1,6-Addition of Tertiary Carbon Radicals Generated From Alcohols or Carboxylic Acids by Visible-Light Photoredox Catalysis

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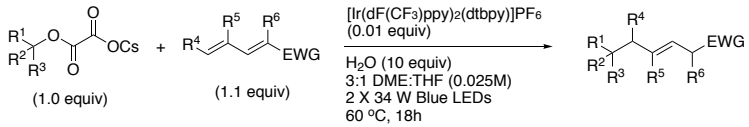
Materials and Methods.

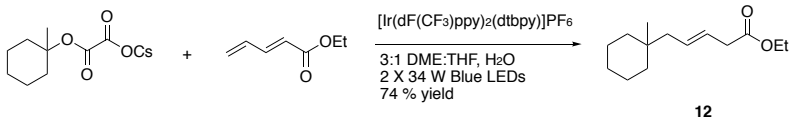
Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen or argon using anhydrous solvents (either freshly distilled or passed through activated alumina columns). For all photoredox reactions, solvents were sparged with argon for five minutes prior to use. All commercially obtained reagents were used as received. $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$.[1] Hemioxalate salts,[1] and ethyl (*E*)-penta-2,4-dienoate,[2] methyl (*E*)-penta-2,4-dienoate, [2] (*E*)-hexa-3,5-dien-2-one,[3] methyl (*E*)-2-methylpenta-2,4-dienoate,[4] (*E*)-5-methylhexa-3,5-dien-2-one,[5] methyl (*E*)-2,4-dimethylpenta-2,4-dienoate,[6] dimethyl (*E*)-2-(but-2-en-1-ylidene)malonate,[7] 3-vinylcyclopent-2-en-1-one,[8] and 3-vinylcyclohex-2-en-1-one[9] were prepared according to literature procedures. Reaction temperatures were controlled using an IKAmag temperature modulator. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 50 F254 pre-coated plates, (0.25 mm), and visualized by exposure to UV light (254 nm) and potassium permanganate staining. EMD silica gel 60 (particle size 0.040−0.063 mm) was used for flash column chromatography. ^{1}H NMR spectra were recorded on Bruker spectrometers (at 500 or 600 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. High-resolution mass spectra were obtained from UC Irvine Mass Spectrometry Facility with a Micromass LCT spectrometer. Kessil KSH150B 34 W LED Grow Light 150, Blue LEDs were purchased from http://www.amazon.com.

Safety Note: Blue light from high-intensity LEDs can be damaging to eyesight. It is important that the reaction setup be surrounded by an appropriate shield to protect researchers from exposure to the light from the LED lamps. Researchers should wear blue-light blocking safety glasses, such as Uvex Skyper Blue Computer Blocking Glasses (model #: S1933X), when the lamps are in operation.

General procedure for the coupling of an oxalate salt with a 1,3-diene:

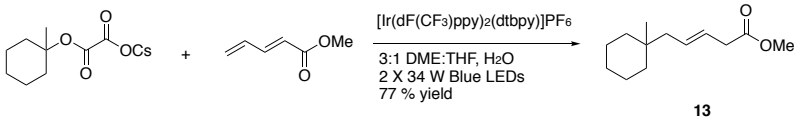


An 8 mL-scintillation vial equipped with a Teflon septum and a magnetic stir bar was charged with the oxalate salt (0.1 mmol, 1.0 equiv) and $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv). A 3:1 mixture of DME/THF (4 mL, 0.025 M) was added, followed by water (18 μL, 1.0 mmol, 10 equiv), and the 1,3-diene (0.11 mmol, 1.1 equiv). The reaction mixture was degassed by sparging with argon for 10 min, and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 18 h with the reaction temperature rising to 60 ^{o}C because of heat given off from the LEDs. The reaction mixture was diluted with water (10 mL) and the aqueous phase was extracted with Et_2O (3 x 10 mL). The combined ethereal extracts were washed with brine (10 mL), dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel to yield corresponding addition products. In some cases, the product contained trace amounts of the *Z* stereoisomer, which had not been removed by chromatographic purification.[10] Results of these experiments are summarized in Schemes 2 and 3 of the publication.



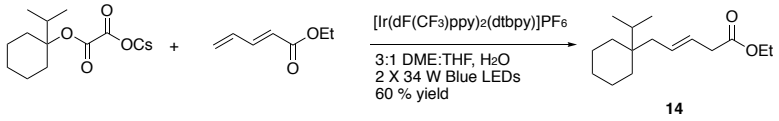
Ethyl (*E*)-5-(1-methylcyclohexyl)pent-3-enoate (12): According to the general procedure, cesium oxalate **10** (35 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and ethyl (*E*)-penta-2,4-dienoate (**11**) (14 mg, 0.11 mmol, 1.1 equiv) was used

the acceptor. The crude residue was purified by flash chromatography (50:1 hexanes/EtOAc) to yield ethyl ester **12** (17 mg, 74%) as a pale yellow oil.[10] R_f 0.2 (50:1 hexanes/EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$) δ 5.59 – 5.54 (m, 1H), 5.52 – 5.47 (m,1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.02 (dd, *J* = 7.2, 1.2 Hz, 2H), 1.94 (d, *J* = 7.2 Hz, 2H), 1.43 – 1.39 (m, 5H), 1.26 – 1.20 (m, 8H), 0.83 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 131.3, 124.0, 60.6, 45.0, 38.5, 37.8, 33.4, 26.6, 25.2, 22.2, 14.4; IR (thin film) 2925, 2860, 1744, 1450, 1249 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{14}H_{24}O_2$ $[M + Na]^+$ 247.1674, observed 247.1680.



13

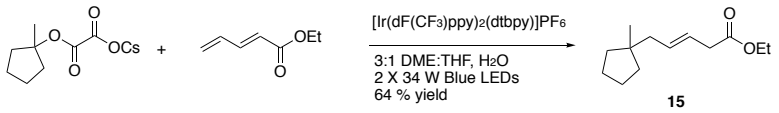
Methyl (*E*)-5-(1-methylcyclohexyl)pent-3-enoate (13): According to the general procedure, cesium oxalate **10** (35 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and methyl (*E*)-penta-2,4-dienoate (12 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (50:1 hexanes/EtOAc) to yield methyl ester **13** (16 mg, 77%) as a pale yellow oil.[10] R_f 0.2 (50:1 hexanes/EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$) δ 5.61 – 5.56 (m, 1H), 5.54 – 5.49 (m,1H), 3.69 (s, 3H), 3.06 (d, *J* = 6.8 Hz, 2H), 1.96 (d, *J* = 7.2 Hz, 2H), 1.47 – 1.40 (m, 5H), 1.32 – 1.20 (m, 5H), 0.85 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 131.6, 123.8, 51.9, 45.0, 38.2, 37.8, 33.5, 26.6, 25.3, 22.2; IR (thin film) 2924, 2847, 1747, 1436, 1251 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{13}H_{22}O_2$ $[M + H]^+$ 211.1698, observed 211.1698.



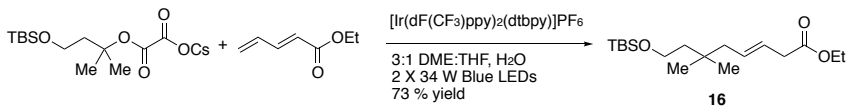
14

Ethyl (*E*)-5-(1-isopropylcyclohexyl)pent-3-enoate (14): According to the general procedure, the cesium oxalate (35 mg, 0.1 mmol, 1.1 equiv) was used as the radical precursor and ethyl (*E*)-penta-2,4-dienoate (**11**) (14 mg, 0.11 mmol, 1.1 equiv) was used

the acceptor. The crude residue was purified by flash chromatography (50:1 hexanes/EtOAc) to yield ethyl ester **14** (15 mg, 60% yield) as a pale yellow oil. R_f 0.2 (40:1 hexanes/EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$) δ 5.59 – 5.50 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.04 (d, *J* = 6.0 Hz, 2H), 2.09 (d, *J* = 7.2 Hz, 2H), 1.70 (sept, *J* = 6.6 Hz, 1H), 1.47 – 1.41 (m, 5H), 1.35 – 1.24 (m, 8H), 0.83 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 131.9, 123.6, 60.7, 38.6, 37.8, 36.0, 32.2, 31.7, 26.6, 21.7, 16.9, 14.4; IR (thin film) 2928, 2863, 1741, 1455, 1369 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{16}H_{28}O_2$ $[M + NH_4]^+$ 270.2433, observed 270.2428.

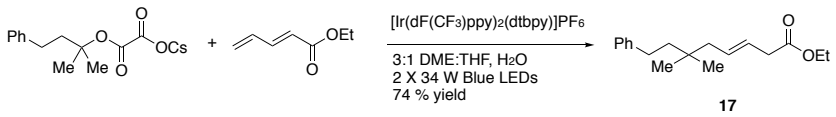


Ethyl (*E*)-5-(1-methylcyclopentyl)pent-3-enoate (15): According to the general procedure, the cesium oxalate (30 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and ethyl (*E*)-penta-2,4-dienoate (**11**) (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (50:1 hexanes/EtOAc) to yield ethyl ester **15** (14 mg, 64% yield) as a pale yellow oil. R_f 0.2 (40:1 hexanes/EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$) δ 5.61 – 5.56 (m, 1H), 5.54 – 5.50 (m, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.04 (d, *J* = 6.6 Hz, 2H), 2.02 (d, *J* = 7.2 Hz, 2H), 1.63 – 1.59 (m, 4H), 1.43 – 1.40 (m, 2H), 1.30 – 1.25 (m, 5H), 0.92 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 132.6, 123.7, 60.7, 45.1, 42.4, 39.1, 38.5, 26.6, 24.7, 14.4; IR (thin film) 2954, 2928, 2867, 1741, 1458 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{13}H_{22}O_2$ $[M + NH_4]^+$ 228.1964, observed 228.1956.

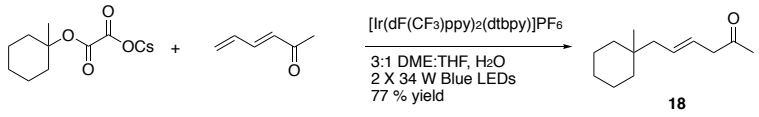


Ethyl (*E*)-8-((*tert*-butyldimethylsilyl)oxy)-6,6-dimethyloct-3-enoate (16): According to the general procedure, the cesium oxalate (42 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and ethyl (*E*)-penta-2,4-dienoate (**11**) (14 mg, 0.11 mmol, 1.1 equiv)

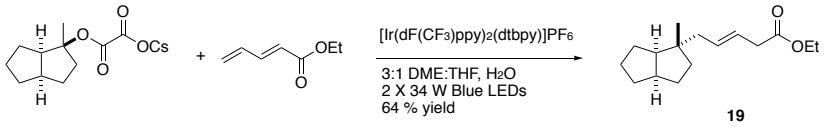
was used the acceptor. The crude residue was purified by flash chromatography (100:1 hexanes/EtOAc) to yield ethyl ester **16** (24 mg, 73% yield) as a pale yellow oil.[11] R_f 0.5 (50:1 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60 – 5.50 (m, 2H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.67 (t, *J* = 7.5 Hz, 2H), 3.04 (d, *J* = 6.0 Hz, 2H), 1.94 (d, *J* = 6.5 Hz, 2H), 1.46 (t, *J* = 7.5 Hz, 2H), 0.89 (s, 9H), 0.88 (s, 6H), 0.05 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 131.5, 124.3, 60.7, 60.2, 45.7, 44.3, 38.5, 32.9, 27.5, 26.2, 18.5, 14.4, -5.1; IR (thin film) 2956, 2929, 2857, 1734, 1471 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{18}H_{36}O_3Si$ $[M + Na]^+$ 351.2332, observed 351.2326.



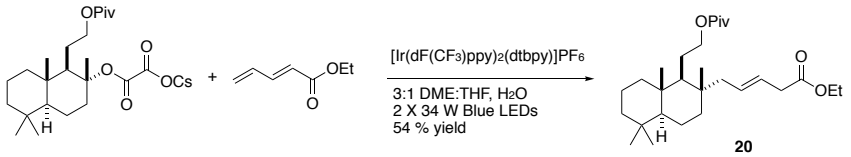
Preparation of Ethyl (*E*)-6,6-dimethyl-8-phenyloct-3-enoate (17) on 1 Mmol Scale: According to the general procedure, the cesium oxalate (368 mg, 1 mmol, 1.0 equiv) was used as the radical precursor and ethyl (*E*)-penta-2,4-dienoate (**11**) (139 mg, 1.1 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (100:1 hexanes/EtOAc) to yield ethyl ester **17** (203 mg, 74% yield) as a pale yellow oil.[10] R_f 0.2 (100:1 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 2H), 7.19 – 7.17 (m, 3H), 5.65 – 5.55 (m, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.07 (d, *J* = 6.6 Hz, 2H), 2.58 – 2.55 (m, 2H), 2.03 (d, *J* = 6.6 Hz, 2H), 1.51 – 1.49 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.95 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 143.6, 131.4, 128.5, 125.7, 124.3, 60.7, 45.0, 44.3, 38.5, 33.7, 30.9, 27.2, 27.1, 14.1; IR (thin film) 3026, 2957, 1744, 1469, 1366 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{18}H_{26}O_2$ $[M + Na]^+$ 297.1830, observed 297.1826.



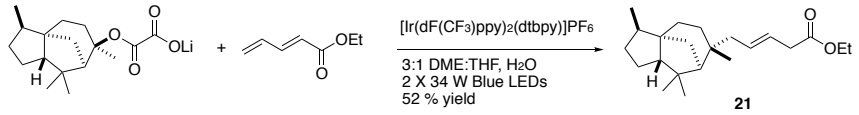
(*E*)-6-(1-methylcyclohexyl)hex-4-en-2-one (18): According to the general procedure, cesium oxalate **10** (35 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and (*E*)-hexa-3,5-dien-2-one (11 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (50:1 hexanes/EtOAc) to yield ketone **18** (15 mg, 0.077 mmol, 77% yield) as a pale yellow oil.[10] R_f 0.6 (85:15 hexanes/EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$) δ 5.61 – 5.56 (m, 1H), 5.53 – 5.48 (m,1H), 3.13 (d, *J* = 7.2 Hz, 2H), 2.16 (s, 3H), 1.98 (d, *J* = 7.2 Hz, 2H), 1.47 – 1.40 (m, 5H), 1.33 – 1.21 (m, 5H), 0.85 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.8, 132.1, 124.1, 48.1, 45.1, 37.8, 33.5, 29.5, 26.6, 25.4, 22.2; IR (thin film) 2935, 2859, 1718, 1450, 1356 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{13}H_{22}O$ $[M + Na]^+$ 217.1568, observed 217.1560.



Ethyl (*E*)-5-((1*S*,3a*R*,6a*R*)-1-methyloctahydropentalen-1-yl)pent-3-enoate (19): According to the general procedure, the cesium oxalate (52 mg, 0.15 mmol, 1.0 equiv) was used as the radical precursor and ethyl (*E*)-penta-2,4-dienoate (21 mg, 0.165 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (50:1 hexanes/EtOAc) to yield ethyl ester **19** (24 mg, 64% yield) as a pale yellow oil. R_f 0.5 (90:10 hexanes/EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$) δ 5.61 – 5.56 (m, 1H), 5.53 – 5.48 (m,1H), 4.14 (q, *J* = 7.1 Hz, 2 H), 3.04 (d, *J* = 6.5 Hz, 2H), 2.49 – 2.43 (m, 1H), 1.99 – 1.91 (m, 3H), 1.90 – 1.84 (m, 1H), 1.82 – 1.77 (m, 1H), 1.64 – 1.60 (m, 1H), 1.53 – 1.50 (m, 1H), 1.39 – 1.30 (m, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.24 – 1.18 (m, 2H), 1.15 – 1.10 (m, 1H), 0.90 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 132.1, 123.6, 60.5, 53.5, 44.5, 44.4, 42.6, 38.4, 37.2, 35.3, 31.5, 29.2, 27.9, 21.6, 14.3; IR (thin film) 2941, 2862, 1736, 1159, 968 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{16}H_{26}O_2$ $[M + Na]^+$ 273.1830, observed 273.1817.

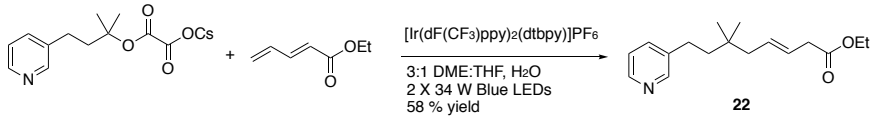


Ethyl (*E*)-5-((1*S*,2*S*,4a*S*,8a*S*)-2,5,5,8a-tetramethyl-1-(2-(pivaloyloxy)ethyl)decahydronaphthalen-2-yl)pent-3-enoate (20): According to the general procedure, the cesium oxalate (81 mg, 0.15 mmol, 1.0 equiv) was used as the radical precursor and ethyl (*E*)-penta-2,4-dienoate (21 mg, 0.165 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (20:1 hexanes/EtOAc) to yield ethyl ester **20** (36 mg, 54% yield) as a pale yellow oil.[10] R_f 0.6 (80:20 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.58 – 5.50 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.03 – 3.99 (m ,1H), 3.95 – 3.91 (m, 1H), 3.04 (d, *J* = 5.7 Hz, 2H), 2.10 – 2.07 (m, 1H), 1.82 – 1.79 (m, 1H), 1.68 (app d, J = 12 Hz, 1 H), 1.60 – 1.47 (m, 5H), 1.43 – 1.30 (m, 3H), 1.27 (app t, J = 7.2 Hz, 4H), 1.20 (s, 9H), 1.16 – 1.09 (m, 1H), 0.86 – 0.84 (m, 7H) 0.82 (s, 3H), 0.80 – 0.78 (m, 4H), 0.71 (t, *J* = 3.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.7, 172.1, 130.8, 124.7, 66.40, 60.6, 56.4, 55.8, 47.2, 42.1, 40.1, 39.6, 39.2, 38.7, 38.4, 38.1, 33.3, 27.3, 25.3, 21.6, 19.8, 18.6, 18.3, 16.1, 14.3; IR (thin film) 2931, 1726, 1282, 1152 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{28}H_{48}O_4$ $[M + Na]^+$ 471.3450, observed 471.3450.

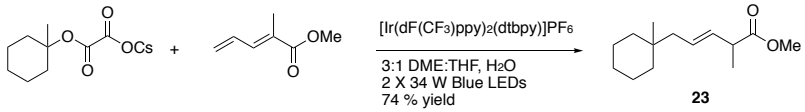


Ethyl (*E*)-5-((3*R*,3a*S*,6*R*,7*S*,8a*S*)-3,6,8,8-tetramethyloctahydro-1*H*-3a,7-methanoazulen-6-yl)pent-3-enoate (21): According to the general procedure, the lithium oxalate (45 mg, 0.15 mmol, 1.0 equiv) was used as the radical precursor and ethyl (*E*)-penta-2,4-dienoate (21 mg, 0.165 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (50:1 hexanes/EtOAc) to yield ethyl ester **21** (26 mg, 52% yield) as a pale yellow oil. R_f 0.5 (90:10 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.56 – 5.48 (m, 2H), 4.14 (q, J = 7.2 Hz, 2H), 3.04 (d, *J* = 5.4 Hz, 2H), 2.47 – 2.44 (m, 1H), 1.87 (sextet, *J* = 6.0 Hz, 1H), 1.76 – 1.70 (m, 2H), 1.65 – 1.56 (m, 3H), 1.53 – 1.45 (m, 3H), 1.39 – 1.32 (m, 4H), 1.28 – 1.24 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.21 (s, 3H), 1.03 (s, 3H), 0.98 (s, 3H), 0.84 (d, *J* = 7.1

Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 131.6, 123.7, 60.5, 57.6, 57.1, 53.6, 45.2, 44.3, 42.0, 39.9, 38.5, 38.1, 37.0, 33.6, 30.4, 29.8, 29.4, 27.0, 25.5, 15.5, 14.3; IR (thin film) 2935, 1738, 1462, 1157 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{22}H_{36}O_2$ [M + Na]$^+$ 355.2613, observed 355.2618.

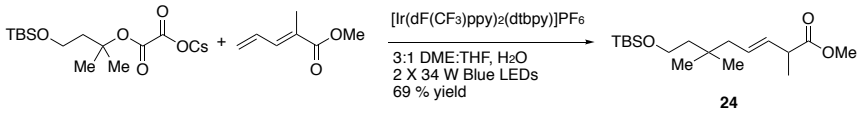


Ethyl (*E*)-6,6-dimethyl-8-(pyridin-3-yl)oct-3-enoate (22): According to the general procedure, the cesium oxalate (55 mg, 0.15 mmol, 1.0 equiv) was used as the radical precursor and ethyl (*E*)-penta-2,4-dienoate (21 mg, 0.165 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (5:1 hexanes/EtOAc) to yield ethyl ester **22** (24mg, 58% yield) as a pale yellow oil. R_f 0.2 (80:20 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, J = 1.8 Hz, 1H), 8.42 (dd, J = 4.8, 1.4 Hz, 1H), 7.48 (td, J = 7.6, 1.8 Hz, 1H), 7.19 (dd, J = 7.6, 4.8 Hz, 1H), 5.62 – 5.54 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.06 (d, *J* = 5.4 Hz, 2H), 2.57 – 2.54 (m, 2H), 2.02 (d, *J* = 6.0 Hz, 2H), 1.49 – 1.46 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H), 0.95 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 149.9, 147.2, 135.8, 131.0, 124.4, 123.3, 60.6, 44.8, 43.8, 38.3, 33.6, 27.9, 20.1, 14.3; IR (thin film) 2954, 2906, 1732, 1172cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for C17H25NO_2 [M + Na]$^+$ 298.1783, observed 298.1789.

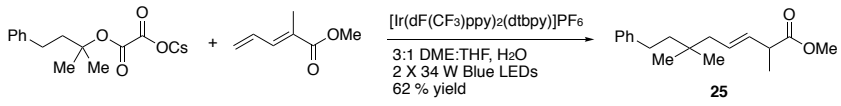


Methyl (*E*)-2-methyl-5-(1-methylcyclohexyl)pent-3-enoate (23): According to the general procedure, cesium oxalate **10** (35 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and methyl (*E*)-2-methylpenta-2,4-dienoate (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (50:1 hexanes/EtOAc) to yield methyl ester **23** (17 mg, 74% yield) as a pale yellow oil.

R_f 0.2 (40:1 hexanes/EtOAc); visualized with $KMnO_4$. ^1H NMR (500 MHz, $CDCl_3$) δ 5.59 – 5.54 (m, 1H), 5.50 – 5.46 (m,1H), 3.68 (s, 3H), 3.13 (p, J = 7.0 Hz, 1H), 1.93 (d, *J* = 7.5 Hz, 2H), 1.43 – 1.22 (m, 13H), 0.83 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 131.2, 129.0, 52.0, 44.9, 43.1, 37.832, 37.826, 33.5, 26.6, 25.3, 22.2, 17.8; IR (thin film) 2925, 2860, 1755, 1452, 1375 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{14}H_{24}O_2$ $[M + Na]^+$ 247.1674, observed 247.1677.

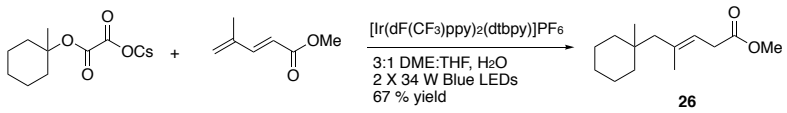


Methyl (*E*)-8-((*tert*-butyldimethylsilyl)oxy)-2,6,6-trimethyloct-3-enoate (24): According to the general procedure, the cesium oxalate (42 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and methyl (*E*)-2-methylpenta-2,4-dienoate (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (95:5 hexanes/EtOAc) to yield methyl ester **24** (23 mg, 69% yield) as a pale yellow oil. R_f 0.7 (85:15 hexanes/EtOAc); visualized with $KMnO_4$. ^1H NMR (500 MHz, $CDCl_3$) δ 5.60 – 5.54 (m, 1H), 5.48 (dd, J = 15.3, 7.5 Hz, 1H), 3.68 – 3.65 (m, 5H), 3.13 (p, *J* = 7.5 Hz, 1H), 1.92 (d, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 7.5 Hz, 2H), 1.25 (d, *J* = 7.5 Hz, 3H), 0.89 (s, 9H), 0.86 (s, 6H), 0.05 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 131.5, 129.0, 60.2, 52.0, 45.6, 44.3, 43.1, 32.9, 27.4, 26.2, 18.5, 17.7, -5.1; IR (thin film) 2955, 2930, 2857, 1730, 1463 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{18}H_{36}O_3Si$ $[M + Na]^+$ 351.2332, observed 351.2342.

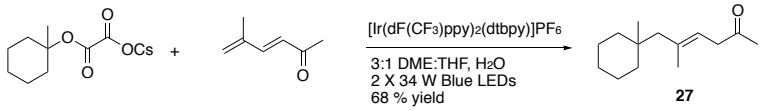


Methyl (*E*)-2,6,6-trimethyl-8-phenyloct-3-enoate (25): According to the general procedure, the cesium oxalate (110 mg, 0.3 mmol, 1.0 equiv) was used as the radical precursor and methyl (*E*)-2-methylpenta-2,4-dienoate (42 mg, 0.33 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (95:5

hexanes/EtOAc) to yield methyl ester **25** (52 mg, 62% yield) as a pale yellow oil. R_f 0.7 (85:15 hexanes/EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 2H), 7.18 – 7.17 (m, 3H), 5.62 – 5.52 (m, 2H), 3.67 (s, 3H), 3.16 (quintet, *J* = 7.2 Hz, 1H), 2.57 – 2.54 (m, 2H), 2.00 (d, *J* = 6.9 Hz, 2H), 1.50 – 1.47 (m, 2H), 1.27 (d, *J* = 7.2 Hz, 3H), 0.93 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 143.5, 131.4, 128.9, 128.4, 128.3, 125.6, 51.8, 44.7, 44.2, 43.0, 33.6, 30.7, 27.09, 27.06, 17.6; IR (thin film) 2953, 2933, 1738, 1454, 1161 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{18}H_{26}O_2$ [M + Na]$^+$297.1830, observed 297.1840.

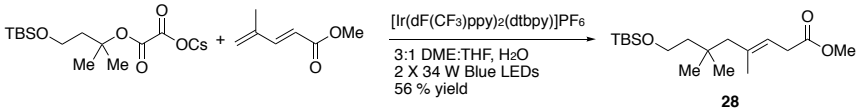


Methyl (E)-4-methyl-5-(1-methylcyclohexyl)pent-3-enoate (26): According to the general procedure, the cesium oxalate **10** (35 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and methyl (*E*)-4-methylpenta-2,4-dienoate (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (40:1 hexanes/EtOAc) to yield methyl ester **26** (15 mg, 67% yield) as a pale yellow oil. R_f 0.2 (50:1 hexanes/EtOAc); visualized with $KMnO_4$. ^1H NMR (500 MHz, $CDCl_3$) δ 5.29 (t, J = 7.0 Hz, 1H), 3.69 (s, 3H), 3.07 (d, J = 7.0 Hz, 2H), 1.99 (s, 2H), 1.69 (s, 3H), 1.50 – 1.41 (m, 5H), 1.29 – 1.26 (m, 5H), 0.87 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 137.2, 119.6, 52.3, 51.9, 38.5, 34.4, 34.0, 26.7, 25.3, 22.4, 19.7; IR (thin film) 2925, 2849, 1758, 1435, 1260 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{14}H_{24}O_2$ [M + NH_4]$^+$ 242.2120, observed 242.2110.

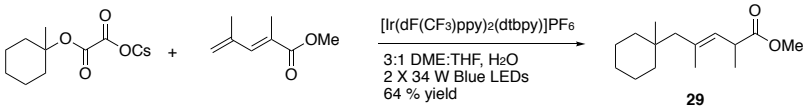


(*E*)-5-methyl-6-(1-methylcyclohexyl)hex-4-en-2-one (27): According to the general procedure, cesium oxalate **10** (35 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and (*E*)-5-methylhexa-3,5-dien-2-one (12 mg, 0.11 mmol, 1.1 equiv) was used

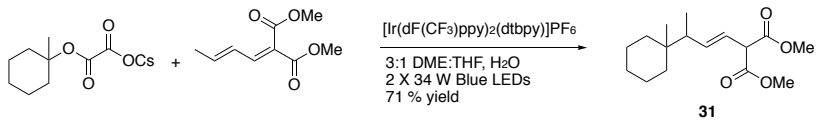
the acceptor. The crude residue was purified by flash chromatography (50:1 hexanes/EtOAc) to yield ketone **27** (14 mg, 68% yield) as a pale yellow oil. R_f 0.2 (50:1 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.29 (tt, *J* = 7.2, 0.6 Hz, 1H), 3.13 (d, *J* = 7.2 Hz, 2H), 2.15 (s, 3H), 2.00 (s, 2H), 1.69 (d, *J* = 0.6 Hz, 3H), 1.49 – 1.41 (m, 5H), 1.30 – 1.25 (m, 5H), 0.87 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.6, 137.6, 119.7, 52.4, 44.0, 38.5, 34.4, 29.6, 26.7, 25.4, 22.4, 19.8; IR (thin film) 2928, 2860, 1716, 1450, 1355 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{14}H_{24}O$ [M + NH_4]$^+$ 226.171, observed 226.2164.



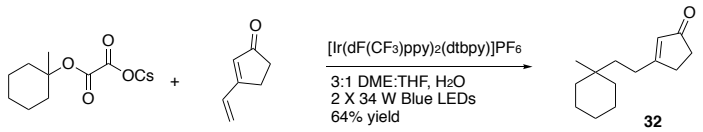
Methyl (*E*)-8-((*tert*-butyldimethylsilyl)oxy)-4,6,6-trimethyloct-3-enoate (28): According to the general procedure, the cesium oxalate (42 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and methyl (*E*)-4-methylpenta-2,4-dienoate (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (95:5 hexanes/EtOAc) to yield methyl ester **28** (18 mg, 56% yield) as a pale yellow oil.[10] R_f 0.7 (85:15 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (t, *J* = 7.0 Hz, 1H), 3.70 – 3.68 (m, 5H), 3.07 (d, *J* = 7.0 Hz, 1H), 1.98 (s, 2H), 1.69 (s, 3H), 1.49 (t, *J* = 7.5 Hz, 2H), 0.90 (s, 6H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 137.0, 120.0, 60.3, 52.4, 51.9, 45.3, 34.0, 33.8, 27.8, 26.2, 19.5, 18.5, -5.0; IR (thin film) 2954, 2857, 1744, 1471, 1255 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{18}H_{36}O_3Si$ [M + Na]$^+$ 351.2332, observed 351.2332.



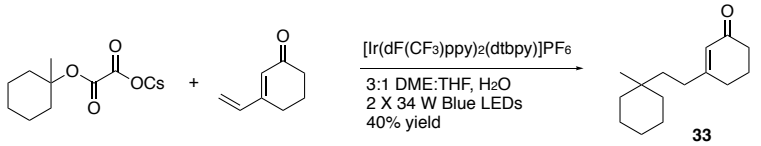
Methyl (*E*)-2,4-dimethyl-5-(1-methylcyclohexyl)pent-3-enoate (29): According to the general procedure, cesium oxalate **10** (35 mg, 0.1 mmol, 1.1 equiv) was used as the radical precursor and methyl (*E*)-2,4-dimethylpenta-2,4-dienoate (15 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (95:5 hexanes/EtOAc) to yield methyl ester **29** (15 mg, 64% yield) as a pale yellow oil. R_f 0.7 (85:15 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.13 (d, *J* = 8.0 Hz, 1H), 3.67 (s, 3H), 3.37 – 3.32 (m, 1H), 1.95 (s, 2H), 1.71 (d, *J* = 1.4 Hz, 3H), 1.49 – 1.40 (m, 5H), 1.26 – 1.21 (m, 8H), 0.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 135.5, 127.8, 52.2, 51.9, 39.2, 38.53, 38.48, 34.4, 26.7, 25.3, 22.4, 19.7, 18.1; IR (thin film) 2925, 2860, 1740, 1452, 1376 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{15}H_{26}O_2$ $[M + NH_4]^+$ 256.2277, observed 256.2270.



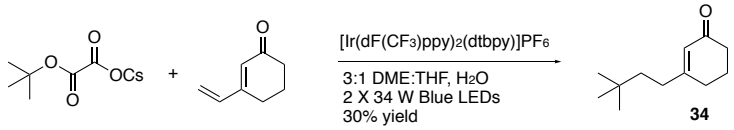
Dimethyl (*E*)-2-(3-(1-methylcyclohexyl)but-1-en-1-yl)malonate (31): According to the general procedure, cesium oxalate **10** (35 mg, 0.1 mmol, 1.1 equiv) was used as the radical precursor and dimethyl (*E*)-2-(but-2-en-1-ylidene)malonate (20 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (25:1 hexanes/EtOAc) to yield malonate **31** (20 mg, 71% yield) as a pale yellow oil. R_f 0.4 (20:1 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.67 – 5.60 (m, 2H), 4.03 (d, *J* = 7.8 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 2.13 (p, *J* = 7.2 Hz, 1H), 1.51 – 1.37 (m, 5H), 1.29 – 1.22 (m, 5H), 0.92 (d, *J* = 7.2 Hz, 3H), 0.78 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.15, 169.13, 140.2, 121.0, 55.6, 52.9, 52.8, 45.6, 36.5, 36.1, 35.4, 26.6, 22.1, 22.0, 20.2, 14.2; IR (thin film) 2925, 2860, 1740, 1452, 1376 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{16}H_{26}O_4$ $[M + Na]^+$ 305.1729, observed 305.1719.



3-(2-(1-Methylcyclohexyl)ethyl)cyclopent-2-en-1-one (32): According to the general procedure, cesium oxalate **10** (35 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and 3-vinylcyclopent-2-en-1-one (12 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (5:1 hexanes/EtOAc) to yield ketone **32** (13 mg, 64% yield) as a pale yellow oil. R_f 0.2 (5:1 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.94 (p, *J* = 1.8 Hz, 1H), 2.60 – 2.58 (m, 2H), 2.41 – 2.39 (m, 2H), 2.36 – 2.33 (m, 2H), 1.49 – 1.43 (m, 7H), 1.33 – 1.26 (m, 5H), 0.90 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 210.3, 184.4, 129.3, 39.5, 37.8, 35.5, 32.7, 31.9, 27.9, 26.6, 24.8, 22.2; IR (thin film) 2923, 2854, 1733, 1615, 1438 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{12}H_{22}O$ $[M + Na]^+$ 229.1568, observed 229.1578.

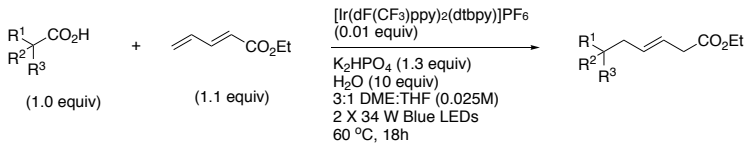


3-(2-(1-Methylcyclohexyl)ethyl)cyclohex-2-en-1-one (33): According to the general procedure, cesium oxalate **10** (35 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and 3-vinylcyclohex-2-en-1-one (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (5:1 hexanes/EtOAc) to yield ketone **33** (9 mg, 40% yield) as a pale yellow oil. R_f 0.2 (5:1 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.89 (t, *J* = 1.2 Hz, 1H), 2.37 – 2.35 (m, 2H), 2.31 (t, *J* = 5.6 Hz, 2H), 2.15 – 2.12 (m, 2H), 1.99 (p, J = 6.6 Hz, 2H), 1.45 – 1.37 (m, 7H), 1.34 – 1.26 (m, 5H), 0.88 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.2, 168.1, 125.6, 39.5, 37.9, 37.5, 32.8, 32.5, 30.2, 26.6, 25.0, 23.0, 22.2; IR (thin film) 2924, 2859, 1690, 1624, 1453 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{15}H_{24}O$ $[M + Na]^+$ 243.1725, observed 243.1725.

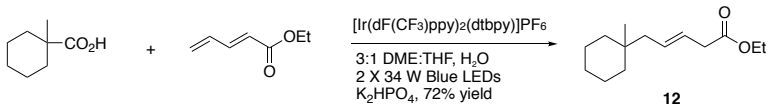


3-(3,3-dimethylbutyl)cyclohex-2-en-1-one (34): According to the general procedure, the cesium oxalate (28 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and 3-vinylcyclohex-2-en-1-one (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (5:1 hexanes/EtOAc) to yield ketone **34** (6 mg, 30% yield) as a pale yellow oil. R_f 0.2 (5:1 hexanes/EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$) δ 5.88 (t, *J* = 1.2 Hz, 1H), 2.36 – 2.34 (m, 2H), 2.30 (t, *J* = 6.0 Hz, 2H), 2.18 – 2.15 (m, 2H), 1.99 (p, J = 6.0 Hz, 2H), 1.38 – 1.35 (m, 2H), 0.92 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.1, 167.8, 125.6, 41.5, 37.5, 33.7, 30.5, 30.1, 29.4, 23.0; IR (thin film) 2953, 2867, 2080, 1673, 1625 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{12}H_{20}O$ $[M + Na]^+$ 203.1412, observed 203.1413.

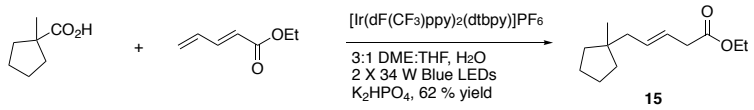
General procedure for the coupling of carboxylic acids with 1,3-dienes:



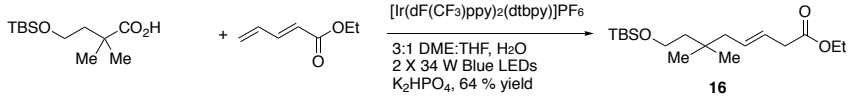
A 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with the carboxylic acid (0.1 mmol, 1.0 equiv) and $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv). A 3:1 mixture of DME/THF (4 mL, 0.025 M) was added, followed by water (18 μL, 1.0 mmol, 10 equiv), K_2HPO_4 (23 mg, 0.13 equiv, 1.3 equiv) and the pentadienoate **11** (14 mg, 0.11 mmol, 1.1 equiv). The reaction mixture was degassed by sparging with argon for 10 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 18 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with water (10 mL) and the aqueous phase was extracted with Et_2O (3 x 10 mL). The combined ethereal extracts were washed with brine (10 mL), dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel to yield corresponding addition products. Results of these experiments are summarized in Scheme 4 of the publication.



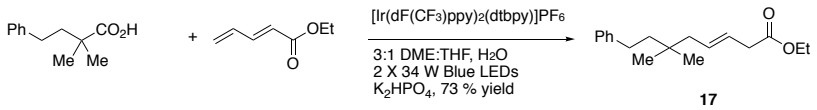
Ethyl (*E*)-5-(1-methylcyclohexyl)pent-3-enoate (12): According to the general procedure, carboxylic acid (14 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and pentadienoate **11** (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (5:1 hexanes/EtOAc) to yield ethyl ester **12** (16 mg, 72% yield) as a pale yellow oil. R_f 0.2 (50:1 hexanes/EtOAc); visualized with $KMnO_4$. Spectral data match those above reported.



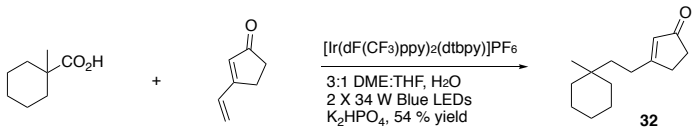
Ethyl (*E*)-5-(1-methylcyclopentyl)pent-3-enoate (15): According to the general procedure, carboxylic acid (13 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and pentadienoate **11** (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (5:1 hexanes/EtOAc) to yield ethyl ester **15** (13 mg, 62% yield) as a pale yellow oil. R_f 0.2 (50:1 hexanes/EtOAc); visualized with $KMnO_4$. Spectral data match those above reported.



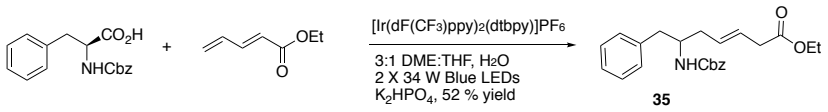
Ethyl (*E*)-8-((*tert*-butyldimethylsilyl)oxy)-6,6-dimethyloct-3-enoate (16): According to the general procedure, carboxylic acid (25 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and pentadienoate **11** (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (5:1 hexanes/EtOAc) to yield ethyl ester **16** (21 mg, 64% yield) as a pale yellow oil. R_f 0.2 (50:1 hexanes/EtOAc); visualized with $KMnO_4$. Spectral data match those above reported.



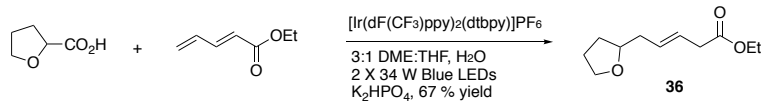
Ethyl (*E*)-6,6-dimethyl-8-phenyloct-3-enoate (17): According to the general procedure, carboxylic acid (19 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and pentadienoate **11** (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (5:1 hexanes/EtOAc) to yield ethyl ester **17** (20 mg, 73% yield) as a pale yellow oil. R_f 0.2 (50:1 hexanes/EtOAc); visualized with $KMnO_4$. Spectral data match those above reported.



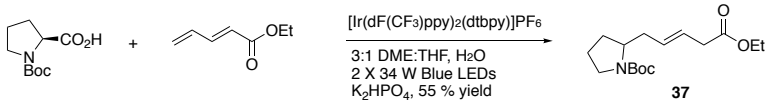
3-(2-(1-Methylcyclohexyl)ethyl)cyclopent-2-en-1-one (32): According to the general procedure, carboxylic acid (14 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and 3-vinylcyclopent-2-en-1-one (12 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (5:1 hexanes/EtOAc) to yield ketone **32** (11 mg, 54% yield) as a pale yellow oil. R_f 0.2 (50:1 hexanes/EtOAc); visualized with $KMnO_4$. Spectral data match those above reported.



Ethyl (*E*)-6-(((benzyloxy)carbonyl)amino)-7-phenylhept-3-enoate (35): According to the general procedure, carboxylic acid (30 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and pentadienoate **11** (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (5:1 hexanes/EtOAc) to yield ethyl ester **35** (20 mg, 52% yield) as a pale yellow oil. R_f 0.2 (5:1 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.18 (m, 10H), 5.65 – 5.60 (m, 1H), 5.58 – 5.53 (m, 1H), 5.11 – 5.06 (m, 2H), 4.67 (d, J = 7.2 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.99 (d, J = 6.0 Hz, 1H), 3.05 (d, J = 6.6 Hz, 2H), 2.84 – 2.77 (m, 2H), 2.31 – 2.27 (m, 1H), 2.18 – 2.13 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 155.8, 137.8, 136.7, 129.8, 129.5, 128.54, 128.49, 128.11, 128.07, 126.5, 125.7, 66.6, 60.7, 51.8, 40.4, 38.1, 36.7, 14.2; IR (thin film) 3342, 2928, 1731, 1528, 1251 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{23}H_{27}NO_4$ $[M + Na]^+$ 404.1838, observed 404.1829.



Ethyl (*E*)-5-(tetrahydrofuran-2-yl)pent-3-enoate (36): According to the general procedure, carboxylic acid (12 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and pentadienoate **11** (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (10:1 hexanes/EtOAc) to yield ethyl ester **36** (13 mg, 67% yield) as a pale yellow oil. R_f 0.2 (10:1 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67 – 5.56 (m, 2H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.87 (p, *J* = 6.5 Hz, 2H), 3.73 (q, *J* = 7.0 Hz, 1H), 3.05 (d, J = 6.0 Hz, 2H), 2.36 – 2.30 (m, 1H), 2.27 – 2.22 (m, 1H), 1.98 – 1.84 (m, 3H), 1.54 – 1.47 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 131.0, 124.3, 78.9, 68.1, 60.8, 38.9, 38.4, 31.0, 25.9, 14.4; IR (thin film) 3541, 2977, 1738, 1645, 1177 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{11}H_{18}O_3$ $[M + Na]^+$ 221.1154, observed 221.1151.

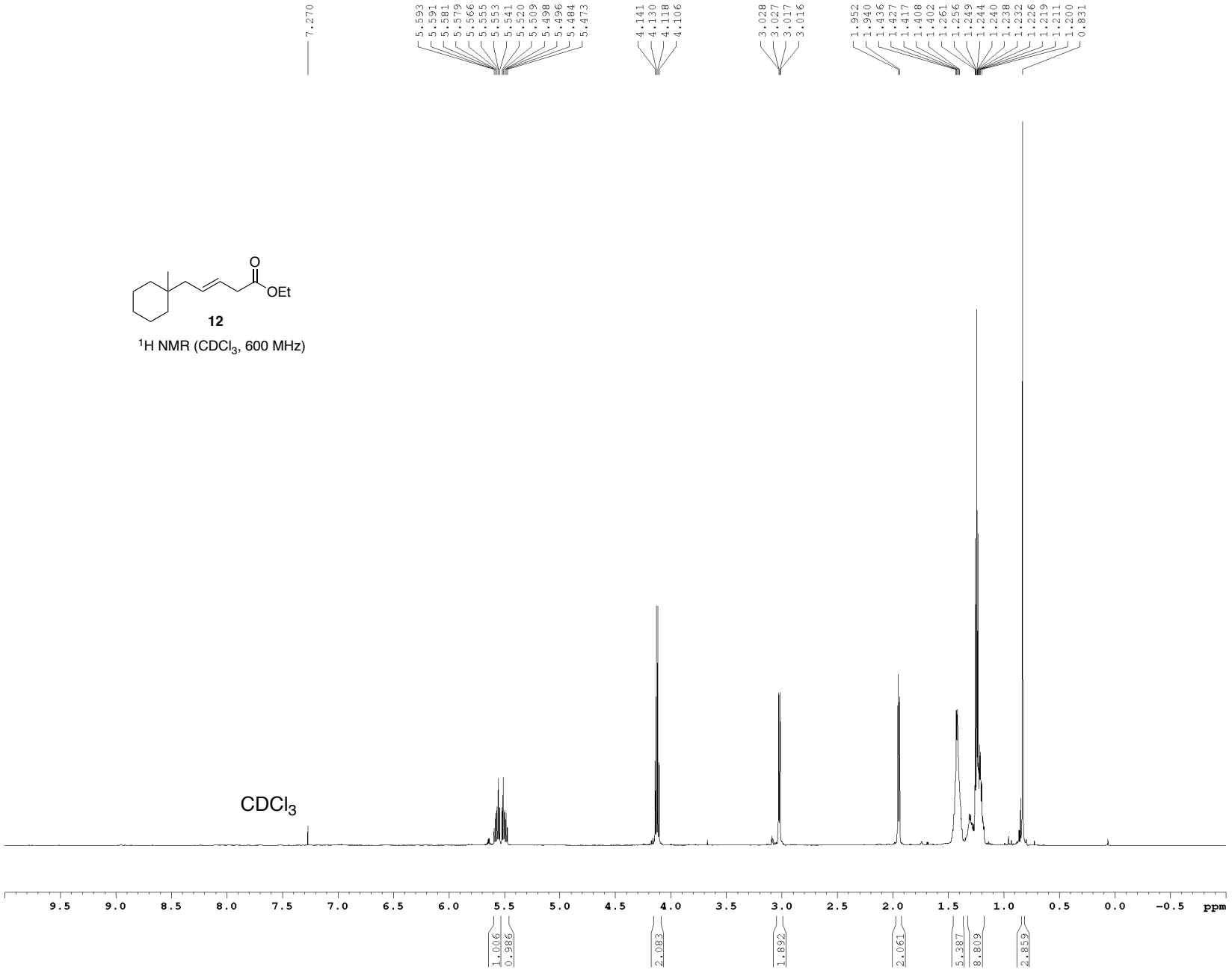


***tert*-Butyl (*E*)-2-(5-ethoxy-5-oxopent-2-en-1-yl)pyrrolidine-1-carboxylate (37):** According to the general procedure, carboxylic acid (22 mg, 0.1 mmol, 1.0 equiv) was used as the radical precursor and pentadienoate **11** (14 mg, 0.11 mmol, 1.1 equiv) was used the acceptor. The crude residue was purified by flash chromatography (5:1 hexanes/EtOAc) to yield ethyl ester **37** (16 mg, 55% yield) as a pale yellow oil.[10] R_f 0.2 (5:1 hexanes/EtOAc); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, C_6D_6) at 70 ^{o}C δ 5.61 – 5.56 (m, 1H), 5.44 – 5.38 (m, 1H), 3.95 (q, *J* = 7.0 Hz, 2H), 3.80 (br, 1H), 3.31 (br, 1H), 3.20 – 3.19 (m, 1H), 2.85 (d, *J* = 7.0 Hz, 2H), 2.46 (br, 1H), 2.12 – 2.09 (m,

1H), 1.54 – 1.33 (m, 15H), 0.98 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, C_6D_6) at 70 ^{o}C δ 170.5, 153.8, 130.5, 124.5, 78.1, 59.7, 56.8, 46.4, 37.9, 37.2, 29.6, 28.3, 23.0, 13.8; IR (thin film) 2979, 2877, 1738, 1696, 1393 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{16}H_{27}NO_4$ $[M + Na]^+$ 320.1838, observed 320.1836.

Spectral Data

1H spectrum

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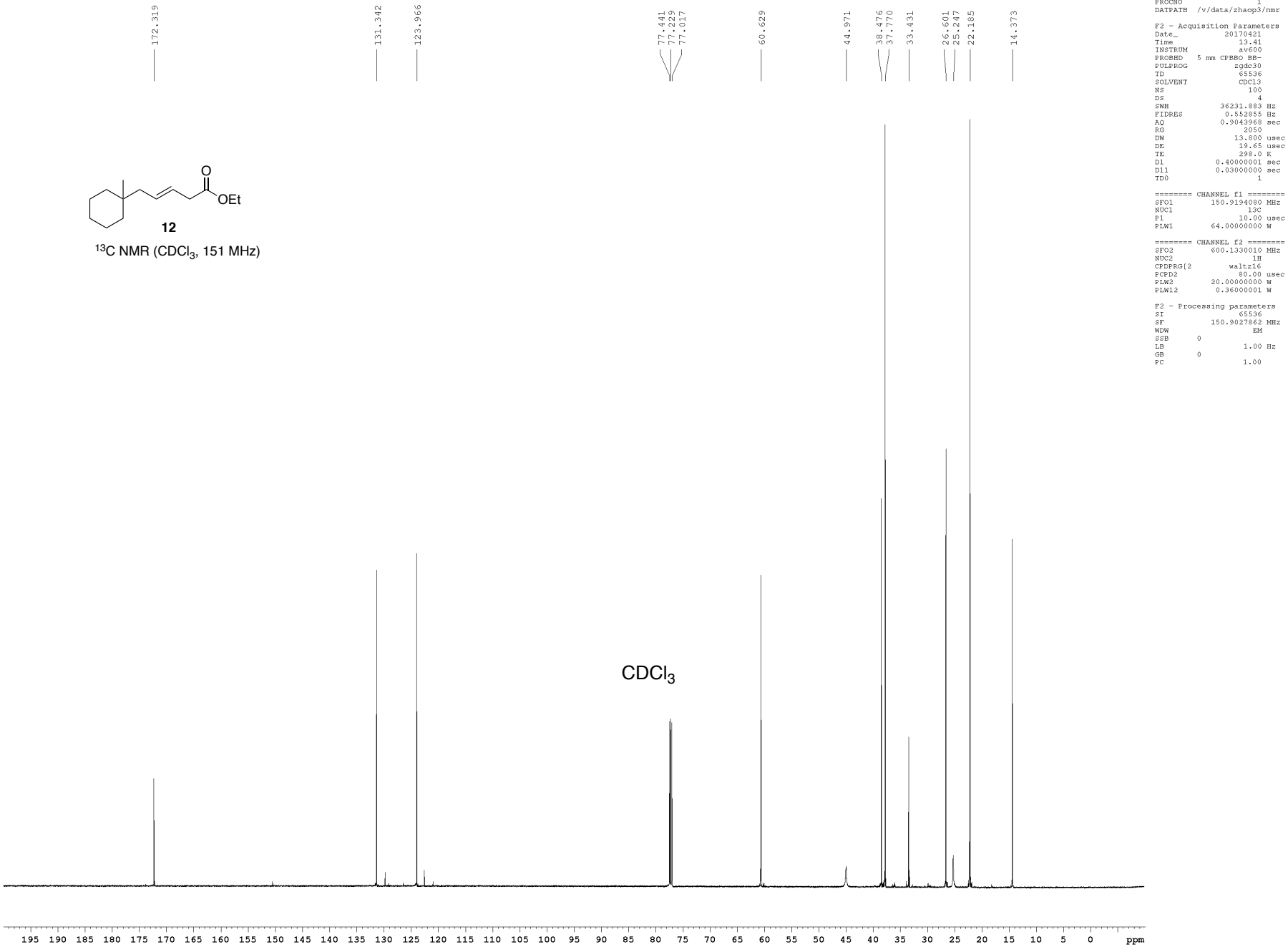
EXPNO                         1
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_              20170421
Time                  13.44
INSTRUM               av600
PROBHD    5 mm CPBBO BB-
PULPROG                zg30
TD                    98074
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                9615.385 Hz
FIDRES            0.098042 Hz
AQ                5.0998478 sec
RG                      22.6
DW                   52.000 usec
DE                   13.70 usec
TE                   298.0 K
D1                0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           600.1342009 MHz
NUC1                      1H
P1                   12.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI                        65536
SF             600.1300279 MHz
WDW                       EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

13C spectrum with 1H decoupling



12

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME                  PZ-2151-E
EXPNO                         2
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

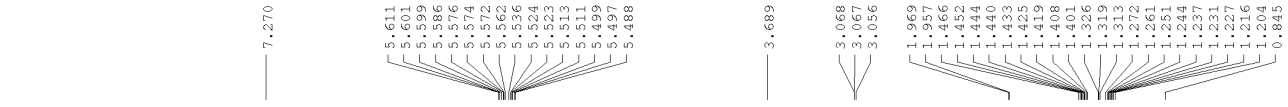
F2 - Acquisition Parameters
Date_              20170421
Time                 13.41
INSTRUM              av600
PROBHD    5 mm CPBBO BB-
PULPROG             zgdc30
TD                   65536
SOLVENT              CDCl3
NS                     100
DS                       4
SWH              36231.883 Hz
FIDRES           0.552855 Hz
AQ               0.9043968 sec
RG                    2050
DW                 13.800 usec
DE                 19.65 usec
TE                  298.0 K
D1              0.40000001 sec
D11             0.03000000 sec
TD0                      1

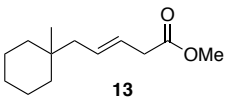
======== CHANNEL f1 ========
SFO1          150.9194080 MHz
NUC1                    13C
P1                   10.00 usec
PLW1          64.00000000 W

======== CHANNEL f2 ========
SFO2          600.1330010 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2          20.00000000 W
PLW12          0.36000001 W

F2 - Processing parameters
SI                   65536
SF            150.9027862 MHz
WDW                     EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.00
```

1H spectrum





13

^{1}H NMR ($CDCl_3$, 600 MHz)

$CDCl_3$

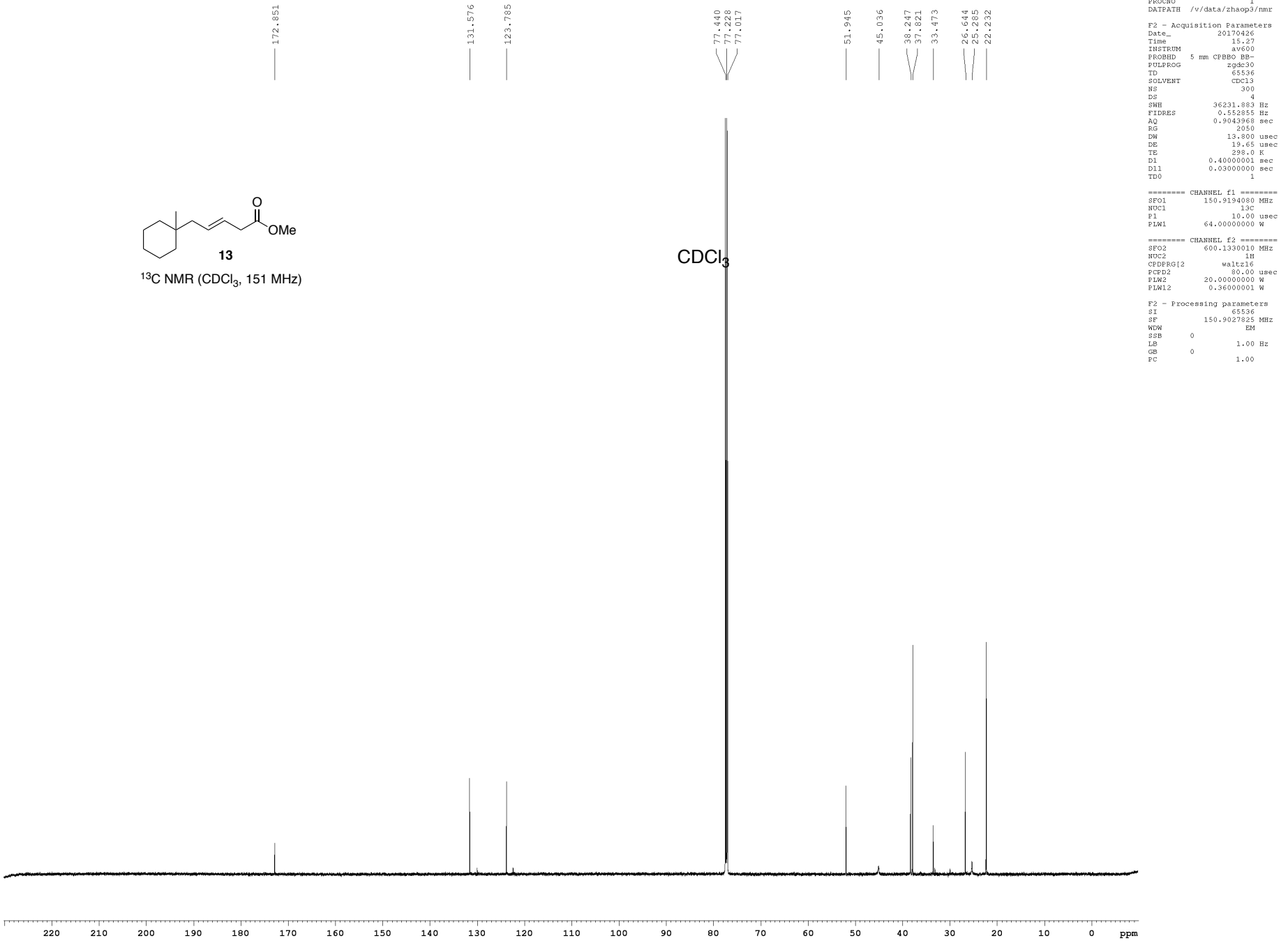

```
Current Data Parameters
NAME            PZ-2151-C
EXPNO                   1
PROCNO                  1
DATPATH   /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_            20170421
Time                11.54
INSTRUM            av600
PROBHD    5 mm CPBBO BB-
PULPROG              zg30
TD                  98074
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              9615.385 Hz
FIDRES           0.098042 Hz
AQ               5.0998478 sec
RG                   22.6
DW                 52.000 usec
DE                 13.70 usec
TE                 298.0 K
D1              0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          600.1342009 MHz
NUC1                   1H
P1                 12.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI                    65536
SF            600.1300281 MHz
WDW                     EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

13C spectrum with 1H decoupling



13

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME                  PZ-2151-C
EXPNO                         4
PROCNO                        1
DATPATH  /v/data/zhaop3/nmr

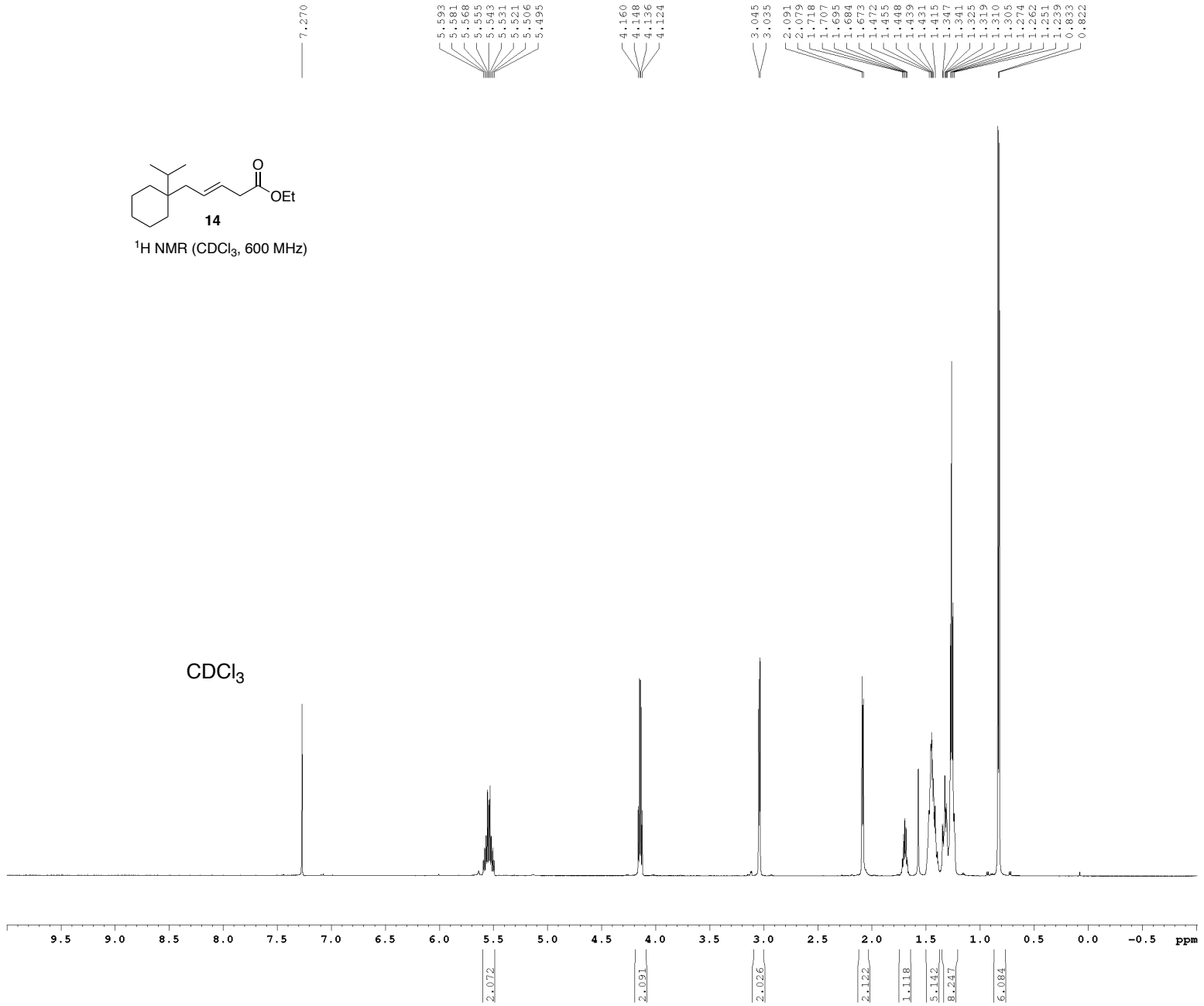
F2 - Acquisition Parameters
Date_              20170426
Time                   15.27
INSTRUM                av600
PROBHD   5 mm CPBBO BB-
PULPROG                zgdc30
TD                      65536
SOLVENT                CDCl3
NS                        300
DS                          4
SWH                36231.883 Hz
FIDRES             0.552855 Hz
AQ                 0.9043968 sec
RG                       2050
DW                     13.800 usec
DE                     19.65 usec
TE                     298.0 K
D1                 0.40000001 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            150.9194080 MHz
NUC1                     13C
P1                     10.00 usec
PLW1           64.00000000 W

======== CHANNEL f2 ========
SFO2            600.1330010 MHz
NUC2                     1H
CPDPRG[2              waltz16
PCPD2                  80.00 usec
PLW2           20.00000000 W
PLW12           0.36000001 W

F2 - Processing parameters
SI                      65536
SF              150.9027825 MHz
WDW                        EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.00
```

1H spectrum with homodecoupling

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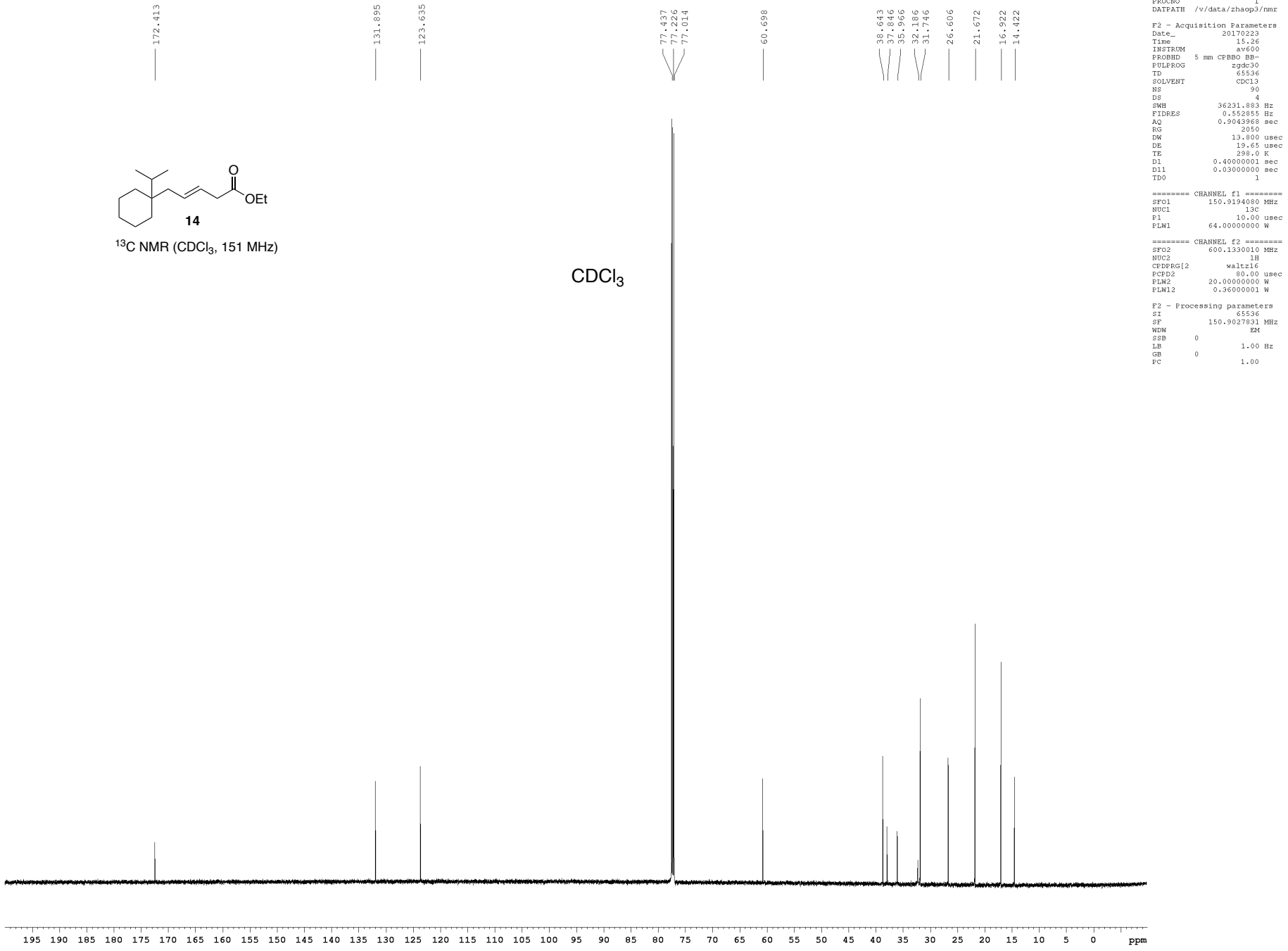
NAME          PZ-2080-#7
EXPNO                  3
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_           20170223
Time               15.15
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG            zg30
TD                98074
SOLVENT           CDCl3
NS                     8
DS                     2
SWH           9615.385 Hz
FIDRES        0.098042 Hz
AQ            5.0998478 sec
RG                  71.8
DW                52.000 usec
DE                13.70 usec
TE                298.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1               1H
P1                12.00 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                 65536
SF          600.1300294 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

13C spectrum with 1H decoupling




```
Current Data Parameters
NAME          PZ-2080-#7
EXPNO                  6
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

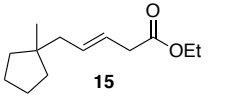
F2 - Acquisition Parameters
Date_           20170223
Time               15.26
INSTRUM            av600
PROBHD  5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                   90
DS                    4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ             0.9043968 sec
RG                 2050
DW                13.800 usec
DE                19.65 usec
TE                298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 =======
SFO1        150.9194080 MHz
NUC1               13c
P1                10.00 usec
PLW1        64.00000000 W

======== CHANNEL f2 =======
SFO2        600.1330010 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                65536
SF          150.9027831 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.00
```

1H spectrum



15

^{1}H NMR ($CDCl_3$, 600 MHz)

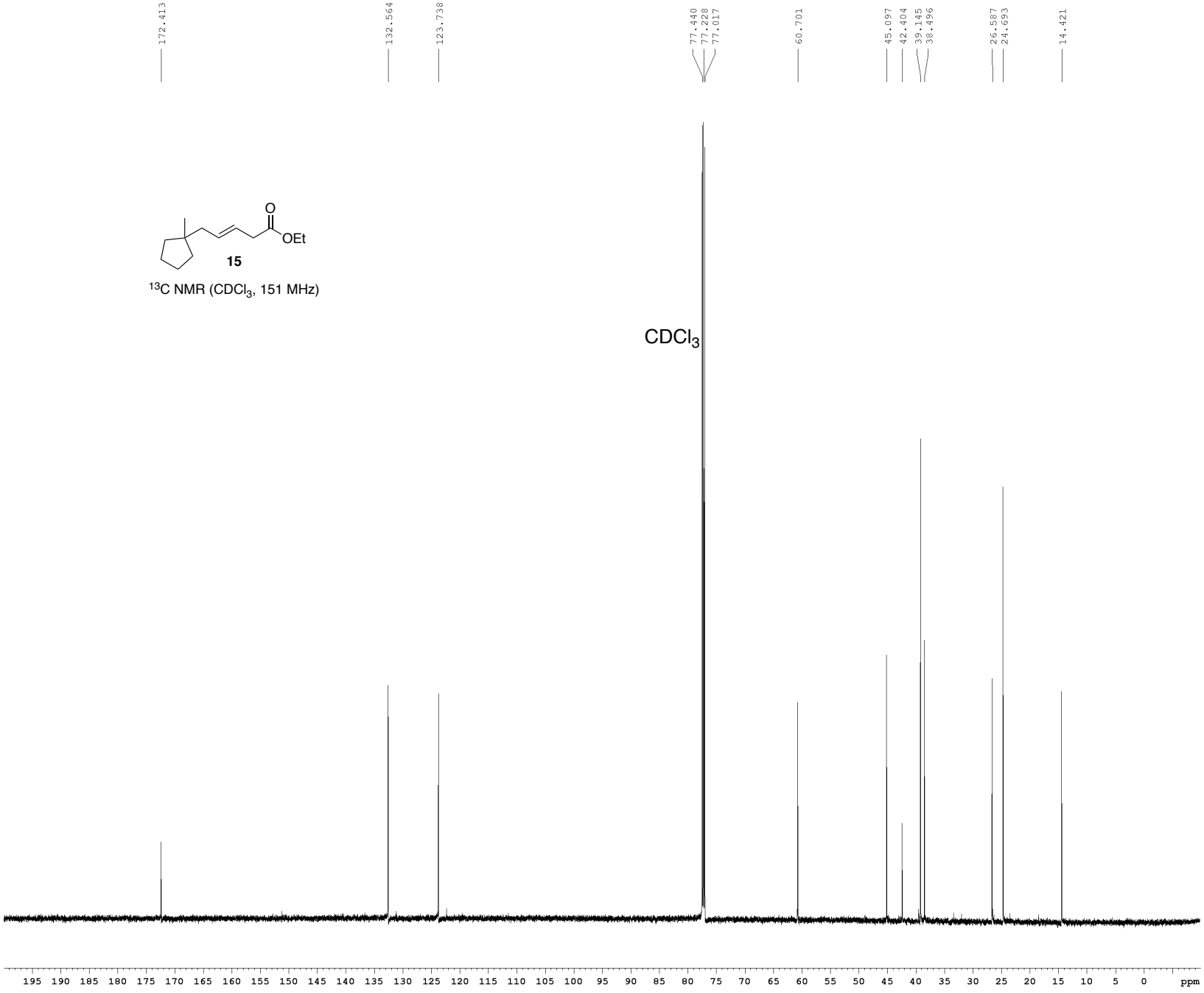

```
Current Data Parameters
NAME                  PZ-2081-P
EXPNO                         4
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_                  20170225
Time                      18.12
INSTRUM                  av600
PROBHD    5 mm CPBBO BB-
PULPROG                   zg30
TD                       98074
SOLVENT                  CDCl3
NS                            8
DS                            2
SWH                   9615.385 Hz
FIDRES                0.098042 Hz
AQ                    5.0998478 sec
RG                         28.5
DW                       52.000 usec
DE                       13.70 usec
TE                       298.0 K
D1                    0.10000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                600.1342009 MHz
NUC1                        1H
P1                       12.00 usec
PLW1                20.00000000 W

F2 - Processing parameters
SI                        65536
SF                  600.1300292 MHz
WDW                          EM
SSB                 0
LB                        0.30 Hz
GB                  0
PC                        1.00
```

13C spectrum with 1H decoupling



15

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME                  PZ-2081-P
EXPNO                         5
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

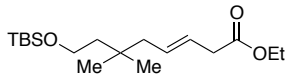
F2 - Acquisition Parameters
Date_              20170225
Time                  18.15
INSTRUM                av600
PROBHD   5 mm CPBBO BB-
PULPROG               zgdc30
TD                     65536
SOLVENT                CDCl3
NS                        58
DS                         4
SWH                36231.883 Hz
FIDRES             0.552855 Hz
AQ                 0.9043968 sec
RG                      2050
DW                    13.800 usec
DE                    19.65 usec
TE                    298.0 K
D1                 0.40000001 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            150.9194080 MHz
NUC1                     13C
P1                    10.00 usec
PLW1           64.00000000 W

======== CHANNEL f2 ========
SFO2            600.1330010 MHz
NUC2                     1H
CPDPRG[2              waltz16
PCPD2                 80.00 usec
PLW2           20.00000000 W
PLW12           0.36000001 W

F2 - Processing parameters
SI                     65536
SF              150.9027831 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.00
```

1H spectrum



16

^{1}H NMR ($CDCl_3$, 600 MHz)

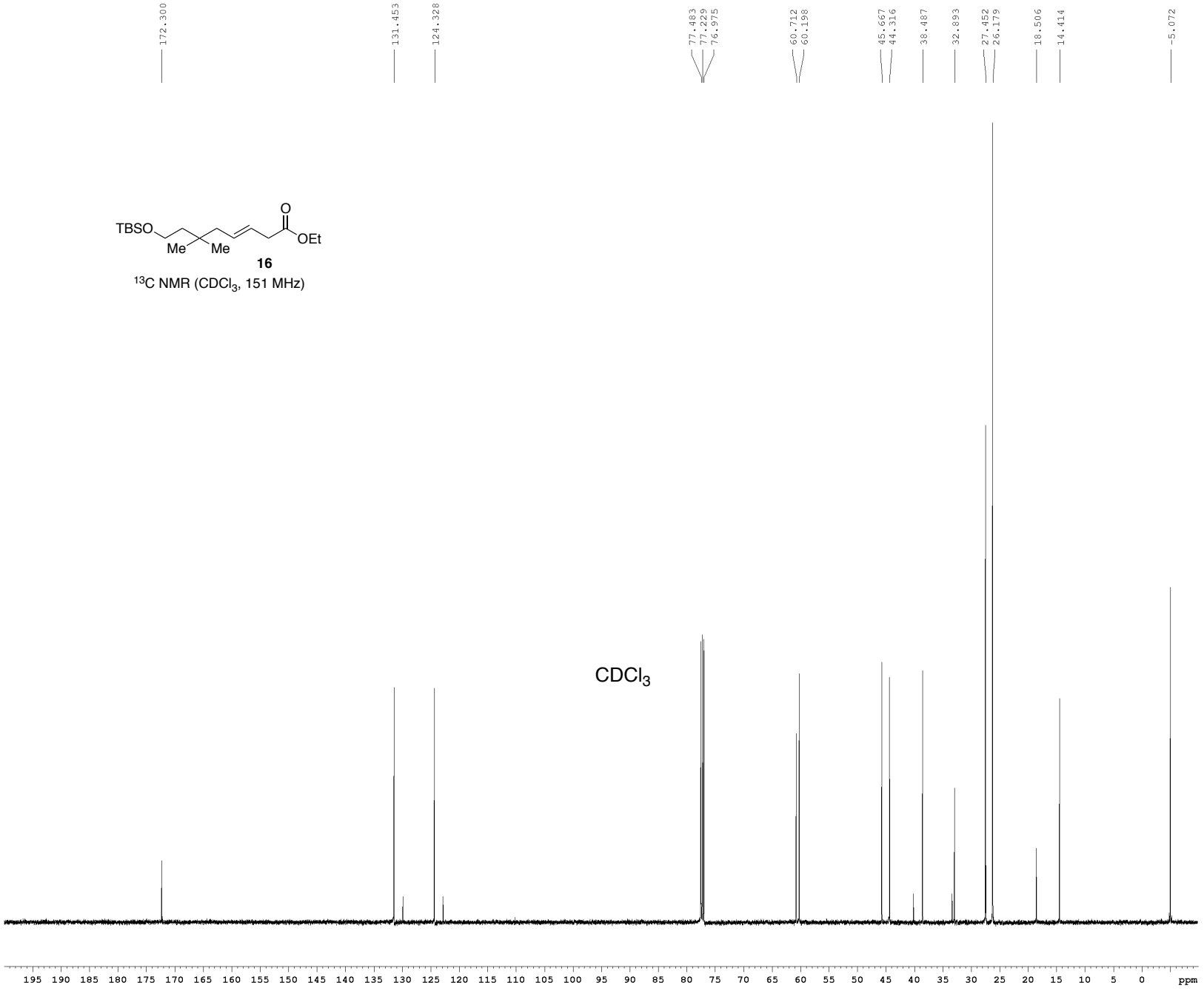

```
Current Data Parameters
NAME            SL-100-1H
EXPNO                   1
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_            20160922
Time                12.19
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998273 sec
RG                    3.6
DW                 62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST    0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                    65536
SF           500.2200267 MHz
WDW                     EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  4.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
NAME          SL-100-13C
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_           20161005
Time              19.50
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  256
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 4096
DW               16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST   0 sec
MCWRK       0.01500000 sec
P2               33.10 usec

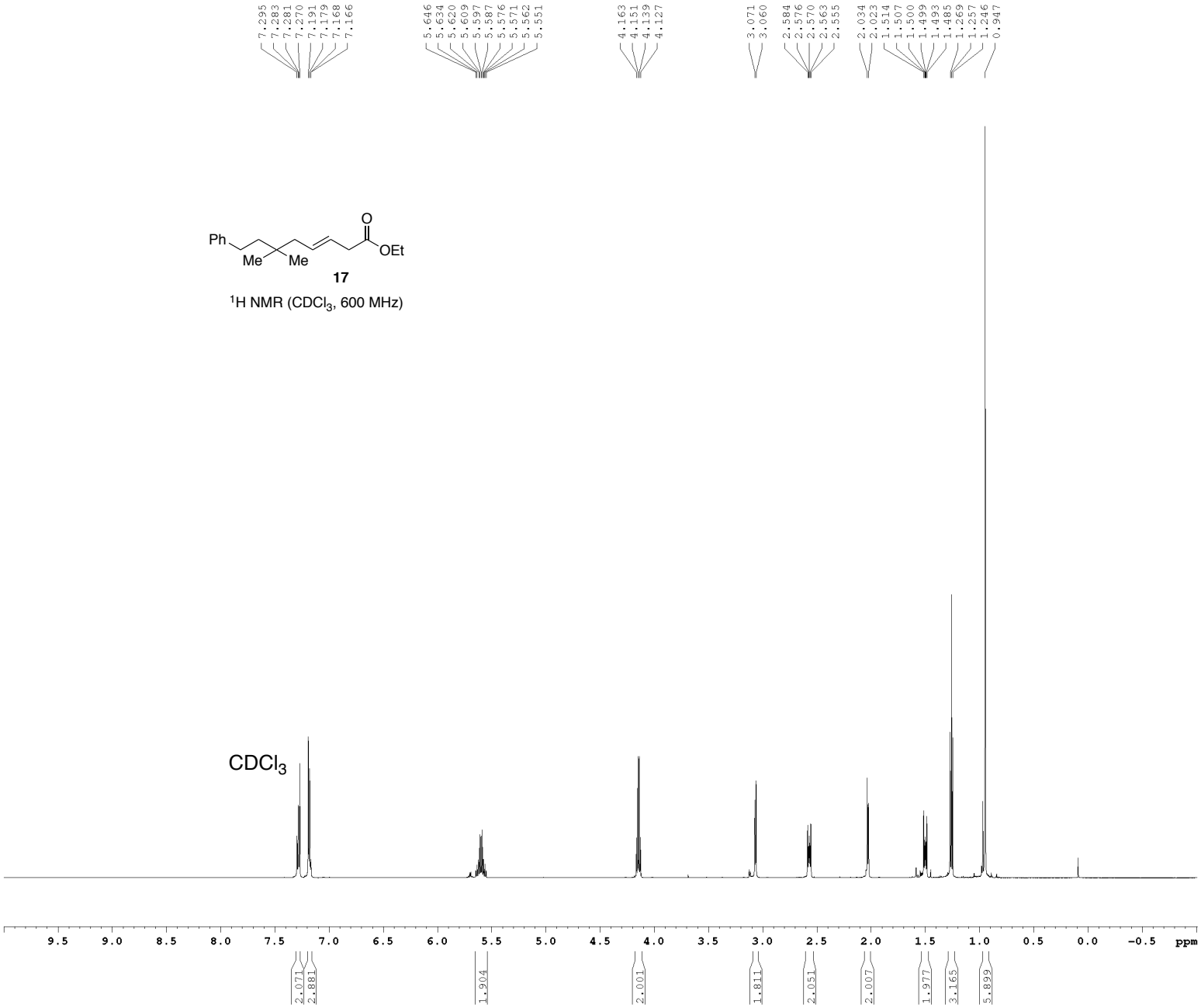
======== CHANNEL f1 ========
NUC1               13C
P1              16.55 usec
PL1            500.00 usec
P12           2000.00 usec
PL0            120.00 dB
PL1             -1.00 dB
SFO1       125.7942548 MHz
SP1              2.70 dB
SP2              2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2               1H
PCPD2           100.00 usec
PL2              1.60 dB
PL12            24.50 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1            30.00 %
GPZ2            50.00 %
p15            500.00 usec
p16           1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803996 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                2.00
```

1H spectrum

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Current Data Parameters
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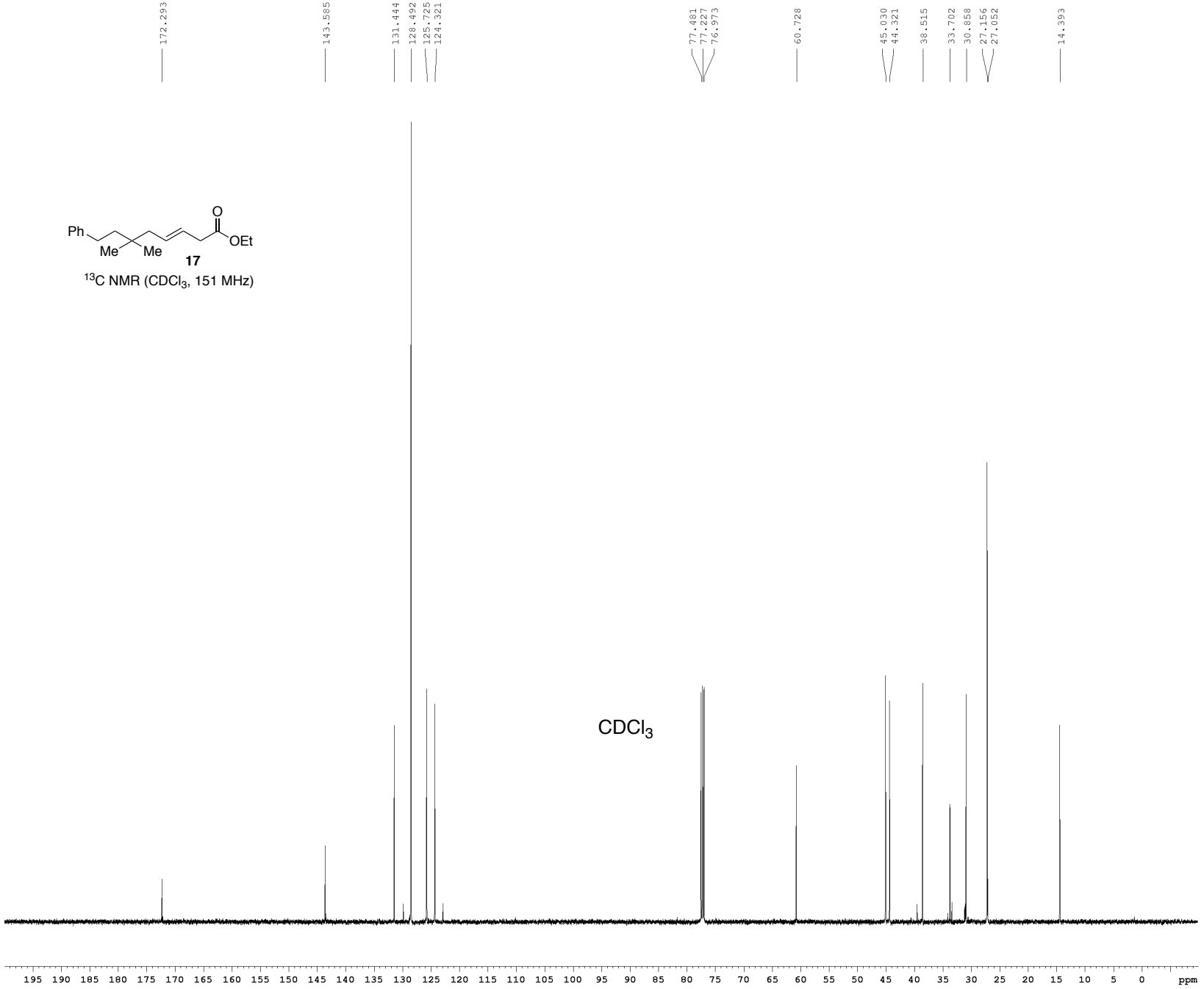
EXPNO                         1
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_               20170421
Time                     11.31
INSTRUM                  av600
PROBHD    5 mm CPBBO BB-
PULPROG                  zg30
TD                      98074
SOLVENT                 CDCl3
NS                          8
DS                          2
SWH                  9615.385 Hz
FIDRES               0.098042 Hz
AQ                   5.0998478 sec
RG                         18
DW                      52.000 usec
DE                      13.70 usec
TE                      298.0 K
D1                   0.10000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1          600.1342009 MHz
NUC1                     1H
P1                    12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                      65536
SF            600.1300279 MHz
WDW                        EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling



17

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME                  SL-96-13C
EXPNO                         1
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_              20161005
Time                 19.18
INSTRUM              cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG   SpinEchopg30gp.prd
TD                    65536
SOLVENT               CDCl3
NS                      256
DS                       16
SWH                30303.031 Hz
FIDRES             0.462388 Hz
AQ                 1.0813440 sec
RG                    7298.2
DW                   16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST    0 sec
MCWRK           0.01500000 sec
P2                   33.10 usec

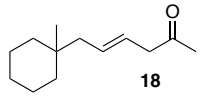
======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1          125.7942548 MHz
SP1                   2.70 dB
SP2                   2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1    0 Hz
SPOFF2    0 Hz

======== CHANNEL f2 ========
CPDPRG[2            waltz16
NUC2                   1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                    65536
SF            125.7804033 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    2.00
```

1H spectrum



18

^{1}H NMR ($CDCl_3$, 600 MHz)

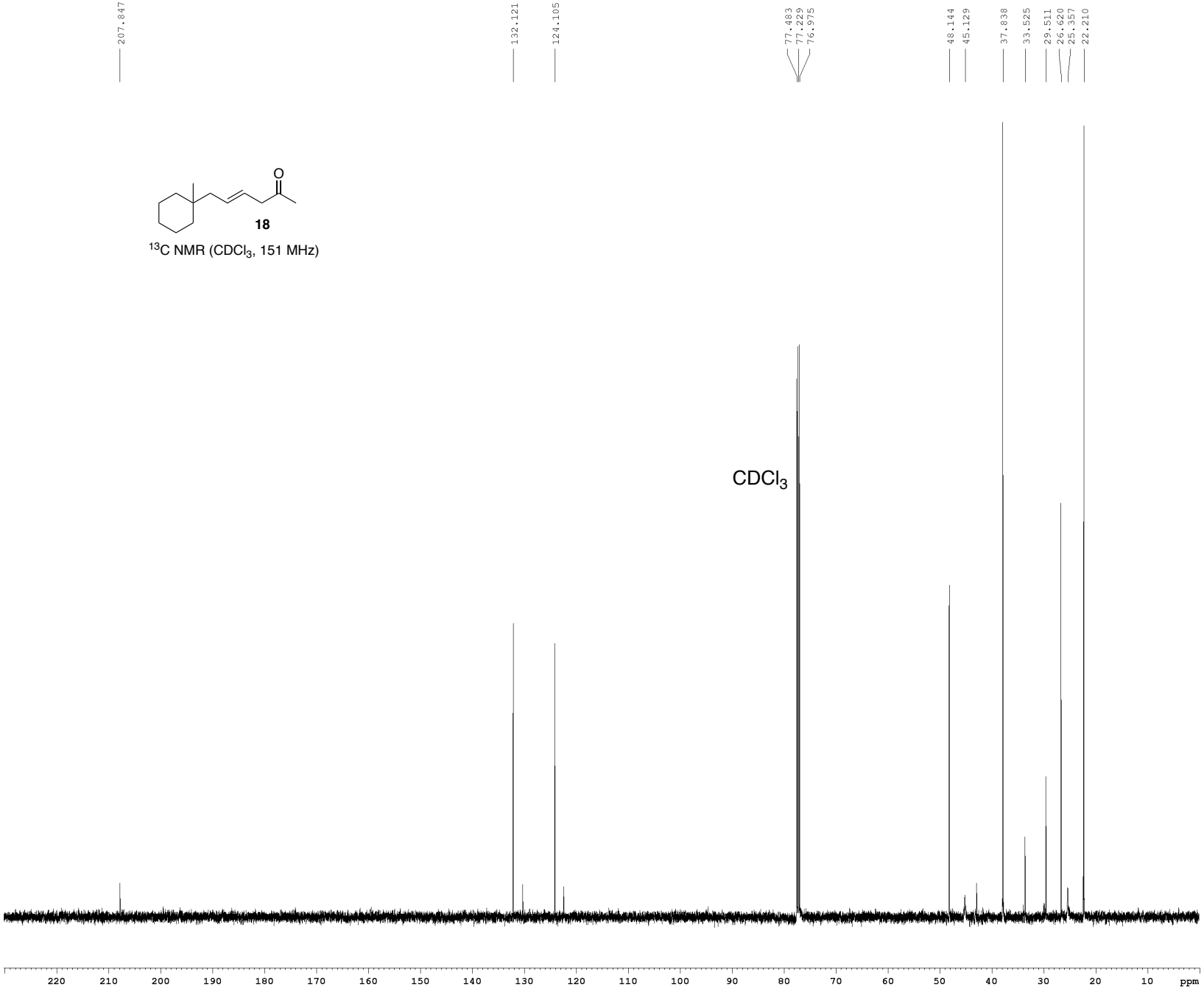

```
Current Data Parameters
NAME                  PZ-2151-B
EXPNO                         1
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_               20170421
Time                    11.44
INSTRUM                 av600
PROBHD    5 mm CPBBO BB-
PULPROG                 zg30
TD                      98074
SOLVENT                 CDCl3
NS                          8
DS                          2
SWH                  9615.385 Hz
FIDRES               0.098042 Hz
AQ                   5.0998478 sec
RG                       20.2
DW                     52.000 usec
DE                     13.70 usec
TE                     298.0 K
D1                0.10000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            600.1342009 MHz
NUC1                       1H
P1                      12.00 usec
PLW1           20.00000000 W

F2 - Processing parameters
SI                      65536
SF              600.1300279 MHz
WDW                        EM
SSB         0
LB                      0.30 Hz
GB          0
PC                      1.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling



18

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME                  PZ-2151-B
EXPNO                         5
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

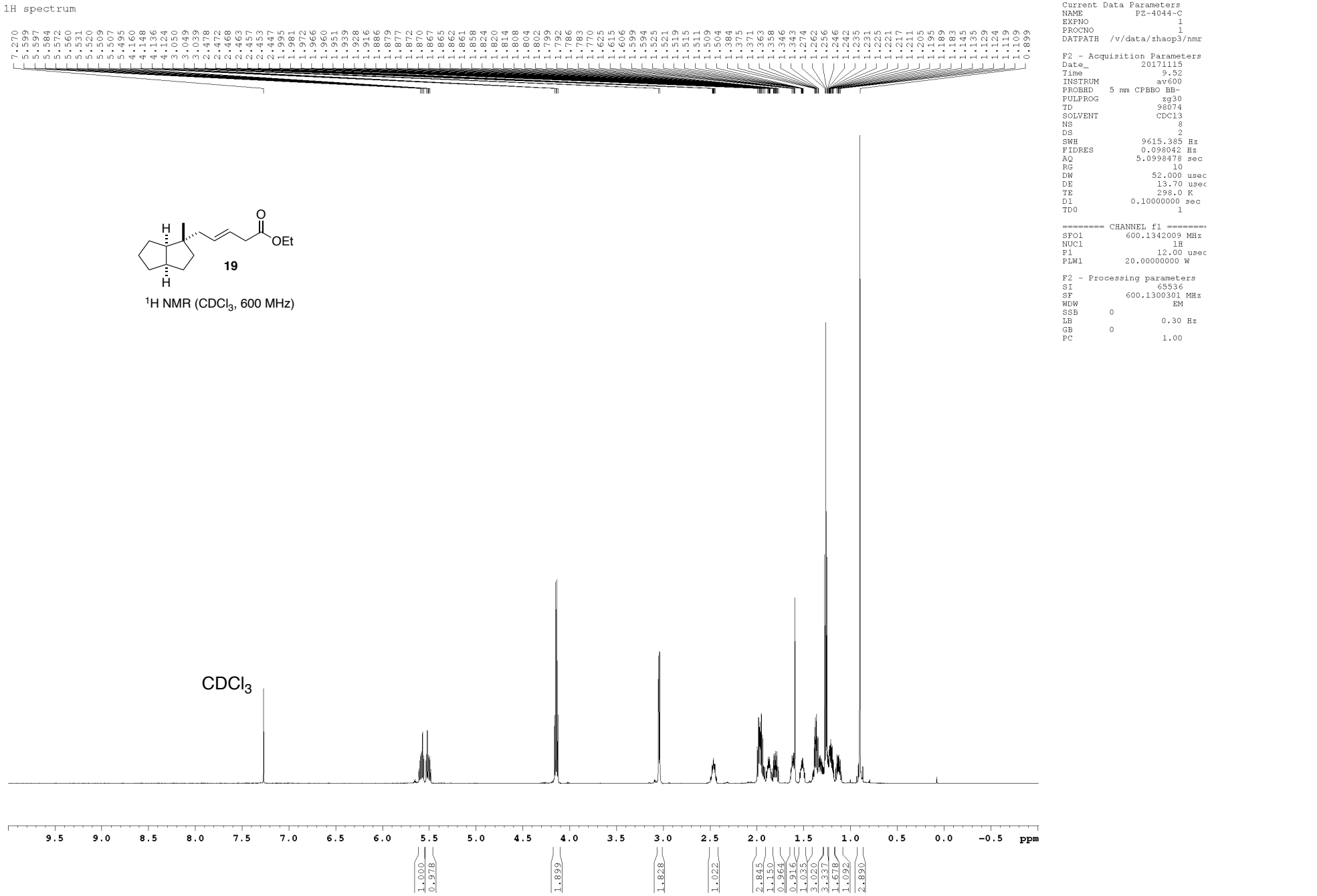
F2 - Acquisition Parameters
Date_              20170421
Time                   17.34
INSTRUM              cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                     65536
SOLVENT                CDCl3
NS                       449
DS                        16
SWH                30303.031 Hz
FIDRES             0.462388 Hz
AQ                 1.0813440 sec
RG                    3649.1
DW                    16.500 usec
DE                     6.00 usec
TE                    298.0 K
D1                 0.25000000 sec
d11                0.03000000 sec
D16                0.00020000 sec
d17                0.00019600 sec
MCREST   0 sec
MCWRK              0.01500000 sec
P2                    33.10 usec

======== CHANNEL f1 ========
NUC1                     13C
P1                    16.55 usec
P11                  500.00 usec
P12                 2000.00 usec
PL0                  120.00 dB
PL1                   -1.00 dB
SFO1            125.7942548 MHz
SP1                    2.70 dB
SP2                    2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                    1.60 dB
PL12                  24.50 dB
SFO2            500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                  30.00 %
GPZ2                  50.00 %
p15                  500.00 usec
p16                 1000.00 usec

F2 - Processing parameters
SI                     65536
SF              125.7803992 MHz
WDW                       EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     2.00
```



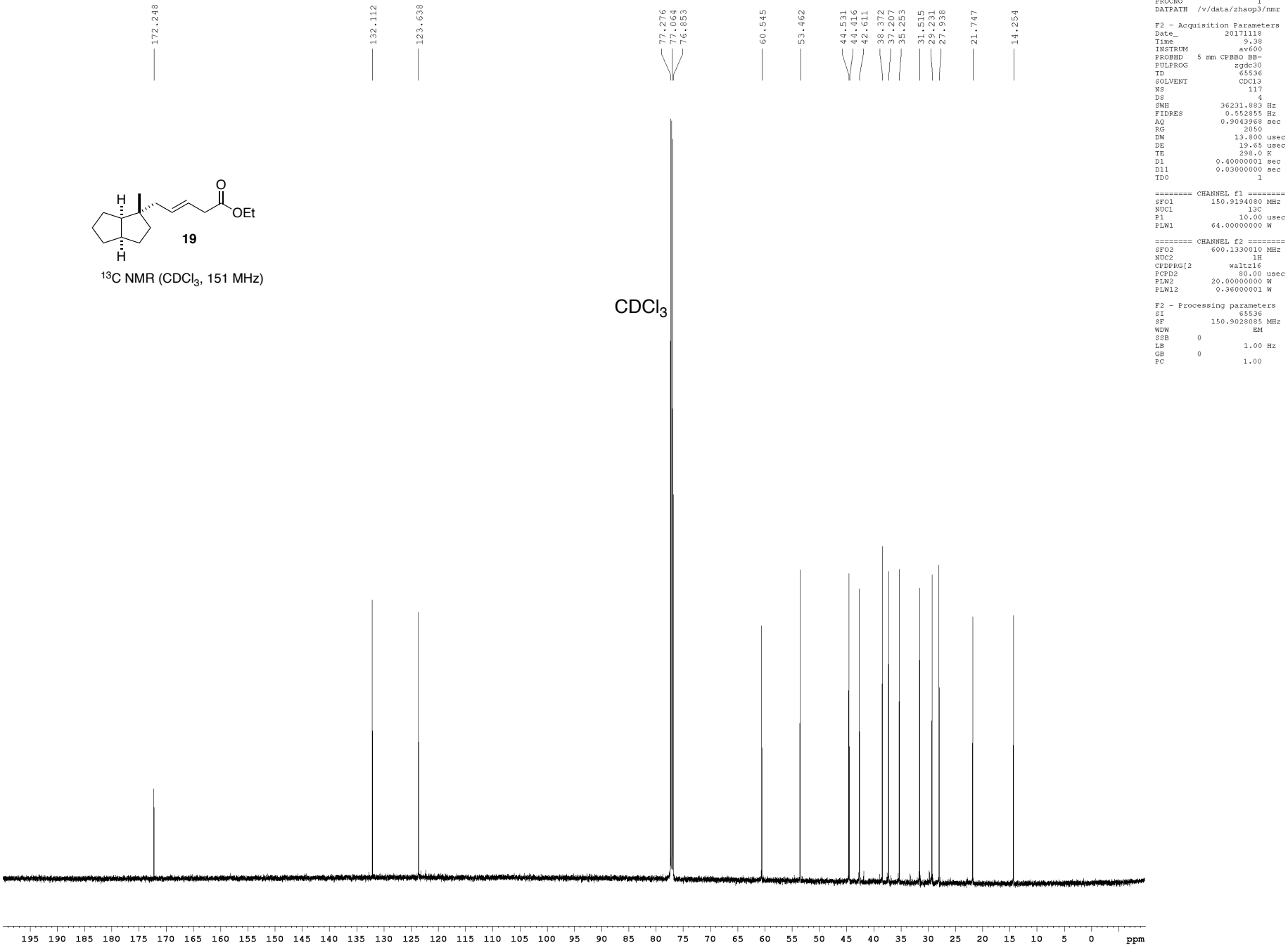

```
Current Data Parameters
NAME            PZ-4044-C
EXPNO                   1
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20171115
Time               9.52
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG           zg30
TD               98074
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           9615.385 Hz
FIDRES        0.098042 Hz
AQ            5.0998478 sec
RG                  10
DW               52.000 usec
DE               13.70 usec
TE               298.0 K
D1            0.10000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1               1H
P1               12.00 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                 65536
SF          600.1300301 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC                 1.00
```

13C spectrum with 1H decoupling



19

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME                  PZ-4044-C
EXPNO                         2
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

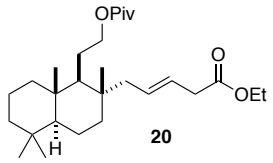
F2 - Acquisition Parameters
Date_              20171118
Time                      9.38
INSTRUM                 av600
PROBHD    5 mm CPBBO BB-
PULPROG                zgdc30
TD                      65536
SOLVENT                 CDCl3
NS                        117
DS                          4
SWH                36231.883 Hz
FIDRES              0.552855 Hz
AQ                  0.9043968 sec
RG                       2050
DW                     13.800 usec
DE                     19.65 usec
TE                     298.0 K
D1                  0.40000001 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             150.9194080 MHz
NUC1                      13C
P1                      10.00 usec
PLW1             64.00000000 W

======== CHANNEL f2 ========
SFO2             600.1330010 MHz
NUC2                      1H
CPDPRG[2              waltz16
PCPD2                  80.00 usec
PLW2             20.00000000 W
PLW12             0.36000001 W

F2 - Processing parameters
SI                        65536
SF               150.9028085 MHz
WDW                         EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.00
```

1H spectrum



20

^{1}H NMR ($CDCl_3$, 600 MHz)

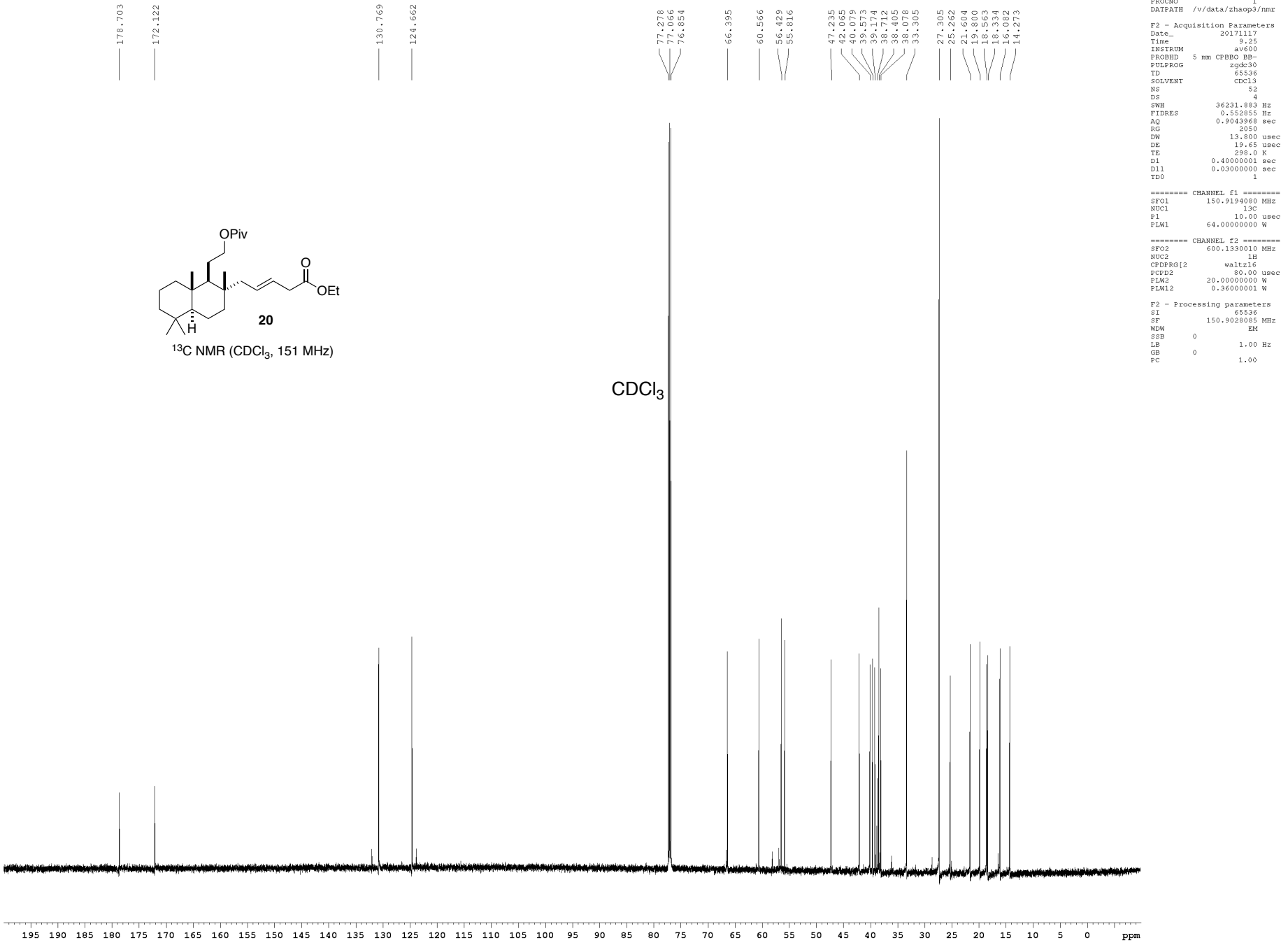

```
Current Data Parameters
NAME            PZ-4044-B
EXPNO                   1
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_            20171115
Time                9.48
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ              5.0998478 sec
RG                    10
DW                52.000 usec
DE                13.70 usec
TE                298.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                   1H
P1                12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300300 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

13C spectrum with 1H decoupling




```
Current Data Parameters
NAME                  PZ-4044-B
EXPNO                         2
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

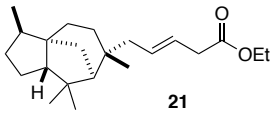
F2 - Acquisition Parameters
Date_              20171117
Time                   9.25
INSTRUM               av600
PROBHD    5 mm CPBBO BB-
PULPROG              zgdc30
TD                    65536
SOLVENT               CDCl3
NS                       52
DS                        4
SWH               36231.883 Hz
FIDRES             0.552855 Hz
AQ                 0.9043968 sec
RG                     2050
DW                   13.800 usec
DE                   19.65 usec
TE                   298.0 K
D1                0.40000001 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          150.9194080 MHz
NUC1                    13C
P1                    10.00 usec
PLW1          64.00000000 W

======== CHANNEL f2 ========
SFO2          600.1330010 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2          20.00000000 W
PLW12          0.36000001 W

F2 - Processing parameters
SI                    65536
SF            150.9028085 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.00
```

1H spectrum



21

^{1}H NMR ($CDCl_3$, 600 MHz)

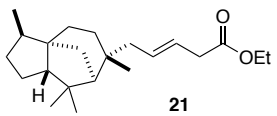

```
Current Data Parameters
NAME            PZ-4044-D
EXPNO                   1
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20171115
Time               9.57
INSTRUM           av600
PROBHD  5 mm CPBBO BB-
PULPROG           zg30
TD               98074
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           9615.385 Hz
FIDRES        0.098042 Hz
AQ            5.0998478 sec
RG                  10
DW             52.000 usec
DE             13.70 usec
TE               298.0 K
D1          0.10000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       600.1342009 MHz
NUC1               1H
P1              12.00 usec
PLW1       20.00000000 W

F2 - Processing parameters
SI                65536
SF         600.1300302 MHz
WDW                  EM
SSB       0
LB              0.30 Hz
GB        0
PC                1.00
```

13C spectrum with 1H decoupling



21

^{13}C NMR ($CDCl_3$, 151 MHz)


```
Current Data Parameters
NAME                  PZ-4044-D
EXPNO                         2
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

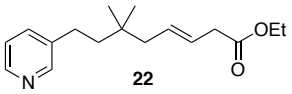
F2 - Acquisition Parameters
Date_              20171120
Time                   11.24
INSTRUM                av600
PROBHD    5 mm CPBBO BB-
PULPROG              zgdc30
TD                    65536
SOLVENT               CDCl3
NS                       33
DS                        4
SWH               36231.883 Hz
FIDRES             0.552855 Hz
AQ                 0.9043968 sec
RG                      2050
DW                   13.800 usec
DE                   19.65 usec
TE                   298.0 K
D1                0.40000001 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          150.9194080 MHz
NUC1                    13C
P1                    10.00 usec
PLW1          64.00000000 W

======== CHANNEL f2 ========
SFO2          600.1330010 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2          20.00000000 W
PLW12          0.36000001 W

F2 - Processing parameters
SI                    65536
SF            150.9028085 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.00
```

1H spectrum



22

^{1}H NMR ($CDCl_3$, 600 MHz)

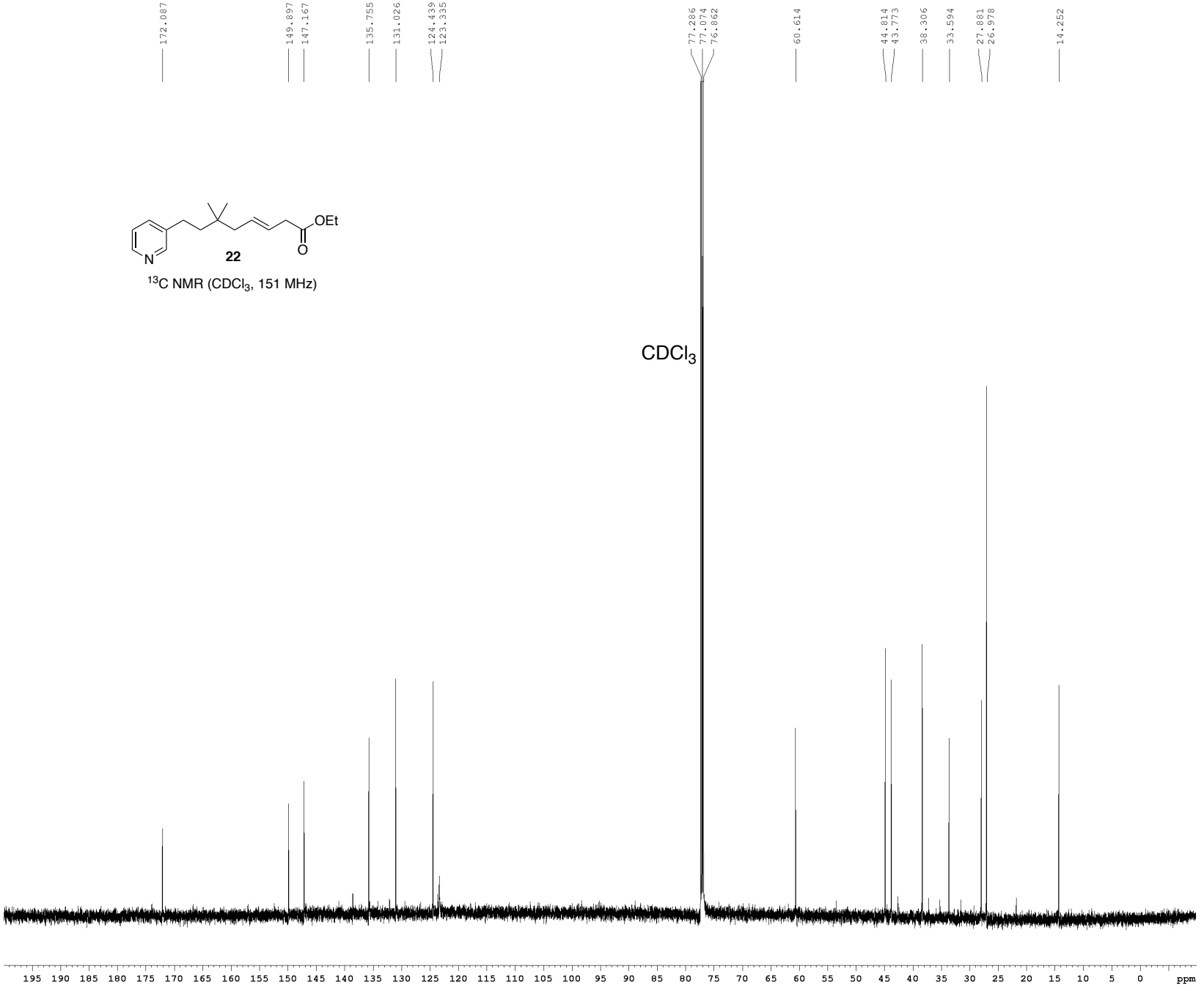

```
Current Data Parameters
NAME                  PZ-4044-E
EXPNO                         1
PROCNO                        1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_                  20171116
Time                       9.34
INSTRUM                   av600
PROBHD    5 mm CPBBO BB-
PULPROG                   zg30
TD                       98074
SOLVENT                  CDCl3
NS                           8
DS                           2
SWH                   9615.385 Hz
FIDRES                0.098042 Hz
AQ                    5.0998478 sec
RG                        20.2
DW                      52.000 usec
DE                      13.70 usec
TE                      298.0 K
D1                    0.10000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                600.1342009 MHz
NUC1                        1H
P1                       12.00 usec
PLW1                20.00000000 W

F2 - Processing parameters
SI                           65536
SF                  600.1300308 MHz
WDW                             EM
SSB                 0
LB                            0.30 Hz
GB                  0
PC                            1.00
```

13C spectrum with 1H decoupling



22

^{13}C NMR ($CDCl_3$, 151 MHz)

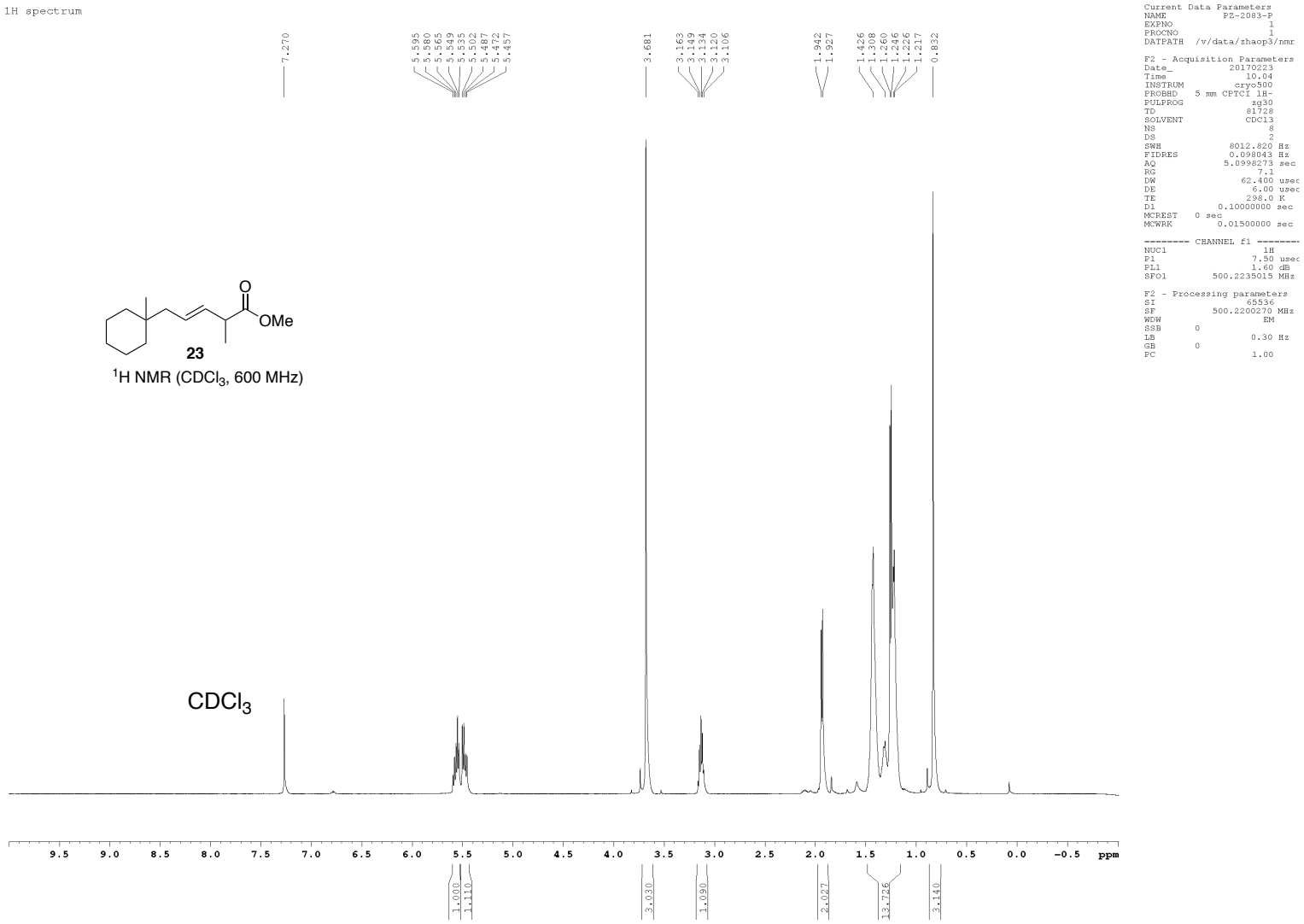
```
Current Data Parameters
NAME            PZ-4044-E
EXPNO                   5
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20171120
Time               11.16
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                   31
DS                    4
SWH           36231.883 Hz
FIDRES        0.552855 Hz
AQ            0.9043968 sec
RG                 2050
DW               13.800 usec
DE               19.65 usec
TE               298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.00 usec
PLW1        64.00000000 W

======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                 65536
SF          150.9028085 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.00
```



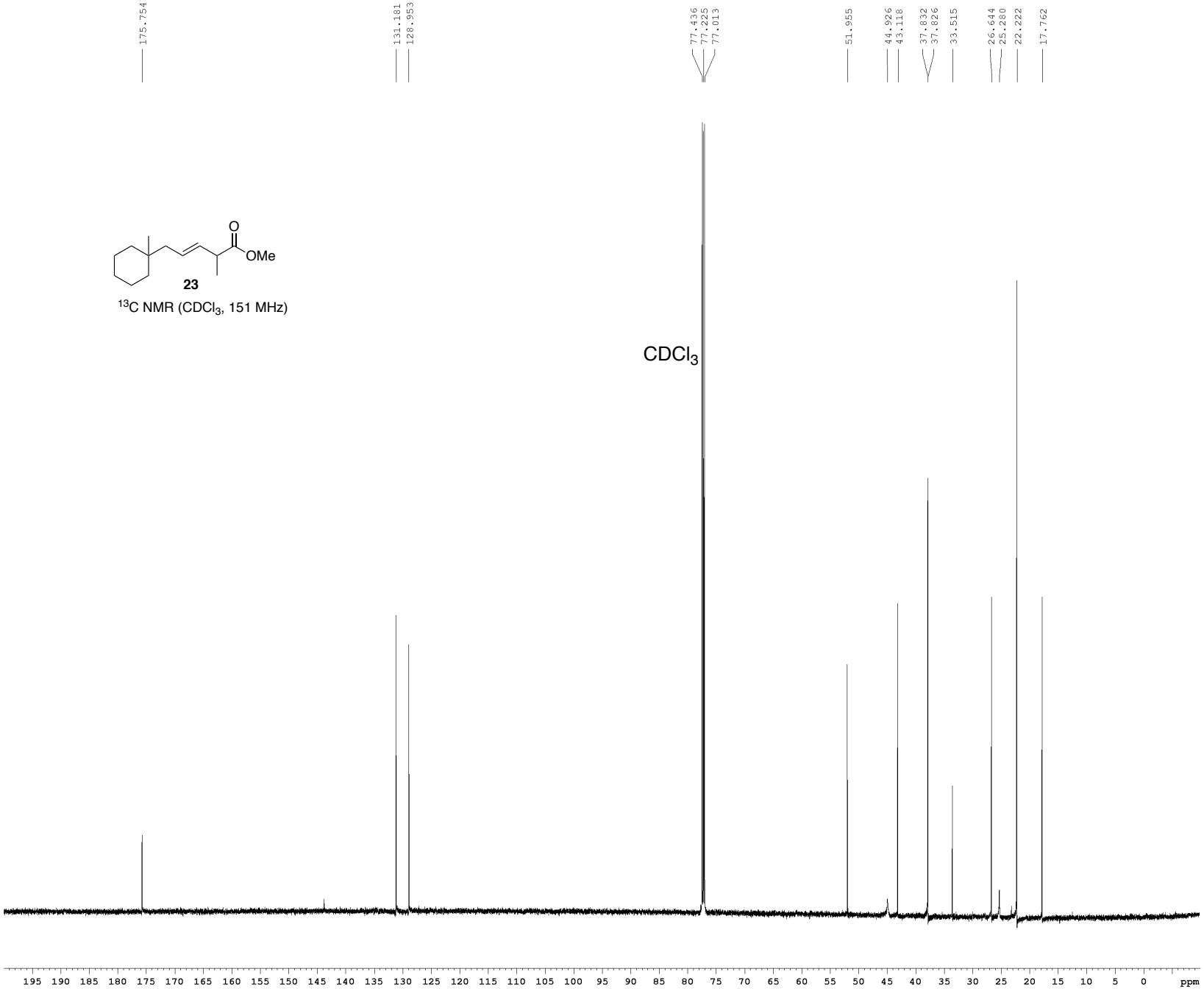

```
Current Data Parameters
NAME                  PZ-2083-P
EXPNO                         1
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_              20170223
Time                  10.04
INSTRUM             cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG                zg30
TD                    81728
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                8012.820 Hz
FIDRES             0.098043 Hz
AQ                 5.0998273 sec
RG                      7.1
DW                   62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1                0.10000000 sec
MCREST    0 sec
MCWRK             0.01500000 sec

-------- CHANNEL f1 --------
NUC1                      1H
P1                     7.50 usec
PL1                    1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                        65536
SF             500.2200270 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

13C spectrum with 1H decoupling



23

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME                  PZ-2083-P
EXPNO                         5
PROCNO                        1
DATPATH  /v/data/zhaop3/nmr

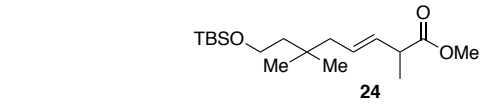
F2 - Acquisition Parameters
Date_              20170225
Time                   23.14
INSTRUM                av600
PROBHD    5 mm CPBBO BB-
PULPROG               zgdc30
TD                     65536
SOLVENT                CDCl3
NS                       126
DS                         4
SWH               36231.883 Hz
FIDRES             0.552855 Hz
AQ                 0.9043968 sec
RG                      2050
DW                    13.800 usec
DE                    19.65 usec
TE                    298.0 K
D1                 0.40000001 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1          150.9194080 MHz
NUC1                    13C
P1                    10.00 usec
PLW1          64.00000000 W

======== CHANNEL f2 ========
SFO2          600.1330010 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                 80.00 usec
PLW2          20.00000000 W
PLW12          0.36000001 W

F2 - Processing parameters
SI                     65536
SF            150.9027833 MHz
WDW                       EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.00
```

1H spectrum



24

^{1}H NMR ($CDCl_3$, 600 MHz)

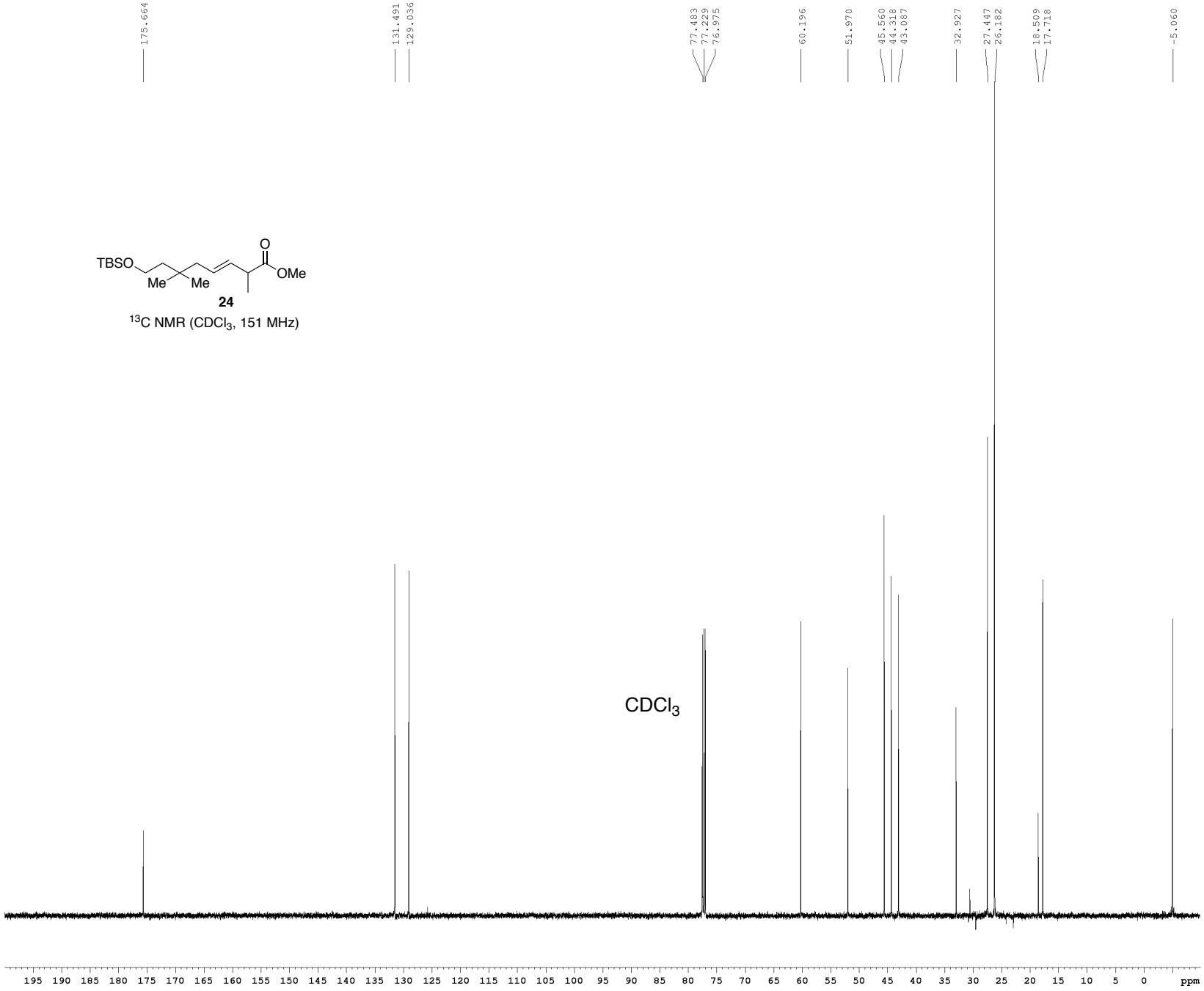

```
Current Data Parameters
NAME            SL-165-1H
EXPNO                   1
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_               20161029
Time                   18.25
INSTRUM              cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG                zg30
TD                    81728
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                8012.820 Hz
FIDRES            0.098043 Hz
AQ                5.0998273 sec
RG                      5.7
DW                   62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST     0 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                    65536
SF            500.2200266 MHz
WDW                     EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   4.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling



24

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME          SL-165-13C
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20161029
Time              18.33
INSTRUM         cryo500
PROBHD  5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  256
DS                   16
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813440 sec
RG               2896.3
DW               16.500 usec
DE                6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2               33.10 usec

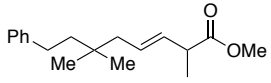
======== CHANNEL f1 ========
NUC1               13C
P1               16.55 usec
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1        125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI                 65536
SF          125.7803993 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 2.00
```

1H spectrum



25

^{1}H NMR ($CDCl_3$, 600 MHz)

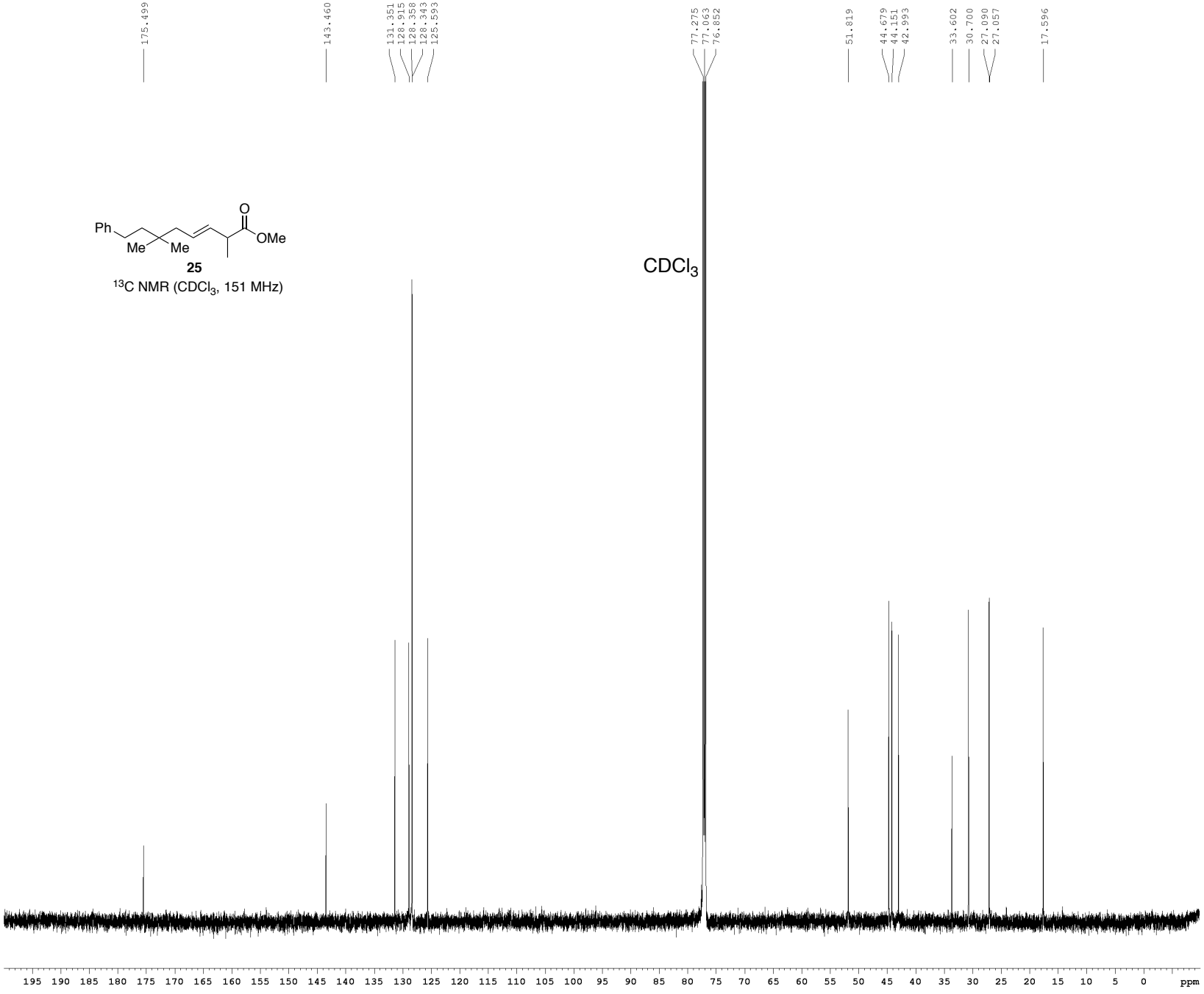

```
Current Data Parameters
NAME          PZ-4039-P1
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_           20171113
Time               16.44
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ              5.0998478 sec
RG                    10
DW                52.000 usec
DE                13.70 usec
TE                298.0 K
D1             0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                   1H
P1                 12.00 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300311 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

13C spectrum with 1H decoupling



25

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME          PZ-4039-P1
EXPNO                  2
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

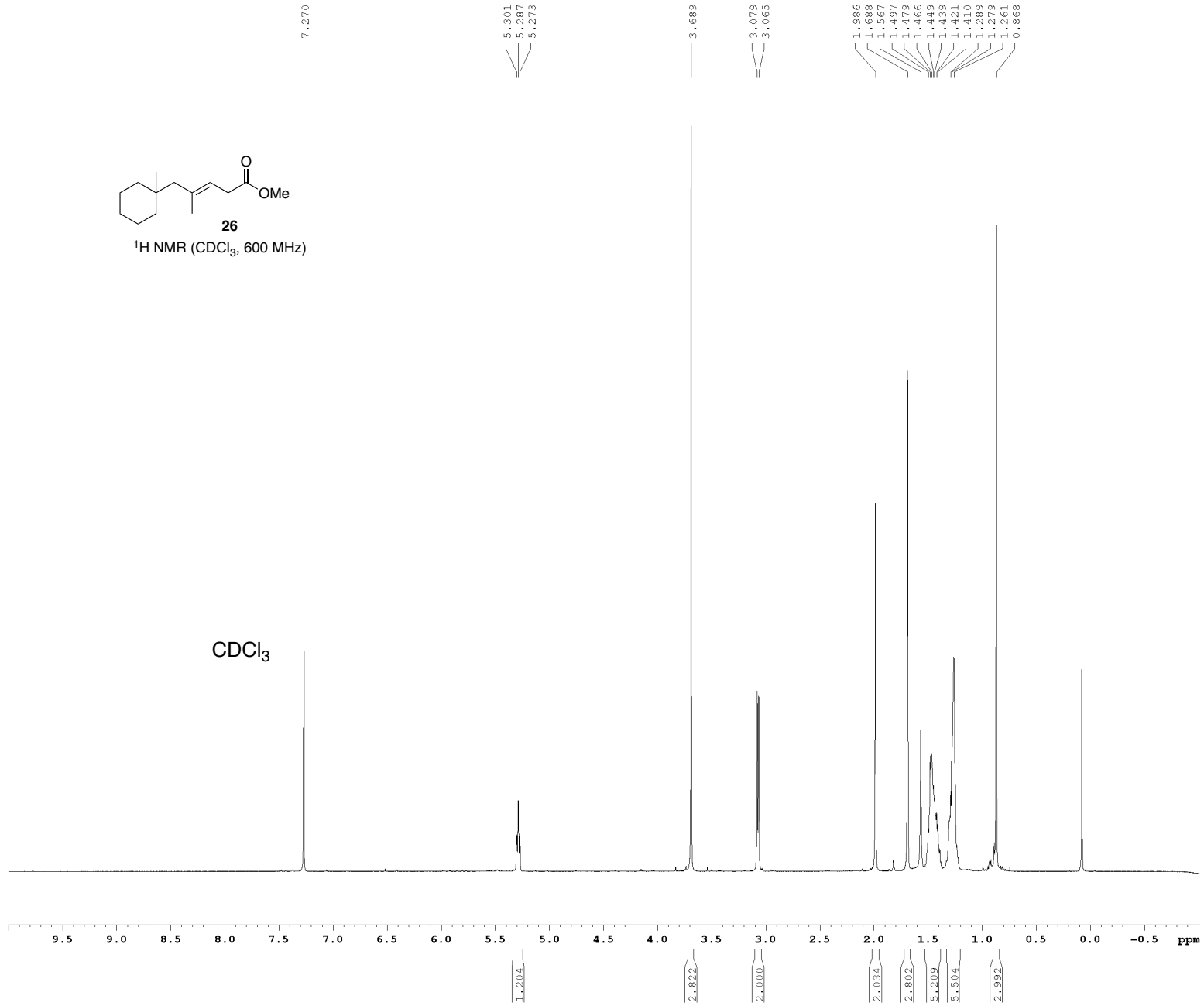
F2 - Acquisition Parameters
Date_           20171113
Time               16.48
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  324
DS                    4
SWH           36231.883 Hz
FIDRES        0.552855 Hz
AQ            0.9043968 sec
RG                 2050
DW               13.800 usec
DE               19.65 usec
TE               298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1               13C
P1               10.00 usec
PLW1        64.00000000 W

======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                65536
SF          150.9028085 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.00
```

1H spectrum



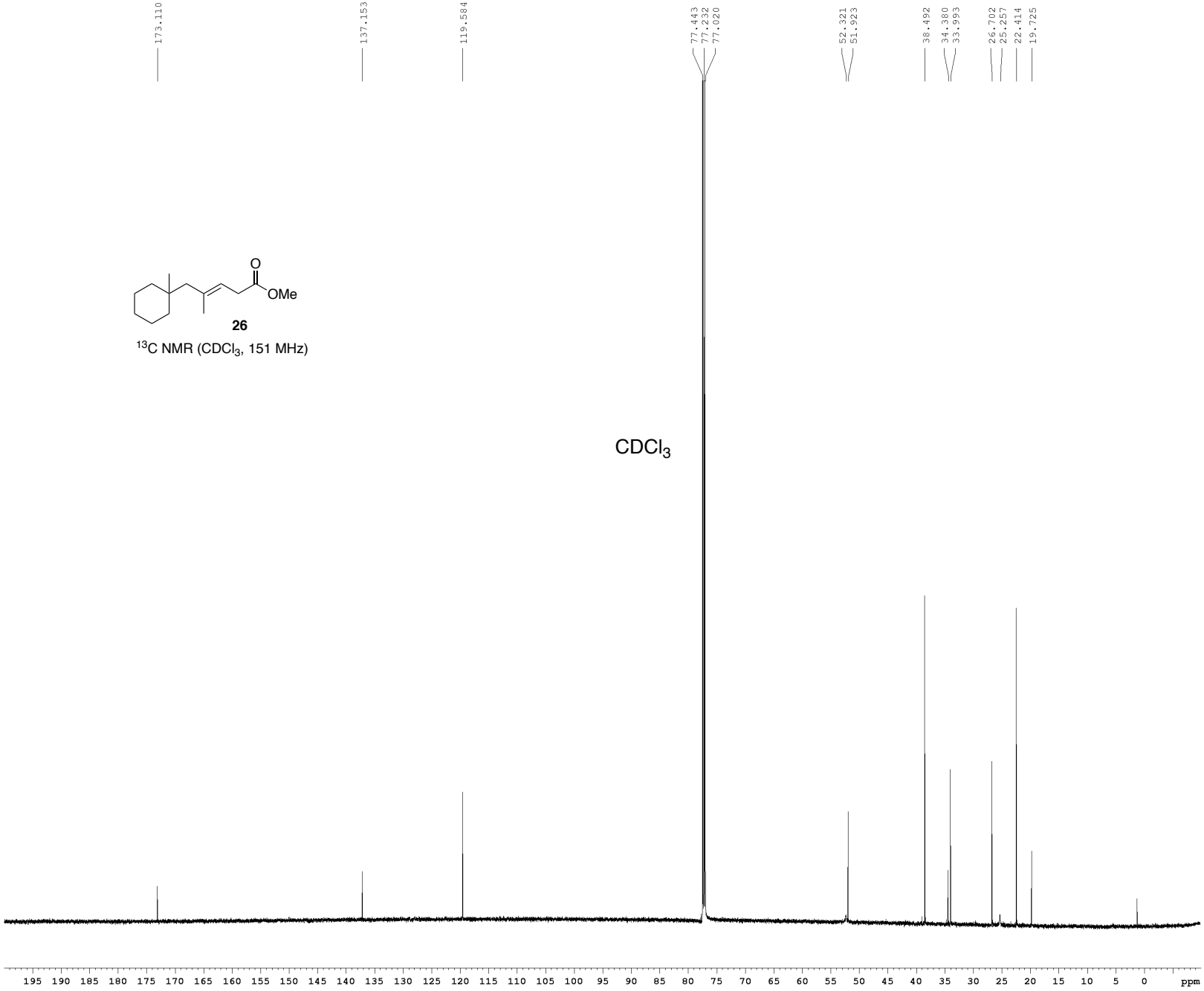

```
Current Data Parameters
NAME         PZ-2112-#10
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_            20170319
Time                16.43
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ                5.0998273 sec
RG                    7.1
DW                 62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1              0.10000000 sec
MCREST    0 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                    65536
SF            500.2200265 MHz
WDW                     EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

13C spectrum with 1H decoupling




```
Current Data Parameters
NAME         PZ-2112-#10
EXPNO                 2
PROCNO                1
DATPATH  /v/data/zhaop3/nmr

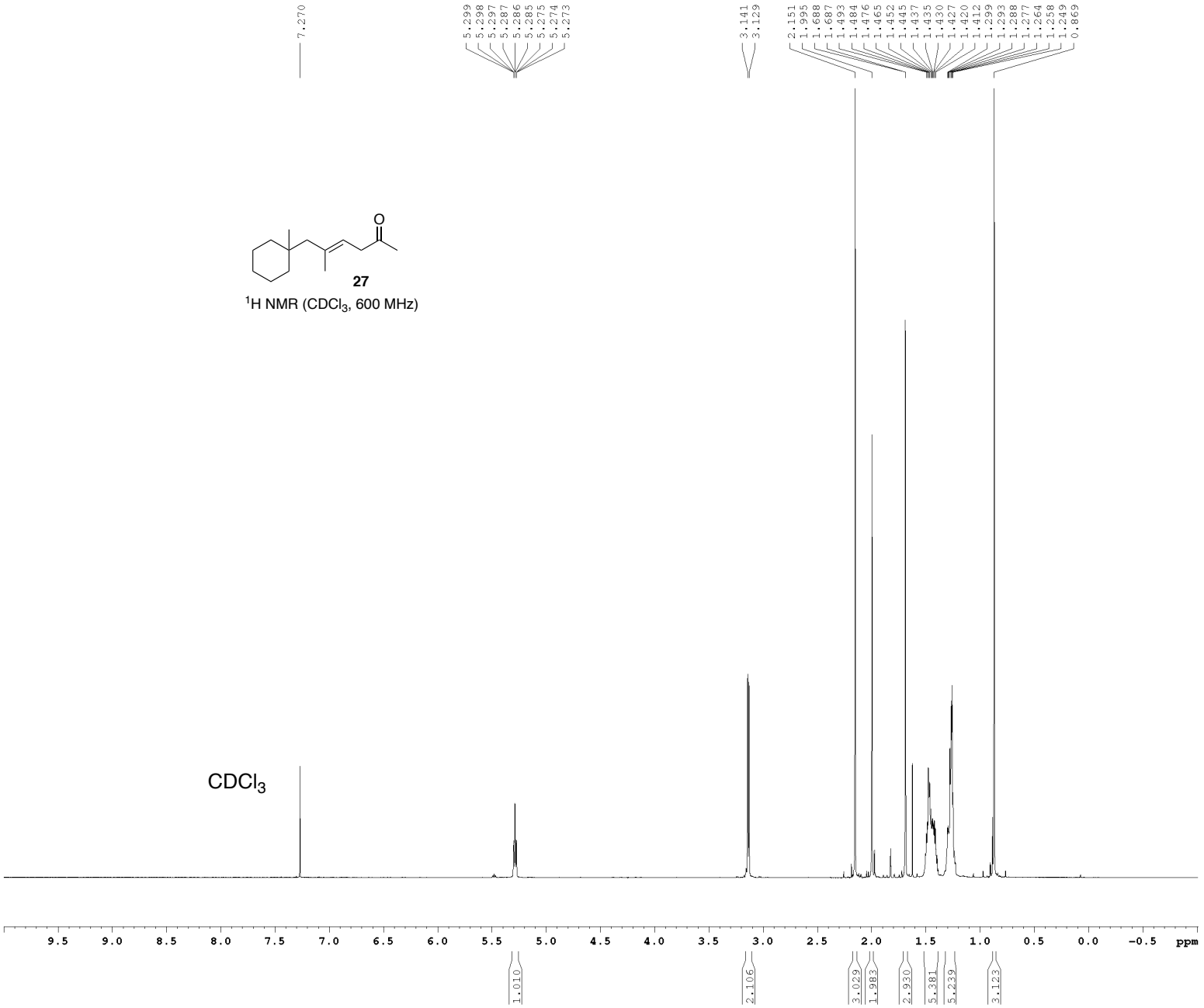
F2 - Acquisition Parameters
Date_          20170320
Time              10.27
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG         zgdc30
TD               65536
SOLVENT          CDCl3
NS                 500
DS                   4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ            0.9043968 sec
RG                2050
DW              13.800 usec
DE              19.65 usec
TE              298.0 K
D1          0.40000001 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       150.9194080 MHz
NUC1               13C
P1               10.00 usec
PLW1       64.00000000 W

======== CHANNEL f2 ========
SFO2       600.1330010 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2       20.00000000 W
PLW12       0.36000001 W

F2 - Processing parameters
SI               65536
SF         150.9027820 MHz
WDW                EM
SSB       0
LB               1.00 Hz
GB        0
PC               1.00
```

1H spectrum



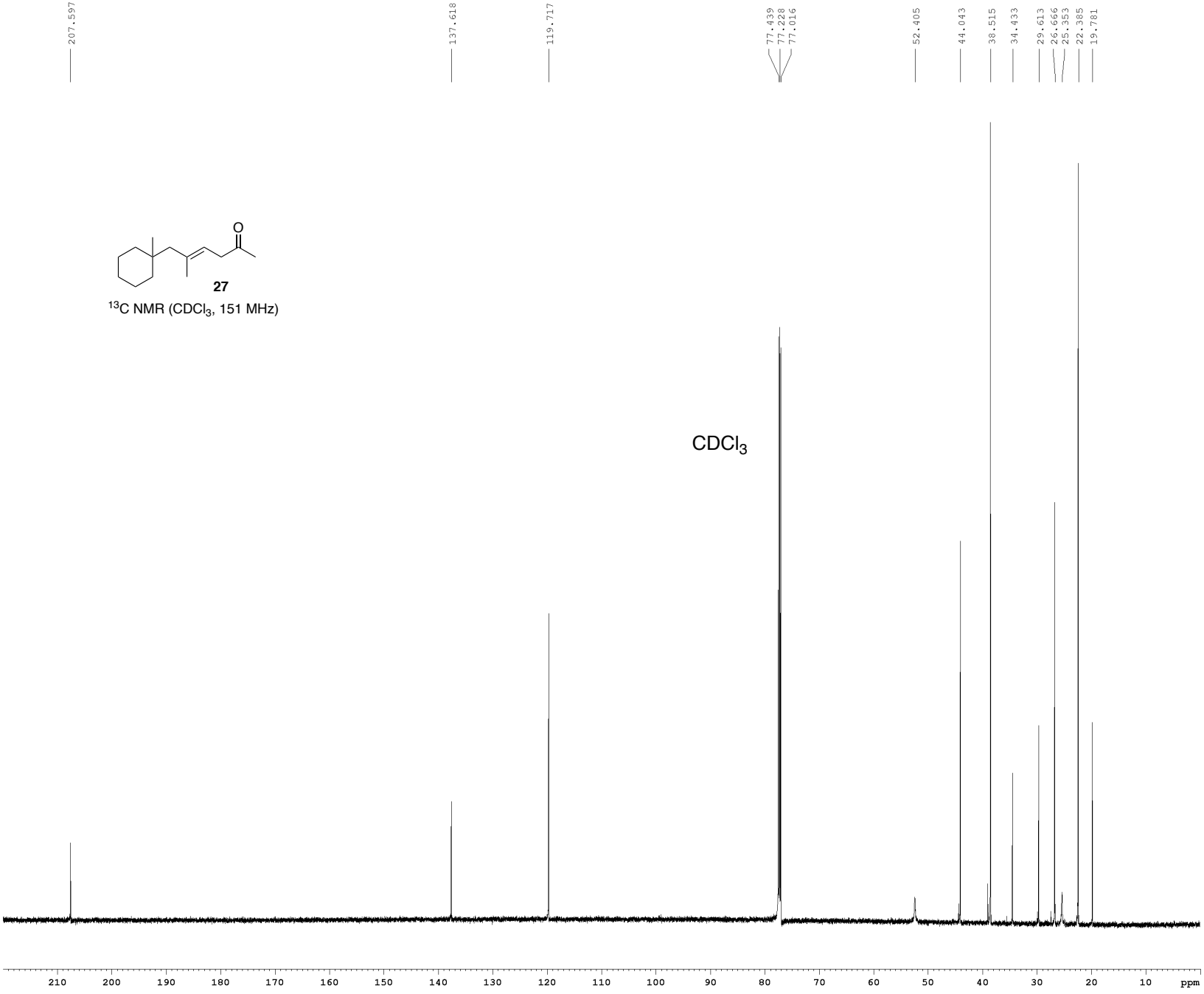

```
Current Data Parameters
NAME                  PZ-2151-P
EXPNO                         2
PROCNO                        1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_               20170419
Time                   14.31
INSTRUM                av600
PROBHD    5 mm CPBBO BB-
PULPROG                 zg30
TD                     98074
SOLVENT                CDCl3
NS                         8
DS                         2
SWH                 9615.385 Hz
FIDRES              0.098042 Hz
AQ                  5.0998478 sec
RG                        10
DW                    52.000 usec
DE                    13.70 usec
TE                    298.0 K
D1                 0.10000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             600.1342009 MHz
NUC1                       1H
P1                    12.00 usec
PLW1            20.00000000 W

F2 - Processing parameters
SI                         65536
SF               600.1300281 MHz
WDW                        EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

13C spectrum with 1H decoupling




```
Current Data Parameters
NAME            PZ-2151-P
EXPNO                   4
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

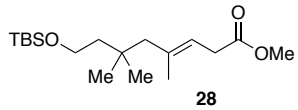
F2 - Acquisition Parameters
Date_           20170419
Time                15.49
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT             CDCl3
NS                    160
DS                      4
SWH             36231.883 Hz
FIDRES          0.552855 Hz
AQ              0.9043968 sec
RG                   2050
DW                13.800 usec
DE                19.65 usec
TE                298.0 K
D1             0.40000001 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         150.9194080 MHz
NUC1                  13C
P1                 10.00 usec
PLW1         64.00000000 W

======== CHANNEL f2 ========
SFO2         600.1330010 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         20.00000000 W
PLW12         0.36000001 W

F2 - Processing parameters
SI                  65536
SF           150.9027836 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```

1H spectrum



28

^{1}H NMR ($CDCl_3$, 600 MHz)

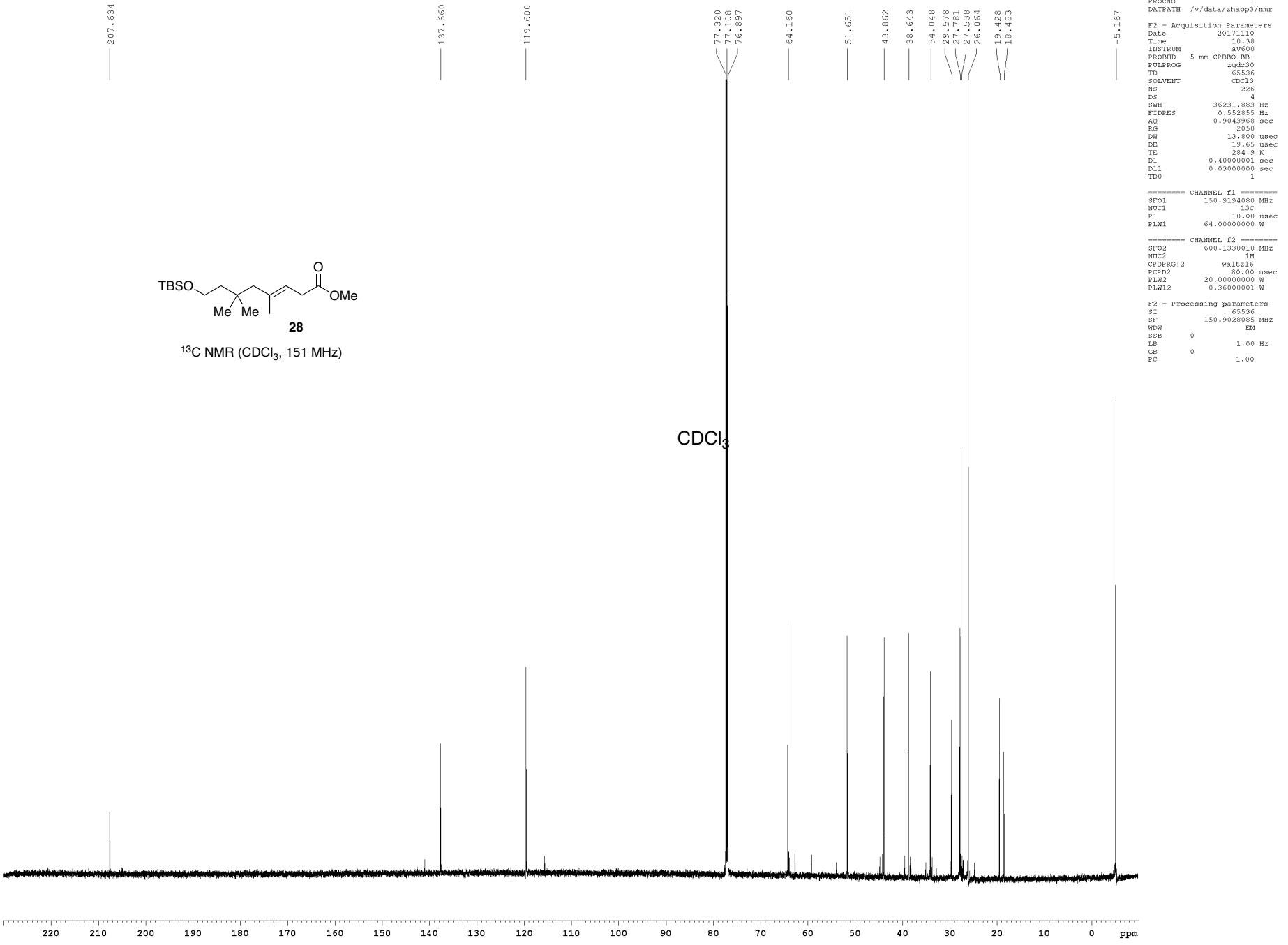

```
Current Data Parameters
NAME         PZ-4040-#19
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_           20171110
Time               10.36
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ              5.0998478 sec
RG                    10
DW                52.000 usec
DE                13.70 usec
TE                284.9 K
D1             0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                1H
P1                 12.00 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300353 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

13C spectrum with 1H decoupling



28

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME         PZ-4040-#19
EXPNO                  2
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

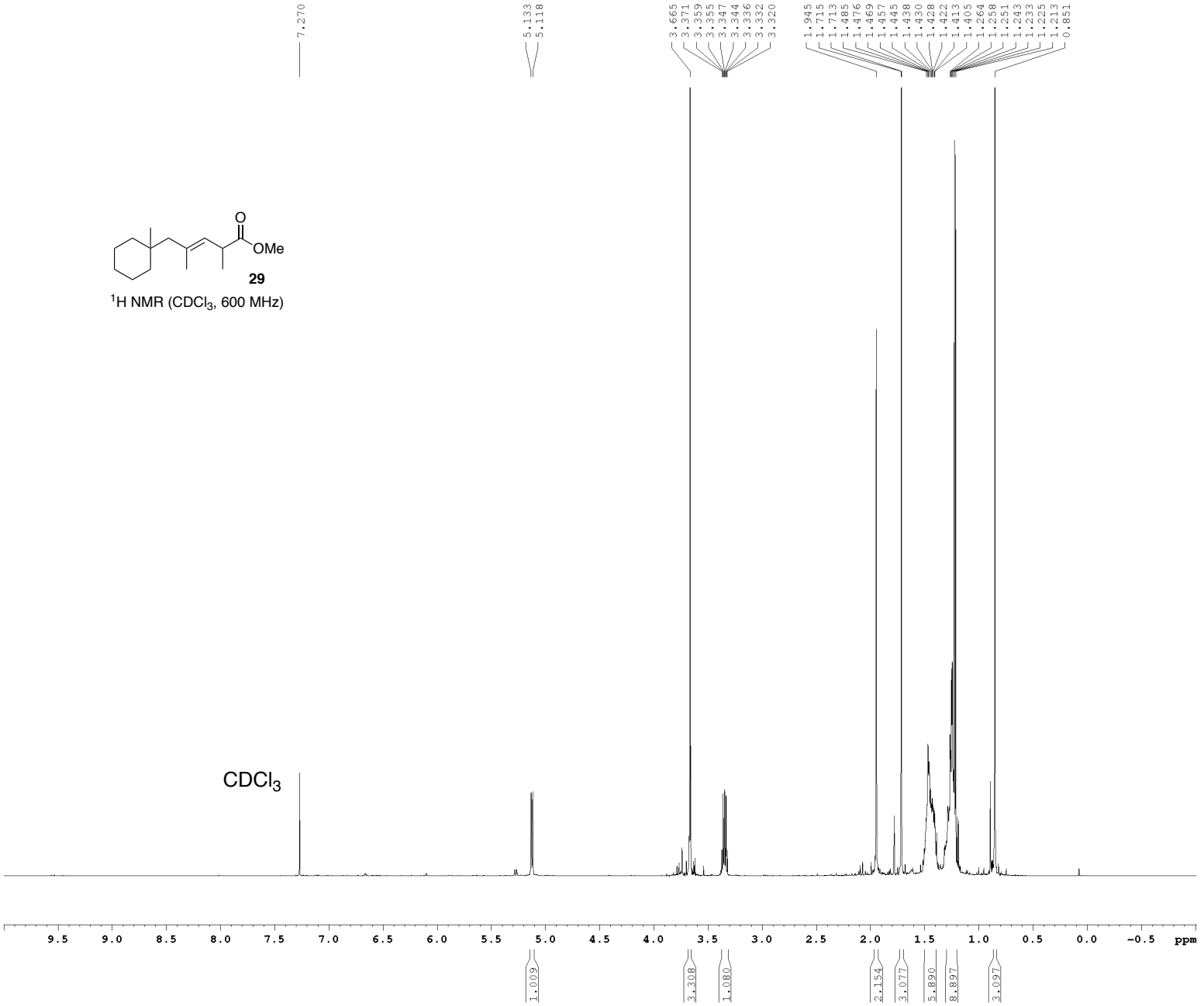
F2 - Acquisition Parameters
Date_           20171110
Time               10.38
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  226
DS                    4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ             0.9043968 sec
RG                 2050
DW               13.800 usec
DE               19.65 usec
TE               284.9 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1               13C
P1               10.00 usec
PLW1        64.00000000 W

======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                65536
SF          150.9028085 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.00
```

1H spectrum



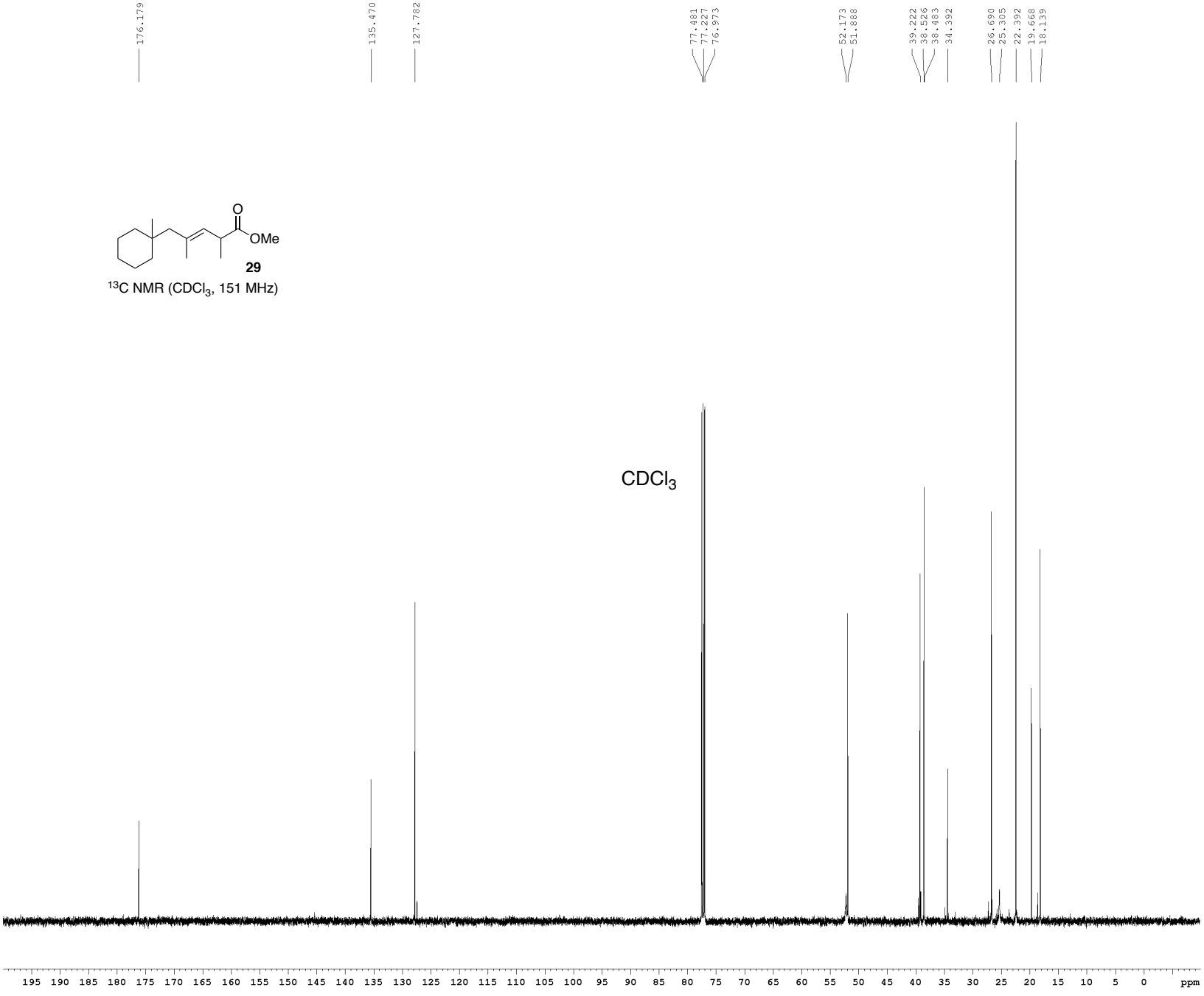

```
Current Data Parameters
NAME            PZ-2151-D
EXPNO                   1
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_            20170421
Time                12.10
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ              5.0998478 sec
RG                  20.2
DW                52.000 usec
DE                13.70 usec
TE                298.0 K
D1             0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                1H
P1                 12.00 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300279 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
NAME          SL-158-13C
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20161030
Time              12.21
INSTRUM         cryo500
PROBHD  5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  256
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813440 sec
RG                 4096
DW               16.500 usec
DE                6.00 usec
TE               298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2               33.10 usec

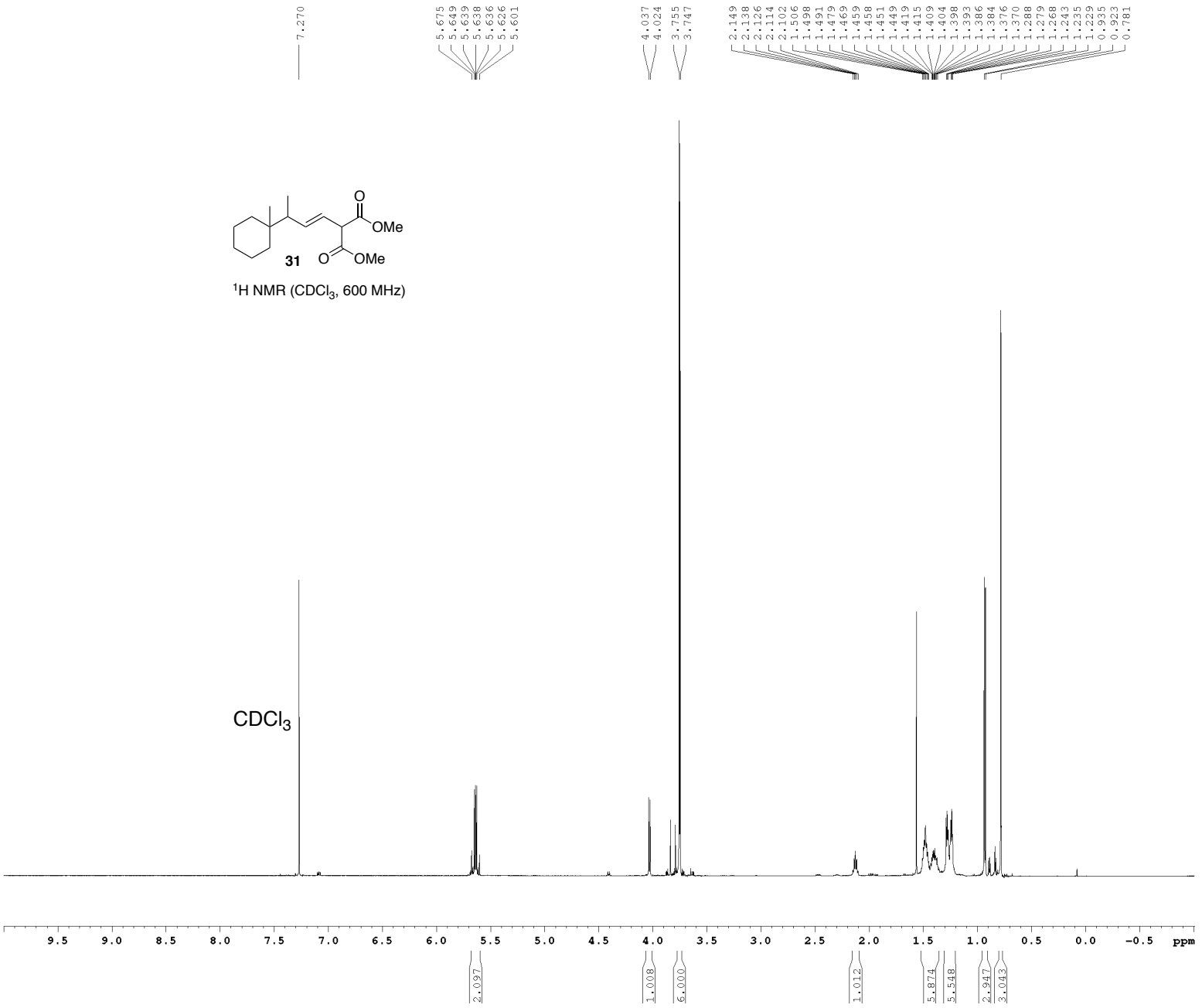
======== CHANNEL f1 ========
NUC1               13C
P1               16.55 usec
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1        125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2               1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1            30.00 %
GPZ2            50.00 %
p15            500.00 usec
p16           1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803996 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                2.00
```

#9



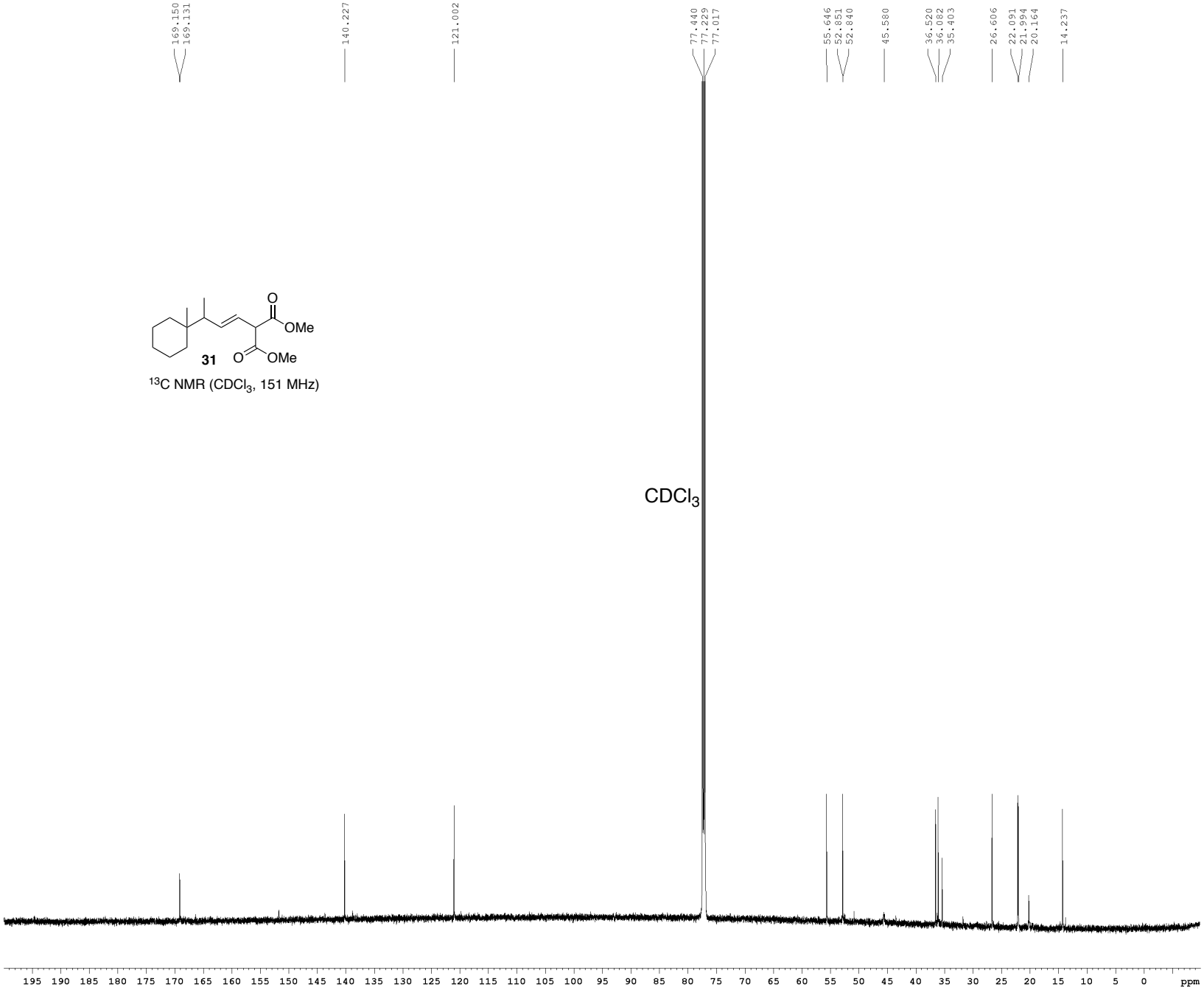

```
Current Data Parameters
NAME            PZ-2150-P
EXPNO                   8
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_            20170420
Time                14.04
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                      8
DS                      2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ              5.0998478 sec
RG                     18
DW                52.000 usec
DE                13.70 usec
TE                298.0 K
D1             0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          600.1342009 MHz
NUC1                   1H
P1                  12.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI                  65536
SF            600.1300281 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

13C spectrum with 1H decoupling



31

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME                  PZ-2150-P
EXPNO                        10
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

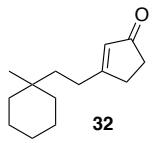
F2 - Acquisition Parameters
Date_              20170420
Time                  14.14
INSTRUM                av600
PROBHD   5 mm CPBBO BB-
PULPROG               zgdc30
TD                     65536
SOLVENT                CDCl3
NS                       366
DS                         4
SWH                36231.883 Hz
FIDRES             0.552855 Hz
AQ                 0.9043968 sec
RG                      2050
DW                    13.800 usec
DE                    19.65 usec
TE                    298.0 K
D1                 0.40000001 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           150.9194080 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           64.00000000 W

======== CHANNEL f2 ========
SFO2           600.1330010 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2           20.00000000 W
PLW12           0.36000001 W

F2 - Processing parameters
SI                     65536
SF             150.9027819 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.00
```

1H spectrum



32

^{1}H NMR ($CDCl_3$, 600 MHz)

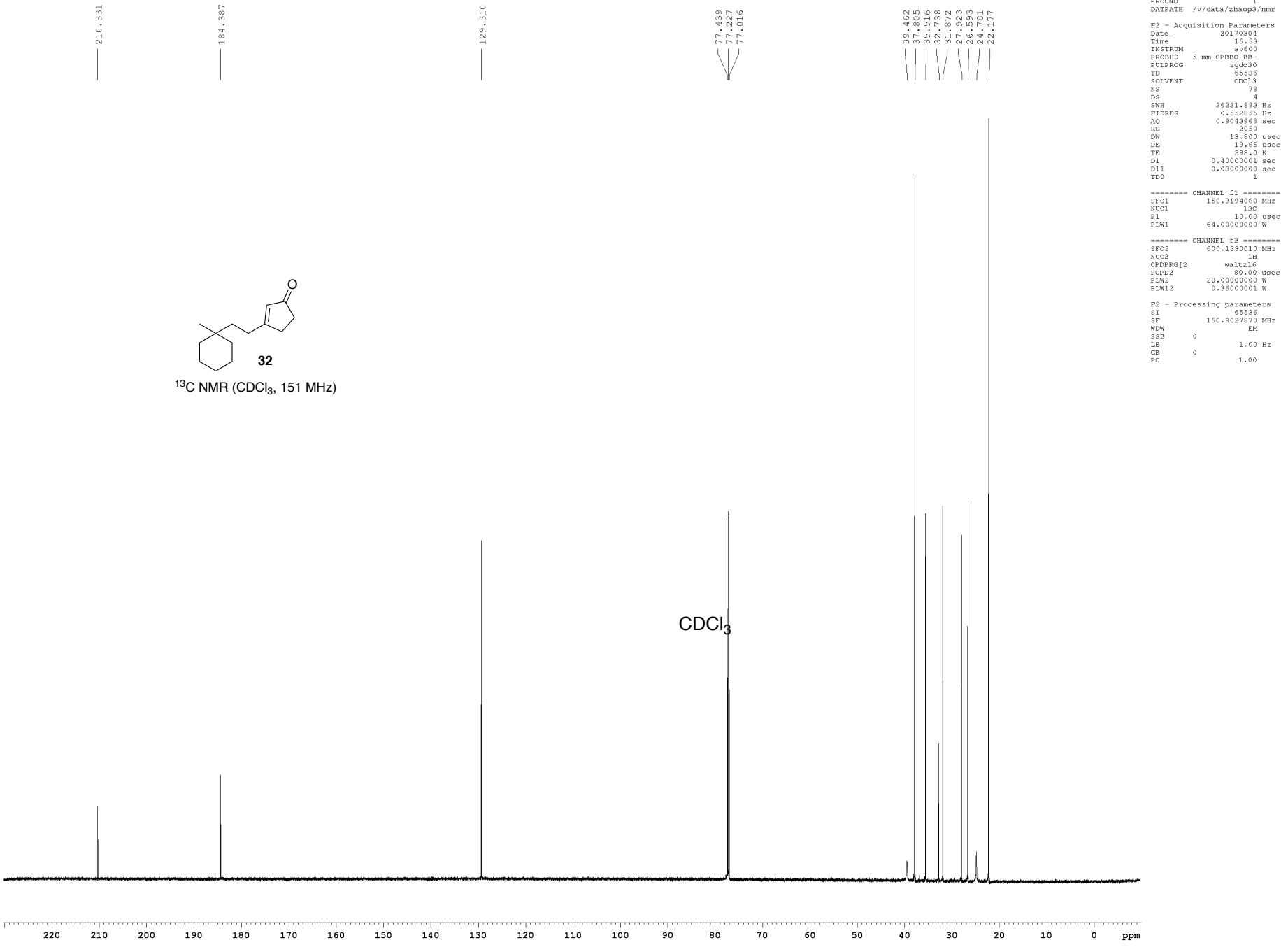

```
Current Data Parameters
NAME                  PZ-2096-P
EXPNO                         1
PROCNO                        1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_               20170304
Time                   15.49
INSTRUM                av600
PROBHD    5 mm CPBBO BB-
PULPROG                 zg30
TD                     98074
SOLVENT                CDCl3
NS                         8
DS                         2
SWH                 9615.385 Hz
FIDRES              0.098042 Hz
AQ                  5.0998478 sec
RG                        18
DW                     52.000 usec
DE                     13.70 usec
TE                     298.0 K
D1                  0.10000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             600.1342009 MHz
NUC1                       1H
P1                     12.00 usec
PLW1            20.00000000 W

F2 - Processing parameters
SI                         65536
SF               600.1300296 MHz
WDW                        EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

13C spectrum with 1H decoupling




```
Current Data Parameters
NAME                  PZ-2096-P
EXPNO                         2
PROCNO                        1
DATPATH  /v/data/zhaop3/nmr

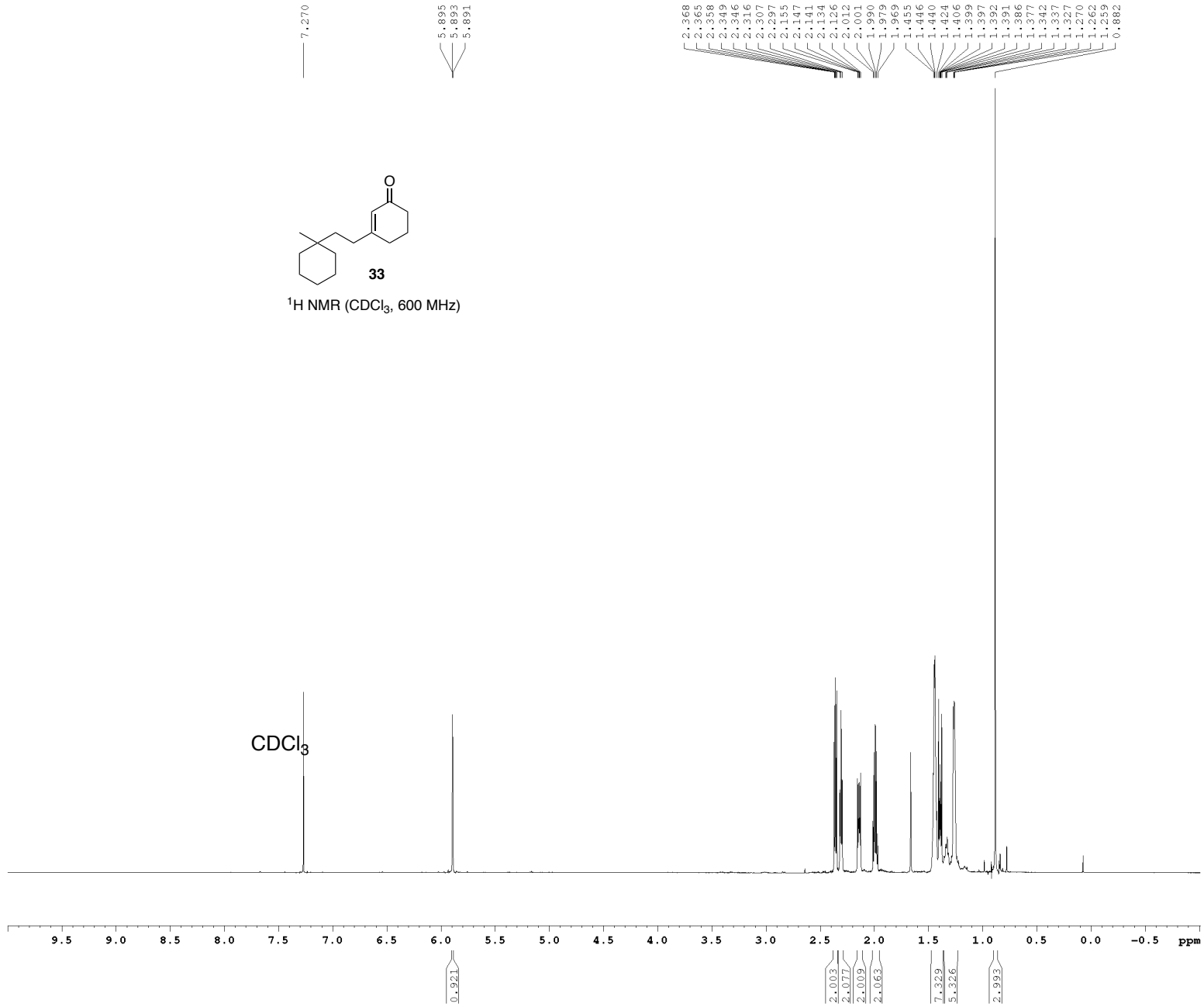
F2 - Acquisition Parameters
Date_              20170304
Time                   15.53
INSTRUM                av600
PROBHD   5 mm CPBBO BB-
PULPROG               zgdc30
TD                     65536
SOLVENT                CDCl3
NS                        78
DS                         4
SWH               36231.883 Hz
FIDRES             0.552855 Hz
AQ                 0.9043968 sec
RG                      2050
DW                    13.800 usec
DE                    19.65 usec
TE                    298.0 K
D1                 0.40000001 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1          150.9194080 MHz
NUC1                    13C
P1                    10.00 usec
PLW1          64.00000000 W

======== CHANNEL f2 ========
SFO2          600.1330010 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2          20.00000000 W
PLW12          0.36000001 W

F2 - Processing parameters
SI                     65536
SF            150.9027870 MHz
WDW                       EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.00
```

1H spectrum



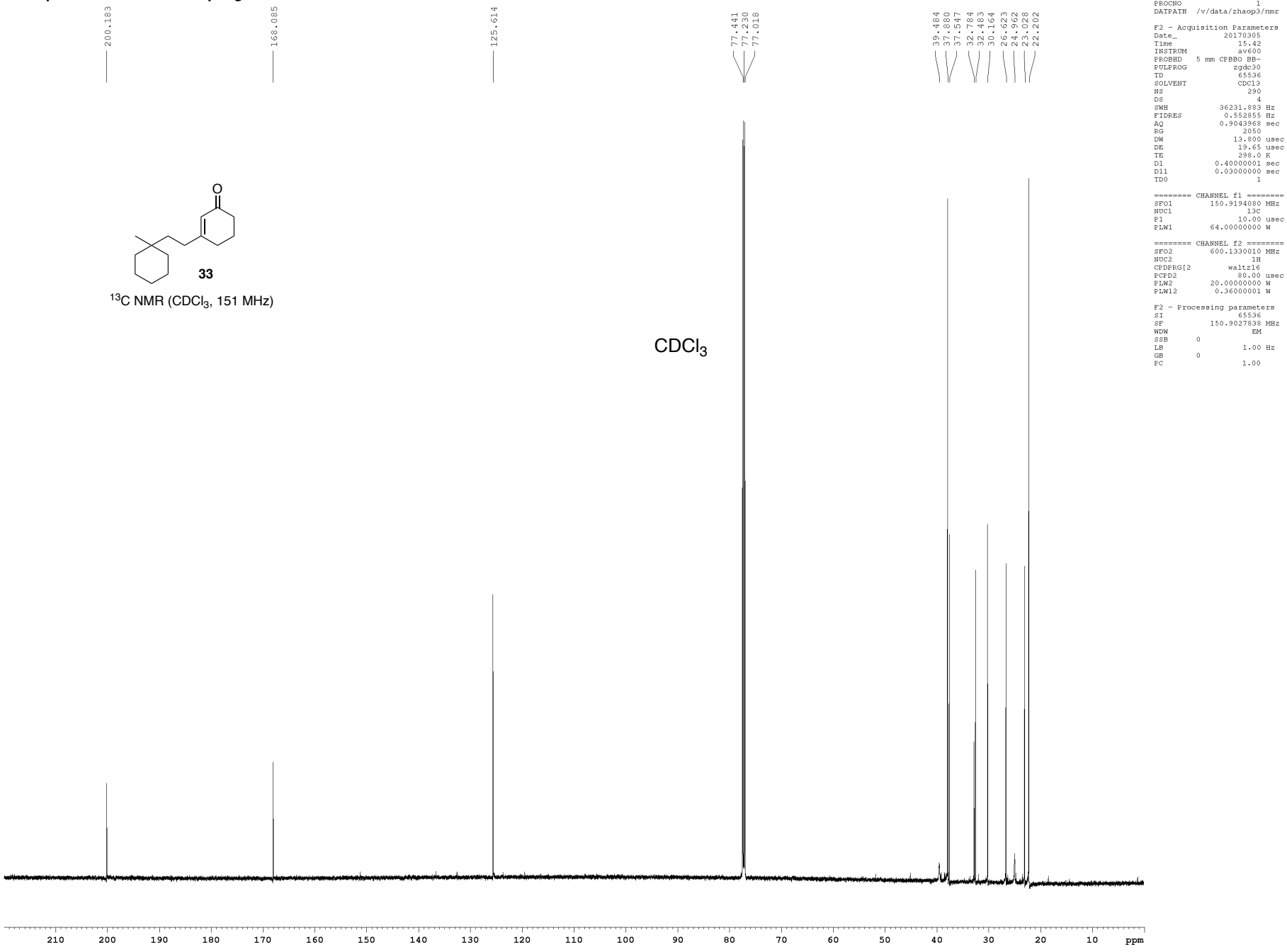

```
Current Data Parameters
NAME                  PZ-2097-P
EXPNO                         1
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_               20170304
Time                   16.42
INSTRUM                av600
PROBHD    5 mm CPBBO BB-
PULPROG                zg30
TD                    98074
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                9615.385 Hz
FIDRES            0.098042 Hz
AQ                5.0998478 sec
RG                       10
DW                   52.000 usec
DE                   13.70 usec
TE                   298.0 K
D1              0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           600.1342009 MHz
NUC1                     1H
P1                   12.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI                    65536
SF             600.1300297 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

13C spectrum with 1H decoupling




```
Current Data Parameters
NAME                  PZ-2097-P
EXPNO                         3
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

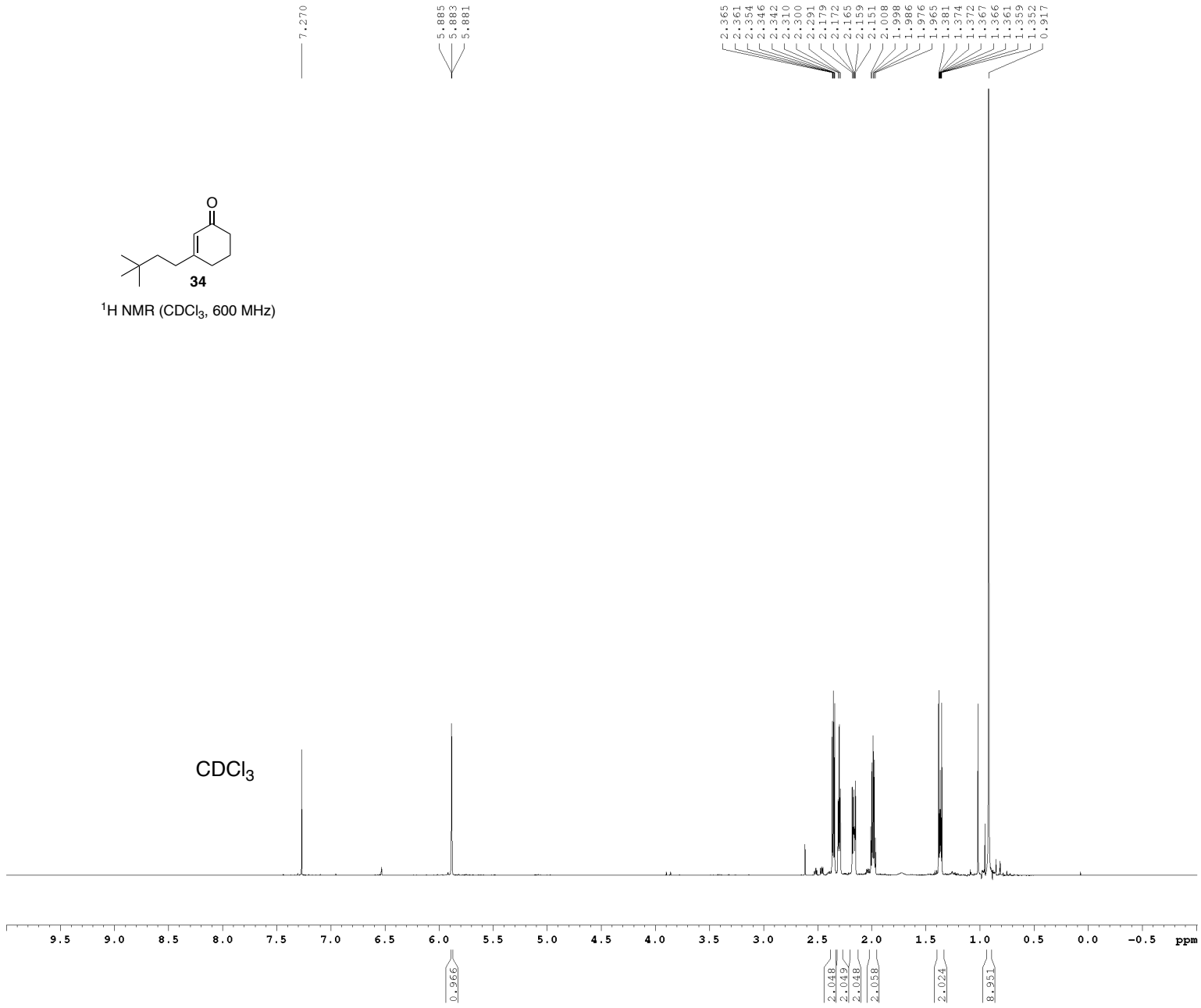
F2 - Acquisition Parameters
Date_              20170305
Time                  15.42
INSTRUM                av600
PROBHD    5 mm CPBBO BB-
PULPROG              zgdc30
TD                    65536
SOLVENT               CDCl3
NS                      290
DS                        4
SWH               36231.883 Hz
FIDRES             0.552855 Hz
AQ                 0.9043968 sec
RG                     2050
DW                   13.800 usec
DE                   19.65 usec
TE                   298.0 K
D1                0.40000001 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            150.9194080 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           64.00000000 W

======== CHANNEL f2 ========
SFO2            600.1330010 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 80.00 usec
PLW2           20.00000000 W
PLW12           0.36000001 W

F2 - Processing parameters
SI                    65536
SF              150.9027838 MHz
WDW                      EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.00
```

1H spectrum



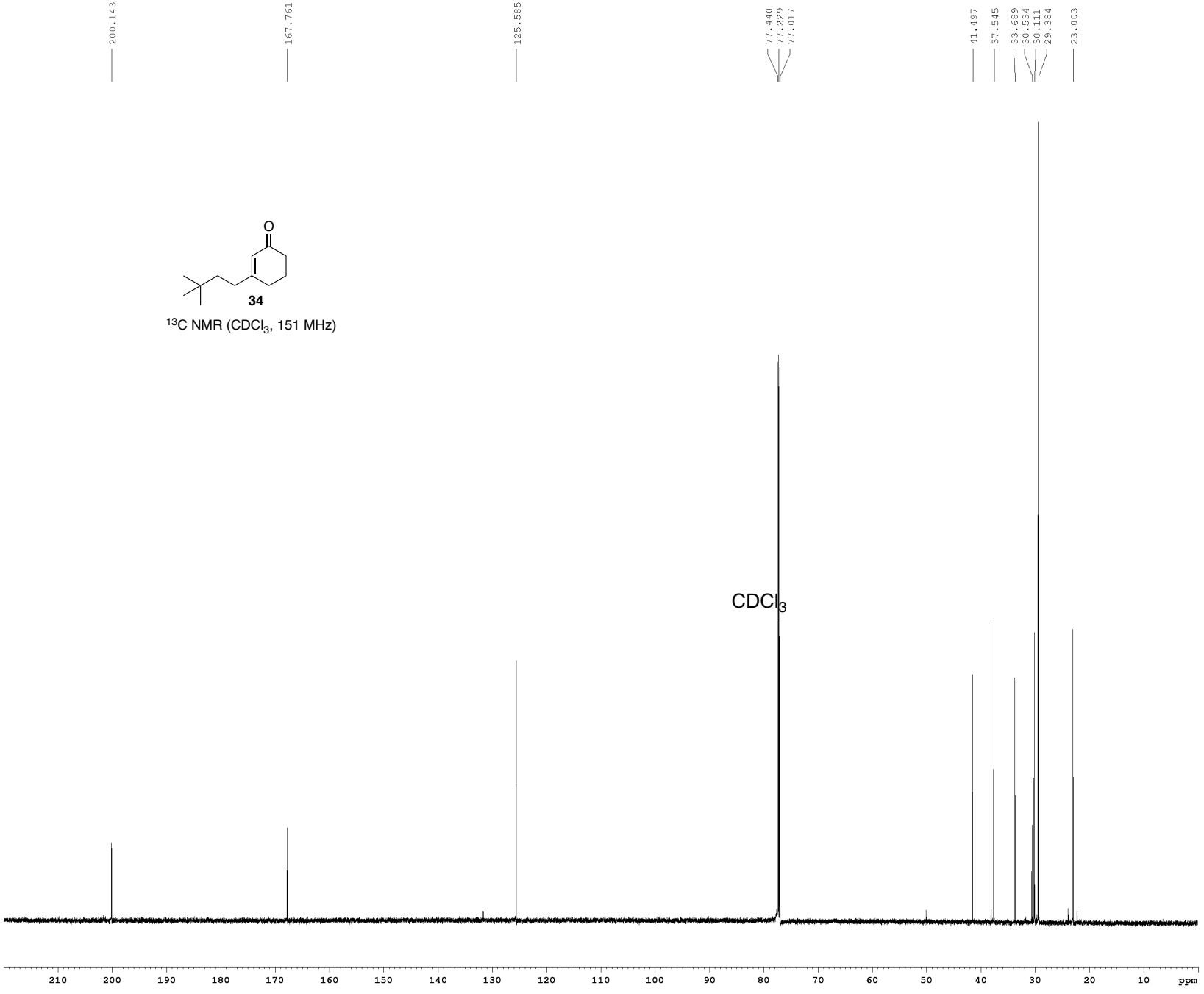

```
Current Data Parameters
NAME                  PZ-2102-P
EXPNO                         1
PROCNO                        1
DATPATH   /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_                  20170307
Time                      17.29
INSTRUM                   av600
PROBHD    5 mm CPBBO BB-
PULPROG                   zg30
TD                        98074
SOLVENT                   CDCl3
NS                            8
DS                            2
SWH                    9615.385 Hz
FIDRES                 0.098042 Hz
AQ                     5.0998478 sec
RG                         40.3
DW                        52.000 usec
DE                        13.70 usec
TE                        298.0 K
D1                   0.10000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                600.1342009 MHz
NUC1                        1H
P1                        12.00 usec
PLW1               20.00000000 W

F2 - Processing parameters
SI                        65536
SF                  600.1300296 MHz
WDW                         EM
SSB          0
LB                         0.30 Hz
GB           0
PC                         1.00
```

13C spectrum with 1H decoupling



34

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME              PZ-2102-P
EXPNO                     2
PROCNO                    1
DATPATH   /v/data/zhaop3/nmr

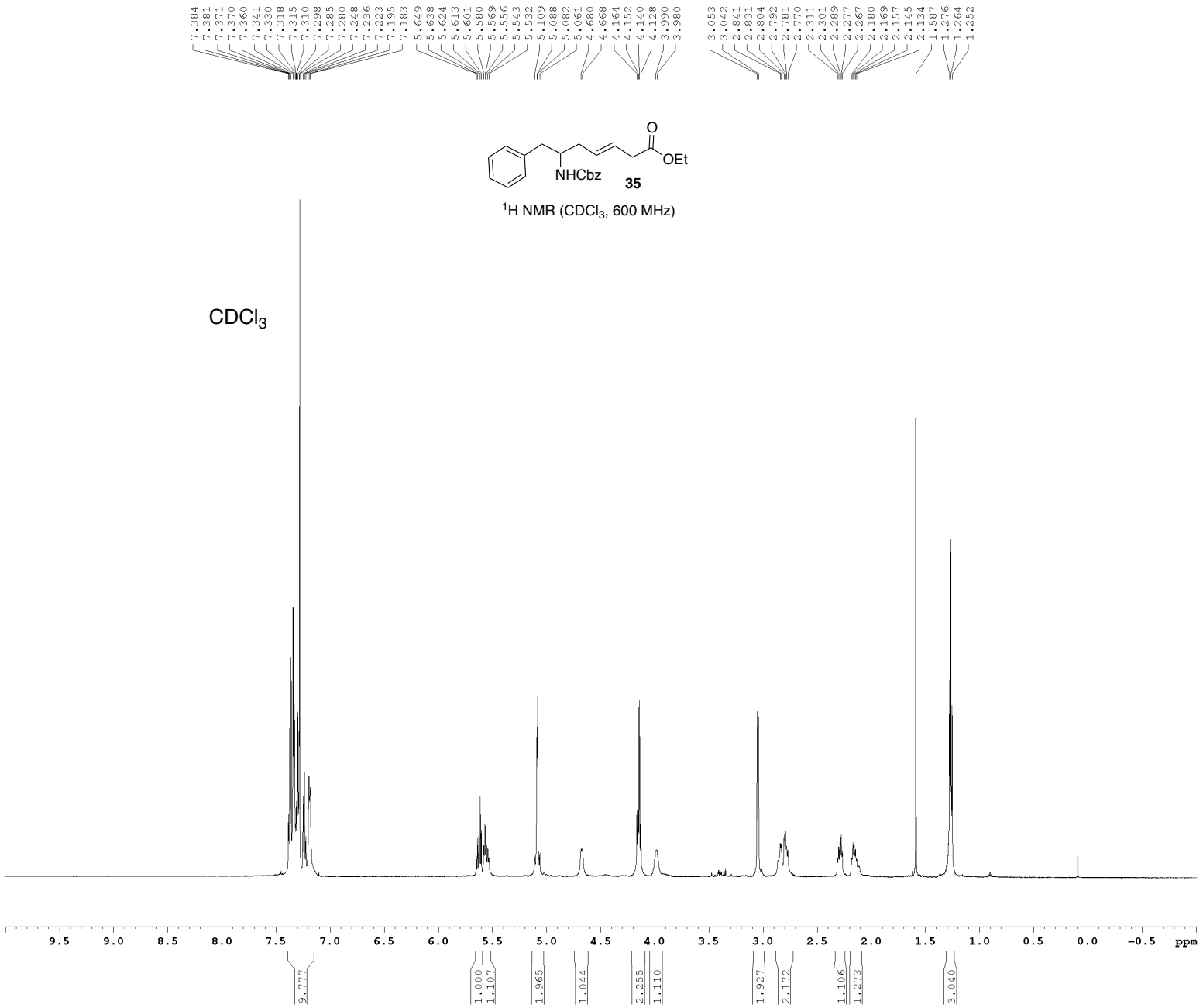
F2 - Acquisition Parameters
Date_              20170307
Time                  17.37
INSTRUM               av600
PROBHD   5 mm CPBBO BB-
PULPROG              zgdc30
TD                    65536
SOLVENT               CDCl3
NS                       46
DS                        4
SWH               36231.883 Hz
FIDRES             0.552855 Hz
AQ                 0.9043968 sec
RG                     2050
DW                   13.800 usec
DE                   19.65 usec
TE                   298.0 K
D1                0.40000001 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          150.9194080 MHz
NUC1                    13C
P1                    10.00 usec
PLW1          64.00000000 W

======== CHANNEL f2 ========
SFO2          600.1330010 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                 80.00 usec
PLW2          20.00000000 W
PLW12          0.36000001 W

F2 - Processing parameters
SI                    65536
SF            150.9027846 MHz
WDW                     EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.00
```

#46



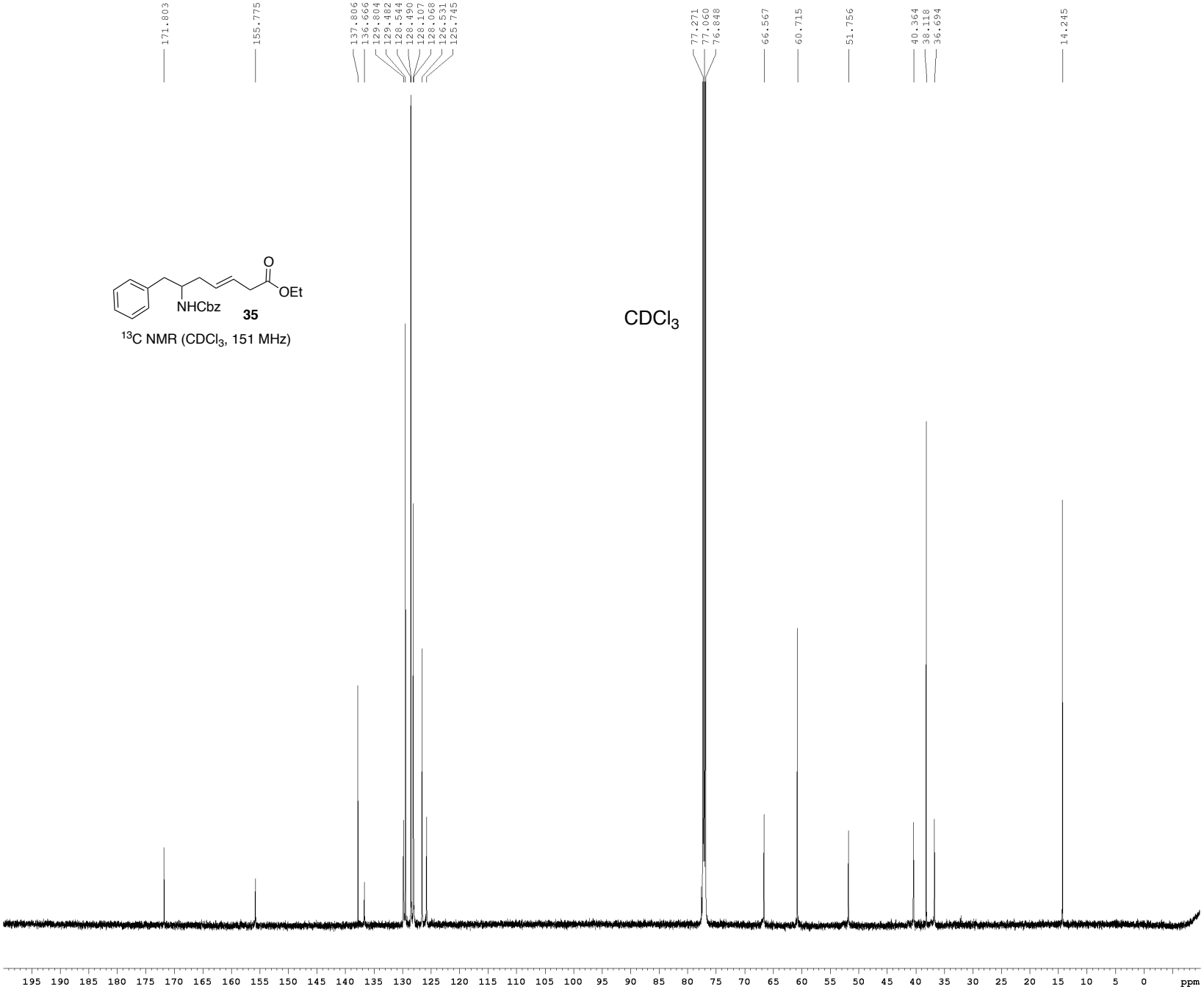

```
Current Data Parameters
NAME            PZ-2128-P
EXPNO                   7
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_            20170423
Time                15.42
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                      8
DS                      2
SWH              9615.385 Hz
FIDRES           0.098042 Hz
AQ               5.0998478 sec
RG                     10
DW                52.000 usec
DE                13.70 usec
TE                298.0 K
D1            0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                    1H
P1                 12.00 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                  65536
SF           600.1300230 MHz
WDW                    EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

13C spectrum with 1H decoupling



35

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME            PZ-2128-P
EXPNO                   8
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

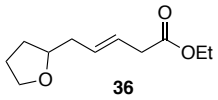
F2 - Acquisition Parameters
Date_           20170423
Time               17.09
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                  2924
DS                     4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ             0.9043968 sec
RG                  2050
DW                13.800 usec
DE                19.65 usec
TE                298.0 K
D1           0.40000001 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1               13C
P1               10.00 usec
PLW1        64.00000000 W

======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                 65536
SF          150.9028085 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.00
```

1H spectrum



36

^{1}H NMR ($CDCl_3$, 600 MHz)

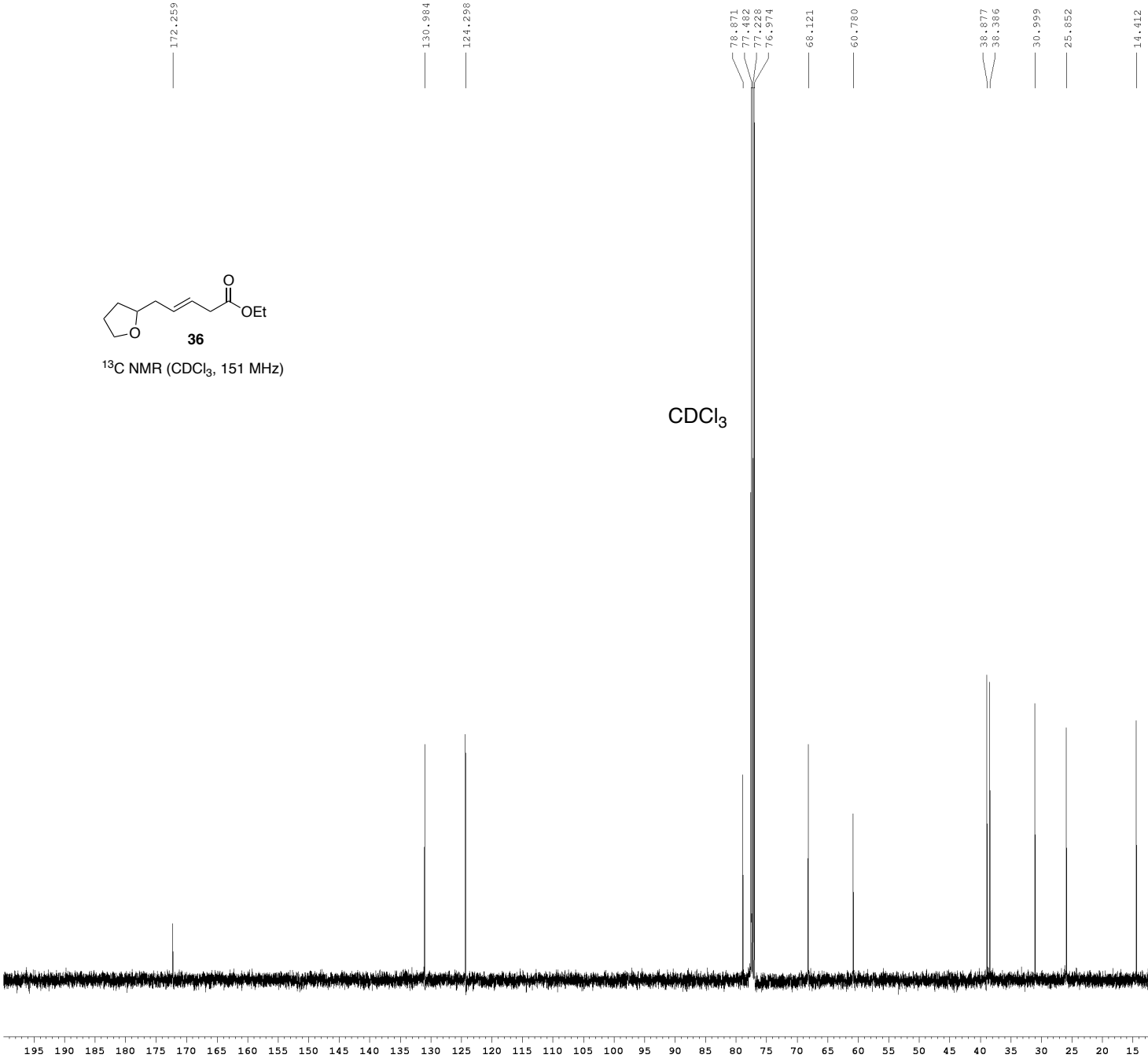

```
Current Data Parameters
NAME         PZ-2129-#17
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_           20170405
Time               12.09
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ              5.0998273 sec
RG                     8
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST    0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.50 usec
PL1                1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200269 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling



36

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME            PZ-2129-P
EXPNO                  11
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20170418
Time              15.45
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  562
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813440 sec
RG                9195.2
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                33.10 usec

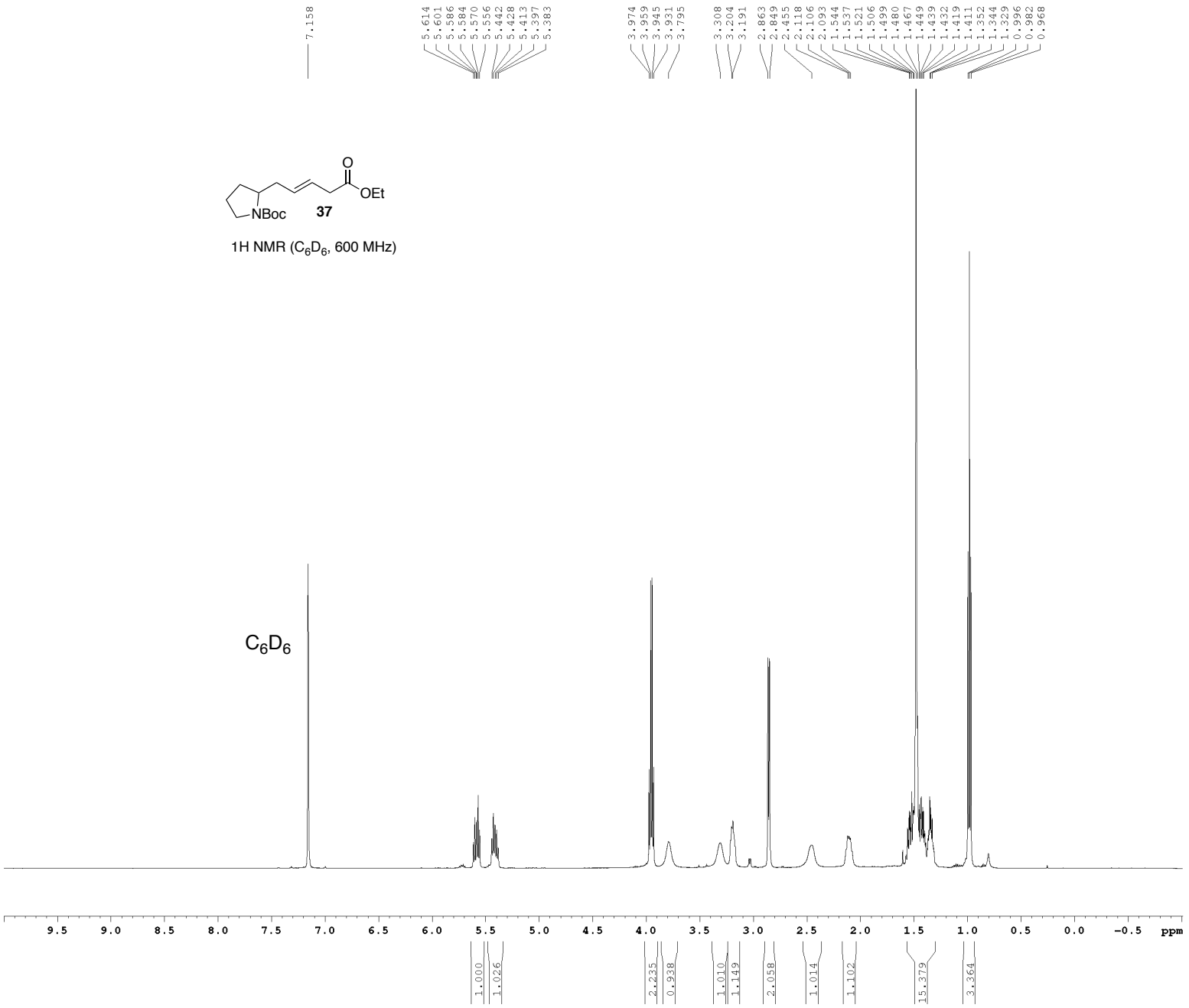
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1         125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803995 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 2.00
```

1H spectrum @ 70oC



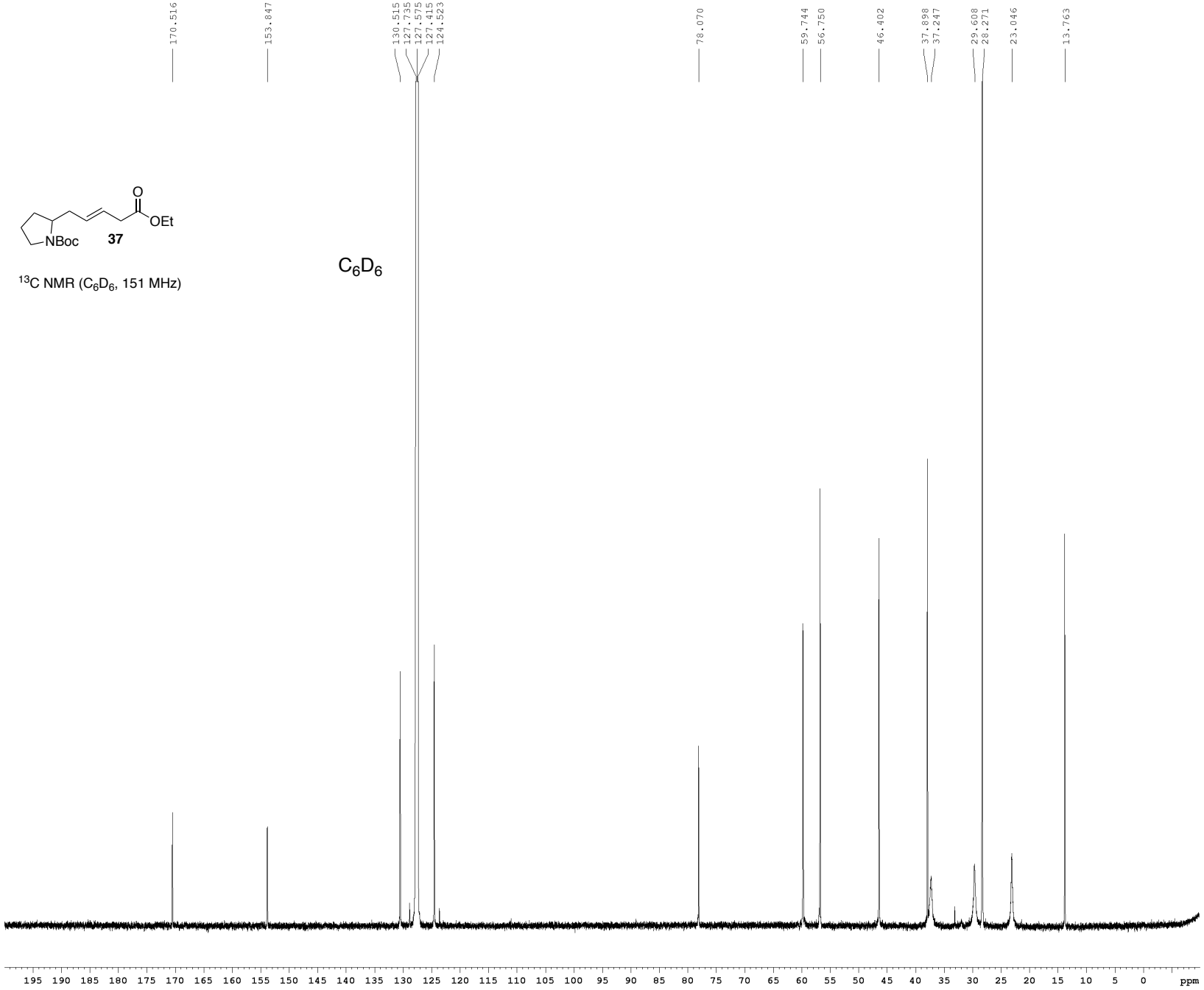

```
Current Data Parameters
NAME            PZ-2126-P
EXPNO                   7
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_            20170417
Time                15.54
INSTRUM             gn500
PROBHD   5 mm broadband
PULPROG              zg30
TD                  81728
SOLVENT              C6D6
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998273 sec
RG                   90.5
DW                 62.400 usec
DE                  6.00 usec
TE                 343.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PL1                -5.80 dB
SFO1         499.0734935 MHz

F2 - Processing parameters
SI                     65536
SF           499.0700000 MHz
WDW                     EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

13C spectrum with 1H decoupling at 70 oC



^{13}C NMR (C_6D_6, 151 MHz)

```
Current Data Parameters
NAME            PZ-2126-P
EXPNO                   3
PROCNO                  1
DATPATH   /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_           20170418
Time              16.23
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT             C6D6
NS                   668
DS                     4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ             0.9043968 sec
RG                  2050
DW               13.800 usec
DE               19.65 usec
TE                343.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 =======
SFO1        150.9194080 MHz
NUC1               13c
P1               10.00 usec
PLW1        64.00000000 W

======== CHANNEL f2 =======
SFO2        600.1330010 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                 65536
SF          150.9028085 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.00
```

References:

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10. This sample contained a trace amount (~5%) of the *Z* stereoisomer as seen by the diagnostic small signals for its vinylic carbons in the ^{13}C NMR spectra.

11. This sample contained ~10% of the *Z* stereoisomer as seen by the diagnostic small signals for its vinylic carbons in the ^{13}C NMR spectra.