Rh(III)-Catalyzed Cyclization of 2,3-Allenoic Acids in the Presence of 2,3-Allenols

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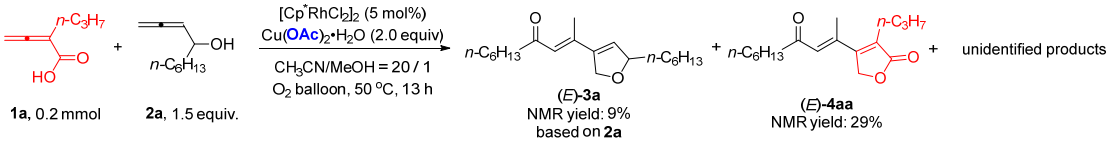
Supporting Information

Table of Contents

1. General Information

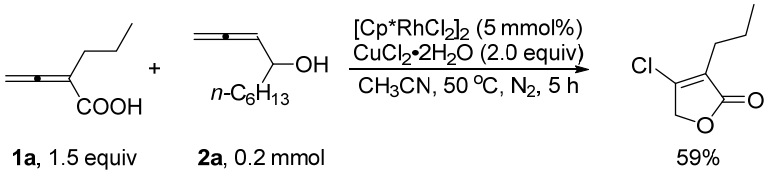
^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded in $CDCl_3$ using a Bruker AM 300 MHz NMR spectrometer (^{1}H at 300 MHz, ^{13}C at 75 MHz, ^{19}F at 282 MHz). All ^{1}H NMR spectra were measured with TMS (0 ppm) in $CDCl_3$. All ^{19}F NMR spectra were measured with $CFCl_3$ (0 ppm) as the internal standard, respectively. All ^{13}C NMR spectra were recorded in relative to the signal of $CDCl_3$ (77.0 ppm). IR spectra were recorded with a Perkin–Elmer 983G instrument. Elemental analyses were conducted with a Carlo-Erba EA1110 elementary analysis instrument. Mass spectrometry was performed with an HP 5989A system. High-resolution mass spectrometry was determined with a Finnigan MAT 8430 or Bruker APEXIII instrument. $[Cp^*RhCl_2]_2$ was purchased from *HWRK CHEM*. CH_3CN was dried over calcium hydride and distilled freshly before use. The range of boiling point of the petroleum ether used for chromatography was 60-90 ^{o}C unless noted otherwise. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise. 2,3-Allenols were prepared according to the literature procedures.[1] 2,3-Allenoic acids **1a** ~ **1c** were prepared according to the literature procedures.[2] 2,3-Allenoic acids **1d** and **1e** were prepared according to the literature procedures.[3]

2. **The Reaction of 2,3-Allenoic Acid 1a and 2,3-Allenol 2a in the Presence of 5 mol% $[Cp^*RhCl_2]_2$ and 2.0 Equiv $Cu(OAc)_2•H_2O$** (Scheme 2). (fjj-4-193)



To a dried Schlenk tube were added $[Cp^*RhCl_2]_2$ (6.1 mg, 0.01 mmol), $Cu(OAc)_2•H_2O$ (80.0 mg, 0.4 mmol), and **1a** (25.4 mg, 0.2 mmol) under air atmosphere. The Schlenk tube was then degassed to remove the air inside completely and refilled with O_2 by a balloon of O_2 for three times. After **2a** (45.3 mg, 0.3 mmol)/CH_3CN (0.6 mL) and MeOH (30 μL) were added sequentially, the reaction tube was put into an oil bath pre-heated at 50 °C. The reaction was complete after stirring for 13 h was monitored by TLC. Then the O_2 balloon was removed, and the reaction mixture was filtered through a short column of silica gel eluted with ethyl acetate (10 mL × 3). The combined filtrate was then concentrated in vacuo and the crude residue was added 9.2 μL of mesitylene as the internal standard. 9% NMR yield of (*E*)-**3a** and 29% NMR yield (*E*)-**4aa** was determined by ^1H NMR spectrum of the crude, and some unindentified products were observed from the spectrum.

3. **The Reaction of 2,3-Allenoic Acid 1a and 2,3-Allenol 2a in the Presence of 5 mol% $[Cp^*RhCl_2]_2$ and 2.0 Equiv $CuCl_2•2H_2O$** (Table 1, Entry 1). (fjj-2-028 and fjj-5-040)

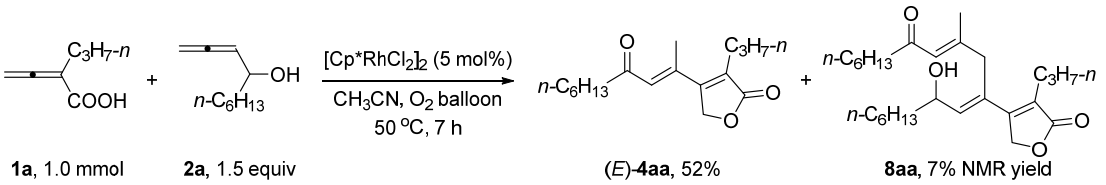


To a Schlenk tube were added $[Cp^*RhCl_2]_2$ (6.3 mg, 0.01 mmol), $CuCl_2 \cdot 2H_2O$ (68.1 mg, 0.4 mmol), and **1a** (38.3 mg, 0.3 mmol) sequentially. The Schlenk tube was degassed under vacuum and backfilled with nitrogen three times at room temperature. Then, **2a** (31.2 mg, 0.2 mmol)/CH_3CN (0.54 mL) were added under nitrogen atmosphere. After being continuously stirred at 50 ^oC for 5 h, the reaction was complete as monitored by thin layer chromatography (TLC). After filteration through a short column of silica gel eluted with ethyl acetate (20 mL × 3). The combined filtrate was then concentrated in vacuo and analyzed by ^1H NMR using 9.2 μL of mesitylene as the internal standard. The reaction afforded **6a** in 2% NMR yield and 4-chloro-3-propyl-2(*5H*)-furanone in 69% NMR yield. The mixture was concentrated in vacuo and the crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ ethyl acetate = 50/1 (500 mL) to 10/1 (500 mL)] to afford 4-chloro-3-propyl-2(*5H*)-furanone as an oil (28.6 mg, 59%): ^1H NMR (400 MHz, $CDCl_3$) δ 4.74 (s, 2 H, OCH_2), 2.34 (t, J = 7.4 Hz, 2 H, CH_2), 1.68-1.52 (m, 2 H, CH_2), 0.95 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 149.7, 128.9, 71.1, 25.4, 20.3, 13.7; IR (neat) ν (cm^{-1}) 2964, 2934, 2875, 1770, 1662, 1456, 1346, 1294, 1219, 1109, 1062, 1033; MS (EI): *m/z* (%) 162 [$M(^{37}Cl)^+$, 14.2], 160 [$M(^{35}Cl)^+$, 43.0], 79 (100); HRMS Calcd for $C_7H_9O_2{}^{35}Cl$ (M^+): 160.0286; Found: 160.0288.

4. Rh(III)-Catalyzed Oxidative Cross-coupling Cyclization of 2,3-Allenoic Acids and 2,3-Allenols

4.1 Synthesis of (*E*)-3-propyl-4-(4-oxodec-2-en-2-yl)-2(*5H*)-furanone (*E*)-**4aa**. (fjj-2-

063)

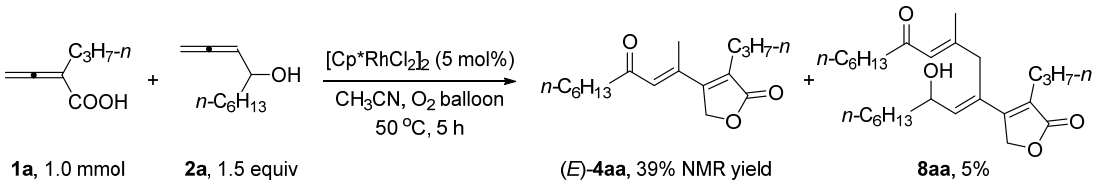


1a, 1.0 mmol **2a**, 1.5 equiv (*E*)-**4aa**, 52% **8aa**, 7% NMR yield

Typical Procedure for synthesis of (*E*)-4aa: To a dry Schlenk tube were added $[Cp^*RhCl_2]_2$ (31.2 mg, 0.05 mmol) and **1a** (125.7 mg, 1.0 mmol) sequentially. The Schlenk tube was degassed under vacuum and backfilled with oxygen three times at room temperature. Then, **2a** (230.2 mg, 1.5 mmol) and CH_3CN (2.7 mL) were added under oxygen atmosphere. After being continuously stirred at 50 °C for 7 h, the reaction was complete as monitored by thin layer chromatography (TLC). After filteration through a short column of silica gel eluted with ethyl acetate (20 mL × 3). The combined filtrate was then concentrated in vacuo and analyzed by ^{1}H NMR using 46 μL of mesitylene as the internal standard: The reaction afforded (*E*)-**4aa** in 59% NMR yield together with 7% NMR of **8aa**. The mixture was concentrated in vacuo and the crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ ethyl acetate = 25/1 (500 mL) to 20/1 (500 mL), then 15/1 (300 mL)] to afford (*E*)-**4aa** as an oil (143.3 mg, 52%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.26 (s, 1 H, =CH), 4.84 (s, 2 H, OCH_2), 2.53 (t, J = 7.2 Hz, 2 H, CH_2), 2.42 (t, J = 7.7 Hz, 2 H, CH_2), 2.35 (s, 3 H, CH_3), 1.72-1.46 (m, 4 H, CH_2 × 2), 1.42-1.15 (m, 6 H, CH_2 × 3), 0.97 (t, J = 7.4 Hz, 3 H, CH_3), 0.93-0.82 (m, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.0, 174.1, 156.8, 143.4, 130.1, 127.1, 70.1, 44.9, 31.5, 28.7, 26.7, 23.9, 22.3, 21.6, 17.4, 14.0, 13.9; IR (neat) ν (cm^{-1}) 2959, 2931, 2872, 1756, 1689, 1589, 1456, 1371, 1348, 1123, 1103, 1077, 1041; MS (EI): *m/z* (%) 278 (M^+, 2.6), 165 (100); HRMS Calcd for $C_{17}H_{26}O_3$

(M^+): 278.1882; Found: 278.1881.

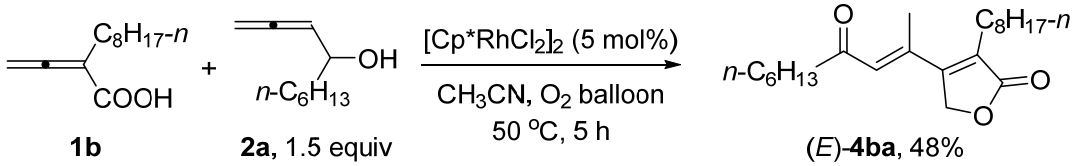
4.2 Synthesis of (*E*)-3-propyl-4-(4-oxodec-2-en-2-yl)-2(5*H*)-furanone **8aa**. (fjj-4-023)



1a, 1.0 mmol **2a**, 1.5 equiv (*E*)-**4aa**, 39% NMR yield **8aa**, 5%

Following **Typical Procedure**, the reaction of **1a** (126.1 mg, 1.0 mmol), **2a** (234.0 mg, 1.5 mmol), and $[Cp^*RhCl_2]_2$ (30.9 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded **8aa** (22.6 mg, 5%) as an oil [eluent: CH_2Cl_2/MeOH = 200/1 (500 mL)]: ^1H NMR (300 MHz, $CDCl_3$) 6.12 (s, 1 H, =CH), 6.00 (d, J = 8.1 Hz, 1 H, =CH), 4.65-4.32 (m, 3 H, OCH_2 and OCH), 3.55 (s, 2 H, CH_2), 2.42 (t, J = 7.4 Hz, 2 H, CH_2), 2.37-2.19 (m, 5 H, CH_2 and CH_3), 1.80-1.12 (m, 21 H, CH_2 × 10 and OH), 0.97 (t, J = 7.4 Hz, 3 H, CH_3), 0.94-0.75 (m, 6 H, CH_3 × 2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.6, 174.6, 157.7, 151.5, 138.0, 137.6, 127.7, 124.0, 71.0, 68.6, 45.0, 38.0, 31.7, 31.6, 29.1, 28.9, 26.6, 25.8, 25.3, 24.1, 22.53, 22.46, 21.2, 16.3, 14.1, 14.01, 13.99; IR (neat) ν (cm^{-1}) 3461, 2957, 2920, 2857, 1755, 1683, 1588, 1456, 1266, 1081, 1037; MS (EI): *m/z* (%) 432 (M^+, 9.0), 43 (100); HRMS Calcd for $C_{27}H_{44}O_4$ (M^+): 432.3240; Found: 432.3235.

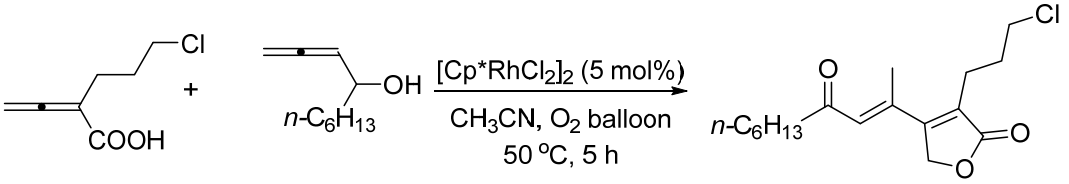
4.2 Synthesis of (*E*)-3-octyl-4-(4-oxodec-2-en-2-yl)-2(5*H*)-furanone (*E*)-**4ba**. (fjj-2-119)



1b **2a**, 1.5 equiv (*E*)-**4ba**, 48%

Following **Typical Procedure**, the reaction of **1b** (98.2 mg, 0.5 mmol), **2a** (115.9 mg, 0.75 mmol), and $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol) in CH_3CN (1.35 mL) afforded (*E*)-**4ba** (83.2 mg, 48%) as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (500 mL) to 10/1 (500 mL)]: ^1H NMR (300 MHz, $CDCl_3$) 6.25 (s, 1 H, =CH), 4.83 (s, 2 H, OCH_2), 2.52 (t, J = 7.4 Hz, 2 H, CH_2), 2.43 (t, J = 7.8 Hz, 2 H, CH_2), 2.35 (s, 3 H, CH_3), 1.69-1.46 (m, 4 H, $CH_2 \times 2$), 1.39-1.15 (m, 16 H, $CH_2 \times 8$), 0.95-0.81 (m, 6 H, $CH_3 \times 2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 174.2, 156.5, 143.6, 130.5, 127.1, 70.2, 45.0, 31.7, 31.5, 29.6, 29.2, 29.1, 28.8, 28.3, 24.9, 24.0, 22.6, 22.4, 17.5, 14.02, 13.95; IR (neat) ν (cm^{-1}) 2955, 2920, 2856, 1753, 1690, 1591, 1452, 1373, 1342, 1128, 1106, 1076, 1039; MS (EI): *m/z* (%) 348 (M^+, 3.9), 43 (100); HRMS Calcd for $C_{22}H_{36}O_3$ (M^+): 348.2664; Found: 348.2665.

4.3 Synthesis of (*E*)-3-(3-chloropropyl)-4-(4-oxodec-2-en-2-yl)-2(5*H*)-furanone (*E*)-**4ca**. (fjj-2-091)

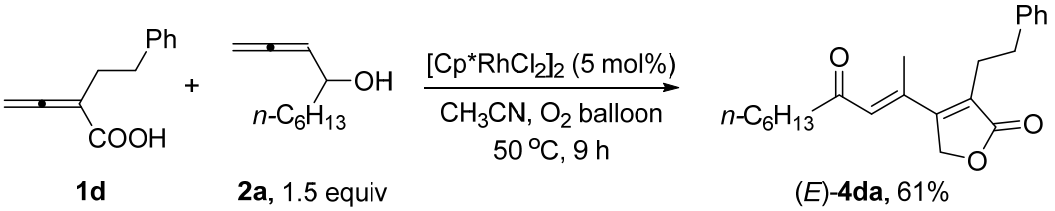


1c **2a**, 1.5 equiv (*E*)-**4ca**, 58%

Following **Typical Procedure**, the reaction of **1c** (79.9 mg, 0.5 mmol), **2a** (115.4 mg, 0.75 mmol), and $[Cp^*RhCl_2]_2$ (15.6 mg, 0.025 mmol) in CH_3CN (1.35 mL) afforded (*E*)-**4ca** (89.6 mg, 58%) as an oil [eluent: petroleum ether/ethyl acetate = 10/1 (500 mL) to 5/1 (1000 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 6.31 (s, 1 H, =CH), 4.87 (s, 2 H, OCH_2), 3.60 (t, J = 5.9 Hz, 2 H, CH_2Cl), 2.64 (t, J = 7.4 Hz, 2 H, CH_2), 2.54 (t,

J = 7.2 Hz, 2 H, CH_2), 2.35 (s, 3 H, CH_3), 2.12-1.97 (m, 2 H, CH_2), 1.70-1.54 (m, 2 H, CH_2), 1.42-1.13 (m, 6 H, $CH_2 \times 3$), 0.95-0.79 (m, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.9, 173.9, 158.1, 142.7, 128.2, 127.6, 70.3, 44.8, 44.4, 31.4, 30.4, 28.7, 23.8, 22.3, 22.1, 17.3, 13.8; IR (neat) ν (cm^{-1}) 2959, 2929, 2858, 1748, 1689, 1593, 1446, 1372, 1341, 1079, 1042; MS (EI): *m/z* (%) 314 [M(^{37}Cl)$^+$, 0.8], 312 [M(^{35}Cl)$^+$, 2.1], 43 (100); HRMS Calcd for $C_{17}H_{25}O_3{}^{35}Cl$ (M^+): 312.1492; Found: 312.1491.

4.4 Synthesis of (*E*)-3-phenethyl-4-(4-oxodec-2-en-2-yl)-2(*5H*)-furanone (*E*)-**4da**. (fjj-3-086)

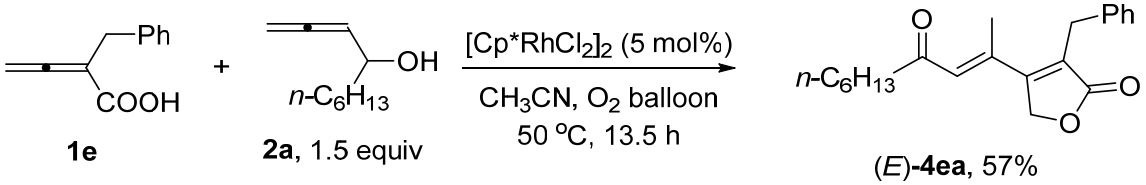


1d **2a**, 1.5 equiv (*E*)-**4da**, 61%

Following **Typical Procedure**, the reaction of **1d** (94.0 mg, 0.5 mmol), **2a** (115.5 mg, 0.75 mmol), and $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol) in CH_3CN (1.35 mL) afforded (*E*)-**4da** (104.2 mg, 61%) as an oil [eluent: petroleum ether/ethyl acetate = 15/1 (500 mL) to 10/1 (1000 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 7.34-7.05 (m, 5 H, ArH), 5.86 (s, 1 H, =CH), 4.78 (s, 2 H, OCH_2), 2.91 (t, J = 7.4 Hz, 2 H, CH_2), 2.72 (t, J = 7.5 Hz, 2 H, CH_2), 2.41 (t, J = 7.4 Hz, 2 H, CH_2), 2.13 (s, 3 H, CH_3), 1.64-1.47 (m, 2 H, CH_2), 1.40-1.17 (m, 6 H, $CH_2 \times 3$), 0.89 (t, J = 6.9 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.9, 174.0, 158.4, 143.1, 140.5, 128.55, 128.53, 128.3, 127.0, 126.3, 70.3, 44.9, 33.6, 31.5, 28.8, 26.9, 23.9, 22.4, 17.4, 14.0; IR (neat) ν (cm^{-1}) 3083, 3062, 3027, 2952, 2930, 2858, 1755, 1689, 1604, 1497, 1454, 1347, 1080, 1045, 1018; MS

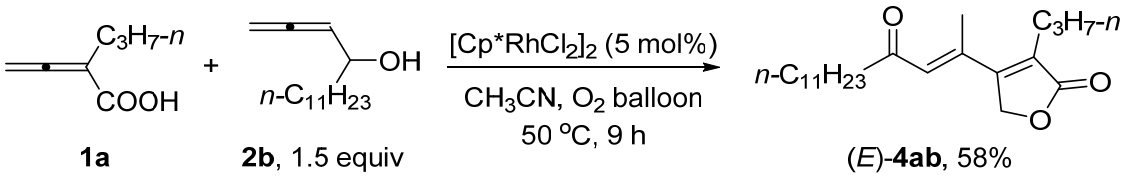
(EI): *m/z* (%) 341 (M^+ + 1, 7.8), 340 (M^+, 2.2), 227 (100); HRMS Calcd for $C_{22}H_{28}O_3$ (M^+): 340.2038; Found: 340.2037.

4.5 Synthesis of (*E*)-3-benzyl-4-(4-oxodec-2-en-2-yl)-2(*5H*)-furanone (*E*)-**4ea**. (fjj-3-023)



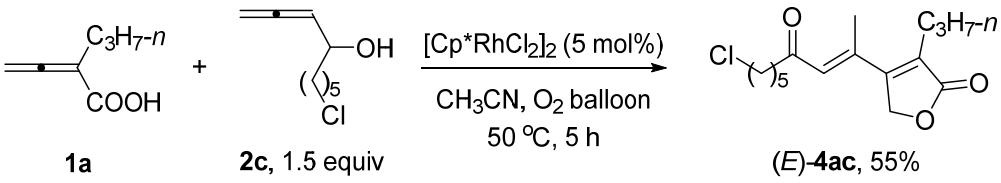
Following **Typical Procedure**, the reaction of **1e** (174.3 mg, 1.0 mmol), **2a** (231.6 mg, 1.5 mmol), and $[Cp^*RhCl_2]_2$ (30.9 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded (*E*)-**4ea** (185.9 mg, 57%) as an oil [eluent: petroleum ether/ethyl acetate = 10/1 (1000 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.10 (m, 5 H, ArH), 6.22 (s, 1 H, =CH), 4.89 (s, 2 H, OCH_2), 3.80 (s, 2 H, CH_2Ph), 2.42 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.29 (s, 3 H, CH_3), 1.60-1.43 (m, 2 H, CH_2), 1.38-1.15 (m, 6 H, CH_2 × 3), 0.88 (t, *J* = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 174.3, 158.5, 142.8, 137.6, 128.7, 128.3, 128.2, 127.9, 126.7, 70.4, 44.9, 31.5, 30.4, 28.8, 23.8, 22.4, 17.3, 14.0; IR (neat) *v* (cm^{-1}) 3062, 3029, 2955, 2929, 2857, 1753, 1688, 1603, 1590, 1496, 1454, 1341, 1081, 1045; MS (EI): *m/z* (%) 326 (M^+, 15.5), 235 (100); HRMS Calcd for $C_{21}H_{26}O_3$ (M^+): 326.1882; Found: 326.1884.

4.6 Synthesis of (*E*)-3-propyl-4-(4-oxopentadec-2-en-2-yl)-2(*5H*)-furanone (*E*)-**4ab**. (fjj-2-160)



Following **Typical Procedure**, the reaction of **1a** (126.0 mg, 1.0 mmol), **2b** (315.7 mg, 1.5 mmol), and $[Cp^*RhCl_2]_2$ (31.0 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded (*E*)-**4ab** (200.5 mg, 58%) as an oil [eluent: petroleum ether/ethyl acetate = 25/1 (500 mL) to 15/1 (800 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.27 (s, 1 H, =CH), 4.85 (s, 2 H, OCH_2), 2.53 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.42 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.36 (s, 3 H, CH_3), 1.70-1.50 (m, 4 H, CH_2 × 2), 1.39-1.17 (m, 16 H, CH_2 × 8), 0.97 (t, *J* = 7.4 Hz, 3 H, CH_3), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.0, 174.1, 156.8, 143.4, 130.1, 127.0, 70.1, 44.9, 31.7, 29.4, 29.31, 29.28, 29.2, 29.0, 26.7, 23.9, 22.5, 21.6, 17.4, 14.0; IR (neat) *v* (cm^{-1}) 2959, 2926, 2854, 1753, 1690, 1591, 1456, 1371, 1348, 1124, 1103, 1070, 1040; MS (EI): *m/z* (%) 348 (M^+, 4.0), 165 (100); HRMS Calcd for $C_{22}H_{36}O_3$ (M^+): 348.2664; Found: 348.2664.

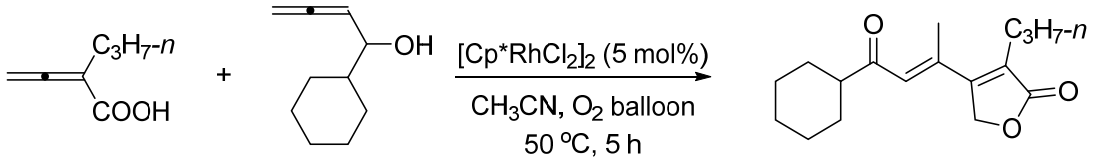
4.7 Synthesis of (*E*)-3-propyl-4-(9-chloro-4-oxonon-2-en-2-yl)-2(5*H*)-furanone (*E*)-**4ac**. (fjj-2-133)



Following **Typical Procedure**, the reaction of **1a** (63.1 mg, 0.5 mmol), **2c** (130.1 mg, 0.75 mmol), and $[Cp^*RhCl_2]_2$ (15.6 mg, 0.025 mmol) in CH_3CN (1.35 mL) afforded (*E*)-**4ac** (82.9 mg, 55%) as an oil [eluent: petroleum ether/ethyl acetate = 20/1

(500 mL) to 10/1 (1000 mL), then 5/1 (300 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.24 (s, 1 H, =CH), 4.84 (s, 2 H, OCH_2), 3.56 (t, *J* = 6.6 Hz, 2 H, CH_2Cl), 2.57 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.42 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.36 (s, 3 H, CH_3), 1.87-1.73 (m, 2 H, CH_2), 1.72-1.41 (m, 6 H, $CH_2 \times 3$), 0.97 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.4, 174.2, 156.7, 143.9, 130.4, 126.9, 70.1, 44.7, 44.6, 32.2, 26.8, 26.3, 23.0, 21.7, 17.5, 14.1; IR (neat) *v* (cm^{-1}) 2963, 2935, 2869, 1753, 1684, 1591, 1455, 1348, 1102, 1070, 1040; MS (EI): *m/z* (%) 300 [M(^{37}Cl)$^+$, 0.8], 298 [M(^{35}Cl)$^+$, 2.1], 165 (100); HRMS Calcd for $C_{16}H_{23}O_3{}^{35}Cl$ (M^+): 298.1336; Found: 298.1337.

4.8 Synthesis of (*E*)-3-propyl-4-(4-oxo-4-cyclohexylbut-2-en-2-yl)-2(*5H*)-furanone (*E*)-**4ad**. (fjj-2-067)

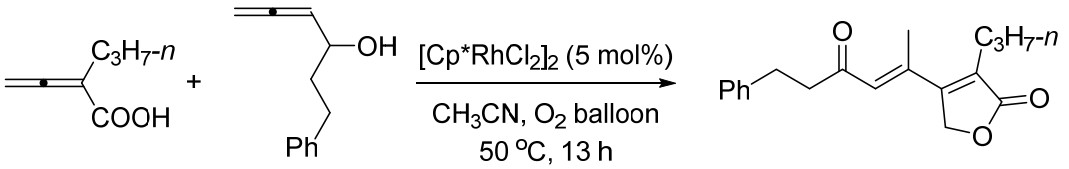


1a **2d**, 1.5 equiv (*E*)-**4ad**, 40%

Following **Typical Procedure**, the reaction of **1a** (126.3 mg, 1.0 mmol), **2d** (228.4 mg, 1.5 mmol), and $[Cp^*RhCl_2]_2$ (31.0 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded (*E*)-**4ad** (115.5 mg, 40%, purity: 95%) as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (500 mL) to 15/1 (1000 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.31 (s, 1 H, =CH), 4.84 (s, 2 H, OCH_2), 2.52-2.11 (m, 6 H, CH, CH_2 and CH_3), 1.97-1.47 (m, 8 H, $CH_2 \times 4$), 1.47-1.15 (m, 4 H, $CH_2 \times 2$), 0.97 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.9, 174.2, 157.0, 143.8, 130.0, 126.5, 70.2, 52.0, 28.3, 26.8, 25.7, 25.5, 21.7, 17.5, 14.0; IR (neat) *v* (cm^{-1}) 2931, 2855, 1755, 1683, 1590, 1450, 1347, 1146, 1038; MS (EI): *m/z* (%) 276 (M^+, 7.4), 83 (100); HRMS Calcd for $C_{17}H_{24}O_3$ (M^+):

276.1725; Found: 276.1724.

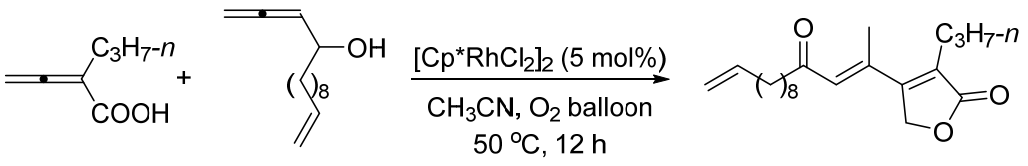
4.9 Synthesis of (*E*)-3-propyl-4-(4-oxo-6-phenylhex-2-en-2-yl)-2(5*H*)-furanone (*E*)-**4ae**. (fjj-3-019)



1a **2e**, 1.5 equiv (*E*)-**4ae**, 49%

Following **Typical Procedure**, the reaction of **1a** (127.0 mg, 1.0 mmol), **2e** (260.3 mg, 1.5 mmol), and $[Cp^*RhCl_2]_2$ (31.1 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded (*E*)-**4ae** (147.2 mg, 49%) as an oil [eluent: petroleum ether/ethyl acetate = 15/1 (500 mL) to 10/1 (1000 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.09 (m, 5 H, ArH), 6.19 (s, 1 H, =CH), 4.77 (s, 2 H, OCH_2), 3.04-2.76 (m, 4 H, CH_2 × 2), 2.47-2.22 (m, 5 H, CH_2 and CH_3), 1.66-1.44 (m, 2 H, CH_2), 0.95 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 174.0, 156.5, 143.6, 140.4, 130.1, 128.2, 128.0, 126.8, 125.9, 69.9, 46.0, 29.6, 26.5, 21.4, 17.3, 13.8; IR (neat) ν (cm^{-1}) 3062, 3027, 2962, 2931, 2873, 1753, 1689, 1588, 1497, 1454, 1348, 1197, 1095, 1072, 1041; MS (EI): *m/z* (%) 298 (M^+, 2.2), 91 (100); HRMS Calcd for $C_{19}H_{22}O_3$ (M^+): 298.1569; Found: 298.1570.

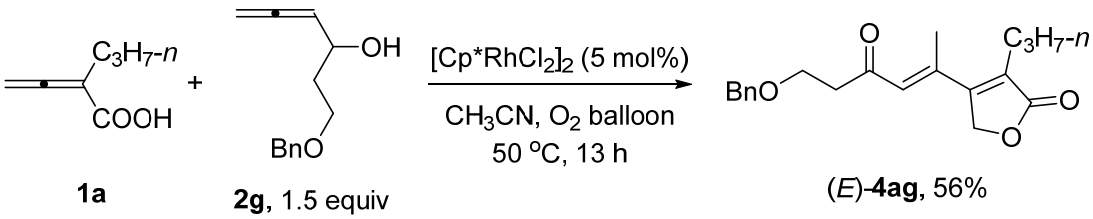
4.10 Synthesis of (*E*)-3-propyl-4-(4-oxotetradeca-2,13-dien-2-yl)-2(5*H*)-furanone (*E*)-**4af**. (fjj-2-188)



1a **2f**, 1.5 equiv (*E*)-**4af**, 49%

Following **Typical Procedure**, the reaction of **1a** (126.2 mg, 1.0 mmol), **2f** (313.0 mg, 1.5 mmol), and $[Cp^*RhCl_2]_2$ (30.9 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded (*E*)-**4af** (164.3 mg, 49%) as an oil [eluent: petroleum ether/ethyl acetate = 25/1 (500 mL) to 20/1 (1000 mL), then 10/1 (500 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.24 (s, 1 H, =CH), 5.90-5.70 (m, 1 H, =CH), 5.06-4.87 (m, 2 H, $=CH_2$), 4.84 (s, 2 H, OCH_2), 2.52 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.42 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.35 (s, 3 H, CH_3), 2.04 (q, *J* = 6.6 Hz, 2 H, CH_2), 1.70-1.48 (m, 4 H, $CH_2 \times 2$), 1.44-1.22 (m, 10 H, $CH_2 \times 5$), 0.97 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 174.2, 156.8, 143.6, 139.1, 130.3, 127.1, 114.1, 70.2, 44.9, 33.7, 29.3, 29.2, 29.1, 29.0, 28.8, 26.8, 24.0, 21.7, 17.5, 14.1; IR (neat) *v* (cm^{-1}) 3076, 2928, 2855, 1755, 1689, 1590, 1456, 1348, 1103, 1072, 1041; MS (EI): *m/z* (%) 332 (M^+, 3.2), 165 (100); HRMS Calcd for $C_{21}H_{32}O_3Na$ $(M+Na)^+$: 355.2244; Found: 355.2246.

4.11 Synthesis of (*E*)-3-propyl-4-(6-(benzyloxy)-4-oxohex-2-en-2-yl)-2(5*H*)-furanone (*E*)-**4ag**. (fjj-2-194)

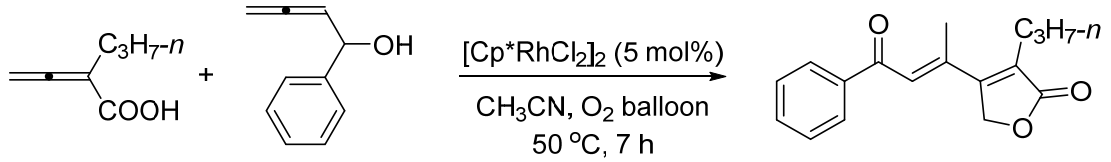


1a **2g**, 1.5 equiv (*E*)-**4ag**, 56%

Following **Typical Procedure**, the reaction of **1a** (126.2 mg, 1.0 mmol), **2g** (316.3 mg, 1.5 mmol), and $[Cp^*RhCl_2]_2$ (30.9 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded (*E*)-**4ag** (183.0 mg, 56%) as an oil [eluent: petroleum ether/ethyl acetate = 10/1 (1000 mL) to 8/1 (500 mL), then 5/1 (500 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.05 (m,

5 H, ArH), 6.27 (s, 1 H, =CH), 4.77 (s, 2 H, OCH_2), 4.52 (s, 2 H, CH_2 of Bn), 3.79 (t, *J* = 6.0 Hz, 2 H, OCH_2), 2.81 (t, *J* = 6.0 Hz, 2 H, CH_2), 2.45-2.27 (m, 5 H, CH_2 and CH_3), 1.62-1.47 (m, 2 H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.8, 174.1, 156.5, 143.9, 137.8, 130.3, 128.2, 127.6, 127.5, 127.0, 73.1, 70.0, 65.2, 44.7, 26.6, 21.5, 17.4, 13.9; IR (neat) *v* (cm^{-1}) 3030, 2962, 2920, 2872, 1748, 1689, 1590, 1496, 1452, 1362, 1199, 1102; MS (EI): *m/z* (%) 328 (M^+, 0.8), 91 (100); HRMS Calcd for $C_{20}H_{24}O_4$ (M^+): 328.1675; Found: 328.1676.

4.12 Synthesis of (*E*)-3-propyl-4-(4-oxo-4-phenylbut-2-en-2-yl)-2(*5H*)-furanone (*E*)-**4ah**. (fjj-2-161, fjj-5-027)

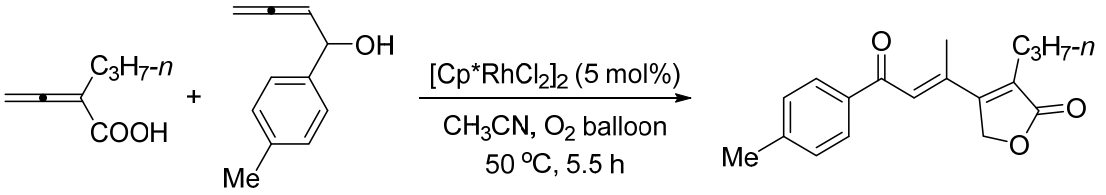


1a **2h**, 1.5 equiv (*E*)-**4ah**, 66%

Following **Typical Procedure**, the reaction of **1a** (63.1 mg, 0.5 mmol), **2h** (109.9 mg, 0.75 mmol), and $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol) in CH_3CN (1.35 mL) afforded (*E*)-**4ah** as an oil (89.7 mg, 66%) [eluent: petroleum ether/ethyl acetate = 25/1 (500 mL) to 15/1 (1000 mL)]. ^1H NMR (300 MHz, $CDCl_3$) δ 8.0-7.85 (m, 2 H, ArH), 7.61 (t, *J* = 7.4 Hz, 1 H, ArH), 7.51 (t, *J* = 7.5 Hz, 2 H, ArH), 6.91 (s, 1 H, =CH), 4.92 (s, 2 H, OCH_2), 2.50 (t, *J* = 8.0 Hz, 2 H, CH_2), 2.37 (s, 3 H, CH_3), 1.74-1.51 (m, 2 H, CH_2), 1.00 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 174.2, 156.7, 144.2, 137.9, 133.2, 129.9, 128.6, 128.1, 125.6, 70.1, 26.8, 21.7, 17.8, 14.0; IR (neat) *v* (cm^{-1}) 3058, 2962, 2932, 2873, 1748, 1659, 1599, 1444, 1348, 1255, 1227, 1190, 1102, 1068, 1038; MS (EI): *m/z* (%) 270 (M^+, 6.4), 105 (100); HRMS Calcd for $C_{17}H_{18}O_3$

(M^+): 270.1256; Found: 270.1255.

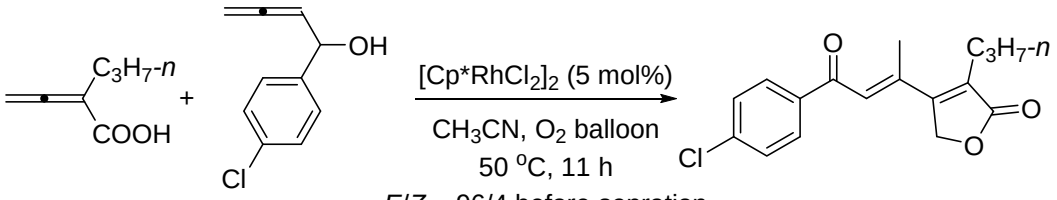
4.13 Synthesis of (*E*)-3-propyl-4-(4-oxo-4-(*p*-tolyl)but-2-en-2-yl)-2(5*H*)-furanone (*E*)-**4ai**. (fjj-2-064)



1a **2i**, 1.5 equiv (*E*)-**4ai**, 56%

Following **Typical Procedure**, the reaction of **1a** (126.0 mg, 1.0 mmol), **2i** (240.3 mg, 1.5 mmol), and $[Cp^*RhCl_2]_2$ (31.2 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded (*E*)-**4ai** (158.0 mg, 56%) as a solid [eluent: petroleum ether/ethyl acetate = 15/1 (500 mL) to 10/1 (500 mL)]: m.p. 64.9-66.7 °C (Et_2O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2 H, ArH), 7.30 (d, *J* = 8.4 Hz, 2 H, ArH), 6.90 (s, 1 H, =CH), 4.92 (s, 2 H, OCH_2), 2.55-2.40 (m, 5 H, CH_2 and CH_3), 2.35 (s, 3 H, CH_3), 1.71-1.53 (m, 2 H, CH_2), 1.00 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 174.3, 156.9, 144.3, 143.6, 135.6, 129.9, 129.4, 128.4, 126.0, 70.2, 26.9, 21.8, 21.6, 17.8, 14.1; IR (neat) *v* (cm^{-1}) 2960, 2929, 2872, 1740, 1653, 1607, 1517, 1445, 1427, 1366, 1354, 1329, 1257, 1233, 1188, 1102, 1068, 1028; MS (EI): *m/z* (%) 284 (M^+, 4.3), 119 (100); Anal. Calcd. for $C_{18}H_{20}O_3$ (%): C, 76.03; H, 7.09; Found: C, 76.23; H, 7.06.

4.14 Synthesis of (*E*)-3-propyl-4-(4-(4-chlorophenyl)-4-oxobut-2-en-2-yl)-2(5*H*)-furanone (*E*)-**4aj**. (fjj-2-170)



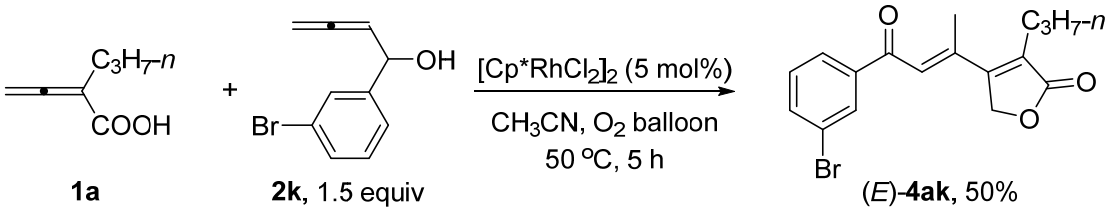
1a **2j**, 1.5 equiv *E*/*Z* = 96/4 before sepration (*E*)-**4aj**, 57% *E*/*Z* = 94/6

Following **Typical Procedure**, the reaction of **1a** (126.1 mg, 1.0 mmol), **2j** (270.8 mg, 1.5 mmol), and $[Cp^*RhCl_2]_2$ (31.0 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded (*E*)-**4aj** as a solid (172.8 mg, 57%, *E*/*Z* = 96/4 according to the ^1H NMR spectrum of the crude product, *E*/*Z* = 94/6 after being purified via chromatography on silica gel) [eluent: petroleum ether/ethyl acetate = 25/1 (500 mL) to 20/1 (500 mL), then 15/1 (1200 mL)]: ^1H NMR (300 MHz, $CDCl_3$) 7.88 (d, *J* = 8.1 Hz, 2 H, ArH), 7.48 (d, *J* = 8.1 Hz, 2 H, ArH), 6.89 (s, 1 H, =CH), 4.94 (s, 2 H, OCH_2), 2.46 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.39 (s, 3 H, CH_3), 1.75-1.51 (m, 2 H, CH_2), 1.00 (t, *J* = 7.2 Hz, 3 H, CH_3); the following signals are disscernible for (*Z*)-**4aj**: δ 7.01 (s, 1 H, =CH), 4.86 (s, 2 H, OCH_2), 2.20 (s, 3 H, CH_3), 2.17-2.06 (m, 2 H, CH_2), 1.50-1.39 (m, 2 H, CH_2), 0.80 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.7, 174.1, 156.6, 145.1, 139.7, 136.4, 130.3, 129.6, 129.0, 125.0, 70.2, 26.8, 21.7, 18.0, 14.1.

The *E*/*Z* mixture recrystallized affording purified (*E*)-**4aj** (120.3 mg): solid, m.p. 78.8-79.6 °C (Et_2O/*n*-hexane); ^1H NMR (300 MHz, $CDCl_3$) 7.88 (d, *J* = 8.1 Hz, 2 H, ArH), 7.48 (d, *J* = 8.1 Hz, 2 H, ArH), 6.88 (s, 1 H, =CH), 4.93 (s, 2 H, OCH_2), 2.49 (t, *J* = 7.5 Hz, 2 H, CH_2), 2.38 (s, 3 H, CH_3), 1.75-1.51 (m, 2 H, CH_2), 1.00 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.8, 174.1, 156.6, 145.2, 139.8, 136.4, 130.4, 129.6, 129.1, 125.0, 70.2, 26.9, 21.8, 18.0, 14.1; IR (neat) *v* (cm^{-1}) 3090, 3062, 2967, 2933, 1739, 1656, 1588, 1459, 1420, 1253, 1226, 1195, 1106, 1089, 1031, 1007;

MS (EI): *m/z* (%) 306 [M(^{37}Cl)$^+$, 1.5], 304 [M(^{35}Cl)$^+$, 4.2], 139 (100); Anal. Calcd. for $C_{17}H_{17}ClO_3$ (%): C, 67.00; H, 5.62; Found: C, 66.85; H, 5.69.

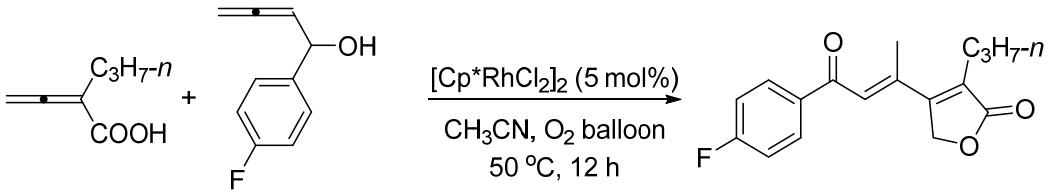
4.15 Synthesis of (*E*)-3-propyl-4-(4-(3-bromophenyl)-4-oxobut-2-en-2-yl)-2(5*H*)-furanone (*E*)-**4ak**. (fjj-2-093)



Following **Typical Procedure**, the reaction of **1a** (63.1 mg, 0.5 mmol), **2k** (169.0 mg, 0.75 mmol), and $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol) in CH_3CN (1.35 mL) afforded (*E*)-**4ak** (87.9 mg, 50%) as an oil [eluent: petroleum ether/Et_2O = 5/1 (500 mL) to 4/1 (1000 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (s, 1 H, ArH), 7.84 (d, *J* = 7.2 Hz, 1 H, ArH), 7.73 (d, *J* = 8.1 Hz, 1 H, ArH), 7.39 (t, *J* = 7.8 Hz, 1 H, ArH), 6.85 (s, 1 H, =CH), 4.92 (s, 2 H, OCH_2), 2.49 (t, *J* = 8.0 Hz, 2 H, CH_2), 2.38 (s, 3 H, CH_3), 1.71-1.56 (m, 2 H, CH_2), 1.01 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 174.1, 156.5, 145.7, 139.8, 136.1, 131.2, 130.5, 130.3, 126.7, 124.8, 123.1, 70.2, 26.9, 21.8, 18.0, 14.1; IR (neat) *v* (cm^{-1}) 3064, 2962, 2931, 2872, 1755, 1662, 1594, 1565, 1431, 1251, 1222, 1188, 1102, 1069, 1038; MS (EI): *m/z* (%) 350 [M(^{81}Br)$^+$, 6.0], 348 [M(^{79}Br)$^+$, 6.2], 183 (100); HRMS Calcd for $C_{17}H_{17}O_3{}^{79}Br$ (M^+): 348.0361; Found: 348.0363.

4.16 Synthesis of (*E*)-3-propyl-4-(4-(4-fluorophenyl)-4-oxobut-2-en-2-yl)-2(5*H*)-

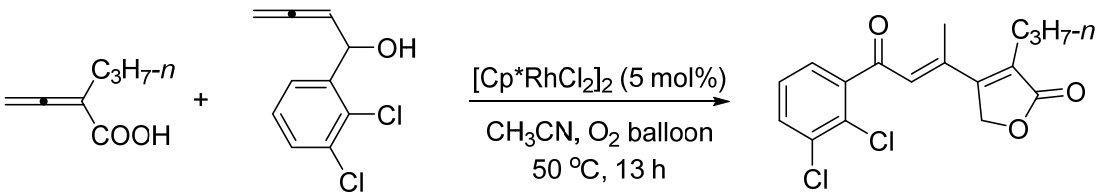
furanone (*E*)-**4al**. (fjj-2-195)



1a **2l**, 1.5 equiv (*E*)-**4al**, 56%

Following **Typical Procedure**, the reaction of **1a** (126.0 mg, 1.0 mmol), **2l** (246.2 mg, 1.5 mmol), and $[Cp^*RhCl_2]_2$ (31.0 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded (*E*)-**4al** (160.9 mg, 56%) as a solid [eluent: petroleum ether/ethyl acetate = 10/1 (500 mL) to 8/1 (500 mL)]: m.p. 59.6-60.1 °C (Et_2O/*n*-hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 8.07-7.84 (m, 2 H, ArH), 7.18 (t, *J* = 8.6 Hz, 2 H, ArH), 6.89 (s, 1 H, =CH), 4.93 (s, 2 H, OCH_2), 2.49 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.38 (s, 3 H, CH_3), 1.74-1.50 (m, 2 H, CH_2), 1.00 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 174.2, 165.8 (d, *J* = 254.4 Hz), 156.6, 144.6, 134.5 (d, *J* = 3.5 Hz), 130.9 (d, *J* = 9.6 Hz), 130.2, 125.3, 115.9 (d, *J* = 21.4 Hz), 70.2, 26.9, 21.8, 18.0, 14.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ 104.7; IR (neat) *v* (cm^{-1}) 3074, 2963, 2929, 2874, 1753, 1661, 1594, 1506, 1453, 1227, 1189, 1157, 1036; MS (EI): *m/z* (%) 288 (M^+, 3.4), 123 (100); Anal. Calcd. for $C_{17}H_{17}FO_3$ (%): C, 70.82; H, 5.94; Found: C, 70.75; H, 6.05.

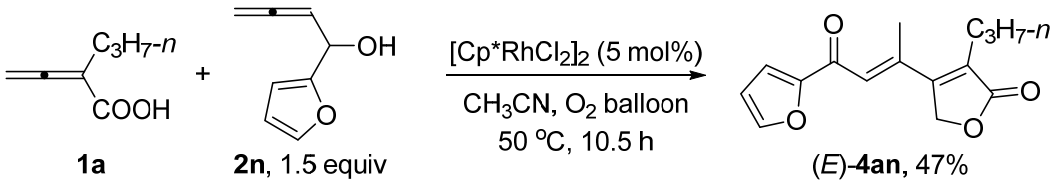
4.17 Synthesis of (*E*)-3-propyl-4-(4-(2,3-dichlorophenyl)-4-oxobut-2-en-2-yl)-2(*5H*)-furanone (*E*)-**4am**. (fjj-3-018)



1a **2m**, 1.5 equiv (*E*)-**4am**, 43%
E/*Z* = 97/3

Following **Typical Procedure**, the reaction of **1a** (126.1 mg, 1.0 mmol), **2m** (322.1 mg, 1.5 mmol), and $[Cp^*RhCl_2]_2$ (30.9 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded (*E*)-**4am** (146.5 mg, 43%, *E*/*Z* = 98/2 according to the ^1H NMR spectrum of the crude product, *E*/*Z* = 97/3 after being purified via chromatography on silica gel) as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (500 mL) to 15/1 (1000 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 1 H, ArH), 7.46 (d, J = 2.1 Hz, 1 H, ArH), 7.37 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1 H, ArH), 6.68 (s, 1 H, =CH), 4.90 (s, 2 H, OCH_2), 2.54-2.36 (m, 5 H, CH_2 and CH_3), 1.67-1.50 (m, 2 H, CH_2), 0.97 (t, J = 7.4 Hz, 3 H, CH_3); the following signals are disscernible for (*Z*)-**4am**: δ 6.76 (s, 1 H, =CH), 4.86 (s, 2 H, OCH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 174.0, 156.1, 145.8, 137.8, 137.7, 132.1, 131.0, 130.9, 130.2, 127.6, 127.2, 70.0, 26.8, 21.7, 18.0, 14.0; IR (neat) ν (cm^{-1}) 3087, 2963, 2932, 2873, 1748, 1668, 1584, 1457, 1374, 1261, 1218, 1188, 1103, 1074, 1031; MS (EI): *m/z* (%) 342 [($M(^{37}Cl^{37}Cl)^+$, 0.8], 340 [($M^{37}Cl^{35}Cl)^+$, 3.8], 338 [$M(^{35}Cl^{35}Cl)^+$, 5.0], 173 (100); HRMS Calcd for $C_{17}H_{16}O_3{}^{35}Cl^{35}Cl$ (M^+): 338.0477; Found: 338.0475.

4.18 Synthesis of (*E*)-4-(4-(furan-2-yl)-4-oxobut-2-en-2-yl)-3-propylfuran-2(5*H*)-one (*E*)-**4an**. (fjj-2-186)

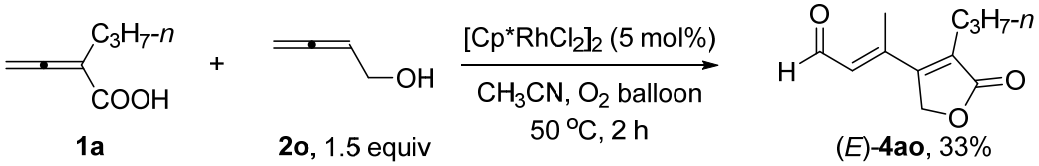


1a **2n**, 1.5 equiv (*E*)-**4an**, 47%

Following **Typical Procedure**, the reaction of **1a** (125.9 mg, 1.0 mmol), **2n** (204.5 mg, 1.5 mmol), and $[Cp^*RhCl_2]_2$ (30.9 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded

(*E*)-**4an** (122.1 mg, 47%) as a solid [eluent: petroleum ether/ethyl acetate = 15/1 (500 mL) to 10/1 (500 mL), then 8/1 (1000 mL)]: m.p. 76.8-77.8 °C (Et_2O/*n*-hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (s, 1 H, ArH), 7.26 (d, *J* = 3.3 Hz, 1 H, ArH), 6.92 (s, 1 H, =CH), 6.64-6.52 (m, 1 H, ArH), 4.92 (s, 2 H, OCH_2), 2.57-2.33 (m, 5 H, CH_2 and CH_3), 1.71-1.54 (m, 2 H, CH_2), 1.00 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.5, 174.2, 156.8, 154.0, 146.5, 146.0, 130.5, 123.7, 117.4, 112.7, 70.2, 26.9, 21.7, 17.8, 14.1; IR (neat) *v* (cm^{-1}) 3137, 3114, 2958, 2932, 2873, 1747, 1647, 1605, 1567, 1467, 1338, 1266, 1200, 1161, 1101, 1014; MS (EI): *m/z* (%) 260 (M^+, 7.1), 95 (100); Anal. Calcd. for $C_{15}H_{16}O_4$ (%): C, 69.22; H, 6.20; Found: C, 69.08; H, 6.29.

4.19 Synthesis of (*E*)-3-propyl-4-(4-oxobutan-2-en-2-yl)-2(*5H*)-furanone (*E*)-**4ao**. (fjj-3-078)

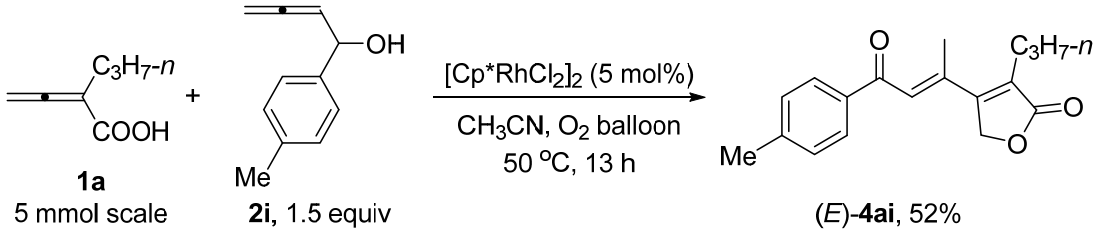


Following **Typical Procedure**, the reaction of **1a** (126.1 mg, 1.0 mmol), **2o** (105.5 mg, 0.75 mmol), and $[Cp^*RhCl_2]_2$ (31.0 mg, 0.05 mmol) in CH_3CN (2.7 mL) afforded (*E*)-**4ao** (64.1 mg, 33%) as an oil [eluent: petroleum ether/ethyl acetate = 4/1 (1000 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 10.18 (d, *J* = 7.5 Hz, 1 H, CHO), 6.07 (dd, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1 H, =CH), 4.89 (s, 2 H, OCH_2), 2.54-2.38 (m, 5 H, CH_2 and CH_3), 1.66-1.51 (m, 2 H, CH_2), 0.99 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.1, 173.8, 154.7, 147.7, 132.0, 129.8, 69.8, 26.9, 21.7, 16.0, 14.0; IR (neat) *v* (cm^{-1}) 2963, 2934, 2873, 1755, 1671, 1455, 1380, 1349, 1197, 1115, 1042; MS (EI): *m/z* (%)

194 (M^+, 3.2), 165 (100); HRMS Calcd for $C_{11}H_{14}O_3$ (M^+): 194.0943; Found: 194.0946.

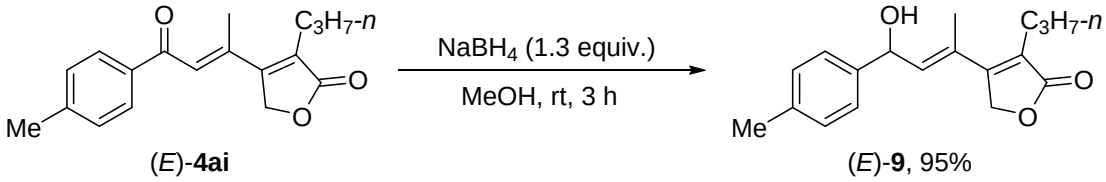
5. 5 mmol Scale Reaction and Transformation

5.1 5 mmol scale reaction for synthesis of (*E*)-**4ai**. (fjj-2-073)



Following **Typical Procedure**, the reaction of **1a** (630.5 mg, 5.0 mmol), **2i** (1200.3 mg, 7.5 mmol), and $[Cp^*RhCl_2]_2$ (153.9 mg, 0.25 mmol) in CH_3CN (13.5 mL) afforded (*E*)-**4ai** (742.6 mg, 52%) as a solid [eluent: petroleum ether/ethyl acetate = 10/1 (1500 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2 H, ArH), 7.30 (d, *J* = 8.1 Hz, 2 H, ArH), 6.89 (s, 1 H, =CH), 4.91 (s, 2 H, OCH_2), 2.49 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.44 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 1.71-1.53 (m, 2 H, CH_2), 1.00 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 156.9, 144.4, 143.6, 135.6, 130.0, 129.5, 128.4, 126.0, 70.3, 26.9, 21.8, 21.6, 17.9, 14.1.

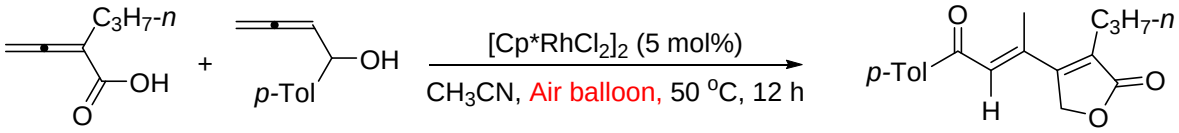
5.2 Preparation of (*E*)-**9**. (fjj-3-095)



To a dry Schlenk tube were added (*E*)-**4ai** (28.3 mg, 0.1 mmol), MeOH (1 mL) and $NaBH_4$ (5.1 mg, 0.13 mmol) sequentially. After being continuously stirred at room temperature for 3 h, the reaction was complete as monitored by thin layer chromatography (TLC). The mixture was concentrated in vacuo and the crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate =

5/1 (500 mL)] to afford (*E*)-**9** as an oil (27.0 mg, 95%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.8 Hz, 2 H, ArH), 7.18 (d, *J* = 7.5 Hz, 2 H, ArH), 5.90 (d, *J* = 8.1 Hz, 1 H, =CH), 5.56 (d, *J* = 8.1 Hz, 1 H, OCH), 4.77 (m, 2 H, OCH_2), 2.49-2.20 (m, 6 H, CH_3, CH_2 and OH), 2.04 (s, 3 H, CH_3), 1.59-1.41 (m, 2 H, CH_2), 0.92 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3, 157.0, 139.6, 137.9, 135.9, 129.5, 128.8, 127.3, 125.9, 70.32, 70.28, 26.6, 22.0, 21.1, 15.8, 14.0; IR (neat) *v* (cm^{-1}) 3430 (OH), 2961, 2929, 2872, 1748, 1512, 1455, 1348, 1194, 1107, 1039; MS (EI): *m/z* (%) 286 (M^+, 6.98), 105 (100); HRMS Calcd for $C_{18}H_{22}O_3$ (M^+): 286.1569; Found: 286.1567.

5.3 Synthesis of (*E*)-**4ai** under air atmosphere. (fjj-4-199)



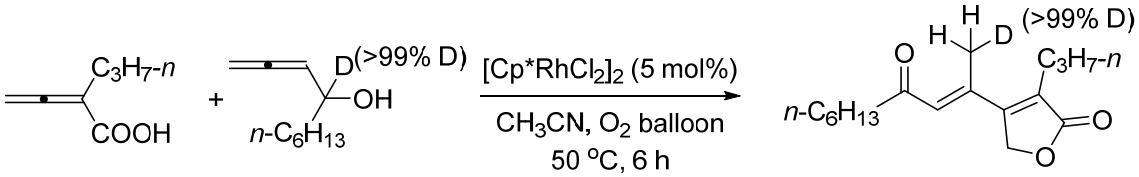
1a, 1 mmol **2i**, 1.5 equiv (*E*)-**4ai**, 54%

To a dry Schlenk tube were added $[Cp^*RhCl_2]_2$ (31.0 mg, 0.05 mmol), **1a** (126.1 mg, 1.0 mmol) and **2i** (240.5 mg, 1.5 mmol) sequentially. The Schlenk tube was degassed under vacuum and backfilled with air three times at room temperature. Then, CH_3CN (2.7 mL) were added under air atmosphere. After being continuously stirred at 50 °C for 13 h, the reaction was complete as monitored by thin layer chromatography (TLC). Then the Air balloon was removed, and the reaction mixture was filtered through a short column of silica gel eluted with ethyl acetate (20 mL × 3). The combined filteration was concentrated in vacuo and the crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ ethyl acetate = 9/1 (1000 mL)] to afford (*E*)-**4ai** as a solid (153.5 mg, 54%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J*

= 8.1 Hz, 2 H, ArH), 7.30 (d, *J* = 8.1 Hz, 2 H, ArH), 6.89 (s, 1 H, =CH), 4.92 (s, 2 H, OCH_2), 2.54-2.41 (m, 5 H, CH_2 and CH_3), 2.35 (s, 3 H, CH_3), 1.72-1.55 (m, 2 H, CH_2), 1.00 (t, *J* = 7.4 Hz, 3 H, CH_3).

6. Mechanistic Studies

The reaction of [D^b]-**2a** and **1a** for the synthesis of [D]-(*E*)-**4aa**. (fjj-2-105)



1a [D^b]-**2a**, 1.5 equiv [D]-(*E*)-**4aa**, 52%

Following **Typical Procedure**, the reaction of **1a** (62.8 mg, 0.5 mmol), [D^b]-**2a** (115.0 mg, 0.75 mmol), and $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol) in CH_3CN (1.35 mL) afforded [D]-(*E*)-**4aa** (71.7 mg, 52%) as an oil [eluent: petroleum ether/ethyl acetate = 10/1 (1000 mL)]: ^1H NMR (300 MHz, $CDCl_3$) 6.24 (d, *J* = 0.9 Hz, 1 H, =CH), 4.84 (s, 2 H, OCH_2), 2.53 (t, *J* = 7.5 Hz, 2 H, CH_2),w 2.42 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.33 (s, 2 H, CH_2D), 1.69-1.49 (m, 4 H, $CH_2 \times 2$), 1.40-1.20 (m, 6 H, $CH_2 \times 3$), 0.97 (t, *J* = 7.4 Hz, 3 H, CH_3), 0.93-0.82 (m, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 174.2, 156.8, 143.4, 130.2, 127.1, 70.1, 44.9, 31.5, 28.7, 26.7, 23.9, 22.4, 21.6, 17.2 (t, *J* = 20.0 Hz), 14.0, 13.9; IR (neat) *v* (cm^{-1}) 2959, 2931, 2872, 1756, 1689, 1589, 1456, 1407, 1349, 1122, 1098, 1072, 1034; MS (EI): *m/z* (%) 279 (M^+, 3.0), 165 (100); HRMS Calcd for $C_{17}H_{25}O_3D$ (M^+): 279.1945; Found: 279.1945.

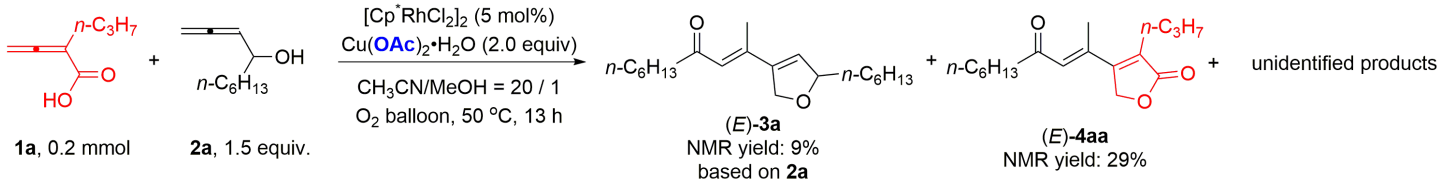
7. References:

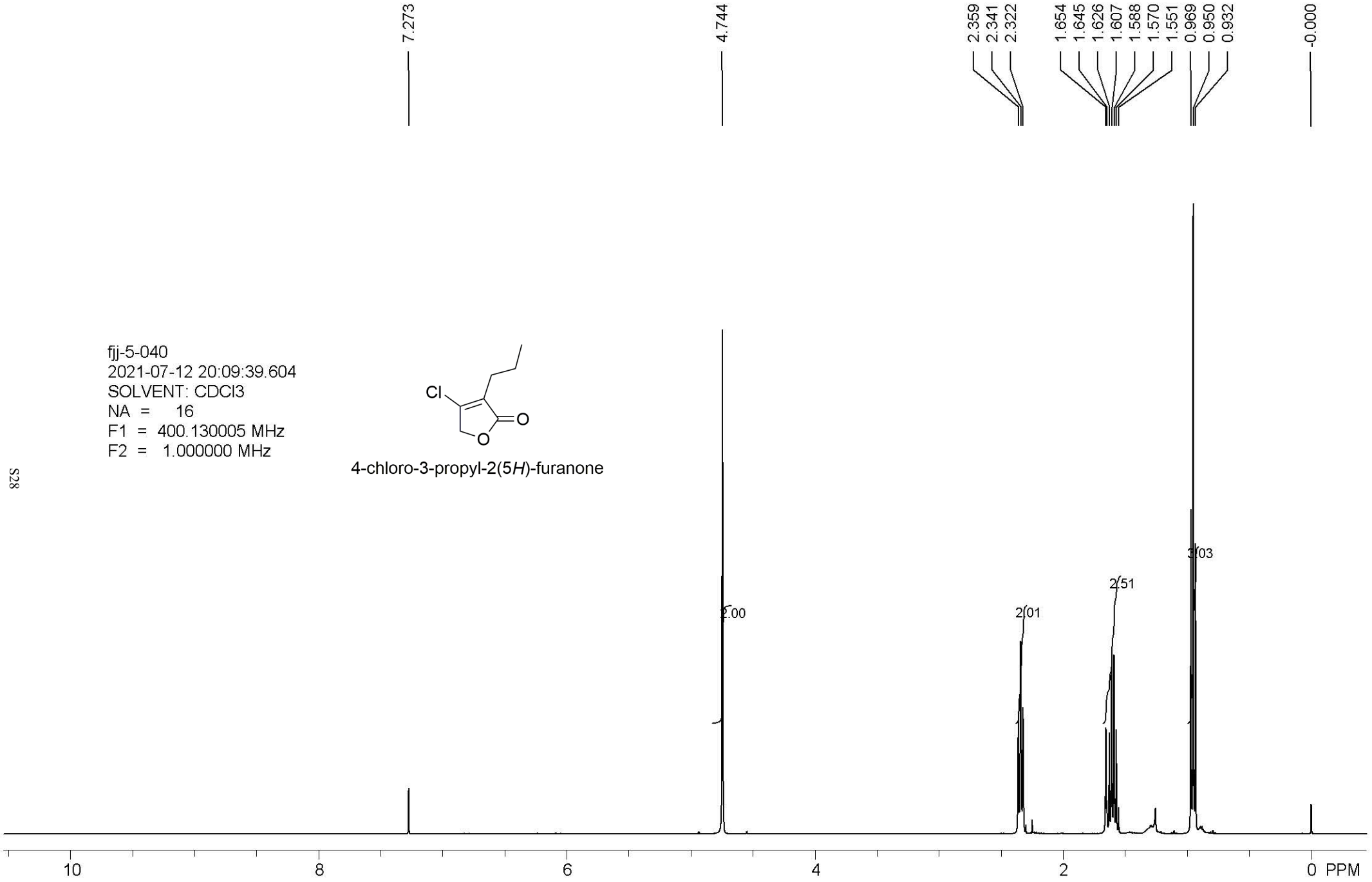
1. Luo, H.; Ma, S. *Eur. J. Org. Chem.* **2013**, 3041.
2. Miao, B.; Li, G.; Ma, S. *Chem. Eur.J.* **2015**, *21*,17224.

3. Castellano, S.; Fiji, H. D. G.; Kinderman, S. S.; Watanabe, M.; de Leon, P.; Tamanoi, F.; Kwon, O. *J. Am. Chem. Soc.* **2007**, *129*, 5843.

8 . ^{1}H NMR, ^{13}C NMR and ^{19}F NMR of the Compounds Prepared.

Spectra of Scheme 2

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2.359
2.341
2.322
1.654
1.645
1.626
1.607
1.588
1.570
1.551
0.969
0.950
0.932
-0.000
fjj-5-040
2021-07-12 20:09:39.604
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F2 = 1.000000 MHz
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O
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S28
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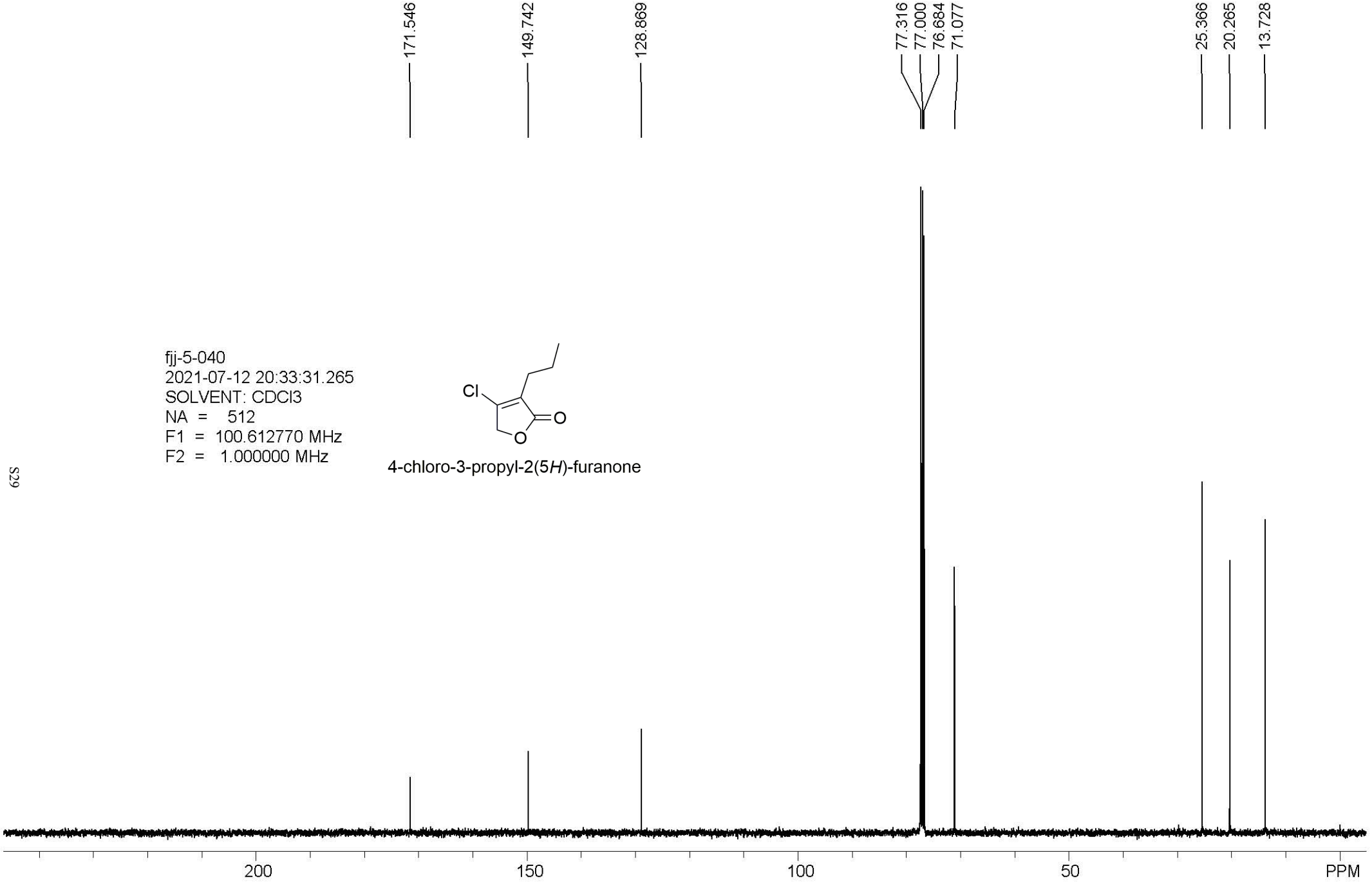
2.01
2.51
3.03
10
8
6
4
2
0 PPM


171.546
149.742
128.869
77.316
77.000
76.684
71.077
25.366
20.265
13.728
fjj-5-040
2021-07-12 20:33:31.265
SOLVENT: CDCl3
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F1 = 100.612770 MHz
F2 = 1.000000 MHz
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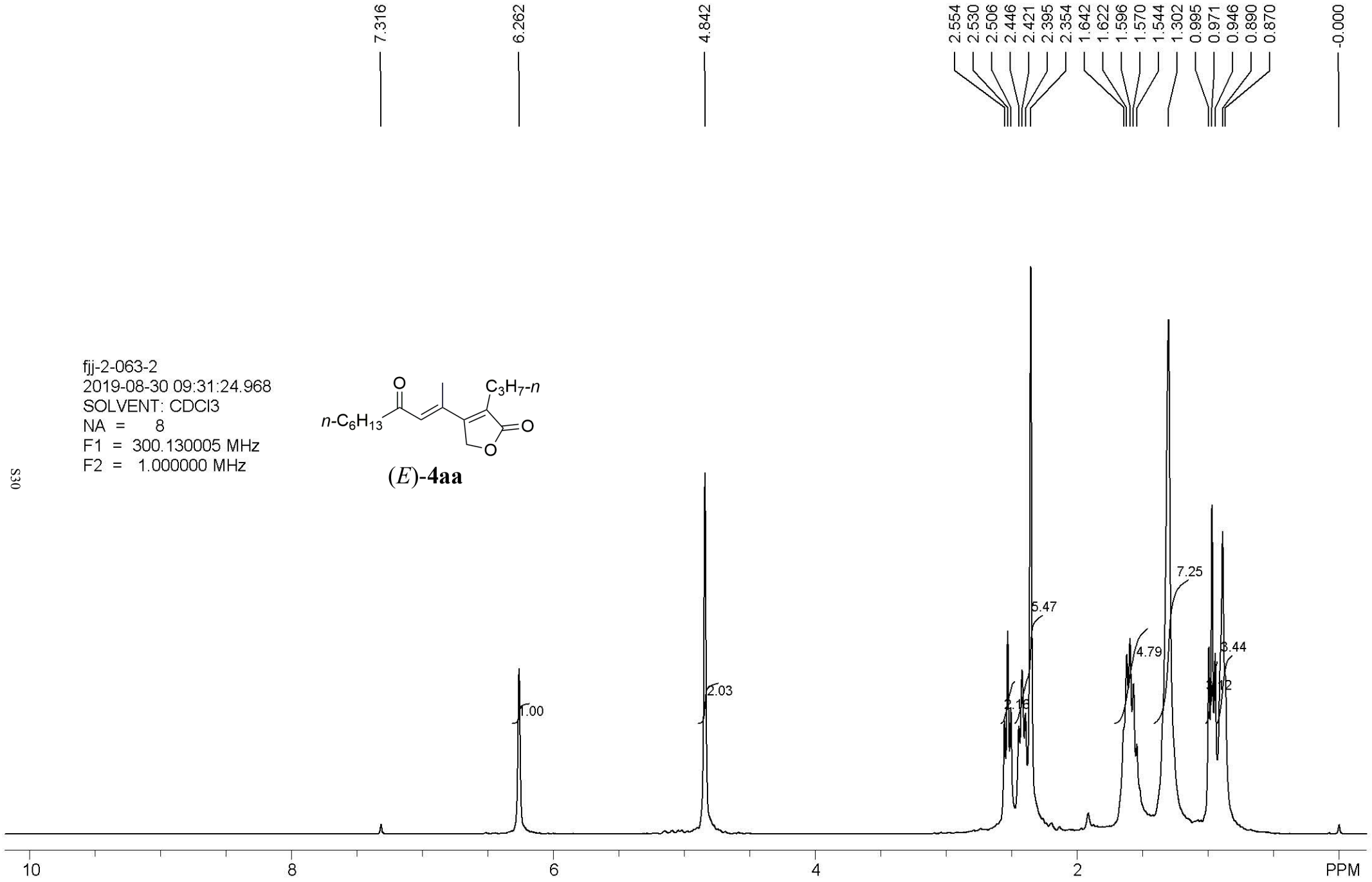
O
4-chloro-3-propyl-2(5H)-furanone
200
150
100
50
PPM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6.262
4.842
2.554
2.530
2.506
2.446
2.421
2.395
2.354
1.642
1.622
1.596
1.570
1.544
1.302
0.995
0.971
0.946
0.890
0.870
-0.000
fjj-2-063-2
2019-08-30 09:31:24.968
SOLVENT: CDCl3
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F1 = 300.130005 MHz
F2 = 1.000000 MHz
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n-C6H13
O
O
(E)-4aa
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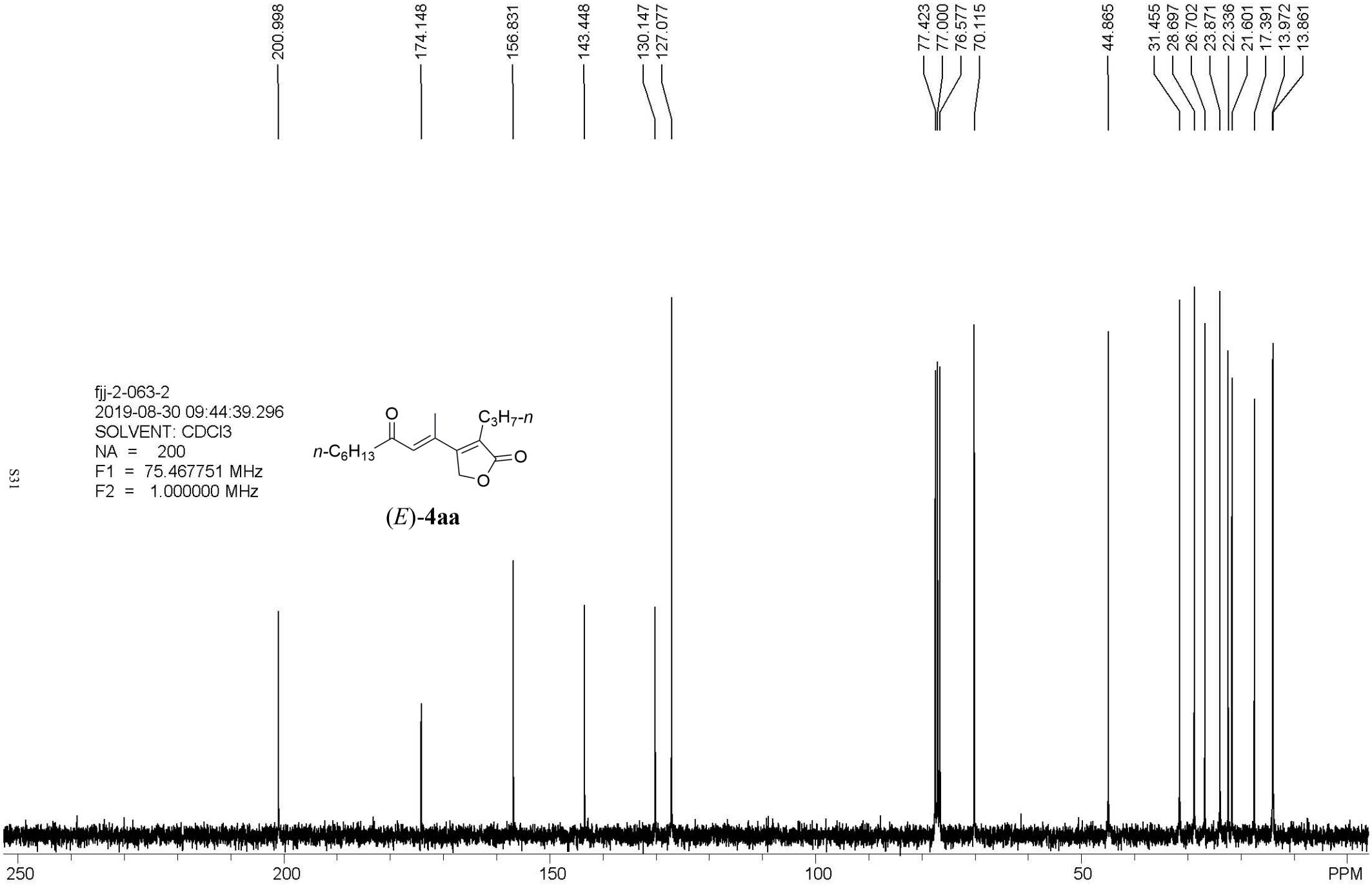
2.03
2.16
5.47
4.79
7.25
3.44
10
8
6
4
2
PPM


200.998
174.148
156.831
143.448
130.147
127.077
77.423
77.000
76.577
70.115
44.865
31.455
28.697
26.702
23.871
22.336
21.601
17.391
13.972
13.861
fjj-2-063-2
2019-08-30 09:44:39.296
SOLVENT: CDCl3
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F1 = 75.467751 MHz
F2 = 1.000000 MHz
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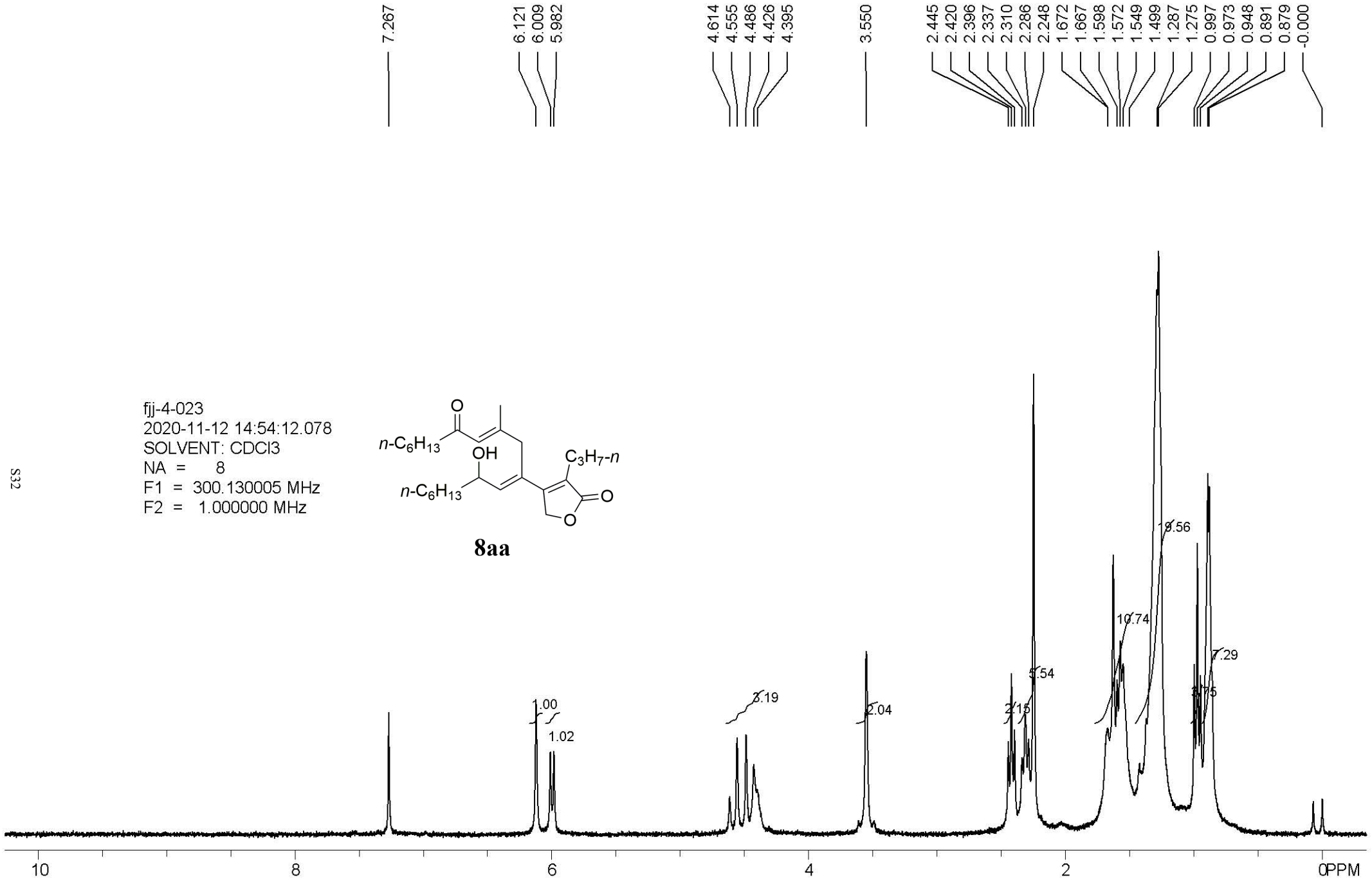
n-C6H13
O
O
250
200
150
100
50
PPM

(*E*)-**4aa**


7.267
6.121
6.009
5.982
4.614
4.555
4.486
4.426
4.395
3.550
2.445
2.420
2.396
2.337
2.310
2.286
2.248
1.672
1.667
1.598
1.572
1.549
1.499
1.287
1.275
0.997
0.973
0.948
0.891
0.879
-0.000
fjj-4-023
2020-11-12 14:54:12.078
SOLVENT: CDCl3
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F1 = 300.130005 MHz
F2 = 1.000000 MHz
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C3H7-n
n-C6H13
O
O
O
8aa
1.00
1.02
3.19
2.04
2.15
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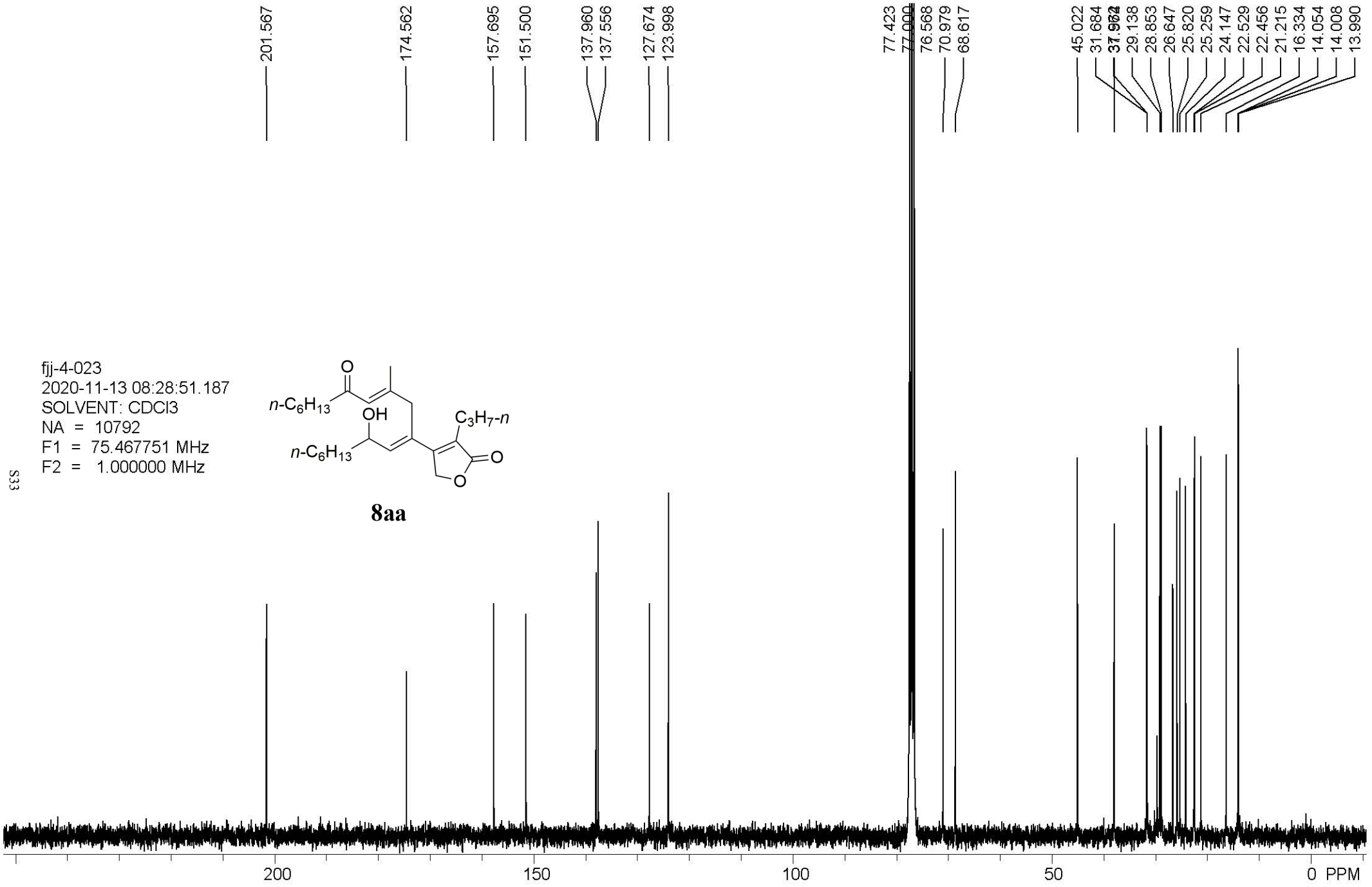
7.29
3.75
10
8
6
4
2
0PPM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70.979
68.617
45.022
31.684
29.138
28.853
26.647
25.820
25.259
24.147
22.529
22.456
21.215
16.334
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14.008
13.990
fjj-4-023
2020-11-13 08:28:51.187
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F2 = 1.000000 MHz
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n-C6H13
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O
O
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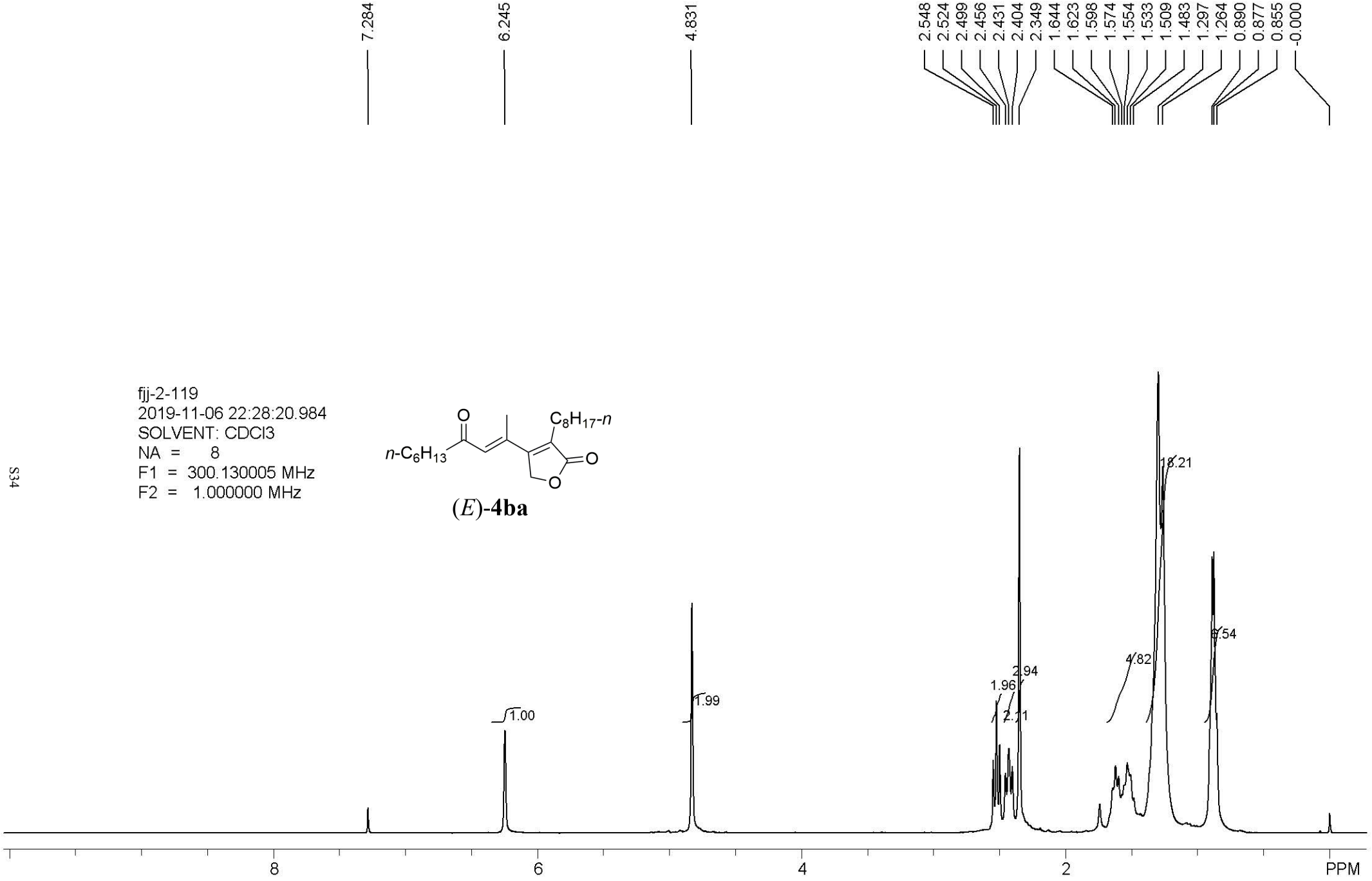
150
100
50
0 PPM

8aa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4.831
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2.524
2.499
2.456
2.431
2.404
2.349
1.644
1.623
1.598
1.574
1.554
1.533
1.509
1.483
1.297
1.264
0.890
0.877
0.855
-0.000
fjj-2-119
2019-11-06 22:28:20.984
SOLVENT: CDCl3
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F1 = 300.130005 MHz
F2 = 1.000000 MHz
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n-C6H13
O
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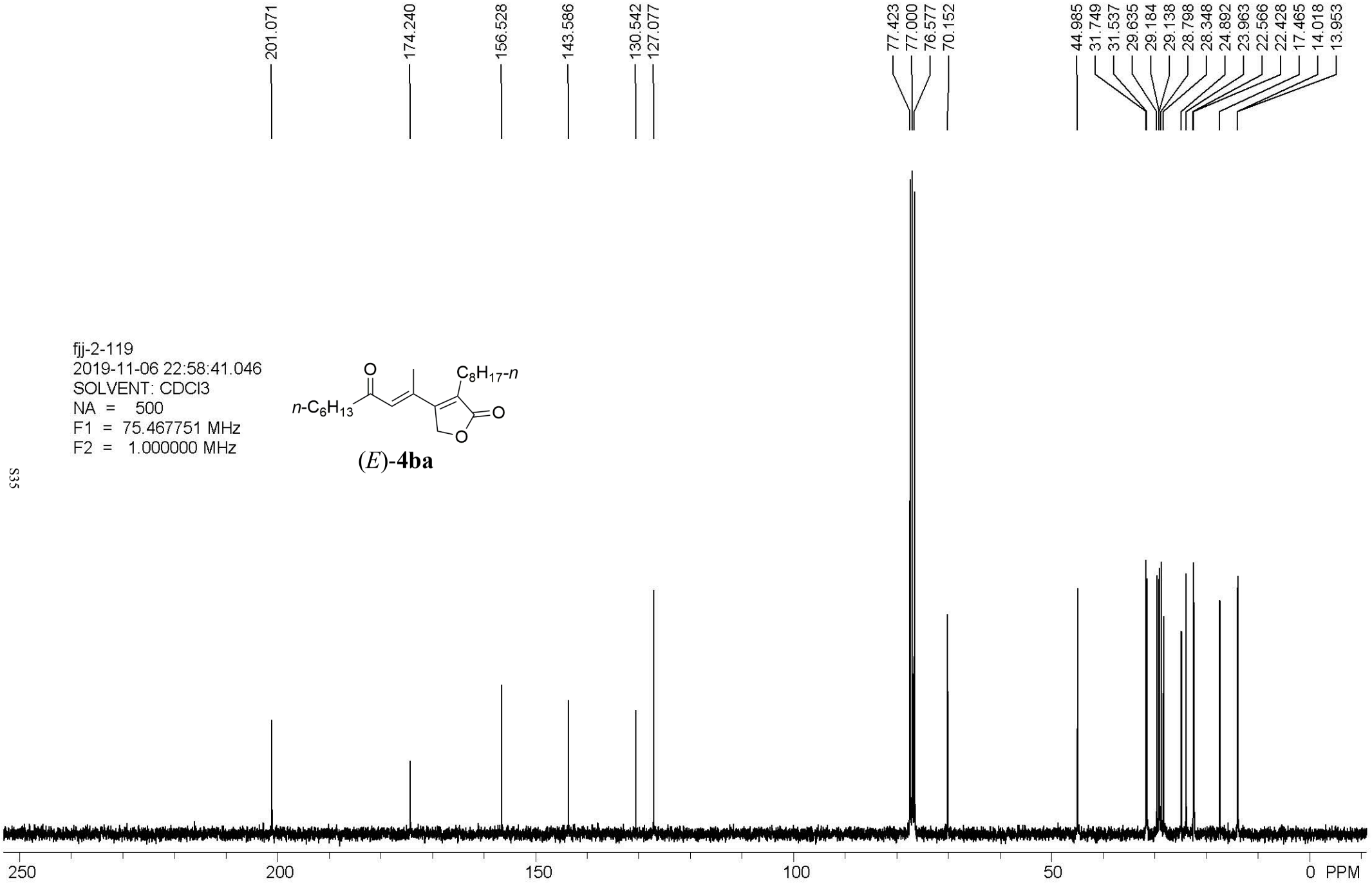
2.11
4.82
8.21
6.54
8
6
4
2
PPM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77.000
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70.152
44.985
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14.018
13.953
fjj-2-119
2019-11-06 22:58:41.046
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F2 = 1.000000 MHz
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n-C6H13
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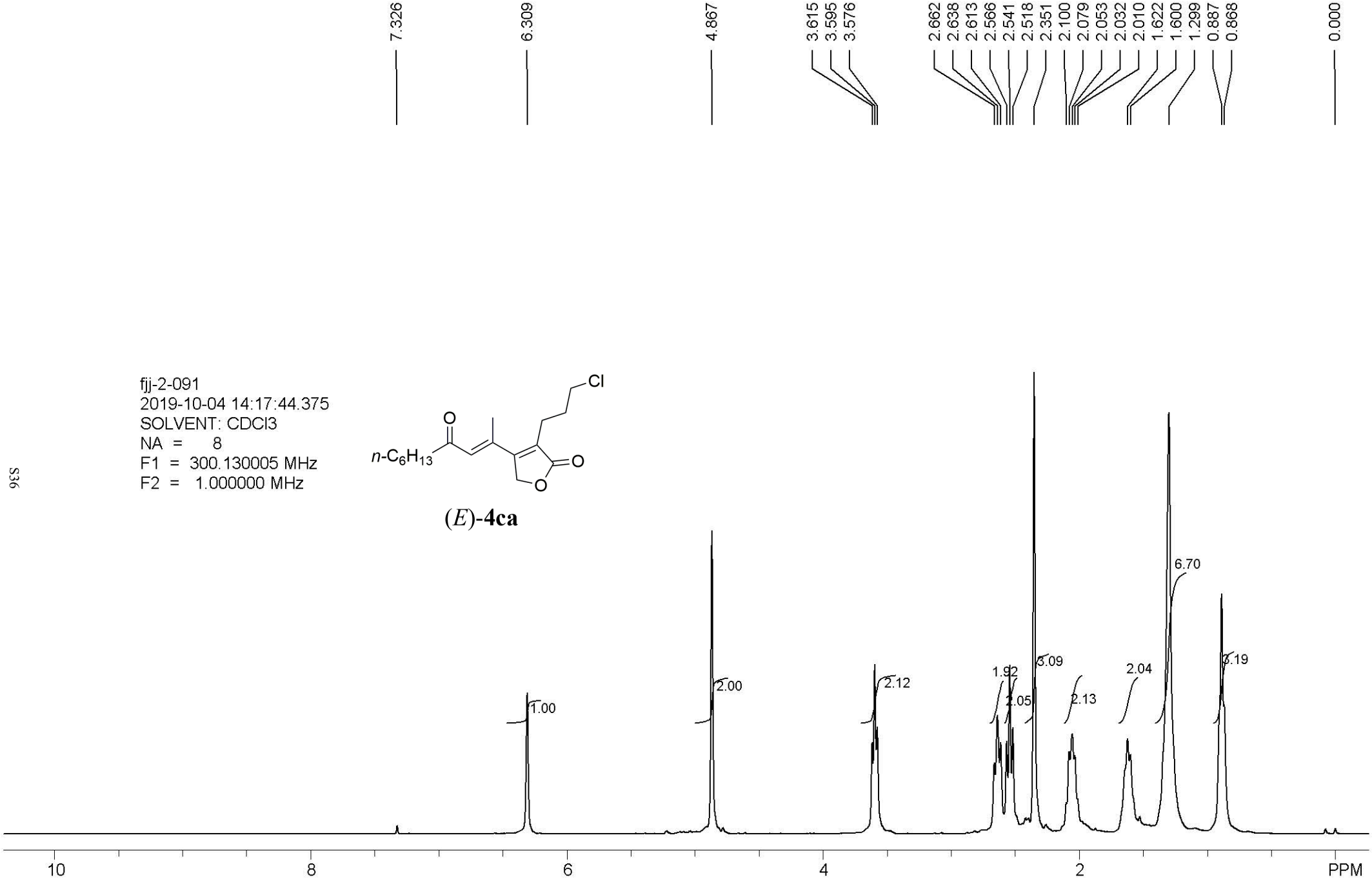
O
(E)-4ba
250
200
150
100
50
0 PPM


7.326
6.309
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3.576
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2.638
2.613
2.566
2.541
2.518
2.351
2.100
2.079
2.053
2.032
2.010
1.622
1.600
1.299
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0.000
fjj-2-091
2019-10-04 14:17:44.375
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F2 = 1.000000 MHz
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2.00
2.12
1.92
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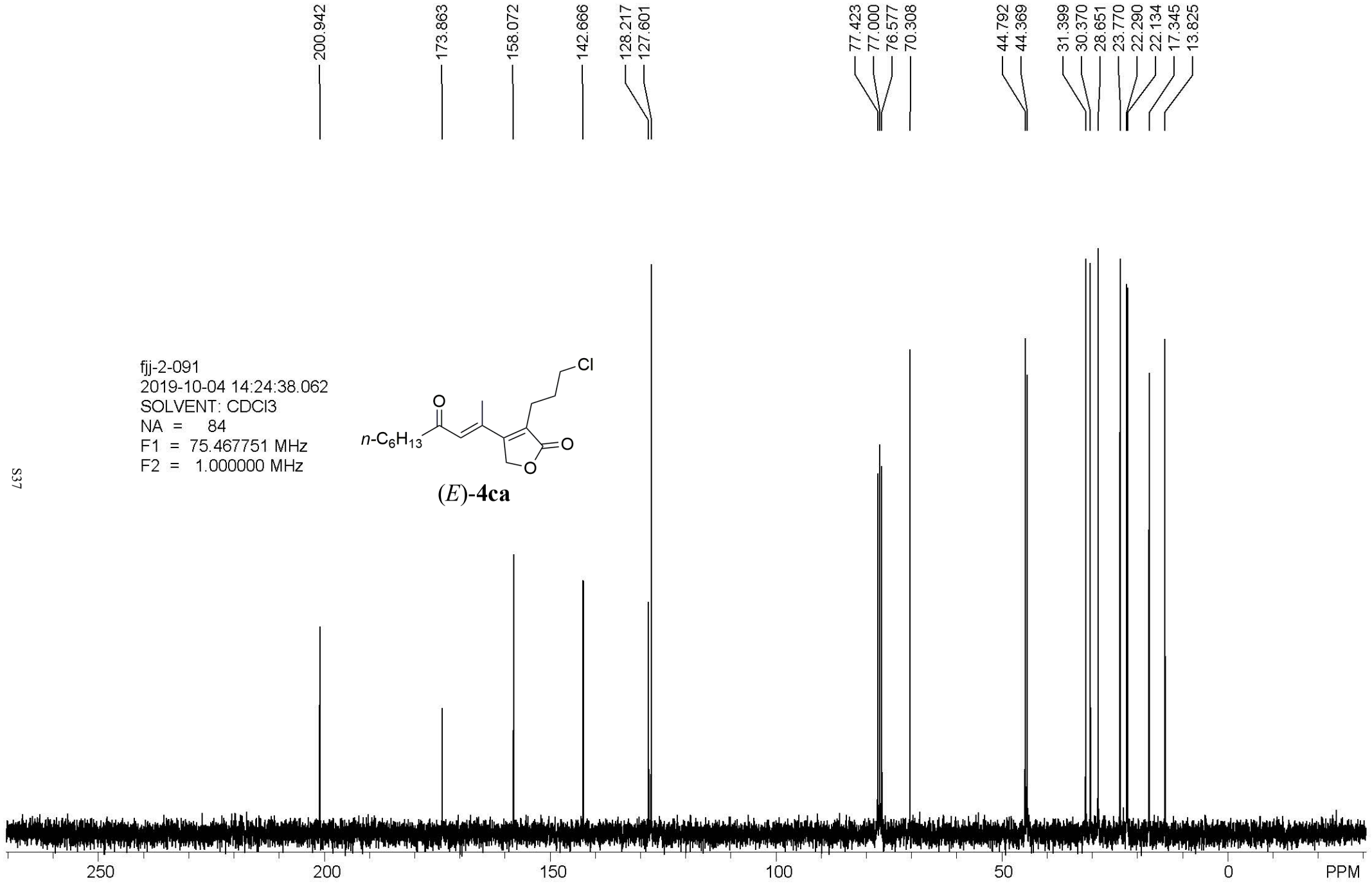
2.13
2.04
6.70
3.19
10
8
6
4
2
PPM

(*E*)-**4ca**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77.000
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31.399
30.370
28.651
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22.134
17.345
13.825
fjj-2-091
2019-10-04 14:24:38.062
SOLVENT: CDCl3
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F1 = 75.467751 MHz
F2 = 1.000000 MHz
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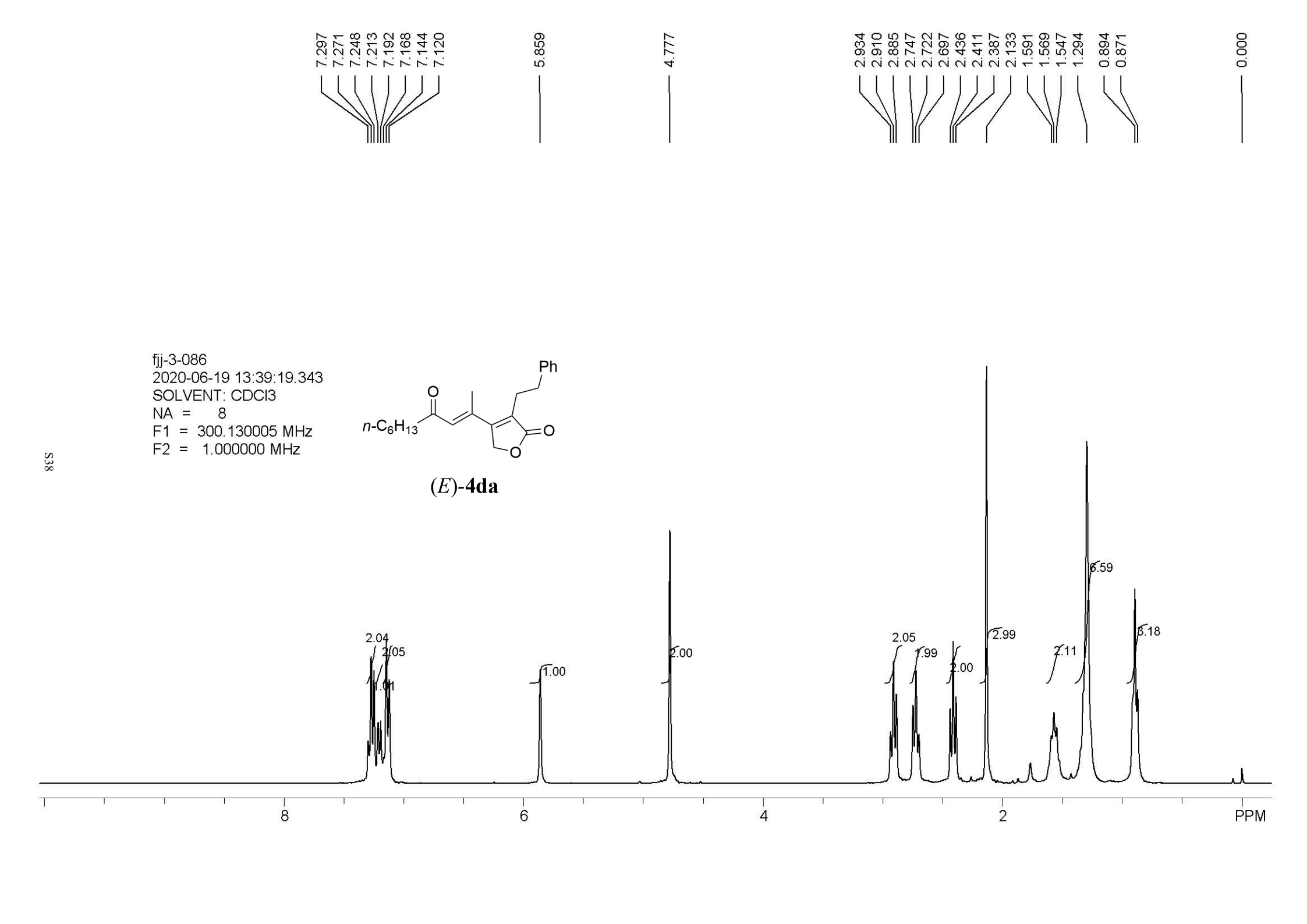
O
O
n-C6H13
250
200
150
100
50
0
PPM

(*E*)-**4ca**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4.777
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2.747
2.722
2.697
2.436
2.411
2.387
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1.591
1.569
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1.294
0.894
0.871
0.000
fjj-3-086
2020-06-19 13:39:19.343
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F2 = 1.000000 MHz
Ph
O
O
O
n-C6H13
(E)-4da
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2.05
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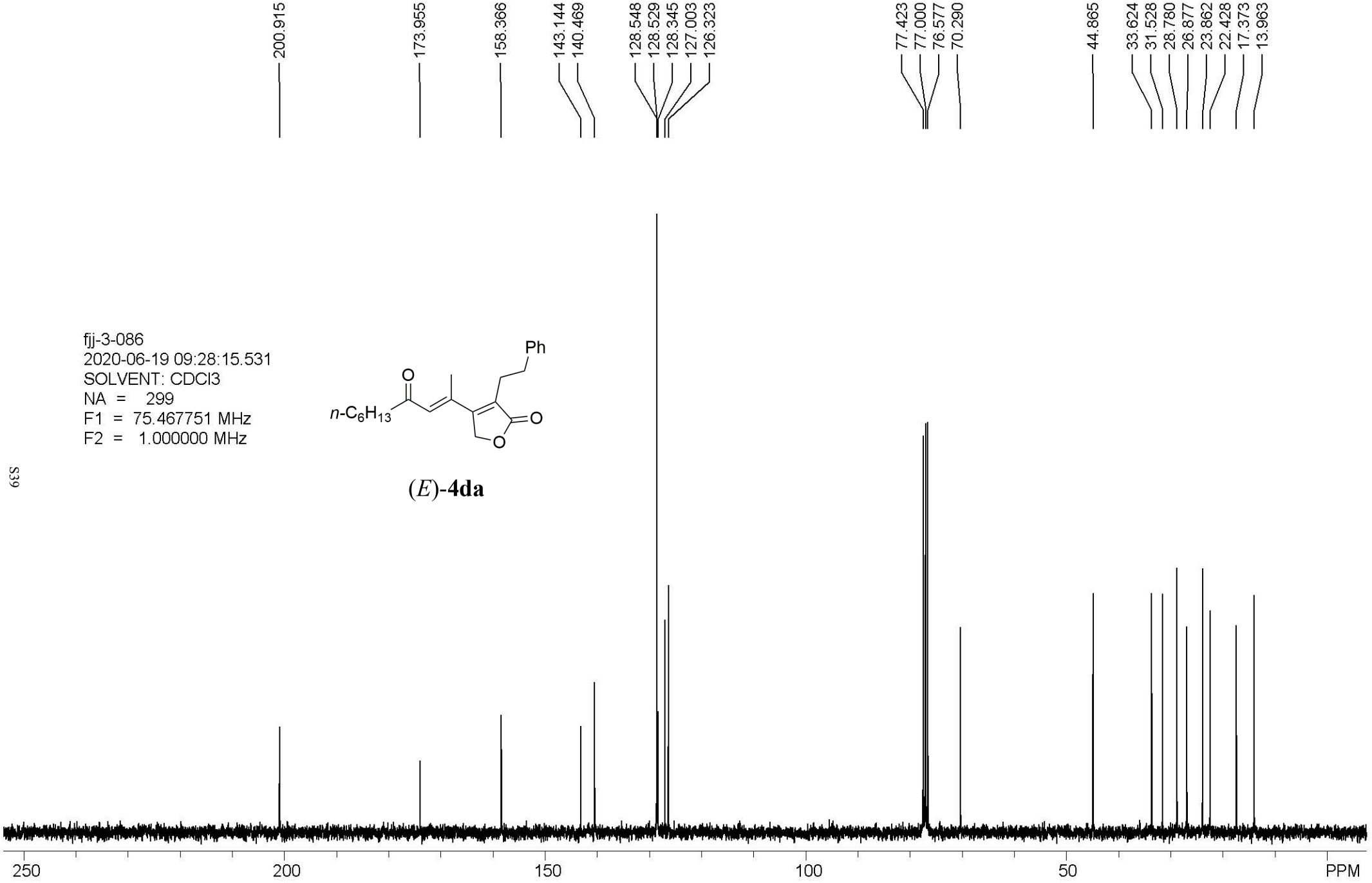
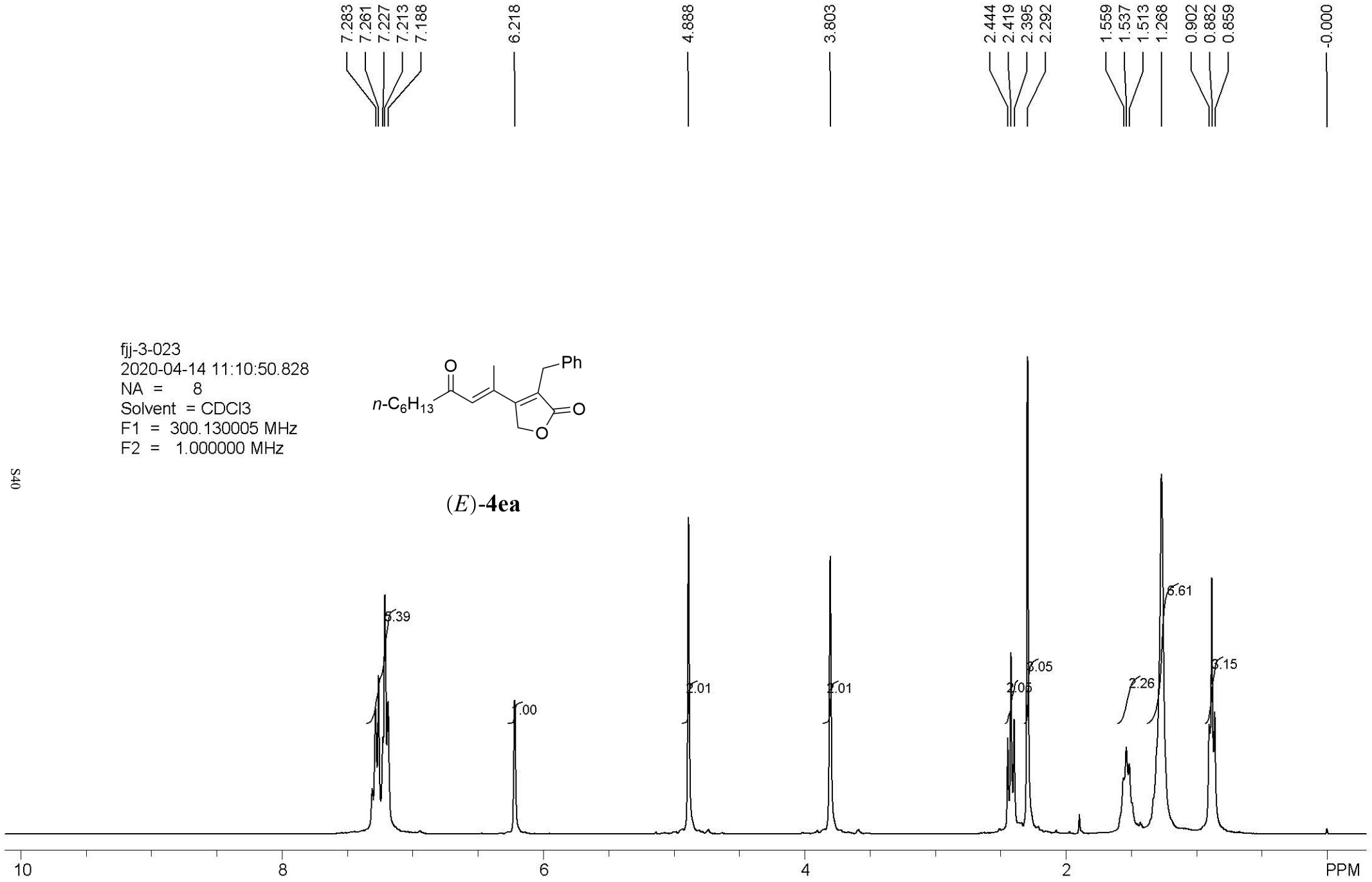
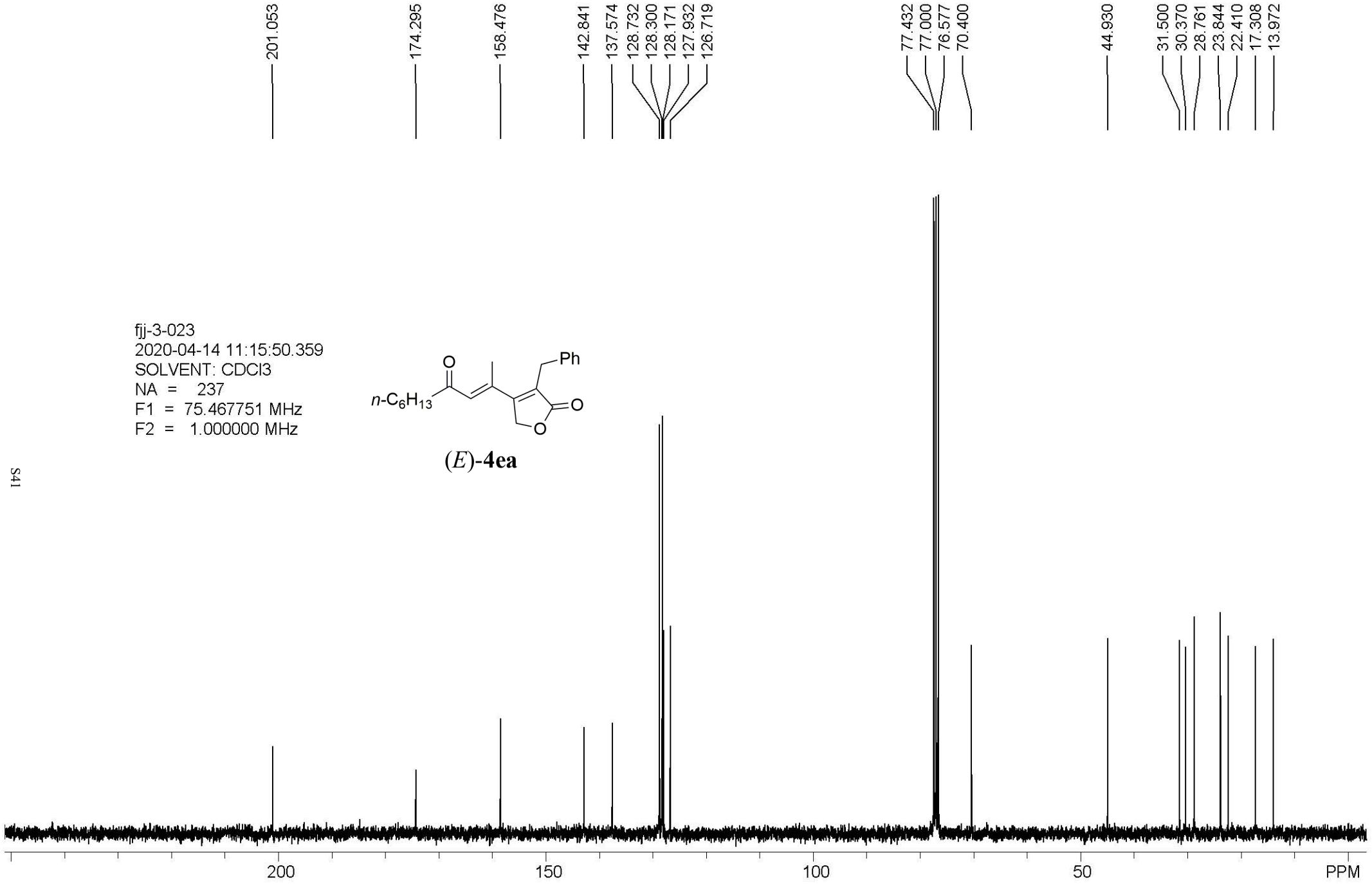
6.59
3.18
8
6
4
2
PPM

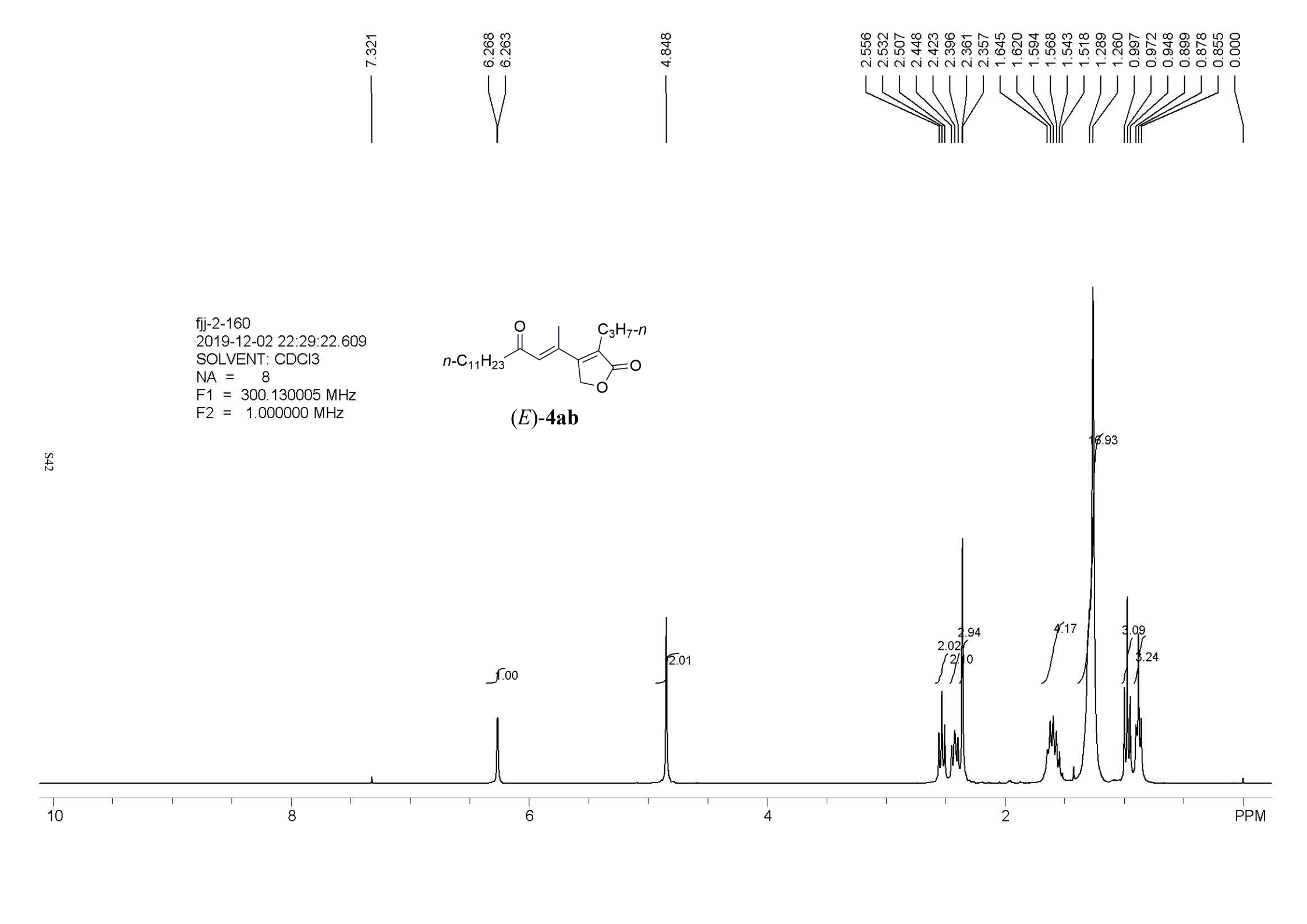

200.915
173.955
158.366
143.144
140.469
128.548
128.529
128.345
127.003
126.323
77.423
77.000
76.577
70.290
44.865
33.624
31.528
28.780
26.877
23.862
22.428
17.373
13.963
fjj-3-086
2020-06-19 09:28:15.531
SOLVENT: CDCl3
NA = 299
F1 = 75.467751 MHz
F2 = 1.000000 MHz
Ph
O
O
O
n-C6H13
250
200
150
100
50
PPM

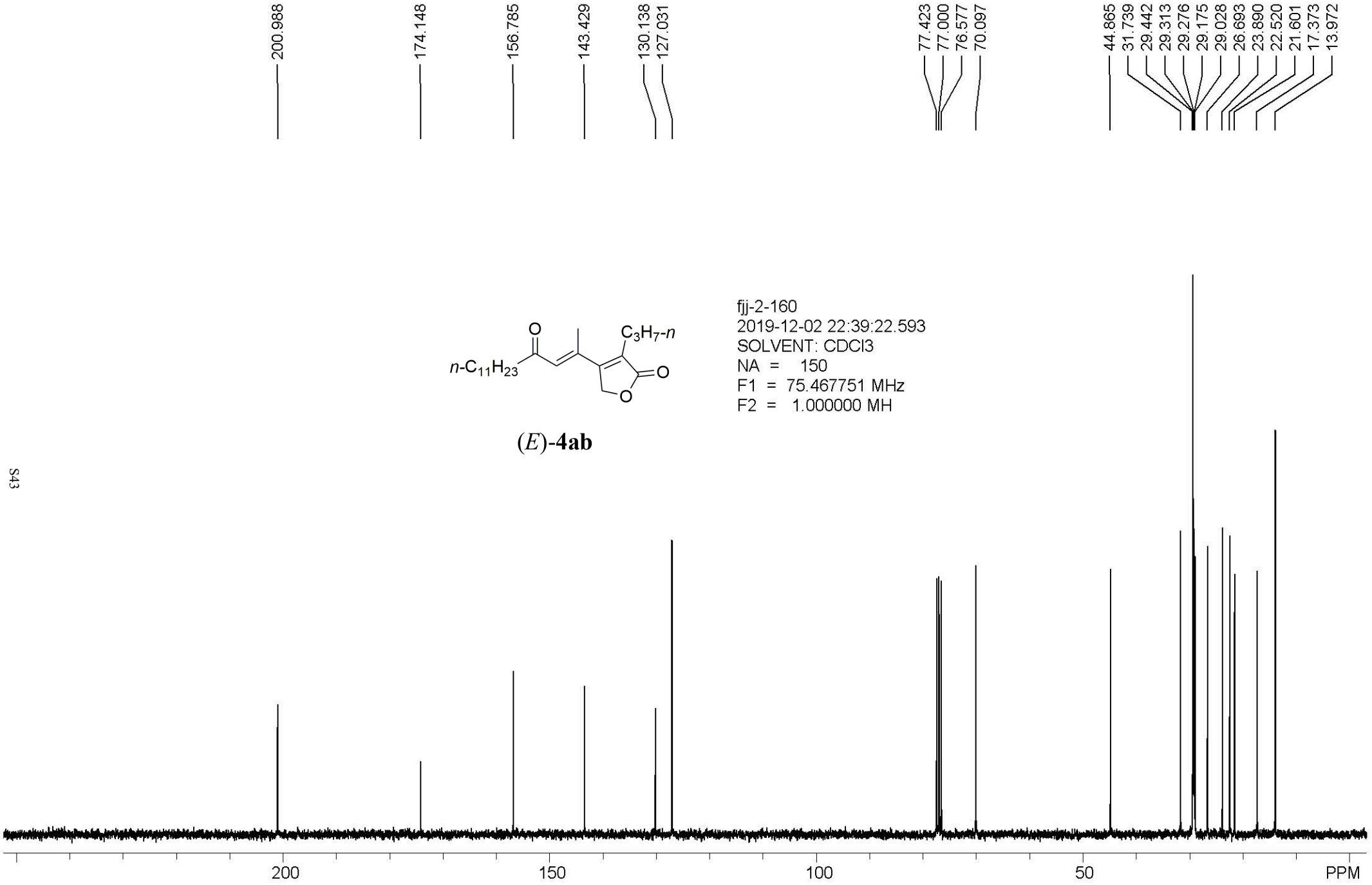
(*E*)-**4da**


7.283
7.261
7.227
7.213
7.188
6.218
4.888
3.803
2.444
2.419
2.395
2.292
1.559
1.537
1.513
1.268
0.902
0.882
0.859
-0.000
fjj-3-023
2020-04-14 11:10:50.828
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
Ph
n-C6H13
O
O
(E)-4ea
S40
5.39
1.00
2.01
2.01
2.05
3.05
2.26
6.61
3.15
10
8
6
4
2
PPM

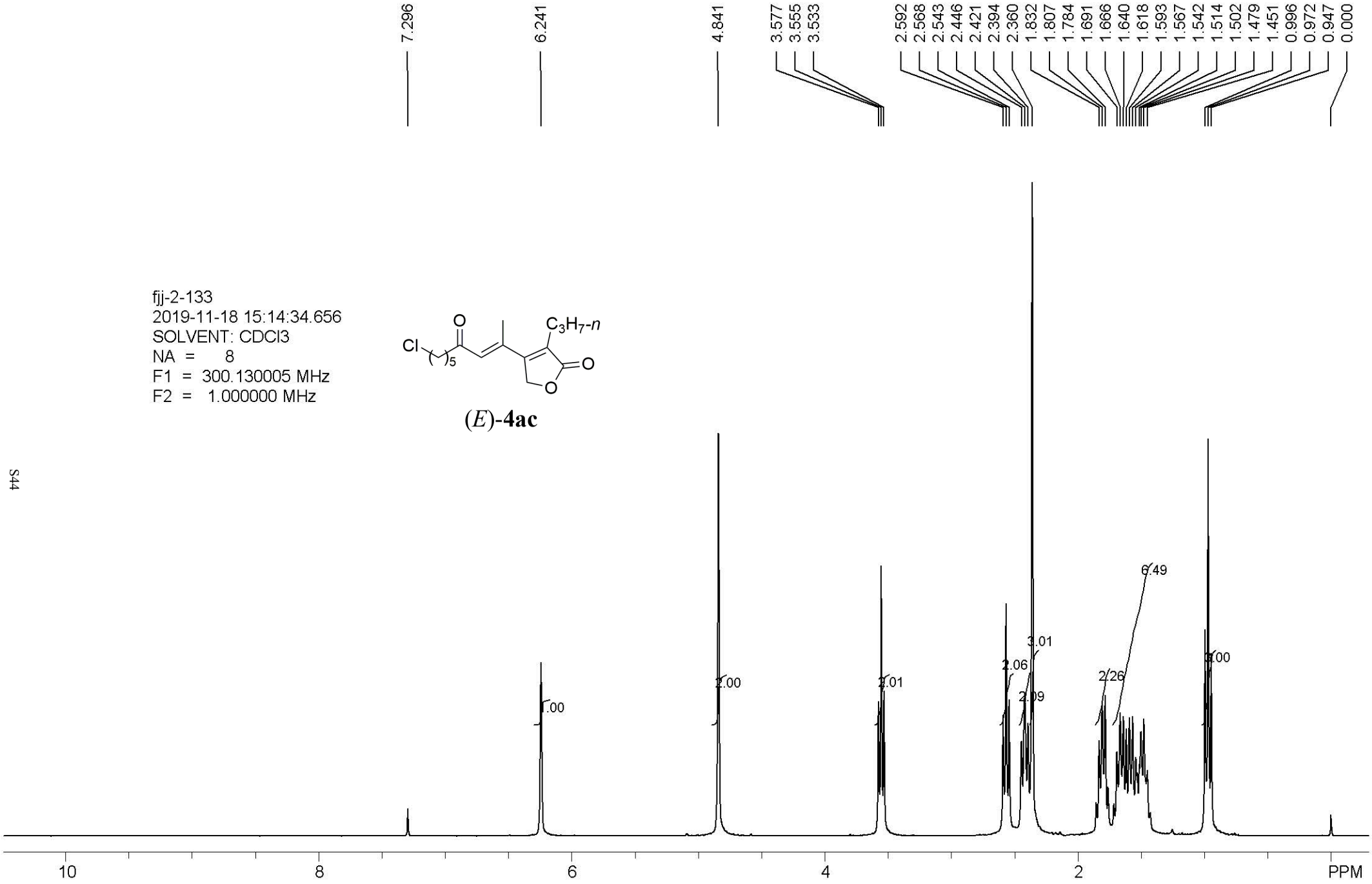

201.053
174.295
158.476
142.841
137.574
128.732
128.300
128.171
127.932
126.719
77.432
77.000
76.577
70.400
44.930
31.500
30.370
28.761
23.844
22.410
17.308
13.972
fjj-3-023
2020-04-14 11:15:50.359
SOLVENT: CDCl3
NA = 237
F1 = 75.467751 MHz
F2 = 1.000000 MHz
O
Ph
n-C6H13
O
O
200
150
100
50
PPM

(*E*)-**4ea**

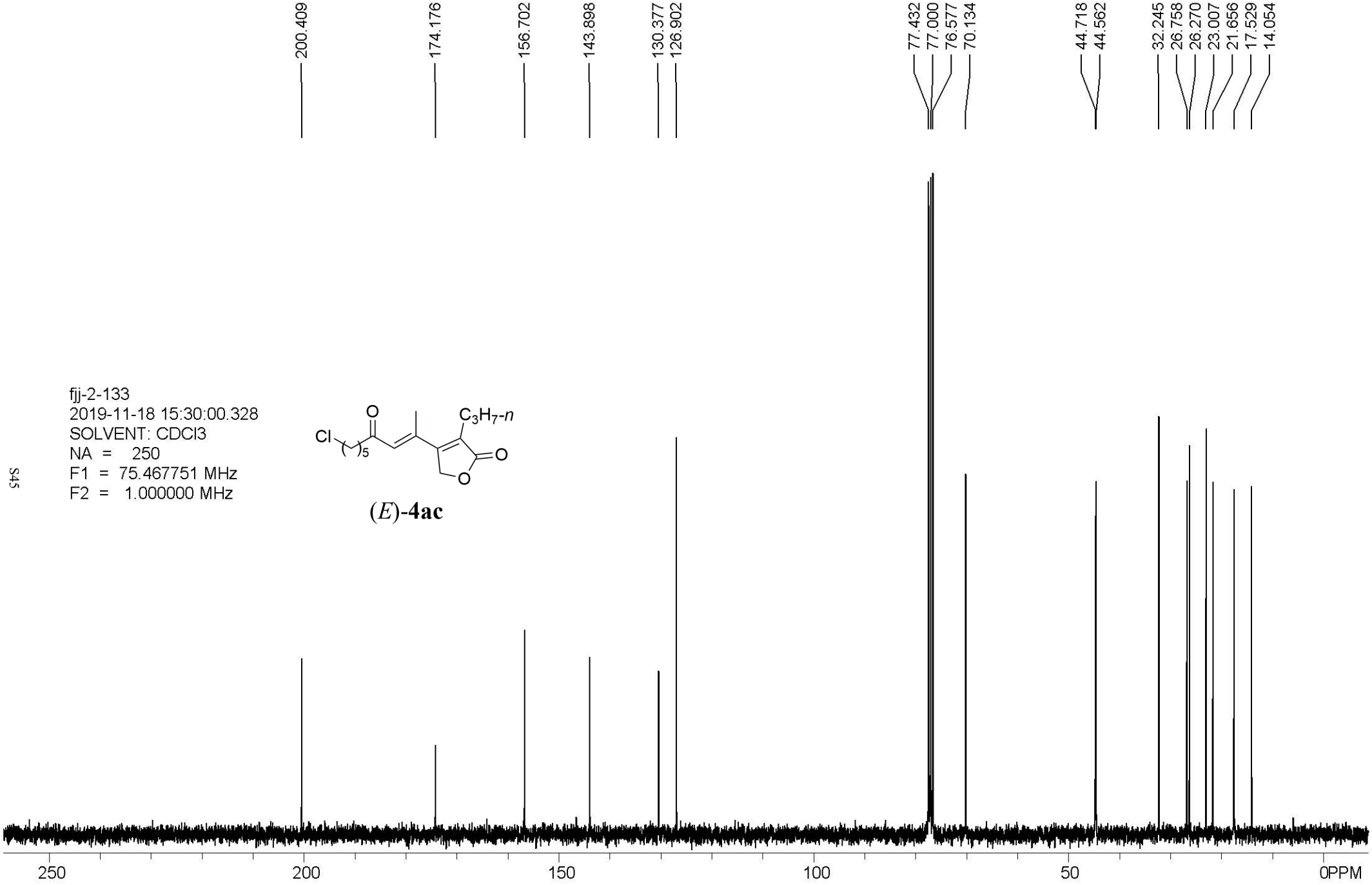

7.321
6.268
6.263
4.848
2.556
2.532
2.507
2.448
2.423
2.396
2.361
2.357
1.645
1.620
1.594
1.568
1.543
1.518
1.289
1.260
0.997
0.972
0.948
0.899
0.878
0.855
0.000
fjj-2-160
2019-12-02 22:29:22.609
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
C3H7-n
n-C11H23
O
O
(E)-4ab
16.93
2.94
2.02
2.10
4.17
3.09
3.24
1.00
2.01
10
8
6
4
2
PPM


200.988
174.148
156.785
143.429
130.138
127.031
77.423
77.000
76.577
70.097
44.865
31.739
29.442
29.313
29.276
29.175
29.028
26.693
23.890
22.520
21.601
17.373
13.972
O
C3H7-n
n-C11H23
O
O
fjj-2-160
2019-12-02 22:39:22.593
SOLVENT: CDCl3
NA = 150
F1 = 75.467751 MHz
F2 = 1.000000 MH
200
150
100
50
PPM

(*E*)-**4ab**

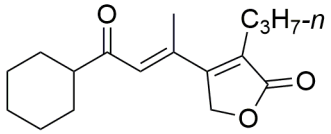

7.296
6.241
4.841
3.577
3.555
3.533
2.592
2.568
2.543
2.446
2.421
2.394
2.360
1.832
1.807
1.784
1.691
1.666
1.640
1.618
1.593
1.567
1.542
1.514
1.502
1.479
1.451
0.996
0.972
0.947
0.000
fjj-2-133
2019-11-18 15:14:34.656
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Cl
5
O
O
O
C3H7-n
1.00
2.00
2.01
2.06
3.01
2.09
2.26
6.49
3.00
10
8
6
4
2
PPM

(*E*)-**4ac**

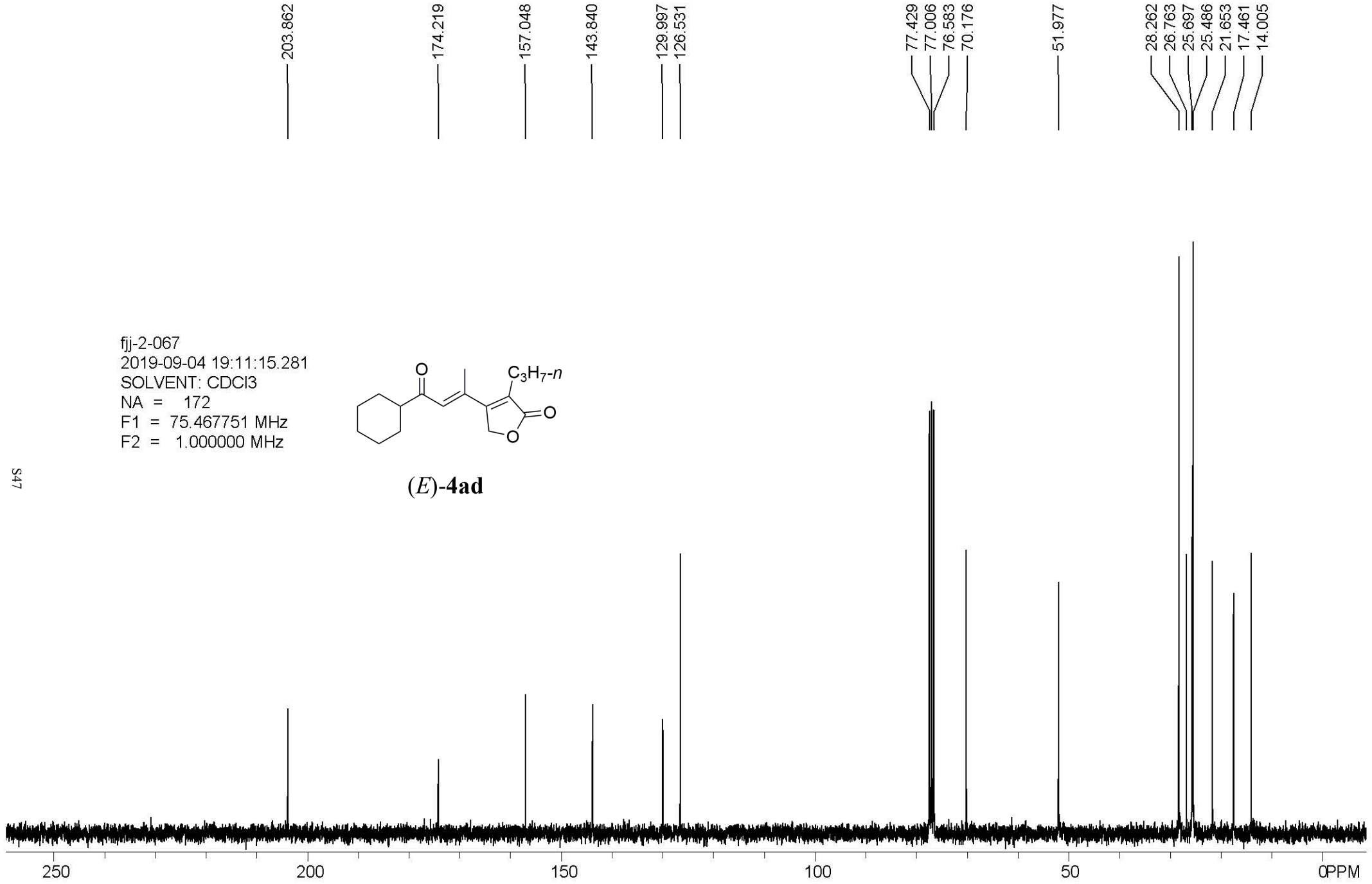

200.409
174.176
156.702
143.898
130.377
126.902
77.432
77.000
76.577
70.134
44.718
44.562
32.245
26.758
26.270
23.007
21.656
17.529
14.054
fjj-2-133
2019-11-18 15:30:00.328
SOLVENT: CDCl3
NA = 250
F1 = 75.467751 MHz
F2 = 1.000000 MHz
Cl
5
O
O
O
C3H7-n
250
200
150
100
50
0PPM

(*E*)-**4ac**

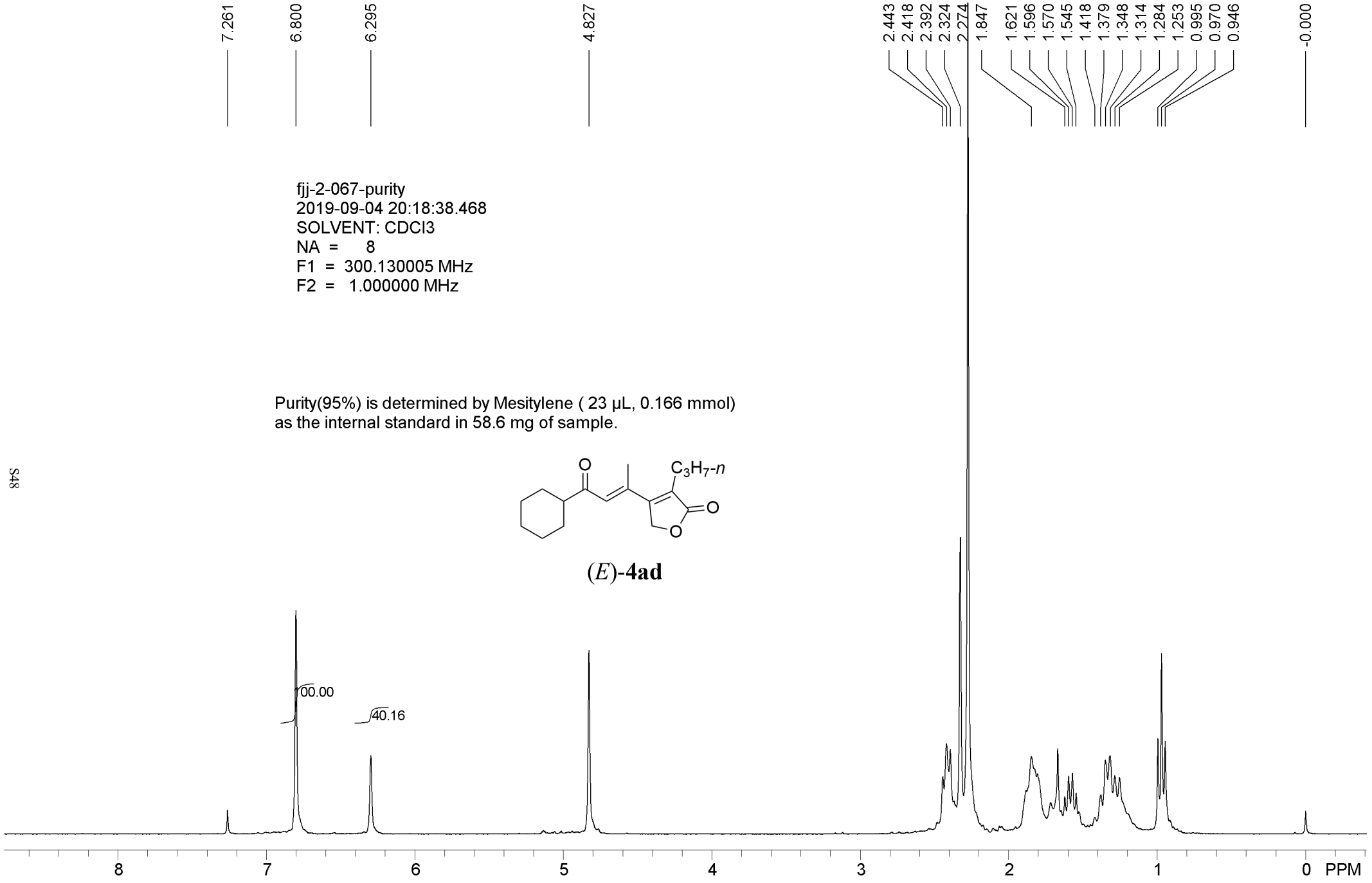
fjj-2-067
2019-09-04 18:59:53.531
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz

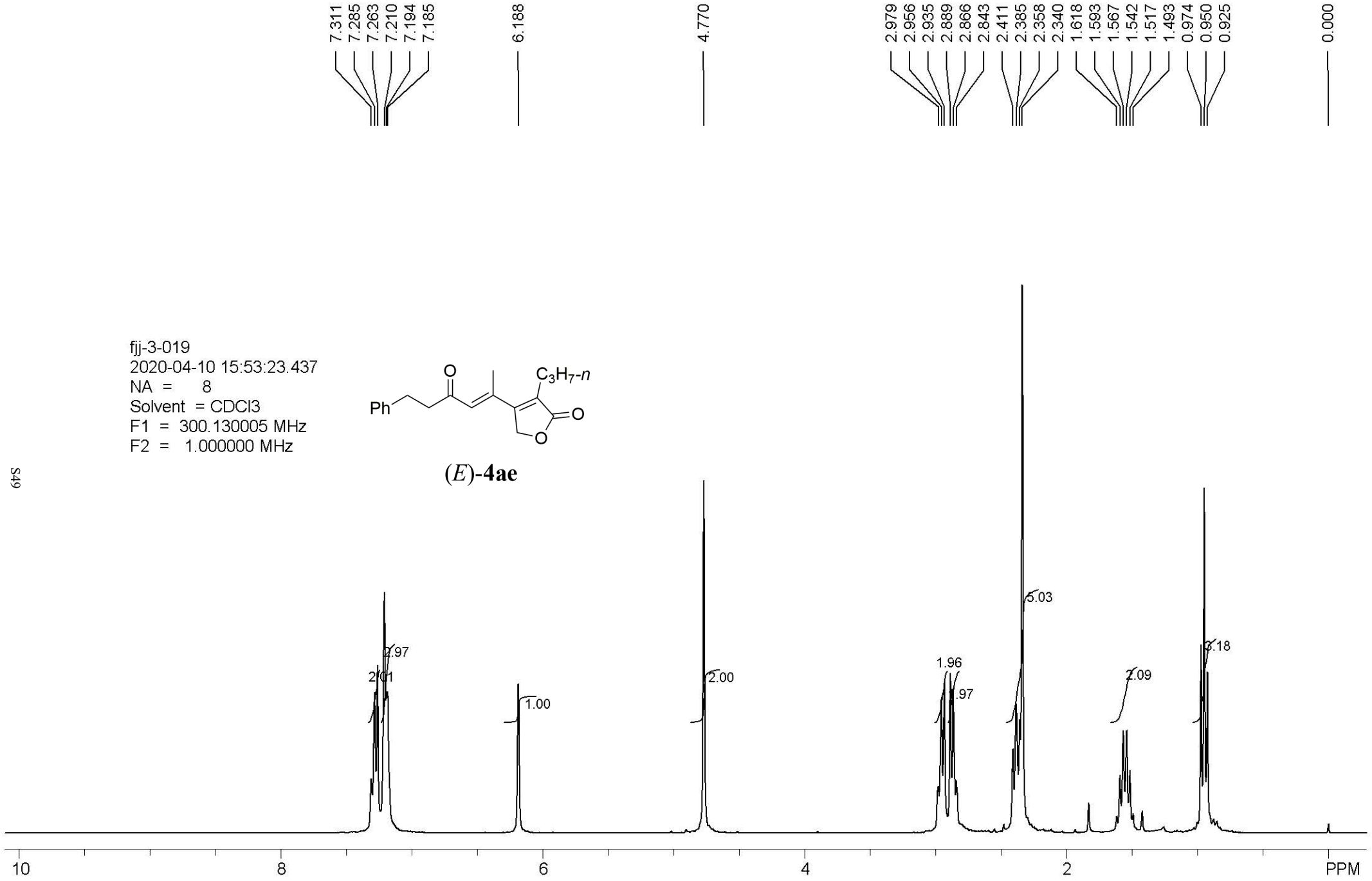


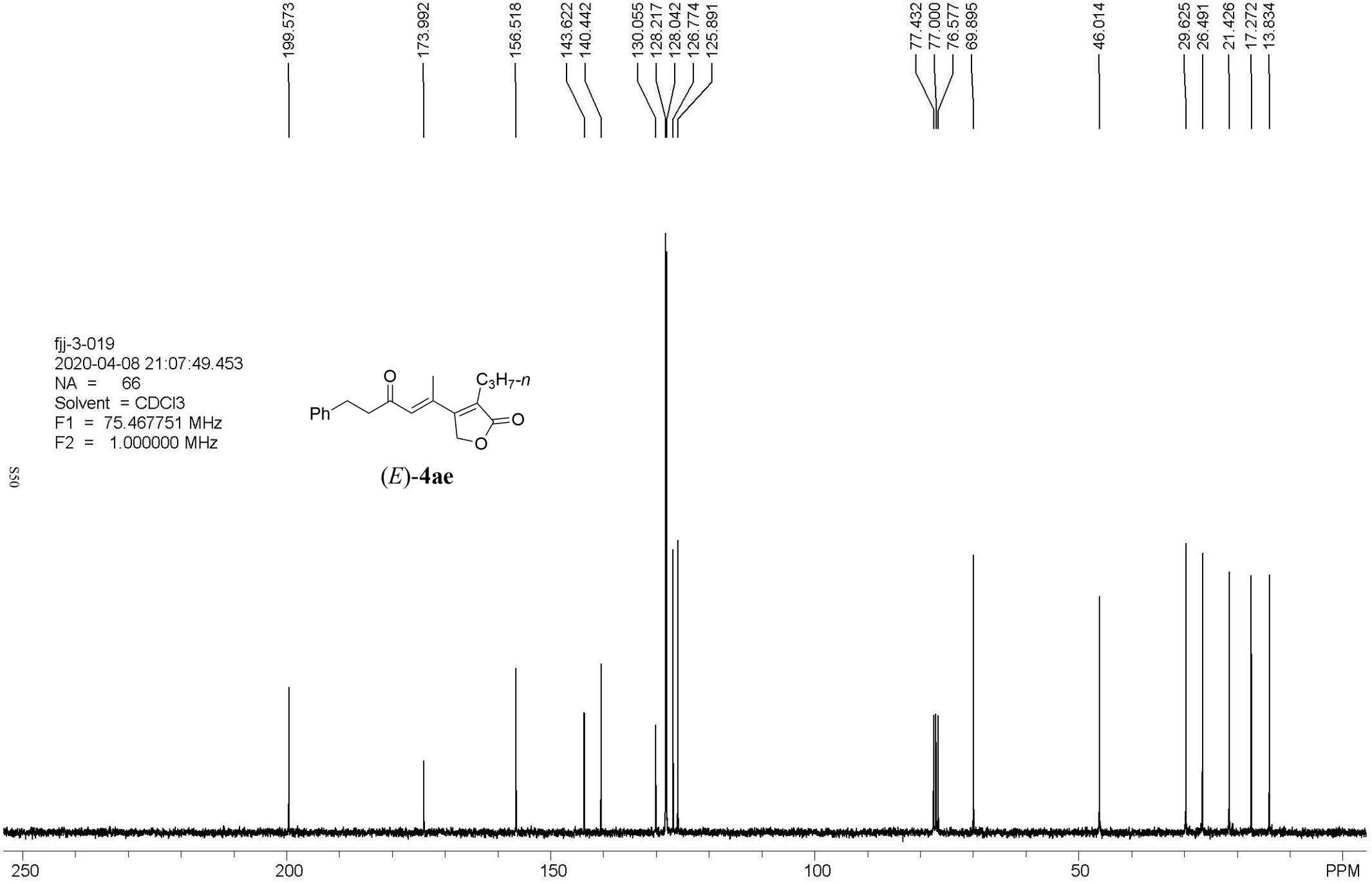
(*E*)-**4ad**


203.862
174.219
157.048
143.840
129.997
126.531
77.429
77.006
76.583
70.176
51.977
28.262
26.763
25.697
25.486
21.653
17.461
14.005
fjj-2-067
2019-09-04 19:11:15.281
SOLVENT: CDCl3
NA = 172
F1 = 75.467751 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
O
250
200
150
100
50
0PPM

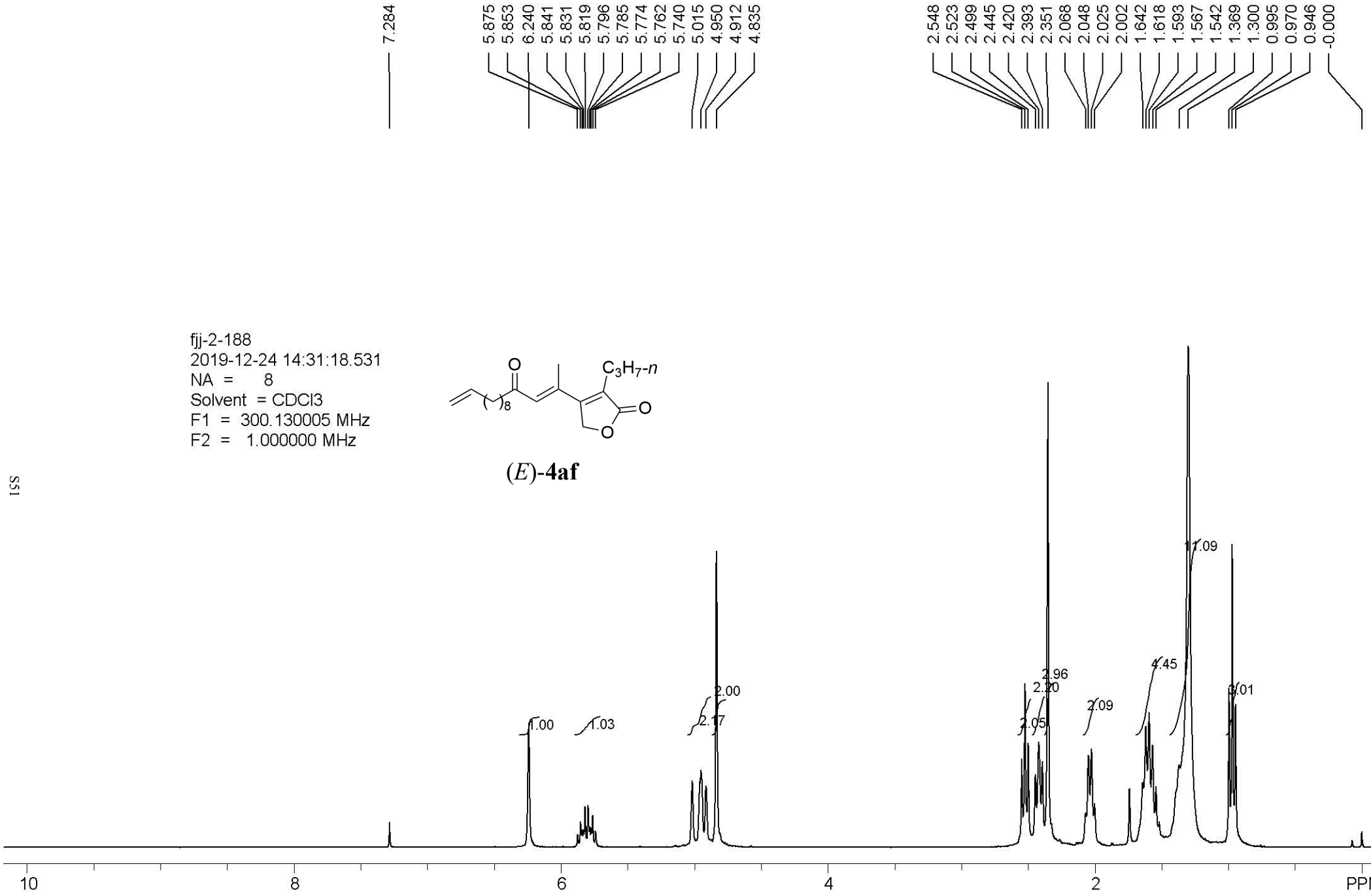
(*E*)-**4ad**


7.261
6.800
6.295
4.827
2.443
2.418
2.392
2.324
2.274
1.847
1.621
1.596
1.570
1.545
1.418
1.379
1.348
1.314
1.284
1.253
0.995
0.970
0.946
-0.000
fjj-2-067-purity
2019-09-04 20:18:38.468
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Purity(95%) is determined by Mesitylene (23 μL, 0.166 mmol)
as the internal standard in 58.6 mg of sample.
O
C3H7-n
O
O
(E)-4ad
00.00
40.16
8
7
6
5
4
3
2
1
0
PPM

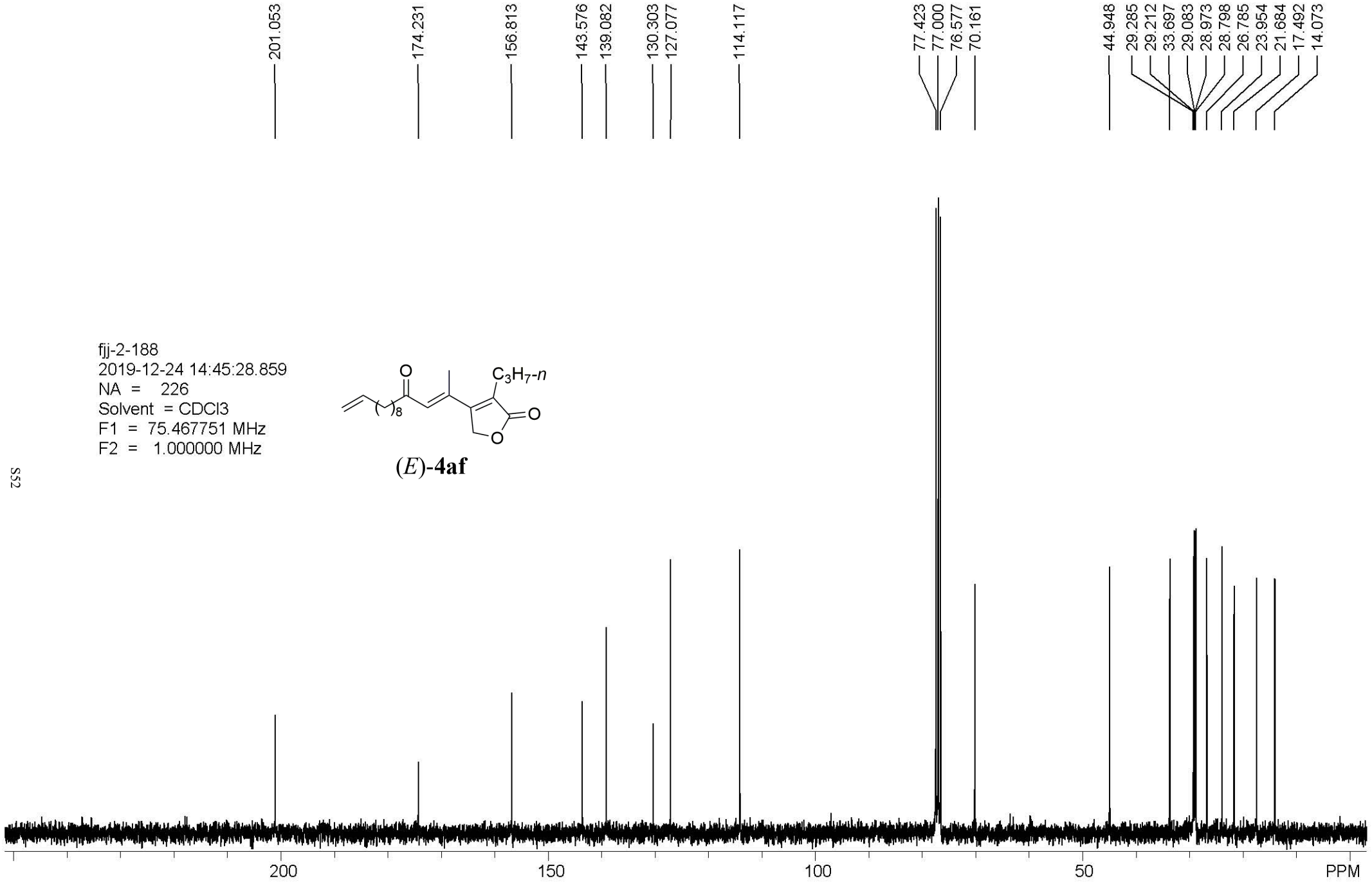

7.311
7.285
7.263
7.210
7.194
7.185
6.188
4.770
2.979
2.956
2.935
2.889
2.866
2.843
2.411
2.385
2.358
2.340
1.618
1.593
1.567
1.542
1.517
1.493
0.974
0.950
0.925
0.000
fjj-3-019
2020-04-10 15:53:23.437
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
C3H7-n
Ph
O
O
(E)-4ae
2.11
2.97
1.00
2.00
1.96
.97
5.03
2.09
3.18
10
8
6
4
2
PPM


199.573
173.992
156.518
143.622
140.442
130.055
128.217
128.042
126.774
125.891
77.432
77.000
76.577
69.895
46.014
29.625
26.491
21.426
17.272
13.834
fjj-3-019
2020-04-08 21:07:49.453
NA = 66
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
Ph
O
C_3H_7-*n*
O
O
250
200
150
100
50
PPM

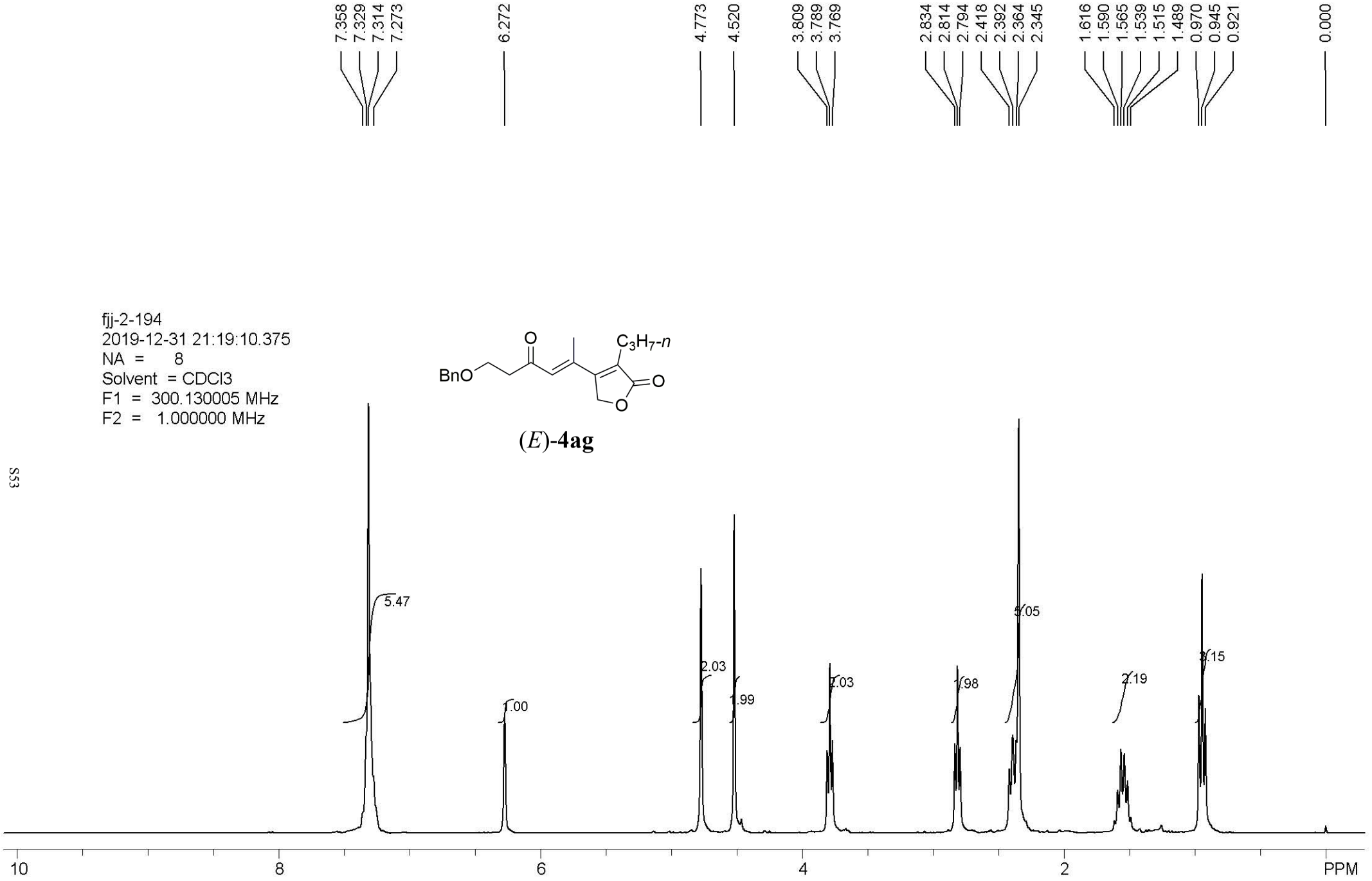
(*E*)-**4ae**

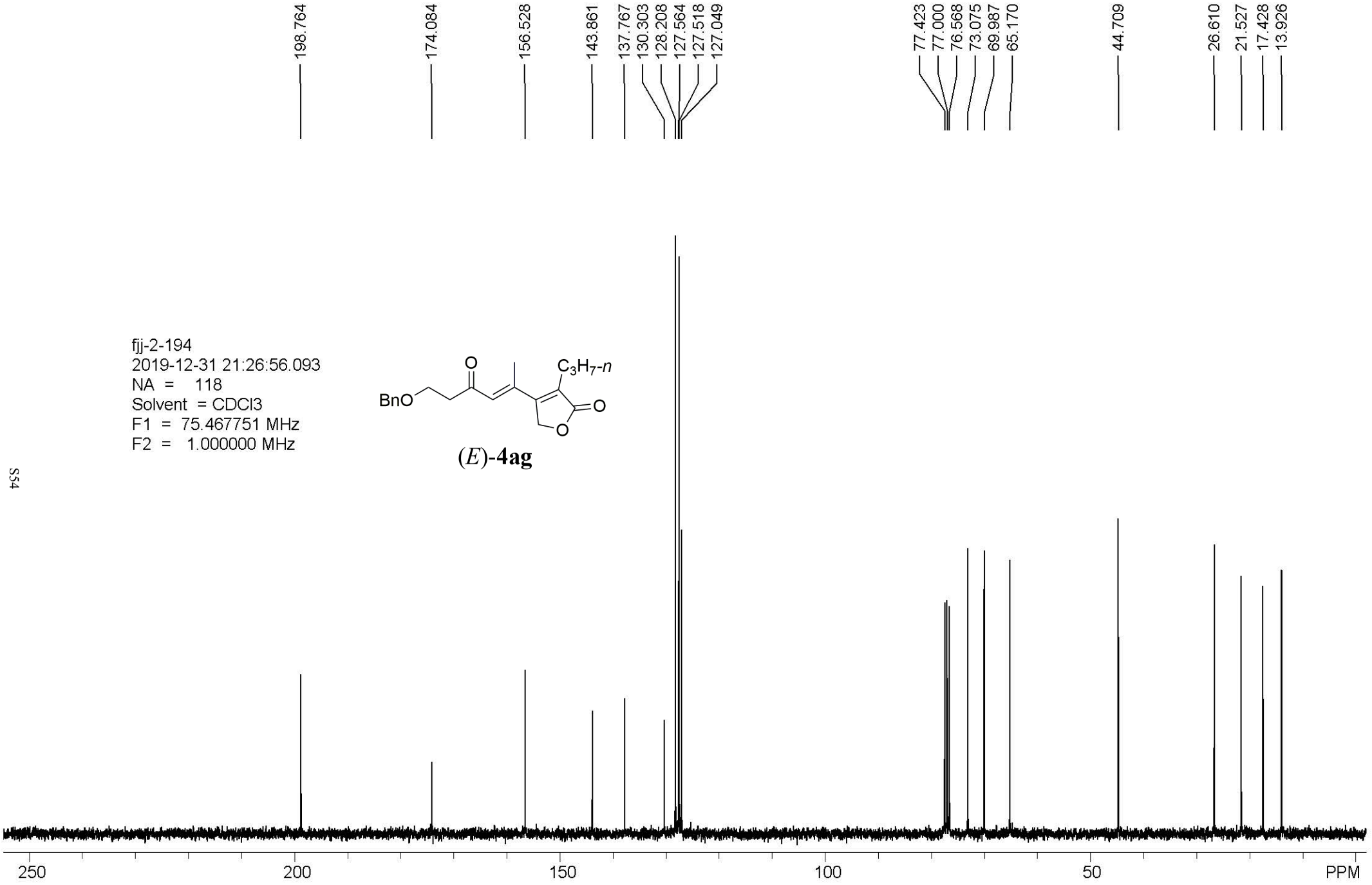

7.284
5.875
5.853
6.240
5.841
5.831
5.819
5.796
5.785
5.774
5.762
5.740
5.015
4.950
4.912
4.835
2.548
2.523
2.499
2.445
2.420
2.393
2.351
2.068
2.048
2.025
2.002
1.642
1.618
1.593
1.567
1.542
1.369
1.300
0.995
0.970
0.946
-0.000
fjj-2-188
2019-12-24 14:31:18.531
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
C3H7-n
8
O
O
1.00
1.03
2.00
2.17
2.96
2.20
2.05
2.09
4.45
11.09
3.01
10
8
6
4
2
PPM

(*E*)-**4af**

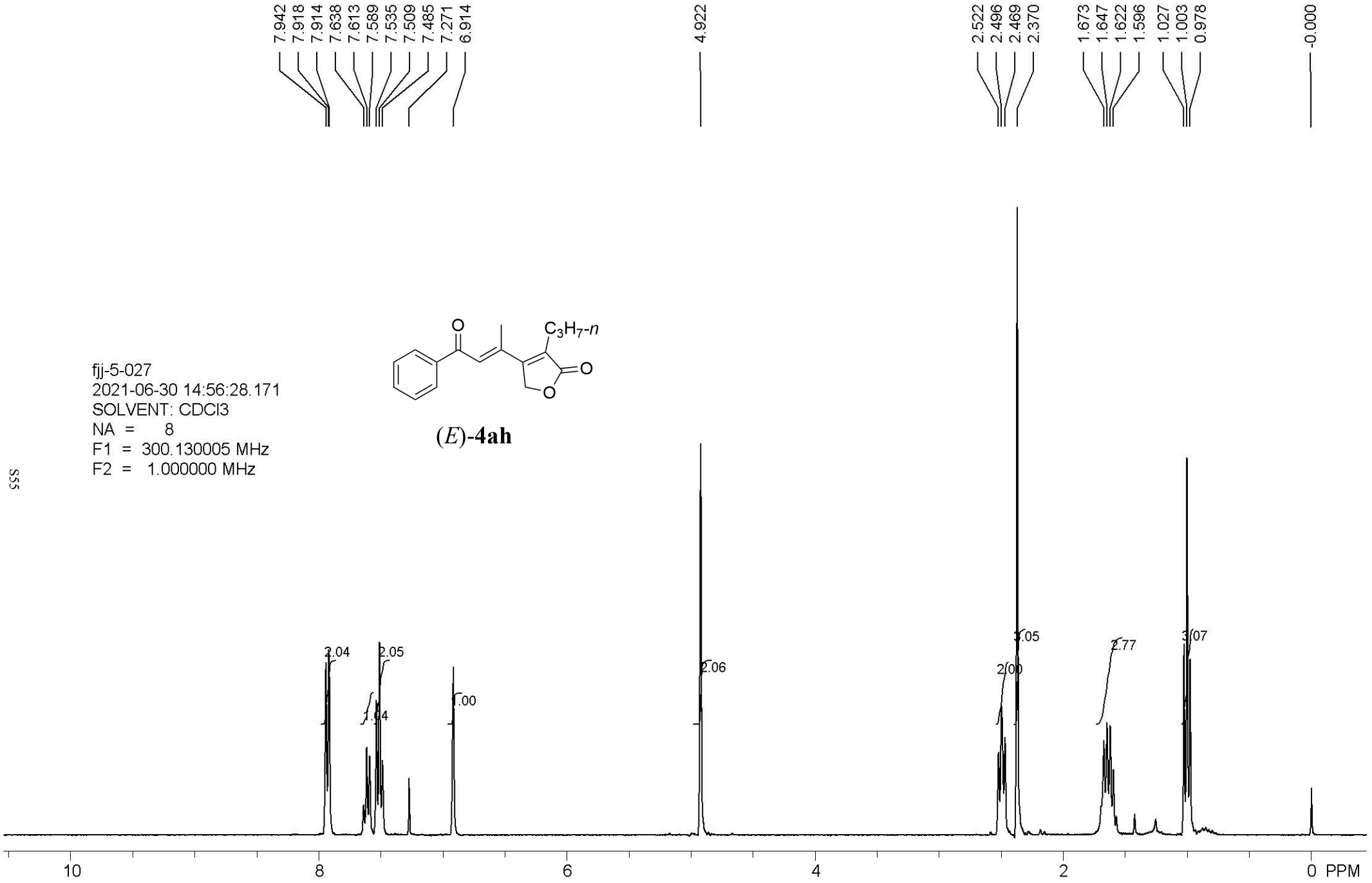

201.053
174.231
156.813
143.576
139.082
130.303
127.077
114.117
77.423
77.000
76.577
70.161
44.948
29.285
29.212
33.697
29.083
28.973
28.798
26.785
23.954
21.684
17.492
14.073
fjj-2-188
2019-12-24 14:45:28.859
NA = 226
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
O
C3H7-n
8
O
O
200
150
100
50
PPM

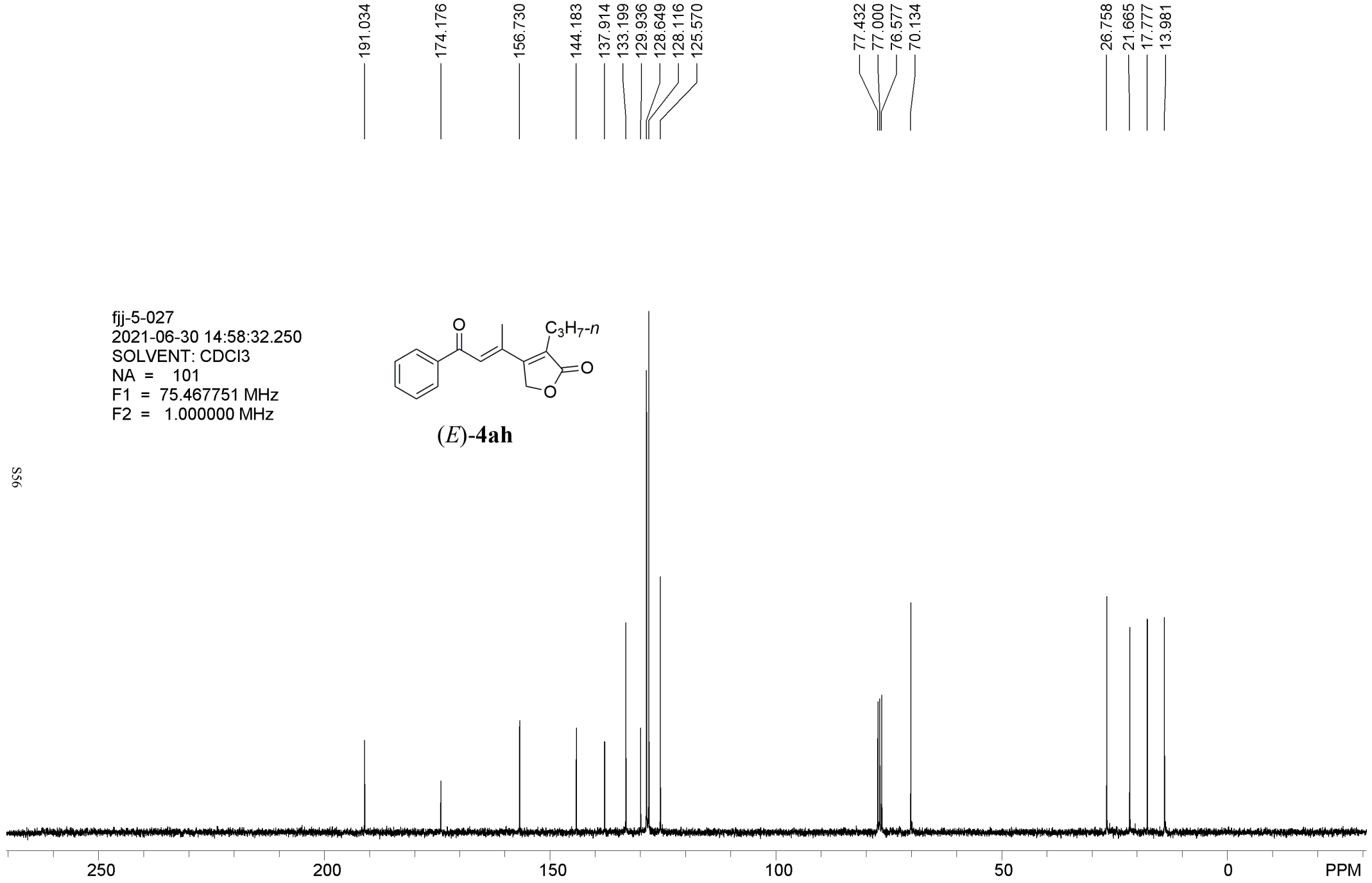
(*E*)-**4af**

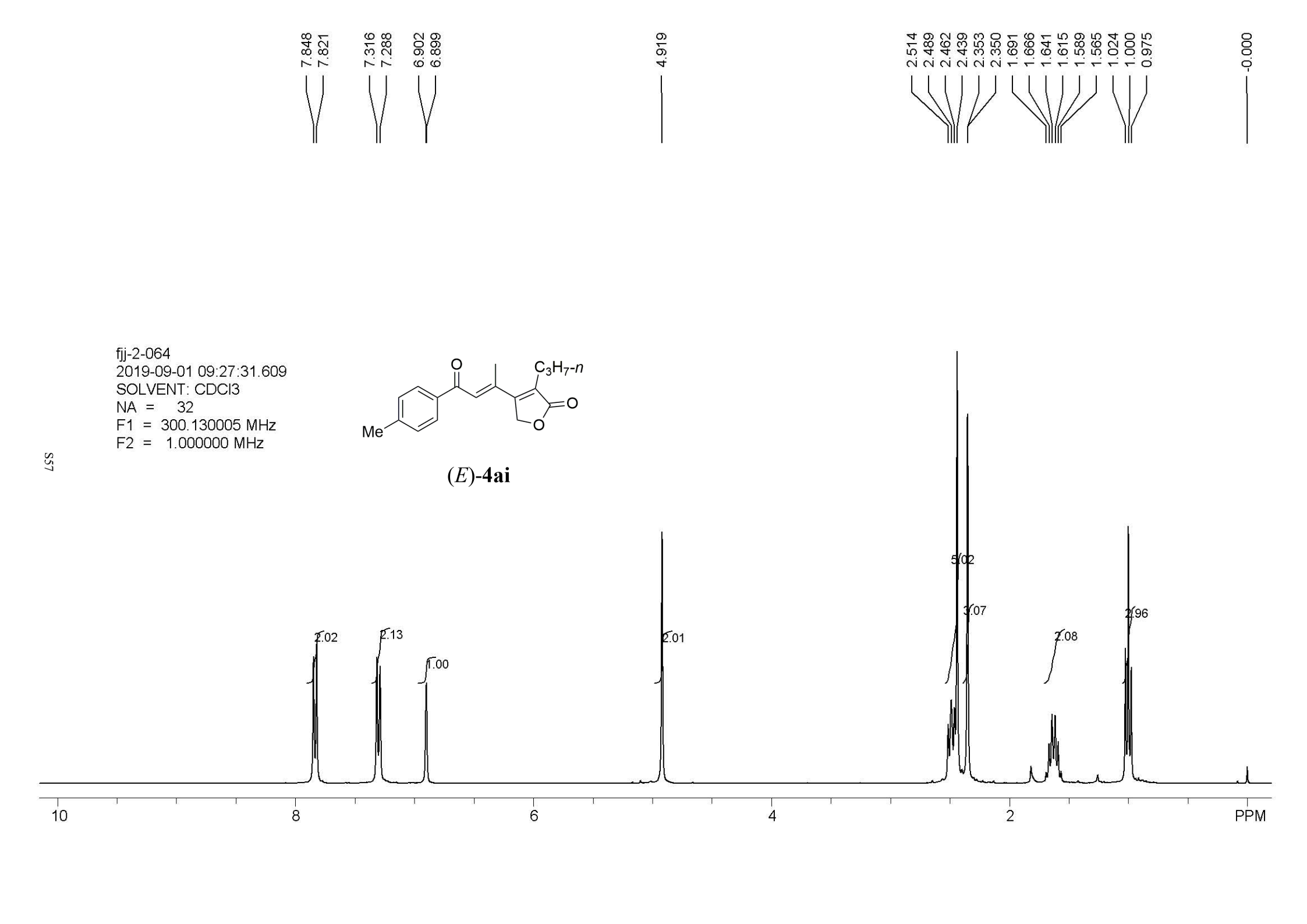

7.358
7.329
7.314
7.273
6.272
4.773
4.520
3.809
3.789
3.769
2.834
2.814
2.794
2.418
2.392
2.364
2.345
1.616
1.590
1.565
1.539
1.515
1.489
0.970
0.945
0.921
0.000
fjj-2-194
2019-12-31 21:19:10.375
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
BnO
O
O
O
C_3H_7-*n*
(*E*)-**4ag**
5.47
1.00
2.03
1.99
2.03
1.98
5.05
2.19
3.15
10
8
6
4
2
PPM


198.764
174.084
156.528
143.861
137.767
130.303
128.208
127.564
127.518
127.049
77.423
77.000
76.568
73.075
69.987
65.170
44.709
26.610
21.527
17.428
13.926
fjj-2-194
2019-12-31 21:26:56.093
NA = 118
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
BnO
O
O
O
C_3H_7-*n*
250
200
150
100
50
PPM

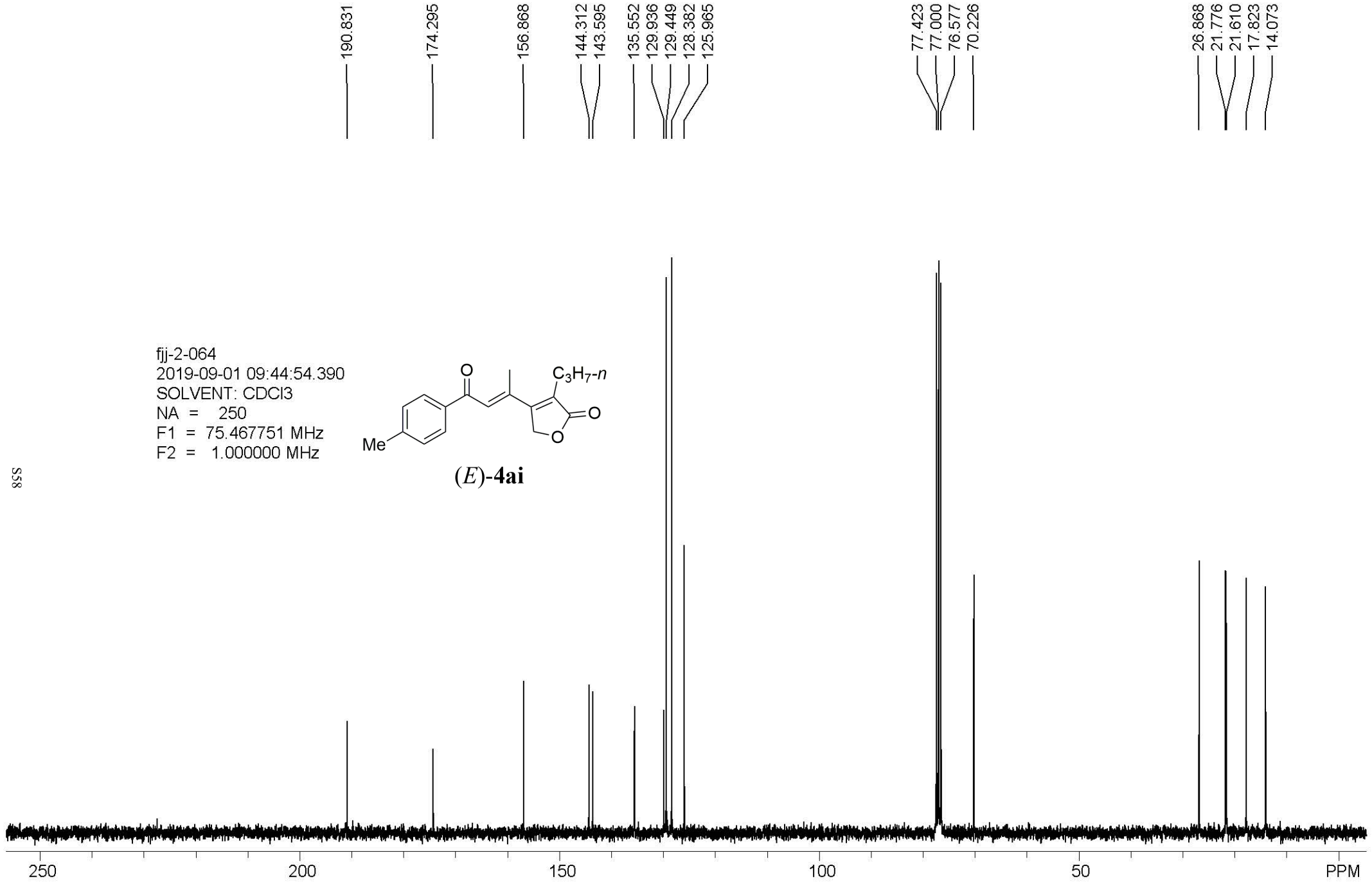
(*E*)-**4ag**


7.942
7.918
7.914
7.638
7.613
7.589
7.535
7.509
7.485
7.271
6.914
4.922
2.522
2.496
2.469
2.370
1.673
1.647
1.622
1.596
1.027
1.003
0.978
-0.000
fjj-5-027
2021-06-30 14:56:28.171
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
S55
O
C3H7-n
O
O
(E)-4ah
2.04
2.05
1.04
1.00
2.06
2.00
3.05
2.77
3.07
10
8
6
4
2
0 PPM


191.034
174.176
156.730
144.183
137.914
133.199
129.936
128.649
128.116
125.570
77.432
77.000
76.577
70.134
26.758
21.665
17.777
13.981
fjj-5-027
2021-06-30 14:58:32.250
SOLVENT: CDCl3
NA = 101
F1 = 75.467751 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
O
(E)-4ah
250
200
150
100
50
0
PPM


7.848
7.821
7.316
7.288
6.902
6.899
4.919
2.514
2.489
2.462
2.439
2.353
2.350
1.691
1.666
1.641
1.615
1.589
1.565
1.024
1.000
0.975
-0.000
fjj-2-064
2019-09-01 09:27:31.609
SOLVENT: CDCl3
NA = 32
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
Me
O
2.02
2.13
1.00
2.01
5.02
3.07
2.08
2.96
10
8
6
4
2
PPM

(*E*)-**4ai**


190.831
174.295
156.868
144.312
143.595
135.552
129.936
129.449
128.382
125.965
77.423
77.000
76.577
70.226
26.868
21.776
21.610
17.823
14.073
fjj-2-064
2019-09-01 09:44:54.390
SOLVENT: CDCl3
NA = 250
F1 = 75.467751 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
Me
O
250
200
150
100
50
PPM

(*E*)-**4ai**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 191031_fjj_2_073_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 191031_fjj_2_073_0m

```
Bond precision:  C-C = 0.0017 A          Wavelength=0.71073

Cell:            a=13.1699(4)    b=6.7473(2)        c=16.9652(6)
                 alpha=90        beta=94.130(1)     gamma=90
Temperature:     170 K

                Calculated                Reported
Volume          1503.63(8)                1503.63(8)
Space group     P 21/c                    P 1 21/c 1
Hall group      -P 2ybc                   -P 2ybc
Moiety formula  C18 H20 O3                C18 H20 O3
Sum formula     C18 H20 O3                C18 H20 O3
Mr              284.34                    284.34
Dx,g cm-3       1.256                     1.256
Z               4                         4
Mu (mm-1)       0.084                     0.084
F000            608.0                     608.0
F000'           608.30
h,k,lmax        16,8,21                   16,8,21
Nref            3322                      3318
Tmin,Tmax       0.988,0.992               0.680,0.746
Tmin'           0.975

Correction method= # Reported T Limits: Tmin=0.680 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 27.105

R(reflections)= 0.0387( 2795)     wR2(reflections)= 0.1060( 3318)

S = 1.025                 Npar= 193
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

```
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O2            108.7 Degree
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         2 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.        19 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by         3 Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   5 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

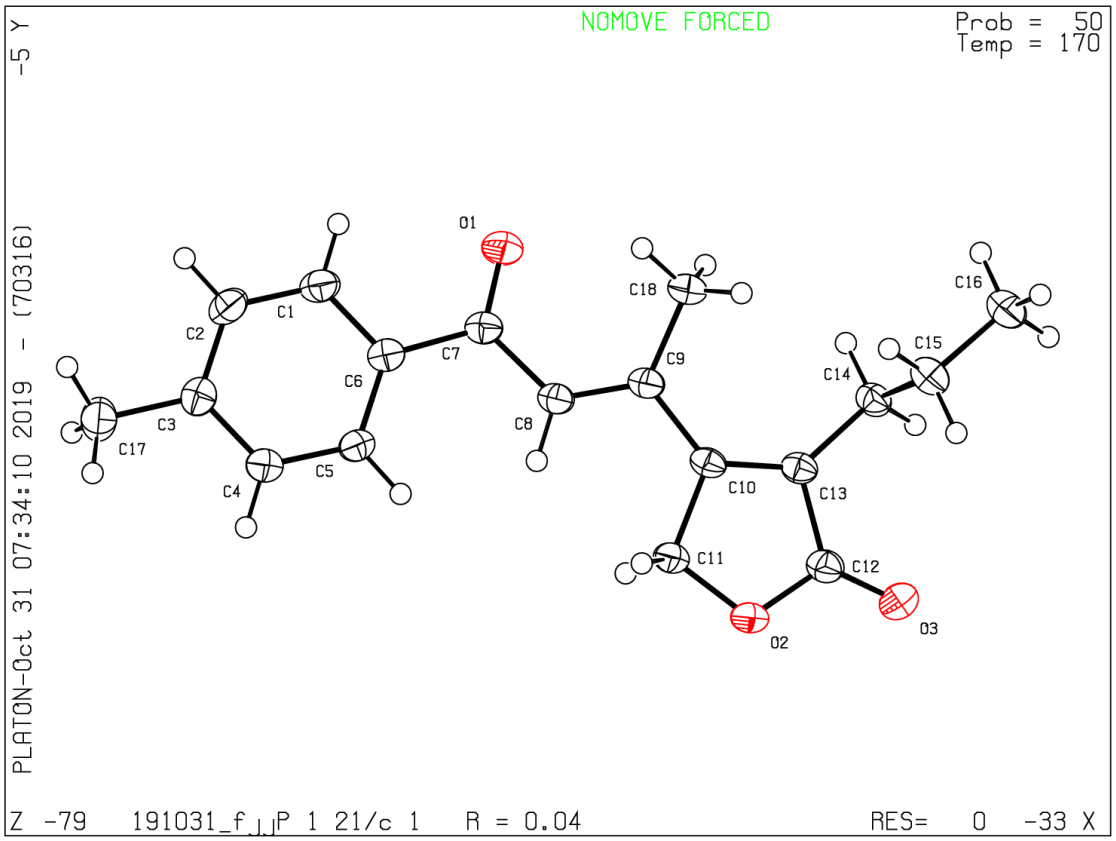
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

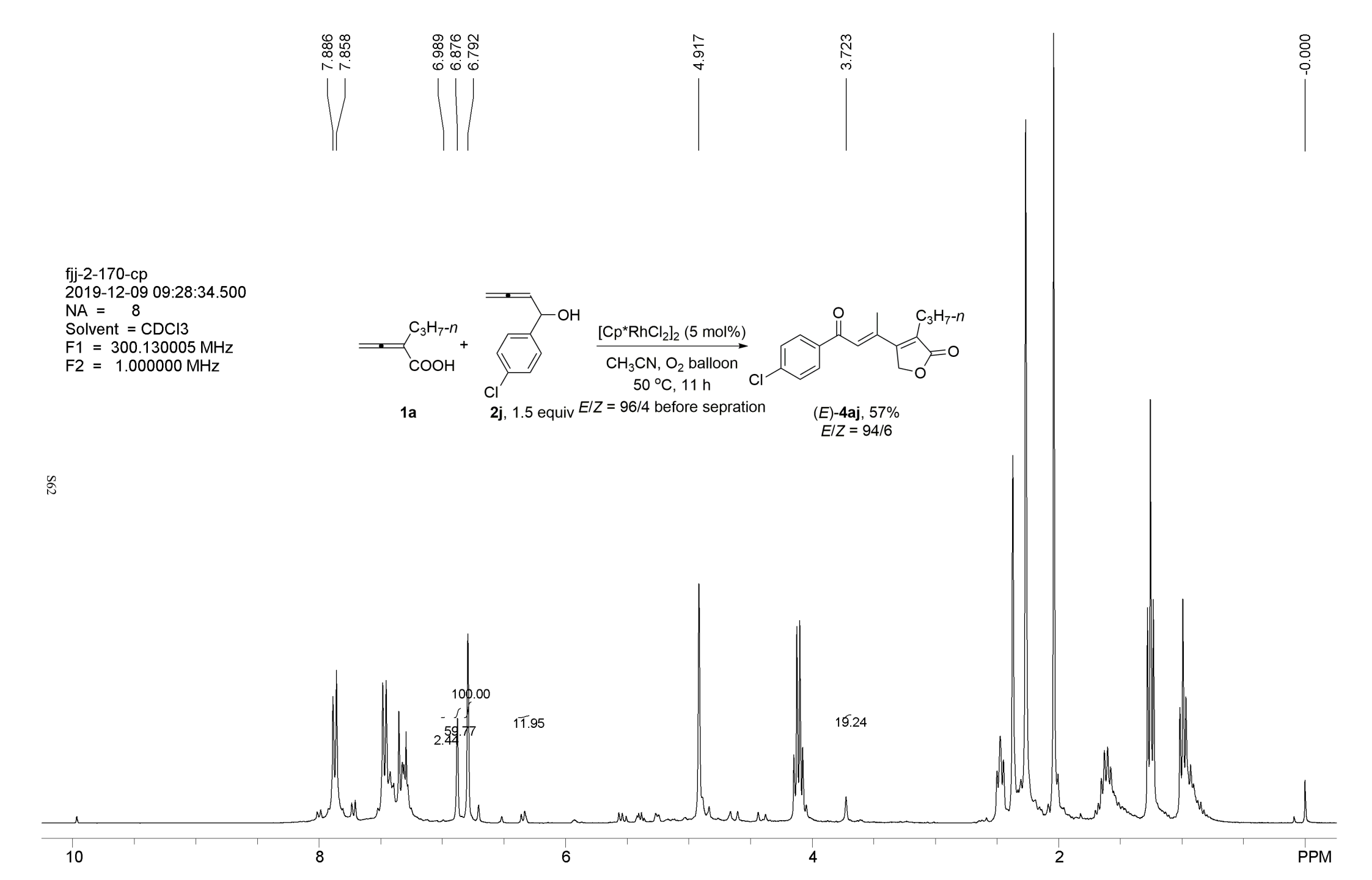
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 191031_fjj_2_073_0m - ellipsoid plot

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6.989
6.876
6.792
4.917
3.723
-0.000
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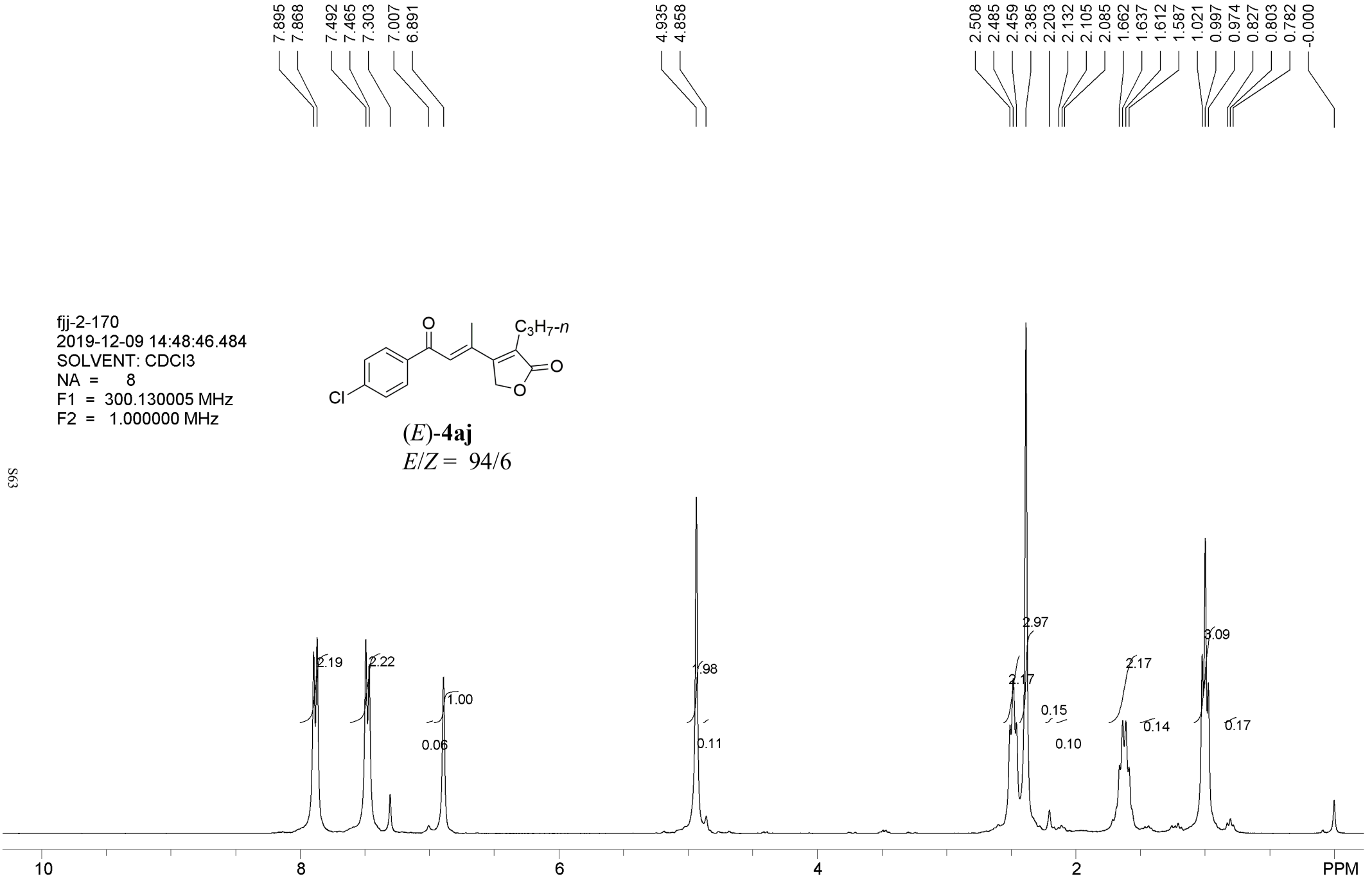
2019-12-09 09:28:34.500
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C3H7-n
COOH
OH
Cl
[Cp*RhCl2]2 (5 mol%)
CH3CN, O2 balloon
50 °C, 11 h
O
C3H7-n
O
O
Cl
1a
2j, 1.5 equiv E/Z = 96/4 before sepration
(E)-4aj, 57%
E/Z = 94/6
S62
100.00
59.77
2.42
11.95
19.24
10
8
6
4
2
PPM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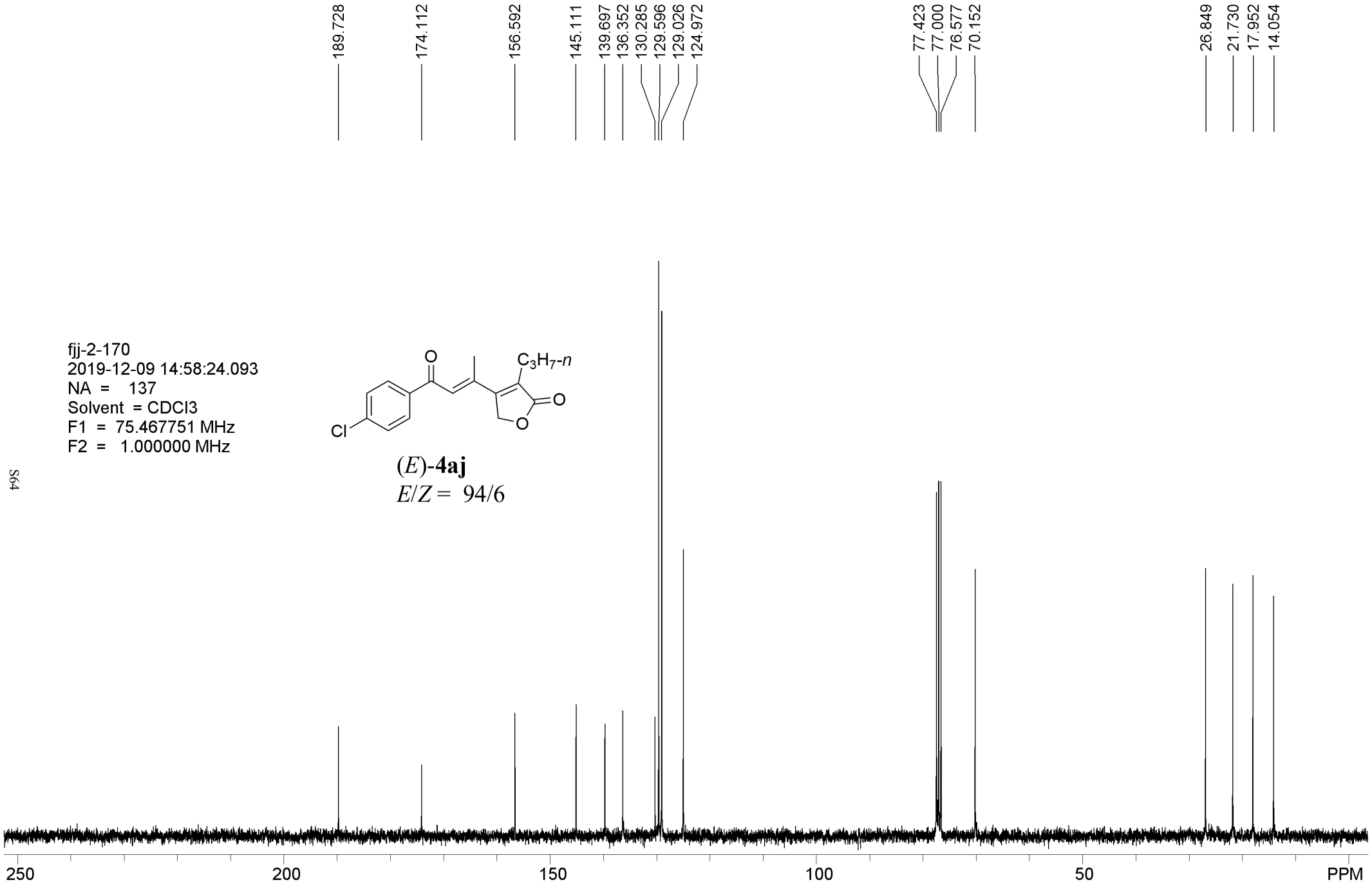
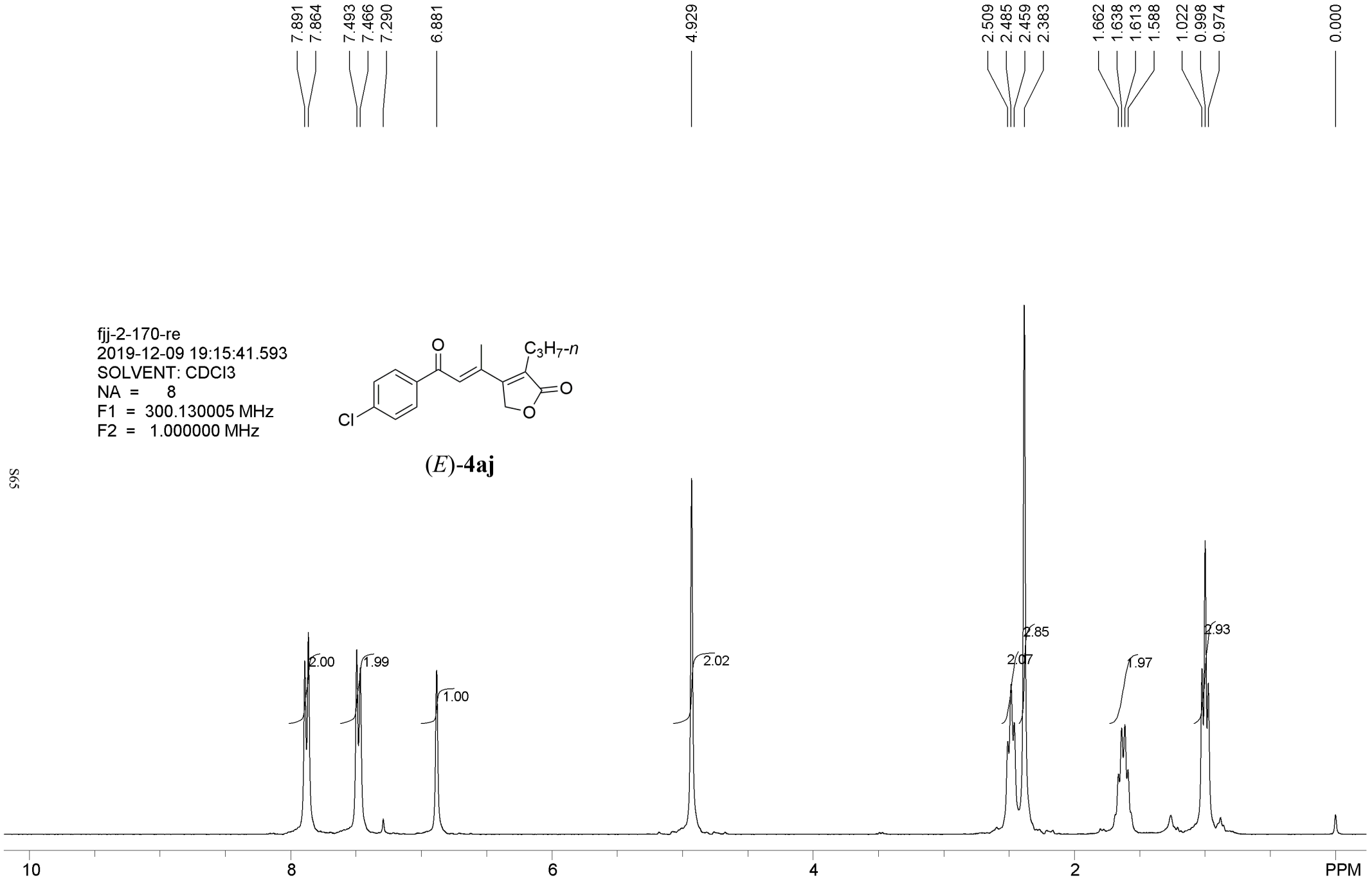
7.868
7.492
7.465
7.303
7.007
6.891
4.935
4.858
2.508
2.485
2.459
2.385
2.203
2.132
2.105
2.085
1.662
1.637
1.612
1.587
1.021
0.997
0.974
0.827
0.803
0.782
-0.000
fjj-2-170
2019-12-09 14:48:46.484
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
Cl
O
(E)-4aj
E/Z = 94/6
2.19
2.22
1.00
0.06
1.98
0.11
2.97
2.17
0.15
0.10
2.17
0.14
3.09
0.17
10
8
6
4
2
PPM


189.728
174.112
156.592
145.111
139.697
136.352
130.285
129.596
129.026
124.972
77.423
77.000
76.577
70.152
26.849
21.730
17.952
14.054
fjj-2-170
2019-12-09 14:58:24.093
NA = 137
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
Cl
O
250
200
150
100
50
PPM

(*E*)-**4aj**

E/*Z* = 94/6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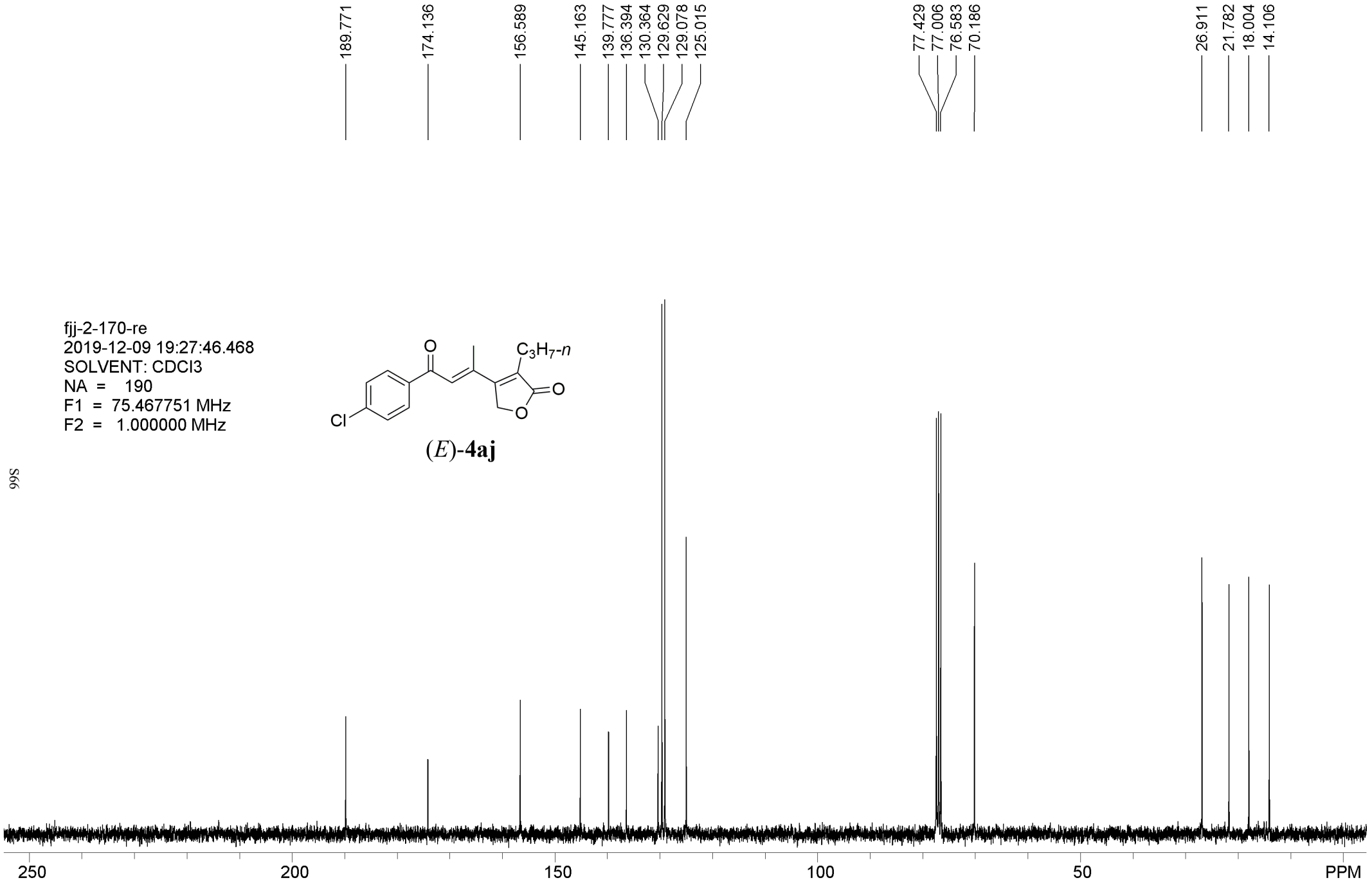
7.864
7.493
7.466
7.290
6.881
4.929
2.509
2.485
2.459
2.383
1.662
1.638
1.613
1.588
1.022
0.998
0.974
0.000
fjj-2-170-re
2019-12-09 19:15:41.593
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
Cl
O
2.00
1.99
1.00
2.02
2.85
2.07
1.97
2.93
10
8
6
4
2
PPM

(*E*)-**4aj**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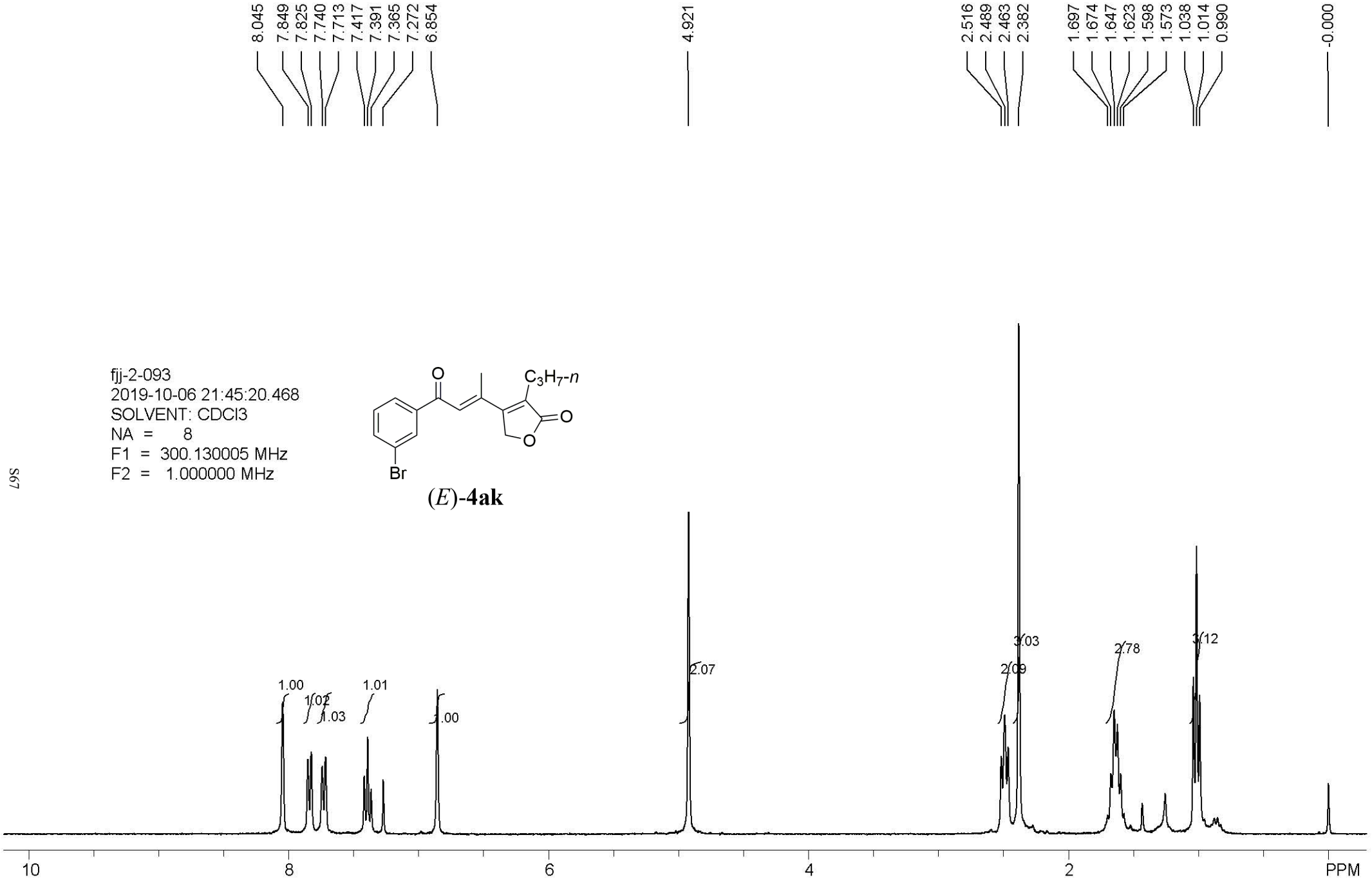
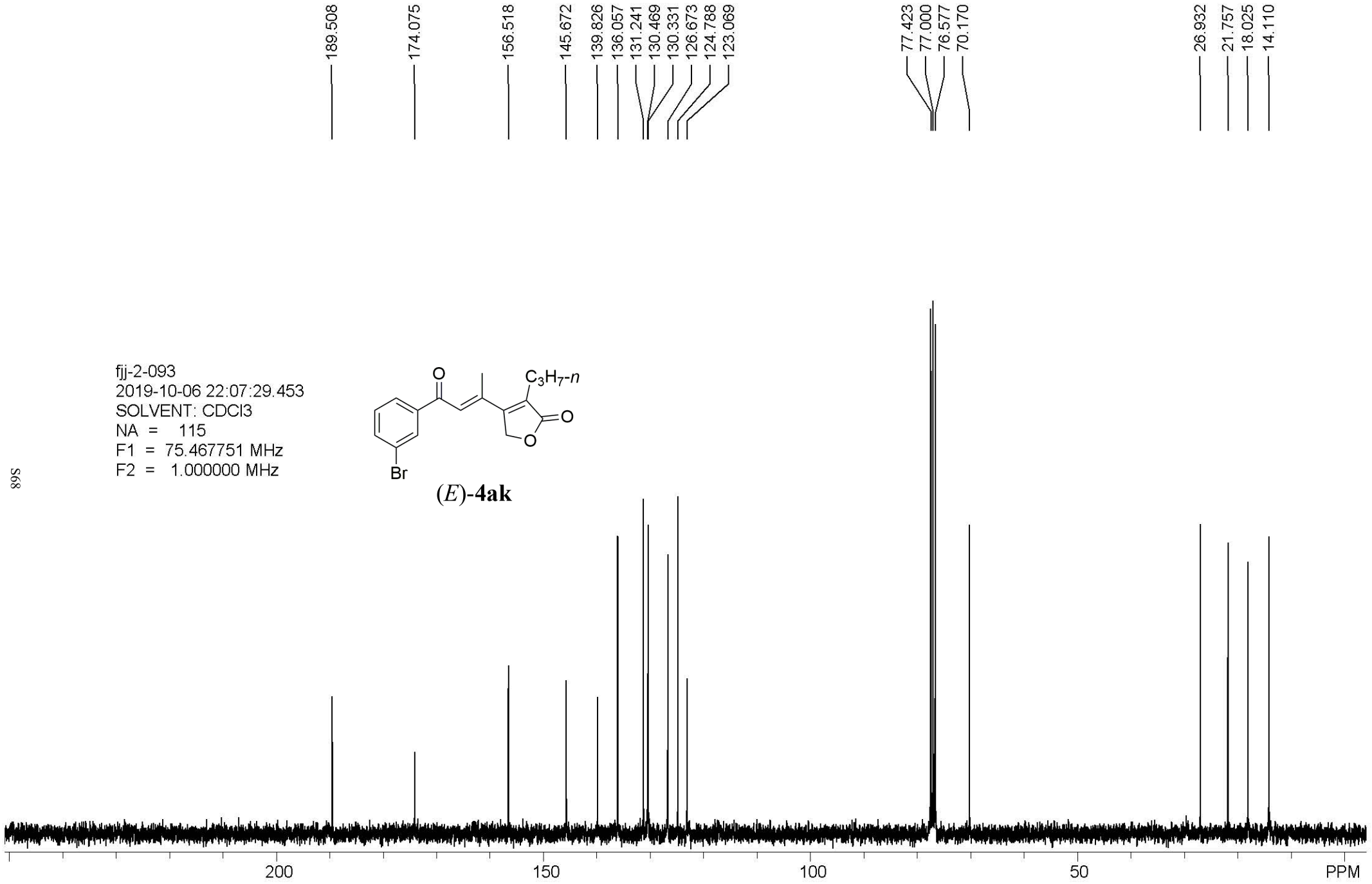
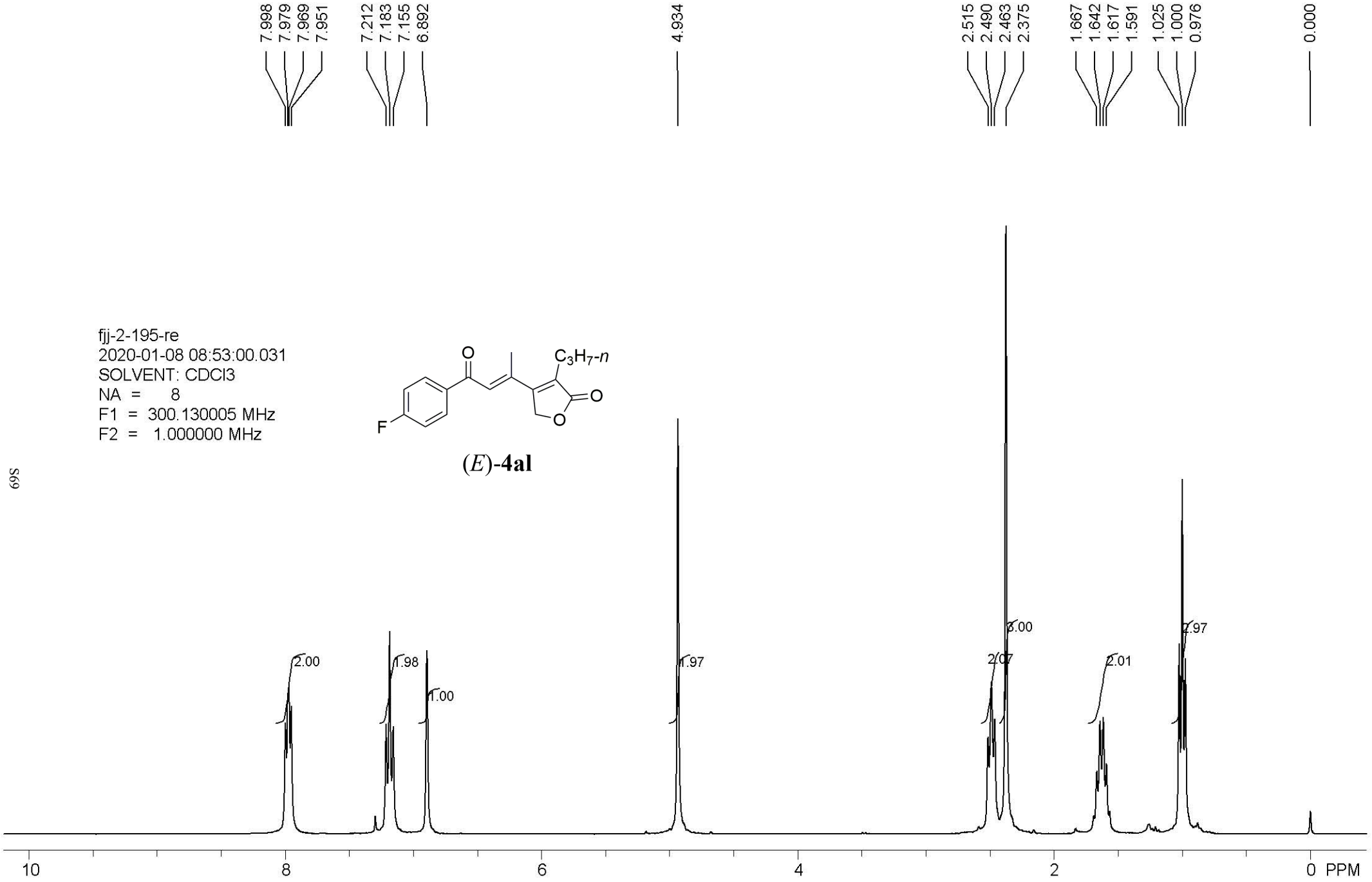
174.136
156.589
145.163
139.777
136.394
130.364
129.629
129.078
125.015
77.429
77.006
76.583
70.186
26.911
21.782
18.004
14.106
fjj-2-170-re
2019-12-09 19:27:46.468
SOLVENT: CDCl3
NA = 190
F1 = 75.467751 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
O
Cl
250
200
150
100
50
PPM

(*E*)-**4aj**


8.045
7.849
7.825
7.740
7.713
7.417
7.391
7.365
7.272
6.854
4.921
2.516
2.489
2.463
2.382
1.697
1.674
1.647
1.623
1.598
1.573
1.038
1.014
0.990
-0.000
fjj-2-093
2019-10-06 21:45:20.468
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
O
Br
(E)-4ak
1.00
1.02
1.03
1.01
1.00
2.07
3.03
2.09
2.78
3.12
10
8
6
4
2
PPM


189.508
174.075
156.518
145.672
139.826
136.057
131.241
130.469
130.331
126.673
124.788
123.069
77.423
77.000
76.577
70.170
26.932
21.757
18.025
14.110
fjj-2-093
2019-10-06 22:07:29.453
SOLVENT: CDCl3
NA = 115
F1 = 75.467751 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
O
Br
(E)-4ak
200
150
100
50
PPM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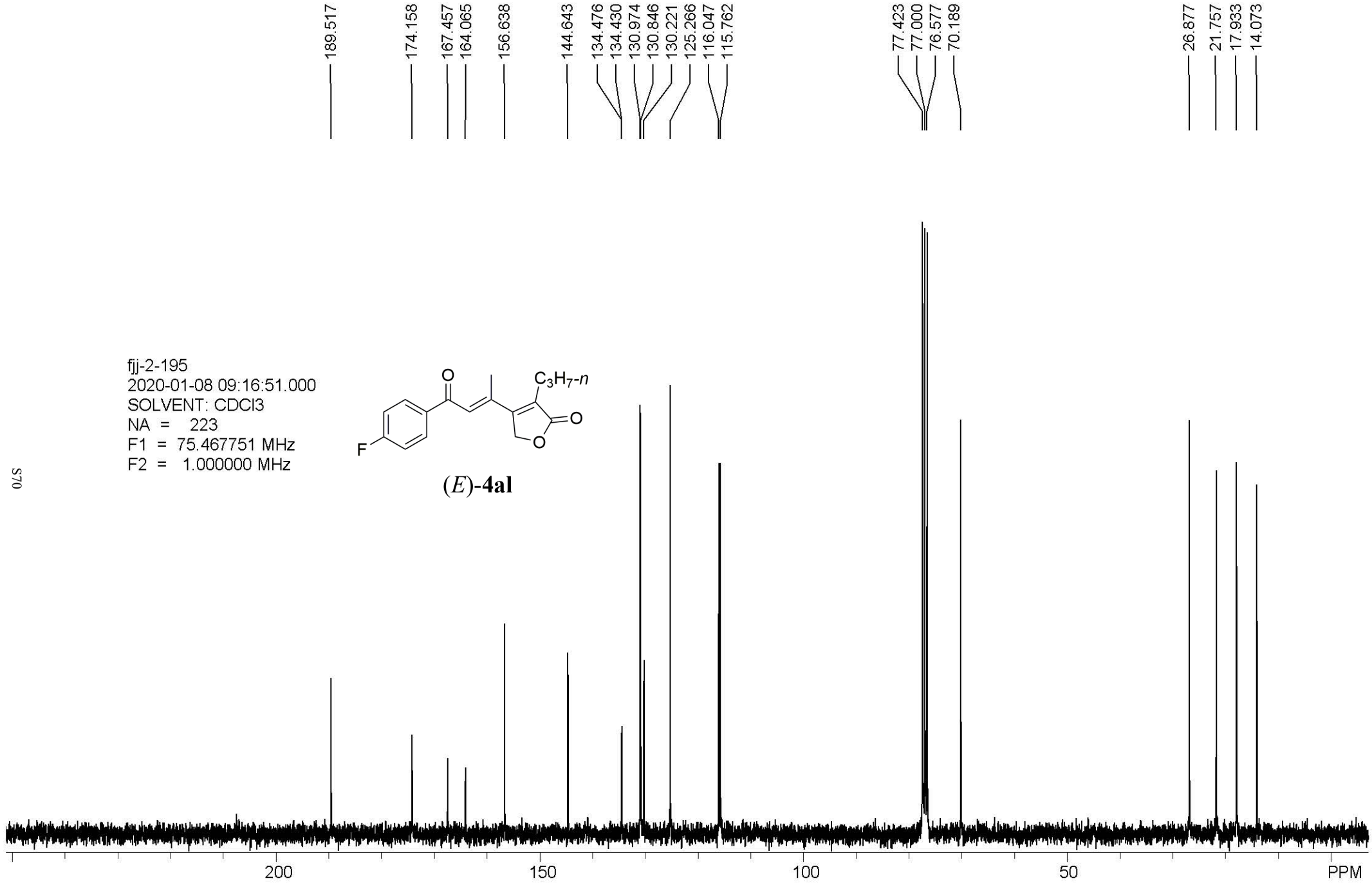
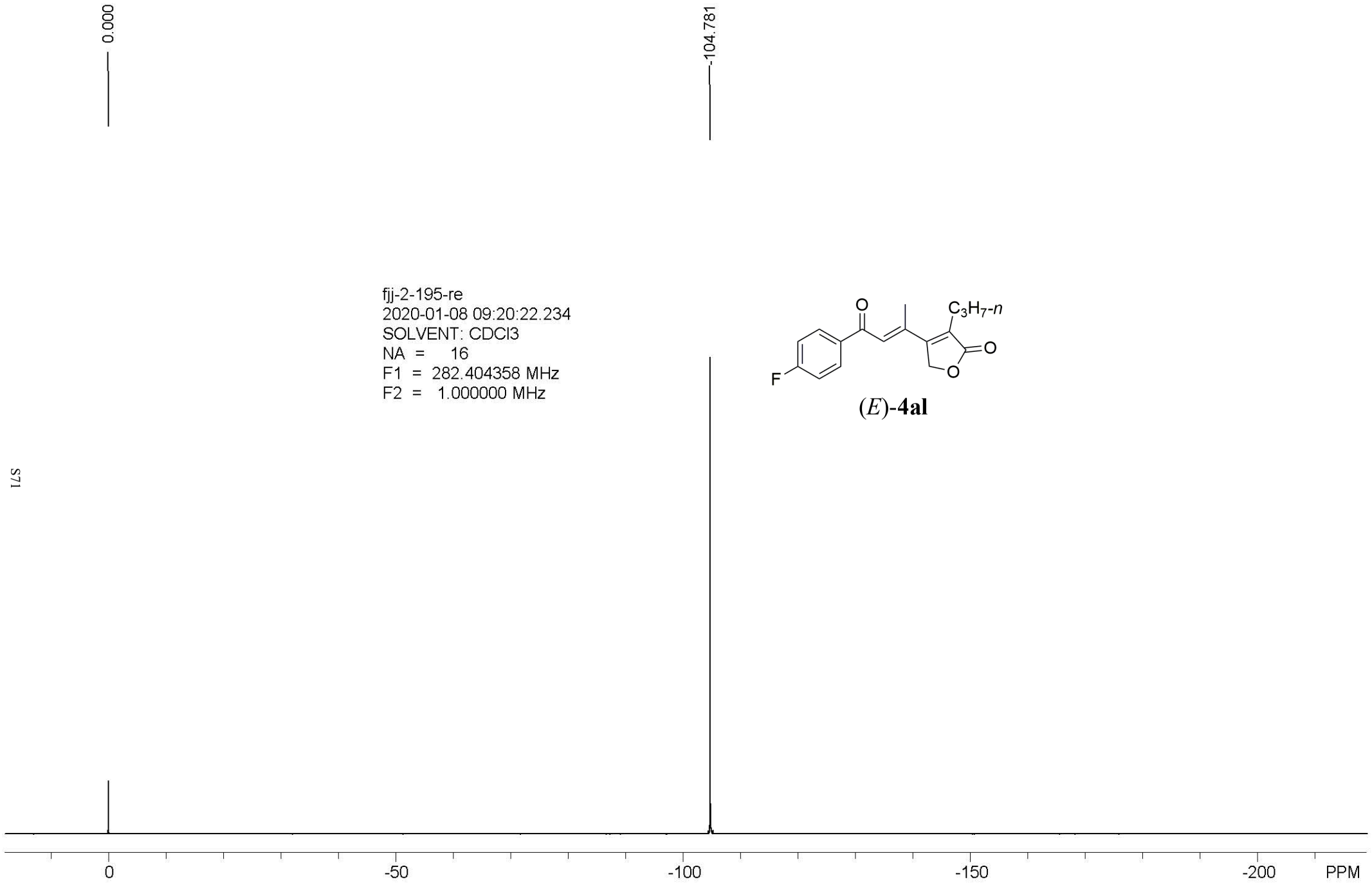
7.979
7.969
7.951
7.212
7.183
7.155
6.892
4.934
2.515
2.490
2.463
2.375
1.667
1.642
1.617
1.591
1.025
1.000
0.976
0.000
fjj-2-195-re
2020-01-08 08:53:00.031
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
F
O
2.00
1.98
1.00
1.97
3.00
2.07
2.01
2.97
10
8
6
4
2
0 PPM

(*E*)-**4al**


189.517
174.158
167.457
164.065
156.638
144.643
134.476
134.430
130.974
130.846
130.221
125.266
116.047
115.762
77.423
77.000
76.577
70.189
26.877
21.757
17.933
14.073
fjj-2-195
2020-01-08 09:16:51.000
SOLVENT: CDCl3
NA = 223
F1 = 75.467751 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
F
O
200
150
100
50
PPM

(*E*)-**4al**


0.000
-104.781
fjj-2-195-re
2020-01-08 09:20:22.234
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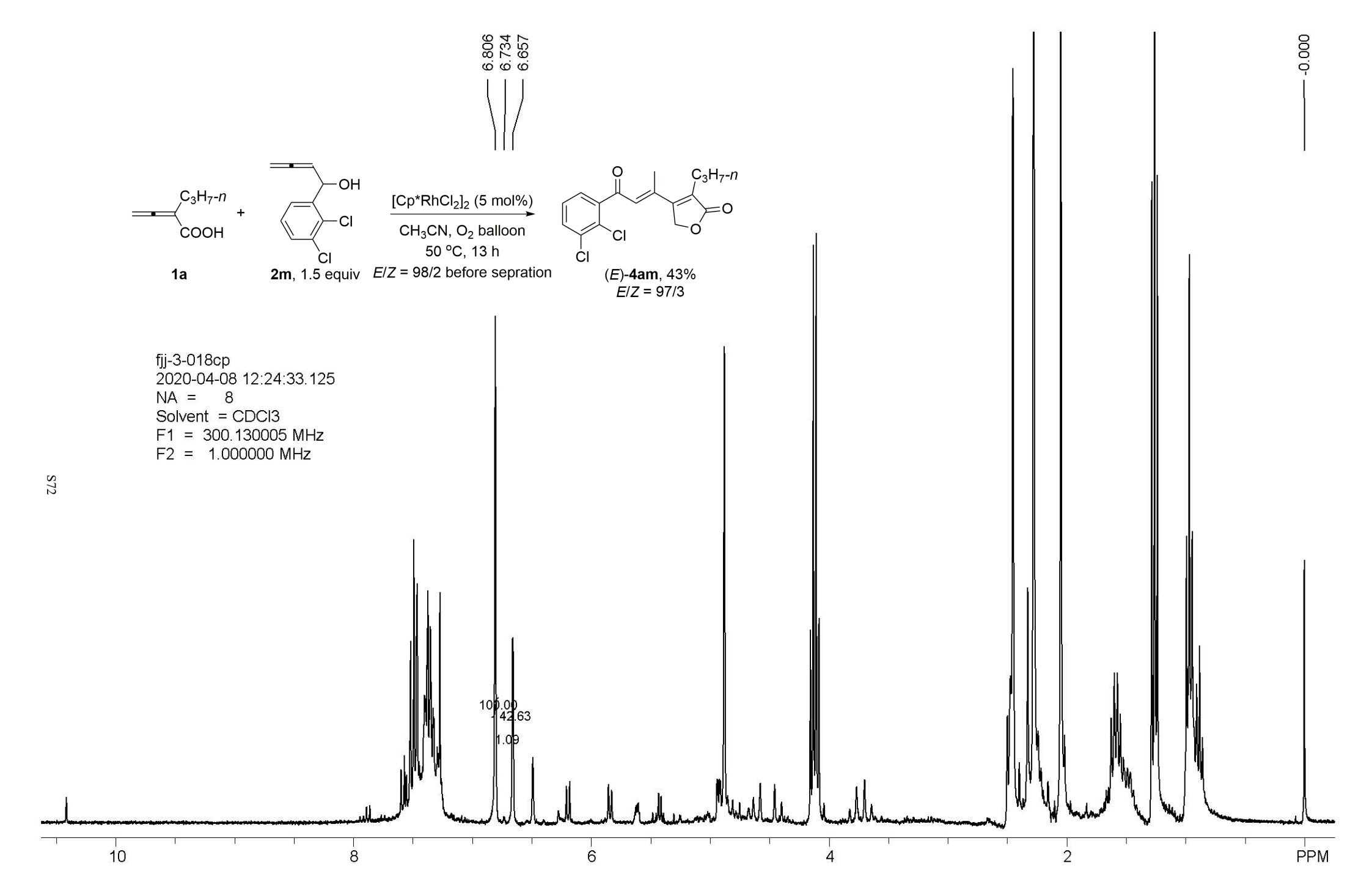
NA = 16
F1 = 282.404358 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
F
O
0
-50
-100
-150
-200
PPM

(*E*)-**4al**


6.806
6.734
6.657
-0.000
C3H7-n
COOH
1a
+
OH
Cl
Cl
2m, 1.5 equiv
[Cp*RhCl2]2 (5 mol%)
CH3CN, O2 balloon
50 °C, 13 h
E/Z = 98/2 before sepration
O
C3H7-n
O
O
Cl
Cl
(E)-4am, 43%
E/Z = 97/3
fjj-3-018cp
2020-04-08 12:24:33.125
NA = 8
Solvent = CDCl3
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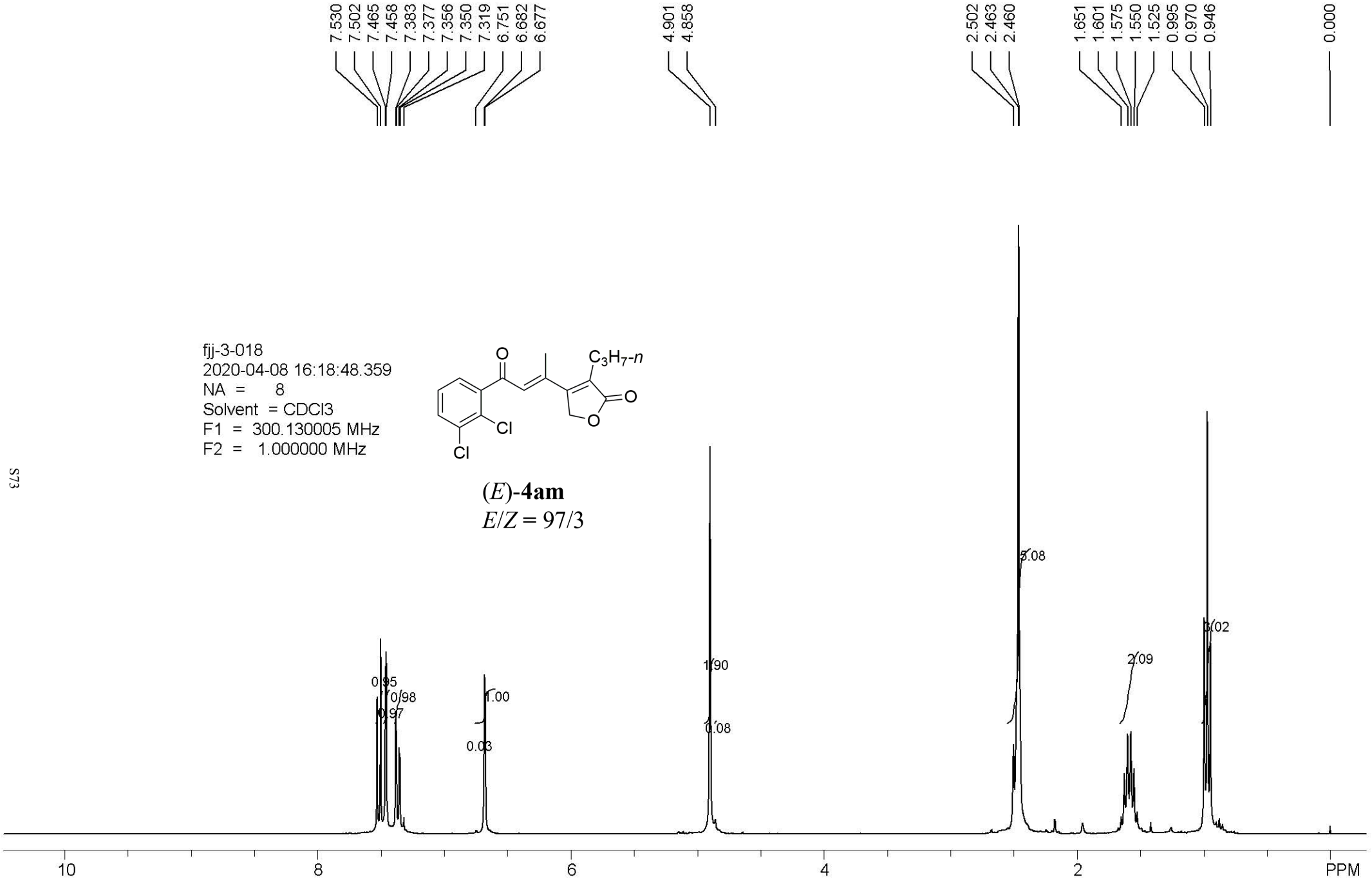
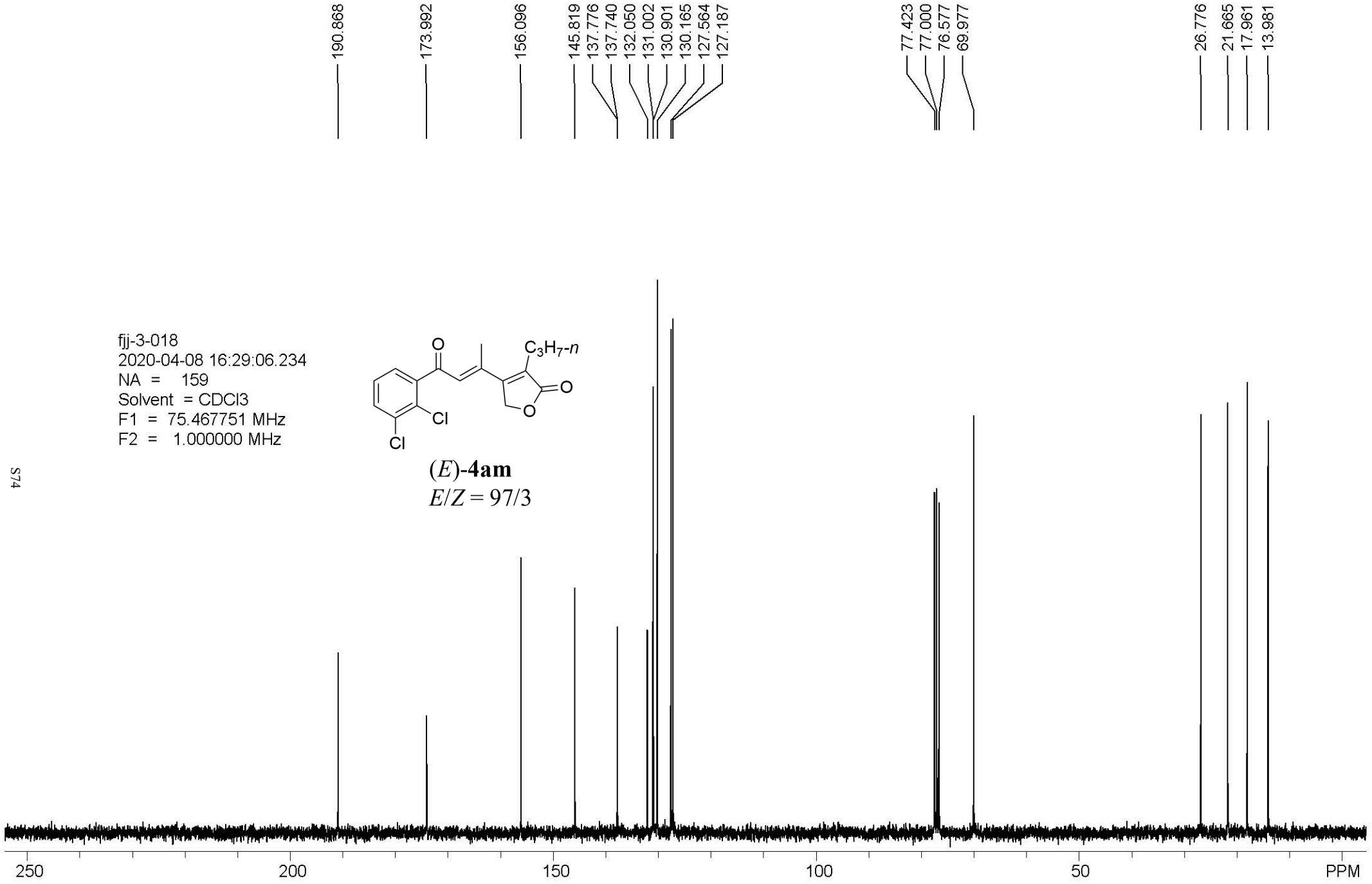
F2 = 1.000000 MHz
100.00
42.63
1.09
10
8
6
4
2
PPM


7.530
7.502
7.465
7.458
7.383
7.377
7.356
7.350
7.319
6.751
6.682
6.677
4.901
4.858
2.502
2.463
2.460
1.651
1.601
1.575
1.550
1.525
0.995
0.970
0.946
0.000
fjj-3-018
2020-04-08 16:18:48.359
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
O
Cl
Cl
0.95
0.98
0.97
1.00
0.03
1.90
0.08
5.08
2.09
3.02
10
8
6
4
2
PPM

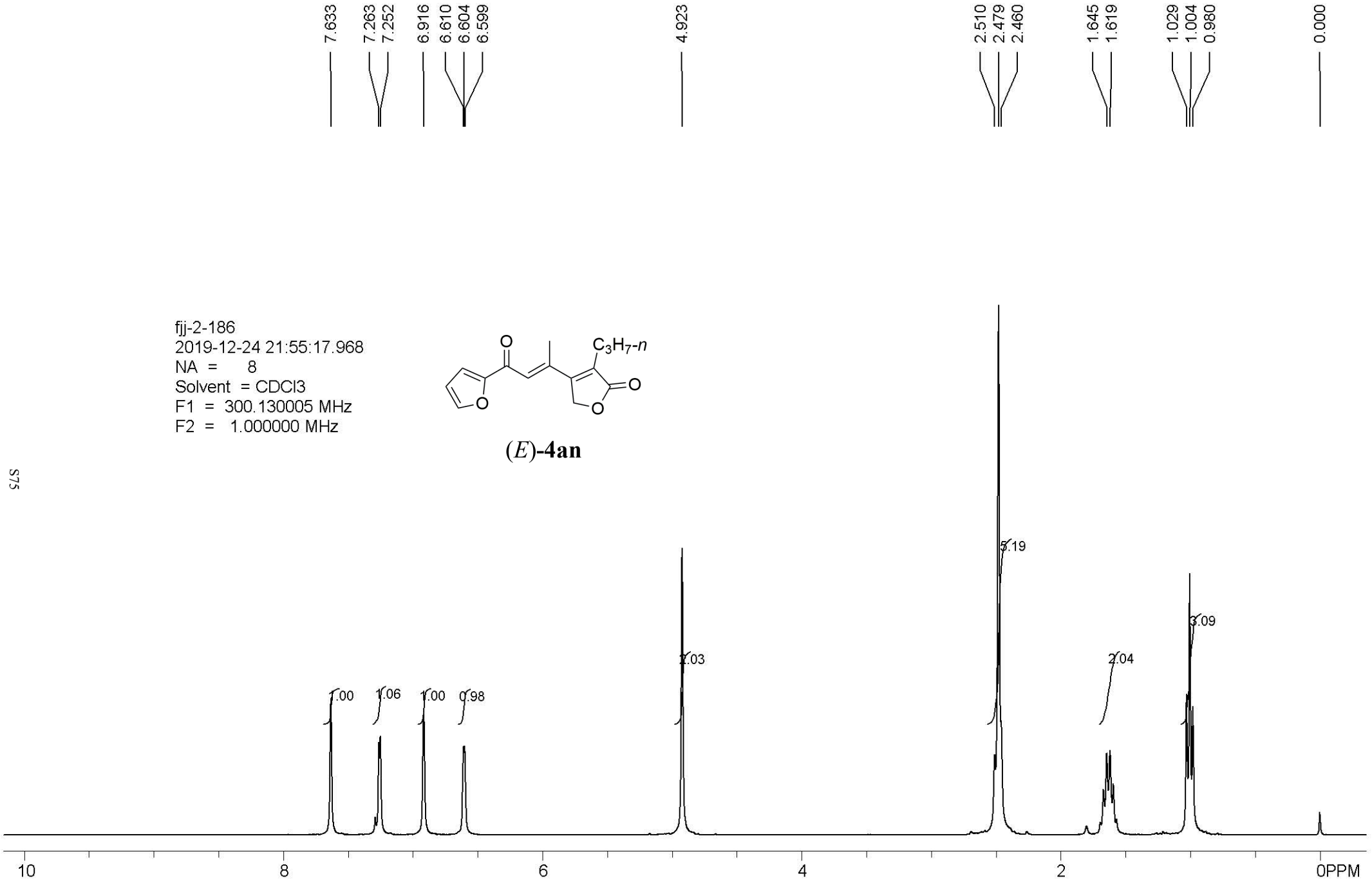
(*E*)-**4am**

E/*Z* = 97/3


190.868
173.992
156.096
145.819
137.776
137.740
132.050
131.002
130.901
130.165
127.564
127.187
77.423
77.000
76.577
69.977
26.776
21.665
17.961
13.981
fjj-3-018
2020-04-08 16:29:06.234
NA = 159
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
O
Cl
Cl
250
200
150
100
50
PPM

(*E*)-4am

$E/Z = 97/3$


7.633
7.263
7.252
6.916
6.610
6.604
6.599
4.923
2.510
2.479
2.460
1.645
1.619
1.029
1.004
0.980
0.000
fjj-2-186
2019-12-24 21:55:17.968
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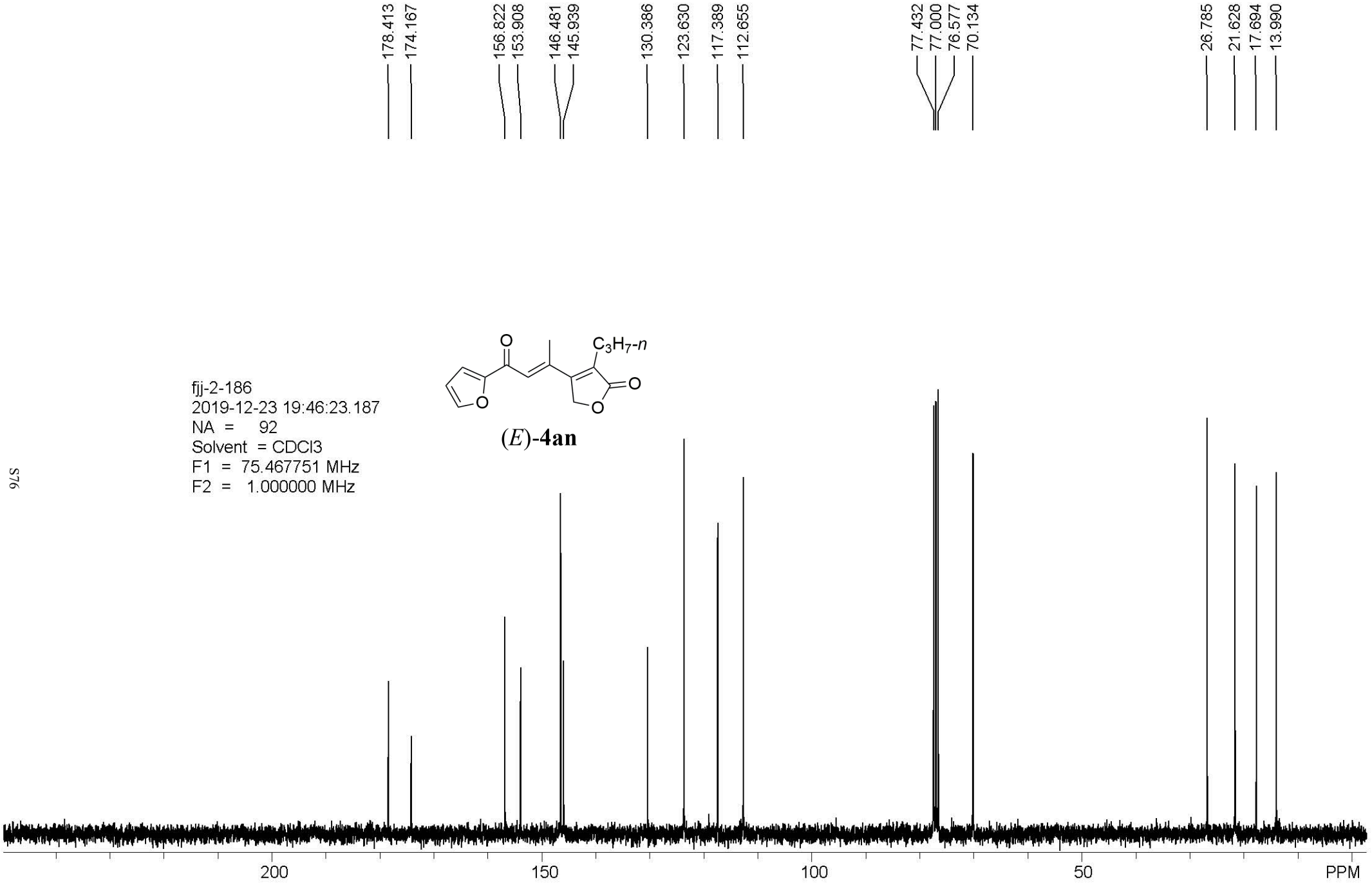
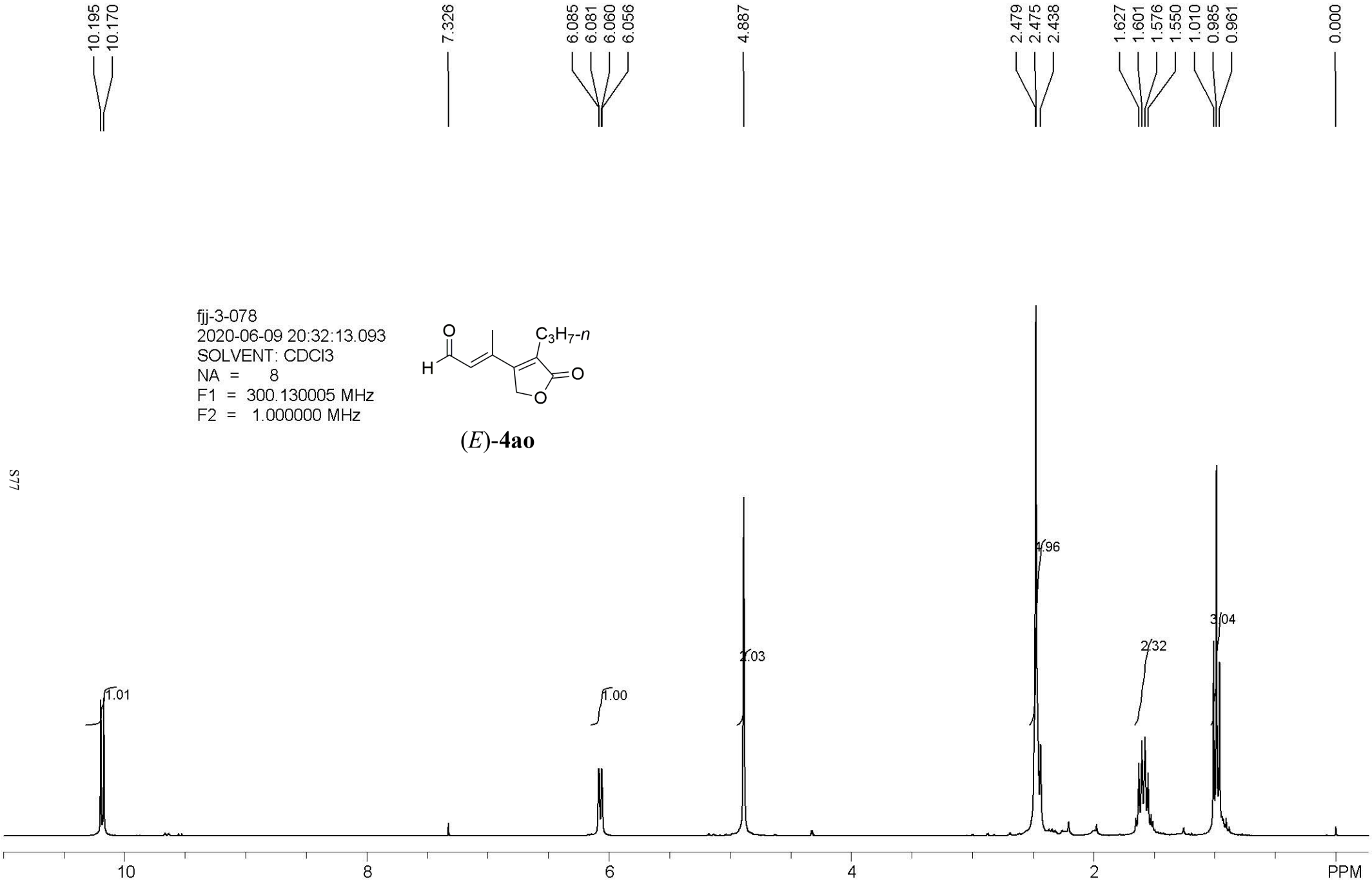
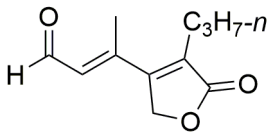
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
O
O
(E)-4an
1.00
1.06
1.00
0.98
2.03
5.19
2.04
3.09
10
8
6
4
2
0PPM


178.413
174.167
156.822
153.908
146.481
145.939
130.386
123.630
117.389
112.655
77.432
77.000
76.577
70.134
26.785
21.628
17.694
13.990
O
C3H7-n
O
O
O
fjj-2-186
2019-12-23 19:46:23.187
NA = 92
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
200
150
100
50
PPM

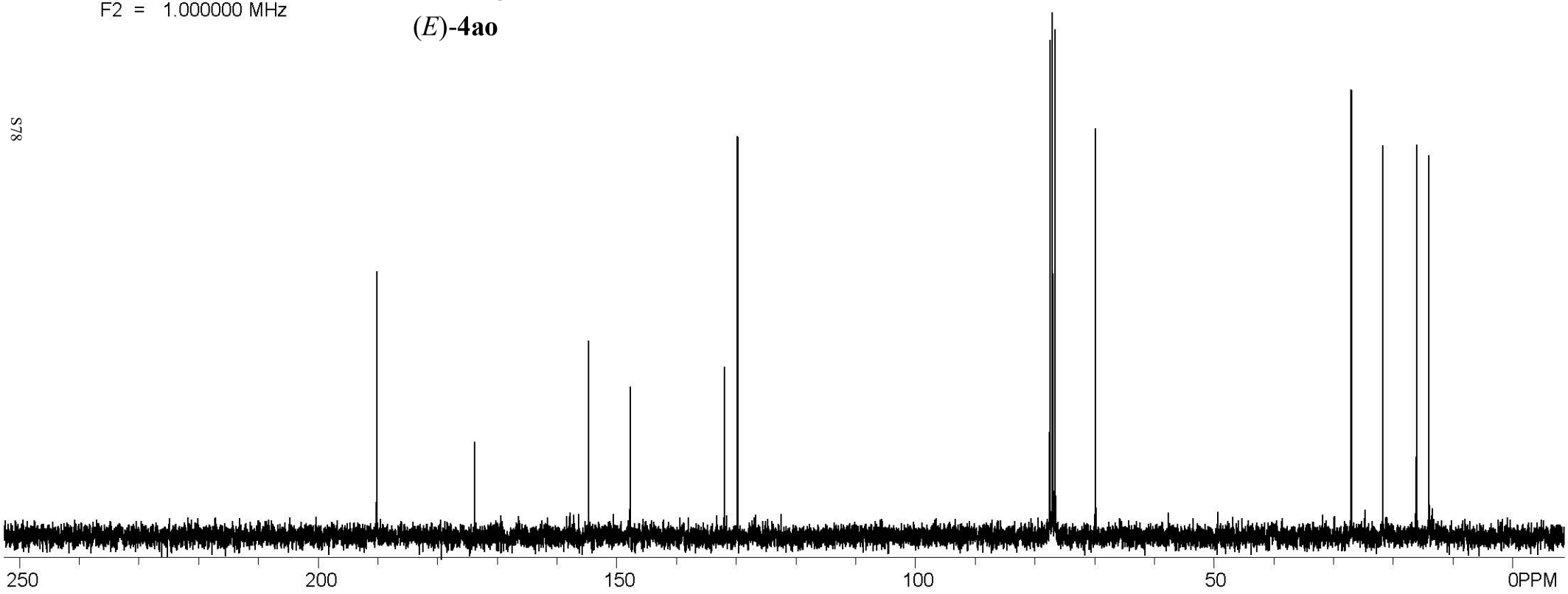
(*E*)-**4an**

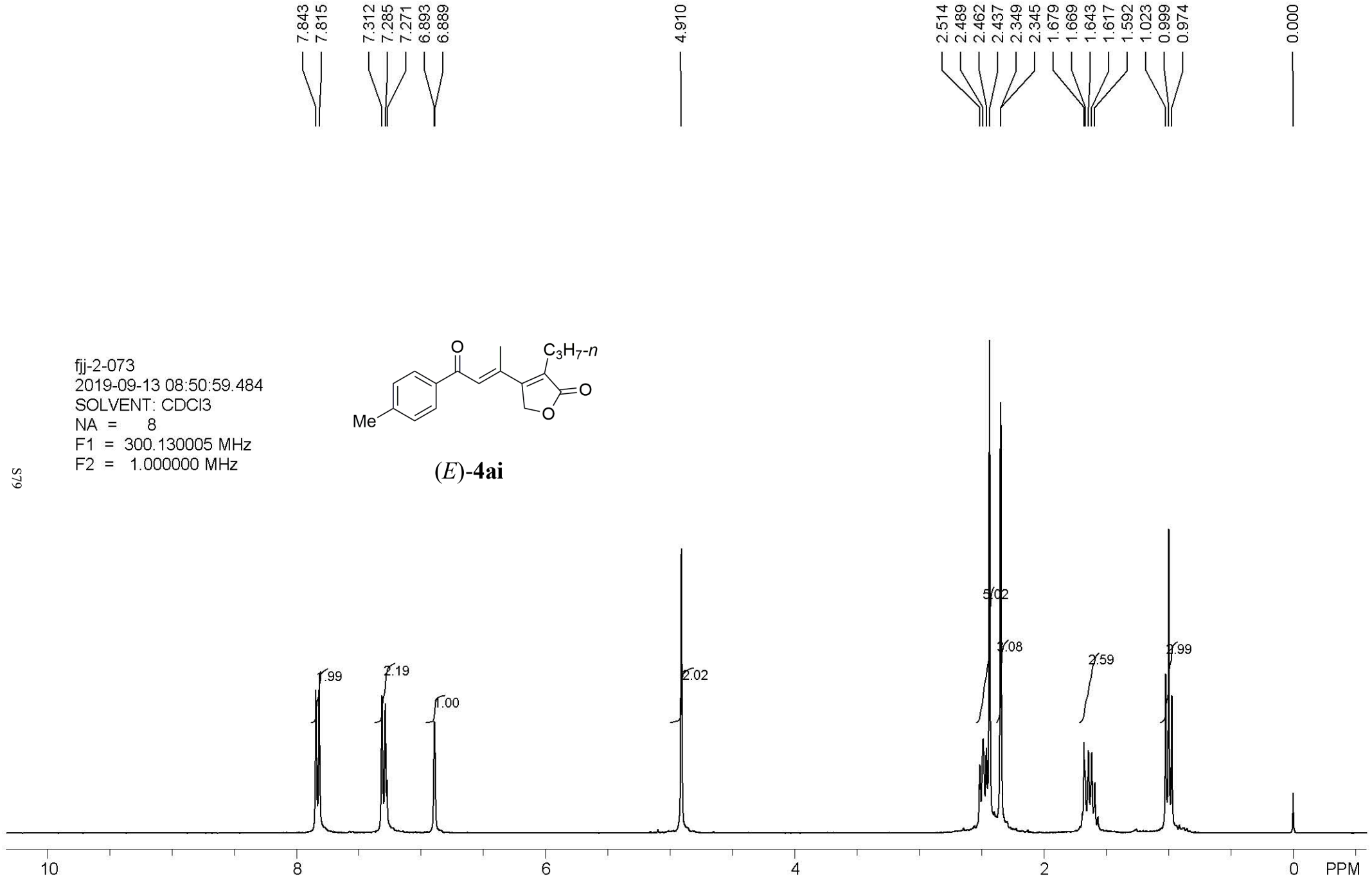

10.195
10.170
7.326
6.085
6.081
6.060
6.056
4.887
2.479
2.475
2.438
1.627
1.601
1.576
1.550
1.010
0.985
0.961
0.000
fjj-3-078
2020-06-09 20:32:13.093
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
H
C3H7-n
O
O
(E)-4ao
S77
1.01
1.00
2.03
4.96
2.32
3.04
10
8
6
4
2
PPM

fjj-3-078
2020-06-09 19:31:47.359
SOLVENT: CDCl3
NA = 72
F1 = 75.467751 MHz
F2 = 1.000000 MHz

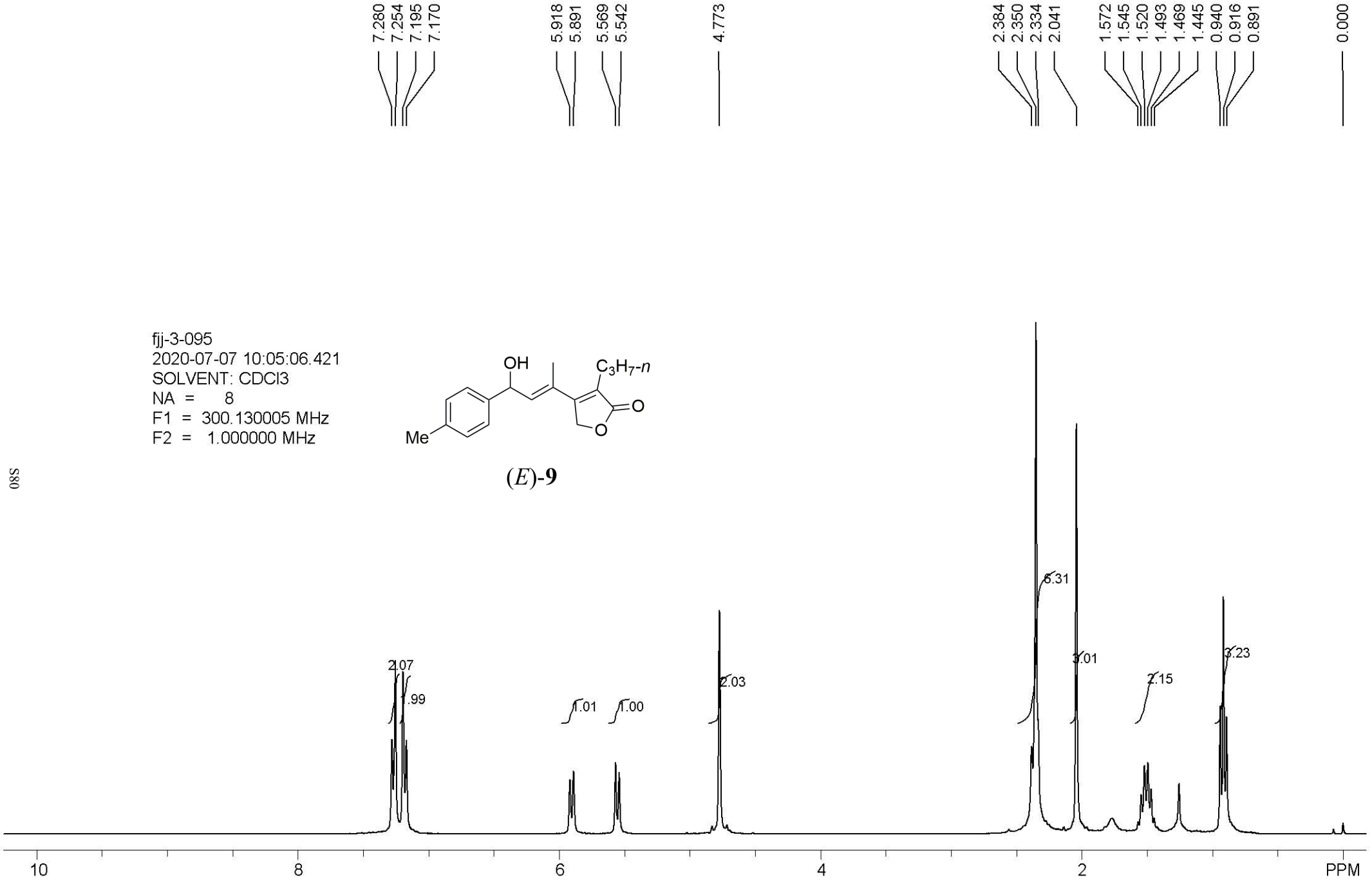


(*E*)-**4ao**

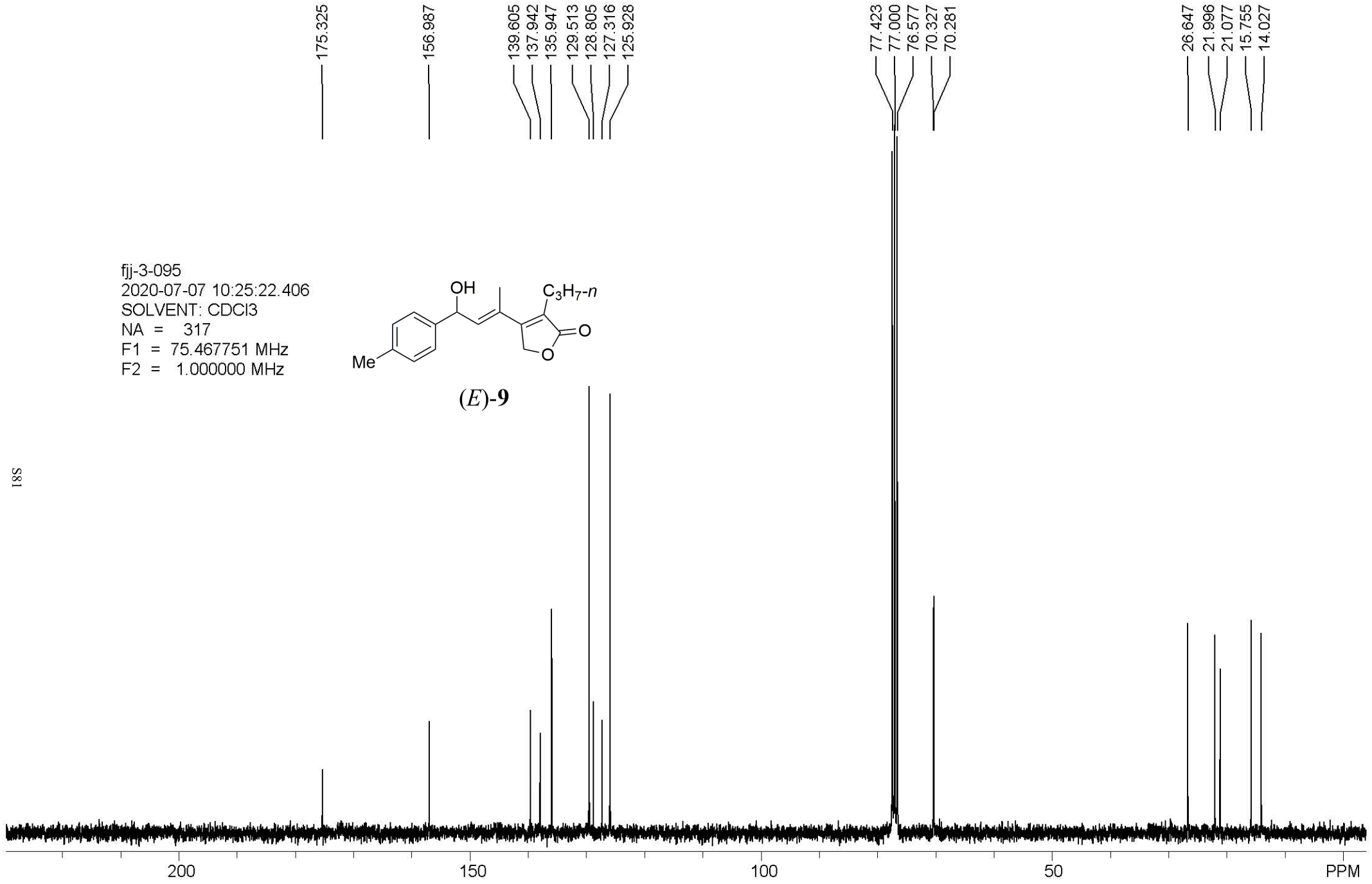



7.843
7.815
7.312
7.285
7.271
6.893
6.889
4.910
2.514
2.489
2.462
2.437
2.349
2.345
1.679
1.669
1.643
1.617
1.592
1.023
0.999
0.974
0.000
fjj-2-073
2019-09-13 08:50:59.484
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
C3H7-n
O
Me
O
1.99
2.19
1.00
2.02
5.02
3.08
2.59
2.99
10
8
6
4
2
0
PPM

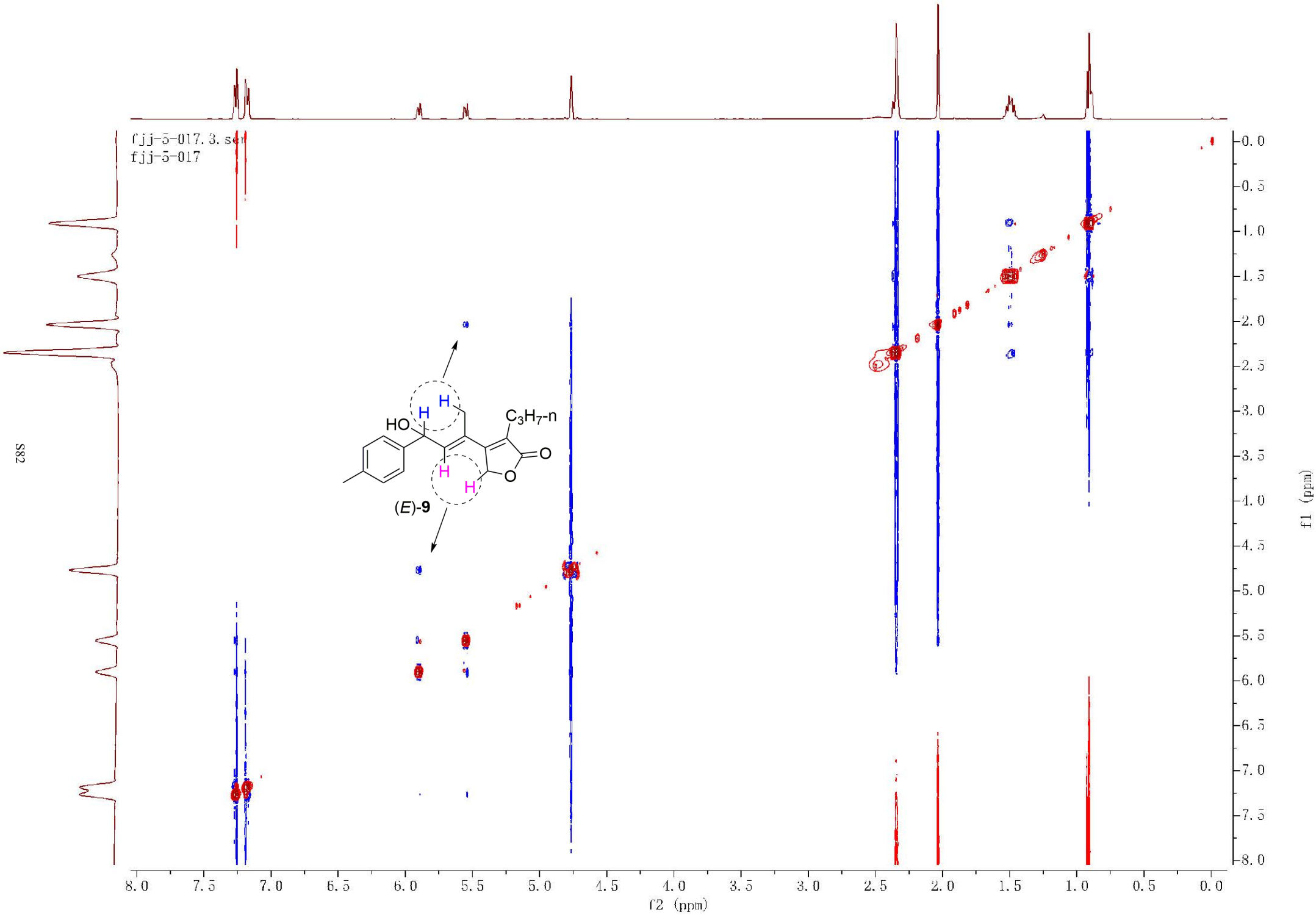
(*E*)-**4ai**

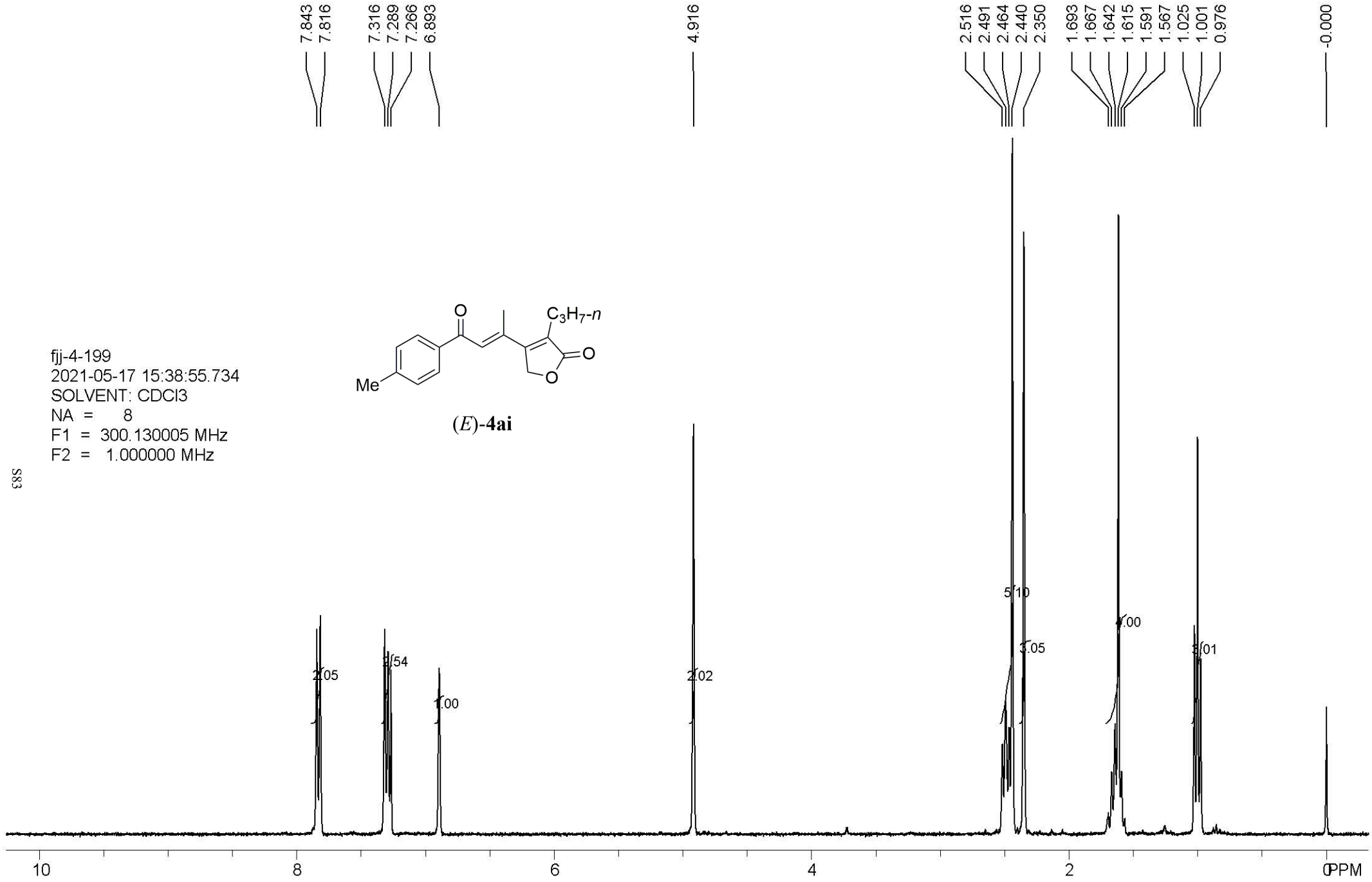

7.280
7.254
7.195
7.170
5.918
5.891
5.569
5.542
4.773
2.384
2.350
2.334
2.041
1.572
1.545
1.520
1.493
1.469
1.445
0.940
0.916
0.891
0.000
fjj-3-095
2020-07-07 10:05:06.421
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
OH
C3H7-n
O
O
Me
2.07
1.99
1.01
1.00
2.03
6.31
3.01
2.15
3.23
10
8
6
4
2
PPM

(*E*)-**9**

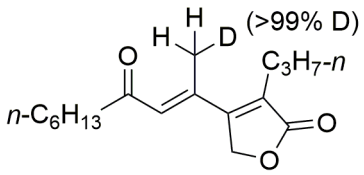

175.325
156.987
139.605
137.942
135.947
129.513
128.805
127.316
125.928
77.423
77.000
76.577
70.327
70.281
26.647
21.996
21.077
15.755
14.027
fjj-3-095
2020-07-07 10:25:22.406
SOLVENT: CDCl3
NA = 317
F1 = 75.467751 MHz
F2 = 1.000000 MHz
OH
C3H7-n
O
O
Me
200
150
100
50
PPM

(*E*)-**9**

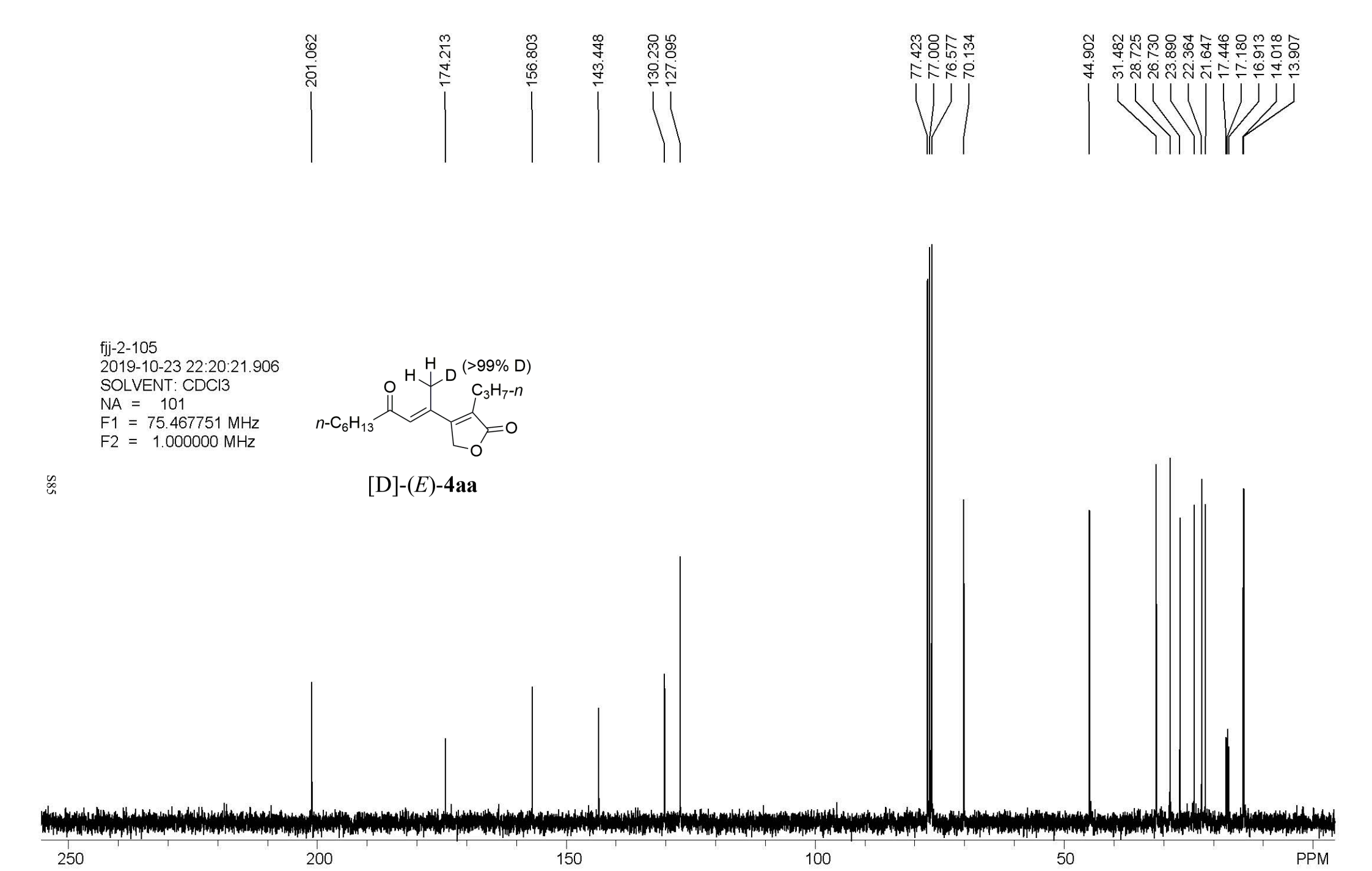

fjj-5-017.3.se
fjj-5-017
S82
HO
H
H
H
H
O
O
C_3H_7-n
(*E*)-**9**
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)


7.843
7.816
7.316
7.289
7.266
6.893
4.916
2.516
2.491
2.464
2.440
2.350
1.693
1.667
1.642
1.615
1.591
1.567
1.025
1.001
0.976
-0.000
fjj-4-199
2021-05-17 15:38:55.734
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
S83
O
C3H7-n
O
Me
O
(E)-4ai
2.05
3.54
1.00
2.02
5.10
3.05
4.00
3.01
10
8
6
4
2
0
PPM

fjj-2-105
2019-11-04 20:46:28.390
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz



[D]-(*E*)-**4aa**


201.062
174.213
156.803
143.448
130.230
127.095
77.423
77.000
76.577
70.134
44.902
31.482
28.725
26.730
23.890
22.364
21.647
17.446
17.180
16.913
14.018
13.907
fjj-2-105
2019-10-23 22:20:21.906
SOLVENT: CDCl3
NA = 101
F1 = 75.467751 MHz
F2 = 1.000000 MHz
H
H
D
(>99% D)
O
C_3H_7-*n*
n-C_6H_{13}
O
O
250
200
150
100
50
PPM

[D]-(*E*)-**4aa**