**Supporting Information**

# Enantio- and Diastereoselective Organocatalytic Conjugate Additions of Nitroalkanes to Enone Diesters

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**General Information:**

**Methods:** Infrared (IR) spectra were obtained using a Jasco 460 Plus Fourier transform infrared spectrometer. Proton and carbon magnetic resonance spectra ($^{1}$H NMR, $^{13}$C NMR, $^{19}$F NMR) were recorded on a Bruker model DRX 400 or 600 ($^{1}$H NMR at 400 MHz or 600 MHz, $^{13}$C NMR at 101 MHz or 151 MHz, $^{19}$F NMR at 376 MHz with solvent resonance as the internal standard ($^{1}$H NMR: $CDCl_3$ at 7.26 ppm and $^{13}$C NMR: $CDCl_3$ at 77.0 ppm). $^{1}$H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, app s = apparent singlet, br s = broad singlet, d = doublet, dd = doublet of doublet, t = triplet , m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were obtained with a Thermo Fisher Scientific Finnigan™ LTQ-ICR FT™ (all samples prepared in methanol). Melting points were obtained using a Thomas Hoover UniMelt Capillary Melting Point Apparatus. Analytical thin layer chromatography was carried out using Whatman 0.25 mm silica gel 60 plates, Sorbent Technologies 0.20 mm Silica Gel TLC plates. Visualization was allowed by UV light, phosphomolybdic acid in ethanol, or aqueous ceric ammonium nitrate solution. HPLC analysis was performed on a Perkin Elmer flexar photodiode array (PDA) system equipped with Daicel IA, IC, AD, and OD-H columns. Asymmetric reactions were carried out in a Thermo Sigma UCR-150N aluminum block UC reactor with stirring. Purification of the reaction products was carried out by using Siliaflash-P60 silica gel (40- 63μm) purchased from Silicycle. Yields refer to isolated yields after flash column chromatography; some samples contain residual minor diastereomers. Since all asymmetric trial results are the averages of two trials, the stereoisomer ratios listed in the paper may not exactly match those represented in the NMR and HPLC data below.

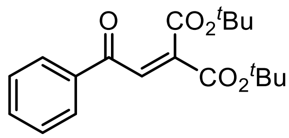
**Materials:** Diethyl ether ($Et_2O$) was passed through a column of neutral alumina under nitrogen prior to use. Wittig reagents were prepared according to a literature procedure.[1] Triaryliminophosphorane catalysts **C1-C3** were prepared according to literature procedures.[2] Commercially available nitroethane and nitropropane were used as received. Raney®-Nickel 2800 (W.R. Grace and Co. Raney®) slurry in $H_2O$ was used as received.

**General procedure for synthesis of enone diesters:**

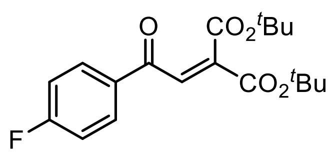
A modification of literature procedures was used.[3-4] A flame-dried 100 mL round-bottomed flask equipped with a reflux condenser was charged with $Rh_2(OAc)_4$ (0.046 mmol, 0.02 equiv), toluene (10 mL), and propylene oxide (22.4 mmol, 10.0 equiv). The mixture was heated to 85 °C in an oil bath for 10 min. A solution of di-*tert*-butyl 2-diazomalonate[5] (2.25 mmol, 1.0 equiv) in toluene (2 mL) was added dropwise. An additional volume of toluene (1 mL) was used as a rinse to complete the addition of the diazomalonate. The reaction was stirred at 85 °C for 1 h then allowed to return to room temperature.

The reaction flask was placed in an ice bath. $MgSO_4$ (500 mg) was added to the reaction, followed by the appropriate Wittig reagent (3.37 mmol, 1.5 equiv). The reaction was allowed to slowly warm to room temperature and was stirred for 16 h. The crude mixture was filtered through a short silica plug with $CH_2Cl_2$ (to remove solids) and concentrated *in vacuo*. The crude materials thusly obtained were purified using flash column chromatography, with the gradient noted below.

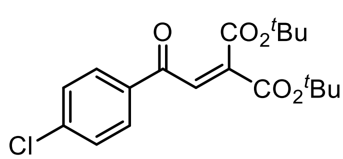
**Characterization data for enone diesters:**



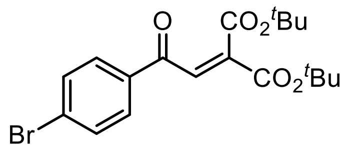

**Di-*tert*-butyl 2-(2-oxo-2-phenylethylidene)malonate (1a):** The title compound was prepared on a larger scale according to the general procedure. Di-*tert*-butyl 2-diazomalonate (8.49 g, 35.0 mmol) was used and all components of the general procedure were scaled proportionally. The crude material was purified using flash column chromatography, with a gradient from 95:5 hexanes/EtOAc to 85:15 hexanes/EtOAc. Yellow solid (8.53 g, 25.7 mmol, 73%), mp 89-90 °C; **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.01-7.99 (m, 2H), 7.68 (s, 1H), 7.65-7.62 (m, 1H), 7.53-7.51 (m, 2H), 1.57 (s, 9H), 1.49 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 189.6, 163.7, 162.2, 138.9, 136.3, 134.0, 133.2, 128.9, 128.9, 83.3, 83.0, 27.9, 27.8. **IR** (thin film) ν 2979, 1724, 1673, 1450, 1369, 1278, 1257, 1156, 1069, 866 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{19}H_{24}NaO_5{}^+$ ([M+Na$^+$]): 355.1516, found 355.1509. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.32.



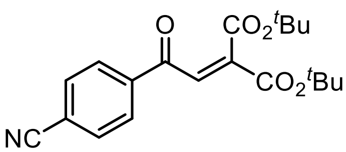

**Di-*tert*-butyl 2-(2-(4-fluorophenyl)-2-oxoethylidene)malonate (1b):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 95:5 hexanes/EtOAc. Yellow oil (544.0 mg, 1.55 mmol, 69%); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.04-8.02 (m, 2H), 7.64 (s, 1H), 7.20-7.18 (m, 2H), 1.56 (s, 9H), 1.50 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 188.0, 166.3 (d, *J* = 256.8 Hz), 163.6, 162.1, 139.1, 132.9, 132.8 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 9.4 Hz), 116.1 (d, *J* = 22.1 Hz), 83.4, 83.1, 27.9, 27.8; **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -103.18. **IR** (thin film) ν 3437, 2980, 1724, 1673, 1598, 1541, 1369, 1279, 1155, 1070 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{19}H_{23}FNaO_5{}^+$ ([M+Na$^+$]): 373.1422, found 373.1413. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.34.



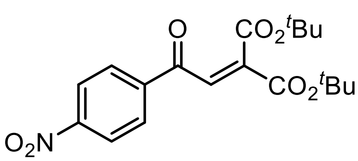

**Di-*tert*-butyl 2-(2-(4-chlorophenyl)-2-oxoethylidene)malonate (1c):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 95:5 hexanes/EtOAc. Yellow solid (528.0 mg, 1.44 mmol, 64%), mp 63-64 °C; **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.63 (s, 1H), 7.49 (d, *J* = 8.6 Hz, 2H), 1.56 (s, 9H), 1.50 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 188.3, 163.6, 162.1, 140.6, 139.4, 134.7, 132.5, 130.2, 129.2, 83.5, 83.2, 27.9, 27.8. **IR** (thin film) ν 2979, 2934, 1725, 1673, 1589, 1369, 1258, 1158, 1092, 847 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{19}H_{23}ClNaO_5^+$ ([M+$Na^+$]): 389.1126, found 389.1119. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.34.



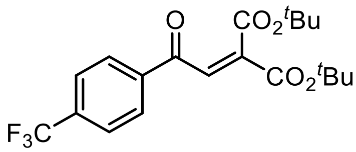

**Di-*tert*-butyl 2-(2-(4-bromophenyl)-2-oxoethylidene)malonate (1d):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 95:5 hexanes/EtOAc. Light yellow solid (626.6 mg, 1.52 mmol, 68%), mp 73-74 °C; **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.62 (s, 1H), 1.56 (s, 9H), 1.50 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 188.5, 163.6, 162.0, 139.5, 135.1, 132.4, 132.2, 130.3, 129.4, 83.5, 83.2, 27.9, 27.8. **IR** (thin film) ν 2979, 2933, 1725, 1672, 1586, 1569, 1369, 1278, 1159, 1071 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{19}H_{23}BrNaO_5^+$ ([M+$Na^+$]): 433.0621, found 433.0611. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.38.



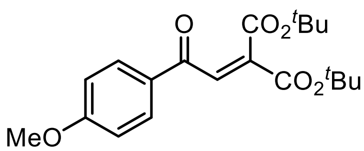

**Di-*tert*-butyl 2-(2-(4-cyanophenyl)-2-oxoethylidene)malonate (1e):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 90:10 hexanes/EtOAc. Yellow solid (407.2 mg, 1.14 mmol, 51%), mp 72-73 °C; **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.62 (s, 1H), 1.56 (s, 9H), 1.51 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 188.3, 163.3, 161.8, 140.4, 139.2, 132.7, 131.6, 129.2, 117.8, 117.1, 83.7, 83.5, 27.9, 27.8. **IR** (thin film) ν 2980, 2935, 2232, 1725, 1677, 1370, 1279, 1158, 1071, 847 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{20}H_{23}NNaO_5^+$ ([M+$Na^+$]): 380.1468, found 380.1463. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.14.



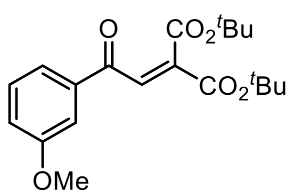

**Di-*tert*-butyl 2-(2-(4-nitrophenyl)-2-oxoethylidene)malonate (1f):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 85:15 hexanes/EtOAc. Yellow solid (598.1 mg, 1.58 mmol, 70%), mp 77-78 °C; **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.9 Hz, 2H), 8.16 (d, *J* = 8.9 Hz, 2H), 7.65 (s, 1H), 1.57 (s, 9H), 1.52 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 188.0, 163.3, 161.8, 150.7, 140.7, 140.5, 131.5, 129.8, 124.1, 83.8, 83.5, 27.9, 27.8. **IR** (thin film) ν 2980, 2360, 1725, 1678, 1530, 1370, 1347, 1278, 1157, 847 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{19}H_{23}NNaO_7^+$ ([M+$Na^+$]): 400.1367, found 400.1358. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.28.



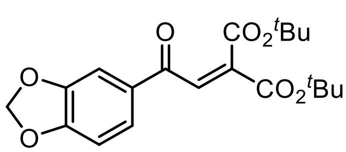
**Di-*tert*-butyl 2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)malonate (1g):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 90:10 hexanes/EtOAc. Yellow oil (550.6 mg, 1.38 mmol, 61%); **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.66 (s, 1H), 1.60 (s, 9H), 1.51 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 188.6, 163.4, 161.9, 140.0, 139.0, 135.1 (q, *J* = 32.8 Hz), 132.0, 129.1, 125.9 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 273.0 Hz), 83.6, 83.3, 27.9, 27.8; **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -63.19. **IR** (thin film) ν 2981, 1726, 1678, 1370, 1326, 1279, 1258, 1161, 1067, 1032 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{20}H_{23}F_3NaO_5^+$ ($[M+Na^+]$): 423.1390, found 423.1383. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.34.



**Di-*tert*-butyl 2-(2-(4-methoxyphenyl)-2-oxoethylidene)malonate (1h):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 90:10 hexanes/EtOAc. White solid (612.8 mg, 1.69 mmol, 75%), mp 93-94 °C; **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.8 Hz, 2H), 7.67 (s, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H), 1.56 (s, 9H), 1.50 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 187.9, 164.3, 163.9, 162.4, 138.3, 133.5, 131.3, 129.5, 114.1, 83.2, 82.8, 55.6, 27.9, 27.8. **IR** (thin film) ν 2979, 1724, 1666, 1599, 1512, 1369, 1281, 1257, 1161, 847 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{20}H_{26}NaO_6^+$ ($[M+Na^+]$): 385.1622, found 385.1613. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.14.

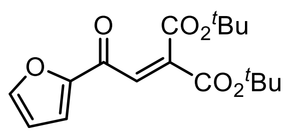


**Di-*tert*-butyl 2-(2-(3-methoxyphenyl)-2-oxoethylidene)malonate (1i):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 90:10 hexanes/EtOAc. Yellow oil (617.3 mg, 1.70 mmol, 76%); **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.58-7.56 (m, 1H), 7.52-7.51 (m, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.19-7.17 (m, 1H), 3.88 (s, 3H), 1.56 (s, 9H), 1.50 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 189.3, 163.7, 162.2, 160.0, 139.0, 137.7, 133.1, 129.8, 121.8, 121.0, 112.4, 83.3, 83.0, 55.5, 27.9, 27.8. **IR** (thin film) ν 2979, 1724, 1672, 1597, 1456, 1369, 1278, 1157, 1032, 848 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{20}H_{26}NaO_6^+$ ($[M+Na^+]$): 385.1622, found 385.1612. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.25.

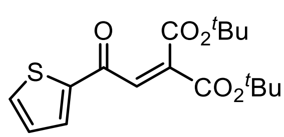


**Di-*tert*-butyl 2-(2-(benzo[*d*][1,3]dioxol-5-yl)-2-oxoethylidene)malonate (1j):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 80:20 hexanes/EtOAc. Yellow solid (506.0

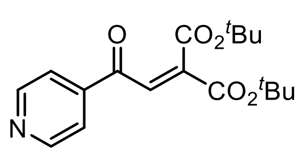
mg, 1.34 mmol, 60%), mp 55-56 °C; **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.59 (d, *J* = 8.2, 1H), 7.48 (s, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.09 (s, 2H), 1.56 (s, 9H), 1.51 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 187.5, 163.8, 162.3, 152.7, 148.6, 138.5, 133.4, 131.3, 126.0, 108.1, 108.1, 102.1, 83.2, 82.9, 27.9, 27.8. **IR** (thin film) ν 2979, 2933, 1723, 1664, 1603, 1505, 1446, 1369, 1259, 1161 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{20}H_{24}NaO_7^+$ ([M+Na$^+$]): 399.1414, found 399.1405. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.21.



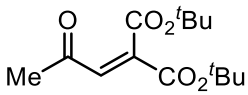
**Di-*tert*-butyl 2-(2-(furan-2-yl)-2-oxoethylidene)malonate (1k):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 80:20 hexanes/EtOAc. White solid (389.0 mg, 1.21 mmol, 54%), mp 67-68 °C; **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.69 (m, 1H), 7.58 (s, 1H), 7.36 (d, *J* = 3.7 Hz, 1H), 6.62 (dd, *J* = 3.6 Hz, 1.6 Hz, 1H), 1.59 (s, 9H), 1.55 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 175.8, 163.9, 162.0, 152.7, 147.9, 140.0, 129.8, 119.6, 113.0, 83.4, 83.1, 27.9, 27.9. **IR** (thin film) ν 2979, 1732, 1669, 1558, 1465, 1370, 1258, 1158, 1071, 846 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{17}H_{22}NaO_6^+$ ([M+Na$^+$]): 345.1309, found 345.1302. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.17.



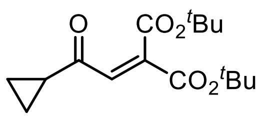
**Di-*tert*-butyl 2-(2-oxo-2-(thiophen-2-yl)ethylidene)malonate (1l):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 90:10 hexanes/EtOAc. Off-white solid (485.8 mg, 1.44 mmol, 64%), mp 84-85 °C; **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 3.9, 1.0 Hz, 1H), 7.76 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.58 (s, 1H), 7.19 (dd, *J* = 4.9, 3.8 Hz, 1H), 1.56 (s, 18H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 180.7, 163.7, 162.1, 144.2, 139.4, 135.8, 133.7, 131.2, 128.6, 83.4, 83.1, 27.9, 27.9. **IR** (thin film) ν 2979, 1726, 1656, 1516, 1415, 1369, 1282, 1257, 1156, 1066 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{17}H_{22}NaO_5S^+$ ([M+Na$^+$]): 361.1080, found 361.1073. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.18.



**Di-*tert*-butyl 2-(2-oxo-2-(pyridin-4-yl)ethylidene)malonate (1m):** The title compound was prepared according to the general procedure, but better results were obtained on larger scale. Di-*tert*-butyl 2-diazomalonate (3.00 g, 12.4 mmol) was used and all components of the general procedure were scaled appropriately. The crude material was purified using flash column chromatography, with a gradient from 95:5 hexanes/EtOAc to 40:60 hexanes/EtOAc. Low-melting red-brown solid (2.23 g, 6.70 mmol, 54%); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.87 (br s, 2H), 7.78 (br s, 2H), 7.61 (s, 1H), 1.57 (s, 9H), 1.52 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 188.8, 163.3, 161.8, 151.2, 142.1, 140.7, 130.9, 121.4, 83.8, 83.5, 27.9, 27.8. **IR** (thin film) ν 2979, 1725, 1682, 1370, 1279, 1223, 1158, 1072, 1032, 847 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{18}H_{23}NNaO_5^+$ ([M+Na$^+$]): 356.1468, found 356.1452. **TLC** (40:60 EtOAc/hexanes): $R_f$ = 0.35.



**Di-*tert*-butyl 2-(2-oxopropylidene)malonate (1n):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 95:5 hexanes/EtOAc. Clear oil (282.4 mg, 1.04 mmol, 46%); **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 6.97 (s, 1H), 2.35 (s, 3H), 1.58 (s, 9H), 1.52 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 196.4, 163.9, 162.0, 138.1, 133.5, 83.4, 83.1, 30.8, 27.9 (2C). **IR** (thin film) ν 2980, 2935, 1730, 1703, 1369, 1274, 1254, 1159, 1075, 848 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{14}H_{22}NaO_5^+$ ([M+Na$^+$]): 293.1359, found 293.1356. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.24.

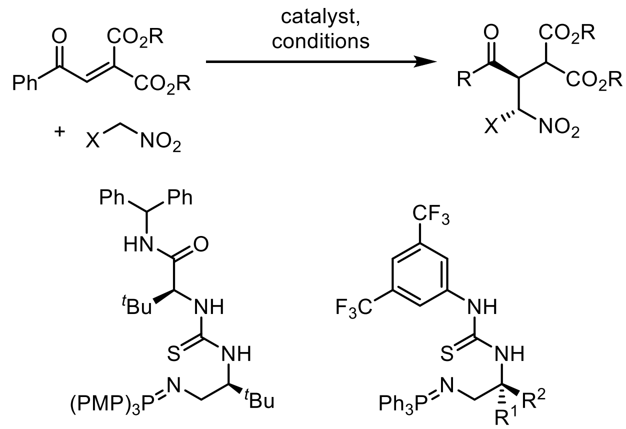


**Di-*tert*-butyl 2-(2-cyclopropyl-2-oxoethylidene)malonate (1o):** The title compound was prepared according to the general procedure. The crude material was purified using flash column chromatography, with a gradient from pure hexanes to 95:5 hexanes/EtOAc. Clear oil (342.4 mg, 1.16 mmol, 51%); **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.11 (s, 1H), 2.14-2.09 (m, 1H), 1.56 (s, 9H), 1.53 (s, 9H), 1.22-1.19 (m, 2H), 1.07-1.04 (m, 2H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 198.7, 164.0, 162.2, 137.4, 133.6, 83.2, 82.9, 27.9, 27.9, 22.2, 12.6. **IR** (thin film) ν 2979, 1729, 1686, 1391, 1369, 1256, 1159, 1087, 1062, 917 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{16}H_{24}NaO_5^+$ ([M+Na$^+$]): 319.1516, found 319.1510. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.29.

**Optimization of asymmetric conjugate addition of nitroalkanes:**

General procedure: A test tube was charged with enone diester (0.1 mmol, 1.0 equiv), nitroalkane (amount listed in table), 1,3,5-trimethoxybenzene (0.1 mmol, 1.0 equiv; internal standard), and solvent (listed in table). The reaction was cooled to -60 °C and catalyst (amount listed in table) was added. The reaction was stirred for the listed amount of time and then quenched with 50 μL of a 0.5 M TFA/toluene solution before flowing it through a short plug of $SiO_2$ with diethyl ether. The filtrate was concentrated *in vacuo* to provide the crude product mixture, which was purified *via* flash column chromatography.

*Observations*: We quickly discovered that we were only able to obtain any reasonable enantioselectivity in the conjugate addition of nitroalkanes using chiral triaryliminophosphorane catalysts (cinchona alkaloid thiourea organocatalysts only gave low levels of enantioselectivity (~10% ee)). Using catalyst **C1** we observed poor reactivity at cryogenic temperatures (and even at room temperature; entries 1-2). We were able to achieve a promising er of 13:87 with **C2** at -60 °C. We were able to improve the yield and enantioselectivity by switching to **C3** (entry 3). A solvent screen (entries 4-8) allowed us to identify diethyl ether as the optimal solvent for the reaction. It was necessary to use 20 mol % catalyst to obtain full conversion. Finding that a large excess of the nitroalkane was required to obtain reasonable conversion, we chose to focus our scope on cheap and commercial nitroalkanes. Switching the diester of the substrate to $^t$Bu (entry 9) and using nitroethane (entry 10) allowed us into achieve our highest yields and stereoselectivities.



**C1** **C2** $R^1$ = H, $R^2$ = $^t$Bu **C3** $R^1$ = Ph, $R^2$ = H

| entry | X (equiv) | R | solvent | catalyst (equiv) | Time (h) | dr | er | Yield[a] |
|---|---|---|---|---|---|---|---|---|
| 1 | H (10.0) | Et | THF | **C1** (0.10) | 21 | n.a. | n.a. | trace |
| 2[b] | H (10.0) | Et | THF | **C1** (0.10) | 19 | n.d. | n.d. | (30) |
| 3 | H (10.0) | Et | THF | **C2** (0.10) | 21 | n.a. | 13:87 | (41) |
| 4 | H (10.0) | Et | THF | **C3** (0.10) | 21 | n.a. | 88:12 | (62) |
| 5 | H (10.0) | Et | EtOAc | **C3** (0.10) | 21 | n.a. | 85.5:14.5 | (45) |
| 6 | H (10.0) | Et | $CH_2Cl_2$ | **C3** (0.10) | 21 | n.a. | 78:22 | (46) |
| 7 | H (10.0) | Et | PhH | **C3** (0.10) | 21 | n.a. | 81:19 | (48) |
| 8 | H (10.0) | Et | $Et_2O$ | **C3** (0.10) | 21 | n.a. | 89:11 | (54) |
| 9 | H (10.0) | $^t$Bu | $Et_2O$ | **C3** (0.10) | 22 | n.a. | 93.5:6.5 | (47) |
| 10[c] | Me (20.0) | $^t$Bu | $Et_2O$ | **C3** (0.20) | 24 | >20:1 | 97:3 | 88 |

[a] Yields in parentheses represent $^1$H NMR yields determined using 1,3,5-trimethoxybenzene as an internal standard. [b] Reaction was run at room temperature [c] The dr, er, and yield values for this entry are an average of two trials. n.a. = not applicable, n.d. = not determined.

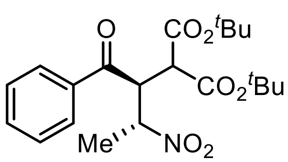
**General procedure for asymmetric conjugate addition of nitroalkanes:**

A flame-dried test tube was charged sequentially with enone diester (0.1 mmol, 1.0 equiv), $Et_2O$ (1.0 mL), and nitroethane (2.1 mmol, 21.0 equiv). The reaction was stirred at -60 °C in a cryogenic cooling apparatus for 15 min, then triaryliminophosphorane catalyst **C1** (0.02 mmol, 0.20 equiv) was added. The reaction was then stirred at -60 °C for 24 h. After this period, the reaction was quenched with a TFA solution in toluene (50 μL, 0.5 M solution) at the same temperature. Additional $Et_2O$ was used to flush the reaction through a short plug of silica and the filtrate was concentrated *in vacuo*. The crude material thusly obtained was purified using flash column chromatography with a gradient from 97.5:2.5 hexanes/EtOAc to 90:10 hexanes/EtOAc unless otherwise noted.

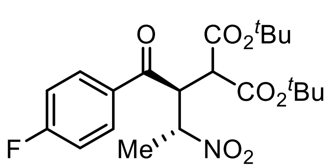
**Gram scale asymmetric conjugate addition reaction:**

A flame-dried 100 mL round-bottomed flask was charged sequentially with enone diester **1a** (1.00 g, 3.01 mmol, 1.0 equiv), $Et_2O$ (30.0 mL), and nitroethane (4.50 mL, 62.6 mmol, 20.8 equiv). The reaction was stirred at -60 °C in a cryogenic cooling apparatus for 15 min, then triaryliminophosphorane catalyst **C1** (401.7 mg, 0.60 mmol, 0.20 equiv) was added. The reaction was then stirred at -60 °C for 24 h. After this period, the reaction was quenched with a TFA solution in toluene (1.5 mL, 0.5M solution) at the same temperature. Additional $Et_2O$ was used to flush the reaction through a short plug of silica and the filtrate was concentrated *in vacuo*. The crude material thusly obtained was purified using flash column chromatography with a gradient from 97.5:2.5 hexanes/EtOAc to 90:10 hexanes/EtOAc, yielding 1.05 g (86%) **2a** as a white solid in >20:1 dr and >99.5:0.5 er.

**Characterization data for conjugate addition products:**

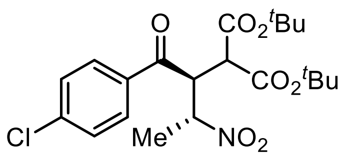



**Di-*tert*-butyl 2-((2*S*,3*R*)-3-nitro-1-oxo-1-phenylbutan-2-yl)malonate (2a):** The title compound was prepared according to the general procedure. No minor diastereomer was observed in the $^1H$ NMR spectrum of the unpurified product. White solid (34.7 mg, 0.085 mmol, 85%), mp 93-94 °C (decomp); **$^1H$ NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.4 Hz, 2H), 7.61 (t, 7.4 Hz, 1H), 7.5 (t, *J* = 7.8 Hz, 2H), 4.92-4.86 (m, 2H), 3.87 (d, *J* = 9.8 Hz, 1H), 1.52 (s, 9H), 1.47 (d, 6.7 Hz, 3H), 1.35 (s, 9H); **$^{13}C$ NMR** (151 MHz, $CDCl_3$) δ 197.3, 166.8, 166.2, 137.1, 133.9, 128.8, 128.6, 83.2, 83.0, 82.4, 55.0, 46.5, 27.8, 27.7, 15.3. **IR** (thin film) ν 2979, 1729, 1682, 1557, 1370, 1257, 1143, 842, 734, 692 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{21}H_{29}NNaO_7^+$ ($[M+Na^+]$): 430.1842, found 430.1831. **HPLC** Derivatized to **4a** for determination of enantiopurity. **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.25. **$[\alpha]_D$** = +80.2 (c = 1.5, $CHCl_3$).

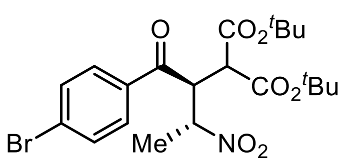



**Di-*tert*-butyl 2-((2*S*,3*R*)-1-(4-fluorophenyl)-3-nitro-1-oxobutan-2-yl)malonate (2b):** The title compound was prepared according to the general procedure. The diastereomeric ratio was determined by $^1H$ NMR spectroscopic analysis of the crude reaction mixture by comparison of the resonances at δ 3.92 (minor diastereomer) and δ 3.86 (major diastereomer). The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 95:5

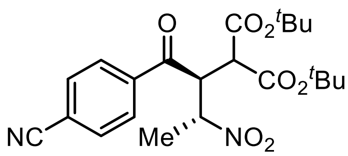
hexanes/EtOAc. White solid (34.9 mg, 0.082 mmol, 82%), mp 89-90 °C (decomp); **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.17 (t, *J* = 8.6 Hz, 2H), 4.88-4.83 (m, 2H), 3.87 (d, *J* = 9.9 Hz, 1H), 1.53 (s, 9H), 1.48 (d, *J* = 6 Hz, 3H), 1.36 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 195.7, 166.7, 166.2, 166.2 (d, *J* = 256.7 Hz), 133.6, 131.3 (d, *J* = 9.1 Hz), 116.0 (d, *J* = 21.14 Hz), 83.3, 83.1, 82.4, 54.9, 46.4, 27.8, 27.8, 15.0; **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -103.8. **IR** (thin film) ν 2980, 1729, 1683, 1599, 1557, 1394, 1370, 1257, 1158, 848 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{21}H_{28}FNNaO_7^+$ ([M+Na$^+$]): 448.1748, found 448.1729. **HPLC** Chiralpak AD column, Hex/$^i$PrOH = 98:2, flow rate = 1.0 mL/min, λ = 210 nm, 9.0 min (minor isomer), 16.4 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.16. **[α]$_D$** = +75.2 (c = 1.5, $CHCl_3$).



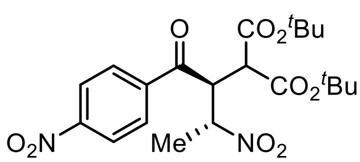

**Di-*tert*-butyl 2-((2*S*,3*R*)-1-(4-chlorophenyl)-3-nitro-1-oxobutan-2-yl)malonate (2c):** The title compound was prepared according to the general procedure. The diastereomeric ratio was determined by $^{1}$H NMR spectroscopic analysis of the crude reaction mixture by comparison of the resonances at δ 3.92 (minor diastereomer) and δ 3.87 (major diastereomer). The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 95:5 hexanes/EtOAc. White solid (39.0 mg, 0.088 mmol, 88%), mp 83-84 °C (decomp); **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 4.89-4.81 (m, 2H), 3.86 (d, *J* = 9.9 Hz, 1H), 1.52 (s, 9H), 1.47 (d, *J* = 6.6 Hz, 3H), 1.36 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 196.1, 166.6, 166.2, 140.4, 135.5, 130.0, 129.1, 83.3, 83.1, 82.4, 55.0, 46.4, 27.8, 27.7, 15.1. **IR** (thin film) ν 2980, 1728, 1683, 1557, 1370, 1258, 1163, 1093, 846, 736 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{21}H_{28}ClNNaO_7^+$ ([M+Na$^+$]): 464.1452, found 464.1435. **HPLC** Chiralpak AD column, Hex/$^i$PrOH = 98:2, flow rate = 1.0 mL/min, λ = 210 nm, 9.1 min (minor isomer), 21.8 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.28. **[α]$_D$** = +68.6 (c = 1.5, $CHCl_3$).



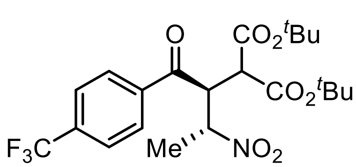

**Di-*tert*-butyl 2-((2*S*,3*R*)-1-(4-bromophenyl)-3-nitro-1-oxobutan-2-yl)malonate (2d):** The title compound was prepared according to the general procedure. The diastereomeric ratio was determined by $^{1}$H NMR spectroscopic analysis of the crude reaction mixture by comparison of the resonances at δ 3.92 (minor diastereomer) and δ 3.86 (major diastereomer). Some residual minor diastereomer was still present in the isolated material. The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 95:5 hexanes/EtOAc. White solid (41.1 mg, 0.085 mmol, 85%), mp 80-81 °C (decomp); **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 4.88-4.81 (m, 2H), 3.86 (d, *J* = 10.1 Hz, 1H), 1.52 (s, 9H), 1.48 (d, *J* = 6.7 Hz, 3H), 1.36 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 196.4, 166.6, 166.2, 135.9, 132.1, 130.1, 129.3, 83.3, 83.1, 82.4, 55.0, 46.4, 27.8, 27.7, 15.1. **IR** (thin film) ν 2979, 1728, 1683, 1557, 1370, 1258, 1144, 1072, 845, 738 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{21}H_{28}BrNNaO_7^+$ ([M+Na$^+$]): 508.0947, found 508.0928. **HPLC** Chiralpak AD column, Hex/$^i$PrOH = 98:2, flow rate = 1.0 mL/min, λ = 210 nm, 12.9 min (minor isomer), 32.9 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.31. **[α]$_D$** = +61.4 (c = 1.5, CHCl$_3$).



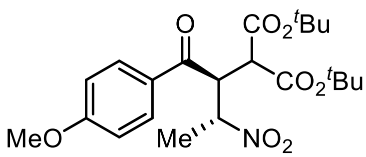

**Di-*tert*-butyl 2-((2*S*,3*R*)-1-(4-cyanophenyl)-3-nitro-1-oxobutan-2-yl)malonate (2e):** The title compound was prepared according to the general procedure. No minor diastereomer was observed in the $^1$H NMR spectrum of the unpurified product. The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 90:10 hexanes/EtOAc. White solid (41.3 mg, 0.95 mmol, 95%), mp 116-117 °C (decomp); **$^1$H NMR** (600 MHz, CDCl$_3$) δ 8.07 (d, $J$ = 8.4 Hz, 2H), 7.80 (d, $J$ = 8.4 Hz, 2H), 4.86-4.81 (m, 2H), 3.89 (d, $J$ = 10.1 Hz, 1H), 1.54 (s, 9H), 1.50 (d, $J$ = 6.7 Hz, 3H), 1.37 (s, 9H); **$^{13}$C NMR** (151 MHz, CDCl$_3$) δ 196.5, 166.4, 166.3, 140.1, 132.6, 128.9, 117.9, 116.8, 83.6, 83.4, 82.3, 55.1, 46.4, 27.8, 27.7, 14.8. **IR** (thin film) ν 2980, 2360, 1727, 1688, 1557, 1370, 1294, 1257, 1143, 848 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{22}H_{28}N_2NaO_7^+$ ([M+Na$^+$]): 455.1794, found 455.1782. **HPLC** Chiralpak IC column, Hex/$^i$PrOH = 99:1, flow rate = 1.0 mL/min, λ = 254 nm, 41.1 min (minor isomer), 43.2 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.11. **[α]$_D$** = +47.5 (c = 1.5, CHCl$_3$).



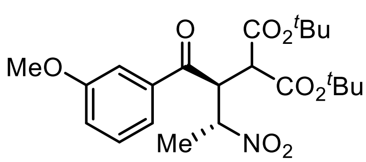

**Di-*tert*-butyl 2-((2*S*,3*R*)-3-nitro-1-(4-nitrophenyl)-1-oxobutan-2-yl)malonate (2f):** The title compound was prepared according to the general procedure. No minor diastereomer was observed in the $^1$H NMR spectrum of the unpurified product. The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 90:10 hexanes/EtOAc. White solid (42.1 mg, 0.093 mmol, 93%), mp 109-110 °C (decomp); **$^1$H NMR** (600 MHz, CDCl$_3$) δ 8.34 (d, $J$ = 8.8 Hz, 2H), 8.14 (d, $J$ = 8.7 Hz, 2H), 4.86 (d, $J$ = 8.8 Hz, 2H), 3.90 (d, $J$ = 10.1 Hz, 1H), 1.54 (s, 9H), 1.52 (d, $J$ = 6.7 Hz, 3H), 1.38 (s, 9H); **$^{13}$C NMR** (151 MHz, CDCl$_3$) δ 196.4, 166.4, 166.3, 150.5, 141.6, 129.6, 123.9, 83.6, 83.5, 82.3, 55.1, 46.7, 27.8, 27.7, 14.8. **IR** (thin film) ν 2980, 2936, 2349, 1727, 1530, 1346, 1258, 1144, 850, 734 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{21}H_{28}N_2NaO_9^+$ ([M+Na$^+$]): 475.1693, found 475.1681. **HPLC** Chiralpak OD-H column, Hex/$^i$PrOH = 99:1, flow rate = 1.0 mL/min, λ = 254 nm, 11.8 min (major isomer), 13.9 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.28. **[α]$_D$** = +47.2 (c = 1.5, CHCl$_3$).



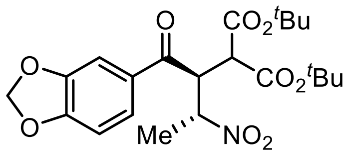

**Di-*tert*-butyl 2-((2*S*,3*R*)-3-nitro-1-oxo-1-(4-(trifluoromethyl)phenyl)butan-2-yl)malonate (2g):** The title compound was prepared according to the general procedure. No minor diastereomer was observed in the $^1$H NMR spectrum of the unpurified product. The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 90:10 hexanes/EtOAc. Yellow solid (46.0 mg, 0.097 mmol, 97%), mp 68-69 °C (decomp); **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.16 Hz, 2H), 4.87 (d, *J* = 7.7 Hz, 2H), 3.89 (d, 9.8 Hz, 1H), 1.53 (s, 9H), 1.50 (d, *J* = 6.1 Hz, 3H), 1.37 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 196.7, 166.5, 166.3, 139.8, 134.8 (q, *J* = 33.2 Hz), 128.9, 125.8 (q, *J* = 3 Hz), 123.5 (q, *J* = 273.3 Hz), 83.4, 83.3, 82.3, 55.0, 46.6, 27.8, 27.7, 15.0; **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -63.2. **IR** (thin film) ν 2981, 2937, 1728, 1689, 1558, 1371, 1325, 1169, 1067, 850 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{22}H_{28}F_3NNaO_7^+$ ([M+Na$^+$]): 498.1716, found 498.1696. **HPLC** Chiralpak AD column, Hex/$^i$PrOH = 98:2, flow rate = 1.0 mL/min, λ = 215 nm, 6.5 min (minor isomer), 20.0 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.29. **[α]$_D$** = +67.1 (c = 1.5, $CHCl_3$).



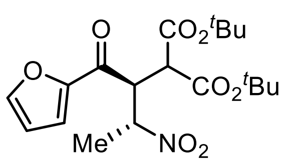
**Di-*tert*-butyl 2-((2*S*,3*R*)-1-(4-methoxyphenyl)-3-nitro-1-oxobutan-2-yl)malonate (2h):** The title compound was prepared according to the general procedure. The diastereomeric ratio was determined by $^{1}$H NMR spectroscopic analysis of the crude reaction mixture by comparison of the resonances at δ 5.05-4.99 (minor diastereomer) and δ 4.90-4.83 (major diastereomer). Some residual minor diastereomer was still present in the isolated material. The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 90:10 hexanes/EtOAc. White solid (37.6 mg, 0.086 mmol, 86%), mp 63-64 °C (decomp); **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.89-4.84 (m, 2H), 3.89 (s, 3H), 3.86 (d, *J* = 9.7 Hz, 1H), 1.52 (s, 9H), 1.47 (d, *J* = 6.5 Hz, 3H), 1.34 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 195.3, 166.9, 166.2, 164.2, 131.0, 130.1, 114.0, 83.1, 82.8, 82.6, 55.5, 54.9, 46.3, 27.8, 27.7, 15.2. **IR** (thin film) ν 2979, 2360, 1729, 1672, 1601, 1556, 1263, 1168, 1030, 846 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{22}H_{31}NNaO_8^+$ ([M+Na$^+$]): 460.1948, found 460.1926. **HPLC** Chiralpak AD column, Hex/$^i$PrOH = 98:2, flow rate = 1.0 mL/min, λ = 210 nm, 20.3 min (minor isomer), 29.0 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.17. **[α]$_D$** = +77.9 (c = 1.5, $CHCl_3$).



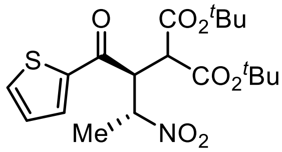
**Di-*tert*-butyl 2-((2*S*,3*R*)-1-(3-methoxyphenyl)-3-nitro-1-oxobutan-2-yl)malonate (2i):** The title compound was prepared according to the general procedure. No minor diastereomer was observed in the $^{1}$H NMR spectrum of the unpurified product. The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 90:10 hexanes/EtOAc. White solid (37.1 mg, 0.085 mmol, 85%), mp 80-81 °C (decomp); **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.49 (s, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.15 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.91-4.84 (m, 2H), 3.88 (s, 3H), 3.85 (d, signal overlap prevents *J* value calculation, 1H), 1.52 (s, 9H), 1.47 (d, *J* = 6.6 Hz, 3H), 1.35 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 196.9, 166.8, 166.2, 159.8, 138.3, 129.8, 121.4, 120.6, 112.5, 83.2, 83.0, 82.4, 55.5, 55.0, 46.7, 27.8, 27.7, 15.4. **IR** (thin film) ν 2979, 2937, 1729, 1683, 1557, 1456, 1370, 1270, 1144, 840 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{22}H_{31}NNaO_8^+$ ([M+Na$^+$]): 460.1948, found 460.1926. **HPLC** Chiralpak OD-H column, Hex/$^i$PrOH = 95:5, flow rate = 1.0 mL/min, λ = 205 nm, 25.3 min (major isomer), 50.5 min (minor isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.17. **[α]$_D$** = +38.3 (c = 1.5, $CHCl_3$).



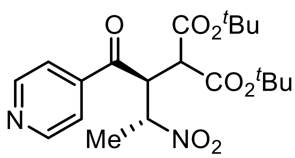
**Di-*tert*-butyl 2-((2*S*,3*R*)-1-(benzo[*d*][1,3]dioxol-5-yl)-3-nitro-1-oxobutan-2-yl)malonate (2j):** The title compound was prepared according to the general procedure. The diastereomeric ratio was determined by $^1$H NMR spectroscopic analysis of the crude reaction mixture by comparison of the resonances at δ 3.93 (minor diastereomer) and δ 3.85 (major diastereomer). The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 90:10 hexanes/EtOAc. White solid (35.8 mg, 0.079 mmol, 79%), mp 91-92 °C (decomp); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.45 (d, *J* = 1.6 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.08 (s, 2H), 4.88-4.83 (m, 1H), 4.79 (dd, *J* = 10.2, 5.3 Hz, 1H), 3.85 (d, *J* = 10.2 Hz), 1.52 (s, 9H), 1.47 (d, *J* = 6.8 Hz, 3H), 1.37 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 194.9, 166.8, 166.2, 152.6, 148.4, 131.9, 125.4, 108.2, 108.1, 102.1, 83.2, 82.9, 82.5, 55.0, 46.4, 27.8, 27.7, 15.2. **IR** (thin film) ν 3443, 2937, 2349, 1728, 1673, 1556, 1444, 1260, 1144, 1038 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{22}H_{29}NNaO_9^+$ ([M+Na$^+$]): 474.1740, found 474.1717. **HPLC** Chiralpak AD column, Hex/$^i$PrOH = 96:4, flow rate = 1.0 mL/min, λ = 205 nm, 13.9 min (minor isomer), 18.5 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.22. **[α]$_D$** = +77.5 (c = 1.5, $CHCl_3$).



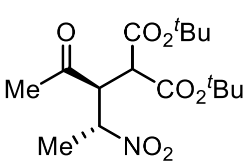
**Di-*tert*-butyl 2-((2*S*,3*R*)-1-(furan-2-yl)-3-nitro-1-oxobutan-2-yl)malonate (2k):** The title compound was prepared according to the general procedure. The diastereomeric ratio was determined by $^1$H NMR spectroscopic analysis of the crude reaction mixture by comparison of the resonances at δ 3.93 (minor diastereomer) and δ 3.81 (major diastereomer). The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 90:10 hexanes/EtOAc. White solid (38.0 mg, 0.096 mmol, 96%), mp 88-89 °C (decomp); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.65 (app s, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 6.59 (dd, *J* = 3.5, 2.7 Hz, 1H), 4.91-4.86 (m, 1H), 4.62 (dd, *J* = 10.4, 5.1 Hz, 1H), 3.82 (d, *J* = 10.4 Hz, 1H), 1.52 (d, signal overlap prevents *J* value calculation, 3H), 1.51 (s, 9H), 1.37 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 184.6, 166.5, 166.0, 152.5, 147.6, 118.9, 112.9, 83.2, 83.0, 82.3, 54.2, 47.6, 27.8, 27.7, 15.0. **IR** (thin film) ν 2980, 2359, 1730, 1674, 1558, 1466, 1296, 1144, 842, 768 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{19}H_{27}NNaO_8^+$ ([M+Na$^+$]): 420.1635, found 420.1623. **HPLC** Chiralpak AD column, Hex/$^i$PrOH = 96:4, flow rate = 1.0 mL/min, λ = 210 nm, 10.4 min (minor isomer), 11.8 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.15. **[α]$_D$** = +65.2 (c = 1.5, $CHCl_3$).



**Di-*tert*-butyl 2-((2*S*,3*R*)-3-nitro-1-oxo-1-(thiophen-2-yl)butan-2-yl)malonate (2l):** The title compound was prepared according to the general procedure. The diastereomeric ratio was determined by $^1$H NMR spectroscopic analysis of the crude reaction mixture by comparison of the resonances at δ 3.93 (minor diastereomer) and δ 3.83 (major diastereomer). The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 90:10 hexanes/EtOAc. White solid (39.4 mg, 0.095 mmol, 95%), mp 100-101 °C (decomp); **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 3.8, 0.8 Hz, 1H), 7.72 (dd, *J* = 4.9, 0.9 Hz, 1H), 7.16 (dd, *J* = 4.8, 4.0 Hz, 1H), 4.94-4.87 (m, 1H), 4.66 (dd, *J* = 10.2, 5.3 Hz, 1H), 3.82 (d, *J* = 10.2 Hz, 1H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.51 (s, 9H), 1.35 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 189.0, 166.6, 165.9, 144.4 135.7, 133.5, 128.6, 83.3, 83.0, 82.5, 54.6, 48.6, 27.8, 27.6, 15.2. **IR** (thin film) ν 2980, 1730, 1660, 1557, 1415, 1370, 1256, 1144, 838, 733 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{19}H_{27}NNaO_7S^+$ ([M+Na$^+$]): 436.1406, found 436.1394. **HPLC** Chiralpak AD column, Hex/$^i$PrOH = 98:2, flow rate = 1.0 mL/min, λ = 215 nm, 14.1 min (minor isomer), 22.6 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.23. **[α]$_D$** = +80.6 (c = 1.5, $CHCl_3$).

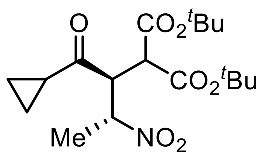


**Di-*tert*-butyl 2-((2*S*,3*R*)-3-nitro-1-oxo-1-(pyridin-4-yl)butan-2-yl)malonate (2m):** The title compound was prepared according to the general procedure. No minor diastereomer was observed in the $^1$H NMR spectrum of the unpurified product. The crude material was purified using flash column chromatography with a gradient from 90:10 hexanes/EtOAc to 60:40 hexanes/EtOAc. White solid (35.3 mg, 0.086 mmol, 86%), mp 95-96 °C (decomp); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.6 Hz, 2H), 7.76 (d, *J* = 4.6 Hz, 2H), 4.88-4.84 (m, 1H), 4.79 (dd, *J* = 10.3, 5.0 Hz, 1H), 3.88 (d, *J* = 10.4 Hz, 1H), 1.53 (s, 9H), 1.51 (d, *J* = 6.9 Hz, 3H), 1.37 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 197.3, 166.4, 166.2, 151.0, 143.0, 121.3, 83.5 (2C), 82.3, 55.1, 46.4, 27.8, 27.7, 15.1. **IR** (thin film) ν 3438, 2980, 2935, 1727, 1696, 1557, 1370, 1257, 1144, 845 cm$^{-1}$. **HRMS** (ESI): Calcd. For $C_{20}H_{29}N_2O_7^+$ ([M+H$^+$]): 409.1974, found 409.1958. **HPLC** Chiralpak IC column, Hex/$^i$PrOH = 95:5, flow rate = 1.0 mL/min, λ = 225 nm, 12.1 min (minor isomer), 18.3 min (major isomer). **TLC** (20:80 EtOAc/hexanes): $R_f$ = 0.19. **[α]$_D$** = +55.5 (c = 1.5, $CHCl_3$).

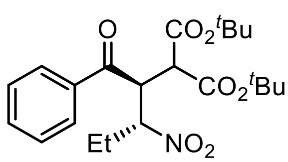


**Di-*tert*-butyl 2-((2*R*,3*S*)-2-nitro-4-oxopentan-3-yl)malonate (2n):** The title compound was prepared according to the general procedure. The diastereomeric ratio was determined by $^1$H NMR spectroscopic analysis of the crude reaction mixture by comparison of the resonances at δ 3.66 (minor diastereomer) and δ 3.60 (major diastereomer). The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 95:5 hexanes/EtOAc. Low-melting white solid (26.3 mg, 0.076

mmol, 76%); **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 4.73-4.69 (m, 1H), 4.02 (dd, *J* = 10.3, 4.7 Hz, 1H), 3.62 (d, *J* = 10.4 Hz, 1H), 2.30 (s, 3H), 1.50 (s, 12H), 1.45 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 205.5, 166.6, 166.4, 83.2, 83.0, 82.0, 54.6, 52.0, 32.5, 27.8 (2C), 14.7. **IR** (thin film) ν 2980, 1724, 1557, 1477, 1458, 1395, 1316, 1144, 1256, 847 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{16}H_{27}NNaO_7^+$ ([M+Na$^+$]): 368.1685, found 368.1671. **HPLC** Chiralpak AD column, Hex/$^i$PrOH = 99:1, flow rate = 1.0 mL/min, λ = 210 nm, 6.3 min (minor isomer), 10.2 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.34. **[α]$_D$** = +30.8 (c = 1.5, $CHCl_3$).



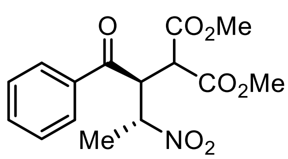

**Di-*tert*-butyl 2-((2*S*,3*R*)-1-cyclopropyl-3-nitro-1-oxobutan-2-yl)malonate (2o):** The title compound was prepared according to the general procedure. The diastereomeric ratio was determined by $^1$H NMR spectroscopic analysis of the crude reaction mixture by comparison of the resonances at δ 3.77 (minor diastereomer) and δ 3.62 (major diastereomer). The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 95:5 hexanes/EtOAc. White solid (33.3 mg, 0.090 mmol, 90%), mp 64-65 °C (decomp); **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 4.76-4.72 (m, 1H), 4.32 (dd, *J* = 10.6, 4.7 Hz, 1H), 3.64 (d, *J* = 10.7 Hz, 1H), 2.02-1.98 (m, 1H), 1.50 (s, 9H), 1.48 (d, *J* = 6.9 Hz, 3H), 1.44 (s, 9H), 1.17-1.12 (m, 1H), 1.05-1.01 (m, 2H), 0.98-0.95 (m, 1H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 207.2 166.7, 166.3, 83.1, 82.7, 81.7, 54.2, 53.3, 27.8 (2C), 22.7, 14.6, 13.3, 12.9. **IR** (thin film) ν 2980, 2359, 1730, 1556, 1393, 1370, 1294, 1256, 1146, 843 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{18}H_{29}NNaO_7^+$ ([M+Na$^+$]): 394.1842, found 394.1826. **HPLC** Chiralpak AD column, Hex/$^i$PrOH = 99:1, flow rate = 1.0 mL/min, λ = 210 nm, 7.9 min (minor isomer), 30.1 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.36. **[α]$_D$** = +36.5 (c = 1.5, $CHCl_3$).




**Di-*tert*-butyl 2-((2*S*,3*R*)-3-nitro-1-oxo-1-phenylpentan-2-yl)malonate (2p):** The title compound was prepared according to the general procedure. No minor diastereomer was observed in the $^1$H NMR spectrum of the unpurified product. The crude material was purified using flash column chromatography, with a gradient from 97.5:2.5 hexanes/EtOAc to 90:10 hexanes/EtOAc. White solid (41.7 mg, 0.099 mmol, 99%), mp 99-100 °C (decomp); **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 4.79 (dd, *J* = 9.4, 6.0 Hz, 1H), 4.73-4.68 (m, 1H), 3.87 (d, *J* = 9.4 Hz, 1H), 1.94-1.82 (m, 1H), 1.78-1.68 (m, 1H), 1.51 (s, 9H), 1.35 (s, 9H), 0.88 (t, *J* = 7.2 Hz, 3H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 197.3, 166.7, 166.2, 137.2, 133.8, 128.8, 128.6, 89.9, 83.1, 83.0, 55.2, 46.4, 27.8, 27.7, 23.5, 10.8. **IR** (thin film) ν 2979, 1741, 1683, 1556, 1370, 1258, 1144, 845, 735, 692 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{22}H_{31}NNaO_7^+$ ([M+Na$^+$]): 444.1999, found 444.1981. **HPLC** Chiralpak AD column, Hex/$^i$PrOH = 98:2, flow rate = 1.0 mL/min, λ = 210 nm, 11.1 min (minor isomer), 14.1 min (major isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.27. **[α]$_D$** = +78.3 (c = 1.5, $CHCl_3$).

**Procedure for transesterification of 2a:**

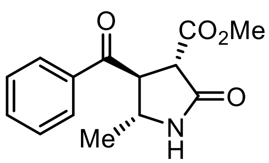
A one dram vial with a stir bar was charged with di-*tert*-butyl ester **2a** (0.058 mmol, 1.0 equiv) and trifluoroacetic acid (0.5 mL). The reaction was stirred for 30 min, then placed under a stream of nitrogen to evaporate volatiles. The residue was dissolved in 3:2 toluene:MeOH (1 mL, 0.06 M) and cooled in an ice bath. A solution of $TMSCHN_2$ (2.0 M in $Et_2O$) was added dropwise until a yellow color persisted. The reaction was stirred for 30 min at room temperature then quenched dropwise with glacial acetic acid; the acid was added until the yellow color disappeared. After stirring for 30 min, ethyl acetate was used to dilute the crude reaction and the organic layer was washed with an aqueous saturated sodium bicarbonate solution. The aqueous layer was extracted twice with ethyl acetate and the combined organic layers were dried with sodium sulfate, filtered, and concentrated *in vacuo*. The crude material thusly obtained was purified using flash column chromatography with a gradient from 97.5:2.5 hexanes/EtOAc to 90:10 hexanes/EtOAc.




**Dimethyl 2-((2*S*,3*R*)-3-nitro-1-oxo-1-phenylbutan-2-yl)malonate (4a):** The diastereomeric ratio of the isolated material was determined by $^1$H NMR spectroscopic analysis by comparison of the resonances at δ 4.22 (minor diastereomer) and δ 4.08 (major diastereomer). Clear oil (16.4 mg, 0.051 mmol, 87%); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.65-7.63 (m, 1H), 7.54-7.51 (m, 2H), 4.98 (dd, *J* = 9.2, 6.5 Hz, 1H), 4.96-4.91 (m, 1H), 4.08 (d, *J* = 9.2 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 1.47 (d, *J* = 6.8 Hz, 3H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 197.3, 167.8, 167.7, 136.8, 134.1, 128.9, 128.7, 82.3, 53.3, 53.2, 52.6, 46.7, 16.5. **IR** (thin film) ν 2956, 1738, 1682, 1596, 1579, 1437, 1281, 1198, 968, 698 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{15}H_{17}NNaO_7^+$ ([M+Na$^+$]): 346.0897, found 346.0893. **HPLC** Chiralpak IC column, Hex/$^i$PrOH = 97:3, flow rate = 1.0 mL/min, λ = 210 nm, 27.3 min (major isomer), 44.1 min (minor isomer). **TLC** (10:90 EtOAc/hexanes): $R_f$ = 0.07. **[α]$_D$** = +58.8 (c = 0.5, $CHCl_3$).

**Local desymmetrization sequence for transesterification/lactamization of 2a:**

A scintillation vial with a stir bar was charged with di-*tert*-butyl ester **2a** (0.25 mmol, 1.0 equiv) and cooled in an ice bath. Trifluoroacetic acid (1.25 mL) was added slowly and the reaction was stirred for 30 min in the ice bath. The reaction was then placed under a stream of nitrogen to evaporate volatiles. The residue was dissolved in 3:2 toluene:MeOH (2.5 mL, 0.1 M) and cooled in an ice bath. A solution of $TMSCHN_2$ (2.0 M in $Et_2O$) was added dropwise until a yellow color persisted. The reaction was stirred for 30 min at room temperature and then cooled in an ice bath while it was quenched dropwise with glacial acetic acid; the acid was added until the yellow color disappeared. The reaction was allowed to return to room temperature and stir for 30 min. Ethyl acetate was used to dilute the crude reaction and the organic layer was washed with an aqueous saturated sodium bicarbonate solution. The aqueous layer was extracted twice with ethyl acetate and the combined organic layers were dried with sodium sulfate, filtered, and concentrated *in vacuo*. $^{1}$H NMR analysis of this crude material indicated that it was >20:1 dr. The material was concentrated into a scintillation vial, where it was dissolved in EtOH (2.0 mL) and treated with Raney®-Nickel 2800 slurry in $H_2O$ (250 mg). The reaction was placed in a high pressure Parr reactor under $H_2$ (60 psi); the vessel was filled and purged three times before finally refilling and allowing the reaction to stir under $H_2$ (60 psi) for 24 h at room temperature. The crude reaction was filtered through a Celite® plug with EtOH and concentrated *in vacuo*. The diastereomeric ratio could not be determined from the $^{1}$H NMR spectrum of the unpurified product. The crude material was purified using flash column chromatography, with a gradient from 60:40 hexanes/EtOAc to 40:60 hexanes/EtOAc to obtain the lactam product.




**Methyl (3*S*,4*S*,5*R*)-4-benzoyl-5-methyl-2-oxopyrrolidine-3-carboxylate (5a):** The title compound was prepared according to the above procedure. The diastereoselectivity could not be determined from the $^{1}$H NMR spectrum of the unpurified product. Once isolated, the product was found to be 9.1:1 dr, which was determined by comparing the signals in the $^{1}$H NMR spectrum at δ 1.38 (major) and δ 1.34 (minor). Clear oil (29.3 mg, 0.11 mmol, 45%); **$^{1}$H NMR** (600 MHz, $CD_3OD$) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.70-7.67 (m, 1H), 7.58-5.55 (m, 2H), 4.38 (dd, *J* = 7.4, 6.0 Hz, 1H), 3.89 (d, *J* = 7.5 Hz, 1H), 3.88-3.85 (m, 1H), 3.75 (s, 3H), 1.38 (d, *J* = 6.2 Hz, 3H); **$^{13}$C NMR** (151 MHz, $CD_3OD$) δ 197.8, 171.1, 169.8, 135.9, 133.7, 128.7, 128.4, 52.0, 51.9, 51.7, 51.7, 20.3. **IR** (thin film) ν 3231, 2954, 2359, 1705, 1596, 1448, 1381, 1264, 1219, 697 $cm^{-1}$. **HRMS** (ESI): Calcd. For $C_{14}H_{15}NNaO_4^+$ ([M+Na$^+$]): 284.0893, found 284.0895. **HPLC** Chiralpak IA column, Hex/$^i$PrOH = 92:8, flow rate = 1.0 mL/min, λ = 210 nm, 16.8 min (minor isomer), 22.7 min (major isomer). **TLC** (50:50 EtOAc/hexanes): $R_f$ = 0.19. **[α]$_D$** = +3.15 (c = 1.25, $CHCl_3$).

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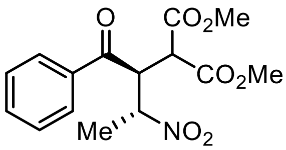
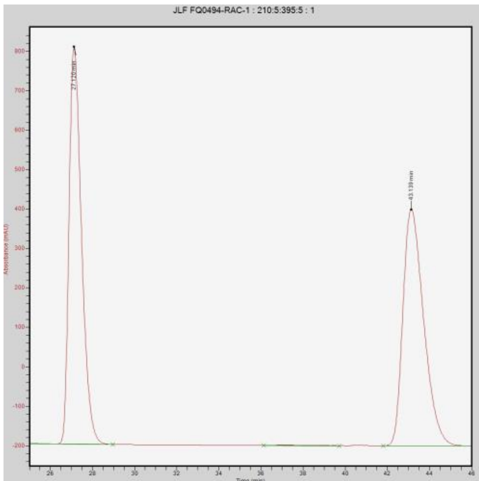
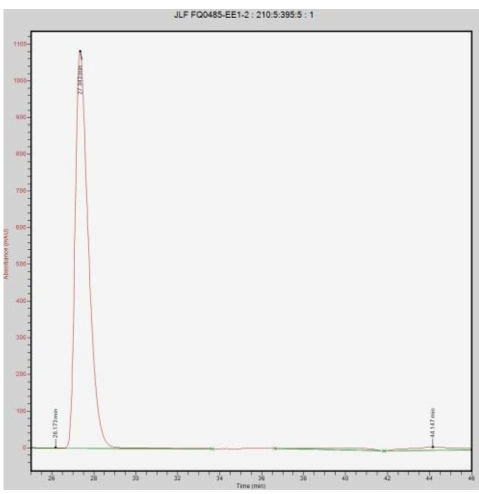
**HPLC traces:**

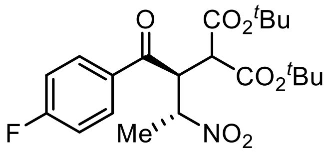



**4a** (used to analyze **2a**)

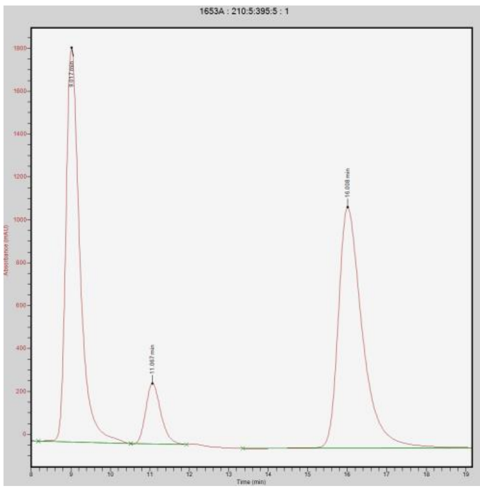


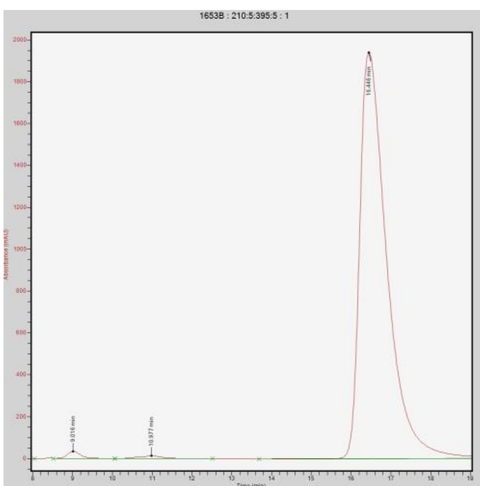


| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 27.1 | 41426094.8 | 50.2 |
| | 43.1 | 41062455.7 | 49.8 |
| Asymmetric | 27.3 | 47660372.2 | 97.2 |
| | 44.1 | 1378617.0 | 2.8 |

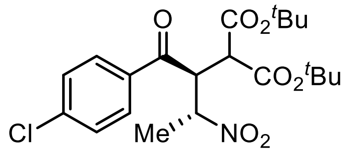



**2b**

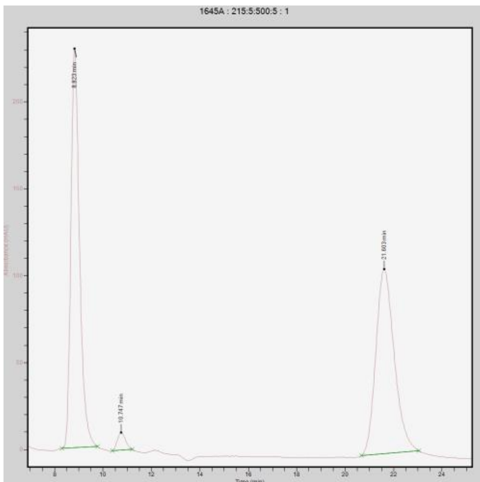


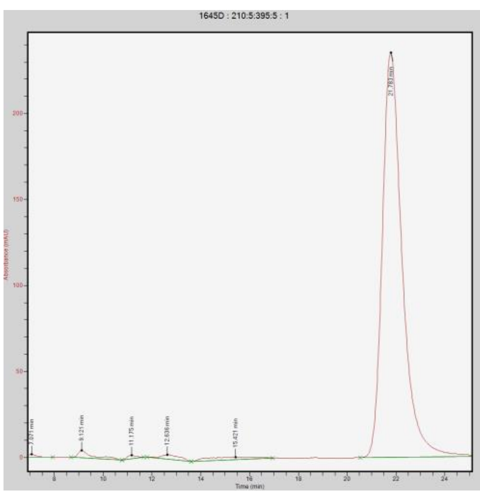




| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 9.0 | 45030634.0 | 48.6 |
| | 16.0 | 47684827.9 | 51.4 |
| Asymmetric | 9.0 | 763945.3 | 0.8 |
| | 16.4 | 91684019.2 | 99.2 |

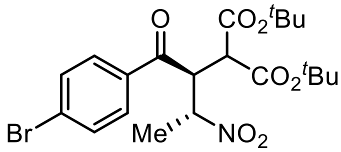



**2c**

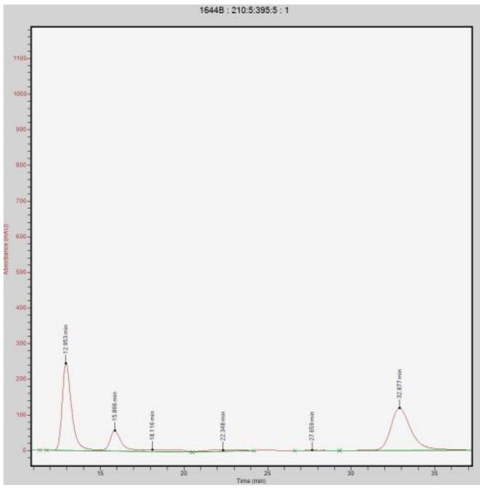


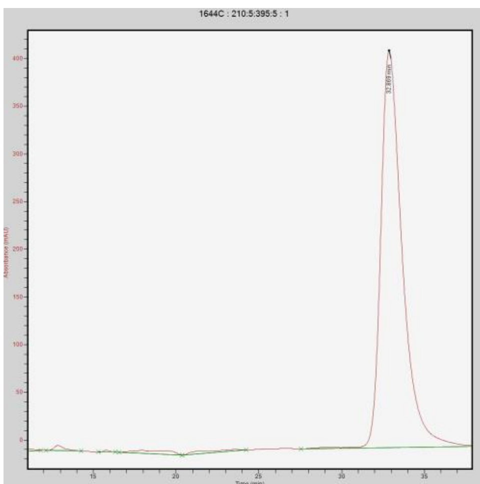




| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 8.8 | 5683251.8 | 50.4 |
| | 21.6 | 5600924.3 | 49.6 |
| Asymmetric | 9.1 | 181195.5 | 1.3 |
| | 21.8 | 13309637.1 | 98.7 |

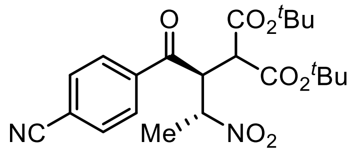


**2d**

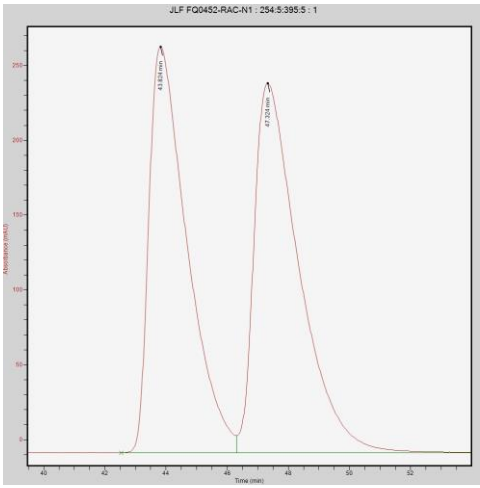


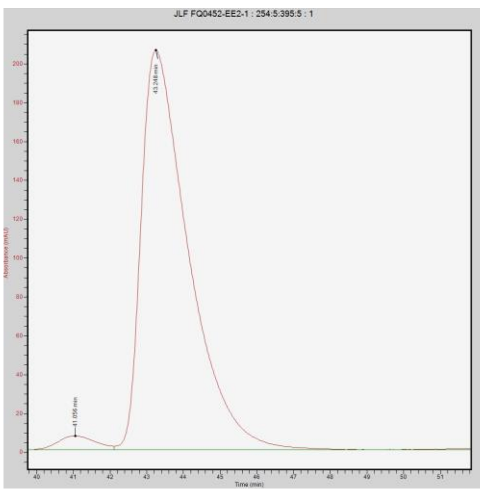


| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 13.0 | 9687260.1 | 49.2 |
| | 32.9 | 10000650.1 | 50.8 |
| Asymmetric | 12.9 | 228774.1 | 0.6 |
| | 32.9 | 37377993.4 | 99.3 |

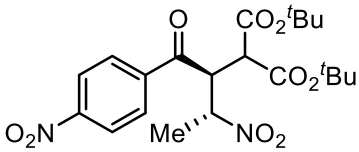



**2e**

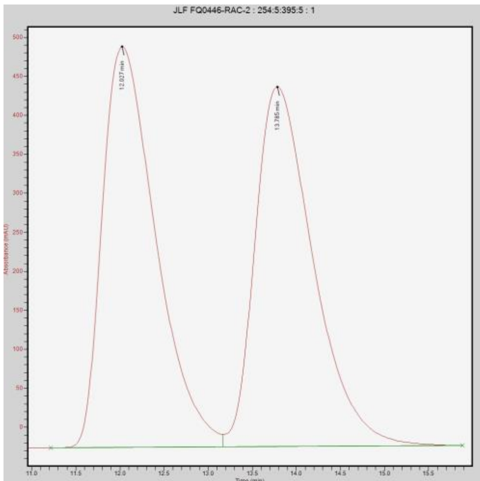


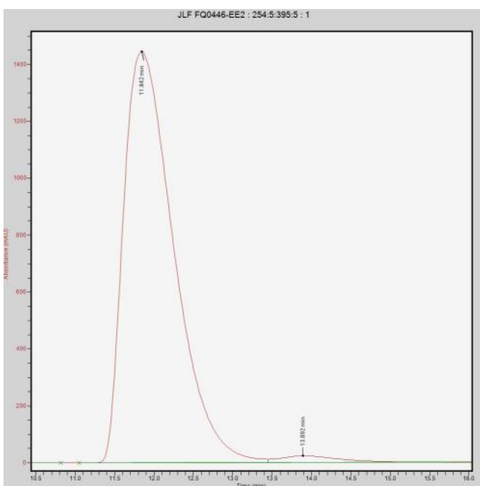


| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 43.8 | 23418578.5 | 48.2 |
| | 47.3 | 25165207.2 | 51.8 |
| Asymmetric | 41.1 | 528693.0 | 2.8 |
| | 43.2 | 18496911.8 | 97.2 |

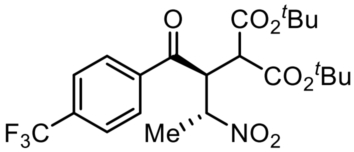



**2f**

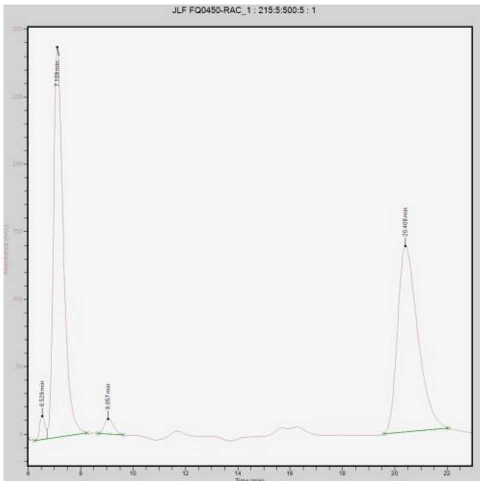


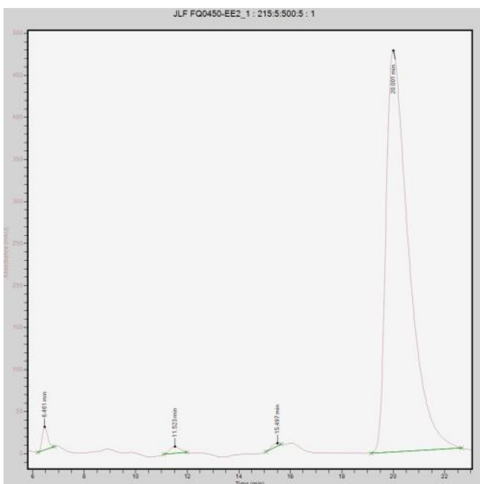




| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 12.0 | 21609139.8 | 50.6 |
| | 13.8 | 21137114.3 | 49.4 |
| Asymmetric | 11.8 | 63975142.0 | 98.1 |
| | 13.9 | 1220289.6 | 1.9 |

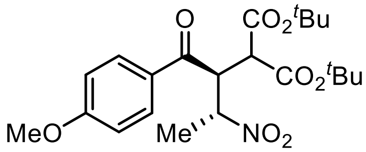


**2g**

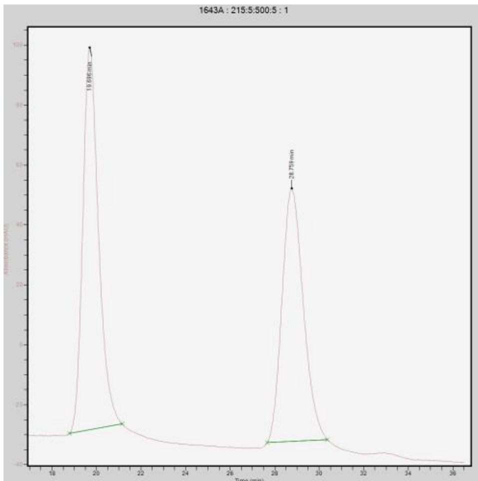


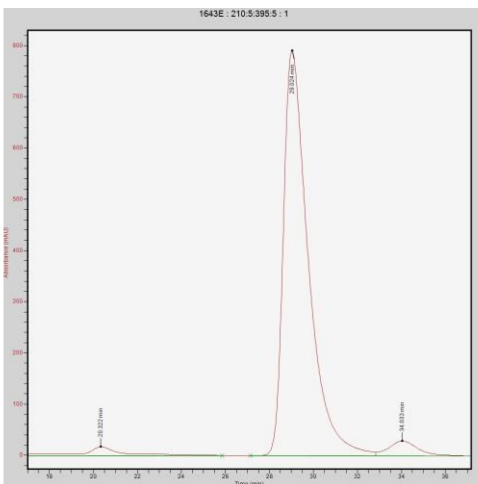




| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 7.1 | 7557428.6 | 50.5 |
| | 20.4 | 7415113.6 | 49.5 |
| Asymmetric | 6.5 | 401910.7 | 1.4 |
| | 20.0 | 29251640.2 | 98.6 |

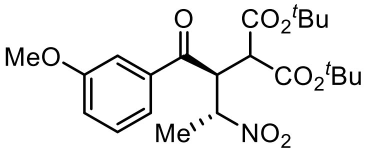



**2h**

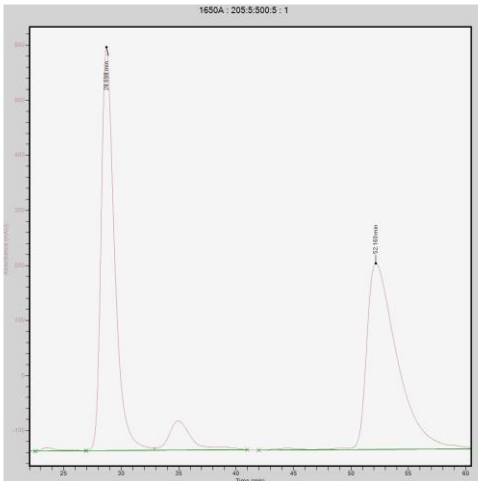


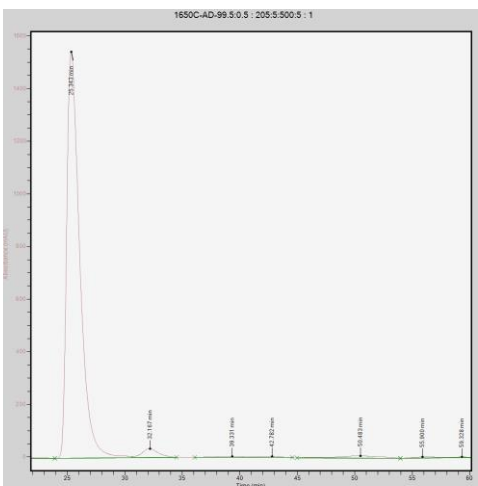


| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 19.7 | 6249220.4 | 52.7 |
| | 28.8 | 5602087.7 | 47.3 |
| Asymmetric | 20.3 | 2916203.6 | 4.5 |
| | 29.0 | 62271509.9 | 95.5 |

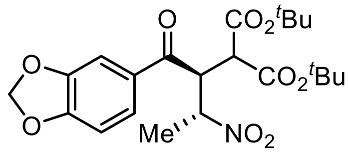



**2i**

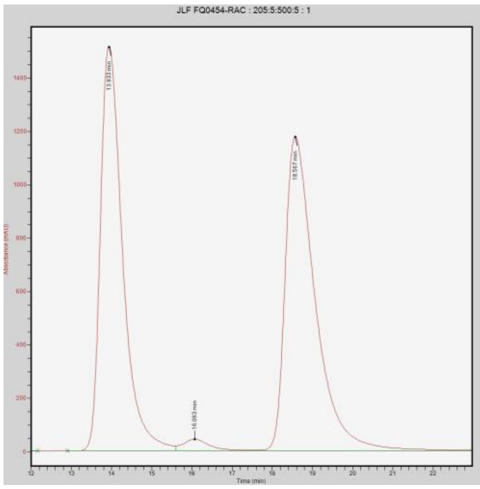


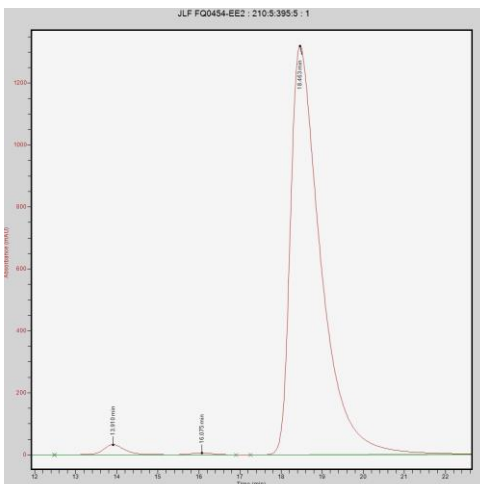




| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 28.7 | 59689929.7 | 49.0 |
| | 52.2 | 61892733.5 | 51.0 |
| Asymmetric | 25.3 | 121702769.4 | 98.5 |
| | 50.5 | 1821839.7 | 1.5 |

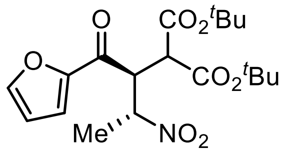



**2j**

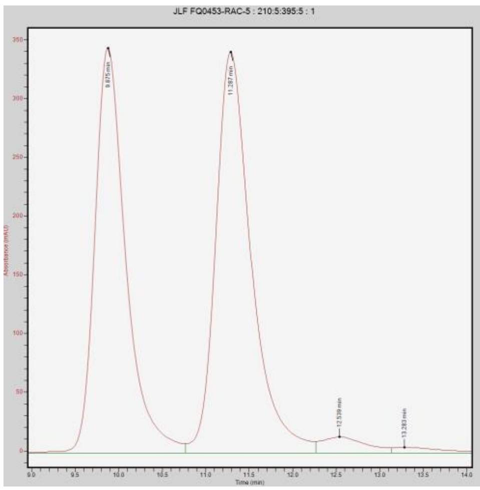


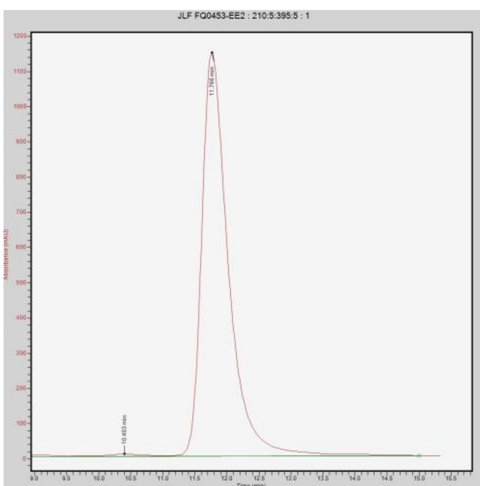




| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 13.9 | 58063205.6 | 48.7 |
| | 18.6 | 61265914.6 | 51.3 |
| Asymmetric | 13.9 | 1234021.9 | 1.8 |
| | 18.5 | 67650046.2 | 98.2 |

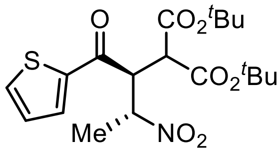



**2k**

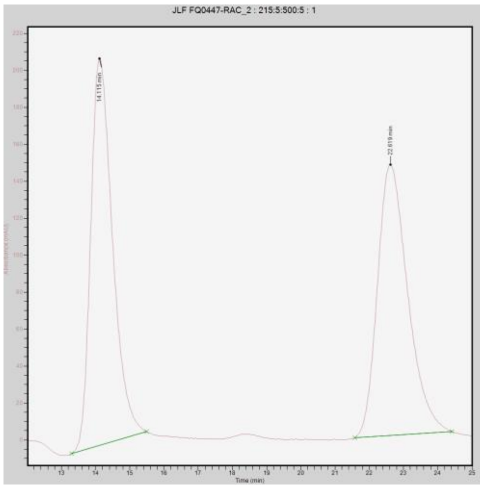


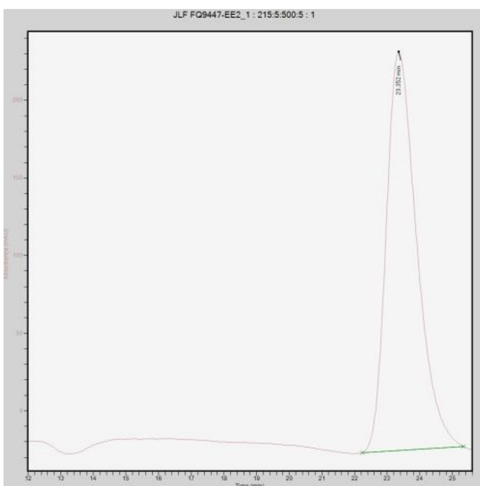




| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 9.9 | 8545601.7 | 46.9 |
| | 11.3 | 9673235.1 | 53.1 |
| Asymmetric | 10.4 | 317256.8 | 0.9 |
| | 11.8 | 33172675.5 | 99.1 |

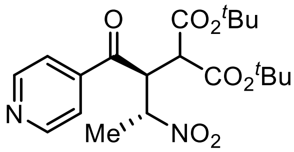


**2l**

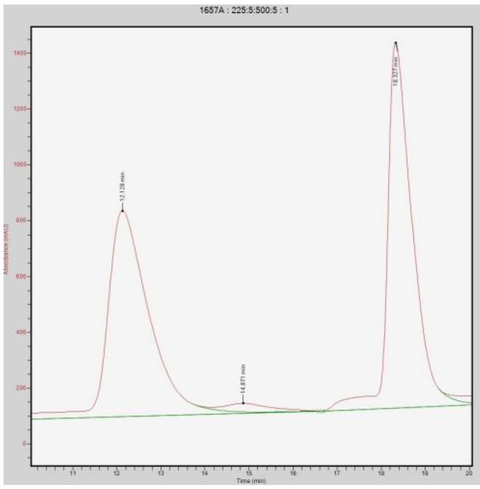


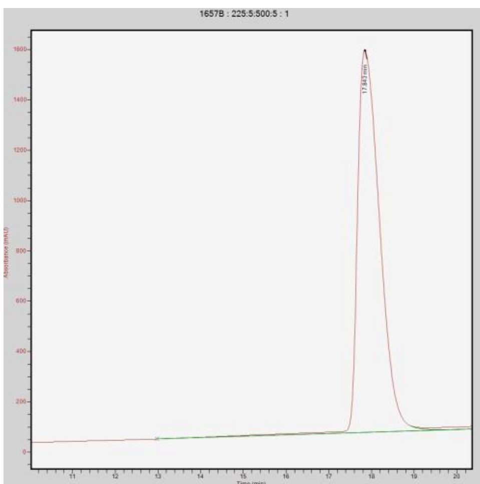


| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 14.1 | 9272413.3 | 50.7 |
| | 22.6 | 9001265.3 | 49.3 |
| Asymmetric | (minor not observed) | N/A | N/A |
| | 23.4 | 16603142.7 | >99 |

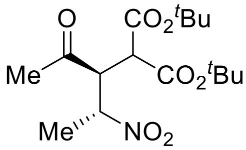


**2m**

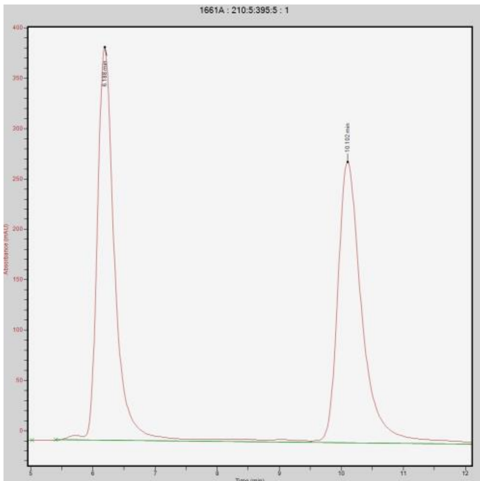


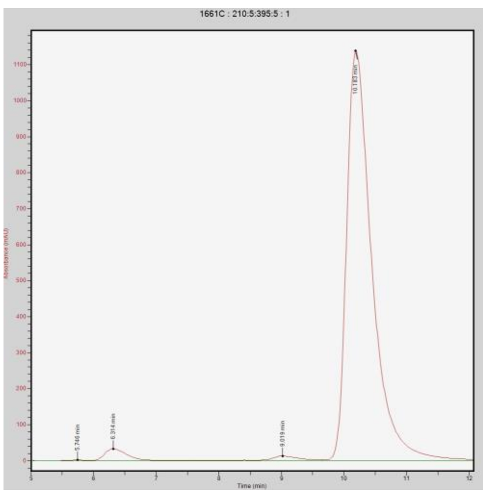




| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 12.1 | 50045253.9 | 49.4 |
| | 18.3 | 51295890.7 | 50.6 |
| Asymmetric | (minor not observed) | N/A | N/A |
| | 17.8 | 54985709.1 | >99 |

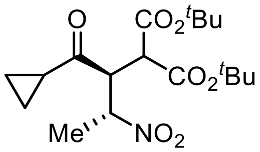


**2n**

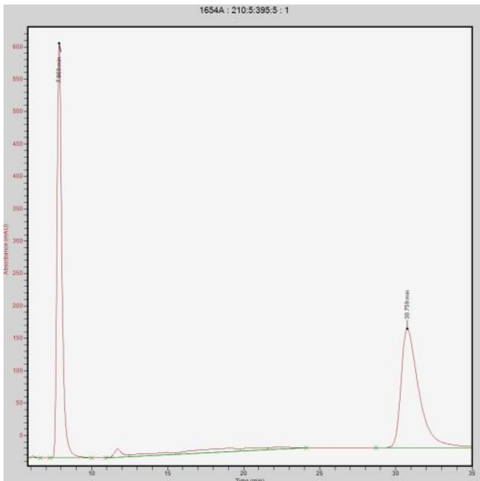


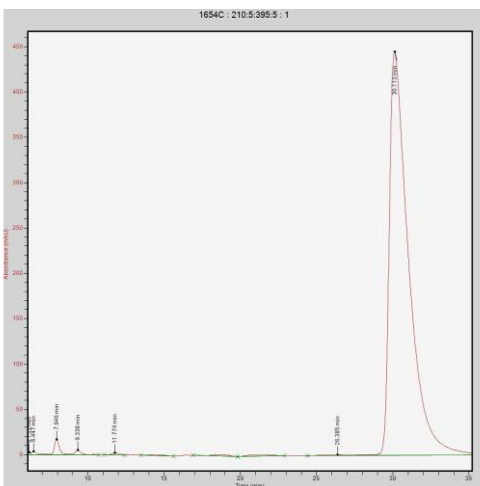




| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 6.2 | 7773174.1 | 50.4 |
| | 10.1 | 7640193.8 | 49.6 |
| Asymmetric | 6.3 | 886800.9 | 2.7 |
| | 10.2 | 32208671.8 | 97.3 |

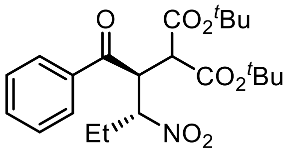


**2o**

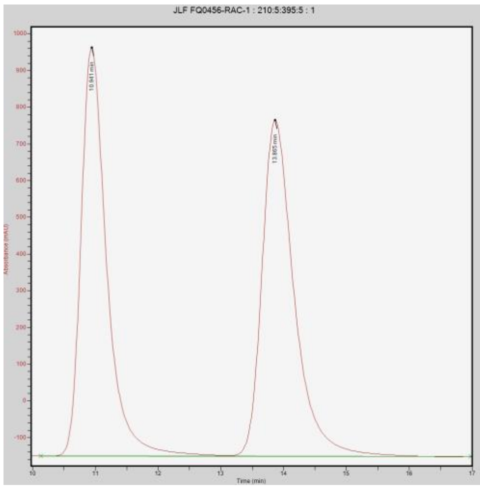


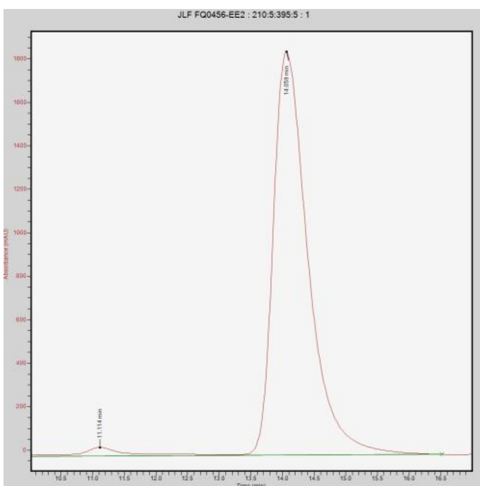


| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 7.9 | 14361728.7 | 48.5 |
| | 30.8 | 15256095.2 | 51.5 |
| Asymmetric | 7.9 | 388824.8 | 1.0 |
| | 30.1 | 39377889.1 | 99.0 |

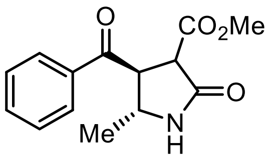



**2p**

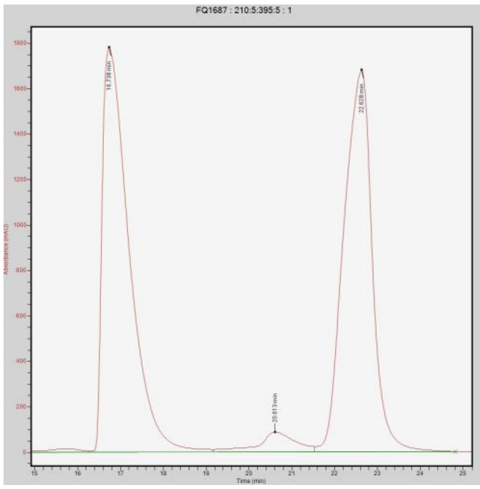


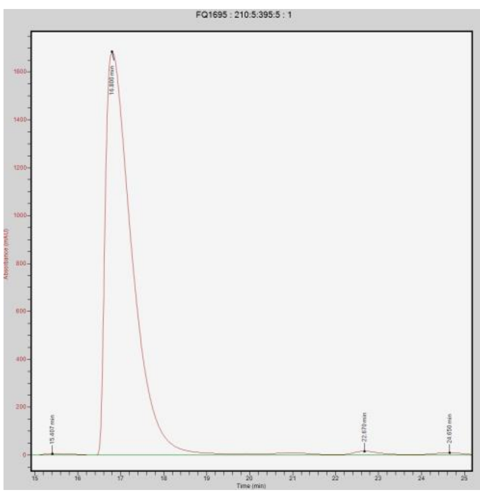




| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 10.9 | 31534207.7 | 49.3 |
| | 13.9 | 32483250.2 | 50.7 |
| Asymmetric | 11.1 | 2221179.1 | 3.0 |
| | 14.1 | 70689759.1 | 97.0 |



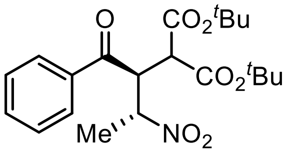
**4a**



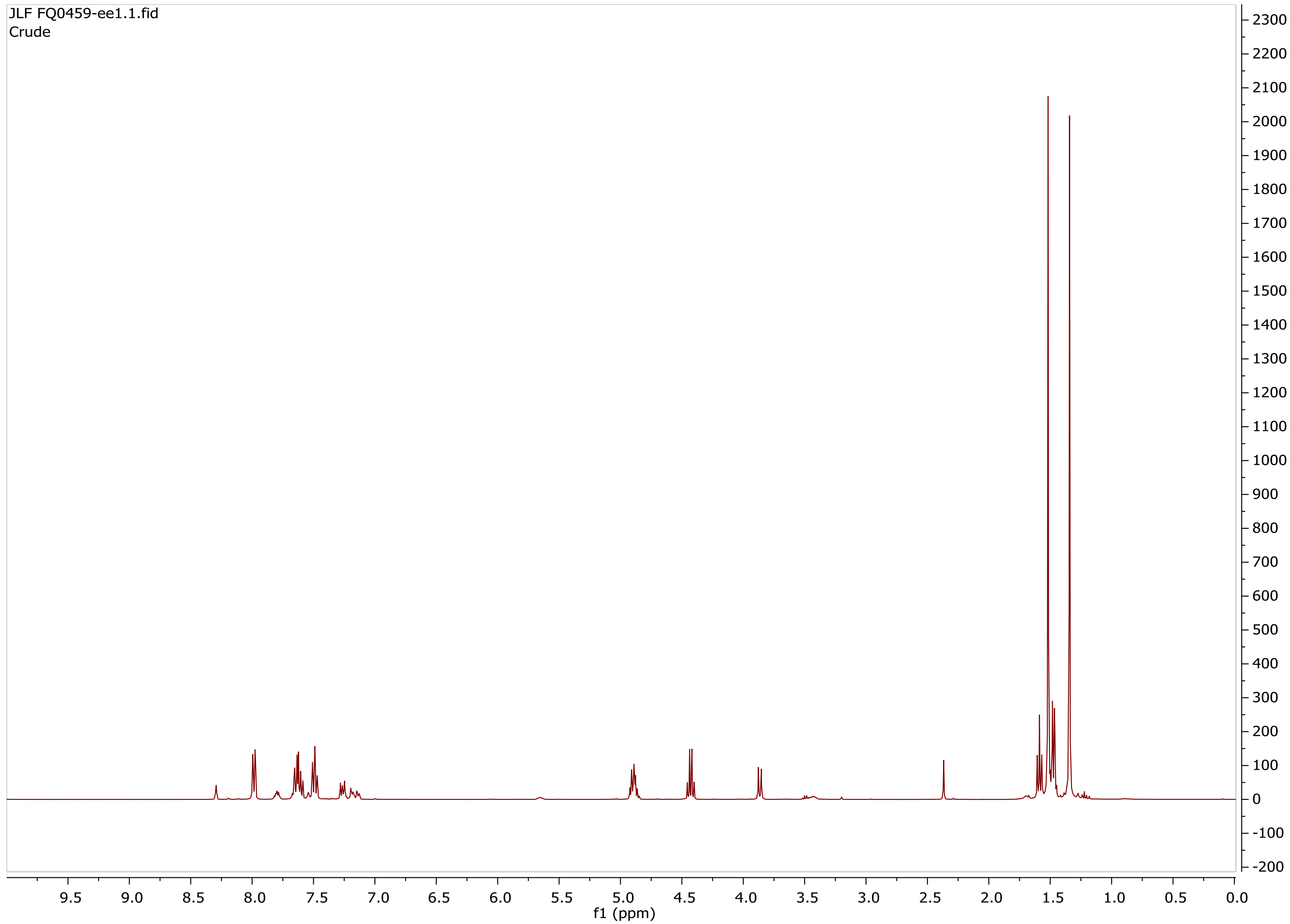


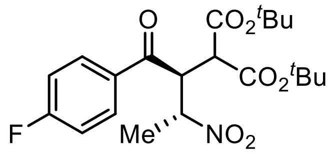
| | Retention Time (min) | Peak Area | % Area |
|---|---|---|---|
| Racemic | 16.7 | 77410170.3 | 50.0 |
| | 22.6 | 77326501.3 | 50.0 |
| Asymmetric | 16.8 | 73153327.6 | 98.9 |
| | 22.7 | 813768.5 | 1.1 |

**Crude $^1$H NMR spectra for the asymmetric reaction:**

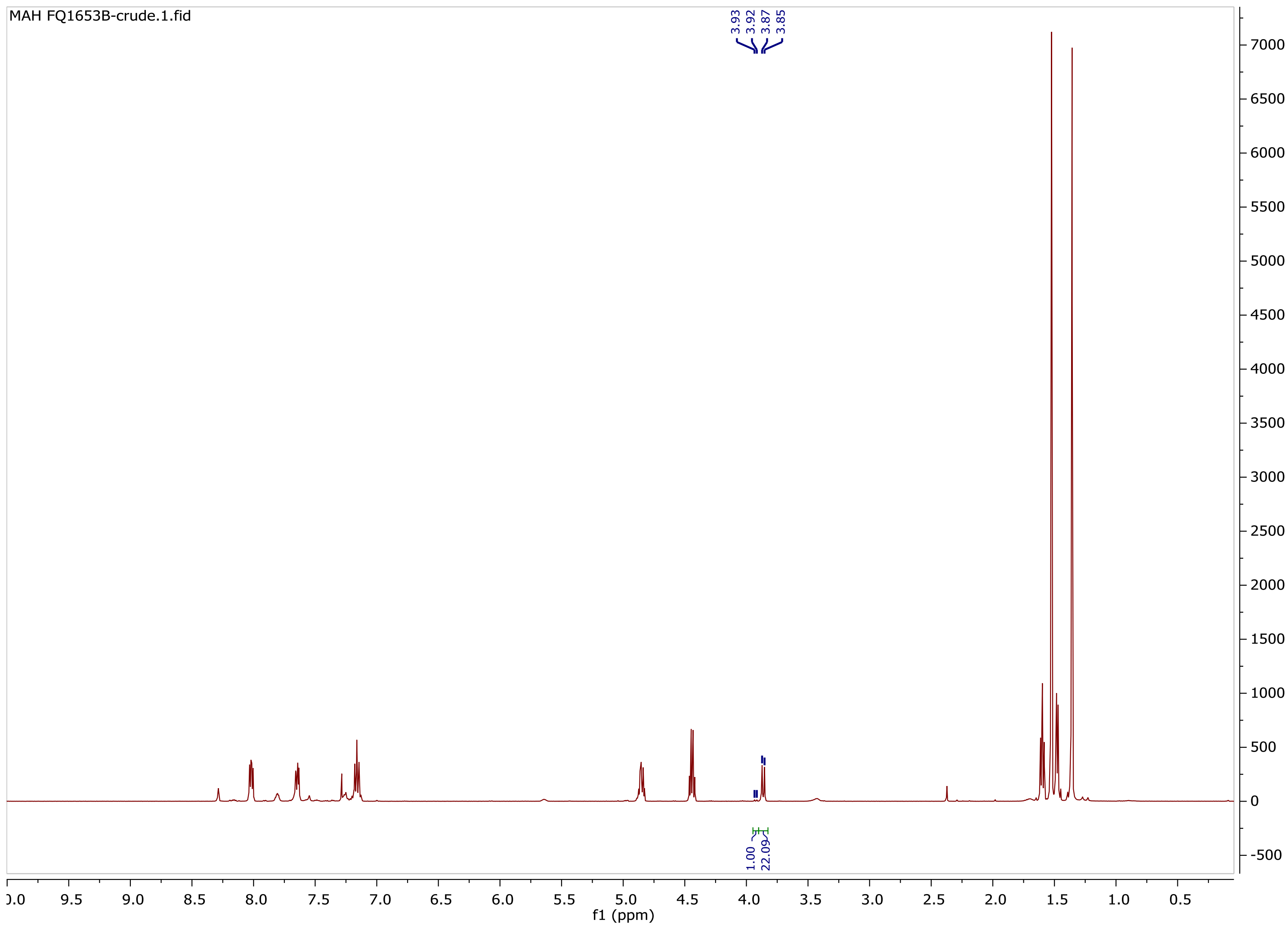


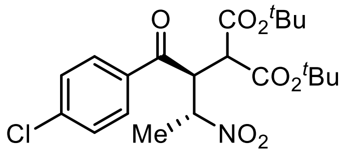
**2a**



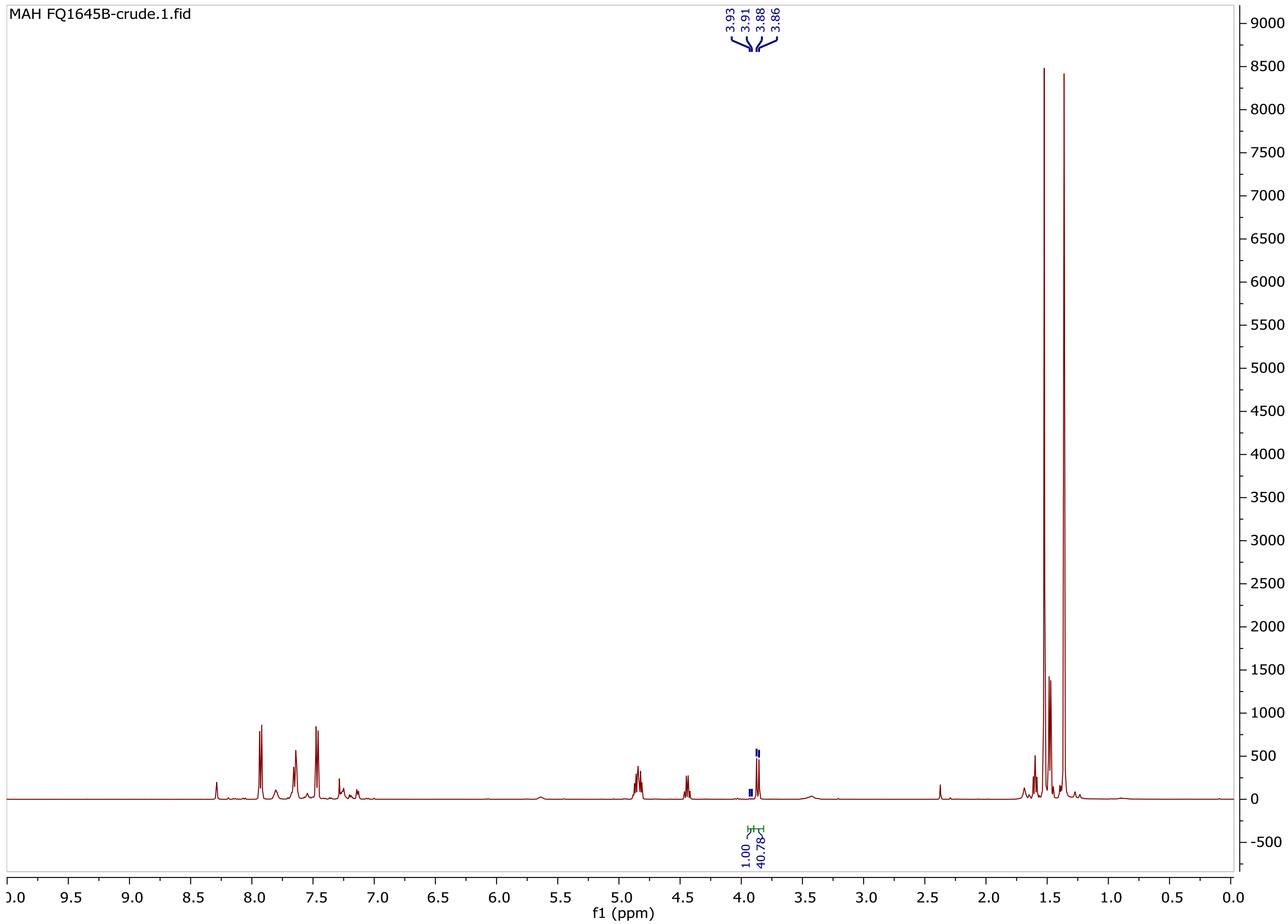


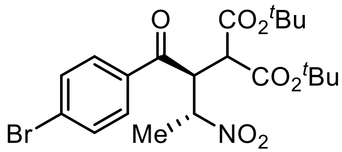
**2b**



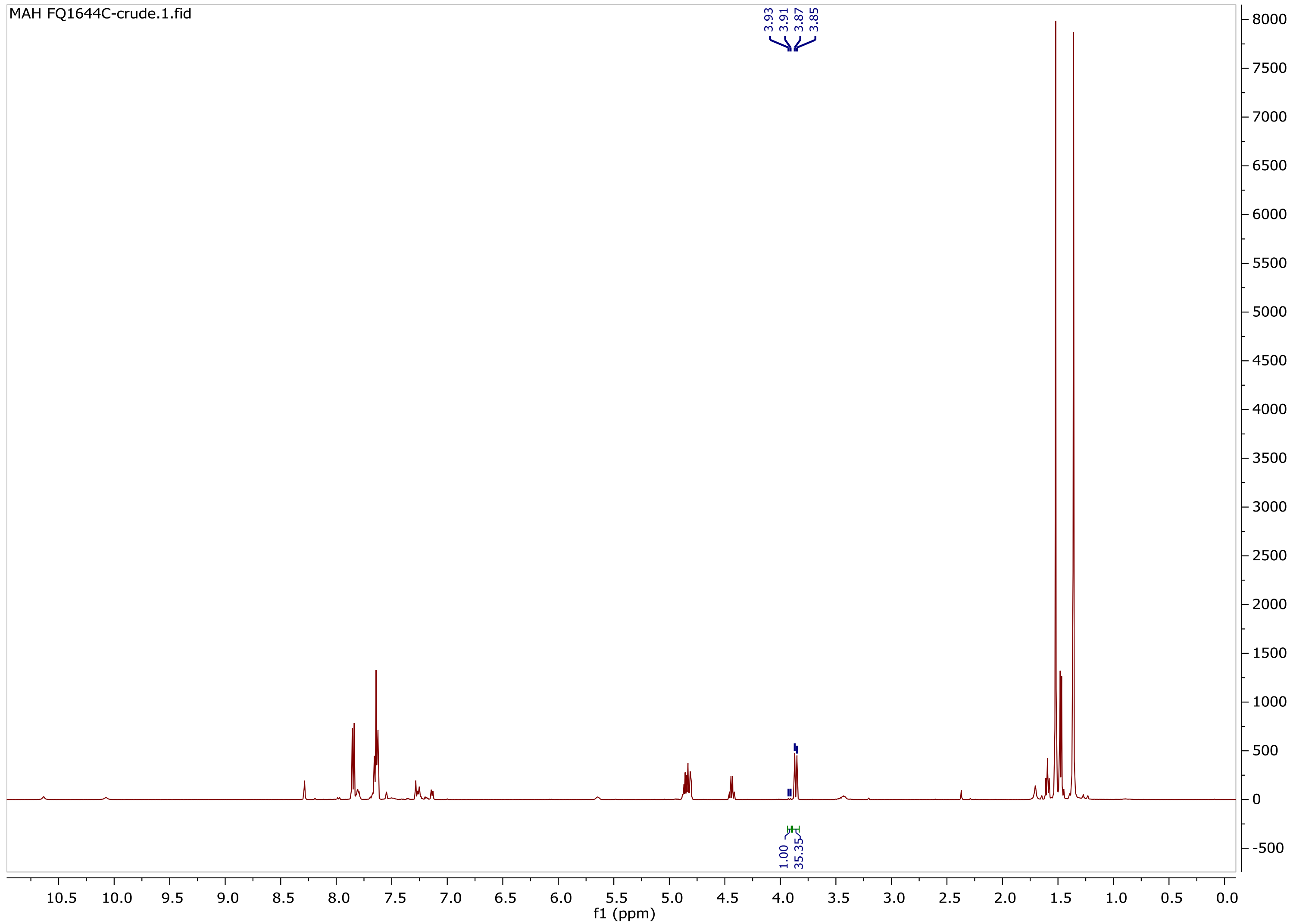

O
$CO_2{}^tBu$
$CO_2{}^tBu$
Cl
Me
$NO_2$

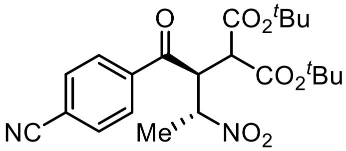
**2c**


MAH FQ1645B-crude.1.fid
3.93
3.91
3.88
3.86
1.00
40.78
f1 (ppm)

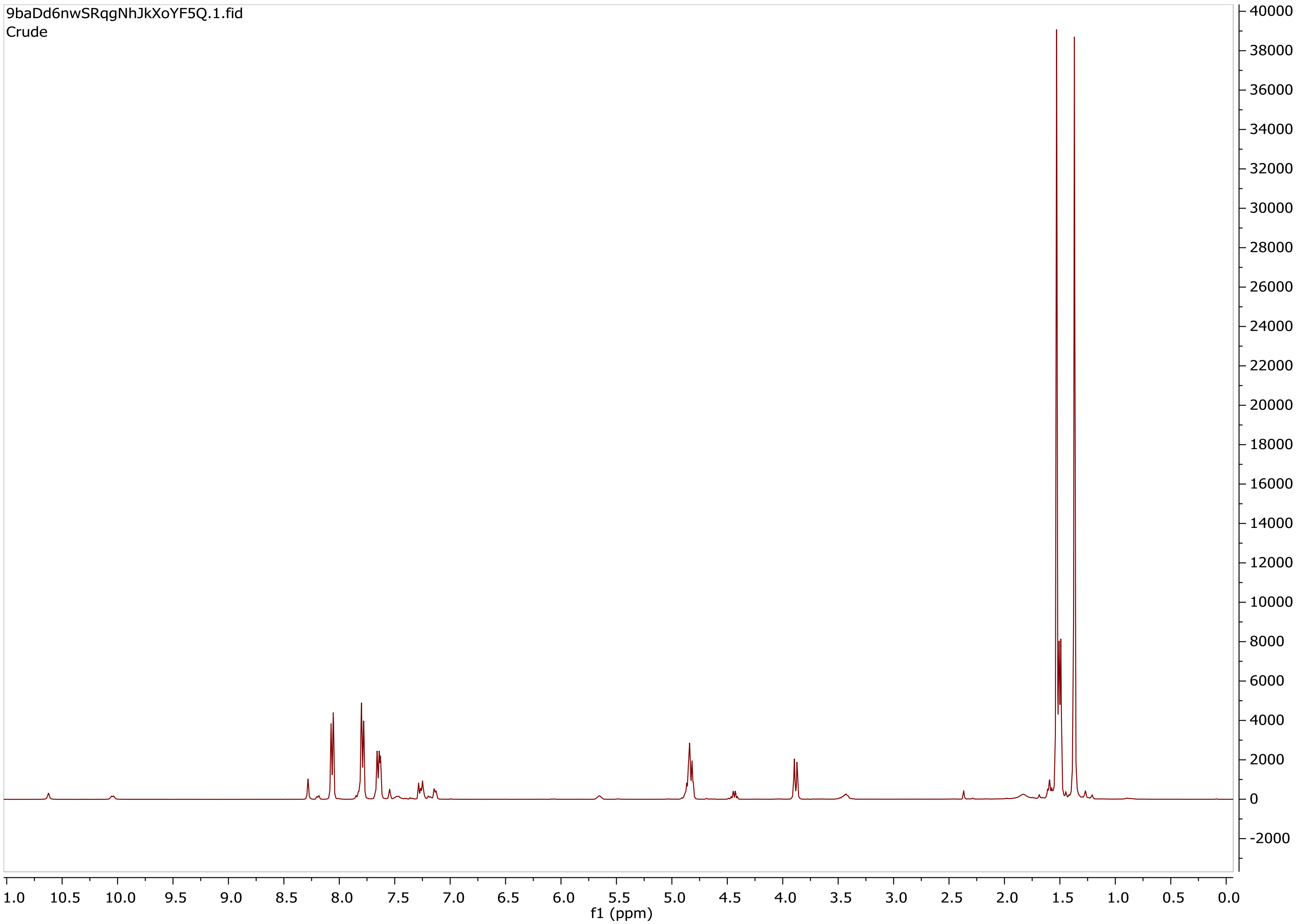


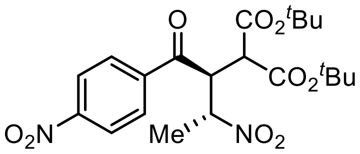
**2d**



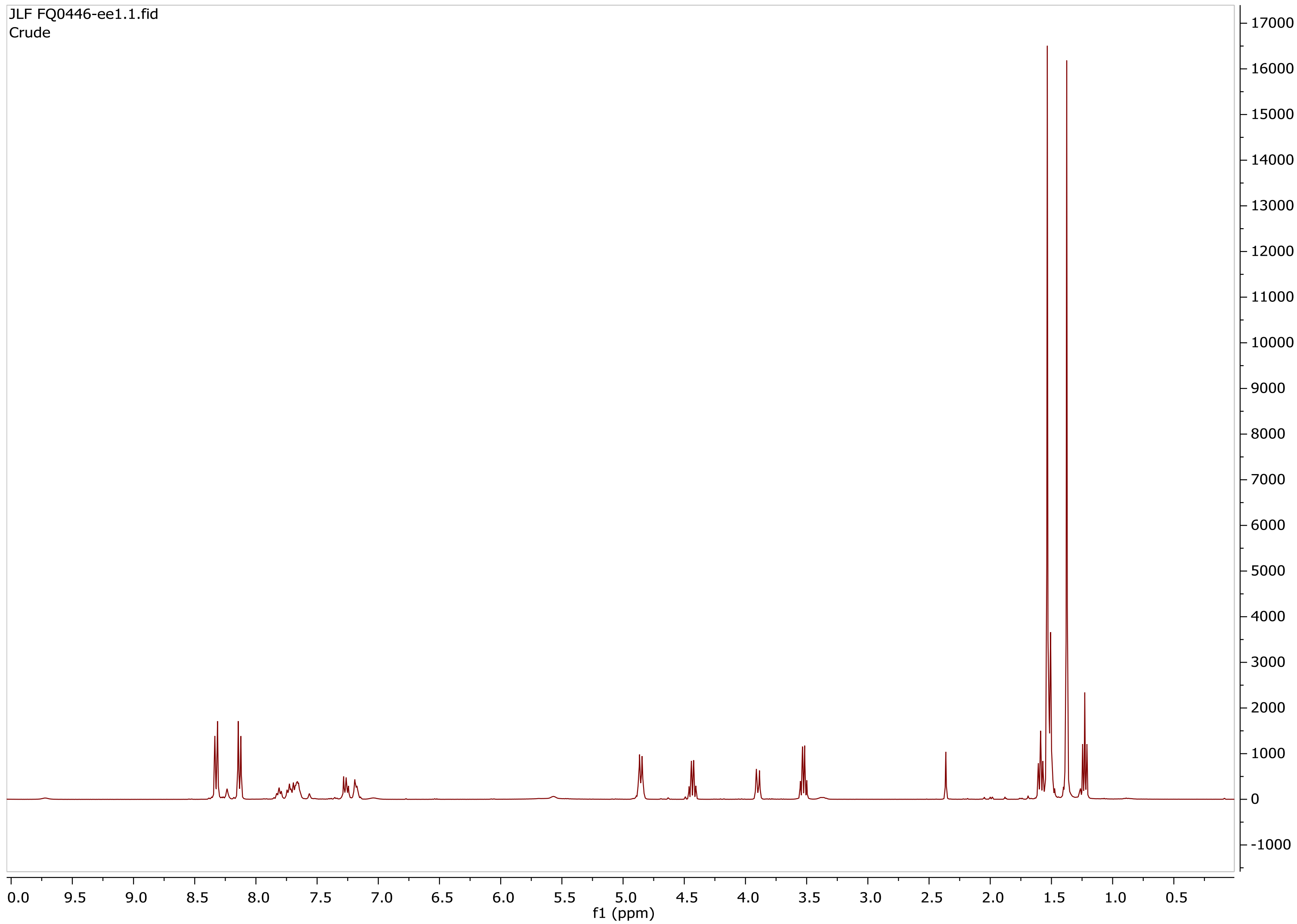


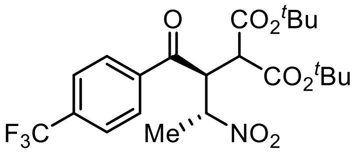
**2e**





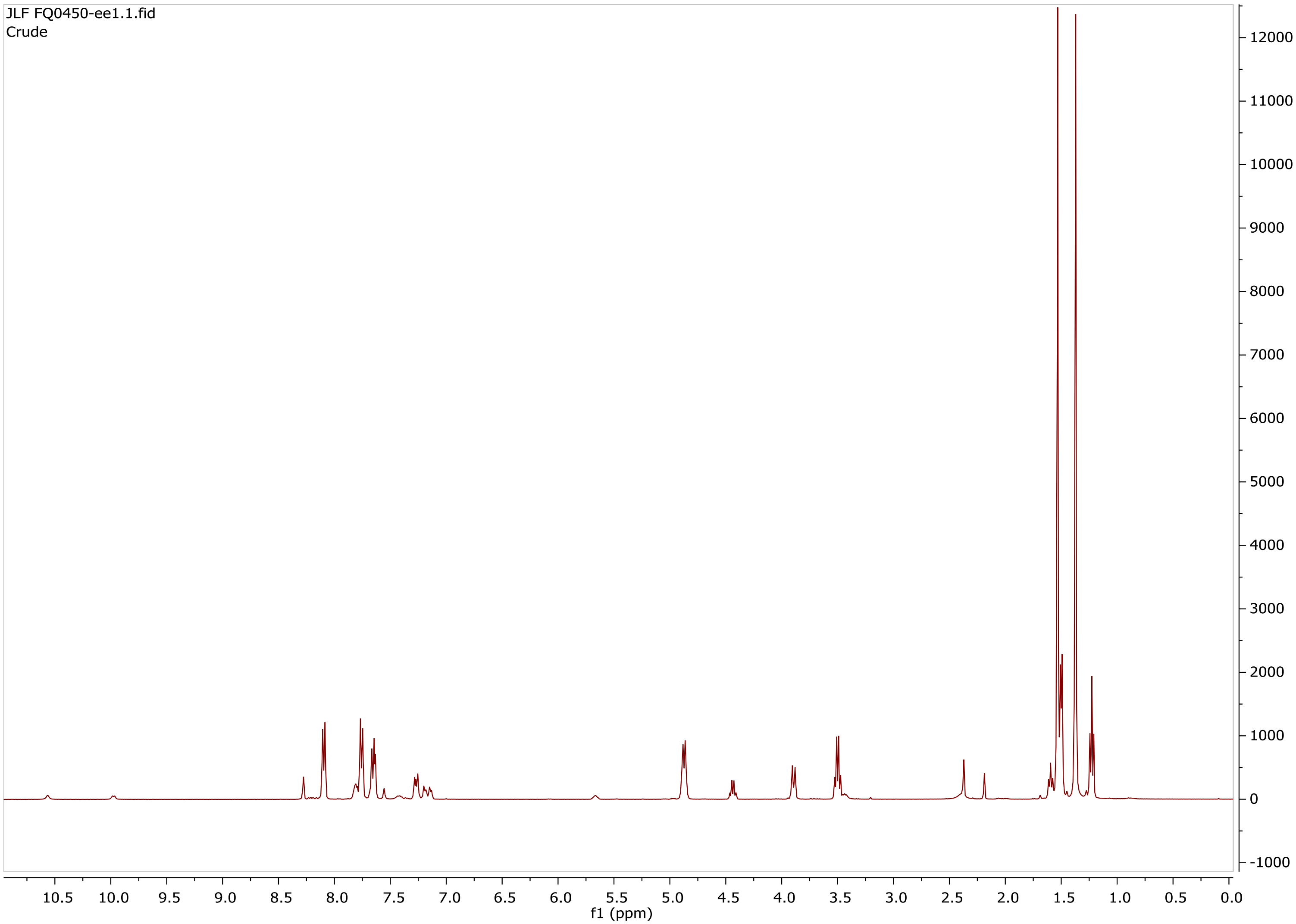

**2f**



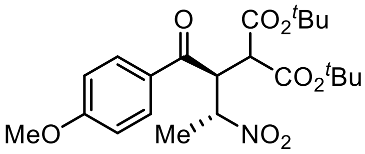


O
$CO_2{}^tBu$
$CO_2{}^tBu$
$F_3C$
Me
$NO_2$

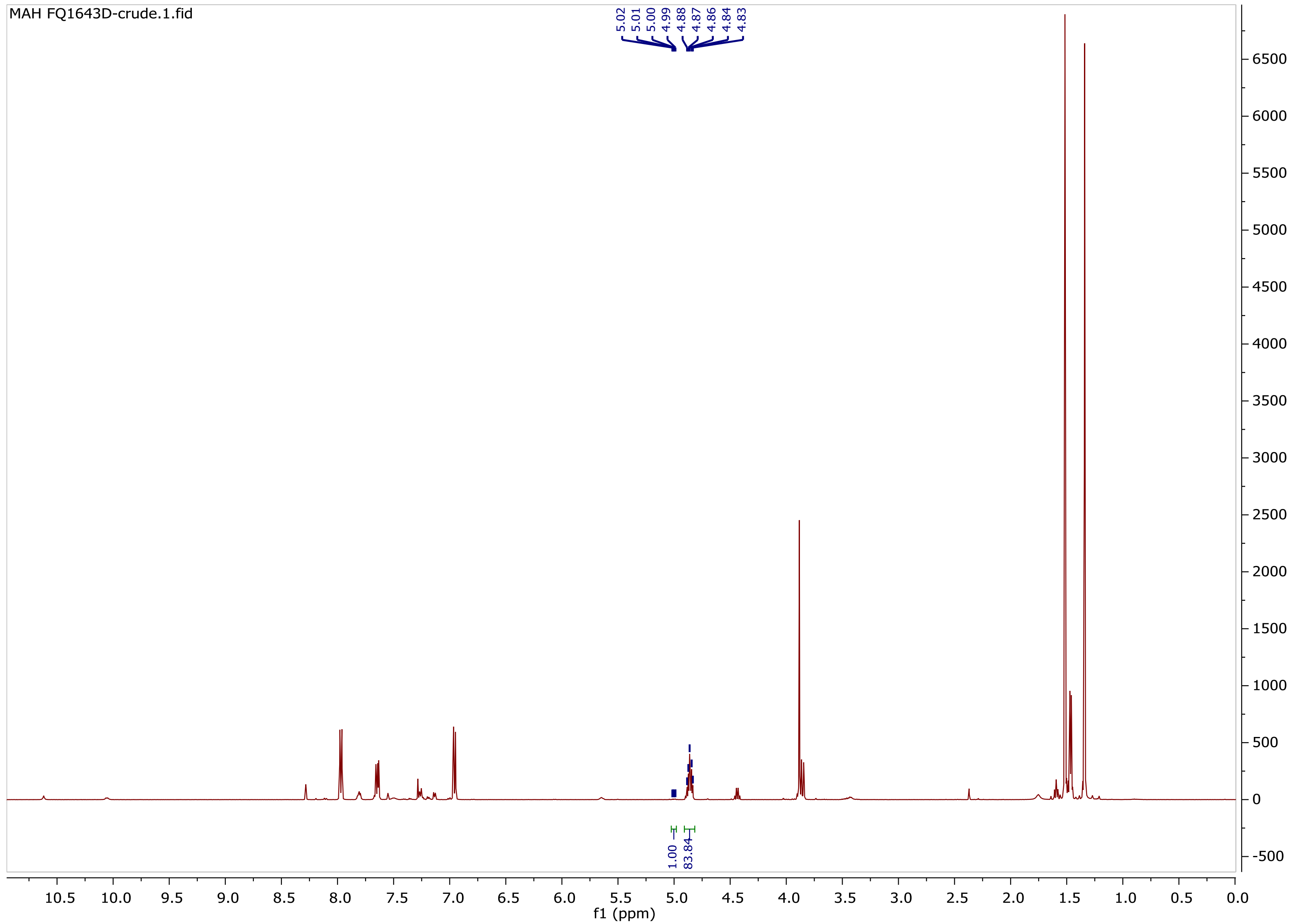

**2g**

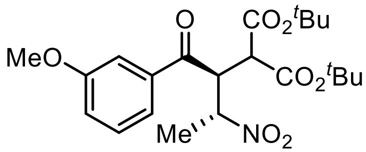


JLF FQ0450-ee1.1.fid
Crude
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

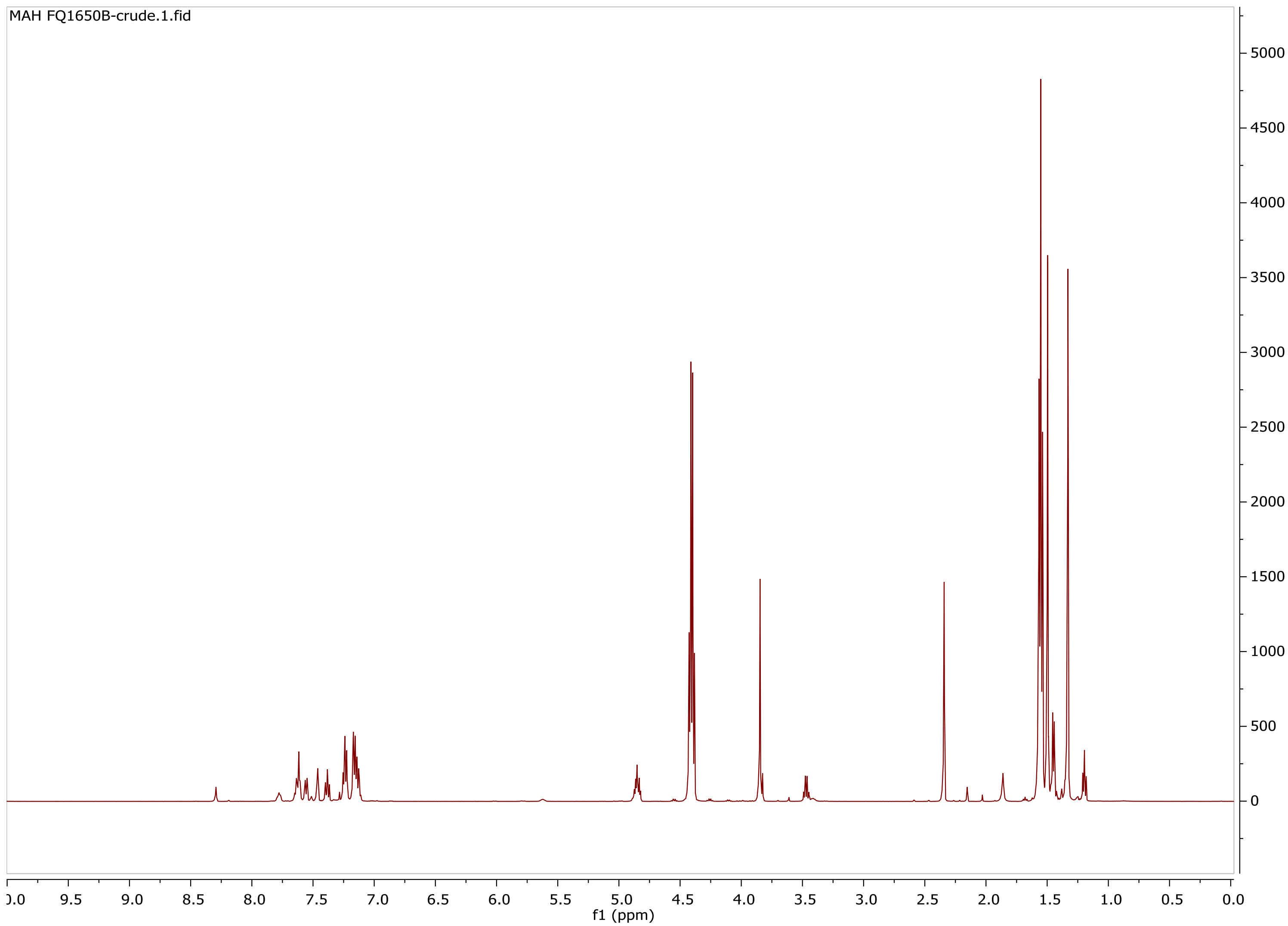


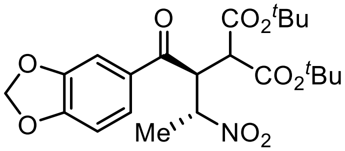
**2h**


MAH FQ1643D-crude.1.fid
5.02
5.01
5.00
4.99
4.88
4.87
4.86
4.84
4.83
1.00
83.84
f1 (ppm)

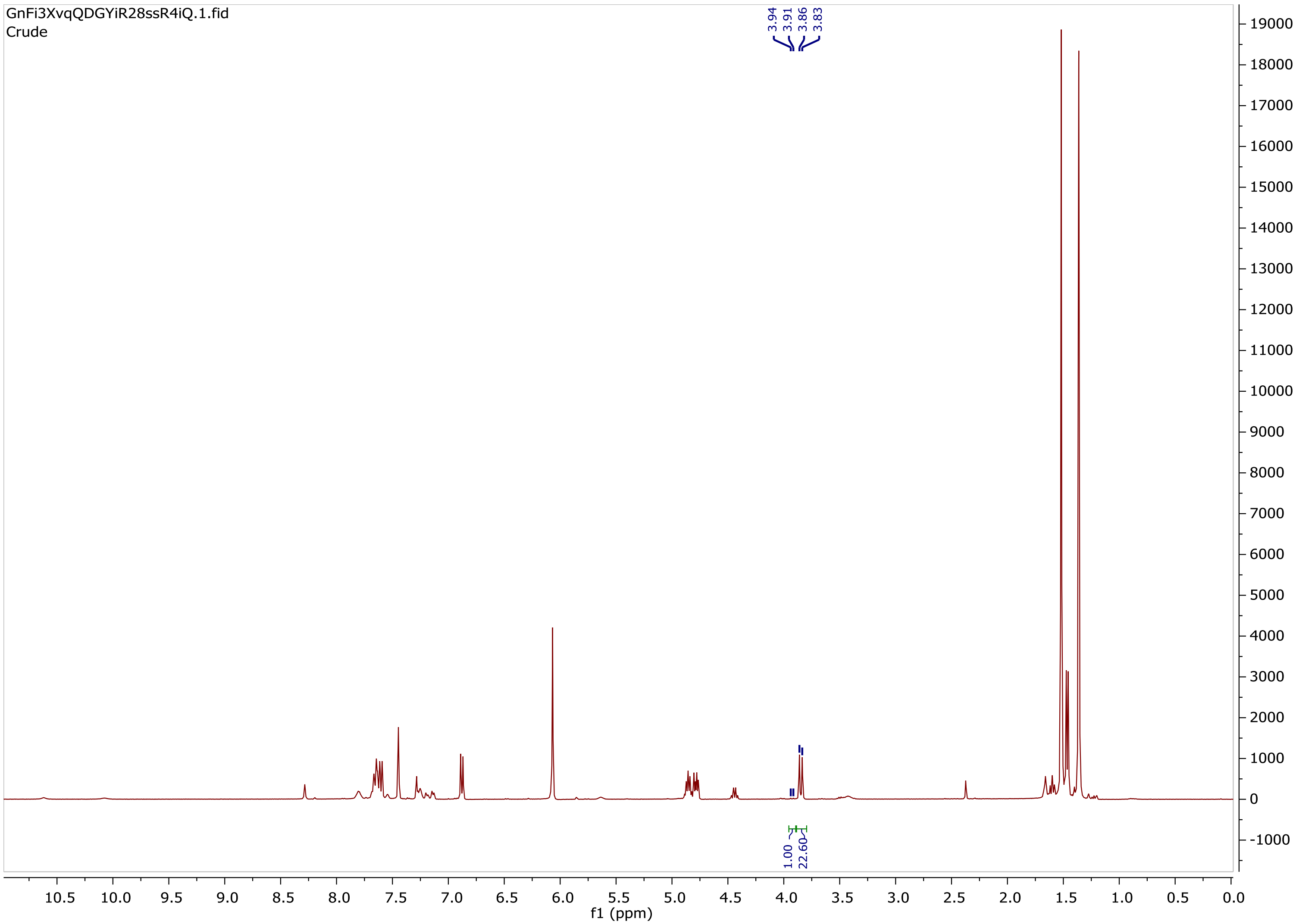

MeO
O
$CO_2{}^tBu$
$CO_2{}^tBu$
Me
$NO_2$

**2h**

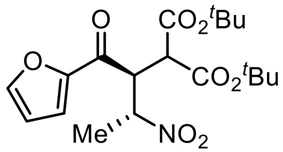

MAH FQ1650B-crude.1.fid
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



**2j**

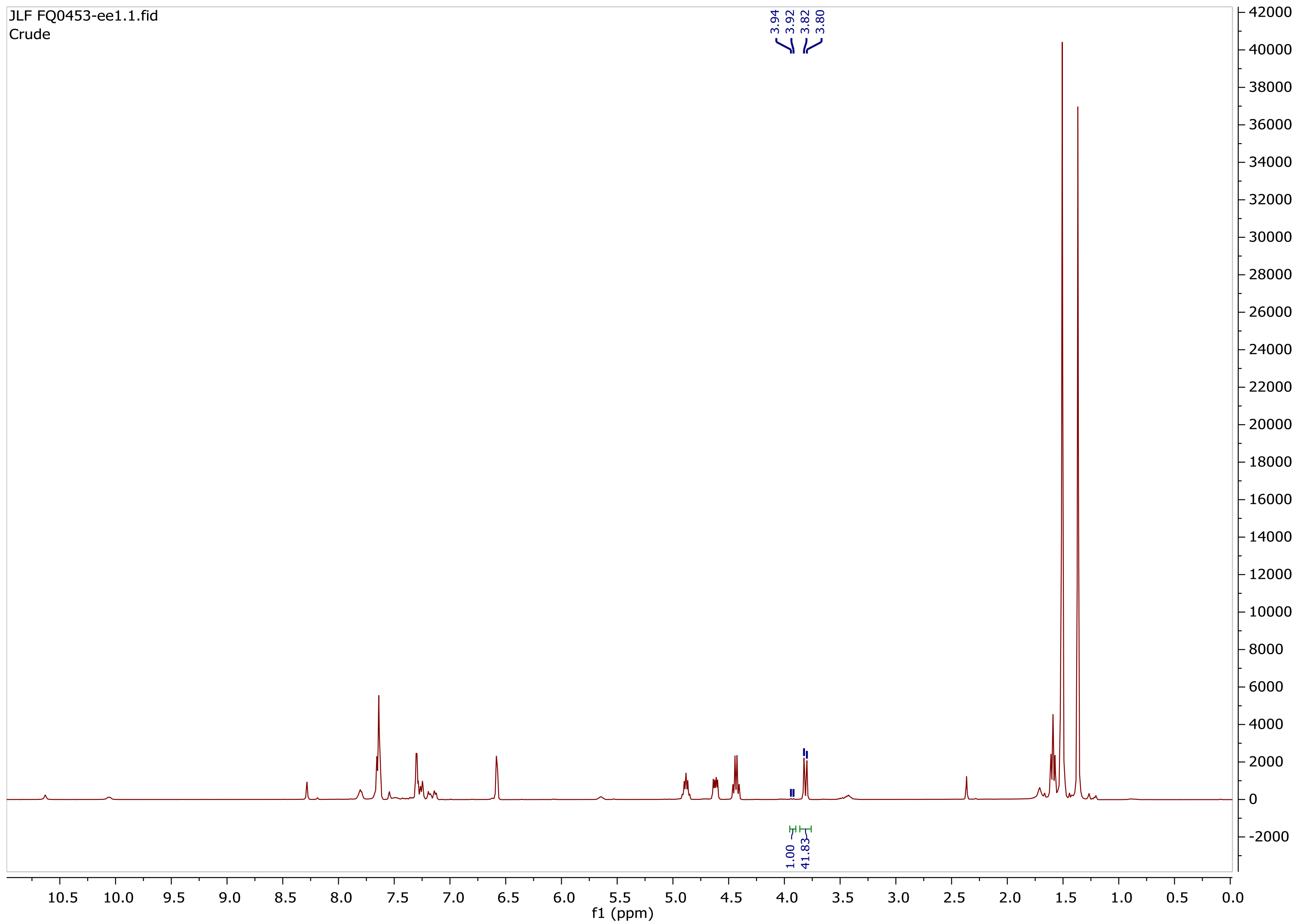


GnFi3XvqQDGYiR28ssR4iQ.1.fid
Crude
3.94
3.91
3.86
3.83
1.00
22.60
f1 (ppm)

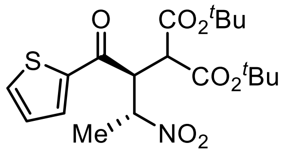


O
$CO_2{}^tBu$
$CO_2{}^tBu$
Me
$NO_2$

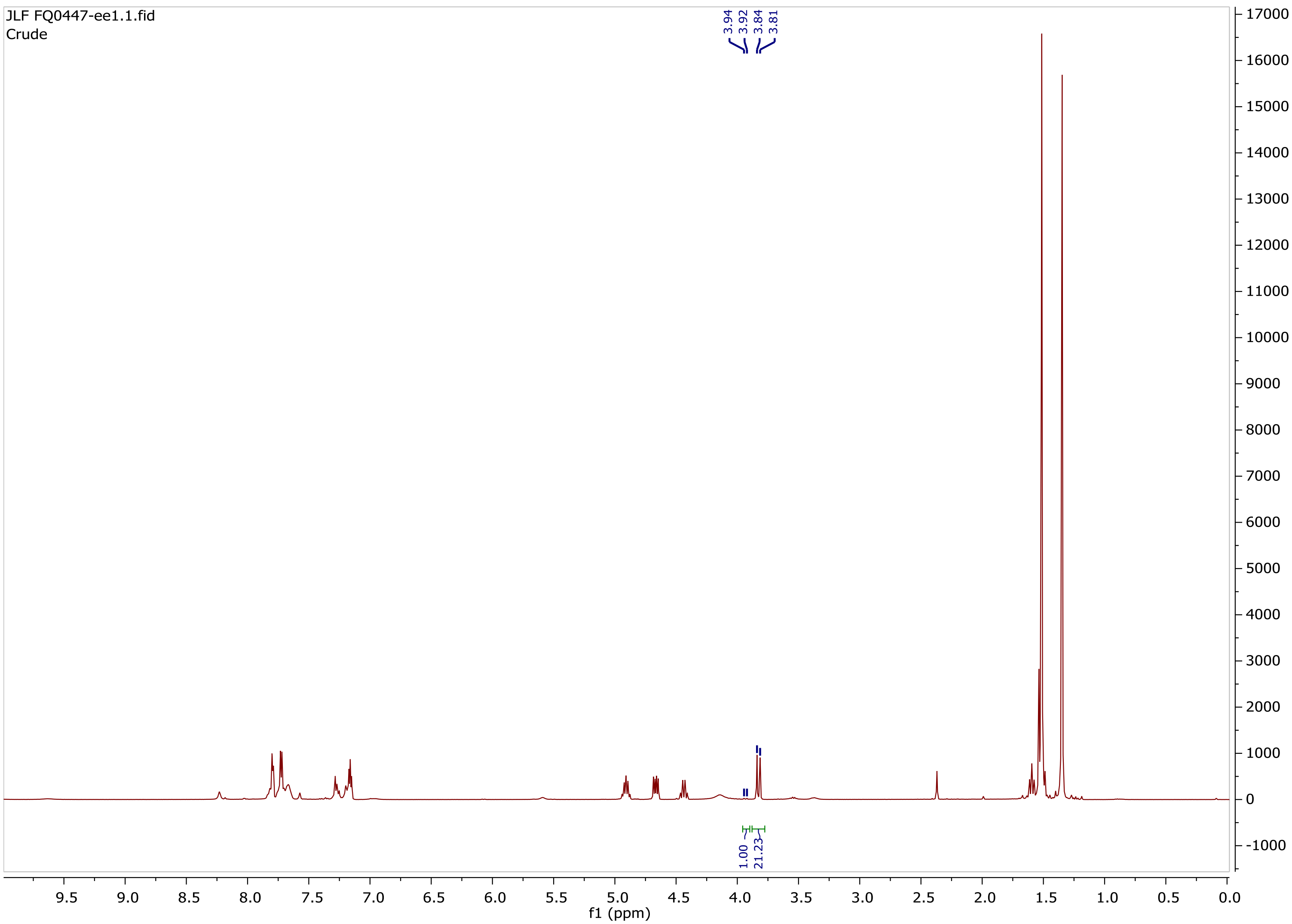

**2k**

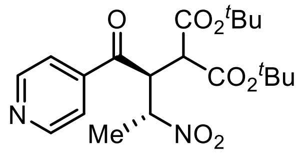


JLF FQ0453-ee1.1.fid
Crude
3.94
3.92
3.82
3.80
1.00
41.83
f1 (ppm)

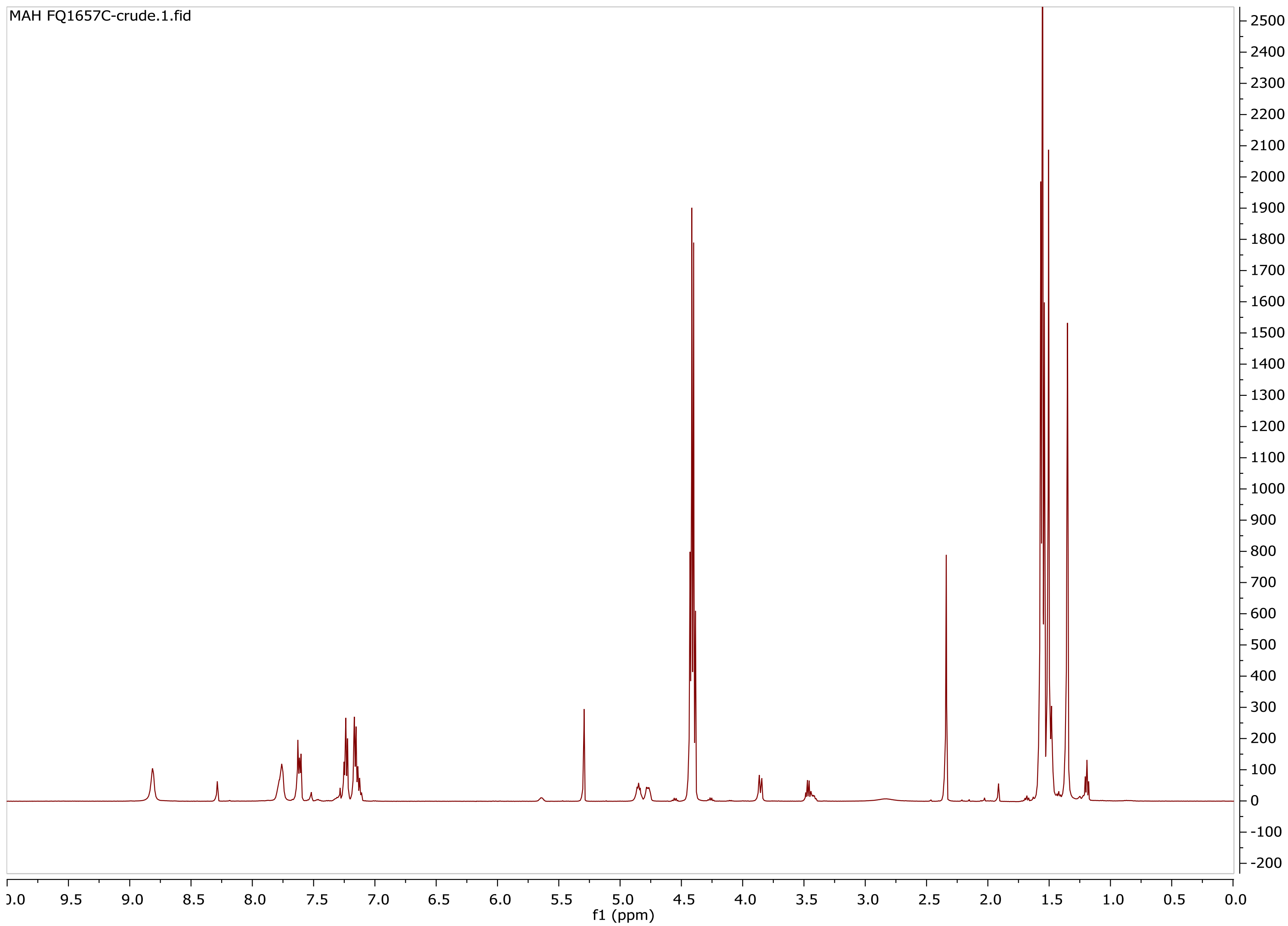


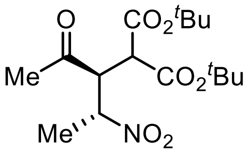
**2l**



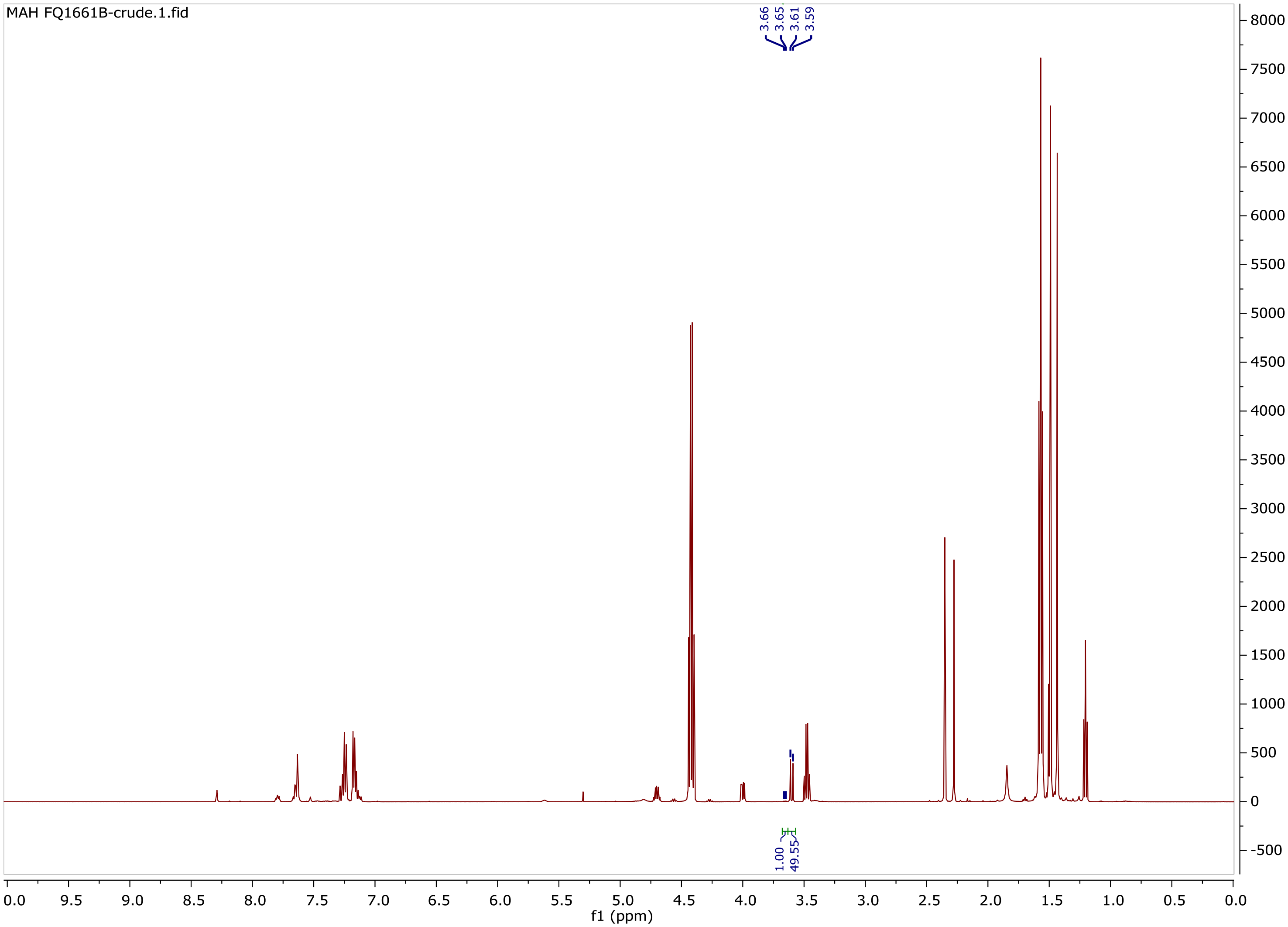


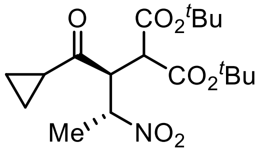

**2m**



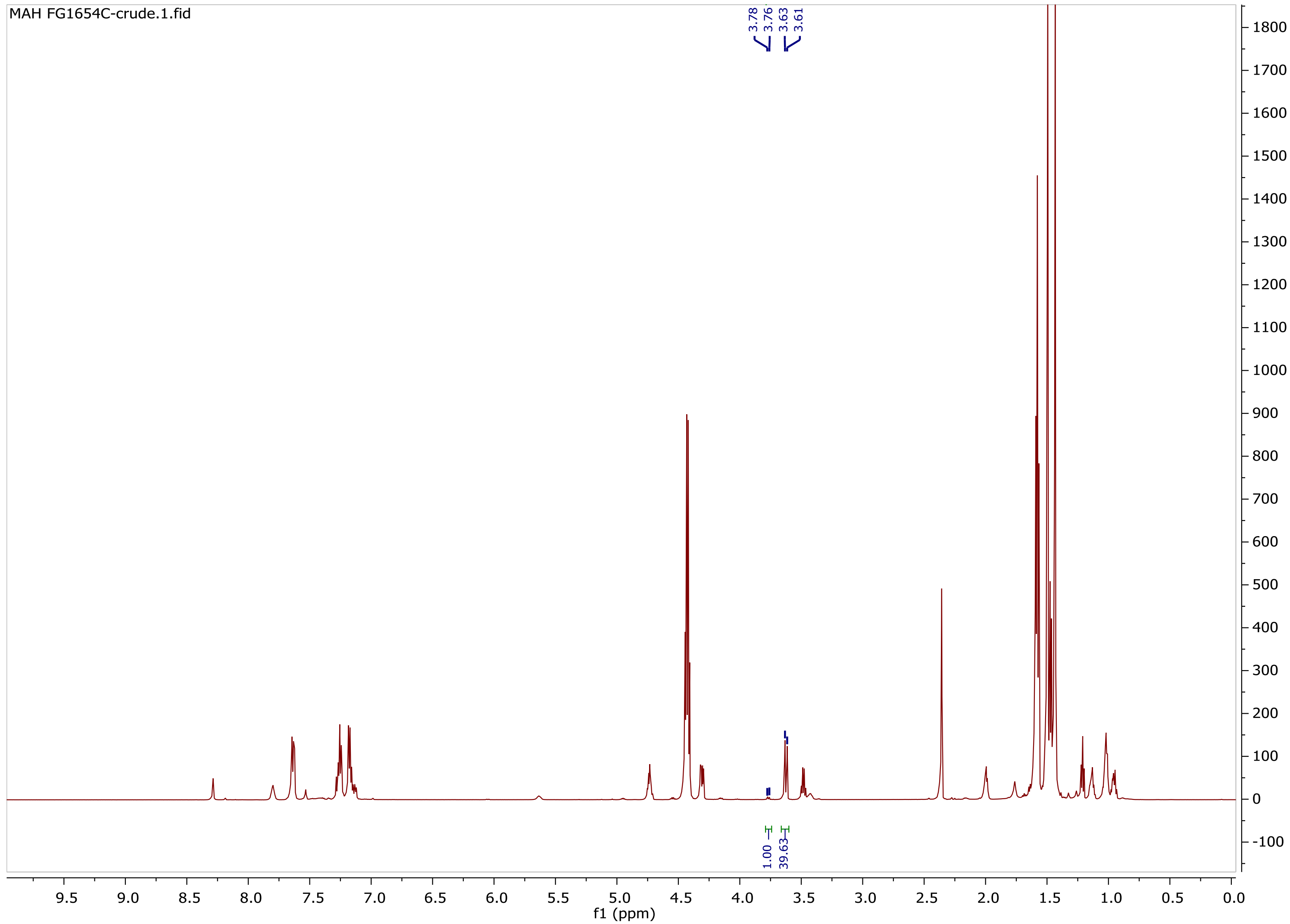


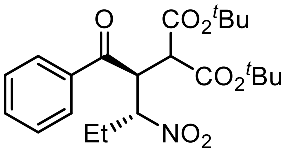
**2n**



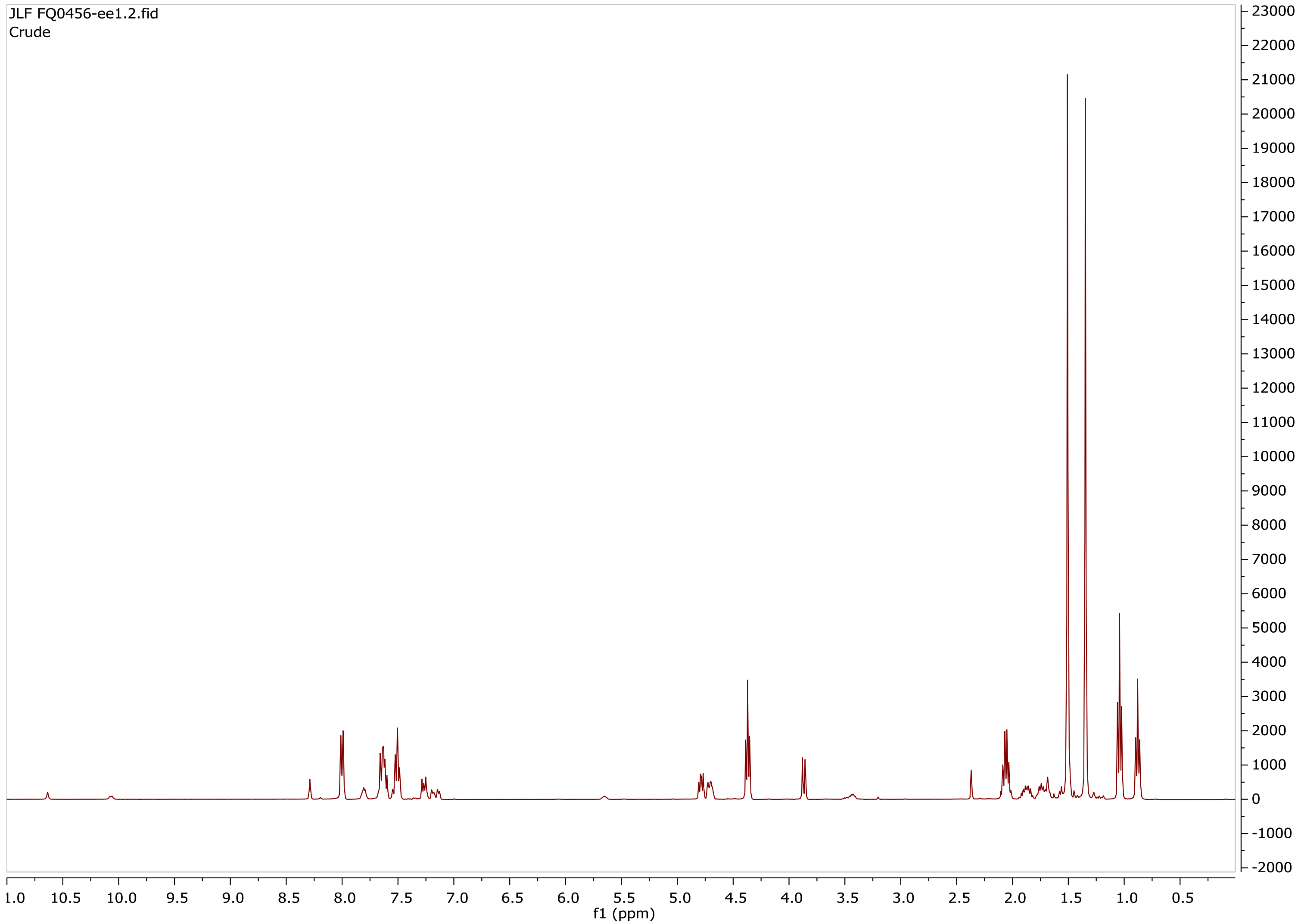


**2o**

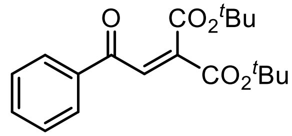




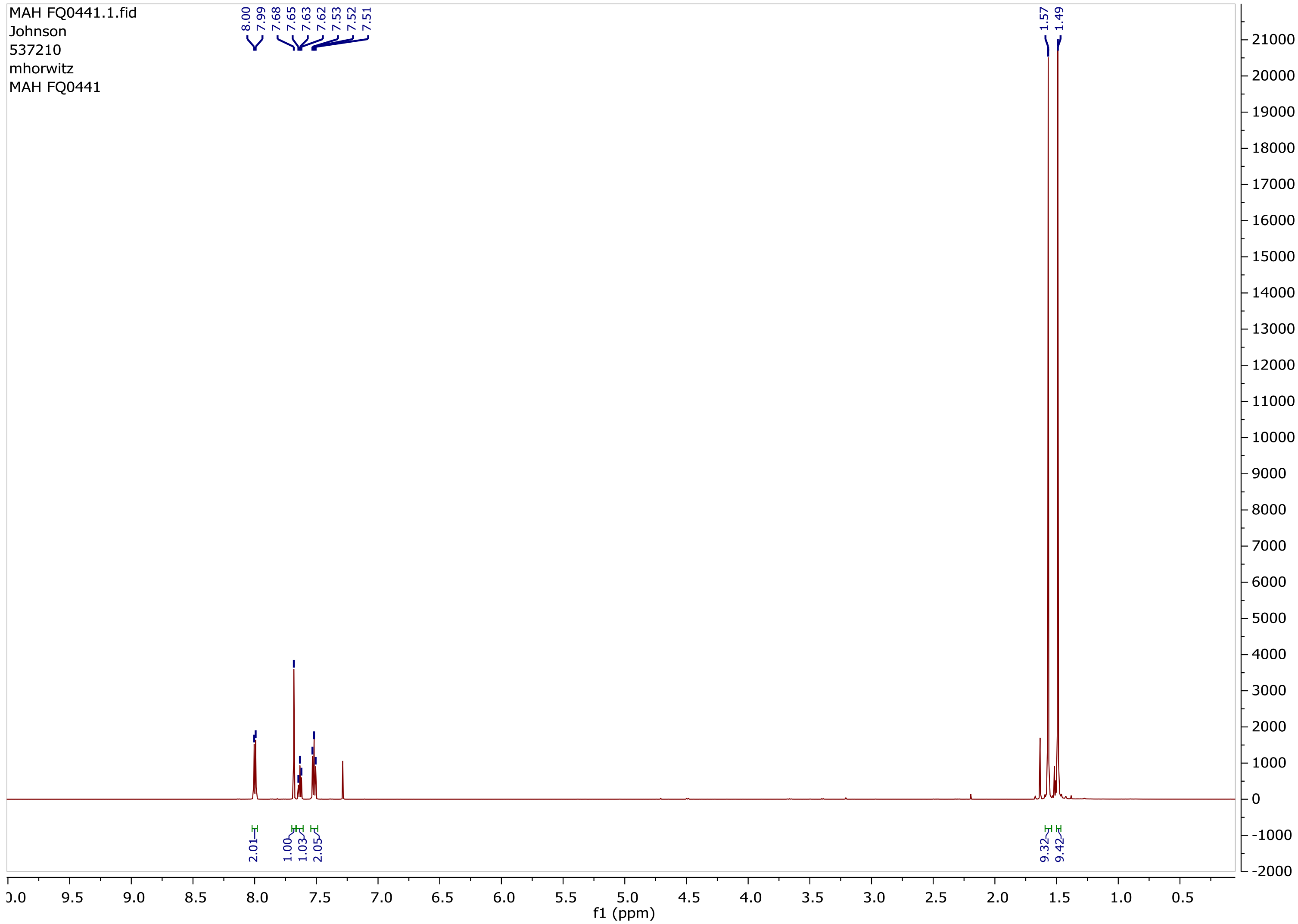
**2p**

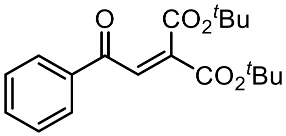


**$^{1}H$ and $^{13}C$ NMR spectra of new compounds:**

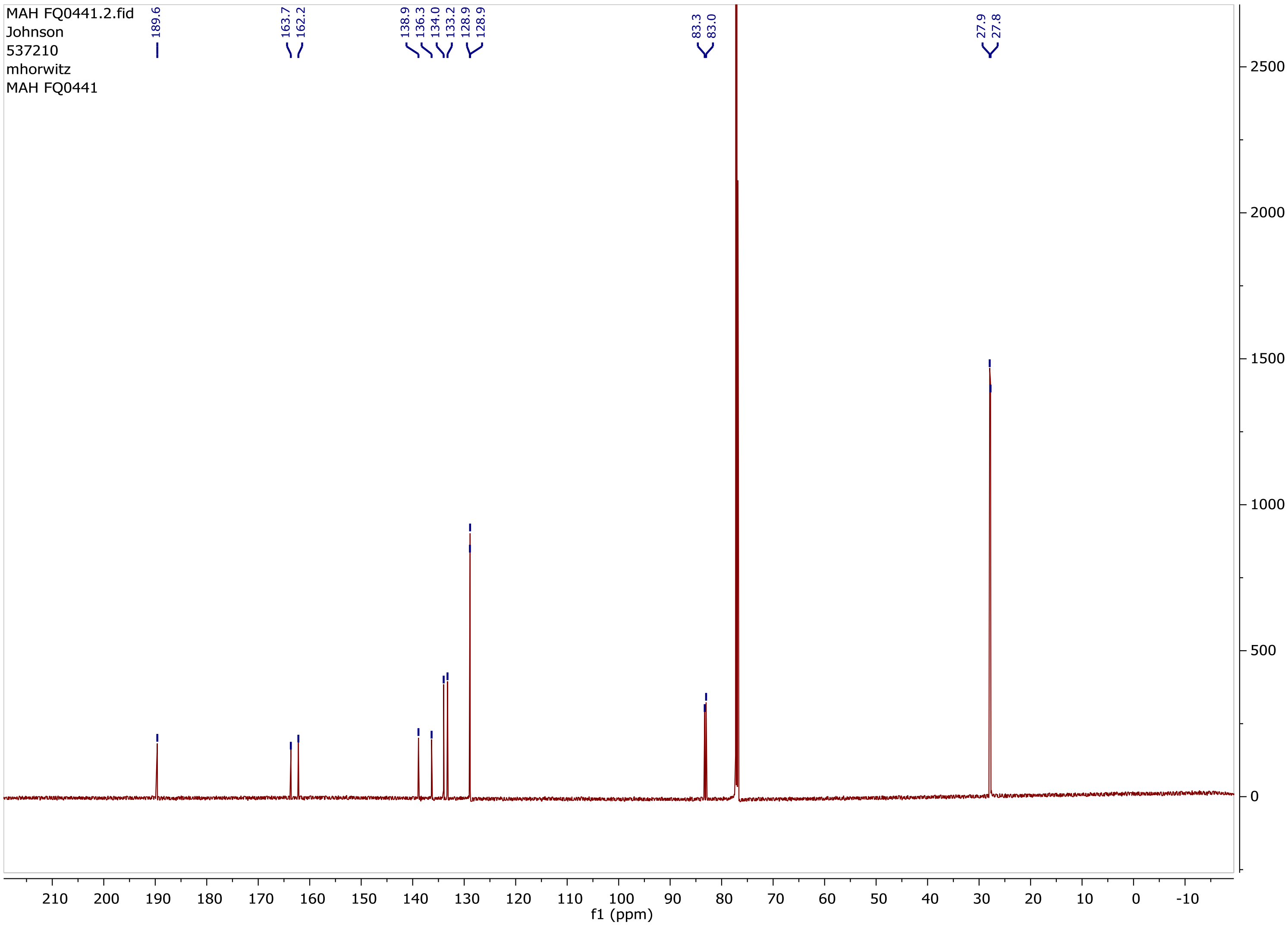


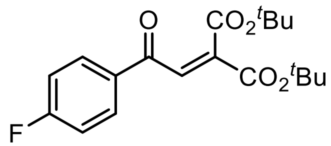

**1a**



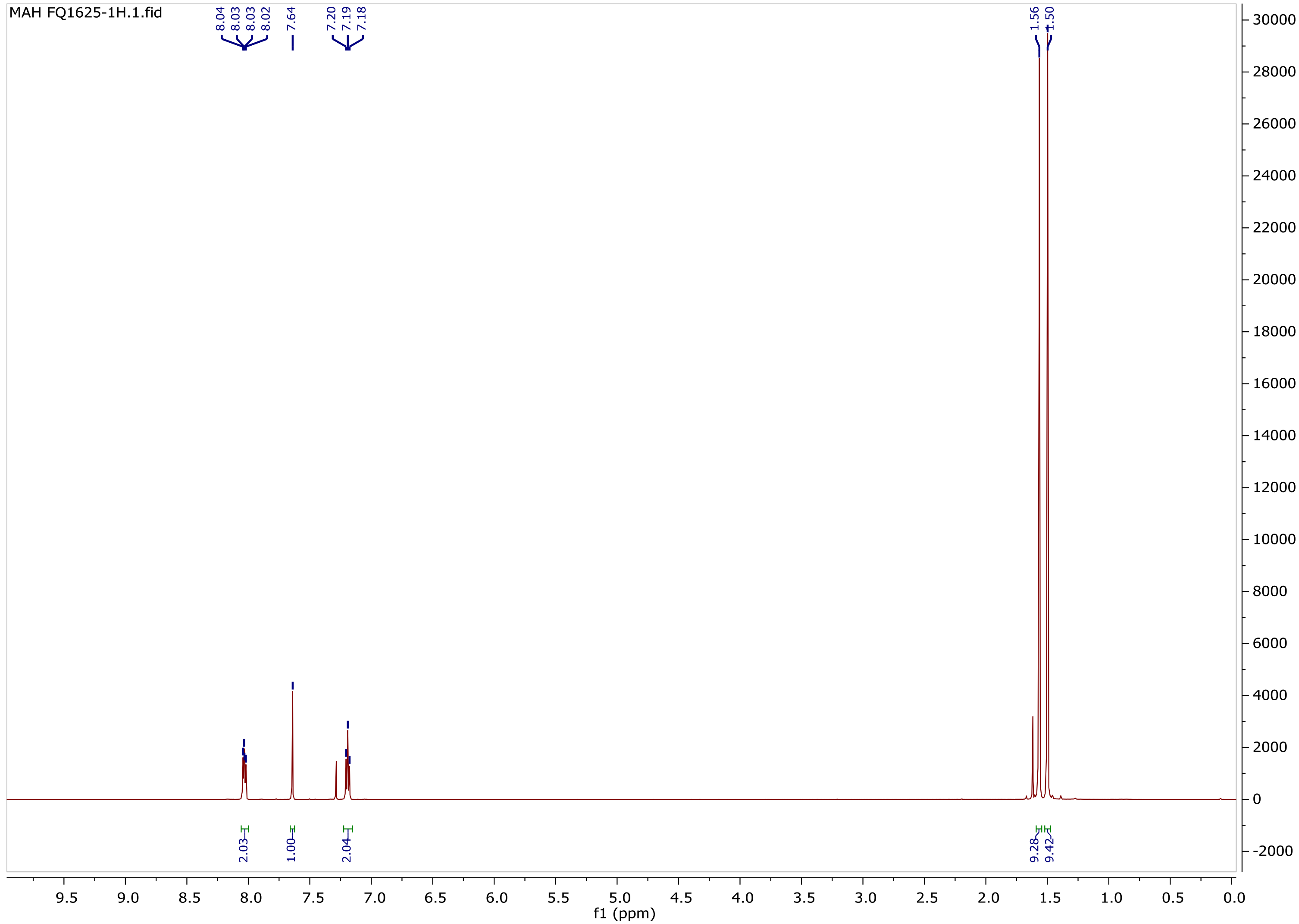

O
CO2tBu
CO2tBu

**1a**

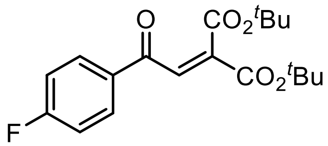

MAH FQ0441.2.fid
Johnson
537210
mhorwitz
MAH FQ0441
189.6
163.7
162.2
138.9
136.3
134.0
133.2
128.9
128.9
83.3
83.0
27.9
27.8
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



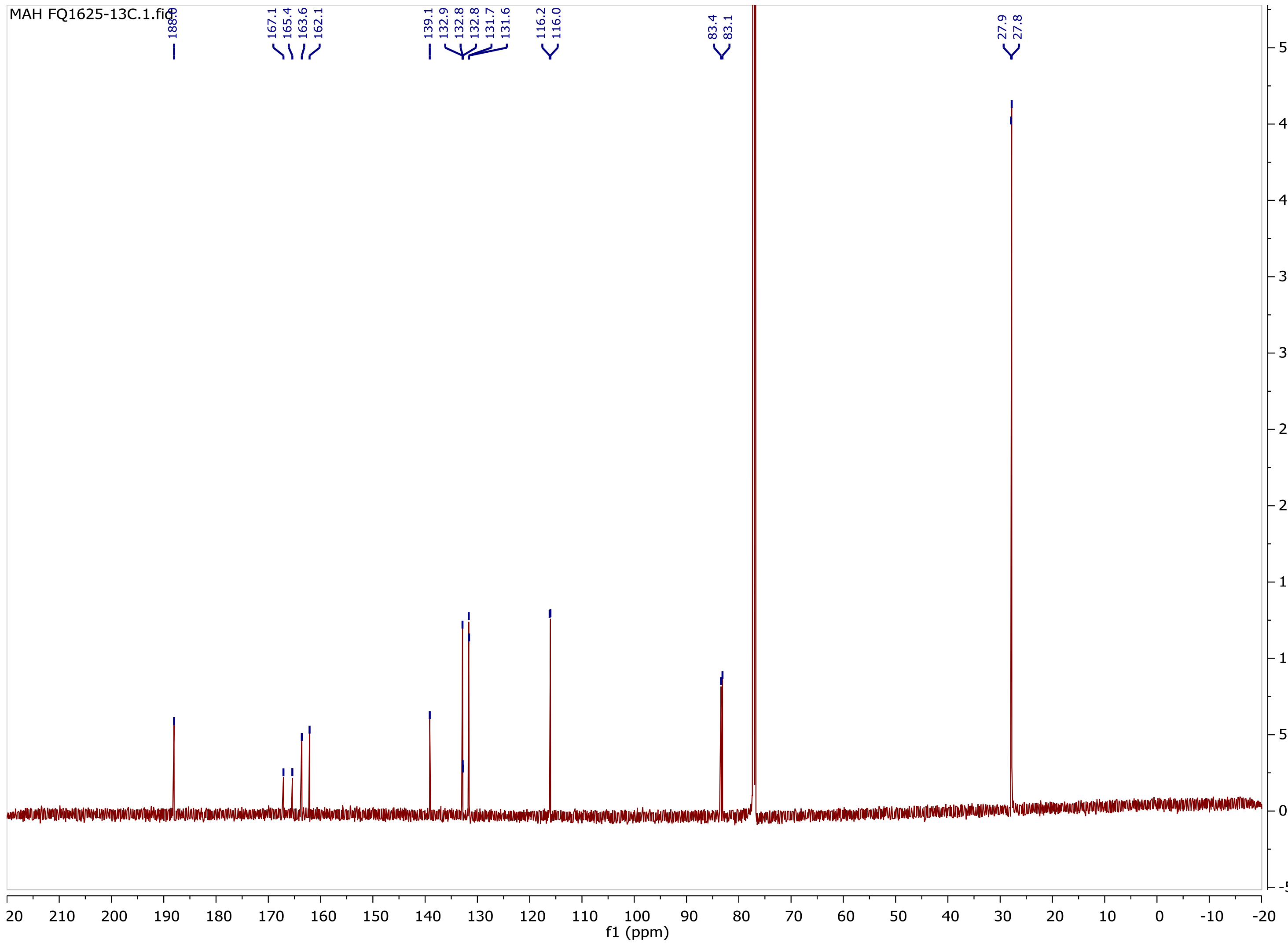
**1b**

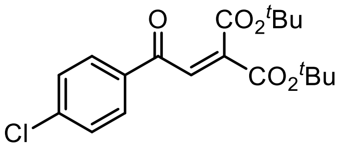


MAH FQ1625-1H.1.fid
8.04
8.03
8.03
8.02
7.64
7.20
7.19
7.18
1.56
1.50
2.03
1.00
2.04
9.28
9.42
f1 (ppm)

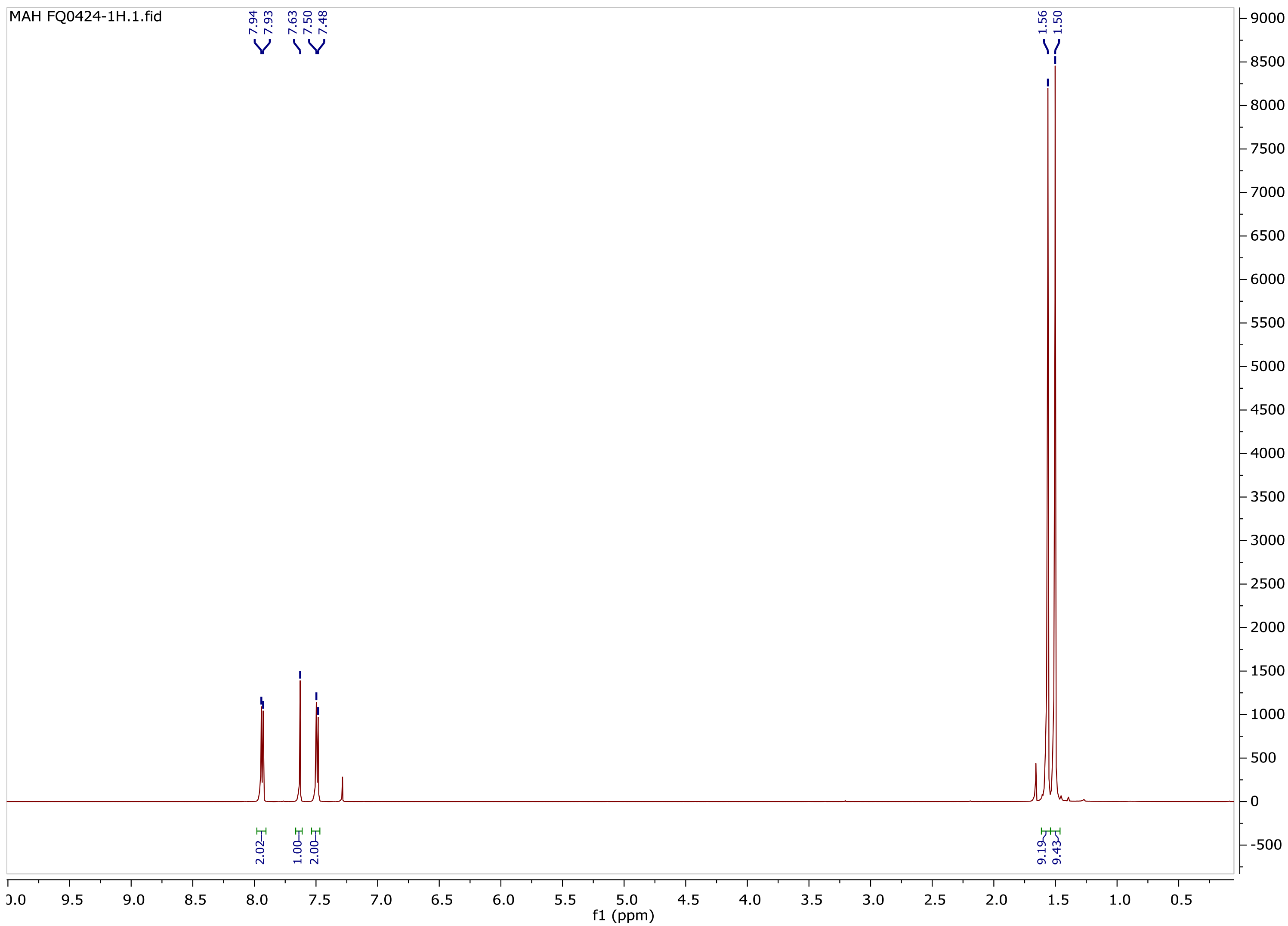

O
CO2tBu
CO2tBu
F

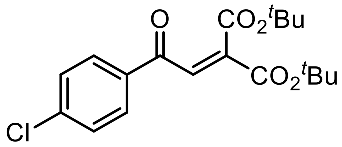
**1b**


MAH FQ1625-13C.1.fid
188.0
167.1
165.4
163.6
162.1
139.1
132.9
132.8
132.8
131.7
131.6
116.2
116.0
83.4
83.1
27.9
27.8
f1 (ppm)

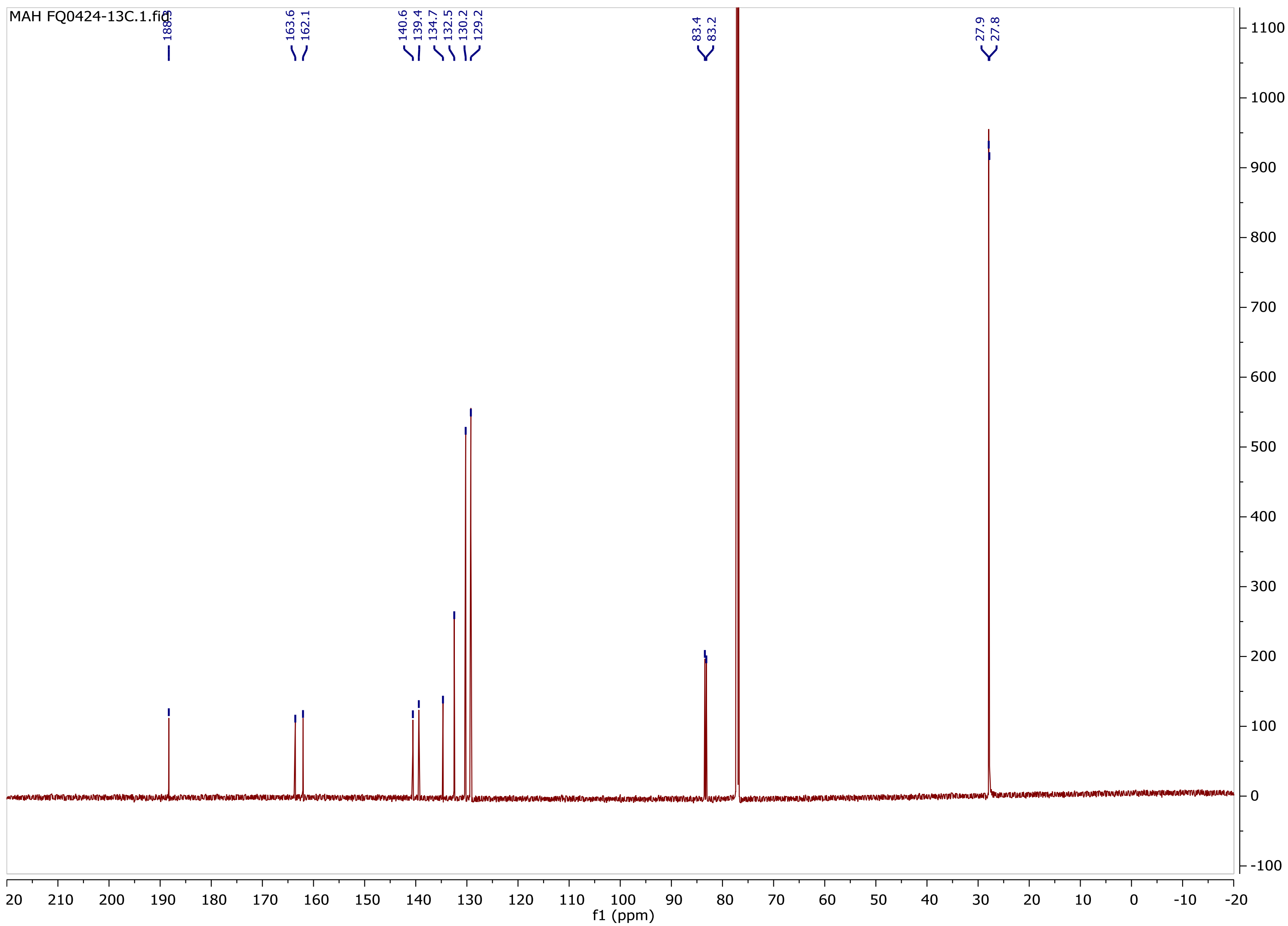

O
CO2tBu
CO2tBu
Cl

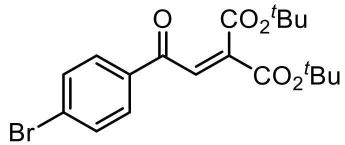
**1c**


MAH FQ0424-1H.1.fid
7.94
7.93
7.63
7.50
7.48
1.56
1.50
2.02
1.00
2.00
9.19
9.43
f1 (ppm)

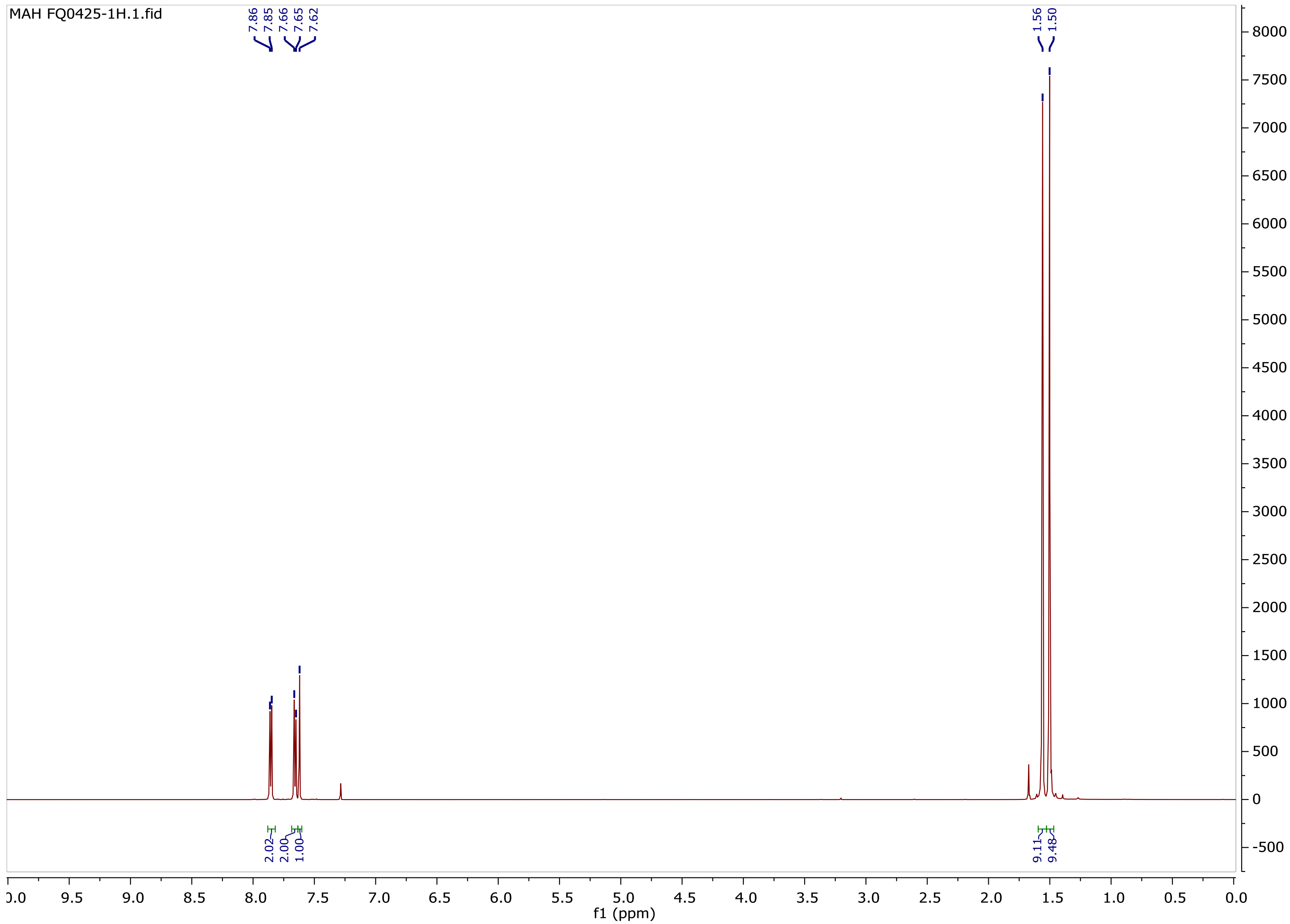

O
CO2tBu
CO2tBu
Cl

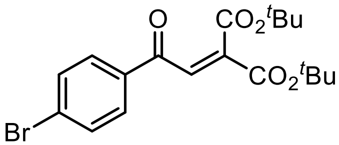
**1c**


MAH FQ0424-13C.1.fid
188.3
163.6
162.1
140.6
139.4
134.7
132.5
130.2
129.2
83.4
83.2
27.9
27.8
f1 (ppm)

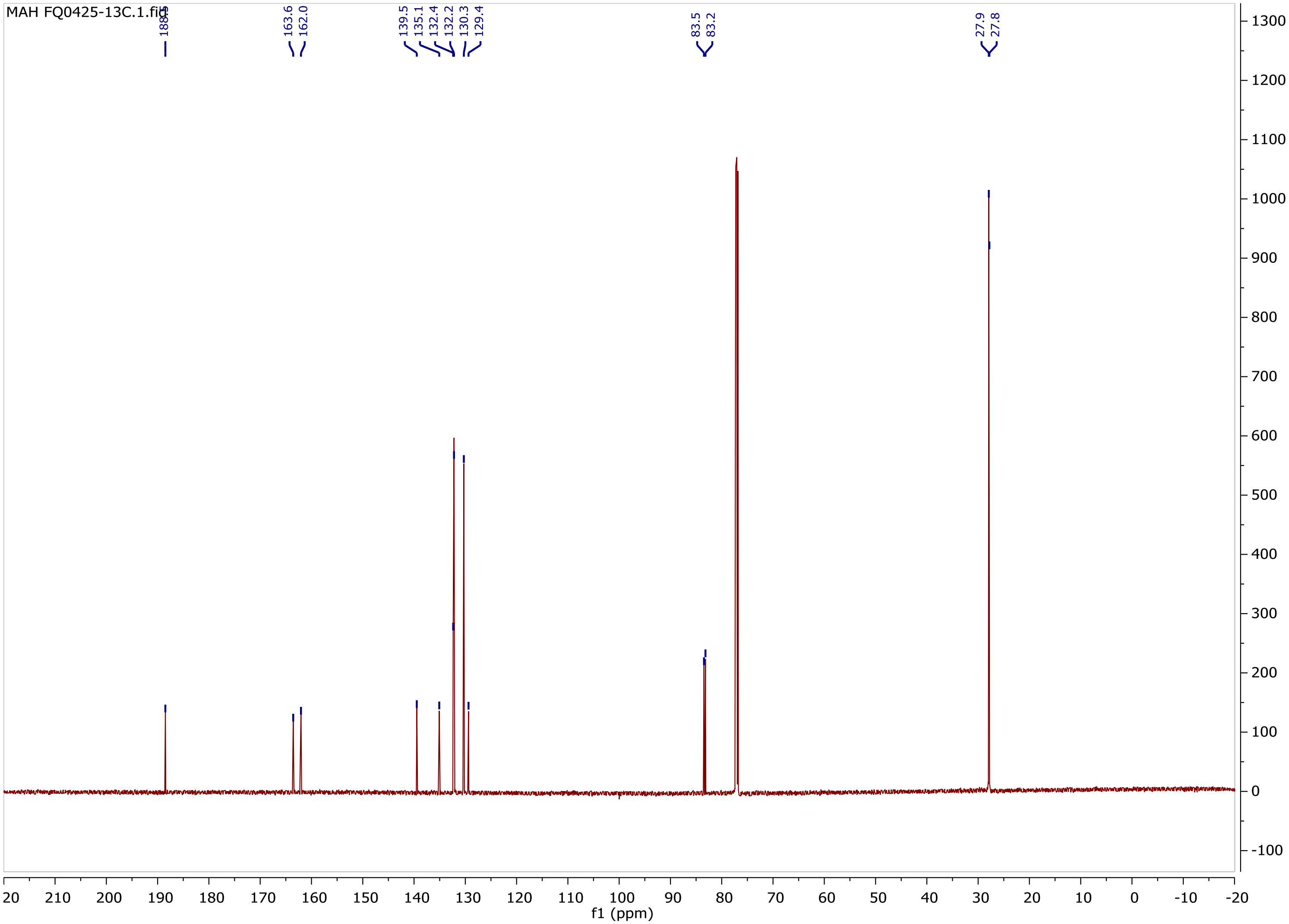

O
$CO_2{}^tBu$
$CO_2{}^tBu$
Br

**1d**

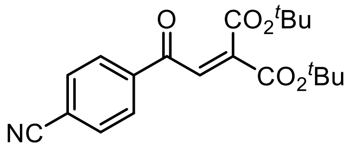

MAH FQ0425-1H.1.fid
7.86
7.85
7.66
7.65
7.62
1.56
1.50
2.02
2.00
1.00
9.11
9.48
f1 (ppm)



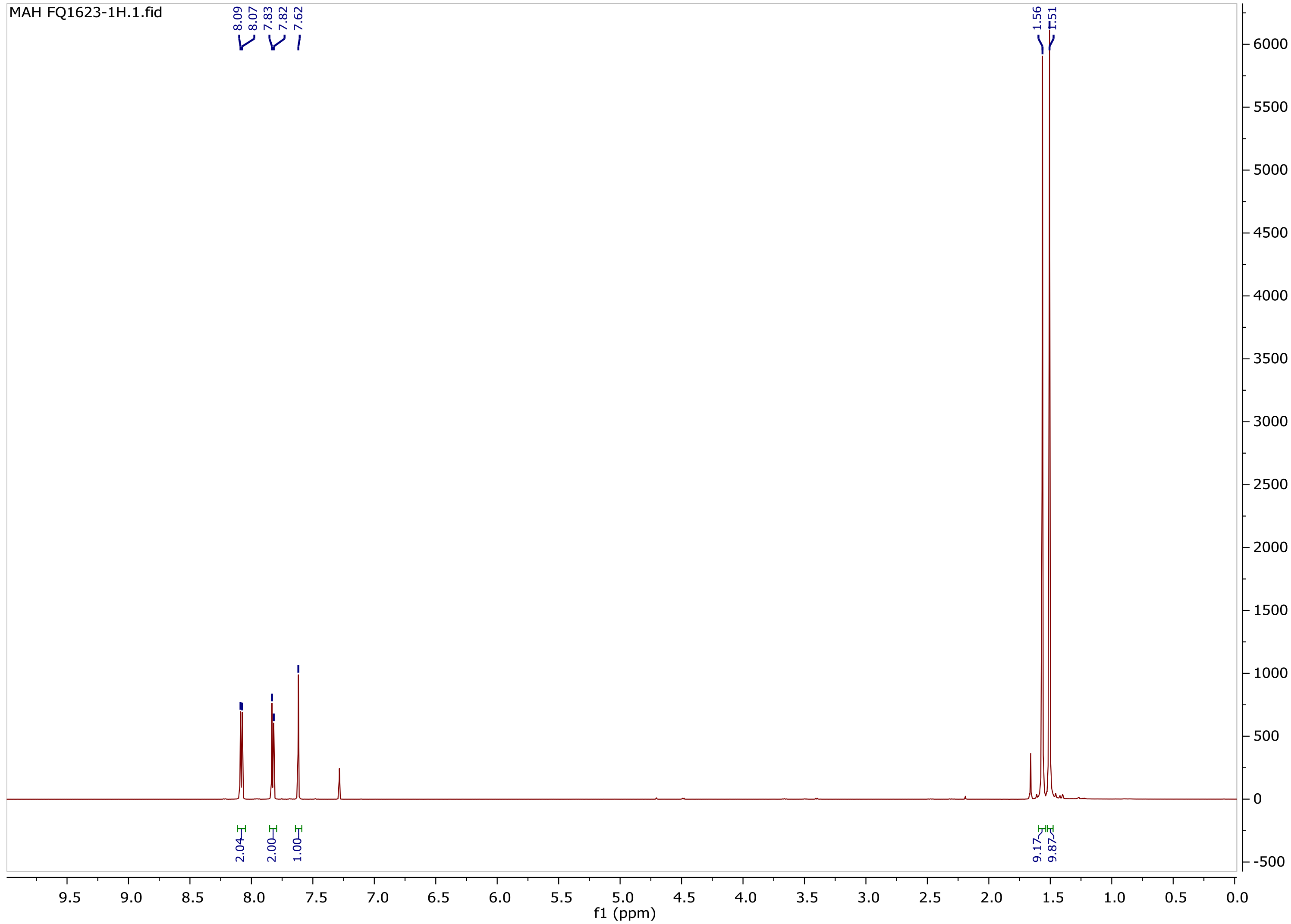
**1d**



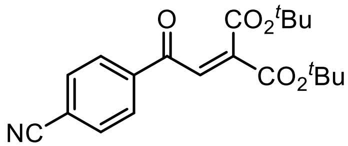
MAH FQ0425-13C.1.fid
188.5
163.6
162.0
139.5
135.1
132.4
132.2
130.3
129.4
83.5
83.2
27.9
27.8
f1 (ppm)



**1e**

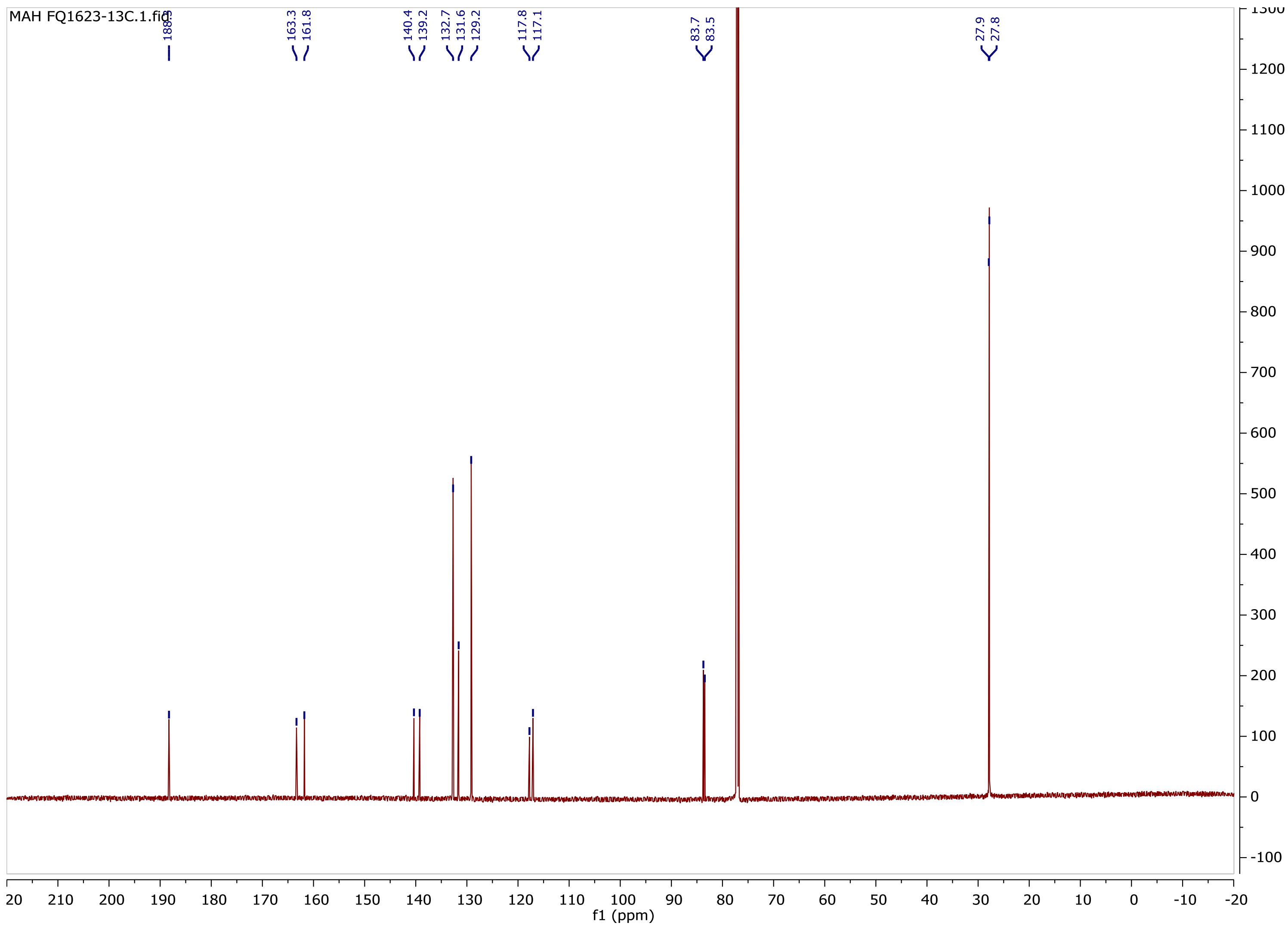


MAH FQ1623-1H.1.fid
8.09
8.07
7.83
7.82
7.62
1.56
1.51
2.04
2.00
1.00
9.17
9.87
f1 (ppm)

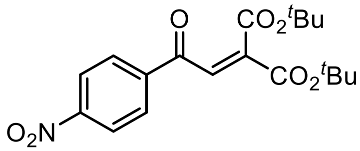


O
$CO_2{}^tBu$
$CO_2{}^tBu$
NC

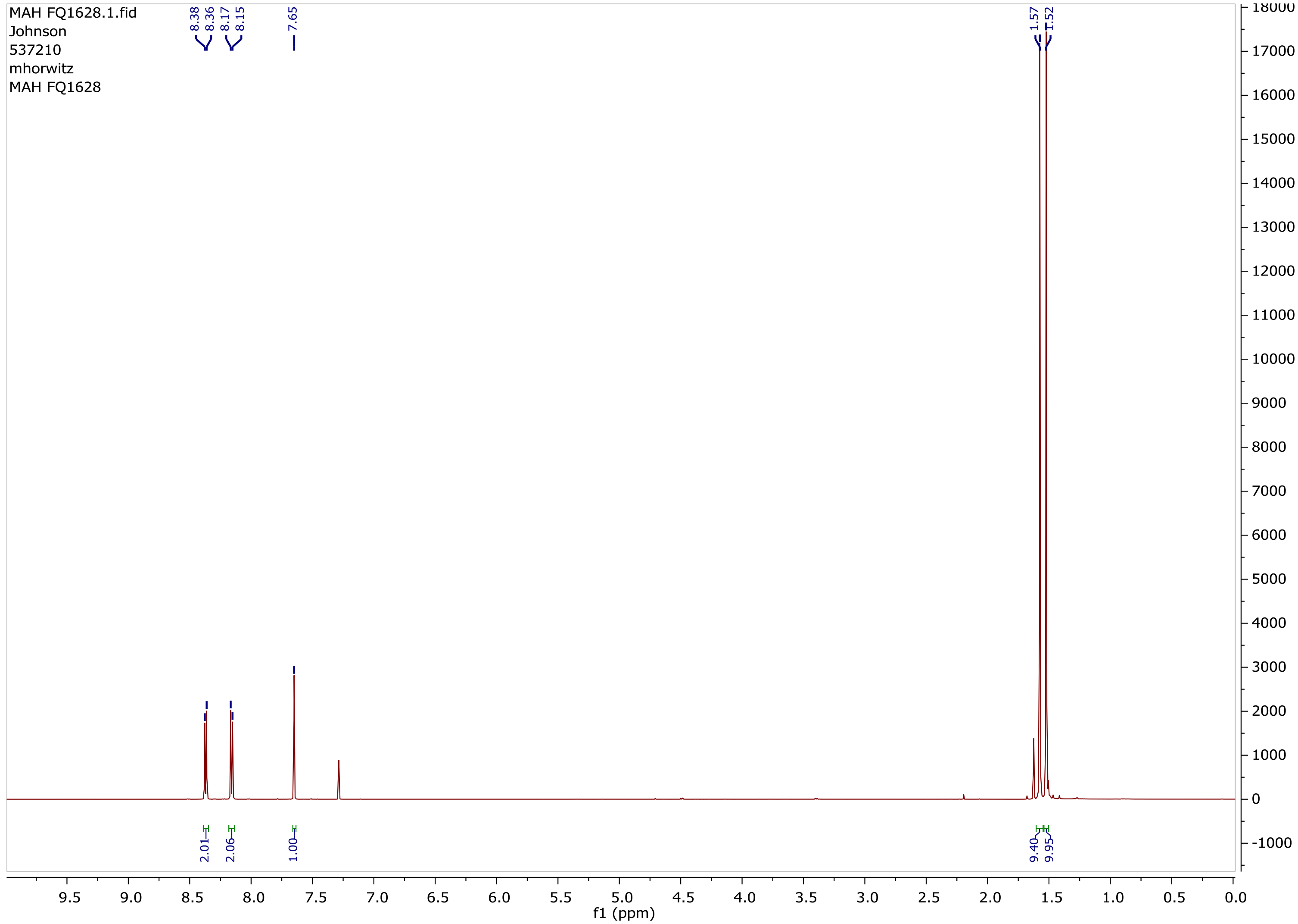

**1e**

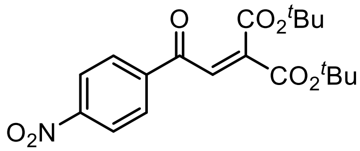


MAH FQ1623-13C.1.fid
188.3
163.3
161.8
140.4
139.2
132.7
131.6
129.2
117.8
117.1
83.7
83.5
27.9
27.8
f1 (ppm)

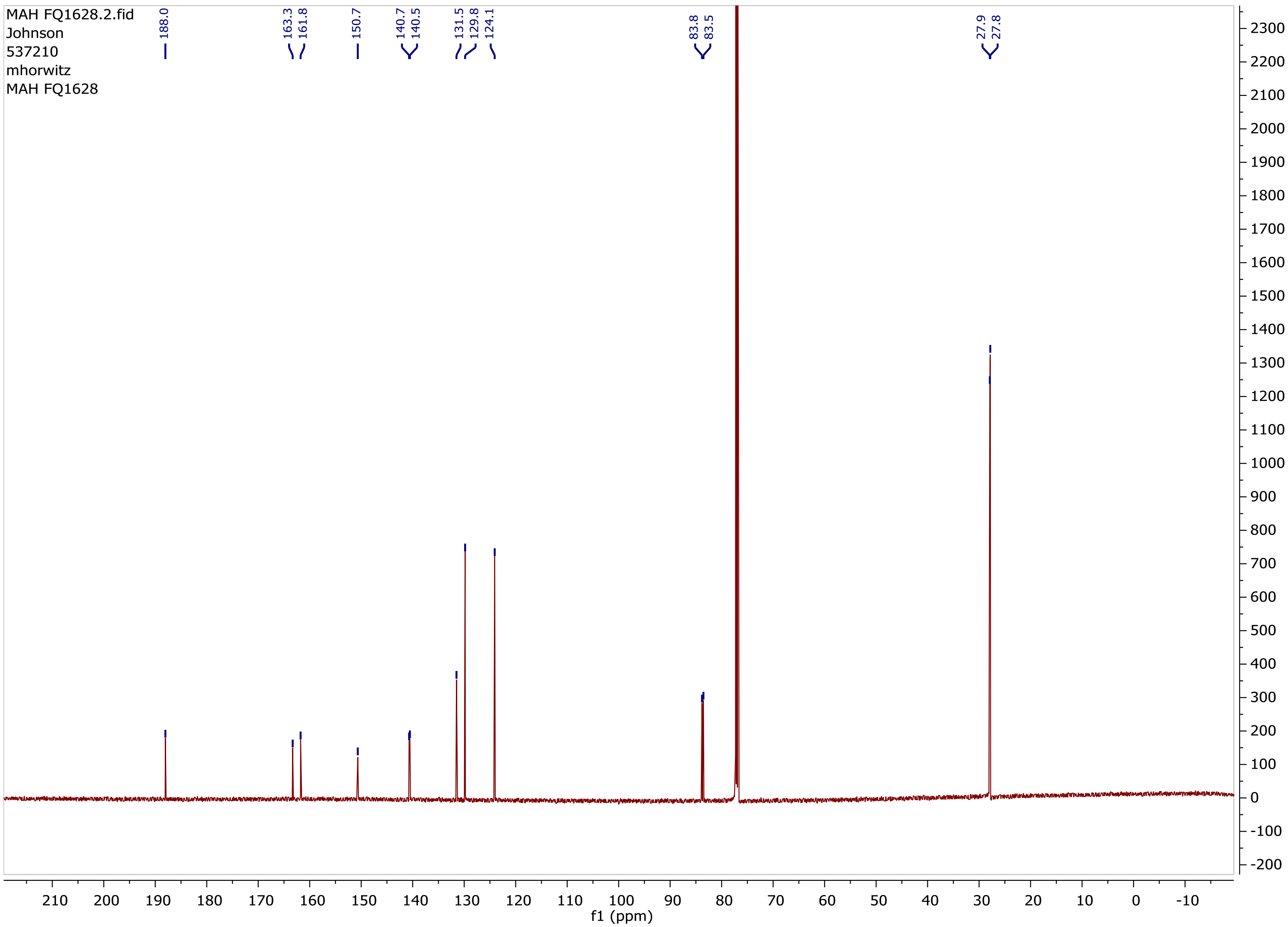


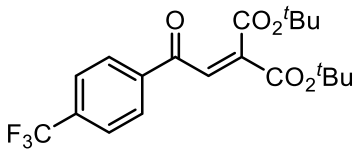
**1f**


MAH FQ1628.1.fid
Johnson
537210
mhorwitz
MAH FQ1628
8.38
8.36
8.17
8.15
7.65
1.57
1.52
2.01
2.06
1.00
9.40
9.95
f1 (ppm)


O
$CO_2{}^tBu$
$CO_2{}^tBu$
$O_2N$

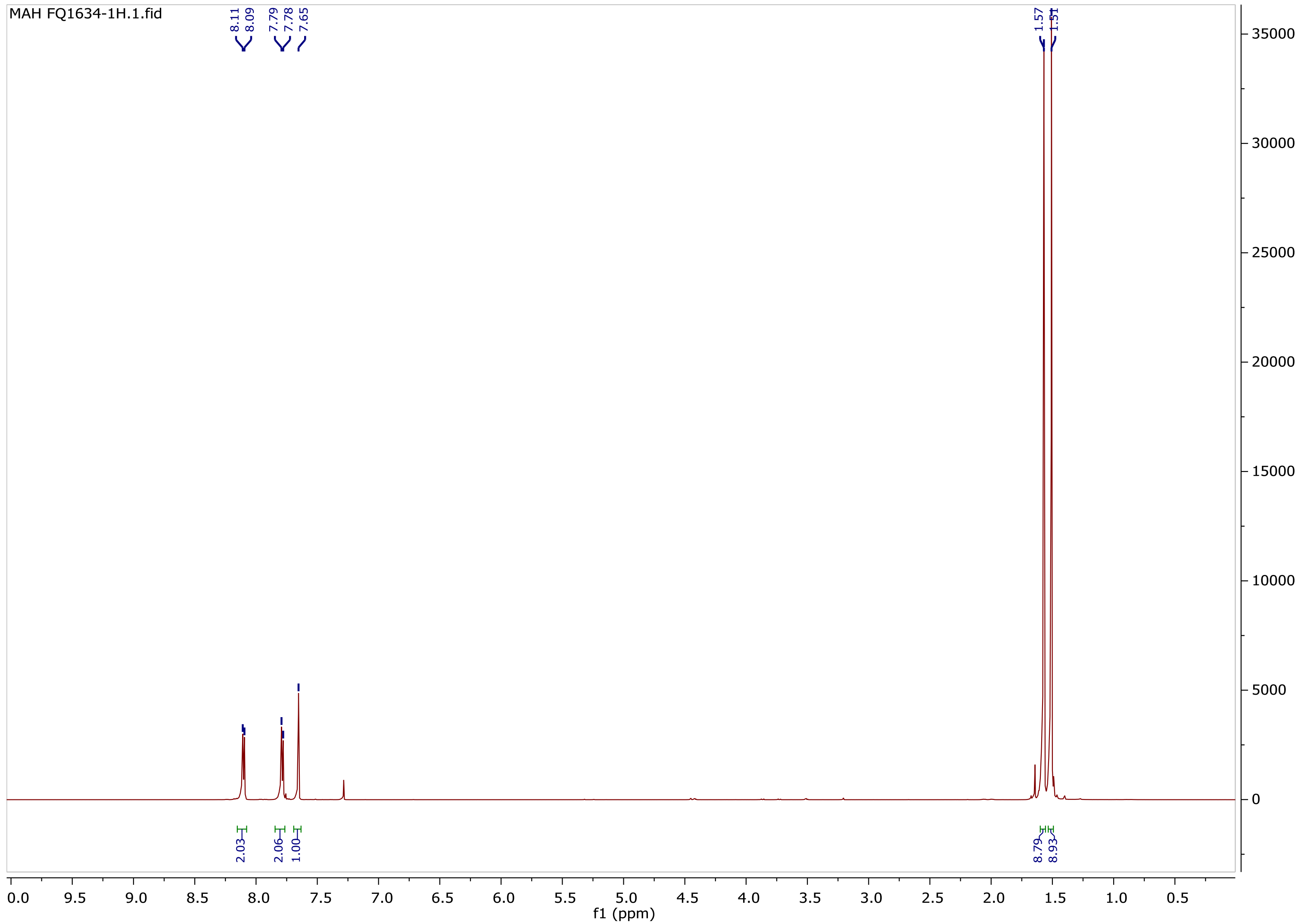
**1f**


MAH FQ1628.2.fid
Johnson
537210
mhorwitz
MAH FQ1628
188.0
163.3
161.8
150.7
140.7
140.5
131.5
129.8
124.1
83.8
83.5
27.9
27.8
f1 (ppm)

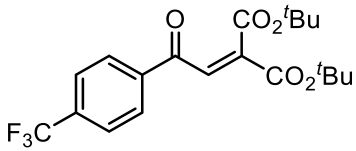


O
$CO_2{}^tBu$
$CO_2{}^tBu$
$F_3C$

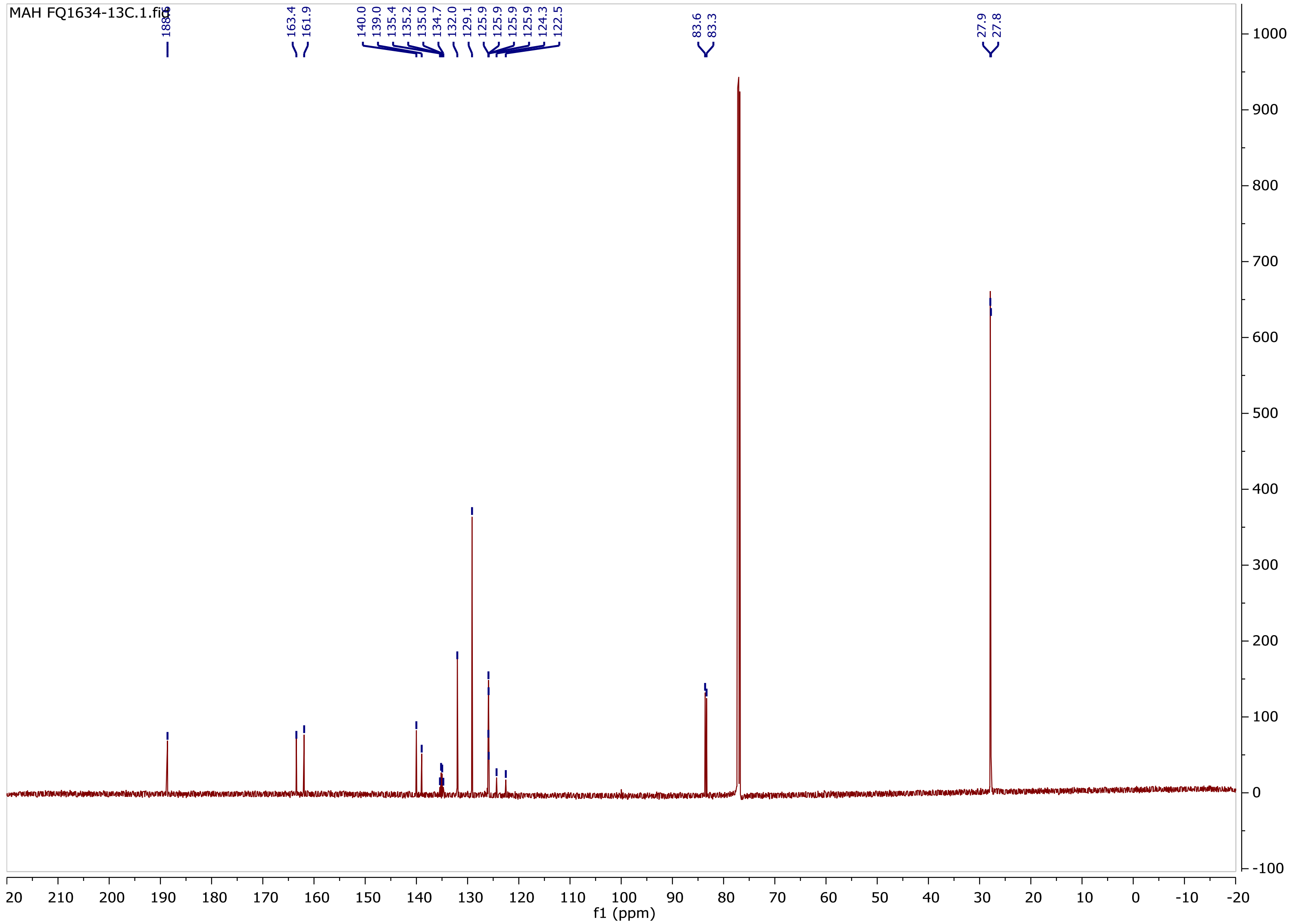

**1g**

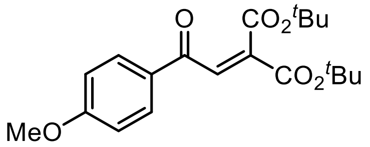


MAH FQ1634-1H.1.fid
8.11
8.09
7.79
7.78
7.65
1.57
1.51
2.03
2.06
1.00
8.79
8.93
f1 (ppm)

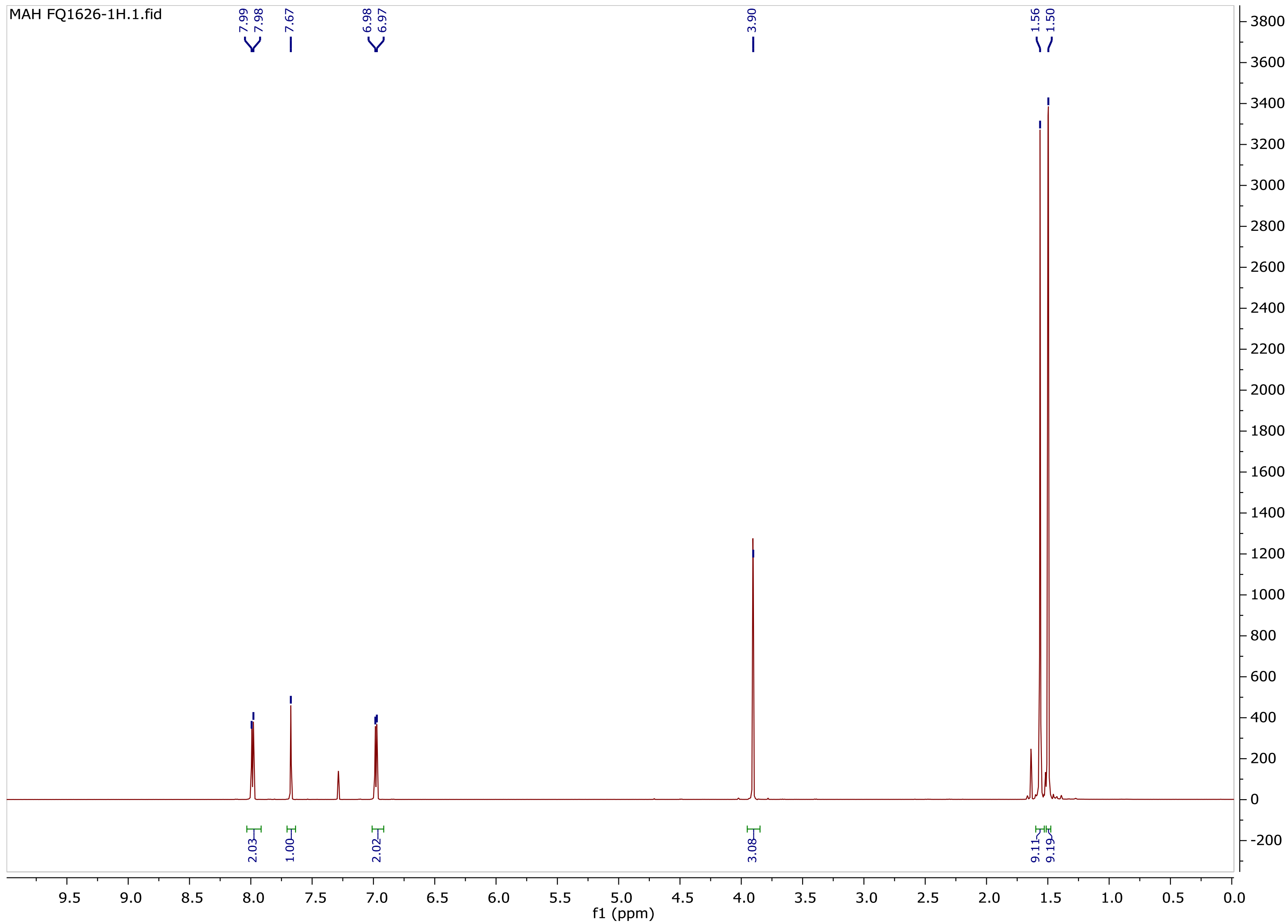

O
CO2tBu
CO2tBu
F3C

**1g**

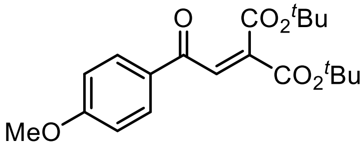

MAH FQ1634-13C.1.fid
188.6
163.4
161.9
140.0
139.0
135.4
135.2
135.0
134.7
132.0
129.1
125.9
125.9
125.9
125.9
124.3
122.5
83.6
83.3
27.9
27.8
f1 (ppm)



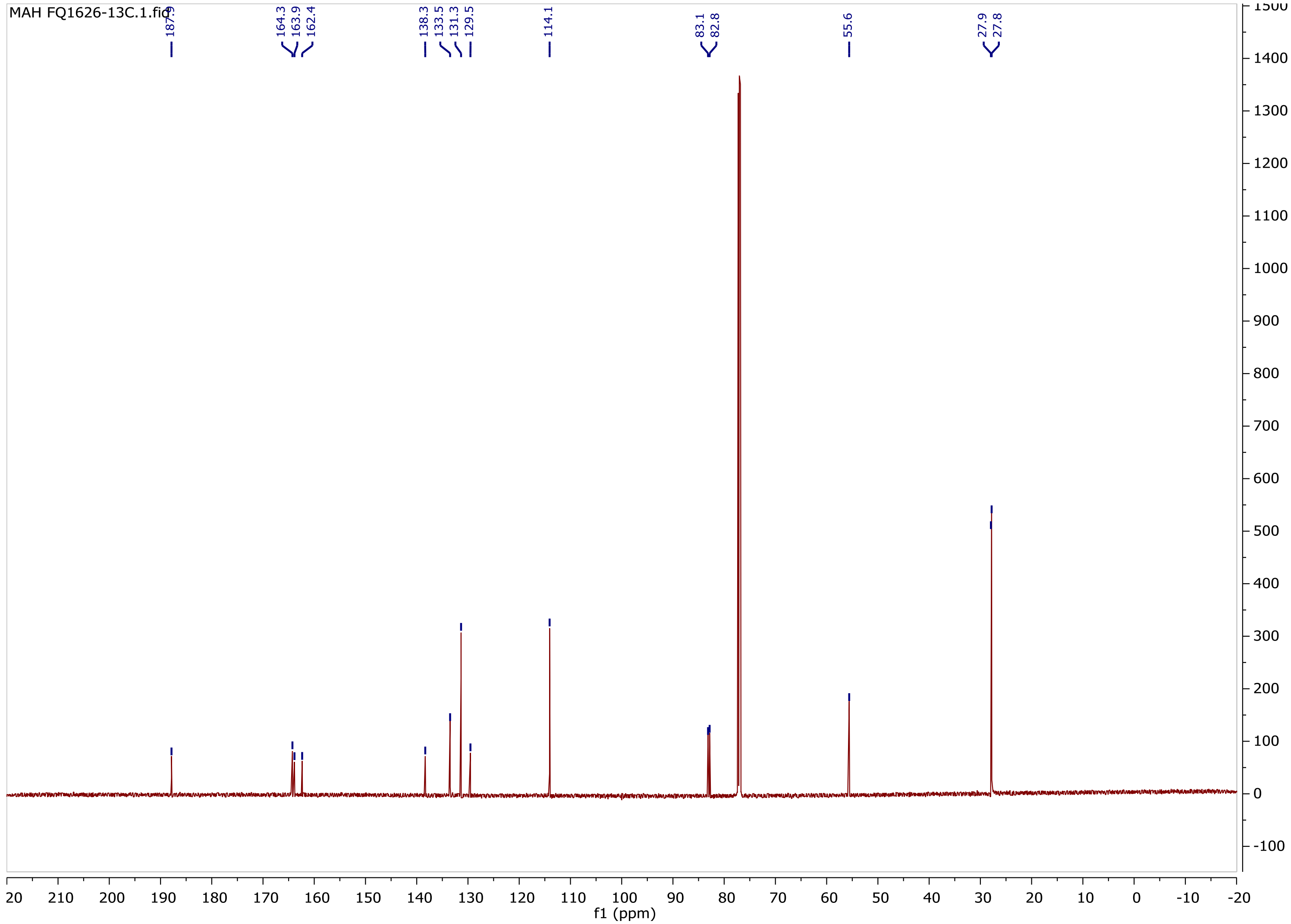
**1h**



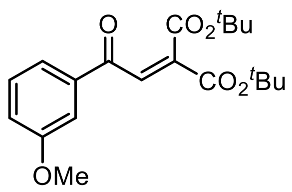
MAH FQ1626-1H.1.fid
7.99
7.98
7.67
6.98
6.97
3.90
1.56
1.50
2.03
1.00
2.02
3.08
9.11
9.19
f1 (ppm)



**1h**

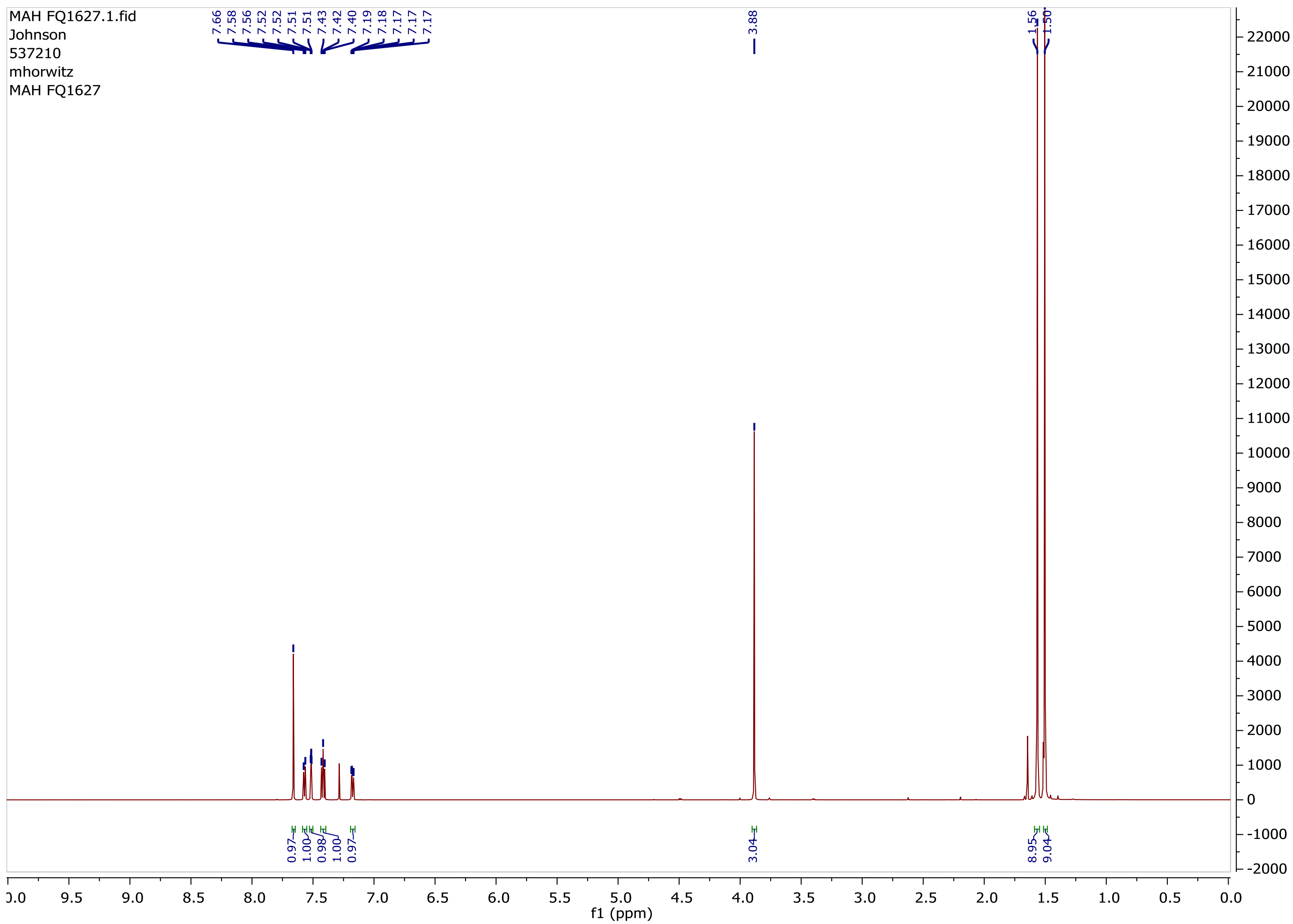


MAH FQ1626-13C.1.fid
187.9
164.3
163.9
162.4
138.3
133.5
131.3
129.5
114.1
83.1
82.8
55.6
27.9
27.8
f1 (ppm)

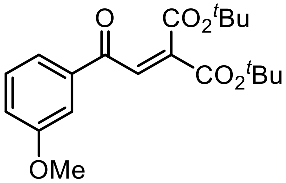


O
$CO_2{}^tBu$
$CO_2{}^tBu$
OMe

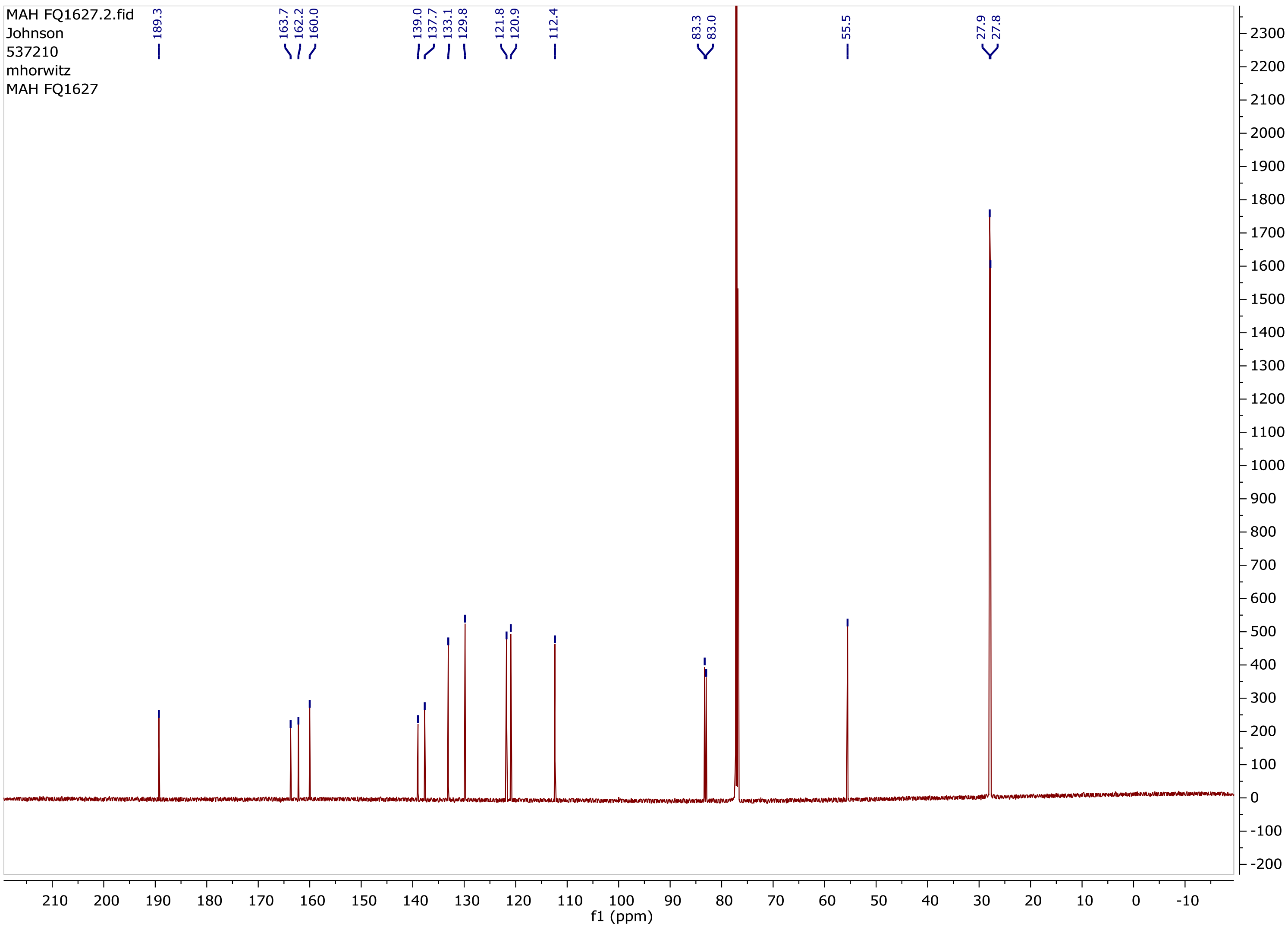

**1i**



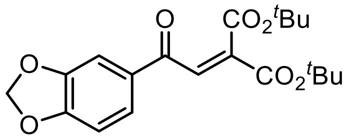
MAH FQ1627.1.fid
Johnson
537210
mhorwitz
MAH FQ1627
7.66 7.58 7.56 7.52 7.52 7.52 7.51 7.51 7.51 7.43 7.42 7.40 7.19 7.18 7.17 7.17 7.17
3.88
1.56 1.50
0.97 1.00 1.00 0.98 1.00 0.97
3.04
8.95 9.04
f1 (ppm)



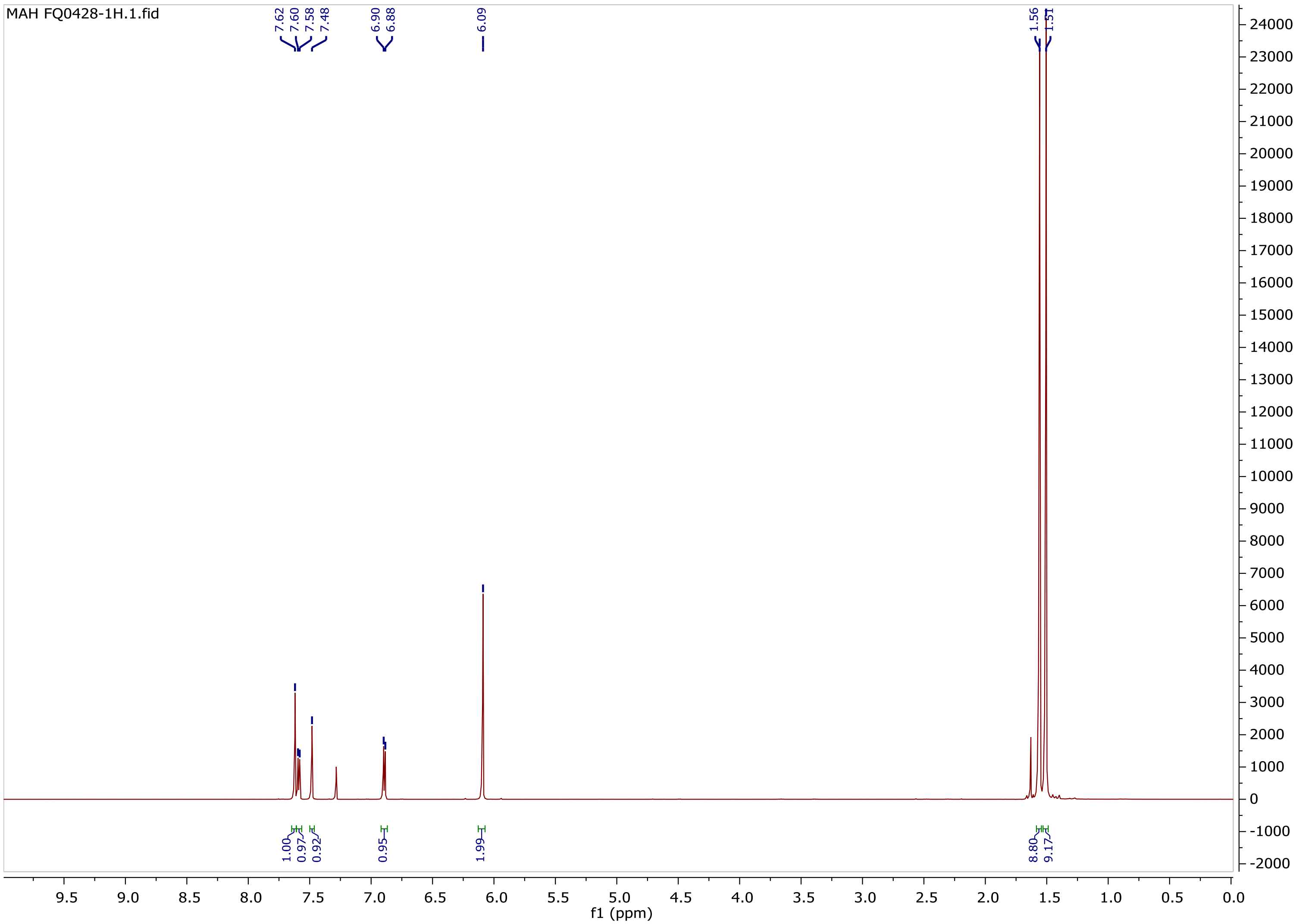
**1i**



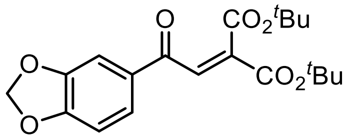
MAH FQ1627.2.fid
Johnson
537210
mhorwitz
MAH FQ1627
189.3
163.7
162.2
160.0
139.0
137.7
133.1
129.8
121.8
120.9
112.4
83.3
83.0
55.5
27.9
27.8
f1 (ppm)



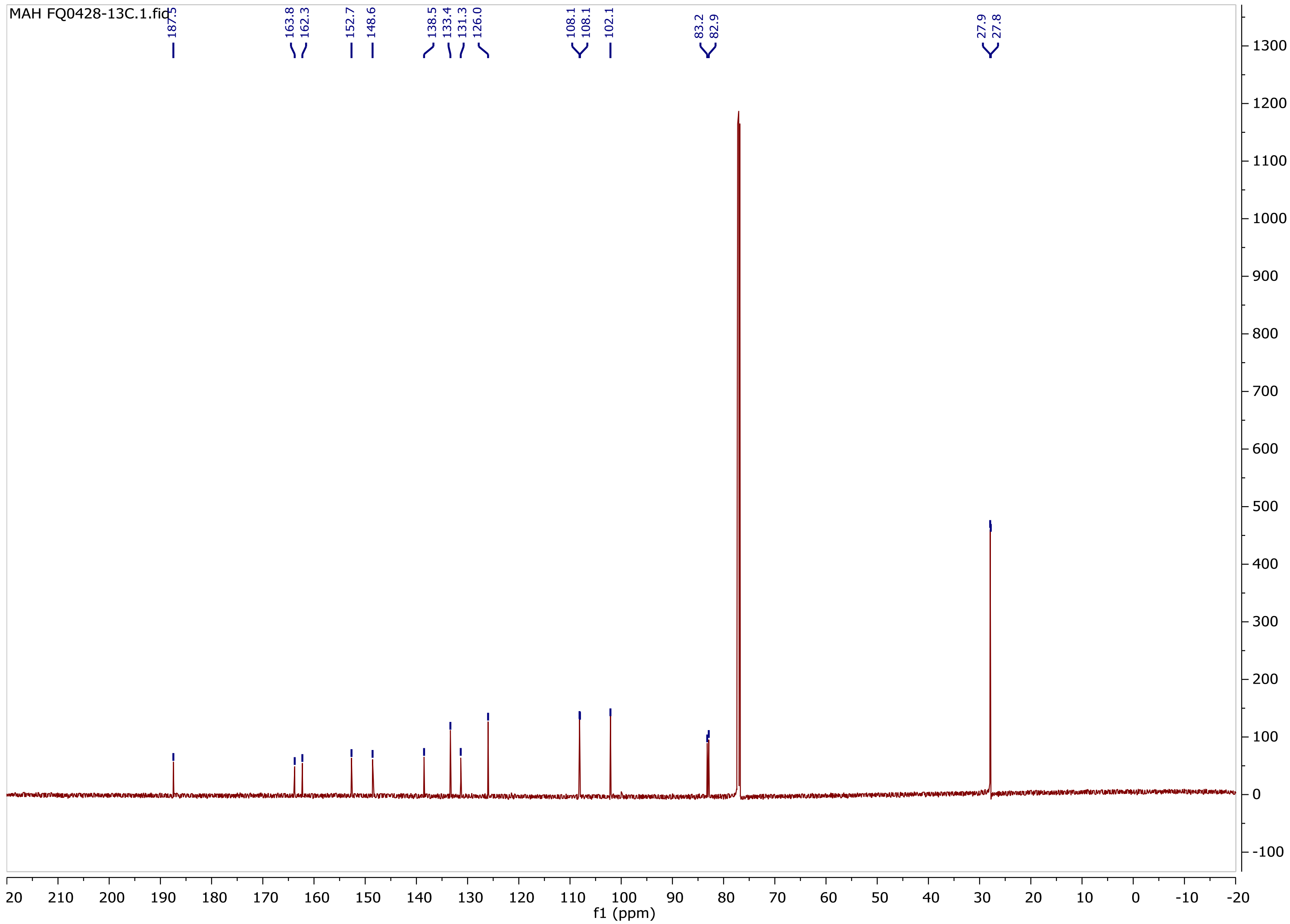
**1j**



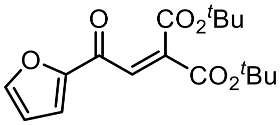
MAH FQ0428-1H.1.fid
7.62
7.60
7.58
7.48
6.90
6.88
6.09
1.56
1.51
1.00
0.97
0.92
0.95
1.99
8.80
9.17
f1 (ppm)



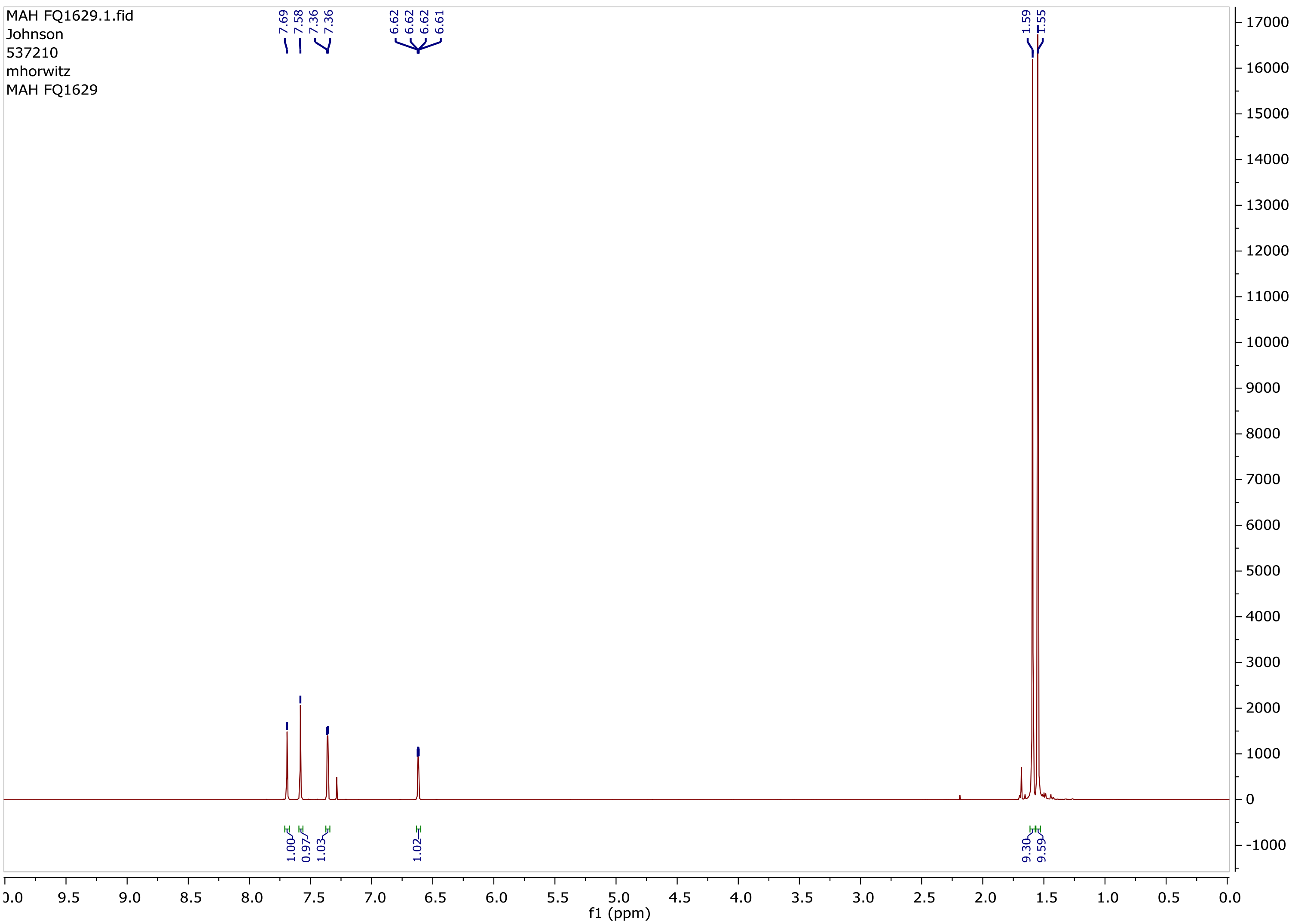
**1j**

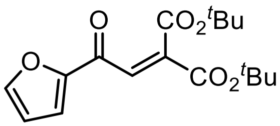


MAH FQ0428-13C.1.fid
187.5
163.8
162.3
152.7
148.6
138.5
133.4
131.3
126.0
108.1
108.1
102.1
83.2
82.9
27.9
27.8
f1 (ppm)

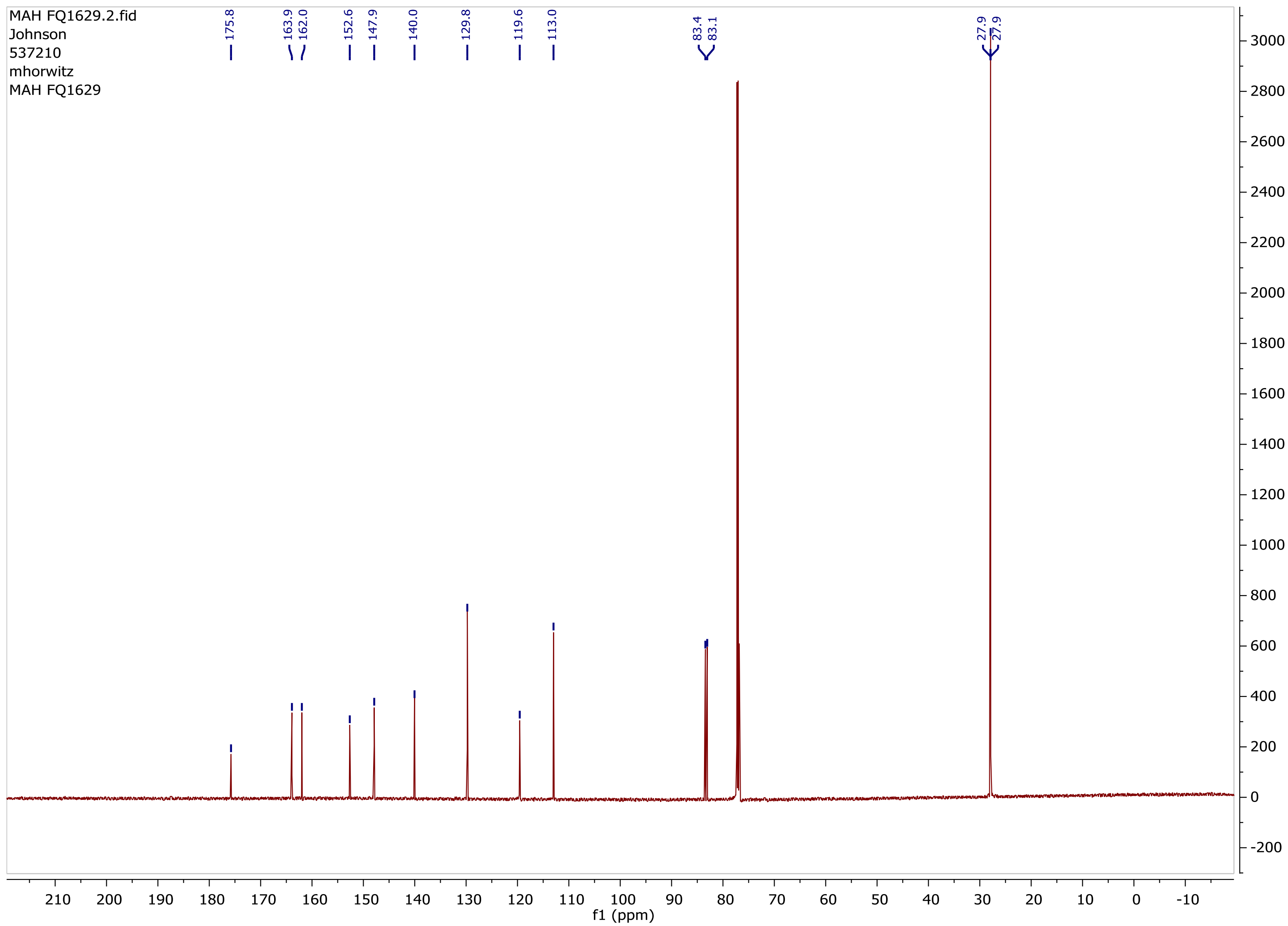


**1k**

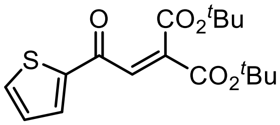

MAH FQ1629.1.fid
Johnson
537210
mhorwitz
MAH FQ1629
7.69
7.58
7.36
7.36
6.62
6.62
6.62
6.61
1.59
1.55
1.00
0.97
1.03
1.02
9.30
9.59
f1 (ppm)



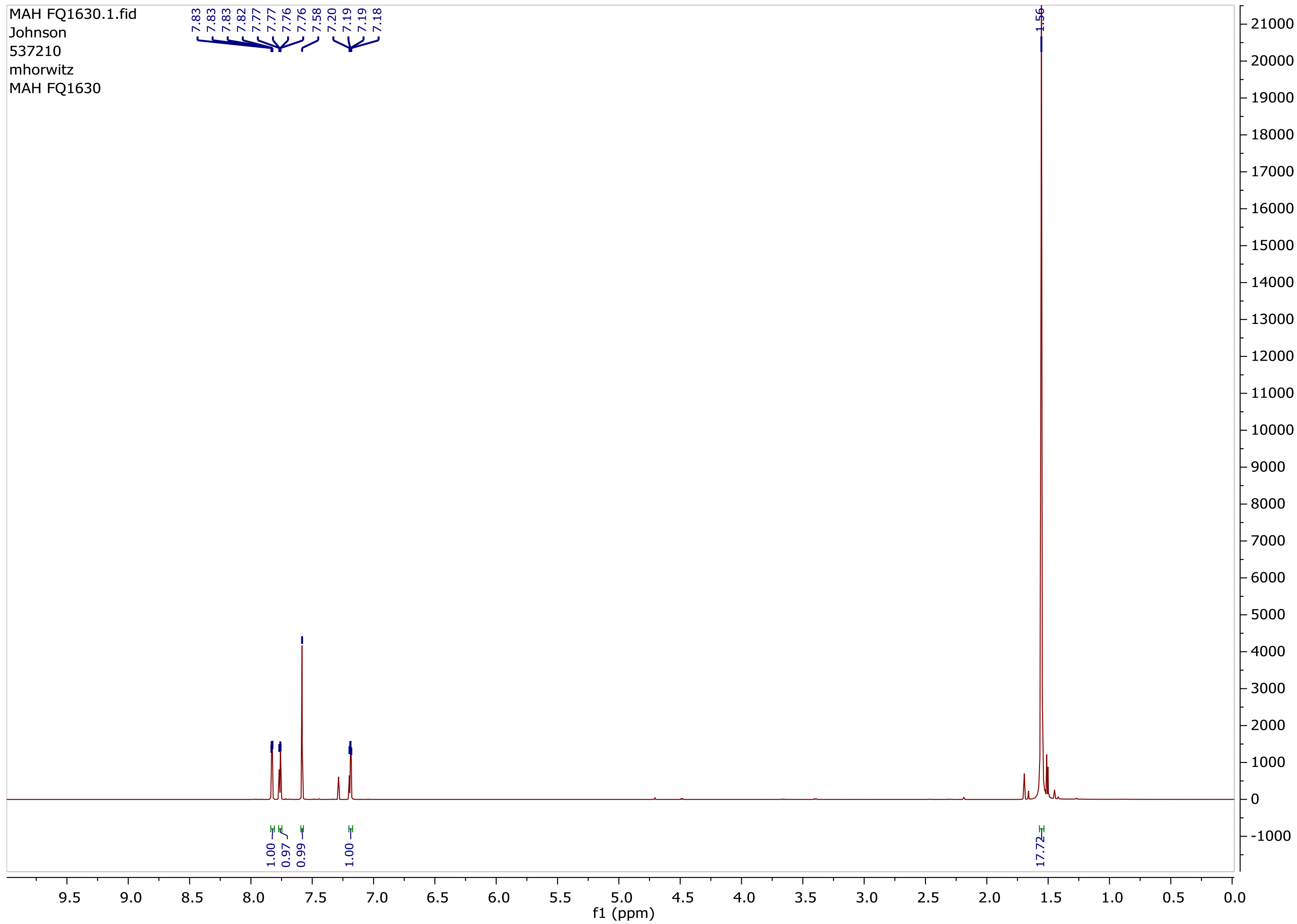
**1k**



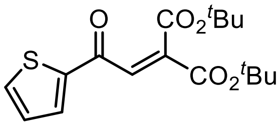
MAH FQ1629.2.fid
Johnson
537210
mhorwitz
MAH FQ1629
175.8
163.9
162.0
152.6
147.9
140.0
129.8
119.6
113.0
83.4
83.1
27.9
27.9
f1 (ppm)



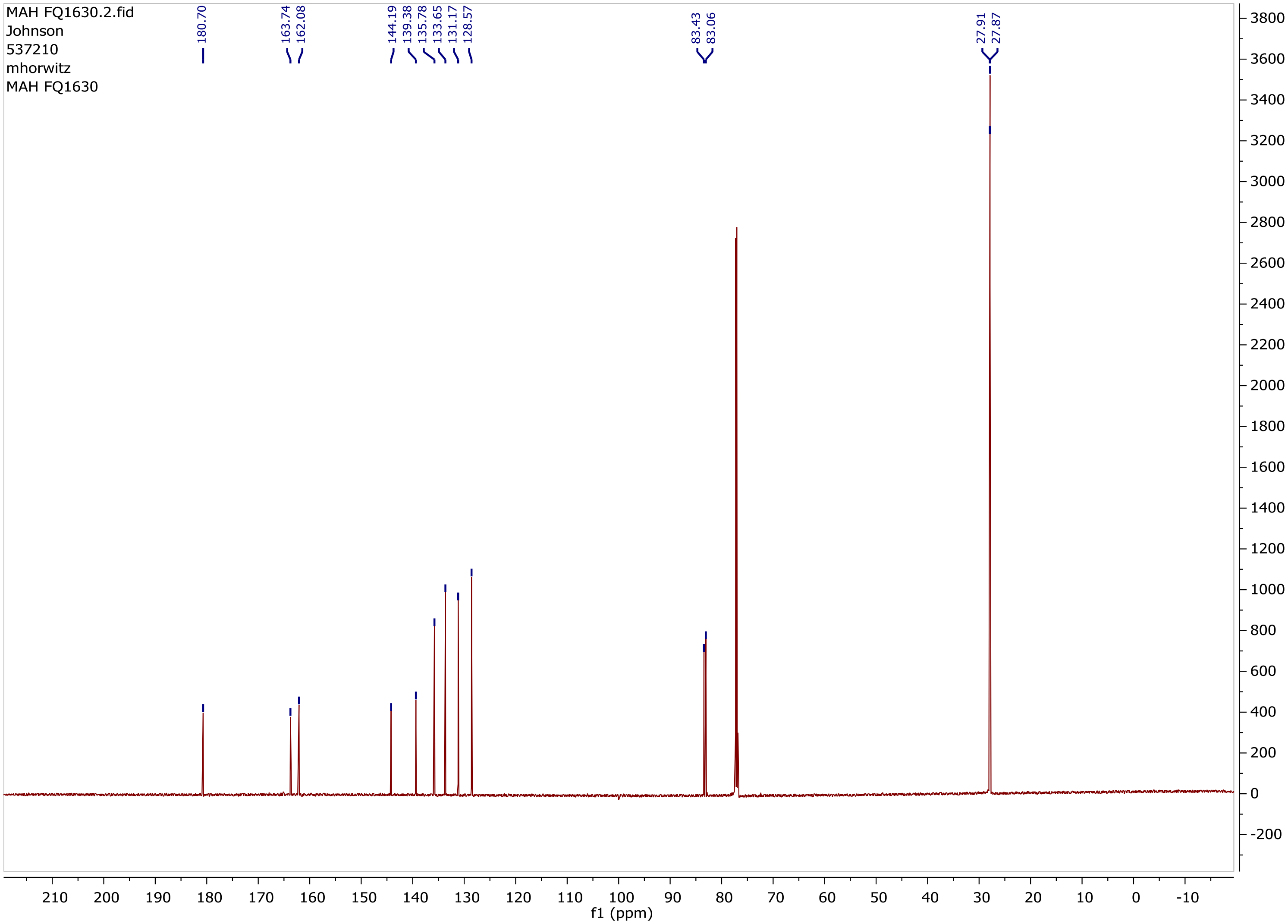
**1l**

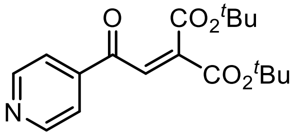


MAH FQ1630.1.fid
Johnson
537210
mhorwitz
MAH FQ1630
7.83
7.83
7.83
7.82
7.77
7.77
7.76
7.76
7.58
7.20
7.19
7.19
7.18
1.56
1.00
0.97
0.99
1.00
17.72
f1 (ppm)

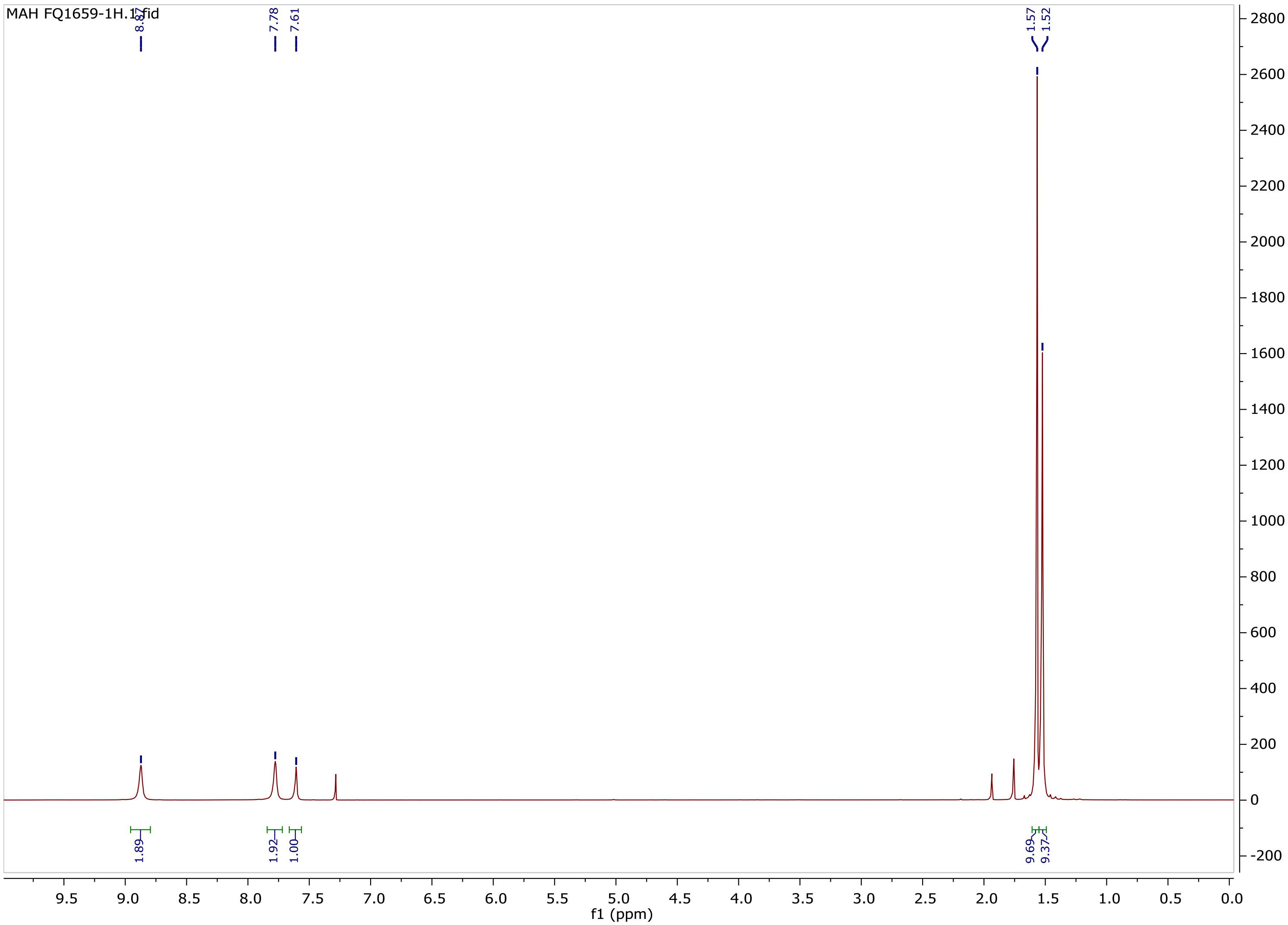


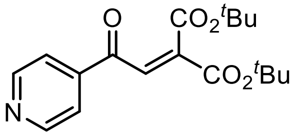
**1l**


MAH FQ1630.2.fid
Johnson
537210
mhorwitz
MAH FQ1630
180.70
163.74
162.08
144.19
139.38
135.78
133.65
131.17
128.57
83.43
83.06
27.91
27.87
f1 (ppm)

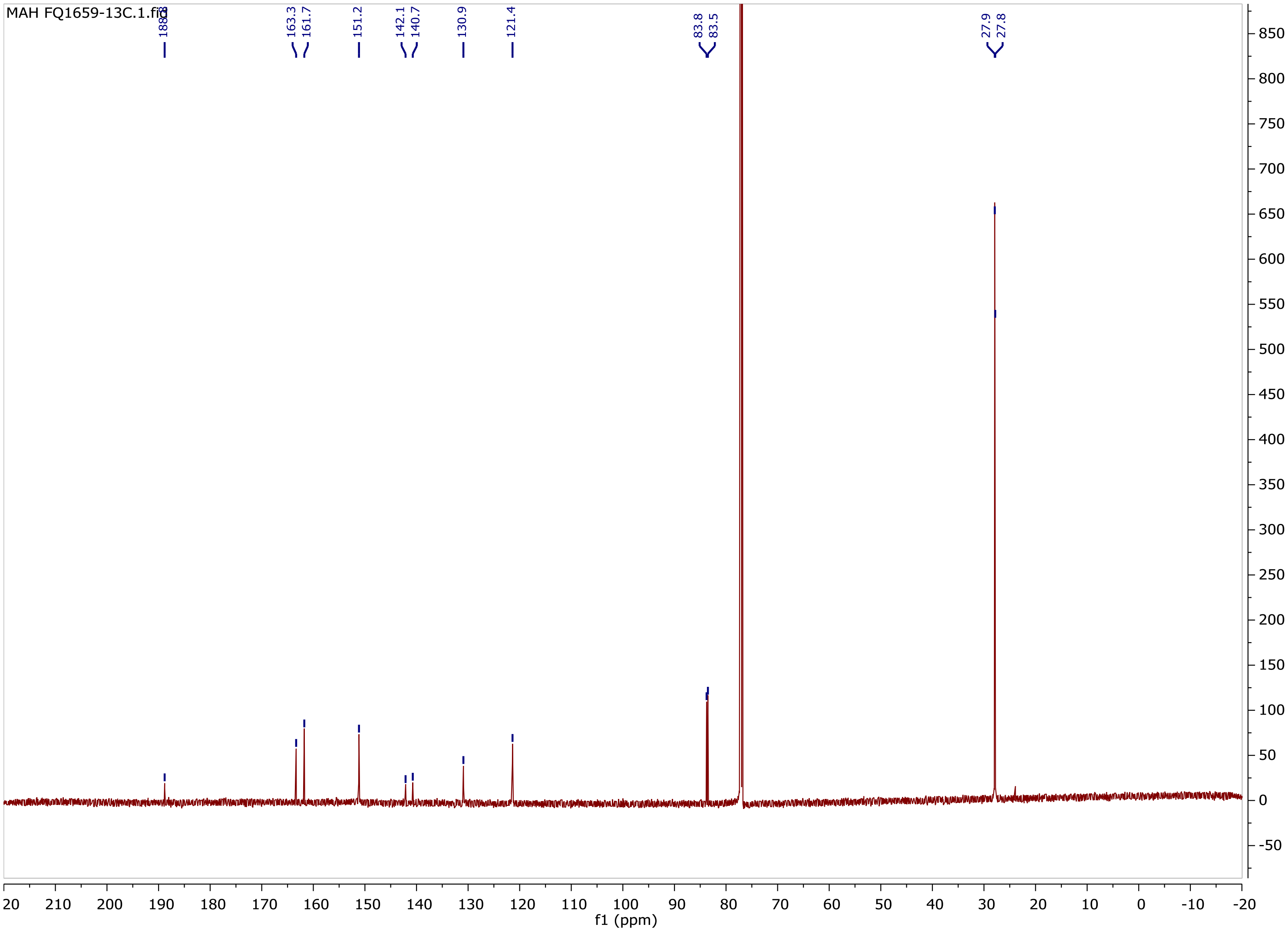


**1m**

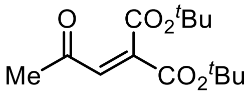

MAH FQ1659-1H.1.fid
8.87
7.78
7.61
1.57
1.52
1.89
1.92
1.00
9.69
9.37
f1 (ppm)



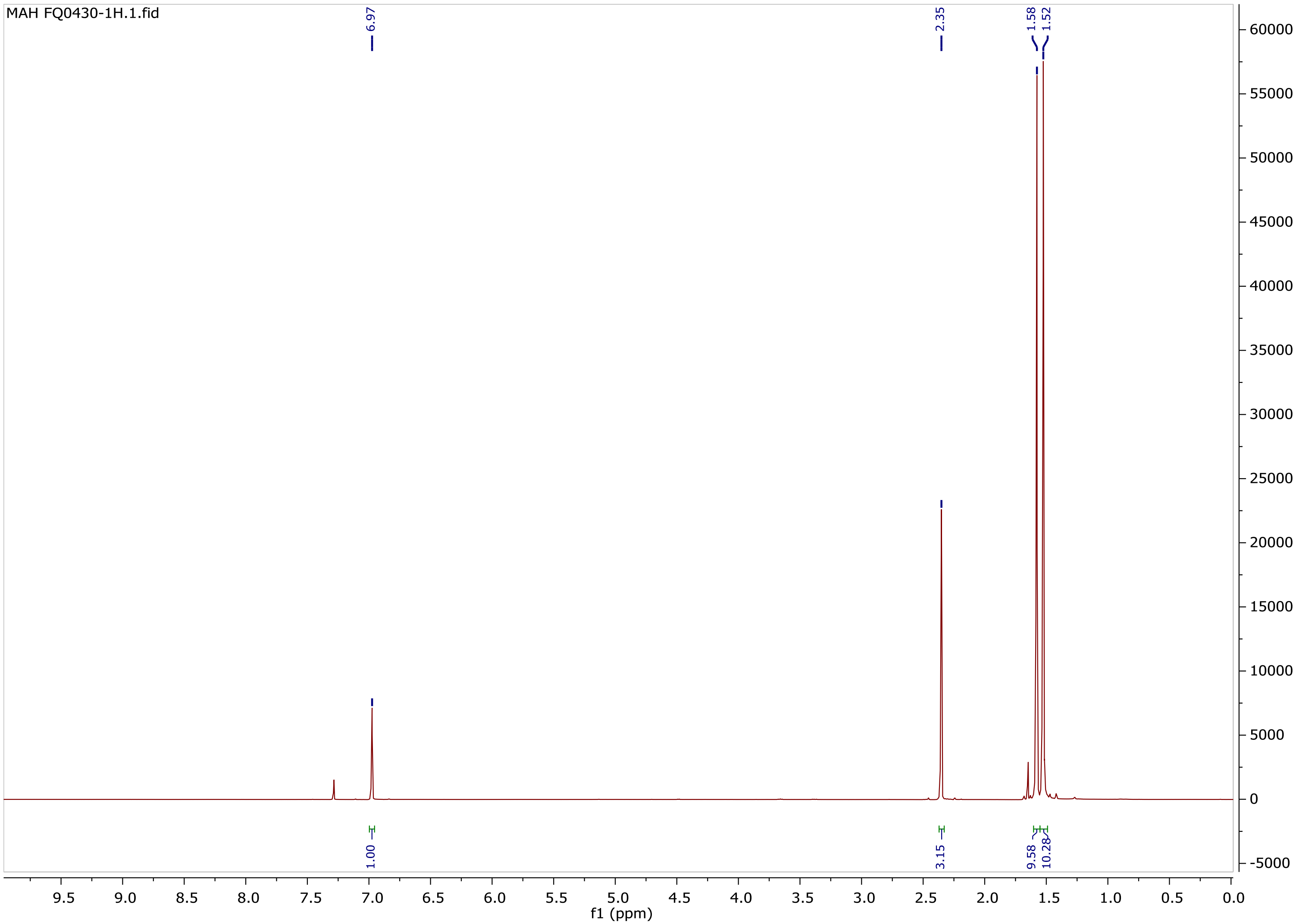
**1m**

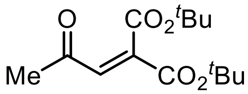


MAH FQ1659-13C.1.fid
163.3
161.7
151.2
142.1
140.7
130.9
121.4
83.8
83.5
27.9
27.8
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

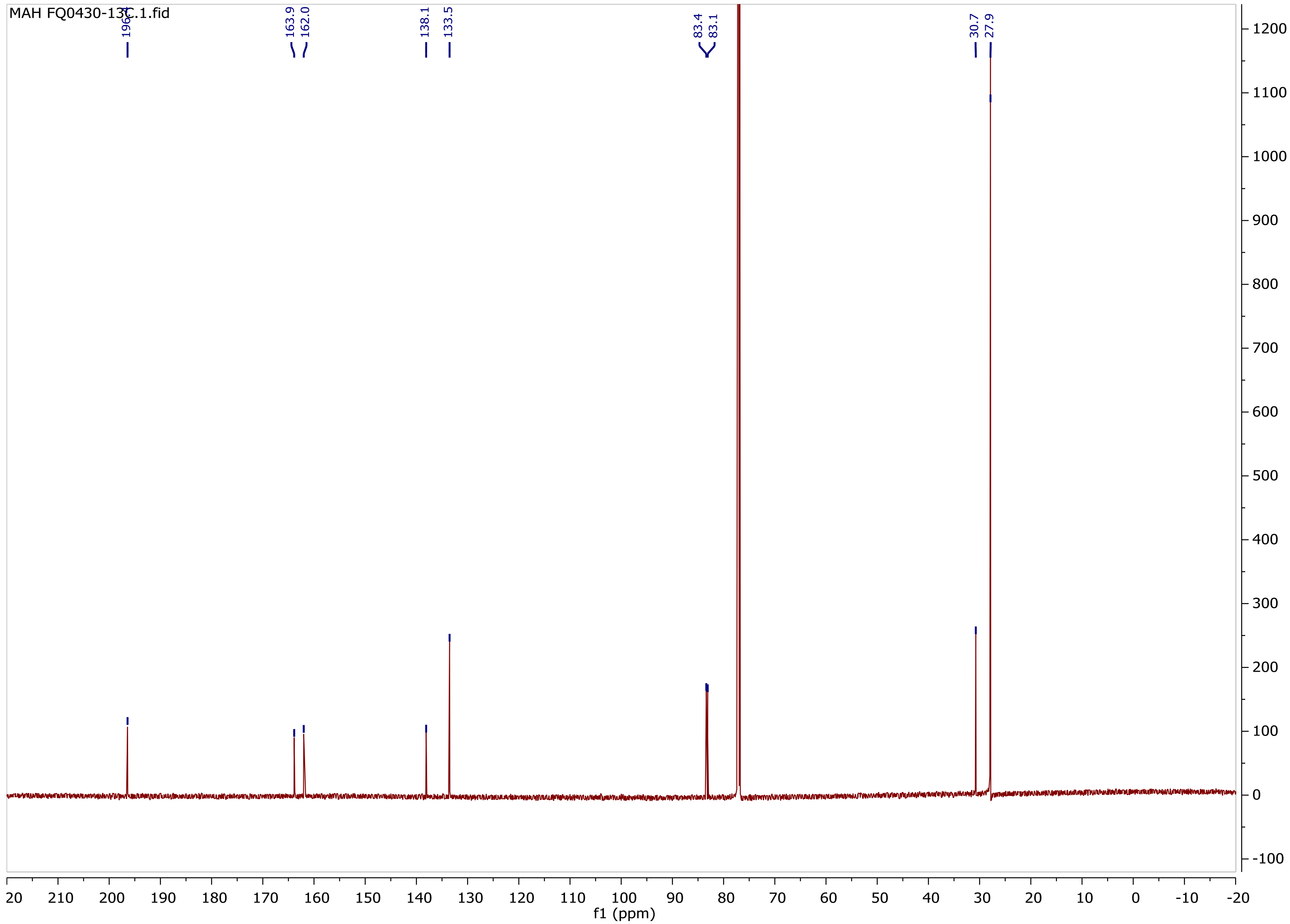

Me
O
$CO_2{}^tBu$
$CO_2{}^tBu$

**1n**

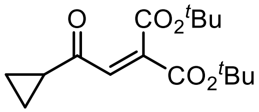

MAH FQ0430-1H.1.fid
6.97
2.35
1.58
1.52
1.00
3.15
9.58
10.28
f1 (ppm)



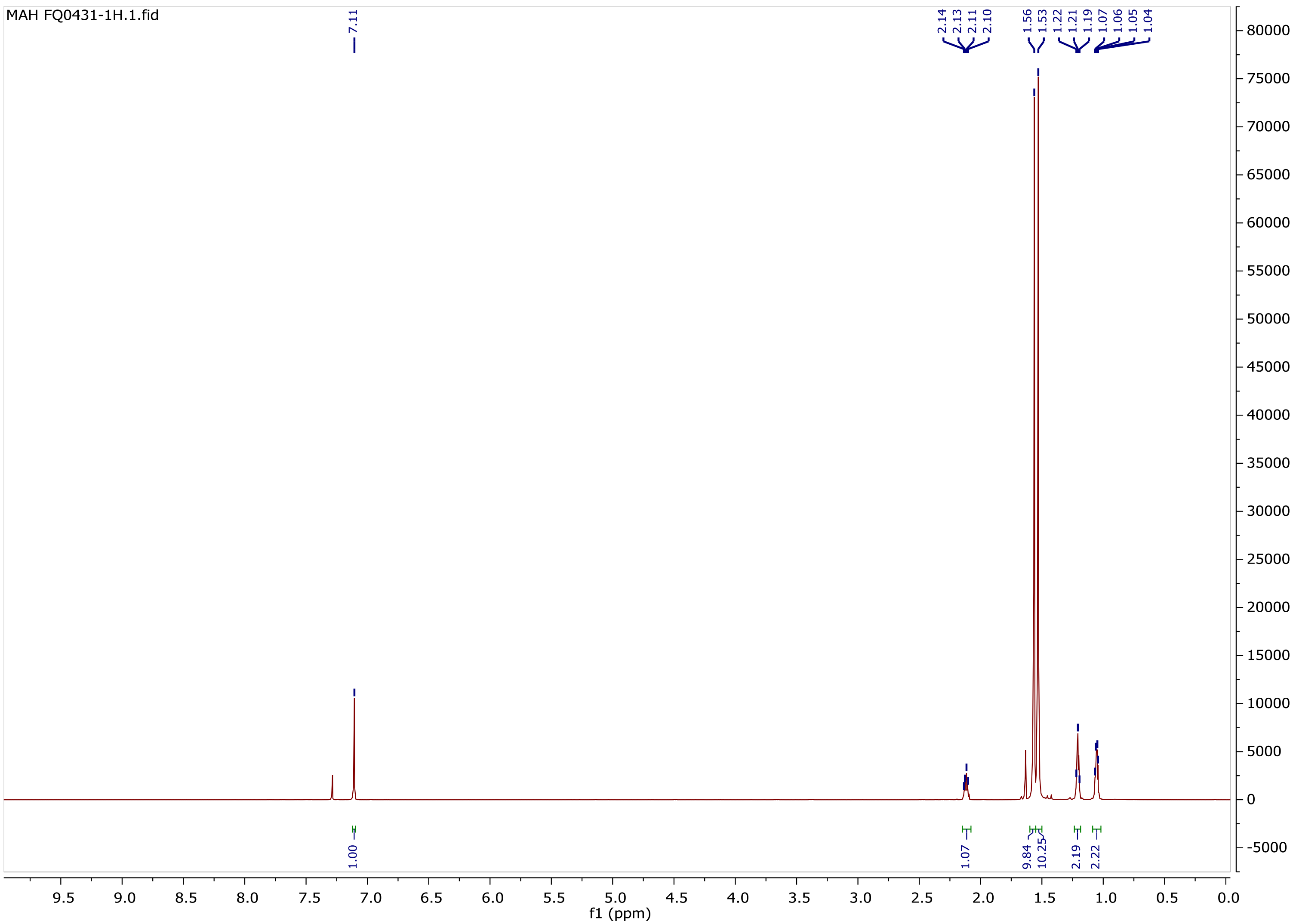
**1n**

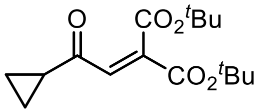


MAH FQ0430-13C.1.fid
196.7
163.9
162.0
138.1
133.5
83.4
83.1
30.7
27.9
f1 (ppm)

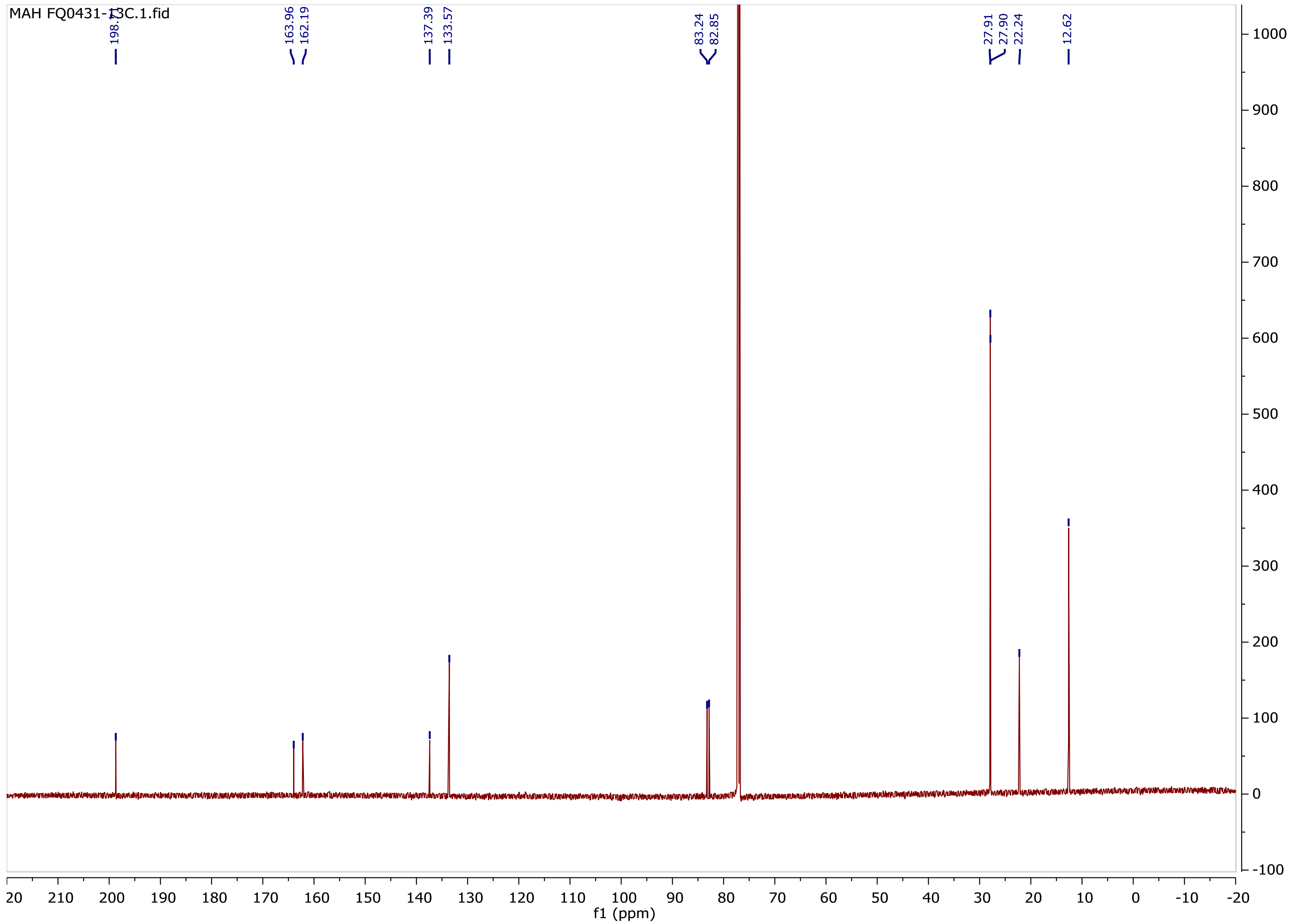


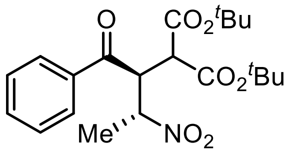
**1o**


MAH FQ0431-1H.1.fid
7.11
2.14
2.13
2.11
2.10
1.56
1.53
1.22
1.21
1.19
1.07
1.06
1.05
1.04
1.00
1.07
9.84
10.25
2.19
2.22
f1 (ppm)

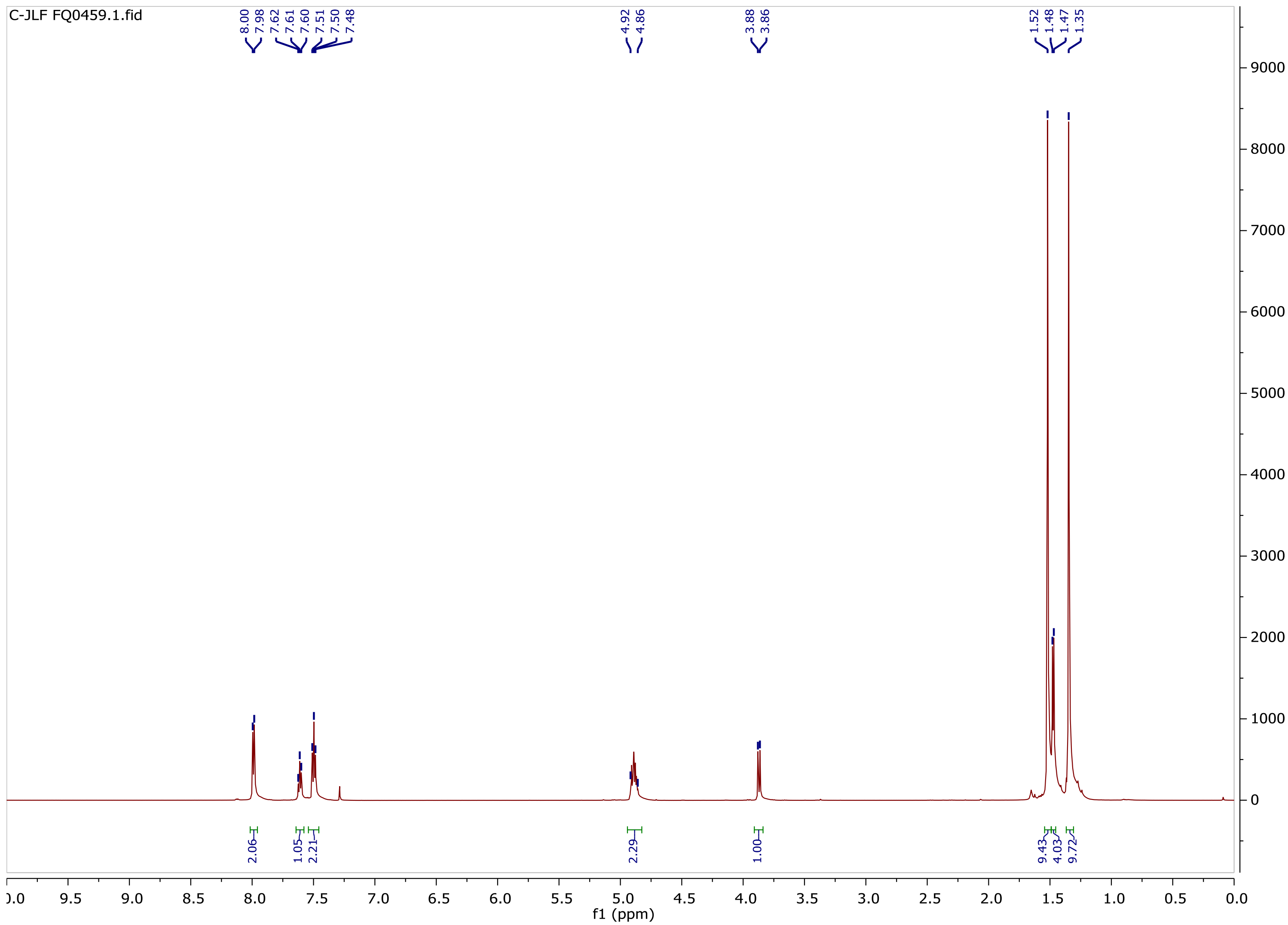

O
CO2tBu
CO2tBu

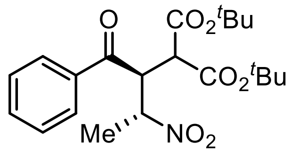
**1o**


MAH FQ0431-13C.1.fid
198.1
163.96
162.19
137.39
133.57
83.24
82.85
27.91
27.90
22.24
12.62
1000
900
800
700
600
500
400
300
200
100
0
-100
f1 (ppm)

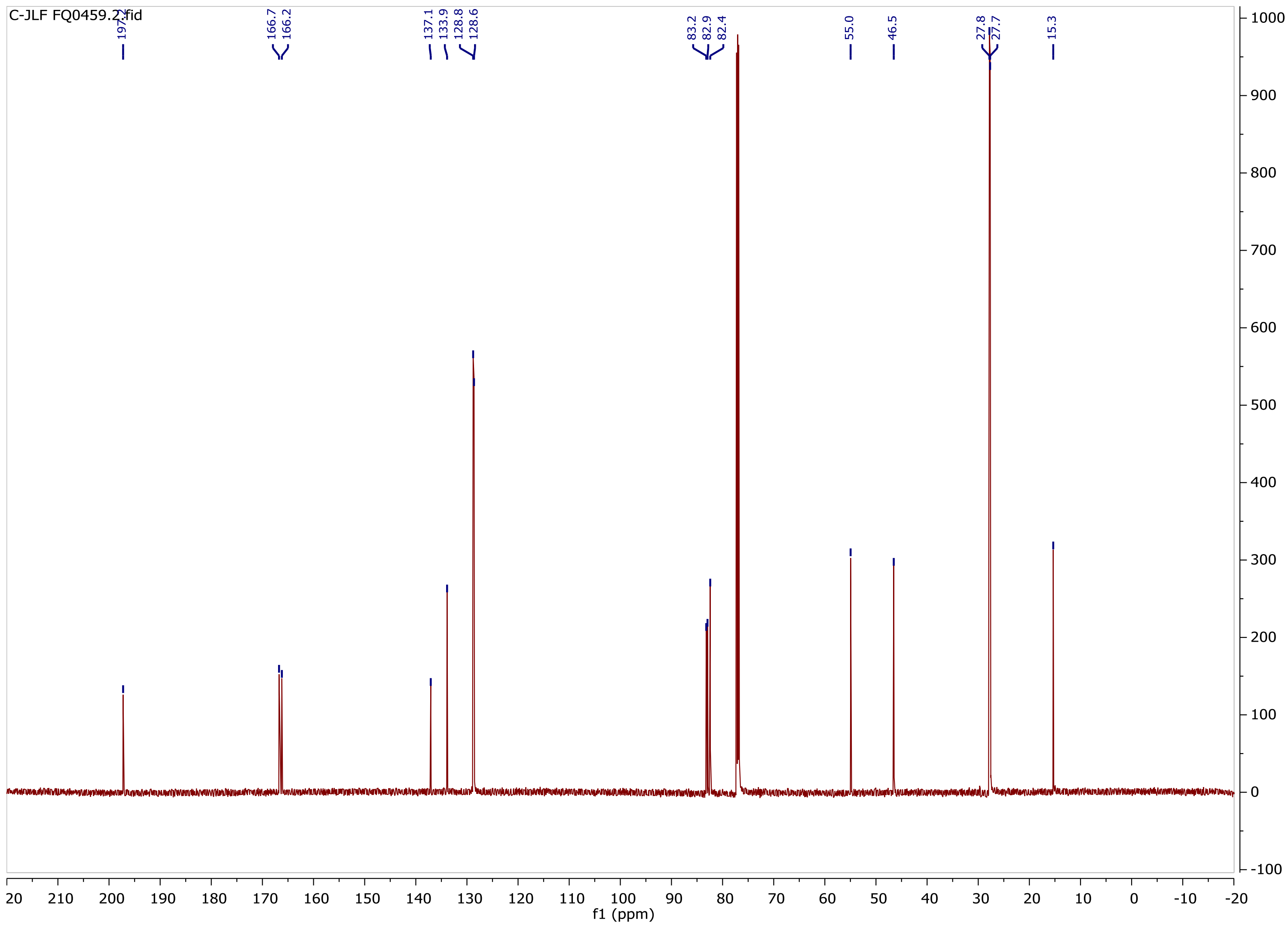

O
CO2tBu
CO2tBu
Me
NO2

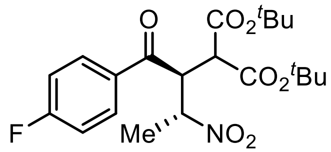
**2a**


C-JLF FQ0459.1.fid
8.00
7.98
7.62
7.61
7.60
7.51
7.50
7.48
4.92
4.86
3.88
3.86
1.52
1.48
1.47
1.35
2.06
1.05
2.21
2.29
1.00
9.43
4.03
9.72
f1 (ppm)

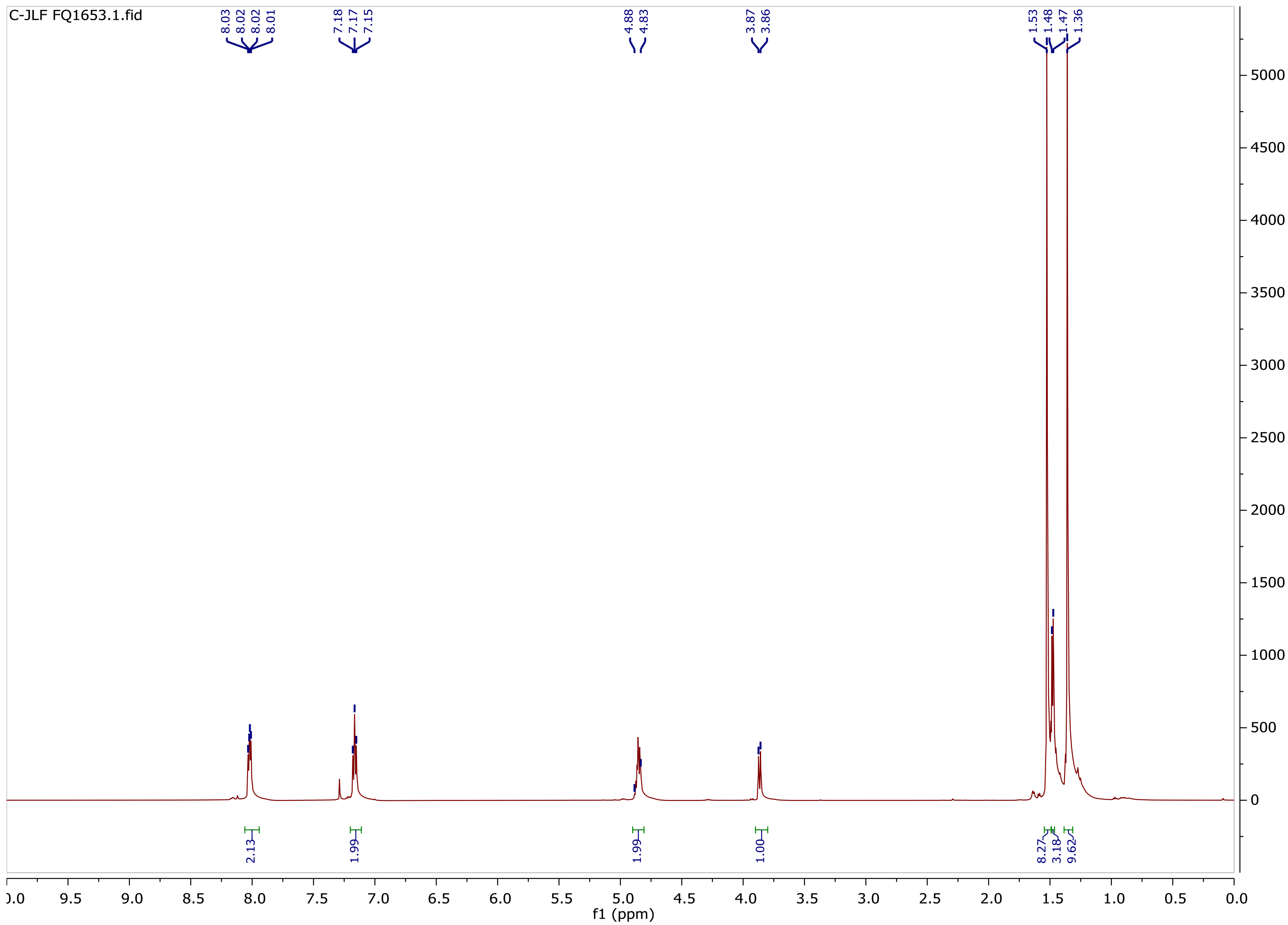

O
CO2tBu
CO2tBu
Me
NO2

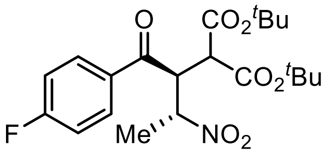
**2a**


C-JLF FQ0459.2.fid
197.2
166.7
166.2
137.1
133.9
128.8
128.6
83.2
82.9
82.4
55.0
46.5
27.8
27.7
15.3
f1 (ppm)

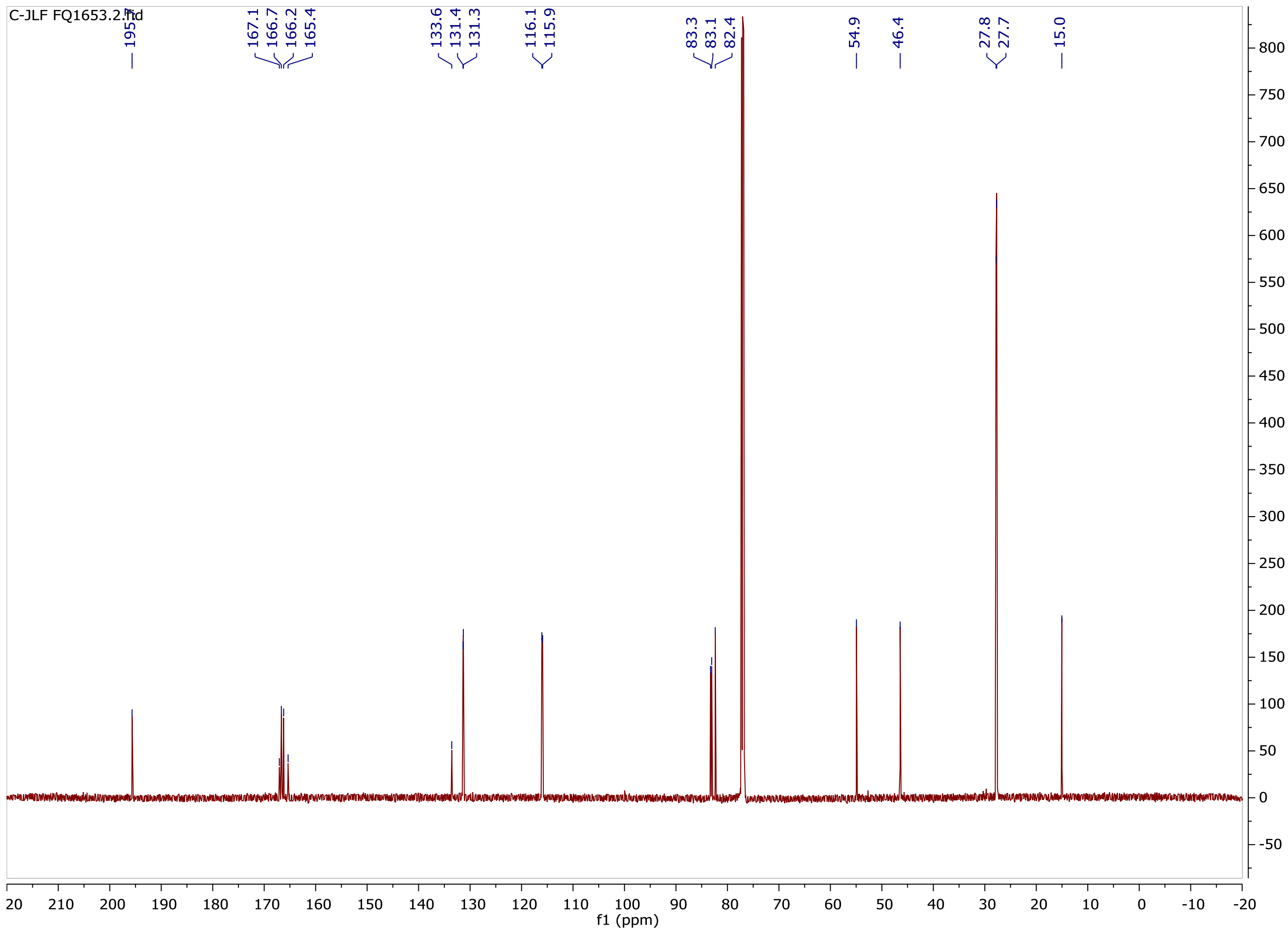

O
$CO_2{}^tBu$
$CO_2{}^tBu$
F
Me
$NO_2$

**2b**

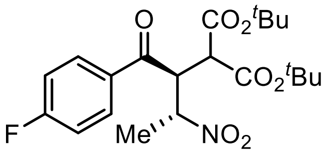

C-JLF FQ1653.1.fid
8.03
8.02
8.02
8.01
7.18
7.17
7.15
4.88
4.83
3.87
3.86
1.53
1.48
1.47
1.36
2.13
1.99
1.99
1.00
8.27
3.18
9.62
f1 (ppm)



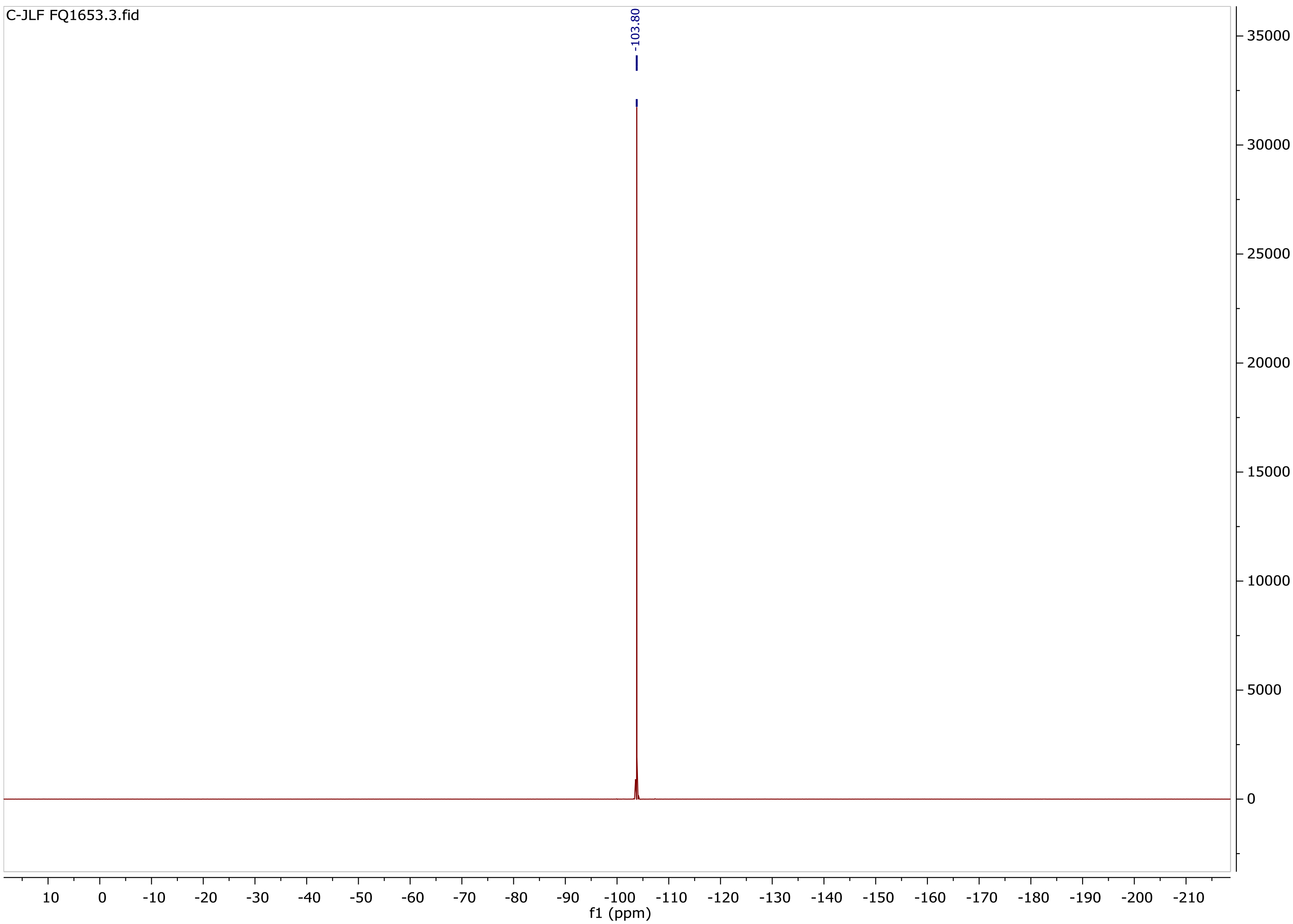
**2b**



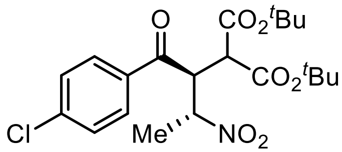
C-JLF FQ1653.2.fid
195.7
167.1
166.7
166.2
165.4
133.6
131.4
131.3
116.1
115.9
83.3
83.1
82.4
54.9
46.4
27.8
27.7
15.0
f1 (ppm)



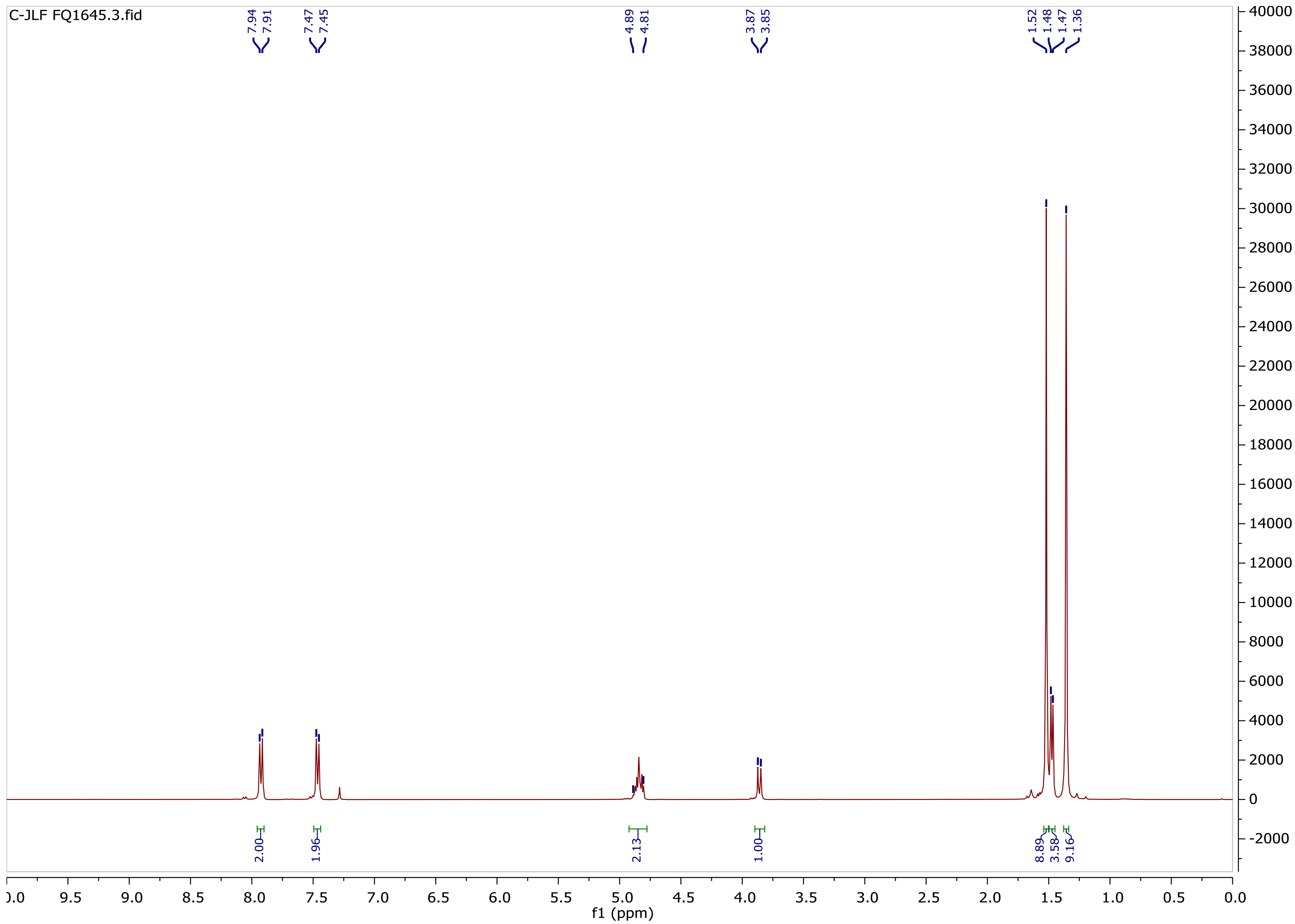
**2b**

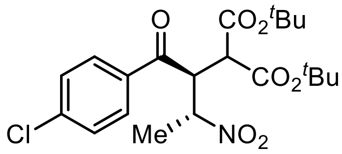


C-JLF FQ1653.3.fid
-103.80
35000
30000
25000
20000
15000
10000
5000
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



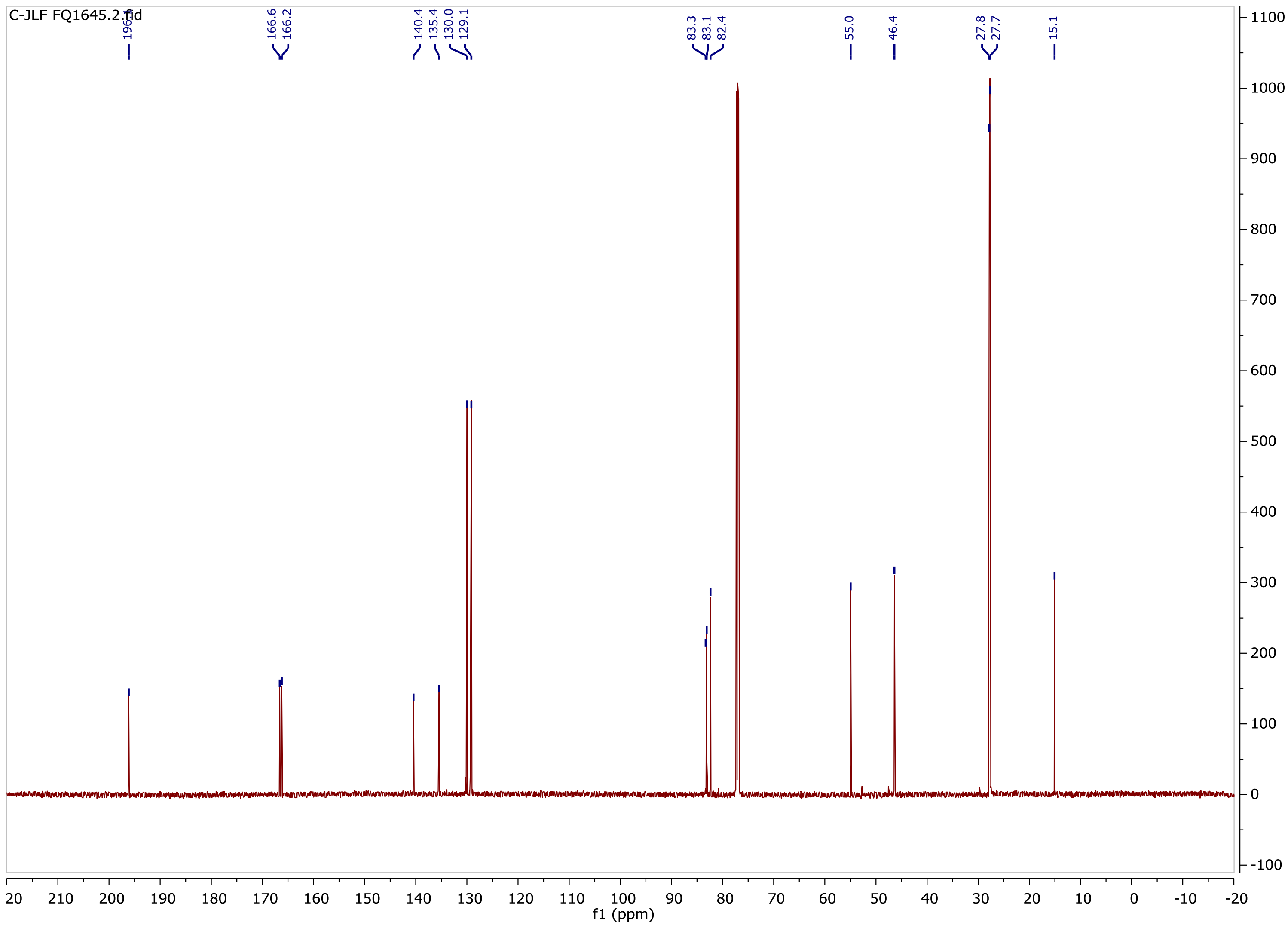
**2c**


C-JLF FQ1645.3.fid
7.94
7.91
7.47
7.45
4.89
4.81
3.87
3.85
1.52
1.48
1.47
1.36
2.00
1.96
2.13
1.00
8.89
3.58
9.16
f1 (ppm)

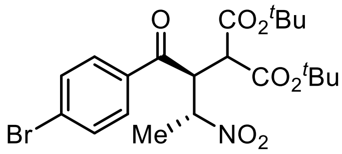


O
CO2tBu
CO2tBu
Cl
Me
NO2

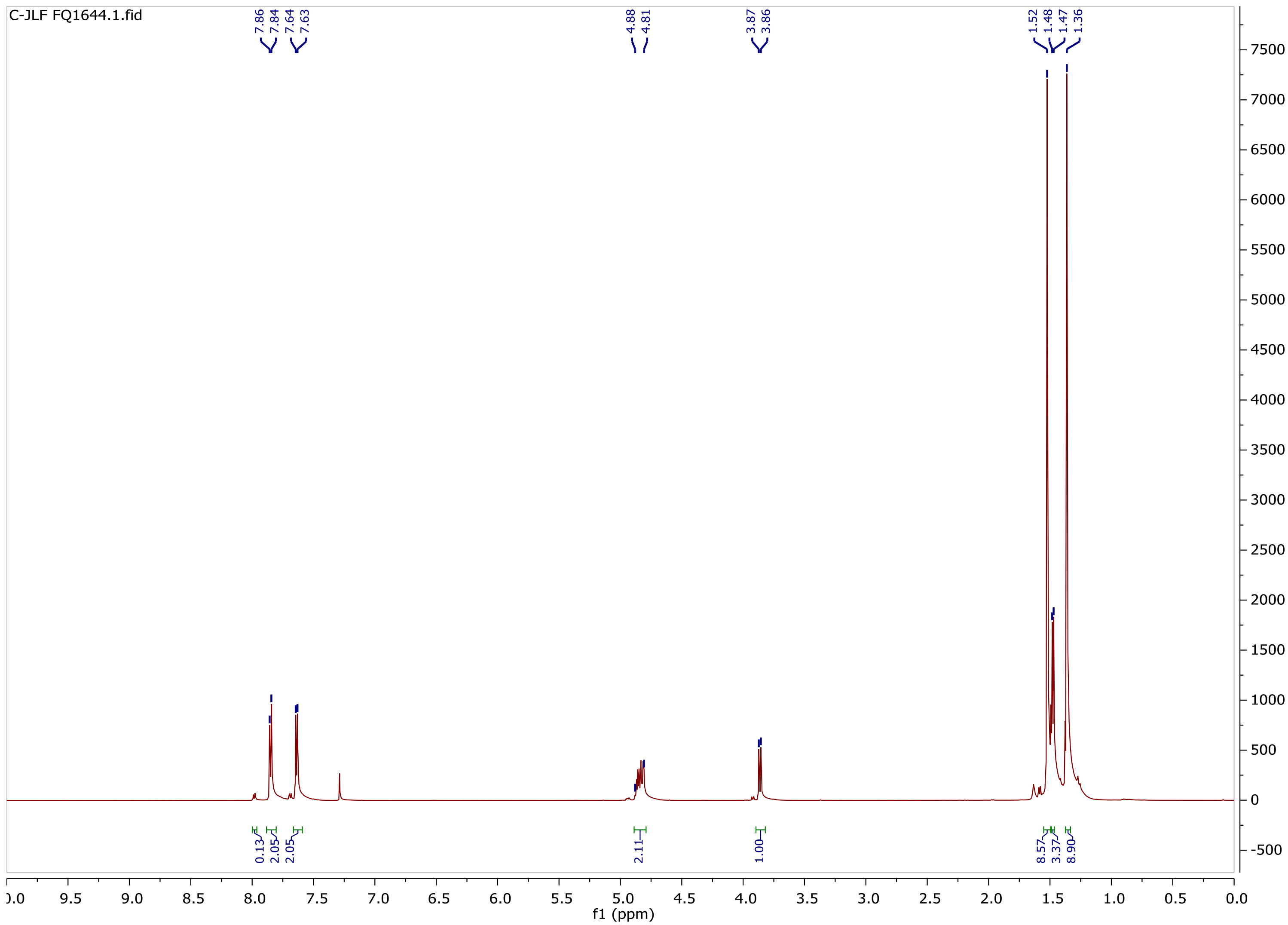

**2c**

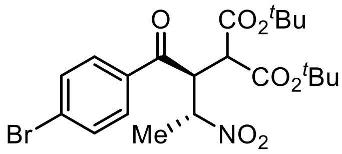


C-JLF FQ1645.2.fid
196.3
166.6
166.2
140.4
135.4
130.0
129.1
83.3
83.1
82.4
55.0
46.4
27.8
27.7
15.1
f1 (ppm)

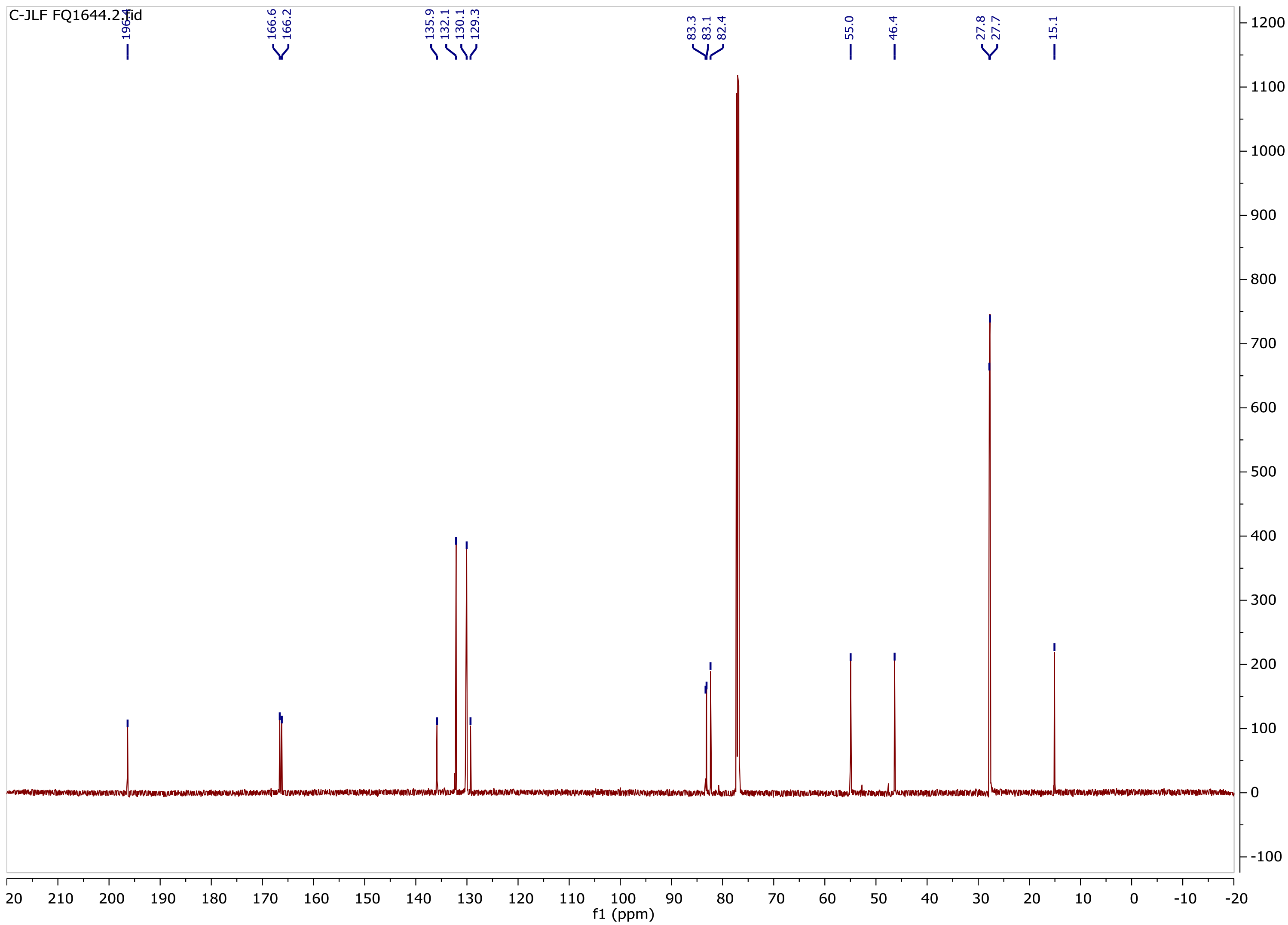

O
CO2tBu
CO2tBu
Br
Me
NO2

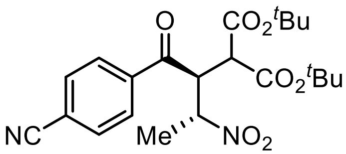
**2d**


C-JLF FQ1644.1.fid
7.86
7.84
7.64
7.63
4.88
4.81
3.87
3.86
1.52
1.48
1.47
1.36
0.13
2.05
2.05
2.11
1.00
8.57
3.37
8.90
f1 (ppm)

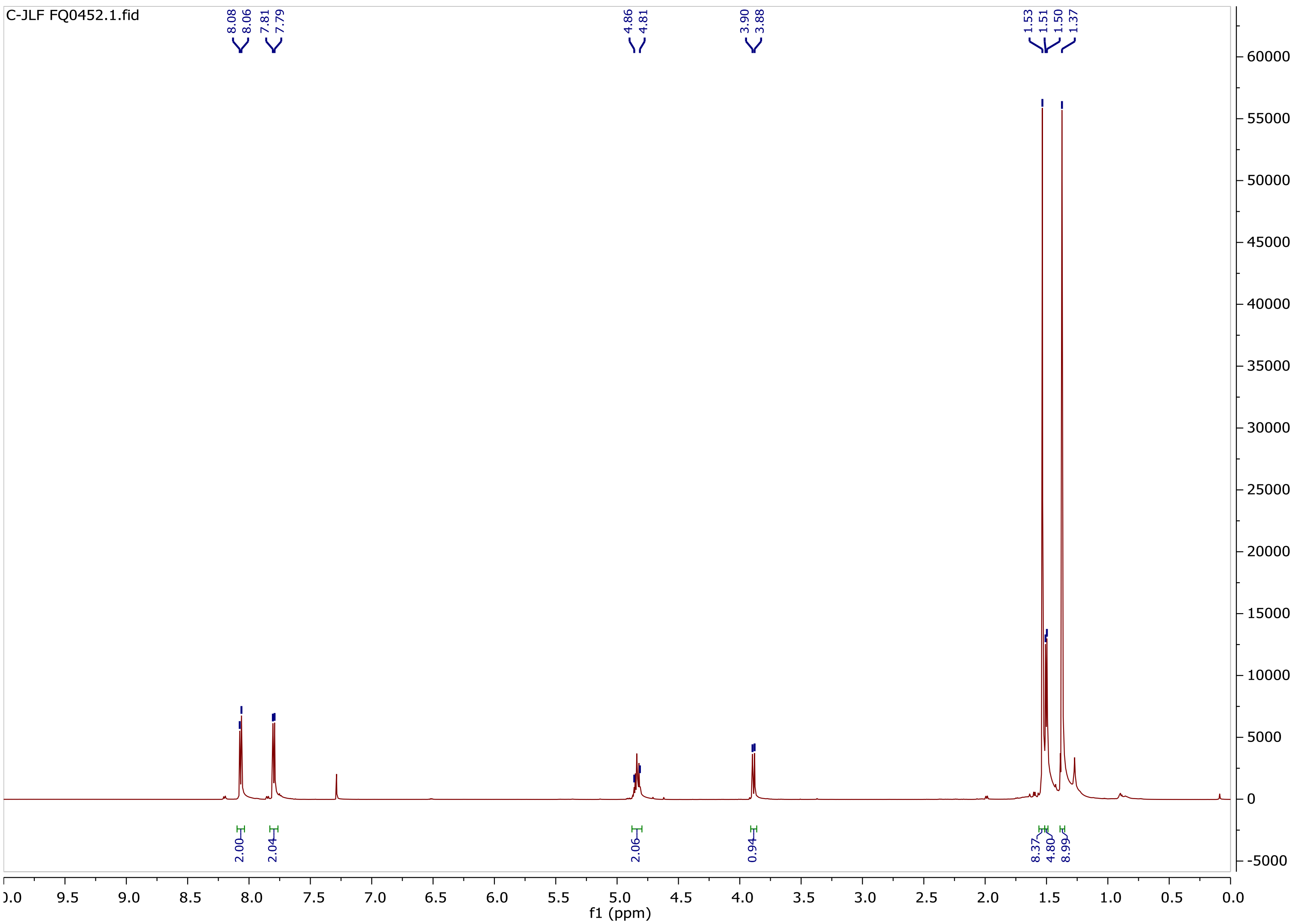

O
CO2tBu
CO2tBu
Br
Me
NO2

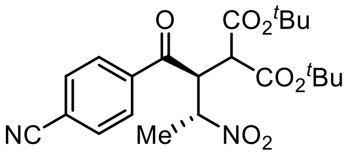
**2d**


C-JLF FQ1644.2.fid
196.4
166.6
166.2
135.9
132.1
130.1
129.3
83.3
83.1
82.4
55.0
46.4
27.8
27.7
15.1
f1 (ppm)

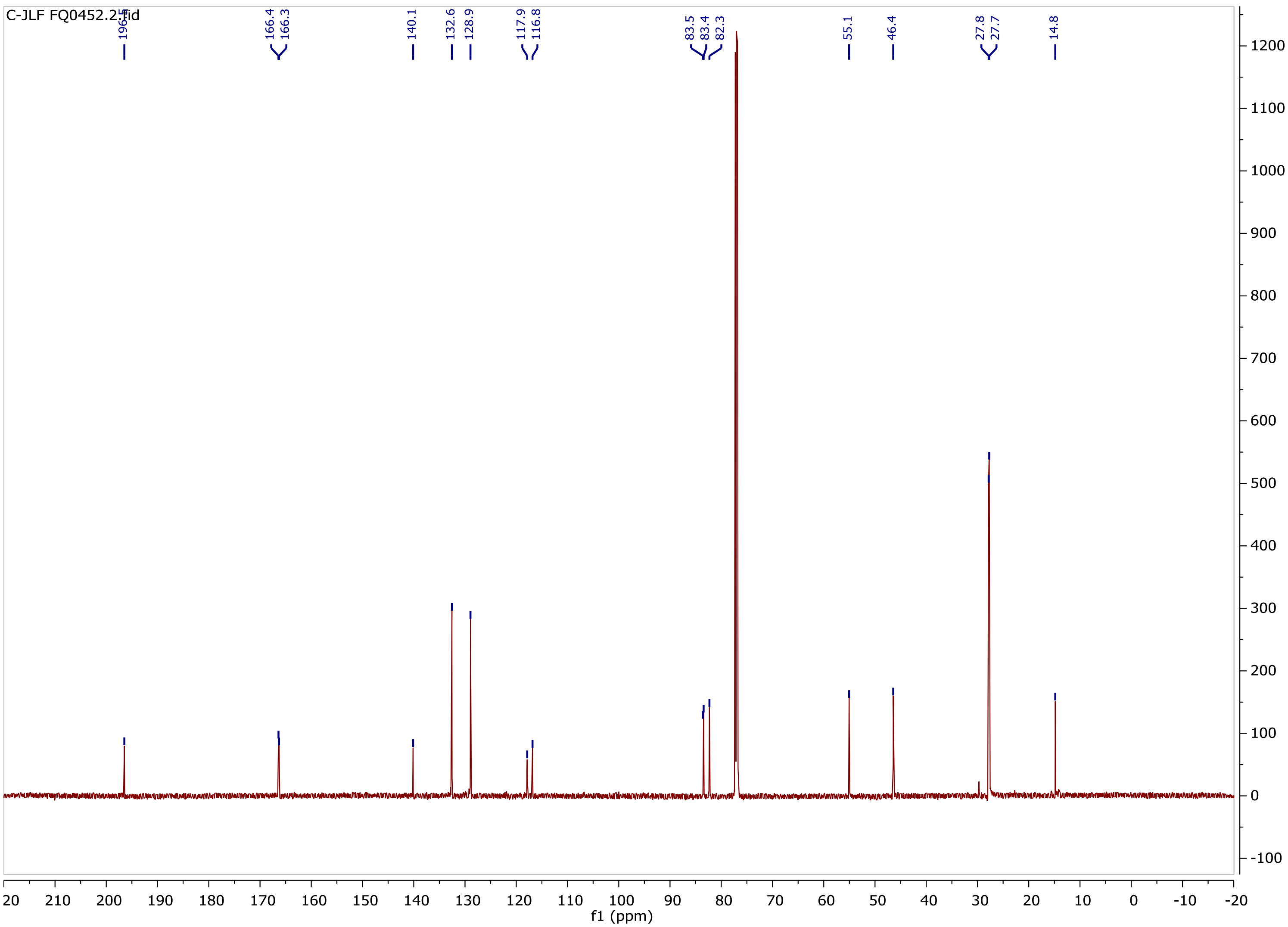


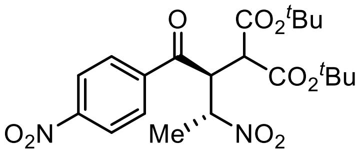
**2e**


C-JLF FQ0452.1.fid
8.08
8.06
7.81
7.79
4.86
4.81
3.90
3.88
1.53
1.51
1.50
1.37
2.00
2.04
2.06
0.94
8.37
4.80
8.99
f1 (ppm)

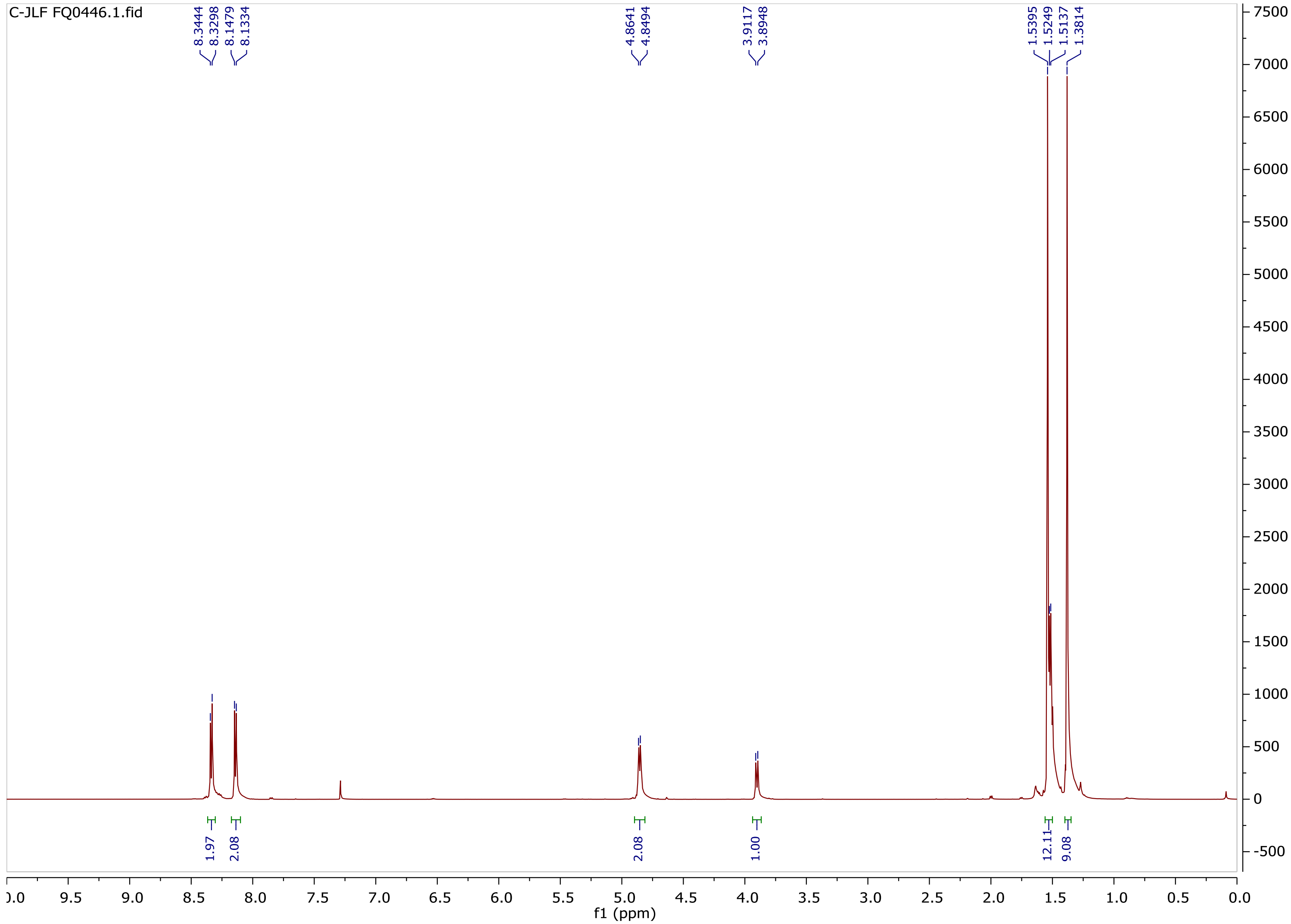

O
CO2tBu
CO2tBu
NC
Me
NO2

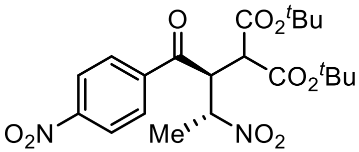
**2e**


C-JLF FQ0452.2.fid
196.5
166.4
166.3
140.1
132.6
128.9
117.9
116.8
83.5
83.4
82.3
55.1
46.4
27.8
27.7
14.8
f1 (ppm)

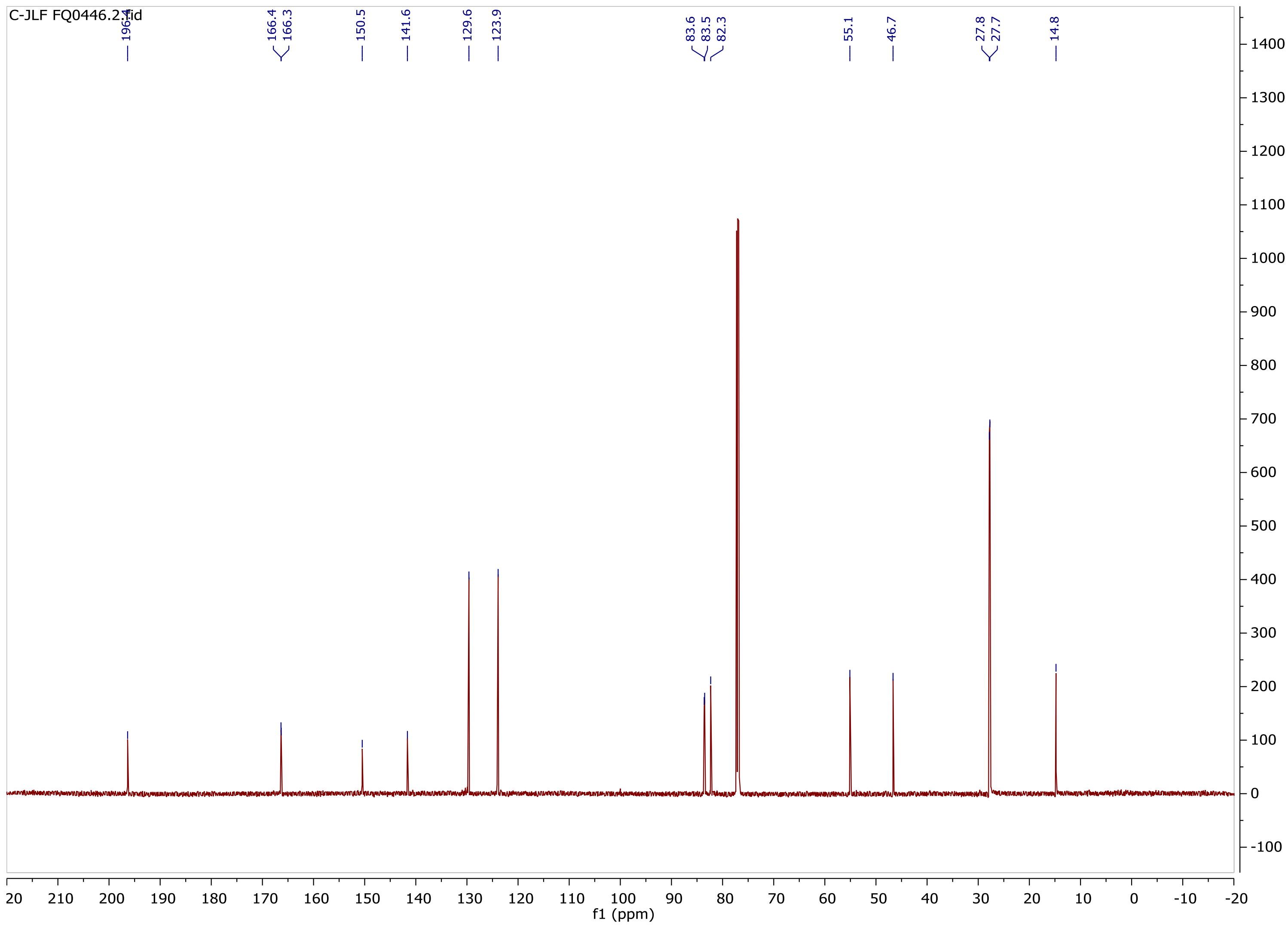


**2f**

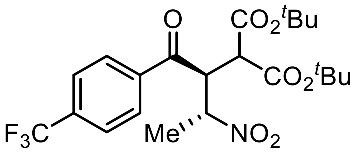

C-JLF FQ0446.1.fid
8.3444
8.3298
8.1479
8.1334
4.8641
4.8494
3.9117
3.8948
1.5395
1.5249
1.5137
1.3814
1.97
2.08
2.08
1.00
12.11
9.08
f1 (ppm)



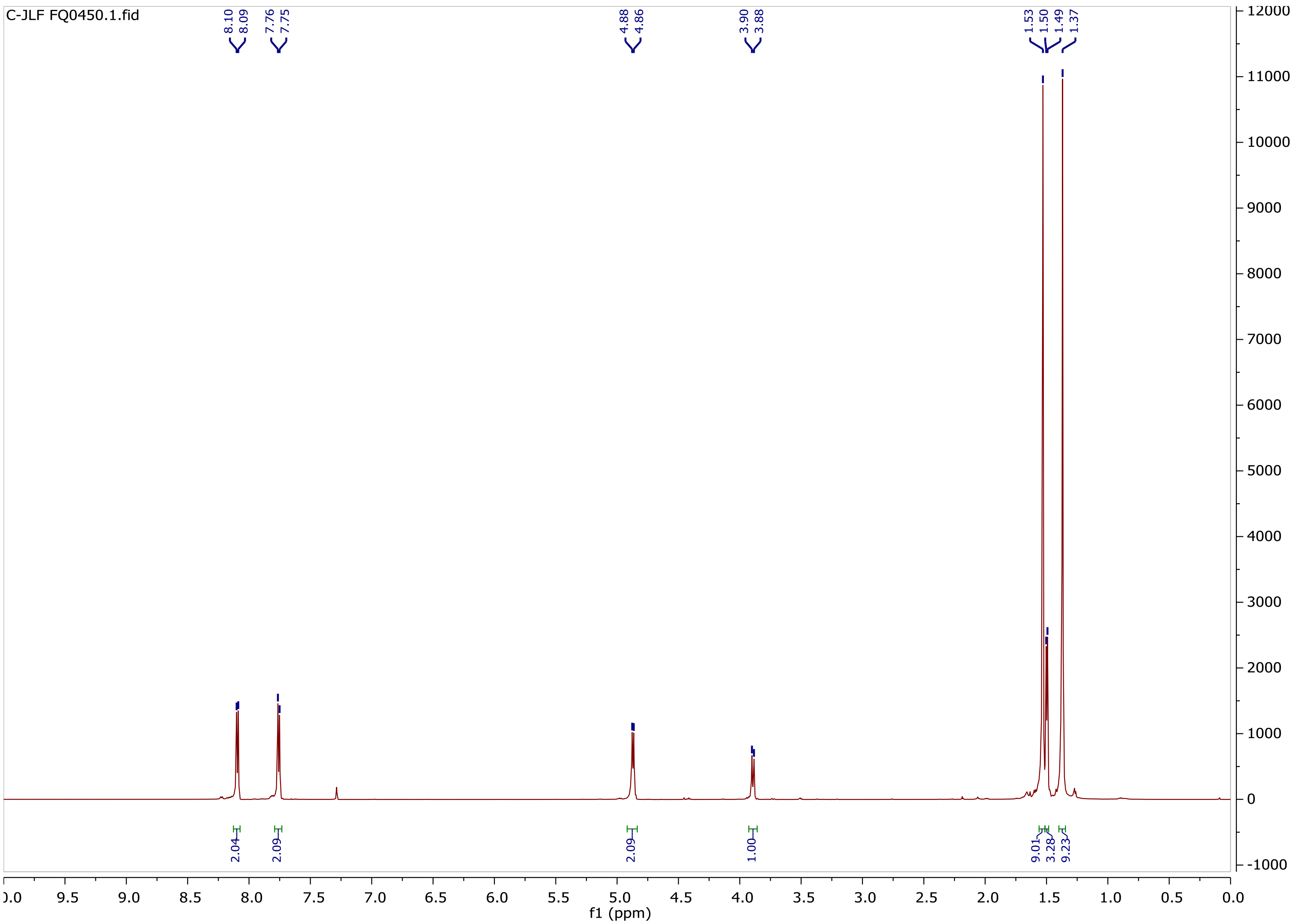
**2f**

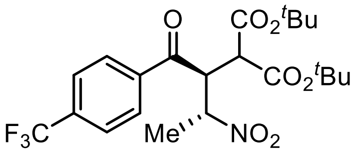


C-JLF FQ0446.2.fid
196.4
166.4
166.3
150.5
141.6
129.6
123.9
83.6
83.5
82.3
55.1
46.7
27.8
27.7
14.8
f1 (ppm)

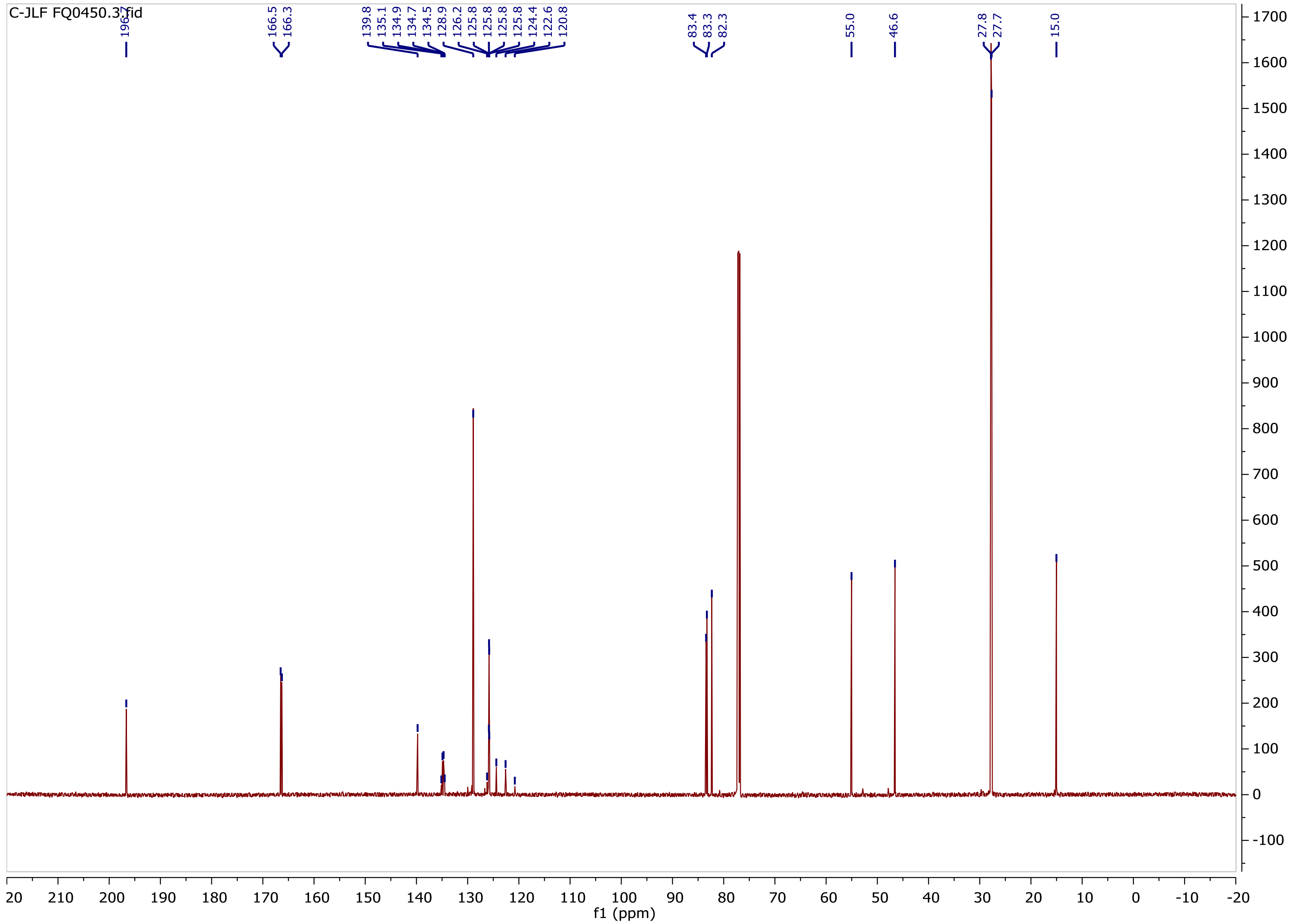


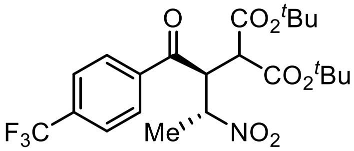
**2g**


C-JLF FQ0450.1.fid
8.10
8.09
7.76
7.75
4.88
4.86
3.90
3.88
1.53
1.50
1.49
1.37
2.04
2.09
2.09
1.00
9.01
3.28
9.23
f1 (ppm)

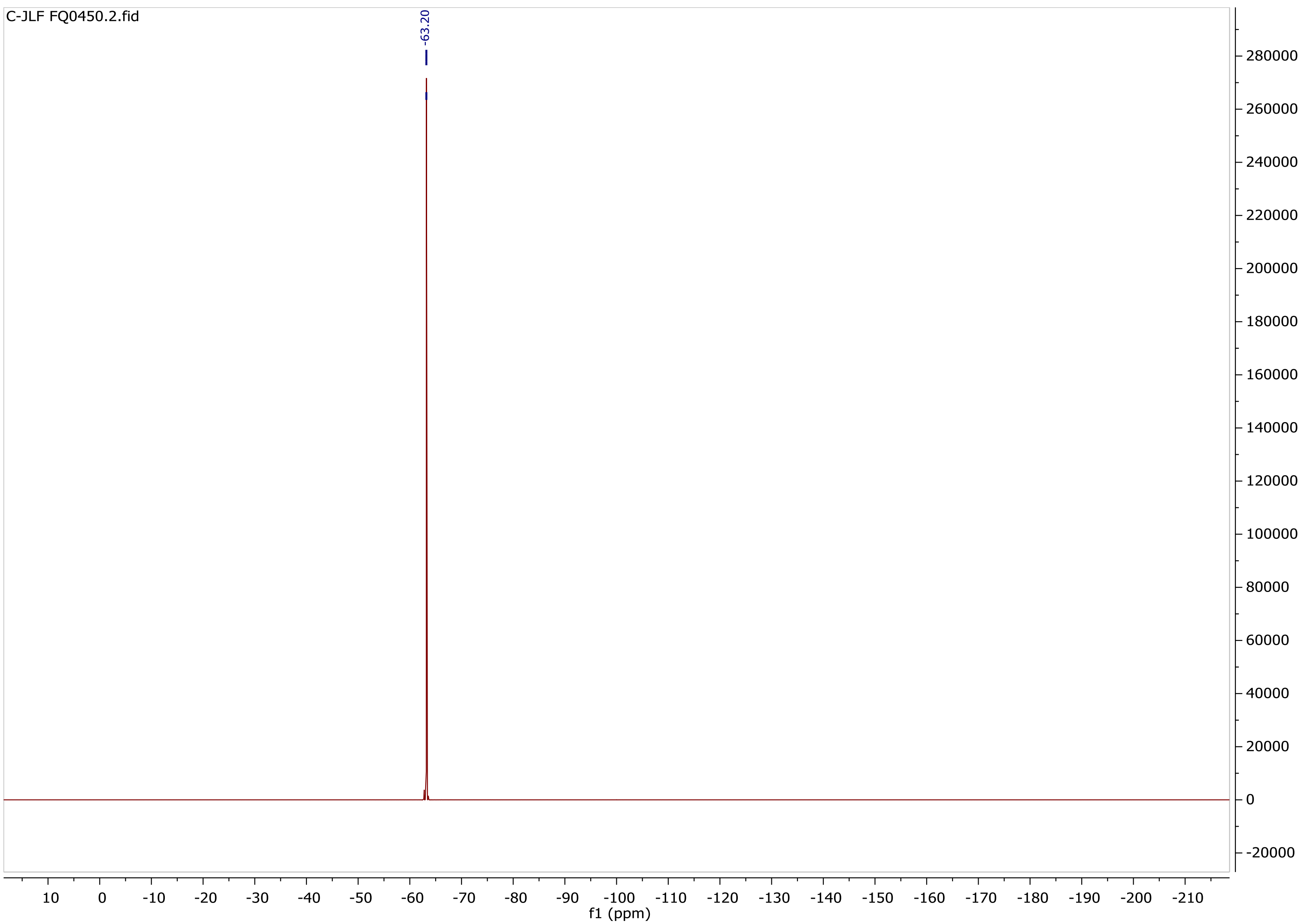

O
$CO_2{}^tBu$
$CO_2{}^tBu$
$F_3C$
Me
$NO_2$

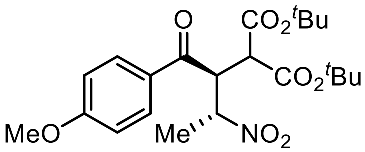
**2g**


C-JLF FQ0450.
166.5
166.3
139.8
135.1
134.9
134.7
134.5
128.9
126.2
125.8
125.8
125.8
125.8
124.4
122.6
120.8
83.4
83.3
82.3
55.0
46.6
27.8
27.7
15.0
f1 (ppm)

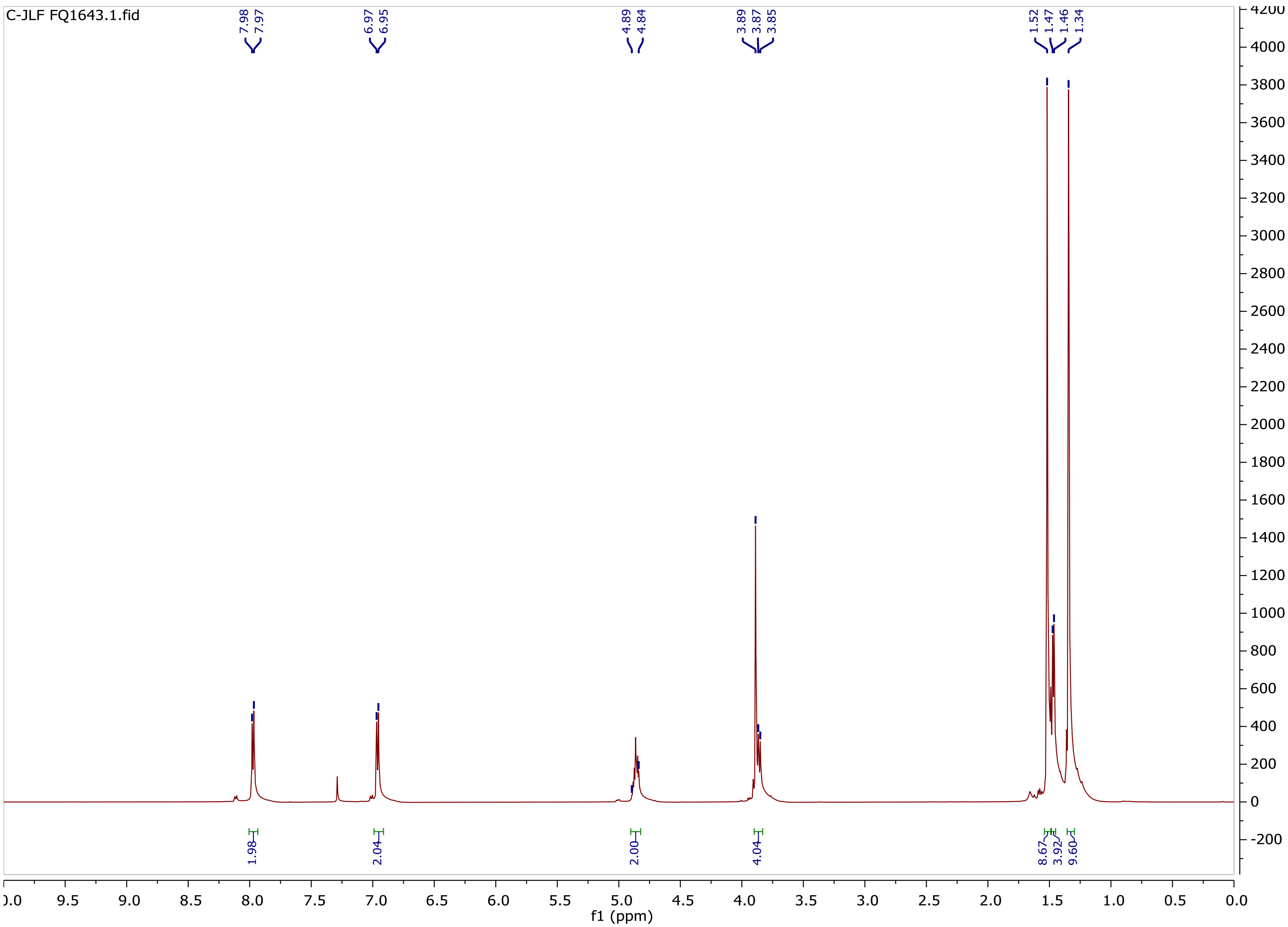


**2g**

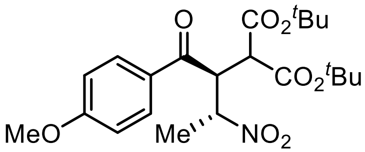




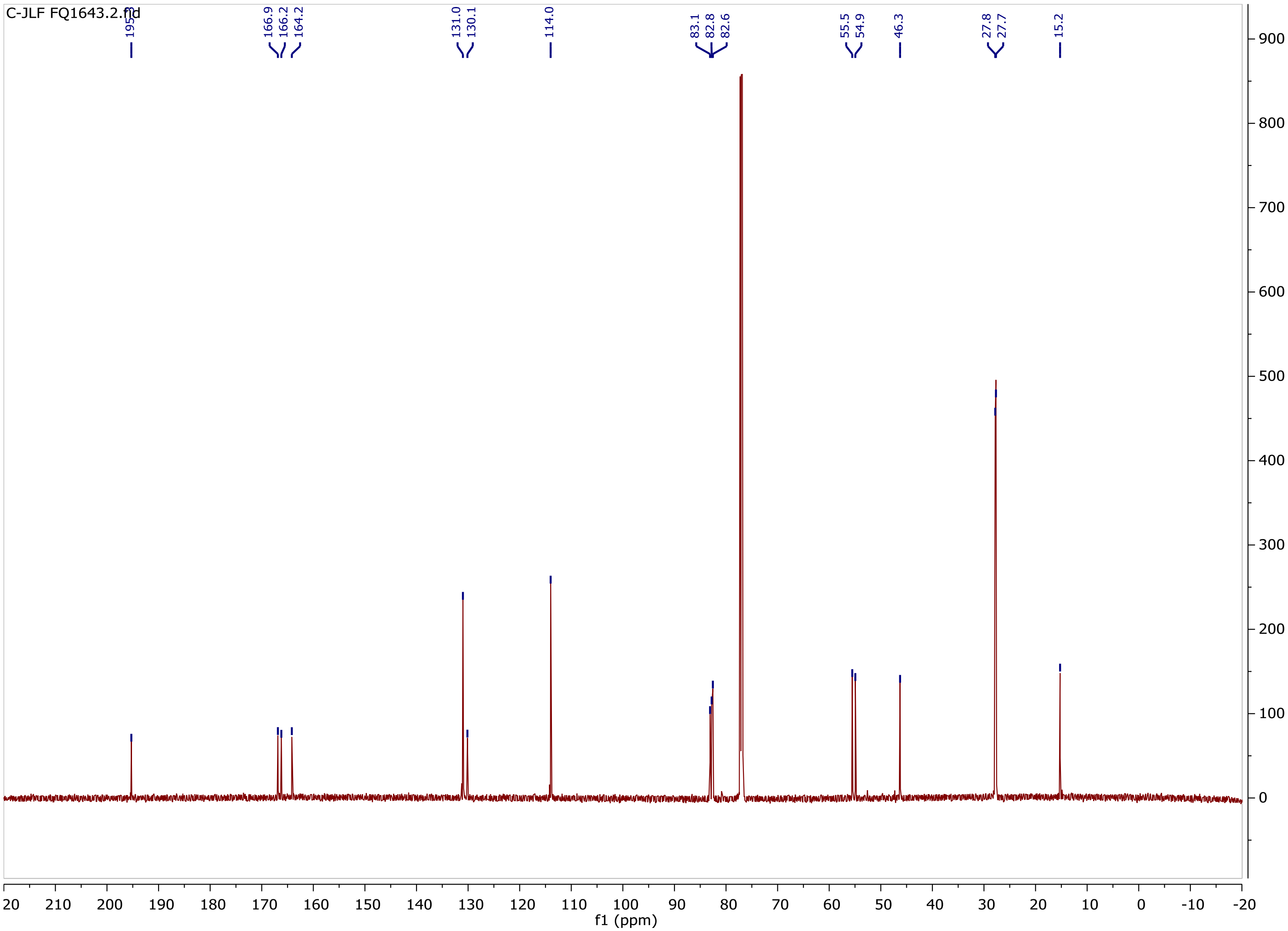
**2h**



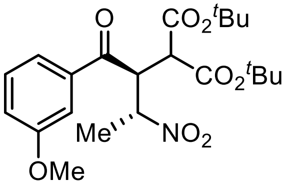
C-JLF FQ1643.1.fid
7.98
7.97
6.97
6.95
4.89
4.84
3.89
3.87
3.85
1.52
1.47
1.46
1.34
1.98
2.04
2.00
4.04
8.67
3.92
9.60
f1 (ppm)



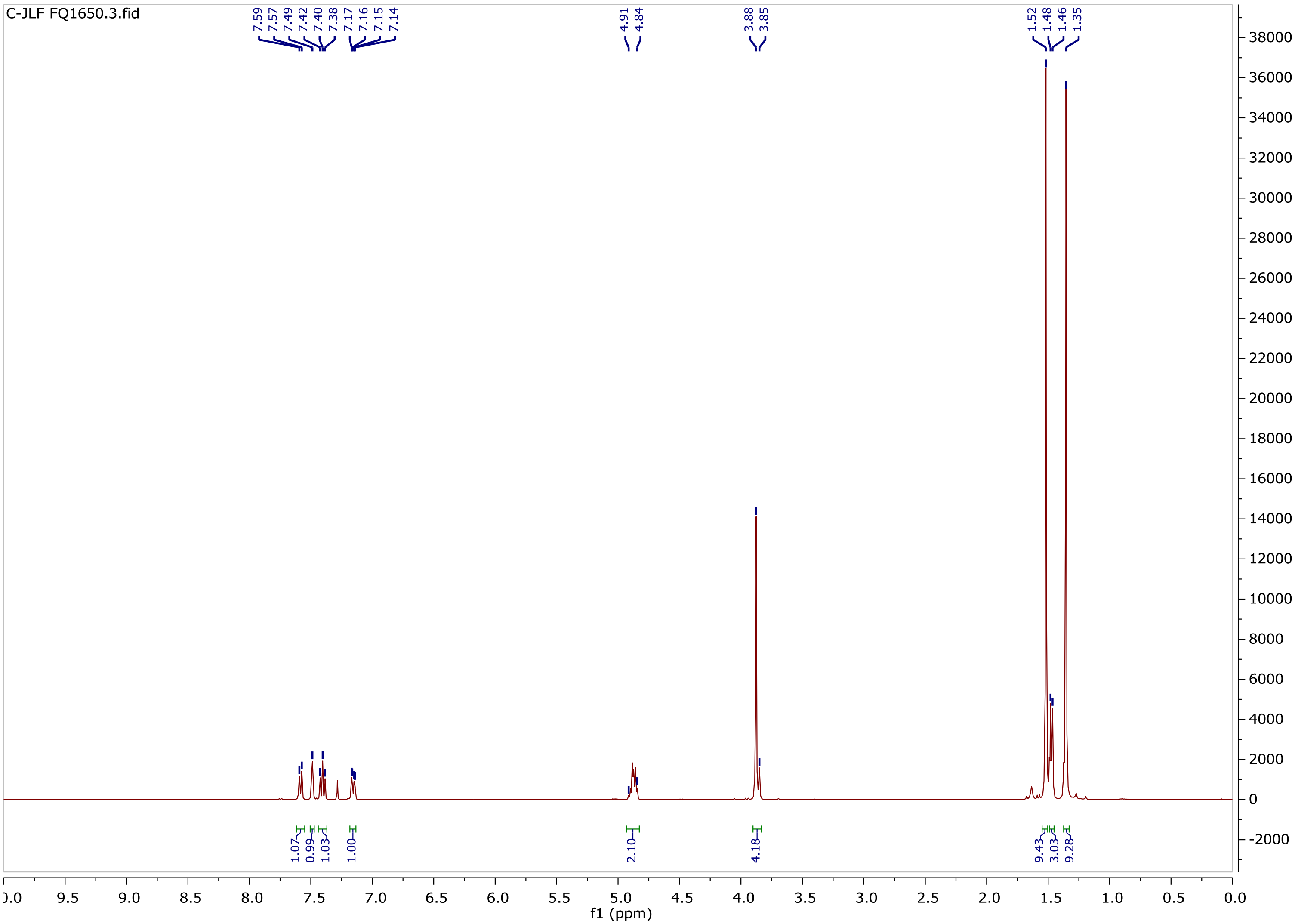
**2h**

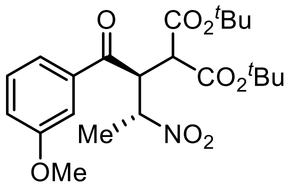


C-JLF FQ1643.2.fid
195.
166.9
166.2
164.2
131.0
130.1
114.0
83.1
82.8
82.6
55.5
54.9
46.3
27.8
27.7
15.2
f1 (ppm)

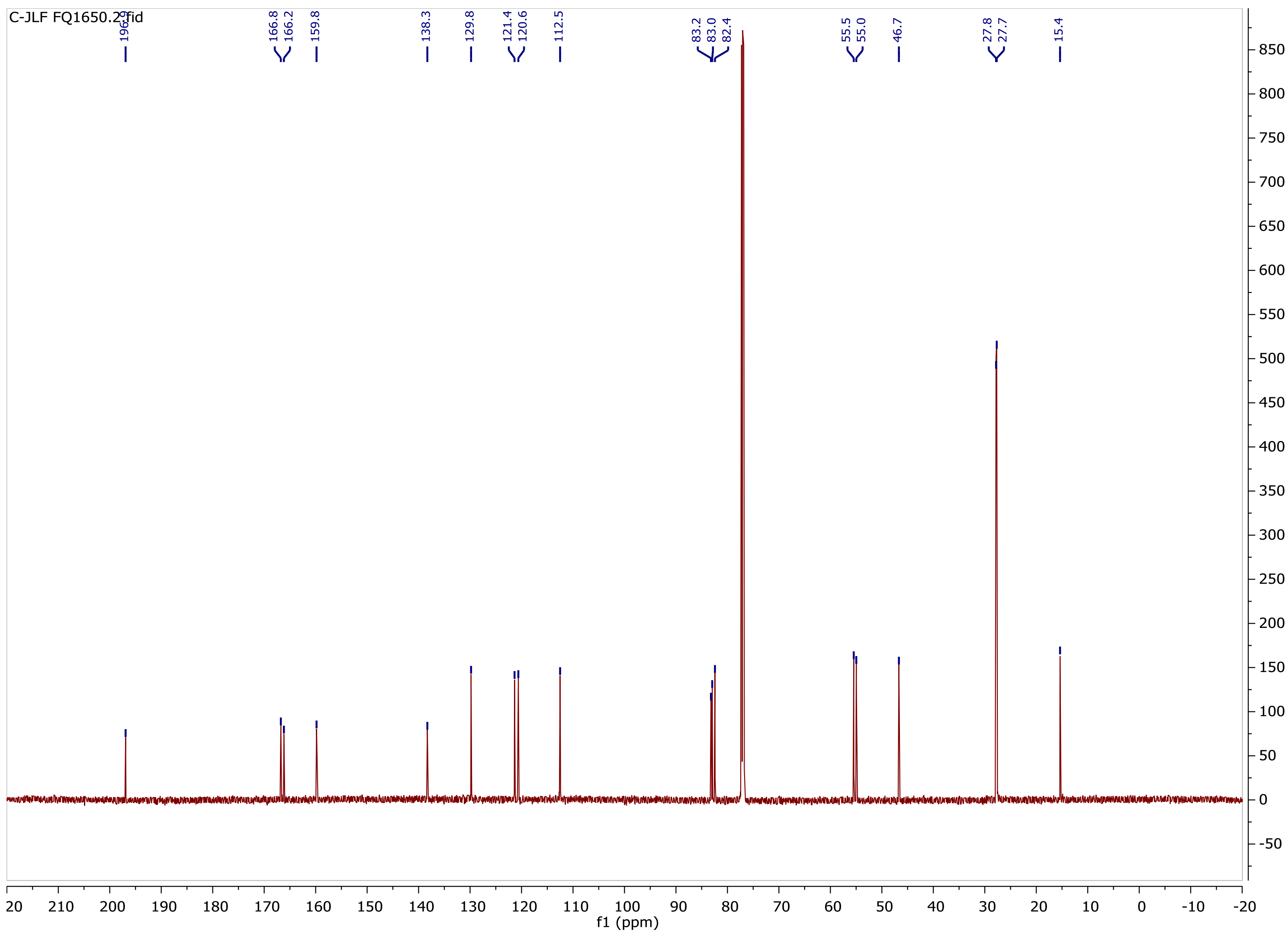


**2i**

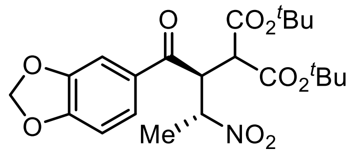

C-JLF FQ1650.3.fid
7.59
7.57
7.49
7.42
7.40
7.38
7.17
7.16
7.15
7.14
4.91
4.84
3.88
3.85
1.52
1.48
1.46
1.35
1.07
0.99
1.03
1.00
2.10
4.18
9.43
3.03
9.28
f1 (ppm)



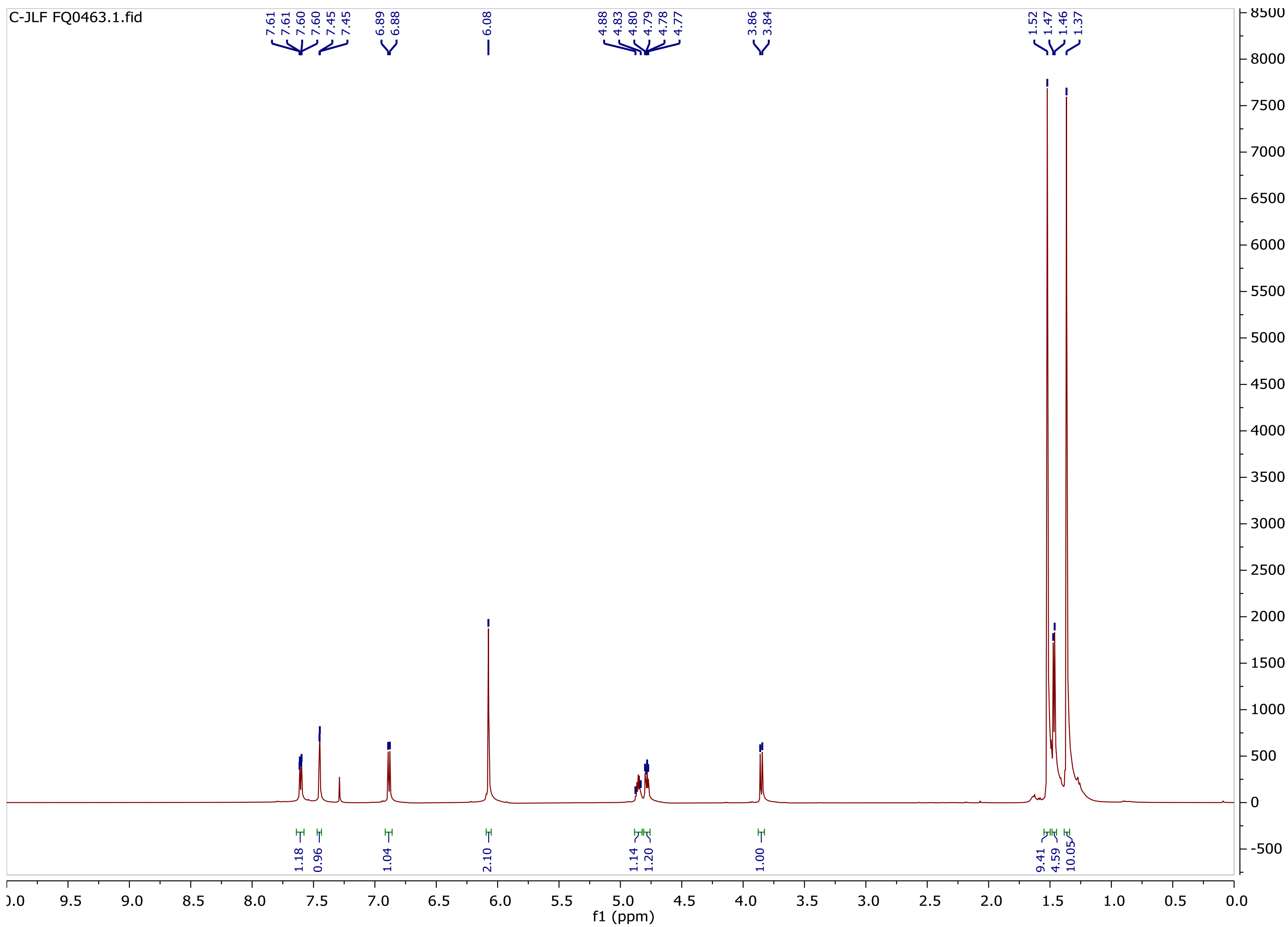
**2i**

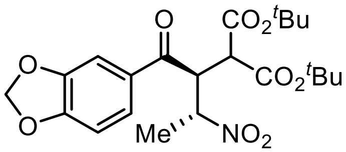


C-JLF FQ1650.2.fid
196.9
166.8
166.2
159.8
138.3
129.8
121.4
120.6
112.5
83.2
83.0
82.4
55.5
55.0
46.7
27.8
27.7
15.4
f1 (ppm)

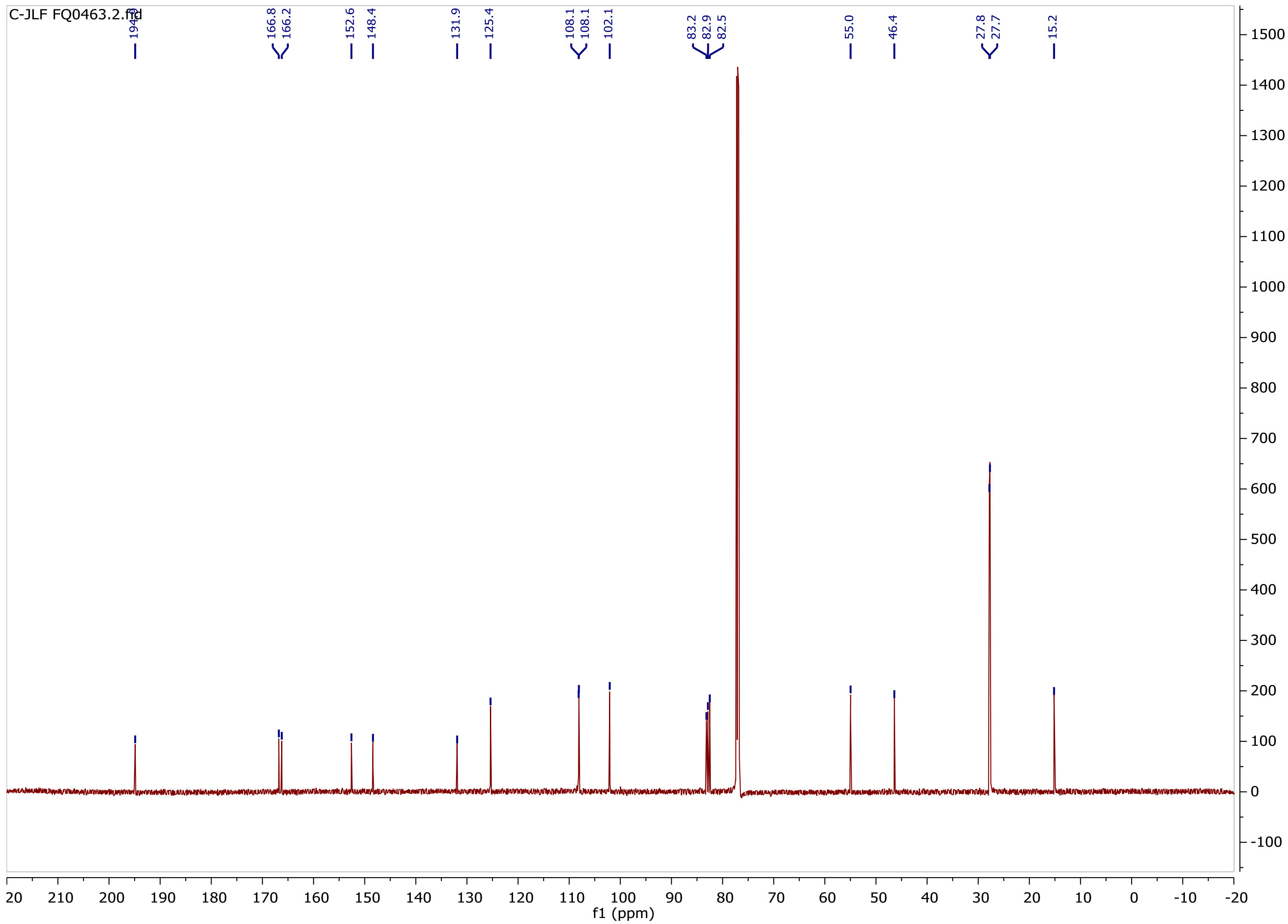

CO2tBu
CO2tBu
O
O
O
Me
NO2

**2j**

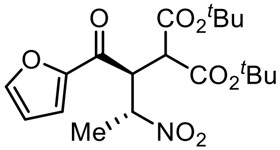

C-JLF FQ0463.1.fid
7.61
7.61
7.60
7.60
7.45
7.45
6.89
6.88
6.08
4.88
4.83
4.80
4.79
4.78
4.77
3.86
3.84
1.52
1.47
1.46
1.37
1.18
0.96
1.04
2.10
1.14
1.20
1.00
9.41
4.59
10.05
f1 (ppm)



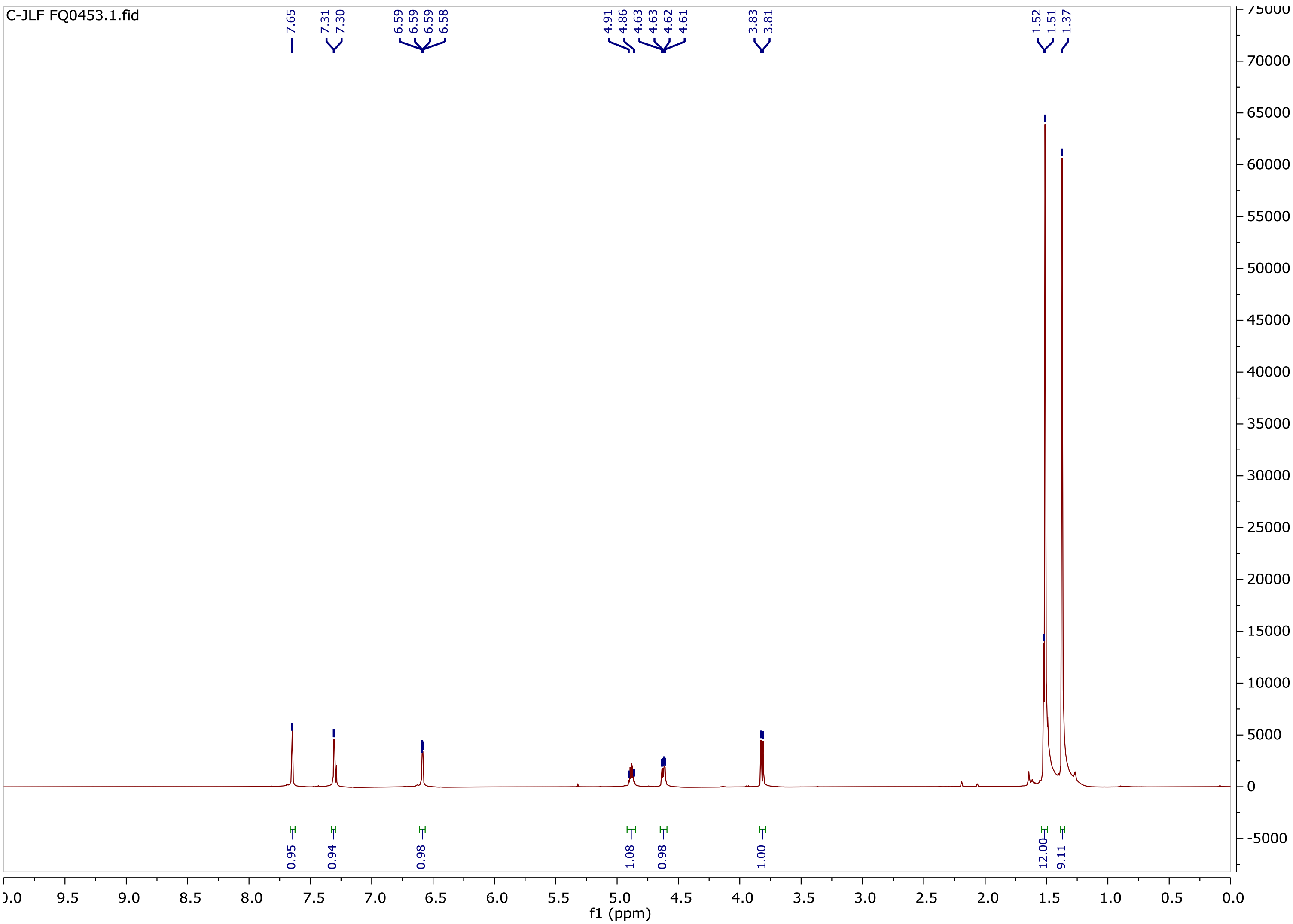
**2j**



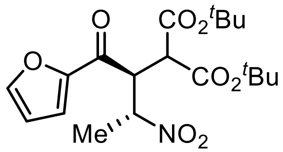
C-JLF FQ0463.2.fid
194.8
166.8
166.2
152.6
148.4
131.9
125.4
108.1
108.1
102.1
83.2
82.9
82.5
55.0
46.4
27.8
27.7
15.2
f1 (ppm)



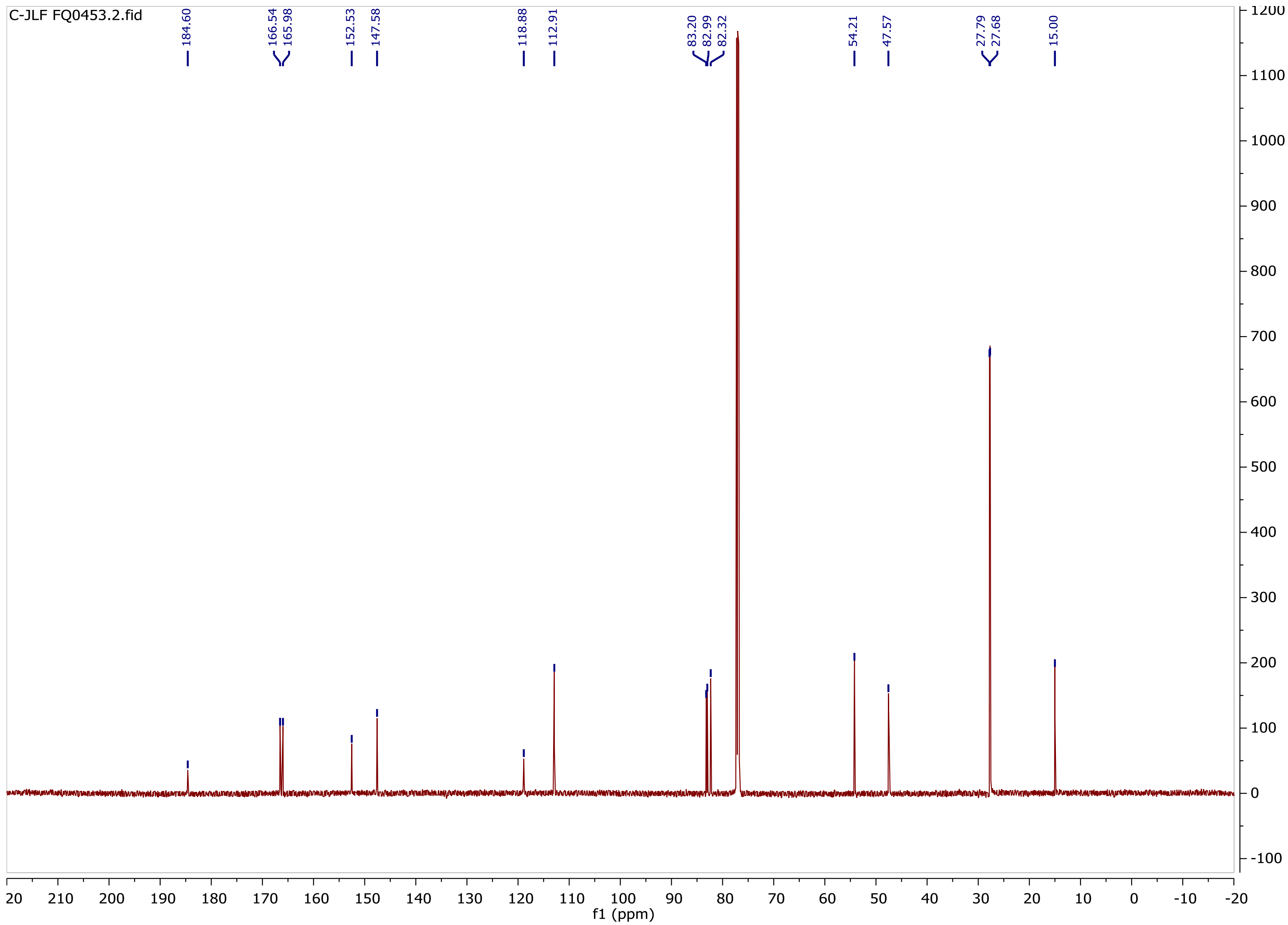
**2k**



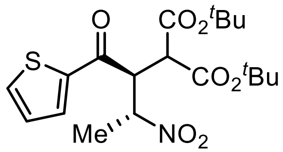
C-JLF FQ0453.1.fid
7.65
7.31
7.30
6.59
6.59
6.59
6.58
4.91
4.86
4.63
4.63
4.62
4.61
3.83
3.81
1.52
1.51
1.37
0.95
0.94
0.98
1.08
0.98
1.00
12.00
9.11
f1 (ppm)



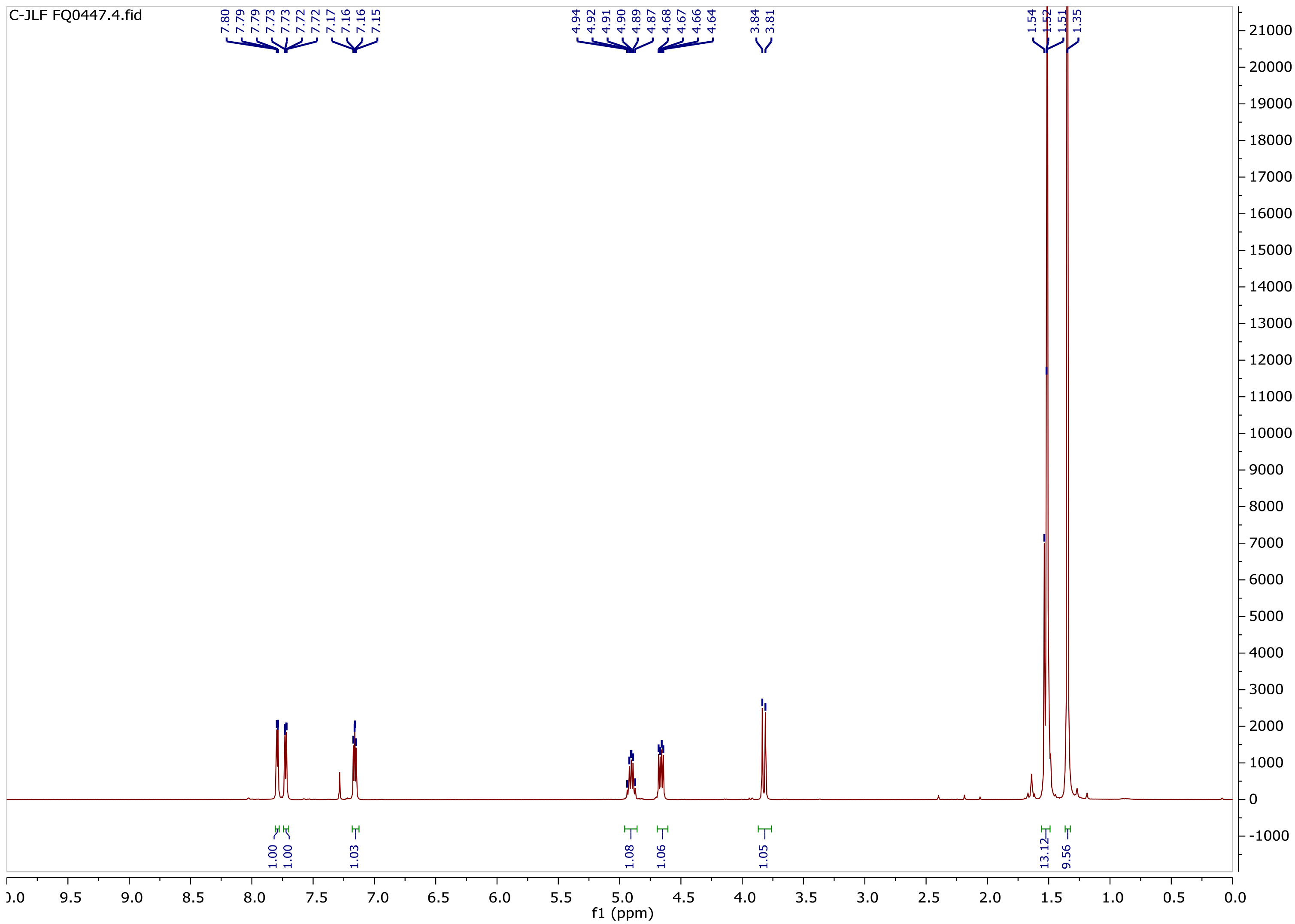
**2k**



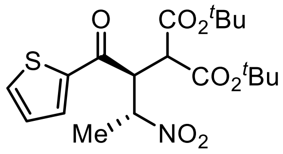
C-JLF FQ0453.2.fid
184.60
166.54
165.98
152.53
147.58
118.88
112.91
83.20
82.99
82.32
54.21
47.57
27.79
27.68
15.00
f1 (ppm)



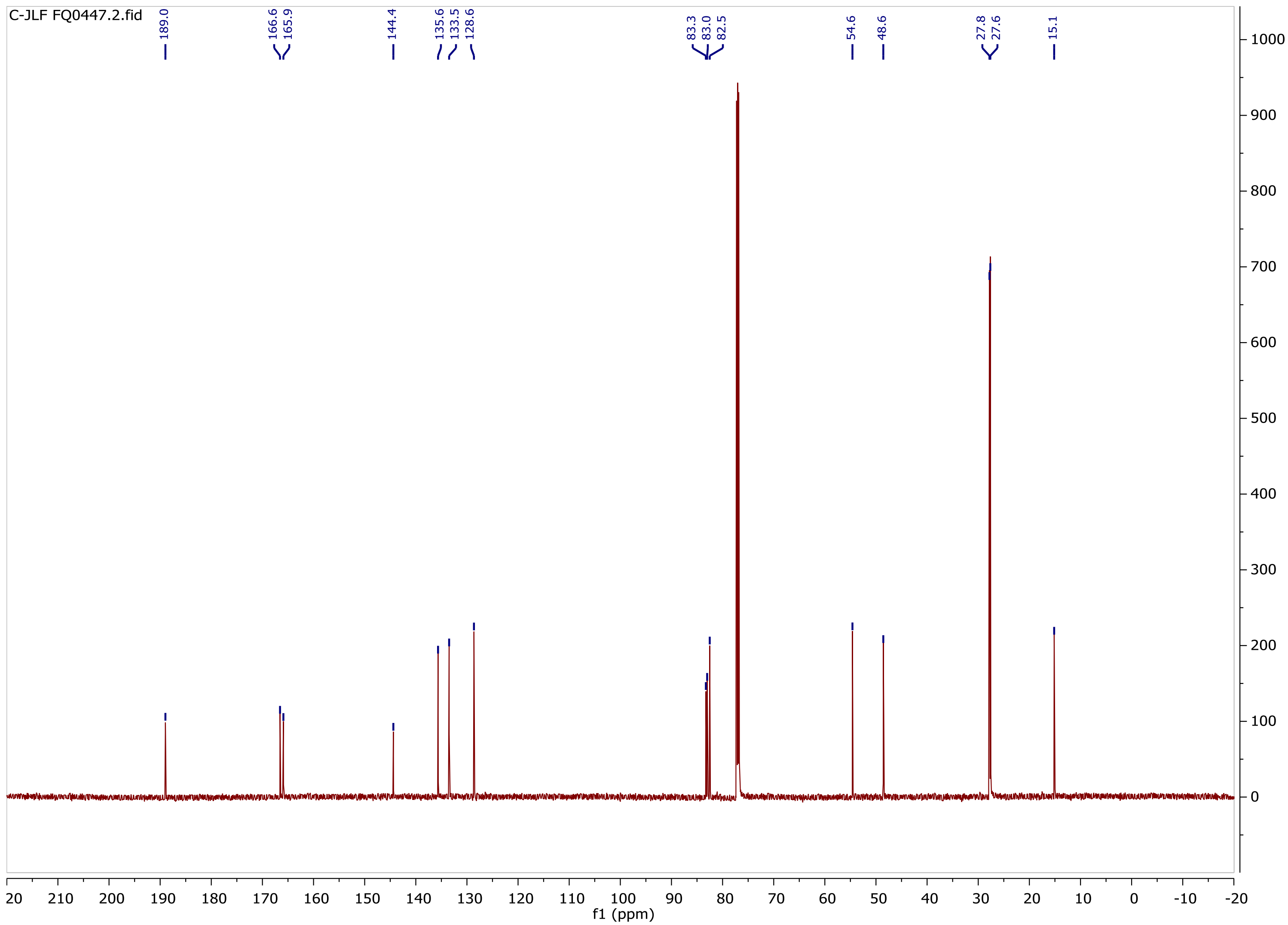
**2l**

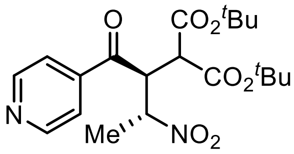


C-JLF FQ0447.4.fid
7.80
7.79
7.79
7.73
7.73
7.72
7.72
7.17
7.16
7.16
7.15
4.94
4.92
4.91
4.90
4.89
4.87
4.68
4.67
4.66
4.64
3.84
3.81
1.54
1.52
1.51
1.35
1.00
1.00
1.03
1.08
1.06
1.05
13.12
9.56
f1 (ppm)

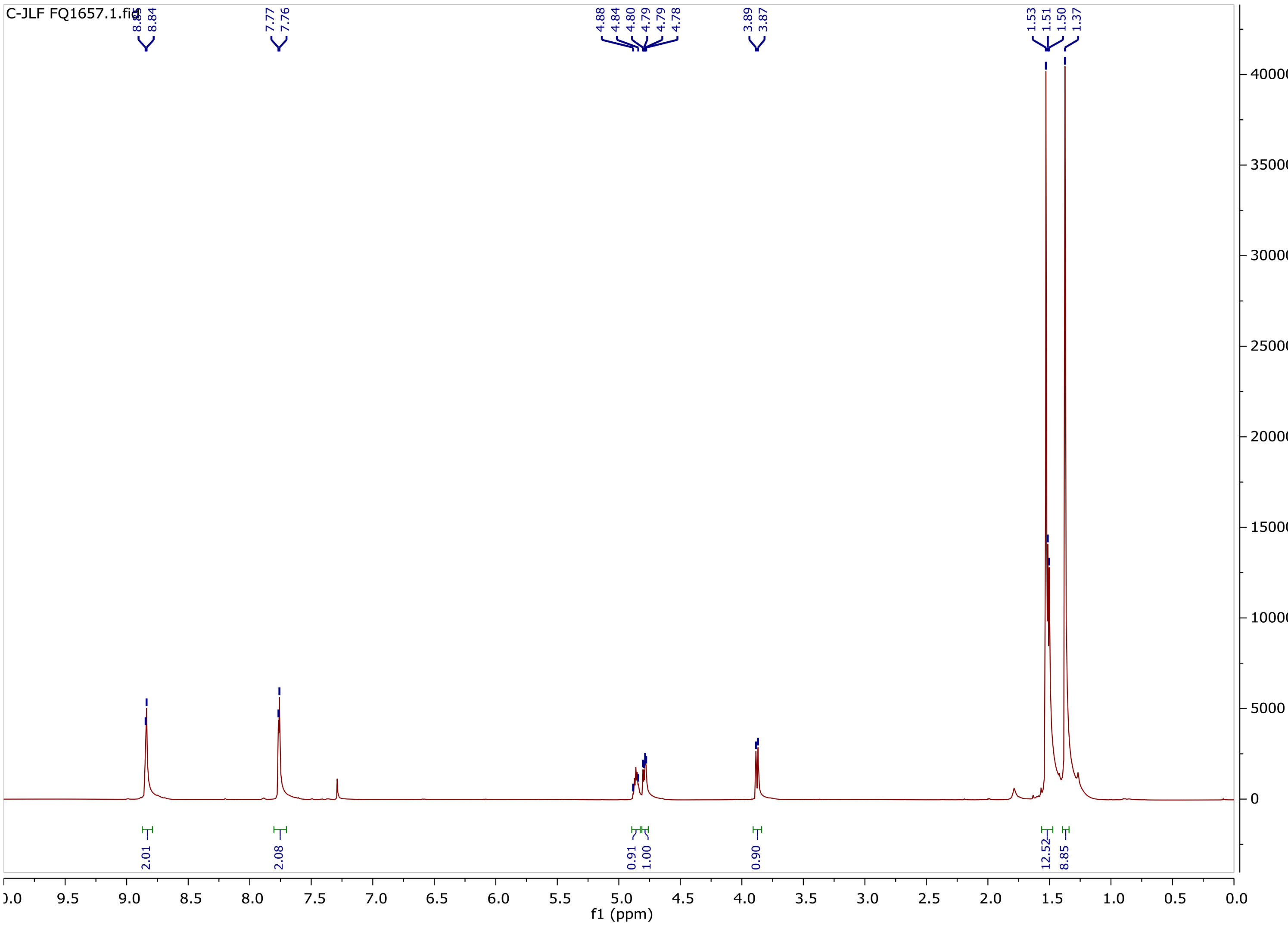


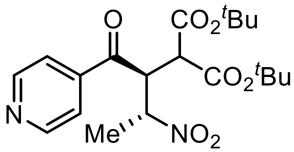
**2l**


C-JLF FQ0447.2.fid
189.0
166.6
165.9
144.4
135.6
133.5
128.6
83.3
83.0
82.5
54.6
48.6
27.8
27.6
15.1
f1 (ppm)

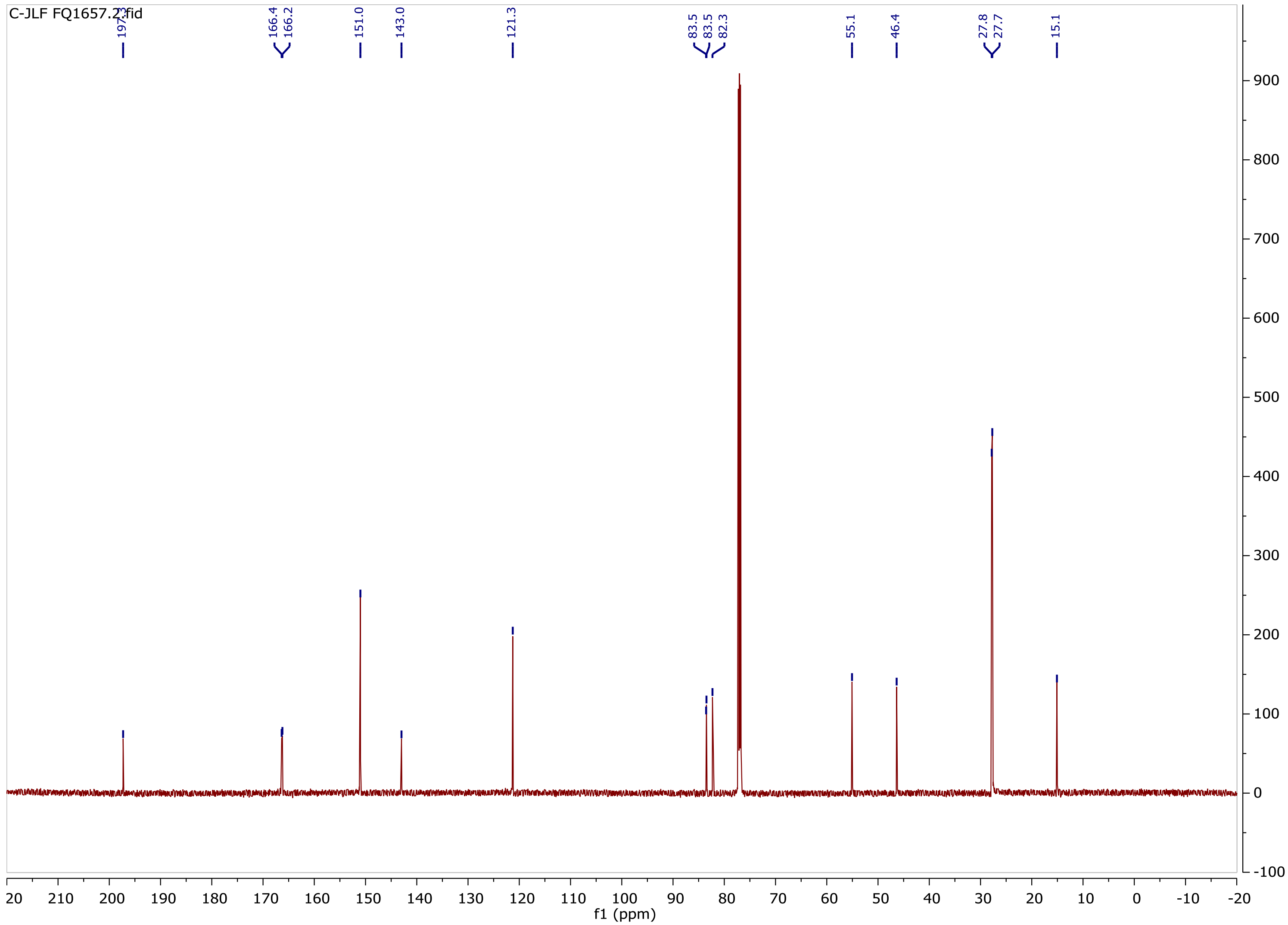


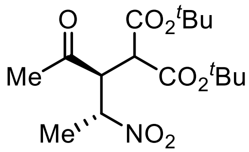
**2m**


C-JLF FQ1657.1.fid
8.85
8.84
7.77
7.76
4.88
4.84
4.80
4.79
4.79
4.78
3.89
3.87
1.53
1.51
1.50
1.37
2.01
2.08
0.91
1.00
0.90
12.52
8.85
f1 (ppm)

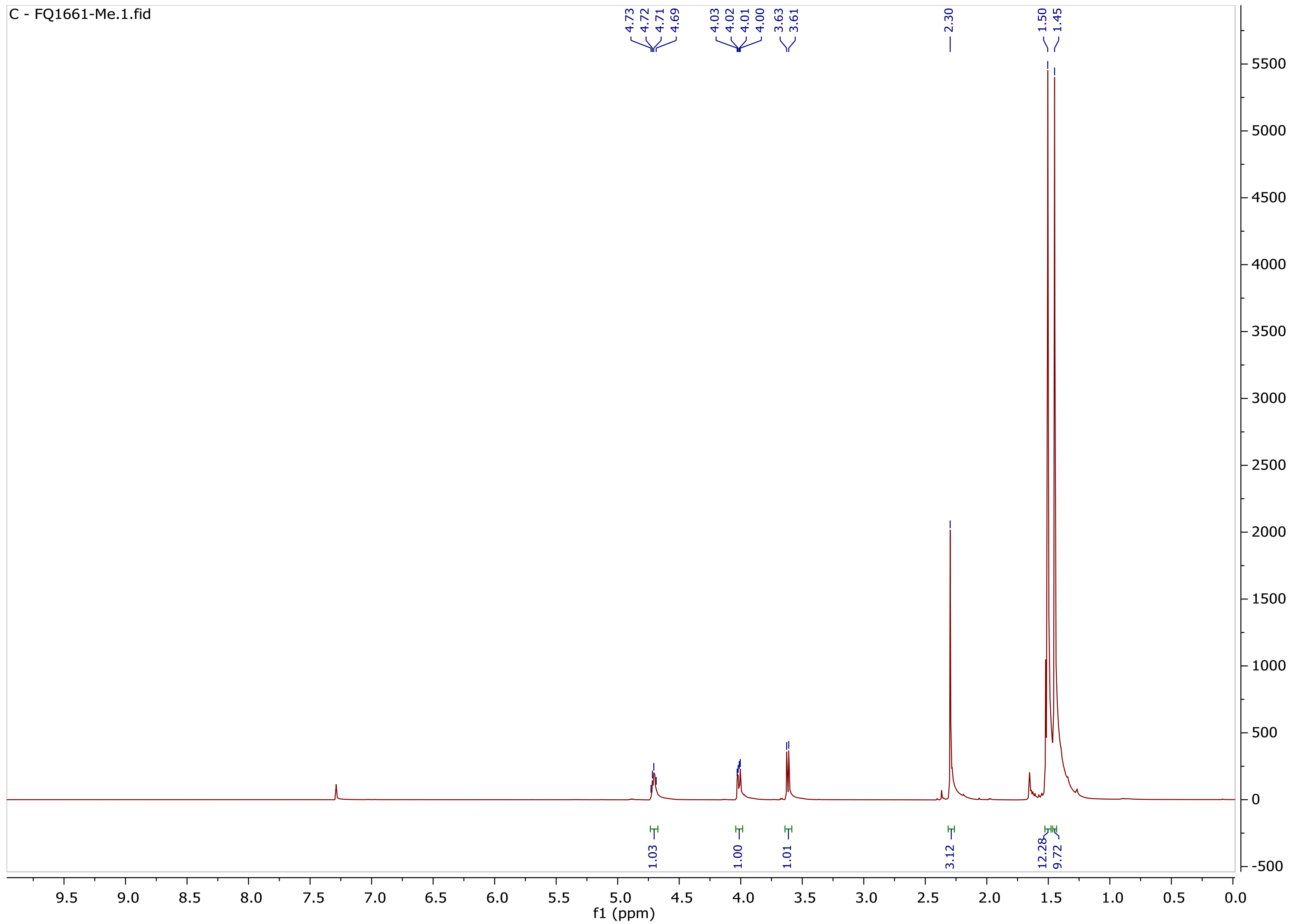


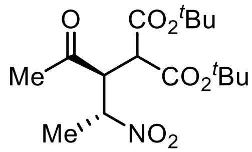
**2m**


C-JLF FQ1657.2.fid
197.
166.4
166.2
151.0
143.0
121.3
83.5
83.5
82.3
55.1
46.4
27.8
27.7
15.1
f1 (ppm)

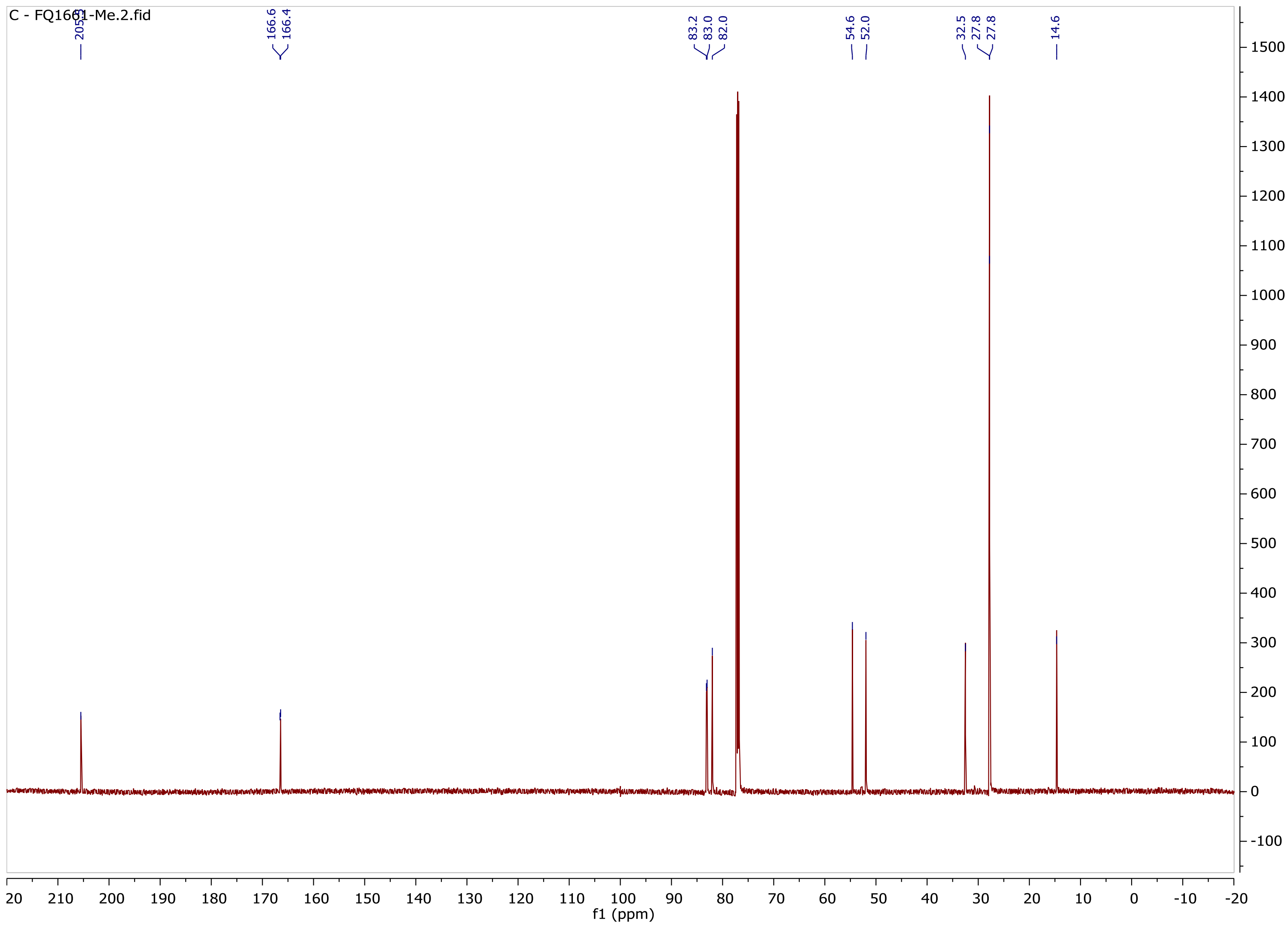


**2n**

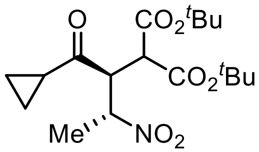

C - FQ1661-Me.1.fid
4.73
4.72
4.71
4.69
4.03
4.02
4.01
4.00
3.63
3.61
2.30
1.50
1.45
1.03
1.00
1.01
3.12
12.28
9.72
f1 (ppm)



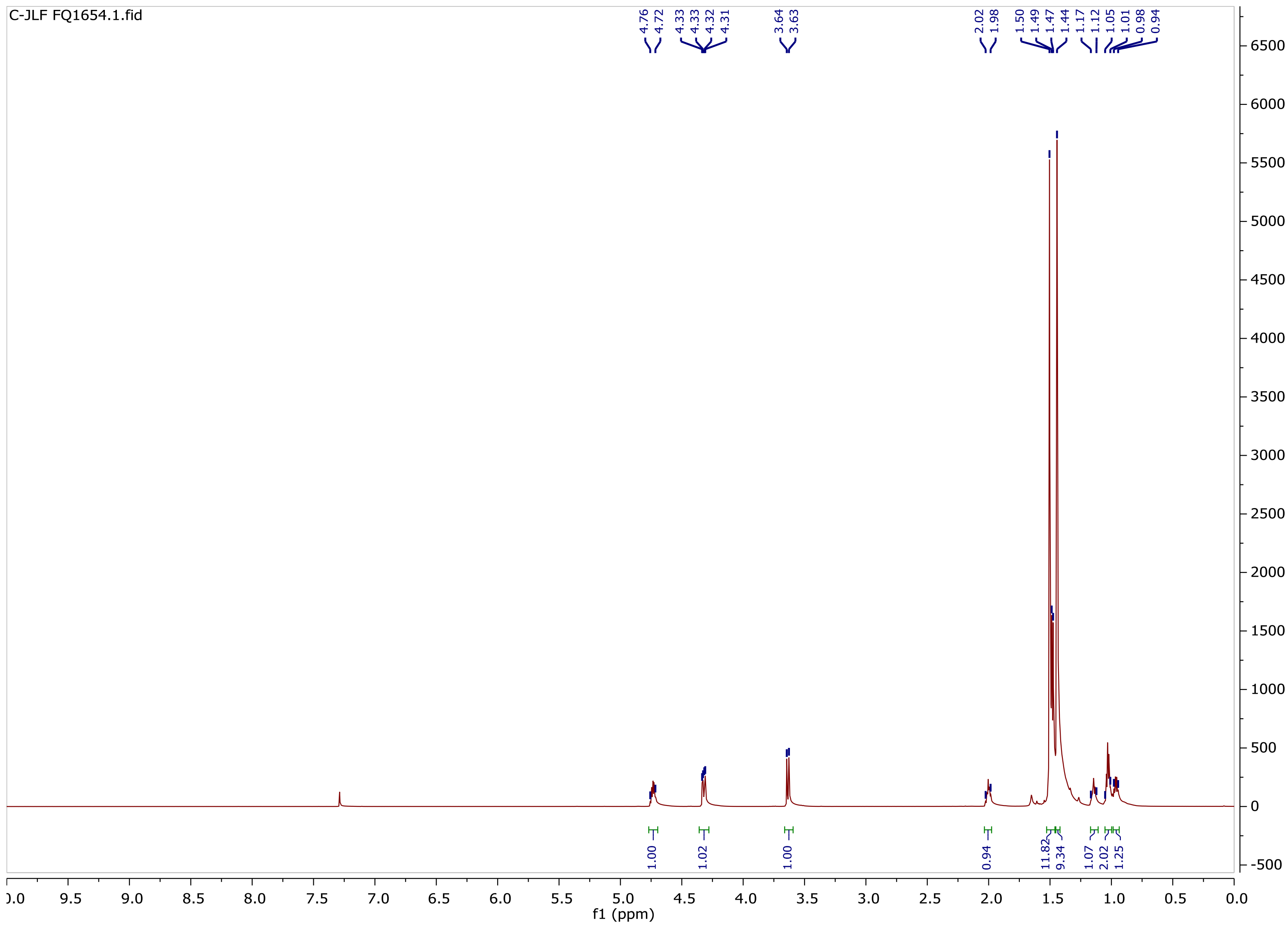
**2n**

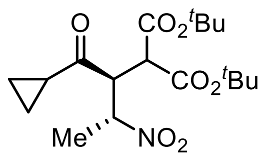


C - FQ1661-Me.2.fid
205.1
166.6
166.4
83.2
83.0
82.0
54.6
52.0
32.5
27.8
27.8
14.6
f1 (ppm)

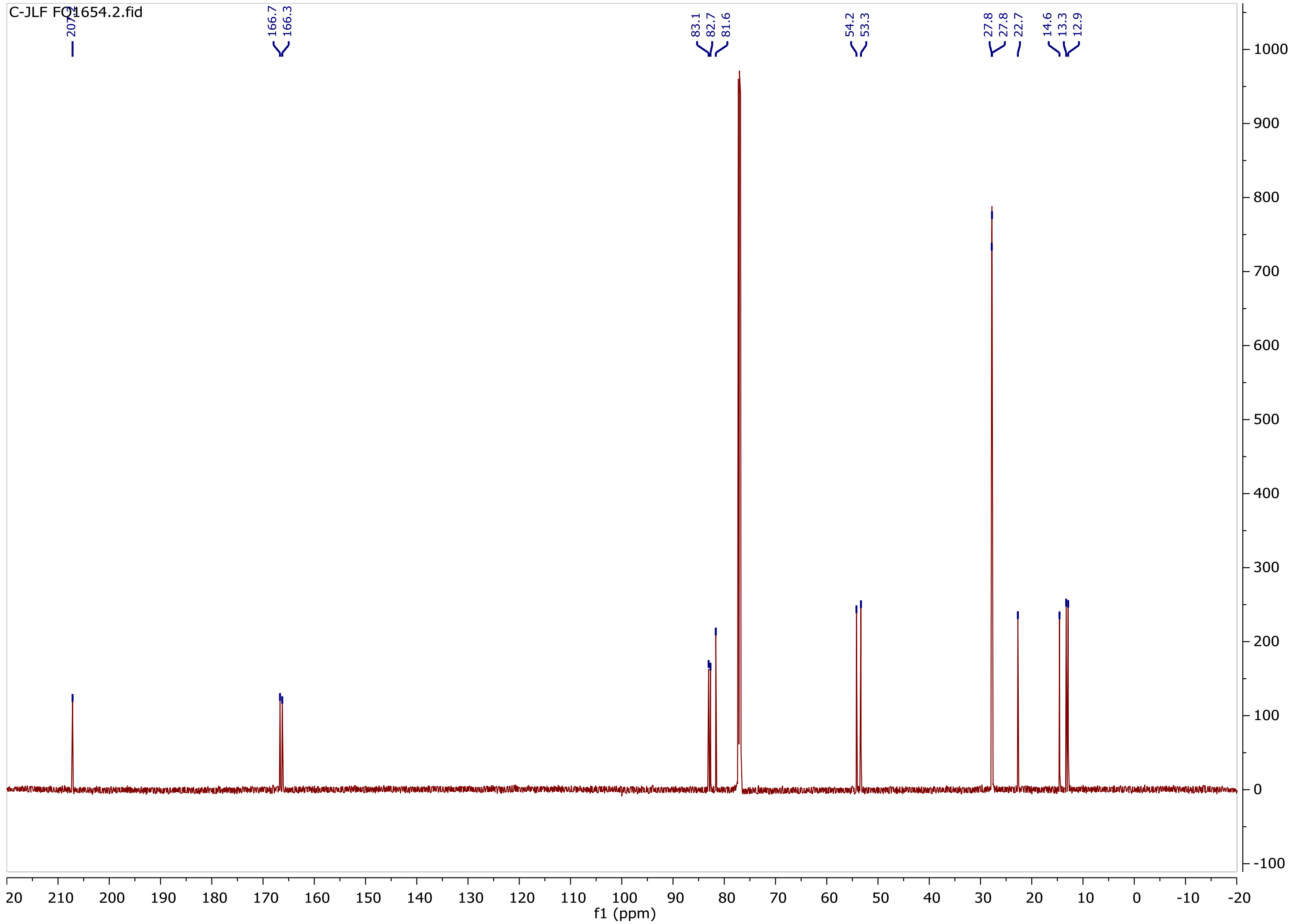


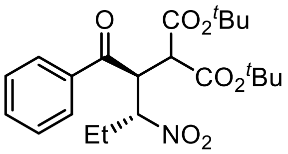
**2o**


C-JLF FQ1654.1.fid
4.76
4.72
4.33
4.33
4.32
4.31
3.64
3.63
2.02
1.98
1.50
1.49
1.47
1.44
1.17
1.12
1.05
1.01
0.98
0.94
1.00
1.02
1.00
0.94
11.82
9.34
1.07
2.02
1.25
f1 (ppm)

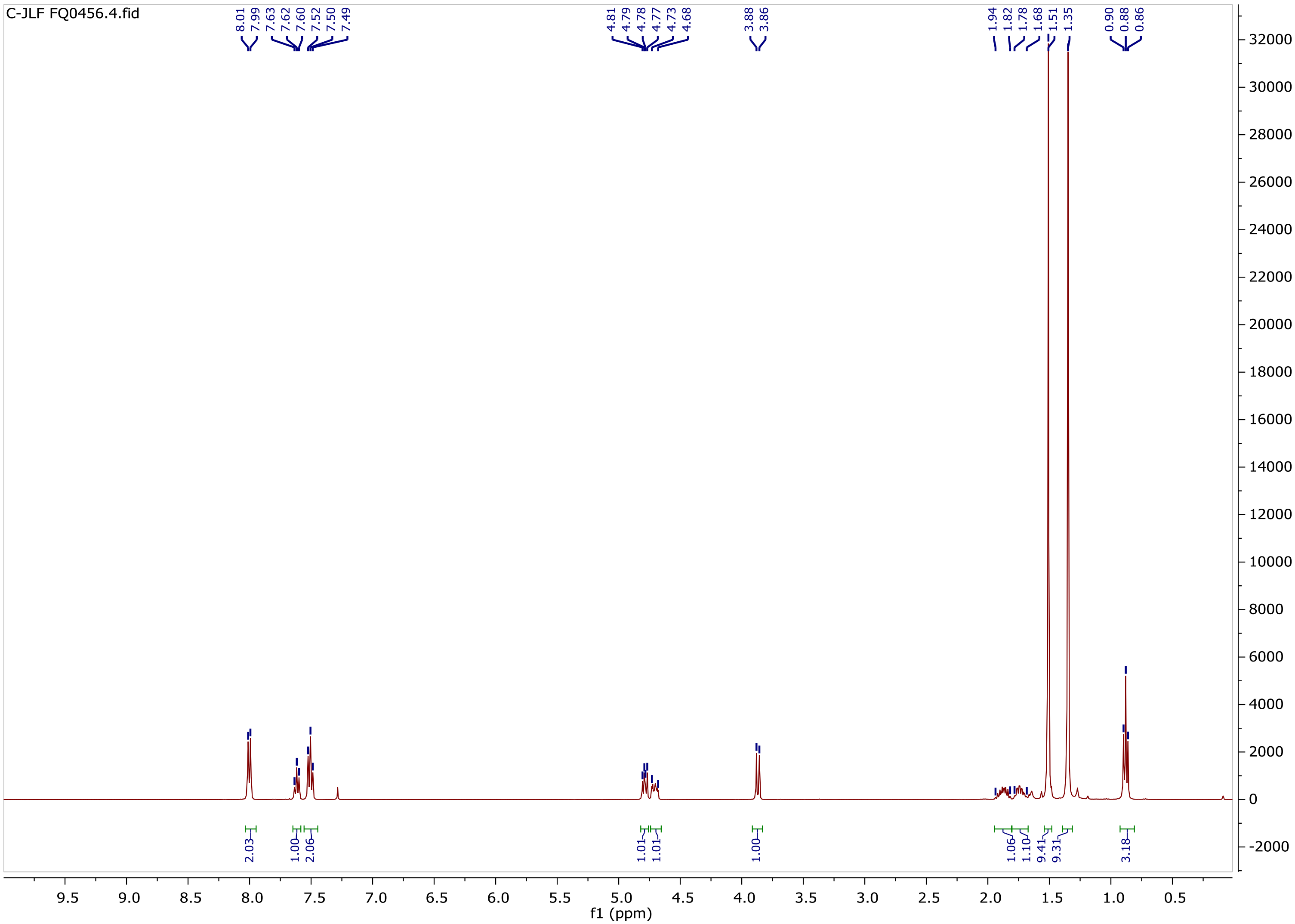

O
$CO_2{}^tBu$
$CO_2{}^tBu$
Me
$NO_2$

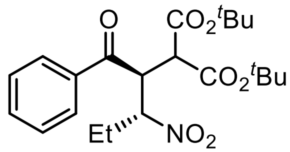
**2o**


C-JLF FQ1654.2.fid
207.1
166.7
166.3
83.1
82.7
81.6
54.2
53.3
27.8
27.8
22.7
14.6
13.3
12.9
f1 (ppm)

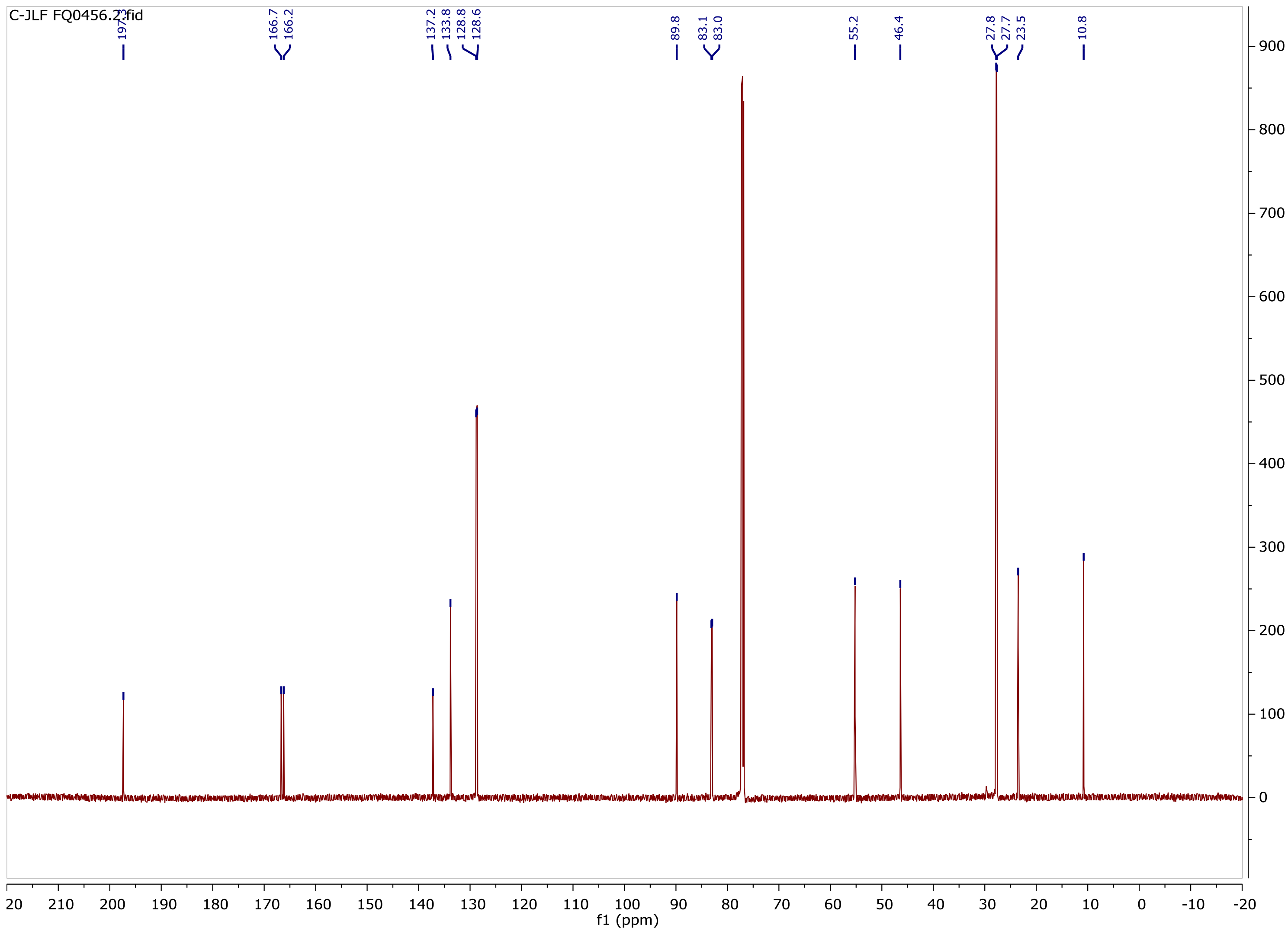


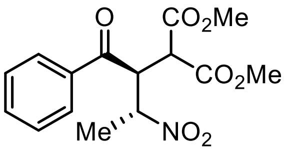
**2p**


C-JLF FQ0456.4.fid
8.01
7.99
7.63
7.62
7.60
7.52
7.50
7.49
4.81
4.79
4.78
4.77
4.73
4.68
3.88
3.86
1.94
1.82
1.78
1.68
1.51
1.35
0.90
0.88
0.86
2.03
1.00
2.06
1.01
1.01
1.00
1.06
1.10
9.41
9.31
3.18
f1 (ppm)

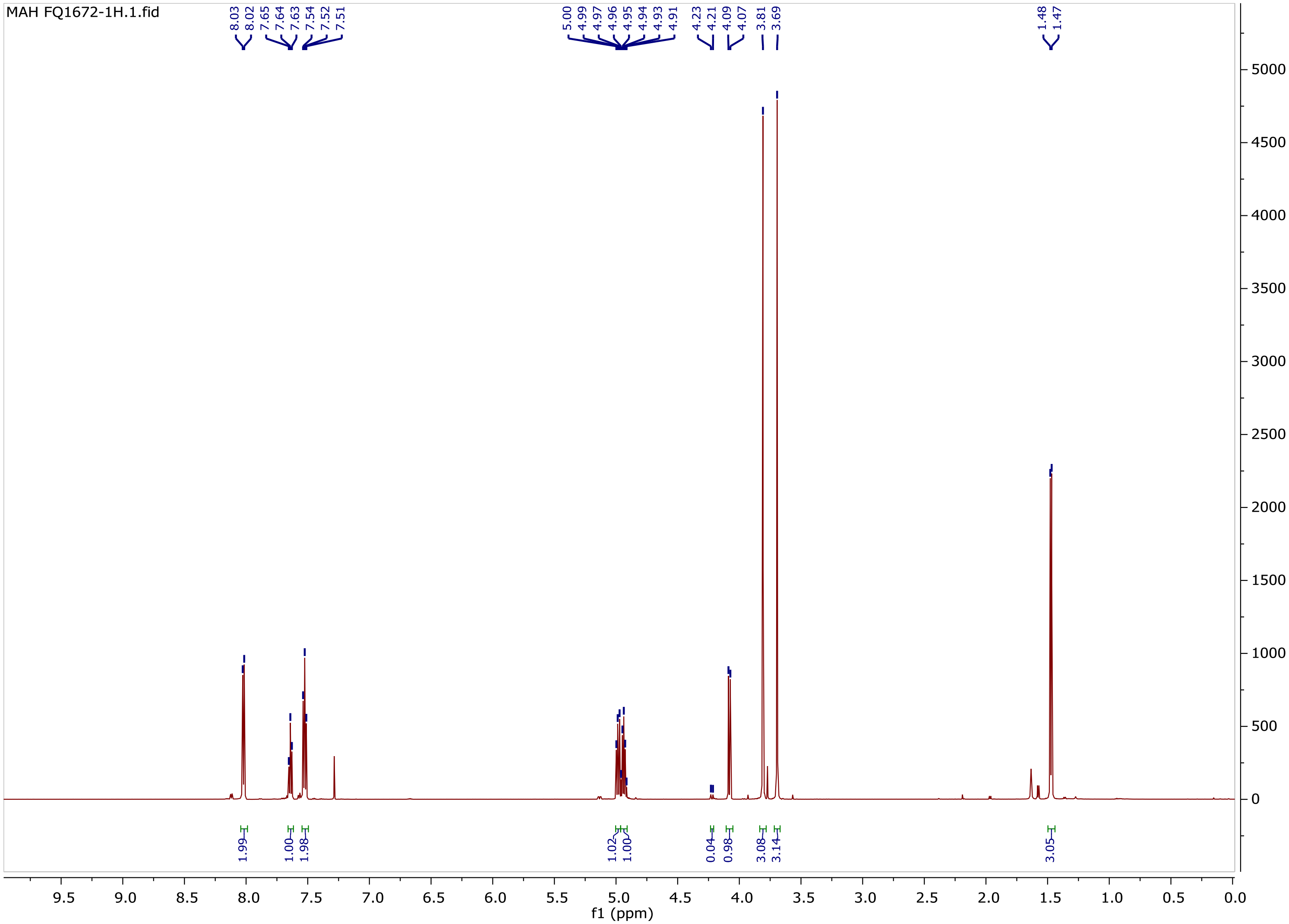


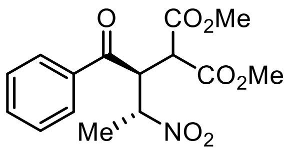
**2p**


C-JLF FQ0456.2.fid
197.2
166.7
166.2
137.2
133.8
128.8
128.6
89.8
83.1
83.0
55.2
46.4
27.8
27.7
23.5
10.8
f1 (ppm)

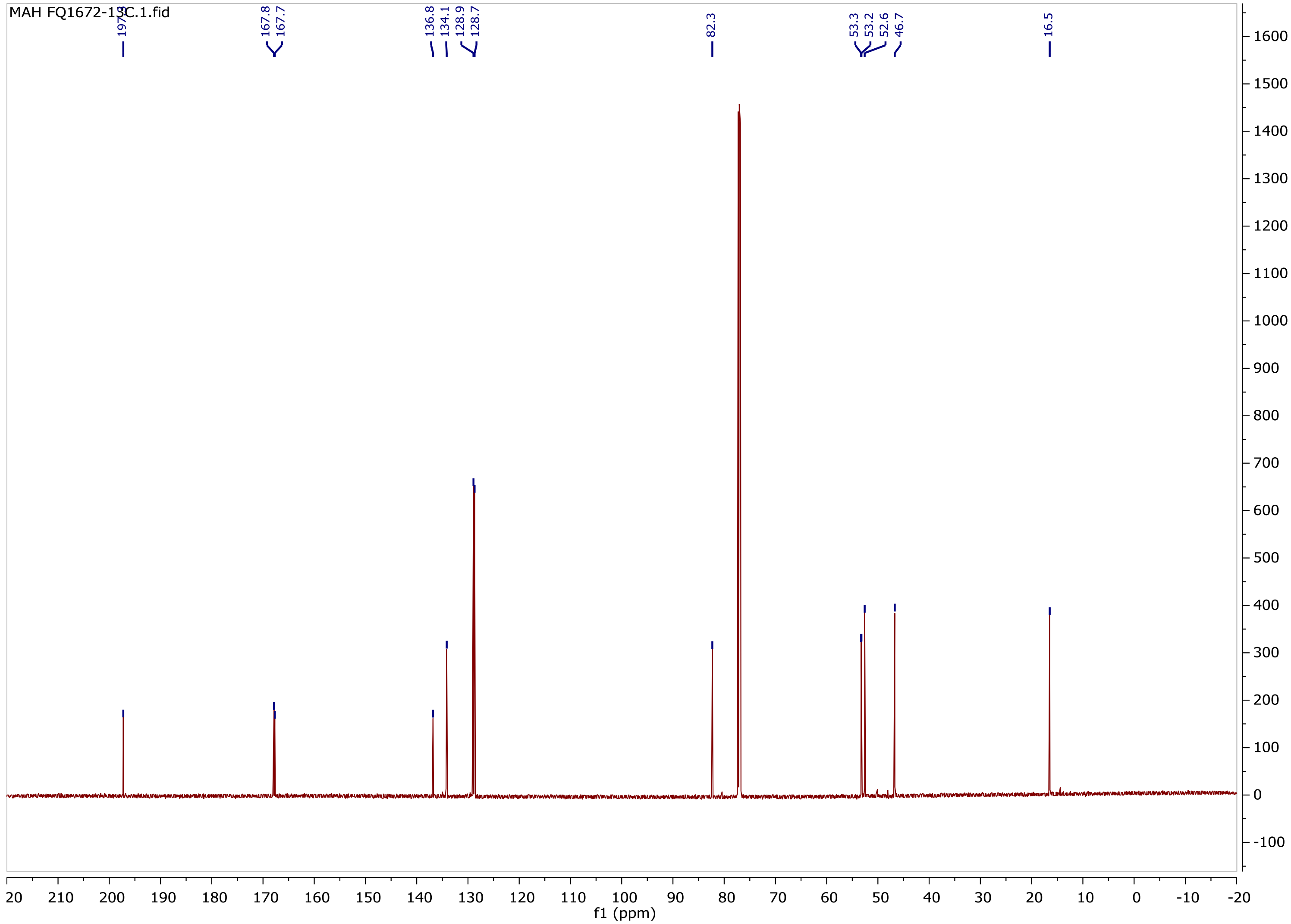


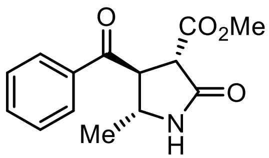
**4a**





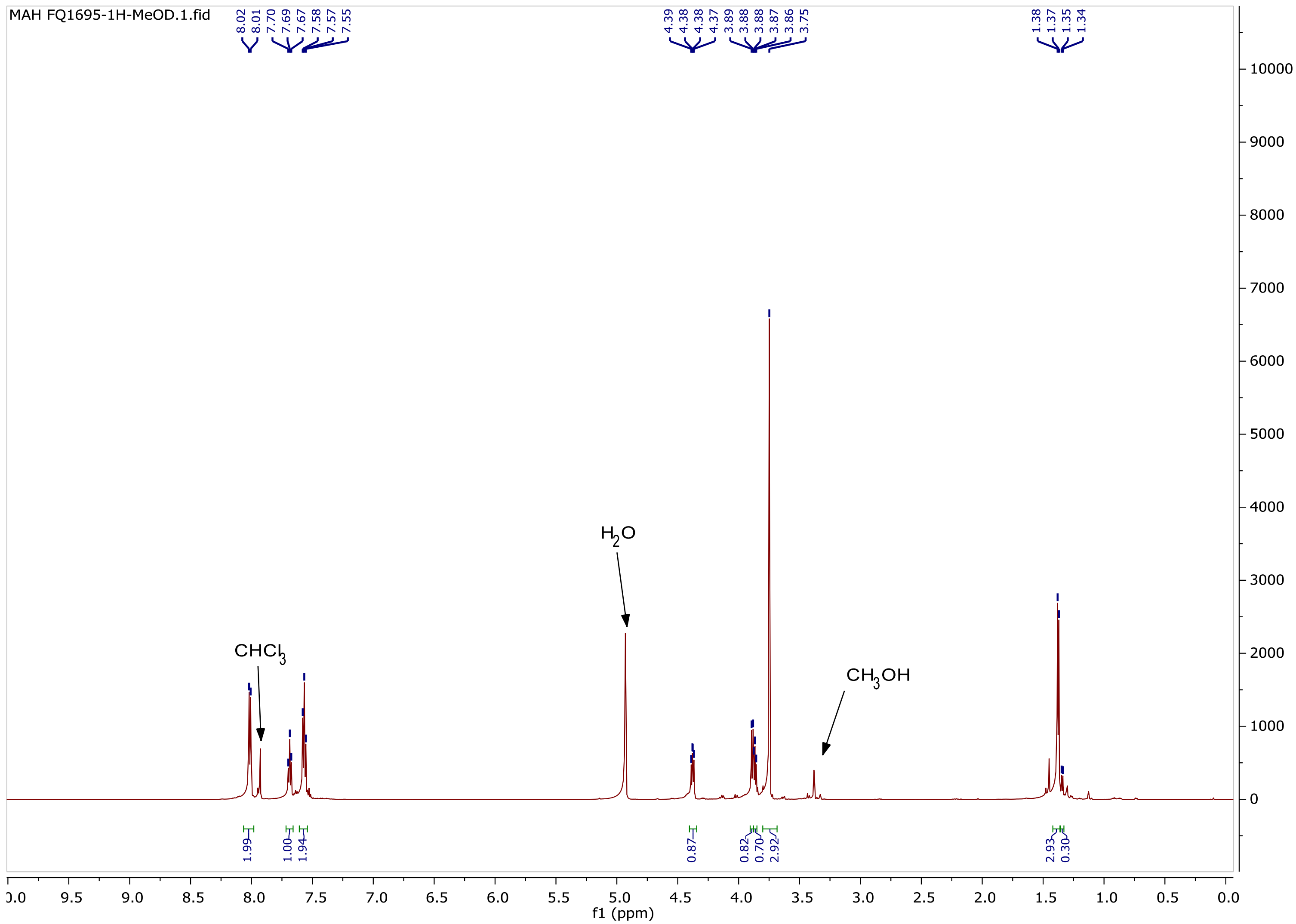
**4a**


MAH FQ1672-13C.1.fid
197.3
167.8
167.7
136.8
134.1
128.9
128.7
82.3
53.3
53.2
52.6
46.7
16.5
f1 (ppm)

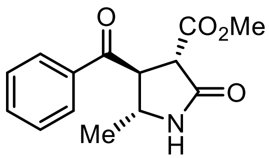


CO2Me
O
O
Me
N
H

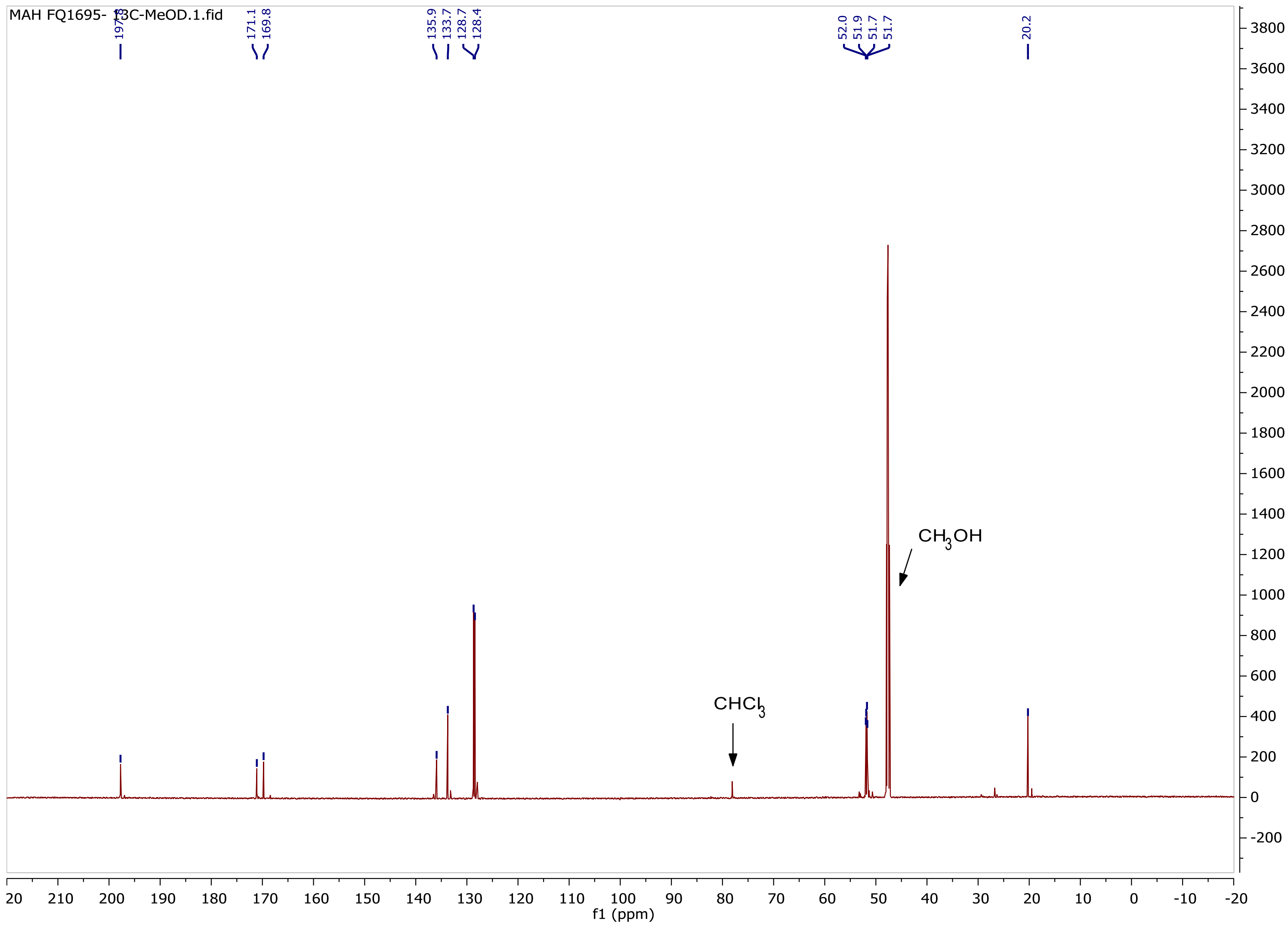

**5a**



MAH FQ1695-1H-MeOD.1.fid
8.02
8.01
7.70
7.69
7.67
7.58
7.57
7.55
4.39
4.38
4.38
4.37
3.89
3.88
3.88
3.87
3.86
3.75
1.38
1.37
1.35
1.34
CHCl3
H2O
CH3OH
1.99
1.00
1.94
0.87
0.82
0.70
2.92
2.93
0.30
f1 (ppm)



**5a**



MAH FQ1695- 13C-MeOD.1.fid
171.1
169.8
135.9
133.7
128.7
128.4
52.0
51.9
51.7
51.7
20.2
CHCl3
CH3OH
f1 (ppm)