Pd-Catalyzed Highly Selective Three-Component Protocol for Trisubstituted Allenes

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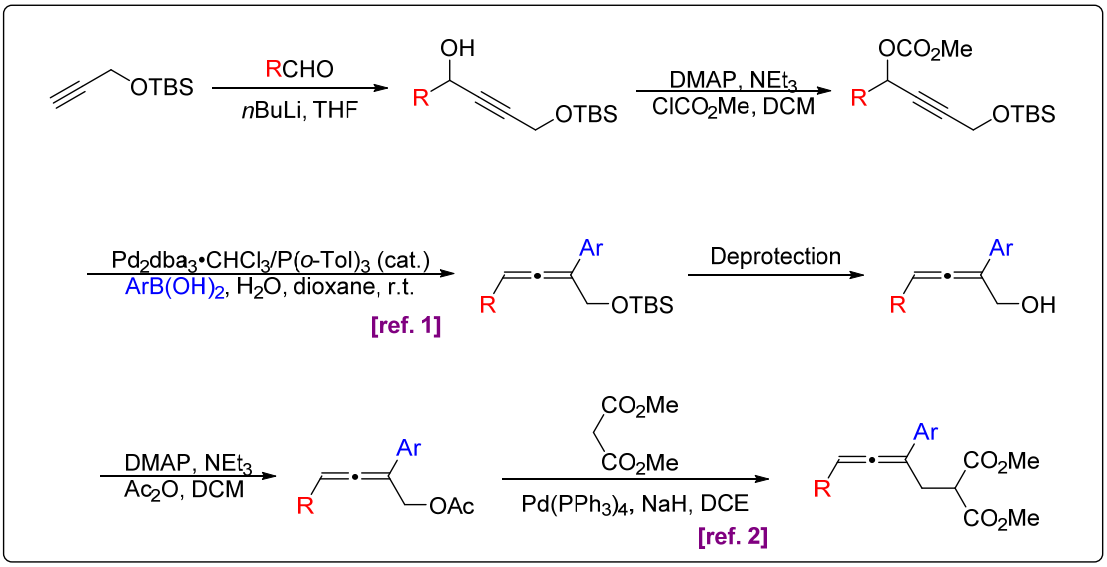
General Information

NMR spectra were taken with Agilent, Varian Mercury, or Bruker 400 MHz NMR spectrometer (400 MHz for ^{1}H NMR; 100 MHz for ^{13}C NMR; 376 MHz for ^{19}F NMR). All ^{1}H NMR experiments were measured with tetramethylsilane (0 ppm) in $CDCl_3$ as the internal reference; ^{13}C NMR experiments were measured in relative to the signal of $CDCl_3$ (77.0 ppm); ^{19}F NMR experiments were measured in relative to the signal of $CFCl_3$ (0 ppm) in $CDCl_3$. $[Pd(allyl)Cl]_2$ was purchased from Bidepharm and J&K. SPhos was purchased from Bidepharm and Strem Chemicals. Petroleum ether (b.p. 60~90 ^{o}C), ethyl acetate, and dichloromethane were purchased from Shanghai Titan Scientific Co. Ltd. THF and toluene were dried over sodium wire with benzophenone as the indicator and distilled freshly before use. Other reagents were all commercially available and used as received without further purification. All the temperatures are referred to the oil baths used.



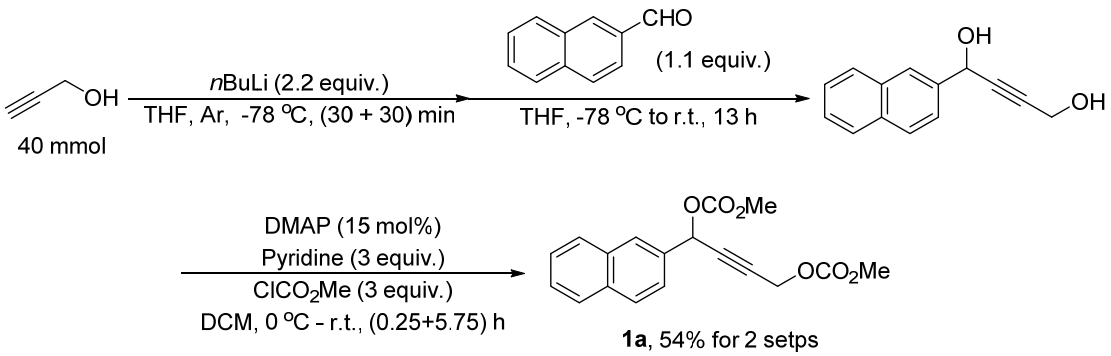
Scheme S1. The traditional protocol for the synthesis of the trisubstituted allenyl malonates.[1-2]

Experimental details and analytical data

1. Synthesis of 2-alkynyl-1,4-diol dicarbonate

Compound **1b** was synthesized according to the reported procedure.[3]

(1) Dimethyl 1-(2-naphthyl)but-2-yn-1,4-diyl dicarbonate **1a** [3] (lican-05-077)

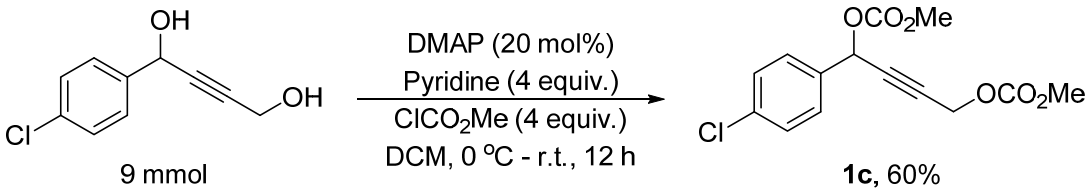


Typical Procedure I: To a solution of propargyl alcohol (2.32 mL, d = 0.963 g/mL, 2.2342 g, 40 mmol) in THF (60 mL) was added dropwise *n*BuLi (2.5 M in hexane, 35.2 mL, 88 mmol) at -78 °C within 30 minutes. After lithiation for 30 minutes at -78 °C, a solution of 2-naphthaldehyde (6.8714 g, 44 mmol) in THF (40 mL) was added dropwise at -78 °C within 10 minutes. The resulting mixture was stirred for 13 h while gradually warming up to room temperature, quenched with NH_4Cl (aq., 50 mL), and extracted with ethyl acetate (50 mL × 3). The combined organic extract layer was washed with brine (50 mL × 3) and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was used in the next step without further purification.

Typical Procedure II: To a three-neck flask were added the above residue, CH_2Cl_2 (100 mL), DMAP (0.7371 g, 6 mmol), and pyridine (9.7 mL, d = 0.983 g/mL, 9.5351 g, 121 mmol) sequentially. The resulting mixture was stirred at 0 °C and then methyl chloroformate (9.3 mL, d = 1.22 g/mL, 11.3460 g, 120 mmol) was added dropwise within 15 min at 0 °C. After the addition, the resulting mixture was stirred for 5.75 h while gradually warming up to room temperature. After the reaction was complete as monitored by TLC, it was quenched with a saturated solution of NH_4Cl (aq., 50 mL). The aqueous phase was extracted with CH_2Cl_2 (50 mL × 3). The

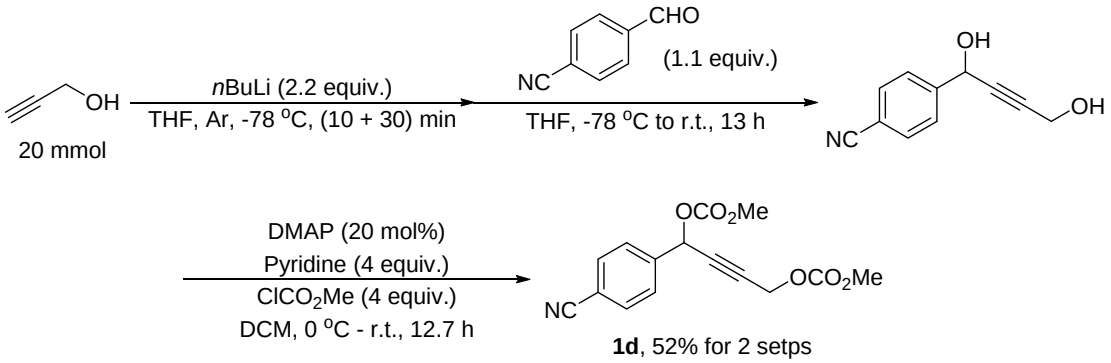
combined organic layer was washed with brine (50 mL × 3) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, chromatography on silica gel (eluent: petroleum ether / CH_2Cl_2 = 1/1 (2400 mL)) afforded **1a** (7.0411 g, 54% for 2 steps) as a yellowish solid: **m.p.** 68.0-69.2 °C (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (s, 1 H, ArH), 7.91-7.78 (m, 3 H, ArH), 7.61 (d, *J* = 8.0 Hz, 1 H, ArH), 7.55-7.45 (m, 2 H, ArH), 6.50 (s, 1 H, CH), 4.84 (s, 2 H, CH_2), 3.79 (s, 6 H, 2 × OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.1, 154.7, 133.5, 133.0, 132.9, 128.7, 128.3, 127.7, 127.2, 126.8, 126.5, 124.8, 83.3, 81.8, 69.5, 55.4, 55.2, 55.1; **IR** (neat): ν 2963, 2858, 1744, 1442, 1376, 1327, 1245, 1140, 935 cm^{-1}; **Raman**: ν 3057, 2963, 2939, 2289, 2223, 1750, 1634, 1577, 1470, 1389, 1328, 1176, 1105, 1020 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 328 (M^+, 7.48), 165 (100); **Elem. Anal.** Calcd. for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91, found C, 65.64; H, 4.91.

(2) Dimethyl 1-(4-chlorophenyl)but-2-yn-1,4-diyl dicarbonate **1c**[3] (zzn-1-047)



Following the **Typical Procedure II**, the reaction of 1-(4-chlorophenyl)but-2-yn-1,4-diol (1.7640 g, 9 mmol), CH_2Cl_2 (40 mL), DMAP (220.4 mg, 1.8 mmol), pyridine (2.9 mL, d = 0.983 g/mL, 2.85 g, 36 mmol) and methyl chloroformate (2.8 mL, d = 1.22 g/mL, 3.4160 g, 36 mmol) afforded **1c** (1.6868 g, 60%) (eluent: petroleum ether / ethyl acetate = 6/1 (1400 mL)) as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47-7.44 (m, 2 H, ArH), 7.36-7.34 (m, 2 H, ArH), 6.30 (s, 1 H, CH), 4.82 (d, *J* = 1.6 Hz, 2 H, CH_2), 3.81 (m, 6 H, 2 × OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.0, 154.5, 135.2, 134.2, 129.1, 128.9, 82.7, 81.8, 68.5, 55.2, 55.1; **IR** (neat): ν 3007, 2959, 2855, 1746, 1597, 1493, 1442, 1374, 1242 cm^{-1}; **MS** (ESI) *m/z* 335.0 [M(^{35}Cl)+Na]$^+$; **HRMS** (ESI) Calcd for $C_{14}H_{13}O_6{}^{35}ClNa$ [M(^{35}Cl)+Na]$^+$: 335.0293, Found: 335.0291.

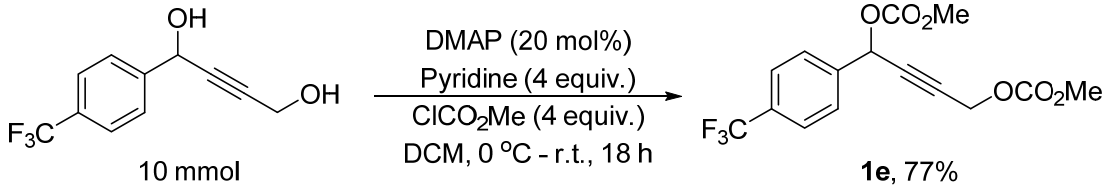
(3) Dimethyl 1-(4-cyanophenyl)but-2-yn-1,4-diyl dicarbonate **1d**[3] (lican-05-070)



Following the **Typical Procedure I**, the reaction of propargyl alcohol (1.16 mL, d = 0.963 g/mL, 1.1171 g, 20 mmol), *n*BuLi (2.5 M in hexane, 17.6 mL, 44 mmol), 4-cyanobenzaldehyde (2.8872 g, 22 mmol) in THF (60 mL) afforded the crude product, and which was used in the next step without further purification.

Following the **Typical Procedure II**, the reaction of the crude product, CH_2Cl_2 (60 mL), DMAP (0.4841 g, 4 mmol), pyridine (6.4 mL, d = 0.983 g/mL, 6.2912 g, 80 mmol) and methyl chloroformate (6.2 mL, d = 1.22 g/mL, 7.5640 g, 80 mmol) afforded **1d** (3.1588 g, 52% for 2 steps) (eluent: petroleum ether / ethyl acetate = 5/1 (1800 mL)) as a white solid: **m.p.** 85.7-87.3 °C (hexane / ethyl acetate): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.4 Hz, 2 H, ArH), 7.64 (d, *J* = 8.0 Hz, 2 H, ArH), 6.36 (s, 1 H, CH), 4.82 (s, 2 H, CH_2), 3.83 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.8, 154.3, 140.4, 132.4, 128.0, 118.0, 113.0, 82.5, 81.9, 68.0, 55.2, 55.1, 55.0; **IR** (neat): ν 2965, 2229, 1742, 1610, 1507, 1441, 1245, 1140, 946 cm^{-1}; **MS** (70 eV, EI) *m*/*z* (%): 303 (M^+, 1.12), 140 (100); **Elem. Anal.** Calcd. for $C_{15}H_{13}NO_6$: C, 59.41; H, 4.32, found C, 59.54; H, 4.33.

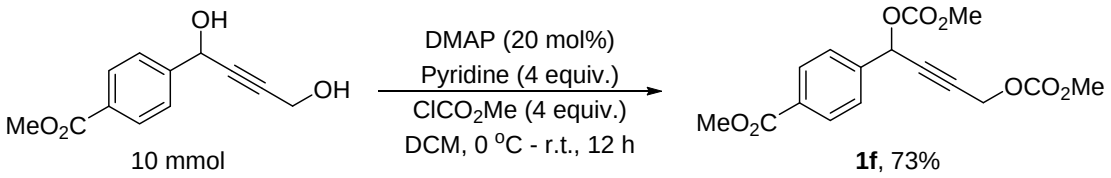
(4) Dimethyl 1-(4-trifluoromethyl)but-2-yn-1,4-diyl dicarbonate **1e**[3] (zzn-1-057)



Following the **Typical Procedure II**, the reaction of 1-(4-trifluoromethyl)but-2-yn-1,4-diol (2.3012 g, 10 mmol), CH_2Cl_2 (40 mL), DMAP

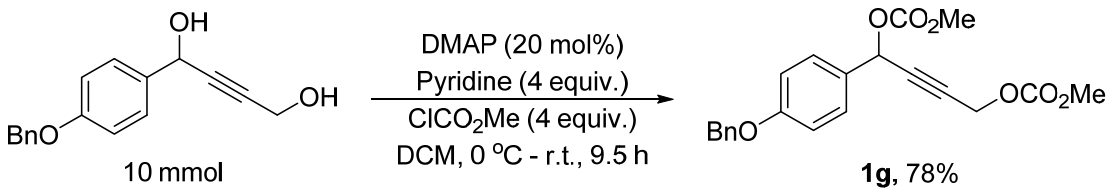
(244.9 mg, 2 mmol), pyridine (3.2 mL, d = 0.983 g/mL, 3.1456 g, 40 mmol) and methyl chloroformate (3.1 mL, d = 1.22 g/mL, 3.78 g, 40 mmol) afforded **1e** (2.6750 g, 77%) (eluent: petroleum ether / ethyl acetate = 8/1 (900 mL) to petroleum ether / ethyl acetate = 5/1 (480 mL)) as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (s, 4 H, ArH), 6.39 (s, 1 H, CH), 4.83 (s, 2 H, CH_2), 3.82 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.0, 154.5, 139.5, 131.2 (q, *J* = 32.4 Hz), 127.9, 125.6 (q, *J* = 3.8 Hz), 123.7 (t, *J* = 270.6 Hz), 82.4, 82.2, 68.3, 55.17, 55.12, 55.07; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -63.2; **IR** (neat): ν 2961, 1749, 1621, 1443, 1376, 1244, 1123 cm^{-1}; **MS** (ESI) *m/z* 369.1 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{15}H_{13}O_6F_3Na$ $[M+Na]^+$: 369.0556, Found: 369.0559.

(5) Dimethyl 1-(4-methoxycarbonyl)but-2-yn-1,4-diyl dicarbonate **1f** [3] (zzn-1-041)



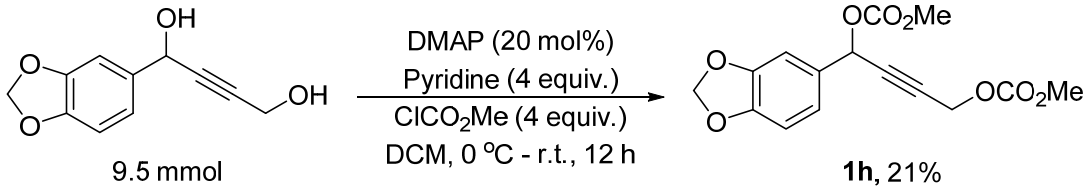
Following the **Typical Procedure II**, the reaction of 1-(4-methoxycarbonyl)but-2-yn-1,4-diol (2.2021 g, 10 mmol), CH_2Cl_2 (40 mL), DMAP (245.0 mg, 2 mmol), pyridine (3.2 mL, d = 0.983 g/mL, 3.1456 g, 40 mmol) and methyl chloroformate (3.1 mL, d = 1.22 g/mL, 3.78 g, 40 mmol) afforded **1f** (2.4680 g, 73%) (eluent: petroleum ether / ethyl acetate = 6/1 (1050 mL)) as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 2 H, ArH), 7.59 (d, *J* = 8.4 Hz, 2 H, ArH), 6.37 (s, 1 H, CH), 4.83 (d, *J* = 0.8 Hz, 2 H, CH_2), 3.92 (s, 3 H, OCH_3), 3.82 (m, 6 H, 2 × OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.3, 155.0, 154.5, 140.3, 130.9, 129.9, 127.4, 82.5, 82.1, 68.5, 55.2, 55.1, 52.2; **IR** (neat): ν 3005, 2958, 2854, 2350, 1749, 1721, 1613, 1440, 1375, 1242; **MS** (ESI) *m/z* 359.1 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{16}H_{16}O_8Na$ $[M+Na]^+$: 359.0737, Found: 359.0734.

(6) Dimethyl 1-(4-(benzyloxy)phenyl)but-2-yn-1,4-diyl dicarbonate **1g** [3] (lican-05-076)



Following the **Typical Procedure II**, the reaction of 1-(4-(benzyloxy)phenyl)but-2-yn-1,4-diol (2.6816 g, 10 mmol), CH_2Cl_2 (40 mL), DMAP (244.9 mg, 2 mmol), pyridine (3.2 mL, d = 0.983, 3.1456 g, 40 mmol) and methyl chloroformate (3.1 mL, d = 1.22 g/mL, 3.78 g, 40 mmol) afforded **1g** (3.0082 g, 78%) (eluent: petroleum ether (0.5% NEt_3) / ethyl acetate = 5/1 (1800 mL)) as a yellowish solid: **m.p.** 80.3-81.9 °C (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51-7.26 (m, 7 H, ArH), 6.95 (d, *J* = 8.4 Hz, 2 H, ArH), 6.28 (s, 1 H, CH), 5.04 (s, 2 H, CH_2), 4.79 (d, *J* = 1.6 Hz, 2 H, CH_2), 3.77 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.5, 155.0, 154.7, 136.6, 129.3, 128.5, 128.1, 127.9, 127.3, 114.8, 83.3, 81.3, 69.9, 69.0, 55.3, 55.0, 54.9; **IR** (neat): ν 2964, 2910, 2863, 1747, 1512, 1443, 1247 cm^{-1}; **MS** (70 eV, EI) *m*/*z* (%): 384 (M^+, 0.53), 309 [$(M\text{-}OCO_2Me)^+$, 9.17], 91 (100); **Elem. Anal.** Calcd. for $C_{21}H_{20}O_7$: C, 65.62; H, 5.24, found C, 65.25; H, 5.18.

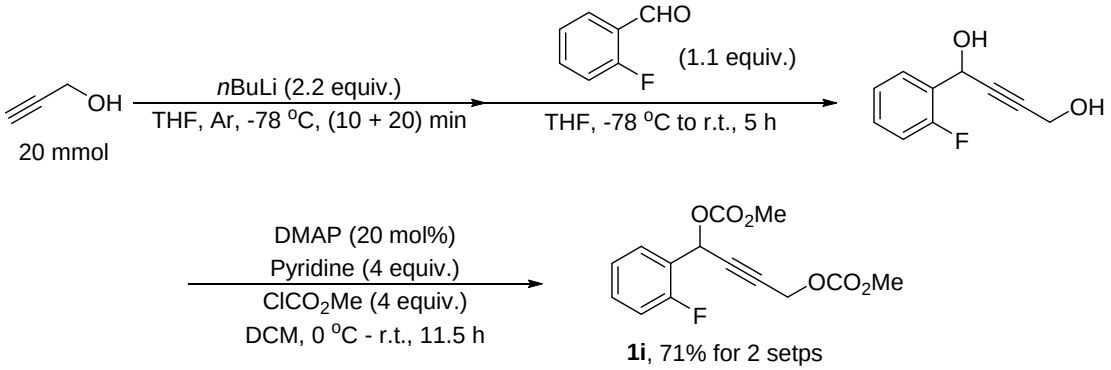
(7) Dimethyl 1-(benzo[*d*][1,3]dioxol-5-yl)but-2-yn-1,4-diyl dicarbonate **1h** [3] (zzn-1-081)



Following the **Typical Procedure II**, the reaction of 1-(benzo[*d*][1,3]dioxol-5-yl)but-2-yn-1,4-diol (1.9580 g, 9.5 mmol), CH_2Cl_2 (40 mL), DMAP (232.6 mg, 1.9 mmol), pyridine (3.1 mL, d = 0.983, 3.0473 g, 38.5 mmol) and methyl chloroformate (3.0 mL, d = 1.22 g/mL, 3.6600 g, 39 mmol) afforded **1h** (634.6 mg, 21%) (eluent: petroleum ether / ethyl acetate = 8/1 (900 mL)) as an orange oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.00-6.98 (m, 2 H, ArH), 6.78 (d, *J* = 7.6 Hz, 1 H, ArH), 6.23 (s, 1 H, CH), 5.97 (s, 2 H, CH_2), 4.81 (s, 2 H, CH_2), 3.81 (s, 3 H, OCH_3), 3.79 (s,

3 H, OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.9, 154.6, 148.4, 147.8, 129.4, 121.9, 108.1, 108.0, 101.3, 83.1, 81.3, 69.1, 55.3, 55.1, 55.0; **IR** (neat): ν 2959, 2902, 1745, 1611, 1503, 1489, 1442, 1374, 1234; **MS** (ESI) *m/z* 345.1 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{15}H_{14}O_8Na$ $[M+Na]^+$: 345.0581, Found: 345.0582.

(8) Dimethyl 1-(2-fluorophenyl)but-2-yn-1,4-diyl dicarbonate **1i**[3] (zzn-1-013)

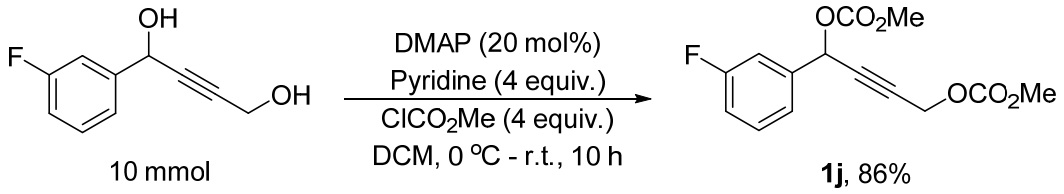


1i, 71% for 2 setps

Following the **Typical Procedure I**, the reaction of propargyl alcohol (1.16 mL, d = 0.963 g/mL, 1.1171 g, 20 mmol), *n*BuLi (2.5 M in hexane, 17.6 mL, 44 mmol), 2-fluorobenzaldehyde (2.5601 g, 22 mmol) in THF (60 mL) afforded the crude product, and which was used in the next step without further purification.

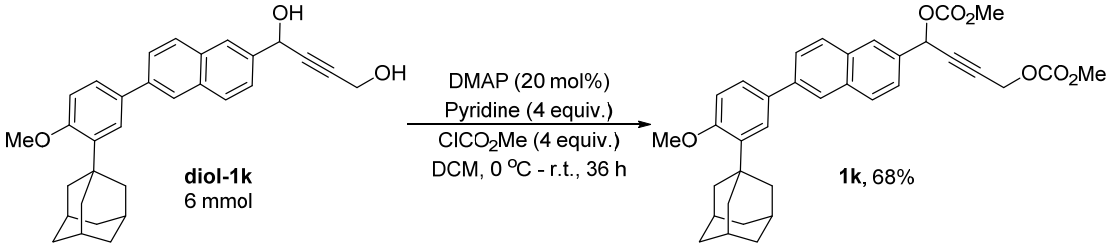
Following the **Typical Procedure II**, the reaction of the crude product, CH_2Cl_2 (60 mL), DMAP (489.0 mg, 4 mmol), pyridine (6.4 mL, d = 0.983 g/mL, 6.2912 g, 80 mmol) and methyl chloroformate (6.2 mL, d = 1.22 g/mL, 7.5640 g, 80 mmol) afforded **1i** (4.2259 g, 71% for 2 steps) (eluent: petroleum ether / ethyl acetate = 15/1 (480 mL) to petroleum ether / ethyl acetate = 12/1 (520 mL) to petroleum ether / ethyl acetate = 7/1 (800 mL)) as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 (td, J_1 = 7.4 Hz, J_2 = 1.6 Hz, 1 H, ArH), 7.42-7.33 (m, 1 H, ArH), 7.23-7.15 (m, 1 H, ArH), 7.13-7.04 (m, 1 H, ArH), 6.61 (s, 1 H, CH), 4.83 (d, J = 1.6 Hz, 2 H, CH_2), 3.88-3.77 (m, 6 H, 2 × OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.1 (d, J = 249.0 Hz), 155.0, 154.5, 131.3 (d, J = 8.4 Hz), 129.5 (d, J = 3.1 Hz), 124.4 (d, J = 3.1 Hz), 123.1 (d, J = 13.0 Hz), 115.7 (d, J = 21.4 Hz), 82.3, 81.6, 63.3 (d, J = 5.4 Hz), 55.4, 55.22, 55.20; **^{19}F NMR** (376 MHz, $CDCl_3$): -118.0; **IR** (neat): ν 2960, 1748, 1617, 1591, 1493, 1442, 1244 cm^{-1}; **MS** (ESI) *m/z* 319.1 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{14}H_{13}O_6FNa$ $[M+Na]^+$: 319.0588, Found: 319.0588.

(9) Dimethyl 1-(3-fluorophenyl)but-2-yn-1,4-diyl dicarbonate **1j** [3] (zzn-1-011)



Following the **Typical Procedure II**, the reaction of 1-(3-fluorophenyl)but-2-yn-1,4-diol (1.8081 g, 10 mmol), CH_2Cl_2 (40 mL), DMAP (244.5 mg, 2 mmol), pyridine (3.2 mL, d = 0.983, 3.1456 g, 40 mmol) and methyl chloroformate (3.1 mL, d = 1.22 g/mL, 3.78 g, 40 mmol) afforded **1j** (2.5650 g, 86%) (eluent: petroleum ether / ethyl acetate = 9/1 (1000 mL)) as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39-7.23 (m, 3 H, ArH), 7.07 (t, *J* = 7.6 Hz, 1 H, ArH), 6.32 (s, 1 H, CH), 4.86 (s, 2 H, CH_2), 3.82 (s, 6 H, 2 × OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.7 (d, *J* = 245.7 Hz), 155.0, 154.6, 138.0 (d, *J* = 7.2 Hz), 130.3 (d, *J* = 8.1 Hz), 123.2 (d, *J* = 2.8 Hz), 116.3 (d, *J* = 21.0 Hz), 114.7 (d, *J* = 23.0 Hz), 82.6, 81.9, 68.4 (d, *J* = 2.1 Hz), 55.3, 55.22, 55.18; **^{19}F NMR** (376 MHz, $CDCl_3$): -112.5; **IR** (neat): ν 3010, 2960, 2857, 1747, 1616, 1594, 1488, 1442, 1375, 1241 cm^{-1}; **MS** (ESI) *m/z* 319.1 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{14}H_{13}O_6FNa$ $[M+Na]^+$: 319.0588, Found: 319.0588.

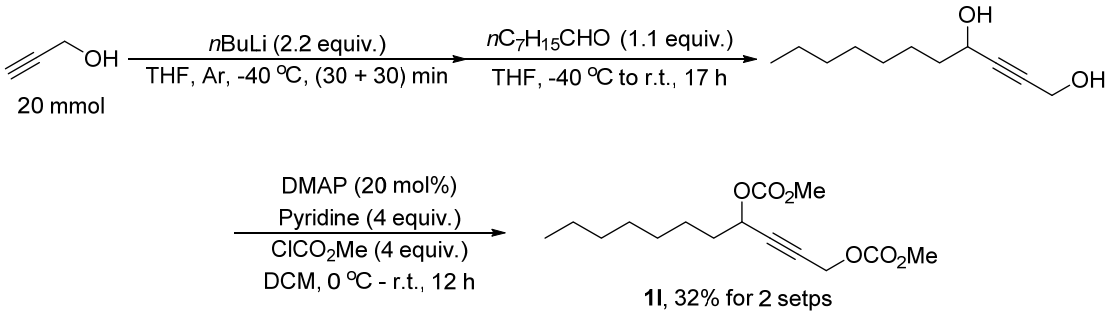
(10) Compound **1k** [3] (zzn-1-065)



Following the **Typical Procedure II**, the reaction of **diol-1k** (2.7132 g, 6 mmol), CH_2Cl_2 (40 mL), DMAP (149.0 mg, 1.2 mmol), pyridine (1.93 mL, d = 0.983, 1.8972 g, 24 mmol) and methyl chloroformate (1.9 mL, d = 1.22 g/mL, 2.3180 g, 25 mmol) afforded **1k** (2.3240 g, 68%) (eluent: petroleum ether / ethyl acetate = 8/1 (1350 mL)) as a yellow solid (we were not able to obtain the crystal from the solvent tested, the **m.p.** was determined by using the solid after evaporation of the eluent. When the

white solid was heated up to 49.2 °C, it shrank. At 58.0 °C, the solid started melting. At 64.5 °C, the sample was completely melted and the color of the liquid was yellow); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (s, 2 H, ArH), 7.90 (d, *J* = 8.4 Hz, 2 H, ArH), 7.76 (d, *J* = 8.4 Hz, 1 H, ArH), 7.65-7.57 (m, 2 H, ArH), 7.53 (d, *J* = 8.0 Hz, 1 H, ArH), 6.99 (d, *J* = 8.4 Hz, 1 H, ArH), 6.50 (s, 1 H, CH), 4.86 (s, 2 H, CH_2), 3.90 (s, 3 H, OCH_3), 3.82 (s, 6 H, 2 × OCH_3), 2.19 (s, 6 H, 3 × CH_2), 2.10 (s, 3 H, 3 × CH), 1.80 (s, 6 H, 3 × CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.7, 155.1, 154.8, 139.9, 138.9, 134.0, 132.8, 132.6, 131.7, 128.9, 128.7, 127.1, 126.3, 125.8, 125.6, 125.1, 124.7, 112.1, 83.3, 81.8, 69.6, 55.5, 55.20, 55.15, 55.14, 40.6, 37.2, 37.1, 29.1; **IR** (neat): ν 2901, 2847, 1748, 1604, 1496, 1441, 1372, 1321, 1235; **MS** (ESI) *m/z* 591.2 $[M+Na]^+$; **Elem. Anal.** Calcd. for $C_{35}H_{36}O_7$: C, 73.92; H, 6.38, found C, 74.04; H, 6.25.

(11) Dimethyl undec-2-yn-1,4-diyl dicarbonate **1l**[3] (zzn-1-060)

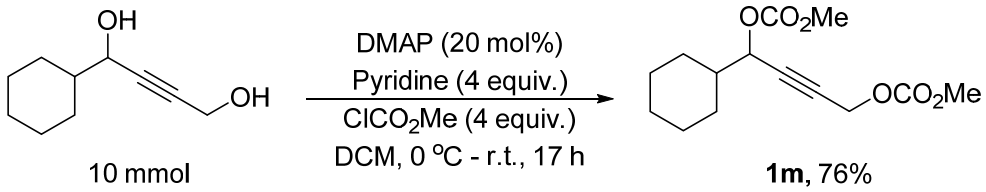


Following the **Typical Procedure I**, the reaction of propargyl alcohol (1.16 mL, d = 0.963 g/mL, 1.1171 g, 20 mmol), *n*BuLi (2.5 M in hexane, 17.6 mL, 44 mmol), octanal (3.44 mL, d = 0.821 g/mL, 2.8242 g, 22 mmol) in THF (60 mL) afforded the crude product, and which was used in the next step without further purification.

Following the **Typical Procedure II**, the reaction of the crude product, CH_2Cl_2 (40 mL), DMAP (0.2279 g, 1.8 mmol), pyridine (2.9 mL, d = 0.983 g/mL, 2.85 g, 36 mmol) and methyl chloroformate (2.8 mL, d = 1.22 g/mL, 3.4160 g, 36 mmol) afforded **1l** (1.9264 g, 32% for 2 steps) (eluent: petroleum ether / ethyl acetate = 18/1 (950 mL)) as a colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.25 (t, *J* = 6.6 Hz, 1 H, CH), 4.77 (d, *J* = 1.6 Hz, 2 H, CH_2), 3.90-3.71 (m, 6 H, 2 × OCH_3), 1.84-1.77 (m, 2 H, CH_2), 1.46-1.41 (m, 2 H, CH_2), 1.30-1.28 (m, 8 H, 4 × CH_2), 0.88 (t, *J* = 6.6 Hz, 3 H,

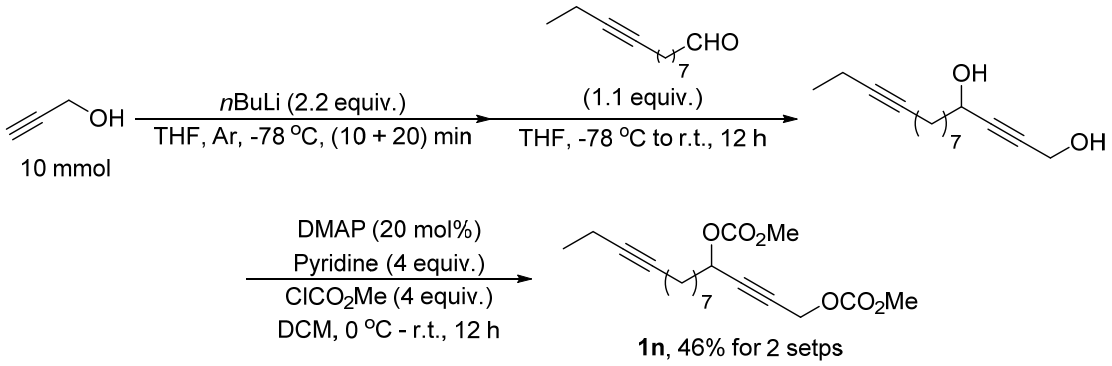
CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): 154.9, 154.8, 84.2, 79.5, 67.7, 55.3, 54.9, 54.7, 34.3, 31.5, 28.9, 28.8, 24.6, 22.4, 13.9; **IR** (neat): ν 2956, 2928, 2857, 1749, 1442, 1375, 1246, 1159 cm^{-1}; **MS** (ESI) *m/z* 323.1 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{15}H_{24}O_6Na$ $[M+Na]^+$: 323.1465, Found: 323.1466.

(12) Dimethyl 1-cyclohexylbut-2-yn-1,4-diyl dicarbonate **1m** [3] (zzn-1-076)



Following the **Typical Procedure II**, the reaction of 1-cyclohexylbut-2-yn-1,4-diol (1.6820 g, 10 mmol), CH_2Cl_2 (40 mL), DMAP (244.9 mg, 2 mmol), pyridine (3.2 mL, d = 0.983, 3.1456 g, 40 mmol) and methyl chloroformate (3.1 mL, d = 1.22 g/mL, 3.78 g, 40 mmol) afforded **1m** (2.2034 g, 76%) (eluent: petroleum ether / ethyl acetate = 5/1 (1200 mL)) as a colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$): 5.09 (d, *J* = 4.8 Hz, 1 H, CH), 4.78 (s, 2 H, CH_2), 3.95-3.64 (m, 6 H, 2 × OCH_3), 1.98-1.53 (m, 6 H), 1.35-0.94 (m, 5 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.0, 83.3, 80.3, 72.1, 55.4, 55.1, 54.9, 41.7, 28.2, 27.9, 26.0, 25.6, 25.5; **IR** (neat): ν 2930, 2855, 1747, 1442, 1375, 1347, 1245; **MS** (ESI) *m/z* 307.1 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{14}H_{20}O_6Na$ $[M+Na]^+$: 307.1152, Found: 307.1153.

(13) Dimethyl pentadeca-2,12-diyn-1,4-diyl dicarbonate **1n** [6] (lican-06-047)



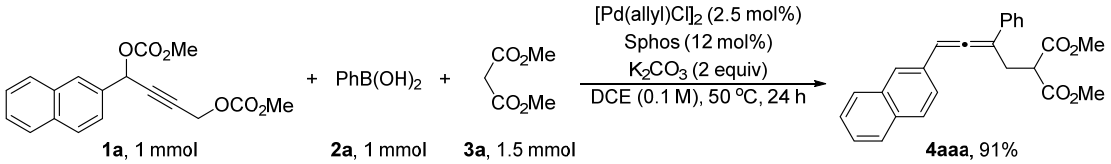
Following the **Typical Procedure I**, the reaction of propargyl alcohol (583 μL, d = 0.963 g/mL, 561.4 mg, 10 mmol), *n*BuLi (2.5 M in hexane, 8.8 mL, 22 mmol),

dodec-9-ynal[4] (1.9872 g, 11 mmol) in THF (60 mL) afforded the reaction mixture. After quenching, filtration, evaporation of the solvent and chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 1.5/1 (1500 mL)) afforded crude product (1.3301 g, 56%) as a yellowish oil. The crude product was used in the next step without further purification.

Following the **Typical Procedure II**, the reaction of the crude product (1.1802 g, 5 mmol), CH_2Cl_2 (20 mL), DMAP (122.4 mg, 1 mmol), pyridine (1.61 mL, d = 0.983 g/mL, 1.5778 g, 20 mmol) and methyl chloroformate (1.55 mL, d = 1.22 g/mL, 1.89 g, 20 mmol) afforded **1n** (1.4372 g, 46% for 2 steps) (eluent: petroleum ether / ethyl acetate = 15/1 (960 mL)) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.24 (t, *J* = 6.6 Hz, 1 H, CH), 4.77 (s, 2 H, CH_2), 3.89-3.72 (m, 6 H, 2 × OCH_3), 2.21-2.08 (m, 4 H, 2 × CH_2), 1.86-1.73 (m, 2 H, CH_2), 1.52-1.40 (m, 4 H, 2 × CH_2), 1.40-1.25 (m, 6 H, 3 × CH_2), 1.11 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.9, 154.7, 84.1, 81.4, 79.5, 79.2, 67.6, 55.2, 54.9, 54.7, 34.3, 28.8, 28.71, 28.69, 28.5, 24.5, 18.5, 14.2, 12.2; **IR** (neat): ν 2932, 2857, 1749, 1442, 1375, 1248, 1163 cm^{-1}; **MS** (FI) *m*/*z* 352 $[M]^+$; **HRMS** (FI) Calcd for $C_{19}H_{28}O_6$ $[M]^+$: 352.1880, Found: 352.1885.

2. Synthesis of trisubstituted 2,3-allenyl malonates

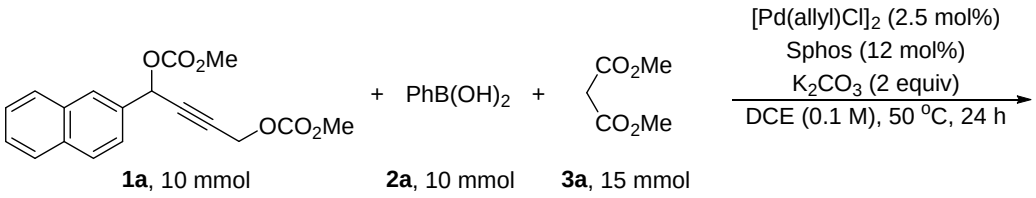
(1) Dimethyl 2-(2-phenyl-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aaa** (lican-05-072)

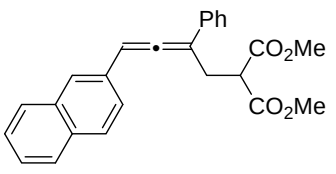


Typical Procedure III: To a flame-dried Schlenk tube were added **1a** (328.3 mg, 1 mmol), $[Pd(allyl)Cl]_2$ (9.2 mg, 0.025 mmol), Sphos (49.5 mg, 0.12 mmol), **2a** (122.3 mg, 1 mmol), and K_2CO_3 (275.0 mg, 2 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then DCE (5 mL), **3a** (171 μL, d = 1.156 g/mL, 197.7 mg, 1.5 mmol), and DCE

(5 mL) were added sequentially under argon atmosphere. The resulting mixture was stirred at 50 °C for 24 h as monitored by TLC, filtered through a short column of silica gel (3 cm) eluted with ethyl acetate (30 mL), and concentrated. The residue was purified by column chromatography on silica gel to afford **4aaa** (351.8 mg, 91%) [eluent: petroleum ether / ethyl ether = 9/1 (1000 mL)] as a white solid: **m.p.** 113.7-115.1 °C (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85-7.73 (m, 3 H, ArH), 7.70 (s, 1 H, ArH), 7.53-7.38 (m, 5 H, ArH), 7.34 (t, J = 7.6 Hz, 2 H, ArH), 7.26 (t, J = 6.0 Hz, 1 H, ArH), 6.78 (t, J = 3.2 Hz, 1 H, CH), 3.79 (dd, J_1 = 8.8 Hz, J_2 = 6.0 Hz, 1 H, CH), 3.72 (s, 3 H, OCH_3), 3.42-3.27 (m, 4 H, OCH_3 and one proton of CH_2), 3.22-3.11 (m, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.7, 169.5, 169.1, 135.1, 133.6, 132.9, 131.1, 128.6, 128.3, 127.8, 127.7, 127.6, 126.3, 126.02, 126.01, 125.9, 124.7, 107.9, 100.7, 52.7, 52.5, 50.2, 29.1; **IR** (neat): ν 3049, 2959, 2921, 1936, 1723, 1596, 1439, 1294, 1249, 1196, 1157 cm^{-1}; **Raman**: ν 3056, 2954, 2913, 1936, 1749, 1626, 1597, 1506, 1468, 1435, 1380, 1226, 1161 cm^{-1};**MS** (70 eV, EI) *m*/*z* (%): 386 (M^+, 7.16), 254 (100); **Elem. Anal.** Calcd. for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74, found C, 77.48; H, 5.87.

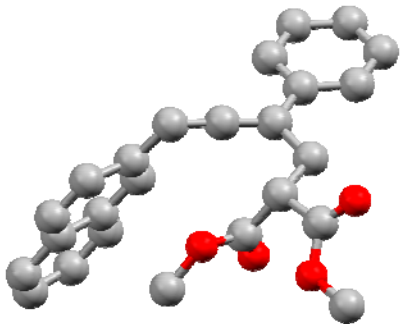
(2) Preparation of dimethyl 2-(2-phenyl-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aaa** on gram scale (lican-05-094)





4aaa, 90%, 3.4834 g

≡

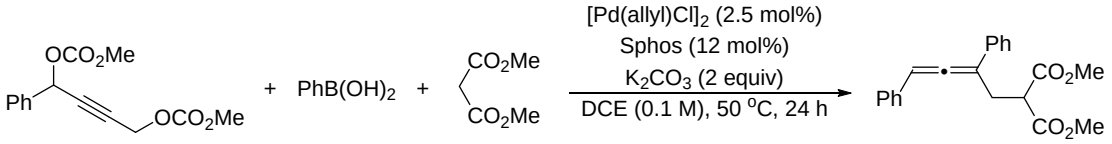


CCDC = 2202991

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (91.9 mg, 0.25 mmol), Sphos (495.0 mg, 1.2 mmol), **1a** (3.2851 g, 10 mmol), **2a** (1.2186 g, 10 mmol), K_2CO_3 (2.7674 g, 20 mmol), **3a** (1.7 mL, d = 1.156, 1.9652 g, 15 mmol), and DCE (10 mL) afforded **4aaa** (3.4834 g, 90%) [eluent: petroleum ether / ethyl acetate = 9/1 (1000 mL) to petroleum ether / ethyl acetate = 4/1 (1000 mL)] as a light brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87-7.73 (m, 3 H, ArH), 7.70 (s, 1 H, ArH), 7.56-7.39 (m, 5 H, ArH), 7.34 (t, J = 7.6 Hz, 2 H, ArH), 7.29-7.21 (m, 1 H, ArH), 6.78 (t, J = 3.4 Hz, 1 H, CH), 3.79 (dd, J_1 = 8.8 Hz, J_2 = 6.0 Hz, 1 H, CH), 3.72 (s, 3 H, OCH_3), 3.46-3.27 (m, 4 H, OCH_3 and one proton of CH_2), 3.29 (ddd, J_1 = 15.8 Hz, J_2 = 5.8 Hz, J_3 = 3.8 Hz, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.7, 169.5, 169.1, 135.2, 133.7, 132.9, 131.2, 128.7, 128.3, 127.8, 127.7, 127.6, 126.0, 126.3, 125.9, 124.8, 107.9, 100.7, 52.7, 52.5, 50.2, 29.2.

Single crystal of **4aaa** (CCDC number: 2202991) was obtained by slow diffusion of hexane (4.0 mL) to a solution of **4aaa** (70 mg) in ethyl acetate (1 mL).

(3) Dimethyl 2-(2,4-diphenylbuta-2,3-dienyl) malonate **4baa** (lican-05-189)

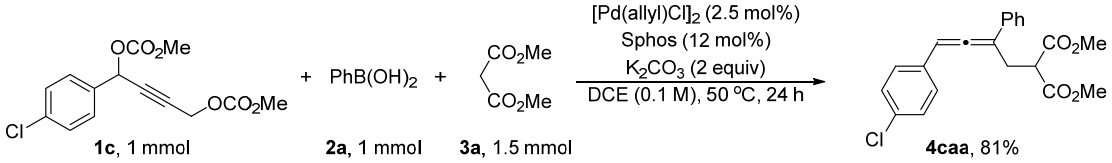


1b, 1 mmol **2a**, 1 mmol **3a**, 1.5 mmol **4baa**, 80%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.2 mg, 0.025 mmol), Sphos (49.4 mg, 0.12 mmol), **1b** (279.2 mg, 1 mmol), **2a** (122.3 mg, 1 mmol), K_2CO_3 (278.8 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4baa** (285.1 mg, 80%, purity = 95%) [eluent: petroleum ether / ethyl acetate = 15/1 (320 mL)] as a light green oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49-7.42 (m, 2 H, ArH), 7.36-7.29 (m, 3 H, ArH), 7.29-7.18 (m, 5 H, ArH), 6.59 (t, J = 3.6 Hz, 1 H, =CH), 3.76 (dd, J_1 = 8.8 Hz, J_2 = 6.0 Hz, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.40 (s, 3 H, OCH_3), 3.29 (ddd, J_1 = 15.7 Hz, J_2 = 8.7 Hz, J_3 = 3.5 Hz, 1 H, one proton of CH_2), 3.13 (ddd, J_1 = 15.8 Hz, J_2 = 6.0 Hz, J_3 = 3.8 Hz, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.1, 169.5, 169.0, 135.1, 133.5, 128.63,

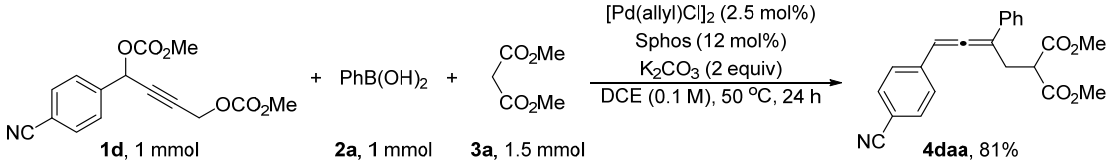
128.56, 127.5, 127.0, 125.9, 107.6, 100.3, 52.7, 52.3, 50.1, 29.0; **IR** (neat): ν 3028, 2952, 2845, 1936, 1732, 1596, 1493, 1434, 1331, 1148 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 336 (M^+, 7.43), 204 (100); **HRMS** (FI) Calcd for $C_{21}H_{20}O_4$ $[M]^+$: 336.1356, Found: 336.1360.

(4) Dimethyl 2-(2-phenyl-4-(4-chlorophenyl)buta-2,3-dienyl) malonate **4caa** (lican-06-016)



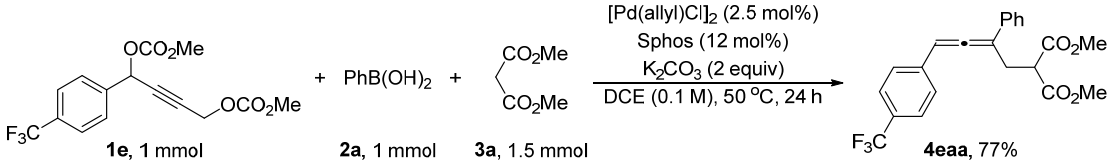
Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.2 mg, 0.025 mmol), Sphos (49.5 mg, 0.12 mmol), **1c** (313.0 mg, 1 mmol), **2a** (122.3 mg, 1 mmol), K_2CO_3 (277.5 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4caa** (300.2 mg, 81%) [eluent: petroleum ether / ethyl acetate = 15/1 (640 mL)] as a white solid: **m.p.** 63.4-65.0 °C (hexane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.6 Hz, 2 H, ArH), 7.33 (d, *J* = 7.4 Hz, 2 H, ArH), 7.30-7.16 (m, 5 H, ArH), 6.60-6.51 (m, 1 H, =CH), 3.83-3.64 (m, 4 H, OCH_3 and CH), 3.44 (s, 3 H, OCH_3), 3.29 (ddd, J_1 = 15.7 Hz, J_2 = 8.9 Hz, J_3 = 3.3 Hz, 1 H, one proton of CH_2), 3.18-3.06 (m, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.3, 169.4, 169.0, 134.8, 133.1, 132.1, 128.8, 128.6, 128.2, 127.7, 125.9, 108.1, 99.3, 52.7, 52.5, 50.1, 29.0; **IR** (neat): ν 3085, 3052, 2955, 2919, 1935, 1748, 1731, 1596, 1489, 1434, 1345, 1263 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 370 ($M(^{35}Cl)^+$, 9.37), 372 ($M(^{37}Cl)^+$, 3.34), 238 (100); **Elem. Anal.** Calcd. for $C_{21}H_{19}ClO_4$: C, 68.02; H, 5.16, found C, 67.92; H, 5.28.

(5) Dimethyl 2-(2-phenyl-4-(4-cyanophenyl)buta-2,3-dienyl) malonate **4daa** (lican-05-116)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.2 mg, 0.025 mmol), Sphos (49.5 mg, 0.12 mmol), **1d** (304.0 mg, 1 mmol), **2a** (121.7 mg, 1 mmol), K_2CO_3 (275.0 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4daa** (294.2 mg, 81%) [eluent: petroleum ether / acetone = 15/1 (960 mL)] as a yellowish oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.4 Hz, 2 H, ArH), 7.43 (d, *J* = 7.2 Hz, 2 H, ArH), 7.39-7.30 (m, 4 H, ArH), 7.26 (t, *J* = 7.4 Hz, 1 H, ArH), 6.62 (t, *J* = 3.4 Hz, 1 H, =CH), 3.78-3.66 (m, 4 H, CH_3 and one proton of CH_2), 3.43 (s, 3 H, OCH_3), 3.32 (ddd, J_1 = 16.0 Hz, J_2 = 8.8 Hz, J_3 = 3.6 Hz, 1 H, one proton of CH_2), 3.15 (ddd, J_1 = 15.9 Hz, J_2 = 5.7 Hz, J_3 = 3.7 Hz, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 206.4, 168.8, 168.5, 138.4, 133.7, 132.1, 128.4, 127.6, 127.1, 125.7, 118.5, 110.2, 108.4, 98.9, 52.4, 52.0, 49.6, 28.6; **IR** (neat): ν 2954, 2254, 2227, 1936, 1732, 1603, 1435, 1151 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 361 (M^+, 12.81), 229 (100); **HRMS** (ESI) Calcd for $C_{22}H_{20}O_4N$ $[M+H]^+$: 362.1387, Found: 362.1384.

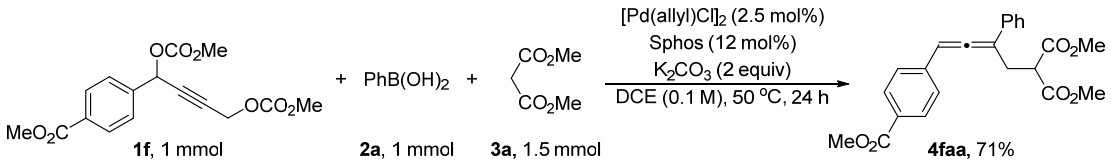
(6) Dimethyl 2-(2-phenyl-4-(4-(trifluoromethyl)phenyl)buta-2,3-dienyl) malonate **4eaa** (lican-06-034)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.3 mg, 0.025 mmol), Sphos (49.3 mg, 0.12 mmol), **1e** (346.7 mg, 1 mmol), **2a** (121.9 mg, 1 mmol), K_2CO_3 (277.0 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4eaa** (310.4 mg, 77%) [eluent: petroleum ether / ethyl acetate = 15/1 (480 mL)] as a white solid: **m.p.** 69.5-71.1 °C (hexane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.4 Hz, 2 H, ArH), 7.44 (d, *J* = 7.6 Hz, 2 H, ArH), 7.41-7.31 (m,

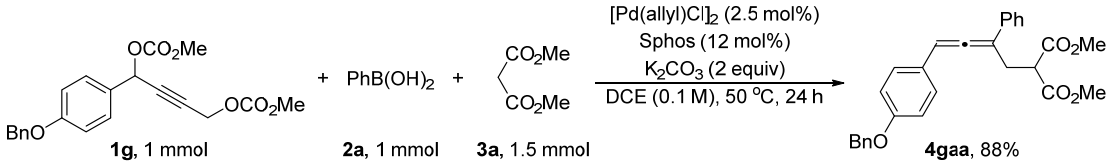
4 H, ArH), 7.27 (t, J = 7.4 Hz, 1 H, ArH), 6.62 (t, J = 3.4 Hz, 1 H, =CH), 3.78-3.67 (m, 4 H, OCH_3 and CH), 3.43 (s, 3 H, OCH_3), 3.31 (ddd, J_1 = 16.0 Hz, J_2 = 8.6 Hz, J_3 = 3.4 Hz, 1 H, one proton of CH_2), 3.15 (ddd, J_1 = 16.0 Hz, J_2 = 5.8 Hz, J_3 = 3.8 Hz, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 206.2, 169.3, 168.9, 137.6, 134.4, 129.3 (q, J = 32.2 Hz), 128.7, 127.9, 127.1, 126.0, 125.6 (q, J = 3.6 Hz), 124.1 (q, J = 270.3 Hz), 108.4, 99.3, 52.7, 52.4, 50.0, 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$): -63.0; **IR** (neat): ν 3058, 2962, 2923, 1938, 1734, 1612, 1493, 1436, 1322, 1258, 1107 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 404 (M^+, 22.57), 272 (100); **Elem. Anal.** Calcd. for $C_{22}H_{19}F_3O_4$: C, 65.34; H, 4.74, found C, 65.17; H, 4.93.

(7) Dimethyl 2-(2-phenyl-4-(4-(methoxycarbonyl)phenyl)buta-2,3-dienyl) malonate **4faa** (lican-06-003)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.3 mg, 0.025 mmol), Sphos (49.3 mg, 0.12 mmol), **1f** (336.5 mg, 1 mmol), **2a** (122.1 mg, 1 mmol), K_2CO_3 (276.8 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4faa** (281.2 mg, 71%) [eluent: petroleum ether / ethyl acetate = 20/1 (630 mL)] as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.0 Hz, 2 H, ArH), 7.4 (d, J = 8.0 Hz, 2 H, ArH), 7.38-7.27 (m, 4 H, ArH), 7.23 (t, J = 7.4 Hz, 1 H, ArH), 6.66-6.59 (m, 1 H, =CH), 3.86 (s, 3 H, OCH_3), 3.75 (dd, J_1 = 8.6 Hz, J_2 = 5.8 Hz, 1 H, CH), 3.69 (s, 3 H, OCH_3), 3.40 (s, 3 H, OCH_3), 3.32 (ddd, J_1 = 15.9 Hz, J_2 = 8.9 Hz, J_3 = 3.1 Hz, 1 H, one proton of CH_2), 3.20-3.09 (m, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 206.1, 168.9, 168.5, 166.3, 138.3, 134.2, 129.7, 128.6, 128.4, 127.5, 126.6, 125.7, 107.9, 99.4, 52.3, 52.0, 51.6, 49.7, 28.7; **IR** (neat): ν 3000, 2952, 2849, 1936, 1745, 1730, 1714, 1604, 1493, 1437, 1274, 1109 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 394 (M^+, 12.61), 262 (100); **HRMS** (FI) Calcd for $C_{23}H_{22}O_6$ $[M]^+$: 394.1411, Found: 394.1416.

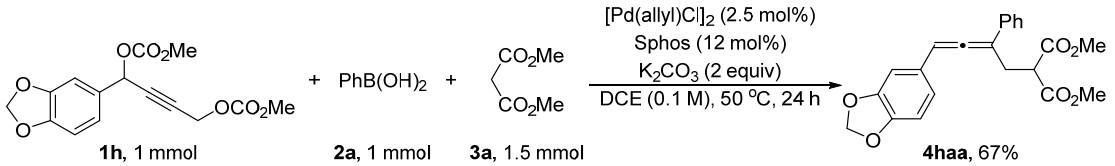
(8) Dimethyl 2-(2-phenyl-4-(4-(benzyloxy)phenyl)buta-2,3-dienyl) malonate **4gaa** (lican-05-115)



1g, 1 mmol **2a**, 1 mmol **3a**, 1.5 mmol **4gaa**, 88%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.0 mg, 0.025 mmol), Sphos (49.3 mg, 0.12 mmol), **1g** (384.5 mg, 1 mmol), **2a** (122.2 mg, 1 mmol), K_2CO_3 (277.0 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4gaa** (389.8 mg, 88%) [eluent: petroleum ether / acetone = 10/1 (1100 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.6 Hz, 2 H, ArH), 7.35 (d, *J* = 7.2 Hz, 2 H, ArH), 7.33-7.21 (m, 5 H, ArH), 7.20-7.12 (m, 3 H, ArH), 6.88 (d, *J* = 8.4 Hz, 2 H, ArH), 6.59-6.47 (m, 1 H, =CH), 4.79 (s, 2 H, OCH_2), 3.75 (dd, J_1 = 9.0 Hz, J_2 = 5.8 Hz, 1 H, CH), 3.64 (s, 3 H, OCH_3), 3.38-3.21 (m, 4 H, CH_3 and one proton of CH_2), 3.15-3.04 (m, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 204.3, 169.2, 168.8, 158.0, 136.6, 135.1, 128.34, 128.26, 128.0, 127.7, 127.1, 125.8, 125.6, 114.9, 107.3, 99.6, 69.6, 52.4, 52.1, 49.9, 28.9; **IR** (neat): ν 3033, 2951, 2844, 2106, 1939, 1726, 1603, 1239, 1229 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 442 (M^+, 19.96), 91 (100); **HRMS** (EI) Calcd for $C_{28}H_{26}O_5$ $[M]^+$: 442.1775, Found: 442.1779.

(9) Dimethyl 2-(2-phenyl-4-(benzo[*d*][1,3]dioxol-5-yl)buta-2,3-dienyl) malonate **4haa** (zzn-1-090)

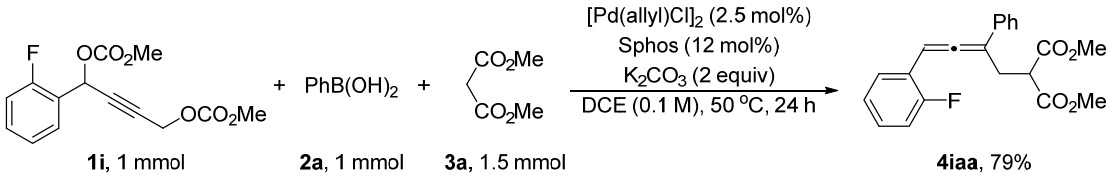


1h, 1 mmol **2a**, 1 mmol **3a**, 1.5 mmol **4haa**, 67%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.4 mg, 0.12 mmol), **1g** (322.1 mg, 1 mmol), **2a** (121.8 mg, 1 mmol), K_2CO_3 (276.6 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and

DCE (10 mL) afforded **4gaa** (258.9 mg, 67%, purity = 99%) [eluent: petroleum ether / ethyl acetate = 10/1 (880 mL)] as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.6 Hz, 2 H, ArH), 7.33 (t, *J* = 7.6 Hz, 2 H, ArH), 7.26-7.22 (m, 1 H, ArH), 6.77-6.76 (m, 3 H, ArH), 6.52 (t, *J* = 3.4 Hz, 1 H, =CH), 5.94 (d, *J* = 2.8 Hz, 2 H, CH_2), 3.73 (m, 4 H, CH and OCH_3), 3.52 (s, 3 H, OCH_3), 3.30-3.32 (m, 1 H, one proton of CH_2), 3.15-3.09 (m, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 204.6, 169.5, 169.1, 148.1, 147.2, 135.3, 128.6, 127.6, 127.5, 126.0, 121.0, 108.4, 107.8, 106.8, 101.1, 100.1, 52.7, 52.5, 50.2, 29.2; **IR** (neat): ν 3002, 2952, 2895, 2778, 1936, 1731, 1597, 1487, 1439, 1341, 1240 cm^{-1}; **MS** (ESI) *m/z* 381.1 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{22}H_{21}O_6$ $[M+H]^+$: 381.1333 , Found: 381.1333.

(10) Dimethyl 2-(2-phenyl-4-(2-fluorophenyl)buta-2,3-dienyl) malonate **4iaa** (zzn-1-016)

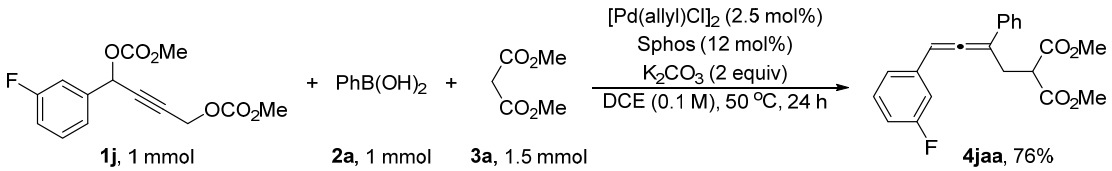


1i, 1 mmol **2a**, 1 mmol **3a**, 1.5 mmol **4iaa**, 79%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.5 mg, 0.12 mmol), **1i** (296.0 mg, 1 mmol), **2a** (121.8 mg, 1 mmol), K_2CO_3 (276.5 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4iaa** (280.4 mg, 79%) [eluent: petroleum ether / ethyl acetate = 60/1 (1280 mL)] as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46-7.44 (m, 2 H, ArH), 7.35-7.15 (m, 5 H, ArH), 7.07-7.01 (m, 2 H, ArH), 6.82 (t, *J* = 3.2 Hz, 1 H, =CH), 3.77-3.72 (m, 4 H, CH and OCH_3), 3.46 (s, 3 H, OCH_3), 3.31-3.24 (m, 1 H, one proton of CH_2), 3.17-3.11 (m, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.8 (d, *J* = 2.0 Hz), 169.3, 169.0, 159.6 (d, *J* = 248.2 Hz), 134.8, 128.8 (d, *J* = 8.1 Hz), 128.6, 128.3 (d, *J* = 3.2 Hz), 127.5, 125.9, 124.1 (d, *J* = 3.7 Hz), 121.1 (d, *J* = 12.2 Hz), 115.6 (d, *J* = 21.0 Hz), 107.7, 92.5 (d, *J* = 6.4 Hz), 52.62 (d, *J* = 1.2 Hz), 52.3, 50.0. 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$): -119.7; **IR** (neat): ν 2953, 2847, 1938, 1732, 1581, 1492, 1435, 1232, 1148 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 354 (M^+, 11.59),

222 (100); **HRMS** (ESI) Calcd for $C_{21}H_{20}O_4F$ $[M+H]^+$: 355.1340, Found: 355.1339.

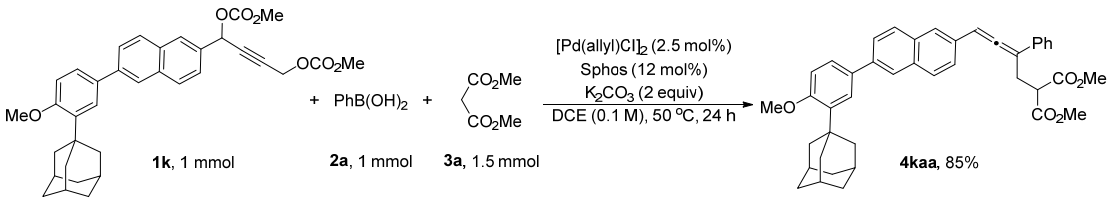
(11) Dimethyl 2-(2-phenyl-4-(3-fluorophenyl)buta-2,3-dienyl) malonate **4jaa** (zzn-1-015)



1j, 1 mmol **2a**, 1 mmol **3a**, 1.5 mmol **4jaa**, 76%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.2 mg, 0.12 mmol), **1j** (297.0 mg, 1 mmol), **2a** (121.7 mg, 1 mmol), K_2CO_3 (276.6 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4jaa** (276.6 mg, 76%, purity = 97%) [eluent: petroleum ether / ethyl acetate = 40/1 (1230 mL)] as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45-7.43 (m, 2 H, ArH), 7.33 (t, *J* = 7.4 Hz, 2 H, ArH), 7.30-7.21 (m, 2 H, ArH), 7.06 (t, *J* = 7.6 Hz, 1 H, ArH), 6.98 (t, *J* = 10.0 Hz, 1 H, ArH), 6.91 (t, *J* = 8.0 Hz, 1 H, ArH), 6.61-6.47 (m, 1 H, =CH), 3.76-3.72 (m, 4 H, CH and OCH_3), 3.47 (s, 3 H, OCH_3), 3.33-3.26 (m, 1 H, one proton of CH_2), 3.17-3.11 (m, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.5, 169.3, 168.9, 163.1 (d, *J* = 243.6 Hz), 136.1 (d, *J* = 7.6 Hz), 134.7, 130.1 (d, *J* = 8.4 Hz), 128.6, 127.7, 126.0, 122.7 (d, *J* = 3.1 Hz), 114.3 (d, *J* = 21.4 Hz), 113.4 (d, *J* = 22.2 Hz), 108.1, 99.4 (d, *J* = 2.3 Hz), 52.7, 52.4, 50.0, 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$): -113.6; **IR** (neat): ν 2954, 1938, 1732, 1610, 1585, 1489, 1435, 1150 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 354 (M^+, 17.25), 222 (100); **HRMS** (ESI) Calcd for $C_{21}H_{20}O_4F$ $[M+H]^+$: 355.1340, Found: 355.1341.

(12) Compound **4kaa** (zzn-1-067)

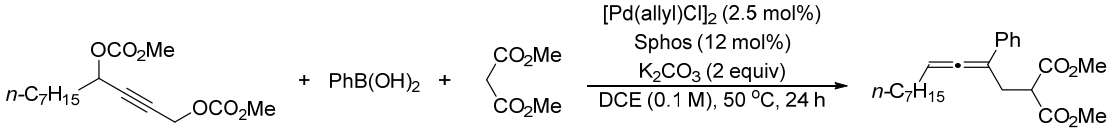


1k, 1 mmol **2a**, 1 mmol **3a**, 1.5 mmol **4kaa**, 85%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.2 mg, 0.025 mmol), Sphos (49.4 mg, 0.12 mmol), **1k** (568.1 mg, 1 mmol), **2a** (121.9 mg, 1

mmol), K_2CO_3 (276.6 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4kaa** (531.2 mg, 85%) [eluent: petroleum ether / ethyl acetate = 25/1 (520 mL) to petroleum ether / ethyl acetate = 18/1 (380 mL) to petroleum ether / ethyl acetate = 12/1 (520 mL)] as a yellow solid (we were not able to obtain the crystal from the solvent tested, the **m.p.** was determined by using the solid after evaporation of the eluent. When the white solid was heated up to 68.5 °C, it shrank. At 78.4 °C, the solid started melting. At 87.1 °C, the sample was completely melted and the color of the liquid was yellow); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (s, 1 H, ArH), 7.83-7.78 (m, 2 H, ArH), 7.72-7.69 (m, 2 H, ArH), 7.58 (d, *J* = 1.6 Hz, 1 H, ArH), 7.55-7.46 (m, 3 H, ArH), 7.41 (d, *J* = 8.4 Hz, 1 H, ArH), 7.35 (t, *J* = 7.6 Hz, 2 H, ArH), 7.27-7.24 (m, 1 H, ArH), 6.97 (d, *J* = 8.4 Hz, 1 H, ArH), 6.84-6.73 (m, 1 H, =CH), 3.89 (s, 3 H, OCH_3), 3.80 (t, *J* = 6.8 Hz, 1 H, CH), 3.72 (s, 3 H, OCH_3), 3.37-3.31 (m, 4 H, OCH_3 and one proton of CH_2), 3.20-3.17 (m, 1 H, one proton of CH_2), 2.18 (br, 6 H, 3 × CH_2), 2.09 (br, 3 H, 3 × CH), 1.79 (br, 6 H, 3 × CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.7, 169.5, 169.1, 158.5, 138.9, 138.8, 135.2, 133.2, 132.9, 132.4, 130.7, 128.6, 128.5, 128.1, 127.5, 126.05, 126.01, 125.78, 125.76, 125.5, 125.1, 124.8, 112.0, 107.8, 100.8, 55.1, 52.7, 52.5, 50.2, 40.6, 37.13, 37.09, 29.2, 29.1; **IR** (neat): ν 2901, 2848, 1748, 1604, 1495, 1441, 1234 cm^{-1}; **MS** (ESI) *m/z* 649.3 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{42}H_{42}O_5Na$ $[M+Na]^+$: 649.2924, Found: 649.2933.

(13) Dimethyl 2-(2-phenylundeca-2,3-dienyl) malonate **4laa** (lican-06-038)

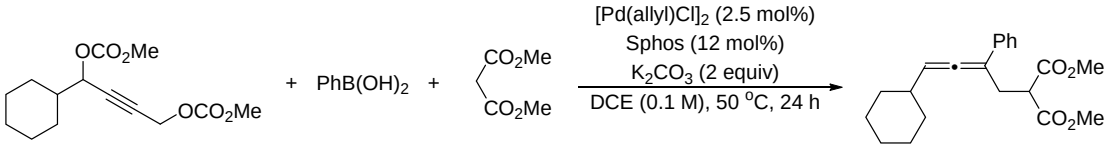


1l, 1 mmol **2a**, 1 mmol **3a**, 1.5 mmol **4laa**, 59%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.4 mg, 0.12 mmol), **1l** (301.2 mg, 1 mmol), **2a** (122.3 mg, 1 mmol), K_2CO_3 (276.4 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4laa** (215.8 mg, 59%, purity = 98%) [eluent: petroleum ether / ethyl acetate = 20/1 (630 mL)] as a yellowish oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ

7.38 (d, *J* = 8.0 Hz, 2 H, ArH), 7.30 (t, *J* = 7.6 Hz, 2 H, ArH), 7.18 (t, *J* = 7.0 Hz, 1 H, ArH), 5.59-5.52 (m, 1 H, =CH), 3.75-3.67 (m, 7 H, 2 × OCH_3 and CH), 3.13-2.96 (m, 2 H, CH_2), 2.07 (q, *J* = 7.6 Hz, 2 H, CH_2), 1.52-1.40 (m, 2 H, CH_2), 1.40-1.24 (m, 8 H, 4 × CH_2), 0.87 (t, *J* = 6.6 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.4, 169.3, 169.2, 136.2, 128.1, 126.6, 125.6, 103.0, 96.8, 52.3, 50.3, 31.6, 29.1, 28.9, 28.7, 22.4, 13.8; **IR** (neat): ν 2953, 2924, 2854, 1949, 1735, 1597, 1494, 1435, 1149 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 358 (M^+, 3.92), 142 (100); **HRMS** (FI) Calcd for $C_{22}H_{30}O_4$ $[M]^+$: 358.2139, Found: 358.2145.

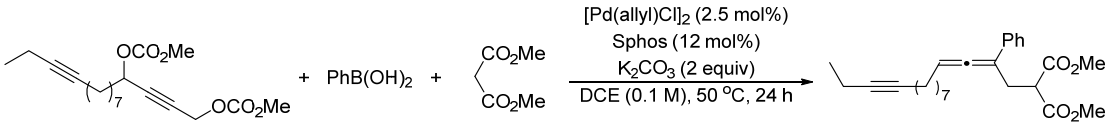
(14) Dimethyl 2-(2-phenyl-4-cyclohexylbuta-2,3-dienyl) malonate **4maa** (zzn-1-079)



1m, 1 mmol **2a**, 1 mmol **3a**, 1.5 mmol **4maa**, 50%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.2 mg, 0.12 mmol), **1m** (284.2 mg, 1 mmol), **2a** (121.8 mg, 1 mmol), K_2CO_3 (276.5 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4maa** (172.7 mg, 50%) [eluent: petroleum ether / ethyl acetate = 15/1 (960 mL)] as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41-7.39 (m, 2 H, ArH), 7.31 (t, *J* = 7.8 Hz, 2 H, ArH), 7.21-7.18 (m, 1 H, ArH), 5.59-5.50 (m, 1 H, =CH), 3.74-3.39 (m, 7 H, CH and 2 × OCH_3), 3.06-3.04 (m, 2 H, CH_2), 2.07 (br, 1 H, CH)，1.81-1.64 (m, 5 H), 1.33-1.10 (m, 5 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.3, 169.49, 169.46, 136.4, 128.3, 126.7, 125.6, 103.9, 103.0, 52.6, 52.5, 50.5, 38.0, 33.0, 32.9, 28.8, 26.01, 26.00, 25.97; **IR** (neat): ν 3028, 2923, 2850, 1946, 1753, 1734, 1597, 1494, 1435, 1342, 1265, 1229, 1148 cm^{-1}; **MS** (ESI) *m/z* 343.2 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{21}H_{27}O_4$ $[M+H]^+$: 343.1904, Found: 343.1906.

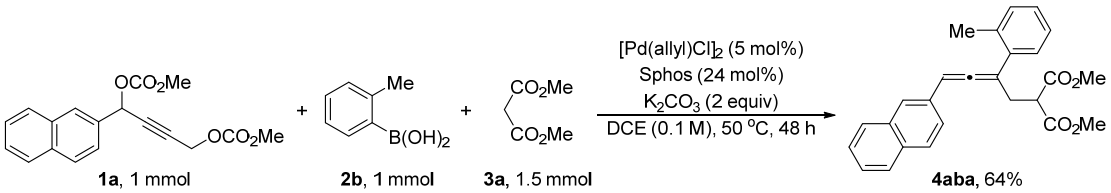
(15) Dimethyl 2-(2-phenylpentadeca-2,3-dien-12-ynyl) malonate **4naa** (lican-06-056)



1n, 1 mmol **2a**, 1 mmol **3a**, 1.5 mmol **4naa**, 63%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.5 mg, 0.12 mmol), **1n** (353.6 mg, 1 mmol), **2a** (121.9 mg, 1 mmol), K_2CO_3 (278.1 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4naa** (269.4 mg, 63%, purity = 96%) [eluent: petroleum ether / ethyl acetate = 25/1 (520 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.6 Hz, 2 H, ArH), 7.30 (t, *J* = 7.6 Hz, 2 H, ArH), 7.19 (t, *J* = 7.2 Hz, 1 H, ArH), 5.63-5.49 (m, 1 H, =CH), 3.81-3.63 (m, 7 H, 2 × OCH_3 and CH), 3.13-2.95 (m, 2 H, CH_2), 2.21-1.99 (m, 6 H, 3 × CH_2), 1.52-1.40 (m, 4 H, 2 × CH_2), 1.40-1.25 (m, 6 H, 3 × CH_2), 1.10 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.5, 169.4, 169.3, 136.2, 128.2, 126.7, 125.6, 103.1, 96.9, 81.5, 79.3, 52.4, 50.4, 29.1, 29.0, 28.94, 28.92, 28.82, 28.78, 28.66, 18.6, 14.2, 12.3; **IR** (neat): ν 2929, 2854, 1949, 1735, 1435, 1330, 1265, 1150 cm^{-1}; **MS** (ESI) *m/z* 411 $[M+H]^+$; **HRMS** (DART) Calcd for $C_{26}H_{35}O_4$ $[M+H]^+$: 411.2530, Found: 411.2526.

(16) Dimethyl 2-(2-(*o*-tolyl)-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aba** (zzn-1-029)

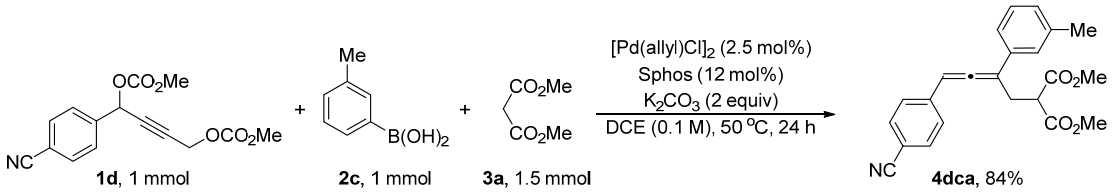


1a, 1 mmol **2b**, 1 mmol **3a**, 1.5 mmol **4aba**, 64%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (18.3 mg, 0.05 mmol), Sphos (98.4 mg, 0.24 mmol), **1a** (328.5 mg, 1 mmol), **2b** (135.8 mg, 1 mmol), K_2CO_3 (276.6 mg, 2 mmol), **3a** (229 μL, d = 1.156, 264.7 mg, 2 mmol) and DCE (10 mL) afforded **4aba** (256.0 mg, 64%) [eluent: petroleum ether / ethyl acetate = 18/1 (950 mL)] as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 6.8 Hz, 3 H, ArH), 7.64 (s, 1 H, ArH), 7.46-7.36 (m, 4 H, ArH), 7.22-7.19 (m, 3 H, ArH), 6.56-6.42 (m, 1 H, =CH), 3.76-3.70 (m, 4 H, CH and OCH_3), 3.46 (s, 3 H, OCH_3), 3.23-3.16 (m, 1 H, one proton of CH_2), 3.04-2.98 (m, 1 H, one proton of CH_2) , 2.41

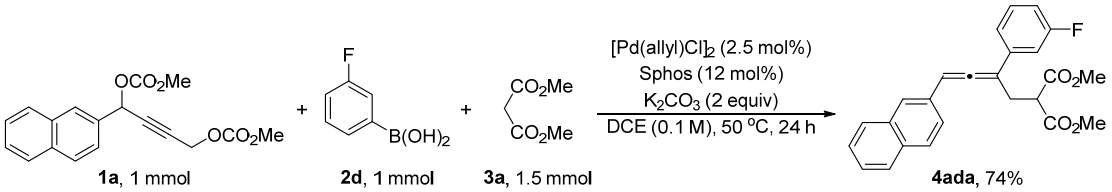
(s, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.4, 169.4, 169.2, 136.0, 136.0, 133.5, 132.7, 131.5, 130.6, 128.12, 128.10, 127.7, 127.6, 127.5, 126.2, 126.0, 125.9, 125.7, 124.9, 106.6, 97.6, 52.6, 52.5, 50.1, 32.9, 20.4; **IR** (neat): ν 3055, 2952, 1943, 1731, 1598, 1508, 1433, 1380, 1148 cm^{-1}; **MS** (ESI) *m/z* 401.2 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{26}H_{25}O_4$ $[M+H]^+$: 401.1747, Found: 401.1745.

(17) Dimethyl 2-(2-(*m*-tolyl)-4-(4-cyanophenyl)buta-2,3-dienyl) malonate **4dca** (zzn-1-036)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.3 mg, 0.12 mmol), **1d** (303.3 mg, 1 mmol), **2c** (135.9 mg, 1 mmol), K_2CO_3 (276.6 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4dca** (315.5 mg, 84%) [eluent: petroleum ether / ethyl acetate = 25/1 (520 mL) to petroleum ether / ethyl acetate = 12/1 (520 mL) to petroleum ether / ethyl acetate = 5/1 (480 mL)] as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60-7.58 (m, 2 H, ArH), 7.38-7.36 (m, 2 H, ArH), 7.26-7.22 (m, 3 H, ArH), 7.16-7.05 (m, 1 H, ArH), 6.64-6.55 (m, 1 H, =CH), 3.73-3.69 (m, 4 H, CH and OCH_3), 3.44 (s, 3 H, OCH_3), 3.33-3.26 (m, 1 H, one proton of CH_2), 3.14-3.10 (m, 1 H, one proton of CH_2), 2.34 (s, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 206.8, 169.2, 168.9, 138.9, 138.4, 134.0, 132.4, 128.8, 128.6, 127.4, 126.7, 123.2, 118.9, 110.6, 108.8, 99.1, 52.8, 52.5, 50.0, 29.1, 21.4; **IR** (neat): ν 3002, 2953, 2226, 1935, 1732, 1602, 1502, 1434, 1381, 1149 cm^{-1}; **MS** (ESI) *m/z* 398.1 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{23}H_{21}O_4NNa$ $[M+Na]^+$: 398.1363, Found: 398.1362.

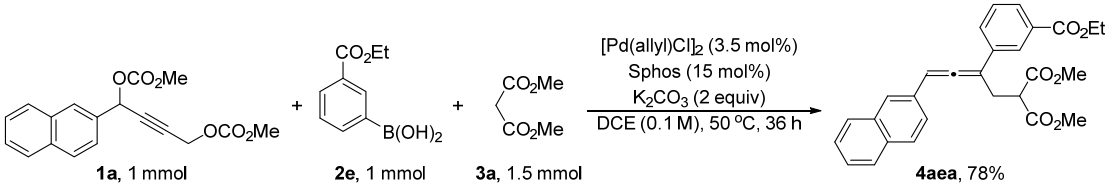
(18) Dimethyl 2-(2-(3-fluorophenyl)-4-(2-naphthyl)buta-2,3-dienyl) malonate **4ada** (zzn-1-088)



1a, 1 mmol **2d**, 1 mmol **3a**, 1.5 mmol **4ada**, 74%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.3 mg, 0.12 mmol), **1a** (328.2 mg, 1 mmol), **2d** (140.1 mg, 1 mmol), K_2CO_3 (276.5 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4ada** (298.1 mg, 74%) [eluent: petroleum ether / ethyl acetate = 15/1 (960 mL)] as a white solid: **m.p.** 104.9-105.9 ℃ (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86-7.72 (m, 3 H, ArH), 7.70 (s, 1 H, ArH), 7.52-7.35 (m, 3 H, ArH), 7.34-7.23 (m, 2 H, ArH), 7.18 (d, *J* = 10.2 Hz, 1 H, ArH), 6.95 (t, *J* = 7.6 Hz, 1 H, ArH), 6.84-6.74 (m, 1 H, =CH), 3.80-3.73 (m, 4 H, CH and OCH_3), 3.38-3.28 (m, 4 H, OCH_3 and one proton of CH_2), 3.16-3.11 (m, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.8, 169.3, 169.0, 163.1 (d, *J* = 244.4 Hz), 137.7 (d, *J* = 7.7 Hz), 133.6, 133.0, 130.6, 130.0 (d, *J* = 8.4 Hz), 128.4, 127.8 (d, *J* = 8.4 Hz), 126.4, 126.2, 126.0, 124.7, 121.6 (d, *J* = 3.0 Hz), 114.4 (d, *J* = 20.6 Hz), 113.0 (d, *J* = 23.0 Hz), 107.2 (d, *J* = 3.1 Hz), 101.1, 52.7, 52.5, 50.1, 29.1.; **^{19}F NMR** (376 MHz, $CDCl_3$): -113.4; **IR** (neat): ν 2969, 1936, 1743, 1726, 1609, 1581, 1485, 1431, 1242 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 404 (M^+, 10.69), 272 (100); **Elem. Anal.** Calcd. for $C_{25}H_{21}FO_4$: C, 74.25; H, 5.23; Found: C, 73.86; H, 5.20.

(19) Dimethyl 2-(2-(3-ethoxycarbonylphenyl)-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aea** (lican-06-009)

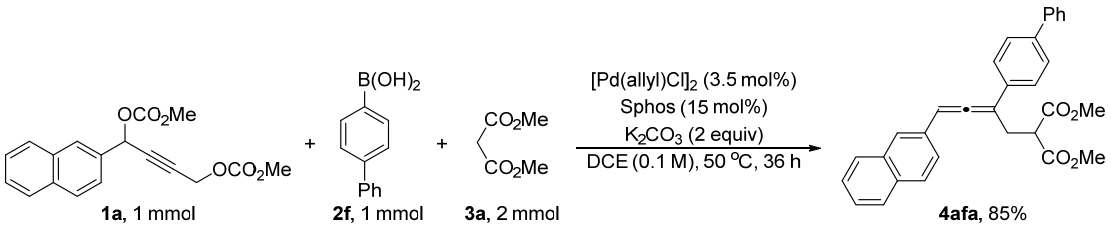


1a, 1 mmol **2e**, 1 mmol **3a**, 1.5 mmol **4aea**, 78%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (12.8 mg, 0.035 mmol), Sphos (61.6 mg, 0.15 mmol), **1a** (328.6 mg, 1 mmol), **2e** (194.5 mg, 1 mmol), K_2CO_3 (276.8 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4aea** (357.9 mg, 78%) [eluent: petroleum ether / ethyl acetate

= 20/1 (630 mL)] as a white solid: **m.p.** 95.5-97.0 °C (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15 (s, 1 H, ArH), 7.94 (d, *J* = 8.0 Hz, 1 H, ArH), 7.84-7.73 (m, 3 H, ArH), 7.68 (d, *J* = 10.4 Hz, 2 H, ArH), 7.51-7.33 (m, 4 H, ArH), 6.82 (t, *J* = 3.4 Hz, 1 H, =CH), 4.37 (q, *J* = 7.1 Hz, 2 H, OCH_2), 3.80 (dd, J_1 = 8.8 Hz, J_2 = 5.6 Hz, 1 H, CH), 3.73 (s, 3 H, OCH_3), 3.46-3.29 (m, 4 H, OCH_3 and one proton of CH_2), 3.25-3.13 (m, 1 H, one proton of CH_2), 1.36 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.7, 169.3, 168.9, 166.3, 135.6, 133.5, 132.9, 130.9, 130.7, 130.6, 128.6, 128.5, 128.3, 127.7, 127.6, 126.6, 126.3, 126.1, 125.9, 124.6, 107.4, 101.1, 61.0, 52.7, 52.4, 50.0, 29.1, 14.2; **IR** (neat): ν 3064, 2985, 2948, 2909, 2110, 1933, 1715, 1599, 1436, 1280, 1240 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 458 (M^+, 10.79), 326 (100); **Elem. Anal.** Calcd. for $C_{28}H_{26}O_6$: C, 73.35; H, 5.72, found C, 73.08; H, 5.85.

(20) Dimethyl 2-(2-(4-biphenyl)-4-(2-naphthyl)buta-2,3-dienyl) malonate **4afa** (lican-05-138)

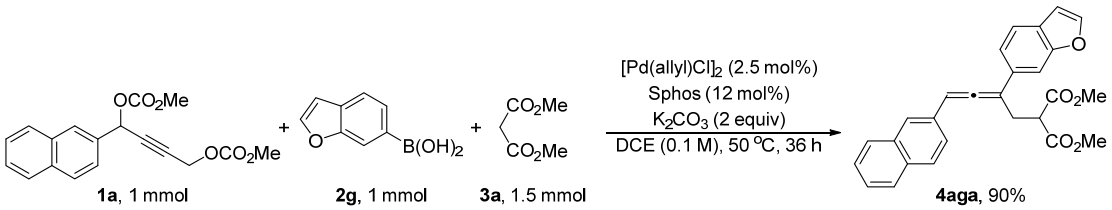


1a, 1 mmol **2f**, 1 mmol **3a**, 2 mmol **4afa**, 85%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (12.9 mg, 0.035 mmol), Sphos (62.0 mg, 0.15 mmol), **1a** (328.5 mg, 1 mmol), **2f** (198.4 mg, 1 mmol), K_2CO_3 (277.3 mg, 2 mmol), **3a** (229 μL, d = 1.156, 264.7 mg, 2 mmol) and DCE (10 mL) afforded **4afa** (393.2 mg, 85%) [eluent: petroleum ether / ethyl acetate = 10/1 (550 mL)] as a white solid: **m.p.** 154.6-155.1 °C (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83-7.74 (m, 3 H, ArH), 7.72 (s, 1 H, ArH), 7.64-7.53 (m, 6 H, ArH), 7.50-7.39 (m, 5 H, ArH), 7.33 (t, *J* = 7.4 Hz, 1 H, ArH), 6.81 (t, *J* = 3.2 Hz, 1 H, =CH), 3.82 (dd, J_1 = 8.8 Hz, J_2 = 6.0 Hz, 1 H, CH), 3.73 (s, 3 H, OCH_3), 3.45-3.31 (m, 4 H, OCH_3 and one proton of CH_2), 3.26-3.15 (m, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.9, 169.5, 169.1, 140.5, 140.4, 134.1, 133.6, 132.9, 131.1, 128.8, 128.4, 127.8, 127.7, 127.4, 127.3, 126.9, 126.4, 126.3, 126.1,

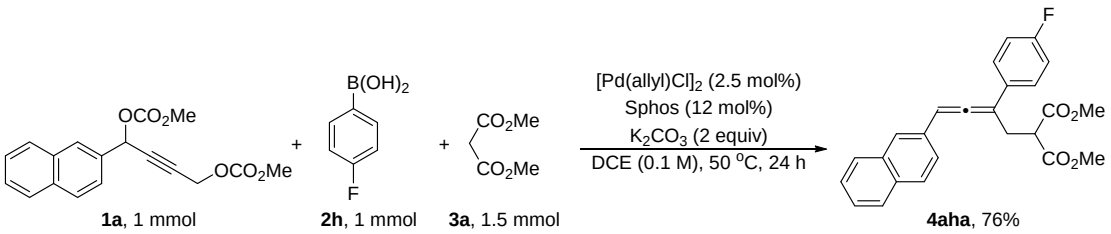
125.9, 124.8, 107.6, 100.8, 52.7, 52.5, 50.2, 29.1; **IR** (neat): ν 3056, 3030, 3002, 2951, 1927, 1748, 1727, 1485, 1435, 1340, 1251, 1149 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 462 (M^+, 4.07), 330 (100); **Elem. Anal.** Calcd. for $C_{31}H_{26}O_4$: C, 80.50; H, 5.67, found C, 80.44; H, 5.68.

(21) Dimethyl 2-(2-(5-benzofuranyl)-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aga** (lican-06-036)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.3 mg, 0.12 mmol), **1a** (328.5 mg, 1 mmol), **2g** (162.4 mg, 1 mmol), K_2CO_3 (278.0 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4aga** (385.6 mg, 90%) [eluent: petroleum ether / ethyl acetate = 20/1 (840 mL)] as a white solid: **m.p.** 130.6-132.2 °C (hexane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83-7.74 (m, 3 H, ArH), 7.71 (s, 2 H, ArH), 7.60 (s, 1 H, ArH), 7.50-7.38 (m, 5 H, ArH), 6.81-6.76 (m, 1 H, =CH), 6.74 (s, 1 H, ArH), 3.82 (dd, 1 H, J_1 = 8.4 Hz, J_2 = 6.0 Hz, CH), 3.73 (s, 3 H, OCH_3), 3.46-3.32 (m, 4 H, OCH_3 and one proton of CH_2), 3.28-3.18 (m, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.5, 169.5, 169.1, 154.4, 145.5, 133.6, 132.8, 131.3, 129.9, 128.3, 127.77, 127.72, 127.65, 126.2, 126.0, 125.8, 124.7, 123.0, 118.3, 111.4, 108.0, 106.6, 100.4, 52.7, 52.4, 50.2, 29.6; **IR** (neat): ν 3120, 3003, 2952, 2926, 2846, 1933, 1722, 1436, 1284, 1239 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 426 (M^+, 9.61), 294 (100); **Elem. Anal.** Calcd. for $C_{27}H_{22}O_5$: C, 76.04; H, 5.20, found C, 75.90; H, 5.27.

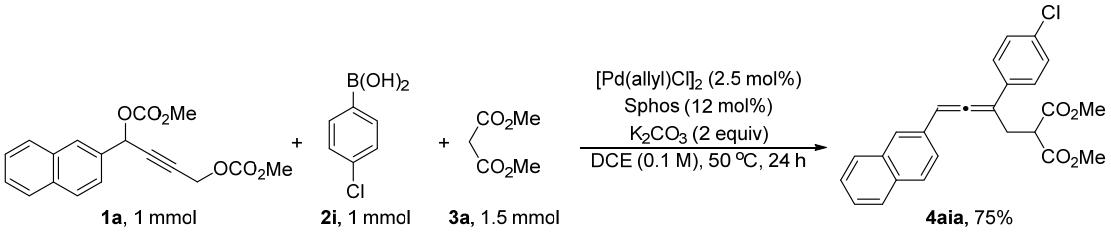
(22) Dimethyl 2-(2-(4-fluorophenyl)-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aha** (zzn-1-089)



1a, 1 mmol **2h**, 1 mmol **3a**, 1.5 mmol **4aha**, 76%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.2 mg, 0.025 mmol), Sphos (49.5 mg, 0.12 mmol), **1a** (328.3 mg, 1 mmol), **2h** (140.1 mg, 1 mmol), K_2CO_3 (276.3 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4aha** (307.1 mg, 76%) [eluent: petroleum ether / ethyl acetate = 15/1 (960 mL)] as a white solid: **m.p.** 118.7-120.1 ℃ (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80-7.75 (m, 3 H, ArH), 7.69 (s, 1 H, ArH), 7.46-7.39 (m, 5 H, ArH), 7.05-7.01 (m, 2 H, ArH), 6.82-6.73 (m, 1 H, =CH), 3.79-3.72 (m, 4 H, CH and OCH_3), 3.37-3.27 (m, 4 H, OCH_3 and one proton of CH_2), 3.16-3.10 (m, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.4 (d, *J* = 1.5 Hz), 169.4, 169.1, 162.3 (d, *J* = 245.9 Hz), 133.6, 132.9, 131.1 (d, *J* = 3.0 Hz), 131.0, 128.4, 127.8 (d, *J* = 6.9 Hz), 127.7, 127.6, 126.4, 126.1, 125.9, 124.6, 115.6 (d, *J* = 21.5 Hz), 107.1, 100.9, 52.7, 52.5, 50.1, 29.3.; **^{19}F NMR** (376 MHz, $CDCl_3$): -115.1; **IR** (neat): ν 2960, 1934, 1725, 1596, 1506, 1438, 1357, 1289 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 404 (M^+, 10.68), 272 (100); **Elem. Anal.** Calcd. for $C_{25}H_{21}FO_4$: C, 74.25; H, 5.23; Found: C, 73.94; H, 5.20.

(23) Dimethyl 2-(2-(4-chlorophenyl)-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aia** (lican-05-093)

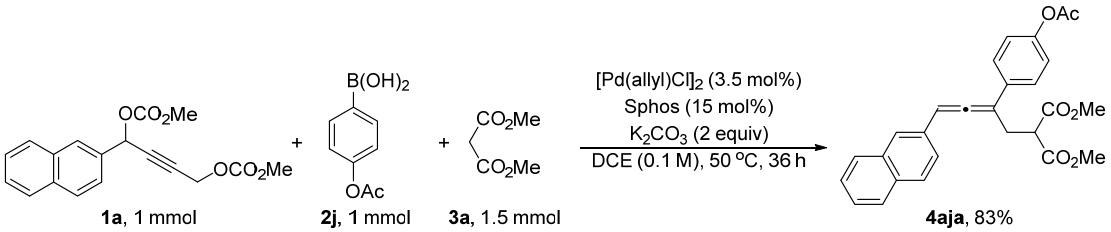


1a, 1 mmol **2i**, 1 mmol **3a**, 1.5 mmol **4aia**, 75%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.2 mg, 0.12 mmol), **1a** (328.5 mg, 1 mmol), **2i** (156.9 mg, 1 mmol), K_2CO_3 (277.0 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4aia** (316.9 mg, 75%) [eluent: petroleum ether / ethyl acetate

= 9/1 (500 mL)] as a white solid: **m.p.** 136.0-137.4 °C (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85-7.72 (m, 3 H, ArH), 7.68 (s, 1 H, ArH), 7.51-7.34 (m, 5 H, ArH), 7.29 (d, J = 8.4 Hz, 2 H, ArH), 6.83-6.73 (m, 1 H, =CH), 3.77 (dd, J_1 = 8.6 Hz, J_2 = 5.8 Hz, 1 H, CH), 3.72 (s, 3 H, OCH_3), 3.36 (s, 3 H, OCH_3), 3.36-3.23 (m, 1 H, one proton of CH_2), 3.19-3.06 (m, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.6, 169.3, 169.0, 133.7, 133.6, 133.3, 132.9, 130.7, 128.7, 128.4, 127.8, 127.7, 127.2, 126.3, 126.2, 126.0, 124.6, 107.1, 101.0, 52.7, 52.5, 50.0, 29.0; **IR** (neat): ν 3063, 2949, 2924, 2845, 1933, 1725, 1488, 1437, 1329, 1160 cm^{-1}; **MS** (ESI) *m/z* 443 [M(^{35}Cl)+Na]$^+$; **Elem. Anal.** Calcd. for $C_{25}H_{21}ClO_4$: C, 71.34; H, 5.03, found C, 71.60; H, 5.41.

(24) Dimethyl 2-(2-(4-acetoxyphenyl)-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aja** (lican-06-008)

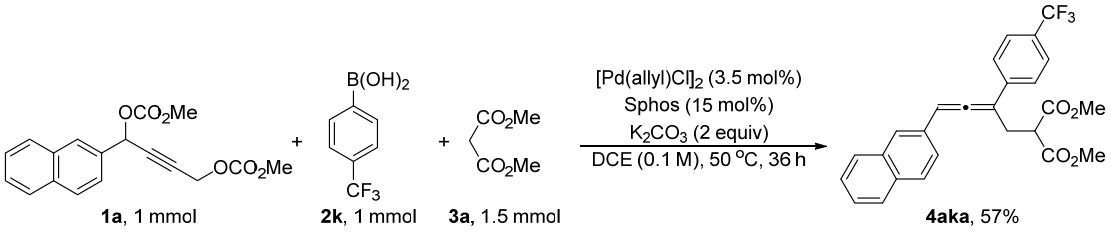


1a, 1 mmol **2j**, 1 mmol **3a**, 1.5 mmol **4aja**, 83%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (12.9 mg, 0.035 mmol), Sphos (61.8 mg, 0.15 mmol), **1a** (328.7 mg, 1 mmol), **2j** (180.5 mg, 1 mmol), K_2CO_3 (277.5 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4aja** (370.3 mg, 83%) [eluent: petroleum ether / ethyl acetate = 15/1 (960 mL)] as a yellow solid: **m.p.** 123.2-124.9 °C (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84-7.72 (m, 3 H, ArH), 7.69 (s, 1 H, ArH), 7.54-7.47 (m, 2 H, ArH), 7.47-7.42 (m, 2 H, ArH), 7.42-7.36 (m, 1 H, ArH), 7.07 (d, J = 8.8 Hz, 2 H, ArH), 6.78 (t, J = 3.4 Hz, 1 H, =CH), 3.78 (dd, J_1 = 8.8 Hz, J_2 = 6.0 Hz, 1 H, CH), 3.72 (s, 3 H, OCH_3), 3.42-3.25 (m, 4 H, OCH_3 and one proton of CH_2), 3.20-3.08 (m, 1 H, one proton of CH_2), 2.29 (s, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.7, 169.44, 169.41, 169.0, 150.0, 133.6, 132.90, 132.85, 130.9, 128.4, 127.8, 127.7, 127.0, 126.3, 126.1, 125.9, 124.7, 121.8, 107.2, 100.9, 52.7, 52.5, 50.1, 29.2, 21.1; **IR** (neat): ν 3667, 2958, 2903, 2113, 1927, 1749, 1721, 1503, 1431, 1216 cm^{-1}; **MS** (70 eV, EI)

m/z (%): 444 (M^+, 6.85), 270 (100); **Elem. Anal.** Calcd. for $C_{27}H_{24}O_6$: C, 72.96; H, 5.44, found C, 72.66; H, 5.66.

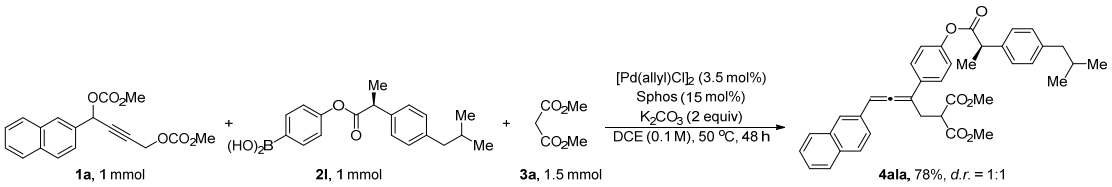
(25) Dimethyl 2-(2-(4-(trifluoromethyl)phenyl)-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aka** (lican-06-035)



1a, 1 mmol **2k**, 1 mmol **3a**, 1.5 mmol **4aka**, 57%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (13.0 mg, 0.036 mmol), Sphos (61.6 mg, 0.15 mmol), **1a** (328.5 mg, 1 mmol), **2k** (190.6 mg, 1 mmol), K_2CO_3 (276.0 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4aka** (259.4 mg, 57%) [eluent: petroleum ether / ethyl acetate = 20/1 (840 mL)] as a light brown solid: **m.p.** 94.1-95.8 °C (hexane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86-7.74 (m, 3 H, ArH), 7.71 (s, 1 H, ArH), 7.59 (s, 4 H, ArH), 7.52-7.42 (m, 2 H, ArH), 7.65 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1 H, ArH), 6.84 (t, J = 3.4 Hz, 1 H, =CH), 3.79 (dd, J_1 = 8.8 Hz, J_2 = 6.0 Hz, 1 H, CH), 3.74 (s, 3 H, OCH_3), 3.42-3.28 (m, 4 H, OCH_3 and one proton of CH_2), 3.16 (ddd, J_1 = 15.9 Hz, J_2 = 5.9 Hz, J_3 = 3.9 Hz, 1 H, one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 206.3, 169.3, 168.9, 139.0, 133.6, 133.0, 130.3, 129.4 (q, J = 32.2 Hz), 128.5, 127.8, 127.7, 126.4, 126.3, 126.2, 126.1, 125.5 (q, J = 3.8 Hz), 124.6, 124.1 (q, J = 270.4 Hz), 107.1, 101.2, 52.7, 52.5, 50.0, 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$): -63.0; **IR** (neat): ν 3067, 2952, 1928, 1748, 1726, 1612, 1506, 1434, 1413, 1321, 1257, 1123, 1107 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 454 (M^+, 13.91), 322 (100); **Elem. Anal.** Calcd. for $C_{26}H_{21}F_3O_4$: C, 68.72; H, 4.66, found C, 68.57; H, 4.86.

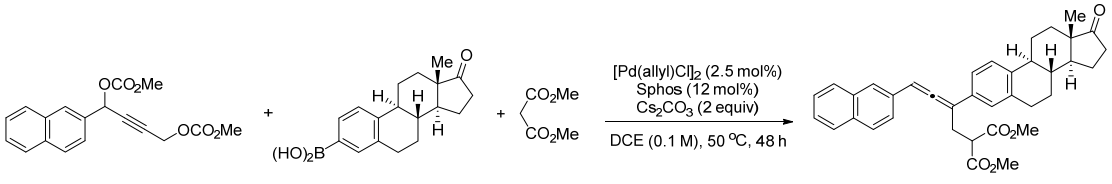
(26) Compound **4ala** (zzn-1-063)



1a, 1 mmol **2l**, 1 mmol **3a**, 1.5 mmol **4ala,** 78%, *d.r.* = 1:1

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (12.8 mg, 0.035 mmol), Sphos (61.7 mg, 0.15 mmol), **1a** (328.8 mg, 1 mmol), **2l**[5] (326.1 mg, 1 mmol), K_2CO_3 (276.6 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4ala** (458.3 mg, 78%, *d.r.* = 1:1) [eluent: petroleum ether / ethyl acetate = 40/1 (820 mL) to petroleum ether / ethyl acetate = 20/1 (840 mL) to petroleum ether / ethyl acetate = 10/1 (440 mL)] (HPLC conditions: Chiralcel OD-H column, *n*hexane / *i*PrOH = 80/20, 1.0 mL/min, λ = 214 nm, t_{R1} = 7.5 min, t_{R2} = 9.2 min) as a white solid: m.p. 62.0-63.3 ℃ (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 3 H, ArH), 7.67 (s, 1 H, ArH), 7.46-7.37 (m, 5 H, ArH), 7.28 (d, *J* = 8.0 Hz, 2 H, ArH), 7.12 (d, *J* = 8.0 Hz, 2 H, ArH), 6.97 (d, *J* = 8.4 Hz, 2 H, ArH), 6.75 (t, *J* = 3.4 Hz, 1 H, =CH), 3.91 (q, *J* = 7.1 Hz, 1 H, CH), 3.76 (dd, J_1 = 5.6 Hz, J_2 = 3.2 Hz, 1 H, CH), 3.70 (s, 3 H, OCH_3), 3.44-3.25 (m, 4 H, one proton of CH_2 and OCH_3), 3.15-3.09 (m, 1 H, one proton of CH_2), 2.45 (d, *J* = 7.6 Hz, 2 H, CH_2), 1.91-1.79 (m, 1 H, CH), 1.58 (d, *J* = 7.2 Hz, 3 H, CH_3), 0.89 (d, *J* = 6.8 Hz, 6 H, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.6, 173.1, 169.4, 169.0, 150.2, 140.7, 137.1, 133.6, 132.8, 132.6, 130.9, 129.4, 128.3, 127.73, 127.65, 127.1, 126.9, 126.3, 126.0, 125.9, 124.6, 121.6, 107.2, 100.8, 52.7, 52.4, 50.1, 45.2, 44.9, 30.1, 29.2, 22.3, 18.4; **IR** (neat): ν 2961, 2870, 1938, 1905, 1743, 1731, 1599, 1505, 1432, 1340, 1264 cm^{-1}; **MS** (ESI) *m/z* 591.3 $[M+H]^+$; **HRMS** (DART) Calcd for $C_{38}H_{39}O_6$ $[M+H]^+$: 591.2741, Found: 591.2738. **Elem. Anal.** Calcd. for $C_{38}H_{38}O_6$: C, 77.27; H, 6.48; Found: C, 77.54; H, 6.25.

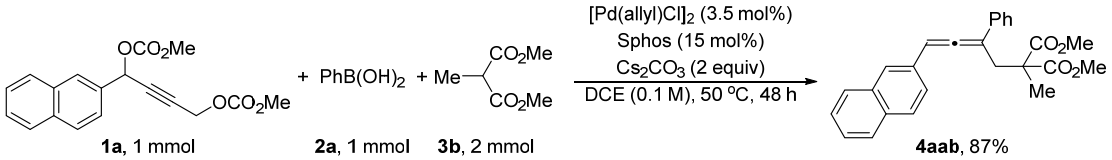
(27) Compound **4ama** (zzn-1-151)



1a, 1 mmol **2m**, 1 mmol **3a**, 1.5 mmol **4ama**, 55%, *d.r.* = 1:1

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.4 mg, 0.12 mmol), **1a** (328.2 mg, 1 mmol), **2m**[6] (298.2 mg, 1 mmol), Cs_2CO_3 (651.3 mg, 2 mmol), **3a** (171 μL, d = 1.156, 197.7 mg, 1.5 mmol) and DCE (10 mL) afforded **4ama** (309.7 mg, 55%, *d.r.* = 1:1) [eluent: petroleum ether / ethyl acetate = 10/1 (1100 mL) to petroleum ether / ethyl acetate = 8/1 (450 mL) to petroleum ether / ethyl acetate = 5/1 (600 mL) to petroleum ether / ethyl acetate = 2/1 (600 mL)] (HPLC conditions: Chiralcel AD-H column, *n*hexane / *i*PrOH = 80/20, 1.0 mL/min, λ = 214 nm, t_{R1} = 19.7 min, t_{R2} = 26.3 min) as a yellow solid (we were not able to obtain the crystal from the solvent tested, the **m.p.** was determined by using the solid after evaporation of the eluent. When the white solid was heated up to 63.6 °C, it shrank. At 82.5 °C, the sample was completely melted and the color of the liquid was yellow); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88-7.72 (m, 3 H, ArH), 7.69 (s, 1 H, ArH), 7.46-7.39 (m, 3 H, ArH), 7.28-7.22 (m, 3 H, ArH), 6.82-6.70 (m, 1 H, =CH), 3.80-3.73 (m, 4 H), 3.36-3.29 (m, 4 H), 3.15-3.11 (m, 1 H), 3.01-2.82 (m, 2 H), 2.54-2.40 (m, 2 H), 2.33-2.26 (m, 1 H), 2.19-1.95 (m, 4 H), 1.68-1.41 (m, 6 H), 0.90 (s, 3 H); **IR** (neat): ν 2925, 1932, 1732, 1500, 1434, 1340, 1258, 1149, 1084cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 562 (M^+, 1.8), 281 (100); **Elem. Anal.** Calcd. for $C_{37}H_{38}O_5$: C, 78.98; H, 6.81; Found: C, 78.66; H, 7.18.

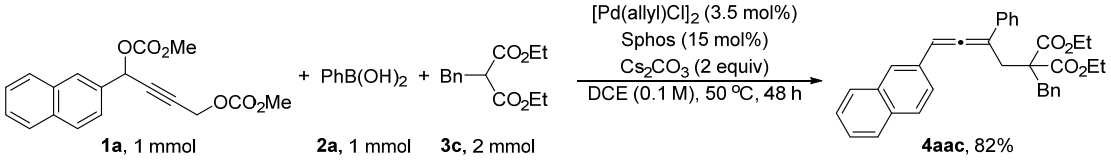
(28) Dimethyl 2-methyl-2-(2-phenyl-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aab** (lican-06-126)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (12.9 mg, 0.035 mmol), Sphos (62.3 mg, 0.15 mmol), **1a** (328.3 mg, 1 mmol), **2a** (121.9 mg, 1 mmol), Cs_2CO_3 (652.7 mg, 2 mmol), **3b** (266 μL, d = 1.098 g/mL, 292.1 mg, 2 mmol) and DCE (10 mL) afforded **4aab** (349.2 mg, 87%) [eluent: petroleum ether / ethyl acetate = 40/1 (410 mL) to petroleum ether / ethyl acetate = 20/1 (630 mL)] as a light

yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 3 H, ArH), 7.69 (s, 1 H, ArH), 7.55-7.45 (m, 3 H, ArH), 7.44-7.34 (m, 2 H, ArH), 7.29 (t, *J* = 7.4 Hz, 2 H, ArH), 7.19 (t, *J* = 7.2 Hz, 1 H, ArH), 6.70-6.60 (m, 1 H, =CH), 3.54 (s, 3 H, OCH_3), 3.45-3.32 (m, 4 H, OCH_3 and one proton of CH_2), 3.25 (d, *J* = 15.2 Hz, 1 H, one proton of CH_2), 1.55 (s, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.4, 172.1, 171.7, 136.1, 133.5, 132.7, 131.1, 128.4, 128.2, 127.63, 127.58, 127.3, 126.22, 126.15, 125.9, 125.7, 124.7, 105.3, 98.6, 53.4, 52.4, 52.3, 35.6, 20.0; **IR** (neat): ν 3054, 2997, 2950, 2841, 1934, 1729, 1596, 1493, 1434, 1377, 1242, 1103 cm^{-1}; **MS** (ESI) *m/z* 423 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{26}H_{24}O_4Na$ $[M+Na]^+$: 423.1567, Found: 423.1570.

(29) Diethyl 2-benzyl-2-(2-phenyl-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aac** (lican-06-119)

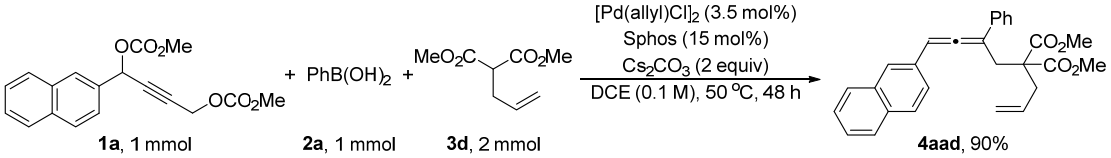


1a, 1 mmol **2a**, 1 mmol **3c**, 2 mmol **4aac**, 82%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (12.8 mg, 0.035 mmol), Sphos (61.6 mg, 0.15 mmol), **1a** (328.6 mg, 1 mmol), **2a** (121.8 mg, 1 mmol), Cs_2CO_3 (651.4 mg, 2 mmol), **3c** (501.8 mg, 2 mmol) and DCE (10 mL) afforded **4aac** (430.3 mg, 82%, purity = 97%) [eluent: petroleum ether / ethyl acetate = 30/1 (310 mL) to petroleum ether / ethyl acetate = 20/1 (840 mL)] as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85-7.66 (m, 4 H, ArH), 7.74 (d, *J* = 8.4 Hz, 1 H, ArH), 7.49 (d, *J* = 7.6 Hz, 2 H, ArH), 7.42-7.30 (m, 2 H, ArH), 7.26 (t, *J* = 7.2 Hz, 2 H, ArH), 7.21-7.03 (m, 6 H, ArH), 6.87-6.69 (m, 1 H, =CH), 4.03 (q, *J* = 6.9 Hz, 2 H, OCH_2), 3.89-3.77 (m, 1 H, one proton of OCH_2), 3.76-3.62 (m, 1 H, one proton of OCH_2), 3.49 (s, 2 H, CH_2), 3.10 (d, *J* = 16.0 Hz, 1 H, one proton of CH_2), 3.15 (d, *J* = 16.0 Hz, 1 H, one proton of CH_2), 1.11 (t, *J* = 7.2 Hz, 3 H, CH_3), 0.98 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.3, 170.2, 170.0, 136.2, 136.1, 133.5, 132.7, 131.1, 129.9, 128.3, 128.2, 128.0, 127.6, 127.5, 127.2, 126.7, 126.2, 126.1, 126.0, 125.6, 124.6, 105.4, 99.6, 61.1, 58.2, 37.2, 31.2, 13.7, 13.5; **IR** (neat): ν 3059,

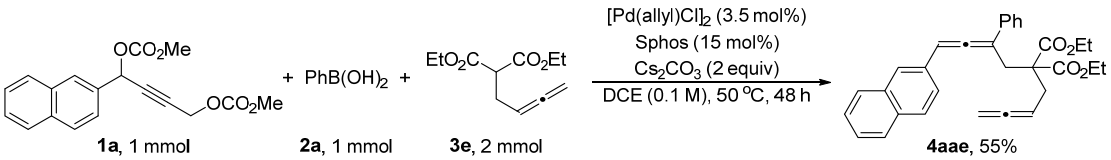
3030, 2981, 2252, 1935, 1727, 1597, 1494, 1444, 1283, 1244, 1180 cm^{-1}; **MS** (ESI) *m/z* 505 $[M+H]^+$; **HRMS** (DART) Calcd for $C_{34}H_{33}O_4$ $[M+H]^+$: 505.2373, Found: 505.2368.

(30) Dimethyl 2-allyl-2-(2-phenyl-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aad** (lican-06-127)



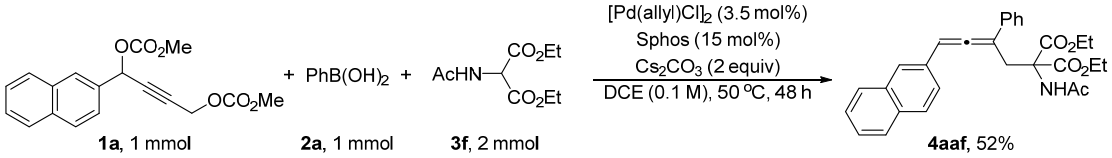
Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (12.9 mg, 0.035 mmol), Sphos (62.0 mg, 0.15 mmol), **1a** (328.7 mg, 1 mmol), **2a** (122.4 mg, 1 mmol), Cs_2CO_3 (651.9 mg, 2 mmol), **3d** (322 μL, d = 1.071 g/mL, 344.9 mg, 2 mmol) and DCE (10 mL) afforded **4aad** (382.9 mg, 90%) [eluent: petroleum ether / ethyl acetate = 25/1 (1040 mL)] as a yellowish oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87-7.75 (m, 3 H, ArH), 7.72 (s, 1 H, ArH), 7.58-7.38 (m, 5 H, ArH), 7.32 (t, *J* = 7.0 Hz, 2 H, ArH), 7.28-7.17 (m, 1 H, ArH), 6.77-6.58 (m, 1 H, =CH), 5.75-5.54 (m, 1 H, =CH), 5.11-4.89 (m, 2 H, $=CH_2$), 3.56 (s, 3 H, OCH_3), 3.41 (s, 3 H, OCH_3), 3.33 (d, *J* = 15.2 Hz, 1 H, one proton of CH_2), 3.24 (d, *J* = 15.2 Hz, 1 H, one proton of CH_2), 2.81 (d, *J* = 6.8 Hz, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.6, 170.9, 170.8, 136.2, 133.6, 132.8, 132.3, 131.2, 128.43, 128.36, 127.73, 127.68, 127.4, 126.5, 126.2, 126.0, 125.8, 124.8, 119.5, 105.2, 98.6, 57.4, 52.4, 52.3, 36.4, 32.3; **IR** (neat): ν 3056, 2980, 2950, 2841, 1938, 1754, 1731, 1595, 1494, 1437, 1295, 1204 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 426 (M^+, 54.36), 256 (100); **HRMS** (FI) Calcd for $C_{28}H_{26}O_4$ $[M]^+$: 426.1826, Found: 426.1832.

(31) Diethyl 2-(buta-2,3-dienyl)-2-(2-phenyl-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aae** (lican-06-138)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (12.8 mg, 0.035 mmol), Sphos (62.0 mg, 0.15 mmol), **1a** (328.5 mg, 1 mmol), **2a** (122.1 mg, 1 mmol), Cs_2CO_3 (651.0 mg, 2 mmol), **3e** (424.7 mg, 2 mmol) and DCE (10 mL) afforded **4aae** (257.5 mg, 55%) [eluent: petroleum ether / ethyl acetate = 25/1 (520 mL)] as a light green solid: **m.p.** 73.9-74.6 °C (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84-7.73 (m, 3 H, ArH), 7.70 (s, 1 H, ArH), 7.55-7.46 (m, 3 H, ArH), 7.45-7.38 (m, 2 H, ArH), 7.30 (t, *J* = 7.4 Hz, 2 H, ArH), 7.21 (t, *J* = 7.0 Hz, 1 H, ArH), 6.74-6.57 (m, 1 H, =CH), 4.95 (quint, *J* = 7.1 Hz, 1 H, =CH), 4.60-4.45 (m, 2 H, $=CH_2$), 4.09-3.89 (m, 3 H, OCH_2 and one proton of OCH_2), 3.88-3.77 (m, 1 H, one proton of OCH_2), 3.41-3.27 (m, 2 H, CH_2), 2.86-2.72 (m, 2 H, CH_2), 1.14 (t, *J* = 7.2 Hz, 3 H, OCH_3), 1.08 (t, *J* = 7.0 Hz, 3 H, OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 210.0, 207.7, 170.4, 170.3, 136.3, 133.6, 132.8, 131.3, 128.4, 128.3, 127.72, 127.66, 127.3, 126.5, 126.2, 125.9, 125.7, 124.8, 105.2, 98.7, 84.3, 74.5, 61.3, 57.4, 32.0, 31.3, 13.8, 13.7; **IR** (neat): ν 3053, 2987, 2942, 2904, 1949, 1744, 1719, 1595, 1442, 1321, 1275, 1237, 1192, 1065, 1018 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 466 (M^+, 37.44), 319 (100); **Elem. Anal.** Calcd. for $C_{31}H_{30}O_4$: C, 79.80; H, 6.48, found C, 79.58; H, 6.57.

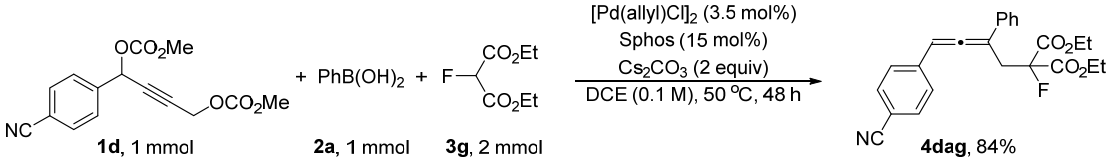
(32) Diethyl 2-acetamido-2-(2-phenyl-4-(2-naphthyl)buta-2,3-dienyl) malonate **4aaf** (lican-06-135)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (12.8 mg, 0.035 mmol), Sphos (61.6 mg, 0.15 mmol), **1a** (328.6 mg, 1 mmol), **2a** (122.1 mg, 1 mmol), Cs_2CO_3 (652.7 mg, 2 mmol), **3f** (433.1 mg, 2 mmol) and DCE (10 mL) afforded **4aaf** (247.4 mg, 52%) [eluent: petroleum ether / ethyl acetate = 4/1 (500 mL)] as a light yellow solid: **m.p.** 147.4-147.9 °C (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.0 Hz, 3 H, ArH), 7.74 (s, 1 H, ArH), 7.53 (d, *J* = 8.4 Hz, 1 H, ArH), 7.51-7.39 (m, 4 H, ArH), 7.32 (t, *J* = 7.4 Hz, 2 H, ArH), 7.26-7.19 (m, 1 H, ArH), 6.79-6.70 (m, 1 H, =CH), 6.65 (s, 1 H, NH), 4.22-4.05 (m, 3 H, OCH_2 and one

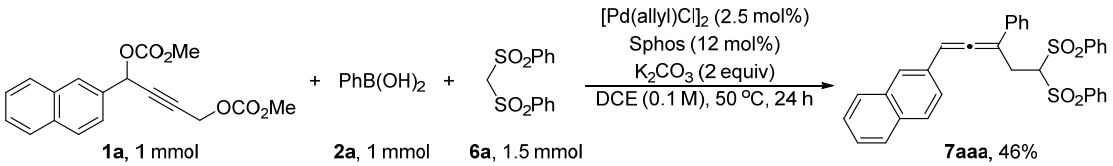
proton of OCH_2), 3.97-3.85 (m, 1 H, one proton of OCH_2), 3.79-3.65 (m, 2 H, CH_2), 1.50 (s, 3 H, CH_3), 1.26-1.04 (m, 6 H, 2 × OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.2, 169.1, 167.5, 167.4, 135.9, 133.6, 132.8, 131.3, 128.51, 128.48, 127.7, 127.4, 126.40, 126.37, 125.89, 125.86, 124.6, 104.8, 98.1, 66.0, 62.5, 32.5, 22.4, 13.8, 13.7; **IR** (neat): ν 3348, 3059, 3019, 2987, 2905, 1933, 1734, 1504, 1443, 1366, 1294, 1279, 1225, 1197, 1088 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 471 (M^+, 38.72), 429 (100); **Elem. Anal.** Calcd. for $C_{29}H_{29}NO_5$: C, 73.87; H, 6.20; N, 2.97, found C, 73.74; H, 6.14; N, 2.65.

(33) Diethyl 2-fluoro-2-(2-phenyl-4-(4-cyanophenyl)buta-2,3-dienyl) malonate **4dag** (lican-06-164)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (12.8 mg, 0.035 mmol), Sphos (61.6 mg, 0.15 mmol), **1d** (303.8 mg, 1 mmol), **2a** (122.1 mg, 1 mmol), Cs_2CO_3 (652.7 mg, 2 mmol), **3g** (324 μL, 365.8 mg, d = 1.129 g/mL, 2 mmol) and DCE (10 mL) afforded **4dag** (342.3 mg, 84%) [eluent: petroleum ether / ethyl acetate = 12/1 (1000 mL)] as a light green oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.6 Hz, 2 H, ArH), 7.45 (d, *J* = 8.0 Hz, 2 H, ArH), 7.42-7.30 (m, 4 H, ArH), 7.30-7.22 (m, 1 H, ArH), 6.56 (s, 1 H, =CH), 4.19 (q, *J* = 6.9 Hz, 2 H, OCH_2), 3.99 (q, *J* = 6.9 Hz, 2 H, OCH_2), 3.64-3.37 (m, 2 H, CH_2), 1.23 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.16 (t, *J* = 7.0 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.6, 165.4 (d, *J* = 6.1 Hz), 165.2 (d, *J* = 6.1 Hz), 138.5, 134.2, 132.2, 128.4, 127.7, 127.5, 126.1, 118.7, 110.4, 103.4, 97.7, 93.1 (d, *J* = 201.1 Hz), 62.5 (d, *J* = 8.4 Hz), 34.6 (d, *J* = 20.5 Hz), 13.5 (d, *J* = 9.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ -165.8, **IR** (neat): ν 2983, 2939, 2226, 1936, 1747, 1603, 1495, 1247, 1304, 1076 cm^{-1}; **MS** (ESI) *m/z* 425.2 $[M+NH_4]^+$; **HRMS** (DART) Calcd for $C_{24}H_{23}O_4NF$ $[M+H]^+$: 408.1606, Found: 408.1605.

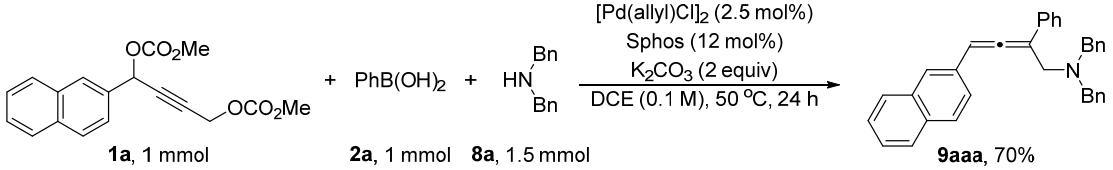
(34) 5,5-bis(phenylsulfonyl)-3-phenyl-1-(2-naphthyl)penta-1,2-diene **7aaa** (lican-06-001)



1a, 1 mmol **2a**, 1 mmol **6a**, 1.5 mmol **7aaa**, 46%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.2 mg, 0.025 mmol), Sphos (49.5 mg, 0.12 mmol), **1a** (328.6 mg, 1 mmol), **2a** (121.9 mg, 1 mmol), K_2CO_3 (276.5 mg, 2 mmol), **6a** (444.8 mg, 1.5 mmol) and DCE (10 mL) afforded **7aaa** (252.2 mg, 46%) [eluent: petroleum ether / ethyl acetate = 9/1 (1000 mL) to petroleum ether / ethyl acetate = 4/1 (1000 mL)] as a yellow solid: **m.p.** 158.6-160.7 °C (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.2 Hz, 2 H, ArH), 7.84-7.68 (m, 6 H, ArH), 7.62 (t, *J* = 7.4 Hz, 1 H, ArH), 7.53-7.40 (m, 6 H, ArH), 7.39-7.29 (m, 4 H, ArH), 7.28-7.18 (m, 3 H, ArH), 6.71 (t, *J* = 3.2 Hz, 1 H, =CH), 4.92 (t, *J* = 5.2 Hz, 1 H, CH), 3.58 (ddd, J_1 = 17.5 Hz, J_2 = 4.7 Hz, J_3 = 3.7 Hz, 1 H, CH), 3.44 (ddd, J_1 = 17.5 Hz, J_2 = 5.5 Hz, J_3 = 3.7 Hz, 1 H, CH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.6, 138.0, 137.5, 134.6, 134.3, 134.1, 133.5, 133.0, 130.2, 129.5, 129.2, 129.0, 128.9, 128.7, 128.6, 127.9, 127.8, 127.7, 126.44, 126.42, 126.41, 124.7, 107.3, 101.8, 81.1, 25.9; **IR** (neat): ν 3064, 2973, 2900, 1937, 1626, 1489, 1446, 1316, 1148 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 550 (M^+, 4.96), 267 (100); **Elem. Anal.** Calcd. for $C_{33}H_{26}O_4S_2$: C, 71.98, H, 4.76; found C, 72.14; H, 4.85.

(35) *N*-(2-phenyl-4-(2-naphthyl)buta-2,3-dienyl) dibenzyl amine **9aaa** (lican-09-013, lican-09-019)

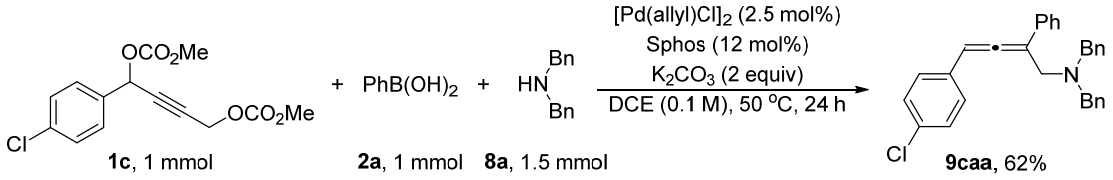


1a, 1 mmol **2a**, 1 mmol **8a**, 1.5 mmol **9aaa**, 70%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.5 mg, 0.12 mmol), **1a** (328.5 mg, 1 mmol), **2a** (121.6 mg, 1 mmol), K_2CO_3 (276.6 mg, 2 mmol), **8a** (288 μL, d = 1.026, 295.5 mg, 1.5 mmol) and

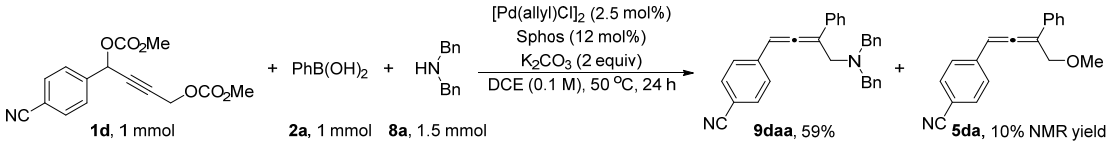
DCE (10 mL) afforded **9aaa** (317.3 mg, 70%) [eluent: petroleum ether /dichloromethane = 9/1 (1000 mL)] as a light green oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83-7.69 (m, 4 H, ArH), 7.53-7.36 (m, 5 H, ArH), 7.34-7.16 (m, 13 H, ArH), 6.79-6.69 (m, 1 H, =CH), 3.73 (d, *J* = 13.6 Hz, 2 H, 2 × one proton of CH_2), 3.68-3.55 (m, 4 H, CH_2 + 2 × one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.5, 139.3, 135.0, 133.7, 132.7, 131.7, 129.1, 128.4, 128.2, 128.1, 127.7, 127.1, 126.90, 126.86, 126.2, 125.8, 125.7, 124.8, 107.9, 97.8, 58.1, 54.5; **IR** (neat): ν 3029, 2920, 2800, 1937, 1598, 1494, 1450, 1365, 1263, 1120, 1073, 1027 cm^{-1}; **MS** (ESI) *m*/*z* 452.2 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{34}H_{30}N$ $[M+H]^+$: 452.2373, Found: 452.2375.

(36) *N*-(2-phenyl-4-(4-chlorophenyl)buta-2,3-dienyl) dibenzyl amine **9caa** (lican-09-021)



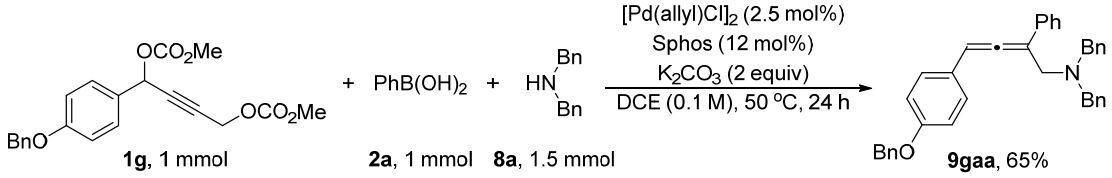
Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.0 mg, 0.025 mmol), Sphos (49.3 mg, 0.12 mmol), **1c** (312.9 mg, 1 mmol), **2a** (122.2 mg, 1 mmol), K_2CO_3 (276.0 mg, 2 mmol), **8a** (288 μL, d = 1.026, 295.5 mg, 1.5 mmol) and DCE (10 mL) afforded **9caa** (271.0 mg, 62%) [eluent: petroleum ether /ethyl ether = 100/1 (1000 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37-7.30 (m, 2 H, ArH), 7.29-7.12 (m, 17 H, ArH), 6.52-6.49 (m, 1 H, =CH), 3.66 (d, *J* = 13.6 Hz, 2 H, 2 × one proton of CH_2), 3.68-3.55 (m, 4 H, CH_2 + 2 × one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.9, 139.2, 134.7, 132.72, 132.68, 129.0, 128.8, 128.2, 128.1, 128.0, 127.2, 126.9, 126.8, 108.2, 96.6, 58.1, 54.3; **IR** (neat): ν 3028, 2972, 2901, 2797, 1937, 1599, 1491, 1451, 1367, 1264, 1240, 1091 cm^{-1}; **MS** (ESI) *m*/*z* 436.2 $[M(^{35}Cl)+H]^+$; **HRMS** (ESI) Calcd for $C_{30}H_{27}N^{35}Cl$ $[M(^{35}Cl)+H]^+$: 436.1827, Found: 436.1828.

(37) *N*-(2-phenyl-4-(4-cyanophenyl)buta-2,3-dienyl) dibenzyl amine **9daa** (lican-09-022)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.3 mg, 0.12 mmol), **1d** (303.6 mg, 1 mmol), **2a** (121.9 mg, 1 mmol), K_2CO_3 (278.0 mg, 2 mmol), **8a** (288 μL, d = 1.026, 295.5 mg, 1.5 mmol) and DCE (10 mL) afforded **9daa** (253.5 mg, 59%) [eluent: petroleum ether /ethyl ether = 30/1 (900 mL)] as a light green oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.4 Hz, 2 H, ArH), 7.37-7.28 (m, 4 H, ArH), 7.28-7.15 (m, 13 H, ArH), 6.56-6.51 (m, 1 H, =CH), 3.66 (d, *J* = 13.2 Hz, 2 H, 2 × one proton of CH_2), 3.63-3.54 (m, 4 H, CH_2 + 2 × one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.1, 139.3, 138.9, 133.9, 132.4, 128.8, 128.3, 128.1, 127.5, 127.2, 126.9, 126.7, 118.9, 110.2, 108.9, 96.7, 58.1, 54.1; **IR** (neat): ν 2986, 2901, 2798, 2226, 1935, 1603, 1495, 1451, 1367, 1265, 1203, 1176 cm^{-1}; **MS** (ESI) *m/z* 427.2 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{31}H_{27}N_2$ $[M+H]^+$: 427.2169, Found: 427.2168.

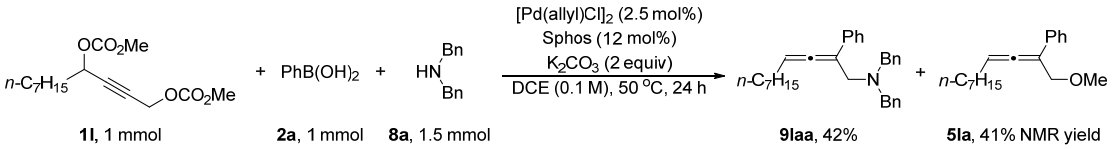
(38) *N*-(2-phenyl-4-(4-(benzyloxy)phenyl)buta-2,3-dienyl) dibenzyl amine **9gaa** (lican-09-020)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.0 mg, 0.025 mmol), Sphos (49.5 mg, 0.12 mmol), **1g** (384.4 mg, 1 mmol), **2a** (122.1 mg, 1 mmol), K_2CO_3 (276.9 mg, 2 mmol), **8a** (288 μL, d = 1.026, 295.5 mg, 1.5 mmol) and DCE (10 mL) afforded **9gaa** (341.6 mg, 65%, purity = 97%) [eluent: petroleum ether /ethyl ether = 60/1 (900 mL)] as a yellowish oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41-7.29 (m, 6 H, ArH), 7.29-7.10 (m, 16 H, ArH), 6.88 (d, *J* = 8.4 Hz, 2 H, ArH), 6.58-6.43 (m, 1 H, =CH), 4.97 (s, 2 H, CH_2), 3.67 (d, *J* = 13.6 Hz, 2 H, 2 × one proton

of CH_2), 3.62-3.43 (m, 4 H, CH_2 + 2 × one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.4, 158.1, 139.3, 136.8, 135.3, 129.1, 128.5, 128.09, 128.05, 128.01, 127.9, 127.4, 126.9, 126.84, 126.79, 126.6, 115.2, 107.5, 96.8, 69.9, 58.0, 54.5; **IR** (neat): ν 3030, 2798, 1605, 1509, 1452, 1374, 1300, 1241, 1171, 1112 cm^{-1}; **MS** (ESI) *m*/*z* 508.3 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{37}H_{34}ON$ $[M+H]^+$: 508.2635, Found: 508.2638.

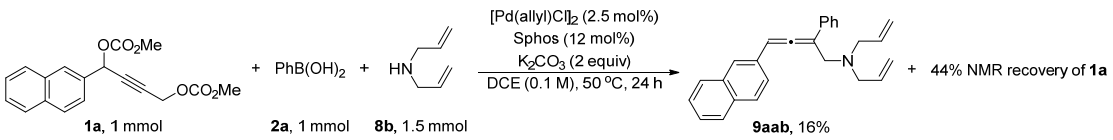
(39) *N*-(2-phenylundeca-2,3-dienyl) dibenzyl amine **9laa** (lican-09-029)



1l, 1 mmol **2a**, 1 mmol **8a**, 1.5 mmol **9laa**, 42% **5la**, 41% NMR yield

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.3 mg, 0.12 mmol), **1l** (300.9 mg, 1 mmol), **2a** (121.9 mg, 1 mmol), K_2CO_3 (278.1 mg, 2 mmol), **8a** (288 μL, d = 1.026, 295.5 mg, 1.5 mmol) and DCE (10 mL) afforded **9laa** (179.2 mg, 42%) [eluent: petroleum ether / dichloromethane = 9/1 (1000 mL)] as a light green oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33-7.24 (m, 11 H, ArH), 7.24-7.20 (m, 3 H, ArH), 7.20-7.13 (m, 1 H, ArH), 5.50 (t, *J* = 6.6 Hz, 1 H, =CH), 3.62 (d, *J* = 13.6 Hz, 2 H, 2 × one proton of CH_2), 3.57 (d, *J* = 13.6 Hz, 2 H, 2 × one proton of CH_2), 3.49-3.38 (m, 2 H, CH_2), 2.12 (dd, J_1 = 14.2 Hz, J_2 = 7.0 Hz, 2 H, CH_2), 1.52-1.42 (m, 2 H, CH_2), 1.38-1.17 (m, 8 H, 4 × CH_2), 0.86 (t, *J* = 6.8 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.7, 139.5, 136.3, 129.1, 128.0, 127.9, 126.80, 126.76, 126.3, 103.2, 93.5, 57.9, 55.0, 31.8, 29.3, 29.2, 29.1, 29.0, 22.6, 14.1; **IR** (neat): ν 3061, 3027, 2926, 2854, 2794, 1947, 1599, 1494, 1452, 1369, 1242, 1118, 1073 cm^{-1}; **MS** (ESI) *m*/*z* 424.3 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{31}H_{38}N$ $[M+H]^+$: 424.2999, Found: 424.2996.

(40) *N*-(2-phenyl-4-(2-naphthyl)buta-2,3-dienyl) diallylamine **9aab** (lican-09-030)

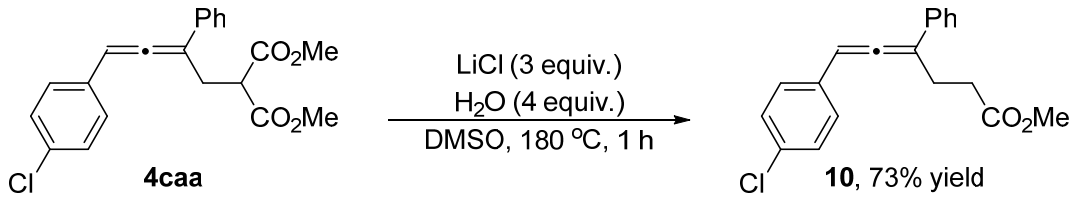


1a, 1 mmol **2a**, 1 mmol **8b**, 1.5 mmol **9aab**, 16%

Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.0 mg, 0.025 mmol), Sphos (49.5 mg, 0.12 mmol), **1a** (328.6 mg, 1 mmol), **2a** (121.9 mg, 1 mmol), K_2CO_3 (277.1 mg, 2 mmol), **8b** (185 μL, d = 0.787, 145.7 mg, 1.5 mmol) and DCE (10 mL) afforded **9aab** (60.5 mg, 16%, purity = 96%) [eluent: petroleum ether /ethyl ether = 80/1 (800 mL)] as a light green oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83-7.67 (m, 4 H, ArH), 7.58 (d, *J* = 7.6 Hz, 2 H, ArH), 7.49 (d, *J* = 8.4 Hz, 1 H, ArH), 7.46-7.37 (m, 2 H, ArH), 7.31 (t, *J* = 7.4 Hz, 2 H, ArH), 7.26-7.15 (m, 1 H, ArH), 6.75-6.63 (m, 1 H, =CH), 5.97-5.77 (m, 2 H, 2 × =CH), 5.27-5.02 (m, 4 H, 2 × $=CH_2$), 3.67 (dd, J_1 = 13.6 Hz, J_2 = 2.0 Hz, 1 H, one proton of CH_2), 3.60 (dd, J_1 = 14.0 Hz, J_2 = 2.0 Hz, 1 H, one proton of CH_2), 3.32-3.09 (m, 4 H, 2 × CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.5, 135.5, 135.3, 133.7, 132.7, 131.7, 128.4, 127.7, 127.2, 126.7, 126.2, 125.8, 125.7, 124.7, 117.7, 107.5, 97.5, 56.5, 54.1; **IR** (neat): ν 3058, 2920, 2807, 1934, 1639, 1597, 1494, 1446, 1417, 1354, 1264 cm^{-1}; **MS** (ESI) *m*/*z* 352.2 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{26}H_{26}N$ $[M+H]^+$: 352.2060, Found: 352.2053.

3 Synthetic Applications

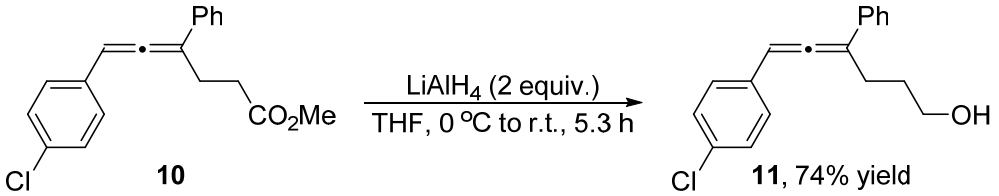
(1) Methyl 6-(4-chlorophenyl)-4-phenylhexa-4,5-dienoate **10** (lican-08-023)



To a flame-dried Schlenk tube were added **4caa** (742.0 mg, 2 mmol) and LiCl (254.4 mg, 6 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then DMSO (10 mL), and H_2O (144 μL, d = 1.0 g/mL, 144.0 mg, 8 mmol) were added sequentially under argon atmosphere. The resulting mixture was stirred at 180 °C for 1 h as monitored by TLC. After cooling to room temperature, the crude reaction mixture was quenched with H_2O (20 mL) and ethyl acetate (20 mL). The aqueous phase was extracted with

ethyl acetate (20 mL × 3). The combined organic layer was washed with brine (40 mL × 3) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 12/1 (650 mL)) afforded **10** (457.2 mg, 73%) as a yellowish solid: **m.p.** 80.0-81.5 °C (hexane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.6 Hz, 2 H, ArH), 7.33 (t, *J* = 7.6 Hz, 2 H, ArH), 7.30-7.18 (m, 5 H, ArH), 6.55 (t, *J* = 3.4 Hz, 1 H, =CH), 3.54 (s, 3 H, OCH_3), 3.03-2.91 (m, 1 H, one proton of CH_2), 2.89-2.78 (m, 1 H, one proton of CH_2), 2.69-2.54 (m, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.8, 173.2, 135.3, 132.9, 132.6, 128.8, 128.6, 128.0, 127.5, 126.0, 109.6, 98.7, 51.6, 32.1, 24.9; **IR** (neat): ν 2989, 2944, 2906, 1938, 1726, 1594, 1489, 1433, 1360, 1228, 1211, 1174, 1151 cm^{-1}; **MS** (ESI) *m/z* 313.1 $[M(^{35}Cl)+H]^+$, 315.0 $[M(^{37}Cl)+H]^+$; **Elem. Anal.** Calcd. for $C_{19}H_{17}ClO_2$: C, 72.96; H, 5.48, found C, 73.30; H, 5.58.

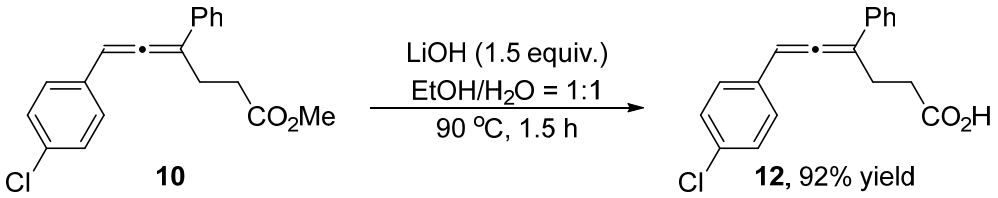
(2) 6-(4-chlorophenyl)-4-phenylhexa-4,5-dien-1-ol **11** (lican-08-029)



To a flame-dried Schlenk tube were added $LiAlH_4$ (15.2 mg, 0.4 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then THF (1 mL) and a solution of **10** (62.8 g, 0.2 mmol) in THF (1 mL) were added dropwise at 0 °C within 20 minutes under argon atmosphere. The resulting mixture was stirred for 5 h while gradually warming up to room temperature as monitored by TLC, quenched with H_2O (0.5 mL) and ethyl acetate (2 mL), filtered through a short column of silica gel (2 cm) and Na_2SO_4 (2 cm) eluted with ethyl acetate (10 mL), and concentrated. After filtration and evaporation of the solvent, chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10/1 (440 mL)) afforded **11** (45.1 mg, 74%, purity = 94%) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.6 Hz, 2 H, ArH), 7.33 (t, *J* = 7.8 Hz, 2 H, ArH), 7.30-7.20 (m, 5 H, ArH), 6.52 (t, *J* = 3.2 Hz, 1 H, =CH), 3.74 (t, *J* = 6.2 Hz, 2 H,

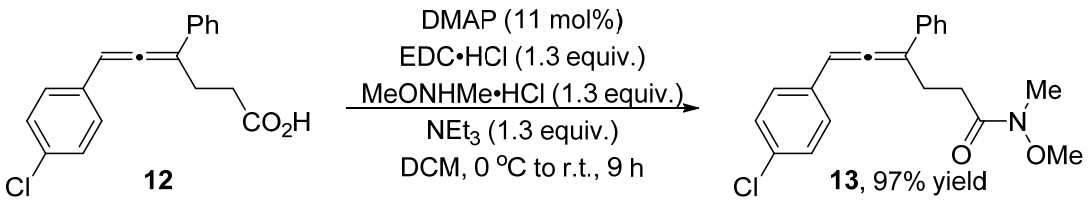
OCH_2), 2.76-2.57 (m, 2 H, CH_2), 1.96-1.75 (m, 2 H, CH_2), 1.35 (s, 1 H, OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 206.3, 135.5, 132.9, 132.6, 128.8, 128.5, 127.8, 127.3, 126.0, 109.9, 97.4, 62.3, 30.8, 26.2; **IR** (neat): ν 3319, 2936, 1932, 1676, 1595, 1488, 1448, 1419, 1381, 1259 cm^{-1}; **MS** (FI) *m/z* 284 $[M(^{35}Cl)]^+$; **HRMS** (FI) Calcd for $C_{18}H_{17}O^{35}Cl$ $[M]^+$: 284.0962, Found: 284.0965.

(3) 6-(4-Chlorophenyl)-4-phenylhexa-4,5-dienoic acid **12** (lican-08-021)



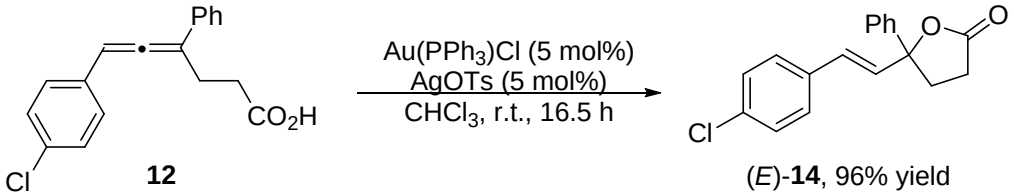
To a flask were added **10** (62.8 mg, 0.2 mmol), EtOH (1 mL), H_2O (1 mL), and LiOH (7.2 mg, 0.3 mmol) sequentially. After stirring for 1.5 h at 90 °C, the reaction was complete as monitored by TLC. After cooling to room temperature, the crude reaction mixture was quenched with an aqueous solution of hydrochloric acid (aq., 3.0 M, 2 mL) and ethyl acetate (2 mL). The aqueous phase was extracted with ethyl acetate (3 mL × 3). The combined organic layer was washed with brine (5 mL × 3) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 15/1 (480 mL)) afforded **12** (55.1 mg, 92%) as a white solid: **m.p.** 141.6-143.3 °C (hexane / ethyl ether); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.6 Hz, 2 H, ArH), 7.34 (t, *J* = 7.6 Hz, 2 H, ArH), 7.29-7.16 (m, 5 H, ArH), 6.57 (t, *J* = 3.2 Hz, 1 H, =CH), 3.00-2.88 (m, 1 H, one proton of CH_2), 2.87-2.75 (m, 1 H, one proton of CH_2), 2.72-2.56 (m, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.8, 178.7, 135.2, 132.8, 132.5, 128.8, 128.6, 128.0, 127.5, 125.9, 109.4, 99.0, 31.9, 24.6; **IR** (neat): ν 3100-2880, 2660, 1935, 1693, 1597, 1490, 1428, 1342, 1285, 1259 cm^{-1}; **MS** (ESI) *m/z* 299.1 $[M(^{35}Cl)+H]^+$; **Elem. Anal.** Calcd. for $C_{18}H_{15}ClO_2$: C, 72.36; H, 5.06, found C, 72.25; H, 5.18.

(4) *N*-methoxy-*N*-methyl-6-(4-chlorophenyl)-4-phenylhexa-4,5-dienamide **13** (lican-08-024)



To a flame-dried Schlenk tube were added *N*,*O*-dimethylhydroxylamine hydrochloride (25.7 mg, 0.26 mmol) and DMAP (2.7 mg, 0.022 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then DCM (1 mL), **12** (59.8 mg, 0.2 mmol), NEt_3 (36 μL, d = 0.728 g/mL, 26.2 mg, 0.26 mmol), and EDC·HCl (49.9 mg, 0.26 mmol) were added sequentially at 0 °C under argon atmosphere. The resulting mixture was stirred for 9 h as monitored by TLC while gradually warming up to room temperature. After evaporation of the solvent, chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 4/1 (250 mL)) afforded **13** (66.6 mg, 97%) as a light green oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51-7.41 (m, 2 H, ArH), 7.36-7.29 (m, 2 H, ArH), 7.28-7.16 (m, 5 H, ArH), 6.53 (t, *J* = 3.4 Hz, 1 H, =CH), 3.54 (s, 3 H, OCH_3), 3.10-2.93 (m, 4 H, NCH_3 and one proton of CH_2), 2.90-2.60 (m, 3 H, CH_2 and one proton of CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 206.0, 173.2 (br), 135.4, 132.8, 132.6, 128.7, 128.5, 128.0, 127.3, 126.0, 110.1, 98.2, 60.9, 32.0 (br), 29.9, 24.4; **IR** (neat): ν 2967, 2935, 2904, 2245, 1934, 1657, 1596, 1489, 1415, 1383, 1177 cm^{-1}; **MS** (ESI) *m/z* 342.1 $[M(^{35}Cl)+H]^+$, 344.1 $[M(^{37}Cl)+H]^+$; **HRMS** (ESI) Calcd for $C_{20}H_{21}NO_2{}^{35}Cl$ $[M+H]^+$: 342.1255, Found: 342.1265.

(5) (*E*)-5-(4-chlorostyryl)-5-phenyldihydro-2(3*H*)-furanone (*E*)-**14** (lican-08-027)

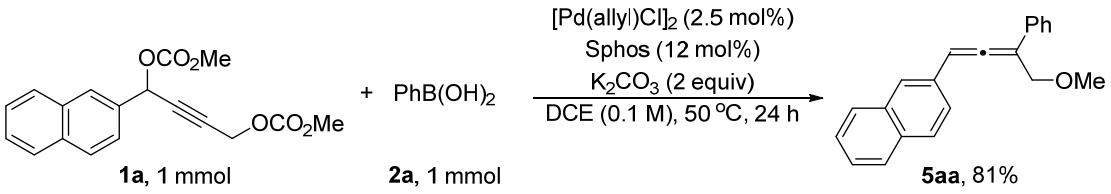


To a flame-dried Schlenk tube were added $Au(PPh_3)Cl$ (4.9 mg, 0.01 mmol) and AgOTs (2.8 mg, 0.01 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then $CHCl_3$ (1.0 mL) was added. After the reaction was stirred at room temperature for 30 min, a

solution of **12** (59.8 g, 0.2 mmol) in $CHCl_3$ (1.0 mL) was added to the reaction mixture. The resulting mixture was stirred at room temperature for 16 h as monitored by TLC, filtered through a short column of silica gel (1 cm) eluted with ethyl acetate (10 mL), and concentrated. The residue was purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5/1 (180 mL)) afforded (*E*)-**14** (57.2 mg, 96%) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49-7.36 (m, 4 H, ArH), 7.35-7.29 (m, 1 H, ArH), 7.29-7.19 (m, 4 H, ArH), 6.56 (d, *J* = 16.0 Hz, 1 H, =CH), 6.38 (d, *J* = 16.0 Hz, 1 H, =CH), 2.74-2.45 (m, 4 H, 2 × CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.0, 141.5, 134.1, 133.8, 131.5, 128.72, 128.67, 128.2, 128.0, 127.9, 124.9, 88.0, 34.8, 28.5; **IR** (neat): ν 2987, 2947, 2889, 1892, 1766, 1644, 1592, 1490, 1450, 1406, 1330, 1291, 1224, 1189, 1160 cm^{-1}; **MS** (FI) *m/z* 298 $[M(^{35}Cl)]^+$; **HRMS** (FI) Calcd for $C_{18}H_{15}O_2{}^{35}Cl$ $[M]^+$: 298.0755, Found: 298.0759.

4 Mechanistic studies

(1) The reaction of **1a** with 1.0 equiv. of **2a** in the absence of malonate (lican-08-015)

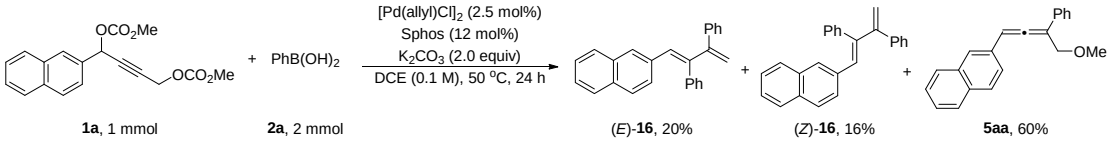


1a, 1 mmol **2a**, 1 mmol **5aa**, 81%

To a flame-dried Schlenk tube were added $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.5 mg, 0.12 mmol), **1a** (328.5 mg, 1 mmol), **2a** (121.9 mg, 1 mmol), and K_2CO_3 (277.0 mg, 2 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then DCE (10 mL) was added under argon atmosphere. The resulting mixture was stirred at 50 °C for 24 h as monitored by TLC, filtered through a short column of silica gel (3 cm) eluted with ethyl acetate (20 mL), and concentrated. The residue was purified by column chromatography on silica gel to afford **5aa** (230.6 mg, 81%) [eluent: petroleum ether / ethyl ether = 30/1 (930 mL)] as a light green solid: **m.p.** 64.7-65.8 °C (hexane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86-7.67 (m, 4 H, ArH), 7.56 (d, *J* = 7.2

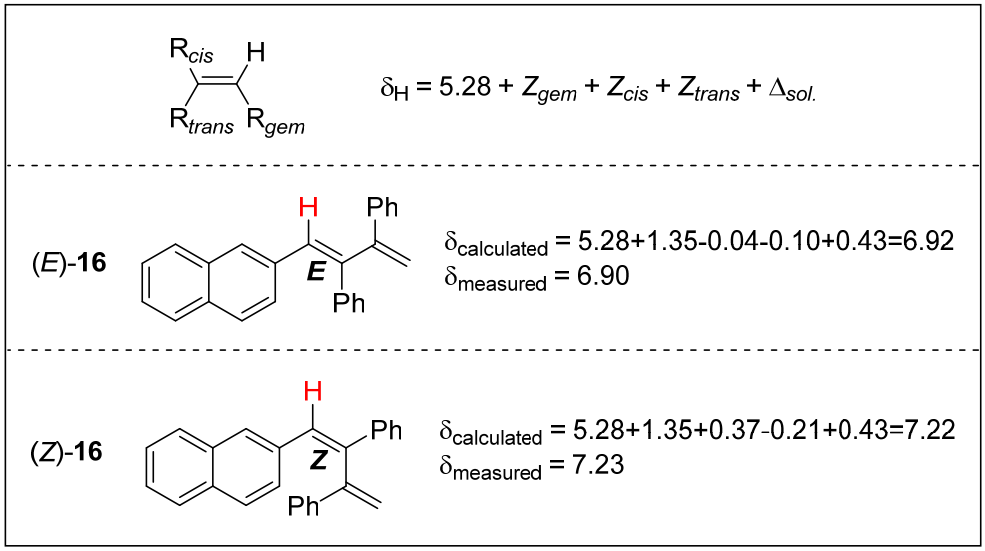
Hz, 2 H, ArH), 7.51 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1 H, ArH), 7.49-7.40 (m, 2 H, ArH), 7.35 (t, J = 7.6 Hz, 2 H, ArH), 7.29-7.22 (m, 1 H, ArH), 6.83-6.75 (m, 1 H, =CH), 4.56 (ddd, J_1 = 17.4 Hz, J_2 = 11.8 Hz, J_3 = 1.8 Hz, 2 H, CH_2), 3.44 (s, 3 H, OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.8, 133.9, 133.6, 132.7, 131.0, 128.5, 128.3, 127.59, 127.56, 127.3, 126.3, 126.2, 125.9, 125.7, 124.5, 106.5, 97.8, 71.7, 57.5; **IR** (neat): ν 3025, 2984, 2916, 2880, 2856, 2814, 2120, 1929, 1754, 1493, 1453, 1188, 1093 cm^{-1}; **MS** (70 eV, EI) *m*/*z* (%): 286 (M^+, 6.13), 241 (100); **Elem. Anal.** Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34, found C, 87.87; H, 6.32.

(2) The reaction of **1a** with 2.0 equiv. of **2a** under standard conditions (lican-09-027)



1a, 1 mmol **2a**, 2 mmol (*E*)-**16**, 20% (*Z*)-**16**, 16% **5aa**, 60%

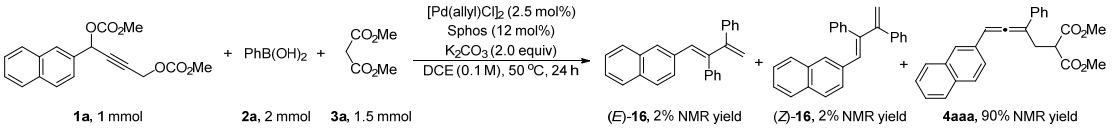
To a flame-dried Schlenk tube were added $[Pd(allyl)Cl]_2$ (9.0 mg, 0.025 mmol), Sphos (49.5 mg, 0.12 mmol), **1a** (328.5 mg, 1 mmol), **2a** (243.6 mg, 2 mmol), and K_2CO_3 (276.9 mg, 2 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then DCE (10 mL) was added under argon atmosphere. The resulting mixture was stirred at 50 °C for 24 h as monitored by TLC, filtered through a short column of silica gel (3 cm) eluted with ethyl acetate (25 mL), and concentrated. The residue was purified by column chromatography on silica gel to afford (*E*)-**16** (66.9 mg, 20%), (*Z*)-**16** (52.8 mg, 16%, purity = 98%) [eluent: petroleum ether (1200 mL)] and **5aa** (171.1 mg, 60%) [eluent: petroleum ether / ethyl ether = 30/1 (600 mL)]. The configurations of (*E*)-**16** and (*Z*)-**16** were determined by comparing ^{1}H-NMR data with the previous literature,[7-8] and by comparing the calculated δ value with the measured δ value of the alkenyl proton according to Shoolery's rule.[9]



(*E*)-**16**: colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66-7.60 (m, 1 H, ArH), 7.55-7.50 (m, 1 H, ArH), 7.49-7.42 (m, 3 H, ArH), 7.40-7.22 (m, 11 H, ArH), 6.90 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 1 H, =CH), 6.70 (s, 1 H, ArH), 5.33 (d, J = 1.6 Hz, 1 H, =CH), 5.09 (d, J = 1.2 Hz, 1 H, =CH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.7, 143.4, 141.5, 139.6, 134.6, 133.1, 132.2, 131.2, 130.2, 129.1, 128.8, 128.6, 128.1, 127.9, 127.40, 127.37, 127.32, 127.1, 127.0, 125.85, 125.83, 118.0; **IR** (neat): ν 2924, 1832, 1577, 1498, 1443, 1382, 1273, 1121, 1073 cm^{-1}; **MS** (70 eV, EI) *m*/*z* (%): 332 (M^+, 100); **HRMS** (EI) Calcd for $C_{26}H_{20}$ $[M]^+$: 332.1560, Found: 332.1564.

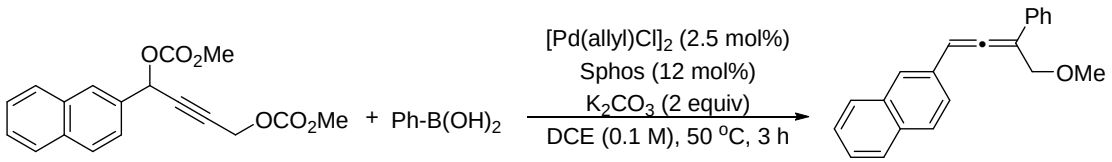
(*Z*)-**16**: colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.87 (s, 1 H, ArH), 7.76-7.68 (m, 2 H, ArH), 7.67-7.60 (m, 2 H, ArH), 7.59-7.53 (m, 4 H, ArH), 7.44-7.36 (m, 2 H, ArH), 7.34-7.18 (m, 7 H, ArH), 5.92 (s, 1 H, =CH), 5.33 (s, 1 H, =CH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.3, 142.3, 141.4, 138.8, 134.9, 133.3, 132.5, 129.6, 128.7, 128.6, 128.4, 128.0, 127.9, 127.6, 127.5, 127.3, 126.7, 126.5, 125.9, 125.8, 117.2; **IR** (neat): ν 3055, 3023, 2988, 1598, 1572, 1493, 1444, 1406, 1270, 1191, 1125, 1075 cm^{-1}; **MS** (70 eV, EI) *m*/*z* (%): 332 (M^+, 100); **HRMS** (EI) Calcd for $C_{26}H_{20}$ $[M]^+$: 332.1560, Found: 332.1563.

(3) The reaction of **1a** with 2.0 equiv. of **2a** and **3a** under standard conditions (lican-08-195)



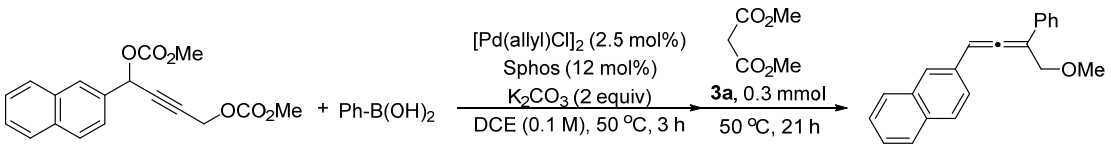
To a flame-dried Schlenk tube were added $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol), Sphos (49.4 mg, 0.12 mmol), **1a** (328.5 mg, 1 mmol), **2a** (243.6 mg, 2 mmol), and K_2CO_3 (278.0 mg, 2 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then DCE (5 mL), **3a** (171 μL, d = 1.156 g/mL, 197.7 mg, 1.5 mmol) and DCE (5 mL) was added under argon atmosphere. The resulting mixture was stirred at 50 °C for 24 h as monitored by TLC, filtered through a short column of silica gel (2 cm) eluted with ethyl acetate (25 mL), and concentrated. 2% NMR yield of (*E*)-**16**, 2% NMR yield of (*Z*)-**16** and 90% NMR yield of **4aaa** was formed as determined by the ^{1}H NMR analysis with CH_2Br_2 as the internal standard.

(4) The reaction of **1a** with **2a** for 3 h (lican-08-200)



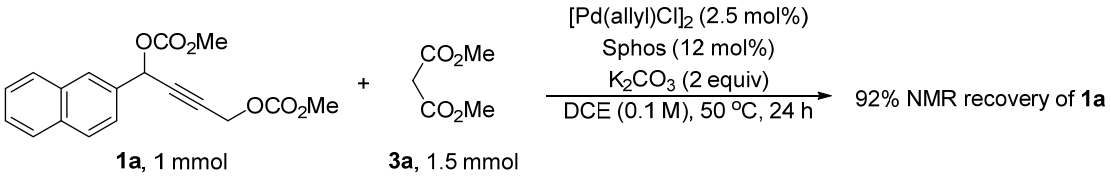
To a flame-dried Schlenk tube were added $[Pd(allyl)Cl]_2$ (1.9 mg, 0.005 mmol), Sphos (9.8 mg, 0.024 mmol), **1a** (65.8 mg, 0.2 mmol), **2a** (24.4 mg, 0.2 mmol), and K_2CO_3 (55.5 mg, 0.4 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then DCE (2 mL) was added under argon atmosphere. The resulting mixture was stirred at 50 °C for 3 h, filtered through a short column of silica gel (1 cm) eluted with ethyl acetate (10 mL), and concentrated. 79% NMR yield of **5aa** was formed as determined by the ^{1}H NMR analysis with CH_2Br_2 as the internal standard.

(5) The reaction of **1a** with **2a** for 3 h followed by the addition of **3a** (lican-07-173)



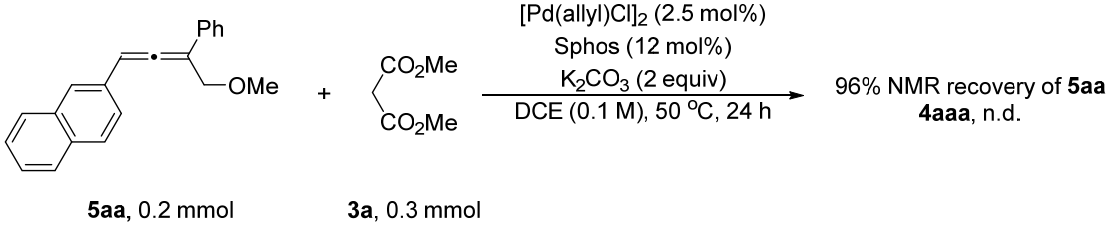
To a flame-dried Schlenk tube were added $[Pd(allyl)Cl]_2$ (1.9 mg, 0.005 mmol), Sphos (9.9 mg, 0.024 mmol), **1a** (65.7 mg, 0.2 mmol), **2a** (24.4 mg, 0.2 mmol), and K_2CO_3 (55.8 mg, 0.4 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then DCE (2 mL) was added under argon atmosphere. The resulting mixture was stirred at 50 °C for 3 h. Dimethyl malonate **3a** was then added under argon atmosphere and the resulting mixture was stirred for extra 21 h at 50 °C, filtered through a short column of silica gel (2 cm) eluted with ethyl acetate (10 mL), and concentrated. 73% NMR yield of **5aa** was formed without the formation of **15** or **4aaa** as determined by the ^{1}H NMR analysis with CH_2Br_2 as the internal standard.

(6) The reaction of **1a** with **3a** (lican-06-160)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (9.3 mg, 0.025 mmol), Sphos (49.3 mg, 0.12 mmol), **1a** (328.5 mg, 1 mmol), K_2CO_3 (277.0 mg, 2 mmol), and **3a** (171 μL, d = 1.156 g/mL, 197.7 mg, 1.5 mmol) in DCE (10 mL) failed to afford product and 92% of **1a** was recovered as determined by the ^{1}H NMR analysis with CH_2Br_2 as the internal standard.

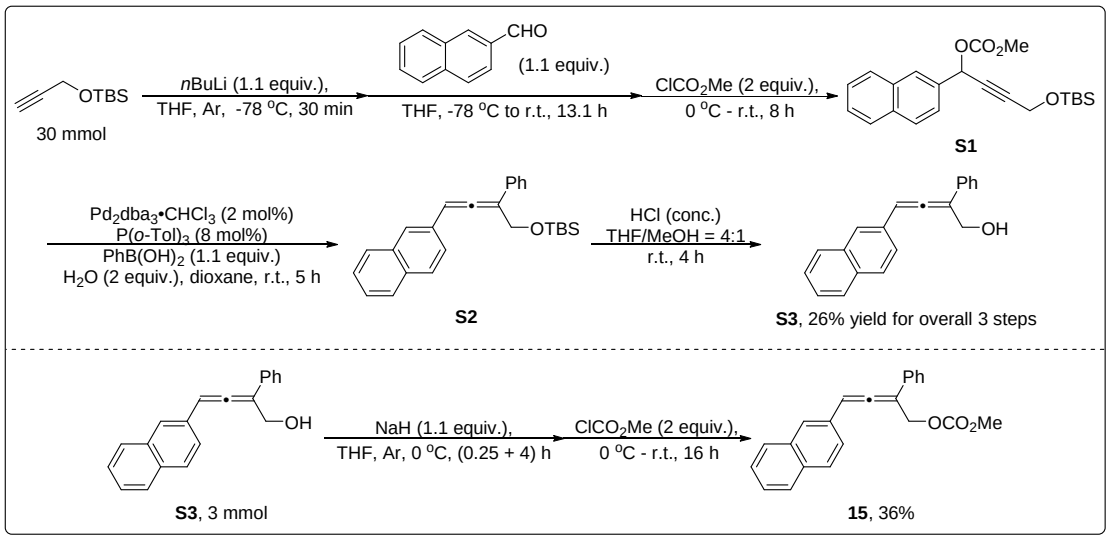
(7) The reaction of **5aa** with **3a** (lican-08-014)



Following the **Typical Procedure III**, the reaction of $[Pd(allyl)Cl]_2$ (1.8 mg, 0.005 mmol), Sphos (9.8 mg, 0.024 mmol), **5aa** (57.3 mg, 0.2 mmol), K_2CO_3 (55.9 mg, 0.4 mmol), and **3a** (34 μL, d = 1.156 g/mL, 39.3 mg, 0.3 mmol) in DCE (2 mL) failed to afford product **4aaa** and 96% of **5aa** was recovered as determined by the ^1H NMR analysis with CH_2Br_2 as the internal standard.

(8) Preparation and reaction of methyl 4-(2-naphthyl)-2-phenylbuta-2,3-dienyl carbonate **15** [1] (lican-07-193, lican-08-004 and lican-08-007)

8.1 Preparation of compound **15** [1]



Step I: To a solution of *t*-butyldimethylsilyl propargyl ether (6.1 mL, d = 0.84 g/mL, 5.1096 g, 30 mmol) in THF (60 mL) was added dropwise *n*BuLi (2.5 M in hexane, 13.2 mL, 33 mmol) at -78 °C within 30 minutes. Then a solution of 2-naphthaldehyde (5.1633 g, 33 mmol) in THF (40 mL) was added dropwise at -78 °C within 10 minutes. The resulting mixture was stirred for 13 h while gradually warming up to room temperature. The resulting mixture was cooled down to 0 °C again and methyl chloroformate (4.6 mL, d = 1.22 g/mL, 5.6120 g, 59 mmol) was added. The resulting mixture was warmed up to room temperature gradually and stirred at rt for 8 h. After the reaction was complete as monitored by TLC (eluent: petroleum ether / ethyl ether = 50/1), it was quenched with H_2O (50 mL) and ethyl ether (50 mL). The aqueous phase was extracted with ethyl ether (30 mL × 3). The combined organic extract was washed with brine (50 mL × 3) and dried over

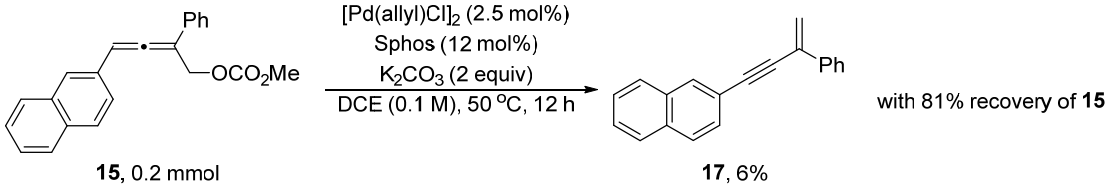
anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on silica gel to afford crude product **S1** (eluent: petroleum ether / ethyl ether = 50/1) as an oil, which was used in the next step without further purification.

Step II:[1] To an oven-dried three-neck flask were added $Pd_2(dba)_3 \cdot CHCl_3$ (622.4 mg, 0.6 mmol), tri(*o*-tolyl)phosphine (728.5 mg, 2.4 mmol), and $PhB(OH)_2$ (4.0249 g, 33 mmol). After replacing air with argon for three times at rt by using a vacuum line, dioxane (30 mL), H_2O (1080 μL, 60 mmol), and the crude product **S1**/dioxane (30 mL) were added sequentially. The resulting mixture was stirred for 5 h at room temperature and then filtered through a short pad of silica gel (5 cm) with ethyl acetate (30 mL) as the eluent. After evaporation, the residue was purified by flash chromatography on silica gel to afford crude product **S2** (eluent: petroleum ether (b.p. 60~90 °C)/ethyl ether = 50/1, 1020 mL) as a yellow oil, which was used in the next step without further purification.

Step III: To a round-bottomed flask were added the crude product **S2**, 100 mL of the mixed solvent (V_{MeOH}/V_{DCM} = 1/4), and HCl (conc., 1 mL) sequentially. The resulting mixture was stirred at room temperature for 4 h, quenched with a saturated aqueous solution of $NaHCO_3$ (50 mL), and extracted with ethyl acetate (50 mL × 3). The combined organic extract was washed with brine (50 mL × 3) and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by recrystallization (petroleum ether / ethyl acetate) to afford 4-(2-naphthyl)-2-phenylbuta-2,3-dienol **S3** (2.1605 g, 26% yield for overall 3 steps) as a light brown solid: **m.p.** 139.2-140.6 °C (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88-7.68 (m, 4 H, ArH), 7.57-7.41 (m, 5 H, ArH), 7.36 (t, *J* = 7.8 Hz, 2 H, ArH), 7.27 (t, *J* = 7.8 Hz, 1 H, ArH), 6.89 (t, *J* = 2.2 Hz, 1 H, =CH), 4.83-4.66 (m, 2 H, OCH_2), 1.78 (t, *J* = 6.4 Hz, 1 H, OH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.6, 133.7, 133.6, 132.9, 130.9, 128.8, 128.5, 127.78, 127.75, 127.69, 126.4, 126.3, 126.1, 126.0, 124.6, 111.0, 100.5, 61.6; **IR** (neat): ν 3417, 3050, 2859, 2116, 1931, 1627, 1595, 1492, 1068 cm^{-1}; **MS** (ESI) *m*/*z* 273.1 $[M+H]^+$; **Elem. Anal.** Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92, found C, 87.89; H, 5.76.

Step IV: To a suspension of sodium hydride (60% in mineral oil, 133.5 mg, 3.3 mmol) in THF (8 mL) was added a solution of **S3** (816.8 mg, 3 mmol) in THF (4 mL) dropwise at 0 °C for 15 min. The resulting mixture was stirred at 0 °C for 4 hours in an ice-water bath followed by the addition of methyl chloroformate (465 μL, d = 1.22 g/mL, 567.3 mg, 6 mmol), stirred for extra 16 h while gradually warming up to room temperature, and quenched with H_2O (10 mL) followed by the addition of ethyl ether (15 mL). The aqueous phase was extracted with ethyl ether (10 mL × 3). The combined organic extract was washed with brine (30 mL × 3), dried over anhydrous Na_2SO_4, filtrated, and evaporated. The residue was purified by chromatography on silica gel to afford **15** (357.1 mg, 36%) as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88-7.71 (m, 4 H, ArH), 7.58-7.40 (m, 5 H, ArH), 7.35 (t, *J* = 7.6 Hz, 2 H, ArH), 7.27 (t, *J* = 7.2 Hz, 1 H, ArH), 6.91-6.81 (m, 1 H, =CH), 5.28 (dd, J_1 = 12.4 Hz, J_2 = 2.0 Hz, 1 H, one proton of CH_2), 5.18 (dd, J_1 = 12.2 Hz, J_2 = 1.8 Hz, 1 H, one proton of CH_2), 3.73 (s, 3 H, OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.0, 155.6, 133.6, 133.2, 132.9, 130.4, 128.8, 128.4, 127.8, 127.73, 127.71, 126.35, 126.32, 126.1, 126.0, 124.8, 105.9, 99.6, 66.2, 54.9; **IR** (neat): ν3054, 2955, 2853, 1939, 1744, 1597, 1495, 1441, 1370, 1252 cm^{-1}; **MS** (ESI) *m*/*z* 353.1 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{22}H_{18}O_3Na$ $[M+Na]^+$: 353.1148, Found: 353.1145.

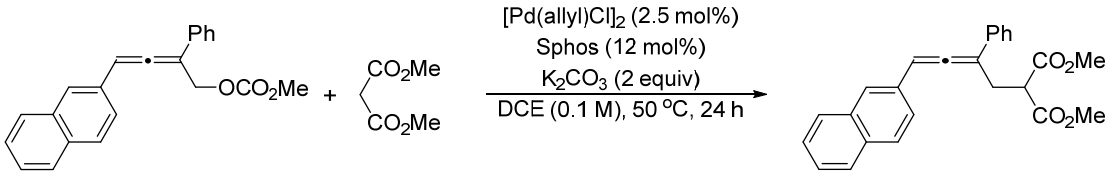
8.2 The reaction of methyl 4-(2-naphthyl)-2-phenylbuta-2,3-dienyl carbonate **15** under standard conditions (lican-08-011)



To a flame-dried Schlenk tube were added $[Pd(allyl)Cl]_2$ (1.9 mg, 0.005 mmol), Sphos (9.9 mg, 0.024 mmol), and K_2CO_3 (55.9 mg, 0.4 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then DCE (1 mL) and a solution of **15** (66.0 mg, 0.2 mmol) in DCE (1 mL) were added under argon atmosphere. The resulting mixture was stirred at 50

°C for 12 h, filtered through a short column of silica gel (2 cm) eluted with ethyl acetate (10 mL), and concentrated. The residue was purified by column chromatography on silica gel to afford **17** (3.1 mg, 6%) [eluent: petroleum ether (200 mL)] as a yellowish oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (s, 1 H, ArH), 7.91-7.72 (m, 5 H, ArH), 7.58 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1 H, ArH), 7.54-7.46 (m, 2 H, ArH), 7.45-7.38 (m, 2 H, ArH), 7.37-7.30 (m, 1 H, ArH), 6.02 (s, 1 H, one proton of $=CH_2$), 5.81 (s, 1 H, one proton of $=CH_2$); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.3, 133.0, 132.9, 131.6, 130.7, 128.45, 128.39, 128.0, 127.8, 126.7, 126.6, 126.1, 120.8, 120.4, 91.2, 88.9; **IR** (neat): ν 3053, 2291, 2200, 2117, 1802, 1595, 1567, 1492, 1443, 1347, 1323 cm^{-1}; **MS** (70 eV, EI) *m*/*z* (%): 254 (M^+, 100); **HRMS** (FI) Calcd for $C_{20}H_{14}$ $[M]^+$: 254.1090, Found: 254.1095.

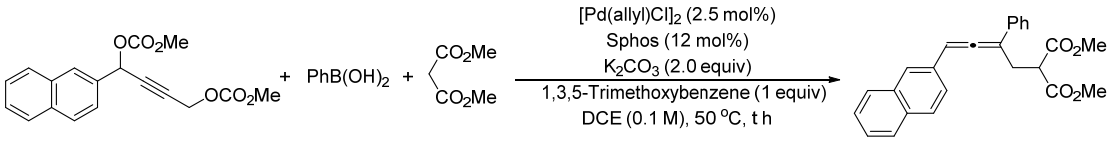
(9) The reaction of methyl 4-(2-naphthyl)-2-phenylbuta-2,3-dienyl carbonate **15** with **3a** under standard conditions (lican-09-005)



15, 0.2 mmol **3a**, 0.3 mmol **4aaa**, 62% NMR yield

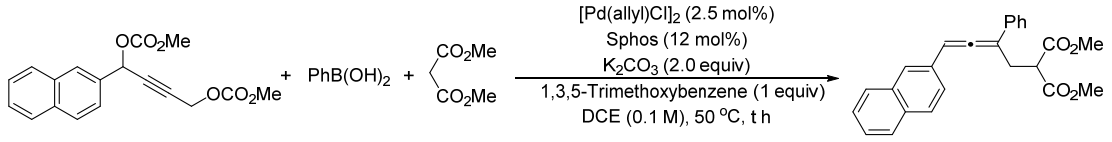
To a flame-dried Schlenk tube were added $[Pd(allyl)Cl]_2$ (1.8 mg, 0.005 mmol), Sphos (9.8 mg, 0.024 mmol), and K_2CO_3 (55.8 mg, 0.4 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then DCE (1 mL), a solution of **15** (66.2 mg, 0.2 mmol) in DCE (1 mL) and **3a** (34 μL, d = 1.156 g/mL, 39.6 mg, 0.3 mmol) were added under argon atmosphere. The resulting mixture was stirred at 50 °C for 24 h, filtered through a short column of silica gel (1 cm) eluted with ethyl acetate (10 mL), and concentrated. 62% NMR yield of **4aaa** was formed as determined by the ^{1}H NMR analysis with CH_2Br_2 as the internal standard.

(10) The monitoring experiment of **1a** with **2a** and **3a** (lican-09-009)



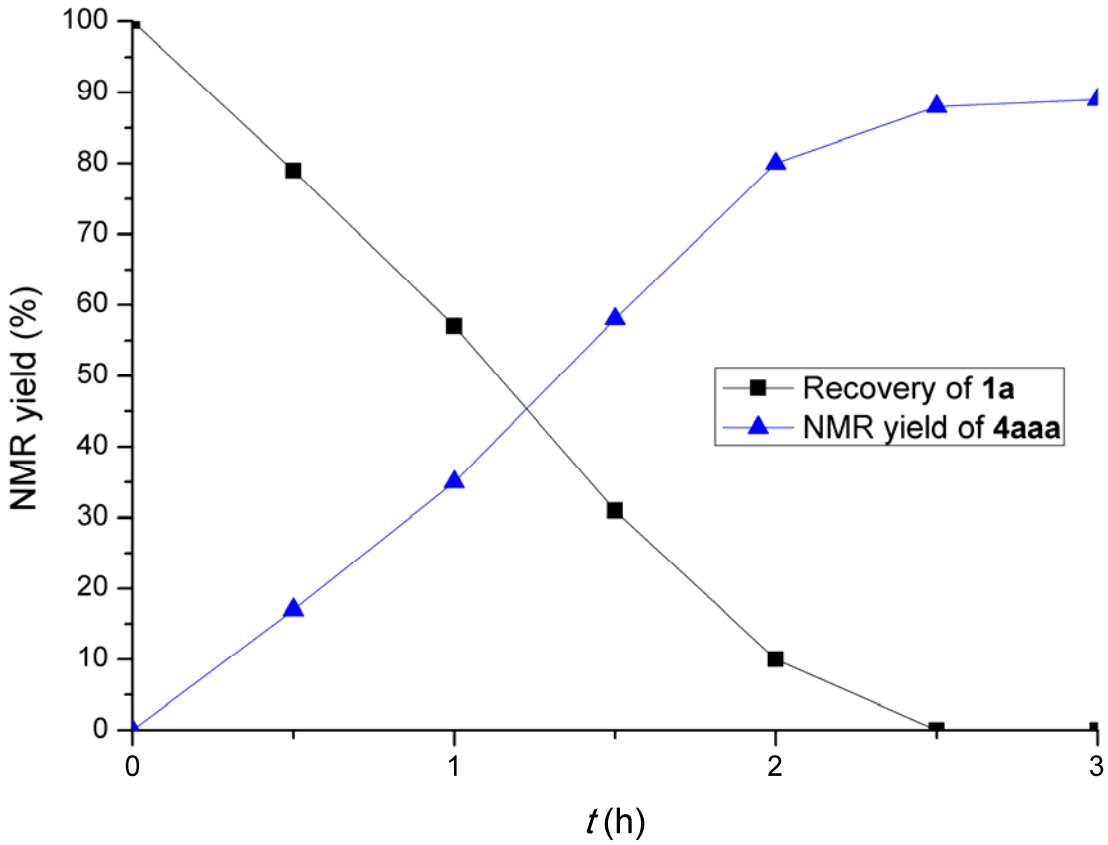
1a, 2 mmol **2a**, 2 mmol **3a**, 3 mmol **4aaa**

To a flame-dried Schlenk tube were added **1a** (656.7 mg, 2 mmol), $[Pd(allyl)Cl]_2$ (18.3 mg, 0.05 mmol), Sphos (98.7 mg, 0.24 mmol), **2a** (243.9 mg, 2 mmol), 1,3,5-Trimethoxybenzene (336.4 mg, 2 mmol) and K_2CO_3 (552.9 mg, 4 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. Then DCE (20 mL) and **3a** (396.9 mg, 3 mmol) were added sequentially under argon atmosphere. The resulting mixture was stirred at 50 °C. 0.2 mL each of the aliquot was taken with an Ar-purged syringes after 0.5 h, 1.0 h, 1.5 h, 2.0 h, 2.5 h, 3.0 h and analyzed by ^1H NMR spectra with 1,3,5-trimethoxybenzene as the internal standard to determine the yields of **4aaa** and the recoveries of **1a**. All the data acquired were analyzed by Origin 8.0.



1a, 2 mmol **2a**, 2 mmol **3a**, 3.0 mmol **4aaa**

entry	t (h)	NMR yield of **4aaa** (%)	recovery of **1a** (%)
1	0.5	17	79
2	1.0	35	57
3	1.5	58	31
4	2.0	80	10
5	2.5	88	/
6	3.0	89	/


NMR yield (%)
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90
80
70
60
50
40
30
20
10
0
0
1
2
3
t (h)
Recovery of 1a
NMR yield of 4aaa

References

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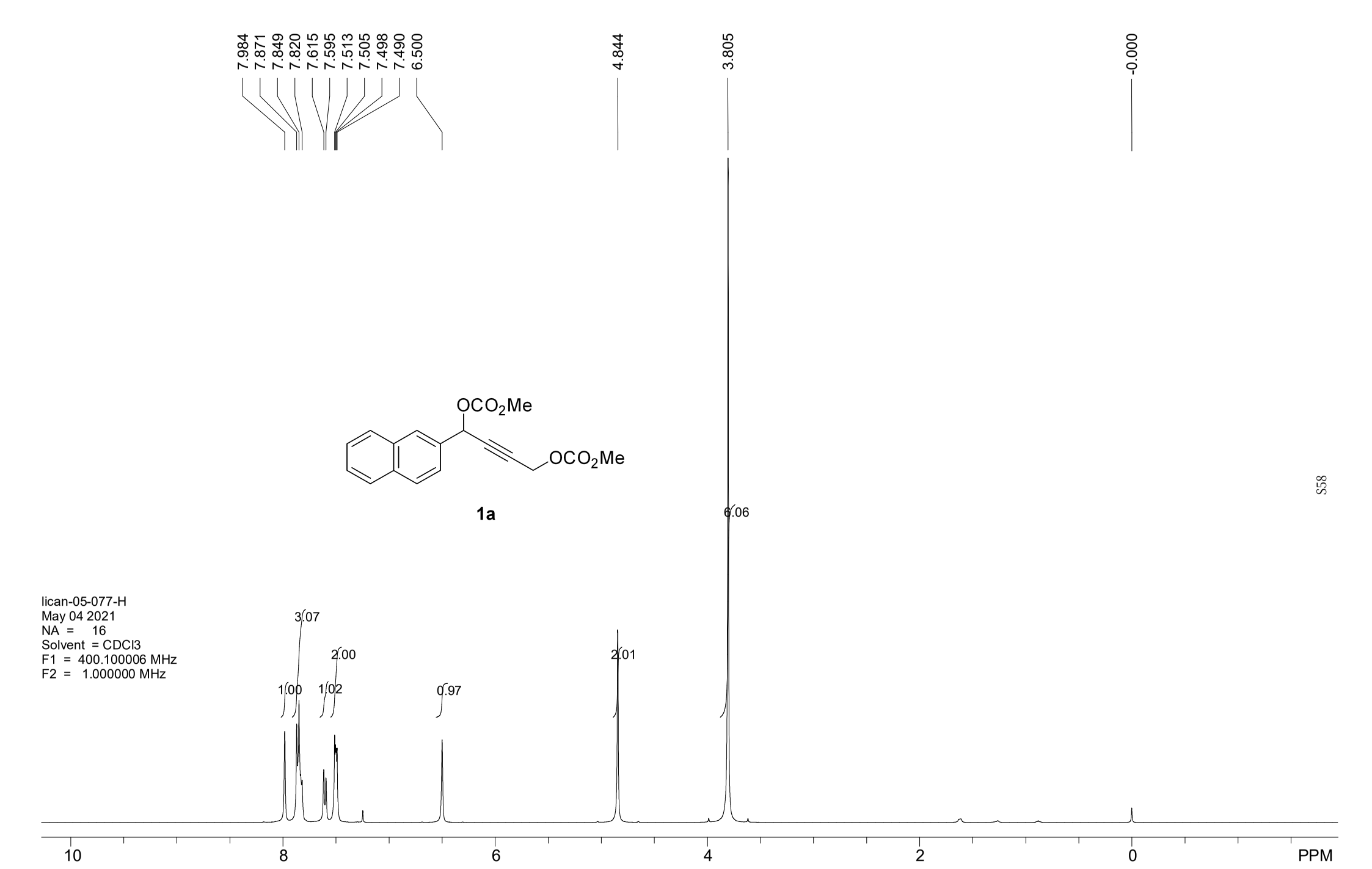
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10
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6
4
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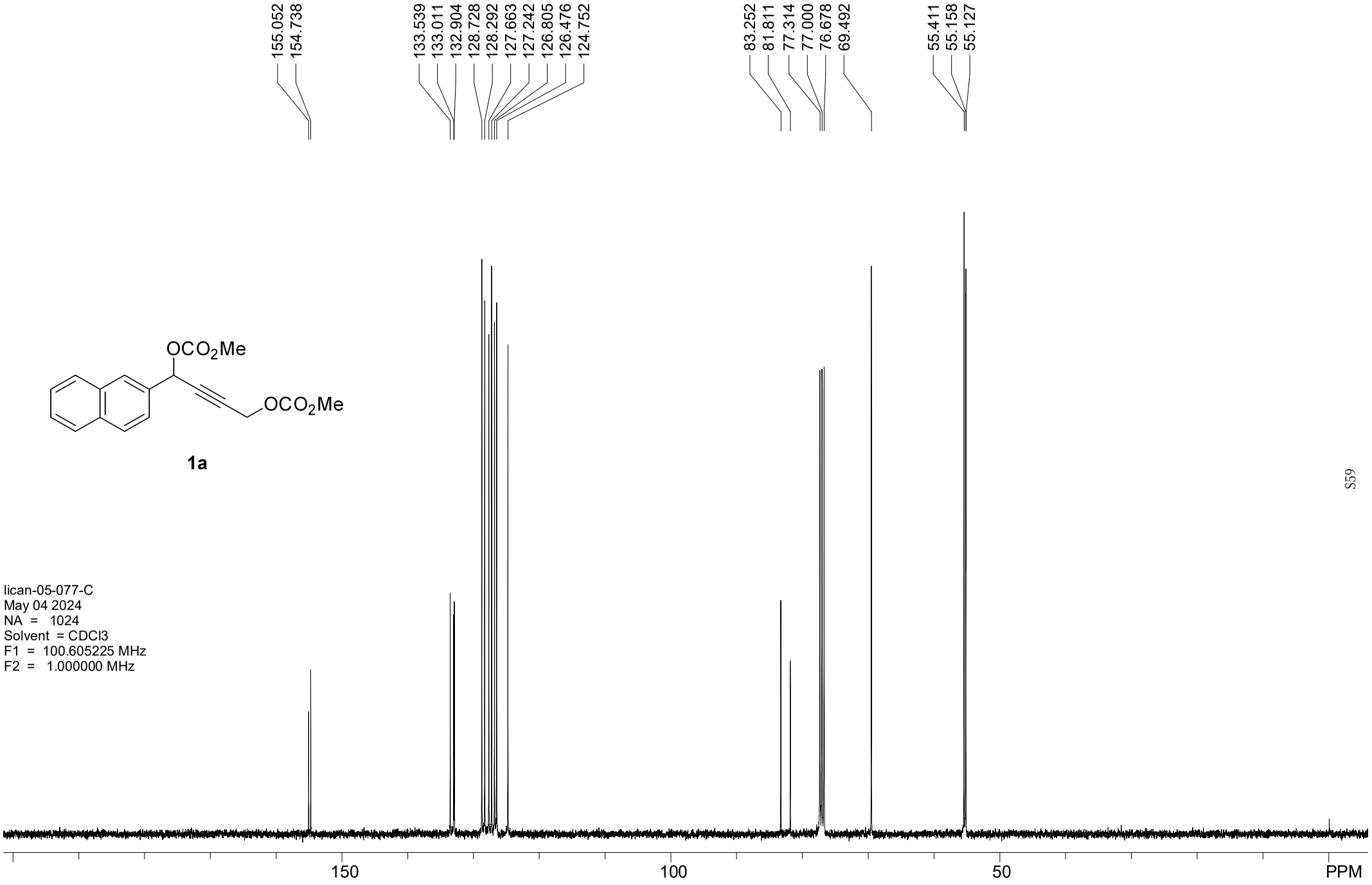
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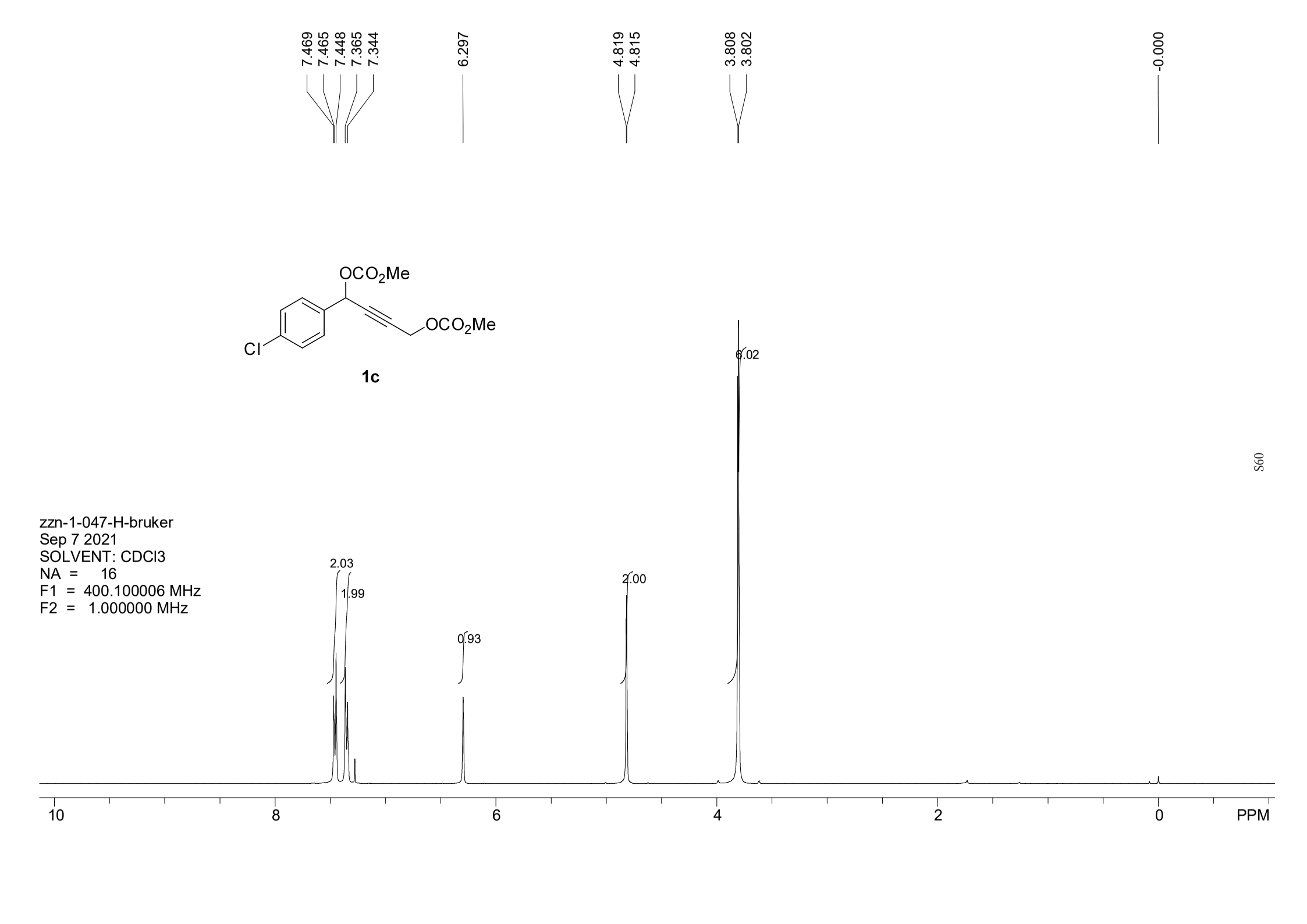
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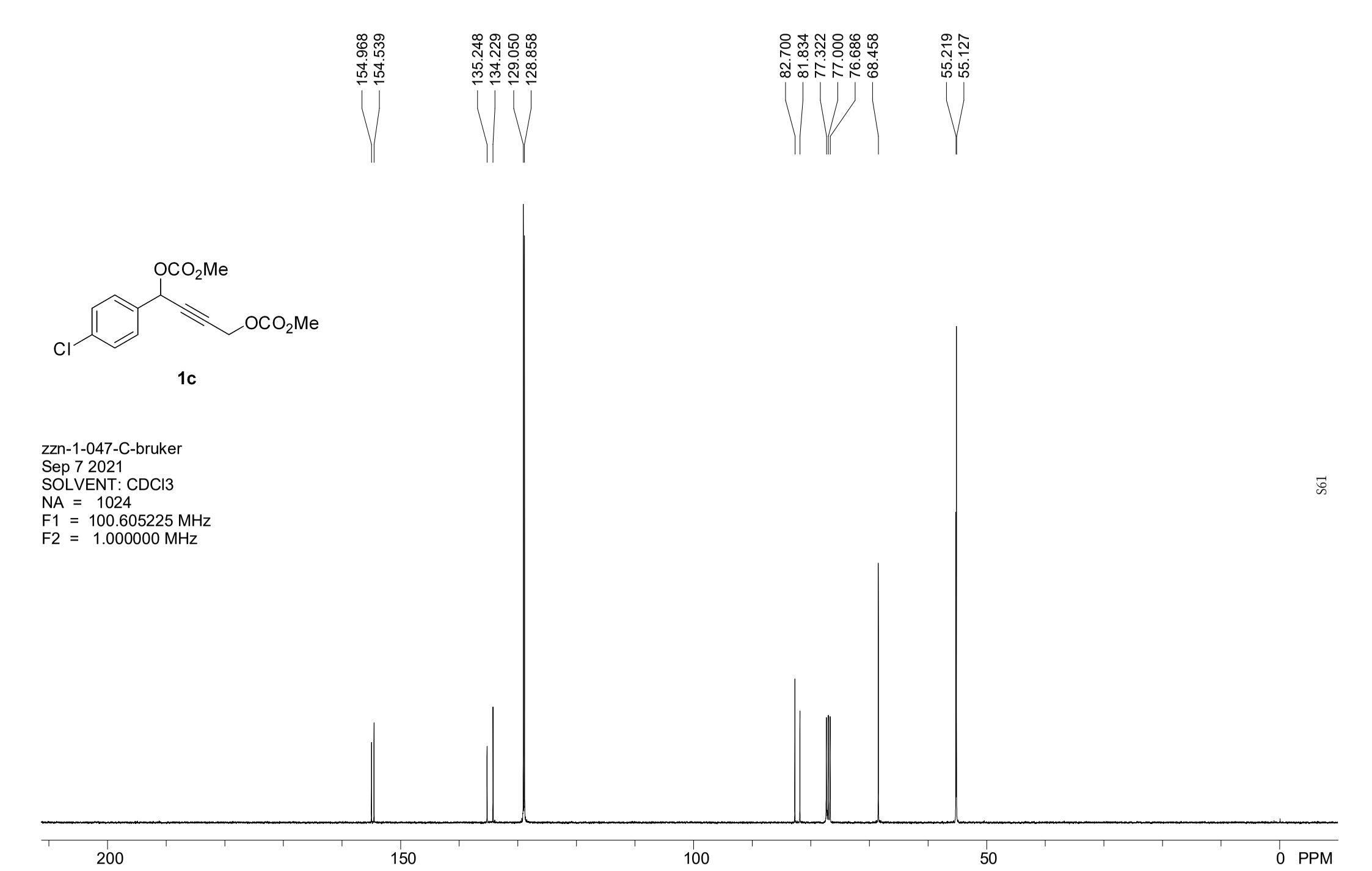
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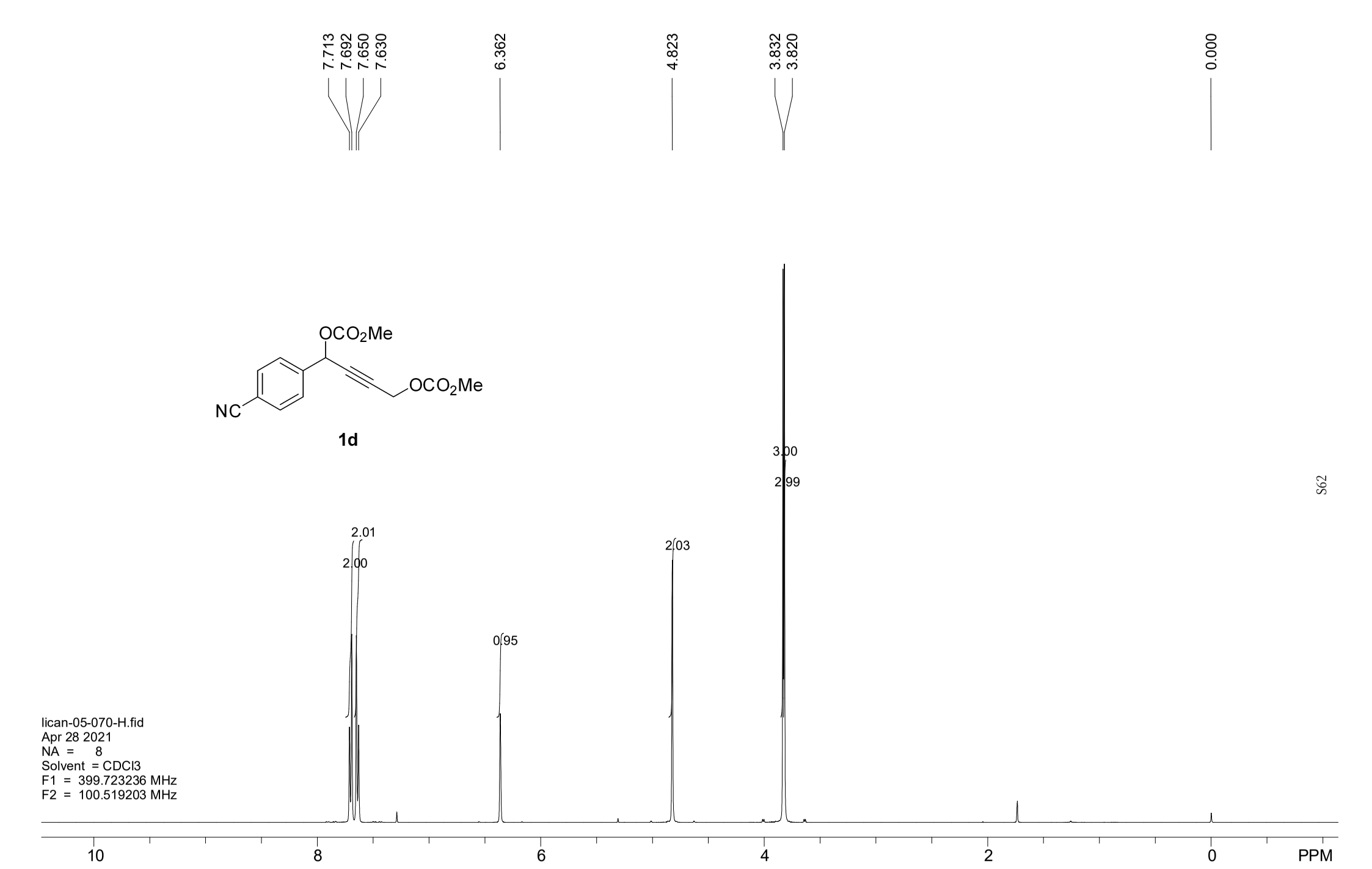
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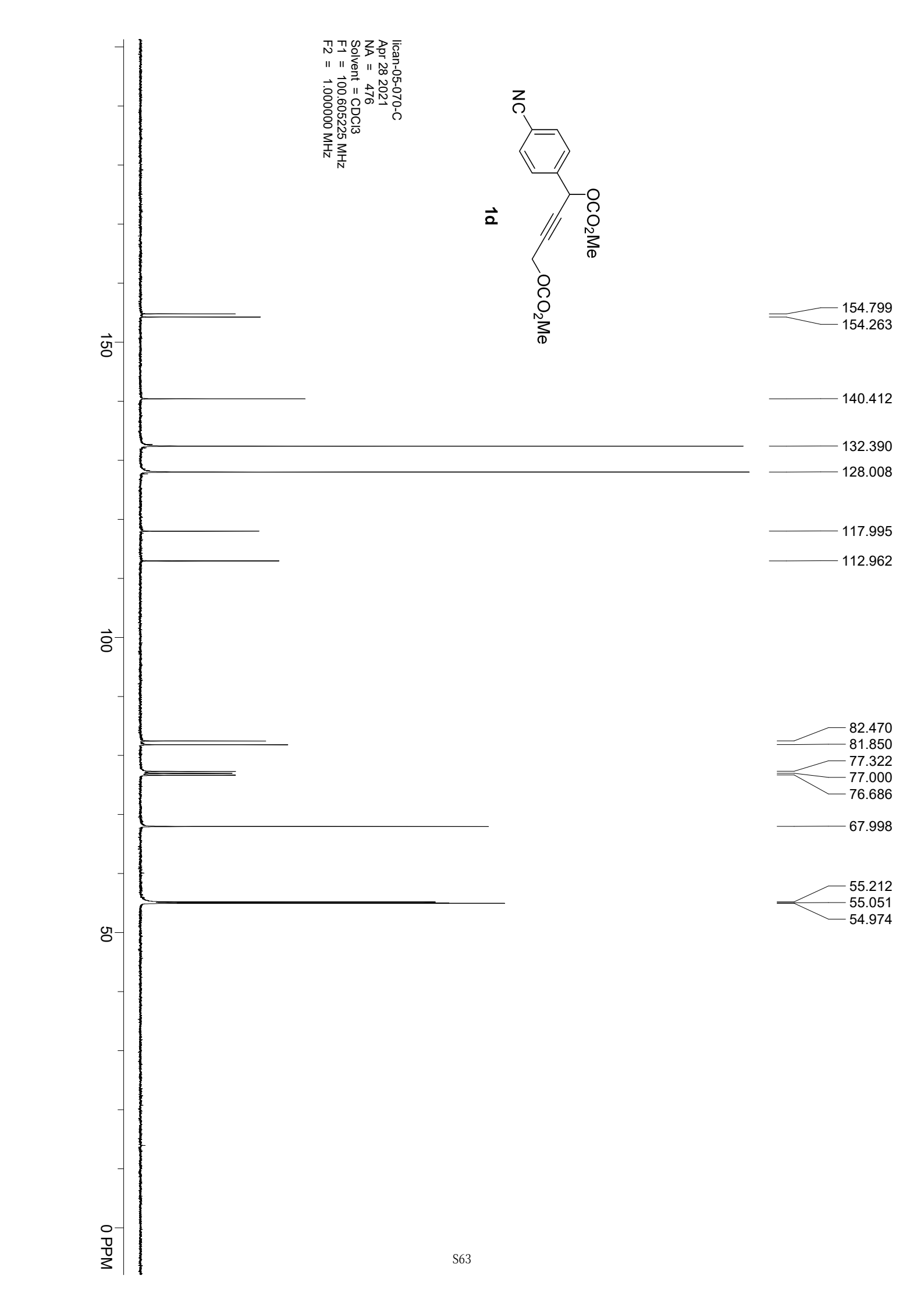
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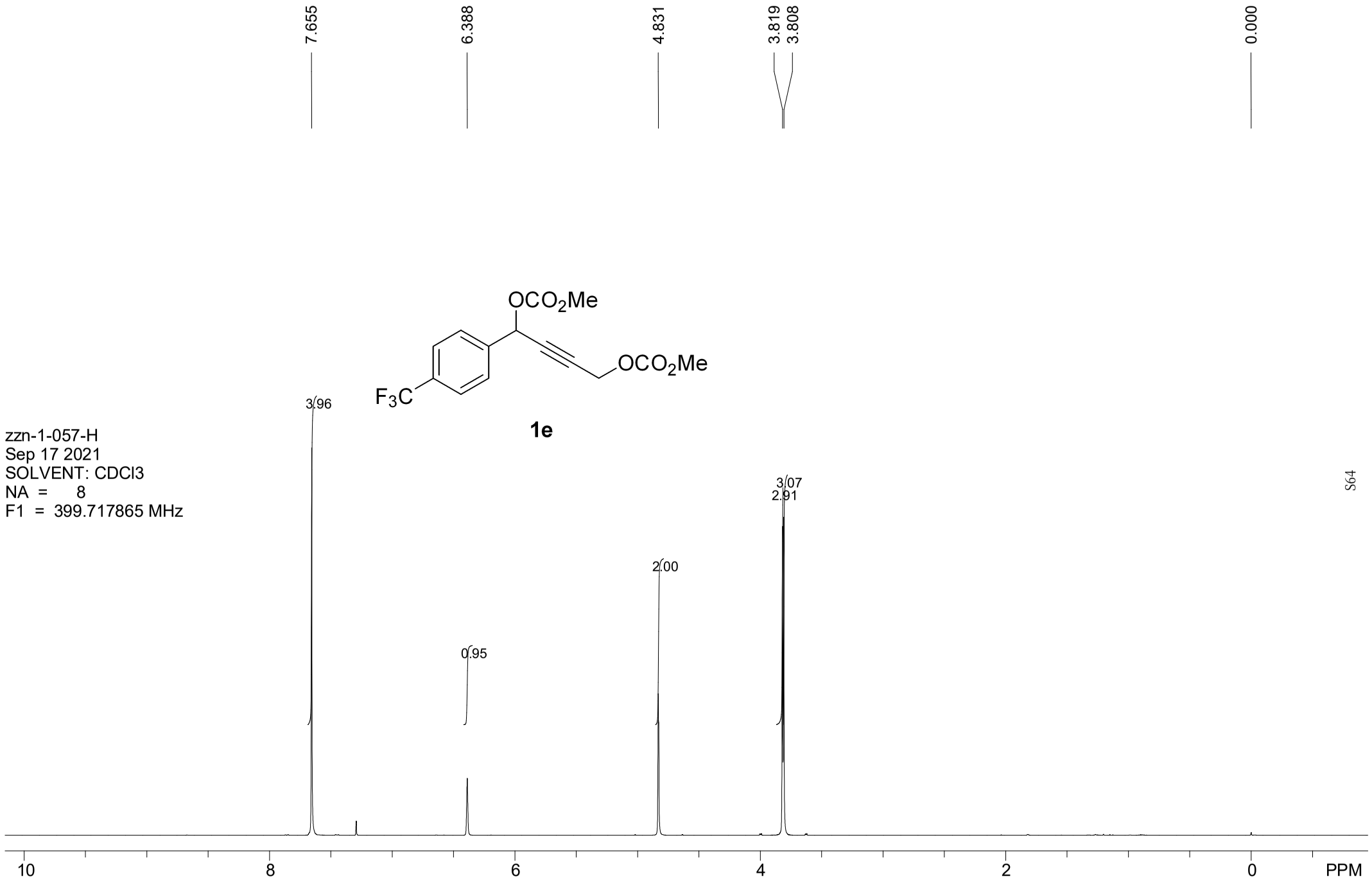
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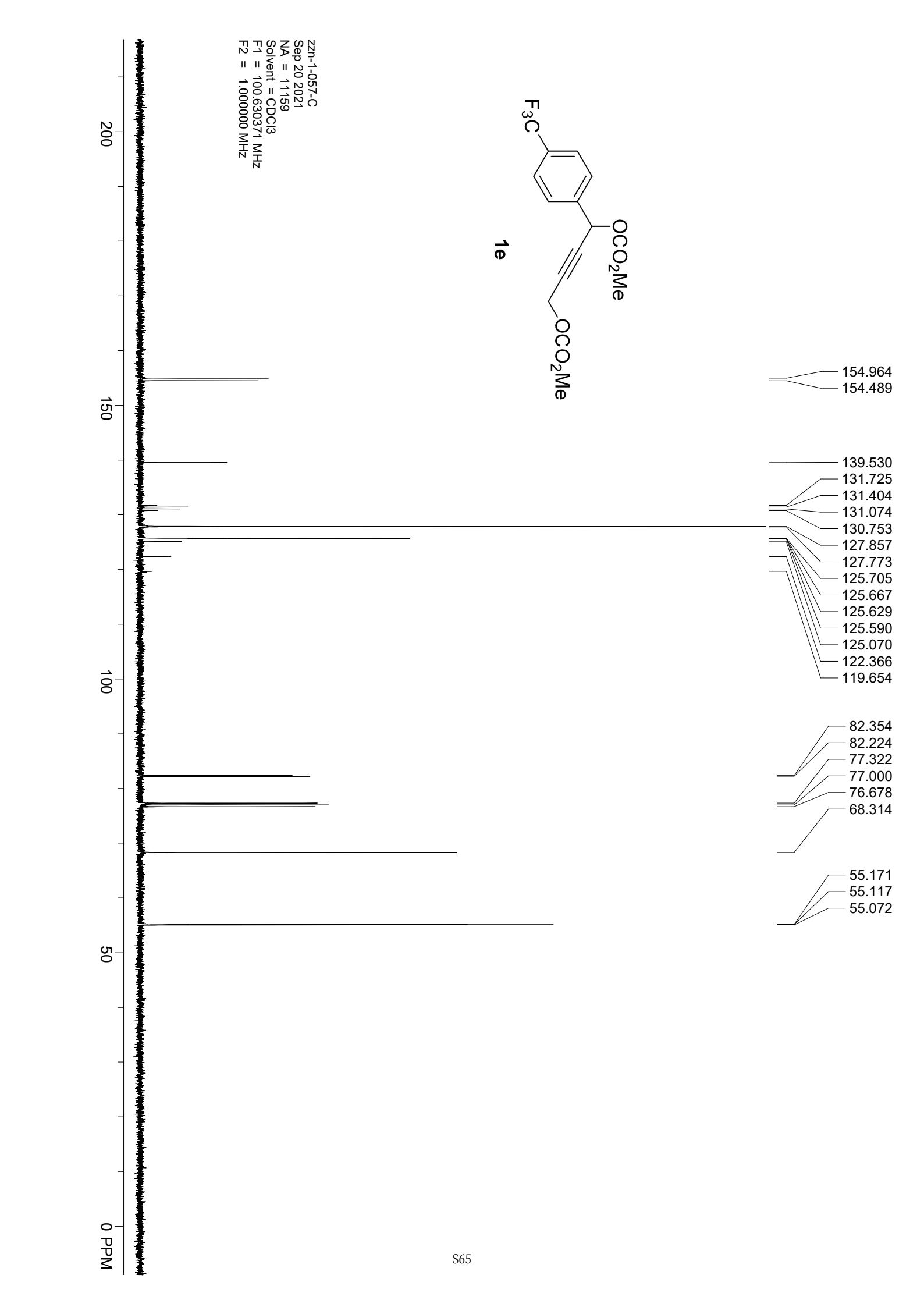
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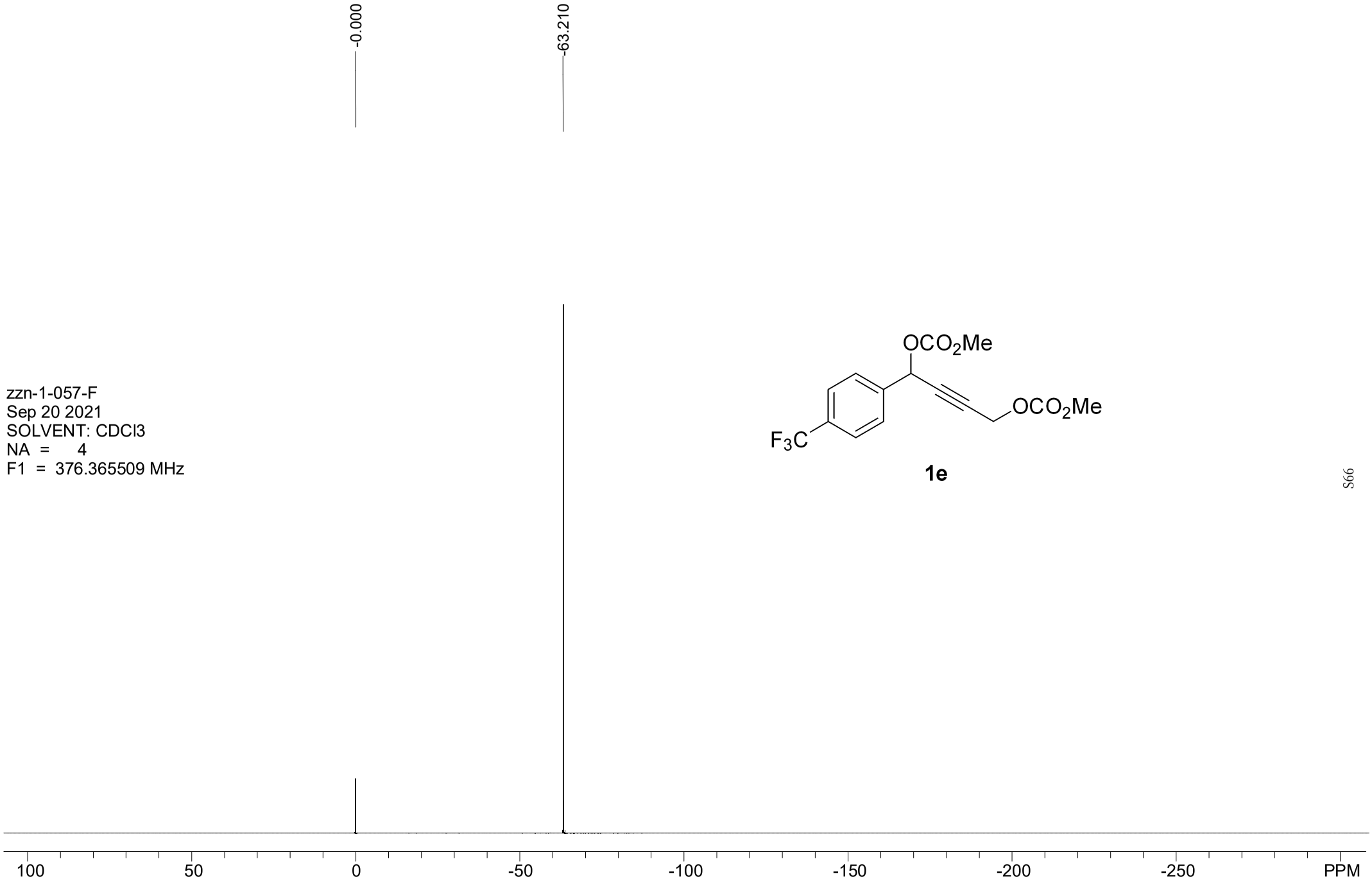
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Sep 20 2021
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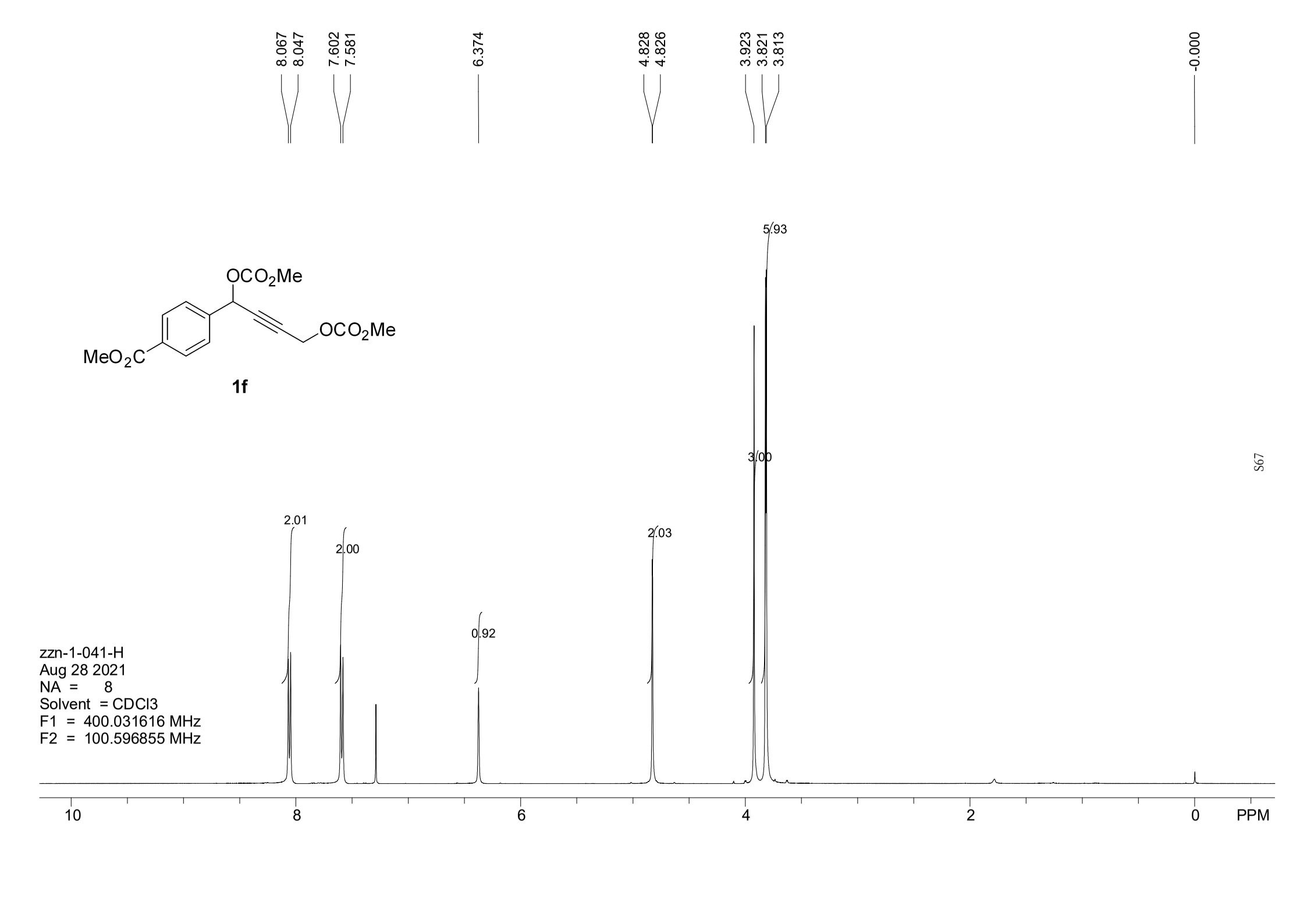
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Aug 28 2021
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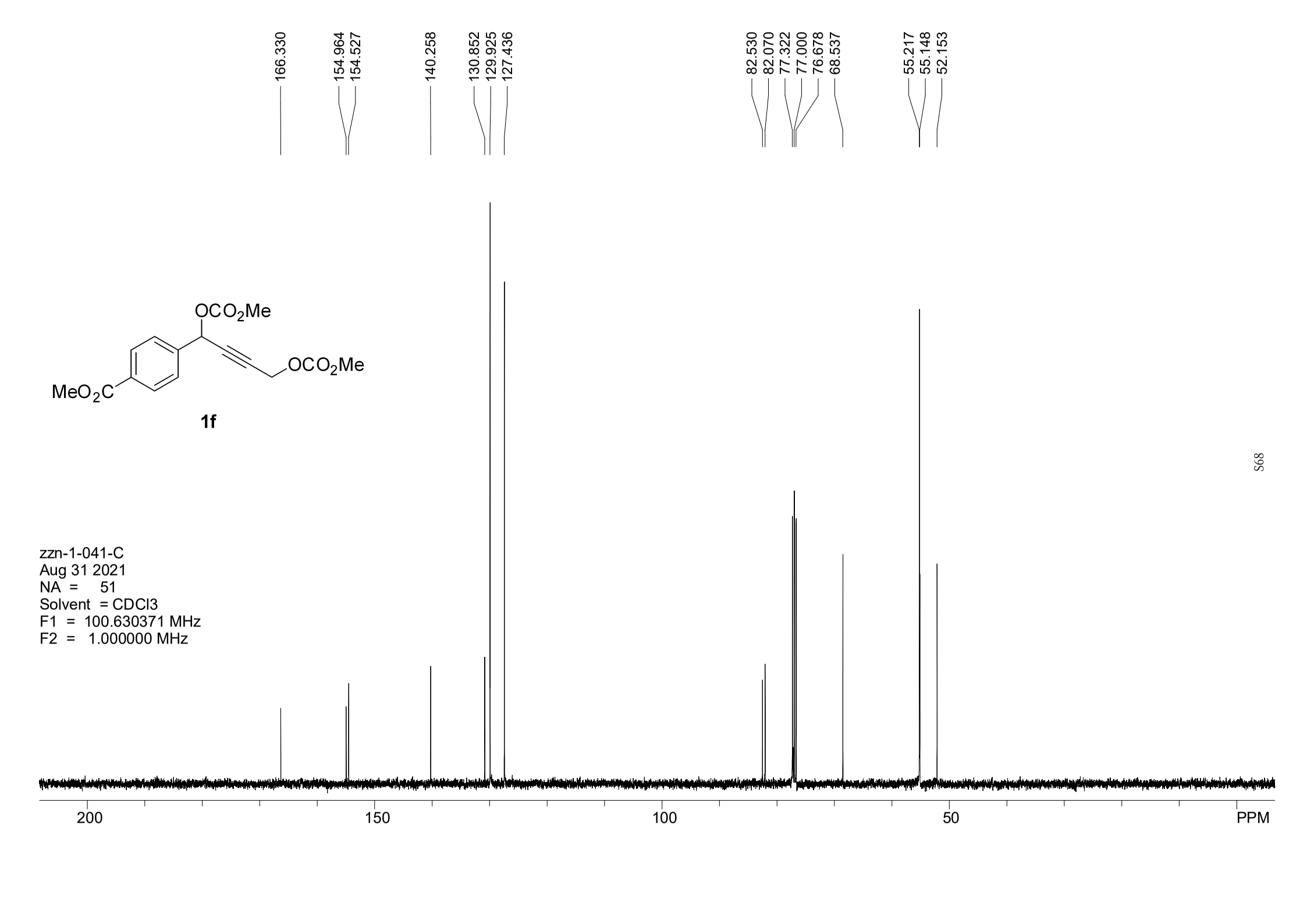
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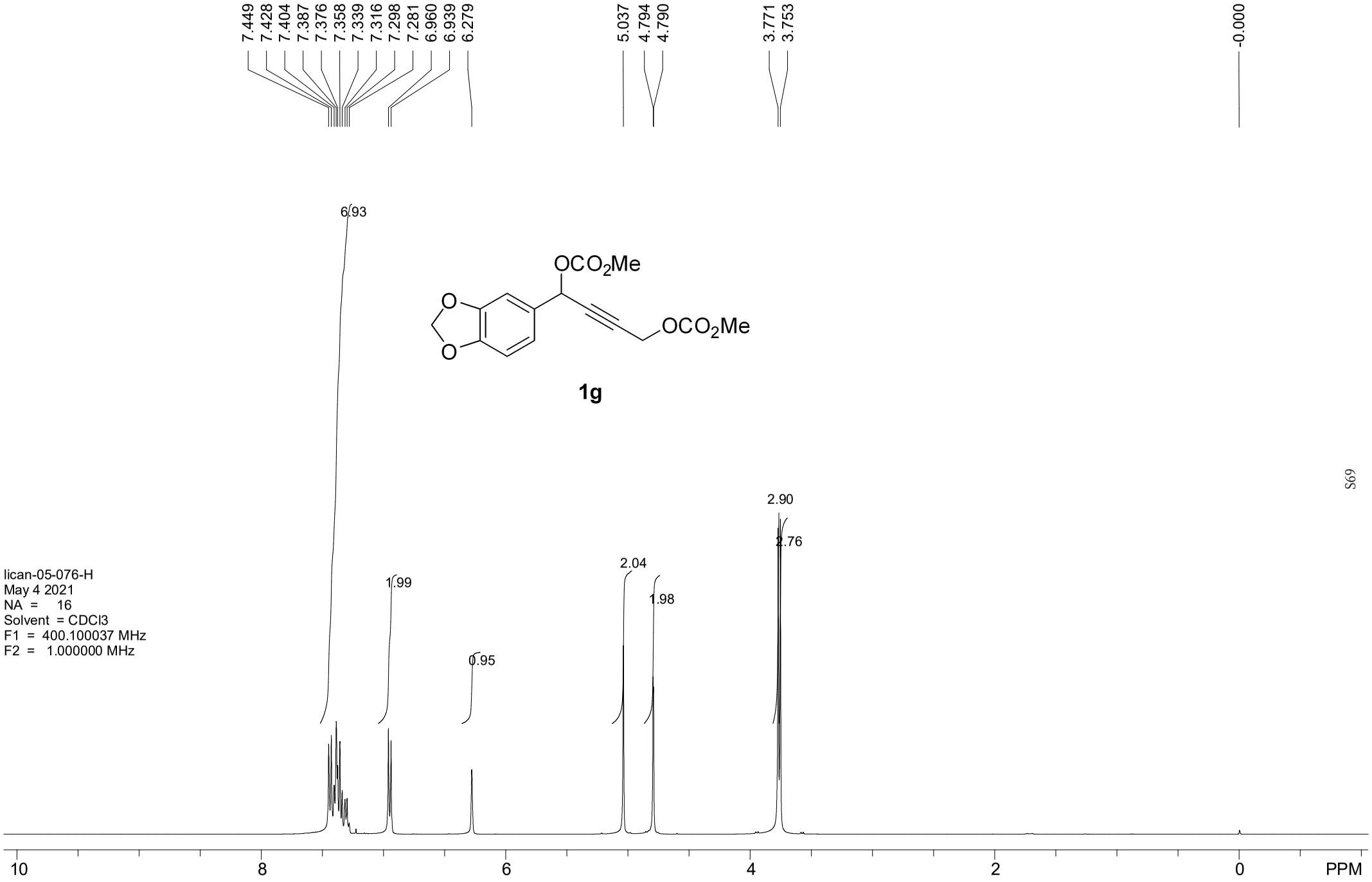
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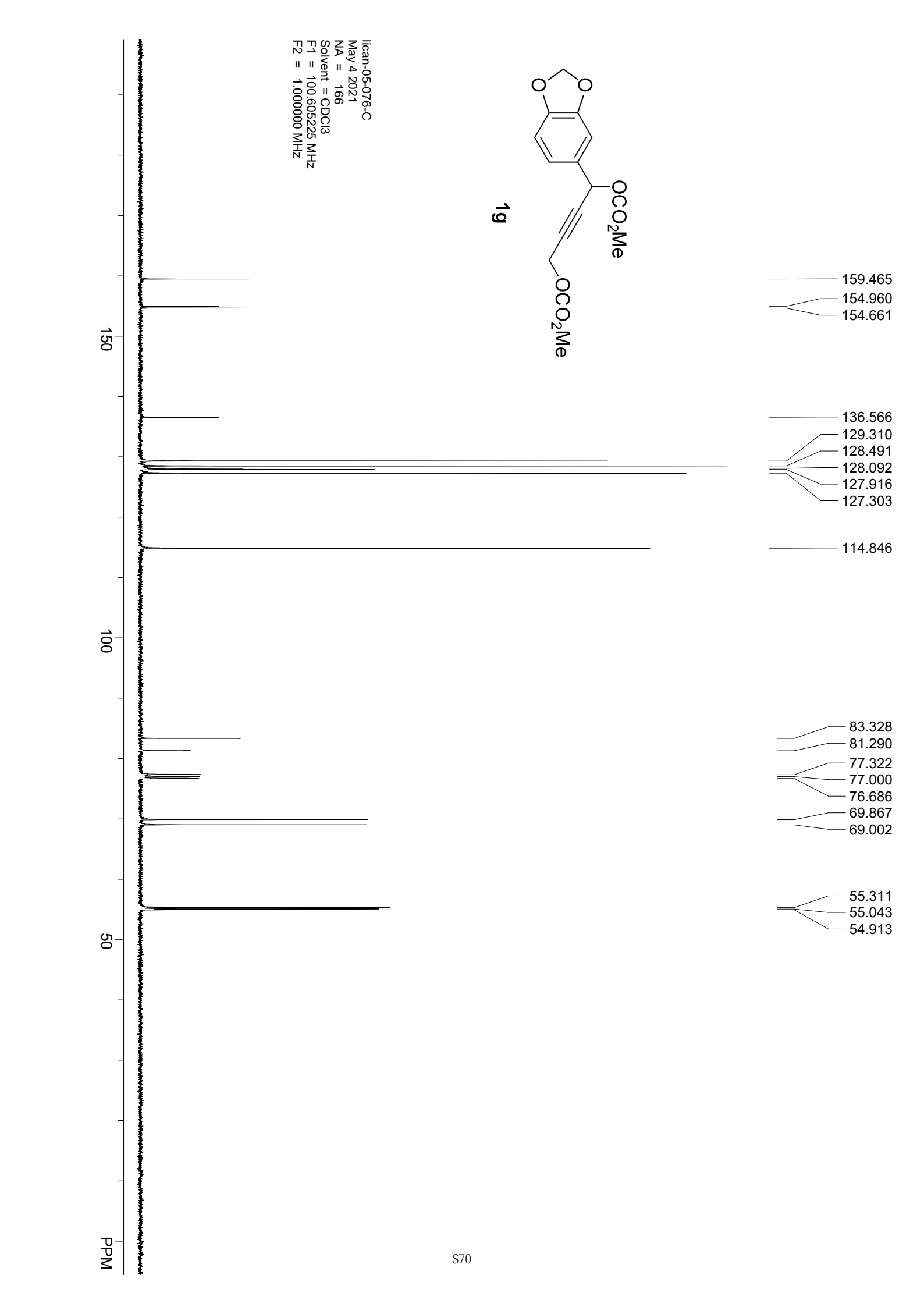
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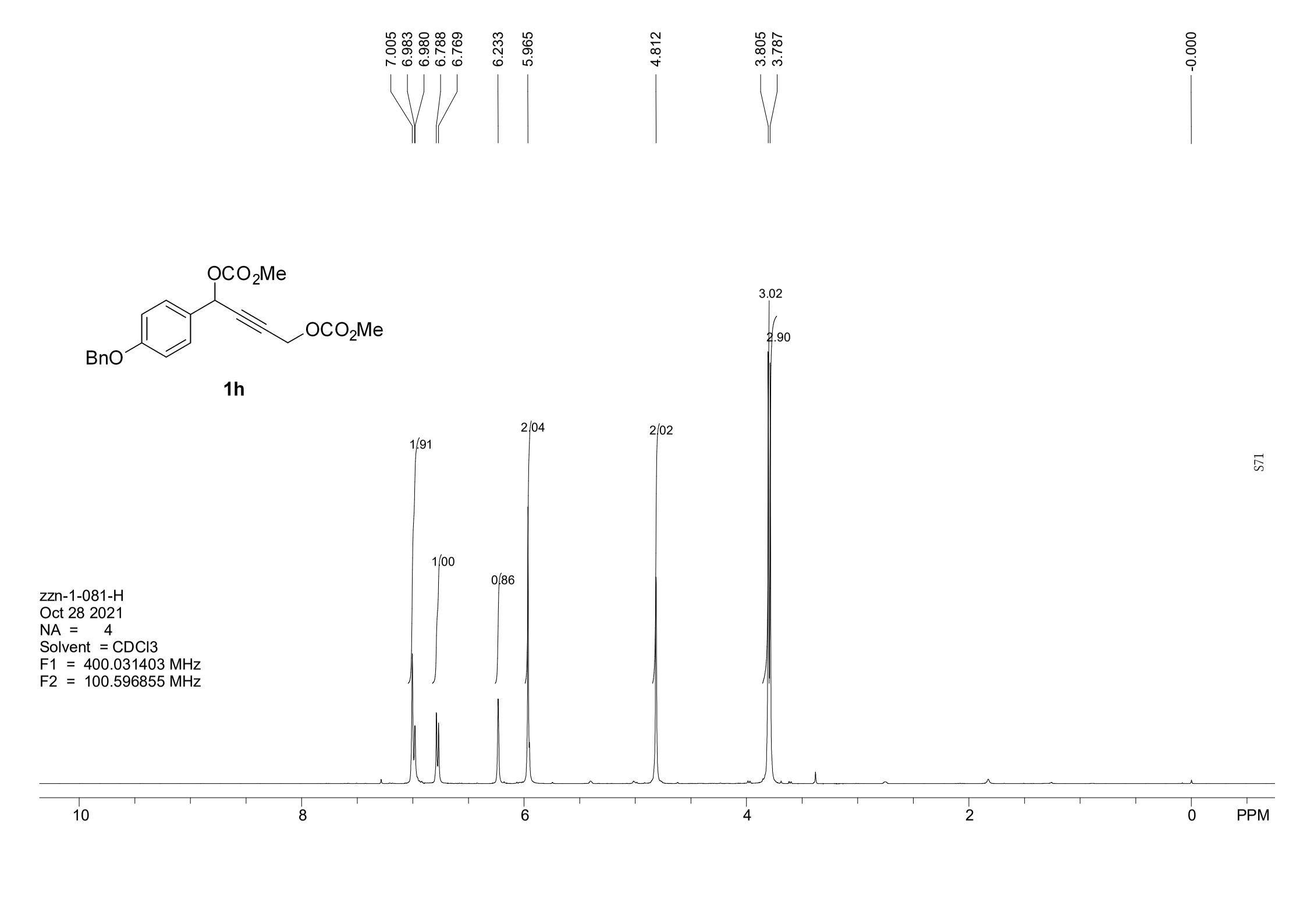
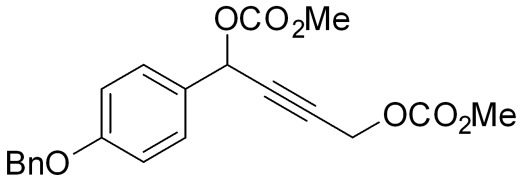
50
PPM

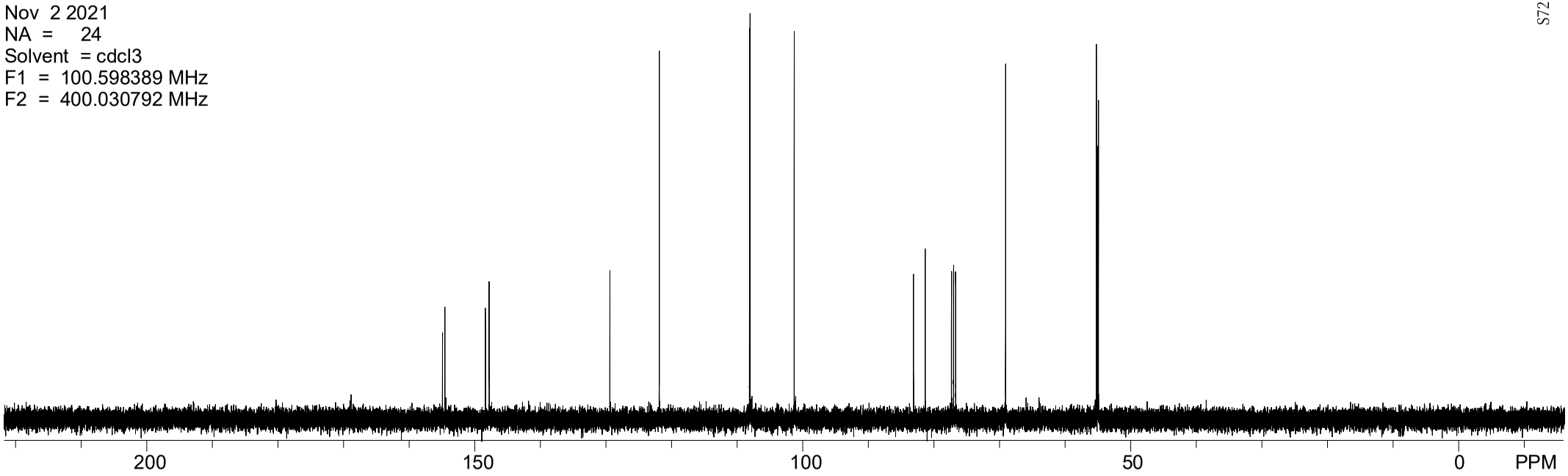

7.005
6.983
6.980
6.788
6.769
6.233
5.965
4.812
3.805
3.787
-0.000
OCO2Me
OCO2Me
BnO
1h
3.02
2.90
2.04
2.02
1.91
1.00
0.86
zzn-1-081-H
Oct 28 2021
NA = 4
Solvent = CDCl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz
10
8
6
4
2
0
PPM

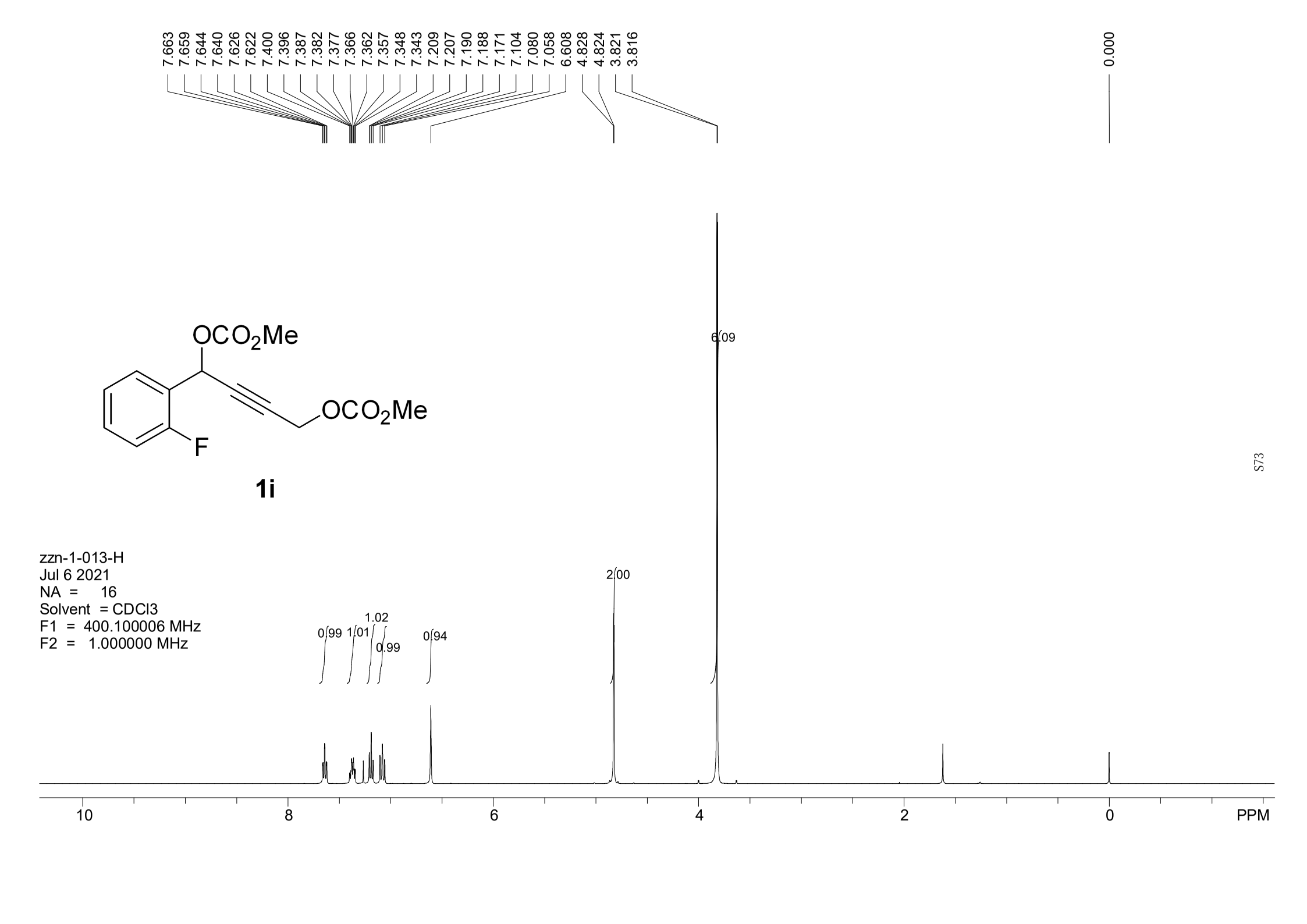
154.931
154.552
148.375
147.806
129.409
121.868
108.110
108.042
101.304
83.104
81.317
77.319
77.000
76.685
69.084
55.250
55.064
54.959

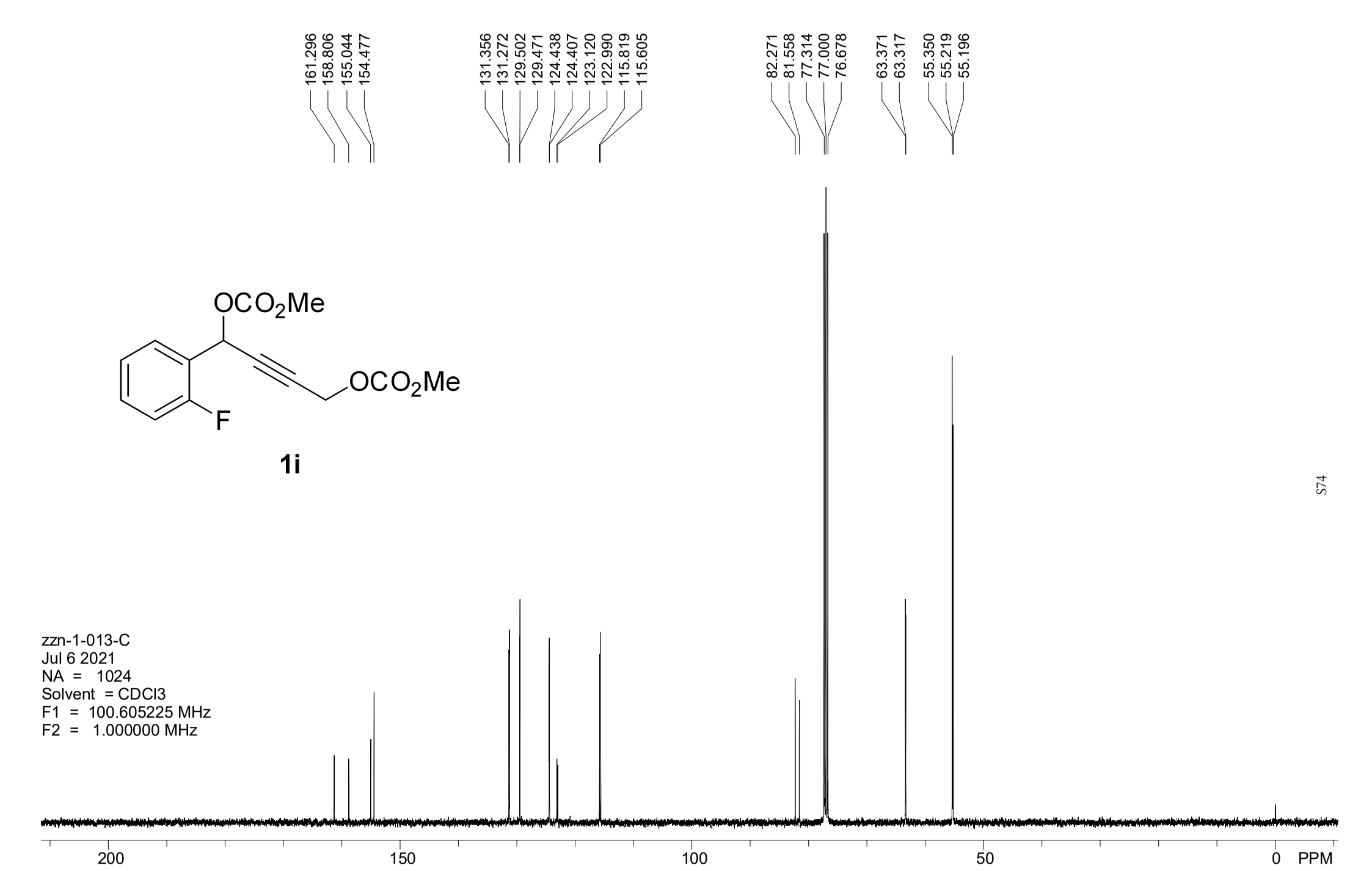


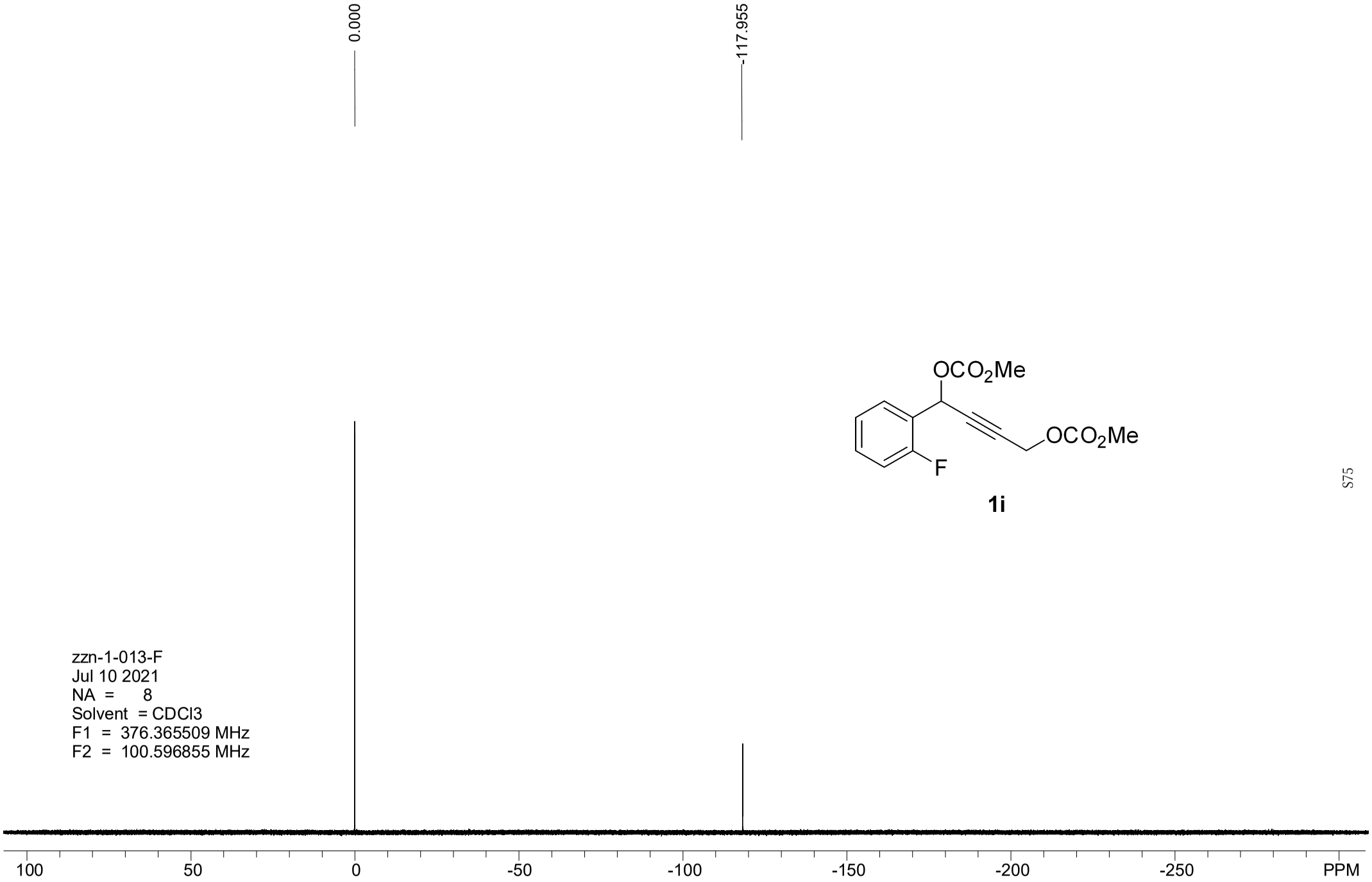
1h

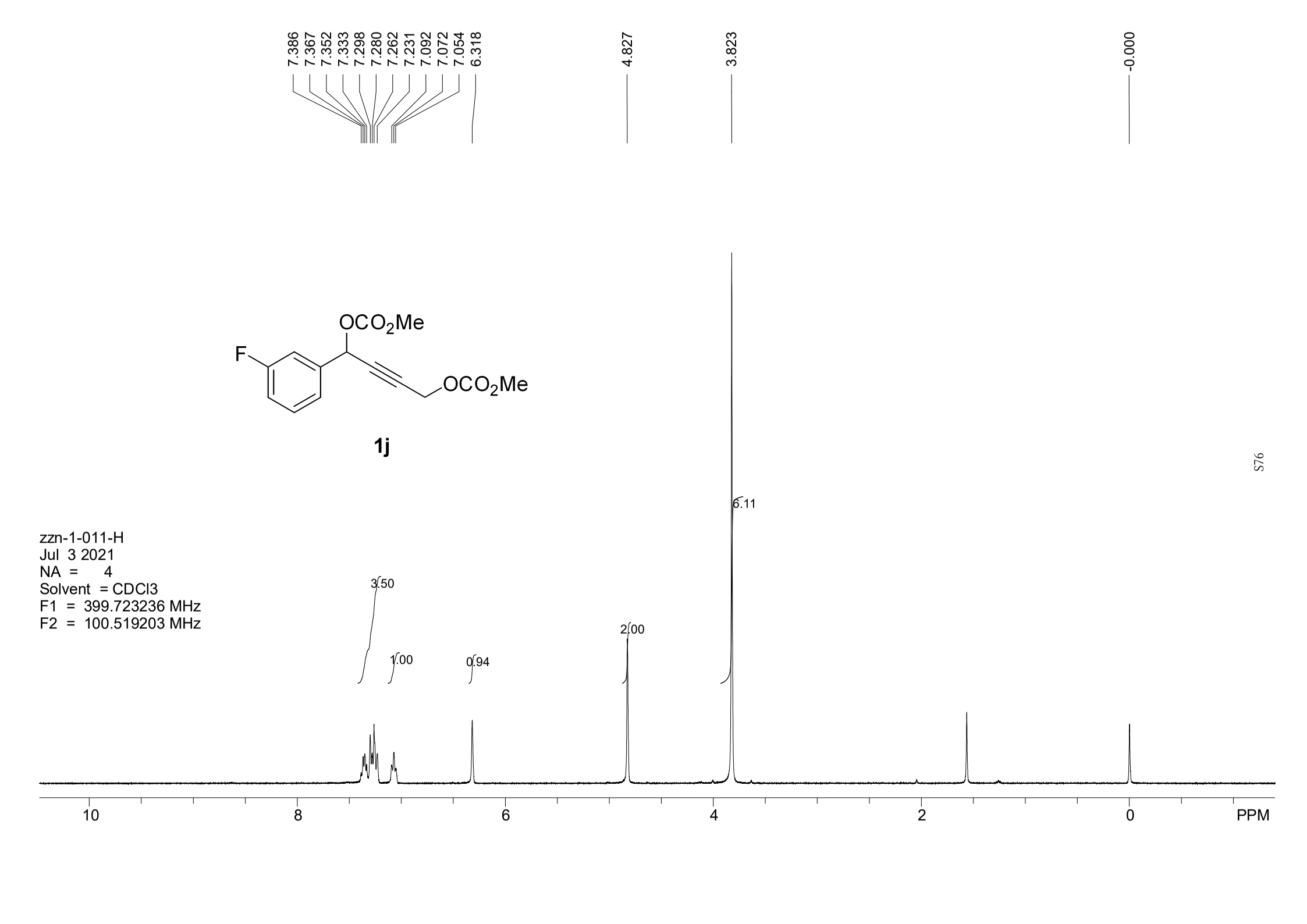
zzn-1-081-C
Nov 2 2021
NA = 24
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz

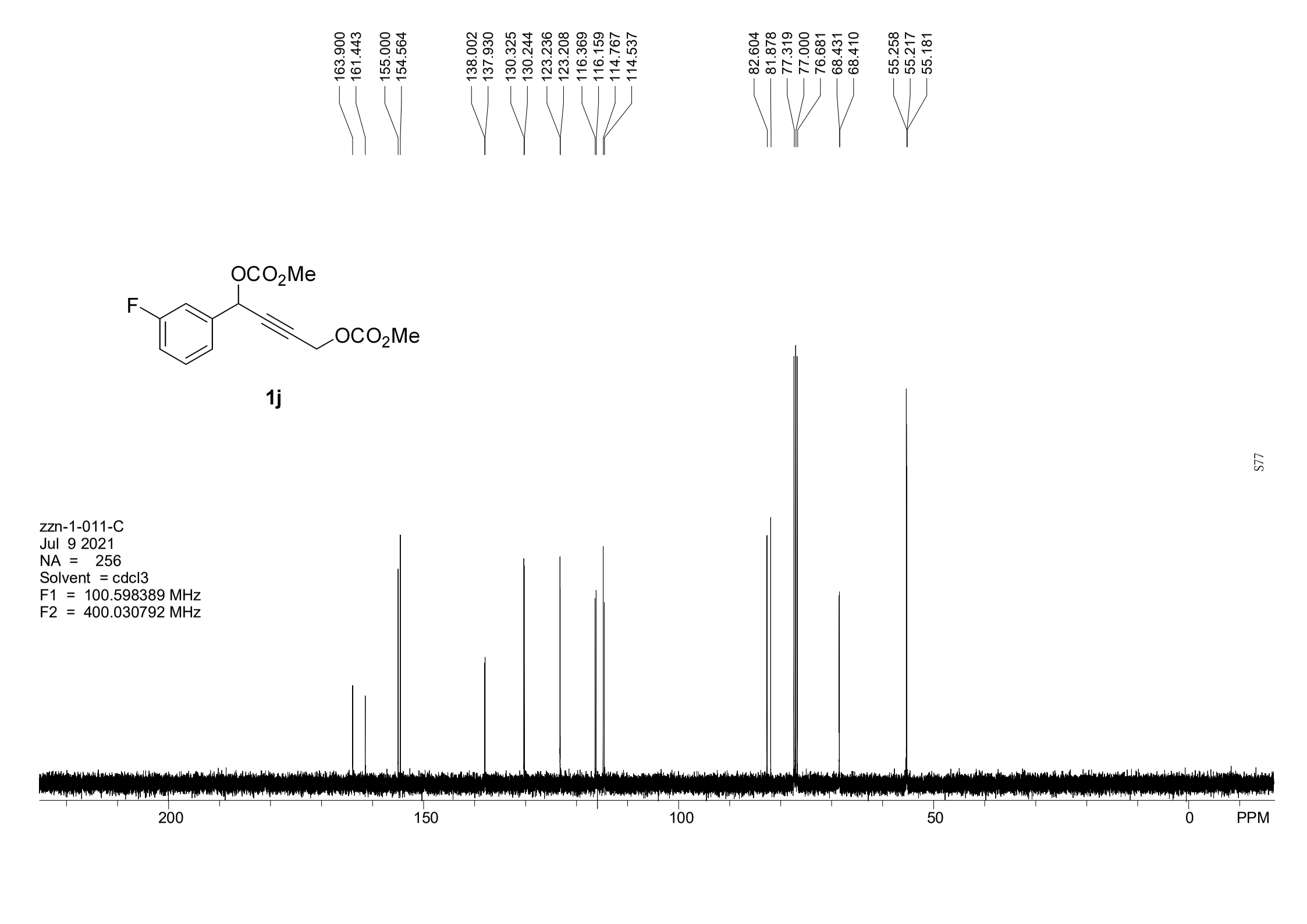


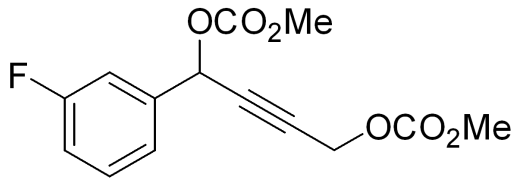

7.663
7.659
7.644
7.640
7.626
7.622
7.400
7.396
7.387
7.382
7.377
7.366
7.362
7.357
7.348
7.343
7.209
7.207
7.190
7.188
7.171
7.104
7.080
7.058
6.608
4.828
4.824
3.821
3.816
0.000
OCO2Me
OCO2Me
F
1i
6.09
2.00
1.02
0.99
1.01
0.99
0.94
zzn-1-013-H
Jul 6 2021
NA = 16
Solvent = CDCl3
F1 = 400.100006 MHz
F2 = 1.000000 MHz
10
8
6
4
2
0
PPM


161.296
158.806
155.044
154.477
131.356
131.272
129.502
129.471
124.438
124.407
123.120
122.990
115.819
115.605
82.271
81.558
77.314
77.000
76.678
63.371
63.317
55.350
55.219
55.196
OCO2Me
OCO2Me
F
1i
zzn-1-013-C
Jul 6 2021
NA = 1024
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
200
150
100
50
0
PPM


0.000
-117.955
OCO2Me
OCO2Me
F
1i
zzn-1-013-F
Jul 10 2021
NA = 8
Solvent = CDCl3
F1 = 376.365509 MHz
F2 = 100.596855 MHz
100
50
0
-50
-100
-150
-200
-250
PPM

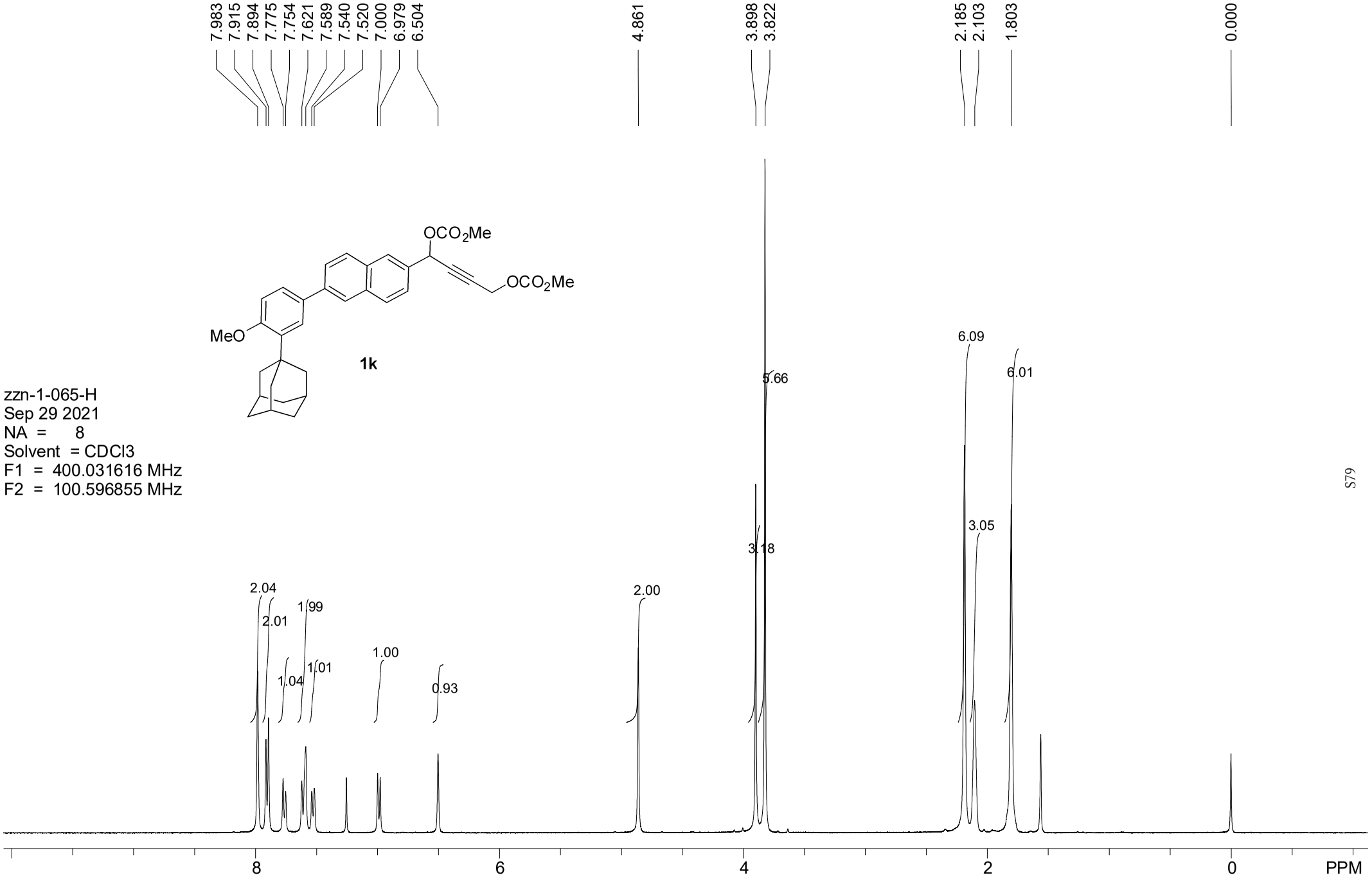

7.386
7.367
7.352
7.333
7.298
7.280
7.262
7.231
7.092
7.072
7.054
6.318
4.827
3.823
-0.000
OCO2Me
F
OCO2Me
1j
S76
zzn-1-011-H
Jul 3 2021
NA = 4
Solvent = CDCl3
F1 = 399.723236 MHz
F2 = 100.519203 MHz
3.50
1.00
0.94
2.00
6.11
10
8
6
4
2
0
PPM

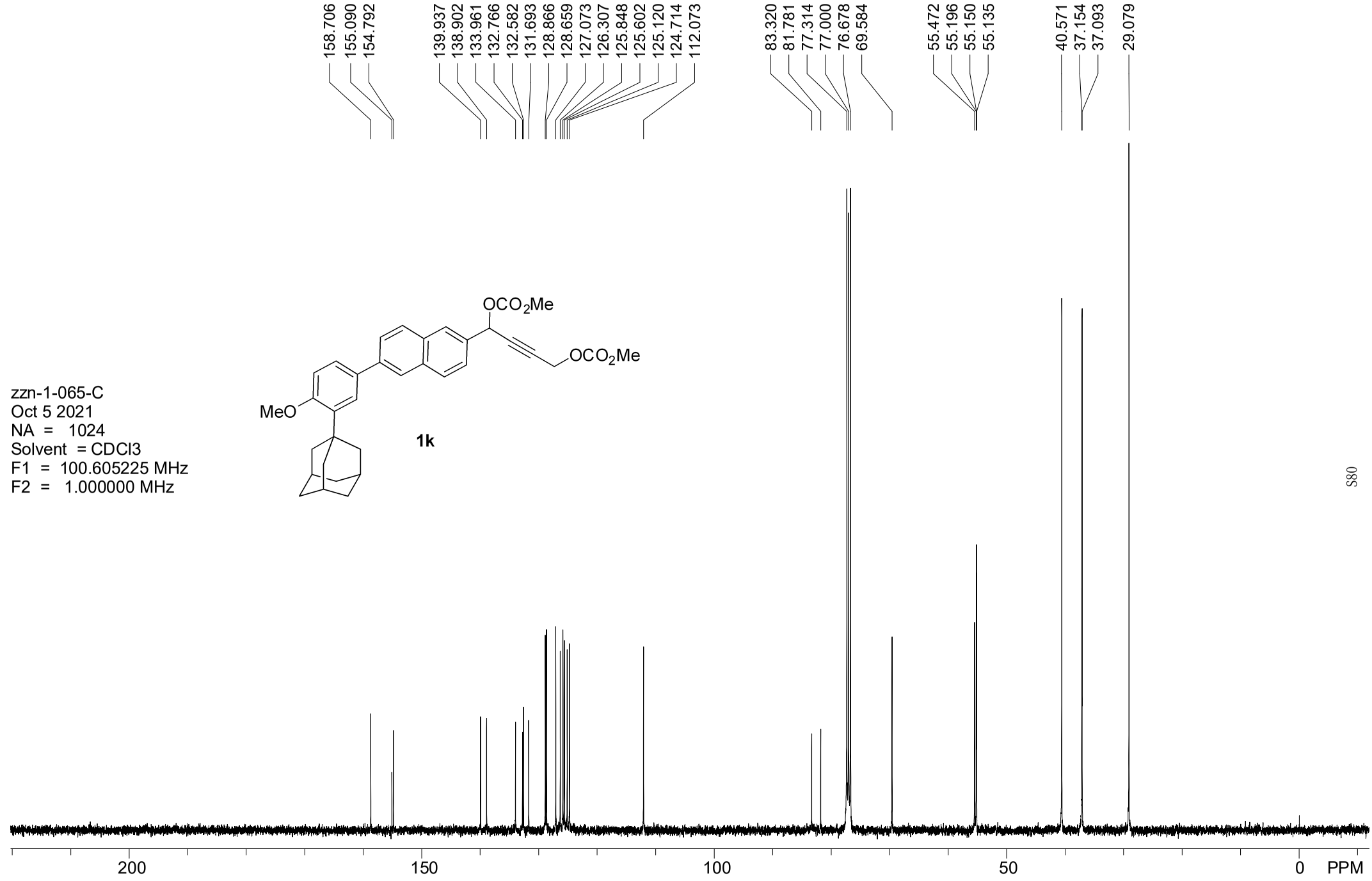

163.900
161.443
155.000
154.564
138.002
137.930
130.325
130.244
123.236
123.208
116.369
116.159
114.767
114.537
82.604
81.878
77.319
77.000
76.681
68.431
68.410
55.258
55.217
55.181
OCO2Me
F
OCO2Me
1j
zzn-1-011-C
Jul 9 2021
NA = 256
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
200
150
100
50
0
PPM

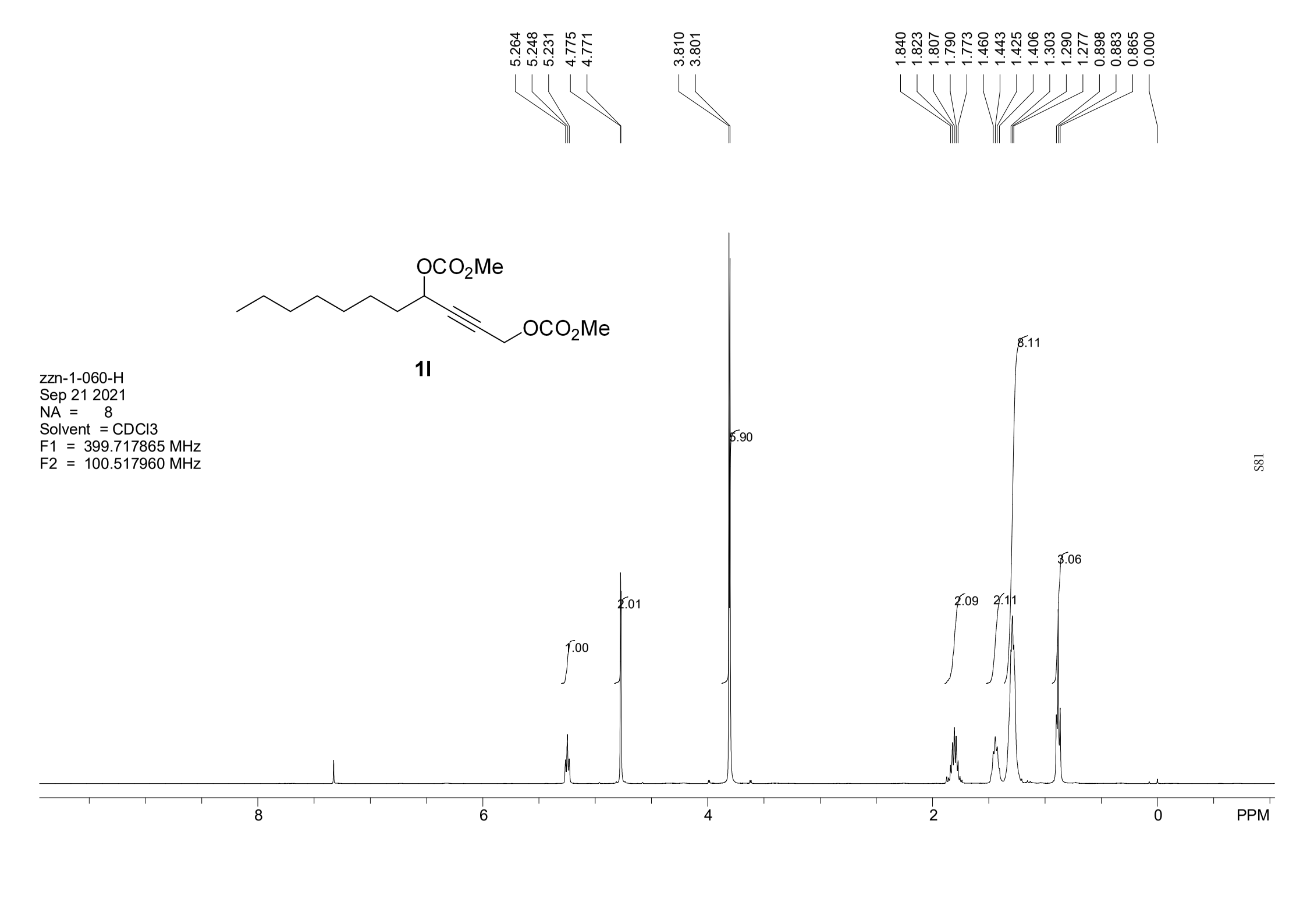


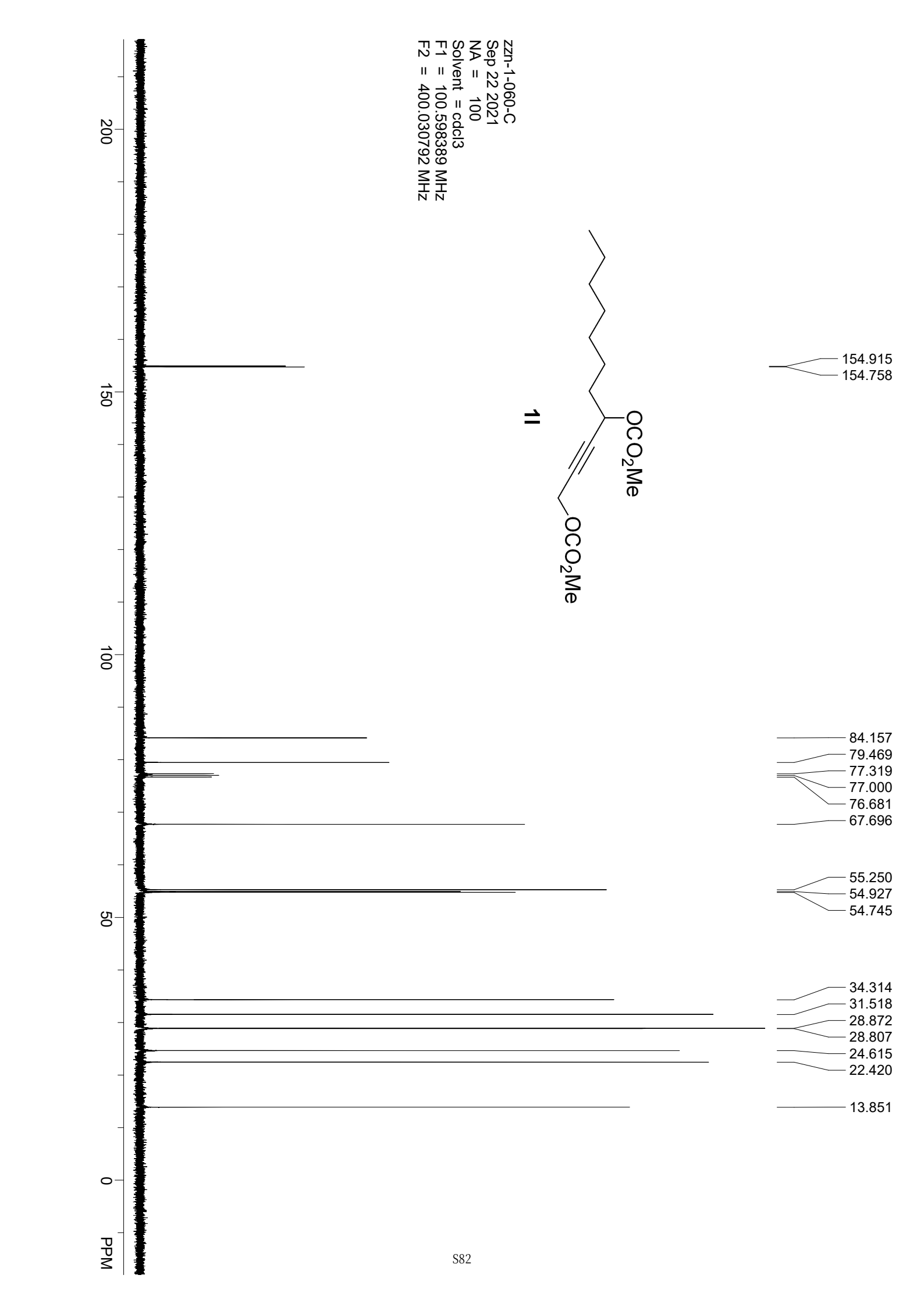
1j

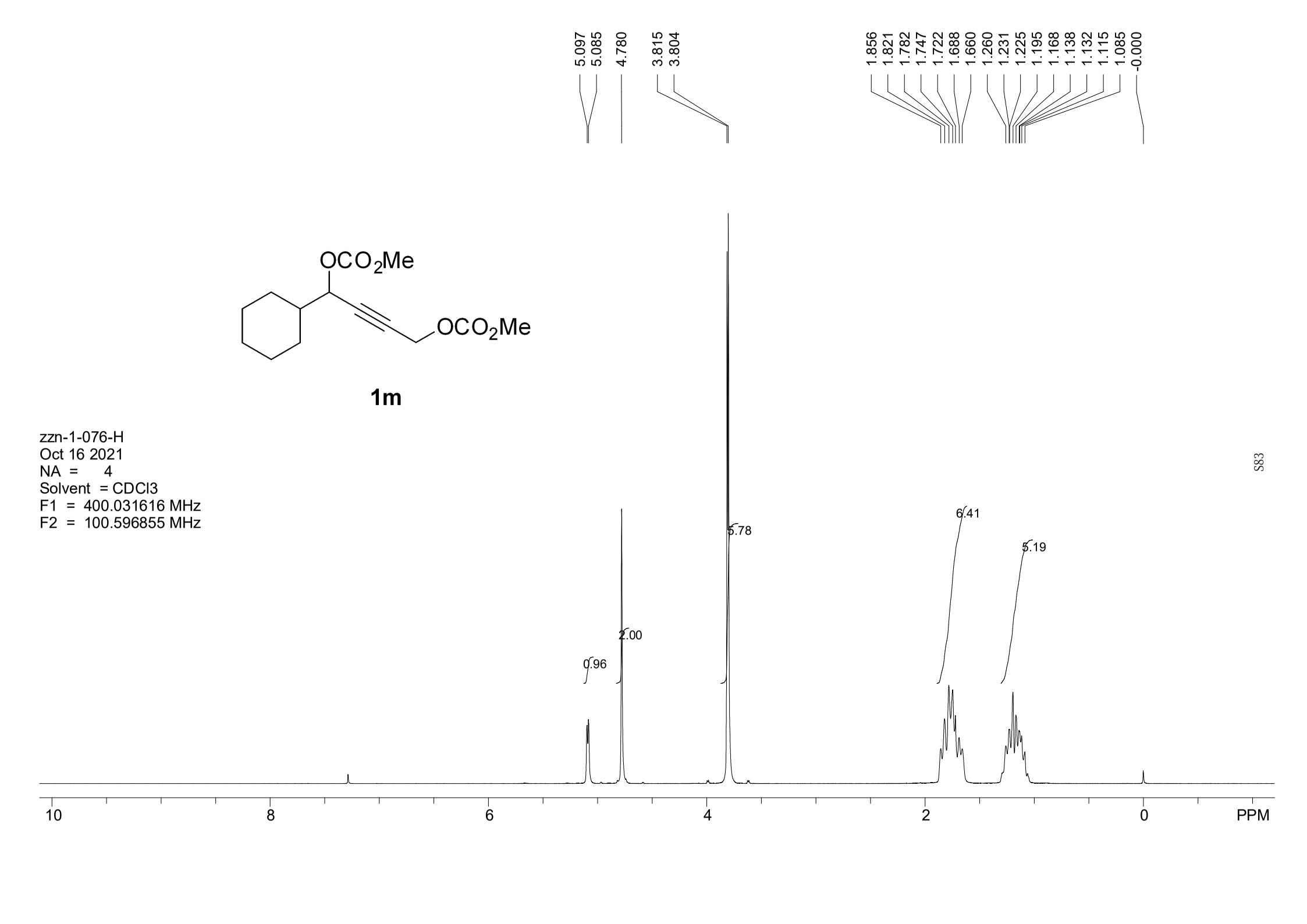
zzn-1-011-F
Jul 10 2021
NA = 4
Solvent = CDCl3
F1 = 376.365509 MHz
F2 = 100.596855 MHz

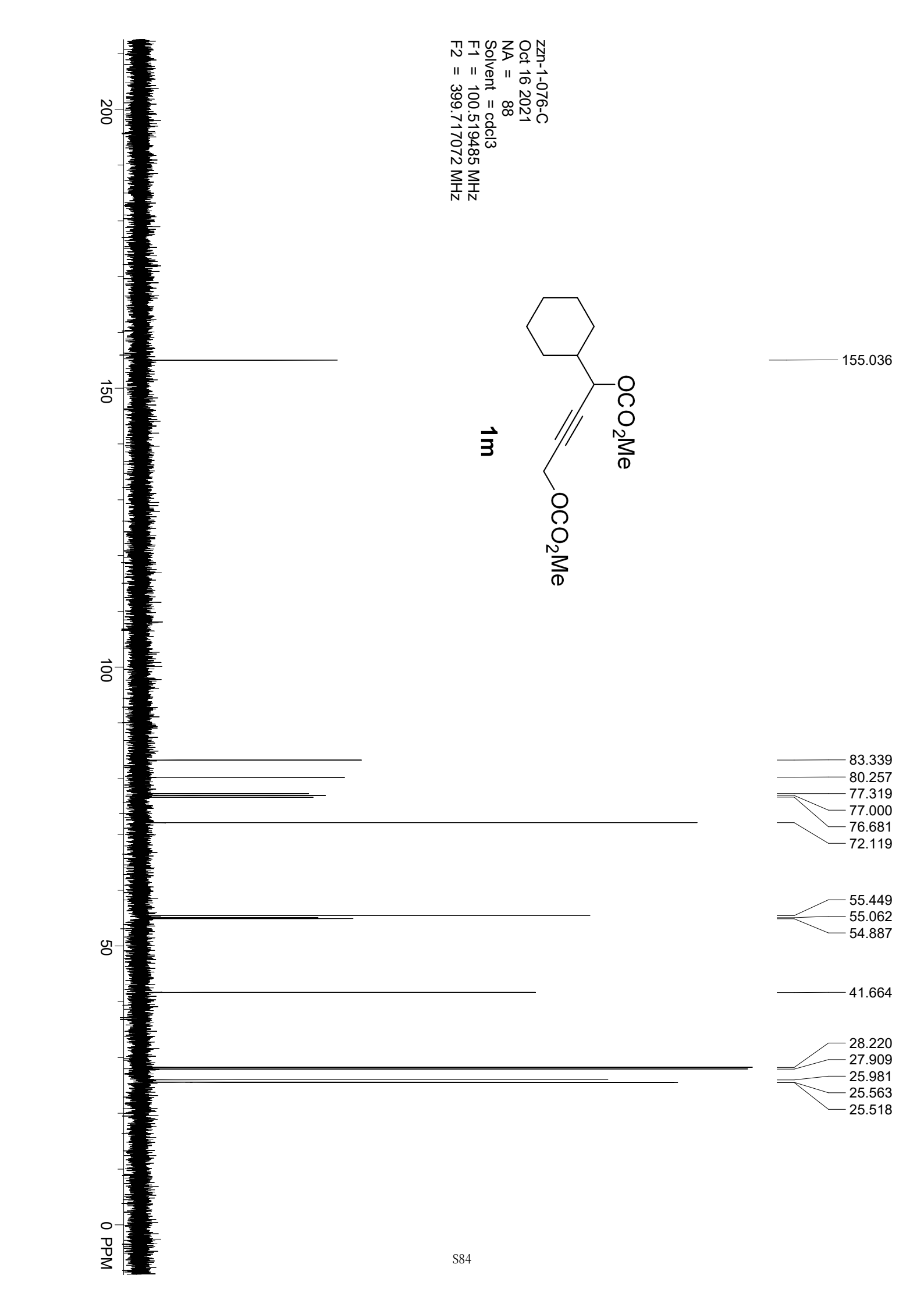

7.983
7.915
7.894
7.775
7.754
7.621
7.589
7.540
7.520
7.000
6.979
6.504
4.861
3.898
3.822
2.185
2.103
1.803
0.000
OCO2Me
OCO2Me
MeO
1k
zzn-1-065-H
Sep 29 2021
NA = 8
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
2.04
2.01
1.99
1.04
1.01
1.00
0.93
2.00
5.66
3.18
6.09
6.01
3.05
8
6
4
2
0
PPM

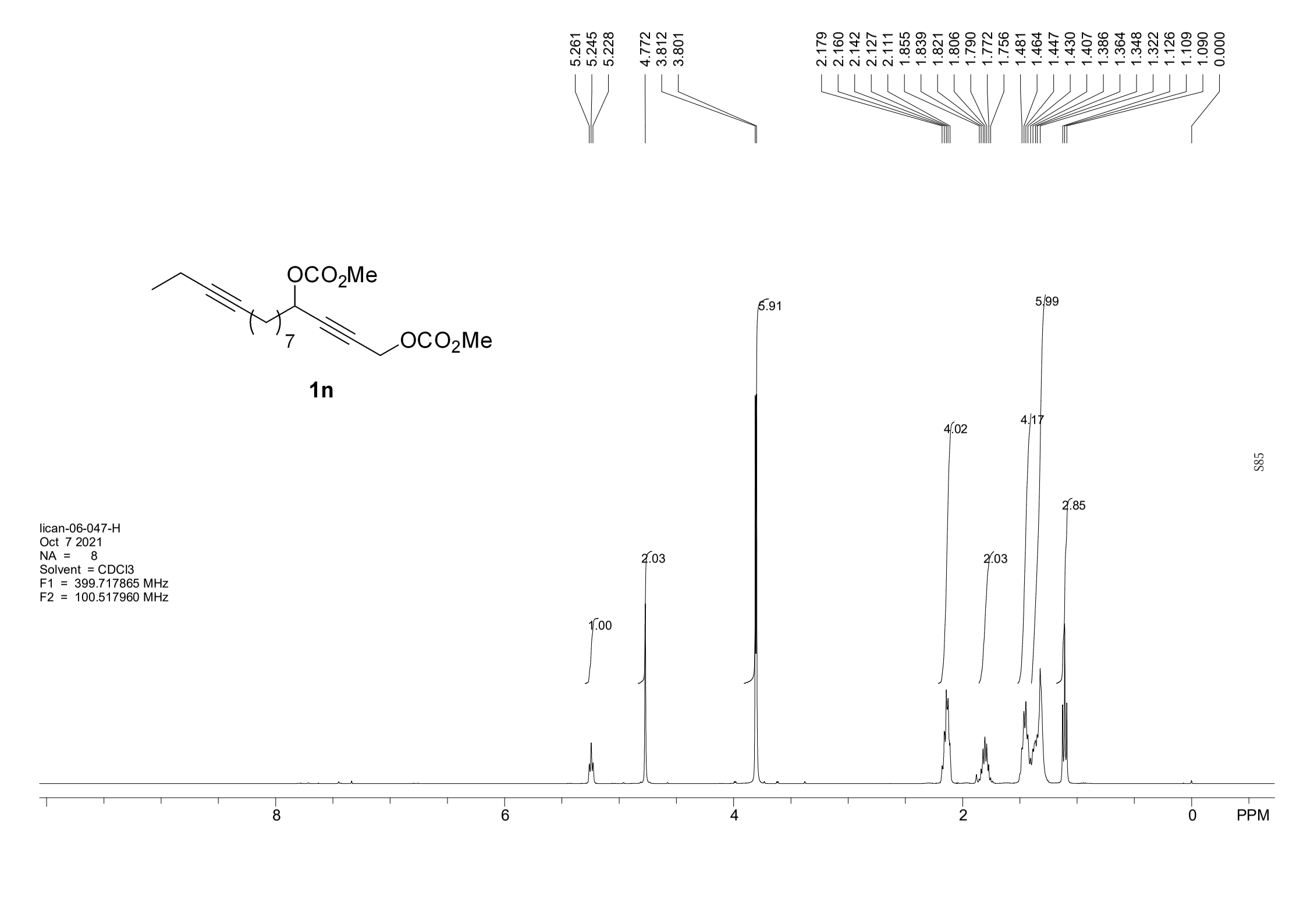

158.706
155.090
154.792
139.937
138.902
133.961
132.766
132.582
131.693
128.866
128.659
127.073
126.307
125.848
125.602
125.120
124.714
112.073
83.320
81.781
77.314
77.000
76.678
69.584
55.472
55.196
55.150
55.135
40.571
37.154
37.093
29.079
OCO2Me
OCO2Me
MeO
1k
zzn-1-065-C
Oct 5 2021
NA = 1024
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
200
150
100
50
0
PPM

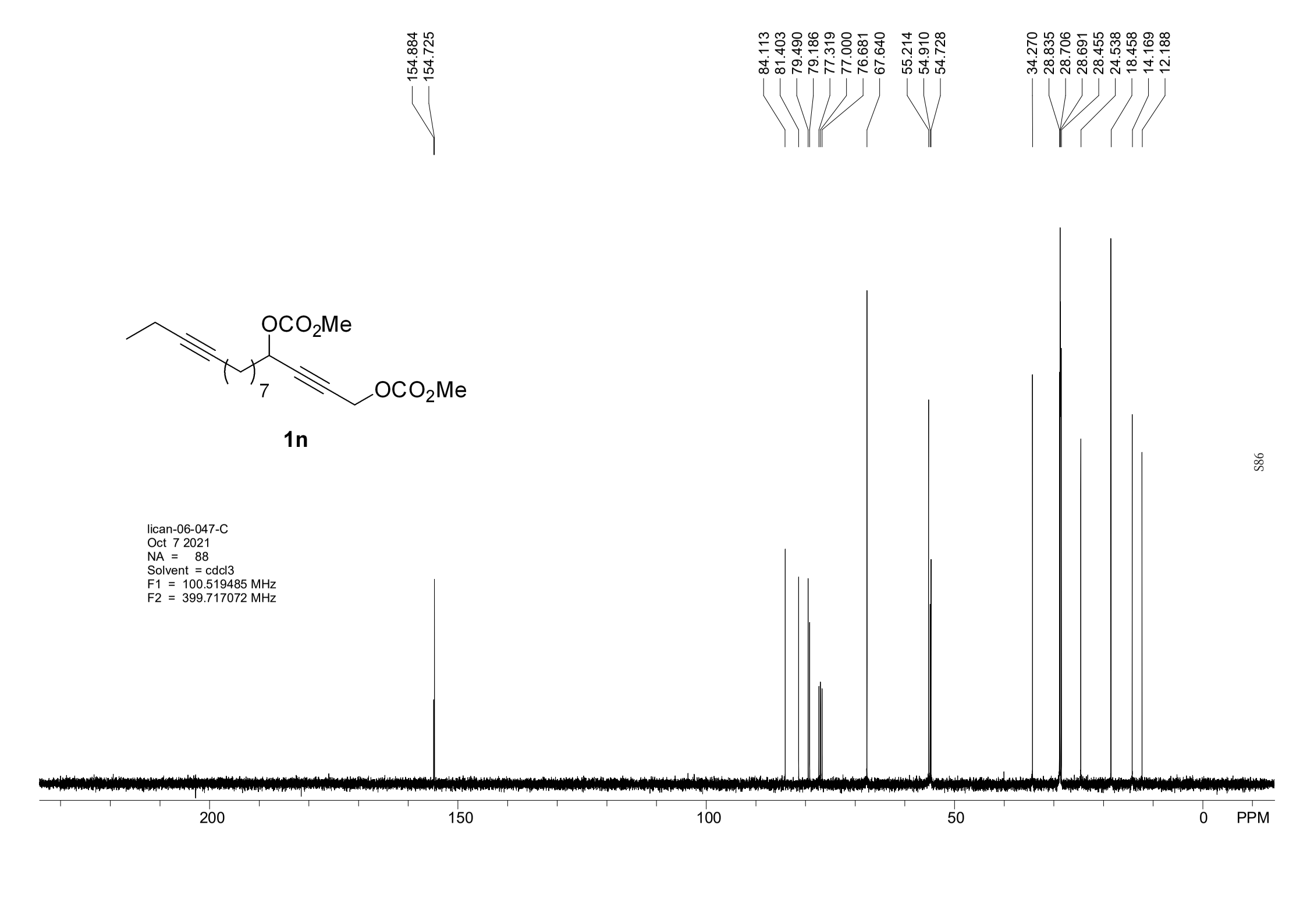

5.264
5.248
5.231
4.775
4.771
3.810
3.801
1.840
1.823
1.807
1.790
1.773
1.460
1.443
1.425
1.406
1.303
1.290
1.277
0.898
0.883
0.865
0.000
OCO2Me
OCO2Me
1l
zzn-1-060-H
Sep 21 2021
NA = 8
Solvent = CDCl3
F1 = 399.717865 MHz
F2 = 100.517960 MHz
1.00
2.01
5.90
2.09
2.11
8.11
3.06
S81
8
6
4
2
0
PPM

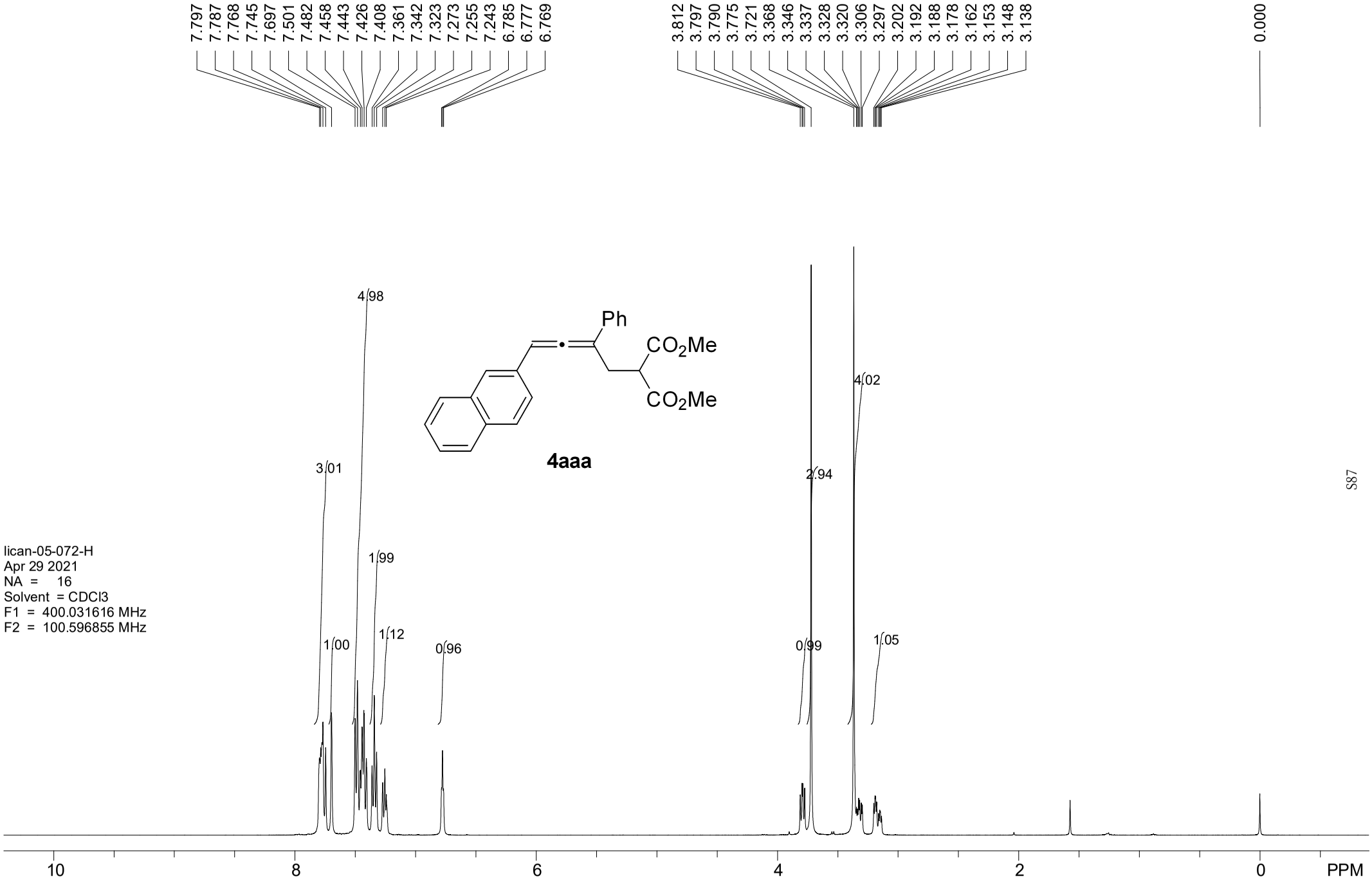

zzn-1-060-C
Sep 22 2021
NA = 100
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
1l
OCO2Me
OCO2Me
154.915
154.758
84.157
79.469
77.319
77.000
76.681
67.696
55.250
54.927
54.745
34.314
31.518
28.872
28.807
24.615
22.420
13.851
200
150
100
50
0
PPM

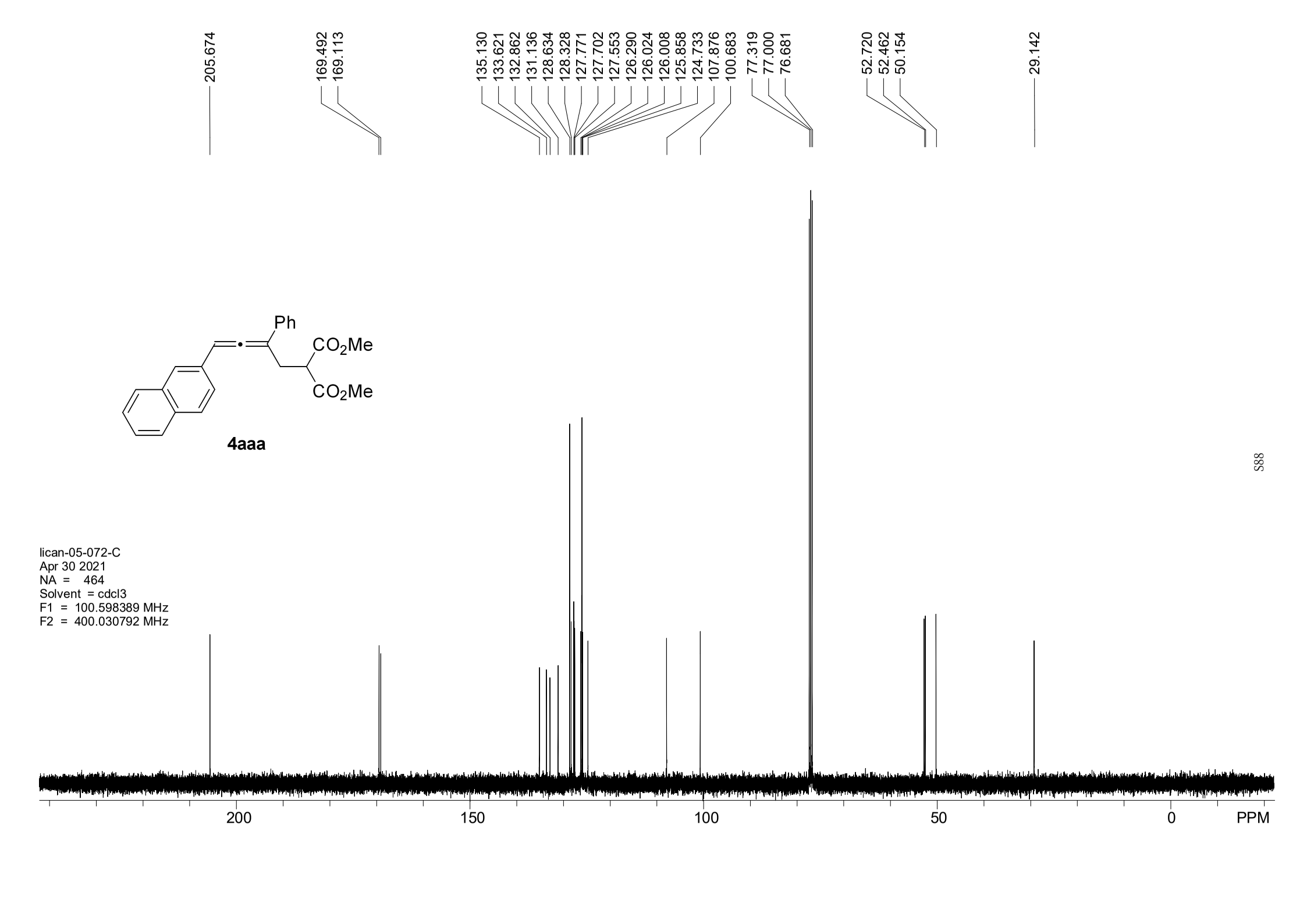

5.097
5.085
4.780
3.815
3.804
1.856
1.821
1.782
1.747
1.722
1.688
1.660
1.260
1.231
1.225
1.195
1.168
1.138
1.132
1.115
1.085
-0.000
OCO2Me
OCO2Me
1m
zzn-1-076-H
Oct 16 2021
NA = 4
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
S83
0.96
2.00
5.78
6.41
5.19
10
8
6
4
2
0
PPM

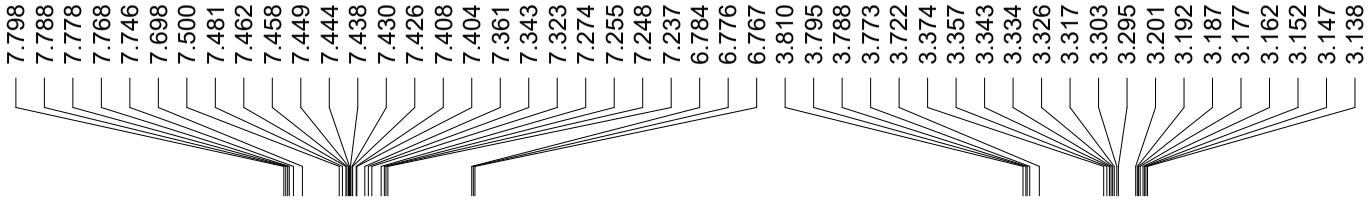

zzn-1-076-C
Oct 16 2021
NA = 88
Solvent = cdcl3
F1 = 100.519485 MHz
F2 = 399.717072 MHz
OCO2Me
OCO2Me
1m
155.036
83.339
80.257
77.319
77.000
76.681
72.119
55.449
55.062
54.887
41.664
28.220
27.909
25.981
25.563
25.518
200
150
100
50
0 PPM

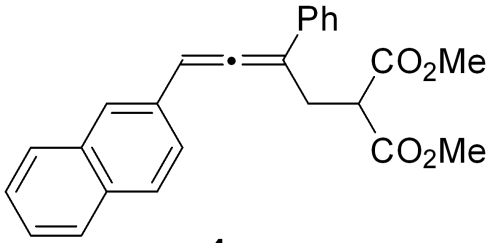

5.261
5.245
5.228
4.772
3.812
3.801
2.179
2.160
2.142
2.127
2.111
1.855
1.839
1.821
1.806
1.790
1.772
1.756
1.481
1.464
1.447
1.430
1.407
1.386
1.364
1.348
1.322
1.126
1.109
1.090
0.000
OCO2Me
7
OCO2Me
1n
lican-06-047-H
Oct 7 2021
NA = 8
Solvent = CDCl3
F1 = 399.717865 MHz
F2 = 100.517960 MHz
1.00
2.03
5.91
4.02
2.03
4.17
5.99
2.85
S85
8
6
4
2
0
PPM


154.884
154.725
84.113
81.403
79.490
79.186
77.319
77.000
76.681
67.640
55.214
54.910
54.728
34.270
28.835
28.706
28.691
28.455
24.538
18.458
14.169
12.188
OCO2Me
7
OCO2Me
1n
lican-06-047-C
Oct 7 2021
NA = 88
Solvent = cdcl3
F1 = 100.519485 MHz
F2 = 399.717072 MHz
200
150
100
50
0
PPM

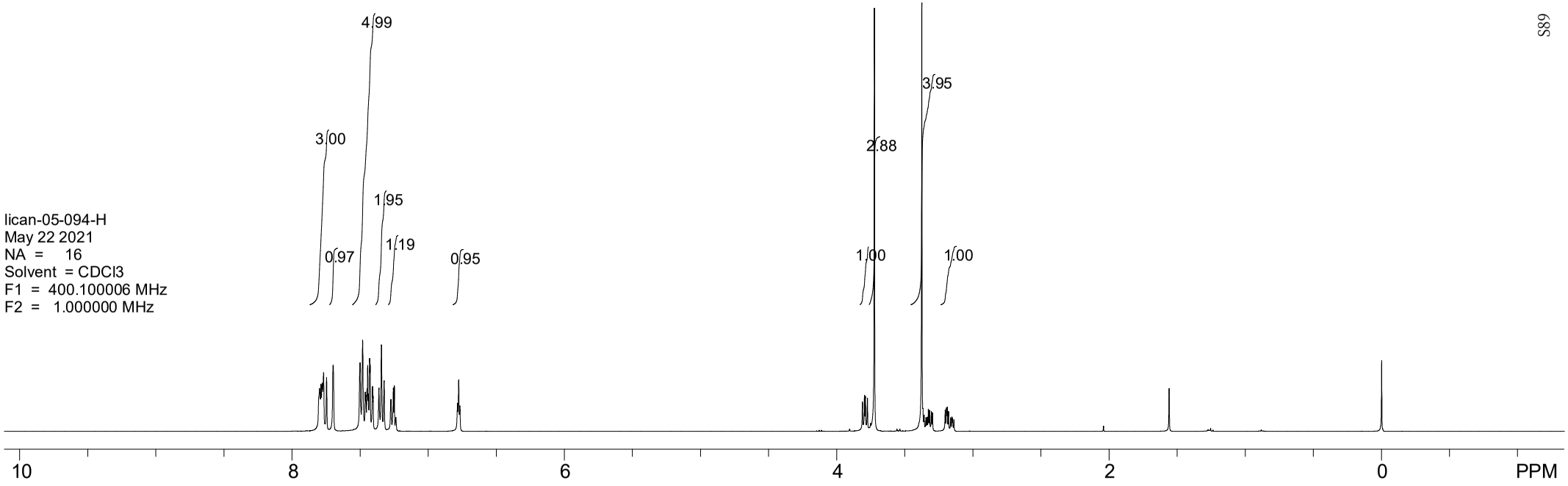

7.797
7.787
7.768
7.745
7.697
7.501
7.482
7.458
7.443
7.426
7.408
7.361
7.342
7.323
7.273
7.255
7.243
6.785
6.777
6.769
3.812
3.797
3.790
3.775
3.721
3.368
3.346
3.337
3.328
3.320
3.306
3.297
3.202
3.192
3.188
3.178
3.162
3.153
3.148
3.138
0.000
Ph
CO2Me
CO2Me
4aaa
4.98
3.01
1.99
1.00
1.12
0.96
2.94
4.02
0.99
1.05
lican-05-072-H
Apr 29 2021
NA = 16
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
10
8
6
4
2
0
PPM

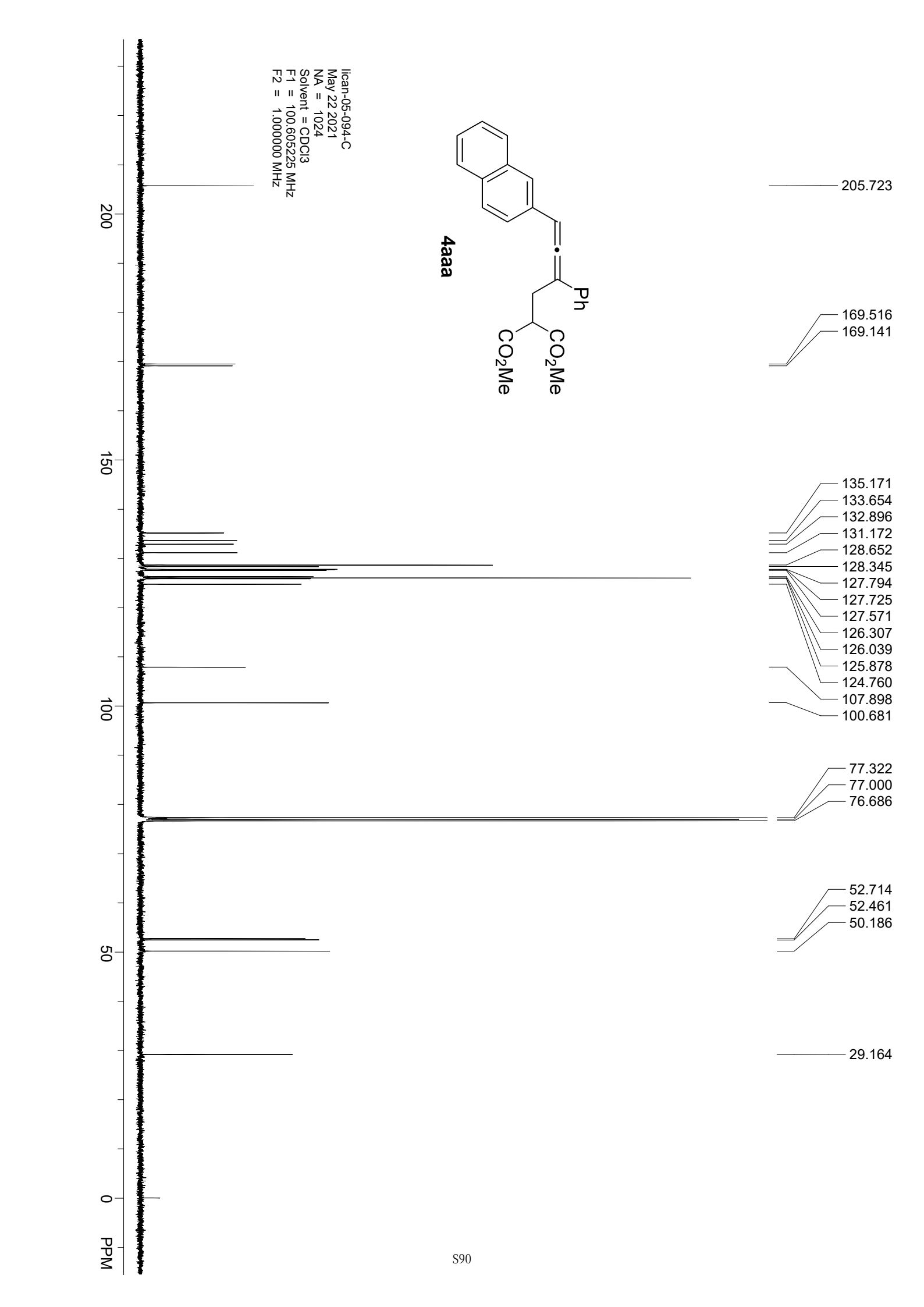

205.674
169.492
169.113
135.130
133.621
132.862
131.136
128.634
128.328
127.771
127.702
127.553
126.290
126.024
126.008
125.858
124.733
107.876
100.683
77.319
77.000
76.681
52.720
52.462
50.154
29.142
Ph
CO2Me
CO2Me
4aaa
S88
lican-05-072-C
Apr 30 2021
NA = 464
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
200
150
100
50
0
PPM

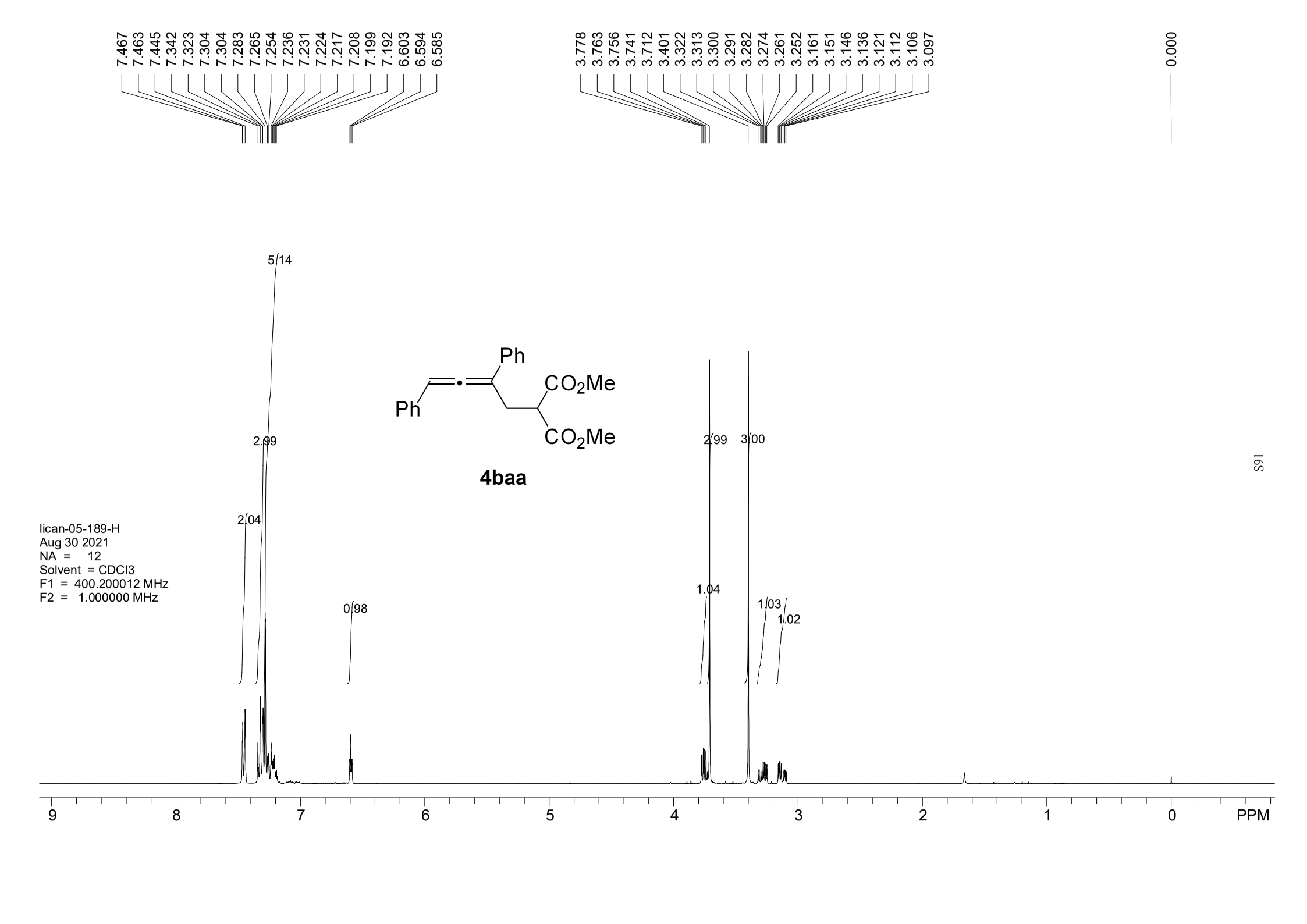

7.798
7.788
7.778
7.768
7.746
7.698
7.500
7.481
7.462
7.458
7.449
7.444
7.438
7.430
7.426
7.408
7.404
7.361
7.343
7.323
7.274
7.255
7.248
7.237
6.784
6.776
6.767
3.810
3.795
3.788
3.773
3.722
3.374
3.357
3.343
3.334
3.326
3.317
3.303
3.295
3.201
3.192
3.187
3.177
3.162
3.152
3.147
3.138
-0.000

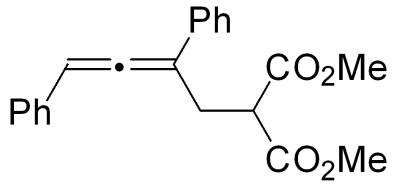

Ph
CO2Me
CO2Me

4aaa


S89
lican-05-094-H
May 22 2021
NA = 16
Solvent = CDCl3
F1 = 400.100006 MHz
F2 = 1.000000 MHz
3.00
4.99
1.95
1.19
0.97
0.95
2.88
3.95
1.00
1.00
10
8
6
4
2
0
PPM

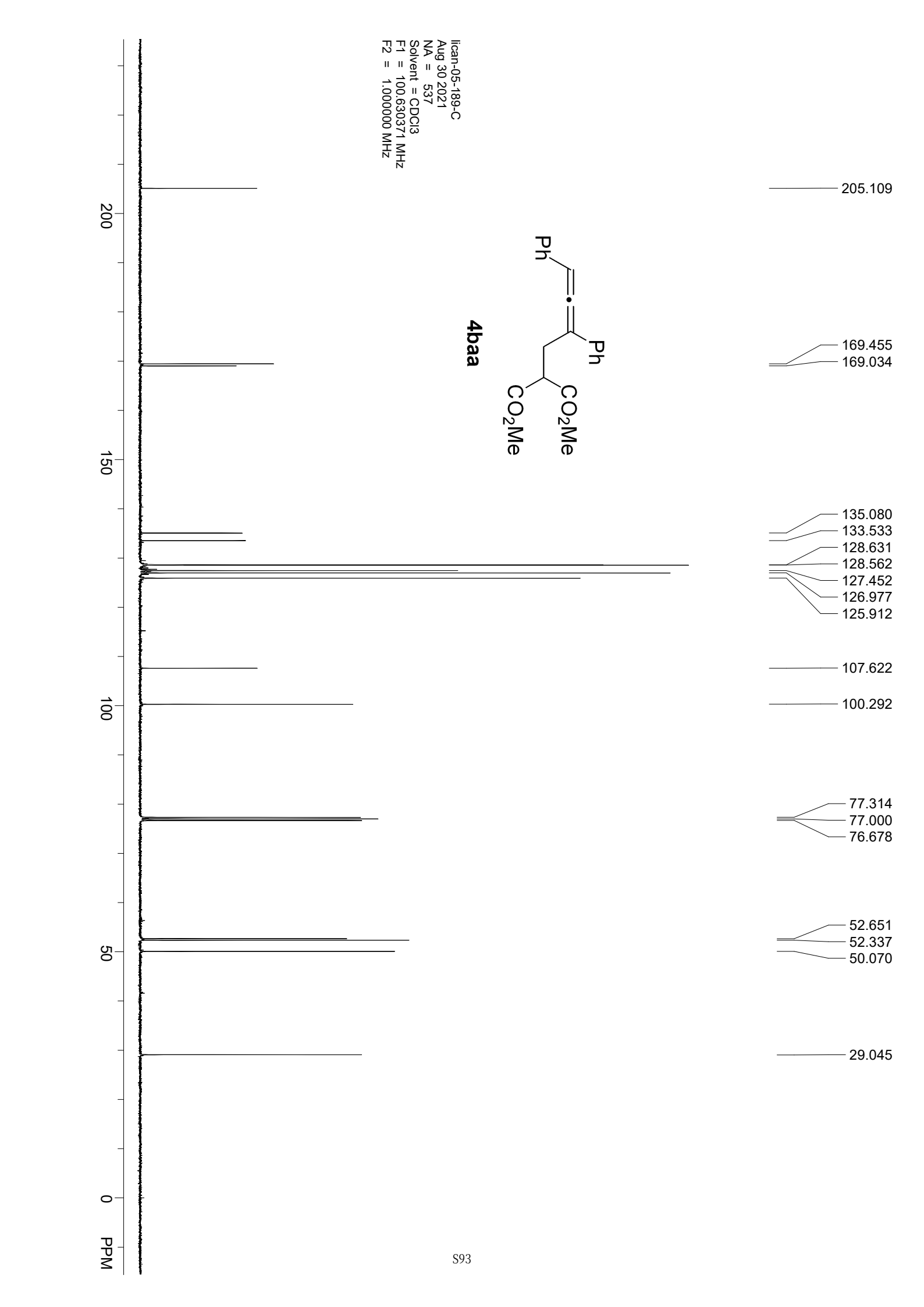

lican-05-094-C
May 22 2021
NA = 1024
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
4aaa
Ph
CO2Me
CO2Me
205.723
169.516
169.141
135.171
133.654
132.896
131.172
128.652
128.345
127.794
127.725
127.571
126.307
126.039
125.878
124.760
107.898
100.681
77.322
77.000
76.686
52.714
52.461
50.186
29.164
200
150
100
50
0
PPM

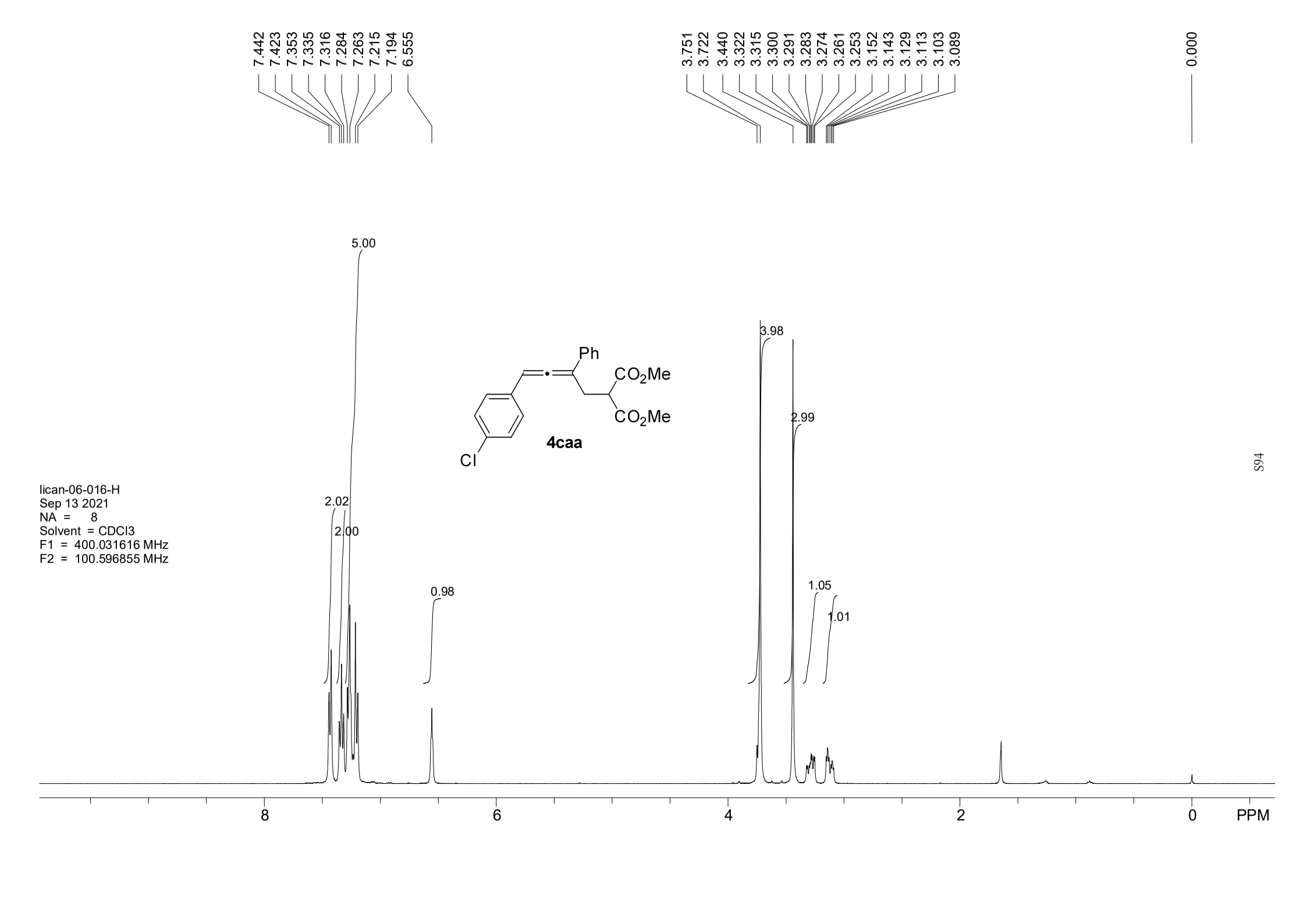

7.467
7.463
7.445
7.342
7.323
7.304
7.304
7.283
7.265
7.254
7.236
7.231
7.224
7.217
7.208
7.199
7.192
6.603
6.594
6.585
3.778
3.763
3.756
3.741
3.712
3.401
3.322
3.313
3.300
3.291
3.282
3.274
3.261
3.252
3.161
3.151
3.146
3.136
3.121
3.112
3.106
3.097
0.000
5.14
2.99
2.04
0.98
2.99
3.00
1.04
1.03
1.02
Ph
Ph
CO2Me
CO2Me
4baa
lican-05-189-H
Aug 30 2021
NA = 12
Solvent = CDCl3
F1 = 400.200012 MHz
F2 = 1.000000 MHz
9
8
7
6
5
4
3
2
1
0
PPM

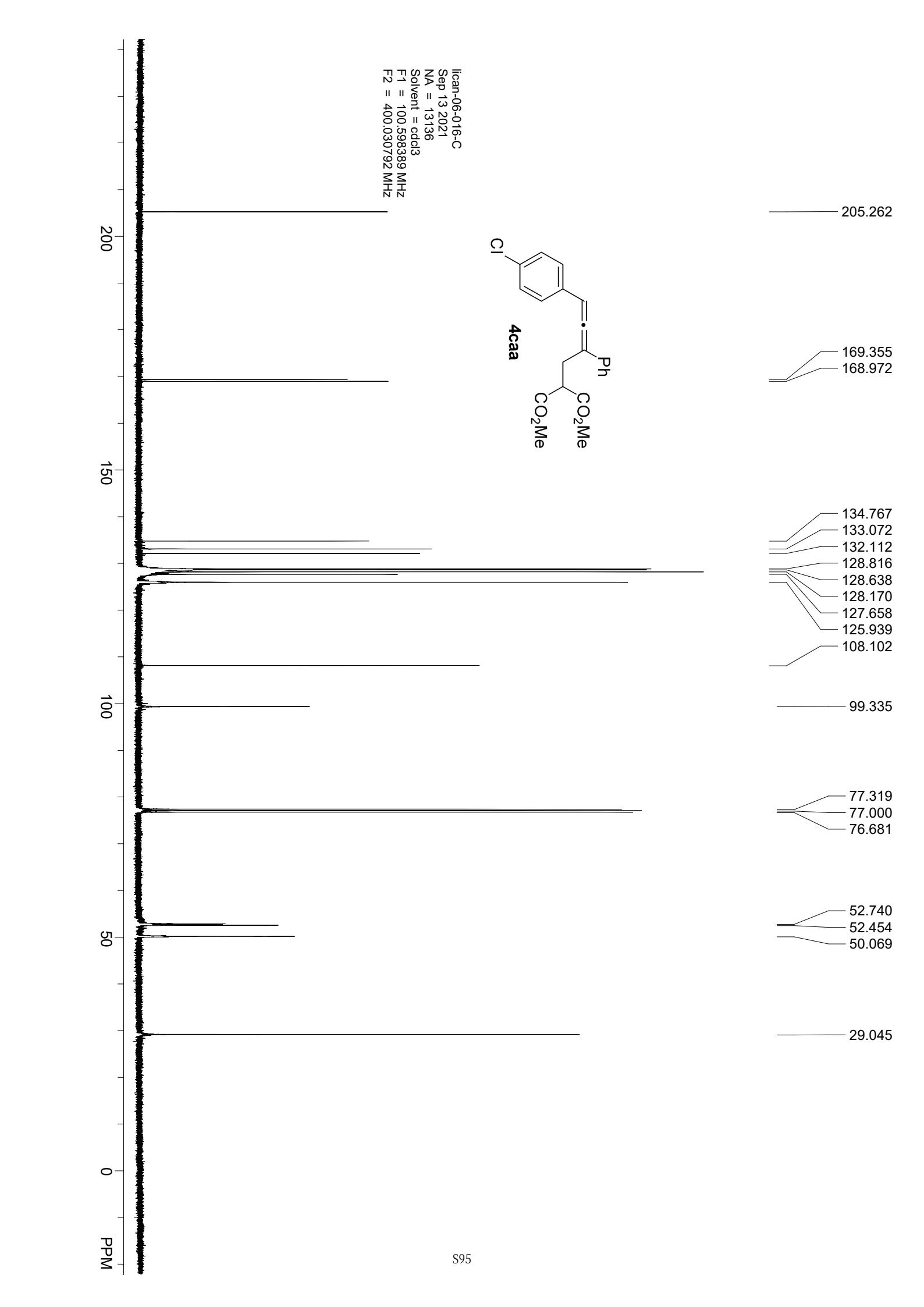


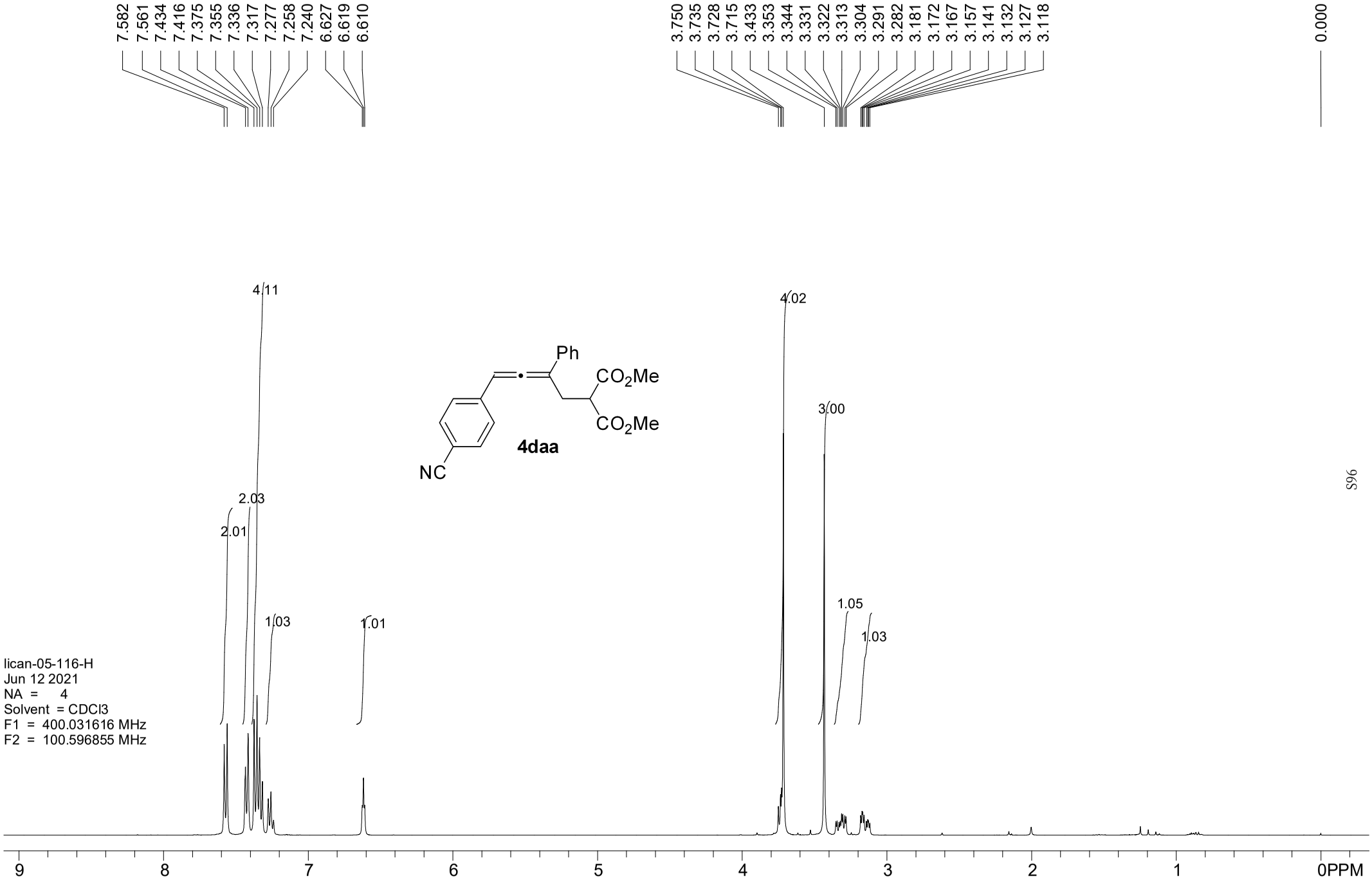
4baa

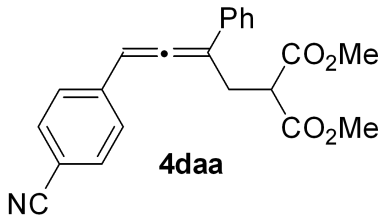
lican-05-189-H-purity
purity = 95%
48.9 mg product with 35 uL dibromomethane
NA = 6
Solvent = CDCl3
F1 = 400.200012 MHz
F2 = 1.000000 MHz


lican-05-189-C
Aug 30 2021
NA = 537
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
4baa
Ph
Ph
CO2Me
CO2Me
205.109
169.455
169.034
135.080
133.533
128.631
128.562
127.452
126.977
125.912
107.622
100.292
77.314
77.000
76.678
52.651
52.337
50.070
29.045
200
150
100
50
0
PPM


7.442
7.423
7.353
7.335
7.316
7.284
7.263
7.215
7.194
6.555
3.751
3.722
3.440
3.322
3.315
3.300
3.291
3.283
3.274
3.261
3.253
3.152
3.143
3.129
3.113
3.103
3.089
0.000
5.00
2.02
2.00
0.98
3.98
2.99
1.05
1.01
Ph
CO2Me
CO2Me
Cl
4caa
lican-06-016-H
Sep 13 2021
NA = 8
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
8
6
4
2
0
PPM


lican-06-016-C
Sep 13 2021
NA = 13136
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
Cl
Ph
CO2Me
CO2Me
4caa
205.262
169.355
168.972
134.767
133.072
132.112
128.816
128.638
128.170
127.658
125.939
108.102
99.335
77.319
77.000
76.681
52.740
52.454
50.069
29.045
200
150
100
50
0
PPM


7.582
7.561
7.434
7.416
7.375
7.355
7.336
7.317
7.277
7.258
7.240
6.627
6.619
6.610
3.750
3.735
3.728
3.715
3.433
3.353
3.344
3.331
3.322
3.313
3.304
3.291
3.282
3.181
3.172
3.167
3.157
3.141
3.132
3.127
3.118
0.000
4.11
2.03
2.01
1.03
1.01
4.02
3.00
1.05
1.03
Ph
CO2Me
CO2Me
NC
4daa
lican-05-116-H
Jun 12 2021
NA = 4
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
9
8
7
6
5
4
3
2
1
0PPM



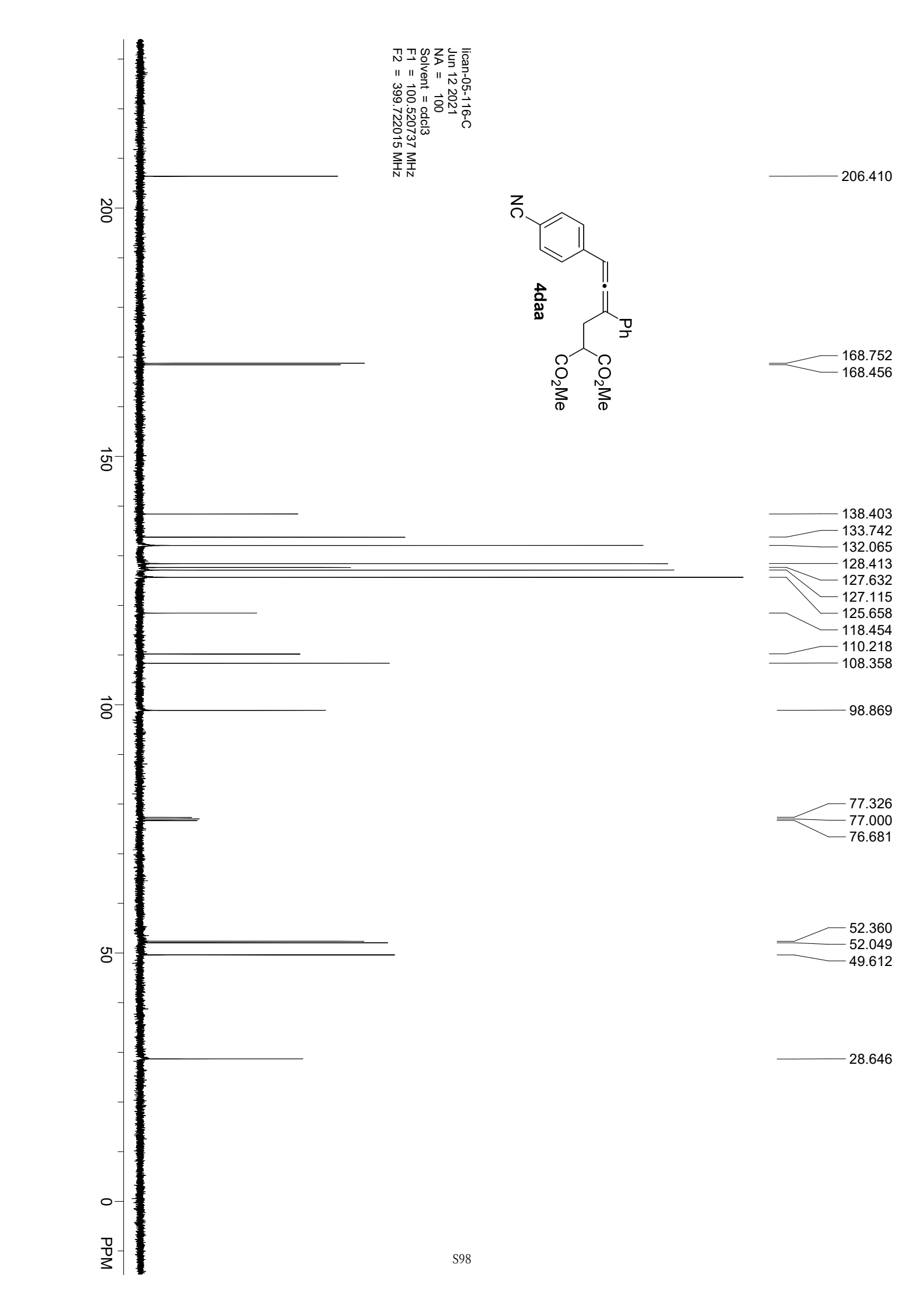
4daa

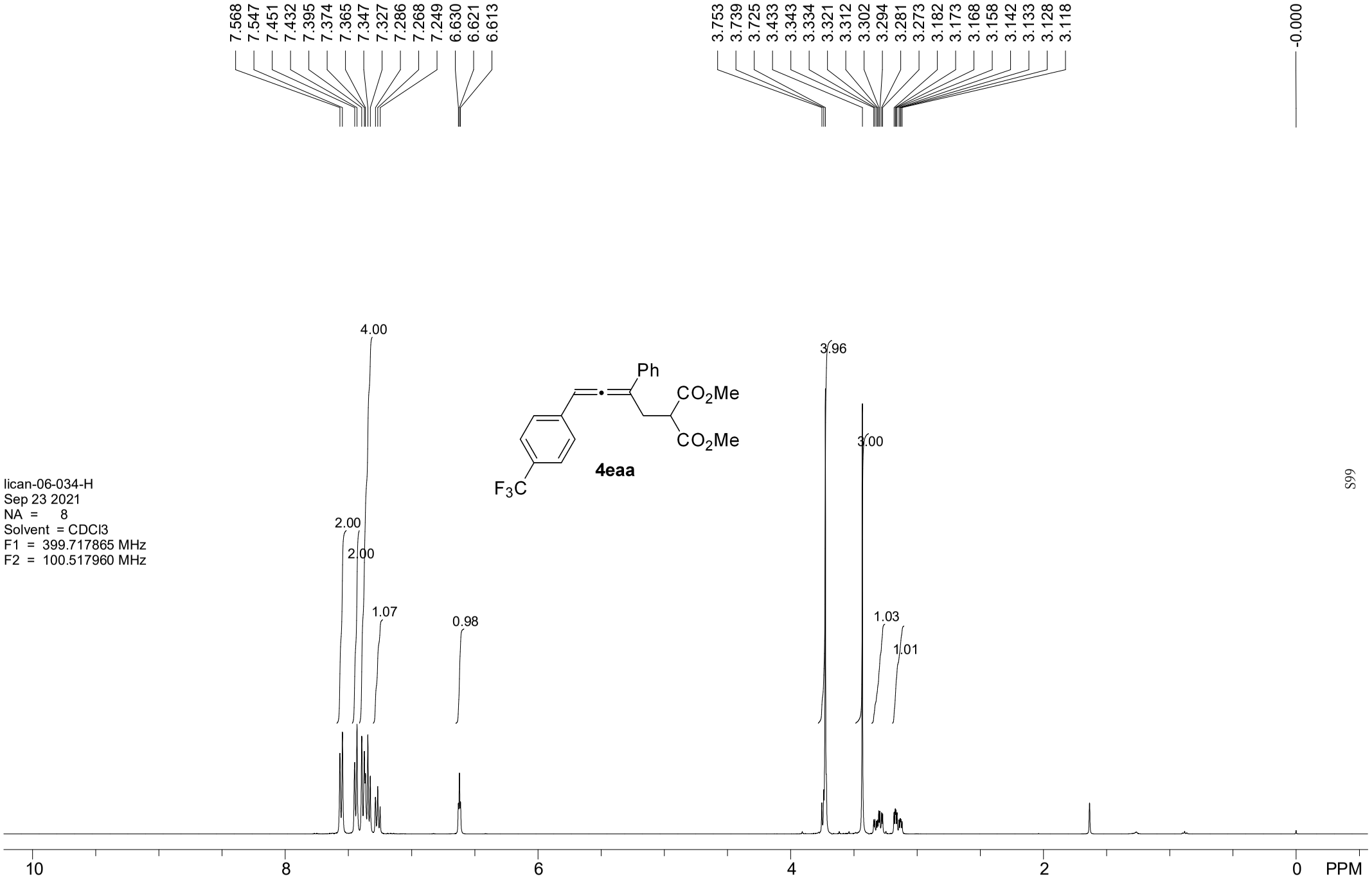
lican-05-116-purity
Jun 12 2021
purity = 95%
187.2 mg product with 35 uL dibromomethane
NA = 4
Solvent = CDCl3
F1 = 399.723236 MHz
F2 = 100.519203 MHz

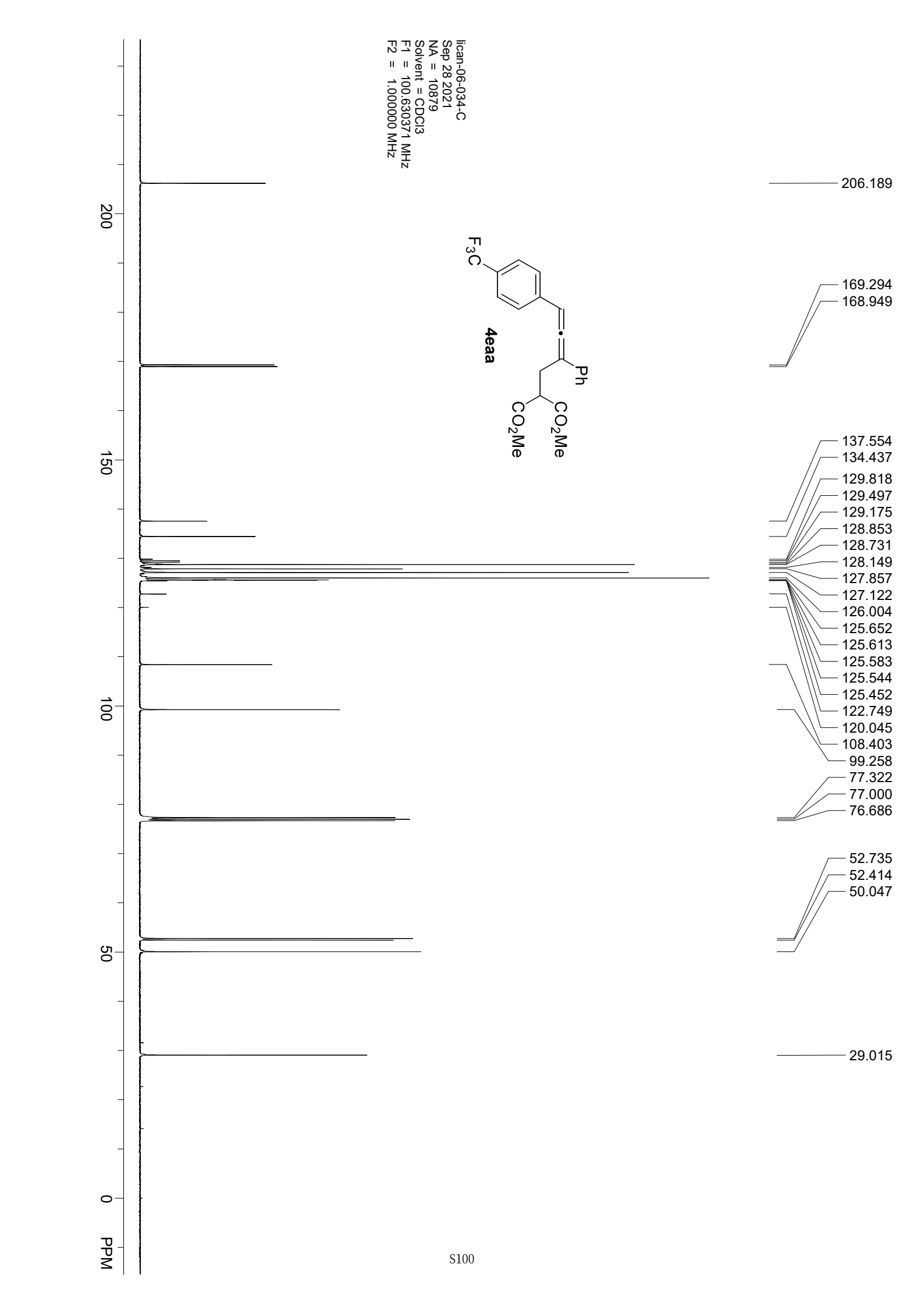
100.00
49.11
48.97

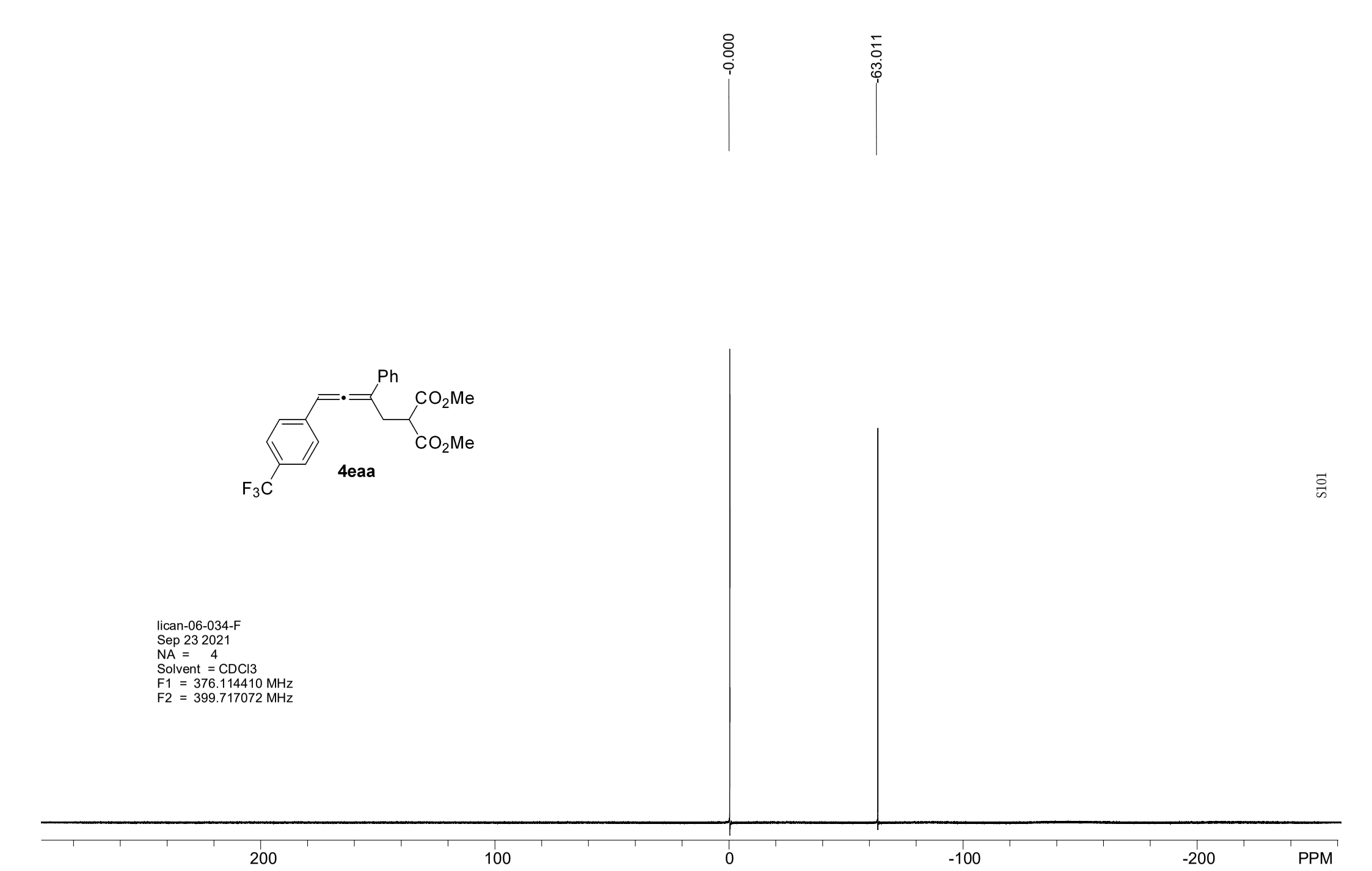
S97

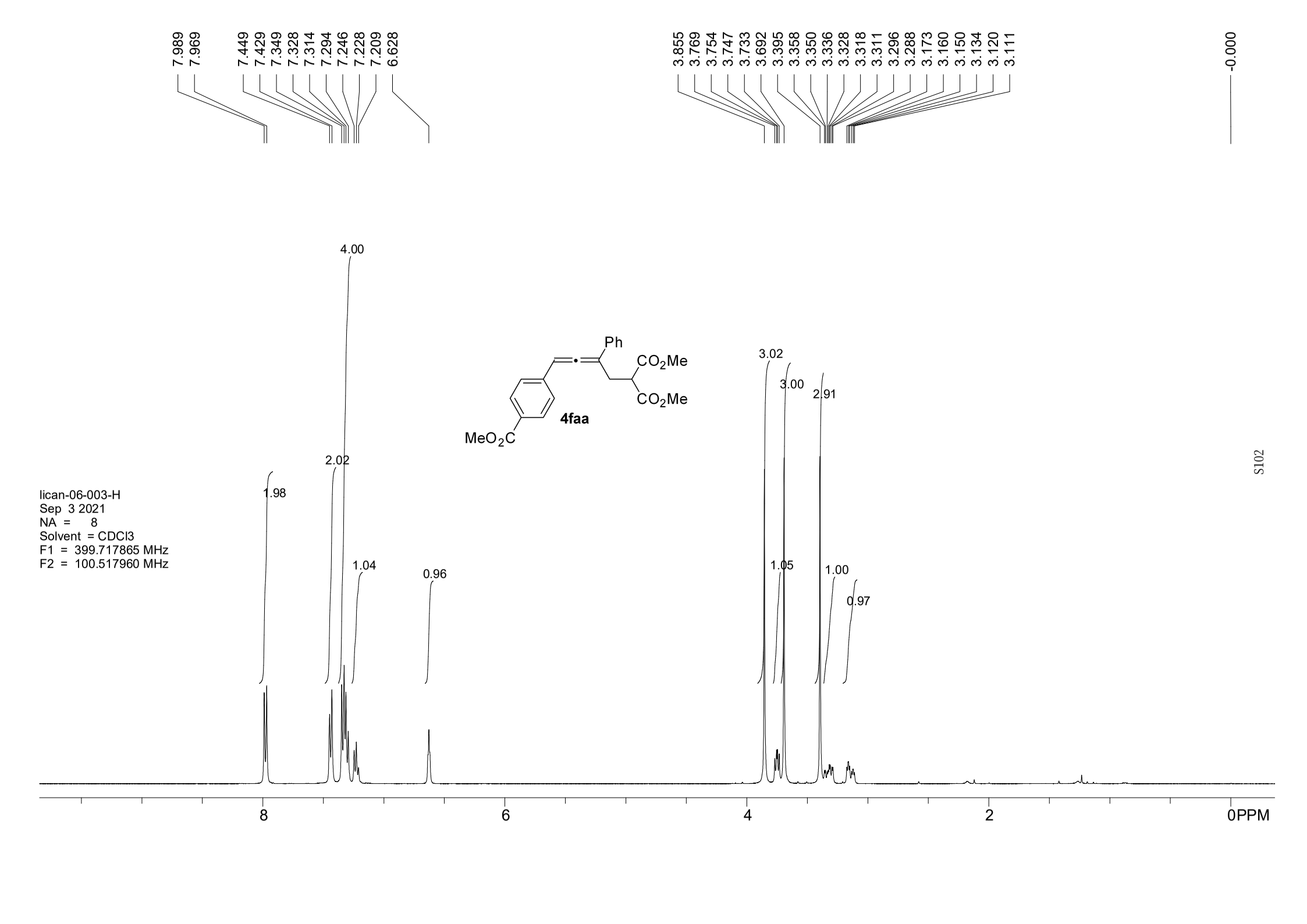
8 7 6 5 4 3 2 1 0 PPM

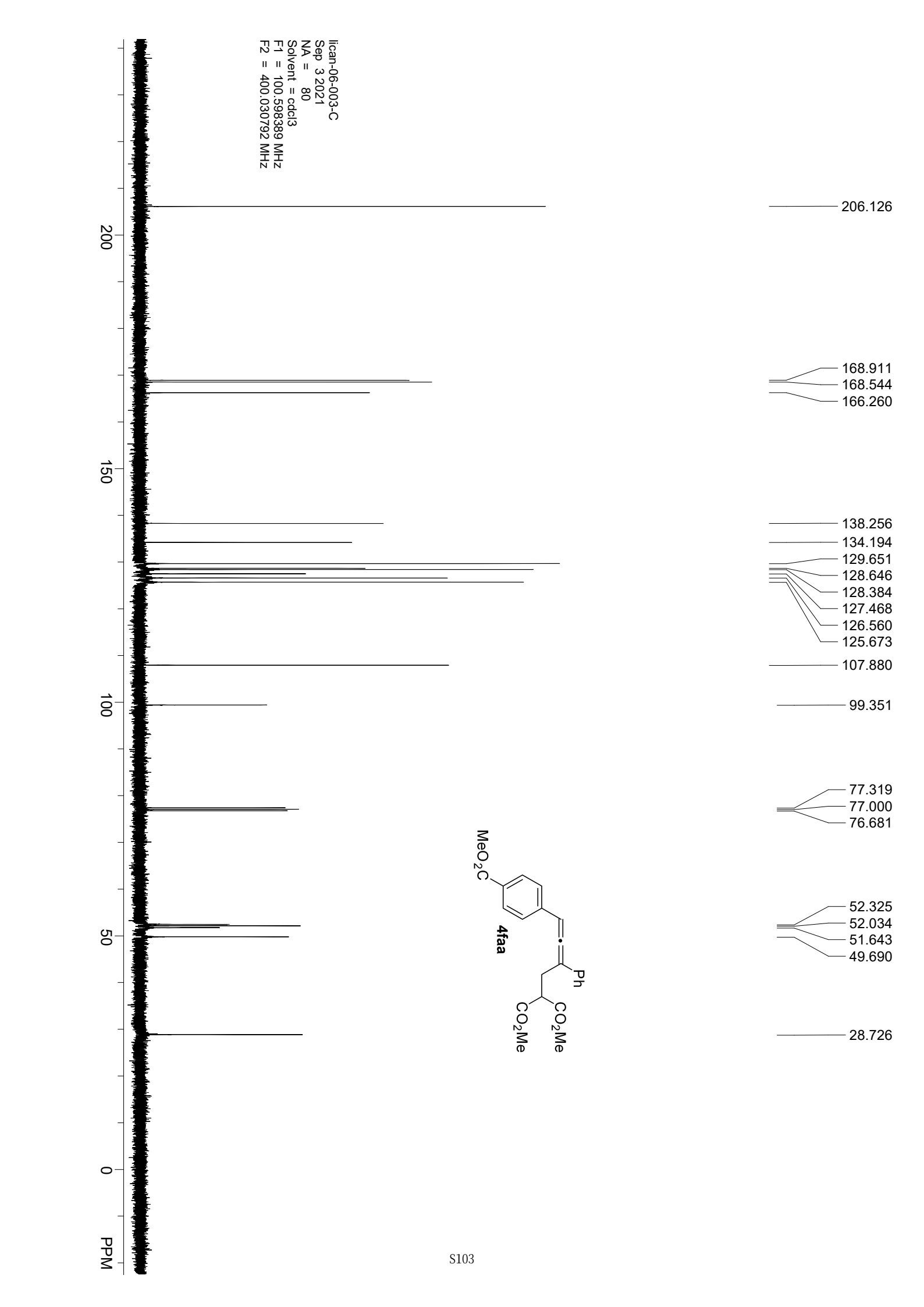

lican-05-116-C
Jun 12 2021
NA = 100
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
NC
Ph
CO2Me
CO2Me
4daa
206.410
168.752
168.456
138.403
133.742
132.065
128.413
127.632
127.115
125.658
118.454
110.218
108.358
98.869
77.326
77.000
76.681
52.360
52.049
49.612
28.646
200
150
100
50
0
PPM

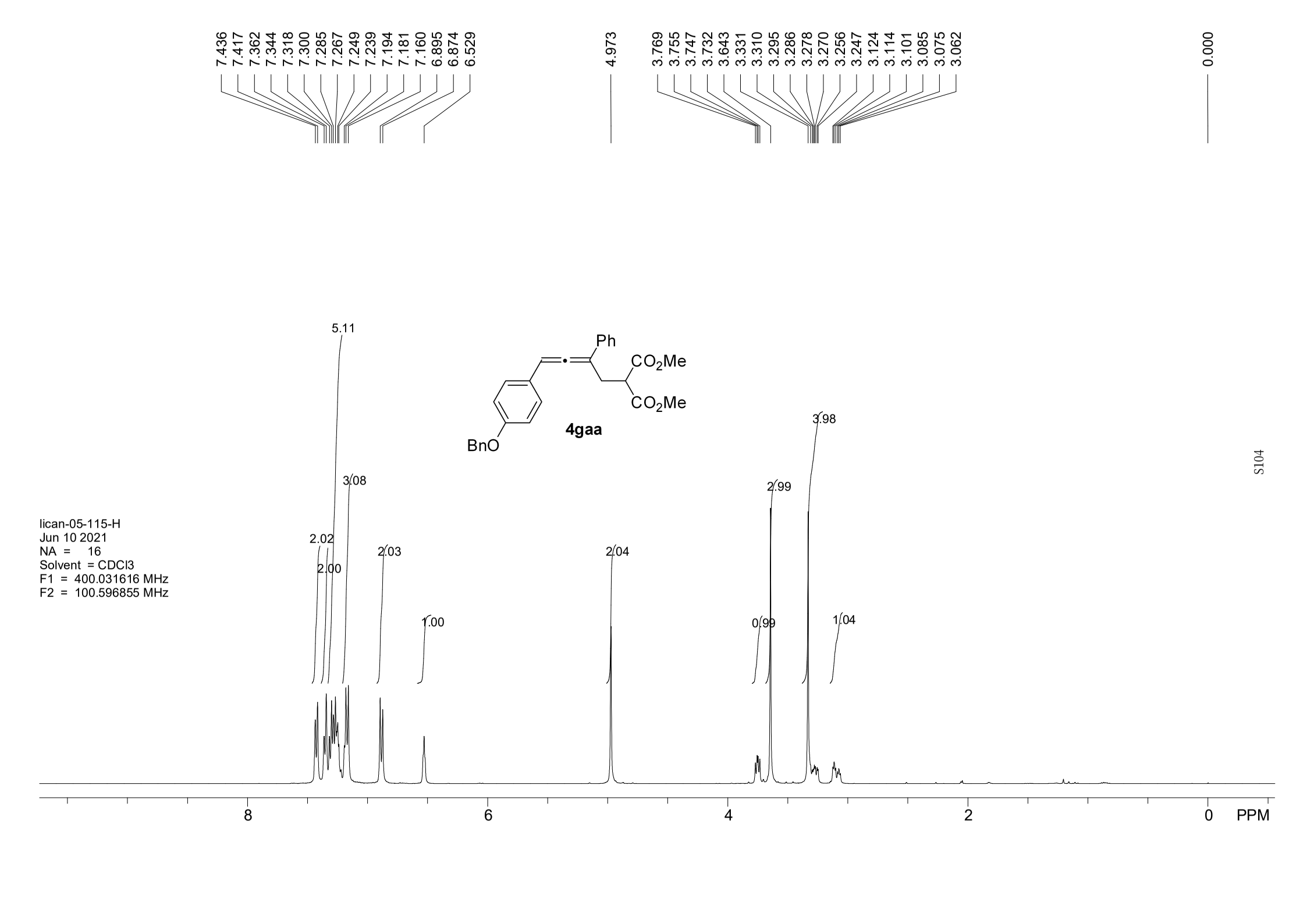

7.568
7.547
7.451
7.432
7.395
7.374
7.365
7.347
7.327
7.286
7.268
7.249
6.630
6.621
6.613
3.753
3.739
3.725
3.433
3.343
3.334
3.321
3.312
3.302
3.294
3.281
3.273
3.182
3.173
3.168
3.158
3.142
3.133
3.128
3.118
-0.000
lican-06-034-H
Sep 23 2021
NA = 8
Solvent = CDCl3
F1 = 399.717865 MHz
F2 = 100.517960 MHz
4.00
2.00
2.00
1.07
0.98
3.96
3.00
1.03
1.01
Ph
CO2Me
CO2Me
F3C
4eaa
S99
10
8
6
4
2
0
PPM

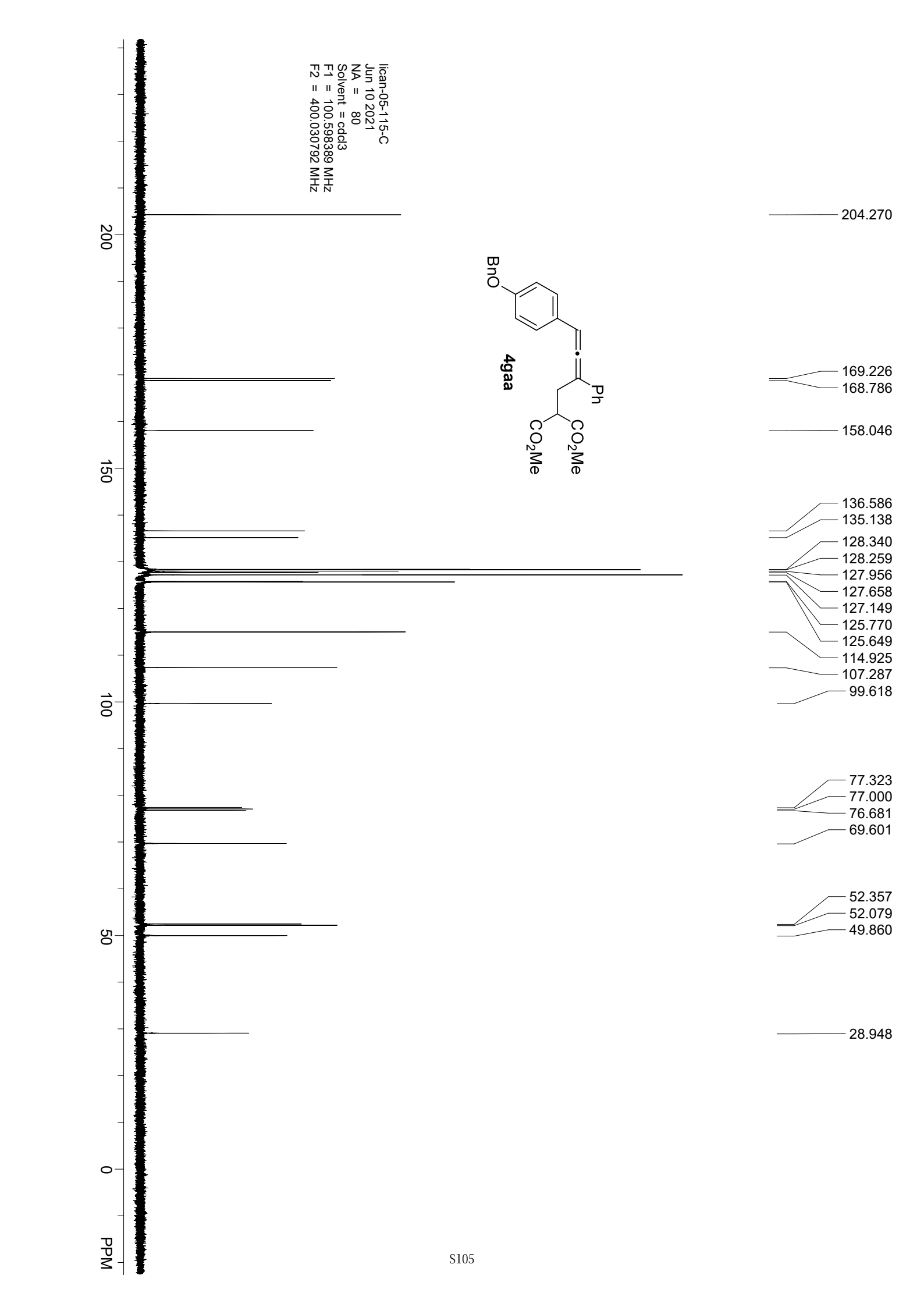

lican-06-034-C
Sep 28 2021
NA = 10879
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
4eaa
206.189
169.294
168.949
137.554
134.437
129.818
129.497
129.175
128.853
128.731
128.149
127.857
127.122
126.004
125.652
125.613
125.583
125.544
125.452
122.749
120.045
108.403
99.258
77.322
77.000
76.686
52.735
52.414
50.047
29.015
200
150
100
50
0
PPM

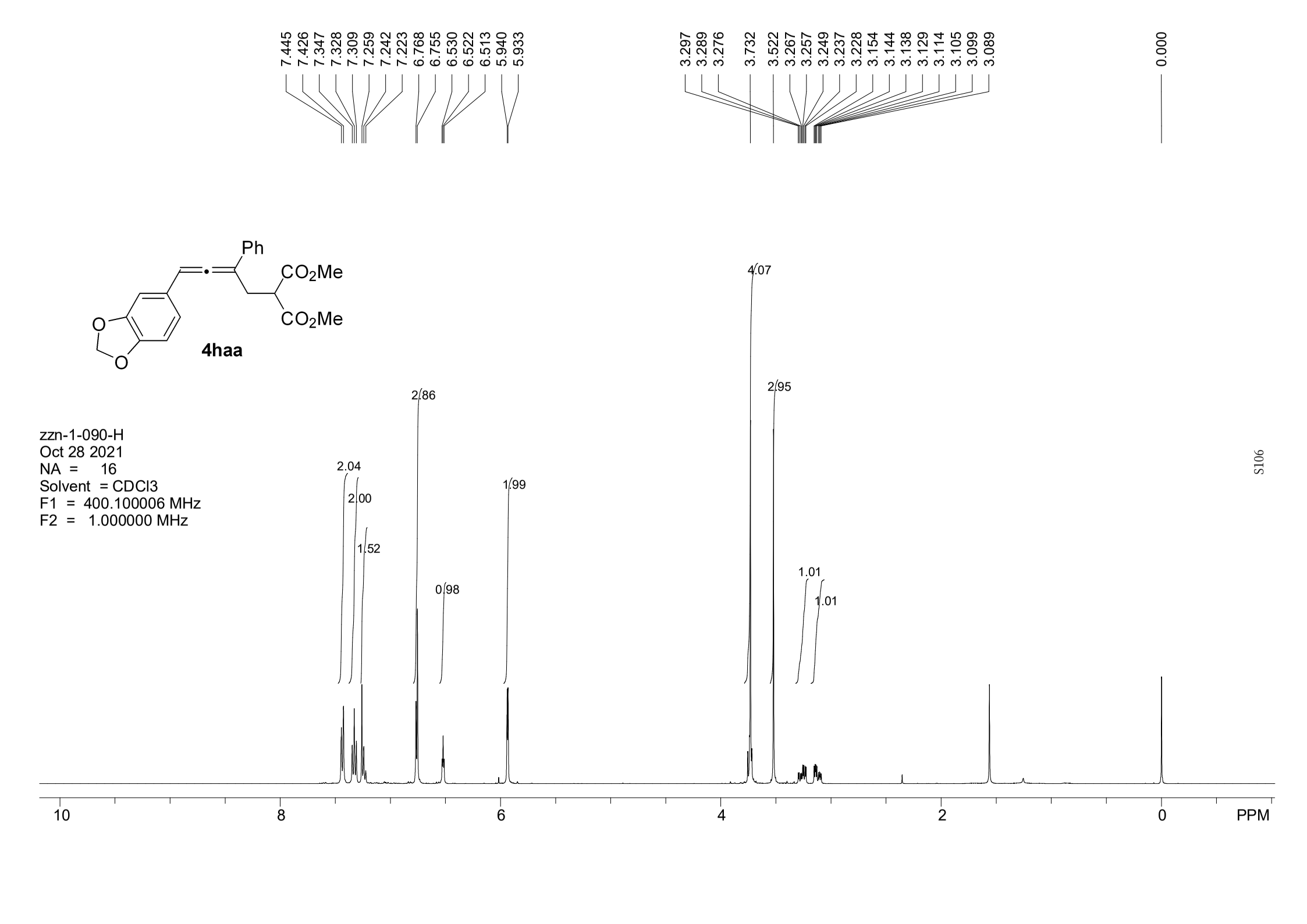

-0.000
-63.011
Ph
CO2Me
CO2Me
F3C
4eaa
lican-06-034-F
Sep 23 2021
NA = 4
Solvent = CDCl3
F1 = 376.114410 MHz
F2 = 399.717072 MHz
200
100
0
-100
-200
PPM

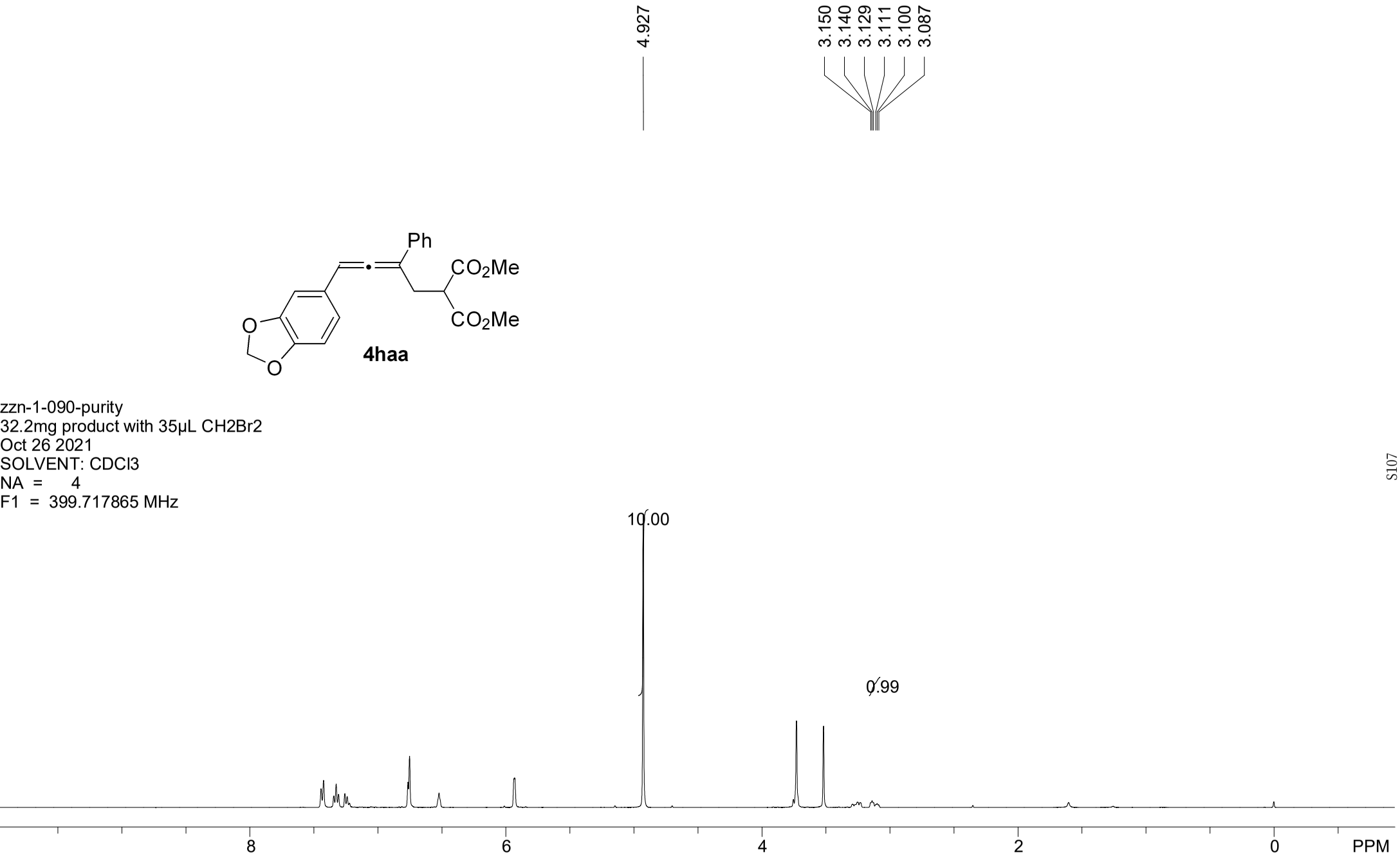

7.989
7.969
7.449
7.429
7.349
7.328
7.314
7.294
7.246
7.228
7.209
6.628
3.855
3.769
3.754
3.747
3.733
3.692
3.395
3.358
3.350
3.336
3.328
3.318
3.311
3.296
3.288
3.173
3.160
3.150
3.134
3.120
3.111
-0.000
Ph
CO2Me
CO2Me
MeO2C
4faa
4.00
2.02
1.98
1.04
0.96
3.02
3.00
2.91
1.05
1.00
0.97
lican-06-003-H
Sep 3 2021
NA = 8
Solvent = CDCl3
F1 = 399.717865 MHz
F2 = 100.517960 MHz
S102
8
6
4
2
0PPM

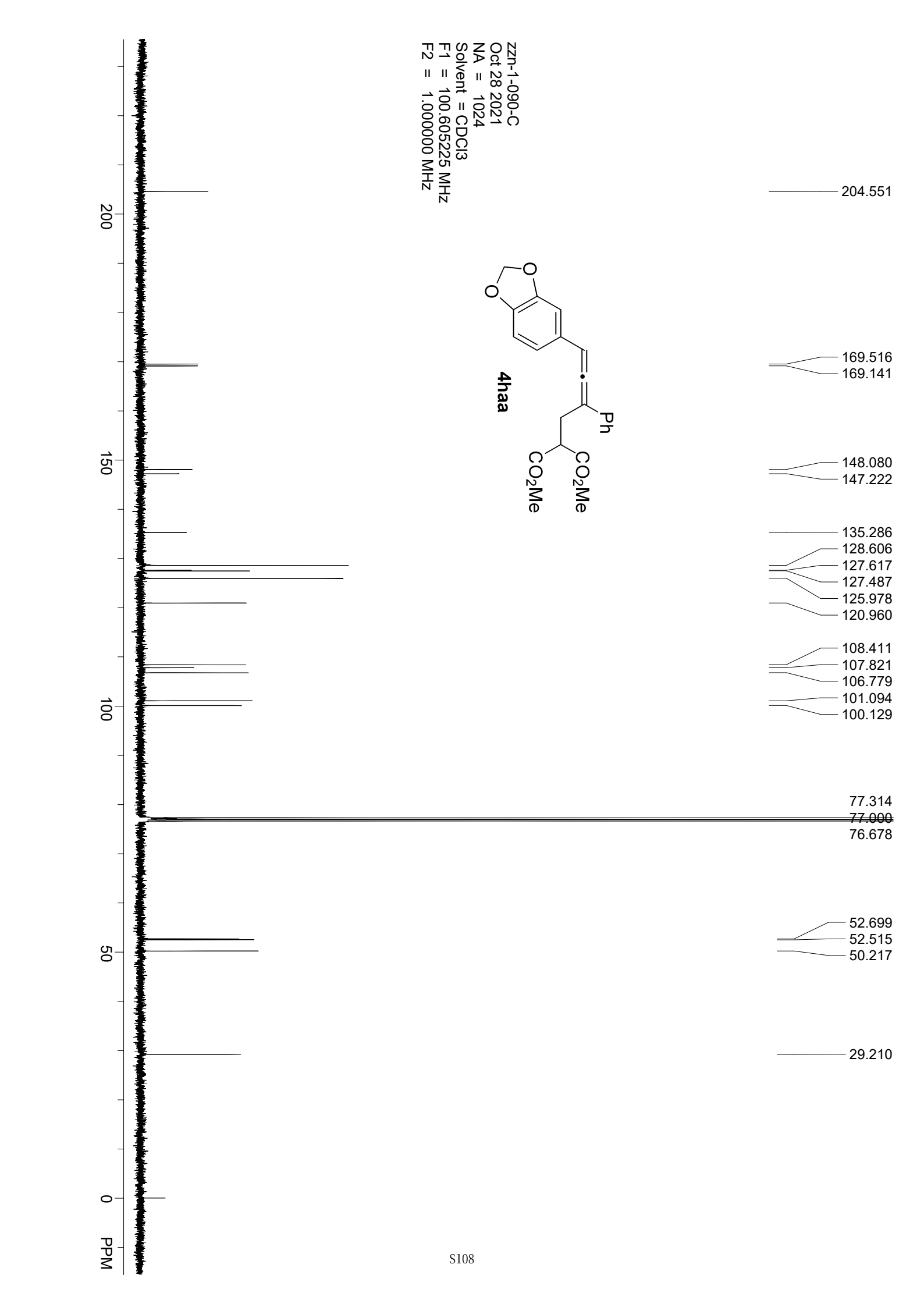

lican-06-003-C
Sep 3 2021
NA = 80
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
206.126
168.911
168.544
166.260
138.256
134.194
129.651
128.646
128.384
127.468
126.560
125.673
107.880
99.351
77.319
77.000
76.681
52.325
52.034
51.643
49.690
28.726
200
150
100
50
0
PPM
MeO2C
4faa
Ph
CO2Me
CO2Me

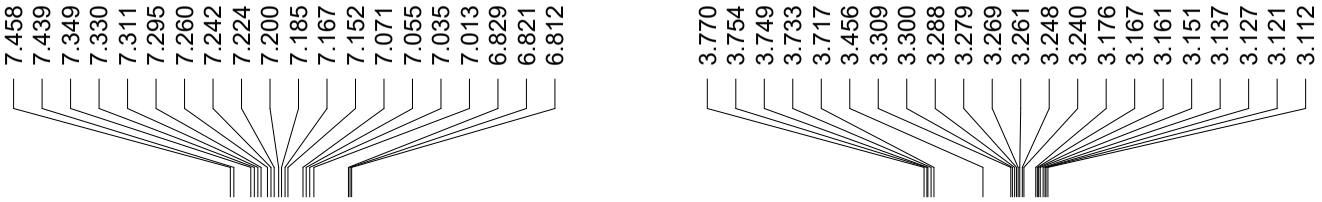

7.436
7.417
7.362
7.344
7.318
7.300
7.285
7.267
7.249
7.239
7.194
7.181
7.160
6.895
6.874
6.529
4.973
3.769
3.755
3.747
3.732
3.643
3.331
3.310
3.295
3.286
3.278
3.270
3.256
3.247
3.124
3.114
3.101
3.085
3.075
3.062
0.000
Ph
CO2Me
CO2Me
BnO
4gaa
5.11
3.08
2.02
2.00
2.03
1.00
2.04
3.98
2.99
0.99
1.04
lican-05-115-H
Jun 10 2021
NA = 16
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
8
6
4
2
0
PPM
S104

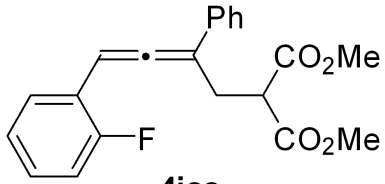

lican-05-115-C
Jun 10 2021
NA = 80
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
BnO
Ph
CO2Me
CO2Me
4gaa
204.270
169.226
168.786
158.046
136.586
135.138
128.340
128.259
127.956
127.658
127.149
125.770
125.649
114.925
107.287
99.618
77.323
77.000
76.681
69.601
52.357
52.079
49.860
28.948
200
150
100
50
0
PPM


7.445
7.426
7.347
7.328
7.309
7.259
7.242
7.223
6.768
6.755
6.530
6.522
6.513
5.940
5.933
3.297
3.289
3.276
3.732
3.522
3.267
3.257
3.249
3.237
3.228
3.154
3.144
3.138
3.129
3.114
3.105
3.099
3.089
0.000
Ph
CO2Me
CO2Me
O
O
O
4haa
zzn-1-090-H
Oct 28 2021
NA = 16
Solvent = CDCl3
F1 = 400.100006 MHz
F2 = 1.000000 MHz
2.04
2.00
1.52
2.86
0.98
1.99
4.07
2.95
1.01
1.01
S106
10
8
6
4
2
0
PPM


4.927
3.150
3.140
3.129
3.111
3.100
3.087
Ph
CO2Me
CO2Me
O
O
4haa
zzn-1-090-purity
32.2mg product with 35μL CH2Br2
Oct 26 2021
SOLVENT: CDCl3
NA = 4
F1 = 399.717865 MHz
10.00
0.99
8
6
4
2
0
PPM

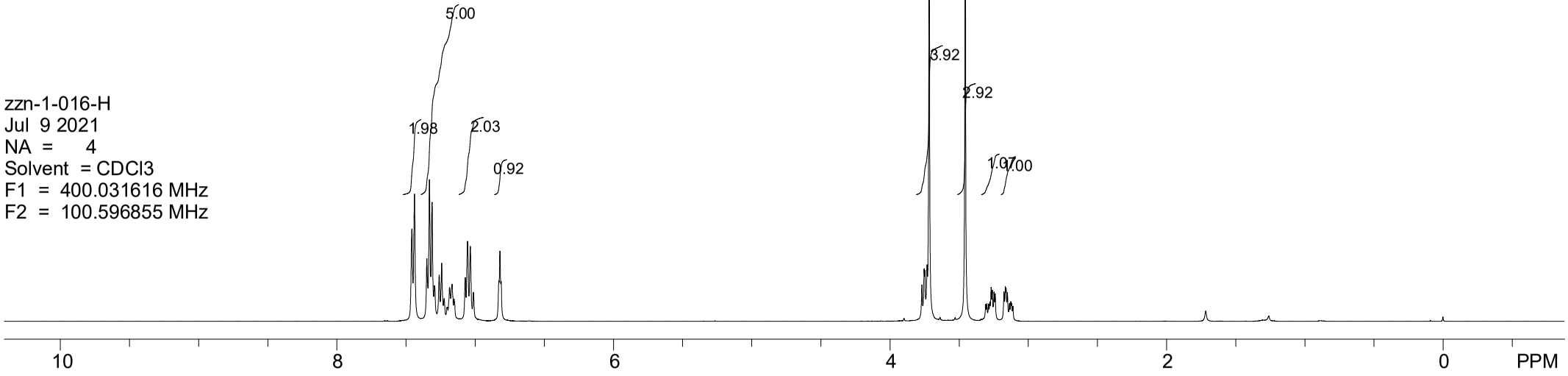

zzn-1-090-C
Oct 28 2021
NA = 1024
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
4haa
Ph
CO2Me
CO2Me
204.551
169.516
169.141
148.080
147.222
135.286
128.606
127.617
127.487
125.978
120.960
108.411
107.821
106.779
101.094
100.129
77.314
77.000
76.678
52.699
52.515
50.217
29.210
200
150
100
50
0
PPM

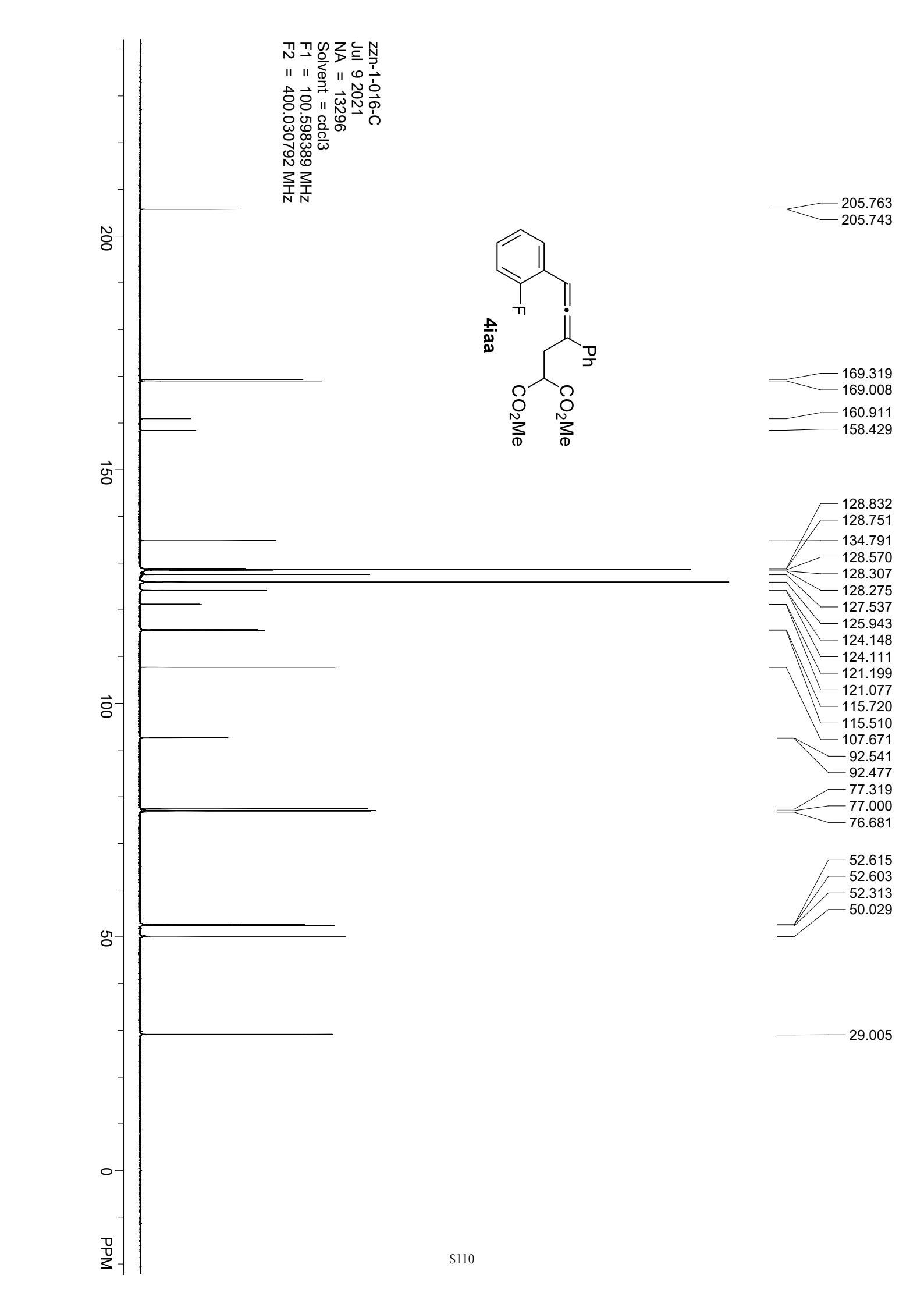


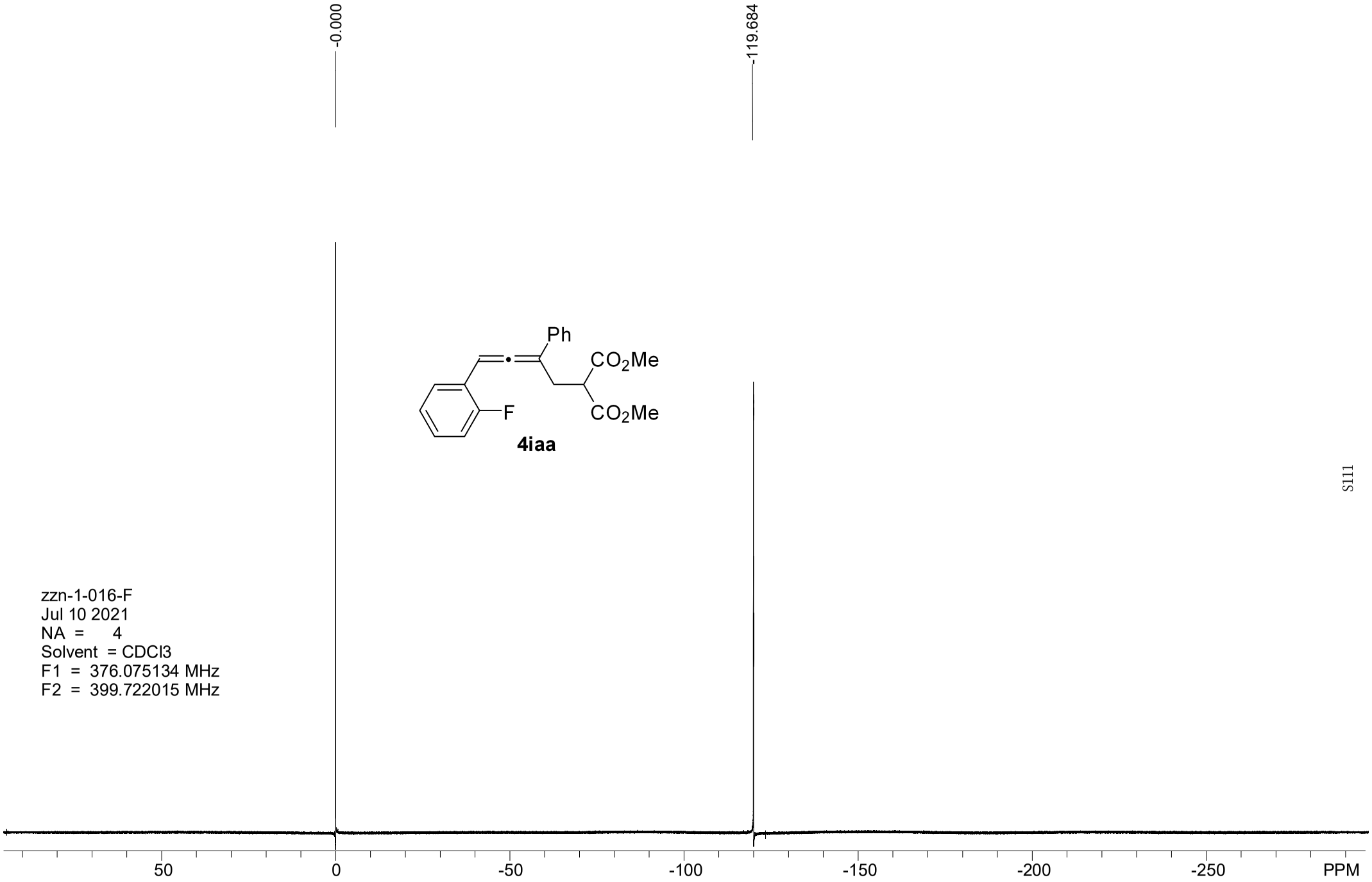


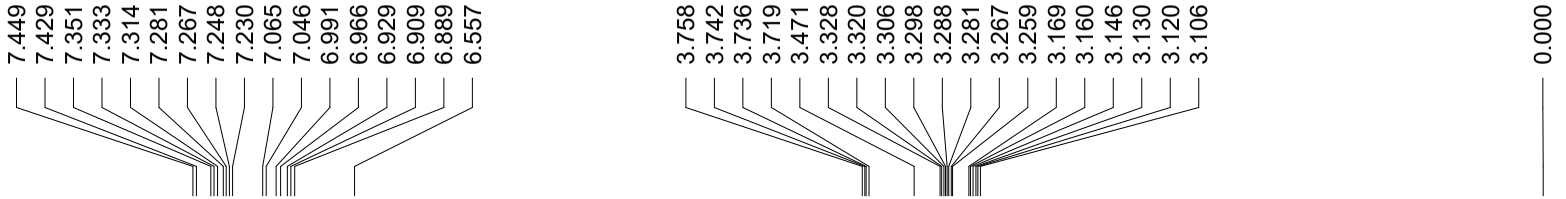
4iaa

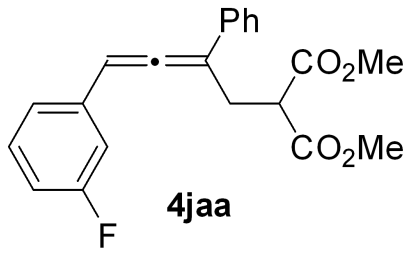
zzn-1-016-H
Jul 9 2021
NA = 4
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz




zzn-1-016-C
Jul 9 2021
NA = 13296
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
4iaa
F
Ph
CO2Me
CO2Me
205.763
205.743
169.319
169.008
160.911
158.429
128.832
128.751
134.791
128.570
128.307
128.275
127.537
125.943
124.148
124.111
121.199
121.077
115.720
115.510
107.671
92.541
92.477
77.319
77.000
76.681
52.615
52.603
52.313
50.029
29.005
200
150
100
50
0
PPM

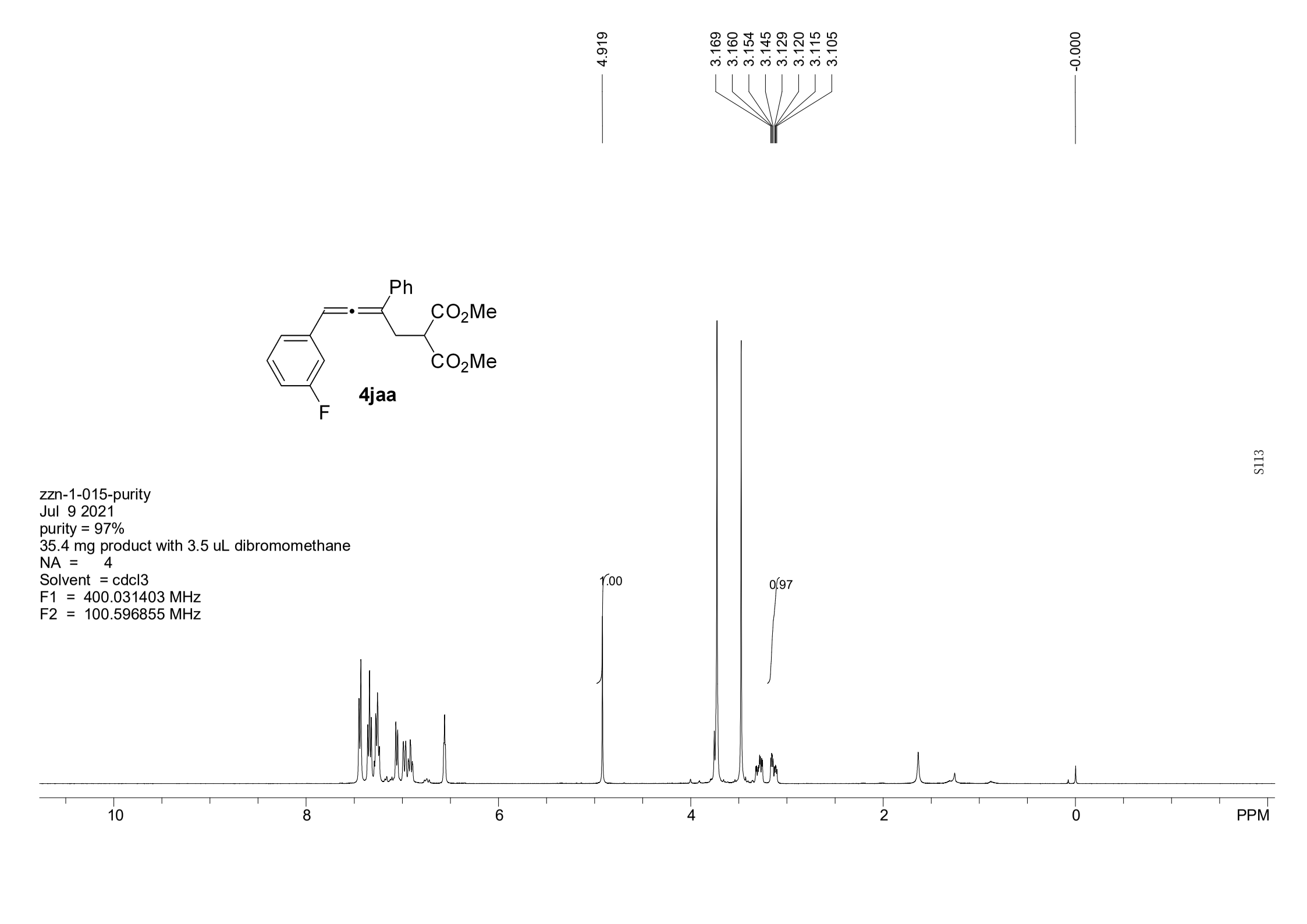

-0.000
-119.684
Ph
CO2Me
CO2Me
F
4iaa
zzn-1-016-F
Jul 10 2021
NA = 4
Solvent = CDCl3
F1 = 376.075134 MHz
F2 = 399.722015 MHz
50
0
-50
-100
-150
-200
-250
PPM

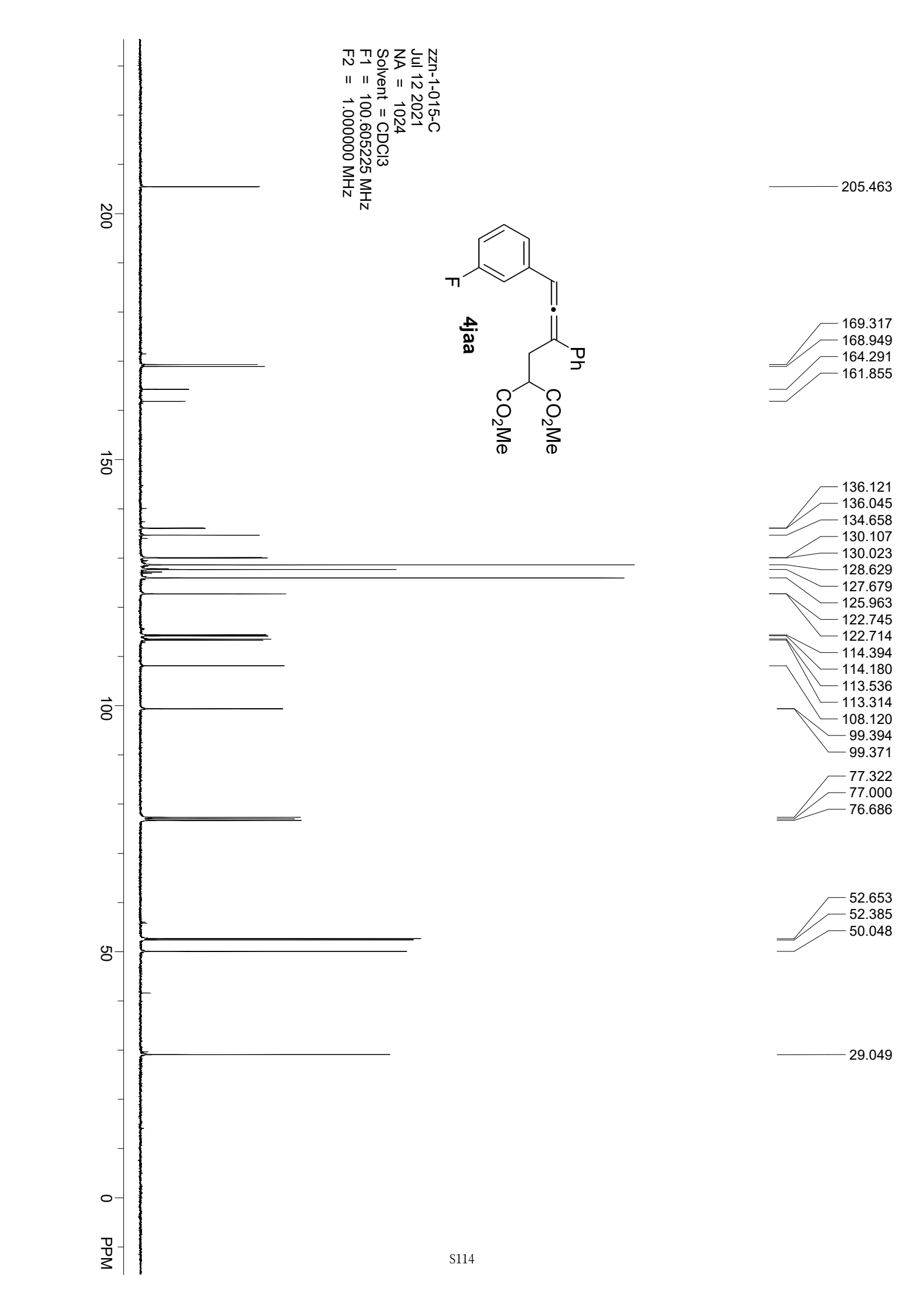

7.449
7.429
7.351
7.333
7.314
7.281
7.267
7.248
7.230
7.065
7.046
6.991
6.966
6.929
6.909
6.889
6.557
3.758
3.742
3.736
3.719
3.471
3.328
3.320
3.306
3.298
3.288
3.281
3.267
3.259
3.169
3.160
3.146
3.130
3.120
3.106
0.000

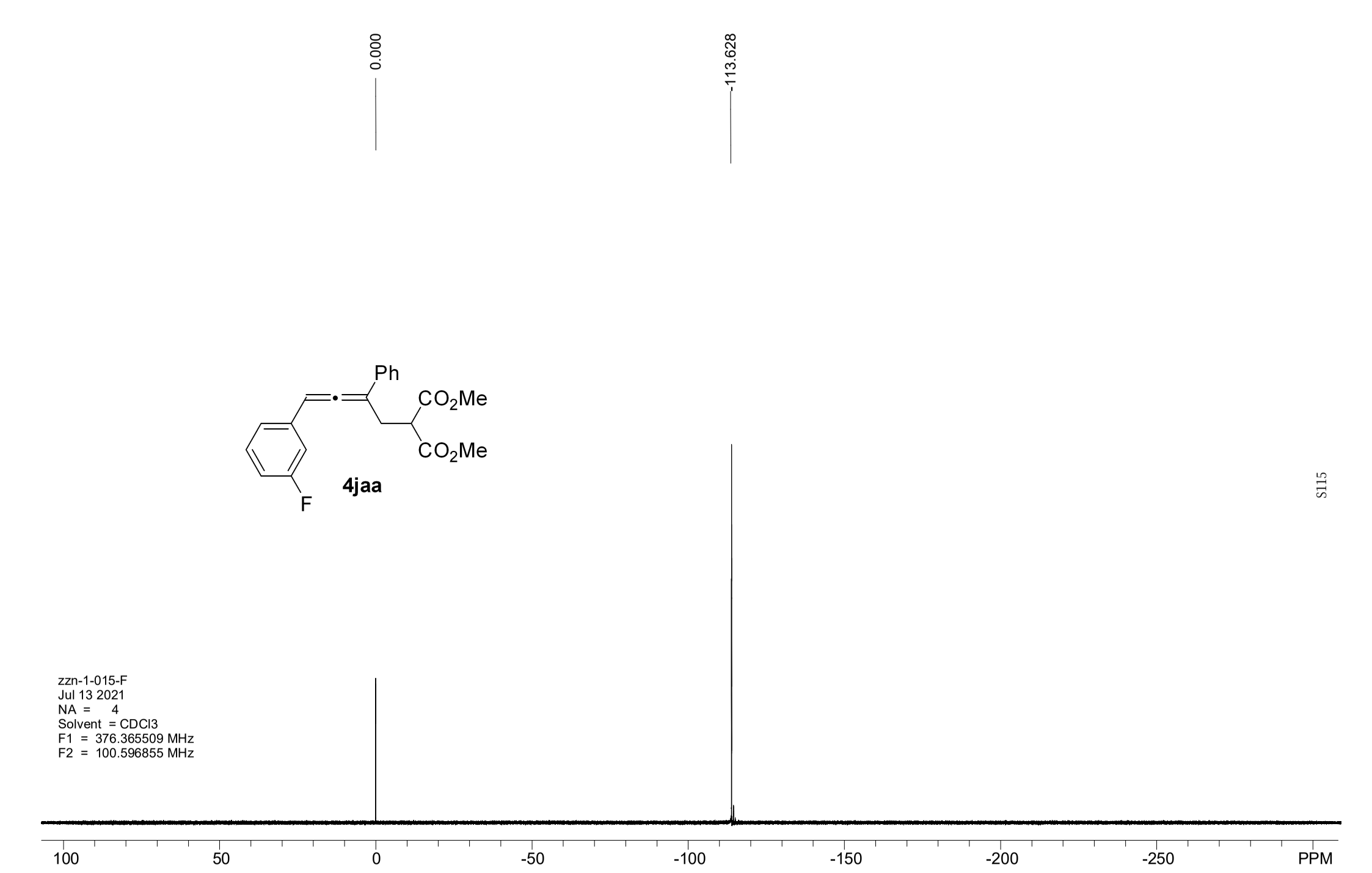

Ph
CO2Me
CO2Me
F

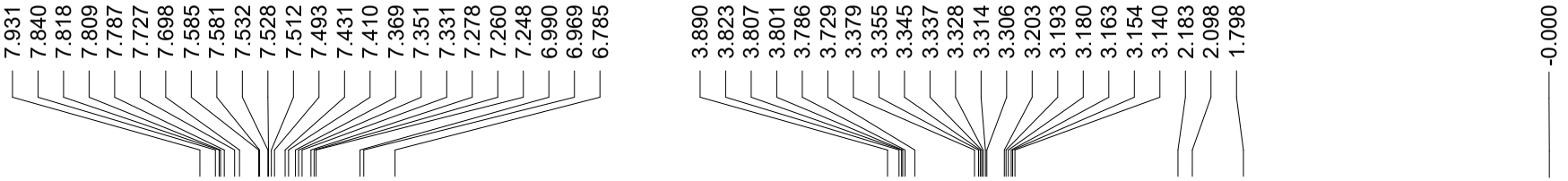
4jaa

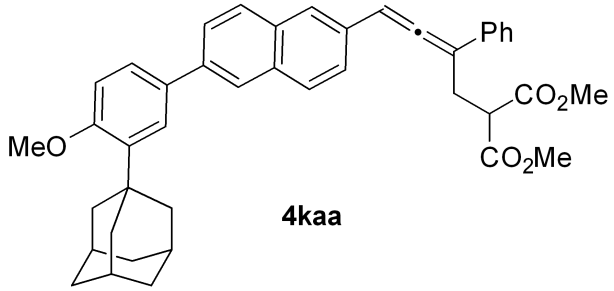
zzn-1-015-H
Jul 16 2021
NA = 16
Solvent = CDCl3
F1 = 400.100067 MHz
F2 = 1.000000 MHz
2.05
1.99
1.99
1.07
0.98
0.97
0.92
4.06
2.97
1.07
1.00
10
8
6
4
2
0
PPM


4.919
3.169
3.160
3.154
3.145
3.129
3.120
3.115
3.105
-0.000
Ph
CO2Me
CO2Me
F
4jaa
S113
zzn-1-015-purity
Jul 9 2021
purity = 97%
35.4 mg product with 3.5 uL dibromomethane
NA = 4
Solvent = cdcl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz
1.00
0.97
10
8
6
4
2
0
PPM


zzn-1-015-C
Jul 12 2021
NA = 1024
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
4jaa
F
Ph
CO2Me
CO2Me
205.463
169.317
168.949
164.291
161.855
136.121
136.045
134.658
130.107
130.023
128.629
127.679
125.963
122.745
122.714
114.394
114.180
113.536
113.314
108.120
99.394
99.371
77.322
77.000
76.686
52.653
52.385
50.048
29.049
200
150
100
50
0
PPM


0.000
-113.628
Ph
CO2Me
CO2Me
F
4jaa
zzn-1-015-F
Jul 13 2021
NA = 4
Solvent = CDCl3
F1 = 376.365509 MHz
F2 = 100.596855 MHz
100
50
0
-50
-100
-150
-200
-250
PPM

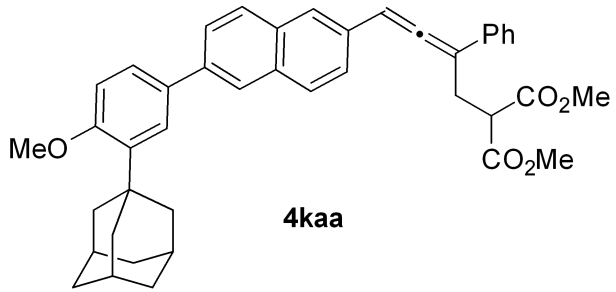




4kaa

zzn-1-067-H
Oct 7 2021
NA = 16
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz

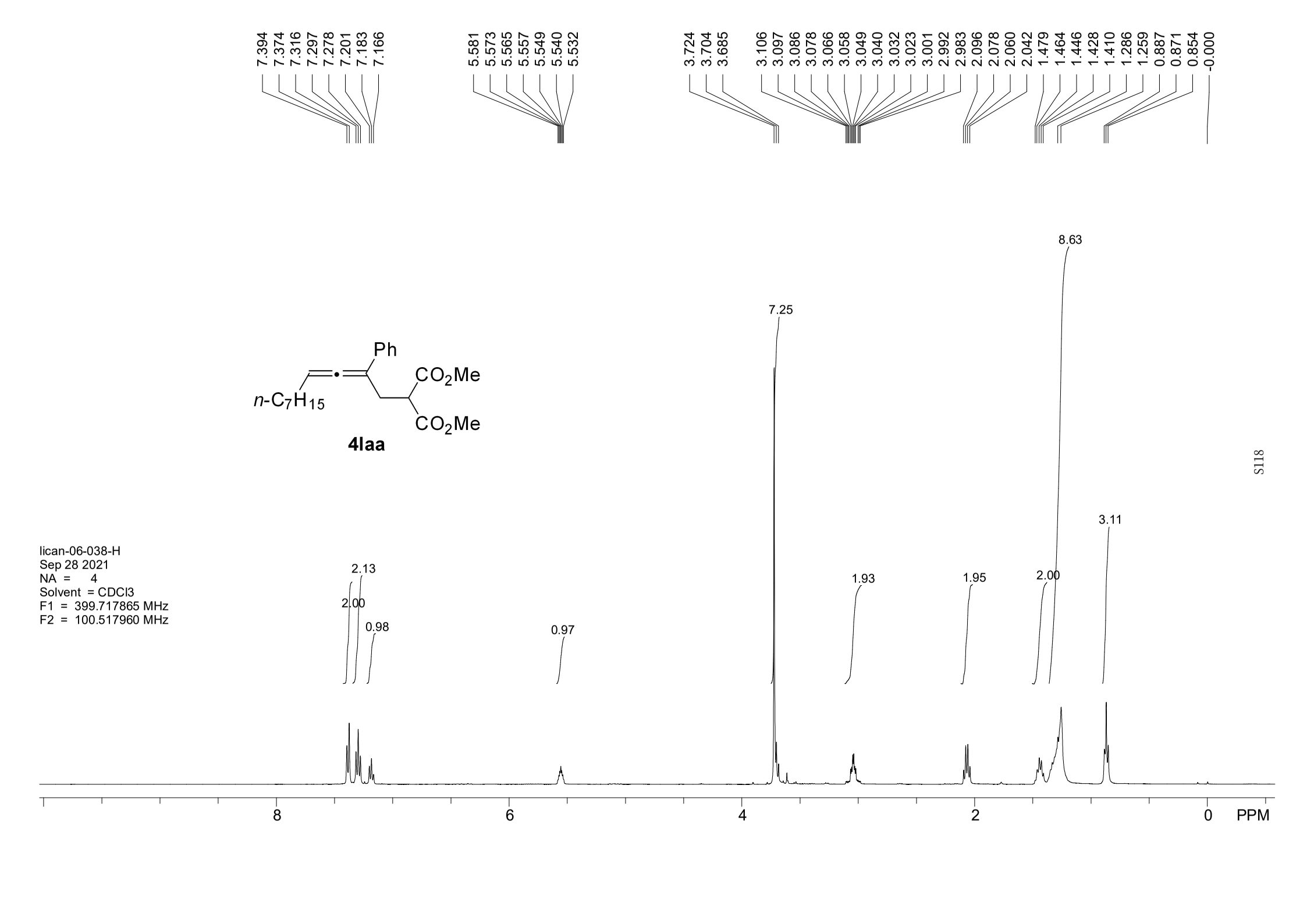
205.674
169.520
169.125
158.546
138.934
138.817
135.178
133.238
132.907
132.394
130.720
128.630
128.473
128.126
127.533
126.048
126.012
125.782
125.757
125.471
125.055
124.809
112.024
107.848
100.784
77.319
77.000
76.685
55.108
52.720
52.486
50.154
40.564
37.134
37.094
29.170
29.073

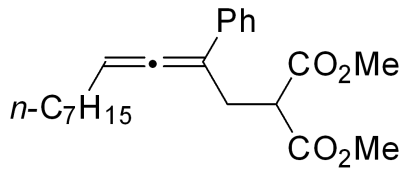


4kaa

zzn-1-067-C
Oct 7 2021
NA = 416
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz

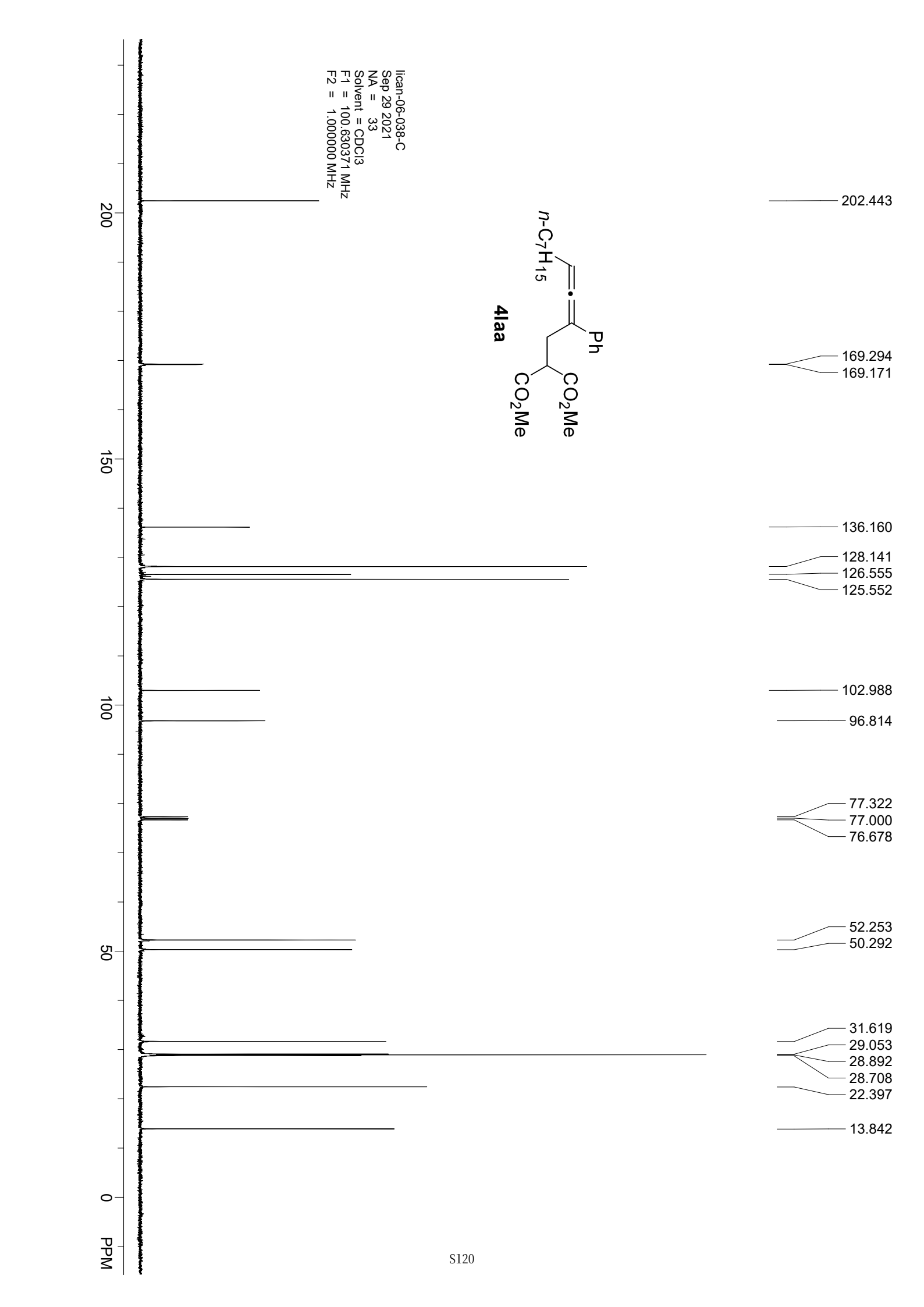
200 150 100 50 0 PPM

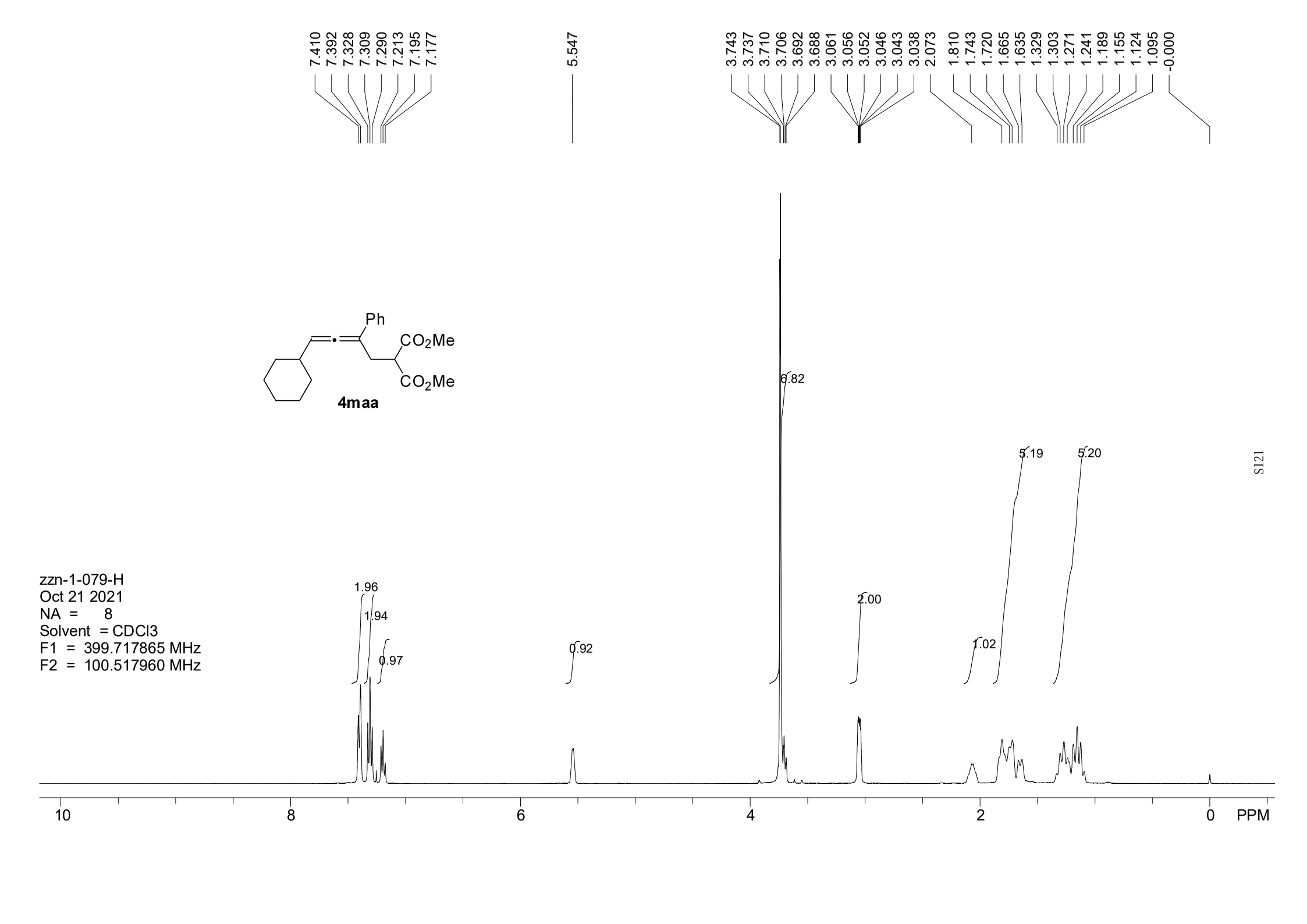

7.394
7.374
7.316
7.297
7.278
7.201
7.183
7.166
5.581
5.573
5.565
5.557
5.549
5.540
5.532
3.724
3.704
3.685
3.106
3.097
3.086
3.078
3.066
3.058
3.049
3.040
3.032
3.023
3.001
2.992
2.983
2.096
2.078
2.060
2.042
1.479
1.464
1.446
1.428
1.410
1.286
1.259
0.887
0.871
0.854
-0.000
Ph
CO2Me
CO2Me
n-C7H15
4laa
S118
lican-06-038-H
Sep 28 2021
NA = 4
Solvent = CDCl3
F1 = 399.717865 MHz
F2 = 100.517960 MHz
2.13
2.00
0.98
0.97
7.25
1.93
1.95
2.00
8.63
3.11
8
6
4
2
0
PPM

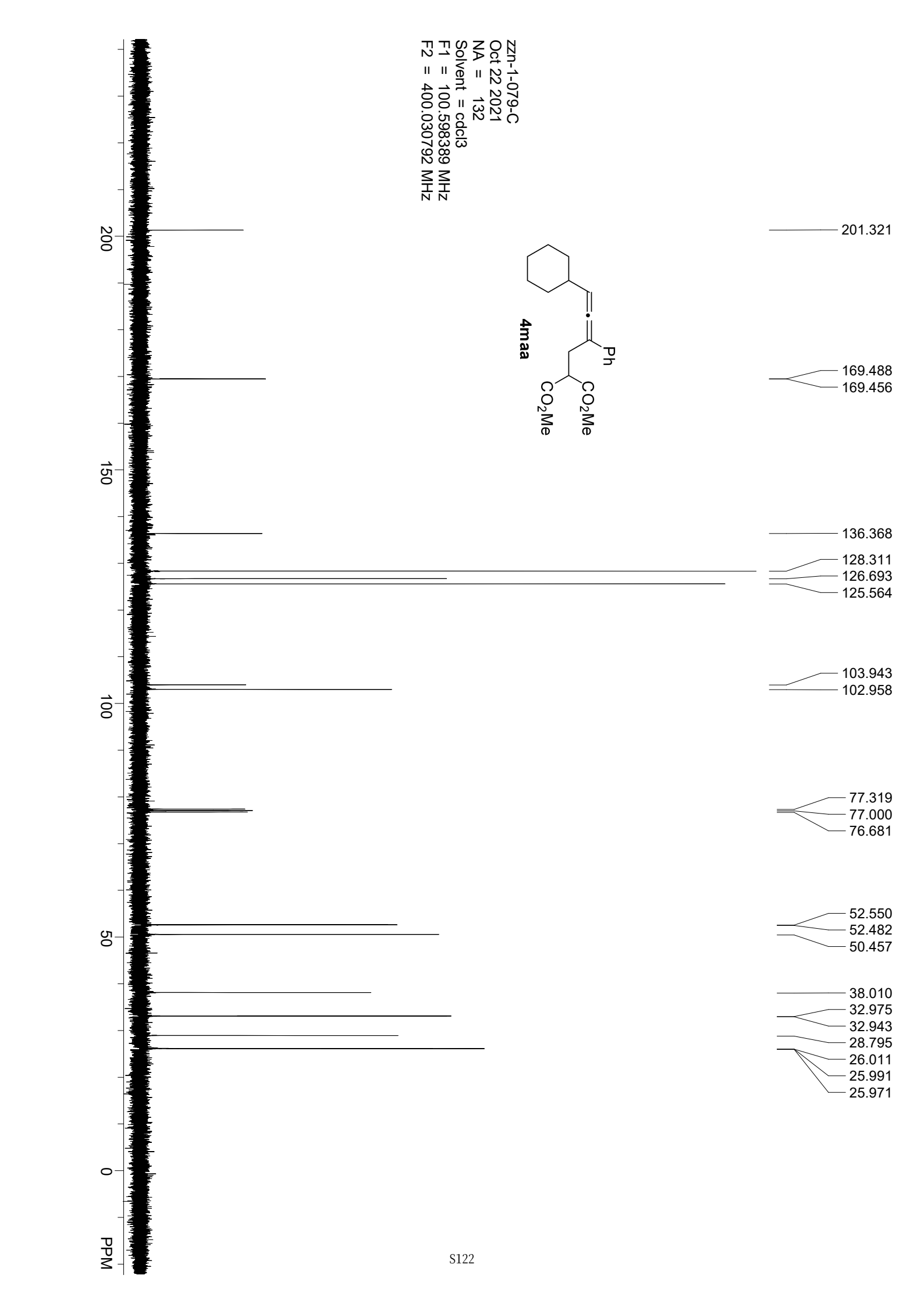


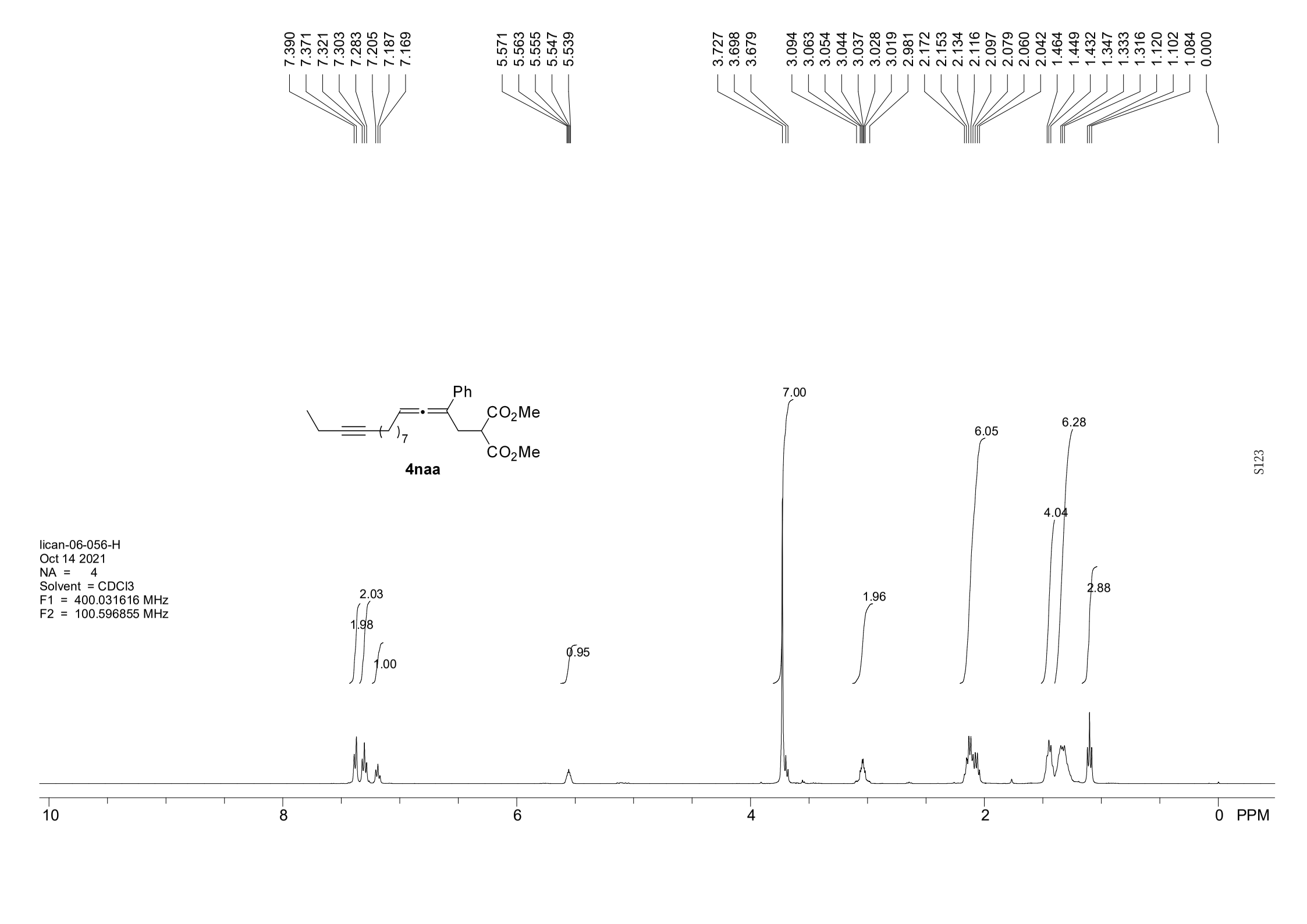
4laa

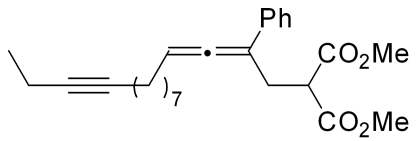
lican-06-038-purity
Sep 29 2021
purity = 98%
78.1 mg product with 35 uL dibromomethane
NA = 4
Solvent = cdcl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz


lican-06-038-C
Sep 29 2021
NA = 33
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
n-C7H15
Ph
CO2Me
CO2Me
4laa
202.443
169.294
169.171
136.160
128.141
126.555
125.552
102.988
96.814
77.322
77.000
76.678
52.253
50.292
31.619
29.053
28.892
28.708
22.397
13.842
200
150
100
50
0
PPM


7.410
7.392
7.328
7.309
7.290
7.213
7.195
7.177
5.547
3.743
3.737
3.710
3.706
3.692
3.688
3.061
3.056
3.052
3.046
3.043
3.038
2.073
1.810
1.743
1.720
1.665
1.635
1.329
1.303
1.271
1.241
1.189
1.155
1.124
1.095
-0.000
Ph
CO2Me
CO2Me
4maa
6.82
5.19
5.20
S121
zzn-1-079-H
Oct 21 2021
NA = 8
Solvent = CDCl3
F1 = 399.717865 MHz
F2 = 100.517960 MHz
1.96
1.94
0.97
0.92
2.00
1.02
10
8
6
4
2
0
PPM


zzn-1-079-C
Oct 22 2021
NA = 132
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
4maa
Ph
CO2Me
CO2Me
201.321
169.488
169.456
136.368
128.311
126.693
125.564
103.943
102.958
77.319
77.000
76.681
52.550
52.482
50.457
38.010
32.975
32.943
28.795
26.011
25.991
25.971
200
150
100
50
0
PPM

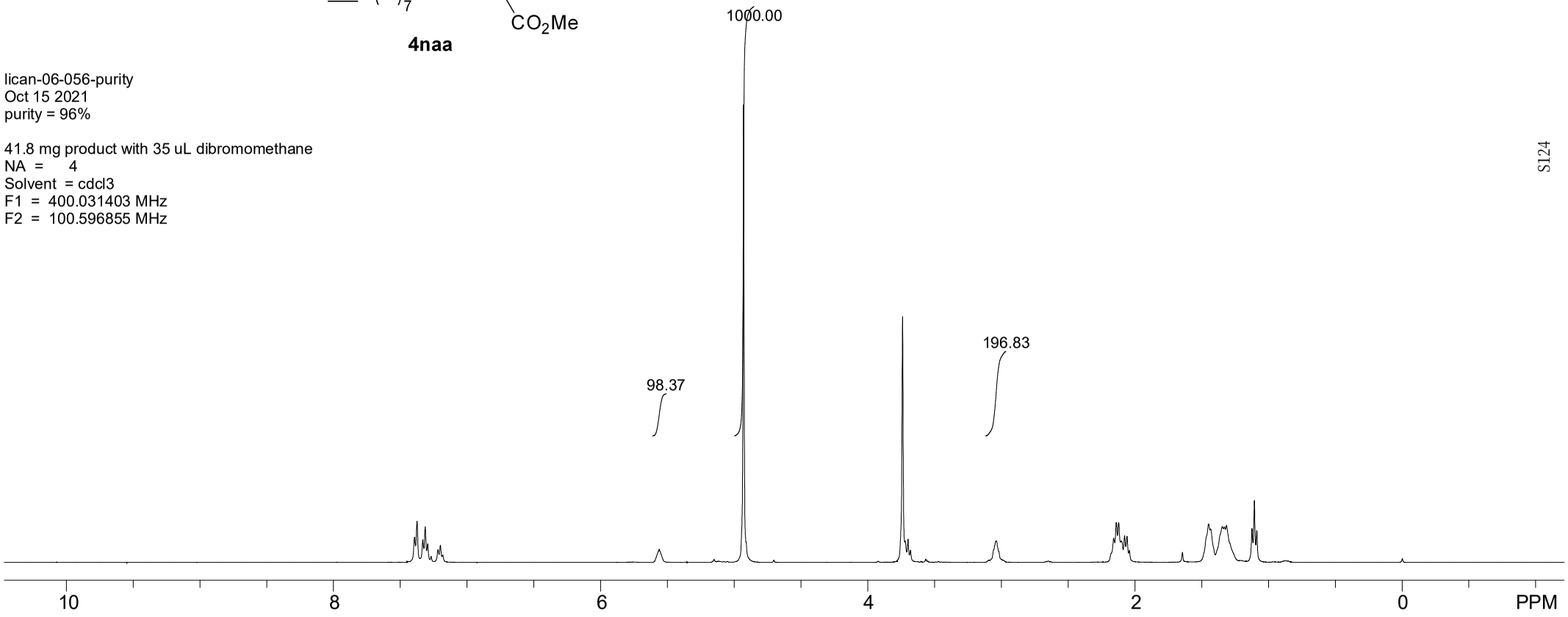

7.390
7.371
7.321
7.303
7.283
7.205
7.187
7.169
5.571
5.563
5.555
5.547
5.539
3.727
3.698
3.679
3.094
3.063
3.054
3.044
3.037
3.028
3.019
2.981
2.172
2.153
2.134
2.116
2.097
2.079
2.060
2.042
1.464
1.449
1.432
1.347
1.333
1.316
1.120
1.102
1.084
0.000
Ph
CO2Me
CO2Me
7
4naa
lican-06-056-H
Oct 14 2021
NA = 4
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
2.03
1.98
1.00
0.95
7.00
1.96
6.05
6.28
4.04
2.88
S123
10
8
6
4
2
0
PPM

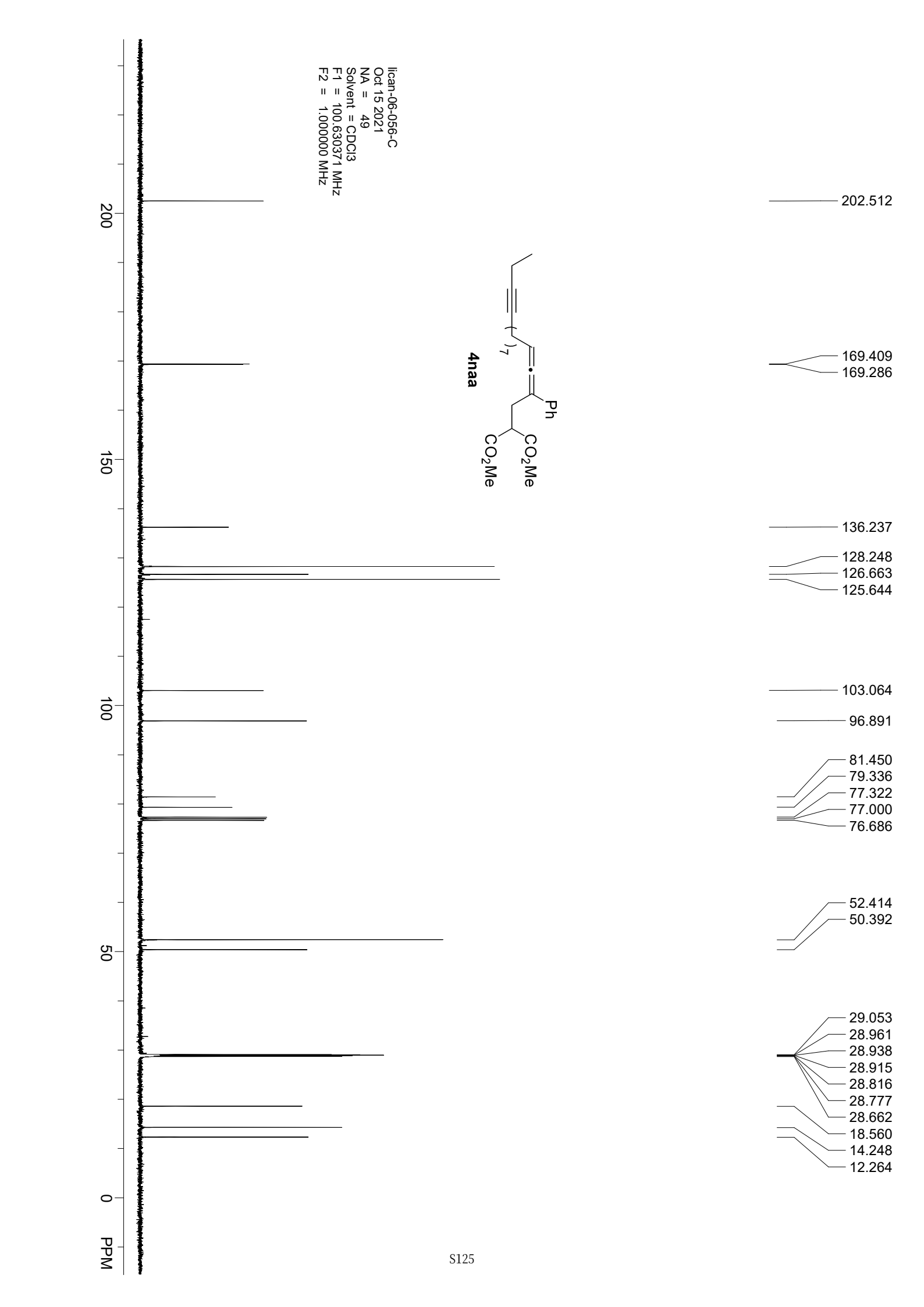


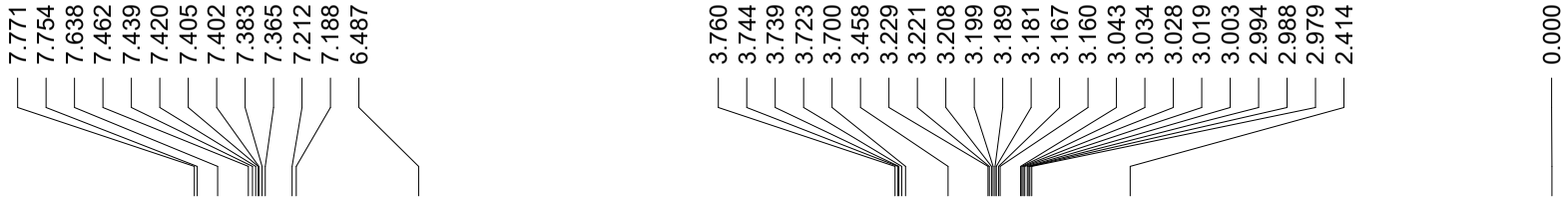
4naa

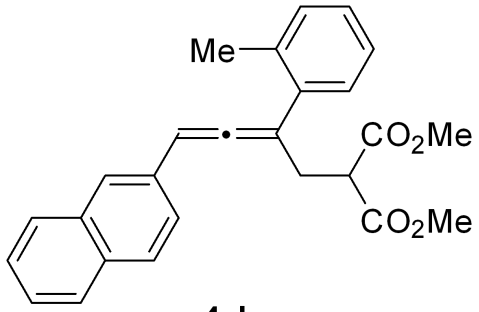
lican-06-056-purity
Oct 15 2021
purity = 96%

41.8 mg product with 35 uL dibromomethane
NA = 4
Solvent = cdcl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz



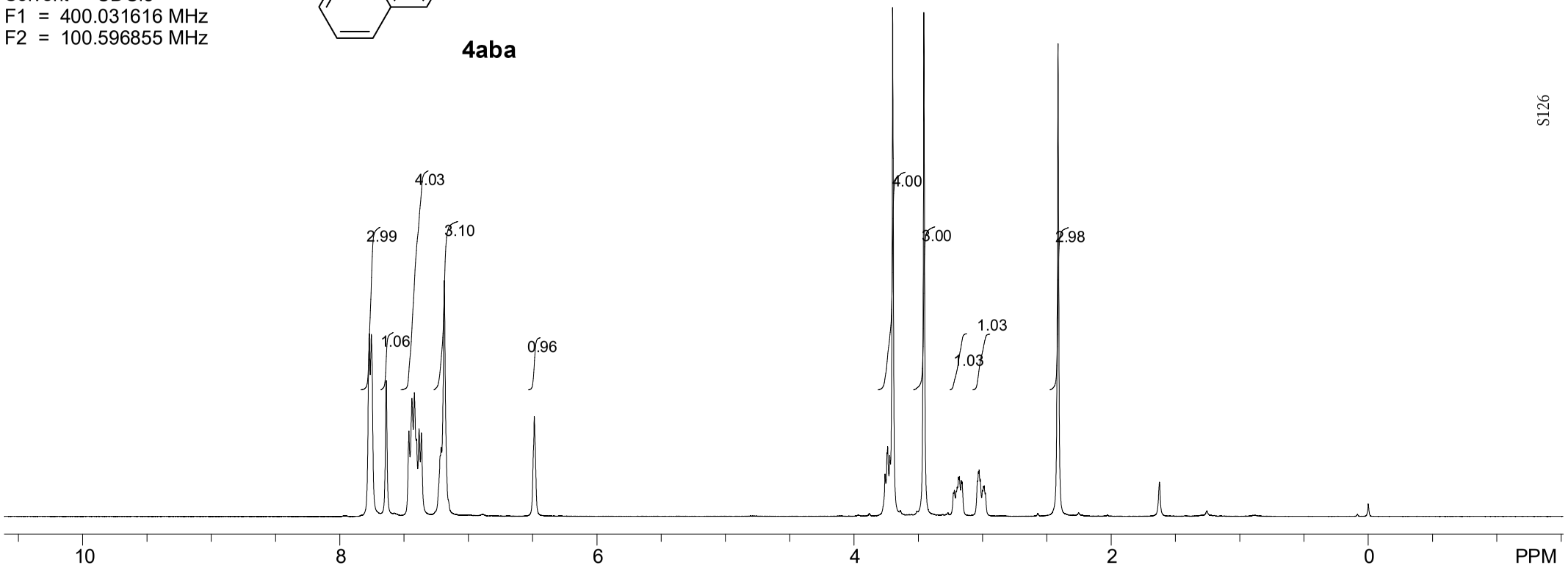

lican-06-056-C
Oct 15 2021
NA = 49
Solvent = CDCl3
F1 = 100.63071 MHz
F2 = 1.000000 MHz
4naa
Ph
CO2Me
CO2Me
7
202.512
169.409
169.286
136.237
128.248
126.663
125.644
103.064
96.891
81.450
79.336
77.322
77.000
76.686
52.414
50.392
29.053
28.961
28.938
28.915
28.816
28.777
28.662
18.560
14.248
12.264
200
150
100
50
0
PPM

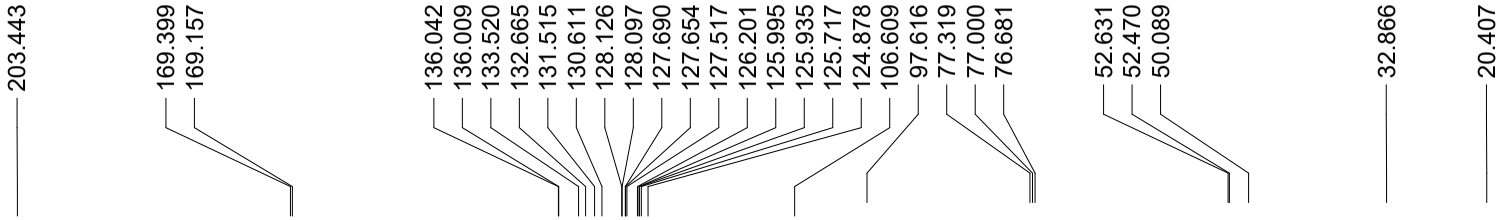


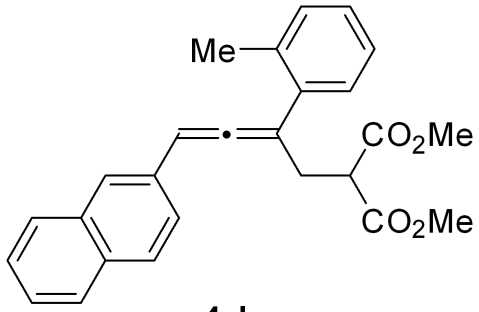


4aba

zzn-1-029-H
Aug 19 2021
NA = 4
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz

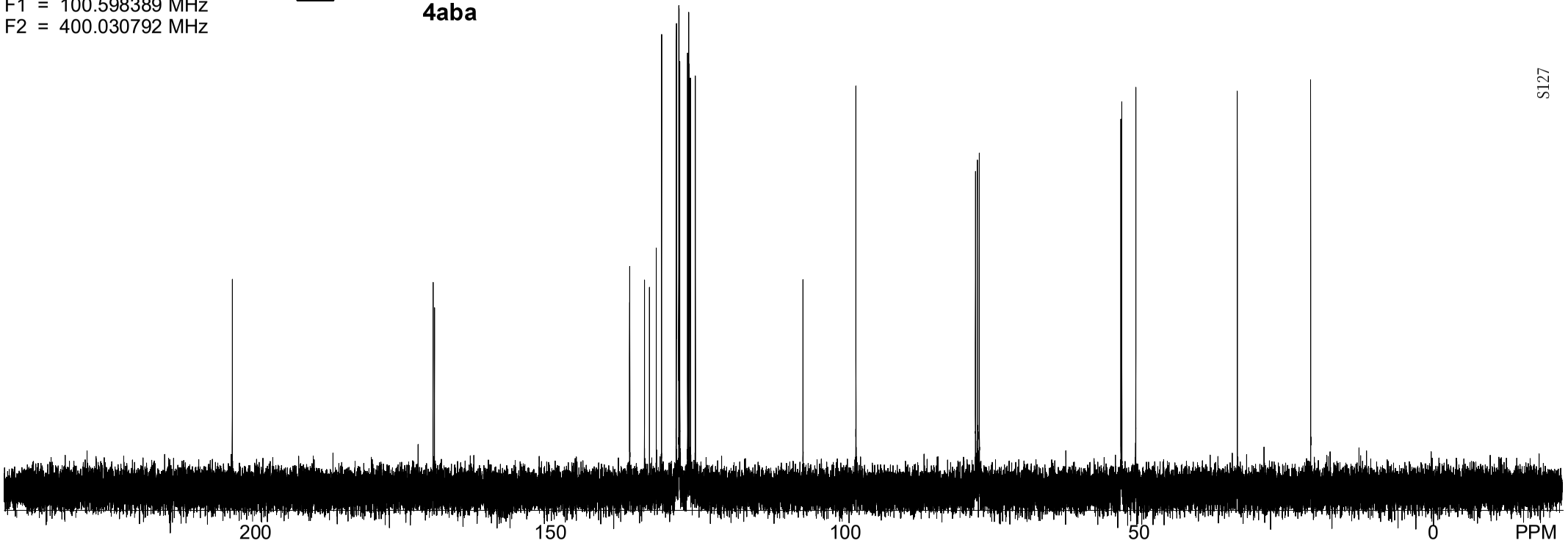


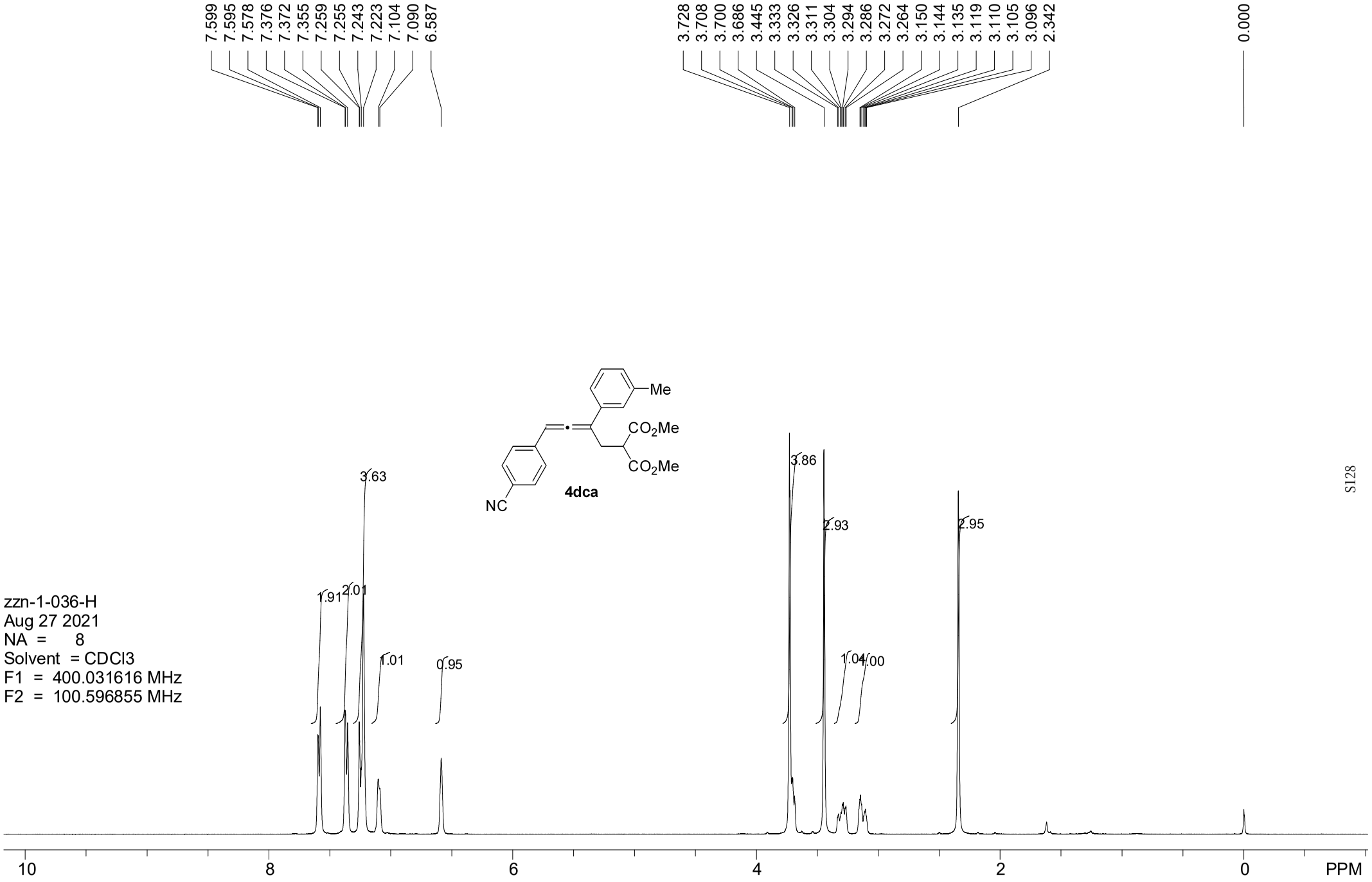


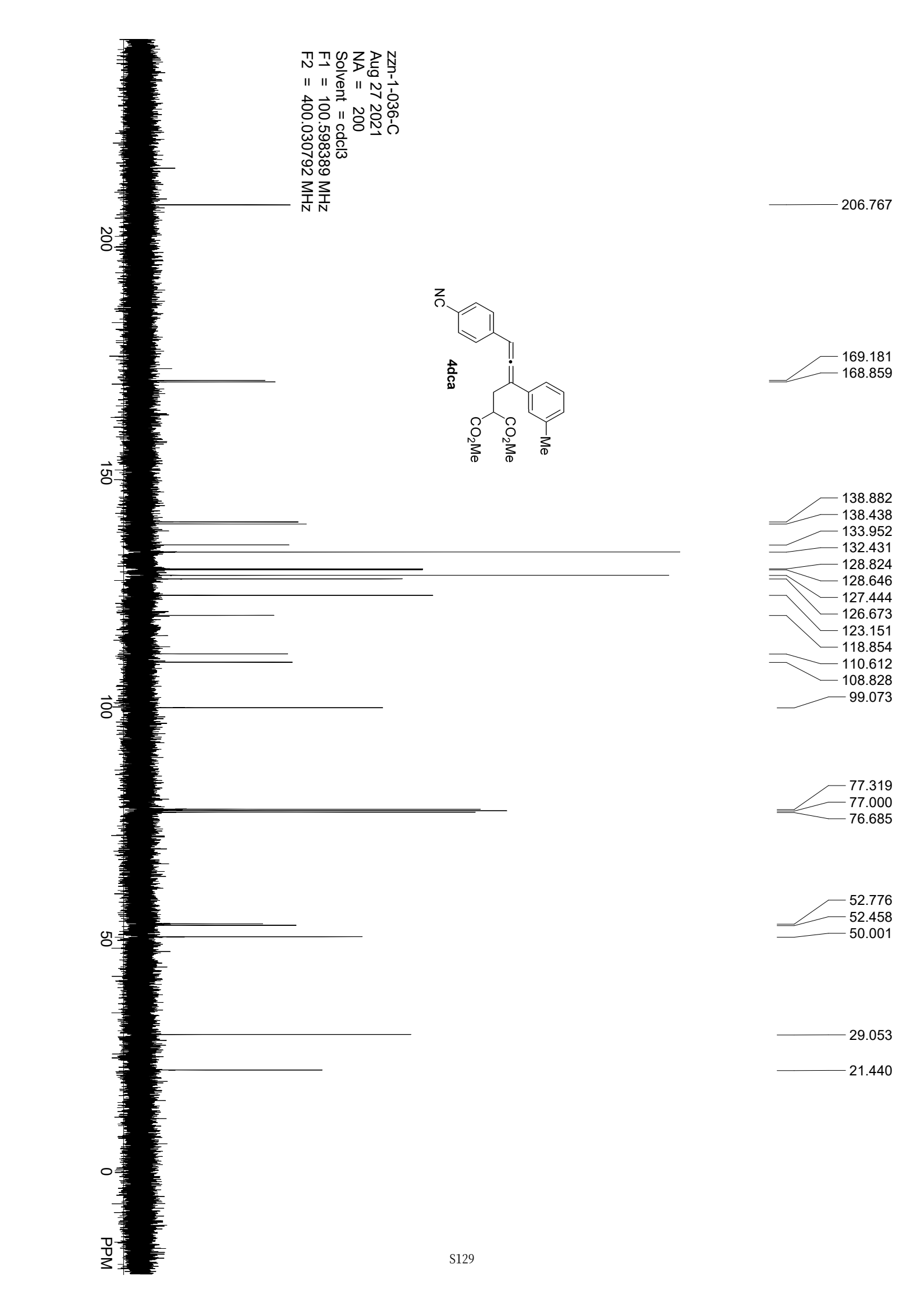


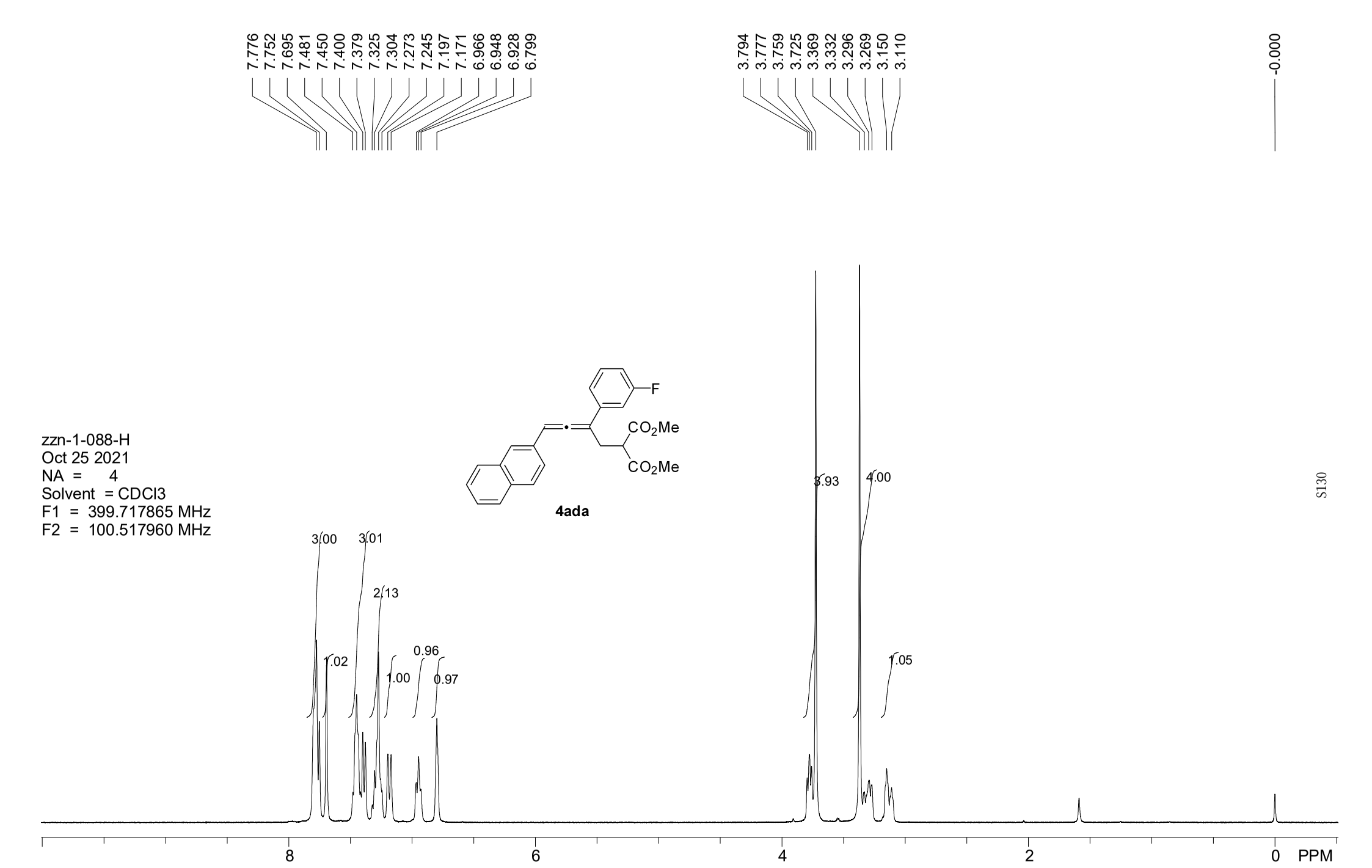
4aba

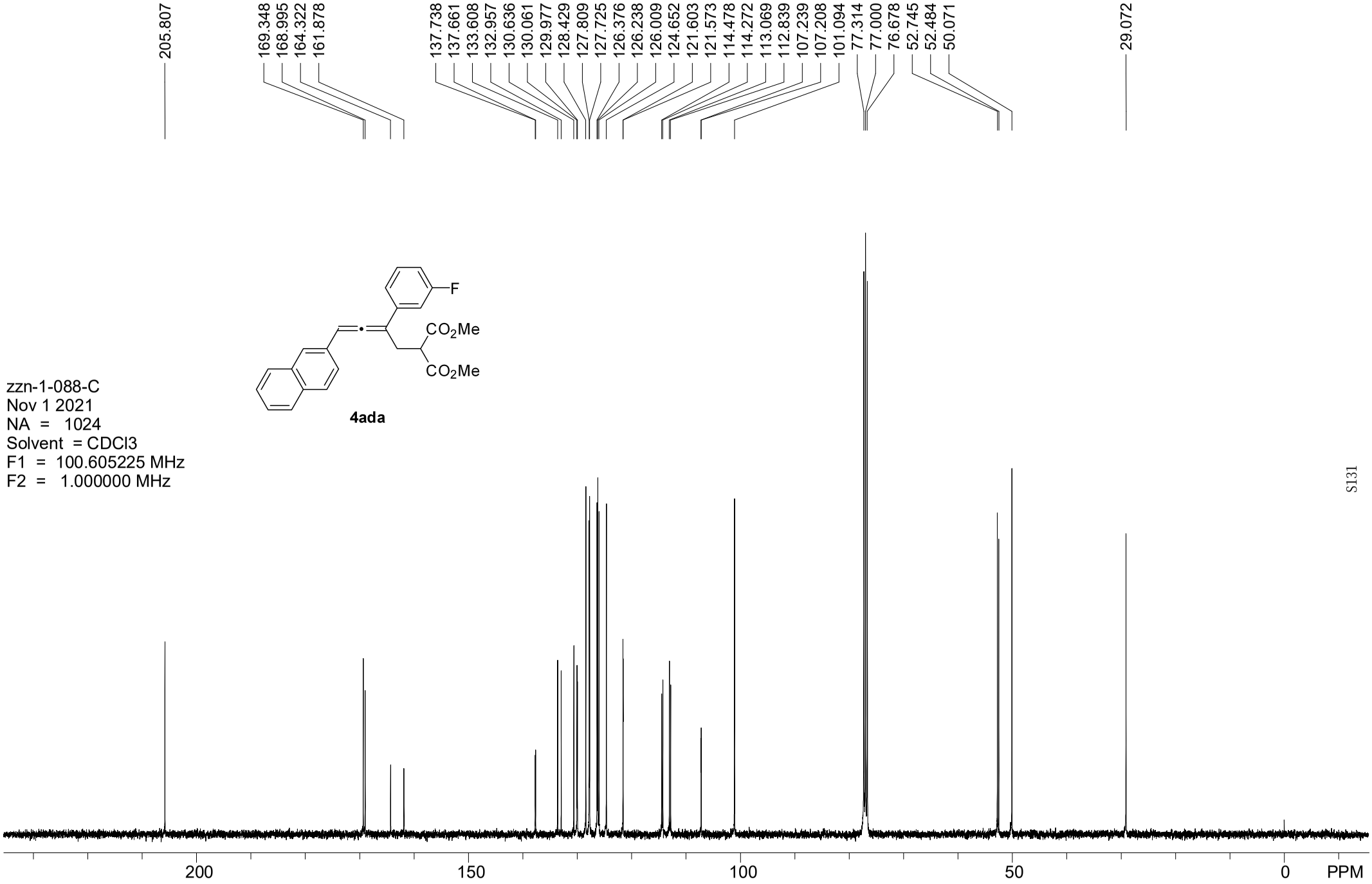
zzn-1-029-C
Aug 19 2021
NA = 80
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz

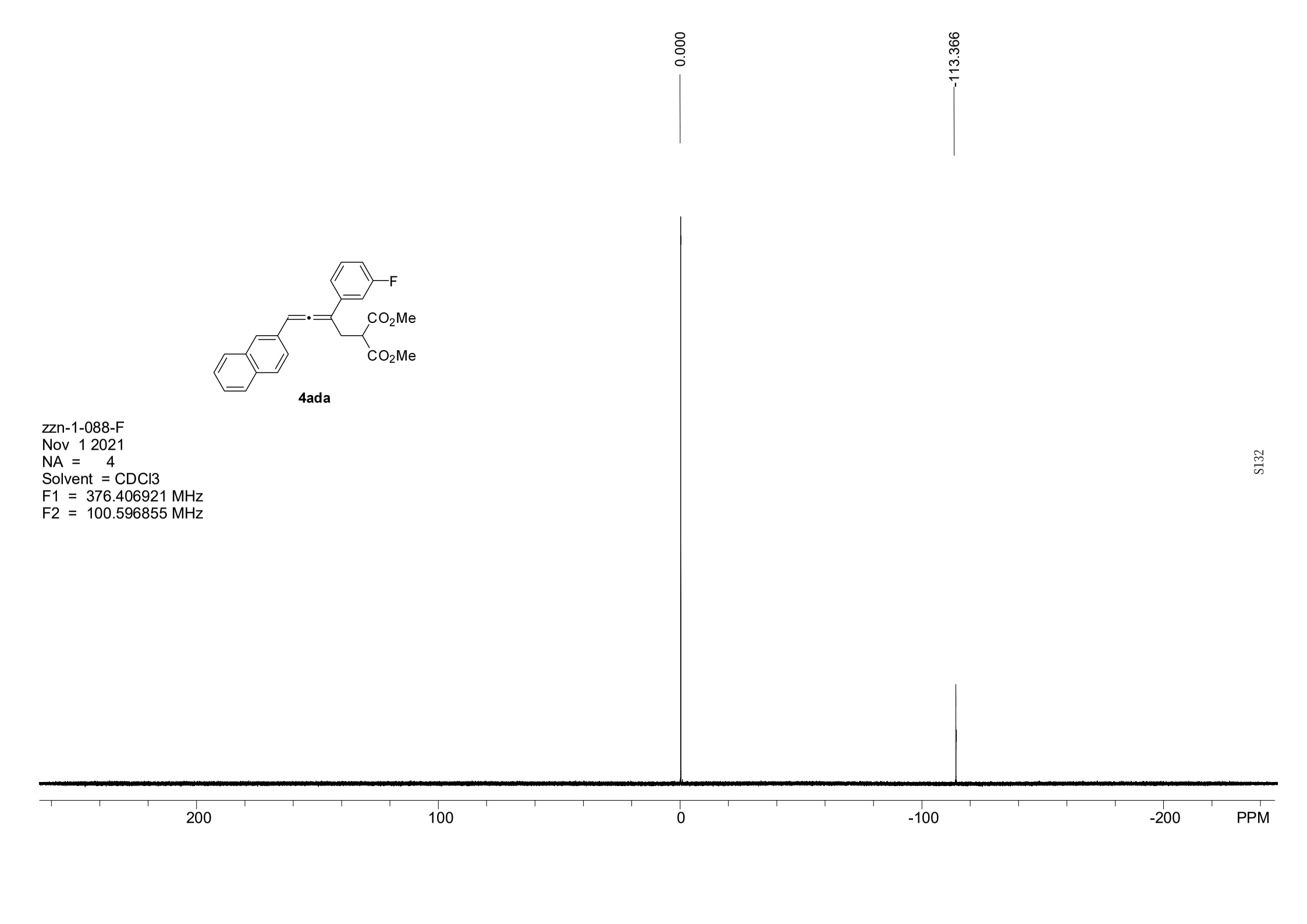


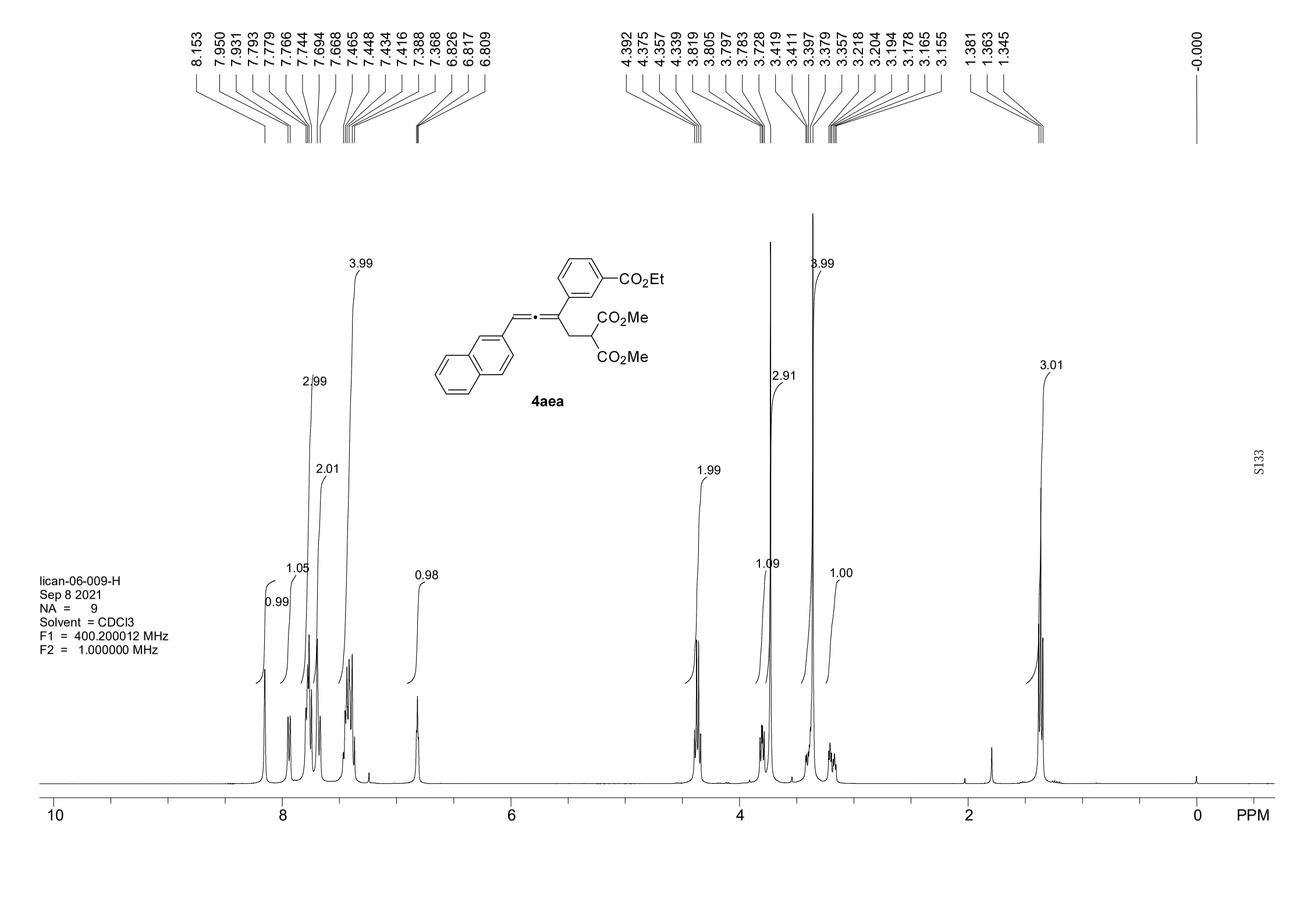

7.599
7.595
7.578
7.376
7.372
7.355
7.259
7.255
7.243
7.223
7.104
7.090
6.587
3.728
3.708
3.700
3.686
3.445
3.333
3.326
3.311
3.304
3.294
3.286
3.272
3.264
3.150
3.144
3.135
3.119
3.110
3.105
3.096
2.342
0.000
Me
CO2Me
CO2Me
NC
4dca
3.63
1.91
2.01
1.01
0.95
3.86
2.93
2.95
1.04
1.00
zzn-1-036-H
Aug 27 2021
NA = 8
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
S128
10
8
6
4
2
0
PPM

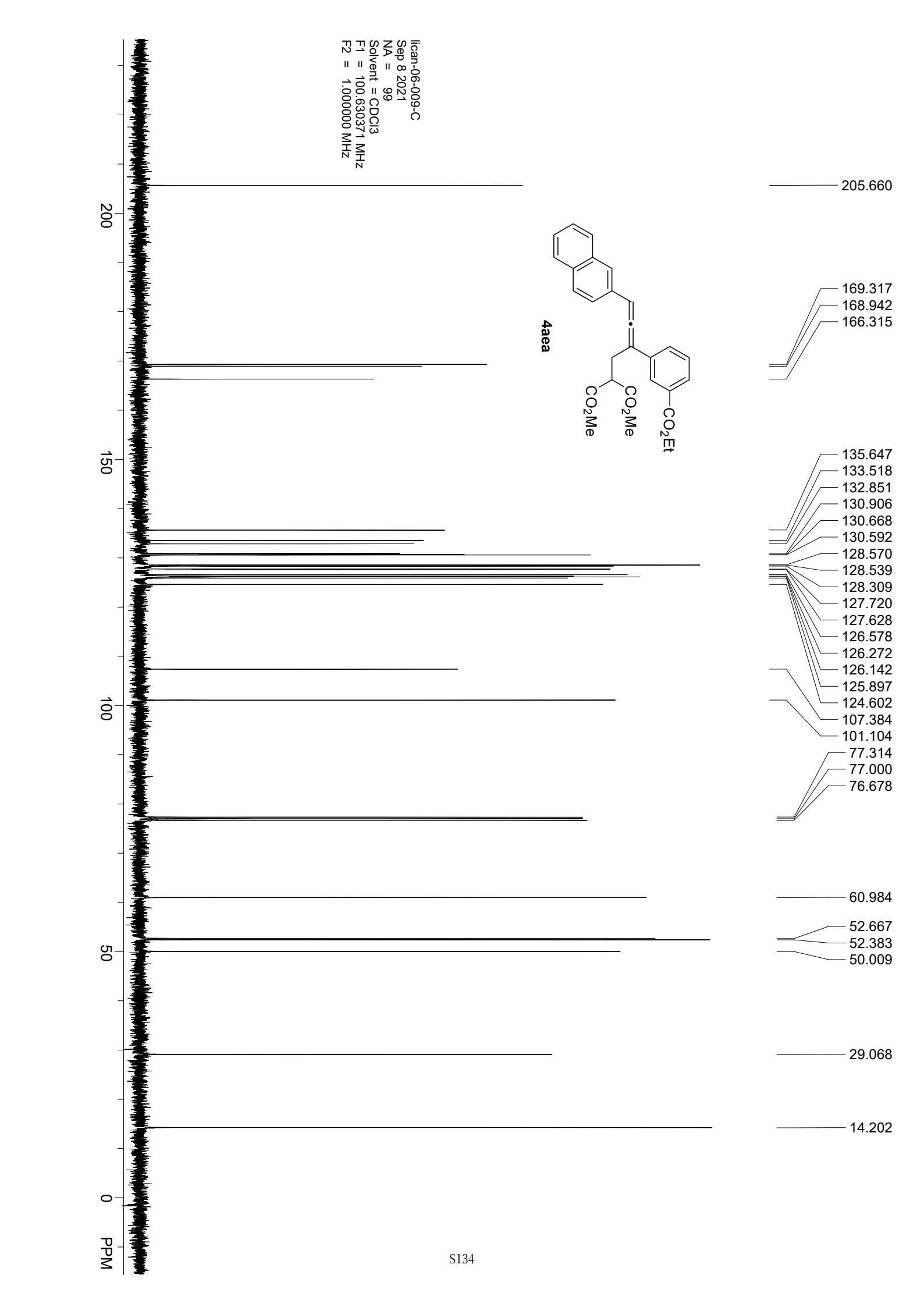

zzn-1-036-C
Aug 27 2021
NA = 200
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
NC
4dca
CO2Me
CO2Me
Me
206.767
169.181
168.859
138.882
138.438
133.952
132.431
128.824
128.646
127.444
126.673
123.151
118.854
110.612
108.828
99.073
77.319
77.000
76.685
52.776
52.458
50.001
29.053
21.440
200
150
100
50
0
PPM

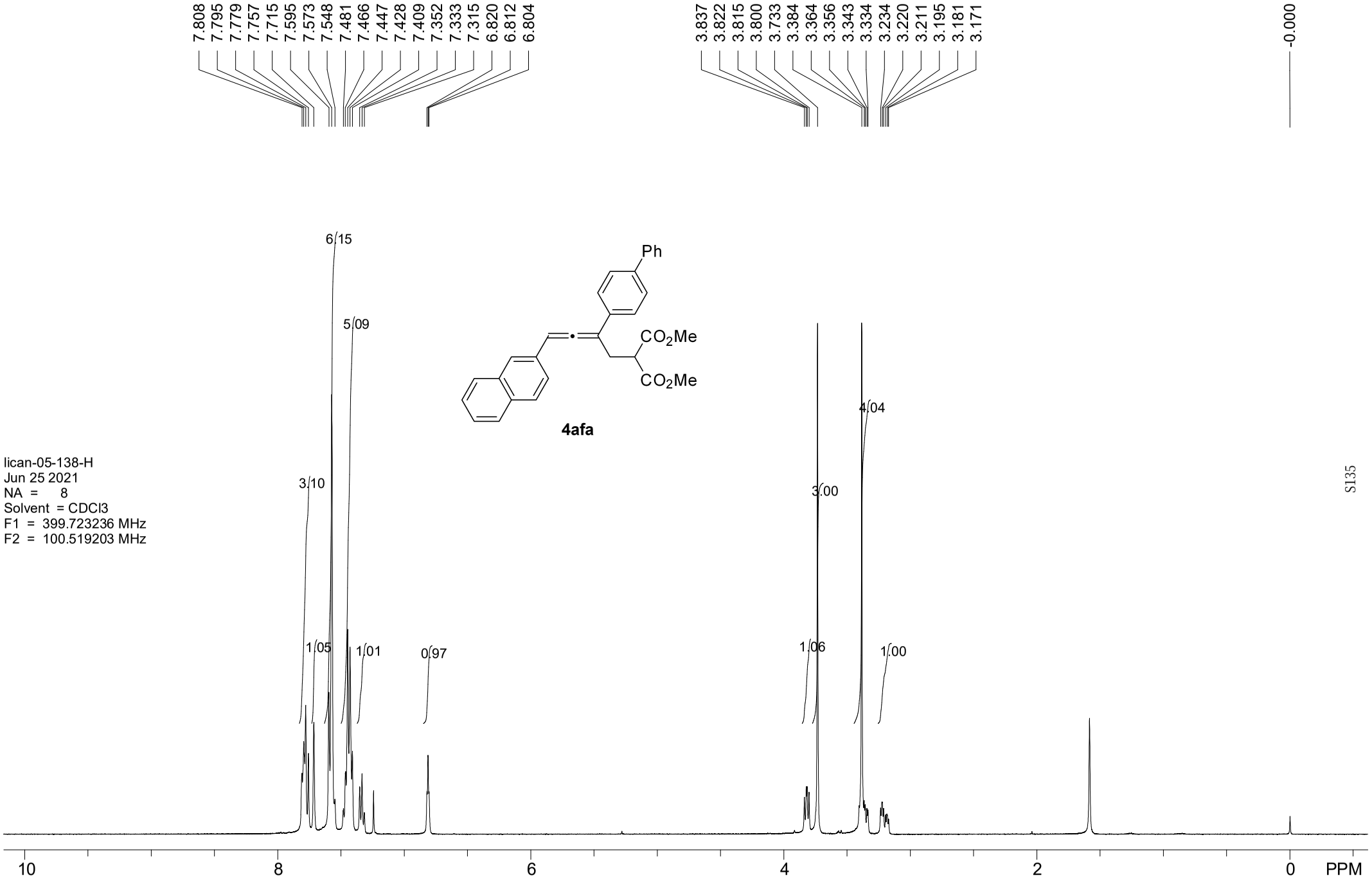

7.776
7.752
7.695
7.481
7.450
7.400
7.379
7.325
7.304
7.273
7.245
7.197
7.171
6.966
6.948
6.928
6.799
3.794
3.777
3.759
3.725
3.369
3.332
3.296
3.269
3.150
3.110
-0.000
zzn-1-088-H
Oct 25 2021
NA = 4
Solvent = CDCl3
F1 = 399.717865 MHz
F2 = 100.517960 MHz
F
CO2Me
CO2Me
4ada
3.00
3.01
2.13
1.02
1.00
0.96
0.97
3.93
4.00
1.05
S130
8
6
4
2
0
PPM

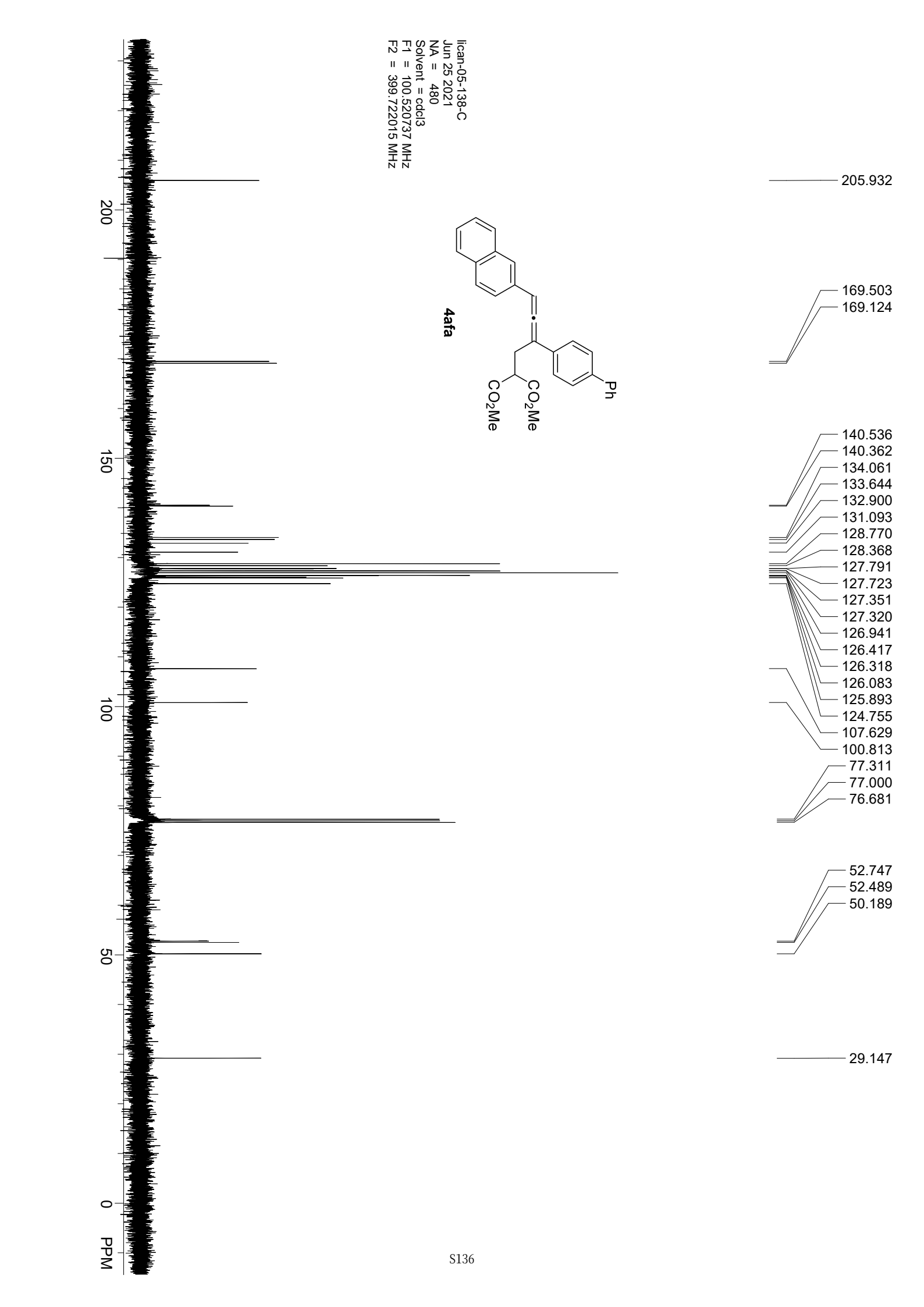

205.807
169.348
168.995
164.322
161.878
137.738
137.661
133.608
132.957
130.636
130.061
129.977
128.429
127.809
127.725
126.376
126.238
126.009
124.652
121.603
121.573
114.478
114.272
113.069
112.839
107.239
107.208
101.094
77.314
77.000
76.678
52.745
52.484
50.071
29.072
F
CO2Me
CO2Me
4ada
zzn-1-088-C
Nov 1 2021
NA = 1024
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
S131
200
150
100
50
0
PPM

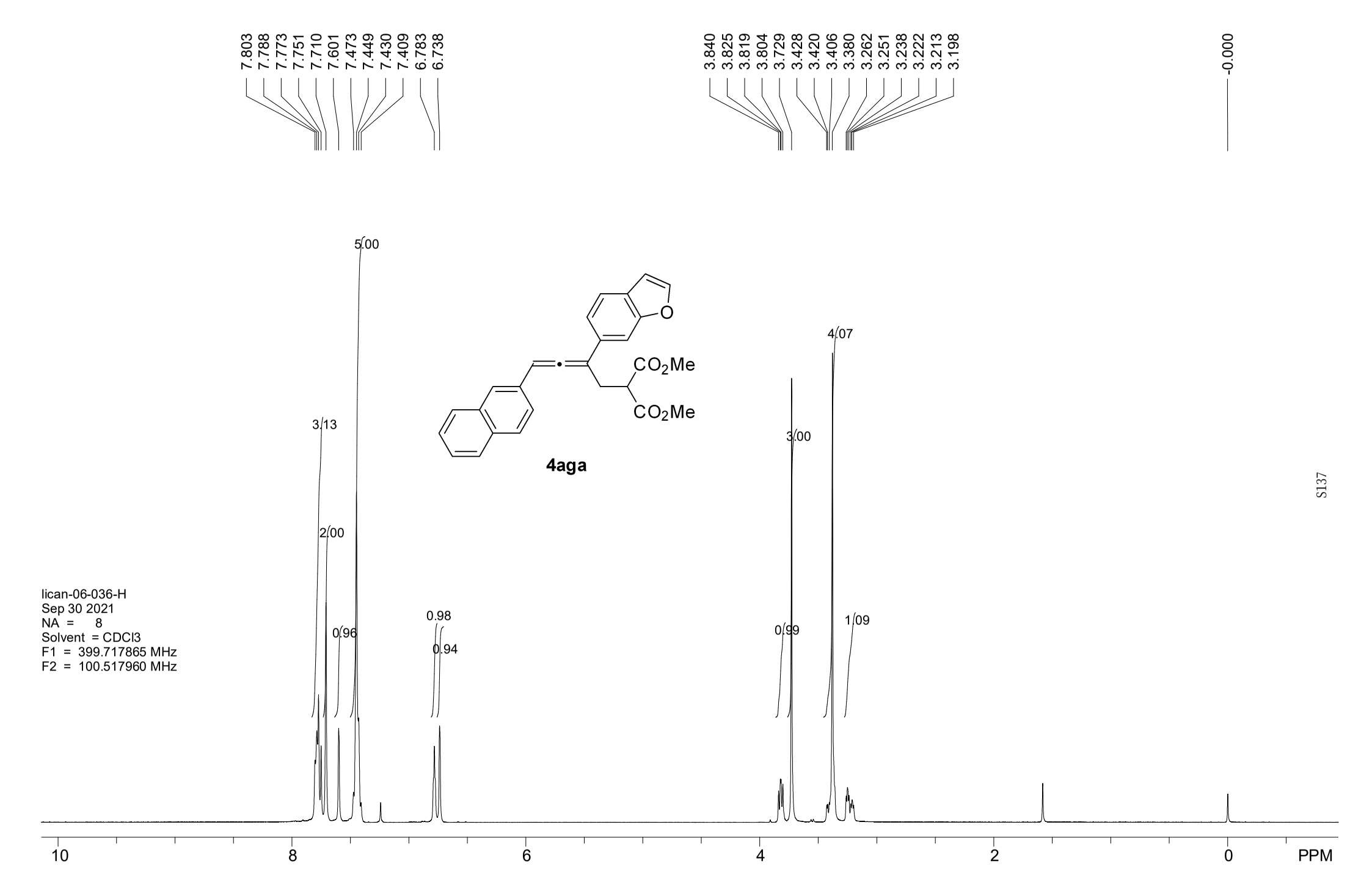

0.000
-113.366
F
CO2Me
CO2Me
4ada
zzn-1-088-F
Nov 1 2021
NA = 4
Solvent = CDCl3
F1 = 376.406921 MHz
F2 = 100.596855 MHz
S132
200
100
0
-100
-200
PPM

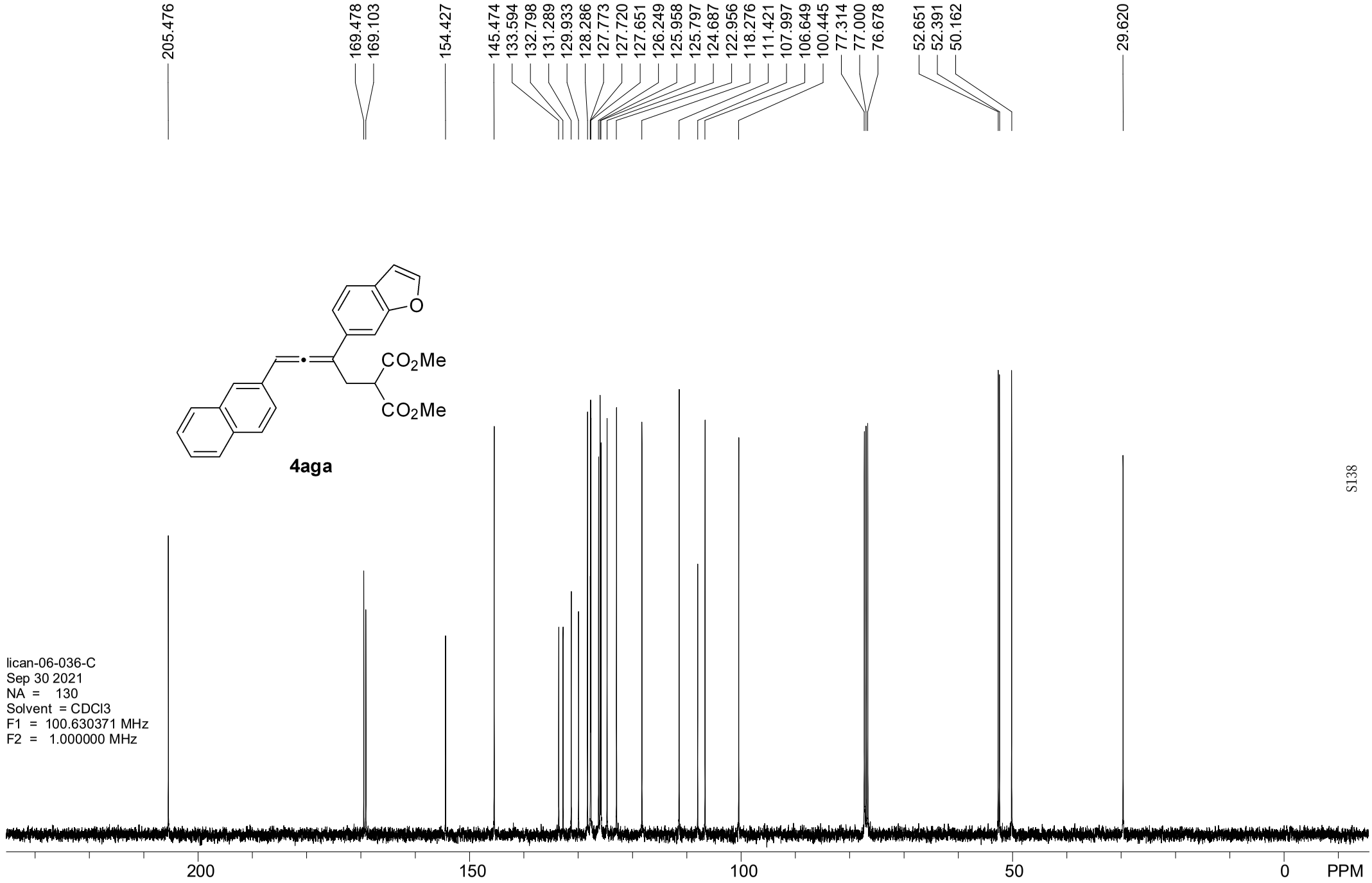

8.153
7.950
7.931
7.793
7.779
7.766
7.744
7.694
7.668
7.465
7.448
7.434
7.416
7.388
7.368
6.826
6.817
6.809
4.392
4.375
4.357
4.339
3.819
3.805
3.797
3.783
3.728
3.419
3.411
3.397
3.379
3.357
3.218
3.204
3.194
3.178
3.165
3.155
1.381
1.363
1.345
-0.000
CO2Et
CO2Me
CO2Me
4aea
3.99
2.99
2.01
1.05
0.99
0.98
1.99
2.91
1.09
3.99
1.00
3.01
lican-06-009-H
Sep 8 2021
NA = 9
Solvent = CDCl3
F1 = 400.200012 MHz
F2 = 1.000000 MHz
S133
10
8
6
4
2
0
PPM

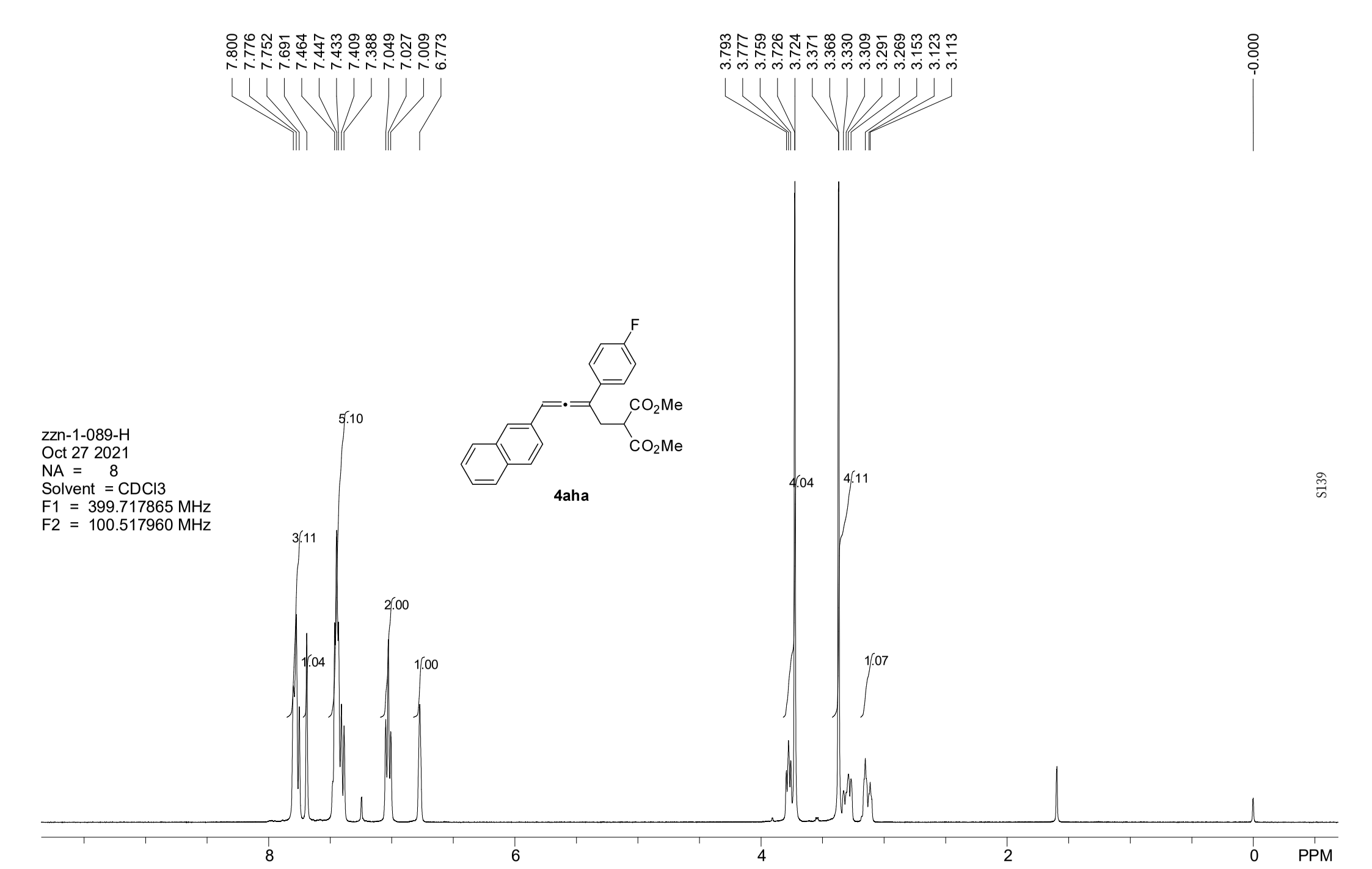

lican-06-009-C
Sep 8 2021
NA = 99
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
4aea
CO2Me
CO2Me
CO2Et
205.660
169.317
168.942
166.315
135.647
133.518
132.851
130.906
130.668
130.592
128.570
128.539
128.309
127.720
127.628
126.578
126.272
126.142
125.897
124.602
107.384
101.104
77.314
77.000
76.678
60.984
52.667
52.383
50.009
29.068
14.202
200
150
100
50
0
PPM

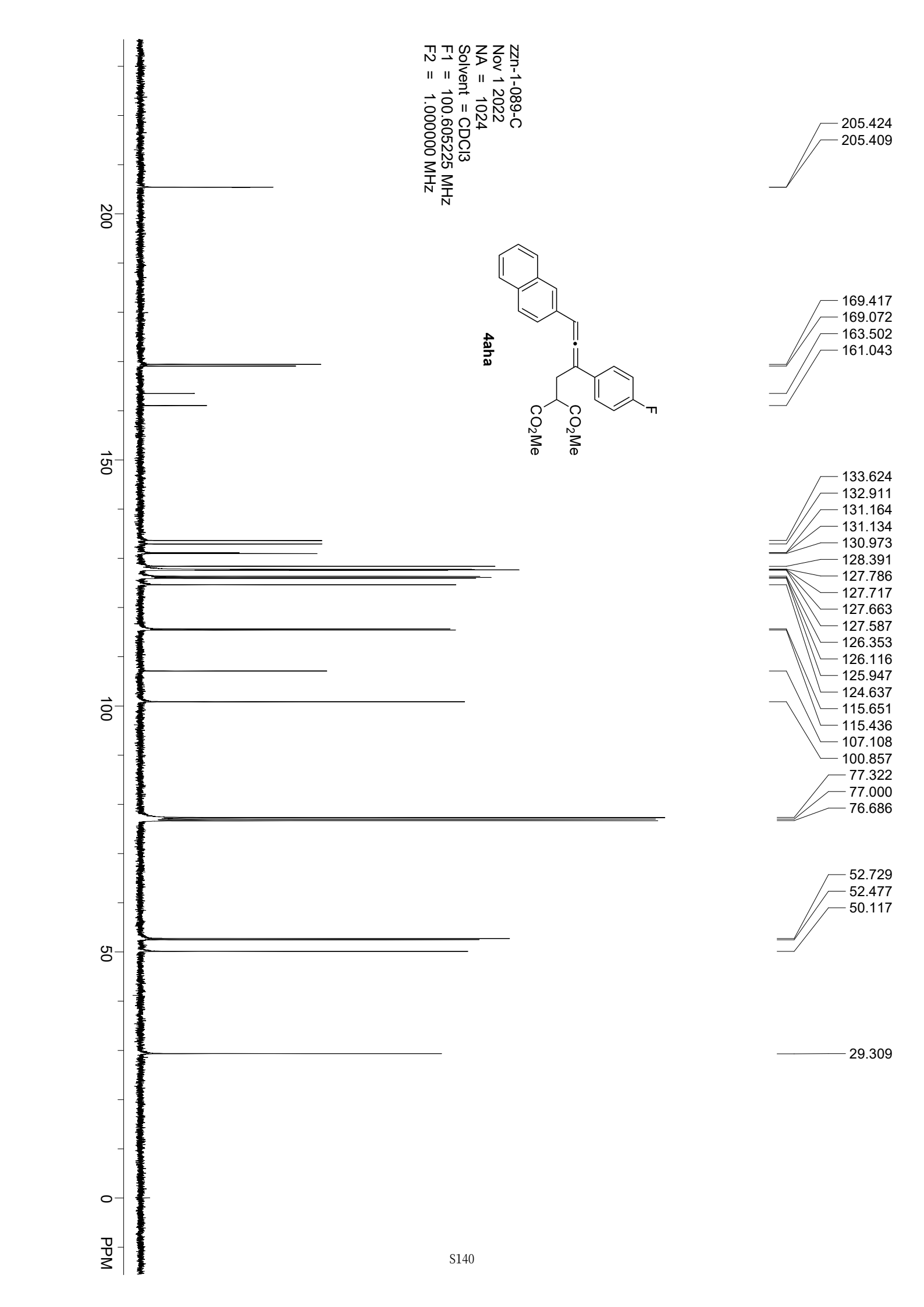

7.808
7.795
7.779
7.757
7.715
7.595
7.573
7.548
7.481
7.466
7.447
7.428
7.409
7.352
7.333
7.315
6.820
6.812
6.804
3.837
3.822
3.815
3.800
3.733
3.384
3.364
3.356
3.343
3.334
3.234
3.220
3.211
3.195
3.181
3.171
-0.000
Ph
CO2Me
CO2Me
4afa
lican-05-138-H
Jun 25 2021
NA = 8
Solvent = CDCl3
F1 = 399.723236 MHz
F2 = 100.519203 MHz
6.15
5.09
3.10
1.05
1.01
0.97
3.00
1.06
4.04
1.00
S135
10
8
6
4
2
0
PPM

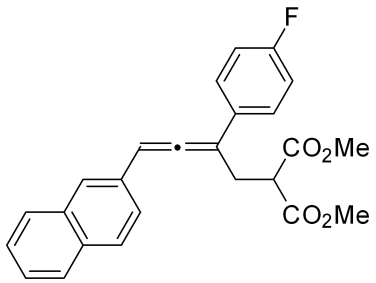

lican-05-138-C
Jun 25 2021
NA = 480
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
4afa
CO2Me
CO2Me
Ph
205.932
169.503
169.124
140.536
140.362
134.061
133.644
132.900
131.093
128.770
128.368
127.791
127.723
127.351
127.320
126.941
126.417
126.318
126.083
125.893
124.755
107.629
100.813
77.311
77.000
76.681
52.747
52.489
50.189
29.147
200
150
100
50
0
PPM


7.803
7.788
7.773
7.751
7.710
7.601
7.473
7.449
7.430
7.409
6.783
6.738
3.840
3.825
3.819
3.804
3.729
3.428
3.420
3.406
3.380
3.262
3.251
3.238
3.222
3.213
3.198
-0.000
5.00
3.13
2.00
0.96
0.98
0.94
3.00
4.07
0.99
1.09
O
CO2Me
CO2Me
4aga
lican-06-036-H
Sep 30 2021
NA = 8
Solvent = CDCl3
F1 = 399.717865 MHz
F2 = 100.517960 MHz
10
8
6
4
2
0
PPM


205.476
169.478
169.103
154.427
145.474
133.594
132.798
131.289
129.933
128.286
127.773
127.720
127.651
126.249
125.958
125.797
124.687
122.956
118.276
111.421
107.997
106.649
100.445
77.314
77.000
76.678
52.651
52.391
50.162
29.620
O
CO2Me
CO2Me
4aga
S138
lican-06-036-C
Sep 30 2021
NA = 130
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
200
150
100
50
0
PPM

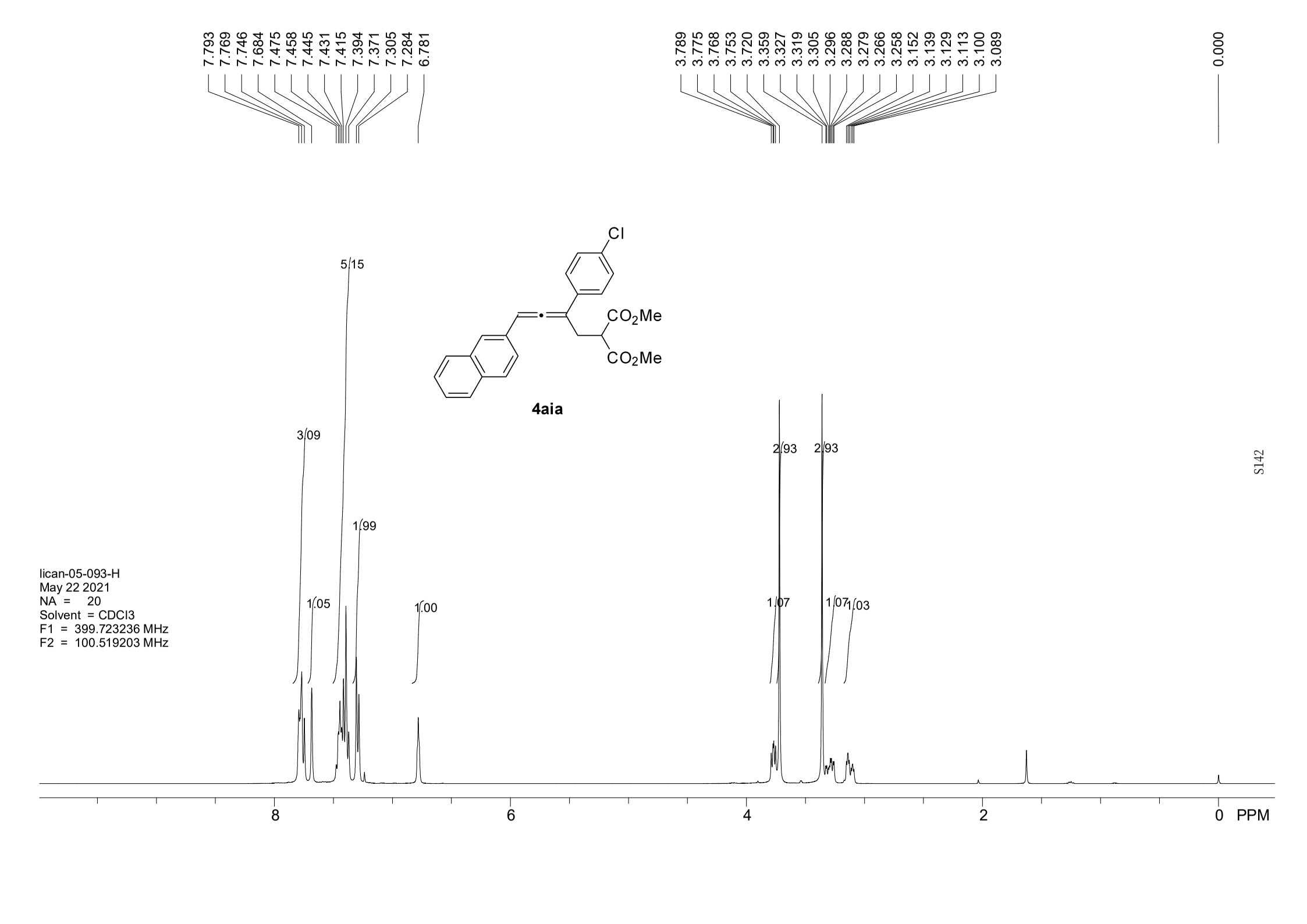

7.800
7.776
7.752
7.691
7.464
7.447
7.433
7.409
7.388
7.049
7.027
7.009
6.773
3.793
3.777
3.759
3.726
3.724
3.371
3.368
3.330
3.309
3.291
3.269
3.153
3.123
3.113
-0.000
zzn-1-089-H
Oct 27 2021
NA = 8
Solvent = CDCl3
F1 = 399.717865 MHz
F2 = 100.517960 MHz
F
CO2Me
CO2Me
4aha
3.11
5.10
1.04
2.00
1.00
4.04
4.11
1.07
S139
8
6
4
2
0
PPM

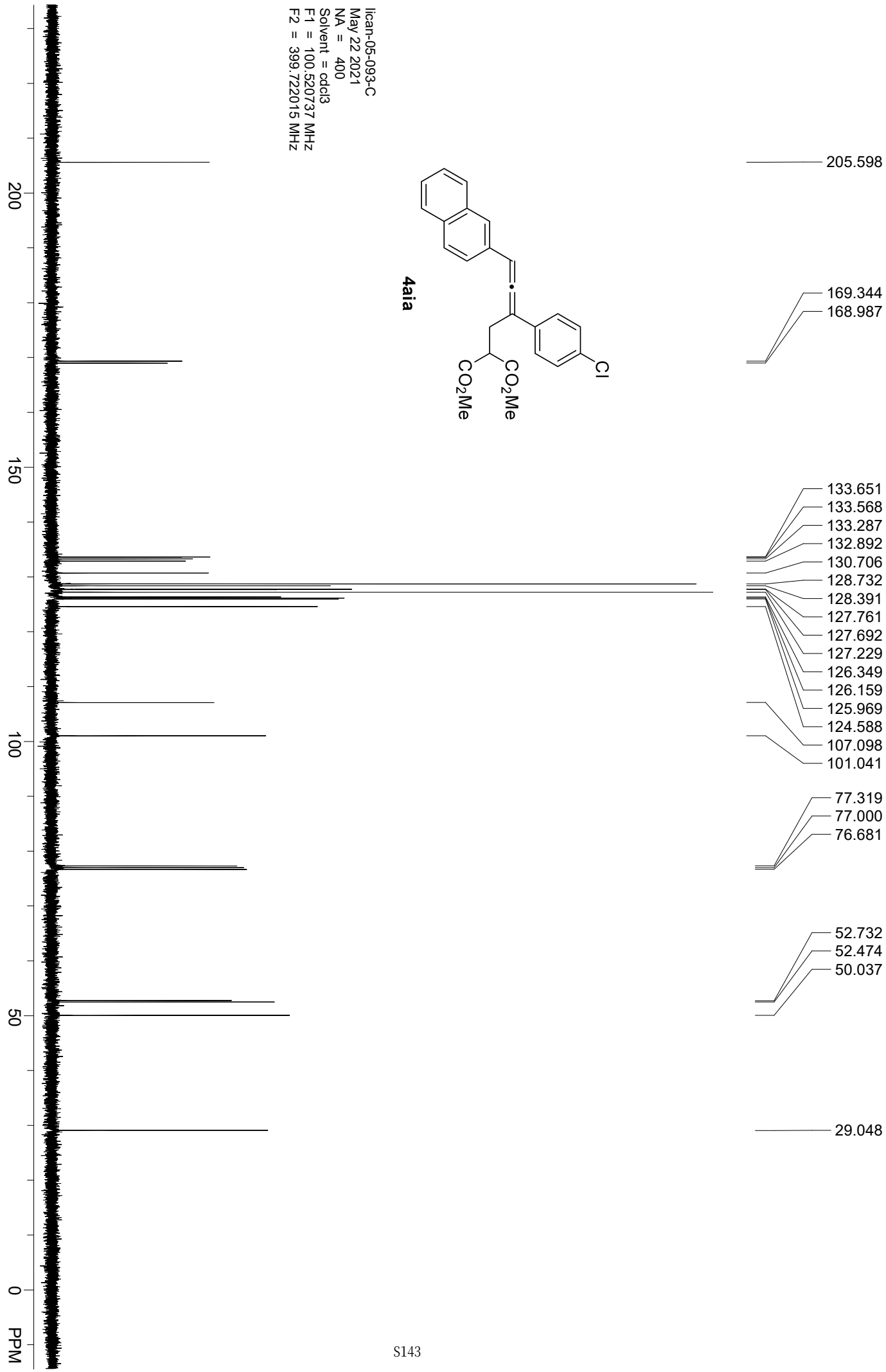

zzn-1-089-C
Nov 1 2022
NA = 1024
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
4aha
CO2Me
CO2Me
F
205.424
205.409
169.417
169.072
163.502
161.043
133.624
132.911
131.164
131.134
130.973
128.391
127.786
127.717
127.663
127.587
126.353
126.116
125.947
124.637
115.651
115.436
107.108
100.857
77.322
77.000
76.686
52.729
52.477
50.117
29.309
200
150
100
50
0
PPM

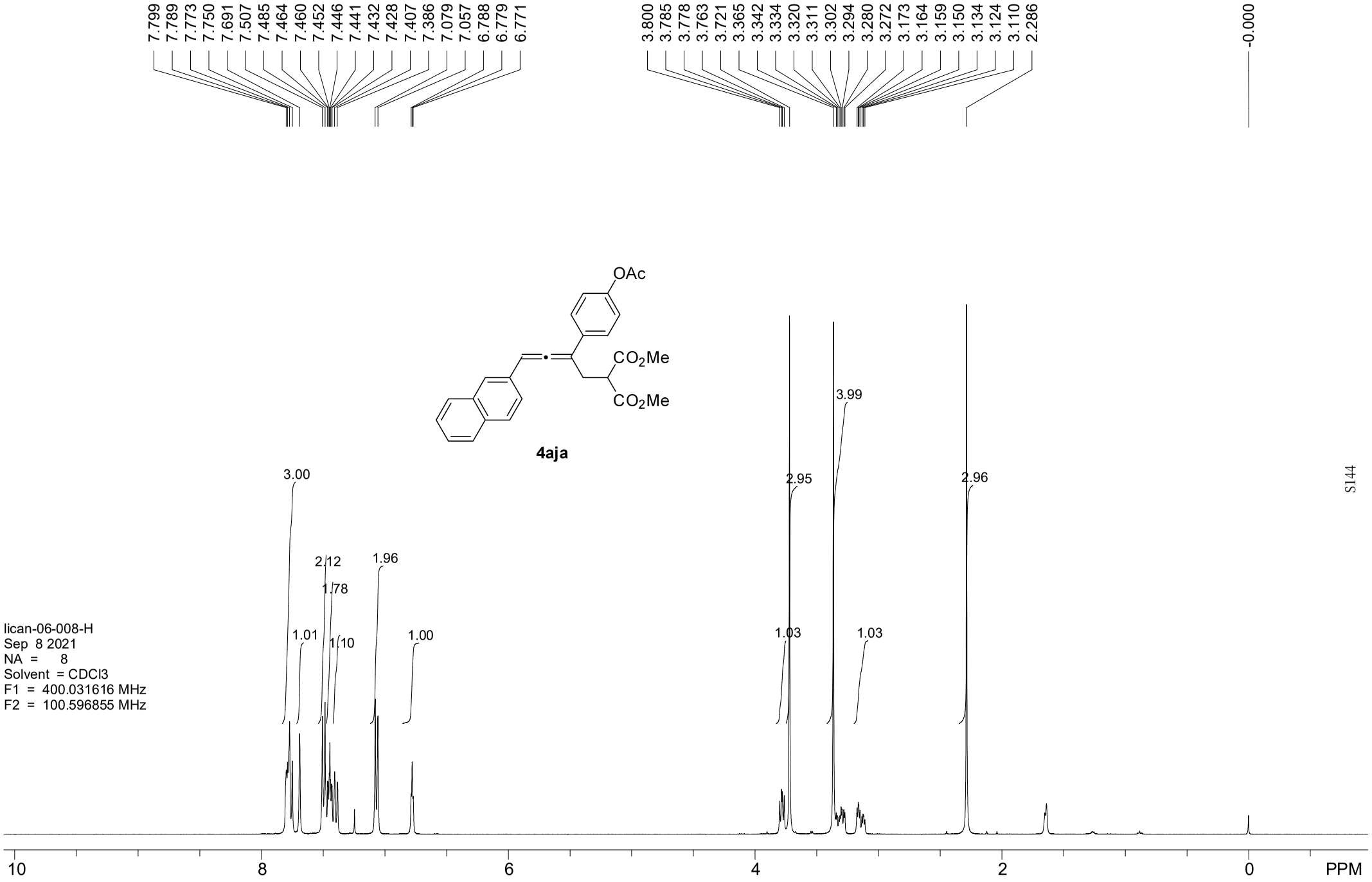


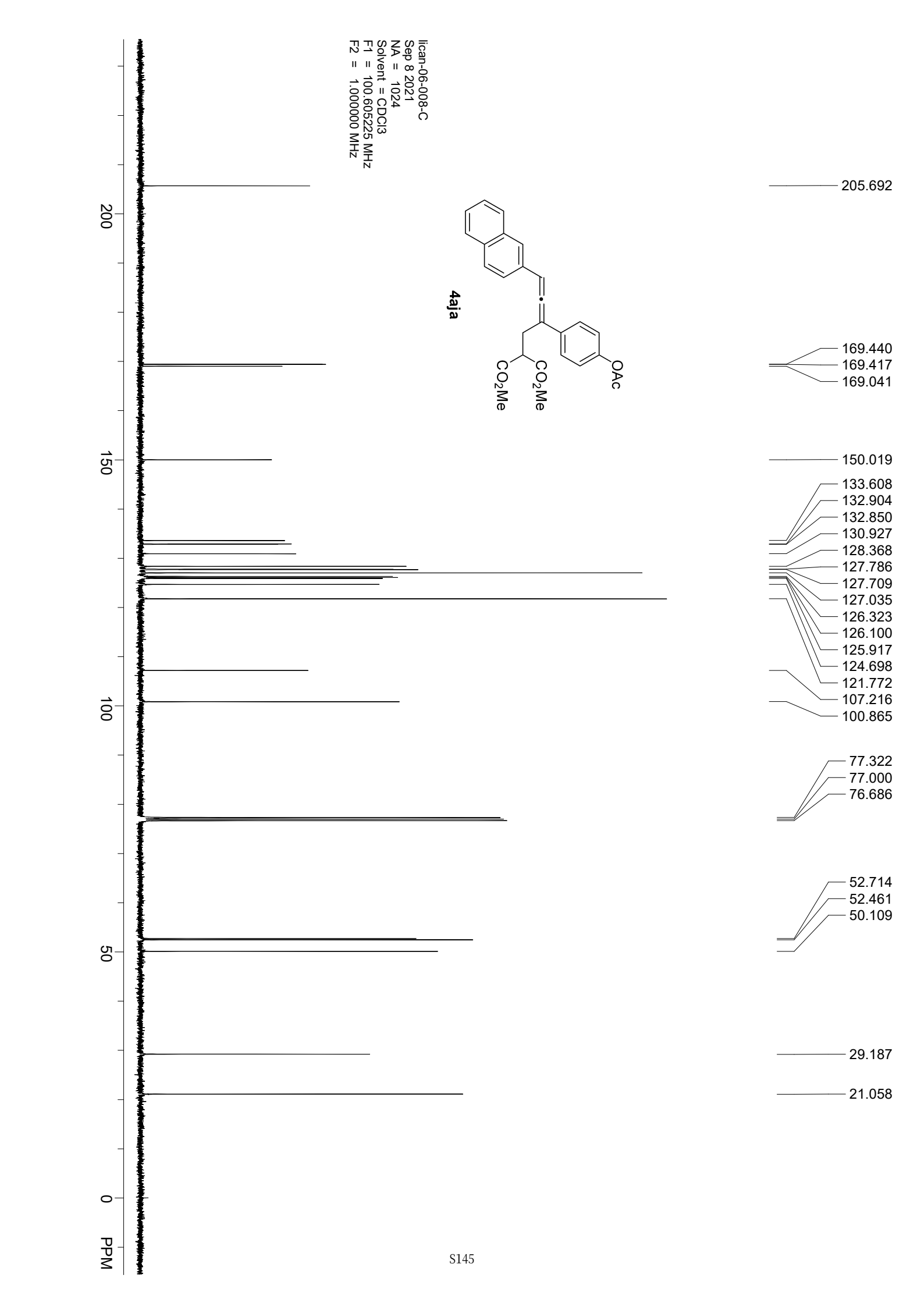
4aha

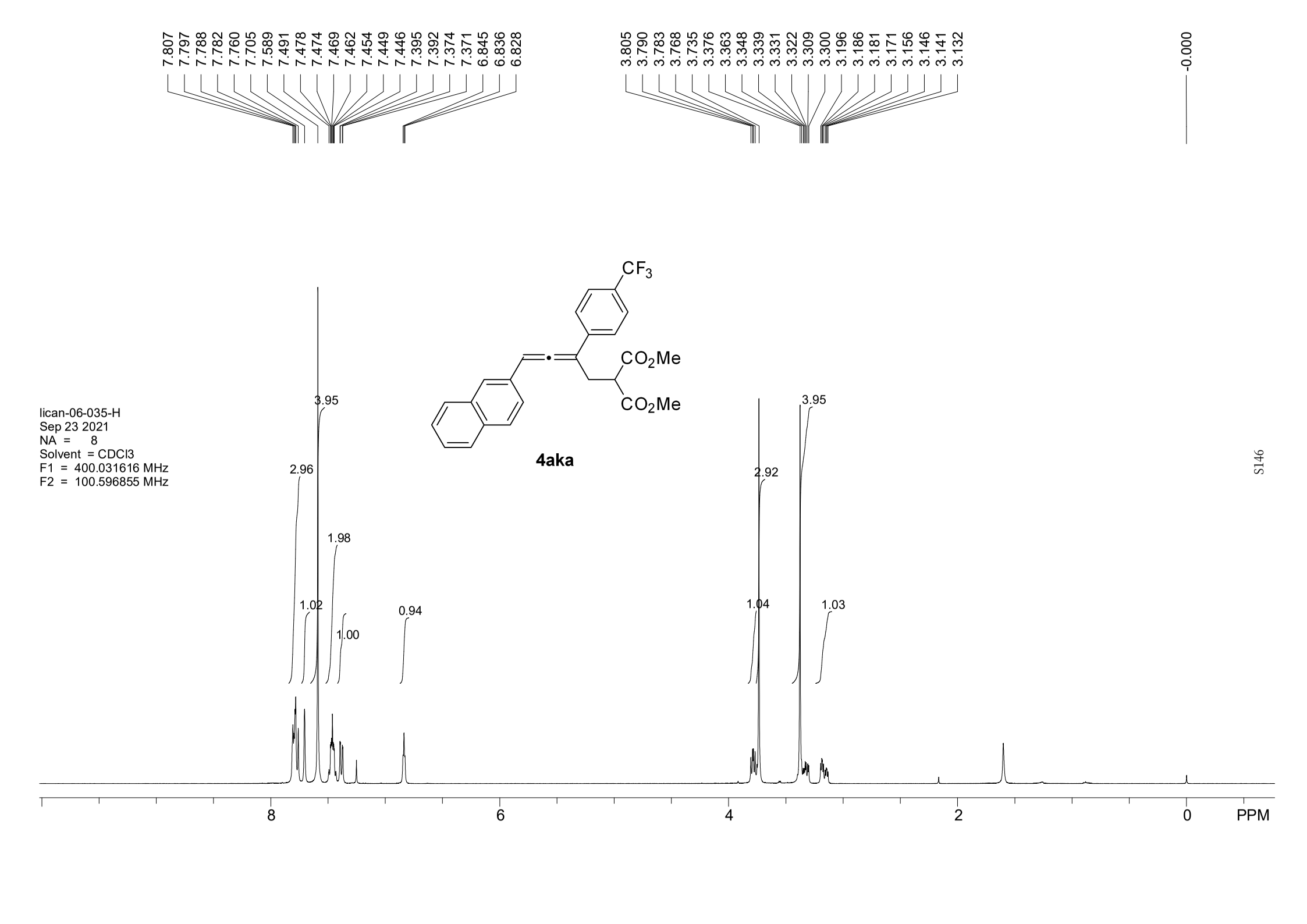
zzn-1-089-F
Nov 1 2021
NA = 4
Solvent = CDCl3
F1 = 376.406921 MHz
F2 = 100.596855 MHz

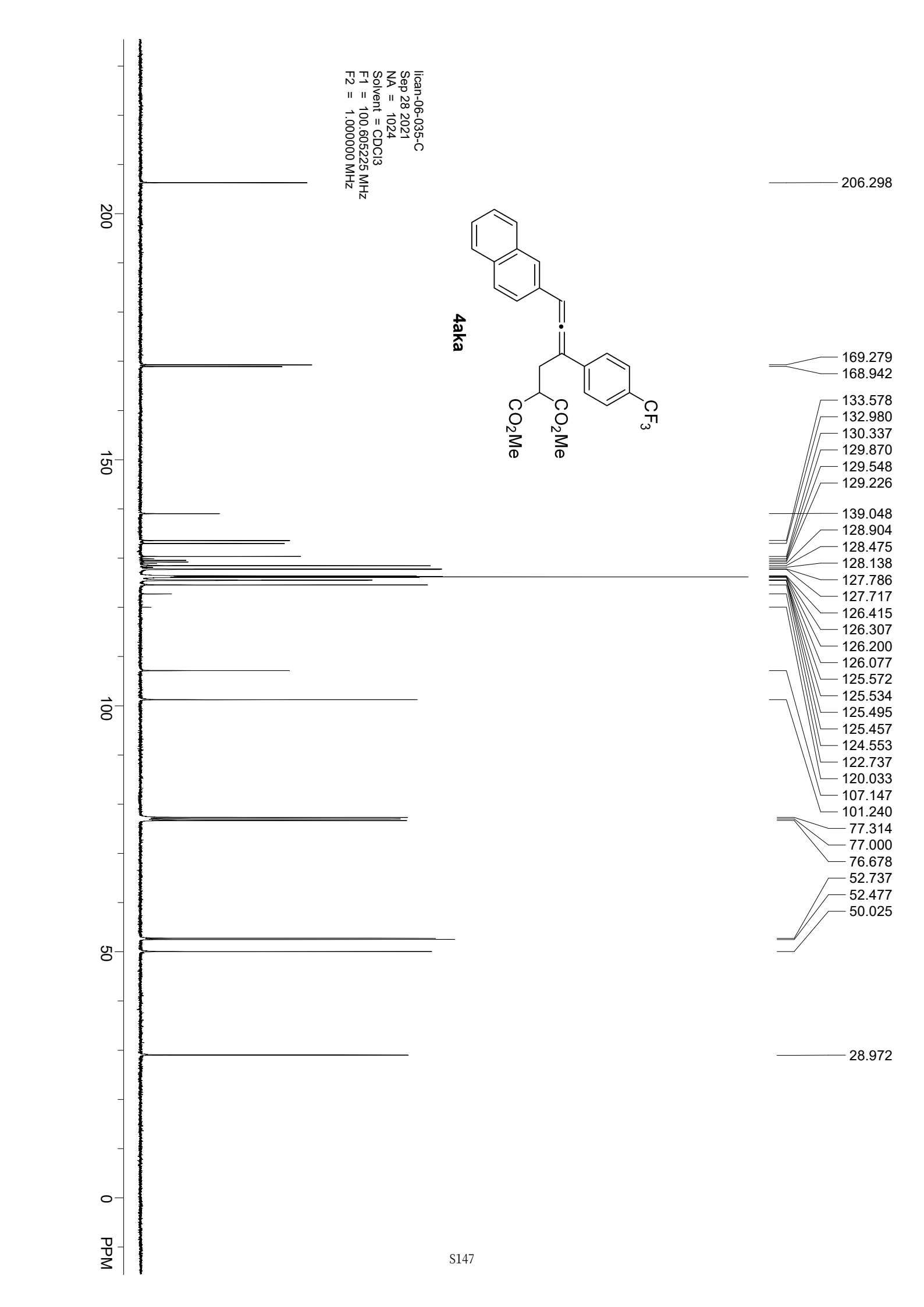

7.793
7.769
7.746
7.684
7.475
7.458
7.445
7.431
7.415
7.394
7.371
7.305
7.284
6.781
3.789
3.775
3.768
3.753
3.720
3.359
3.327
3.319
3.305
3.296
3.288
3.279
3.266
3.258
3.152
3.139
3.129
3.113
3.100
3.089
0.000
Cl
CO2Me
CO2Me
4aia
5.15
3.09
1.99
1.05
1.00
2.93
2.93
1.07
1.07
1.03
lican-05-093-H
May 22 2021
NA = 20
Solvent = CDCl3
F1 = 399.723236 MHz
F2 = 100.519203 MHz
S142
8
6
4
2
0
PPM

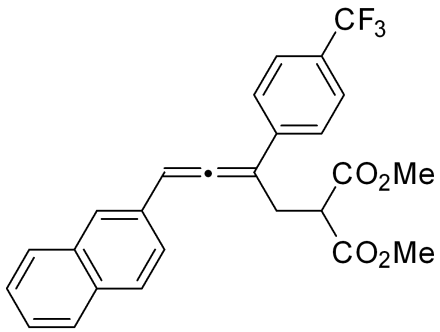

lican-05-093-C
May 22 2021
NA = 400
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
4aia
CO2Me
CO2Me
Cl
205.598
169.344
168.987
133.651
133.568
133.287
132.892
130.706
128.732
128.391
127.761
127.692
127.229
126.349
126.159
125.969
124.588
107.098
101.041
77.319
77.000
76.681
52.732
52.474
50.037
29.048
200
150
100
50
0
PPM


7.799
7.789
7.773
7.750
7.691
7.507
7.485
7.464
7.460
7.452
7.446
7.441
7.432
7.428
7.407
7.386
7.079
7.057
6.788
6.779
6.771
3.800
3.785
3.778
3.763
3.721
3.365
3.342
3.334
3.320
3.311
3.302
3.294
3.280
3.272
3.173
3.164
3.159
3.150
3.134
3.124
3.110
2.286
-0.000
OAc
CO2Me
CO2Me
4aja
3.00
2.12
1.78
1.96
1.01
1.10
1.00
2.95
3.99
2.96
1.03
1.03
lican-06-008-H
Sep 8 2021
NA = 8
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
S144
10
8
6
4
2
0
PPM


lican-06-008-C
Sep 8 2021
NA = 1024
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
4aja
CO2Me
CO2Me
OAc
205.692
169.440
169.417
169.041
150.019
133.608
132.904
132.850
130.927
128.368
127.786
127.709
127.035
126.323
126.100
125.917
124.698
121.772
107.216
100.865
77.322
77.000
76.686
52.714
52.461
50.109
29.187
21.058
200
150
100
50
0
PPM

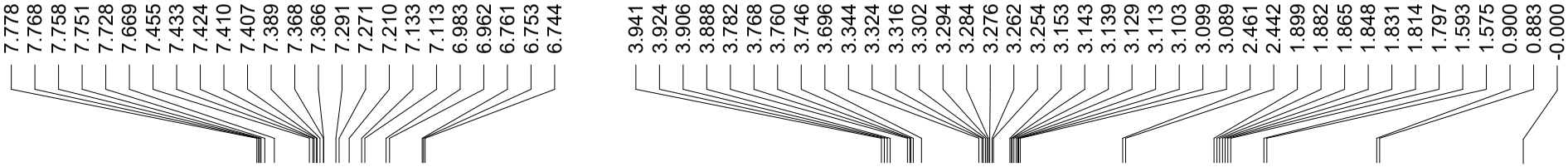

7.807
7.797
7.788
7.782
7.760
7.705
7.589
7.491
7.478
7.474
7.469
7.462
7.454
7.449
7.446
7.395
7.392
7.374
7.371
6.845
6.836
6.828
3.805
3.790
3.783
3.768
3.735
3.376
3.363
3.348
3.339
3.331
3.322
3.309
3.300
3.196
3.186
3.181
3.171
3.156
3.146
3.141
3.132
-0.000
lican-06-035-H
Sep 23 2021
NA = 8
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
CF3
CO2Me
CO2Me
4aka
3.95
2.96
1.98
1.02
1.00
0.94
2.92
3.95
1.04
1.03
S146
8
6
4
2
0
PPM

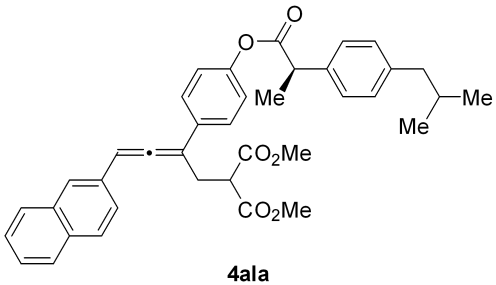

lican-06-035-C
Sep 28 2021
NA = 1024
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
4aka
CO2Me
CO2Me
CF3
206.298
169.279
168.942
133.578
132.980
130.337
129.870
129.548
129.226
139.048
128.904
128.475
128.138
127.786
127.717
126.415
126.307
126.200
126.077
125.572
125.534
125.495
125.457
124.553
122.737
120.033
107.147
101.240
77.314
77.000
76.678
52.737
52.477
50.025
28.972
200
150
100
50
0
PPM



4aka

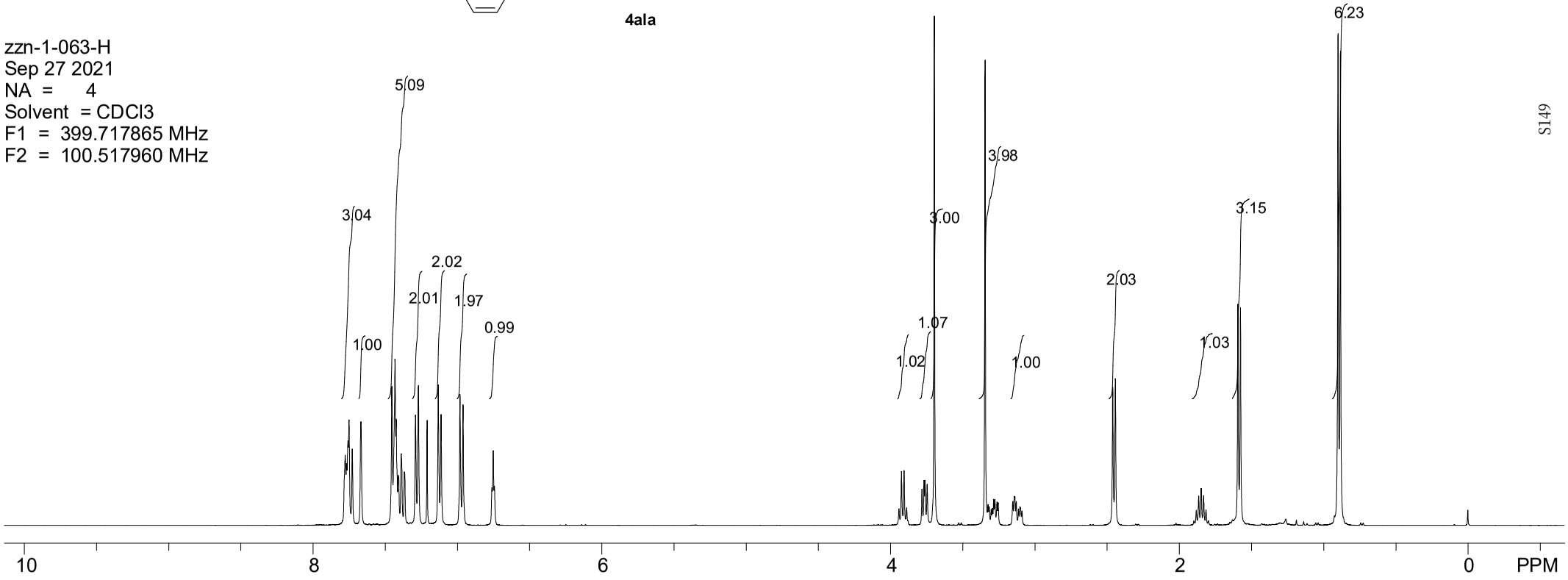
lican-06-035-F
Sep 23 2021
NA = 4
Solvent = CDCl3
F1 = 376.114410 MHz
F2 = 399.717072 MHz

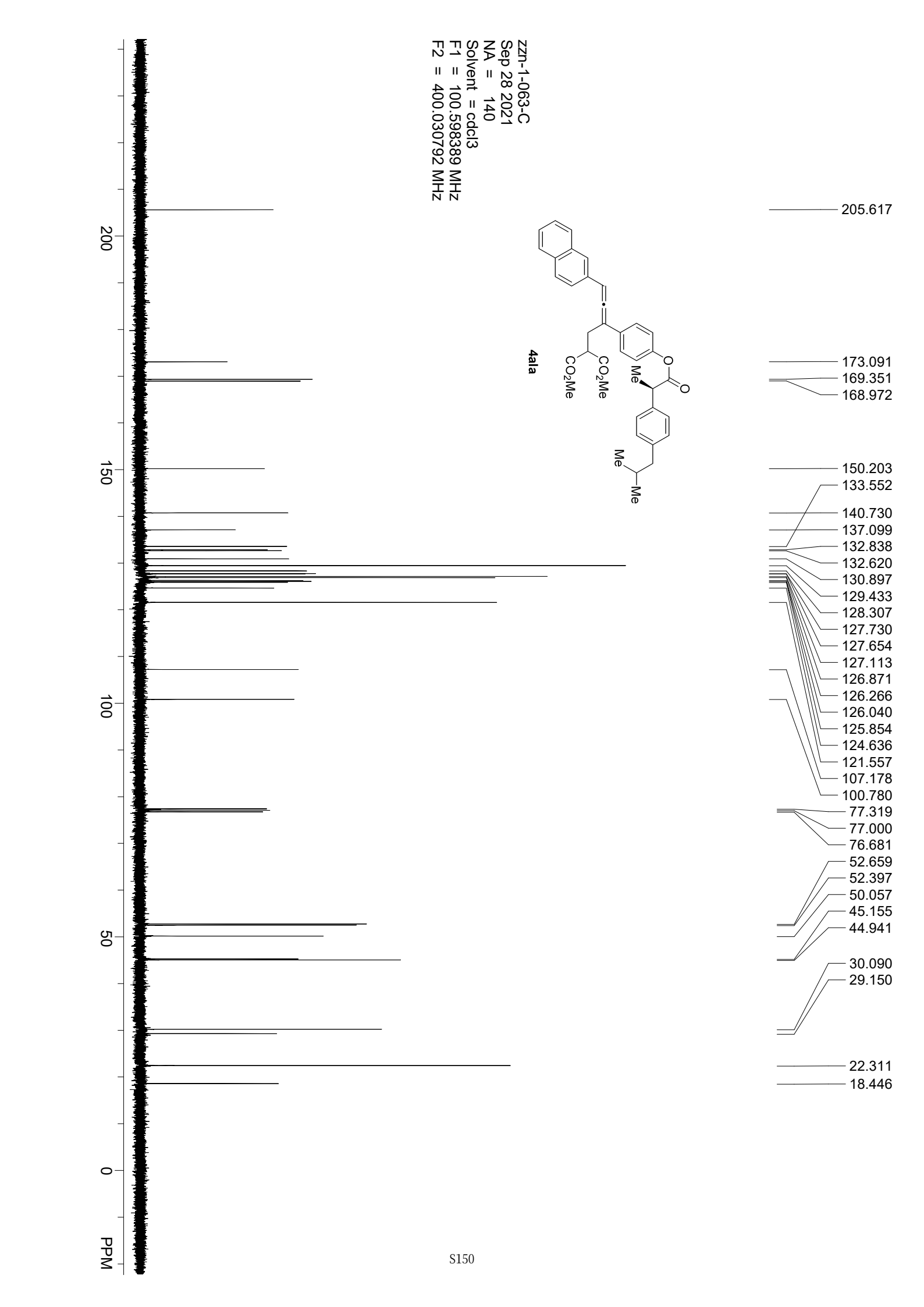




4ala

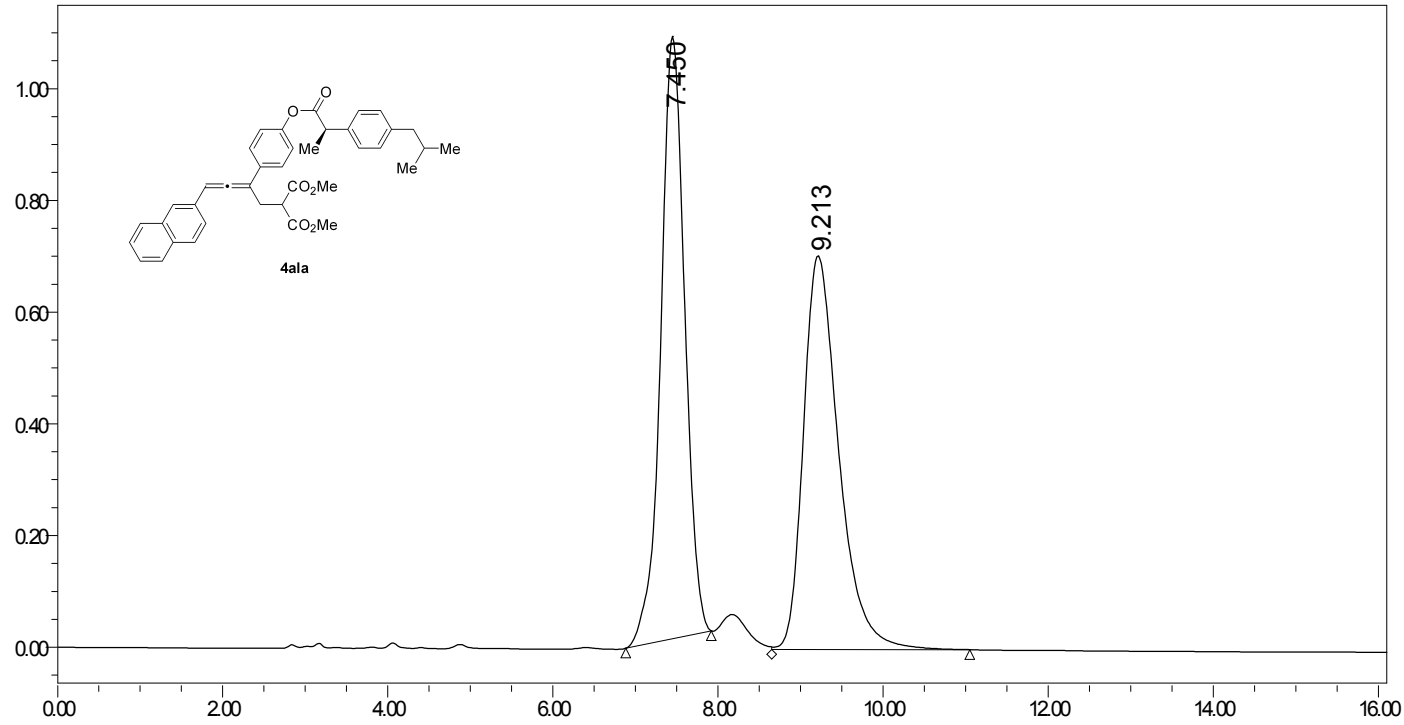
zzn-1-063-H
Sep 27 2021
NA = 4
Solvent = CDCl3
F1 = 399.717865 MHz
F2 = 100.517960 MHz



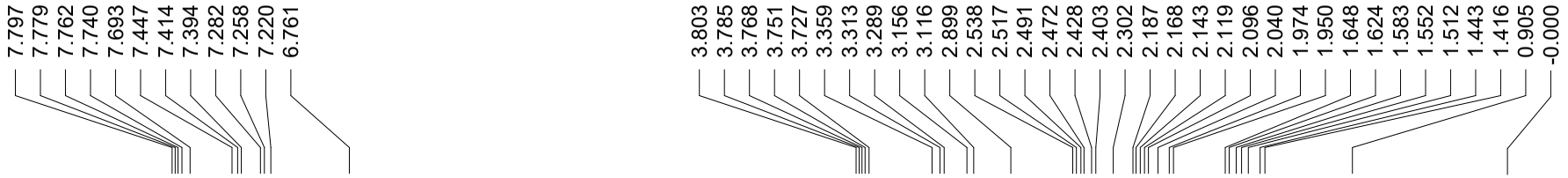

zzn-1-063-C
Sep 28 2021
NA = 140
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
4ala
205.617
173.091
169.351
168.972
150.203
133.552
140.730
137.099
132.838
132.620
130.897
129.433
128.307
127.730
127.654
127.113
126.871
126.266
126.040
125.854
124.636
121.557
107.178
100.780
77.319
77.000
76.681
52.659
52.397
50.057
45.155
44.941
30.090
29.150
22.311
18.446
200
150
100
50
0
PPM

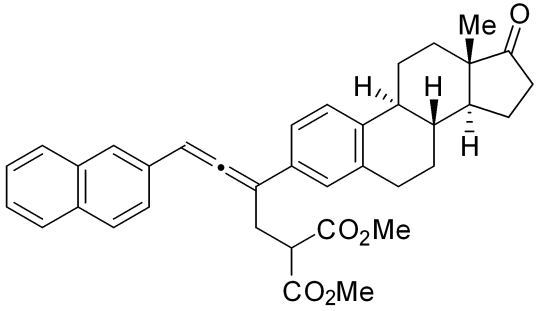
SAMPLE INFORMATION

Sample Name:	zzn-1-063-od-h-80-20-1.0-214-1	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	HPLC
Injection #:	2	Processing Method:	20181124
Injection Volume:	5.00 ul	Channel Name:	W2489 ChA
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 214nm
Date Acquired:	11/4/2021 1:04:14 AM CST		
Date Processed:	11/4/2021 1:21:26 AM CST		



	RT	Area	%Area	Height
1	7.450	21738816	50.88	1078621
2	9.213	20988918	49.12	704686

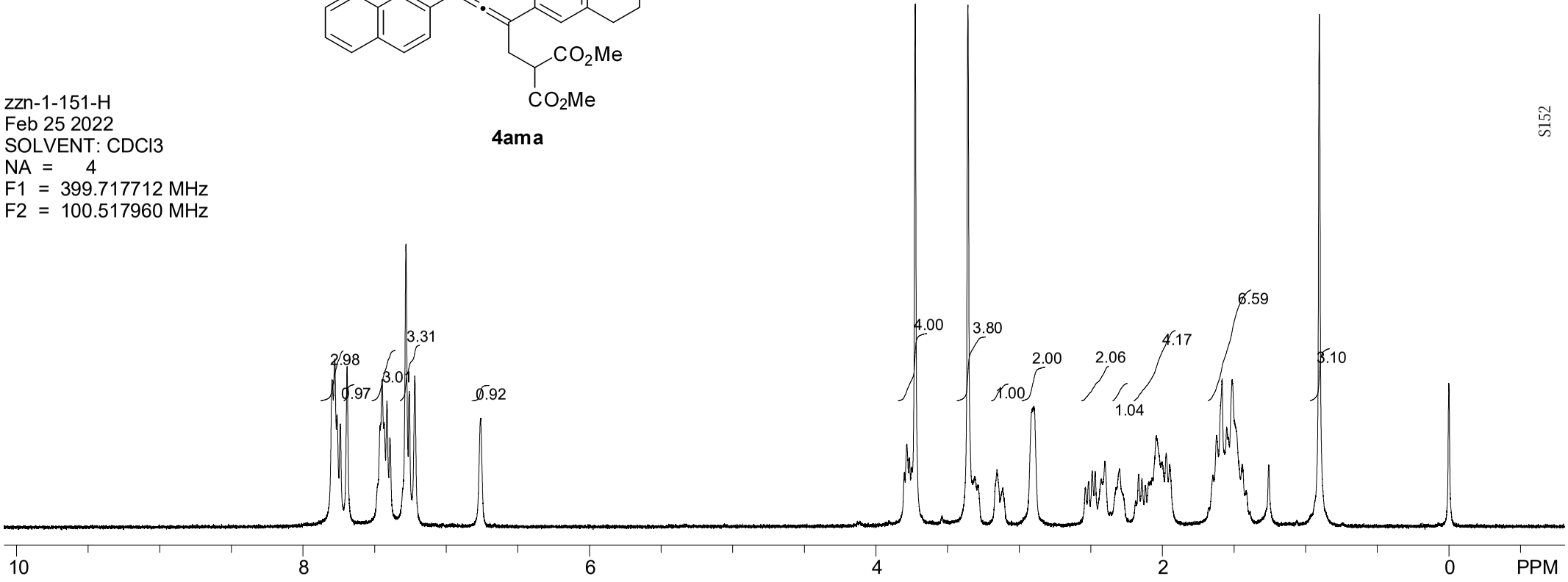


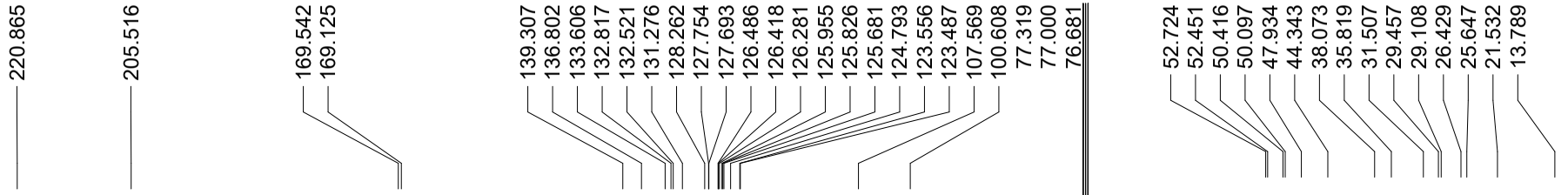


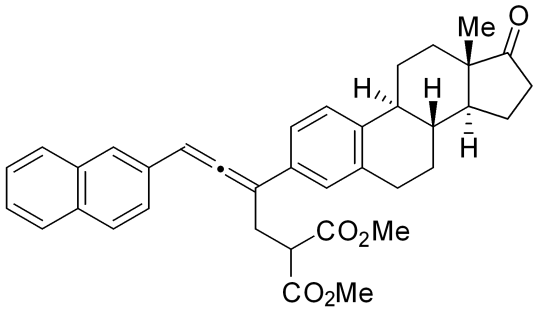
4ama

zzn-1-151-H
Feb 25 2022
SOLVENT: CDCl3
NA = 4
F1 = 399.717712 MHz
F2 = 100.517960 MHz

S152

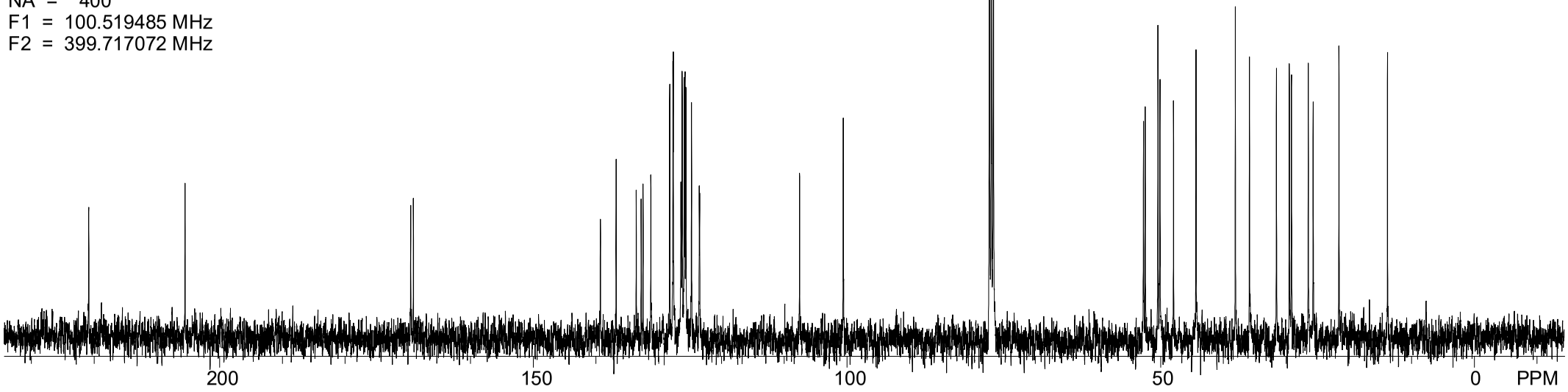






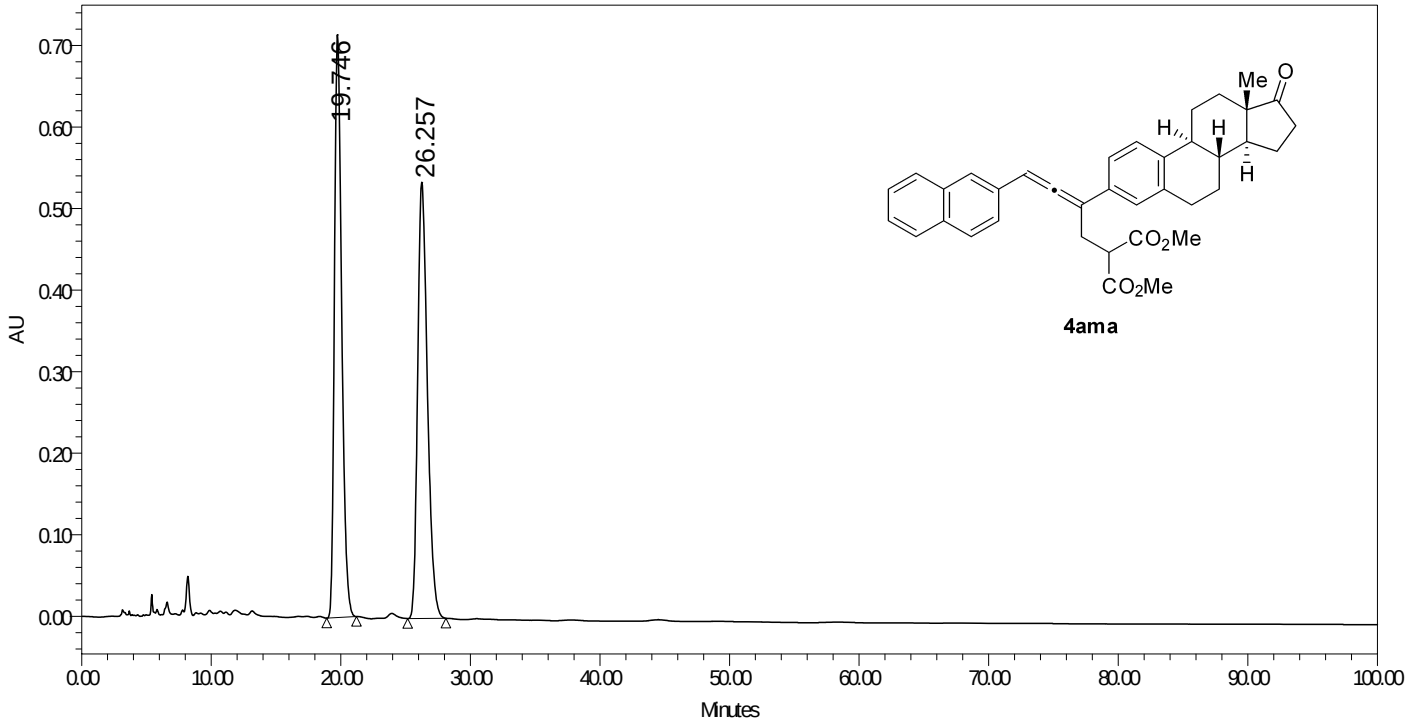
4ama

zzn-1-151-C
Feb 25 2022
SOLVENT: cdcl3
NA = 400
F1 = 100.519485 MHz
F2 = 399.717072 MHz



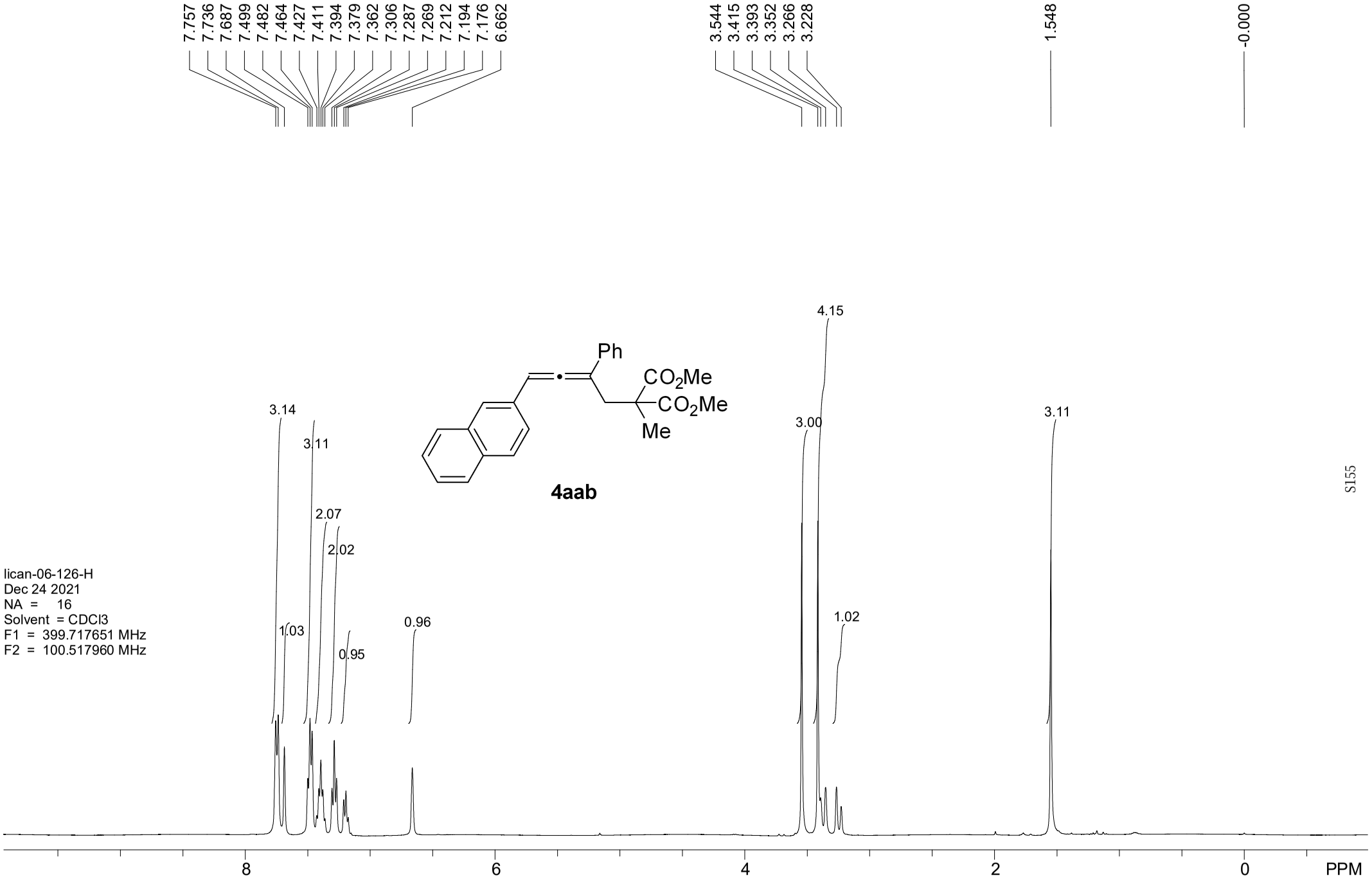
SAMPLE INFORMATION

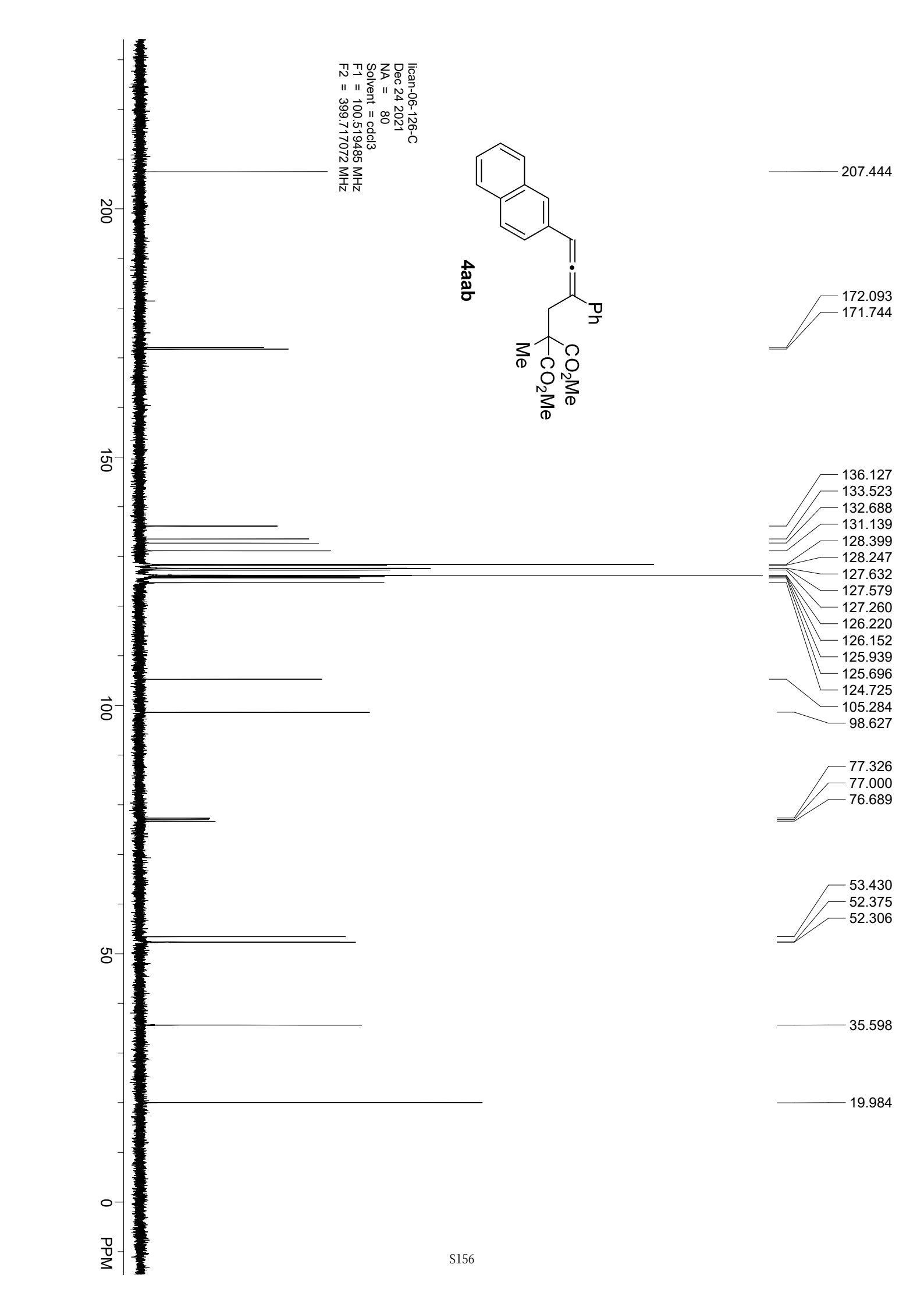
Sample Name:	zzn-1-151-ad-h-80-20-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	HPLC
Injection #:	5	Processing Method:	LC PQ
Injection Volume:	5.00 ul	Channel Name:	W2489 ChA
Run Time:	100.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 214nm
Date Acquired:	3/9/2022 5:52:05 PM EST		
Date Processed:	3/10/2022 6:30:30 PM EST		

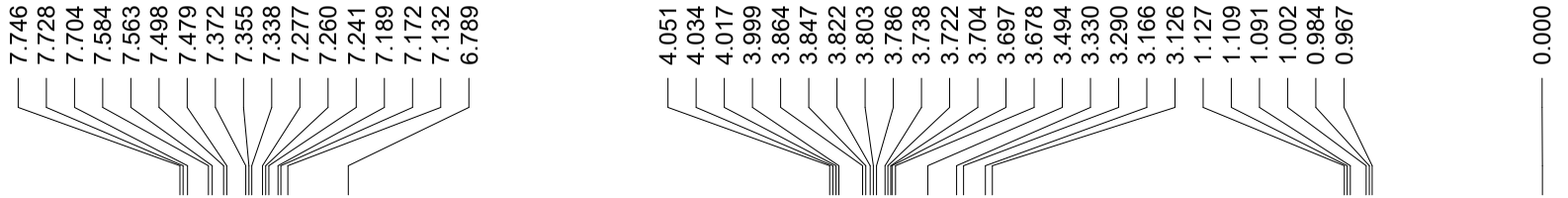


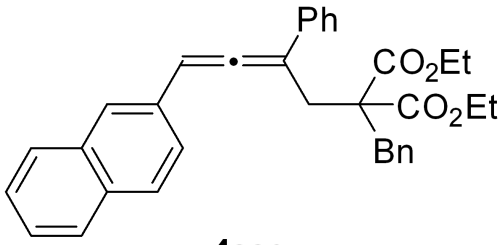
4ama

	RT	Area	%Area	Height
1	19.746	27899647	49.90	714841
2	26.257	28016707	50.10	535137

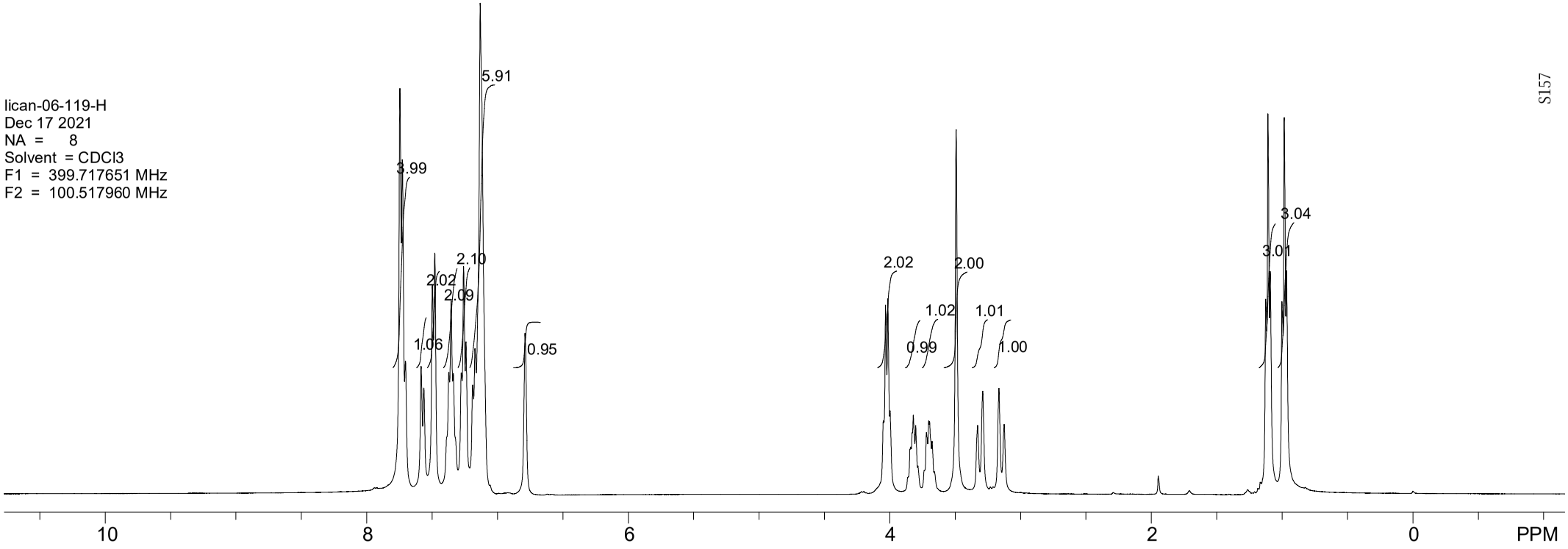

7.757
7.736
7.687
7.499
7.482
7.464
7.427
7.411
7.394
7.379
7.362
7.306
7.287
7.269
7.212
7.194
7.176
6.662
3.544
3.415
3.393
3.352
3.266
3.228
1.548
-0.000
Ph
CO2Me
CO2Me
Me
4aab
4.15
3.14
3.11
3.00
3.11
2.07
2.02
1.03
0.96
1.02
0.95
lican-06-126-H
Dec 24 2021
NA = 16
Solvent = CDCl3
F1 = 399.717651 MHz
F2 = 100.517960 MHz
8
6
4
2
0
PPM


lican-06-126-C
Dec 24 2021
NA = 80
Solvent = cdcl3
F1 = 100.519485 MHz
F2 = 399.717072 MHz
4aab
Ph
CO2Me
CO2Me
Me
207.444
172.093
171.744
136.127
133.523
132.688
131.139
128.399
128.247
127.632
127.579
127.260
126.220
126.152
125.939
125.696
124.725
105.284
98.627
77.326
77.000
76.689
53.430
52.375
52.306
35.598
19.984
200
150
100
50
0
PPM

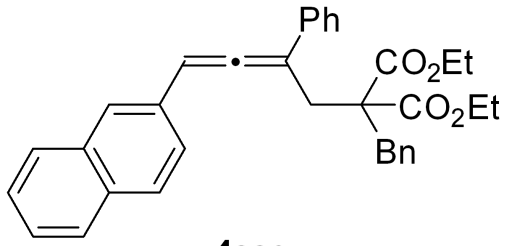

7.746
7.728
7.704
7.584
7.563
7.498
7.479
7.372
7.355
7.338
7.277
7.260
7.241
7.189
7.172
7.132
6.789
4.051
4.034
4.017
3.999
3.864
3.847
3.822
3.803
3.786
3.738
3.722
3.704
3.697
3.678
3.494
3.330
3.290
3.166
3.126
1.127
1.109
1.091
1.002
0.984
0.967
0.000


Ph
CO2Et
CO2Et
Bn

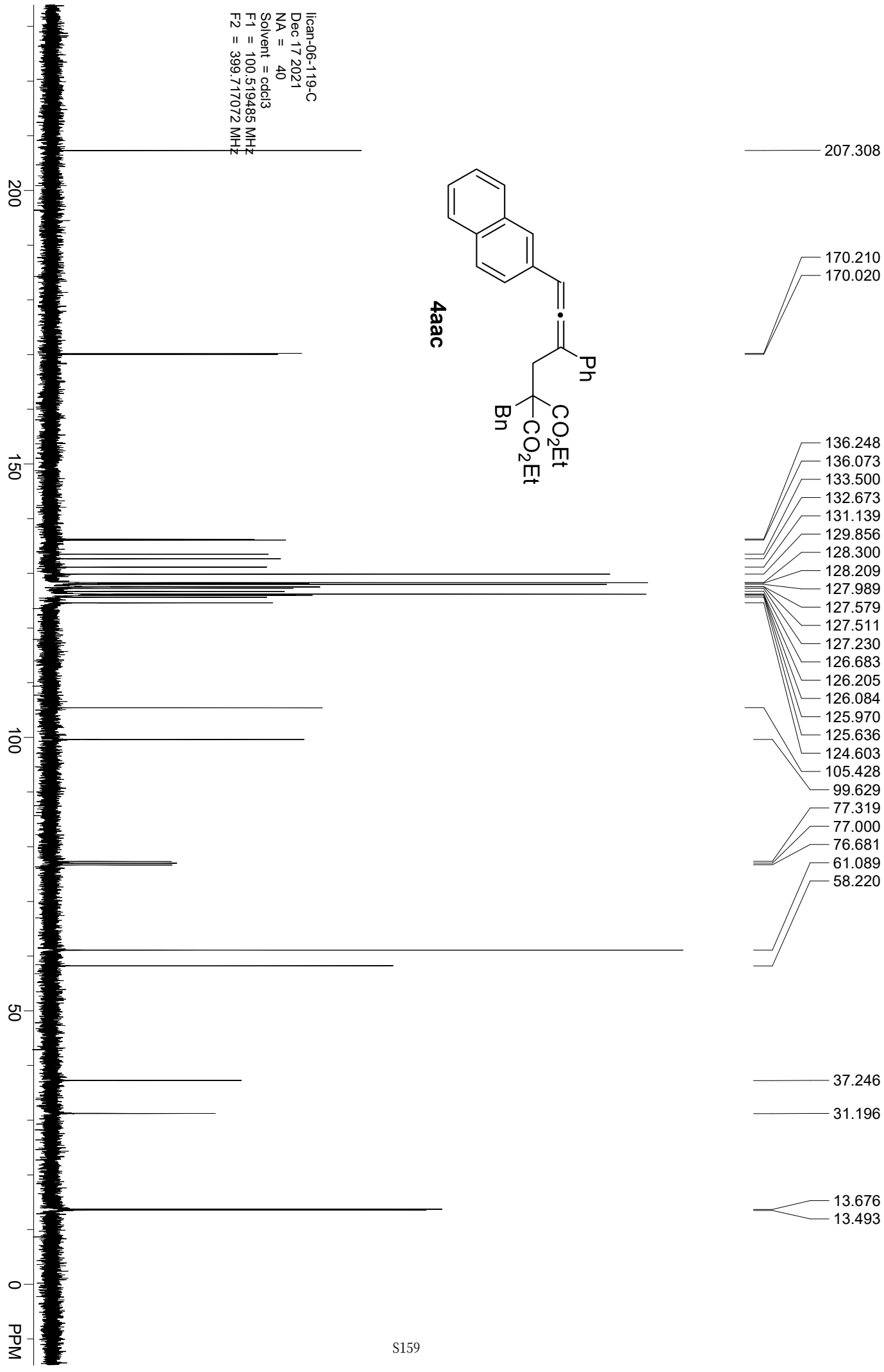
4aac

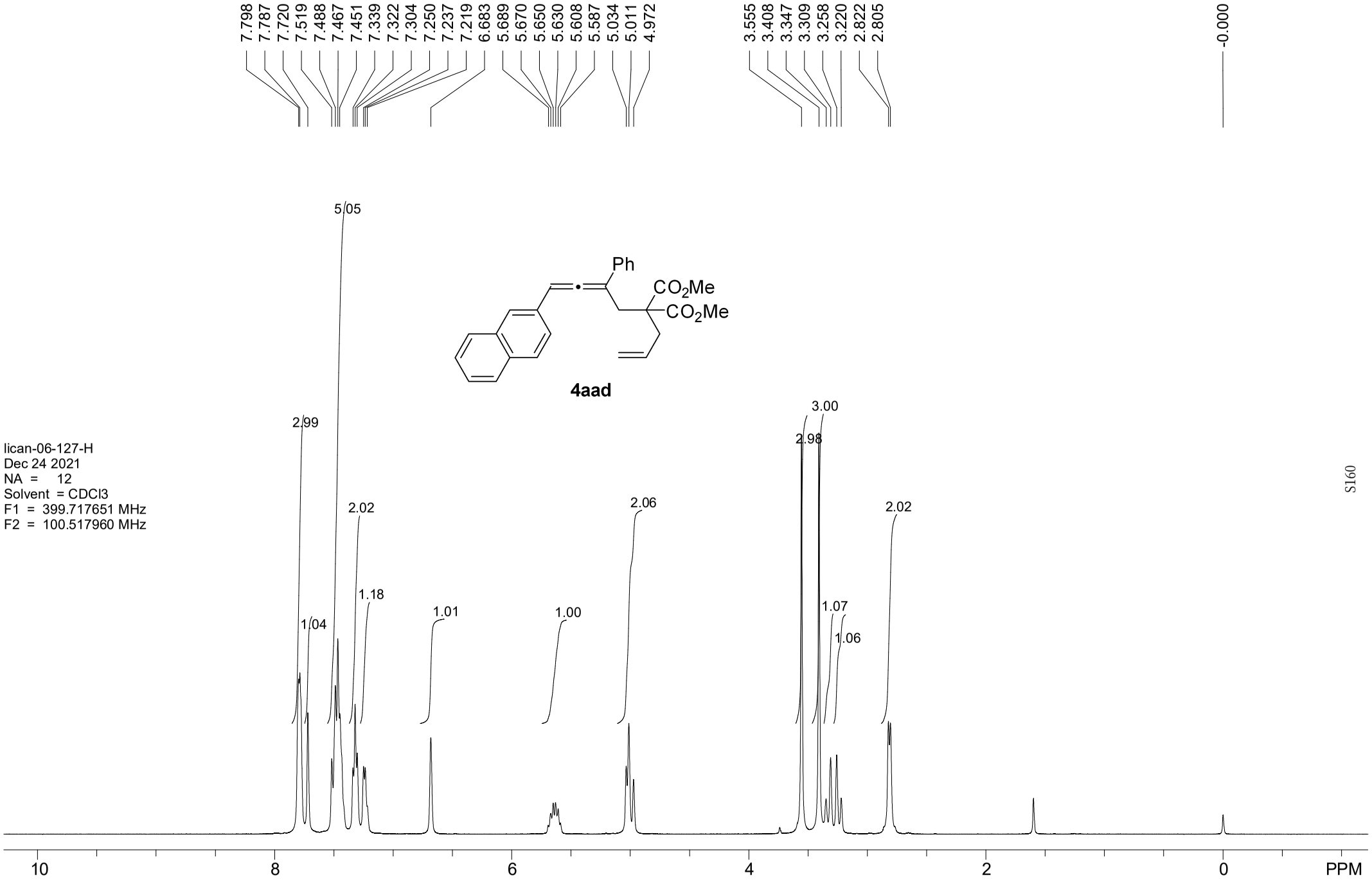

lican-06-119-H
Dec 17 2021
NA = 8
Solvent = CDCl3
F1 = 399.717651 MHz
F2 = 100.517960 MHz
3.99
1.06
2.02
2.09
2.10
5.91
0.95
2.02
0.99
1.02
2.00
1.01
1.00
3.01
3.04
10
8
6
4
2
0
PPM

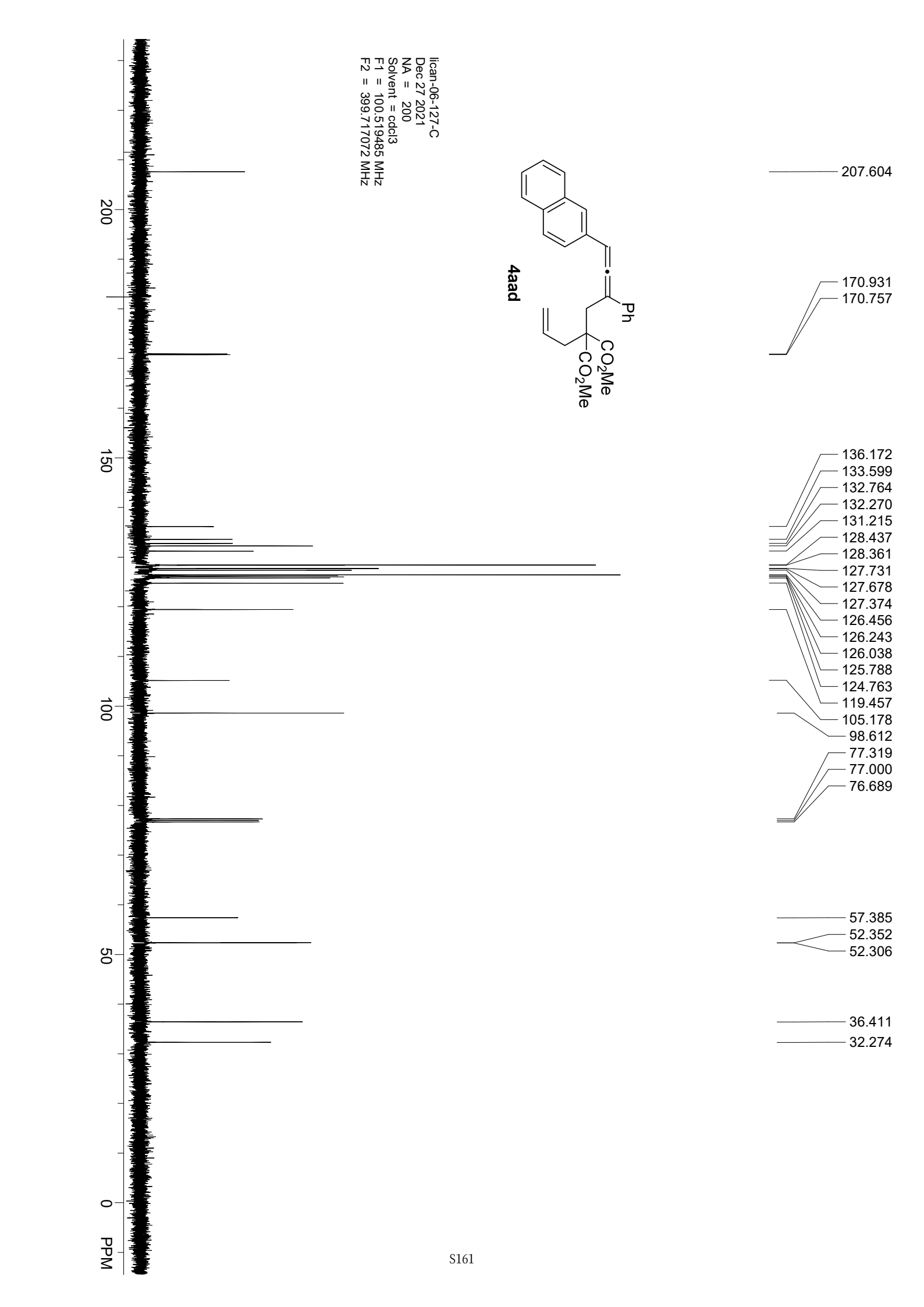
lican-06-119-purity
purity = 97%
31.6 mg product with 35 uL dibromomethane
Dec 18 2021
NA = 8
Solvent = CDCl3
F1 = 399.717651 MHz
F2 = 100.517960 MHz

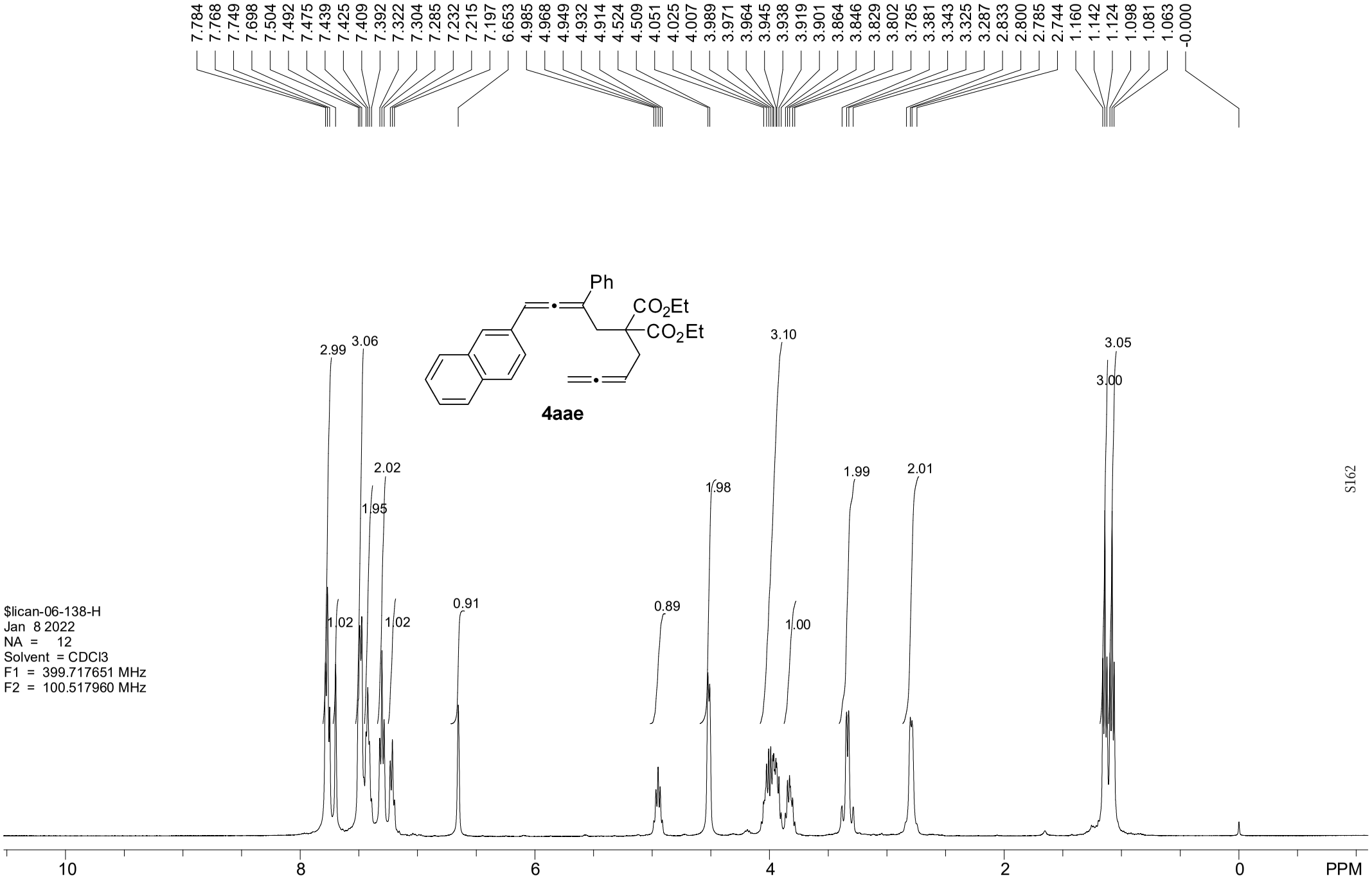


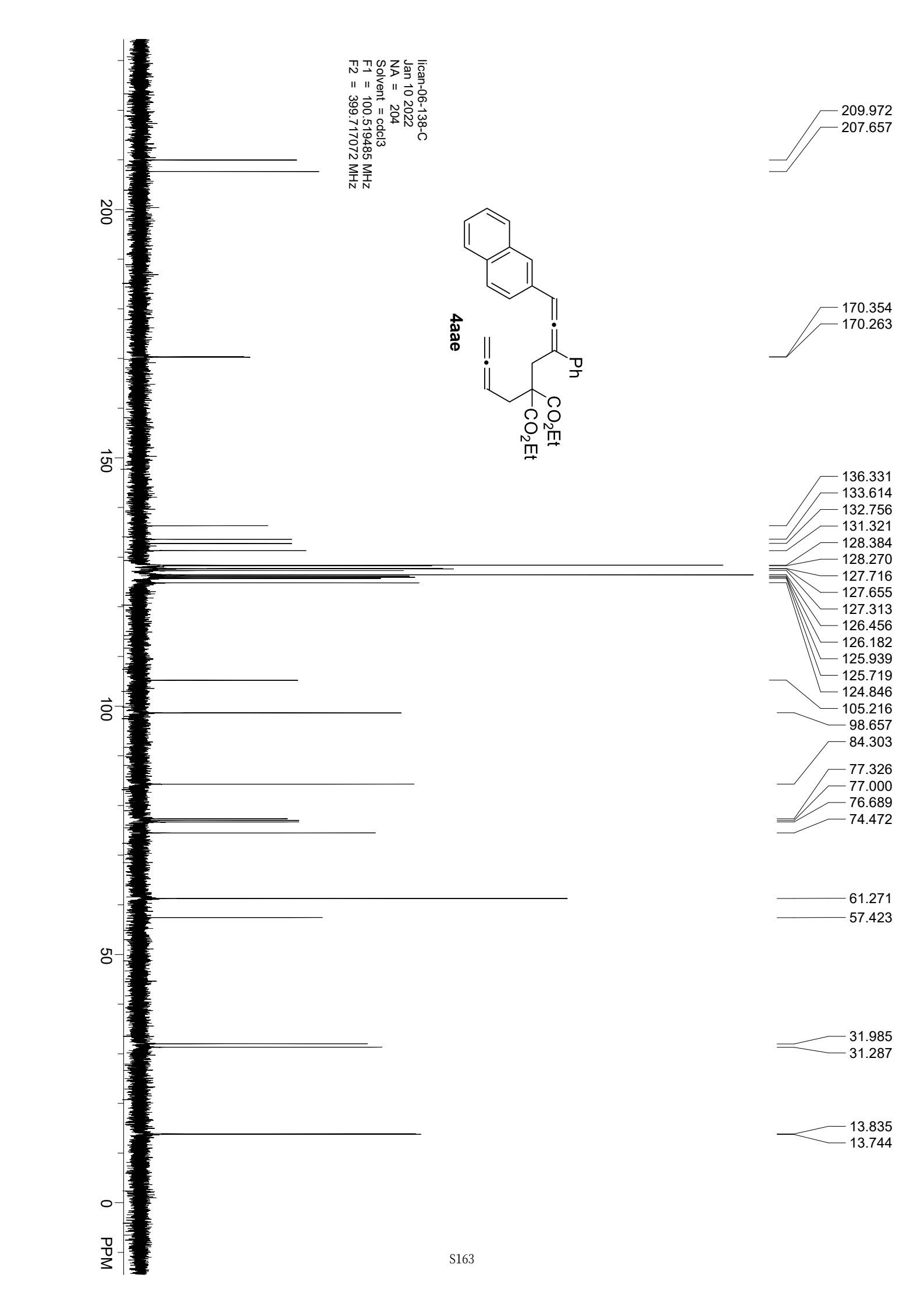
4aac

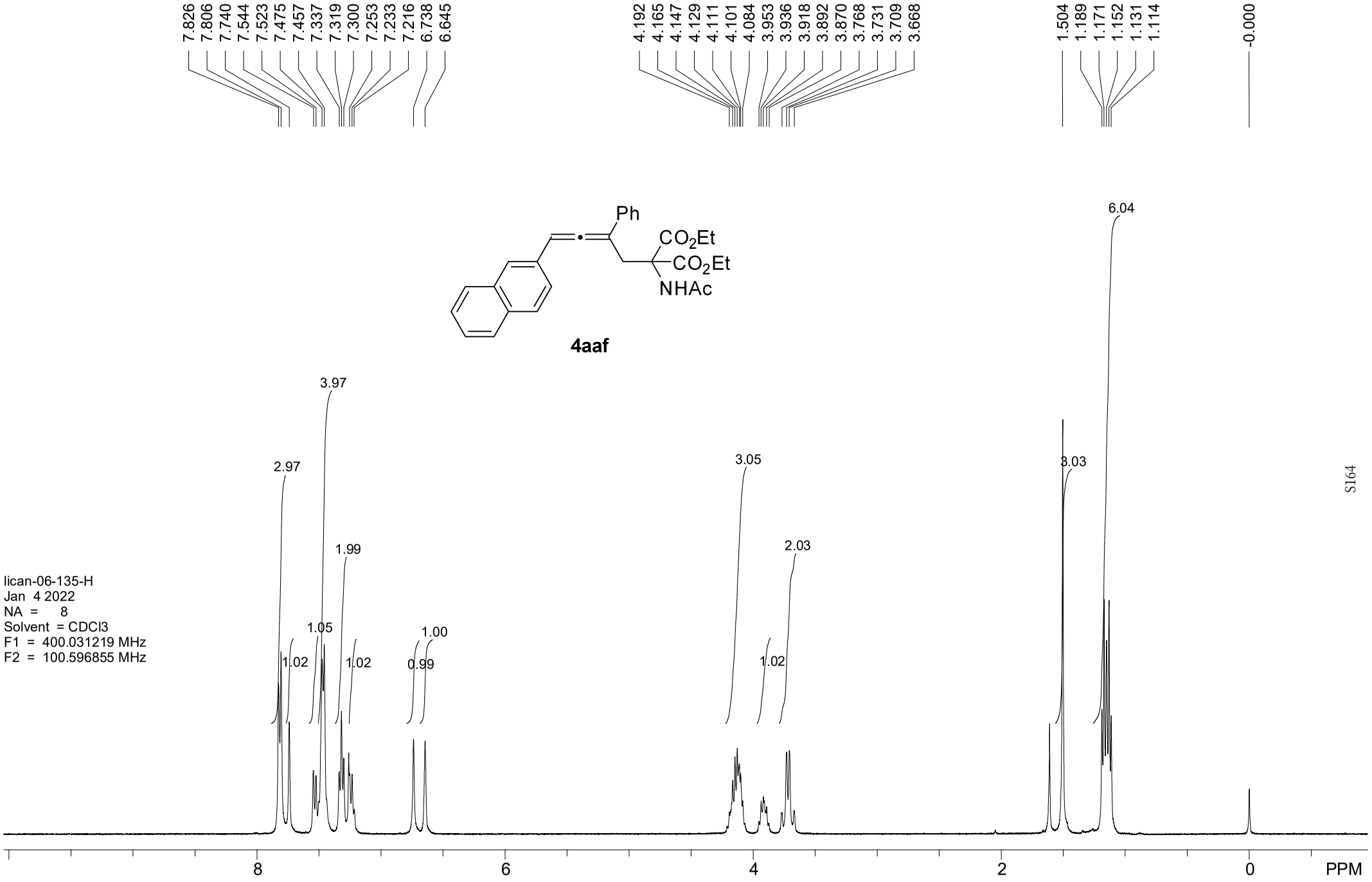

lican-06-119-C
Dec 17 2021
NA = 40
Solvent = cdcl3
F1 = 100.519485 MHz
F2 = 399.717072 MHz
4aac
Ph
Bn
CO2Et
CO2Et
207.308
170.210
170.020
136.248
136.073
133.500
132.673
131.139
129.856
128.300
128.209
127.989
127.579
127.511
127.230
126.683
126.205
126.084
125.970
125.636
124.603
105.428
99.629
77.319
77.000
76.681
61.089
58.220
37.246
31.196
13.676
13.493
200
150
100
50
0
PPM

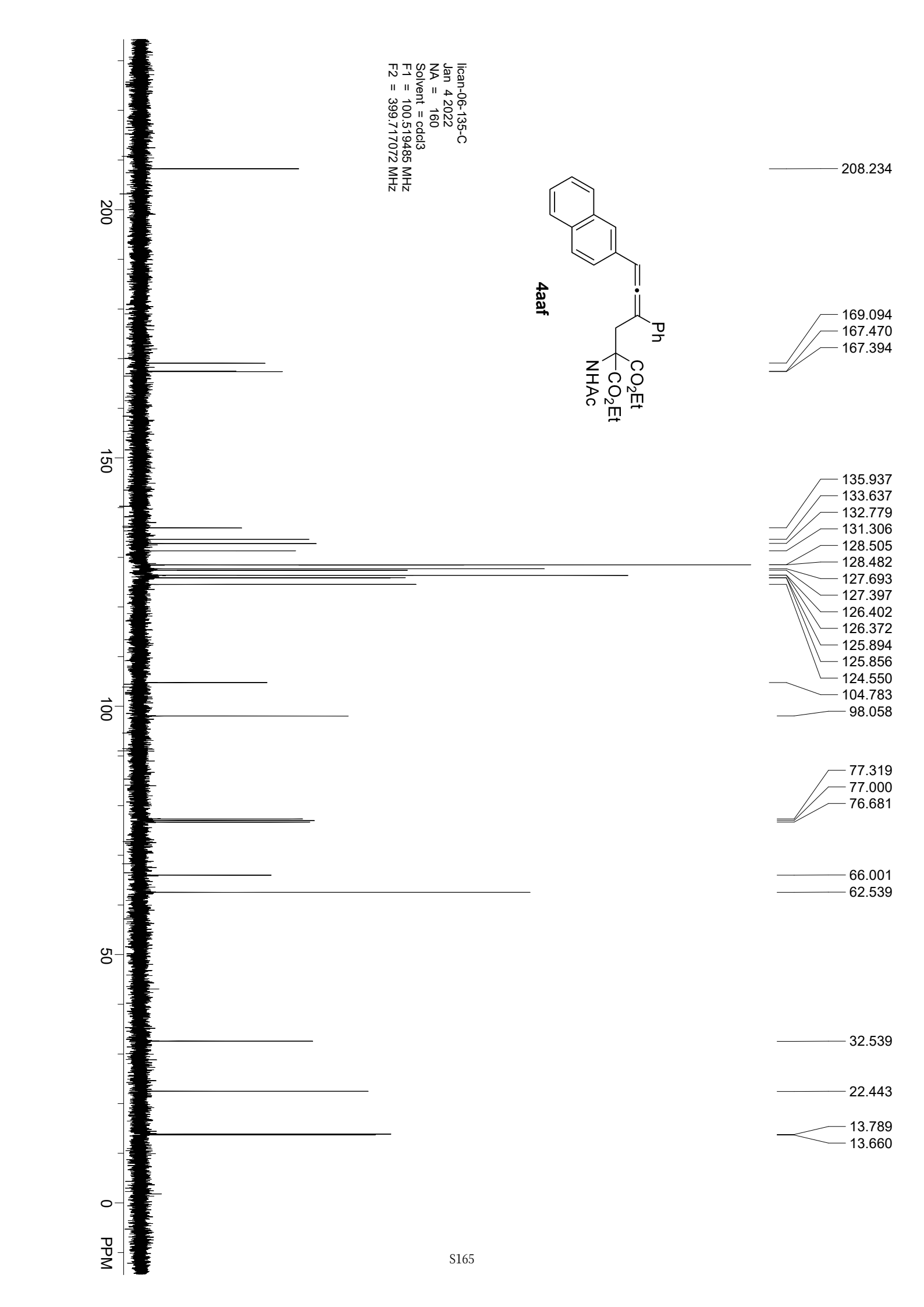

7.798
7.787
7.720
7.519
7.488
7.467
7.451
7.339
7.322
7.304
7.250
7.237
7.219
6.683
5.689
5.670
5.650
5.630
5.608
5.587
5.034
5.011
4.972
3.555
3.408
3.347
3.309
3.258
3.220
2.822
2.805
-0.000
Ph
CO2Me
CO2Me
4aad
lican-06-127-H
Dec 24 2021
NA = 12
Solvent = CDCl3
F1 = 399.717651 MHz
F2 = 100.517960 MHz
5.05
2.99
2.02
1.18
1.04
1.01
1.00
2.06
3.00
2.98
1.07
1.06
2.02
S160
10
8
6
4
2
0
PPM

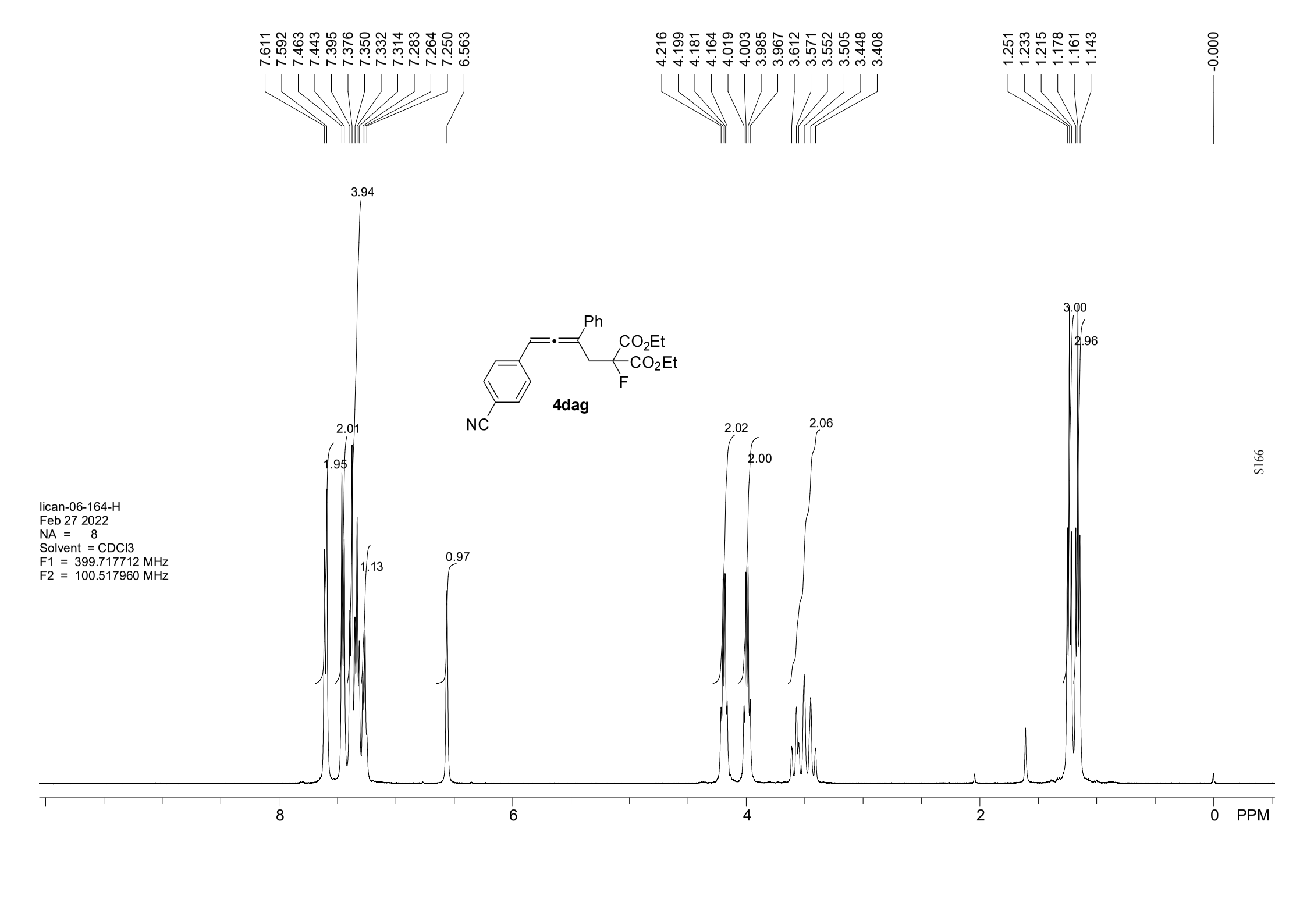

lican-06-127-C
Dec 27 2021
NA = 200
Solvent = cdcl3
F1 = 100.519485 MHz
F2 = 399.717072 MHz
4aad
Ph
CO2Me
CO2Me
207.604
170.931
170.757
136.172
133.599
132.764
132.270
131.215
128.437
128.361
127.731
127.678
127.374
126.456
126.243
126.038
125.788
124.763
119.457
105.178
98.612
77.319
77.000
76.689
57.385
52.352
52.306
36.411
32.274
200
150
100
50
0
PPM

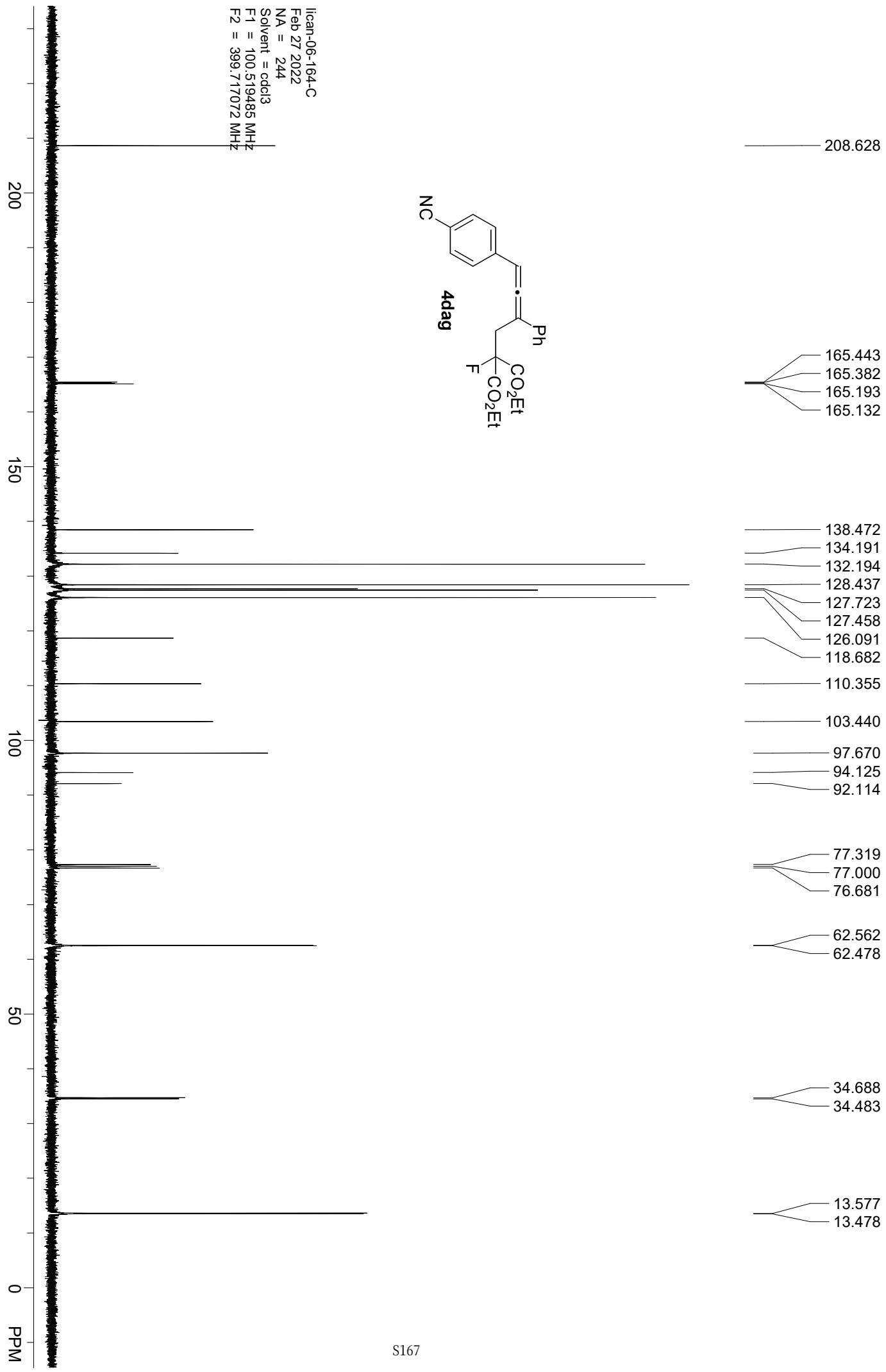

7.784
7.768
7.749
7.698
7.504
7.492
7.475
7.439
7.425
7.409
7.392
7.322
7.304
7.285
7.232
7.215
7.197
6.653
4.985
4.968
4.949
4.932
4.914
4.524
4.509
4.051
4.025
4.007
3.989
3.971
3.964
3.945
3.938
3.919
3.901
3.864
3.846
3.829
3.802
3.785
3.381
3.343
3.325
3.287
2.833
2.800
2.785
2.744
1.160
1.142
1.124
1.098
1.081
1.063
-0.000
Ph
CO2Et
CO2Et
4aae
2.99
3.06
2.02
1.95
1.02
1.02
0.91
0.89
1.98
3.10
1.00
1.99
2.01
3.05
3.00
S162
$lican-06-138-H
Jan 8 2022
NA = 12
Solvent = CDCl3
F1 = 399.717651 MHz
F2 = 100.517960 MHz
10
8
6
4
2
0
PPM

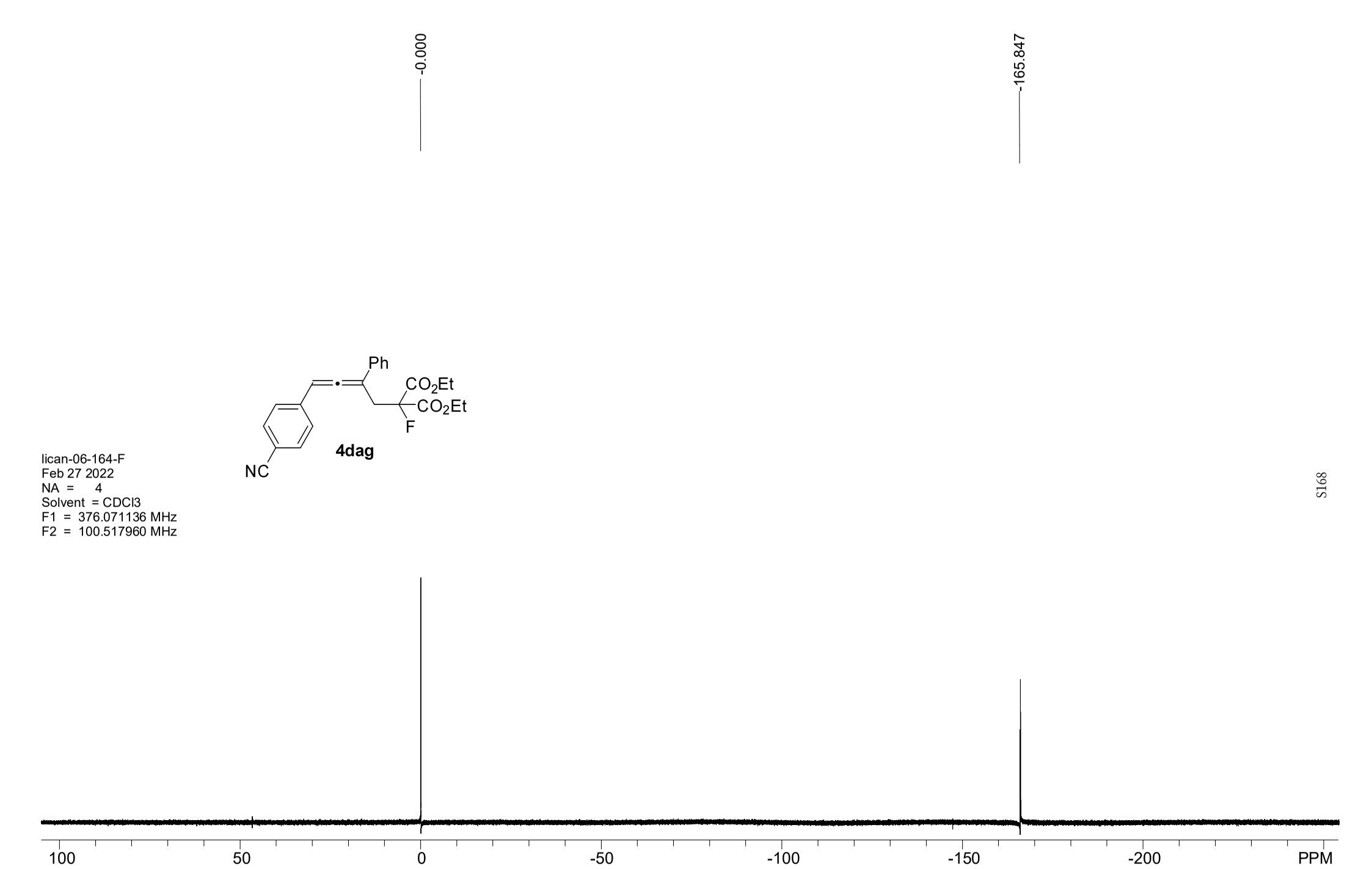

lican-06-138-C
Jan 10 2022
NA = 204
Solvent = cdcl3
F1 = 100.519485 MHz
F2 = 399.717072 MHz
4aae
Ph
CO2Et
CO2Et
209.972
207.657
170.354
170.263
136.331
133.614
132.756
131.321
128.384
128.270
127.716
127.655
127.313
126.456
126.182
125.939
125.719
124.846
105.216
98.657
84.303
77.326
77.000
76.689
74.472
61.271
57.423
31.985
31.287
13.835
13.744
200
150
100
50
0
PPM

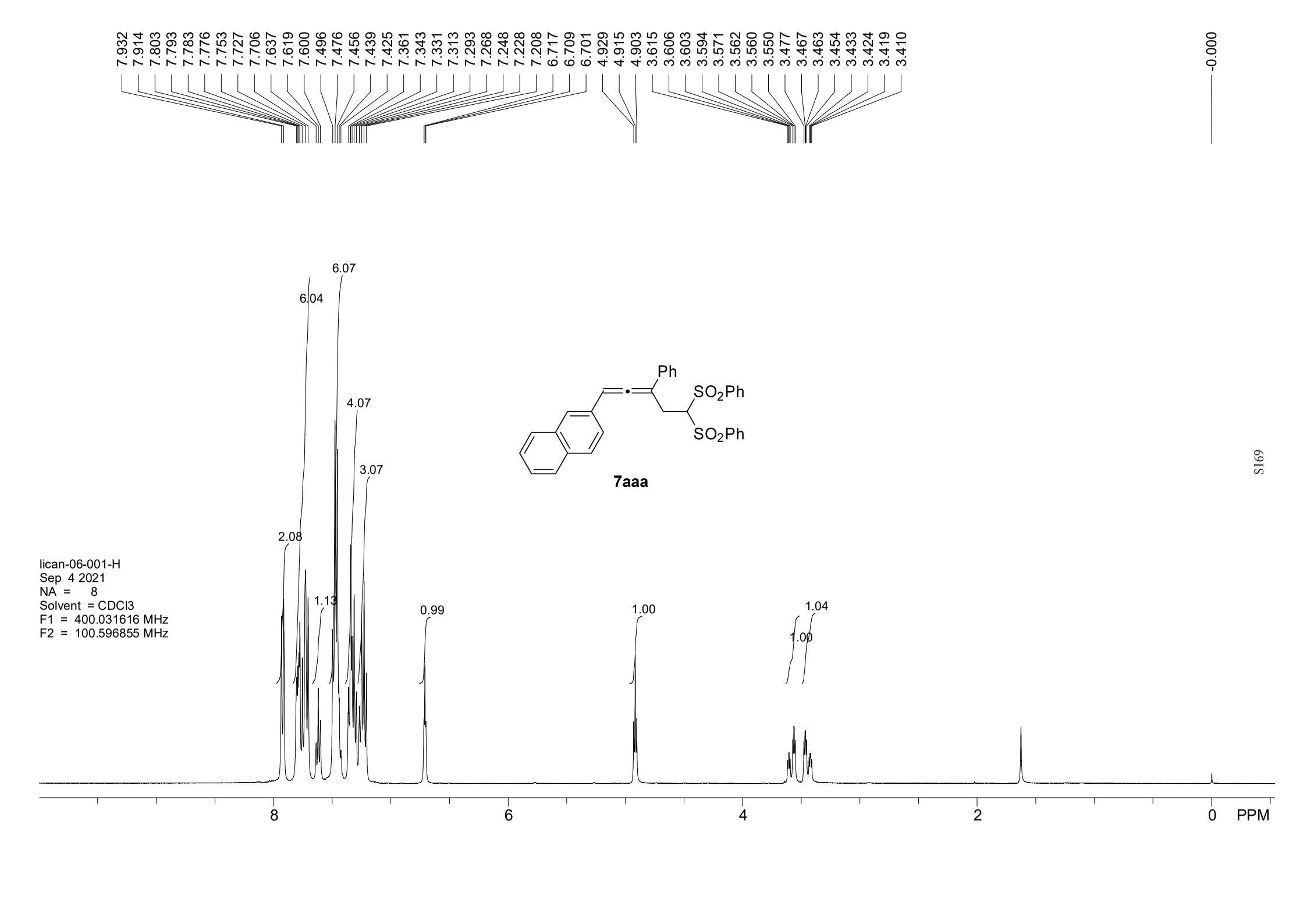

7.826
7.806
7.740
7.544
7.523
7.475
7.457
7.337
7.319
7.300
7.253
7.233
7.216
6.738
6.645
4.192
4.165
4.147
4.129
4.111
4.101
4.084
3.953
3.936
3.918
3.892
3.870
3.768
3.731
3.709
3.668
1.504
1.189
1.171
1.152
1.131
1.114
-0.000
Ph
CO2Et
CO2Et
NHAc
4aaf
6.04
3.97
3.05
3.03
2.97
2.03
1.99
1.05
1.00
1.02
1.02
0.99
1.02
lican-06-135-H
Jan 4 2022
NA = 8
Solvent = CDCl3
F1 = 400.031219 MHz
F2 = 100.596855 MHz
S164
8
6
4
2
0
PPM


lican-06-135-C
Jan 4 2022
NA = 160
Solvent = cdcl3
F1 = 100.519485 MHz
F2 = 399.717072 MHz
4aaf
Ph
CO2Et
CO2Et
NHAc
208.234
169.094
167.470
167.394
135.937
133.637
132.779
131.306
128.505
128.482
127.693
127.397
126.402
126.372
125.894
125.856
124.550
104.783
98.058
77.319
77.000
76.681
66.001
62.539
32.539
22.443
13.789
13.660
200
150
100
50
0
PPM

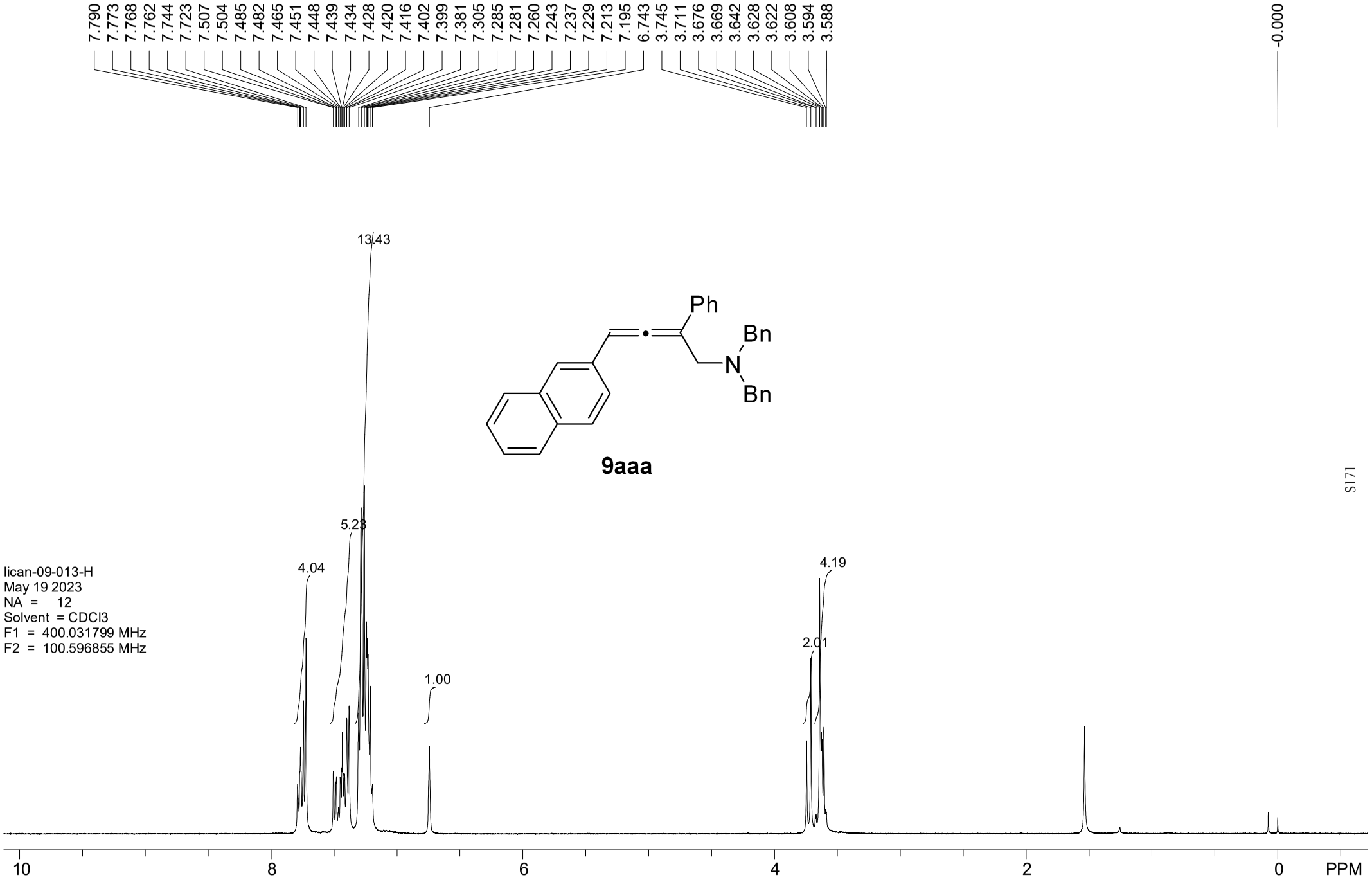

7.611
7.592
7.463
7.443
7.395
7.376
7.350
7.332
7.314
7.283
7.264
7.250
6.563
4.216
4.199
4.181
4.164
4.019
4.003
3.985
3.967
3.612
3.571
3.552
3.505
3.448
3.408
1.251
1.233
1.215
1.178
1.161
1.143
-0.000
3.94
2.01
1.95
1.13
0.97
2.02
2.00
2.06
3.00
2.96
Ph
CO2Et
CO2Et
F
NC
4dag
lican-06-164-H
Feb 27 2022
NA = 8
Solvent = CDCl3
F1 = 399.717712 MHz
F2 = 100.517960 MHz
S166
8
6
4
2
0
PPM

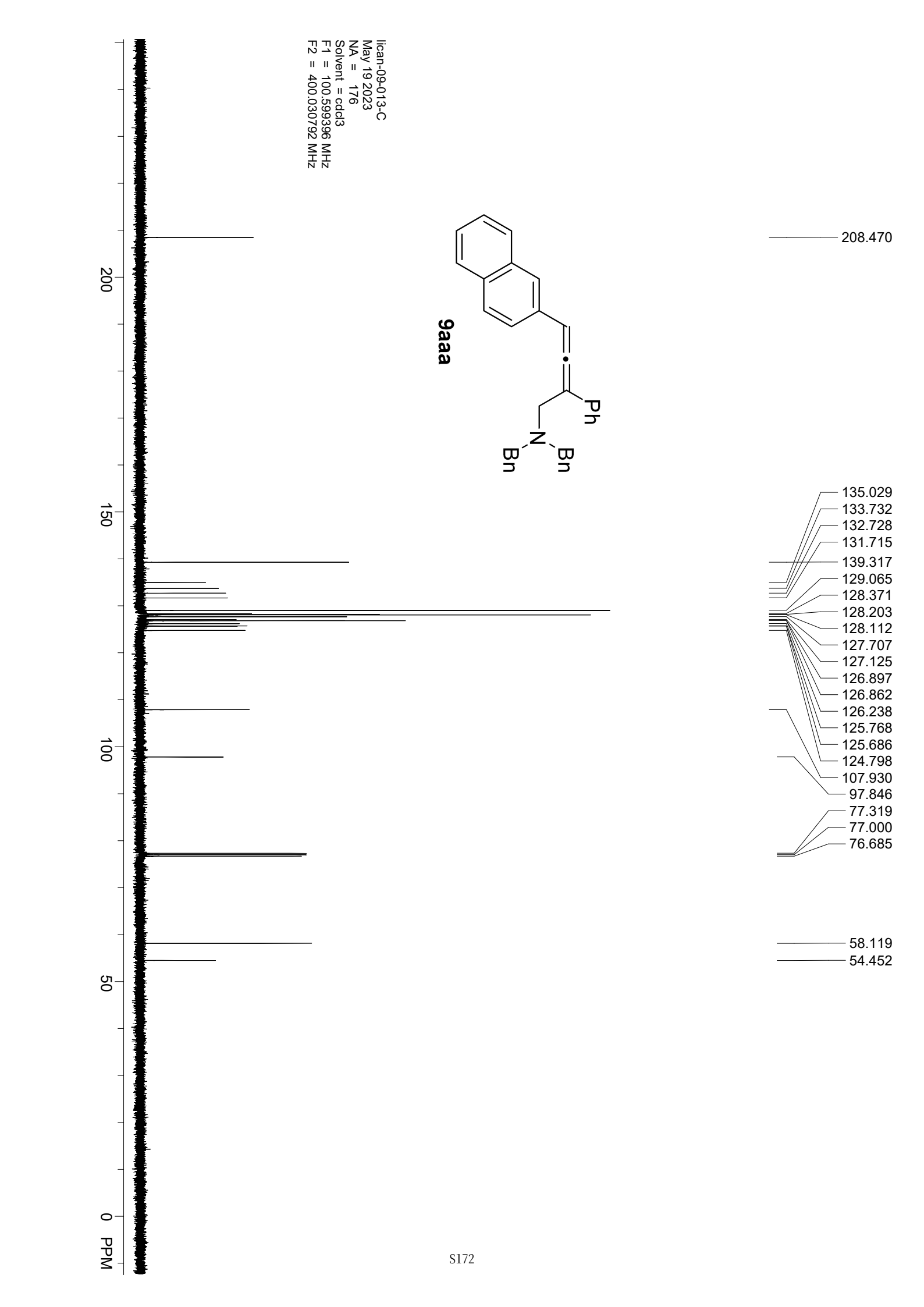

lican-06-164-C
Feb 27 2022
NA = 244
Solvent = cdcl3
F1 = 100.519485 MHz
F2 = 399.717072 MHz
NC
Ph
F
CO2Et
CO2Et
4dag
208.628
165.443
165.382
165.193
165.132
138.472
134.191
132.194
128.437
127.723
127.458
126.091
118.682
110.355
103.440
97.670
94.125
92.114
77.319
77.000
76.681
62.562
62.478
34.688
34.483
13.577
13.478
200
150
100
50
0
PPM

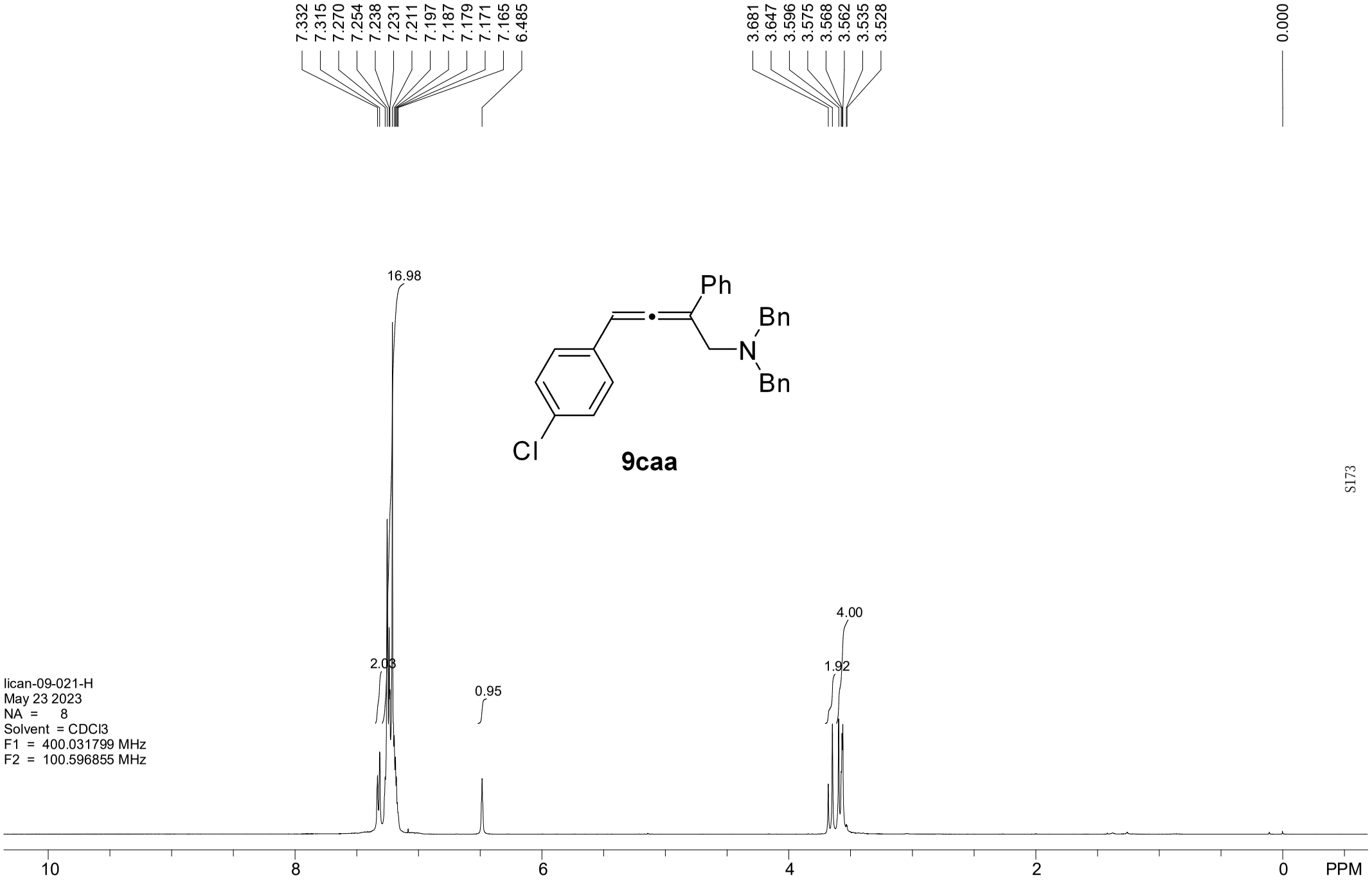

-0.000
-165.847
Ph
CO2Et
CO2Et
F
NC
4dag
lican-06-164-F
Feb 27 2022
NA = 4
Solvent = CDCl3
F1 = 376.071136 MHz
F2 = 100.517960 MHz
100
50
0
-50
-100
-150
-200
PPM

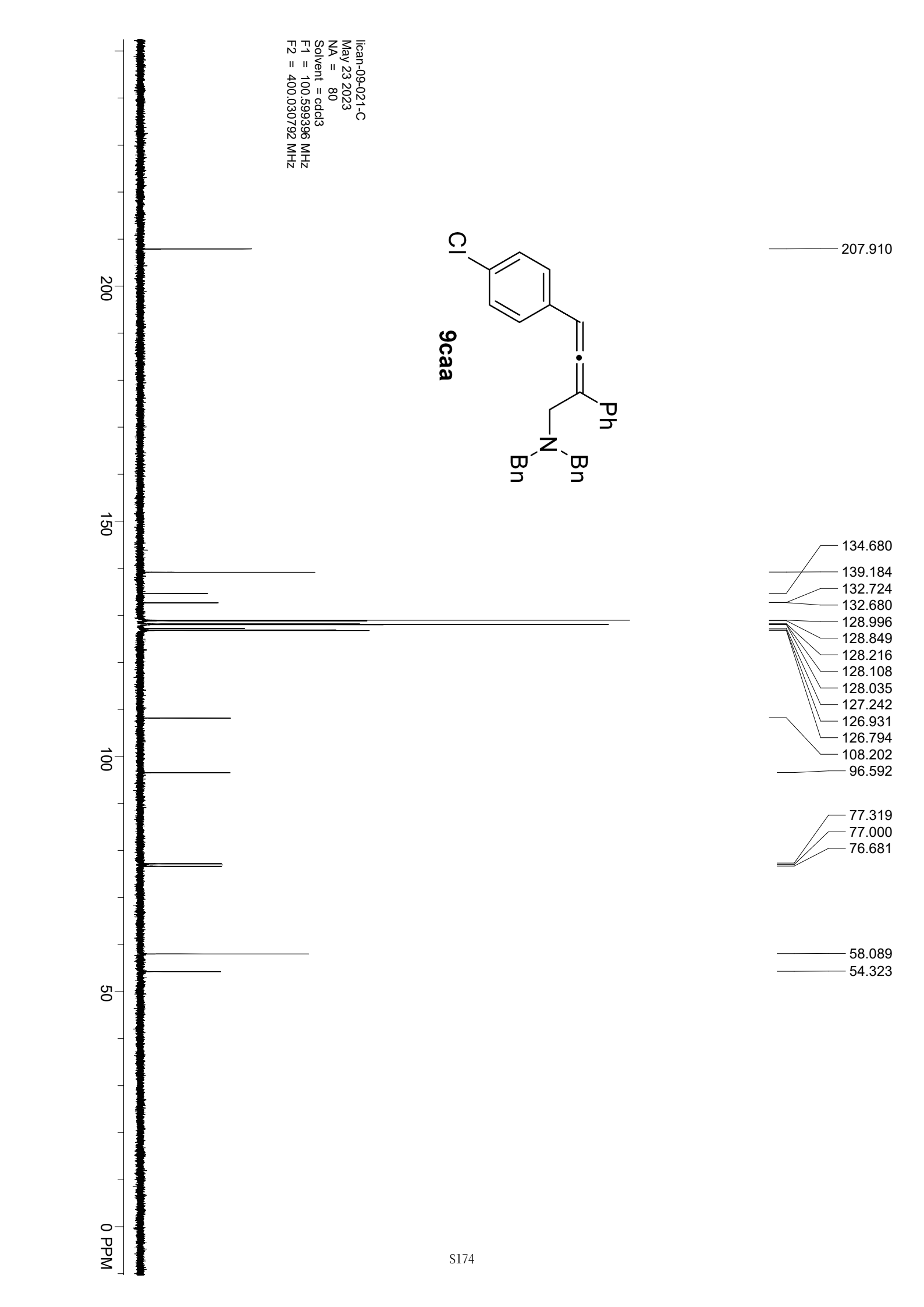

7.932
7.914
7.803
7.793
7.783
7.776
7.753
7.727
7.706
7.637
7.619
7.600
7.496
7.476
7.456
7.439
7.425
7.361
7.343
7.331
7.313
7.293
7.268
7.248
7.228
7.208
6.717
6.709
6.701
4.929
4.915
4.903
3.615
3.606
3.603
3.594
3.571
3.562
3.560
3.550
3.477
3.467
3.463
3.454
3.433
3.424
3.419
3.410
-0.000
6.07
6.04
4.07
3.07
2.08
1.13
0.99
1.00
1.04
1.00
Ph
SO2Ph
SO2Ph
7aaa
lican-06-001-H
Sep 4 2021
NA = 8
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
8
6
4
2
0
PPM

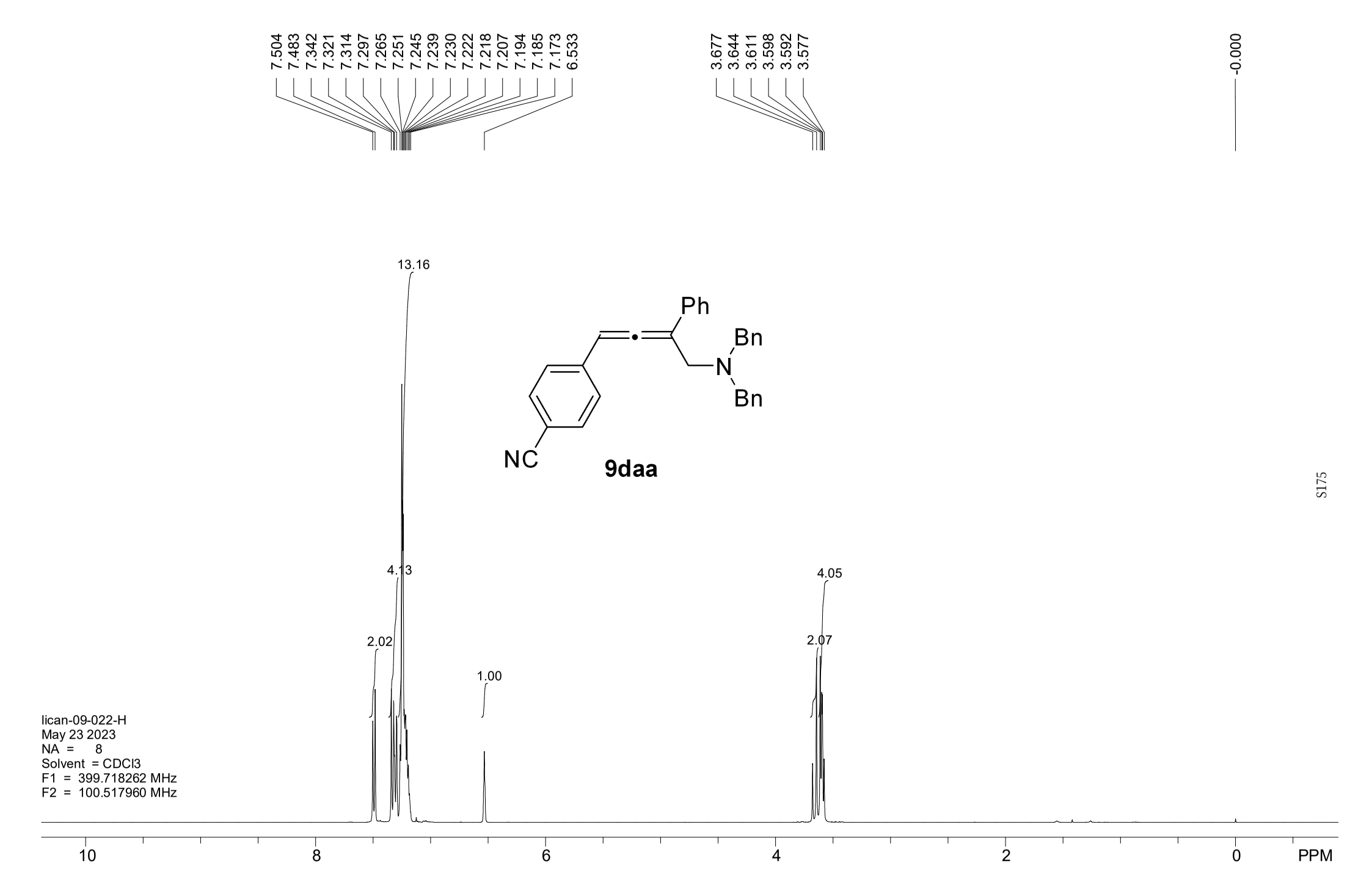

lican-06-001-C
Sep 4 2021
NA = 97
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
7aaa
Ph
SO2Ph
SO2Ph
205.607
138.037
137.546
134.605
134.284
134.069
133.510
132.982
130.316
129.520
129.152
129.037
128.914
128.738
128.639
127.934
127.781
127.704
126.440
126.418
126.142
124.732
107.338
101.755
81.121
77.314
77.000
76.678
25.943
200
150
100
50
0
PPM

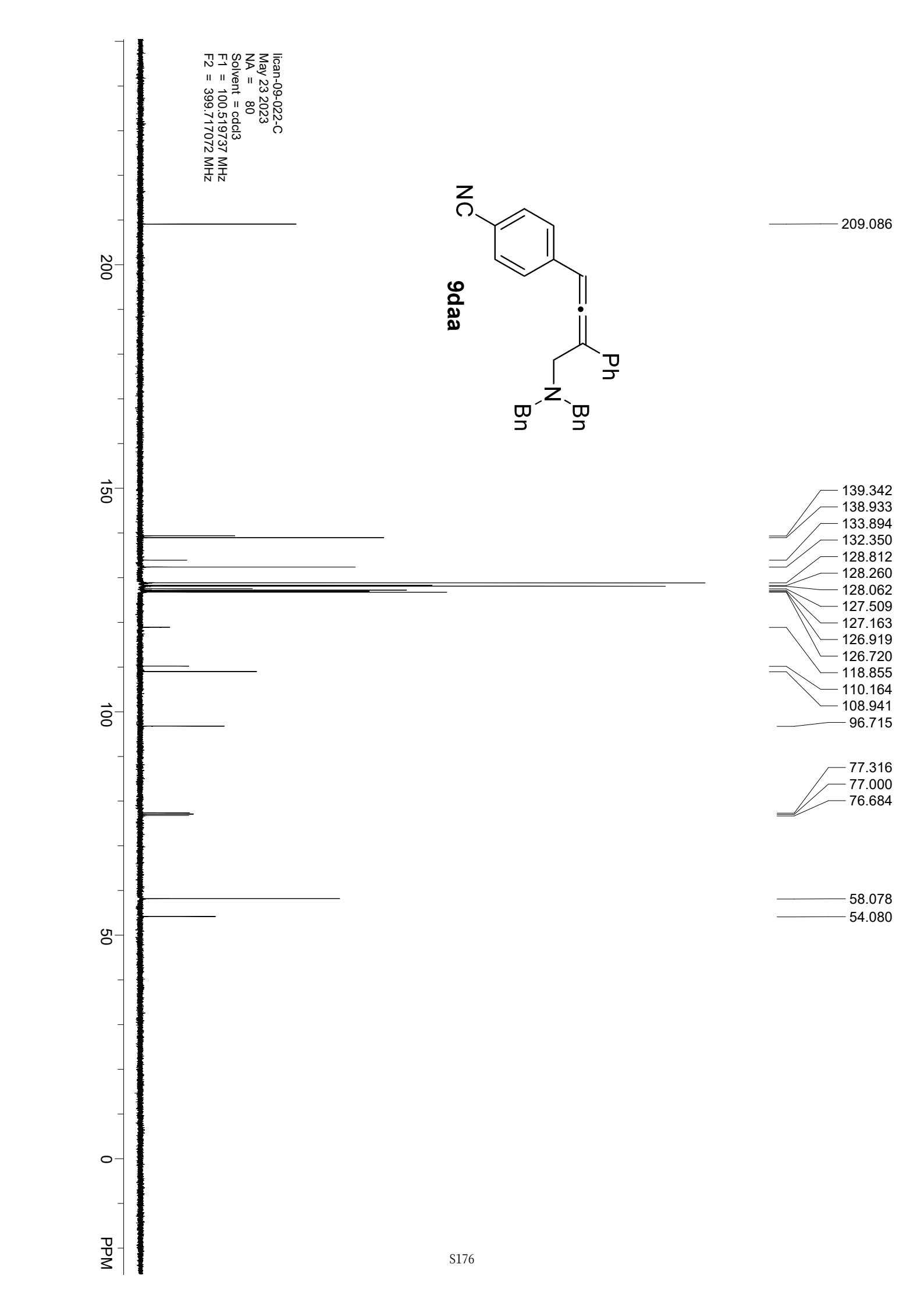

7.790
7.773
7.768
7.762
7.744
7.723
7.507
7.504
7.485
7.482
7.465
7.451
7.448
7.439
7.434
7.428
7.420
7.416
7.402
7.399
7.381
7.305
7.285
7.281
7.260
7.243
7.237
7.229
7.213
7.195
6.743
3.745
3.711
3.676
3.669
3.642
3.628
3.622
3.608
3.594
3.588
-0.000
13.43
5.23
4.04
1.00
4.19
2.01
Ph
Bn
N
Bn
9aaa
lican-09-013-H
May 19 2023
NA = 12
Solvent = CDCl3
F1 = 400.031799 MHz
F2 = 100.596855 MHz
S171
10
8
6
4
2
0
PPM

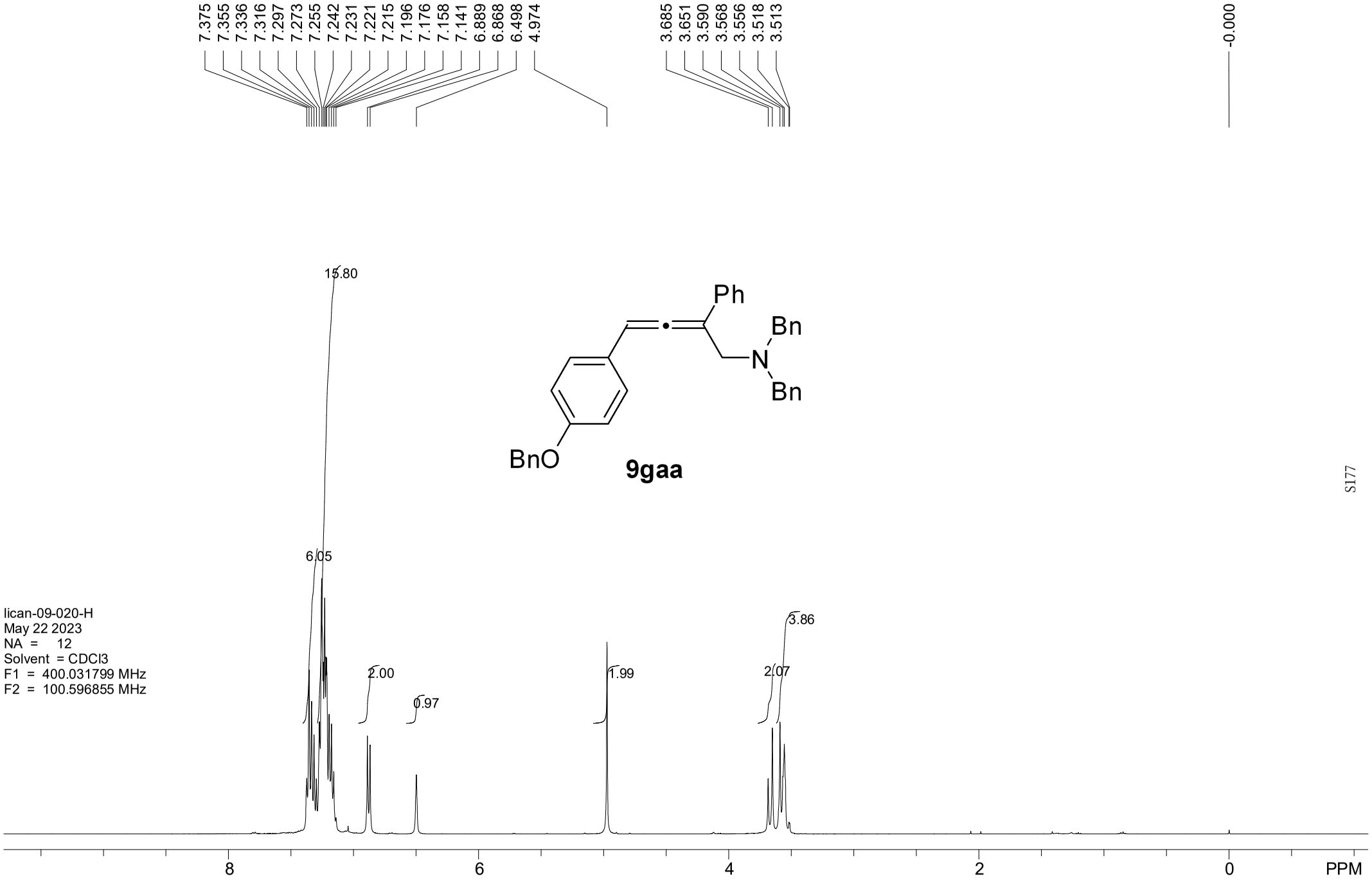

lican-09-013-C
May 19 2023
NA = 176
Solvent = cdcl3
F1 = 100.599396 MHz
F2 = 400.030792 MHz
9aaa
Ph
N
Bn
Bn
208.470
135.029
133.732
132.728
131.715
139.317
129.065
128.371
128.203
128.112
127.707
127.125
126.897
126.862
126.238
125.768
125.686
124.798
107.930
97.846
77.319
77.000
76.685
58.119
54.452
200
150
100
50
0
PPM

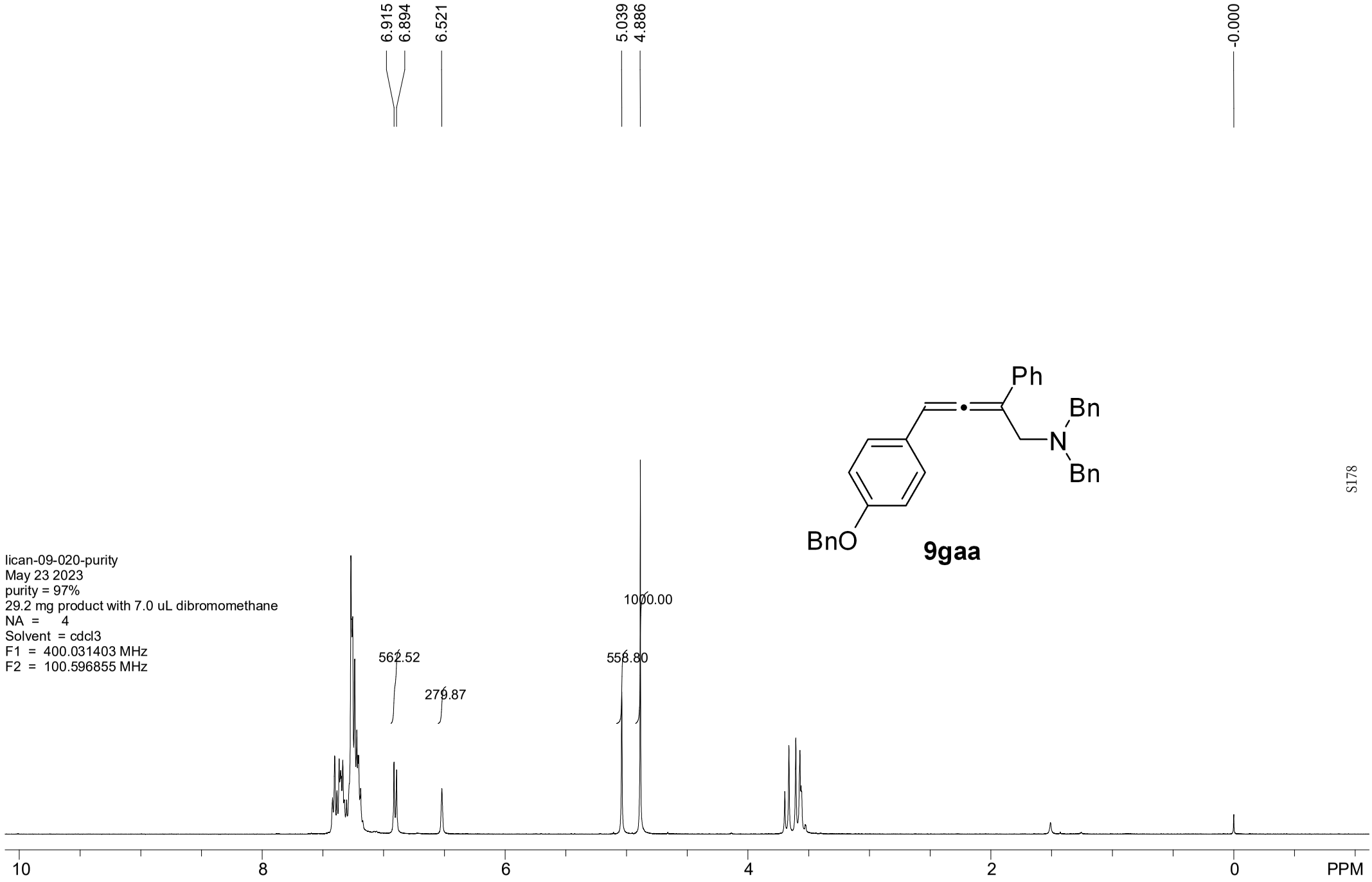

7.332
7.315
7.270
7.254
7.238
7.231
7.211
7.197
7.187
7.179
7.171
7.165
6.485
3.681
3.647
3.596
3.575
3.568
3.562
3.535
3.528
0.000
16.98
Ph
Bn
N
Bn
Cl
9caa
S173
4.00
2.03
1.92
0.95
lican-09-021-H
May 23 2023
NA = 8
Solvent = CDCl3
F1 = 400.031799 MHz
F2 = 100.596855 MHz
10
8
6
4
2
0
PPM

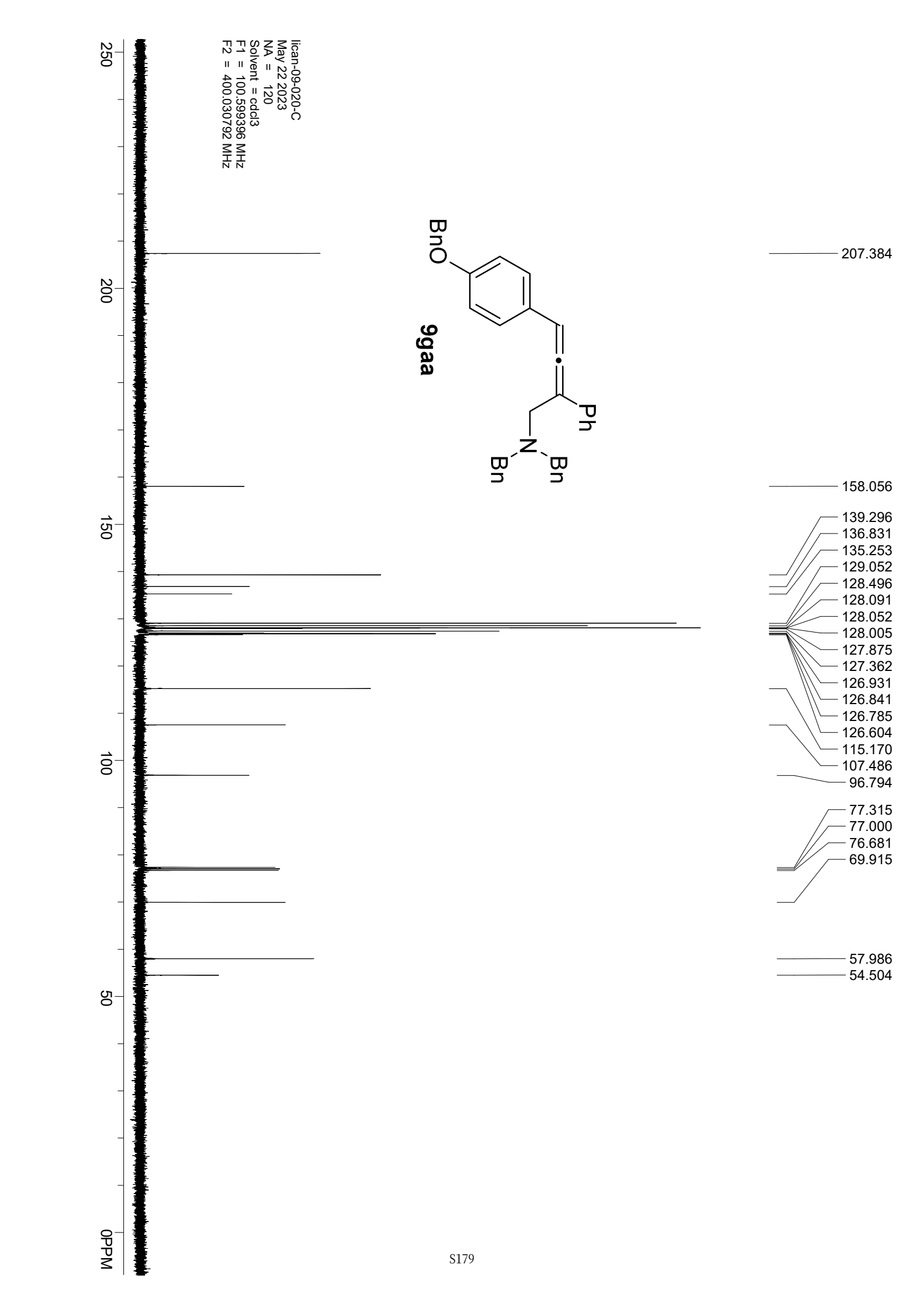

lican-09-021-C
May 23 2023
NA = 80
Solvent = cdcl3
F1 = 100.599396 MHz
F2 = 400.030792 MHz
Cl
Ph
N
Bn
Bn
9caa
207.910
134.680
139.184
132.724
132.680
128.996
128.849
128.216
128.108
128.035
127.242
126.931
126.794
108.202
96.592
77.319
77.000
76.681
58.089
54.323
200
150
100
50
0 PPM

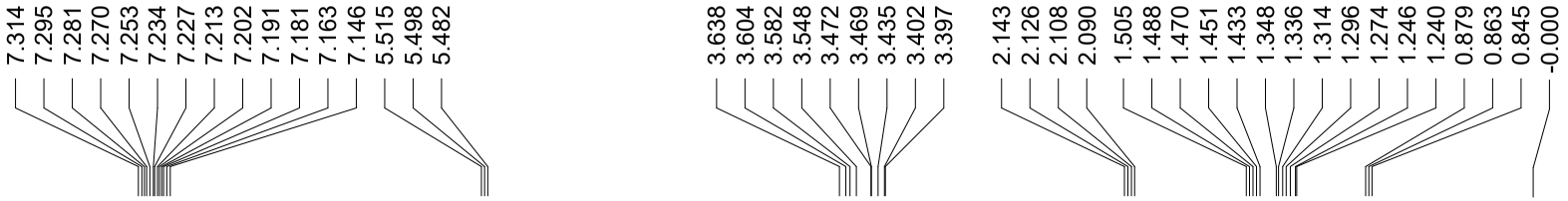

7.504
7.483
7.342
7.321
7.314
7.297
7.265
7.251
7.245
7.239
7.230
7.222
7.218
7.207
7.194
7.185
7.173
6.533
3.677
3.644
3.611
3.598
3.592
3.577
-0.000
13.16
4.13
2.02
1.00
4.05
2.07
Ph
Bn
N
Bn
NC
9daa
lican-09-022-H
May 23 2023
NA = 8
Solvent = CDCl3
F1 = 399.718262 MHz
F2 = 100.517960 MHz
10
8
6
4
2
0
PPM

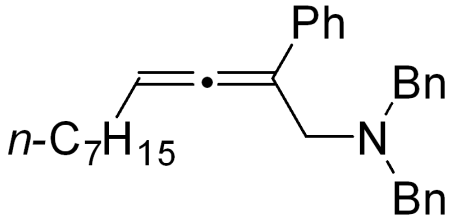

lican-09-022-C
May 23 2023
NA = 80
Solvent = cdcl3
F1 = 100.519737 MHz
F2 = 399.717072 MHz
NC
Ph
N
Bn
Bn
9daa
209.086
139.342
138.933
133.894
132.350
128.812
128.260
128.062
127.509
127.163
126.919
126.720
118.855
110.164
108.941
96.715
77.316
77.000
76.684
58.078
54.080
200
150
100
50
0
PPM


7.375
7.355
7.336
7.316
7.297
7.273
7.255
7.242
7.231
7.221
7.215
7.196
7.176
7.158
7.141
6.889
6.868
6.498
4.974
3.685
3.651
3.590
3.568
3.556
3.518
3.513
-0.000
15.80
6.05
2.00
0.97
1.99
2.07
3.86
Ph
Bn
N
Bn
BnO
9gaa
lican-09-020-H
May 22 2023
NA = 12
Solvent = CDCl3
F1 = 400.031799 MHz
F2 = 100.596855 MHz
8
6
4
2
0
PPM

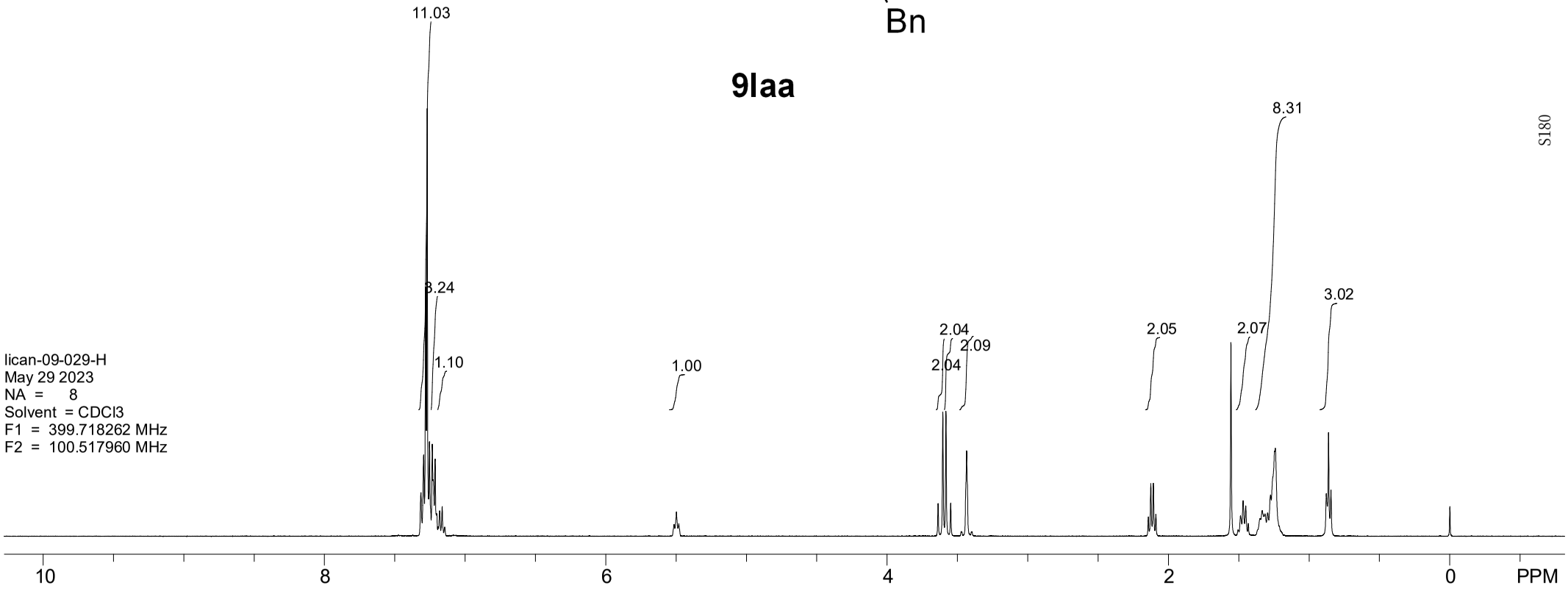

6.915
6.894
6.521
5.039
4.886
-0.000
Ph
Bn
N
Bn
BnO
9gaa
S178
lican-09-020-purity
May 23 2023
purity = 97%
29.2 mg product with 7.0 uL dibromomethane
NA = 4
Solvent = cdcl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz
562.52
279.87
558.80
1000.00
10
8
6
4
2
0
PPM

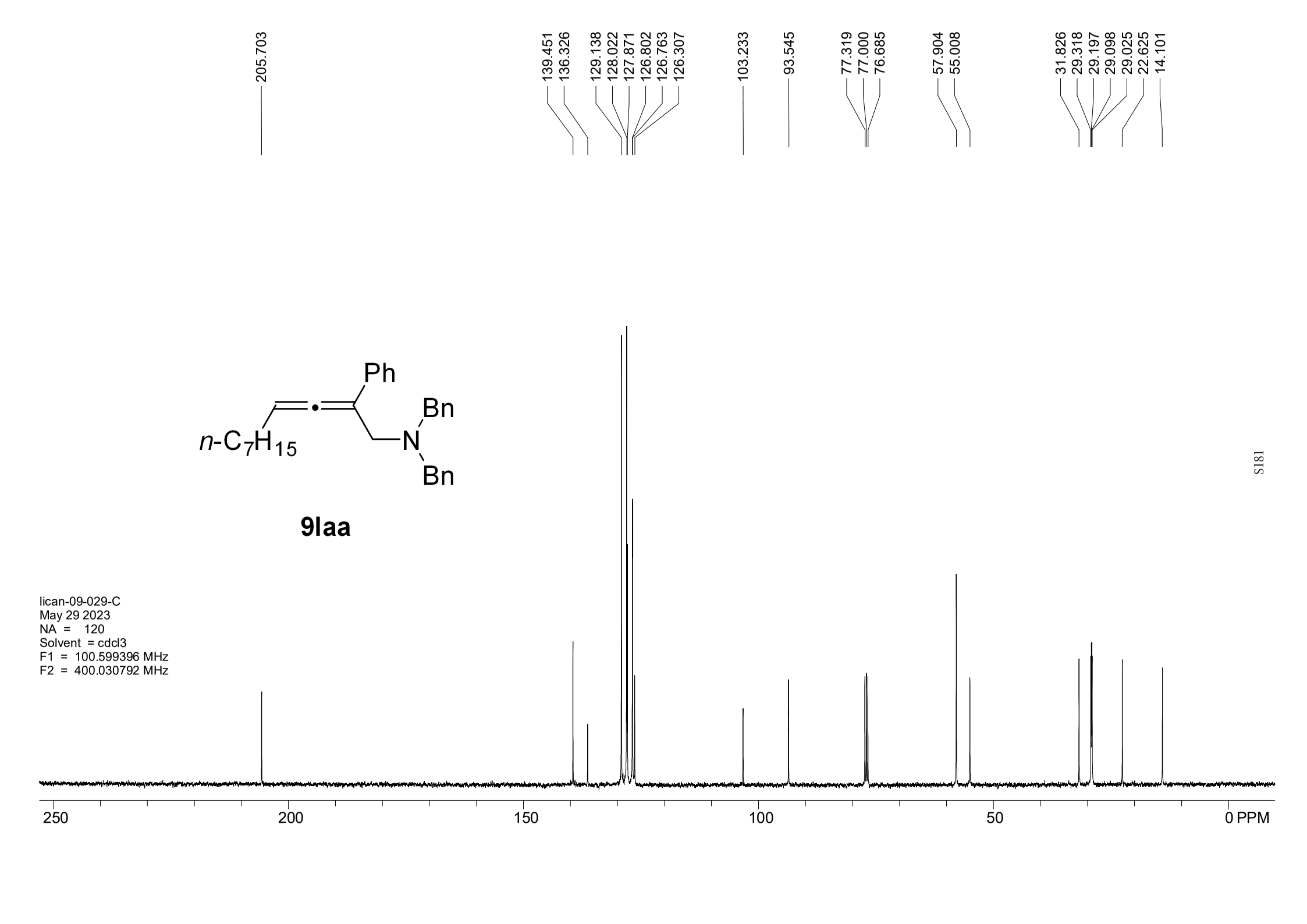

lican-09-020-C
May 22 2023
NA = 120
Solvent = cdcl3
F1 = 100.599396 MHz
F2 = 400.030792 MHz
BnO
Ph
N
Bn
Bn
9gaa
207.384
158.056
139.296
136.831
135.253
129.052
128.496
128.091
128.052
128.005
127.875
127.362
126.931
126.841
126.785
126.604
115.170
107.486
96.794
77.315
77.000
76.681
69.915
57.986
54.504
250
200
150
100
50
0PPM

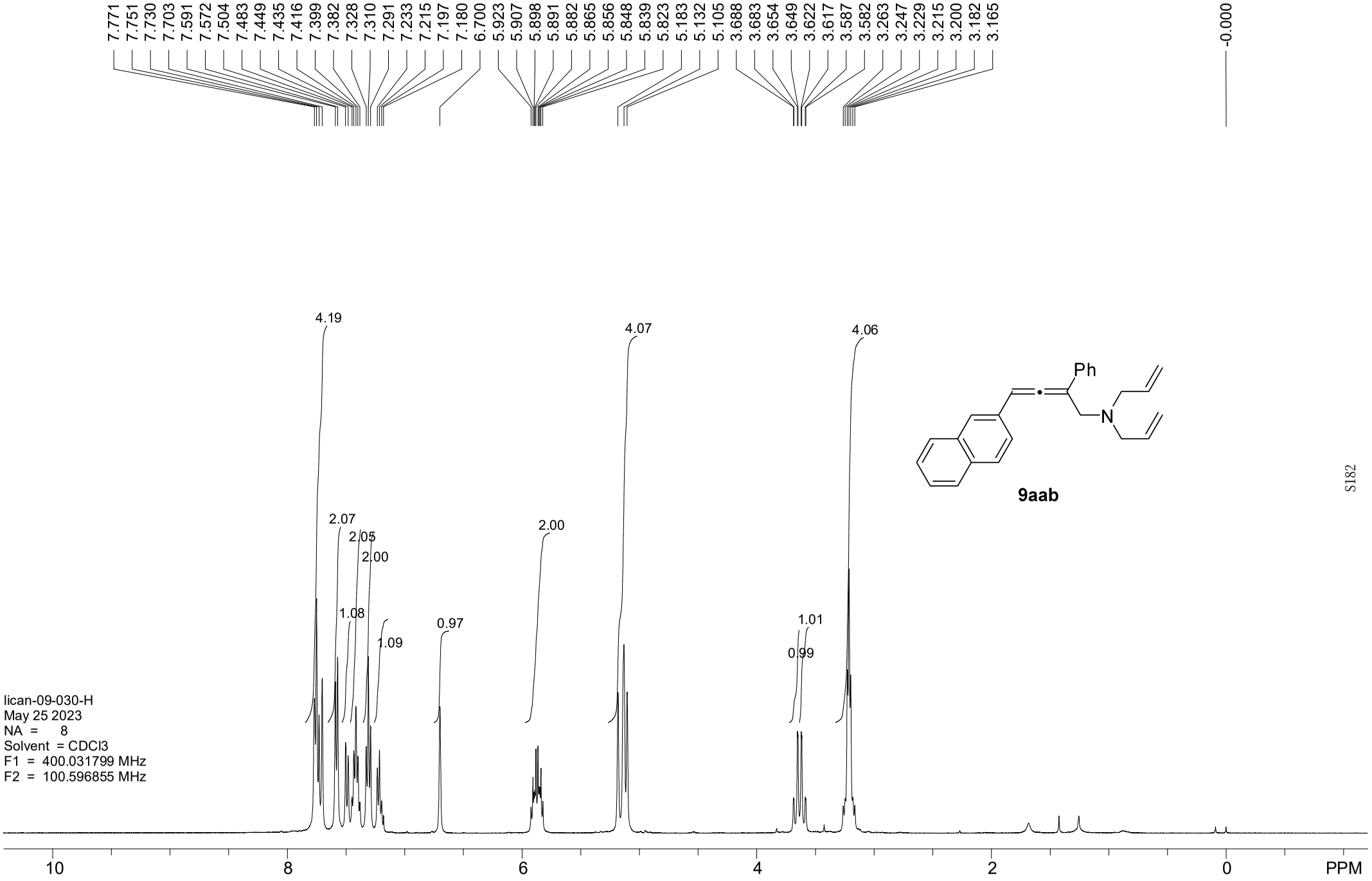

7.314
7.295
7.281
7.270
7.253
7.234
7.227
7.213
7.202
7.191
7.181
7.163
7.146
5.515
5.498
5.482
3.638
3.604
3.582
3.548
3.472
3.469
3.435
3.402
3.397
2.143
2.126
2.108
2.090
1.505
1.488
1.470
1.451
1.433
1.348
1.336
1.314
1.296
1.274
1.246
1.240
0.879
0.863
0.845
-0.000

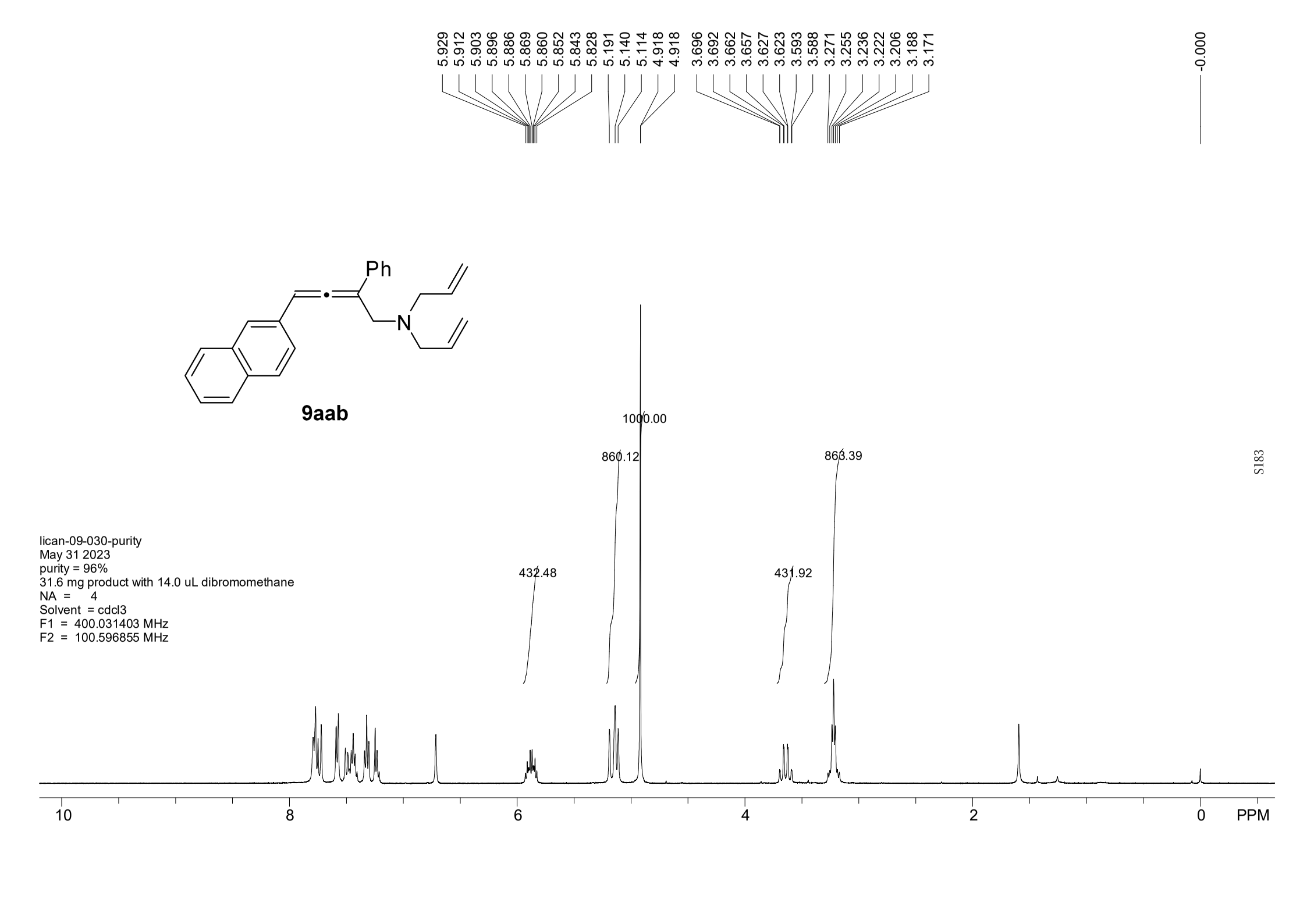

Ph
Bn
N
Bn
n-C7H15

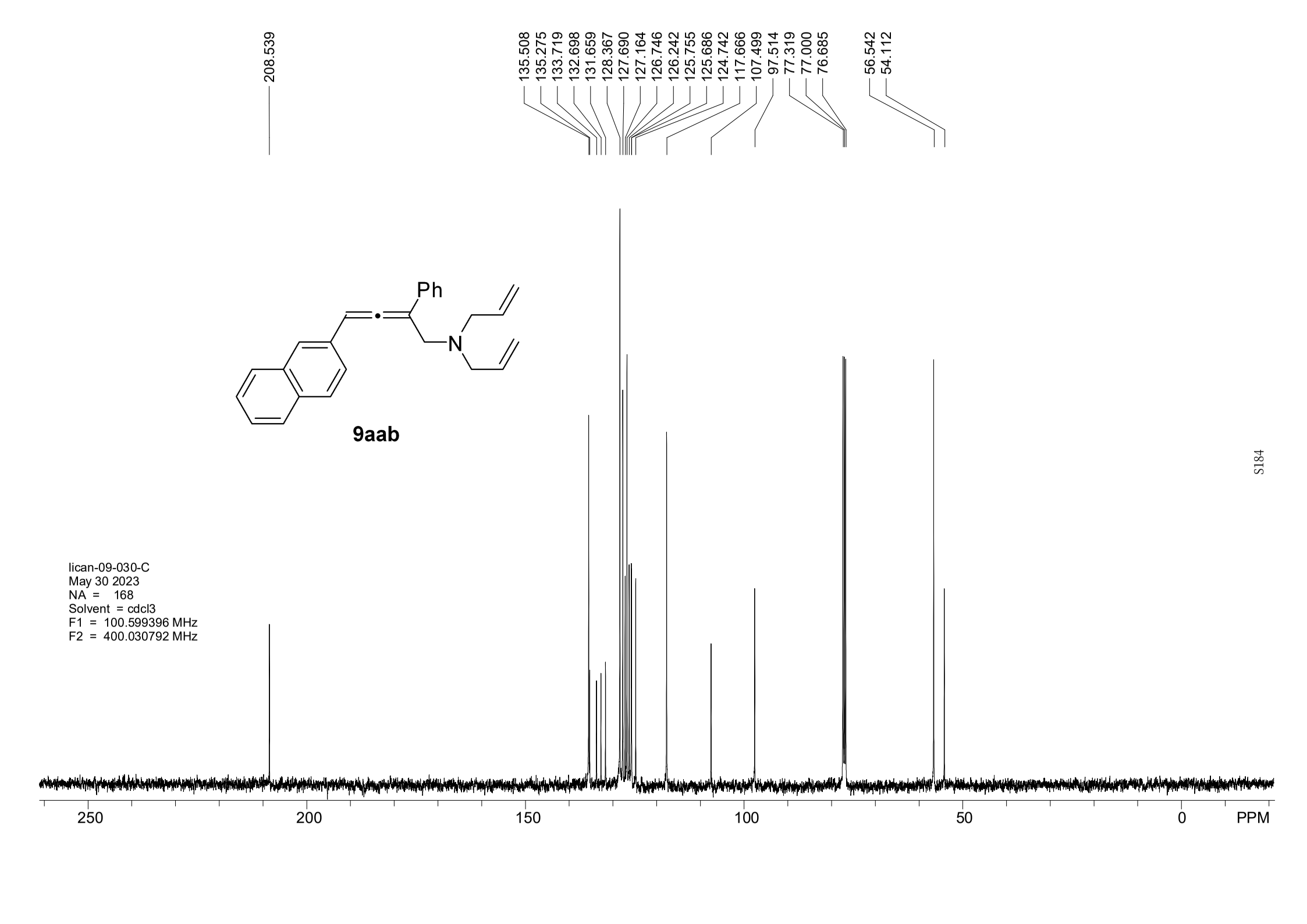
9laa

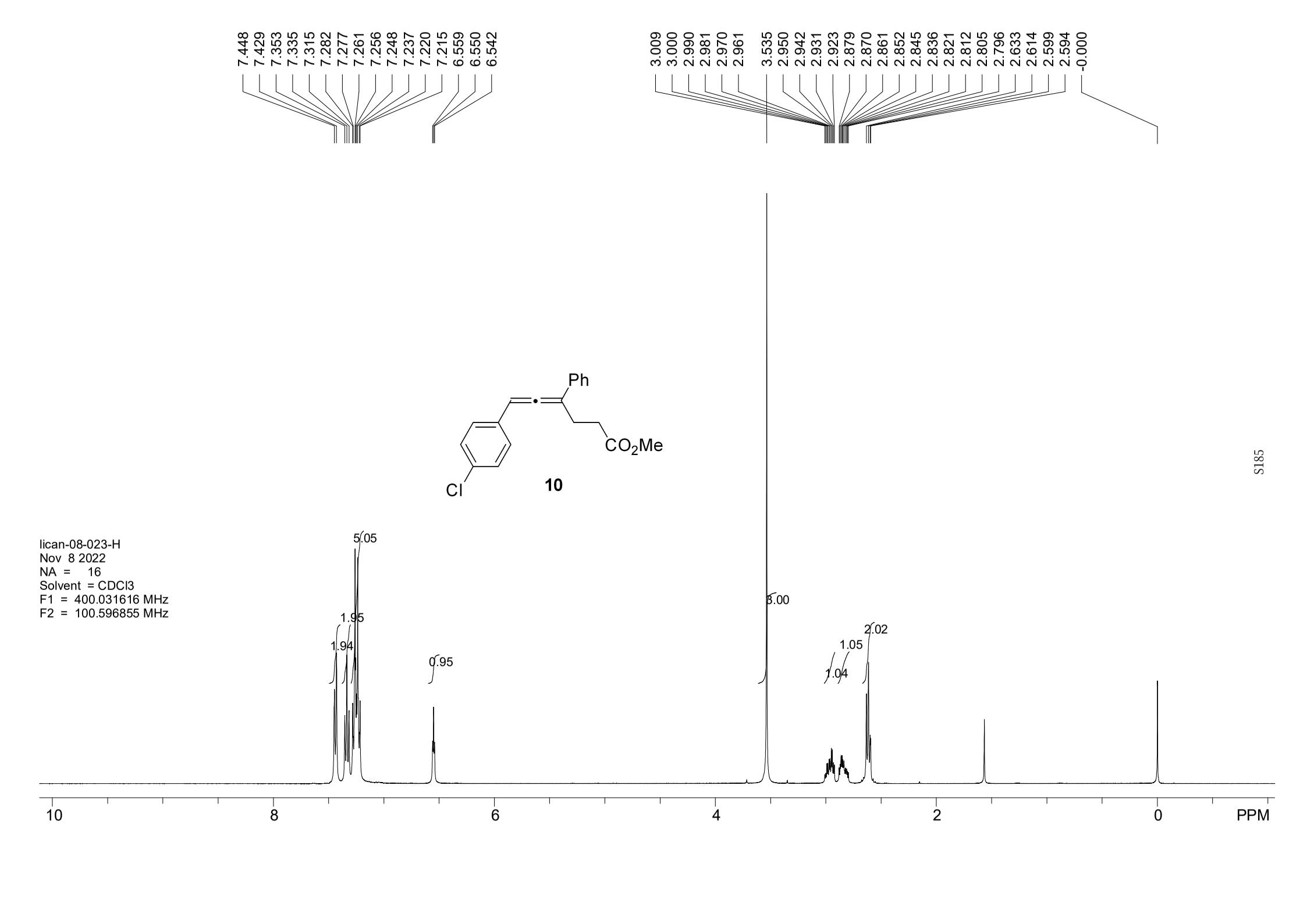

11.03
3.24
1.10
1.00
2.04
2.04
2.09
2.05
2.07
8.31
3.02
lican-09-029-H
May 29 2023
NA = 8
Solvent = CDCl3
F1 = 399.718262 MHz
F2 = 100.517960 MHz
10
8
6
4
2
0
PPM

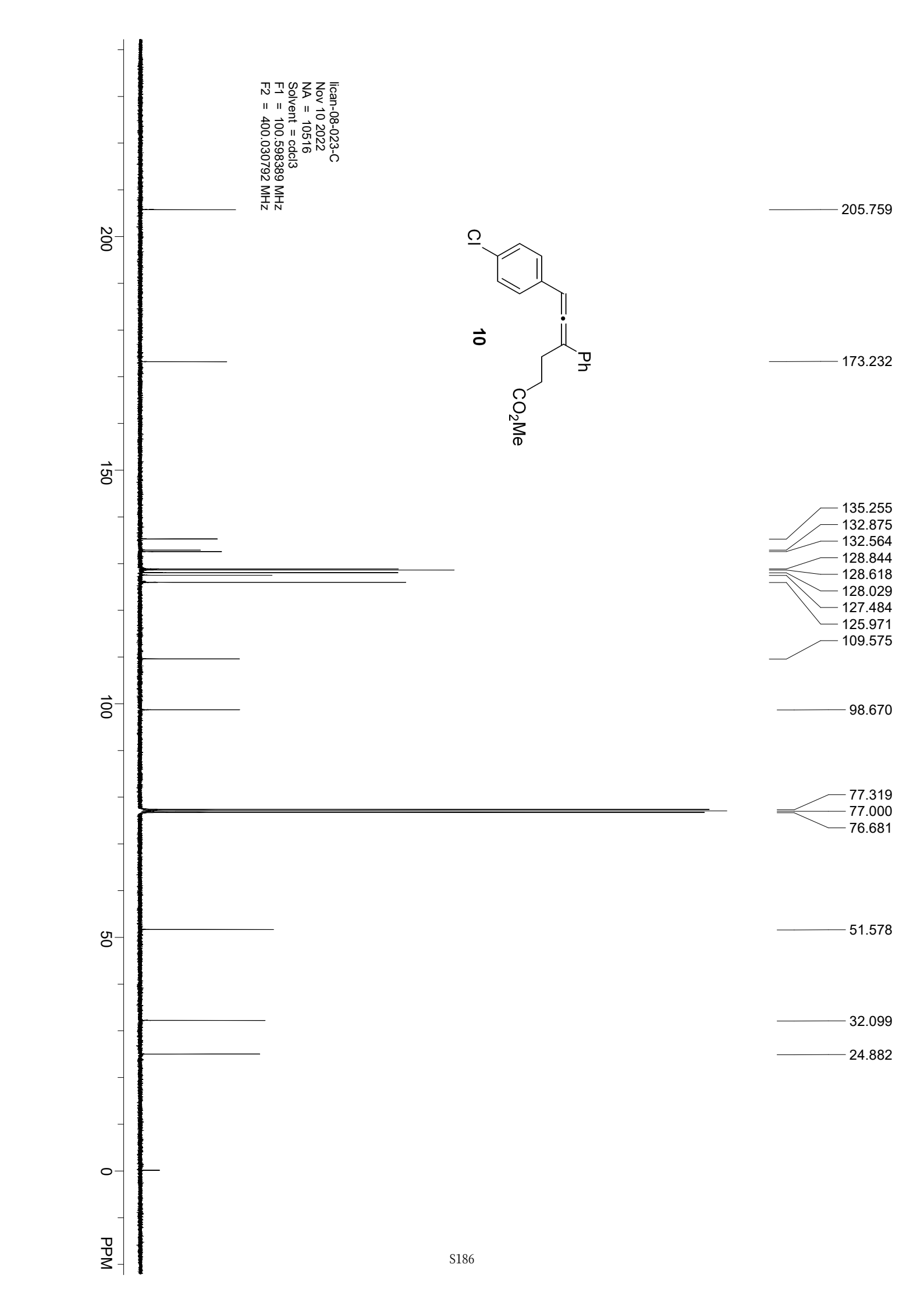

205.703
139.451
136.326
129.138
128.022
127.871
126.802
126.763
126.307
103.233
93.545
77.319
77.000
76.685
57.904
55.008
31.826
29.318
29.197
29.098
29.025
22.625
14.101
Ph
Bn
N
Bn
n-C7H15
9laa
lican-09-029-C
May 29 2023
NA = 120
Solvent = cdcl3
F1 = 100.599396 MHz
F2 = 400.030792 MHz
250
200
150
100
50
0 PPM

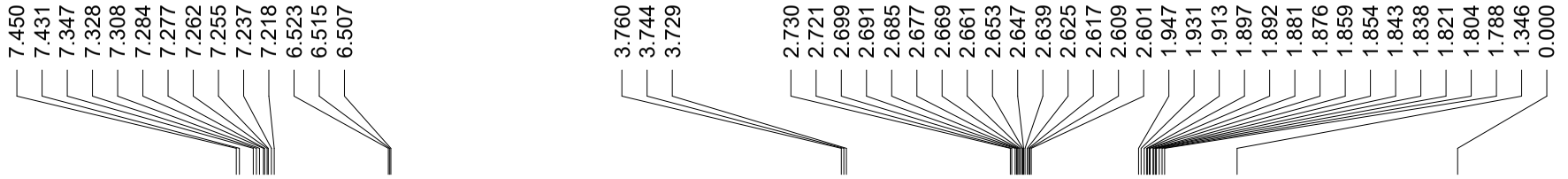

7.771
7.751
7.730
7.703
7.591
7.572
7.504
7.483
7.449
7.435
7.416
7.399
7.382
7.328
7.310
7.291
7.233
7.215
7.197
7.180
6.700
5.923
5.907
5.898
5.891
5.882
5.865
5.856
5.848
5.839
5.823
5.183
5.132
5.105
3.688
3.683
3.654
3.649
3.622
3.617
3.587
3.582
3.263
3.247
3.229
3.215
3.200
3.182
3.165
-0.000
4.19
2.07
2.05
2.00
1.08
1.09
0.97
2.00
4.07
1.01
0.99
4.06
Ph
N
9aab
lican-09-030-H
May 25 2023
NA = 8
Solvent = CDCl3
F1 = 400.031799 MHz
F2 = 100.596855 MHz
10
8
6
4
2
0
PPM

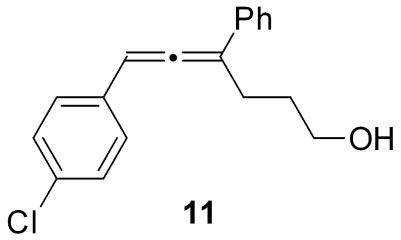

5.929
5.912
5.903
5.896
5.886
5.869
5.860
5.852
5.843
5.828
5.191
5.140
5.114
4.918
4.918
3.696
3.692
3.662
3.657
3.627
3.623
3.593
3.588
3.271
3.255
3.236
3.222
3.206
3.188
3.171
-0.000
Ph
N
9aab
1000.00
860.12
863.39
S183
lican-09-030-purity
May 31 2023
purity = 96%
31.6 mg product with 14.0 uL dibromomethane
NA = 4
Solvent = cdcl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz
432.48
431.92
10
8
6
4
2
0
PPM


208.539
135.508
135.275
133.719
132.698
131.659
128.367
127.690
127.164
126.746
126.242
125.755
125.686
124.742
117.666
107.499
97.514
77.319
77.000
76.685
56.542
54.112
Ph
N
9aab
lican-09-030-C
May 30 2023
NA = 168
Solvent = cdcl3
F1 = 100.599396 MHz
F2 = 400.030792 MHz
250
200
150
100
50
0
PPM

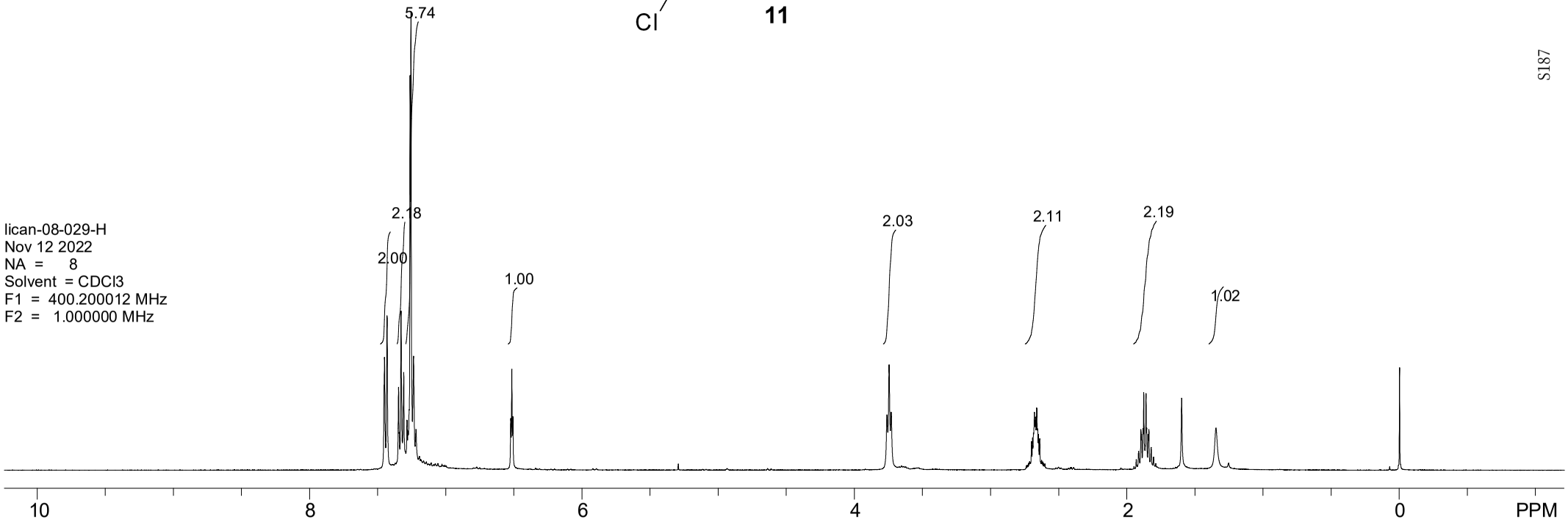

7.448
7.429
7.353
7.335
7.315
7.282
7.277
7.261
7.256
7.248
7.237
7.220
7.215
6.559
6.550
6.542
3.009
3.000
2.990
2.981
2.970
2.961
3.535
2.950
2.942
2.931
2.923
2.879
2.870
2.861
2.852
2.845
2.836
2.821
2.812
2.805
2.796
2.633
2.614
2.599
2.594
-0.000
Ph
CO2Me
Cl
10
S185
lican-08-023-H
Nov 8 2022
NA = 16
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
5.05
1.95
1.94
0.95
3.00
2.02
1.05
1.04
10
8
6
4
2
0
PPM

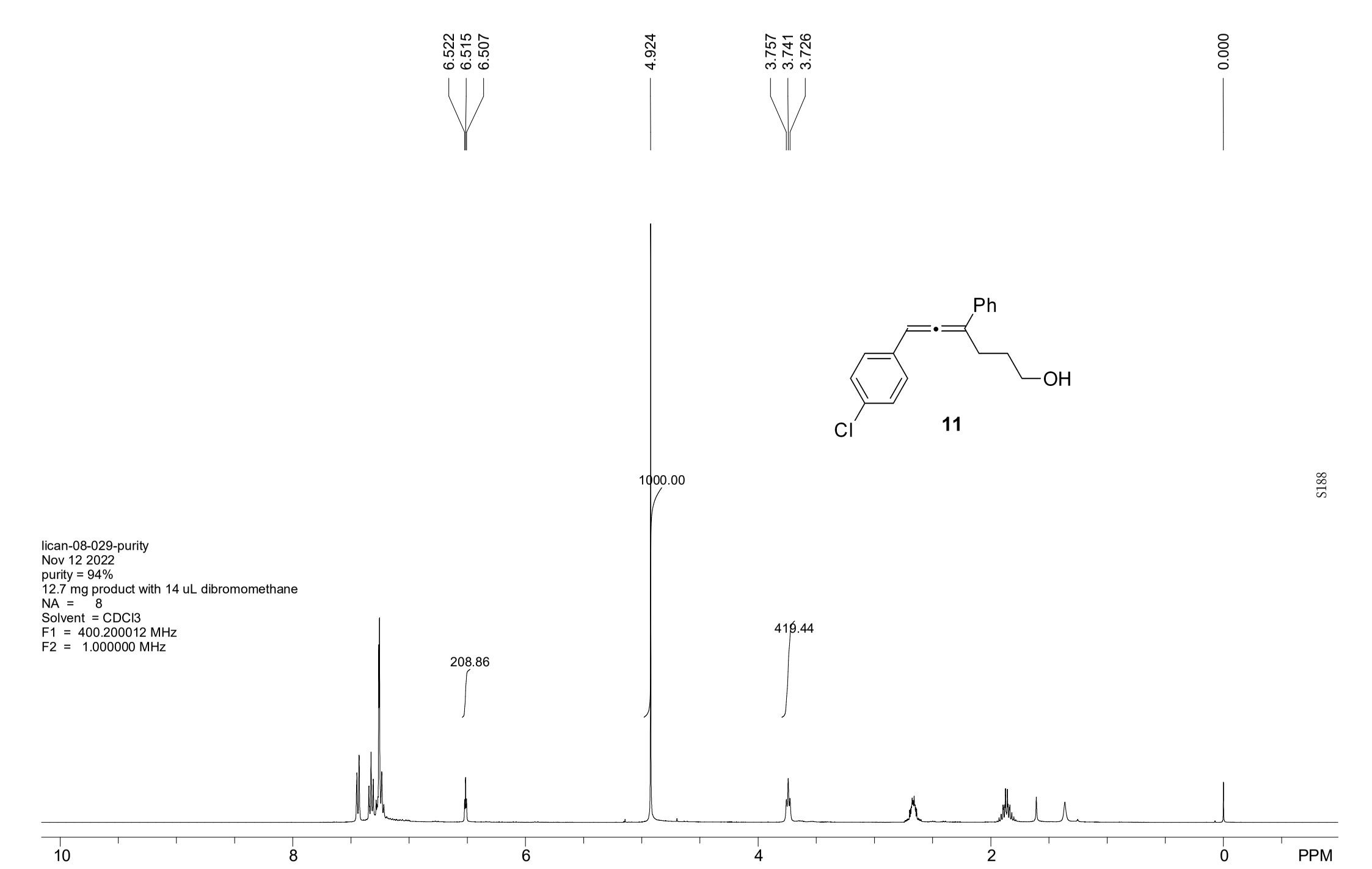

lican-08-023-C
Nov 10 2022
NA = 10516
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
Cl
Ph
CO2Me
10
205.759
173.232
135.255
132.875
132.564
128.844
128.618
128.029
127.484
125.971
109.575
98.670
77.319
77.000
76.681
51.578
32.099
24.882
200
150
100
50
0
PPM

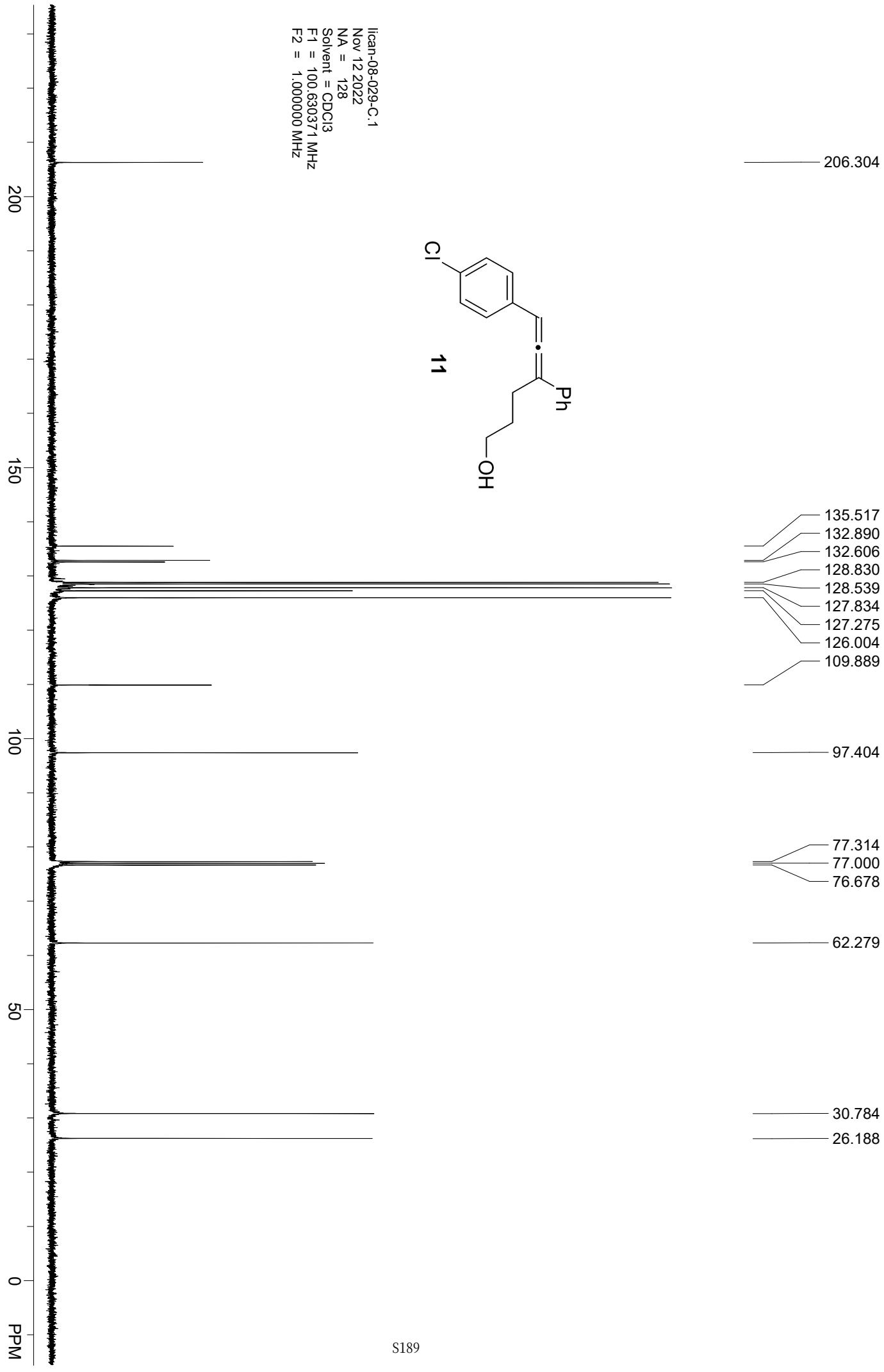

7.450
7.431
7.347
7.328
7.308
7.284
7.277
7.262
7.255
7.237
7.218
6.523
6.515
6.507
3.760
3.744
3.729
2.730
2.721
2.699
2.691
2.685
2.677
2.669
2.661
2.653
2.647
2.639
2.625
2.617
2.609
2.601
1.947
1.931
1.913
1.897
1.892
1.881
1.876
1.859
1.854
1.843
1.838
1.821
1.804
1.788
1.346
0.000

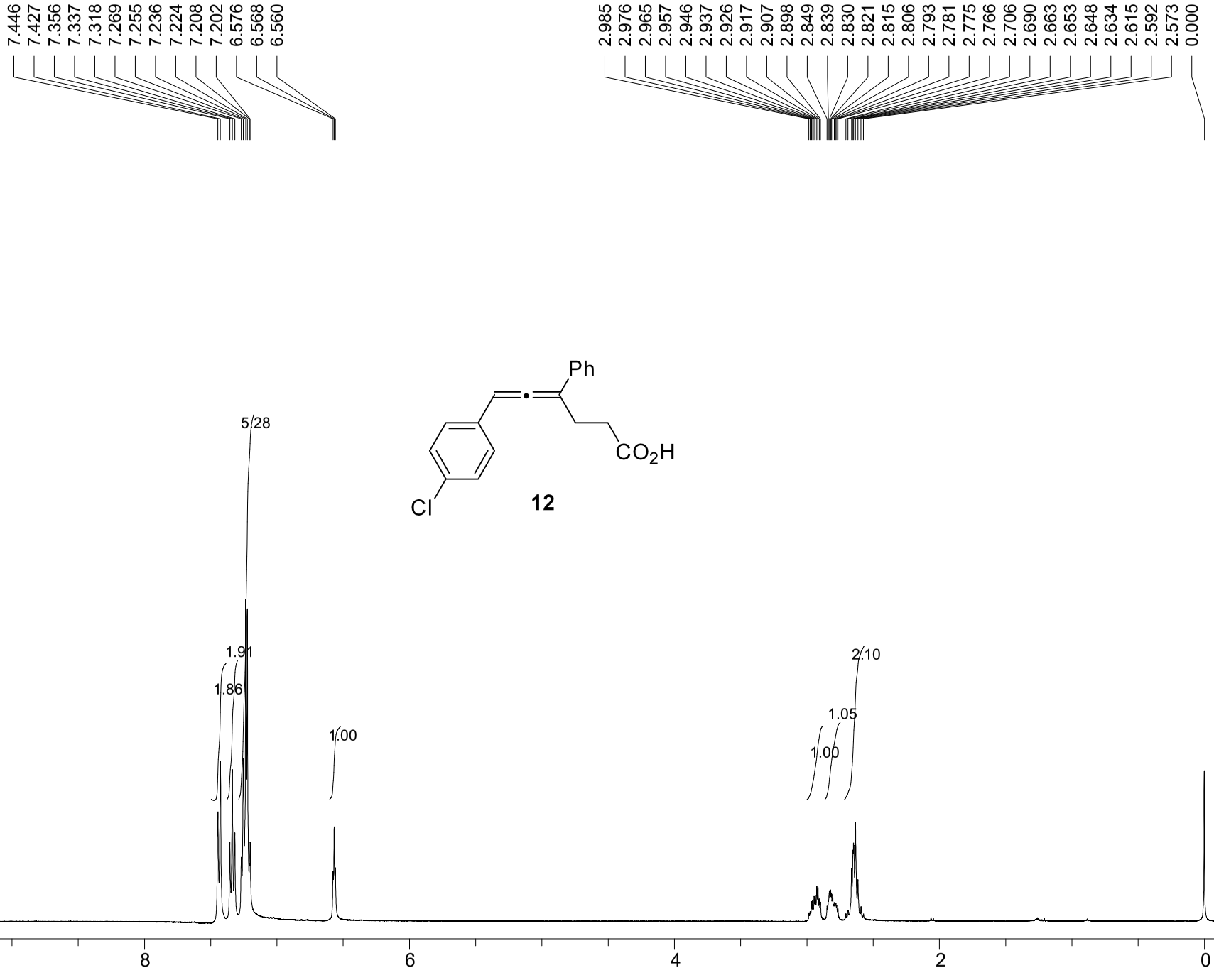

Ph
OH
Cl

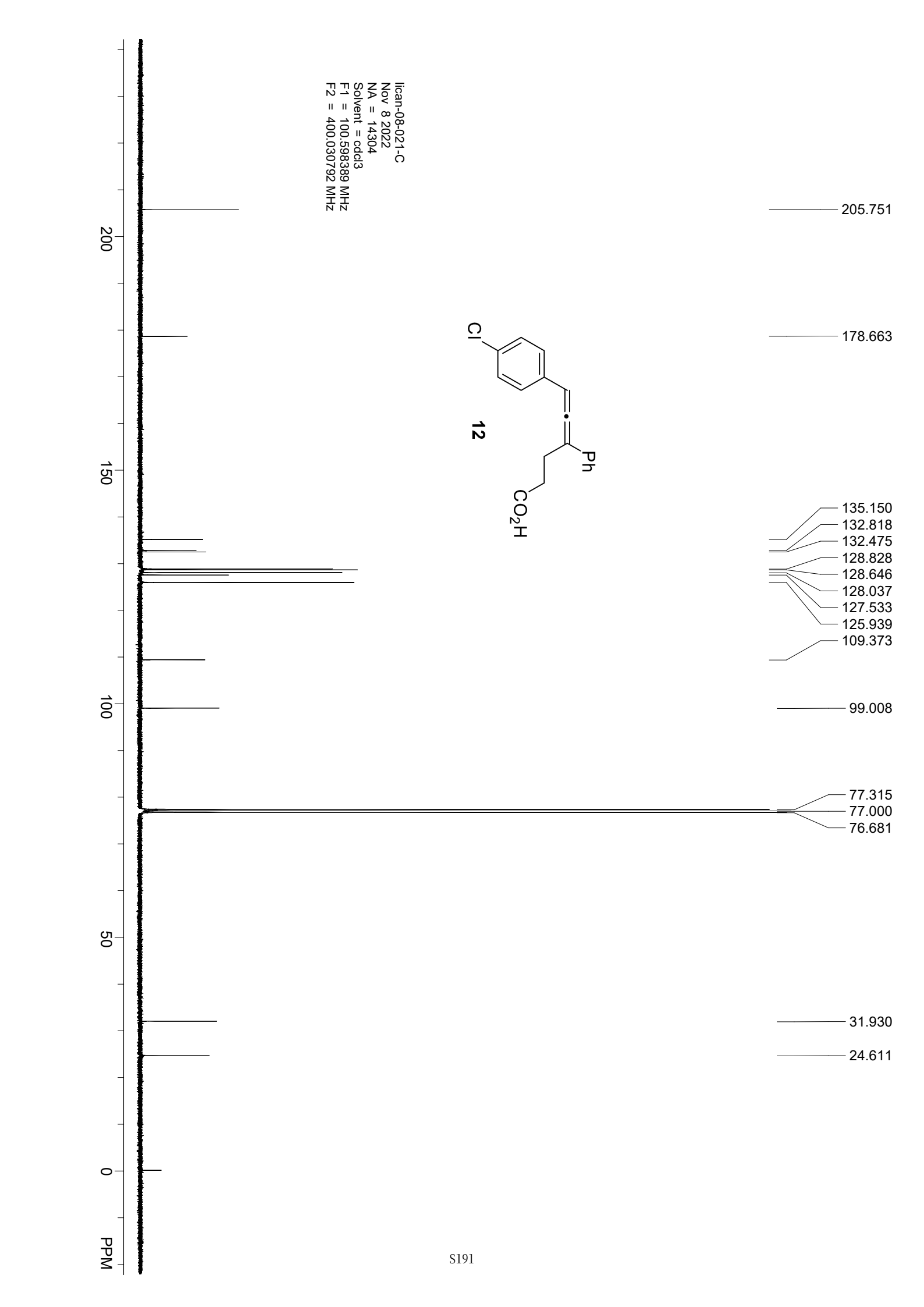
11

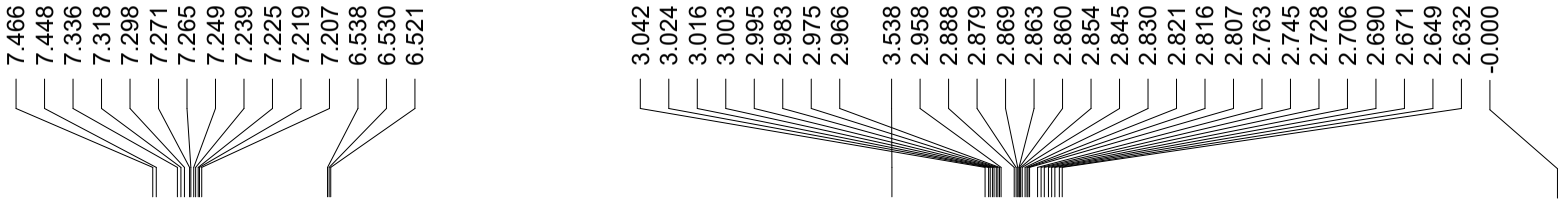

lican-08-029-H
Nov 12 2022
NA = 8
Solvent = CDCl3
F1 = 400.200012 MHz
F2 = 1.000000 MHz
5.74
2.18
2.00
1.00
2.03
2.11
2.19
1.02
10
8
6
4
2
0
PPM

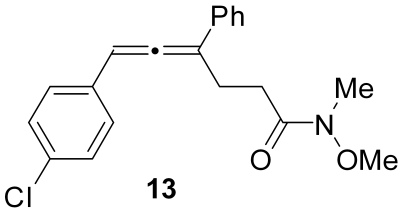

6.522
6.515
6.507
4.924
3.757
3.741
3.726
0.000
Ph
OH
Cl
11
1000.00
208.86
419.44
S188
lican-08-029-purity
Nov 12 2022
purity = 94%
12.7 mg product with 14 uL dibromomethane
NA = 8
Solvent = CDCl3
F1 = 400.200012 MHz
F2 = 1.000000 MHz
10
8
6
4
2
0
PPM


lican-08-029-C.1
Nov 12 2022
NA = 128
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
Cl
Ph
OH
11
206.304
135.517
132.890
132.606
128.830
128.539
127.834
127.275
126.004
109.889
97.404
77.314
77.000
76.678
62.279
30.784
26.188
200
150
100
50
0
PPM

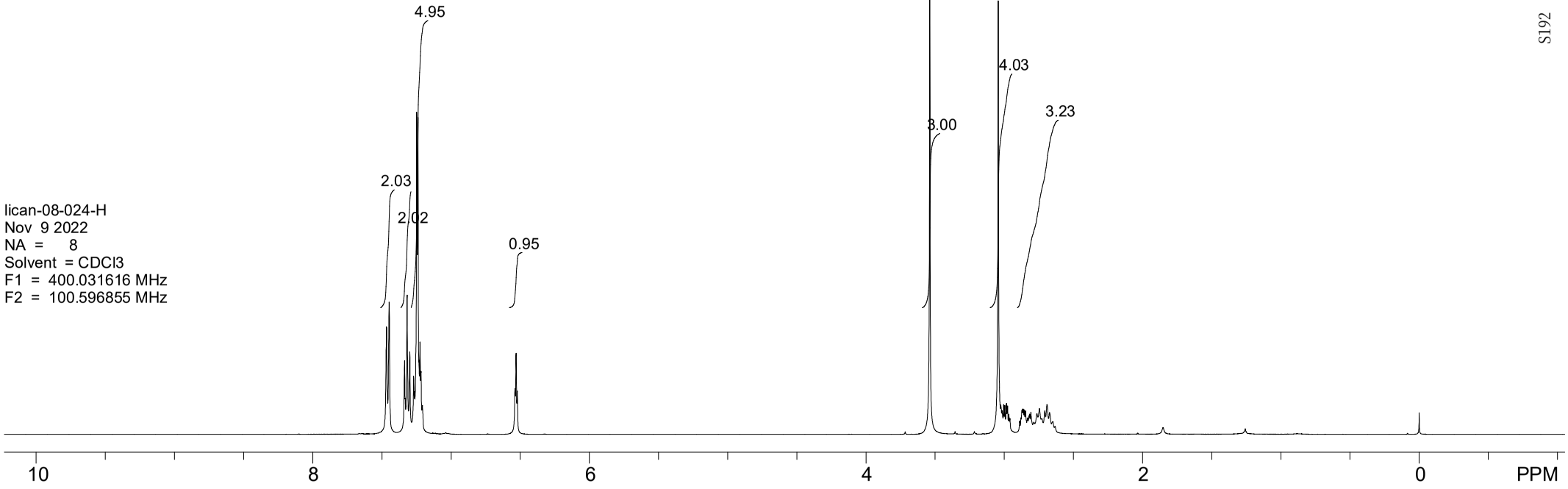

7.446
7.427
7.356
7.337
7.318
7.269
7.255
7.236
7.224
7.208
7.202
6.576
6.568
6.560
2.985
2.976
2.965
2.957
2.946
2.937
2.926
2.917
2.907
2.898
2.849
2.839
2.830
2.821
2.815
2.806
2.793
2.781
2.775
2.766
2.706
2.690
2.663
2.653
2.648
2.634
2.615
2.592
2.573
0.000
Ph
CO2H
Cl
12
5.28
1.91
1.86
1.00
2.10
1.05
1.00
lican-08-021-H
Nov 8 2022
NA = 8
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
10
8
6
4
2
0
PPM

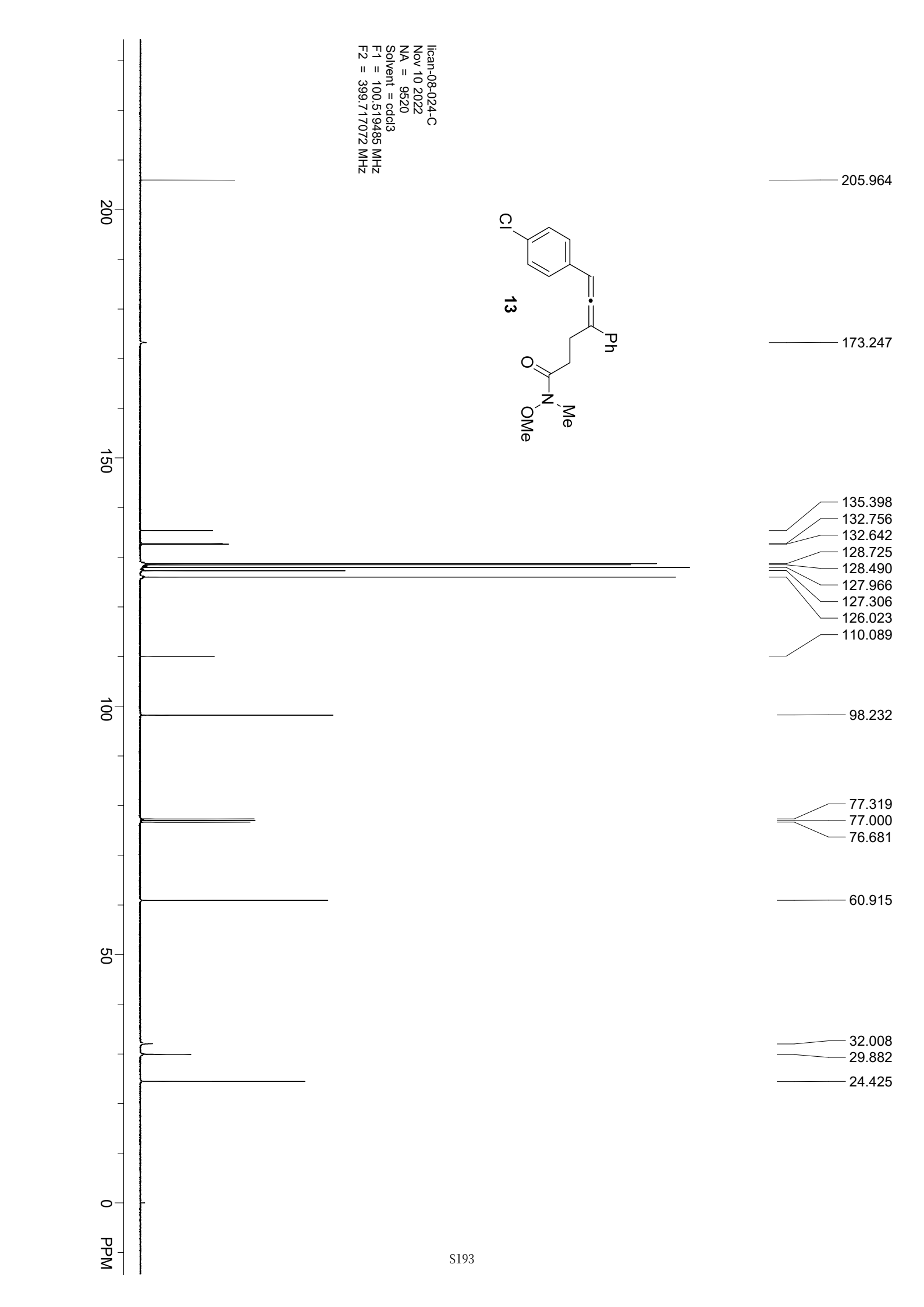

lican-08-021-C
Nov 8 2022
NA = 14304
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
Cl
Ph
CO2H
12
205.751
178.663
135.150
132.818
132.475
128.828
128.646
128.037
127.533
125.939
109.373
99.008
77.315
77.000
76.681
31.930
24.611
200
150
100
50
0
PPM

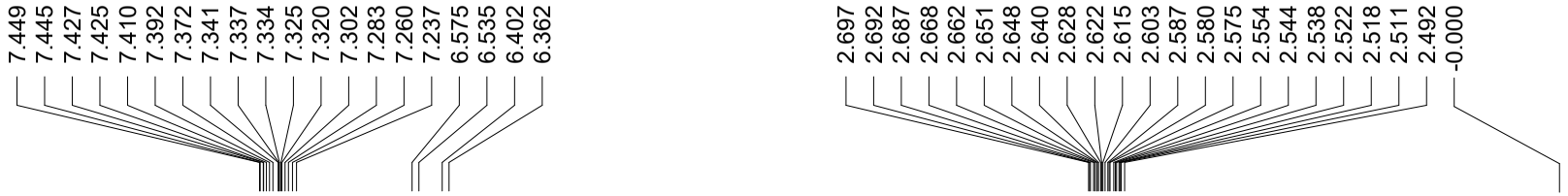

7.466
7.448
7.336
7.318
7.298
7.271
7.265
7.249
7.239
7.225
7.219
7.207
6.538
6.530
6.521
3.042
3.024
3.016
3.003
2.995
2.983
2.975
2.966
3.538
2.958
2.888
2.879
2.869
2.863
2.860
2.854
2.845
2.830
2.821
2.816
2.807
2.763
2.745
2.728
2.706
2.690
2.671
2.649
2.632
-0.000

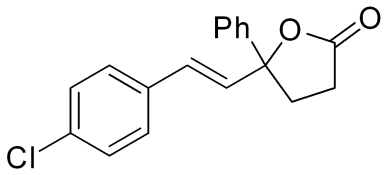

Ph
Me
N
O
OMe
Cl

13


4.95
2.03
2.02
0.95
3.00
4.03
3.23
lican-08-024-H
Nov 9 2022
NA = 8
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
10
8
6
4
2
0
PPM

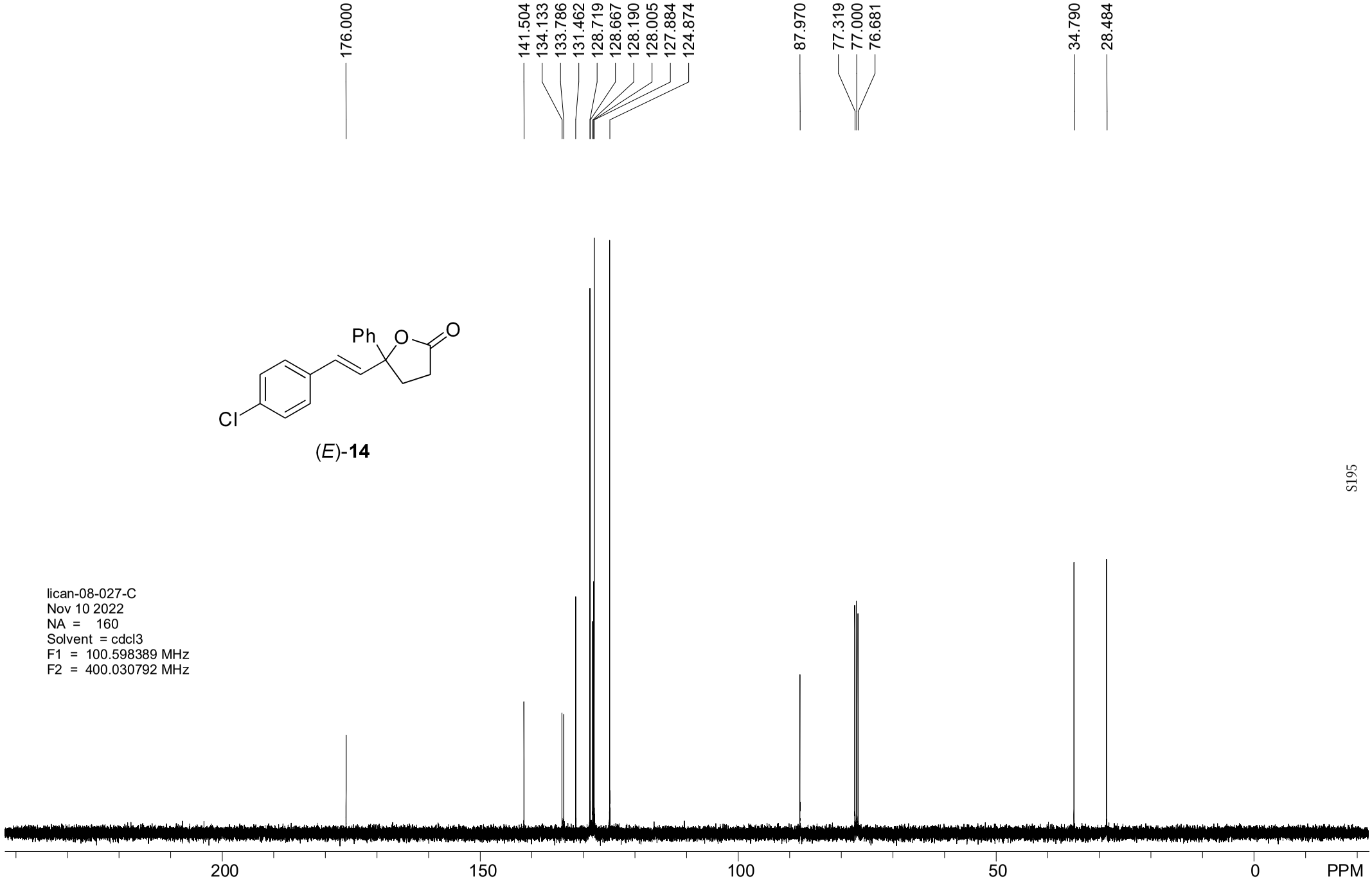

lican-08-024-C
Nov 10 2022
NA = 9520
Solvent = cdcl3
F1 = 100.519485 MHz
F2 = 399.717072 MHz
Cl
13
Ph
O
N
Me
OMe
205.964
173.247
135.398
132.756
132.642
128.725
128.490
127.966
127.306
126.023
110.089
98.232
77.319
77.000
76.681
60.915
32.008
29.882
24.425
200
150
100
50
0
PPM

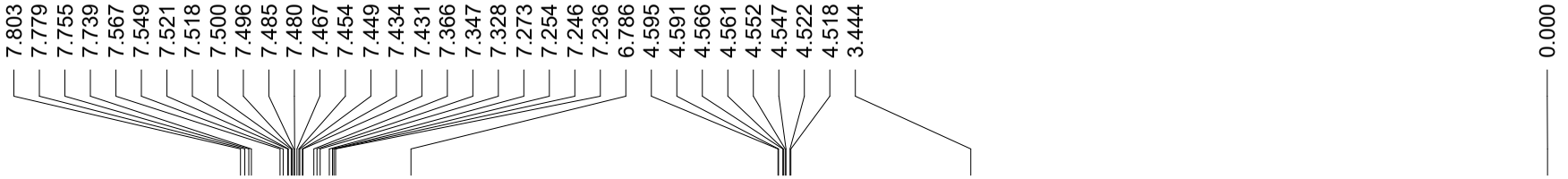

7.449
7.445
7.427
7.425
7.410
7.392
7.372
7.341
7.337
7.334
7.325
7.320
7.302
7.283
7.260
7.237
6.575
6.535
6.402
6.362
2.697
2.692
2.687
2.668
2.662
2.651
2.648
2.640
2.628
2.622
2.615
2.603
2.587
2.580
2.575
2.554
2.544
2.538
2.522
2.518
2.511
2.492
-0.000

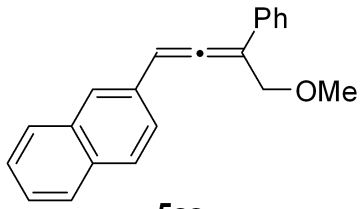

Ph
O
O
Cl

(*E*)-**14**

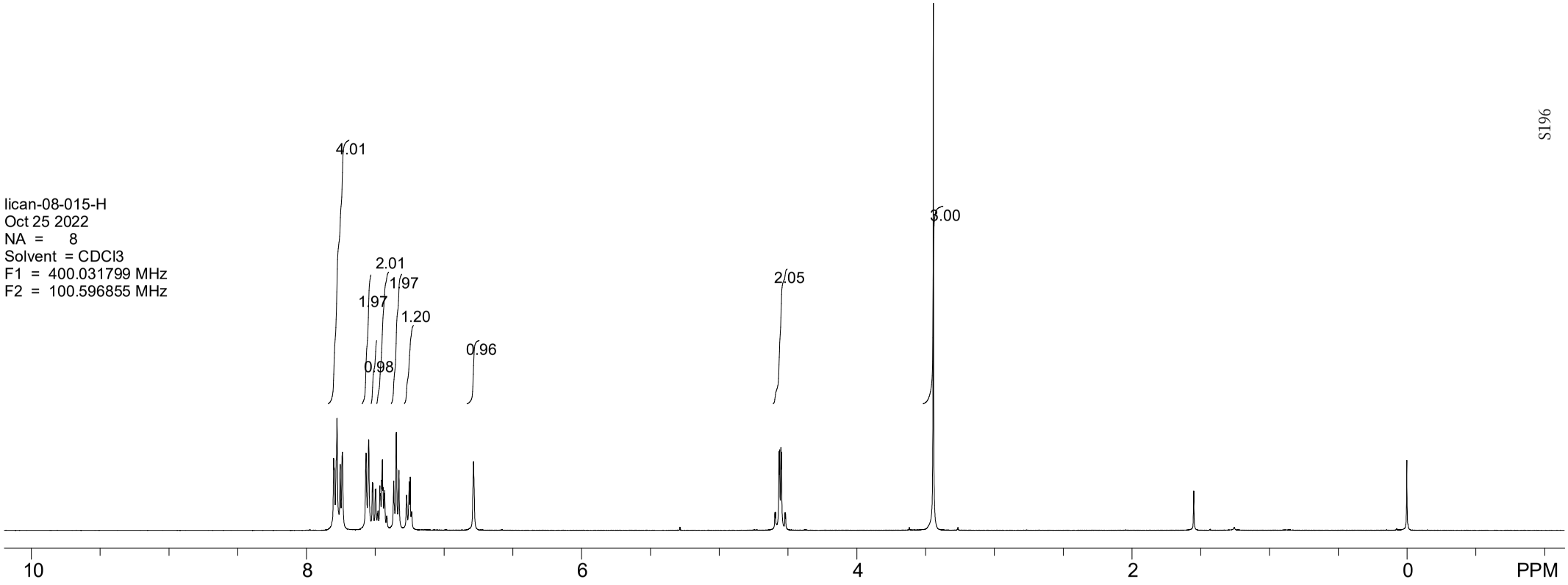
4.01
3.99
0.99
1.00
0.98
4.22
lican-08-027-H
Nov 10 2022
NA = 12
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
10
8
6
4
2
0
PPM

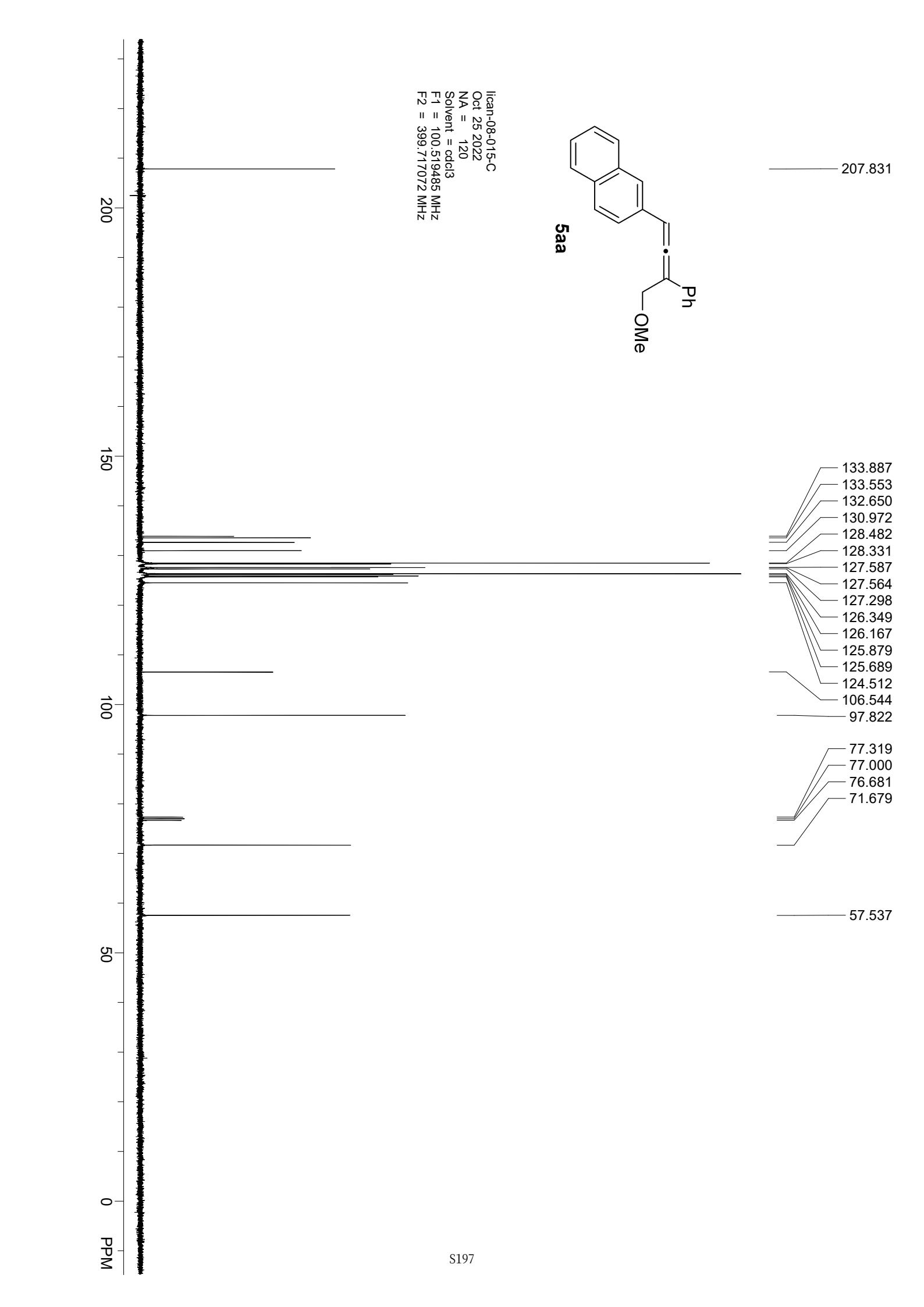

176.000
141.504
134.133
133.786
131.462
128.719
128.667
128.190
128.005
127.884
124.874
87.970
77.319
77.000
76.681
34.790
28.484
Ph
O
O
Cl
(E)-14
lican-08-027-C
Nov 10 2022
NA = 160
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
200
150
100
50
0
PPM

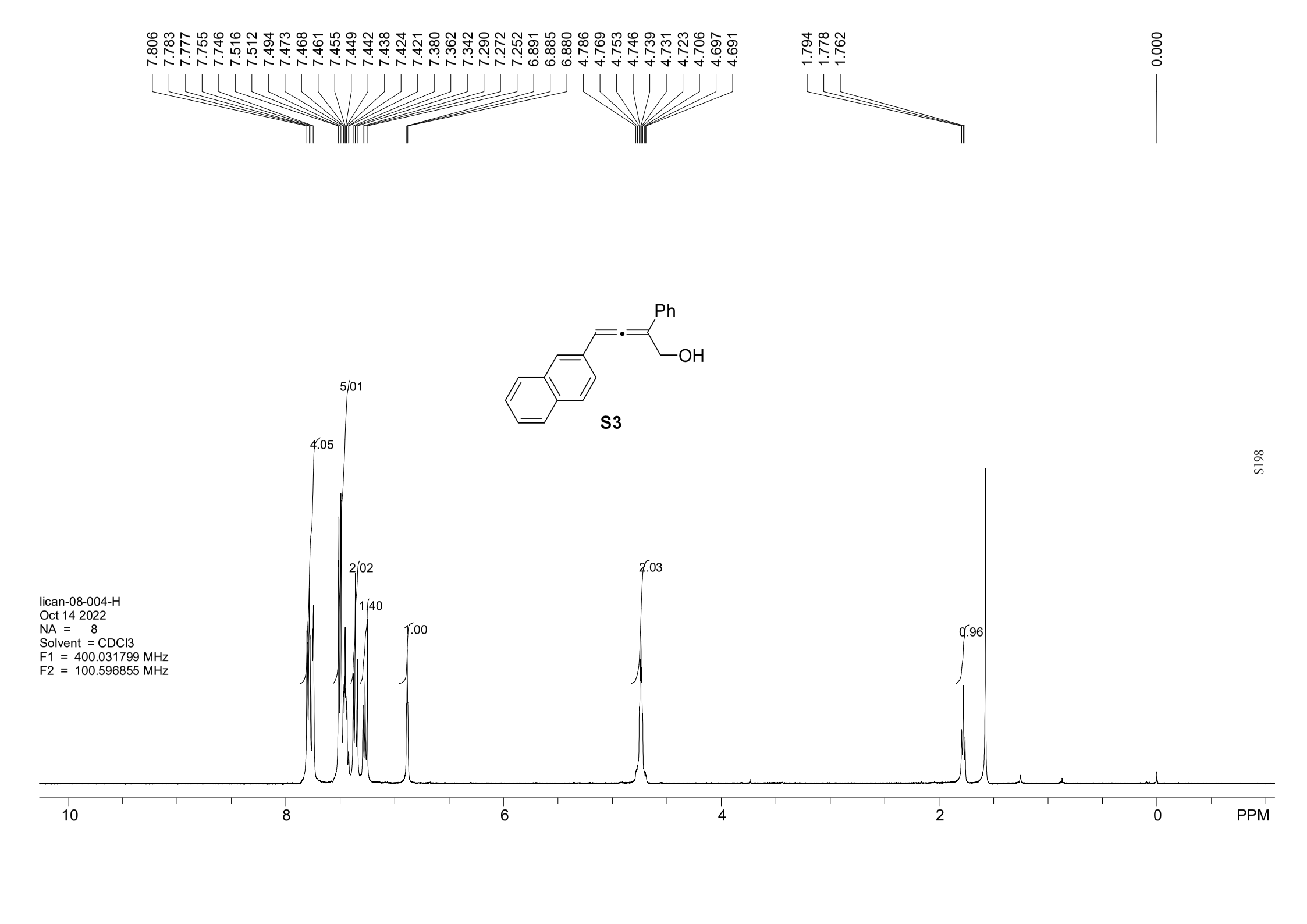

7.803
7.779
7.755
7.739
7.567
7.549
7.521
7.518
7.500
7.496
7.485
7.480
7.467
7.454
7.449
7.434
7.431
7.366
7.347
7.328
7.273
7.254
7.246
7.236
6.786
4.595
4.591
4.566
4.561
4.552
4.547
4.522
4.518
3.444
0.000

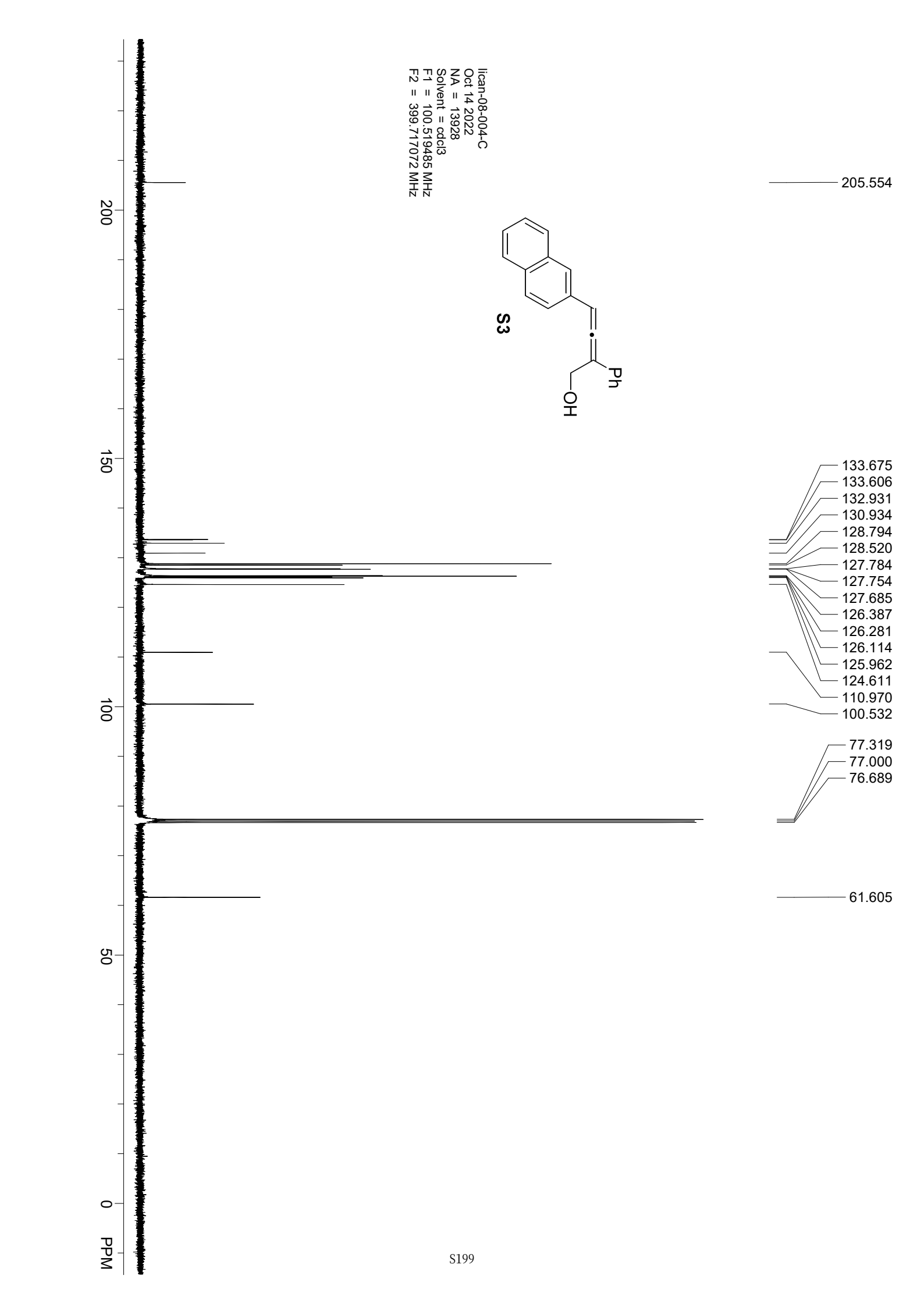

Ph
OMe

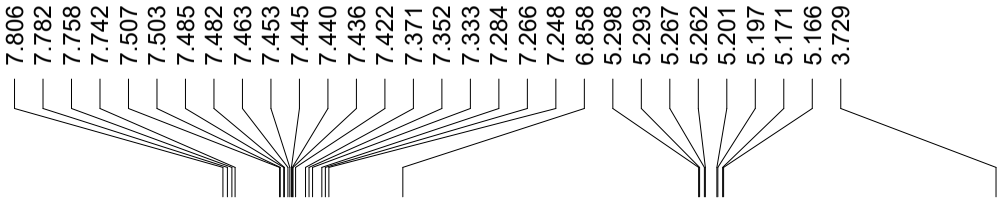
5aa

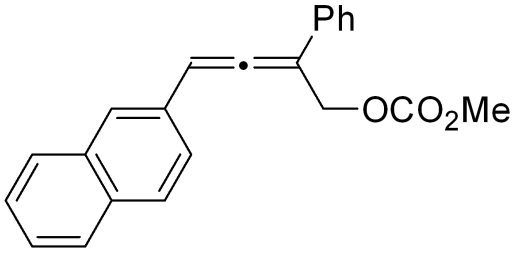

lican-08-015-H
Oct 25 2022
NA = 8
Solvent = CDCl3
F1 = 400.031799 MHz
F2 = 100.596855 MHz
4.01
2.01
1.97
1.97
1.20
0.98
0.96
2.05
3.00
10
8
6
4
2
0
PPM


lican-08-015-C
Oct 25 2022
NA = 120
Solvent = cdcl3
F1 = 100.519485 MHz
F2 = 399.717072 MHz
5aa
Ph
OMe
207.831
133.887
133.553
132.650
130.972
128.482
128.331
127.587
127.564
127.298
126.349
126.167
125.879
125.689
124.512
106.544
97.822
77.319
77.000
76.681
71.679
57.537
200
150
100
50
0
PPM

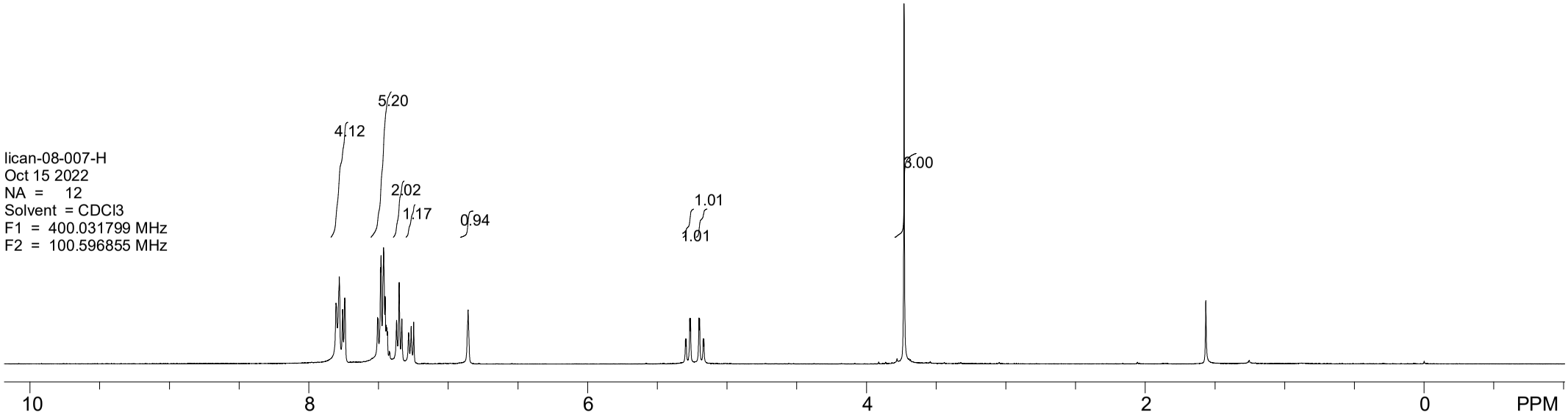

7.806
7.783
7.777
7.755
7.746
7.516
7.512
7.494
7.473
7.468
7.461
7.455
7.449
7.442
7.438
7.424
7.421
7.380
7.362
7.342
7.290
7.272
7.252
6.891
6.885
6.880
4.786
4.769
4.753
4.746
4.739
4.731
4.723
4.706
4.697
4.691
1.794
1.778
1.762
0.000
Ph
OH
S3
5.01
4.05
2.02
1.40
1.00
2.03
0.96
lican-08-004-H
Oct 14 2022
NA = 8
Solvent = CDCl3
F1 = 400.031799 MHz
F2 = 100.596855 MHz
10
8
6
4
2
0
PPM
S198

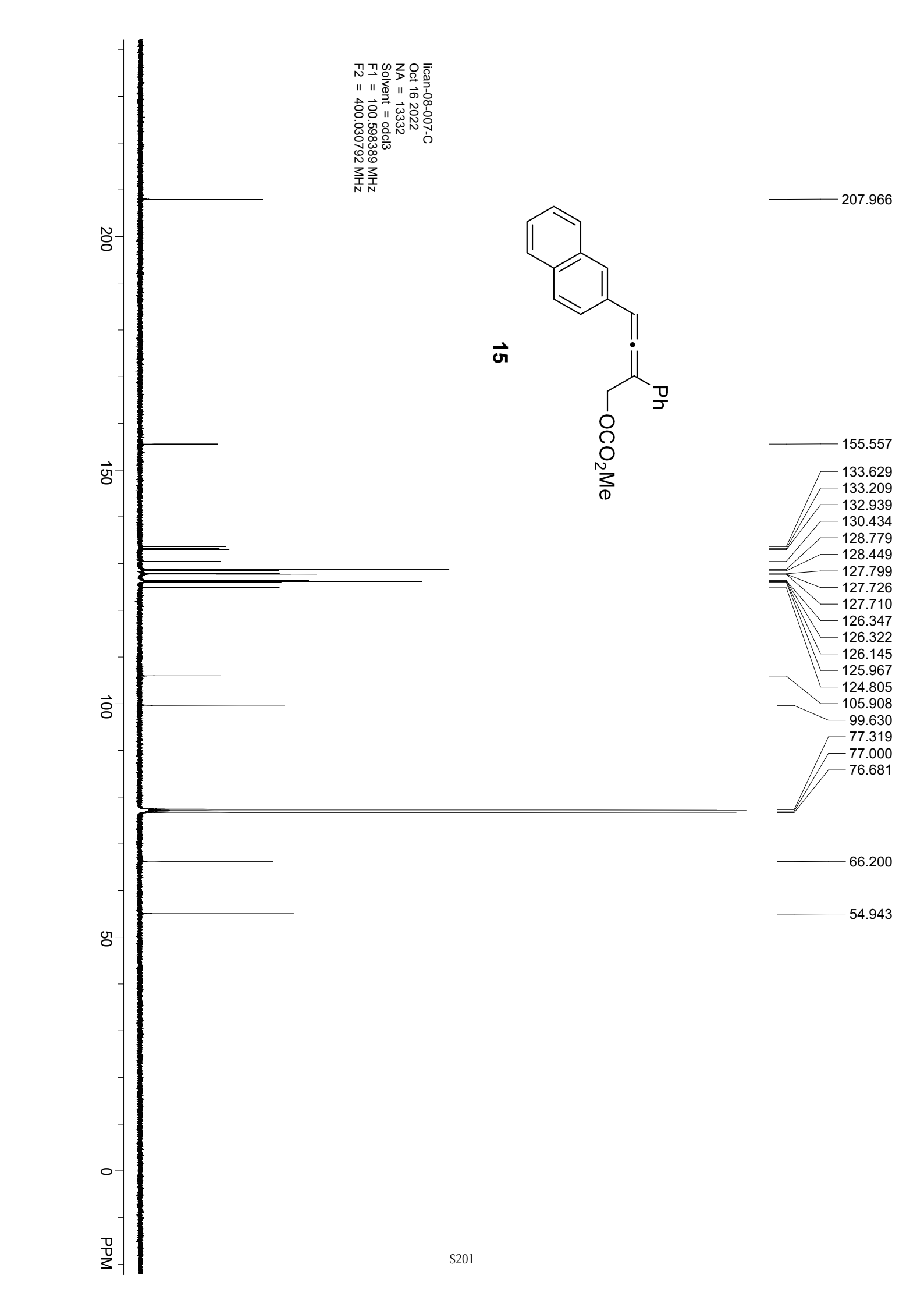

lican-08-004-C
Oct 14 2022
NA = 13928
Solvent = cdcl3
F1 = 100.519485 MHz
F2 = 399.717072 MHz
S3
Ph
OH
205.554
133.675
133.606
132.931
130.934
128.794
128.520
127.784
127.754
127.685
126.387
126.281
126.114
125.962
124.611
110.970
100.532
77.319
77.000
76.689
61.605
200
150
100
50
0
PPM

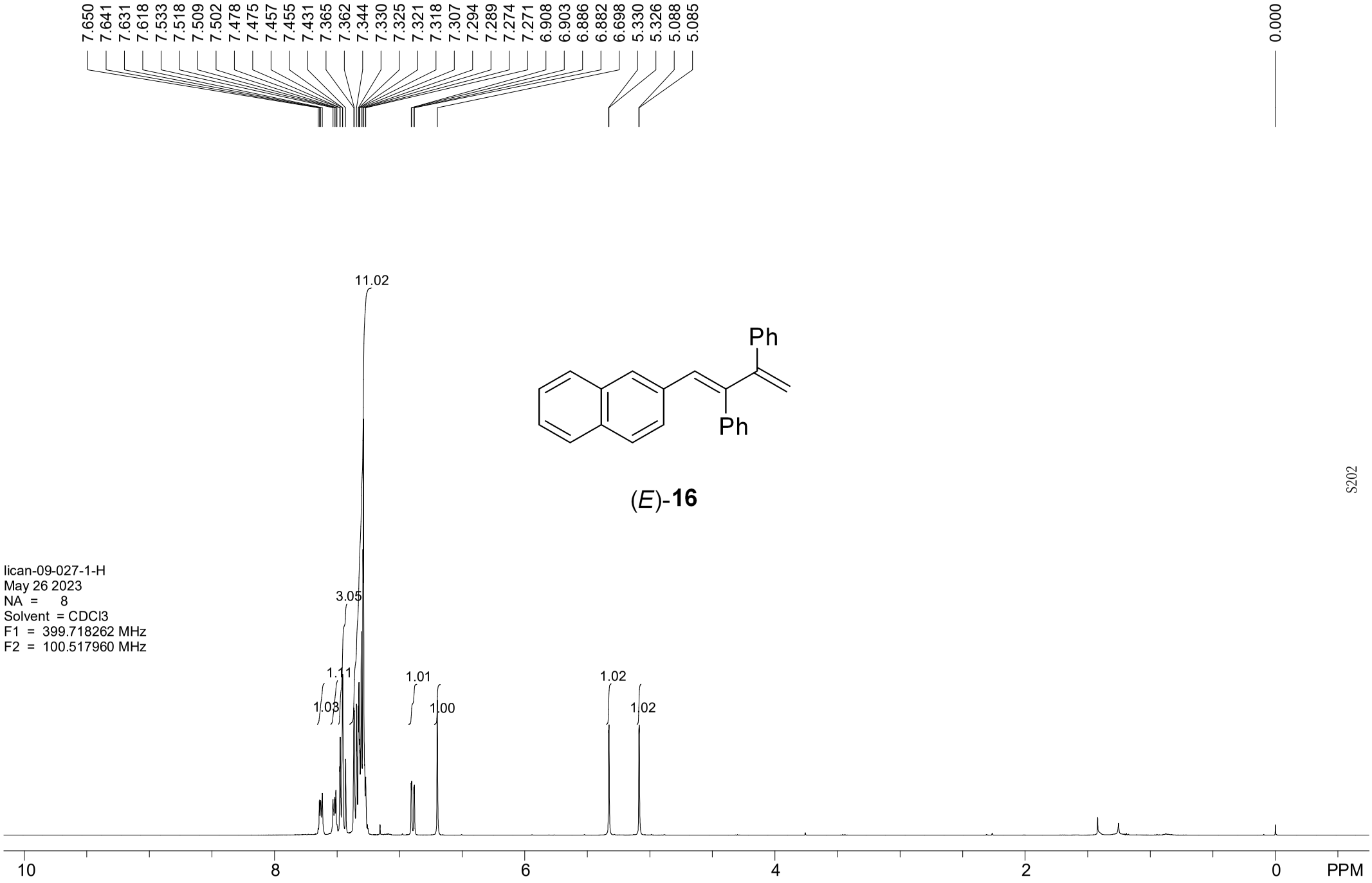

7.806
7.782
7.758
7.742
7.507
7.503
7.485
7.482
7.463
7.453
7.445
7.440
7.436
7.422
7.371
7.352
7.333
7.284
7.266
7.248
6.858
5.298
5.293
5.267
5.262
5.201
5.197
5.171
5.166
3.729
0.000

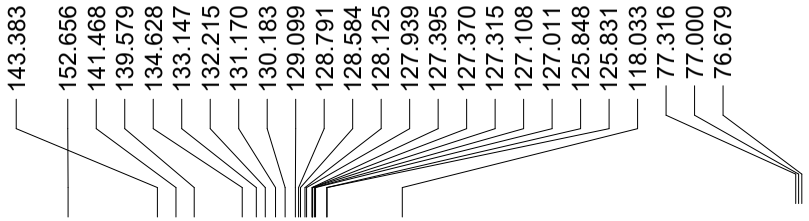

Ph
OCO2Me

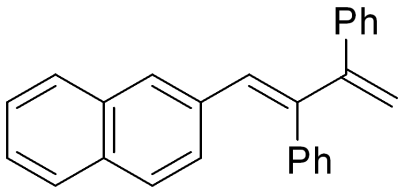
15


lican-08-007-H
Oct 15 2022
NA = 12
Solvent = CDCl3
F1 = 400.031799 MHz
F2 = 100.596855 MHz
4.12
5.20
2.02
1.17
0.94
1.01
1.01
3.00
10
8
6
4
2
0
PPM


lican-08-007-C
Oct 16 2022
NA = 13332
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
15
Ph
OCO2Me
207.966
155.557
133.629
133.209
132.939
130.434
128.779
128.449
127.799
127.726
127.710
126.347
126.322
126.145
125.967
124.805
105.908
99.630
77.319
77.000
76.681
66.200
54.943
200
150
100
50
0
PPM

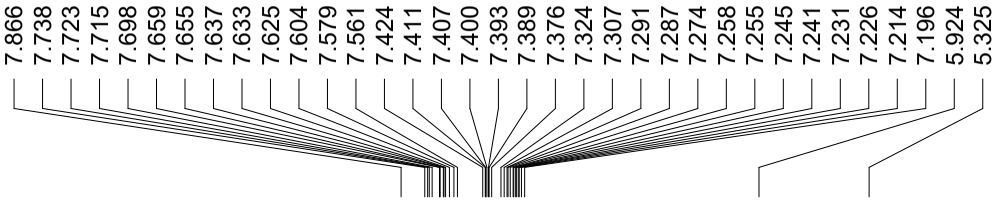

7.650
7.641
7.631
7.618
7.533
7.518
7.509
7.502
7.478
7.475
7.457
7.455
7.431
7.365
7.362
7.344
7.330
7.325
7.321
7.318
7.307
7.294
7.289
7.274
7.271
6.908
6.903
6.886
6.882
6.698
5.330
5.326
5.088
5.085
0.000
11.02
Ph
Ph
(E)-16
S202
lican-09-027-1-H
May 26 2023
NA = 8
Solvent = CDCl3
F1 = 399.718262 MHz
F2 = 100.517960 MHz
3.05
1.11
1.03
1.01
1.00
1.02
1.02
10
8
6
4
2
0
PPM



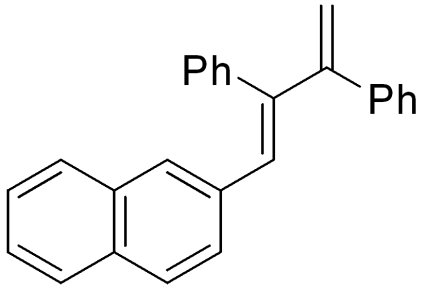


(*E*)-**16**

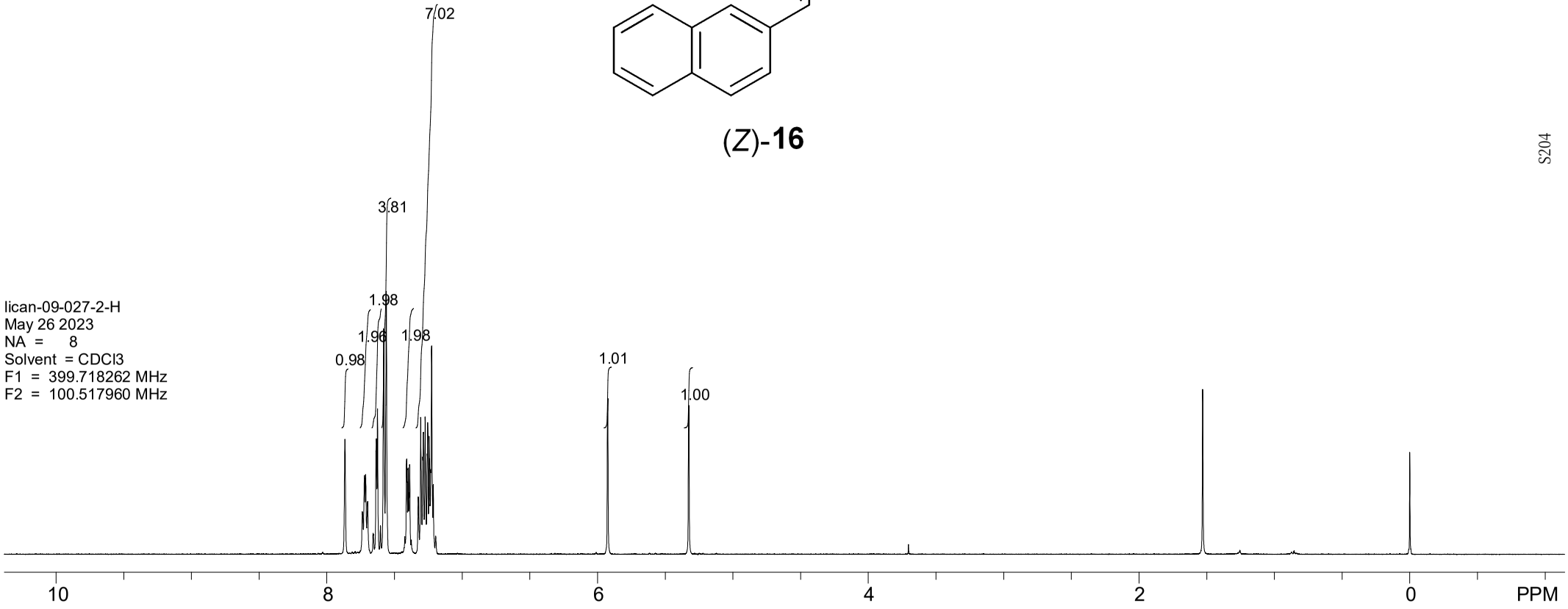
lican-09-027-1-C
May 26 2023
NA = 76
Solvent = cdcl3
F1 = 100.519737 MHz
F2 = 399.717072 MHz

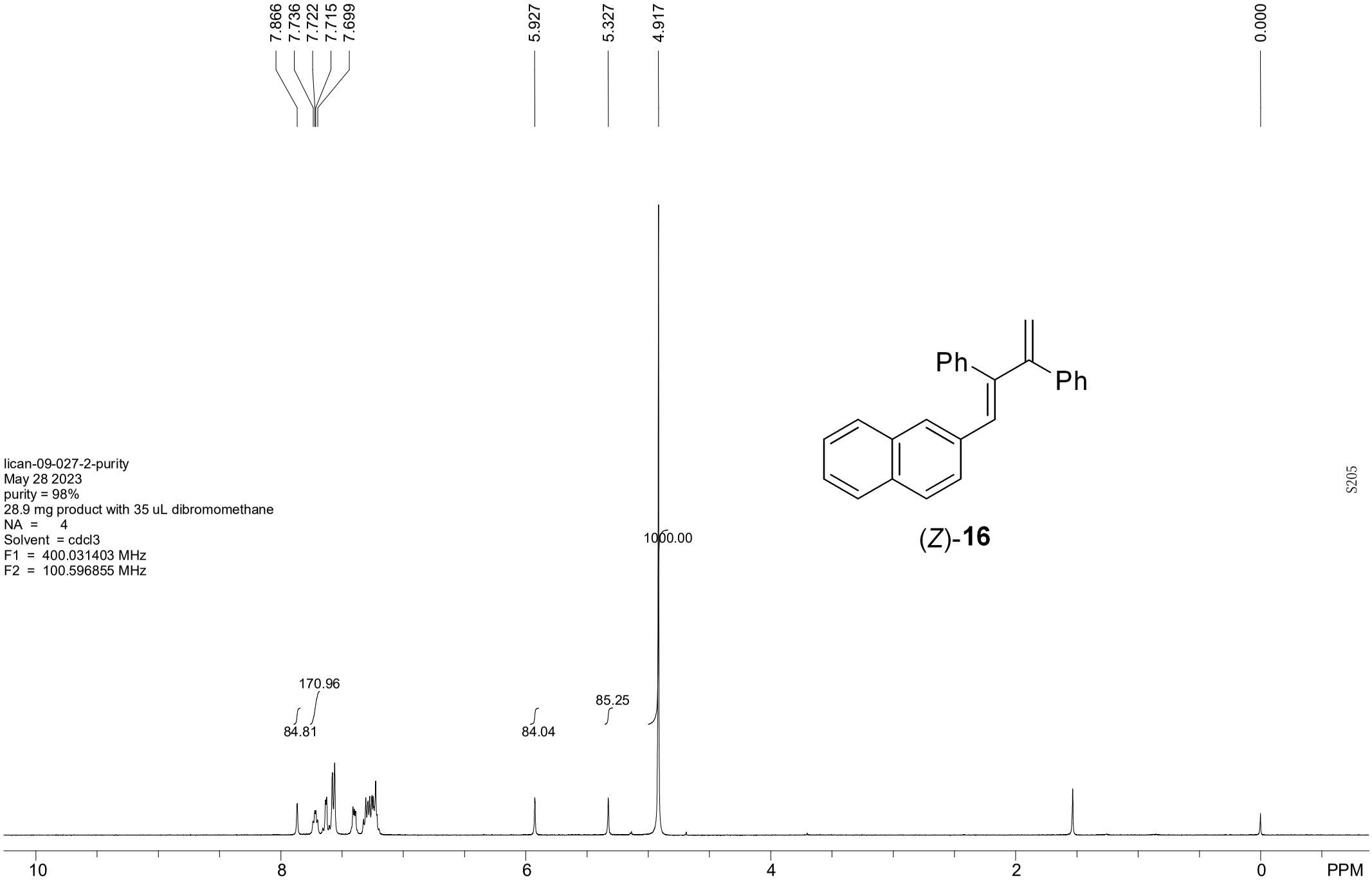

7.866
7.738
7.723
7.715
7.698
7.659
7.655
7.637
7.633
7.625
7.604
7.579
7.561
7.424
7.411
7.407
7.400
7.393
7.389
7.376
7.324
7.307
7.291
7.287
7.274
7.258
7.255
7.245
7.241
7.231
7.226
7.214
7.196
5.924
5.325

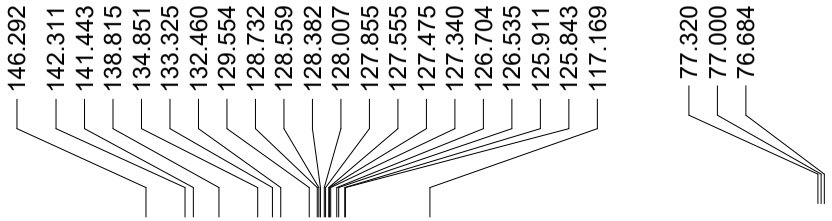
-0.000

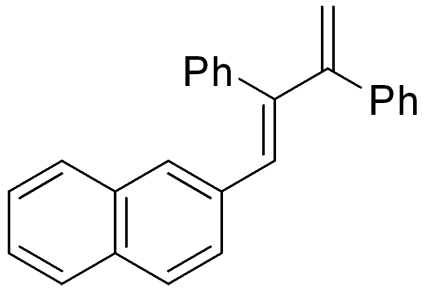

Ph
Ph

(*Z*)-**16**


lican-09-027-2-H
May 26 2023
NA = 8
Solvent = CDCl3
F1 = 399.718262 MHz
F2 = 100.517960 MHz
7.02
3.81
1.98
1.96
1.98
0.98
1.01
1.00
10
8
6
4
2
0
PPM

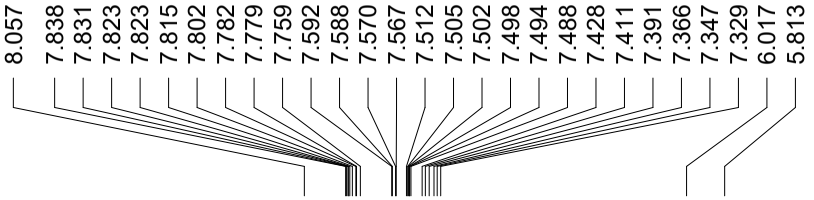

7.866
7.736
7.722
7.715
7.699
5.927
5.327
4.917
0.000
lican-09-027-2-purity
May 28 2023
purity = 98%
28.9 mg product with 35 uL dibromomethane
NA = 4
Solvent = cdcl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz
1000.00
170.96
84.81
84.04
85.25
Ph
Ph
(Z)-16
S205
10
8
6
4
2
0
PPM


146.292
142.311
141.443
138.815
134.851
133.325
132.460
129.554
128.732
128.559
128.382
128.007
127.855
127.555
127.475
127.340
126.704
126.535
125.911
125.843
117.169
77.320
77.000
76.684

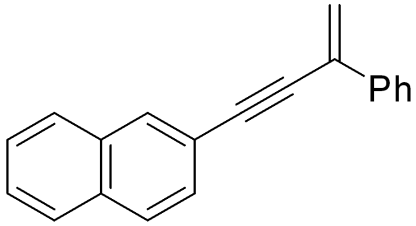

Ph
Ph

(*Z*)-**16**

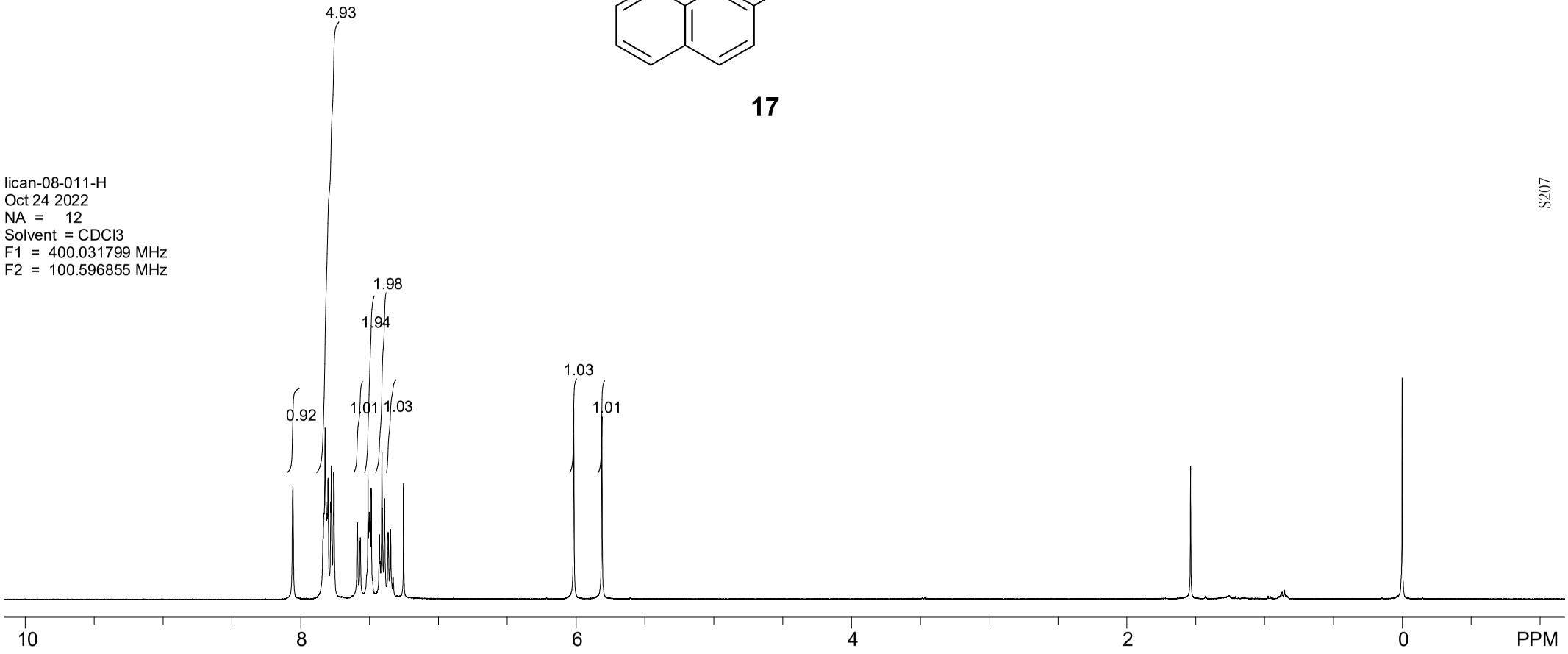
lican-09-027-2-C
May 28 2023
NA = 200
Solvent = cdcl3
F1 = 100.519737 MHz
F2 = 399.717072 MHz
200
150
100
50
0
PPM

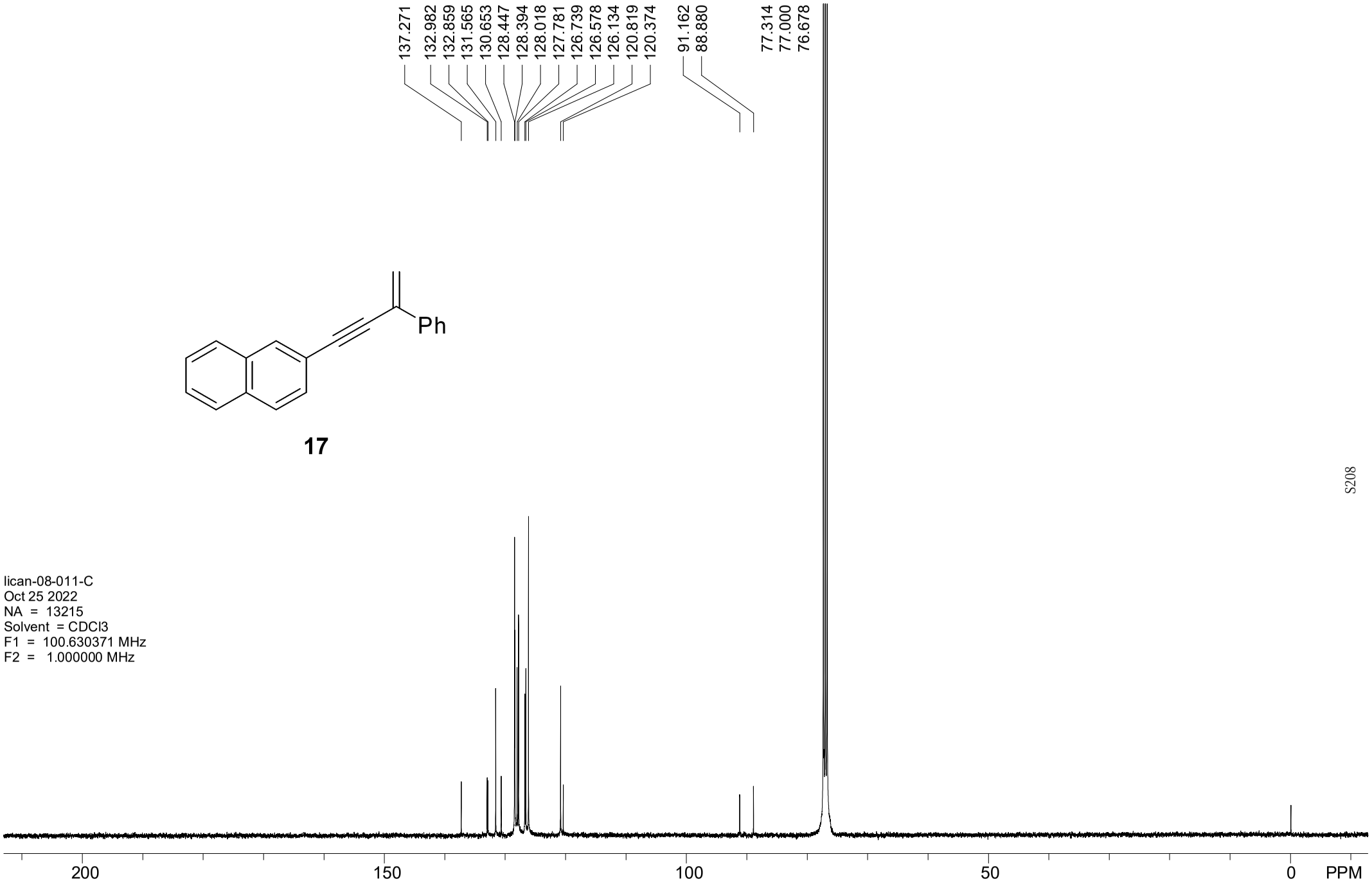

8.057
7.838
7.831
7.823
7.823
7.815
7.802
7.782
7.779
7.759
7.592
7.588
7.570
7.567
7.512
7.505
7.502
7.498
7.494
7.488
7.428
7.411
7.391
7.366
7.347
7.329
6.017
5.813


0.000


Ph

17


lican-08-011-H
Oct 24 2022
NA = 12
Solvent = CDCl3
F1 = 400.031799 MHz
F2 = 100.596855 MHz
4.93
1.98
1.94
1.03
1.01
0.92
1.01
1.03
10
8
6
4
2
0
PPM


137.271
132.982
132.859
131.565
130.653
128.447
128.394
128.018
127.781
126.739
126.578
126.134
120.819
120.374
91.162
88.880
77.314
77.000
76.678
Ph
17
lican-08-011-C
Oct 25 2022
NA = 13215
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
200
150
100
50
0
PPM