ELECTRONIC SUPPLEMENTARY INFORMATION

For

Regioselective installation of enolizable ketones and unprotected mercaptoacetic acid into olefins using GO as phase transfer catalyst

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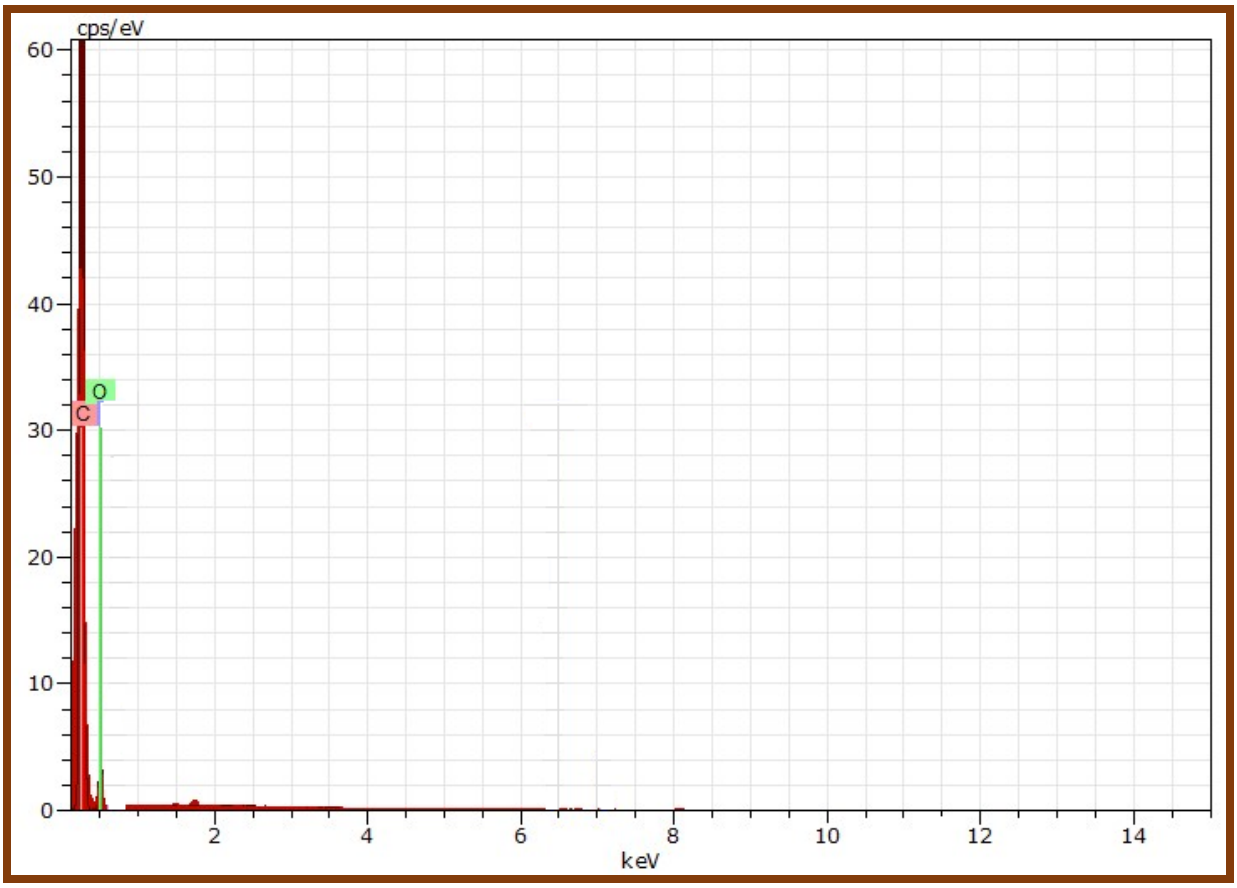
I EDAX of Graphene Oxide:



II. General Methods

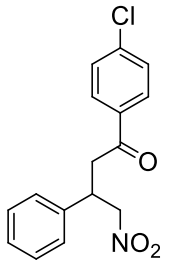
A. General Information: Reagents were obtained from commercial suppliers, and used without further purification unless otherwise specified by a reference. All reactions were performed using oven-dried glassware under a nitrogen atmosphere. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over silica gel (Merck 60-120 mesh) and TLC was performed using silica gel GF254 (Merck) plates. IR spectra in KBr were recorded on a Shimadzu 400-4000 cm^{-1} FTIR spectrophotometer, ^{1}H NMR spectra were recorded on a Bruker AVIII 500 spectrometer in $CDCl_3$, D_2O, DMSO with chemical shift value being reported in ppm. All coupling constants (*J*) are reported in Hertz (Hz). ^{13}C NMR spectra were recorded on the same

instrument at 125 MHz in $CDCl_3$. Elemental analyses were carried out in a Coleman automatic carbon, hydrogen and nitrogen analyzer.

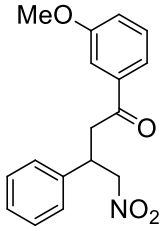
B. General procedure for the synthesis of Michael adduct 3: To a mixture of GO (10mg), KOH (0.185gm, 3.3 mmol, 2.2 equiv.), Michael acceptor (1.5 mmol, 1 equiv), Michael donor (2.25 mmol, 1.5 equiv.) added 4 mL mixture of DCM:H_2O (1:1) solvent. The reaction mixture was stirred at room temperature for 25h. After completion of reaction (as monitored by TLC; 30%EtOAc/*n*-hexane), the reaction mixture was undergoing simple filtration and washing of residue (GO) by diethyl ether (5 mL×3). The catalyst was then washed with water and ethanol, dried under vacuum and was reused for further experiment. Then, the reaction mixture was washed sequentially with DCM (10 mL×3) and water (10 mL×2). The combined organic extracts were dried over sodium sulfate and concentrated to give the crude product. Then the crude product was purified by column chromatography over silica gel to afford the analytically pure sample 3. The structure of all the synthesized compounds 3 were confirmed by their elemental and spectral analyses.

C. General method for the synthesis of Michael adduct 5: To a mixture of GO (10mg), KOH (0.092 g, 1.65 mmol, 1.1 equiv.), Michael acceptor (1.5 mmol, 1 equiv), Michael donor (2.25 mmol, 1.5 equiv.) added 4 mL mixture of DCM:H_2O (1:1) solvent. The reaction mixture was stirred at room temperature. After completion of reaction (as monitored by TLC; 50% EtOAc/*n*-hexane), the reaction mixture was filtered and residue (GO) was washed by diethyl ether (5 mL×3). The catalyst was then washed with water and ethanol, dried under vacuum and was reused for further experiment. Then, the reaction mixture was used as such as crude product. This crude product was purified by column chromatography over silica gel to afford the analytically pure sample 5. The structure of all the synthesized compounds 5 were confirmed by their elemental and spectral analyses.

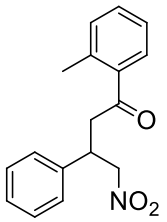
III. Spectroscopic and analytical data for compounds 3.



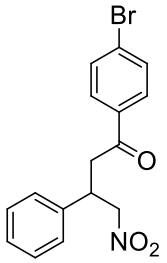
Compound 3a: 1-(4-chlorophenyl)-4-nitro-3-phenylbutan-1-one. Eluent in chromatography: *n*-hexane/EtOAc 24:1. Yellow crystal, Yield 79%, M.P. 82-83°C. IR (KBr): (ν) 3054, 1707, 1599, 1566, 1458, 1372, 1341, 722. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.76 (d, 2H, *J* = 8 Hz), 7.55 (d, 2H, *J* = 7.5 Hz), 7.37 (d, 2H, *J* = 7 Hz), 7.32 (t, 2H, *J* = 7 Hz), 7.25 (d, 1H, *J* = 7 Hz), 5.29 (d, 2H, *J* = 8 Hz), 3.35 (s, 1H), 3.31-3.23 (m, 2H). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 196.8, 143.0, 135.6, 132.2, 129.8, 129.1, 128.8, 128.0, 125.9, 79.6, 41.7, 39.4. EIMS (m/z): 303 (M^+) Anal. Calcd. for $C_{16}H_{14}ClNO_3$: C, 63.27; H, 4.65; N, 4.61. Found: C, 62.97; H, 4.38; N, 4.96.



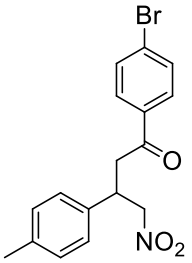
Compound 3b: 1-(3-methoxyphenyl)-4-nitro-3-phenylbutan-1-one. Eluent in chromatography: *n*-hexane/EtOAc 24:1. Reddish yellow oil, Yield 70%. IR (KBr): (ν) 3063, 1708, 1603, 1563, 1457, 1451, 1379, 1338, 1249. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.56-7.54 (m, 1H), 7.46 (d, 1H, *J* = 7.5 Hz), 7.42 (s, 1H), 7.39-7.29 (m, 5H), 7.07 (d, 1H, J = 7.5 Hz), 5.29 (br s, 2H), 4.32-4.20 (m, 1H), 3.80 (s,3H), 3.31-3.23 (m, 2H). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 196.7, 159.9, 139.2, 137.8, 129.8, 129.2, 127.9, 127.7, 120.6, 120.0, 112.3, 79.6, 55.5, 41.7, 39.5. EIMS (m/z): 299 (M^+) Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.72; N, 4.68. Found: C, 68.44; H, 5.43; N, 4.59.



Compound 3c: 4-nitro-3-phenyl-1-(*o*-tolyl)butan-1-one. Eluent in chromatography: *n*-hexane/EtOAc 24:1. Dark yellow oil, Yield 71%. IR (KBr): (ν) 3063, 2940, 1706, 1604, 1568, 1459, 1452, 1376, 1342. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.49 (d, 1H, *J* = 8 Hz), 7.30-7.29 (m, 1H), 7.28-7.25 (m, 2H), 7.19-7.15 (m, 5H), 4.49 (dd, 2H, J = 12.5 Hz, 7.5 Hz), 3.82-3.78 (m, 1H), 3.40 (dd, 2H, 13 Hz, 6.5 Hz), 2.11 (s, 3H). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 200.7, 138.9, 138.5, 137.2, 132.1, 131.7, 129.2, 128.3, 127.9, 127.5, 125.8, 79.7, 44.3, 39.6, 21.1. EIMS (m/z): 283 (M^+) Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.39; H, 6.24; N, 5.16.

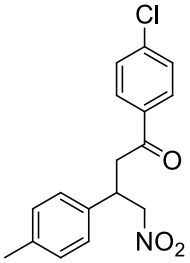


Compound 3d: 1-(4-bromophenyl)-4-nitro-3-phenylbutan-1-one. Eluent in chromatography: *n*-hexane/EtOAc 24:1. Reddish brown oil, Yield 78%. IR (KBr): (ν) 3061, 1708, 1603, 1563, 1458, 1448, 1378, 1340, 680. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.84 (d, 2H, *J* = 7 Hz), 7.39-7.25 (m, 7H), 4.82-4.64 (m, 2H), 3.94-3.87 (m, 1H), 3.36-3.27 (m, 2H). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 196.4, 139.1, 135.3, 129.8, 129.2, 128.8, 128.3, 128.0, 125.9, 79.2, 41.4, 39.3. EIMS (m/z): 347 (M^+) Anal. Calcd for $C_{16}H_{14}BrNO_3$: C, 55.19; H, 4.05; N, 4.02. Found: C, 55.39; H, 4.36; N, 3.87.

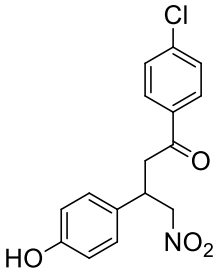


Compound 3e: 1-(4-bromophenyl)-4-nitro-3-(*p*-tolyl)butan-1-one. Eluent in chromatography: *n*-hexane/EtOAc 24:1. Reddish brown oil, Yield 81%. IR (KBr): (ν) 3061, 2944, 1705, 1605, 1566, 1456, 1450, 1379, 1339, 677. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.73-7.64 (m, 2H), 7.52-7.44 (m, 2H), 7.18-7.12 (m, 4H), 4.79 (dd, 1H, *J* = 12.5 Hz, 6.5 Hz), 4.68 (dd, 1H, *J* = 12.5 Hz, 8.5 Hz), 4.24-4.18 (m, 1H), 3.46-3.40 (m, 2H), 2.13 (s,

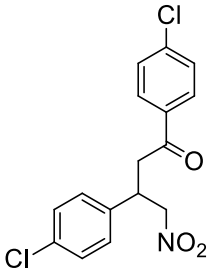
3H). $^{13}C\{^{1}H\}$NMR (125 MHz; $CDCl_3$) δ: 197.5, 137.6, 136.09, 136.06, 131.4, 129.8, 129.7, 128.3, 127.9, 79.5, 41.7, 38.7, 21.1. EIMS (m/z): 361 (M^+) Anal. Calcd for $C_{17}H_{16}BrNO_3$: C, 56.37; H, 4.45; N, 3.87. Found: C, 56.10; H, 4.55; N, 3.68.



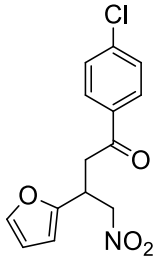
Compound 3f: 1-(4-chlorophenyl)-4-nitro-3-(*p*-tolyl)butan-1-one. Eluent in chromatography: *n*-hexane/EtOAc 24:1. Dark yellow oil, Yield 82%. IR (KBr): (ν) 3058, 2938, 1706, 1601, 1562, 1454, 1447, 1374, 1343, 724. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.77 (d, 2H, *J* = 8 Hz), 7.56 (d, 2H, *J* = 8 Hz), 7.18-7.11 (m, 4H), 4.78 (dd, 1H, *J* = 12.5 Hz, 6.5 Hz), 4.67 (dd, 1H, *J* = 12.5 Hz, 8.5 Hz), 4.22-4.17 (m, 1H), 3.48-3.40 (m, 2H), 2.12 (s, 3H). $^{13}C\{^{1}H\}$NMR (125 MHz; $CDCl_3$) δ: 196.8, 139.0, 137.6, 136.2, 135.3, 129.7, 129.6, 128.7, 128.3, 79.7, 41.6, 38.9, 21.1. EIMS (m/z): 317 (M^+) Anal. Calcd for $C_{17}H_{16}ClNO_3$: C, 64.26; H, 5.08; N, 4.41. Found: C, 64.46; H, 4.77; N, 4.76.



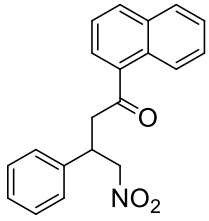
Compound 3g: 1-(4-chlorophenyl)-3-(4-hydroxyphenyl)-4-nitrobutan-1-one. Eluent in chromatography: *n*-hexane / EtOAc 47:3. Light yellow oil, Yield 92%. IR (KBr): (ν) 3360, 3061, 2785, 1707, 1596, 1562, 1472, 1459, 1378, 1342, 726. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.78 (d, 2H, *J* = 8 Hz), 7.40 (d, 2H, *J* = 8 Hz), 7.25 (d, 2H, *J* = 7.5 Hz), 6.87 (d, 2H, 7.5 Hz), 4.86-4.80 (m, 1H), 4.63-4.58 (m, 1H), 4.18-4.12 (m, 1H), 3.36-3.32 (m, 2H). $^{13}C\{^{1}H\}$NMR (125 MHz; $CDCl_3$) δ:196.7, 155.8, 138.9, 135.1, 131.7, 130.1, 128.9, 127.8, 115.9, 79.8, 41.7, 39.3. EIMS (m/z): 319 (M^+) Anal. Calcd for $C_{16}H_{14}ClNO_4$: C, 60.10; H, 4.41; N, 4.38. Found: C, 59.75; H, 4.71; N, 4.13.



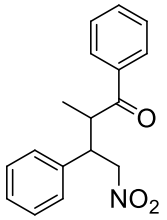
Compound 3h: 1,3-bis(4-chlorophenyl)-4-nitrobutan-1-one. Eluent in chromatography: *n*-hexane / EtOAc 19:1. Yellow oil, Yield 65%. IR (KBr): (ν) 3058, 1709, 1602, 1568, 1460, 1455, 1374, 1344, 729, 722. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.78 (d, 2H, *J* = 8 Hz), 7.39 (d, 2H, *J* = 8 Hz), 7.26 (d, 2H, *J* = 5 Hz), 7.16 (d, 2H, *J* = 5 Hz), 4.75-4.70 (m, 1H), 4.61-4.57 (m, 1H), 4.16-4.12 (m,1H), 3.36-3.32 (m, 2H).). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 195.5, 140.1, 137.6, 134.7, 134.0, 129.6, 129.5, 129.3, 129.1, 79.5, 41.5, 38.7. EIMS (m/z): 337 (M^+) Anal. Calcd for $C_{16}H_{13}Cl_2NO_3$: C, 56.82; H, 3.87; N, 4.14. Found: C, 57.14; H, 3.58; N, 4.36.



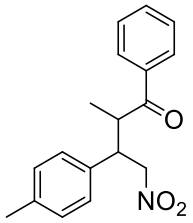
Compound 3i: 1-(4-chlorophenyl)-3-(furan-2-yl)-4-nitrobutan-1-one. Eluent in chromatography: *n*-hexane / EtOAc 24:1. Yellow oil, Yield 77%. IR (KBr): (ν) 3053, 1706, 1603, 1462, 1458, 1336, 1078, 728. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.76 (d, 2H, J = 8 Hz), 7.56 (d, 2H, J = 8 Hz), 7.33-732 (m, 1H), 6.32-6.28 (m, 1H), 6.21-6.16 (m,1H), 4.82-4.72 (m, 2H), 4.39-4.32 (m,1H), 3.51-3.43 (m, 2H). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 196.4, 151.4, 142.2, 139.4, 135.2, 129.2, 128.3, 110.3, 107.2, 77.7, 38.7, 33.3. EIMS (m/z): 293 (M^+) Anal. Calcd for $C_{14}H_{12}ClNO_4$: C, 57.25; H, 4.12; N, 4.77. Found: C, 57.04; H, 3.96; N, 5.12.



Compound 3j: 1-(naphthalen-1-yl)-4-nitro-3-phenylbutan-1-one. Eluent in chromatography: *n*-hexane / EtOAc 19:1. Yellow oil, Yield 73%. IR (KBr): (ν) 3066, 3061, 1707, 1605, 1603, 1600, 1562, 1457, 1450, 1372, 1333. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 8.58 (d, 1H, *J* = 9 Hz), 7.91-7.74 (m, 4H), 7.57-7.48 (m, 2H), 7.43-7.32 (m, 5H), 4.63-4.57 (m, 2H), 4.11-4.06 (m, 1H), 3.57 (dd, 2H, *J* = 15 Hz, 6 Hz). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 196.5, 139.1, 135.5, 133.8, 133.1, 130.4, 129.1, 128.7, 128.4, 128.1, 128.0, 127.7, 126.4, 126.0, 124.4, 79.6, 41.4, 39.3. EIMS (m/z): 319 (M^+) Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39. Found: C, 75.57; H, 5.63; N, 4.09.

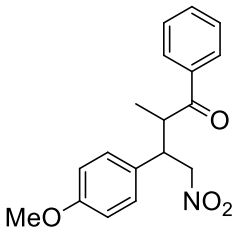


Compound 3k: 2-methyl-4-nitro-1,3-diphenylbutan-1-one. Eluent in chromatography: *n*-hexane / EtOAc 24:1. Yellow crystal, Yield 66%, M.P. 105-106^{o}C. IR (KBr): (ν) 3068, 2938, 1706, 1604, 1602, 1568, 1456, 1377, 1344, 1340. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.92 (d, 2H, *J* = 8 Hz), 7.51 (t, 1H, *J* = 7 Hz), 7.41 (t, 2H, *J* = 7.5 Hz), 7.36 (d, 2H, *J* = 7.5 Hz), 7.30 (t, 2H, *J* = 7.5 Hz), 7.23 (t, 1H, *J* = 7 Hz), 4.94 (d, 2H, *J* = 8 Hz), 3.81-3.75 (m, 1H), 2.96 (br s, 1H), 1.01 (d, 3H, *J* = 7 Hz). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 205.1, 142.4, 137.0, 133.5, 128.8, 128.7, 128.6, 128.1, 126.9, 78.4, 48.2, 43.3, 15.9. EIMS (m/z): 283 (M^+) Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.37; H, 5.70; N, 4.73.

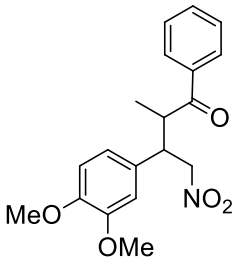


Compound 3l: 2-methyl-4-nitro-1-phenyl-3-(*p*-tolyl)butan-1-one. Eluent in chromatography: *n*-hexane / EtOAc 24:1. Yellow oil, Yield 67%. IR (KBr): (ν) 3061, 2944, 2940, 1707, 1604, 1569, 1462, 1379, 1343, 1338. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.93 (d, 2H, *J* = 7 Hz), 7.54-7.50 (m,3 H), 7.24 (t, 2H, *J* = 8 Hz), 7.11 (t, 2H, *J* = 7.5 Hz),

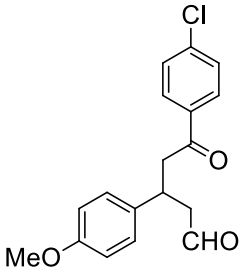
5.17 (dd, 1H, *J* = 19 Hz, 3 Hz), 4.92 (dd, 1H, *J* = 18.5 Hz, 8.5 Hz), 3.79-3.73 (m, 1H), 3.66-3.61 (m, 1H), 2.29 (s, 3H), 0.99 (d, 3H, *J* = 7 Hz). $^{13}C\{^{1}H\}$NMR (125 MHz; $CDCl_3$) δ: 201.8, 137.8, 137.1, 133.6, 133.4, 129.3, 128.8, 128.6, 126.9, 77.6, 48.2, 43.8, 21.3, 15.8. EIMS (m/z): 297 (M^+) Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.42; H, 6.75; N, 4.86.



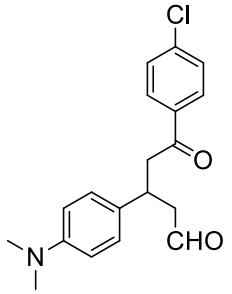
Compound 3m: 3-(4-methoxyphenyl)-2-methyl-4-nitro-1-phenylbutan-1-one. Eluent in chromatography: *n*-hexane / EtOAc 19:1. Yellow oil, Yield 68%. IR (KBr): (ν) 3070, 2942, 1706, 1600, 1570, 1464, 1374, 1339, 1334, 1252. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.88 (d, 2H, *J* = 9 Hz), 7.45-7.42 (m, 5H), 6.86 (d, 2H, J = 9 Hz), 4.90 (d, 2H, *J* = 8 Hz), 3.84-3.81 (m, 1H), 3.77 (s, 3H), 2.82-2.78 (m, 1H). 0.98 (d, 3H, *J* = 7 Hz). $^{13}C\{^{1}H\}$NMR (125 MHz; $CDCl_3$) δ: 201.5, 159.1, 142.3, 133.4, 131.1, 128.7, 128.4, 128.3, 114.9, 77.7, 55.5, 45.4, 43.2, 15.8. EIMS (m/z): 313 (M^+) Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 68.85; H, 5.82; N, 4.82.



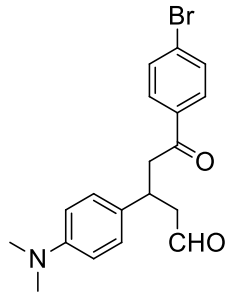
Compound 3n: 3-(3,4-dimethoxyphenyl)-2-methyl-4-nitro-1-phenylbutan-1-one. Eluent in chromatography: *n*-hexane / EtOAc 19:1. Yellow oil, Yield 69%. IR (KBr): (ν) 3088, 3082, 2949, 1707, 1603, 1561, 1473, 1374, 1343, 1338, 1261, 1257. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.73 (s, 2H), 7.53-7.52 (m, 3H), 7.45 (s, 1H), 6.83 (d, 1H, *J* = 3.5 Hz), 6.52-6.51 (m, 1H), 4.66 (d, 2H, J = 8 Hz), 3.92 (s, 3H), 3.89 (s, 3H), 3.85-3.83 (m, 1H), 3.60-3.55 (m, 1H), 0.93 (d, 3H, J = 7 Hz). $^{13}C\{^{1}H\}$NMR (125 MHz; $CDCl_3$) δ: 201.1, 149.5, 148.7, 139.2, 133.7, 131.4, 128.8, 128.2, 119.1, 111.6, 110.6, 77.8, 55.9, 55.8, 45.1, 43.2, 15.7. EIMS (m/z): 343 (M^+) Anal. Calcd for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16; N, 4.08. Found: C, 66.68; H, 5.82; N, 3.92.



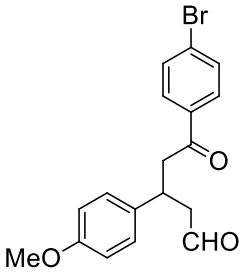
Compound 3o: 5-(4-chlorophenyl)-3-(4-methoxyphenyl)-5-oxopentanal. Eluent in chromatography: *n*-hexane / EtOAc 19:1. Yellow oil, Yield 85%. IR (KBr): (ν) 3082, 1724, 1707, 1601, 1466, 1451, 1336, 1264, 729. . ^{1}H NMR (500 MHz; $CDCl_3$) δ: 9.59 (d, 1H, *J* = 2 Hz), 7.86 (d, 2H, *J* = 8 Hz), 7.40 (d, 2H, *J* = 8 Hz), 7.27 (d, 2H, *J* = 8.5 Hz), 6.81 (d, 2H, *J* = 8.5 Hz), 3.87-3.78 (m, 1H), 3.76 (s, 3H), 3.20 (d, 2H, *J* = 7 Hz), 2.73-2.67 (m, 2H). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 201.5, 196.6, 158.3, 139.6, 135.8, 131.1, 129.4, 128.9, 128.7, 114.6, 55.5, 49.7, 44.5, 35.4. EIMS (m/z): 316 (M^+) Anal. Calcd for $C_{18}H_{17}ClO_3$: C, 68.25; H, 5.41. Found: C, 68.01; H, 5.33.



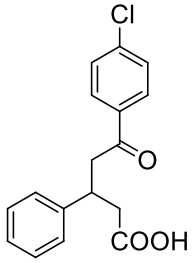
Compound 3p: 5-(4-chlorophenyl)-3-(4-(dimethylamino)phenyl)-5-oxopentanal. Eluent in chromatography: *n*-hexane / EtOAc 97:3. Yellow oil, Yield 88%. IR (KBr): (ν) 3069, 2883, 2880, 1725, 1707, 1603, 1601, 1463, 1460, 1340, 736. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 9.55 (d, 1H, *J* = 2 Hz), 7.87 (d, 2H, *J* = 7.5 Hz), 7.40 (d, 2H, *J* = 7.5 Hz), 7.36 (d, 2H, *J* = 8.5 Hz), 6.64 (d, 2H, *J* = 8.5), 3.87-3.83 (m, 1H), 3.05 (br s, 2H), 2.98 (s, 6H), 2.84-2.75 (m, 2H). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 201.1, 197.7, 150.3, 139.5, 135.7, 130.1, 129.8, 128.9, 128.4, 113.4, 49.4, 44.7, 41.0, 35.8. EIMS (m/z): 329 (M^+) Anal. Calcd for $C_{19}H_{20}ClNO_2$: C, 69.19; H, 6.11; N, 4.25. Found: C, 68.91; H, 5.78; N, 4.48.



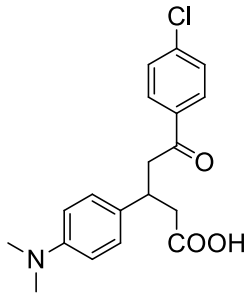
Compound 3q: 5-(4-bromophenyl)-3-(4-(dimethylamino)phenyl)-5-oxopentanal. Eluent in chromatography: *n*-hexane / EtOAc 19:1. Brownish oil, Yield 87%. IR (KBr): (ν) 3063, 2892, 2889, 1724, 1706, 1605, 1602, 1466, 1459, 1335, 687. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 9.53 (d, 1H, *J* = 2 Hz), 7.72-7.66 (m, 2H), 7.50-7.44 (m, 2H), 7.34 (d, 2H, *J* = 8 Hz), 6.62 (d, 2H, *J* = 8.5 Hz), 3.85 (br s, 1H), 3.02 (br s, 2H), 2.96 (s, 6H), 2.82-2.74 (m, 2H). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 200.8, 197.1, 150.0, 135.6, 131.7, 129.9, 129.7, 128.7, 128.3, 113.8, 49.6, 44.8, 41.0, 35.2. EIMS (m/z): 373 (M^+) Anal. Calcd for $C_{19}H_{20}BrNO_2$: C, 60.97; H, 5.39; N, 3.74. Found: C, 61.17; H, 5.74; N, 3.60.



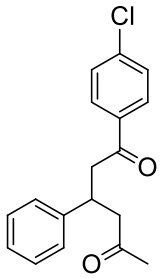
Compound 3r: 5-(4-bromophenyl)-3-(4-methoxyphenyl)-5-oxopentanal. Eluent in chromatography: *n*-hexane / EtOAc 19:1. Brownish oil, Yield 83%. IR (KBr): (ν) 3072, 1722, 1706, 1598, 1466, 1463, 1342, 1258, 686. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 9.58 (d, 1H, *J* = 2 Hz), 7.75-7.69 (m, 2H), 7.52-7.47 (m, 2H), 7.26 (d, 2H, *J* = 8.5 Hz), 6.79 (d, 2H, *J* = 8.5), 3.83-3.77 (m, 1H), 3.74 (s, 3H), 3.18 (d, 2H, *J* = 7 Hz), 2.72-2.65 (m, 2H). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 201.3,196.4, 158.4, 135.9, 131.8, 131.3, 129.3, 128.3, 127.8, 114.0, 55.5, 49.2, 44.2, 35.2. EIMS (m/z): 360 (M^+) Anal. Calcd for $C_{18}H_{17}BrO_3$: C, 59.85; H, 4.74. Found: C, 60.18; H, 4.53.



Compound 3s: 5-(4-chlorophenyl)-5-oxo-3-phenylpentanoic acid. Eluent in chromatography: *n*-hexane / EtOAc 1:24.White powder, M.P. 136-138°C, Yield 76%. IR (KBr): (ν) 3052, 1706, 1702, 1597, 1453, 1450, 1336, 719. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.85 (d, 2H, *J* = 8.5 Hz), 7.38 (d, 2H, *J* = 8.5 Hz), 7.30-7.23 (m, 4H), 7.19-7.14 (m, 1H), 3.84-3.78 (m, 1H), 3.38-3.30 (m, 2H), 2.84 (q, 1H, *J* = 7 Hz), 2.74 (q, 1H, *J* = 7.5 Hz). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 196.9, 176.9, 142.8, 139.6, 135.1, 129.5, 128.9, 128.7, 127.4, 127.0, 44.5, 40.4, 37.2. EIMS (m/z): 302 (M^+) Anal. Calcd for $C_{17}H_{15}ClO_3$: C, 67.44; H, 4.99. Found: C, 67.14; H, 4.77.

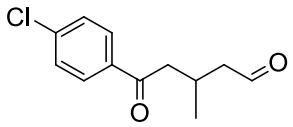


Compound 3t: 5-(4-chlorophenyl)-3-(4-(dimethylamino)phenyl)-5-oxopentanoic acid. Eluent in chromatography: *n*-hexane / EtOAc 1:24. Yellow oil, Yield 90%. IR (KBr): (ν) 3066, 2894, 2884, 1713, 1706, 1604, 1461, 1453, 1341, 732. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.89 (d, 2H, *J* = 8.5 Hz), 7.49 (d, 2H, *J* = 8.5 Hz), 7.41 (d, 2H, *J* = 8.5 Hz), 6.64 (d, 2H, *J* = 8.5 Hz), 3.42-3.36 (m, 1H), 3.07-3.01 (m, 2H), 2.99 (s, 6H), 2.15-2.09 (m, 2H). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 196.8, 177.1, 149.1, 139.8, 135.5, 129.7, 129.1, 128.9, 127.0, 113.2, 44.6, 41.2, 40.1, 37.7. EIMS (m/z): 345 (M^+) Anal. Calcd for $C_{19}H_{20}ClNO_3$: C, 65.99; H, 5.83; N, 4.05. Found: C, 65.76; H, 5.48; N, 4.20.

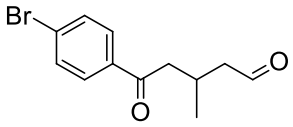


Compound 3u: 1-(4-chlorophenyl)-3-phenylhexane-1,5-dione. Eluent in chromatography: *n*-hexane / EtOAc 24:1. Yellow oil, Yield 74%. IR (KBr): (ν) 3054, 1709, 1707, 1603, 1458, 1450, 1337, 734. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.79 (d, 2H, *J* = 8.5 Hz), 7.38-7.31 (m, 7H), 3.82-3.75 (m, 1H), 3.27 (dd, 1H, *J* = 16.5 Hz, 7 Hz), 3.17 (dd, 1H, *J* = 16.5 Hz, 7 Hz), 2.86 (dd, 1H, *J* = 17 Hz, 7 Hz), 2.78 (dd, 1H, *J* = 17 Hz, 7 Hz),

2.03 (s, 3H). $^{13}C\{^{1}H\}$NMR (125 MHz; $CDCl_3$) δ: 207.1, 200.3, 144.2, 143.2, 134.4, 129.2, 128.7, 128.6, 127.9, 125.9, 49.2, 44.7, 36.7, 30.5. EIMS (m/z): 300 (M^+) Anal. Calcd for $C_{18}H_{17}ClO_2$: C, 71.88; H, 5.70. Found: C, 72.25; H, 5.93.

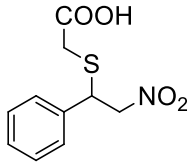


Compound 3v: 5-(4-chlorophenyl)-3-methyl-5-oxopentanal. Eluent in chromatography: *n*-hexane / EtOAc 49:1. Yellow oil, Yield 64%. IR (KBr): (ν) 3066, 2948, 1723, 1707, 1601, 1598,1462, 1447, 1342, 731. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 9.43 (d, 1H, *J* = 2 Hz), 7.88 (d, 2H, *J* = 8.5 Hz), 7.38 (d, 2H, *J* = 8.5 Hz), 3.25-3.18 (m, 1H), 3.11-3.04 (m, 2H), 2.80-2.71 (m, 2H), 1.01 (d, 3H, *J* = 6.5 Hz). $^{13}C\{^{1}H\}$NMR (125 MHz; $CDCl_3$) δ: 202.3, 199.3, 139.0, 134.8, 129.8, 128.6, 50.7, 44.9, 24.7, 20.6. EIMS (m/z): 224 (M^+) Anal. Calcd for $C_{12}H_{13}ClO_2$: C, 64.15; H, 5.83. Found: 63.83; H, 5.56.



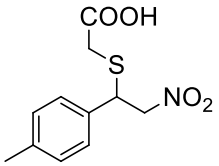
Compound 3w: 5-(4-bromophenyl)-3-methyl-5-oxopentanal. Eluent in chromatography: *n*-hexane / EtOAc 49:1. Brown oil, Yield 61%. IR (KBr): (ν) 3068, 2944, 1720, 1707, 1602, 1452, 1448, 1337, 692. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 9.41 (d, 1H, *J* = 2 Hz), 7.87 (d, 2H, *J* = 8 Hz), 7.54 (d, 2H, *J* = 8 Hz), 3.10 (br s, 1H), 3.06 (br s, 2H), 2.80 (br s, 2H), 0.94 (d, 3H, *J* = 6.5 Hz). $^{13}C\{^{1}H\}$NMR (125 MHz; $CDCl_3$) δ: 200.7, 198.0, 136.1, 131.5, 129.8, 128.5, 50.4, 44.8, 24.4, 21.4. EIMS (m/z): 268 (M^+) Anal. Calcd for $C_{12}H_{13}BrO_2$: C, 53.55; H, 4.87. Found: C, 53.36; H, 4.99.

IV. Spectroscopic and analytical data for compounds 5.

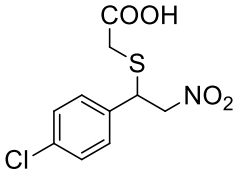


Compound 5a: 2-((2-nitro-1-phenylethyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 3:97. Yellow solid, M.P. 71-72°C, Yield 86%. IR (KBr): (ν) 1702, 1508, 1379, 1318, 1220, 709. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 9.51 (br s, 1H), 7.29-7.23 (m, 5H),

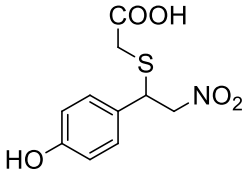
4.82-4.73 (m, 3H), 3.13-3.00 (m, 2H). $^{13}C\{^{1}H\}$NMR (125 MHz; $CDCl_3$) δ: 175.5, 135.9, 129.2, 128.9, 127.9, 78.4, 46.5, 32.5. EIMS (m/z): 241 (M^+) Anal. Calcd for $C_{10}H_{11}NO_4S$: C, 49.78; H, 4.60; N, 5.81. Found: 49.47; H, 4.26; N, 5.93.



Compound 5b: 2-((2-nitro-1-(*p*-tolyl)ethyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 3:97. Yellow semisolid, Yield 83%. IR (KBr): (ν) 2942, 1700, 1504, 1378, 1310, 1218, 712. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 10.51 (br s, 1H), 7.23 (d, 2H, *J* = 8.5 Hz), 7.16 (d, 2H, *J* = 8 Hz), 4.84-4.77 (m, 3H), 3.18-3.05 (m, 2H), 2.32 (s, 3H). $^{13}C\{^{1}H\}$NMR (125 MHz; $CDCl_3$) δ: 176.2, 138.8, 132.7, 129.9, 127.8, 78.5, 46.3, 32.4, 21.2. EIMS (m/z): 255 (M^+) Anal. Calcd for $C_{11}H_{13}NO_4S$: C, 51.75; H, 5.13; N, 5.49. Found: C, 51.91; H, 5.33; N, 5.14.

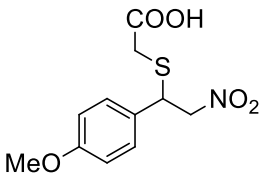


Compound 5c: 2-((1-(4-chlorophenyl)-2-nitroethyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 3:97. Yellow viscous solid, Yield 75%. IR (KBr): (ν) 1704, 1502, 1382, 1312, 1216, 724, 708. ^{1}H NMR (500 MHz; D_2O) δ: 8.07 (s,1H), 7.28-7.20 (m, 4H), 4.60 (br s, 3H), 3.31 (d, 2H, *J* = 3H). $^{13}C\{^{1}H\}$NMR (125 MHz; D_2O) δ: 175.3, 138.8, 133.6, 129.3, 128.4, 78.8, 46.5, 32.5. EIMS (m/z): 275 (M^+) Anal. Calcd for $C_{10}H_{10}ClNO_4S$: C, 43.56; H, 3.66; N, 5.08. Found: C, 43.80; H, 3.35; N, 5.19.

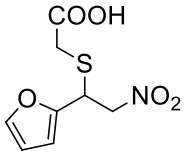


Compound 5d: 2-((1-(4-hydroxyphenyl)-2-nitroethyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 3:97. Yellow semisolid, Yield 90%. IR (KBr): (ν) 3362, 2872, 1703, 1507, 1373, 1310, 1214, 704. ^{1}H NMR (500 MHz; D_2O) δ: 10.18 (br s, 1H), 7.07 (d, 2H, *J* = 8.5 Hz), 6.71 (d, 2H, *J* = 8.5 Hz), 5.00 (s, 1H), 4.76 (br s, 3H), 3.15-3.11 (m, 2H). $^{13}C\{^{1}H\}$NMR (125 MHz; D_2O) δ: 174.9, 155.7, 129.3, 127.9, 115.7, 77.7,

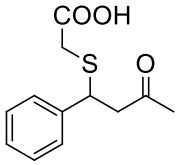
48.8, 33.7. EIMS (m/z): 257 (M^+) Anal. Calcd for $C_{10}H_{11}NO_5S$: C, 46.69; H, 4.31; N, 5.44. Found: C, 46.34; H, 4.65; N, 5.25.



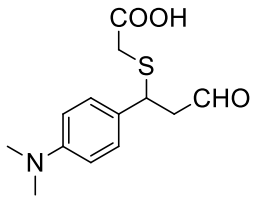
Compound 5e: 2-((1-(4-methoxyphenyl)-2-nitroethyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 3:97. Yellow semisolid, Yield 89%. IR (KBr): (ν) 1718, 1510, 1370, 1315, 1247, 1216, 718. ^{1}H NMR (500 MHz; DMSO) δ: 9.59 (s, 1H), 7.25 (d, 2H, *J* = 8 Hz), 6.72 (d, 2H, *J* = 8 Hz), 4.94 (br s, 3H), 3.81 (s, 3H), 3.14 (d, 2H, *J* = 2 Hz). ^{13}C{^{1}H}NMR (125 MHz; DMSO) δ: 175.5, 159.1, 131.0, 129.5, 114.2, 78.2, 55.4, 46.3, 32.4. EIMS (m/z): 271 (M^+) Anal. Calcd for $C_{11}H_{13}NO_5S$: C, 48.70; H, 4.83; N, 5.16. Found: C, 48.54; H, 4.54; N, 5.50.



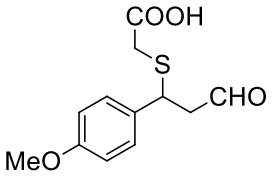
Compound 5f: 2-((1-(furan-2-yl)-2-nitroethyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 3:47. Yellow semisolid, Yield 84%. IR (KBr): (ν) 1714, 1568, 1473, 1448, 1373, 1343. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.53 (br s, 1H), 7.31-7.30 (m, 1H), 6.27 (d, 1H, *J* = 3.5 Hz), 6.24-6.23 (m, 1H), 4.86-4.75 (m, 3H), 3.15 (s, 2H). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 174.7, 148.1, 143.4, 110.7, 109.5, 76.1, 39.6, 32.3. EIMS (m/z): 231 (M^+) Anal. Calcd for $C_8H_9NO_5S$: C, 41.55; H, 3.92; N, 6.06. Found: 41.88; H, 3.67; N, 6.24.



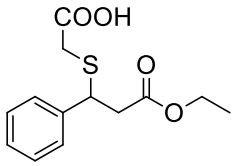
Compound 5g: 2-((3-oxo-1-phenylbutyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 2:23. Light yellow semisolid, Yield 79%. IR (KBr): (ν) 3068, 1721, 1714, 1597, 1478, 1462, 1338. ^{1}H NMR (500 MHz; $CDCl_3$) δ: 7.51-7.25 (m, 5H), 4.39 (br s, 1H), 3.54 (br s, 2H), 2.92 (br s, 2H), 1.96 (s, 3H). ^{13}C{^{1}H}NMR (125 MHz; $CDCl_3$) δ: 206.9, 177.0, 143.6, 129.1, 128.4, 127.2, 49.6, 43.9, 35.6, 30.6. EIMS (m/z): 238 (M^+) Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C, 60.26; H, 5.63.



Compound 5h: 2-((1-(4-(dimetylamino)phenyl)-3-oxopropyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 1:98. Yellowish semisolid, Yield 85%. IR (KBr): (ν) 2967, 2898, 2793, 1732, 1712, 1603, 1567, 1467, 1458, 1343. ^{1}H NMR (500 MHz; DMSO) δ: 9.58 (s, 1H), 7.08 (d, 2H, *J* = 8.5 Hz), 6.74 (d, 2H, *J* = 8.5 Hz), 3.96-3.92 (m, 1H), 3.53 (s, 6H), 3.14 (s, 2H), 2.82 (br s, 2H). ^{13}C{^{1}H}NMR (125 MHz; DMSO) δ: 201.4, 175.0, 150.1, 129.5, 128.3, 113.6, 52.4, 46.5, 41.2, 31.2. EIMS (m/z): 267 (M^{+}) Anal. Calcd for $C_{13}H_{17}NO_3S$: C, 58.40; H, 6.41; N, 5.24. Found: C, 58.13; H, 6.26; N, 5.48.

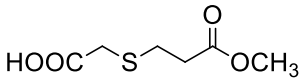


Compound 5i: 2-((1-(4-methoxyphenyl)-3-oxopropyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 1:98. Yellowish semisolid, Yield 84%. IR (KBr): (ν) 3062, 1728, 1720, 1604, 1454, 1448, 1343, 1248. ^{1}H NMR (500 MHz; DMSO) δ: 9.60 (d, 1H, *J* = 2 Hz), 7.25 (d, 2H, J = 8 Hz), 6.73 (d, 2H, J = 8 Hz), 3.81 (s, 3H), 3.75-3.70 (m 1H) 3.49 (s, 2H), 2.75-2.68 (m, 2H). ^{13}C{^{1}H}NMR (125 MHz; DMSO) δ: 202.4, 174.3, 159.0, 130.3, 129.5, 114.3, 55.4, 52.2, 46.3, 31.0. EIMS (m/z): 254 (M^{+}) Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.68; H, 5.55. Found: C, 56.96; H, 5.32.

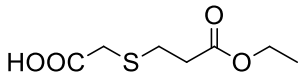


Compound 5j: 2-((3-ethoxy-3-oxo-1-phenylpropyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 1:19. Yellow oil, Yield 74%. IR (KBr): (ν) 3063, 1742, 1723,1605, 1468, 1455, 1343. ^{1}H NMR (500 MHz; DMSO) δ: 9.67 (br s, 1H), 7.39-7.26 (m, 5H), 4.64 (br s, 1H), 4.13 (q, 2H, *J* = 7 Hz), 3.18 (S, 2H), 2.65-2.62 (m, 2H), 1.20 (t, 3H, *J* = 7 Hz). ^{13}C{^{1}H}NMR (125 MHz; DMSO) δ: 174.5,170.8, 143.4, 128.2, 127.7,

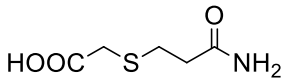
126.3, 60.2, 42.4, 42.0, 35.7, 14.1. EIMS (m/z): 268 (M^+) Anal. Calcd for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01. Found: C, 58.30; H, 5.70.



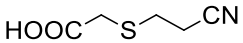
Compound 5k: 2-((3-methoxy-3-oxopropyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 1:19. Yellow oil, Yield 67%. IR (KBr): (ν) 1748, 1722, 1469, 1454. ^{1}H NMR (500 MHz; DMSO) δ: 3.58 (s, 3H), 3.14 (s, 2H), 2.73 (s, 2H), 2.60 (s, 2H). ^{13}C{^{1}H}NMR (125 MHz; DMSO) δ: 173.3, 171.4, 51.7, 43.6, 34.3, 28.0. EIMS (m/z): 178 (M^+) Anal. Calcd for $C_6H_{10}O_4S$: C, 40.44; H, 5.66. Found: C, 40.63; H, 5.98.



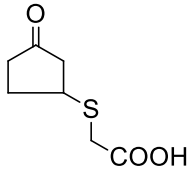
Compound 5l: 2-((3-ethoxy-3-oxopropyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 1:19. Yellow oil, Yield 62%. IR (KBr): (ν) 1742, 1722, 1458, 1454, 1187. ^{1}H NMR (500 MHz; DMSO) δ: 4.03, (br s, 2H), 3.13 (br s, 2H), 2.72 (br s, 2H), 2.56 (br s, 2H), 1.15 (br s, 3H). ^{13}C{^{1}H}NMR (125 MHz; DMSO) δ: 173.0, 172.0, 60.4, 43.8, 34.3, 27.0, 14.3. EIMS (m/z): 192 (M^+) Anal. Calcd for $C_7H_{12}O_4S$: C, 43.74; H, 6.29. Found: C, 43.61; H, 6.55.



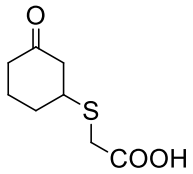
Compound 5m: 2-((3-amino-3-oxopropyl)thio)acetic acid. . Eluent in chromatography: *n*-hexane / EtOAc 3:97. Yellow liquid, Yield 51%. IR (KBr): (ν) 1714, 1692, 1597, 1472, 1458. ^{1}H NMR (500 MHz; DMSO) δ: 7.59 (s, 1H), 6.91 (s, 1H), 3.07 (br s, 2H), 2.66 (br s, 2H), 2.33 (br s, 2H). ^{13}C{^{1}H}NMR (125 MHz; DMSO) δ: 174.2, 167.5, 44.7, 35.5, 27.9. EIMS (m/z): 163 (M^+) Anal. Calcd for $C_5H_9NO_3S$: C, 36.80; H, 5.56; N, 8.58. Found: C, 36.57; H, 5.89; N, 8.23.



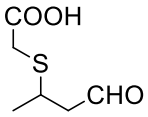
Compound 5n: 2-((2-cyanoethyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 1:24.White solid, M.P. 74-76^{o}C, Yield 72%. IR (KBr): (ν)3082, 2263, 1734, 1477, 1464. . ^{1}H NMR (500 MHz; DMSO) δ: 9.43 (s, 1H), 3.21 (s, 2H), 2.85-2.78 (m, 4H). ^{13}C{^{1}H}NMR (125 MHz; DMSO) δ: 171.5, 119.8, 42.8, 27.2, 17.7. EIMS (m/z): 145 (M^+) Anal. Calcd for $C_5H_7NO_2S$: C, 41.36; H, 4.86; N, 9.65. Found: 41.60; H, 5.11; N, 9.48.



Compound 5o: 2-((3-oxocyclopentyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 1:24, Light yellow oil, Yield 59%. IR (KBr): (ν) 1746, 1719, 1453, 1448, 1343. ^{1}H NMR (500 MHz; DMSO) δ: 10.60 (s, 1H), 3.48 (br s, 2H), 3.22 (s, 1H), 2.68-2.57 (m, 1H), 2.26-1.84 (m, 5H). ^{13}C{^{1}H}NMR (125 MHz; DMSO) δ: 216.9, 172.6, 45.2, 40.4, 36.7, 34.5, 29.1. EIMS (m/z): 174 (M^{+}) Anal. Calcd for $C_7H_{10}O_3S$: C, 48.26; H, 5.79. Found: C, 48.57; H, 5.53.

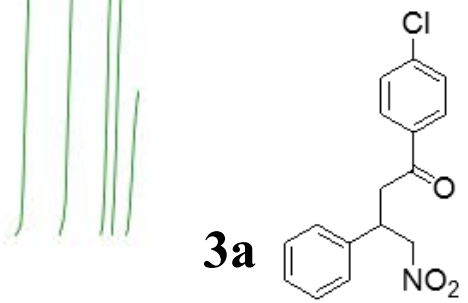


Compound 5p: 2-((3-oxocyclohexyl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 1:24, Light yellow oil, Yield 56%. IR (KBr): (ν) 1720, 1715, 1467, 1448. ^{1}H NMR (500 MHz; DMSO) δ: 3.51 (br s, 3H), 3.28 (s, 2H), 2.07-1.22 (m, 6H).). ^{13}C{^{1}H}NMR (125 MHz; DMSO) δ: 208.5, 171.3, 47.4, 42.7, 37.3, 32.3, 25.0, 22.2. EIMS (m/z): 188 (M^{+}) Anal. Calcd for $C_8H_{12}O_3S$: C, 51.04; H, 6.43. Found: C, 50.70; H, 6.60.



Compound 5q: 2((4-oxobutan-2yl)thio)acetic acid. Eluent in chromatography: *n*-hexane / EtOAc 1:49, Yellow oil, Yield 55%. IR (KBr): (ν) 2879, 1732, 1714, 1476, 1443, 1342. ^{1}H NMR (500 MHz; DMSO) δ: 11.10 (br s, 1H), 9.58 (s, 1H), 3.34-3.28 (m, 1H), 3.14 (s, 2H), 2.58 (d, 2H, *J* = 7 Hz), 1.21 (d, 3H, *J* = 7 Hz). ^{13}C{^{1}H}NMR (125 MHz; DMSO) δ: 201.1, 174.3, 50.3, 41.5, 32.3, 22.2. EIMS (m/z): 162 (M^{+}) Anal. Calcd for $C_6H_{10}O_3S$: C, 44.43; H, 6.21. Found: C, 44.73; H, 6.55.

V. 1 H NMR Spectra 3a -3w



3a

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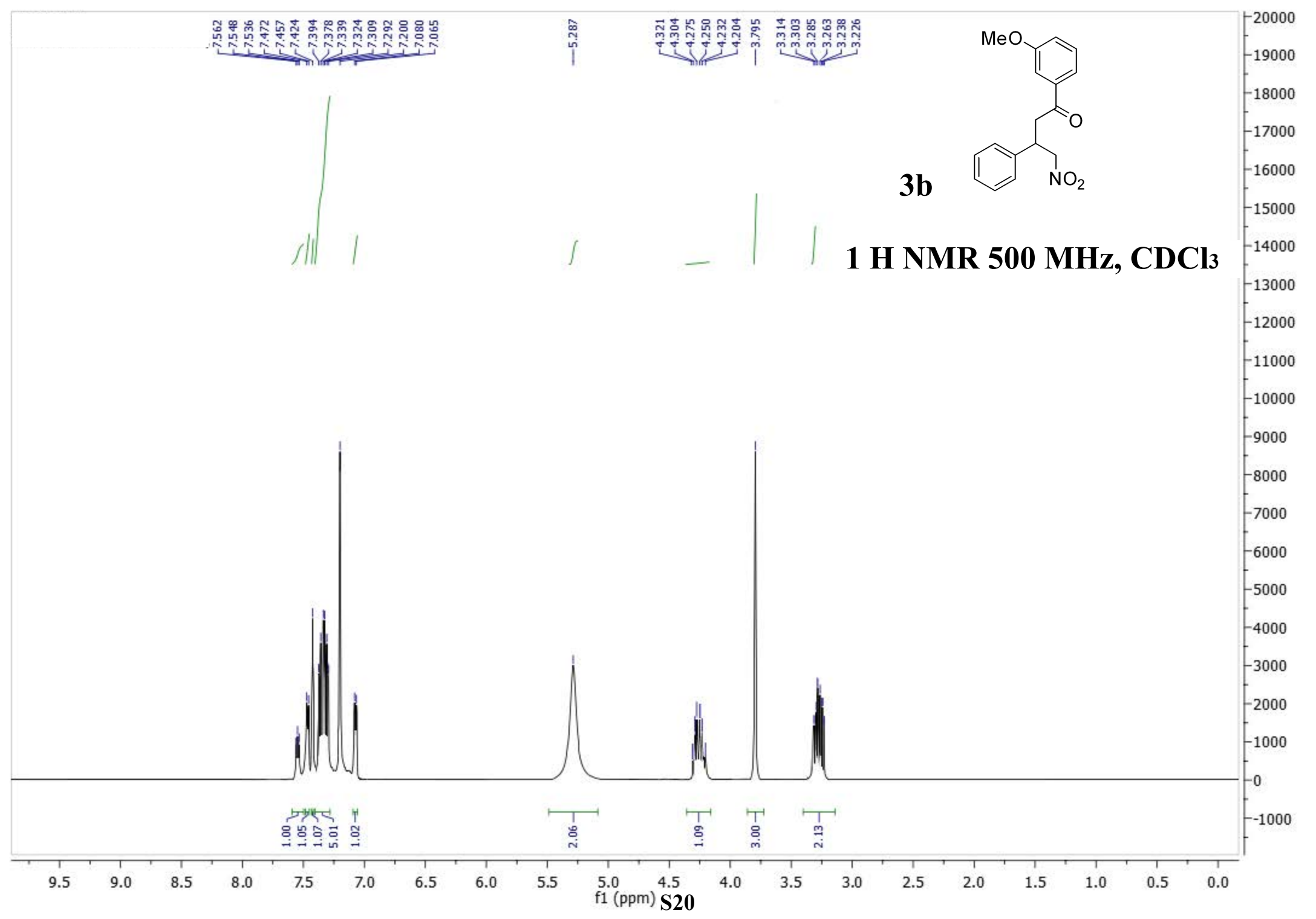
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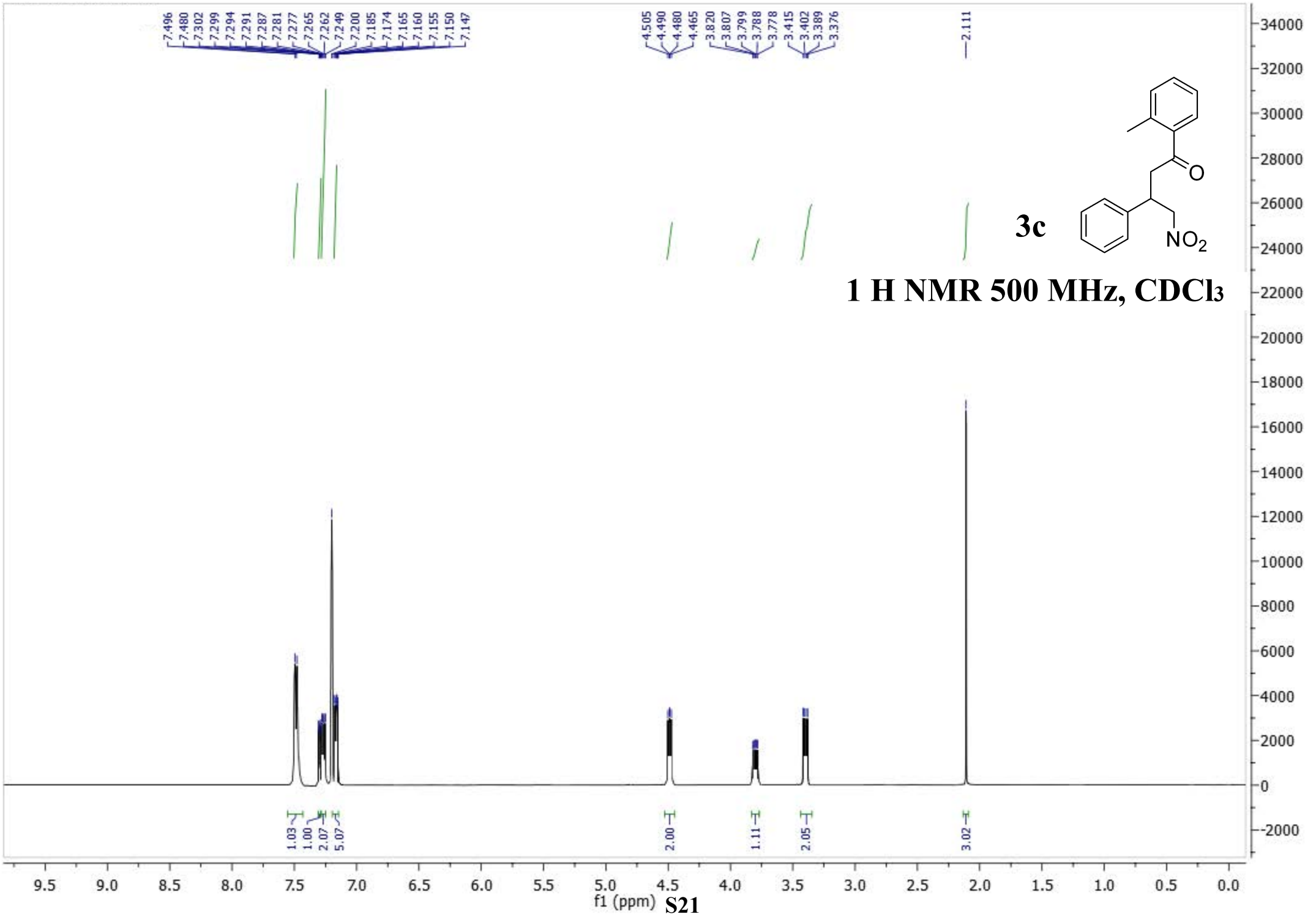
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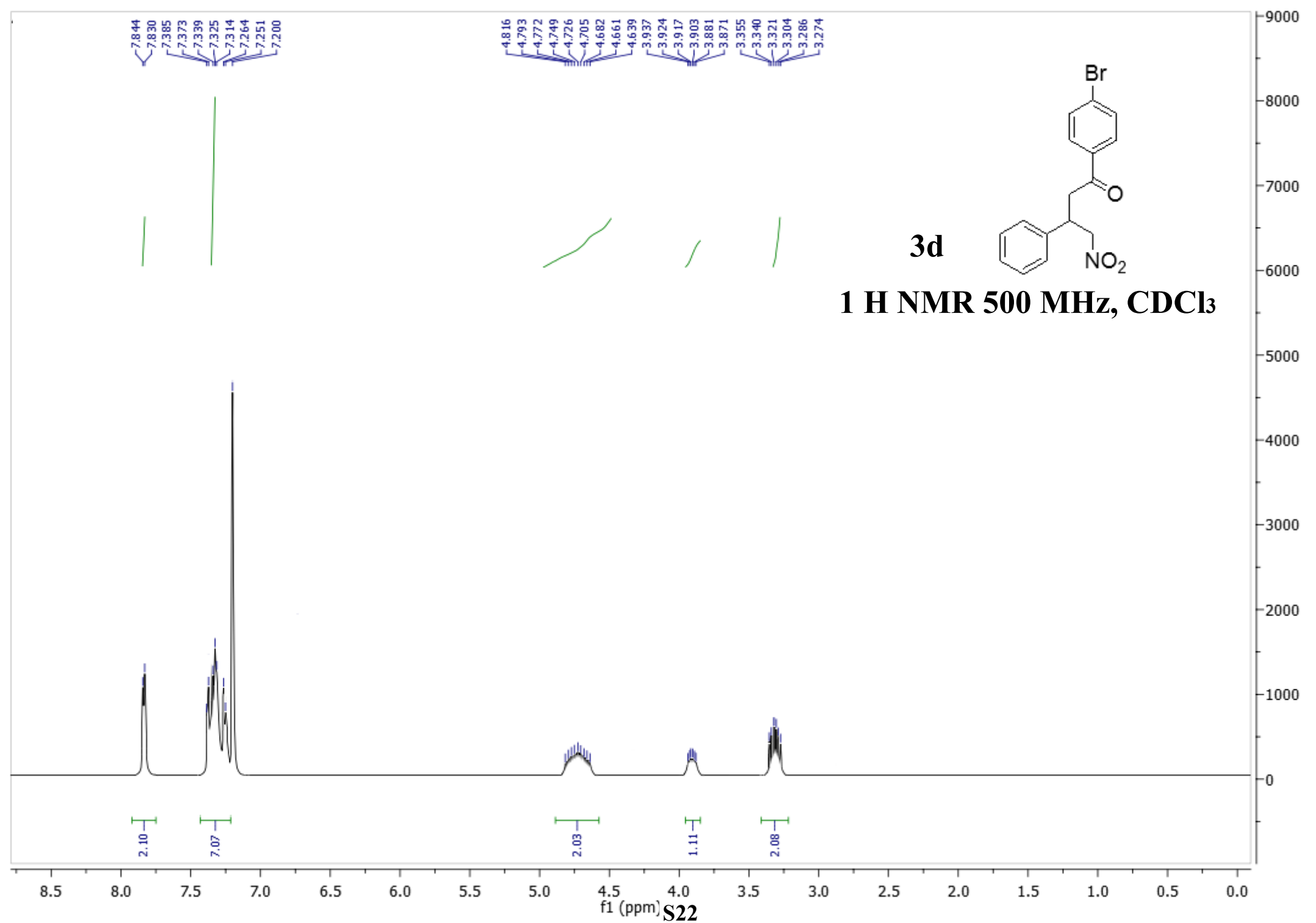
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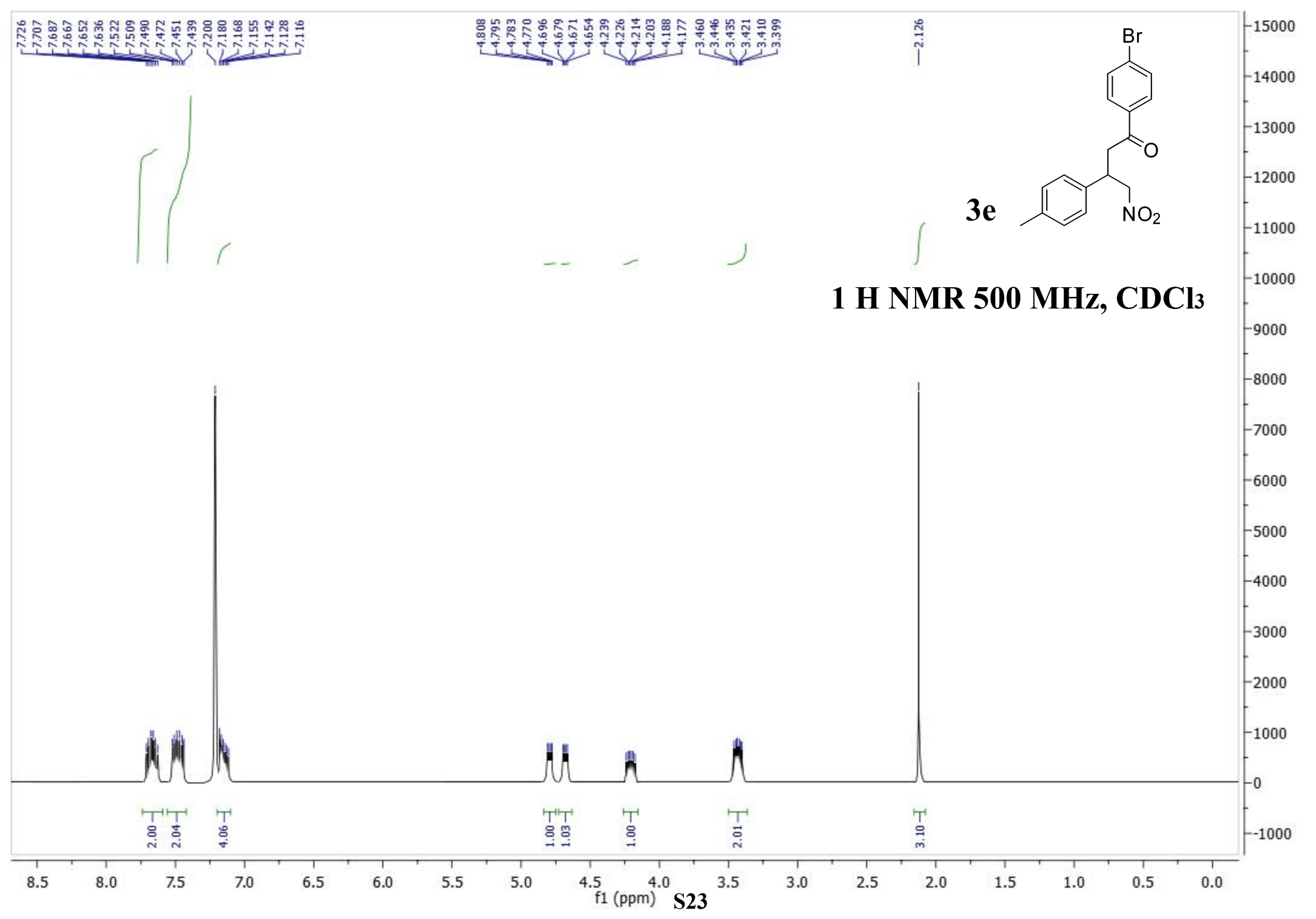
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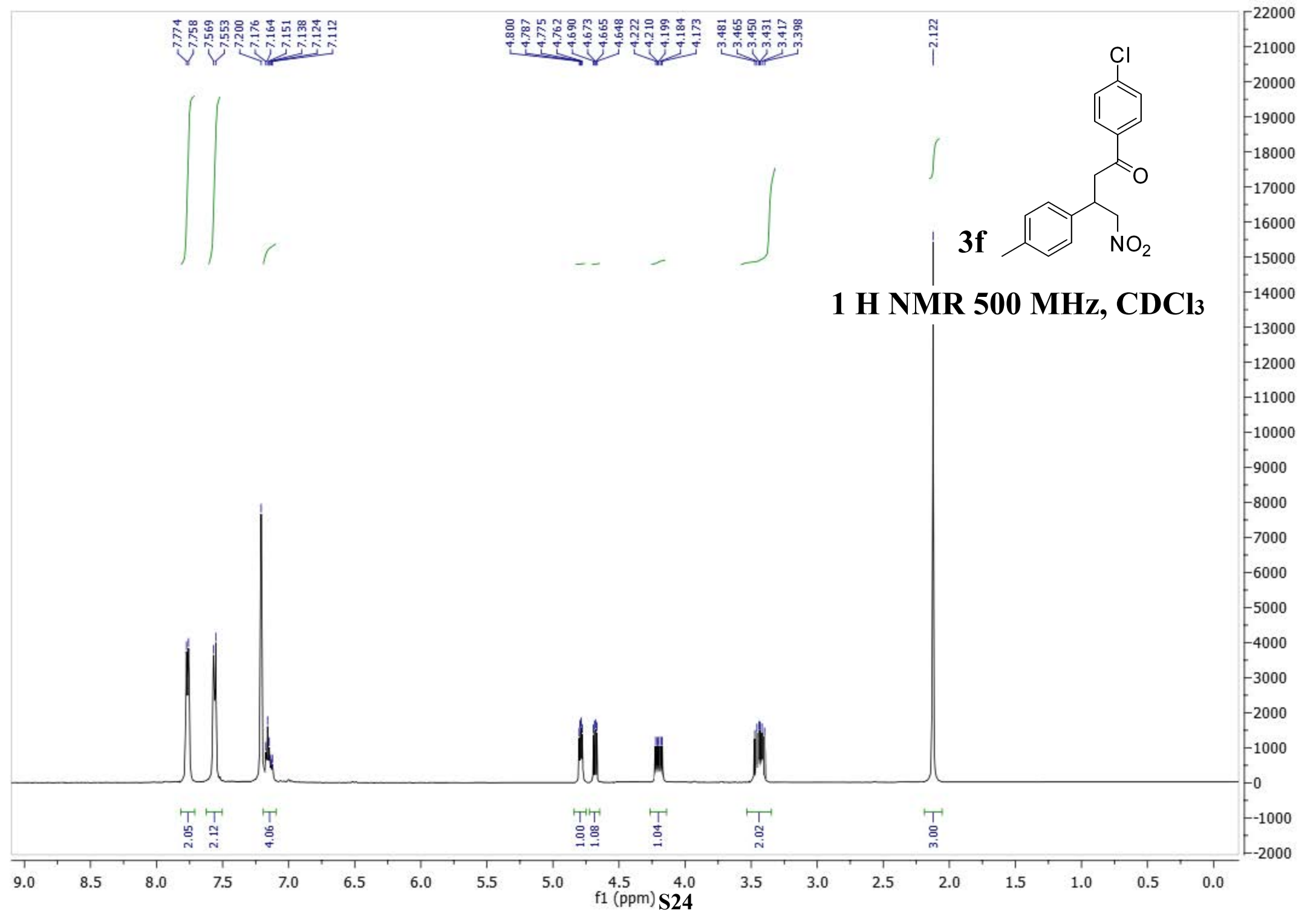
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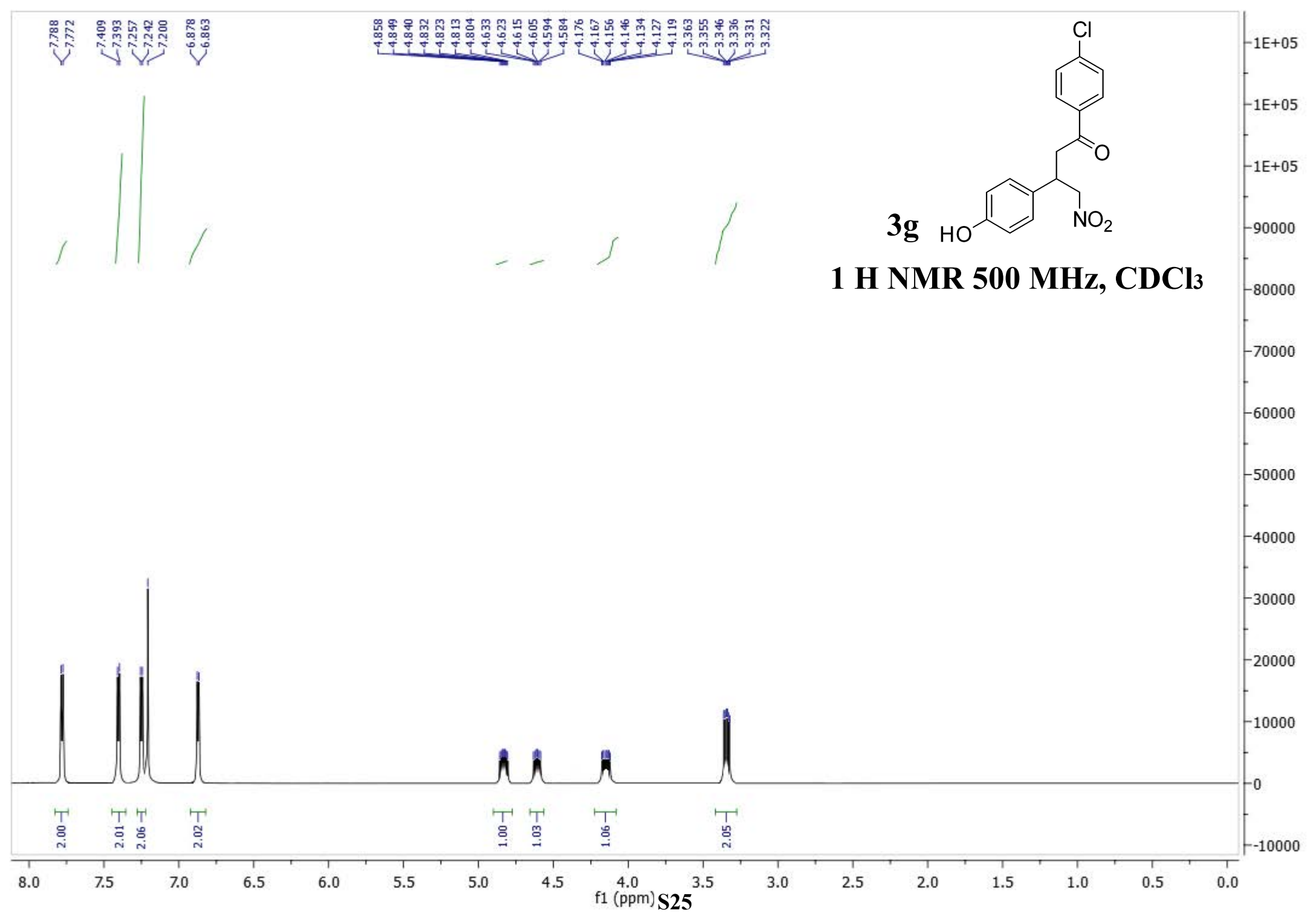
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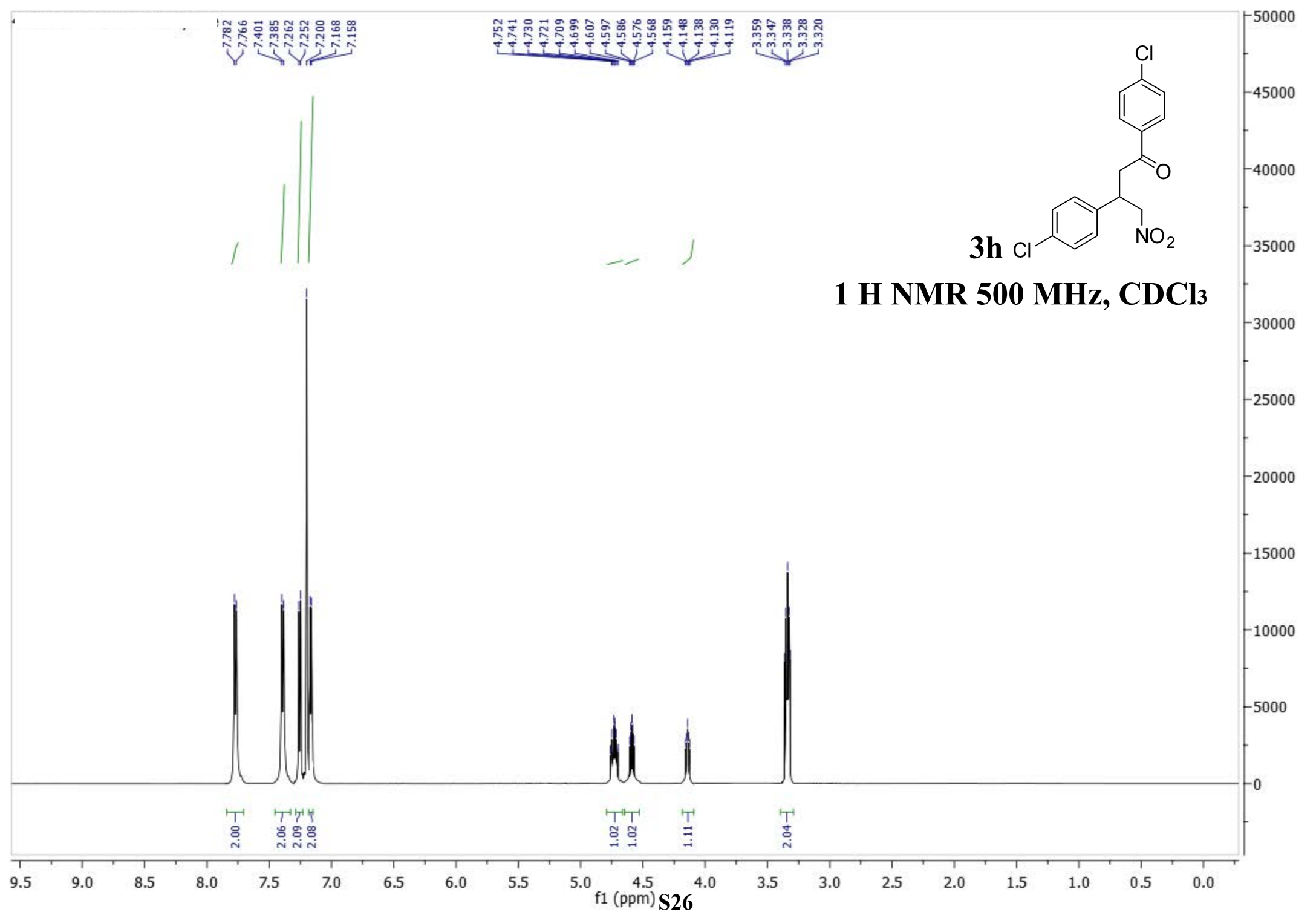
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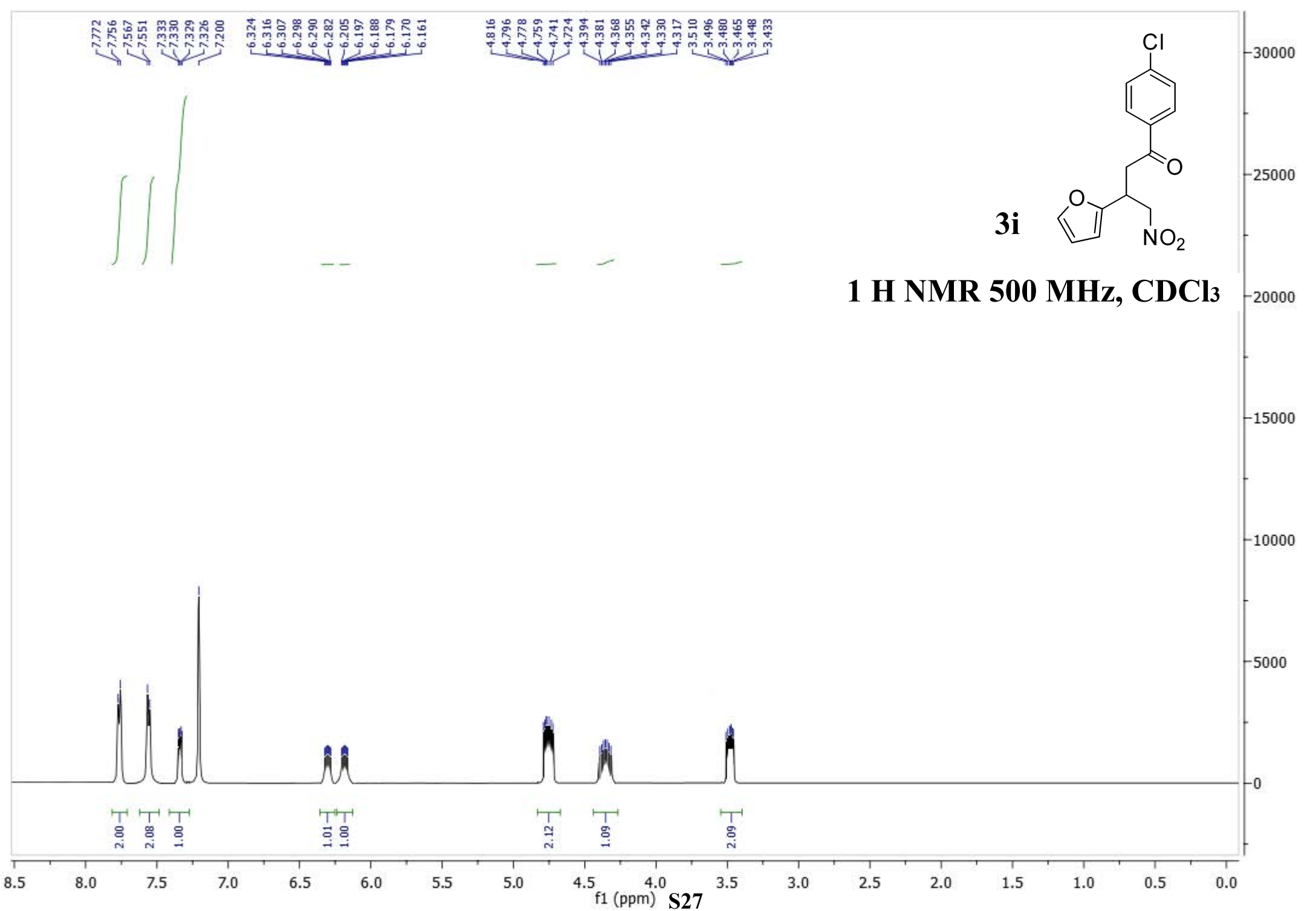
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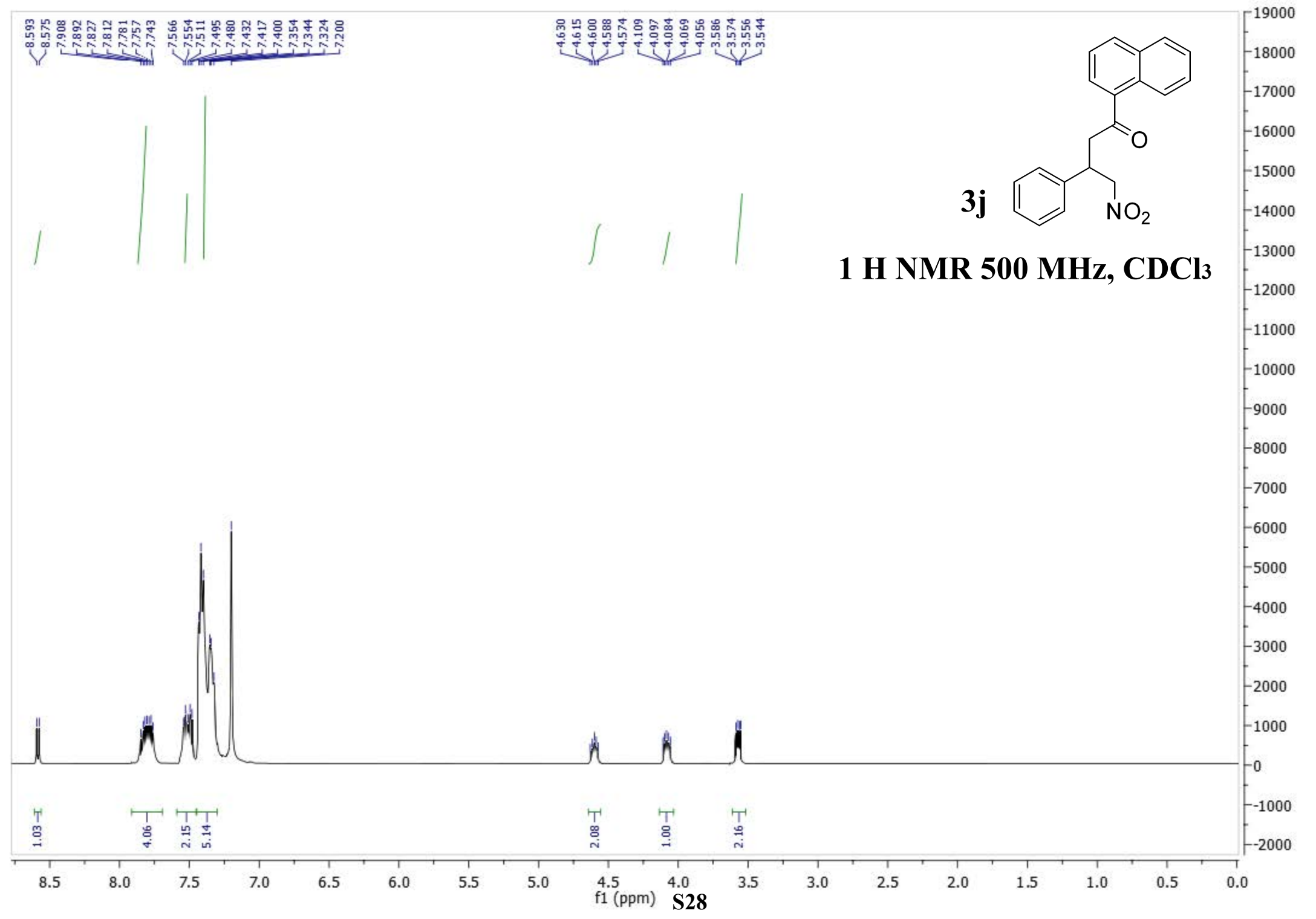
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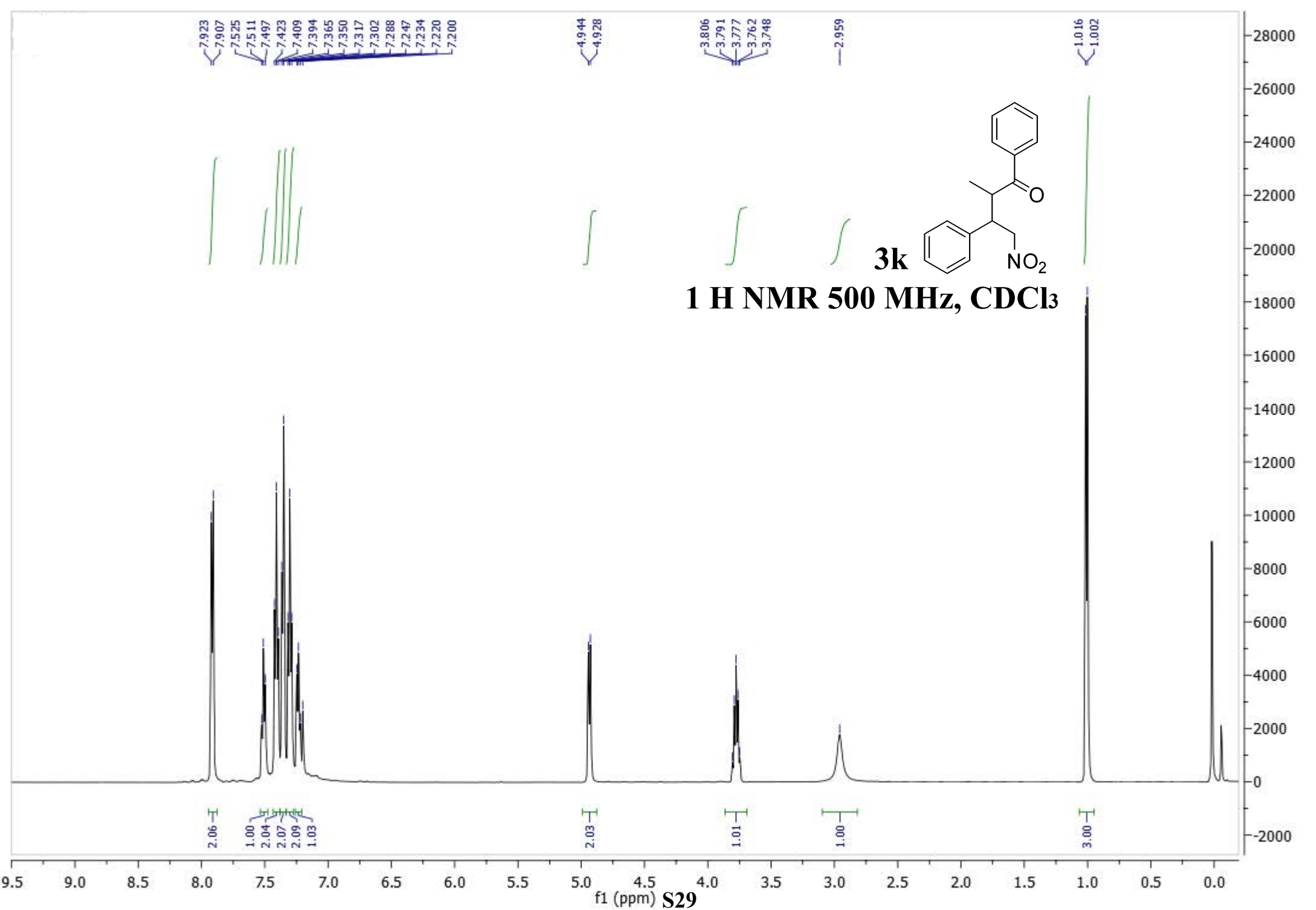
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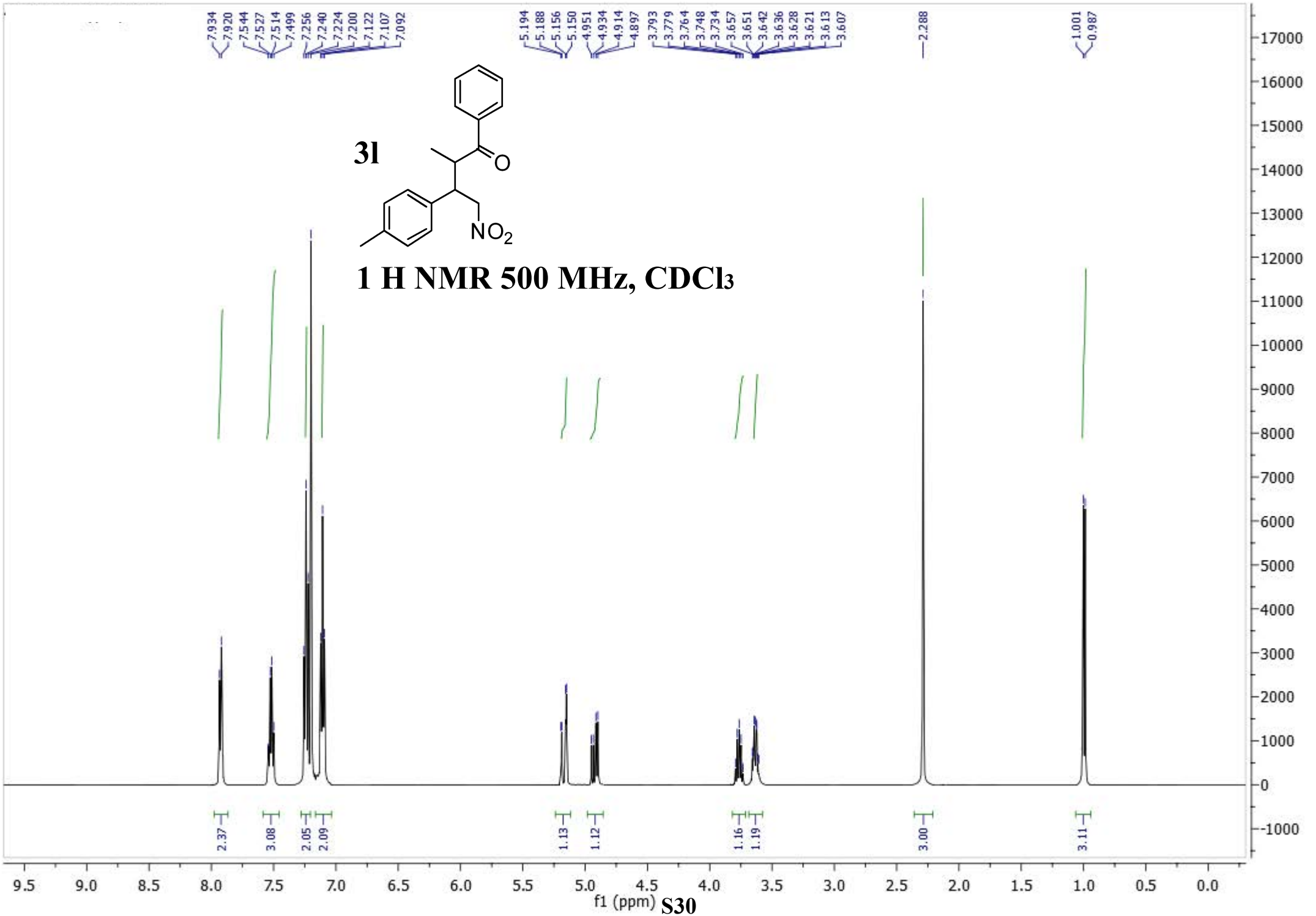
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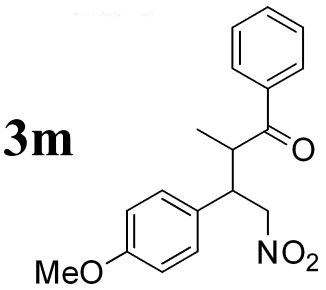
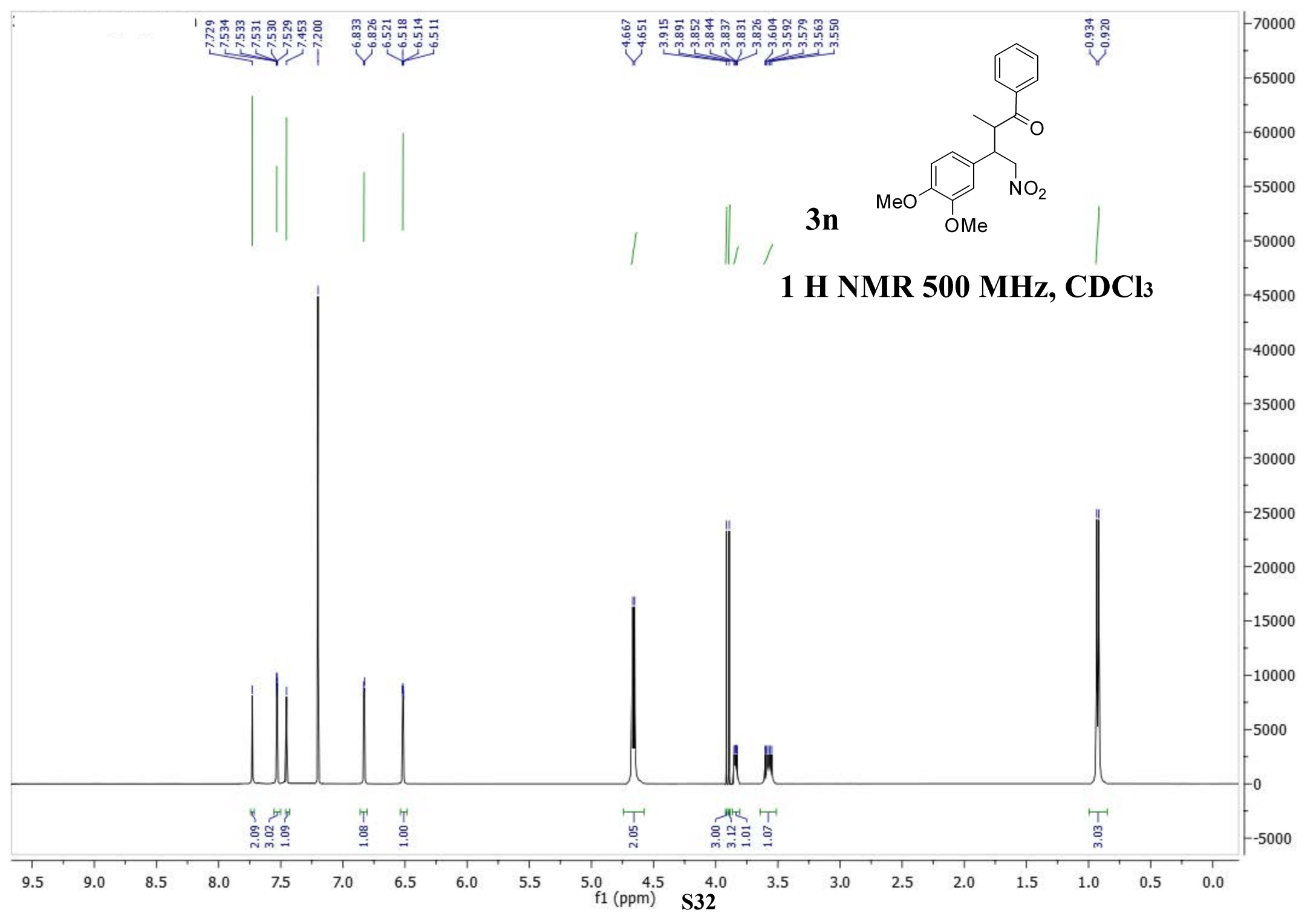
7.499
7.256
7.240
7.224
7.200
7.122
7.107
7.092
5.194
5.188
5.156
5.150
4.951
4.934
4.914
4.897
3.793
3.779
3.764
3.748
3.734
3.657
3.651
3.642
3.636
3.628
3.621
3.613
3.607
2.288
1.001
0.987
3l
O
NO2
1 H NMR 500 MHz, CDCl3
2.37
3.08
2.05
2.09
1.13
1.12
1.16
1.19
3.00
3.11
f1 (ppm)

3m

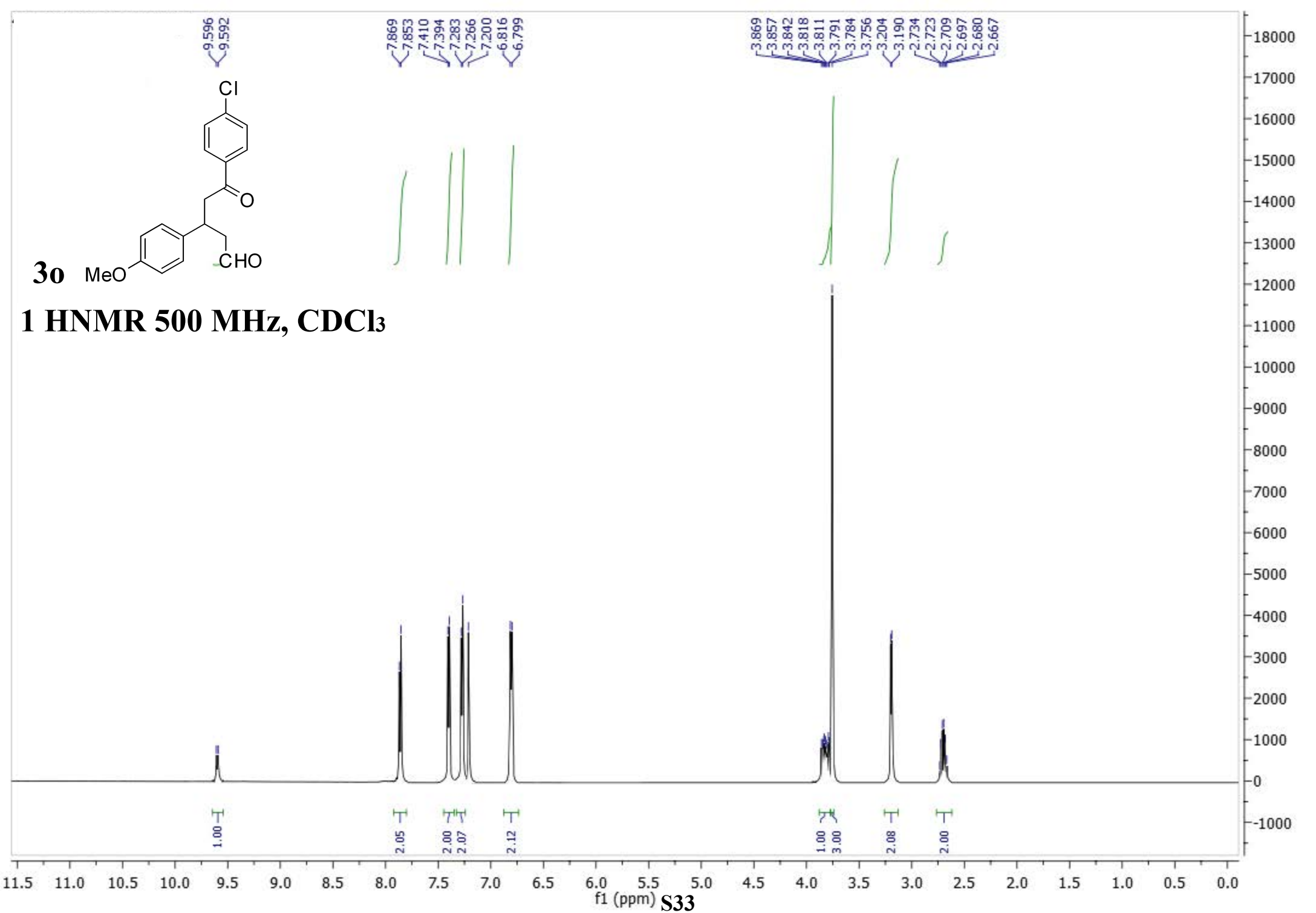


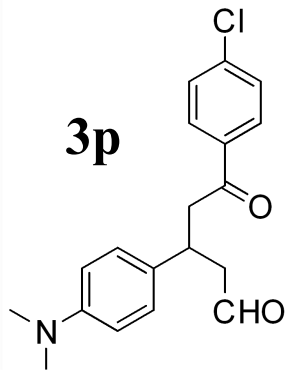
1 H NMR 500 MHz, CDCl3



3n

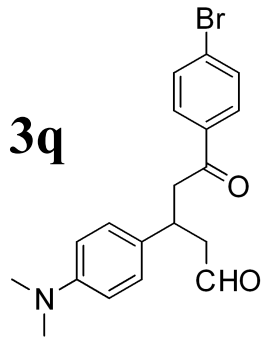
1 H NMR 500 MHz, $CDCl_3$


9.596
9.592
7.869
7.853
7.410
7.394
7.283
7.266
7.200
6.816
6.799
3.869
3.857
3.842
3.818
3.811
3.791
3.784
3.756
3.204
3.190
2.734
2.723
2.709
2.697
2.680
2.667
Cl
O
CHO
MeO
3o
1 HNMR 500 MHz, CDCl3
1.00
2.05
2.00
2.07
2.12
1.00
3.00
2.08
2.00
f1 (ppm)



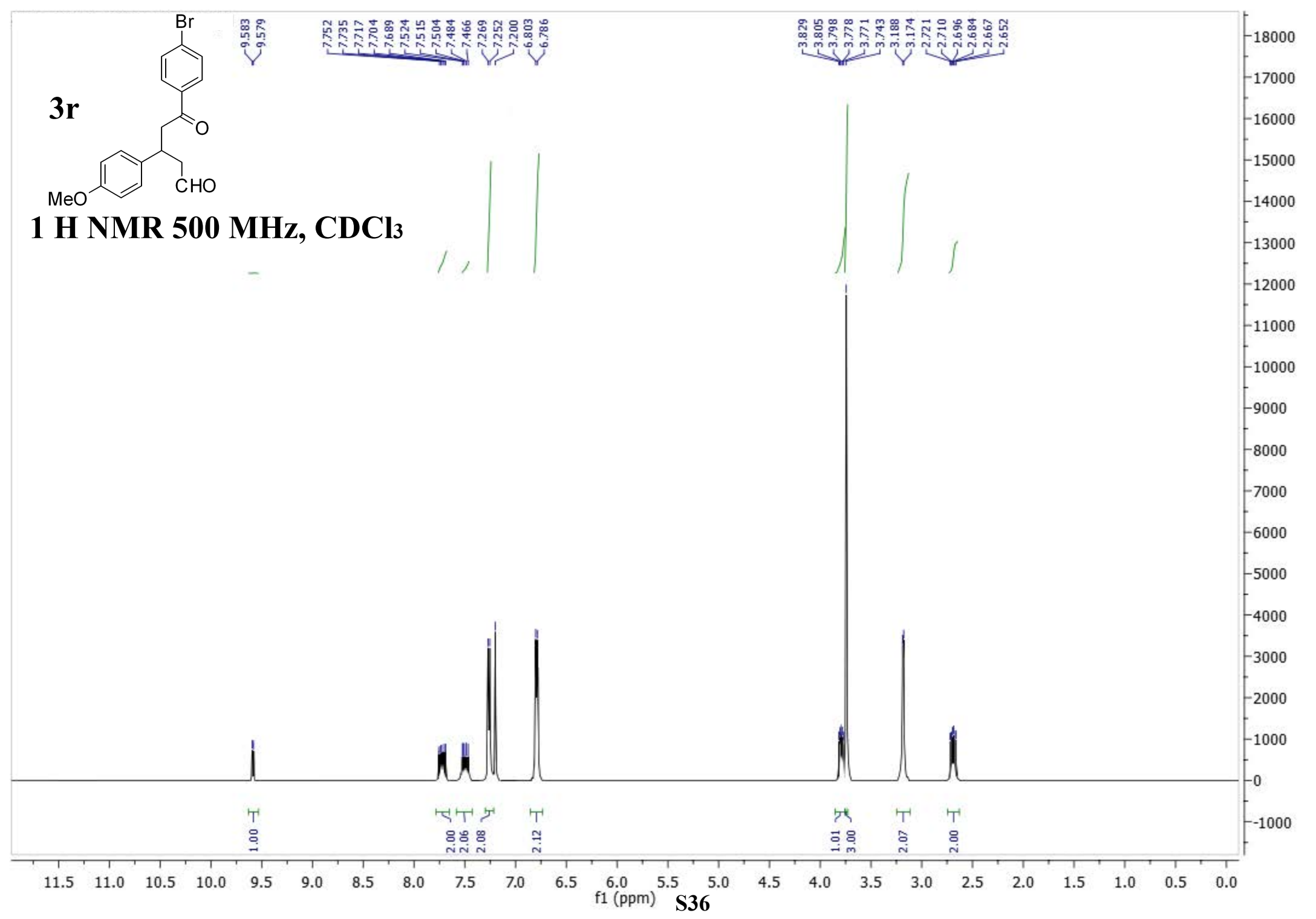
3p

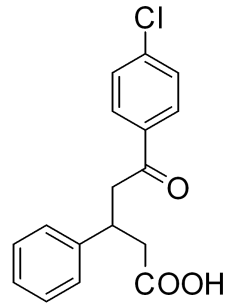
1 H NMR 500 MHz, $CDCl_3$



3q

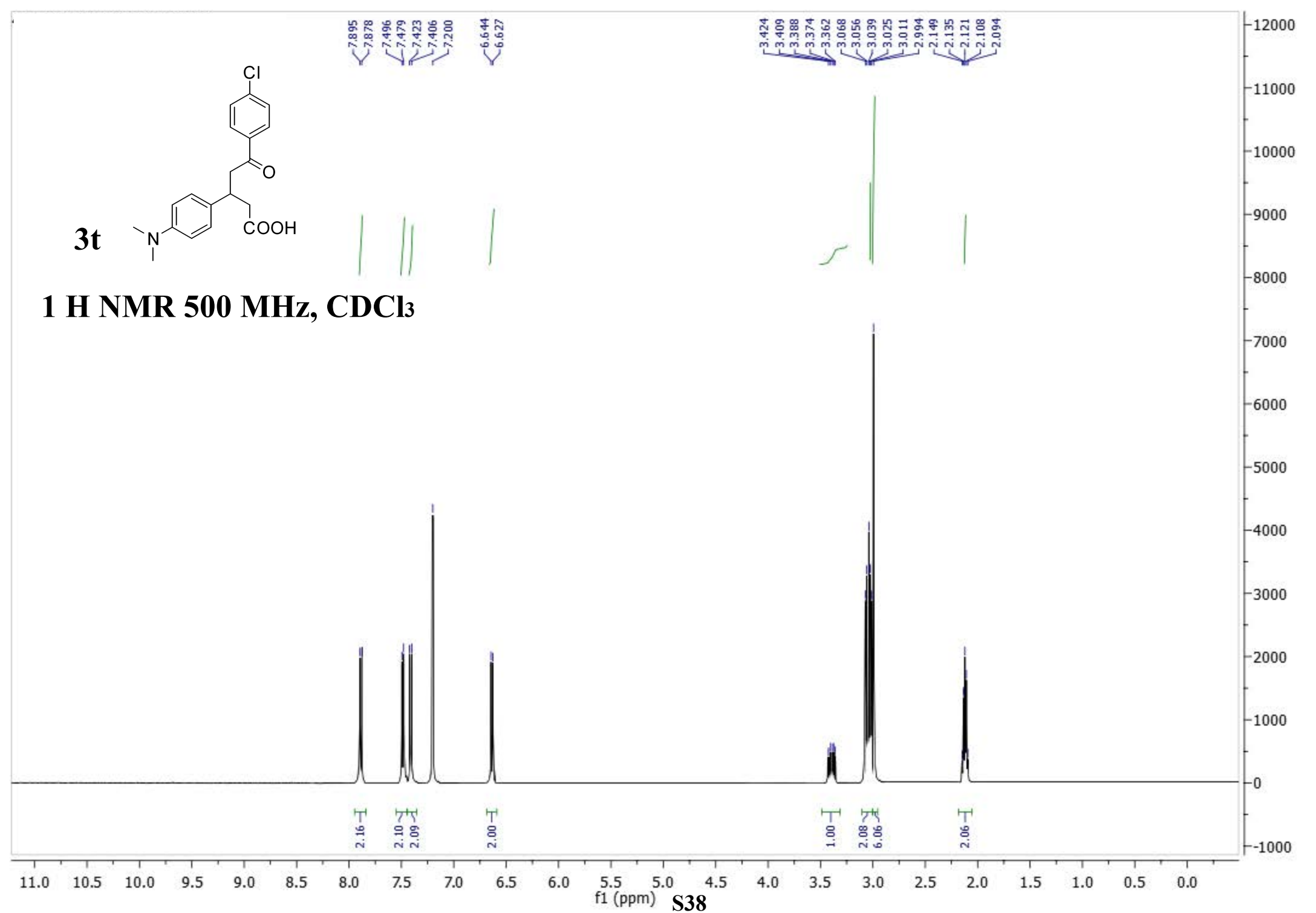
1 H NMR 500 MHz, $CDCl_3$

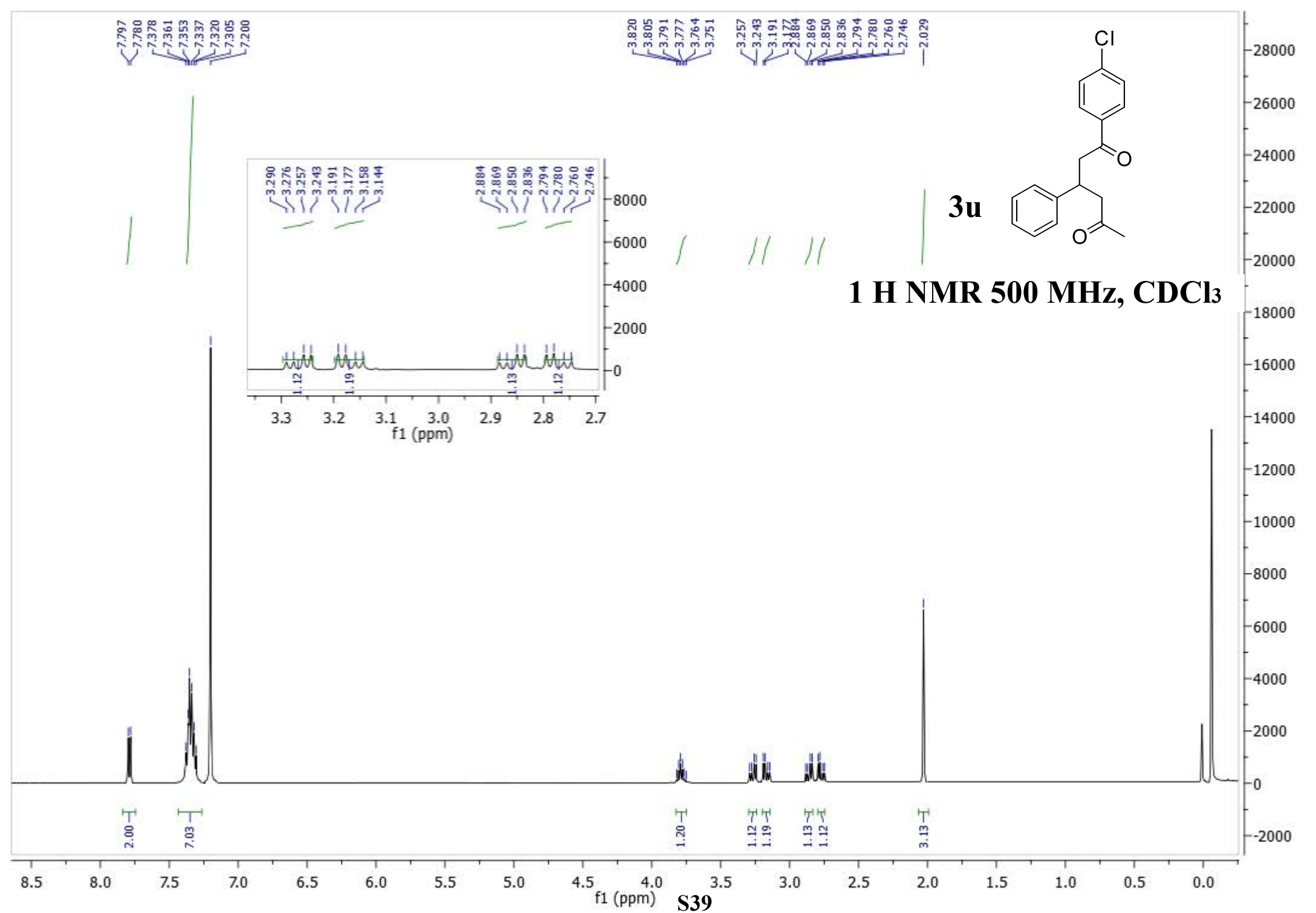

3r
Br
O
CHO
MeO
1 H NMR 500 MHz, CDCl3
9.583
9.579
7.752
7.735
7.717
7.704
7.689
7.524
7.515
7.504
7.484
7.466
7.269
7.252
7.200
6.803
6.786
3.829
3.805
3.798
3.778
3.771
3.743
3.188
3.174
2.721
2.710
2.696
2.684
2.667
2.652
1.00
2.00
2.06
2.08
2.12
1.01
3.00
2.07
2.00
f1 (ppm)

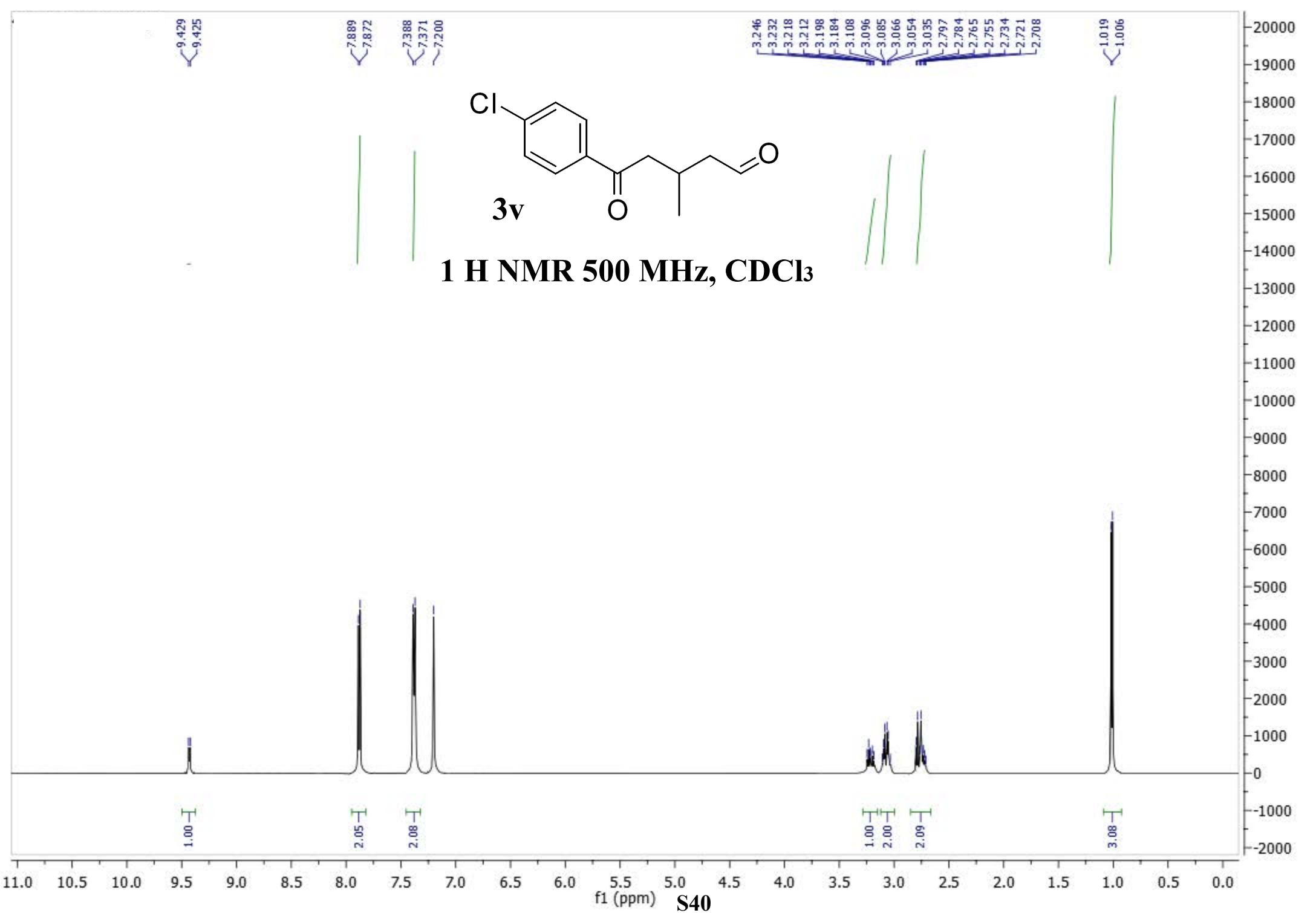


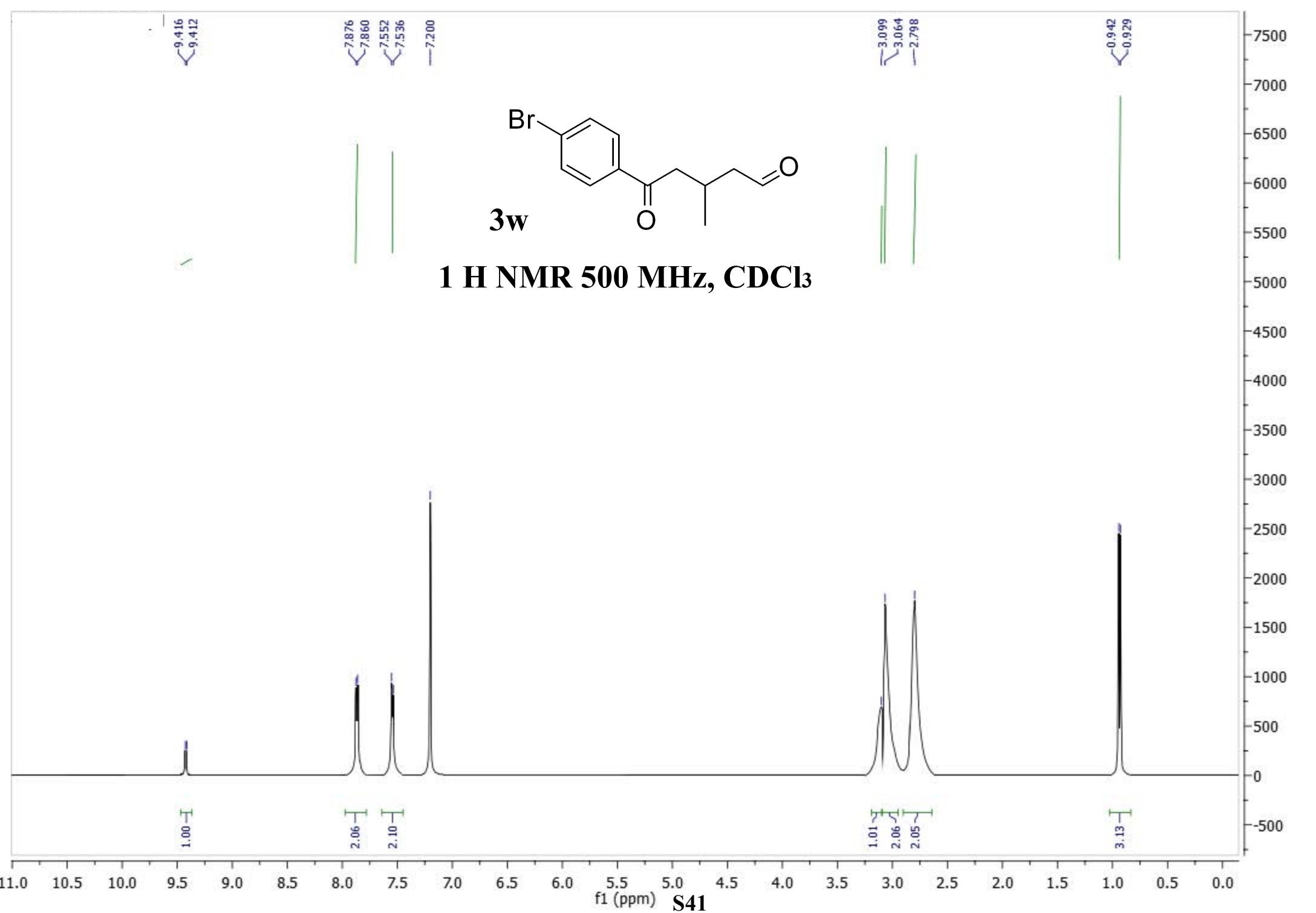
3s

1 H NMR 500 MHz, $CDCl_3$

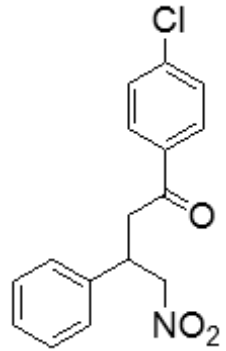

3t
Cl
O
COOH
N
1 H NMR 500 MHz, CDCl3
7.895
7.878
7.496
7.479
7.423
7.406
7.200
6.644
6.627
3.424
3.409
3.388
3.374
3.362
3.068
3.056
3.039
3.025
3.011
2.994
2.149
2.135
2.121
2.108
2.094
2.16
2.10
2.09
2.00
1.00
2.08
6.06
2.06
f1 (ppm)


3u
1 H NMR 500 MHz, CDCl3
f1 (ppm)


9.429
9.425
7.889
7.872
7.388
7.371
7.200
3.246
3.232
3.218
3.212
3.198
3.184
3.108
3.096
3.085
3.066
3.054
3.035
2.797
2.784
2.765
2.755
2.734
2.721
2.708
1.019
1.006
Cl
O
O
3v
1 H NMR 500 MHz, CDCl3
1.00
2.05
2.08
1.00
2.00
2.09
3.08
f1 (ppm)

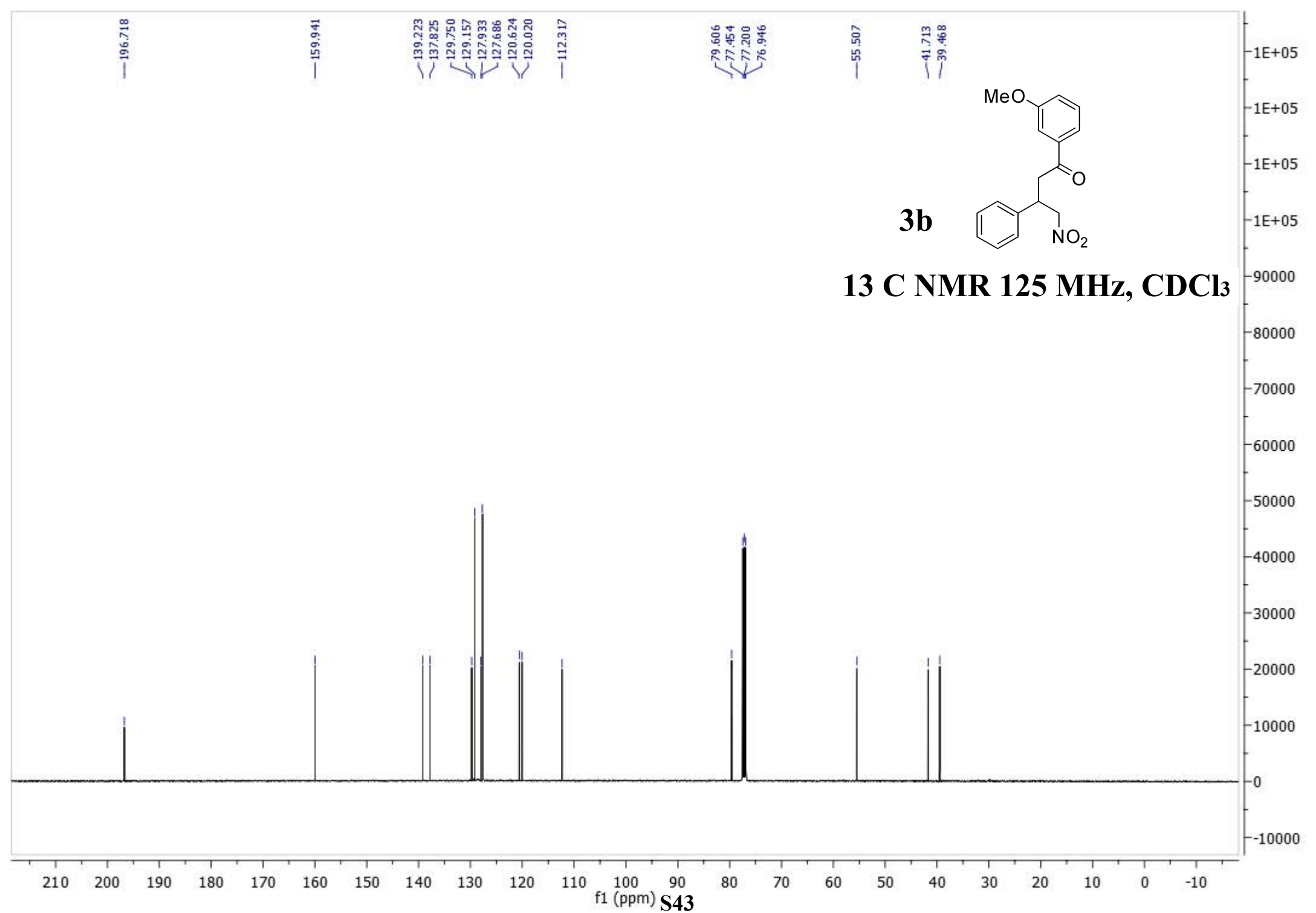

9.416
9.412
7.876
7.860
7.552
7.536
7.200
3.099
3.064
2.798
0.942
0.929
Br
O
O
3w
1 H NMR 500 MHz, CDCl3
1.00
2.06
2.10
1.01
2.06
2.05
3.13
f1 (ppm)

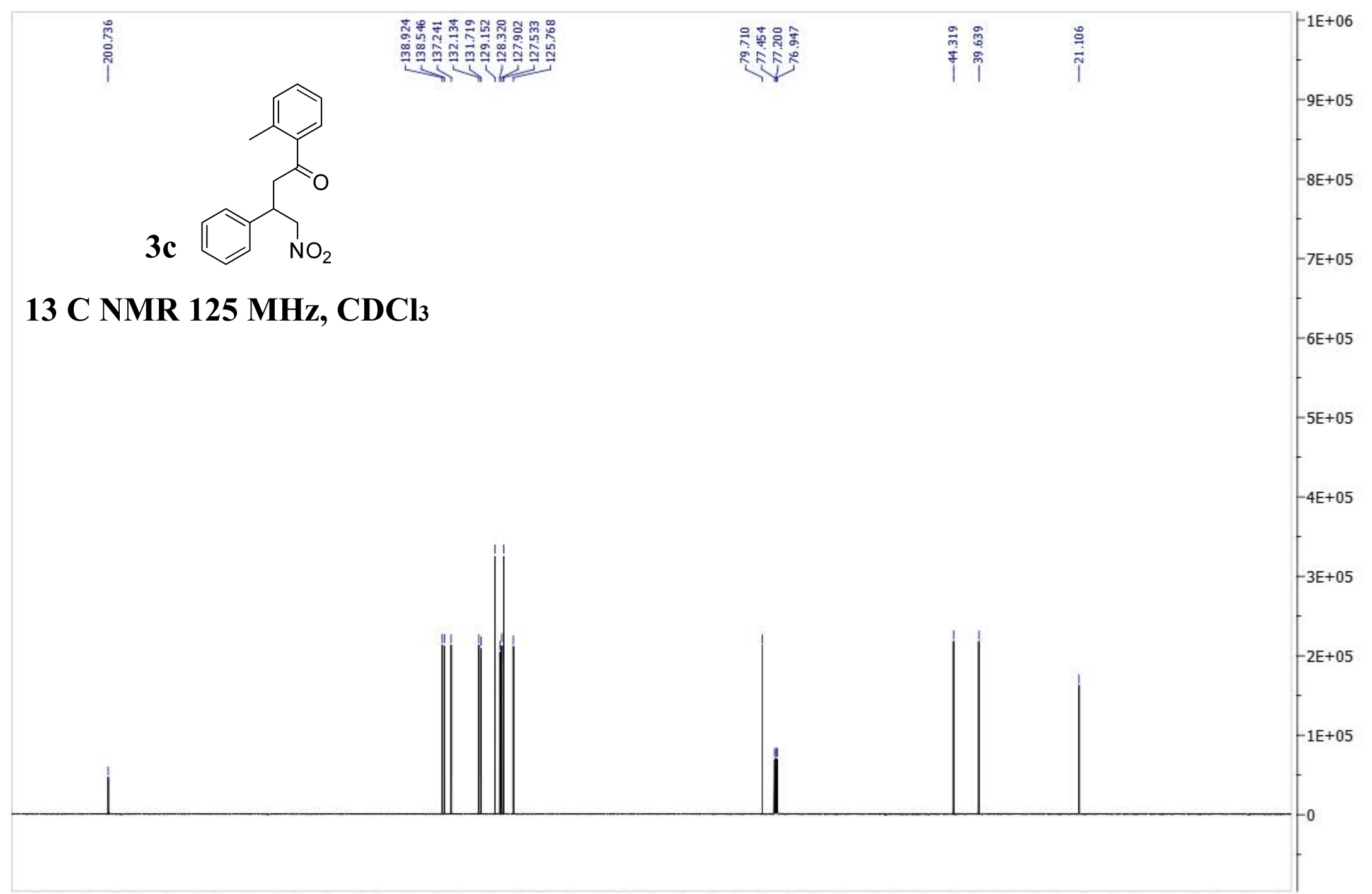
V. 13 C NMR Spectra 3a -3w

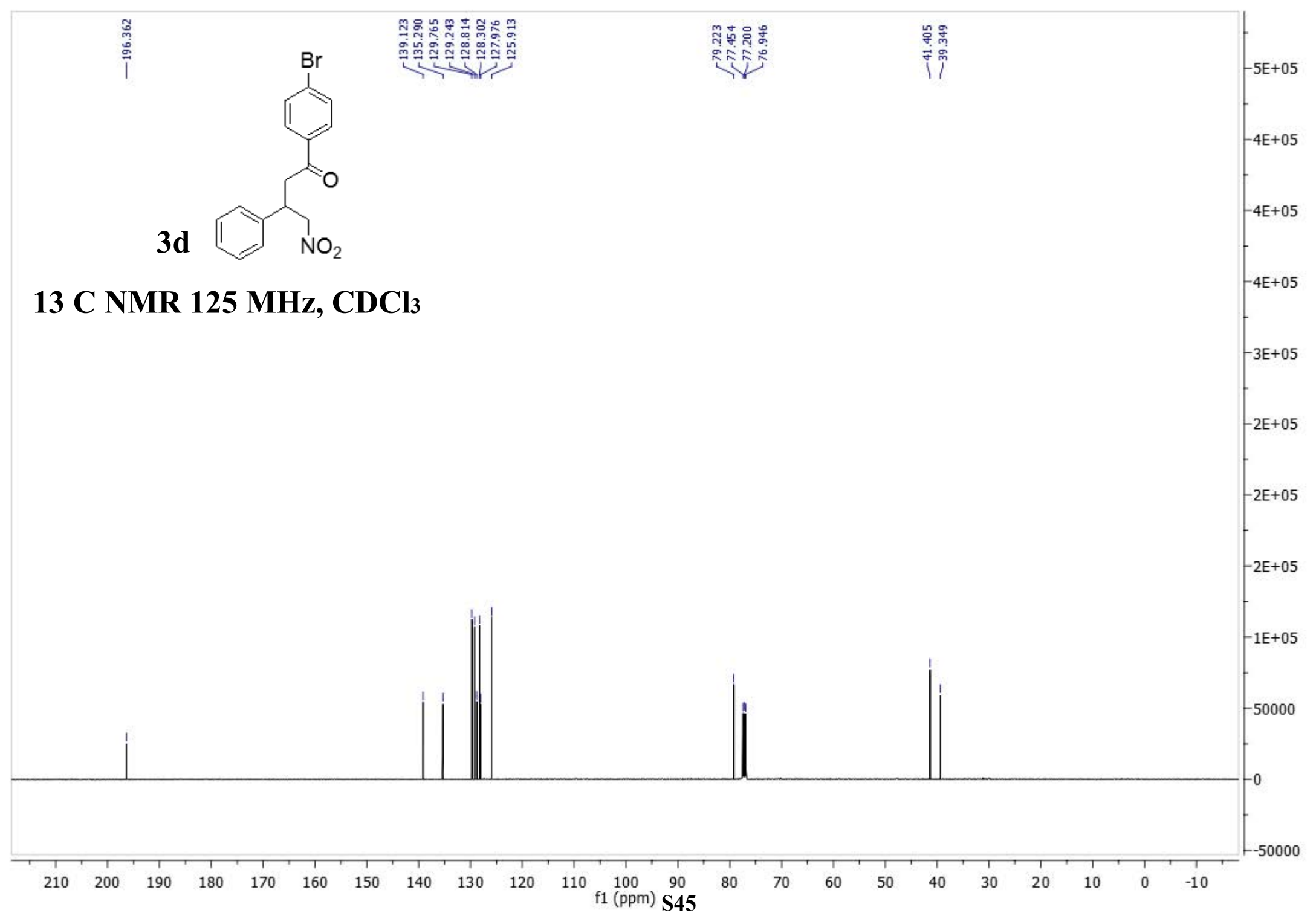


3a

13 C NMR 125 MHz, $CDCl_3$

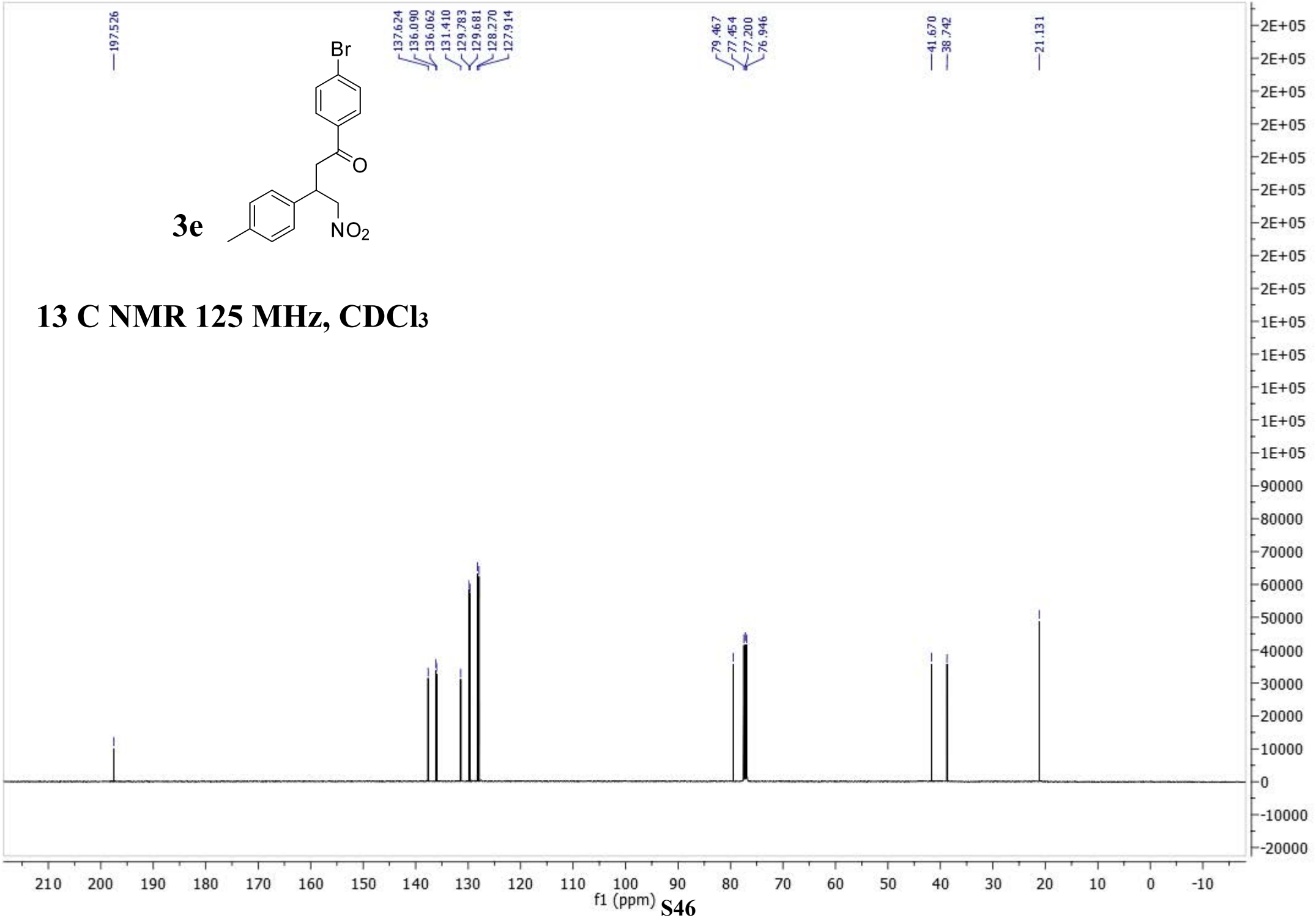

196.718
159.941
139.223
137.825
129.750
129.157
127.933
127.686
120.624
120.020
112.317
79.606
77.454
77.200
76.946
55.507
41.713
39.468
MeO
O
NO2
3b
13 C NMR 125 MHz, CDCl3
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

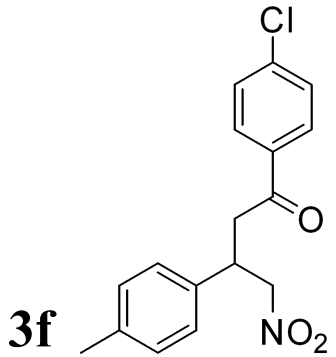

200.736
138.924
138.546
137.241
132.134
131.719
129.152
128.320
127.902
127.533
125.768
79.710
77.454
77.200
76.947
44.319
39.639
21.106
O
NO2
3c
13 C NMR 125 MHz, CDCl3
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3d

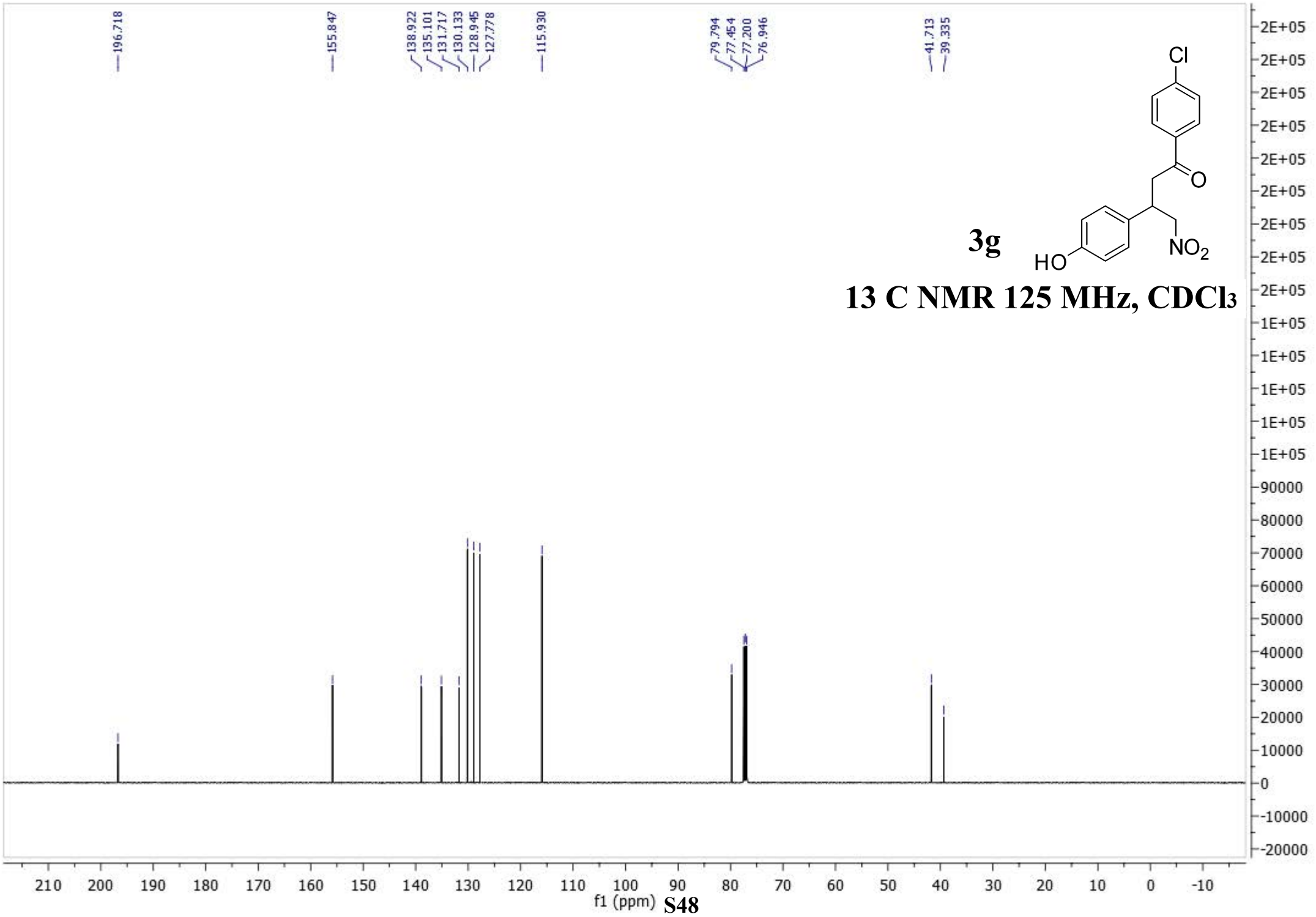
13 C NMR 125 MHz, $CDCl_3$

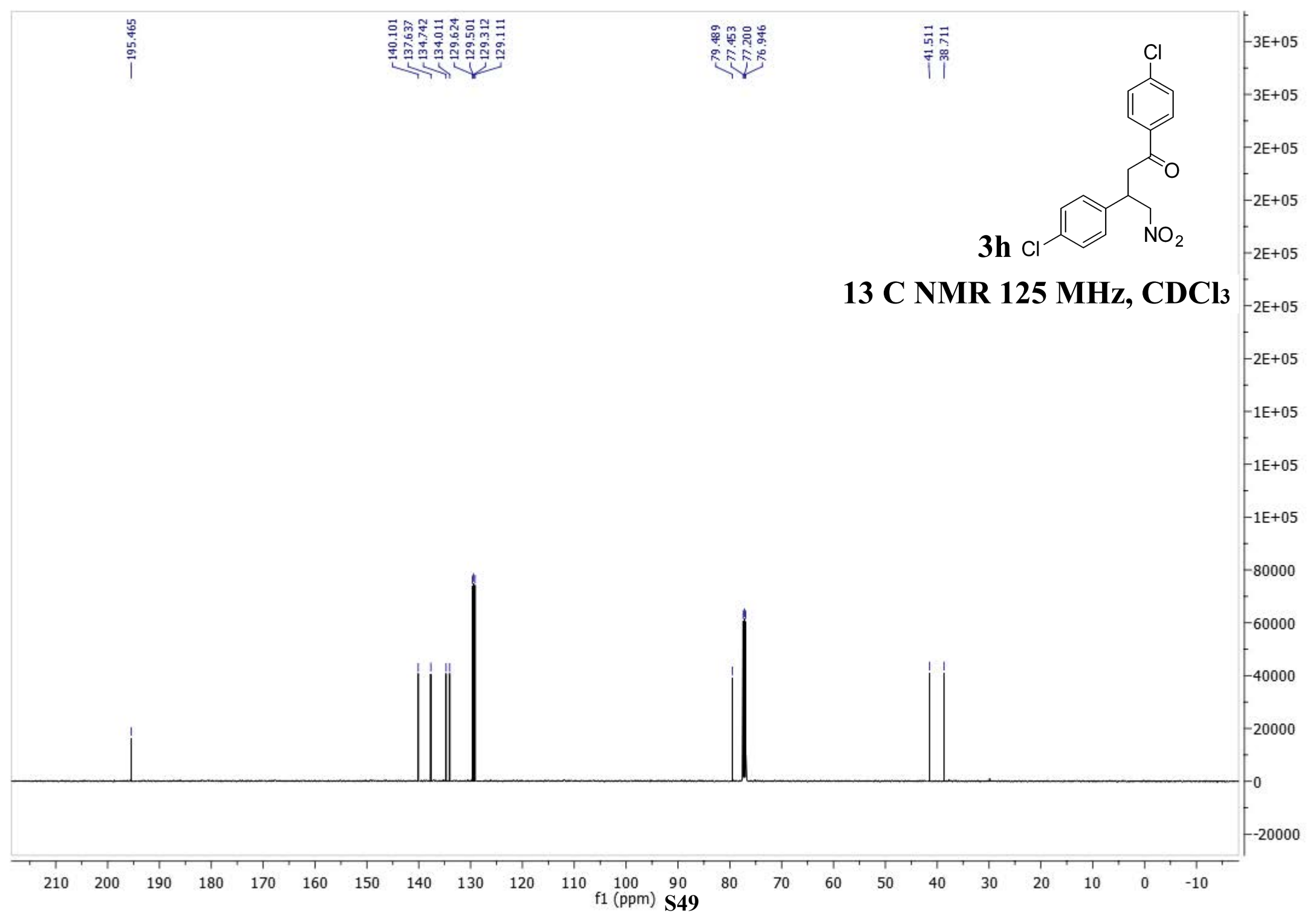

197.526
137.624
136.090
136.062
131.410
129.783
129.681
128.270
127.914
79.467
77.454
77.200
76.946
41.670
38.742
21.131
Br
O
NO2
3e
13 C NMR 125 MHz, CDCl3
f1 (ppm)

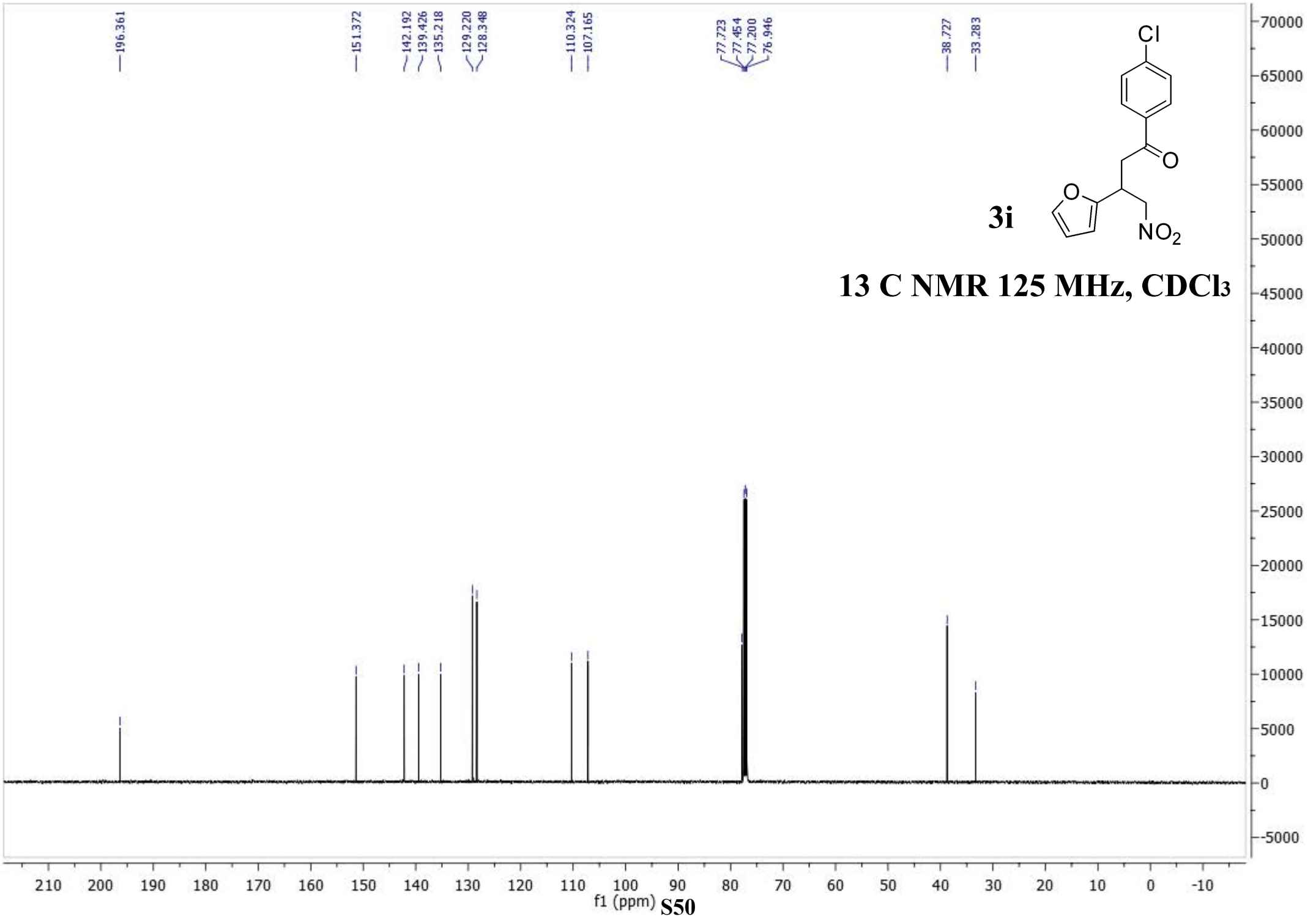


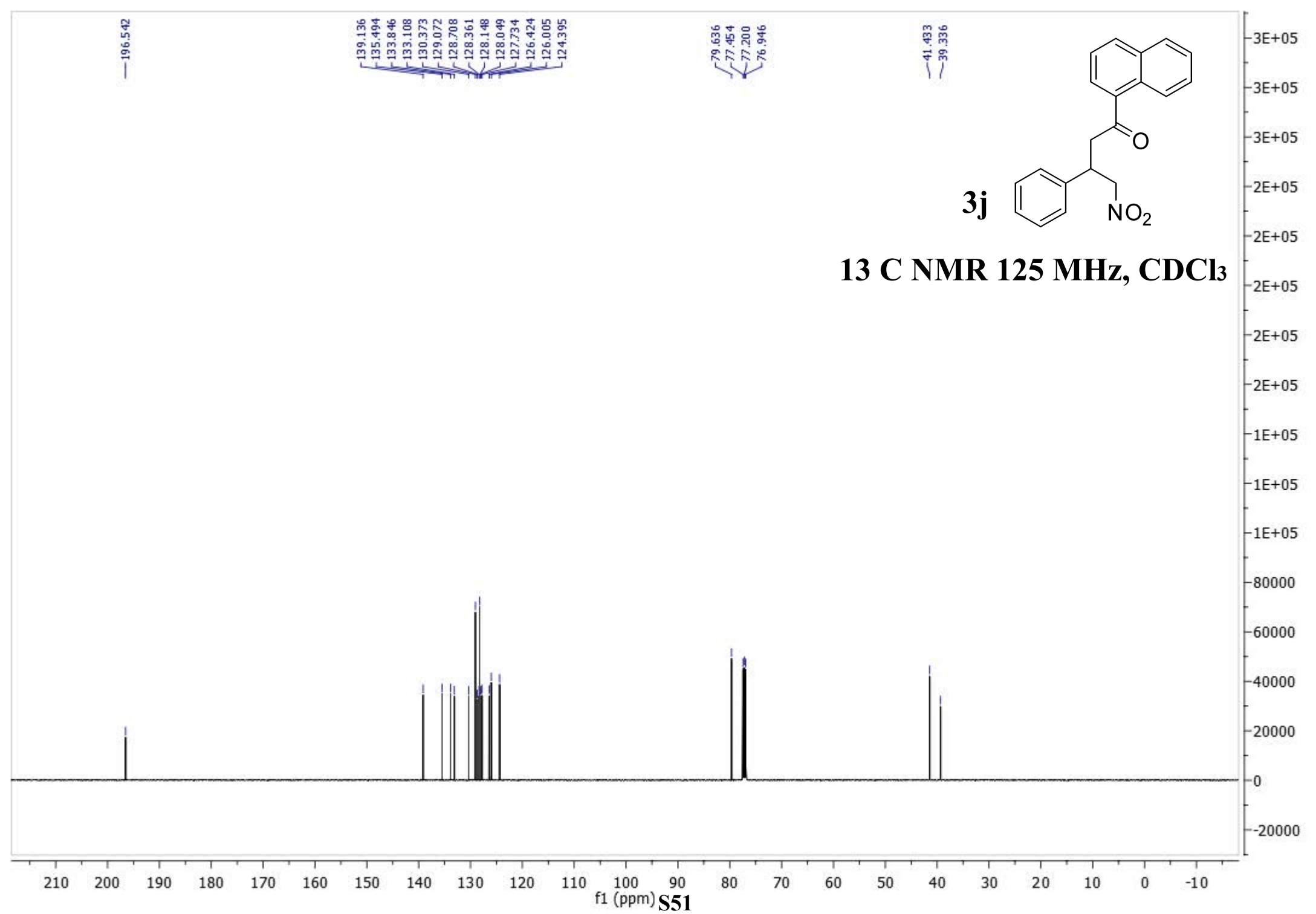
3f

13 C NMR 125 MHz, $CDCl_3$


196.718
155.847
138.922
135.101
131.717
130.133
128.945
127.778
115.930
79.794
77.454
77.200
76.946
41.713
39.335
Cl
O
HO
NO2
3g
13 C NMR 125 MHz, CDCl3
f1 (ppm)

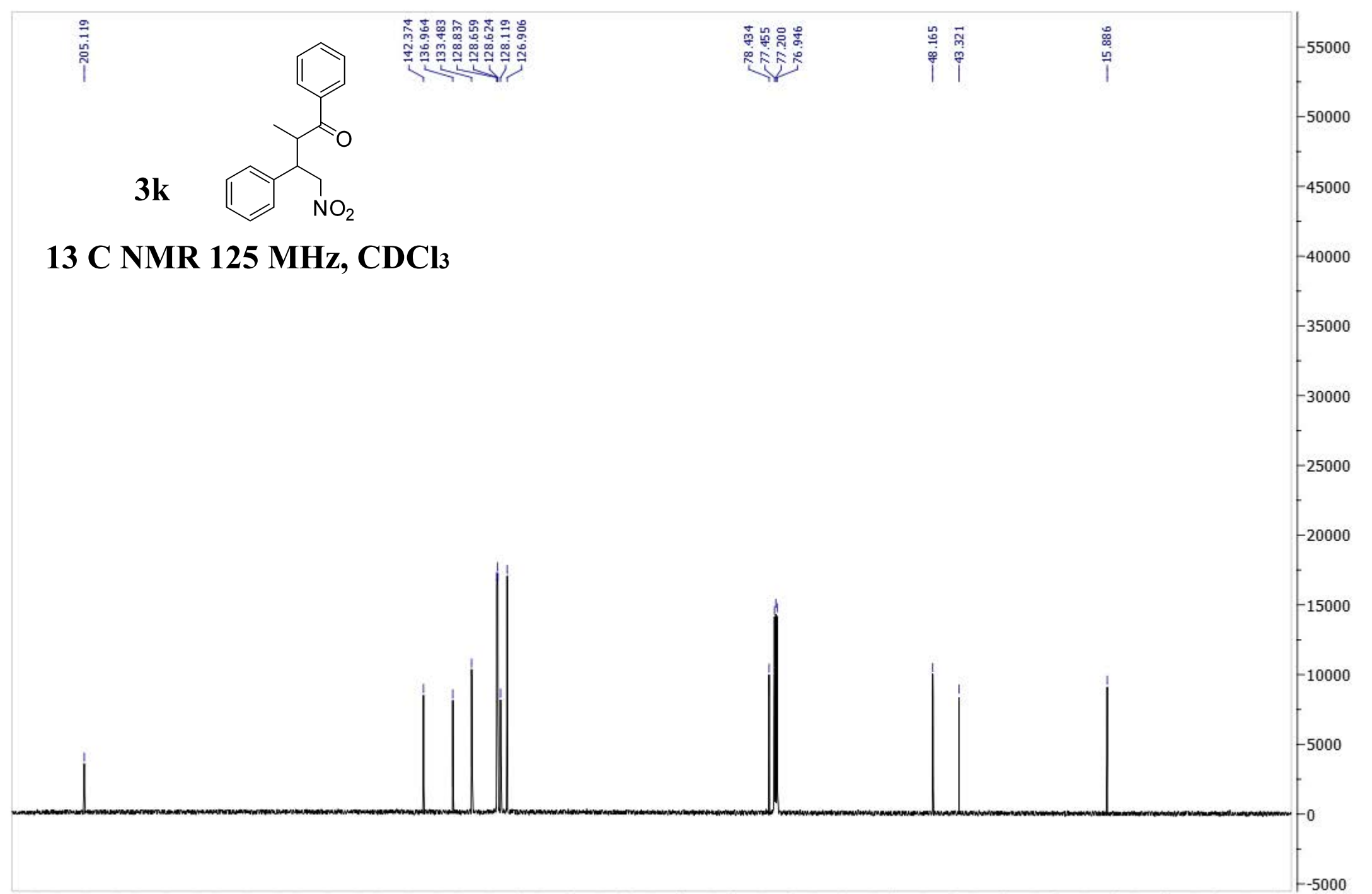

195.465
140.101
137.637
134.742
134.011
129.624
129.501
129.312
129.111
79.489
77.453
77.200
76.946
41.511
38.711
Cl
O
NO2
Cl
3h
13 C NMR 125 MHz, CDCl3
3E+05
2E+05
1E+05
80000
60000
40000
20000
0
-20000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


196.361
151.372
142.192
139.426
135.218
129.220
128.348
110.324
107.165
77.723
77.454
77.200
76.946
38.727
33.283
Cl
O
O
NO2
3i
13 C NMR 125 MHz, CDCl3
f1 (ppm)



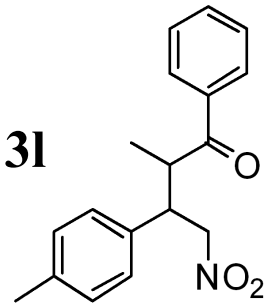
3j

13 C NMR 125 MHz, $CDCl_3$



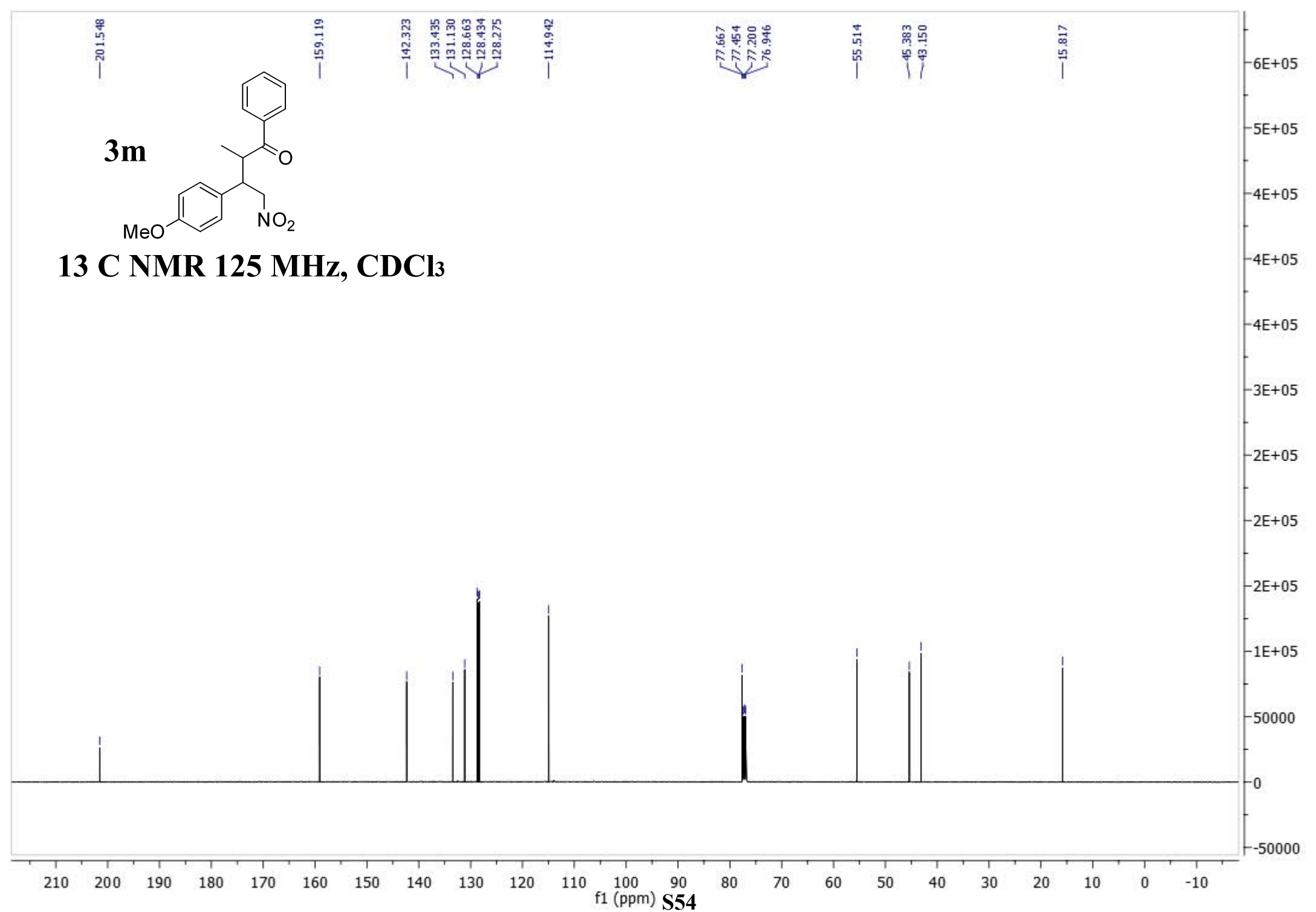
3k

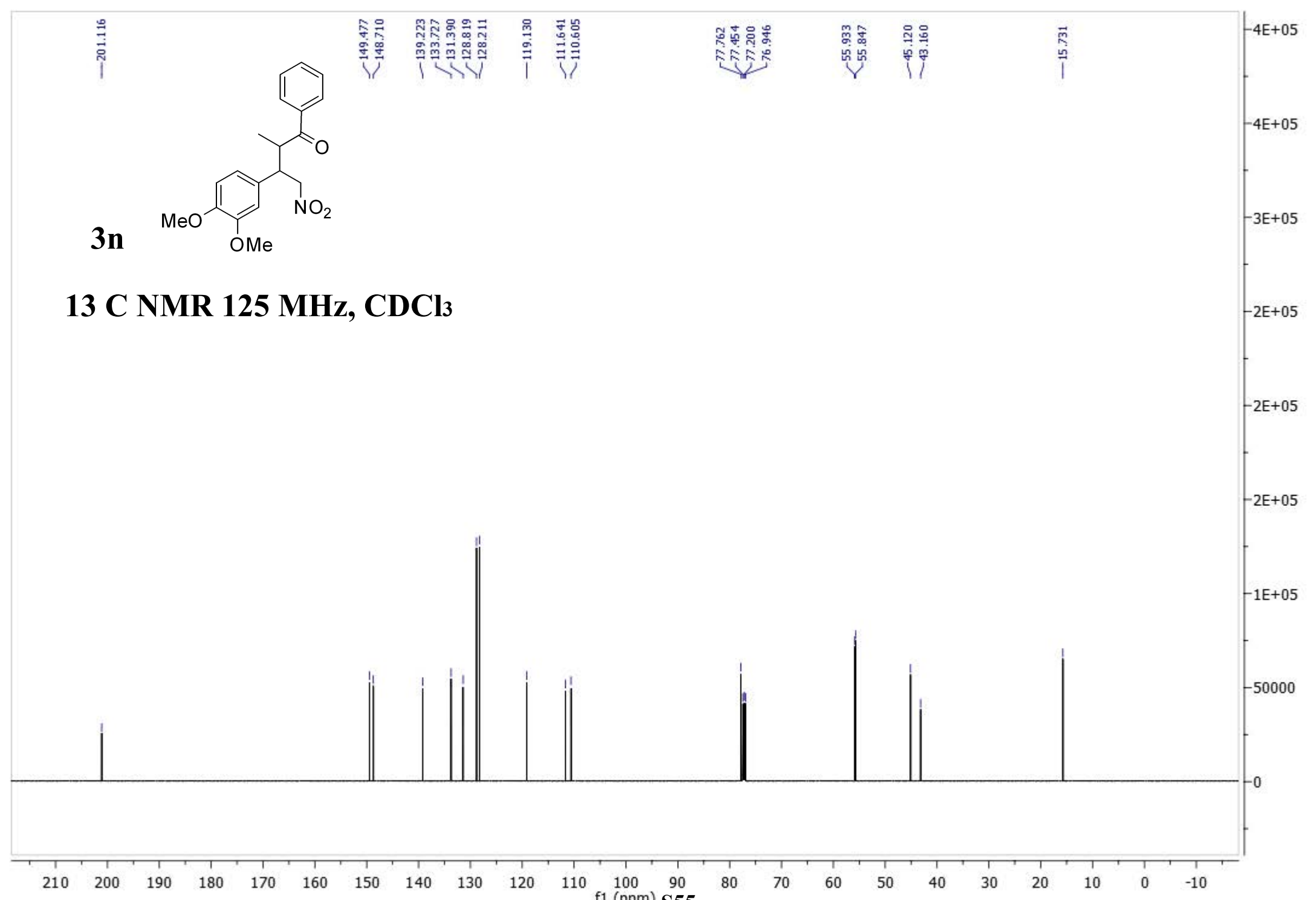
13 C NMR 125 MHz, $CDCl_3$



3l

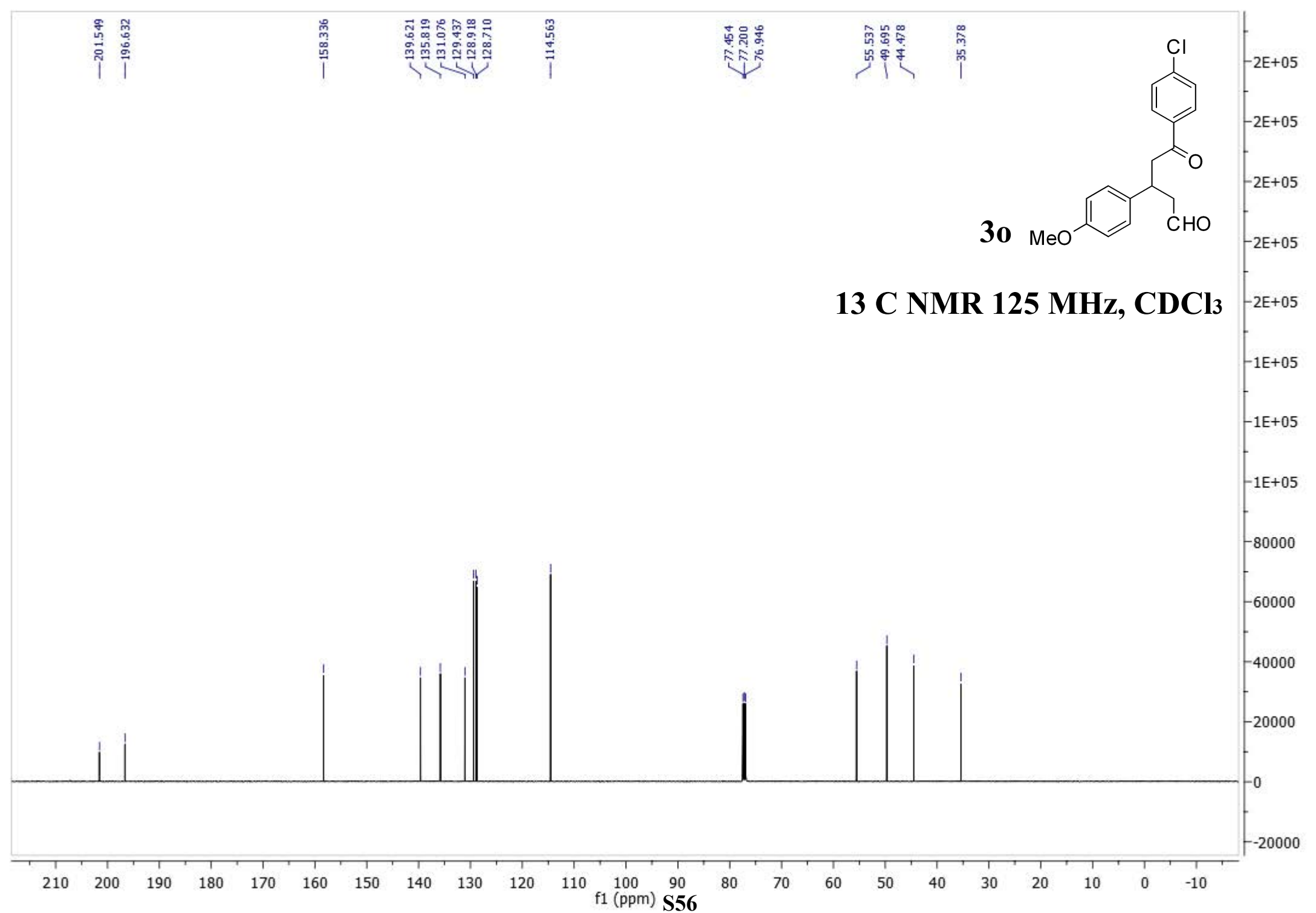
13 C NMR 125 MHz, $CDCl_3$


201.548
159.119
142.323
133.435
131.130
128.663
128.434
128.275
114.942
77.667
77.454
77.200
76.946
55.514
45.383
43.150
15.817
3m
O
NO2
MeO
13 C NMR 125 MHz, CDCl3
6E+05
5E+05
4E+05
4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
50000
0
-50000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



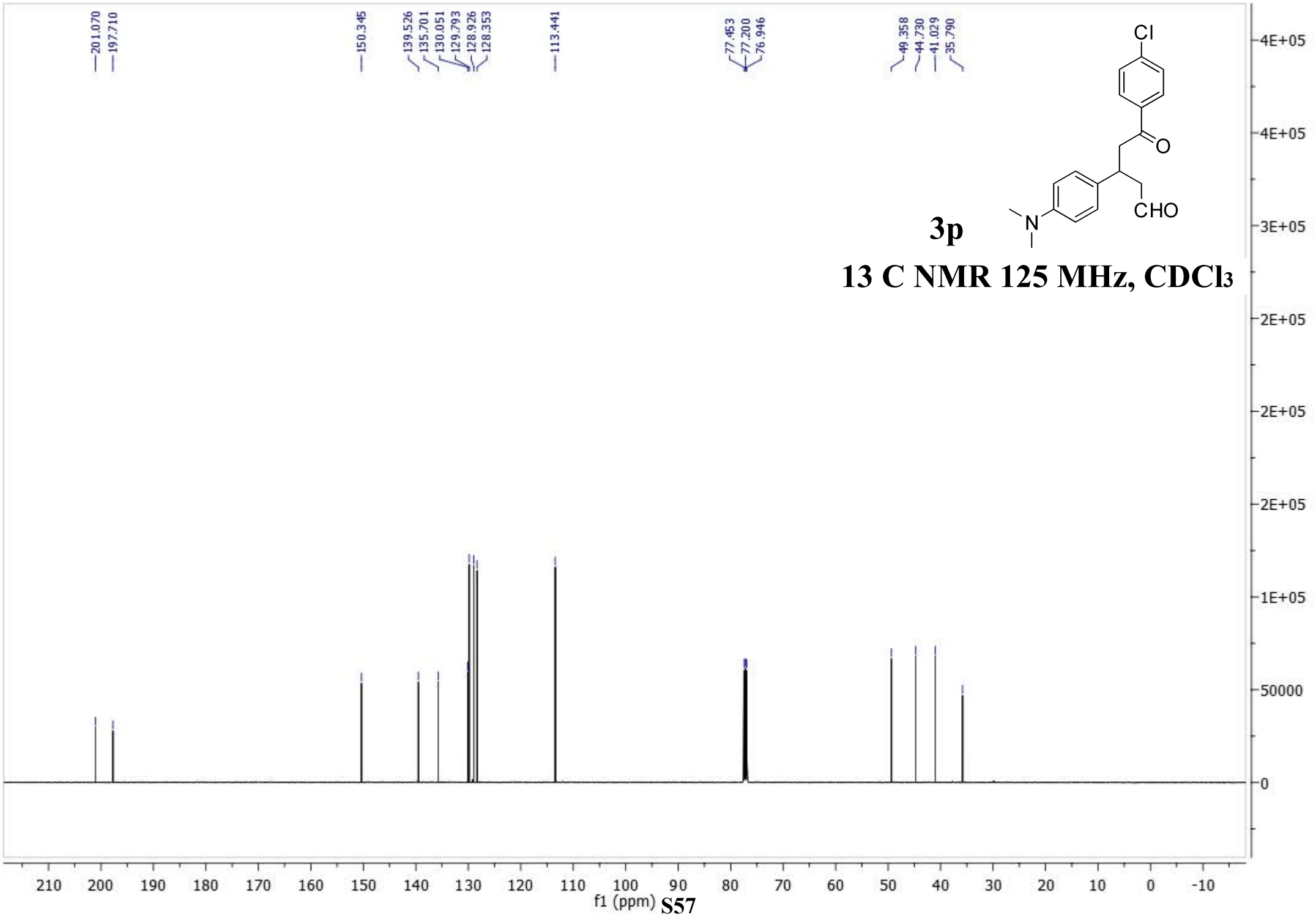
3n

13 C NMR 125 MHz, $CDCl_3$



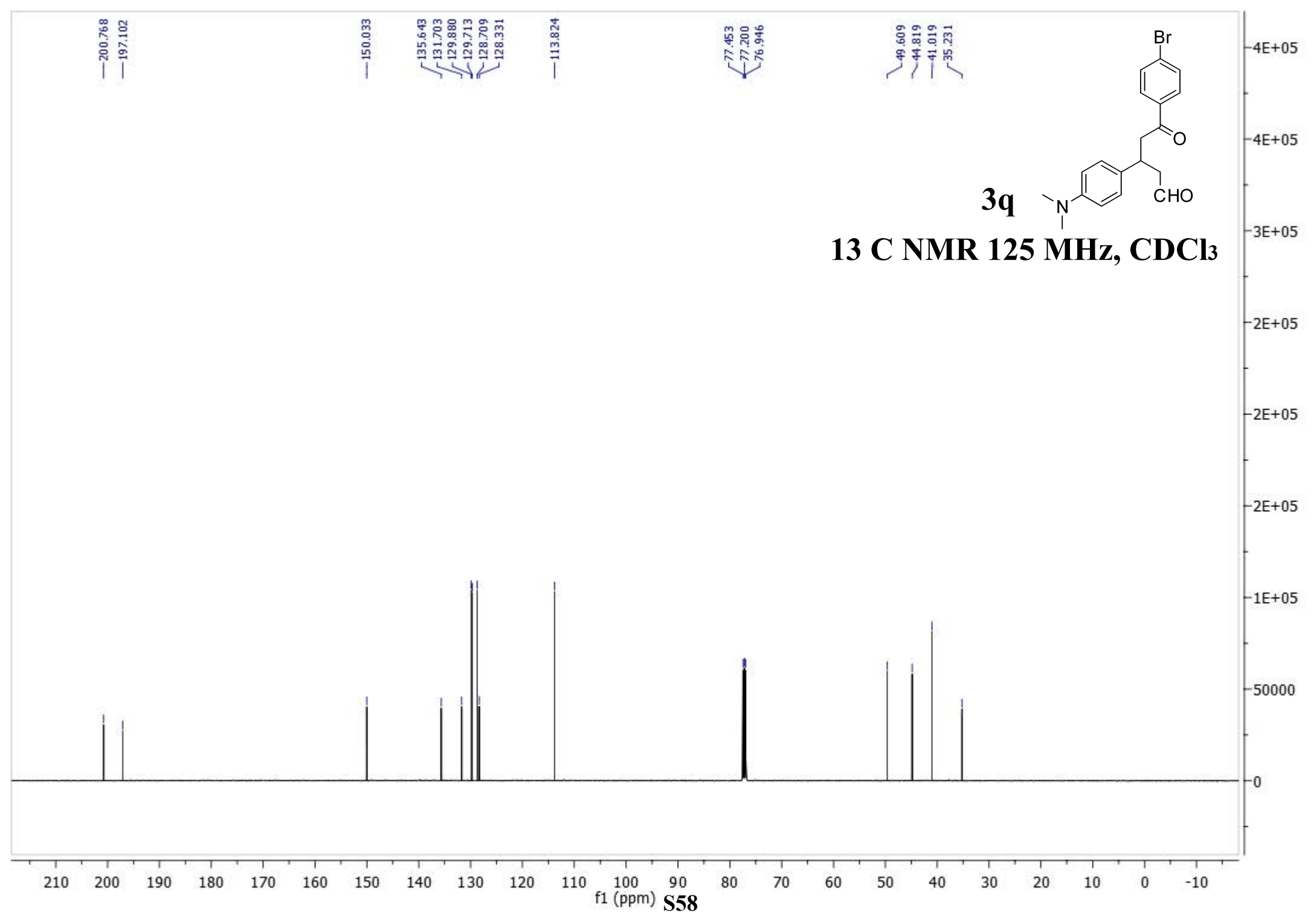
3o

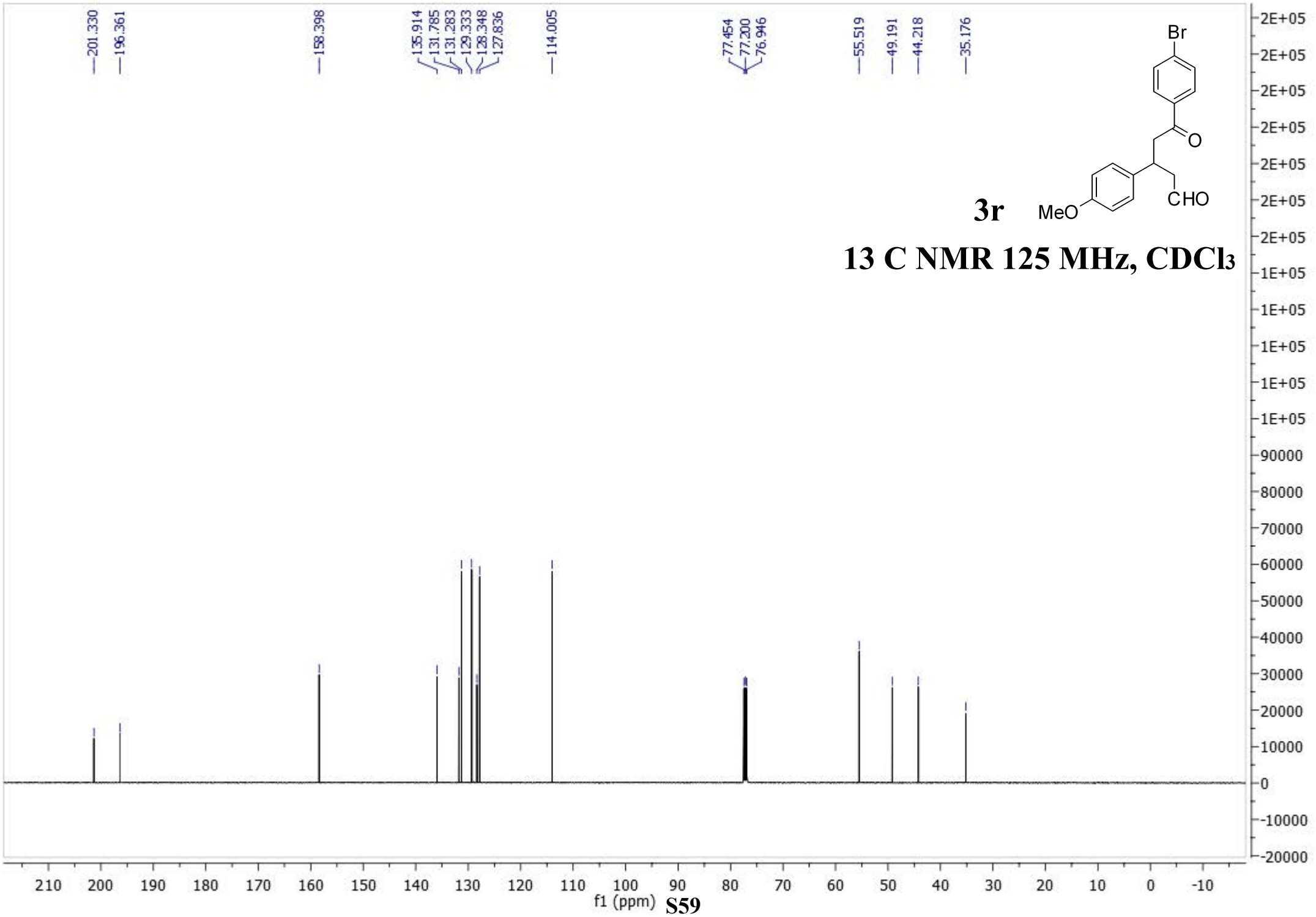
13 C NMR 125 MHz, $CDCl_3$

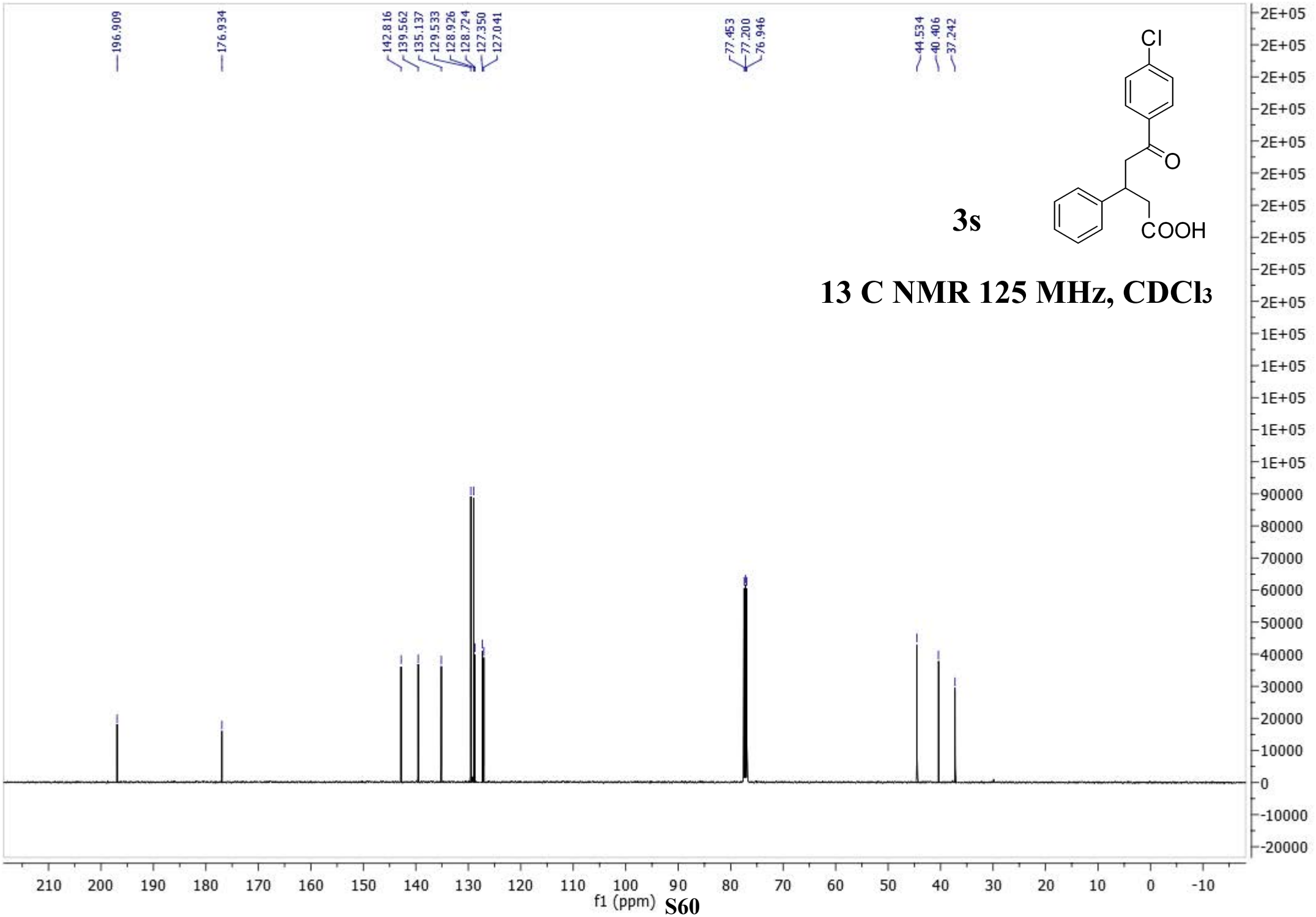


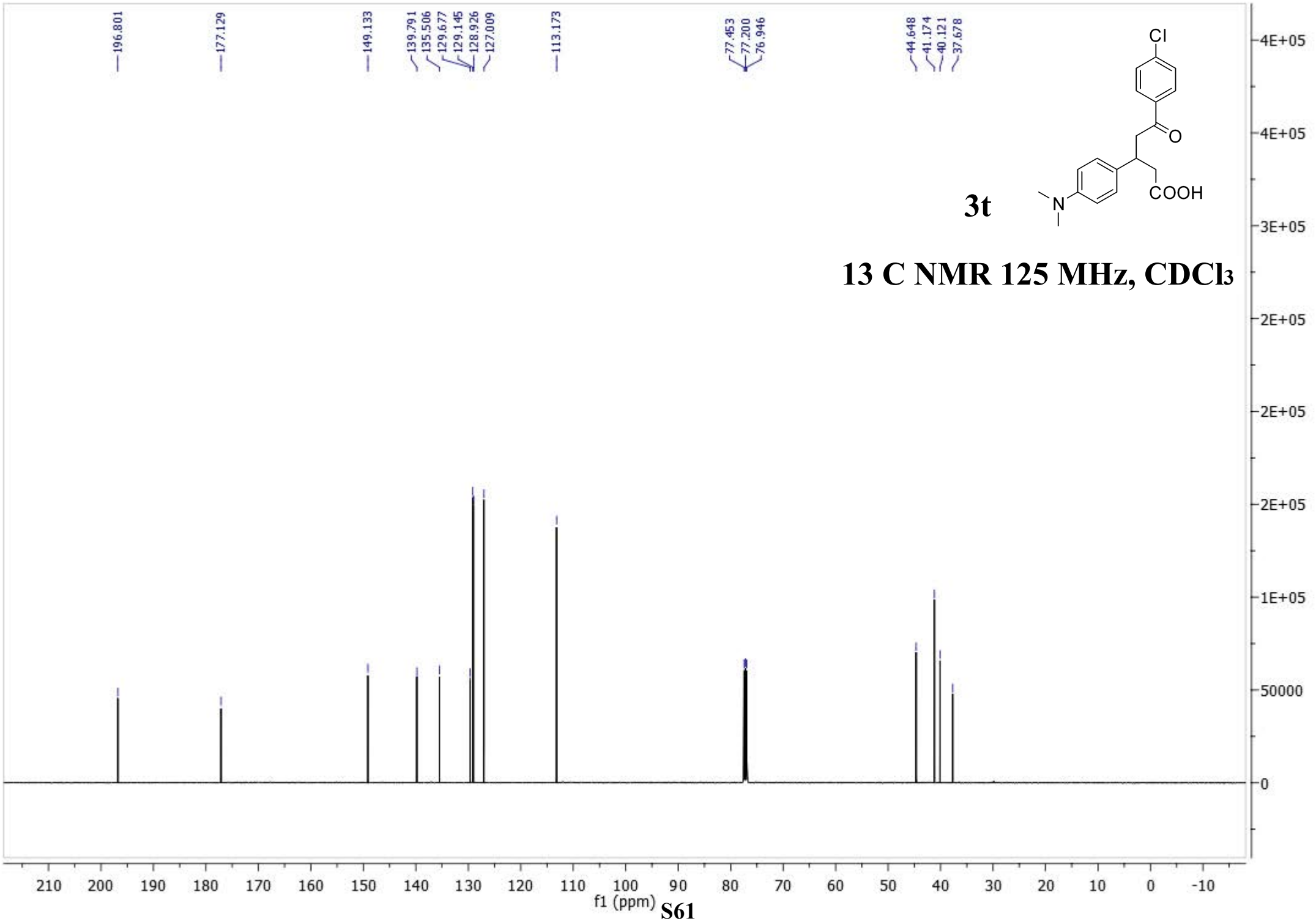
3p

13 C NMR 125 MHz, $CDCl_3$


200.768
197.102
150.033
135.643
131.703
129.880
129.713
128.709
128.331
113.824
77.453
77.200
76.946
49.609
44.819
41.019
35.231
Br
O
CHO
N
3q
13 C NMR 125 MHz, CDCl3
4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
50000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

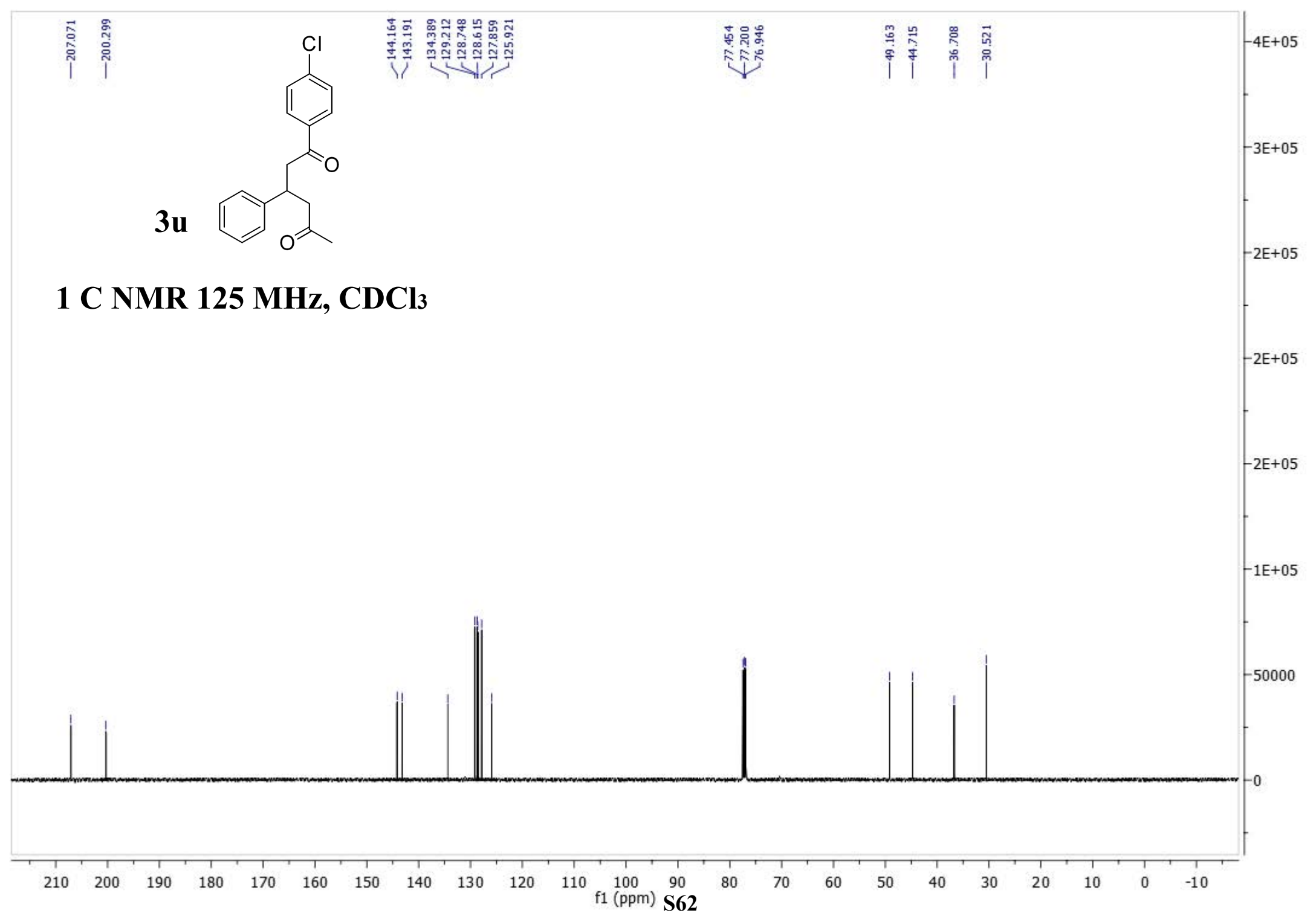

201.330
196.361
158.398
135.914
131.785
131.283
129.333
128.348
127.836
114.005
77.454
77.200
76.946
55.519
49.191
44.218
35.176
Br
O
CHO
MeO
3r
13 C NMR 125 MHz, CDCl3
f1 (ppm)


196.909
176.934
142.816
139.562
135.137
129.533
128.926
128.724
127.350
127.041
77.453
77.200
76.946
44.534
40.406
37.242
Cl
O
COOH
3s
13 C NMR 125 MHz, CDCl3
2E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



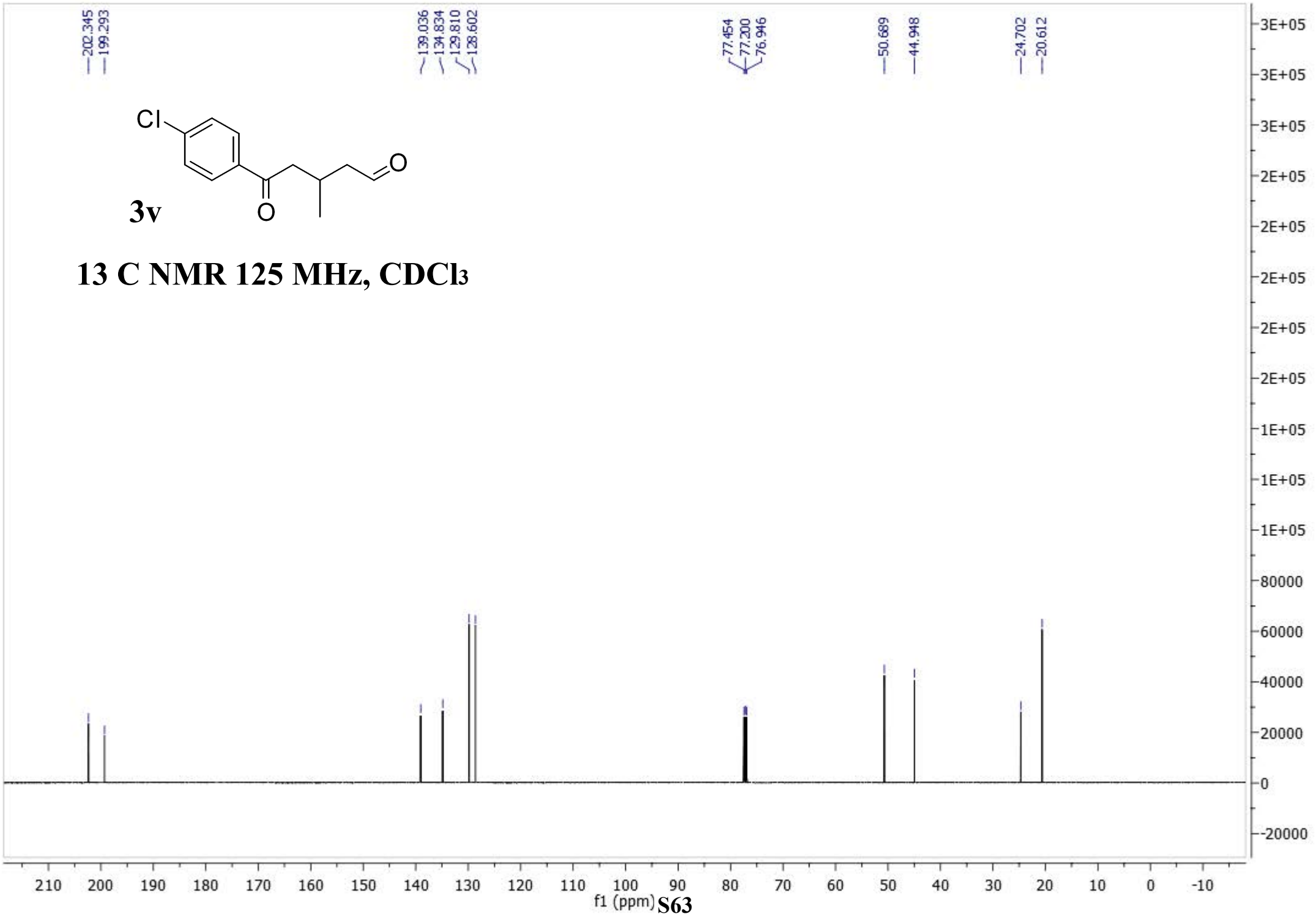
3t

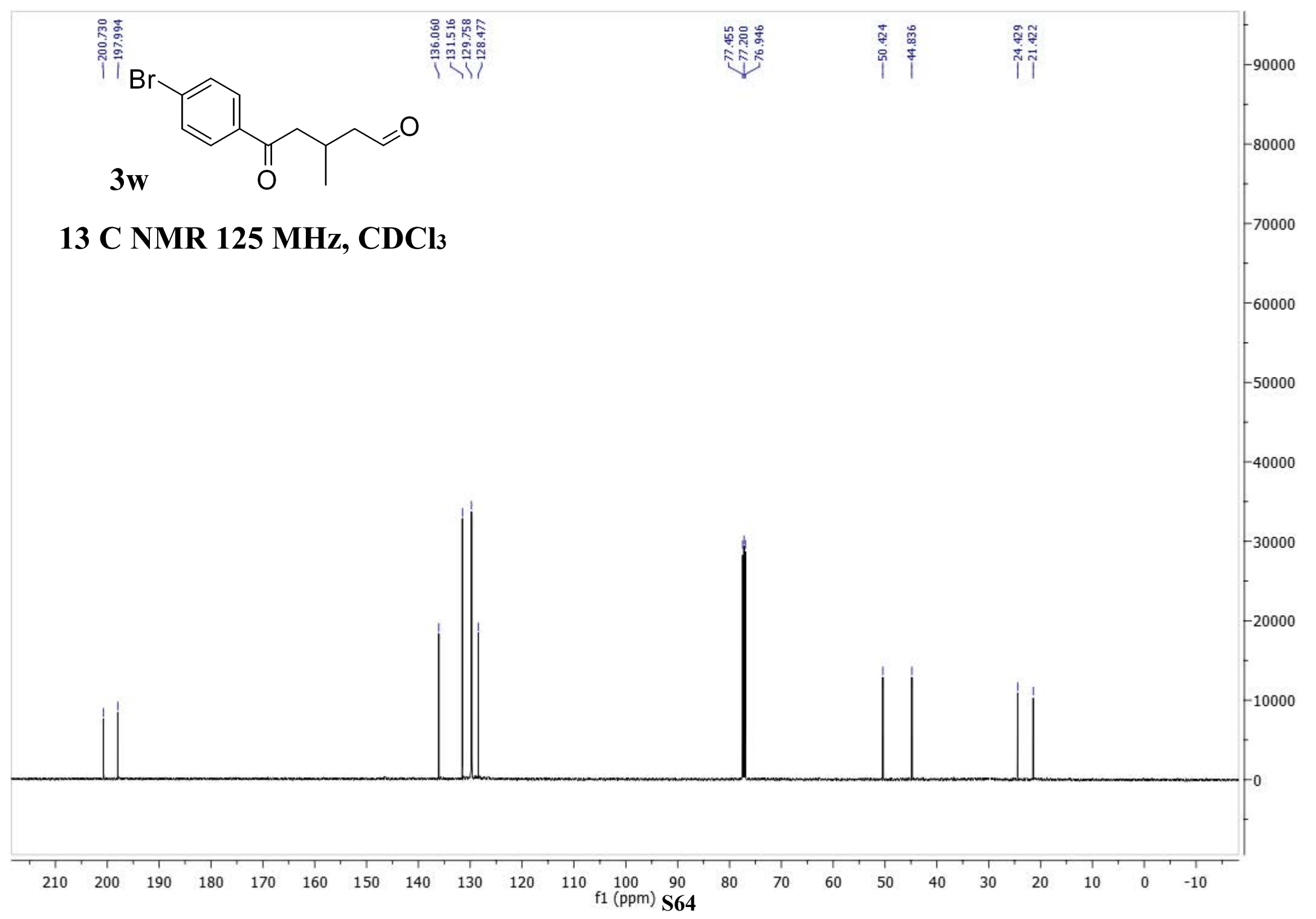
13 C NMR 125 MHz, $CDCl_3$



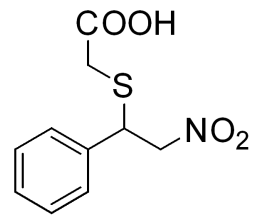
3u

1 C NMR 125 MHz, $CDCl_3$


202.345
199.293
139.036
134.834
129.810
128.602
77.454
77.200
76.946
50.689
44.948
24.702
20.612
Cl
O
O
3v
13 C NMR 125 MHz, CDCl3
f1 (ppm)

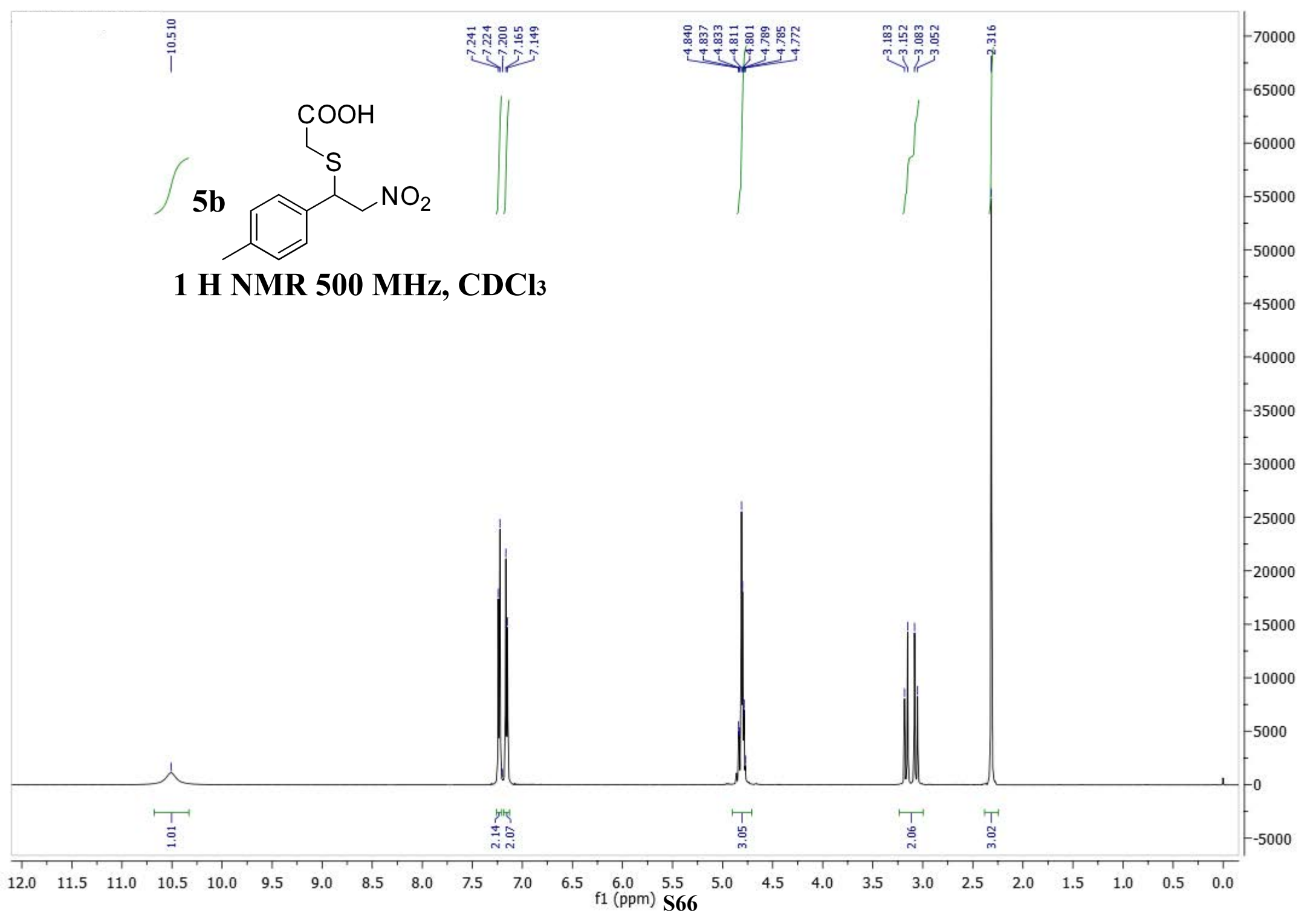

200.730
197.994
136.060
131.516
129.758
128.477
77.455
77.200
76.946
50.424
44.836
24.429
21.422
Br
O
O
3w
13 C NMR 125 MHz, CDCl3
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

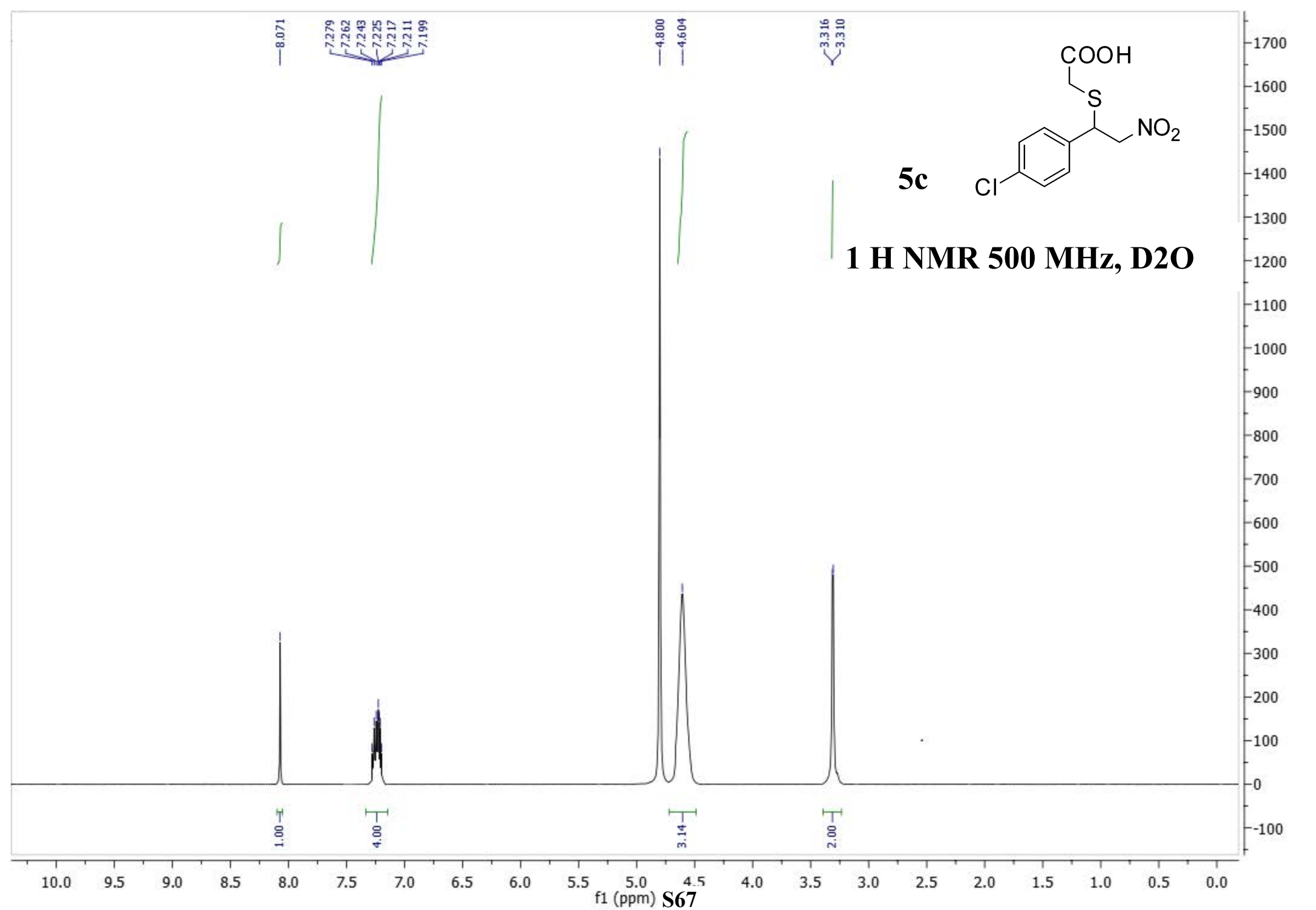
VI. 1 H NMR Spectra 5a -5q



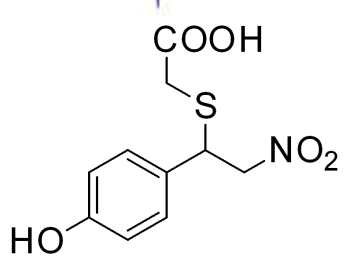
5a

1 H NMR 500 MHz, $CDCl_3$

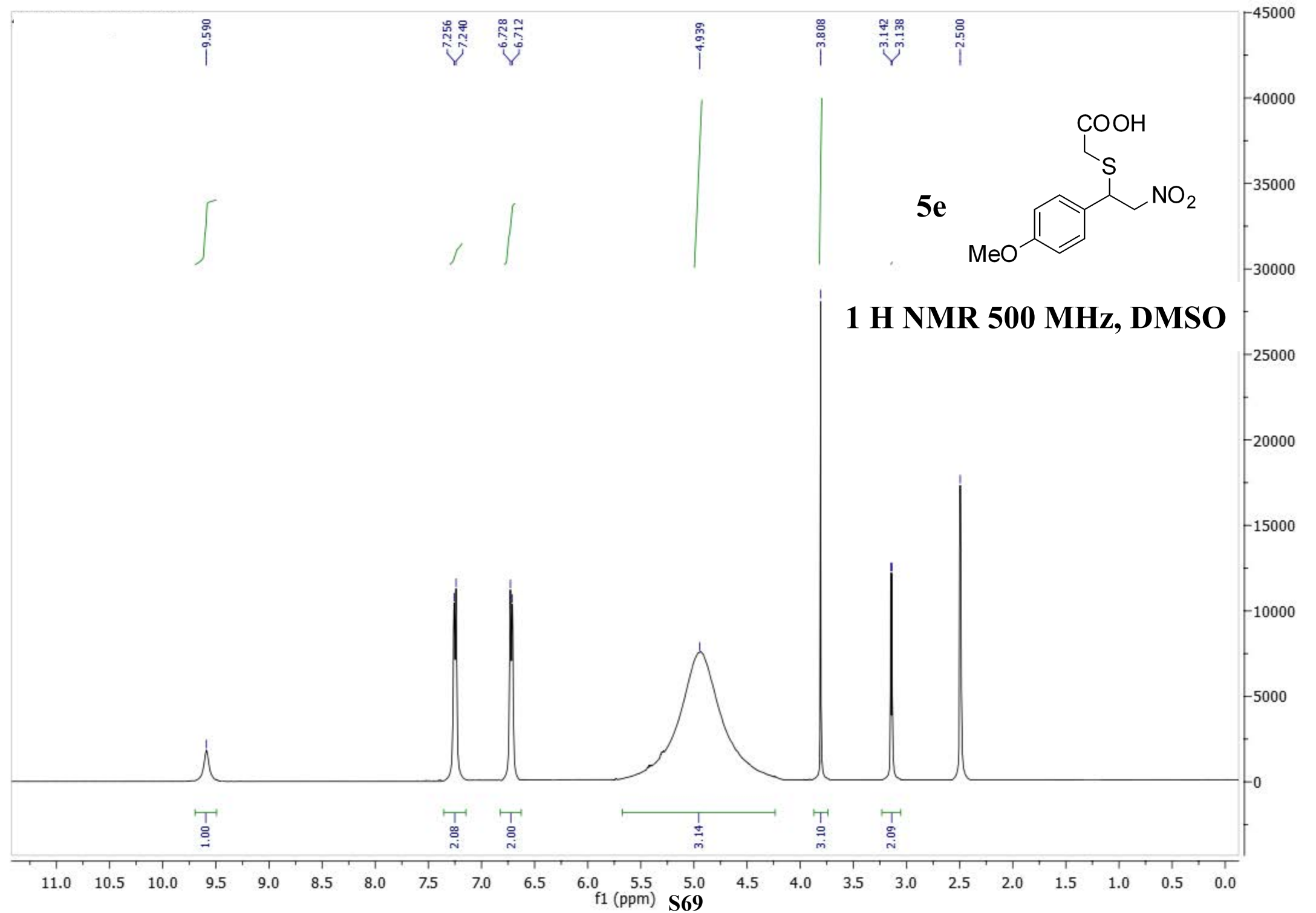

10.510
7.241
7.224
7.200
7.165
7.149
4.840
4.837
4.833
4.811
4.801
4.789
4.785
4.772
3.183
3.152
3.083
3.052
2.316
COOH
S
NO2
5b
1 H NMR 500 MHz, CDCl3
1.01
2.14
2.07
3.05
2.06
3.02
f1 (ppm)

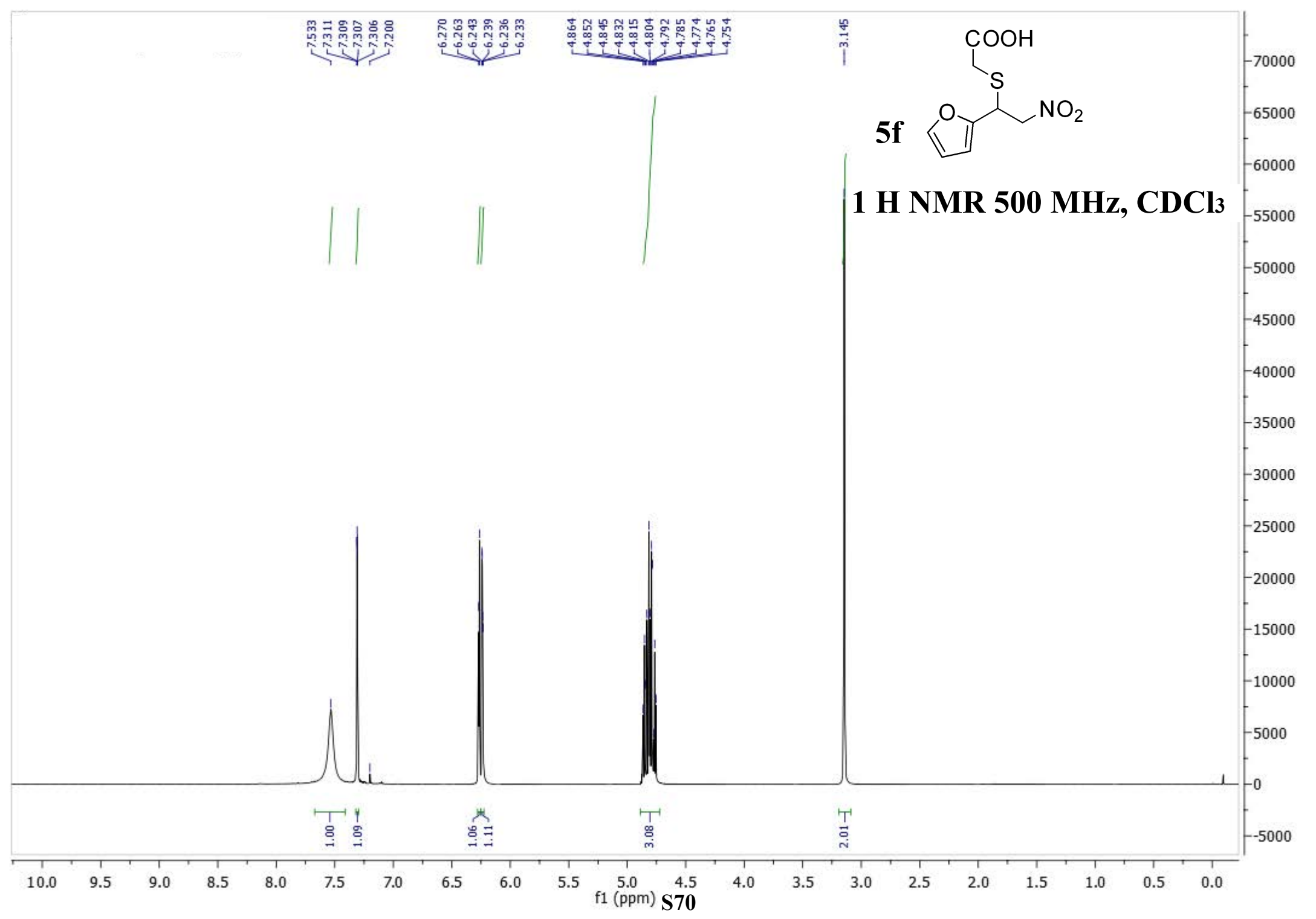

8.071
7.279
7.262
7.243
7.225
7.217
7.211
7.199
4.800
4.604
3.316
3.310
COOH
S
NO2
Cl
5c
1 H NMR 500 MHz, D2O
1.00
4.00
3.14
2.00
f1 (ppm)

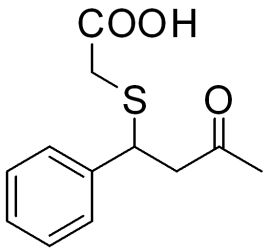
5d



1 H NMR 500 MHz, D2O

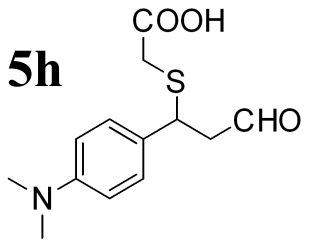

9.590
7.256
7.240
6.728
6.712
4.939
3.808
3.142
3.138
2.500
5e
COOH
S
NO2
MeO
1 H NMR 500 MHz, DMSO
1.00
2.08
2.00
3.14
3.10
2.09
f1 (ppm)


7.533
7.311
7.309
7.307
7.306
7.200
6.270
6.263
6.243
6.239
6.236
6.233
4.864
4.852
4.845
4.832
4.815
4.804
4.792
4.785
4.774
4.765
4.754
3.145
COOH
S
O
NO2
5f
1 H NMR 500 MHz, CDCl3
1.00
1.09
1.06
1.11
3.08
2.01
f1 (ppm)



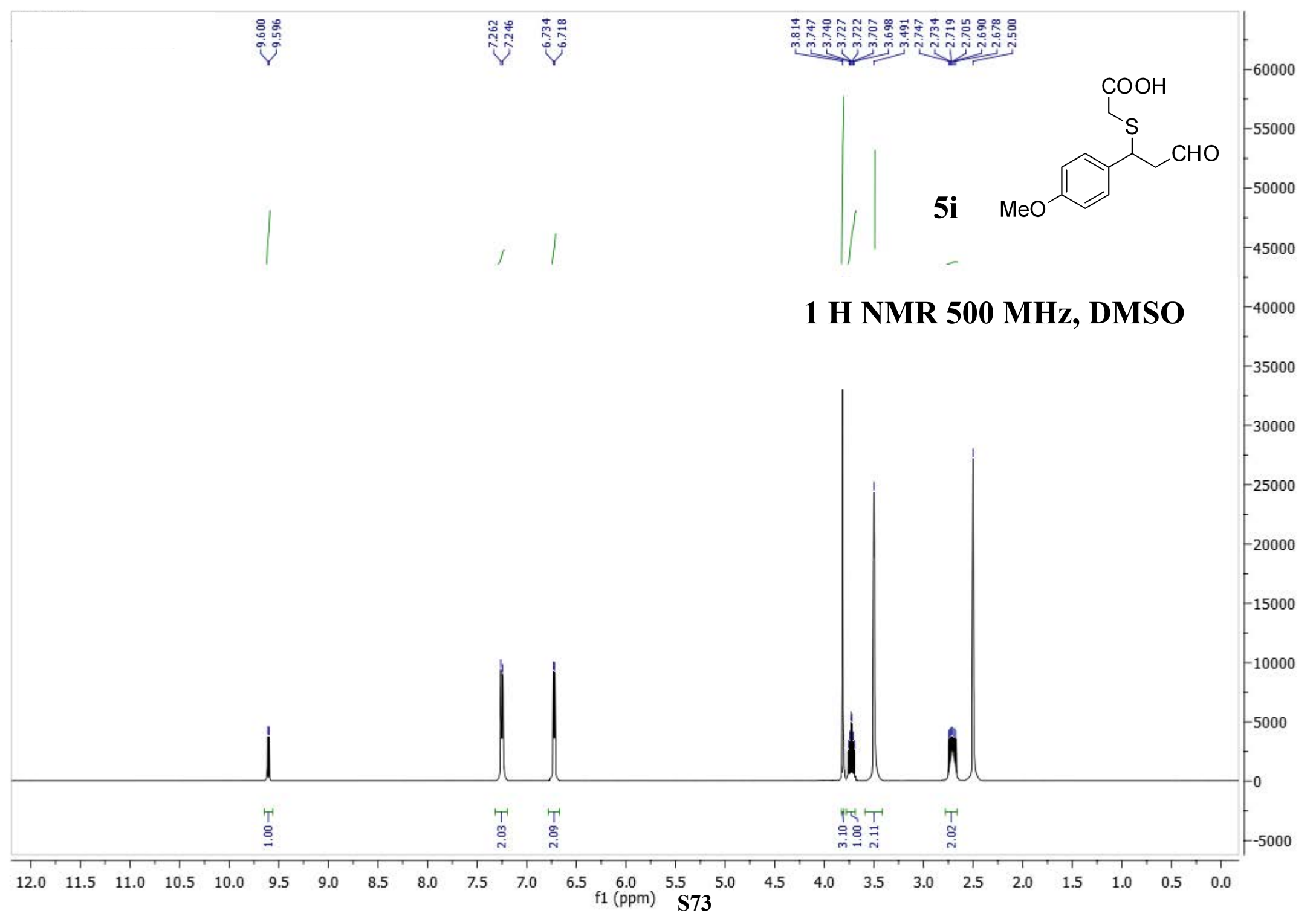
5g

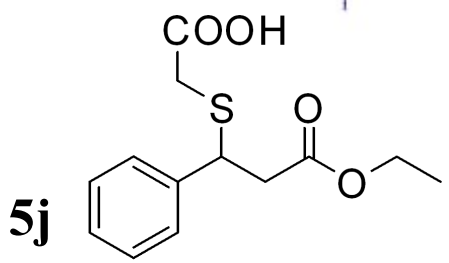
1 H NMR 500 MHz, $CDCl_3$



5h

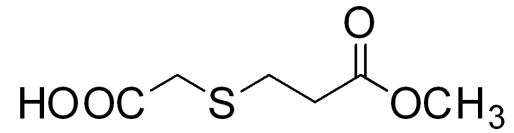
1 H NMR 500 MHz, DMSO


9.600
9.596
7.262
7.246
6.734
6.718
3.814
3.747
3.740
3.727
3.722
3.707
3.698
3.491
2.747
2.734
2.719
2.705
2.690
2.678
2.500
COOH
S
CHO
MeO
5i
1 H NMR 500 MHz, DMSO
1.00
2.03
2.09
3.10
1.00
2.11
2.02
f1 (ppm)



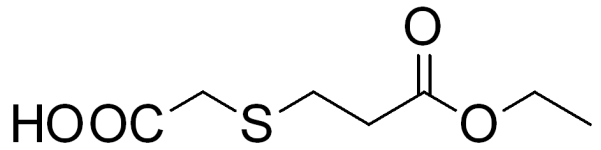
5j

1 H NMR 500 MHz, DMSO

5k 

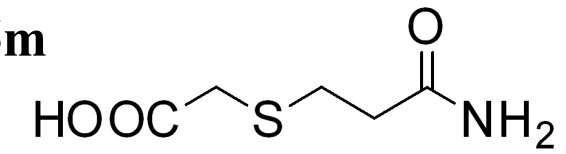
1 H NMR 500 MHz, DMSO

5l



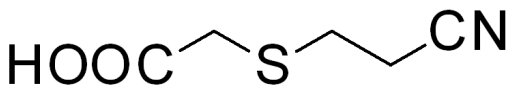
1 H NMR 500 MHz, DMSO

5m

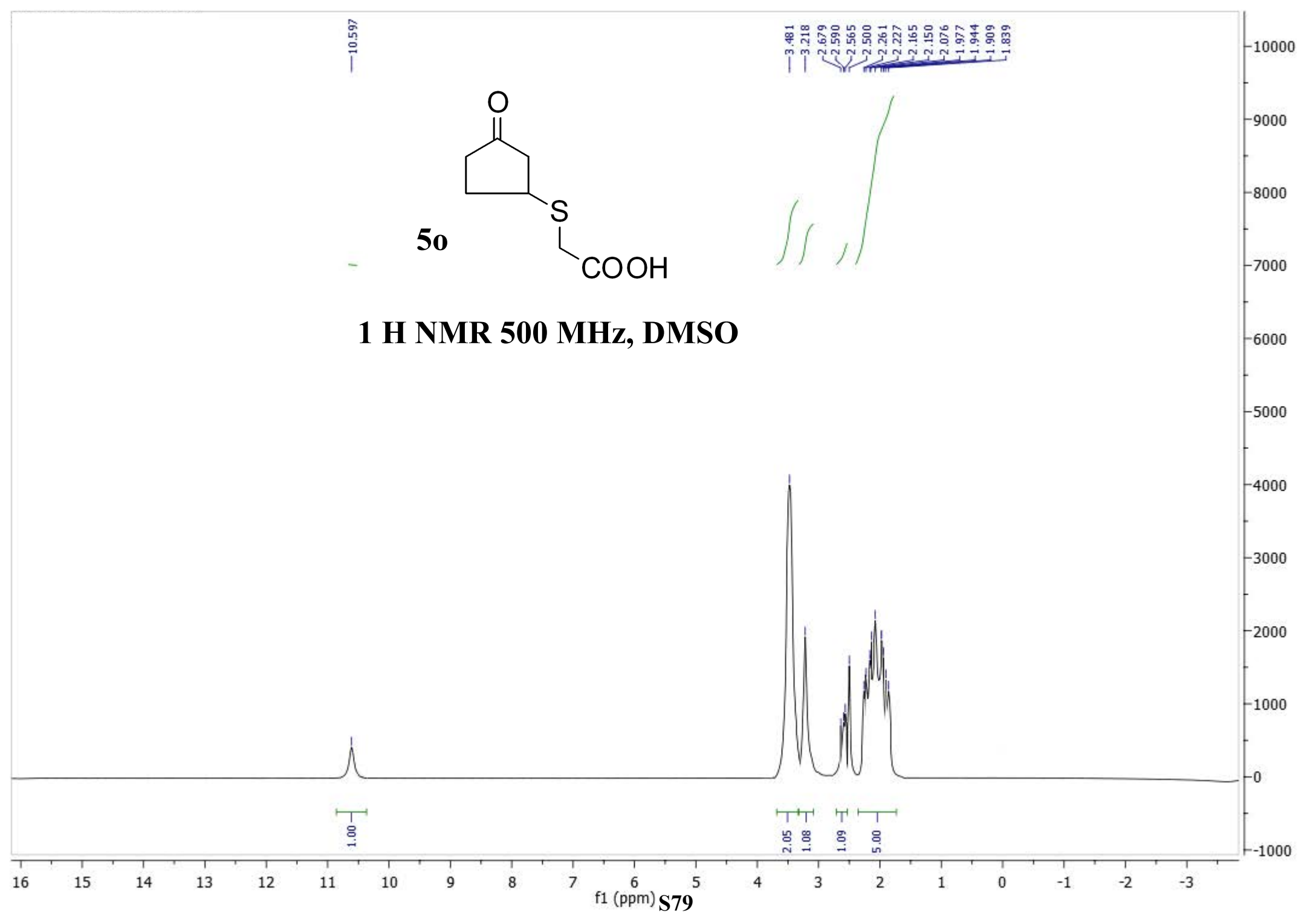


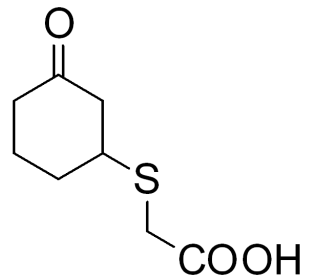
1 H NMR 500 MHz, DMSO

5n



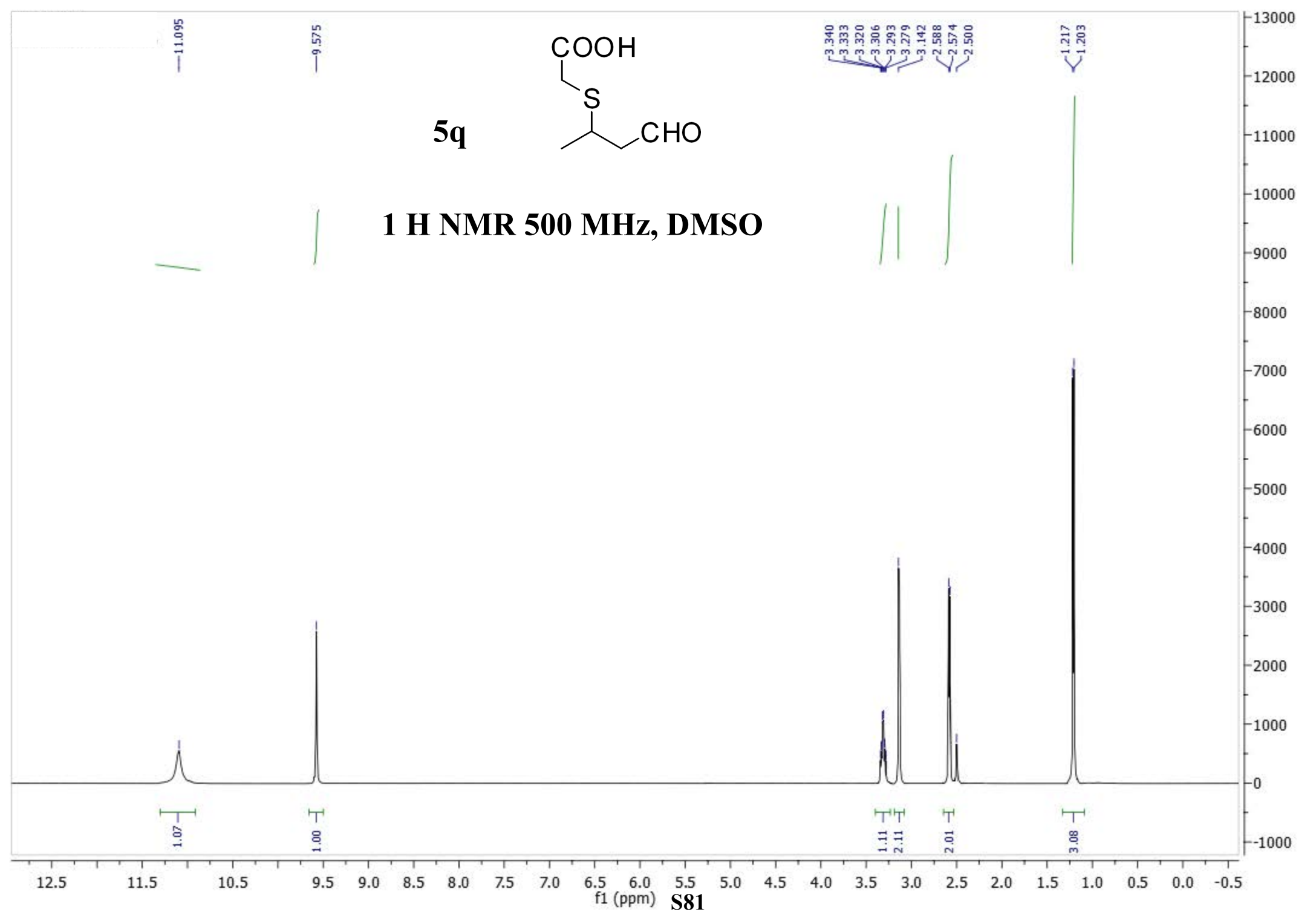
1 H NMR 500 MHz, DMSO


10.597
3.481
3.218
2.679
2.590
2.565
2.500
2.261
2.227
2.165
2.150
2.076
1.977
1.944
1.909
1.839
O
S
COOH
5o
1 H NMR 500 MHz, DMSO
1.00
2.05
1.08
1.09
5.00
f1 (ppm)

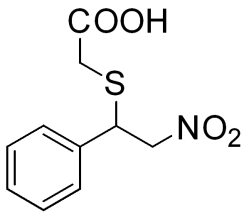


5p

1 H NMR 500 MHz, DMSO

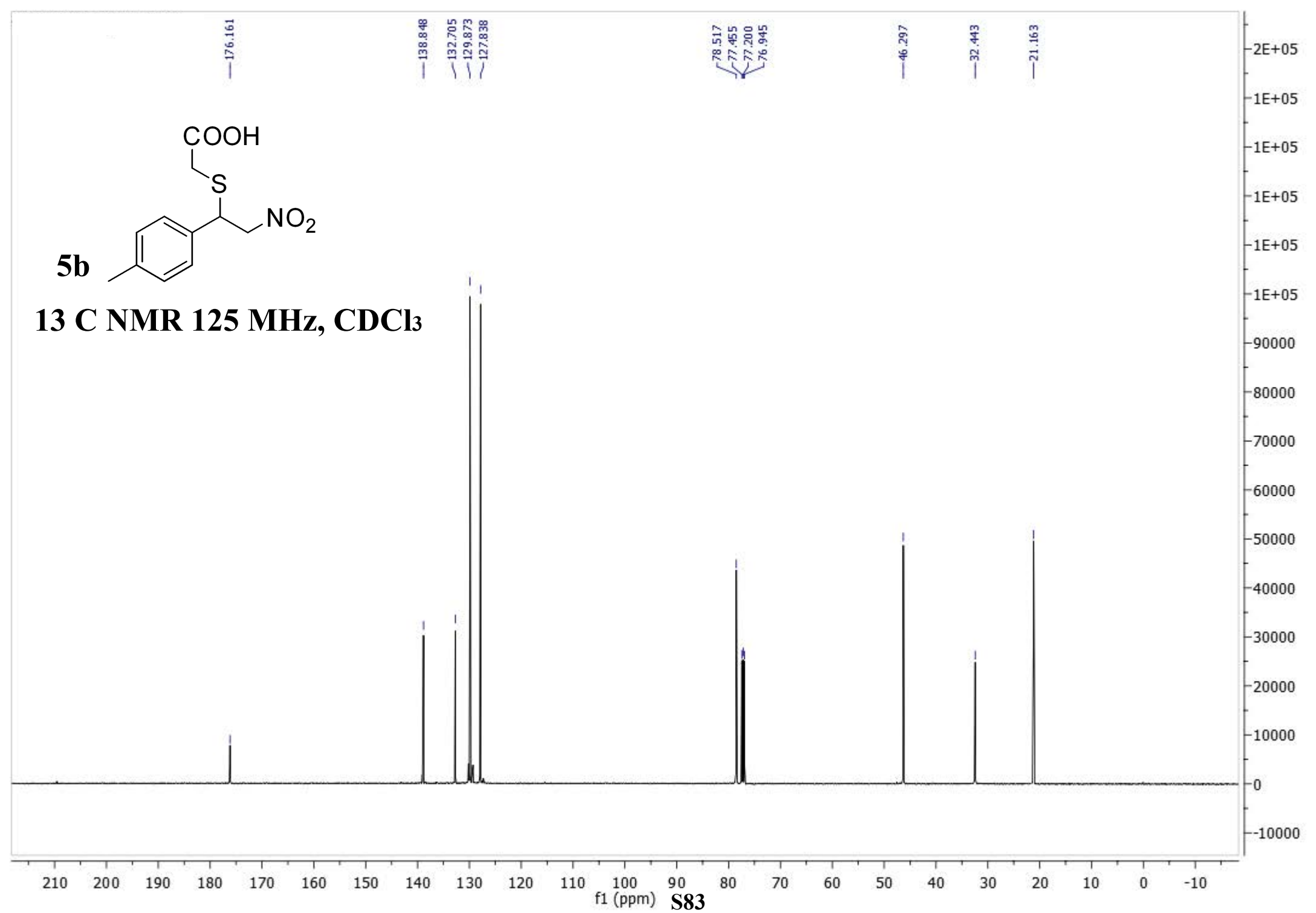

11.095
9.575
3.340
3.333
3.320
3.306
3.293
3.279
3.142
2.588
2.574
2.500
1.217
1.203
COOH
S
CHO
5q
1 H NMR 500 MHz, DMSO
1.07
1.00
1.11
2.11
2.01
3.08
f1 (ppm)

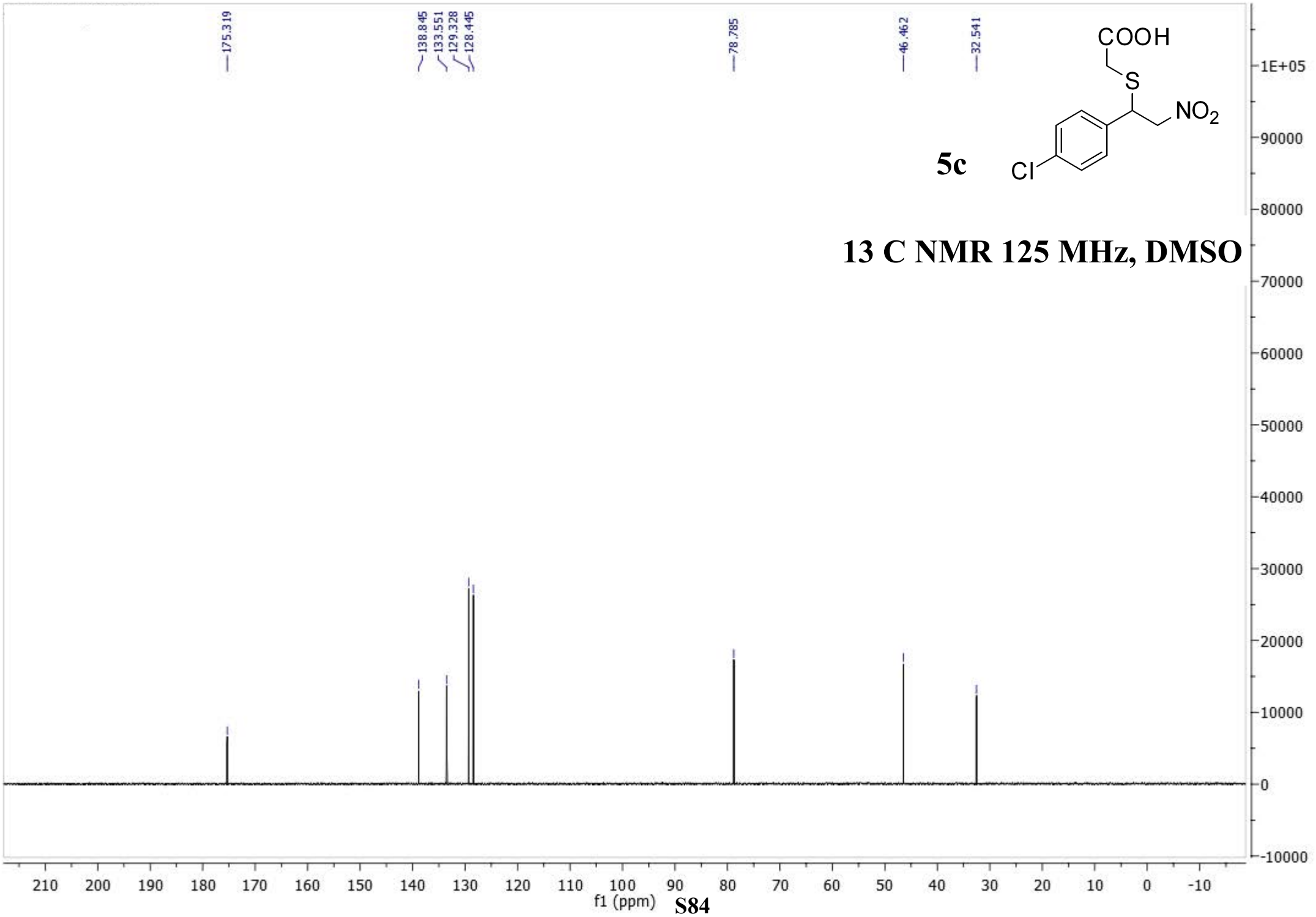
VI. 13 C NMR Spectra 5a -5q

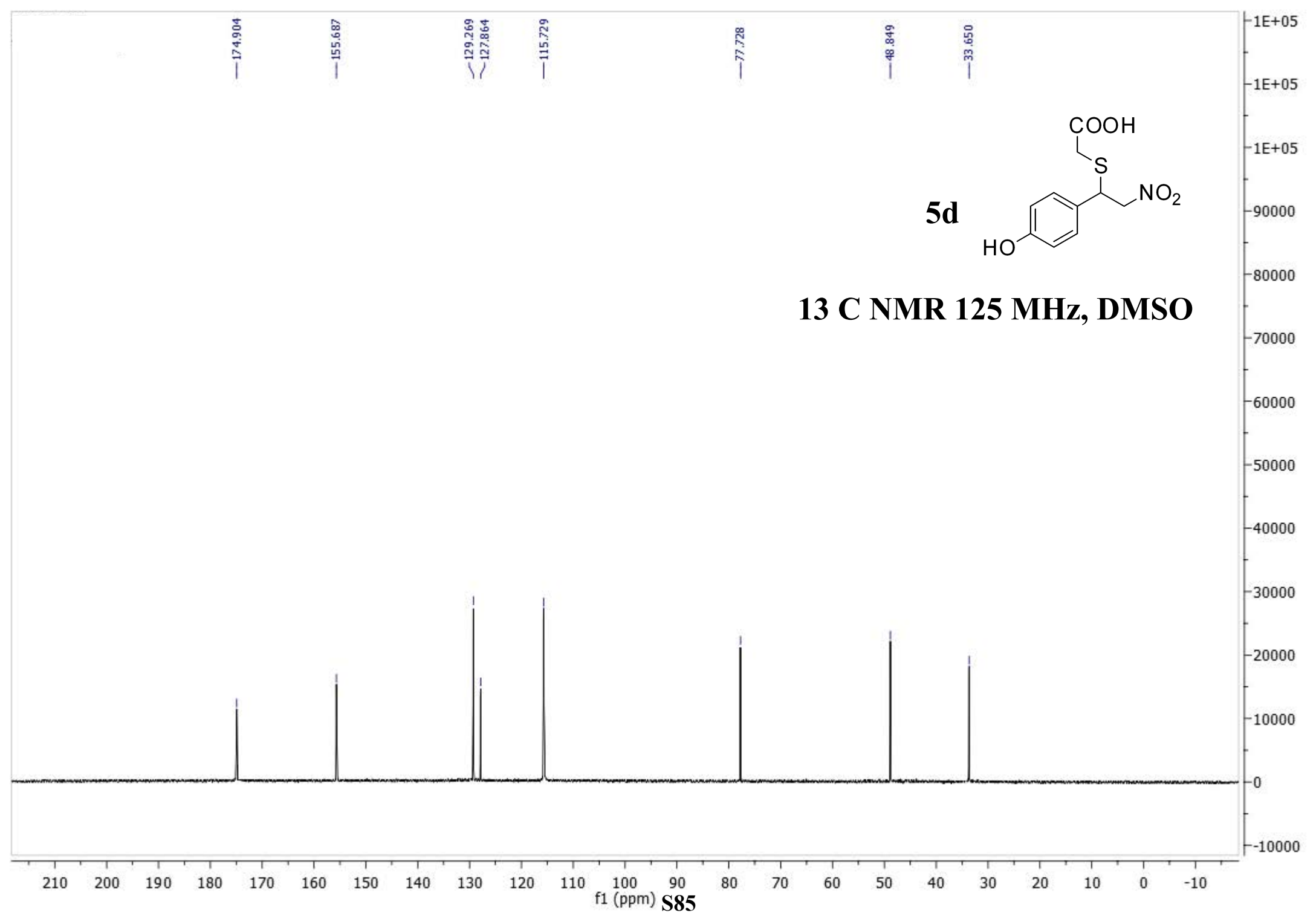


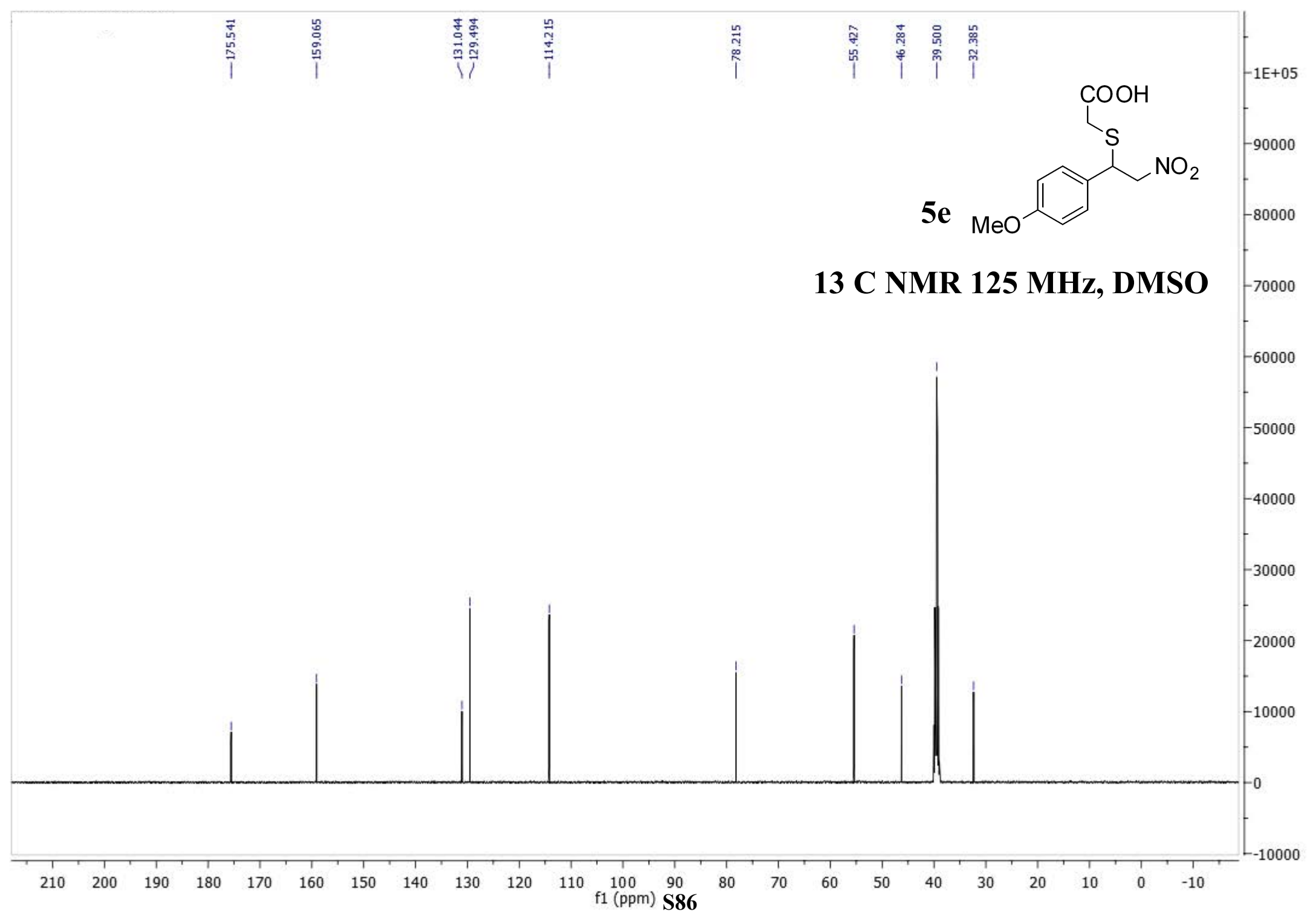
5a

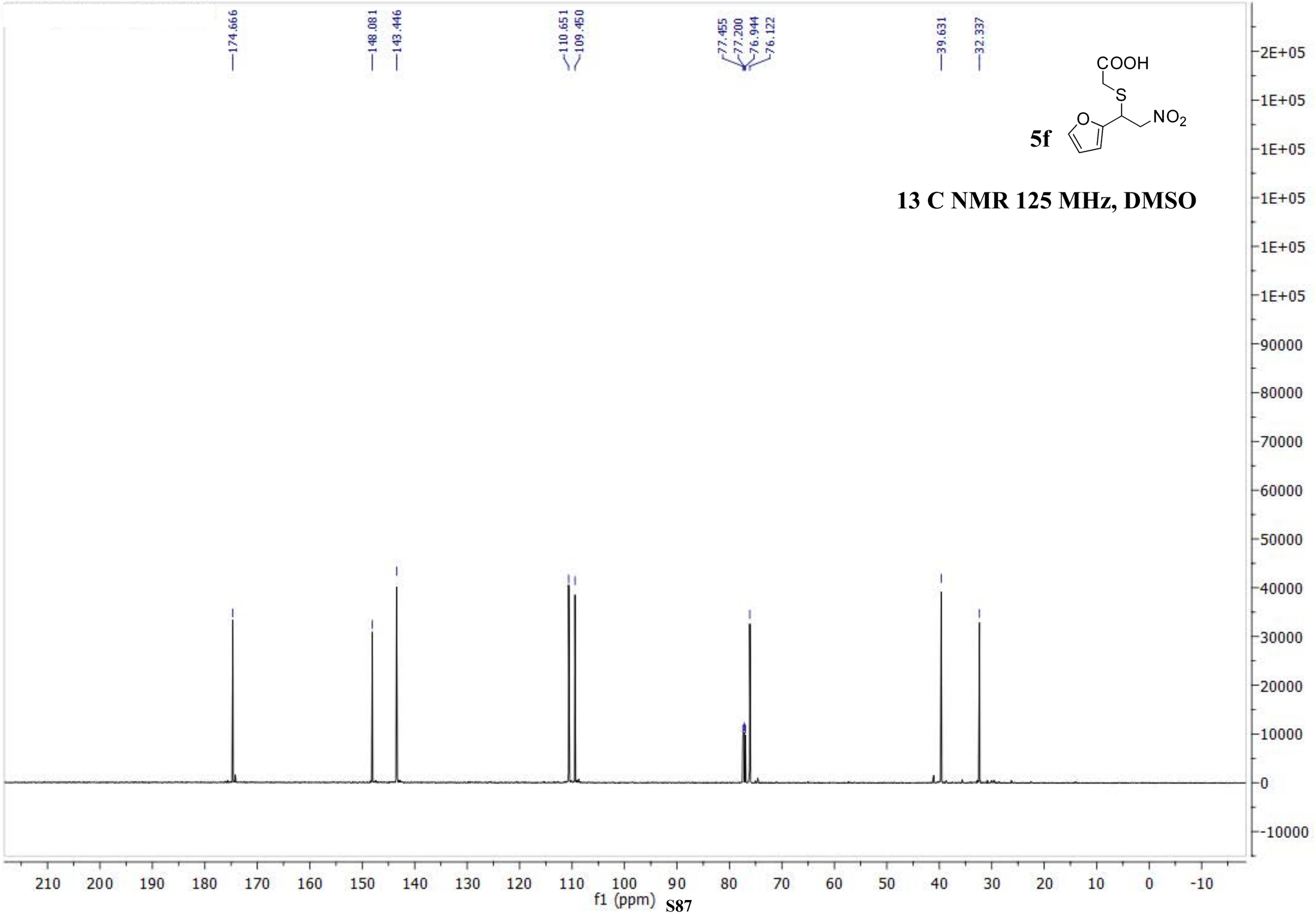
13 C NMR 125 MHz, $CDCl_3$

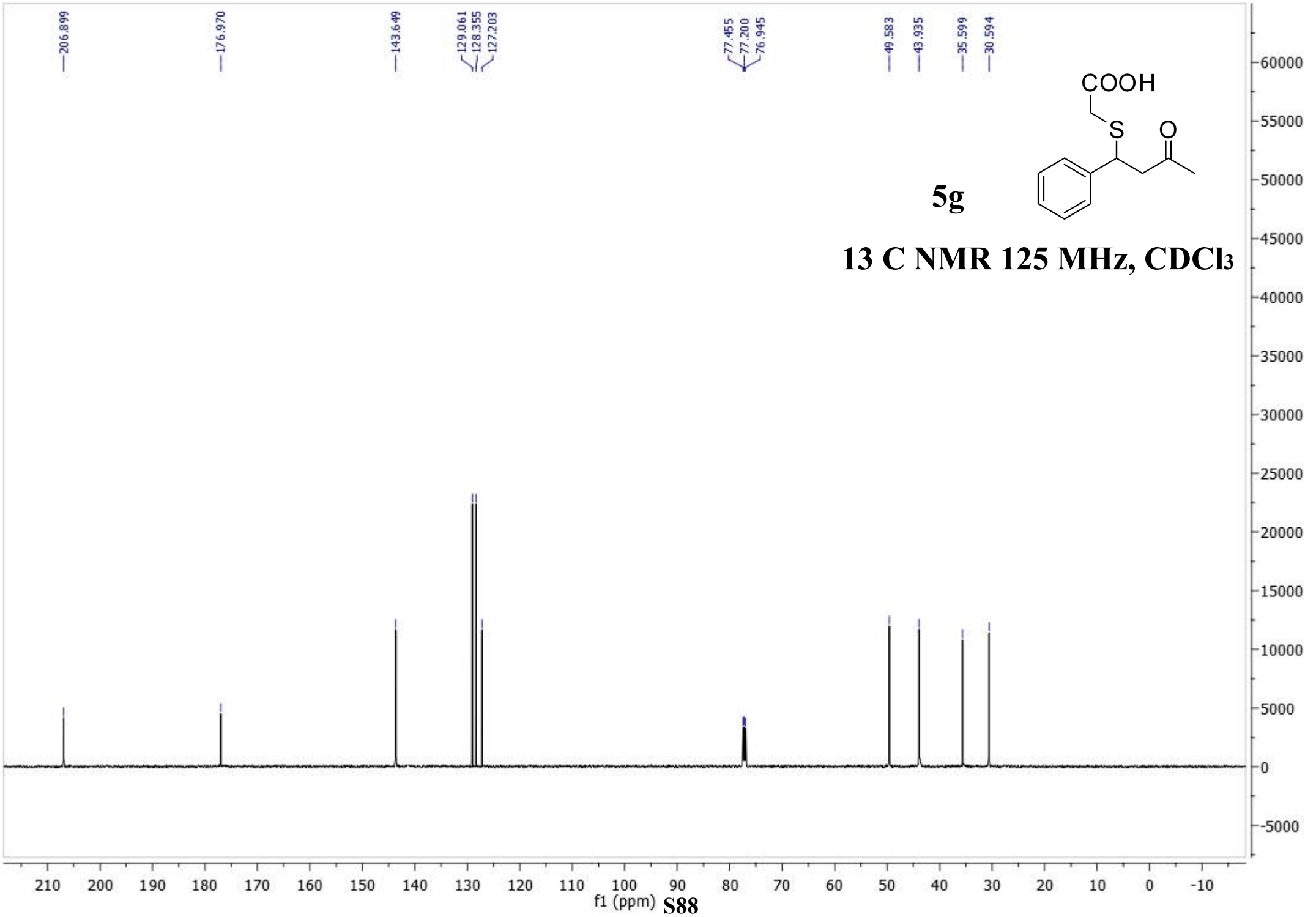

176.161
138.848
132.705
129.873
127.838
78.517
77.455
77.200
76.945
46.297
32.443
21.163
COOH
S
NO2
5b
13 C NMR 125 MHz, CDCl3
2E+05
1E+05
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

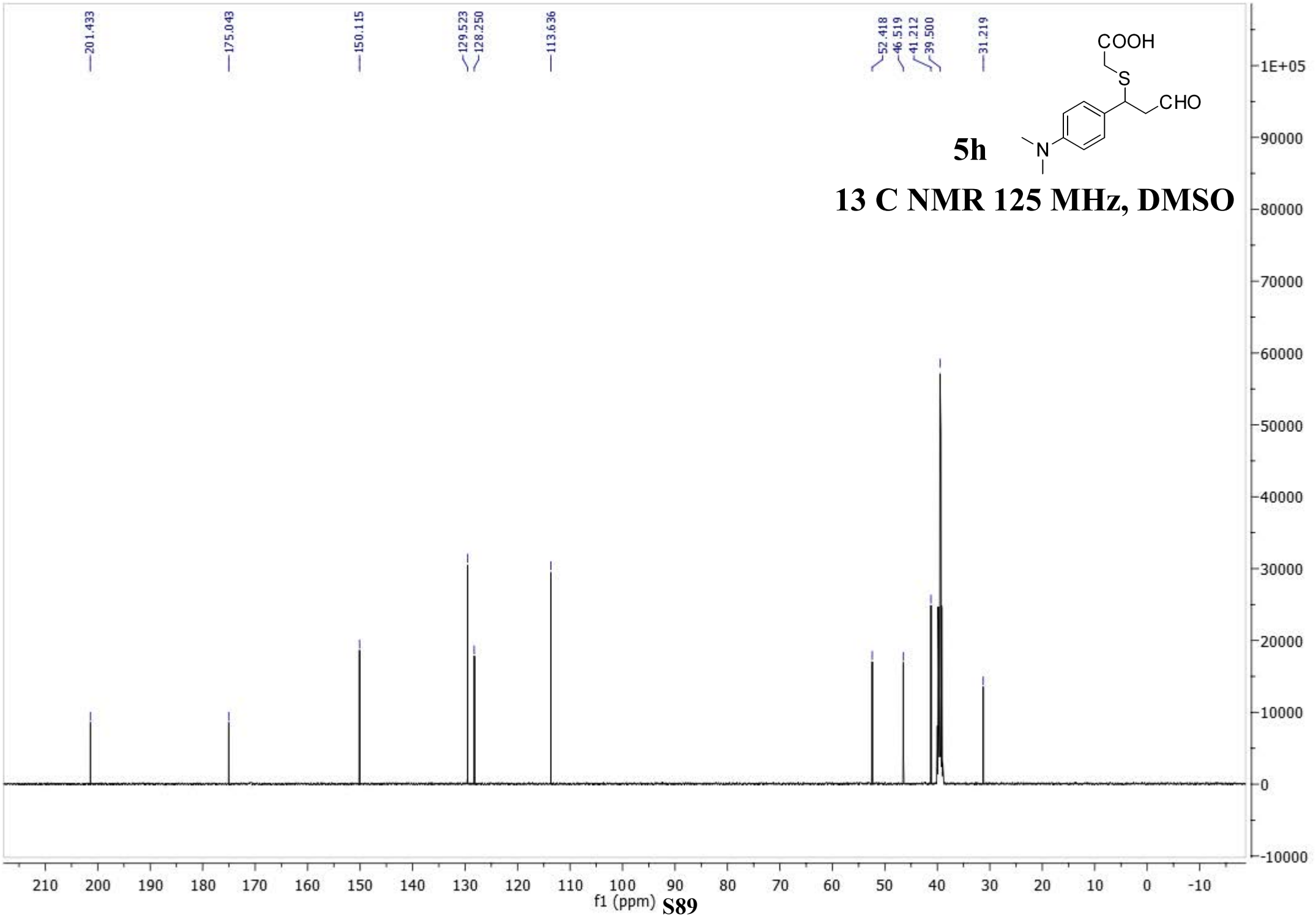

175.319
138.845
133.551
129.328
128.445
78.785
46.462
32.541
COOH
S
NO2
Cl
5c
13 C NMR 125 MHz, DMSO
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

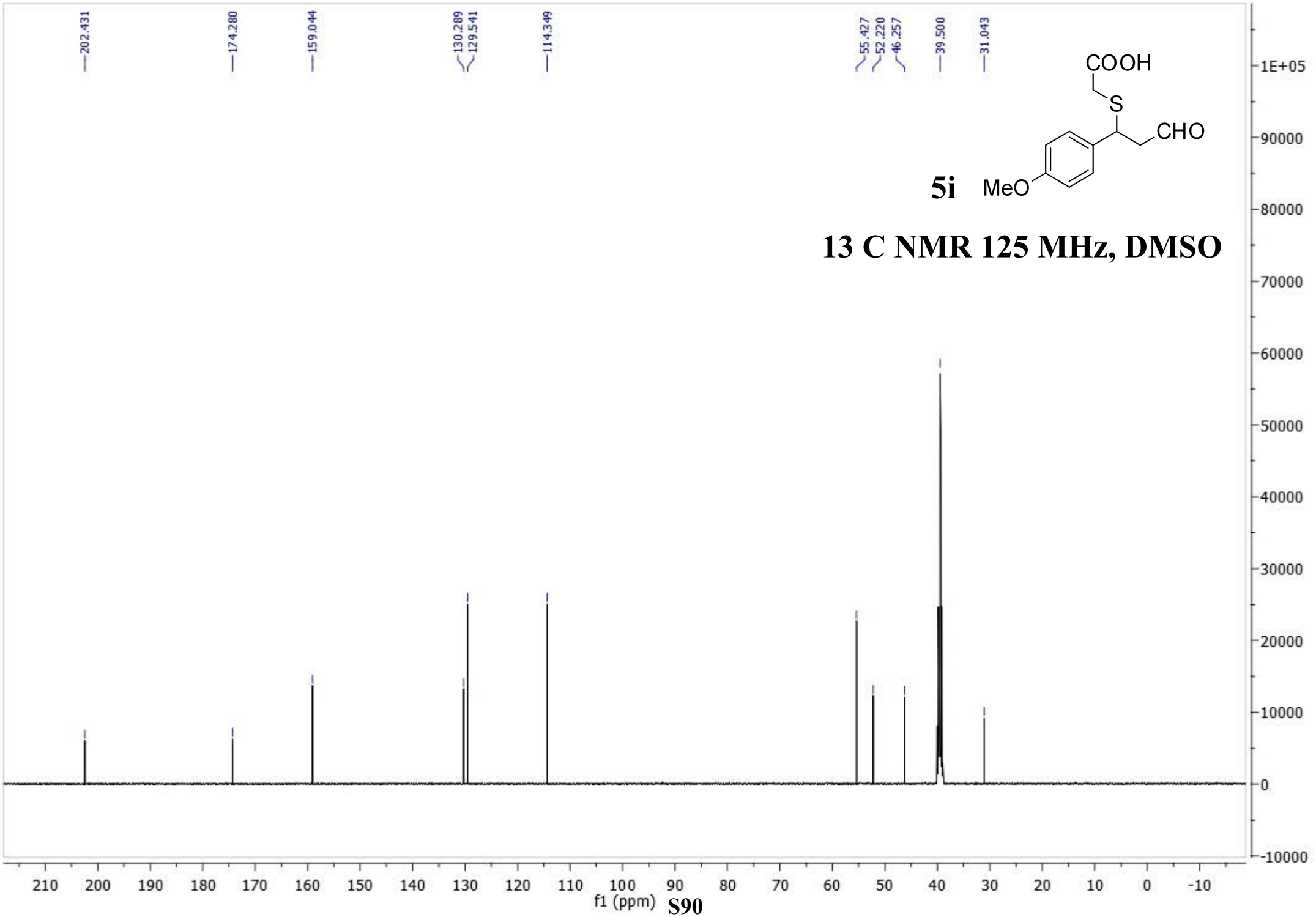

174.904
155.687
129.269
127.864
115.729
77.728
48.849
33.650
COOH
S
NO2
HO
5d
13 C NMR 125 MHz, DMSO
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

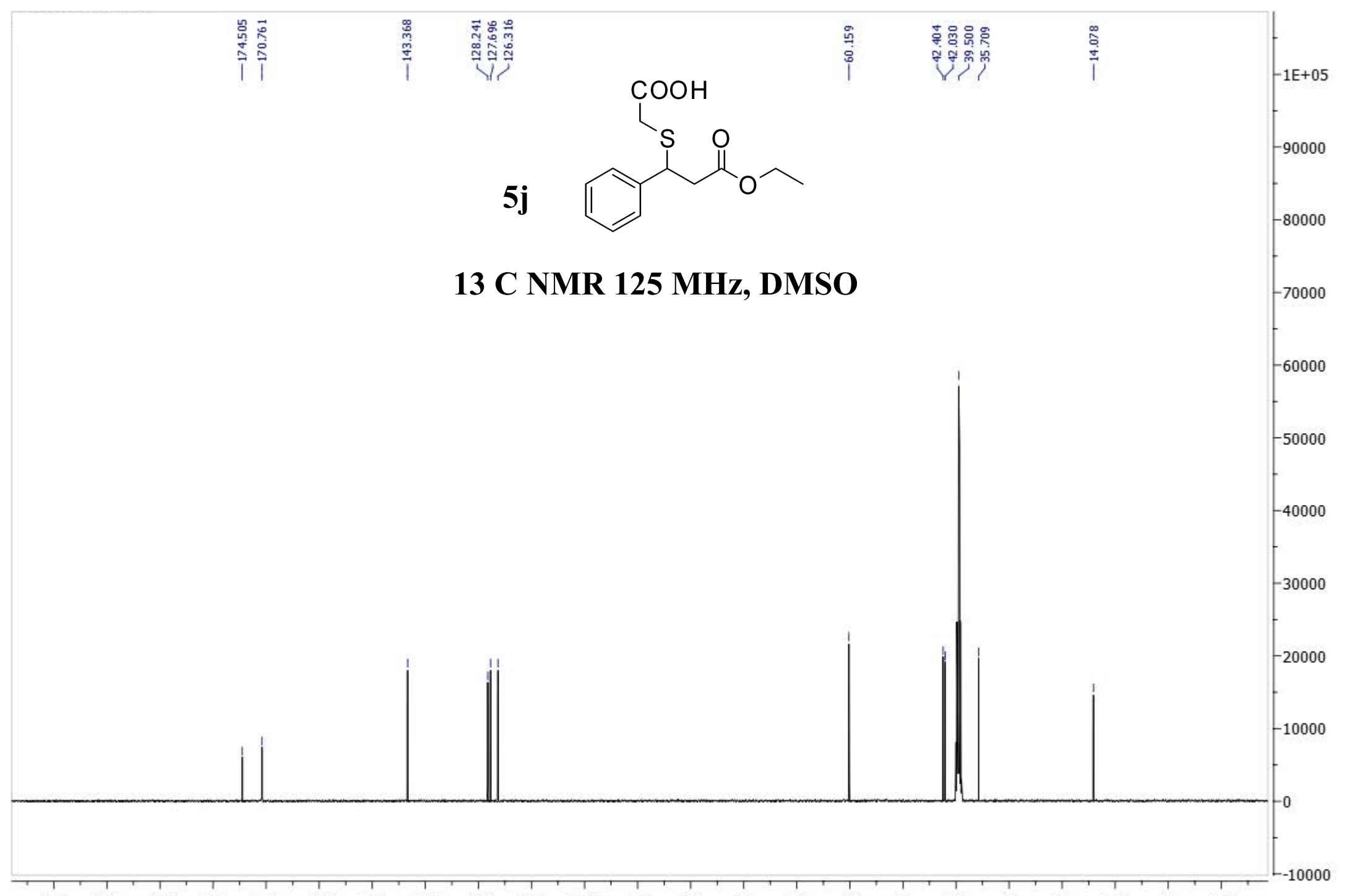

175.541
159.065
131.044
129.494
114.215
78.215
55.427
46.284
39.500
32.385
COOH
S
NO2
MeO
5e
13 C NMR 125 MHz, DMSO
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

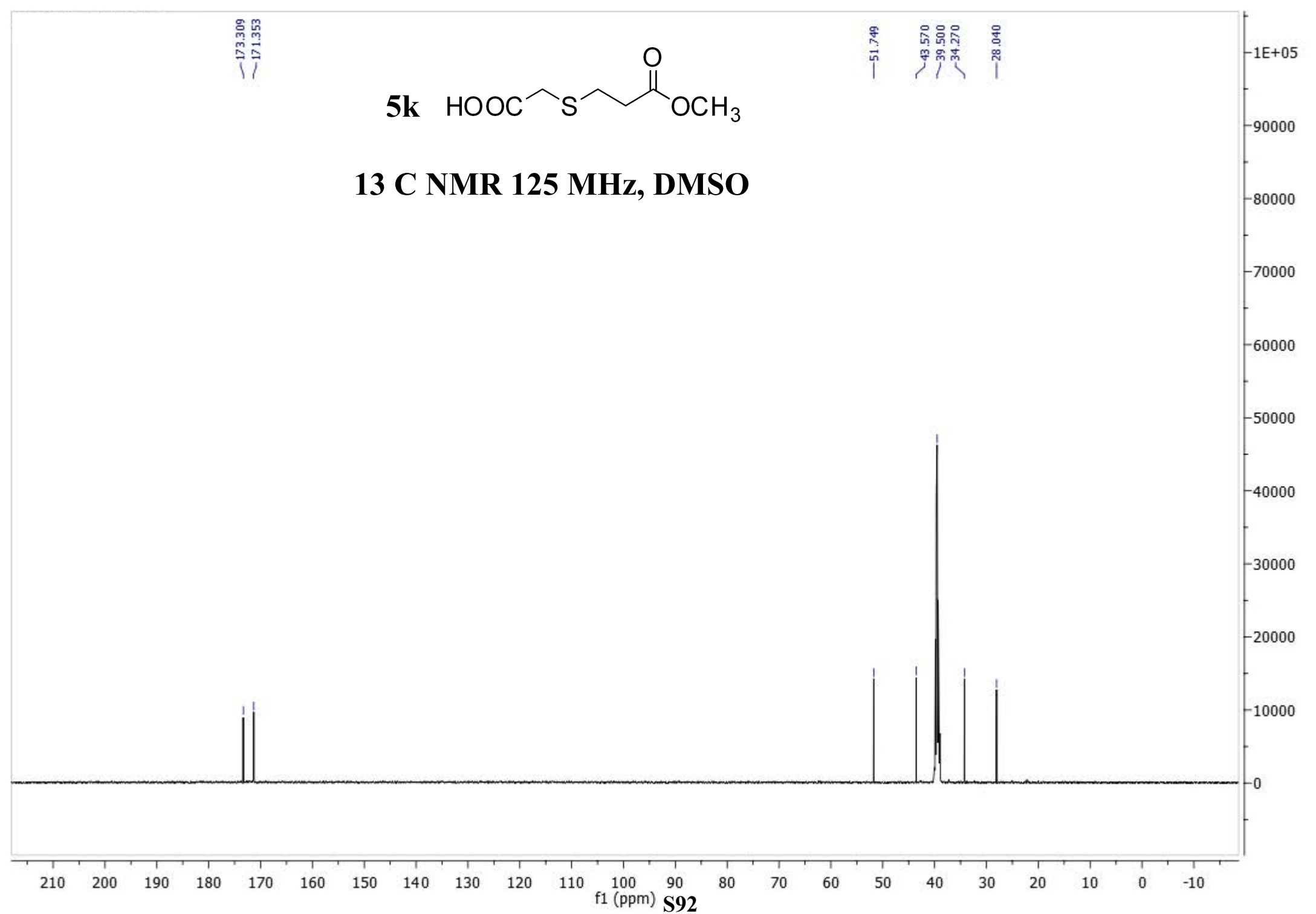

174.666
148.081
143.446
110.651
109.450
77.455
77.200
76.944
76.122
39.631
32.337
COOH
S
O
NO2
5f
13 C NMR 125 MHz, DMSO
2E+05
1E+05
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

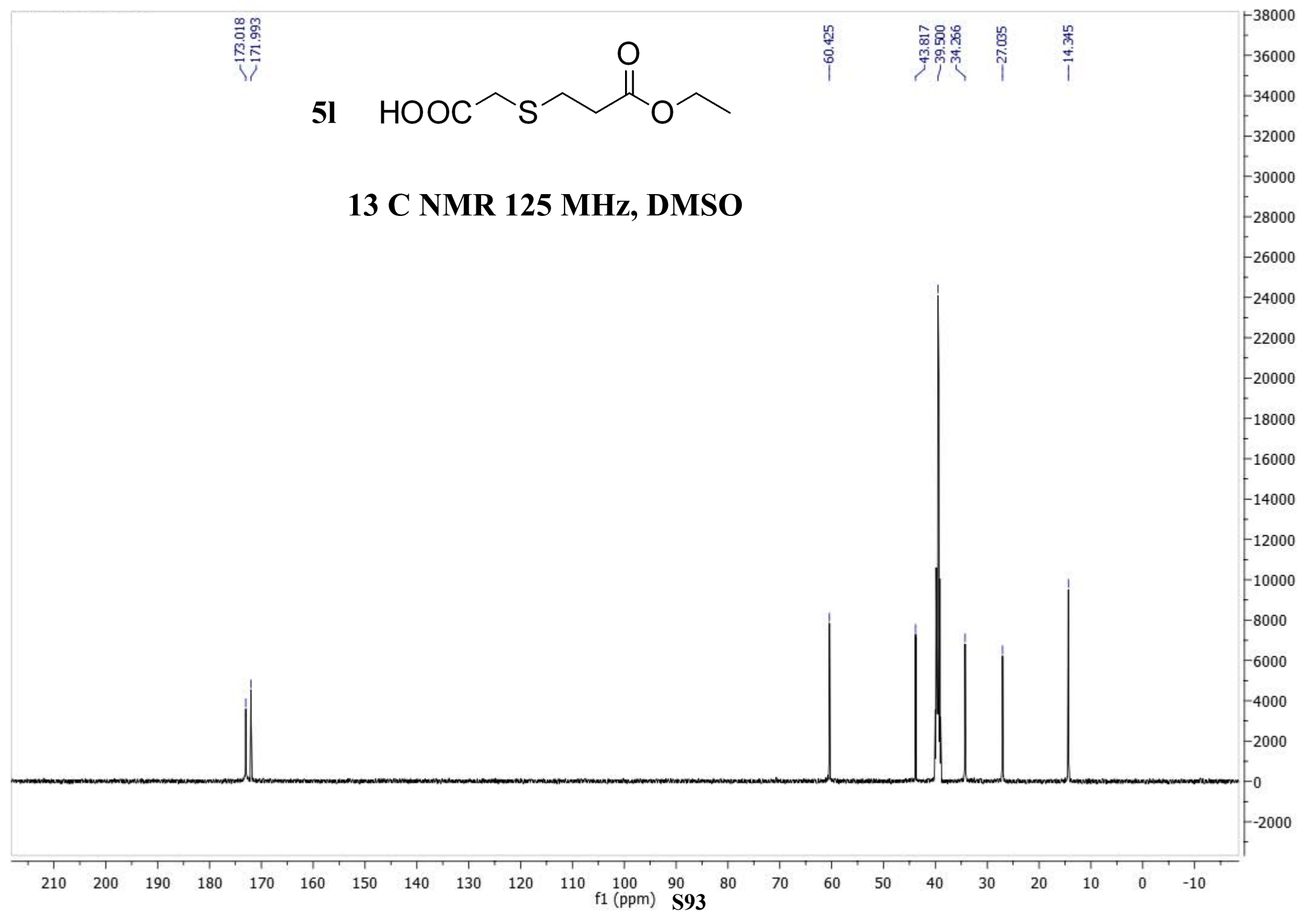

206.899
176.970
143.649
129.061
128.355
127.203
77.455
77.200
76.945
49.583
43.935
35.599
30.594
COOH
S
O
5g
13 C NMR 125 MHz, CDCl3
f1 (ppm)


201.433
175.043
150.115
129.523
128.250
113.636
52.418
46.519
41.212
39.500
31.219
COOH
S
CHO
N
5h
13 C NMR 125 MHz, DMSO
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

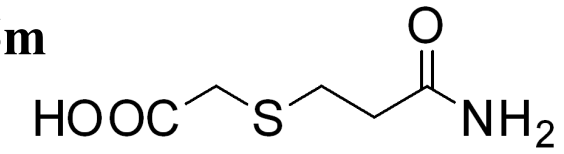

202.431
174.280
159.044
130.289
129.541
114.349
55.427
52.220
46.257
39.500
31.043
COOH
S
CHO
MeO
5i
13 C NMR 125 MHz, DMSO
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


174.505
170.761
143.368
128.241
127.696
126.316
60.159
42.404
42.030
39.500
35.709
14.078
COOH
S
O
O
5j
13 C NMR 125 MHz, DMSO
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


173.309
171.353
51.749
43.570
39.500
34.270
28.040
5k HOOC S OCH3
O
13 C NMR 125 MHz, DMSO
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

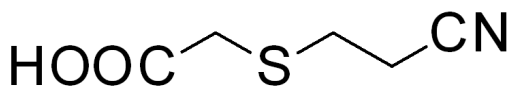

173.018
171.993
60.425
43.817
39.500
34.266
27.035
14.345
5l
HOOC
S
O
O
13 C NMR 125 MHz, DMSO
f1 (ppm)

5m

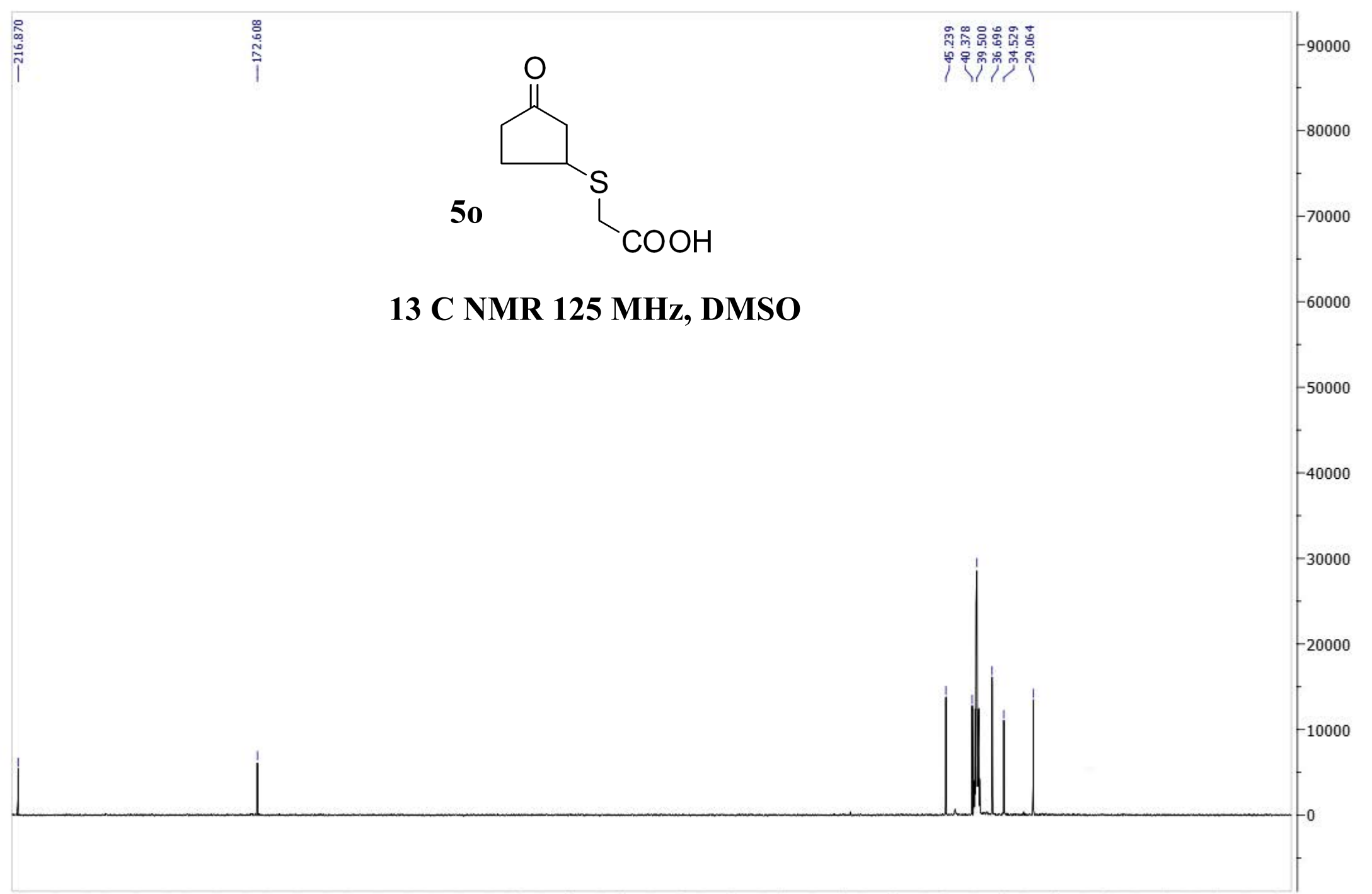


13 C NMR 125 MHz, DMSO

5n

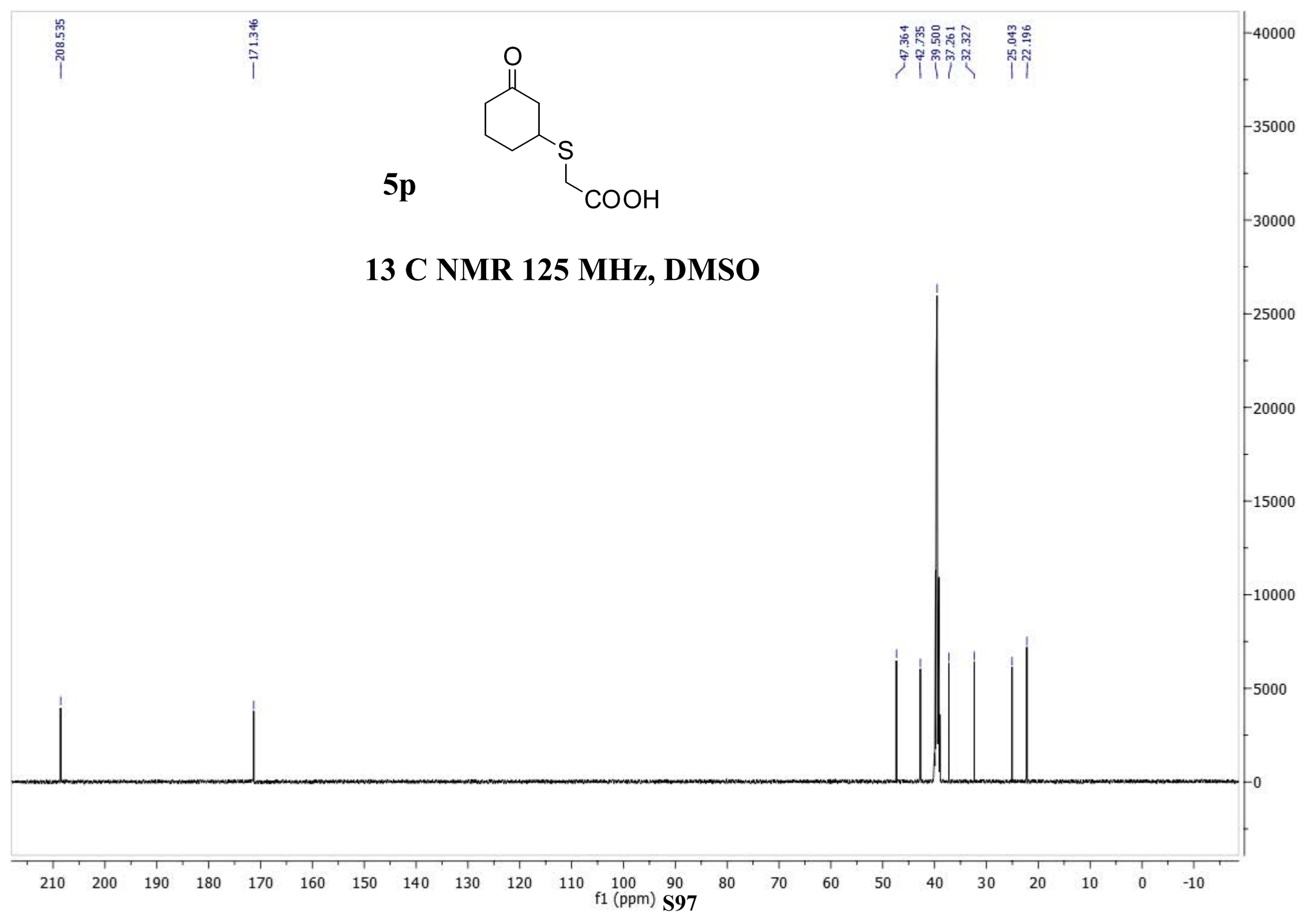


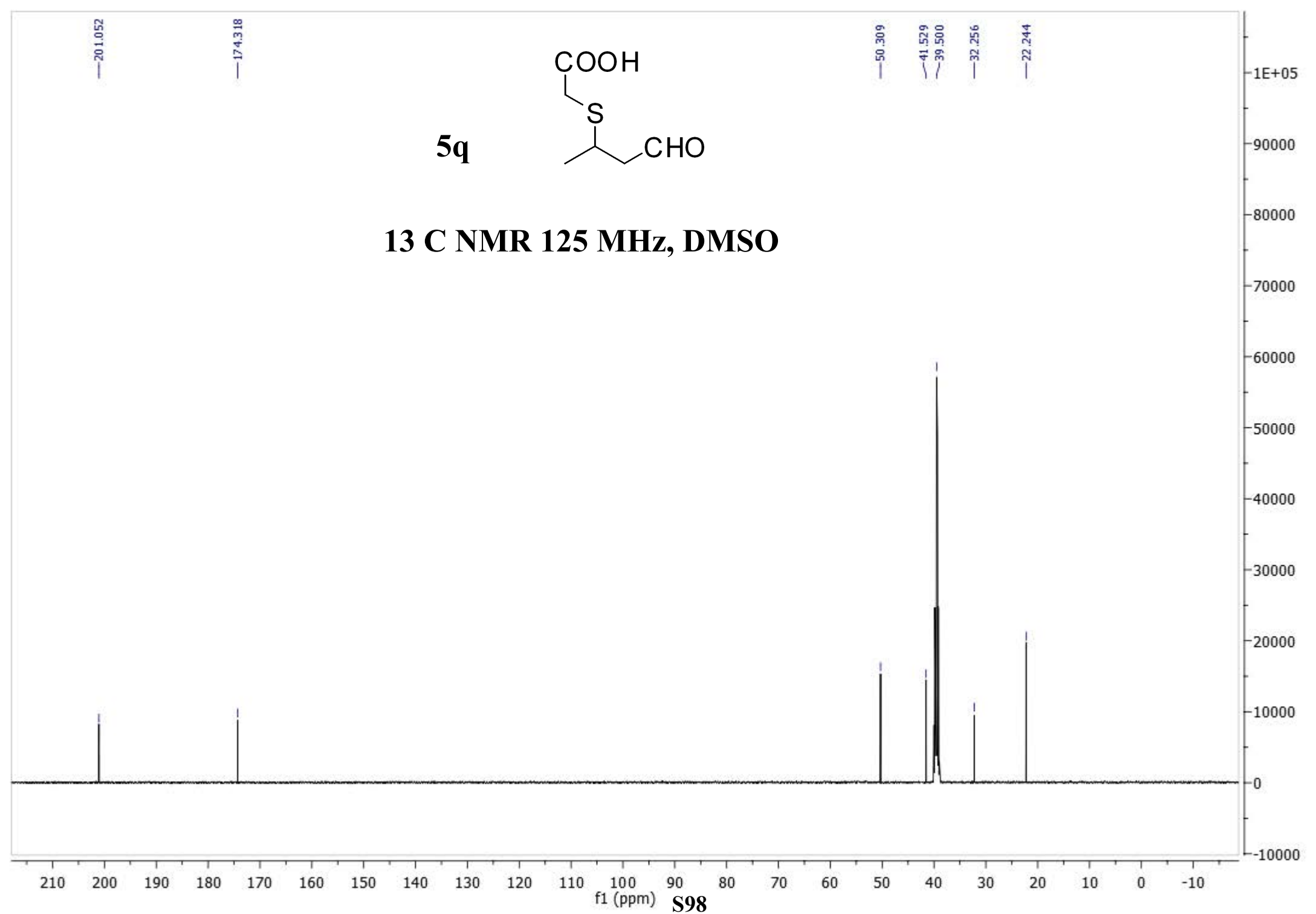
13 C NMR 125 MHz, DMSO



5o

13 C NMR 125 MHz, DMSO


208.535
171.346
47.364
42.735
39.500
37.261
32.327
25.043
22.196
O
S
COOH
5p
13 C NMR 125 MHz, DMSO
40000
35000
30000
25000
20000
15000
10000
5000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


201.052
174.318
50.309
41.529
39.500
32.256
22.244
COOH
S
CHO
5q
13 C NMR 125 MHz, DMSO
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)