Supporting Information

General Experimental

Air and/or moisture sensitive reactions were performed under an atmosphere of argon in flame dried apparatus. Tetrahydrofuran (THF), toluene, dichloromethane and diethyl ether were purified using a Pure-Solv^{TM} 500 Solvent Purification System. Other dry organic solvents and starting materials were obtained from commercial sources and used as received unless otherwise specified. Petroleum ether used for column chromatography was the 40–60 °C fraction.

All reactions were monitored by thin layer chromatography (TLC) using Merck silica gel 60 covered aluminium plates F_{254}. TLC plates were visualised under UV light and stained with a solution of potassium permanganate, acidic ethanolic anisaldehyde. Flash column chromatography was performed with silica gel (Geduran Si 60 35–70 µm) as solid support.

IR spectra were recorded using a Shimadzu FT IR-8400S ATR instrument. The IR spectrum of each compound (solid or liquid) was acquired directly on a thin layer at ambient temperature.

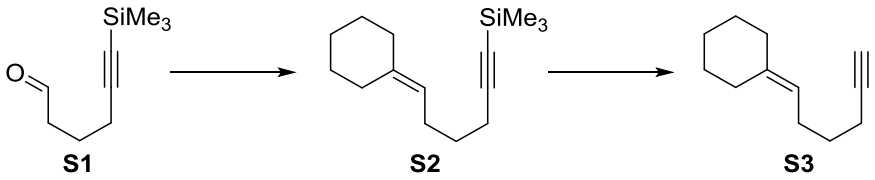
All ^{1}H NMR spectra were recorded using Bruker Avance III 400 MHz and 500 MHz spectrometers at ambient temperature. Data are reported as follows: chemical shift in ppm relative to $CHCl_3$ (7.26) on the δ scale, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, app. = apparent, or a combination of these), coupling constant(s) *J* (Hz) and assignment. All ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz and 500 MHz spectrometers at 101 MHz and 126 MHz at ambient temperature and multiplicities were obtained using a DEPT sequence. Data are reported as follows: chemical shift in ppm relative to $CDCl_3$ (77.16) on the δ scale.

High resolution mass spectra (HRMS) were recorded using positive chemical ionization (CI+) or positive ion impact (EI+) ionization on a Jeol MStation JMS-700 instrument, or using positive or negative ion electrospray (ESI+/ESI-) on a Bruker micrOTOF-Q instrument. Low resolution mass spectra (LRMS) were carried out using the same instruments and the intensity of each peak is quoted as a percentage of the largest, where this information was available.

Melting points were recorded with an Electrothermal IA 9100 apparatus.

X-ray crystallography was performed using an Enraf Nonius FR590 with Mo *K* source and a Kappa CCD. The computer programs used to obtain the crystallographic data were: Collect (Bruker AXS BV, 1997-2004), HKL Scalepack[1],HKL Denzo and Scalepack[1], SIR 92[2], SHELXL-2013[3], Ortep-3 for windows[4] and WinGX publication routines.[4]

Hex-5-yn-1-ylidenecyclohexane (S3).

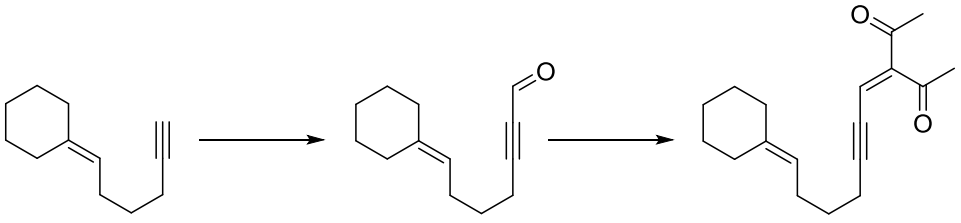


S1 **S2** **S3**

n-BuLi (10.3 mL of a 2.5 M solution in hexanes, 25.8 mmol) was added dropwise to a suspension of cyclohexyltriphenylphosphonium bromide (11.0 g, 25.9 mmol) in THF (25 mL) at 0 °C and the solution was allowed to warm to rt and then stirred for 30 min. A solution of aldehyde **S1**[5] (2.72 g, 16.2 mmol) in THF (10 mL) was added and the reaction mixture stirred at rt for 2 h. The reaction was quenched with 10% aqueous NH_4Cl (20 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by filtration through a short plug of silica gel (petroleum ether-Et_2O, 100:1) to afford the crude alkene **S2** as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (1H, b t, J = 7.4 Hz), 2.21 (2H, t, J = 7.1 Hz), 2.15–2.03 (6H, m), 1.58–1.45 (8H, m), 0.14 (9H, s).

Solid K_2CO_3 (2.69 g, 19.5 mmol) was added to a solution of crude alkene **S2** in MeOH (80 mL) at rt. The mixture was stirred at rt for 20 h before the reaction was quenched with 10% aqueous NH_4Cl (100 mL). The mixture was extracted with Et_2O (3 × 100 mL) and the organic extracts were combined and washed with brine (50 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (pentane-Et_2O, 100:1) to afford the enyne **S3** (1.42 g, 54% over 2 steps) as a colourless oil. R_f = 0.83 (petroleum ether-EtOAc, 9:1); ν_{max} 3310, 2930, 2857, 905, 729, 650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (1H, t, J = 7.3 Hz), 2.18 (2H, td, J = 7.2, 2.6 Hz), 2.14–2.03 (6H, m), 1.94 (1H, t, J = 2.6 Hz), 1.60–1.45 (8H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 120.1, 84.8, 68.3, 37.4, 29.1, 28.9, 28.9, 28.0, 27.1, 26.2, 17.9; LRMS (CI, *iso*-butane) *m/z* (intensity) 163.1 $[M+H]^+$ (36), 109.1 (25), 89.1 (100), 81.1 (56); HRMS (CI, *iso*-butane) calcd for $C_{12}H_{19}$ $[M+H]^+$ 163.1487, found 163.1482.

3-(7-Cyclohexylidenehept-2-yn-1-ylidene)pentane-2,4-dione (6a).



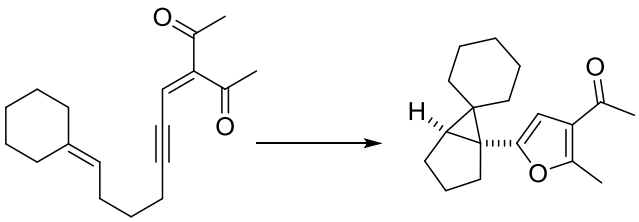
S3 **9a** **6a**

n-BuLi (1.73 mL of a 2.5 M solution in hexanes, 4.33 mmol) was added to a solution of enyne **S3** (581 mg, 3.58 mmol) in THF (10 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 10

min after which DMF (0.67 mL, 8.6 mmol) was added. The mixture was stirred for a further 30 min at –78 °C and the reaction was quenched by addition of 10% aqueous KH_2PO_4 (10 mL). The mixture was stirred at 0 °C for 30 min and then extracted with Et_2O (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude aldehyde **9a** as a colourless oil which was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (1H, t, *J* = 0.9 Hz), 5.01 (1H, tt, *J* = 7.4, 1.0 Hz), 2.40 (2H, td, *J* = 7.1, 0.9 Hz), 2.15–2.04 (6H, m), 1.63 (2H, quintet, *J* = 7.1 Hz), 1.56–1.45 (6H, m).

Solid $MgSO_4$ (72 mg, 0.60 mmol) was added to a mixture of the aldehyde **9a**, 2,4-pentanedione (0.31 mL, 3.0 mmol), AcOH (0.10 mL, 1.8 mmol) and piperidine (0.03 mL, 0.3 mmol) in toluene (3 mL) at rt. The resulting solution was heated to 30 °C and stirred at this temperature for 2.5 h. The reaction was quenched by addition of H_2O (5 mL) and the resulting mixture was extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 19:1) to provide ynenedione **6a** (728 mg, 75%, over 2 steps) as a colourless solid. R_f = 0.19 (petroleum ether-EtOAc, 19:1); ν_{max} 2921, 2850, 1676, 1569, 951 cm^{-1}; m.p. = 79–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.70 (1H, t, *J* = 2.4 Hz), 5.02 (1H, t, *J* = 7.3 Hz), 2.47 (3H, s), 2.42 (2H, td, *J* = 7.2, 2.4 Hz), 2.31 (3H, s), 2.13–2.04 (6H, m), 1.59 (2H, quintet, *J* = 7.2 Hz), 1.57–1.46 (6H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 195.8, 149.6, 141.3, 123.3, 119.7, 110.6, 77.0, 37.3, 31.0, 28.8, 28.8, 28.6, 28.0, 27.3, 27.0, 26.2, 19.7; HRMS (ESI) calcd for $C_{18}H_{24}O_2Na$ $[M+Na]^+$ 295.1669, found 295.1658.

1-[2-Methyl-5-{spiro(bicyclo[3.1.0]hexane-6,1'-cyclohexan)-1-yl}furan-3-yl]ethanone (7a).

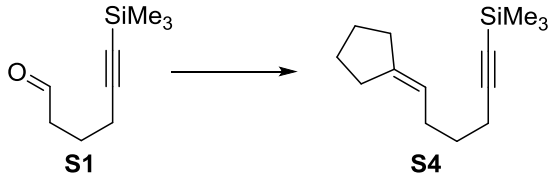


6a **7a**

Chloroacetic acid (35 mg, 0.37 mmol) was added to a solution of ynenedione **6a** (100 mg, 0.37 mmol) in CH_2Cl_2 (1.5 mL) at rt. The resulting solution was heated at reflux for 20 h then cooled to rt. The reaction mixture was washed sequentially with saturated aqueous $NaHCO_3$ (3 × 1.5 mL) and brine (1.5 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (petroleum ether-EtOAc, 19:1) to afford cyclopropyl furan **7a** (86 mg, 86%) as a colourless solid. The product was crystallised from petroleum ether-Et_2O (19:1) to afford colourless crystals. R_f = 0.26 (petroleum ether-EtOAc, 15:1); m.p. = 87–89 °C; ν_{max} 2924, 2851, 1676, 951 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13 (1H, s), 2.53 (3H, s), 2.35 (3H, s), 2.06–1.93 (4H, m), 1.62–1.39 (9H, m), 1.33–1.29 (2H, m), 1.22–1.10 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 156.8, 156.6, 121.8,

105.7, 37.8, 37.3, 34.8, 34.0, 30.9, 29.8, 29.2, 26.7, 26.6, 26.1, 25.5, 25.3, 14.6; HRMS (ESI) calcd for $C_{18}H_{24}O_2Na$ $[M+Na]^+$ 295.1669, found 295.1656.

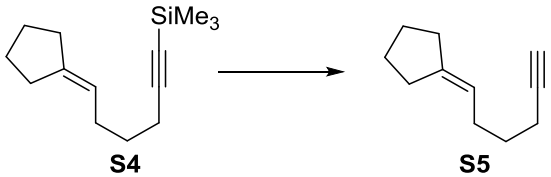
(6-Cyclopentylidenehex-1-yn-1-yl)trimethylsilane (S4).



S1 **S4**

n-BuLi (7.72 mL of a 2.5 M solution in hexanes, 19.3 mmol) was added dropwise to a suspension of cyclopentyltriphenylphosphonium bromide (7.94 g, 19.3 mmol) in THF (20 mL) at 0 °C. The solution was allowed to warm to rt and stirred for 30 min and then a solution of aldehyde **S1** (2.03 g, 12.1 mmol) in THF (5 mL) was added. The solution was stirred at rt for 2.5 h and the reaction was quenched with 10% aqueous NH_4Cl (20 mL). The resulting mixture was extracted with Et_2O (3 × 20 mL) and the combined organic extracts were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-Et_2O, 100:1) to afford enyne **S4** (1.99 g, 75%) as a colourless oil. R_f = 0.91 (petroleum ether-EtOAc, 9:1); ν_{max} 2957, 2944, 1249, 907, 840, 730 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.24–5.17 (1H, m), 2.22 (4H, t, *J* = 7.2 Hz), 2.23–2.16 (2H, m), 2.09 (1H, dt, *J* = 7.3, 1.3 Hz), 2.05 (1H, dt, *J* = 7.3, 1.3 Hz), 1.69–1.52 (6H, m), 0.14 (9H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 119.1, 107.9, 84.5, 33.7, 28.8, 28.8, 28.8, 26.6, 26.5, 19.5, 0.3; LRMS (CI, *iso*-butane) *m/z* (intensity) 221.3 $[M+H]^+$ (50), 147.2 (100); HRMS (CI, *iso*-butane) calcd for $C_{14}H_{25}Si$ $[M+H]^+$ 221.1726, found 221.1724.

Hex-5-yn-1-ylidenecyclopentane (S5).

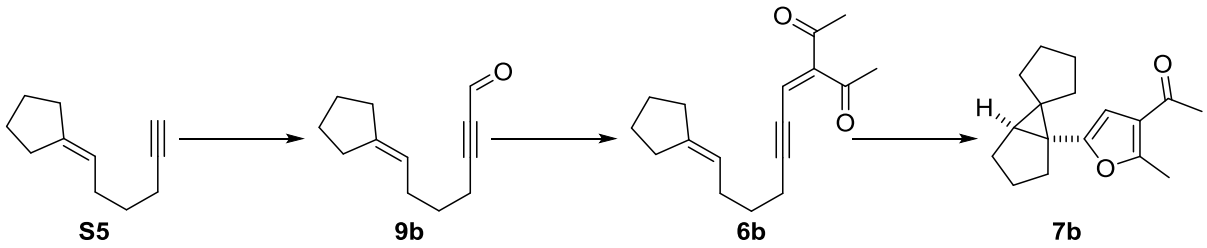


S4 **S5**

Solid K_2CO_3 (1.2 g, 8.7 mmol) was added to a solution of alkene **S4** (1.6 g, 7.3 mmol) in MeOH (35 mL) at rt. The mixture was stirred at rt for 20 h and the reaction was quenched with 10% aq. NH_4Cl (40 mL). The mixture was extracted with Et_2O (3 × 20 mL) and the combined organic phases were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (pentane-Et_2O, 100:1) to afford the enyne **S5** (796 mg, 74%) as a colourless liquid. R_f = 0.77 (petroleum ether-EtOAc, 19:1); ν_{max} 3309, 2943, 908, 733 $cm^{-1;}$ ^1H NMR (500 MHz, $CDCl_3$) δ 5.20 (1H, dtd, *J* = 7.2, 4.7, 2.2 Hz), 2.24–2.16 (6H, m), 2.08 (2H, b q, *J* = 7.2 Hz), 1.94 (1H, t, *J* = 2.6 Hz), 1.66 (2H, dt, *J* = 13.2, 6.6 Hz), 1.62–1.55 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 119.0, 84.9, 68.2, 33.7, 28.8,

28.7, 28.7, 26.6, 26.5, 18.1; LRMS (CI, *iso*-butane) *m/z* (intensity) 149.2 $[M+H]^+$ (100), 135.1 (25),109.1 (25); HRMS (CI, *iso*-butane) calcd for $C_{11}H_{17}$ $[M+H]^+$ 149.1330, found 149.1334.

1-[2-Methyl-5-{spiro(bicyclo[3.1.0]hexane-6,1'-cyclopentan)-1-yl}furan-3-yl]ethanone (7b).



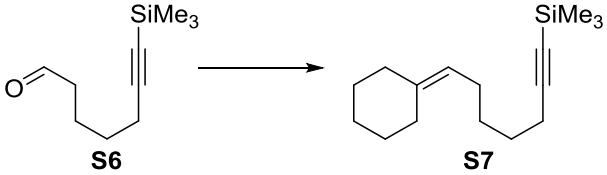
S5 **9b** **6b** **7b**

n-BuLi (2.3 mL of a 2.5 M solution in hexanes, 5.8 mmol) was added to a solution of enyne **S5** (790 mg, 5.33 mmol) in THF (13 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 10 min after which DMF (0.89 mL, 12 mmol) was added. The mixture was stirred for a further 30 min at –78 °C and the reaction was then quenched by addition of 10% aqueous KH_2PO_4 (10 mL). The mixture was stirred at 0 °C for 30 min and then extracted with Et_2O (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude aldehyde **9b** as a colourless oil which was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (1H, t, *J* = 0.8 Hz), 5.22–5.16 (1H, m), 2.41 (2H, td, *J* = 7.1, 0.8 Hz), 2.25–2.15 (4H, m), 2.13–2.06 (2H, m), 1.71–1.54 (6H, m).

Solid $MgSO_4$ (96 mg, 0.80 mmol) was added to a mixture of the crude aldehyde **9b**, 2,4-pentanedione (0.41 mL, 4.0 mmol), AcOH (0.14 mL, 2.4 mmol) and piperidine (0.04 mL, 0.4 mmol) in toluene (4 mL) at rt. The resulting mixture was heated to 30 °C and stirred at this temperature for 2.5 h. The reaction was quenched by addition of H_2O (5 mL) and extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford crude ynenedione **6b** which was immediately used in the next step without further purification. *Attempted purification of ynenedione **6b** by flash column chromatography on silica gel resulted in partial cyclisation to give the furan **7b**.*

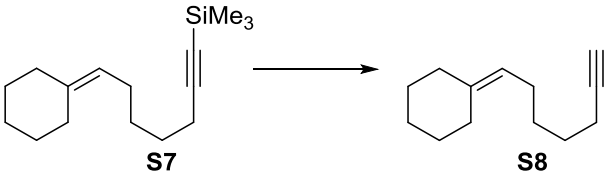
Chloroacetic acid (378 mg, 4.00 mmol) was added to a solution of crude ynenedione **6b** in CH_2Cl_2 (16 mL) at rt. The resulting solution was heated at reflux for 18 h then cooled to rt. The reaction mixture was washed sequentially with saturated aqueous $NaHCO_3$ (3 × 15 mL) and brine (15 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (petroleum ether-EtOAc, 20:1) to afford the cyclopropyl furan **7b** (677 mg, 49% over 3 steps; 66% over 2 steps based on diketone as the limiting reagent) as a pale yellow oil. R_f = 0.30 (petroleum ether-EtOAc, 19:1); ν_{max} 2949, 1676, 1568, 947 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (1H, s), 2.54 (3H, s), 2.37 (3H, s), 2.06–1.95 (3H, m), 1.83–1.63 (4H, m), 1.61 (1H, d, *J* = 5.1 Hz), 1.55–1.32 (7H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.6, 156.8, 156.5, 122.0, 105.3, 37.2, 35.9, 35.7, 34.8, 31.2, 29.3, 27.4, 26.9, 26.3, 25.7, 25.2, 14.6; HRMS (ESI) calcd for $C_{17}H_{22}O_2Na$ $[M+Na]^+$ 281.1512, found 281.1518.

(7-Cyclohexylidenehept-1-yn-1-yl)trimethylsilane (S7).



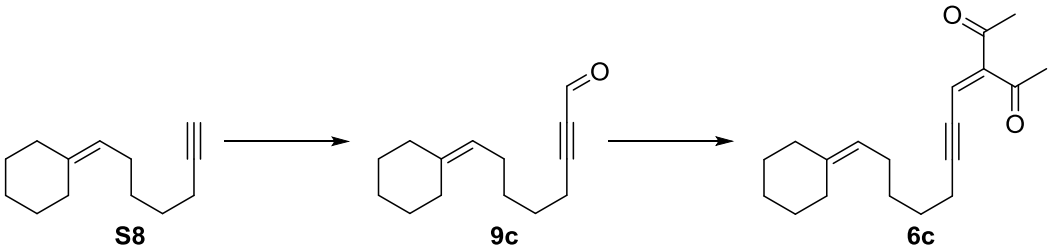
n-BuLi (3.38 mL of 2.5 M in hexanes, 8.44 mmol) was added dropwise to a suspension of cyclohexyltriphenylphosphonium bromide (3.59 g, 8.73 mmol) in THF (10 mL) at 0 °C. The solution was allowed to warm to rt and stirred for 30 min. A solution of aldehyde **S6**[6] (987 mg, 5.41 mmol) in THF (2.5 mL) was added and the reaction mixture stirred at rt for 2.5 h. The reaction was quenched with 10% aqueous NH_4Cl (10 mL) and the mixture was extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-Et_2O, 100:1) to afford the enyne **S7** (901 mg, 67%) as a colourless oil. R_f = 0.83 (petroleum ether-EtOAc, 9:1); ν_{max} 2955, 2926, 2855, 839, 760 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.06 (1H, tt, *J* = 7.3, 1.0 Hz), 2.22 (2H, t, *J* = 7.1 Hz), 2.13–2.10 (2H, m), 2.08–2.04 (2H, m), 1.99 (2H, q, *J* = 7.3 Hz), 1.57–1.46 (8H, m), 1.45–1.38 (2H, m), 0.14 (9H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0, 121.1, 107.8, 84.4, 37.3, 29.5, 28.9, 28.9, 28.4, 28.0, 27.1, 26.6, 19.9, 0.3 (3C); LRMS (CI, *iso*-butane) *m/z* (intensity) 249.3 $[M+H]^+$ (86), 175.2 (100); HRMS (CI, *iso*-butane) calcd for $C_{16}H_{29}Si$ $[M+H]^+$ 249.2039, found 249.2034.

Hept-6-yn-1-ylidenecyclohexane (S8).



Solid K_2CO_3 (752 mg, 5.44 mmol) was added to a solution of alkene **S7** (901 mg, 3.63 mmol) in MeOH (18 mL) at rt. The mixture was stirred at rt for 20 h and the reaction was quenched with 10% aq. NH_4Cl (40 mL). The resulting mixture was extracted with Et_2O (3 × 20 mL) and the combined organic phases were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (pentane-Et_2O, 100:1) to afford the enyne **S8** (527 mg, 82%) as a colourless liquid. R_f = 0.85 (petroleum ether-EtOAc, 20:1); ν_{max} 3312, 2926, 2855, 841, 629 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.05 (1H, tt, *J* = 7.3, 1.0 Hz), 2.18 (2H, td, *J* = 7.1, 2.6 Hz), 2.13–2.09 (2H, m), 2.08–2.04 (2H, m), 2.00 (2H, q, *J* = 7.3 Hz), 1.94 (1H, t, *J* = 2.6 Hz), 1.57–1.47 (8H, m), 1.46–1.39 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 121.0, 84.9, 68.2, 37.3, 29.4, 28.9, 28.9, 28.2, 28.0, 27.1, 26.6, 18.5.

3-(8-Cyclohexylideneoct-2-yn-1-ylidene)pentane-2,4-dione (6c)

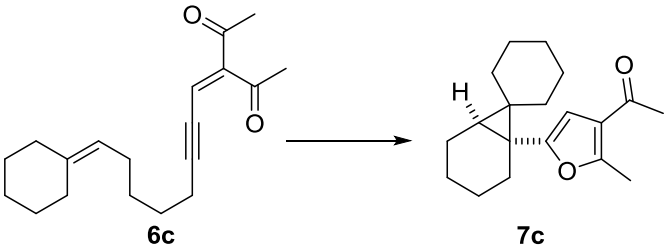


S8 **9c** **6c**

n-BuLi (1.44 mL of a 2.5 M in hexanes, 3.60 mmol) was added to a solution of enyne **S8** (527 mg, 2.99 mmol) in THF (8 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 10 min after which DMF (0.56 mL, 7.2 mmol) was added. The mixture was stirred for a further 30 min at –78 °C and the reaction was quenched by addition of 10% aqueous KH_2PO_4 (10 mL). The resulting mixture was stirred at 0 °C for 30 min. and then extracted with Et_2O (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude aldehyde **9c** as a pale yellow oil which was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (1H, t, *J* = 0.8 Hz), 5.04 (1H, tt, *J* = 7.3, 1.0 Hz), 2.41 (2H, td, *J* = 7.1, 0.8 Hz), 2.14–2.08 (2H, m), 2.08–2.04 (2H, m), 2.01 (2H, q, *J* = 7.3 Hz), 1.65–1.40 (10H, m).

Solid $MgSO_4$ (60 mg, 0.50 mmol) was added to a mixture of the aldehyde **9c**, 2,4-pentanedione (0.26 µL, 2.5 mmol), AcOH (0.86 mL, 1.5 mmol) and piperidine (0.03 mL, 0.3 mmol) in toluene (3.5 mL) at rt. The resulting mixture was heated to 30 °C and stirred at this temperature for 2.5 h. The reaction was quenched by addition of H_2O (5 mL) and the mixture was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 15:1) to provide ynenedione **6c** (484 mg, 57% over 2 steps; 68% based on diketone as the limiting reagent) as a pale yellow oil. R_f = 0.36 (petroleum ether-EtOAc, 9:1); ν_{max} 2926, 2853, 1715, 1690, 1667, 1576, 972, 912, 733, 624 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70 (1H, t, *J* = 2.4 Hz), 5.04 (1H, t, *J* = 7.3 Hz), 2.47 (3H, s), 2.43 (2H, td, *J* = 7.1, 2.4 Hz), 2.31 (3H, s), 2.12–2.09 (2H, m), 2.07–2.04 (2H, m), 2.00 (2H, q, *J* = 7.3 Hz), 1.60–1.46 (8H, m), 1.45–1.38 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.4, 195.9, 149.6, 140.4, 123.4, 120.7, 110.6, 77.1, 37.3, 31.1, 29.5, 28.9, 28.8, 28.0, 27.8, 27.4, 27.1, 26.5, 20.3.

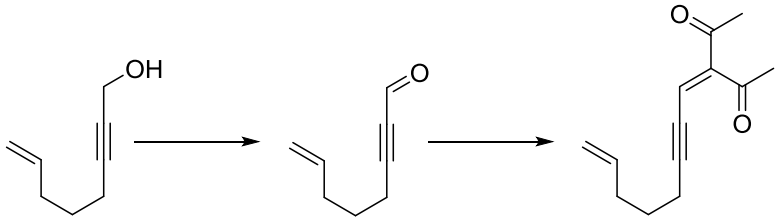
1-[2-Methyl-5-{spiro(bicyclo[4.1.0]heptane-7,1'-cyclohexan)-1-yl}furan-3-yl]ethanone (7c).



6c **7c**

Chloroacetic acid (102 mg, 1.08 mmol) was added to a solution of ynenedione **6c** (310 mg, 1.08 mmol) in CH_2Cl_2 (4.3 mL) at rt. The resulting solution was heated at reflux for 18 h then cooled to rt. The reaction was washed sequentially with saturated aqueous $NaHCO_3$ (3 × 4 mL) and brine (4 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (petroleum ether-EtOAc, 20:1) to afford cyclopropyl furan **7c** (265 mg, 85%) as a white solid. The product was crystallised from petroleum ether-EtOAc (20:1) to afford colourless crystals. R_f = 0.60 (petroleum ether-EtOAc, 9:1); m.p. = 77–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (1H, s), 2.54 (3H, s), 2.36 (3H, s), 2.00–1.88 (2H, m), 1.69 (1H, ddd, *J* = 14.6, 8.8, 5.6 Hz), 1.59–1.35 (8H, m), 1.35–1.20 (4H, m), 1.14–1.00 (3H, m), 0.91–0.81 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.6, 159.5, 156.6, 121.7, 105.8, 34.7, 31.4, 29.2, 27.6, 26.6, 25.6, 25.5, 24.5, 24.4, 21.8, 21.6, 18.4, 14.7; LRMS (EI+) *m/z* (intensity) 286.4 $[M]^+$ (100), 243.2 (30), 204.2 (90); HRMS (EI+) calcd for $C_{19}H_{26}O_2$ $[M]^+$ 286.1933, found 286.1928.

3-(Oct-7-en-2-yn-1-ylidene)pentane-2,4-dione (6d).

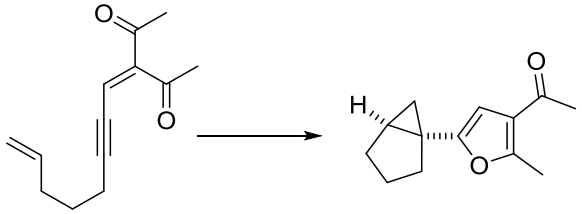


Dess-Martin periodinane (410 mg, 0.967 mmol) was added to a solution of alcohol **S9**[7] (100 mg, 0.805 mmol) in CH_2Cl_2 (8 mL) at rt. The mixture was stirred at rt for 1h and the reaction was quenched by the sequential addition of H_2O (2 mL), saturated aqueous $Na_2S_2O_3$ (8 mL) and saturated aqueous $NaHCO_3$ (8 mL). The resulting mixture was stirred vigorously until two clear phases were obtained. The biphasic mixture was poured into saturated aqueous NH_4Cl (8 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude aldehyde **9d** as a colourless oil which was used directly in the next reaction without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (1H, t, *J* = 0.7 Hz), 5.77 (1H, ddt, *J* = 17.0, 10.2, 6.7 Hz), 5.06 (1H, ddt, *J* = 17.0, 1.7, 1.6 Hz), 5.03 (1H, ddt, *J* = 10.2, 1.7, 1.1 Hz), 2.43 (2H, td, *J* = 7.1, 0.7 Hz), 2.25–2.10 (2H, m), 1.71 (2H, quintet, *J* = 7.2 Hz).

Solid $MgSO_4$ (22 mg, 0.18 mmol) was added to a mixture of aldehyde **9d**, 2,4-pentanedione (70 mg, 0.70 mmol), AcOH (0.02 mL, 0.4 mmol) and piperidine (0.01 mL, 0.1 mmol) in toluene (500 µL) at rt. The resulting mixture was heated to 30 °C and stirred at this temperature for 2 h. The reaction was quenched by addition of H_2O (3 mL) and the mixture was extracted with Et_2O (3 × 5 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel

(petroleum ether-EtOAc, 19:1) to provide the ynenedione **6d** (90 mg, 46% over 2 steps; 63% based on diketone as the limiting reagent) as a colourless oil. R_f = 0.09 (petroleum ether-EtOAc, 19:1); ν_{max} 2934, 2210, 1715, 1691, 1665, 1578, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.67 (1H, t, *J* = 2.5 Hz), 5.74 (1H, ddt, *J* = 17.1, 10.2, 6.7 Hz), 5.02 (1H, ddt, *J* = 17.1, 2.0, 1.5 Hz), 4.98 (1H, ddt, *J* = 10.2, 2.0, 1.2 Hz), 2.44 (3H, s), 2.42 (2H, td, *J* = 7.1, 2.5 Hz), 2.29 (3H, s), 2.16–2.09 (2H, m), 1.64 (2H, quintet, *J* = 7.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 195.8, 149.8, 137.3, 123.2, 115.8, 109.9, 77.1, 32.8, 31.0, 27.3, 27.2, 19.6; HRMS (ESI+) calcd for $C_{13}H_{16}O_2Na$ $[M+Na]^+$ 227.1048, found 227.1043.

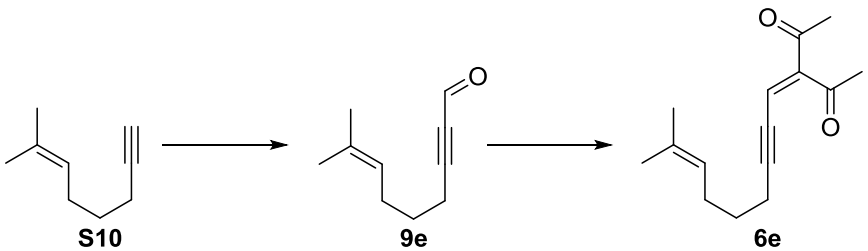
1-{5-(Bicyclo[3.1.0]hexan-1-yl)-2-methylfuran-3-yl}ethanone (7d).



6d **7d**

Chloroacetic acid (37 mg, 0.39 mmol) was added to a solution of ynenedione **6d** (80 mg, 0.39 mmol) in CH_2Cl_2 (1.6 mL) at rt. The resulting solution was heated at reflux for 22 h then cooled to rt. The reaction was washed sequentially with saturated aqueous $NaHCO_3$ (3 × 2 mL) and brine (2 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 20:1) to afford cyclopropyl furan **7d** (75 mg, 94%) as a colourless oil. R_f = 0.14 (petroleum ether-EtOAc, 19:1); ν_{max} 2934, 2864, 1676, 1572, 1393, 1221, 945 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.18 (1H, s), 2.51 (3H, s), 2.35 (3H, s), 2.06–1.97 (1H, m), 1.94 (1H, ddd, *J* = 12.2, 8.0, 0.9 Hz), 1.90–1.65 (3H, m), 1.59 (1H, dt, *J* = 8.6, 4.4 Hz), 1.34–1.23 (1H, m), 0.98 (1H, dd, *J* = 8.3, 4.8 Hz), 0.78 (1H, t, *J* = 4.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 156.8, 156.2, 122.2, 103.8, 30.0, 29.2, 27.5, 26.6, 26.3, 20.9, 14.4, 13.6; HRMS (ESI+) calcd for $C_{13}H_{16}O_2Na$ $[M+Na]^+$ 227.1043, found 227.1041.

3-(8-Methylnon-7-en-2-yn-1-ylidene)pentane-2,4-dione (6e).



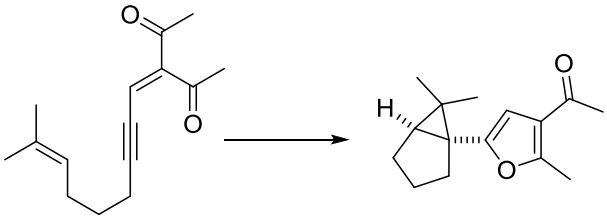
S10 **9e** **6e**

n-BuLi (1.96 mL of a 2.5 M solution in hexanes, 4.91 mmol) was added to a solution of alkyne **S10**[8] (400 mg, 3.27 mmol) in THF (11 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 10 min after which DMF (0.76 mL, 9.8 mmol) was added. The mixture was stirred for a further

30 min at –78 °C and the reaction was quenched by addition of 10% aqueous KH_2PO_4 (10 mL). The resulting mixture was stirred at 0 °C for 30 min. and then extracted with Et_2O (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude aldehyde **9e** as a colourless oil which was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (1H, t, *J* = 0.8 Hz), 5.07 (1H, tdt, *J* = 7.2, 2.8, 1.2 Hz), 2.40 (2H, td, *J* = 7.1, 0.8 Hz), 2.10 (2H, q, *J* = 7.2 Hz), 1.70 (3H, d, *J* = 1.2 Hz), 1.63 (2H, tt, *J* = 7.2, 7.1 Hz), 1.59 (3H, s).

Solid $MgSO_4$ (66 mg, 0.55 mmol) was added to a mixture of the aldehyde **9e**, 2,4-pentanedione (0.28 mL, 2.7 mmol), AcOH (0.094 mL, 1.6 mmol) and piperidine (0.03 mL, 0.3 mmol) in toluene (2 mL) at rt. The resulting mixture was heated to 30 °C and stirred at this temperature for 2 h. The reaction was quenched by addition of H_2O (5 mL) and the mixture was extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 20:1) to provide the ynenedione **6e** (374 mg, 49% over 2 steps; 60% based on the diketone as limiting reagent) as a pale yellow oil. R_f = 0.41 (petroleum ether-EtOAc, 9:1); ν_{max} 2928, 2916, 1686, 1665, 1578, 905, 729, 650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71–6.68 (1H, m), 5.07 (1H, tq, *J* = 7.3, 1.3 Hz), 2.47 (3H, d, *J* = 1.6 Hz), 2.42 (2H, tdd, *J* = 7.2, 2.3, 1.2 Hz), 2.31 (3H, d, *J* = 1.3 Hz), 2.07 (2H, q, *J* = 7.2 Hz), 1.69 (3H, s), 1.64–1.55 (2H, m), 1.60 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 195.9, 149.6, 133.1, 123.4, 123.1, 110.6, 77.0, 31.1, 28.4, 27.4, 27.3, 25.9, 19.8, 17.9; HRMS (ESI+) calcd for $C_{15}H_{20}O_2Na$ $[M+Na]^+$ 255.1356, found 255.1350.

1-{5-(6,6-Dimethylbicyclo[3.1.0]hexan-1-yl)-2-methylfuran-3-yl}ethanone (7e).

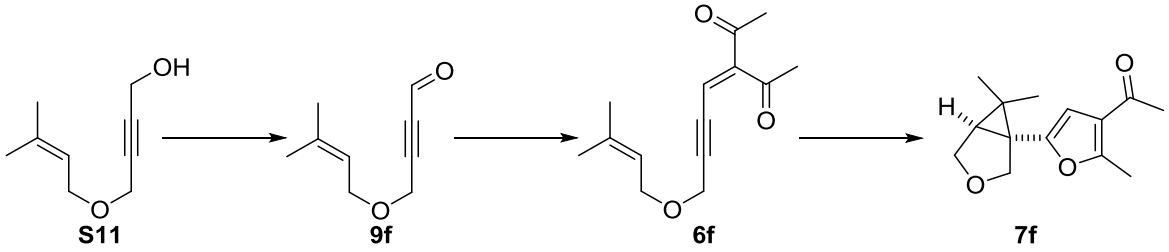


6e **7e**

Chloroacetic acid (85 mg, 0.90 mmol) was added to a solution of ynenedione **6e** (210 mg, 0.90 mmol) in CH_2Cl_2 (9 mL) at rt. The resulting solution was heated at reflux for 20 h then cooled to rt. The reaction was washed sequentially with saturated aqueous $NaHCO_3$ (3 × 9 mL) and brine (9 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 30:1) to afford the cyclopropyl furan **7e** (149 mg, 71%) as a colourless oil. R_f = 0.27 (petroleum ether-EtOAc, 19:1); ν_{max} 2961, 2926, 2874, 1694, 1670, 1566, 1452, 1416, 903, 723, 648 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (1H, s), 2.53 (3H, s), 2.36 (3H, s), 2.10–1.90 (4H, m), 1.72–1.64 (1H, m), 1.61–1.52 (1H, m), 1.50 (1H, d, *J* = 6.1 Hz), 1.08 (3H, s), 0.91 (3H, s); ^{13}C NMR

(101 MHz, $CDCl_3$) δ 194.5, 156.9, 156.6, 121.9, 105.8, 37.6, 36.9, 31.3, 29.2, 28.1, 26.9, 25.6, 24.5, 15.8, 14.6; HRMS (ESI+) calcd for $C_{15}H_{20}O_2Na$ $[M+Na]^+$ 255.1356, found 255.1356.

1-{5-(6,6-Dimethyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-methylfuran-3-yl}ethanone (7f).

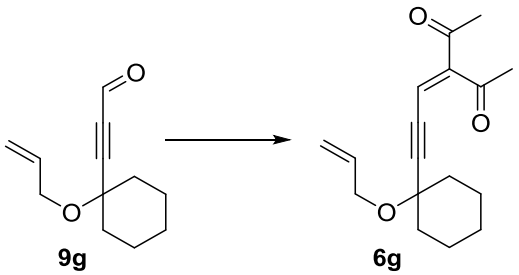


To a solution of propargyl alcohol **S11**[9] (300 mg, 1.95 mmol) in CH_2Cl_2 (20 mL) at rt was added Dess-Martin periodinane (990 mg, 2.33 mmol). The resulting mixture was stirred at rt for 30 min and the reaction was then quenched by the sequential addition of H_2O (6 mL), saturated aqueous $Na_2S_2O_3$ (20 mL) and saturated aqueous $NaHCO_3$ (20 mL). The resulting mixture was stirred vigorously until two clear phases were obtained. The biphasic mixture was poured into saturated aqueous NH_4Cl (20 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to deliver the crude aldehyde **9f** which was used directly in the next step without further purification. ^1H NMR (400 MHz, $CDCl_3$) δ 9.25 (1H, s), 5.33 (1H, tqq, *J* = 7.1, 1.4, 1.4 Hz), 4.32 (2H, s), 4.08 (2H, d, *J* = 7.1 Hz), 1.77 (3H, b s), 1.71 (3H, b s).

Ethylenediamine diacetate (35 mg, 0.19 mmol) was added to a solution of crude aldehyde **9f** and 2,4-pentandione (0.20 mL, 1.9 mmol) in toluene (4.3 mL) at rt. The resulting mixture was stirred at rt for 3 h. The reaction was quenched by addition of H_2O (5 mL) and the mixture was extracted with Et_2O (3 × 5 mL). The combined organic extracts were washed with brine (5 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford the crude ynenedione **6f** which was used directly in the next step without further purification.

Chloroacetic acid (194 mg, 2.06 mmol) was added to a solution of the crude ynenedione **6f** in CH_2Cl_2 (7.7 mL) at rt. The resulting solution was heated at reflux for 18 h then cooled to rt. The reaction mixture was washed sequentially with saturated aqueous $NaHCO_3$ (3 × 8 mL) and brine (8 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (petroleum ether-EtOAc, 19:1) to yield the cyclopropyl furan **7f** (276 mg, 61% over 3 steps) as a colourless oil. R_f = 0.36 (petroleum ether-EtOAc, 9:1); ν_{max} 2919, 2863, 1677, 1569, 949 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.26 (1H, s), 4.03 (1H, dd, *J* = 8.7, 3.9 Hz), 4.02 (1H, d, *J* = 8.5 Hz), 3.89 (1H, d, *J* = 8.7 Hz), 3.88 (1H, d, *J* = 8.5 Hz), 2.52 (3H, s), 2.35 (3H, s), 1.77 (1H, d, *J* = 3.9 Hz), 1.18 (3H, s), 0.96 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 157.4, 151.8, 122.0, 107.7, 71.6, 68.4, 35.7, 35.5, 29.2, 25.6, 23.2, 14.5, 13.5; HRMS (ESI+) calcd for $C_{14}H_{18}O_3Na$ $[M+Na]^+$ 257.1148, found 257.1140.

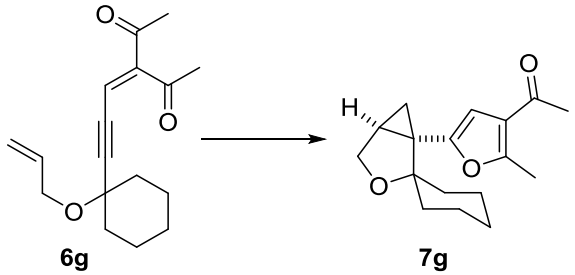
3-{3-[1-(Allyloxy)cyclohexyl]prop-2-yn-1-ylidene}pentane-2,4-dione (6g).



9g **6g**

Ethylenediamine diacetate (36 mg, 0.20 mmol) was added to a solution of the aldehyde **9g**[10] (461 mg, 2.10 mmol) and 2,4-pentanedione (0.21 mL, 2.0 mmol) in toluene (2 mL) at rt. The resulting mixture was stirred at rt for 2 h and the reaction was then quenched by addition of H_2O (5 mL). The mixture was extracted with Et_2O (3 × 5 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 10:1) to provide the ynenedione **6g** (500 mg, 81%) as a pale yellow oil. R_f = 0.20 (petroleum ether-EtOAc, 10:1); ν_{max} 2936, 2859, 1715, 1694, 1667, 1580, 995, 926 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.72 (1H, s), 5.93 (1H, ddt, *J* = 17.1, 10.4, 5.5 Hz), 5.30 (1H, dq, *J* = 17.1, 1.6 Hz), 5.15 (1H, dq, *J* = 10.4, 1.6 Hz), 4.06 (2H, dt, *J* = 5.5, 1.6 Hz), 2.46 (3H, s), 2.33 (3H, s), 1.97–1.89 (2H, m), 1.73–1.63 (4H, m), 1.56–1.41 (3H, m), 1.36–1.26 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.0, 195.6, 150.5, 135.2, 121.7, 116.7, 109.5, 81.4, 74.6, 65.0, 36.9, 31.0, 27.2, 25.4, 22.7; HRMS (ESI+) calcd for $C_{17}H_{22}O_3Na$ $[M+Na]^+$ 297.1461, found 297.1466.

1-{5-(6,6-Dimethyl-3-oxaspirobicyclo[3.1.0]hexane-2,1'-cyclohexan-1-yl)-2-methylfuran-3-yl}-ethanone (7g).

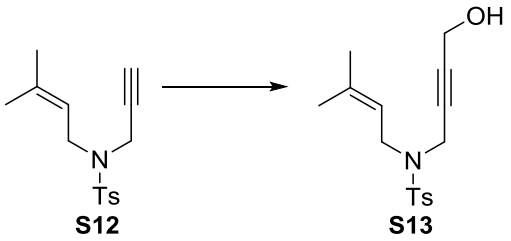


6g **7g**

Chloroacetic acid (170 mg, 1.80 mmol) was added to a solution of ynenedione **6g** (500 mg, 1.65 mmol) in CH_2Cl_2 (7.2 mL) at rt and the resulting solution was heated at reflux for 48 h then cooled to rt. The reaction mixture was washed with saturated aqueous $NaHCO_3$ (3 × 8 mL) and brine (8 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 10:1) to afford the cyclopropyl furan **7g** (440 mg, 88%) as a colourless oil. R_f = 0.20 (petroleum ether-EtOAc, 9:1); ν_{max} 2930, 2857, 1676, 1568, 993, 959, 926, 824, 633 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.30 (1H, s), 3.89 (1H, dd, *J* = 8.6, 2.7 Hz), 3.75 (1H, d, *J* = 8.6 Hz), 2.55 (3H, s), 2.36 (3H, s), 1.83 (1H, ddd, *J* = 7.8, 4.4, 2.7 Hz), 1.72–1.56 (5H, m), 1.55–1.39 (3H, m), 1.14–

1.05 (2H, m), 1.03 (1H, t, *J* = 4.4 Hz), 0.73 (1H, dd, *J* = 7.8, 4.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 157.6, 152.6, 122.0, 108.5, 82.2, 66.3, 33.2, 32.9, 31.5, 29.2, 25.7, 23.1 (2C), 21.8, 14.7, 13.6; HRMS (ESI+) calcd for $C_{17}H_{22}O_3Na$ $[M+Na]^+$ 297.1461, found 297.1460.

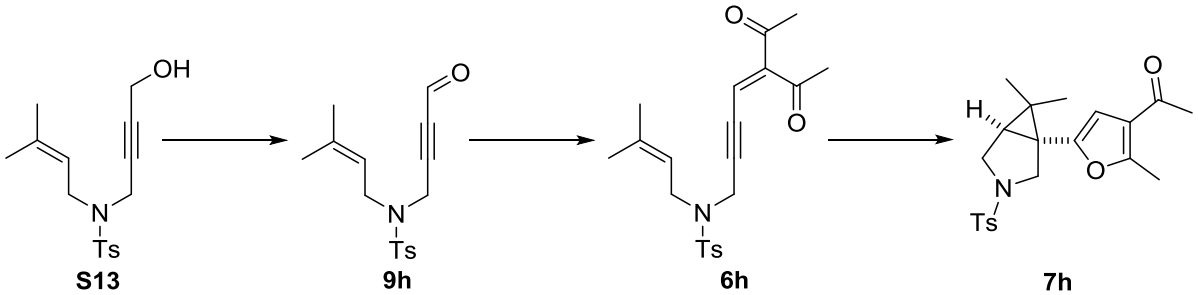
_N_-(4-Hydroxybut-2-yn-1-yl)-4-methyl-_N_-(3-methylbut-2-en-1-yl)benzenesulfonamide (S13).



S12 **S13**

n-BuLi (0.52 mL of a 2.5 M solution in hexanes, 1.3 mmol) was added to a solution of enyne **S12**[11] (300 mg, 1.08 mmol) in THF (4.5 mL) at –78 °C. The reaction was stirred for at –78 °C for 4 h and then paraformaldehyde powder (39 mg, 1.30 mmol) was added. The resulting mixture was stirred at –78 °C for 2 h, then slowly warmed to rt over 20 h. The reaction was quenched by addition of saturated aqueous NH_4Cl (5 mL) and the resulting mixture was extracted with Et_2O (3 × 5 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 3:1) to provide the alcohol **S13** (259 mg, 78%) as a colourless oil. R_f = 0.26 (petroleum ether-EtOAc, 3:1); ν_{max} 3518, 2972, 2919, 2864, 901, 738, 658 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (2H, d, *J* = 8.2 Hz), 7.29 (2H, d, *J* = 8.2 Hz), 5.10–5.04 (1H, m), 4.04 (2H, t, *J* = 1.7 Hz), 3.95 (2H, dt, *J* = 6.0, 1.7 Hz), 3.77 (2H, d, *J* = 7.3 Hz), 2.41 (3H, s), 1.70 (3H, s), 1.68 (1H, t, *J* = 6.0 Hz), 1.64 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 139.1, 136.2, 129.4, 128.0, 117.9, 83.6, 78.9, 50.7, 44.2, 35.8, 25.9, 21.6, 17.9; HRMS (ESI+) calcd for $C_{16}H_{21}NO_3NaS$ $[M+Na]^+$ 330.1134, found 330.1119.

1-{5-(6,6-Dimethyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)-2-methylfuran-3-yl}ethanone (7h).



S13 **9h** **6h** **7h**

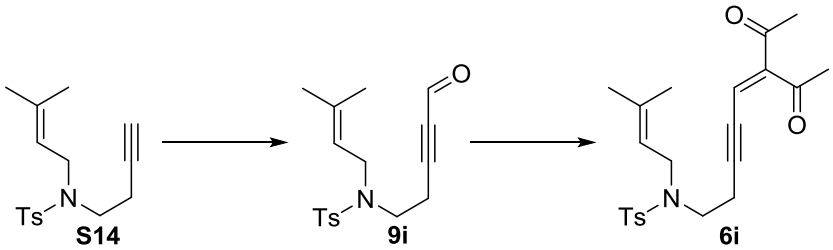
To a solution of propargyl alcohol **S13** (250 mg, 0.813 mmol) in CH_2Cl_2 (8.4 mL) at rt was added Dess-Martin periodinane (416 mg, 0.981 mmol). The resulting mixture was stirred at rt for 30 min and the reaction was then quenched by the sequential addition of H_2O (3 mL), saturated aqueous $Na_2S_2O_3$ (10 mL) and saturated aqueous $NaHCO_3$ (10 mL). The resulting mixture was stirred vigorously until two clear phases were obtained. The biphasic mixture was poured into saturated

aqueous NH_4Cl (10 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to deliver the crude aldehyde **9h** which was used directly in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (1H, s), 7.73 (2H, d, *J* = 8.2 Hz), 7.31 (2H, d, *J* = 8.2 Hz), 5.10 (1H, tqq, J = 7.3, 1.4, 1.4 Hz), 4.24 (2H, s), 3.81 (2H, d, *J* = 7.3 Hz), 2.43 (3H, s), 1.73 (3H, s), 1.66 (3H, s).

Ethylenediamine diacetate (15 mg, 0.083 mmol) was added to a solution of the crude aldehyde **9h** and 2,4-pentanedione (80 mg, 0.80 mmol) in toluene (2 mL) at rt and the resulting mixture was stirred at rt for 3 h. The reaction was quenched by addition of H_2O (2 mL) and the mixture was extracted with Et_2O (3 × 2 mL). The combined organic extracts were washed with brine (2 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford the crude ynenedione **6h** which was used directly in the next step without further purification.

Chloroacetic acid (76.5 mg, 0.810 mmol) was added to a solution of the crude ynenedione **6h** in CH_2Cl_2 (3.2 mL) at rt. The resulting solution was heated at reflux for 18 h then cooled to rt. The mixture was washed sequentially with saturated aqueous $NaHCO_3$ (3 × 3 mL) and brine (3 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure and the resulting residue was purified by flash chromatography on silica gel (petroleum ether-EtOAc, 4:1) to yield the cyclopropyl furan **7h** (182 mg, 60% over 3 steps) as a colourless oil. R_f = 0.31 (petroleum ether-EtOAc, 3:1); ν_{max} 2926, 2872, 1676, 1568, 1344, 1229, 1167, 1099, 949, 814, 667, 611 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (2H, d, *J* = 8.1 Hz), 7.30 (2H, d, *J* = 8.1 Hz), 6.17 (1H, s), 3.68 (1H, d, *J* = 9.6 Hz), 3.48 (2H, d, *J* = 3.0 Hz), 3.37 (1H, d, *J* = 9.6 Hz), 2.49 (3H, s), 2.41 (3H, s), 2.33 (3H, s), 1.67 (1H, t, *J* = 3.0 Hz), 1.14 (3H, s), 0.90 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0, 157.5, 151.6, 143.6, 134.2, 129.8, 127.5, 122.1, 107.6, 51.7, 47.7, 33.7, 33.6, 29.2, 26.7, 23.5, 21.6, 14.5, 13.8; LRMS (EI+) *m/z* (intensity) 248.0 $[M]^+$ (30), 205.0 (25), 179.0 (40),164.0 (100), 149.0 (78); HRMS (ESI+) calcd for $C_{21}H_{25}O_4SNa$ $[M+Na]^+$ 410.1397, found 410.1383.

3-{5-[*N*-Tosyl-(3-methylbut-2-en-1-yl)aza]pent-2-yn-1-ylidene}pentane-2,4-dione (6i).

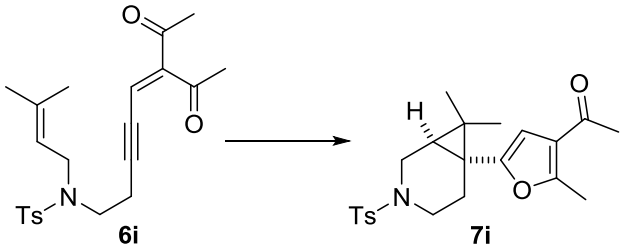


n-BuLi (0.54 mL of a 1.4 M solution in hexanes, 0.76 mmol) was added to a solution of the alkyne **S14**[12] (200 mg, 0.69 mmol) in THF (4.5 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 10 min and then DMF (0.33 mL, 4.2 mmol) in THF (1.5 mL) was added. The mixture was stirred for a further 30 min at –78 °C and the reaction was then quenched by the addition of 5% aqueous H_2SO_4 (6 mL) followed by stirring at rt for 1 h. The resulting mixture was extracted with Et_2O (3 ×

10 mL) and the combined organic extracts were washed with saturated aqueous $NaHCO_3$ (10 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude aldehyde **9i** as a colourless oil. This crude material was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (1H, t, *J* = 0.8 Hz), 7.70 (2H, d, *J* = 8.1 Hz), 7.31 (2H, d, *J* = 8.1 Hz), 5.04–4.98 (1H, m), 3.81 (2H, d, *J* = 7.1 Hz), 3.28 (2H, t, *J* = 7.4 Hz), 2.72 (2H, t, *J* = 7.4 Hz), 2.43 (3H, s), 1.69 (3H, s), 1.63 (3H, s).

Solid $MgSO_4$ (20 mg, 0.17 mmol) was added to a mixture of the aldehyde **9i**, 2,4-pentanedione (0.06 mL, 0.6 mmol), AcOH (0.02 mL, 0.3 mmol) and piperidine (0.01 mL, 0.1 mmol) in toluene (600 µL) at rt. The resulting mixture was heated to 30 °C and stirred at this temperature for 2.5 h. The reaction was quenched by addition of H_2O (5 mL) and the mixture was extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether-EtOAc, 4:1) to provide the ynenedione **6i** (168 mg, 66% over 2 steps) as a colourless oil. R_f = 0.29 (petroleum ether-EtOAc, 4:1); ν_{max} 2969, 2924, 2868, 2212, 1713, 1690, 1665, 1591, 721, 654 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (2H, d, *J* = 8.1 Hz), 7.29 (2H, d, *J* = 8.1 Hz), 6.62 (1H, t, *J* = 2.4 Hz), 5.01–4.94 (1H, m), 3.79 (2H, b d, *J* = 7.1 Hz), 3.25 (2H, t, *J* = 7.4 Hz), 2.71 (2H, ddd, *J* = 7.8, 7.1, 2.4 Hz), 2.44 (3H, s), 2.42 (3H, s), 2.30 (3H, s), 1.66 (3H, d, *J* = 0.9 Hz), 1.61 (3H, d, *J* = 0.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 195.7, 150.2, 143.5, 137.8, 136.9, 129.8, 127.3, 122.4, 118.7, 105.9, 78.2, 46.4, 45.7, 31.0, 27.3, 25.9, 21.6, 21.5, 17.9; LRMS (EI+) *m/z* (intensity) 401 $[M]^+$ (8), 358.0 (12), 246.1 (100), 217.1 (45), 91.0 (25); HRMS (EI+) calcd for $C_{22}H_{27}O_4NS$ $[M]^+$ 401.1661, found 401.1660.

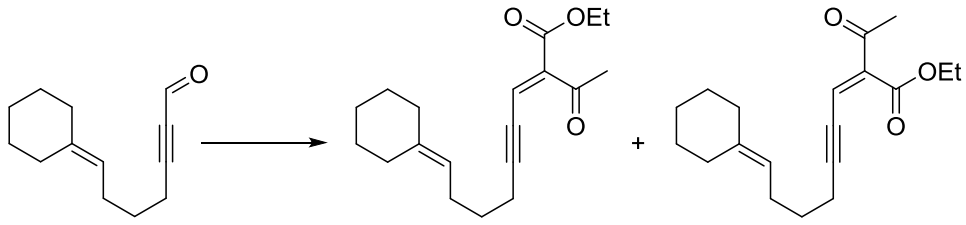
1-{5-(7,7-Dimethyl-3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)-2-methylfuran-3-yl}ethanone (7i).



Chloroacetic acid (28.5 mg, 0.302 mmol) was added to a solution of the ynenedione **6i** (120 mg, 0.31 mmol) in CH_2Cl_2 (1.2 mL) at rt. The resulting solution was heated at reflux for 72 h then cooled to rt. The reaction mixture was washed with saturated aqueous $NaHCO_3$ (3 × 2 mL) and brine (2 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 40:1) to afford the cyclopropyl furan **7i** (98 mg, 82%) as a colourless foam. R_f = 0.32 (petroleum ether-EtOAc, 4:1); ν_{max} 2947, 2924, 2870, 1674, 1566, 936, 816, 714, 677 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (2H, d, *J* = 8.1 Hz), 7.32 (2H, d, *J* = 8.1 Hz), 6.03 (1H, s), 3.68 (1H, d, *J* = 12.1 Hz), 3.55 (1H, dt, *J* = 10.9, 3.3 Hz), 2.92 (1H, dd, *J* = 12.1, 6.2 Hz), 2.49

(3H, s), 2.42 (3H, s), 2.31 (3H, s), 2.21–2.14 (1H, m), 2.10–2.06 (2H, m), 1.30 (3H, s), 1.12 (1H, dd, *J* = 6.2, 1.5 Hz), 0.85 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 157.1, 156.7, 143.6, 133.2, 129.8, 127.8, 121.8, 106.3, 42.2, 40.7, 29.2, 25.6, 25.5, 24.3, 23.9, 23.1, 21.6, 16.4, 14.6; LRMS (EI+) *m/z* (intensity) 401.0 $[M]^+$ (10), 358.0 (25), 246.1 (100), 217.0 (90), 91.0 (45); HRMS (EI+) calcd for $C_{22}H_{27}O_4NS$ $[M]^+$ 401.1661, found 401.1658.

Ethyl 2-acetyl-9-cyclohexylidenenon-2-en-4-ynoate (6j).



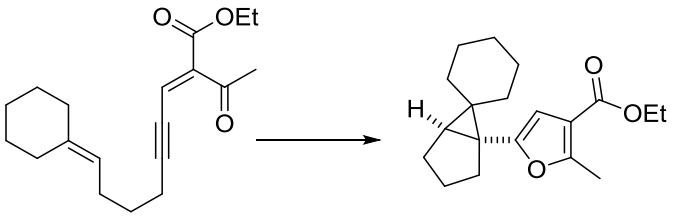
9a ***E*-6j** ***Z*-6j**

Solid $MgSO_4$ (8 mg, 0.07 mmol) was added to a mixture of the aldehyde **9a** (68.5 mg, 0.360 mmol), ethyl acetoacetate (0.04 mL, 0.3 mmol), AcOH (0.01 mL, 2 mmol) and piperidine (0.01 mL, 0.1 mmol) in toluene (330 µL) at rt. The resulting mixture was heated to 35 °C and stirred at this temperature for 3 h. The reaction was quenched by addition of H_2O (5 mL) and the reaction mixture was extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 49:1 to 19:1) to provide the ester ***E*-6j** (34.3 mg, 32%) and the ester ***Z*-6j** (30.7 mg, 28%) as a colourless oils.

***E*-6j**: R_f = 0.25 (petroleum ether-EtOAc, 19:1); ν_{max} 2928, 2853, 1717, 1699, 1684, 1541, 910, 733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (1H, t, *J* = 2.5 Hz), 5.02 (1H, t, *J* = 7.3 Hz), 4.25 (2H, q, *J* = 7.1 Hz), 2.44 (3H, s), 2.40 (2H, td, *J* = 7.2, 2.5 Hz), 2.13–2.04 (6H, m), 1.58 (2H, quintet, *J* = 7.2 Hz), 1.56–1.45 (6H, m), 1.30 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 164.2, 142.3, 141.3, 124.1, 119.8, 108.6, 76.8, 61.7, 37.4, 30.6, 28.9, 28.7, 28.0, 27.1, 26.3, 26.2, 19.7, 14.3; LRMS (EI+) *m/z* (intensity) 302.2 $[M]^+$ (100), 259.1 (85), 246.1 (20), 220.1 (70), 191.1 (30), 85.9 (100), 83.9 (100); HRMS (EI+) calcd for $C_{19}H_{26}O_3$ $[M]^+$ 302.1882, found 302.1879.

***Z*-6j**: R_f = 0.15 (petroleum ether-EtOAc, 19:1); ν_{max} 2930, 2855, 1713, 1586, 910, 733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (1H, t, *J* = 2.4 Hz), 5.02 (1H, t, *J* = 7.3 Hz), 4.34 (2H, q, *J* = 7.1 Hz), 2.43 (2H, td, *J* = 7.2, 2.4 Hz), 2.35 (3H, s), 2.14–2.04 (6H, m), 1.59 (2H, quintet, *J* = 7.2 Hz), 1.57–1.45 (6H, m), 1.35 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.2, 165.8, 141.7, 141.3, 125.6, 119.8, 109.9, 77.7, 61.6, 37.4, 28.9, 28.9, 28.7, 28.0, 27.6, 27.1, 26.3, 19.8, 14.3; LRMS (EI+) *m/z* (intensity) 302.2 $[M]^+$ (40), 259.1 (20), 246.1 (5), 220.1 (15), 193.1 (11), 191.1 (10), 84.0 (100); HRMS (EI+) calcd for $C_{19}H_{26}O_3$ $[M]^+$ 302.1882, found 302.1883.

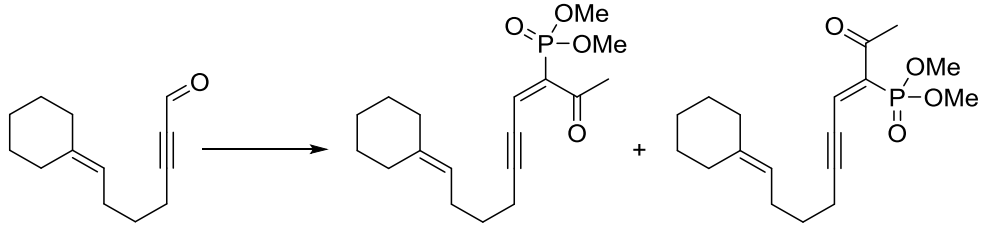
Ethyl 2-methyl-5-{spiro(bicyclo[3.1.0]hexane-6,1'-cyclohexan)-1-yl}furan-3-carboxylate (7j).



***E*-6j** **7j**

Chloroacetic acid (10.3 mg, 0.109 mmol) was added to a solution of ester ***E*-6j** (33 mg, 0.11 mmol) in CH_2Cl_2 (400 µL) at rt. The resulting solution was heated at reflux for 20 h then cooled to rt. The reaction mixture was diluted with CH_2Cl_2 (1 mL) and then washed with saturated aqueous $NaHCO_3$ (3 × 1.5 mL) and brine (1.5 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 20:1) to afford the cyclopropyl furan **7j** (19.7 mg, 60%) as a colourless oil. R_f = 0.22 (petroleum ether-EtOAc, 20:1); ν_{max} 2926, 2853, 1717, 1586, 910, 779, 733 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.17 (1H, s), 4.26 (2H, qd, *J* = 7.1, 1.8 Hz), 2.53 (3H, s), 2.06–1.94 (4H, m), 1.65–1.40 (9H, m), 1.33 (3H, t, *J* = 7.1 Hz), 1.35–1.29 (2H, m), 1.23–1.11 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 157.4, 156.9, 113.6, 106.0, 60.0, 37.9, 37.3, 34.9, 34.0, 30.9, 29.9, 26.7, 26.7, 26.2, 25.5, 25.4, 14.6, 14.0; LRMS (EI+) *m/z* (intensity) 302.2 $[M]^+$ (100), 259.1 (50), 246.1 (10), 220.1 (40), 191.1 (15), 84.0 (93); HRMS (EI+) calcd for $C_{19}H_{26}O_3$ $[M]^+$ 302.1882, found 302.1883.

(*E*)-Dimethyl(10-cyclohexylidene-2-oxodec-3-en-5-yn-3-yl)phosphonate (*E*-6k).



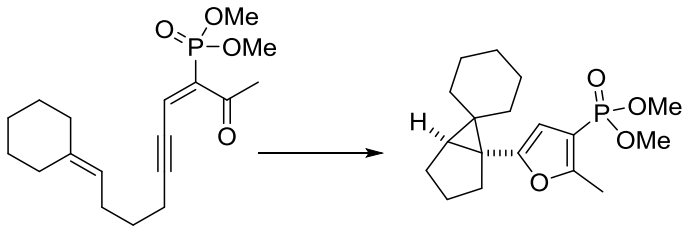
9a ***E*-6k** ***Z*-6k**

Ethylenediamine diacetate (8 mg, 0.04 mmol) was added to a solution of aldehyde **9a** (251 mg, 1.32 mmol) and dimethyl 2-oxopropylphosphonate (0.12 mL, 0.88 mmol) in toluene (1 mL) at rt. The resulting mixture was stirred at rt for 3 h and the reaction was quenched by addition of H_2O (5 mL). The mixture was extracted with Et_2O (3 × 5 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 3:1) to provide the phosphonates ***E*-6k** (190 mg, 64%) and ***Z*-6k** (36 mg, 12%) as colourless oils.

***E*-6k**: R_f = 0.15 (petroleum ether-EtOAc, 3:1); ν_{max} 2926, 2851, 2209, 1709, 1692, 1678, 1572, 827, 775, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.94 (1H, t, *J* = 2.4 Hz, J_{PH} = 22.1 Hz), 5.01 (1H, b t, *J* = 7.3 Hz), 3.79 (3H, s), 3.76 (3H, s), 2.51 (3H, s), 2.48–2.41 (2H, m), 2.12–2.04 (6H, m), 1.60 (2H, quintet, *J* = 7.2 Hz), 1.56–1.45 (6H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.4, 141.4, 139.6 (d, *J* =

176.7 Hz), 131.3 (d, *J* = 11.4 Hz), 119.7, 110.3, 77.6, 53.3 (d, *J* = 5.7 Hz), 37.3, 30.8 (d, *J* = 3.6 Hz), 28.9, 28.8, 28.6, 28.0, 27.0, 26.3, 19.7; HRMS (ESI+) calcd for $C_{18}H_{27}O_4NaP$ $[M+Na]^+$ 361.1539, found 361.1523.

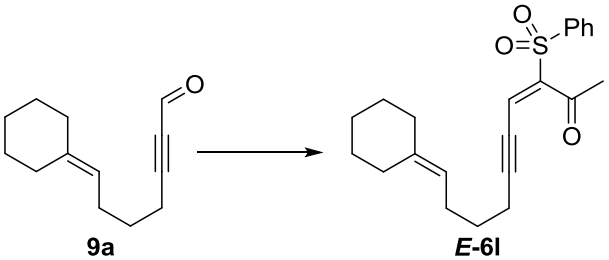
Dimethyl[2-methyl-5-{spiro(bicyclo[3.1.0]hexane-6,1'-cyclohexan)-1-yl)}furan-3-yl]-phosphonate (7k).



***E*-6k** **7k**

Chloroacetic acid (28.4 mg, 0.301 mmol) was added to a solution of ynenone ***E*-6k** (100 mg, 0.30 mmol) in CH_2Cl_2 (1.2 mL) at rt. The resulting solution was heated at reflux for 48 h then cooled to rt. The reaction mixture was washed sequentially with saturated aqueous $NaHCO_3$ (3 × 1.5 mL) and brine (1.5 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 3:1) to afford the cyclopropyl furan **7k** (88 mg, 88%) as a colourless oil. R_f = 0.19 (petroleum ether-EtOAc, 3:1); ν_{max} 2922, 2849, 1570, 826, 777 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.96 (1H, d, J_{PH} = 3.1 Hz), 3.73 (3H, d, J_{PH} = 4.9 Hz), 3.70 (3H, d, J_{PH} = 4.9 Hz), 2.47 (3H, d, J_{PH} = 2.1 Hz), 2.07–1.91 (4H, m), 1.65–1.37 (9H, m), 1.33–1.09 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7 (d, *J* = 26.6 Hz), 158.1 (d, *J* = 15.7 Hz), 107.3 (d, *J* = 11.7 Hz), 105.3 (d, *J* = 216.6 Hz), 52.4 (d, *J* = 2.7 Hz), 52.4 (d, *J* = 2.5 Hz), 37.8, 37.4, 34.9, 33.9, 30.9, 29.8, 26.7, 26.6, 26.2, 25.5, 25.4, 13.7; HRMS (ESI+) calcd for $C_{18}H_{27}O_4NaP$ $[M+Na]^+$ 361.1539, found 361.1524.

(*E*)-10-Cyclohexylidene-3-(phenylsulfonyl)dec-3-en-5-yn-2-one (*E*-6l).

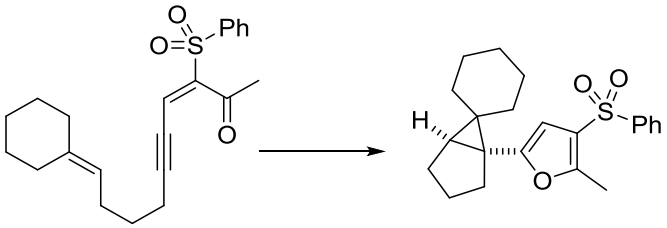


9a ***E*-6l**

Ethylenediamine diacetate (17 mg, 0.094 mmol) was added to a solution of the aldehyde **9a** (329 mg, 1.73 mmol) and 1-(phenylsulfonyl)propan-2-one (285 mg, 1.44 mmol) in toluene (1 mL) at rt. The resulting mixture was stirred at rt for 4 h and the reaction was then quenched by addition of H_2O (5 mL). The mixture was and extracted with Et_2O (3 × 5 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-Et_2O, 9:1) to

provide sulfone ***E*-6l** (309 mg, 58%) as a pale yellow oil. R_f = 0.18 (petroleum ether-Et_2O, 9:1); ν_{max} 2926, 2851, 1572, 914, 731, 689, 610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93–7.88 (2H, m), 7.63–7.57 (1H, m), 7.54–7.49 (2H, m), 7.42 (1H, t, *J* = 2.5 Hz), 5.00 (1H, t, *J* = 7.3 Hz), 2.52 (3H, s), 2.48 (2H, td, *J* = 7.1, 2.5 Hz), 2.12–2.02 (6H, m), 1.61 (2H, tt, *J* = 7.3, 7.1 Hz), 1.56–1.44 (6H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 148.6, 141.5, 140.1, 133.7, 129.0, 128.7, 128.2, 126.8, 119.4, 115.2, 105.0, 76.2, 37.3, 31.4, 28.8, 28.7, 28.3, 28.0, 26.9, 26.2, 19.9; HRMS (ESI+) calcd for $C_{22}H_{26}O_3NaS$ $[M+Na]^+$ 393.1495, found 393.1484.

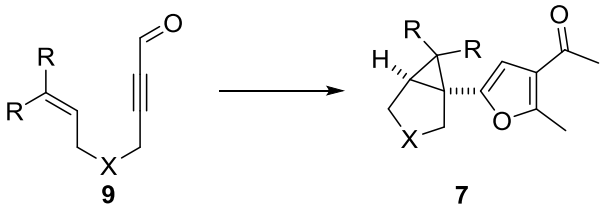
2-Methyl-3-(phenylsulfonyl)-5-{spiro(bicyclo[3.1.0]hexane-6,1'-cyclohexan)-1-yl}furan (7l).



***E*-6l** **7l**

Chloroacetic acid (30 mg, 0.32 mmol) was added to a solution of sulfone **6l** (119 mg, 0.321 mmol) in CH_2Cl_2 (1.3 mL) at rt. The resulting solution was heated at reflux for 18 h and then cooled to rt. The reaction mixture was washed sequentially with saturated aqueous $NaHCO_3$ (3 × 1.5 mL) and brine (1.5 mL) and the organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 15:1) to afford the cyclopropyl furan **7l** (103 mg, 87%) as a pale yellow solid. R_f = 0.18 (petroleum ether-EtOAc, 15:1); m.p. = 89–91 °C; ν_{max} 2945, 2922, 2851, 1559, 804, 733, 692, 611 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94–7.88 (2H, m), 7.60–7.48 (3H, m), 6.10 (1H, s), 2.52 (3H, s), 2.03–1.88 (4H, m), 1.65–1.57 (2H, m), 1.56–1.35 (7H, m), 1.28 (2H, quintet, *J* = 5.8 Hz), 1.18–1.05 (2H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 154.7, 143.0, 133.0, 129.3, 126.9, 122.3, 105.0, 37.7, 37.6, 35.2, 33.9, 30.7, 29.7, 26.6, 26.6, 26.1, 25.4, 25.3, 13.2; HRMS (ESI+) calcd for $C_{22}H_{26}O_3NaS$ $[M+Na]^+$ 393.1495, found 393.1477.

General Procedure for One-pot Knoevenagel Condensation and Cascade Cyclisation

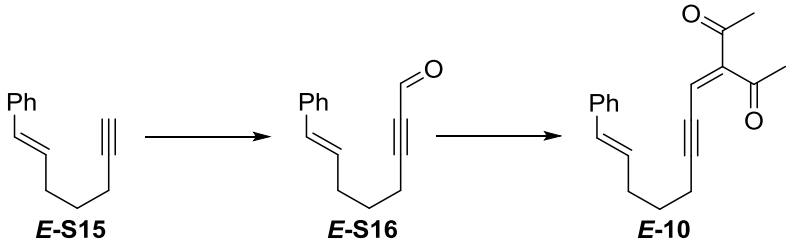


9 **7**

$MgSO_4$ (0.4 equiv.) was added to a solution of aldehyde **9** (1.0 equiv.), 2,4-pentanedione (1.0 equiv) and chloroacetic acid (1.0 equiv) in toluene (4 mL per mmol) at rt. The resulting mixture was heated at 60 °C and stirred at this temperature until complete consumption of the starting aldehyde (reaction monitored by TLC and ^1H NMR). The reaction was quenched by addition of H_2O (4 mL per mmol) and extracted with Et_2O (3 × 4 mL per mmol). The combined organic layers were

washed with saturated aqueous $NaHCO_3$ (3 × 4 mL per mmol) and brine (4 mL per mmol), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel to provide the corresponding cyclopropyl furan **7**.

(*E*)-3-(8-Phenyloct-7-en-2-yn-1-ylidene)pentane-2,4-dione (*E*-10).

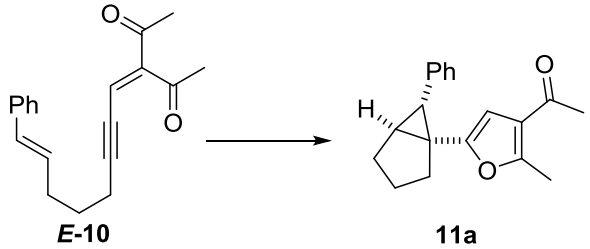


***E*-S15** ***E*-S16** ***E*-10**

n-BuLi (0.99 mL of a 2.5 M solution in hexanes, 2.5 mmol) was added to a solution of the enyne ***E*-S15**[11] (280 mg, 1.64 mmol) in THF (5 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 10 min after which DMF (0.31 mL, 3.9 mmol) was added. The reaction mixture was stirred for a further 30 min at –78 °C and the reaction was then quenched by addition of 10% aqueous KH_2PO_4 (10 mL). The resulting mixture was stirred at 0 °C for 30 min and then extracted with Et_2O (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude aldehyde ***E*-S16** (287.7 mg) as a colourless oil which was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (1H, t, J = 0.7 Hz), 7.37–7.25 (4H, m), 7.24–7.18 (1H, m), 6.43 (1H, bd, J = 15.8 Hz), 6.23–613 (1H, m), 2.48 (2H, td, J = 7.1, 0.7 Hz), 2.34 (2H, td, J = 7.3, 1.2 Hz), 1.75 (2H, tt, J = 7.3, 7.1 Hz).

Solid $MgSO_4$ (14 mg, 0.12 mmol) was added to a mixture of the crude aldehyde ***E*-S16** (142.7 mg, 0.720 mmol), 2,4-pentanedione (60 µL, 0.6 mmol), AcOH (20 µL, 0.4 mmol) and piperidine (10 µL, 0.1 mmol) in toluene (0.6 mL) at rt. The resulting mixture was heated to 30 °C and stirred at this temperature for 3 h. The reaction was quenched by addition of H_2O (5 mL) and the resulting mixture was extracted with Et_2O (3 × 5 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 20:1) to provide the ynenedione ***E*-10** (95.3 mg, 48% over 2 steps) as a pale yellow oil. R_f = 0.31 (petroleum ether-EtOAc, 10:1); ν_{max} 2936, 2864, 2210, 1713, 1674, 1665, 1572, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (4H, m), 7.23–7.18 (1H, m), 6.69 (1H, t, J = 2.5 Hz), 6.42 (1H, b d, J = 15.8 Hz), 6.17 (1H, dt, J = 15.8, 7.0 Hz), 2.50 (2H, td, J = 7.2, 2.5 Hz), 2.48 (3H, s), 2.36–2.30 (2H, m), 2.32 (3H, s), 1.75 (2H, quintet, J = 7.2 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.4, 195.9, 149.9, 137.6, 131.3, 129.2, 128.7 (2C), 127.3 (2C), 126.2, 123.2, 109.9, 77.7, 32.2, 31.1, 27.9, 27.3, 19.8; HRMS (ESI+) calcd for $C_{19}H_{20}O_2Na$ $[M+Na]^+$ 303.1356, found 303.1350.

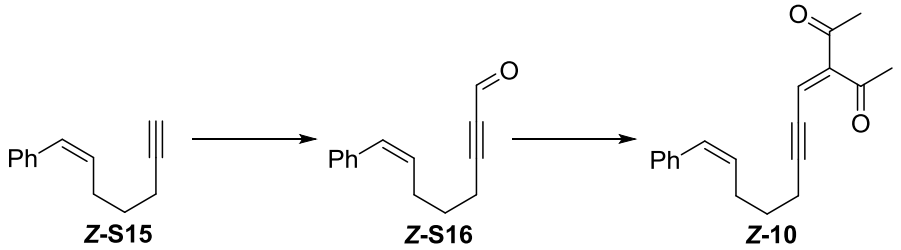
1-{2-Methyl-5-(6-phenylbicyclo[3.1.0]hexan-1-yl)furan-3-yl}ethanone (11a).



***E*-10** **11a**

Chloroacetic acid (57 mg, 0.60 mmol) was added to a solution of ynenedione ***E*-10** (168 mg, 0.60 mmol) in CH_2Cl_2 (2.4 mL) at rt. The resulting solution was heated at reflux for 18 h then cooled to rt. The mixture was washed sequentially with saturated aqueous $NaHCO_3$ (3 × 3 mL) and brine (3 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 20:1) to afford the furan **11a** (140 mg, 83%) as a colourless oil. R_f = 0.35 (petroleum ether-EtOAc, 10:1); ν_{max} 2955, 2938, 2864, 1674, 1568, 951, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.17–7.12 (2H, m), 7.11–7.05 (1H, m), 7.04–7.00 (2H, m), 5.91 (1H, s), 2.37 (3H, s), 2.29 (1H, d, *J* = 4.7 Hz), 2.28–2.21 (2H, m), 2.22 (3H, s), 2.09–1.99 (3H, m), 1.89–1.80 (1H, m), 1.58–1.46 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.4, 156.7, 153.4, 138.4, 128.5, 127.8, 125.9, 121.8, 107.0, 34.9, 33.4, 30.8, 30.5, 29.1, 27.9, 22.0, 14.3; HRMS (ESI+) calcd for $C_{19}H_{20}O_2Na$ $[M+Na]^+$ 303.1356, found 303.1348.

(*Z*)-3-(8-Phenyloct-7-en-2-yn-1-ylidene)pentane-2,4-dione (*Z*-10).

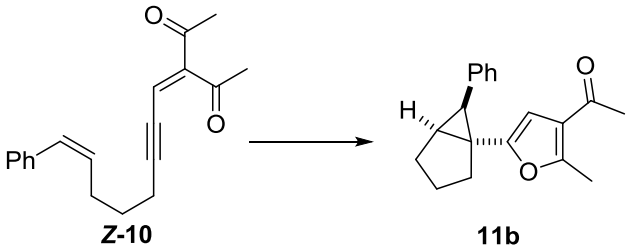


***Z*-S15** ***Z*-S16** ***Z*-10**

n-BuLi (1.92 mL of a 2.5 M solution in hexanes, 4.80 mmol) was added to a solution of the enyne ***Z*-S15** (680 mg, 3.99 mmol) in THF (12 mL) at –78 °C. The mixture was stirred at –78 °C for 10 min and then DMF (0.75 mL, 9.6 mmol) was added. The mixture was stirred for a further 30 min at –78 °C and then the reaction was quenched by the addition of 10% aqueous KH_2PO_4 (10 mL). The mixture was stirred at 0 °C for 30 min and then extracted with Et_2O (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude aldehyde ***Z*-S16** as a colourless oil which was used directly in the next step without further purification. ^1H NMR (400 MHz, $CDCl_3$) δ 9.10 (1H, t, *J* = 0.7 Hz), 7.36–7.21 (5H, m), 6.50 (1H, dt, *J* = 11.7, 1.5 Hz), 5.62 (1H, dt, *J* = 11.7, 7.3 Hz), 2.50–2.41 (4H, m), 1.75 (2H, quintet, *J* = 7.3 Hz). Solid $MgSO_4$ (81 mg, 0.67 mmol) was added to a mixture of the aldehyde ***Z*-S16**, 2,4-pentanedione (0.34 mL, 3.3 mmol), AcOH (0.11 mL, 2.0 mmol) and piperidine (0.03 mL, 0. 3 mmol) in toluene (3.6 mL) at rt. The resulting mixture was heated to 30 °C and stirred at this temperature for 3 h.

The reaction was quenched by addition of H_2O (6 mL) and mixture was extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 20:1) to provide the ynenedione ***Z*-10** (461 mg, 41%) as a pale yellow oil. R_f = 0.23 (petroleum ether-EtOAc, 10:1); ν_{max} 3009, 2932, 2862, 2209, 1713, 1690, 1663, 1576, 770, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.30 (2H, m), 7.28–7.20 (3H, m), 6.62 (1H, t, *J* = 2.5 Hz), 6.48 (1H, d, *J* = 11.6 Hz), 5.61 (1H, dt, *J* = 11.6, 7.3 Hz), 2.49–2.42 (4H, m), 2.41 (3H, s), 2.30 (3H, s), 1.72 (2H, quintet, *J* = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 195.9, 149.7, 137.5, 131.2, 130.3, 128.9, 128.3, 126.8, 123.2, 109.8, 77.3, 31.0, 28.4, 27.8, 27.4, 19.9; LRMS (EI+) *m/z* (intensity) 280.1 $[M]^+$ (100), 219.1 (45), 189.1 (40), 163.1 (95), 115.1 (38), 91.1 (40); HRMS (EI+) calcd for $C_{19}H_{20}O_2$ $[M]^+$ 280.1463, found 2801466.

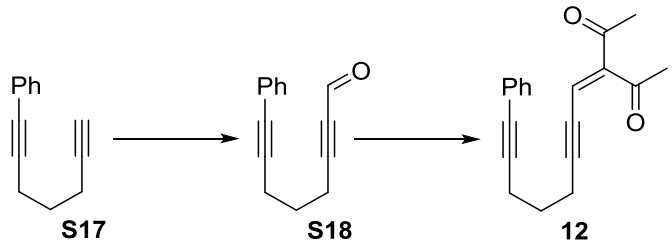
1-{2-Methyl-5-(6-phenylbicyclo[3.1.0]hexan-1-yl)furan-3-yl}ethanone (11b).



***Z*-10** **11b**

Chloroacetic acid (55 mg, 0.60 mmol) was added to a solution of ynenedione ***Z*-10** (162 mg, 0.58 mmol) in toluene (2.3 mL) at rt. The resulting solution was heated at reflux for 24 h and then cooled to rt. The reaction was washed sequentially with saturated aqueous $NaHCO_3$ (3 × 3 mL) and brine (3 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 20:1) to afford the furan **11b** (92 mg, 57%) as a colourless oil. R_f = 0.48 (petroleum ether-EtOAc, 9:1); ν_{max} 2955, 2938, 2864, 1674, 1568, 951 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.21 (5H, m), 6.30 (1H, s), 2.67 (1H, d, *J* = 8.4 Hz), 2.56 (3H, s), 2.40 (3H, s), 2.22–2.13 (1H, m), 2.08–1.98 (2H, m), 1.98 (1H, ddd, *J* = 12.9, 8.4, 0.9 Hz), 1.91–1.83 (1H, m), 1.46–1.36 (1H, m), 0.27–0.13 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.3, 157.0, 156.4, 137.1, 128.7, 128.5, 126.4, 122.3, 104.1, 32.5 (2C), 31.0, 29.2, 28.8, 26.2, 23.0, 14.5; LRMS (EI+) *m/z* (intensity) 280.1 $[M]^+$ (100), 219 (20), 189 (25); HRMS (EI+) calcd for $C_{19}H_{20}O_2$ $[M]^+$ 280.1463, found 280.1469.

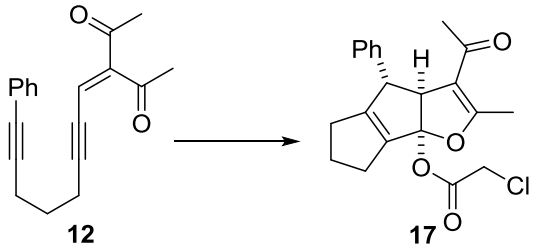
3-(8-Phenylocta-2,7-diyn-1-ylidene)pentane-2,4-dione (12).



S17 **S18** **12**

n-BuLi (1.22 mL of a 2.5 M solution in hexanes, 3.05 mmol) was added to a solution of the alkyne **S17**[13] (342 mg, 2.03 mmol) in THF (7 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 10 min after which DMF (0.47 mL, 6.1 mmol) was added. The mixture was stirred for a further 30 min at –78 °C and the reaction was then quenched by addition of 10% aqueous KH_2PO_4 (10 mL). The mixture was stirred at 0 °C for 30 min and then extracted with Et_2O (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude aldehyde **S18** as a colourless oil which was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (1H, t, *J* = 0.7 Hz), 7.41–7.37 (2H, m), 7.31–7.26 (3H, m), 2.63 (2H, td, *J* = 7.0, 0.7 Hz), 2.57 (2H, t, *J* = 7.0 Hz), 1.91 (2H, quintet, *J* = 7.0 Hz).
Solid $MgSO_4$ (41 mg, 0.34 mmol) was added to a mixture of the aldehyde **S18**, 2,4-pentanedione (0.17 mL, 1.7 mmol), AcOH (0.06 µL, 1.0 mmol) and piperidine (0.02 mL, 0.2 mmol) in toluene (1.3 mL) at rt. The resulting mixture was heated to 30 °C and stirred at this temperature for 2 h. The reaction was quenched by addition of H_2O (5 mL) and the mixture was extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 20:1) to provide the ynenedione **12** (156 mg, 28% over 3 steps) as a pale yellow oil. R_f = 0.37 (petroleum ether-EtOAc, 20:1); ν_{max} 2936, 2866, 2203, 1664, 1618, 1568, 758, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.37 (2H, m), 7.30–7.27 (3H, m), 6.69 (1H, t, *J* = 2.5 Hz), 2.65 (2H, td, *J* = 7.0, 2.5 Hz), 2.54 (2H, t, *J* = 7.0 Hz), 2.48 (3H, s), 2.31 (3H, s), 1.87 (2H, quintet, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.4, 195.9, 150.0, 131.7, 128.4, 127.9, 123.8, 123.0, 109.1, 88.5, 81.9, 77.5, 31.1, 27.3, 19.5, 18.8; LRMS (CI, *iso*-butane) *m/z* (intensity) 279.0 $[M+H]^+$ (15), 113.1 (25), 81.1 (78), 69.1 (100); HRMS (CI, *iso*-butane) calcd for $C_{19}H_{19}O_2$ $[M+H]^+$ 279.1385, found 279.1382.

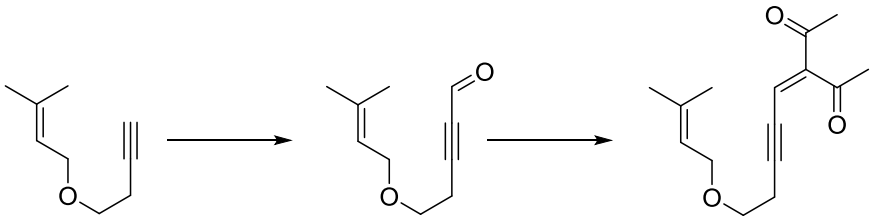
3-Acetyl-2-methyl-4-phenyl-4,5,6,7-tetrahydropentaleno[1,2-b]furan-7b(3aH)-yl 2-chloroacetate (17).



Chloroacetic acid (52 mg, 0.55 mmol) was added to a solution of ynenedione **12** (153 mg, 0.55 mmol) in CH_2Cl_2 (2.2 mL) at rt. The resulting solution was heated at reflux for 26 h then cooled to rt. The solvent was removed by concentration under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 10:1) to afford tricyclic product **17** (63 mg, 31%) as a colourless solid. The product was crystallised from Et_2O to

afford colourless crystals. R_f = 0.36 (petroleum ether-EtOAc, 10:1); m.p. = 118–120 °C; ν_{max} 3026, 2953, 2924, 2857, 1778, 1757, 1674, 1626, 1601, 982, 930, 783, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (2H, m), 7.26–7.19 (3H, m), 4.19–4.16 (1H, m), 4.12 (2H, s), 3.60 (1H, b d, *J* = 1.2 Hz), 2.54–2.48 (2H, m), 2.33–2.22 (2H, m), 2.26 (3H, d, *J* = 1.5 Hz), 2.19 (3H, s), 2.16–2.07 (1H, m), 2.06–1.96 (1H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 165.0, 159.6, 142.4, 142.0, 128.9, 127.6, 127.1, 118.0, 117.9, 77.4, 66.8, 53.7, 41.4, 30.1, 28.3, 27.4, 26.3, 15.2; LRMS (CI, *iso*-butane) *m/z* (intensity) 373.0 $[M+H]^+$ (30), 339.0 (50), 279.0 (100), 113.1 (25), 71.1 (55); HRMS (CI, *iso*-butane) calcd for $C_{21}H_{22}O_4Cl$ $[M+H]^+$ 373.1207, found 373.1210.

3-{5-[(3-Methylbut-2-en-1-yl)oxy]pent-2-yn-1-ylidene}pentane-2,4-dione (6m).



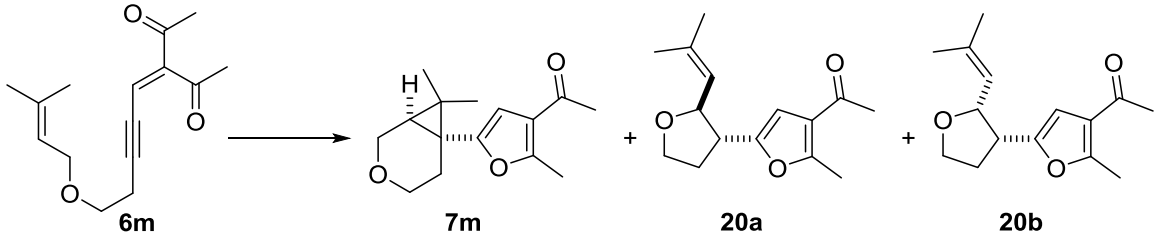
S19 **9m** **6m**

n-BuLi (1.6 mL of a 2.5 M solution in hexanes, 4.0 mmol) was added to a solution of the enyne **S19**[14] (500 mg, 3.62 mmol) in THF (24 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 10 min after which DMF (1.73 mL, 22.3 mmol) in THF (8 mL) was added. The mixture was stirred for a further 30 min at –78 °C and the reaction was quenched by the addition of 5% aqueous H_2SO_4 (10 mL) and stirred at rt for 1 h. The resulting mixture was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (30 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude aldehyde **9m** as a colourless oil which was used directly in the next step without further purification. ^1H NMR (400 MHz, $CDCl_3$) δ 9.18 (1H, t, *J* = 0.7 Hz), 5.37–5.31 (1H, m), 4.01 (2H, d, *J* = 7.0 Hz), 3.60 (2H, t, *J* = 6.8 Hz), 2.69 (2H, td, *J* = 6.8, 0.7 Hz), 1.76 (3H, s), 1.68 (3H, s).

Solid $MgSO_4$ (100 mg, 0.831 mmol) was added to a mixture of the aldehyde **9m**, 2,4-pentanedione (0.31 mL, 3.0 mmol), AcOH (0.10 mL, 1.8 mmol) and piperidine (0.03 mL, 0.3 mmol) in toluene (3 mL) at rt. The resulting mixture was heated to 30 °C and stirred at this temperature for 2.5 h. The reaction was quenched by addition of H_2O (5 mL) and the mixture was extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 9:1) to provide the ynenedione **6m** (520 mg, 58%, over 2 steps, 70% based on the diketone as the limiting reagent) as a pale yellow oil. R_f = 0.26 (petroleum ether-EtOAc, 9:1); ν_{max} 2972, 2916, 2862, 2214, 1715, 1690, 1665, 1578 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.68 (1H, t, *J* = 2.4 Hz), 5.36–5.30 (1H, m), 3.99 (2H, b d, *J* = 7.0 Hz), 3.56 (2H, t, *J* = 6.7 Hz), 2.71 (2H, td, *J* = 6.7, 2.4 Hz), 2.48 (3H, d, *J* = 0.4 Hz), 2.30 (3H, d, *J* = 0.4 Hz), 1.75 (3H, s), 1.67 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 195.9, 150.0, 137.6, 123.0, 120.8, 107.0, 77.7,

67.6, 67.5, 31.1, 27.4, 25.9, 21.9, 18.2; LRMS (EI+) *m/z* (intensity) 248.0 $[M]^+$ (30), 205.0 (25), 179,0 (40), 164.0 (100), 149.0 (80); HRMS (EI+) calcd for $C_{15}H_{20}O_3$ $[M]^+$ 248.1412, found 248.1410.

1-{5-(7,7-Dimethyl-3-oxabicyclo[4.1.0]heptan-6-yl)-2-methylfuran-3-yl}ethanone (7m).



Acid-catalyzed reaction

Chloroacetic acid (152 mg, 1.61 mmol) was added to a solution of ynenedione **6m** (400 mg, 1.61 mmol) in CH_2Cl_2 (6.5 mL) at rt. The resulting solution was heated at reflux for 18 h then cooled to rt. The reaction mixture was washed with saturated aqueous $NaHCO_3$ (3 × 8 mL) and brine (8 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 20:1) to afford the cyclopropyl furan **7m** (276 mg, 69%) along with the diastereomeric tetrahydrofurans **20a** (60 mg, 15%) and **20b** (16 mg, 4%) as colourless oils.

$ZnCl_2$ catalyzed reaction

Solid $ZnCl_2$ (16.5 mg, 0.121 mmol) was added to a solution of ynenedione **6m** (300 mg, 1.21 mmol) in CH_2Cl_2 (4.8 mL) at rt. The resulting solution was heated at reflux for 1.5 h then cooled to rt and then concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 20:1) to afford the cyclopropyl furan **7m** (39 mg, 13%) along with the diastereomeric tetrahydrofurans **20a** (141 mg, 47%) and **20b** (72 mg, 24%) as colourless oils.

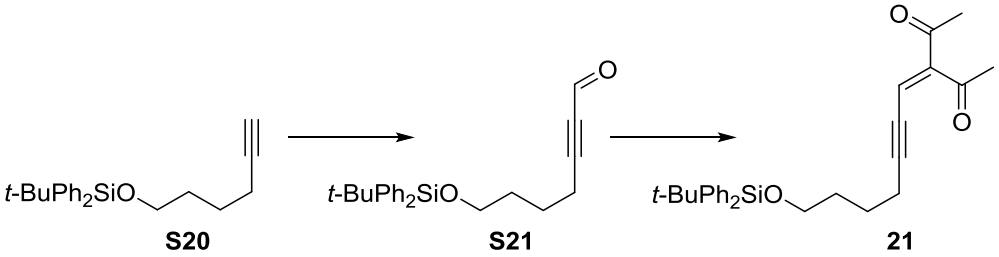
7m: R_f = 0.26 (petroleum ether-EtOAc, 9:1); ν_{max} 2972, 2915, 2862, 2214, 1715, 1690, 1665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.16 (1H, s), 3.99 (1H, d, *J* = 11.8 Hz), 3.92 (1H, dd, *J* = 11.8, 4.5 Hz), 3.65 (1H, ddd, *J* = 11.2, 5.6, 1.1 Hz), 3.07 (1H, ddd, *J* = 12.7, 11.2, 3.5 Hz), 2.52 (3H, s), 2.35 (3H, s), 2.05 (1H, ddd, *J* = 14.8, 12.7, 5.6 Hz), 1.83 (1H, ddd, *J* = 14.8, 3.5, 1.1 Hz), 1.26 (3H, s), 0.95 (1H, d, *J* = 4.5 Hz), 0.86 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.3, 157.8, 157.0, 121.8, 105.9, 62.7, 62.5, 29.2, 25.2, 24.9, 23.6, 22.9, 22.6, 16.4, 14.6; HRMS (ESI+) calcd for $C_{15}H_{20}O_3Na$ $[M+Na]^+$ 271.1305, found 271.1295.

20a: R_f = 0.16 (petroleum ether-EtOAc, 9:1); ν_{max} 2972, 2916, 2873, 1676, 1569, 949, 732, 633 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.21 (1H, s), 5.15 (1H, d quintet, *J* = 8.5, 1.2 Hz), 4.43 (1H, t, *J* = 8.5 Hz), 3.95 (1H, dt, *J* = 8.5, 7.3 Hz), 3.90 (1H, td, *J* = 8.5, 5.5 Hz), 2.92 (1H, q, *J* = 8.5 Hz), 2.48 (3H, s), 2.30 (3H, s), 2.29–2.22 (1H, m), 2.10 (1H, dtd, *J* = 12.3, 8.6, 7.0 Hz), 1.66 (3H, d, *J* = 1.2 Hz), 1.49 (3H, d, *J* = 1.2 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.2, 157.5, 152.7, 138.0, 123.9,

122.1, 106.1, 79.8, 67.3, 44.8, 32.2, 29.2, 26.0, 18.4, 14.4; HRMS (ESI+) calcd for $C_{15}H_{20}O_3Na$ $[M+Na]^+$ 271.1305, found 271.1296.

20b: R_f = 0.13 (petroleum ether-EtOAc, 9:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.24 (1H, s), 4.89 (1H, d quintet, *J* = 8.8, 1.3 Hz), 4.69 (1H, dd, *J* = 8.8, 6.6 Hz), 4.13 (1H, td, *J* = 8.3, 4.9 Hz), 3.84 (1H, ddd, *J* = 8.3, 8.0, 7.8 Hz), 3.41 (1H, dt, *J* = 7.9, 6.6 Hz), 2.52 (3H, s), 2.36 (3H, s), 2.32 (1H, dddd, *J* = 12.6, 8.0, 7.9, 4.9 Hz), 2.20–2.12 (1H, m), 1.65 (3H, d, *J* = 1.2 Hz), 1.60 (3H, d, *J* = 1.2 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.4, 157.3, 153.2, 137.2, 122.0, 121.7, 106.7, 78.1, 66.8, 41.9, 31.2, 29.2, 26.0, 18.4, 14.4.

3-[7-(*tert*-Butyldiphenylsilyloxy)hept-2-yn-1-ylidene]pentane-2,4-dione (21).



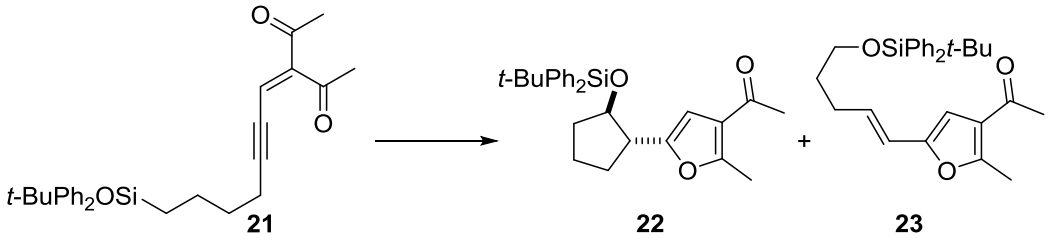
S20 **S21** **21**

n-BuLi (0.71 mL of a 2.5 M solution in hexanes, 1.8 mmol) was added to a solution of the alkyne **S20**[15] (500 mg, 1.49 mmol) in THF (4 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 10 min after which DMF (0.28 mL, 3.6 mmol) was added. The mixture was stirred for a further 30 min at –78 °C and the reaction was quenched by addition of 10% aqueous KH_2PO_4 (10 mL). The resulting mixture was stirred at 0 °C for 30 min and then extracted with Et_2O (3 × 20 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude aldehyde **S21** as a colourless oil which was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (1H, t, *J* = 0.7 Hz), 7.68–7.64 (4H, m), 7.46–7.36 (6H, m), 3.69 (2H, t, *J* = 5.8 Hz), 2.42 (2H, td, *J* = 6.8, 0.7 Hz), 1.76–1.63 (4H, m), 1.05 (9H, s).

Solid $MgSO_4$ (40 mg, 0.33 mmol) was added to a mixture of the aldehyde **S21**, 2,4-pentanedione (0.13 µL, 1.2 mmol), AcOH (0.04 mL, 0.7 mmol) and piperidine (0.01 µL, 0.1 mmol) in toluene (1.3 mL) at rt. The resulting mixture was heated to 30 °C and stirred at this temperature for 2.5 h. The reaction was quenched by addition of H_2O (5 mL) and the mixture was extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 12:1) to provide the ynenedione **21** (450 mg, 68% over 2 steps) as a pale yellow oil. R_f = 0.08 (petroleum ether-EtOAc, 19:1); ν_{max} 2932, 2858, 2211, 1691, 1666, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.64 (4H, m), 7.46–7.36 (6H, m), 6.70 (1H, t, *J* = 2.4 Hz), 3.69 (2H, t, *J* = 5.8 Hz), 2.46 (3H, s), 2.45 (2H, td, *J* = 6.7, 2.4 Hz), 2.32 (3H, s), 1.74–1.62 (4H, m), 1.06 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 195.9, 149.7, 135.6, 134.0, 129.7, 127.8, 123.3,

110.3, 77.1, 63.2, 31.7, 31.0, 27.3, 27.0, 24.8, 20.1, 19.3; HRMS (ESI+) calcd for $C_{28}H_{34}O_3NaSi$ $[M]^+$ 469.2169, found 469.2149.

1-{5-[(1*R,2*R**)-2-(*tert*-Butyldiphenylsilyloxy)cyclopentyl]-2-methylfuran-3-yl}ethanone (22) and (*E*)-1-{5-[5-(*tert*-Butyldiphenylsilyloxy)pent-1-en-1-yl]-2-methylfuran-3-yl}ethanone (23).**



Acid-catalysed reaction

Chloroacetic acid (63.6 mg, 0.673 mmol) was added to a solution of ynenedione **21** (301 mg, 0.672 mmol) in CH_2Cl_2 (2.7 mL) at rt. The resulting solution was heated at reflux for 48 h then cooled to rt. The reaction mixture was washed with saturated aqueous $NaHCO_3$ (3 × 3 mL) and brine (3 mL) and the organic phase was dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (petroleum ether-EtOAc, 30:1) delivered unreacted ynenedione **21** (295 mg, 98%) as a colourless oil.

Zinc(II) chloride catalysed reaction

Solid $ZnCl_2$ (9 mg, 0.07 mmol) was added to a solution of ynenedione **21** (295 mg, 0.659 mmol) in CH_2Cl_2 (2.6 mL) at rt. The resulting solution was heated at reflux for 1.5 h then cooled to rt and concentrated under reduced pressure. The residual material was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 30:1) to afford the cyclopentane **22** (109 mg, 37%; 6.2:1 *anti*:*syn* isomers) and the *E*-alkene **23** (165 mg, 56%) as colourless oils. *The products **22** and **23** could not be separated fully by flash column chromatography on silica gel.*

22: R_f = 0.14 (petroleum ether-EtOAc, 20:1); ν_{max} 2959, 2932, 2857, 1676, 1568, 939, 741, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61–7.56 (2H, m), 7.43–7.32 (6H, m), 7.31–7.25 (2H, m), 6.30 (1H, s), 4.44 (1H, dt, *J* = 4.8, 3.0 Hz), 2.93–2.87 (1H, ddd, *J* = 11.1, 7.8, 4.8 Hz), 2.47 (3H, s), 2.33 (3H, s), 2.18–2.08 (1H, m), 1.99–1.87 (2H, m), 1.66–1.58 (3H, m), 0.94 (9H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.6, 156.9, 153.9, 136.0, 135.8, 134.6, 134.2, 129.6, 129.5, 127.6 (2C), 127.5 (2C), 122.1, 107.3, 76.3, 45.1, 34.8, 29.2, 27.3, 26.9, 21.5, 19.3, 14.5; HRMS (ESI+) calcd for $C_{28}H_{34}O_3NaSi$ $[M]^+$ 469.2169, found 469.2150.

23: R_f = 0.16 (petroleum ether-EtOAc, 20:1); ν_{max} 2955, 2930, 2857, 1678, 951, 822, 739, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61–7.58 (4H, m), 7.36–7.27 (6H, m), 6.22 (1H, s), 6.10 (1H, dt, *J* = 15.8, 6.6 Hz), 6.02 (1H, d, *J* = 15.8 Hz), 3.63 (2H, t, *J* = 6.2 Hz), 2.51 (3H, s), 2.31 (3H, s), 2.22 (2H, dt, *J* = 7.5, 7.0 Hz), 1.68–1.60 (2H, m), 0.98 (9H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.3, 157.5, 151.1, 135.7, 134.1, 130.7, 129.7, 127.8, 118.1, 106.2, 63.3, 32.1, 29.3, 27.0, 26.9, 19.4, 14.6; HRMS (ESI+) calcd for $C_{28}H_{34}NaO_3Si$ $[M]^+$ 469.2169, found 469.2150.

References

[1] Z. Otwinowski and W. Minor, *Methods Enzymol.* **1997**, 276, 307–326.

[2] A. Altomare, G. Cascarano, C. Giacovazzo, A. Gualiardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst*. **1994**, *27*, 435.

[3] G. M. Sheldrick, *Acta Cryst. A*, **2008**, *A64*, 112–122.

[4] L. J. Farrugia, *J. Appl. Cryst.* **2012**, *45*, 849–854.

[5] B. Witulski, U. Bergsträßer, M. Gößmann, *Tetrahedron* **2000**, 56, 4747–4752

[6] S. S. Goh, H. Baars,B. Gockel, E. A. Anderson, *Org. Lett.* **2012**, *14*, 6278–6281.

[7] F. Giacomina, A. Alexakis, *Eur. J. Org. Chem.* **2013**, *29*, 6710–6721.

[8] C. A. Broka, D. E. C. Reichert, *Tetrahedron Lett.* **1987**, *28*, 1503–1506.

[9] B. M. Trost, A. W. Franz, *J. Am. Chem. Soc.* **2010**, *132*, 18429–18429.

[10] R. Vicente, J. González, L. Riesgo, J. González, L. A. López, *Angew. Chem. Int. Ed.* **2012**, *51*, 8063–8067.

[11] L. S. Kocsis, E. Benedetti, K. M. Brummond, *Org. Lett.* **2012**, *14*, 4430–4433.

[12] B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **2002**, *124*, 5025–5036.

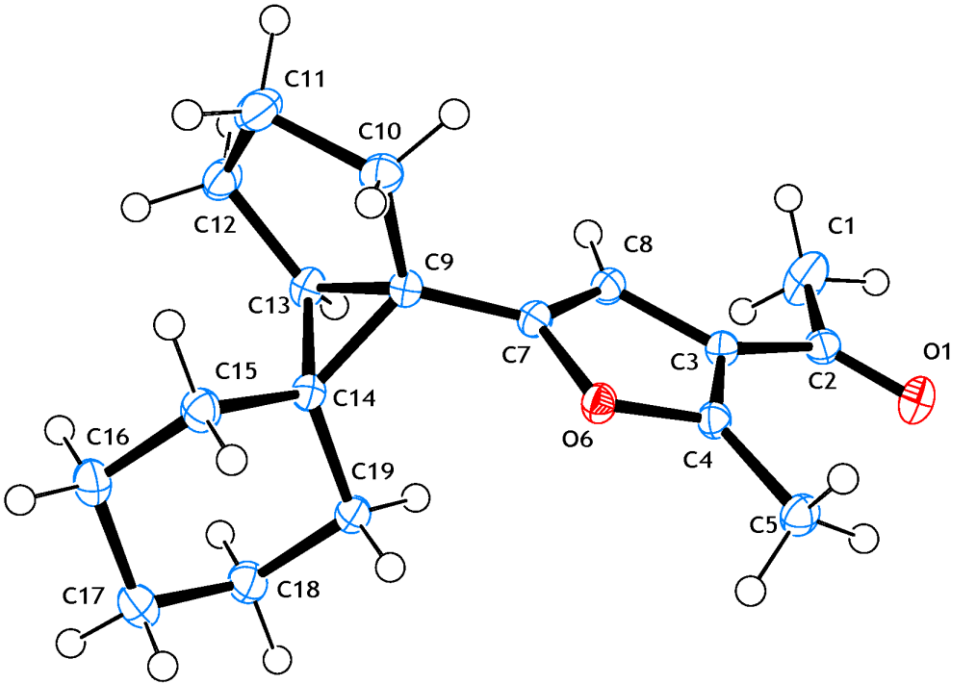
[13] H.-T. Chang, M. Jeganmohan, C.-H. Cheng, *Org. Lett.* **2007**, *9*, 505–508.

[14] L. Li, S. B. Herzon, *J. Am. Chem. Soc.* **2012**, *134*, 17376–17379.

[15] D. Brandt, V. Bellosta, J. Cossy, *Org. Lett.* **2012**, *14*, 5594–5597.

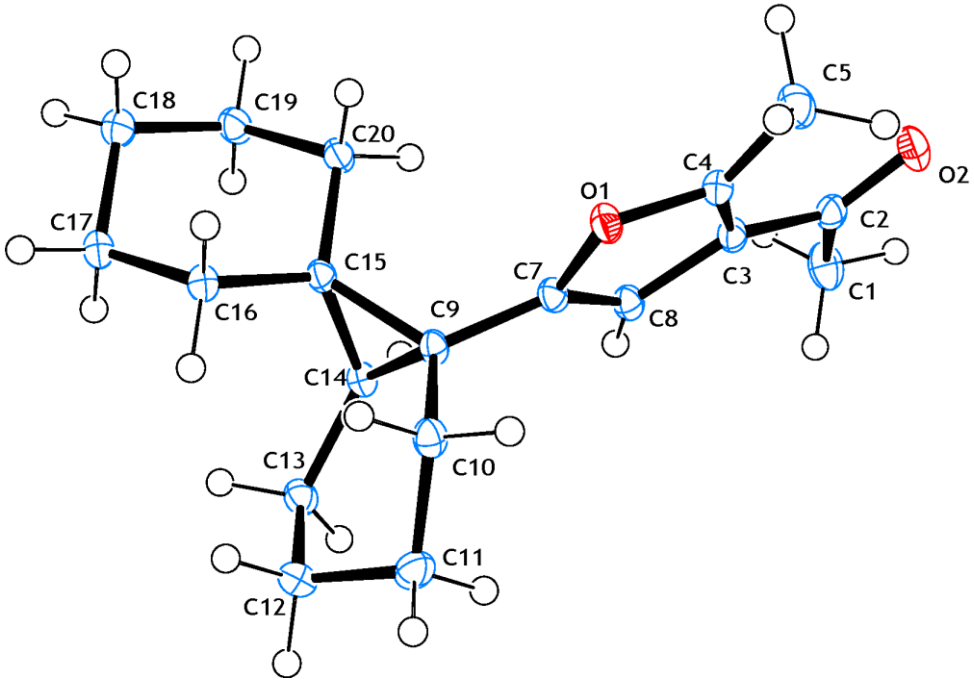
X-Ray Crystal Structure Data and Structure Refinement

7a (CCDC 1043529).



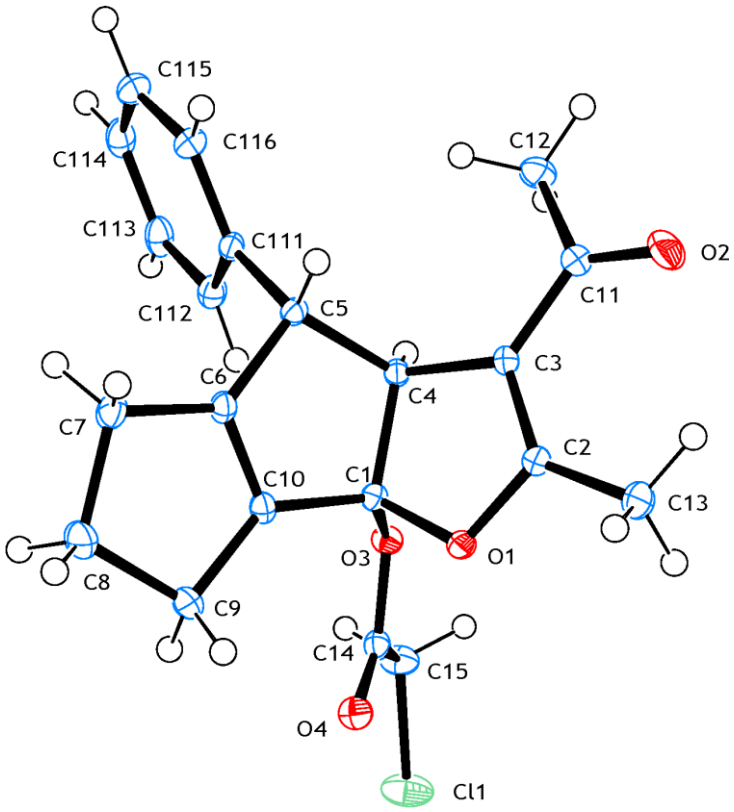
Empirical formula	$C_{18}H_{24}O_2$	
Formula weight	272.37	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/a$	
Unit cell dimensions	a = 10.4571(2) Å	α = 90°
	b = 12.2467(3) Å	β = 113.0010(10)°
	c = 12.6054(3) Å	γ = 90°
Volume	1485.97(6) Å^3	
Z	4	
Density (calculated)	1.217 mg m^{-3}	
Absorption coefficient	0.077 mm^{-1}	
F(000)	592	
Crystal size	0.500 × 0.400 × 0.300 mm^3	
θ range for data collection	2.418 to 30.029°	
Index ranges	–14 ≤ h ≤ 14; –17 ≤ k ≤ 17; –17 ≤ l ≤ 17	
Reflections collected	66311	
Independent reflections	4337	
R_{int}	0.034	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.862 and 0.63	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4337 / 0 / 207	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2σ(I)]	R_1 = 0.0387, wR_2 = 0.1060	
R indices (all data)	R_1 = 0.0438, wR_2 = 0.1088	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.387 and –0.168 e.Å^{-3}	

7c (CCDC 1043528).



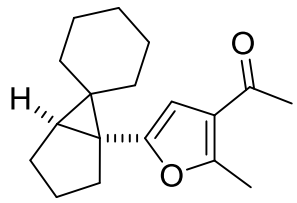
Empirical formula	$C_{19}H_{26}O_2$	
Formula weight	286.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/a$	
Unit cell dimensions	a = 10.4669(8) Å	α = 90°
	b = 12.1945(8) Å	β = 93.856(4)°
	c = 12.2239(9) Å	γ = 90°
Volume	1556.71(19) Å^3	
Z	4	
Density (calculated)	1.222 mg m^{-3}	
Absorption coefficient	0.077 mm^{-1}	
F(000)	624	
Crystal size	0.500 × 0.300 × 0.200 mm^3	
θ range for data collection	1.670 to 30.021°.	
Index ranges	–14 ≤ h ≤ 14; –17 ≤ k ≤ 17; –17 ≤ l ≤ 17	
Reflections collected	46896	
Independent reflections	4559	
R_{int}	0.102	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.77 and 0.661	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4559 / 0 / 218	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2σ(I)]	R_1 = 0.0525, wR_2 = 0.1361	
R indices (all data)	R_1 = 0.0763, wR_2 = 0.1480	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.577 and –0.268 e.Å^{-3}	

17 (CCDC 1043527).

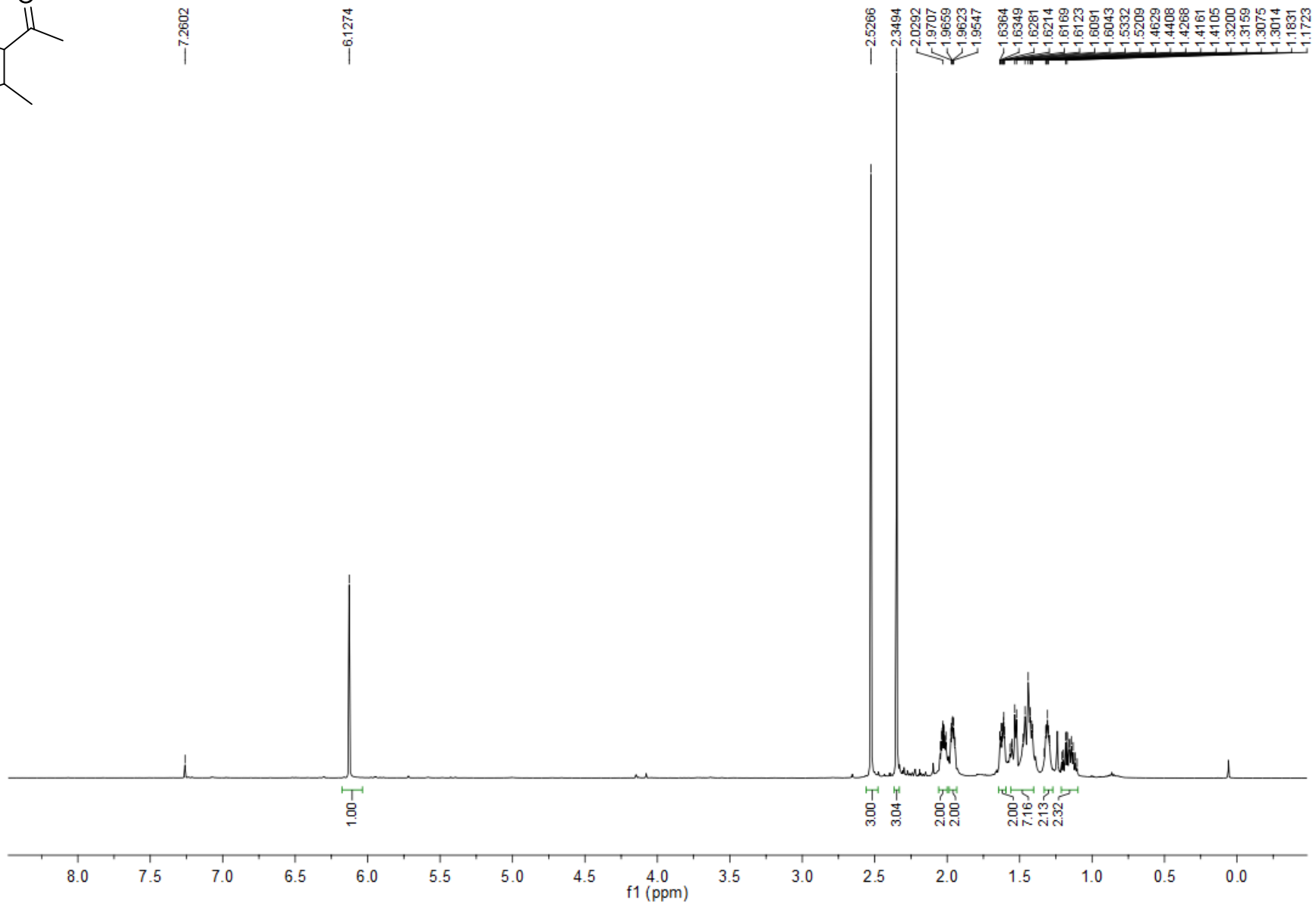


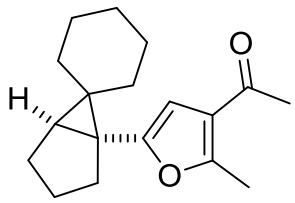
Empirical formula	$C_{21}H_{21}ClO_4$	
Formula weight	372.83	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.0310(8) Å	α = 90°
	b = 13.2689(13) Å	β = 99.262(5)°
	c = 8.5938(8) Å	γ = 90°
Volume	903.84(15) Å^3	
Z	2	
Density (calculated)	1.370 mg m^{-3}	
Absorption coefficient	0.235 mm^{-1}	
F(000)	392	
Crystal size	0.500 × 0.450 × 0.250 mm^3	
θ range for data collection	2.401 to 31.253°	
Index ranges	–11 ≤ h ≤ 11; –19 ≤ k ≤ 19; –12 ≤ l ≤ 12	
Reflections collected	5897	
Independent reflections	5897	
R_{int}	0.069	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.747 and 0.659	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5897 / 1 / 258	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2σ(I)]	R_1 = 0.0326, wR_2 = 0.0852	
R indices (all data)	R_1 = 0.0351, wR_2 = 0.0870	
Absolute structure parameter	0.048(19)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.362 and –0.185 e.Å^{-3}	

^{1}H and ^{13}C NMR Spectra

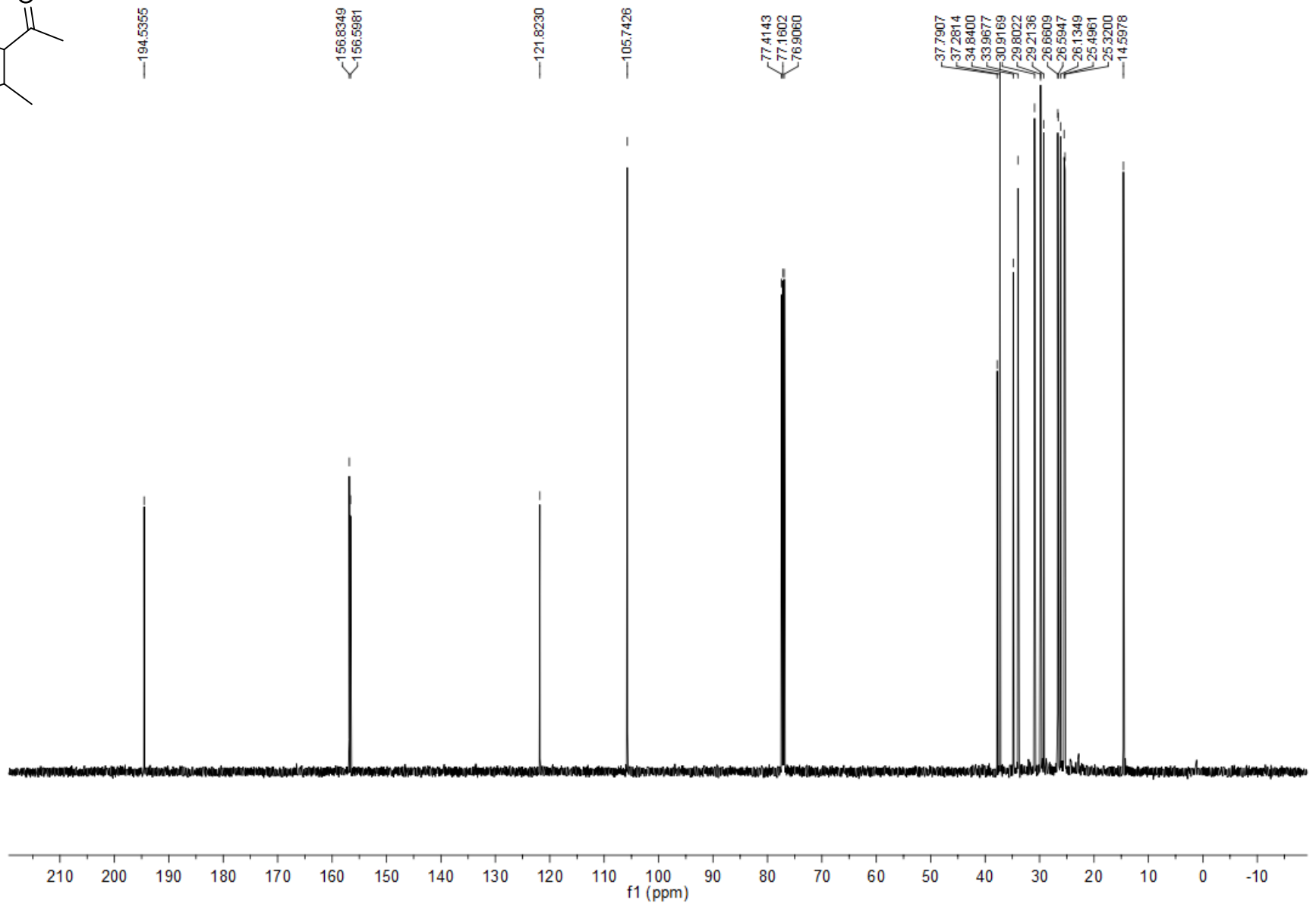

H
O
O

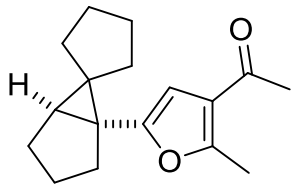
7a


7.2602
6.1274
2.5266
2.3494
2.0292
1.9707
1.9659
1.9623
1.9547
1.6364
1.6349
1.6281
1.6214
1.6169
1.6123
1.6091
1.6043
1.5332
1.5209
1.4629
1.4408
1.4268
1.4161
1.4105
1.3200
1.3159
1.3075
1.3014
1.1831
1.1723
1.00
3.00
3.04
2.00
2.00
2.00
7.16
2.13
2.32
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

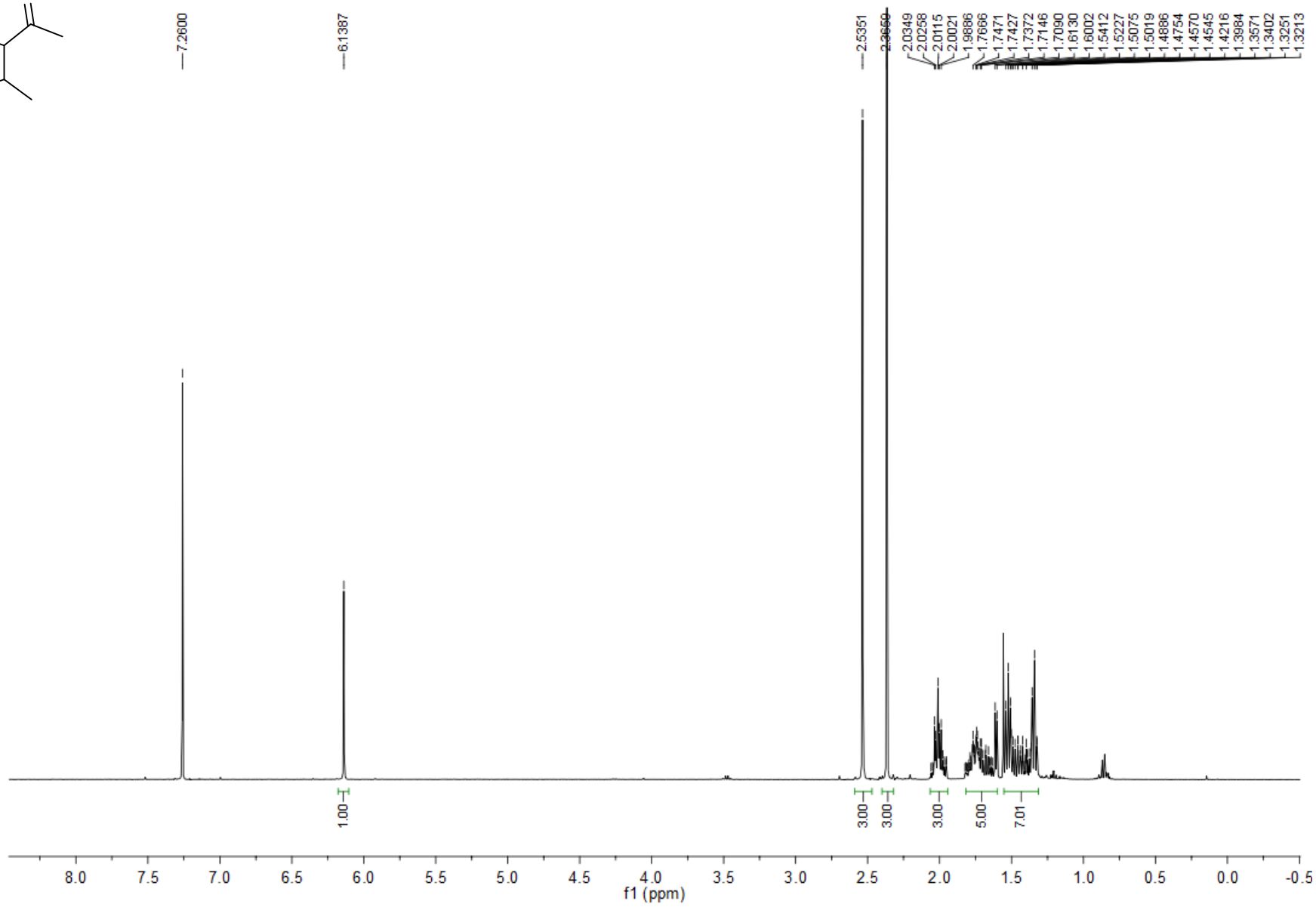

H
O
O

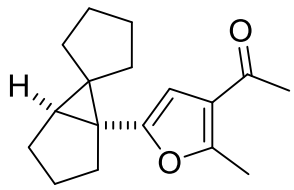
7a


194.5355
156.8349
156.5981
121.8230
105.7426
77.4143
77.1602
76.9060
37.7907
37.2814
34.8400
33.9677
30.9169
29.8022
29.2136
26.6609
26.5947
26.1349
25.4961
25.3200
14.5978
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

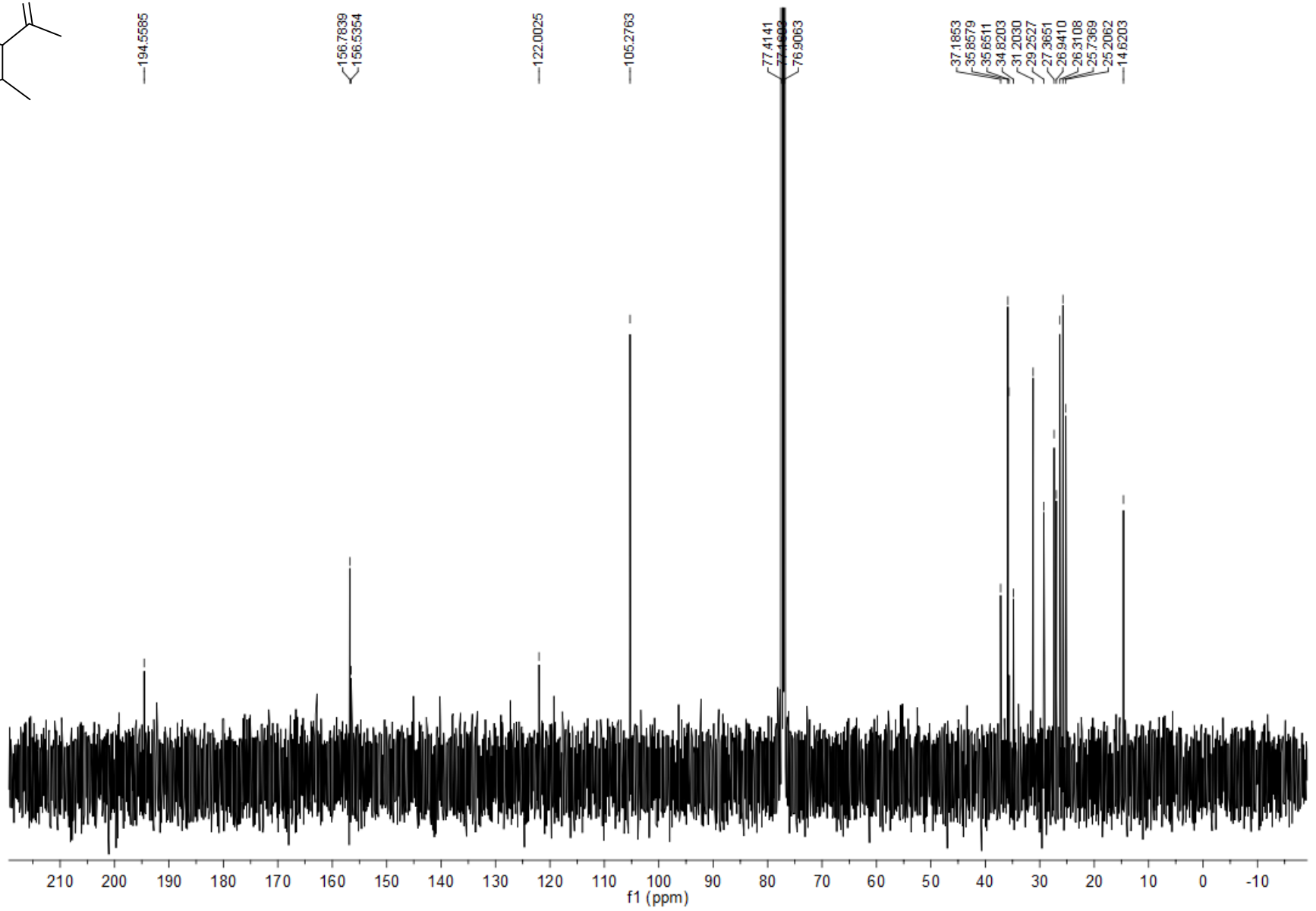

H
O
O

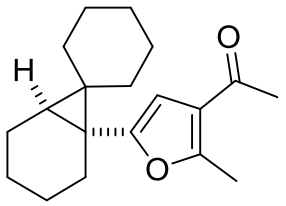
7b


7.2600
6.1387
2.5351
2.3659
2.0349
2.0258
2.0115
2.0021
1.9886
1.7666
1.7471
1.7427
1.7372
1.7146
1.7090
1.6130
1.6002
1.5412
1.5227
1.5075
1.5019
1.4886
1.4754
1.4570
1.4545
1.4216
1.3984
1.3571
1.3402
1.3251
1.3213
1.00
3.00
3.00
3.00
5.00
7.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

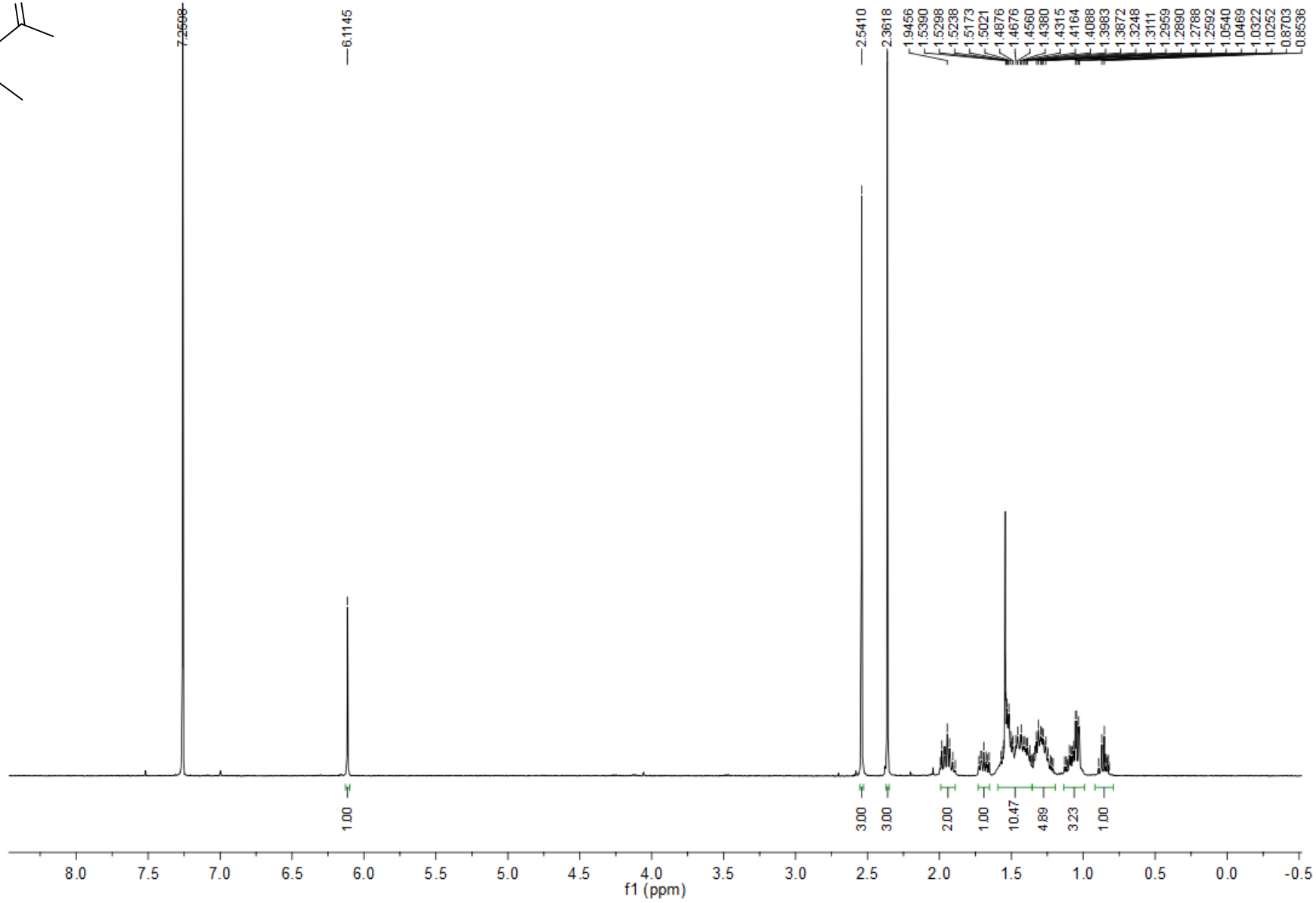

H
O
O

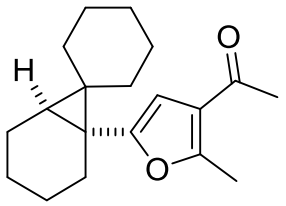
7b


194.5585
156.7839
156.5354
122.0025
105.2763
77.4141
77.0000
76.9063
37.1853
36.8579
35.6511
34.8203
31.2030
29.2527
27.3651
26.9410
26.3108
25.7369
25.2062
14.6203
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

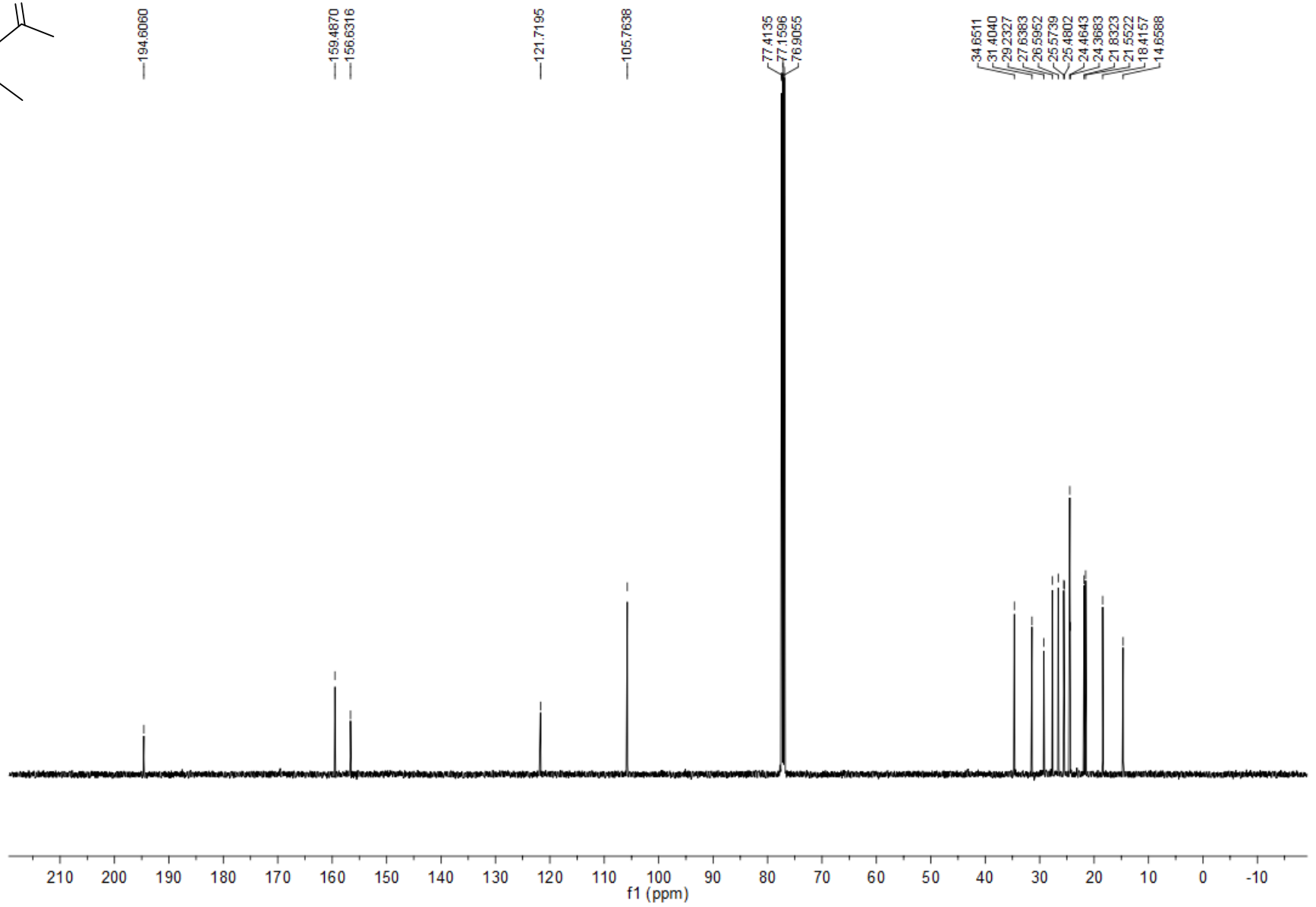

H
O
O

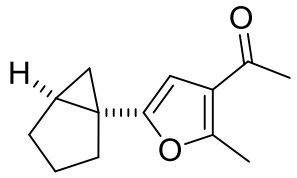
7c


7.2598
6.1145
2.5410
2.3618
1.9456
1.5390
1.5298
1.5238
1.5173
1.5021
1.4876
1.4676
1.4560
1.4380
1.4315
1.4164
1.4088
1.3983
1.3872
1.3248
1.3111
1.2959
1.2890
1.2788
1.2592
1.0540
1.0469
1.0322
1.0252
0.8703
0.8536
1.00
3.00
3.00
2.00
1.00
10.47
4.89
3.23
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

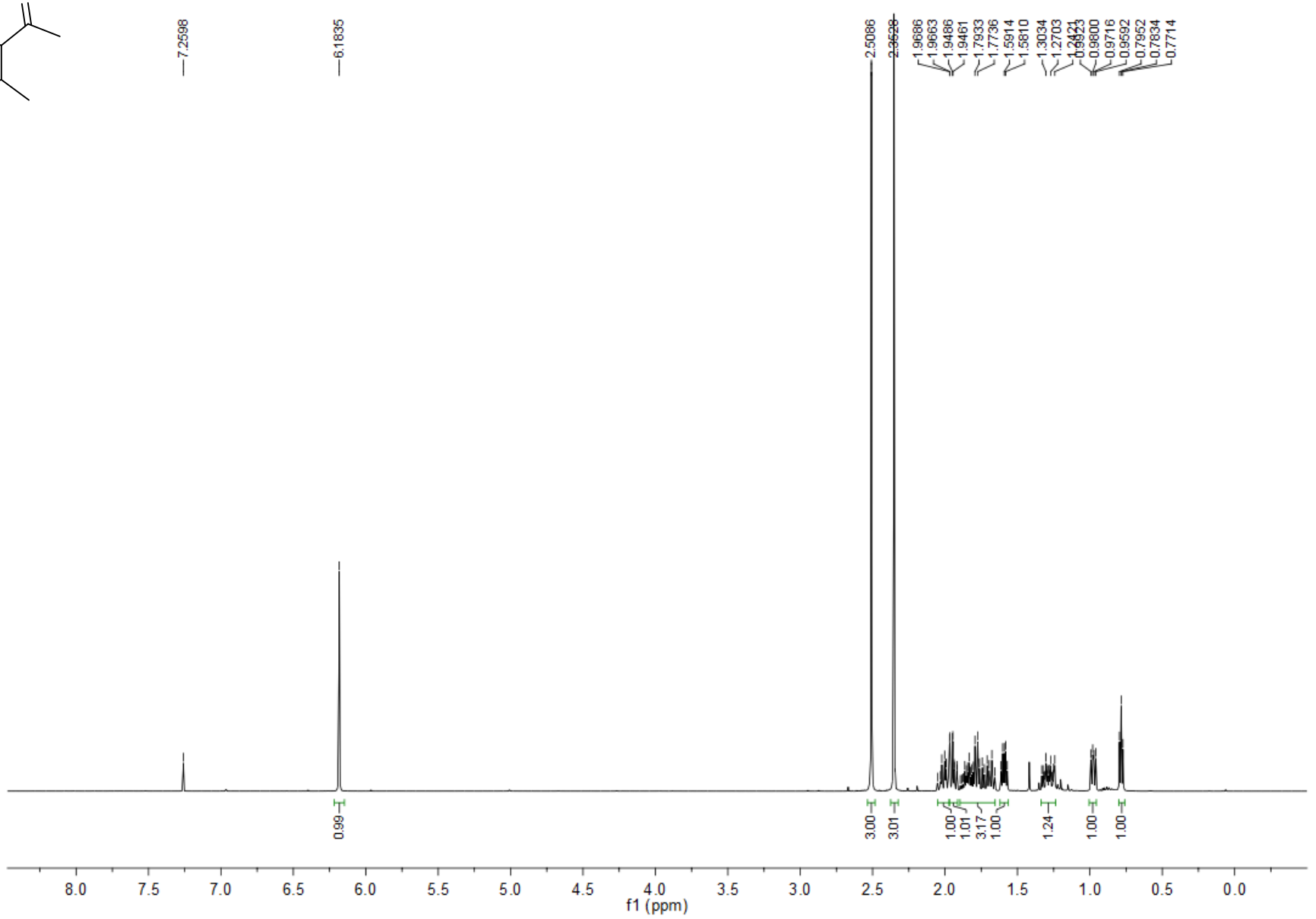

H
O
O

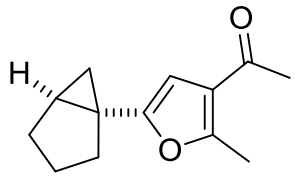
7c


194.6060
159.4870
156.6316
121.7195
105.7638
77.4135
77.1596
76.9055
34.6511
31.4040
29.2327
27.6383
26.5952
25.5739
25.4802
24.4643
24.3683
21.8323
21.5522
18.4157
14.6588
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

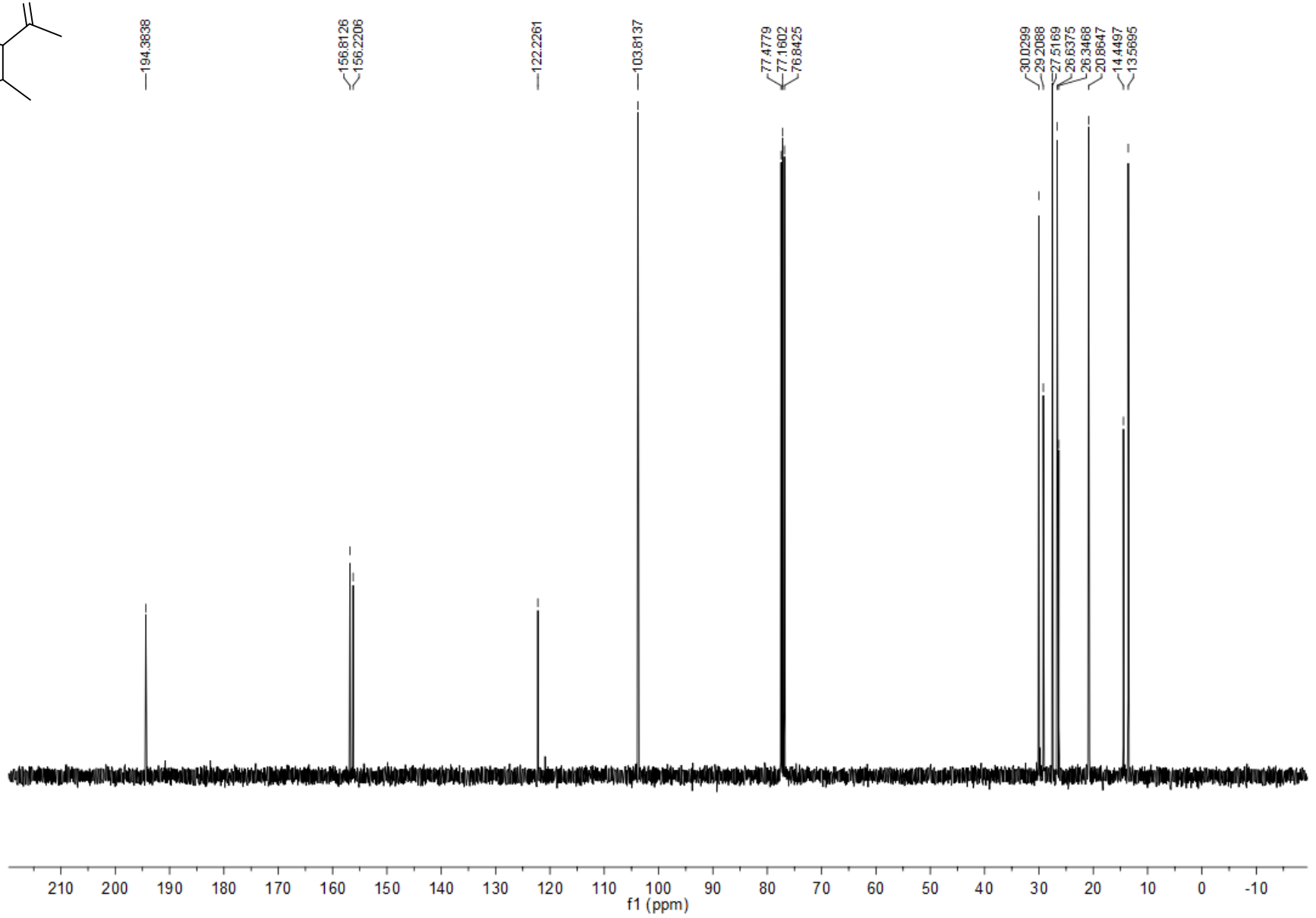

H
O
O

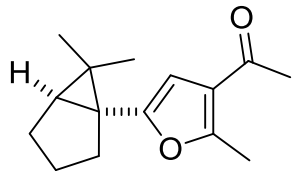
7d


7.2598
6.1835
2.5086
2.3628
1.9686
1.9663
1.9486
1.9461
1.7933
1.7736
1.5914
1.5810
1.3034
1.2703
0.9923
0.9800
0.9716
0.9592
0.7952
0.7834
0.7714
0.99
3.00
3.01
1.00
1.01
3.17
1.00
1.24
1.00
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

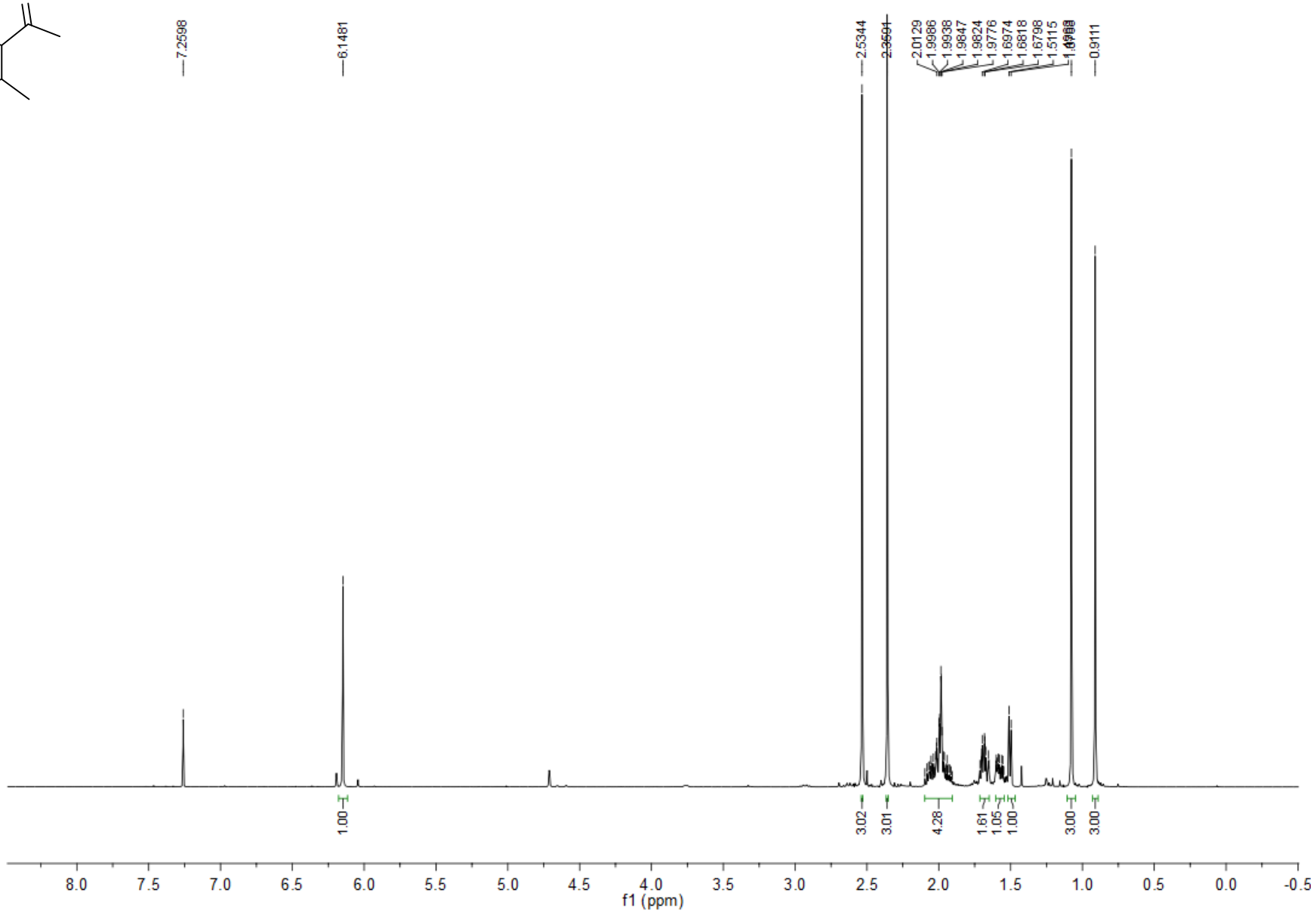

H
O
O

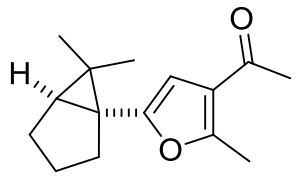
7d


194.3838
156.8126
156.2206
122.2261
103.8137
77.4779
77.1602
76.8425
30.0299
29.2088
27.5169
26.6375
26.3468
20.8647
14.4497
13.5695
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

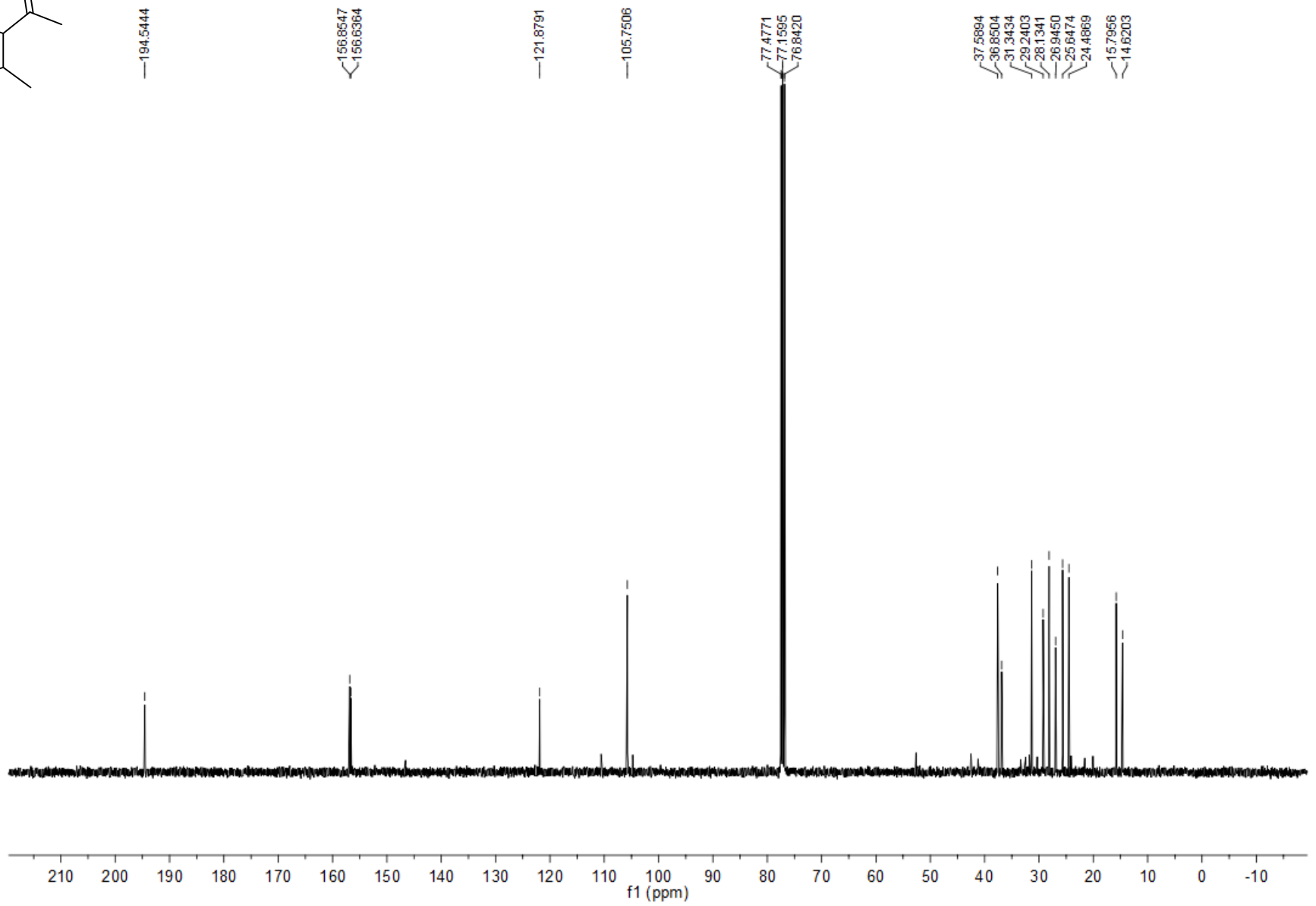

H
O
O

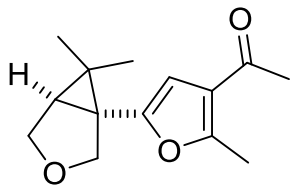
7e


7.2598
6.1481
2.5344
2.3591
2.0129
1.9986
1.9938
1.9847
1.9824
1.9776
1.6974
1.6818
1.6798
1.5115
0.9111
1.00
3.02
3.01
4.28
1.61
1.05
1.00
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

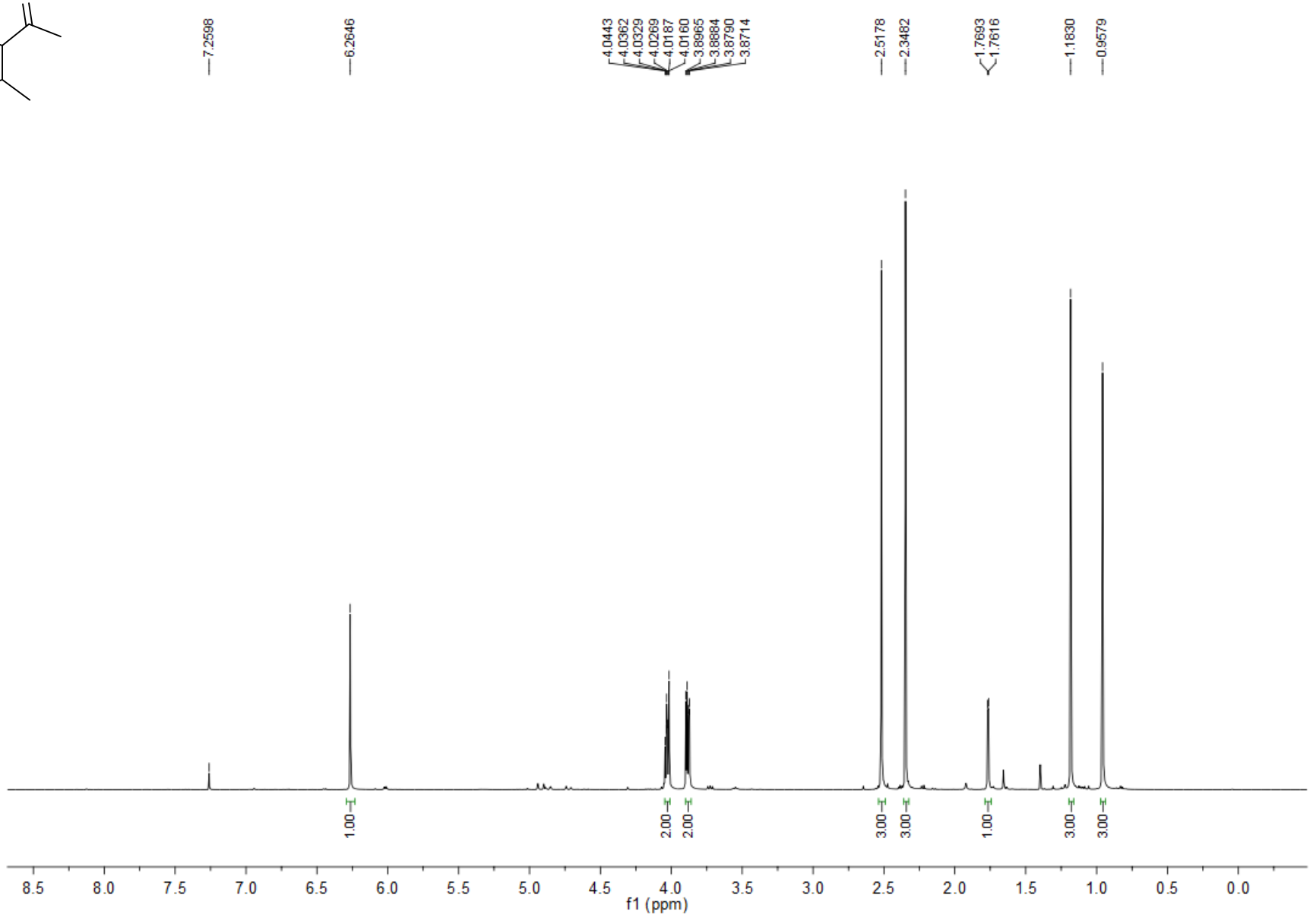

H
O
O

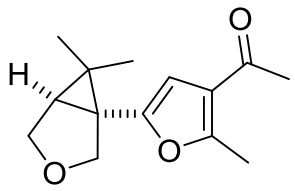
7e


194.5444
156.8547
156.6364
121.8791
105.7506
77.4771
77.1595
76.8420
37.5894
36.8504
31.3434
29.2403
28.1341
26.9450
25.6474
24.4869
15.7956
14.6203
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

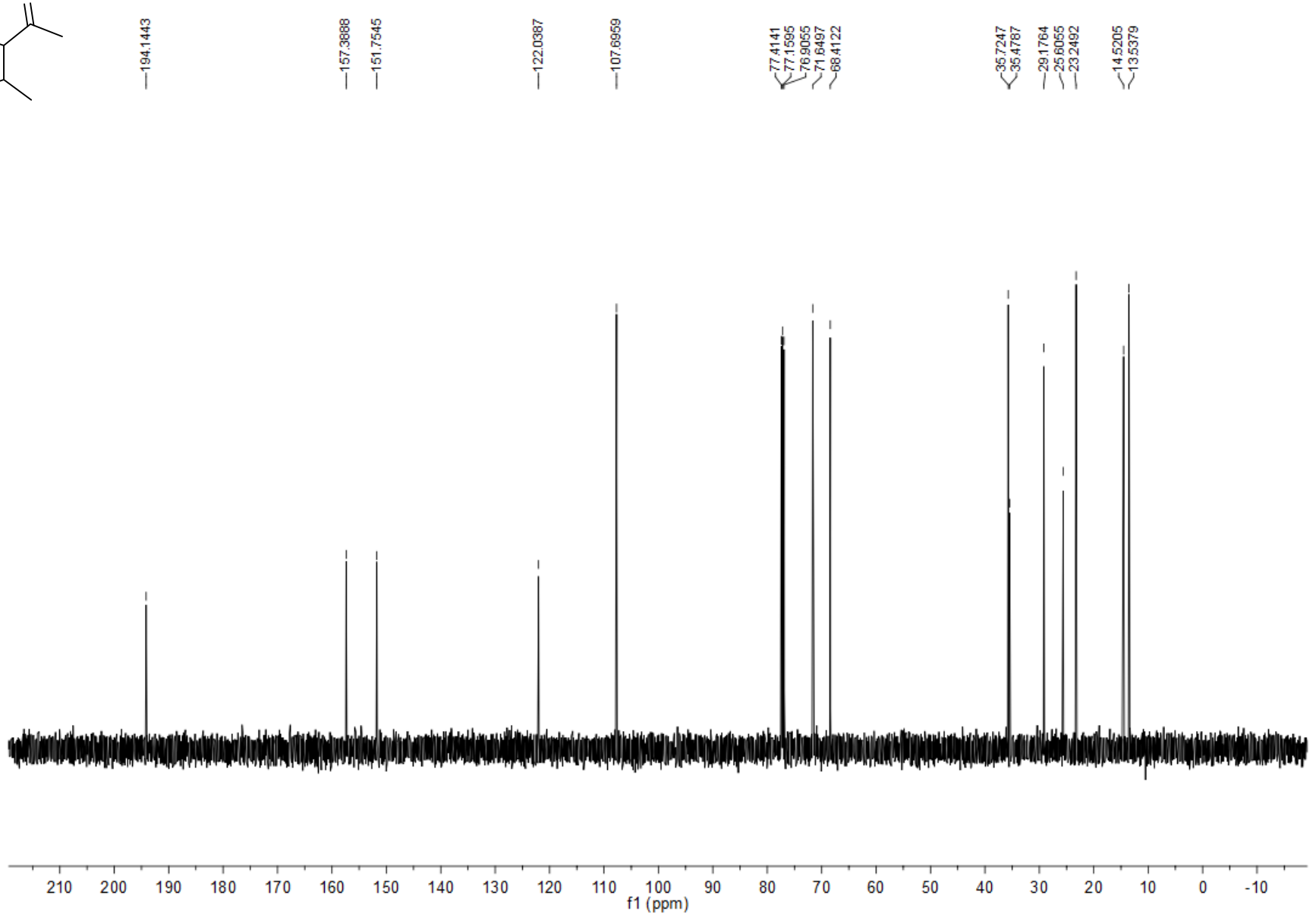

H
O
O
O

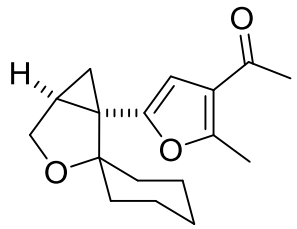
7f


7.2598
6.2646
4.0443
4.0362
4.0329
4.0269
4.0187
4.0160
3.8965
3.8884
3.8790
3.8714
2.5178
2.3482
1.7693
1.7616
1.1830
0.9579
1.00
2.00
2.00
3.00
3.00
1.00
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

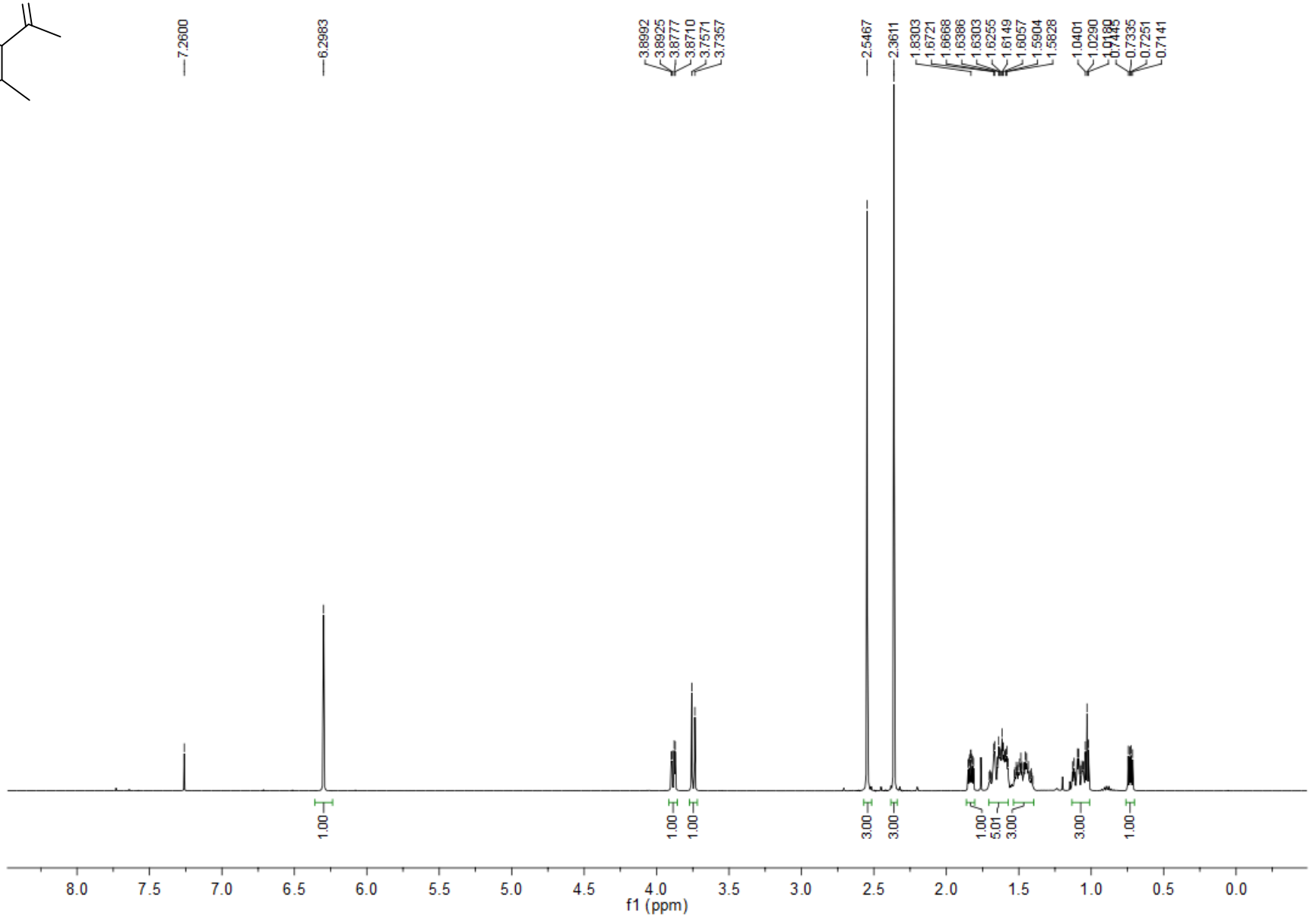

H
O
O
O

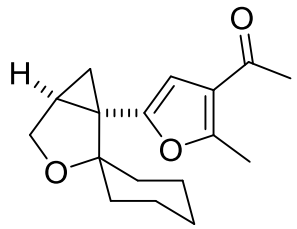
7f


194.1443
157.3888
151.7545
122.0387
107.6959
77.4141
77.1595
76.9055
71.6497
68.4122
35.7247
35.4787
29.1764
25.6055
23.2492
14.5205
13.5379
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

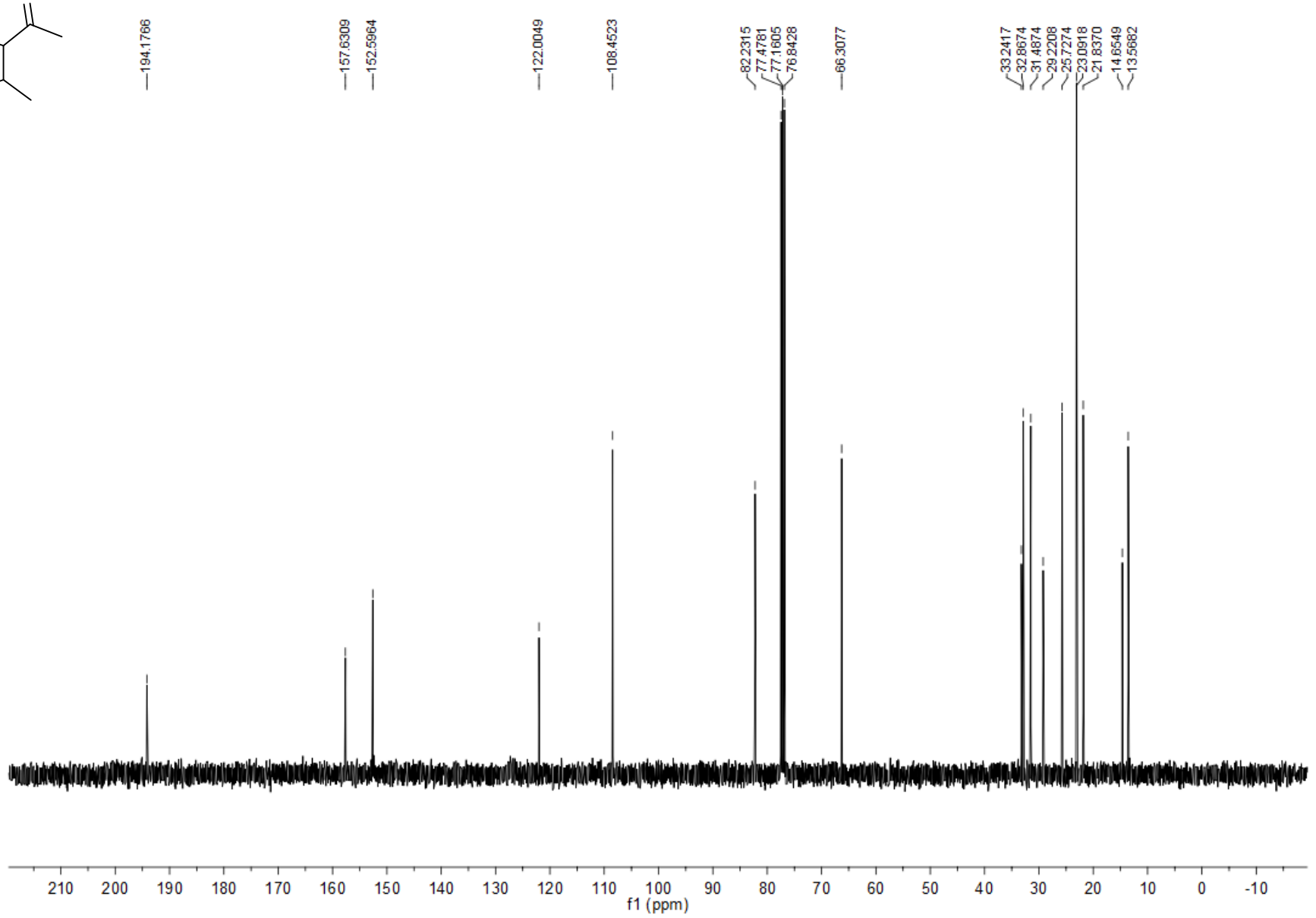

H
O
O
O

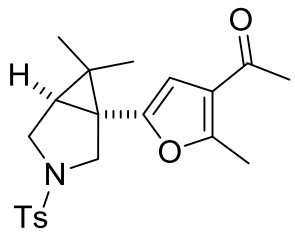
7g


7.2600
6.2983
3.8992
3.8925
3.8777
3.8710
3.7571
3.7357
2.5467
2.3611
1.8303
1.6721
1.6668
1.6386
1.6303
1.6255
1.6149
1.6057
1.5904
1.5828
1.0401
1.0290
0.7335
0.7251
0.7141
1.00
1.00
1.00
3.00
3.00
1.00
5.01
3.00
3.00
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

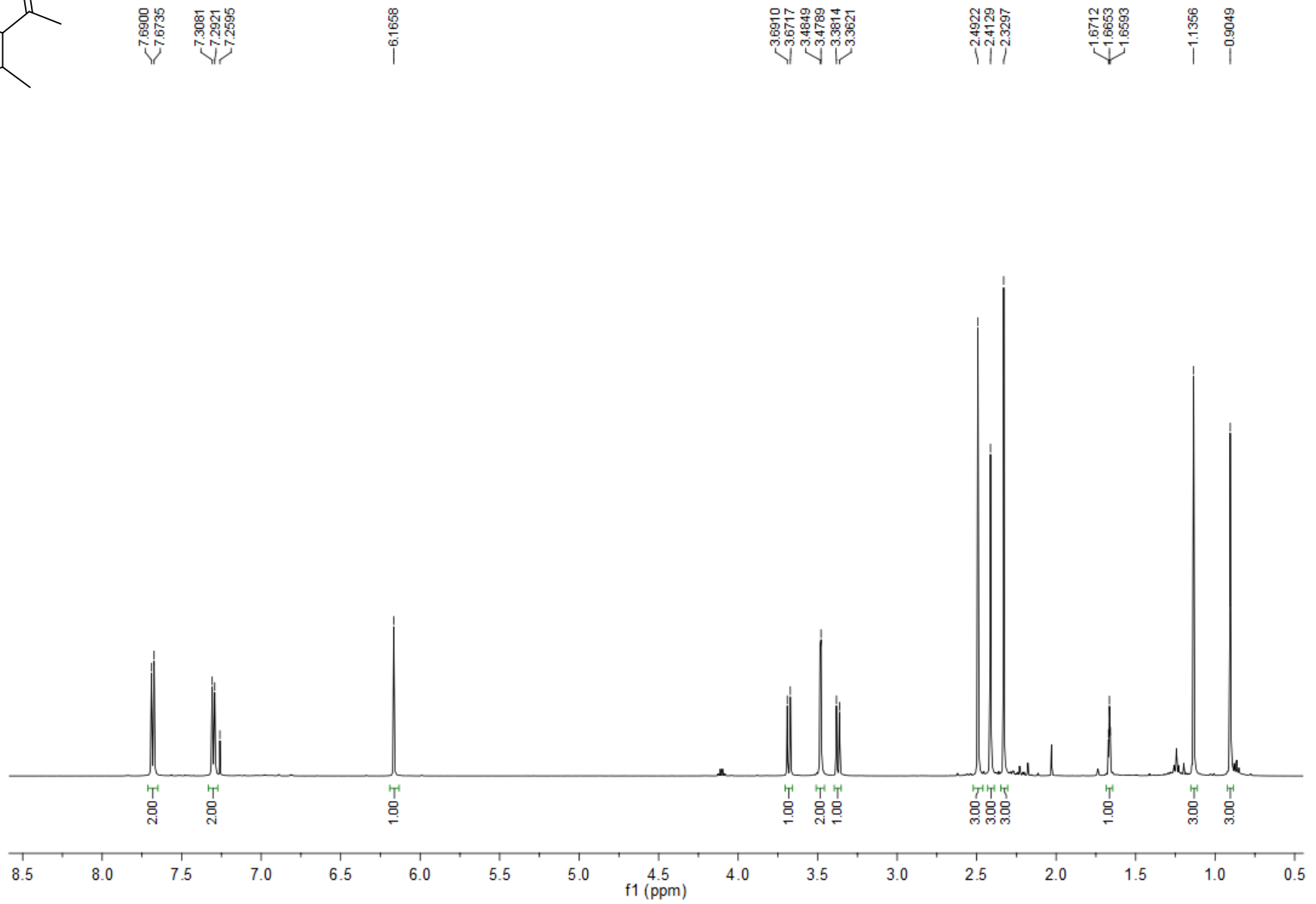

H
O
O
O

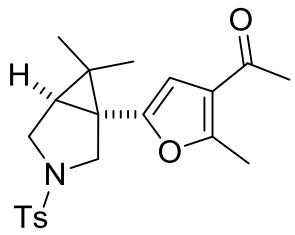
7g


194.1766
157.6309
152.5964
122.0049
108.4523
82.2315
77.4781
77.1605
76.8428
66.3077
33.2417
32.8674
31.4874
29.2208
25.7274
23.0918
21.8370
14.6549
13.5682
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

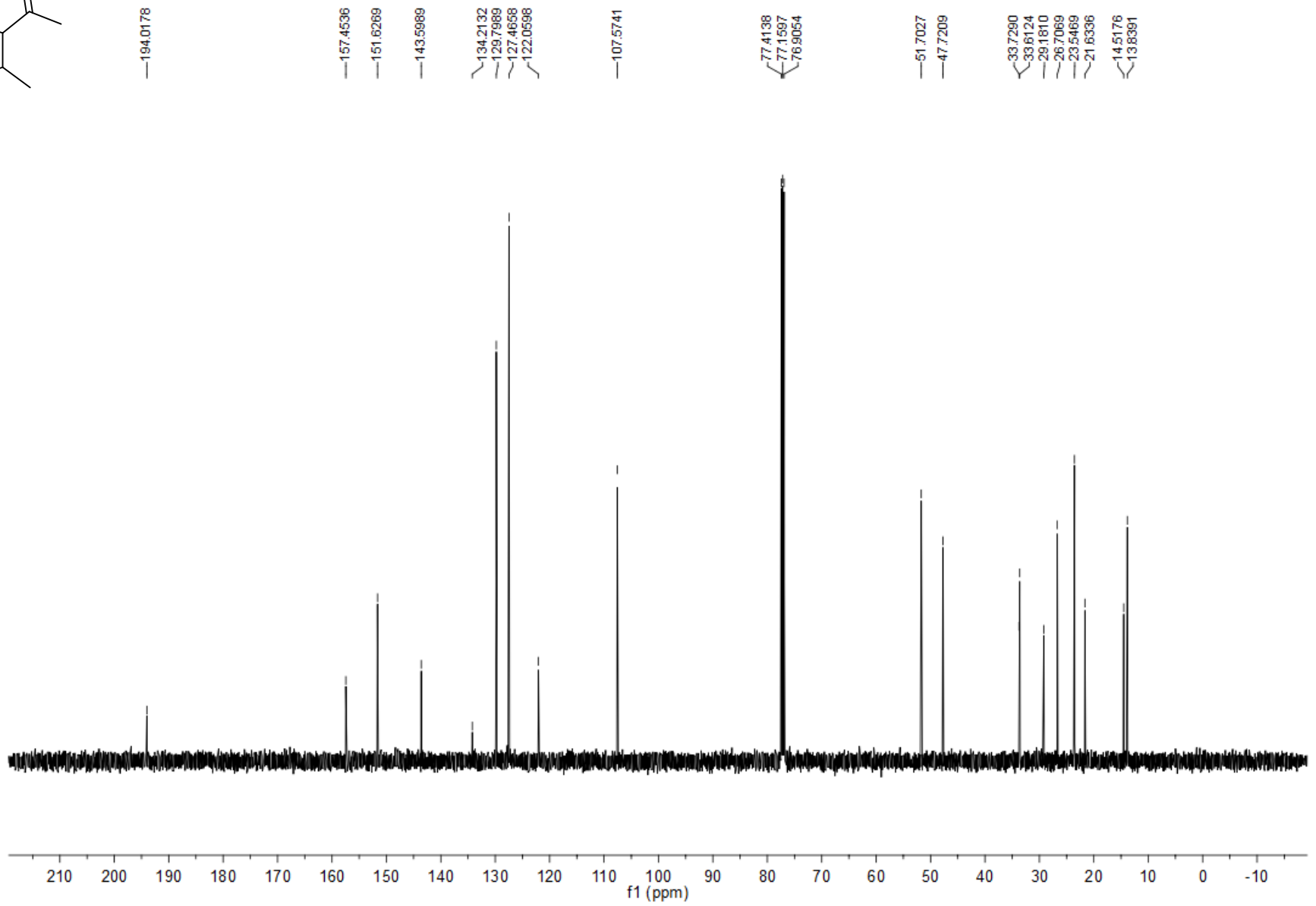

H
O
N
Ts
O

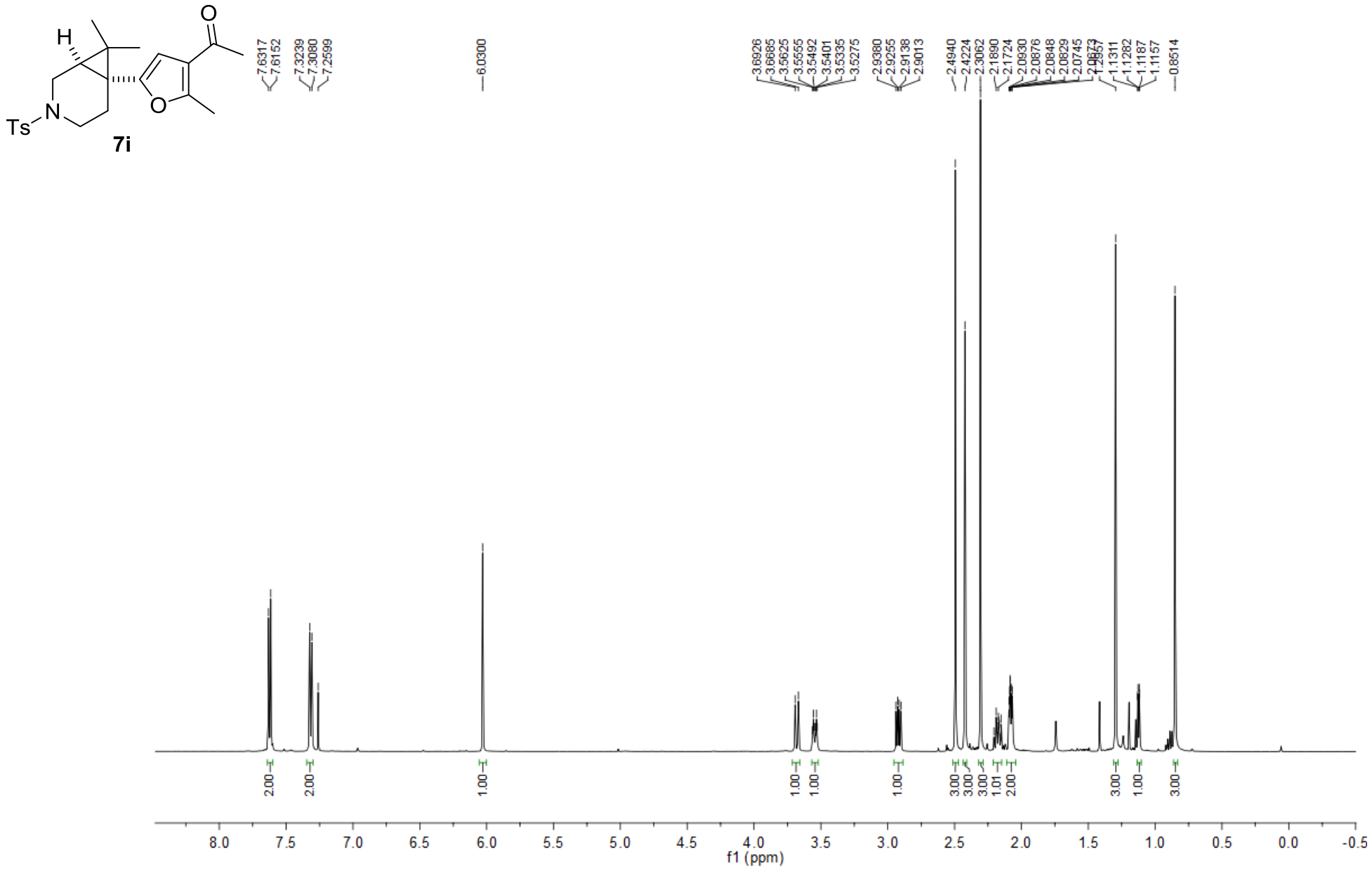
7h

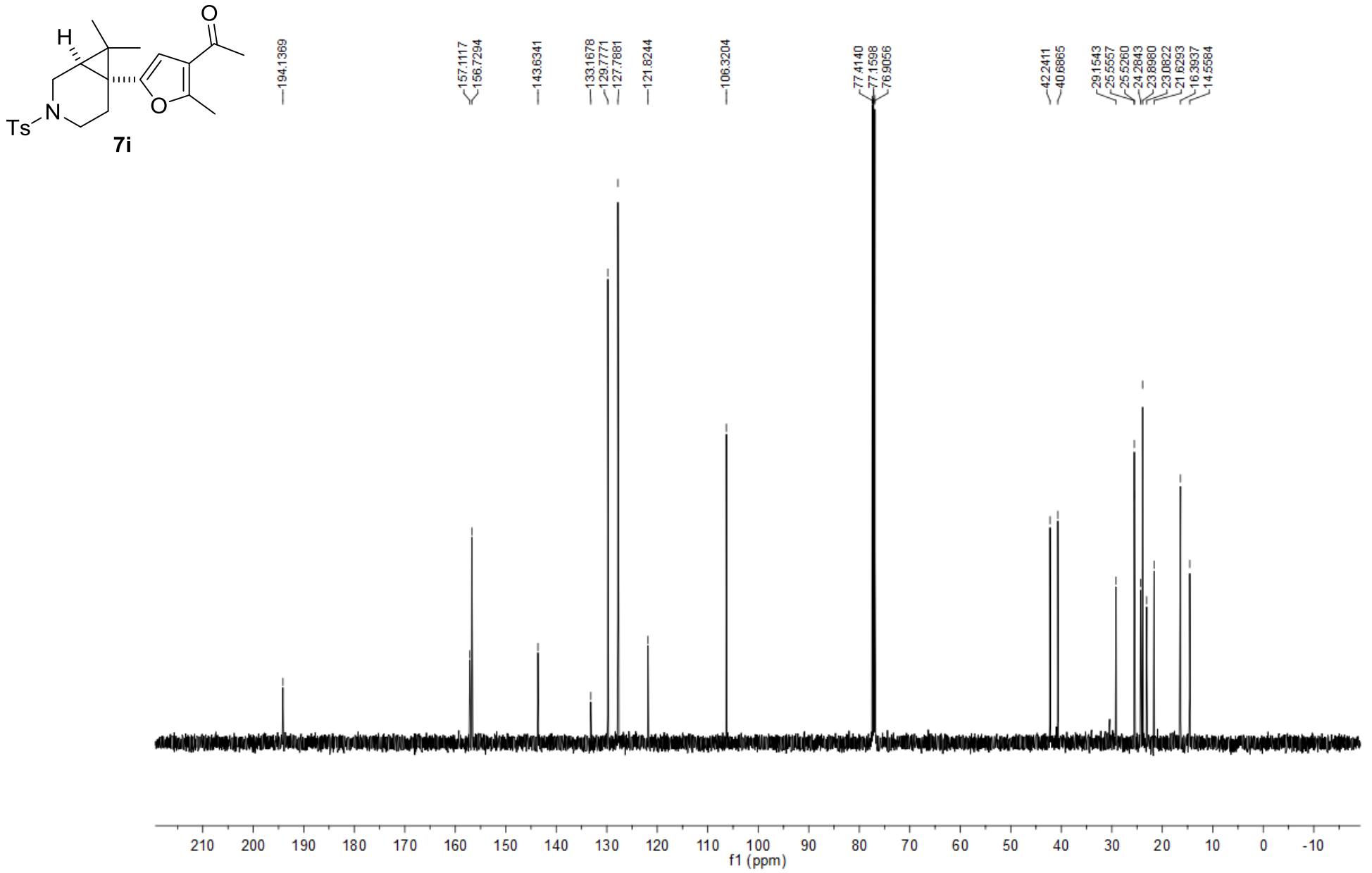

7.6900
7.6735
7.3081
7.2921
7.2595
6.1658
3.6910
3.6717
3.4849
3.4789
3.3814
3.3621
2.4922
2.4129
2.3297
1.6712
1.6653
1.6593
1.1356
0.9049
2.00
2.00
1.00
1.00
2.00
1.00
3.00
3.00
3.00
1.00
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

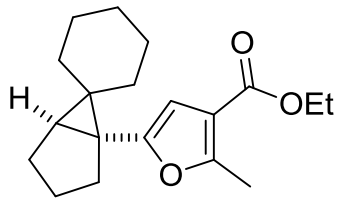

O
H
O
N
Ts

7h

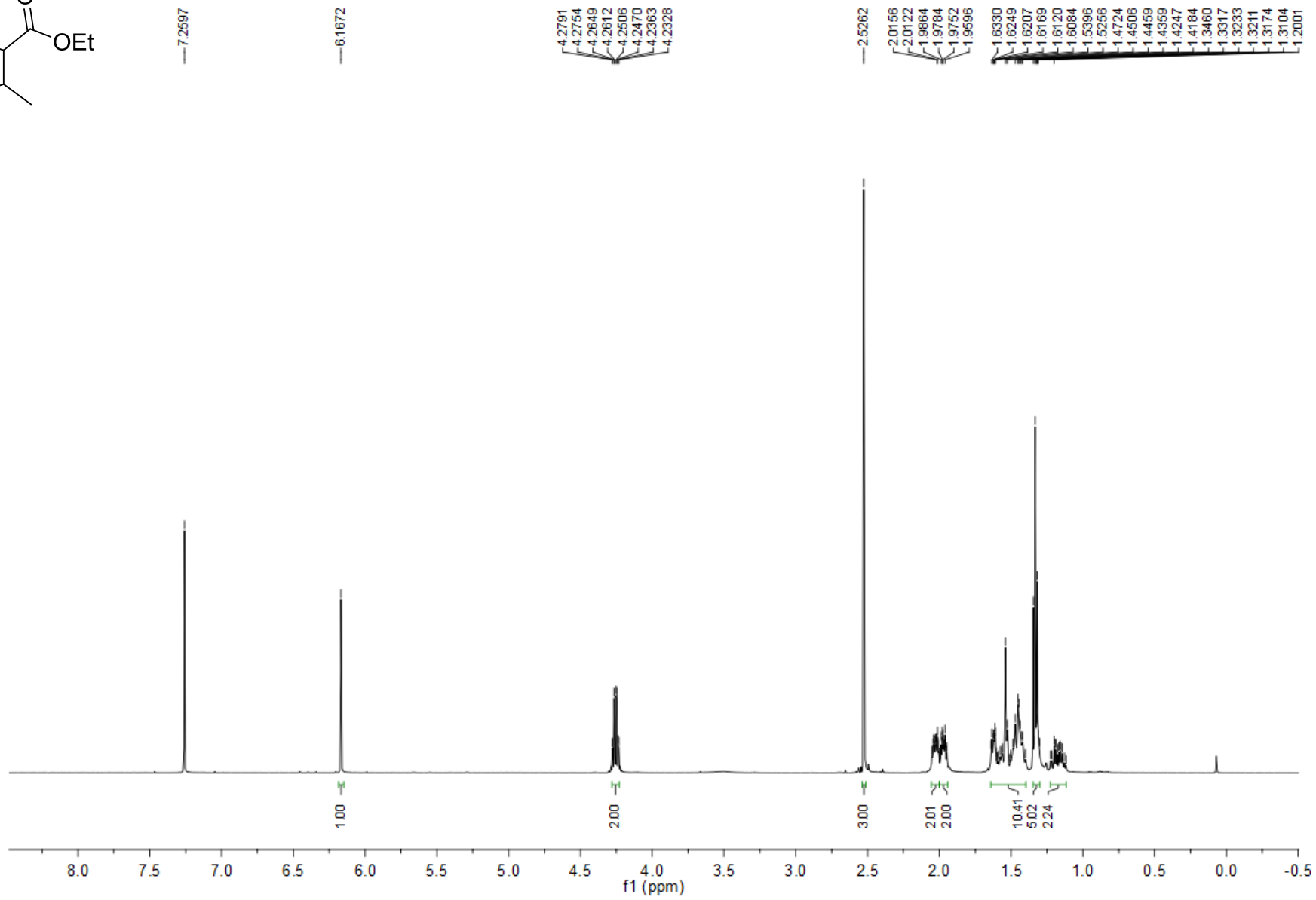

194.0178
157.4536
151.6269
143.5989
134.2132
129.7989
127.4658
122.0598
107.5741
77.4138
77.1597
76.9054
51.7027
47.7209
33.7290
33.6124
29.1810
26.7069
23.5469
21.6336
14.5176
13.8391
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

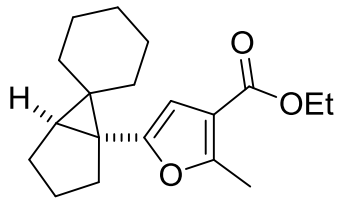

H
O
Ts
N
O
7i
7.6317
7.6152
7.3239
7.3080
7.2599
6.0300
3.6926
3.6685
3.5625
3.5555
3.5492
3.5401
3.5335
3.5275
2.9380
2.9255
2.9138
2.9013
2.4940
2.4224
2.3062
2.1890
2.1724
2.0930
2.0876
2.0848
2.0829
2.0745
1.1311
1.1282
1.1187
1.1157
0.8514
2.00
2.00
1.00
1.00
1.00
1.00
3.00
3.00
1.01
2.00
3.00
1.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


H
O
Ts
N
O
7i
194.1369
157.1117
156.7294
143.6341
133.1678
129.7771
127.7881
121.8244
106.3204
77.4140
77.1598
76.9056
42.2411
40.6865
29.1543
25.5557
25.5260
24.2843
23.8980
23.0822
21.6293
16.3937
14.5584
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

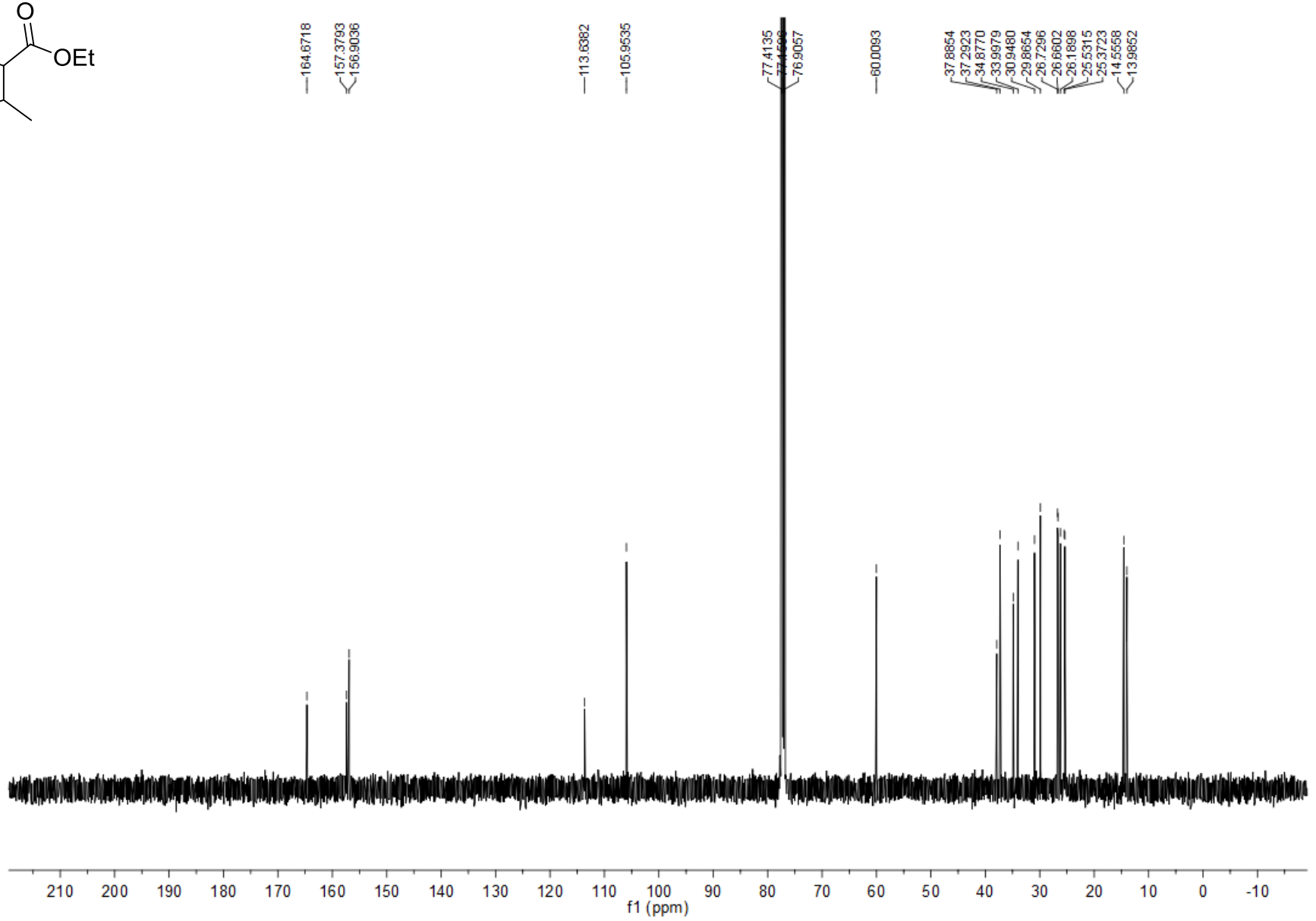

H
O
OEt
O

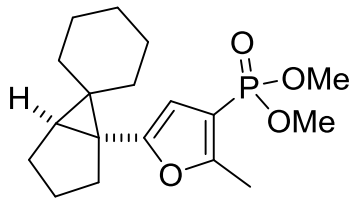
7j


7.2597
6.1672
4.2791
4.2754
4.2649
4.2612
4.2506
4.2470
4.2363
4.2328
2.5262
2.0156
2.0122
1.9864
1.9784
1.9752
1.9596
1.6330
1.6249
1.6207
1.6169
1.6120
1.6084
1.5396
1.5256
1.4724
1.4506
1.4459
1.4359
1.4247
1.4184
1.3460
1.3317
1.3233
1.3211
1.3174
1.3104
1.2001
1.00
2.00
3.00
2.01
2.00
10.41
5.02
2.24
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

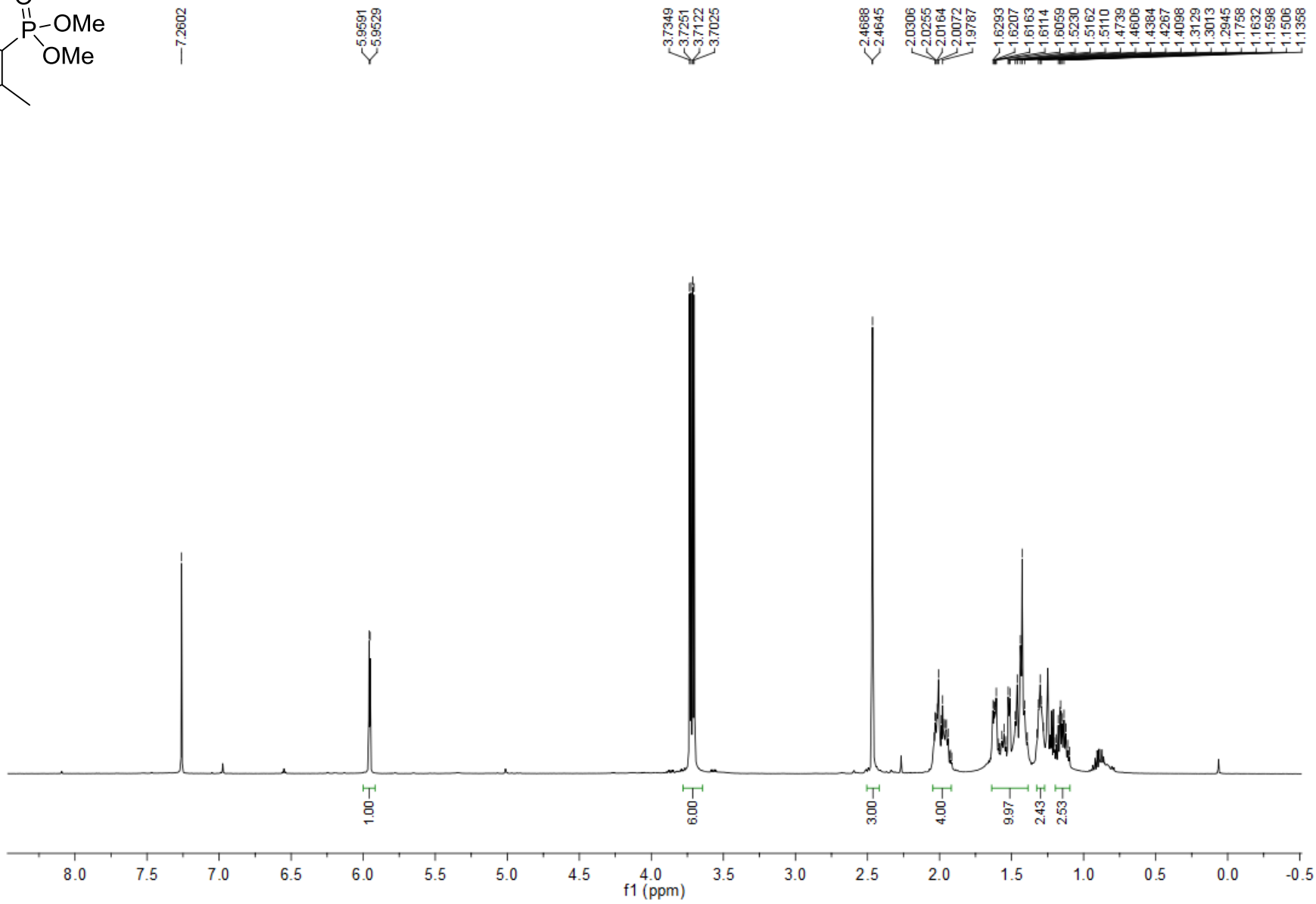

H
O
OEt
O

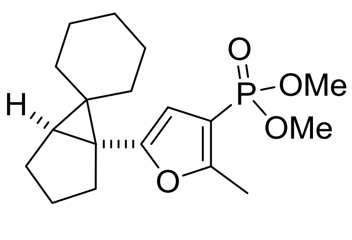
7j


164.6718
157.3793
156.9036
113.6382
105.9535
77.4135
76.9057
60.0093
37.8854
37.2923
34.8770
33.9979
30.9480
29.8654
26.7296
26.6602
26.1898
25.5315
25.3723
14.5558
13.9852
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

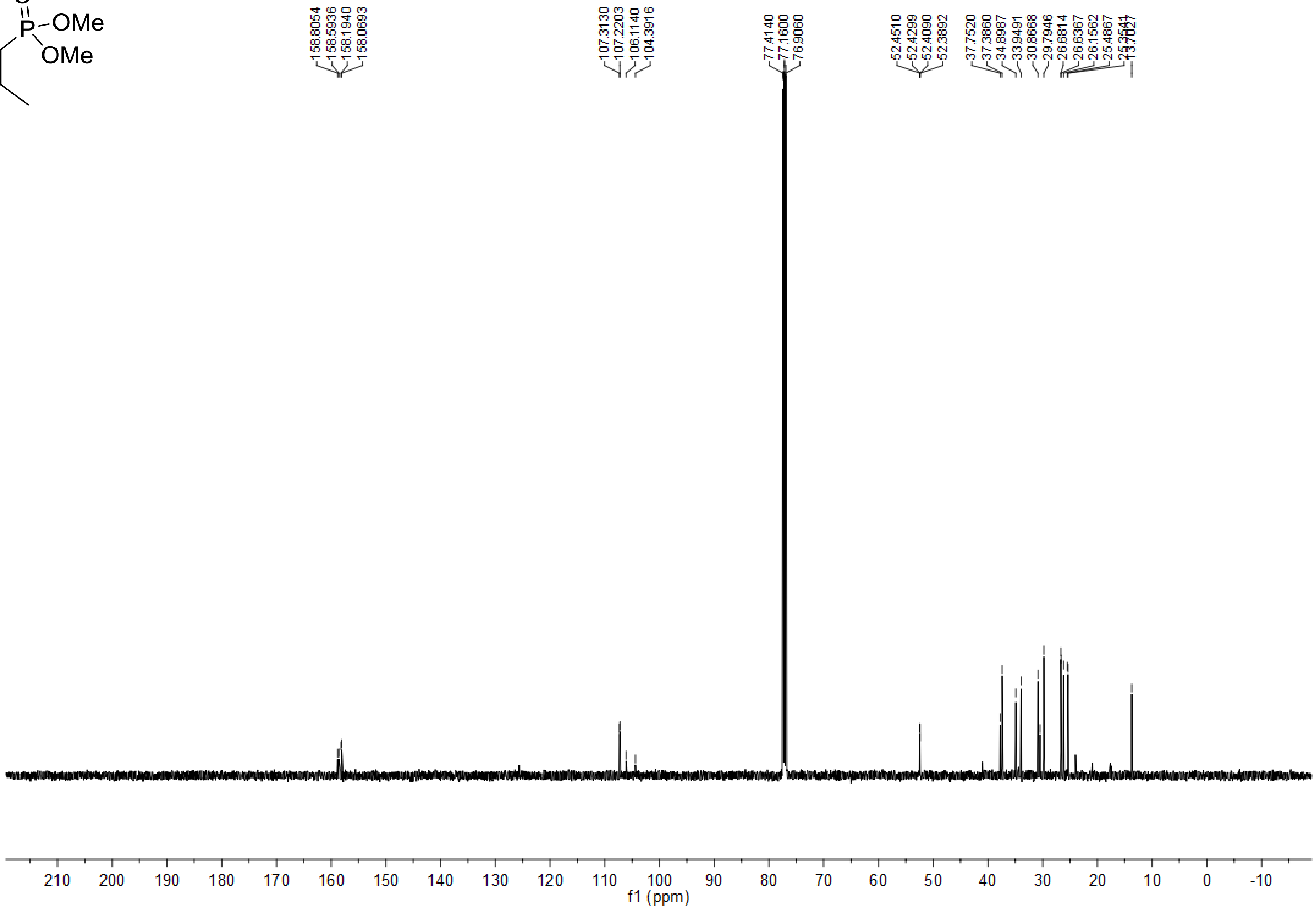

H
O
P
OMe
OMe
O

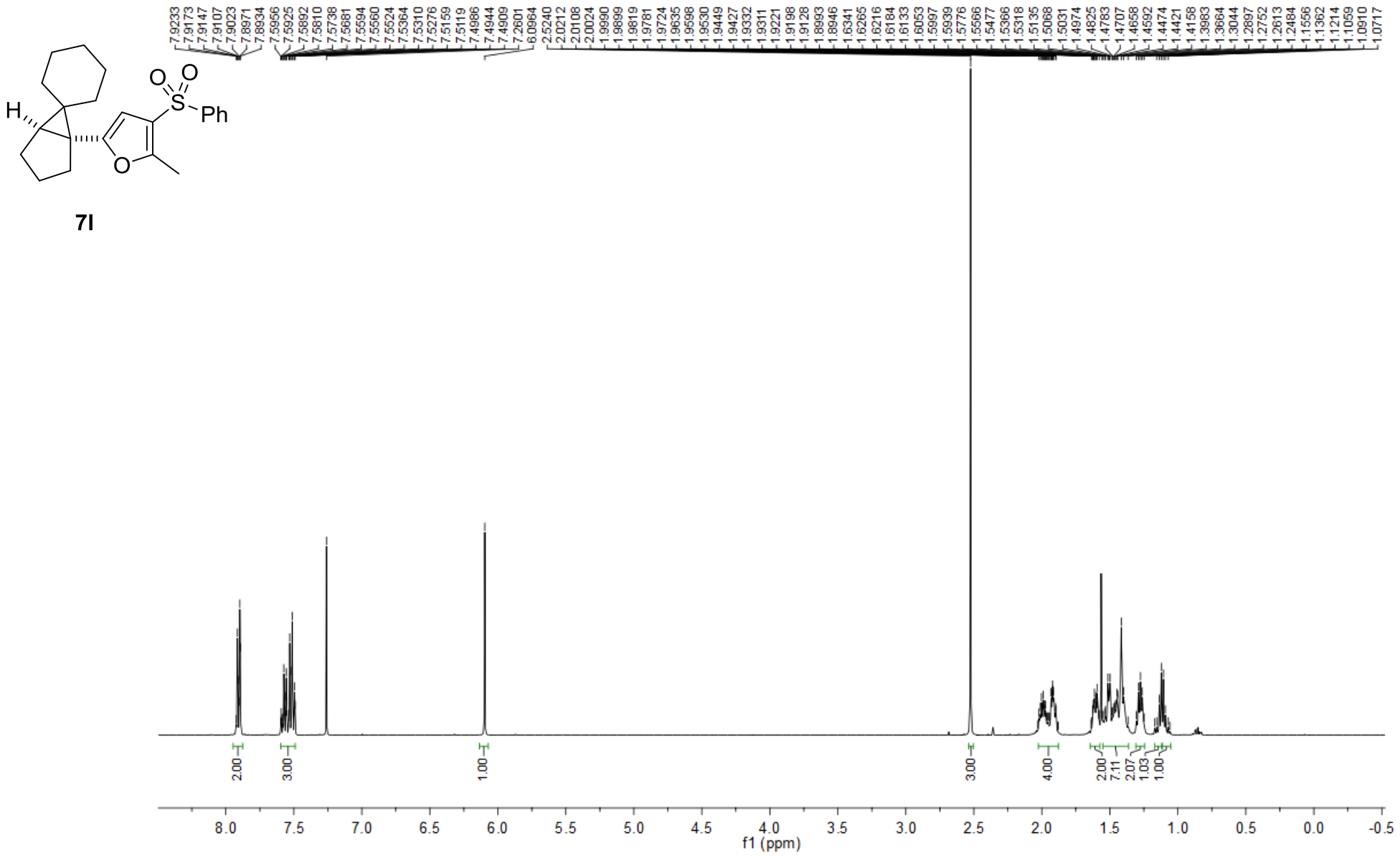
7k


7.2602
5.9591
5.9529
3.7349
3.7251
3.7122
3.7025
2.4688
2.4645
2.0306
2.0255
2.0164
2.0072
1.9787
1.6293
1.6207
1.6163
1.6114
1.6059
1.5230
1.5162
1.5110
1.4739
1.4606
1.4384
1.4267
1.4098
1.3129
1.3013
1.2945
1.1758
1.1632
1.1598
1.1506
1.1358
1.00
6.00
3.00
4.00
9.97
2.43
2.53
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

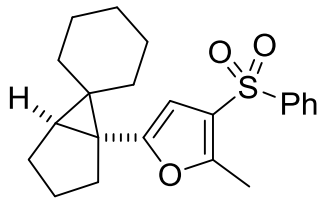

O
P
OMe
OMe
H
O

7k

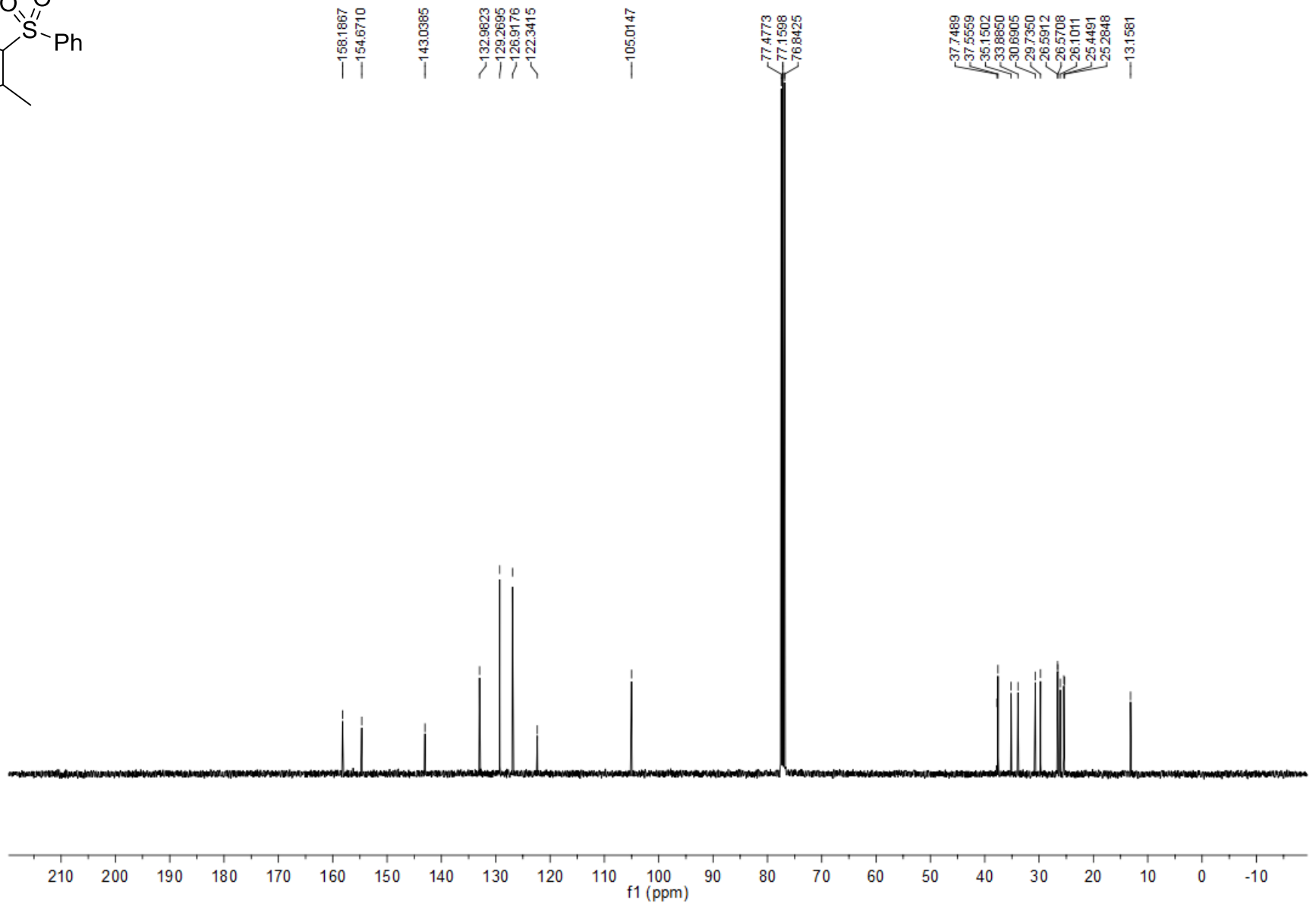

158.8054
158.5936
158.1940
158.0693
107.3130
107.2203
106.1140
104.3916
77.4140
77.1600
76.9060
52.4510
52.4299
52.4090
52.3892
37.7520
37.3860
34.8987
33.9491
30.8668
29.7946
26.6814
26.6367
26.1562
25.4867
25.3541
13.7027
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

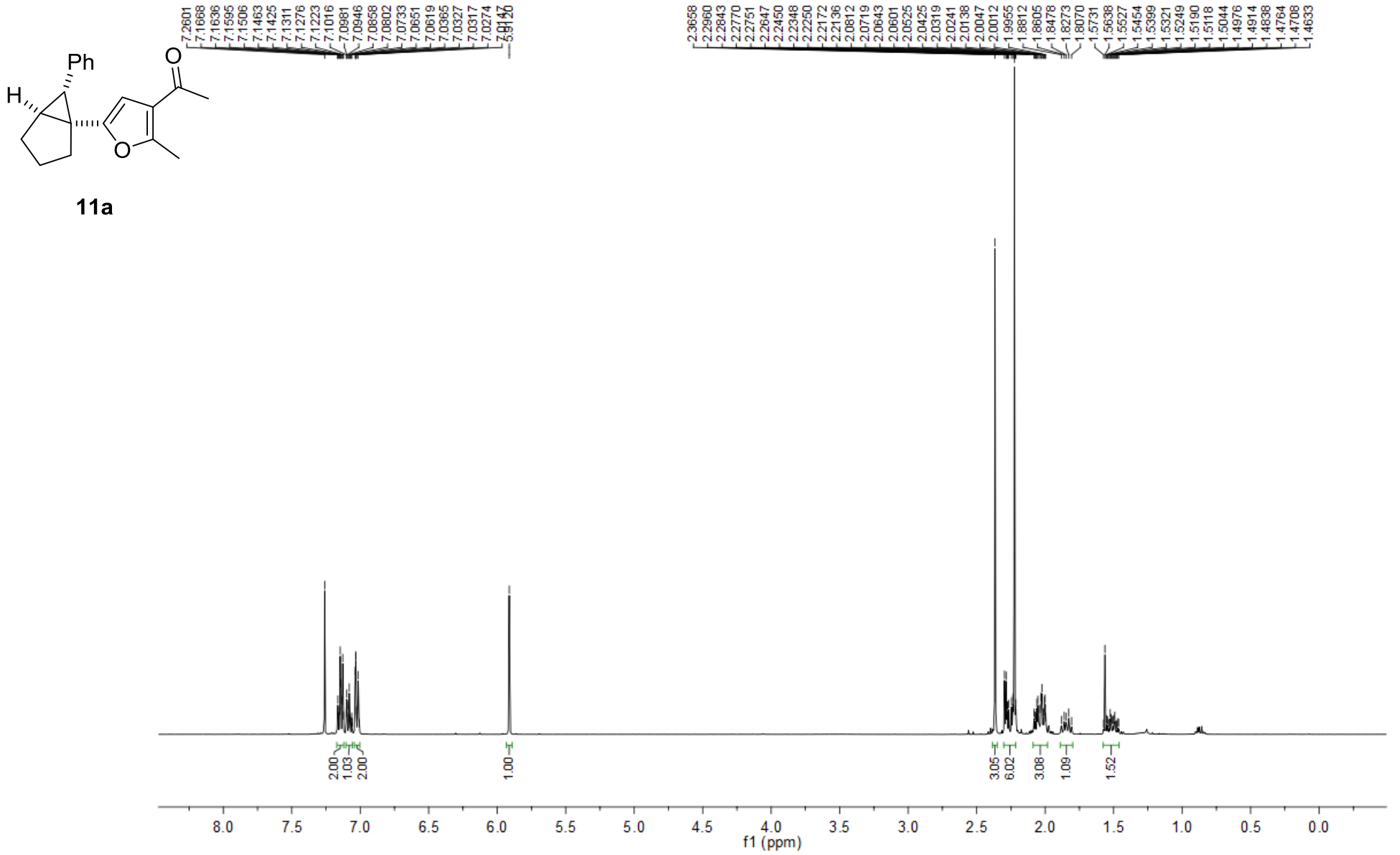

H
O
O
S
Ph
O
7.9233
7.9173
7.9147
7.9107
7.9023
7.8971
7.8934
7.5956
7.5925
7.5892
7.5810
7.5738
7.5681
7.5594
7.5560
7.5524
7.5364
7.5310
7.5276
7.5159
7.5119
7.4986
7.4944
7.4909
7.2601
6.0964
2.5240
2.0212
2.0108
2.0024
1.9990
1.9899
1.9819
1.9781
1.9724
1.9635
1.9598
1.9530
1.9449
1.9427
1.9332
1.9311
1.9221
1.9198
1.9128
1.8993
1.8946
1.6341
1.6265
1.6216
1.6184
1.6133
1.6053
1.5997
1.5939
1.5776
1.5566
1.5477
1.5366
1.5318
1.5135
1.5068
1.5031
1.4974
1.4825
1.4783
1.4707
1.4658
1.4592
1.4474
1.4421
1.4158
1.3983
1.3664
1.3044
1.2897
1.2752
1.2613
1.2484
1.1556
1.1362
1.1214
1.1059
1.0910
1.0717
2.00
3.00
1.00
3.00
4.00
2.00
7.11
2.07
1.03
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

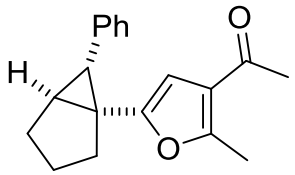
7l


H
O
O
S
Ph
O

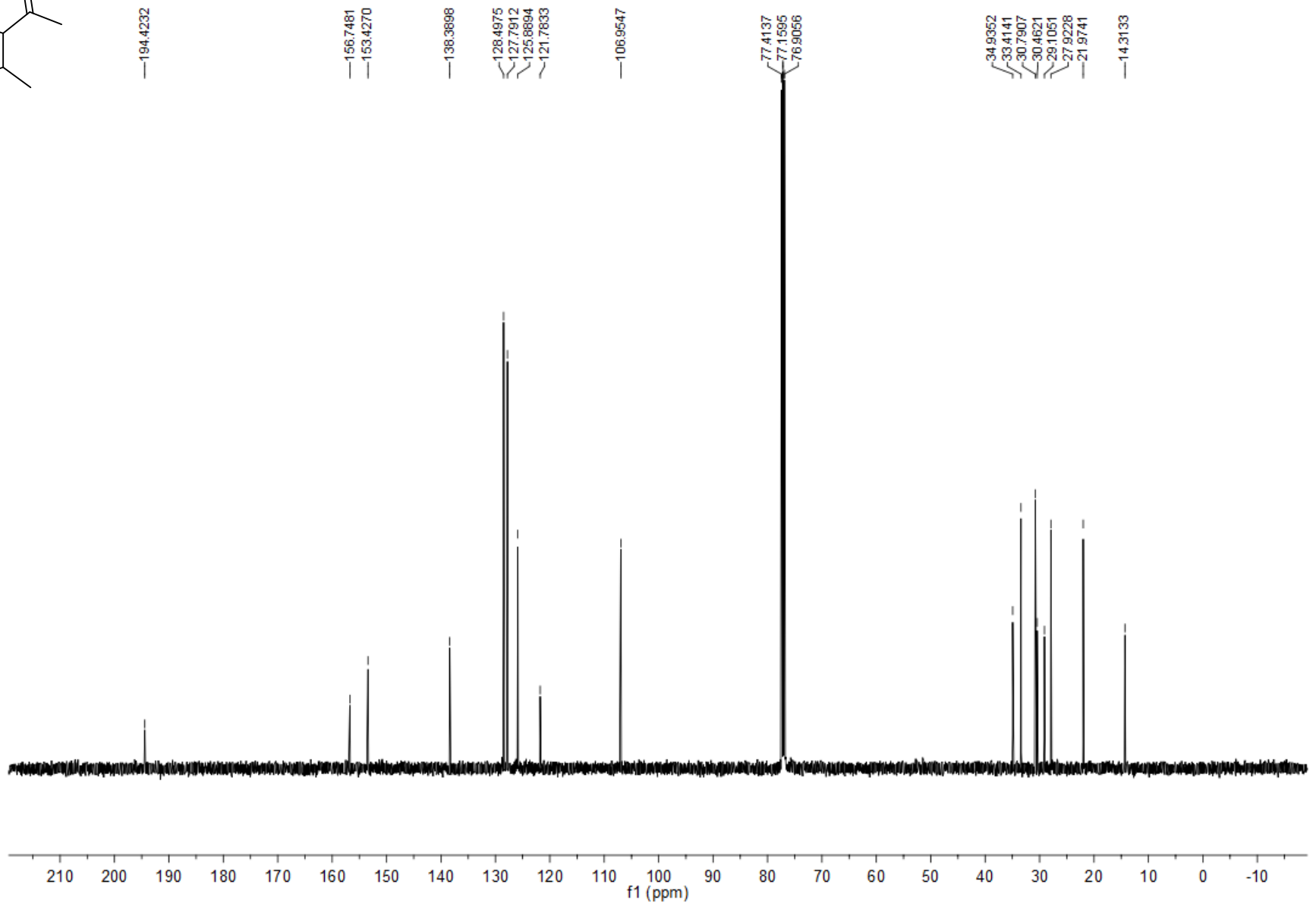
7l

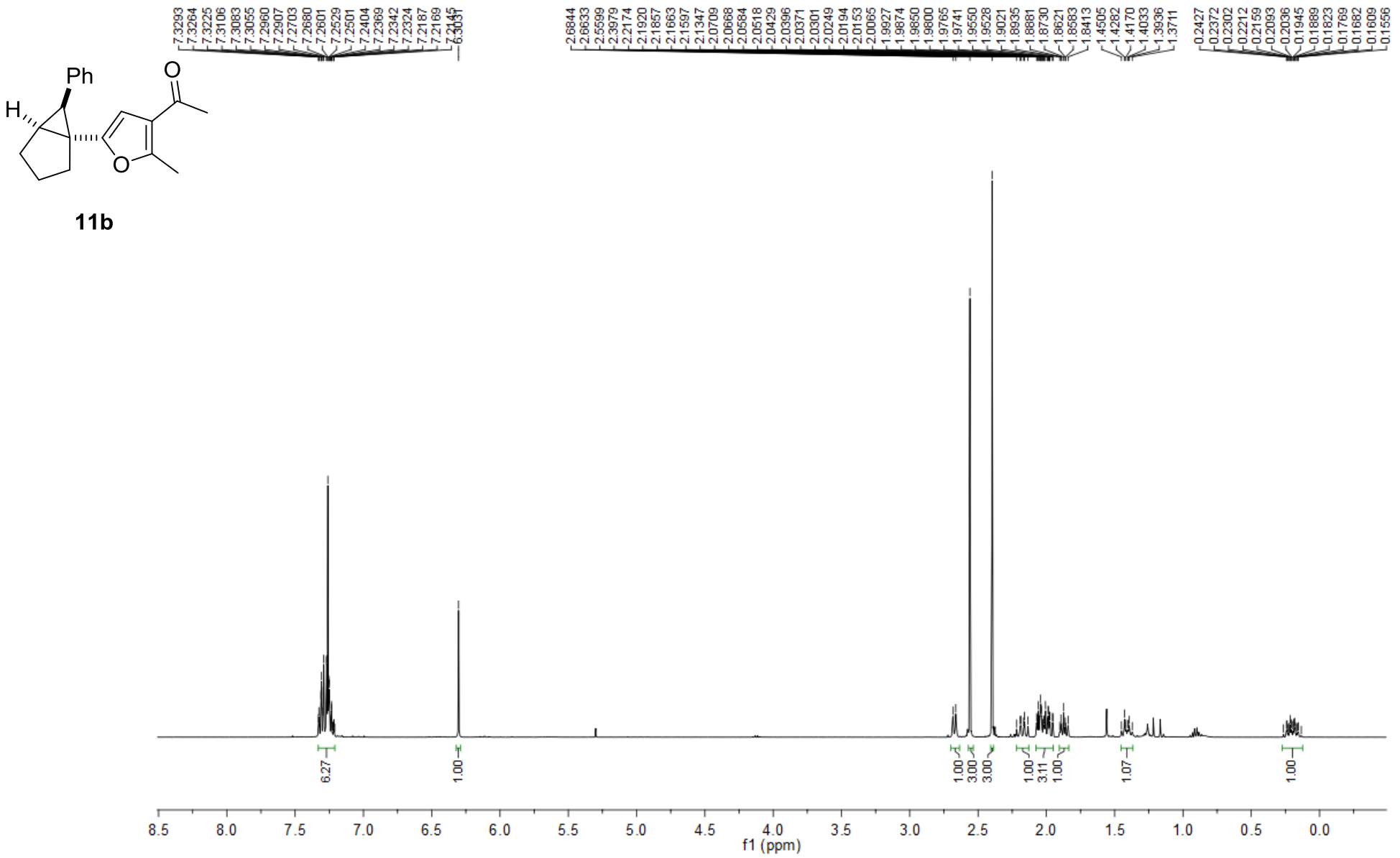

158.1867
154.6710
143.0385
132.9823
129.2695
126.9176
122.3415
105.0147
77.4773
77.1598
76.8425
37.7489
37.5559
35.1502
33.8850
30.6905
29.7350
26.5912
26.5708
26.1011
25.4491
25.2848
13.1581
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

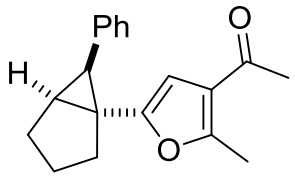

Ph
H
O
O
11a
f1 (ppm)


Ph
H
O
O

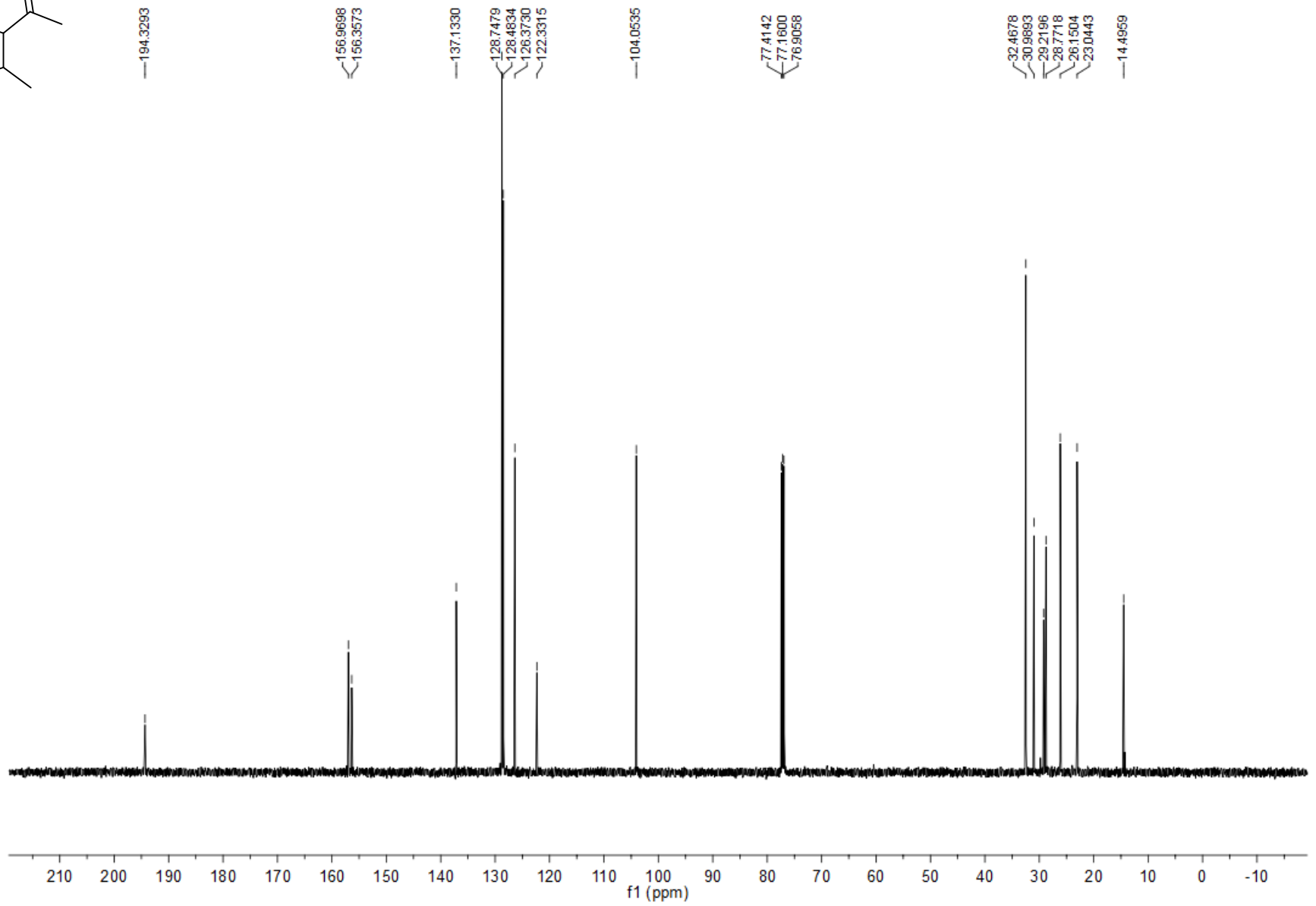
11a

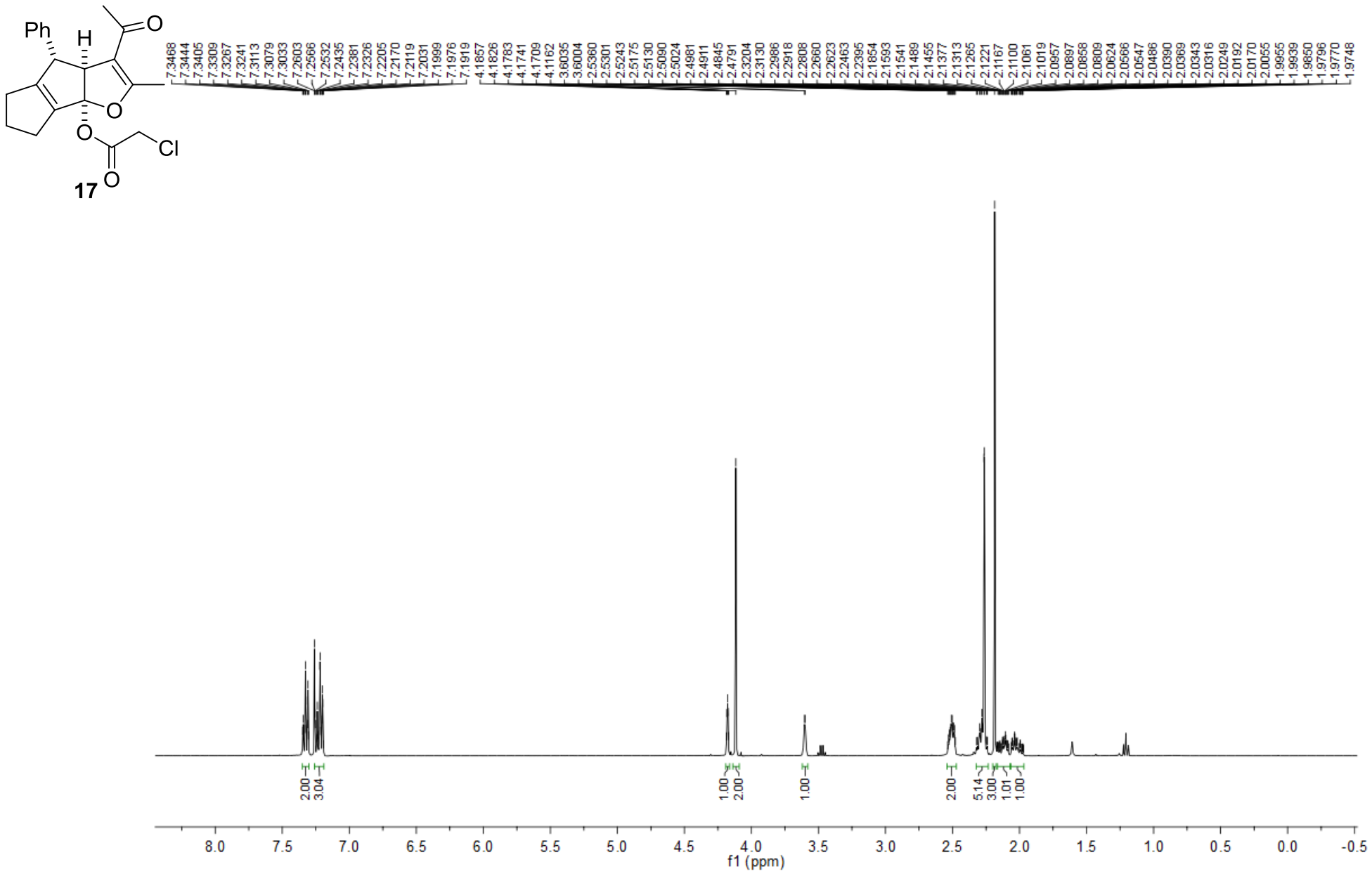

194.4232
156.7481
153.4270
138.3898
128.4975
127.7912
125.8894
121.7833
106.9547
77.4137
77.1595
76.9056
34.9352
33.4141
30.7907
30.4621
29.1051
27.9228
21.9741
14.3133
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

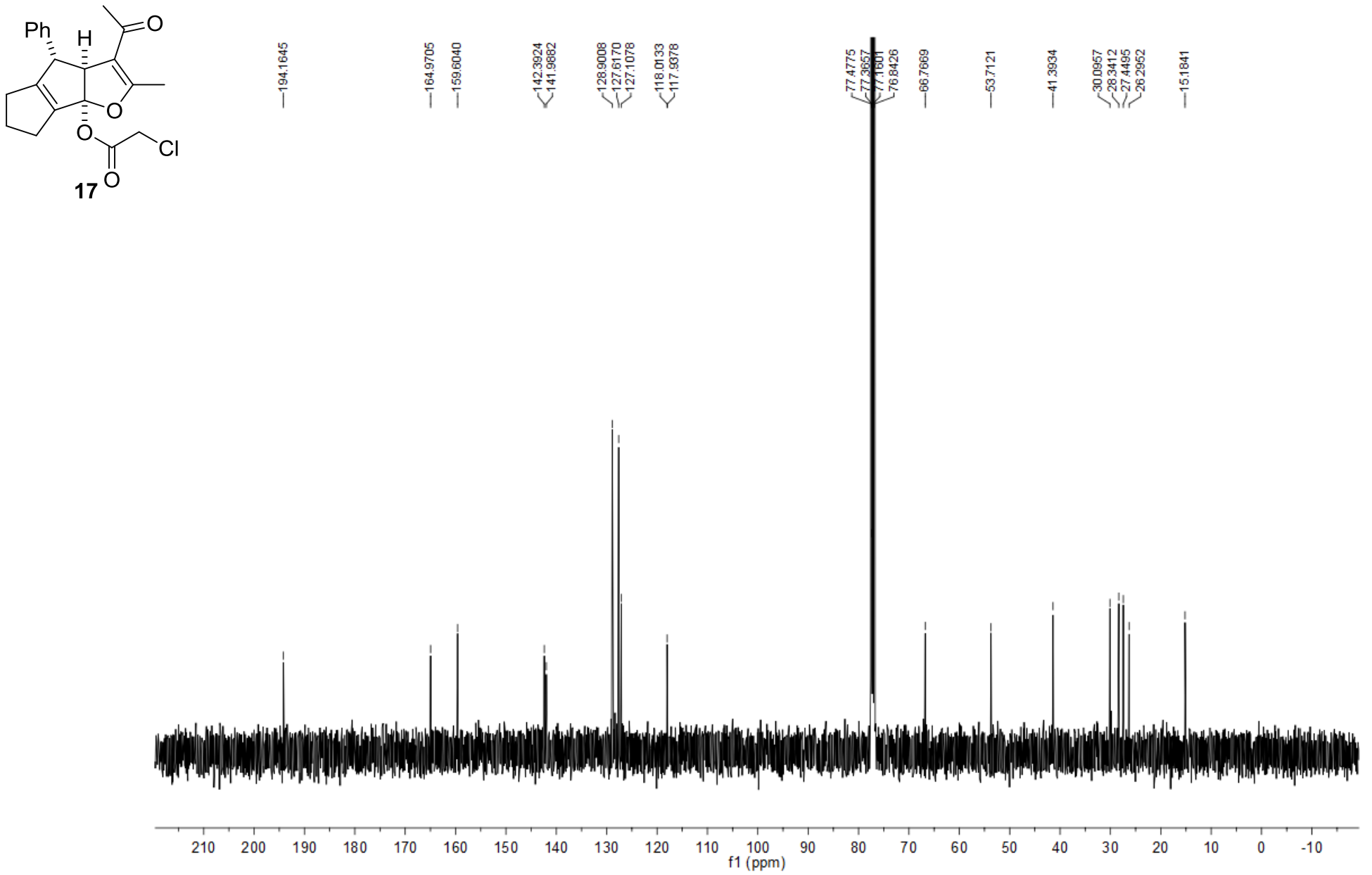

Ph
H
O
O
11b
7.3293
7.3264
7.3225
7.3106
7.3083
7.3055
7.2960
7.2907
7.2703
7.2680
7.2601
7.2529
7.2501
7.2404
7.2369
7.2342
7.2324
7.2187
7.2169
7.2145
7.2031
2.6844
2.6633
2.5599
2.3979
2.2174
2.1920
2.1857
2.1663
2.1597
2.1347
2.0709
2.0668
2.0584
2.0518
2.0429
2.0396
2.0371
2.0301
2.0249
2.0194
2.0153
2.0065
1.9927
1.9874
1.9850
1.9800
1.9765
1.9741
1.9550
1.9528
1.9021
1.8935
1.8881
1.8730
1.8621
1.8583
1.8413
1.4505
1.4282
1.4170
1.4033
1.3936
1.3711
0.2427
0.2372
0.2302
0.2212
0.2159
0.2093
0.2036
0.1945
0.1889
0.1823
0.1769
0.1682
0.1609
0.1556
6.27
1.00
1.00
3.00
3.00
1.00
3.11
1.00
1.07
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

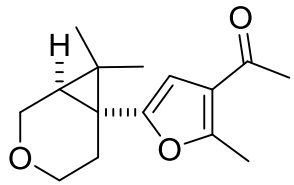

Ph
H
O
O

11b

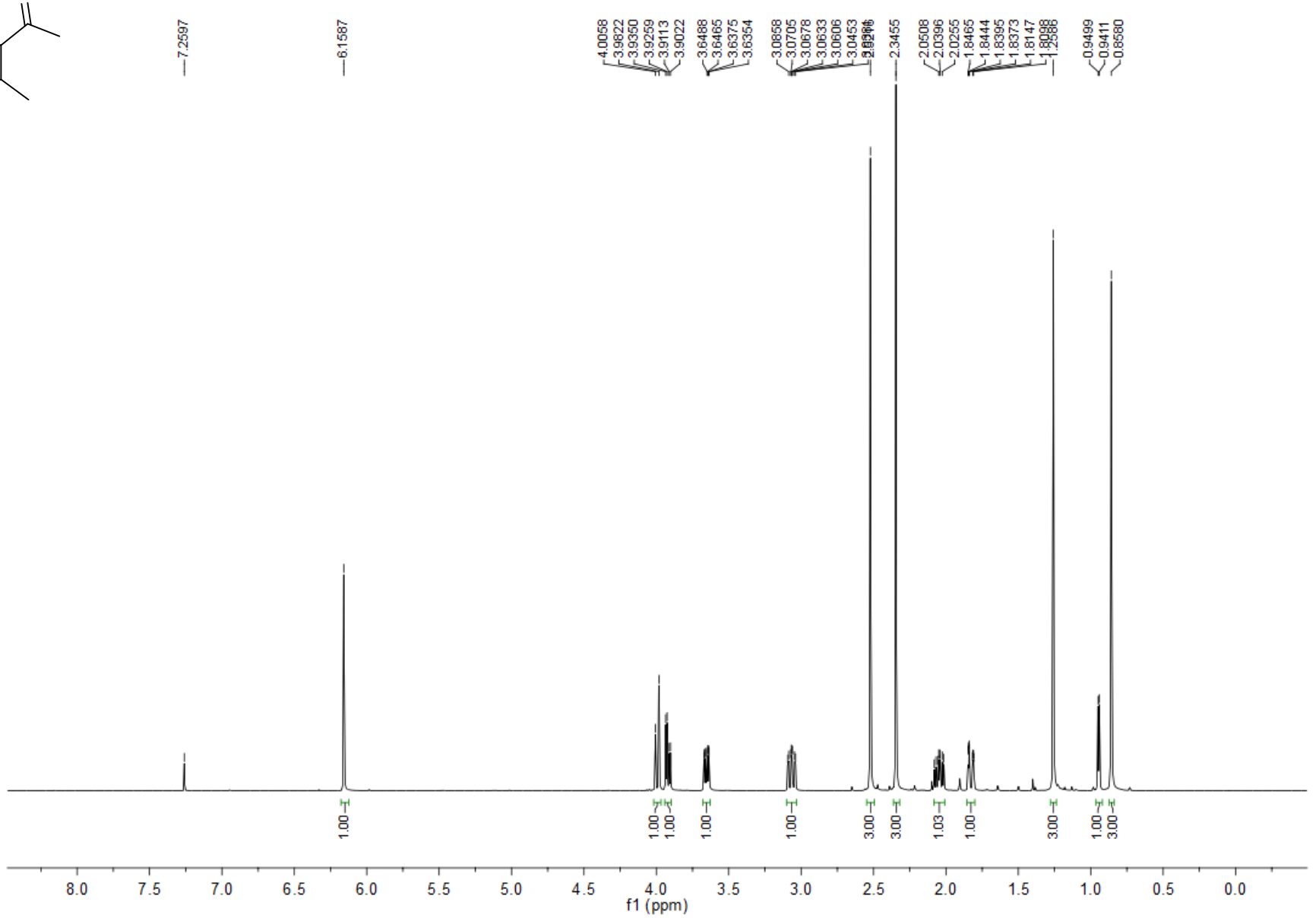

194.3293
156.9698
156.3573
137.1330
128.7479
128.4834
126.3730
122.3315
104.0535
77.4142
77.1600
76.9058
32.4678
30.9893
29.2196
28.7718
26.1504
23.0443
14.4959
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

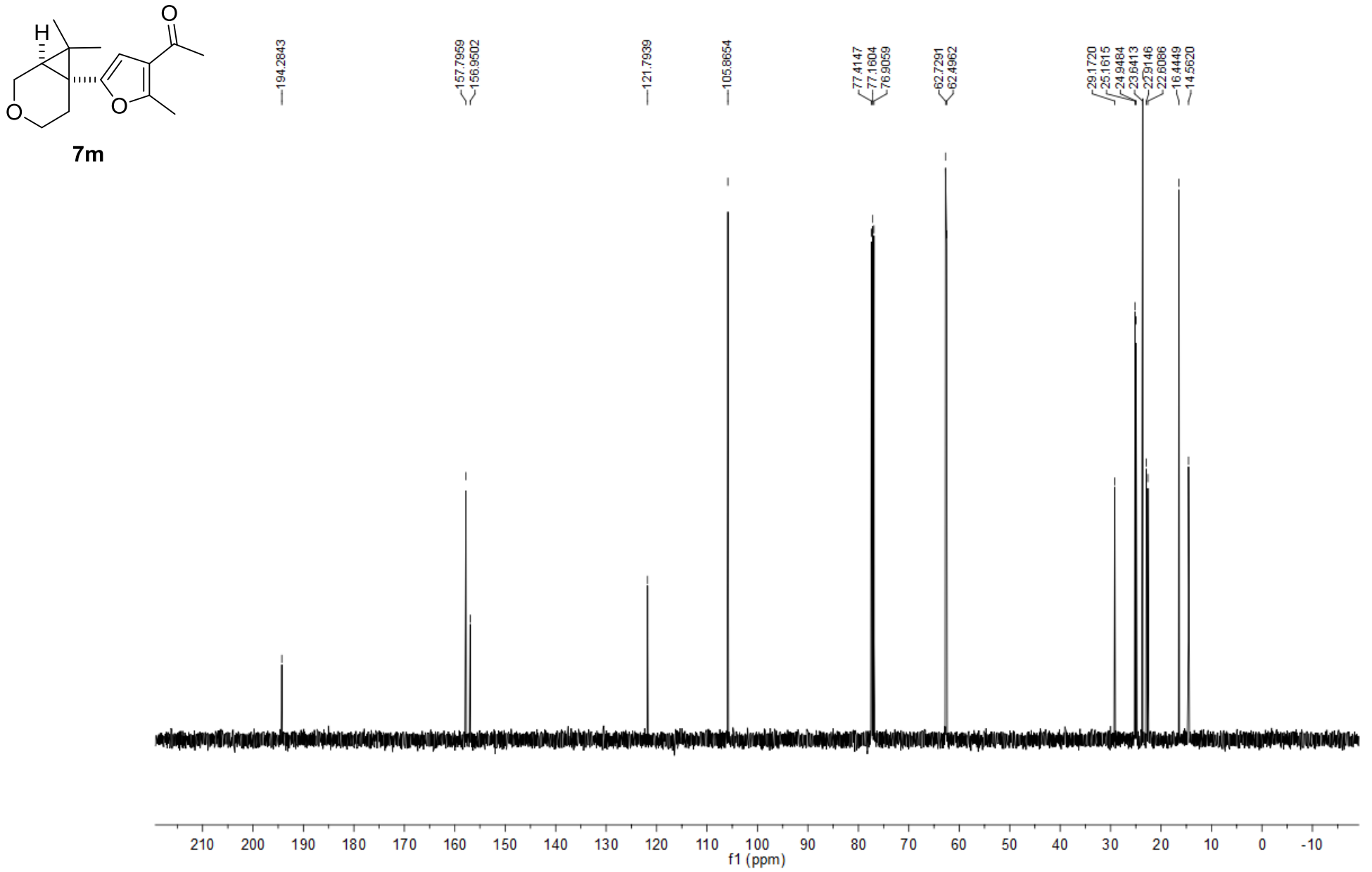

Ph
H
O
O
O
Cl
O
17
7.3468
7.3444
7.3405
7.3309
7.3267
7.3241
7.3113
7.3079
7.3033
7.2603
7.2566
7.2532
7.2435
7.2381
7.2326
7.2205
7.2170
7.2119
7.2031
7.1999
7.1976
7.1919
4.1857
4.1826
4.1783
4.1741
4.1709
4.1162
3.6035
3.6004
2.5360
2.5301
2.5243
2.5175
2.5130
2.5090
2.5024
2.4981
2.4911
2.4845
2.4791
2.3204
2.3130
2.2986
2.2918
2.2808
2.2660
2.2623
2.2463
2.2395
2.1854
2.1593
2.1541
2.1489
2.1455
2.1377
2.1313
2.1265
2.1221
2.1167
2.1100
2.1061
2.1019
2.0957
2.0897
2.0858
2.0809
2.0624
2.0566
2.0547
2.0486
2.0390
2.0369
2.0343
2.0316
2.0249
2.0192
2.0170
2.0055
1.9955
1.9939
1.9850
1.9796
1.9770
1.9748
2.00
3.04
1.00
2.00
1.00
2.00
5.14
3.00
1.01
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

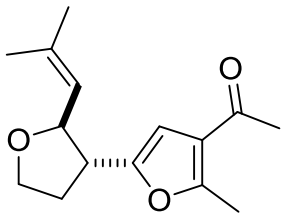

Ph
H
O
O
O
O
Cl
17
194.1645
164.9705
159.6040
142.3924
141.9882
128.9008
127.6170
127.1078
118.0133
117.9378
77.4775
77.3657
77.1601
76.8426
66.7669
53.7121
41.3934
30.0957
28.3412
27.4495
26.2952
15.1841
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
O
O
O

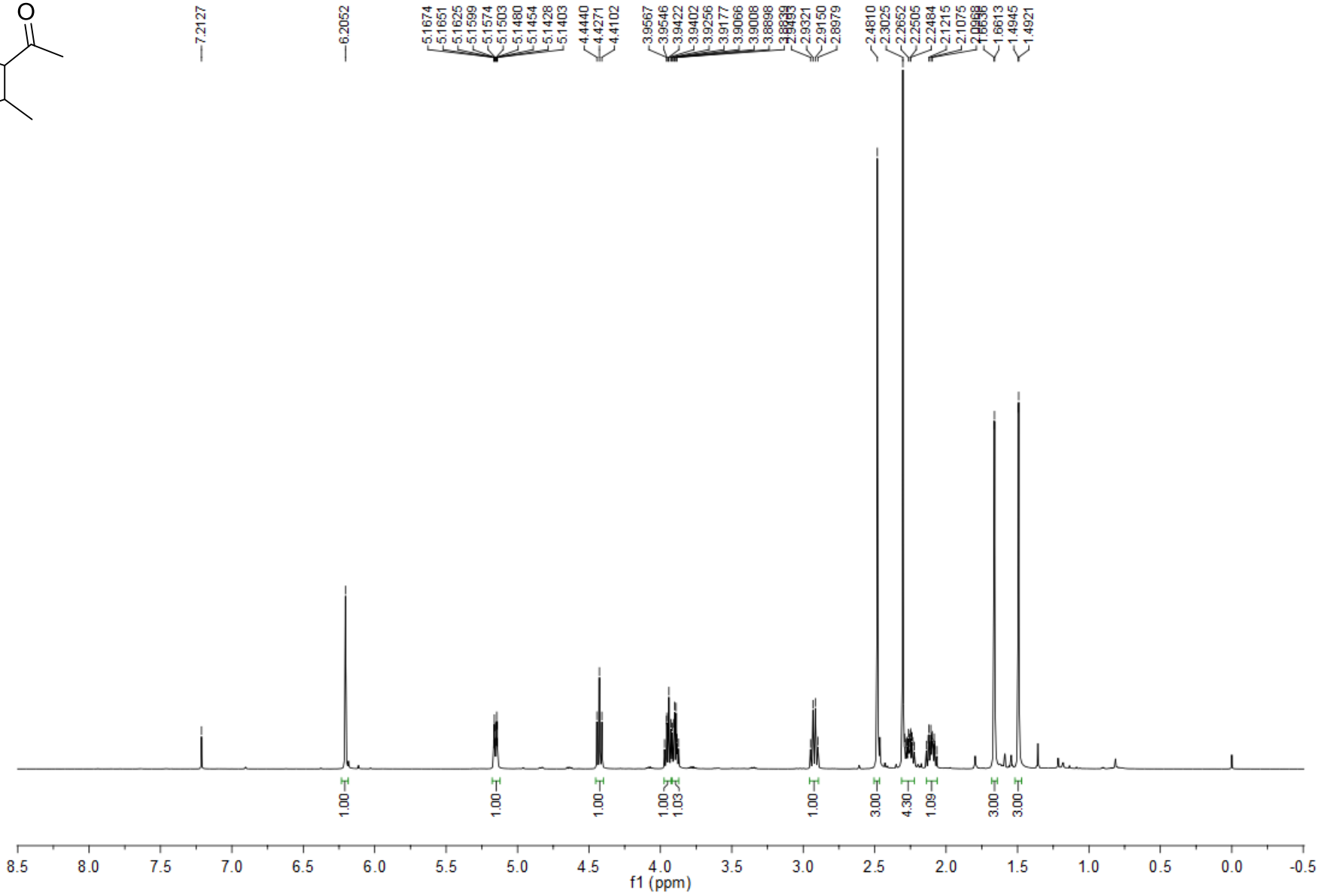
7m

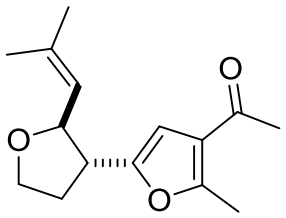

7.2597
6.1587
4.0058
3.9822
3.9350
3.9259
3.9113
3.9022
3.6488
3.6465
3.6375
3.6354
3.0858
3.0705
3.0678
3.0633
3.0606
3.0453
2.3455
2.0508
2.0396
2.0255
1.8465
1.8444
1.8395
1.8373
1.8147
0.9499
0.9411
0.8580
1.00
1.00
1.00
1.00
1.00
3.00
3.00
1.03
1.00
3.00
1.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


H
O
O
O
7m
194.2843
157.7959
156.9502
121.7939
105.8654
77.4147
77.1604
76.9059
62.7291
62.4962
29.1720
25.1615
24.9484
23.6413
22.9146
22.6086
16.4449
14.5620
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

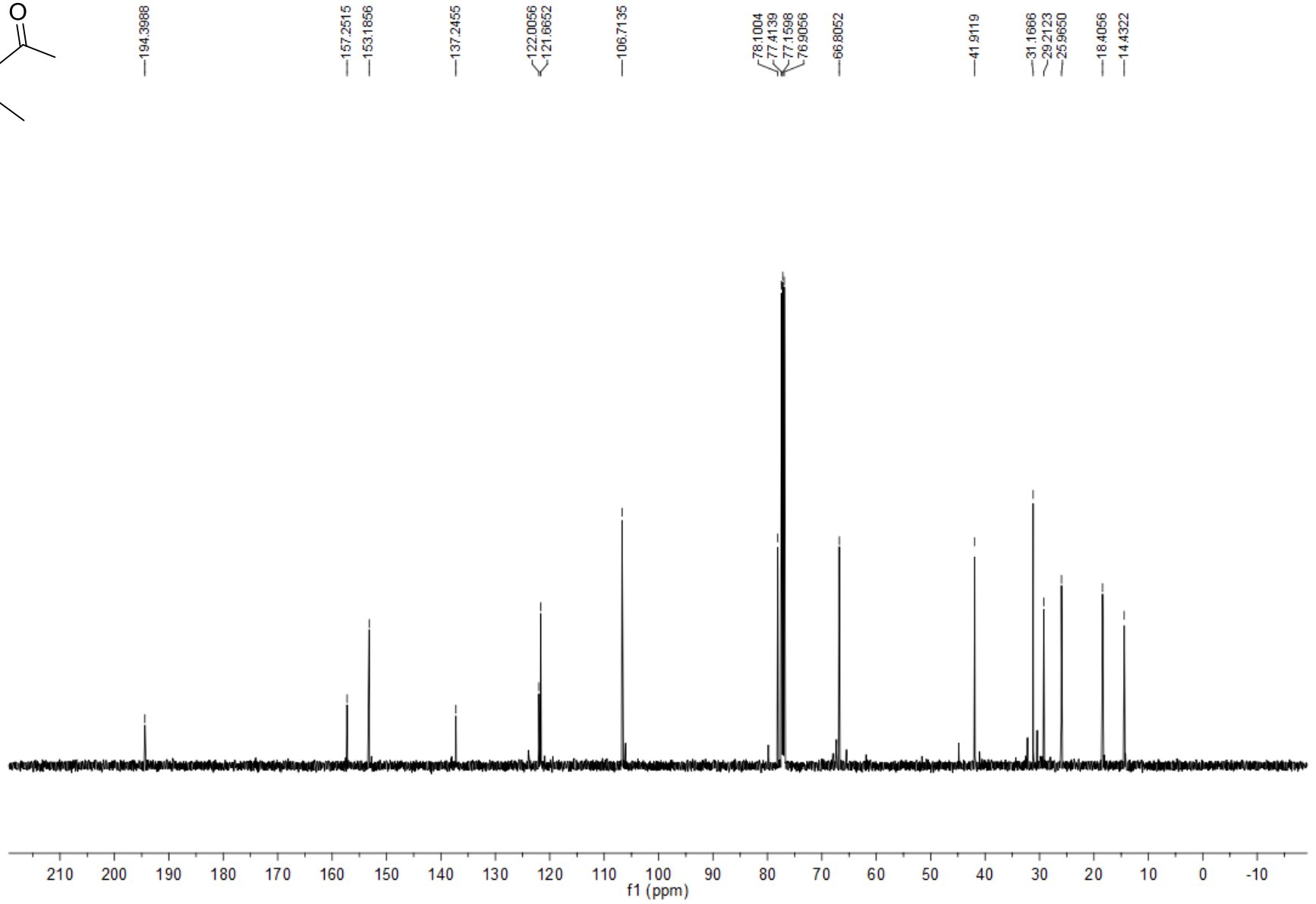


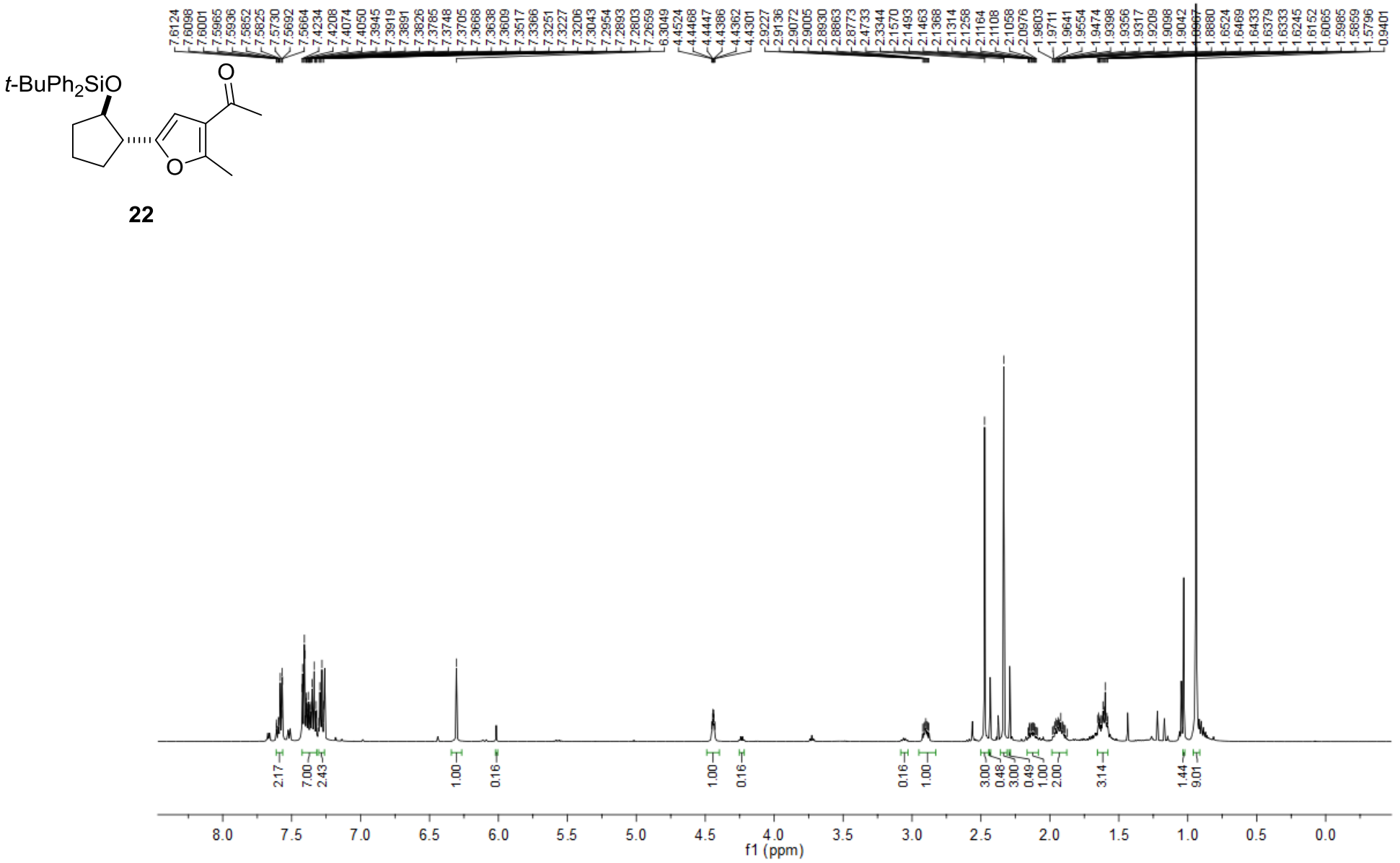
20a

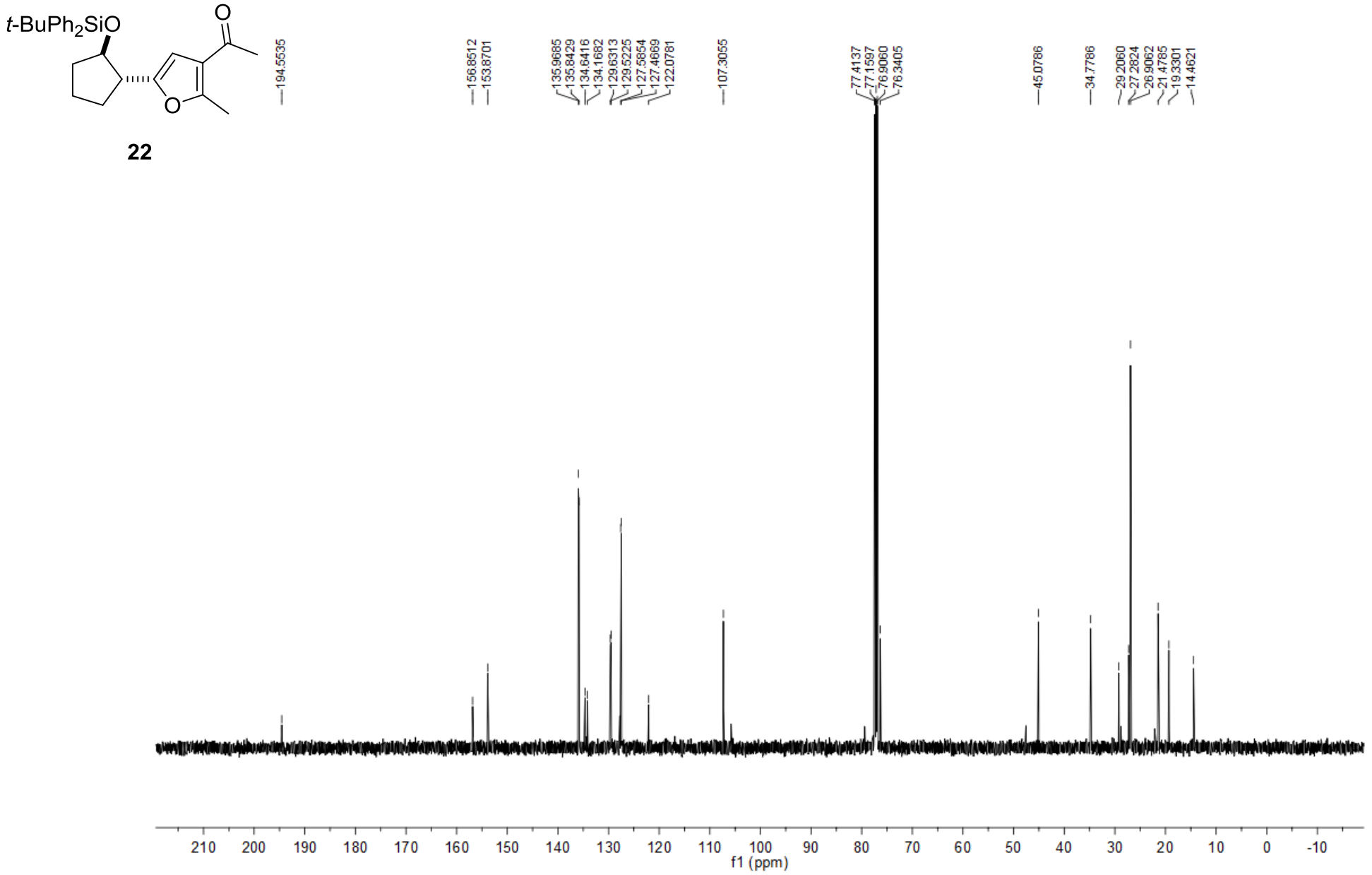

7.2127
6.2052
5.1674
5.1651
5.1625
5.1599
5.1574
5.1503
5.1480
5.1454
5.1428
5.1403
4.4440
4.4271
4.4102
3.9567
3.9546
3.9422
3.9402
3.9256
3.9177
3.9066
3.9008
3.8898
2.9321
2.9150
2.8979
2.4810
2.3025
2.2652
2.2505
2.2484
2.1215
2.1075
1.6613
1.4945
1.4921
1.00
1.00
1.00
1.00
1.03
1.00
3.00
4.30
1.09
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



20a


194.3988
157.2515
153.1856
137.2455
122.0056
121.6652
106.7135
78.1004
77.4139
77.1598
76.9056
66.8052
41.9119
31.1666
29.2123
25.9650
18.4056
14.4322
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


t-BuPh2SiO
O
O
22
f1 (ppm)


t-BuPh2SiO
O
O
22
194.5535
156.8512
153.8701
135.9685
135.8429
134.6416
134.1682
129.6313
129.5225
127.5854
127.4669
122.0781
107.3055
77.4137
77.1597
76.9060
76.3405
45.0786
34.7786
29.2060
27.2824
26.9062
21.4785
19.3301
14.4621
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)