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Aerobic Bimetallic Catalysis for Oxy-alkynylation of Allenes

Junjie Fan, [¶a] Dongjie Zhang, [¶a] Yaqi Shi,[a] Chunling Fu,[a] and Shengming Ma*[a]

[a] Laboratory of Molecular Recognition and Synthesis, Department of Chemistry, Zhejiang University, Hangzhou 310027, Zhejiang, P. R. China. E-mail: masm@sioc.ac.cn

[¶] equal contribution

Supporting Information

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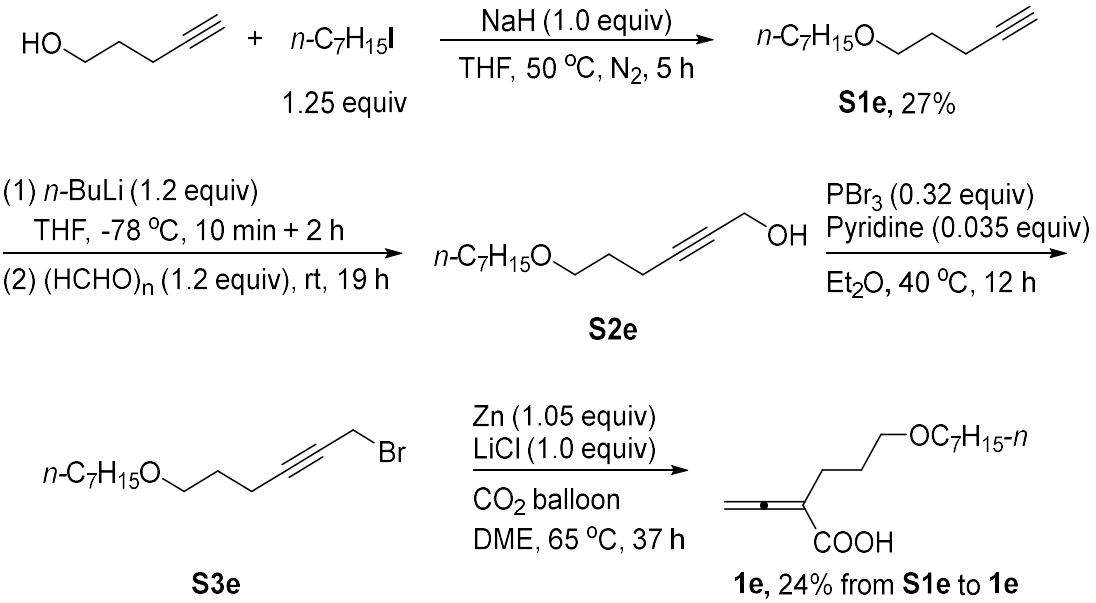
General Information

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded using a Bruker AM 300 MHz NMR spectrometer (^{1}H at 300 MHz, ^{13}C at 75 MHz, ^{19}F at 282 MHz) unless noted otherwise: 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; 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* and Laajoo. The range of boiling point of the petroleum ether used for chromatography was 60-90 ^{o}C unless noted otherwise. 2,3-Butadienoic acids **1a**-**1c**,[1] **1f** -**1p,**[1] **1d**,[2] and **1e**[2] were prepared according to the literature procedures. Other commercially available reagents were purchased and used as received.

1 Synthesis of Starting Materials

1.1 Synthesis of 2-(3-heptyloxypropyl)-2,3-butadienoic acid **1e**.[2] (fjj-2-123, fjj-2-139, fjj-2-143, and fjj-4-093)



To an over dried three-necked flask were added NaH (3.2733 g, 60% dispersion in mineral oil, 81.8 mmol), THF (100 mL), and 1-iodoheptane (16.8 mL, d = 1.3791 g/mL, 23.1689 g, 102.5 mmol) sequentially under N_2 atmosphere at room temperature. Then 4-pentynol (7.65 mL, d = 0.904 g/mL, 6.9156 g, 82.2 mmol) were added dropwise for 15 min at room temperature. The reaction was complete after stirring in an oil bath preheated at 50 °C for 5 h as monitored by TLC. The resulting mixture was cooled to room temperature, quenched with a saturated aqueous NH_4Cl solution, and extracted with ethyl ether (20 mL × 3). The combined organic extract was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude residual was purified via chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 50/1 (1500 mL)] to afford **S1e** (4.0305 g, 27%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.50 (t, J = 6.2 Hz, 2 H, OCH_2), 3.41 (t, J = 6.6 Hz, 2 H, OCH_2), 2.29 (td, J_1 = 7.0 Hz, J_2 = 2.4 Hz,

2 H, CH_2), 1.95 (t, J = 2.6 Hz, 1 H, ≡CH), 1.85-1.72 (m, 2 H, CH_2), 1.61-1.72 (m, 2 H, CH_2), 1.40-1.18 (m, 8 H, CH_2 × 2), 0.88 (t, J = 6.0 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 84.1, 71.1, 69.0, 68.3, 31.8, 29.7, 29.1, 28.6, 26.1, 22.6, 15.2, 14.1. **S1e** was used for the next step without further identification.

To an over dried three-necked flask were added **S1e** (3.9858 g, 21.7 mmol) and THF (80 mL) sequentially under N_2 atmosphere at room temperature. Then the resulting mixture was cooled to -78 °C. *n*-BuLi (13.0 mL, 2.5 M in hexane, 32.5 mmol) were added dropwise for 10 min at -78 °C. After being stirred for 2.5 h at -78 °C, and removing the ethanol bath, polyformaldehyde (990.0 mg, 33 mmol) was added under N_2 atmosphere. The reaction was complete after stirring for 19 h as monitored by TLC. The resulting mixture was quenched with a saturated aqueous NH_4Cl solution (50 mL) and HCl (3 M). After the separation of the organic phase, the aqueous phase was extracted with ethyl ether (30 mL × 3). The combined organic extract was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude residual was purified via chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 15/1 (500 mL) to 10/1 (1000 mL)] to afford **S2e** as a liquid (2.8011 g). **S2e** was used for the next step without further purification.

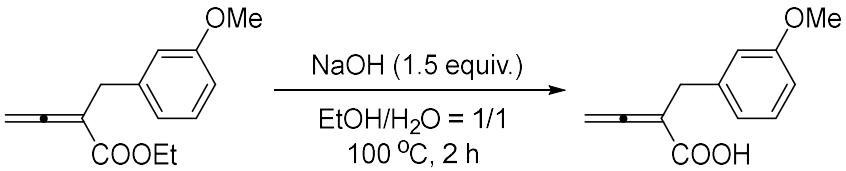
To an over dried three-necked flask were added **S2e** (2.7599 g) and Et_2O (15 mL). Then PBr_3 (0.4 mL, d = 2.85 g/mL, 1.14 g, 4.2 mmol,) and pyridine (36.0 mg, 0.46 mmol) were added dropwise sequentially. After being refluxed at 40 °C for 12 h, the resulting mixture was cooled to room temperature and then poured into an ice-water mixture (50 g). After the separation of the organic phase, the aqueous phase was

extracted with diethyl ether (30 mL × 3). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude residual was purified via chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 50/1 (800 mL)] to afford **S3e** as a liquid (3.2199 g). **S3e** was used for the next step without further purification.

To an over dried Schlenk tube were added zinc powder (590.0 mg) and anhydrous LiCl (365.0 mg, 8.6 mmol) sequentially under N_2 atmosphere. The Schlenk tube was then dried under vacuum with a heating gun. After cooling to room temperature, **S3e** (2.3600 g, 8.6 mmol) and DME (43 mL) were added sequentially under N_2 atmosphere. The resulting mixture was then frozen with a liquid nitrogen bath and the N_2 atmosphere was completely replaced with CO_2 via a balloon. After being thawed, the resulting mixture was put into an oil bath preheated at 65 ºC and stirred at 65 ºC for 37 h. The resulting mixture was quenched with an aqueous solution of HCl (3 M), and extracted with ethyl acetate (40 mL × 5). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residual was purified via chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 5/1 (600 mL)] to afford **1e** (0.9302 g, 24% from **S1e** to **1e**) as a solid, m.p. < 30 ºC (determined without recrystallization): ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.8 (bs, 1 H, COOH), 5.20 (t, J = 3.0 Hz, 2 H, =CH_2), 3.74-3.10 (m, 4 H, OCH_2 × 2), 2.45-2.15 (m, 2 H, CH_2), 1.84-1.65 (m, 2 H, CH_2), 1.64-1.48 (m, 2 H, CH_2), 1.43-1.15 (m, 8 H, CH_2 × 4), 0.88 (t, J = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.6, 172.6, 99.6, 79.4, 71.0, 69.8, 31.7, 29.6, 29.1, 27.8, 26.0, 24.4, 22.6, 14.0; IR (KBr) ν (cm^{-1}) 2936,

2852, 1961, 1921, 1676, 1465, 1419, 1378, 1287, 1270, 1244, 1116; MS (EI): *m*/*z* (%) 195 [(M-COOH)$^+$, 2.16), 57 (100); Anal. Calcd. for $C_{14}H_{24}O_3$ (%): C, 69.96; H, 10.07; Found: C, 70.01; H, 10.24.

1.2 Synthesis of 2-(3-methoxybenzyl)-2,3-butadienoic acid **1l**.[1] (zdj-1-118)

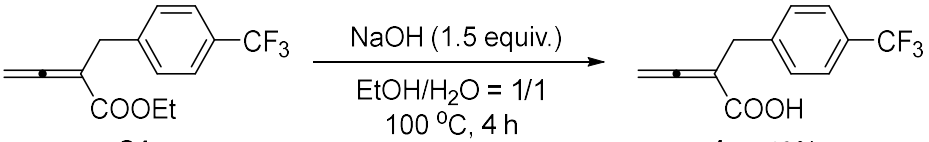


S1l **1l**, 54%

To a round bottomed flask equipped with a magnetic stirring bar were added 2-(3-methoxybenzyl)-2,3-butadienoic acid ethyl ester **S1l**[3] (2.9373 g, 12.6 mmol), EtOH (10 mL), H_2O (10 mL), and NaOH (0.7624 g, 19.1 mmol) sequentially. The reaction flask was then equipped with a condenser and put into an oil bath preheated at 100 °C. The reaction was complete after being stirred for 2 h at 100 °C as monitored by TLC. The resulting mixture was then cooled to room temperature, quenched with an aqueous solution of HCl (3 M), and extracted with ethyl acetate (20 mL × 5). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude residual was purified via chromatography on silica gel [eluent: dichloromethane (300 mL) to dichloromethane/methanol = 200/1 (800 mL), then 150/1 (900 mL)] to afford **1l** (1.3848 g, 54%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.63 (bs, 1 H, COOH), 7.18 (t, *J* = 7.8 Hz, 1 H, ArH), 6.92-6.68 (m, 3 H, ArH), 5.17 (t, *J* = 2.1 Hz, 2 H, =CH_2), 3.77 (s, 3 H, OCH_3), 3.51 (s, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.5, 172.7, 159.4, 140.2, 129.2, 121.1, 114.5, 111.7, 99.6,

79.5, 55.0, 34.3; IR (neat) ν (cm^{-1}) 3437-2538, 1963, 1929, 1683, 1600, 1585, 1490, 1465, 1455, 1435, 1384, 1287, 1263, 1152, 1048; MS (EI): *m*/*z* (%) 204 (M^+, 69.02), 159 (100); HRMS Calcd for $C_{12}H_{12}O_3$ (M^+): 204.0786; Found: 204.0786.

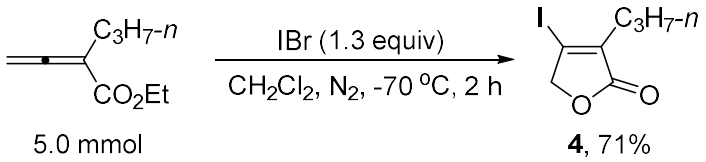
1.3 Synthesis of 2-(4-(trifluoromethyl)benzyl)-2,3-butadienoic acid **1m**.[1] (zdj-1-087)



To a round-bottom flask equipped with a magnetic stirring bar were added ethyl 2-(4-(trifluoromethyl)benzyl)buta-2,3-dienoic acid ethyl ester **S1m**[4] (1.4371 g, 5.3 mmol), EtOH (25 mL), H_2O (25 mL), and NaOH (0.3279 g, 8.2 mmol) sequentially. The reaction flask was then equipped with a condenser and put into an oil bath preheated at 100 °C. The reaction was complete after being stirred for 4 h at 100 °C as monitored by TLC. The resulting mixture was cooled to room temperature and quenched with an aqueous solution of HCl (3 M), and extracted with ethyl acetate (50 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude residual was purified by recrystallization (dichloromethane/petroleum ether) to afford **1m** (629.1 mg, 49%) as a white solid: m.p. 118.6-120.3 °C (dichloromethane/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.42 (bs, 1 H, COOH), 7.53 (d, *J* = 8.1 Hz, 2 H, ArH), 7.34 (d, *J* = 7.8 Hz, 2 H, ArH), 5.22 (t, *J* = 2.4 Hz, 2 H, =CH_2), 3.59 (s, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.4, 172.2, 142.8, 129.1, 128.9 (q, *J* = 32.2 Hz), 125.3 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 270.2 Hz), 99.1, 80.0, 34.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ 62.9; IR (neat) ν (cm^{-1}) 3351-2211,

1963, 1927, 1686, 1617, 1424, 1327, 1304, 1283, 1261, 1196, 1175, 1101, 1066, 1016; MS (EI): *m/z* (%) 242 (M^+, 23.92), 197 (100); Anal. Calcd. for $C_{12}H_9F_3O_2$ (%): C, 59.51; H, 3.75; Found: C, 59.41; H, 3.83.

1.4 Synthesis of 4-iodo-3-propylfuran-2(*5H*)-one **4**.[5] (zdj-1-013)

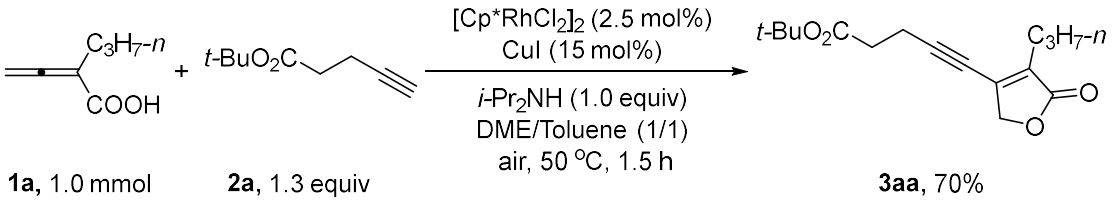


5.0 mmol **4**, 71%

To a dried three-necked flask were added ethyl 2-vinylidenepentanoate (774.9 mg, 5.0 mmol) and freshly distilled CH_2Cl_2 (50 mL) under nitrogen atmosphere. After cooling to -70 °C, a solution of IBr (1.3463 g, 6.5 mmol) in CH_2Cl_2 (9.3 mL) was added. The resulting mixture was stirred at -70 °C for 2 h, then removed cold bath. After returned to room temperature, the resulting mixture was quenched with 30 mL of water, extracted with CH_2Cl_2 (50 mL × 3), washed with a saturated aqueous solution of $Na_2S_2O_3$, dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude residual was purified via chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 100/1 (1000 mL) to 30/1 (300 mL)] to afford 4-iodo-3-propylfuran-2(*5H*)-one **4** (897.2 mg, 71%) as a white solid, m.p. 82.3-82.5 °C (dichloromethane/ petroleum ether): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.79 (s, 2 H, OCH_2), 2.32 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.68-1.46 (m, 2 H, CH_2), 0.96 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 138.4, 114.2, 76.1, 28.6, 20.3, 13.6; IR (neat) *ν* (cm^{-1}) 2971, 2954, 2928, 2868, 1734, 1633, 1463, 1440, 1336, 1312, 1270, 1220, 1118, 1103, 1047, 1010; MS (EI): *m/z* (%) 252 (M^+, 48.71), 125 (100); Anal. Calcd. for $C_7H_9IO_2$ (%): C, 33.36; H, 3.60; Found: C, 33.39; H, 3.59.

2. Aerobic Bimetallic Catalysis for Oxy-alkynylation of Allenes

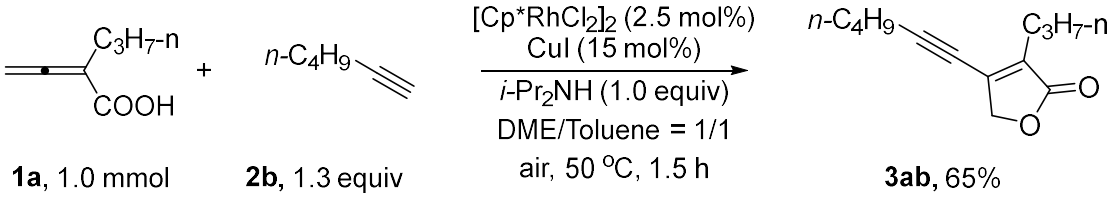
2.1 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-propylfuran-2(*5H*)-one **3aa**. (zdj-1-053 and zdj-1-023)



1a, 1.0 mmol **2a**, 1.3 equiv **3aa**, 70%

Typical Procedure：To a 100 mL dry Schlenk tube were added $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), **1a** (126.1 mg, 1.0 mmol), **2a** (200.9 mg, 1.3 mmol), *i*-Pr_2NH (0.14 mL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol), toluene (2.5 mL), and DME (2.5 mL) sequentially. After being stirred at 50 °C under air atmosphere for 1.5 h, the reaction was complete as monitored by TLC. The resulting mixture was filtrated 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 purified via chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 20/1 (400 mL) to 15/1 (300 mL)] to afford **3aa** (193.8 mg, 70%) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.66 (s, 2 H, OCH_2), 2.75 (t, *J* = 7.2 Hz, 2 H, CH_2), 2.53 (t, *J* = 7.1 Hz, 2 H, CH_2), 2.35 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.67-1.52 (m, 2 H, CH_2), 1.47 (s, 9 H, CH_3 × 3), 0.94 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 170.5, 140.1, 135.1, 105.3, 81.0, 71.8, 71.1, 33.9, 27.9, 26.7, 20.7, 15.8, 13.7; IR (neat) *v* (cm^{-1}) 2966, 2934, 2874, 2227, 1760, 1732, 1641, 1456, 1368, 1343, 1248, 1152, 1085, 1038, 1006; MS (EI): *m/z* (%) 223 [[(M-C_4H_8) + H]$^+$, 100]; HRMS Calcd for $C_{12}H_{15}O_4$ [(M-C_4H_8) + H]$^+$: 223.0970; Found: 223.0970.

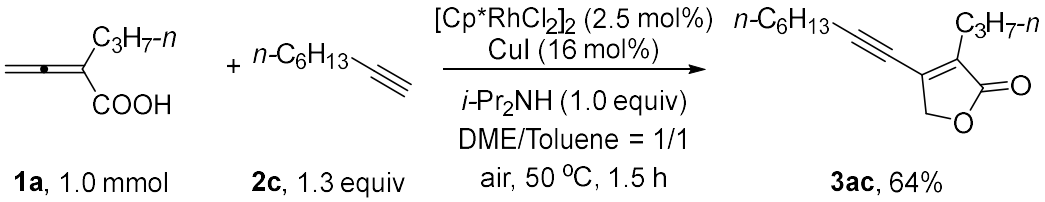
2.2 Synthesis of 4-(hexynyl)-3-propylfuran-2(*5H*)-one **3ab**. (fjj-4-070)



1a, 1.0 mmol **2b**, 1.3 equiv **3ab**, 65%

Following **Typical Procedure**, the reaction of **1a** (126.2 mg, 1.0 mmol), **2b** (106.8 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.4 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ab** (133.6 mg, 65%) as a brown oil [eluent: petroleum ether/ethyl acetate = 60/1 (600 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.67 (s, 2 H, OCH_2), 2.48 (t, *J* = 6.9 Hz, 2 H, CH_2), 2.36 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.68-1.53 (m, 4 H, CH_2 × 2), 1.53-1.37 (m, 2 H, CH_2), 1.03-0.86 (m, 6 H, CH_3 × 2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 140.7, 134.6, 107.6, 71.5, 71.2, 30.1, 26.7, 21.8, 20.8, 19.5, 13.8, 13.4; IR (neat) *v* (cm^{-1}) 2961, 2934, 2873, 2223, 1761, 1640, 1456, 1369, 1339, 1193, 1084, 1041, 1009; MS (EI): *m/z* (%) 207 [$(M + H)^+$, 12.29], 206 (M^+, 17.59), 119 (100); HRMS Calcd for $C_{13}H_{18}O_2$ (M^+): 206.1307; Found: 206.1306.

2.3 Synthesis of 4-(octynyl)-3-propylfuran-2(*5H*)-one **3ac**. (zdj-1-003, fjj-3-196)

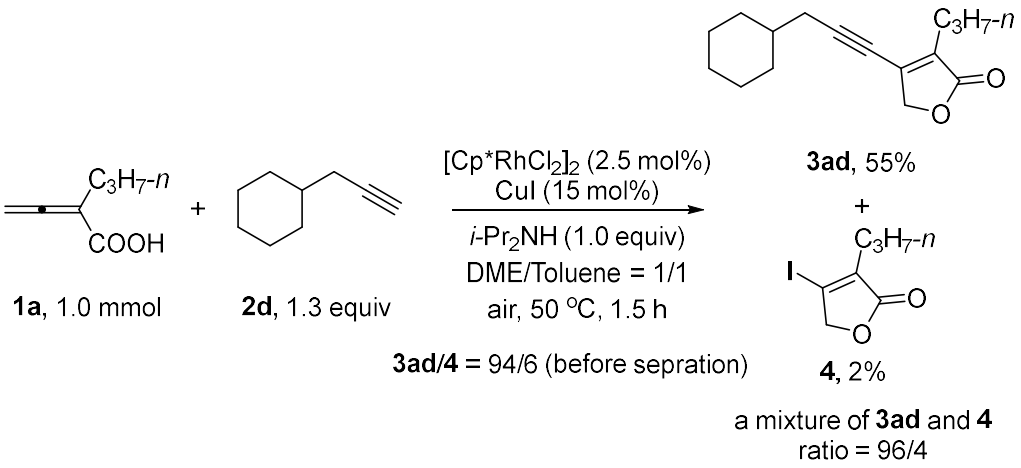


1a, 1.0 mmol **2c**, 1.3 equiv **3ac**, 64%

Following **Typical Procedure**, the reaction of **1a** (126.0 mg, 1.0 mmol), **2c** (146.6 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (30.7 mg, 0.16 mmol), and *i*-Pr_2NH (0.14 mL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in (0.65 mL) and toluene

(0.65 mL) afforded **3ac** (149.5 mg, 64%) as a light yellow oil [eluent: petroleum ether/ethyl acetate = 60/1 (600 mL) to 50 /1 (200 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.67 (s, 2 H, OCH_2), 2.47 (t, J = 6.9 Hz, 2 H, CH_2), 2.36 (t, J = 7.5 Hz, 2 H, CH_2), 1.70-1.51 (m, 4 H, CH_2 × 2), 1.50-1.19 (m, 6 H, CH_2 × 3), 1.11-0.84 (m, 6 H, CH_3 × 2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 140.7, 134.6, 107.7, 71.5, 71.2, 31.1, 28.4, 28.0, 26.7, 22.4, 20.8, 19.8, 13.9, 13.8; IR (neat) v (cm^{-1}) 2960, 2933, 2872, 2223, 1761, 1640, 1456, 1369, 1338, 1192, 1084, 1042; MS (EI): *m/z* (%) 234 (M^+, 2.56), 91 (100); HRMS Calcd for $C_{15}H_{22}O_2$ (M^+): 234.1620; Found: 234.1619.

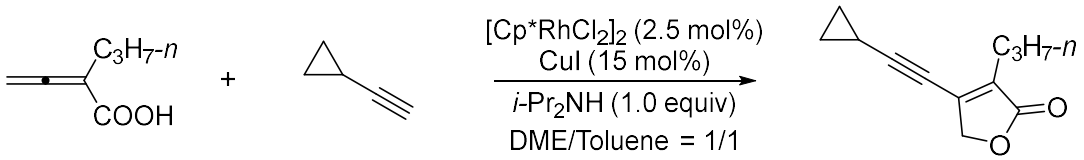
2.4 Synthesis of 4-(3-cyclohexylpropynyl)-3-propylfuran-2(*5H*)-one **3ad**. (fjj-4-041)



Following **Typical Procedure**, the reaction of **1a** (126.3 mg, 1.0 mmol), **2d** (160.0 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.7 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded a mixture of **3ad** (55%) and **4** (2%) (139.8 mg, **3ad**/**4** = 94/6 according to the ^{1}H NMR spectrum of the crude product, **3ad**/**4** = 96/4 after being purified via chromatography on silica gel) as a red oil [eluent: petroleum ether/ethyl

acetate = 100/1 (600 mL) to 50/1 (300 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.67 (s, 2 H, OCH_2), 2.50-2.20 (m, 4 H, CH_2 × 2), 1.90-1.46 (m, 8 H, CH_2 × 4), 1.39-0.77 (m, 8 H, CH, CH_2 × 2 and CH_3); the following signal is discernible for **4**: δ 4.78 (s, 0.08 H, OCH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 140.8, 134.5, 106.7, 72.4, 71.2, 37.0, 32.5, 27.5, 26.7, 26.0, 25.9, 20.8, 13.8; IR (neat) *v* (cm^{-1}) 2960, 2926, 2852, 2221, 1762, 1639, 1450, 1370, 1339, 1116, 1084, 1041, 1001; MS (EI): *m/z* (%) 247 [$(M + H)^+$, 23.63], 246 (M^+, 30.48), 164 (100); HRMS Calcd for $C_{16}H_{22}O_2$ (M^+): 246.1620; Found: 246.1618.

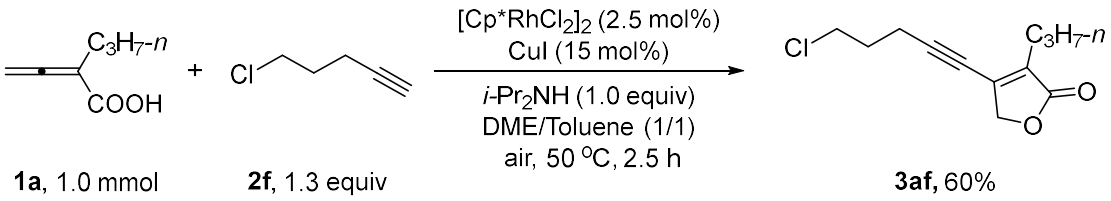
2.5 Synthesis of 4-(cyclopropylethynyl)-3-propylfuran-2(*5H*)-one **3ae**. (fjj-4-104)



1a, 1.0 mmol **2e**, 1.3 equiv **3ae**, 33%

Following **Typical Procedure**, the reaction of **1a** (126.0 mg, 1.0 mmol), **2e** (85.0 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.3 mg, 0.025 mmol), CuI (28.5 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ae** (63.6 mg, 33%) as a yellow oil [eluent: petroleum ether/ethyl acetate = 50/1 (800 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.64 (s, 2 H, OCH_2), 2.33 (t, *J* = 7.7 Hz, 2 H, CH_2), 1.70-1.42 (m, 3 H, CH_2 and CH), 1.07-0.78 (m, 7 H, CH_3 and CH_2 × 2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 140.6, 134.2, 110.9, 71.1, 66.7, 26.7, 20.7, 13.7, 9.4, 0.5; IR (neat) *v* (cm^{-1}) 3014, 2962, 2934, 2873, 2217, 1755, 1638, 1454, 1386, 1344, 1202, 1073, 1037; MS (EI): *m/z* (%) 190 (M^+, 44.01), 91 (100); HRMS Calcd for $C_{12}H_{14}O_2$ (M^+): 190.0994; Found: 190.0995.

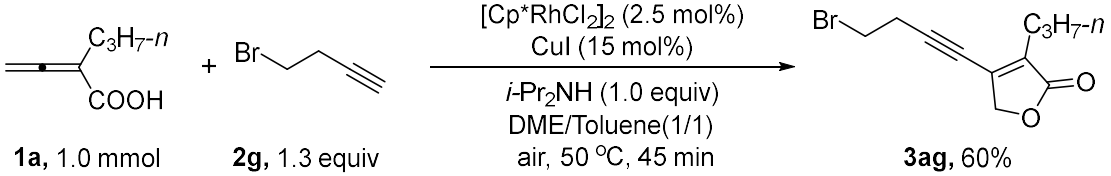
2.6 Synthesis of 4-(5-chloropentynyl)-3-propylfuran-2(5*H*)-one **3af**. (zdj-1-024, zdj-1-054)



1a, 1.0 mmol **2f**, 1.3 equiv **3af,** 60%

Following **Typical Procedure**, the reaction of **1a** (126.2 mg, 1.0 mmol), **2f** (133.8 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.4 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), and *i*-Pr_2NH (0.14 mL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3af** (135.3 mg, 60%) as a yellow oil [eluent: petroleum ether/ethyl acetate = 20/1 (800 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.68 (s, 2 H, OCH_2), 3.67 (t, *J* = 6.2 Hz, 2 H, CH_2), 2.70 (t, *J* = 6.9 Hz, 2 H, CH_2), 2.36 (t, *J* = 7.5 Hz, 2 H, CH_2), 2.16-1.93 (m, 2 H, CH_2), 1.75-1.53 (m, 2 H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 140.0, 135.4, 105.0, 72.3, 71.1, 43.2, 30.7, 26.8, 20.8, 17.3, 13.8; IR (neat) *v* (cm^{-1}) 2962, 2933, 2873, 2226, 1756, 1640, 1453, 1370, 1340, 1116, 1085, 1043, 1014; MS (EI): *m/z* (%) 228 [M(^{37}Cl)$^+$, 2.71], 226 [M(^{35}Cl)$^+$, 5.90], 164 (100); HRMS Calcd for $C_{12}H_{15}{}^{35}ClO_2$ (M^+): 226.0761; Found: 226.0759.

2.7 Synthesis of 4-(4-bromobutynyl)-3-propylfuran-2(5*H*)-one **3ag**. (zdj-1-079)

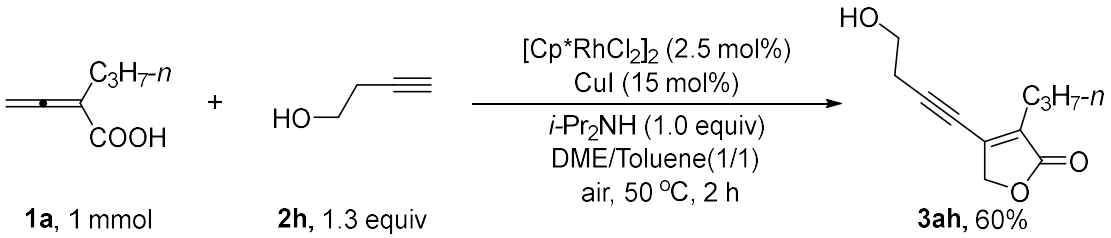


1a, 1.0 mmol **2g,** 1.3 equiv **3ag,** 60%

Following **Typical Procedure**, the reaction of **1a** (126.4 mg, 1.0 mmol), **2g** (172.9

mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.4 mg, 0.15 mmol), and *i*-Pr_2NH (0.14 mL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ag** (155.1 mg, 60%) as a brown oil [eluent: petroleum ether/ethyl acetate = 30/1 (300 mL) to 15/1 (750 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.70 (s, 2 H, OCH_2), 3.51 (t, *J* = 6.9 Hz, 2 H, CH_2Br), 3.06 (t, *J* = 6.8 Hz, 2 H, CH_2), 2.38 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.73-1.49 (m, 2 H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 139.5, 136.1, 103.1, 73.2, 71.0, 28.5, 26.8, 24.1, 20.8, 13.8; IR (neat) *v* (cm^{-1}) 2962, 2933, 2872, 2232, 1755, 1640, 1451, 1409, 1370, 1339, 1272, 1216, 1194, 1116, 1086, 1044, 1021; MS (EI): *m/z* (%) 258 [M(^{81}Br)$^+$, 15.29], 256 [M(^{79}Br)$^+$, 15.49], 177 (100); HRMS Calcd for $C_{11}H_{13}O_2{}^{79}Br$ (M^+): 256.0099; Found: 256.0098.

2.8 Synthesis of 4-(4-hydroxybutynyl)-3-propylfuran-2(*5H*)-one **3ah**. (fjj-3-180, zdj-1-192)

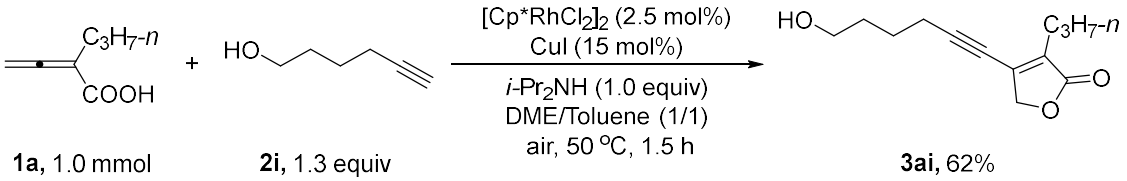


1a, 1 mmol **2h**, 1.3 equiv **3ah**, 60%

Following **Typical Procedure**, the reaction of **1a** (126.3 mg, 1.0 mmol), **2h** (91.3 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.3 mg, 0.025 mmol), CuI (28.5 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ah** (116.5 mg, 60%) as a brown oil [eluent: petroleum ether/ethyl acetate = 4/1 (1500 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.69 (s, 2 H, OCH_2), 3.83 (q,

J = 6.1 Hz, 2 H, OCH_2), 2.76 (t, J = 6.5 Hz, 2 H, CH_2), 2.63 (t, J = 5.4 Hz, 1 H, OH), 2.36 (t, J = 7.5 Hz, 2 H, CH_2), 1.69-1.50 (m, 2 H, CH_2), 0.94 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 140.4, 135.0, 104.2, 72.5, 71.2, 60.4, 26.7, 24.0, 20.7, 13.7; IR (neat) ν (cm^{-1}) 3445, 2962, 2929, 2874, 2262, 1747, 1639, 1455, 1372, 1344, 1192, 1040; MS (EI): *m/z* (%) 194 (M^+, 5.69), 91 (100); HRMS Calcd for $C_{11}H_{14}O_3$ (M^+): 194.0943; Found: 194.0942.

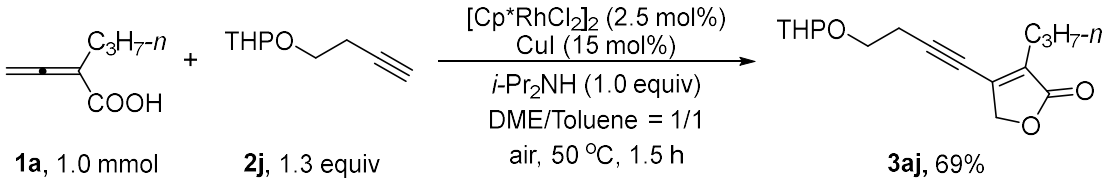
2.9 Synthesis of 4-(6-hydroxyhexynyl)-3-propylfuran-2(*5H*)-one **3ai**. (zdj-1-059)



1a, 1.0 mmol **2i**, 1.3 equiv **3ai**, 62%

Following **Typical Procedure**, the reaction of **1a** (126.3 mg, 1.0 mmol), **2i** (128.0 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.3 mg, 0.025 mmol), CuI (28.8 mg, 0.15 mmol), and *i*-Pr_2NH (0.14 mL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ai** (138.0 mg, 62%) as a yellow oil [eluent: petroleum ether/ethyl acetate = 4/1 (1000 mL) to 3/1 (400 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.67 (s, 2 H, OCH_2), 3.70 (s, 2 H, OCH_2), 2.53 (s, 2 H, CH_2), 2.35 (t, J = 7.4 Hz, 2 H, CH_2), 1.88-1.42 (m, 7 H, CH_2 × 3 and OH), 0.94 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 140.6, 134.8, 107.1, 71.8, 71.2, 62.0, 31.6, 26.8, 24.5, 20.8, 19.7, 13.8; IR (neat) v (cm^{-1}) 3435, 2955, 2935, 2872, 2222, 1755, 1638, 1454, 1371, 1342, 1192, 1117, 1086, 1066, 1041; MS (EI): *m/z* (%) 223 (M^+ +1, 75.97), 91 (100); HRMS Calcd for $C_{13}H_{18}O_3$ (M^+): 222.1255; Found: 222.1256.

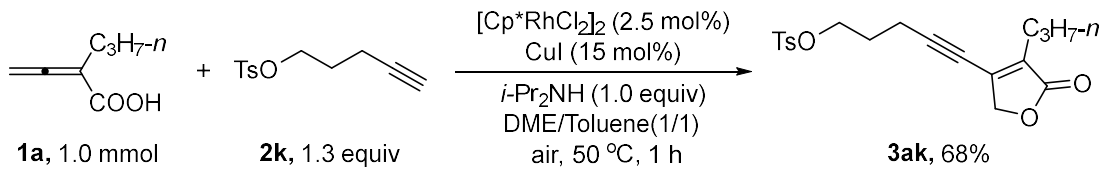
2.10 Synthesis of 3-propyl-4-(4-((tetrahydro-*2H*-pyran-2-yl)oxy)butynyl)furan-2(*5H*)-one **3aj**. (fjj-4-071)



1a, 1.0 mmol **2j**, 1.3 equiv **3aj**, 69%

Following **Typical Procedure**, the reaction of **1a** (126.1 mg, 1.0 mmol), **2j** (200.5 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3aj** (193.1 mg, 69%) as a yellow oil [eluent: petroleum ether/ethyl acetate = 5/1 (800 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.80-4.52 (s, 3 H, OCH_2 and OCH), 4.00-3.80 (m, 2 H, OCH_2), 3.71-3.46 (m, 2 H, OCH_2), 2.78 (t, *J* = 6.6 Hz, 2 H, CH_2), 2.36 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.95-1.45 (m, 8 H, CH_2 × 4), 0.94 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 140.2, 135.0, 104.3, 98.7, 72.1, 71.1, 64.9, 62.1, 30.4, 26.7, 25.2, 21.3, 20.7, 19.2, 13.7; IR (neat) *v* (cm^{-1}) 2941, 2873, 2227, 1760, 1641, 1454, 1343, 1201, 1122, 1081, 1035; MS (EI): *m/z* (%) 279 [$(M + H)^+$, 6.14], 278 (M^+, 3.71), 85 (100); HRMS Calcd for $C_{16}H_{22}O_4$ (M^+): 278.1518; Found: 278.1517.

2.11 Synthesis of 4-(5-(tosyloxy)pentynyl)-3-propylfuran-2(*5H*)-one **3ak**. (zdj-1-094)

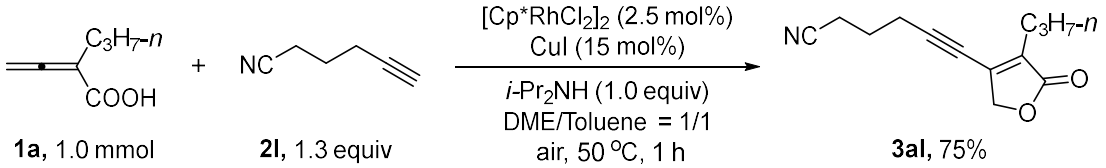


1a, 1.0 mmol **2k**, 1.3 equiv **3ak**, 68%

Following **Typical Procedure**, the reaction of **1a** (126.0 mg, 1.0 mmol), **2k** (310.1

mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.7 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded impure **3ak** (287.0 mg) after chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 8/1, 900 mL to 6/1, 700 mL]. The impure **3ak** was further purified via chromatography on silica gel [eluent: dichloromethane/ethyl acetate = 500/1 (1000 mL)] to afford pure **3ak** (247.4 mg, 68%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2 H, ArH), 7.37 (d, *J* = 8.1 Hz, 2 H, ArH), 4.62 (s, 2 H, OCH_2), 4.15 (t, *J* = 5.9 Hz, 2 H, OCH_2), 2.59 (t, *J* = 6.8 Hz, 2 H, CH_2), 2.45 (s, 3 H, CH_3), 2.31 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.04-1.87 (m, 2 H, CH_2), 1.68-1.48 (m, 2 H, CH_2), 0.92 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 144.9, 139.9, 135.0, 132.6, 129.8, 127.7, 104.6, 72.3, 71.0, 68.3, 27.3, 26.6, 21.4, 20.7, 16.1, 13.7; IR (neat) *v* (cm^{-1}) 2962, 2932, 2873, 2226, 1755, 1640, 1598, 1493, 1454, 1363, 1304, 1292, 1189, 1176, 1118, 1097, 1038, 1013; MS (EI): *m/z* (%) 363 [(M + H)$^+$, 27.25], 362 (M^+, 7.30), 91 (100); HRMS Calcd for $C_{19}H_{22}O_5S$ (M^+): 362.1188; Found: 362.1190.

2.12 Synthesis of 4-(5-cyanopentynyl)-3-propylfuran-2(*5H*)-one **3al**. (zdj-2-083, zdj-1-090)

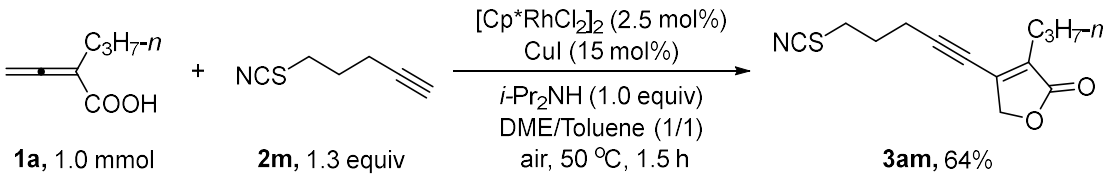


1a, 1.0 mmol **2l**, 1.3 equiv **3al**, 75%

Following **Typical Procedure**, the reaction of **1a** (126.1 mg, 1.0 mmol), **2l** (120.9 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.6 mg, 0.025 mmol), CuI (28.7 mg, 0.15 mmol), and

i-Pr_2NH (140 μL, d = 0.718 g/ml, 100.5mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3al** (162.9 mg, 75%) as a brown oil [eluent: petroleum ether/dichloromethane = 1/2 (900 mL) to dichloromethane (300 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 4.69 (s, 2 H, OCH_2), 2.69 (t, *J* = 6.9 Hz, 2 H, CH_2), 2.54 (t, *J* = 7.1 Hz, 2 H, CH_2), 2.36 (t, *J* = 7.5 Hz, 2 H, CH_2), 2.08-1.91 (m, 2 H, CH_2), 1.69-1.52 (m, 2 H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 139.6, 135.6, 118.6, 103.7, 73.0, 71.0, 26.8, 23.9, 20.7, 18.8, 16.2, 13.7; IR (neat) *v* (cm^{-1}) 2962, 2925, 2873, 2254, 2227, 1755, 1640, 1454, 1429, 1370, 1341, 1315, 1191, 1116, 1087, 1039, 1010; MS (EI): *m/z* (%) 217 (M^+, 20.52), 91 (100); HRMS Calcd for $C_{13}H_{15}NO_2Na$ (M + Na)$^+$: 240.9995; Found: 240.9994.

2.13 Synthesis of 3-propyl-4-(5-thiocyanatopentynyl)furan-2(*5H*)-one **3am**. (zdj-1-115)

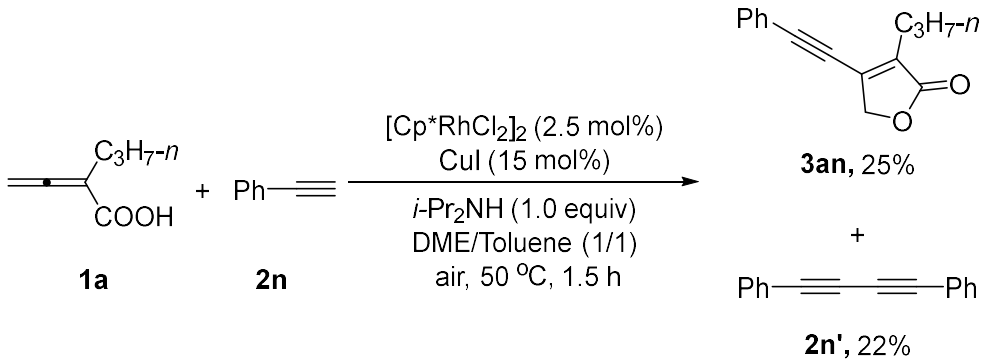


1a, 1.0 mmol **2m,** 1.3 equiv **3am,** 64%

Following **Typical Procedure**, the reaction of **1a** (126.2 mg, 1.0 mmol), **2m** (162.8 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.6 mg, 0.025 mmol), CuI (28.7 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3am** (159.5 mg, 64%) as a red oil [the reaction crude was afforded by filtrated through a short column of silica gel eluted with ethyl acetate (15 mL × 3); eluent: petroleum ether/dichloromethane = 2/3 (1200 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 4.69 (s, 2 H, OCH_2), 3.10 (t, *J* = 6.9 Hz, 2 H, CH_2), 2.73 (t, *J* = 6.8 Hz, 2 H, CH_2), 2.36 (t, *J* = 7.5 Hz, 2 H, CH_2), 2.24-2.07 (m, 2 H, CH_2), 1.70-1.48 (m, 2 H,

CH_2), 0.95 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 139.6, 135.5, 111.4, 103.9, 72.9, 71.0, 32.5, 28.0, 26.8, 20.7, 18.1, 13.7; IR (neat) ν (cm^{-1}) 2962, 2933, 2873, 2225, 2154, 1755, 1640, 1451, 1369, 1340, 1283, 1261, 1192, 1116, 1086, 1041, 1011; MS (EI): *m/z* (%) 249 (M^+, 14.03), 91 (100); HRMS Calcd for $C_{13}H_{15}NO_2SNa$ $(M + Na)^+$: 272.0716; Found: 272.0717.

2.14 Synthesis of 4-(phenylethynyl)-3-propylfuran-2(5*H*)-one **3an**. (zdj-2-080, zdj-1-199)

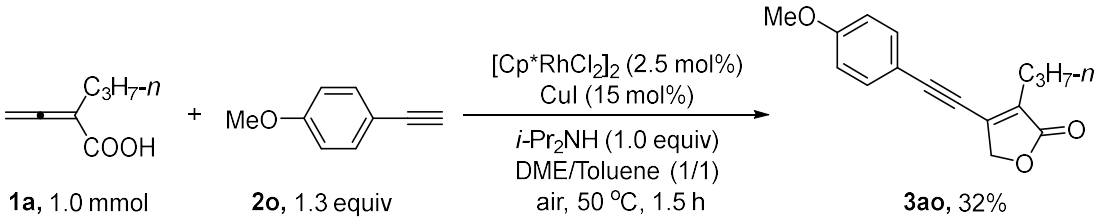


Following **Typical Procedure**, the reaction of **1a** (126.1 mg, 1.0 mmol), **2n** (132.8 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded 1,4-diphenylbutadiyne **2n'** (28.9 mg, 22%) and **3an** (56.4 mg, 25%) [eluent: petroleum ether (200 mL) to petroleum ether/ethyl acetate = 30/1 (600 mL)]:

2n': light yellow solid, m.p. 81.4-82.2 °C (determined without recrystallization) (reported value for **2n'** [6]: 84−86 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.61-7.47 (m, 4 H, ArH), 7.45-7.28 (m, 6 H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.5, 129.2, 128.4, 121.7, 81.5, 73.9; IR (KBr) ν (cm^{-1}) 3049, 2150, 1592, 1564, 1485, 1439; MS (EI): *m/z* (%) 202 (M^+, 100).

3an: brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.48 (m, 2 H, ArH), 7.46-7.33 (m, 3 H, ArH), 4.81 (t, *J* = 1.2 Hz, 2 H, OCH_2), 2.47 (t, *J* = 7.7 Hz, 2 H, CH_2), 1.80-1.59 (m, 2 H, CH_2), 0.99 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 139.5, 135.7, 131.8, 129.9, 128.6, 121.3, 104.7, 79.5, 70.9, 27.0, 20.9, 13.9; IR (neat) *v* (cm^{-1}) 2962, 2932, 2872, 2206, 1759, 1640, 1490, 1444, 1373, 1339, 1213, 1114, 1071, 1036; MS (EI): *m/z* (%) 227 [$(M + H)^+$, 23.65], 226 (M^+, 100); HRMS Calcd for $C_{15}H_{14}O_2$ (M^+): 226.0994; Found: 226.0996.

2.15 Synthesis of 4-((4-methoxyphenyl)ethynyl)-3-propylfuran-2(*5H*)-one **3ao**. (zdj-1-088)

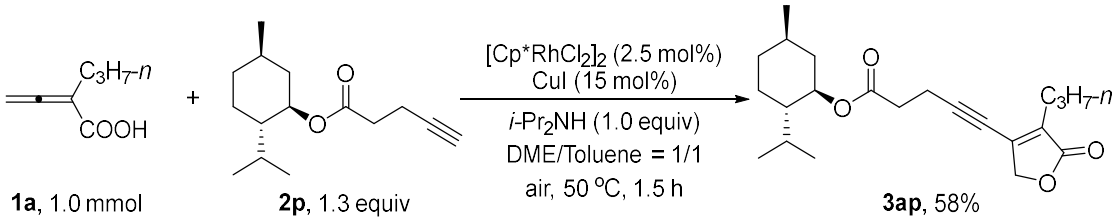


1a, 1.0 mmol **2o**, 1.3 equiv **3ao**, 32%

Following **Typical Procedure**, the reaction of **1a** (126.2 mg, 1.0 mmol), **2o** (171.8 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.7 mg, 0.025 mmol), CuI (28.8 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ao** (80.8 mg, 32%) as a brown oil [eluent: petroleum ether/ethyl acetate = 20/1 (1000 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2 H, ArH), 6.91 (d, *J* = 8.7 Hz, 2 H, ArH), 4.79 (s, 2 H, OCH_2), 3.85 (s, 3 H, OCH_3), 2.45 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.76-1.59 (m, 2 H, CH_2), 0.99 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 160.8, 139.9, 134.4, 133.4, 114.2, 113.2, 105.3, 78.6, 70.9, 55.2, 26.9, 20.8, 13.8; IR (neat) *v* (cm^{-1}) 2961, 2933, 2872, 2840, 2201, 1754,

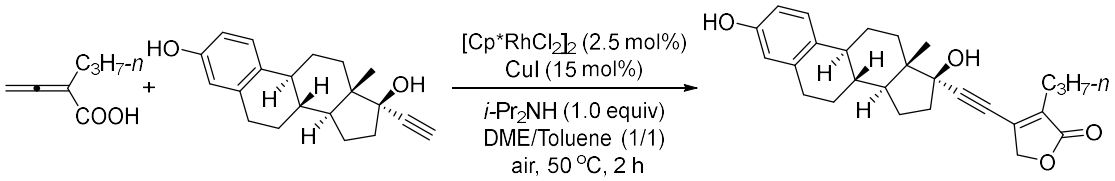
1639, 1602, 1568, 1510, 1462, 1418, 1375, 1342, 1294, 1252, 1218, 1173, 1111, 1073, 1034; MS (EI): *m/z* (%) 257 [(M + H)$^+$, 25.35], 256 (M$^+$, 100); HRMS Calcd for $C_{16}H_{16}O_3$ (M$^+$): 256.1099; Found: 256.1100.

2.16 Synthesis of **3ap**. (fjj-4-025)



Following **Typical Procedure**, the reaction of **1a** (126.1 mg, 1.0 mmol), **2p** (307.5 mg, 1.3 mmol), [Cp*RhCl$_2$]$_2$ (15.5 mg, 0.025 mmol), CuI (28.5 mg, 0.15 mmol), and *i*-Pr$_2$NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ap** (207.6 mg, 58%) as a brown oil [eluent: petroleum ether/ethyl acetate = 25/1 (1000 mL)]: $[\alpha]_D^{20}$ = -47.4 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.73 (td, J_1 = 10.8 Hz, J_2 = 4.5 Hz, 1 H, OCH), 4.65 (s, 2 H, OCH_2), 2.80 (t, *J* = 7.2 Hz, 2 H, CH_2), 2.60 (t, *J* = 7.2 Hz, 2 H, CH_2), 2.35 (t, *J* = 7.5 Hz, 2 H, CH_2), 2.04-1.92 (m, 1 H, CH), 1.91-1.77 (m, 1 H, one proton of CH_2), 1.76-1.20 (m, 7 H, CH_2, CH × 2, and one proton of CH_2 × 3), 1.19-0.80 (m, 11 H, CH_3 × 3, and CH_2 × 2), 0.75 (d, *J* = 6.9 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 170.8, 140.0, 135.3, 105.1, 74.8, 72.0, 71.1, 46.9, 40.9, 34.1, 33.2, 31.3, 26.8, 26.3, 23.4, 21.9, 20.8, 20.7, 16.3, 15.8, 13.8; IR (neat) *v* (cm^{-1}) 2958, 2932, 2872, 2227, 1761, 1732, 1642, 1456, 1371, 1340, 1258, 1176, 1083, 1039; MS (EI): *m/z* (%) 361 [(M + H)$^+$, 10.6], 178 (100); HRMS Calcd for $C_{22}H_{32}O_4$ (M$^+$): 360.2301; Found: 360.2298.

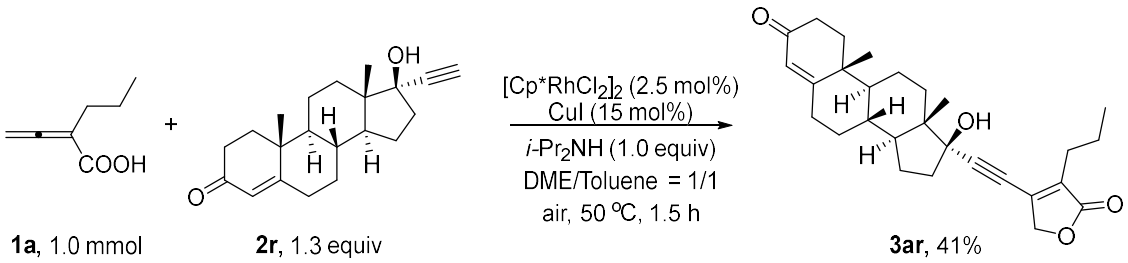
2.17 Synthesis of **3aq**. (zdj-1-055)



1a, 1.0 mmol **2q,** 1.3 equiv **3aq,** 67%

Following **Typical Procedure**, the reaction of **1a** (126.1 mg, 1.0 mmol), **2q** (385.4 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.6 mg, 0.025 mmol), CuI (28.5 mg, 0.15 mmol), and *i*-Pr_2NH (0.14 mL, 0.718 g/mL, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3aq** (280.8 mg, 67%) as a red oil [eluent: petroleum ether/ethyl acetate = 4/1 (500 mL) to 3/1 (800 mL)]: $[\alpha]_D^{20}$ = -48.6 (*c* = 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.4 Hz, 1 H, ArH), 6.65 (dd, J_1 = 8.4 Hz, J_2 = 2.7 Hz, 1 H, ArH), 6.59 (d, *J* = 2.4 Hz, 1 H, ArH), 5.49 (bs, 1 H, OH), 4.73 (s, 2 H, OCH_2), 2.91-2.77 (m, 2 H, CH_2), 2.47-2.29 (m, 4 H, CH_2, CH and OH), 2.22-2.05 (m, 2 H, CH_2), 1.95-1.18 (m, 12 H, $CH_2 \times 6$), 1.04-0.80 (m, 6 H, $CH_3 \times 2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 153.7, 139.8, 137.9, 135.8, 131.7, 126.3, 115.3, 112.8, 109.3, 80.7, 76.5, 71.1, 50.1, 47.8, 43.6, 39.3, 39.0, 33.0, 29.5, 27.2, 27.0, 26.3, 22.8, 21.0, 13.9, 12.7; IR (neat) *v* (cm^{-1}) 3389, 2931, 2871, 2249, 1737, 1636, 1611, 1584, 1500, 1448, 1381, 1369, 1347, 1315, 1287, 1248, 1144, 1097, 1060, 1034; MS (EI): *m/z* (%) 421 [$(M + H)^+$, 16.18], 420 (M^+, 49.53), 84 (100); HRMS Calcd for $C_{27}H_{32}O_4$ (M^+): 420.2301; Found: 420.2303.

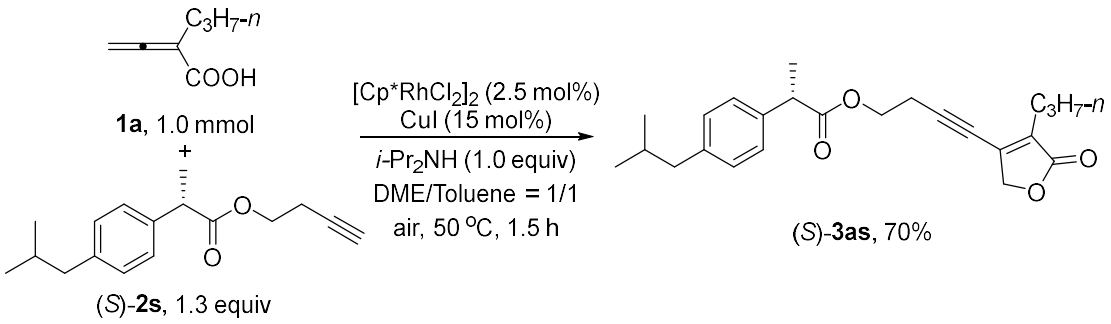
2.18 Synthesis of **3ar**. (fjj-4-036)



1a, 1.0 mmol **2r**, 1.3 equiv **3ar**, 41%

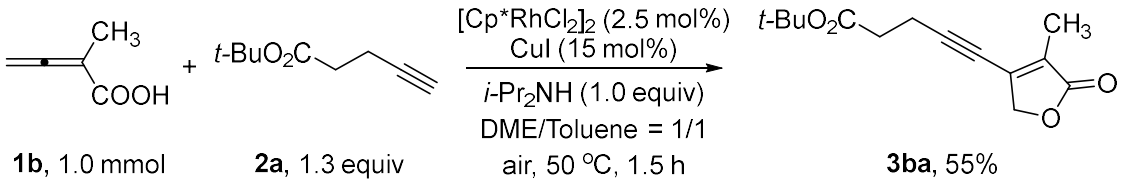
Following **Typical Procedure**, the reaction of **1a** (126.2 mg, 1.0 mmol), **2r** (406.4 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.7 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ar** (179.6 mg, 41%) as a light yellow oil [eluent: petroleum ether/ethyl acetate = 2/1 (800 mL)]: $[\alpha]_D^{20}$ = -18.8 (*c* = 0.80, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 5.74 (s, 1 H, =CH), 4.71 (s, 2 H, OCH_2), 3.54 (bs, 1 H, OH), 2.59-2.23 (m, 7 H, CH_2 × 3 and one proton of CH_2), 2.22-1.98 (m, 2 H, CH_2), 1.97-1.33 (m, 12 H, CH_2 × 4, CH × 3 and one proton of CH_2), 1.22 (s, 3 H, CH_3), 1.14-0.80 (m, 8 H, CH_2 and CH_3 × 2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 173.8, 171.2, 139.6, 135.4, 123.6, 109.3, 79.9, 76.0, 70.8, 53.4, 50.3, 47.1, 38.7, 38.4, 35.9, 35.4, 33.6, 32.5, 32.4, 31.3, 26.8, 22.9, 20.8, 20.5, 17.1, 13.8, 12.5; IR (neat) *v* (cm^{-1}) 3419, 2945, 2872, 2214, 1755, 1661, 1454, 1273, 1232, 1125, 1058, 1037; MS (EI): *m/z* (%) 437 [$(M + H)^+$, 18.01], 436 (M^+, 32.31), 364 (100); HRMS Calcd for $C_{28}H_{36}O_4$ (M^+): 436.2614; Found: 436.2613.

2.19 Synthesis of (*S*)-**3as**. (fjj-4-027)



Following **Typical Procedure**, the reaction of **1a** (126.2 mg, 1.0 mmol), **2s** (335.5 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.6 mg, 0.025 mmol), CuI (28.4 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3as** (267.6 mg, 70%) as a yellow oil [eluent: petroleum ether/ethyl acetate = 25/1 (1000 mL) to 20/1 (200 mL)]: $[\alpha]_D^{20}$ = +14.8 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.1 Hz, 2 H, ArH), 7.08 (d, *J* = 8.1 Hz, 2 H, ArH), 4.58 (s, 2 H, OCH_2), 4.24 (t, *J* = 6.3 Hz, 2 H, OCH_2), 3.72 (q, *J* = 7.2 Hz, 1 H, CH), 2.77 (t, *J* = 6.6 Hz, 2 H, CH_2), 2.44 (d, *J* = 7.2 Hz, 2 H, CH_2), 2.33 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.92-1.75 (m, 1 H, CH), 1.66-1.52 (m, 2 H, CH_2), 1.50 (d, *J* = 7.2 Hz, 3 H, CH_3), 0.99-0.82 (m, 9 H, CH_3 × 3) ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 174.0, 140.6, 139.7, 137.3, 135.5, 129.2, 127.0, 102.3, 72.6, 71.0, 61.6, 44.90, 44.87, 30.1, 26.7, 22.2, 20.7, 20.3, 18.4, 13.8; IR (neat) *v* (cm^{-1}) 2960, 2933, 2871, 2229, 1760, 1641, 1512, 1456, 1383, 1338, 1162, 1091; MS (EI): *m/z* (%) 383 [$(M + H)^+$, 7.38], 382 (M^+, 20.29), 161 (100); HRMS Calcd for $C_{24}H_{30}O_4$ (M^+): 382.2144; Found: 382.2147.

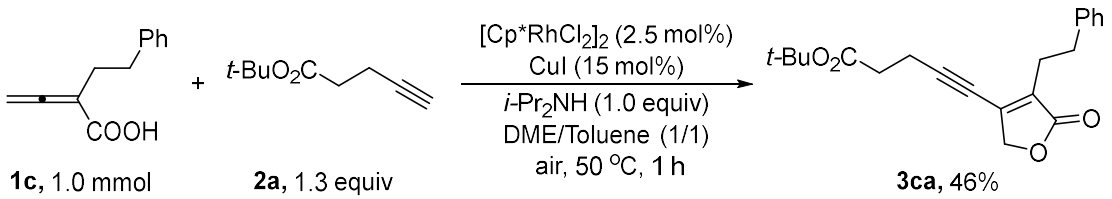
2.20 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-methylfuran-2(*5H*)-one **3ba**. (fjj-4-030)



1b, 1.0 mmol **2a**, 1.3 equiv **3ba**, 55%

Following **Typical Procedure**, the reaction of **1b** (98.1 mg, 1.0 mmol), **2a** (201.0 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.7 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ba** (140.0 mg, 55%) as a brown oil [eluent: petroleum ether/ethyl acetate = 25/1 (500 mL) to 20/1 (500 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.66 (d, *J* = 1.8 Hz, 2 H, OCH_2), 2.75 (t, *J* = 7.2 Hz, 2 H, CH_2), 2.54 (t, *J* = 7.2 Hz, 2 H, CH), 1.94 (s, 3 H, CH_3), 1.47 (s, 9 H, $CH_3 \times 3$) ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 170.5, 140.0, 131.4, 105.7, 81.1, 71.7, 71.2, 34.0, 28.0, 15.8, 9.9; IR (neat) *v* (cm^{-1}) 2979, 2933, 2226, 1762, 1731, 1648, 1393, 1367, 1337, 1248, 1210, 1152, 1076, 1037; MS (EI): *m/z* (%) 251 [$(M + H)^+$, 7.84], 194 (100); HRMS Calcd for $C_{14}H_{18}O_4$ (M^+): 250.1205; Found: 250.1207.

2.21 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-phenethylfuran-2(*5H*)-one **3ca**.(zdj-1-109)

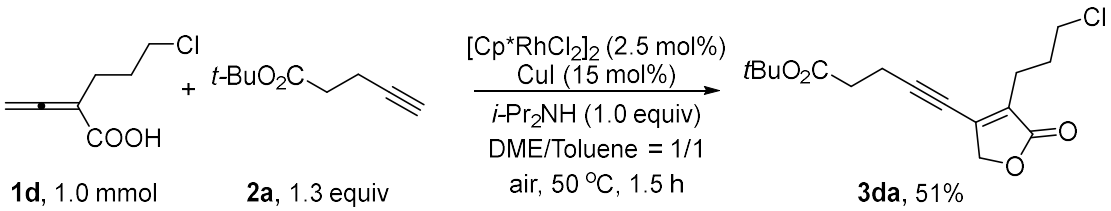


1c, 1.0 mmol **2a,** 1.3 equiv **3ca,** 46%

Following **Typical Procedure**, the reaction of **1c** (188.2 mg, 1.0 mmol), **2a** (201.1 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene

(2.5 mL) afforded **3ca** (158.1 mg, 46%) as a yellow oil [the reaction crude was afforded by filtrated through a short column of silica gel eluted with ethyl acetate (15 mL × 3); eluent: petroleum ether/ ethyl acetate = 20/1 (1200 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.24 (m, 2 H, ArH), 7.24-7.14 (m, 3 H, ArH), 4.63 (m, 2 H, OCH_2), 2.89 (t, *J* = 7.7 Hz, 2 H, CH_2), 2.73-2.63 (m, 4 H, CH_2 × 2), 2.49 (t, *J* = 7.4 Hz, 2 H, CH_2), 1.45 (s, 9 H, CH_3 × 3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 170.5, 140.7, 140.6, 134.1, 128.4, 128.3, 126.1, 105.8, 81.1, 71.5, 71.1, 33.9, 33.2, 28.0, 26.7, 15.7; IR (neat) *v* (cm^{-1}) 3062, 3032, 2978, 2929, 2865, 2227, 1758, 1731, 1642, 1455, 1392, 1367, 1343, 1247, 1210, 1151, 1079, 1038; MS (EI): *m/z* (%) 284 [(M – *t*-Bu + H)$^+$, 15.94], 91 (100); Anal. Calcd. for $C_{21}H_{24}O_4$ (%): C, 74.09; H, 7.11; Found: C, 74.15; H, 7.21.

2.22 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-(3-chloropropyl)furan-2(*5H*)-one **3da**. (fjj-4-079)

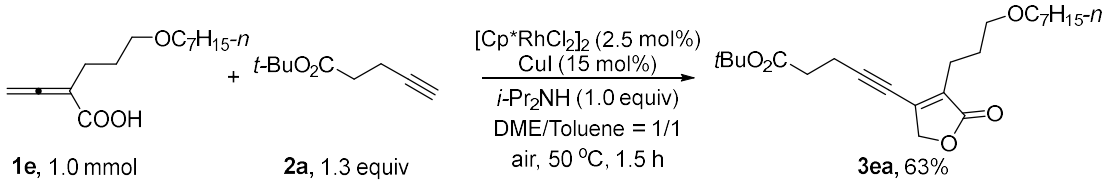


1d, 1.0 mmol **2a**, 1.3 equiv **3da**, 51%

Following **Typical Procedure**, the reaction of **1d** (160.7 mg, 1.0 mmol), **2a** (200.5 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3da** (158.4 mg, 51%) as a brown oil [eluent: petroleum ether/ethyl acetate = 50/1 (1000 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.68 (s, 2 H, OCH_2), 3.55 (t, *J* = 6.3 Hz, 2 H, CH_2Cl), 2.75 (t, *J* = 7.2 Hz, 2 H, CH_2), 2.60-2.48 (m, 4 H, CH_2 × 2),

2.14-1.98 (m, 2 H, CH_2), 1.47 (s, 9 H, CH_3 × 3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 170.5, 141.2, 133.7, 106.6, 81.2, 71.4, 71.2, 44.1, 33.9, 30.0, 28.0, 22.2, 15.9; IR (neat) *v* (cm^{-1}) 2978, 2931, 2228, 1760, 1731, 1642, 1368, 1152, 1092, 1071, 1039; MS (EI): *m/z* (%) 259 [$(M(^{37}Cl) - C_4H_7)^+$, 20.22], 257 [$(M(^{35}Cl) - C_4H_7)^+$, 54.72], 57 (100); HRMS Calcd for $C_{16}H_{21}{}^{35}ClO_4Na$ $(M + Na)^+$: 335.1021; Found: 335.1024.

2.23 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-(3-(heptyloxy)propyl)furan-2(*5H*)-one **3ea**. (fjj-4-103)

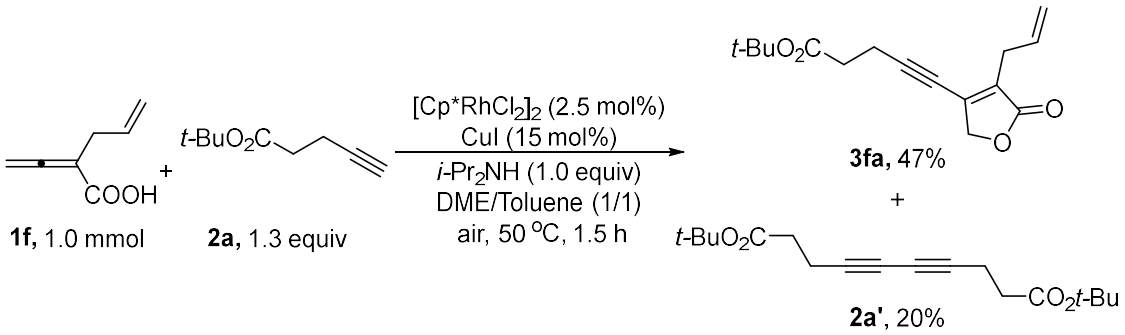


1e, 1.0 mmol **2a**, 1.3 equiv **3ea**, 63%

Following **Typical Procedure**, the reaction of **1e** (240.2 mg, 1.0 mmol), **2a** (200.6 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.6 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ea** (248.1 mg, 63%) as a brown oil [eluent: petroleum ether/ethyl acetate = 20/1 (500 mL) to 15/1 (500 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 4.65 (s, 2 H, OCH_2), 3.49-3.30 (m, 4 H, OCH_2 × 2), 2.74 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.53 (t, *J* = 7.2 Hz, 2 H, CH_2), 2.45 (t, *J* = 7.4 Hz, 2 H, CH_2), 1.93-1.78 (m, 2 H, CH_2), 1.63-1.40 (m, 11 H, CH_2 and CH_3 × 3), 1.37-1.21 (m, 8 H, CH_2 × 4), 0.88 (m, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 170.4, 139.9, 134.8, 105.6, 80.9, 71.6, 71.0, 70.8, 69.8, 33.8, 31.6, 29.6, 29.0, 27.9, 27.2, 26.0, 22.4, 21.7, 15.7, 13.9; IR (neat) *v* (cm^{-1}) 2931, 2857, 2228, 1762, 1732, 1643, 1456, 1368, 1152, 1116, 1083, 1039; MS (EI): *m/z* (%) 335 $[(M - t\text{-Bu})^+$, 9.13], 57 (100); HRMS Calcd for $C_{23}H_{37}O_5$ $(M + H)^+$: 393.2636; Found:

393.2634.

2.24 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-allylfuran-2(*5H*)-one **3fa**. (zdj-1-132)



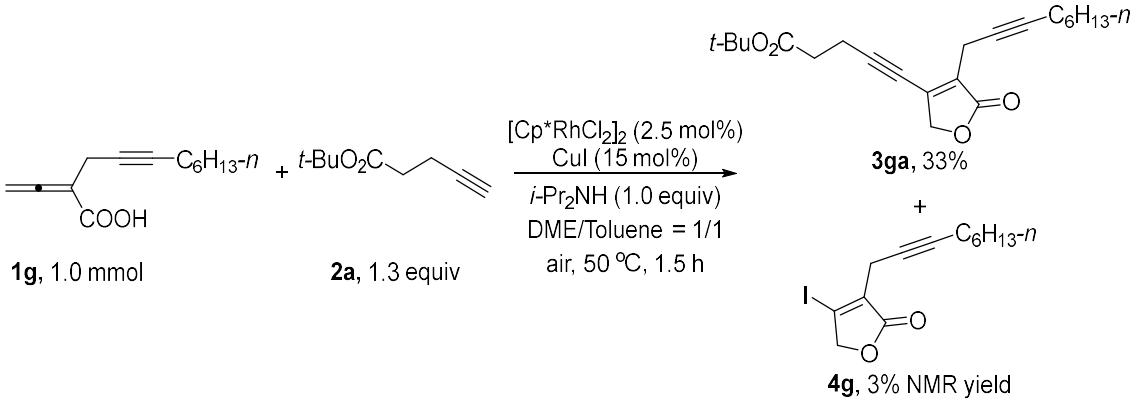
Following **Typical Procedure**, the reaction of **1f** (124.1 mg, 1.0 mmol), **2a** (200.4 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.5 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL), afforded **2a'** (39.5 mg, 20%) and **3fa** (129.9 mg, 47%) [eluent: petroleum ether/ethyl acetate = 20/1 (1200 mL)].

2a': white solid, m.p. 56.0-58.4 °C (determined without recrystallization); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.60-2.33 (m, 8 H, CH_2 × 4), 1.45 (s, 18 H, CH_3 × 6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 80.9, 75.8, 65.6, 34.1, 28.0, 15.2; IR (neat) *ν* (cm^{-1}) 3006, 2979, 2932, 2142, 1728, 1455, 1428, 1388, 1366, 1293, 1254, 1205, 1158; MS (EI): *m/z* (%) 250 [$(M - t\text{-Bu} + H)^+$, 2.14], 57 (100); Anal. Calcd. for $C_{18}H_{26}O_4$ (%): C, 70.56; H, 8.55; Found: C, 70.30; H, 8.35.

3fa: light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.99-5.76 (m, 1 H, =CH), 5.21-5.01 (m, 2 H, $=CH_2$), 4.68 (s, 2 H, OCH_2), 3.12 (d, *J* = 6.6 Hz, 2 H, CH_2), 2.75 (t, *J* = 7.2 Hz, 2 H, CH_2), 2.53 (t, *J* = 7.2 Hz, 2 H, CH_2), 1.47 (s, 9 H, CH_3 × 3); ^{13}C NMR

(75 MHz, $CDCl_3$) δ 173.6, 170.4, 140.6, 132.8, 132.4, 117.0, 106.2, 81.1, 71.5, 71.2, 33.8, 29.0, 27.9, 15.8; IR (neat) *v* (cm^{-1}) 3075, 2979, 2933, 2228, 1760, 1730, 1643, 1455, 1425, 1393, 1367, 1342, 1298, 1248, 1211, 1152, 1082, 1037; MS (EI): *m/z* (%) 219 [(M – *t*-Bu)$^+$, 7.01], 57 (100); Anal. Calcd. for $C_{16}H_{20}O_4$ (%): C, 69.55; H, 7.30; Found: C, 69.58; H, 7.32.

2.25 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-(non-2-ynyl)furan-2(*5H*)-one **3ga**. (fjj-4-120)



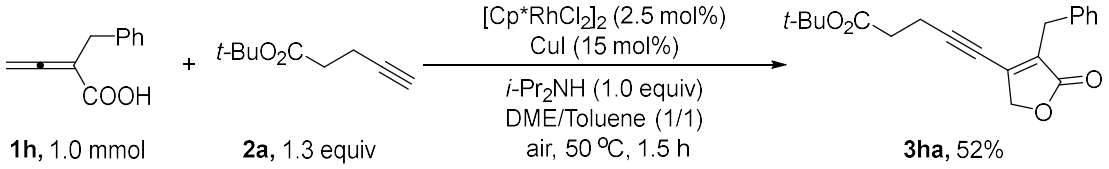
1g, 1.0 mmol **2a**, 1.3 equiv

Following **Typical Procedure**, the reaction of **1g** (206.3 mg, 1.0 mmol), **2a** (200.5 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.6 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ga** (118.6 mg, 33%) as a brown oil [eluent: petroleum ether/ethyl acetate = 50/1 (500 mL) to 25/1 (1000 mL)] together with 3% NMR of **4g**, which was analyzed by ^1H NMR using 46 μL of mesitylene as the internal standard.

3ga: ^1H NMR (300 MHz, $CDCl_3$) δ 4.68 (s, 2 H, OCH_2), 3.24 (s, 2 H, CH_2), 2.76 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.54 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.20-2.05 (m, 2 H, CH_2), 1.57-1.13 (m, 17 H, CH_3 × 3 and CH_2 × 4), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (75

MHz, $CDCl_3$) δ 172.9, 170.4, 140.9, 130.6, 107.3, 81.8, 81.1, 73.5, 71.2, 33.8, 31.2, 28.7, 28.4, 28.0, 22.4, 18.7, 15.9, 14.9, 13.9; IR (neat) *v* (cm^{-1}) 2932, 2859, 2228, 1764, 1732, 1649, 1368, 1342, 1152, 1037; MS (EI): *m/z* (%) 301 [(M – *t*-Bu) $^+$, 4.00], 57 (100); HRMS Calcd for $C_{22}H_{30}O_4Na$ ($M+Na^+$): 381.2036; Found: 381.2039.

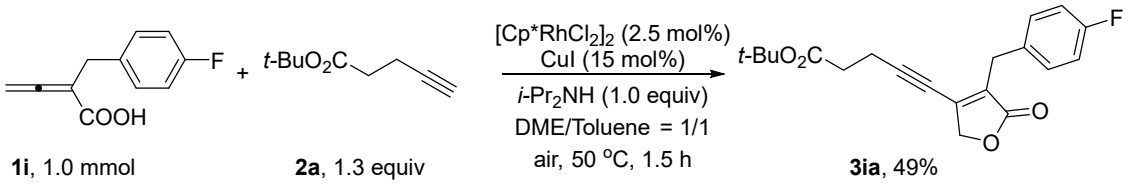
2.26 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-benzylfuran-2(*5H*)-one **3ha**. (zdj-1-083)



1h, 1.0 mmol **2a**, 1.3 equiv **3ha**, 52%

Following **Typical Procedure**, the reaction of **1h** (174.2 mg, 1.0 mmol), **2a** (200.9 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.4 mg, 0.025 mmol), CuI (28.5 mg, 0.15 mmol), and *i*-Pr_2NH (0.14 mL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL), afforded **3ha** (170.5 mg, 52%) as a yellow oil [eluent: petroleum ether/ethyl acetate = 15/1 (900 mL) to 10/1 (200 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.16 (m, 5 H, ArH), 4.65 (s, 2 H, OCH_2), 3.68 (s, 2 H, CH_2), 2.73 (t, *J* = 7.1 Hz, 2 H, CH_2), 2.51 (t, *J* = 7.2 Hz, 2 H, CH_2), 1.46 (s, 9 H, CH_3 × 3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 170.4, 140.5, 137.2, 134.1, 128.8, 128.4, 126.6, 106.3, 81.1, 71.7, 71.1, 33.8, 30.8, 27.9, 15.8; IR (neat) *v* (cm^{-1}) 3062, 3029, 2978, 2931, 2226, 1758, 1729, 1642, 1598, 1495, 1455, 1429, 1393, 1367, 1343, 1247, 1211, 1152, 1085, 1035; MS (EI): *m/z* (%) 327 [$(M + H)^+$, 40.36], 57 (100); HRMS Calcd for $C_{20}H_{22}O_4Na$ $(M + Na)^+$: 349.1410; Found: 349.1408.

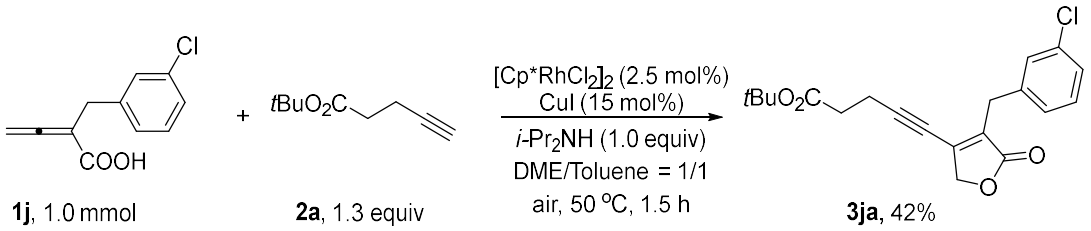
2.27 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-(4-fluorobenzyl)furan-2(*5H*)-one **3ia**. (fjj-4-086)



1i, 1.0 mmol **2a**, 1.3 equiv **3ia**, 49%

Following **Typical Procedure**, the reaction of **1i** (192.2 mg, 1.0 mmol), **2a** (202.0 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.5 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ia** (168.4 mg, 49%) as a brown oil [eluent: petroleum ether/ethyl acetate = 20/1 (1000 mL) to 15/1 (500 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (t, *J* = 6.9 Hz, 2 H, ArH), 6.97 (t, *J* = 8.7 Hz, 2 H, ArH), 4.67 (s, 2 H, OCH_2), 3.65 (s, 2 H, CH_2), 2.75 (t, *J* = 7.2 Hz, 2 H, CH_2), 2.53 (t, *J* = 7.2 Hz, 2 H, CH_2), 1.46 (s, 9 H, CH_3 × 3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 170.5, 161.7 (*J* = 243.4 Hz), 140.6, 134.0, 133.0 (*J* = 3.5 Hz), 130.4 (*J* = 7.6 Hz), 115.3 (*J* = 20.6 Hz), 106.5, 81.2, 71.6, 71.2, 33.8, 30.0, 28.0, 15.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -116.7; IR (neat) *v* (cm^{-1}) 2979, 2930, 2226, 1759, 1729, 1509, 1367, 1343, 1222, 1154, 1036; MS (EI): *m/z* (%) 288 [(M – *t*-Bu + H)$^+$, 41.98], 287 [(M – *t*-Bu)$^+$, 32.05], 57 (100); HRMS Calcd for $C_{20}H_{21}FO_4Na$ ($M+Na^+$): 367.1316; Found: 367.1317.

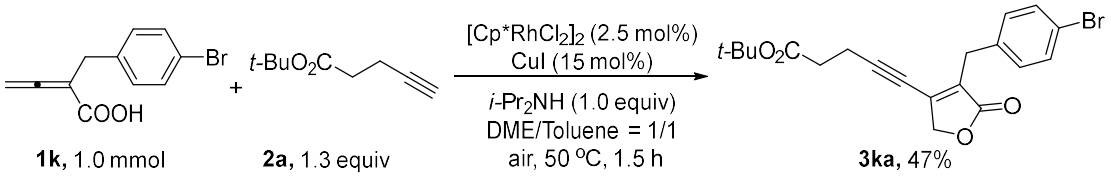
2.28 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-(3-chlorobenzyl)furan-2(*5H*)-one **3ja**. (fjj-4-096)



1j, 1.0 mmol **2a**, 1.3 equiv **3ja**, 42%

Following **Typical Procedure**, the reaction of **1a** (208.6 mg, 1.0 mmol), **2e** (200.6 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3ae** (151.5 mg, 42%) as a yellow oil [eluent: petroleum ether/ethyl acetate = 20/1 (1000 mL) to 15/1 (500 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.14 (m, 4 H, ArH), 4.69 (s, 2 H, OCH_2), 3.66 (s, 2 H, CH_2), 2.75 (t, *J* = 7.2 Hz, 2 H, CH_2), 2.54 (t, *J* = 7.2 Hz, 2 H, CH_2), 1.46 (s, 9 H, CH_3 × 3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 170.4, 141.1, 139.1, 134.1, 133.3, 129.7, 128.9, 127.0, 126.8, 106.9, 81.1, 71.5, 71.2, 33.7, 30.4, 27.9, 15.8; IR (neat) *v* (cm^{-1}) 2979, 2932, 2226, 1760, 1729, 1642, 1475, 1432, 1367, 1341, 1152, 1082, 1036; MS (EI): *m/z* (%) 306 [(M(^{37}Cl) – *t*-Bu + H)$^+$, 9.72], 305 [(M(^{37}Cl) – *t*-Bu)$^+$, 13.06], 304 [(M(^{35}Cl) – *t*-Bu + H)$^+$, 26.39], 304 [(M(^{35}Cl) – *t*-Bu)$^+$, 16.73], 57 (100); HRMS Calcd for $C_{20}H_{22}{}^{35}ClO_4$ (M + H)$^+$: 361.1201; Found: 361.1204.

2.29 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-(4-bromobenzyl)furan-2(*5H*)-one **3ka**. (syq-1-083, syq-1-088)

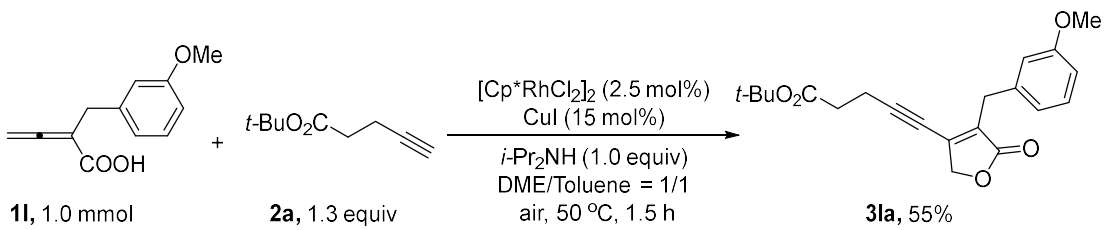


1k, 1.0 mmol **2a,** 1.3 equiv **3ka,** 47%

Following typical procedure: the reaction of **1k** (253.3 mg, 1.0 mmol), **2a** (199.6

mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.3 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded impure **3ka** (198.6 mg) after chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 20/1 (600 mL) to 10/1 (200 mL) then 8/1 (400 mL)]. The impure **3ka** was further purified via chromatography on silica gel [eluent: petroleum ether/dichloromethane = 1/3 (200 mL) to 1/6 (600 mL)] to afford pure **3ka** (189.8 mg, 47%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2 H, ArH), 7.19 (d, *J* = 8.4 Hz, 2 H, ArH), 4.66 (s, 2 H, CH_2), 3.62 (s, 2 H, CH_2), 2.74 (t, *J* = 7.1 Hz, 2 H, CH_2), 2.51 (t, *J* = 7.2 Hz, 2 H, CH_2), 1.46 (s, 9 H, CH_3 × 3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 170.3, 140.8, 136.2, 133.4, 131.4, 130.6, 120.5, 106.7, 81.1, 71.5, 71.2, 33.7, 30.2, 27.9, 15.8; IR (neat) *v* (cm^{-1}) 2978, 2929, 2219, 1760, 1728, 1643, 1488, 1367, 1342, 1247, 1152, 1082, 1036, 1012; MS (EI) *m*/*z* (%): 350 [(M(^{81}Br) – *t*-Bu)$^+$, 6.87], 348 [(M(^{79}Br) – *t*-Bu)$^+$, 7.04], 165 (100); HRMS Calcd for $C_{20}H_{21}{}^{79}BrO_4Na$ (M + Na)$^+$: 427.0515; Found: 427.0517.

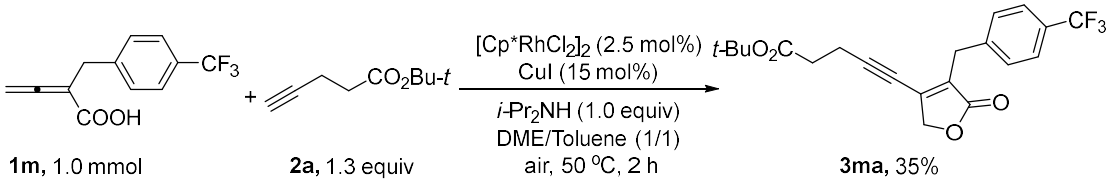
2.30 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-(3-methoxybenzyl)furan-2(*5H*)-one **3la**. (zdj-1-129)



Following **Typical Procedure**, the reaction of **1l** (204.1 mg, 1.0 mmol), **2a** (200.6 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), and

i-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3la** (194.6 mg, 55%) as a brown oil [eluent: petroleum ether/dichloromethane = 1/50 (900 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (t, *J* = 8.0 Hz, 1 H, ArH), 6.98-6.83 (m, 2 H, ArH), 6.80-6.70 (m, 1 H, ArH), 4.66 (s, 2 H, OCH_2), 3.79 (s, 3 H, OCH_3), 3.65 (s, 2 H, CH_2), 2.74 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.52 (t, *J* = 7.4 Hz, 2 H, CH_2), 1.46 (s, 9 H, $CH_3 \times 3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 170,4, 159.6, 140.6, 138.7, 134.0, 129.4, 121.1, 114.5, 112.0, 106.3, 81.1, 71.7, 71.1, 55.0, 33.8, 30.8, 28.0, 15.8; IR (neat) *v* (cm^{-1}) 3058, 2977, 2932, 2834, 2225, 1759, 1729, 1641, 1600, 1585, 1490, 1455, 1436, 1393, 1367, 1341, 1260, 1211, 1151, 1082, 1036; MS (EI): *m/z* (%) 356 (M^+, 8.88), 57 (100); HRMS Calcd for $C_{21}H_{24}O_5Na$ $(M + Na)^+$: 379.1516; Found: 379.1515.

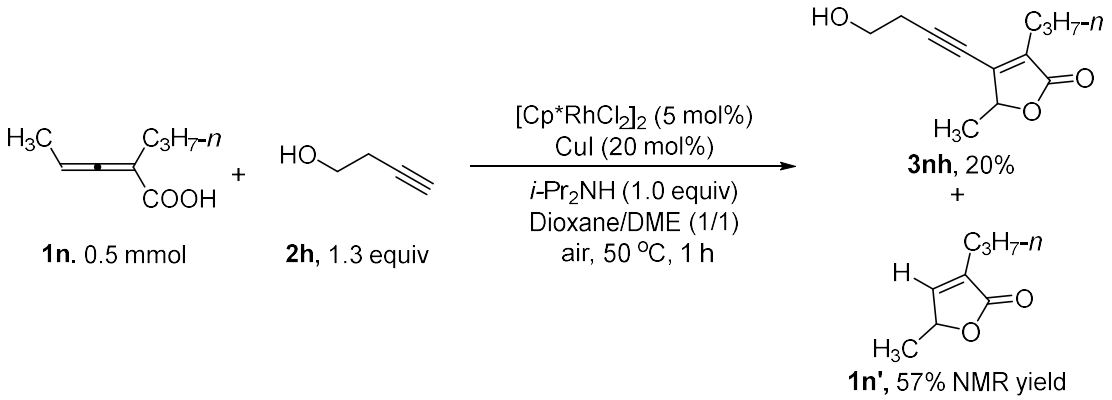
2.31 Synthesis of 4-(5-(*tert*-butoxy)-5-oxopentynyl)-3-(4-(trifluoromethyl)benzyl)furan-2(*5H*)-one **3ma**. (zdj-1-092)



Following **Typical Procedure**, the reaction of **1m** (242.3 mg, 1.0 mmol), **2a** (200.5 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.3 mg, 0.025 mmol), CuI (28.4 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded impure **3ma** (169.5 mg) as a solid after chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 15/1 (1200 mL)]. The impure **3ma** was further purified via recrystallization (petroleum ether) at -20 °C to afford pure **3ma**

(93.2 mg). The mother liquid was further purified via recrystallization (petroleum ether) at -20 °C to afford pure **3ma** (36.1 mg). Repeat it again to afford pure **3ma** (8.0 mg). Total afforded pure **3ma** (137.3 mg, 35%) as a light yellow solid, m.p. 70.3-71.2 °C (petroleum ether): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 2 H, ArH), 7.43 (t, *J* = 8.1 Hz, 2 H, ArH), 4.69 (s, 2 H, OCH_2), 3.74 (s, 2 H, CH_2), 2.73 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.50 (t, *J* = 7.4 Hz, 2 H, CH_2), 1.45 (s, 9 H, CH_3 × 3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 170.4, 141.3, 133.1, 129.2, 129.0 (q, *J* = 32.2 Hz), 125.4 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 270.3 Hz), 107.0, 81.2, 71.5, 71.3, 33.8, 30.6, 27.9, 15.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.0; IR (neat) *v* (cm^{-1}) 2981, 2931, 2226, 1759, 1729, 1644, 1618, 1581, 1420, 1368, 1326, 1248, 1157, 1123, 1111, 1066, 1037, 1020; MS (EI): *m/z* (%) 337 [(M - *t*-Bu)$^+$, 46.75], 57 (100); Anal. Calcd. for $C_{21}H_{21}F_3O_4$ (%): C, 63.95; H, 5.37; Found: C, 63.71; H, 5.43.

2.32 Synthesis of 4-(4-hydroxybutynyl)-5-methyl-3-propylfuran-2(5*H*)-one **3nh**. (zdj-2-003)

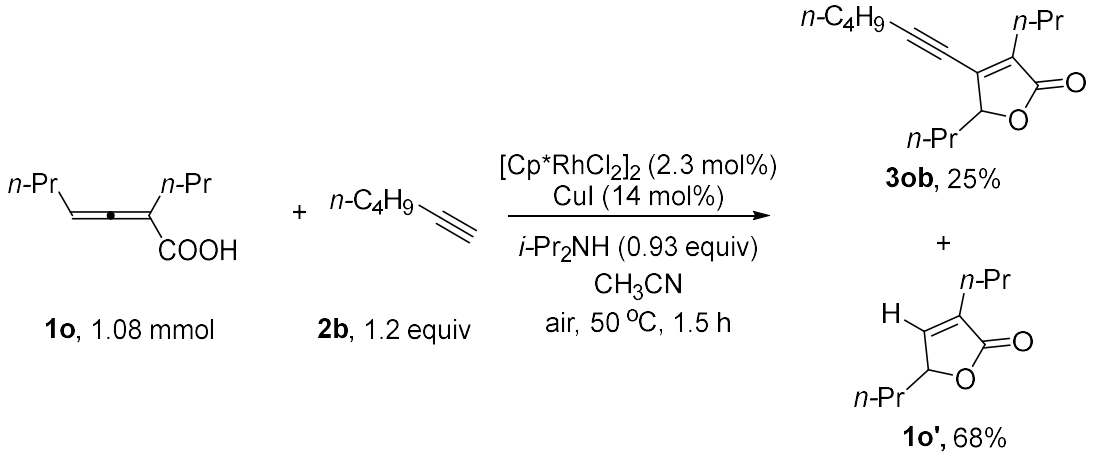


Following **Typical Procedure**, the reaction of **1n** (70.1 mg, 0.5 mmol), **2h** (49 μL, d = 0.926 g/mL, 45.4 mg, 0.65 mmol), $[Cp^*RhCl_2]_2$ (15.6 mg, 0.025 mmol), CuI (19.0

mg, 0.1 mmol), and *i*-Pr_2NH (70 μL, d = 0.718 g/mL, 50.3 mg, 0.5 mmol) in dioxane (3.5 mL) and DME (3.5 mL) afforded **3nh** (20.4 mg, 20%) [eluent: petroleum ether/ethyl acetate = 4/1 (1000 mL)] together with 57% NMR of **1n'**, which was analyzed by ^1H NMR using 23 μL of mesitylene as the internal standard.

3nh: colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 4.87 (q, *J* = 6.7 Hz, 1 H, OCH), 3.84 (t, *J* = 6.5 Hz, 2 H, OCH_2), 2.77 (t, *J* = 6.5 Hz, 2 H, CH_2), 2.34 (t, *J* = 7.7 Hz, 2 H, CH_2), 1.97 (s, 1 H, OH), 1.71-1.52 (m, 2 H, CH_2), 1.47 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.94 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 145.2, 135.0, 104.6, 78.7, 73.0, 60.6, 26.8, 24.1, 20.8, 18.9, 13.8; IR (neat) *v* (cm^{-1}) 3446, 2962, 2933, 2874, 2224, 1756, 1639, 1455, 1365, 1316, 1191, 1112, 1047; MS (EI): *m/z* (%) 208 (M^+, 5.35), 91 (100); HRMS Calcd for $C_{12}H_{16}O_3$ (M^+): 208.1099; Found: 208.1101.

2.33 Synthesis of 4-(hexynyl)-3,5-dipropylfuran-2(*5H*)-one **3ob**. (fjj-6-096)



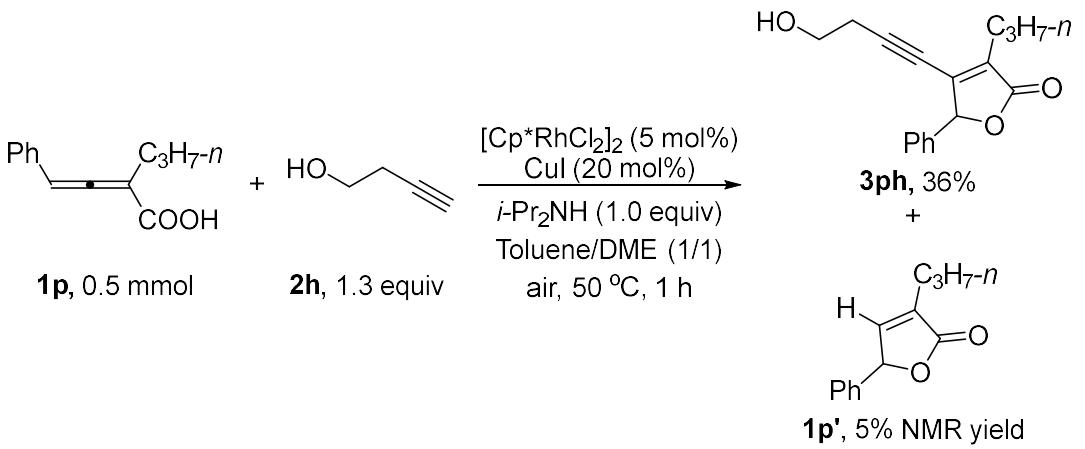
To a 100 mL dry Schlenk tube were added $[Cp^*RhCl_2]_2$ (15.6 mg, 0.025 mmol), CuI (28.6 mg, 0.15 mmol), **1o** (182.1 mg, 1.08 mmol), CH_3CN (2.5 mL), **2b** (107.0 mg, 1.3 mmol), CH_3CN (2.5 mL), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0

mmol) sequentially. After being stirred at 50 °C under air atmosphere for 1.5 h, the reaction was complete as monitored by TLC. The resulting mixture was filtrated through a short column of silica gel eluted with ethyl acetate (20 mL × 3). The combined filtrate was then concentrated in vacuo and the crude residue was purified via chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 20/1 (400 mL) to 15/1 (300 mL)] to afford **3ob** (70.1 mg, 25%, 95% purity) and **1o'** (123.0 mg, 68%).

3ob: brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.78 (dd, J_1 = 7.2 Hz, J_2 = 3.3 Hz, 1 H, OCH), 2.49 (t, J = 7.0 Hz, 2 H, CH_2), 2.33 (t, J = 7.5 Hz, 2 H, CH_2), 1.97-1.87 (m, 1 H, one proton of CH_2), 1.66-1.37 (m, 9 H, CH_2 × 4 and one proton of CH_2), 1.02-0.88 (m, 9 H, CH_3 × 3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 144.7, 134.6, 108.4, 82.1, 71.9, 34.9, 30.2, 26.8, 21.8, 20.9, 19.5, 17.7, 13.7, 13.4; IR (neat) v (cm^{-1}) 2961, 2934, 2874, 2223, 1760, 1640, 1464, 1365, 1333, 1189, 1114, 1093, 1061, 1022; MS (EI): *m/z* (%) 248 (M^+, 3.44), 177 (100); HRMS Calcd for $C_{16}H_{24}O_2Na$ $(M + Na)^+$: 271.1669; Found: 271.1669.

1o': oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 1 H, =CH), 5.02-4.82 (m, 1 H, OCH), 2.25 (t, J = 7.8 Hz, 2 H, CH_2), 1.77-1.68 (m, 1 H, one proton of CH_2), 1.67-1.54 (m, 3 H, CH_2 and one proton of CH_2), 1.54-1.38 (m, 2 H, CH_2), 1.03-0.89 (m, 6 H, CH_3 × 2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 148.1, 133.8, 80.8, 35.3, 26.9, 20.5, 18.1, 13.5, 13.4; IR (neat) v (cm^{-1}) 2962, 2935, 2875, 1755, 1465, 1337, 1200, 1114, 1061, 1026; MS (EI): *m/z* (%) 168 (M^+, 38.16), 97 (100); HRMS Calcd for $C_{10}H_{16}O_2Na$ $(M + Na)^+$: 191.1043; Found: 191.1042.

2.34 Synthesis of 4-(4-hydroxybutynyl)-5-phenyl-3-propylfuran-2(*5H*)-one **3ph**. (fjj-3-177)

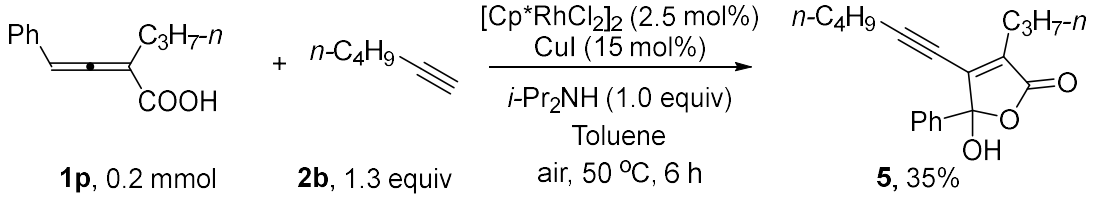


Following **Typical Procedure**, the reaction of **1p** (101.5 mg, 0.5 mmol), **2h** (49 μL, d = 0.963 g/mL, 47.2 mg, 0.65 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (19.2 mg, 0.1 mmol), and *i*-Pr_2NH (70 μL, d = 0.718 g/mL, 50.3 mg, 0.5 mmol) in toluene (3.5 mL) and DME (3.5 mL) afforded **3ph** (48.7 mg, 36%) [eluent: petroleum ether/ethyl acetate = 20/1 (500 mL) to 5/1 (1000 mL)] together with 5% NMR of **1p'**, which was analyzed by ^1H NMR using 23 μL of mesitylene as the internal standard.

3ph: yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44-7.33 (m, 3 H, ArH), 7.33-7.22 (m, 2 H, ArH), 5.72 (s, 1 H, OCH), 3.68 (t, *J* = 6.3 Hz, 2 H, CH_2), 2.63 (t, *J* = 6.3 Hz, 2 H, CH_2), 2.41 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.87 (bs, 1 H, OH), 1.74-1.56 (m, 2 H, CH_2), 0.96 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 143.9, 134.72, 143.65, 129.2, 128.7, 126.5, 105.1, 83.4, 73.3, 60.5, 26.9, 24.1, 20.9, 13.8; IR (neat) *v* (cm^{-1}) 3459, 2962, 2874, 2228, 1753, 1637, 1456, 1364, 1001; MS (EI): *m/z* (%) 270 (M^+, 11.83), 105 (100); HRMS Calcd for $C_{17}H_{18}O_3$ (M^+): 270.1256; Found: 270.1256.

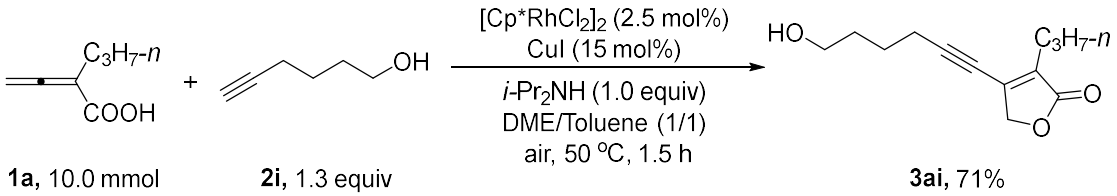
2.35 Synthesis of 4-(hexynyl)-5-hydroxy-5-phenyl-3-propylfuran-2(*5H*)-one **5**. (fjj-6-

094)



Following **Typical Procedure**, the reaction of **1p** (40.4 mg, 0.2 mmol), **2b** (22.0 mg, 0.26 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), CuI (5.6 mg, 0.03 mmol), and *i*-Pr_2NH (28 μL, d = 0.718 g/mL, 20.1 mg, 0.2 mmol) in toluene (1 mL) afforded **5** (20.8 mg, 35%) as an oil [eluent: petroleum ether/ethyl acetate = 10/1 (500 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.48 (m, 2 H, ArH), 7.48-7.30 (m, 3 H, ArH), 3.92 (s, 1 H, OH), 2.44 (t, *J* = 7.0 Hz, 2 H, CH_2), 2.35 (t, *J* = 7.8 Hz, 2 H, CH_2), 1.67-1.57 (m, 2 H, CH_2), 1.57-1.47 (m, 2 H, CH_2), 1.43-1.33 (m, 2 H, CH_2), 0.98-0.84 (m, 6 H, CH_3 × 2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 145.0, 137.1, 134.8, 129.4, 128.4, 125.8, 110.3, 104.2, 71.6, 30.1, 26.8, 21.8, 20.9, 19.7, 13.8, 13.4; IR (neat) *v* (cm^{-1}) 3367, 2961, 2933, 2873, 2222, 1764, 1647, 1452, 1362, 1213, 1142, 1072; MS (EI): *m/z* (%) 298 (M^+, 10.51), 176 (100); HRMS Calcd for $C_{19}H_{22}O_3Na$ $(M + Na)^+$: 321.1461; Found: 321.1462.

3. Gram-Scale Reaction (zdj-1-148)

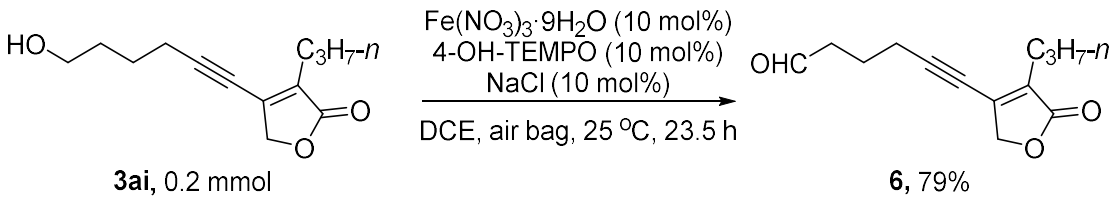


1a, 10.0 mmol **2i**, 1.3 equiv **3ai**, 71%

To a 1000 mL three-necked flask equipped with a magnetic stirring bar were added $[Cp^*RhCl_2]_2$ (154.3 mg, 0.25 mmol), CuI (285.8 mg, 1.5 mmol), **1a** (1.2625 g, 10.0 mmol), **2i** (1.2741 g, 13.0 mmol), toluene (25 mL), DME (25 mL), and *i*-Pr_2NH (1.4 mL, d = 0.718 g/mL, 1005.2 mg, 10.0 mmol) sequentially. The reaction flask was put into an oil bath preheated at 50 °C and the reaction was complete after being stirred for 1.5 h as monitored by TLC. The resulting mixture was filtered through a short column of silica gel eluted with ethyl acetate (100 mL × 3) and concentrated in vacuo. The crude residual was purified via chromatography on silica gel to afford **3ai** (1.5718 g, 71%) as a yellow oil [eluent: petroleum ether/ethyl acetate = 4/1 (2500 mL) to 2/1 (600 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.68 (s, 2 H, OCH_2), 3.69 (s, 2 H, OCH_2), 2.53 (t, *J* = 6.5 Hz, 2 H, CH_2), 2.43-2.16 (m, 3 H, CH_2 and OH), 1.82-1.43 (m, 6 H, CH_2 × 3), 0.94 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 140.7, 134.5, 107.3, 71.6, 71.2, 61.8, 31.5, 26.6, 24.4, 20.7, 19.6, 13.7.

4. Synthetic Applications.

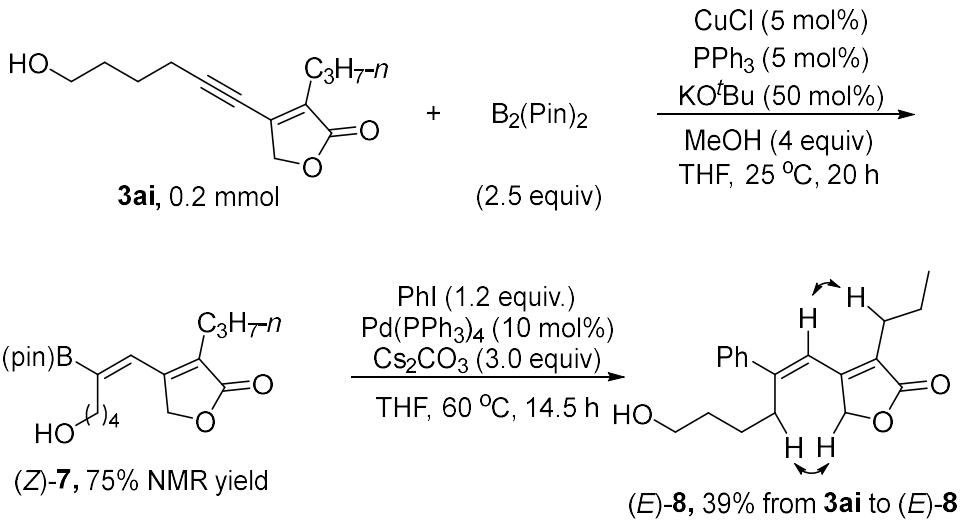
4.1 Synthesis of 4-(6-oxohexynyl)-3-propylfuran-2(*5H*)-one **6**.[7] (zdj-1-180)



3ai, 0.2 mmol **6,** 79%

To a 25 mL Schlenk tube equipped with a magnetic stirring bar were added $Fe(NO_3)_3·9H_2O$ (8.1 mg, 0.02 mmol), 4-OH-TEMPO (3.5 mg, 0.02 mmol), NaCl (1.2 mg, 0.02 mmol), **3ai** (44.3 mg, 0.2 mmol), and DCE (0.8 mL) sequentially. The Schlenk tube was then connected with an air bag. The resulting mixture was stirred at 25 °C for 23.5 h as monitored by TLC, filtered through a short column of silica gel eluted with ethyl ether (10 mL × 3), and concentrated in vacuo. The crude residual was purified via chromatography on silica gel to afford **6** (32.1 mg, 79%) as a colorless oil [eluent: petroleum ether/ethyl ether = 3/1 (600 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.83 (s, 1 H, CHO), 4.67 (s, 2 H, OCH_2), 2.73-2.46 (m, 4 H, CH_2 × 2), 2.36 (t, *J* = 7.7 Hz, 2 H, CH_2), 2.05-1.86 (m, 2 H, CH_2), 1.69-1.50 (m, 2 H, CH_2), 0.94 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 174.2, 140.1, 135.2, 105.7, 72.4, 71.1, 42.5, 26.8, 20.8, 20.5, 19.2, 13.8; IR (neat) *v* (cm^{-1}) 2963, 2874, 2219, 1754, 1637, 1452, 1370, 1344, 1085, 1028; MS (EI): *m/z* (%) 191 [$(M - CHO)^+$, 67.20], 91 (100); HRMS Calcd for $C_{13}H_{16}O_3$ (M^+): 220.1099; Found: 220.1099.

4.2. Synthesis of (*E*)-4-(5-hydroxy-2-phenylpentenyl)-3-propylfuran-2(*5H*)-one (*E*)-**8**.[8] (zdj-1-169, zdj-1-170)



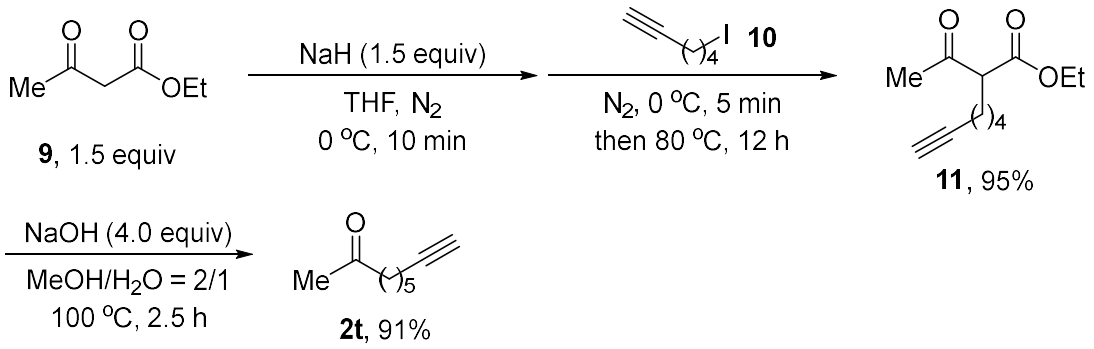
To a 25 mL Schlenk tube with polytetrafluoroethylene plug were added PPh_3 (2.5 mg, 0.01 mmol), KO^{t}Bu (11.1 mg, 0.1 mmol), $B_2(pin)_2$ (127.0 mg, 0.5 mmol), and CuCl (1.1 mg, 0.01 mmol) THF (1 mL) sequentially under nitrogen atmosphere. The resulting mixture was stirred for 5 min, followed by the addition **3ai** (44.5 mg, 0.2 mmol), THF (1 mL), and MeOH (32 μL, d = 0.7918 g/mL, 25.3 mg, 0.8 mmol) under nitrogen atmosphere. The resulting mixture was stirred at 25 °C for 20 h, filtered through a short column of silica gel eluted with ethyl acetate (10 mL × 3), and concentrated in vacuo. To the crude residue was added 9.2 μL of mesitylene as the internal standard: 75% NMR yield of (*Z*)-**7** was determined by ^{1}H NMR analysis of the crude product. After removing $CDCl_3$ in vacuo, the crude product (*Z*)-**7** was used without further purification.

To a 25 mL flame-dried Schlenk tube were added $Pd(PPh_3)_4$ (23.2 mg, 0.02 mmol), Cs_2CO_3 (196.1 mg, 0.6 mmol), a solution of the above crude product (*Z*)-**7** in THF (2 mL), and PhI (27 μL, d = 1.82 g/mL, 49.2 mg, 0.24 mmol) sequentially under nitrogen atmosphere. The resulting mixture was stirred at 60 °C for 14.5 h, filtered through a

short column of silica gel (3 cm) eluted with ethyl acetate (10 mL × 3), and concentrated in vacuo. The crude residual was purified via chromatography on silica gel to afford (*E*)-**8** (23.5 mg, 39% from **3ai** to (*E*)-**8**) as a colorless oil [eluent: petroleum ether/ethyl acetate = 4/1 (1000 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.30 (m, 5 H, ArH), 6.50 (s, 1 H, =CH), 5.12 (s, 2 H, OCH_2), 3.62 (t, *J* = 6.0 Hz, 2 H, OCH_2), 2.62 (t, *J* = 7.7 Hz, 2 H, CH_2), 2.36 (t, *J* = 7.7 Hz, 2 H, CH_2), 1.80-1.32 (m, 7 H, OH and CH_2 × 3), 0.94 (t, *J* = 7.4 Hz, 3 H, CH_3) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 153.6, 149.9, 142.0, 129.0, 128.6, 128.4, 126.6, 118.1, 70.9, 62.1, 32.30, 32.25, 25.8, 25.6, 21.5, 13.9; IR (neat) *v* (cm^{-1}) 3446, 2959, 2932, 2871, 1747, 1626, 1445, 1375, 1344, 1192, 1114, 1074, 1038; MS (EI): *m/z* (%) 300 (M^+, 56.14), 91 (100); HRMS Calcd for $C_{19}H_{24}O_3$ (M^+): 300.1725; Found: 300.1725.

5. Synthesis of naturally occurring *Appenolide A*.

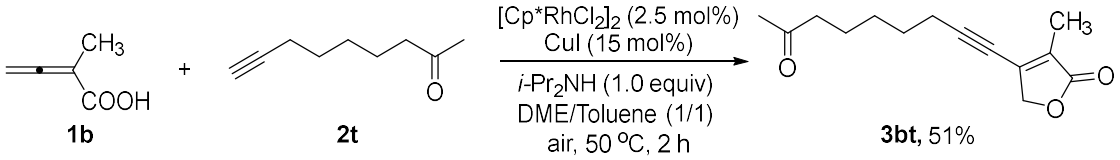
5.1 Synthesis of non-8-yn-2-one **2t**. (zdj-2-035, zdj-2-037)



To an over dried three-necked flask equipped with a magnetic stirring bar were added NaH (0.6021 g, 60% dispersion in mineral oil, 15 mmol). After degassing under vacuum and backfilling with nitrogen for three times, THF (15 mL) was added. Then the resulting mixture was put into an ice-water bath, cooled to 0 °C. Ethyl acetoacetate **9** (1.9 mL, d = 1.0282 g/mL, 1953.6 mg, 15 mmol) was added dropwise for 10 min and 6-iodohexyne **10** (2.0804 g, 10 mmol) was added dropwise for 5 min at 0 °C sequentially under nitrogen atmosphere. Then the resulting mixture was put into an oil bath preheated at 80 °C. The reaction was complete after being stirred for 12 h as monitored by TLC, quenched with a saturated aqueous NH_4Cl solution, and extracted with dichloromethane (30 mL × 3). The combined organic extract was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude residual was purified via chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 20/1 (1000 mL)] to afford **11**[9a] as a liquid (2.0067 g, 95%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20 (q, J = 7.1 Hz, 2 H, OCH_2), 3.42 (t, J = 7.4 Hz, 1 H, CH), 2.31-2.14 (m, 5 H, CH_3 and CH_2), 1.95 (t, J = 2.6 Hz, 1 H, ≡CH), 1.92-1.79 (m, 2 H, CH_2), 1.62-1.48 (m, 2 H, CH_2), 1.48-1.33 (m, 2 H, CH_2), 1.28 (t, J = 7.2 Hz, 3 H, CH_3).

To a round-bottom flask equipped with a magnetic stirring bar were added **11** (2.0020 g, 9.5 mmol), MeOH (30 mL), H_2O (15 mL), and NaOH (1.5469 g, 38 mmol) sequentially. The reaction was complete after stirring in an oil bath preheated at 100 °C for 2.5 h as monitored by TLC. The resulting mixture was cooled to room temperature, evaporated under vacuum, extracted with ethyl ether (20 mL × 3). The combine organic extract was washed with brine three times, dried over Na_2SO_4, filtered, and concentrated to afford **2t**[9b] as a liquid (1.1975 g, 91%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45 (t, J = 7.4 Hz, 2 H, CH_2), 2.22 (td, J_1 = 6.9 Hz, J_2 = 2.7 Hz, 2 H, CH_2), 2.14 (s, 3 H, CH_3), 1.94 (t, J = 2.6 Hz, 1 H, ≡CH), 1.66-1.47 (m, 4 H, CH_2 × 2), 1.47-1.33 (m, 2 H, CH_2).

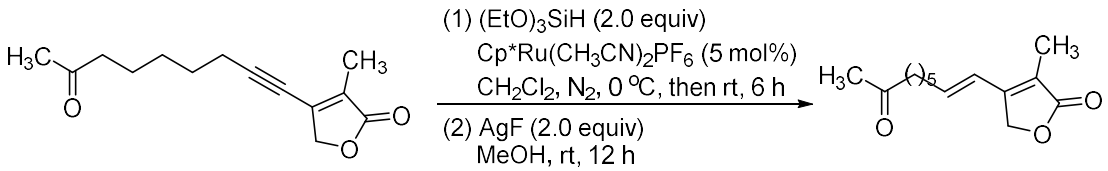
5.2 Synthesis of 3-methyl-4-(8-oxononynyl)-furan-2(*5H*)-one **3bt** (zdj-2-032).



Following **Typical Procedure**, the reaction of **1b** (98.2 mg, 1.0 mmol), **2t** (179.8 mg, 1.3 mmol), $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), CuI (28.7 mg, 0.15 mmol), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) in DME (2.5 mL) and toluene (2.5 mL) afforded **3bt** (119.0 mg, 51%) as a colorless oil [eluent: petroleum ether/ethyl acetate = 5/1 (900 mL)]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71-4.63 (m, 2 H, OCH_2), 2.54-2.42 (m, 4 H, CH_2 × 2), 2.15 (s, 3 H, CH_3), 1.95 (s, 3 H, CH_3), 1.68-1.56 (m, 4 H, CH_2 × 2), 1.50-1.36 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8, 174.6, 140.5, 130.8, 107.5, 71.5, 71.2, 43.3, 29.8, 28.2, 27.9, 23.0, 19.6, 9.9; IR (neat) v (cm^{-1}) 2936,

2862, 2222, 1759, 1714, 1646, 1452, 1338, 1210, 1160, 1076, 1038; MS (EI): *m/z* (%) 234 (M^+, 46.3), 149 (100); HRMS Calcd for $C_{14}H_{18}O_3$ (M^+): 234.1256; Found: 234.1254.

5.3 Synthesis of (*E*)-*Appenolide A*. (fjj-5-045)



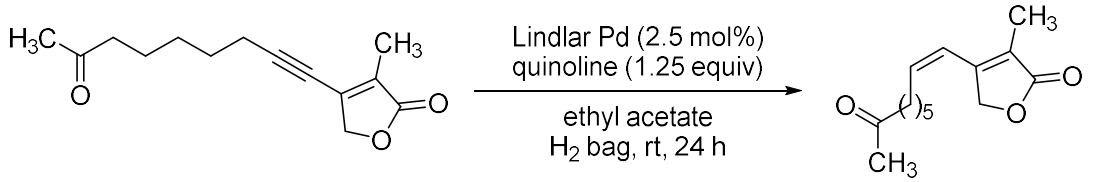
3bt (*E*)-Appenolide A, 88%

To a 25 mL Schlenk tube equipped with a magnetic stirring bar were added **3bt** (68.9 mg, 0.3 mmol) and CH_2Cl_2 (3 mL) under nitrogen atmosphere. After cooling down to 0 ºC, Cp*Ru(CH_3CN)$_2PF_6$ (7.6 mg, 0.015 mmol) and $(EtO)_3SiH$ (111 μL, d = 0.89 g/mL, 98.8 mg, 0.6 mmol,) were added sequentially. Then the reaction was stirring at room temperture for 6 h, filtered through a short column of silica gel eluted with ethyl acetate (10 mL × 3), and concentrated in vacuo to afford crude residual.

To a 25 mL Schlenk tube equipped with a magnetic stirring bar were added the crude residual, MeOH (6 mL), and AgF (76.0 mg, 0.6 mmol) sequentially under nitrogen atmosphere. The reaction was complete after stirring at room temperture for 12 h as monitored by TLC. The resulting mixture was filtered through a short column of silica gel eluted with ethyl acetate (20 mL × 3), and concentrated in vacuo. The crude residual was purified via chromatography on silica gel to afford (*E*)-*Appenolide A*[10] (60.9 mg, 88%) as a colorless oil [eluent: petroleum ether/ ethyl acetate = 4/1 (500 mL)

to 3/1 (500 mL)]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (d, J = 16.0 Hz, 1 H, =CH), 6.02 (dt, J_1 = 16.0 Hz, J_2 = 7.0 Hz, 1 H, =CH), 4.85 (d, J = 1.2 Hz, 2 H, OCH_2), 2.45 (t, J = 7.2 Hz, 2 H, CH_2), 2.25 (q, J = 7.2 Hz, 2 H, CH_2), 2.15 (s, 3 H, CH_3), 1.90 (s, 3 H, CH_3), 1.65-1.54 (m, 2 H, CH_2), 1.54-1.42 (m, 2 H, CH_2), 1.39-1.28 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9 175.5, 153.4, 139.0, 121.3, 120.6, 69.3, 43.3, 33.0, 29.8, 28.5, 28.3, 23.3, 8.5; IR (neat) v (cm^{-1}) 2931, 2858, 1748, 1713, 1661, 1344, 1082, 1033; MS (EI): m/z (%) 236 (M^+, 44.25), 43 (100).

5.4 Synthesis of (*Z*)-*Appenolide A*. (fjj-5-086 and fjj-5-036)



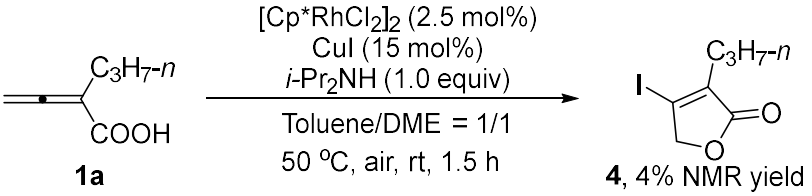
3bt, 0.1 mmol　　*Z*/*E* = 94/6 (before sepration)　(*Z*)-Appenolide A, 84%

To a 25 mL Schlenk tube equipped with a magnetic stirring bar were added 5 wt.% Lindlar Pd (5.4 mg, 0.0025 mmol), **3bt** (23.0 mg, 0.1 mmol), ethyl acetate (2 mL), and quinoline (16.1 mg, 0.125 mmol) sequentially. The Schlenk tube was then connected with a hydrogen bag. After degassing under vacuum and backfilling with hydrogen for three times, the resulting mixture was stirred at room temperture for 24 h as monitored by TLC, filtered through a short column of silica gel eluted with ethyl acetate (20 mL × 3), and concentrated in vacuo. The crude residual (*Z*/*E* = 94/6) was purified via chromatography on silica gel to afford (*Z*)-*Appenolide A* (19.5 mg, 84%) as a colorless oil [eluent: petroleum ether/ ethyl acetate = 7/1 (500 mL) to 5/1 (300 mL)]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (d, J = 12.0 Hz, 1 H, =CH), 5.87 (dt, J_1 = 11.6 Hz, J_2 = 7.6

Hz, 1 H, =CH), 4.95 (d, J = 1.2 Hz, 2 H, OCH_2), 2.45 (t, J = 7.4 Hz, 2 H, CH_2), 2.22-2.08 (m, 5 H, CH_2 and CH_3), 1.89 (t, J = 1.6 Hz, 3 H, CH_3), 1.64-1.54 (m, 2 H, CH_2), 1.54-1.43 (m, 2 H, CH_2), 1.38-1.29 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8, 175.0, 153.5, 139.8, 124.0, 119.0, 71.2, 43.3, 30.0, 29.9, 29.2, 28.7, 23.4, 8.9; IR (neat) ν (cm^{-1}) 2931, 2858, 1748, 1714, 1650, 1360, 1084, 1032; MS (EI): *m/z* (%) 236 (M^+, 74.0), 151 (100); HRMS Calcd for $C_{14}H_{20}O_3Na$ $(M+Na)^+$: 259.1305; Found: 259.1304.

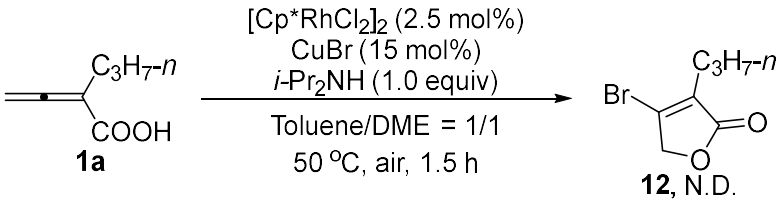
6. Mechanistic Studies

6.1 The reaction of **1a** under the standard conditions without terminal alkyne. (zdj-1-123)



To a 25 mL dried Schlenk tube were added $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), CuI (5.8 mg, 0.03 mmol), **1a** (25.2 mg, 0.2 mmol), DME (0.5 mL), toluene (0.5 mL), and *i*-Pr_2NH (28 μL, d = 0.718 g/mL, 20.1 mg, 0.2 mmol) sequentially under air atmosphere. After being continuously stirred at 50 °C for 1.5 h, the reaction was complete as monitored by thin layer chromatography (TLC). After filtration through a short column of silica gel eluted with ethyl acetate (10 mL × 3), the combined filtrate was concentrated in vacuo. To the crude residue was added 23 μL of mesitylene as the internal standard: 4% NMR yield of **4** was determined by ^1H NMR analysis of the crude product.

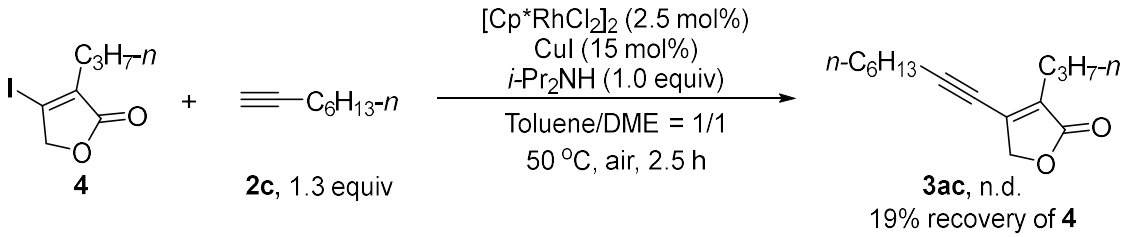
6.2 The reaction of **1a** under the Standard Conditions using CuBr. (zdj-1-128)



To a 25 mL dried Schlenk tube were added CuBr (4.1 mg, 0.03 mmol) in glove box. After being removed from the glove box, $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), **1a** (25.3 mg, 0.2 mmol), DME (0.5 mL), toluene (0.5 mL), and *i*-Pr_2NH (28 μL, d = 0.718 g/mL, 20.1 mg, 0.2 mmol) were added sequentially under air atmosphere. After being

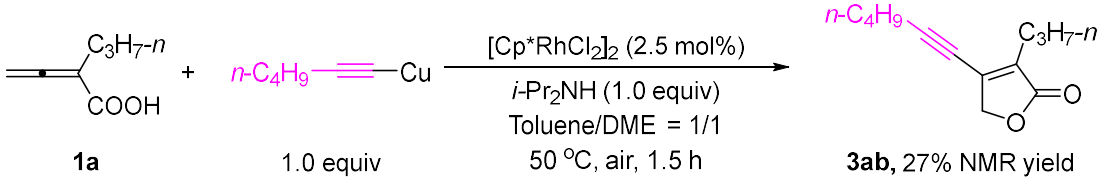
continuously stirred at 50 °C for 1.5 h, the reaction was complete as monitored by thin layer chromatography (TLC). After filtration through a short column of silica gel eluted with ethyl acetate (10 mL × 3), the combined filtrate was then concentrated in vacuo and analyzed by ^{1}H NMR using 23 μL of mesitylene as the internal standard. No signal of 4-bromo-3-propylfuran-2(*5H*)-one **12** was found.

6.3 The reaction of **4** and **2c** under the Standard Conditions. (zdj-1-016)



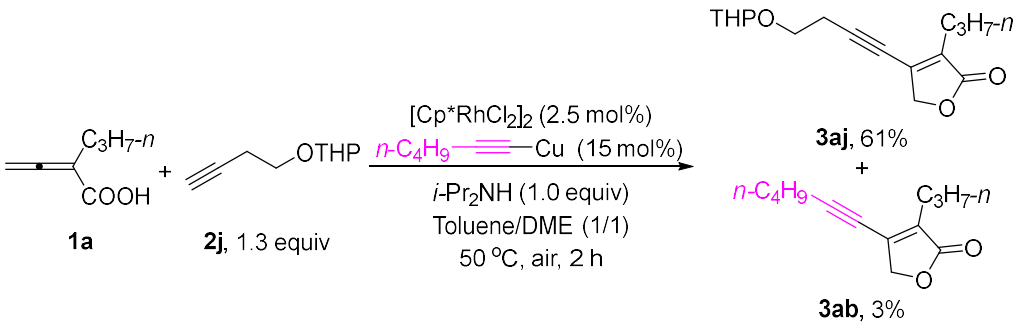
To a 25 mL dry Schlenk tube were added $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), CuI (5.8 mg, 0.03 mmol), **4** (50.5 mg, 0.2 mmol), **2c** (29.1 mg, 0.26 mmol), DME (0.5 mL), toluene (0.5 mL), and *i*-Pr_2NH (28 μL, d = 0.718 g/mL, 20.1 mg, 0.2 mmol) sequentially under air atmosphere. After being continuously stirred at 50 °C for 2.5 h, the resulting mixture was filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3). The combined filtrate was then concentrated in vacuo and analyzed by ^{1}H NMR using 23 μL of mesitylene as the internal standard. No signal of 4-(octynyl)-3-propylfuran-2(*5H*)-one **3ac** was found, and 19% recovery of **4** was determined.

6.4 Synthesis of **3ab** using hexynylcopper instead of alkyne and CuI. (fjj-4-066)



To a 25 mL dry Schlenk tube were added $[Cp^*RhCl_2]_2$ (3.0 mg, 0.005 mmol), **1a** (25.0 mg, 0.2 mmol), hexynylcopper (30.1 mg, 0.2 mmol), toluene (0.5 mL), DME (0.5 mL), and *i*-Pr_2NH (28 μL, d = 0.718 g/mL, 20.1 mg, 0.2 mmol) sequentially under air atmosphere. After being continuously stirred at 50 °C for 1.5 h, the reaction was complete as monitored by thin layer chromatography (TLC). After filtration through a short column of silica gel eluted with ethyl acetate (20 mL × 3), the combined filtrate was concentrated in vacuo and analyzed by ^1H NMR using 9.2 μL of mesitylene as the internal standard. The reaction afforded **3ab** in 27% NMR yield.

6.5 Synthesis of **3aj** using hexynylcopper instead of CuI. (zdj-1-193)



To a 100 mL dry Schlenk tube were added $[Cp^*RhCl_2]_2$ (15.3 mg, 0.025 mmol), hexynyl copper (21.7 mg, 0.15 mmol), **1a** (125.9 mg, 1.0 mmol), **2j** (200.7 mg, 1.3 mmol)/DME (2.5 mL) and toluene (2.5 mL), and *i*-Pr_2NH (140 μL, d = 0.718 g/mL, 100.5 mg, 1.0 mmol) sequentially. After being continuously stirred at 50 °C under air atmosphere for 2 h, the reaction was complete as monitored by TLC. After filtration 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 residual was purified via chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 60/1 (600 mL) to

20/1 (1600 mL)] to afford **3ab** (5.9 mg, 3%) and **3aj** (169.7 mg, 61%).

3ab: brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.66 (s, 2 H, OCH_2), 2.47 (t, J = 6.9 Hz, 2 H, CH_2), 2.36 (t, J = 7.7 Hz, 2 H, CH_2), 1.68-1.53 (m, 4 H, CH_2 × 2), 1.51-1.37 (m, 2 H, CH_2), 1.03-0.86 (m, 6 H, CH_3 × 2).

3aj: yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.67 (s, 3 H, OCH_2 and OCH), 4.00-3.80 (m, 2 H, OCH_2), 3.71-3.46 (m, 2 H, OCH_2), 2.79 (t, J = 6.6 Hz, 2 H, CH_2), 2.36 (t, J = 7.5 Hz, 2 H, CH_2), 1.95-1.45 (m, 8 H, CH_2 × 4), 0.94 (t, J = 7.4 Hz, 3 H, CH_3).

7. References

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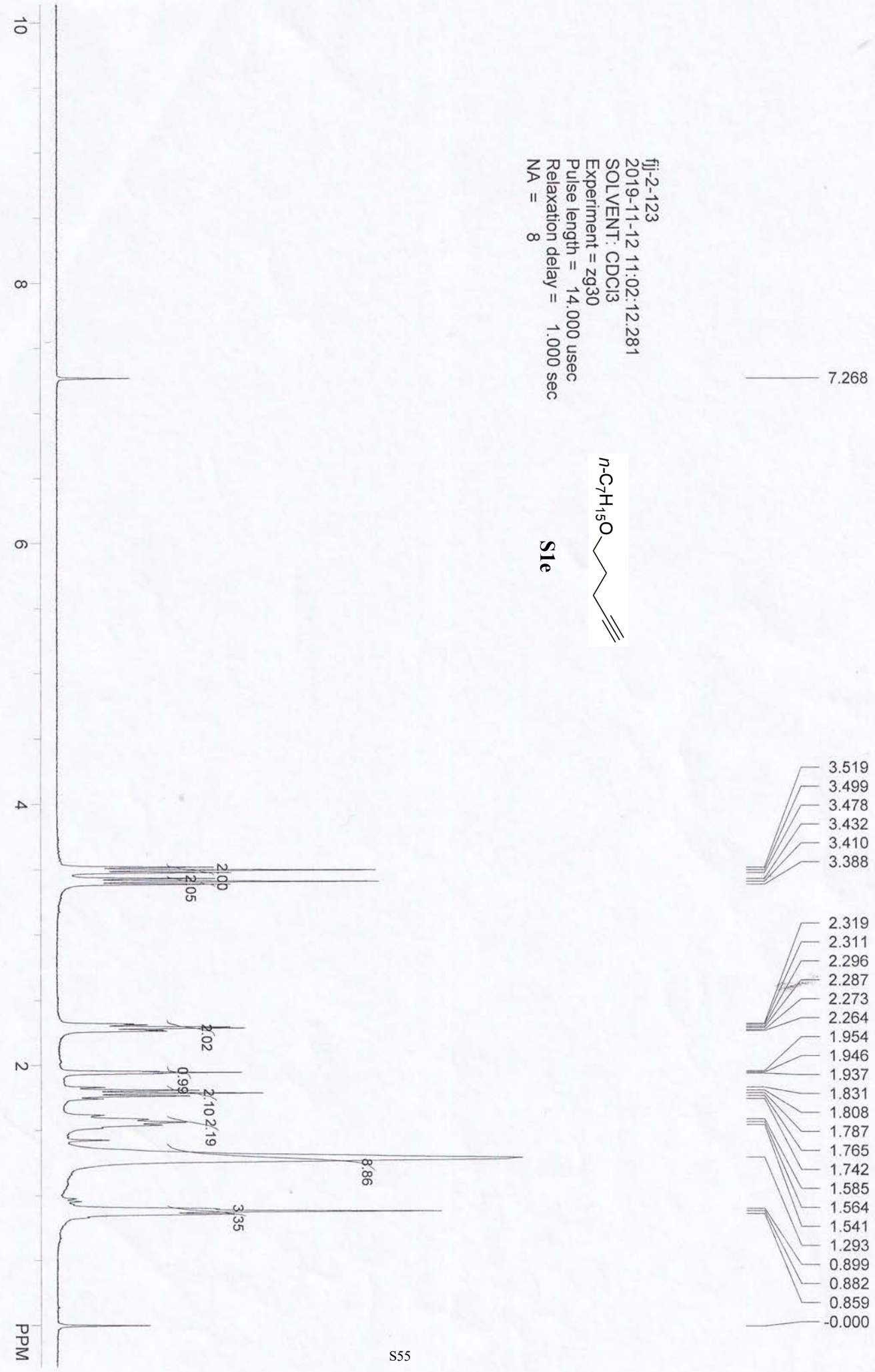
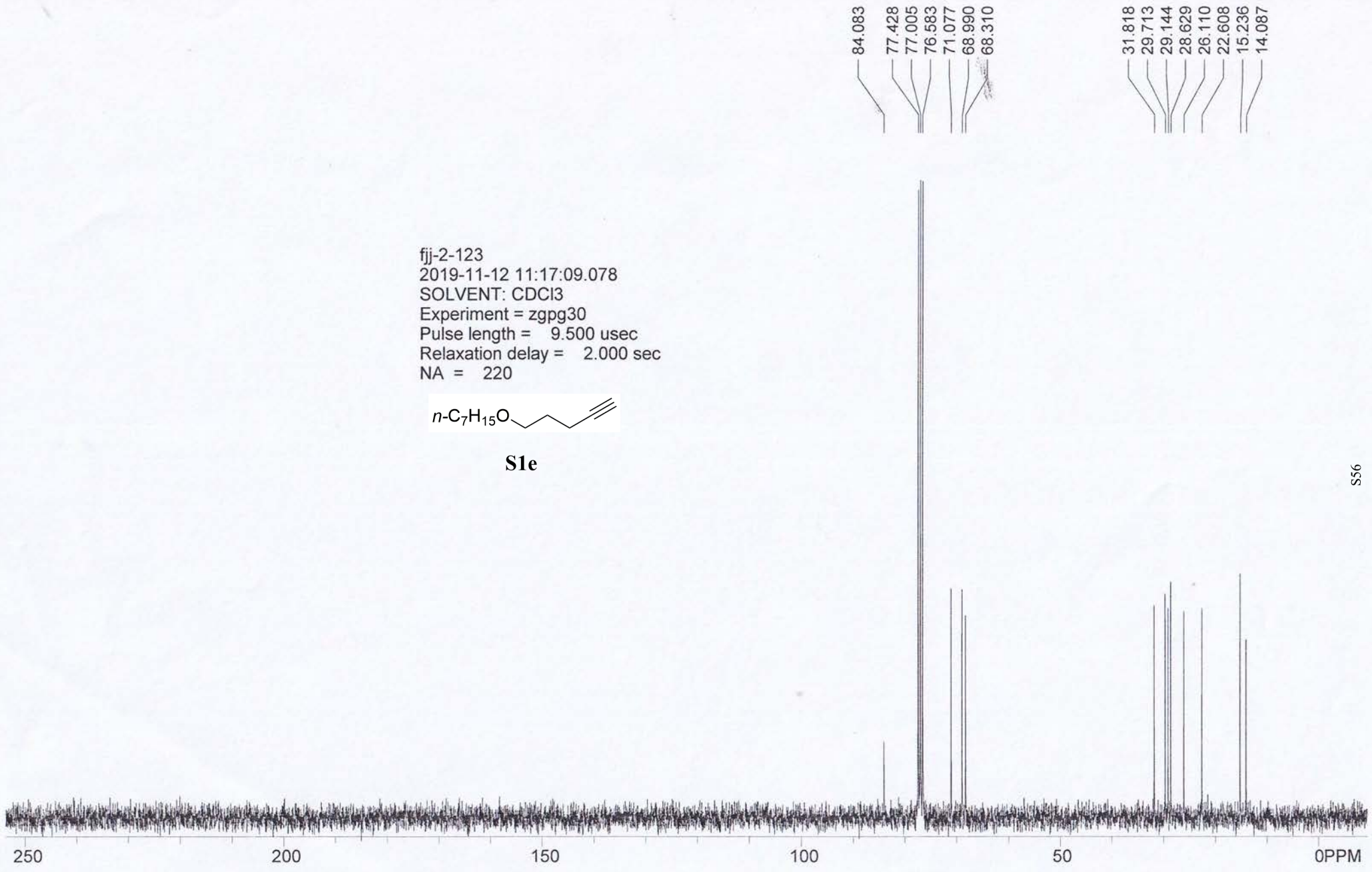
8. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR Spectra of the Compounds Prepared

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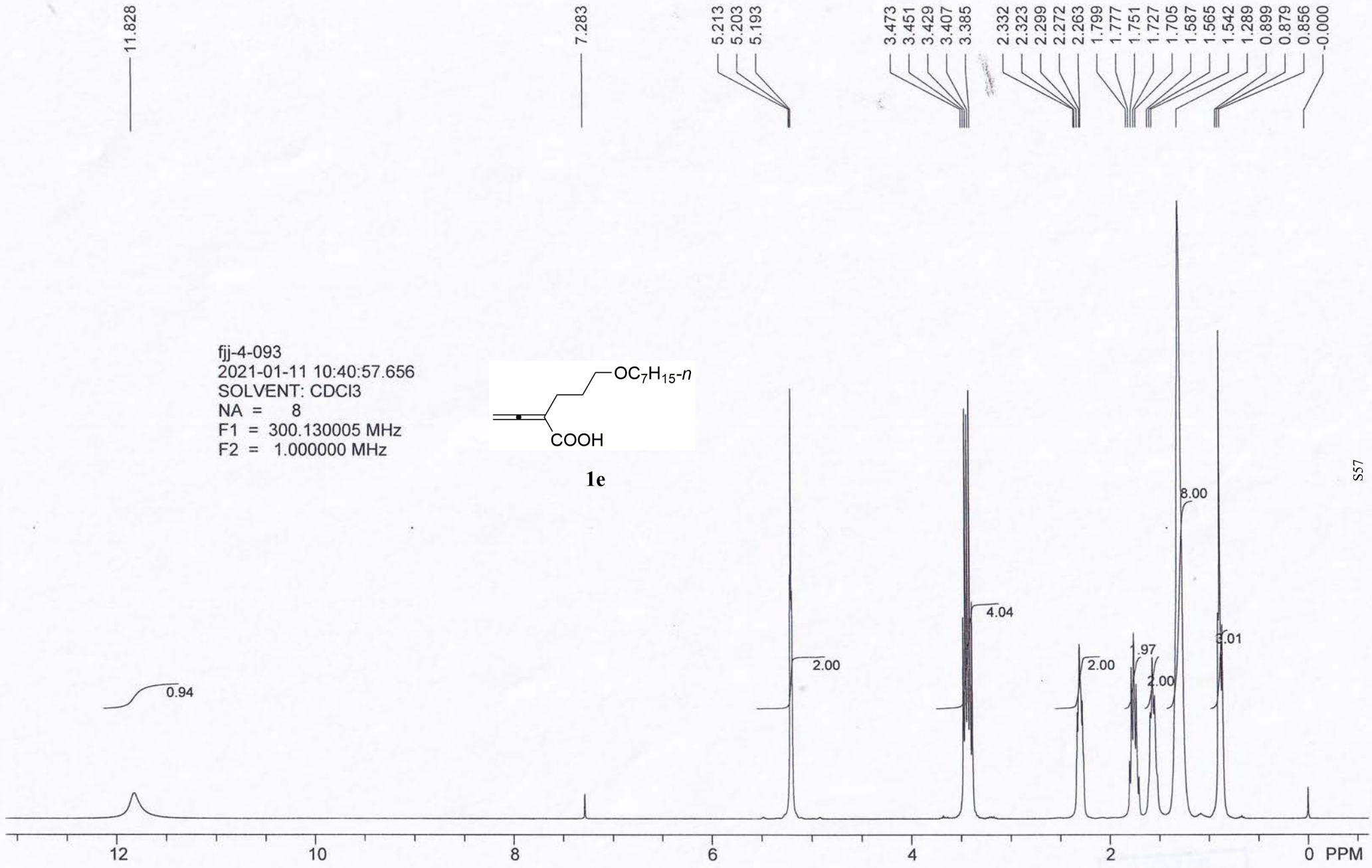
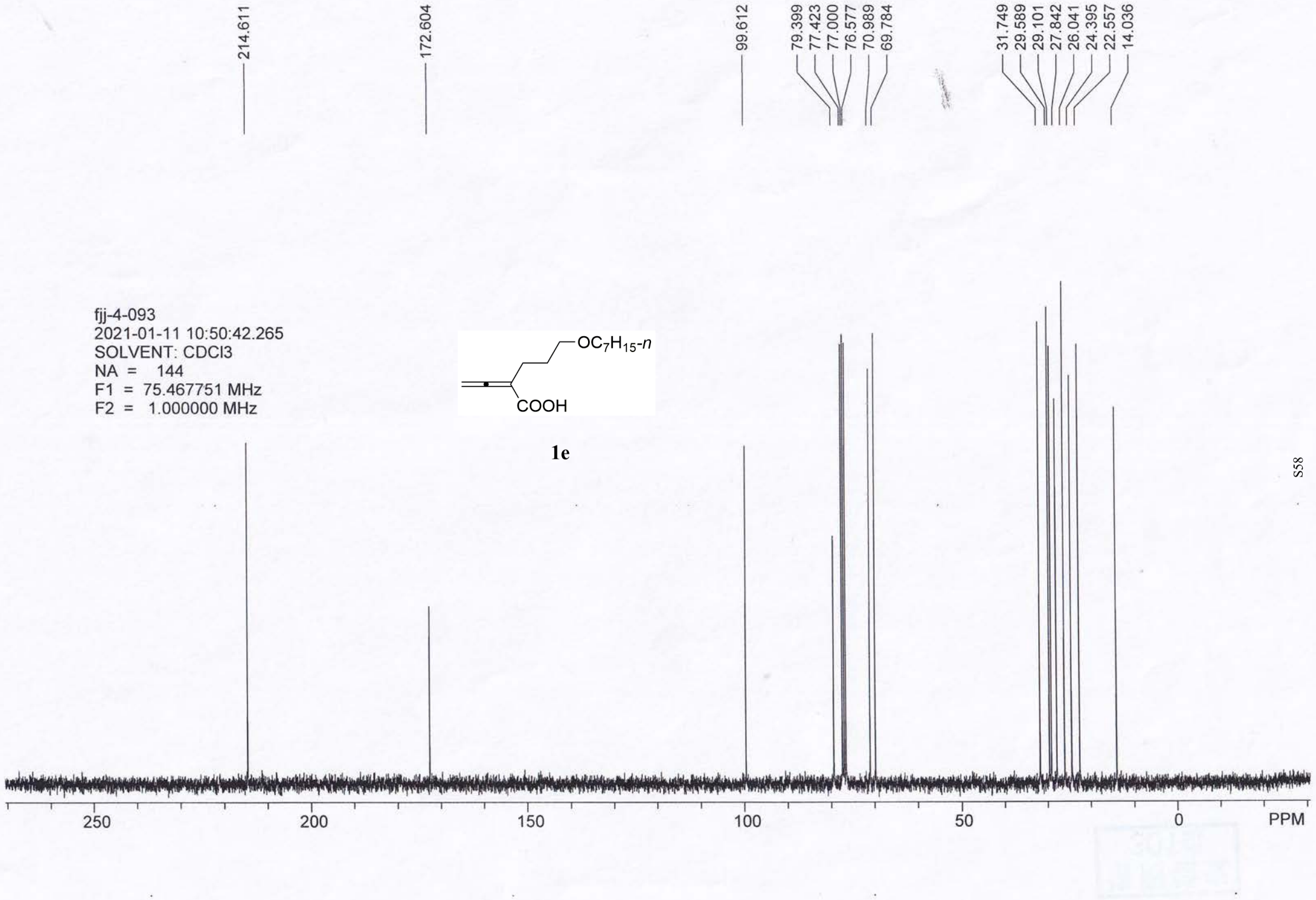
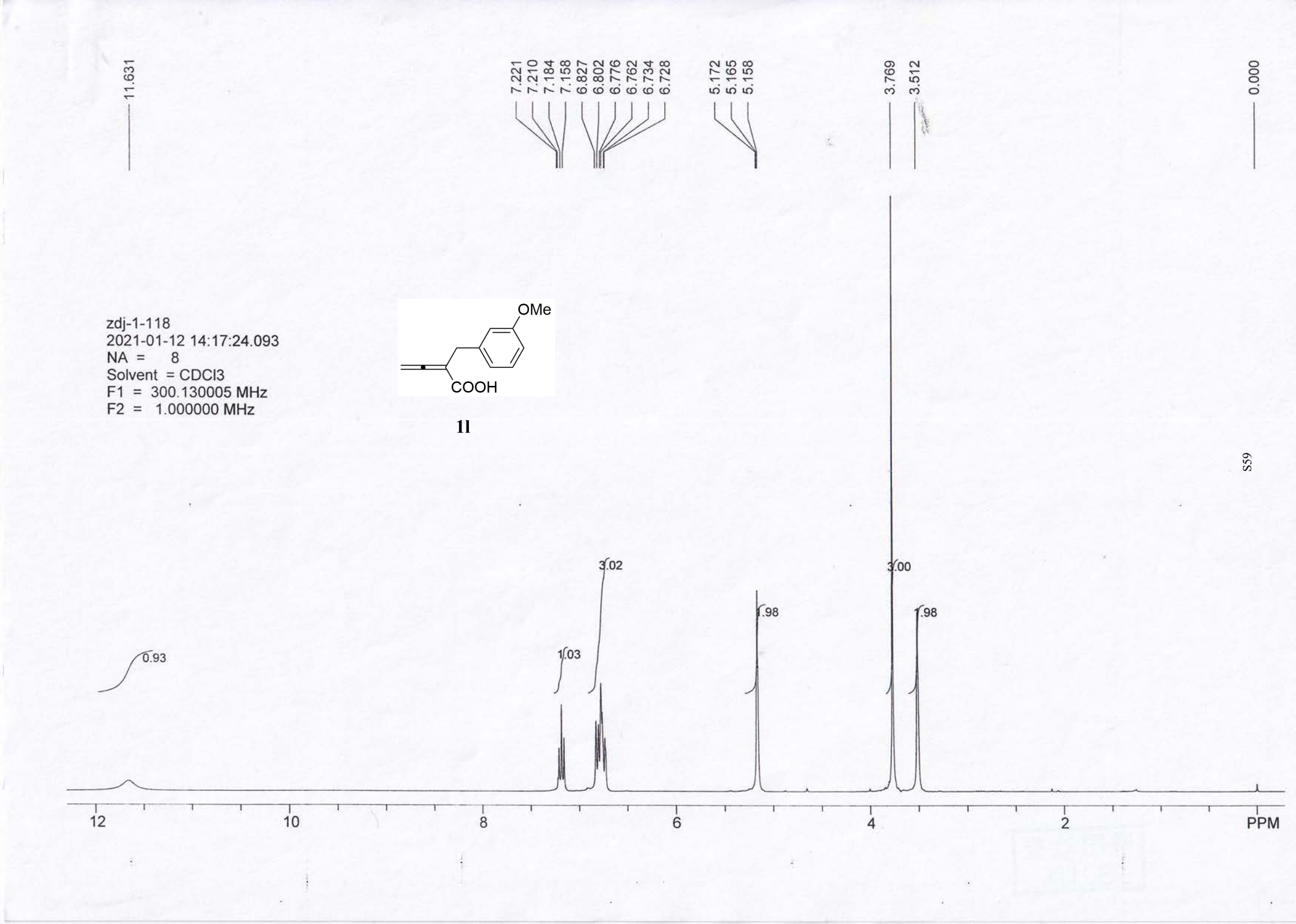
77.428
77.005
76.583
71.077
68.990
68.310
31.818
29.713
29.144
28.629
26.110
22.608
15.236
14.087
fjj-2-123
2019-11-12 11:17:09.078
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 220
n-C7H15O
250
200
150
100
50
0PPM

S1e

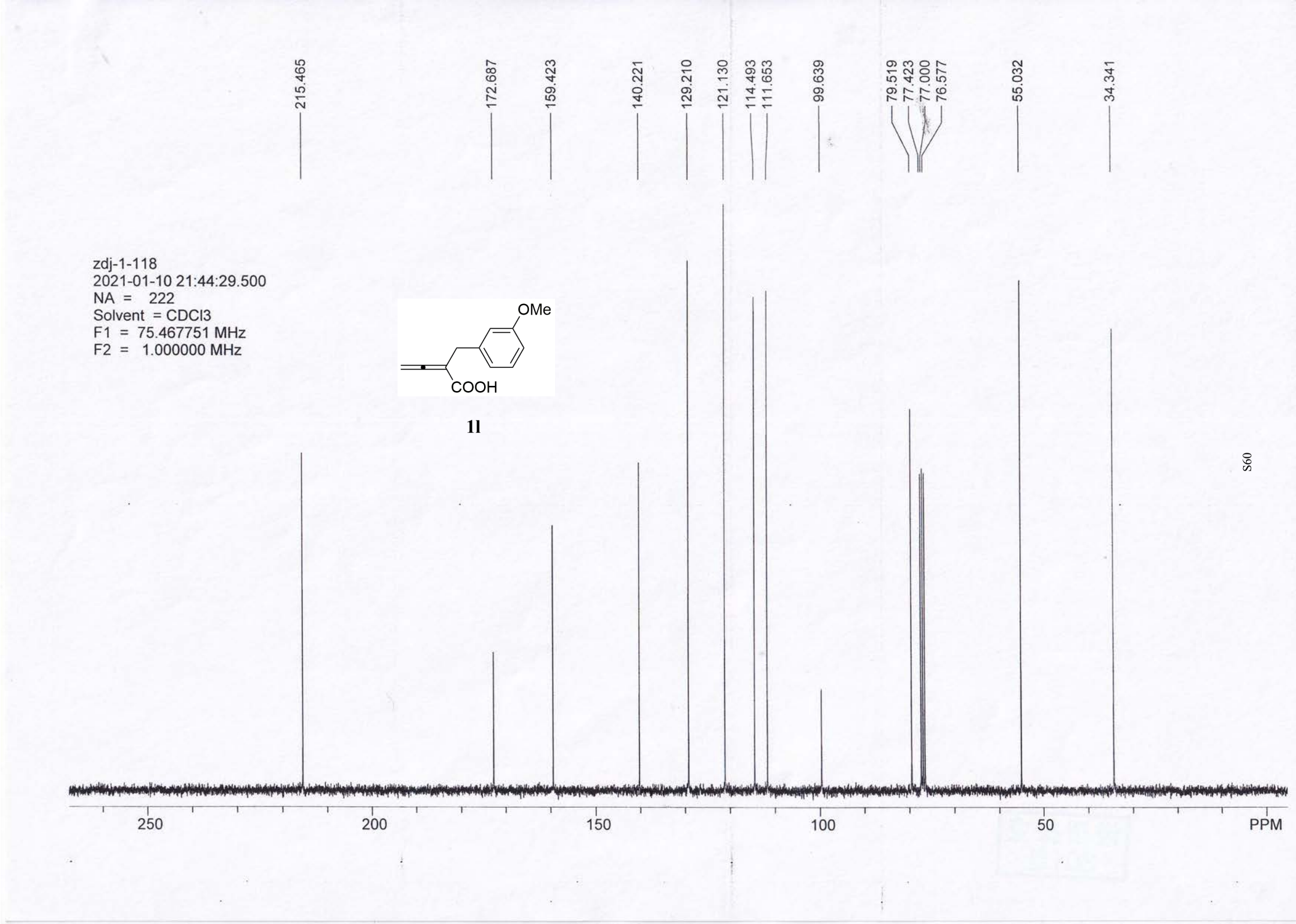

11.828
7.283
5.213
5.203
5.193
3.473
3.451
3.429
3.407
3.385
2.332
2.323
2.299
2.272
2.263
1.799
1.777
1.751
1.727
1.705
1.587
1.565
1.542
1.289
0.899
0.879
0.856
-0.000
fjj-4-093
2021-01-11 10:40:57.656
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
OC7H15-n
COOH
1e
0.94
2.00
4.04
2.00
1.97
2.00
8.00
3.01
12
10
8
6
4
2
0 PPM


214.611
172.604
99.612
79.399
77.423
77.000
76.577
70.989
69.784
31.749
29.589
29.101
27.842
26.041
24.395
22.557
14.036
fjj-4-093
2021-01-11 10:50:42.265
SOLVENT: CDCl3
NA = 144
F1 = 75.467751 MHz
F2 = 1.000000 MHz
OC7H15-n
COOH
250
200
150
100
50
0
PPM

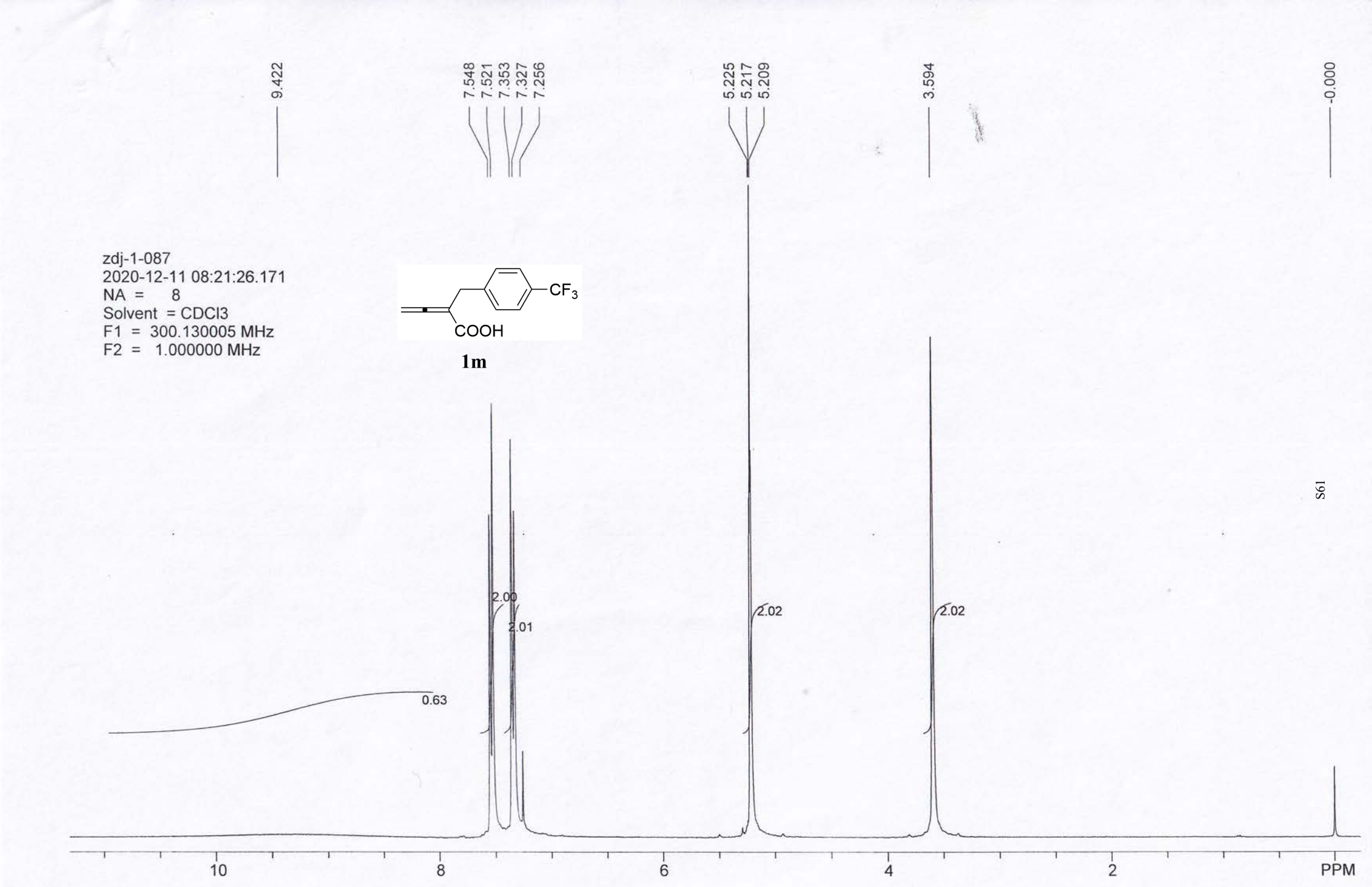
1e

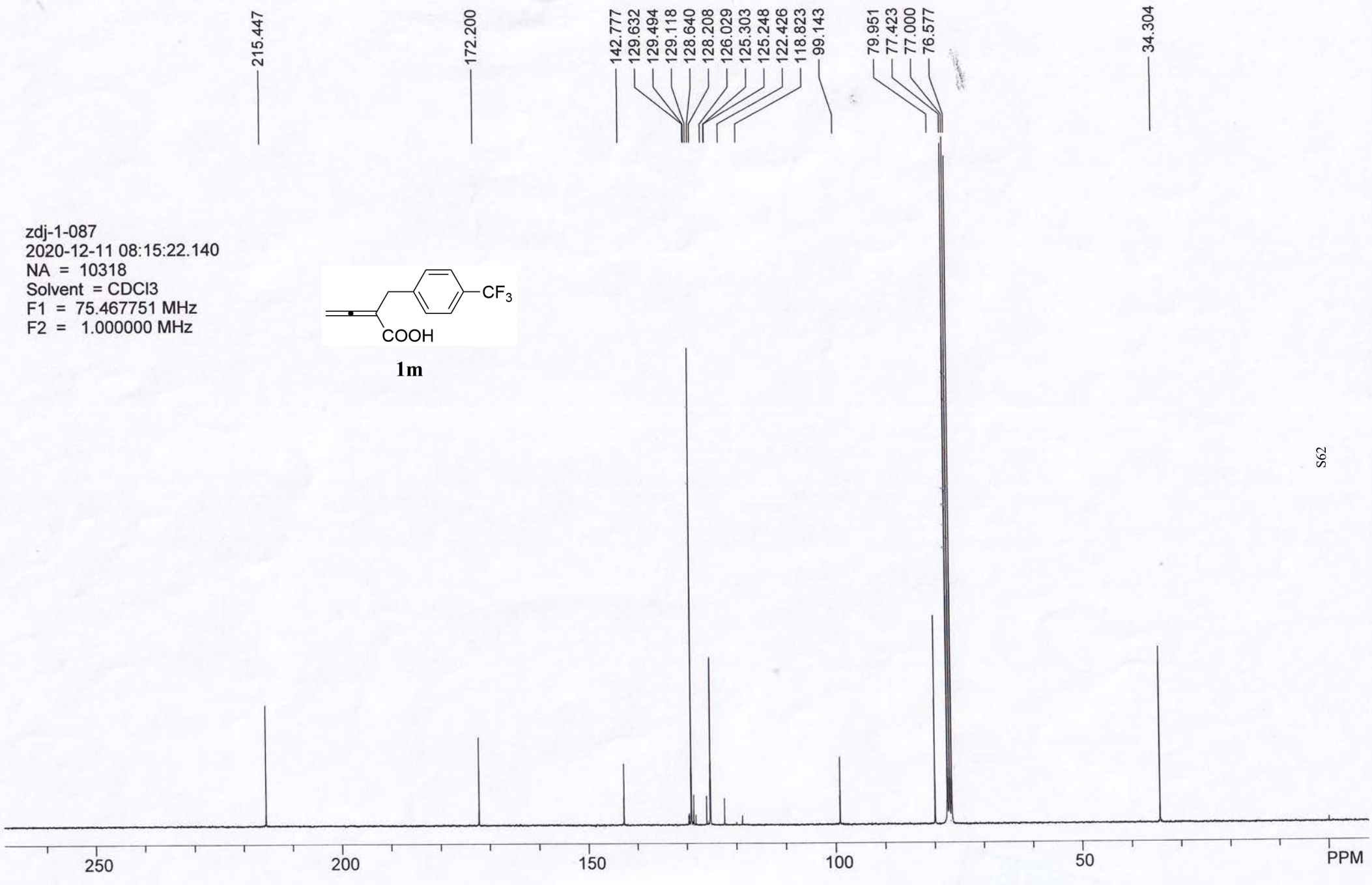

11.631
7.221
7.210
7.184
7.158
6.827
6.802
6.776
6.762
6.734
6.728
5.172
5.165
5.158
3.769
3.512
0.000
zdj-1-118
2021-01-12 14:17:24.093
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
OMe
COOH
0.93
1.03
3.02
1.98
3.00
1.98
12
10
8
6
4
2
PPM

1l

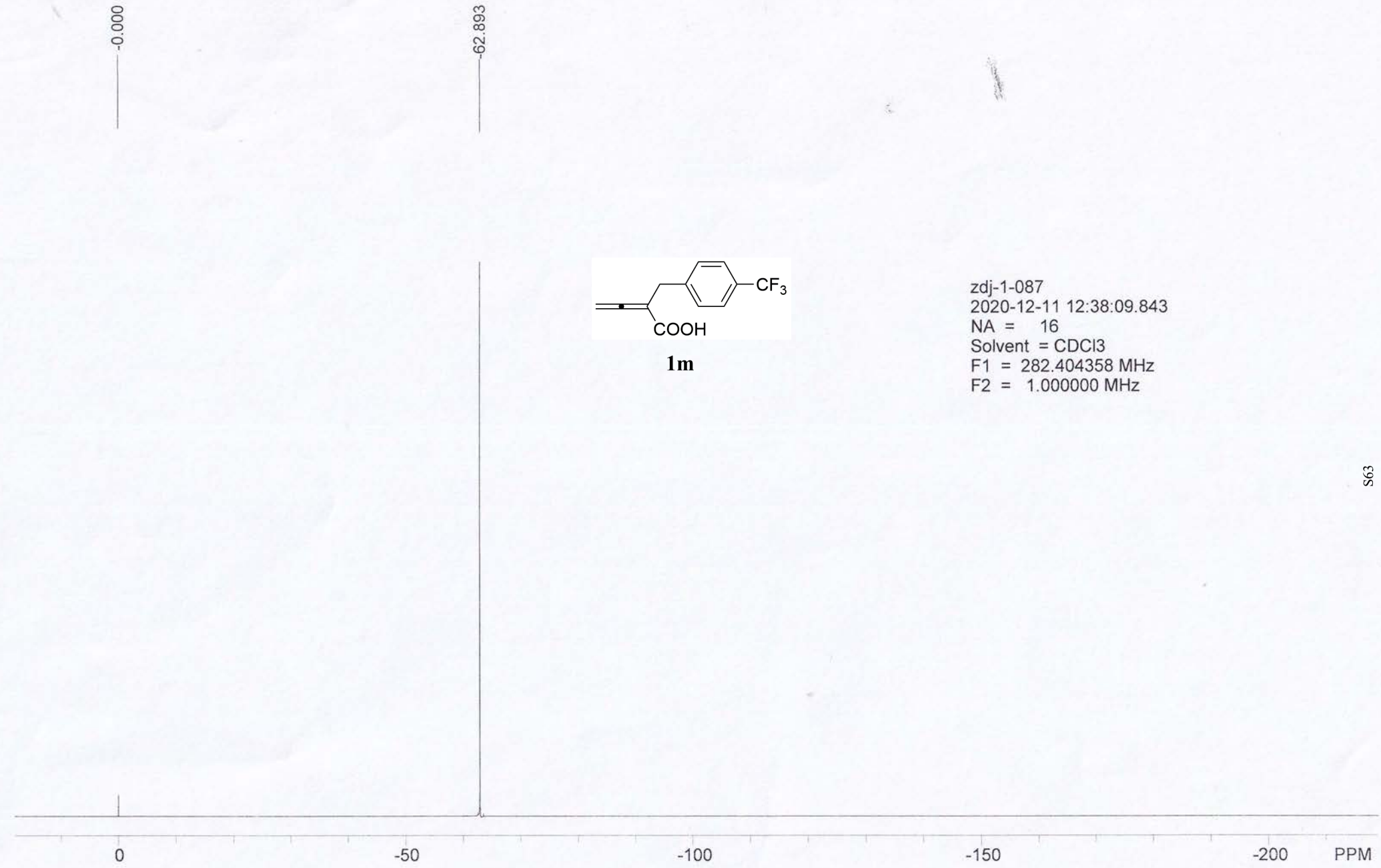

215.465
172.687
159.423
140.221
129.210
121.130
114.493
111.653
99.639
79.519
77.423
77.000
76.577
55.032
34.341
zdj-1-118
2021-01-10 21:44:29.500
NA = 222
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
OMe
COOH
250
200
150
100
50
PPM

1l

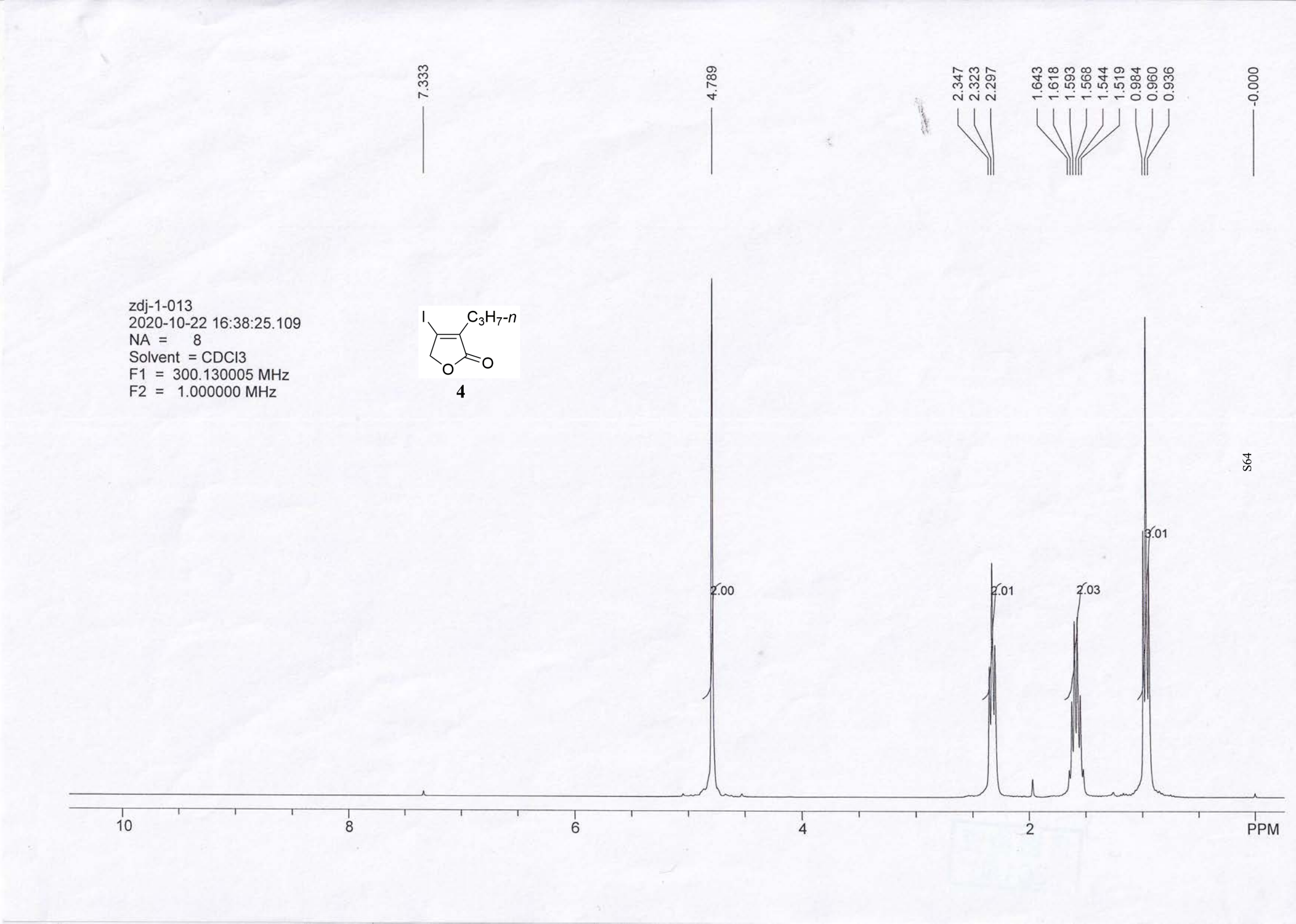

9.422
7.548
7.521
7.353
7.327
7.256
5.225
5.217
5.209
3.594
-0.000
zdj-1-087
2020-12-11 08:21:26.171
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
CF3
COOH
1m
2.00
2.01
2.02
2.02
0.63
10
8
6
4
2
PPM

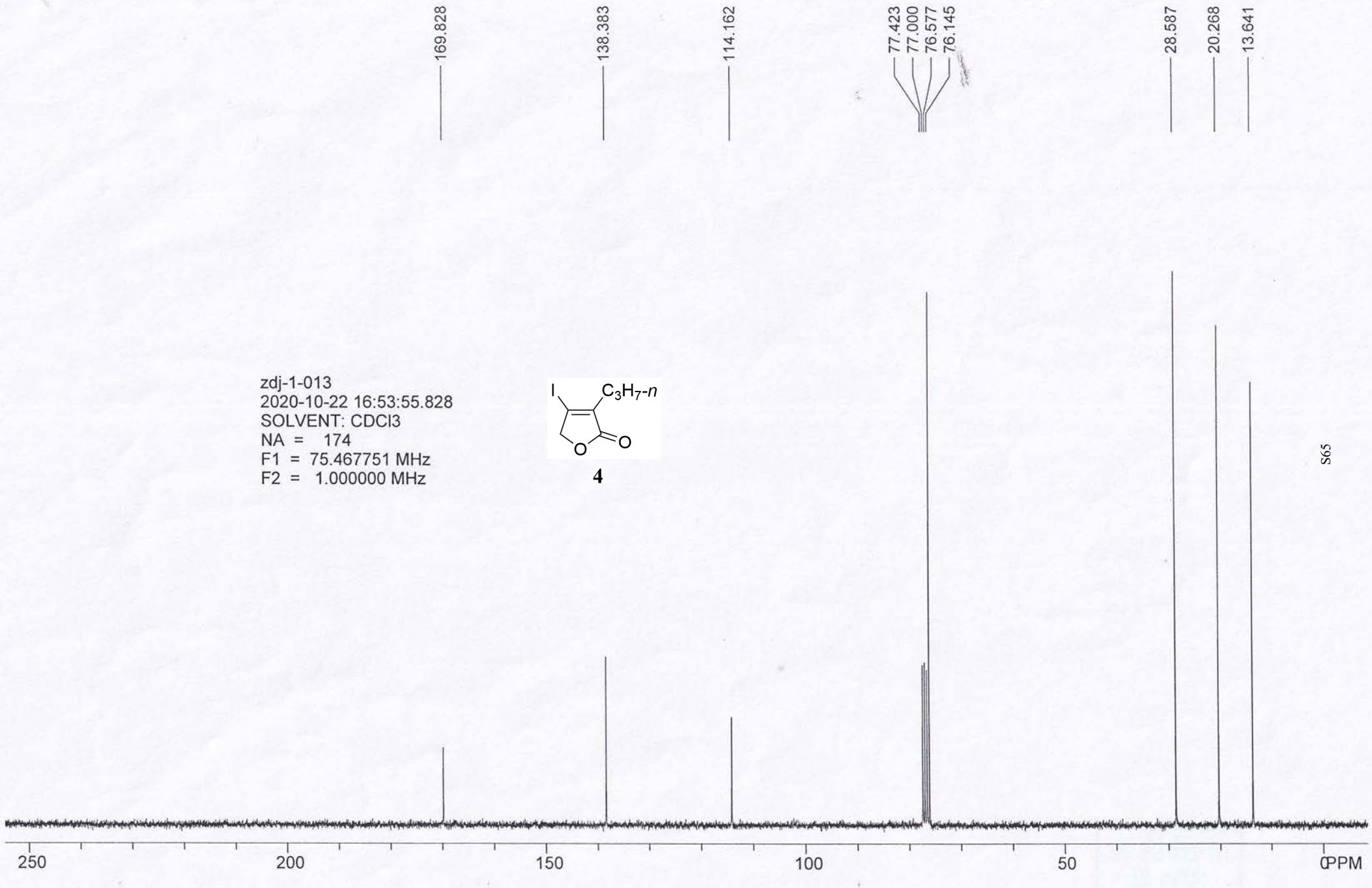

215.447
172.200
142.777
129.632
129.494
129.118
128.640
128.208
126.029
125.303
125.248
122.426
118.823
99.143
79.951
77.423
77.000
76.577
34.304
zdj-1-087
2020-12-11 08:15:22.140
NA = 10318
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
CF3
COOH
250
200
150
100
50
PPM

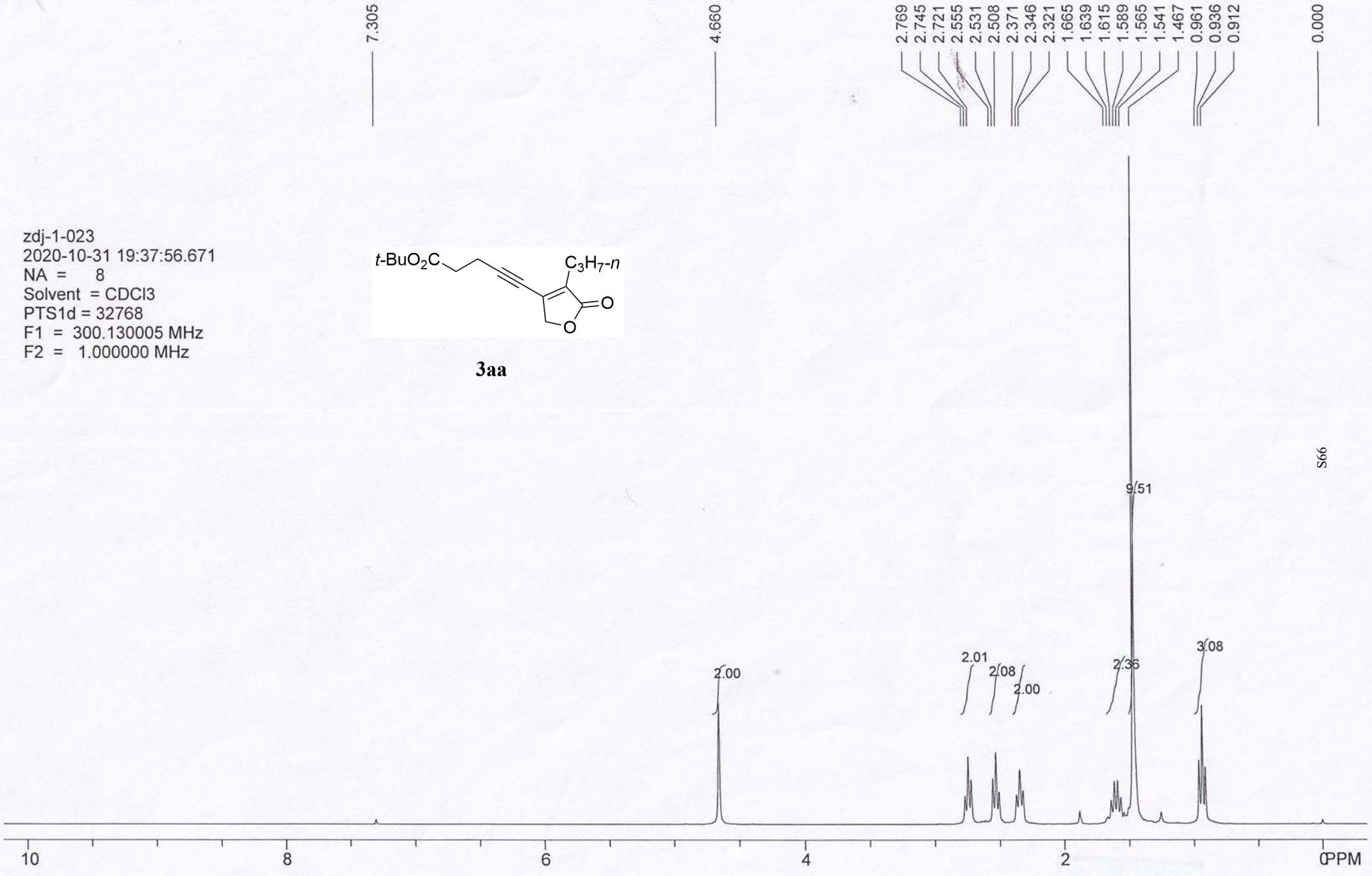
1m


-0.000
-62.893
CF3
COOH
zdj-1-087
2020-12-11 12:38:09.843
NA = 16
Solvent = CDCl3
F1 = 282.404358 MHz
F2 = 1.000000 MHz
0
-50
-100
-150
-200
PPM

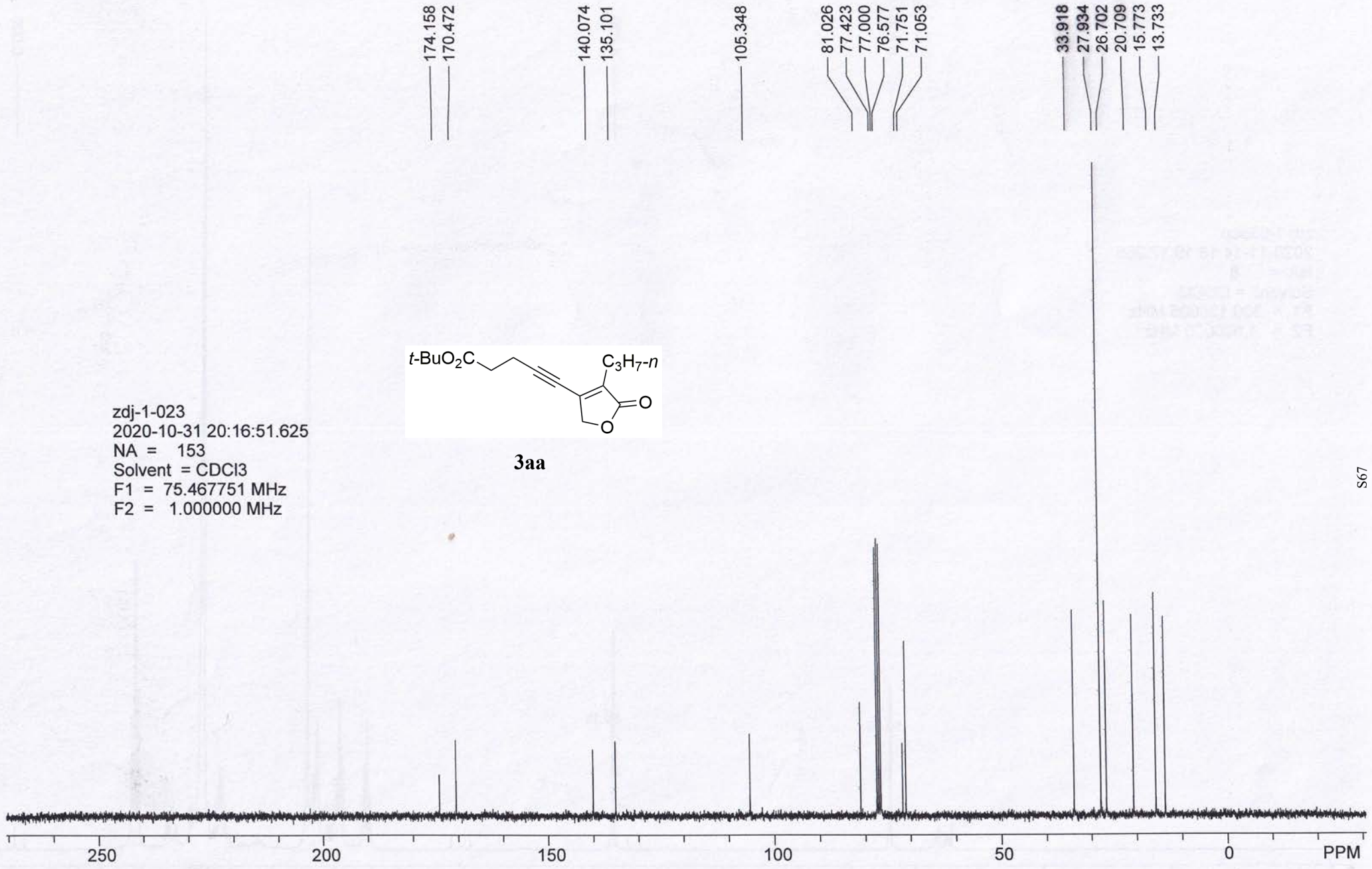
1m


7.333
4.789
2.347
2.323
2.297
1.643
1.618
1.593
1.568
1.544
1.519
0.984
0.960
0.936
-0.000
zdj-1-013
2020-10-22 16:38:25.109
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
I
C3H7-n
O
O
4
2.00
2.01
2.03
3.01
10
8
6
4
2
PPM


169.828
138.383
114.162
77.423
77.000
76.577
76.145
28.587
20.268
13.641
zdj-1-013
2020-10-22 16:53:55.828
SOLVENT: CDCl3
NA = 174
F1 = 75.467751 MHz
F2 = 1.000000 MHz
I
C3H7-n
O
O
4
250
200
150
100
50
0
PPM

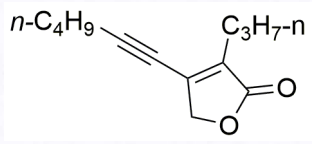

7.305
4.660
2.769
2.745
2.721
2.555
2.531
2.508
2.371
2.346
2.321
1.665
1.639
1.615
1.589
1.565
1.541
1.467
0.961
0.936
0.912
0.000
zdj-1-023
2020-10-31 19:37:56.671
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
t-BuO2C
C3H7-n
O
O
2.00
2.01
2.08
2.00
9.51
2.36
3.08
10
8
6
4
2
0
PPM

3aa

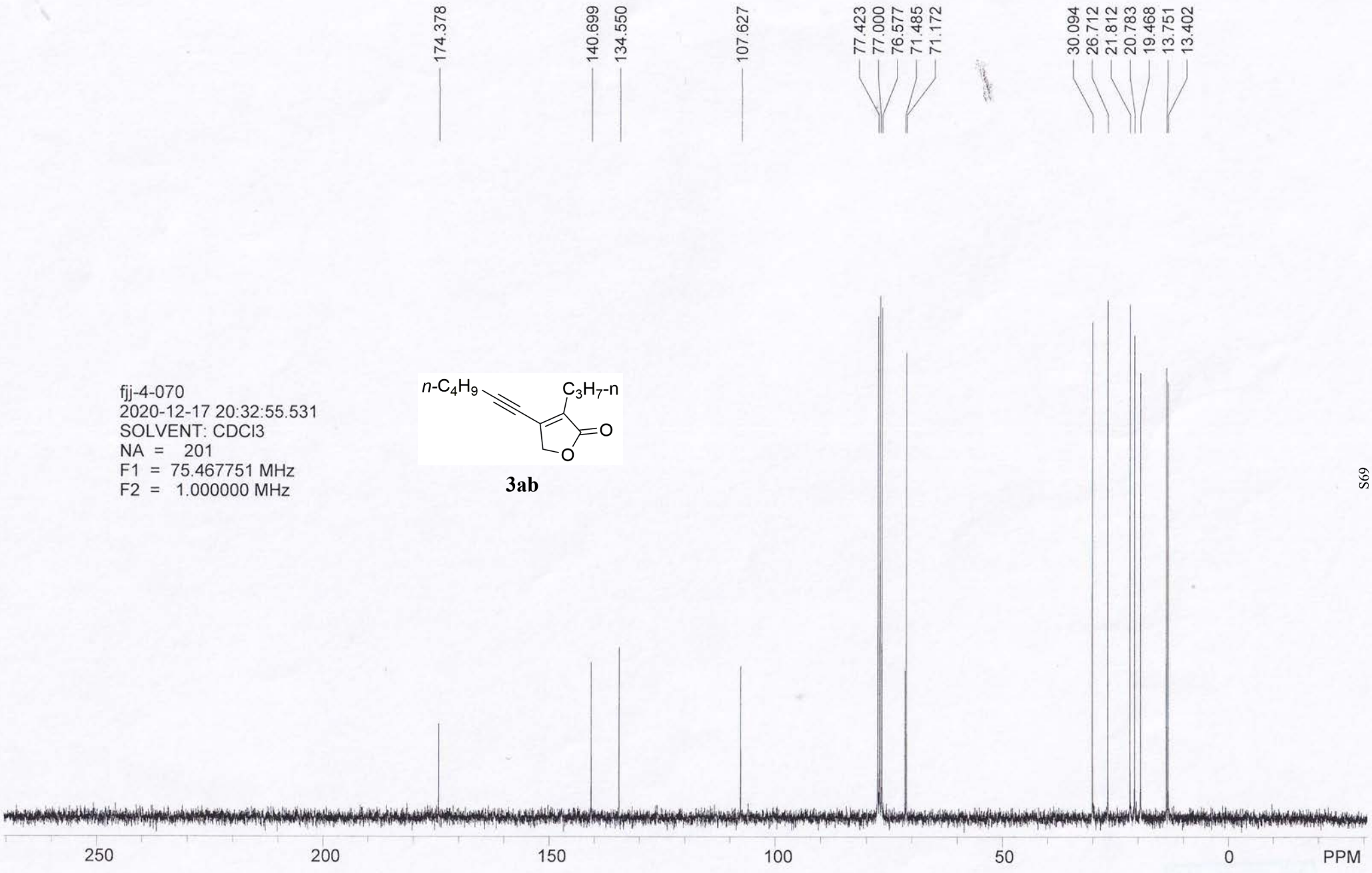

174.158
170.472
140.074
135.101
105.348
81.026
77.423
77.000
76.577
71.751
71.053
33.918
27.934
26.702
20.709
15.773
13.733
t-BuO2C
C3H7-n
O
O
zdj-1-023
2020-10-31 20:16:51.625
NA = 153
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
250
200
150
100
50
0
PPM

3aa

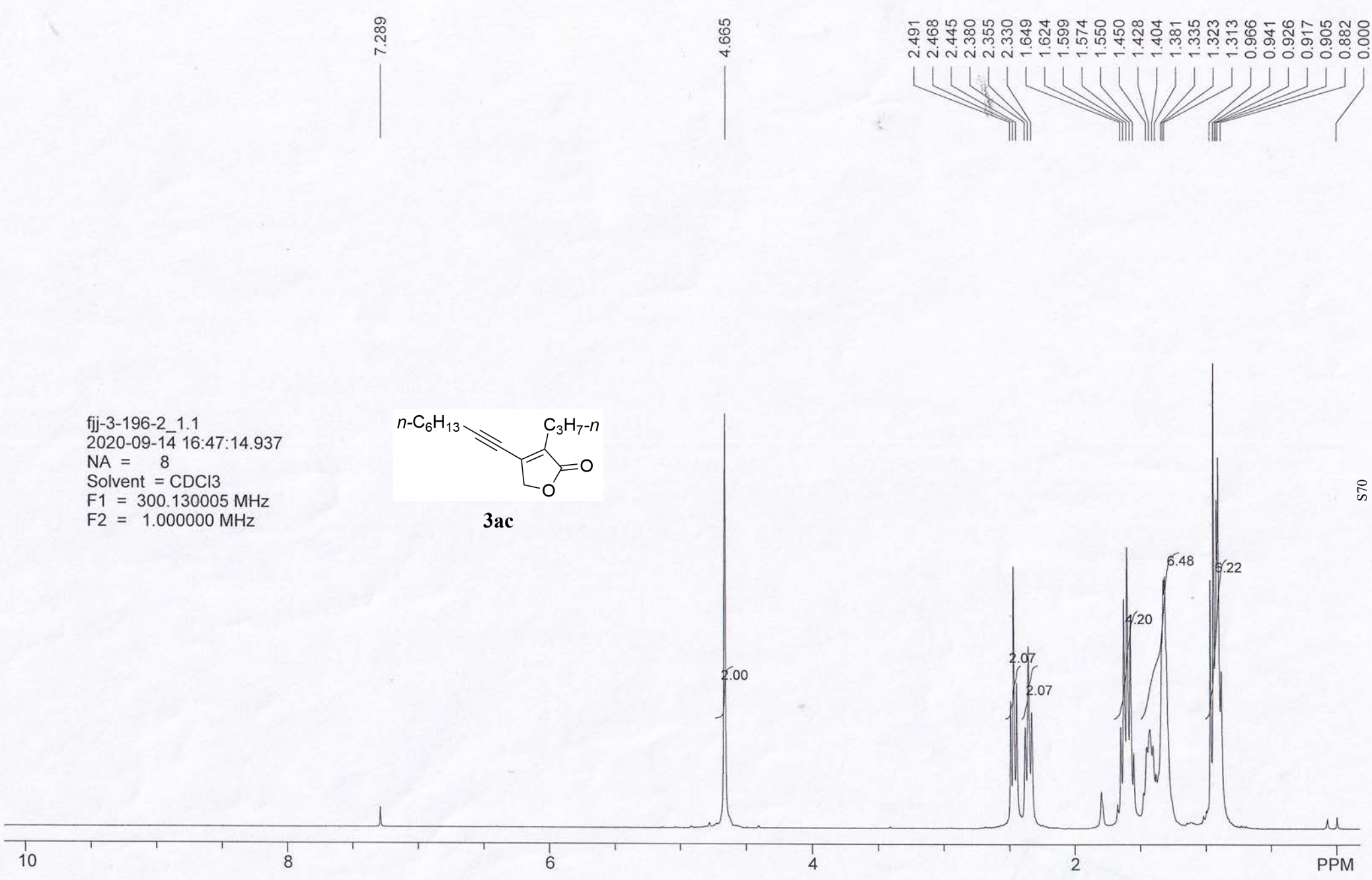
fjj-4-070
2020-12-17 20:19:54.500
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz

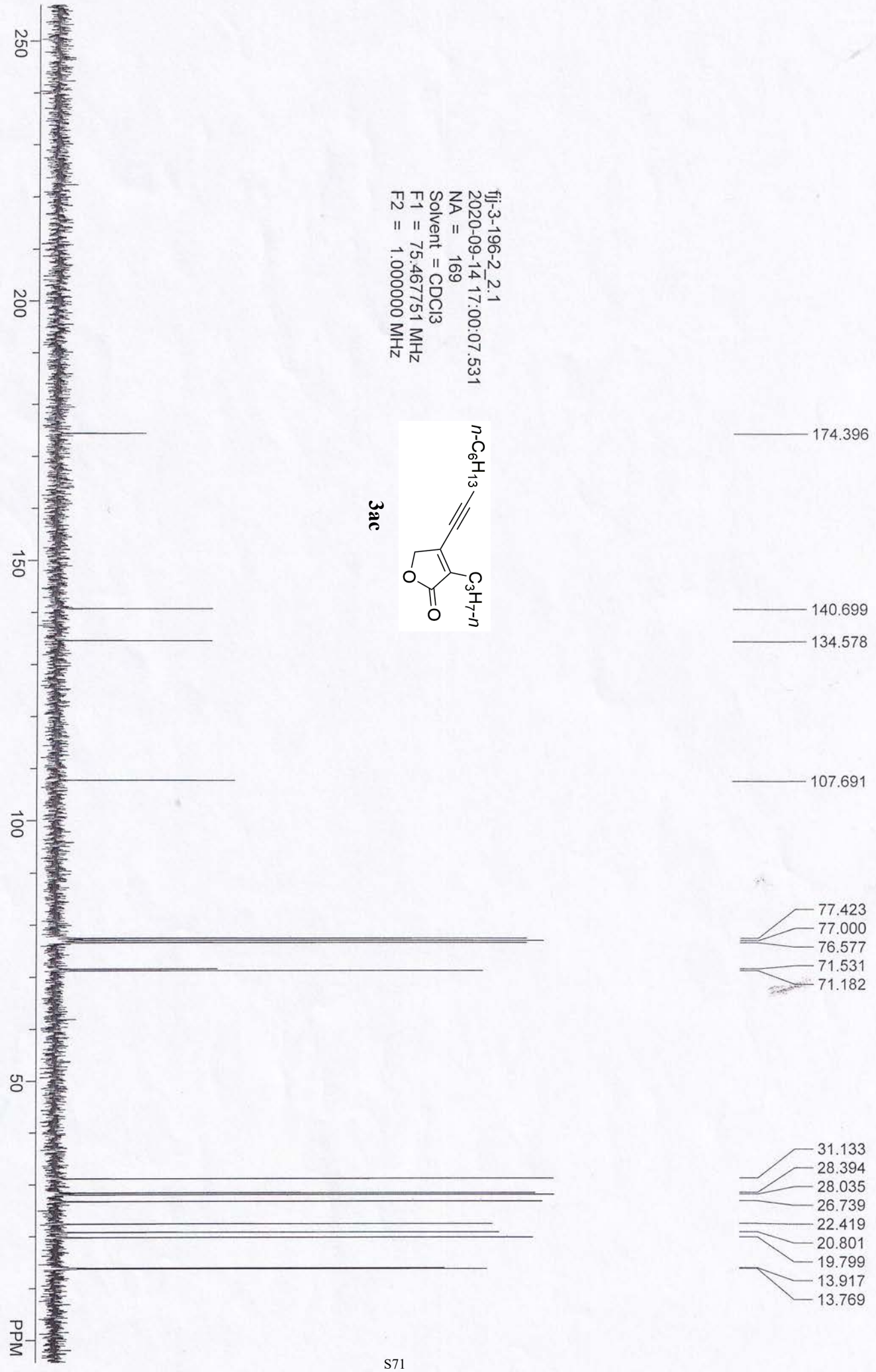


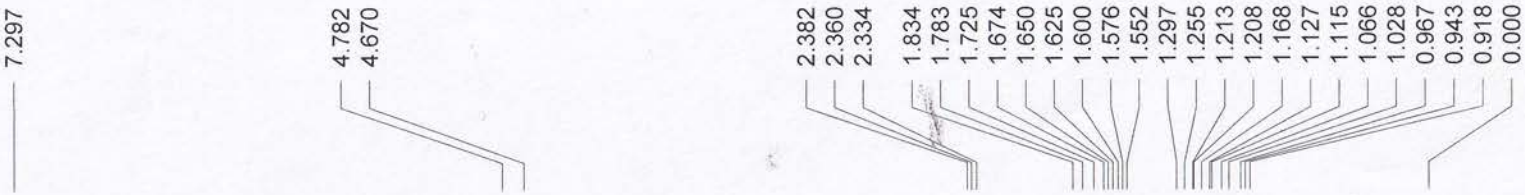
3ab

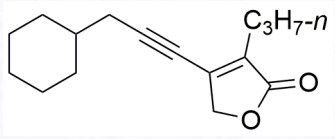

174.378
140.699
134.550
107.627
77.423
77.000
76.577
71.485
71.172
30.094
26.712
21.812
20.783
19.468
13.751
13.402
fjj-4-070
2020-12-17 20:32:55.531
SOLVENT: CDCl3
NA = 201
F1 = 75.467751 MHz
F2 = 1.000000 MHz
n-C4H9
C3H7-n
O
O
250
200
150
100
50
0
PPM

3ab


7.289
4.665
2.491
2.468
2.445
2.380
2.355
2.330
1.649
1.624
1.599
1.574
1.550
1.450
1.428
1.404
1.381
1.335
1.323
1.313
0.966
0.941
0.926
0.917
0.905
0.882
0.000
fjj-3-196-2_1.1
2020-09-14 16:47:14.937
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
n-C6H13
C3H7-n
O
O
3ac
2.00
2.07
2.07
4.20
6.48
6.22
10
8
6
4
2
PPM


fjj-3-196-2_2.1
2020-09-14 17:00:07.531
NA = 169
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
n-C6H13
C3H7-n
O
O
3ac
174.396
140.699
134.578
107.691
77.423
77.000
76.577
71.531
71.182
31.133
28.394
28.035
26.739
22.419
20.801
19.799
13.917
13.769
250
200
150
100
50
PPM





3ad

fjj-4-041
2020-12-01 16:46:22.703
SOLVENT: CDCl3
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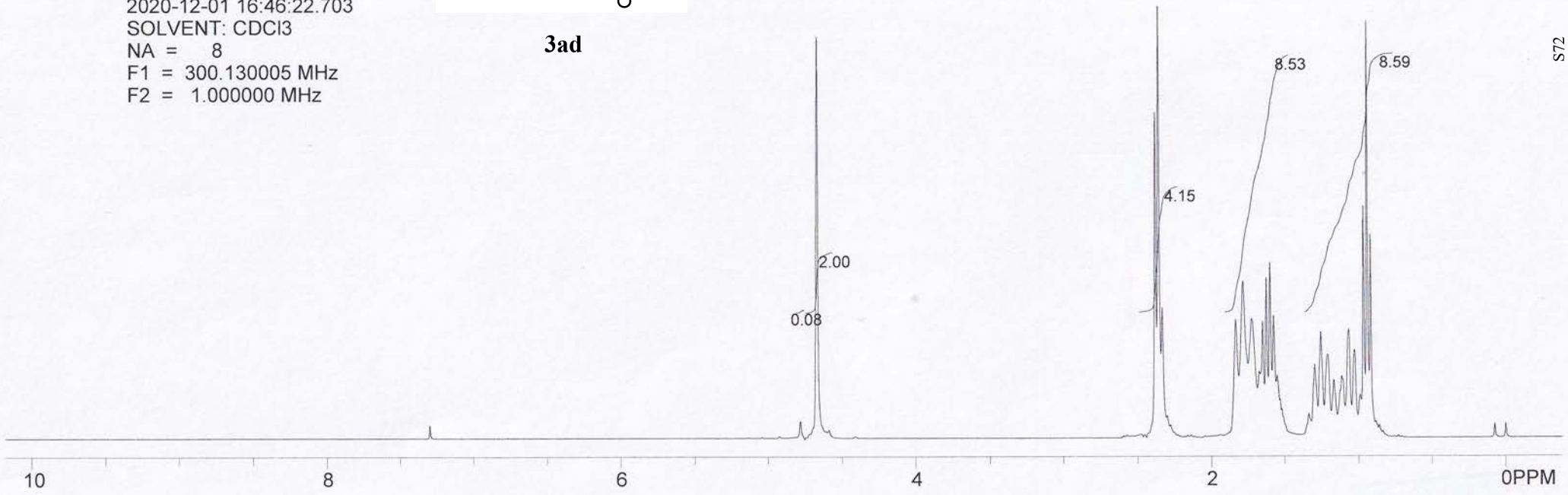
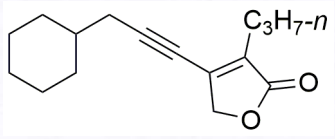
F1 = 300.130005 MHz
F2 = 1.000000 MHz

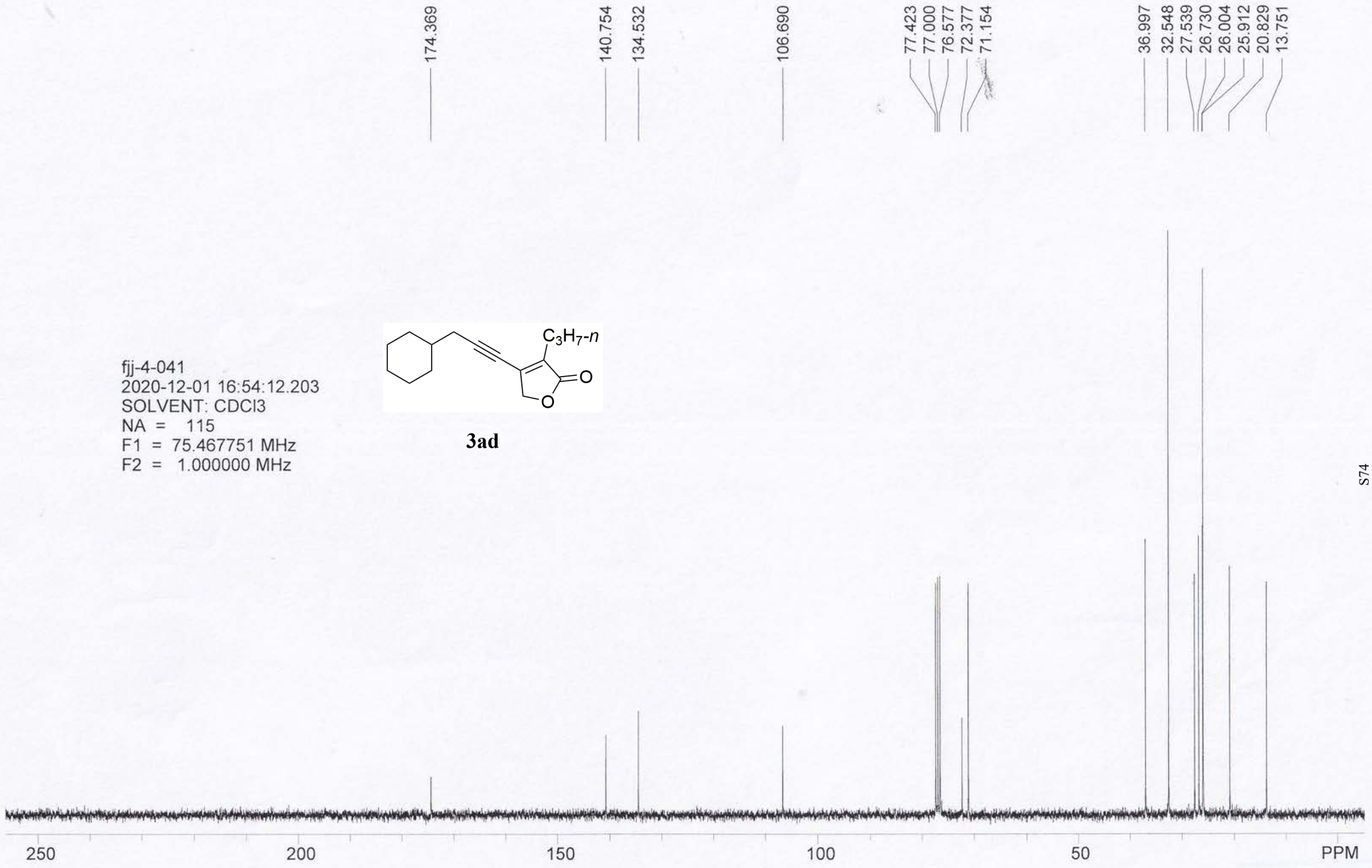


fjj-4-041-purity
2020-12-02 11:34:38.921
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz

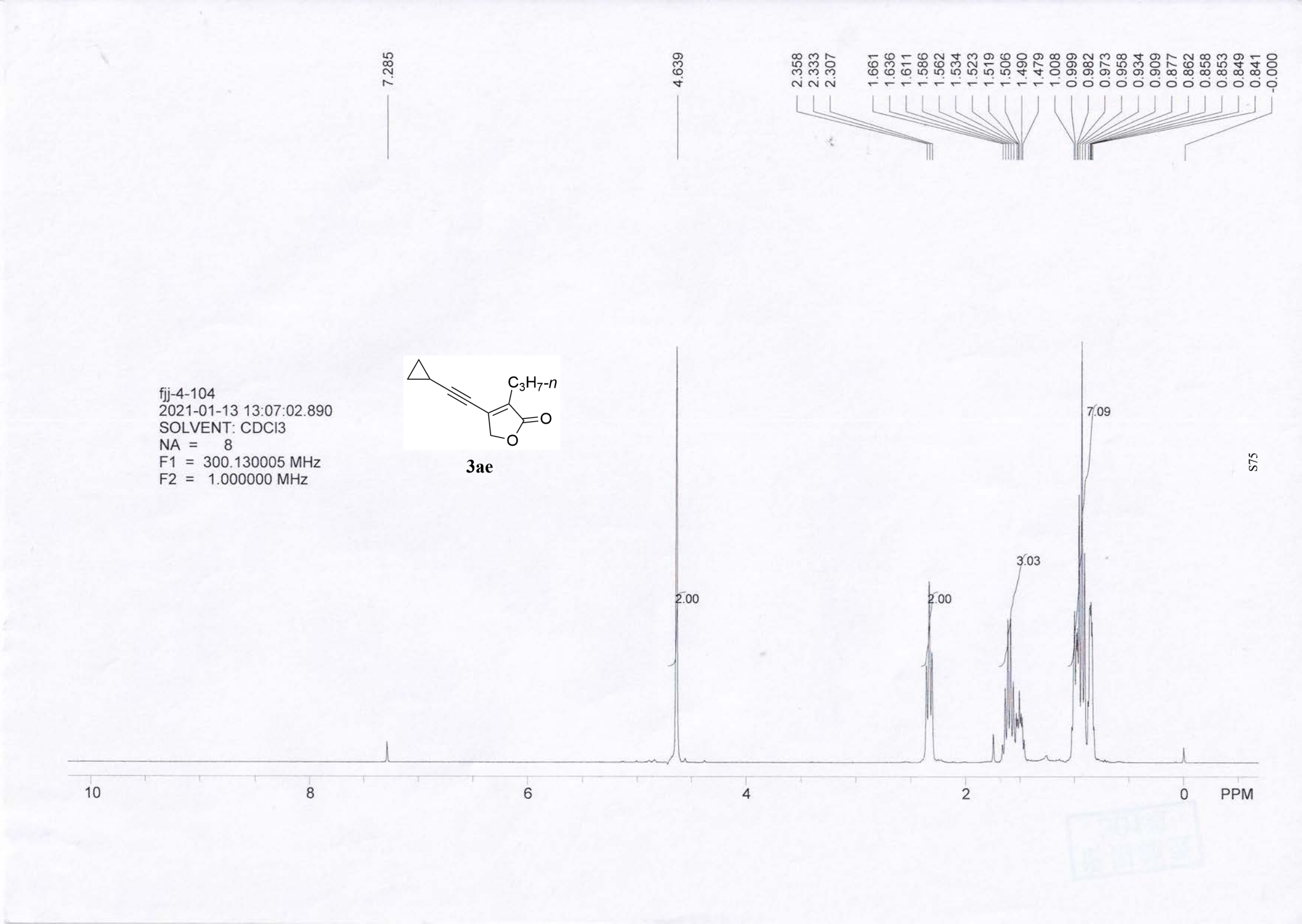


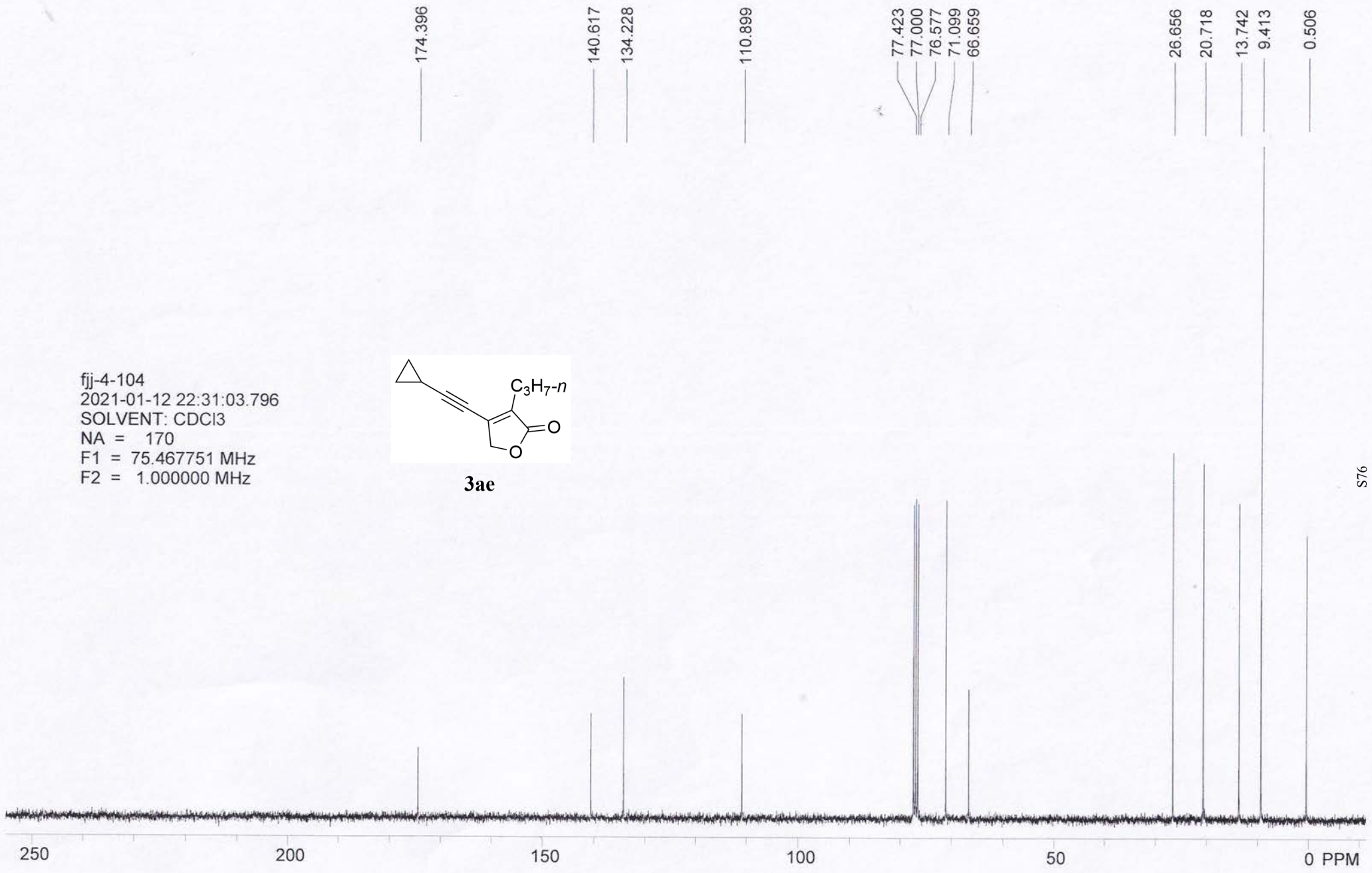
3ad

Purity (97%) is determined by dibromomethane(25 μL, 5/7 mmol) as the intenal standard in 94.5 mg of sample.

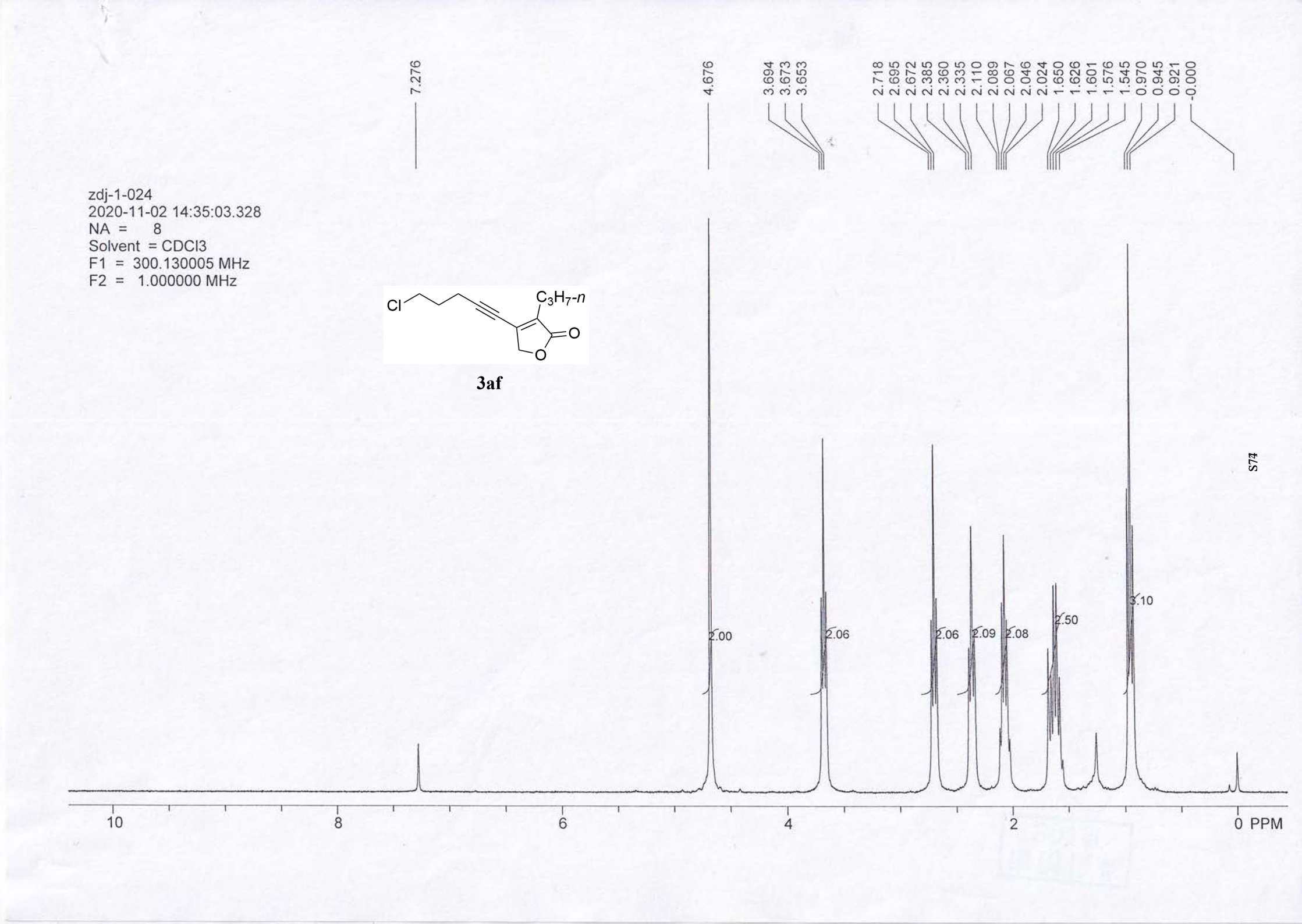

174.369
140.754
134.532
106.690
77.423
77.000
76.577
72.377
71.154
36.997
32.548
27.539
26.730
26.004
25.912
20.829
13.751
fjj-4-041
2020-12-01 16:54:12.203
SOLVENT: CDCl3
NA = 115
F1 = 75.467751 MHz
F2 = 1.000000 MHz
C3H7-n
O
O
250
200
150
100
50
PPM

3ad

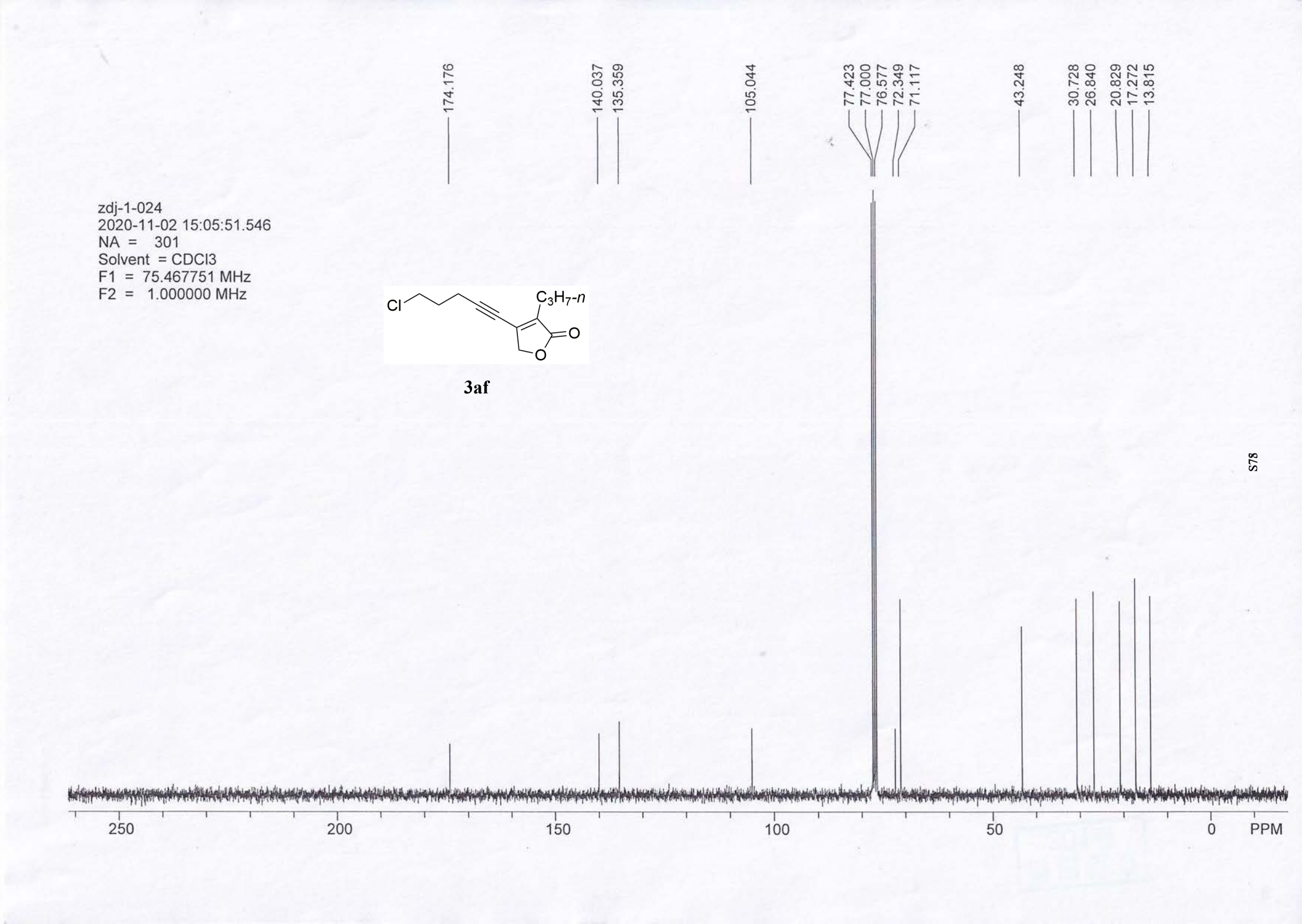

7.285
4.639
2.358
2.333
2.307
1.661
1.636
1.611
1.586
1.562
1.534
1.523
1.519
1.506
1.490
1.479
1.008
0.999
0.982
0.973
0.958
0.934
0.909
0.877
0.862
0.858
0.853
0.849
0.841
-0.000
fjj-4-104
2021-01-13 13:07:02.890
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C3H7-n
O
O
3ae
2.00
2.00
3.03
7.09
S75
10
8
6
4
2
0
PPM

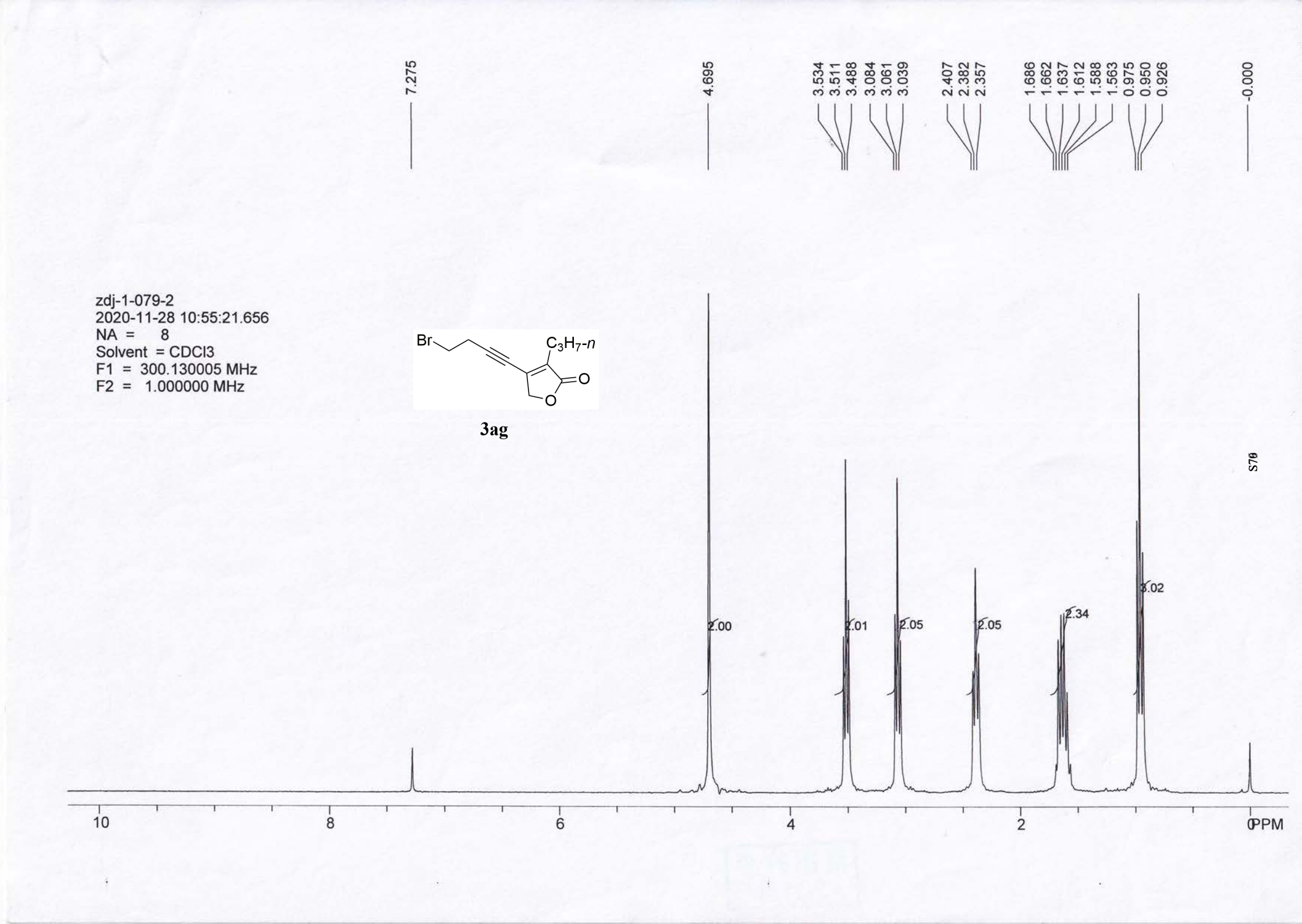

174.396
140.617
134.228
110.899
77.423
77.000
76.577
71.099
66.659
26.656
20.718
13.742
9.413
0.506
fjj-4-104
2021-01-12 22:31:03.796
SOLVENT: CDCl3
NA = 170
F1 = 75.467751 MHz
F2 = 1.000000 MHz
C3H7-n
O
O
250
200
150
100
50
0 PPM

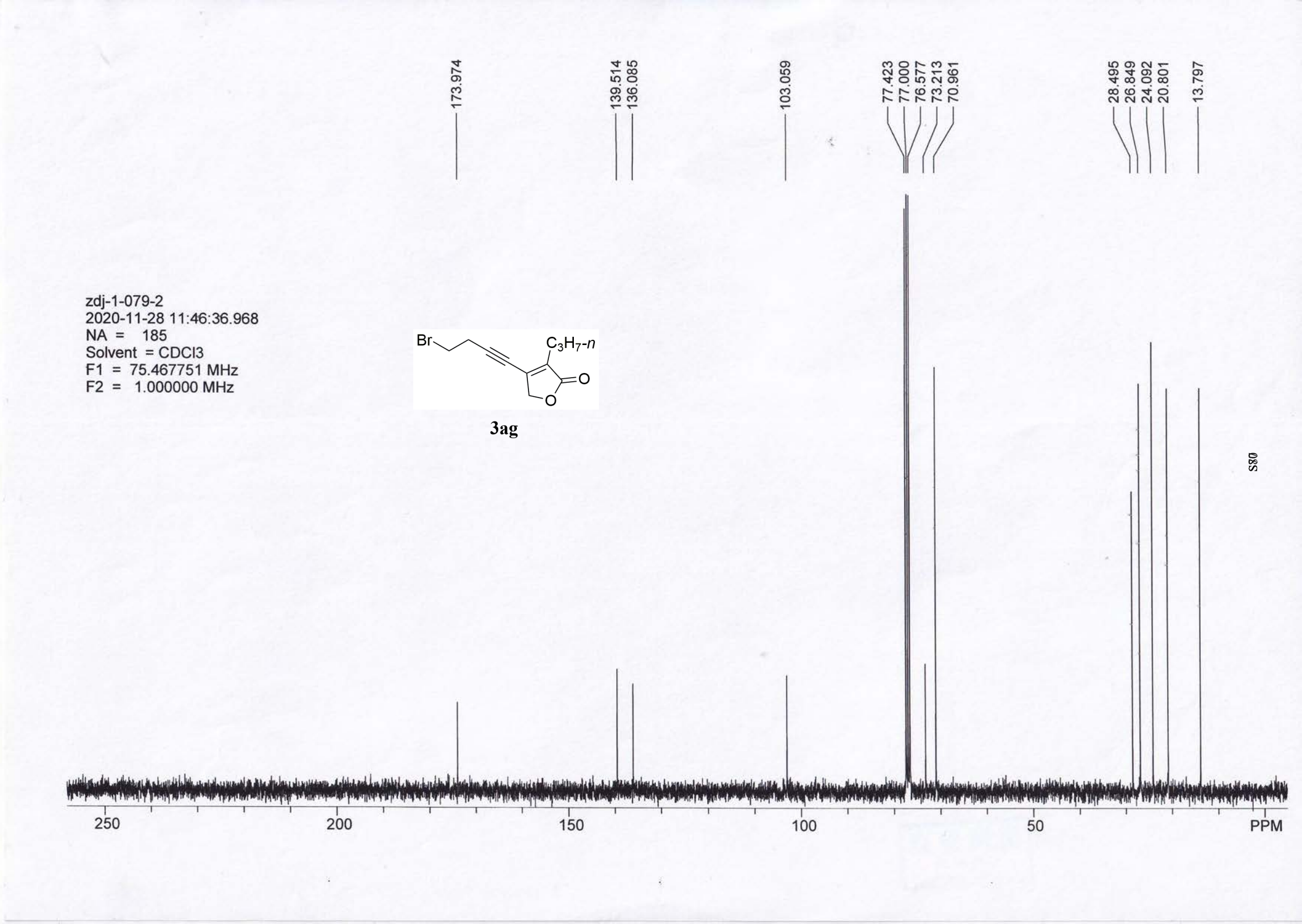
3ae


7.276
4.676
3.694
3.673
3.653
2.718
2.695
2.672
2.385
2.360
2.335
2.110
2.089
2.067
2.046
2.024
1.650
1.626
1.601
1.576
1.545
0.970
0.945
0.921
-0.000
zdj-1-024
2020-11-02 14:35:03.328
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Cl
C_3H_7-*n*
O
O
2.00
2.06
2.06
2.09
2.08
2.50
3.10
10
8
6
4
2
0 PPM

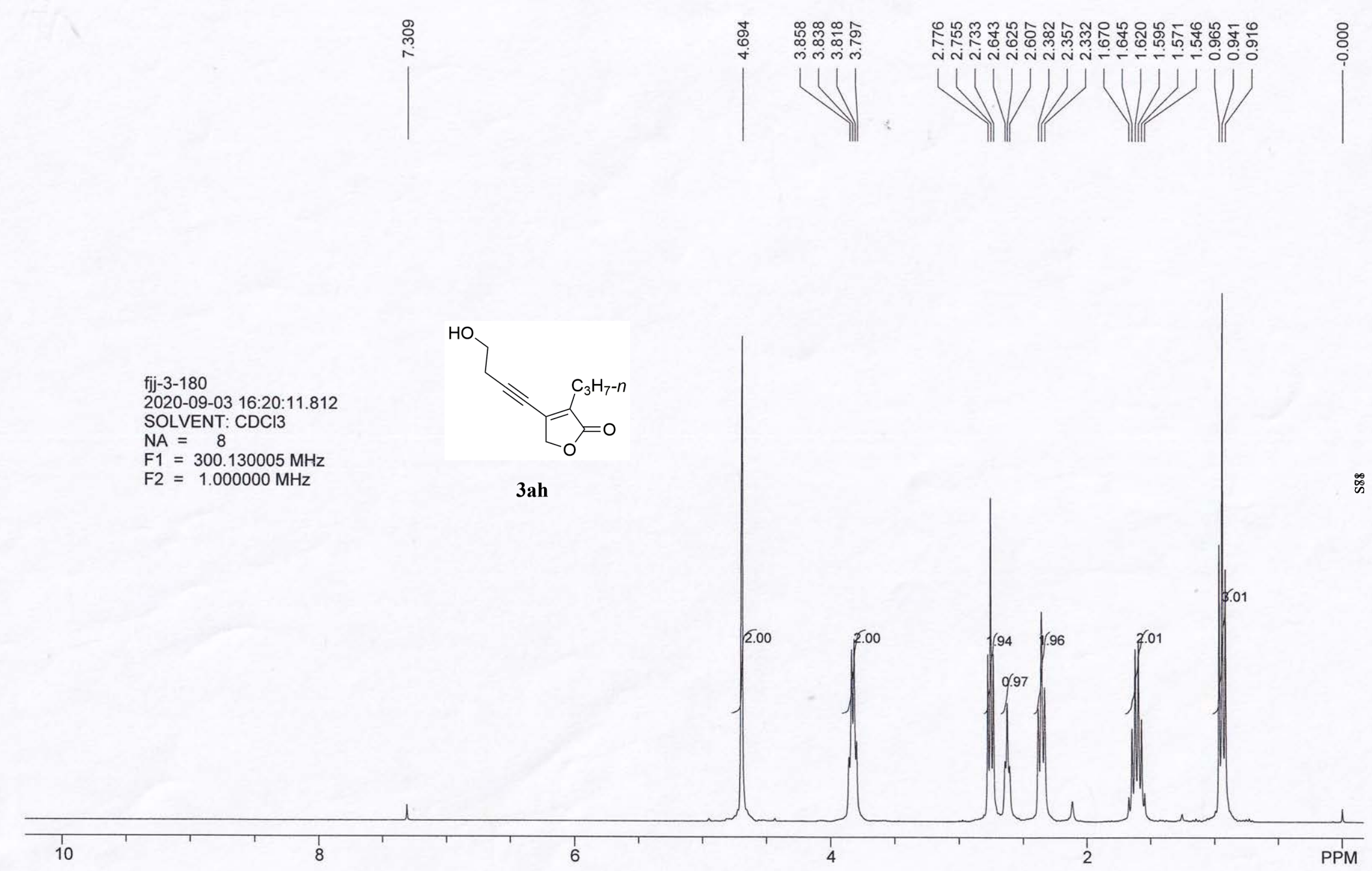
3af

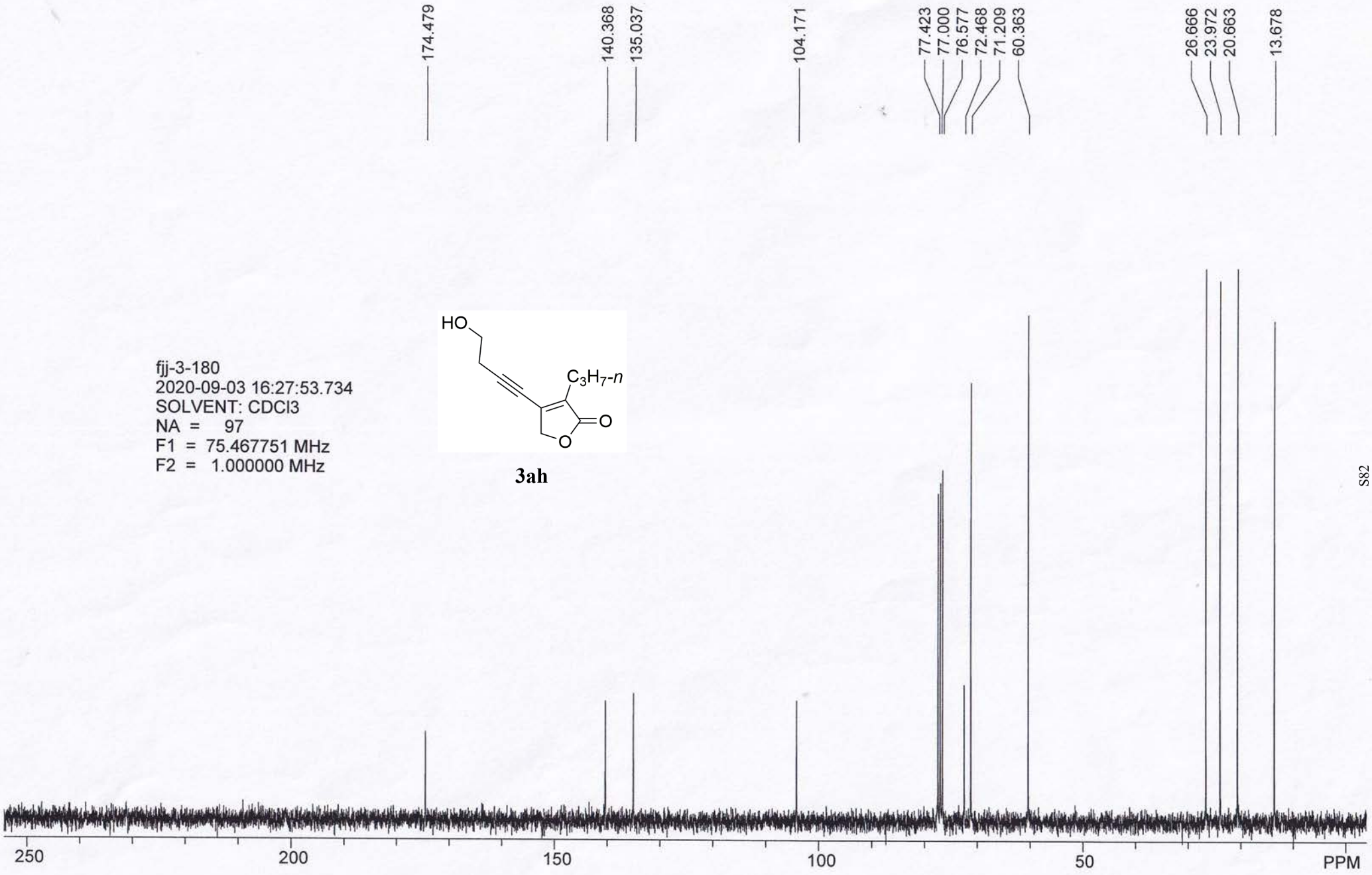

174.176
140.037
135.359
105.044
77.423
77.000
76.577
72.349
71.117
43.248
30.728
26.840
20.829
17.272
13.815
zdj-1-024
2020-11-02 15:05:51.546
NA = 301
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
Cl
C3H7-n
O
O
3af
250
200
150
100
50
0
PPM


7.275
4.695
3.534
3.511
3.488
3.084
3.061
3.039
2.407
2.382
2.357
1.686
1.662
1.637
1.612
1.588
1.563
0.975
0.950
0.926
-0.000
zdj-1-079-2
2020-11-28 10:55:21.656
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Br
C3H7-n
O
O
3ag
2.00
2.01
2.05
2.05
2.34
3.02
S76
10
8
6
4
2
0
PPM

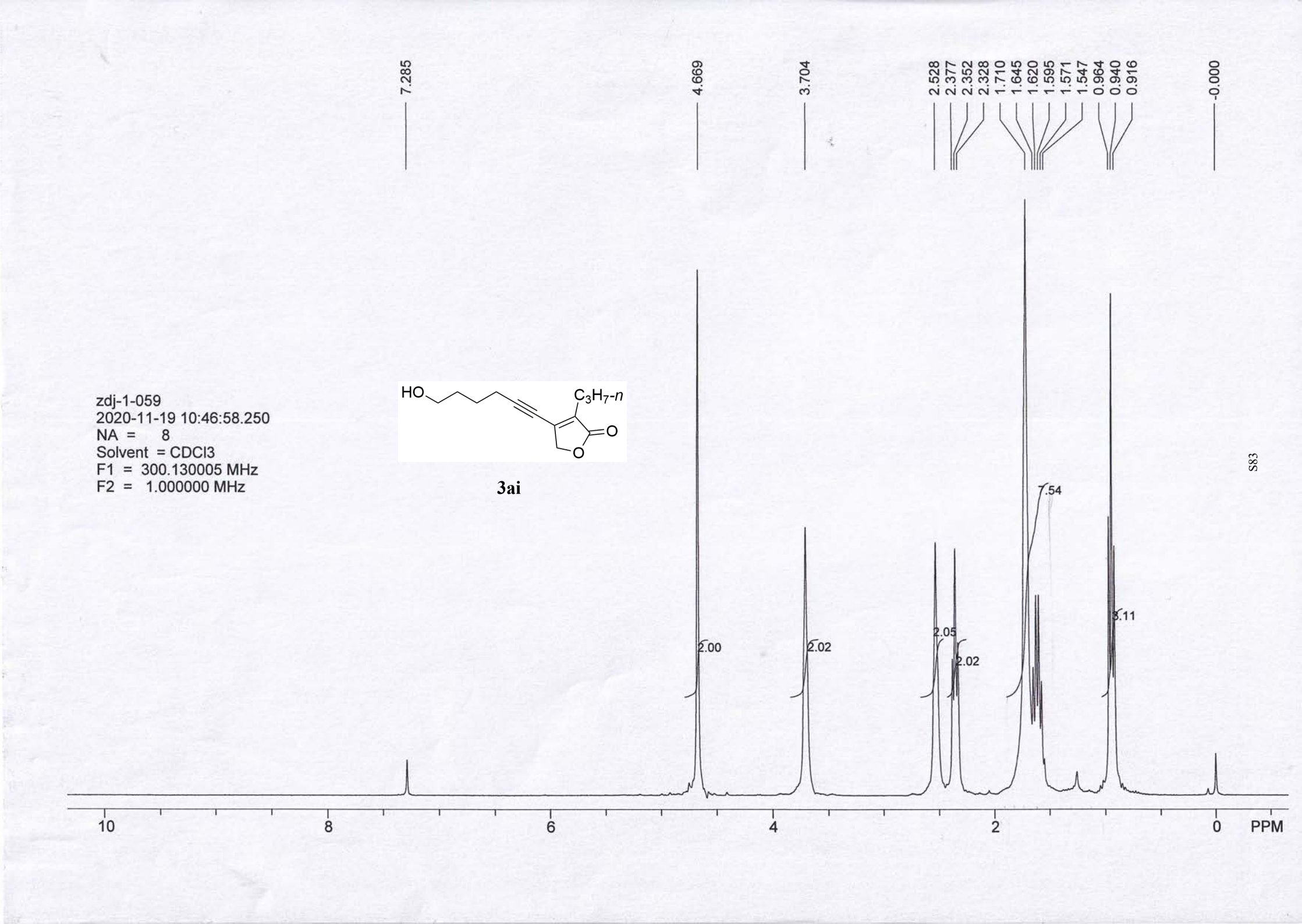

173.974
139.514
136.085
103.059
77.423
77.000
76.577
73.213
70.961
28.495
26.849
24.092
20.801
13.797
zdj-1-079-2
2020-11-28 11:46:36.968
NA = 185
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
Br
C_3H_7-*n*
O
O
S80
250
200
150
100
50
PPM

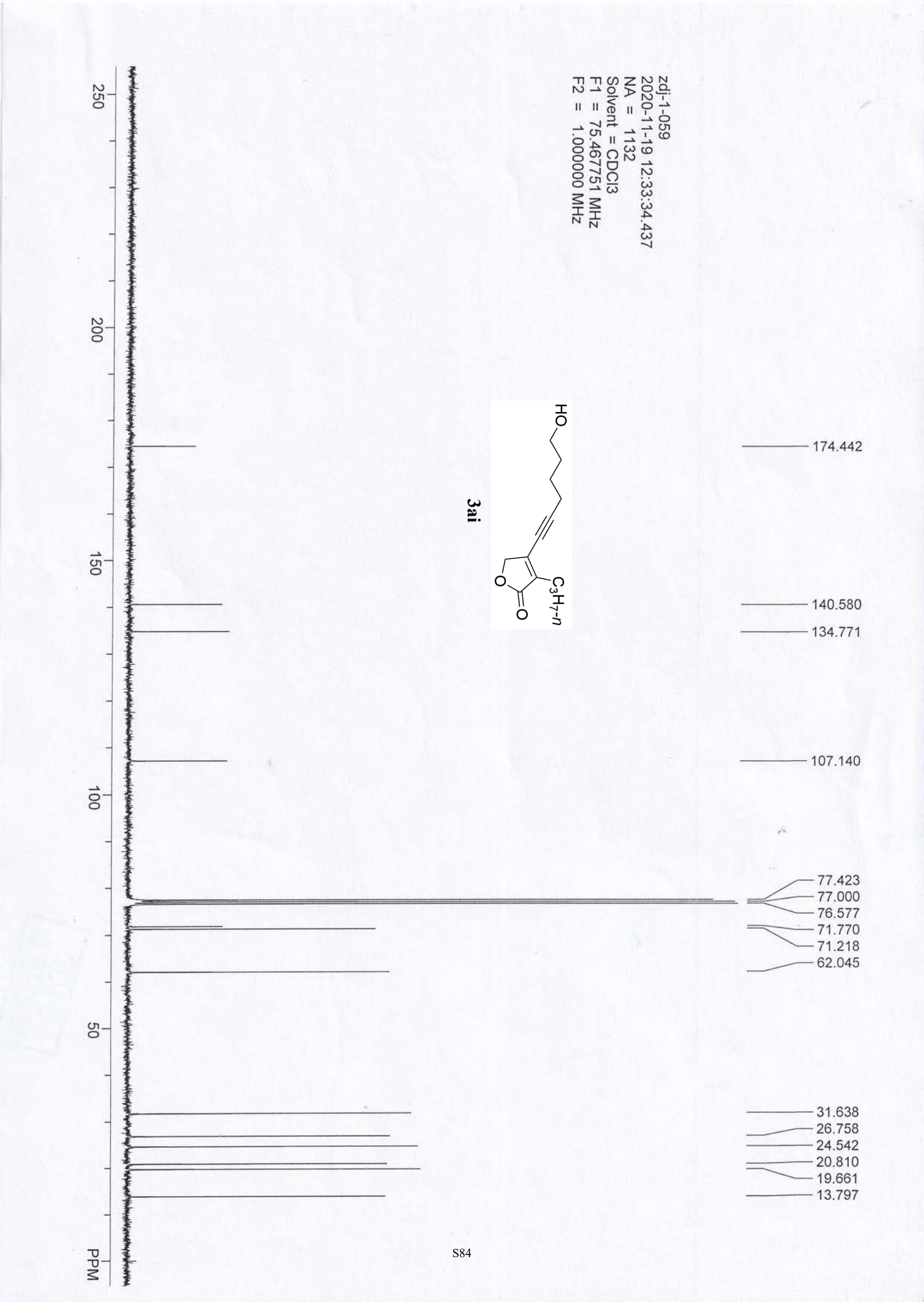
3ag


7.309
4.694
3.858
3.838
3.818
3.797
2.776
2.755
2.733
2.643
2.625
2.607
2.382
2.357
2.332
1.670
1.645
1.620
1.595
1.571
1.546
0.965
0.941
0.916
-0.000
fjj-3-180
2020-09-03 16:20:11.812
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
HO
C3H7-n
O
O
3ah
2.00
2.00
1.94
0.97
1.96
2.01
3.01
10
8
6
4
2
PPM

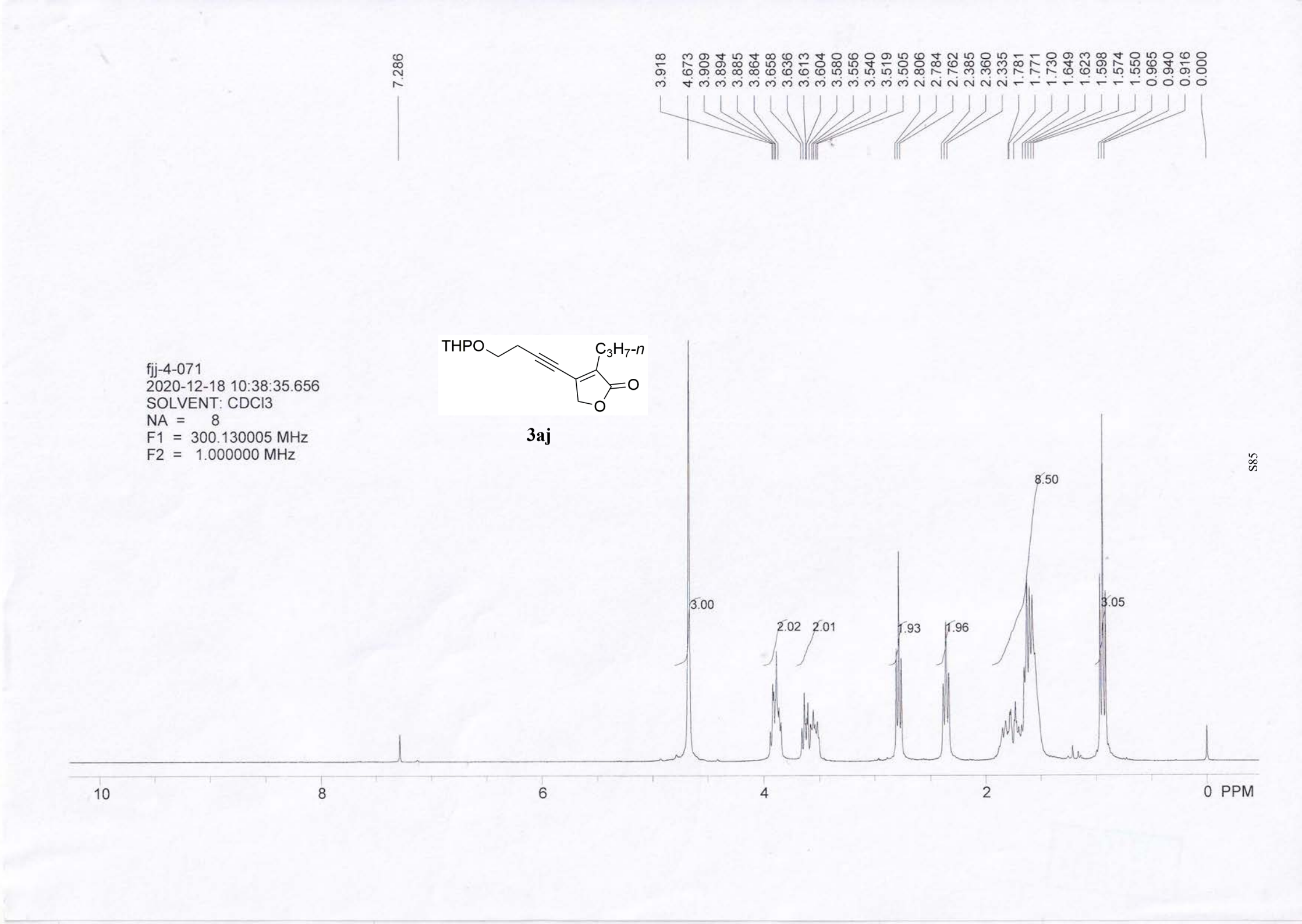

174.479
140.368
135.037
104.171
77.423
77.000
76.577
72.468
71.209
60.363
26.666
23.972
20.663
13.678
fjj-3-180
2020-09-03 16:27:53.734
SOLVENT: CDCl3
NA = 97
F1 = 75.467751 MHz
F2 = 1.000000 MHz
HO
C_3H_7-*n*
O
O
250
200
150
100
50
PPM

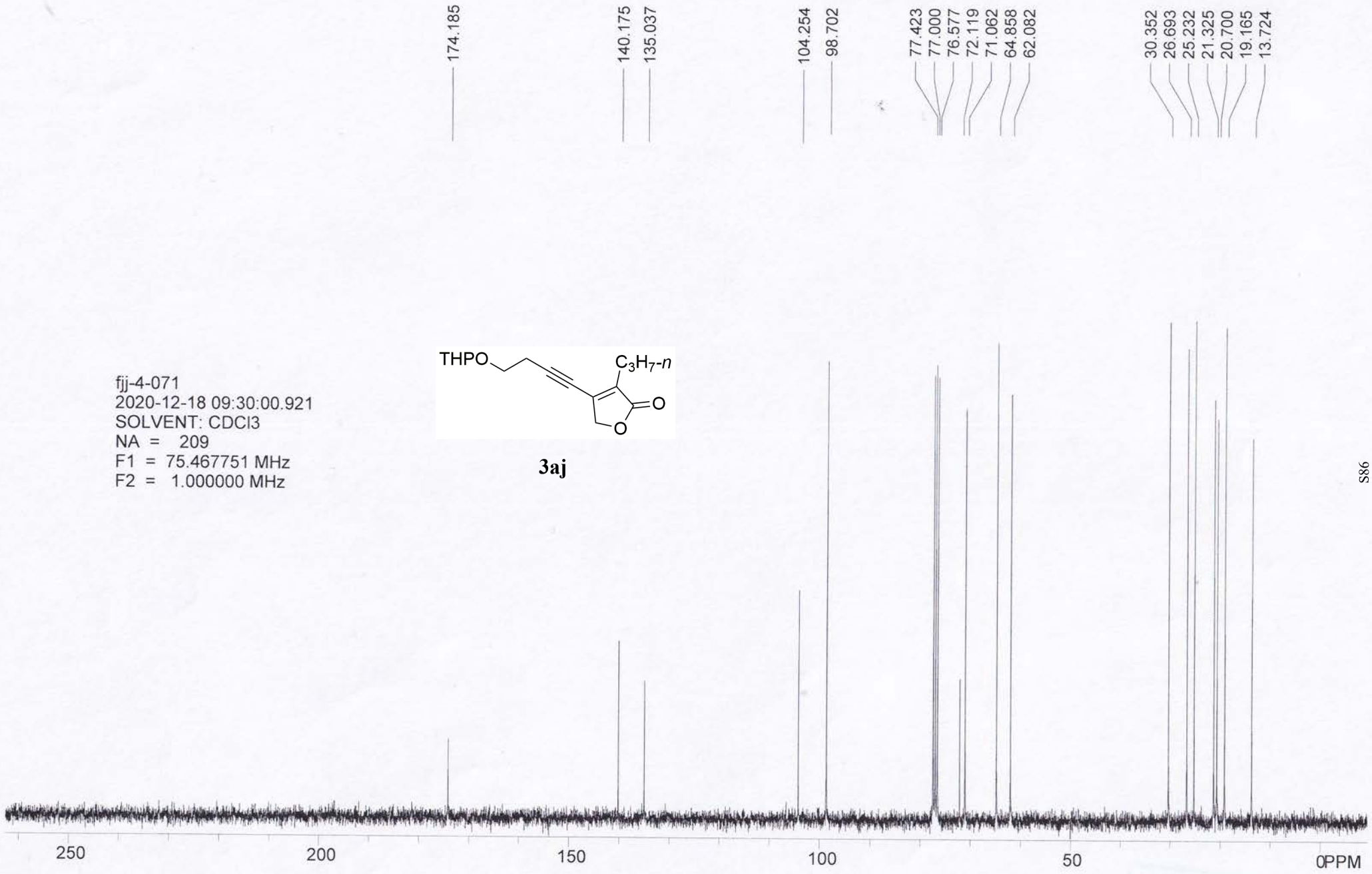
3ah


7.285
4.669
3.704
2.528
2.377
2.352
2.328
1.710
1.645
1.620
1.595
1.571
1.547
0.964
0.940
0.916
-0.000
zdj-1-059
2020-11-19 10:46:58.250
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
HO
C3H7-n
O
O
3ai
2.00
2.02
2.05
2.02
7.54
3.11
S83
10
8
6
4
2
0
PPM

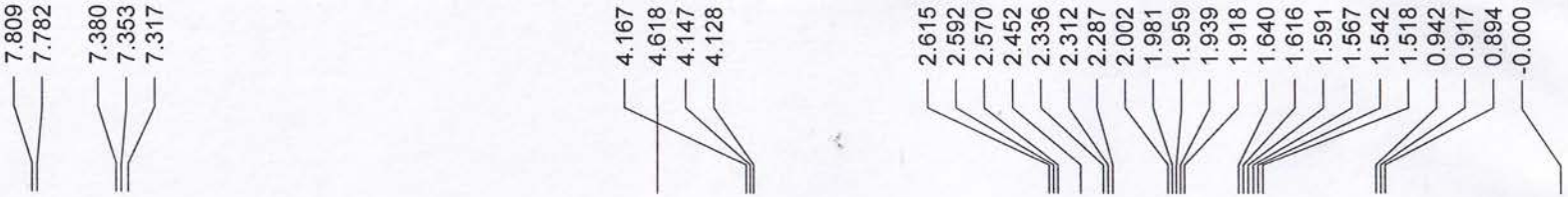

zdj-1-059
2020-11-19 12:33:34.437
NA = 1132
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
HO
O
O
C3H7-n
174.442
140.580
134.771
107.140
77.423
77.000
76.577
71.770
71.218
62.045
31.638
26.758
24.542
20.810
19.661
13.797
250
200
150
100
50
PPM

3ai

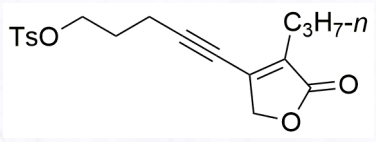

7.286
3.918
4.673
3.909
3.894
3.885
3.864
3.658
3.636
3.613
3.604
3.580
3.556
3.540
3.519
3.505
2.806
2.784
2.762
2.385
2.360
2.335
1.781
1.771
1.730
1.649
1.623
1.598
1.574
1.550
0.965
0.940
0.916
0.000
fjj-4-071
2020-12-18 10:38:35.656
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
THPO
C3H7-n
O
O
3aj
3.00
2.02
2.01
1.93
1.96
8.50
3.05
10
8
6
4
2
0 PPM


174.185
140.175
135.037
104.254
98.702
77.423
77.000
76.577
72.119
71.062
64.858
62.082
30.352
26.693
25.232
21.325
20.700
19.165
13.724
fjj-4-071
2020-12-18 09:30:00.921
SOLVENT: CDCl3
NA = 209
F1 = 75.467751 MHz
F2 = 1.000000 MHz
THPO
C3H7-n
O
O
250
200
150
100
50
0PPM

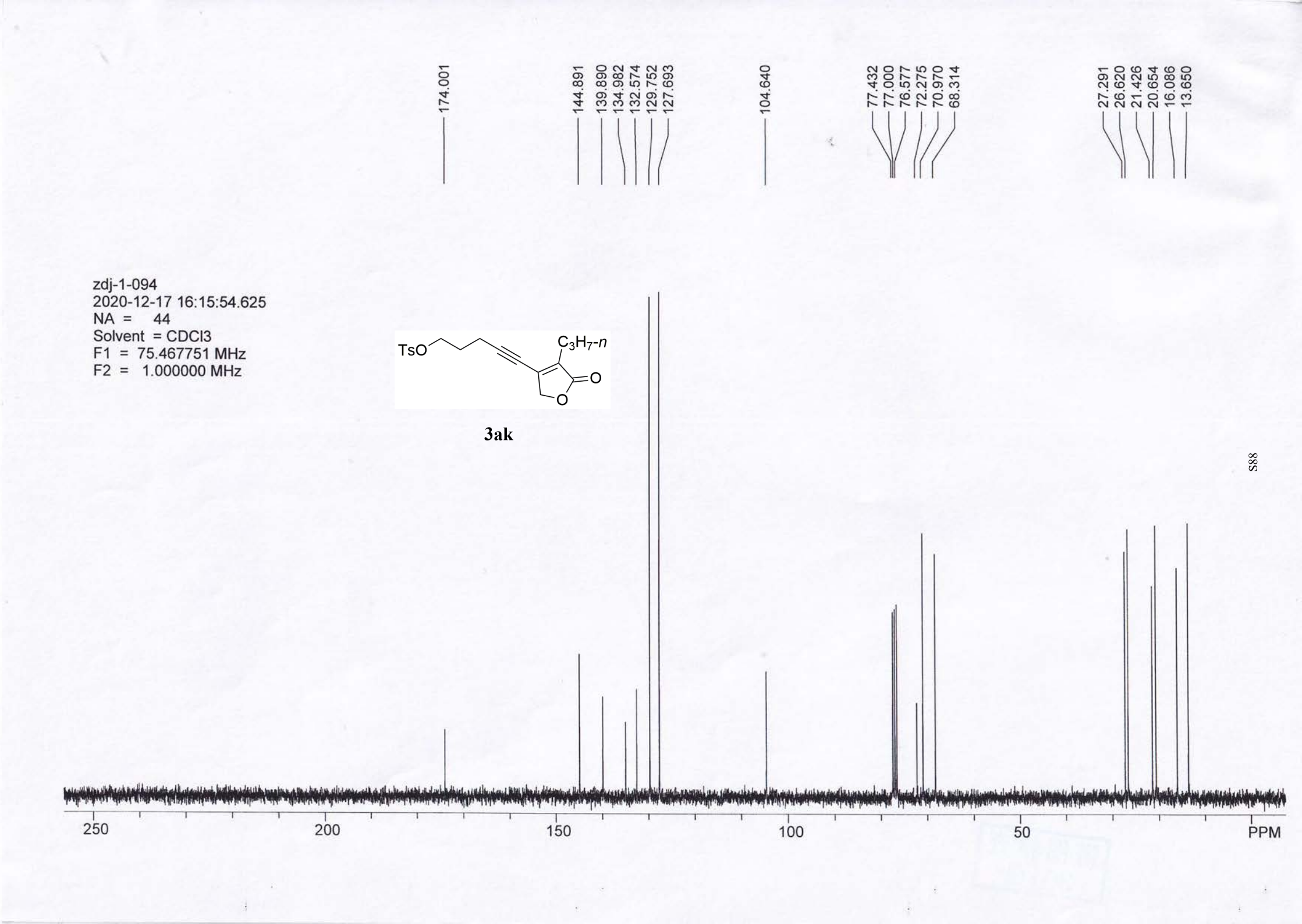
3aj



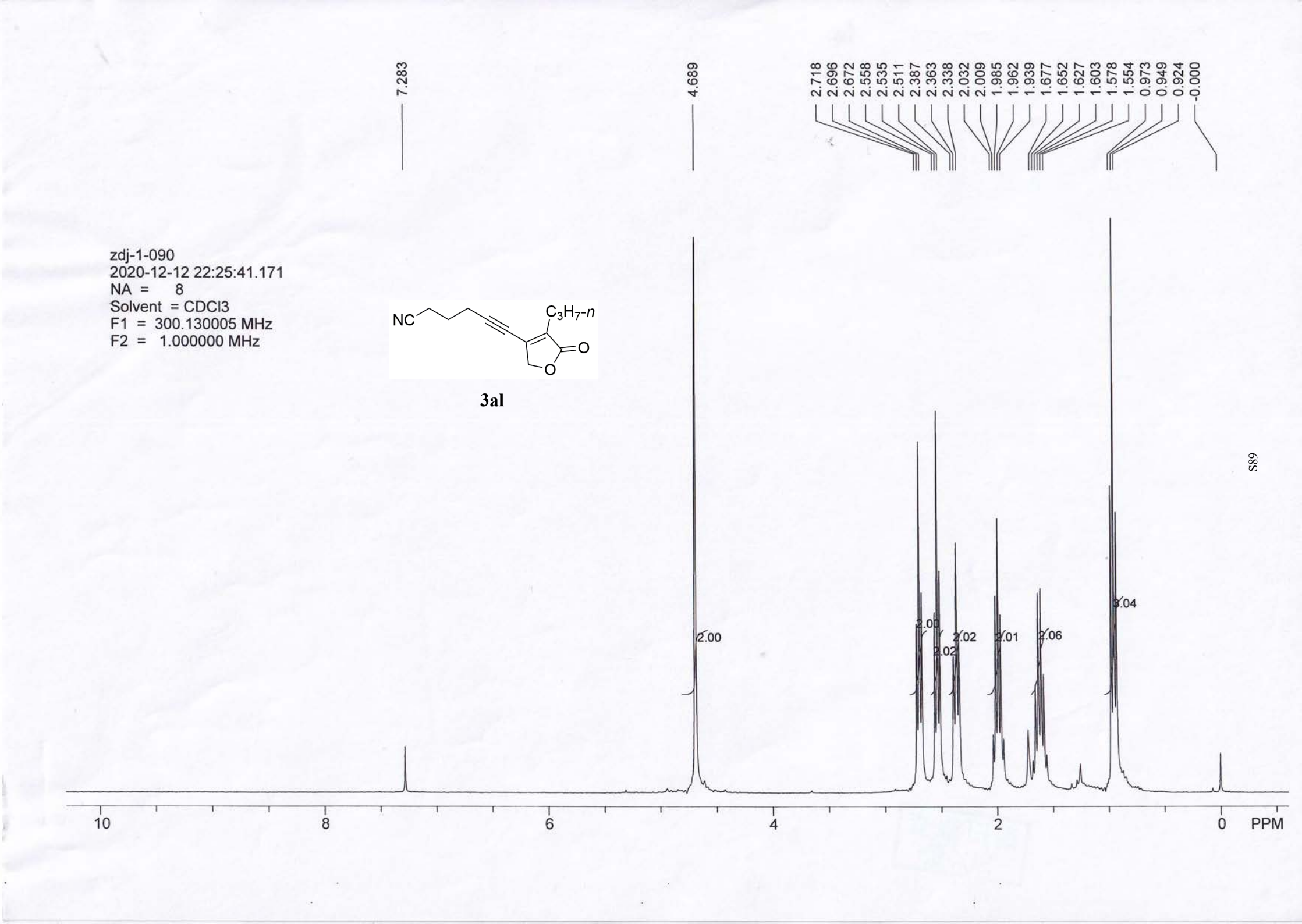
zdj-1-094
2020-12-17 14:07:24.000
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz



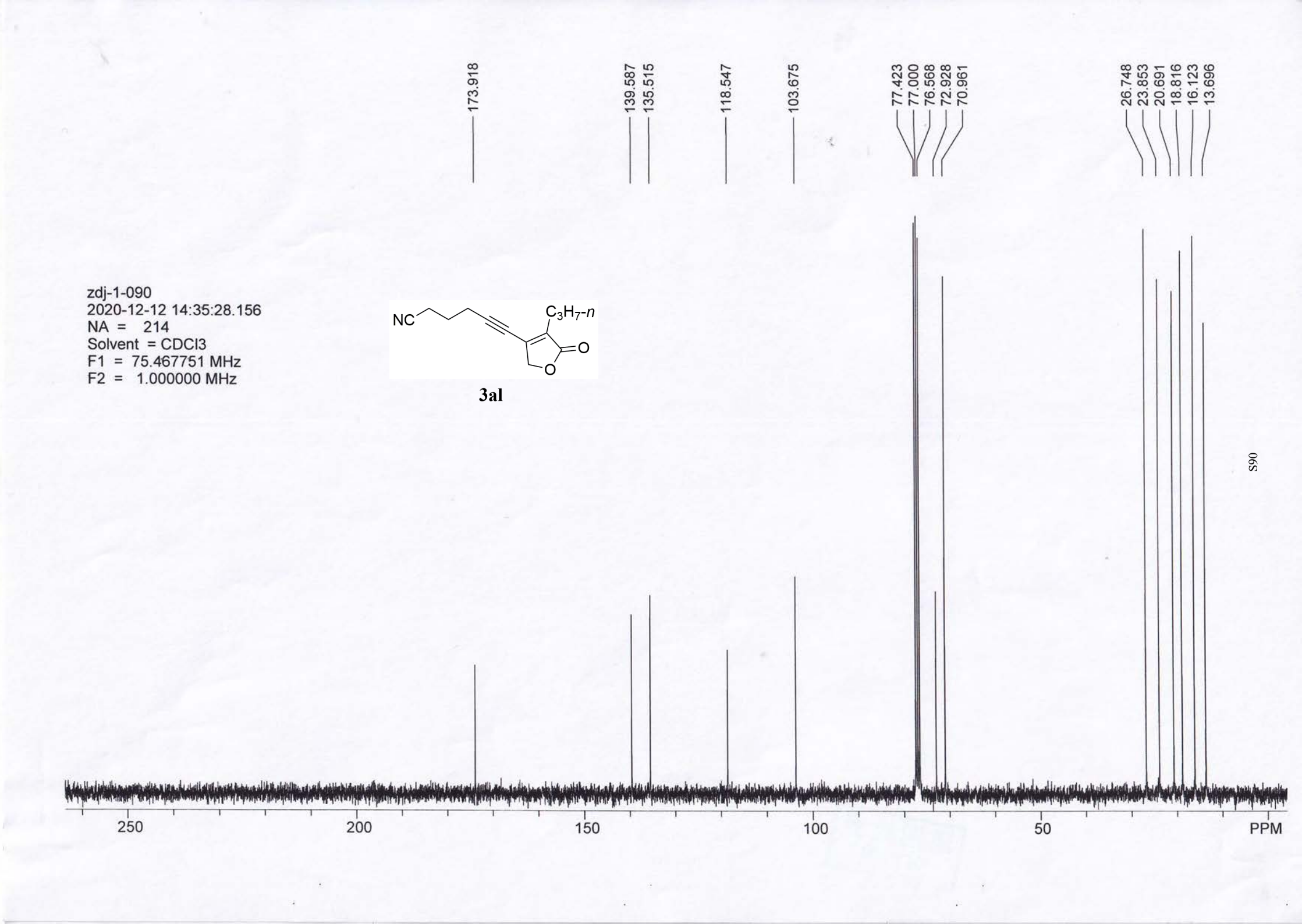
3ak

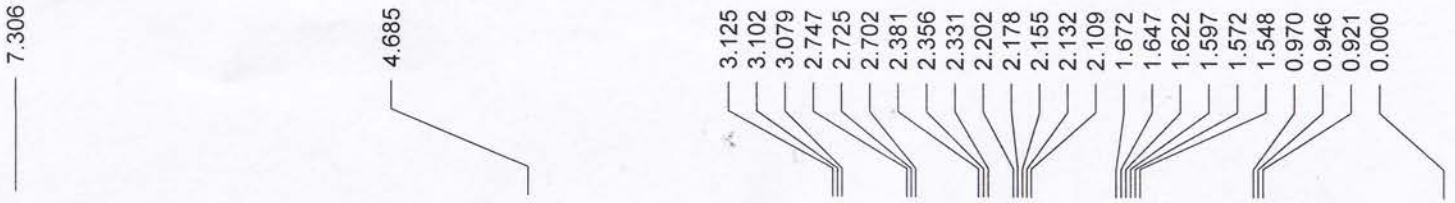

174.001
144.891
139.890
134.982
132.574
129.752
127.693
104.640
77.432
77.000
76.577
72.275
70.970
68.314
27.291
26.620
21.426
20.654
16.086
13.650
zdj-1-094
2020-12-17 16:15:54.625
NA = 44
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
TsO
C3H7-n
O
O
250
200
150
100
50
PPM

3ak

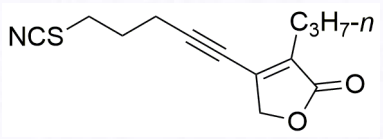

7.283
4.689
2.718
2.696
2.672
2.558
2.535
2.511
2.387
2.363
2.338
2.032
2.009
1.985
1.962
1.939
1.677
1.652
1.627
1.603
1.578
1.554
0.973
0.949
0.924
-0.000
zdj-1-090
2020-12-12 22:25:41.171
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NC
C_3H_7-*n*
O
O
2.00
3.03
2.02
2.02
2.01
2.06
3.04
10
8
6
4
2
0
PPM

3al

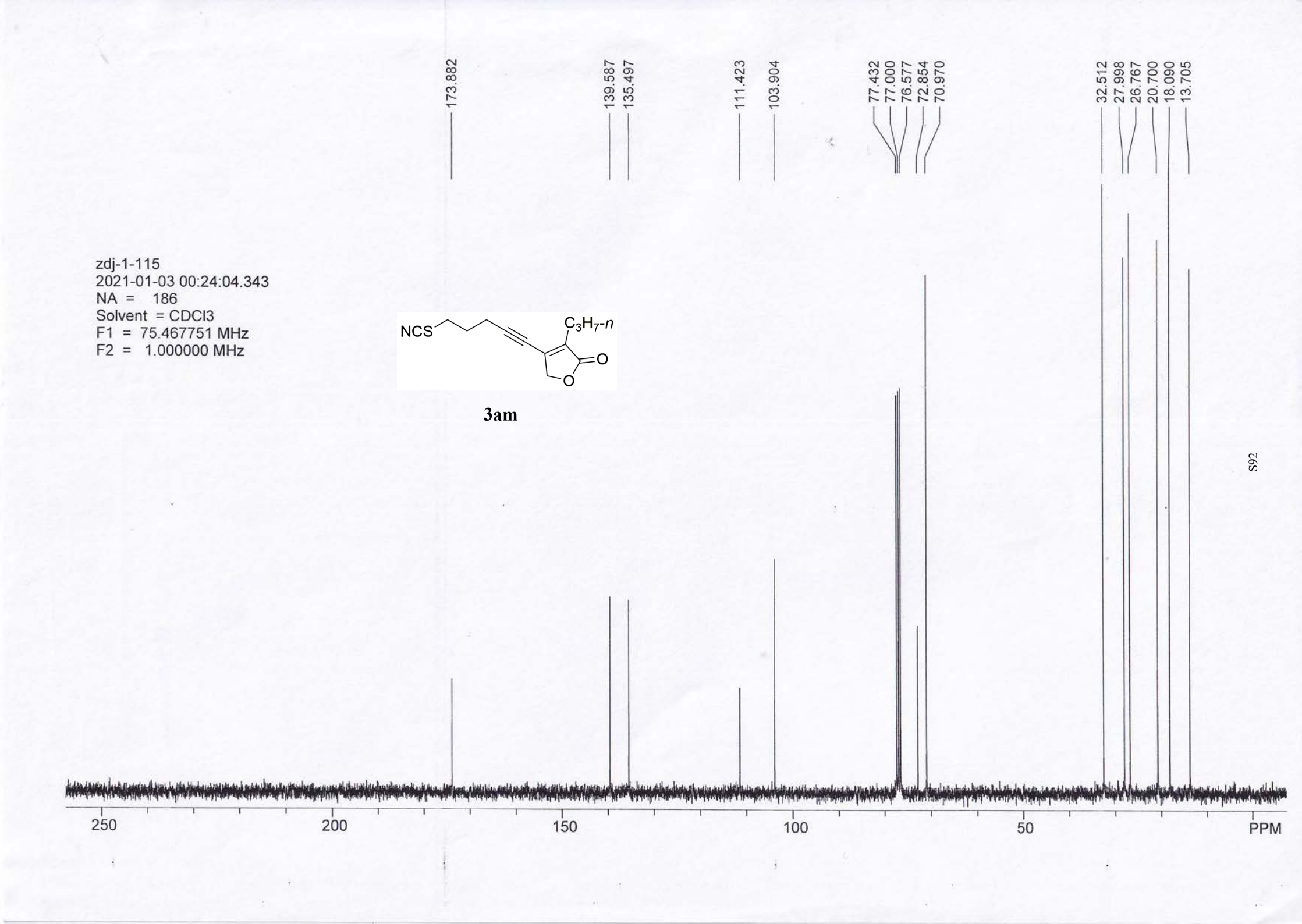

173.918
139.587
135.515
118.547
103.675
77.423
77.000
76.568
72.928
70.961
26.748
23.853
20.691
18.816
16.123
13.696
zdj-1-090
2020-12-12 14:35:28.156
NA = 214
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
NC
C3H7-n
O
O
3al
S90
250
200
150
100
50
PPM



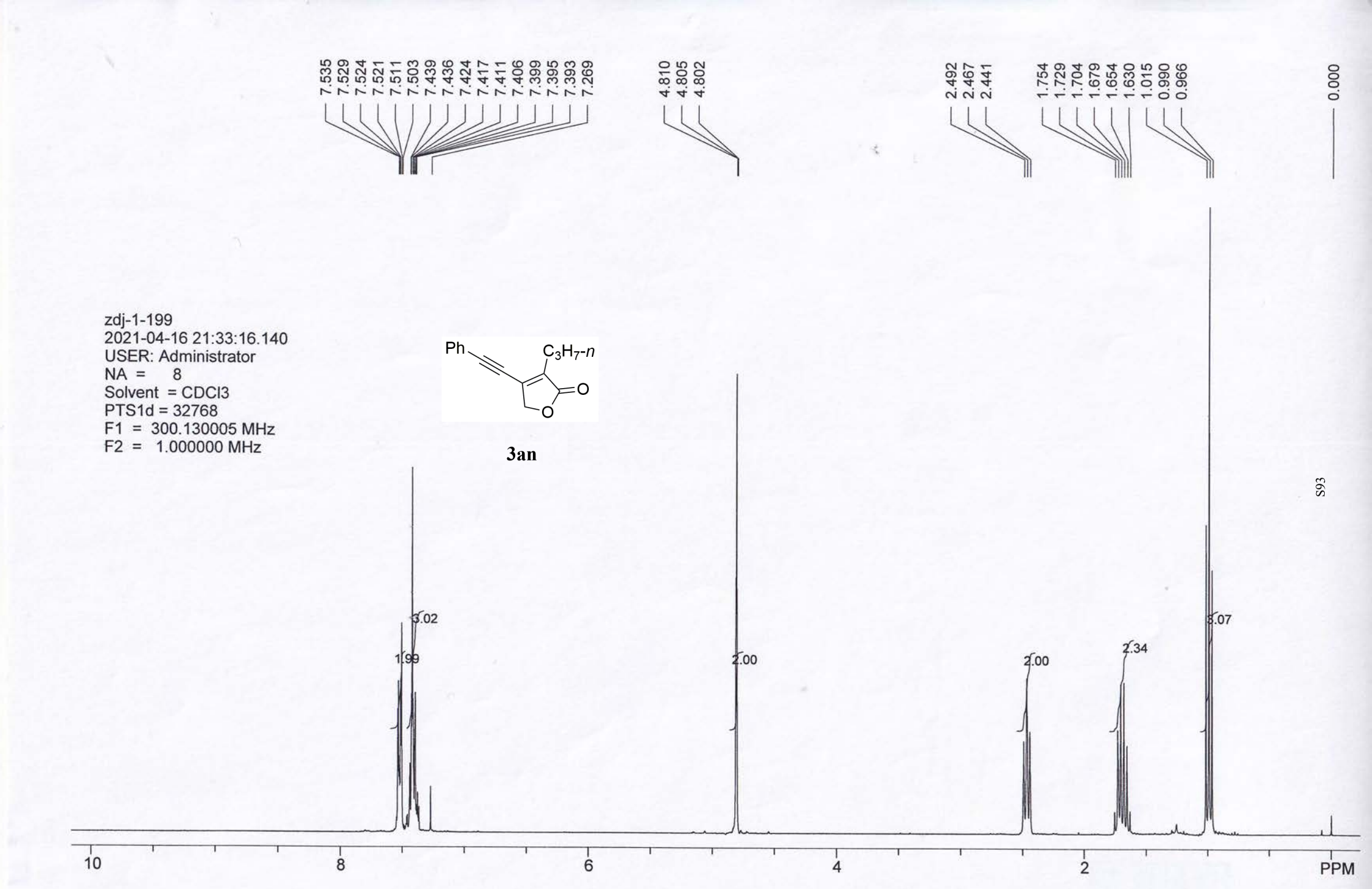
zdj-1-115
2020-12-27 18:39:48.562
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz

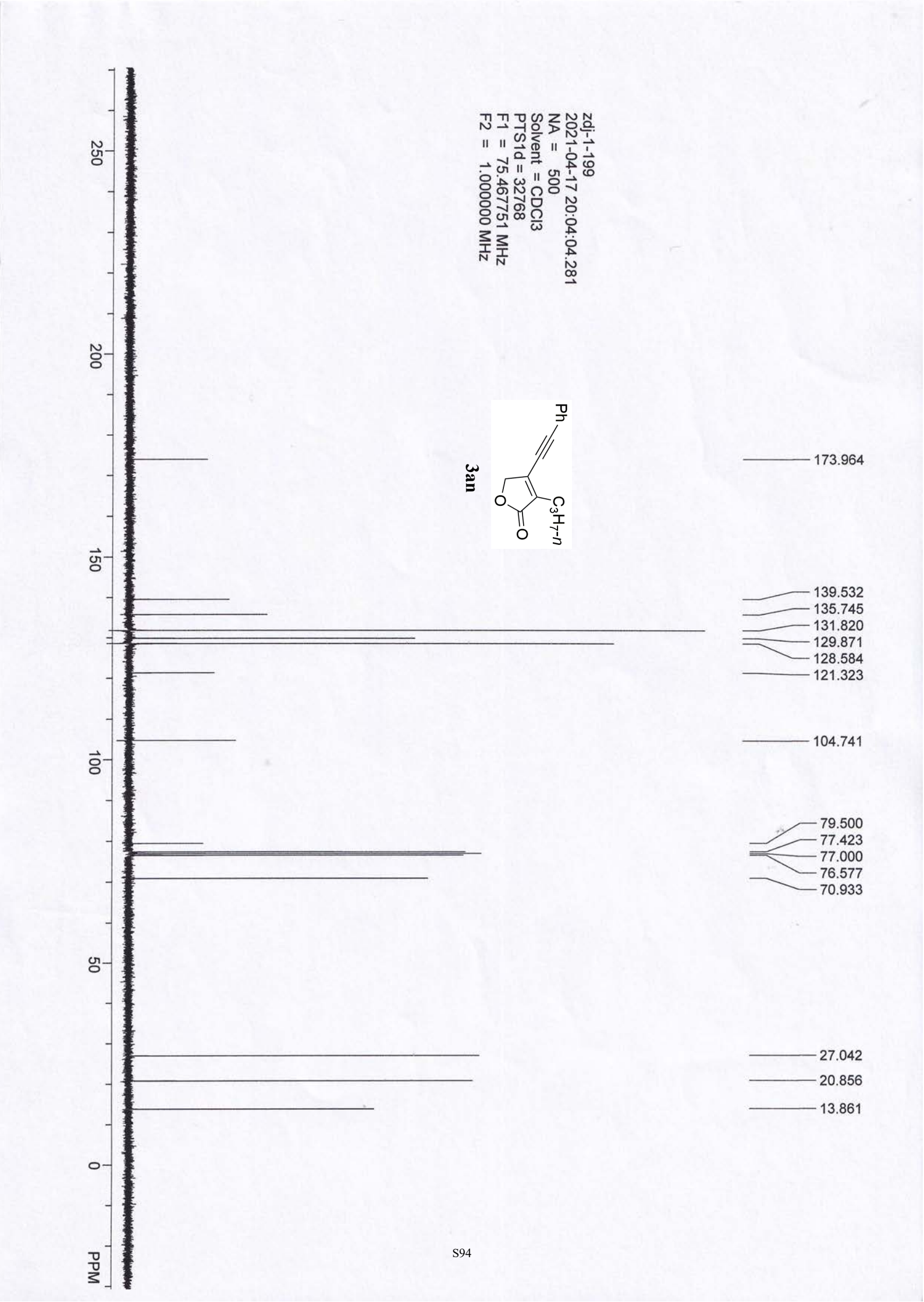


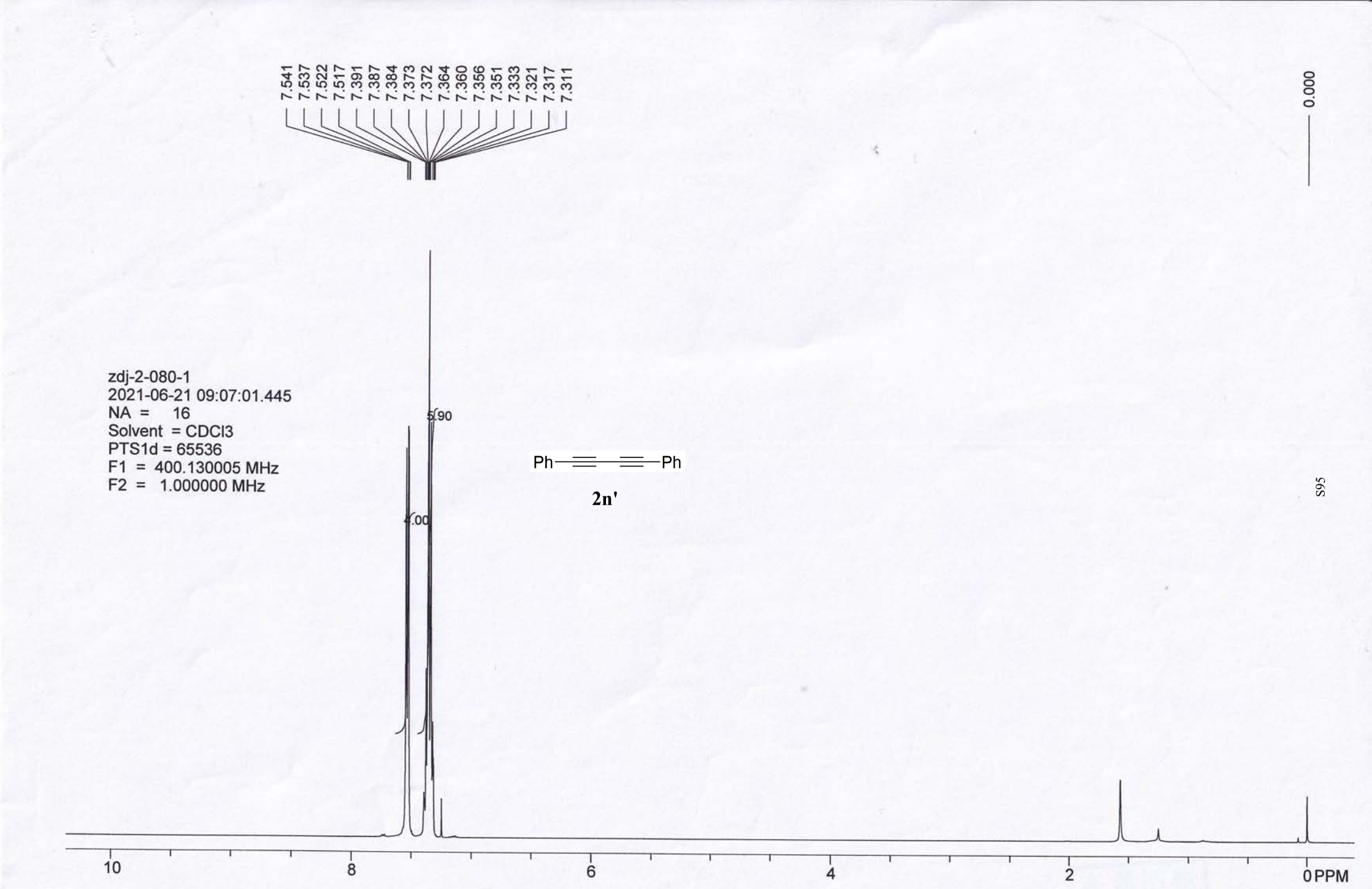
3am

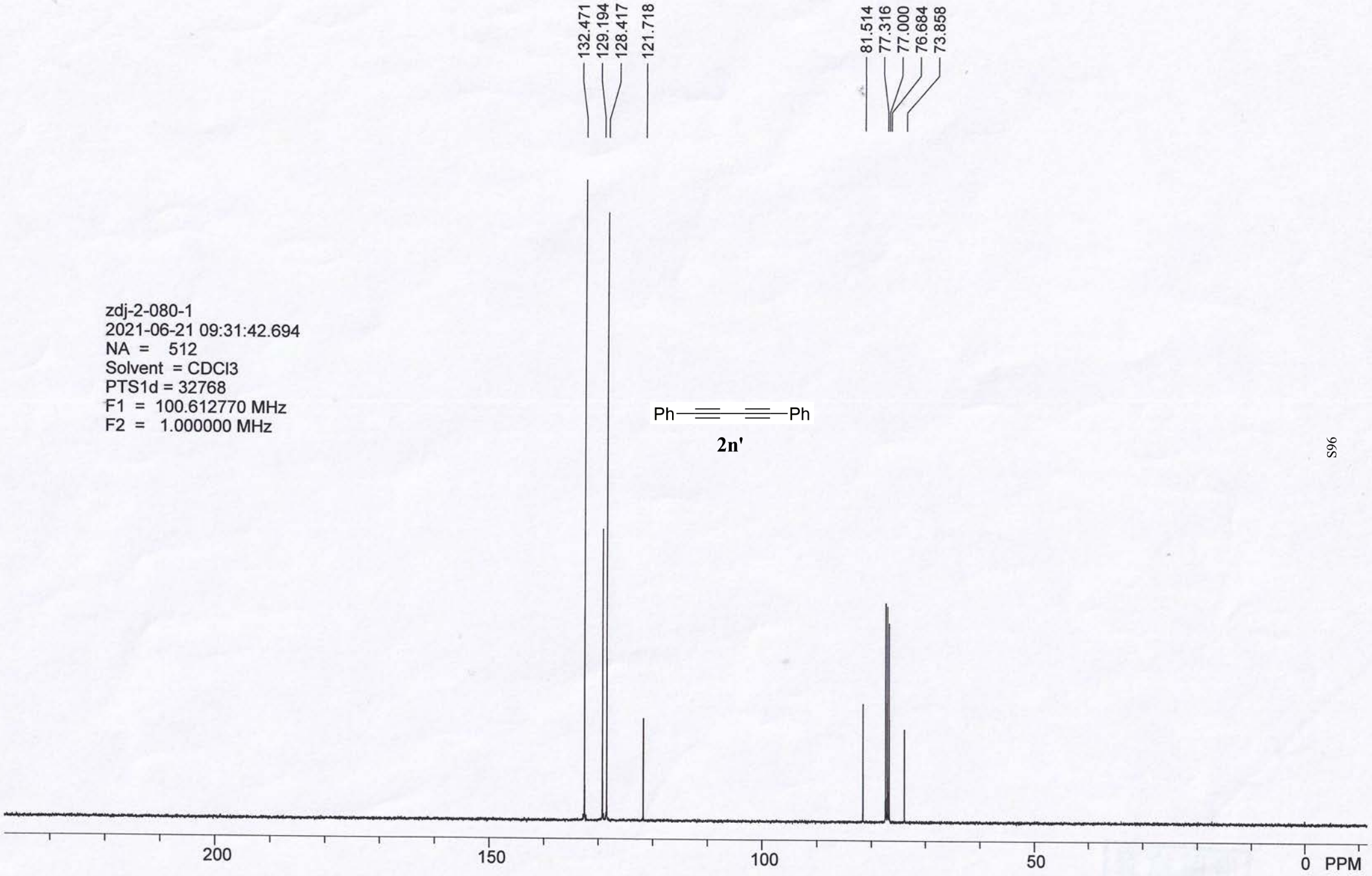

173.882
139.587
135.497
111.423
103.904
77.432
77.000
76.577
72.854
70.970
32.512
27.998
26.767
20.700
18.090
13.705
zdj-1-115
2021-01-03 00:24:04.343
NA = 186
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
NCS
C_3H_7-*n*
O
O
250
200
150
100
50
PPM

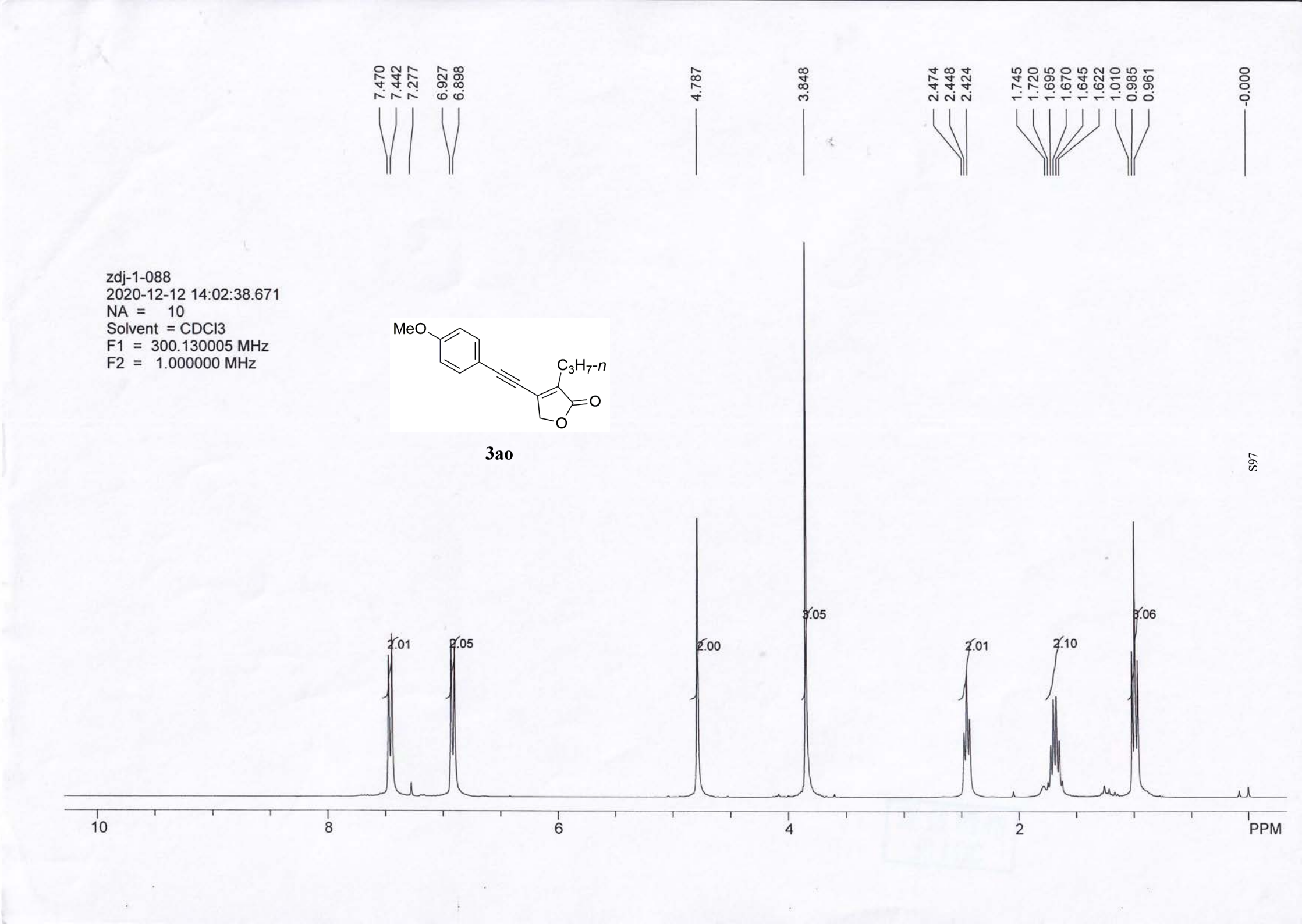
3am


7.535
7.529
7.524
7.521
7.511
7.503
7.439
7.436
7.424
7.417
7.411
7.406
7.399
7.395
7.393
7.269
4.810
4.805
4.802
2.492
2.467
2.441
1.754
1.729
1.704
1.679
1.654
1.630
1.015
0.990
0.966
0.000
zdj-1-199
2021-04-16 21:33:16.140
USER: Administrator
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Ph
C3H7-n
O
O
3an
1.99
3.02
2.00
2.00
2.34
3.07
10
8
6
4
2
PPM
S93

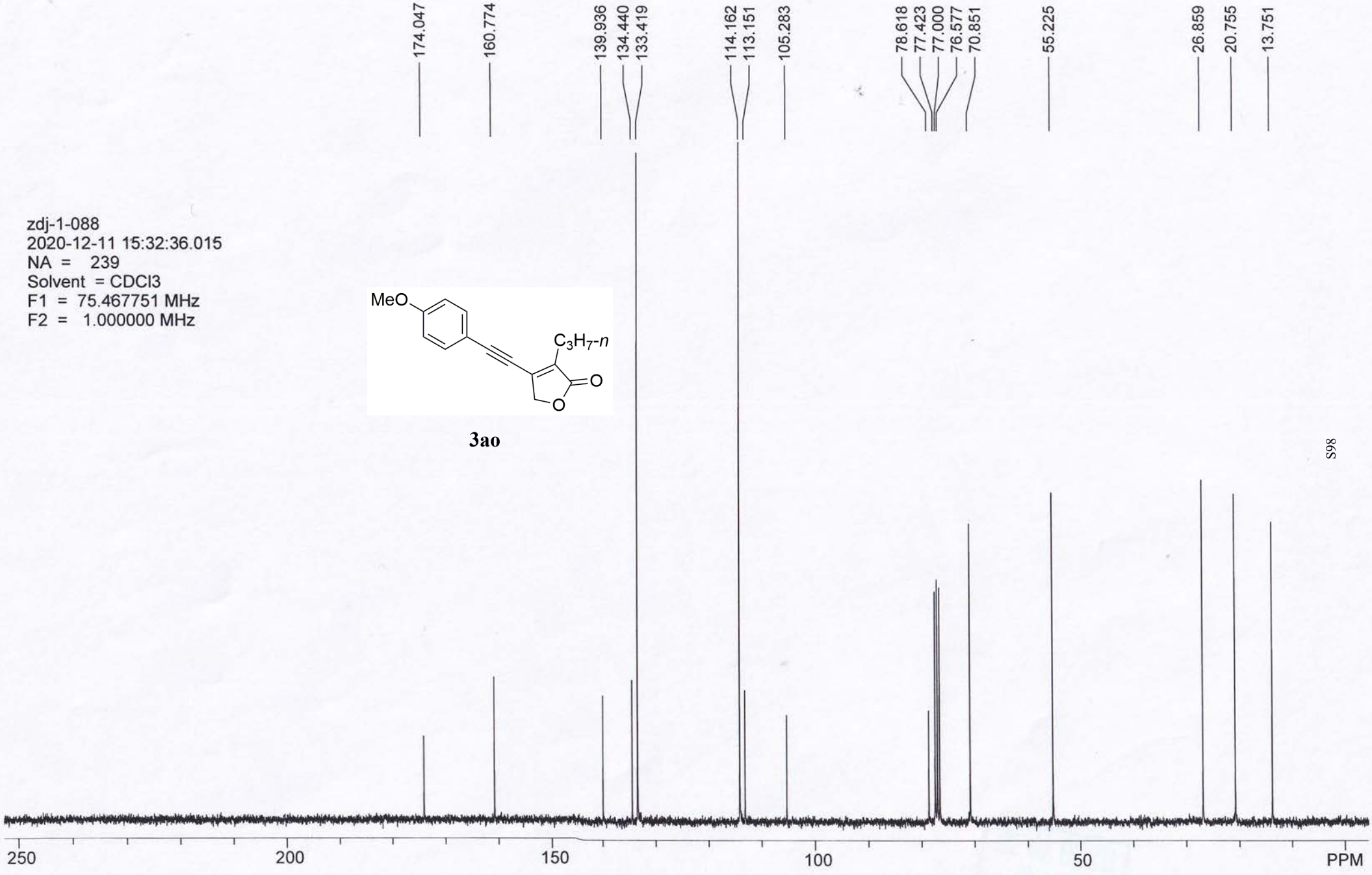

zdj-1-199
2021-04-17 20:04:04.281
NA = 500
Solvent = CDCl3
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
Ph
C_3H_{7}-n
O
O
3an
173.964
139.532
135.745
131.820
129.871
128.584
121.323
104.741
79.500
77.423
77.000
76.577
70.933
27.042
20.856
13.861
250
200
150
100
50
0
PPM


7.541
7.537
7.522
7.517
7.391
7.387
7.384
7.373
7.372
7.364
7.360
7.356
7.351
7.333
7.321
7.317
7.311
0.000
zdj-2-080-1
2021-06-21 09:07:01.445
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
5.90
4.00
Ph
Ph
2n'
10
8
6
4
2
0 PPM

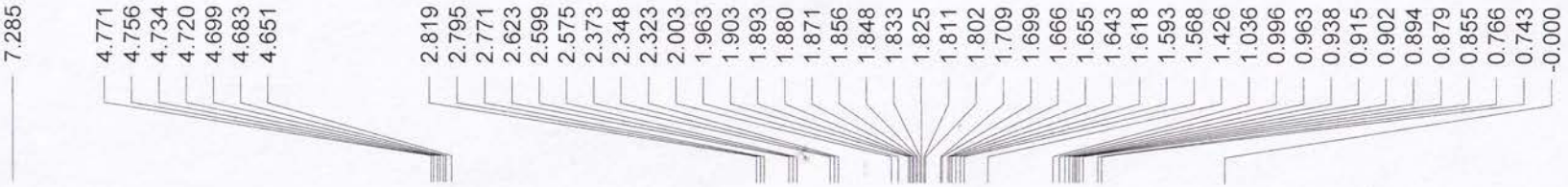

132.471
129.194
128.417
121.718
81.514
77.316
77.000
76.684
73.858
zdj-2-080-1
2021-06-21 09:31:42.694
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
Ph
Ph
2n'
200
150
100
50
0 PPM


7.470
7.442
7.277
6.927
6.898
4.787
3.848
2.474
2.448
2.424
1.745
1.720
1.695
1.670
1.645
1.622
1.010
0.985
0.961
-0.000
zdj-1-088
2020-12-12 14:02:38.671
NA = 10
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
MeO
C3H7-n
O
O
2.01
2.05
2.00
3.05
2.01
2.10
3.06
10
8
6
4
2
PPM

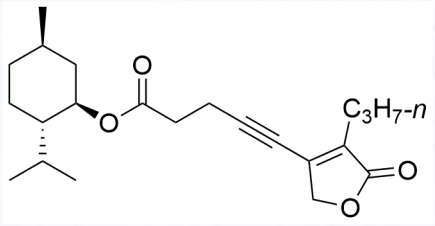
3ao


174.047
160.774
139.936
134.440
133.419
114.162
113.151
105.283
78.618
77.423
77.000
76.577
70.851
55.225
26.859
20.755
13.751
zdj-1-088
2020-12-11 15:32:36.015
NA = 239
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
MeO
C3H7-n
O
O
250
200
150
100
50
PPM

3ao

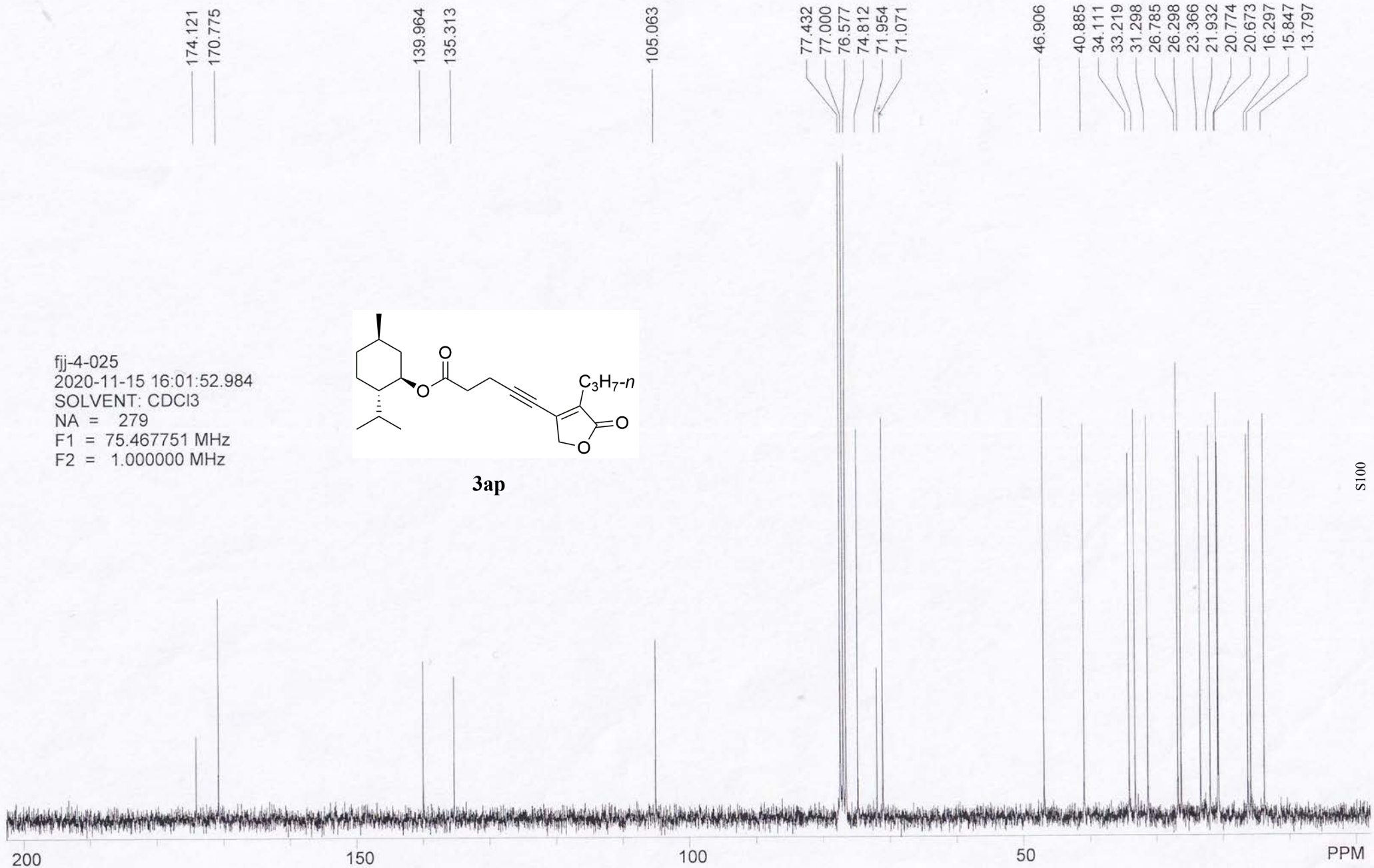


fjj-4-025
2020-11-15 15:43:50.921
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz

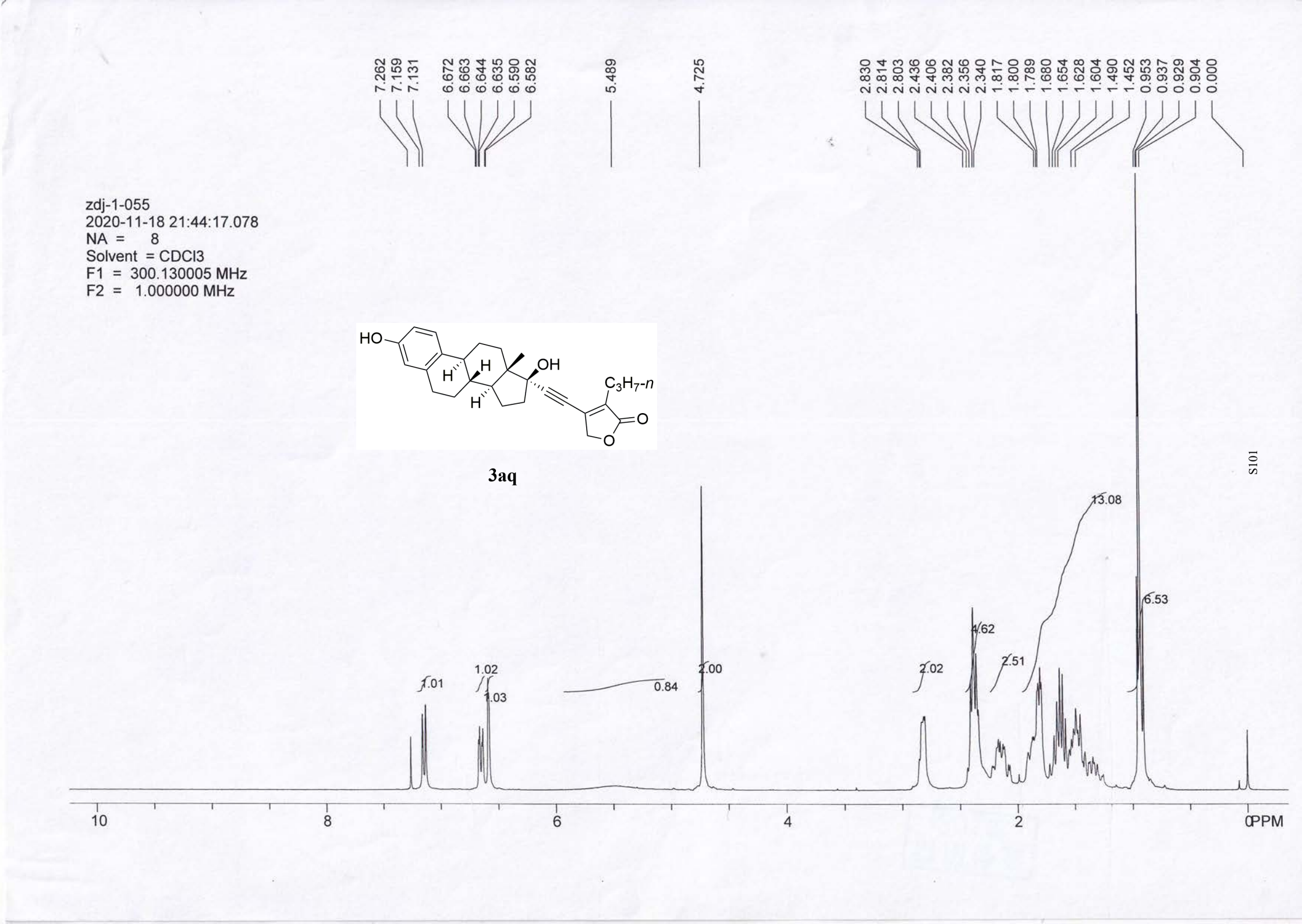


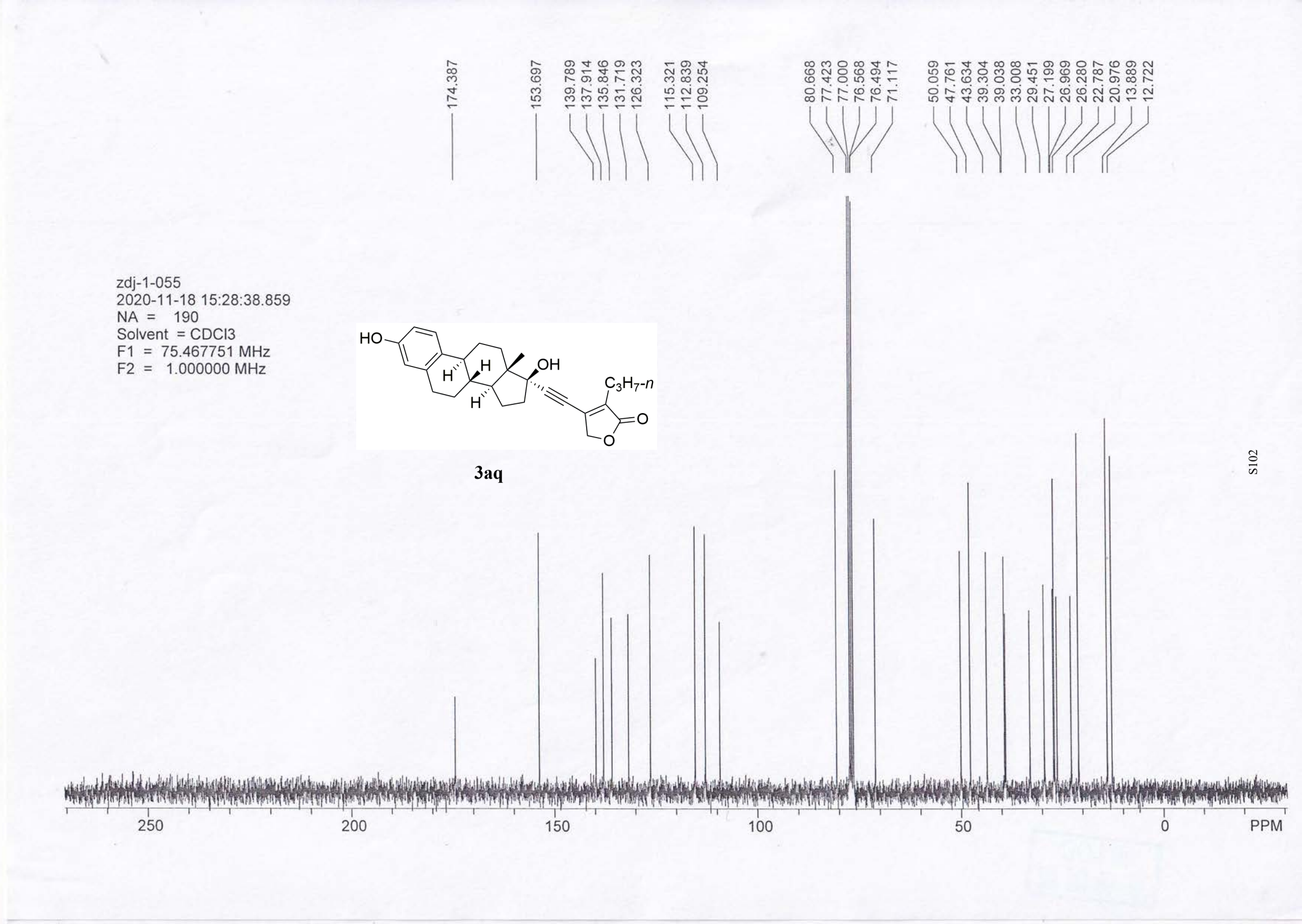
3ap

S99

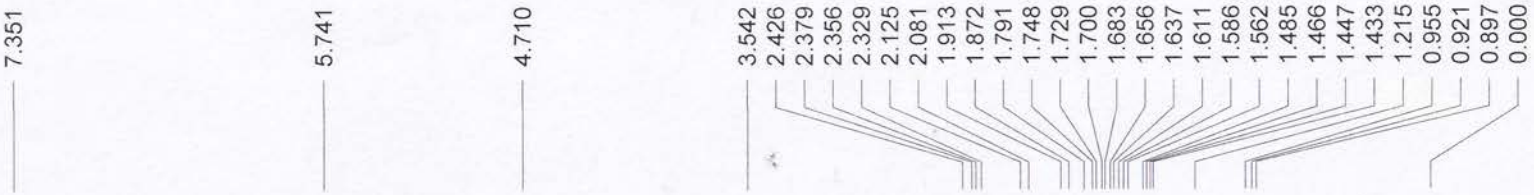

174.121
170.775
139.964
135.313
105.063
77.432
77.000
76.577
74.812
71.954
71.071
46.906
40.885
34.111
33.219
31.298
26.785
26.298
23.366
21.932
20.774
20.673
16.297
15.847
13.797
fjj-4-025
2020-11-15 16:01:52.984
SOLVENT: CDCl3
NA = 279
F1 = 75.467751 MHz
F2 = 1.000000 MHz
O
O
O
O
C_3H_7-*n*
200
150
100
50
PPM

3ap

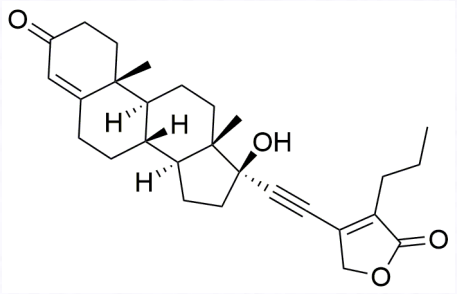

7.262
7.159
7.131
6.672
6.663
6.644
6.635
6.590
6.582
5.489
4.725
2.830
2.814
2.803
2.436
2.406
2.382
2.356
2.340
1.817
1.800
1.789
1.680
1.654
1.628
1.604
1.490
1.452
0.953
0.937
0.929
0.904
0.000
zdj-1-055
2020-11-18 21:44:17.078
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
HO
H
H
H
OH
C3H7-n
O
O
3aq
S101
1.01
1.02
1.03
0.84
2.00
2.02
4.62
2.51
13.08
6.53
10
8
6
4
2
0
PPM


174.387
153.697
139.789
137.914
135.846
131.719
126.323
115.321
112.839
109.254
80.668
77.423
77.000
76.568
76.494
71.117
50.059
47.761
43.634
39.304
39.038
33.008
29.451
27.199
26.969
26.280
22.787
20.976
13.889
12.722
zdj-1-055
2020-11-18 15:28:38.859
NA = 190
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
HO
H
H
H
OH
C3H7-n
O
O
250
200
150
100
50
0
PPM

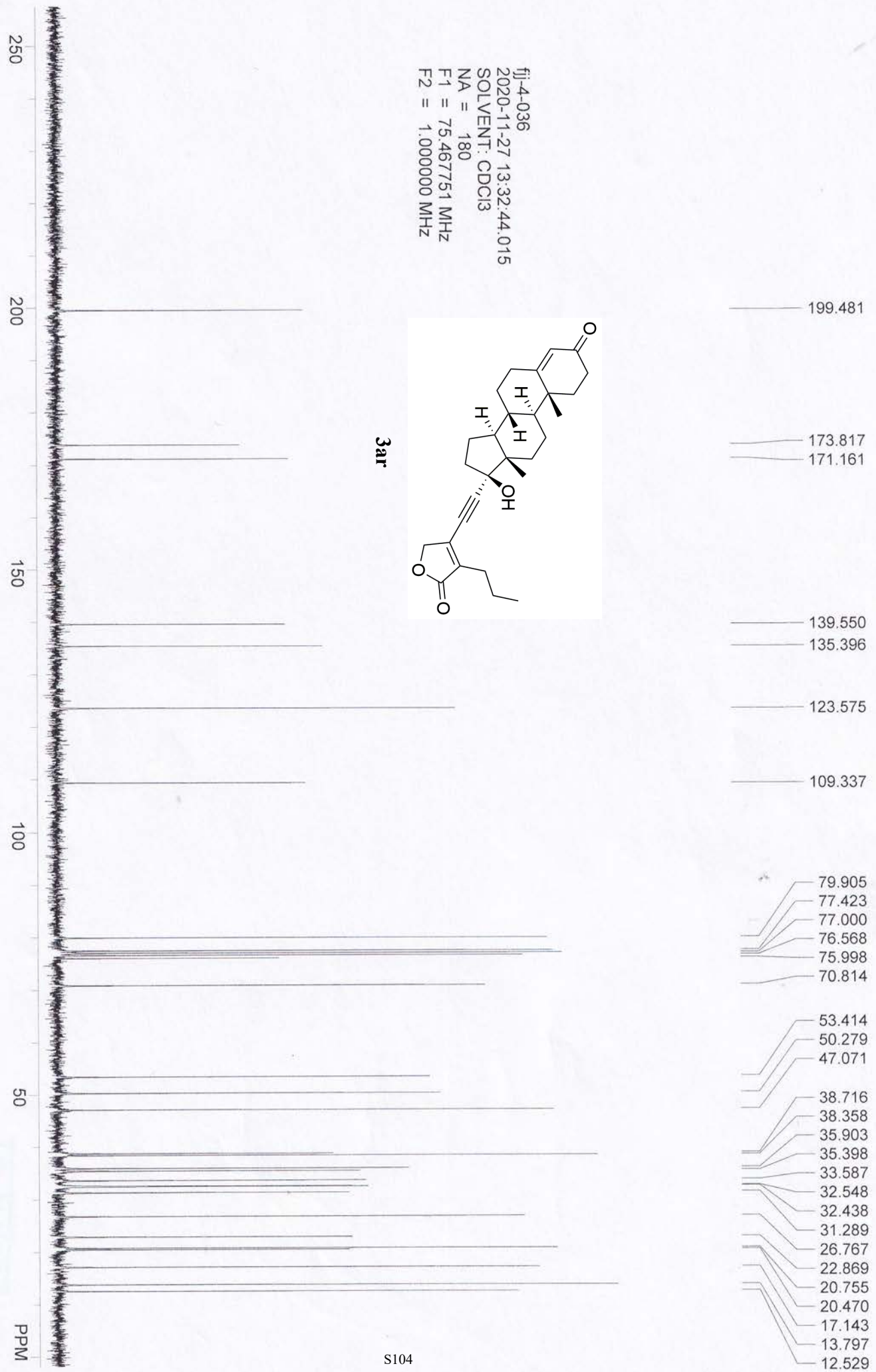
3aq

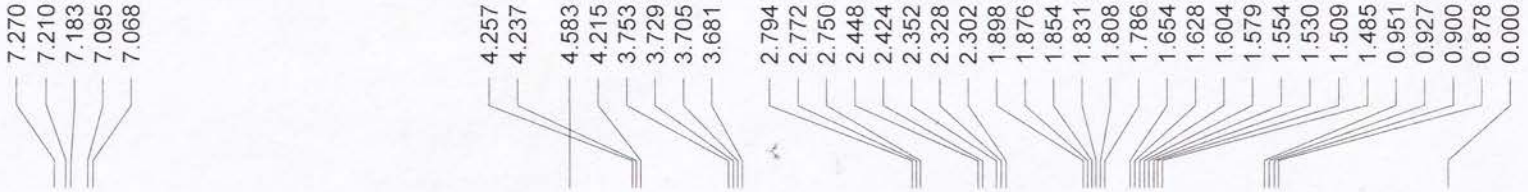


fjj-4-036
2020-11-27 13:21:01.296
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz

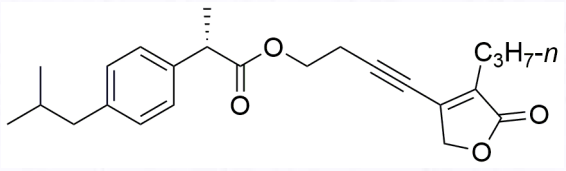


3ar

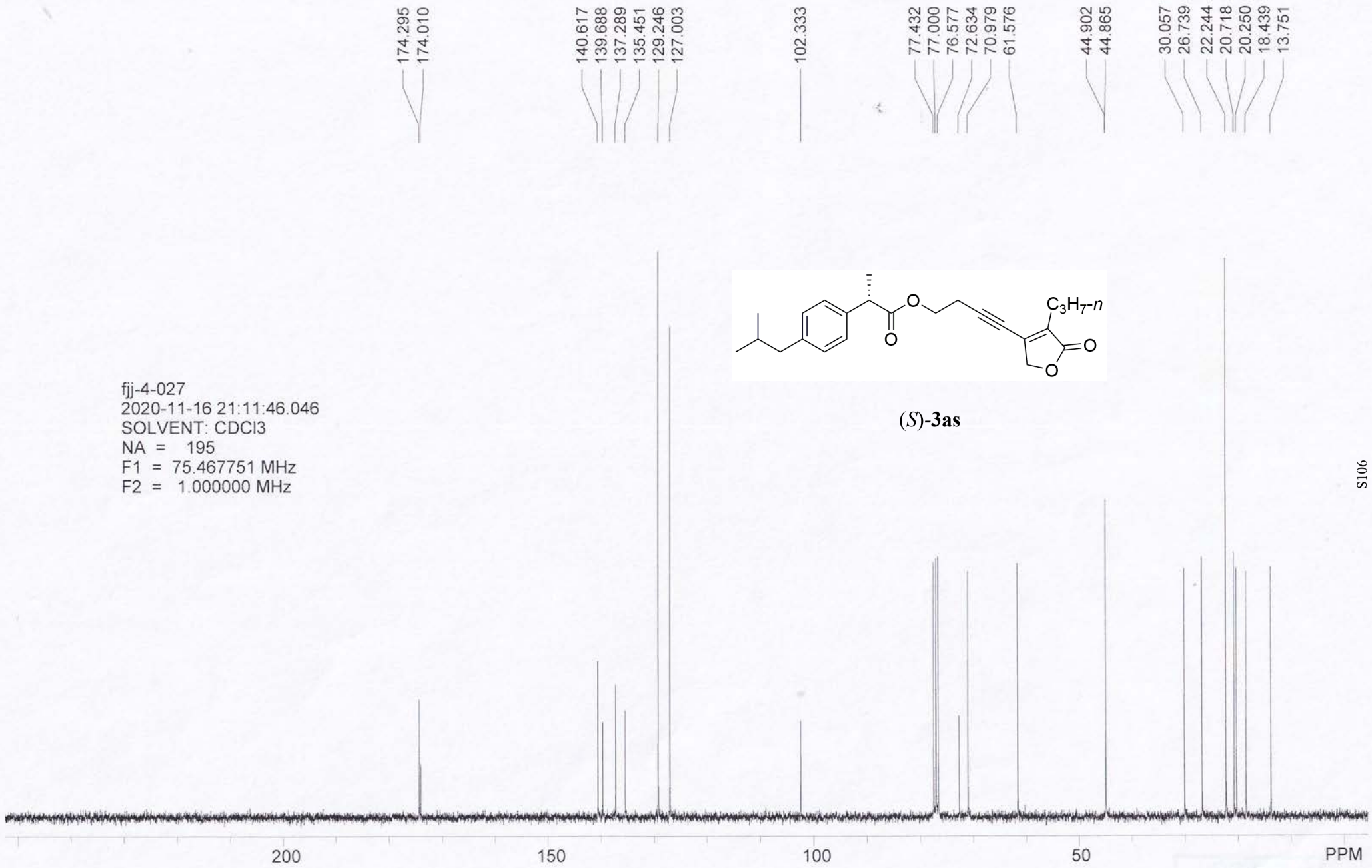

fjj-4-036
2020-11-27 13:32:44.015
SOLVENT: CDCl3
NA = 180
F1 = 75.467751 MHz
F2 = 1.000000 MHz
3ar
199.481
173.817
171.161
139.550
135.396
123.575
109.337
79.905
77.423
77.000
76.568
75.998
70.814
53.414
50.279
47.071
38.716
38.358
35.903
35.398
33.587
32.548
32.438
31.289
26.767
22.869
20.755
20.470
17.143
13.797
12.529
250
200
150
100
50
PPM



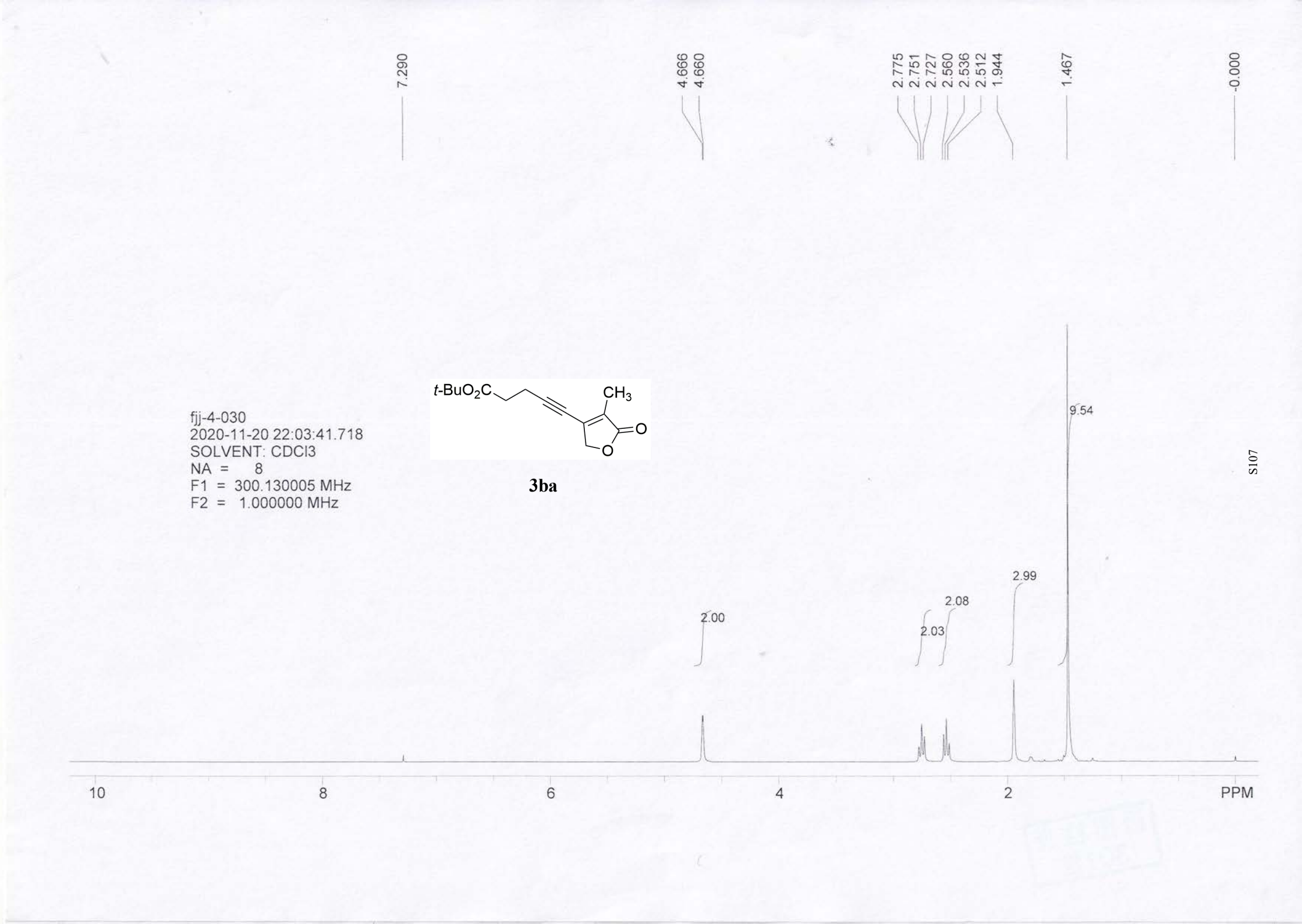
fjj-4-027
2020-11-16 21:38:40.609
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz

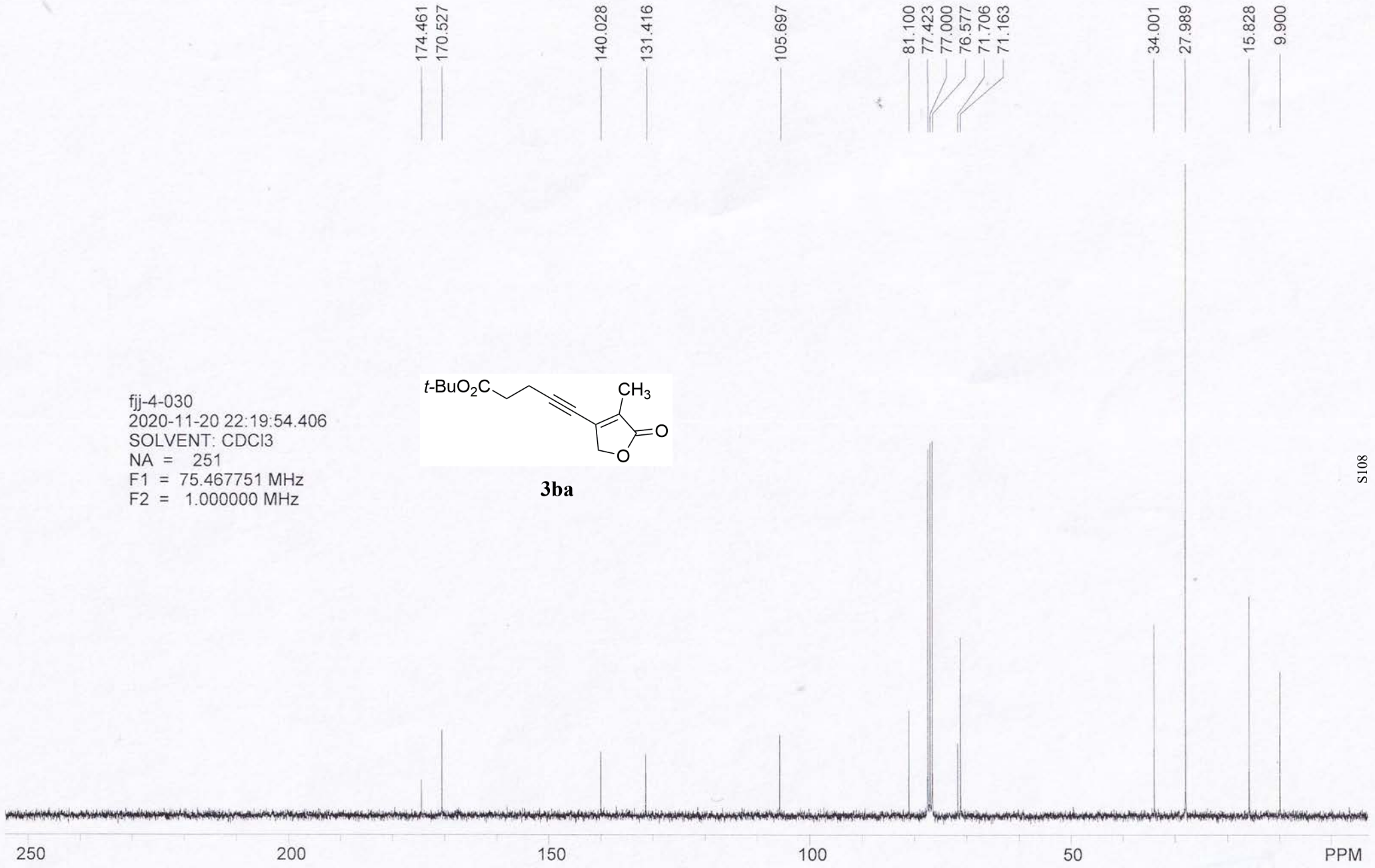


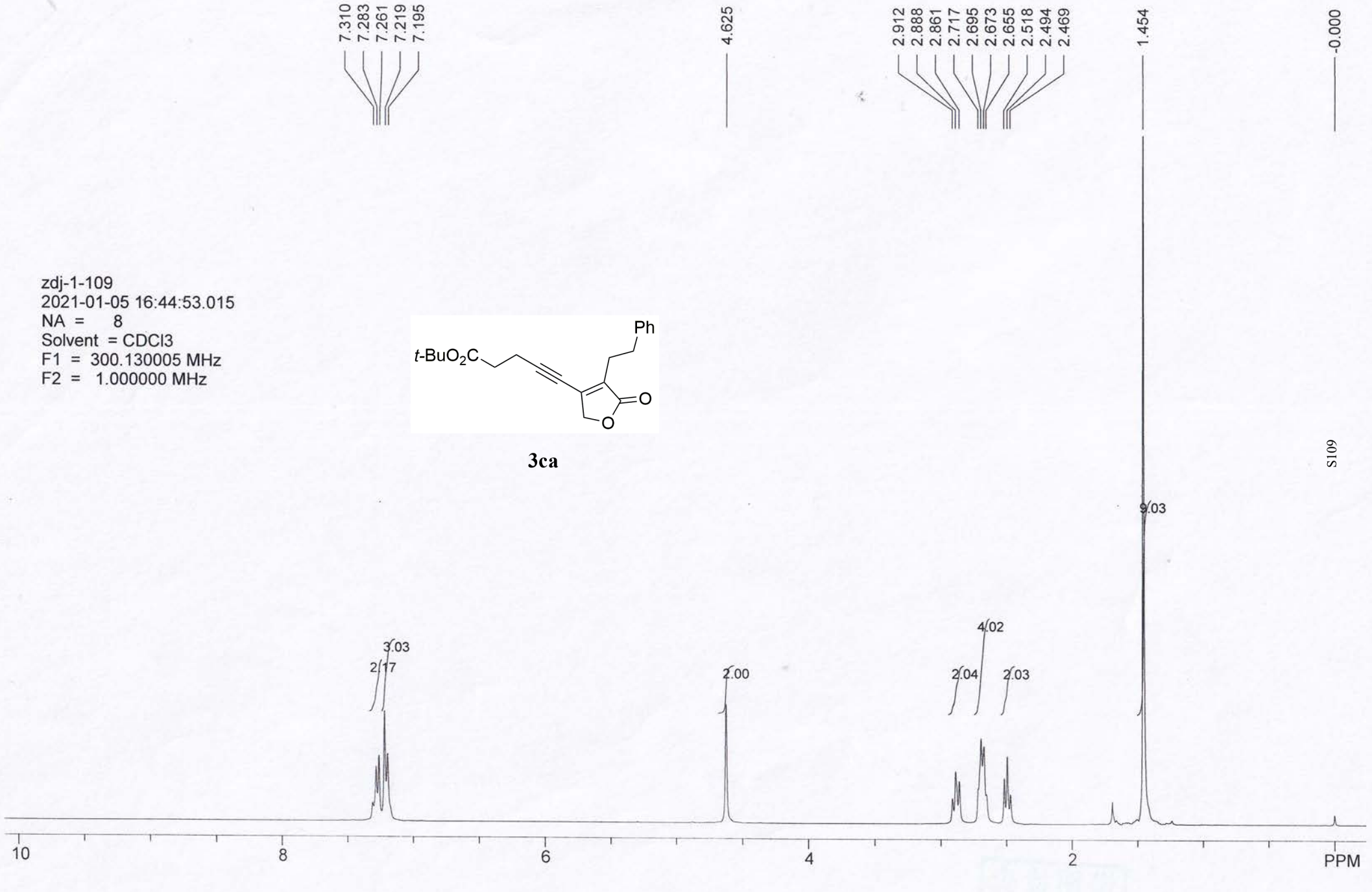
(*S*)-**3as**

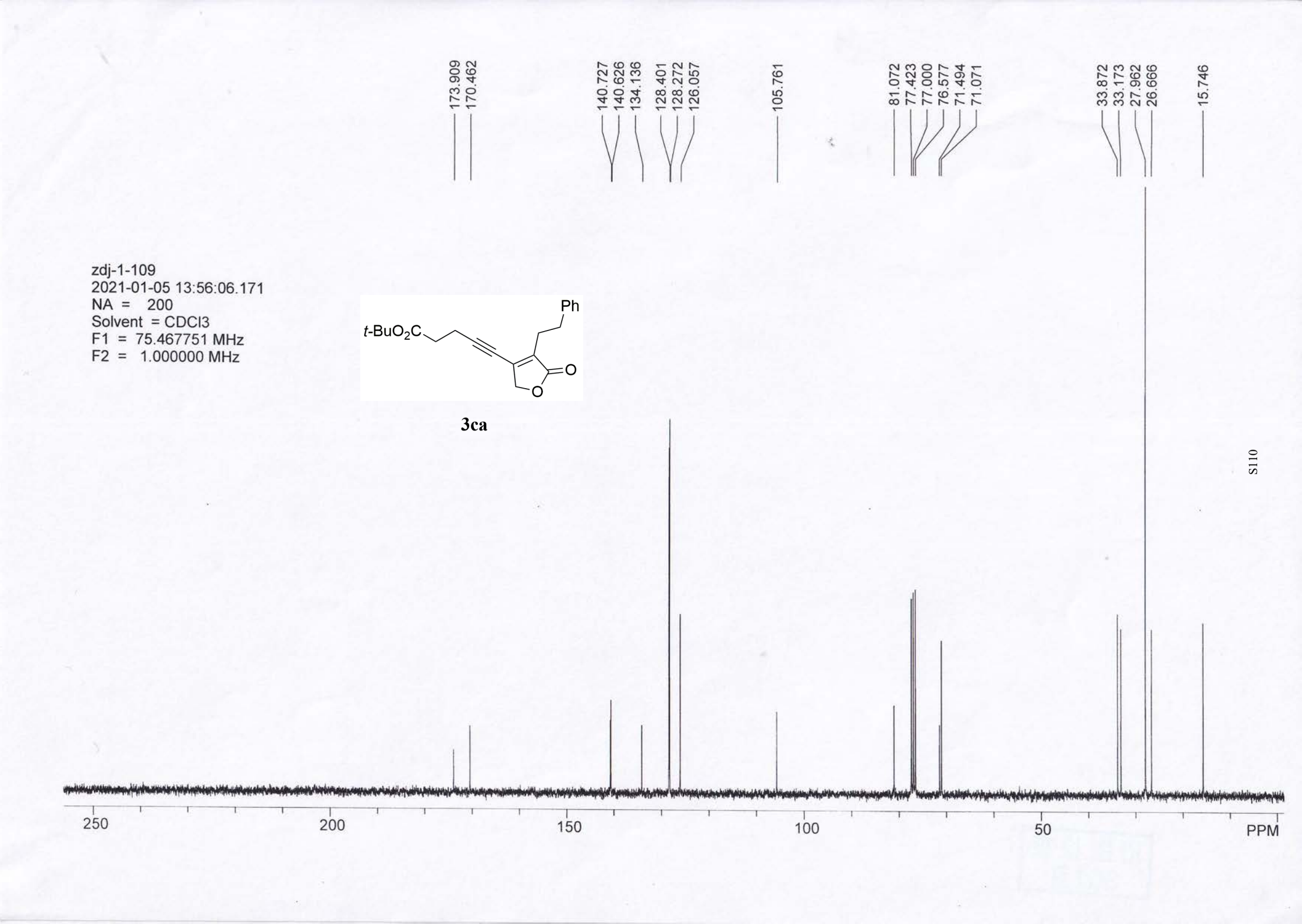

174.295
174.010
140.617
139.688
137.289
135.451
129.246
127.003
102.333
77.432
77.000
76.577
72.634
70.979
61.576
44.902
44.865
30.057
26.739
22.244
20.718
20.250
18.439
13.751
C3H7-n
O
O
O
O
fjj-4-027
2020-11-16 21:11:46.046
SOLVENT: CDCl3
NA = 195
F1 = 75.467751 MHz
F2 = 1.000000 MHz
200
150
100
50
PPM

(*S*)-**3as**

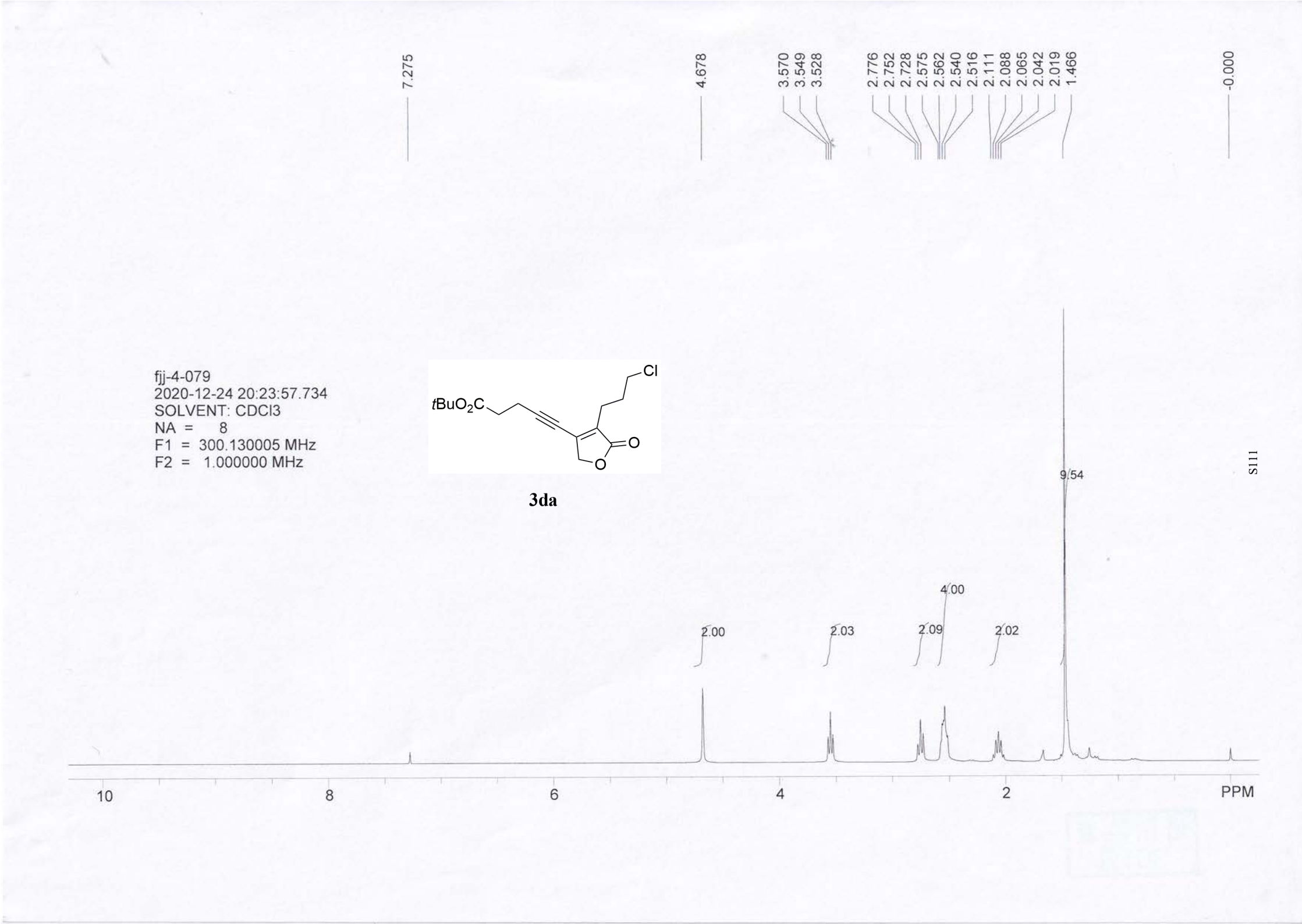

7.290
4.666
4.660
2.775
2.751
2.727
2.560
2.536
2.512
1.944
1.467
-0.000
fjj-4-030
2020-11-20 22:03:41.718
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
t-BuO2C
CH3
O
O
3ba
9.54
2.99
2.08
2.03
2.00
10
8
6
4
2
PPM

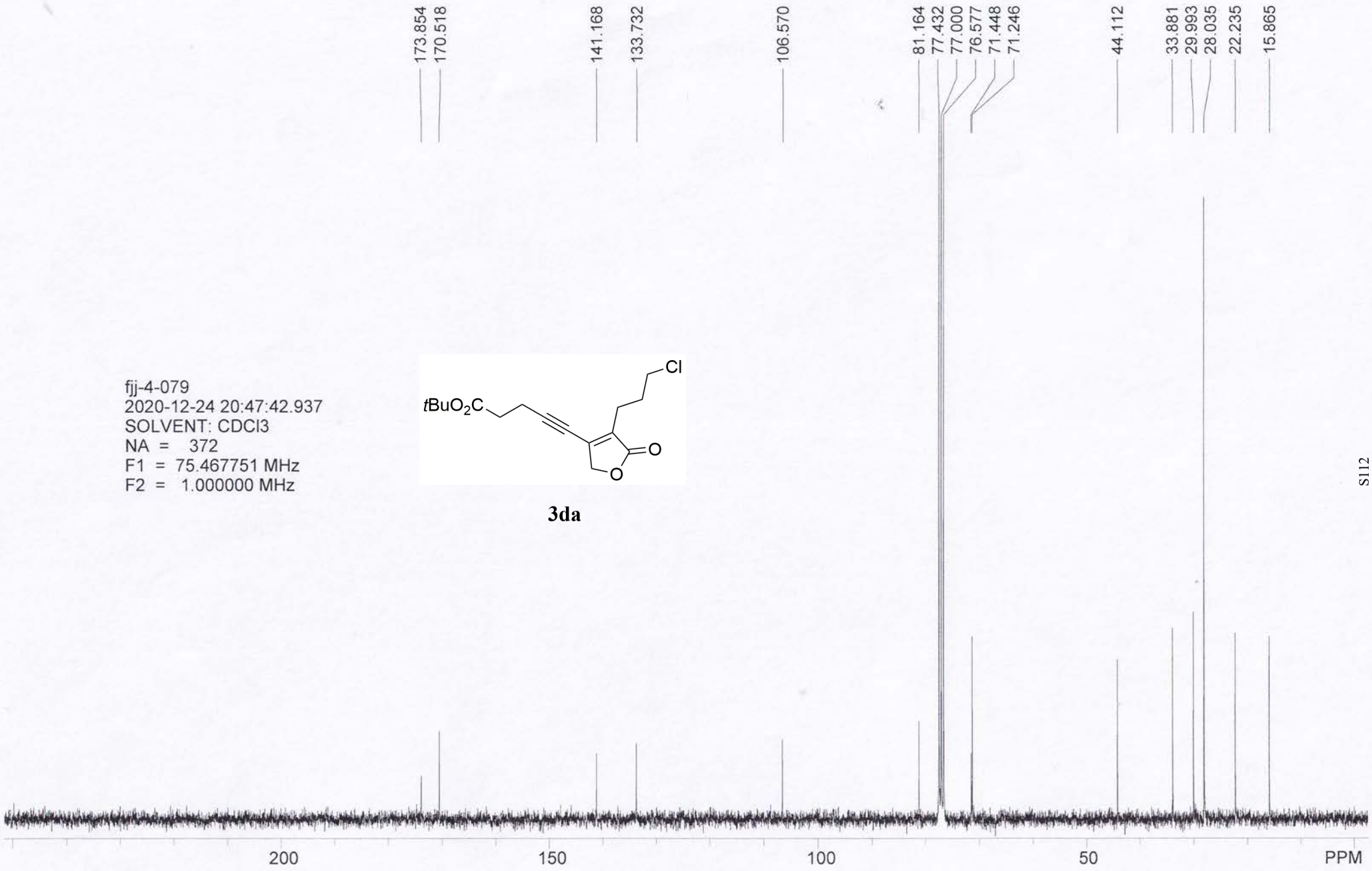

174.461
170.527
140.028
131.416
105.697
81.100
77.423
77.000
76.577
71.706
71.163
34.001
27.989
15.828
9.900
fjj-4-030
2020-11-20 22:19:54.406
SOLVENT: CDCl3
NA = 251
F1 = 75.467751 MHz
F2 = 1.000000 MHz
t-BuO2C
CH3
O
O
3ba
250
200
150
100
50
PPM


7.310
7.283
7.261
7.219
7.195
4.625
2.912
2.888
2.861
2.717
2.695
2.673
2.655
2.518
2.494
2.469
1.454
-0.000
zdj-1-109
2021-01-05 16:44:53.015
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Ph
t-BuO2C
O
O
3ca
S109
9.03
4.02
3.03
2.17
2.00
2.04
2.03
10
8
6
4
2
PPM

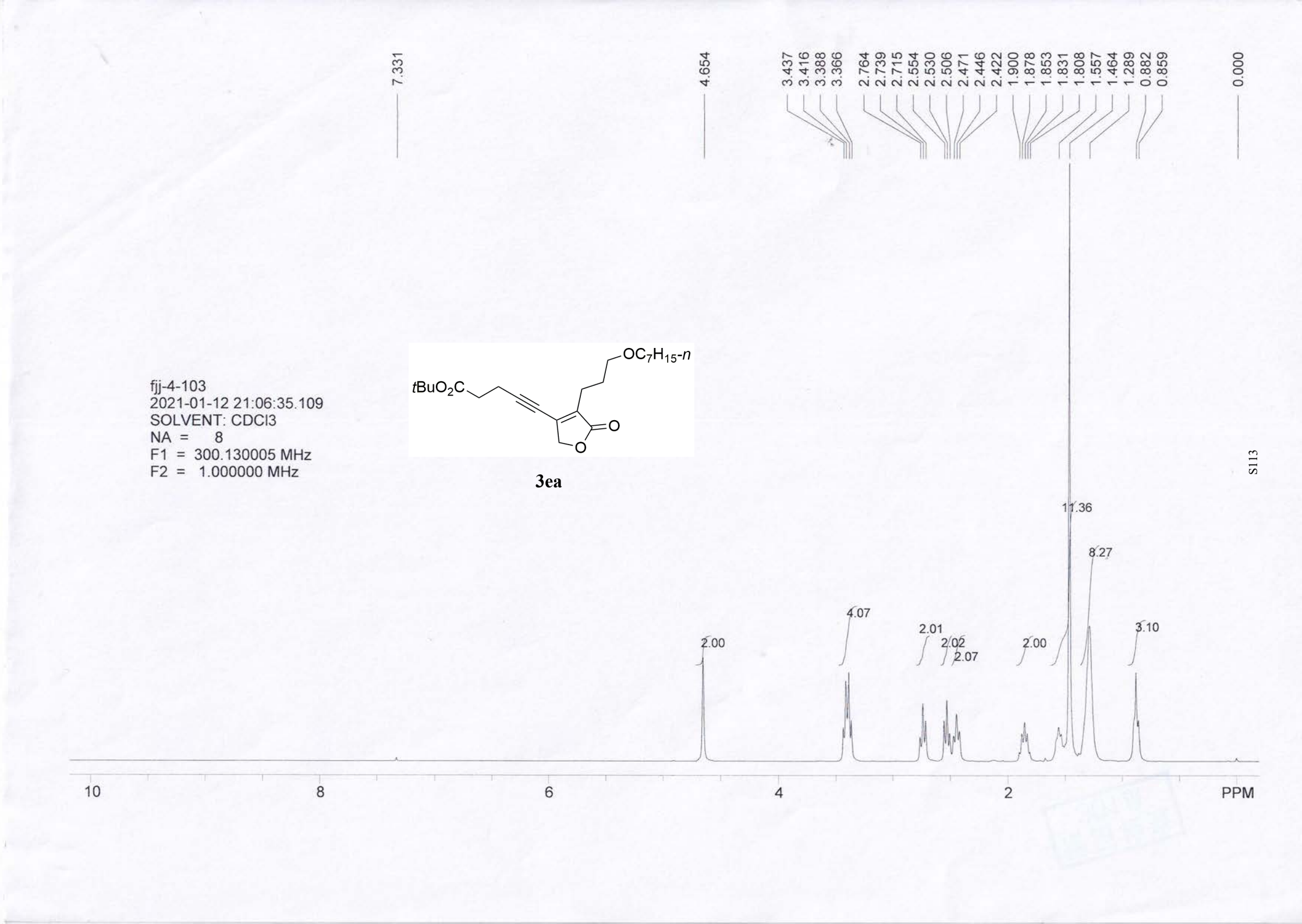

173.909
170.462
140.727
140.626
134.136
128.401
128.272
126.057
105.761
81.072
77.423
77.000
76.577
71.494
71.071
33.872
33.173
27.962
26.666
15.746
zdj-1-109
2021-01-05 13:56:06.171
NA = 200
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
t-BuO2C
Ph
O
O
250
200
150
100
50
PPM

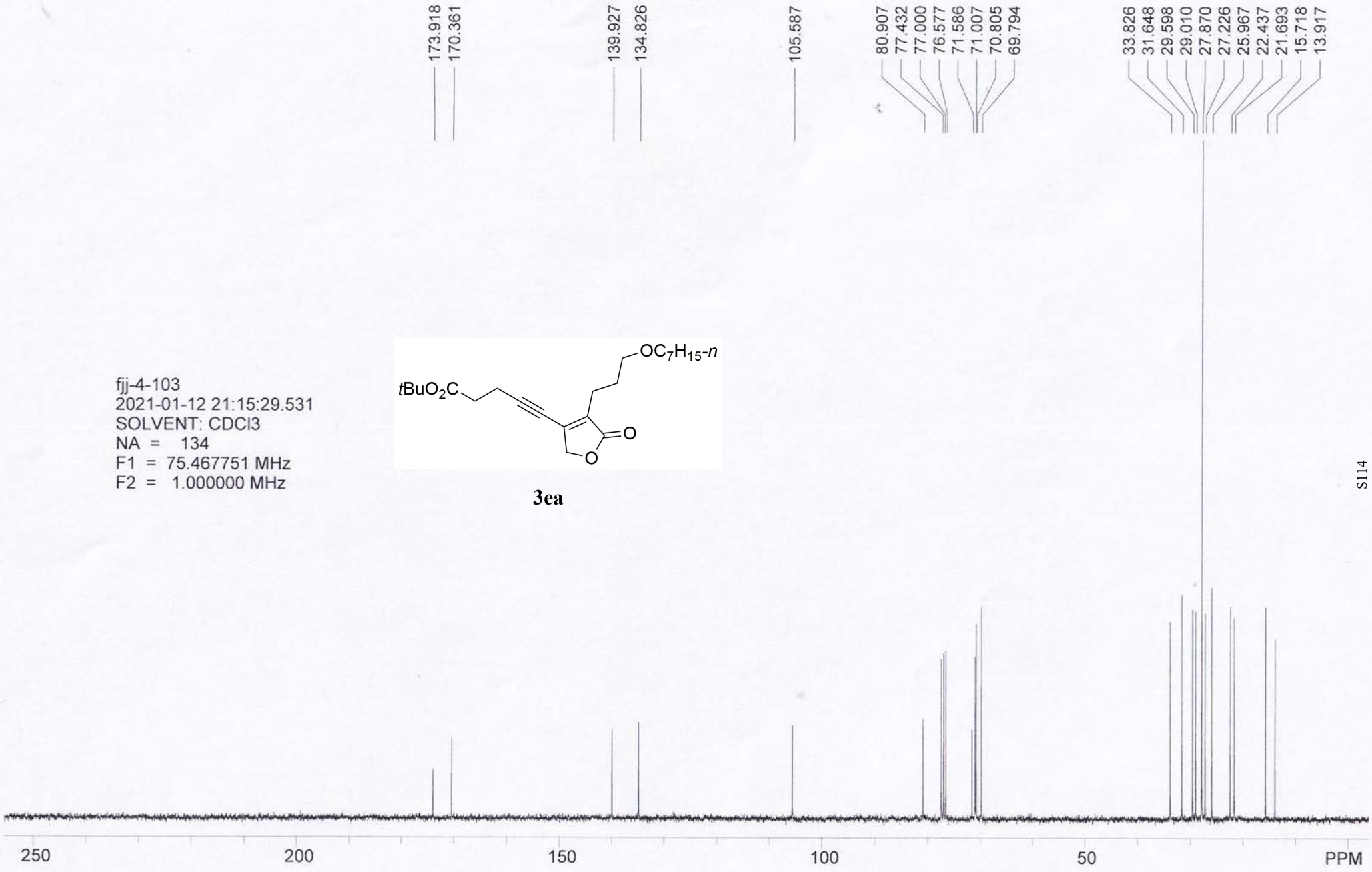
3ca


7.275
4.678
3.570
3.549
3.528
2.776
2.752
2.728
2.575
2.562
2.540
2.516
2.111
2.088
2.065
2.042
2.019
1.466
-0.000
fjj-4-079
2020-12-24 20:23:57.734
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
tBuO2C
Cl
O
O
3da
S111
9.54
4.00
2.00
2.03
2.09
2.02
10
8
6
4
2
PPM

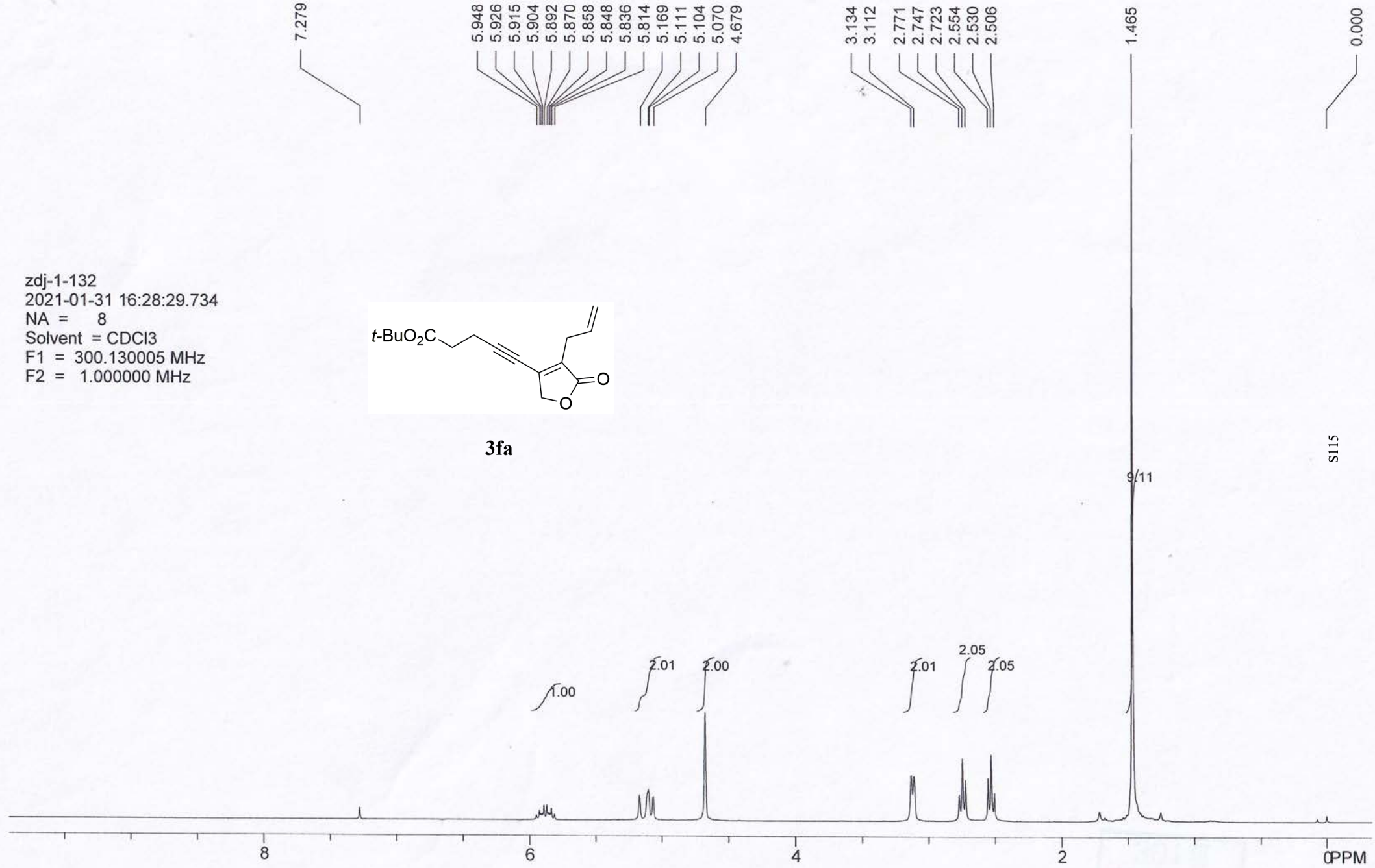

173.854
170.518
141.168
133.732
106.570
81.164
77.432
77.000
76.577
71.448
71.246
44.112
33.881
29.993
28.035
22.235
15.865
fjj-4-079
2020-12-24 20:47:42.937
SOLVENT: CDCl3
NA = 372
F1 = 75.467751 MHz
F2 = 1.000000 MHz
tBuO2C
Cl
O
O
200
150
100
50
PPM

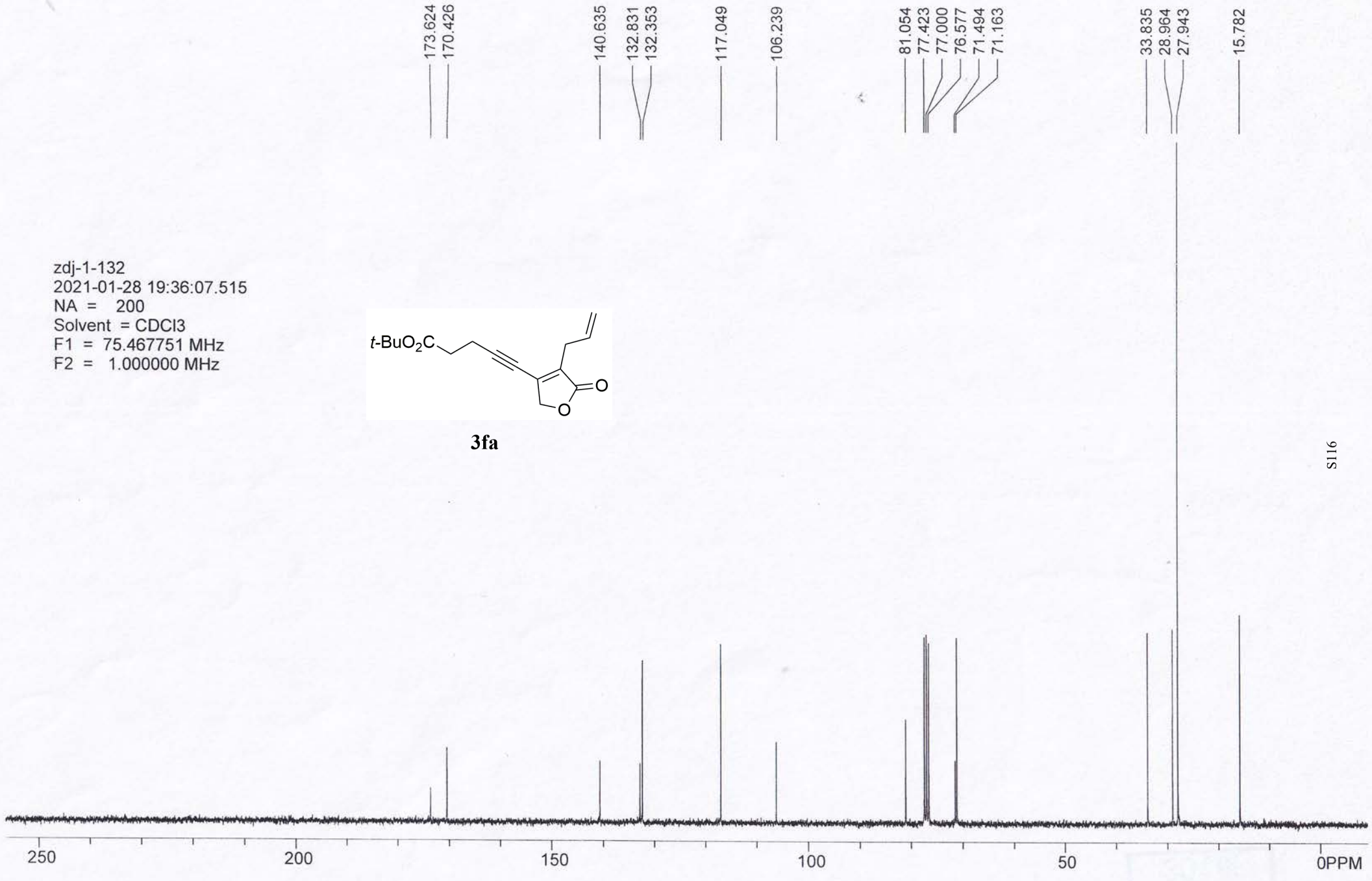
3da


7.331
4.654
3.437
3.416
3.388
3.366
2.764
2.739
2.715
2.554
2.530
2.506
2.471
2.446
2.422
1.900
1.878
1.853
1.831
1.808
1.557
1.464
1.289
0.882
0.859
0.000
fjj-4-103
2021-01-12 21:06:35.109
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
tBuO2C
OC7H15-n
O
O
3ea
S113
2.00
4.07
2.01
2.02
2.07
2.00
11.36
8.27
3.10
10
8
6
4
2
PPM

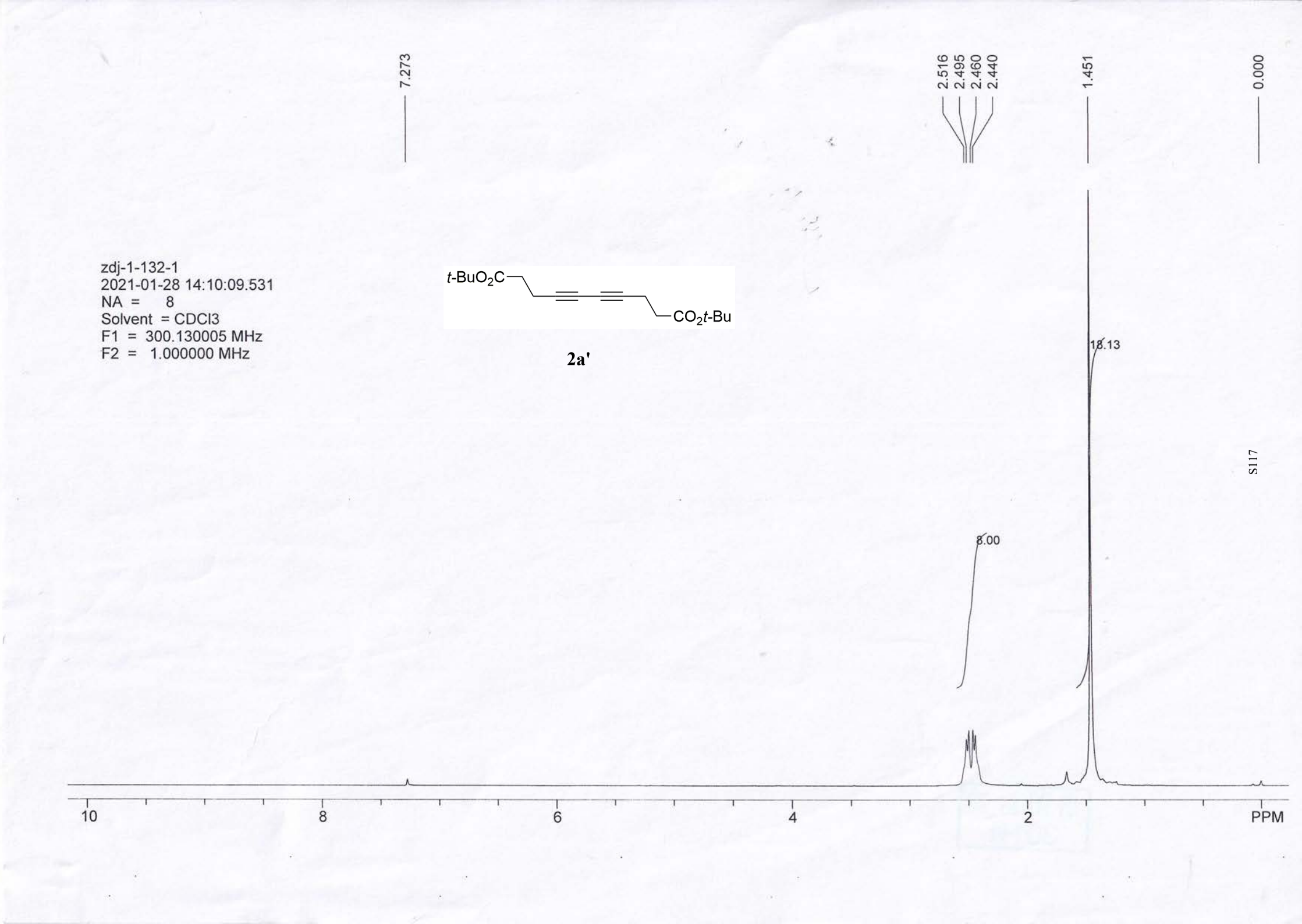

173.918
170.361
139.927
134.826
105.587
80.907
77.432
77.000
76.577
71.586
71.007
70.805
69.794
33.826
31.648
29.598
29.010
27.870
27.226
25.967
22.437
21.693
15.718
13.917
fjj-4-103
2021-01-12 21:15:29.531
SOLVENT: CDCl3
NA = 134
F1 = 75.467751 MHz
F2 = 1.000000 MHz
tBuO2C
OC7H15-n
O
O
250
200
150
100
50
PPM

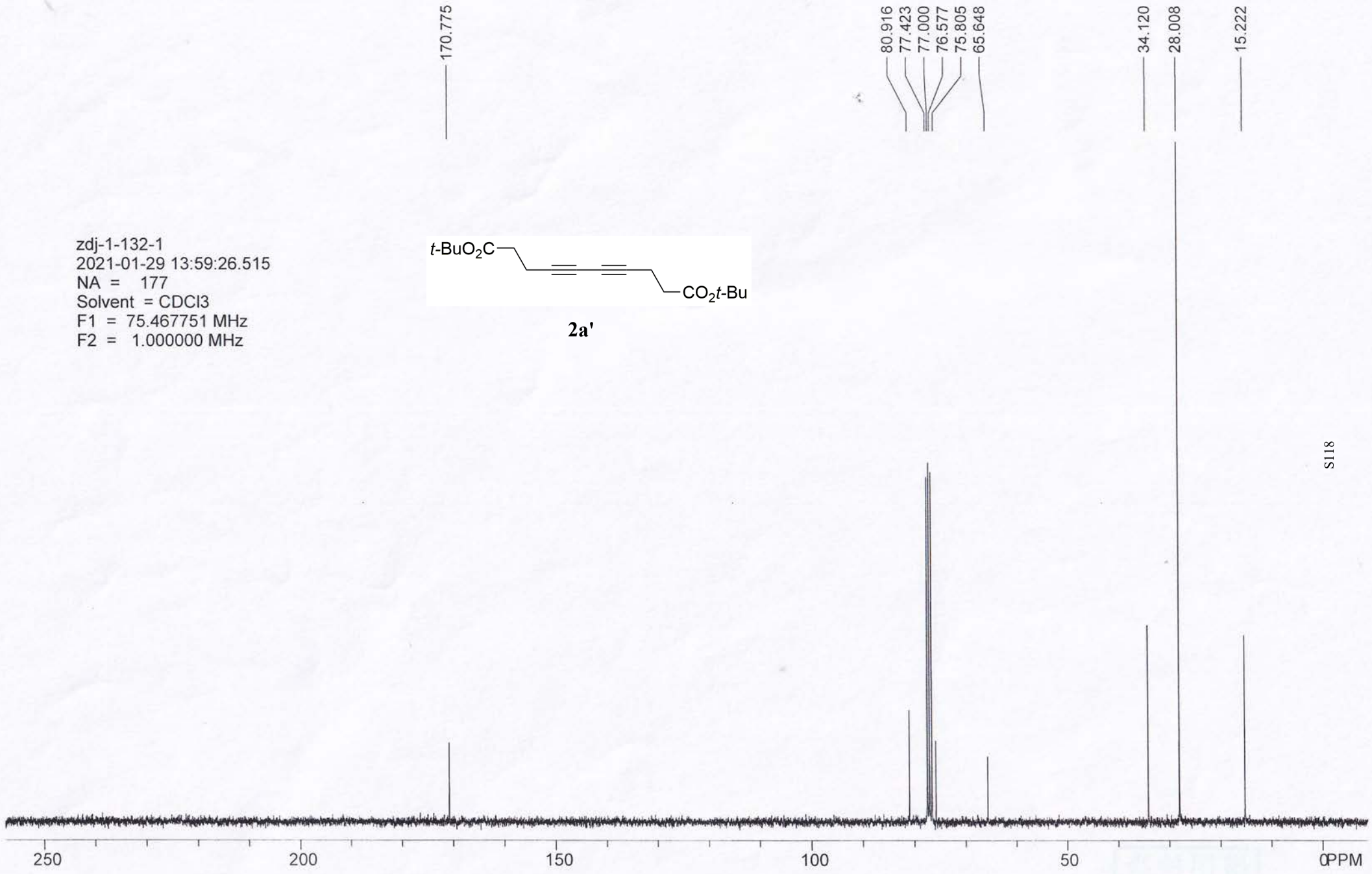
3ea

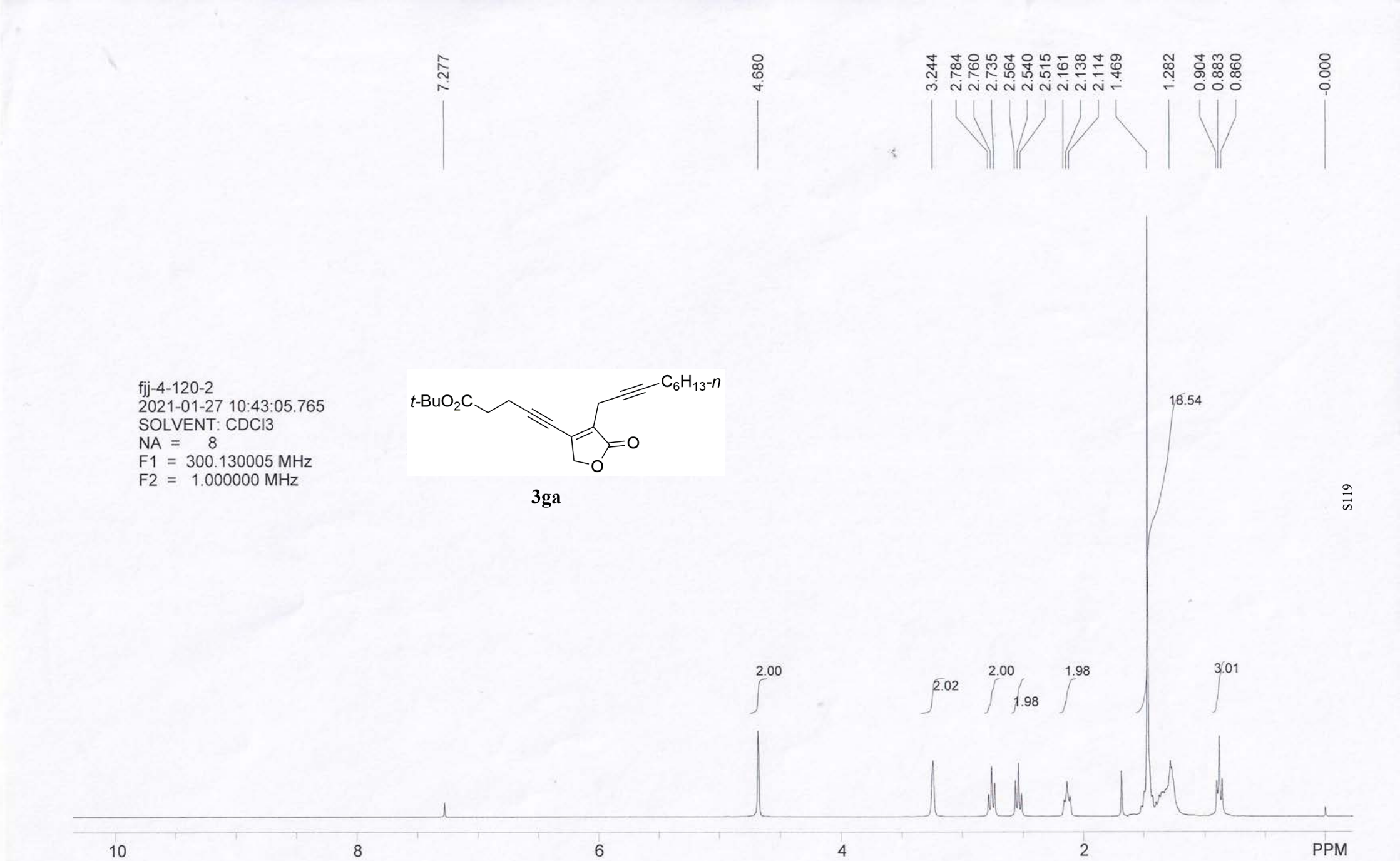

7.279
5.948
5.926
5.915
5.904
5.892
5.870
5.858
5.848
5.836
5.814
5.169
5.111
5.104
5.070
4.679
3.134
3.112
2.771
2.747
2.723
2.554
2.530
2.506
1.465
0.000
zdj-1-132
2021-01-31 16:28:29.734
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
t-BuO2C
O
O
3fa
S115
9.11
1.00
2.01
2.00
2.01
2.05
2.05
8
6
4
2
0PPM

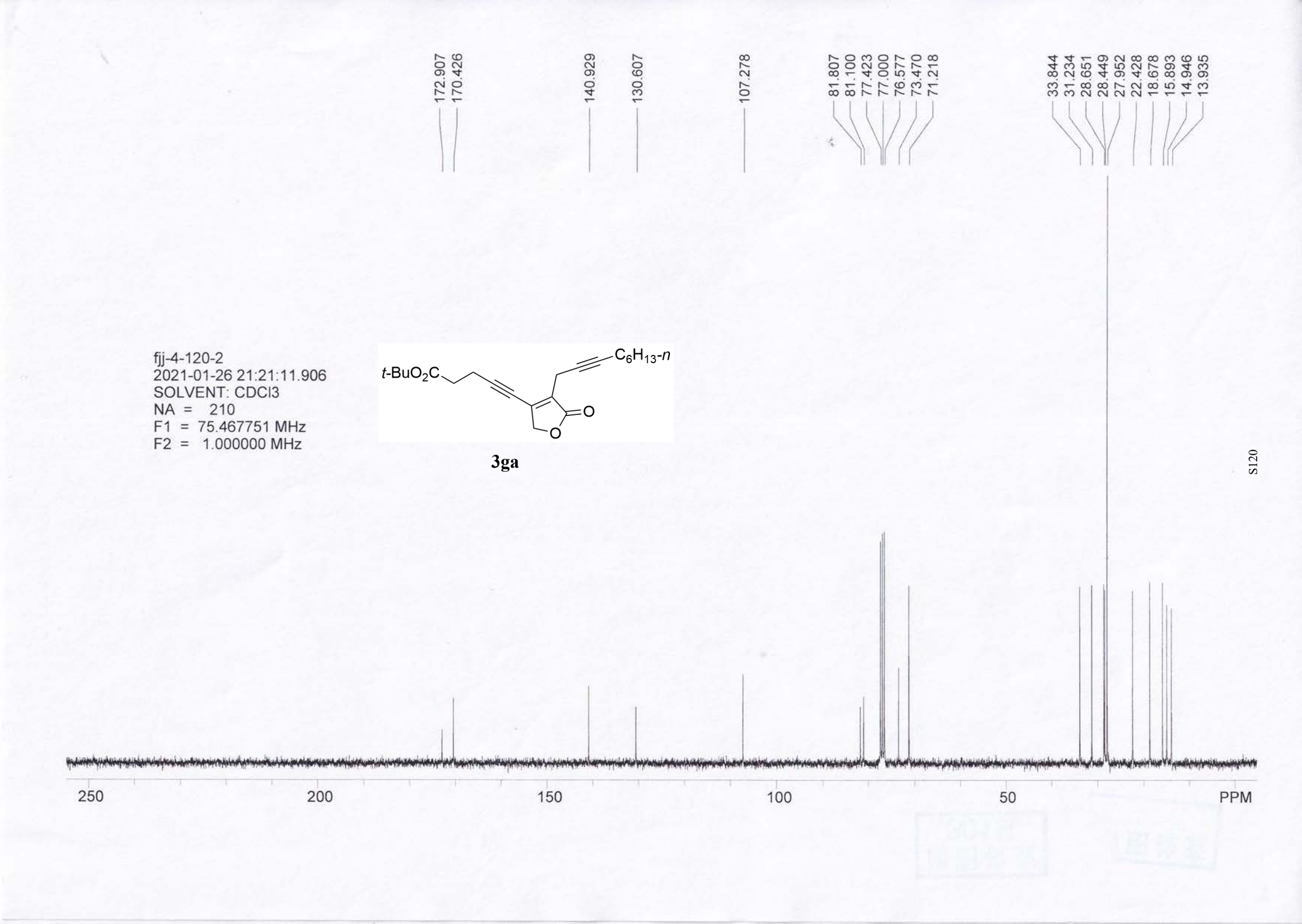

173.624
170.426
140.635
132.831
132.353
117.049
106.239
81.054
77.423
77.000
76.577
71.494
71.163
33.835
28.964
27.943
15.782
zdj-1-132
2021-01-28 19:36:07.515
NA = 200
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
t-BuO2C
O
O
250
200
150
100
50
0PPM

3fa

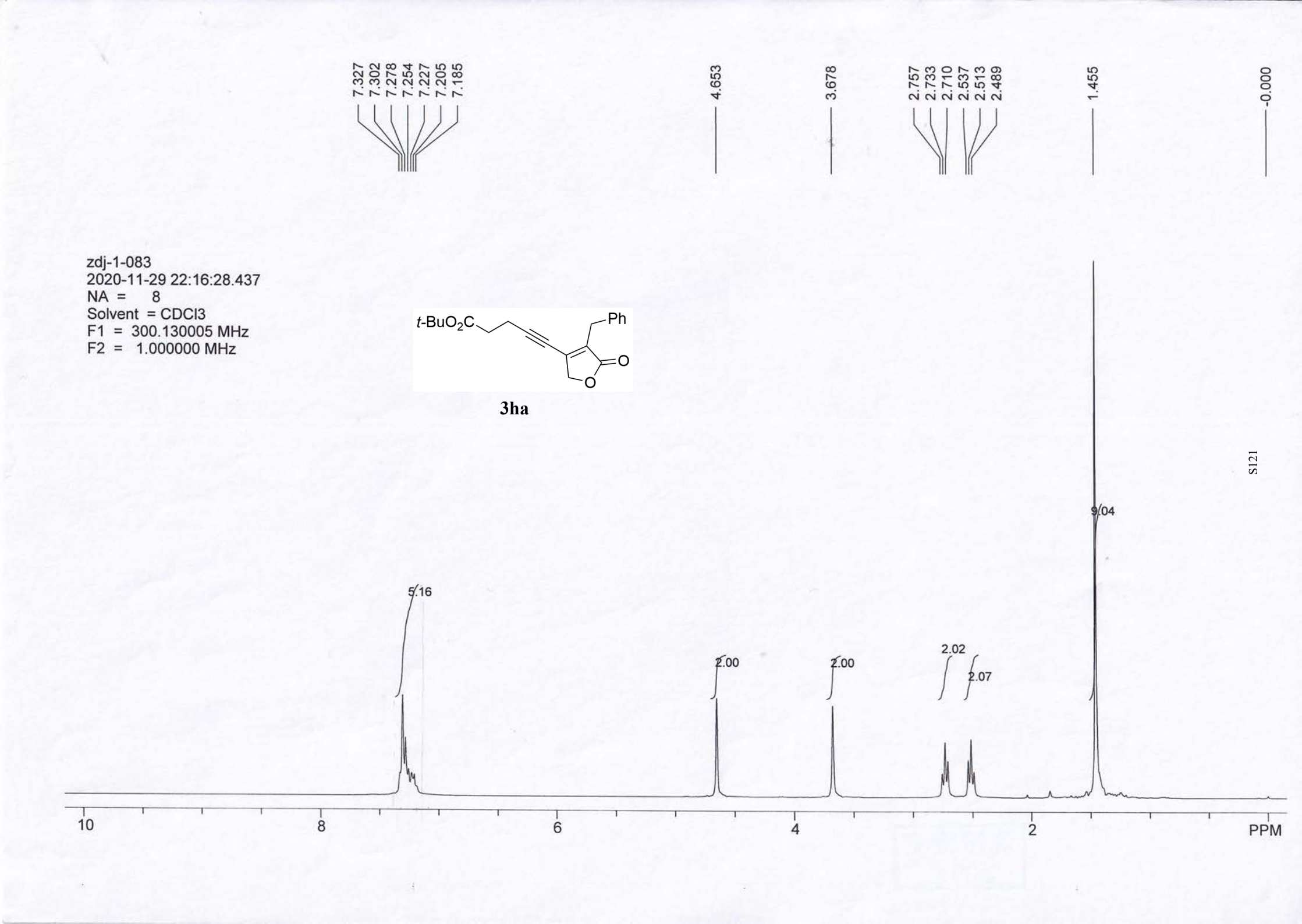

7.273
2.516
2.495
2.460
2.440
1.451
0.000
zdj-1-132-1
2021-01-28 14:10:09.531
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
t-BuO2C
CO2t-Bu
2a'
18.13
8.00
S117
10
8
6
4
2
PPM

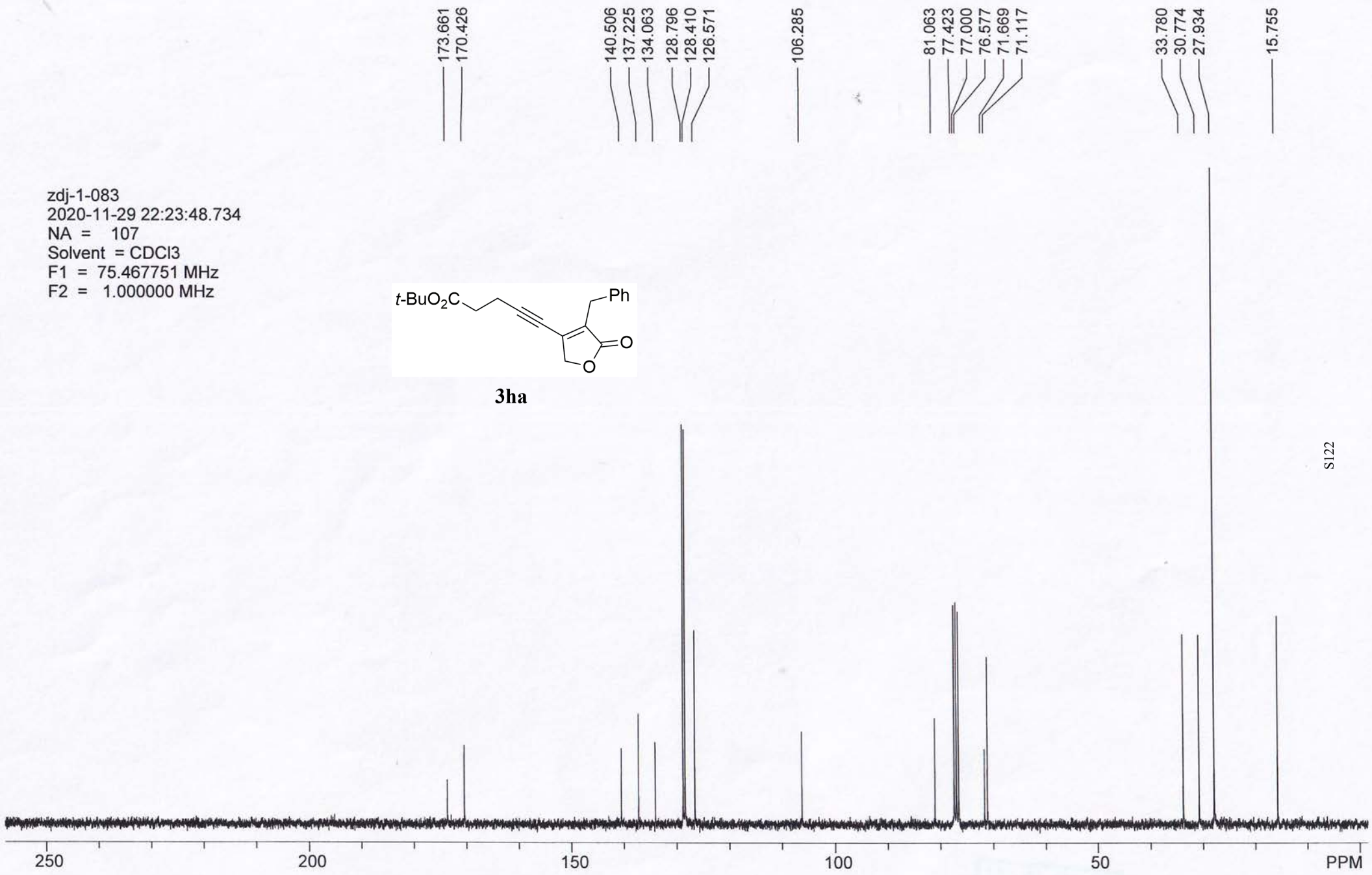

170.775
80.916
77.423
77.000
76.577
75.805
65.648
34.120
28.008
15.222
zdj-1-132-1
2021-01-29 13:59:26.515
NA = 177
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
t-BuO2C
CO2t-Bu
2a'
250
200
150
100
50
0PPM


7.277
4.680
3.244
2.784
2.760
2.735
2.564
2.540
2.515
2.161
2.138
2.114
1.469
1.282
0.904
0.883
0.860
-0.000
fjj-4-120-2
2021-01-27 10:43:05.765
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
t-BuO2C
C6H13-n
O
O
3ga
18.54
2.00
2.02
2.00
1.98
1.98
3.01
10
8
6
4
2
PPM

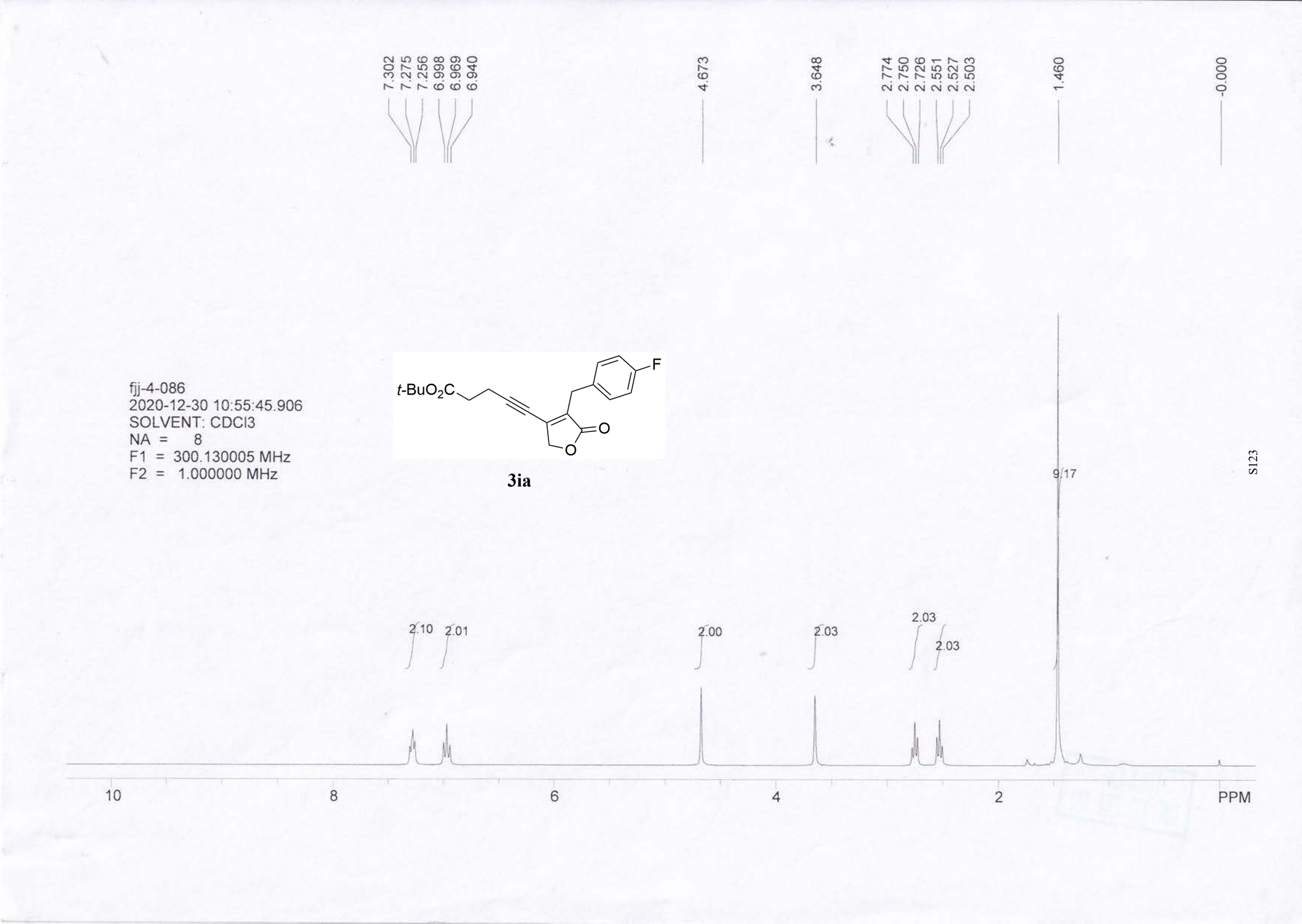

172.907
170.426
140.929
130.607
107.278
81.807
81.100
77.423
77.000
76.577
73.470
71.218
33.844
31.234
28.651
28.449
27.952
22.428
18.678
15.893
14.946
13.935
fjj-4-120-2
2021-01-26 21:21:11.906
SOLVENT: CDCl3
NA = 210
F1 = 75.467751 MHz
F2 = 1.000000 MHz
t-BuO2C
C6H13-n
O
O
250
200
150
100
50
PPM

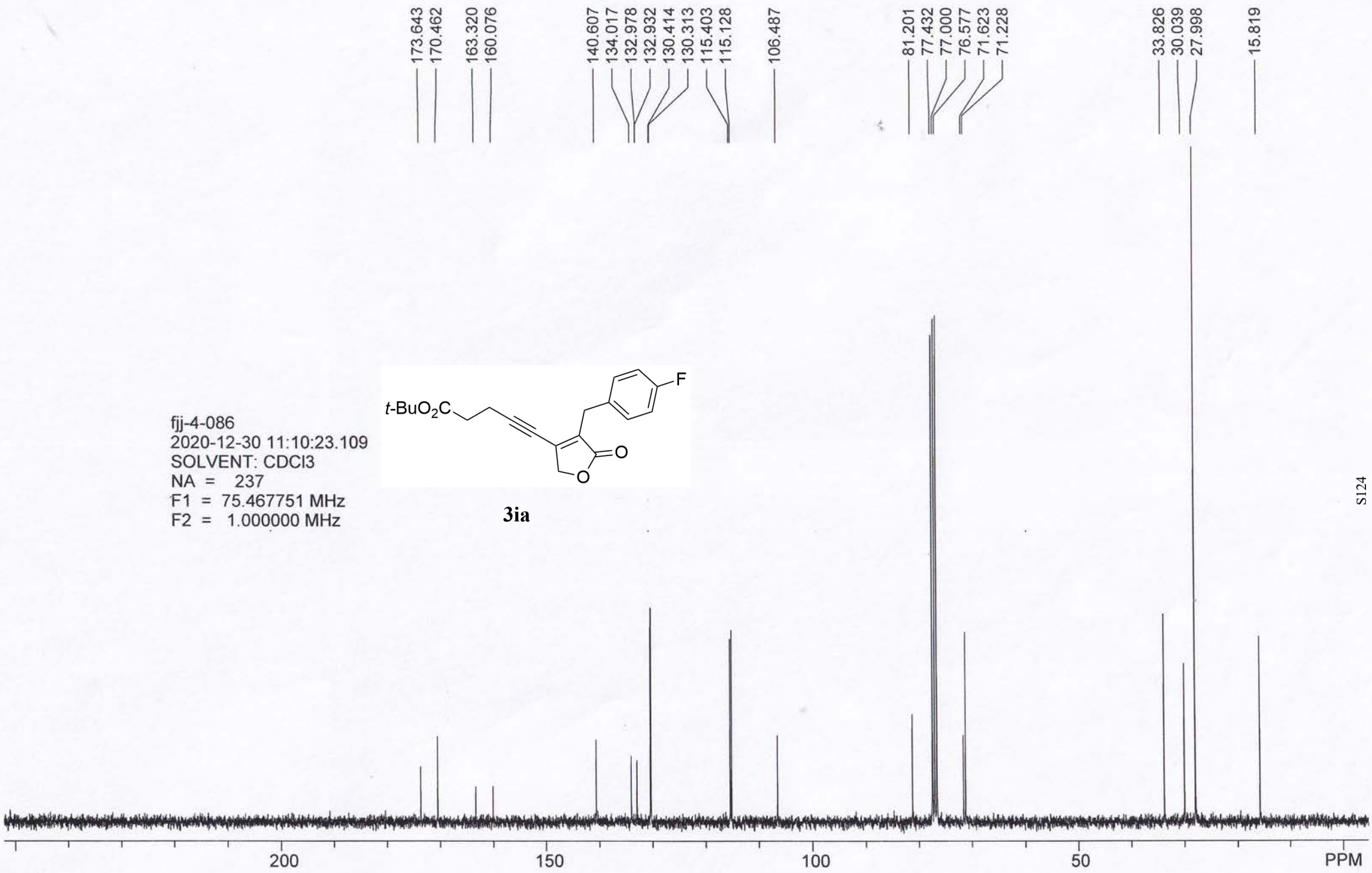
3ga


7.327
7.302
7.278
7.254
7.227
7.205
7.185
4.653
3.678
2.757
2.733
2.710
2.537
2.513
2.489
1.455
-0.000
zdj-1-083
2020-11-29 22:16:28.437
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
t-BuO2C
Ph
O
O
3ha
S121
9.04
5.16
2.00
2.00
2.02
2.07
10
8
6
4
2
PPM

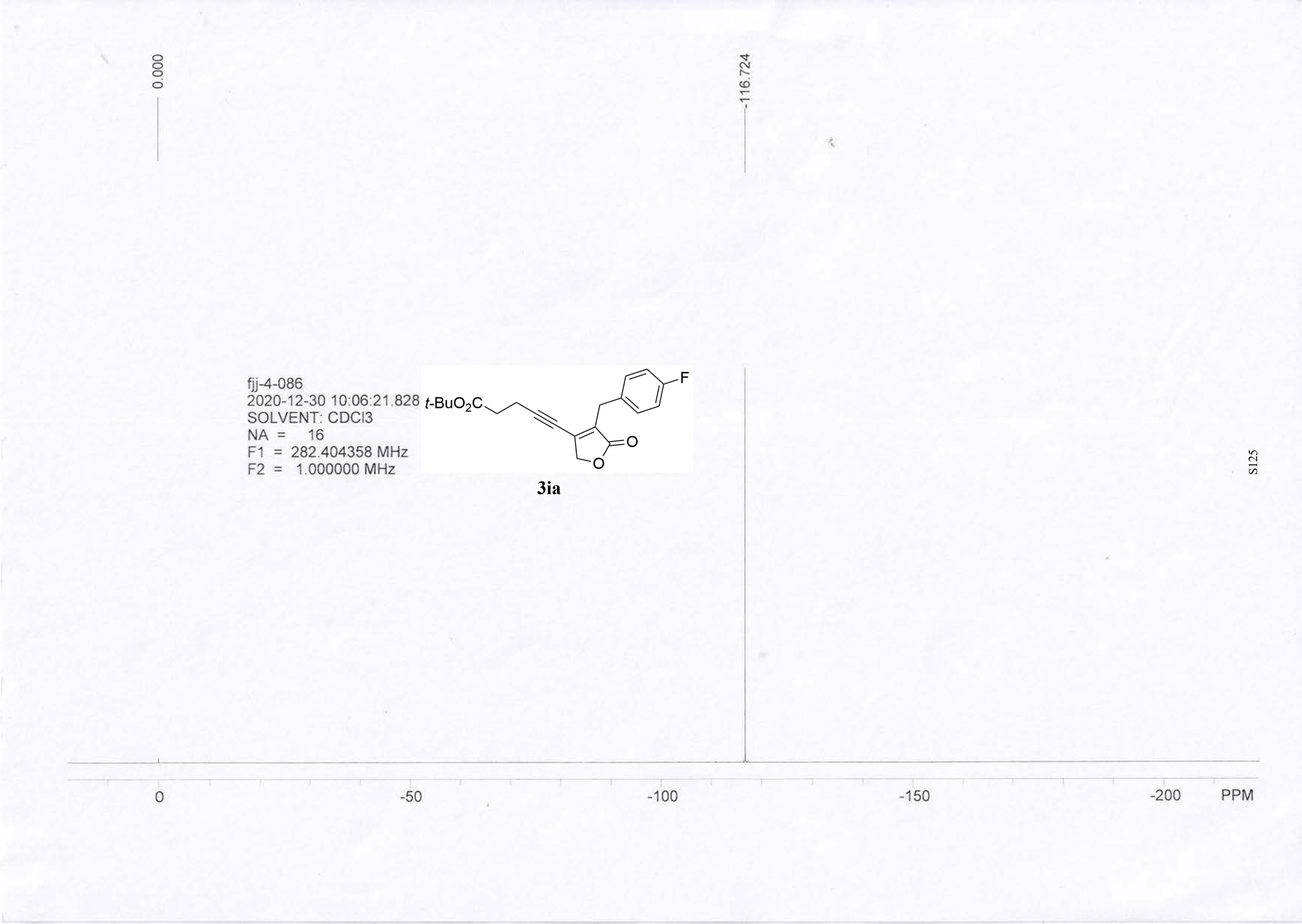

173.661
170.426
140.506
137.225
134.063
128.796
128.410
126.571
106.285
81.063
77.423
77.000
76.577
71.669
71.117
33.780
30.774
27.934
15.755
zdj-1-083
2020-11-29 22:23:48.734
NA = 107
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
t-BuO2C
Ph
O
O
250
200
150
100
50
PPM

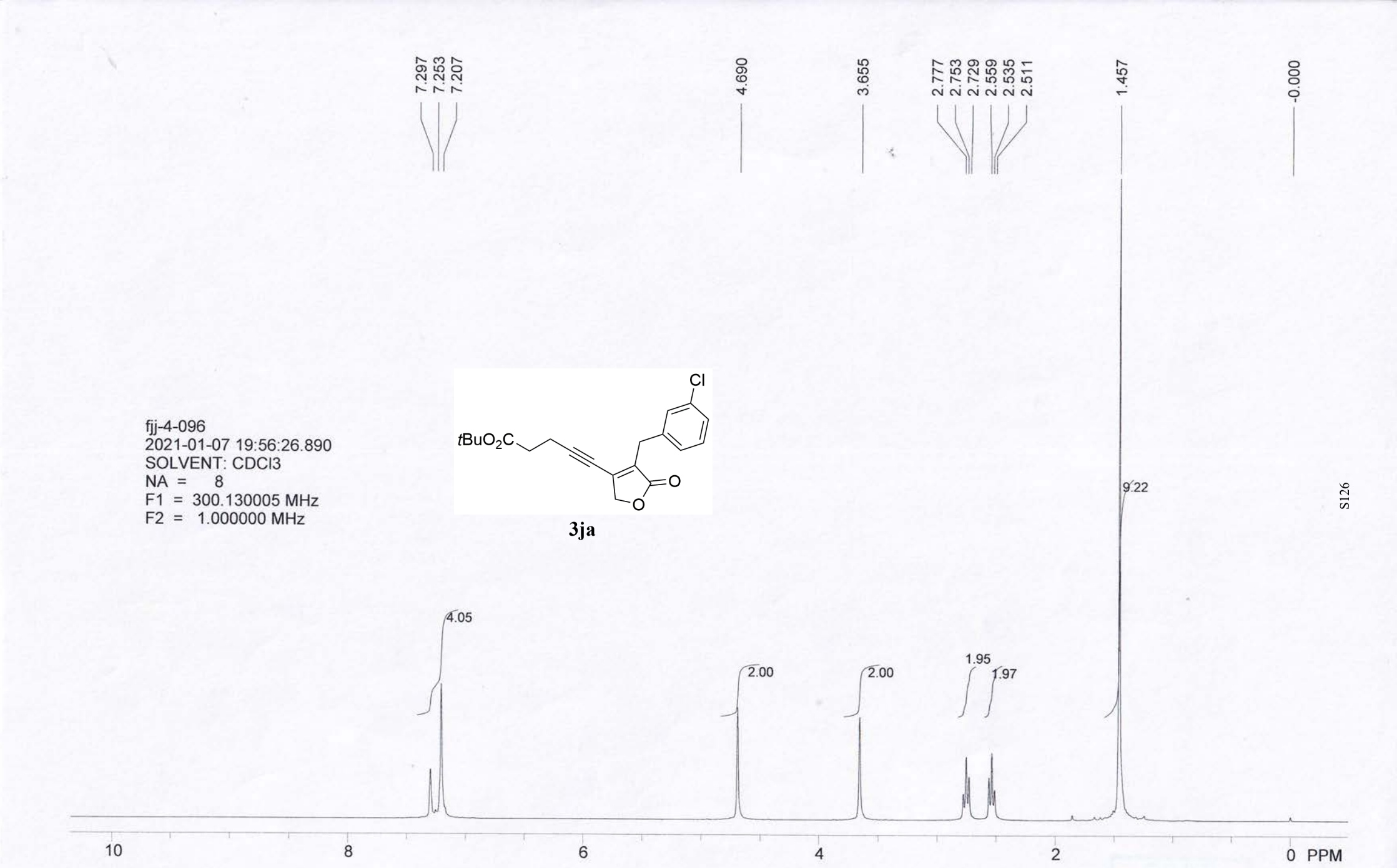
3ha

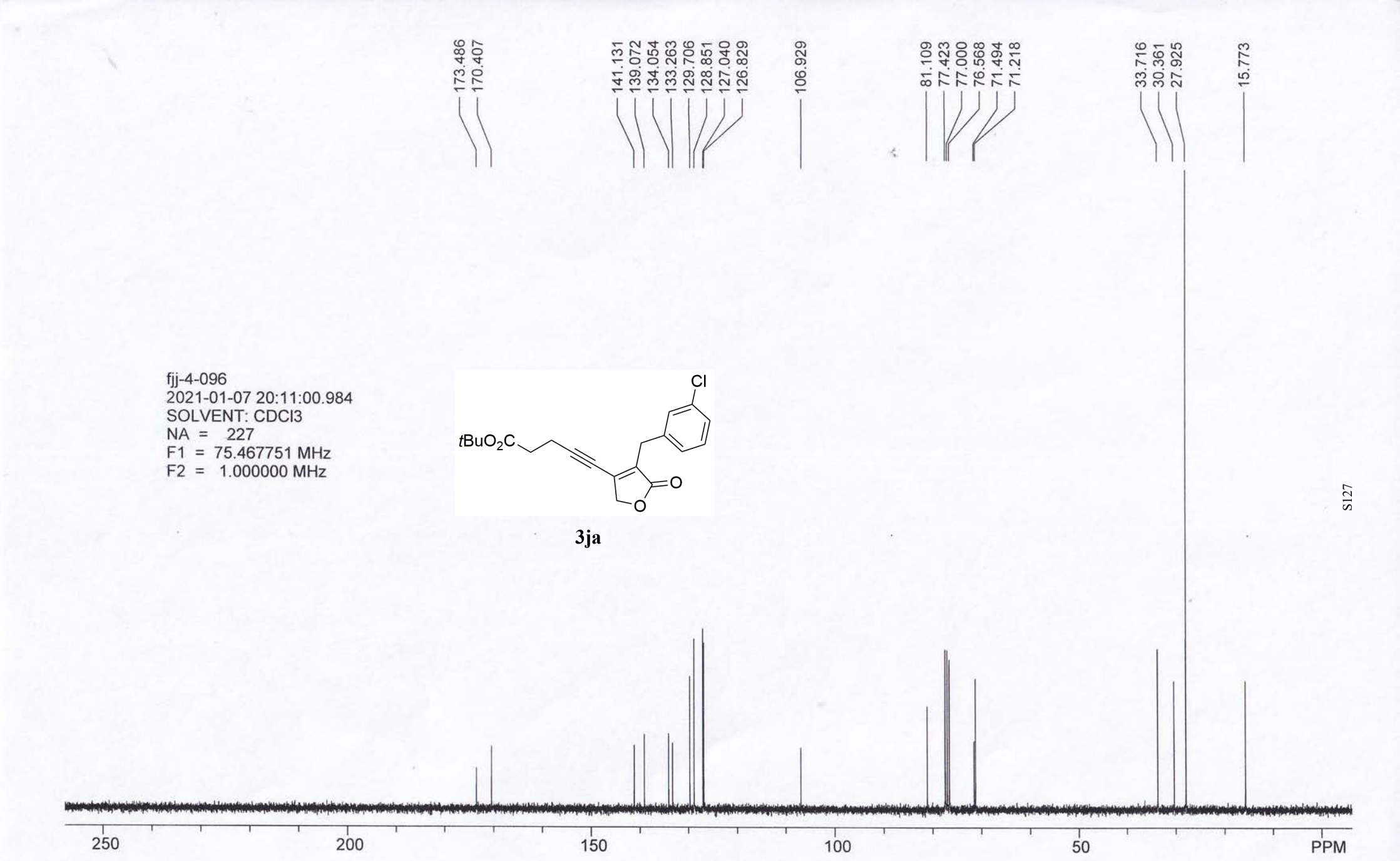

7.302
7.275
7.256
6.998
6.969
6.940
4.673
3.648
2.774
2.750
2.726
2.551
2.527
2.503
1.460
-0.000
fjj-4-086
2020-12-30 10:55:45.906
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
t-BuO2C
F
O
O
3ia
S123
9.17
2.10
2.01
2.00
2.03
2.03
2.03
10
8
6
4
2
PPM


173.643
170.462
163.320
160.076
140.607
134.017
132.978
132.932
130.414
130.313
115.403
115.128
106.487
81.201
77.432
77.000
76.577
71.623
71.228
33.826
30.039
27.998
15.819
fjj-4-086
2020-12-30 11:10:23.109
SOLVENT: CDCl3
NA = 237
F1 = 75.467751 MHz
F2 = 1.000000 MHz
t-BuO2C
F
O
O
200
150
100
50
PPM

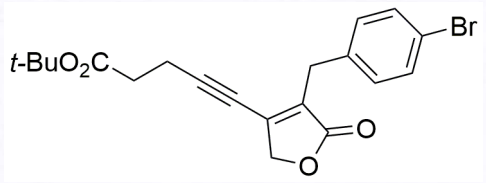
3ia


0.000
-116.724
fjj-4-086
2020-12-30 10:06:21.828
SOLVENT: CDCl3
NA = 16
F1 = 282.404358 MHz
F2 = 1.000000 MHz
t-BuO2C
F
O
O
3ia
S125
0
-50
-100
-150
-200
PPM


7.297
7.253
7.207
4.690
3.655
2.777
2.753
2.729
2.559
2.535
2.511
1.457
-0.000
fjj-4-096
2021-01-07 19:56:26.890
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Cl
tBuO2C
O
O
3ja
4.05
2.00
2.00
1.95
1.97
9.22
10
8
6
4
2
0 PPM


173.486
170.407
141.131
139.072
134.054
133.263
129.706
128.851
127.040
126.829
106.929
81.109
77.423
77.000
76.568
71.494
71.218
33.716
30.361
27.925
15.773
fjj-4-096
2021-01-07 20:11:00.984
SOLVENT: CDCl3
NA = 227
F1 = 75.467751 MHz
F2 = 1.000000 MHz
Cl
tBuO2C
O
O
250
200
150
100
50
PPM

3ja



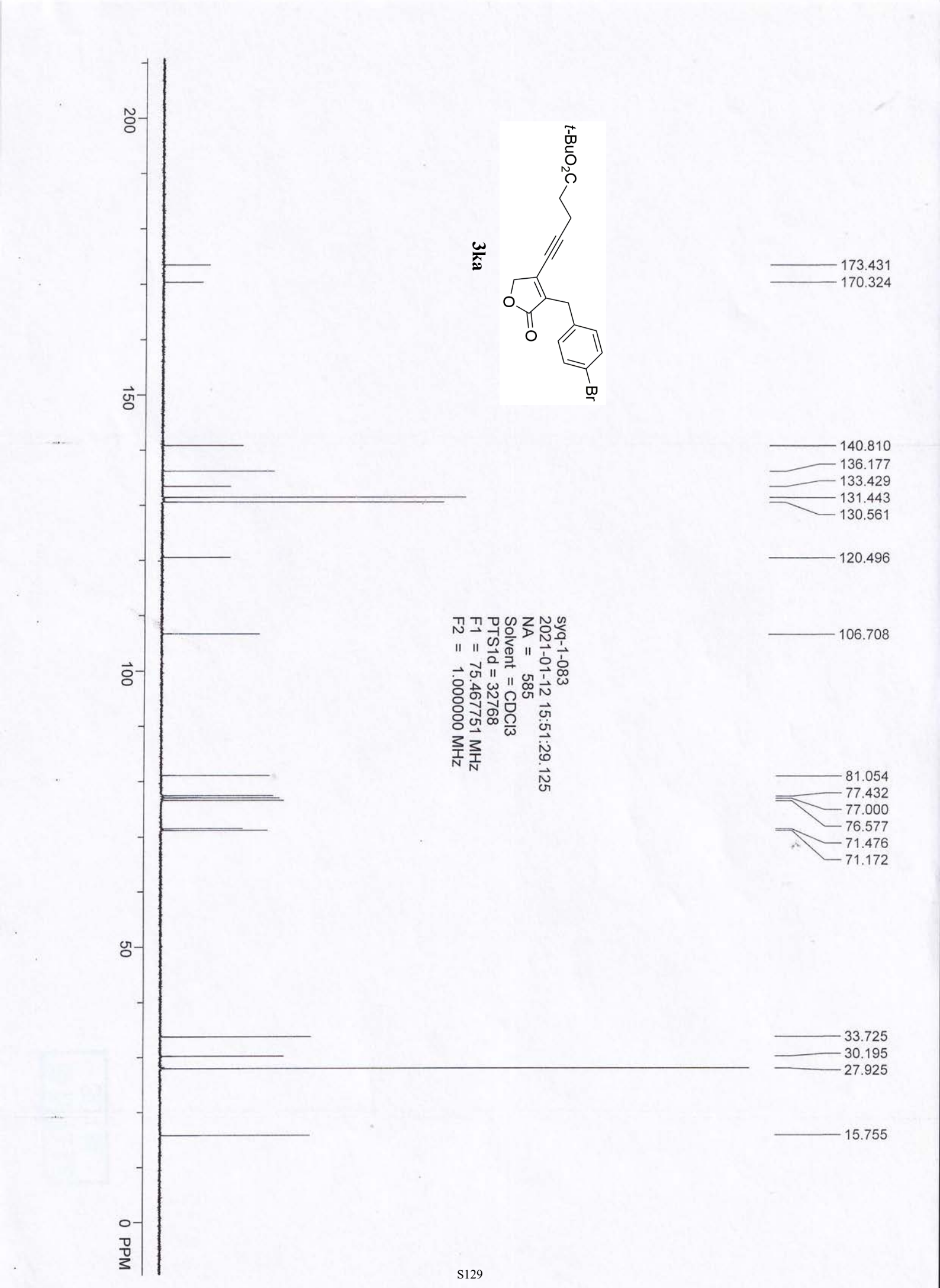
3ka

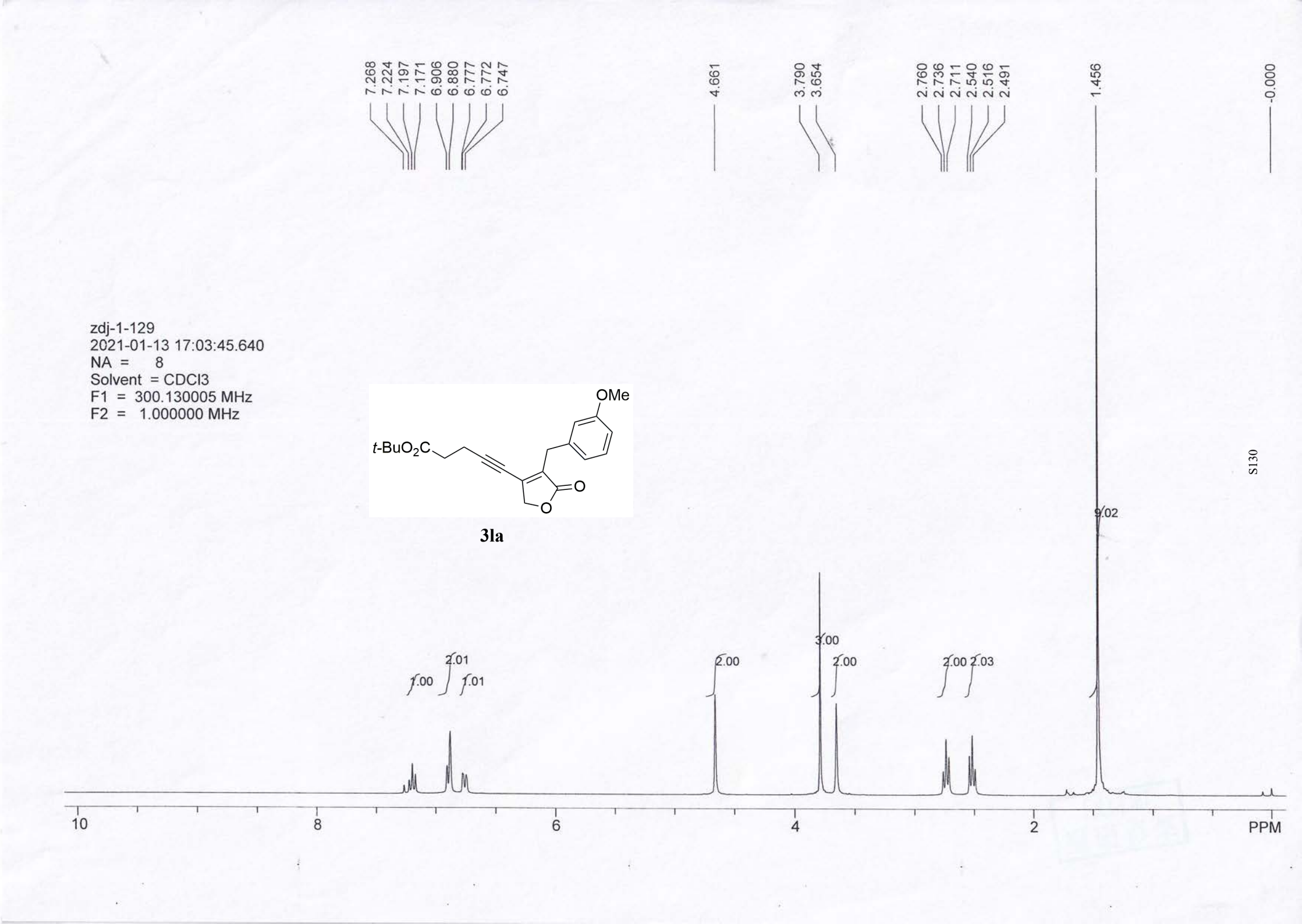
syq-1-083
2021-01-12 14:54:02.140
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

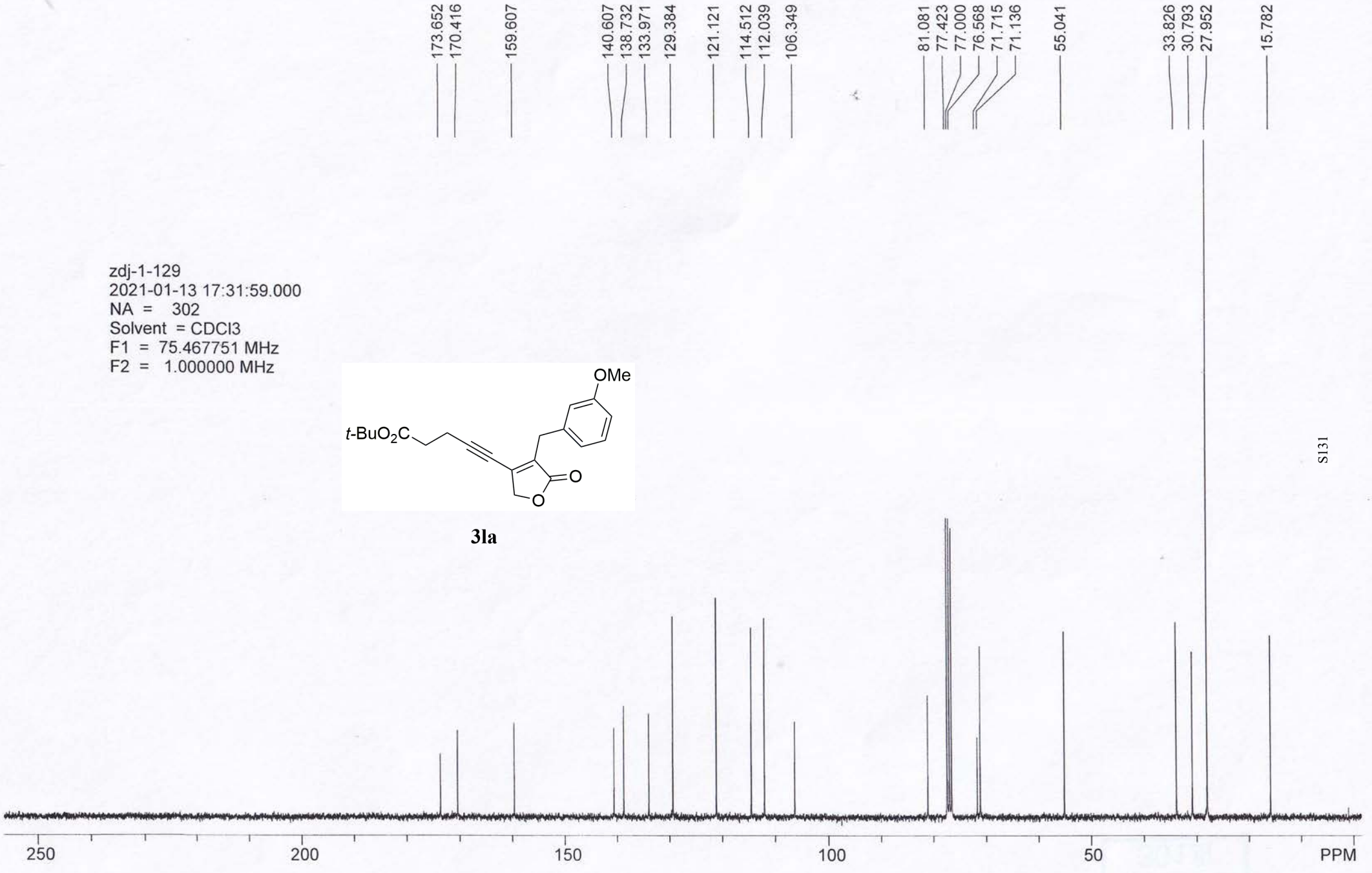
7.411 7.383 7.204 7.176 4.662 3.623 2.759 2.735 2.712 2.536 2.512 2.488 1.457 0.000

1.91 1.98 2.00 1.97 2.06 2.04 9.00

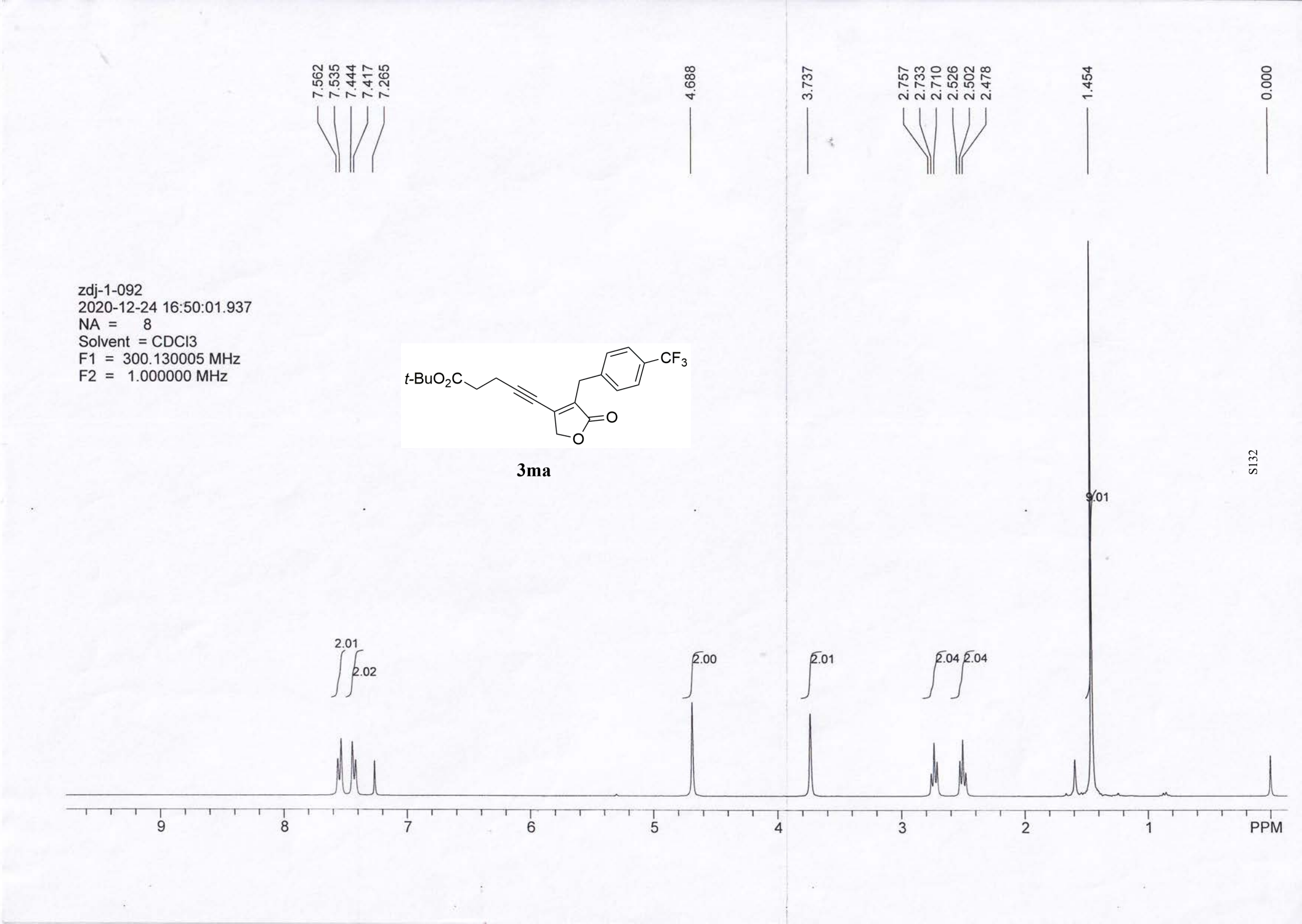
10 8 6 4 2 0 PPM

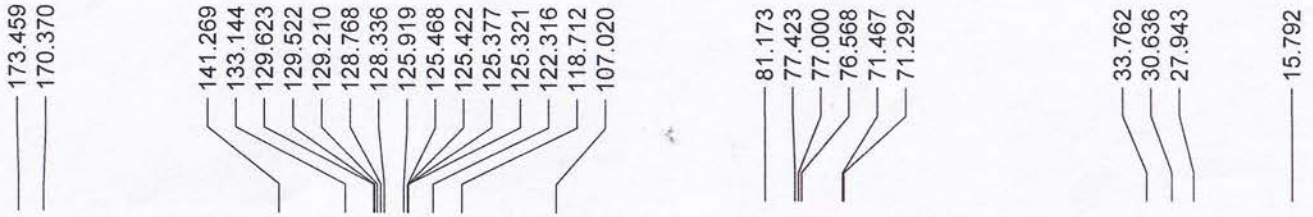

t-BuO2C
O
O
Br
3ka
syq-1-083
2021-01-12 15:51:29.125
NA = 585
Solvent = CDCl3
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
173.431
170.324
140.810
136.177
133.429
131.443
130.561
120.496
106.708
81.054
77.432
77.000
76.577
71.476
71.172
33.725
30.195
27.925
15.755
200
150
100
50
0 PPM


7.268
7.224
7.197
7.171
6.906
6.880
6.777
6.772
6.747
4.661
3.790
3.654
2.760
2.736
2.711
2.540
2.516
2.491
1.456
-0.000
zdj-1-129
2021-01-13 17:03:45.640
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
OMe
t-BuO2C
O
O
3la
S130
1.00
2.01
1.01
2.00
3.00
2.00
2.00
2.03
9.02
10
8
6
4
2
PPM

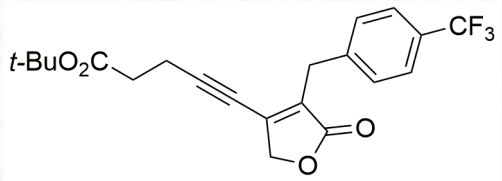

173.652
170.416
159.607
140.607
138.732
133.971
129.384
121.121
114.512
112.039
106.349
81.081
77.423
77.000
76.568
71.715
71.136
55.041
33.826
30.793
27.952
15.782
zdj-1-129
2021-01-13 17:31:59.000
NA = 302
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
OMe
t-BuO2C
O
O
250
200
150
100
50
PPM

3la

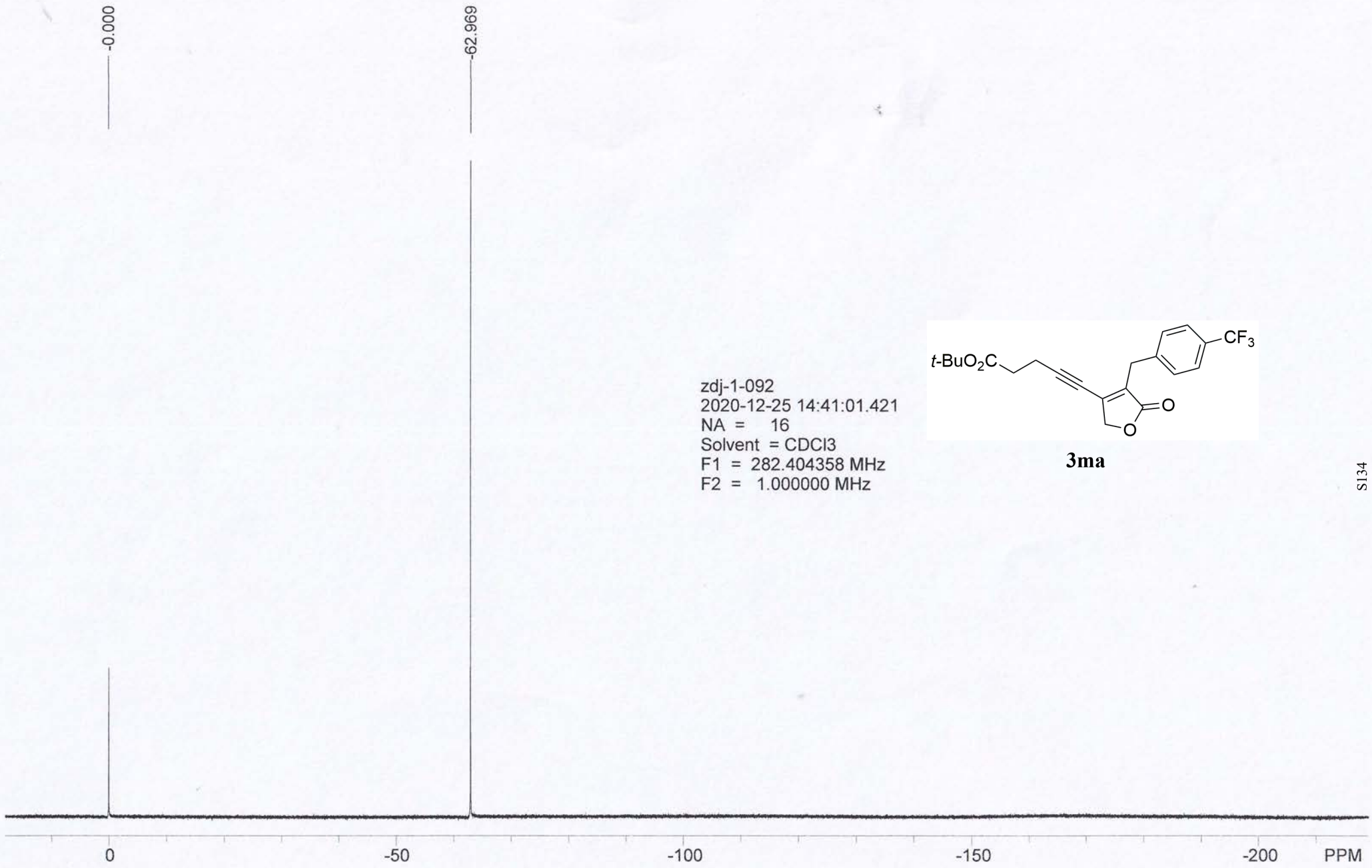

7.562
7.535
7.444
7.417
7.265
4.688
3.737
2.757
2.733
2.710
2.526
2.502
2.478
1.454
0.000
zdj-1-092
2020-12-24 16:50:01.937
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
t-BuO2C
CF3
O
O
3ma
S132
2.01
2.02
2.00
2.01
2.04
2.04
9.01
9
8
7
6
5
4
3
2
1
PPM



zdj-1-092
2020-12-25 08:25:31.609
NA = 10273
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz



3ma


-0.000
-62.969
zdj-1-092
2020-12-25 14:41:01.421
NA = 16
Solvent = CDCl3
F1 = 282.404358 MHz
F2 = 1.000000 MHz
t-BuO2C
CF3
O
O
0
-50
-100
-150
-200
PPM

3ma

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_210107_zdj_1_092_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: mo_210107_zdj_1_092_0m

```
Bond precision:  C-C = 0.0049 A          Wavelength=0.71073

Cell:            a=12.352(3)    b=5.4853(16)          c=15.561(5)
                 alpha=90       beta=111.325(11)      gamma=90
Temperature:     170 K

                 Calculated                Reported
Volume           982.1(5)                  982.1(5)
Space group      P 21                      P 1 21 1
Hall group       P 2yb                     P 2yb
Moiety formula   C21 H21 F3 O4             C21 H21 F3 O4
Sum formula      C21 H21 F3 O4             C21 H21 F3 O4
Mr               394.38                    394.38
Dx,g cm-3        1.334                     1.334
Z                2                         2
Mu (mm-1)        0.110                     0.110
F000             412.0                     412.0
F000'            412.28
h,k,lmax         15,7,19                   15,7,19
Nref             4328[ 2394]               4302
Tmin,Tmax        0.959,0.993               0.673,0.746
Tmin'            0.955

Correction method= # Reported T Limits: Tmin=0.673 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.80/0.99      Theta(max)= 27.105

R(reflections)= 0.0520( 4033)     wR2(reflections)= 0.1426( 4302)

S = 1.061                 Npar= 256
```

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 C

```
STRVA01_ALERT_4_C           Flack parameter is too small
           From the CIF: _refine_ls_abs_structure_Flack   -0.300
           From the CIF: _refine_ls_abs_structure_Flack_su    0.300
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00485 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          3 Report
```

Alert level G

```
PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High .      0.300 Report
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of         C7 Check
PLAT371_ALERT_2_G Long   C(sp2)-C(sp1) Bond  C12      - C13      .       1.43 Ang.
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O2             109.9 Degree
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          1 Note
PLAT916_ALERT_2_G Hooft y and Flack x Parameter Values Differ by .       0.10 Check
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          2 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          1 Info
```

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

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

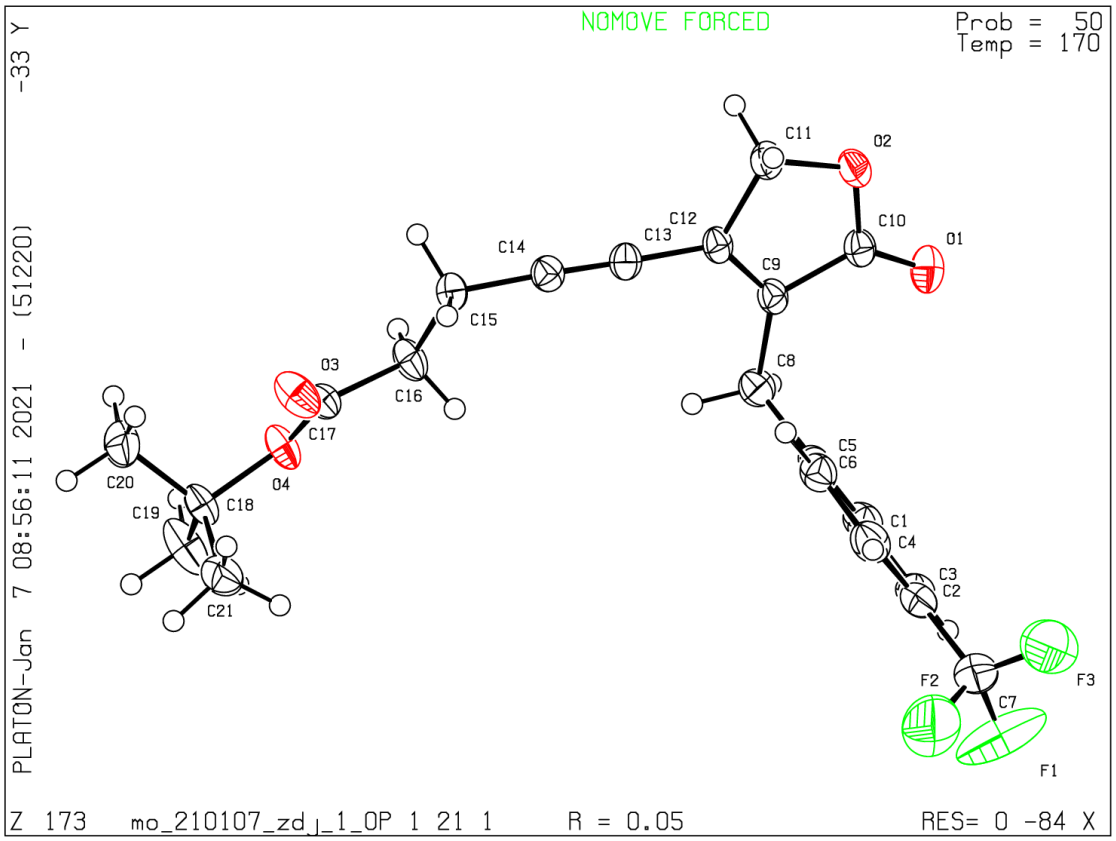
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section 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.

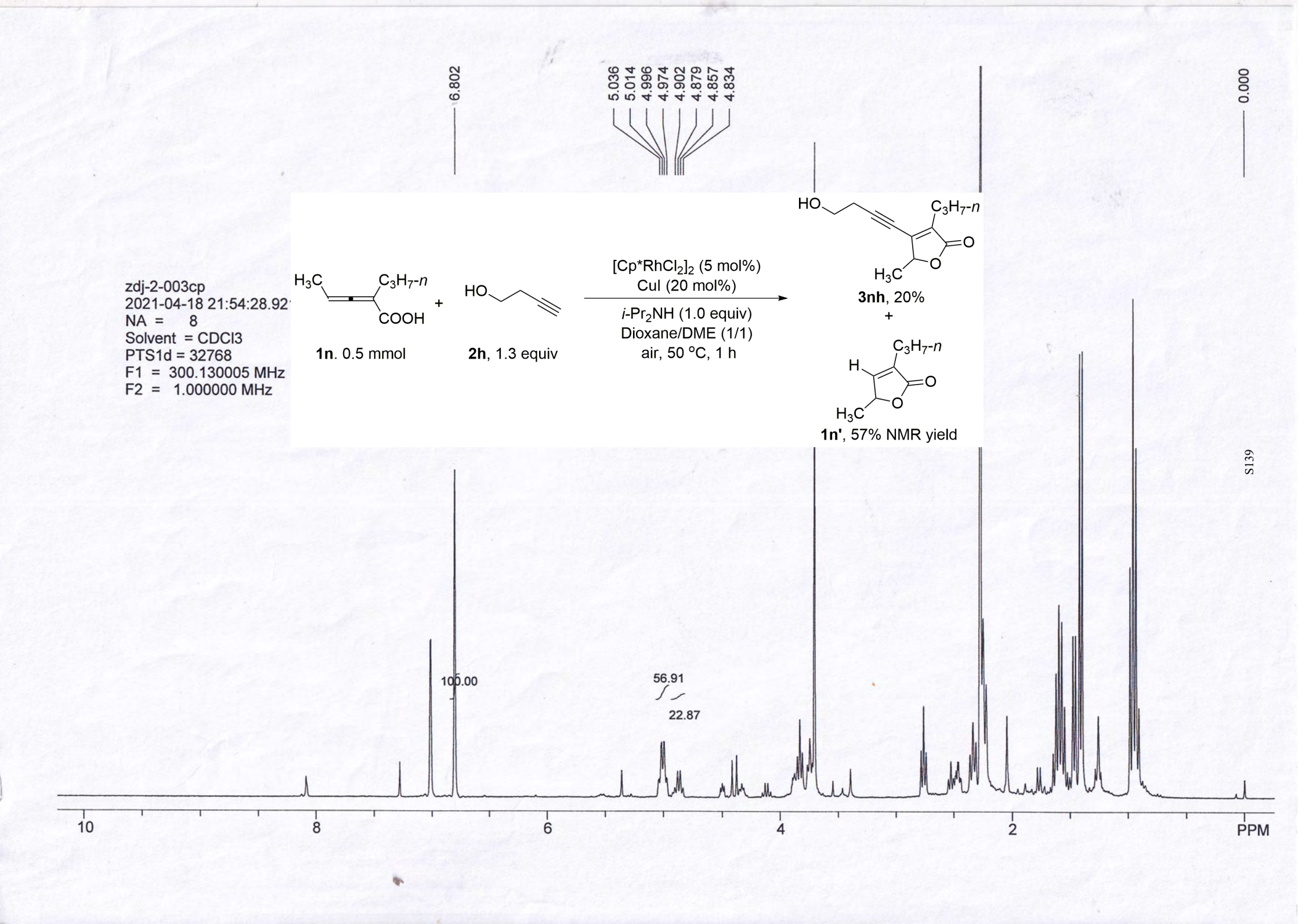
Publication of your CIF in other journals

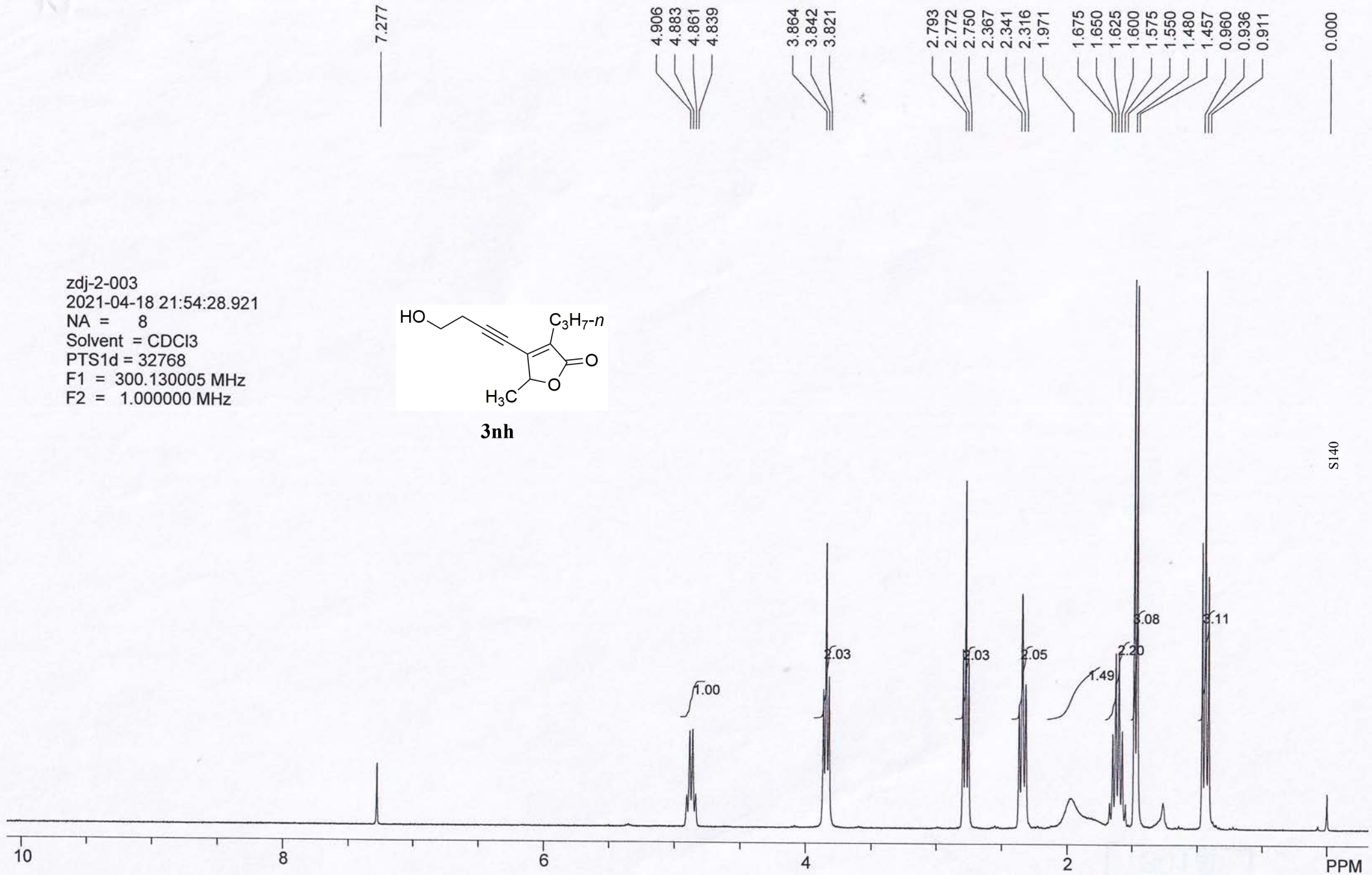
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 05/12/2020; check.def file version of 05/12/2020

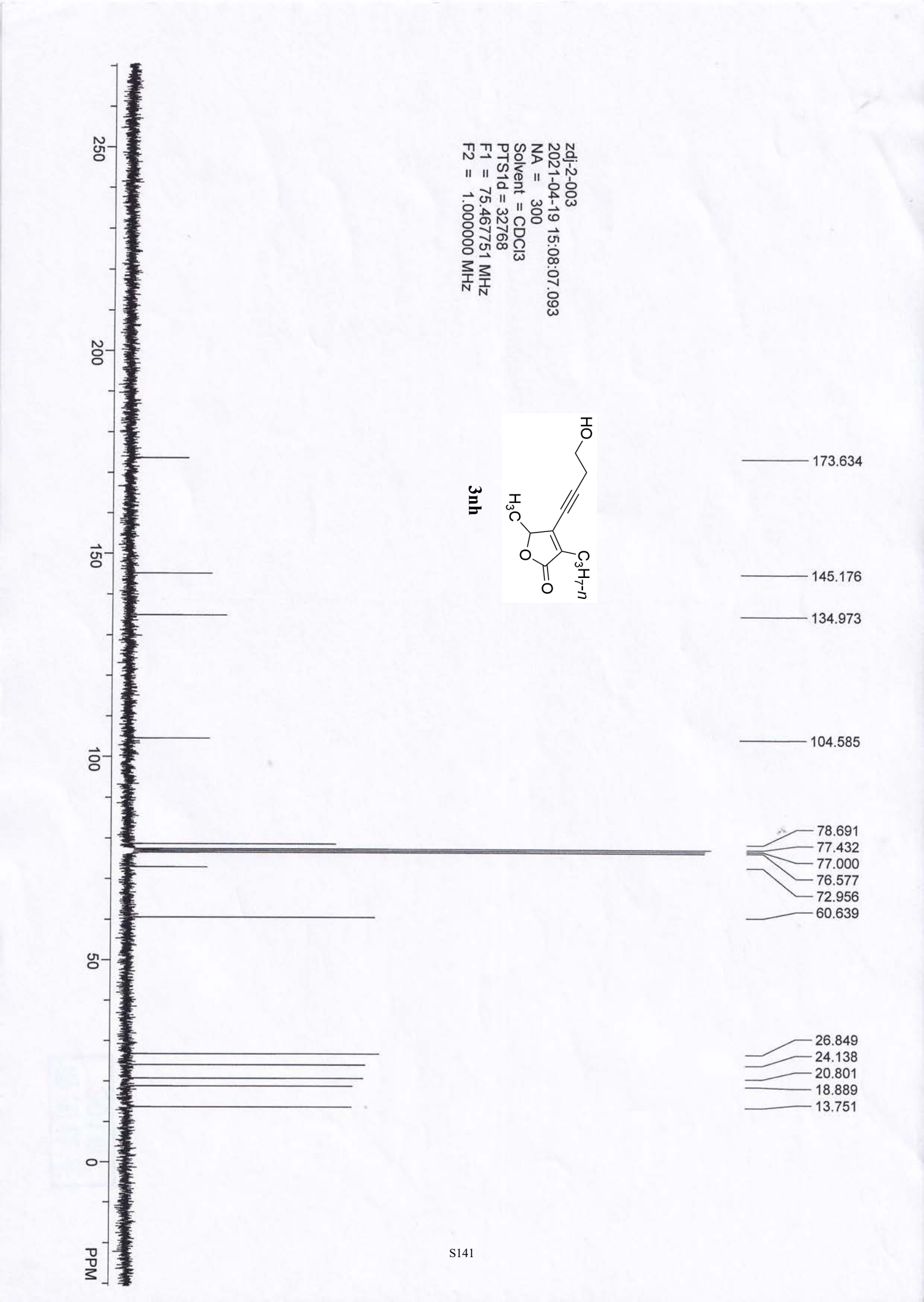
Datablock mo_210107_zdj_1_092_0m - ellipsoid plot

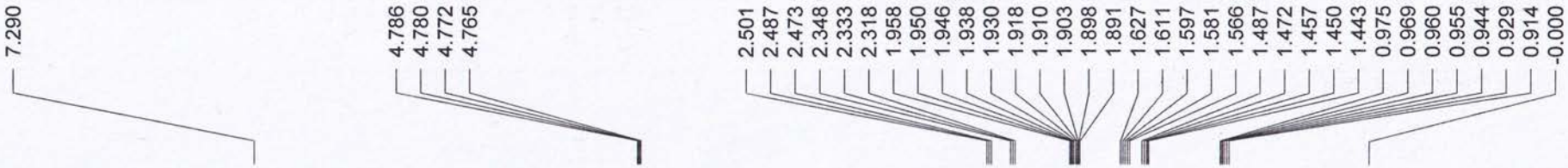


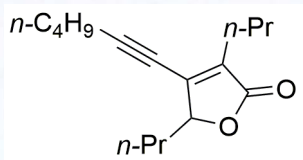

6.802
5.036
5.014
4.996
4.974
4.902
4.879
4.857
4.834
0.000
zdj-2-003cp
2021-04-18 21:54:28.92
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
H3C
C3H7-n
COOH
1n. 0.5 mmol
+
HO
2h, 1.3 equiv
[Cp*RhCl2]2 (5 mol%)
CuI (20 mol%)
i-Pr2NH (1.0 equiv)
Dioxane/DME (1/1)
air, 50 °C, 1 h
HO
C3H7-n
O
O
H3C
3nh, 20%
+
C3H7-n
H
O
O
H3C
1n', 57% NMR yield
100.00
56.91
22.87
10
8
6
4
2
PPM
S139


7.277
4.906
4.883
4.861
4.839
3.864
3.842
3.821
2.793
2.772
2.750
2.367
2.341
2.316
1.971
1.675
1.650
1.625
1.600
1.575
1.550
1.480
1.457
0.960
0.936
0.911
0.000
zdj-2-003
2021-04-18 21:54:28.921
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
HO
C_3H_7-*n*
O
O
H_3C
1.00
2.03
2.03
2.05
1.49
2.20
3.08
3.11
10
8
6
4
2
PPM

3nh

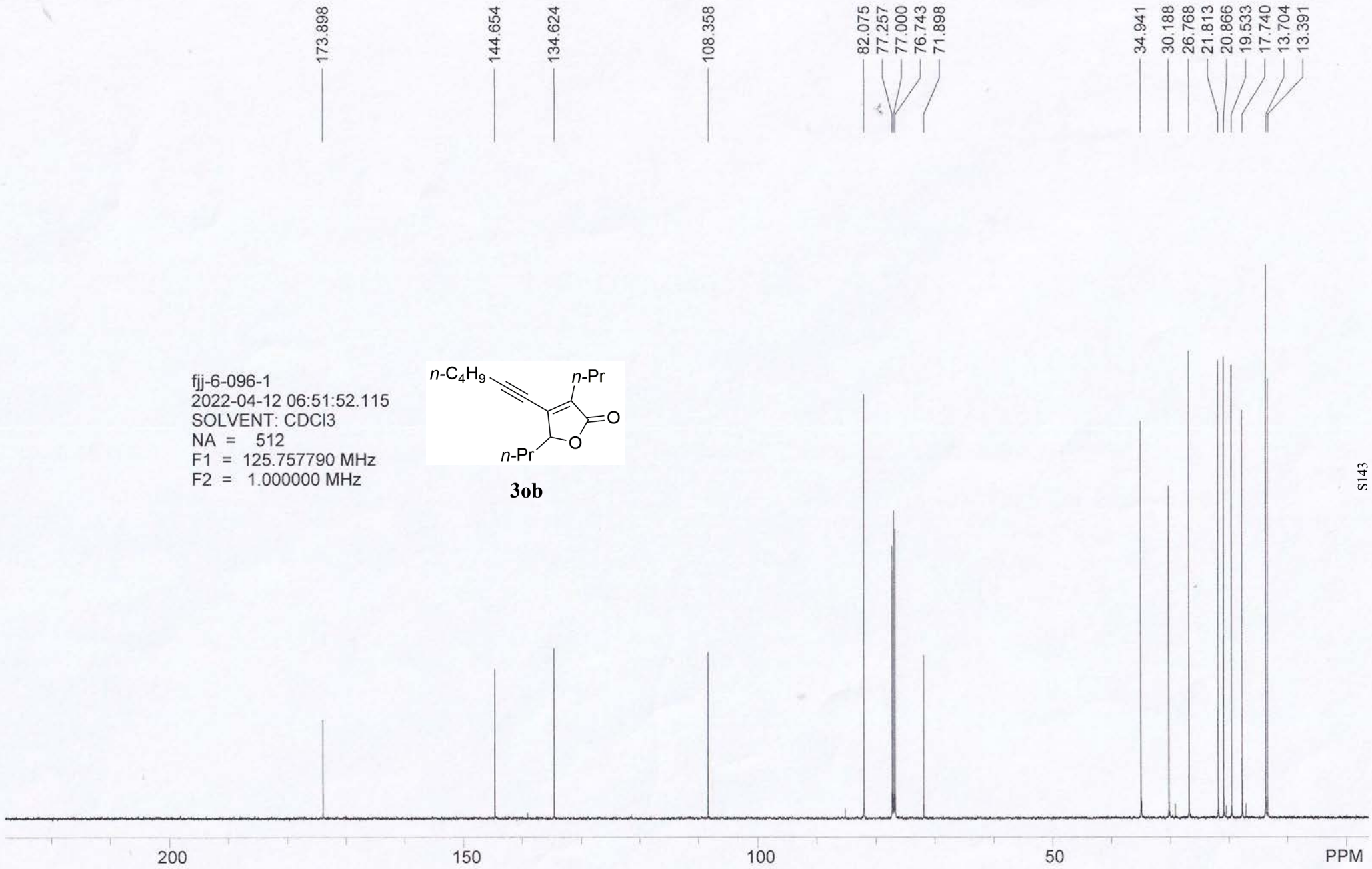

zdj-2-003
2021-04-19 15:08:07.093
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
3nh
HO
H3C
O
O
C3H7-n
173.634
145.176
134.973
104.585
78.691
77.432
77.000
76.577
72.956
60.639
26.849
24.138
20.801
18.889
13.751
250
200
150
100
50
0
PPM



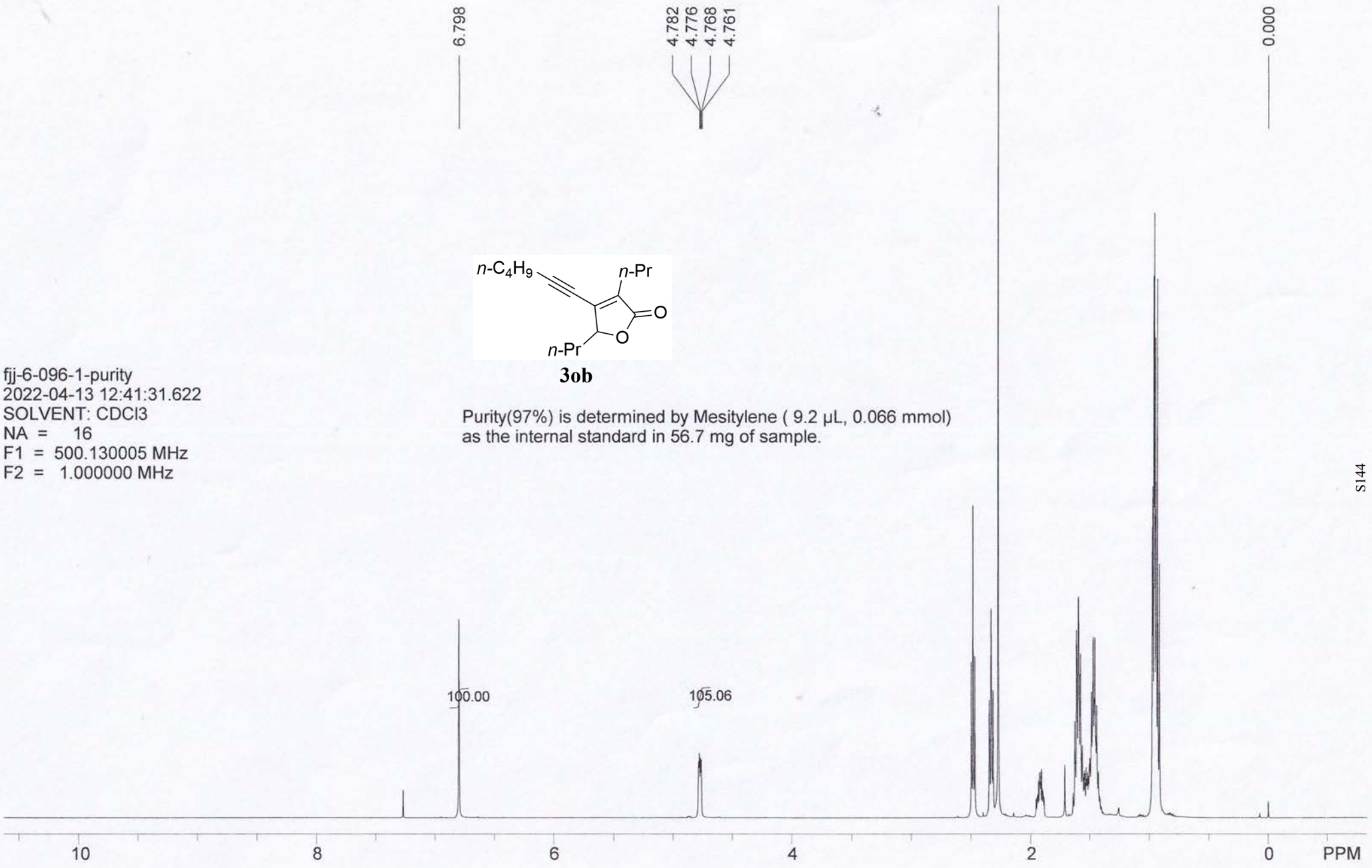


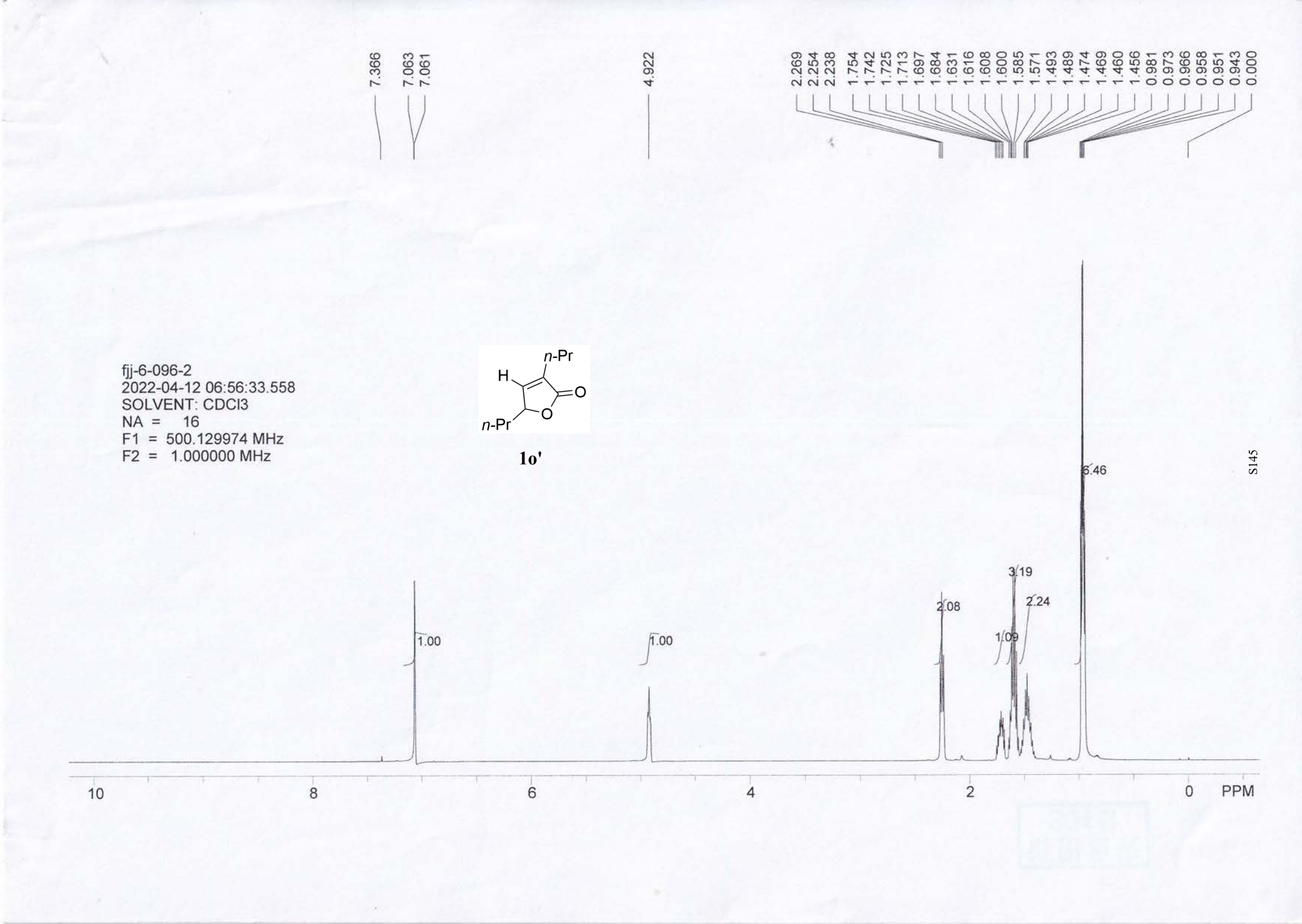
3ob

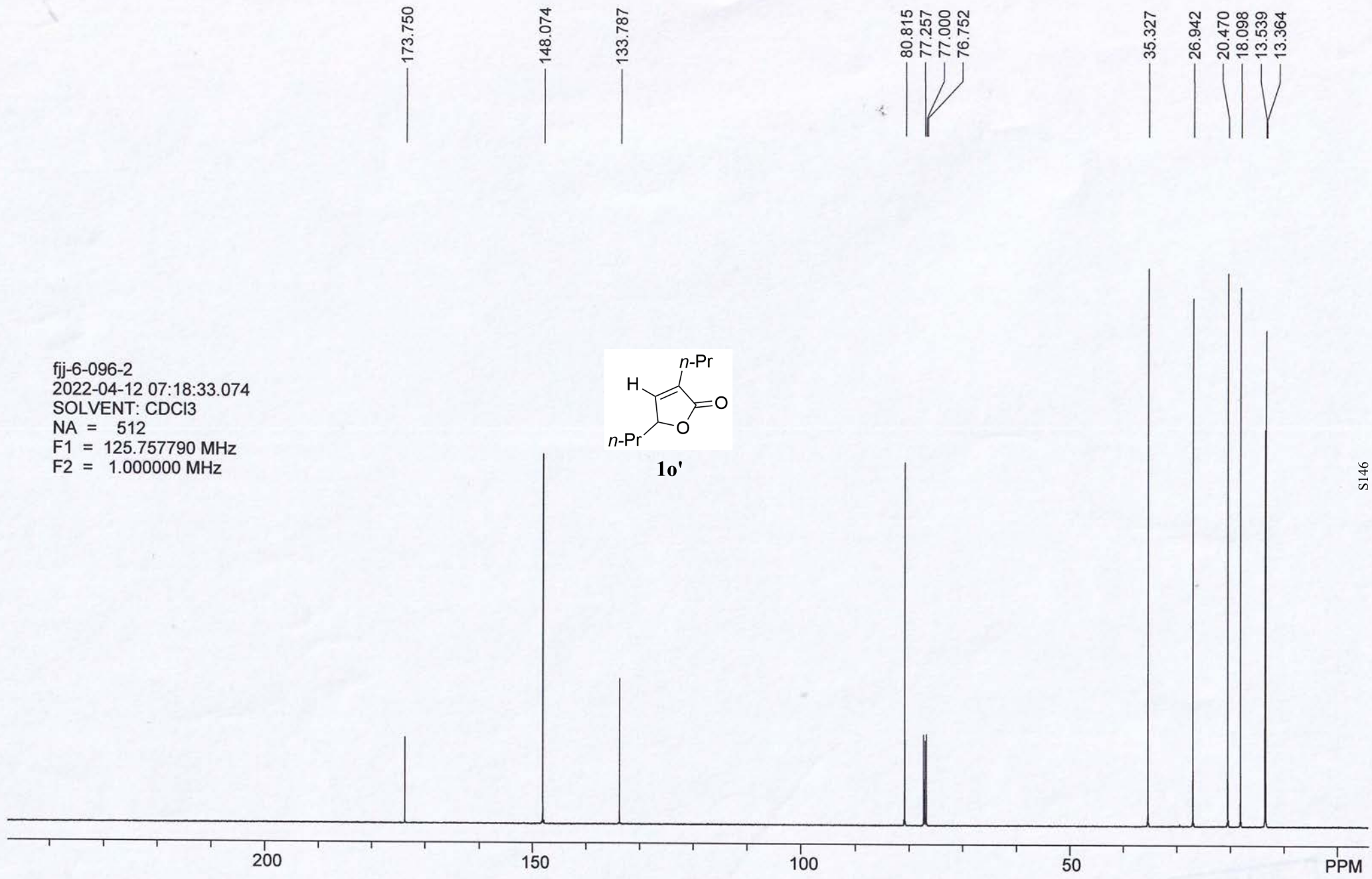
fjj-6-096-1
2022-04-12 06:29:52.195
SOLVENT: CDCl3
NA = 16
F1 = 500.130005 MHz
F2 = 1.000000 MHz

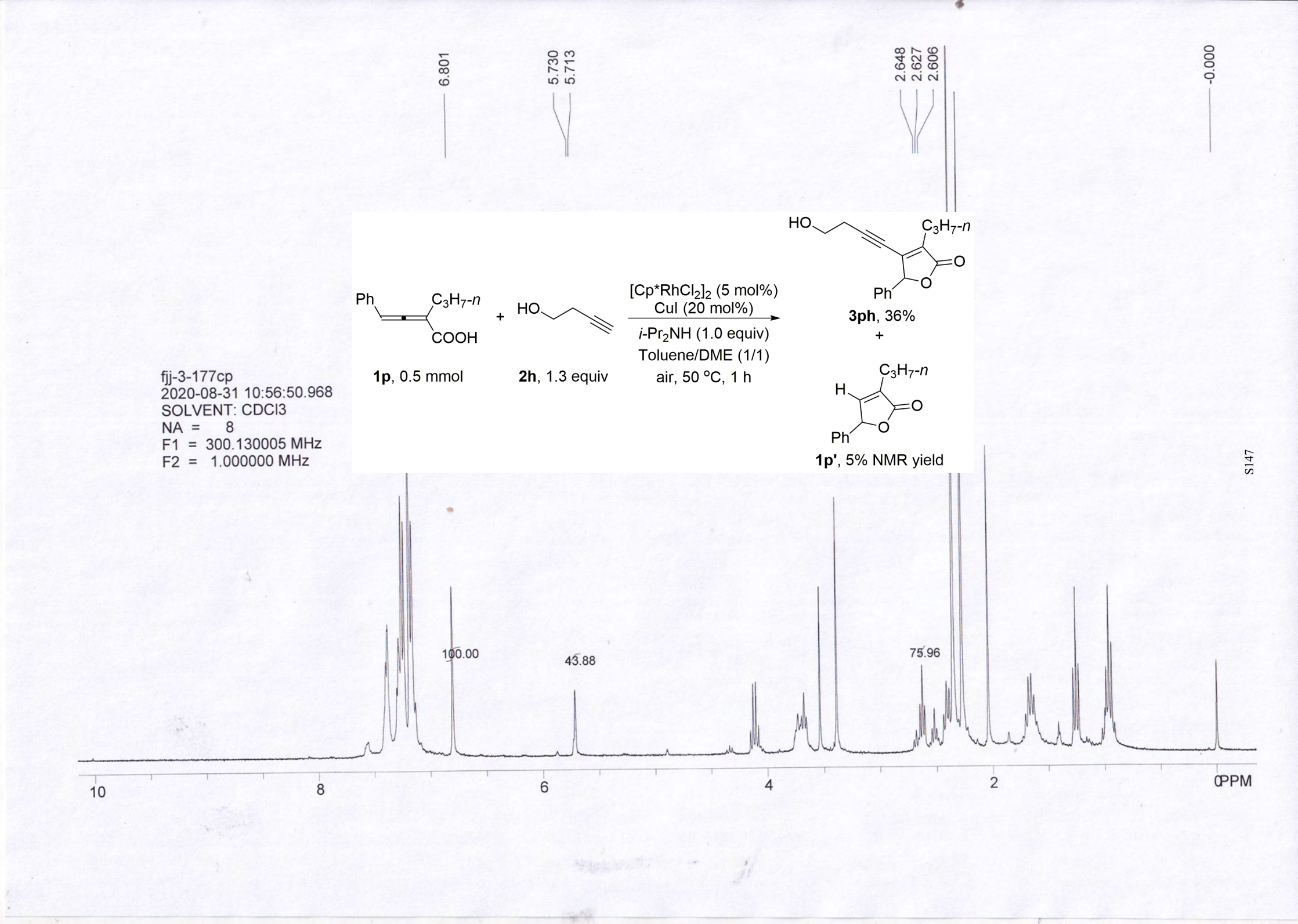

173.898
144.654
134.624
108.358
82.075
77.257
77.000
76.743
71.898
34.941
30.188
26.768
21.813
20.866
19.533
17.740
13.704
13.391
fjj-6-096-1
2022-04-12 06:51:52.115
SOLVENT: CDCl3
NA = 512
F1 = 125.757790 MHz
F2 = 1.000000 MHz
n-C4H9
n-Pr
n-Pr
O
O
200
150
100
50
PPM

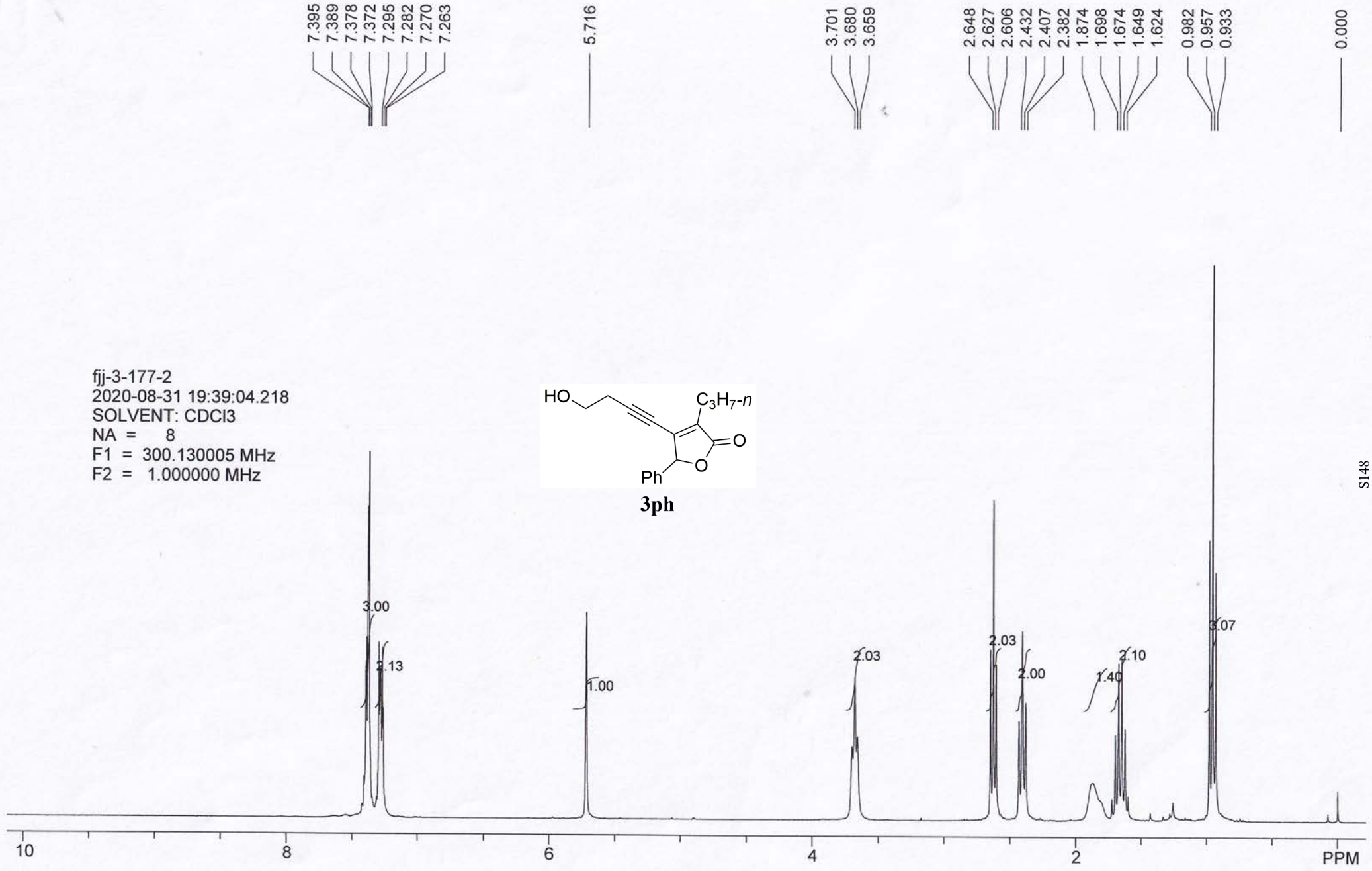
3ob

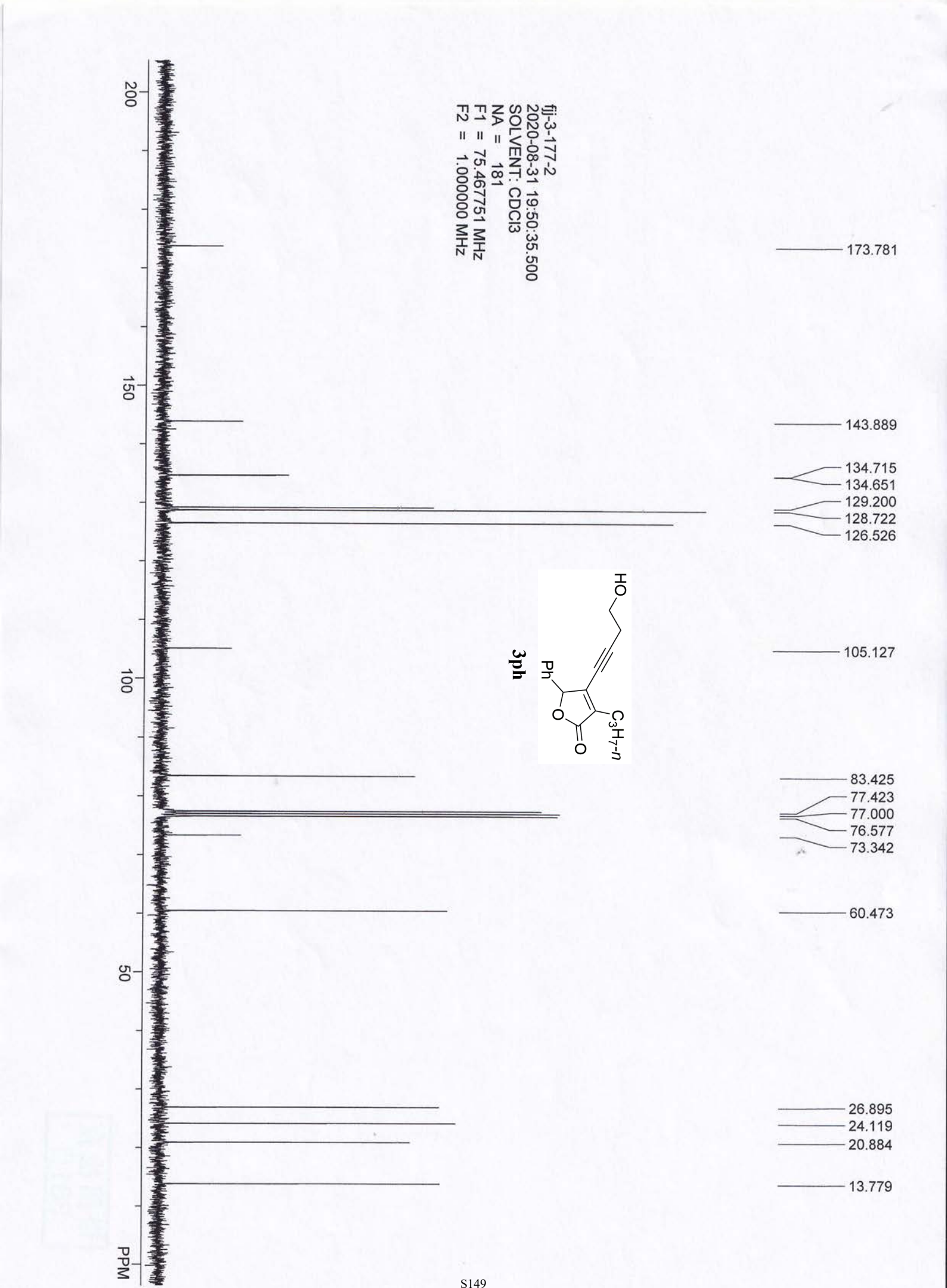

6.798
4.782
4.776
4.768
4.761
0.000
n-C4H9
n-Pr
n-Pr
O
O
3ob
fjj-6-096-1-purity
2022-04-13 12:41:31.622
SOLVENT: CDCl3
NA = 16
F1 = 500.130005 MHz
F2 = 1.000000 MHz
Purity(97%) is determined by Mesitylene (9.2 μL, 0.066 mmol)
as the internal standard in 56.7 mg of sample.
100.00
105.06
10
8
6
4
2
0
PPM

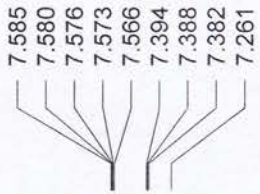

7.366
7.063
7.061
4.922
2.269
2.254
2.238
1.754
1.742
1.725
1.713
1.697
1.684
1.631
1.616
1.608
1.600
1.585
1.571
1.493
1.489
1.474
1.469
1.460
1.456
0.981
0.973
0.966
0.958
0.951
0.943
0.000
fjj-6-096-2
2022-04-12 06:56:33.558
SOLVENT: CDCl3
NA = 16
F1 = 500.129974 MHz
F2 = 1.000000 MHz
n-Pr
H
O
O
n-Pr
1o'
S145
6.46
3.19
2.24
2.08
1.09
1.00
1.00
10
8
6
4
2
0
PPM

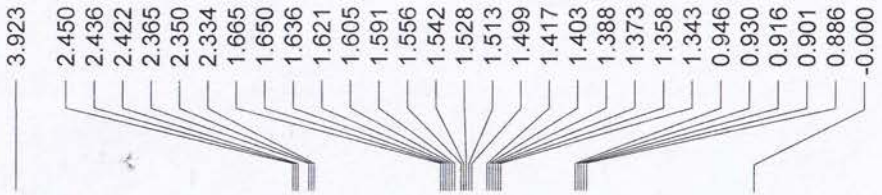

173.750
148.074
133.787
80.815
77.257
77.000
76.752
35.327
26.942
20.470
18.098
13.539
13.364
fjj-6-096-2
2022-04-12 07:18:33.074
SOLVENT: CDCl3
NA = 512
F1 = 125.757790 MHz
F2 = 1.000000 MHz
n-Pr
H
O
O
n-Pr
1o'
200
150
100
50
PPM


6.801
5.730
5.713
2.648
2.627
2.606
-0.000
Ph
C_3H_7-*n*
COOH
1p, 0.5 mmol
+
HO
2h, 1.3 equiv
[Cp*RhCl2]2 (5 mol%)
CuI (20 mol%)
i-Pr2NH (1.0 equiv)
Toluene/DME (1/1)
air, 50 °C, 1 h
HO
C_3H_7-*n*
O
O
Ph
3ph, 36%
+
H
C_3H_7-*n*
O
O
Ph
1p', 5% NMR yield
fjj-3-177cp
2020-08-31 10:56:50.968
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
100.00
43.88
75.96
10
8
6
4
2
0
PPM
S147

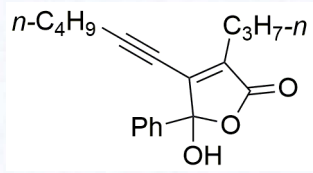

7.395
7.389
7.378
7.372
7.295
7.282
7.270
7.263
5.716
3.701
3.680
3.659
2.648
2.627
2.606
2.432
2.407
2.382
1.874
1.698
1.674
1.649
1.624
0.982
0.957
0.933
0.000
fjj-3-177-2
2020-08-31 19:39:04.218
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
HO
C3H7-n
O
O
Ph
3ph
3.00
2.13
1.00
2.03
2.03
2.00
1.40
2.10
3.07
10
8
6
4
2
PPM


fji-3-177-2
2020-08-31 19:50:35.500
SOLVENT: CDCl3
NA = 181
F1 = 75.467751 MHz
F2 = 1.000000 MHz
3ph
HO
Ph
O
O
C3H7-n
173.781
143.889
134.715
134.651
129.200
128.722
126.526
105.127
83.425
77.423
77.000
76.577
73.342
60.473
26.895
24.119
20.884
13.779
200
150
100
50
PPM

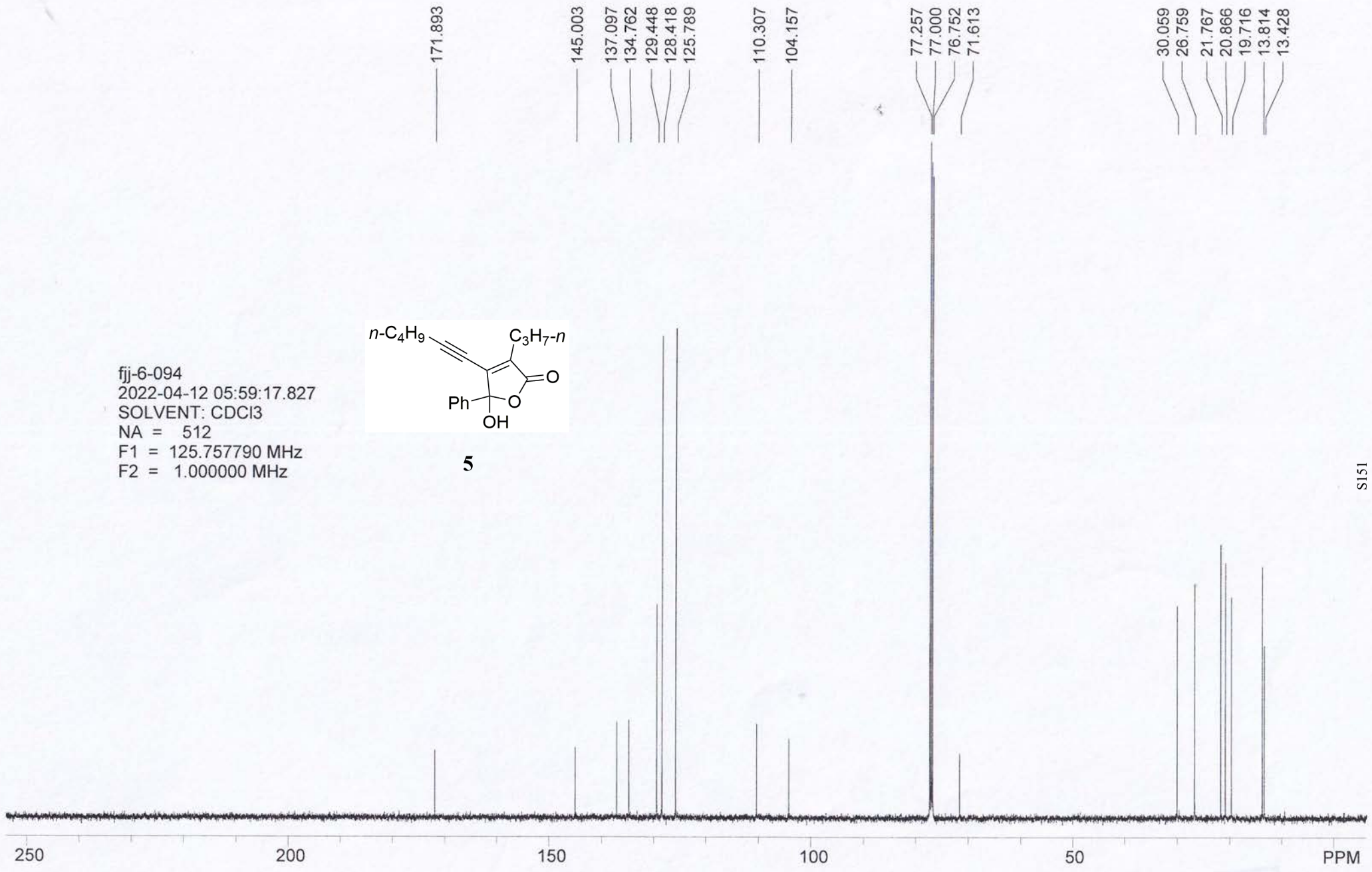




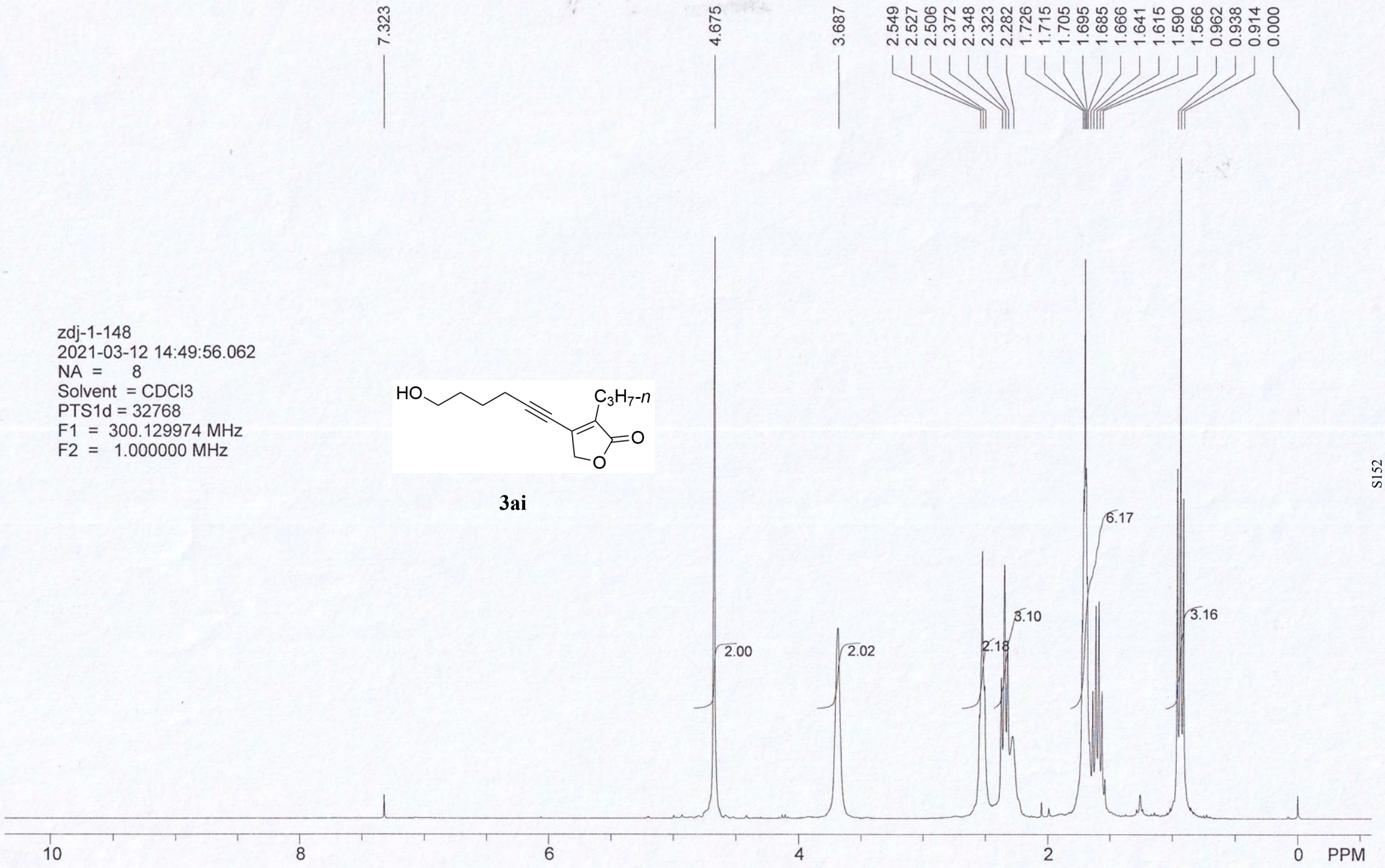
fjj-6-094
2022-04-12 05:37:20.269
SOLVENT: CDCl3
NA = 16
F1 = 500.130005 MHz
F2 = 1.000000 MHz
SW1 = 15000.00 Hz



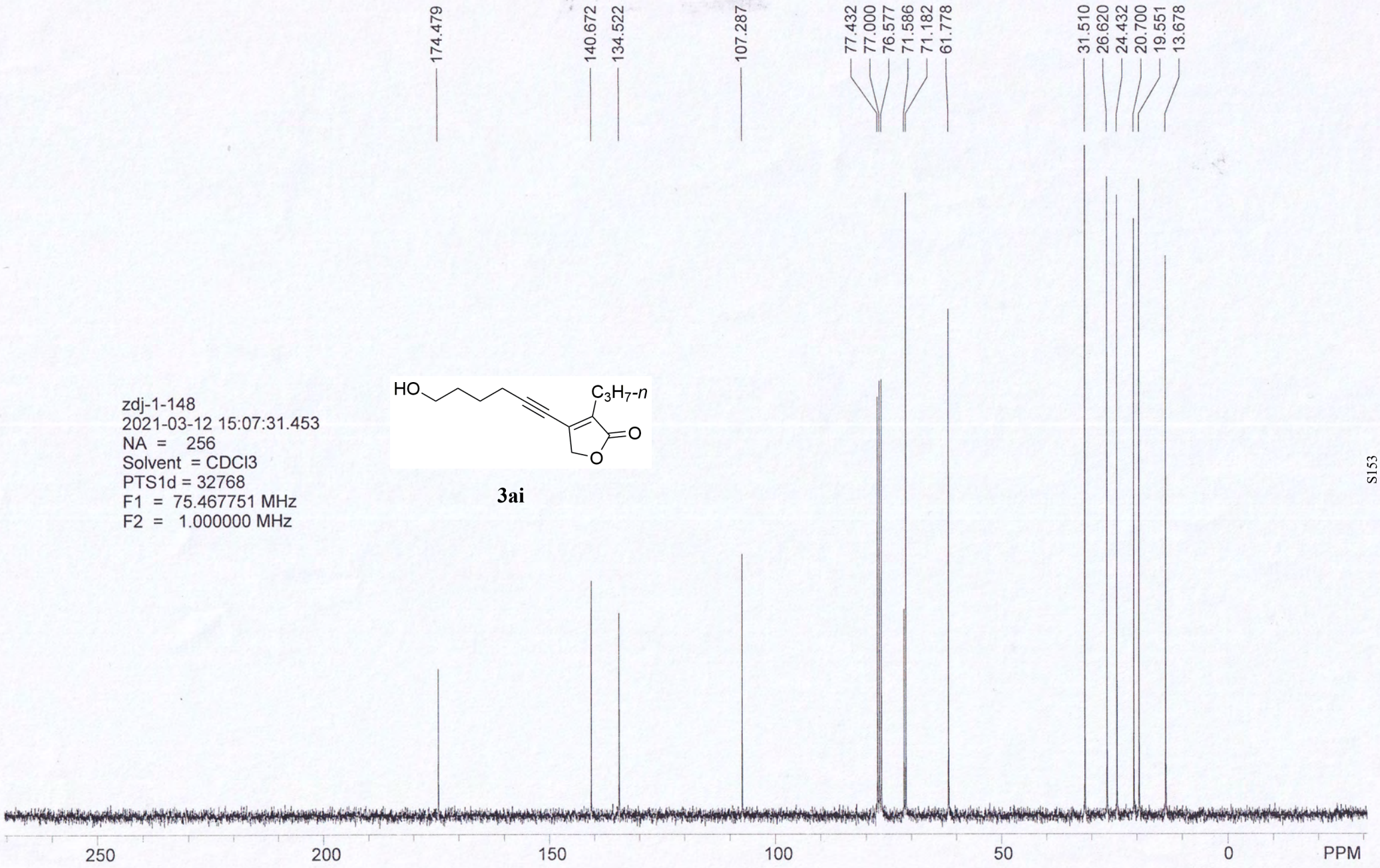
5


171.893
145.003
137.097
134.762
129.448
128.418
125.789
110.307
104.157
77.257
77.000
76.752
71.613
30.059
26.759
21.767
20.866
19.716
13.814
13.428
fjj-6-094
2022-04-12 05:59:17.827
SOLVENT: CDCl3
NA = 512
F1 = 125.757790 MHz
F2 = 1.000000 MHz
n-C4H9
C3H7-n
O
Ph
O
OH
250
200
150
100
50
PPM

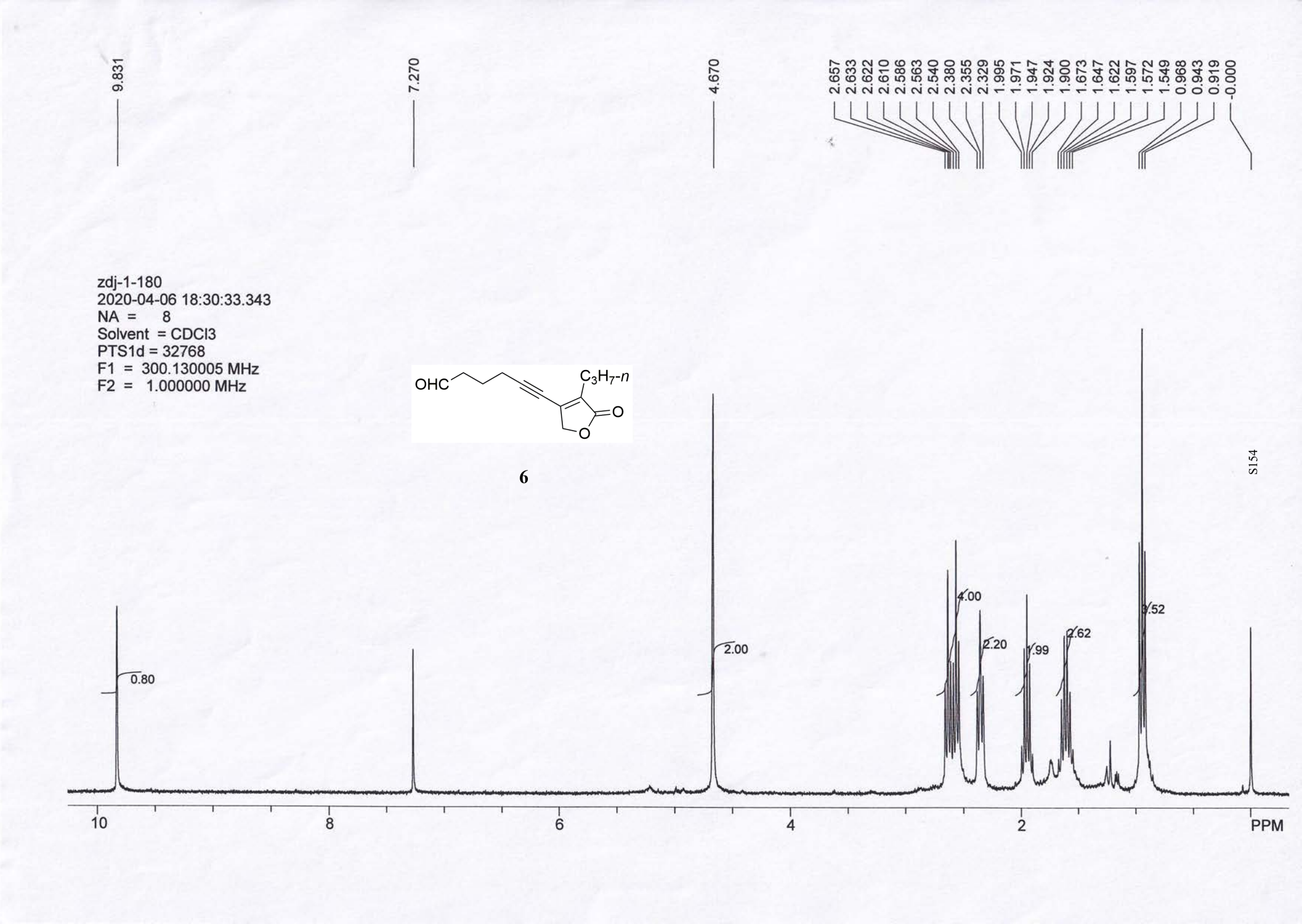
5

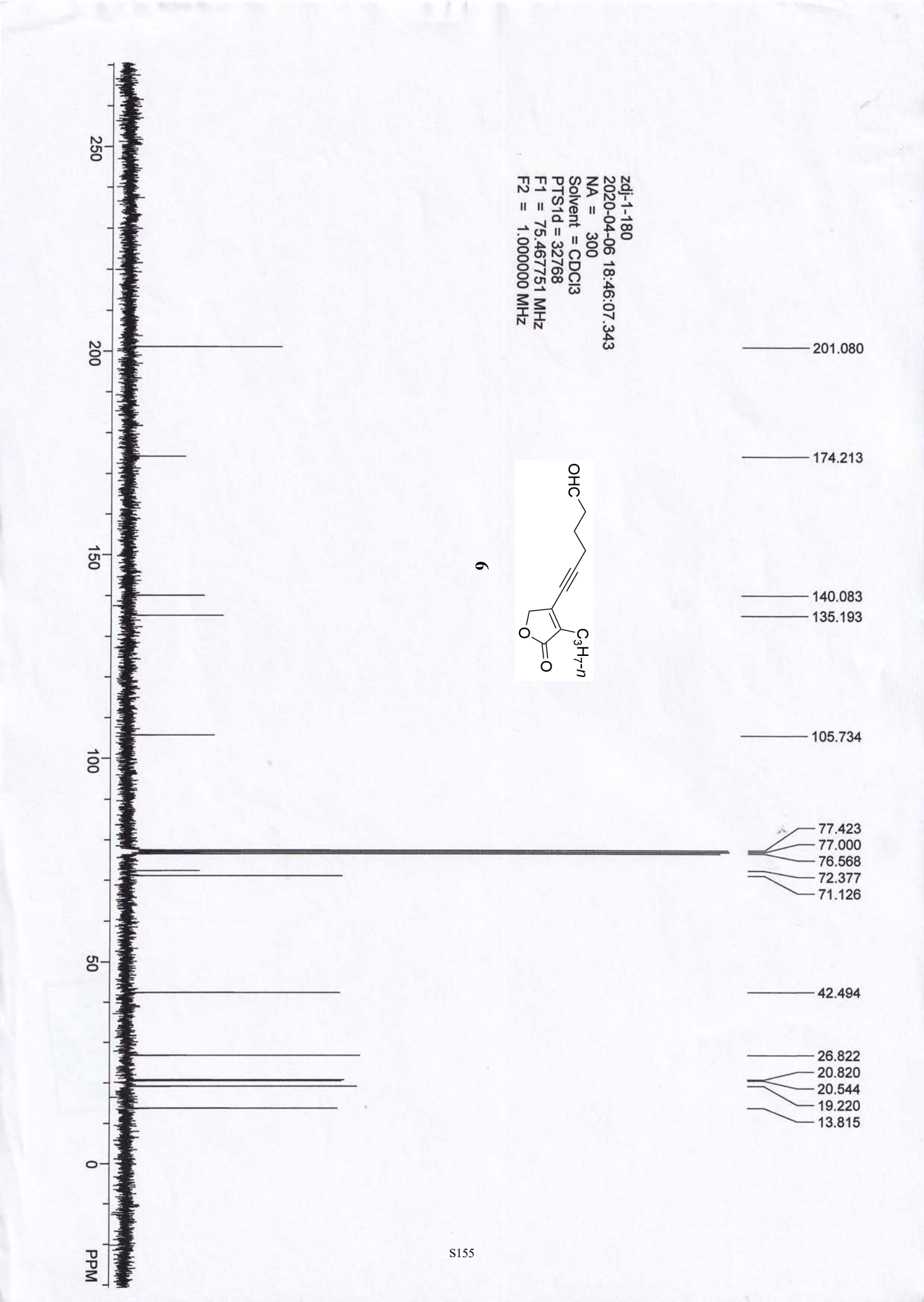

7.323
4.675
3.687
2.549
2.527
2.506
2.372
2.348
2.323
2.282
1.726
1.715
1.705
1.695
1.685
1.666
1.641
1.615
1.590
1.566
0.962
0.938
0.914
0.000
zdj-1-148
2021-03-12 14:49:56.062
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.129974 MHz
F2 = 1.000000 MHz
HO
C3H7-n
O
O
2.00
2.02
2.18
3.10
6.17
3.16
10
8
6
4
2
0
PPM

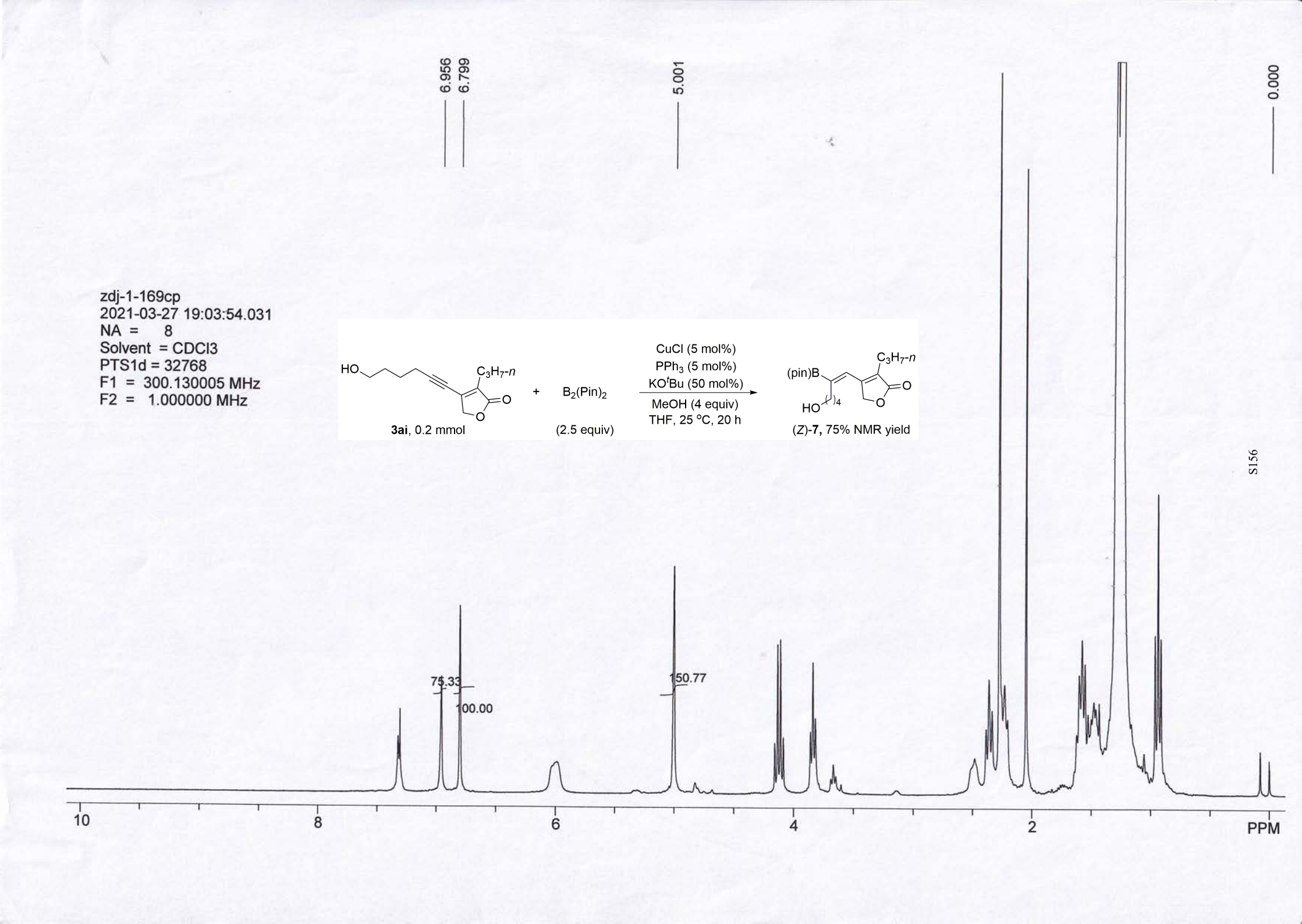
3ai

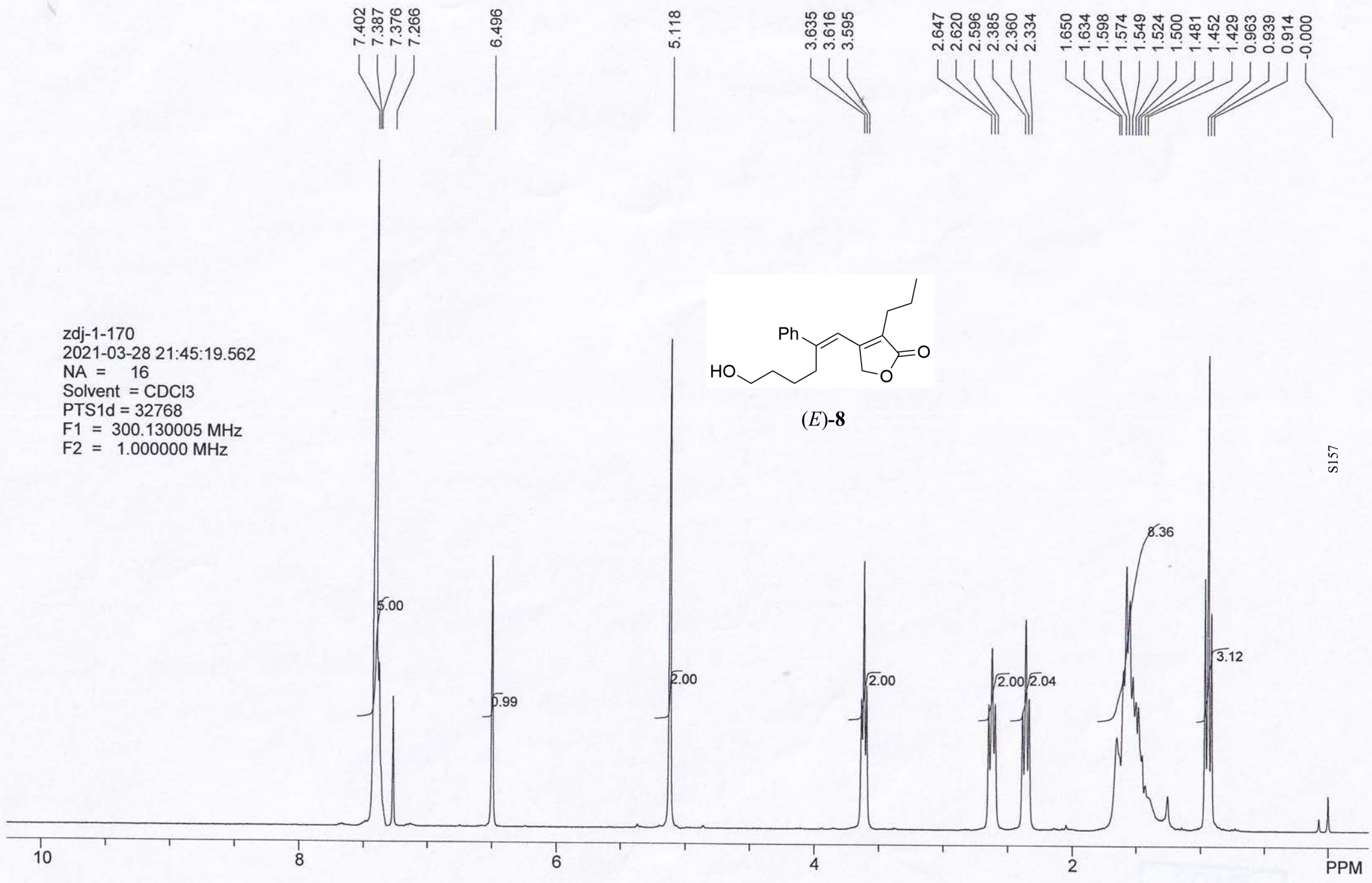

174.479
140.672
134.522
107.287
77.432
77.000
76.577
71.586
71.182
61.778
31.510
26.620
24.432
20.700
19.551
13.678
zdj-1-148
2021-03-12 15:07:31.453
NA = 256
Solvent = CDCl3
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
HO
C3H7-n
O
O
250
200
150
100
50
0
PPM

3ai

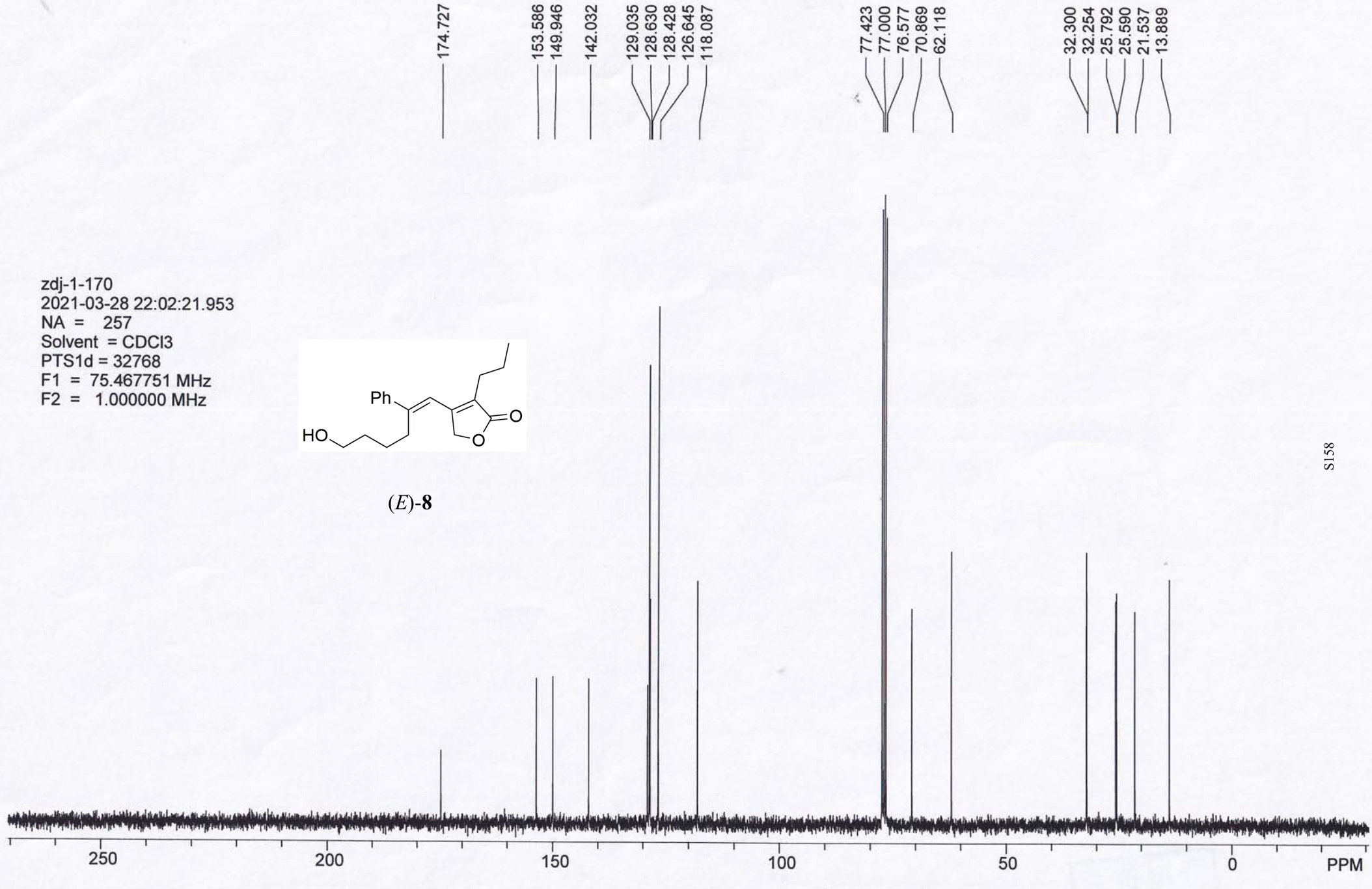

9.831
7.270
4.670
2.657
2.633
2.622
2.610
2.586
2.563
2.540
2.380
2.355
2.329
1.995
1.971
1.947
1.924
1.900
1.673
1.647
1.622
1.597
1.572
1.549
0.968
0.943
0.919
-0.000
zdj-1-180
2020-04-06 18:30:33.343
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
OHC
C_3H_7-*n*
O
O
6
0.80
2.00
4.00
2.20
1.99
2.62
3.52
10
8
6
4
2
PPM
S154


zdj-1-180
2020-04-06 18:46:07.343
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
6
OHC
O
O
O
C_3H_{7-n}
201.080
174.213
140.083
135.193
105.734
77.423
77.000
76.568
72.377
71.126
42.494
26.822
20.820
20.544
19.220
13.815
250
200
150
100
50
0
PPM

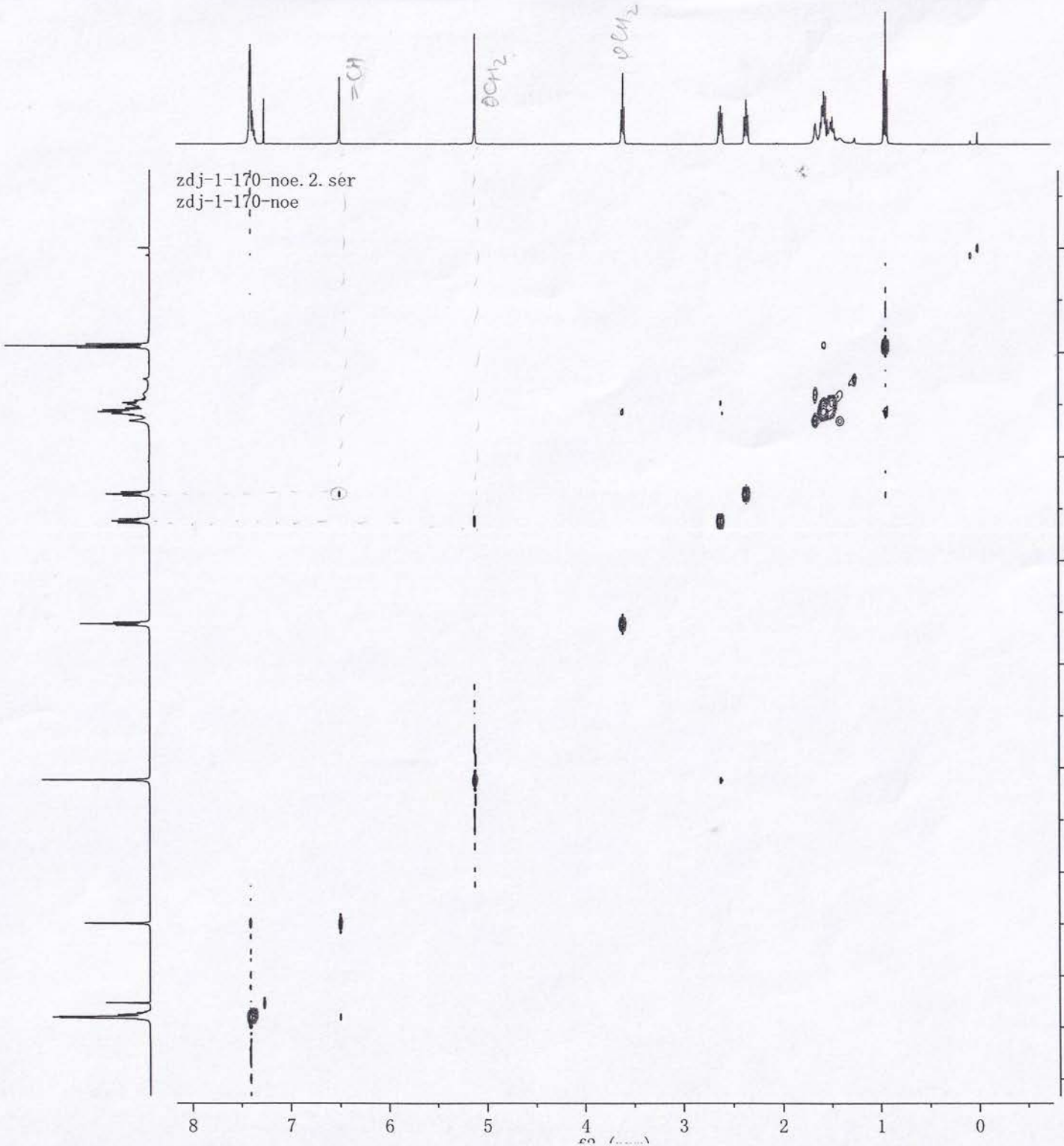

6.956
6.799
5.001
0.000
zdj-1-169cp
2021-03-27 19:03:54.031
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
HO
C_3H_7-n
O
O
3ai, 0.2 mmol
+
$B_2(Pin)_2$
(2.5 equiv)
CuCl (5 mol%)
PPh_3 (5 mol%)
KO^tBu (50 mol%)
MeOH (4 equiv)
THF, 25 °C, 20 h
(pin)B
HO
4
(Z)-7, 75% NMR yield
75.33
100.00
150.77
10
8
6
4
2
PPM

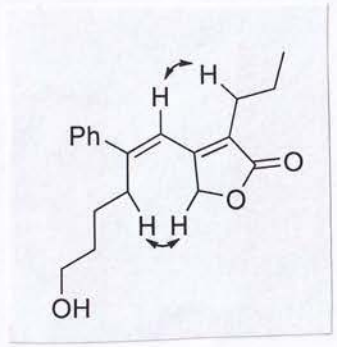

7.402
7.387
7.376
7.266
6.496
5.118
3.635
3.616
3.595
2.647
2.620
2.596
2.385
2.360
2.334
1.650
1.634
1.598
1.574
1.549
1.524
1.500
1.481
1.452
1.429
0.963
0.939
0.914
-0.000
zdj-1-170
2021-03-28 21:45:19.562
NA = 16
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Ph
HO
O
O
5.00
0.99
2.00
2.00
2.00
2.04
8.36
3.12
10
8
6
4
2
PPM

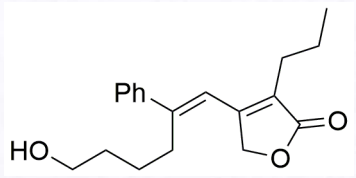
(*E*)-**8**


174.727
153.586
149.946
142.032
129.035
128.630
128.428
126.645
118.087
77.423
77.000
76.577
70.869
62.118
32.300
32.254
25.792
25.590
21.537
13.889
zdj-1-170
2021-03-28 22:02:21.953
NA = 257
Solvent = CDCl3
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
Ph
HO
O
O
250
200
150
100
50
0
PPM

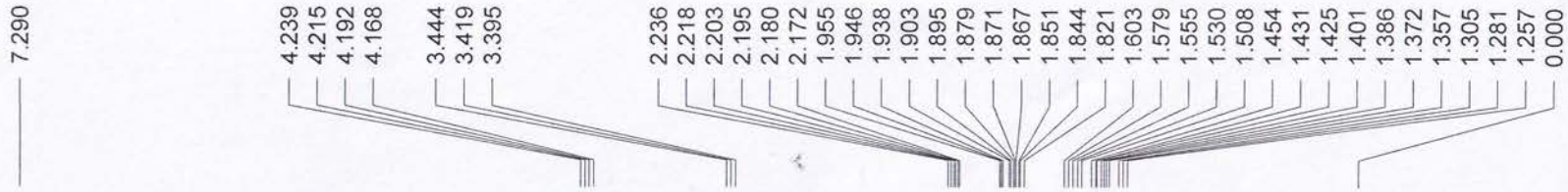
(*E*)-**8**


zdj-1-170-noe.2.ser
zdj-1-170-noe
=CH
OCH2
φCH2
f1 (ppm)
f2 (ppm)

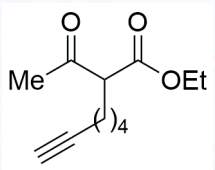

H
H
Ph
O
O
H H
OH


Ph
HO
O
O

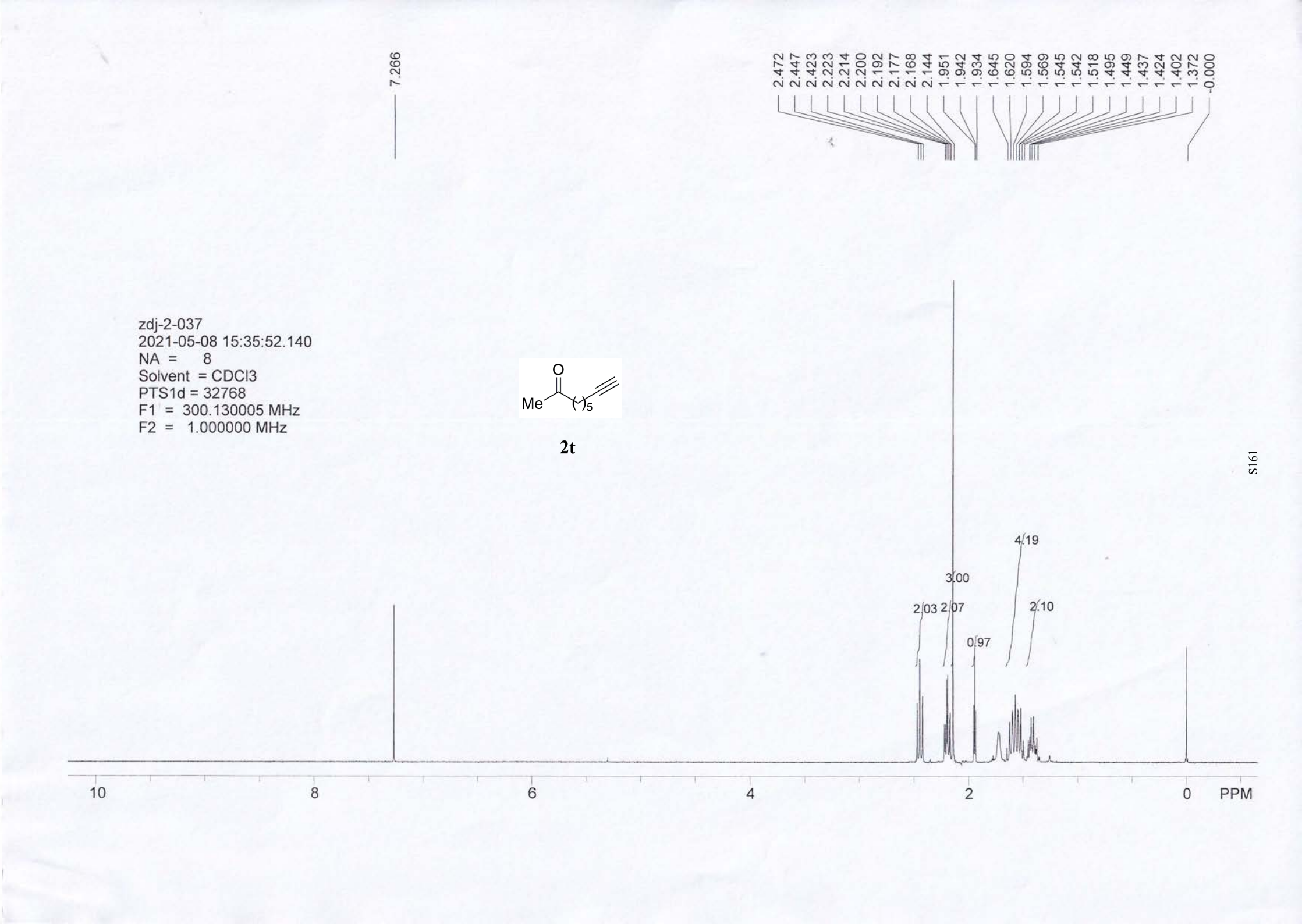
(*E*)-**8**

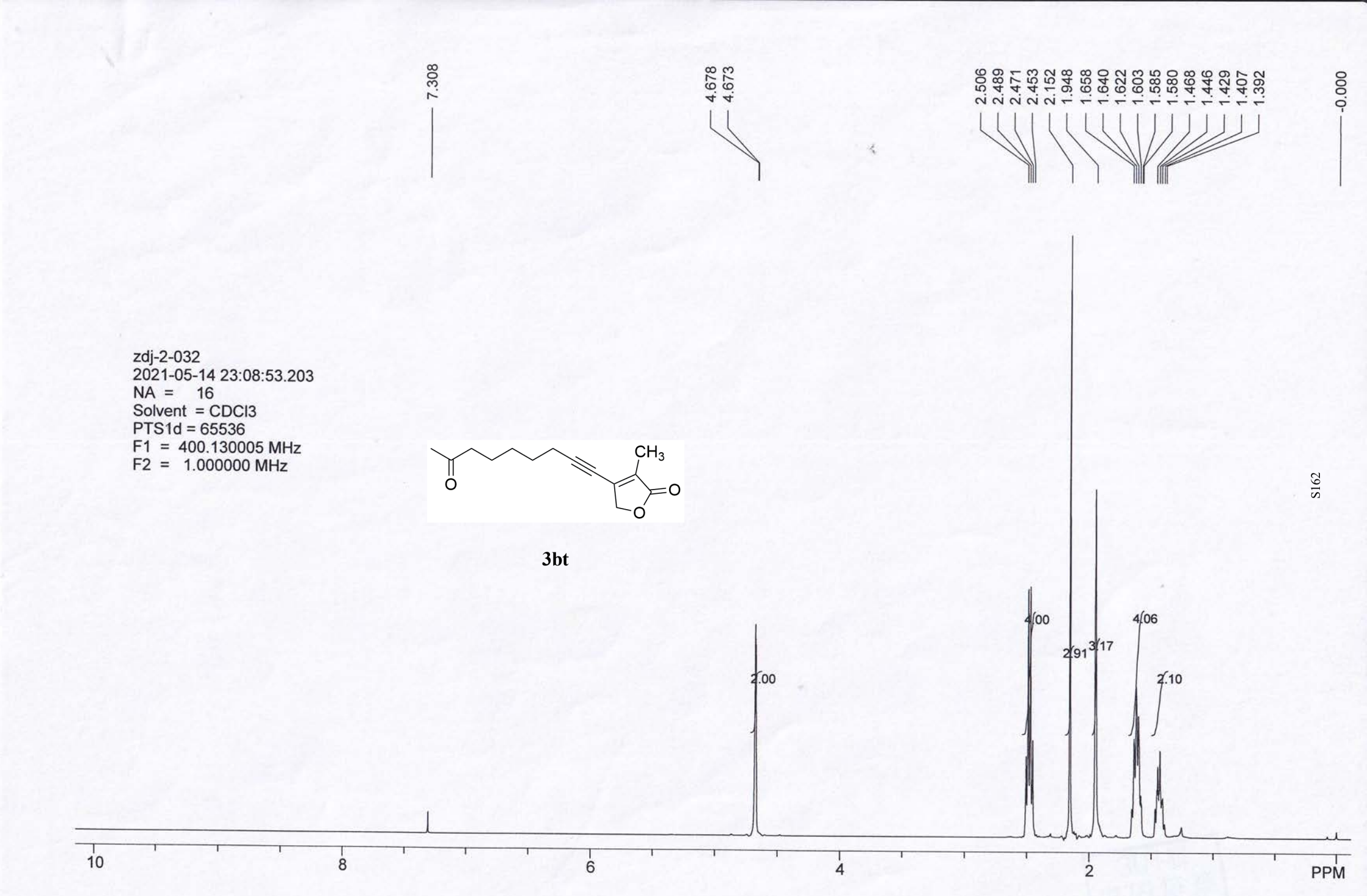


zdj-2-035
2021-05-15 21:53:25.000
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

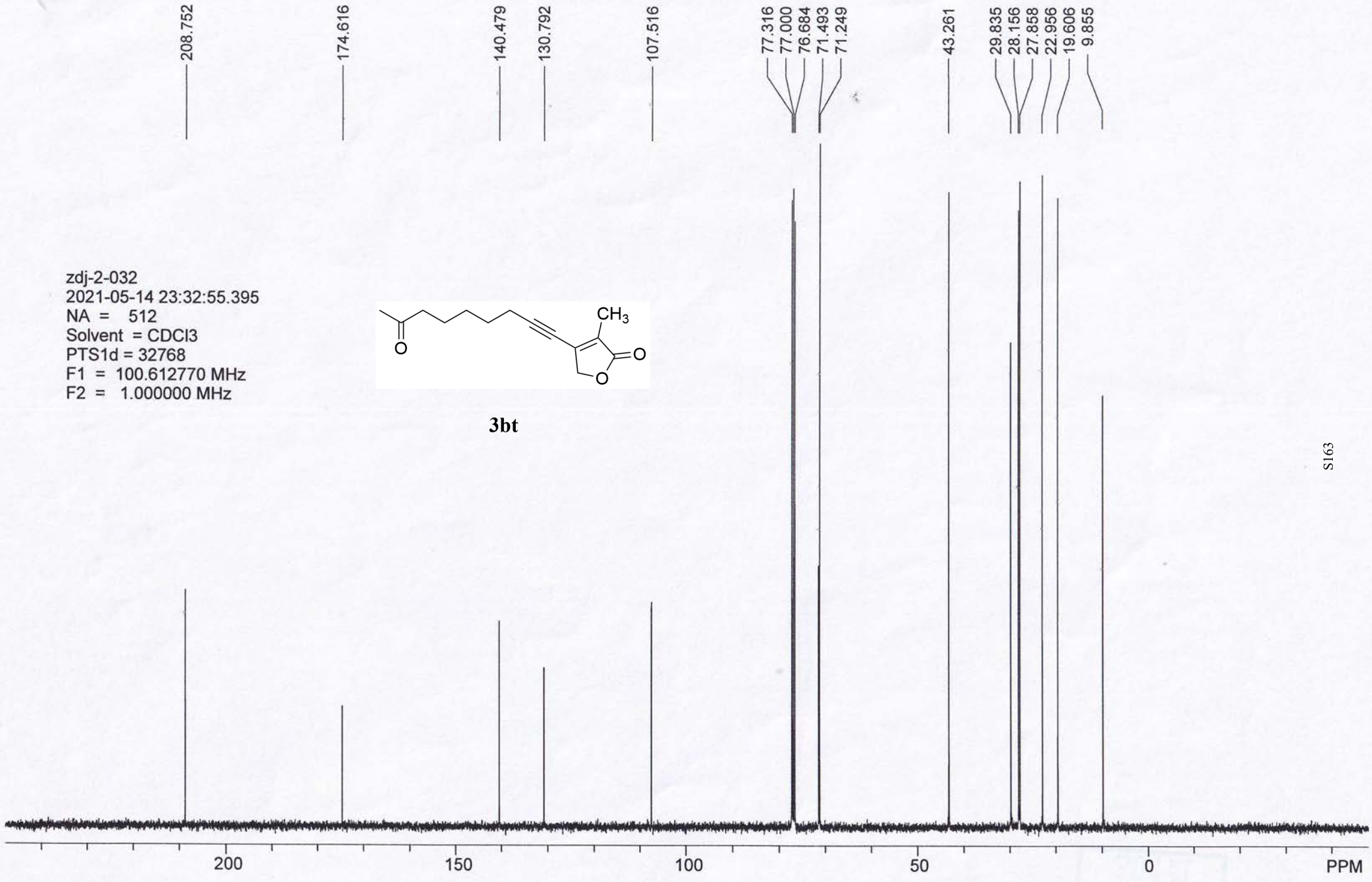


11


7.266
2.472
2.447
2.423
2.223
2.214
2.200
2.192
2.177
2.168
2.144
1.951
1.942
1.934
1.645
1.620
1.594
1.569
1.545
1.542
1.518
1.495
1.449
1.437
1.424
1.402
1.372
-0.000
zdj-2-037
2021-05-08 15:35:52.140
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
O
Me
5
2t
4.19
3.00
2.03
2.07
2.10
0.97
10
8
6
4
2
0
PPM

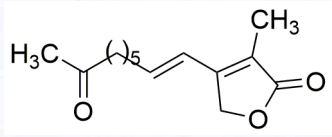

7.308
4.678
4.673
2.506
2.489
2.471
2.453
2.152
1.948
1.658
1.640
1.622
1.603
1.585
1.580
1.468
1.446
1.429
1.407
1.392
-0.000
zdj-2-032
2021-05-14 23:08:53.203
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
CH3
O
O
O
2.00
4.00
2.91
3.17
4.06
2.10
10
8
6
4
2
PPM

3bt

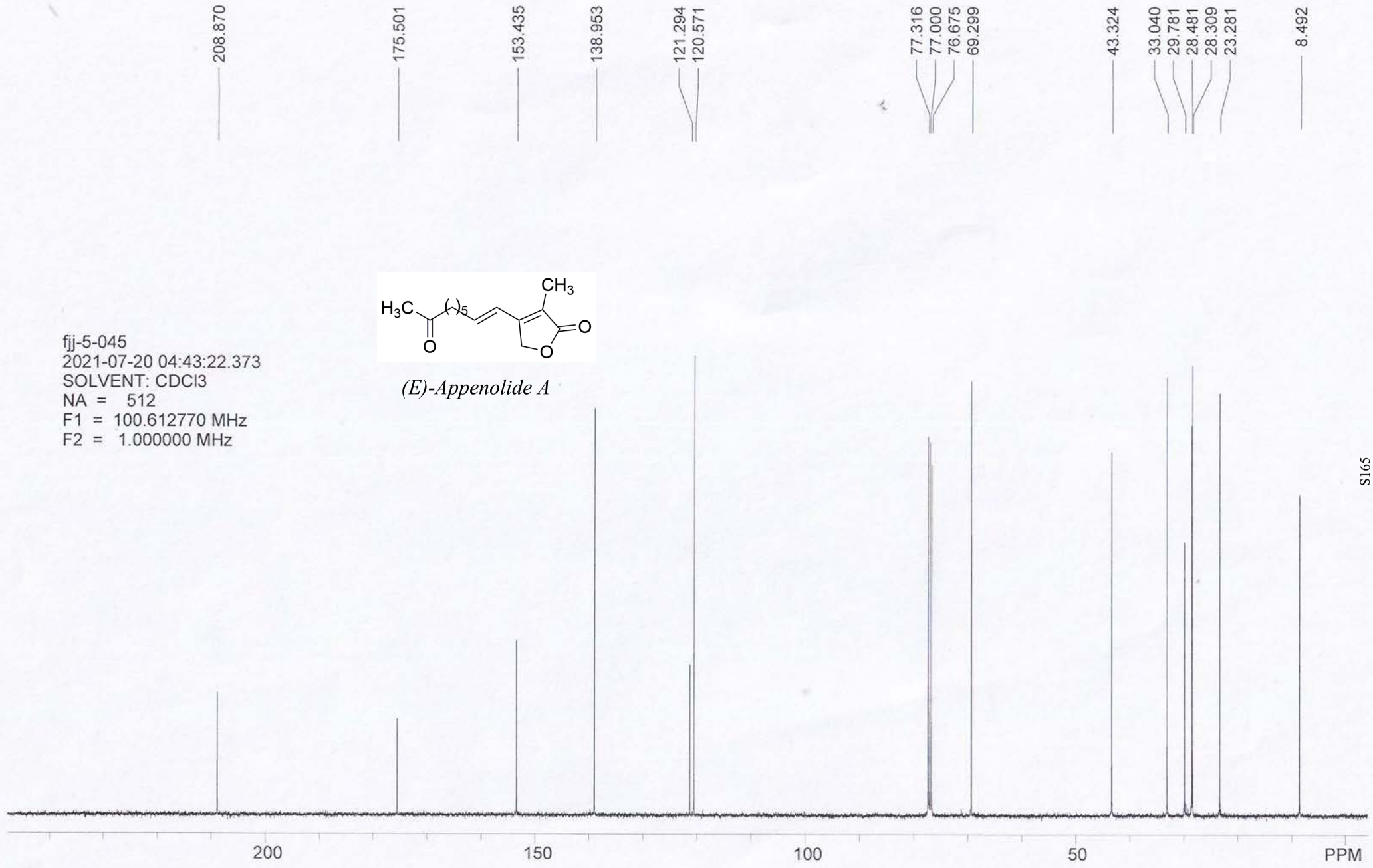

208.752
174.616
140.479
130.792
107.516
77.316
77.000
76.684
71.493
71.249
43.261
29.835
28.156
27.858
22.956
19.606
9.855
zdj-2-032
2021-05-14 23:32:55.395
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
CH3
O
O
O
200
150
100
50
0
PPM

3bt

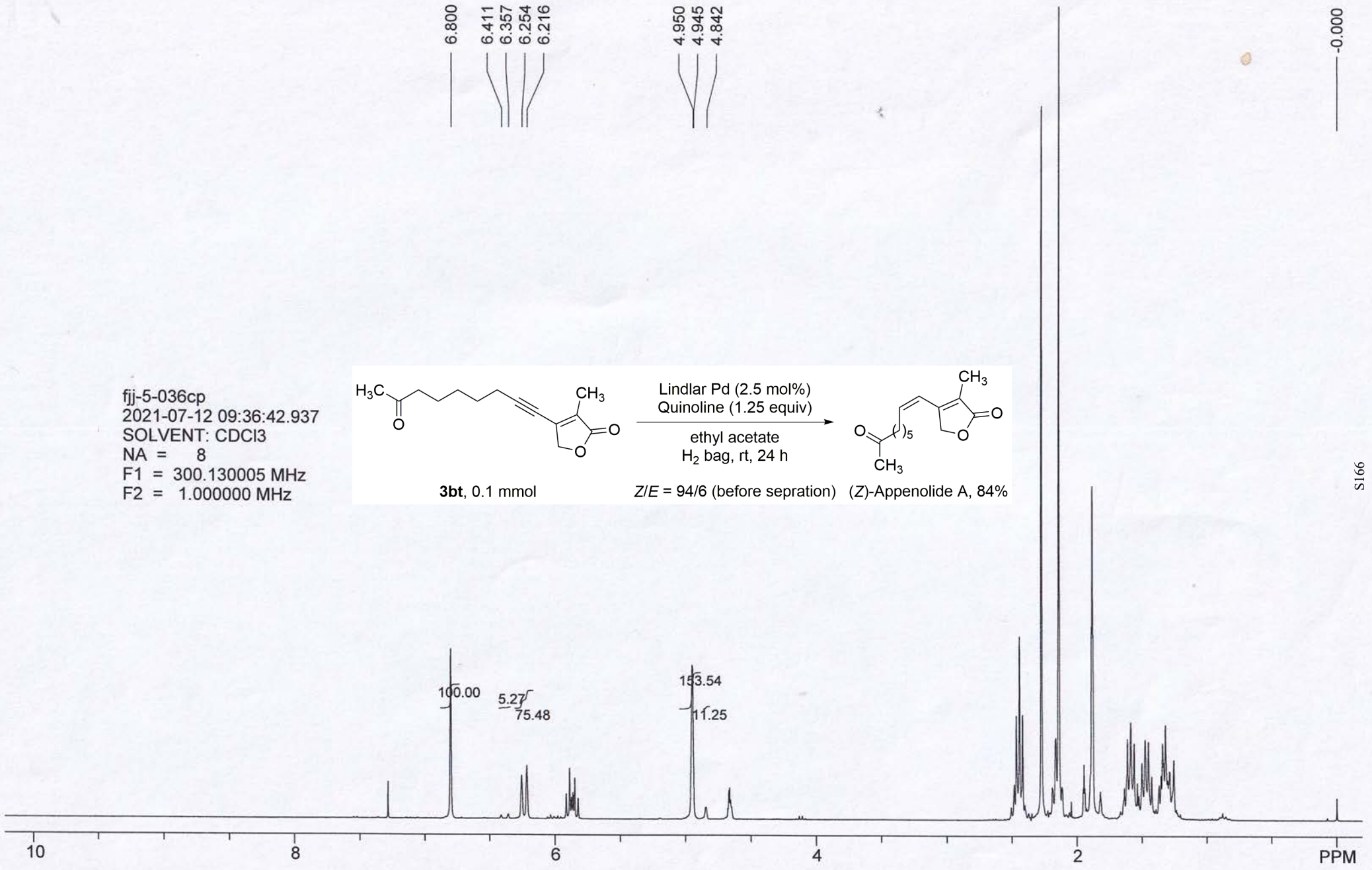
fjj-5-045
2021-07-20 04:19:15.923
SOLVENT: CDCl3
NA = 16
F1 = 400.129974 MHz
F2 = 1.000000 MHz

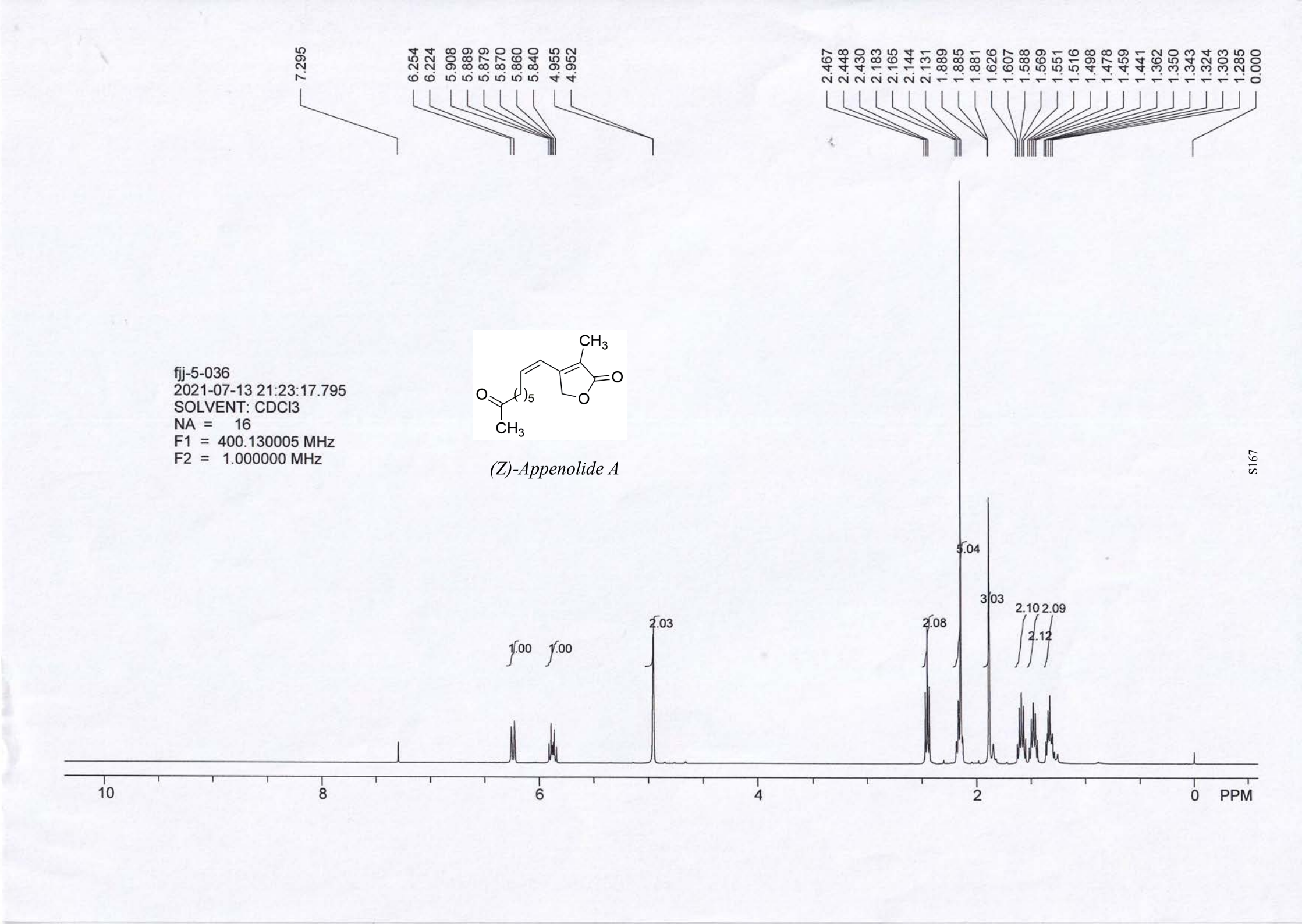


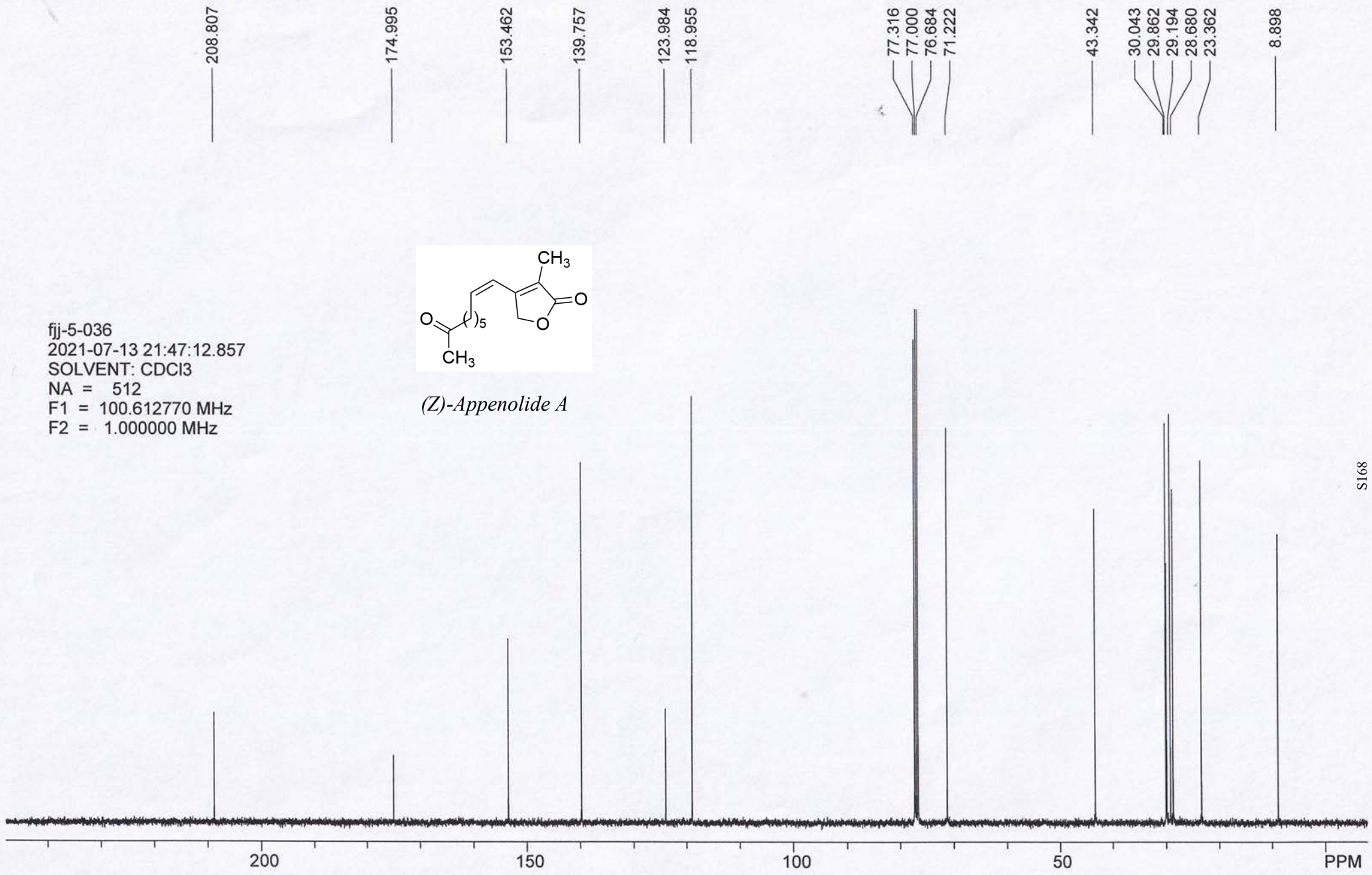
(*E*)-*Appenolide A*



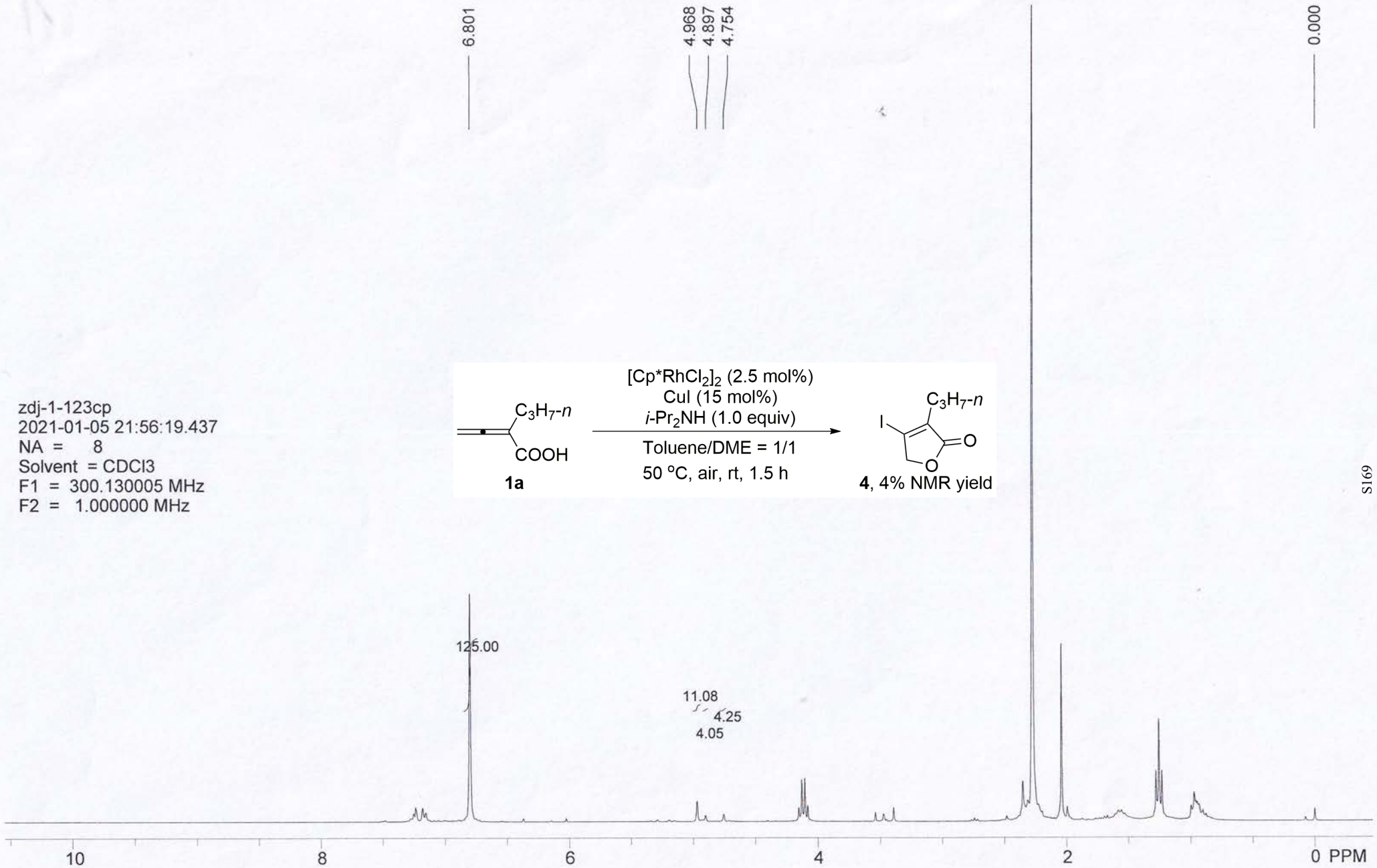
(E)-Appenolide A

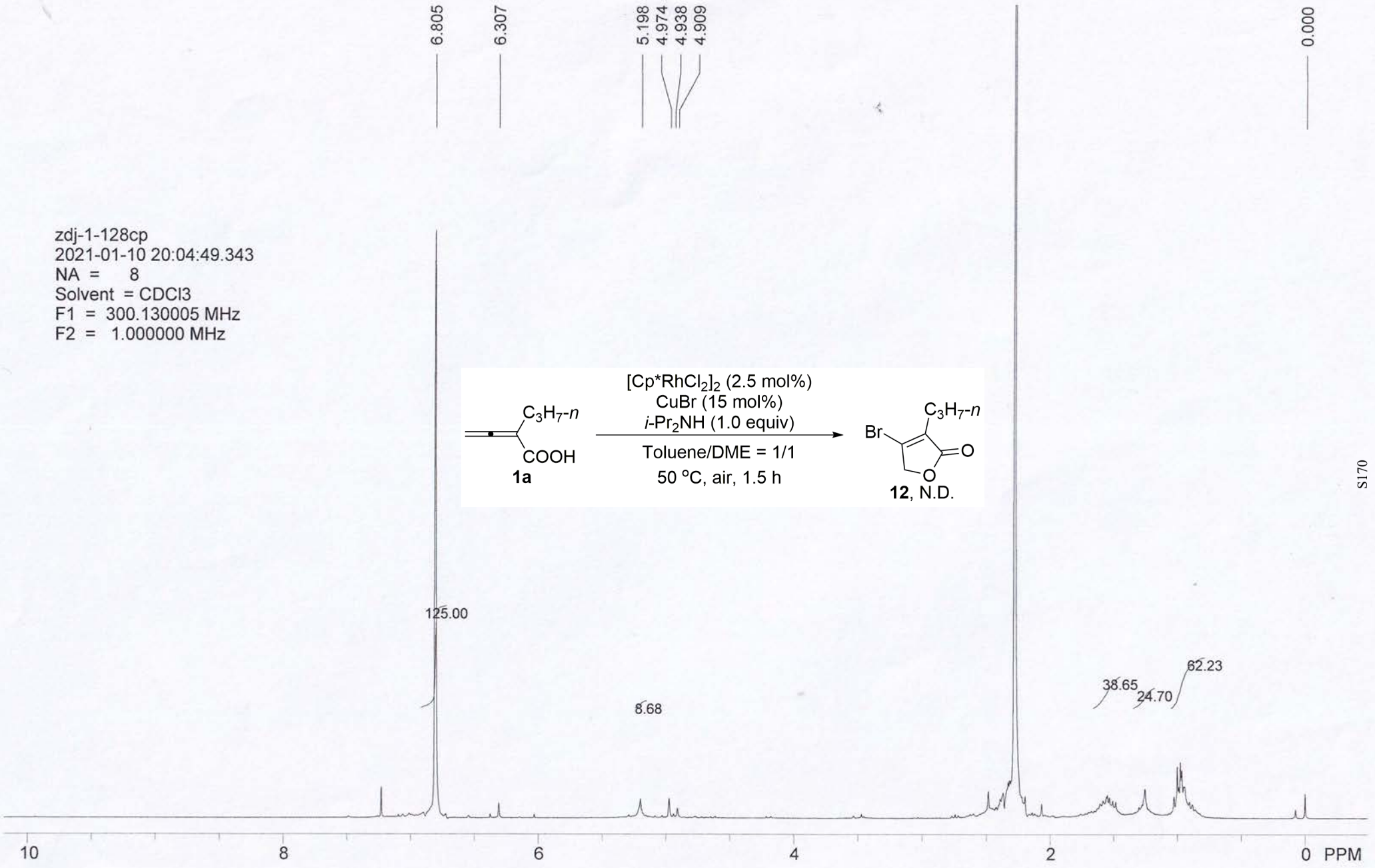

6.800
6.411
6.357
6.254
6.216
4.950
4.945
4.842
-0.000
fjj-5-036cp
2021-07-12 09:36:42.937
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
H3C
O
CH3
O
O
Lindlar Pd (2.5 mol%)
Quinoline (1.25 equiv)
ethyl acetate
H2 bag, rt, 24 h
3bt, 0.1 mmol
Z/E = 94/6 (before sepration)
CH3
O
O
)5
O
CH3
(Z)-Appenolide A, 84%
100.00
5.27
75.48
153.54
11.25
10
8
6
4
2
PPM

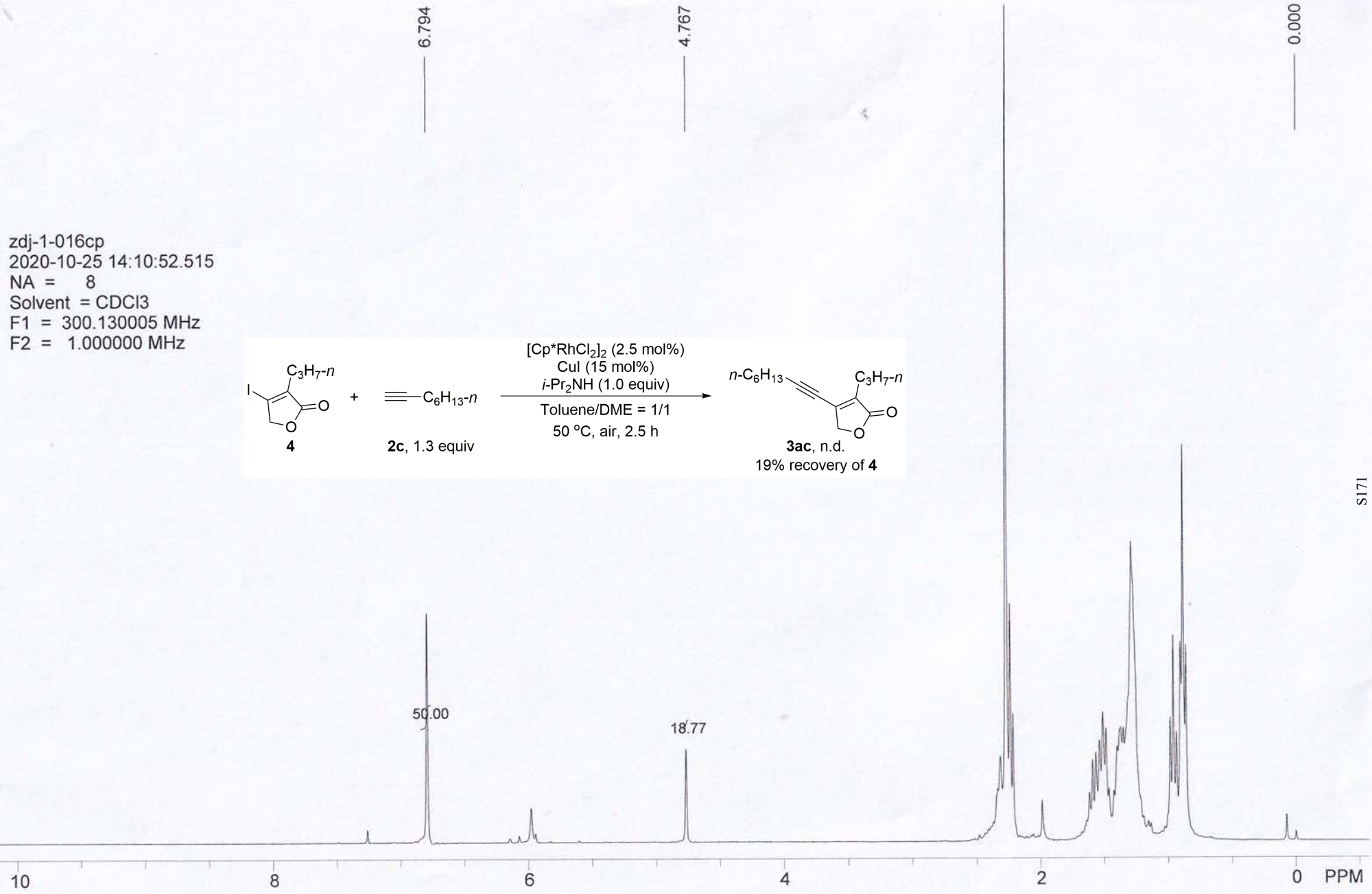

7.295
6.254
6.224
5.908
5.889
5.879
5.870
5.860
5.840
4.955
4.952
2.467
2.448
2.430
2.183
2.165
2.144
2.131
1.889
1.885
1.881
1.626
1.607
1.588
1.569
1.551
1.516
1.498
1.478
1.459
1.441
1.362
1.350
1.343
1.324
1.303
1.285
0.000
fjj-5-036
2021-07-13 21:23:17.795
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
CH3
O
O
O
5
CH3
(Z)-Appenolide A
S167
1.00
1.00
2.03
2.08
5.04
3.03
2.10
2.09
2.12
10
8
6
4
2
0
PPM

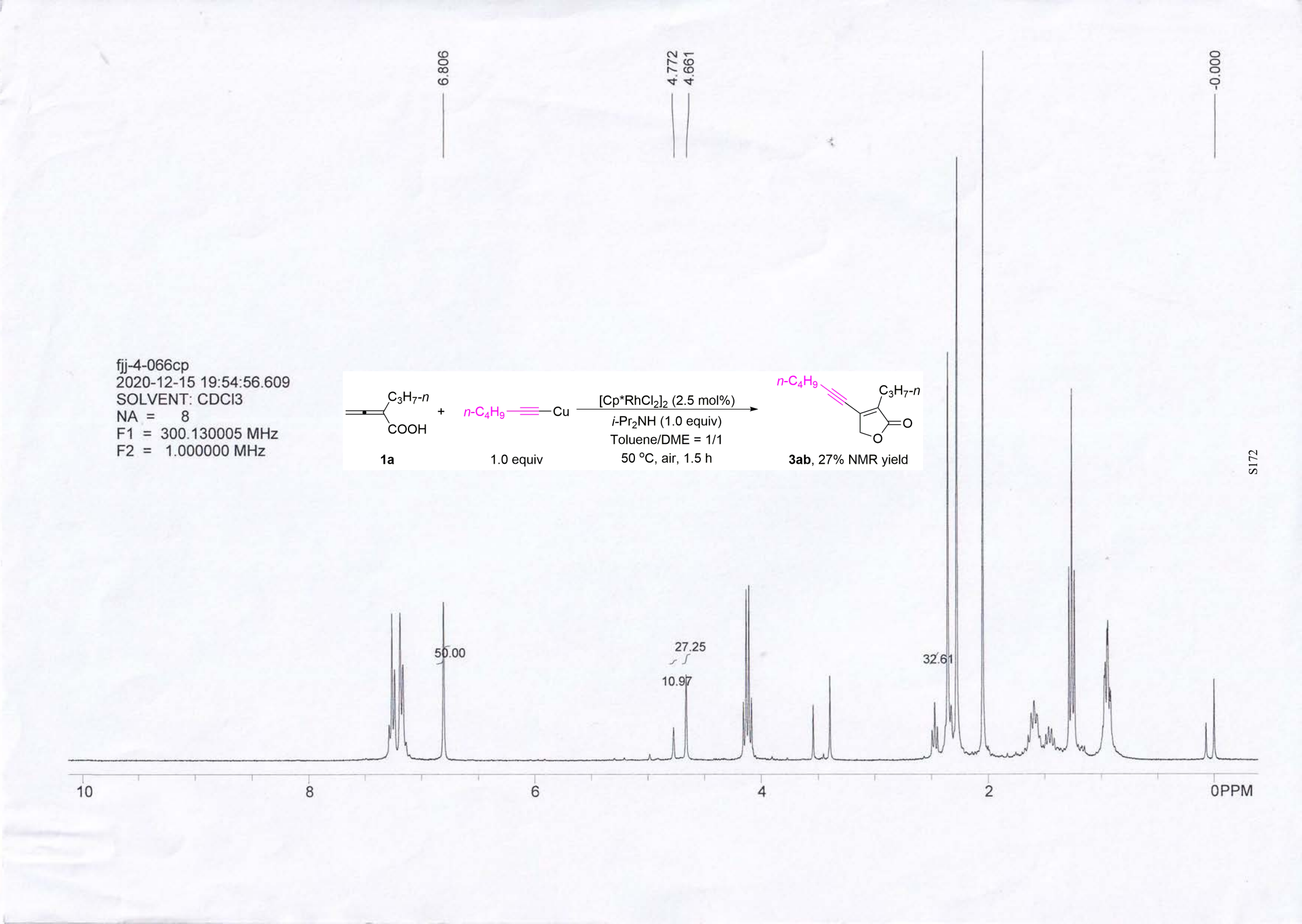


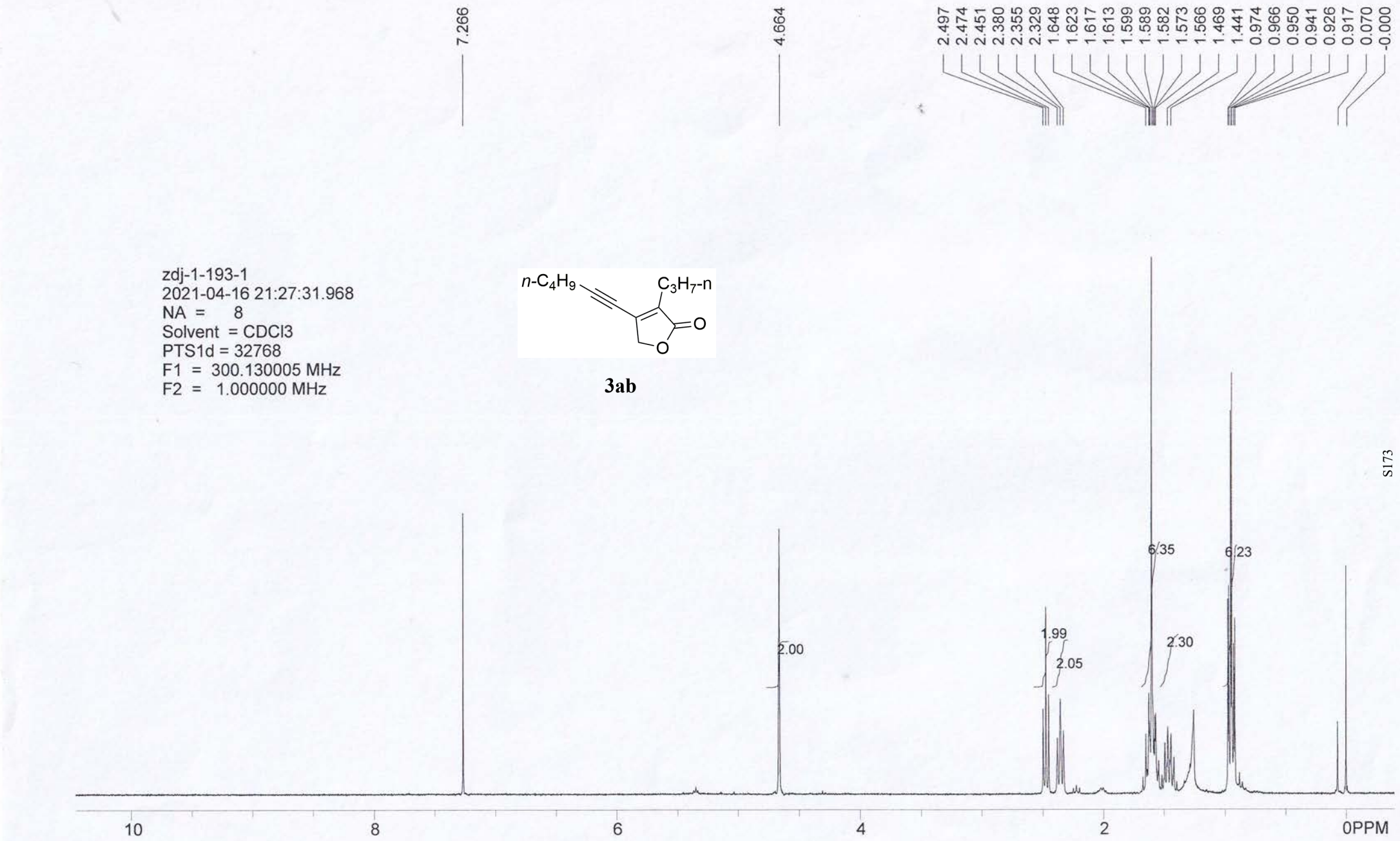
(Z)-Appenolide A

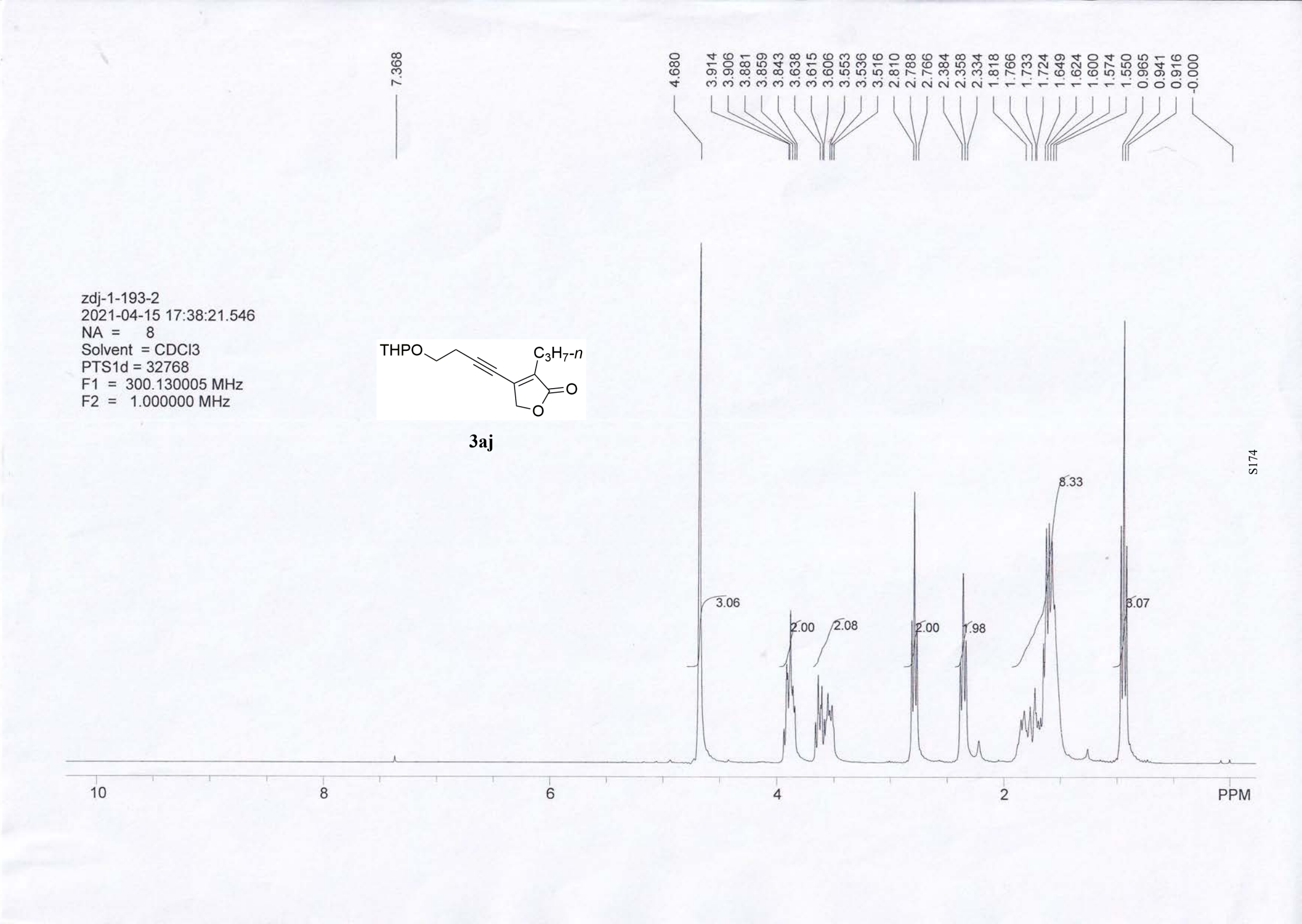

6.801
4.968
4.897
4.754
0.000
zdj-1-123cp
2021-01-05 21:56:19.437
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C3H7-n
COOH
1a
[Cp*RhCl2]2 (2.5 mol%)
CuI (15 mol%)
i-Pr2NH (1.0 equiv)
Toluene/DME = 1/1
50 °C, air, rt, 1.5 h
C3H7-n
I
O
O
4, 4% NMR yield
125.00
11.08
4.25
4.05
10
8
6
4
2
0 PPM


6.805
6.307
5.198
4.974
4.938
4.909
0.000
zdj-1-128cp
2021-01-10 20:04:49.343
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
[Cp*RhCl2]2 (2.5 mol%)
CuBr (15 mol%)
i-Pr2NH (1.0 equiv)
Toluene/DME = 1/1
50 °C, air, 1.5 h
C3H7-n
COOH
1a
Br
O
O
12, N.D.
125.00
8.68
38.65
24.70
62.23
10
8
6
4
2
0 PPM


6.794
4.767
0.000
zdj-1-016cp
2020-10-25 14:10:52.515
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C_3H_7-n
I
O
O
4
+
C_6H_{13}-n
2c, 1.3 equiv
[Cp*RhCl2]2 (2.5 mol%)
CuI (15 mol%)
i-Pr2NH (1.0 equiv)
Toluene/DME = 1/1
50 °C, air, 2.5 h
n-C_6H_{13}
C_3H_7-n
O
O
3ac, n.d.
19% recovery of 4
50.00
18.77
10
8
6
4
2
0
PPM


6.806
4.772
4.661
-0.000
fjj-4-066cp
2020-12-15 19:54:56.609
SOLVENT: CDCl3
NA = 8
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C3H7-n
COOH
1a
+
n-C4H9
Cu
1.0 equiv
[Cp*RhCl2]2 (2.5 mol%)
i-Pr2NH (1.0 equiv)
Toluene/DME = 1/1
50 °C, air, 1.5 h
n-C4H9
C3H7-n
O
O
3ab, 27% NMR yield
S172
50.00
27.25
10.97
32.61
10
8
6
4
2
0PPM


7.266
4.664
2.497
2.474
2.451
2.380
2.355
2.329
1.648
1.623
1.617
1.613
1.599
1.589
1.582
1.573
1.566
1.469
1.441
0.974
0.966
0.950
0.941
0.926
0.917
0.070
-0.000
zdj-1-193-1
2021-04-16 21:27:31.968
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
n-C4H9
C3H7-n
O
O
3ab
S173
2.00
1.99
2.05
6.35
2.30
6.23
10
8
6
4
2
0PPM


7.368
4.680
3.914
3.906
3.881
3.859
3.843
3.638
3.615
3.606
3.553
3.536
3.516
2.810
2.788
2.766
2.384
2.358
2.334
1.818
1.766
1.733
1.724
1.649
1.624
1.600
1.574
1.550
0.965
0.941
0.916
-0.000
zdj-1-193-2
2021-04-15 17:38:21.546
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
THPO
C3H7-n
O
O
3aj
3.06
2.00
2.08
2.00
1.98
8.33
3.07
10
8
6
4
2
PPM
S174