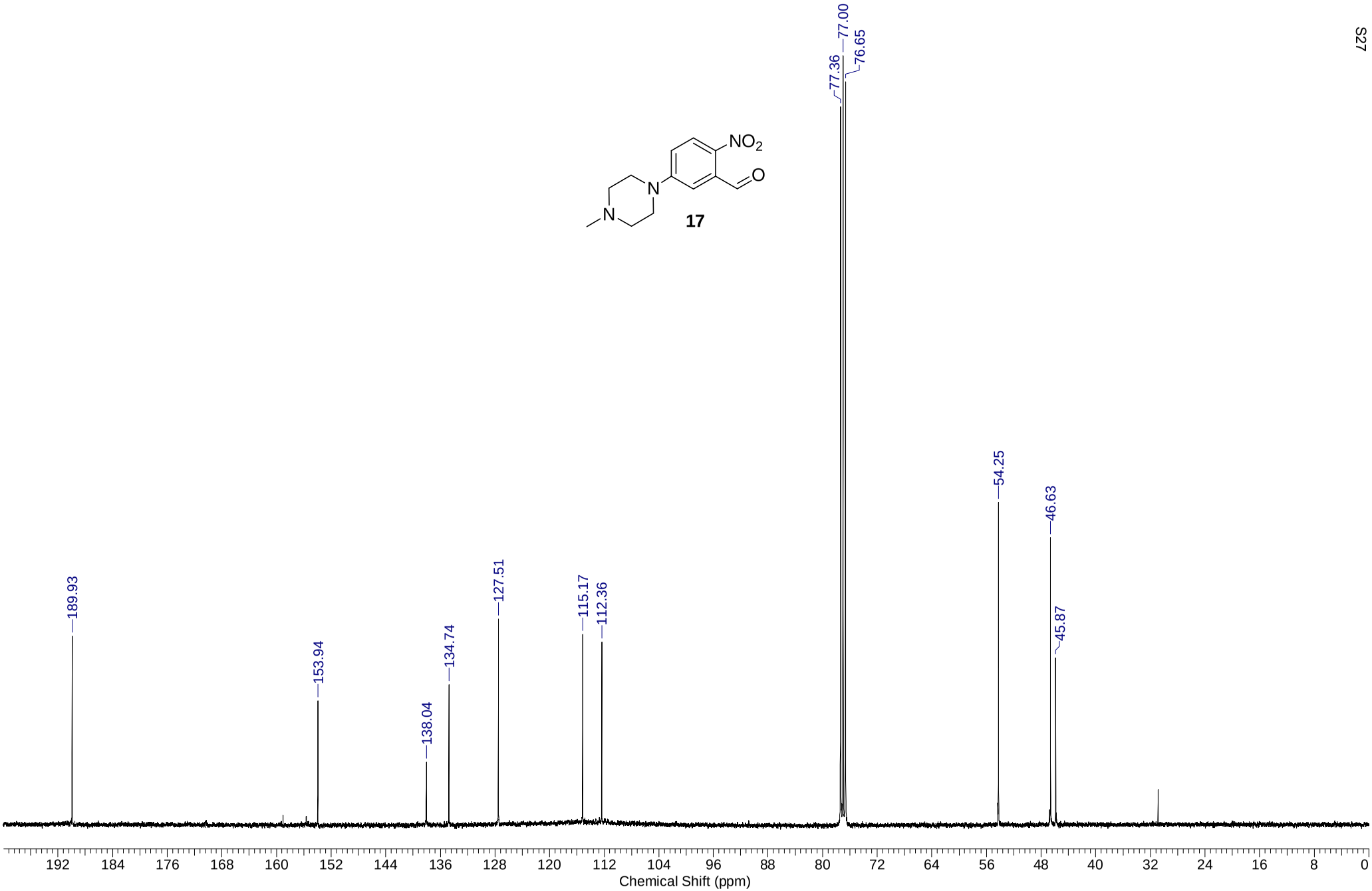
MR121

NO2
O
N
N

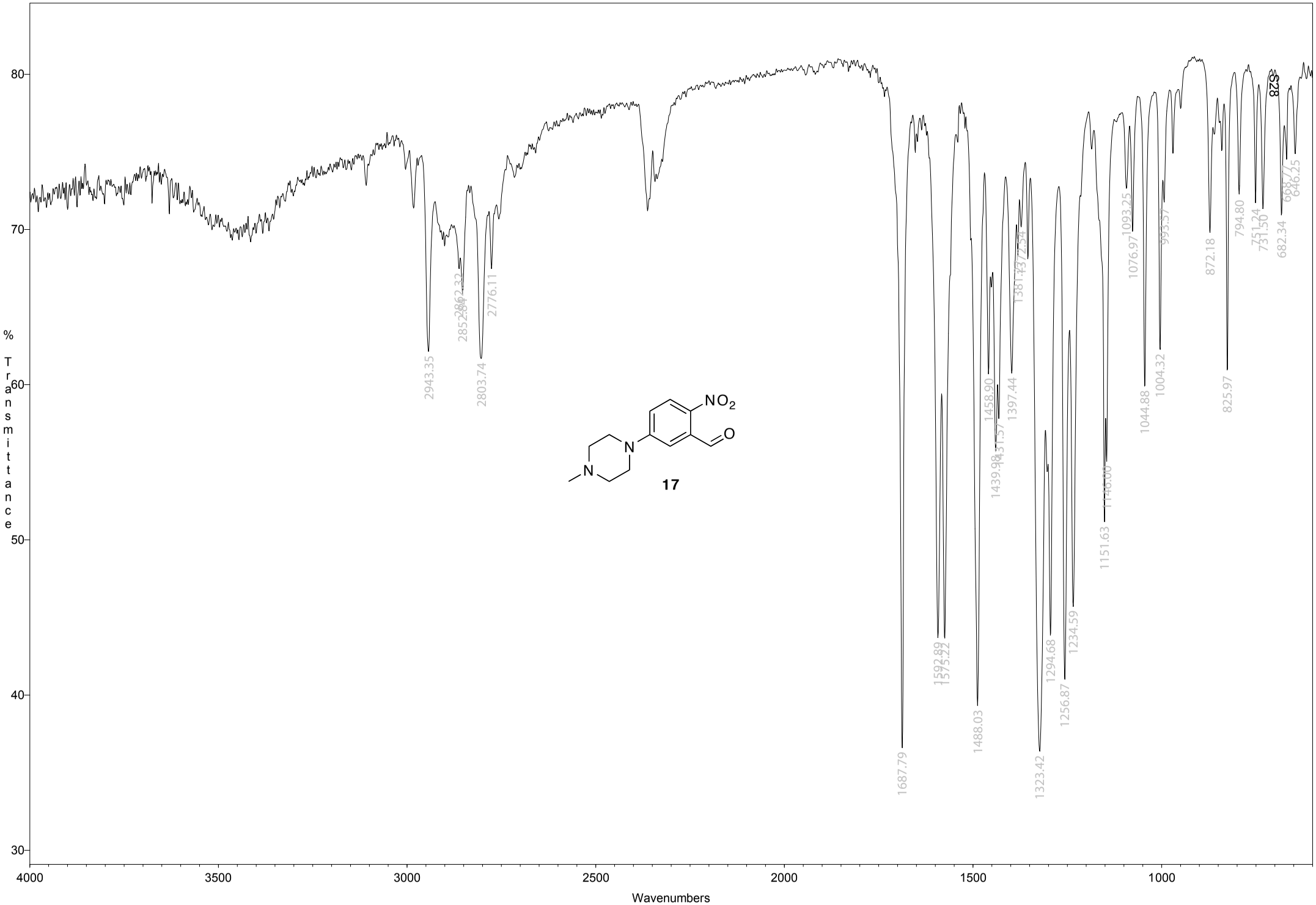
17


10.49
8.10
8.07
7.26
7.12
7.11
6.95
6.94
6.92
6.91
3.49
3.48
3.47
2.55
2.54
2.52
2.34
0.84
0.93
0.99
3.99
3.00
11.5
11.0
10.5
10.0
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
Chemical Shift (ppm)

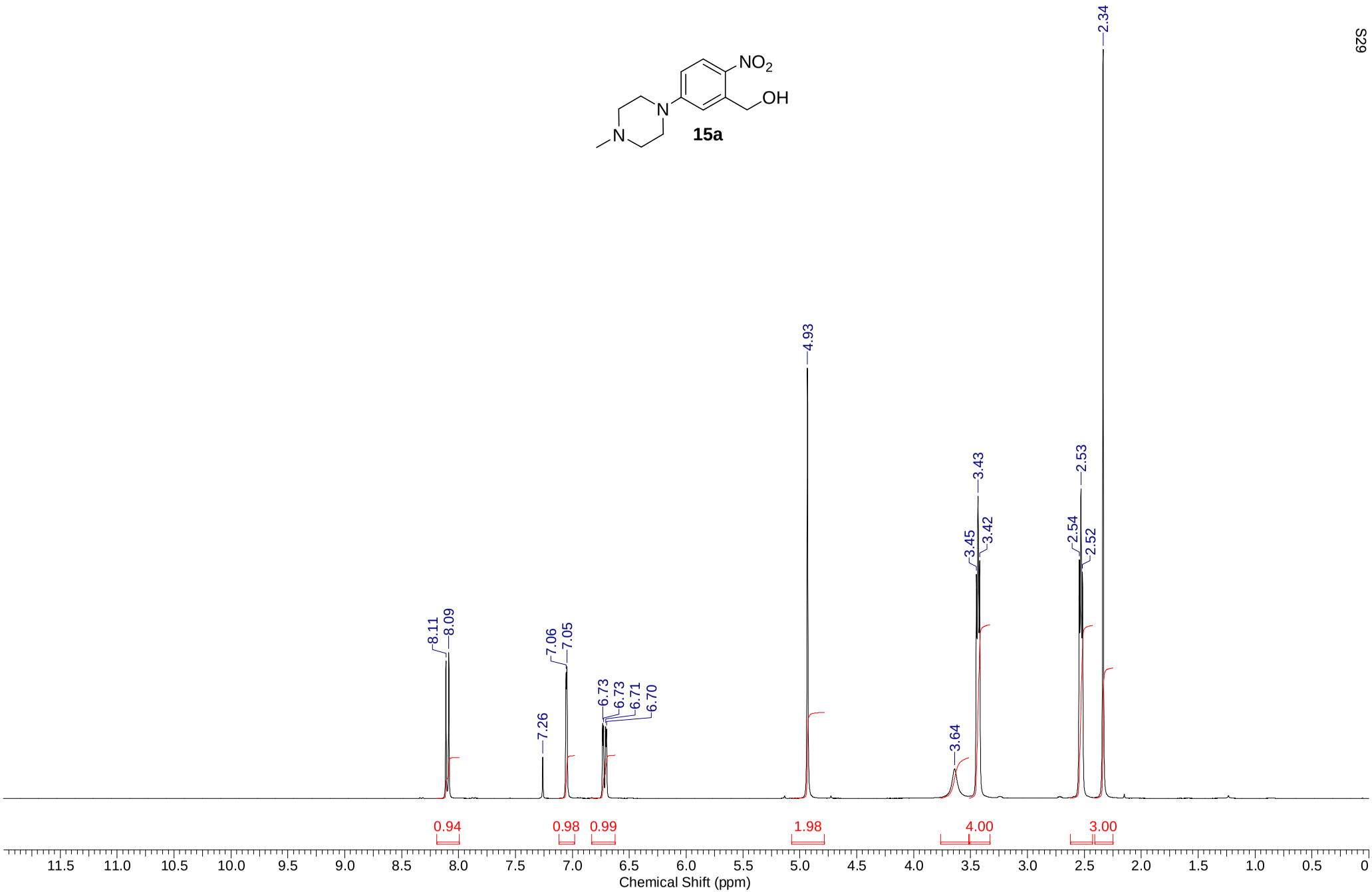
MR121


NO2
O
N
N
17
77.36
77.00
76.65
54.25
46.63
45.87
189.93
153.94
138.04
134.74
127.51
115.17
112.36
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

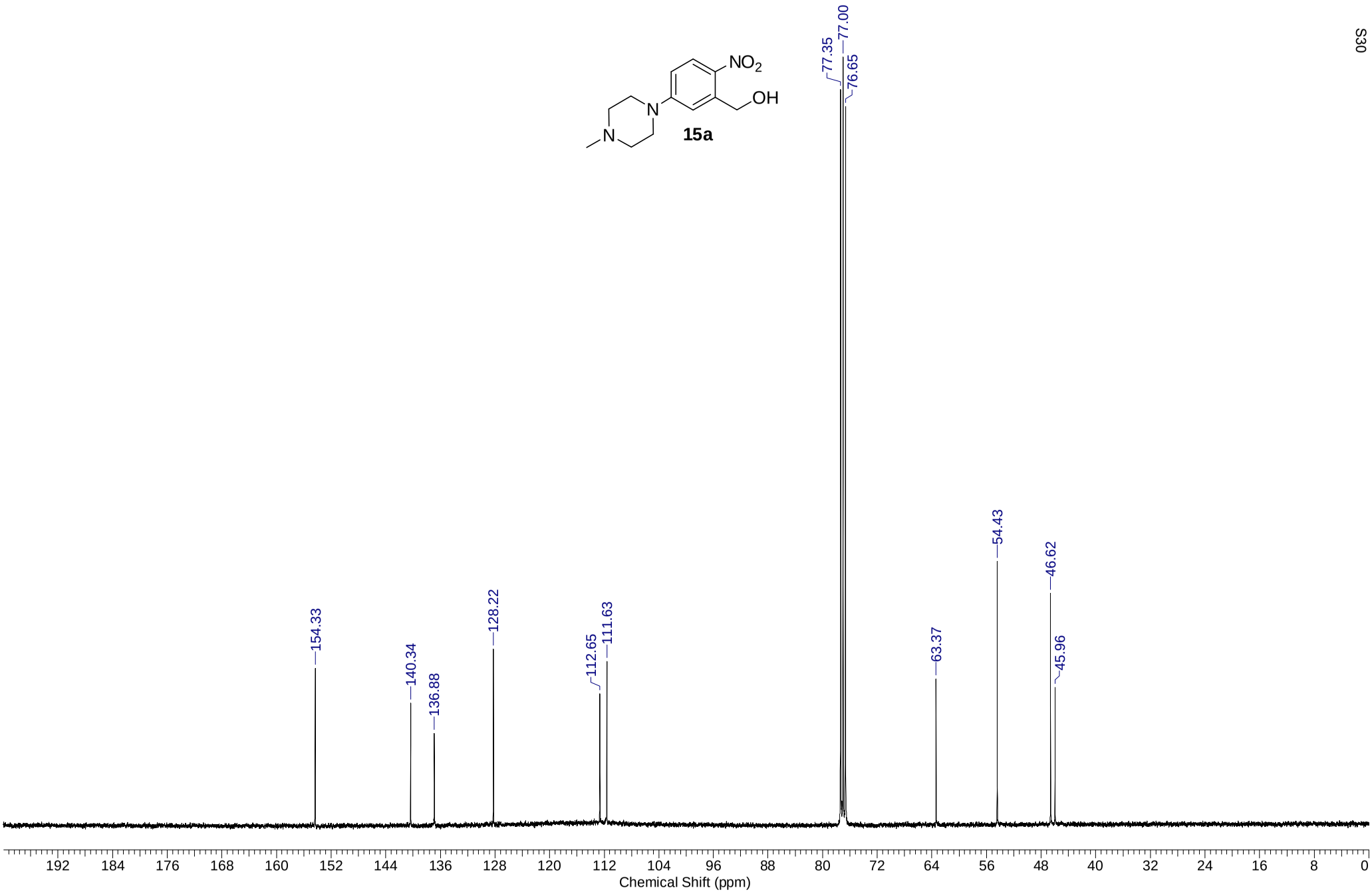
mr121

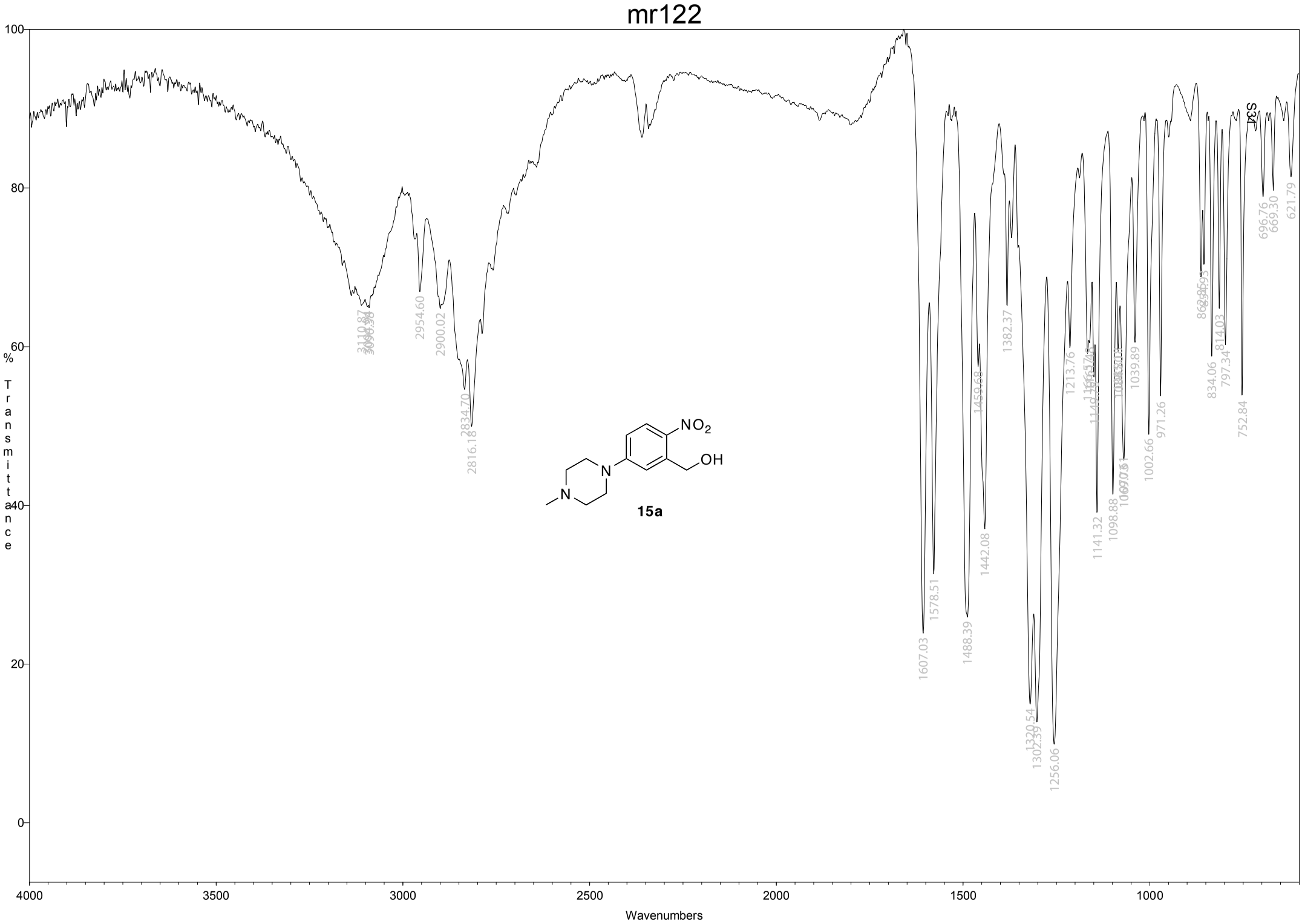

% Transmittance
Wavenumbers
4000
3500
3000
2500
2000
1500
1000
80
70
60
50
40
30
2943.35
2852.32
2803.74
2776.11
1687.79
1592.89
1575.22
1488.03
1458.90
1439.98
1397.44
1381.37
1372.54
1323.42
1294.68
1256.87
1234.59
1151.63
1146.00
1093.25
1076.97
1044.88
1004.32
993.57
872.18
825.97
794.80
751.24
731.50
682.34
668.77
646.25
528
NO_2
O
N
N
17

MR122


NO2
OH
N
N
15a
2.34
4.93
3.43
2.53
3.45
3.42
2.54
2.52
8.11
8.09
7.06
7.05
6.73
6.73
6.71
6.70
7.26
3.64
0.94
0.98
0.99
1.98
4.00
3.00
11.5
11.0
10.5
10.0
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
Chemical Shift (ppm)

MR122

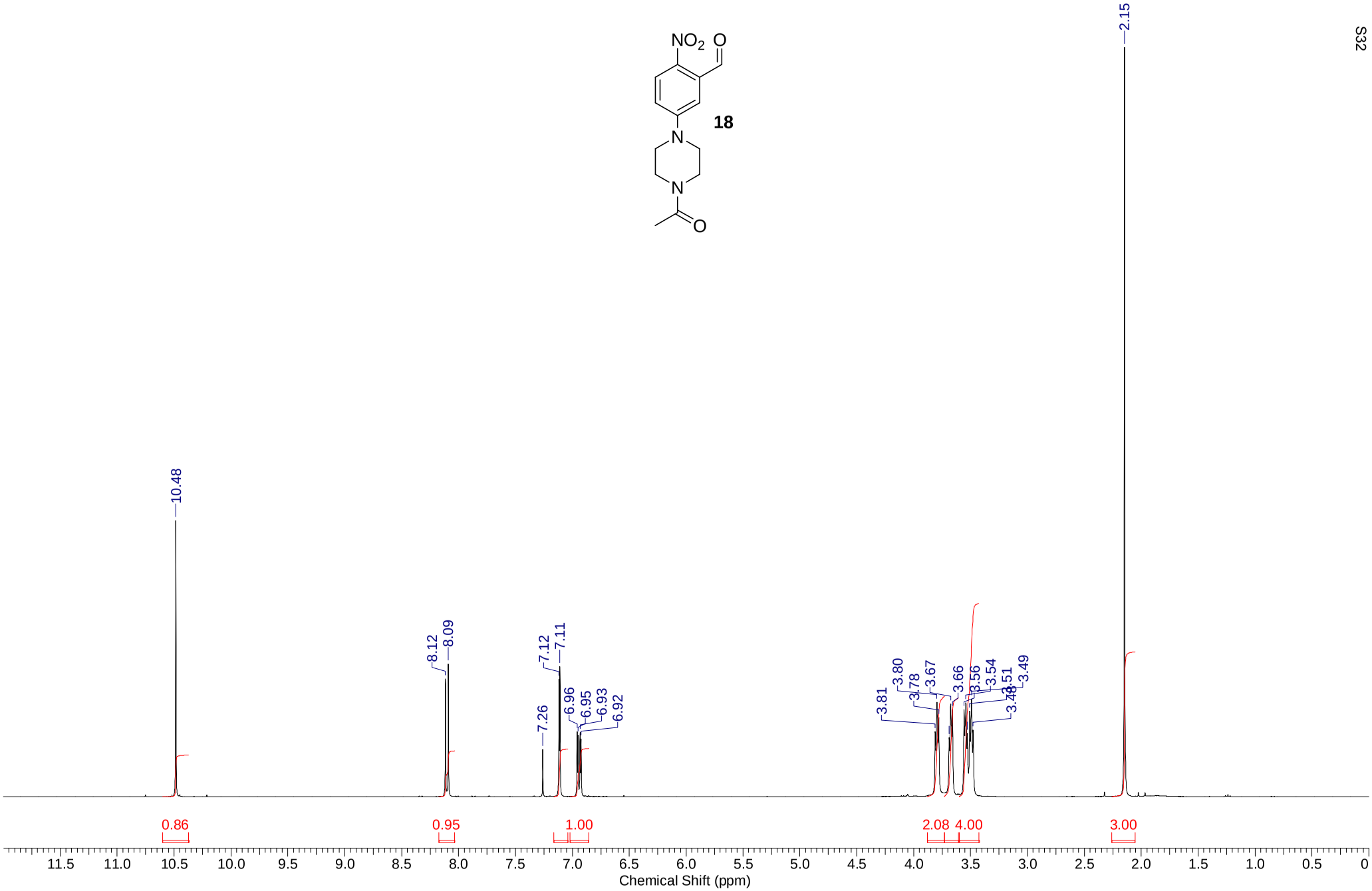

NO2
OH
N
N
15a
77.35
77.00
76.65
154.33
140.34
136.88
128.22
112.65
111.63
63.37
54.43
46.62
45.96
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


mr122
100
80
60
40
20
0
% Transmittance
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
3110.87
2954.60
2900.02
2834.70
2816.18
1607.03
1578.51
1488.39
1459.68
1442.08
1382.37
1320.54
1302.39
1256.06
1213.76
1141.32
1098.88
1039.89
1002.66
971.26
834.06
814.03
797.34
752.84
696.76
669.30
621.79
NO2
OH
N
N
15a
S34

MR138

NO2
O
N
N
O

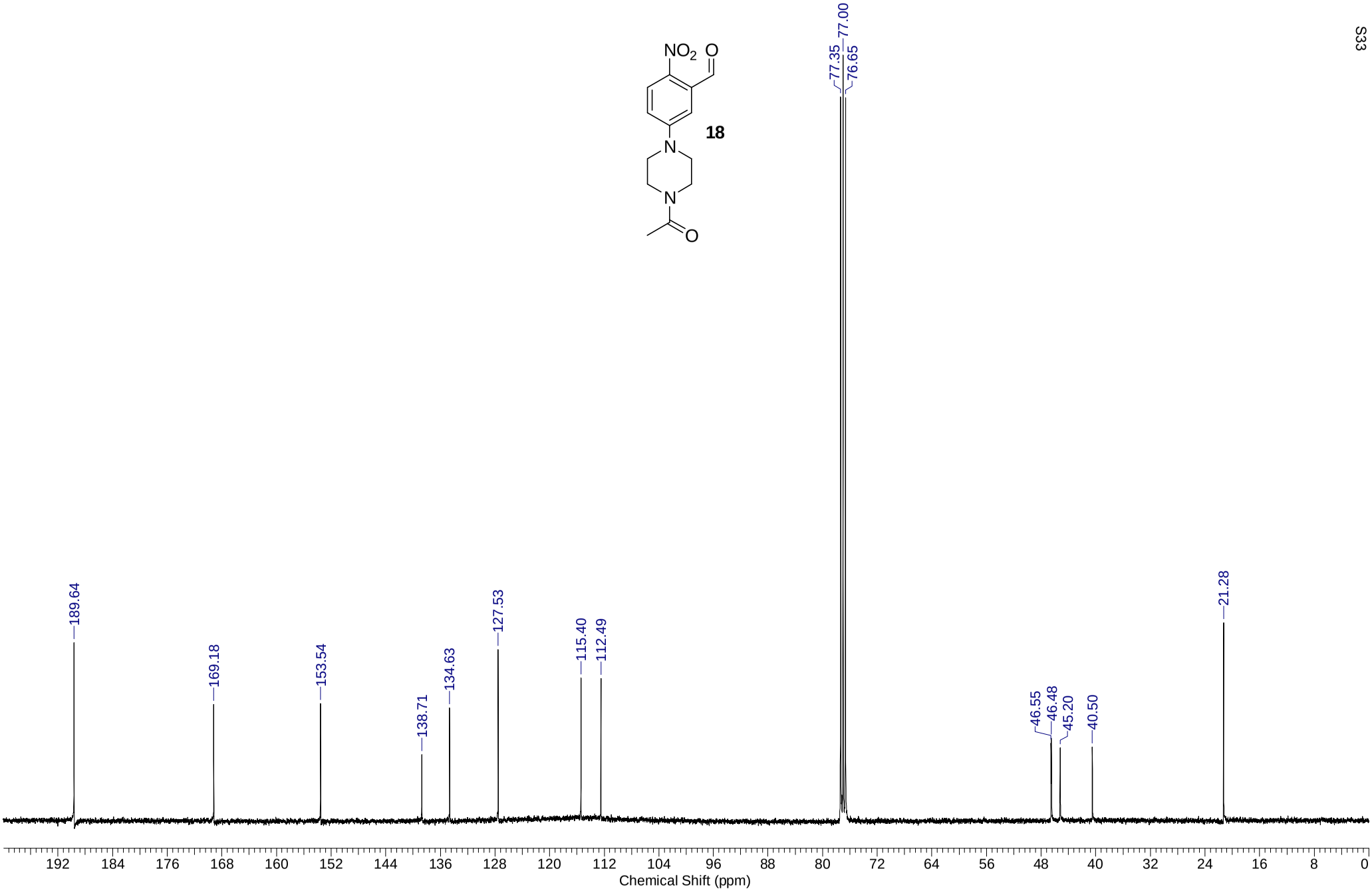
18


10.48
8.12
8.09
7.26
7.12
7.11
6.96
6.95
6.93
6.92
3.81
3.80
3.78
3.67
3.66
3.56
3.54
3.51
3.49
3.48
2.15
0.86
0.95
1.00
2.08
4.00
3.00
11.5
11.0
10.5
10.0
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
Chemical Shift (ppm)

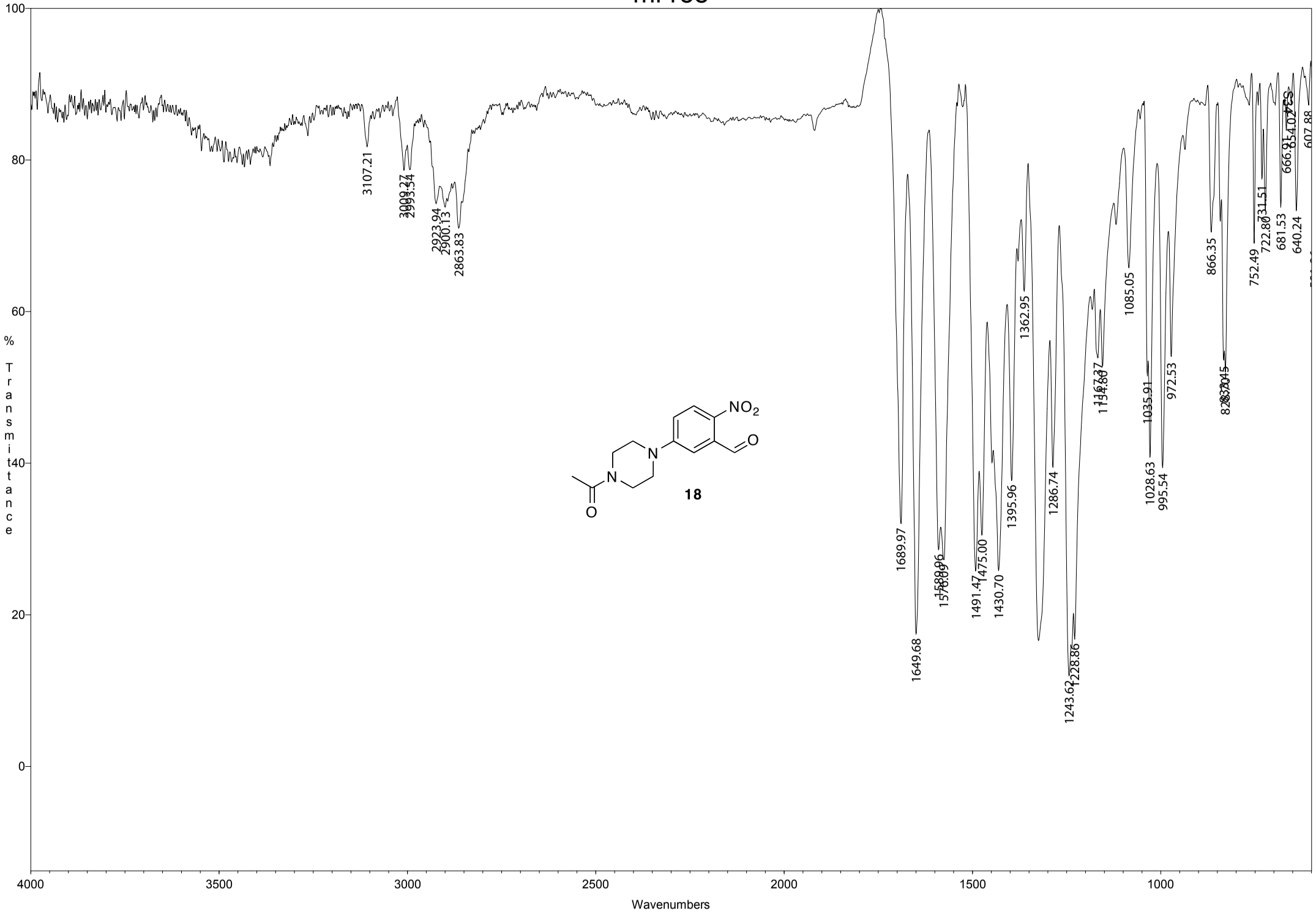
MR138

NO2
O
N
N
O

18


189.64
169.18
153.54
138.71
134.63
127.53
115.40
112.49
77.35
77.00
76.65
46.55
46.48
45.20
40.50
21.28
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

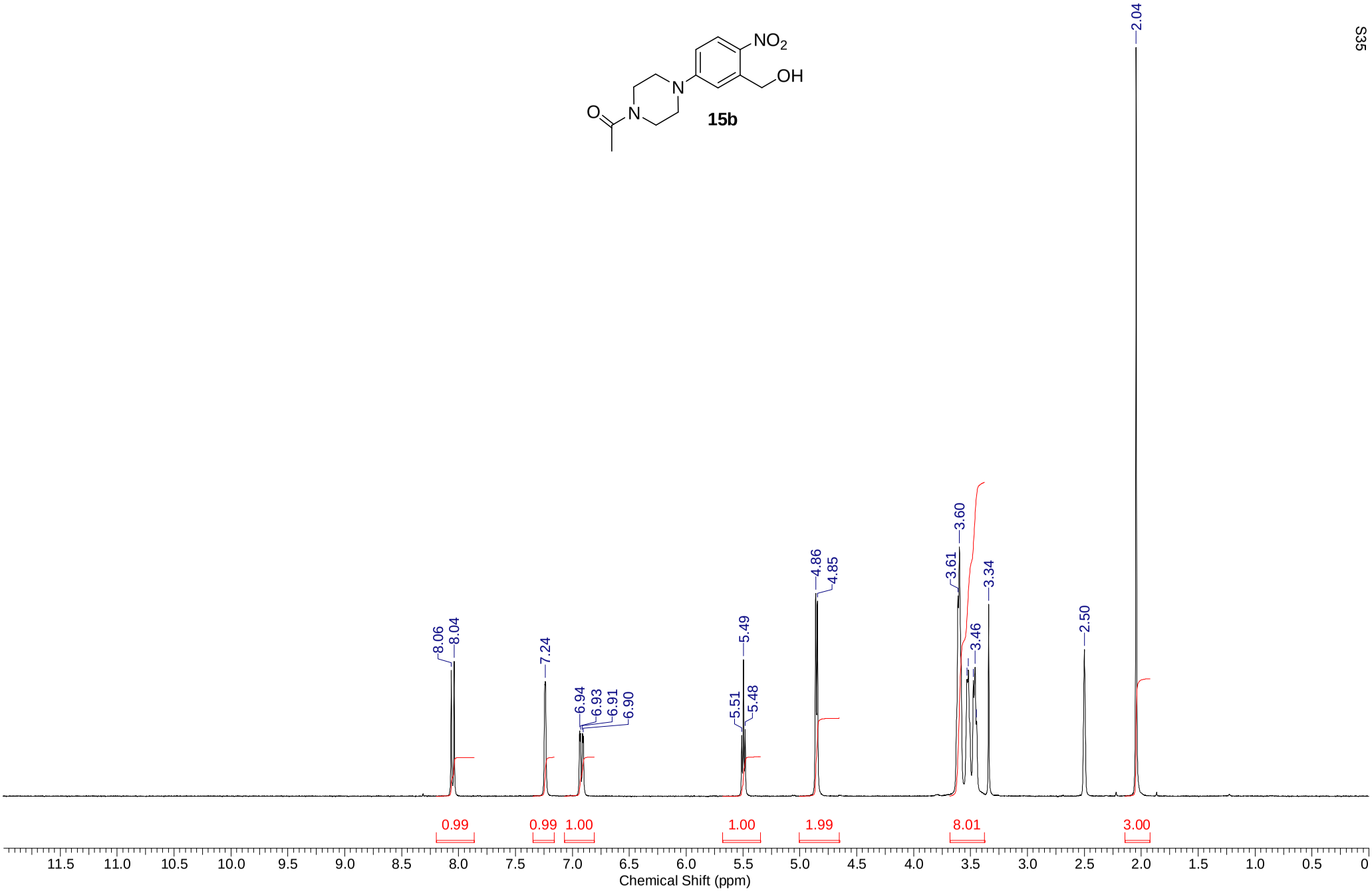
mr138


% Transmittance
Wavenumbers
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
3107.21
2923.94
2900.13
2863.83
1689.97
1649.68
1491.47
1475.00
1430.70
1395.96
1362.95
1286.74
1243.62
1228.86
1085.05
1035.91
1028.63
995.54
972.53
866.35
752.49
722.80
681.53
640.24
607.88
NO2
O
N
N
O
18

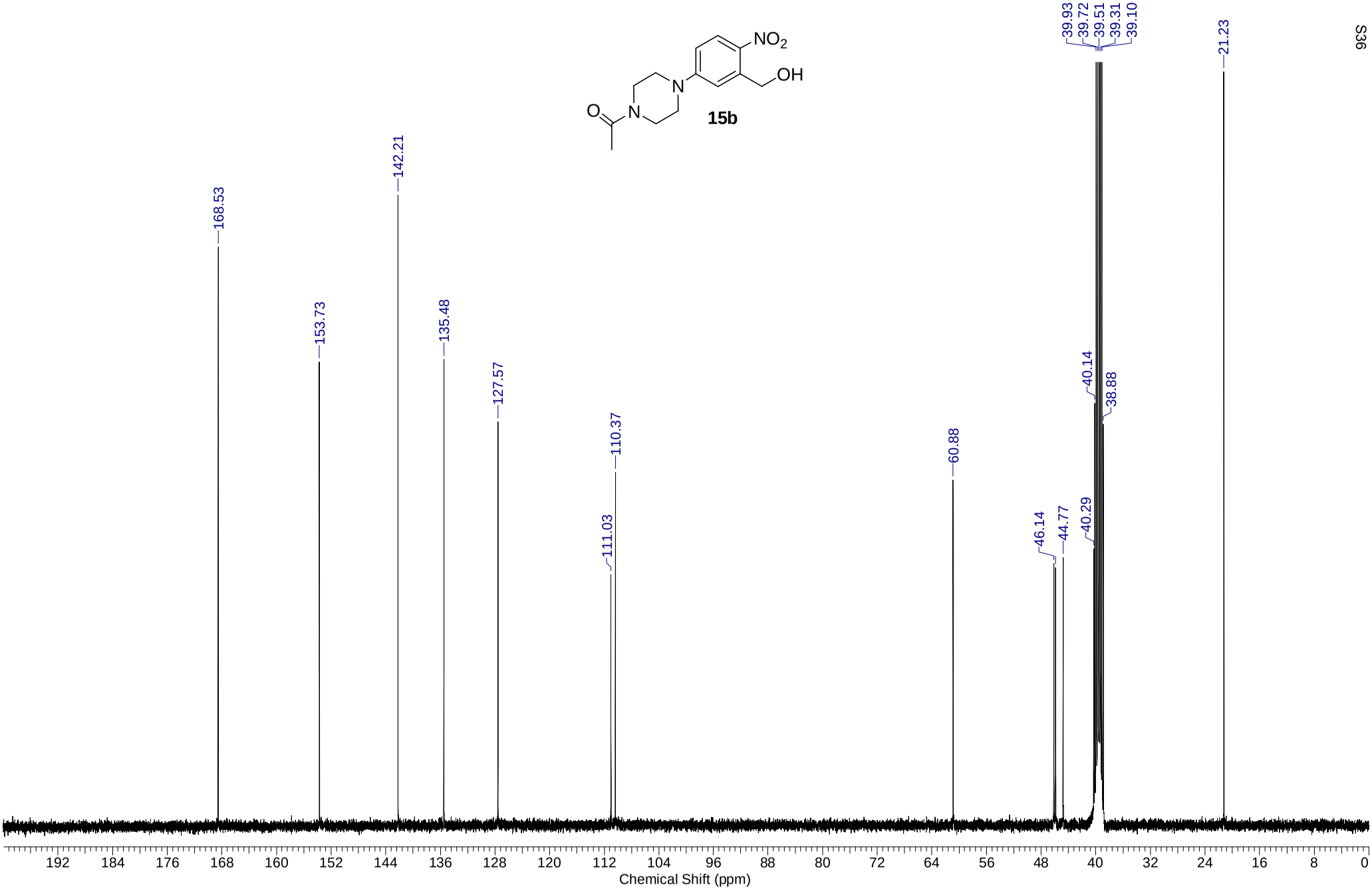
MR141

NO2
OH
N
N
O

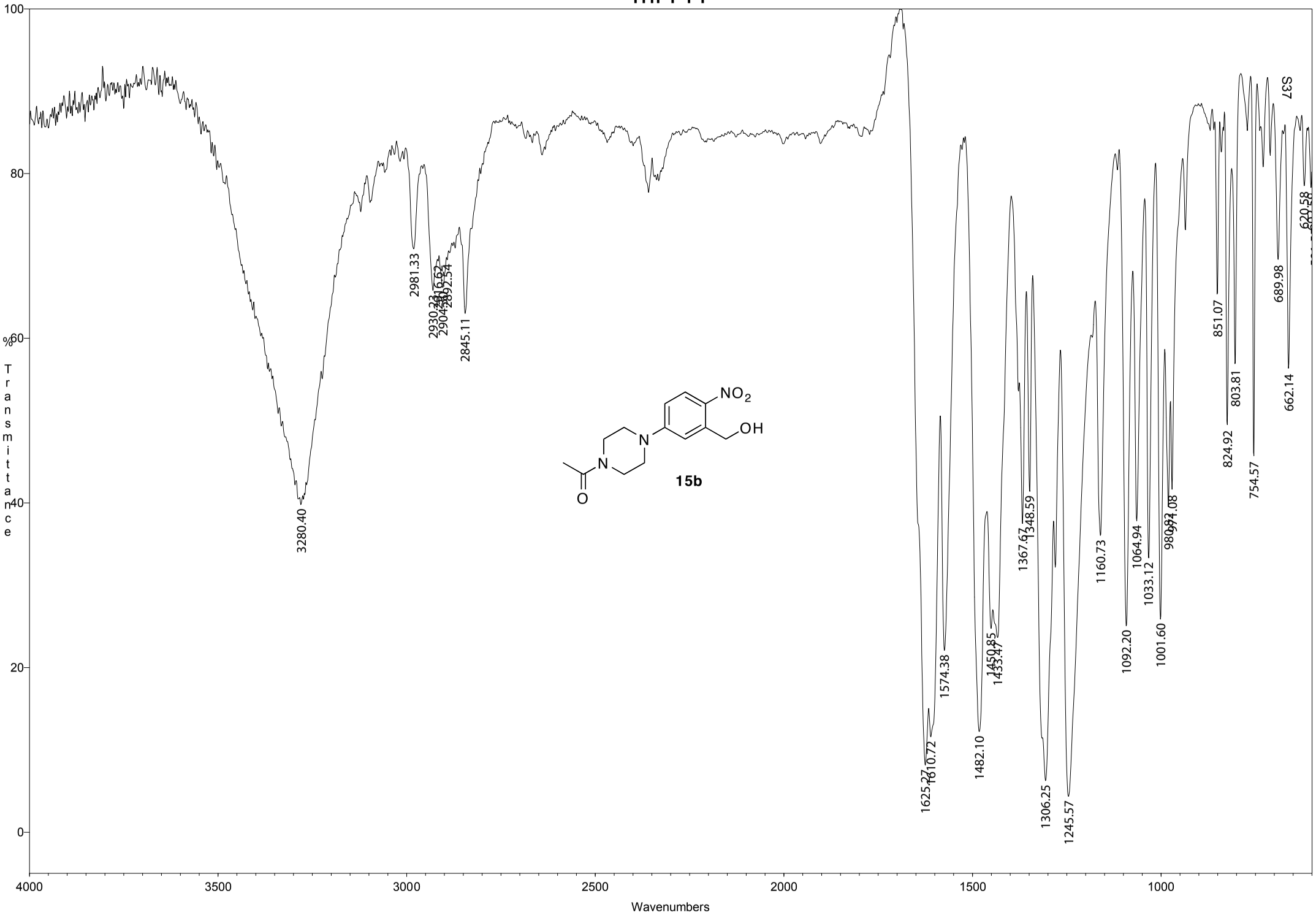
15b


8.06
8.04
7.24
6.94
6.93
6.91
6.90
5.51
5.49
5.48
4.86
4.85
3.61
3.60
3.46
3.34
2.50
2.04
0.99
0.99
1.00
1.00
1.99
8.01
3.00
11.5
11.0
10.5
10.0
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
Chemical Shift (ppm)

MR141

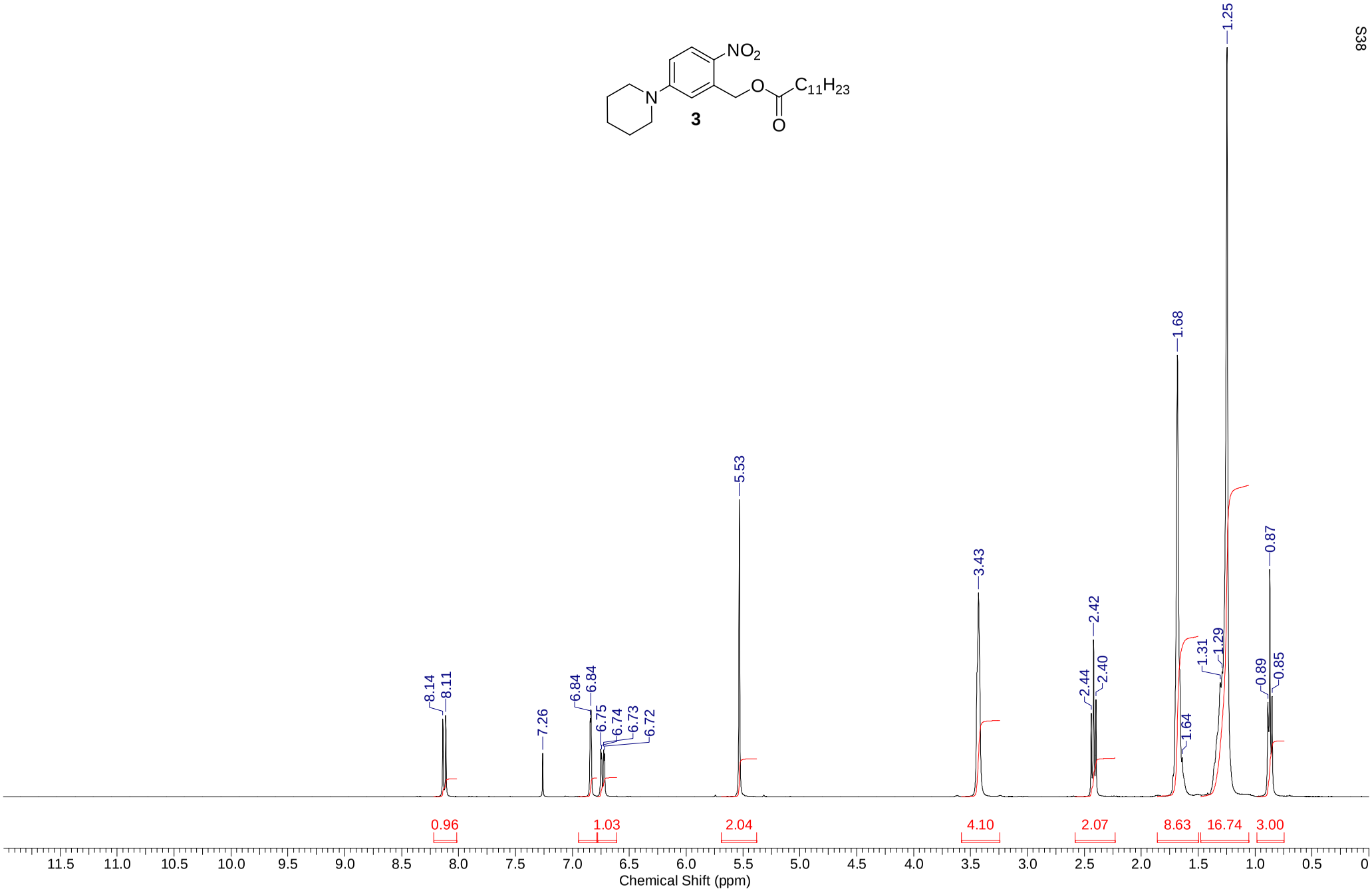

NO2
OH
N
N
O
15b
168.53
153.73
142.21
135.48
127.57
111.03
110.37
60.88
46.14
44.77
40.29
40.14
38.88
39.93
39.72
39.51
39.31
39.10
21.23
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

mr141


100
80
60
40
20
0
% Transmittance
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
3280.40
2981.33
2930.23
2904.54
2892.54
2845.11
1625.27
1610.72
1574.38
1482.10
1450.85
1433.47
1367.67
1348.59
1306.25
1245.57
1160.73
1092.20
1064.94
1033.12
1001.60
980.87
971.08
851.07
824.92
803.81
754.57
689.98
662.14
620.58
NO2
OH
N
N
O
15b

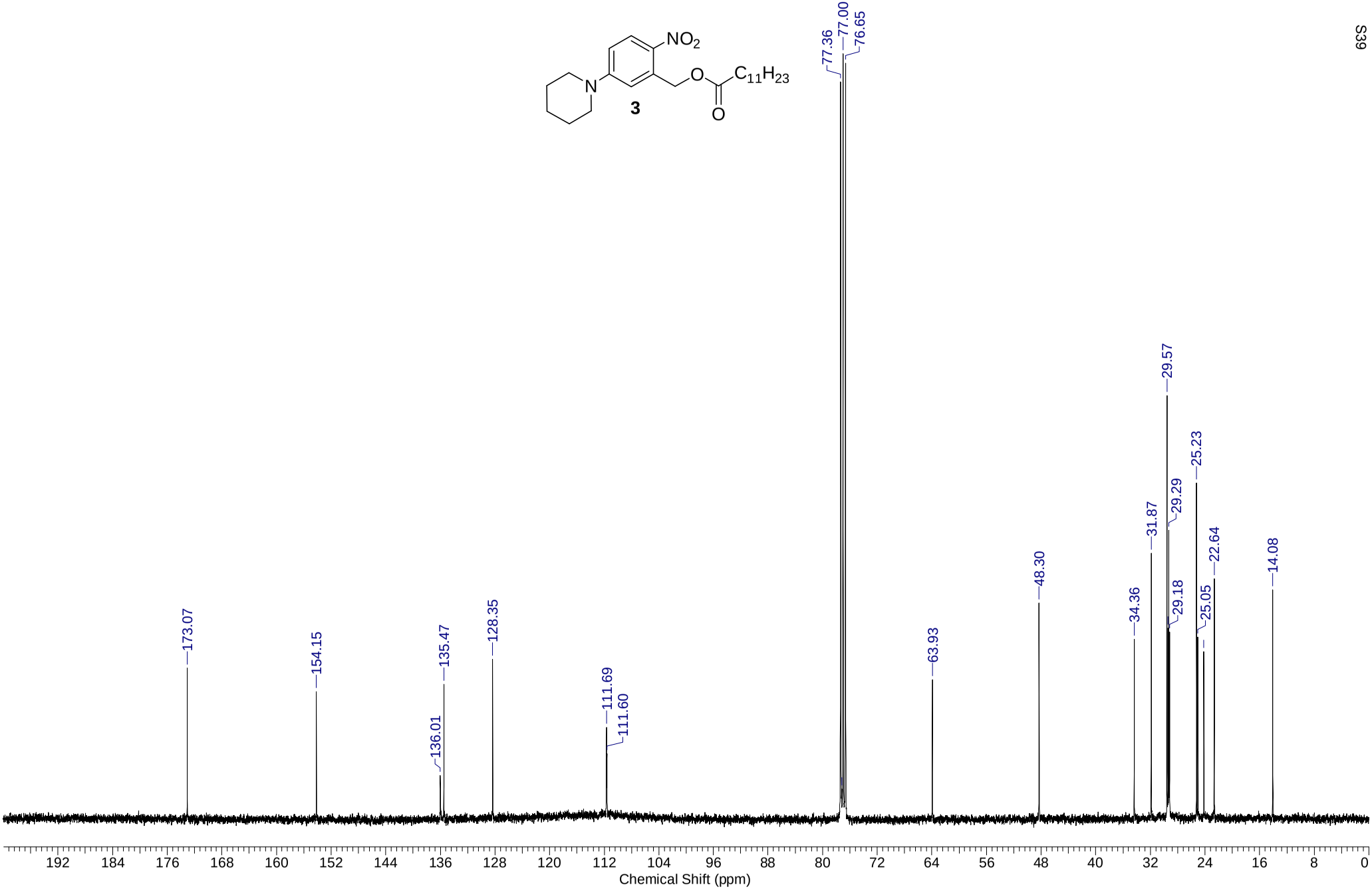
ER84

NO2
N
O
C11H23
O
3

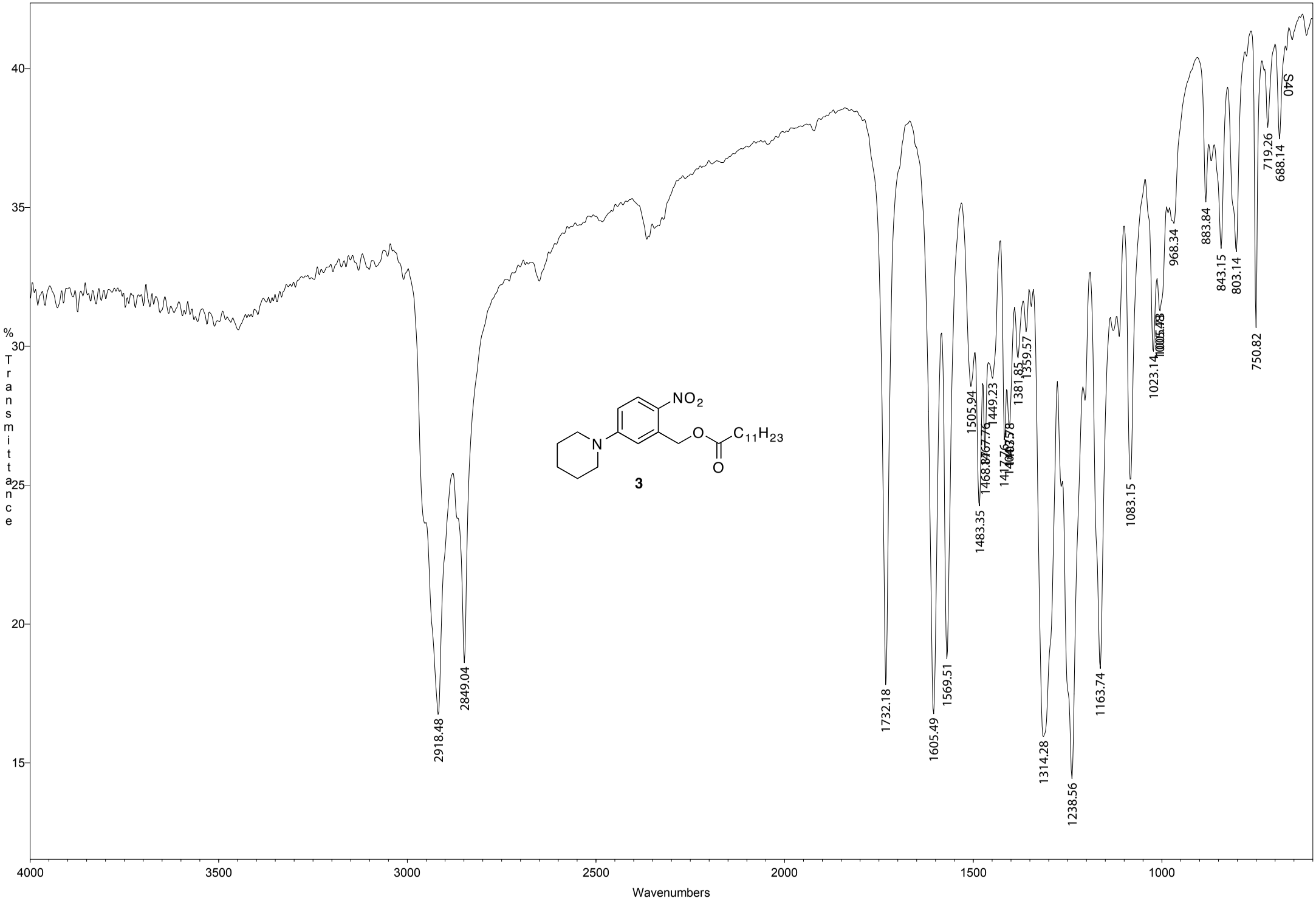

8.14
8.11
7.26
6.84
6.84
6.75
6.74
6.73
6.72
5.53
3.43
2.44
2.42
2.40
1.68
1.64
1.31
1.29
1.25
0.89
0.85
0.87
0.96
1.03
2.04
4.10
2.07
8.63
16.74
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

ER84

NO2
N
O
C11H23
O
3

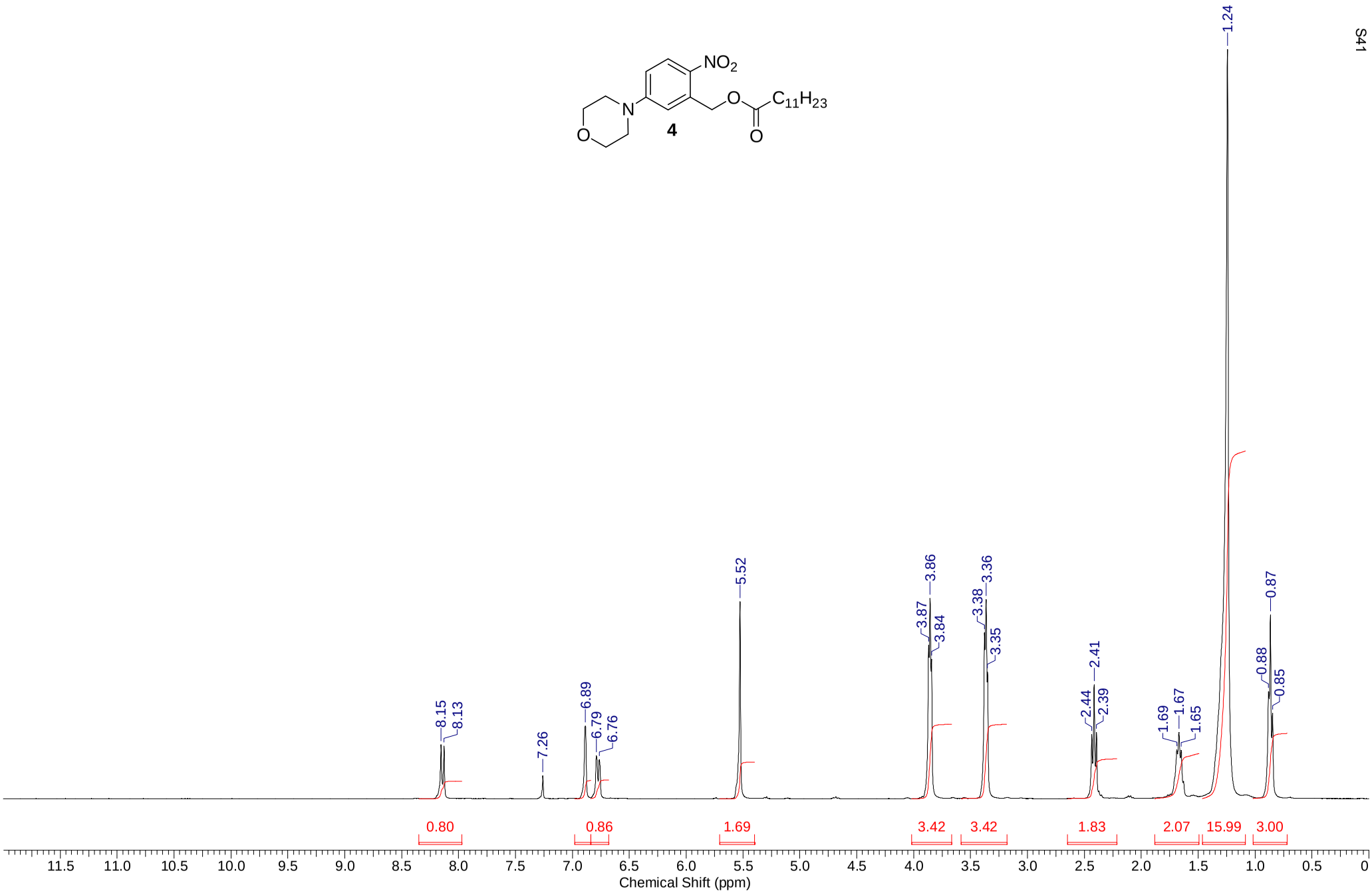

173.07
154.15
136.01
135.47
128.35
111.69
111.60
77.36
77.00
76.65
63.93
48.30
34.36
31.87
29.57
29.29
29.18
25.23
25.05
22.64
14.08
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

ER84


% Transmittance
Wavenumbers
4000
3500
3000
2500
2000
1500
1000
40
35
30
25
20
15
2918.48
2849.04
1732.18
1605.49
1569.51
1505.94
1483.35
1449.23
1381.85
1359.57
1314.28
1238.56
1163.74
1083.15
1023.14
968.34
883.84
843.15
803.14
750.82
719.26
688.14
NO2
N
O
C11H23
O
3

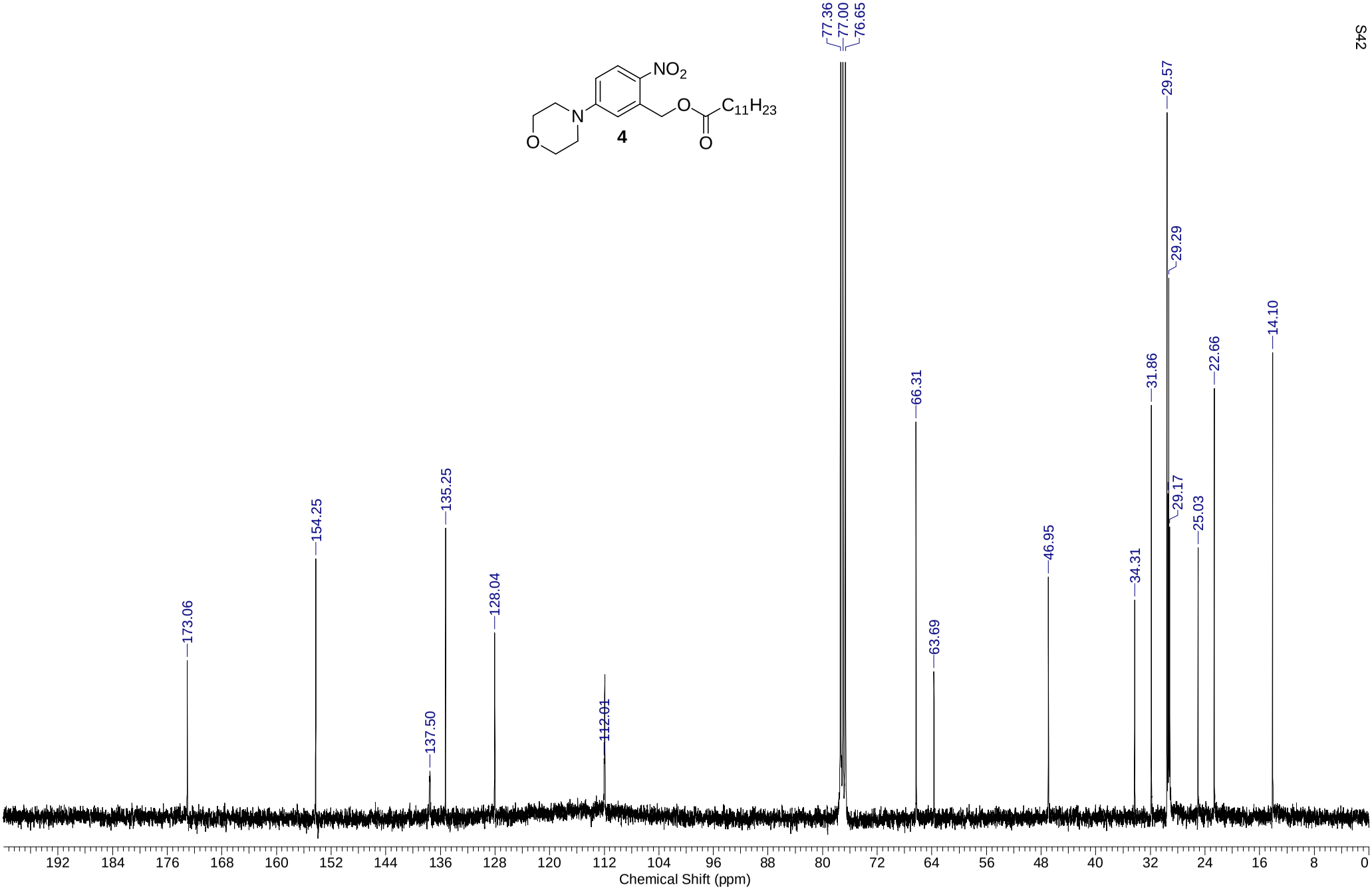
ER19

NO2
N
O
O
C11H23
O
4

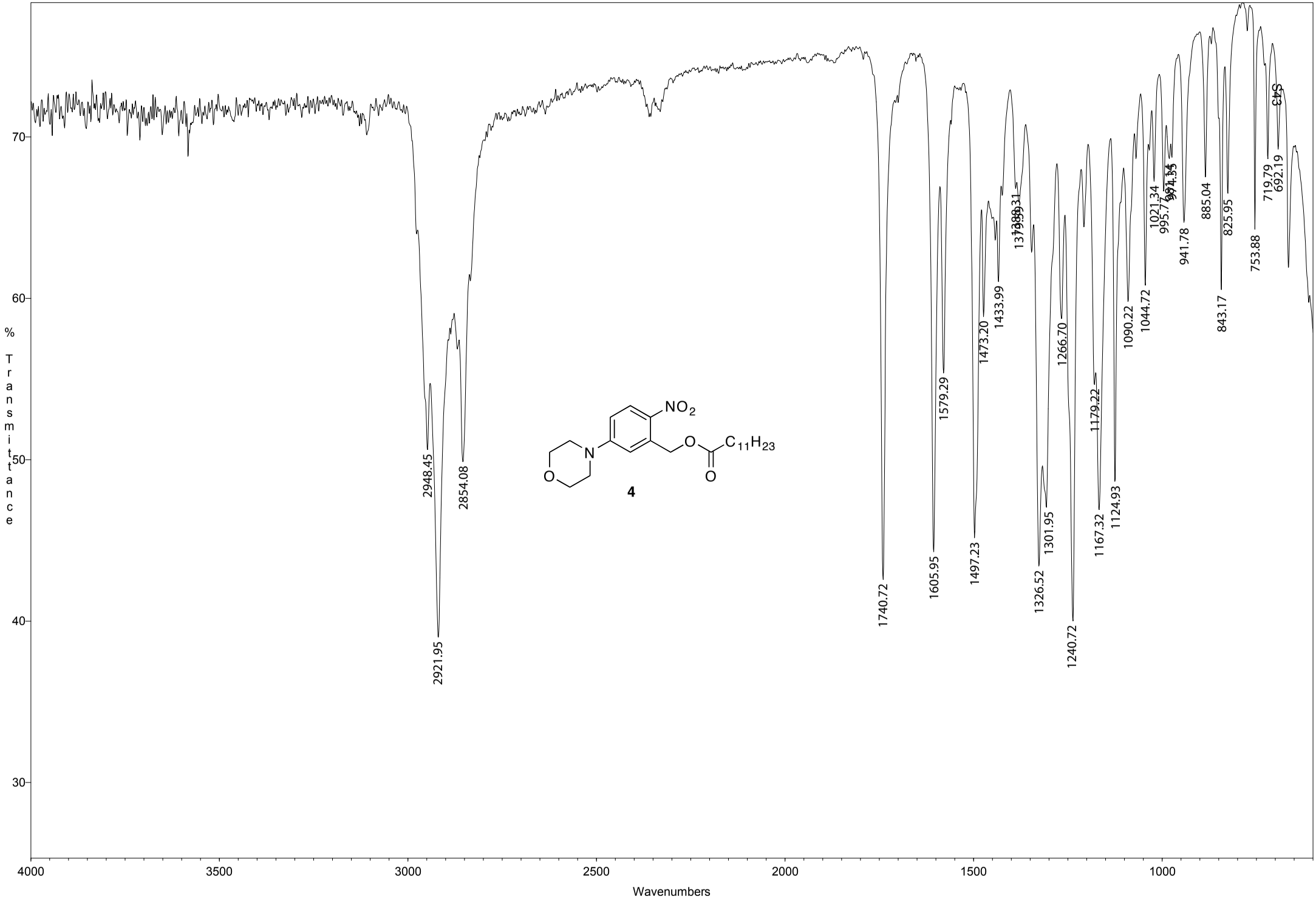

1.24
0.87
0.88
0.85
1.69
1.67
1.65
2.44
2.41
2.39
3.87
3.86
3.84
3.38
3.36
3.35
5.52
8.15
8.13
7.26
6.89
6.79
6.76
0.80
0.86
1.69
3.42
3.42
1.83
2.07
15.99
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

ER19

NO2
N
O
O
C11H23
O
4

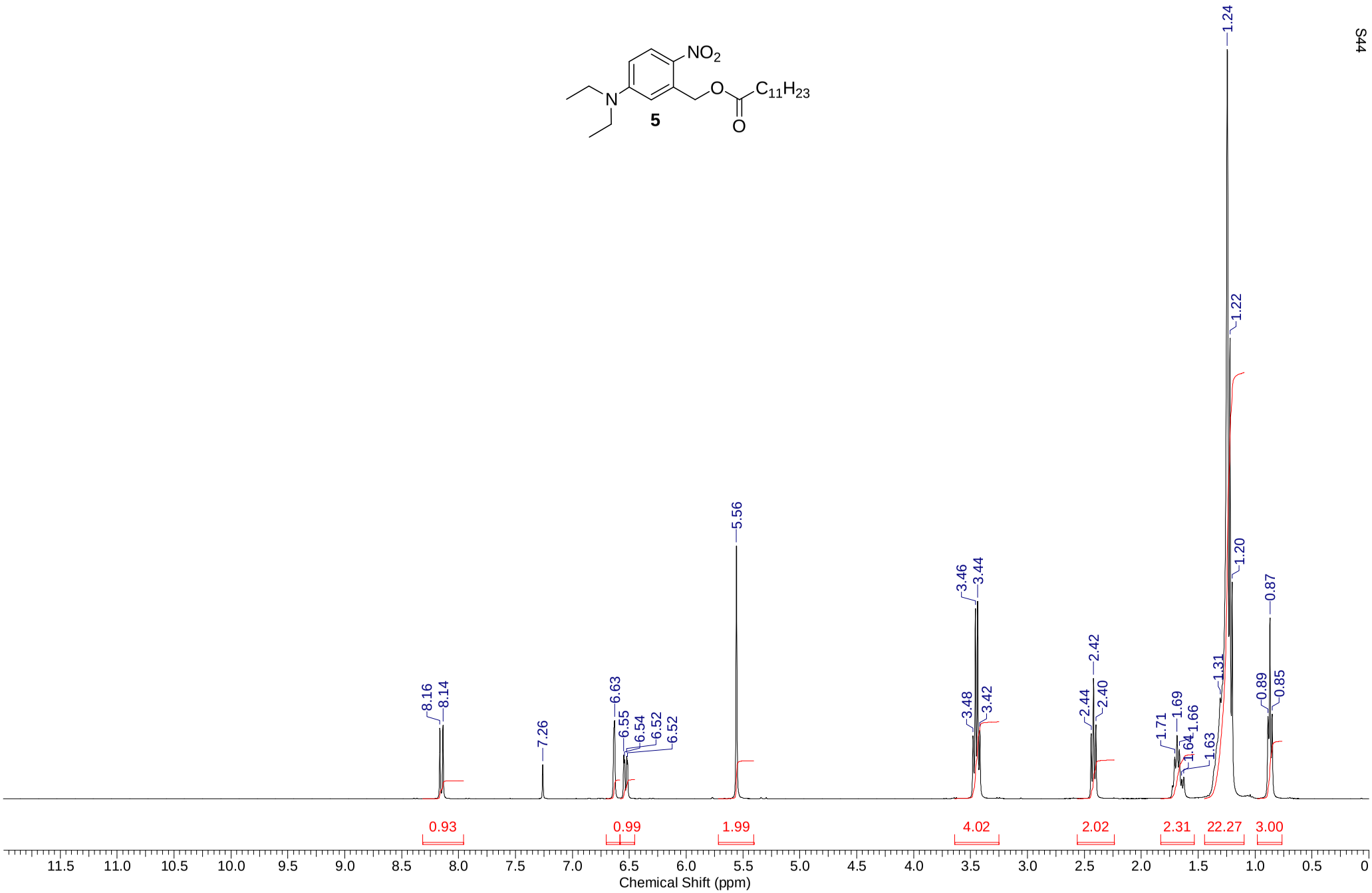

77.36
77.00
76.65
29.57
29.29
29.17
173.06
154.25
137.50
135.25
128.04
112.01
66.31
63.69
46.95
34.31
31.86
25.03
22.66
14.10
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

ER19


% Transmittance
Wavenumbers
4000
3500
3000
2500
2000
1500
1000
70
60
50
40
30
2948.45
2921.95
2854.08
1740.72
1605.95
1579.29
1497.23
1473.20
1433.99
1326.52
1301.95
1266.70
1240.72
1179.22
1167.32
1124.93
1090.22
1044.72
1021.34
941.78
885.04
843.17
825.95
753.88
719.79
692.19
NO2
N
O
O
C11H23
O
4

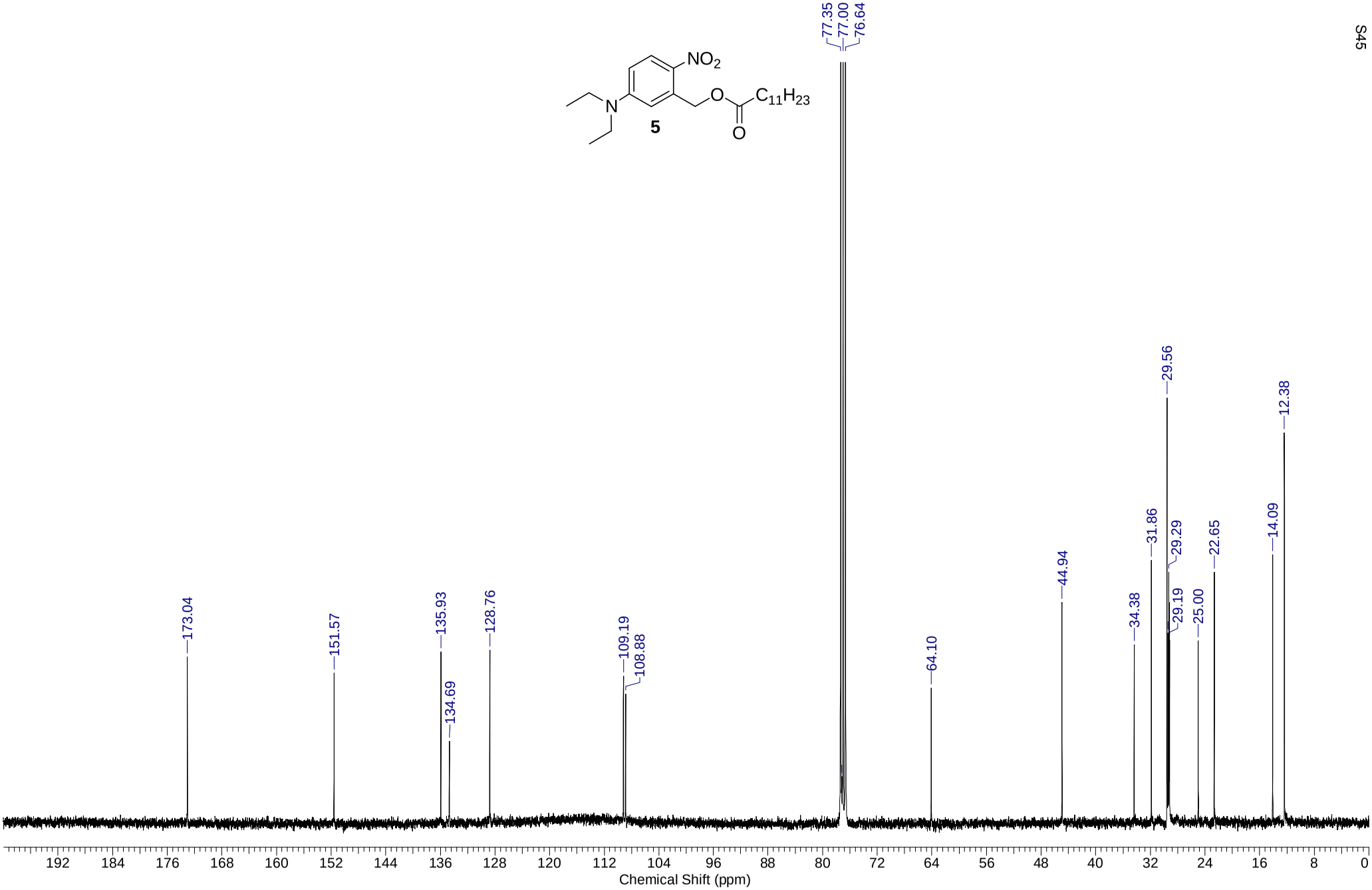
ER86

NO2
N
O
C11H23
O
5

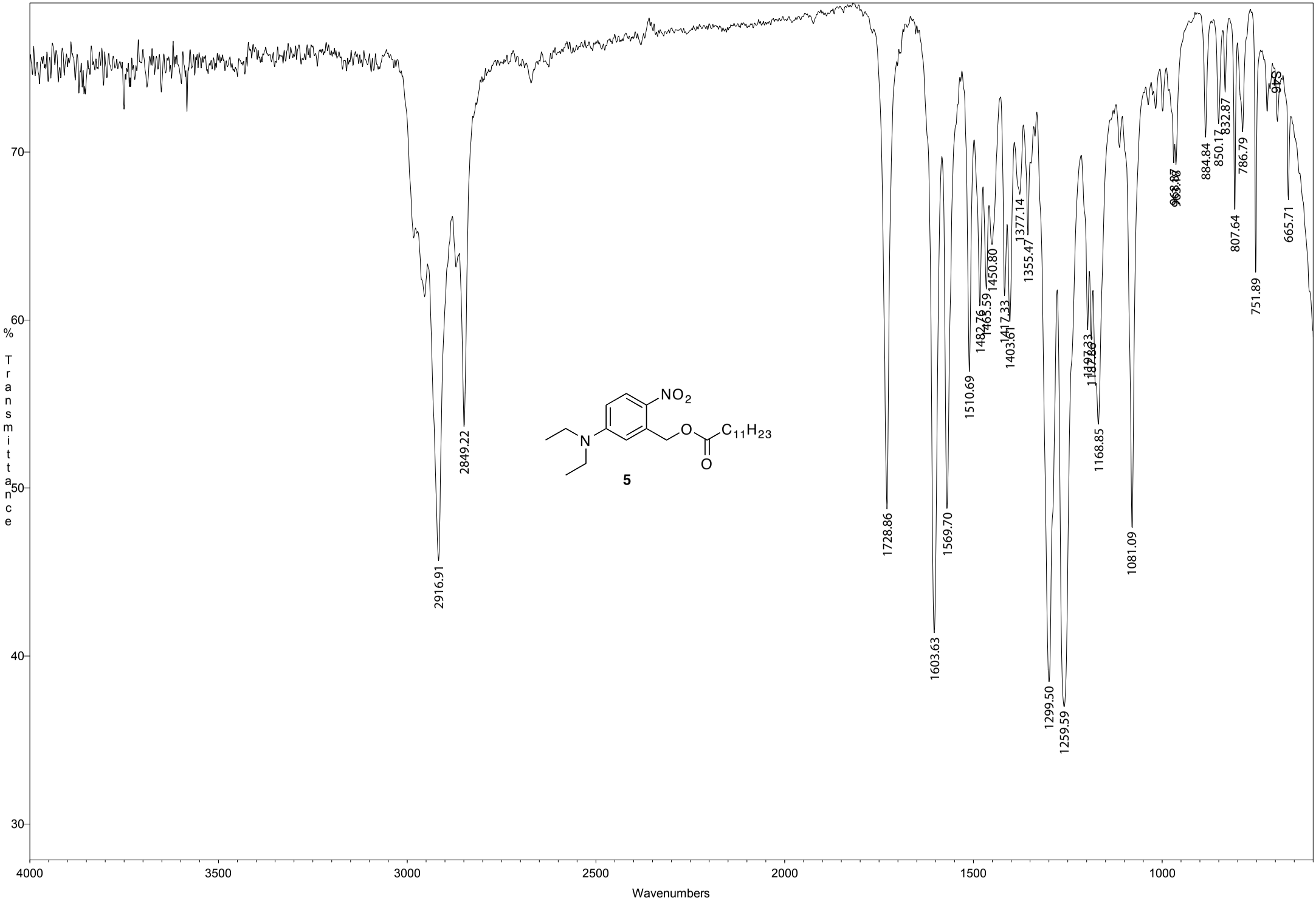

8.16
8.14
7.26
6.63
6.55
6.54
6.52
6.52
5.56
3.46
3.44
3.48
3.42
2.44
2.42
2.40
1.71
1.69
1.66
1.64
1.63
1.31
1.24
1.22
1.20
0.89
0.87
0.85
0.93
0.99
1.99
4.02
2.02
2.31
22.27
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

ER86

NO2
N
O
C11H23
O
5


173.04
151.57
135.93
134.69
128.76
109.19
108.88
77.35
77.00
76.64
64.10
44.94
34.38
31.86
29.56
29.29
29.19
25.00
22.65
14.09
12.38
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

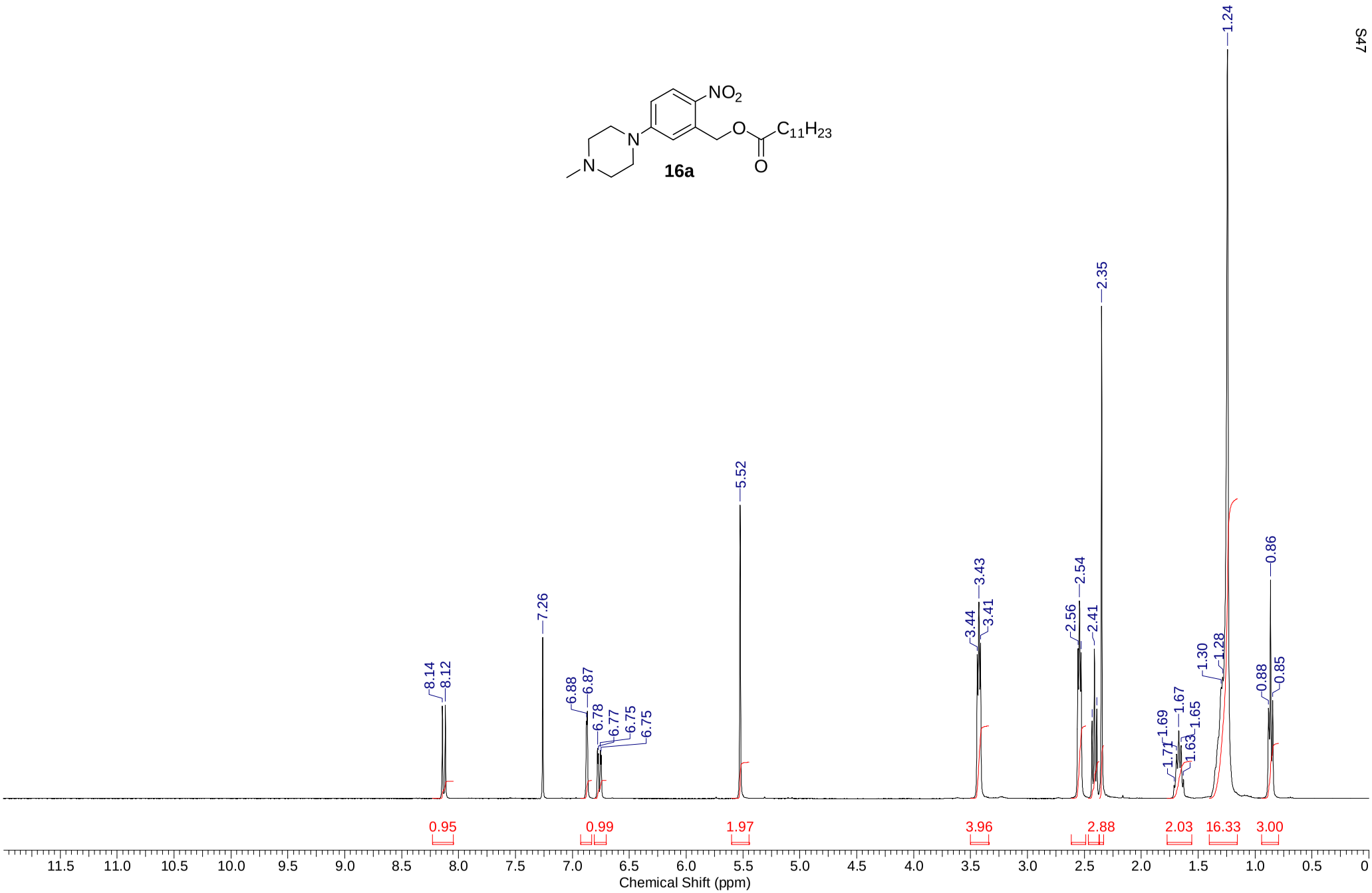
ER86


% Transmittance
Wavenumbers
4000
3500
3000
2500
2000
1500
1000
70
60
50
40
30
2916.91
2849.22
1728.86
1603.63
1569.70
1510.69
1482.76
1465.59
1450.80
1417.33
1403.61
1377.14
1355.47
1299.50
1259.59
1168.85
1081.09
884.84
850.17
832.87
807.64
786.79
751.89
665.71
NO2
N
O
C11H23
O
5

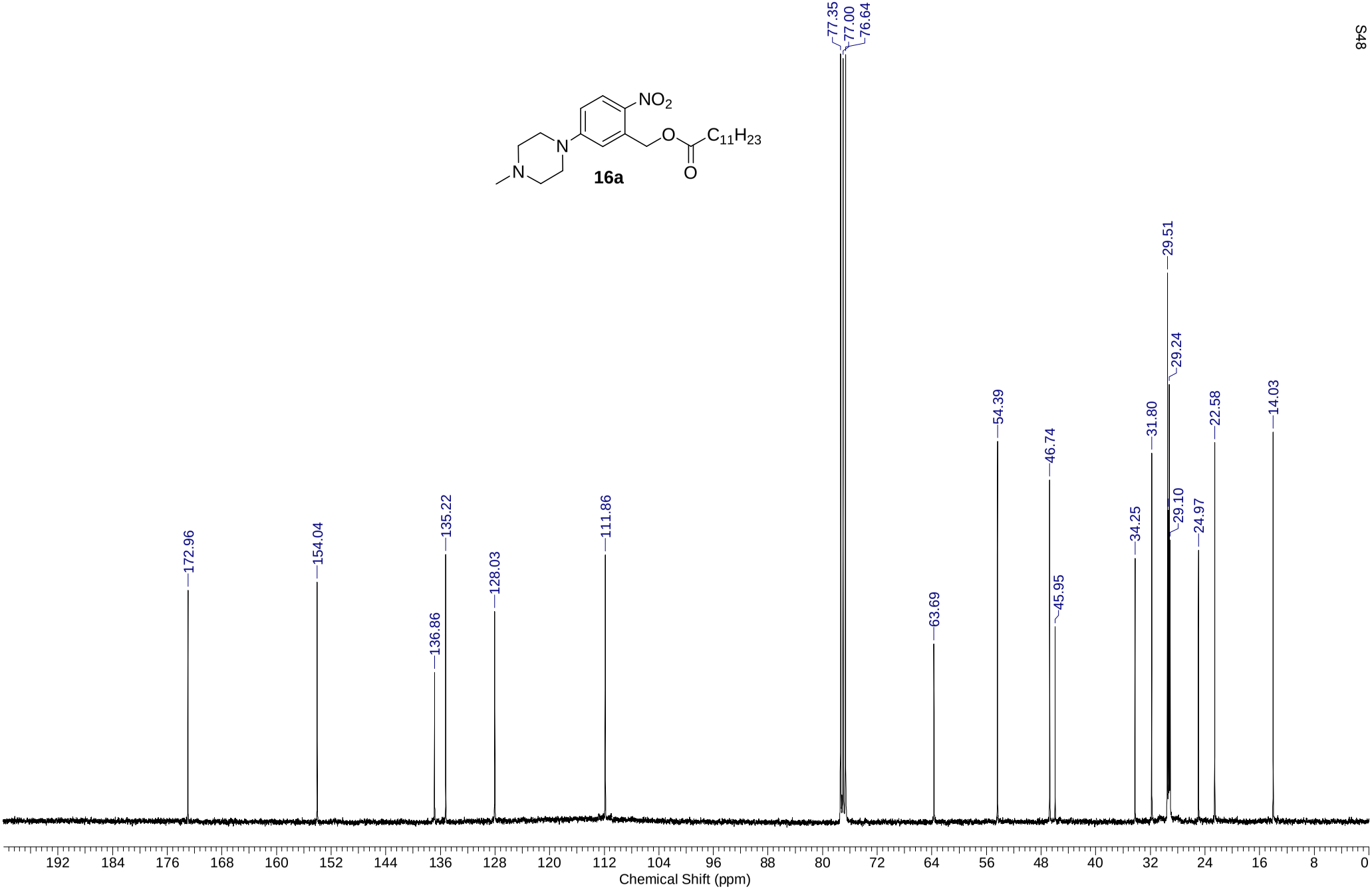
MR123

NO2
N
N
O
C11H23
O

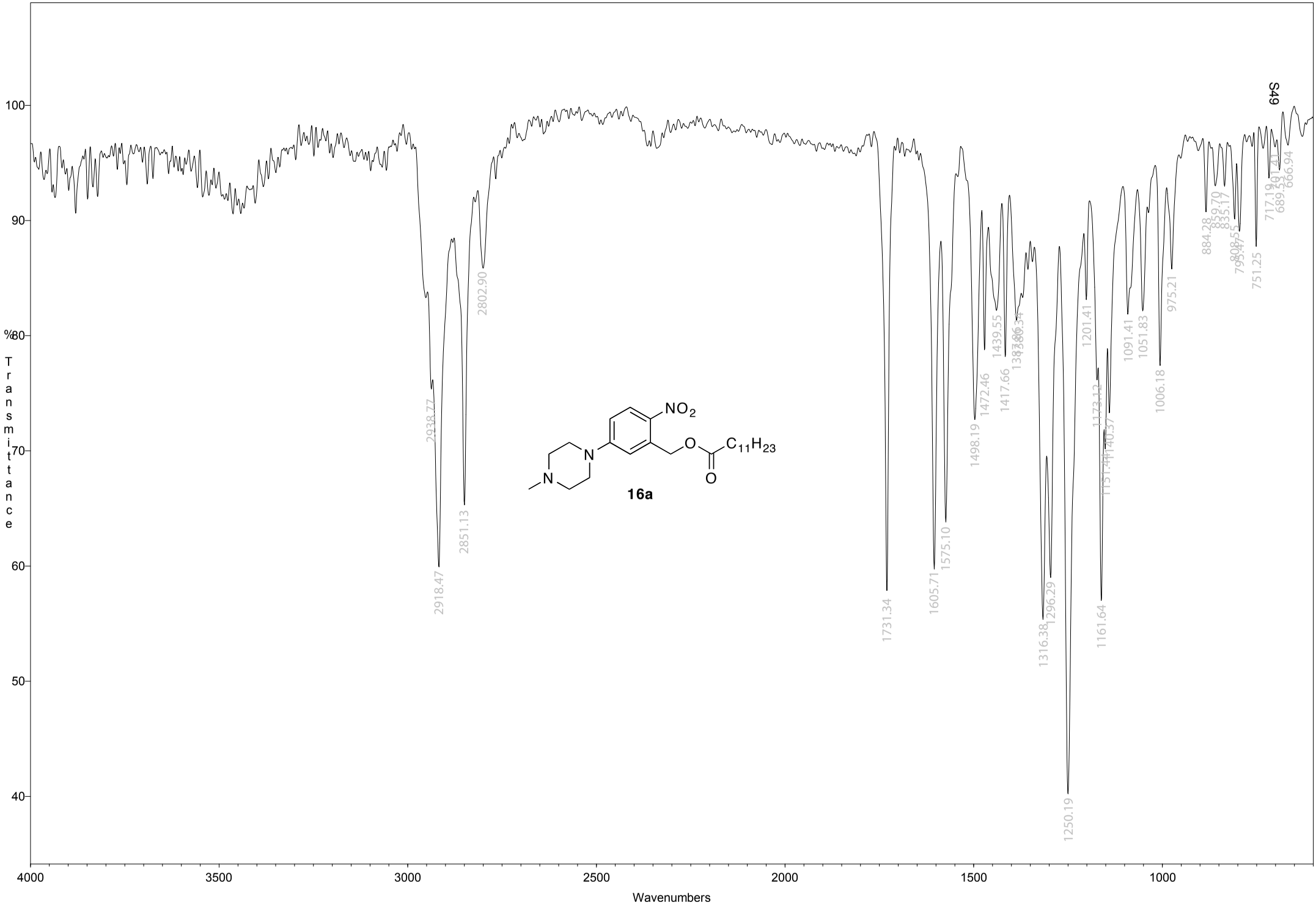
16a


8.14
8.12
7.26
6.88
6.87
6.78
6.77
6.75
6.75
5.52
3.44
3.43
3.41
2.56
2.54
2.41
2.35
1.71
1.69
1.67
1.65
1.63
1.30
1.28
1.24
0.88
0.86
0.85
0.95
0.99
1.97
3.96
2.88
2.03
16.33
3.00
11.5
11.0
10.5
10.0
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
Chemical Shift (ppm)

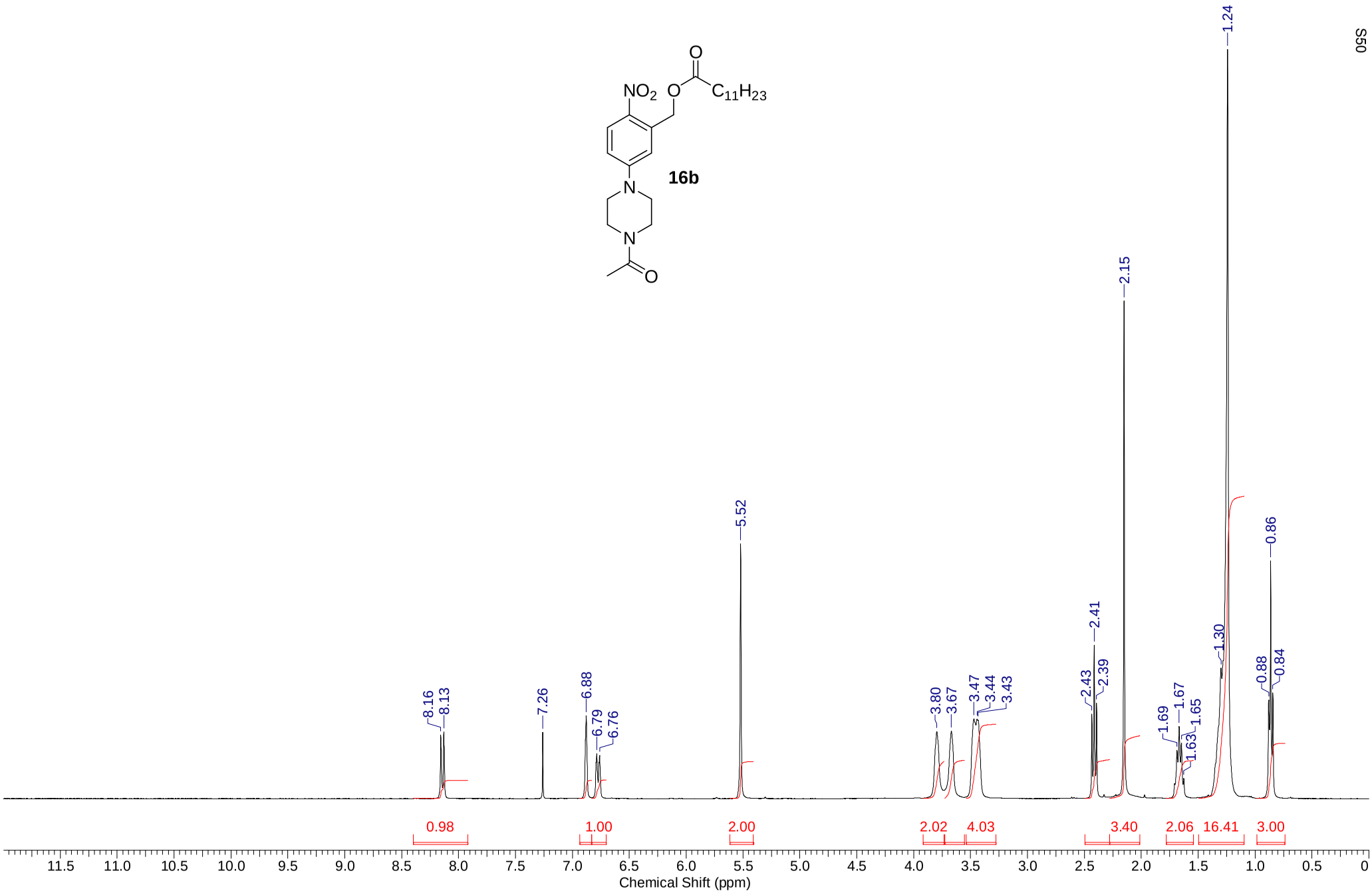
MR123


NO2
N
N
O
C11H23
O
16a
77.35
77.00
76.64
172.96
154.04
136.86
135.22
128.03
111.86
63.69
54.39
46.74
45.95
34.25
31.80
29.51
29.24
29.10
24.97
22.58
14.03
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

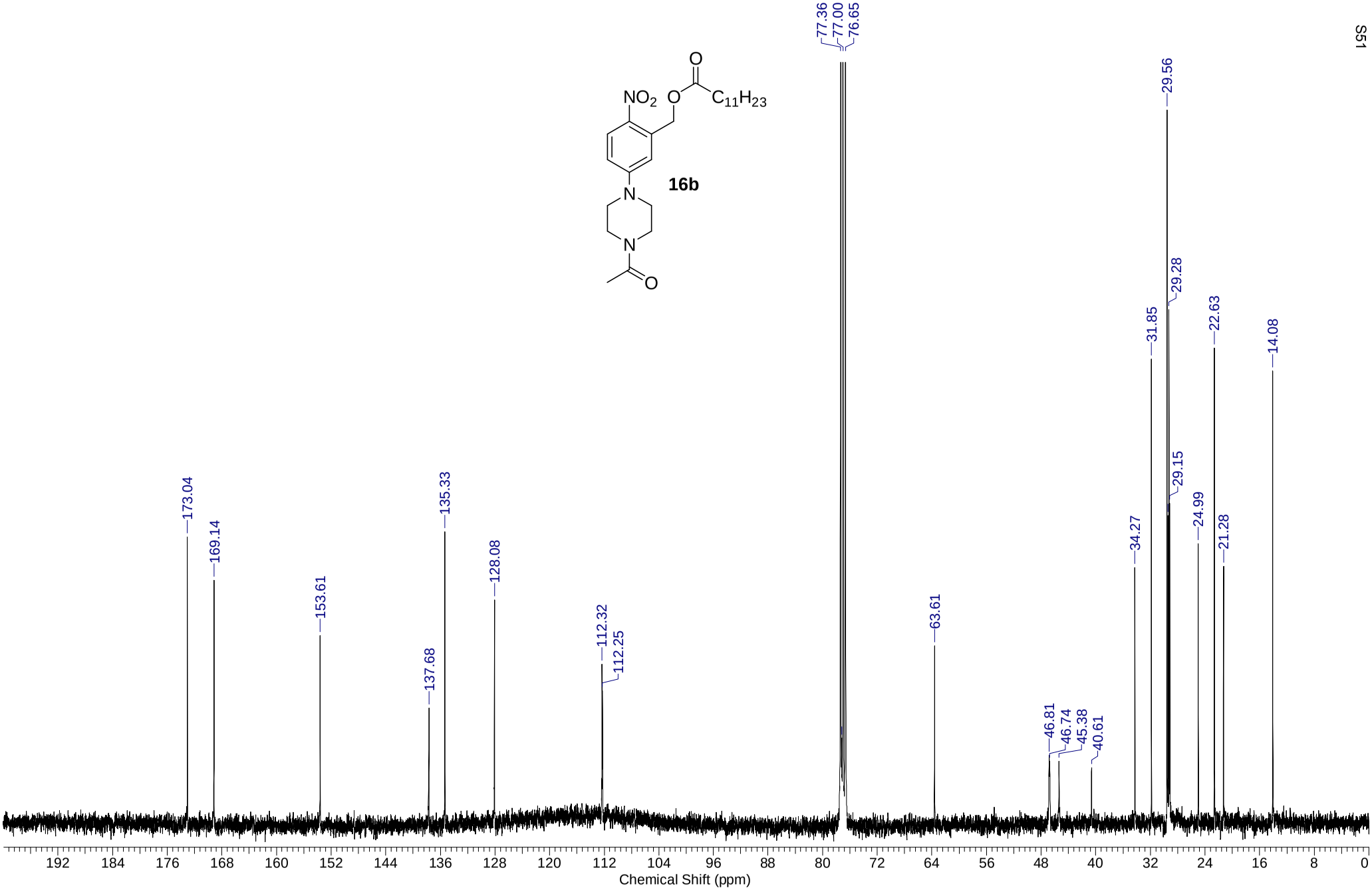
mr123


S49
%Transmittance
Wavenumbers
4000
3500
3000
2500
2000
1500
1000
100
90
80
70
60
50
40
2938.77
2918.47
2851.13
2802.90
1731.34
1605.71
1575.10
1498.19
1472.46
1439.55
1417.66
1316.38
1296.29
1250.19
1201.41
1173.12
1161.64
1091.41
1051.83
1006.18
975.21
884.28
839.70
835.17
808.55
795.47
751.25
717.19
689.53
666.94
NO_2
$C_{11}H_{23}$
16a

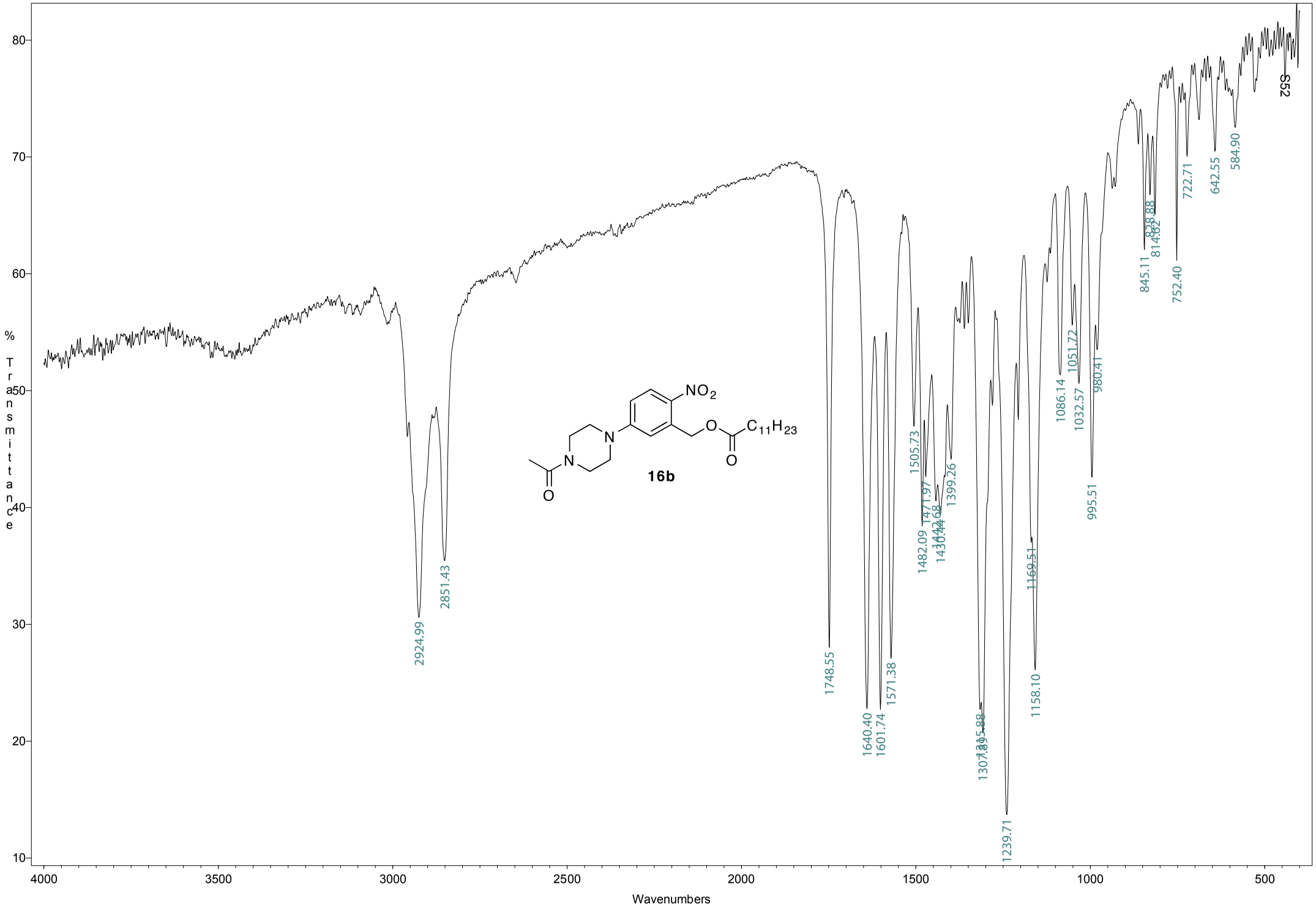
MR142


NO2
O
O
C11H23
N
N
O
16b
8.16
8.13
7.26
6.88
6.79
6.76
5.52
3.80
3.67
3.47
3.44
3.43
2.43
2.41
2.39
2.15
1.69
1.67
1.65
1.63
1.30
1.24
0.88
0.86
0.84
0.98
1.00
2.00
2.02
4.03
3.40
2.06
16.41
3.00
11.5
11.0
10.5
10.0
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
Chemical Shift (ppm)

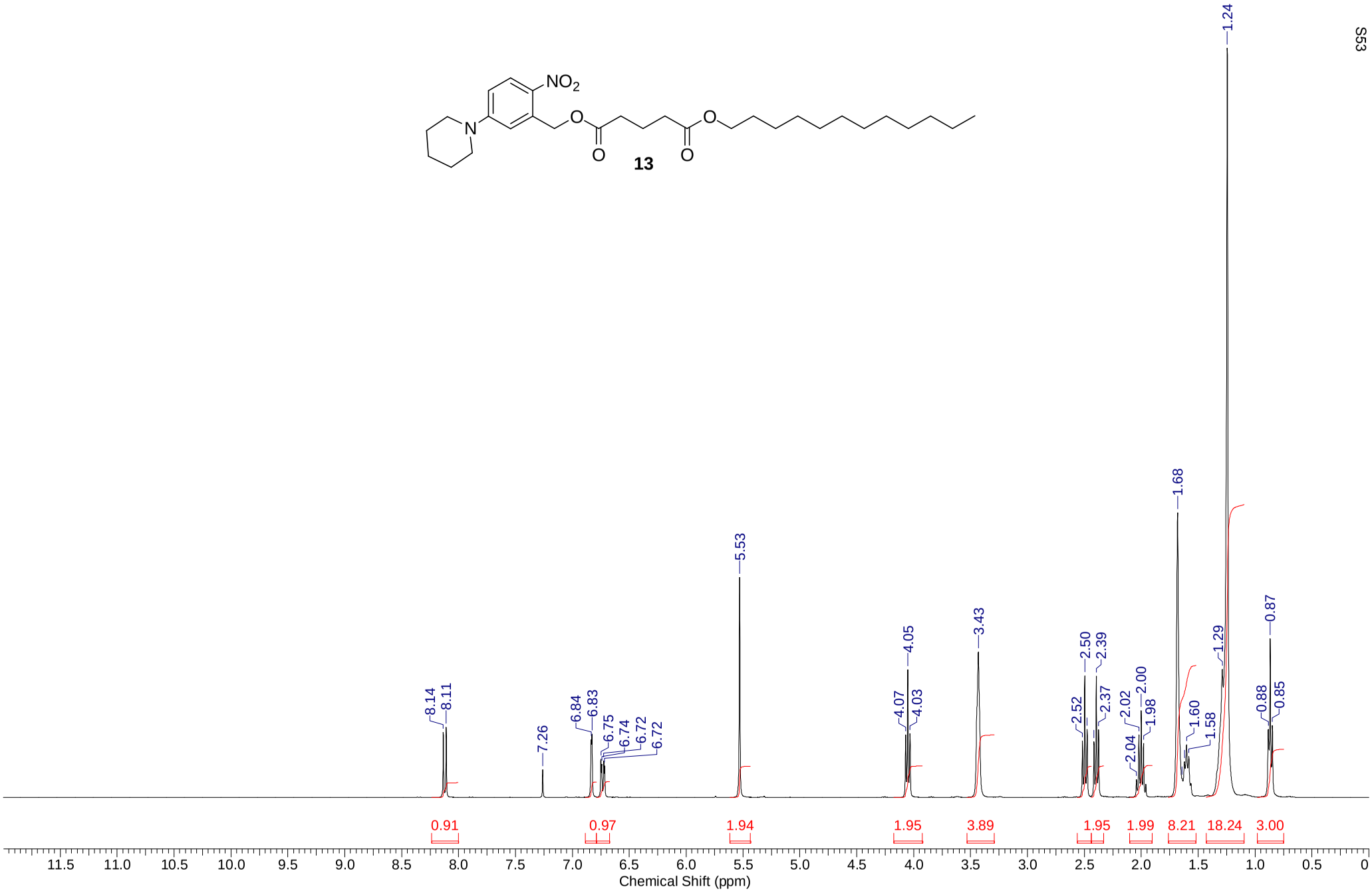
MR142


NO2
O
O
C11H23
N
N
O
16b
173.04
169.14
153.61
137.68
135.33
128.08
112.32
112.25
77.36
77.00
76.65
63.61
46.81
46.74
45.38
40.61
34.27
31.85
29.56
29.28
29.15
24.99
22.63
21.28
14.08
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

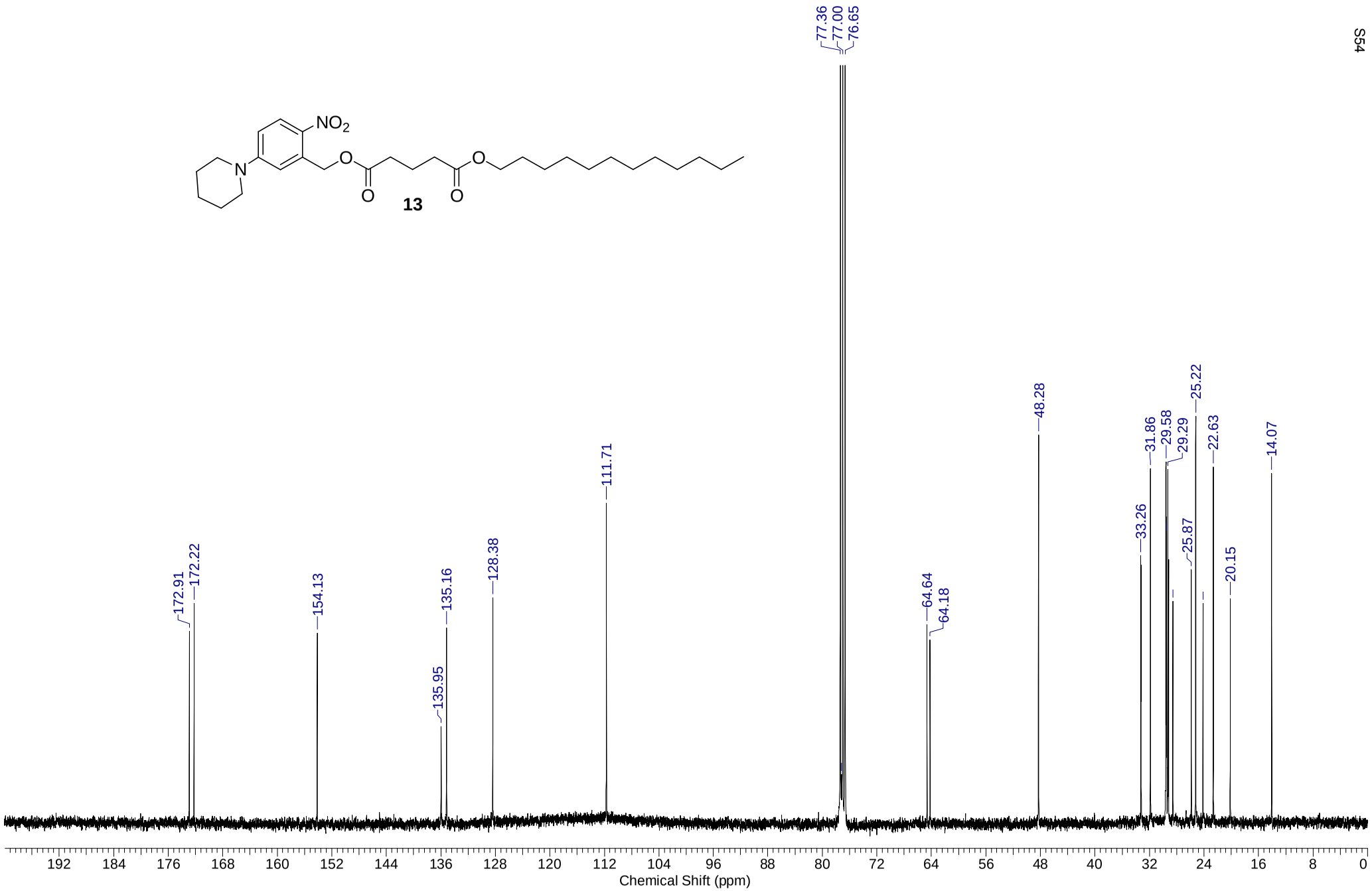
mr142


% Transmittance
Wavenumbers
2924.99
2851.43
1748.55
1640.40
1601.74
1571.38
1505.73
1482.09
1471.97
1399.26
1239.71
1158.10
1086.14
1051.72
1032.57
995.51
980.41
845.11
814.62
752.40
722.71
642.55
584.90
S52
NO2
C11H23
16b

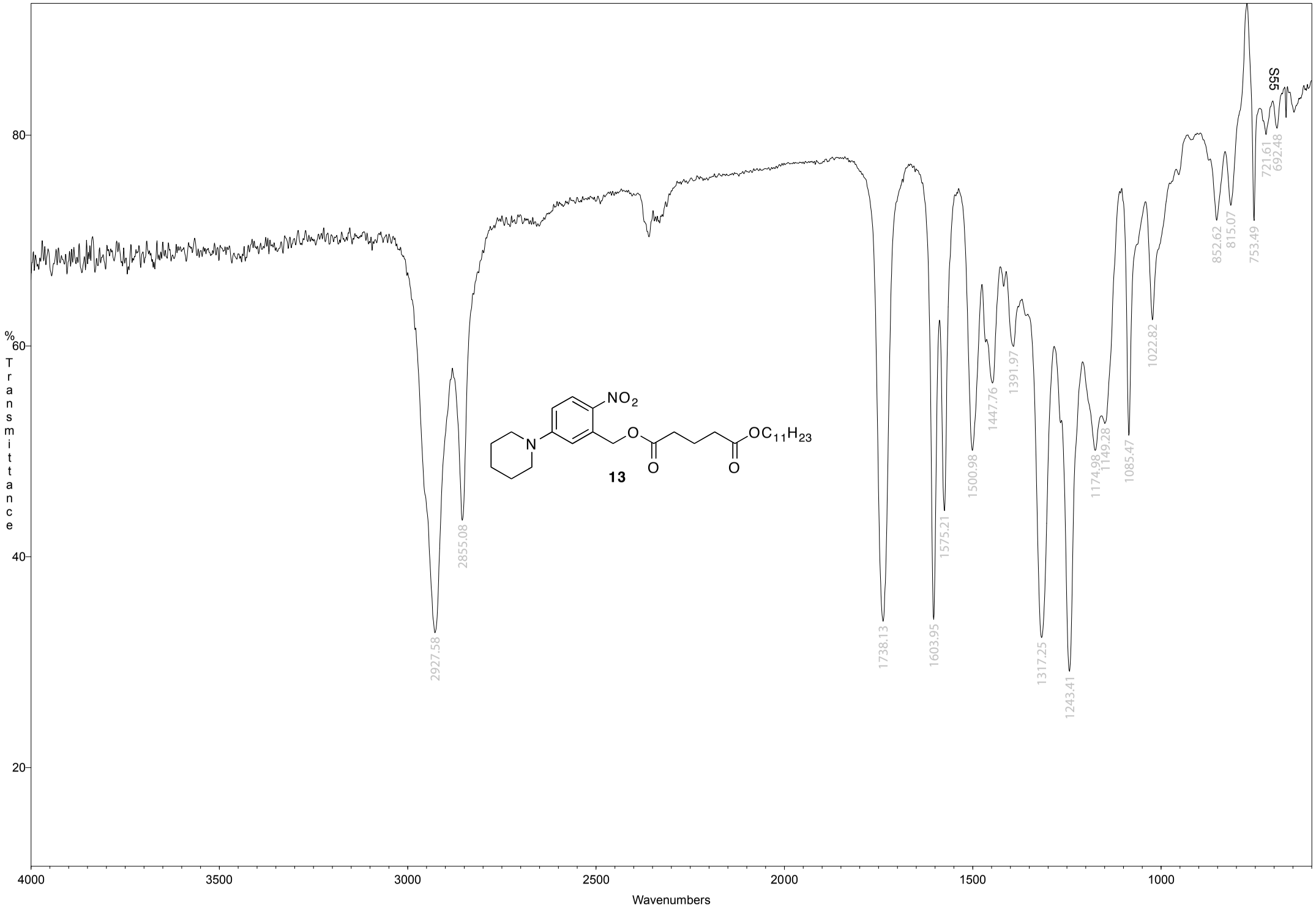
ER72


NO2
N
O
O
O
O
13
8.14
8.11
7.26
6.84
6.83
6.75
6.74
6.72
6.72
5.53
4.07
4.05
4.03
3.43
2.52
2.50
2.39
2.37
2.04
2.02
2.00
1.98
1.68
1.60
1.58
1.29
1.24
0.88
0.87
0.85
0.91
0.97
1.94
1.95
3.89
1.95
1.99
8.21
18.24
3.00
11.5
11.0
10.5
10.0
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
Chemical Shift (ppm)

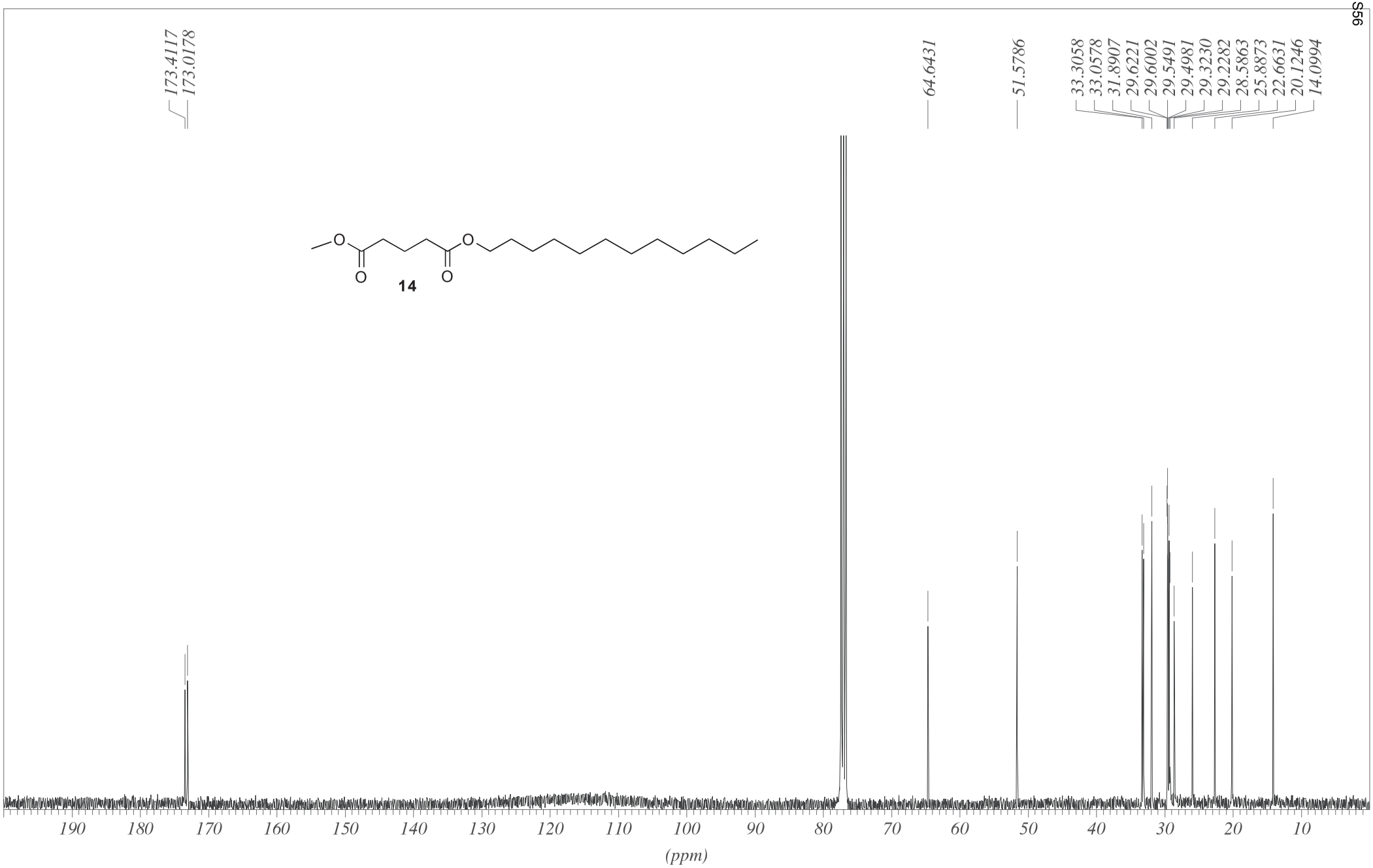
ER72


NO2
N
O
O
O
O
13
77.36
77.00
76.65
172.91
172.22
154.13
135.95
135.16
128.38
111.71
64.64
64.18
48.28
33.26
31.86
29.58
29.29
25.87
25.22
22.63
20.15
14.07
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

er72

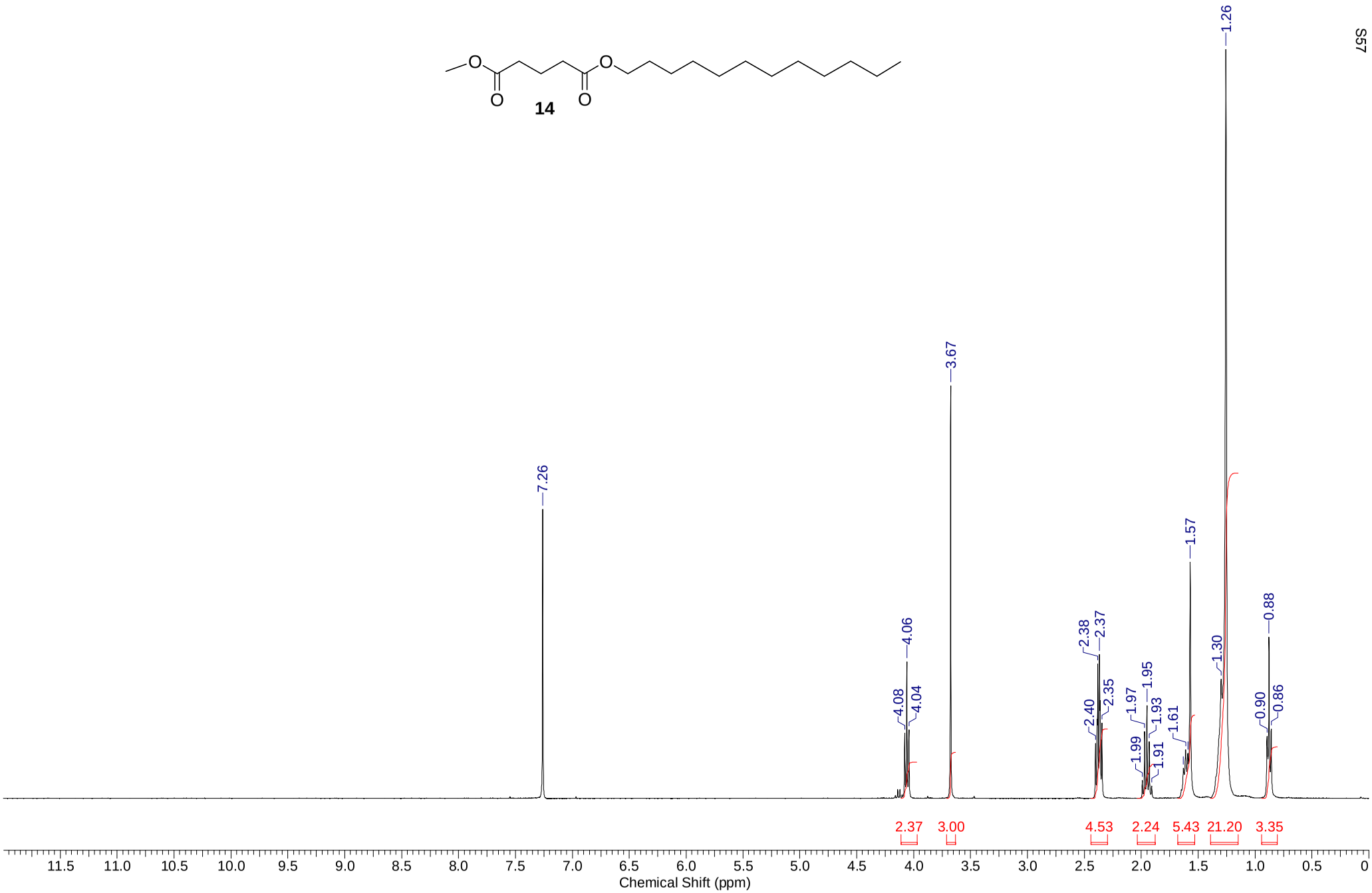

S55
2927.58
2855.08
1738.13
1603.95
1575.21
1500.98
1447.76
1391.97
1317.25
1243.41
1174.98
1149.28
1085.47
1022.82
852.62
815.07
753.49
721.61
692.48
NO2
N
O
O
O
OC11H23
13
% Transmittance
80
60
40
20
4000
3500
3000
2500
2000
1500
1000
Wavenumbers

MR22

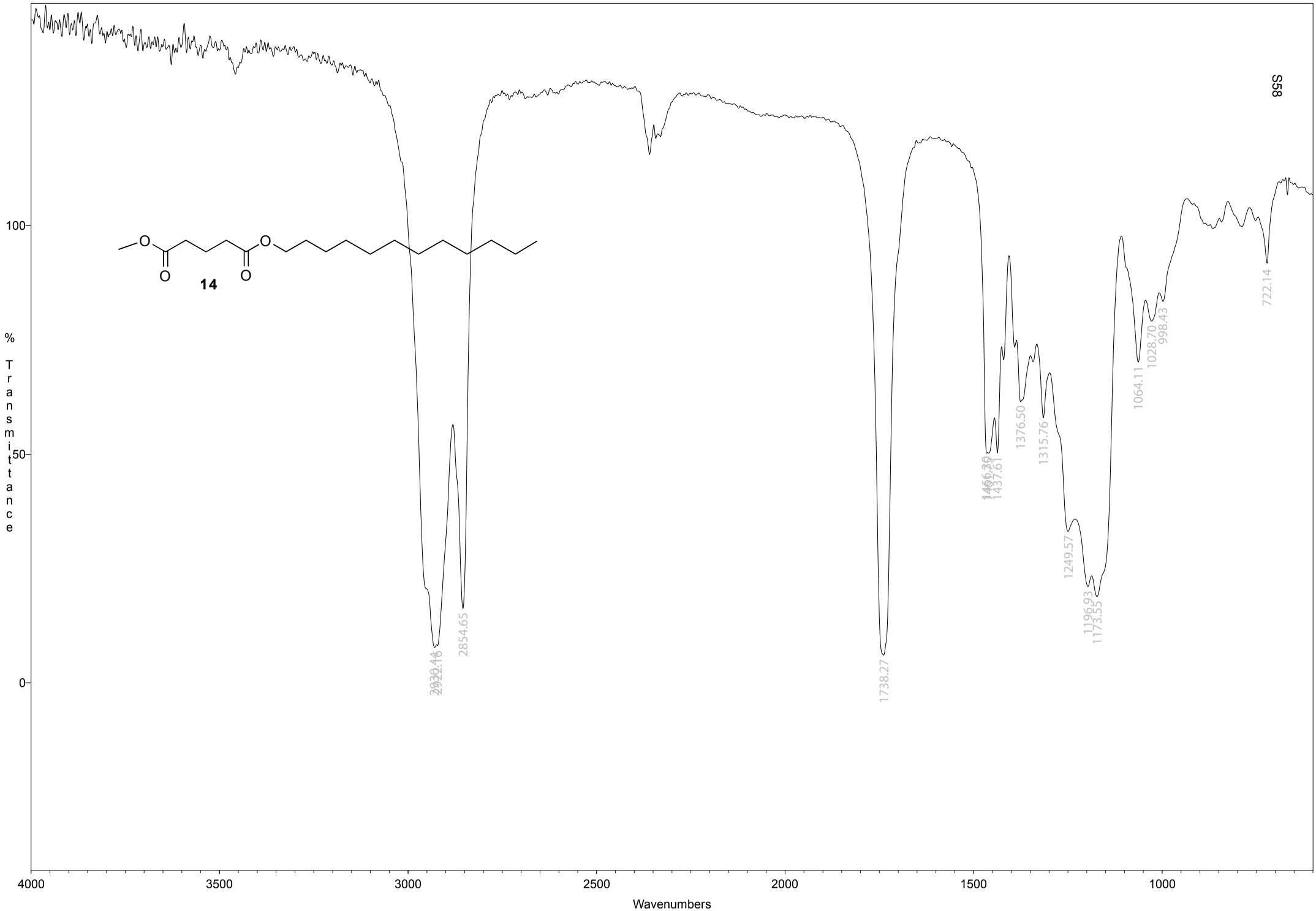

173.4117
173.0178
64.6431
51.5786
33.3058
33.0578
31.8907
29.6221
29.6002
29.5491
29.4981
29.3230
29.2282
28.5863
25.8873
22.6631
20.1246
14.0994
O
O
O
O
14
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

MR22

14


7.26
4.08
4.06
4.04
3.67
2.40
2.38
2.37
2.35
1.99
1.97
1.95
1.93
1.91
1.61
1.57
1.30
1.26
0.90
0.88
0.86
2.37
3.00
4.53
2.24
5.43
21.20
3.35
11.5
11.0
10.5
10.0
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
Chemical Shift (ppm)

mr22


S58
14
% Transmittance
100
50
0
2930.46
2922.16
2854.65
1738.27
1466.30
1462.29
1437.61
1376.50
1315.76
1249.57
1196.93
1173.55
1064.11
1028.70
998.43
722.14
4000
3500
3000
2500
2000
1500
1000
Wavenumbers