Supplementary information for:

A biosynthetically inspired route to substituted furans using the Appel reaction: total synthesis of the furan fatty acid F_5

Robert J. Lee,[a] Martin R. Lindley,[b] Gareth J. Pritchard[a]* and Marc C. Kimber[a]*

[a] School of Science, Department of Chemistry, Loughborough
University, Loughborough, LE11 3TU, UK
Email: M.C.Kimber@lboro.ac.uk
Phone: (+) 44 1509 22 2570
Email: G.J.Pritchard@lboro.ac.uk
Phone: (+) 44 1509 22 2586

[b] Dr. M. R. Lindley
School of Sports, Exercise and Health Science, Loughborough
University, Loughborough, LE11 3TU, UK

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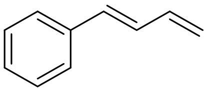
1. General Experimental Details

All reactions requiring the omission of air/water were performed under nitrogen atmosphere, using oven-dried glassware. All solvents and commercially available reagents were purchased from Sigma-Aldrich, Alfa Aesar, or Fischer Scientific, and were used without prior purification apart from THF, which was distilled as required over benzophenone and sodium. ^{1}H and ^{13}C NMR spectra, recorded at 400MHz and 100 MHz respectively, were obtained using a Bruker Avance 400 MHz spectrometer or JEOL ECS-400 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from TMS, with the solvent resonance as the reference standard. Coupling constants (*J*) are reported in Hz. Where compounds were obtained as a mixture of isomers, data for the major isomer is quoted. High resolution mass spectra (HRMS) were obtained using a Thermofischer exactive (orbi) resolution mass spectrometer, with ESI as the ionisation source. Thin layer chromatography (TLC) analysis was performed on aluminium backed silica plates. Plates were visualised by ultraviolet light (254 nm), or with vanillin or $KMnO_4$ stains and heating. Column chromatography was performed using Apollo Scientific ZEOprep-60 silica, with a particle size of 40 – 63 microns; eluents are specified in brackets.

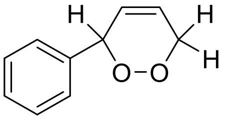
2. Synthetic Procedures

(*E*)-Buta-1,3-dien-1-ylbenzene (16b)



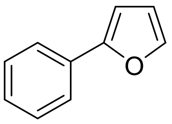
Methyltriphenylphosphonium iodide (2.021 g, 5.00 mmol) was suspended in anhydrous THF (50 mL) and cooled to -78 °C. ^{n}BuLi (3.0 mL, 2.5 M in hexanes, 7.50 mmol) was added dropwise, and the mixture brought to room temperature and stirred for 30 minutes to give a clear orange-red solution. *Trans*-cinnamaldehyde (0.95 mL, 7.50 mL) was added in one portion, and the mixture stirred for 18 hours. Removal of solvents *in vacuo* followed by column chromatography (100% hexanes, R_f = 0.35) afforded the title compound as a colourless oil (397 mg, 3.1 mmol, 61%). **δH** (400 MHz, $CDCl_3$): 7.47 – 7.42 (2H, m), 7.38 – 7.35 (2H, m), 7.30 – 7.25 (1H, m), 6.88 – 6.81 (1H, m), 6.63 – 6.52 (2H, m), 5.39 (1H, d, *J* = 16.8 Hz), 5.23 (1H, d, *J* = 10.4Hz). **δC** (100 MHz, $CDCl_3$): 137.3, 137.3, 133.0, 129.8, 128.8, 127.8, 126.6, 117.8. **IR** (ν_{max}, cm^{-1}): 1804, 1602, 1494, 1449. **MS (**m/z): Found 131.0859, ($C_{10}H_{11}^+$ requires 131.0855).

3-Phenyl-3,6-dihydro-1,2-dioxine (14b)[1]



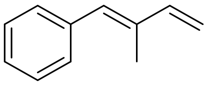
A constant stream of oxygen was passed through a solution of **16b** (0.130 g, 1.00 mmol) and 10^{-4} M disodium Rose Bengal in CH_2Cl_2/MeOH (19:1, 30 mL) whilst exposed to a 400W halogen light source for 30 hours at room temperature. After removal of solvents *in vacuo*, column chromatography (9:1 hexanes/ethyl acetate R_f = 0.45) afforded **14b** as an unstable colourless oil (0.026 g, 0.20 mmol, 16%). **δH** (400 MHz, $CDCl_3$): 7.41 – 7.33 (5H, m), 6.21 – 6.16 (1H, m), 6.14 – 6.10 (1H, m), 5.65 – 5.62 (1H, m), 4.80 – 4.74 (1H, m), 4.62 – 4.56 (1H, m). **δC** (100 MHz, $CDCl_3$): 137.1, 129.0, 128.6, 126.9, 124.9, 80.7, 69.9. **IR** (ν_{max}, cm^{-1}): 1493, 1454, 1379, 1260, 1059, 1033. **MS (**m/z): Found 185.0575, ($C_{10}H_{10}O_2Na^+$requires 185.0573).

2-Phenylfuran (15b)[2]



To a solution of CBr_4 (0.059 g, 0.18 mmol) in CH_2Cl_2 (1.0 mL) cooled to 0 °C was added PPh_3 (0.047 g, 0.18 mmol) and the mixture stirred for 10 minutes. A solution of **14b** (0.026 g, 0.16 mmol) in CH_2Cl_2 (1.0 mL) was added in one portion, brought to r.t. and stirred for 16 hours. Solvents were removed *in vacuo* and the crude product purified by column chromatography (100% hexanes, R_f = 0.48) affording **15b** as an unstable colourless oil (0.021 g, 0.15 mmol, 82%). **δH** (400 MHz, $CDCl_3$): 7.72 – 7.69 (2H, m), 7.50 (1H, d, *J* = 2.0 Hz), 7.43 – 7.39 (2H, m), 7.31 – 7.28 (1H, m), 6.69 (1H, d, *J* = 3.2 Hz), 6.51 (1H, dd, J_1 =3.2 Hz, J_2 = 2.0Hz). **δC** (100 MHz, $CDCl_3$): 154.0, 142.1, 131.0, 128.7, 127.4, 123.8, 111.7, 105.0. **IR** (ν_{max}, cm^{-1}): 1650, 1577, 1540, 1470, 1202, 1113, 1025. **MS (**m/z): Found 145.0648, ($C_{10}H_9O^+$ requires 145.0648).

(*E*)-(2-Methylbuta-1,3-dien-1-yl)benzene (16c)



Methyltriphenylphosphonium iodide (2.021 g, 5.00 mmol) was suspended in anhydrous THF (50 mL) and cooled to -78 °C. ^{n}BuLi (3.0 mL, 2.5 M in hexanes, 7.50 mmol) was added dropwise, and the mixture brought to room temperature and stirred for 30 minutes to give a clear orange-red solution. α-methyl-*trans*-cinnamaldehyde (1.05 mL, 7.50 mmol) was added in one portion, and the mixture stirred for 18 hours. Methanol (5.0 mL) was added, then solvents removed *in vacuo* followed by column chromatography (100% hexanes, R_f = 0.36) affording a colourless oil (0.489 g, 3.50 mmol, 69%). **δH** (400 MHz, $CDCl_3$): 7.49 – 7.33 (5H, m), 6.70 (2H, m), 5.45 (1H, d, *J* = 17.6 Hz), 5.28 (1H, d, *J* = 10.4 Hz), 2.15 (3H, s). **δC** (100 MHz, $CDCl_3$): 142.1, 138.0, 136.2, 131.9, 129.5, 128.4, 126.9, 113.2, 13.4. **IR** (ν_{max}, cm^{-1}): 1804, 1607, 1489, 1444. **MS (**m/z): Found 145.1016, ($C_{11}H_{13}^+$ requires 145.1012).

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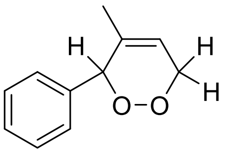
[1] M. Matsumoto, S. Dobashi, K. Kuroda and K. Keiko, *Tetrahedron* 1985, **41**, 2147.

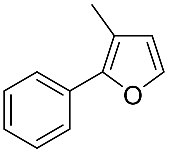
[2] L. N. Pridgen and S. S. Jones, *J. Org. Chem.* 1982, **47**, 1590.

4-Methyl-3-phenyl-3,6-dihydro-1,2-dioxine (14c)[3]



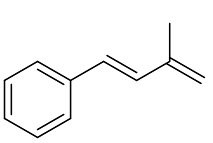
A constant stream of oxygen was passed through a solution of **16c** (0.144 g, 1.00 mmol) and 10^{-4} M disodium Rose Bengal in CH_2Cl_2/MeOH (19:1, 30 mL) whilst exposed to a 400W halogen light source for 18 hours at room temperature. After removal of solvents *in vacuo*, column chromatography (9:1 hexanes/ethyl acetate $R_f = 0.42$) afforded **14c** as a colourless oil (0.030 g, 0.17 mmol, 17%). **δH** (400 MHz, $CDCl_3$): 7.40 – 7.35 (5H, m), 5.89 – 5.87 (1H, m), 5.33 (1H, s), 4.74 – 4.68 (1H, m), 4.63 – 4.58 (1H, m), 1.59 (3H, s). **δC** (100 MHz, $CDCl_3$): 136.6, 133.2, 129.4, 129.1, 128.6, 120.0, 84.6, 70.2, 19.0. **IR** (ν_{max}, cm^{-1}): 1677, 1492, 1453, 1380, 1068, 1020. **MS** (m/z): Found 199.0730 ($C_{11}H_{12}O_2Na^+$ requires 199.0730).

3-Methyl-2-phenylfuran (15c)[4]



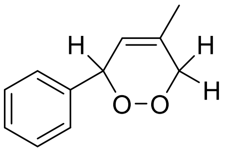
To a solution of CBr_4 (0.062 g, 0.19 mmol) in CH_2Cl_2 (1.0 mL) cooled to 0 °C was added PPh_3 (0.049 g, 0.10 mmol) and the mixture stirred for 10 minutes. A solution of **14c** (0.030 g, 0.17 mmol) in CH_2Cl_2 (1.0 mL) was added in one portion, the mixture brought to r.t. and stirred for 16 hours. Solvents were removed *in vacuo* and the crude product purified by column chromatography (100% hexanes, $R_f = 0.51$) affording **15c** as a colourless oil (0.027 g, 0.17 mmol, 91%). **δH** (400 MHz, $CDCl_3$): 7.65 – 7.63 (2H, m), 7.44 – 7.38 (3H, m), 7.29 – 7.24 (1H, m), 6.34 (1H, d, *J* = 1.6 Hz), 2.30 (3H, s). **δC** (100 MHz, $CDCl_3$): 148.8, 140.8, 131.9, 128.6, 126.8, 125.4, 116.3, 115.2, 12.0. **IR** (ν_{max}, cm^{-1}): 1682, 1608, 1510, 1485, 1443, 1164. **MS** (m/z): Found 159.0804 ($C_{11}H_{11}O^+$ requires 159.0805).

(*E*)-(3-Methylbuta-1,3-dien-1-yl)benzene (16d)



Methyltriphenylphosphonium iodide (2.021 g, 5.00 mmol) was suspended in anhydrous THF (50 mL) and cooled to -78 °C. ^nBuLi (3.0 mL, 2.5 M in hexanes, 7.50 mmol) was added dropwise, and the mixture brought to room temperature and stirred for 30 minutes to give a clear orange-red solution. Benzylideneacetone (0.731 g, 5.50 mmol) was added in one portion, and the mixture stirred for 16 hours, after which point MeOH (5.0 mL) was added, then solvents removed *in vacuo*. Column chromatography (100% hexanes, $R_f = 0.42$) affording a colourless oil (0.576 g, 4.0 mmol, 80%). **δH** (400 MHz, $CDCl_3$): 7.48 – 7.45 (2H, m), 7.37 – 7.33 (2H, m), 7.28 – 7.23 (1H, m), 6.91 (1H, d, *J* = 16.4Hz), 6.57 (1H, d, *J* = 16.4 Hz), 5.15 2H, d, *J* = 16.8 Hz), 2.01 (3H, s). **δC** (100 MHz, $CDCl_3$): 142.2, 137.5, 131.8, 128.8, 128.7, 127.5, 126.6, 117.5, 18.7. **IR** (ν_{max}, cm^{-1}): 1605, 1493, 1446. **MS** (m/z): Found 145.1014 ($C_{11}H_{13}^+$ requires 145.1012).

5-Methyl-3-phenyl-3,6-dihydro-1,2-dioxine (14d)[5]



A constant stream of oxygen was passed through a solution of **16d** (0.100 g, 0.69 mmol) and 10^{-4} M disodium Rose Bengal in CH_2Cl_2/MeOH (19:1, 30 mL) whilst exposed to a 400W halogen light source for 28 hours at room temperature. After removal of solvents *in vacuo*, column chromatography (9:1 hexanes/ethyl acetate $R_f = 0.51$) afforded **14d** as a colourless oil (0.045 g, 0.26 mmol, 26%). **δH** (400 MHz, $CDCl_3$): 7.42 – 7.36 (5H, m), 5.84 – 5.82 (1H, m), 5.62 – 5.60 (1H, m), 4.64 (1H, d, *J* = 16.0 Hz), 4.45 (1H, d, *J* = 16.0 Hz), 1.86 (3H, s). **δC** (100 MHz, $CDCl_3$): 137.8, 132.5, 128.8, 128.5, 128.5, 120.8, 80.4, 73.0, 18.3. **IR** (ν_{max}, cm^{-1}): 1681, 1492, 1453, 1022. **MS** (m/z): Found 199.0730 ($C_{11}H_{12}O_2Na^+$ requires 199.0730).

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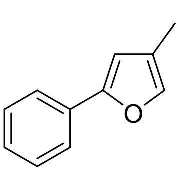
[3] B. W. Greatrex and D. K. Taylor, *J. Org. Chem.* 2004, **69**, 2577.

[4] A. I. Meyers and R. F. Spohn, *J. Org. Chem.* 1985, **50**, 4872.

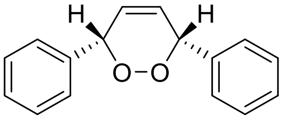
[5] A. Eske, B. Goldfuss, A. G. Griesbeck, A. de Kiff, M. Kleczka, M. Leven, J. –M. Neudoerfl and M. Vollmer, *J. Org. Chem.* 2014, **79**, 1818.

4-Methyl-2-phenylfuran (15d)[6]



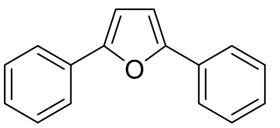
To a solution of CBr_4 (0.093 g, 0.28 mmol) in CH_2Cl_2 (2.0 mL) cooled to 0 °C was added PPh_3 (0.074 g, 0.28 mmol) and the mixture stirred for 10 minutes. A solution of **14d** (0.045 g, 0.26 mmol) in CH_2Cl_2 (1.0 mL) was added in one portion, the mixture brought to r.t., and stirred for 16 hours. Solvents were removed *in vacuo* and the crude product purified by column chromatography (100% hexanes, R_f = 0.50) affording **15d** as a colourless oil (0.036 g, 0.23 mmol, 87%). **δH** (400 MHz, $CDCl_3$): 7.69 – 7.67 (2H, m), 7.43 – 7.39 (2H, m), 7.31 – 7.26 (2H, m), 6.57 (1H, s), 2.12 (3H, s). **δC** (100 MHz, $CDCl_3$): 153.8, 138.9, 131.1, 128.7, 127.2, 123.7, 122.0, 107.7, 9.9. **IR** (ν_{max}, cm^{-1}): 1597, 1539, 1479, 1445, 1387, 1185. **MS (**m/z): Found 159.0809 ($C_{11}H_{11}O^+$ requires 159.0804).

(3*R*,6*S*)-3,6-Diphenyl-3,6-dihydro-1,2-dioxine (14a)[1]



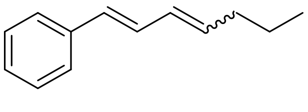
A constant stream of oxygen was passed through a solution of *trans,trans*-1,4-diphenyl-1,3-butadiene (2.066 g, 10.00 mmol) in 19:1 CH_2Cl_2/MeOH (80 mL) containing 10^{-4} M methylene blue for 24 h. Solvents were removed *in vacuo*, followed by column chromatography (5:1 hexanes/ethyl acetate R_f = 0.50) afforded the endoperoxide as pale yellow crystals (1.330 g, 5.60 mmol, 56%). **δH** (400 MHz, $CDCl_3$): 7.50 – 7.25 (10H, m), 6.35 (2H, s), 5.68 (2H, s). **δC** (100 MHz, $CDCl_3$): 137.6, 132.9, 128.8, 128.7, 128.5, 80.2. **IR** (ν_{max}, cm^{-1}): 1595, 1492, 1454, 1265, 1061. **MP** (°C): 79.1 – 84.2. **MS (**m/z): Found 261.0883 ($C_{16}H_{14}O_2Na^+$ requires 261.0886).

2,5-Diphenylfuran (15a)[7]



To a solution of CBr_4 (0.182 g, 0.55 mmol) in CH_2Cl_2 (3.0 mL) cooled to 0 °C was added PPh_3 (0.144 g, 0.55 mmol) and the mixture stirred for 20 minutes. After this period, a solution of **14a** (0.120 g, 0.50 mmol) in CH_2Cl_2 (2.0 mL) was added in one portion, the mixture brought to r.t. and stirred for 16 h. Solvents were removed *in vacuo*, then purified by column chromatography (4:1 hexanes/ethyl acetate R_f = 0.58) affording a pale yellow crystalline solid (0.104 g, 0.48 mmol, 95%). **δH** (400 MHz, $CDCl_3$): 7.77 – 7.25 (10H, m), 6.74 (2H, s). **δH** (400 MHz, $CDCl_3$): 7.77 – 7.25 (10H, m), 6.74 (2H, s). **δC** (100 MHz, $CDCl_3$): 153.4, 130.8, 129.3, 128.7, 123.7, 107.3. **IR** (ν_{max}, cm^{-1}): 1597, 1482, 1443, 1288. **MP** (°C): 86.0 – 90.2. **MS (**m/z): Found 221.0959 ($C_{16}H_{13}O^+$ requires 221.0961).

((1*E*)-Hepta-1,3-dien-1-yl)benzene (*E*/*Z* = 1.0 : 1.7) (16e)



^{n}Butyltriphenylphosphonium bromide (2.00g, 5.00 mmol) was suspended in anhydrous THF (50 mL) and cooled to -78 °C. ^{n}BuLi (3.0 mL, 2.5 M in hexanes, 7.50 mmol) was added dropwise, and the mixture brought to room temperature and stirred for 30 minutes to give a clear orange-red solution. *Trans*-cinnamaldehyde (0.95 mL, 7.50 mmol) was added in one portion, and the mixture stirred for 40 hours. Removal of solvents *in vacuo* followed by column chromatography (100% hexanes, R_f = 0.36) affording a colourless oil (0.707 g, 4.1 mmol, 82%, E/Z = 1.0 : 1.7). **δH** (400 MHz, $CDCl_3$): 7.53 – 7.29 (5H, m), 7.20 (1H, dd, J_1 = 15.6 Hz, J_2 = 11.2 Hz), 6.63 (1H, d, J = 15.6 Hz), 6.35 – 6.26 (1H, m), 5.68 – 5.61 (1H, m), 2.37 (2H, dt, J_1 = 7.8 Hz, J_2 = 7.2 Hz), 1.62 – 1.53 (2H, m), 1.07 (3H, t, J = 7.2 Hz). **δC** (100 MHz, $CDCl_3$): 137.9, 133.2, 132.2, 129.1, 128.8, 127.5, 126.5, 126.3, 30.2, 23.1, 14.0. **IR** (ν_{max}, cm^{-1}): 1595, 1492, 1449. **MS (**m/z): Found 173.1328 ($C_{13}H_{17}^+$ requires 173.1325).

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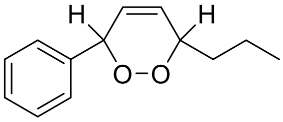
[6] R. Spinam, E. Colacino, J. Martinez and F. Lamaty, *Chem. Eur. J.* 2013, **19**, 3817.

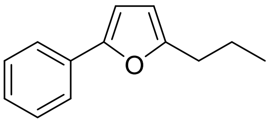
[7] K. E. O'Shea and C. S. Foote, *J. Org. Chem.*, 1989, **54**, 3475.

3-Phenyl-6-propyl-3,6-dihydro-1,2-dioxine (14e)



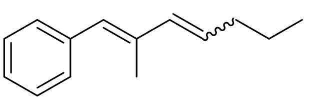
A constant stream of oxygen was passed through a solution of **16e** (0.172 g, 1.00 mmol) in CH_2Cl_2/MeOH (19:1, 30 mL) containing 10^{-4} M disodium Rose Bengal whilst exposed to a 400W halogen light source for 13 hours at room temperature. After removal of solvents *in vacuo*, column chromatography (9:1 hexanes/ethyl acetate R_f = 0.43) afforded **14e** as a pale yellow oil (0.057 g, 0.30 mmol, 28%). **δH** (400 MHz, $CDCl_3$): 7.46 – 7.38 (5H, m), 6.18 – 6.09 (2H, m), 5.57 – 5.55 (1H, m), 4.64 – 4.62 (1H, m), 1.84 – 1.48 (4H, m), 1.00 (3H, t, *J* = 7.2 Hz) **δC** (100 MHz, $CDCl_3$): 137.7, 128.9, 128.8, 128.7, 128.6, 126.3, 80.2, 78.3, 35.2, 18.8, 14.1. **IR** (ν_{max}, cm^{-1}): 1681, 1492, 1453, 1381, 1257, 1108, 1066. **MS (**m/z): Found 227.1042 ($C_{13}H_{16}O_2Na^+$ requires 227.1043).

2-Phenyl-5-propylfuran (15e)[8]



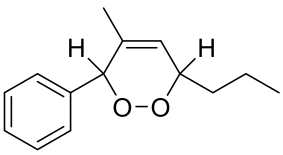
To a solution of CBr_4 (0.091 g, 0.27 mmol) in CH_2Cl_2 (2.0 mL) cooled to 0 °C was added PPh_3 (0.072 g, 0.27 mmol) and the mixture stirred for 25 minutes. A solution of **14e** (0.051 g, 0.25 mmol) in CH_2Cl_2 (1.0 mL) was added in one portion and stirred for 18 hours. Solvents were removed *in vacuo*, then purified by column chromatography (100% hexanes, R_f = 0.48) affording **15e** as a colourless oil (0.036 g, 0.20 mmol, 76%). **δH** (400 MHz, $CDCl_3$): 7.67 – 7.64 (2H, m), 7.39 – 7.35 (2H, m) 7.25 – 7.21 (1H, m), 6.57 (1H, d, *J* = 3.2 Hz), 6.08 (1H, d, *J* = 3.2 Hz), 2.68 (2H, t, *J* = 7.6 Hz) 1.79 – 1.70 (2H, m), 1.02 (3H, t, *J* = 7.2 Hz). **δC** (100 MHz, $CDCl_3$): 156.4, 152.2, 131.4, 128.7, 126.8, 123.4, 107.1, 105.7, 30.3, 21.6, 13.9. **IR** (ν_{max}, cm^{-1}): 1594, 1546, 1487, 1448, 1204, 1015. **MS (**m/z): Found 187.1114 ($C_{13}H_{15}O^+$ requires 187.1117).

(1*E*)-2-Methylhepta-1,3-dien-1-yl)benzene (*E*/*Z* = 1.5 : 1.0) (16f)



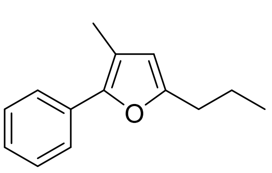
^{n}Butyltriphenylphosphonium bromide (2.000 g, 5.00 mmol) was suspended in anhydrous THF (50 mL) and cooled to -78 °C. ^{n}BuLi (3.0 mL, 2.5 M in hexanes, 7.50 mmol) was added dropwise, and the mixture brought to room temperature and stirred for 30 minutes to give a clear orange-red solution. α-methyl-*trans*-cinnamaldehyde (1.05 mL, 7.50 mmol) was added in one portion, and the mixture stirred for 18 hours. Removal of solvents *in vacuo* followed by column chromatography (100% hexanes, R_f = 0.31) giving a colourless oil (0.654 g, 3.50 mmol, 70%, E/Z = 1.5 : 1.0). **δH** (400 MHz, $CDCl_3$): 7.42 – 7.24 (5H, m), 6.49 (1H, s), 6.31 (1H, d, *J* = 15.6 Hz), 5.85 (1H, dt, J_1 = 15.6 Hz, J_2 = 6.8 Hz), 2.23 (2H, dt, J_1 = 6.8 Hz, J_2 = 7.2 Hz), 2.06 (3H, s), 1.58 – 1.47 (2H, m), 1.01 (3H, t, *J* = 7.6 Hz). **δC** (100 MHz, $CDCl_3$): 138.3, 136.0, 135.5, 130.4, 129.3, 129.2, 128.2, 126.4, 35.3, 23.0, 14.1, 14.0. **IR** (ν_{max}, cm^{-1}): 1598, 1492, 1443, 1379. **MS (**m/z): Found 187.1120 ($C_{13}H_{15}O^+$ requires 187.1117).

4-Methyl-3-phenyl-6-propyl-3,6-dihydro-1,2-dioxine (14f)



A constant stream of oxygen was passed through a solution of **16f** (0.190 g, 1.00 mmol) in CH_2Cl_2/MeOH (19:1, 30 mL) containing 10^{-4} M disodium Rose Bengal whilst exposed to a 400W halogen light source for 3.5 hours at room temperature. After removal of solvents *in vacuo*, column chromatography (9:1 hexanes/ethyl acetate R_f = 0.49) afforded **14f** as a yellow oil (0.103 g, 0.50 mmol, 47%). **δH** (400 MHz, $CDCl_3$): 7.42 – 7.37 (5H, m), 5.87 – 5.83 (1H, m), 5.25 (1H, s), 4.77 – 4.65 (1H, m), 1.79 – 1.47 (7H, m), 1.01 (3H, t, *J* = 7.2 Hz). **δC** (100 MHz, $CDCl_3$): 137.2, 132.7, 129.3, 128.8, 128.5, 124.2, 83.9, 78.3, 35.4, 19.1, 18.7, 14.1. **IR** (ν_{max}, cm^{-1}): 1602, 1493, 1454, 1380, 1254, 1065, 1025. **MS (**m/z): Found 219.1377 ($C_{14}H_{19}O_2^+$ requires 219.1380).

3-Methyl-2-phenyl-5-propylfuran (15f)



To a solution of CBr_4 (0.112 g, 0.34 mmol) in CH_2Cl_2 (2.0 mL) cooled to 0 °C was added PPh_3 (0.089 g, 0.34 mmol) and the mixture stirred for 20 minutes. A solution of **14f** (0.067 g, 0.31 mmol) in CH_2Cl_2 (1.0 mL) was added in one portion, the mixture brought to r.t., and stirred for 18 hours. Solvents were removed *in vacuo*, then column chromatography (100% hexanes, R_f = 0.32) afforded **15f** as a colourless oil (0.031 g, 0.22 mmol, 72%). **δH** (400 MHz, $CDCl_3$): 7.59 (2H, d, *J* = 7.2Hz), 7.39 (2H, t, *J* = 7.6 Hz), 7.23 (1H, t, *J* = 7.2 Hz), 5.94 (1H, s), 2.62 (2H, t, *J* = 7.6 Hz) 2.25

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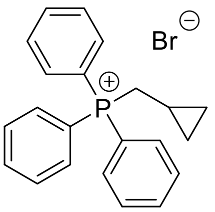
[8] A. Padwa, J. M. Kassir and S. L. Xu, *J. Org. Chem.* 1991, **56**, 6971.

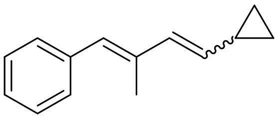
(3H, s), 1.72 – 1.68 (4H, m), 1.00 (3H, t, *J* = 7.2Hz). **δC** (100 MHz, $CDCl_3$): 154.8, 146.8, 137.3, 128.5, 126.1, 125.0, 117.1, 110.8, 30.2, 21.5, 13.9, 12.1. **IR** (ν_{max}, cm^{-1}): 1675, 1616, 1449, 1238. **MS (**m/z): Found 201.1271 ($C_{14}H_{17}O^+$ requires 201.1274).

(Cyclopropylmethyl)triphenylphosphonium bromide (26)



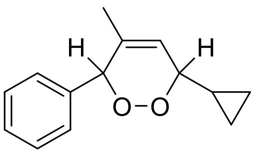
A solution of (bromomethyl)cyclopropane (0.48 mL, 5.00 mmol) and PPh_3 (1.570 g, 6.00 mmol) in toluene (5 mL) was heated to reflux for 16 h. After this period, the mixture was cooled, solvents removed *in vacuo*, and the residue triturated with diethyl ether (3 x 10 mL) affording a white powder (1.160 g, 2.90 mmol, 58 %). **δH** (400 MHz, $CDCl_3$): 7.91 – 7.86 (6H, m), 7.83 – 7.75 (3H, m), 7.71 – 7.64 (6H, m), 3.96 – 3.91 (2H, m), 0.93 – 0.82 (1H, m), 0.61 – 0.53 (4H, m). **δC** (100 MHz, $CDCl_3$):134.9, 134.0, 130.4, 118.9, 28.1, 27.6, 6.4, 4.3. **IR** (ν_{max}, cm^{-1}): 1439, 1265, 1114. **MS (**m/z): Found 317.1455 ($C_{22}H_{22}P^+$ requires 317.1454).

((1*E*)-4-cyclopropyl-2-methylbuta-1,3-dien-1-yl)benzene (*E*/*Z* = 1.0 : 1.2) (16g)



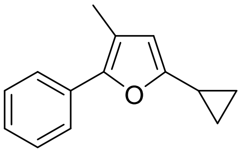
To a suspension of **26** (0.795 g, 2.00 mmol) in anhydrous THF (10 mL) cooled to -78 °C was added ^{n}BuLi (0.9 mL, 2.5 M in hexanes, 2.20 mmol) dropwise. After complete addition, the resulting mixture was brought to r.t. and allowed to stir for 1 h at room temperature. α-methyl-*trans*-cinnamaldehyde (0.35 mL, 2.50 mmol) added dropwise, and the solution stirred at room temperature for 6 h. After this period, MeOH (2 mL) was added, then solvents were removed *in vacuo*, and the crude product purified by column chromatography (19:1 Hexanes/Ethyl acetate, R_f = 0.58) to give a colourless oil (0.247 g, 1.34 mmol, 67%, E/Z = 1.0 : 1.2). **δH** (400 MHz, $CDCl_3$): 7.34 – 7.20 (5H, m), 6.58 (1H, s), 5.91 (1H, d, *J* = 11.6 Hz), 4.81 (1H, dd, J_1 = 11.6 Hz, J_2 = 10.8 Hz), 2.12 (3H, m), 1.53 – 1.45 (1H, m), 0.84 – 0.76 (2H, m), 0.48 – 0.41 (2H, m). **δC** (100 MHz, $CDCl_3$): 138.3, 135.7, 134.3, 133.0, 131.9, 129.2, 128.1, 126.3, 18.8, 11.5, 8.3. **IR** (ν_{max}, cm^{-1}): 1635, 1596, 1490, 1442, 1265. **MS (**m/z): Found 185.1329 ($C_{14}H_{17}^+$ requires 185.1325).

6-Cyclopropyl-4-methyl-3-phenyl-3,6-dihydro-1,2-dioxine (14g)



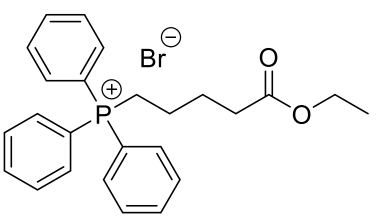
A solution of **16g** (0.184 g, 1.00 mmol) in 19:1 CH_2Cl_2/MeOH (30 mL) containing 10^{-4} M methylene blue was irradiated for 2.5 h at room temperature with a 400W halogen light source, whilst a constant stream of oxygen was passed through the solution. After this period, solvents were removed *in vacuo* and the residue purified by column chromatography (9:1 hexanes/ethyl acetate, R_f = 0.44) to give a colourless oil (0.060 g, 0.28 mmol, 28%). **δH** (400 MHz, $CDCl_3$): 7.42 – 7.31 (5H, m), 5.91 – 5.88 (1H, m), 5.17 (1H, s), 3.90 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz), 1.65 (3H, s), 1.08 – 0.92 (1H, m), 0.66 – 0.32 (4H, m). **δC** (100 MHz, $CDCl_3$): 135.7, 131.5, 127.8, 127.2, 126.9, 121.5, 82.2, 81.3, 17.5, 11.7, 1.8, 0.1. **IR** (ν_{max}, cm^{-1}): 1678, 1493, 1454, 1051, 1027. **MS (**m/z): Found 239.1044 ($C_{14}H_{16}O_2Na^+$ requires 239.1043).

5-Cyclopropyl-3-methyl-2-phenylfuran (15g)



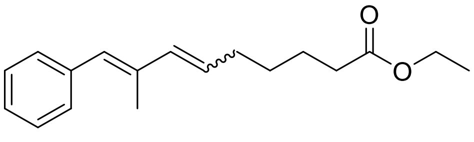
To a solution of CBr_4 (0.074 g, 0.22 mmol) in CH_2Cl_2 (1.0 mL) cooled to 0 °C was added PPh_3 (0.059 g, 0.22 mmol). The resulting mixture was stirred for 10 min, then a solution of **14g** (0.044 g, 0.20 mmol in CH_2Cl_2 (1.0 mL) was added. The solution was brought to r.t. and stirred for 16h. After this period, solvents were removed *in vacuo* and the crude product purified by column chromatography (19:1 hexanes/ethyl acetate, R_f = 0.52) to give the furan as a colourless oil (0.037 g, 0.19 mmol, 93%). **δH** (400 MHz, $CDCl_3$): 7.61 – 7.58 (2H, m), 7.42 – 7.38 (2H, m), 7.26 – 7.21 (1H, m), 5.94 (1H, s), 2.25 (3H, s), 1.95 – 1.90 (1H, m), 0.95 – 0.83 (4H, m). **δC** (100 MHz, $CDCl_3$): 155.6, 146.3, 132.1, 128.4, 126.1, 124.8, 117.2, 109.3, 12.0, 8.8, 6.9, 6.9. **IR** (ν_{max}, cm^{-1}): 1600, 1558, 1444. **MS (**m/z): Found 221.0939 ($C_{14}H_{14}ONa^+$ requires 221.0937).

(5-Ethoxy-5-oxopentyl)triphenylphosphonium bromide (27)



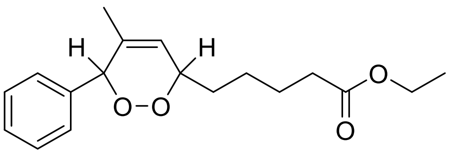
A solution of PPh_3 (3.147 g, 12.00 mmol) and ethyl 6-bromohexanoate (1.8 mL, 10.0 mmol) in MeCN (20 mL) was heated to reflux for 2.5 days. After this period, the mixture was allowed to cool, triturated with diethyl ether (3 x 50 mL), then dried under vacuum to give the phosphonium salt as a white tar (4.330 g, 8.90 mmol, 89%). **δH** (400 MHz, $CDCl_3$): 7.57 – 7.40 (12H, m), 7.10 – 6.94 (3H, m), 3.73 (2H, q, *J* = 7.2Hz), 3.48 – 3.30 (2H, m), 1.91 (2H, t, *J* = 7.6 Hz), 1.42 – 1.28 (6H, m), 0.89 (3H, t, *J* = 7.2Hz). **δC** (100 MHz, $CDCl_3$): 173.2, 133.54, 130.5, 128.4, 60.1, 33.6, 29.6, 24.2, 22.7, 22.2, 14.1. **IR** (ν_{max}, cm^{-1}): 1724, 1440, 1379, 1190, 1113. **MS (**m/z): Found 405.1980 ($C_{26}H_{30}O_2P^+$ requires 405.1978).

ethyl (8*E*)-8-methyl-9-phenylnona-6,8-dienoate (*E*/*Z* = 1.0 : 1.2) (16h)



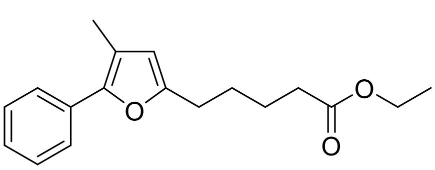
Cs_2CO_3 (6.516 g, 20.00 mmol) was added to a solution of **27** (2.431 g, 5.00 mmol) and α-methyl-*trans*-cinnamaldehyde (0.75 mL, 5.40 mmol) in CH_2Cl_2 (60 mL) and the resulting mixture heated to reflux for 24 h. After this period the mixture was allowed to cool to room temperature, Celite® (c.a. 2.0 g) was added and the mixture stirred for 10 min. The mixture was filtered under vacuum, washing with hexanes (20 mL) and solvents removed *in vacuo*. Purification by column chromatography (9:1 hexanes/ethyl acetate, R_f = 0.42) afforded the diene as a colourless oil (1.086 g, 4.02 mmol, 80%, E/Z = 2.7 : 1.0). **δH** (400 MHz, $CDCl_3$): 7.32 – 7.17 (5H, m), 6.42 (1H, s), 6.22 (1H, d, *J* = 16.0 Hz), 5.75 (1H, dt, J_1 = 16.0 Hz, J_2 = 6.8Hz), 4.12 (2H, q, *J* = 7.6 Hz), 2.38 – 2.16 (4H, m), 1.97 (3H, s), 1.71 – 1.61 (2H, m), 1.51 – 1.41 (2H, m), 1.25 (3H, t, *J* = 7.6Hz). **δC** (100 MHz, $CDCl_3$): 173.8, 138.2, 135.8, 135.6, 129.8, 129.5, 129.2, 128.1, 126.3, 60.3, 34.3, 32.7, 29.1, 27.7, 18.7, 14.2. **IR** (ν_{max}, cm^{-1}): 1742, 1611, 1040. **MS (**m/z): Found 295.1677 ($C_{18}H_{24}O_2Na^+$ requires 295.1669).

Ethyl 5-(5-methyl-6-phenyl-3,6-dihydro-1,2-dioxin-3-yl)pentanoate (14h)



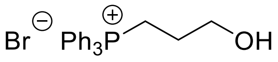
A solution of **16h** (0.273 mg, 1.01 mmol) in 19:1 CH_2Cl_2/MeOH (30 mL) containing 10^{-4} M disodium Rose Bengal was irradiated for 2.5 h at room temperature with a 400W halogen light source, whilst a constant stream of oxygen was passed through the solution. After this period, solvents were removed *in vacuo* and the residue purified by column chromatography (9:1 hexanes/ethyl acetate, R_f = 0.20) to give a colourless oil (0.112 g, 0.39 mmol, 39%). **δH** (400 MHz, $CDCl_3$): 7.36 – 7.30 (5H, m), 5.80 (1H, m), 5.19 (1H, s), 4.58 – 4.55 (1H, m), 4.11 (2H, q, *J* = 7.2Hz), 2.30 (2H, t, *J* = 7.2 Hz), 1.79 – 1.39 (9H, m), 1.24 (3H, t, *J* = 7.2Hz). **δC** (100 MHz, $CDCl_3$): 173.7, 137.0, 133.0, 129.4, 128.9, 128.6, 124.0, 84.0, 78.3, 60.3, 34.3, 33.0, 25.1, 25.0, 19.1, 14.3. **IR** (ν_{max}, cm^{-1}): 1741, 1448, 1374, 1241, 1047. **MS (**m/z): Found 327.1577 ($C_{18}H_{24}O_4Na^+$ requires 327.1567).

Ethyl 5-(4-methyl-5-phenylfuran-2-yl)pentanoate (15h)



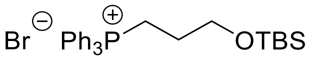
To a solution of CBr_4 (0.092 g, 0.28 mmol) in CH_2Cl_2 (2.0 mL) at 0 °C was added PPh_3 (0.073 g, 0.28 mmol), and the mixture stirred for 10 min. After this period, a solution of **14h** (0.072 g, 0.25 mmol) in CH_2Cl_2 (1.0 mL) was added. The resulting mixture was heated to reflux for 30 h, then the mixture cooled, solvents removed *in vacuo*, and purified by column chromatography (9:1 hexanes/ethyl acetate, R_f = 0.33). The pure furan was obtained as a yellow oil (0.064 g, 0.24 mmol, 94%). **δH** (400 MHz, $CDCl_3$): 7.61 – 7.58 (2H, m), 7.41 – 7.37 (2H, m), 7.25 – 7.20 (1H, m), 5.96 (1H, s), 4.14 (2H, q, *J* = 7.2 Hz), 2.69 – 2.65 (2H, m), 2.38 – 2.33 (2H, m), 2.24 (3H, s), 1.77 – 1.68 (2H, m), 1.26 (3H, t, *J* = 7.6Hz). **δC** (100 MHz, $CDCl_3$): 173.7, 154.2, 147.0, 132.2, 128.5, 126.2, 125.0, 117.1, 111.0, 60.4, 34.2, 27.8, 27.7, 24.6, 14.3, 12.1. **IR** (ν_{max}, cm^{-1}): 1728, 1604, 1558, 1443, 1373, 1180. **MS (**m/z): Found 309.1464 ($C_{18}H_{22}O_3Na^+$ requires 309.1461).

(3-Hydroxypropyl)triphenylphosphonium bromide (28)



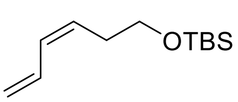
A solution of 3-bromo-1-propanol (2.25 mL, 25.00 mmol) and PPh_3 (7.213 g, 27.50 mmol) in toluene (10 mL) was heated to reflux for 16 hours. After this period the mixture was cooled to room temperature, triturated with diethyl ether (3 x 50 mL), and dried under vacuum affording the phosphonium salt as a white powder (9.887 g, 24.80 mmol, 99%). **MP** = 220.2 – 223.8 °C. **δH** (400 MHz, $CDCl_3$): 7.92 – 7.65 (15H, m), 3.93 – 3.75 (4H, m), 3.35 (1H, s (br)), 1.90 – 1.79 (2H, m). **δC** (100 MHz, $CDCl_3$): 135.1, 133.6, 130.6, 118.5, 60.3, 25.9, 20.2. **IR** (ν_{max}, cm^{-1}): 3314 (br), 2305, 1439, 1264, 1112, 896, 737. **MS** (m/z): Found 321.1397 ($C_{21}H_{22}OP^+$ requires 321.1403).

(3-((*tert*-Butyldimethylsilyl)oxy)propyl)triphenylphosphonium bromide (29)



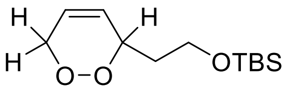
To a solution of **28** (4.013 g, 10.00 mmol) and imidazole (0.749 g, 11.00 mmol) in CH_2Cl_2 (30 mL) was added a solution of TBSCl (1.658 g, 11.00 mmol) in CH_2Cl_2 (10 mL) dropwise. The resulting mixture was stirred at room temperature for 16 h, solvents removed *in vacuo*, then triturated with Et_2O (3 x 100 mL). Removal of residual solvent *in vacuo* afforded the phosphonium salt as a white powder (4.627 g, 9.00 mmol, 90%). **MP** = 107.5 – 111.8 °C. **δH** (400 MHz, $CDCl_3$): 7.84 – 7.63 (15H, m), 3.83 – 3.69 (4H, m), 1.90 – 1.76 (2H, m), 0.09 (9H, s), 0.04 (6H, s). **δC** (100 MHz, $CDCl_3$): 135.4, 133.7, 133.4, 130.7, 118.7, 60.3, 26.0, 19.7, -3.5, -5.3. **IR** (ν_{max}, cm^{-1}): 2306, 1440, 1265, 1113, 998, 743. **MS** (m/z): Found 435.2260 ($C_{27}H_{36}SiOP^+$ requires 435.2268).

(*Z*)-*tert*-Butyl(hexa-3,5-dien-1-yloxy)dimethylsilane (16i)



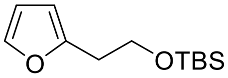
To a suspension of **29** (1.547 g, 3.00 mmol) in anhydrous THF (20 mL) cooled to -78 °C was added KHMDS (6.0 mL, 0.5 M in toluene, 3.00 mmol) dropwise. The mixture was brought to room temperature and stirred for 1 hour, then cooled to -78 °C and acrolein (0.30 mL 4.50 mmol) added. The mixture was stirred for 1h at -78 °C, then brought to room temperature and stirred for a further 2 hours. The mixture was concentrated *in vacuo* (ca. 5 mL), diluted with hexanes (30 mL), washed with water (3 x 25 mL), dried over $MgSO_4$, filtered, and solvents removed *in vacuo.* Column chromatography (9:1 hexanes/ethyl acetate R_f = 0.73) afforded a yellow oil (0.326 g, 1.53 mmol, 51%). **δH** (400 MHz, $CDCl_3$): 6.63 (1H, ddd, J_1 = 17.2 Hz, J_2 = 12.4 Hz, J_3 = 10.0 Hz), 6.06 (1H, dd, J_1 = 12.4 Hz, J_2 = 10.0 Hz), 5.46 (1H, dt, J_1 =10.0 Hz, J_2 = 8.0 Hz), 5.20 (1H, d, J = 17.2Hz), 5.09 (1H, d, J = 10.0Hz), 3.66 (2H, t, J = 5.6 Hz), 2.3 (2H, dt, J_1 = 8.0 Hz, J_2 = 5.6Hz), 0.88 (9H, s), 0.10 (6H, s). **δC** (100 MHz, $CDCl_3$): 132.4, 130.9, 128.7, 117.4, 62.8, 31.6, 26.0, 18.4, -5.2. **IR** (ν_{max}, cm^{-1}): 1676, 1590, 1255, 1118. **MS** (m/z): Found 235.1491 ($C_{12}H_{24}SiONa^+$ requires 235.1489).

***tert*-Butyl(2-(3,6-dihydro-1,2-dioxin-3-yl)ethoxy)dimethylsilane (14i)**



A constant stream of oxygen was passed through a solution of **16i** (0.101 g, 0.47 mmol) in CH_2Cl_2/MeOH (19:1, 30 mL) containing 10^{-4} M disodium Rose Bengal whilst irradiated with a 400W halogen light source for 30 hours. After this period, solvents were removed *in vacuo* and the crude product purified by column chromatography (9:1 hexanes/ethyl acetate R_f = 0.52) affording a colourless oil (0.036 g, 0.15 mmol, 31%). **δH** (400 MHz, $CDCl_3$): 6.00 – 5.95 (2H, m), 4.77 – 4.73 (1H, m), 4.57 – 4.53 (2H, m), 3.82 – 3.71 (2H, m), 1.94 – 1.75 (2H, m), 0.91 (9H, s), 0.03 (6H, s). **δC** (100 MHz, $CDCl_3$): 128.2, 123.9, 75.8, 69.9, 59.1, 35.8, 25.9, 18.3, -5.4. **IR** (ν_{max}, cm^{-1}): 1683, 1471, 1257, 1096. **MS** (m/z): Found 267.1381 ($C_{12}H_{24}SiO_3Na^+$ requires 267.1387).

***tert*-Butyl(2-(furan-2-yl)ethoxy)dimethylsilane (15i)**[9]



A solution of CBr_4 (0.060 g, 0.18 mmol) in CH_2Cl_2 (1.0 mL) was cooled to 0 °C and PPh_3 (0.047 g, 0.18 mmol) added. The mixture was stirred for 20 minutes, then a solution of **14i** (0.039 g, 0.16 mmol) in CH_2Cl_2 (1.0 mL) was added in one portion. The solution was brought to room temperature and stirred with TLC monitoring. After 18 h solvents were removed *in vacuo*. Column chromatography (19:1 hexanes/ethyl acetate R_f = 0.54) afforded a colourless oil (0.034 g, 0.15 mmol, 95%). **δH** (400 MHz, $CDCl_3$): 7.31 – 7.30 (1H, m), 6.29 – 6.28 (1H, m), 6.06 – 6.05 (1H, m), 3.85 (2H, t, J = 7.2Hz), 2.85 (2H, t, J = 7.2Hz), 0.87 (9H, s), 0.01 (6H, s). **δC** (100 MHz, $CDCl_3$): 153.4, 141.0, 110.3, 106.2, 61.7, 32.0, 26.0, 18.4, -5.4. **IR** (ν_{max}, cm^{-1}): 1599, 1507, 1472, 1255, 1105, 1005. **MS** (m/z): Found 249.1285 ($C_{12}H_{22}SiO_2Na^+$ requires 249.1281).

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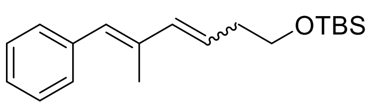
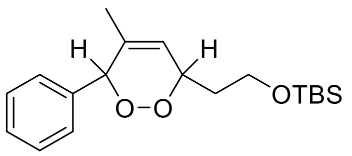
[9] F. Loiseau, J. –M. Simone, D. Carcache, P. Bobal and R. Neier, *Monatsh. Chem.* 2007, **138**, 121.

***tert*-Butyldimethyl(((5E)-5-methyl-6-phenylhexa-3,5-dien-1-yl)oxy)silane (*E/Z* = 2 : 1) (16j)**



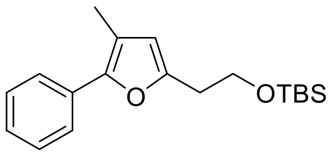
To a suspension of **29** (5.150 g, 10.0 mmol) in anhydrous THF (50 mL) cooled to -78 °C was added ^{n}BuLi (6.0 mL, 2.5 M in hexanes, 15.00 mmol) dropwise. After complete addition, the resulting mixture was brought to r.t. and allowed to stir for 1 h, then α-methyl-*trans*-cinnamaldehyde (3.0 mL, 20.0.0 mmol) added dropwise, and the solution stirred for 12h. After this period, MeOH (10 mL) was added, solvents removed *in vacuo*, and the crude product purified by column chromatography (19:1 Hexanes/Ethyl acetate, R_f = 0.38) affording a colourless oil (2.080 g, 7.80 mmol, 78%, E/Z = 2 : 1). **δH** (400 MHz, $CDCl_3$): 7.38 – 7.23 (5H, m), 6.47 (1H, s), 6.29 (1H, d, *J* = 15.6Hz), 5.79 (1H, dt, J_1 = 15.6Hz, J_2 = 6.8 Hz), 3.73 (2H, t, *J* = 7.2Hz), 2.42 (2H, dt, J_1 = 6.8Hz, J_2 = 7.2Hz), 2.01 (3H, s), 0.92 (9H, s), 0.10 (6H, s). **δC** (100 MHz, $CDCl_3$): 138.1, 137.0, 135.8, 134.9, 129.7, 129.2, 128.0, 126.4, 63.2, 36.6, 26.0, 18.4, 13.9, -5.2. **IR** (ν_{max}, cm^{-1}): 1604, 1472, 1387, 1360, 1254, 1100. **MS (**m/z): Found 325.1962 ($C_{19}H_{30}SiONa^+$ requires 325.1958).

***tert*-Butyldimethyl(2-(5-methyl-6-phenyl-3,6-dihydro-1,2-dioxin-3-yl)ethoxy)silane (14j)**



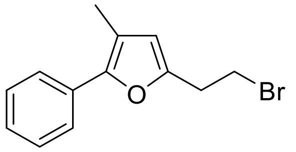
A constant stream of oxygen was passed through a solution of **16j** (0.303 g, 1.00 mmol) in CH_2Cl_2/MeOH (19:1, 30 mL) containing 10^{-4} M methylene blue, under irradiation from a 400W halogen light source for 5 hours. After this period, solvents were removed *in vacuo* and the crude product purified by column chromatography (9:1 hexanes/ethyl acetate R_f = 0.35) affording a colourless oil (0.129 g, 0.38 mmol, 38%). **δH** (400 MHz, $CDCl_3$): 7.40 – 7.38 (5H, m), 5.91 – 5.90 (1H, m), 5.33 (1H, s), 4.90 – 4.78 (1H, m), 3.85 – 3.80 (2H, m), 2.09 – 1.82 (2H, m), 1.62 (3H, s), 0.95 (9H, s), 0.12 (6H, s). **δC** (100 MHz, $CDCl_3$): 136.7, 132.9, 129.3, 128.9, 128.5, 124.2, 84.1, 75.5, 59.3, 36.4, 26.0, 18.9, 18.4, -5.3. **IR** (ν_{max}, cm^{-1}): 1471, 1455, 1387, 1255, 1095. **MS (**m/z): Found 357.1859 ($C_{19}H_{30}SiO_3Na^+$ requires 357.1856).

***tert*-Butyldimethyl(2-(4-methyl-5-phenylfuran-2-yl)ethoxy)silane (15j)**



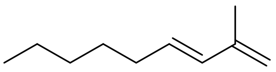
To a solution of CBr_4 (0.054 g, 0.16 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C was added PPh_3 (0.043 g, 0.16 mmol), and the mixture stirred for 10 min. After this period, a solution of **14j** (0.050 mg, 0.15 mmol) in CH_2Cl_2 (1.0 mL) was added, and the mixture brought to r.t. The resulting mixture was allowed to stir for 16 h, then solvents removed *in vacuo*, and purified by column chromatography (9:1 hexanes/ethyl acetate, R_f = 0.57). The pure furan was obtained as a pale yellow oil (0.030 g, 0.09 mmol, 63%). **δH** (400 MHz, $CDCl_3$): 7.62 – 7.60 (2H, m), 7.43 – 7.39 (2H, m), 2.28 – 7.25 (1H, m) 6.03 (1H, s), 3.91 (2H, t, *J* = 6.8 Hz), 2.89 (2H, t, *J* = 6.8 Hz), 2.26 (3H, s), 0.91 (9H, s), 0.06 (6H, s) . **δC** (100 MHz, $CDCl_3$): 151.5, 147.1, 132.2, 128.5, 126.2, 125.0, 117.1, 112.1, 61.8, 32.0, 25.9, 18.6, 12.0, -5.4. **IR** (ν_{max}, cm^{-1}): 1471, 1455, 1387, 1256, 1096. **MS (**m/z): Found 339.1757 ($C_{19}H_{28}SiO_2Na^+$ requires 339.1751).

5-(2-Bromoethyl)-3-methyl-2-phenylfuran (15j')



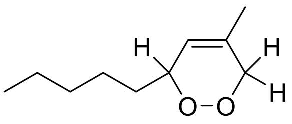
To a solution of CBr_4 (0.292 g, 0.88 mmol) in CH_2Cl_2 (3.0 mL) at 0 °C was added PPh_3 (0.232 g, 0.88 mmol), and the mixture stirred for 10 min. After this period, a solution of **14j** (0.130 g, 0.40 mmol) in CH_2Cl_2 (2.0 mL) was added. The resulting mixture heated to reflux for 16 h, cooled, then solvents removed *in vacuo*, and purified by column chromatography (9:1 hexanes/ethyl acetate, R_f = 0.81). The pure furan was obtained as a pale yellow oil (0.097 g, 0.36 mmol, 91%). **δH** (400 MHz, $CDCl_3$): 7.71 – 7.61 (2H, m), 7.48 – 7.41 (2H, m), 7.31 – 7.26 (1H, m), 6.12 (1H, s), 3.65 (2H, t, *J* = 7.2 Hz), 3.25 (2H, t, *J* = 7.2 Hz), 2.30 (3H, s). **δC** (100 MHz, $CDCl_3$): 150.6, 147.8, 131.8, 128.5, 126.5, 125.1, 117.1, 112.5, 31.9, 29.8, 11.9. **IR** (ν_{max}, cm^{-1}): 1679, 1600, 1551, 1491, 1378, 1071. **MS (**m/z): Found 287.0049 ($C_{13}H_{13}BrONa^+$ requires 287.0042).

(*E*)-2-Methylnona-1,3-diene (16k)



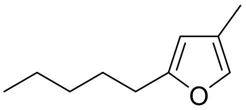
To a suspension of methyltriphenylphosphonium bromide (0.720 g, 2.00 mmol) in anhydrous THF (20 mL) cooled to -78 °C was added ^{n}BuLi (1.0 mL, 2.5 M in hexanes, 2.50 mmol) dropwise. After complete addition, the mixture was brought to r.t. and stirred for 1 h, then 3-nonen-2-one (0.41 mL, 2.50 mmol) added dropwise. The resulting mixture was allowed to stir at room temperature for 2h, then MeOH (2 mL) was added, solvents removed *in vacuo*, and the crude product purified by column chromatography (100% hexanes, R_f = 0.70). The pure diene was obtained as a colourless oil (0.133 mg, 0.96 mmol, 49%). **δH** (400 MHz, $CDCl_3$): 6.16 (1H, d, *J* = 15.6 Hz), 5.69 (1H, dt, J_1 = 15.6Hz, J_2 = 6.8 Hz), 4.89 (2H, s), 2.14 (2H, dt, J_1 = 6.8 Hz, J_2 = 8.4 Hz), 1.86 (3H, s), 1.46 – 1.31 (6H, m), 0.92 (3H, t, *J* = 7.6 Hz). **δC** (100 MHz, $CDCl_3$): 142.3, 132.7, 131.2, 114.1, 32.8, 31.5, 29.1, 22.6, 18.7, 14.1, 12.5. **IR** (ν_{max}, cm^{-1}): 1647, 1609, 1455, 1437, 1377. **MS (**m/z): Found 137.1327 ($C_{10}H_{17}^-$ requires 137.1325).

5-Methyl-3-pentyl-3,6-dihydro-1,2-dioxine (14k)



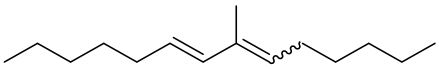
A solution of **16k** (0.133 g, 0.96 mmol) in 19:1 CH_2Cl_2/MeOH (30 mL) containing 10^{-4} M disodium Rose Bengal was irradiated for 20 h at room temperature with a 400W halogen light source, whilst a constant stream of oxygen was passed through the solution. After this period, solvents were removed *in vacuo* and the residue purified by column chromatography (9:1 hexanes/ethyl acetate, R_f = 0.44) to give a colourless oil (0.084 g, 0.49 mmol, 51%). **δH** (400 MHz, $CDCl_3$): 5.54 – 5.52 (1H, m), 4.94 – 4.46 (1H, m), 4.41 (1H, d, *J* = 15.6 Hz), 4.21 (1H, d, *J* = 15.6 Hz), 1.67 (3H, s), 1.57 – 1.30 (8H, m), 0.85 (3H, t, *J* = 7.2Hz). **δC** (100 MHz, $CDCl_3$): 131.4, 122.1, 78.3, 72.8, 32.9, 31.8, 24.8, 22.5, 18.0, 14.0. **IR** (ν_{max}, cm^{-1}): 1682, 1450, 1380, 1175, 1066, 1021. **MS (**m/z): Found 193.1204 ($C_{10}H_{18}O_2Na^+$ requires 193.1199).

4-Methyl-2-pentylfuran (15k)[10]



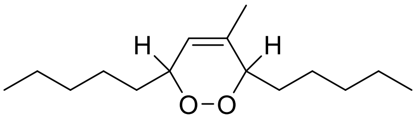
To a solution of CBr_4 (0.179 g, 0.54 mmol) in CH_2Cl_2 (3.0 mL) cooled to 0 °C was added PPh_3 (0.141 g, 0.54 mmol) and the mixture stirred for 10 minutes. A solution of **14k** (0.084 g, 0.49 mmol) in CH_2Cl_2 (2.0 mL) was added in one portion and stirred for 16 hours. Solvents were removed *in vacuo*, and the crude product purified by column chromatography (100% hexanes, R_f = 0.74) afforded **15k** as a colourless oil (0.062 g, 0.41 mmol, 83%). **δH** (400 MHz, $CDCl_3$): 7.08 (1H, s), 5.87 (1H, s), 2.58 (2H, t, *J* = 7.6 Hz), 2.01 (3H, s), 1.67 – 1.59 (2H, m), 1.36 – 1.28 (4H, m), 0.92 (3H, t, *J* = 7.2Hz). **δC** (100 MHz, $CDCl_3$): 156.7, 137.2, 120.4, 107.4, 31.4, 29.7, 28.1, 27.7, 22.5, 14.0, 9.9. **IR** (ν_{max}, cm^{-1}): 1643, 1553, 1468, 1381, 1167, 1096. **MS (**m/z): Found 153.1278 ($C_{10}H_{17}O^+$ requires 153.1274)

(8*E*)-7-Methyltetradeca-6,8-diene (*E*/*Z* = 2.9 : 1.0) (16l)



To a suspension of ⁿhexyltriphenylphosphonium bromide (2.140 g, 5.00 mmol) in anhydrous THF (50 mL) cooled to -78 °C was added ⁿBuLi (2.0 mL, 2.5 M in hexanes, 5.00 mmol) dropwise, the mixture brought to r.t. and stirred for 1 h. After this period, 3-nonen-2-one (0.83 mL, 5.00 mmol) was added dropwise to the ylide solution, and the solution stirred at room temperature for 2 h. MeOH (5 mL) was added, solvents were removed *in vacuo*, and the product purified by column chromatography (100% hexanes, R_f = 0.62). The diene was obtained as a pale yellow oil (0.636 mg, 3.10 mmol, 61%, E/Z = 2.9 : 1.0). **δH** (400 MHz, $CDCl_3$): 6.08 (1H, d, *J* = 15.6 Hz), 5.58 (1H, dt, J_1 = 15.6Hz, J_2 = 6.8 Hz), 5.40 (1H, t, *J* = 7.6 Hz), 2.17 – 2.08 (4H, m), 1.75 (3H, s), 1.47 – 1.29 (12H, m), 0.94 – 0.92 (6H, m). **δC** (100 MHz, $CDCl_3$): 134.7, 133.4, 130.7, 127.6, 32.9, 31.6, 31.6, 29.4, 29.4, 28.1, 22.7, 22.6, 14.1, 14.1, 12.4. **IR** (ν_{max}, cm^{-1}): 1643, 1466, 1379, 1097. **MS (**m/z): Found 209.2265 ($C_{15}H_{29}^+$ requires 209.2265).

4-Methyl-3,6-dipentyl-3,6-dihydro-1,2-dioxine (14l)



A solution of **16l** (0.416 g, 2.00 mmol) in 19:1 CH_2Cl_2/MeOH (30 mL) containing 10^{-4} M disodium Rose Bengal was irradiated for 18 h at room temperature with a 400W halogen light source, whilst a constant stream of oxygen was passed through the solution. After this period, solvents were removed *in vacuo* and the residue purified by column chromatography (9:1 hexanes/ethyl acetate, R_f = 0.52) to give a colourless oil (0.240 g, 1.00 mmol, 50%). **δH** (400 MHz, $CDCl_3$): 5.53 (1H, m), 4.49 (1H, m), 4.25 (1H, m), 1.75 – 1.28 (19H, m), 0.92 (3H, t, *J* =

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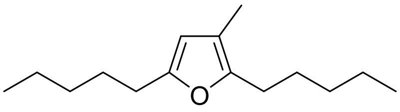
[10] D. Kalaitzakis, T. Montagnon, I. Alexopoulou and G. Vassilikogiannakis, *Angew. Chem. Int. Ed.* 2012, **51**, 8868.

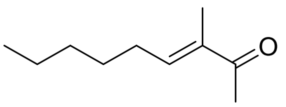
6.8Hz), 0.90 (3H, t, *J* = 6.8Hz). **δC** (100 MHz, $CDCl_3$): 134.5, 122.6, 81.8, 78.2, 33.0, 33.0, 31.8, 31.8, 25.5, 25.5, 22.6, 22.6, 18.9, 14.0, 14.0. **IR** (ν_{max}, cm^{-1}): 1467, 1380, 1056. **MS (**m/z): Found 263.1987 ($C_{15}H_{28}O_2Na^+$ requires 263.1982).

3-Methyl-2,5-dipentylfuran (15l)



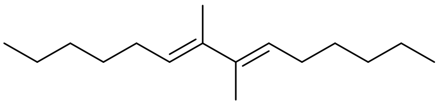
To a solution of CBr_4 (0.365 g, 1.10 mmol) in CH_2Cl_2 (7.0 mL) cooled to 0 °C was added PPh_3 (0.289 g, 1.1 mmol) and the resulting mixture stirred for 10 minutes. After this period, a solution of **14l** (0.239 g, 1.00 mmol) in CH_2Cl_2 (3.0 mL) was added, the solution brought to r.t., and stirred for 16h. Solvents were removed *in vacuo*, and the crude product purified by column chromatography (9:1 hexanes/ethyl acetate, R_f = 0.70). The furan was obtained as a colourless oil (0.160 g, 0.72 mmol, 72%). **δH** (400 MHz, $CDCl_3$): 5.76 (1H, s), 2.54 (2H, t, *J* = 8.0 Hz), 2.53 (2H, t, *J* = 7.6 Hz), 1.93 (3H, s), 1.66 – 1.56 (4H, m), 1.39 – 1.28 (8H, m), 0.94 – 0.90 (6H, m). **δC** (100 MHz, $CDCl_3$): 153.5, 149.4, 113.8, 107.6, 31.5, 31.4, 28.5, 28.0, 27.9, 25.9, 22.5, 22.5, 14.1, 14.0, 9.9. **IR** (ν_{max}, cm^{-1}): 1637, 1576, 1466, 1379, 1219. **MS (**m/z): Found 223.2062 ($C_{15}H_{27}O^+$ requires 223.2056).

(*E*)-3-Methylnon-3-en-2-one (30)



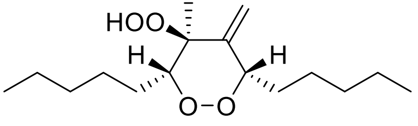
Hexanal (6.0 mL, 50.0 mmol) was added dropwise to a vigorously stirred biphasic mixture of butanone (20 mL, 0.22 mol) and aqueous NaOH (15 mL, 10% w/v) over a 1 h period. After complete addition, the mixture was stirred at room temperature for 60 h, then the layers separated and the aqueous layer extracted into ethyl acetate (2 x 20 mL). Combined organics were dried over $MgSO_4$, filtered, and solvents removed *in vacuo* to give a colourless oil. Aqueous HBr (2 drops, 40% w/v), and the mixture distilled to obtain the crude, wet enone as a colourless oil. The distillate was diluted with ethyl acetate (20 mL), dried over $MgSO_4$, filtered, and solvents removed *in vacuo* affording a colourless oil (5.694 g, 40.10 mmol, 80%). **δH** (400 MHz, $CDCl_3$): 6.65 – 6.61 (1H, t, *J* = 7.2Hz), 2.30 (3H, s), 2.23 (2H, dt, J_1 = 7.2Hz, J_2 = 7.6 Hz), 1.76 (3H, s), 1.50 – 1.43 (2H, m), 1.37 – 1.27 (4H, m), 0.90 (3H, t, *J* = 7.2 Hz). **δC** (100 MHz, $CDCl_3$): 200.1, 144.1, 137.7, 31.7, 29.2, 28.4, 25.5, 22.6, 14.1, 11.2. **IR** (ν_{max}, cm^{-1}): 1669, 1641, 1459, 1366. **MS (**m/z): Found 153.1434 ($C_{10}H_{19}O^+$ requires 155.1430).

(6*E*,8*E*)-7,8-Dimethyltetradeca-6,8-diene (16)



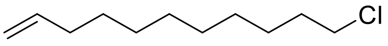
^{n}BuLi (2.2 mL, 2.3 M in hexanes, 5.00 mmol) was added dropwise to a suspension of ^{n}hexyltriphenylphosphonium bromide (2.141 g, 5.00 mmol) in anhydrous THF (50 mL) cooled to -78 °C. After complete addition, the mixture was brought to r.t. and allowed to stir for 1 h, then **30** (0.770 g, 5.00 mmol) added dropwise and the resulting mixture stirred at room temperature for 2 h. MeOH (5 mL) was added to the solution, solvents were removed *in vacuo*, and the crude product purified by column chromatography (100% hexanes, R_f = 0.60) to give a colourless oil (0.660 g, 3.10 mmol, 63%). **δH** (400 MHz, $CDCl_3$): 5.16 – 5.10 (2H, m), 2.23 – 1.97 (4H, m), 1.76 (3H, s), 1.67 (3H, s), 1.43 – 1.32 (12H, m), 0.92 – 0.85 (6H, m). **δC** (100 MHz, $CDCl_3$): 140.0, 135.2, 127.1, 125.3, 31.6, 31.6, 30.1, 29.4, 28.9, 27.8, 23.4, 22.6, 22.6, 15.6, 14.1, 14.1. **IR** (ν_{max}, cm^{-1}): 1641, 1466, 1377. **MS (**m/z): Found 221.2270 ($C_{16}H_{29}^+$ requires 221.2264).

(3*R*,4*S*,6*S*)-4-Hydroperoxy-4-methyl-5-methylene-3,6-dipentyl-1,2-dioxane (18)



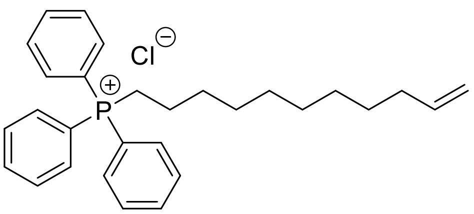
A solution of **16** (0.140 g, 0.63 mmol) in 19:1 CH_2Cl_2/MeOH (30 mL) containing 10^{-4} M disodium Rose Bengal was irradiated for 2.5 h at room temperature with a 400W halogen light source, whilst a constant stream of oxygen was passed through the solution. After this period, solvents were removed *in vacuo* and the residue purified by column chromatography (9:1 hexanes/ethyl acetate, R_f = 0.27) to give a colourless oil (0.155 g, 0.54 mmol, 86%). **δH** (400 MHz, $CDCl_3$): 8.00 (1H, s), 5.32 (1H, t, *J* = 6.8 Hz), 5.26 (1H, s), 4.97 (1H, d, *J* = 2Hz), 4.45 (1H, t, *J* = 6.8Hz), 2.00 (2H, m), 1.81 (3H, s), 1.55 – 1.21 (14H, m), 0.86 (3H, t, *J* = 7.2Hz), 0.86 (3H, t, *J* = 7.2Hz). **δC** (100 MHz, $CDCl_3$): 148.5, 134.9, 129.6, 113.6, 87.4, 32.4, 31.8, 31.7, 30.0, 29.2, 25.6, 24.1, 22.7, 22.6, 14.1, 14.1. **IR** (ν_{max}, cm^{-1}): 3402 (br), 1636, 1458, 1373, 1064. **MS (**m/z): Found 309.2036 ($C_{16}H_{30}O_4Na^+$ requires 309.2036).

11-Chloroundec-1-ene (20)



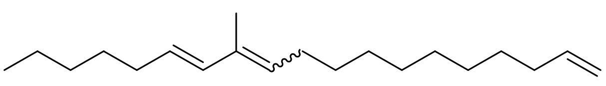
To a mixture of 10-undecen-1-ol (10.0 mL, 49.80 mmol) and pyridine (2.0 mL, 24.80 mmol) under a nitrogen atmosphere was added thionyl chloride (7.2 mL, 99.30 mmol) dropwise over a 1 h period. After complete addition, the resulting mixture was heated to 65°C for 2 h, after which the mixture was cooled and water (25 mL) was added slowly to quench the residual thionyl chloride. The mixture was extracted into ethyl acetate (3 x 25 mL), the combined organics were washed sequentially with 2M HCl solution (10 mL), saturated $NaHCO_3$ (3 x 10mL), and brine (10 mL). The organics were dried over $MgSO_4$, filtered, and solvents removed *in vacuo* to afford a yellow oil. The crude oil was dissolved in hexanes (100 mL), and filtered through a short plug of silica. Removal of solvents *in vacuo* gave the pure compound as a colourless oil (8.506 g, 45.14 mmol, 90%). **δH** (400 MHz, $CDCl_3$): 5.86 – 5.76 (1H, m), 5.02 – 4.91 (2H, m), 3.53 (2H, t, J = 6.8Hz), 2.06 – 2.01 (2H, m), 1.80 – 1.74 (2H, m), 1.44 – 1.28 (12H, m). **δC** (100 MHz, $CDCl_3$): 139.3, 114.2, 45.3, 33.9, 32.7, 29.5, 29.5, 29.2, 29.0, 29.0, 27.0. **IR** (ν_{max}, cm^{-1}): 1640, 1465.

Triphenyl(undec-10-en-1-yl)phosphonium chloride (21)



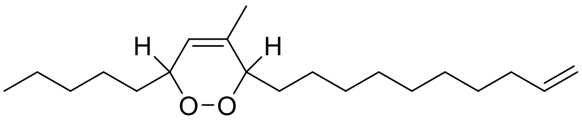
PPh_3 (13.088 g, 49.90 mmol) was dissolved in **20** (8.486 g, 45.00 mmol) in a sealed tube under an atmosphere of nitrogen. The solution was heated to 250°C for 3 days, at which point the hot mixture was poured into a beaker and allowed to cool. The crude phosphonium salt was triturated with diethyl ether (3 x 100 mL), then dried under vacuum to afford the phosphonium salt as a pale yellow tar (15.834 g, 35.12 mmol, 78%). **δH** (400 MHz, $CDCl_3$):7.87 – 7.64 (15H, m), 5.77 (1H, d, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 6.8 Hz), 4.96 (1H, dd, J_1 = 17.2 Hz, J_2 = 1.6 Hz), 4.90 (1H, dd, J_1 = 10.4 Hz, J_2 = 1.6 Hz), 3.97 – 3.81 (2H, m), 2.00 (2H, dt, J_1 = 6.8 Hz, J_2 = 7.2 Hz), 1.66 – 1.59 (4H, m), 1.31 – 1.20 (10H, m). **δC** (100 MHz, $CDCl_3$):139.2, 134.9, 133.9, 130.4, 119.1, 114.1, 33.8, 30.6, 30.4, 29.4, 29.3, 29.2, 29.0, 28.8, 22.8. **IR** (ν_{max}, cm^{-1}): 1627, 1588, 1438, 1267, 1114. **MS (**m/z): Found 415.2554 ($C_{29}H_{26}P^+$ requires 415.2549).

(13*E*)-12-Methylnonadeca-1,11,13-triene (E/Z = 1.0 : 2.2) (23)



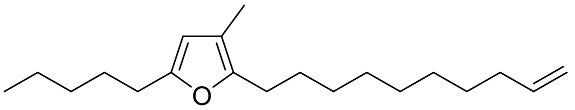
21 (2.253 g, 5.00 mmol) was dissolved in anhydrous THF (20 mL) under a nitrogen atmosphere and cooled to -78°C, ^nBuLi (2.0 mL, 2.5 M in hexanes, 5.00 mmol) added dropwise to produce an orange-red solution of ylide then allowed to warm to room temperature, and stirred for 1 h. After this period, 3-nonen-2-one (0.92 mL, 5.50 mmol) was added dropwise to the ylide, and the resulting mixture stirred 16 h. MeOH (5 mL) was added to quench the reaction, and solvents were removed *in vacuo*. The crude product was purified by column chromatography (100% hexanes, R_f = 0.57) affording the pure compound as a colourless oil (0.448 g, 1.62 mmol, 32 %, E/Z = 1.0 : 2.2). **δH** (400 MHz, $CDCl_3$): 6.04 (1H, d, J = 15.6 Hz), 5.80 (1H, m), 5.54 (1H, dt, J_1 = 15.6Hz, J_2 = 6.8 Hz), 5.37 (1H, t, J = 7.6Hz), 5.01 – 4.95 (1H, m), 4.94 – 4.90 (1H, m), 2.14 – 2.00 (6H, m), 1.40 – 1.27 (18H, m), 0.90 – 0.84 (3H, m). **δC** (100 MHz, $CDCl_3$): 139.3, 134.8, 133.5, 130.8, 127.7, 114.2, 33.9, 33.0, 31.6, 29.8, 29.6, 29.5, 29.5, 29.5, 29.2, 29.0, 28.2, 22.7, 14.2, 12.5. **IR** (ν_{max}, cm^{-1}): 1640, 1465, 1378. **MS (**m/z): Found 275.2738 ($C_{20}H_{35}^-$ requires 275.2733).

3-(Dec-9-en-1-yl)-4-methyl-6-pentyl-3,6-dihydro-1,2-dioxine (14m)



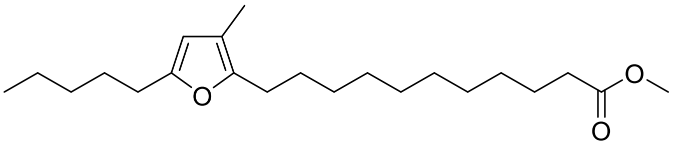
A stream of oxygen was passed through a solution of **23** (0.200 g, 0.72 mmol) in CH_2Cl_2/MeOH (19:1, 30 mL) containing 10^{-4} M methylene blue whilst irradiated for 15 minutes at room temperature with a 400W halogen light source. After this period, solvents were removed *in vacuo*, and the crude product purified by column chromatography (9:1 peteroleum ether/ethyl acetate, R_f = 0.81) affording a colourless oil (0.108 g, 0.35 mmol, 49%). **δH** (400 MHz, CDCl3): 5.83 (1H, m), 5.53 (1H, d, $J = 10.4$ *Hz*), 5.03 (1H, dd, $J_1 = 17.2$ *Hz*, $J_2 = 3.6$ *Hz*), 4.94 (1H, dd, J_1 = 10.0 Hz, $J_2 = 2.4$ *Hz*), 4.54 (1H, m), 4.13 (1H, m), 2.07 – 1.98 (2H, m), 1.75 (3H, s), 1.67 – 1.32 (22H, m), 0.91 (3H, t, $J = 6.8$ *Hz*). **δC** (100 MHz, $CDCl_3$): 134.7, 133.2, 125.8, 122.6, 81.8, 78.3, 33.0, 32.6, 32.0, 31.9, 31.4, 31.1, 29.8, 29.7, 29.4, 29.2, 24.9, 22.6, 19.0, 14.1. **IR** (ν_{max}, cm^{-1}): 1645, 1560, 1466, 1096, 1017. **MS (**m/z): Found 331.2615 ($C_{20}H_{36}O_2Na^+$ requires 331.2608).

2-(Dec-9-en-1-yl)-3-methyl-5-pentylfuran (15m)[11]



A solution of CBr_4 (0.047 g, 0.14 mmol) in CH_2Cl_2 (1.0 mL) was cooled to 0°C and PPh_3 (0.037 g, 0.14 mmol) added. The mixture was stirred for 10 minutes, then a solution of 1,2-dioxine **14m** (0.040 g, 0.13 mmol) in CH_2Cl_2 (1.0 mL) added and the solution brought to r.t. The resulting mixture was allowed to stir for 40 h, then solvents removed *in vacuo*. The crude product was purified by column chromatography (99:1 hexanes/ethyl acetate, R_f = 0.42) affording the furan as a colourless oil (0.025 g, 0.09 mmol, 66%). **δH** (400 MHz, $CDCl_3$): 5.85 – 5.75 (1H, m), 5.72 (1H, s), 5.00 – 4.90 (2H, m), 2.51 (2H, t, *J* = 7.6 Hz), 2.48 (2H, t, *J* = 7.6 Hz), 2.06 – 2.01 (2H, m), 1.89 (3H, s), 1.61 – 1.52 (4H, m), 1.37 – 1.25 (14H, m), 0.91 – 0.88 (3H, m). **δC** (100 MHz, $CDCl_3$): 153.6, 149.5, 139.3, 114.2, 113.9, 107.7, 33.9, 33.9, 31.5, 29.8, 29.5, 29.4, 29.3, 29.2, 29.0, 27.1, 26.0, 22.5, 14.1, 10.0. **IR** (ν_{max}, cm^{-1}): 1640, 1576, 1463, 1378. **MS (**m/z): Found 291.2680 ($C_{20}H_{35}O^+$ requires 291.2682).

Methyl 11-(3-methyl-5-pentylfuran-2-yl)undecanoate (1e)



A solution of **15m** (0.020 g, 0.07 mmol) and Grubbs 2nd generation catalyst (0.006 g, 0.01 mmol, 10 mol%) in toluene (5 mL) was degassed with ethylene for 30 min, then maintained under an atmosphere of nitrogen. Methyl acrylate (0.062 mL, 0.75 mmol) was added, and the resulting mixture was heated to 100 °C for 4 hours after which point TLC monitoring showed complete consumption of the starting furan. After this period the mixture was cooled, PtO_2 (0.002 g, 0.01 mmol, 10 mol%) was added and the mixture degassed with hydrogen. The mixture was stirred for 15 h at room temperature under a hydrogen atmosphere, then solvents were removed *in vacuo* and the crude product adsorbed onto silica. Purification by column chromatography (19:1 hexanes/ethyl acetate, R_f = 0.36) afforded the methyl ester of F_5 as a colourless oil (0.024 mg, 0.07 mmol, 98%). **δH** (400 MHz, $CDCl_3$): 5.76 (1H, s), 3.66 (3H, s), 2.54 (2H, t, *J* = 7.6Hz), 2.51 (2H, t, *J* = 7.6 Hz), 2.30 (2H, t, *J* = 8.4Hz), 1.87 (3H, s), 1.65 – 1.52 (7H, m), 1.35 – 1.24 (15H, m), 0.89 (3H, t, *J* = 7.2Hz). **δC** (100 MHz, $CDCl_3$): 174.4, 153.5, 149.4, 113.8, 107.6, 51.4, 34.1, 31.4, 29.5, 29.4, 29.4, 29.2, 29.2, 29.2, 28.8, 28.0, 27.9, 25.9, 25.0, 22.4, 14.0, 9.9. **IR** (ν_{max}, cm^{-1}): 1743, 1638, 1576, 1462, 1436. **MS,** m/z Found (373.2712, $C_{22}H_38O_3Na^+$ requires 373.2713).

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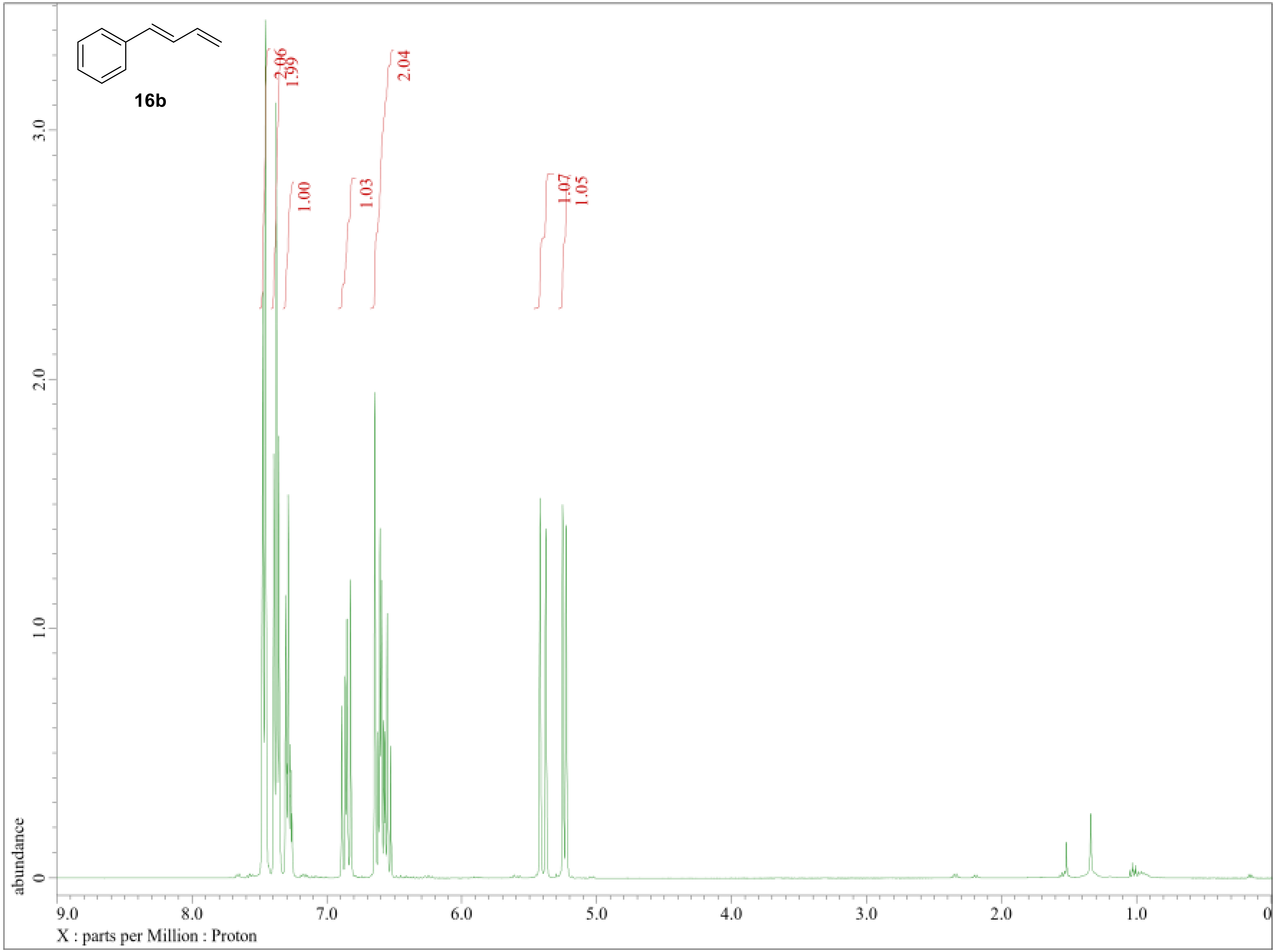
[11] D. W. Knight and A. W. T. Smith, *Tetrahedron* 2015, **71**, 7436.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1.00
1.03
2.04
1.07
1.05
3.0
2.0
1.0
0
abundance
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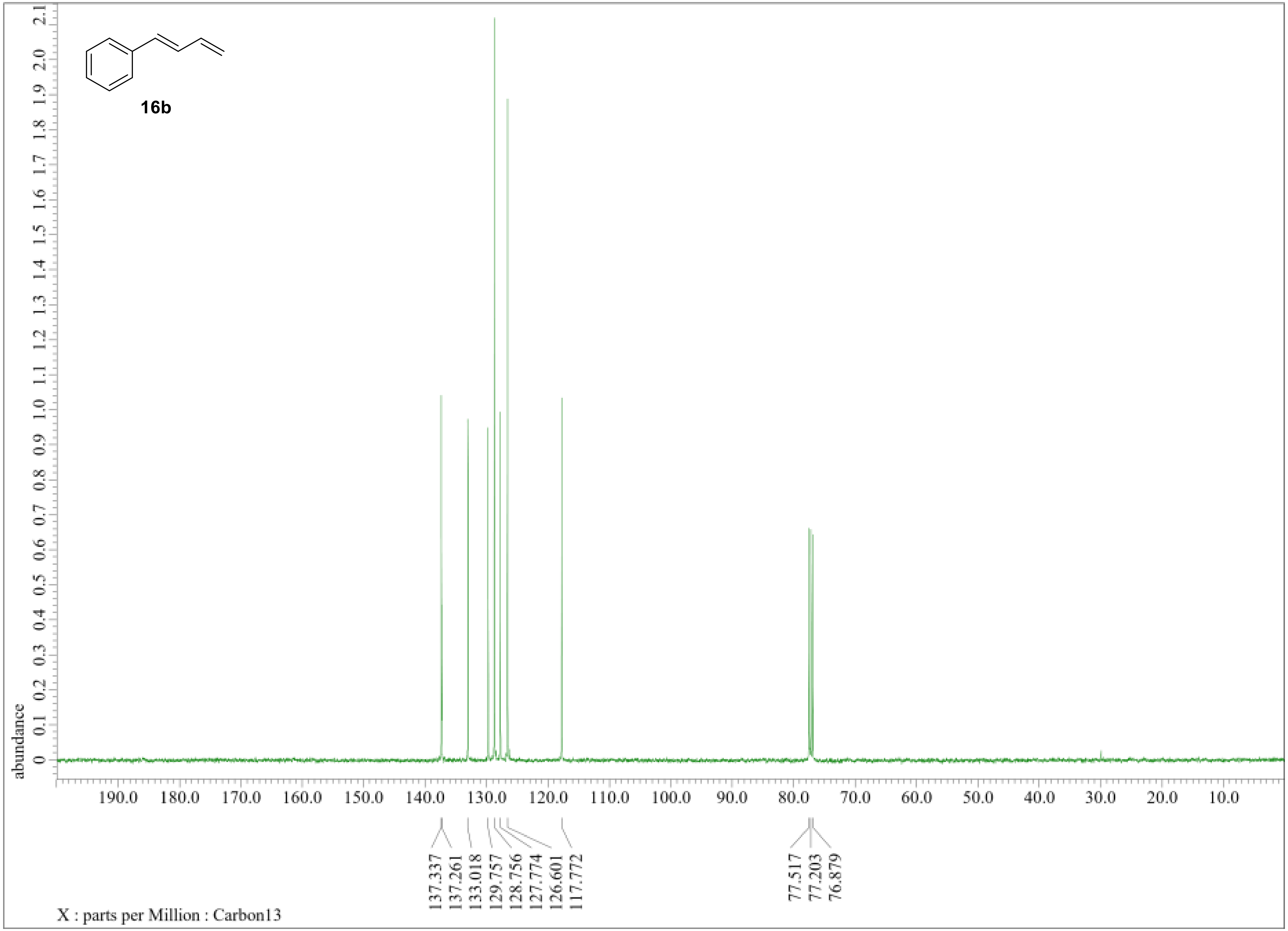
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


16b
abundance
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0.4
0.5
0.6
0.7
0.8
0.9
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1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
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127.774
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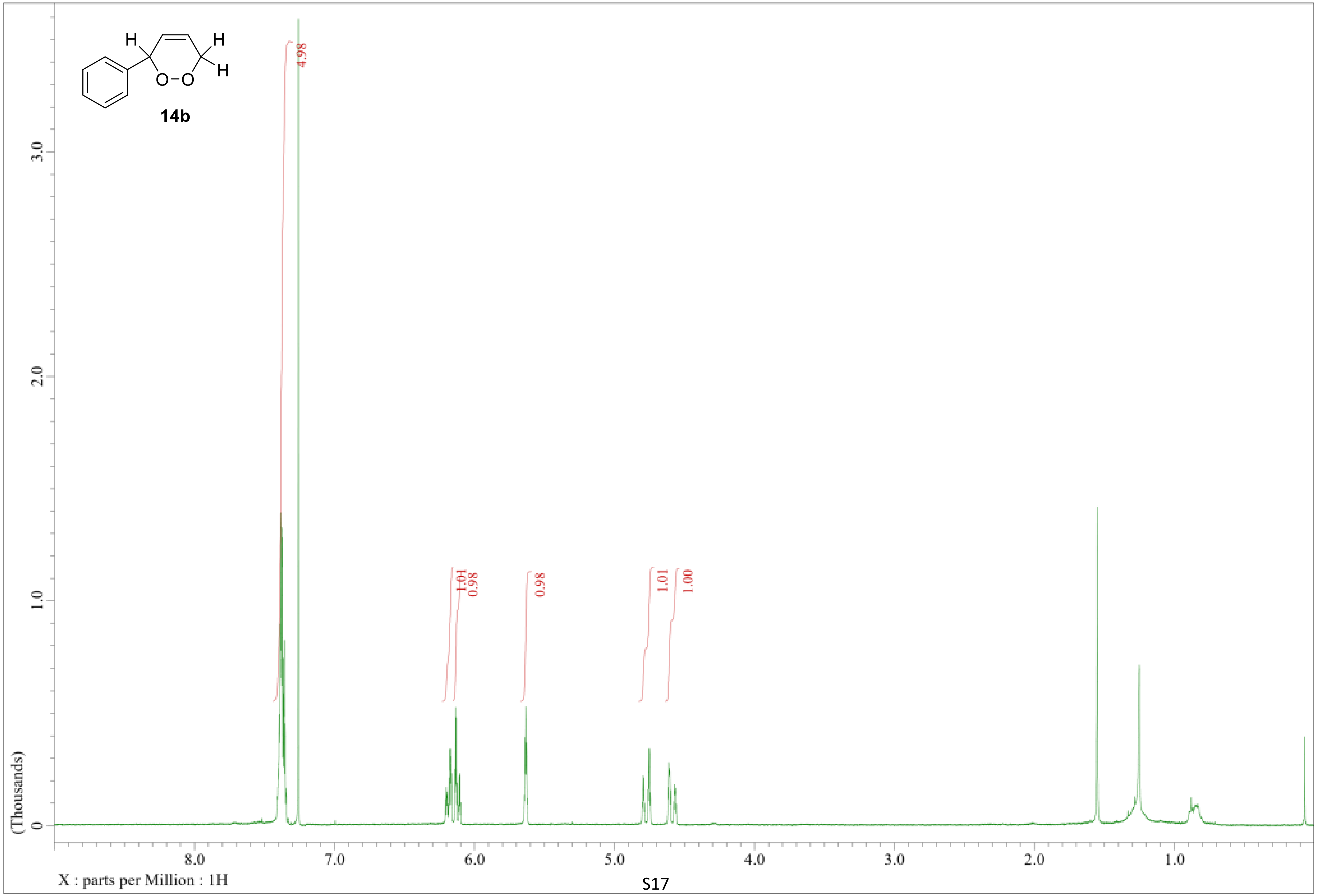
77.517
77.203
76.879
X : parts per Million : Carbon13


H
H
H
O–O
14b
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1.01
0.98
0.98
1.01
1.00
3.0
2.0
1.0
0
(Thousands)
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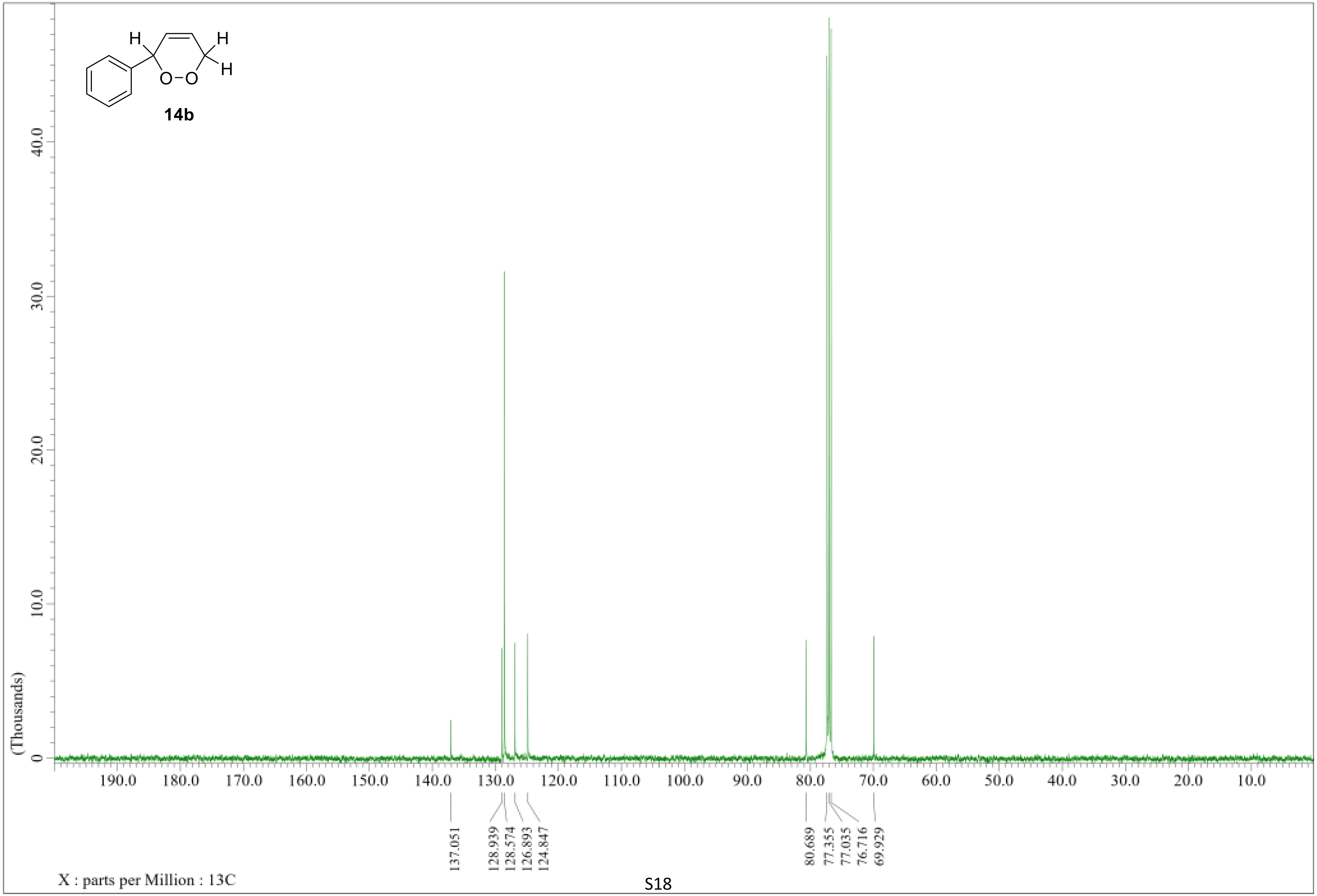
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H


H
H
H
O–O
14b
(Thousands)
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10.0
0
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180.0
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
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126.893
124.847
80.689
77.355
77.035
76.716
69.929
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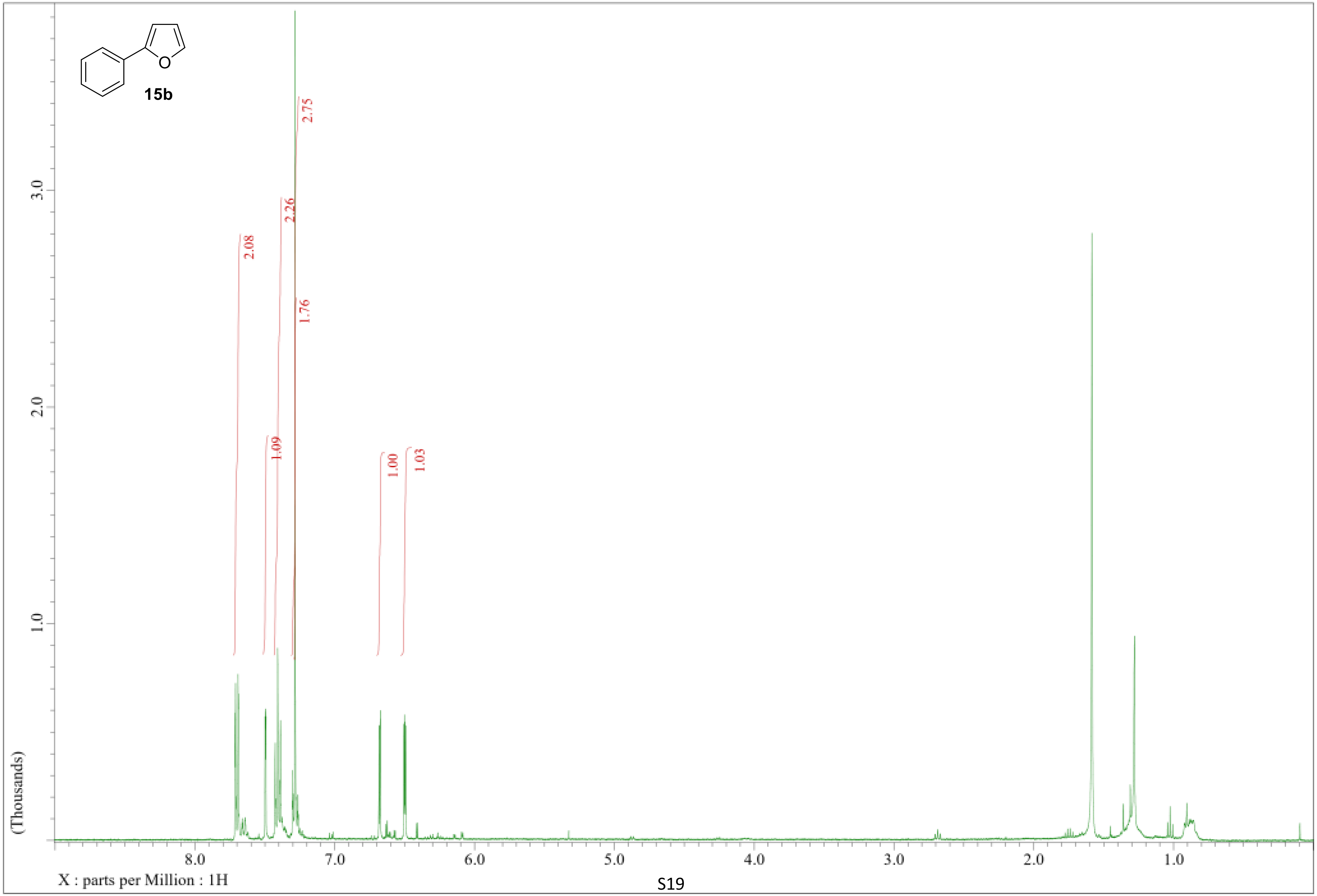
O
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1.76
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1.03
3.0
2.0
1.0
(Thousands)
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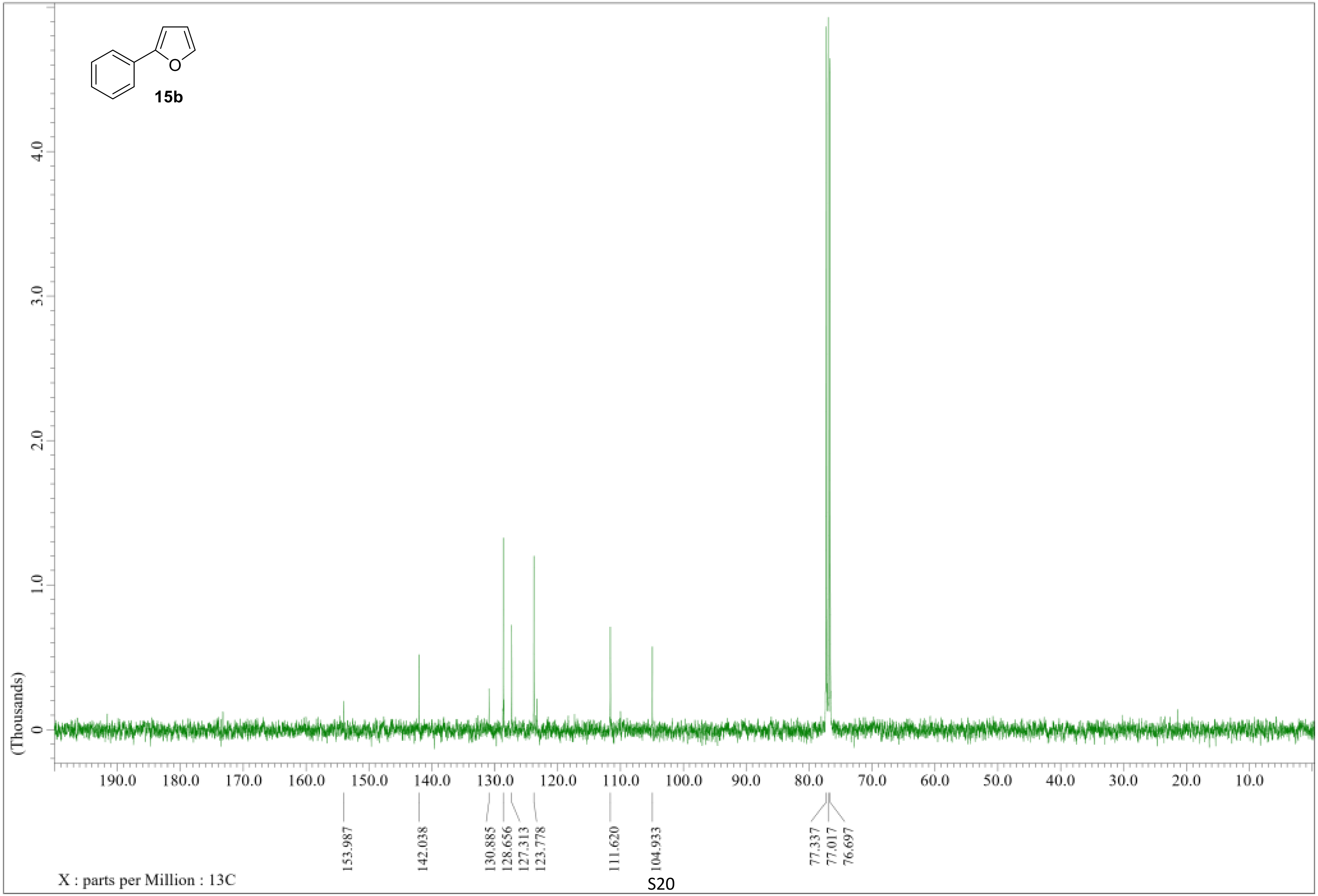
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H


15b
O
(Thousands)
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2.0
3.0
4.0
190.0
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
153.987
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111.620
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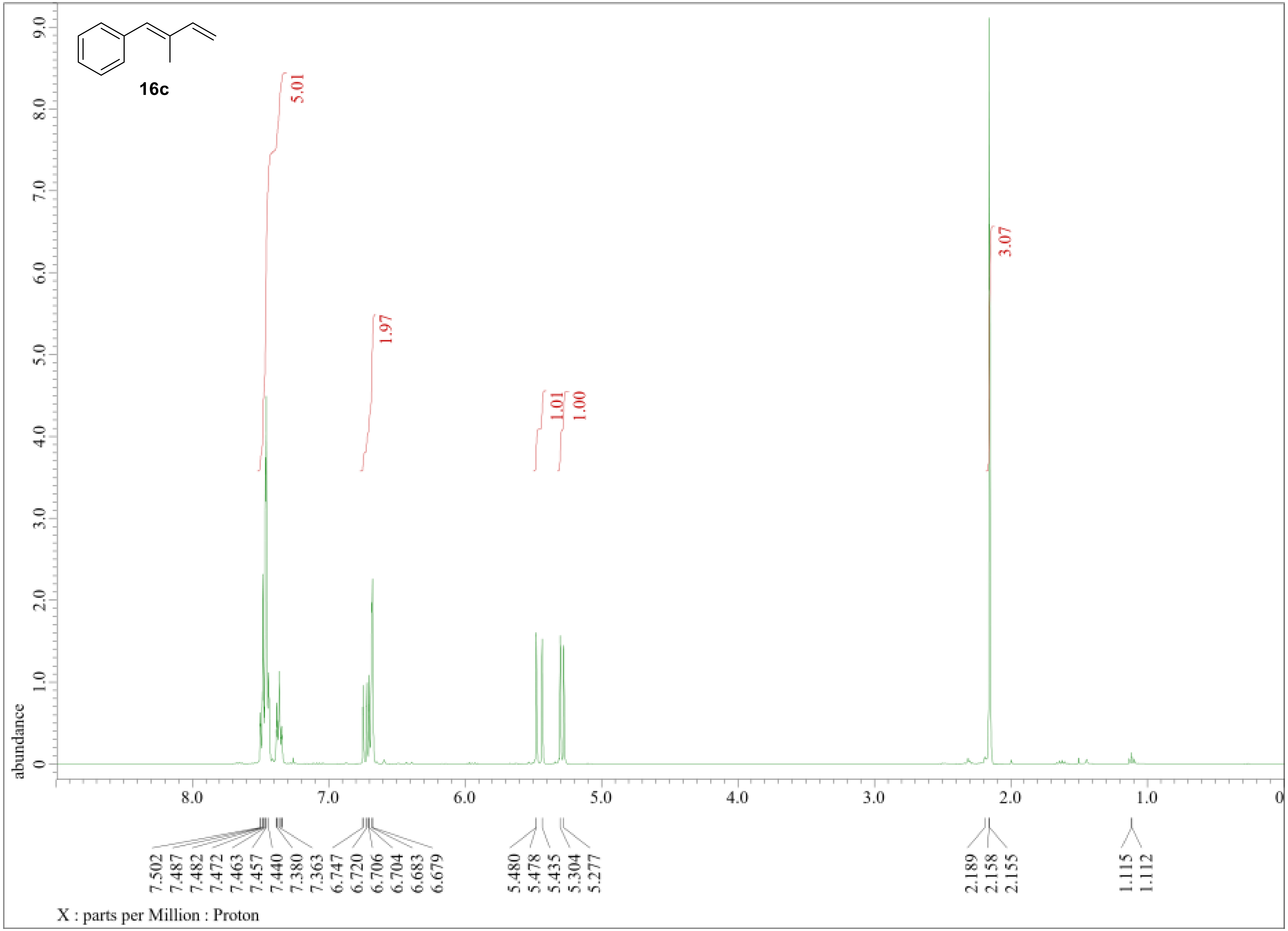
X : parts per Million : 13C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2.0
1.0
0
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1.97
1.01
1.00
3.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.502
7.487
7.482
7.472
7.463
7.457
7.440
7.380
7.363
6.747
6.720
6.706
6.704
6.683
6.679
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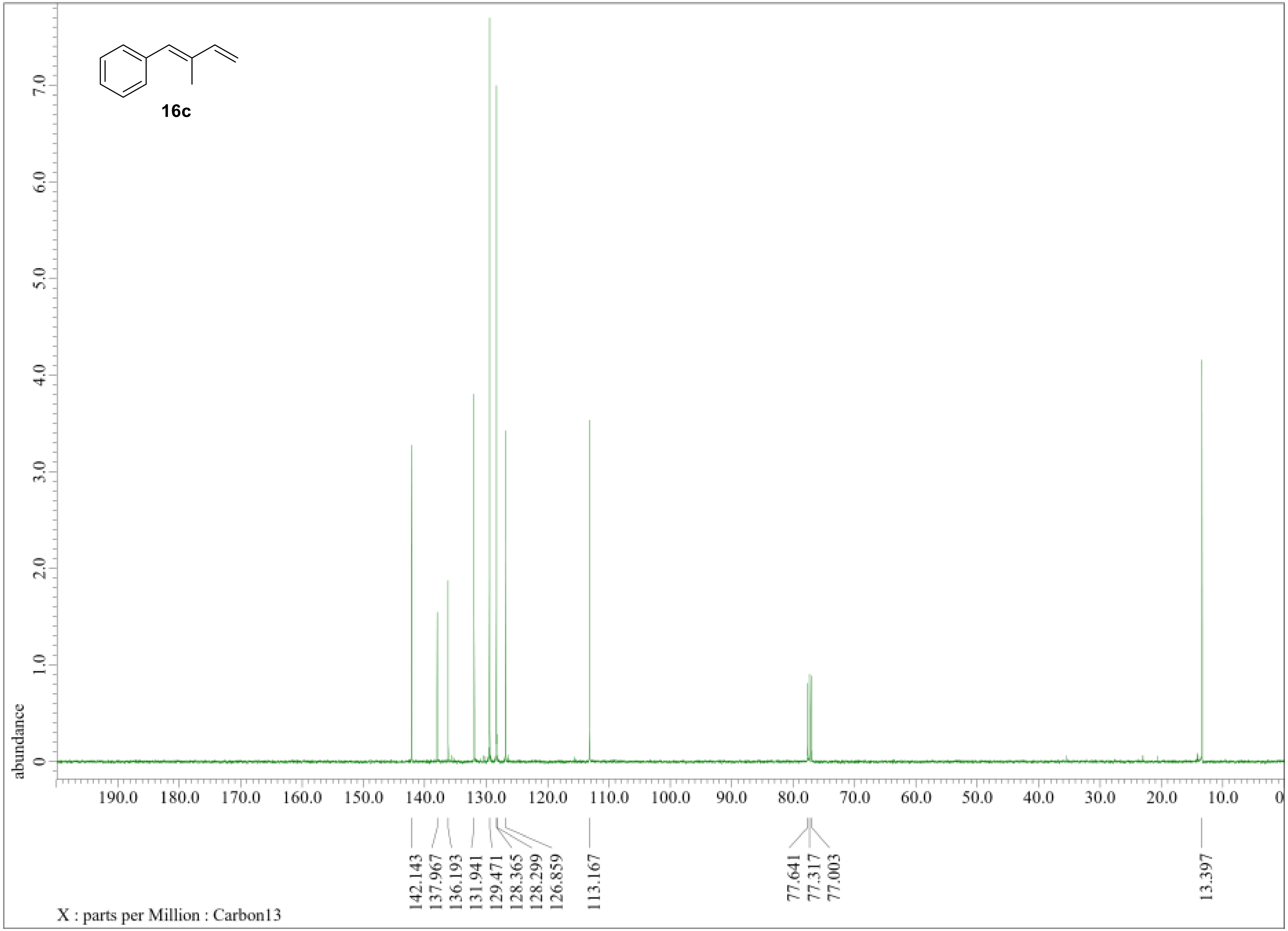
X : parts per Million : Proton


16c

abundance
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2.0
3.0
4.0
5.0
6.0
7.0
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180.0
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150.0
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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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137.967
136.193
131.941
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128.299
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113.167
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77.317
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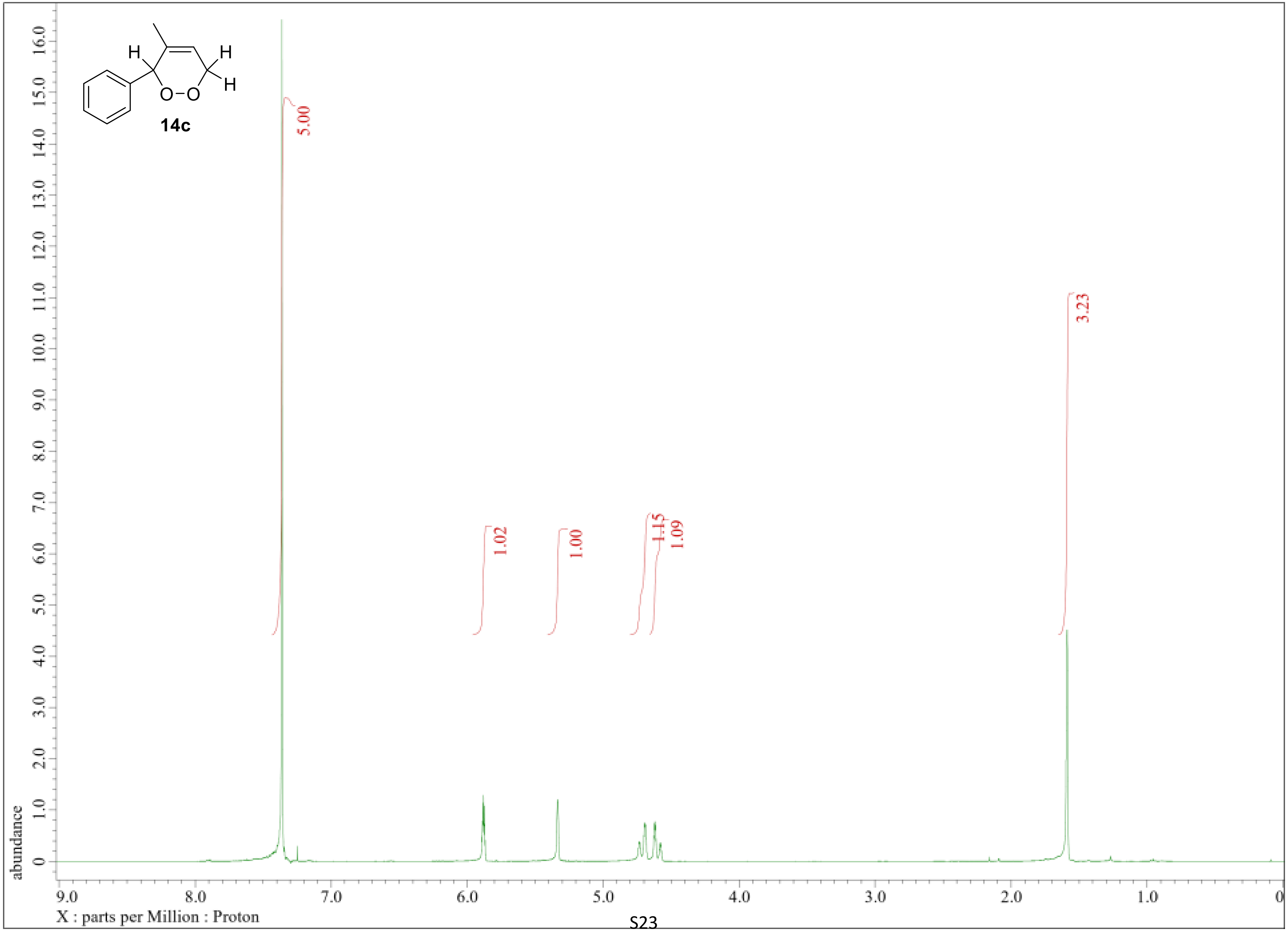
X : parts per Million : Carbon13



H
H
H
O–O
14c
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1.02
1.00
1.15
1.09
3.23
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
abundance
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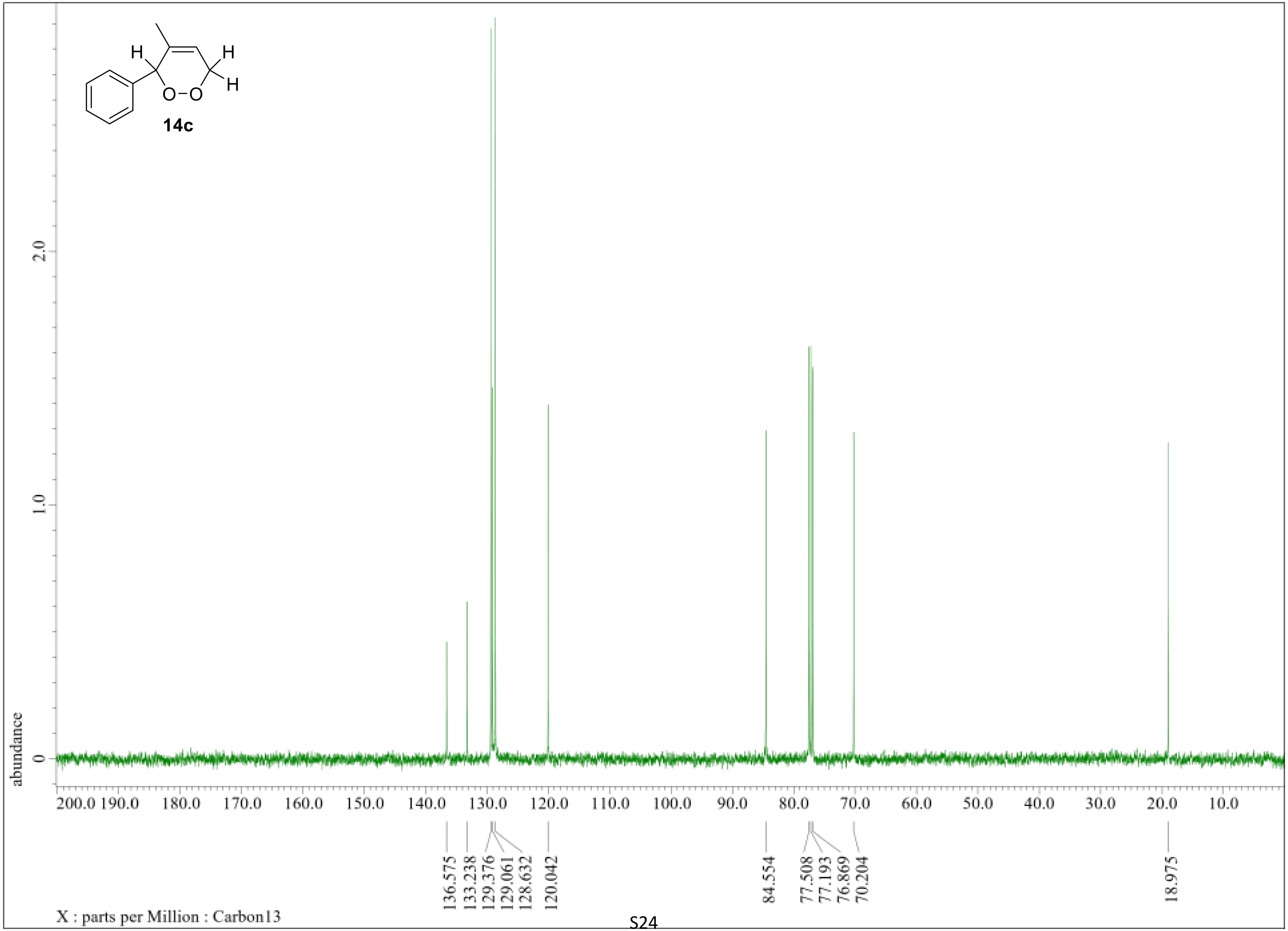
X : parts per Million : Proton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H
H
O–O
14c
abundance
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
136.575
133.238
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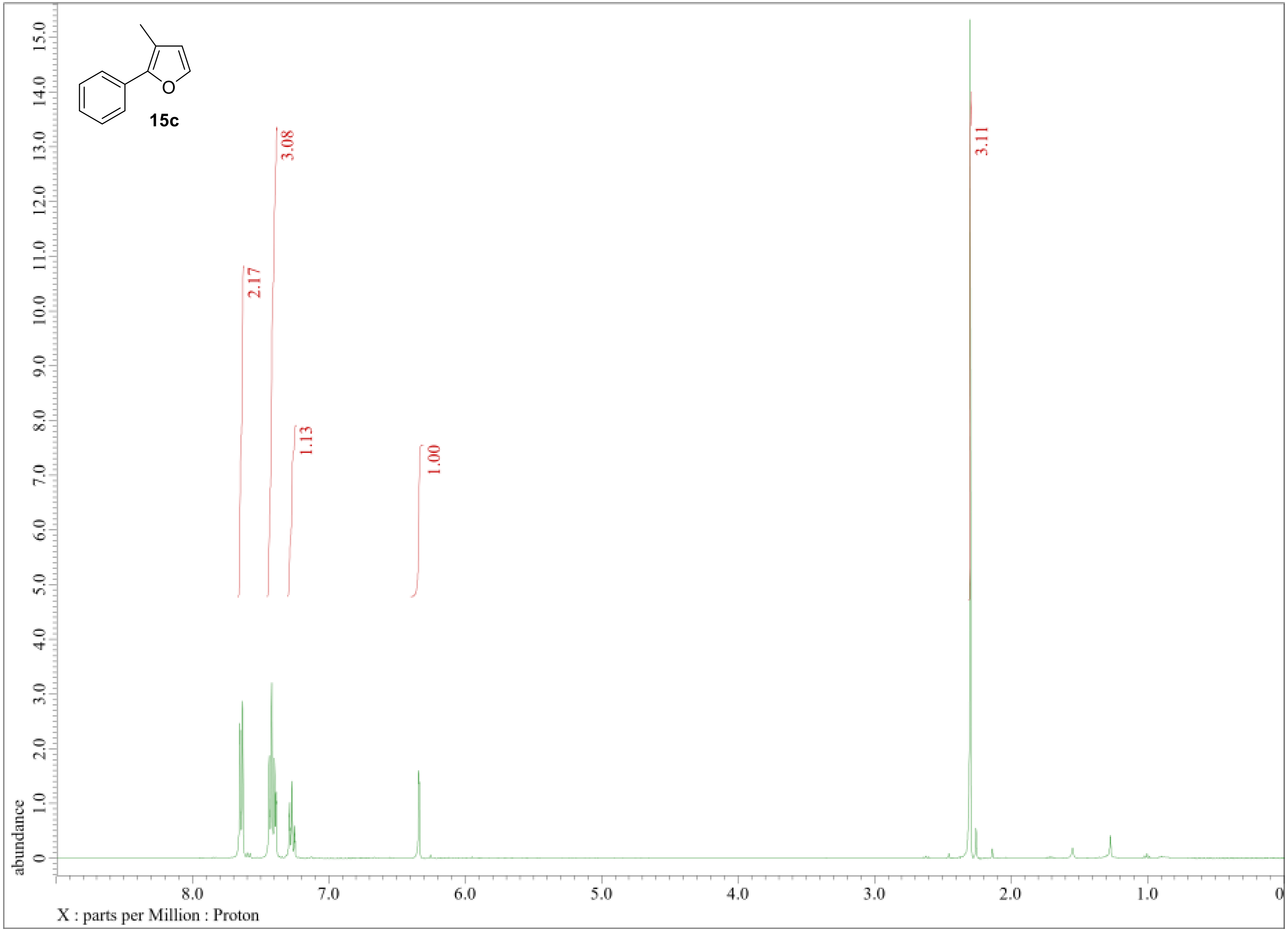
X : parts per Million : Carbon13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abundance
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3.0
2.0
1.0
0
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6.0
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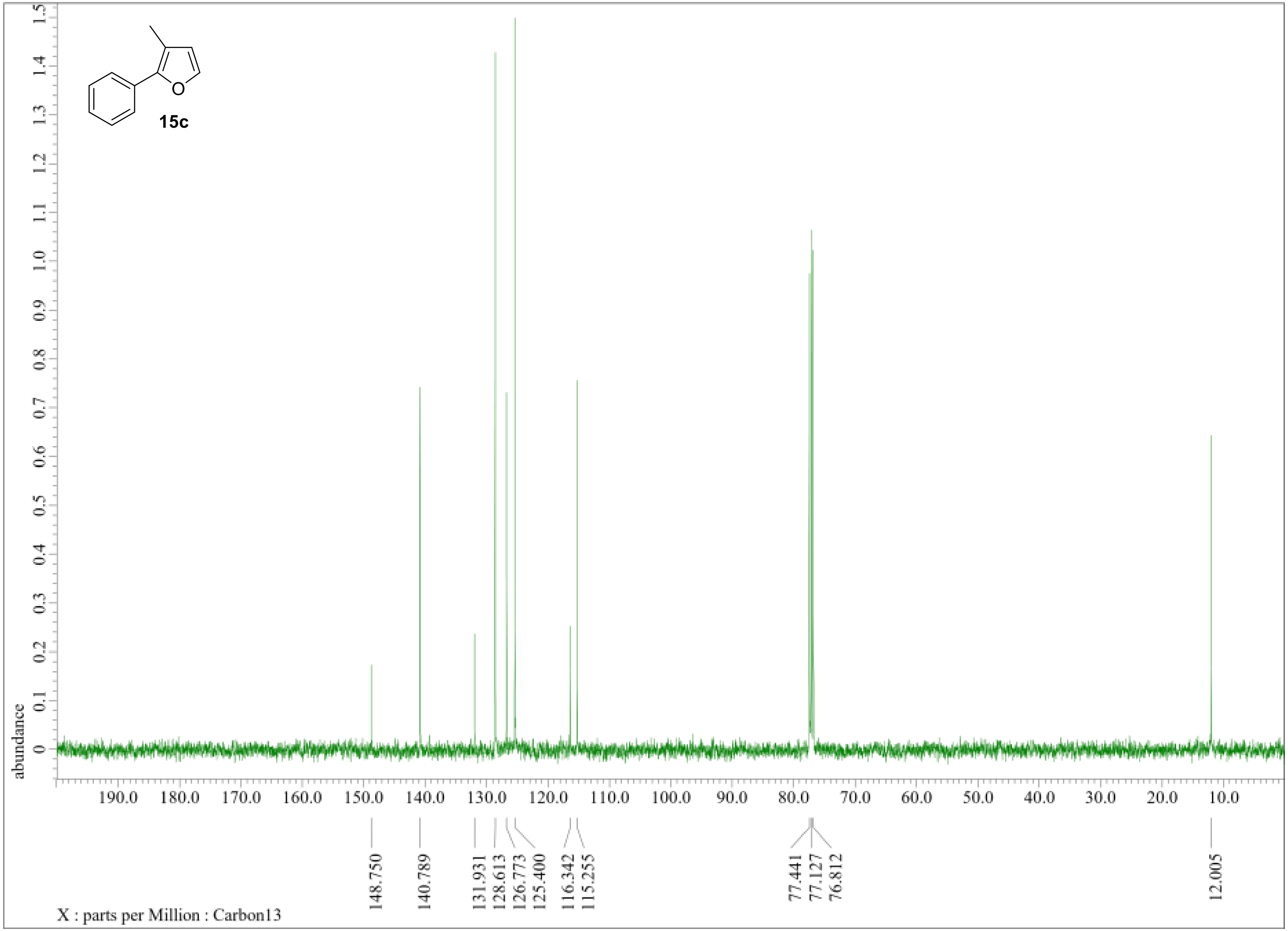
2.0
1.0
0
X : parts per Million : Proton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1.1
1.2
1.3
1.4
1.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
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140.789
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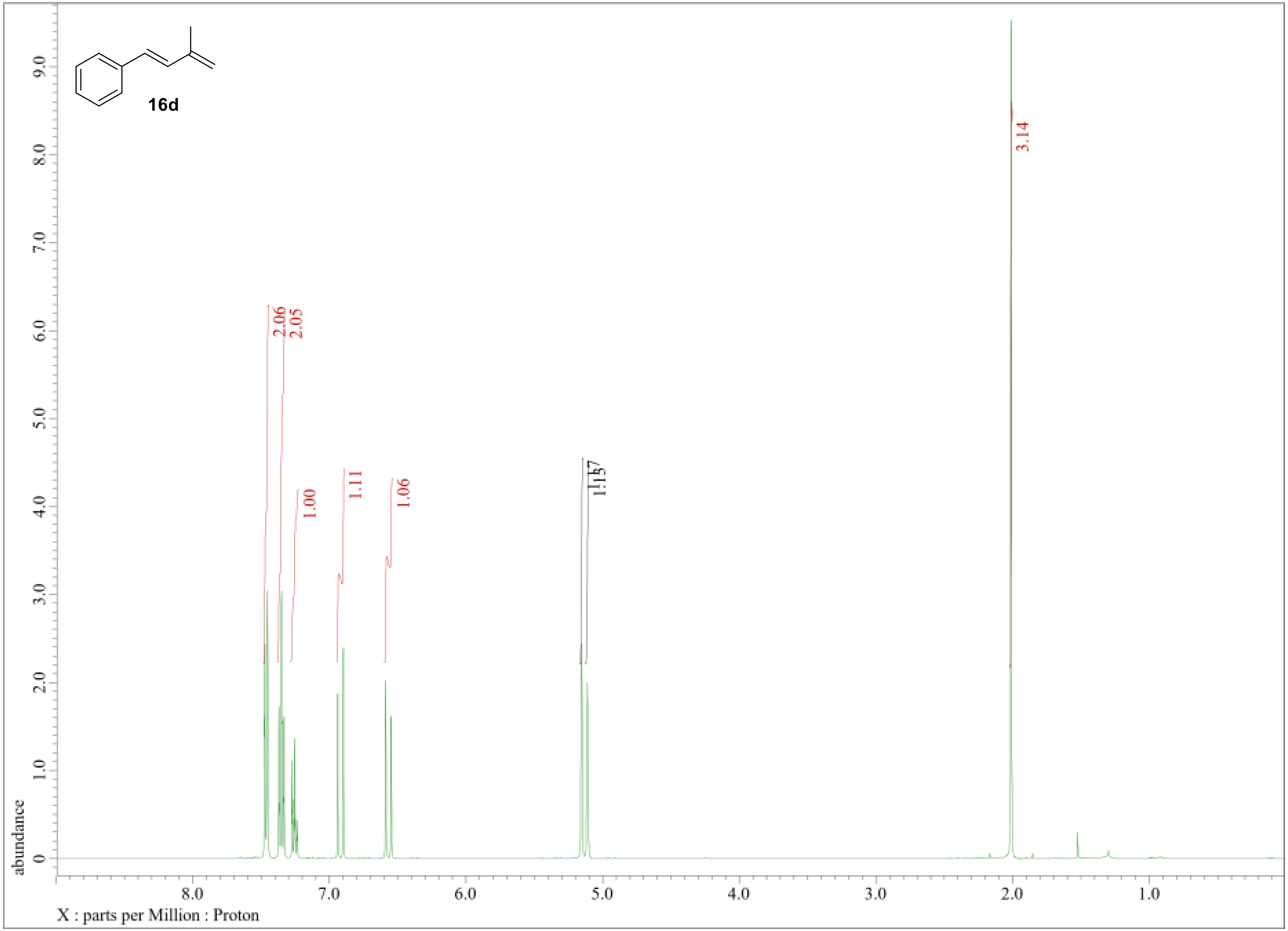
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abundance
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4.0
5.0
6.0
7.0
8.0
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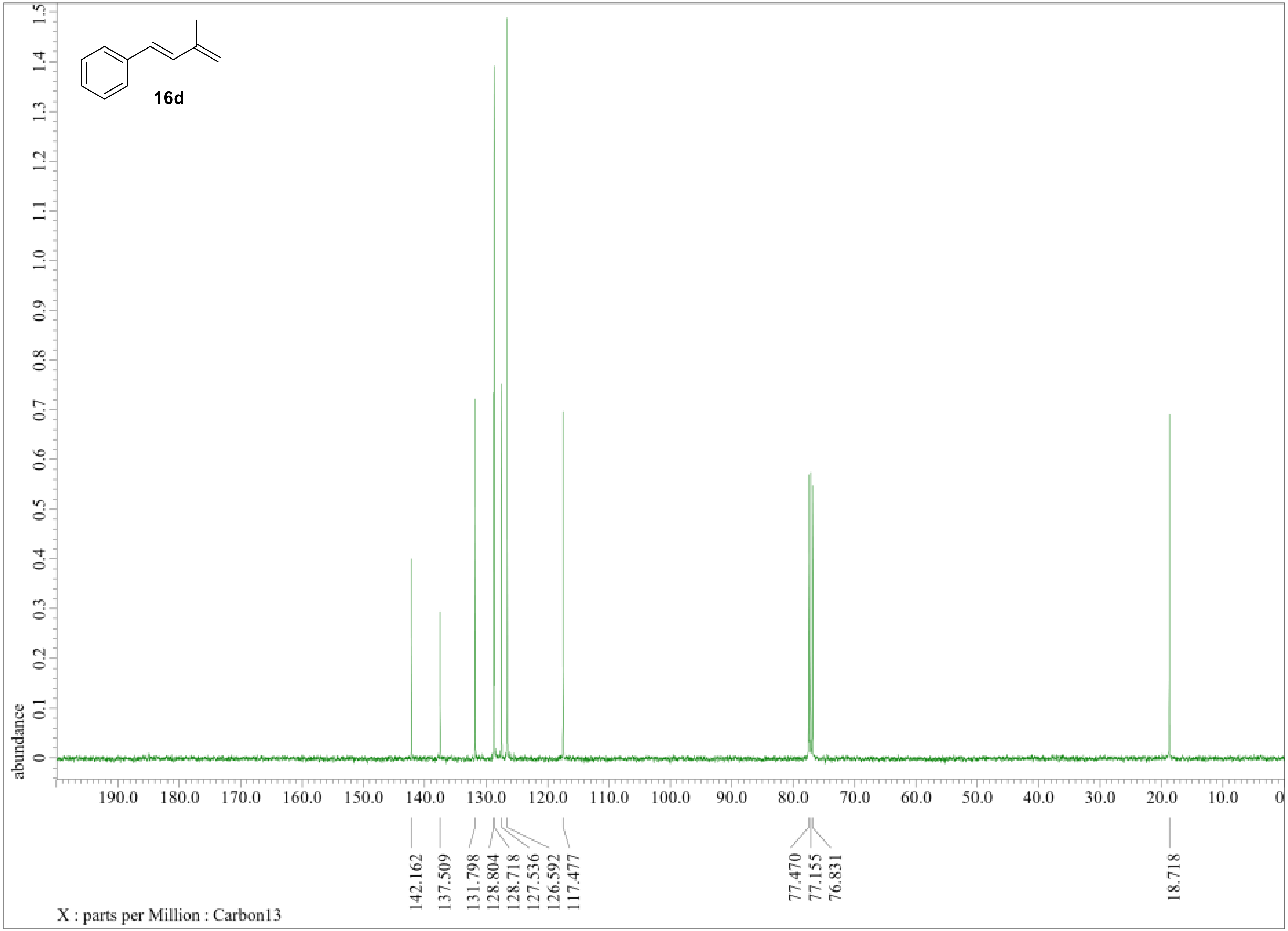
X : parts per Million : Proton


16d
abundance
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0.2
0.3
0.4
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0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
142.162
137.509
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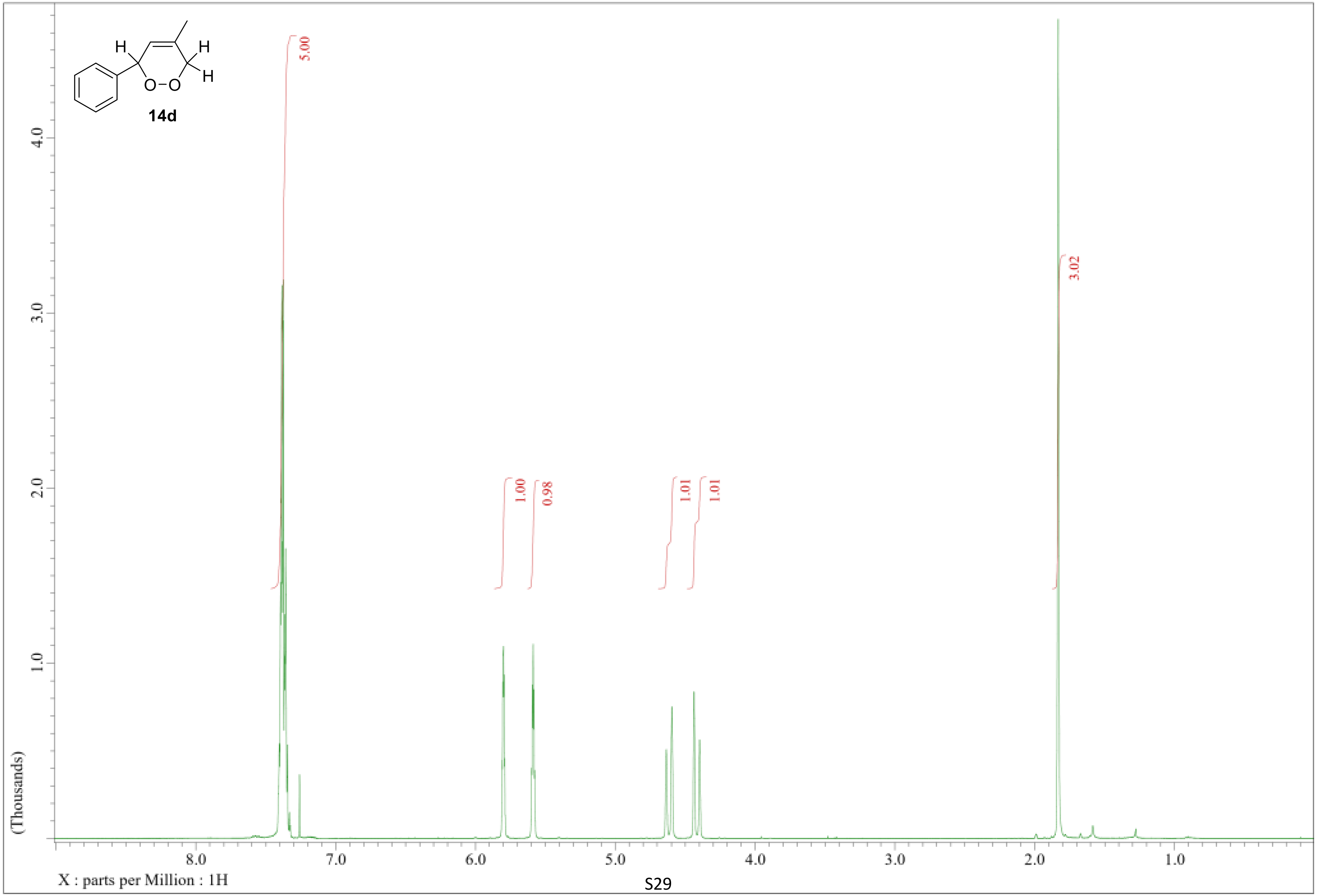
X : parts per Million : Carbon13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H
H
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1.01
3.02
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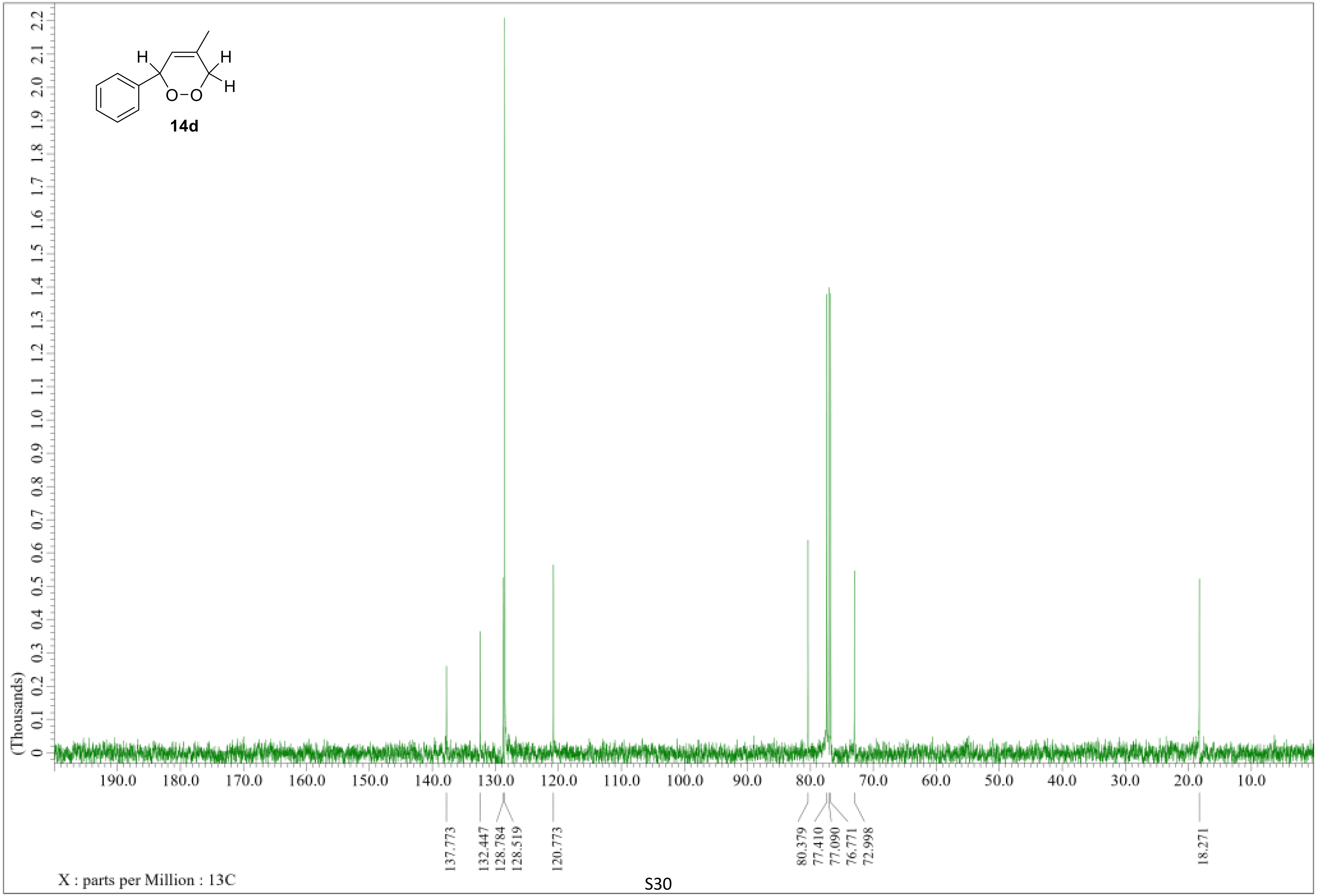
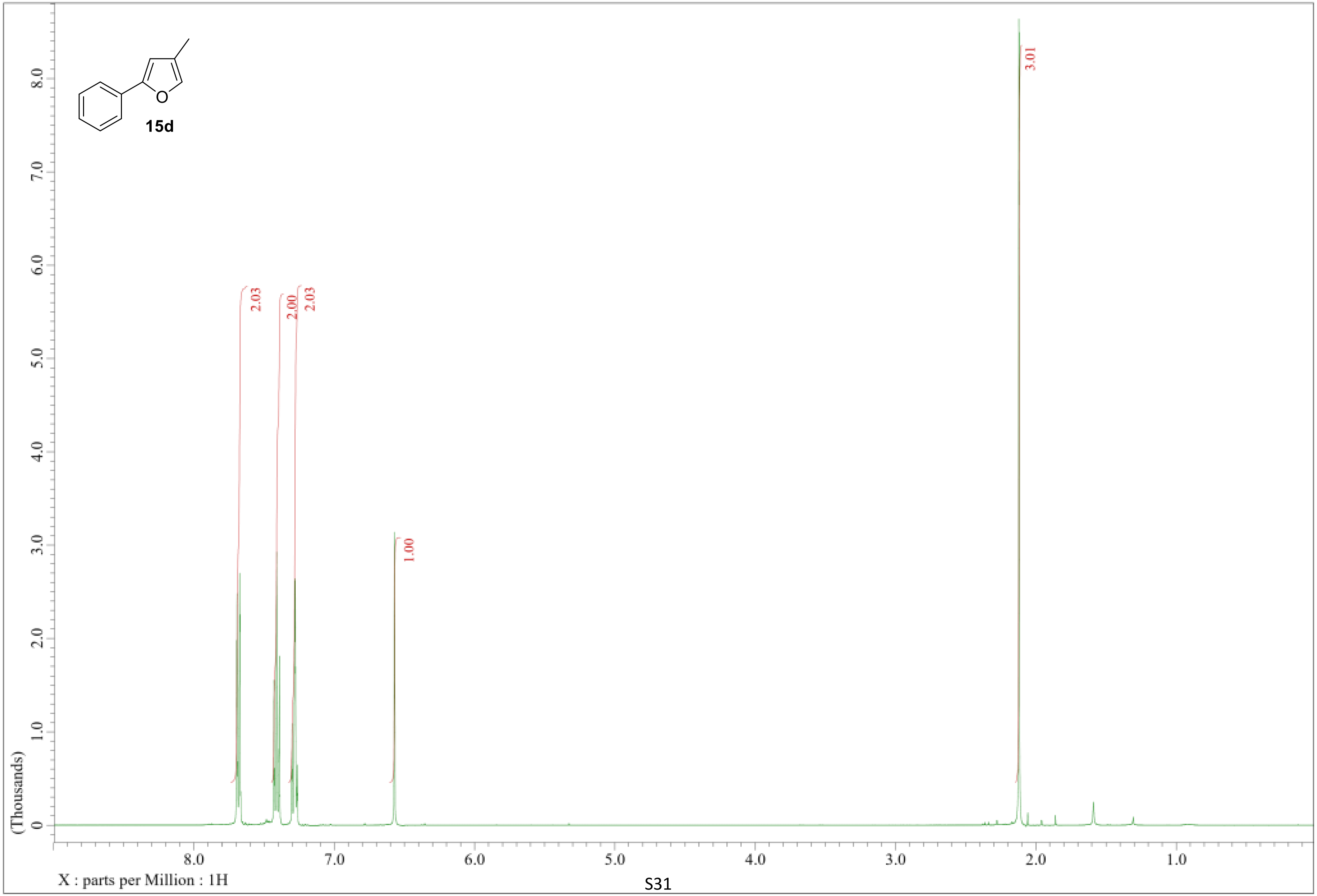
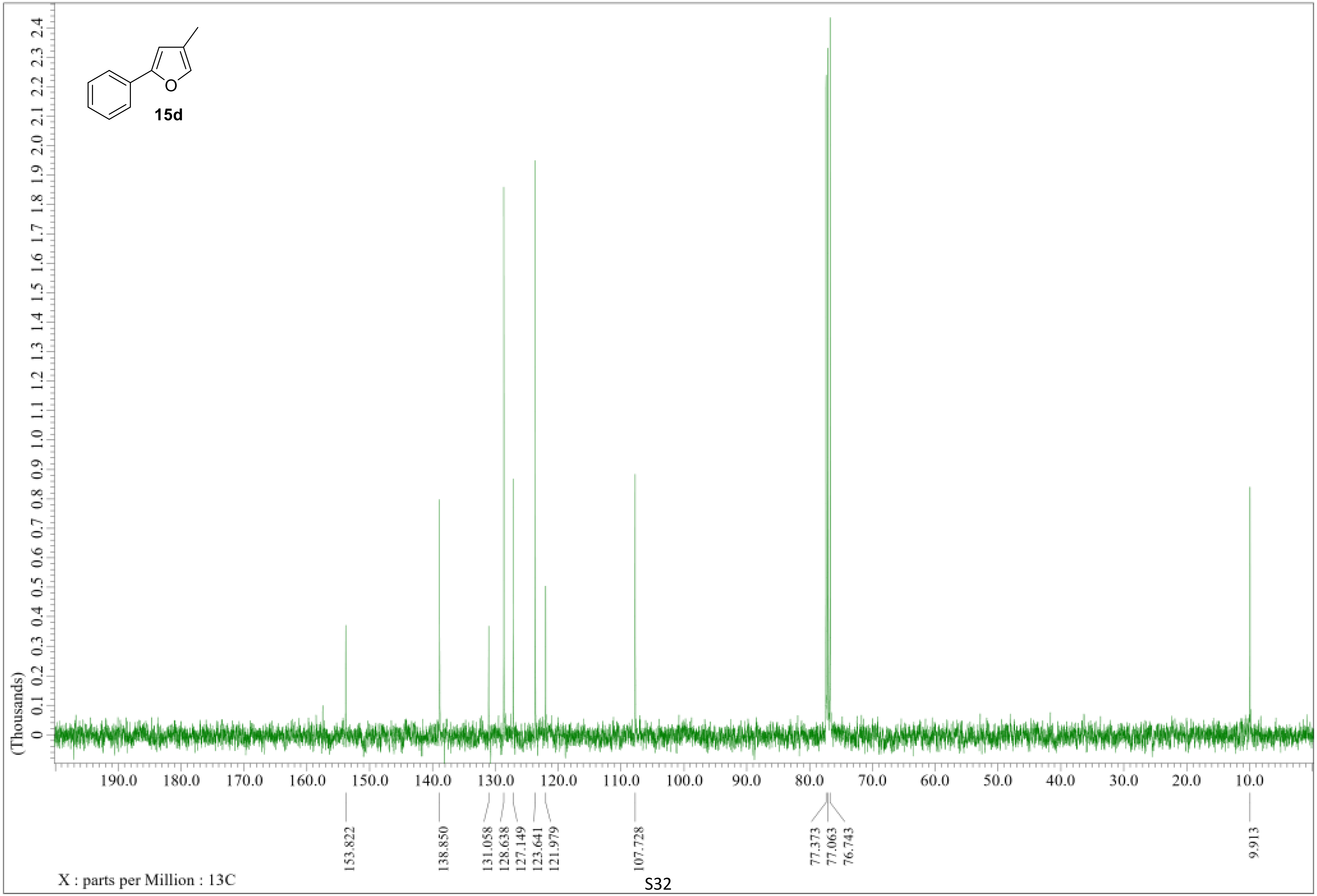
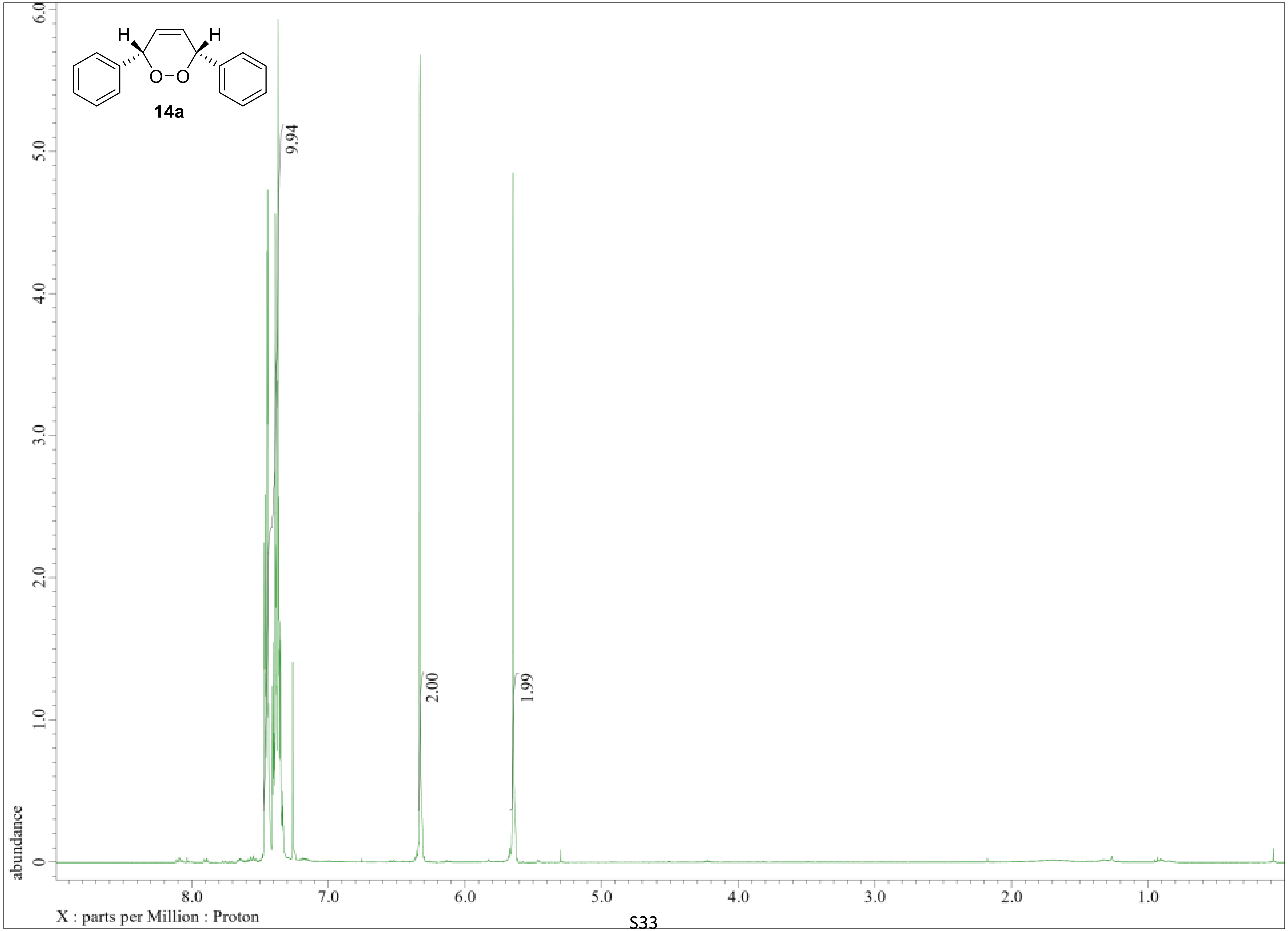
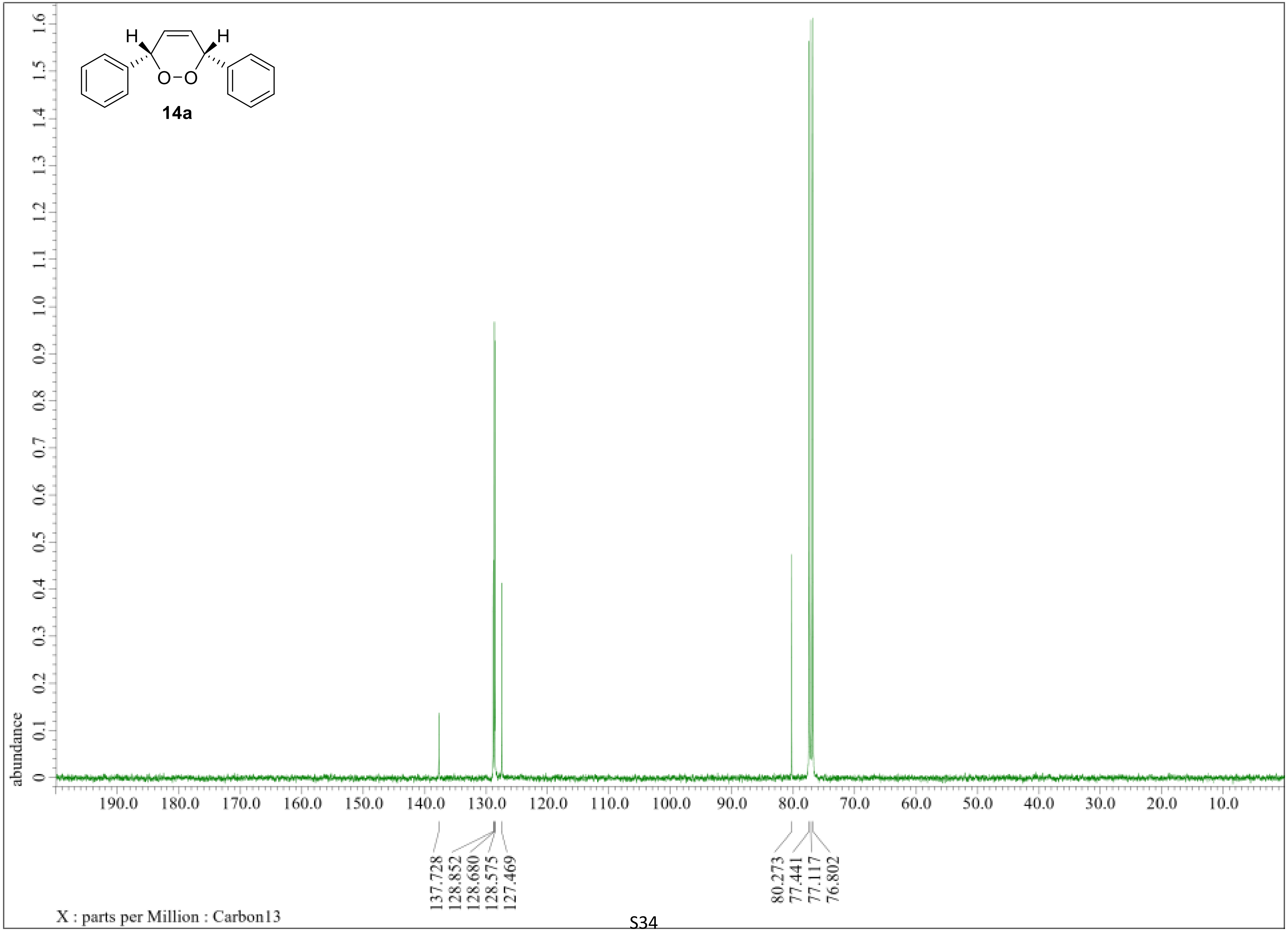
3.0
2.0
1.0
(Thousands)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H

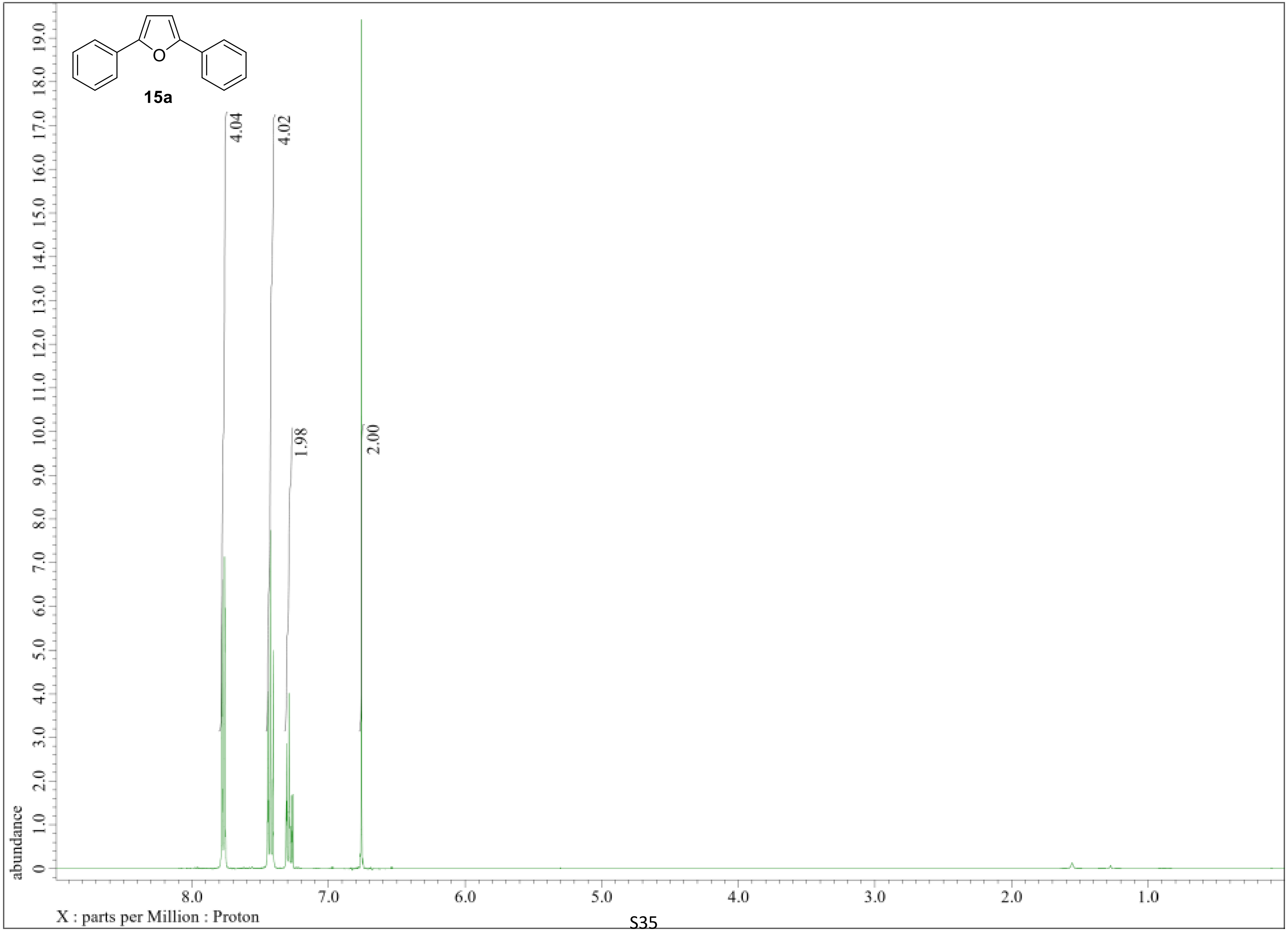

H
H
H
O–O
14d
(Thousands)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
137.773
132.447
128.784
128.519
120.773
80.379
77.410
77.090
76.771
72.998
18.271
X : parts per Million : 13C

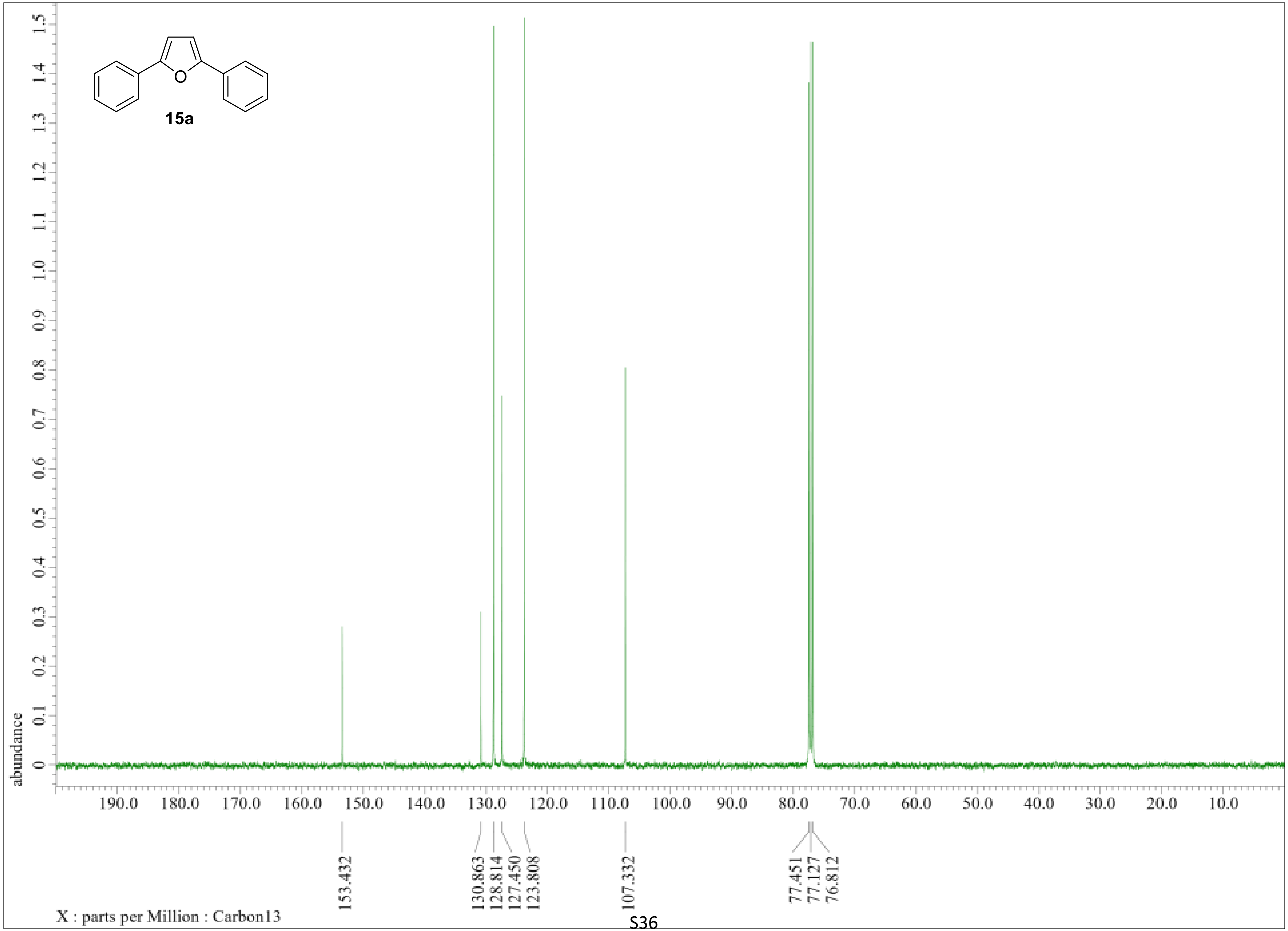

15d
O
2.03
2.00
2.03
1.00
3.01
(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H

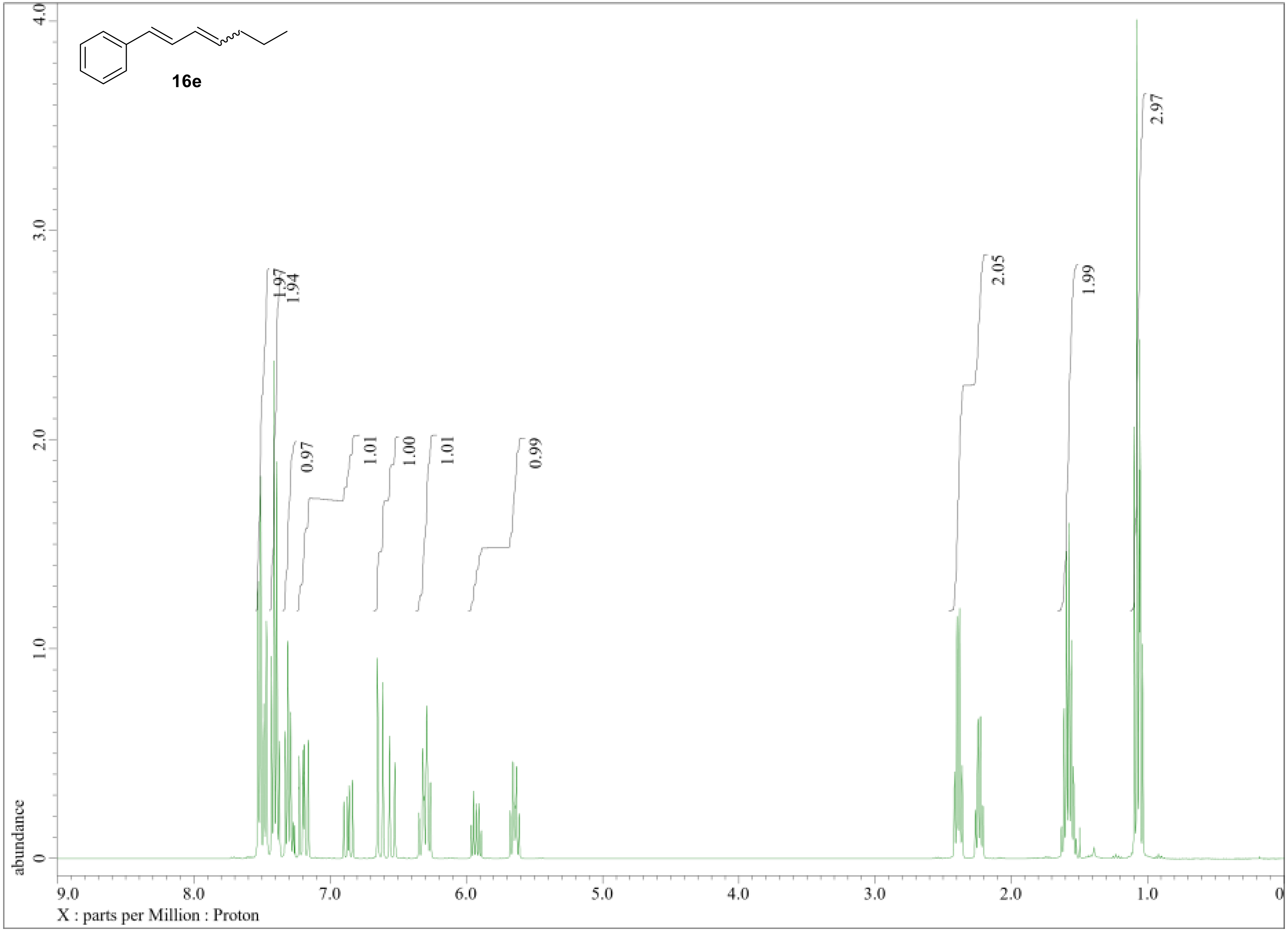

15d
(Thousands)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
153.822
138.850
131.058
128.638
127.149
123.641
121.979
107.728
77.373
77.063
76.743
9.913
X : parts per Million : 13C


14a
H
H
O
O
6.0
5.0
4.0
3.0
2.0
1.0
0
abundance
9.94
2.00
1.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton

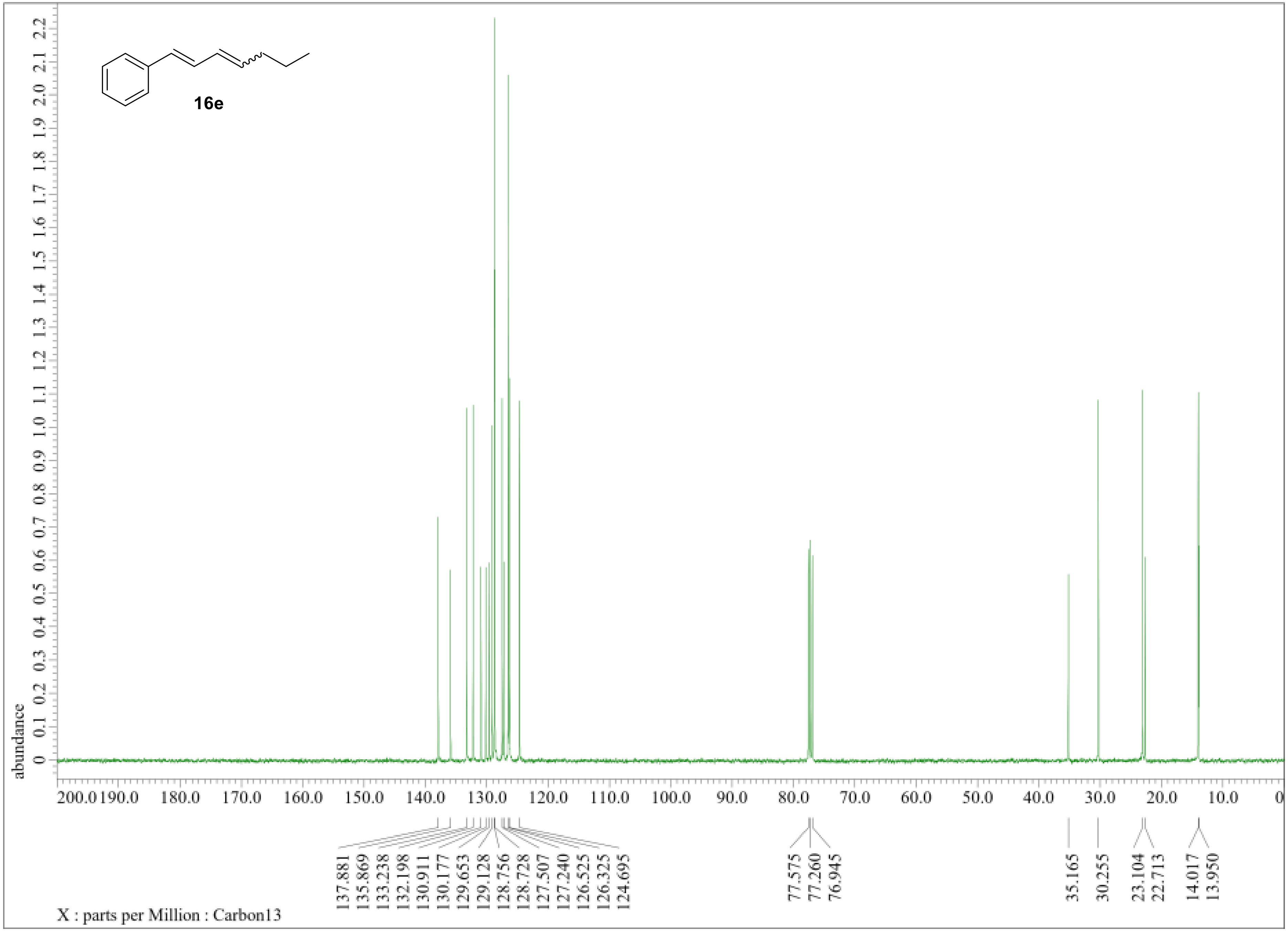

14a
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
137.728
128.852
128.680
128.575
127.469
80.273
77.441
77.117
76.802
X : parts per Million : Carbon13

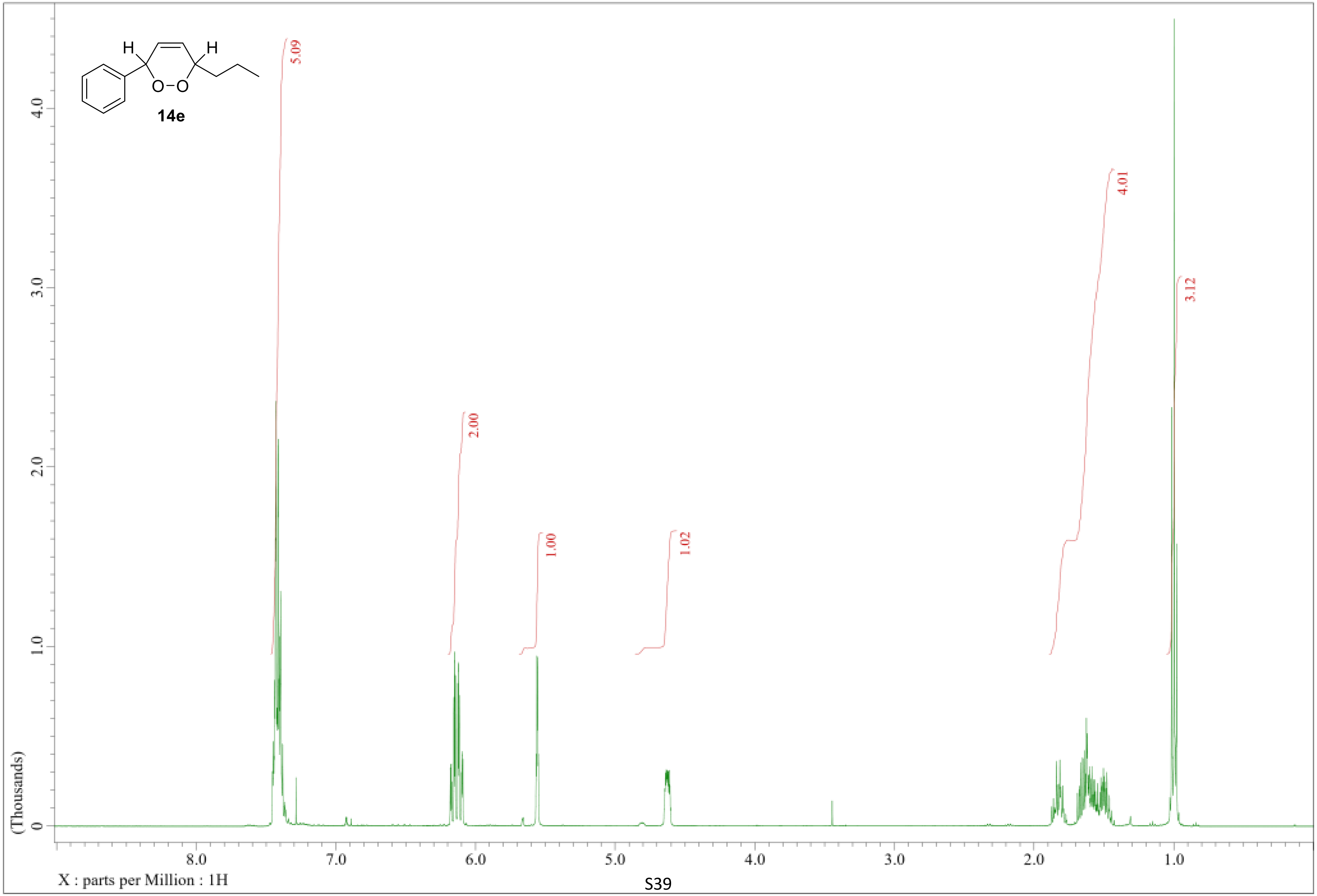

15a
O
4.04
4.02
1.98
2.00
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton

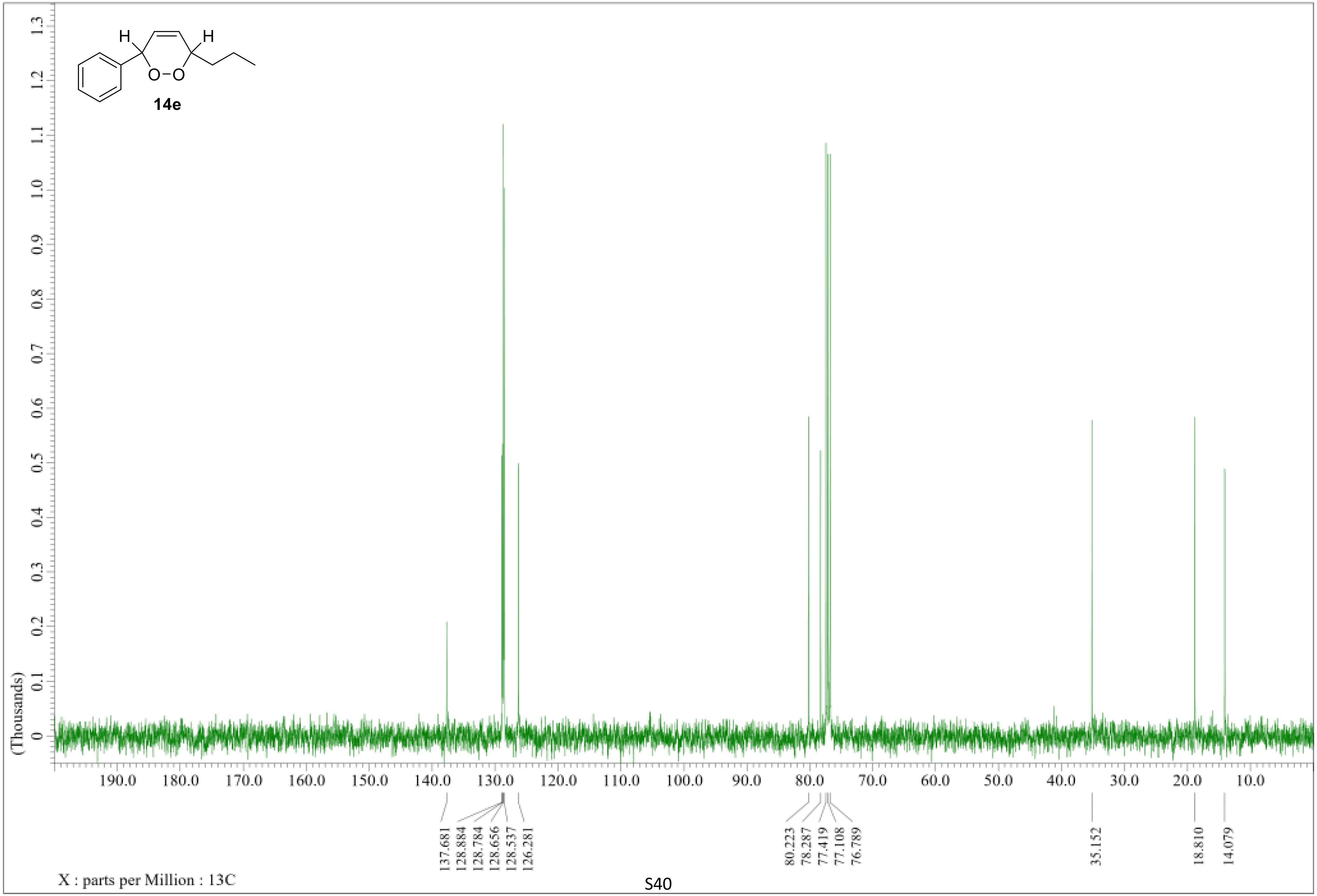

15a
O
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
153.432
130.863
128.814
127.450
123.808
107.332
77.451
77.127
76.812
X : parts per Million : Carbon13

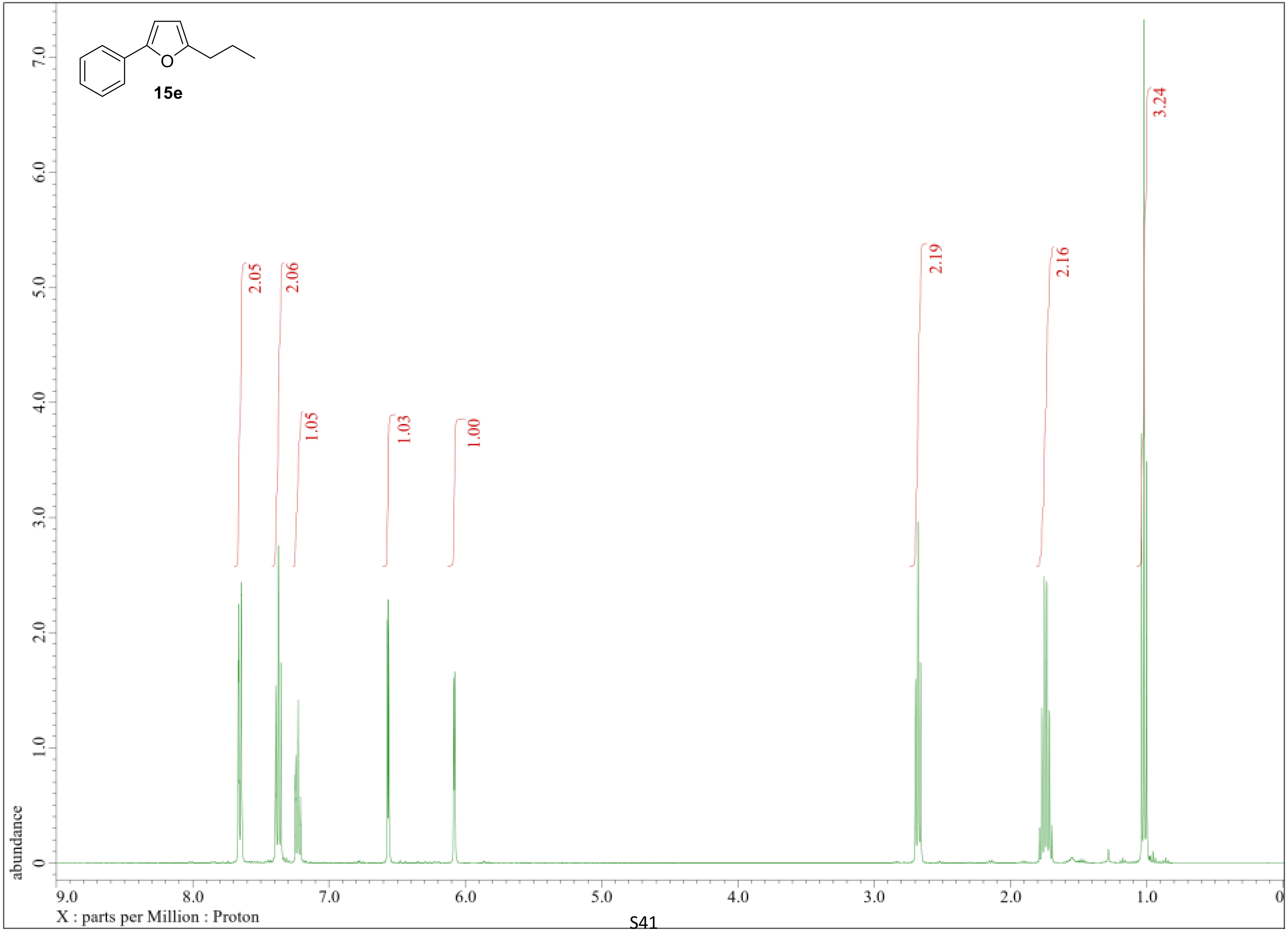

16e

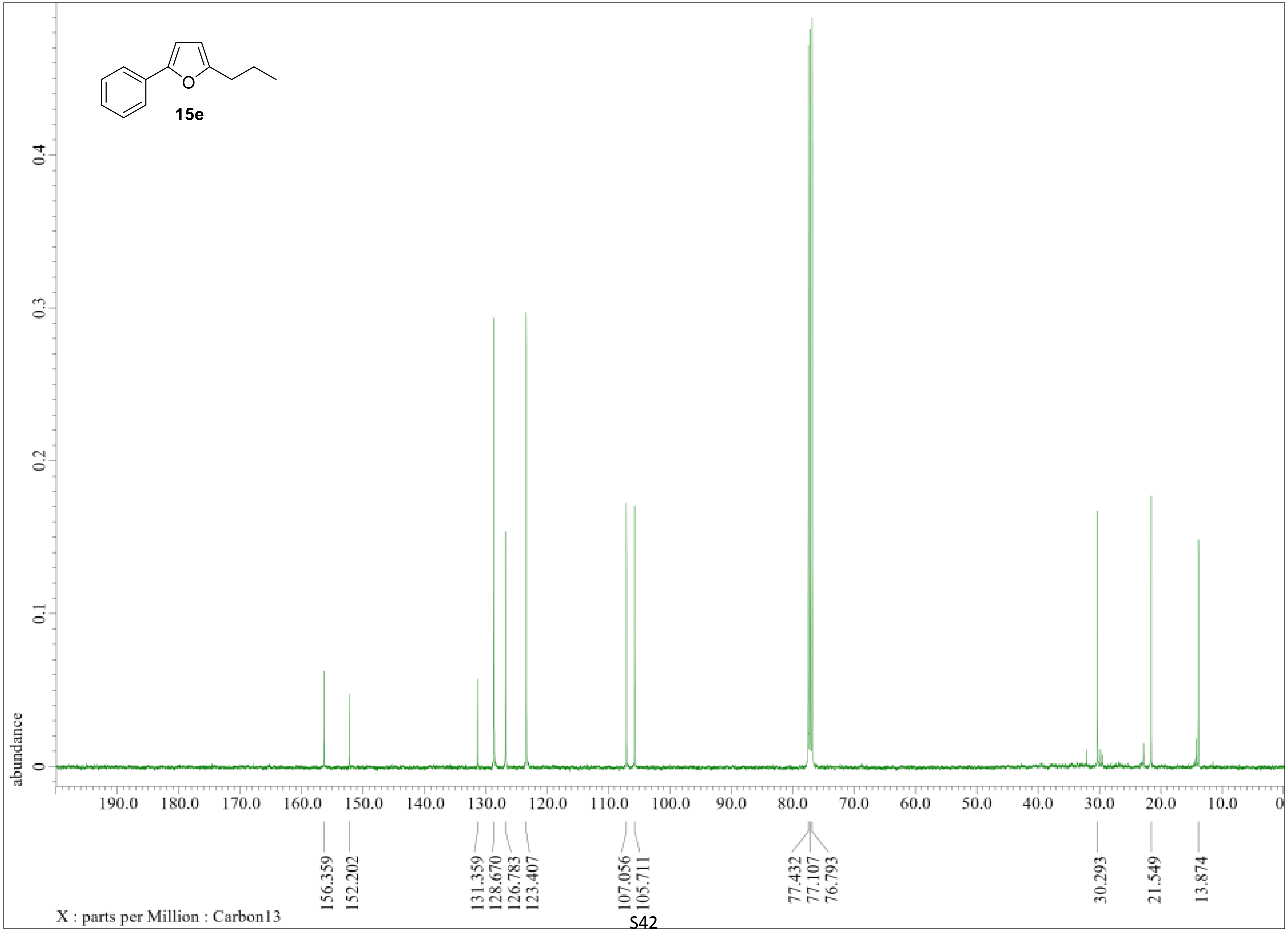
abundance
0
1.0
2.0
3.0
4.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton
1.97
1.94
0.97
1.01
1.00
1.01
0.99
2.05
1.99
2.97

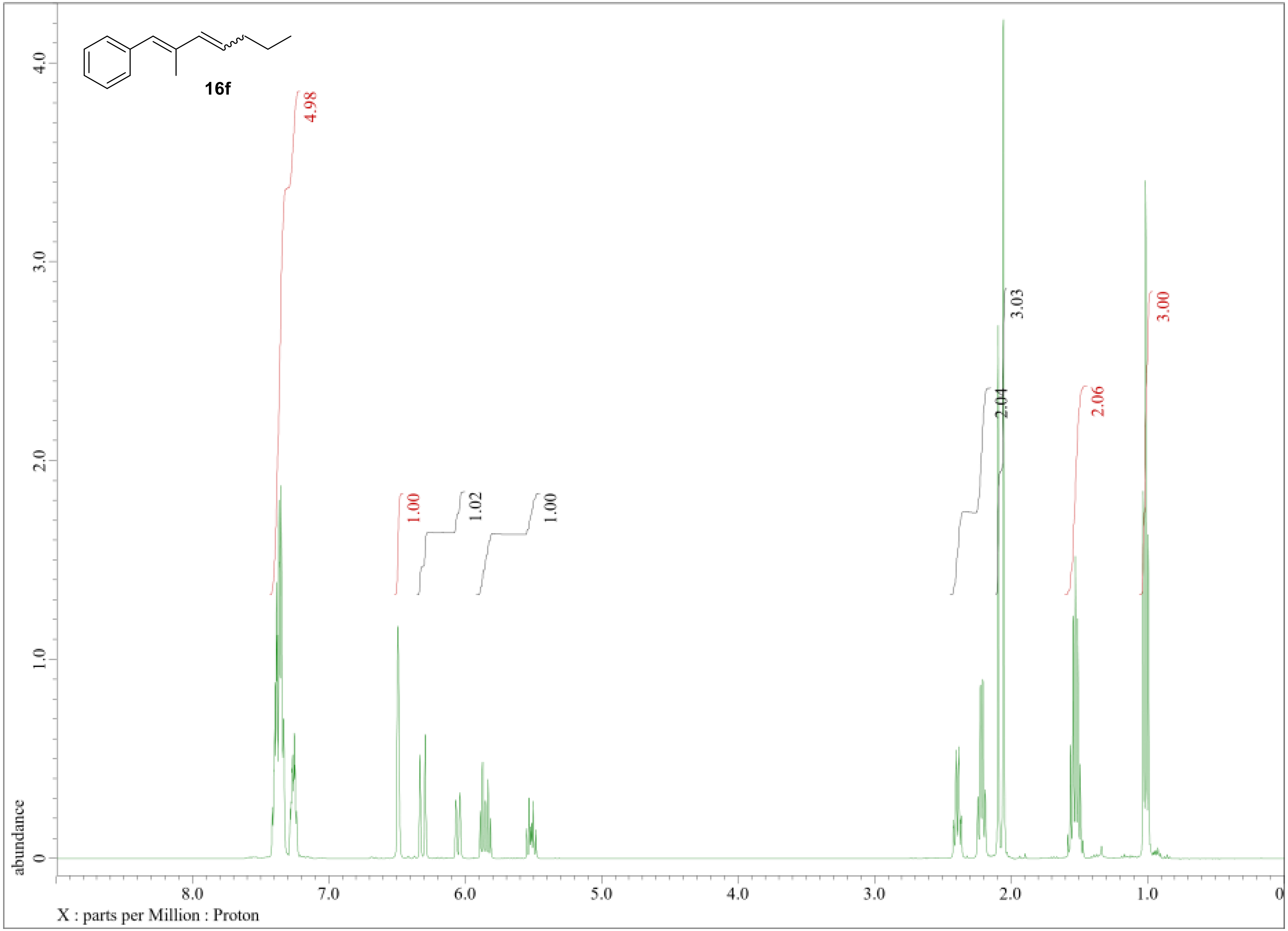

16e
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
137.881
135.869
133.238
132.198
130.911
130.177
129.653
129.128
128.756
128.728
127.507
127.240
126.525
126.325
124.695
77.575
77.260
76.945
35.165
30.255
23.104
22.713
14.017
13.950
X : parts per Million : Carbon13


14e
H
H
O–O
5.09
2.00
1.00
1.02
4.01
3.12
4.0
3.0
2.0
1.0
0
(Thousands)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H


H
H
O–O
14e
(Thousands)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
137.681
128.884
128.784
128.656
128.537
126.281
80.223
78.287
77.419
77.108
76.789
35.152
18.810
14.079
X : parts per Million : 13C

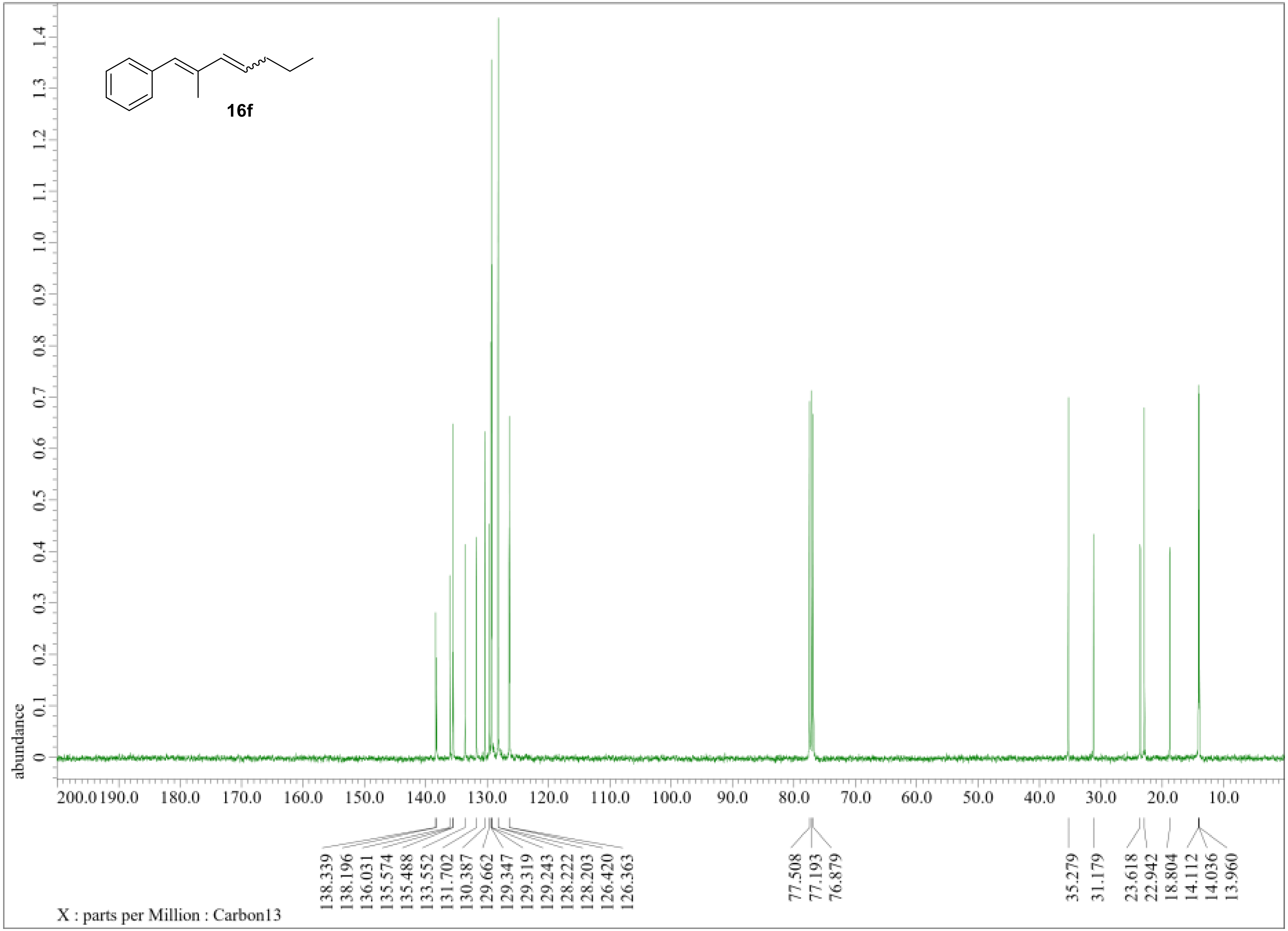

15e
O
2.05
2.06
1.05
1.03
1.00
2.19
2.16
3.24
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

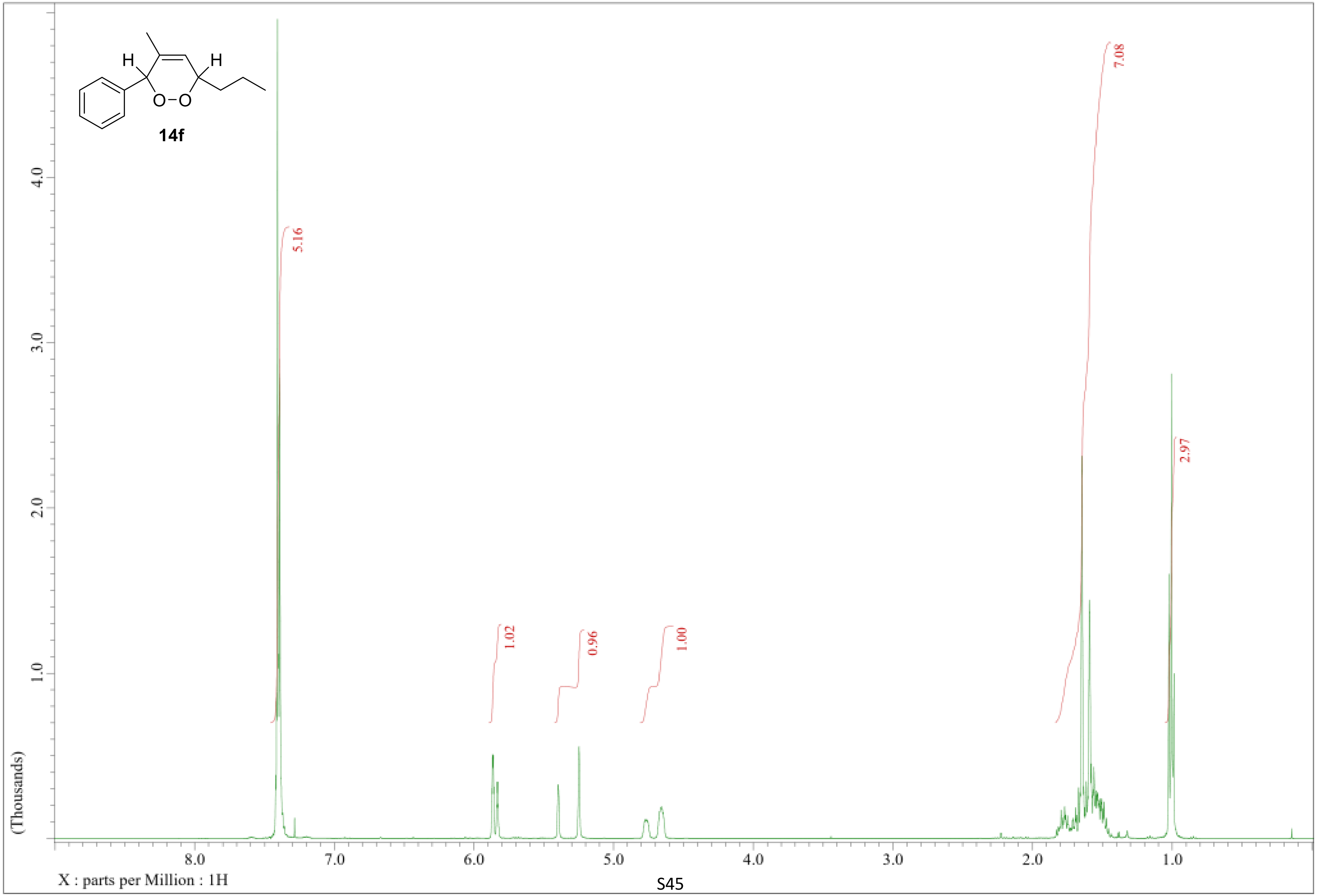

15e
O
abundance
0
0.1
0.2
0.3
0.4
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
156.359
152.202
131.359
128.670
126.783
123.407
107.056
105.711
77.432
77.107
76.793
30.293
21.549
13.874
X : parts per Million : Carbon13

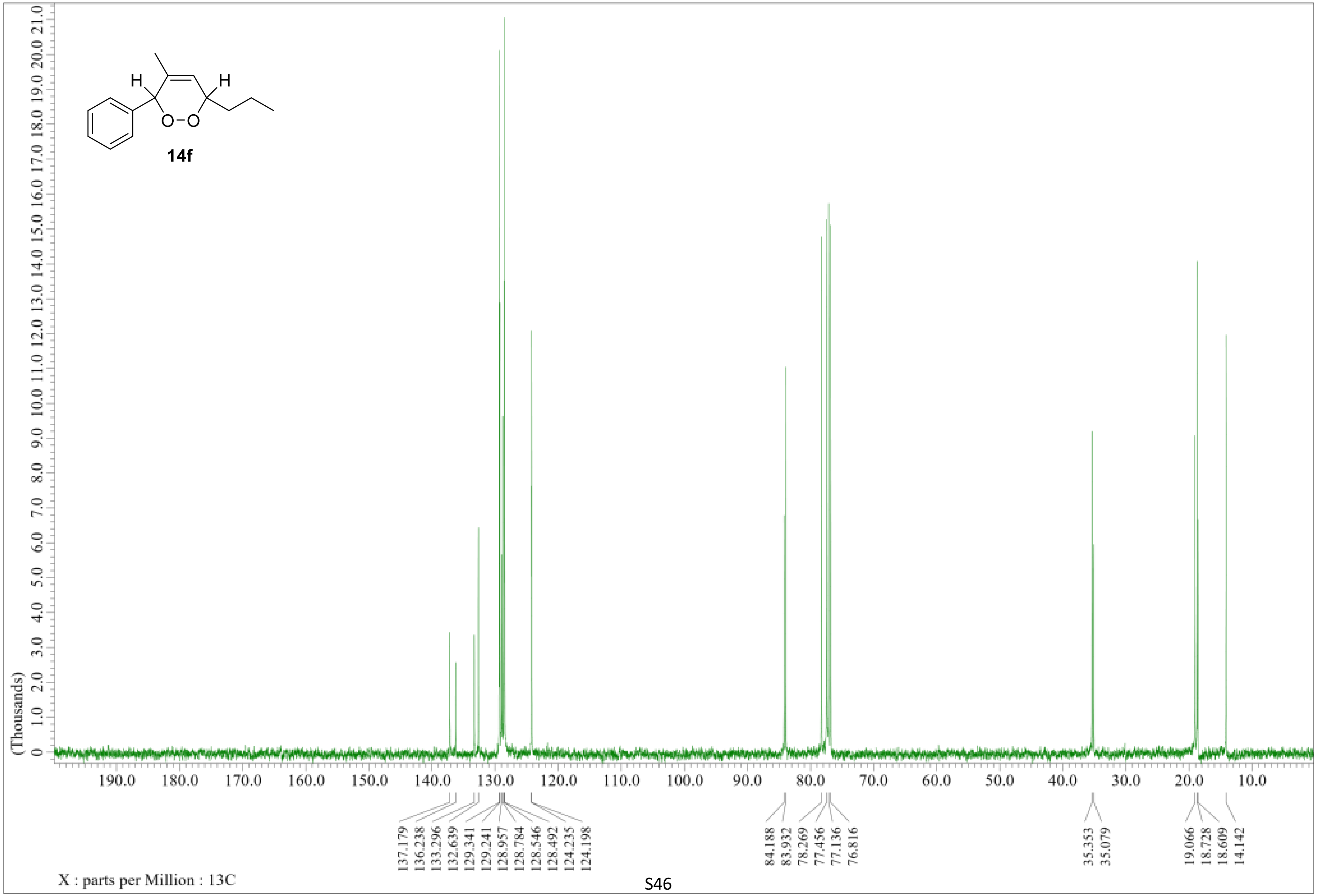


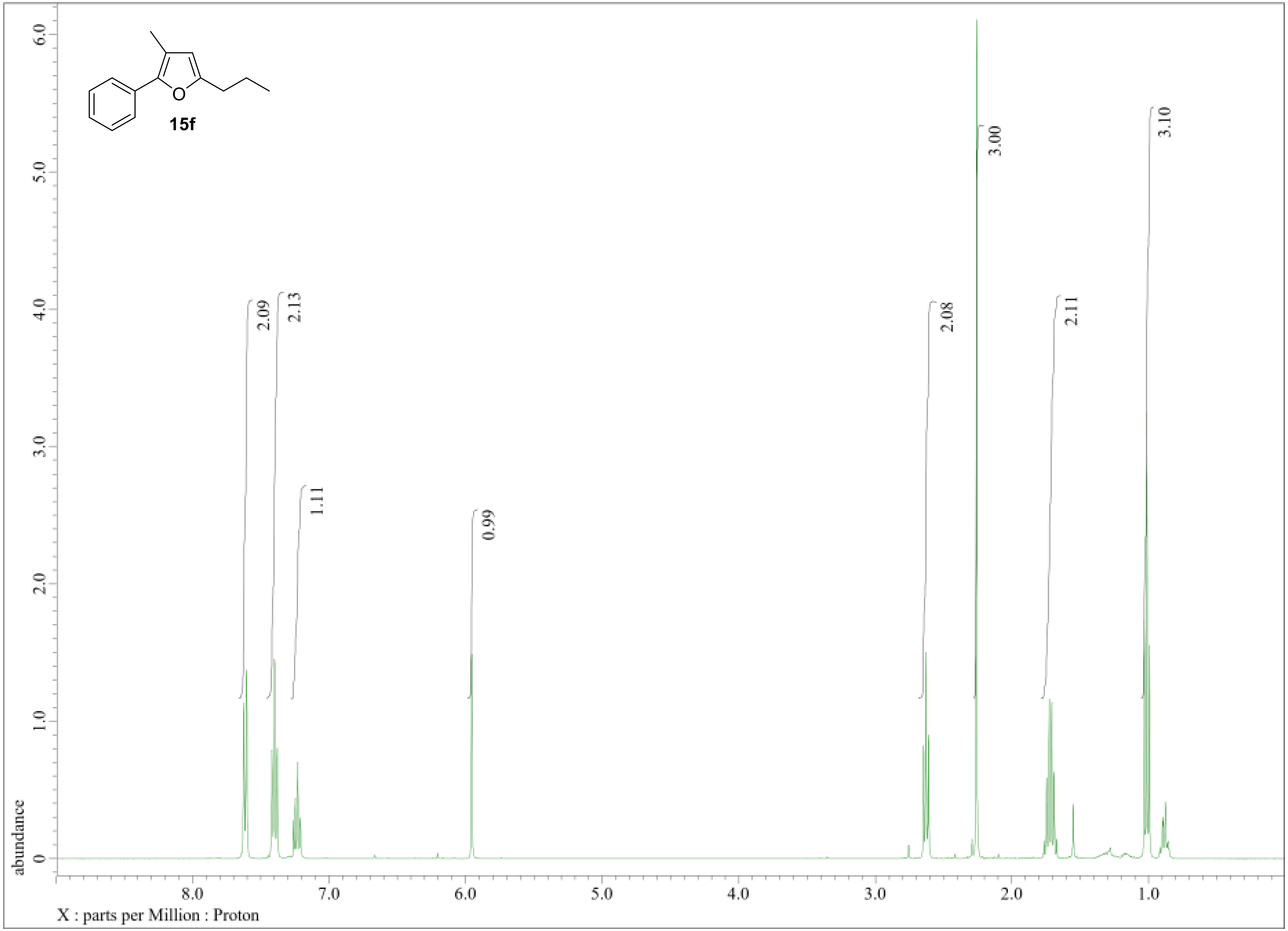
16f

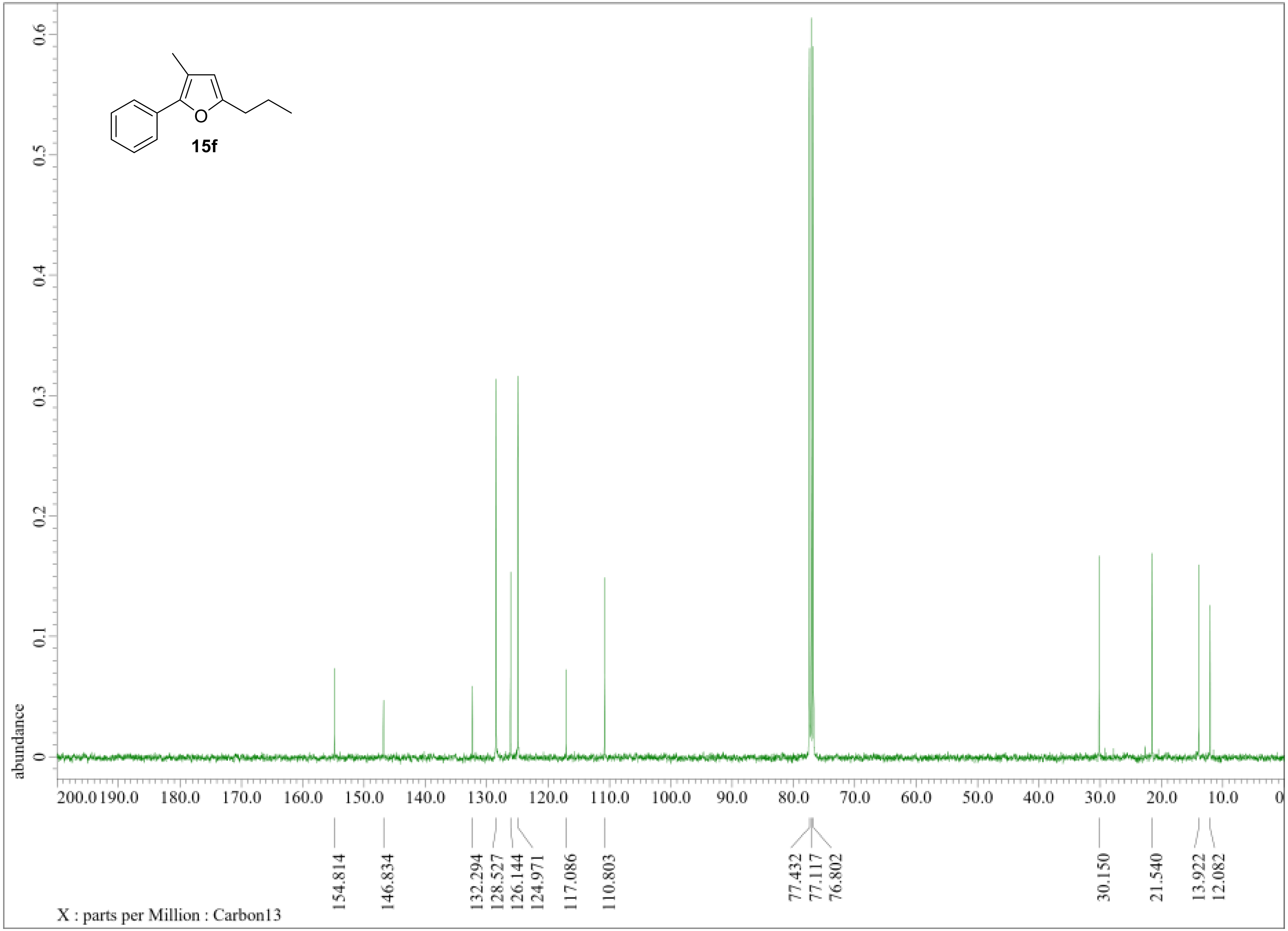
4.98
1.00
1.02
1.00
2.04
3.03
2.06
3.00
abundance
0
1.0
2.0
3.0
4.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

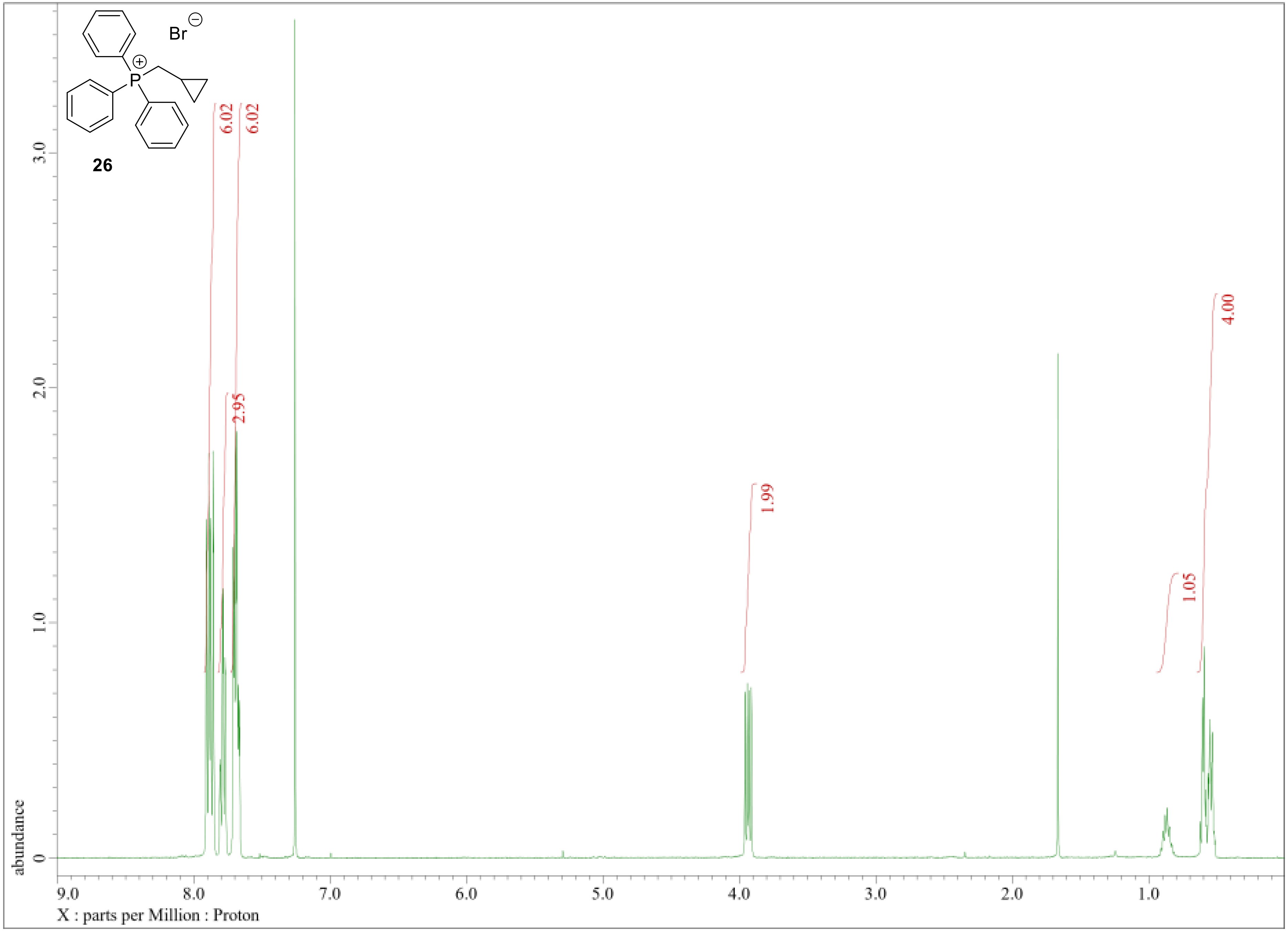

16f
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
138.339
138.196
136.031
135.574
135.488
133.552
131.702
130.387
129.662
129.347
129.319
129.243
128.222
128.203
126.420
126.363
77.508
77.193
76.879
35.279
31.179
23.618
22.942
18.804
14.112
14.036
13.960
X : parts per Million : Carbon13

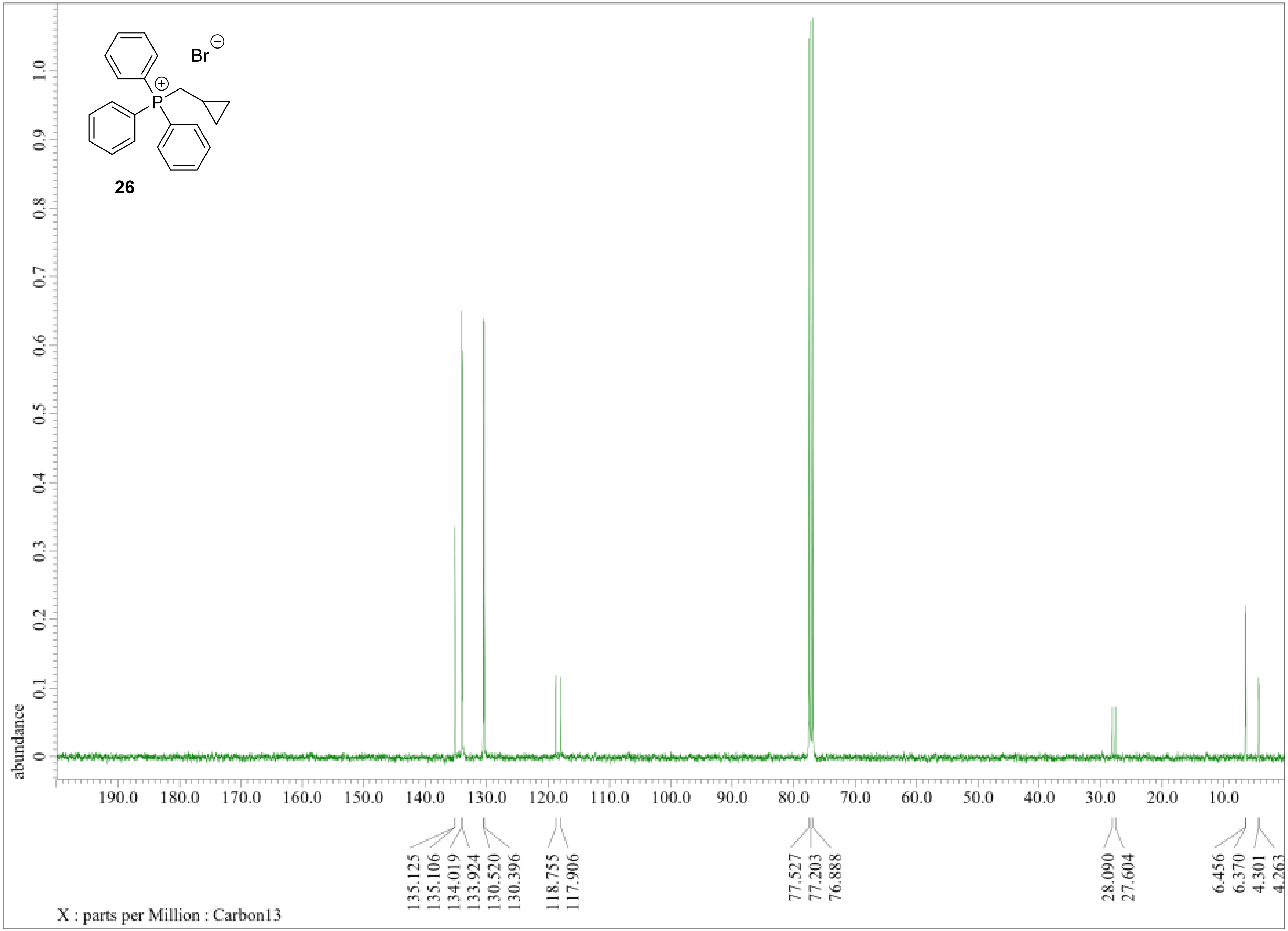

14f
H
H
O–O
5.16
1.02
0.96
1.00
7.08
2.97
(Thousands)
1.0
2.0
3.0
4.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H

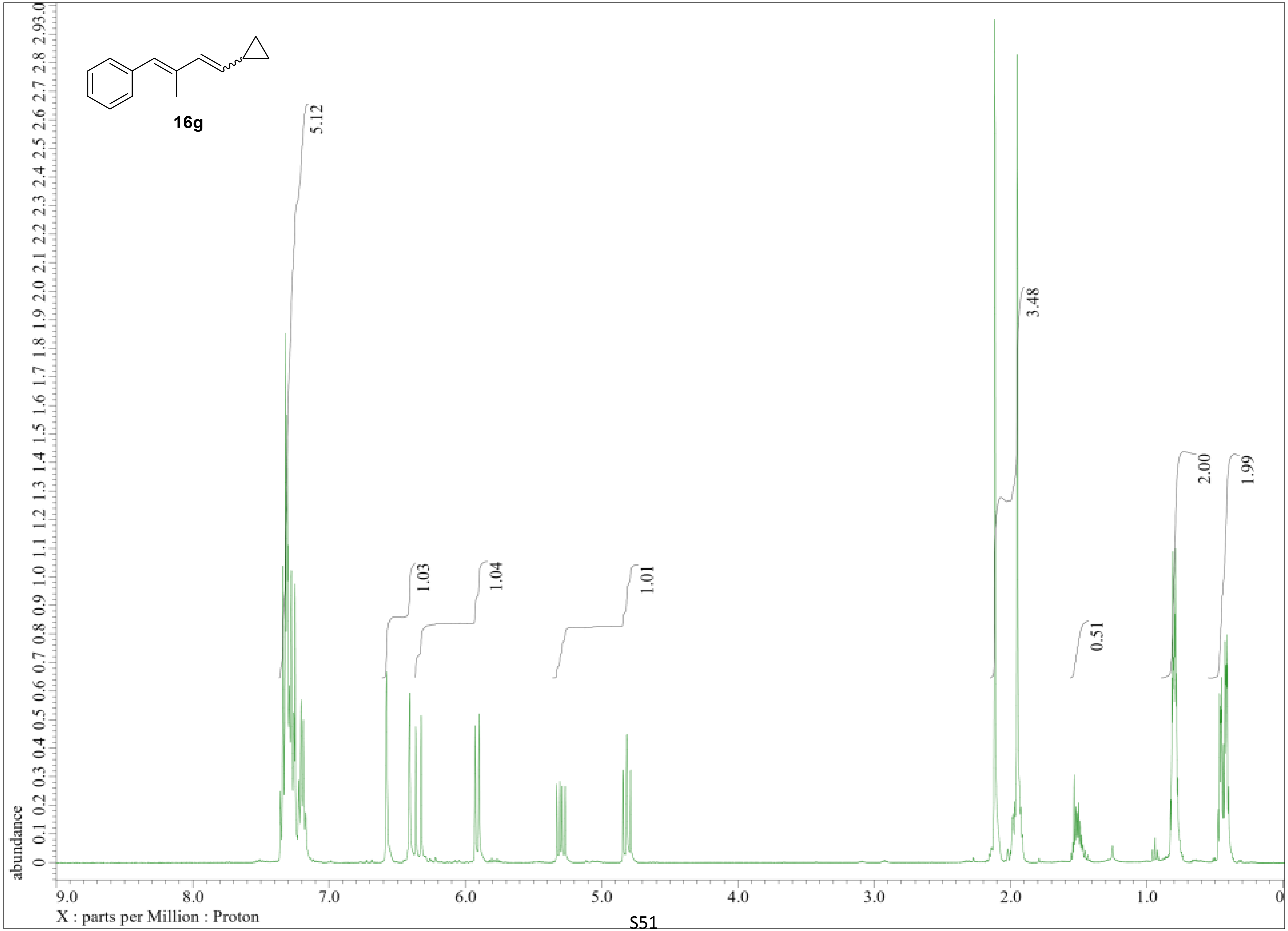

H
H
O–O
14f
(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
137.179
136.238
133.296
132.639
129.341
129.241
128.957
128.784
128.546
128.492
124.235
124.198
84.188
83.932
78.269
77.456
77.136
76.816
35.353
35.079
19.066
18.728
18.609
14.142
X : parts per Million : 13C

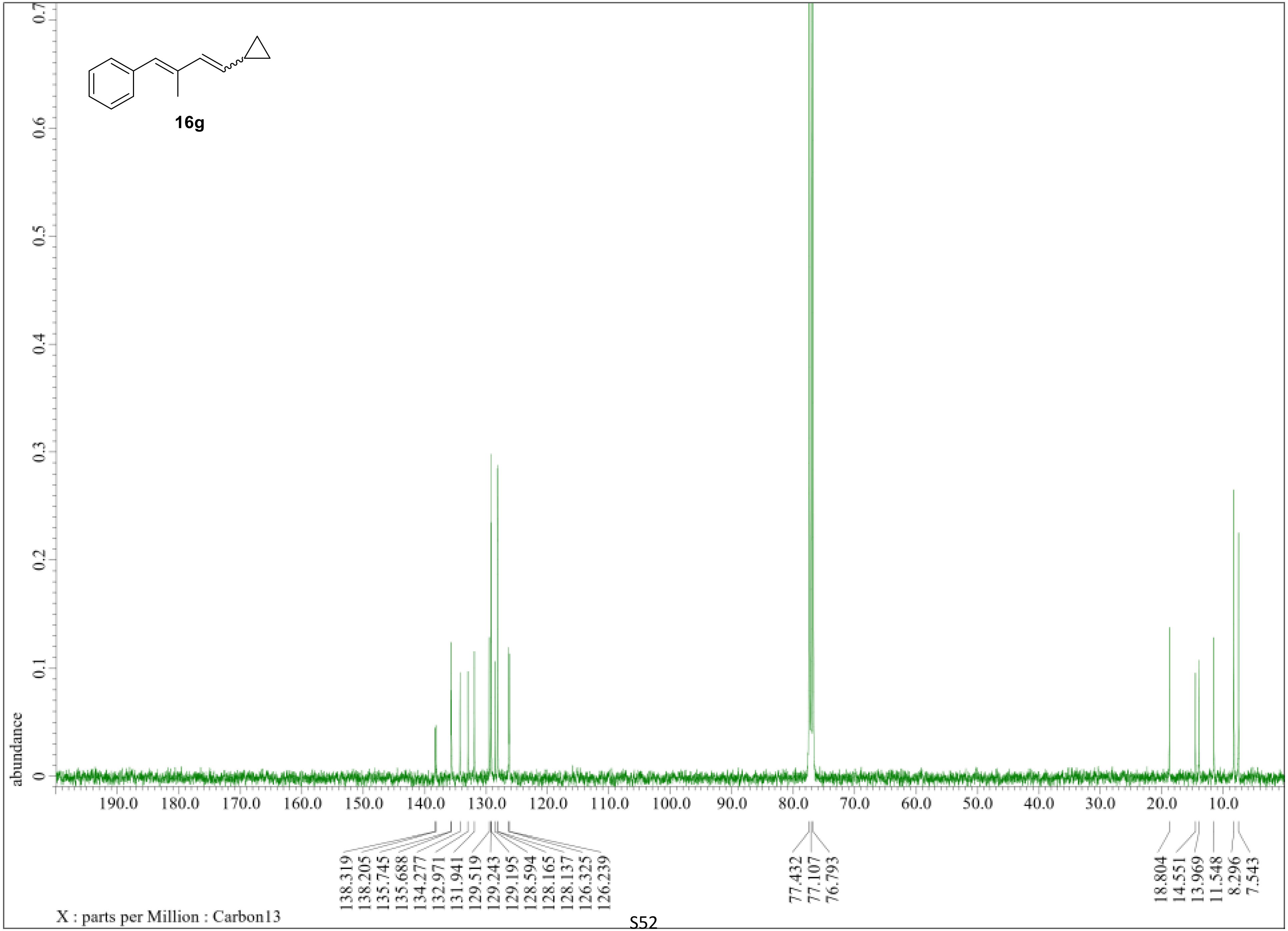

15f
O
2.09
2.13
1.11
0.99
2.08
3.00
2.11
3.10
6.0
5.0
4.0
3.0
2.0
1.0
0
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton

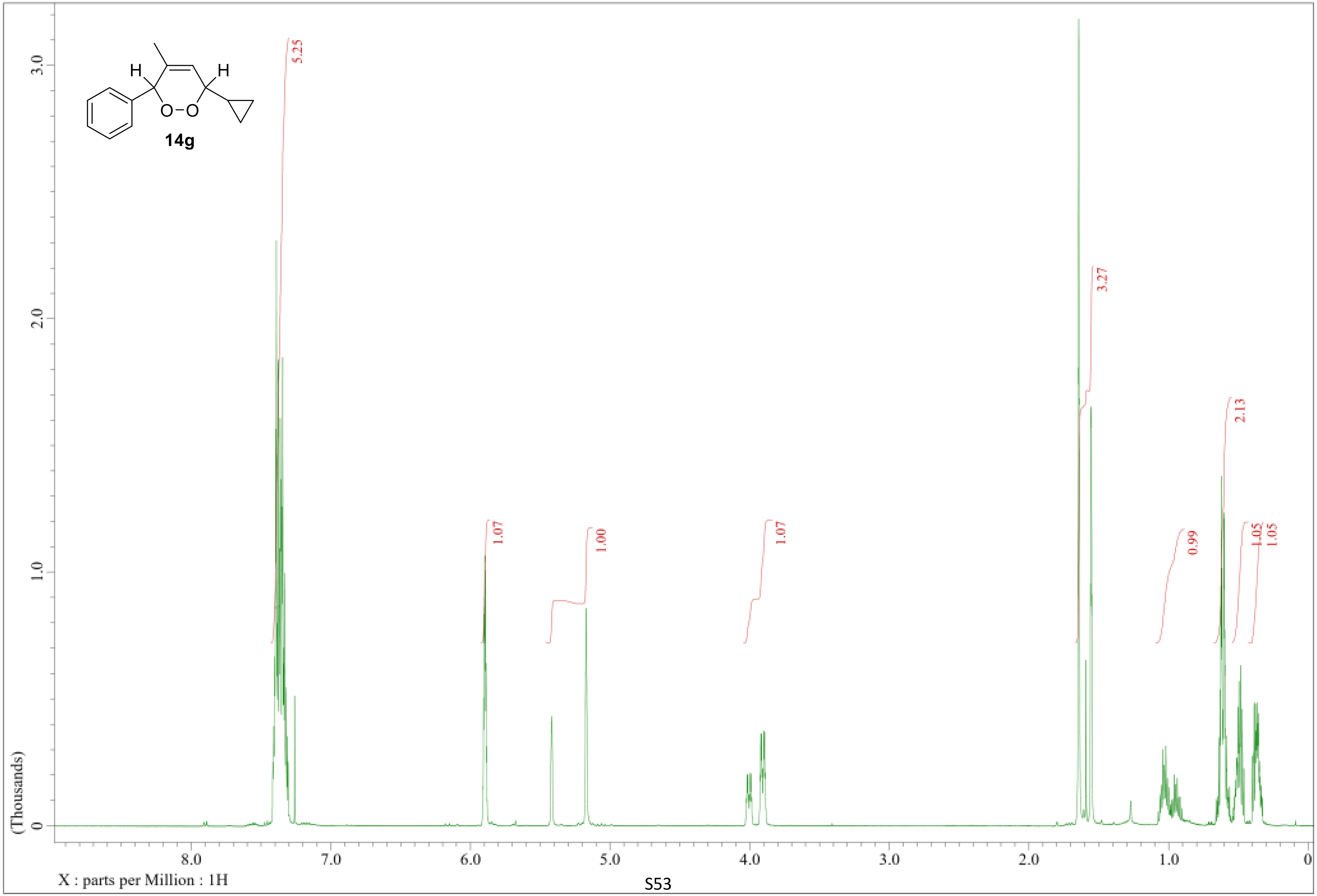

15f
O
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
154.814
146.834
132.294
128.527
126.144
124.971
117.086
110.803
77.432
77.117
76.802
30.150
21.540
13.922
12.082
X : parts per Million : Carbon13

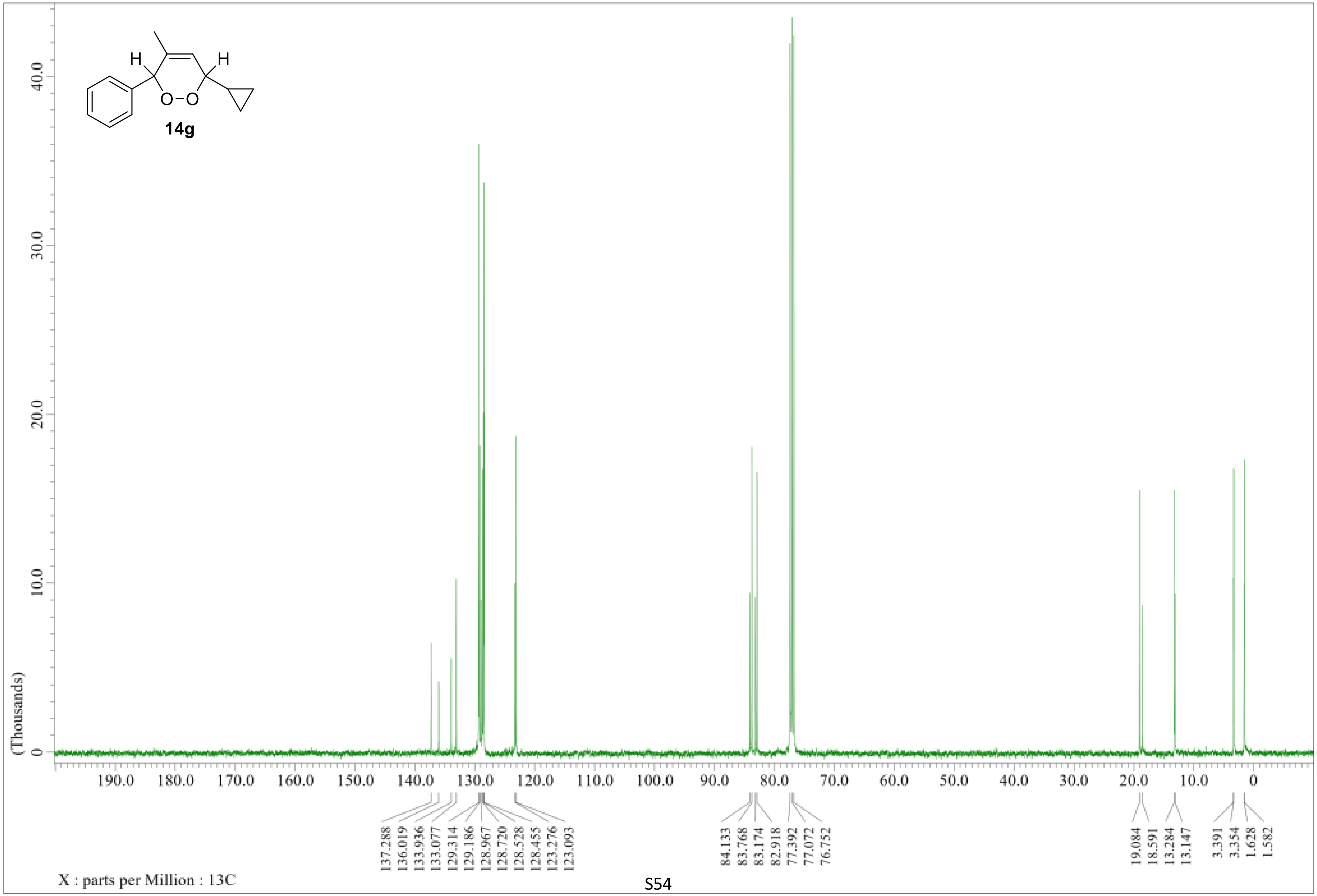

Br
P
26
6.02
6.02
2.95
1.99
1.05
4.00
3.0
2.0
1.0
0
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton

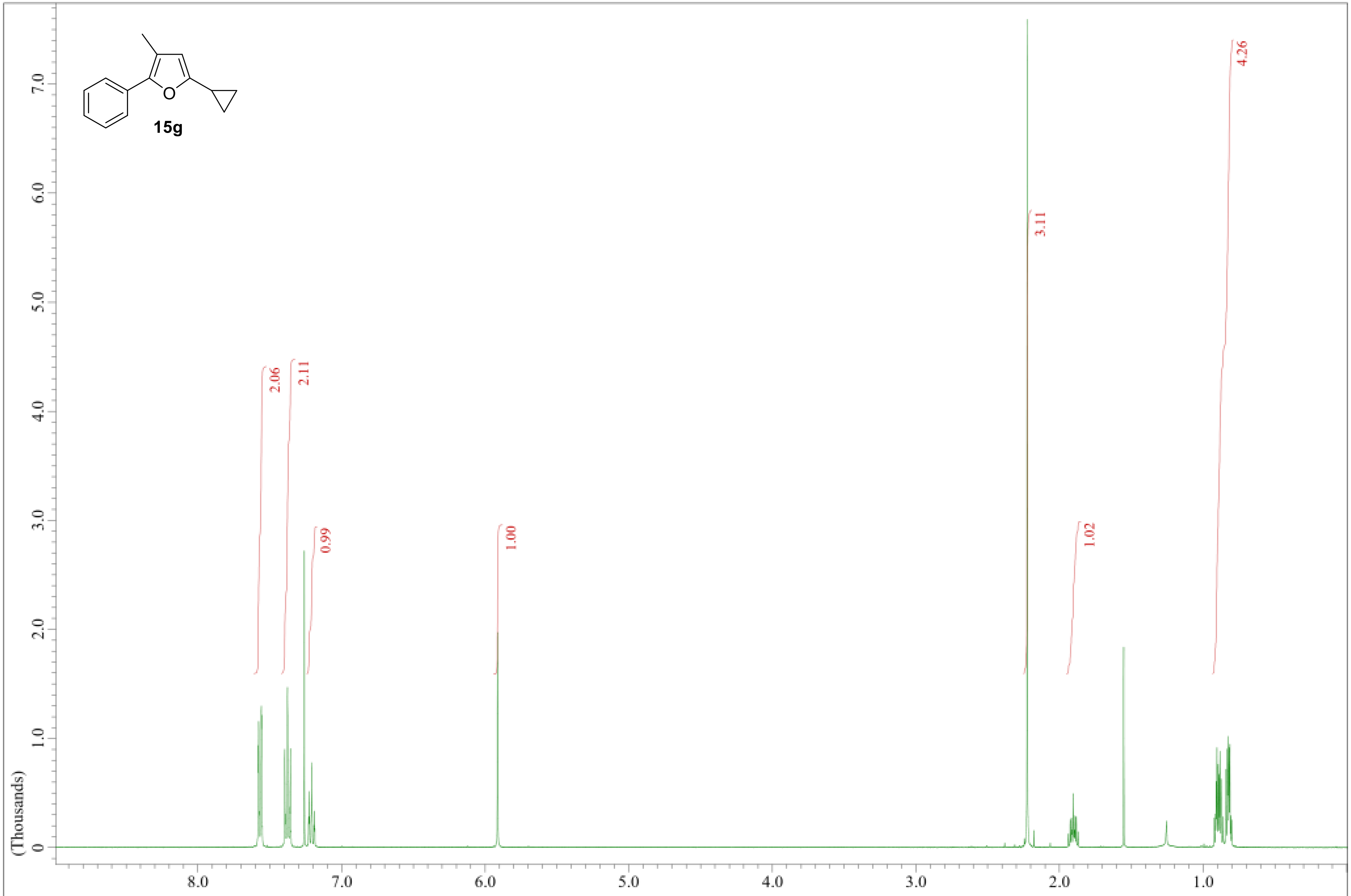

Br⊖
P⊕
26
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
135.125
135.106
134.019
133.924
130.520
130.396
118.755
117.906
77.527
77.203
76.888
28.090
27.604
6.456
6.370
4.301
4.263
X : parts per Million : Carbon13


16g
5.12
1.03
1.04
1.01
3.48
0.51
2.00
1.99
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.93.0
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton

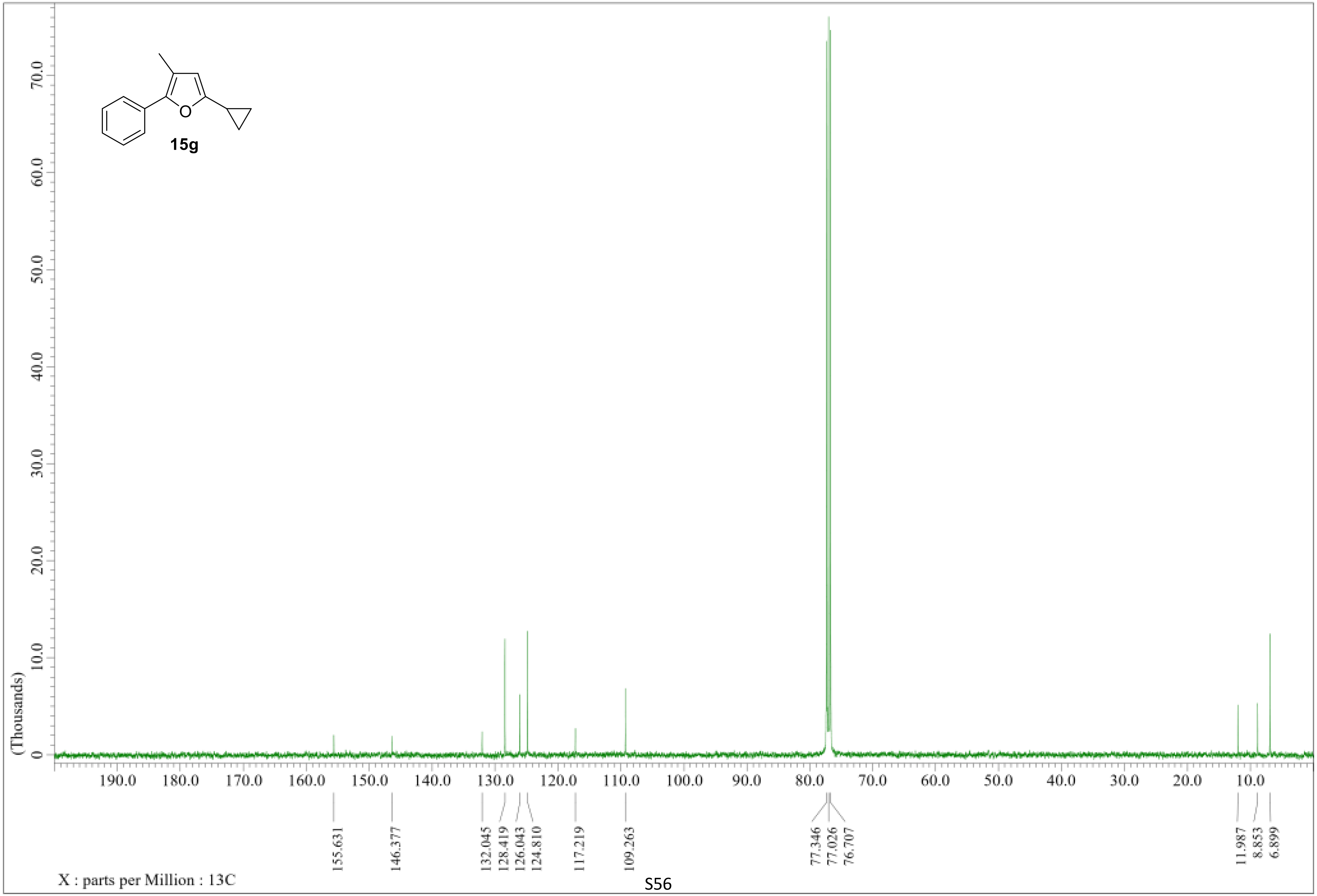

16g
abundance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
138.319
138.205
135.745
135.688
134.277
132.971
131.941
129.519
129.243
129.195
128.594
128.165
128.137
126.325
126.239
77.432
77.107
76.793
18.804
14.551
13.969
11.548
8.296
7.543
X : parts per Million : Carbon13

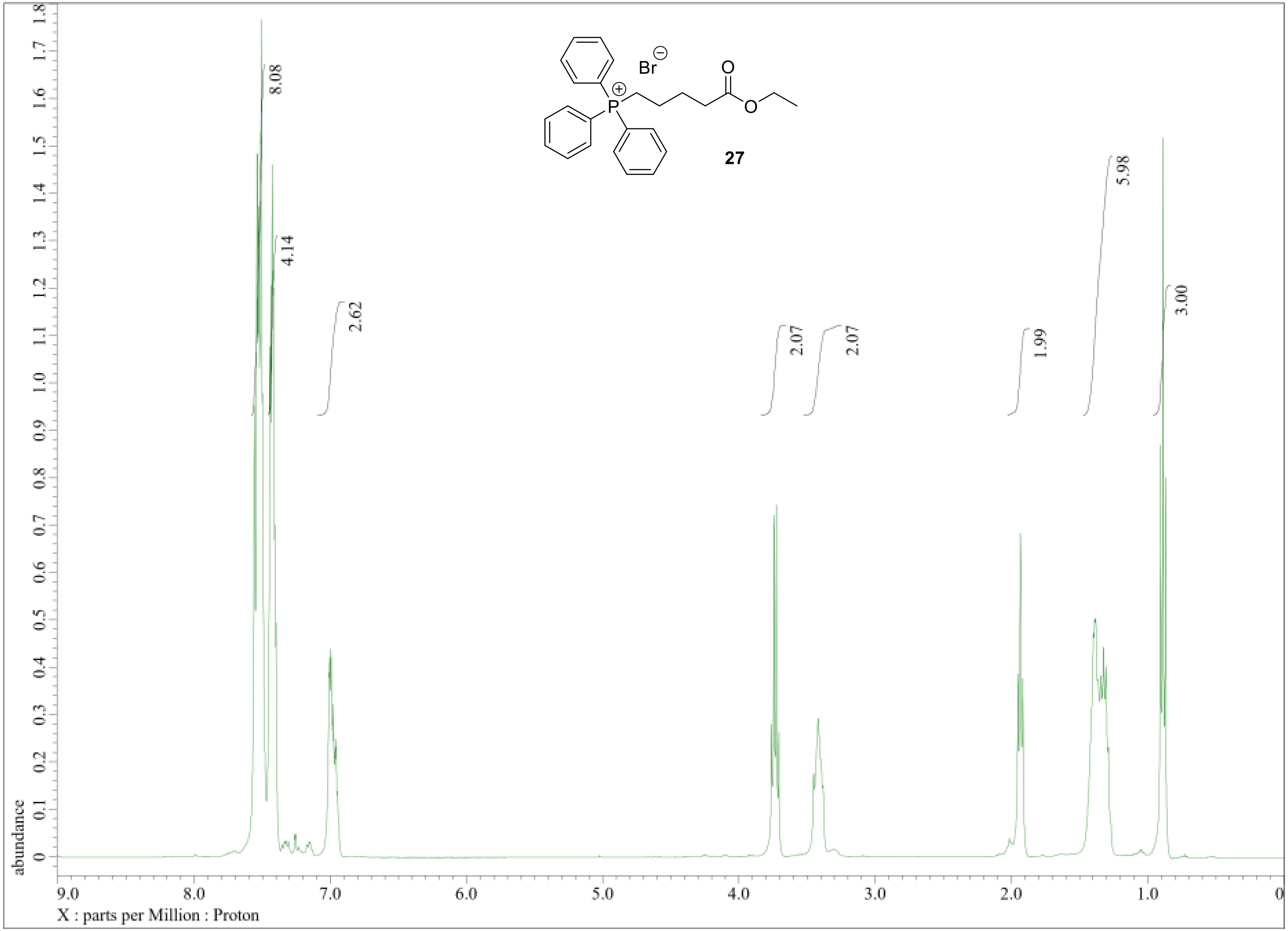

14g
H
H
O–O
5.25
1.07
1.00
1.07
3.27
2.13
0.99
1.05
1.05
3.0
2.0
1.0
0
(Thousands)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

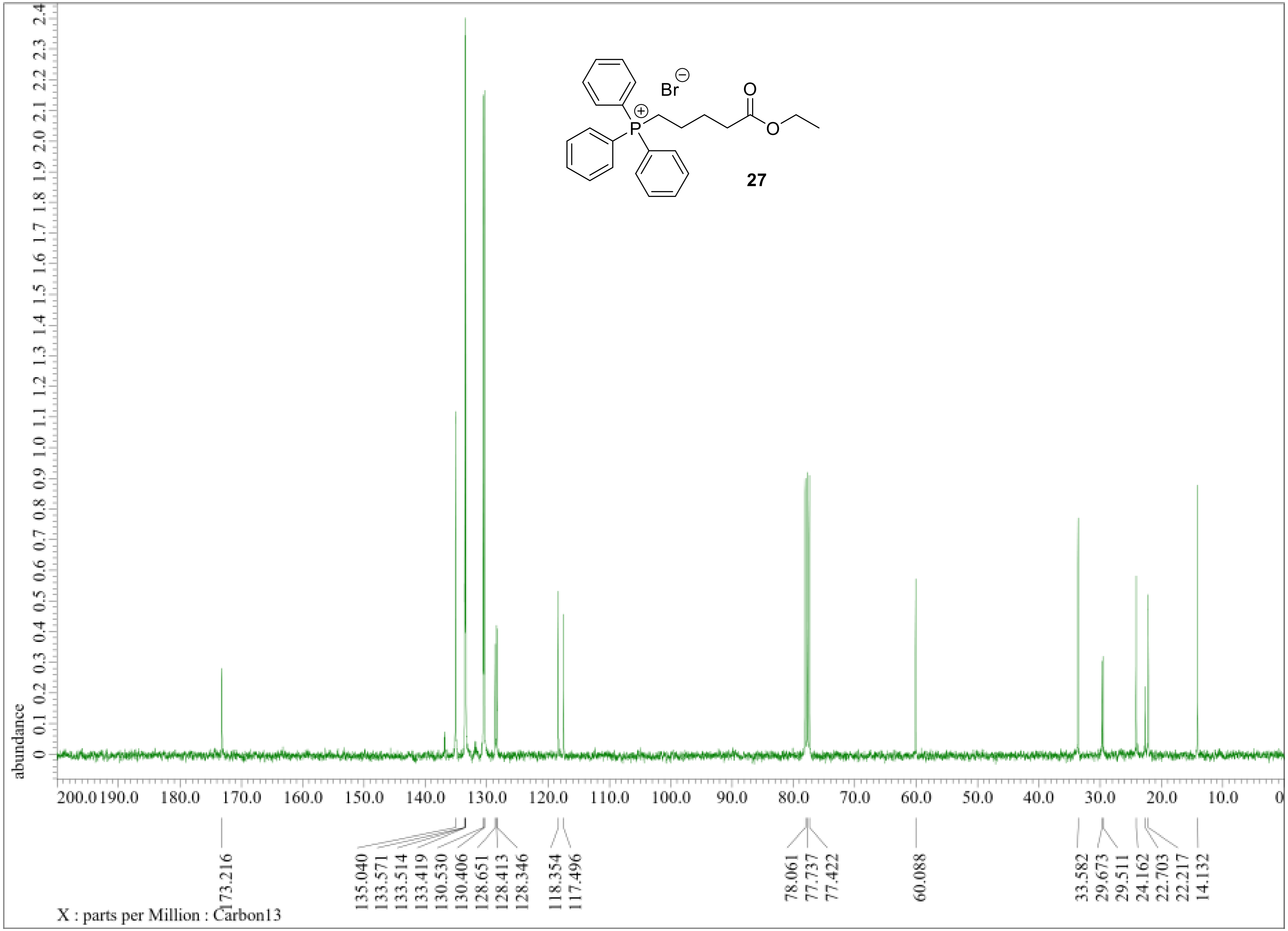

14g
H
H
O–O
(Thousands)
40.0
30.0
20.0
10.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
137.288
136.019
133.936
133.077
129.314
129.186
128.967
128.720
128.528
128.455
123.276
123.093
84.133
83.768
83.174
82.918
77.392
77.072
76.752
19.084
18.591
13.284
13.147
3.391
3.354
1.628
1.582
X : parts per Million : 13C

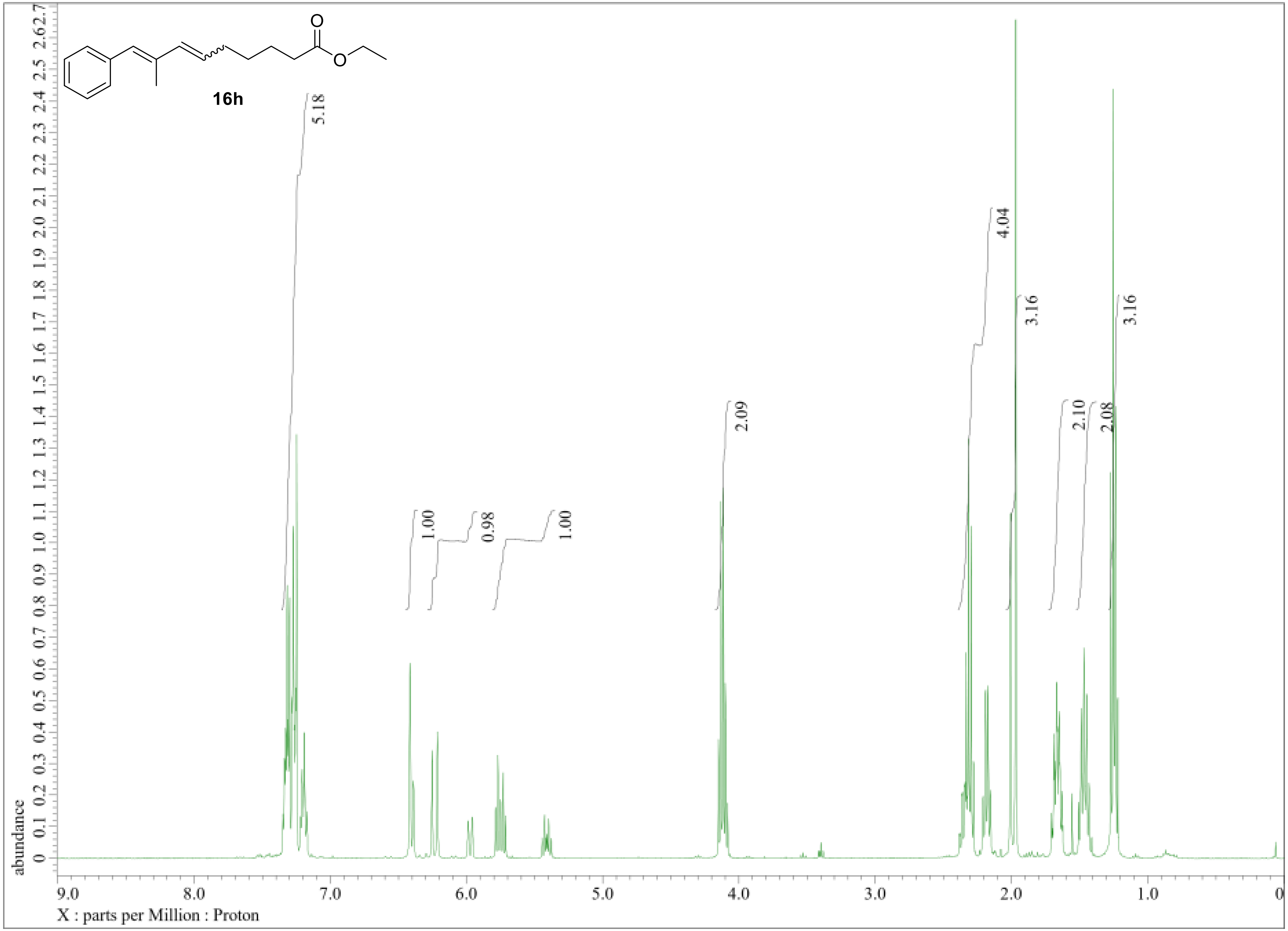


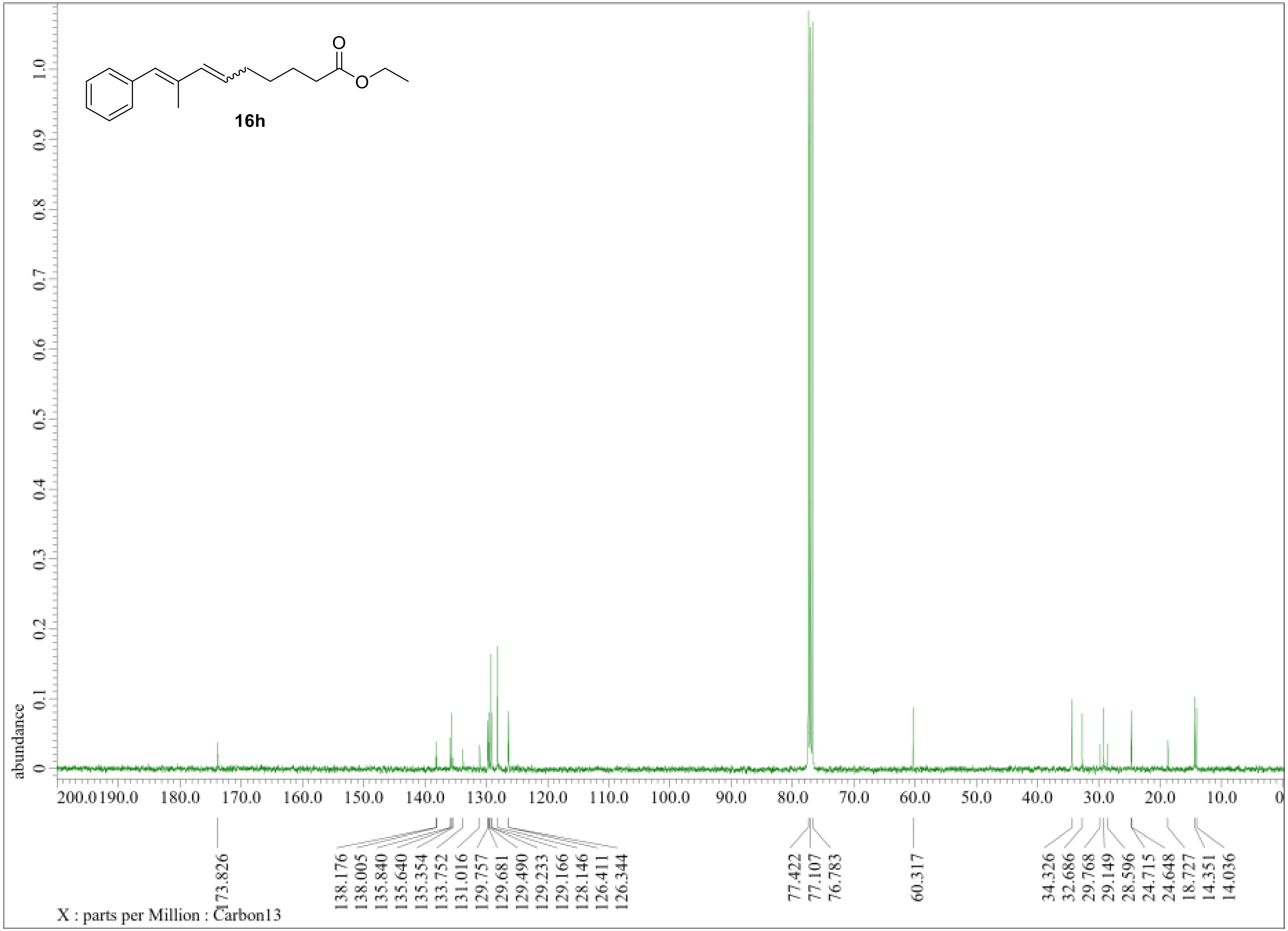
O
15g
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
(Thousands)
2.06
2.11
0.99
1.00
3.11
1.02
4.26
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H

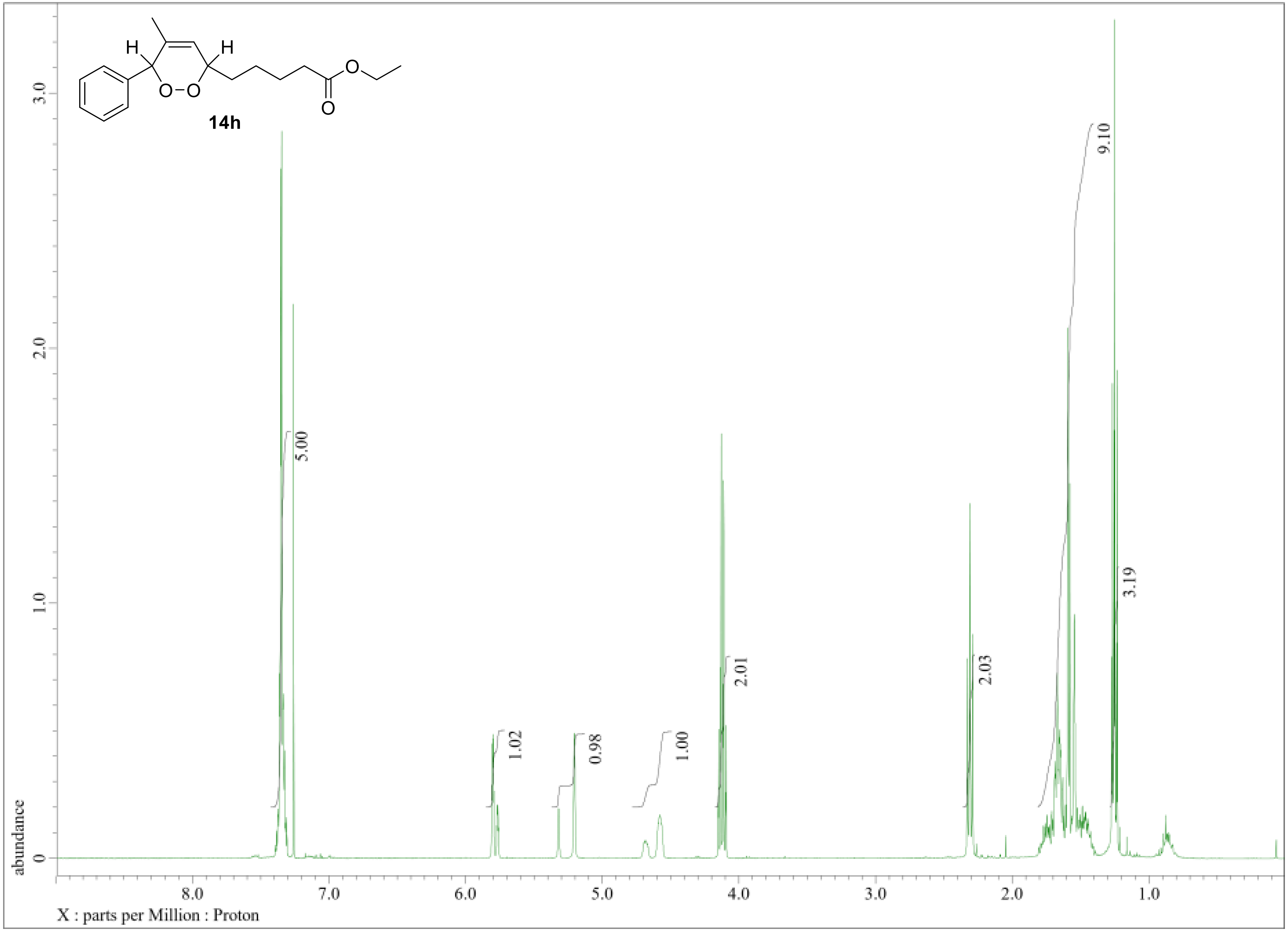

O
15g
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
(Thousands)
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
155.631
146.377
132.045
128.419
126.043
124.810
117.219
109.263
77.346
77.026
76.707
11.987
8.853
6.899
X : parts per Million : 13C

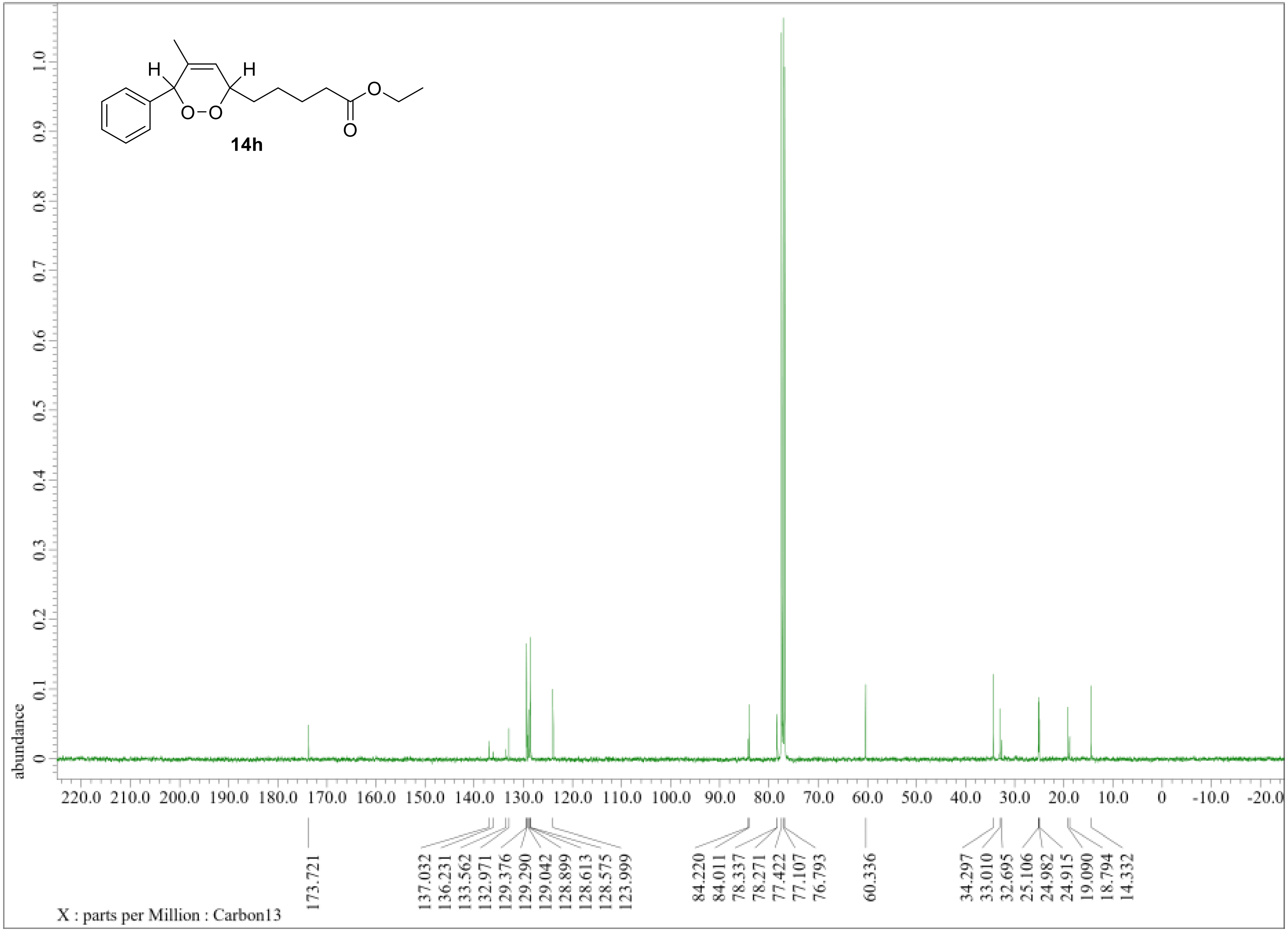

Br⊖
O
P⊕
O
27
8.08
4.14
2.62
2.07
2.07
1.99
5.98
3.00
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

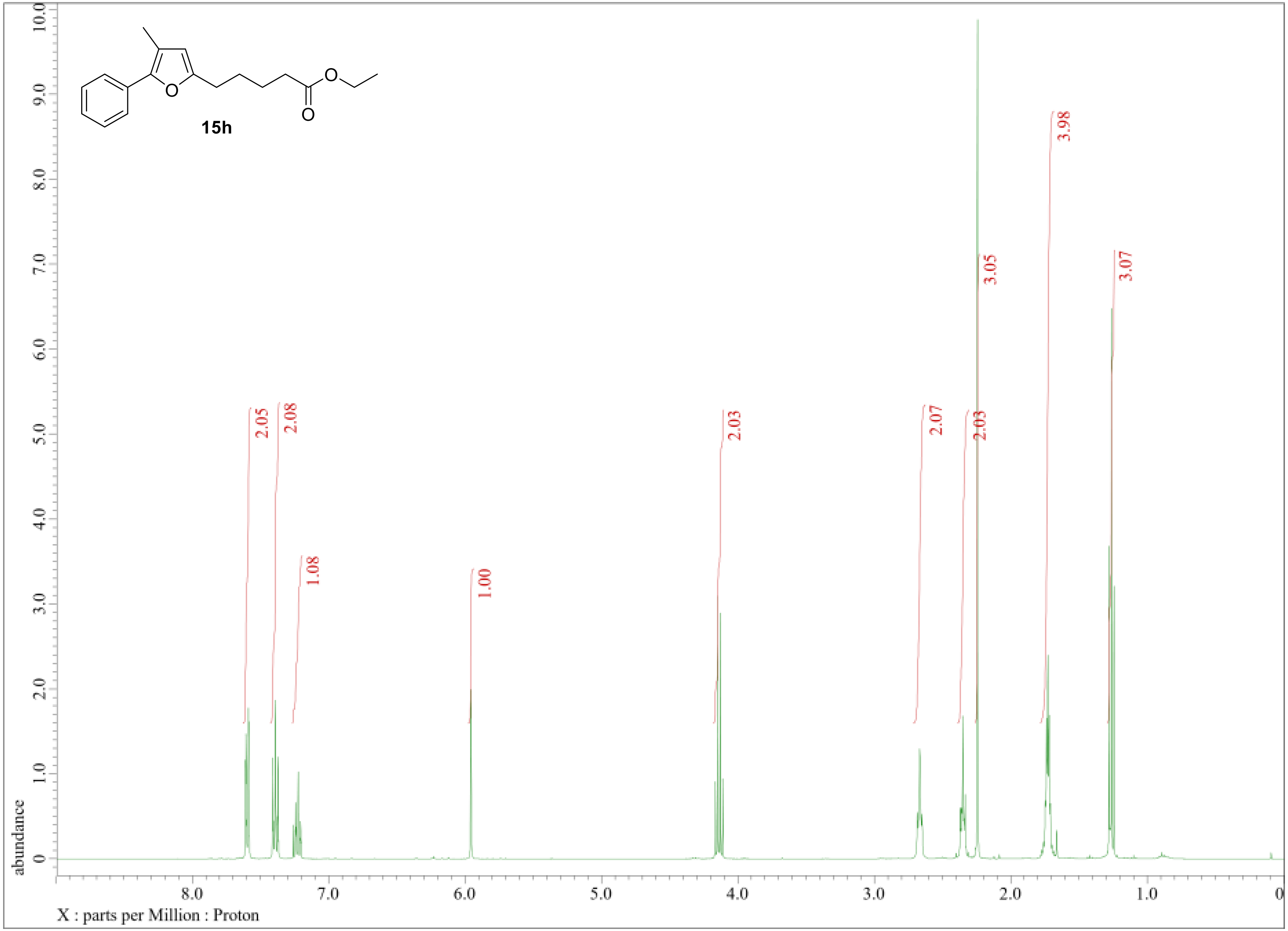

Br
P
O
O
27
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.216
135.040
133.571
133.514
133.419
130.530
130.406
128.651
128.413
128.346
118.354
117.496
78.061
77.737
77.422
60.088
33.582
29.673
29.511
24.162
22.703
22.217
14.132
X : parts per Million : Carbon13

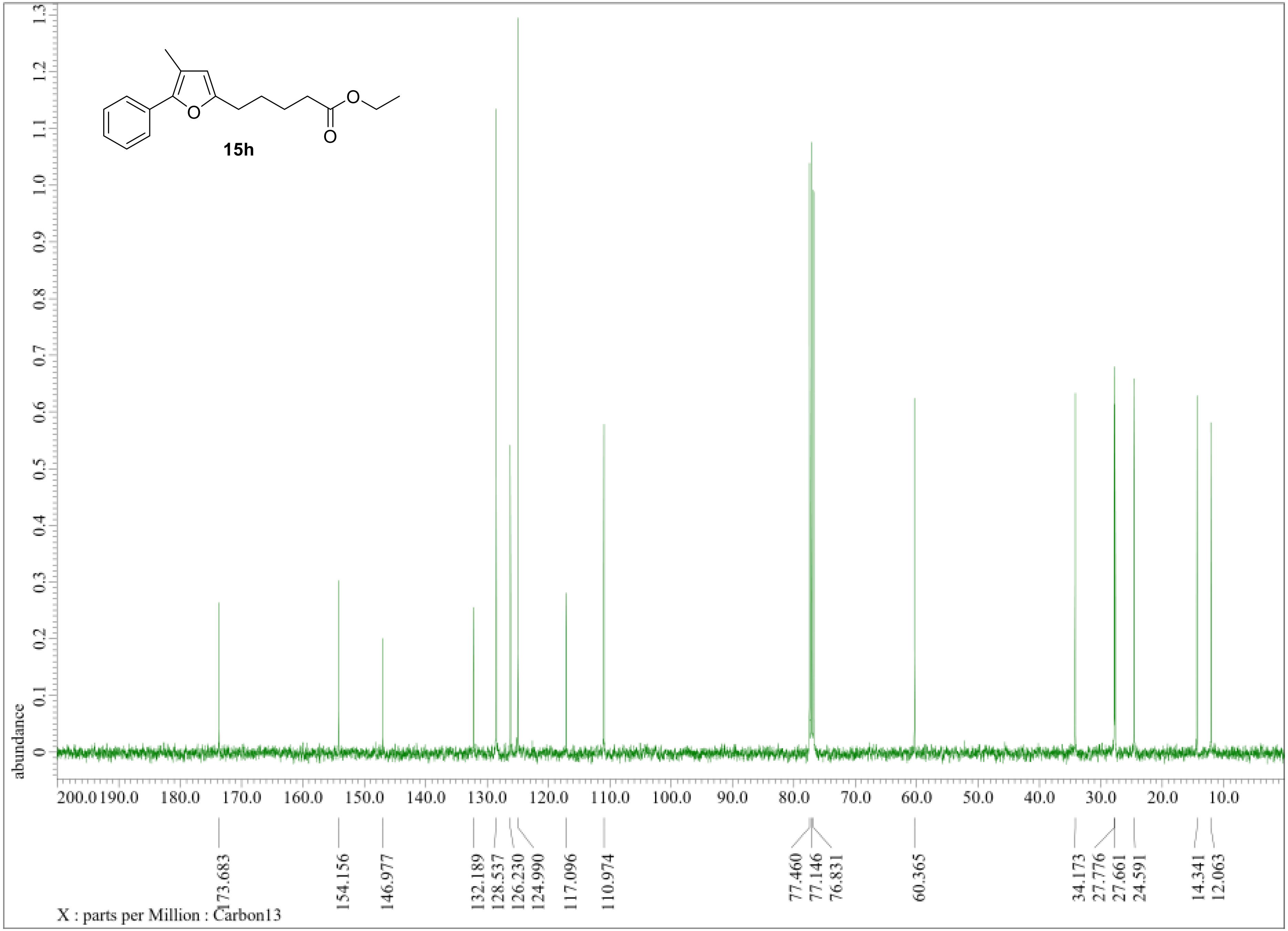

16h
O
O
5.18
1.00
0.98
1.00
2.09
4.04
3.16
2.10
2.08
3.16
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

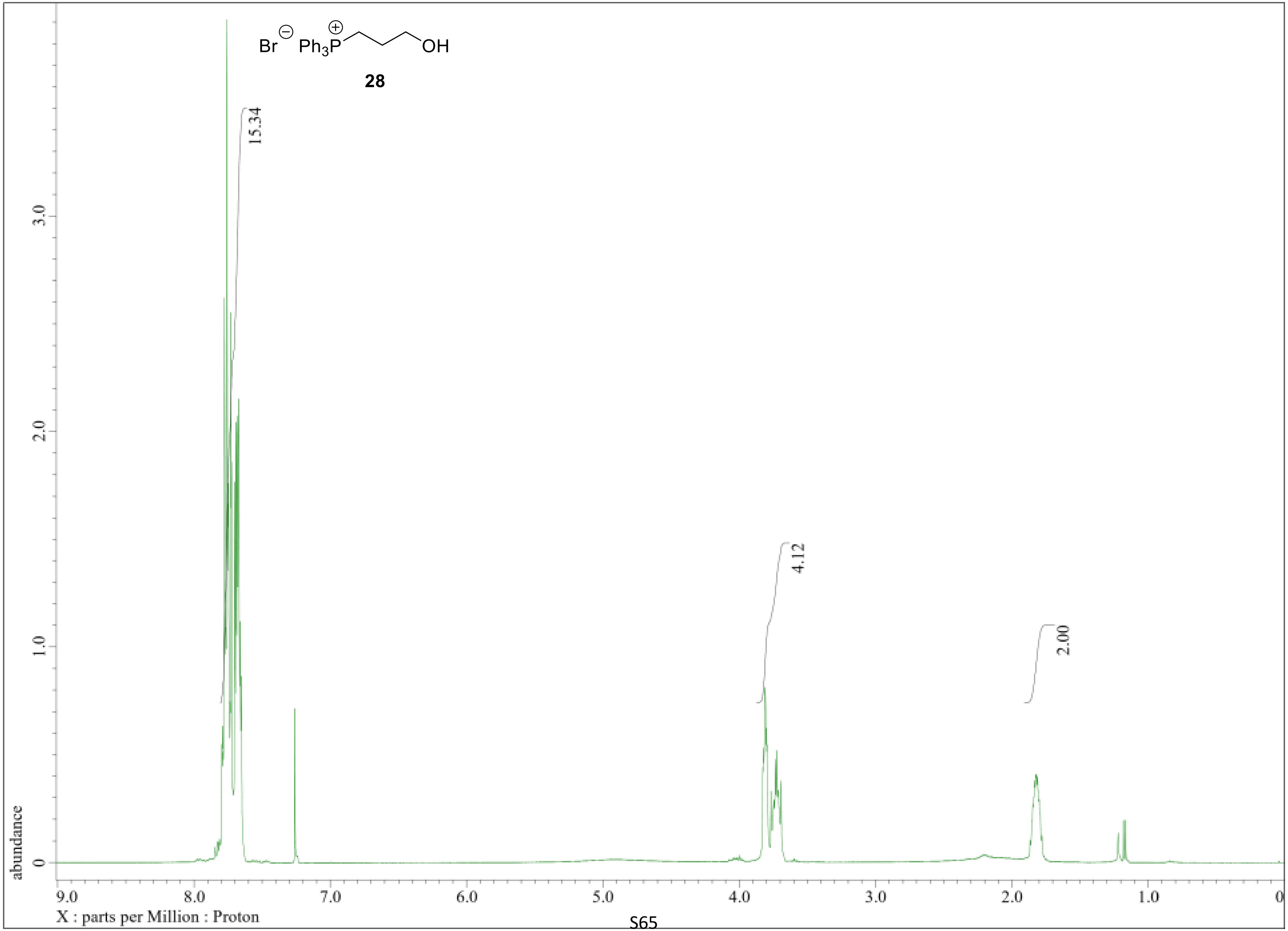

16h
O
O
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.826
138.176
138.005
135.840
135.640
135.354
133.752
131.016
129.757
129.681
129.490
129.233
129.166
128.146
126.411
126.344
77.422
77.107
76.783
60.317
34.326
32.686
29.768
29.149
28.596
24.715
24.648
18.727
14.351
14.036
X : parts per Million : Carbon13


14h
H
H
O
O
O
O
3.0
2.0
1.0
0
abundance
5.00
1.02
0.98
1.00
2.01
2.03
9.10
3.19
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton

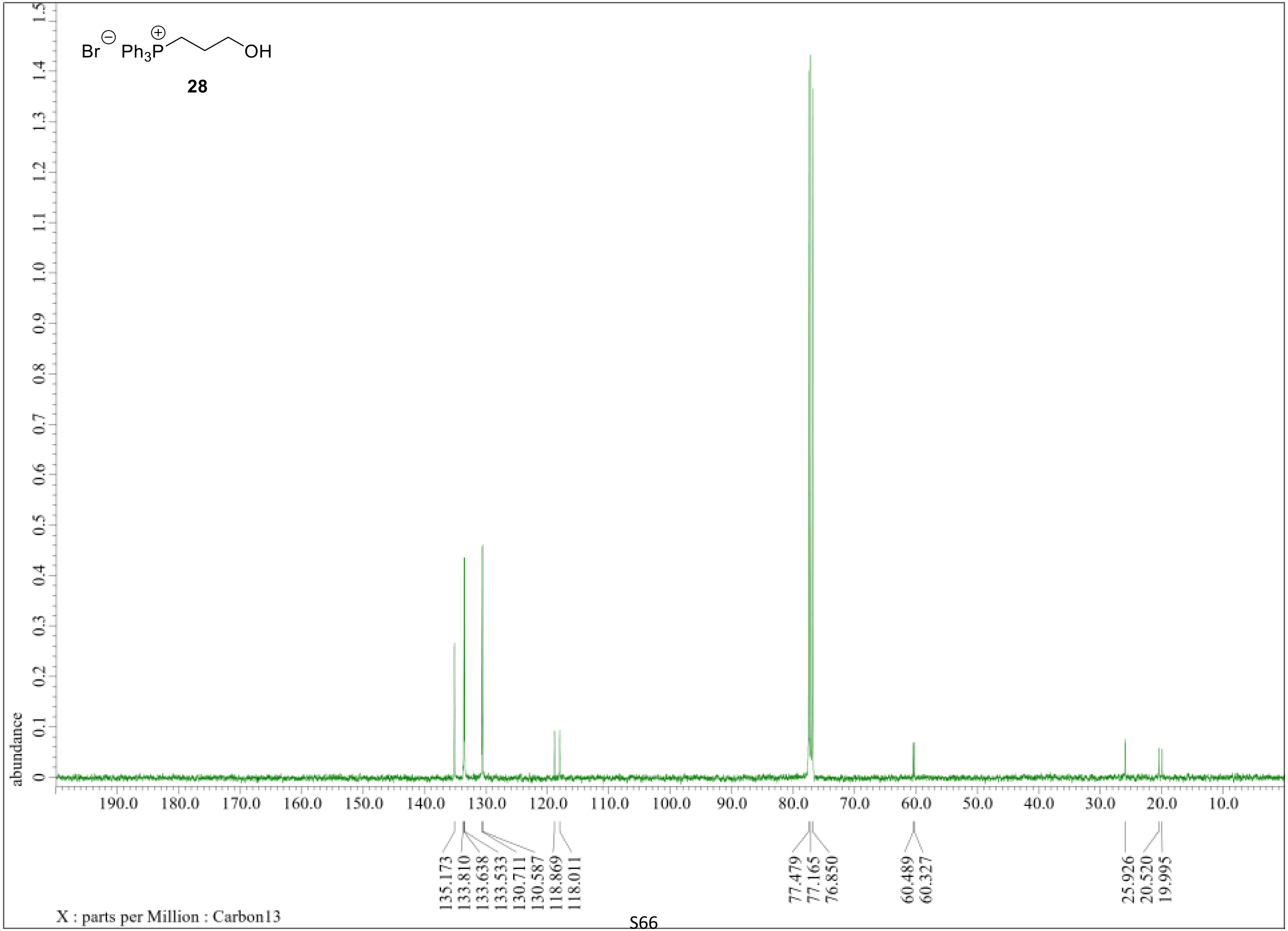

14h
H
H
O
O
O
O
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
173.721
137.032
136.231
133.562
132.971
129.376
129.290
129.042
128.899
128.613
128.575
123.999
84.220
84.011
78.337
78.271
77.422
77.107
76.793
60.336
34.297
33.010
32.695
25.106
24.982
24.915
19.090
18.794
14.332
X : parts per Million : Carbon13

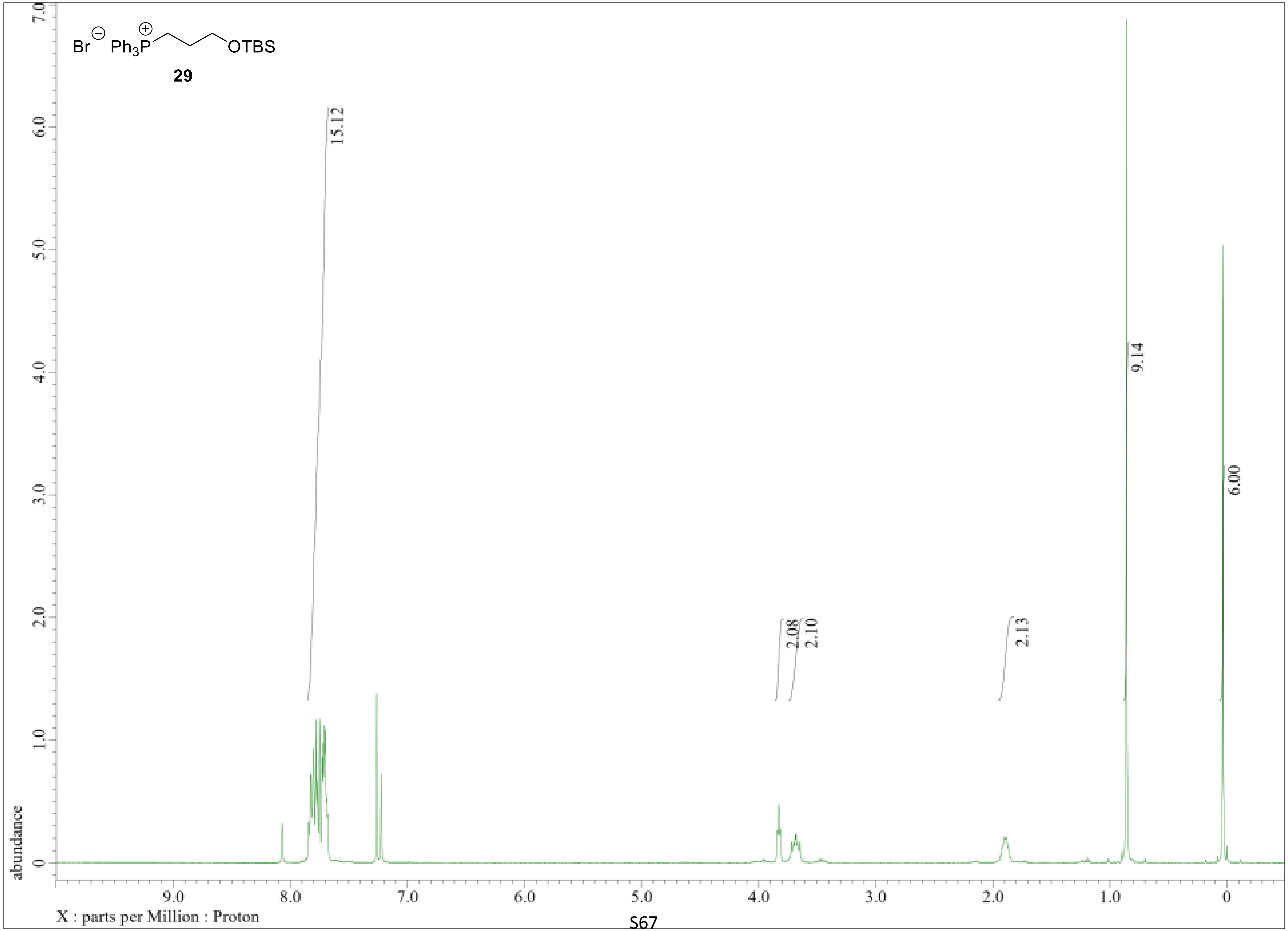

15h
O
O
O
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.05
2.08
1.08
1.00
2.03
2.07
2.03
3.05
3.98
3.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


15h
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
173.683
154.156
146.977
132.189
128.537
126.230
124.990
117.096
110.974
77.460
77.146
76.831
60.365
34.173
27.776
27.661
24.591
14.341
12.063
X : parts per Million : Carbon13

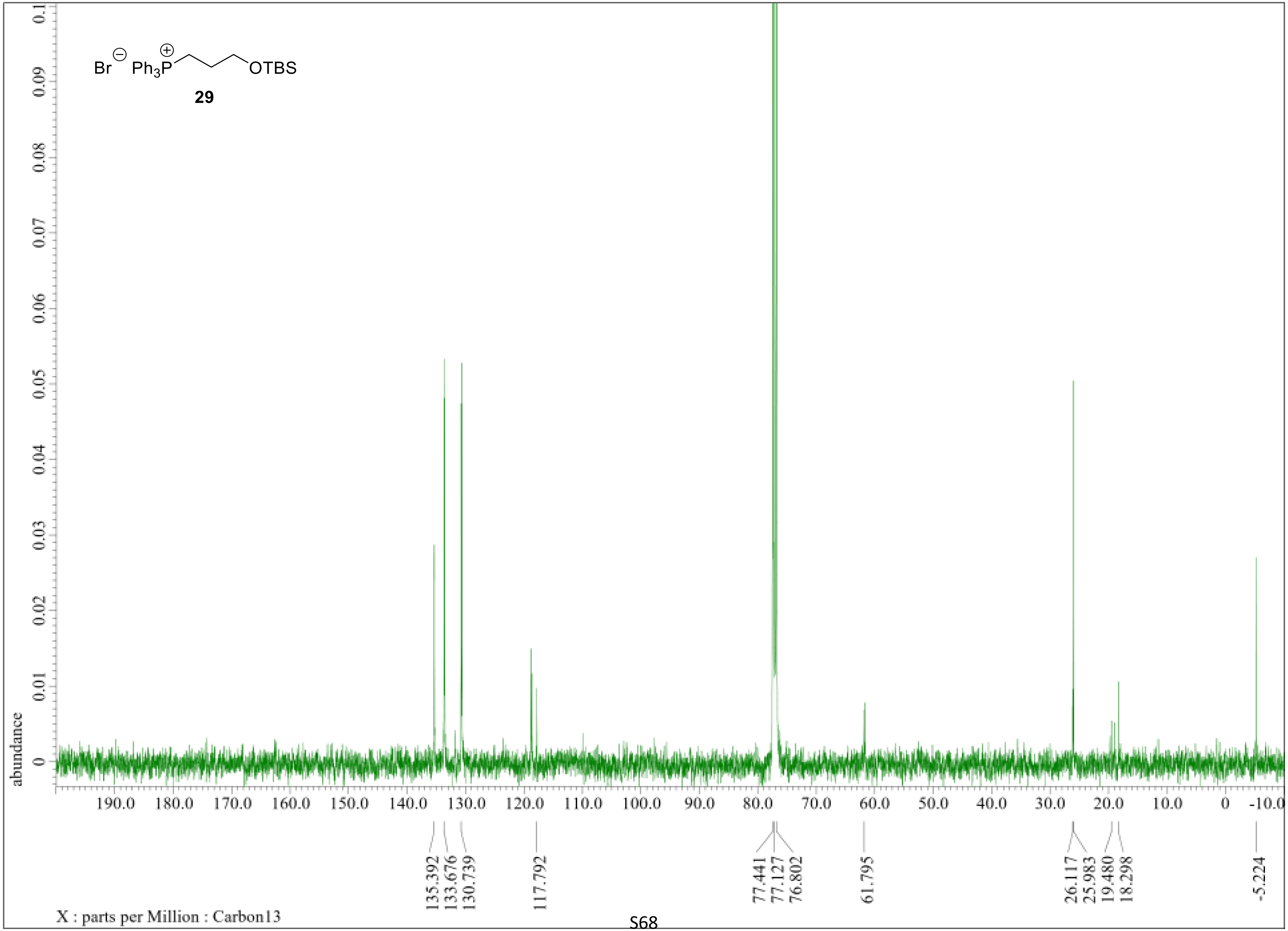

28

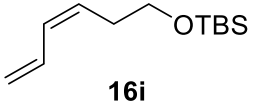
Br
Ph3P
OH
15.34
4.12
2.00
3.0
2.0
1.0
0
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


Br⊖ Ph3P⊕ OH
28
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
135.173
133.810
133.638
133.533
130.711
130.587
118.869
118.011
77.479
77.165
76.850
60.489
60.327
25.926
20.520
19.995
X : parts per Million : Carbon13

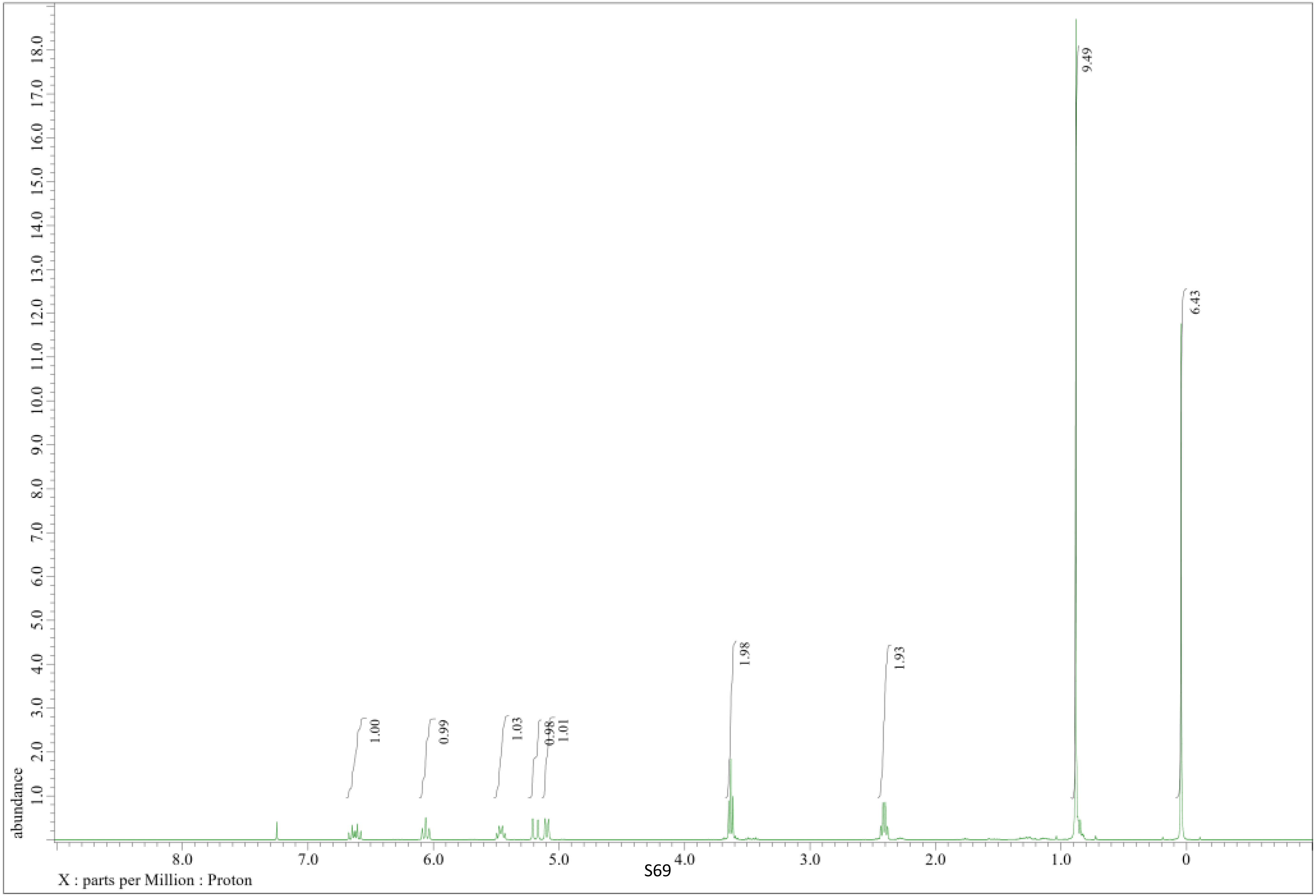

Br
Ph3P
OTBS
15.12
2.08
2.10
2.13
9.14
6.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

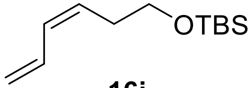
29


Br⁻ Ph3P⁺ OTBS
29
abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
135.392
133.676
130.739
117.792
77.441
77.127
76.802
61.795
26.117
25.983
19.480
18.298
-5.224
X : parts per Million : Carbon13

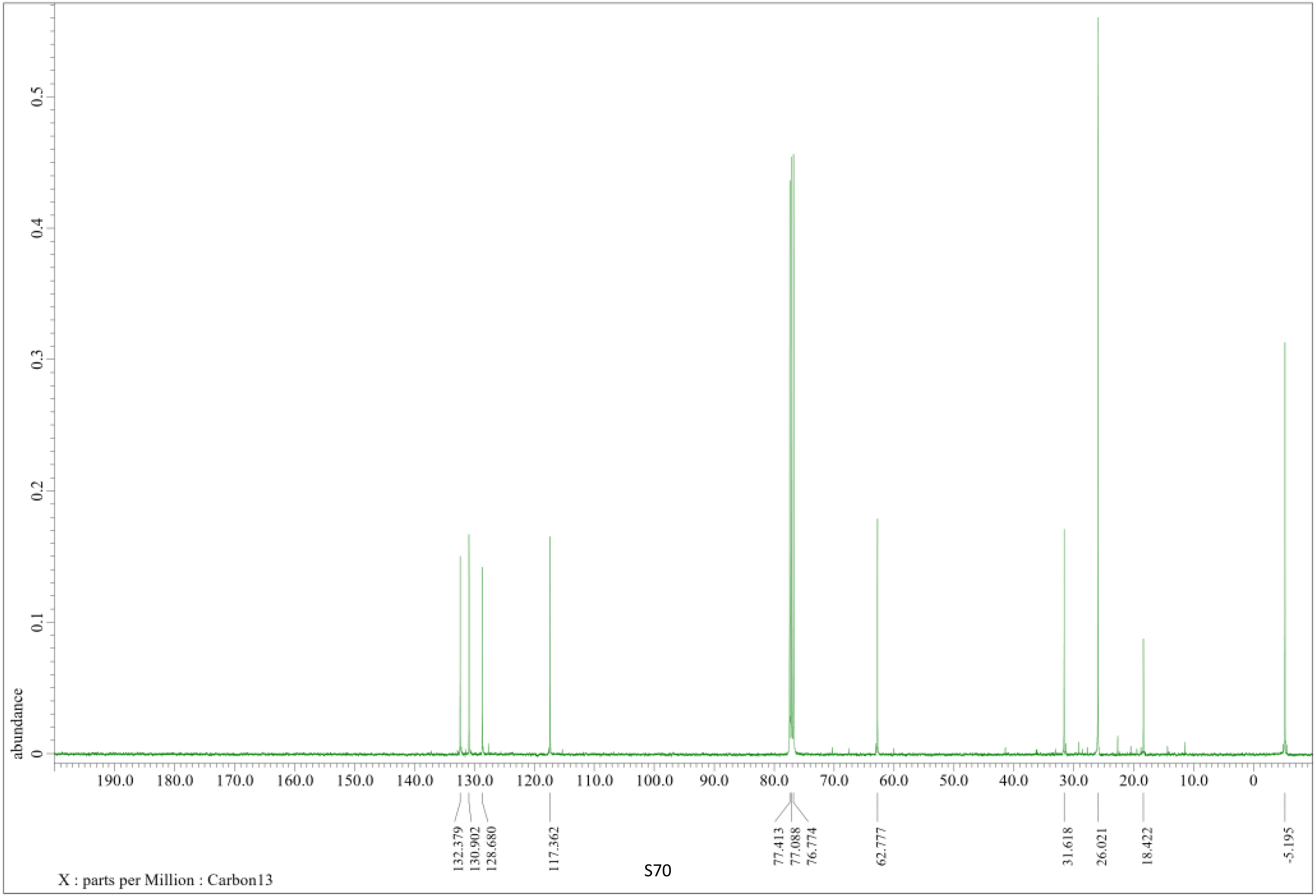

OTBS

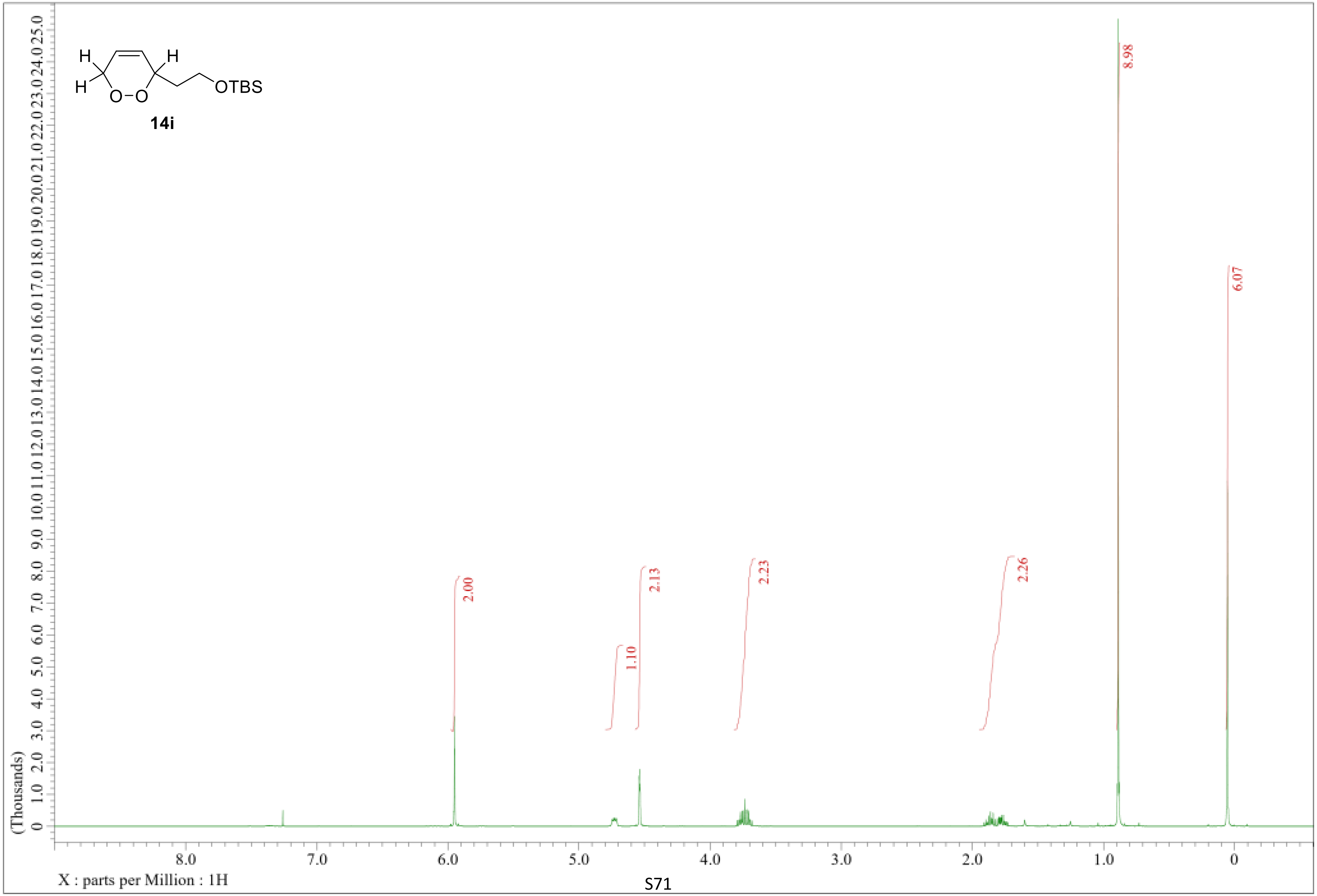
16i

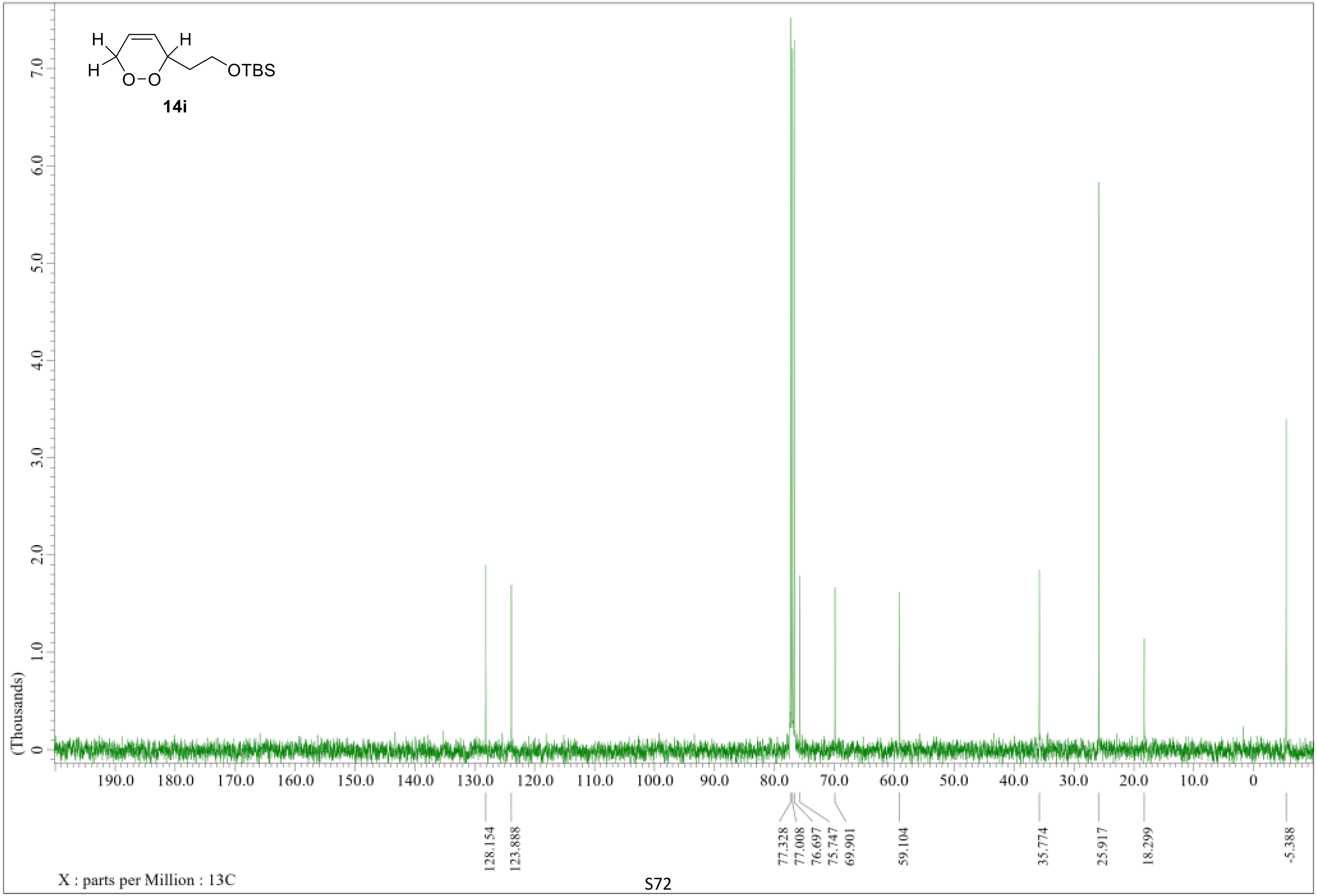

abundance
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
1.00
0.99
1.03
0.98
1.01
1.98
1.93
9.49
6.43
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

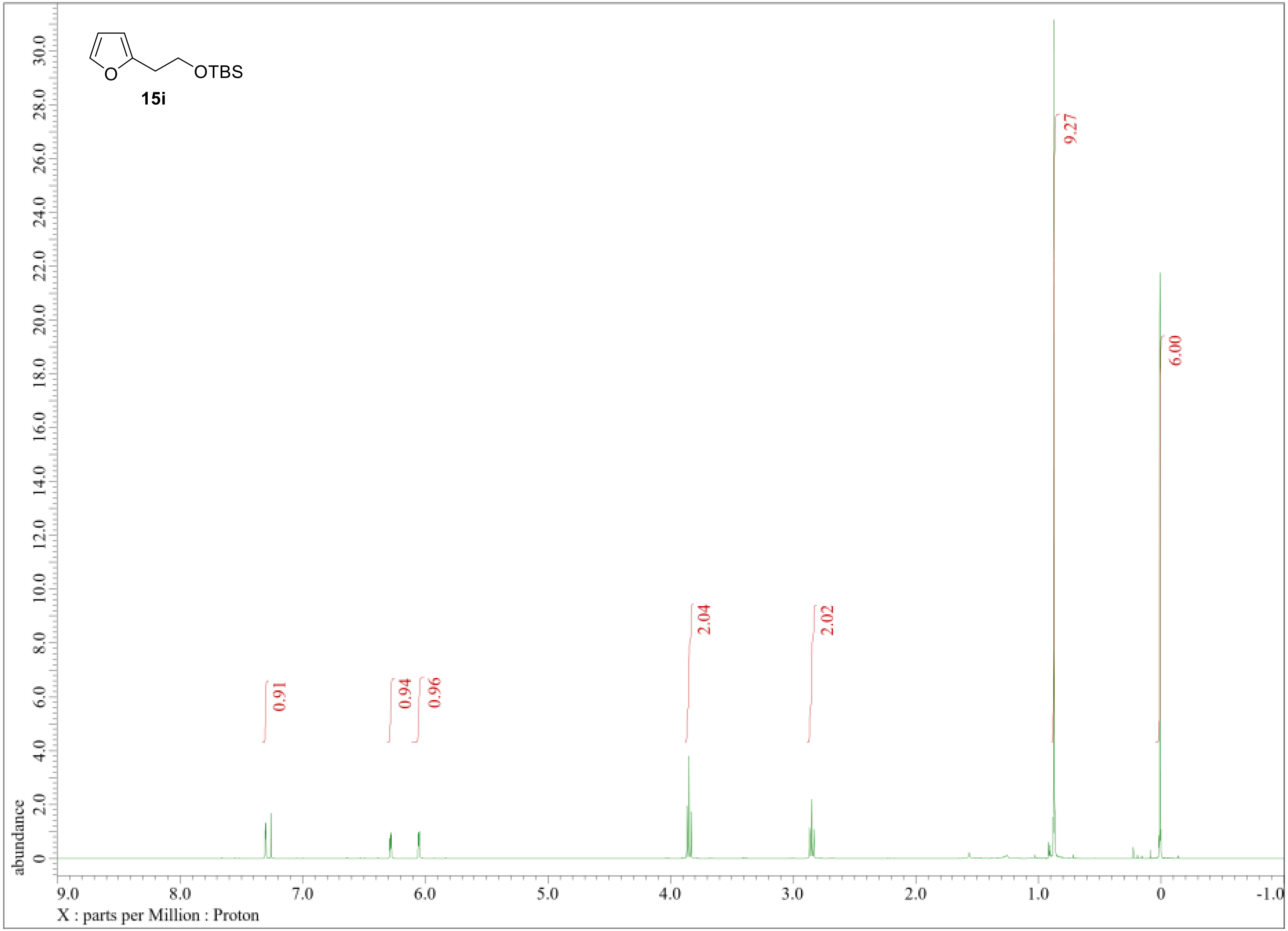

OTBS

16i


abundance
0
0.1
0.2
0.3
0.4
0.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
132.379
130.902
128.680
117.362
77.413
77.088
76.774
62.777
31.618
26.021
18.422
-5.195
X : parts per Million : Carbon13

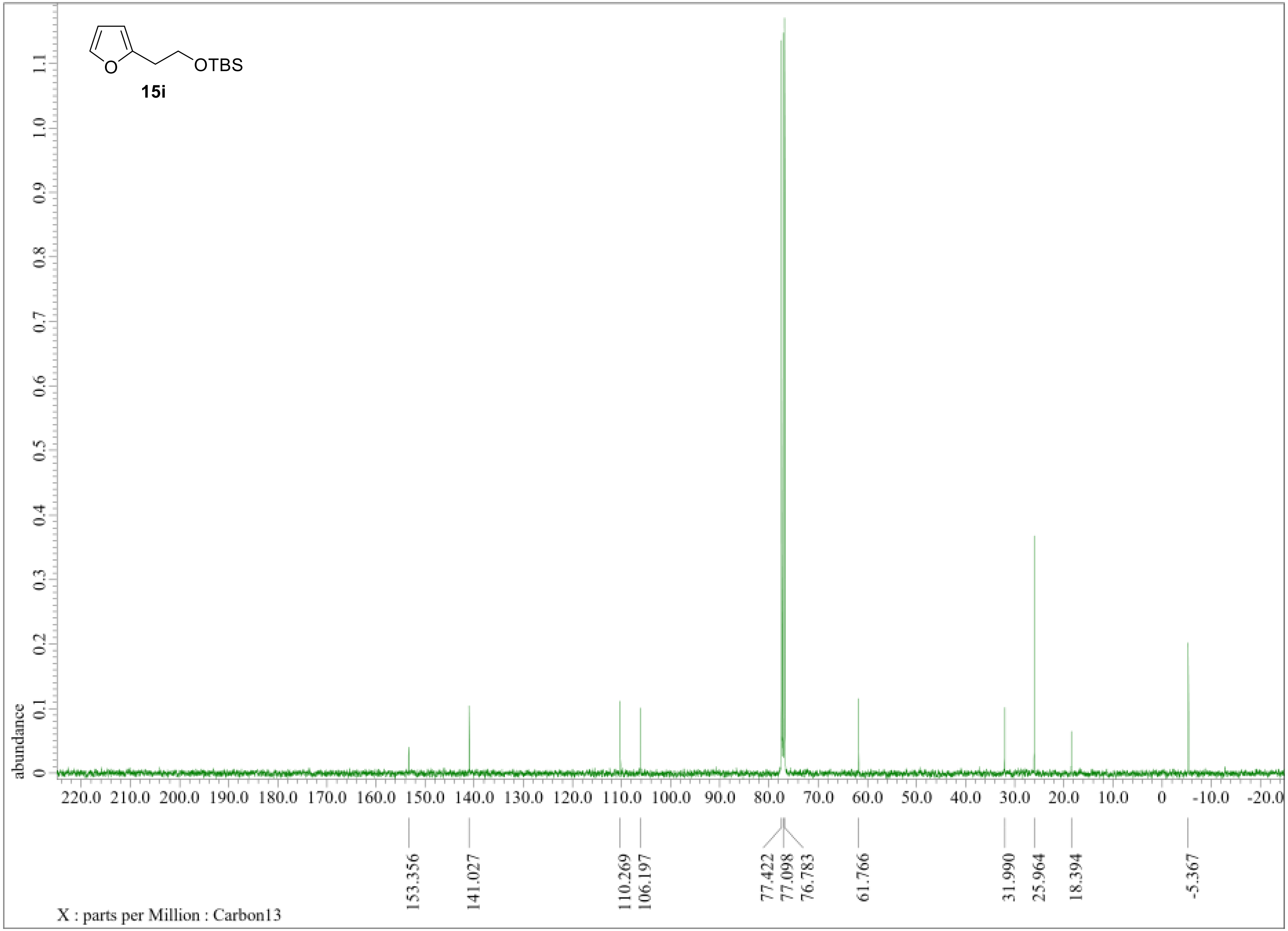

14i
OTBS
(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
23.0
24.0
25.0
2.00
1.10
2.13
2.23
2.26
8.98
6.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

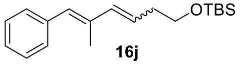

H
H
H
O–O
OTBS
14i
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
(Thousands)
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
128.154
123.888
77.328
77.008
76.697
75.747
69.901
59.104
35.774
25.917
18.299
-5.388
X : parts per Million : 13C



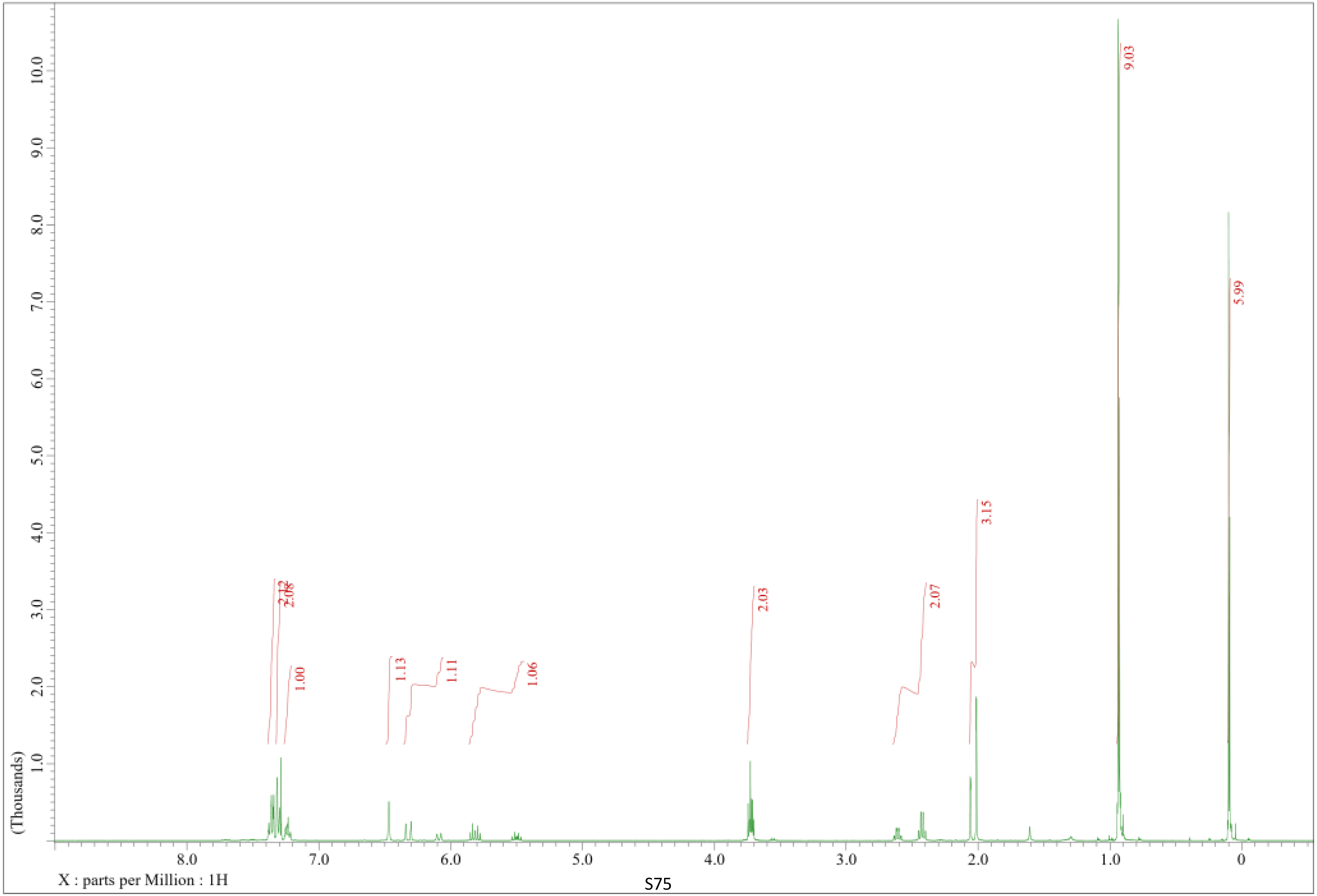
15i

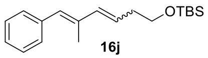
OTBS
O
abundance
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
26.0
28.0
30.0
0.91
0.94
0.96
2.04
2.02
9.27
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
X : parts per Million : Proton


OTBS
O
15i
abundance
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
153.356
141.027
110.269
106.197
77.422
77.098
76.783
61.766
31.990
25.964
18.394
-5.367
X : parts per Million : Carbon13

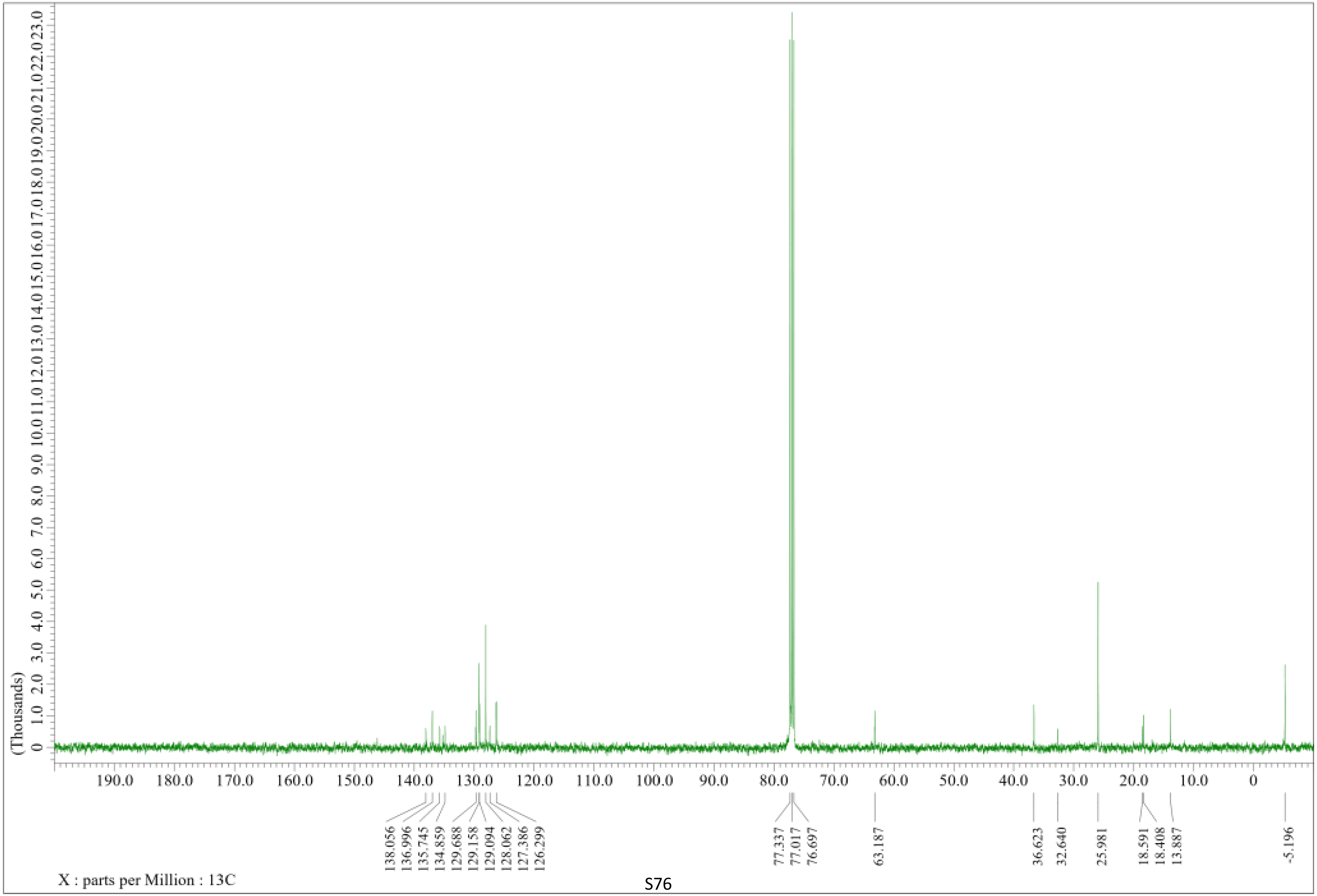

OTBS

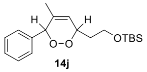
16j


(Thousands)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
2.12
2.08
1.00
1.13
1.11
1.06
2.03
2.07
3.15
9.03
5.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

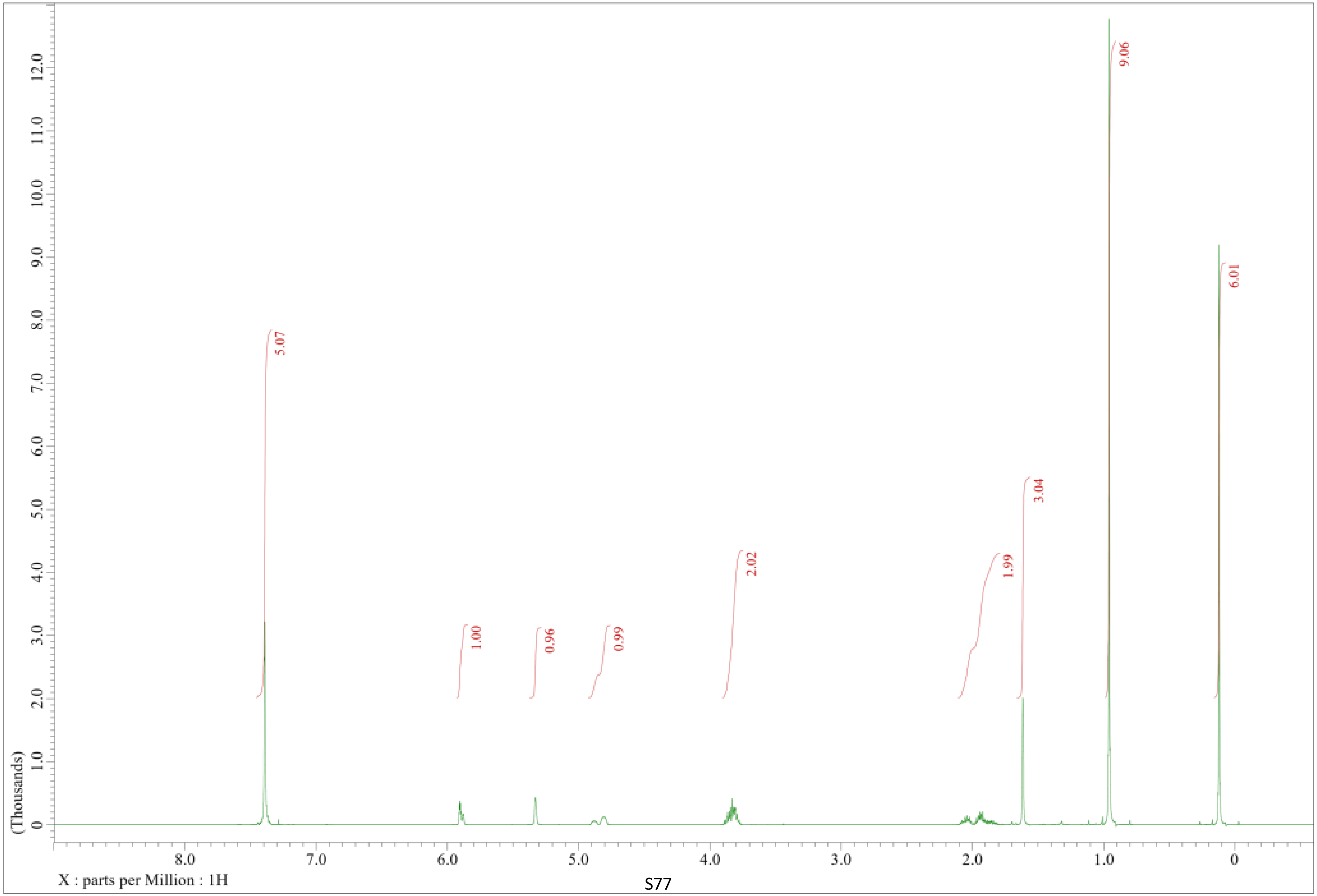

OTBS

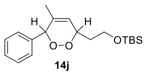
16j


(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
23.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.056
136.996
135.745
134.859
129.688
129.158
129.094
128.062
127.386
126.299
77.337
77.017
76.697
63.187
36.623
32.640
25.981
18.591
18.408
13.887
-5.196
X : parts per Million : 13C

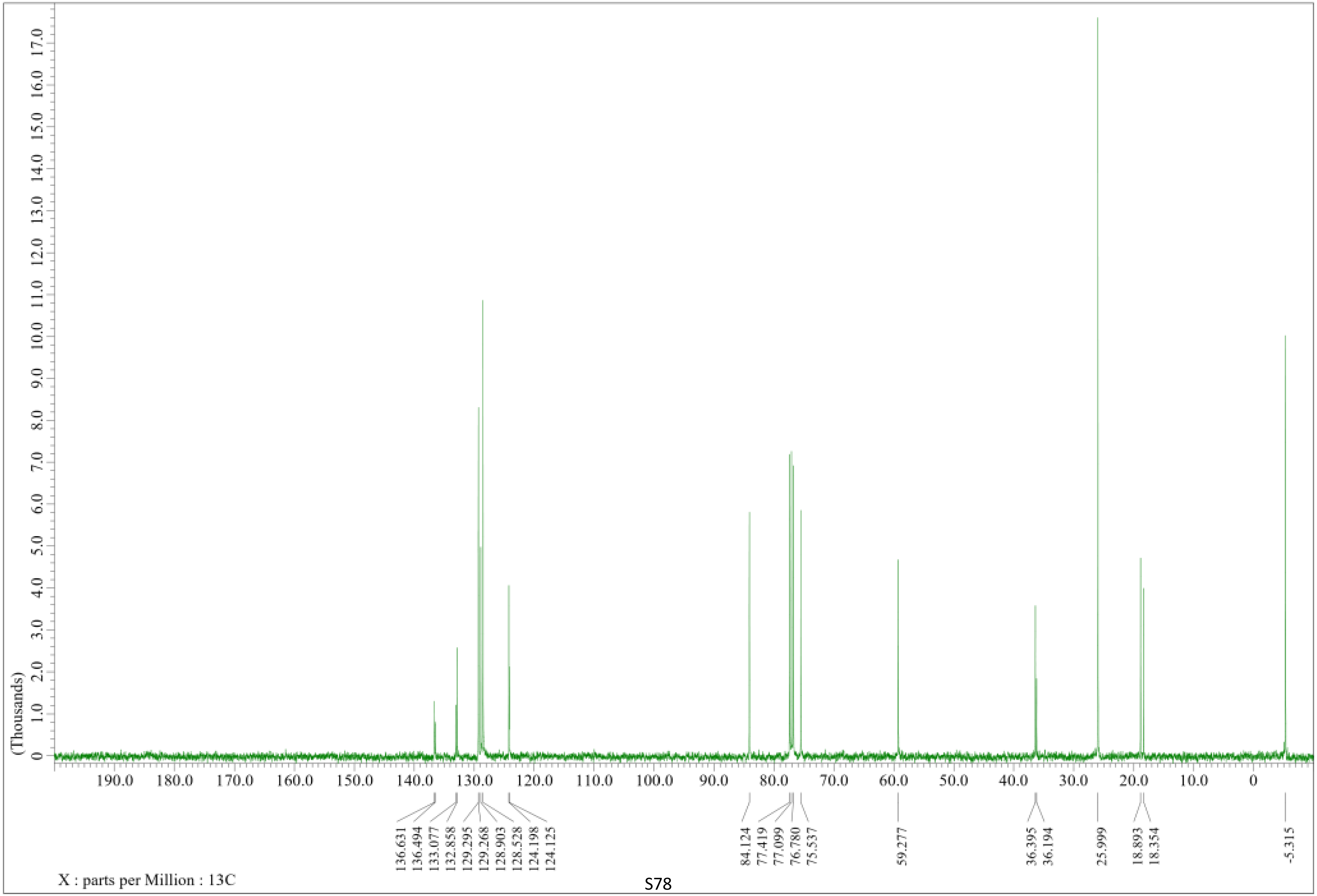

H
H
O–O
OTBS

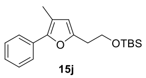
14j


5.07
1.00
0.96
0.99
2.02
1.99
3.04
9.06
6.01
(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

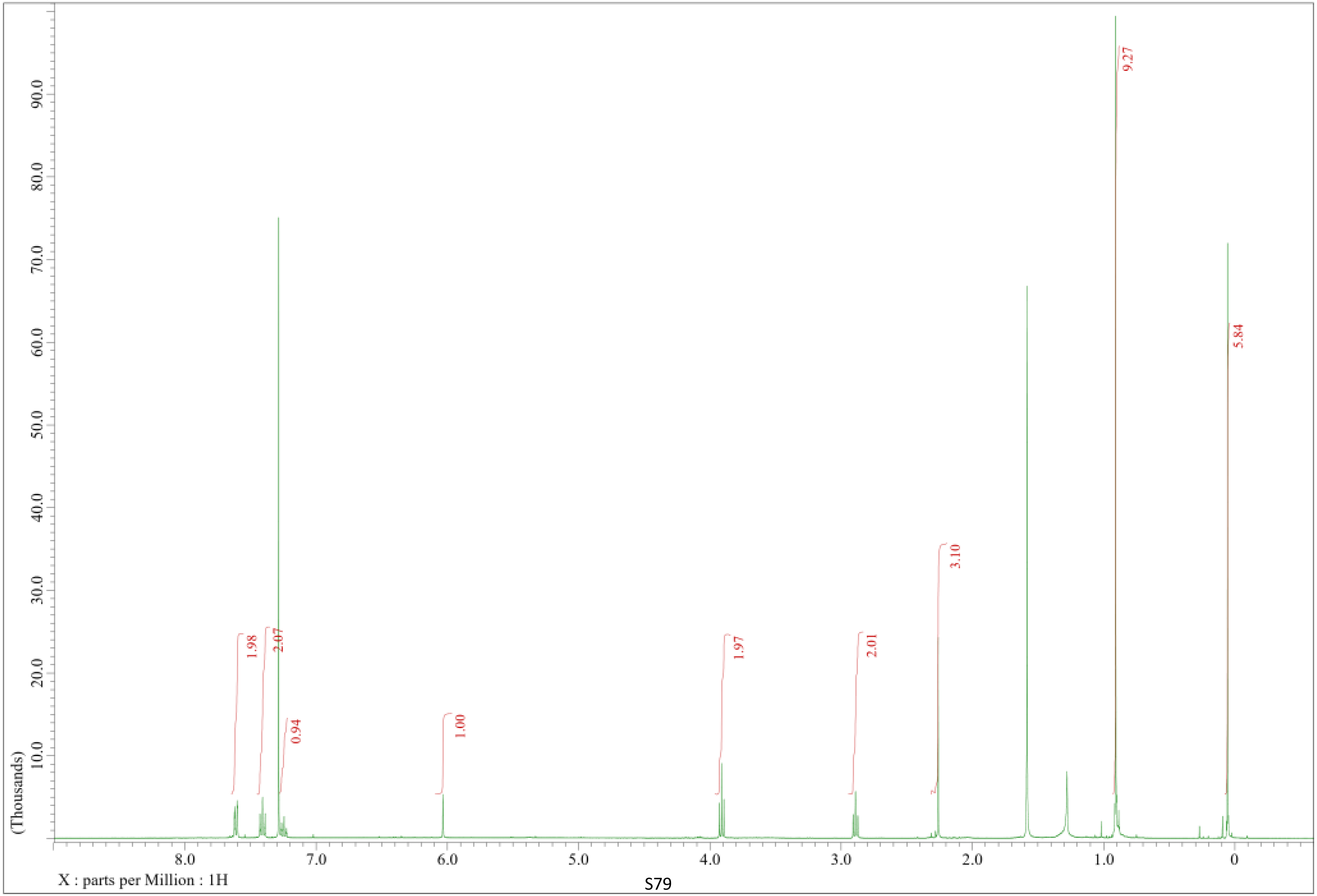

H
H
O–O
OTBS

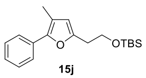
14j


(Thousands)
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
136.631
136.494
133.077
132.858
129.295
129.268
128.903
128.528
124.198
124.125
84.124
77.419
77.099
76.780
75.537
59.277
36.395
36.194
25.999
18.893
18.354
-5.315
X : parts per Million : 13C

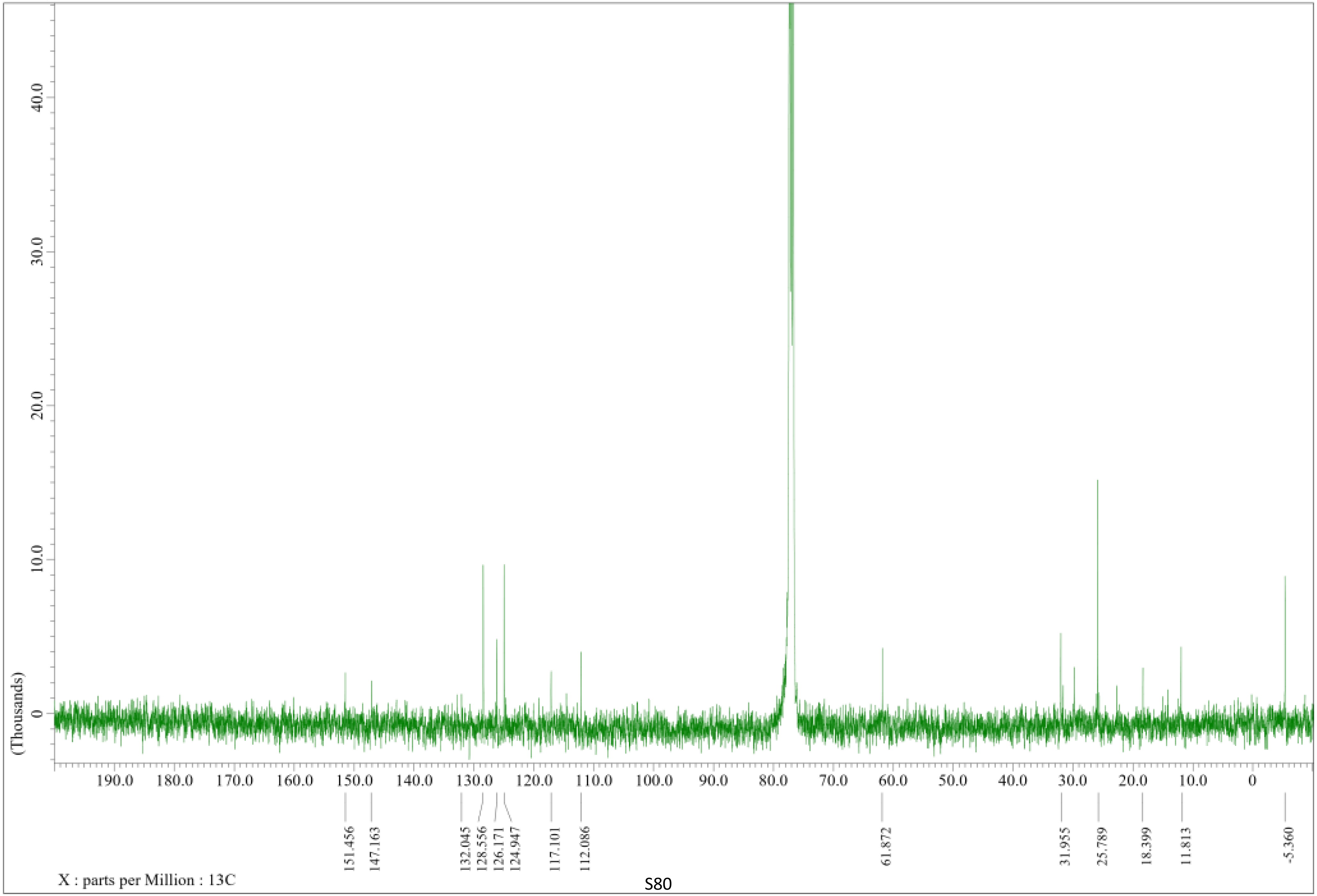

OTBS
O

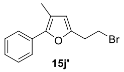
15j


(Thousands)
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
1.98
2.07
0.94
1.00
1.97
2.01
3.10
9.27
5.84
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

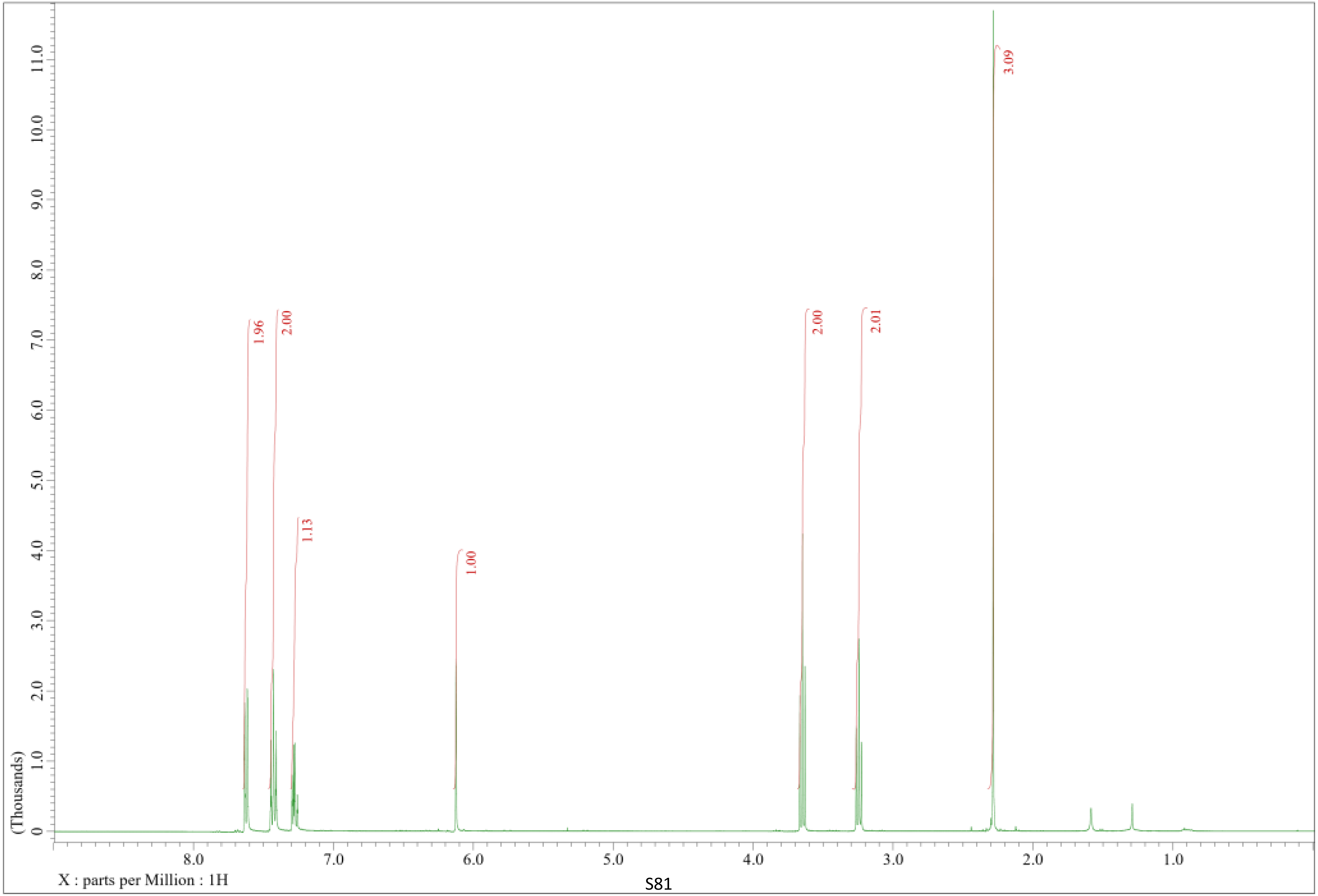

OTBS
O

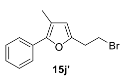
15j


(Thousands)
40.0
30.0
20.0
10.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
151.456
147.163
132.045
128.556
126.171
124.947
117.101
112.086
61.872
31.955
25.789
18.399
11.813
-5.360
X : parts per Million : 13C

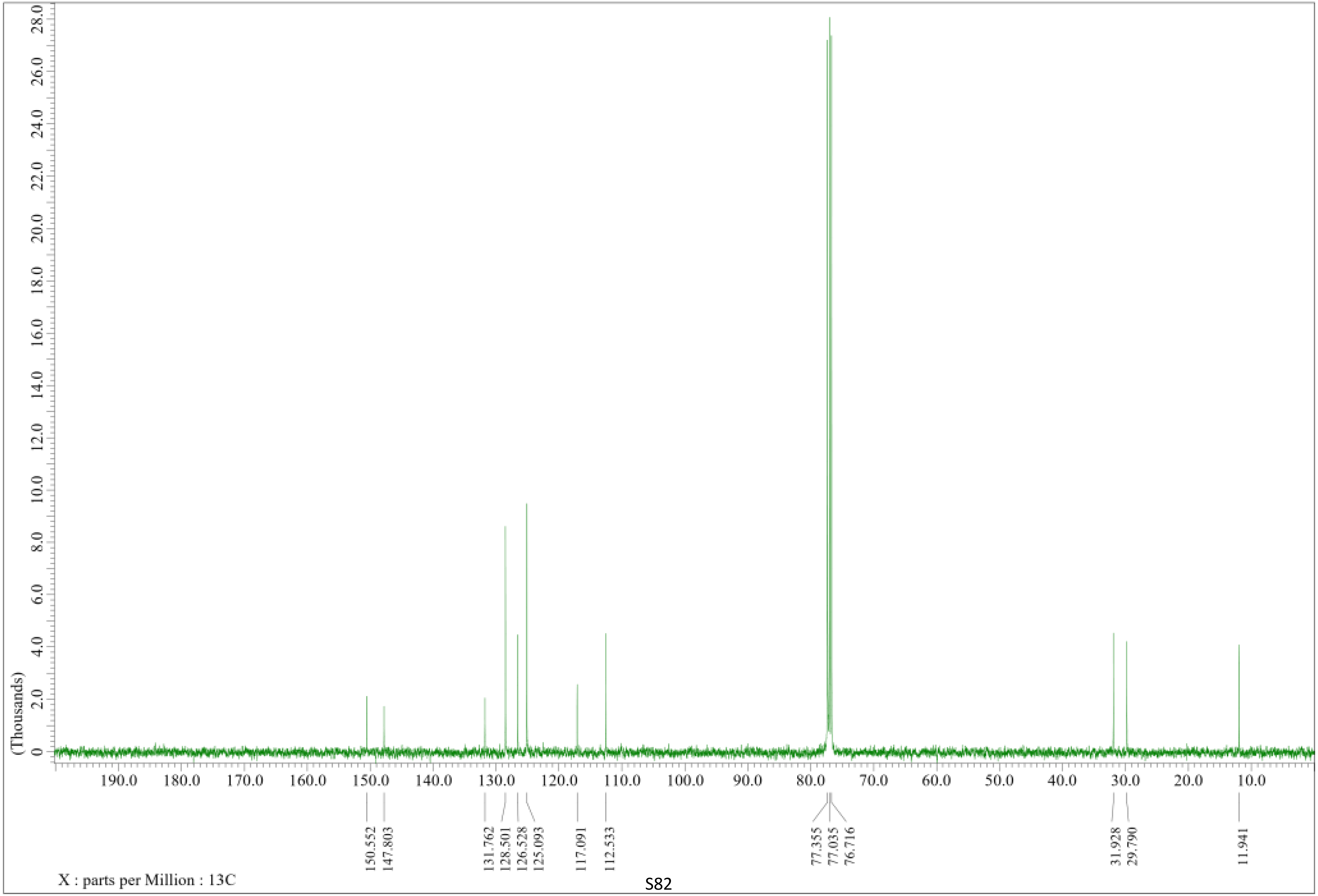

O
Br

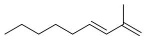
15j'


1.96
2.00
1.13
1.00
2.00
2.01
3.09
(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H

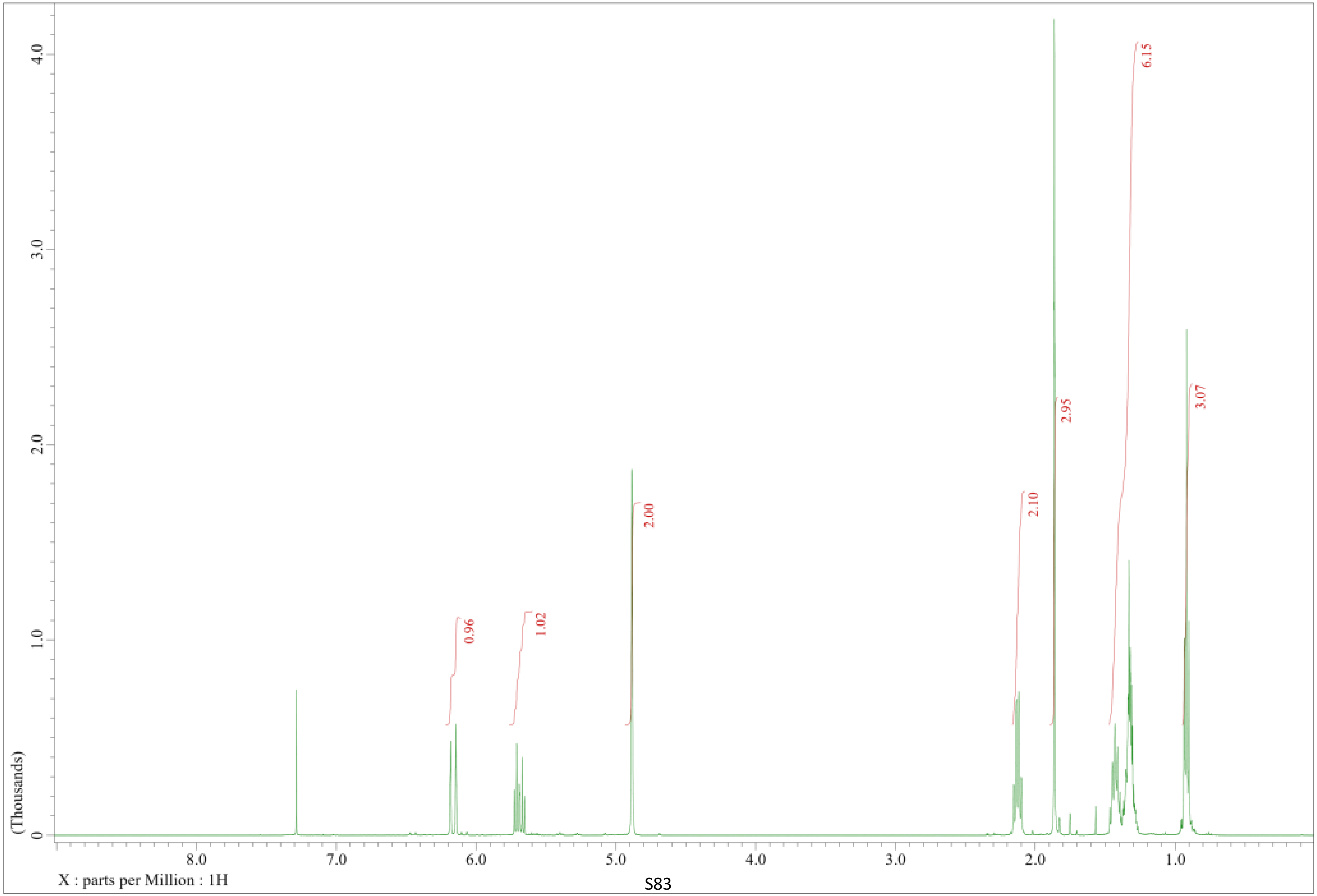


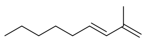
15j'


(Thousands)
28.0
26.0
24.0
22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
150.552
147.803
131.762
128.501
126.528
125.093
117.091
112.533
77.355
77.035
76.716
31.928
29.790
11.941
X : parts per Million : 13C

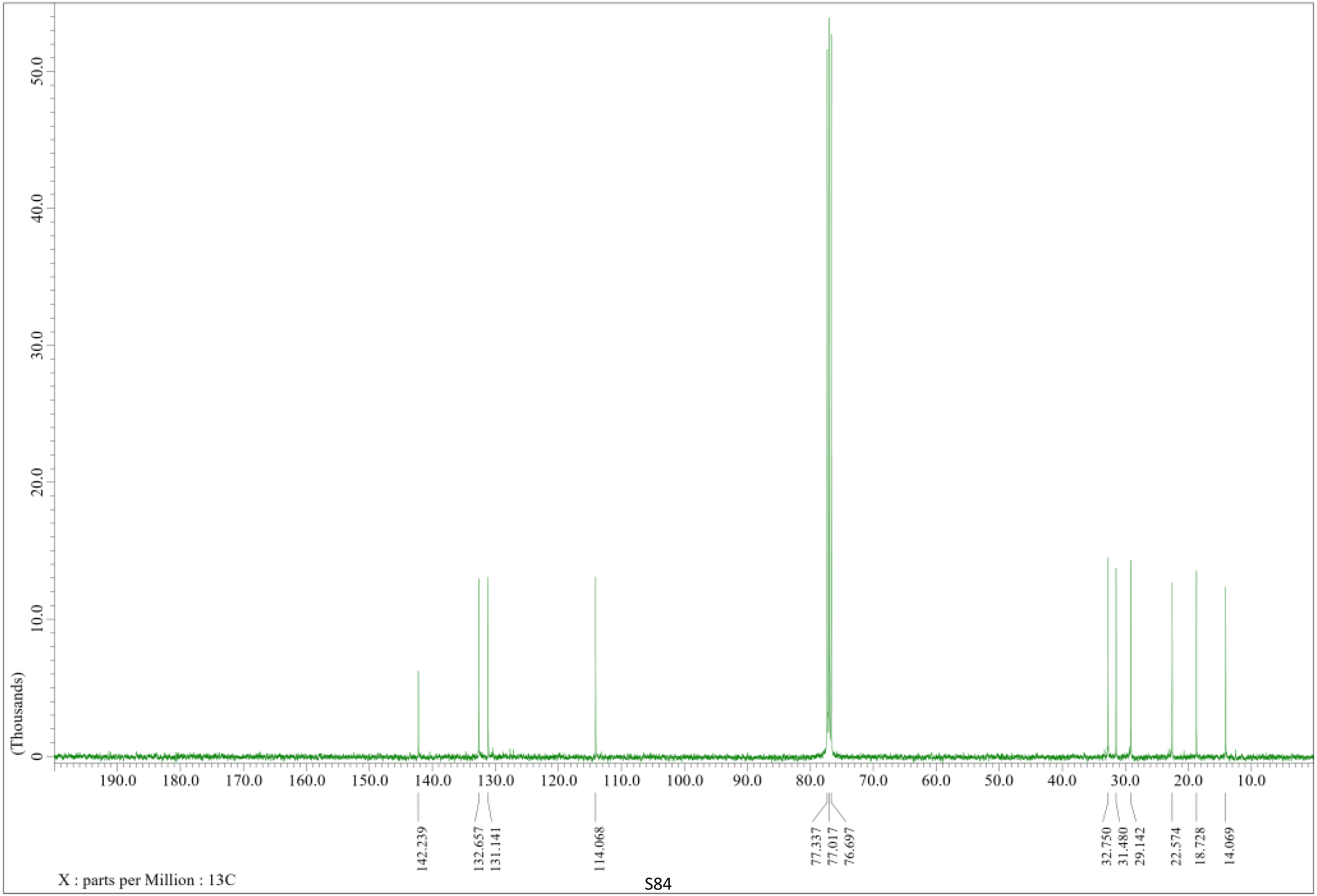


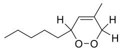
16k


4.0
3.0
2.0
1.0
0
(Thousands)
0.96
1.02
2.00
2.10
2.95
6.15
3.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H

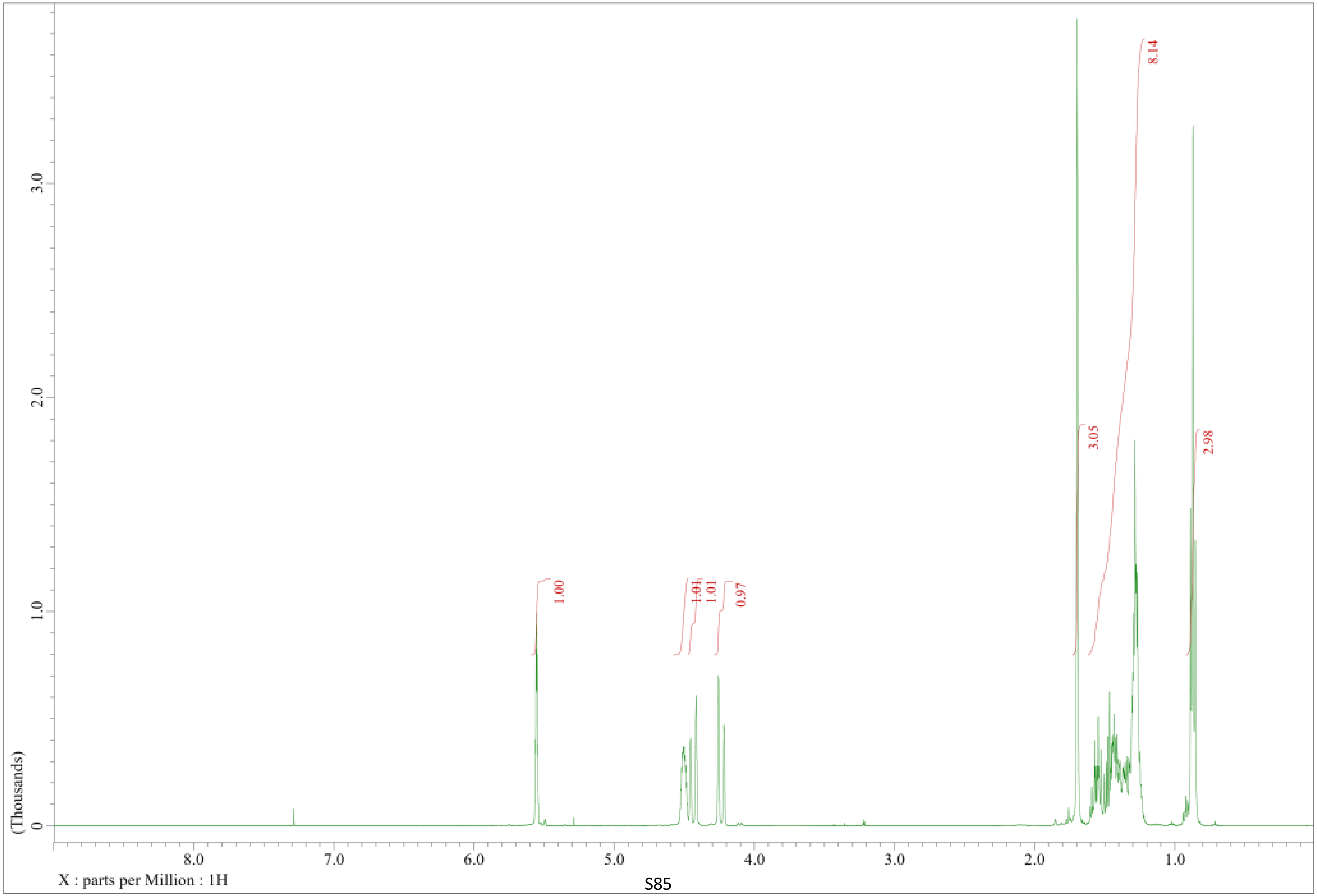


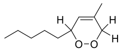
16k


50.0
40.0
30.0
20.0
10.0
0
(Thousands)
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
142.239
132.657
131.141
114.068
77.337
77.017
76.697
32.750
31.480
29.142
22.574
18.728
14.069
X : parts per Million : 13C

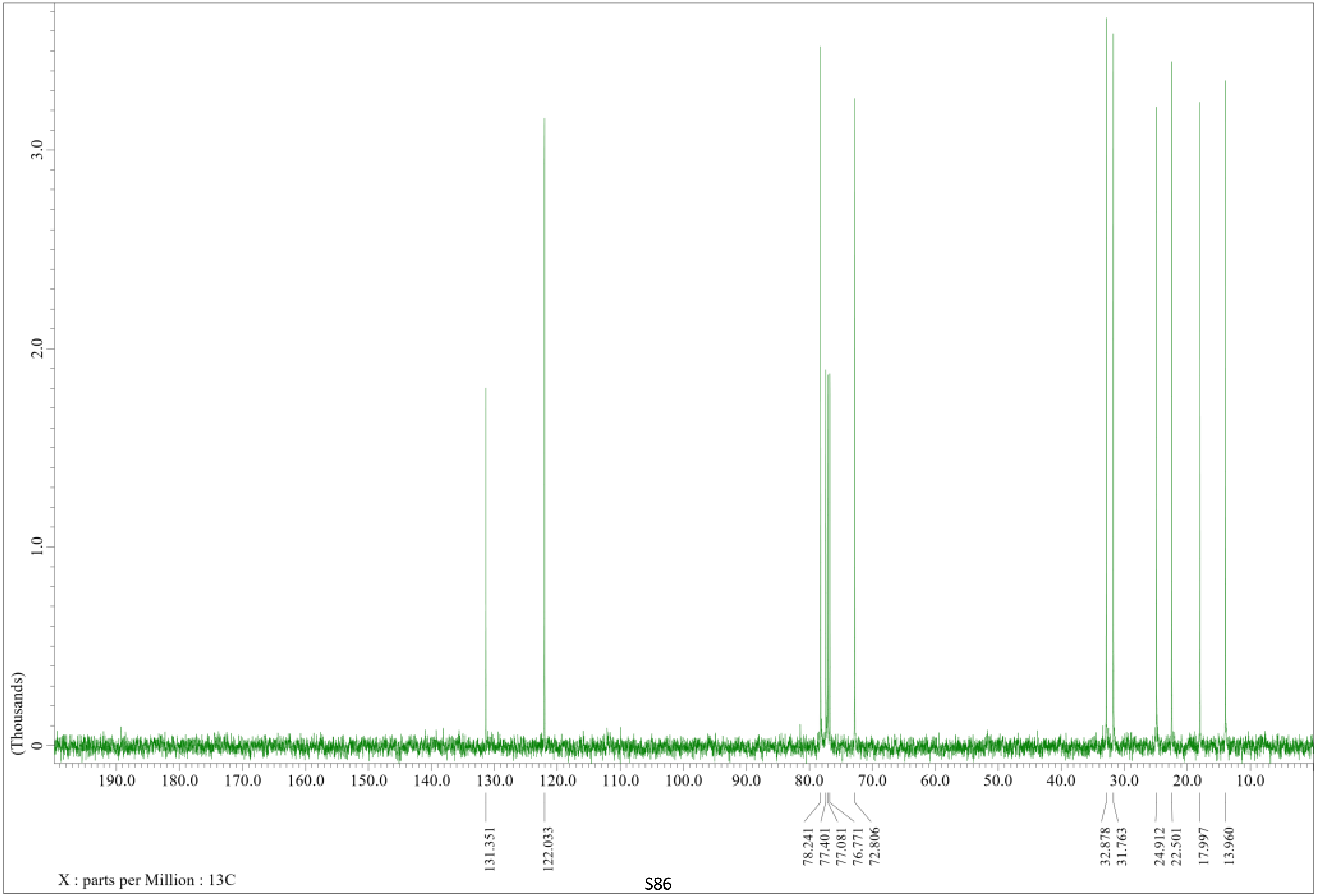

H
H
H
O–O

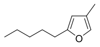
14k


(Thousands)
0
1.0
2.0
3.0
1.00
1.01
1.01
0.97
3.05
8.14
2.98
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H

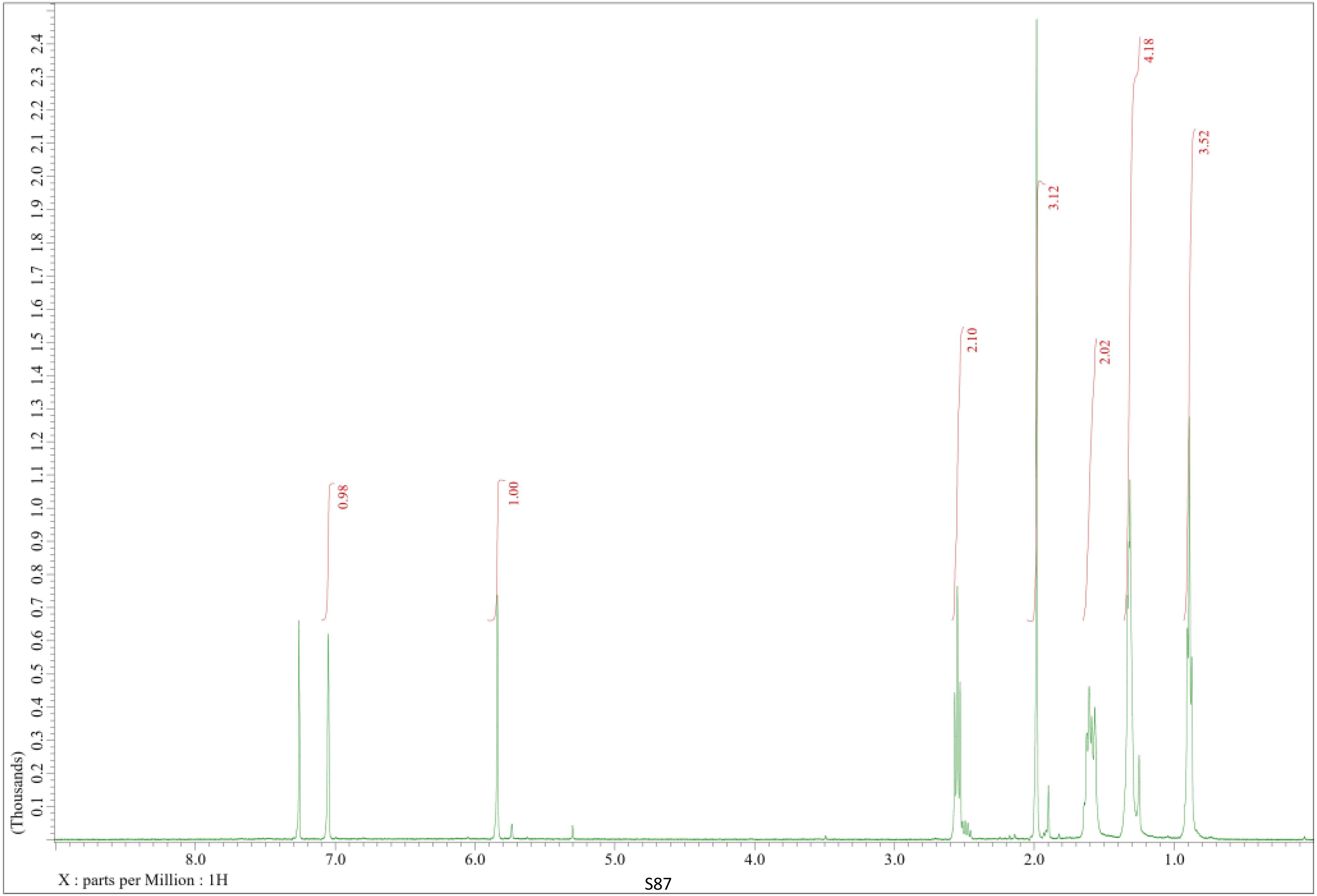

H
H
H
O–O

14k

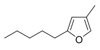

(Thousands)
0
1.0
2.0
3.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
131.351
122.033
78.241
77.401
77.081
76.771
72.806
32.878
31.763
24.912
22.501
17.997
13.960
X : parts per Million : 13C



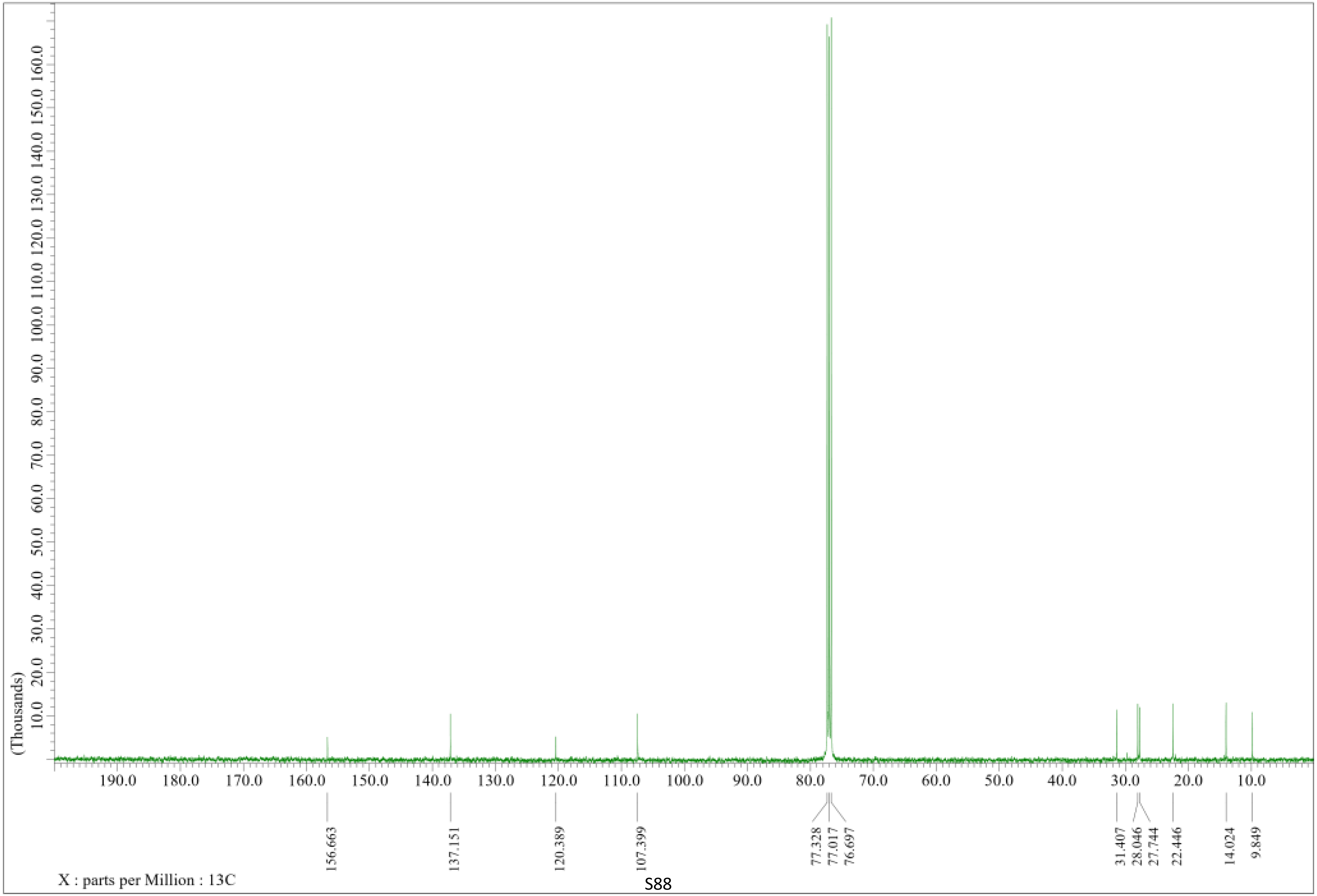
15k

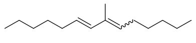


0.98
1.00
2.10
3.12
2.02
4.18
3.52
(Thousands)
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H

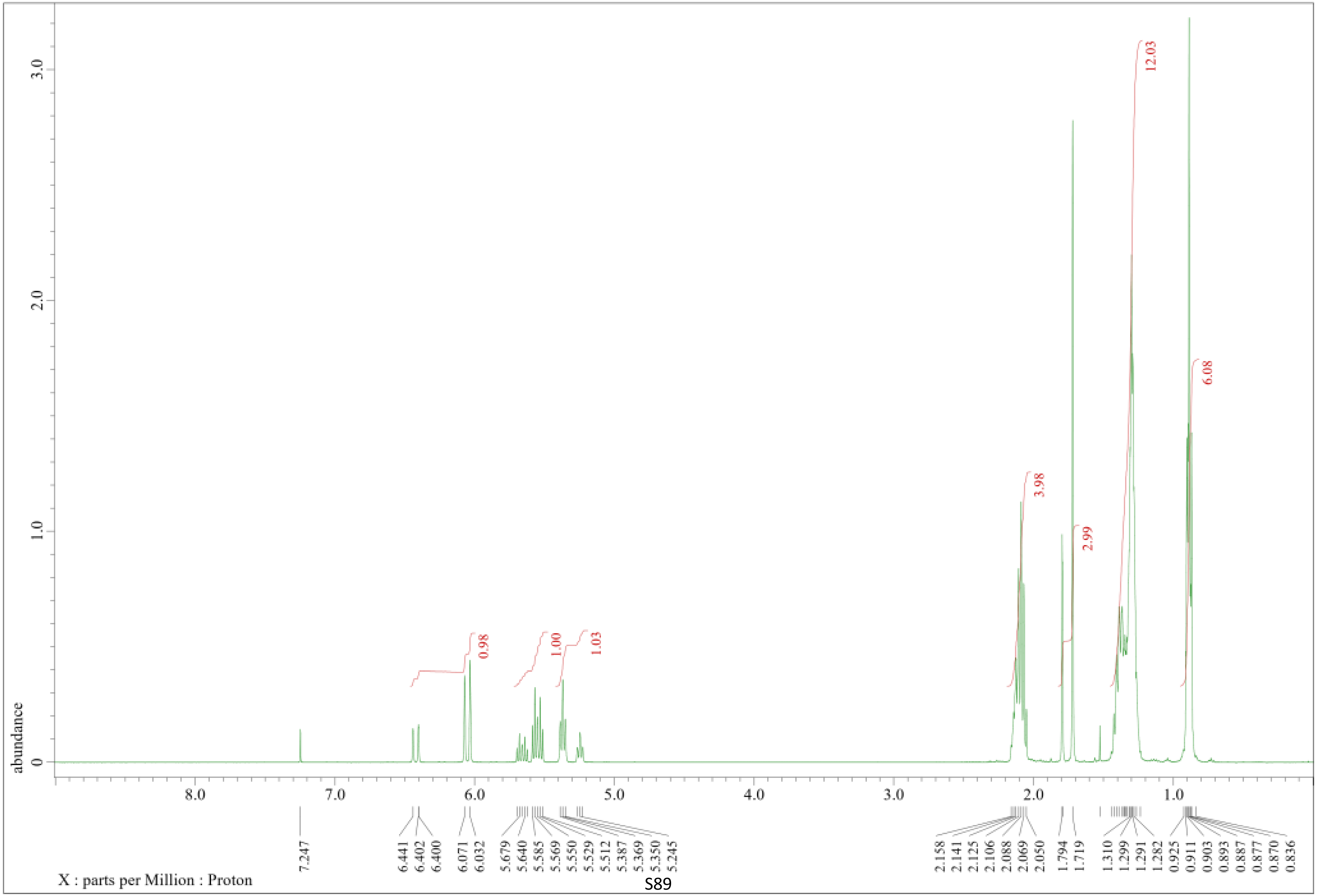


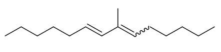
15k


(Thousands)
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
156.663
137.151
120.389
107.399
77.328
77.017
76.697
31.407
28.046
27.744
22.446
14.024
9.849
X : parts per Million : 13C

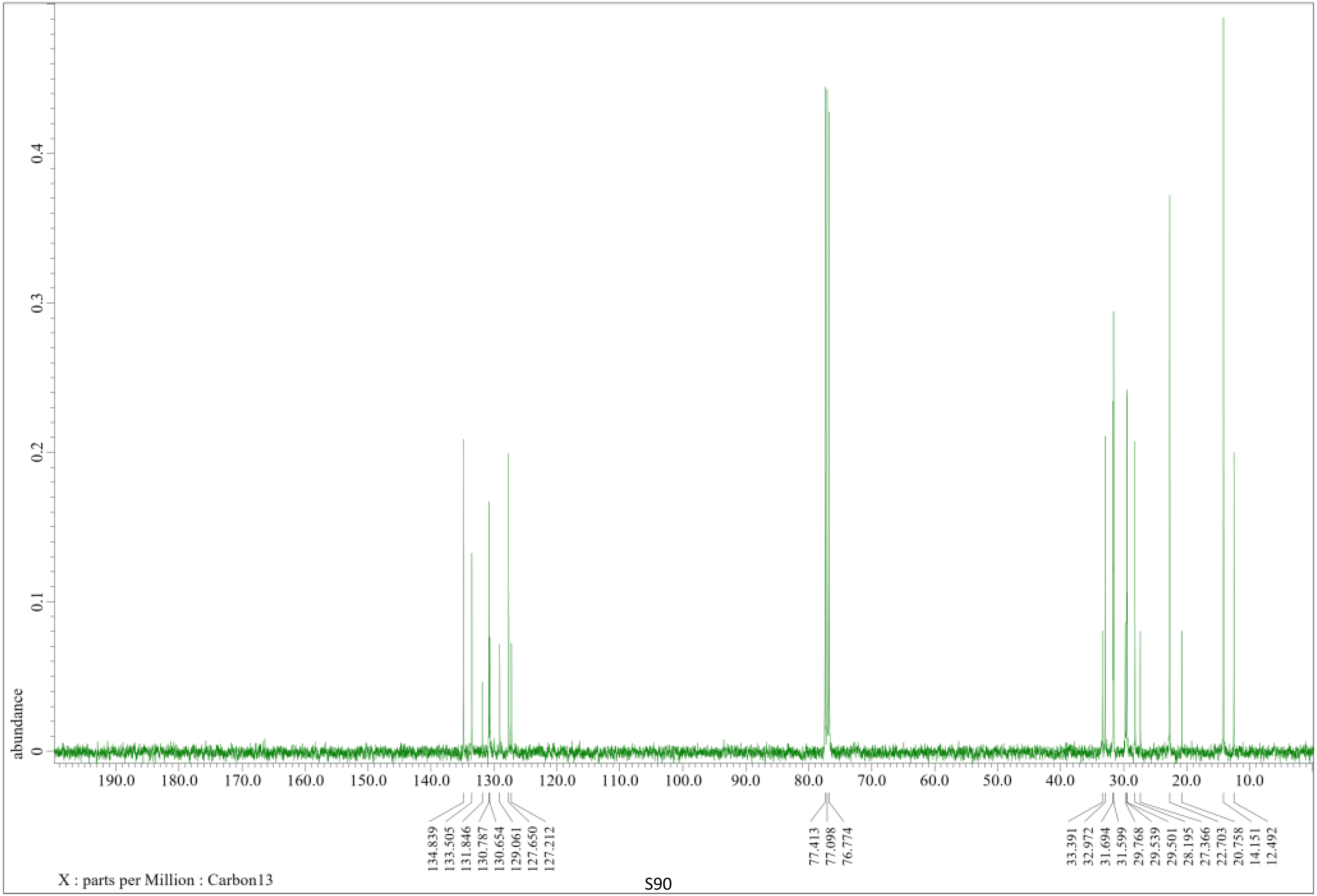


16l

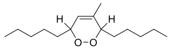

abundance
0
1.0
2.0
3.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton
0.98
1.00
1.03
3.98
2.99
12.03
6.08
7.247
6.441
6.402
6.400
6.071
6.032
5.679
5.640
5.585
5.569
5.550
5.529
5.512
5.387
5.369
5.350
5.245
2.158
2.141
2.125
2.106
2.088
2.069
2.050
1.794
1.719
1.310
1.299
1.291
1.282
0.925
0.911
0.903
0.893
0.887
0.877
0.870
0.836



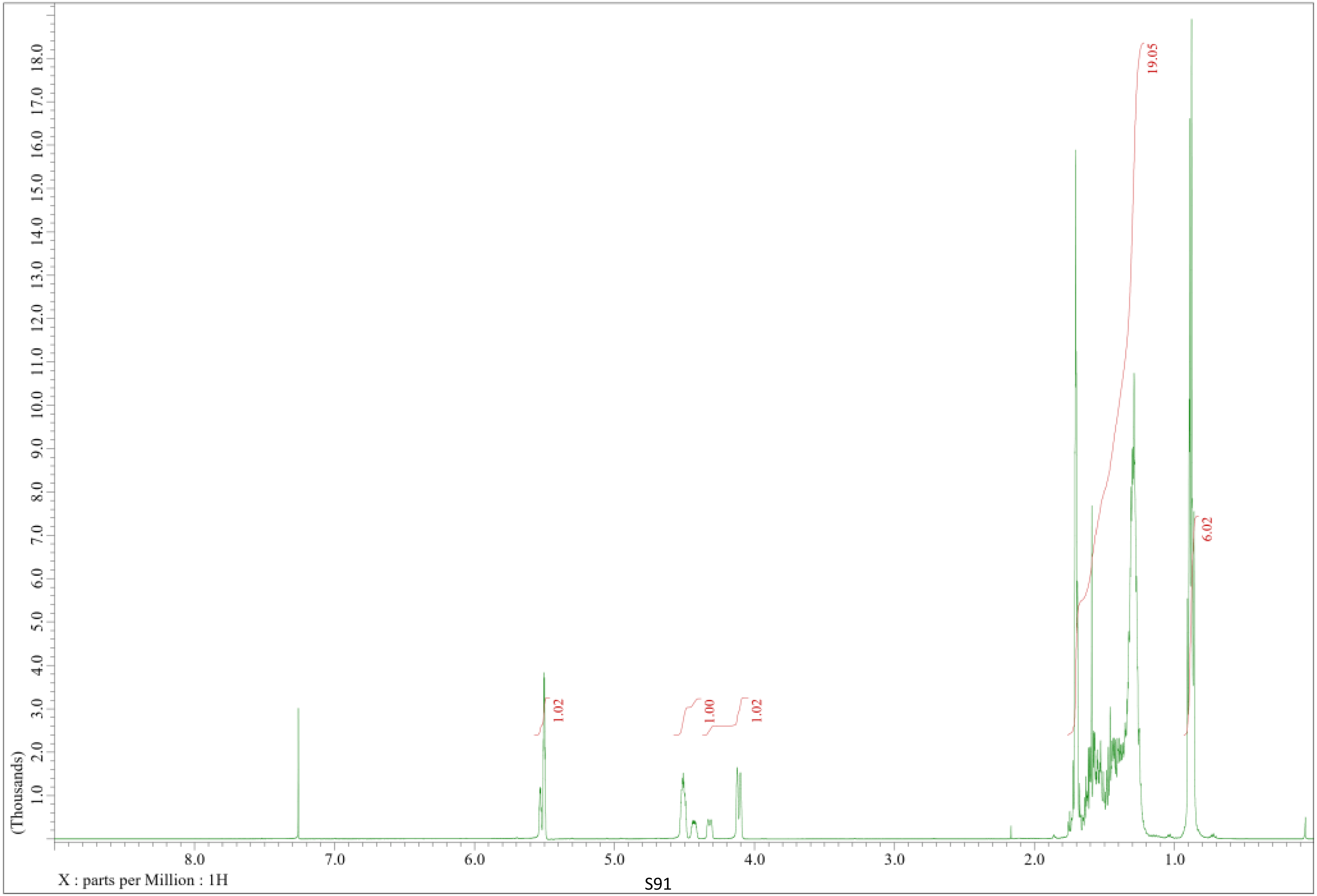
16l

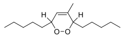


abundance
0
0.1
0.2
0.3
0.4
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
134.839
133.505
131.846
130.787
130.654
129.061
127.650
127.212
77.413
77.098
76.774
33.391
32.972
31.694
31.599
29.768
29.539
29.501
28.195
27.366
22.703
20.758
14.151
12.492
X : parts per Million : Carbon13

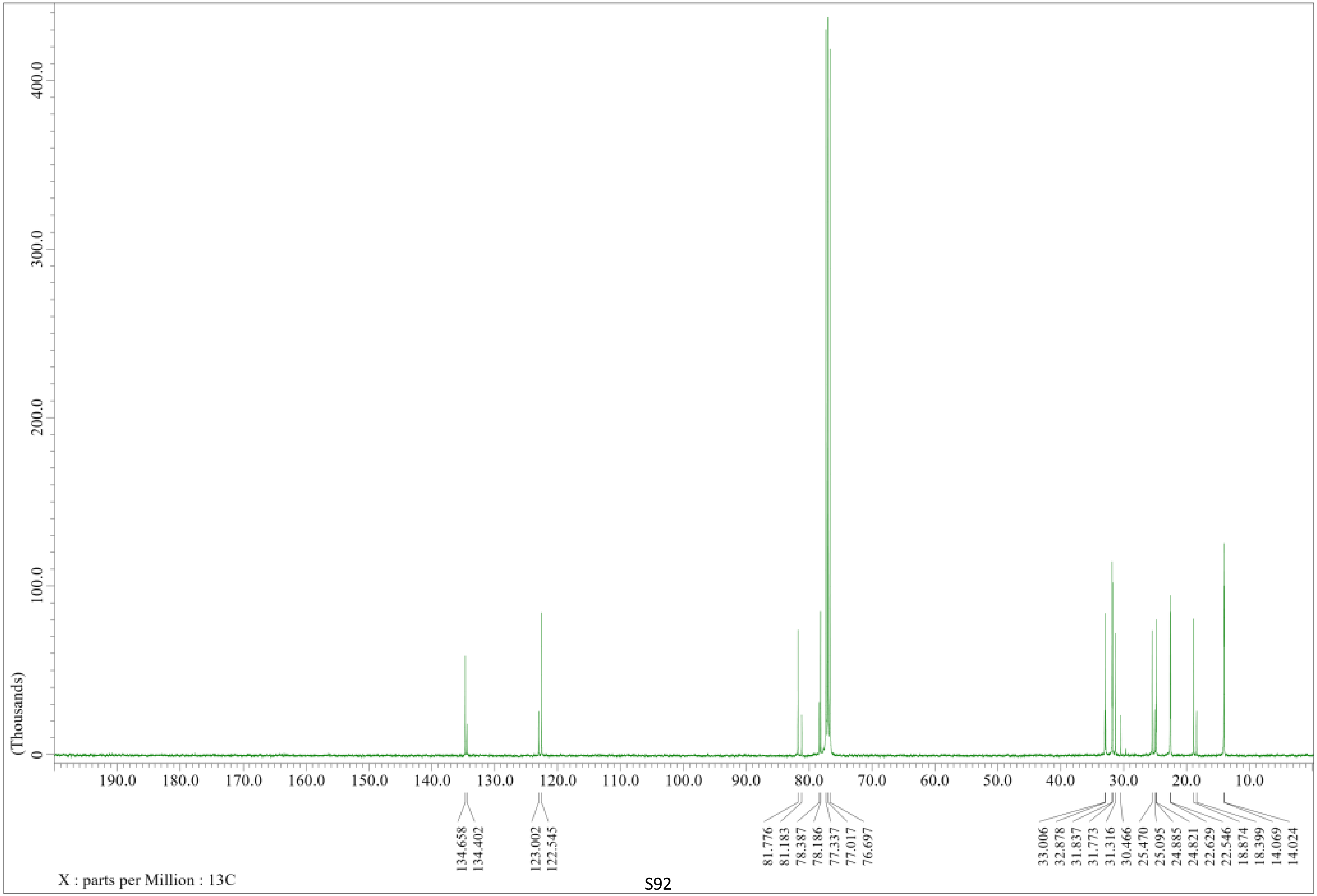

H
H
O–O

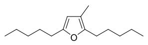
14l


(Thousands)
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
1.02
1.00
1.02
19.05
6.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H

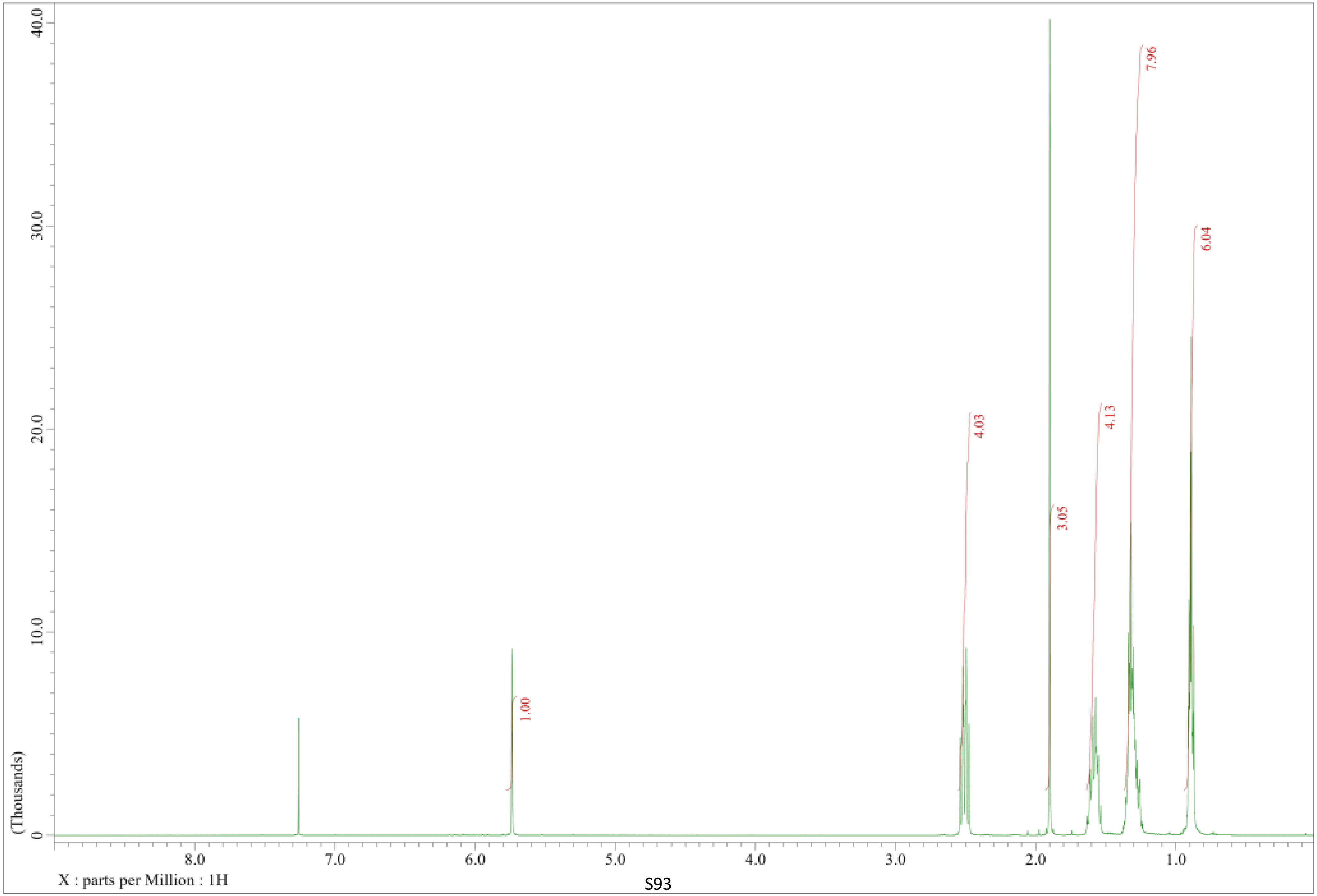


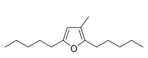
14l


(Thousands)
400.0
300.0
200.0
100.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
134.658
134.402
123.002
122.545
81.776
81.183
78.387
78.186
77.337
77.017
76.697
33.006
32.878
31.837
31.773
31.316
30.466
25.470
25.095
24.885
24.821
22.629
22.546
18.874
18.399
14.069
14.024
X : parts per Million : 13C

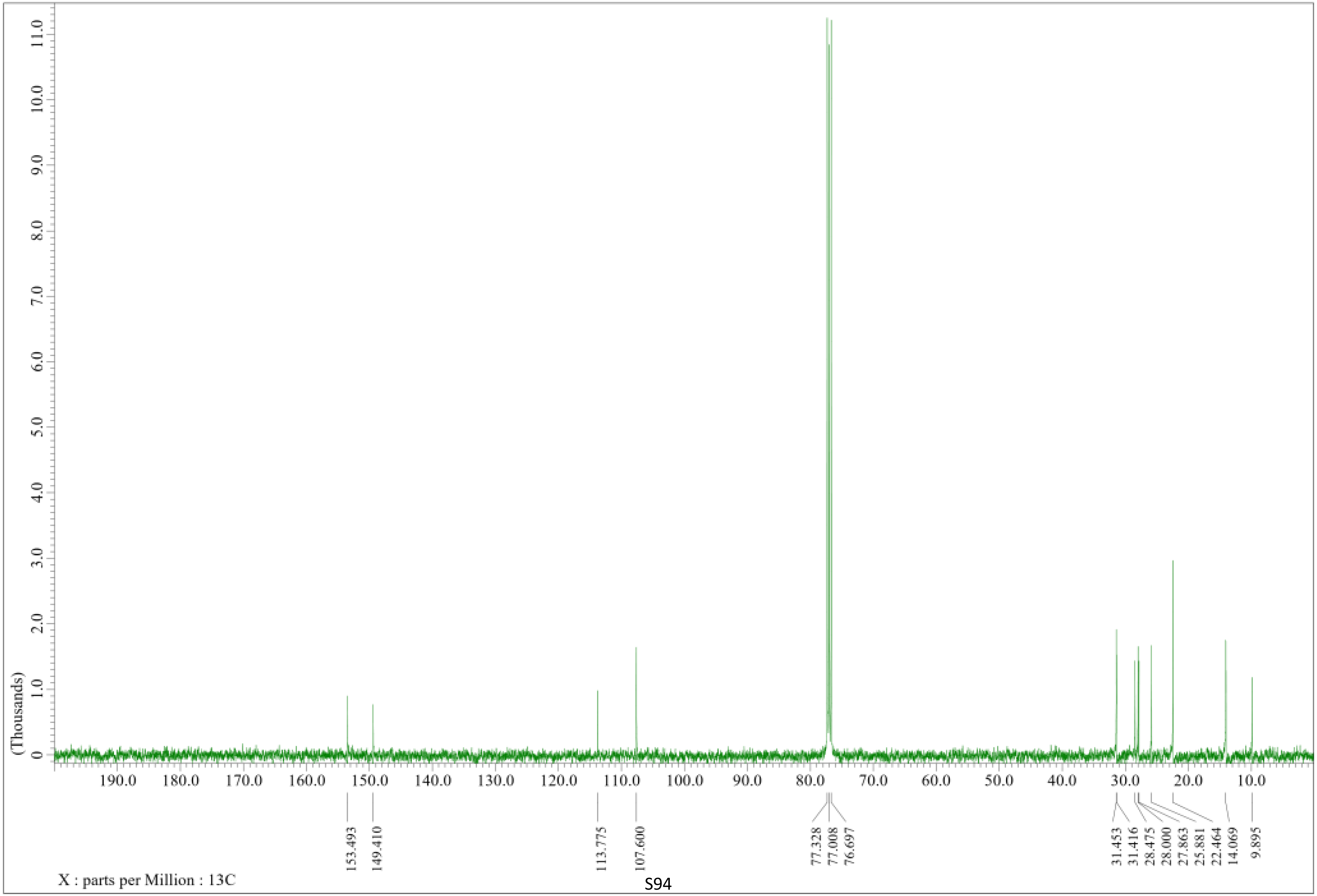


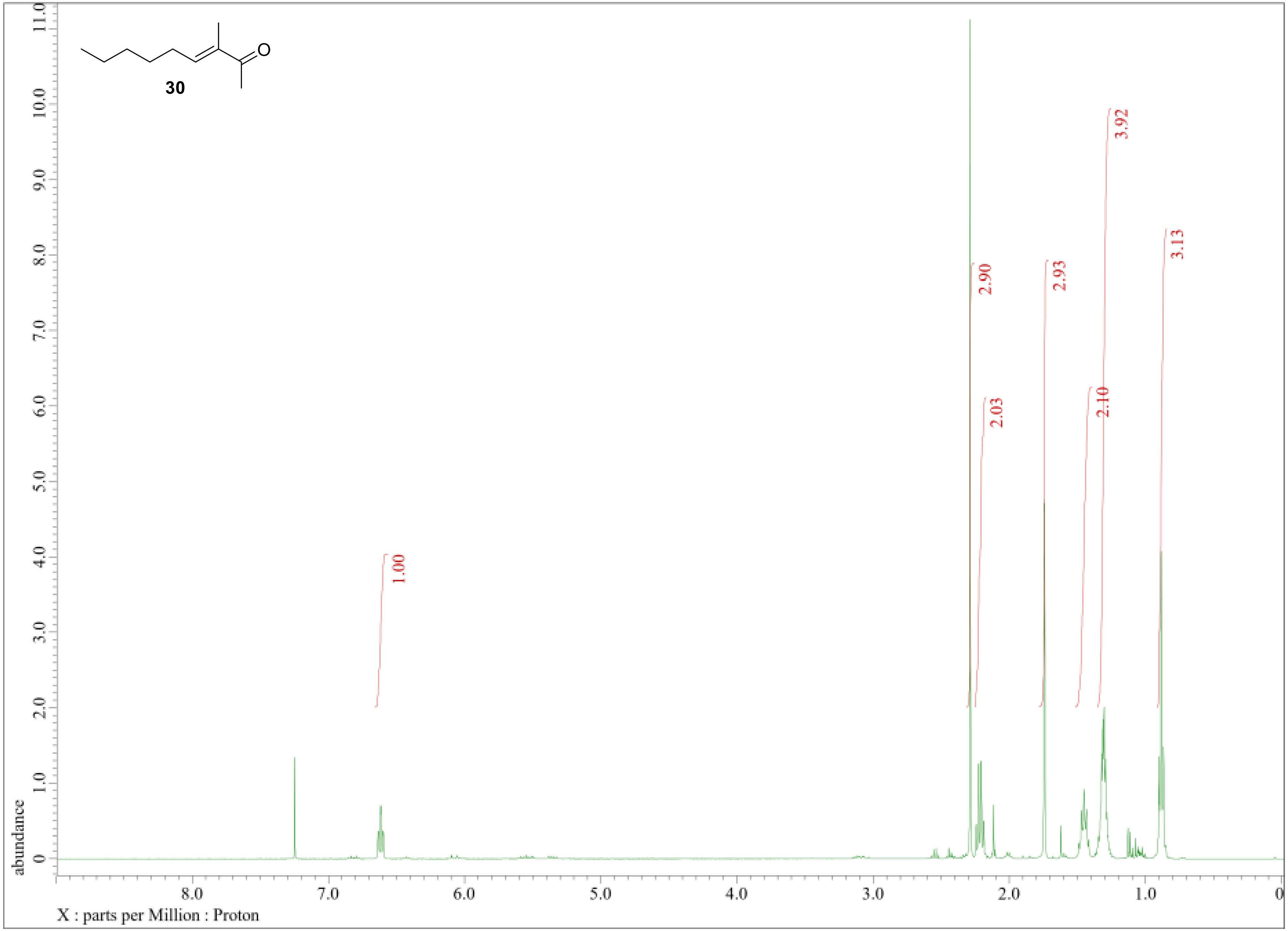
15l

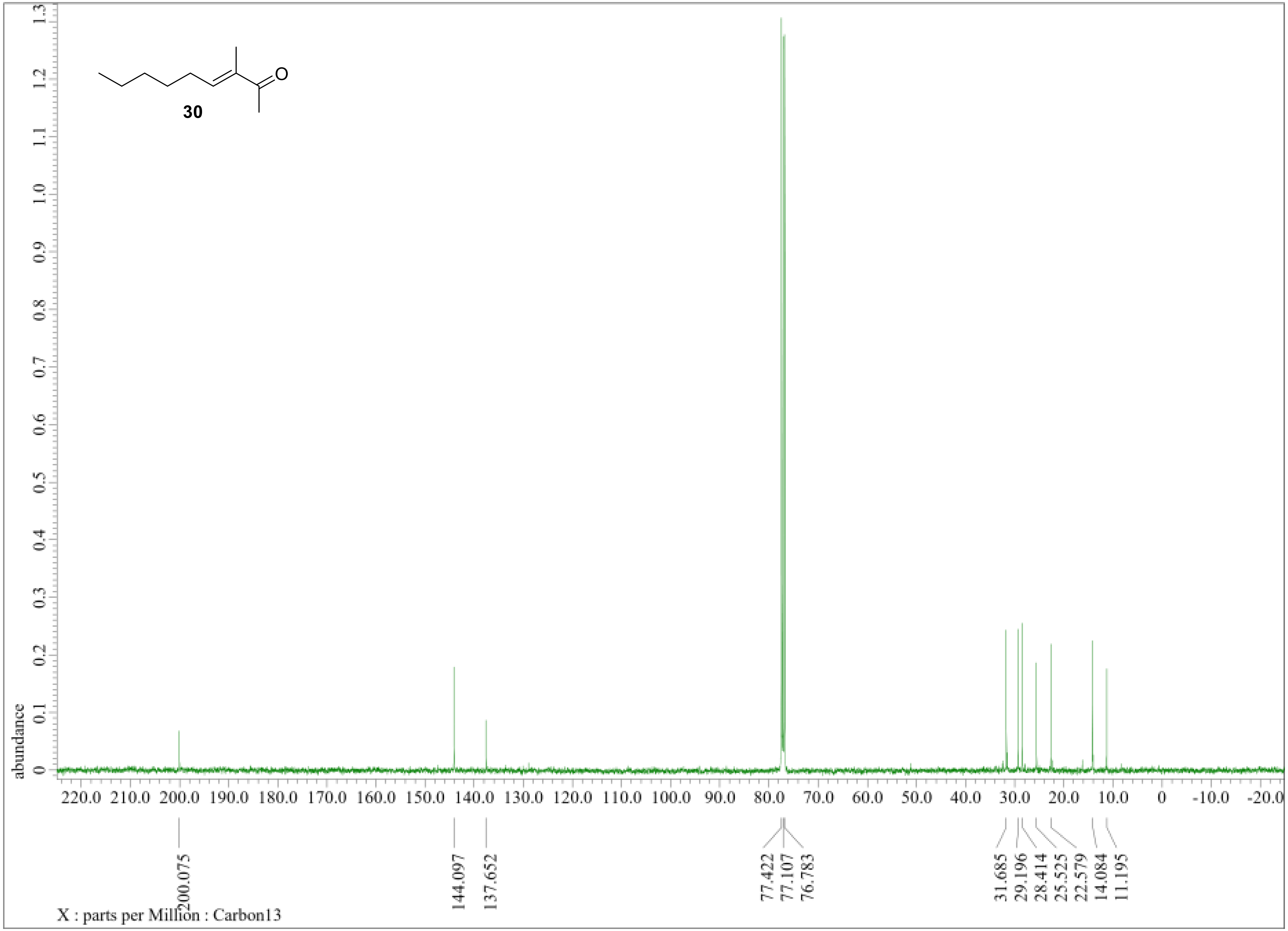

40.0
30.0
20.0
10.0
0
(Thousands)
1.00
4.03
3.05
4.13
7.96
6.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H

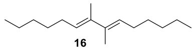


15l

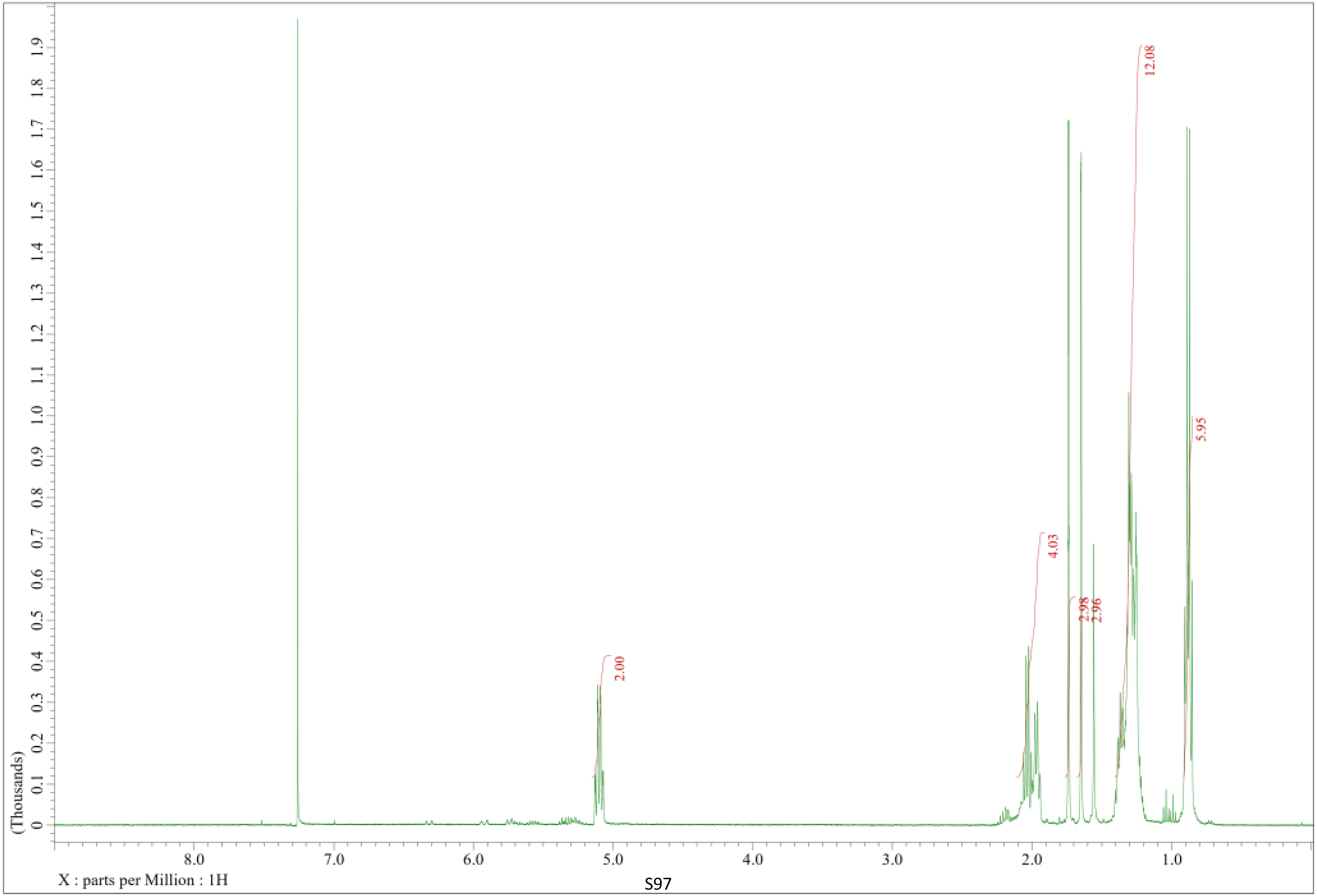

(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
153.493
149.410
113.775
107.600
77.328
77.008
76.697
31.453
31.416
28.475
28.000
27.863
25.881
22.464
14.069
9.895
X : parts per Million : 13C

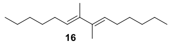

30
O
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
abundance
1.00
2.90
2.03
2.93
2.10
3.92
3.13
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


30
O
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
200.075
144.097
137.652
77.422
77.107
76.783
31.685
29.196
28.414
25.525
22.579
14.084
11.195
X : parts per Million : Carbon13

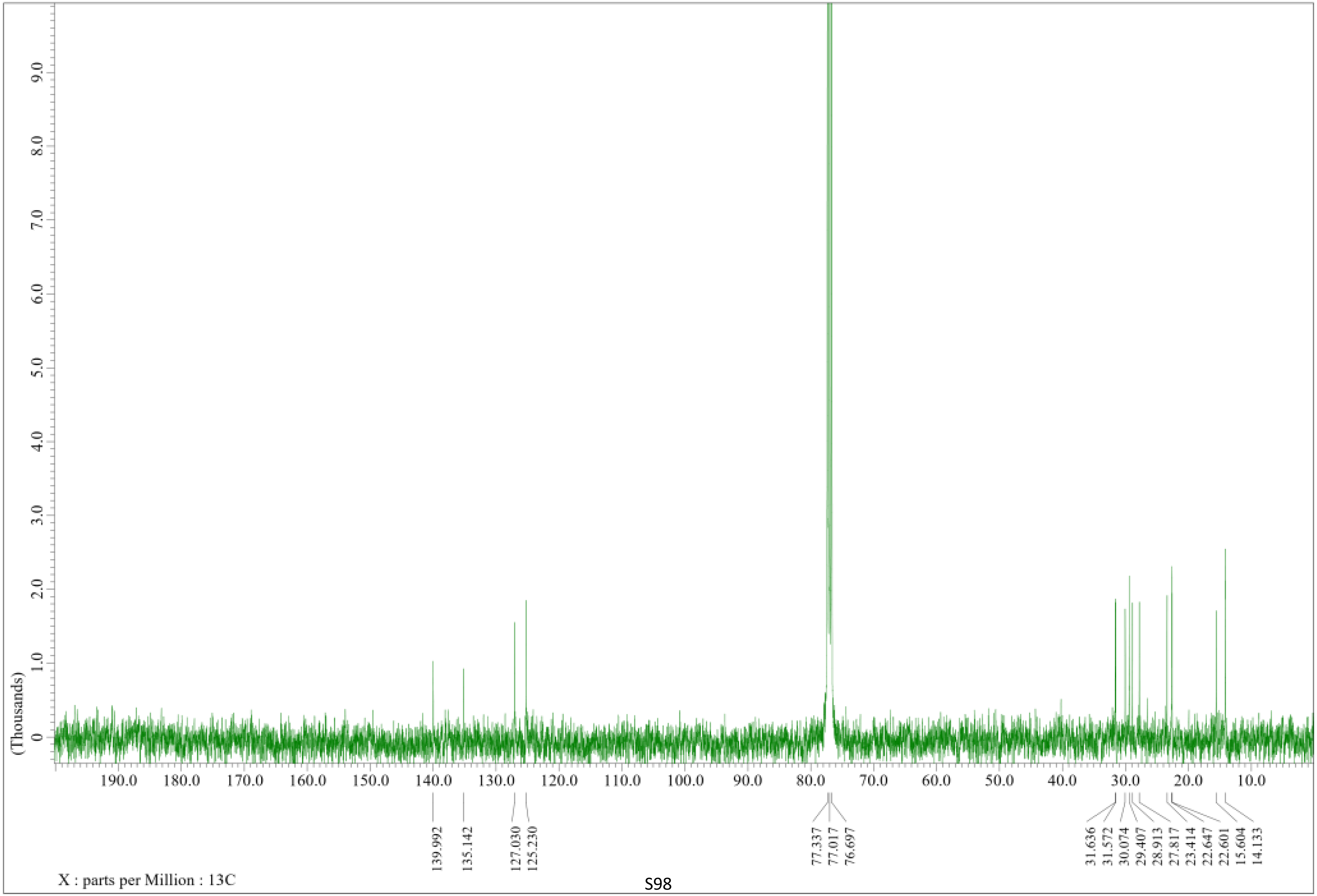


16

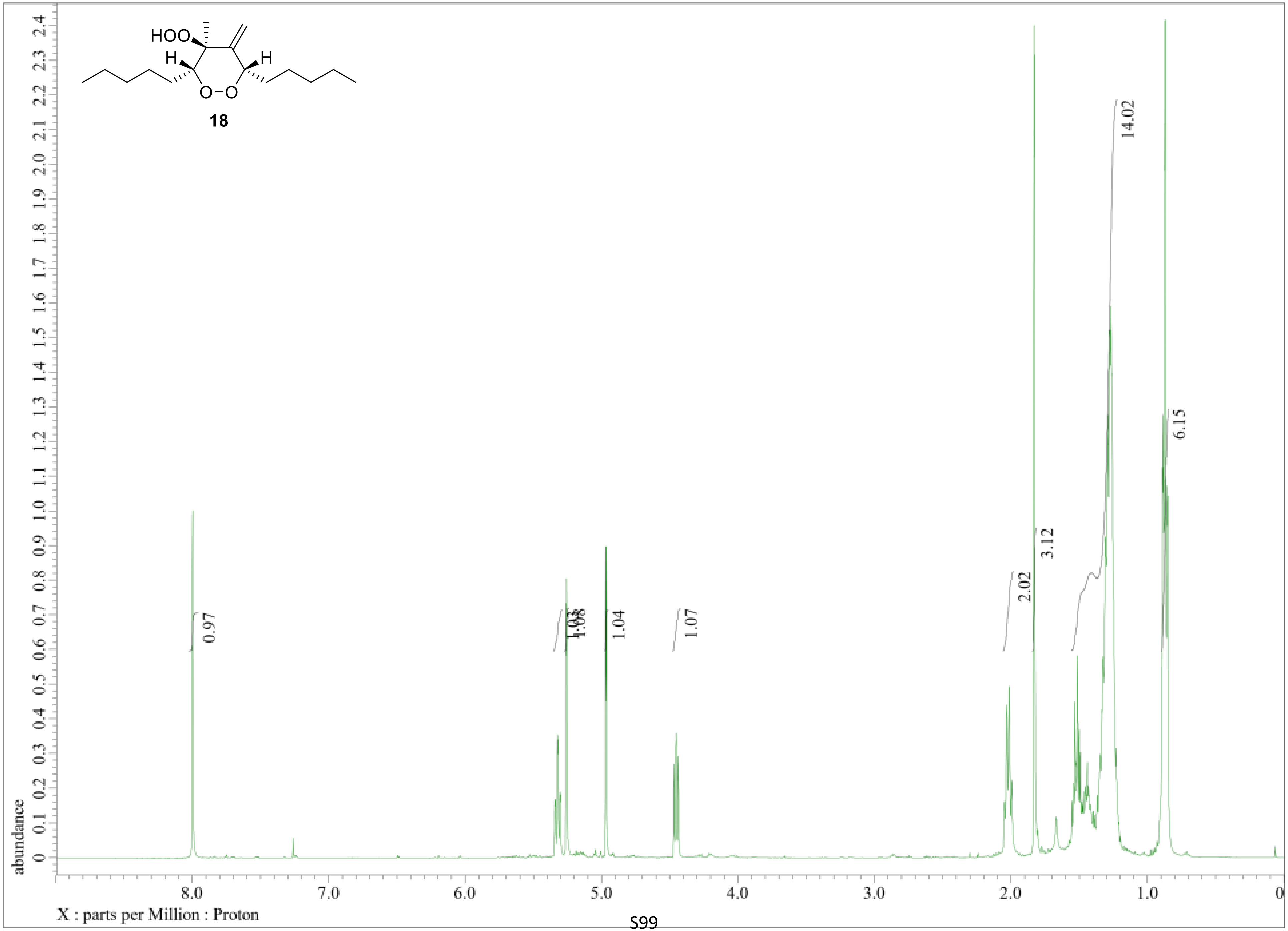

(Thousands)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.00
4.03
2.98
2.96
12.08
5.95
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H

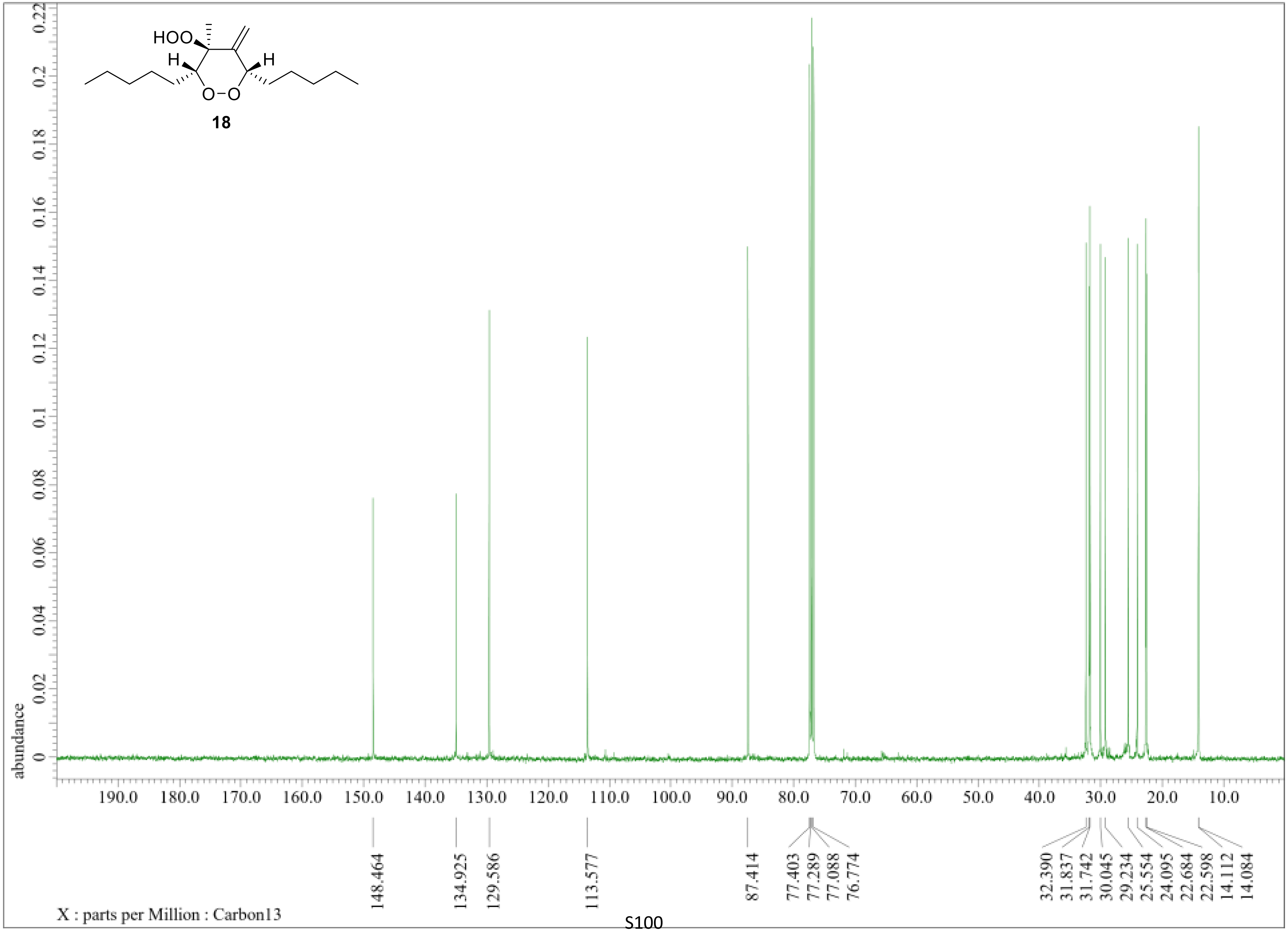


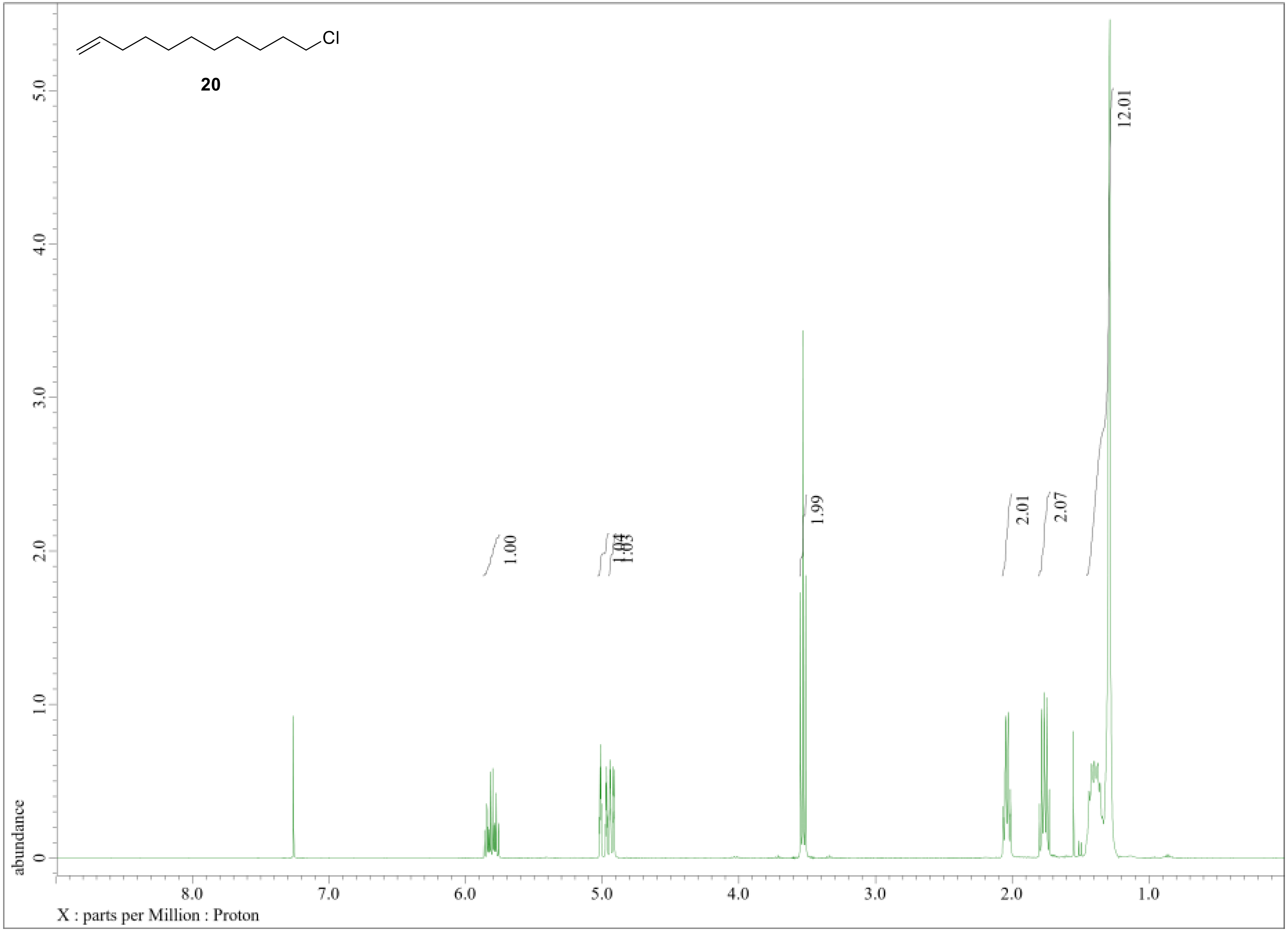
16

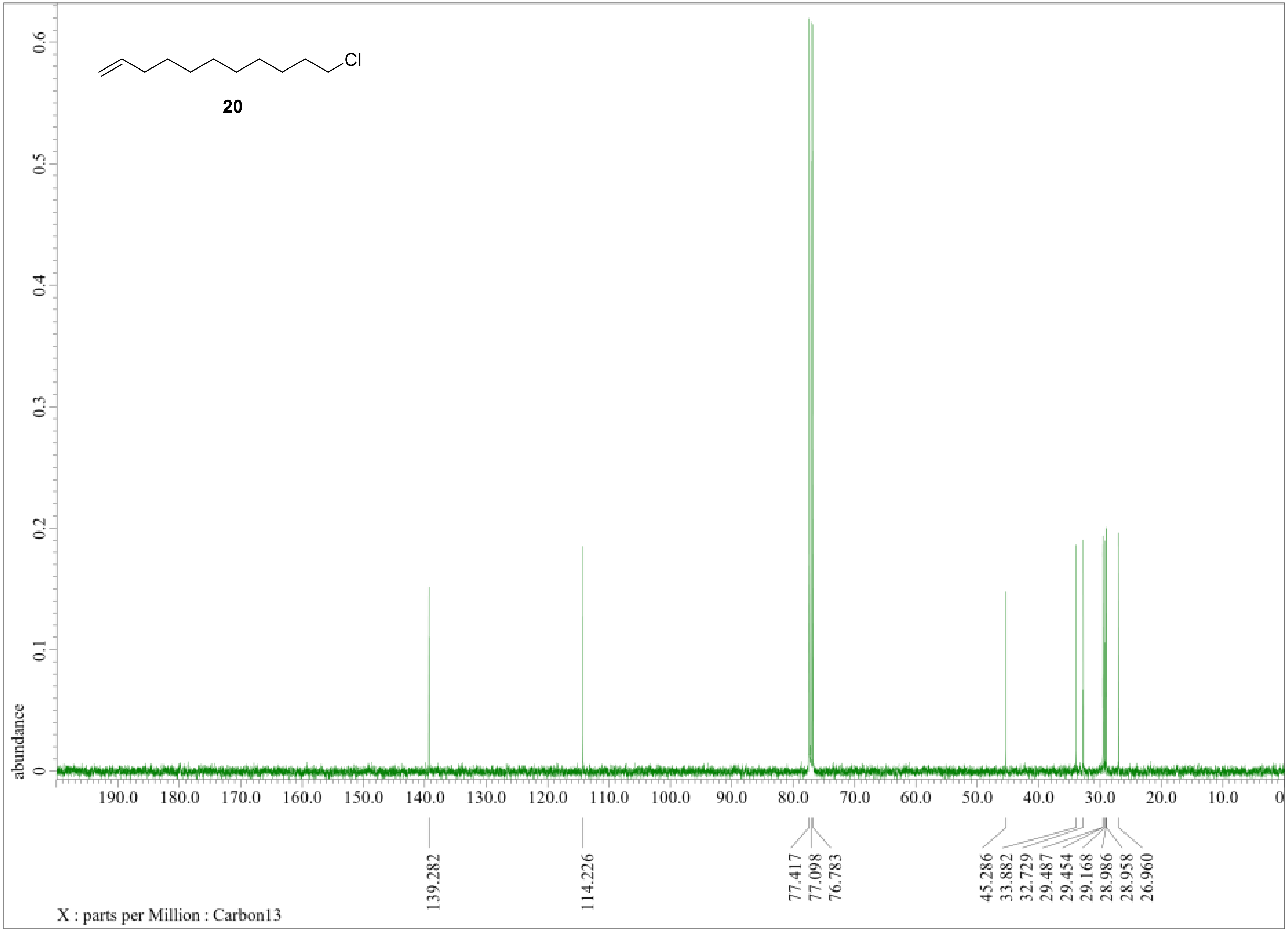


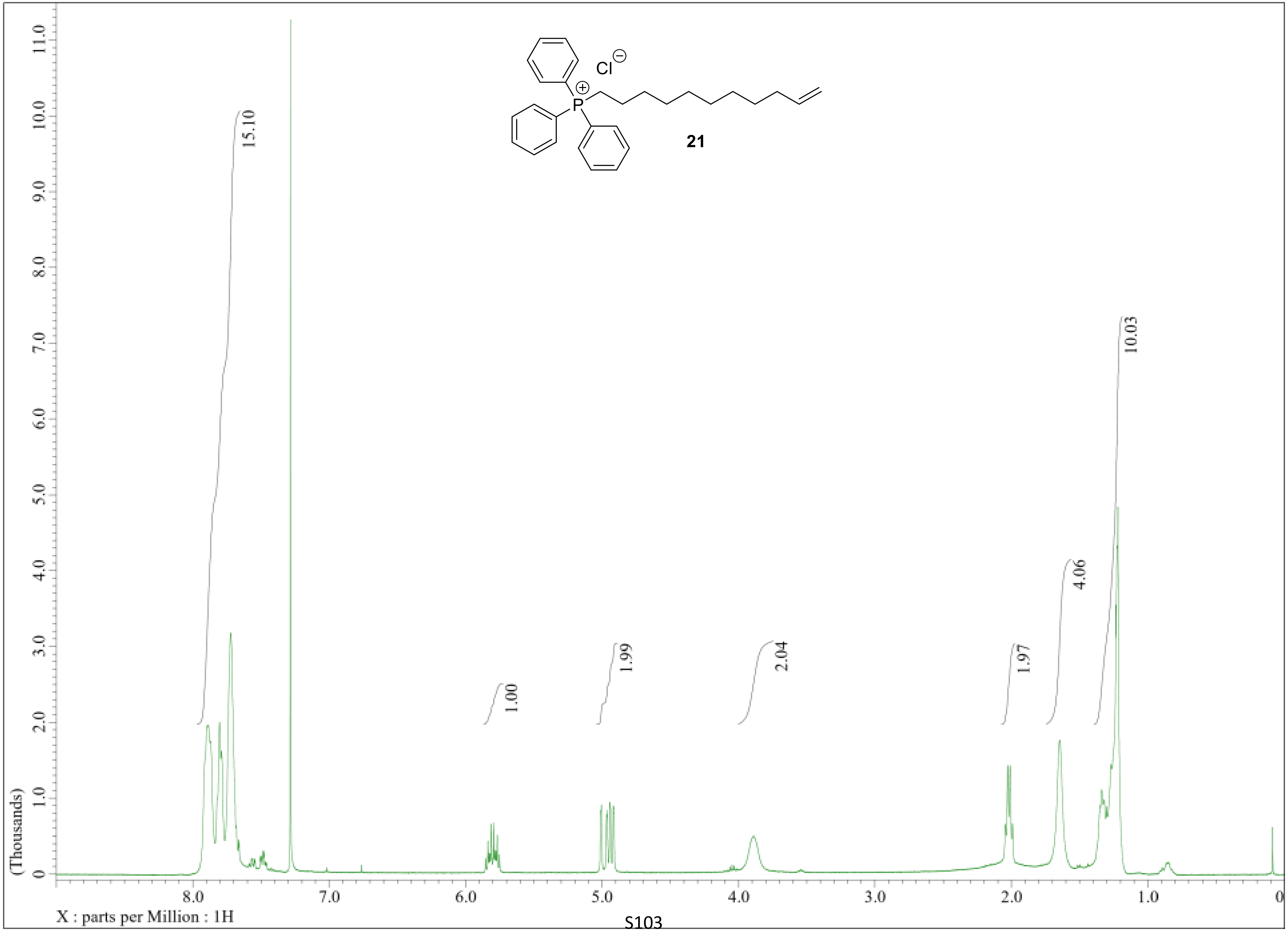
(Thousands)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
139.992
135.142
127.030
125.230
77.337
77.017
76.697
31.636
31.572
30.074
29.407
28.913
27.817
23.414
22.647
22.601
15.604
14.133
X : parts per Million : 13C

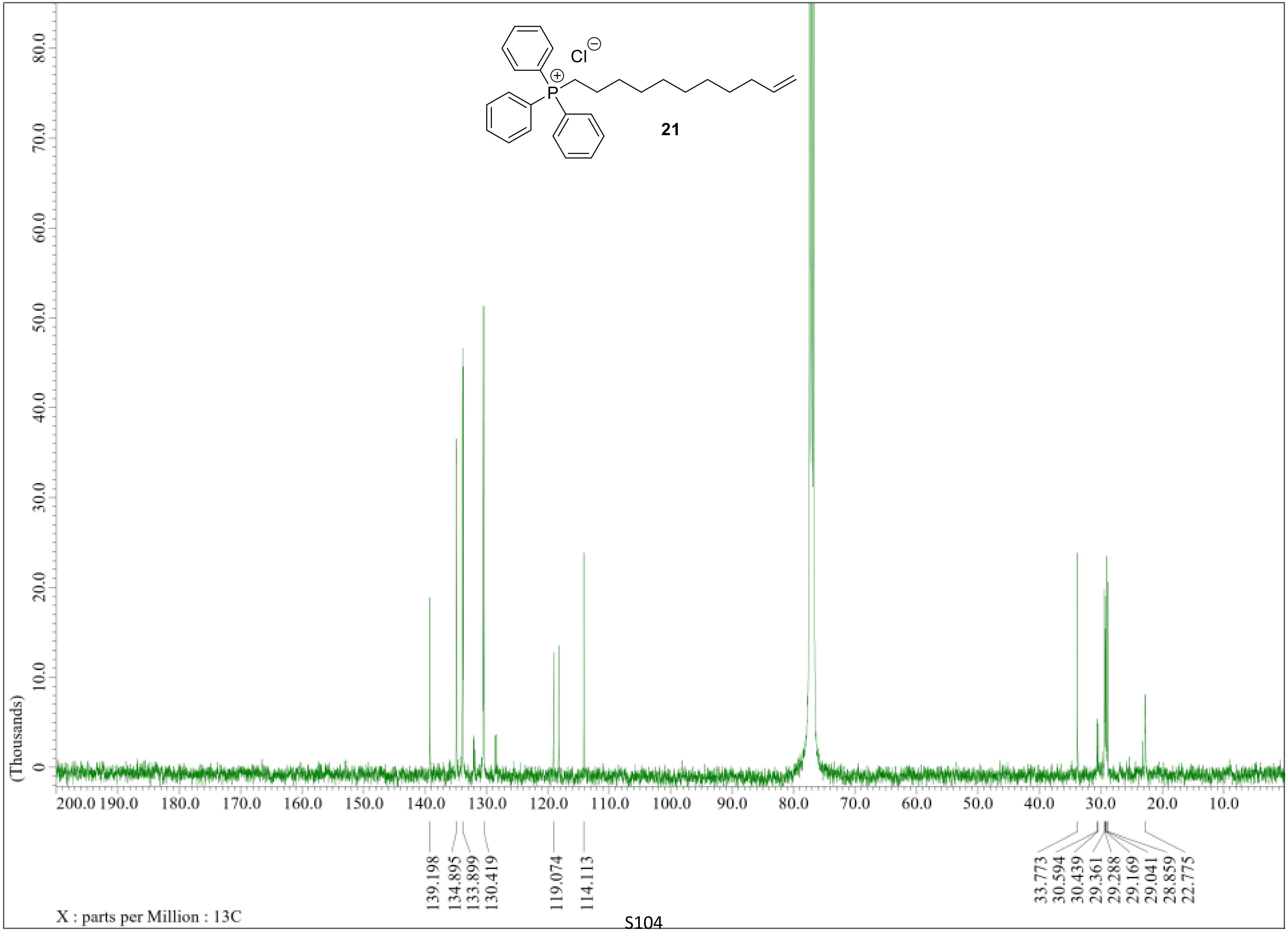

HOO
H
H
O–O
18
0.97
1.03
1.08
1.04
1.07
2.02
3.12
14.02
6.15
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


HOO
H
H
O–O
18
abundance
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
148.464
134.925
129.586
113.577
87.414
77.403
77.289
77.088
76.774
32.390
31.837
31.742
30.045
29.234
25.554
24.095
22.684
22.598
14.112
14.084
X : parts per Million : Carbon13

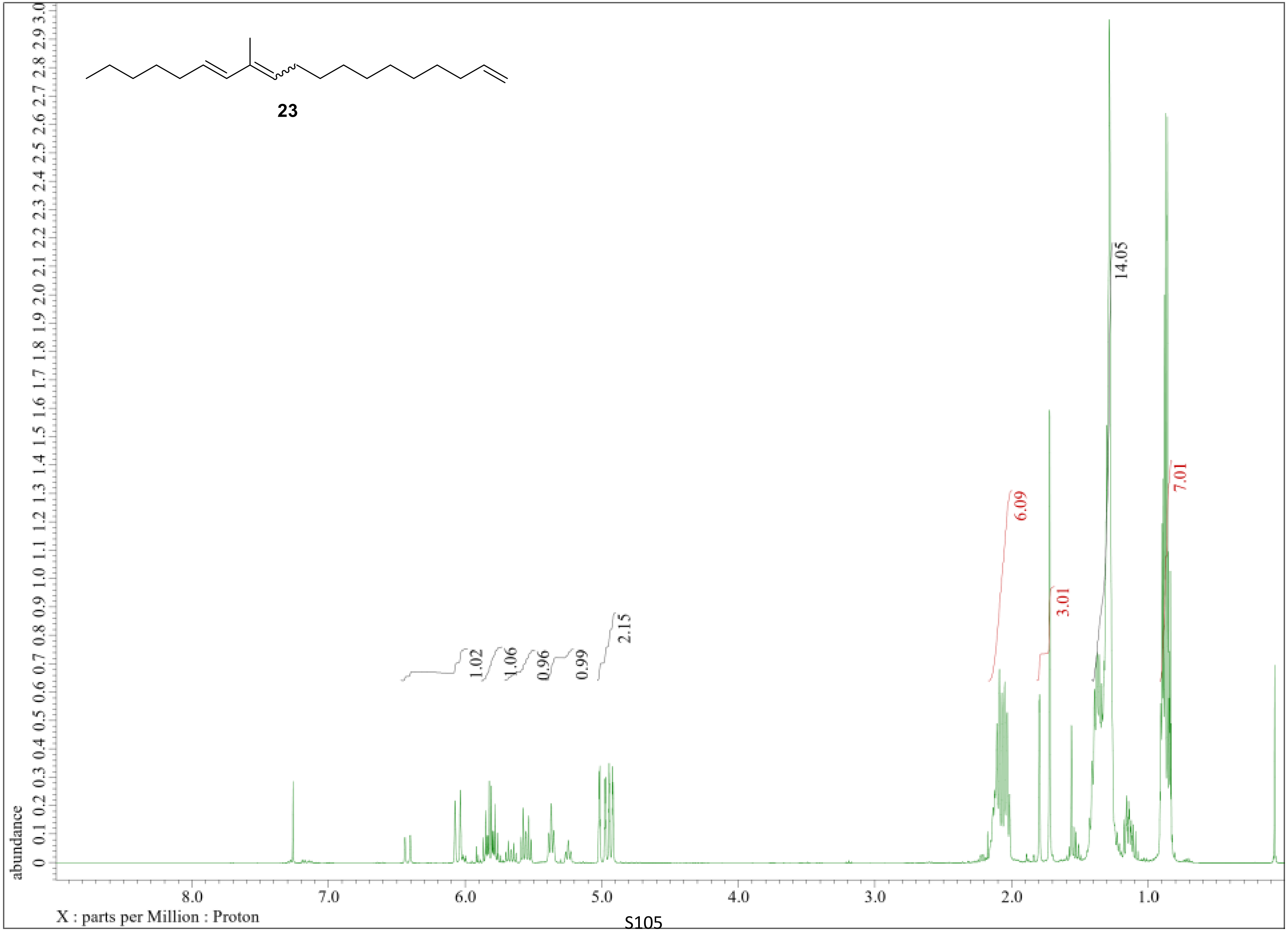

Cl
20
abundance
0
1.0
2.0
3.0
4.0
5.0
1.00
1.04
1.03
1.99
2.01
2.07
12.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton

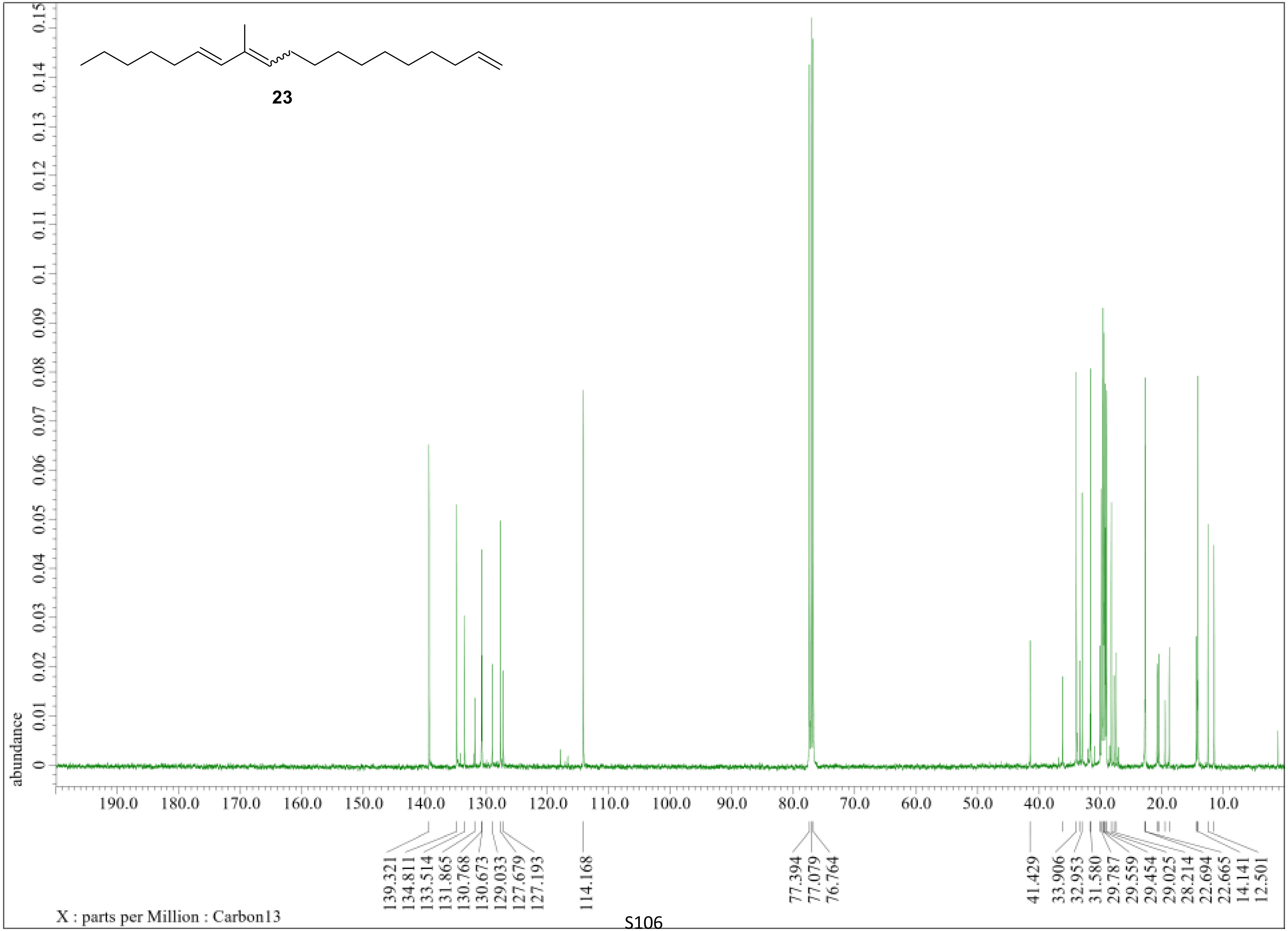

Cl
20
abundance
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
139.282
114.226
77.417
77.098
76.783
45.286
33.882
32.729
29.487
29.454
29.168
28.986
28.958
26.960
X : parts per Million : Carbon13

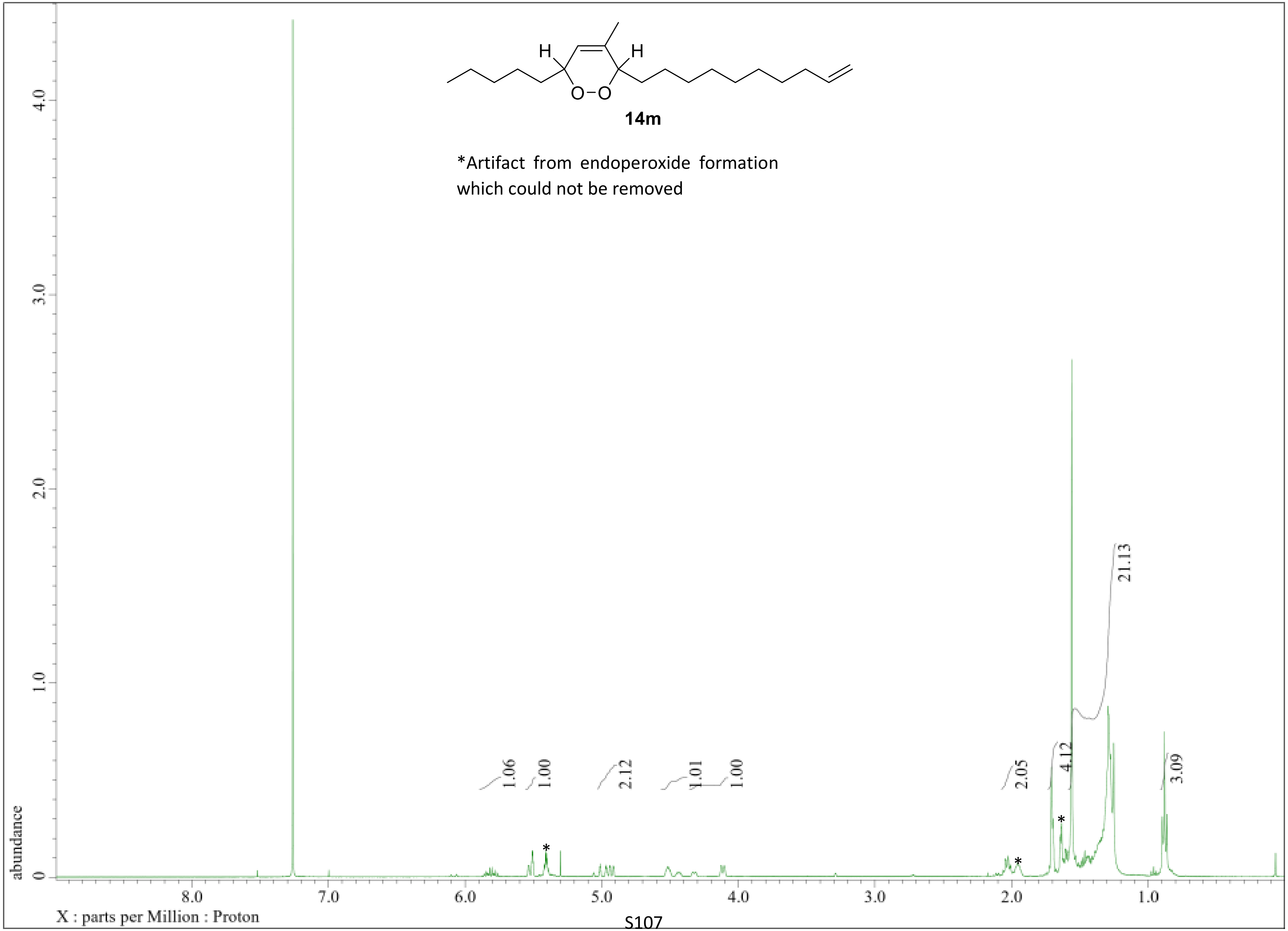

Cl⊖
P⊕
21
15.10
1.00
1.99
2.04
1.97
4.06
10.03
(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


Cl
P
(Thousands)
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
139.198
134.895
133.899
130.419
119.074
114.113
33.773
30.594
30.439
29.361
29.288
29.169
29.041
28.859
22.775
X : parts per Million : 13C

21

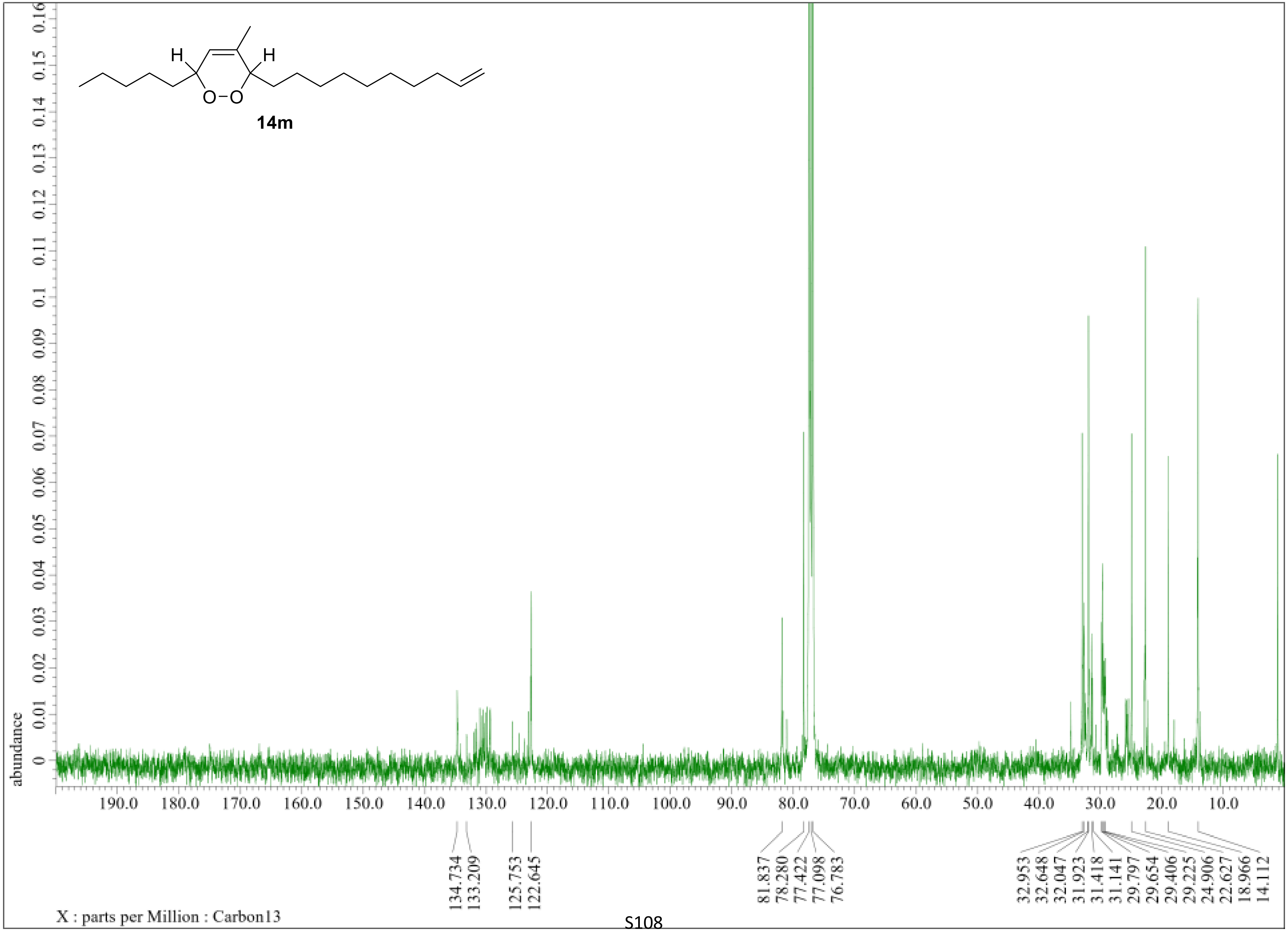

23
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3.0
1.02
1.06
0.96
0.99
2.15
6.09
3.01
14.05
7.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton


23
abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
139.321
134.811
133.514
131.865
130.768
130.673
129.033
127.679
127.193
114.168
77.394
77.079
76.764
41.429
33.906
32.953
31.580
29.787
29.559
29.454
29.025
28.214
22.694
22.665
14.141
12.501
X : parts per Million : Carbon13

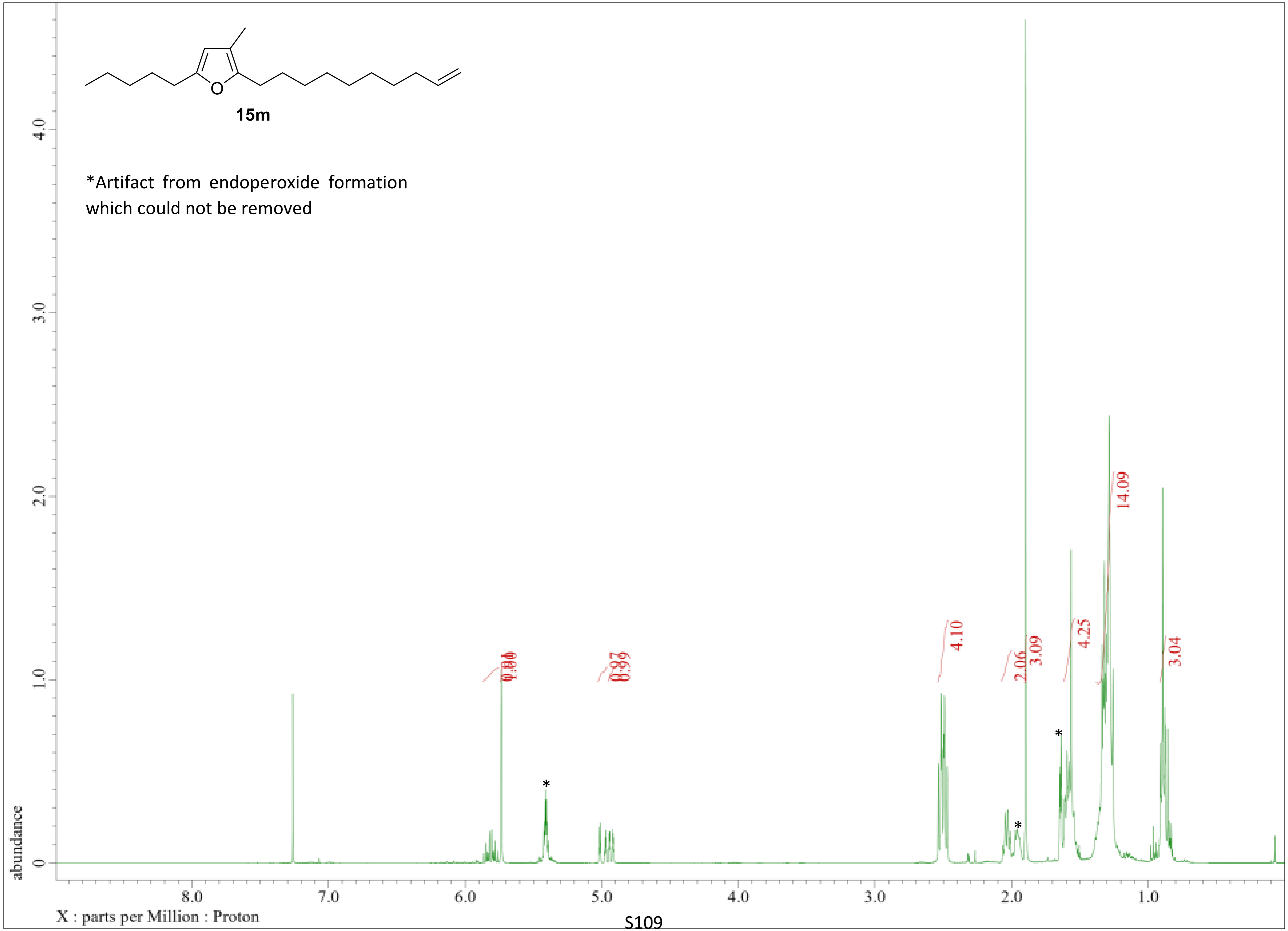


14m

*Artifact from endoperoxide formation which could not be removed

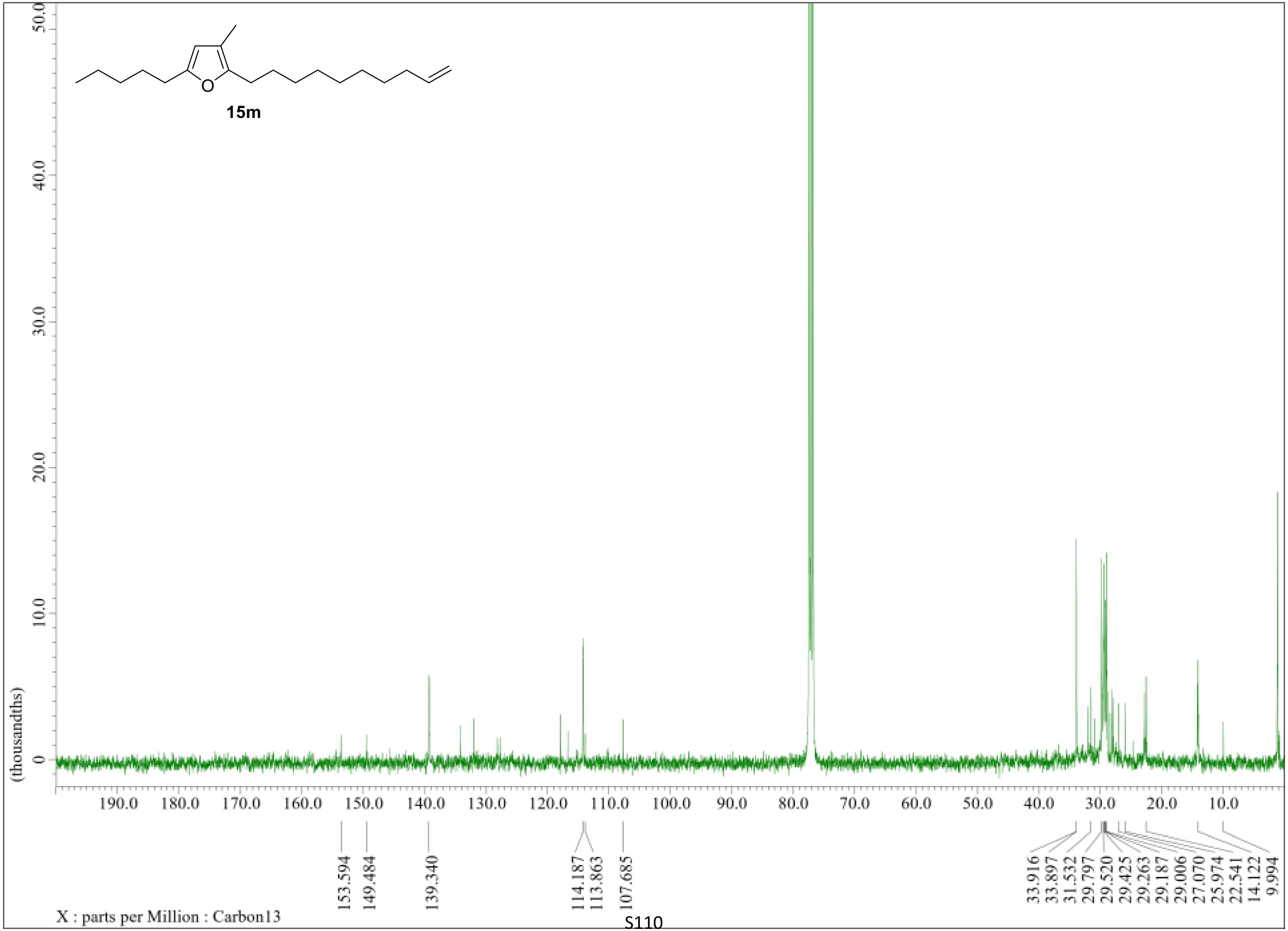


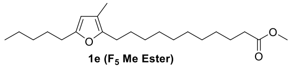
14m
H
H
O–O
abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
0.16
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
134.734
133.209
125.753
122.645
81.837
78.280
77.422
77.098
76.783
32.953
32.648
32.047
31.923
31.418
31.141
29.797
29.654
29.406
29.225
24.906
22.627
18.966
14.112
X : parts per Million : Carbon13



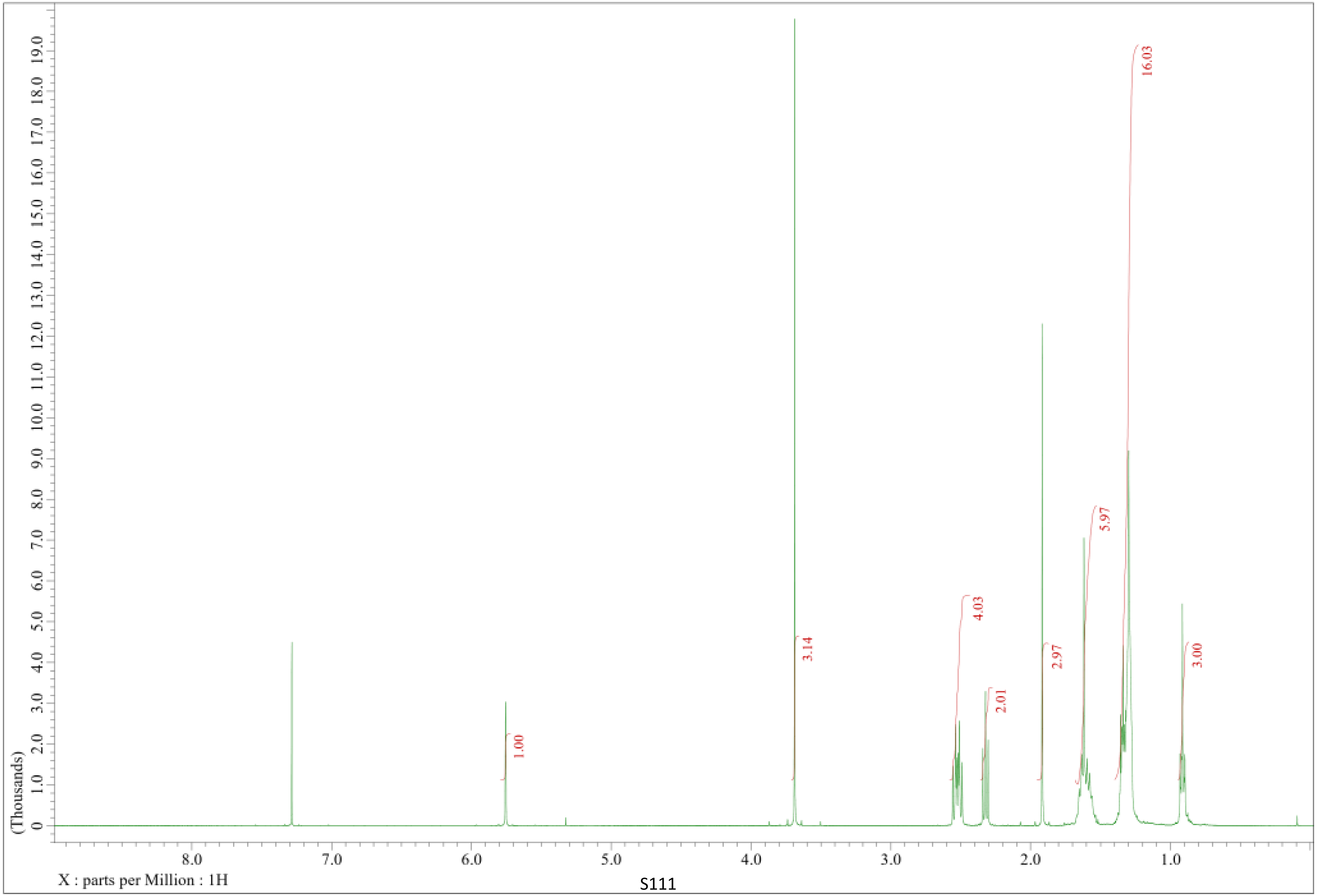
15m

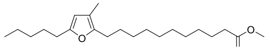
*Artifact from endoperoxide formation which could not be removed


15m
O
50.0
40.0
30.0
20.0
10.0
0
(thousandths)
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
153.594
149.484
139.340
114.187
113.863
107.685
33.916
33.897
31.532
29.797
29.520
29.425
29.263
29.187
29.006
27.070
25.974
22.541
14.122
9.994
X : parts per Million : Carbon13



1e (F$_5$ Me Ester)





1e (F$_5$ Me Ester)