Reactivity of Vinylidene-π-Allyl Palladium(II) Species

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Supporting Information

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 in $CDCl_3$ with tetramethylsilane (0 ppm) as the internal standard; ^{13}C NMR experiments were measured in relative to the signal of $CDCl_3$ (77.0 ppm); ^{19}F NMR experiments were measured in $CDCl_3$ with $CFCl_3$ (0 ppm) as the internal standard. THF was dried over sodium wire and distilled freshly before use. Petroleum ether (b.p. 60-90 ^{o}C) was purchased from Shanghai Titan Scientific Co. Ltd. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise. Room temperature in laboratory was in the range of 20 to 26 ^{o}C.

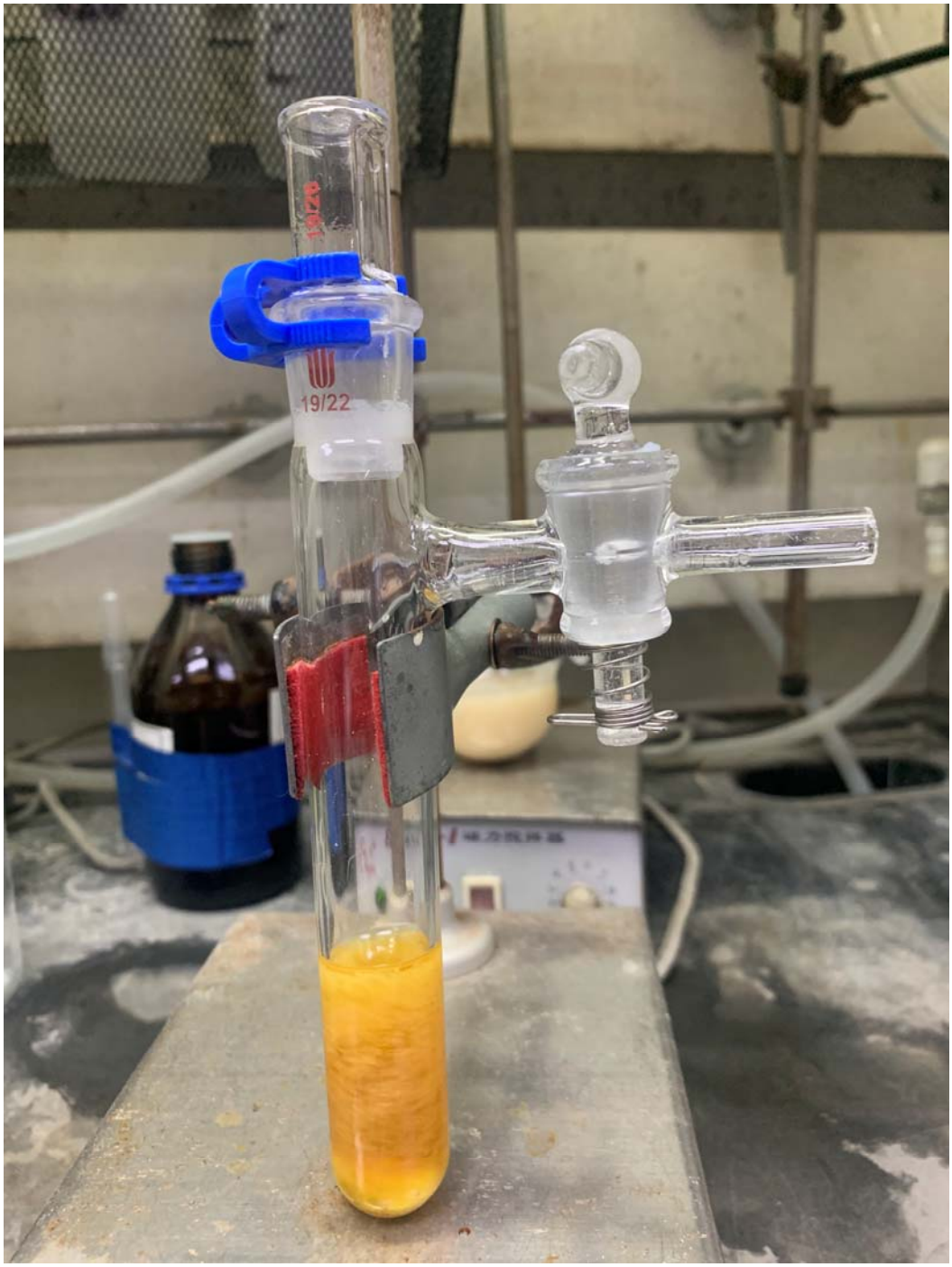
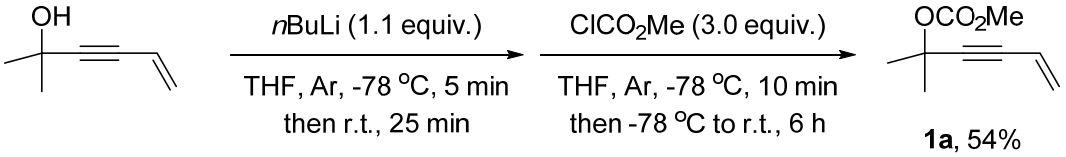


Figure S1. The photo of the apparatus for preparation of 1,2,3-butatrienes.

1. Preparation of 4-alken-2-ynyl carbonates.

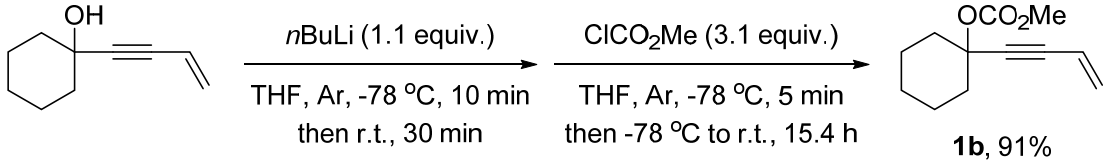
2-Methylhex-5-en-3-yn-2-yl acetate **1a'** was prepared according to the literature.[1]

(1) Preparation of methyl 2-methylhex-5-en-3-yn-2-yl carbonate **1a** (lican-02-123)



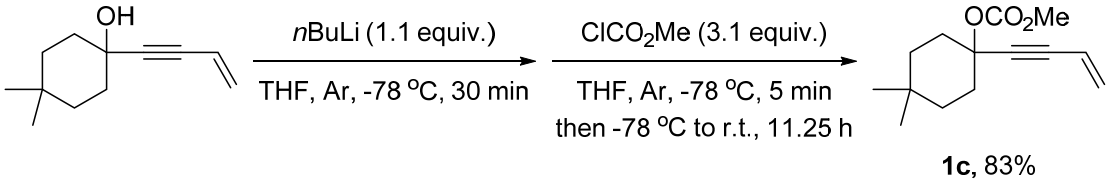
Typical Procedure I: To an oven-dried Schlenk tube with a polytetrafluoroethylene plug were added 2-methylhex-5-en-3-yn-2-ol (1.7312 g, 15.7 mmol) and freshly distilled THF (40 mL) under argon atmosphere. After cooling to -78 °C via a dry ice-acetone bath, *n*BuLi (2.5 M in hexane, 7.1 mL, 17.8 mmol) was added dropwise over 5 min. The resulting mixture was stirred for 25 min at room temperature and subsequently cooled to -78 °C via a dry ice-acetone bath, which was followed by the dropwise addition of methyl chloroformate (3.7 mL, d = 1.223, 4.525 g, 48 mmol) over 10 min. The resulting mixture was stirred for 6 h, during which time it was gradually warmed up to room temperature. After the reaction was complete as monitored by TLC (eluent: petroleum ether / ethyl acetate = 8:1), it was quenched with an aqueous solution of NH_4Cl and extracted with ethyl acetate (40 mL × 3). The combined organic extract was washed with brine (50 mL × 3), dried over anhydrous Na_2SO_4, and filtrated. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel to afford **1a** (1.4283 g, 54%) [eluent: petroleum ether / ethyl acetate = 60:1 (1200+20 mL)] as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.82 (dd, J_1 = 17.8 Hz, J_2 = 11.0 Hz, 1 H, =CH), 5.66 (dd, J_1 = 17.6 Hz, J_2 = 2.0 Hz, 1 H, one proton of $=CH_2$), 5.50 (dd, J_1 = 11.2 Hz, J_2 = 2.0 Hz, 1 H, one proton of $=CH_2$), 3.77 (s, 3 H, OCH_3), 1.72 (s, 6 H, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 153.4, 127.6, 116.4, 89.8, 83.0, 74.4, 54.2, 28.7; **IR** (neat): ν = 2992, 2953, 1751, 1441, 1256, 1133, 940 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 168 (M^+, 22.0), 93 (100); **HRMS** (EI) Calcd. for $C_9H_{12}O_3$ [M^+]: 168.0781, found 168.0777.

(2) Preparation of methyl 1,1-pentamethylenepent-4-en-2-ynyl carbonate **1b** (lican-02-075)



Following **Typical Procedure I**, the reaction of 1,1-pentamethylenepent-4-en-2-yn-1-ol (1.5760 g, 10 mmol), *n*BuLi (2.5 M in hexane, 4.4 mL, 11 mmol), methyl chloroformate (2.4 mL, d = 1.223, 2.9352 g, 31 mmol), and THF (20 mL) for 15.4 h afforded **1b** (1.9795 g, 91%) via column chromatography on silica gel [petroleum ether / ethyl acetate = 60:1 (1200+20 mL)] as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.85 (dd, J_1 = 17.6 Hz, J_2 = 11.2 Hz, 1 H, =CH), 5.66 (dd, J_1 = 17.6 Hz, J_2 = 2.4 Hz, 1 H, one proton of $=CH_2$), 5.50 (dd, J_1 = 11.0 Hz, J_2 = 2.4 Hz, 1 H, one proton of $=CH_2$), 3.77 (s, 3 H, OCH_3), 2.22-2.11 (m, 2 H), 1.94-1.82 (m, 2 H), 1.73-1.47 (m, 5 H), 1.40-1.28 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 153.1, 127.3, 116.5, 88.7, 85.0, 77.8, 54.0, 36.7, 24.9, 22.5; **IR** (neat): ν = 2936, 2860, 1749, 1441, 1270, 1235, 1183, 1015 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 208 (M^+, 94.4), 91 (100); **HRMS** (EI) Calcd. for $C_{12}H_{16}O_3$ [M^+]: 208.1099, found 208.1101.

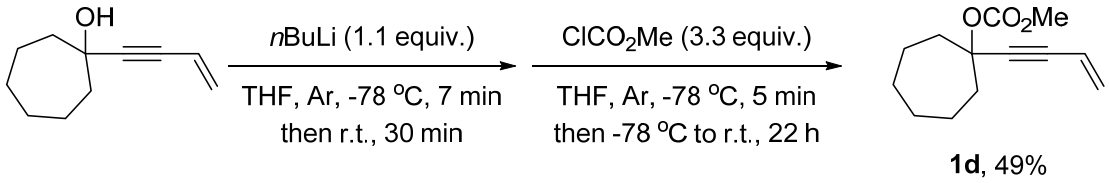
(3) Preparation of methyl 1,1-(3,3-dimethylpentamethylene)pent-4-en-2-ynyl carbonate **1c** (lican-04-078)



Following **Typical Procedure I**, the reaction of 1,1-(3,3-dimethylpentamethylene)pent-4-en-2-ynol (1.8351 g, 10 mmol), *n*BuLi (2.5 M in hexane, 4.4 mL, 11 mmol), methyl chloroformate (2.4 mL, d = 1.223, 2.9352 g, 31 mmol), and THF (30 mL) for 11.25 h afforded **1c** (1.9504 g, 83%) via column chromatography on silica gel [petroleum ether / ethyl ether = 30:1 (900+30 mL)] as a light green oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.85 (dd, J_1 = 17.6 Hz, J_2 = 11.2 Hz,

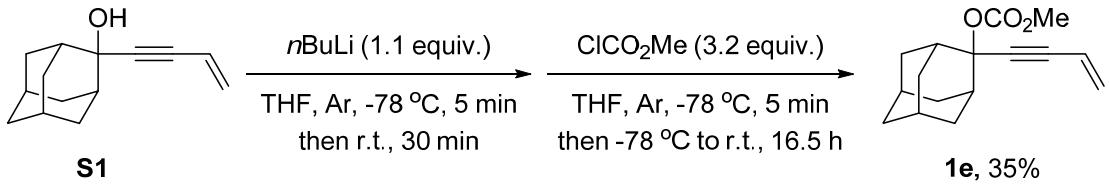
1 H, =CH), 5.66 (dd, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1 H, one proton of =CH_2), 5.50 (dd, J_1 = 11.2 Hz, J_2 = 2 Hz, 1 H, one proton of =CH_2), 3.77 (s, 3 H, OCH_3), 2.19-1.95 (m, 4 H, 2 × CH_2), 1.52-1.34 (m, 4 H, 2 × CH_2), 1.02-0.84 (m, 6 H, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 153.3, 127.5, 116.5, 88.7, 84.7, 77.9, 54.2, 35.1, 32.8, 29.2, 28.8 (br), 27.1 (br); **IR** (neat): ν = 2952, 2915, 2867, 1752, 1440, 1286, 1445, 1205, 1170, 1127 cm^{-1}; **MS** (ESI) *m/z* 259 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{14}H_{20}O_3Na$ $[M+Na]^+$: 259.1305, Found: 259.1304.

(4) Preparation of methyl 1,1-hexamethylenepent-4-en-2-ynyl carbonate **1d** (zzn-1-010)



Following **Typical Procedure I**, the reaction of 1,1-hexamethylene-pent-4-en-1-yn-1-ol (1.8030 g, 11 mmol), *n*BuLi (2.5 M in hexane, 5 mL, 12.5 mmol), methyl chloroformate (2.8 mL, d = 1.223, 3.4244 g, 36 mmol), and THF (60 mL) at -78 °C to r.t. for 22 h afforded **1d** (1.2499 g, 49%, 97% purity) via column chromatography on silica gel [First round: petroleum ether / ethyl acetate = 15:1 (1800+120 mL)] afforded impure **1d**. Second round: petroleum ether / ethyl acetate = 60:1 (900+15 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.84 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1 H, =CH), 5.64 (dd, J_1 = 17.6 Hz, J_2 = 2.0 Hz, 1 H, one proton of =CH_2), 5.48 (dd, J_1 = 11.0 Hz, J_2 = 1.8 Hz, 1 H, one proton of =CH_2), 3.75 (s, 3 H, OCH_3), 2.30-2.25(m, 2 H, CH_2), 2.16-2.10 (m, 2 H, CH_2), 1.68-1.58 (m, 8 H, 4 × CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 153.2, 127.2, 116.5, 89.9, 84.2, 81.2, 54.0, 39.9. 28.1, 21.9; **IR** (neat): ν = 2931, 2858, 1750, 1601, 1460, 1440, 1287, 1249, 1188, 1006, 956, 885, 789 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 222 (M^+, 32.3), 91 (100); **HRMS** (EI) Calcd. for $C_{13}H_{18}O_3$ $[M^+]$: 222.1256, found 222.1253.

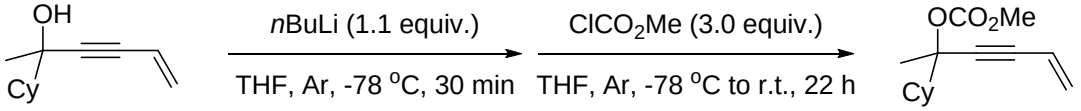
(5) Preparation of compound **1e** (zzn-1-017)



S1 **1e**, 35%

Following **Typical Procedure I**, the reaction of **S1** (2.4266 g, 12 mmol), *n*BuLi (2.5 M in hexane, 5.6 mL, 14 mmol), methyl chloroformate (3.0 mL, d = 1.223, 3.6690 g, 38.8 mmol), and THF (60 mL) at -78 °C to r.t. for 16.5 h afforded **1e** (1.0808 g, 35%) via column chromatography on silica gel [petroleum ether / ethyl ether = 60:1 (1800+30 mL)] as a white solid: **m.p.** 55.1-55.9 °C (hexane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.87 (dd, J_1 = 17.2 Hz, J_2 = 11.2 Hz, 1 H, =CH), 5.66 (dd, J_1 = 17.8 Hz, J_2 = 2.2 Hz, 1 H, one proton of $=CH_2$), 5.49 (dd, J_1 = 11.2 Hz, J_2 = 2.0 Hz, 1 H, one proton of $=CH_2$), 3.78 (s, 3 H, OCH_3), 2.50 (s, 2 H, 2 × CH), 2.24-2.12 (m, 2 H, CH_2), 2.09-1.98 (m, 2 H, CH_2), 1.89-1.76 (m, 4 H, 2 × CH_2), 1.73 (m, 2 H, CH_2) 1.67-1.58 (m, 2 H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 153.2, 127.3, 116.7, 89.3, 85.9, 82.3, 54.2, 37.3. 36.0, 34.9. 31.8, 26.7, 26.2; **IR** (neat): ν = 2907, 2858, 1748, 1601, 1437, 1359, 1252, 1100, 967, 912, 787, 503 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 260 (M^+, 100); **Elem. Anal.** Calcd. for $C_{16}H_{20}O_3$: C 73.82, H 7.74, found C 74.16, H 7.93.

(6) Preparation of methyl 2-cyclohexylhex-5-en-3-yn-2-yl carbonate **1f** (lican-06-080)

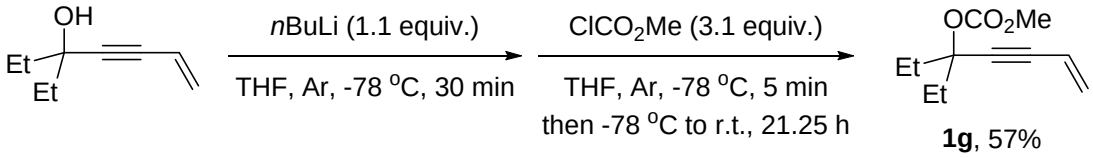


1f, 71%

Following **Typical Procedure I**, the reaction of 2-cyclohexyl-hex-5-en-3-yn-2-ol (0.5362 g, 3 mmol), *n*BuLi (2.5 M in hexane, 1.3 mL, 3.3 mmol), methyl chloroformate (0.7 mL, d = 1.223, 856.1 mg, 9 mmol), and THF (20 mL) at -78 °C to r.t. for 22 h afforded **1f** (0.5065 g, 71%) via column chromatography on silica gel [petroleum ether / ethyl ether = 30:1 (600+20 mL)] as a light green oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.84 (dd, J_1 = 17.8 Hz, J_2 = 11.0 Hz, 1 H, =CH), 5.70 (dd, J_1 = 17.6 Hz, J_2 = 2.0 Hz, 1 H, one proton of $=CH_2$), 5.49 (dd, J_1 = 11.2 Hz, J_2 = 2.0 Hz, 1 H, one proton of $=CH_2$), 3.75 (s, 3 H, OCH_3), 2.04-1.92 (m, 1 H, CH), 1.91-1.75 (m, 4 H), 1.68 (m, 4 H), 1.34-1.06 (m, 5 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 153.4, 127.3,

116.5, 88.6, 84.7, 80.9, 54.1, 47.1, 27.3, 27.0, 26.10, 26.05, 26.00, 23.2; **IR** (neat): ν = 2931, 2855, 1751, 1607, 1440, 1373, 1251, 1215, 1145, 1059, 942 cm^{-1}; **MS** (ESI) *m/z* 259 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{14}H_{20}O_3Na$ $[M+Na]^+$: 259.1305, Found: 259.1304.

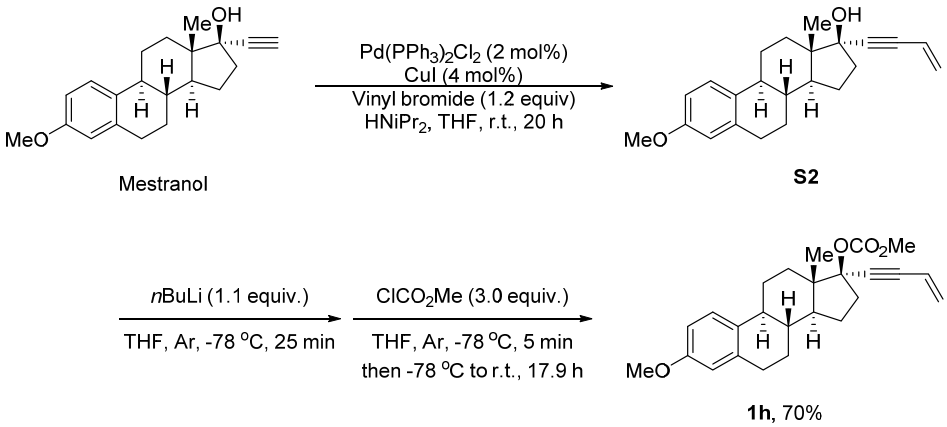
(7) Preparation of methyl 3-ethylhept-6-en-4-yn-3-yl carbonate **1g** (lican-04-059)



1g, 57%

Following **Typical Procedure I**, the reaction of 3-ethyl-hept-6-en-4-yn-3-ol (0.9571 g, 7 mmol), *n*BuLi (2.5 M in hexane, 3.1 mL, 7.8 mmol), methyl chloroformate (1.7 mL, d = 1.223, 2.0791 g, 22 mmol) and THF (30 mL) at -78 °C to r.t. for 21.25 h afforded **1g** (0.7870 g, 57%) via column chromatography on silica gel [petroleum ether / ethyl ether = 30:1 (900+30 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.85 (dd, J_1 = 17.2 Hz, J_2 = 10.8 Hz, 1 H, =CH), 5.66 (dd, J_1 = 17.6 Hz, J_2 = 1.2 Hz, 1 H, one proton of $=CH_2$), 5.50 (dd, J_1 = 11.6 Hz, J_2 = 2.0 Hz, 1 H, one proton of $=CH_2$), 3.75 (s, 3 H, OCH_3), 2.12-1.89 (m, 4 H, 2 × CH_2), 1.00 (t, *J* = 7.4 Hz, 6 H, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 153.3, 127.4, 116.5, 88.2, 85.0, 81.9, 54.1, 30.6, 8.2; **IR** (neat): ν = 2976, 2884, 1752, 1441, 1251, 1212, 952 cm^{-1}; **MS** (ESI) *m/z* 197 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{11}H_{17}O_3$ $[M+H]^+$: 197.1172, Found: 197.1168.

(8) Preparation of compound **1h** (lican-04-104)

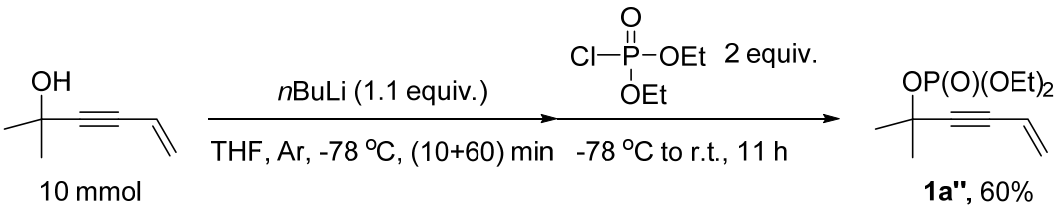


1h, 70%

To a three-neck flask were added mestranol (3.0916 g, 10 mmol), $Pd(PPh_3)_2Cl_2$ (0.1421 g, 0.2 mmol), CuI (0.0758 g, 0.4 mmol), THF (40 mL), *i*Pr_2NH (3.5 mL), and vinyl bromide (1 M in THF, 12 mL, 12 mmol) sequentially under Argon atmosphere. The resulting mixture was then stirred at room temperature for 20 hours as monitored by TLC, quenched with an aqueous solution of NH_4Cl (40 mL), and extracted with ethyl acetate (40 mL × 3). The combined organic extract was washed with brine (50 mL × 3), dried over anhydrous Na_2SO_4, and filtrated. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel [eluent: petroleum ether / acetone = 8:1 (1200+150 mL)] to afford **S2** (3.3093 g, 98%), which was used in next step without further characterization.

Following **Typical Procedure I**, the reaction of **S2** (3.3688 g, 10 mmol), *n*BuLi (2.5 M in hexane, 4.4 mL, 11 mmol), methyl chloroformate (2.4 mL, d = 1.223, 2.9352 g, 31 mmol), and THF (40 mL) at -78 °C to r.t. for 17.9 h afforded **1h** (2.7523 g, 70%) via column chromatography on silica gel [petroleum ether / ethyl ether = 15:1 (900+60 mL)] as a white solid: **m.p.** 106.7-107.7 °C (hexane); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.21 (d, J = 8.8 Hz, 1 H, ArH), 6.71 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1 H, ArH), 6.65 (d, J = 2.8 Hz, 1 H, ArH), 5.87 (dd, J_1 = 17.6 Hz, J_2 = 11.6 Hz, 1 H, =CH), 5.67 (dd, J_1 = 18.0 Hz, J_2 = 2.0 Hz, 1 H, =CH), 5.50 (dd, J_1 = 11.0 Hz, J_2 = 2.2 Hz, 1 H, =CH), 3.84-3.70 (m, 6 H, 2 × OCH_3), 2.93-2.81 (m, 2 H, CH_2), 2.80-2.68 (m, 1 H, CH), 2.42-2.31 (m, 1 H, CH), 2.30-2.13 (m, 2 H, CH_2), 2.03-1.92 (m, 1 H, CH), 1.92-1.79 (m, 3 H, CH_2 and CH), 1.77-1.66 (m, 1 H, CH), 1.55-1.32 (m, 4 H, 2 × CH_2), 0.94 (s, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.4, 154.2, 137.8, 132.3, 127.4, 126.3, 116.7, 113.7, 111.4, 88.9, 87.1, 85.8, 55.1, 54.5, 48.4, 48.3, 43.4, 39.1, 37.3, 33.2, 29.7, 27.2, 26.3, 23.1, 13.4; **IR** (neat): ν = 2989, 2936, 2867, 2836, 1755, 1610, 1500, 1441, 1275, 1255, 1235 cm^{-1}; **MS** (ESI) *m/z* 395 $[M+H]^+$; **Elem. Anal.** Calcd. for $C_{25}H_{30}O_4$: C 76.11, H 7.67, found C 76.44, H 7.84.

(9) Preparation of diethyl 2-methylhex-5-en-3-yn-2-yl phosphate **1a"** (lican-08-074)

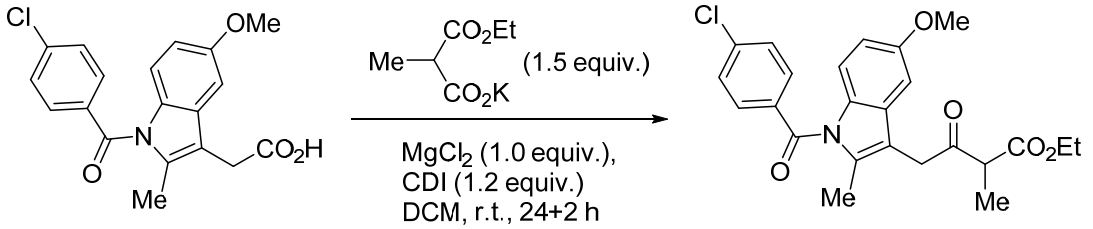


To an oven-dried Schlenk tube with a polytetrafluoroethylene plug were added 2-methylhex-5-en-3-yn-2-ol (1.1071 g, 10 mmol) and freshly distilled THF (40 mL) under argon atmosphere. After cooling to -78 °C via a dry ice-acetone bath, *n*BuLi (2.5 M in hexane, 4.4 mL, 11.0 mmol) was added dropwise over 10 min. The resulting mixture was stirred for 60 min at -78 °C with a dry ice-acetone bath, which was followed by the addition of diethyl chlorophosphate (3.4552 g, 20 mmol). The resulting mixture was stirred for 11 h, during which time it was gradually warmed up to room temperature. After the reaction was complete as monitored by TLC (eluent: petroleum ether / ethyl acetate = 2:1), it was quenched with an aqueous solution of NH_4Cl (50 mL) and extracted with ethyl acetate (30 mL × 4). The combined organic extract was washed with brine (50 mL × 3), dried over anhydrous Na_2SO_4, and filtrated. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel to afford **1a"** (1.5853 g, 60%, purity = 93%) [eluent: petroleum ether / ethyl acetate = 2:1 (800+400 mL)] as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.83 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1 H, =CH), 5.67 (dd, J_1 = 17.6 Hz, J_2 = 2.0 Hz, 1 H, one proton of $=CH_2$), 5.51 (dd, J_1 = 11.0 Hz, J_2 = 2.2 Hz, 1 H, one proton of $=CH_2$), 4.17-4.07 (m, 4 H, 2 × OCH_2), 1.75 (s, 6 H, 2 × CH_3), 1.38-1.30 (m, 6 H, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 127.8, 116.4, 90.4 (d, *J* = 4.6 Hz), 83.4, 74.7 (d, *J* = 6.9 Hz), 63.5 (d, *J* = 6.1 Hz), 30.7 (d, *J* = 4.5 Hz), 16.0 (d, *J* = 7.6 Hz); **IR** (neat): ν = 2987, 1603, 1445, 1389, 1368, 1264, 1166 cm^{-1}; **MS** (ESI) *m/z* 247.1 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{11}H_{20}O_4P$ $[M+H]^+$: 247.10937, Found: 247.10890.

2. Preparation of β-ketocarbonyls.

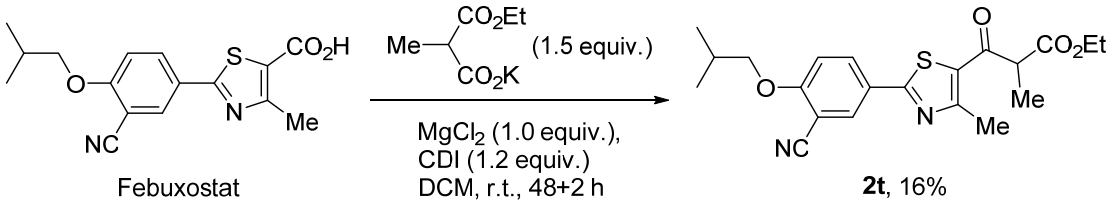
β-Ketocarbonyls **2a-2c**,[2] **2d**,[3] **2e**,[4] **2f**,[5] **2g-2m**[2] were prepared according to literatures.

(1) Preparation of compound **2q** (lican-03-141)



To an oven-dried Schlenk flask (100 mL) with a polytetrafluoroethylene plug replaced air with argon for three times at room temperature by vacuum were added indomethacin (3.5764 g, 10 mmol), CDI (1.9457 g, 12 mmol), and freshly distilled CH_2Cl_2 (50 mL, 0.2 M). After stirring for 2 h at room temperature, to the resulting solution were added $MgCl_2$ (954.4 mg, 10 mmol) and potassium 3-ethoxy-2-methyl-3-oxopropanoate (2.7309 g, 15 mmol). After stirring for extra 24 h, the resulting mixture was filtered through a short column of silica gel (5 cm) eluted with ethyl acetate (30 mL) and concentrated. The residue was purified by column chromatography on silica gel to afford **2q** (1.0380 g, 23%) [eluent: petroleum ether / ethyl acetate = 8/1 (800+100 mL)] as a light green solid: **m.p.** 90.4-91.8 ºC (hexane/ ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2 H, ArH), 7.47 (d, *J* = 8.4 Hz, 2 H, ArH), 6.97-6.79 (m, 2 H, ArH), 6.67 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1 H, ArH), 4.14 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.00-3.74 (m, 5 H, CH_2 and CH_3), 3.73-3.60 (m, 1 H, CH), 2.34 (s, 3 H, CH_3), 1.34 (d, *J* = 7.2 Hz, 3 H, CH_3), 1.24 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.6, 170.2, 168.2, 156.0, 139.2, 136.2, 133.7, 131.1, 130.8, 130.5, 129.0, 114.9, 111.8, 111.6, 101.1, 61.4, 55.6, 55.5, 51.2, 37.8, 13.9, 13.3, 12.9; **IR** (neat): ν = 3086, 2993, 2945, 2904, 2834, 1717, 1677, 1613, 1590, 1477, 1367, 1205, 1180, 1087 cm^{-1}; **MS** (ESI) *m/z* 442 $[M(^{35}Cl)+H]^+$; **Elem. Anal.** Calcd. for $C_{24}H_{24}ClNO_5$: C 65.23, H 5.47, found C 65.03, H 5.56.

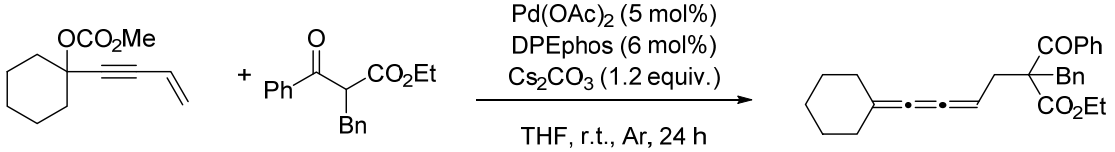
(2) Preparation of compound **2t** (lican-03-155)



To an oven-dried Schlenk flask (100 mL) with a polytetrafluoroethylene plug replaced air with argon for three times at room temperature by vacuum were added Febuxostat (3.1662 g, 10 mmol), CDI (1.9477 g, 12 mmol), and freshly distilled CH_2Cl_2 (50 mL, 0.2 M). After stirring for 2 h at room temperature, to the resulting solution were added $MgCl_2$ (953.4 mg, 10 mmol) and potassium 3-ethoxy-2-methyl-3-oxopropanoate (2.7338 g, 15 mmol). After stirring for extra 48 h, the resulting mixture was filtered through a short column of silica gel (5 cm) eluted with ethyl acetate (30 mL) and concentrated. The residue was purified by column chromatography on silica gel to afford **2t** (0.6372 g, 16%) [eluent: petroleum ether / ethyl acetate = 4/1 (800+200 mL)] as a light green solid: **m.p.** 90.9-92.3 ºC (hexane / ethyl acetate); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 2.4 Hz, 1 H, ArH), 8.13 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1 H, ArH), 7.03 (d, *J* = 8.8 Hz, 1 H, ArH), 4.20 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.04 (q, *J* = 7.1 Hz, 1 H, CH), 3.92 (d, *J* = 6.4 Hz, 2 H, OCH_2), 2.79 (s, 3 H, CH_3), 2.27-2.16 (m, 1 H, CH), 1.51 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.25 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.10 (d, *J* = 6.8 Hz, 6 H, 2 × CH_3),; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 188.6, 169.8, 167.0, 162.7, 161.7, 132.7, 132.2, 129.2, 125.6, 115.3, 112.7, 103.0, 75.7, 61.7, 52.8, 28.1, 19.0, 18.5, 14.0, 13.7; **IR** (neat): ν = 3077, 2959, 2937, 2878, 2031, 1731, 1665, 1602, 1421, 1368, 1289 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 400 (M^+, 12.30), 243 (100); **Elem. Anal.** Calcd. for $C_{21}H_{24}N_2O_4S$: C 62.98, H 6.04, found C 62.80, H 5.91.

3. Preparation of 1,2,3-butatrienes

(1) Preparation of ethyl 2-benzoyl-2-benzyl-7,7-(pentamethylene)hepta-4,5,6-trien-oate **3bb** (lican-03-060)



1b 0.5 mmol

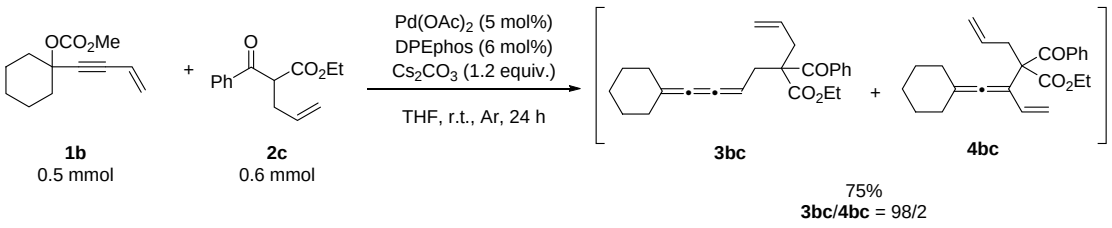
2b 0.6 mmol

3bb, 81%

Typical Procedure II: To a flame-dried Schlenk tube (25 mL) were added $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), DPEphos (16.3 mg, 0.03 mmol), and Cs_2CO_3 (195.1

mg, 0.6 mmol). After the addition, the Schlenk tube was degassed and refilled with Ar for three times to ensure the complete exclusion of air. THF (5 mL), **1b** (104.4 mg, 0.5 mmol), **2b** (169.2 mg, 0.6 mmol), and THF (5 mL) were sequentially under argon atmosphere. After that, the Ar gas line was closed. The resulting mixture was stirred at room temperature for 24 h. After completion of the reaction as monitored by TLC, the resulting mixture was filtered through a short column of silica gel (3 cm) eluted with ethyl acetate (10 mL) and concentrated. The residue was purified by column chromatography on silica gel to afford **3bb** (169.3 mg, 81%) [eluent: petroleum ether / ethyl ether = 100/1 (1500+15 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2 H, ArH), 7.52 (t, *J* = 7.4 Hz, 1 H, ArH), 7.41 (t, *J* = 7.8 Hz, 2 H, ArH), 7.21-7.13 (m, 3 H, ArH), 7.10-7.02 (m, 2 H, ArH), 5.09 (t, *J* = 8.0 Hz, 1 H, =CH), 4.20-4.01 (m, 2 H, OCH_2), 3.48 (s, 2 H, CH_2 of Bn), 2.96-2.78 (m, 2 H, CH_2), 2.33-2.16 (m, 4 H, 2 × CH_2), 1.69-1.50 (m, 6 H, 3 × CH_2), 1.06 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.9, 172.2, 162.4, 152.5, 136.1, 135.9, 132.6, 130.3, 128.44, 128.42, 128.0, 126.8, 124.4, 95.7, 62.5, 61.3, 38.4, 35.5, 34.9, 34.8, 27.7, 27.6, 25.8, 13.7; **IR** (neat) *ν* = 2930, 2855, 2064, 1731, 1680, 1598, 1495, 1444, 1366, 1271, 1236, 1181, 1082, 1045 cm^{-1}; **MS** (ESI) *m/z* 415 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{28}H_{31}O_3$ $[M+H]^+$: 415.2268, Found: 415.2260.

(2) Preparation of ethyl 2-allyl-2-benzoyl-7,7-(pentamethylene)hepta-4,5,6-trienoate **3bc** (lican-03-066)



1b 0.5 mmol

2c 0.6 mmol

3bc

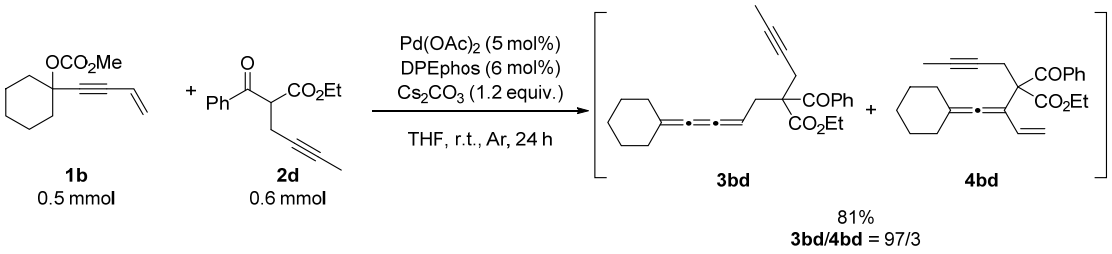
4bc

75%
3bc/**4bc** = 98/2

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.7 mg, 0.025 mmol), DPEphos (16.4 mg, 0.03 mmol), Cs_2CO_3 (195.7 mg, 0.6 mmol), THF (10 mL), **1b** (104.7 mg, 0.5 mmol), and **2c** (139.9 mg, 0.6 mmol) afforded (**3bc** + **4bc**) (136.8 mg, 75%, **3bc**/**4bc** = 98/2) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 100/1 (1500+15 mL)] as a colorless oil: **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 7.89-7.81 (m, 2 H, ArH), 7.51 (t, *J* = 7.8 Hz, 1 H, ArH), 7.41 (t, *J* = 7.8 Hz, 2 H, ArH), 5.68-5.55 (m, 1 H, =CH), 5.11-4.98 (m, 3 H, $CH=CH_2$), 4.14 (q, *J* = 7.2 Hz, 2 H, OCH_2), 2.98-2.85 (m, 4 H, 2 × CH_2), 2.26-2.12 (m, 4 H, 2 × CH_2), 1.66-1.50 (m, 6 H, 3 × CH_2), 1.10 (t, *J* = 7.0 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.9, 172.3, 162.1, 152.3, 135.9, 132.5, 132.0, 128.35, 128.31, 124.1, 119.4, 95.4, 61.3, 61.2, 37.1, 35.9, 34.9, 34.7, 27.6, 27.5, 25.8, 13.8; **IR** (neat) *v* = 3075, 2980, 2929, 2855, 2063, 1731, 1681, 1642, 1597, 1443, 1367, 1278, 1245, 1201, 1136 cm^{-1}; **MS** (ESI) *m/z* 365 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{24}H_{29}O_3$ $[M+H]^+$: 329.2111, Found: 329.2095.

(3) Preparation of ethyl 2-benzoyl-2-(but-2-yn-1-yl)-7,7-(pentamethylene)hepta-4,5,6-trienoate **3bd** (lican-03-070)



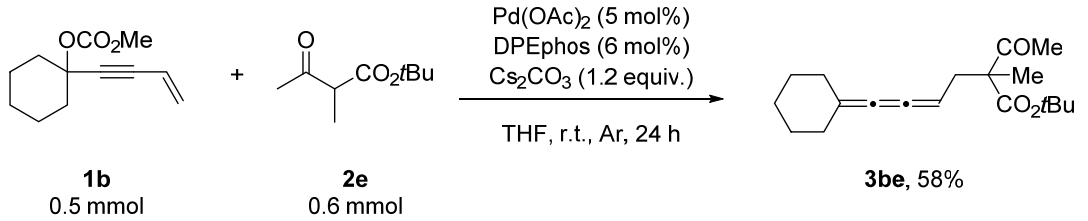
1b 0.5 mmol + **2d** 0.6 mmol → **3bd** + **4bd**

81%
3bd/4bd = 97/3

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.5 mg, 0.024 mmol), DPEphos (16.3 mg, 0.03 mmol), Cs_2CO_3 (195.1 mg, 0.6 mmol), THF (10 mL), **1b** (104.4 mg, 0.5 mmol), and **2d** (146.1 mg, 0.6 mmol) afforded (**3bd** + **4bd**) (152.2 mg, 81%, **3bd**/**4bd** = 97/3) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 100/1 (1000+10 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.78 (m, 2 H, ArH), 7.55-7.46 (m, 1 H, ArH), 7.44-7.36 (m, 2 H, ArH), 5.05 (t, *J* = 8.0 Hz, 1 H, C=CH), 4.16 (q, *J* = 7.2 Hz, 2 H, OCH_2), 3.17-3.02 (m, 2 H, CH_2), 2.97 (q, *J* = 2.4 Hz, 2 H, $C\equiv CCH_2$), 2.27-2.18 (m, 2 H, CH_2), 2.17-2.07 (m, 2 H, CH_2), 1.73 (t, *J* = 2.4 Hz, 3 H, $C\equiv CCH_3$), 1.67-1.48 (m, 6 H, 3 × CH_2), 1.12 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.4, 171.6, 162.1, 152.3, 135.8, 132.5, 128.4, 128.2, 124.2, 95.2, 79.3, 73.3, 61.6, 61.1, 35.9, 34.9, 34.7, 27.6, 27.5, 25.8, 23.8, 13.8, 3.4; **IR** (neat) *v* = 2928, 2855, 2063, 1733, 1682, 1598, 1580, 1443, 1366, 1279, 1241, 1189 cm^{-1}; **MS** (ESI) *m/z* 377 $[M+H]^+$; **HRMS** (ESI) Calcd for

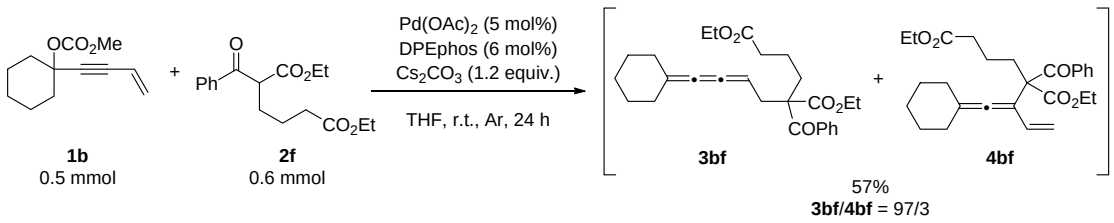
$C_{25}H_{29}O_3$ $[M+H]^+$: 377.2111, Found: 377.2103.

(4) Preparation of *tert*-butyl 2-acetyl-2-methyl-7,7-(pentamethylene)hept-4,5,6-trienoate **3be** (lican-03-056)



Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), DPEphos (16.5 mg, 0.03 mmol), Cs_2CO_3 (195.1 mg, 0.6 mmol), THF (10 mL), **1b** (104.1 mg, 0.5 mmol), and **2e** (103.4 mg, 0.6 mmol) afforded **3be** (88.0 mg, 58%) via column chromatography on silica gel [eluent: petroleum ether / ethyl acetate = 100/1 (1000+10 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.14 (t, J = 8.0 Hz, 1 H, =CH), 2.72 (dd, J_1 = 14.4 Hz, J_2 = 8.0 Hz, 1 H, one proton of CH_2), 2.61 (dd, J_1 = 14.4 Hz, J_2 = 8.0 Hz, 1 H, one proton of CH_2), 2.33-2.21 (m, 4 H, 2 × CH_2), 2.17 (s, 3 H, CH_3), 1.69-1.54 (m, 6 H, 3 × CH_2), 1.46 (s, 9 H, 3 × CH_3), 1.36 (s, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.2, 171.3, 161.4, 152.4, 123.6, 96.6, 81.8, 60.5, 38.1, 34.9, 34.8, 27.7, 27.58, 27.56, 26.1, 25.8, 18.8; **IR** (neat) ν = 2978, 2930, 2856, 2064, 1710, 1534, 1447, 1392, 1369, 1282, 1248, 1153, 1113 cm^{-1}; **MS** (ESI) *m/z* 327 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{19}H_{28}O_3Na$ $[M+Na]^+$: 327.1931, Found: 327.1922.

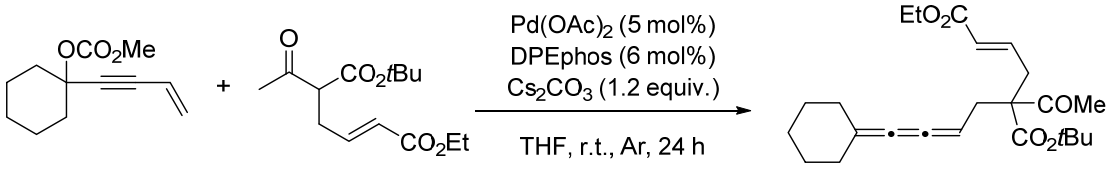
(5) Preparation of ethyl 5-benzoyl-5-(ethoxycarbonyl)-10,10-(pentamethylene)-deca-7,8,9-trienoate **3bf** (lican-03-102)



Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), DPEphos (16.3 mg, 0.03 mmol), Cs_2CO_3 (195.3 mg, 0.6 mmol), THF (10 mL), **1b** (104.7 mg, 0.5 mmol), and **2f** (184.4 mg, 0.6 mmol) afforded (**3bf** + **4bf**) (126.0 mg,

57%, **3bf**/**4bf** = 97/3) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 15/1 (900+60 mL)] as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2 H, ArH), 7.51 (t, *J* = 6.8 Hz, 1 H, ArH), 7.41 (t, *J* = 7.6 Hz, 2 H, ArH), 5.04 (t, *J* = 8.2 Hz, 1 H, =CH), 4.20-3.99 (m, 4 H, 2 × CH_2), 3.04-2.87 (m, 2 H, CH_2), 2.30-2.20 (m, 4 H, 2 × CH_2), 2.20-2.11 (m, 4 H, 2 × CH_2), 1.67-1.52 (m, 7 H, 3 × CH_2 and one proton of CH_2), 1.50-1.37 (m, 1 H, one proton of CH_2), 1.20 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.08 (t, *J* = 6.8 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.3, 172.7, 172.6, 161.9, 152.1, 135.7, 132.5, 128.3, 128.2, 124.1, 95.4, 61.3, 61.0, 60.1, 35.7, 34.9, 34.7, 34.2, 31.7, 27.6, 27.5, 25.7, 19.0, 14.0, 13.7; **IR** (neat) *v* = 2978, 2932, 2855, 2063, 1730, 1679, 1445, 1256, 1176, 1094, 1023 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 438 (M^+, 1.16), 105 (100); **HRMS** (EI) Calcd. for $C_{27}H_{34}O_5$ [M^+]: 438.2406, found: 438.2408.

(6) Preparation of ethyl (2*E*)-5-acetyl-5-(*tert*-butoxycarbonyl)-10,10-(penta-methylene)deca-2,7,8,9-tetraenoate **3bg** (lican-03-100)

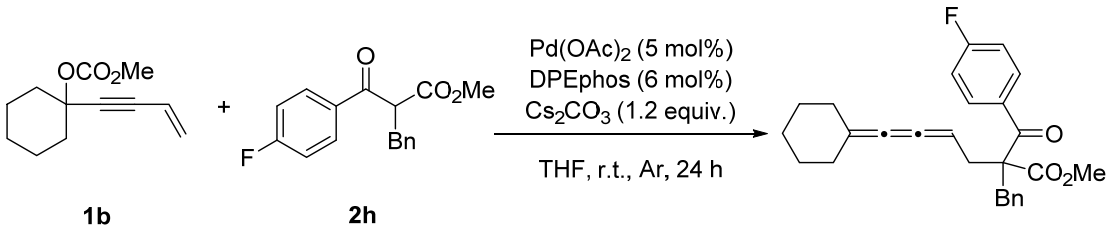


1b 0.5 mmol + **2g** 0.6 mmol → **3bg**, 87%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), DPEphos (16.3 mg, 0.03 mmol), Cs_2CO_3 (195.7 mg, 0.6 mmol), THF (10 mL), **1b** (104.3 mg, 0.5 mmol), and **2g** (162.9 mg, 0.6 mmol) afforded **3bg** (175.4 mg, 87%) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 25/1 (1600+64 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.83-6.70 (m, 1 H, =CH), 5.89 (d, *J* = 15.6 Hz, 1 H, =CH), 5.01 (t, *J* = 8.2 Hz, 1 H, =CH), 4.16 (q, *J* = 7.2 Hz, 2 H, OCH_2), 2.83 (ddd, J_1 = 14.4 Hz, J_2 = 7.6 Hz, J_2 = 1.2 Hz, 1 H, one proton of CH_2), 2.77-2.67 (m, 3 H, one proton of CH_2 and CH_2), 2.34-2.23 (m, 4 H, 2 × CH_2), 2.19 (s, 3 H, CH_3), 1.71-1.54 (m, 6 H, 3 × CH_2), 1.47 (s, 9 H, 3 × CH_3), 1.27 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.0, 169.5, 165.6, 161.9, 152.2, 142.8, 125.0, 124.7, 95.0, 82.4, 63.8, 60.0, 34.7, 34.0, 27.6, 27.5, 27.4, 26.3, 25.7,

14.0; **IR** (neat) ν = 2978, 2931, 2856, 2062, 1710, 1655, 1442, 1368, 1268, 1145 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 402 (M^+, 5.99), 43 (100); **HRMS** (EI) Calcd. for $C_{24}H_{34}O_5$ [M^+]: 402.2406, found: 402.2408.

(7) Preparation of methyl 2-(4-fluorobenzoyl)-2-benzyl-7,7-(pentamethylene)hepta-4,5,6-trienoate **3bh** (lican-03-146)



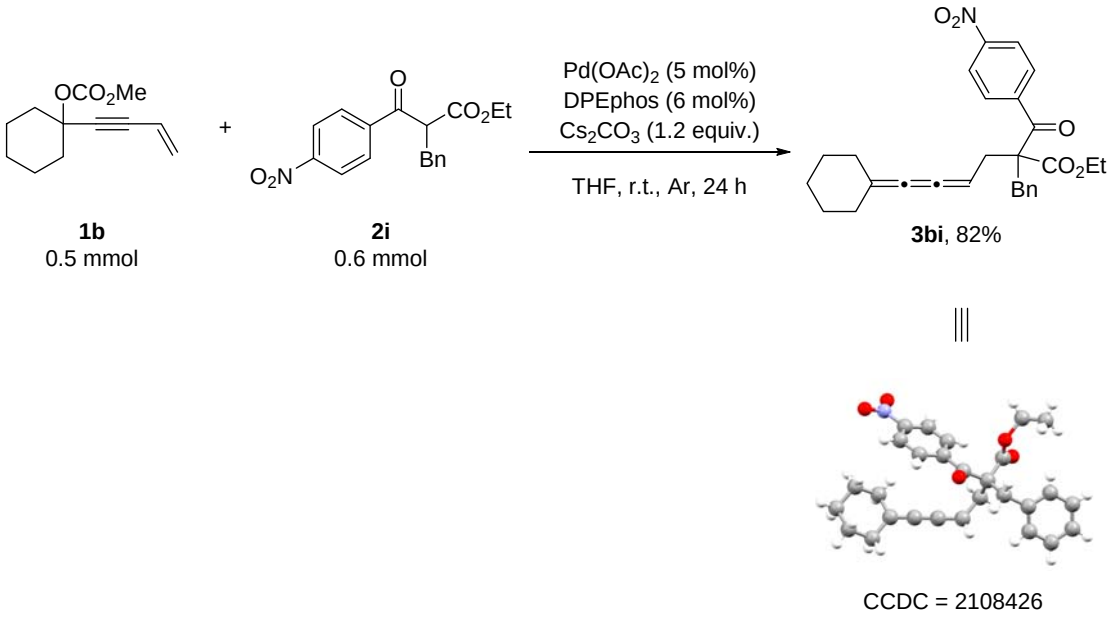
1b 0.5 mmol

2h 0.6 mmol

3bh, 61%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.4 mg, 0.025 mmol), DPEphos (16.4 mg, 0.03 mmol), Cs_2CO_3 (195.7 mg, 0.6 mmol), THF (10 mL), **1b** (104.7 mg, 0.5 mmol), and **2h** (170.9 mg, 0.6 mmol) afforded **3bh** (127.2 mg, 61%) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 60/1 (1200+20 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94-7.85 (m, 2 H, ArH), 7.26-7.16 (m, 3 H, ArH), 7.14-6.97 (m, 4 H, ArH), 5.06 (t, *J* = 8.0 Hz, 1 H, =CH), 3.64 (s, 3 H, CH_3), 3.53-3.37 (m, 2 H, CH_2 of Bn), 2.97-2.77 (m, 2 H, CH_2), 2.34-2.16 (m, 4 H, 2 ×CH_2), 1.73-1.51 (m, 6 H, 3 × CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.1, 172.7, 165.2 (d, *J* = 253.8 Hz), 162.5, 152.4, 135.7, 132.4 (d, *J* = 3.2 Hz), 131.7 (d, *J* = 8.9 Hz), 130.2, 128.1, 126.9, 124.8, 115.7 (d, *J* = 21.8 Hz), 95.3, 62.5, 52.3, 38.4, 35.4, 34.9, 34.8, 27.7, 27.6, 25.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.7; **IR** (neat) ν = 3064, 3030, 2931, 2854, 2063, 1735, 1680, 1597, 1505, 1436, 1273, 1235, 1200, 1158, 1081 cm^{-1}; **MS** (DART) *m/z* 419 $[M+H]^+$; **HRMS** (DART) Calcd for $C_{27}H_{28}O_3F$ $[M+H]^+$: 419.2017, Found: 419.2012.

(8) Preparation of ethyl 2-(4-nitrobenzoyl)-2-benzyl-7,7-(pentamethylene)hepta-4,5,6-trienoate **3bi** (lican-03-075)



1b
0.5 mmol

2i
0.6 mmol

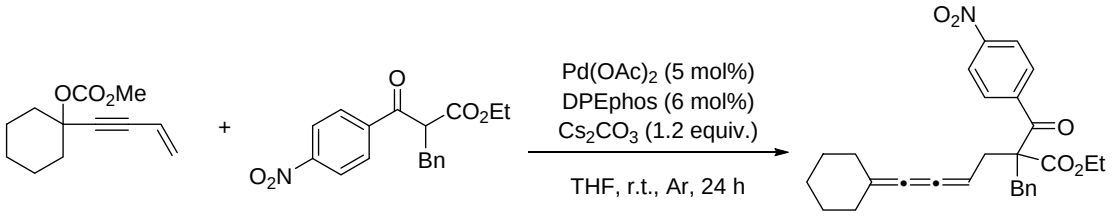
3bi, 82%

CCDC = 2108426

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.7 mg, 0.025 mmol), DPEphos (16.2 mg, 0.03 mmol), Cs_2CO_3 (195.7 mg, 0.6 mmol), THF (10 mL), **1b** (104.7 mg, 0.5 mmol), and **2i** (196.5 mg, 0.6 mmol) afforded **3bi** (188.4 mg, 82%) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 60/1 (1200+20 mL)] as a green solid: **m.p.** 81.4-82.9 °C (hexane / chloroform); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28-8.22 (m, 2 H, ArH), 7.99-7.92 (m, 2 H, ArH), 7.24-7.19 (m, 3 H, ArH), 7.12-7.03 (m, 2 H, ArH), 5.09 (t, *J* = 8.0 Hz, 1 H, =CH), 4.22-4.06 (m, 2 H, OCH_2), 3.51 (d, *J* = 14.0 Hz, 1 H, one proton of CH_2), 3.45 (d, *J* = 14.0 Hz, 1 H, one proton of CH_2), 2.88 (d, *J* = 8.4 Hz, 2 H, CH_2), 2.30-2.14 (m, 4 H, 2 × CH_2), 1.69-1.51 (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 195.2, 171.4, 162.5, 152.3, 149.6, 141.1, 135.4, 130.2, 129.3, 128.1, 127.0, 125.2, 123.5, 94.8, 63.0, 61.7, 38.4, 35.4, 34.8, 34.7, 27.6, 27.5, 25.7, 13.6; IR (neat) *v* = 3109, 2979, 2931, 2856, 2064, 1732, 1680, 1516, 1443, 1347, 1180 cm^{-1}; **MS** (ESI) *m/z* 460 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{28}H_{30}O_5N$ $[M+H]^+$: 460.2118, Found: 460.2110.

Single crystal of **3bi** (CCDC number: 2108426) was obtained by slow diffusion of hexane (1.0 mL) to a solution of **3bi** (30 mg) in chloroform (0.2 mL).

(9) Preparation of ethyl 2-(4-nitrobenzoyl)-2-benzyl-7,7-(pentamethylene)hepta-4,5,6-trienoate in gram scale **3bi** (lican-04-068)



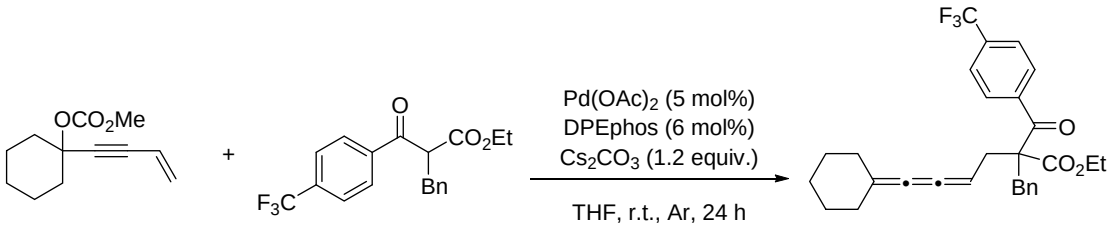
1b
3 mmol

2i
3.6 mmol

3bi,
1.1246 g, 82%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (34.1 mg, 0.15 mmol), DPEphos (98.0 mg, 0.18 mmol), Cs_2CO_3 (1.1688 g, 3.6 mmol), THF (60 mL), **1b** (626.4 mg, 3 mmol), and **2i** (1.1788 g, 3.6 mmol) afforded **3bi** (1.1246 mg, 82%) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 20/1 (1000+50 mL)] as a green oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 2 H, ArH), 7.94 (m, *J* = 8.8 Hz, 2 H, ArH), 7.23-7.20 (m, 3 H, ArH), 7.10-7.05 (m, 2 H, ArH), 5.09 (t, *J* = 7.8 Hz, 1 H, =CH), 4.21-4.05 (m, 2 H, OCH_2), 3.51 (d, *J* = 14.0 Hz, 1 H, one proton of CH_2), 3.45 (d, *J* = 14.0 Hz, 1 H, one proton of CH_2), 2.88 (d, *J* = 8.0 Hz, 2 H, CH_2), 2.27-2.12 (m, 4 H, 2 × CH_2), 1.69-1.50 (m, 6 H, 3 × CH_2), 1.09 (t, *J* = 7.0 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.1, 171.4, 162.4, 152.2, 149.5, 140.9, 135.3, 130.1, 129.2, 128.1, 126.9, 125.2, 123.5, 94.7, 62.9, 61.7, 38.2, 35.3, 34.70, 34.65, 27.6, 27.5, 25.6, 13.6.

(10) Preparation of ethyl 2-(4-(trifluoromethyl)benzoyl)-2-benzyl-7,7-(penta-methylene)hepta-4,5,6-trienoate **3bj** (lican-03-128)



1b
0.5 mmol

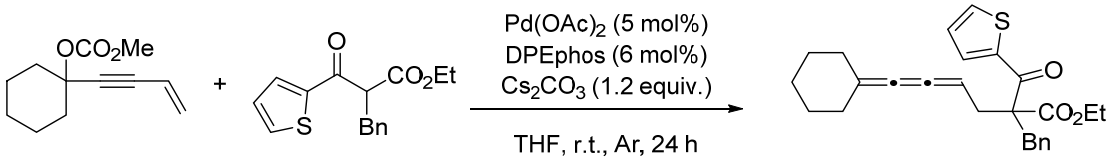
2j
0.6 mmol

3bj, 75%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.8 mg, 0.026 mmol), DPEphos (16.6 mg, 0.03 mmol), Cs_2CO_3 (195.4 mg, 0.6 mmol), THF (10 mL), **1b** (104.6 mg, 0.5 mmol), and **2j** (211.0 mg, 0.6 mmol) afforded **3bj** (181.8 mg, 75%) via

column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 60/1 (900+15 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2 H, ArH), 7.69 (d, *J* = 8.4 Hz, 2 H, ArH), 7.25-7.15 (m, 3 H, ArH), 7.12-6.98 (m, 2 H, ArH), 5.08 (t, *J* = 8.2 Hz, 1 H, =CH), 4.22-4.02 (m, 2 H, OCH_2), 3.50 (d, *J* = 14.0 Hz, 1 H, one proton of CH_2), 3.44 (d, *J* = 14.4 Hz, 1 H, one proton of CH_2), 2.99-2.78 (m, 2 H, CH_2), 2.36-2.09 (m, 4 H, 2 × CH_2), 1.71-1.54 (m, 6 H, 3 × CH_2), 1.08 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.6, 171.9, 162.6, 152.4, 139.2, 135.7, 133.9 (q, *J* = 32.4 Hz), 130.3, 128.8, 128.2, 127.1, 125.5 (q, *J* = 3.6 Hz), 125.2, 123.5 (q, *J* = 271.2 Hz), 95.1, 62.9, 61.7, 38.4, 35.5, 34.92, 34.86, 27.7, 27.6, 25.9, 13.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.6; **IR** (neat) *v* = 3064, 3031, 2933, 2855, 2064, 1735, 1687, 1496, 1440, 1325, 1168, 1129, 1068 cm^{-1}; **MS** (ESI) *m/z* 505 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{29}H_{29}O_3F_3Na$ $[M+Na]^+$: 505.1961, Found: 505.1961.

(11) Preparation of ethyl 2-((thien-2-yl)carbonyl)-2-benzyl-7,7-(pentamethylene)-hepta-4,5,6-trienoate **3bk** (lican-03-105)



1b 0.5 mmol

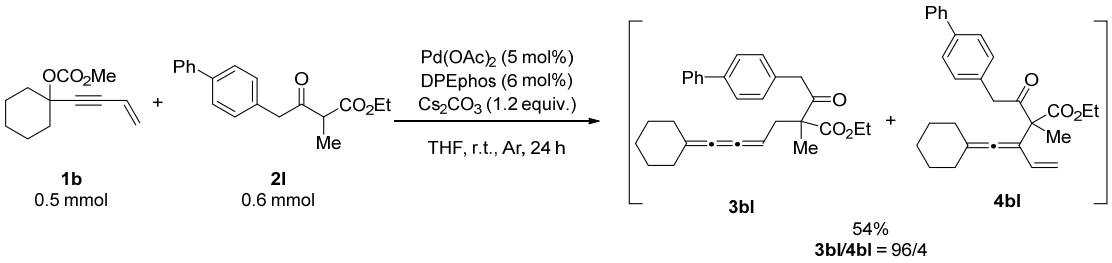
2k 0.6 mmol

3bk, 50%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.7 mg, 0.025 mmol), DPEphos (16.0 mg, 0.03 mmol), Cs_2CO_3 (195.9 mg, 0.6 mmol), THF (10 mL), **1b** (104.4 mg, 0.5 mmol), and **2k** (173.5 mg, 0.6 mmol) afforded **3bk** (105.9 mg, 50%) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 50/1 (1000+20 mL)] as a light green oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 4.0 Hz, 1 H, ArH), 7.62 (d, *J* = 5.2 Hz, 1 H, ArH), 7.24-7.15 (m, 3 H, ArH), 7.12-7.02 (m, 3 H, ArH), 5.11 (t, *J* = 8.2 Hz, 1 H, =CH), 4.25-4.01 (m, 2 H, CH_2), 3.47 (dd, J_1 = 18.8 Hz, J_2 = 4.8 Hz, 2 H, CH_2), 2.96-2.77 (m, 2 H, CH_2), 2.36-2.19 (m, 4 H, 2 × CH_2), 1.73-1.50 (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 188.8, 172.0, 162.5, 152.5, 142.9, 135.7, 133.7, 131.2, 130.2, 128.1, 128.0,

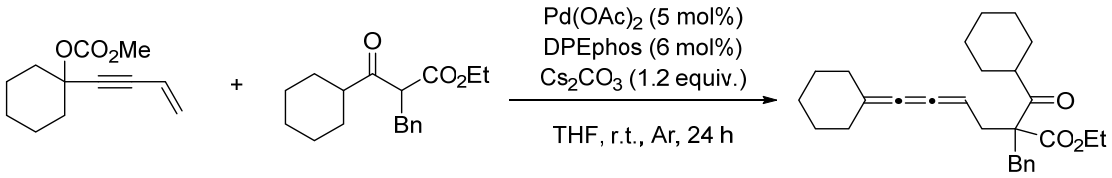
126.8, 124.6, 95.6, 62.8, 61.5, 38.2, 35.3, 34.9, 34.8, 27.7, 27.6, 25.8, 13.7; **IR** (neat) ν = 3086, 3029, 2930, 2854, 2064, 1729, 1658, 1441, 1411, 1353, 1274, 1242, 1200, 1181, 1082 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 420 (M^+, 2.00), 111 (100); **HRMS** (EI) Calcd. for $C_{26}H_{28}O_3S$ [M^+]: 420.1759, found: 420.1761.

(12) Preparation of ethyl 2-(2-(*para*-phenylphenyl-4-yl)acetyl)-2-methyl-7,7-(penta-methylene)hepta-4,5,6-trienoate **3bl** (lican-03-143)



Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.4 mg, 0.024 mmol), DPEphos (16.4 mg, 0.03 mmol), Cs_2CO_3 (195.7 mg, 0.6 mmol), THF (10 mL), **1b** (104.5 mg, 0.5 mmol), and **2l** (177.6 mg, 0.6 mmol) afforded (**3bl** + **4bl**) (116.3 mg, 54%, **3bl**/**4bl** = 96/4) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 50/1 (1000+20 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60-7.49 (m, 4 H, ArH), 7.40 (t, *J* = 7.6 Hz, 2 H, ArH), 7.31 (t, *J* = 7.4 Hz, 1 H, ArH), 7.23 (d, *J* = 7.6 Hz, 2 H, ArH), 5.17 (t, *J* = 8.0 Hz, 1 H, =CH), 4.25-4.07 (m, 2 H, OCH_2), 3.83 (s, 2 H, CH_2), 2.89-2.67 (m, 2 H, CH_2), 2.32-2.21 (m, 4 H, 2 × CH_2), 1.69-1.52 (m, 6 H, 3 × CH_2), 1.49 (s, 3 H, CH_3), 1.23 (t, *J* = 7.0 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.2, 172.2, 161.6, 152.3, 140.7, 139.7, 132.9, 129.9, 128.6, 127.1, 127.0, 126.9, 124.1, 96.2, 61.4, 60.0, 44.7, 38.2, 34.9, 34.8, 27.6, 27.5, 25.8, 19.0, 13.9; **IR** (neat) ν = 3029, 2981, 2930, 2854, 2062, 1713, 1487, 1446, 1377, 1229, 1191, 1103, 1024 cm^{-1}; **MS** (DART) *m/z* 429 $[M+H]^+$; **HRMS** (DART) Calcd for $C_{29}H_{33}O_3$ $[M+H]^+$: 429.2424, Found: 429.2419.

(13) Preparation of ethyl 2-benzyl-2-(cyclohexanecarbonyl)- 7,7-(pentamethylene)-hepta-4,5,6-trienoate **3bm** (lican-03-109)



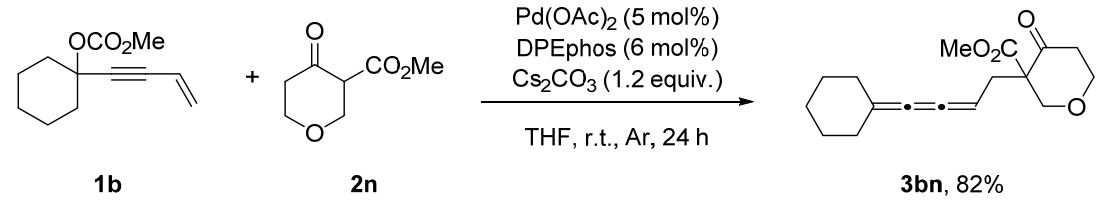
1b
0.5 mmol

2m
0.6 mmol

3bm, 75%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.7 mg, 0.025 mmol), DPEphos (16.1 mg, 0.03 mmol), Cs_2CO_3 (196.0 mg, 0.6 mmol), THF (10 mL), **1b** (104.7 mg, 0.5 mmol), and **2m** (196.5 mg, 0.6 mmol) afforded **3bm** (157.4 mg, 75%) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 50/1 (1000+20 mL)] as a white solid: **m.p.** 103.2-104.6 °C (hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.16 (m, 3 H, ArH), 7.15-7.05 (m, 2 H, ArH), 5.05 (t, *J* = 7.4 Hz, 1 H, =CH), 4.28-4.02 (m, 2 H, OCH_2), 3.29 (d, *J* = 14.0 Hz, 1 H, one proton of CH_2), 3.22 (d, *J* = 14.4 Hz, 1 H, one proton of CH_2), 2.88-2.66 (m, 2 H, CH_2), 2.65-2.51 (m, 1 H, CH), 2.42-2.21 (m, 4 H, 2 × CH_2), 1.82-1.56 (m, 11 H), 1.53-1.33 (m, 2 H), 1.32-1.12 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.5, 171.2, 162.0, 152.6, 136.5, 130.0, 128.0, 126.6, 124.5, 96.1, 65.0, 61.2, 48.0, 36.6, 34.8, 34.7, 33.4, 30.2, 29.8, 27.7, 27.6, 25.8, 25.5, 25.4, 13.9; **IR** (neat) *v* = 3062, 3027, 2934, 2852, 2066, 1739, 1700, 1447, 1369, 1259, 1181 cm^{-1}; **MS** (70 eV, EI) *m/z* (%): 420 (M^+, 5.18), 83 (100); **Elem. Anal.** Calcd. for $C_{28}H_{36}O_3$: C 79.96, H, 8.63, found C 79.47, H, 8.76.

(14) Preparation of 3-(methoxycarbonyl)-3-(5,5-(pentamethylene)penta-2,3,4-trienyl) tetrahydro-4*H*-pyran-4-one **3bn** (lican-03-090)



1b
0.5 mmol

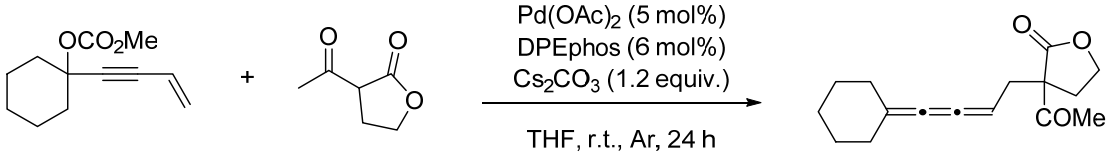
2n
0.6 mmol

3bn, 82%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), DPEphos (16.3 mg, 0.03 mmol), Cs_2CO_3 (195.7 mg, 0.6 mmol), THF (10 mL), **1b** (104.1 mg, 0.5 mmol), and **2n** (95.4 mg, 0.6 mmol) afforded **3bn** (119.4 mg, 82%) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 9/1 (900+100 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.21 (t, *J* = 7.8 Hz, 1

H, =CH), 4.53 (d, J = 11.6 Hz, 1 H, one proton of CH_2), 4.23-4.11 (m, 1 H, one proton of CH_2), 3.82-3.69 (m, 4 H, CH_3 and one proton of CH_2), 3.59 (d, J = 12.0 Hz, 1 H, one proton of CH_2), 2.88-2.76 (m, 1 H, one proton of CH_2), 2.71-2.62 (m, 1 H, one proton of CH_2), 2.58-2.43 (m, 2 H, 2 × one proton of CH_2), 2.32-2.20 (m, 4 H, 2 ×CH_2), 1.73-1.51 (m, 6 H, 3 × CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.9, 170.4, 161.3, 152.0, 124.1, 95.7, 73.7, 68.4, 62.9, 52.5, 41.3, 34.9, 34.7, 33.7, 27.5, 27.4, 25.7; **IR** (neat) ν = 2928, 2853, 2061, 1714, 1435, 1312, 1206, 1092, 975 cm^{-1}; **MS** (ESI) *m/z* 291 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{17}H_{23}O_4$ $[M+H]^+$: 291.1591, Found: 291.1583.

(15) Preparation of 3-acetyl-3-(5,5-(pentamethylene)penta-2,3,4-trienyl)dihydrofuran-2(3*H*)-one **3bo** (lican-03-054)



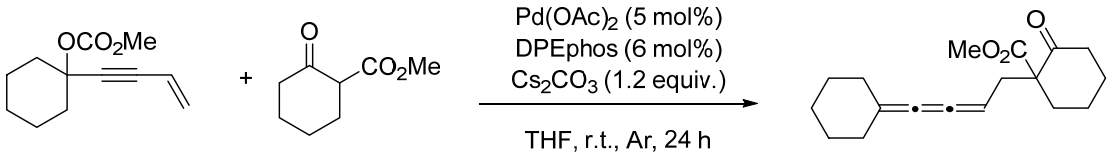
1b 0.5 mmol

2o 0.6 mmol

3bo, 74%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.5 mg, 0.024 mmol), DPEphos (16.2 mg, 0.03 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol), THF (10 mL), **1b** (104.4 mg, 0.5 mmol), and **2o** (76.7 mg, 0.6 mmol) afforded **3bo** (96.3 mg, 74%) via column chromatography on silica gel [eluent: petroleum ether / ethyl acetate = 50/1 (1000+20 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.12 (t, J = 7.2 Hz, 1 H, =CH), 4.33 (td, J_1 = 8.8 Hz, J_2 = 3.2 Hz, 1 H, one proton of OCH_2), 4.28-4.18 (m, 1 H, OCH one proton of OCH_2), 3.05-2.91 (m, 2 H, 2 × one proton of CH_2), 2.72 (dd, J_1 = 16 Hz, J_2 = 6.6 Hz, 1 H, one proton of CH_2) 2.36 (s, 3 H, CH_3), 2.33-2.24 (m, 4 H, 2 × CH_2), 2.24-2.15 (m, 1 H, one proton of CH_2), 1.71-1.54 (m, 6 H, 3 × CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.0, 274.8, 161.6, 152.4, 125.7, 94.6, 66.5, 61.1, 37.4, 34.7, 34.3, 29.2, 27.5, 27.4, 25.7; **IR** (neat) ν = 2961, 2928, 2855, 1746, 1711, 1441, 1327, 1246, 1140, 935 cm^{-1}; **MS** (ESI) *m/z* 283 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{16}H_{20}O_3Na$ $[M+Na]^+$: 283.1305, Found: 283.1295.

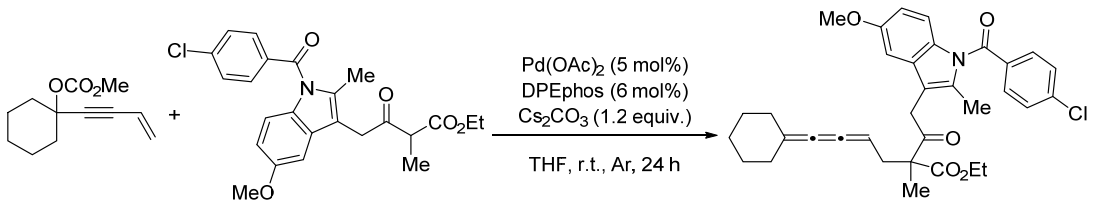
(16) Preparation of 2-(methoxycarbonyl)-2-(5,5-(pentamethylene)penta-2,3,4-trienyl) cyclohexan-1-one **3bp** (lican-03-055)



1b 0.5 mmol　　**2p** 0.6 mmol　　**3bp**, 72%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.7 mg, 0.025 mmol), DPEphos (16.5 mg, 0.03 mmol), Cs_2CO_3 (196.1 mg, 0.6 mmol), THF (10 mL), **1b** (104.6 mg, 0.5 mmol), and **2p** (93.9 mg, 0.6 mmol) afforded **3bp** (103.8 mg, 72%) via column chromatography on silica gel [eluent: petroleum ether / ethyl acetate = 40/1 (800+20 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.21 (t, J = 8.2 Hz, 1 H, =CH), 3.72 (s, 3 H, CH_3), 2.70 (dd, J_1 = 14.0 Hz, J_2 = 8.0 Hz, 1 H, one proton of CH_2), 2.57-2.48 (m, 2 H, CH_2), 2.48-2.40 (m, 2 H, CH_2), 2.31-2.21 (m, 4 H, 2 × CH_2), 2.05-1.95 (m, 1 H, one proton of CH_2), 1.82-1.71 (m, 1 H, one proton of CH_2), 1.71-1.53 (m, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.2, 171.8, 161.1, 152.2, 123.2, 97.0, 61.6, 52.2, 40.8, 37.9, 35.4, 35.0, 34.7, 27.6, 27.5, 27.3, 25.8, 22.2; **IR** (neat) v = 2934, 2857, 1743, 1712, 1441, 1375, 1246, 1121, 935 cm^{-1}; **MS** (ESI) *m/z* 289 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{18}H_{25}O_3$ $[M+H]^+$: 289.1798, Found: 289.1789.

(17) Preparation of compound ethyl 2-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetyl)-2-methyl-7,7-(pentamethylene)hepta-4,5,6-trienoate **3bq** (lican-03-147)

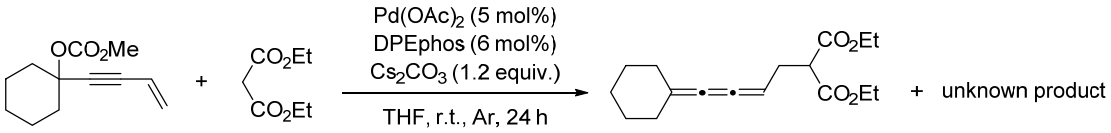


1b 0.5 mmol　　**2q** 0.6 mmol　　**3bq**, 60%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.7 mg, 0.025 mmol), DPEphos (16.4 mg, 0.03 mmol), Cs_2CO_3 (195.4 mg, 0.6 mmol), THF (10 mL), **1b** (104.4 mg, 0.5 mmol), and **2q** (265.7 mg, 0.6 mmol) afforded **3bq** (172.5 mg, 60%)

via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 8/1 (800+100 mL)] as a green oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74-7.61 (m, 2 H, ArH), 7.51-7.43 (m, 2 H, ArH), 6.90 (d, *J* = 9.2 Hz, 1 H, ArH), 6.80 (d, *J* = 2.4 Hz, 1 H, ArH), 6.64 (dd, J_1 = 9.0 Hz, J_2 = 2.6 Hz, 1 H, ArH), 5.19 (t, *J* = 7.8 Hz, 1 H, =CH), 4.20 (q, *J* = 7.1 Hz, 2 H, OCH_2), 3.88 (d, *J* = 1.2 Hz, 2 H, CH_2), 3.81 (s, 3 H, CH_3), 2.86 (d, *J* = 8.0 Hz, 2 H, CH_2), 2.38-2.13 (m, 7 H, 2 × CH_2 and CH_3), 1.67-1.56 (m, 9 H, 3 × CH_2 and CH_3), 1.28 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.1, 172.3, 168.0, 161.6, 155.8, 152.3, 138.9, 135.9, 133.9, 131.0, 130.8, 130.7, 128.9, 124.5, 114.7, 112.3, 111.0, 101.5, 96.0, 61.5, 59.6, 55.5, 38.3, 34.78, 34.76, 34.4, 27.5, 27.4, 25.7, 19.4, 13.9, 13.4; **IR** (neat) *v* = 2975, 2931, 2855, 2835, 2065, 1746, 1710, 1670, 1608, 1475, 1458, 1361, 1326, 1227, 1149, 1106, 1031 cm^{-1}; **MS** (ESI) *m/z* 574 $[M(^{35}Cl)+H]^+$; **HRMS** (ESI) Calcd for $C_{34}H_{37}O_5N^{35}Cl$ $[M+H]^+$: 574.2355, Found: 574.2345.

(18) Preparation of ethyl 2-(ethoxycarbonyl)-7,7-(pentamethylene)hepta-4,5,6-trienoate **3br** (lican-04-031)

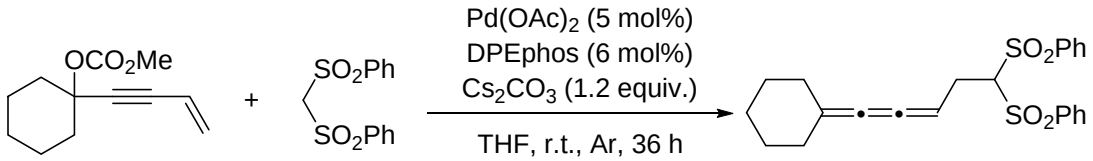


1b 0.5 mmol + **2r** 0.6 mmol → **3br**, 45%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.7 mg, 0.025 mmol), DPEphos (16.4 mg, 0.03 mmol), Cs_2CO_3 (195.2 mg, 0.6 mmol), THF (10 mL), **1b** (104.3 mg, 0.5 mmol), and **2r** (96.0 mg, 0.6 mmol) afforded **3br** (65.5 mg, 45%) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 10/1 (400+40 mL)] as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.31 (t, *J* = 6.6 Hz, 1 H, =CH), 4.28-4.13 (m, 4 H, 2 × OCH_2), 3.61 (t, *J* = 7.4 Hz, 1 H, CH), 2.78 (t, *J* = 7.0 Hz, 2 H, CH_2), 2.35-2.21 (m, 4 H, 2 × CH_2), 1.69-1.52 (m, 6 H, 3 × CH_2), 1.27 (t, *J* = 7.0 Hz, 6 H, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 159.2, 153.4, 123.2, 98.2, 61.3, 51.2, 34.8, 34.6, 31.1, 27.6, 27.5, 25.8, 14.0; **IR** (neat) *v* = 2974, 2928, 2854, 2063, 1735, 1707, 1607, 1462, 1367, 1252, 1149 cm^{-1}; **MS** (ESI) *m/z* 315 $[M+Na]^+$;

HRMS (ESI) Calcd for $C_{17}H_{24}O_4Na$ $[M+Na]^+$: 315.1567, Found: 315.1565.

(19) Preparation of 6,6-bis(phenylsulfonyl)-1,1-(pentamethylene)hexa-1,2,3-triene **3bs** (lican-05-013)



1b 0.5 mmol | **2s** 0.6 mmol | **3bs**, 55%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.8 mg, 0.026 mmol), DPEphos (16.7 mg, 0.03 mmol), Cs_2CO_3 (196.1 mg, 0.6 mmol), THF (10 mL), **1b** (104.6 mg, 0.5 mmol), and **2s** (177.4 mg, 0.6 mmol) afforded **3bs** (124.1 mg, 55%, 95% purity) via column chromatography on silica gel [eluent: petroleum ether / ethyl acetate = 9/1 (900+100 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 4 H, ArH), 7.68 (t, *J* = 7.4 Hz, 2 H, ArH), 7.56 (t, *J* = 7.6 Hz, 4 H, ArH), 5.24 (t, *J* = 6.6 Hz, 1 H, =CH), 4.78 (t, *J* = 6.0 Hz, 1 H, CH), 3.04 (t, *J* = 6.2 Hz, 2 H, CH_2), 2.37-2.14 (m, 4 H, 2 × CH_2), 1.79-1.51 (m, 6 H, 3 × CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 153.4, 137.9, 134.5, 129.5, 129.0, 124.9, 95.8, 82.6, 35.2, 34.6, 28.1, 27.6, 27.4, 25.7; **IR** (neat) *v* = 3066, 2931, 2855, 2256, 2063, 1584, 1447, 1329, 1151, 1078 cm^{-1}; **MS** (DART) *m/z* 429 $[M+H]^+$; **HRMS** (DART) Calcd for $C_{23}H_{25}O_4S_2$ $[M+H]^+$: 429.1189, Found: 429.1179.

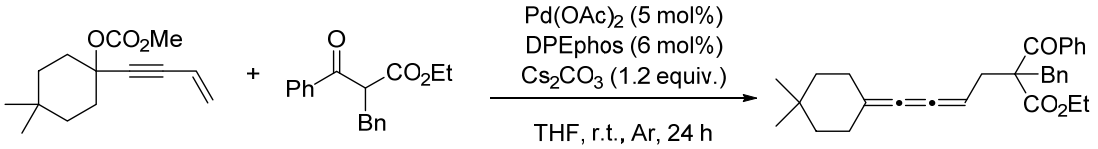
(20) Preparation of ethyl 2-benzoyl-2-benzyl-2,7-dimethylocta-4,5,6-trienoate **3aa** (lican-06-079)

1a 0.5 mmol | **2a** 0.6 mmol | **3aa** + **4aa** 77% | **3aa/4aa** = 96/4

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), DPEphos (16.2 mg, 0.03 mmol), Cs_2CO_3 (196.0 mg, 0.6 mmol), THF (10 mL), **1a**

(84.1 mg, 0.5 mmol), and **2a** (123.9 mg, 0.6 mmol) afforded (**3aa** + **4aa**) (120.4 mg, 77%, **3aa**/**4aa** = 96/4, 96% purity) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 25/1 (500+20 mL)] as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2 H, ArH), 7.51 (t, *J* = 7.2 Hz, 1 H, ArH), 7.40 (t, *J* = 7.6 Hz, 2 H, ArH), 5.13 (t, *J* = 8.0 Hz, 1 H, =CH), 4.20-4.04 (m, 2 H, OCH_2), 2.89 (d, *J* = 8.0 Hz, 2 H, CH_2), 1.92-1.78 (m, 6 H, 2 × CH_3), 1.59 (s, 3 H, CH_3), 1.07 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.9, 173.3, 161.2, 154.9, 135.4, 132.5, 128.34, 128.26, 115.2, 95.9, 61.2, 57.4, 39.7, 24.2, 24.0, 20.8, 13.6; **IR** (neat) *v* = 2982, 2934, 2908, 2849, 2255, 2063, 1733, 1682, 1598, 1580, 1446, 1376, 1276, 1236, 1190, 1102 cm^{-1}; **MS** (ESI) *m/z* 299 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1642, Found: 299.1642.

(21) Preparation of ethyl 2-benzoyl-2-benzyl-7,7-(3,3-dimethylpentamethylene)hepta-4,5,6-trienoate **3cb** (lican-04-081)



1c 0.5 mmol

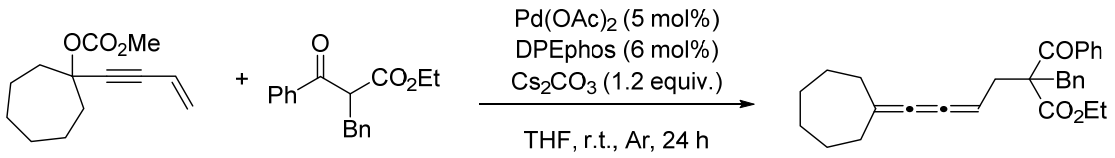
2b 0.6 mmol

3cb, 76%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), DPEphos (16.4 mg, 0.03 mmol), Cs_2CO_3 (197.1 mg, 0.6 mmol), THF (10 mL), **1c** (118.6 mg, 0.5 mmol), and **2b** (170.0 mg, 0.6 mmol) afforded **3cb** (167.4 mg, 76%) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 20/1 (400+20 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 2 H, ArH), 7.51 (t, *J* = 7.2 Hz, 1 H, ArH), 7.41 (t, *J* = 7.6 Hz, 2 H, ArH), 7.22-7.14 (m, 3 H, ArH), 7.10-7.01 (m, 2 H, ArH), 5.09 (t, *J* = 8.2 Hz, 1 H, =CH), 4.21-4.02 (m, 2 H, OCH_2), 3.49 (s, 2 H, CH_2 of Bn), 2.97-2.79 (m, 2 H, CH_2), 2.37-2.19 (m, 4 H, 2 × CH_2), 1.49-1.37 (m, 4 H, 2 × CH_2), 1.05 (t, *J* = 7.0 Hz, 3 H, CH_3), 0.97 (s, 6 H, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.8, 172.2, 162.4, 152.5, 136.0, 135.8, 132.6, 130.2, 128.40, 128.36, 127.9, 126.7, 124.0, 95.8, 62.4, 61.3, 39.9, 39.7, 38.3, 35.4, 30.8, 30.7, 29.9, 27.9, 27.8, 13.6; **IR** (neat) *v* = 3063, 2951, 2914, 2063, 1732, 1681,

1446, 1270, 1177 cm^{-1}; **MS** (ESI) *m/z* 443 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{30}H_{35}O_3$ $[M+H]^+$: 443.2581, Found: 443.2571.

(22) Preparation of ethyl 2-benzoyl-2-benzyl-7,7-hexamethylenehepta-4,5,6-trienoate **3db** (lican-03-095)



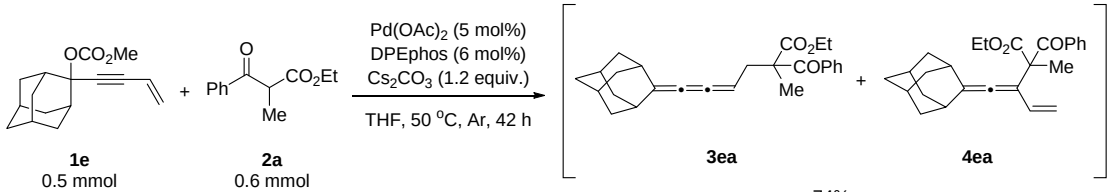
1d 0.5 mmol

2b 0.6 mmol

3db, 60%

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), DPEphos (16.4 mg, 0.03 mmol), Cs_2CO_3 (195.7 mg, 0.6 mmol), THF (10 mL), **1d** (111.5 mg, 0.5 mmol), and **2b** (169.2 mg, 0.6 mmol) afforded **3db** (129.4 mg, 60%) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 100/1 (1000+10 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28-8.22 (m, 2 H, ArH), 7.56-7.48 (m, 1 H, ArH), 7.46-7.37 (m, 2 H, ArH), 7.23-7.14 (m, 3 H, ArH), 7.10-7.02 (m, 2 H, ArH), 5.04 (t, *J* = 8.2 Hz, 1 H, =CH), 4.21-4.02 (m, 2 H, OCH_2), 3.48 (s, 2 H, CH_2 of Bn), 2.97-2.79 (m, 2 H, CH_2), 2.50-2.33 (m, 4 H, 2 × CH_2), 1.73-1.61 (m, 4 H, 2 × CH_2), 1.60-1.48 (m, 4 H, 2 × CH_2), 1.06 (t, *J* = 7.0 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.0, 172.3, 161.7, 154.7, 136.1, 135.9, 132.6, 130.3, 128.5, 128.4, 128.0, 126.8, 126.4, 95.3, 62.5, 61.4, 38.4, 36.23, 36.15, 35.5, 29.58, 29.55, 28.0, 27.8, 13.7; **IR** (neat) *v* = 3062, 3031, 2925, 2851, 2058, 1732, 1680, 1445, 1271, 1180 cm^{-1}; **MS** (ESI) *m/z* 451 $[M+Na]^+$; **HRMS** (ESI) Calcd for $C_{29}H_{33}O_3$ $[M+H]^+$: 429.2424, Found: 429.2415.

(23) Preparation of compound **3ea** (lican-04-115)



1e 0.5 mmol

2a 0.6 mmol

3ea **4ea**

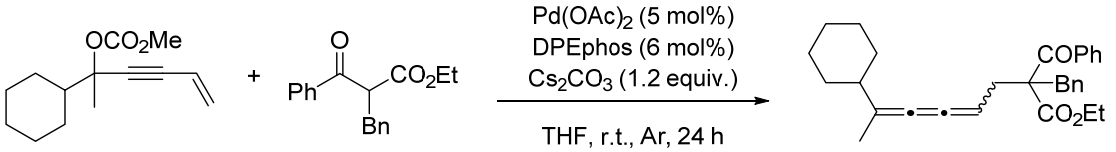
74%
3ea/4ea = 95/5

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.5 mg, 0.024 mmol),

DPEphos (16.4 mg, 0.03 mmol), Cs_2CO_3 (197.0 mg, 0.6 mmol), THF (10 mL), **1e** (131.0 mg, 0.5 mmol), and **2a** (124.6 mg, 0.6 mmol) afforded (**3ea** + **4ea**) (172.5 mg, 74%, **3ea**/**4ea** = 95/5,) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 30/1 (900+30 mL)] as a light yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2 H, ArH), 7.51 (t, *J* = 7.4 Hz, 1 H, ArH), 7.40 (t, *J* = 7.6 Hz, 2 H, ArH), 5.14 (t, *J* = 8.2 Hz, 1 H, =CH), 4.21-4.01 (m, 2 H, OCH_2), 2.89 (d, *J* = 7.6 Hz, 2 H, CH_2), 2.60 (s, 1 H, CH), 2.52 (s, 1 H, CH), 1.97 (s, 2 H, CH_2), 1.94-1.79 (m, 10 H, 5 × CH_2), 1.60 (s, 3 H, CH_3), 1.08 (t, *J* = 7.2 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.1, 173.5, 162.5, 147.7, 135.5, 132.7, 132.5, 128.4, 128.3, 95.0, 61.3, 57.6, 39.8, 39.04, 39.00, 38.7, 38.5, 36.8, 27.8, 20.9, 13.7; **IR** (neat) *ν* = 3062, 2926, 2851, 2061, 1731, 1680, 1598, 1581, 1446, 1271, 1179 cm^{-1}; **MS** (DART) *m/z* 391 $[M+H]^+$; **HRMS** (DART) Calcd for $C_{26}H_{31}O_3$ $[M+H]^+$: 391.2268, Found: 391.2264.

The following signals are discernible for **4ea**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2 H, ArH), 6.30 (dd, J_1 = 17.0 Hz, J_2 = 10.2 Hz, 1 H, =CH), 5.36 (d, *J* = 16.8 Hz, 1 H, one proton of $=CH_2$), 2.42 (s, 1 H, CH), 2.32 (s, 1 H, CH).

(24) Preparation of ethyl 2-benzoyl-2-benzyl-7-cyclohexylocta-4,5,6-trienoate **3fb** (lican-04-095)

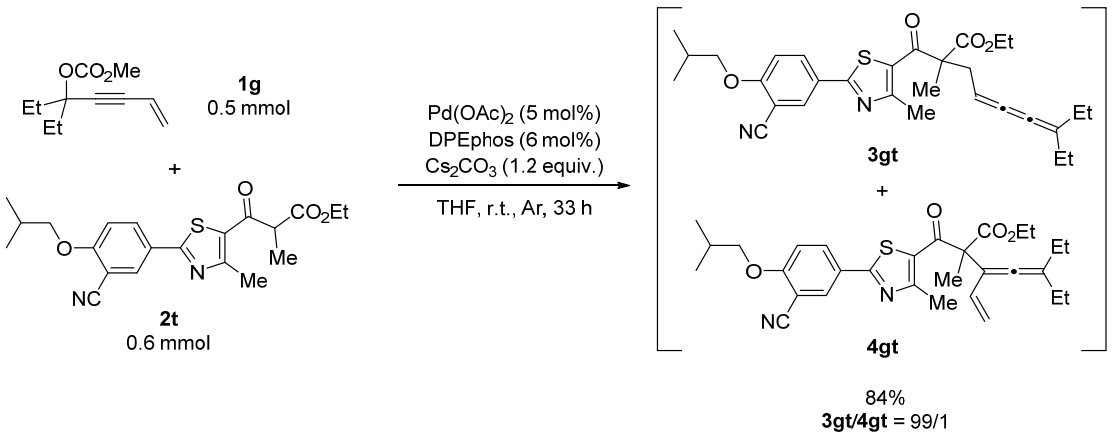


1f 0.5 mmol | **2b** 0.6 mmol | **3fb** 73%, *Z/E* = 1:1

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.7 mg, 0.025 mmol), DPEphos (16.2 mg, 0.03 mmol), Cs_2CO_3 (195.1 mg, 0.6 mmol), THF (10 mL), **1f** (118.9 mg, 0.5 mmol), and **2b** (169.0 mg, 0.6 mmol) afforded (*Z*-**3fb** + *E*-**3fb**) (154.3 mg, 73%, *Z/E* = 1:1) (the *Z*/*E* ratio of the product was determined via the ^{13}C NMR analysis) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 60/1 (900+15 mL)] as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.78 (m, 2 H, ArH), 7.58-7.41 (m, 1 H, ArH), 7.46-7.36 (m, 2 H, ArH), 7.23-7.13

(m, 3 H, ArH), 7.11-6.99 (m, 2 H, ArH), 5.13-4.97 (m, 1 H, =CH), 4.21-4.01 (m, 2H, OCH_2), 3.55-3.38 (m, 2 H, CH_2 of Bn), 3.03-2.78 (m, 2 H, CH_2), 2.04-1.91 (m, 1 H, CH), 1.91-1.87 (m, 3 H, CH_3), 1.87-1.71 (m, 4 H), 1.70-1.60 (m, 1 H), 1.33-1.09 (m, 5 H), 1.89-1.01 (m, 3 H, CH_3); **IR** (neat) ν = 2925, 2851, 2061, 1732, 1680, 1598, 1581, 1495, 1446, 1367, 1271, 1236, 1179 cm^{-1}; **MS** (ESI) *m/z* 443 $[M+H]^+$; **Elem. Anal.** Calcd. for $C_{30}H_{34}O_3$: C 81.41, H 7.74, found C 81.76, H 7.76.

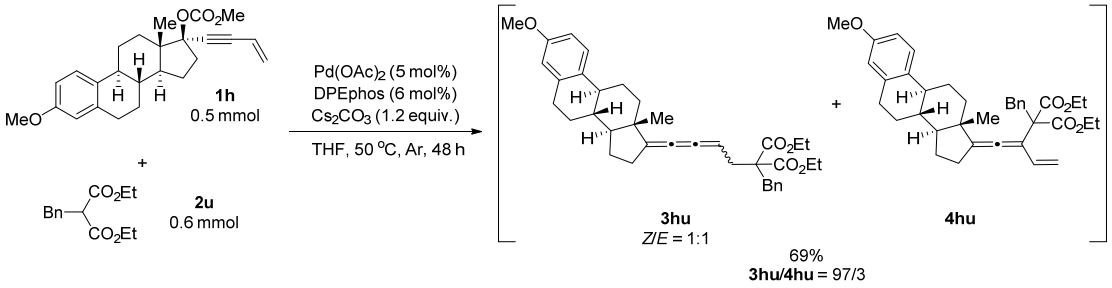
(25) Preparation of compound **3gt** (lican-04-063)



Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.4 mg, 0.024 mmol), DPEphos (16.4 mg, 0.03 mmol), Cs_2CO_3 (196.1 mg, 0.6 mmol), THF (10 mL), **1g** (98.5 mg, 0.5 mmol), and **2t** (240.5 mg, 0.6 mmol) afforded (**3gt** + **4gt**) (219.1 mg, 84%, **3gt**/**4gt** = 99/1) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 4/1 (600+150 mL)] as a light yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, J = 2.0 Hz, 1 H, ArH), 8.11 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1 H, ArH), 7.07 (d, J = 9.2 Hz, 1 H, ArH), 5.12 (t, J = 8.0 Hz, 1 H, =CH), 4.23 (q, J = 7.1 Hz, 2 H, OCH_2), 3.93 (d, J = 6.4 Hz, 2 H, $ArOCH_2$), 2.98-2.84 (m, 2 H, CH_2), 2.73 (s, 3 H, $ArCH_3$), 2.28-2.06 (m, 5 H, CH and 2 × CH_2), 1.61 (s, 3 H, CH_3), 2.44 (t, J = 7.0 Hz, 3 H, CH_3), 1.10 (d, J = 6.4 Hz, 6 H, 2 × CH_3), 1.05 (t, J = 7.2 Hz, 3 H, CH_3), 0.98 (t, J = 7.4 Hz, 3 H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.2, 172.2, 165.73, 165.72, 162.7, 162.3, 152.5, 132.4, 131.8, 128.7, 125.8, 125.2, 115.0, 112.4, 102.6, 94.6, 75.4, 61.5, 59.6, 39.5, 29.1, 29.0, 27.9, 20.2, 18.7, 18.4, 13.7, 11.8, 11.7; **IR** (neat) ν = 2967, 2933, 2876, 2254, 2230, 2061, 1733, 1664, 1605, 1509, 1430, 1369, 1279, 1118 cm^{-1};

MS (ESI) *m/z* 521 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{30}H_{37}O_4N_2S$ $[M+H]^+$: 521.2469, Found: 521.2464.

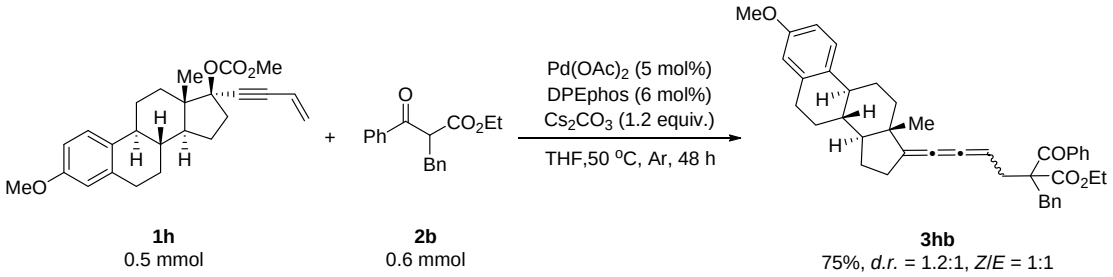
(26) Preparation of compound **3hu** (lican-04-156)



Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.5 mg, 0.024 mmol), DPEphos (16.6 mg, 0.03 mmol), Cs_2CO_3 (196.9 mg, 0.6 mmol), THF (10 mL), **1h** (198.1 mg, 0.5 mmol), and **2u** (150.7 mg, 0.6 mmol) afforded (**3hu** + **4hu**) (196.5 mg, 69%, **3hu**/**4hu** = 97/3, *Z*/*E* = 1:1 for **3hu**) (the *Z*/*E* ratio of the product was determined via the ^{13}C NMR analysis and *r.r.* of the product was determined via the ^1H NMR analysis) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 9/1 (900+100 mL)] as a white solid: **m.p.** 114.7-115.7 °C (hexane / ethyl ether); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.09 (m, 6 H, ArH), 6.76-6.66 (m, 1 H, ArH), 6.66-6.57 (m, 1 H, ArH), [5.20 (t, *J* = 7.8 Hz, 0.49 H), 5.12 (t, *J* = 7.8 Hz, 0.48 H), 1 H, =CH], 4.30-4.10 (m, 4 H, 2 × CH_2), 3.81-3.68 (m, 3 H, CH_3), 3.37-3.25 (m, 2 H, CH_2), 2.96-2.80 (m, 2 H, CH_2), 2.79-2.61 (m, 3 H, CH_2 and CH), 2.59-2.44 (m, 1 H, CH), 2.43-2.30 (m, 1 H, CH), 2.28-2.16 (m, 1 H, CH), 2.11-1.85 (m, 3 H), 1.62-1.34 (m, 6 H), 1.30-1.18 (m, 6 H, 2 × CH_3), 1.00-0.87 (m, 3 H, CH_3); **IR** (neat) *v* = 2927, 2066, 1728, 1611, 1575, 1497, 1437, 1278, 1197, 1176 cm^{-1}; **MS** (ESI) *m/z* 569 $[M+H]^+$; **Elem. Anal.** Calcd. for $C_{37}H_{44}O_5$: C 78.14, H 7.80, found C 77.89, H 7.80.

The following signals are discernible for **4hu**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.15-6.04 (m, 1 H, =CH), 5.38-5.32 (m, 1 H, one proton of $=CH_2$), 5.05-4.98 (m, 1 H, one proton of $=CH_2$).

(27) Preparation of compound **3hb** (lican-04-118)



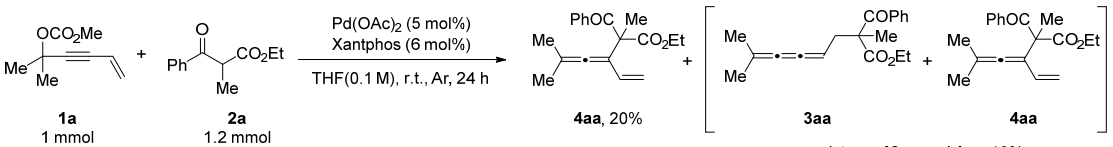
1h
0.5 mmol

2b
0.6 mmol

3hb
75%, *d.r.* = 1.2:1, *Z*/*E* = 1:1

Following **Typical Procedure II**, the reaction of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), DPEphos (16.4 mg, 0.03 mmol), Cs_2CO_3 (198.0 mg, 0.6 mmol), THF (10 mL), **1h** (197.6 mg, 0.5 mmol), and **2b** (169.9 mg, 0.6 mmol) afforded **3hb** (224.9 mg, 75%, *d.r.* = 1.2:1, *Z*/*E* = 1:1) (the *d.r.* and *Z*/*E* ratio of the product were determined via the ^{13}C NMR analysis) via column chromatography on silica gel [eluent: petroleum ether / ethyl ether = 20/1 (800+40 mL)] as a white solid: **m.p.** 104.6-105.6 °C (hexane / ethyl ether); **^{1}H NMR** (400 MHz, $CDCl_3$. It's difficult to assign the signals for the *Z*/*E* isomers. δ 7.95-7.82 (m, 2 H, ArH), 7.60-7.49 (m, 1 H, ArH), 7.48-7.39 (m, 2 H, ArH), 7.62-7.16 (m, 4 H, ArH), 7.13-7.01 (m, 2 H, ArH), 6.78-6.68 (m, 1 H, ArH), 6.67-6.59 (m, 1 H, ArH), 5.15-4.99 (m, 1 H, =CH), 4.21-4.03 (m, 2 H, CH_2), 3.84-3.70 (m, 3 H, CH_3), 3.55-3.41 (m, 2 H, CH_2), 3.03-2.78 (m, 4 H, 2 × CH_2), 2.72-2.57 (m, 1 H, CH), 2.54-2.40 (m, 1 H, CH), 2.39-2.29 (m, 1 H, CH), 2.28-2.16 (m, 1 H, CH), 2.00-1.81 (m, 3 H), 1.57-1.32 (m, 6 H), 1.12-1.02 (m, 3 H, CH_3), 0.96-0.88 (m, 2 H, 2 × CH), 0.88-0.81 (m, 1 H, CH); **IR** (neat) ν = 2989, 2935, 2867, 2835, 1755, 1679, 1610, 1500, 1442, 1275, 1225, 1235 cm^{-1}; **MS** (ESI) *m/z* 601 $[M+H]^+$; **Elem. Anal.** Calcd. for $C_{41}H_{44}O_4$: C 81.97, H 7.38, found C 81.86, H 7.39.

4. Isolation and confirmation of the regioisomer 4aa via a large scale reaction (lican-08-061, lican-08-089)



1a
1 mmol

2a
1.2 mmol

4aa, 20%

3aa

4aa

a mixture of **3aa** and **4aa**, 10%
3aa/4aa = 95/5

To a flame-dried Schlenk tube were added $Pd(OAc)_2$ (11.5 mg, 0.05 mmol) and Xantphos (34.5 mg, 0.06 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 (5 mL), **1a** (168.3 mg, 1 mmol), **2a** (247.9 mg, 1.2 mmol), and THF (5 mL) were sequentially added under argon atmosphere. After that, the Ar gas line was closed. The resulting mixture was stirred at room temperature for 24 h, 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 pure **4aa** (60.9 mg, 20%) and a mixture of **3aa** and **4aa** (30.1 mg, 10%, **3aa**/**4aa** = 95/5) [eluent: petroleum ether / dichloromethane = 10/1 (1000+100 mL) to petroleum ether / dichloromethane = 4/1 (800+200 mL)].

4aa: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 2 H, ArH), 7.54-7.43 (m, 1 H, ArH), 7.42-7.25 (m, 2 H, ArH), 6.21 (dd, J_1 = 16.6 Hz, J_2 = 10.6 Hz, 1 H, =CH), 5.27 (d, J = 17.2 Hz, 1 H, one proton of $=CH_2$), 5.10 (d, J = 10.0 Hz, 1 H, one proton of $=CH_2$), 4.22-3.98 (m, 2 H, OCH_2), 1.71 (s, 3 H, CH_3), 1.63 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3), 1.06 (t, J = 6.6 Hz, 3 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.3, 196.6, 172.2, 135.7, 132.2, 132.1, 129.0, 127.9, 115.2, 104.6, 101.0, 61.1, 60.4, 22.5, 19.5, 19.0, 13.6; **IR** (neat) v = 3061, 2984, 2940, 2910, 1736, 1688, 1598, 1448, 1377, 1254, 1227, 1095 cm^{-1}; **MS** (ESI) m/z 299.2 $[M+H]^+$; **HRMS** (ESI) Calcd for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1642, Found: 299.1636.

5. The effect of leaving group

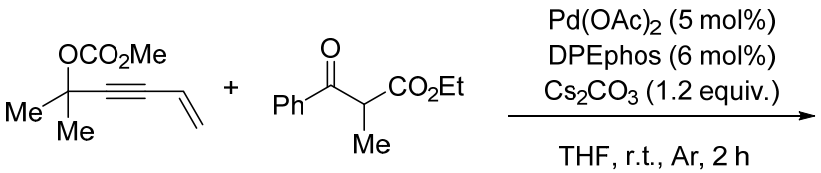
1 **2a** **3aa** **4aa**

Entry	LG	Recovery of **1** (%)	Yield of **3aa** (%)	Yield of **4aa** (%)
1	OCO_2Me (**1a**)	/	81	3
2[a]	OAc (**1a'**)	78	8	/
3	$OP(O)(OEt)_2$ (**1a''**)	2	1	/

Reaction conditions: **1** (0.2 mmol), **2a** (1.2 equiv), $Pd(OAc)_2$ (5 mol%), Dpephos (6 mol%), and Cs_2CO_3 (1.2 equiv.) in THF (2 mL) unless otherwise noted. The yield was determined by ^{1}H-NMR analysis with dibromomethane or CH_3NO_2 as the internal standard, [a] a small amount of unknown product was detected.

SAESI-MS Experiment[6]

Preparation of the sample for SAESI-MS analysis



1a
0.2 mmol

2a
0.24 mmol

To a flame-dried Schlenk tube (10 mL) were added $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), DPEphos (6.5 mg, 0.012 mmol), Cs_2CO_3 (78.4 mg, 0.24 mmol), THF (1 mL), **1a** (33.8 mg, 34.5 μL, 0.5 mmol), **2a** (49.4 mg, 46 μL, 0.24 mmol), and THF (1 mL) sequentially under argon atmosphere. After being stirred at room temperature for 2 h, the mixture was sealed and submitted to SAESI-MS analysis.

SAESI-MS conditions

SAESI-MS spectra were recorded on a Thermo TSQ Quantum Access triple-quadrupole mass spectrometer (Thermo Fisher Scientific, Waltham, MA) equipped with a home-made SAESI ion source in positive mode. The basic SAESI conditions were: vacuum, 3.2×10^{-6} torr; spray voltage, 3600 V; capillary temperature, 275°C; sheath gas pressure of two sprayers, 3 arb. units; the collision energy of CID, 30 eV. Data acquisition and analysis were done with the Xcalibur (version 2.0, Thermo Fisher Scientific) software package.

In solvent-assisted electrospray ionization mass spectrometric experiment, the angle (α) between the two sprayers is 45° and the distance (b) between the tip of sprayers and the inlet to the mass is 6 mm. The chemical solutions were injected by a 500-μL air-tight syringe with a speed at 5 μL/min to SAESI-MS. The assisted solvent of anhydrous acetonitrile was injected by another 500-μL air-tight syringe with a speed at 500 μL/min.

SAESI-MS device

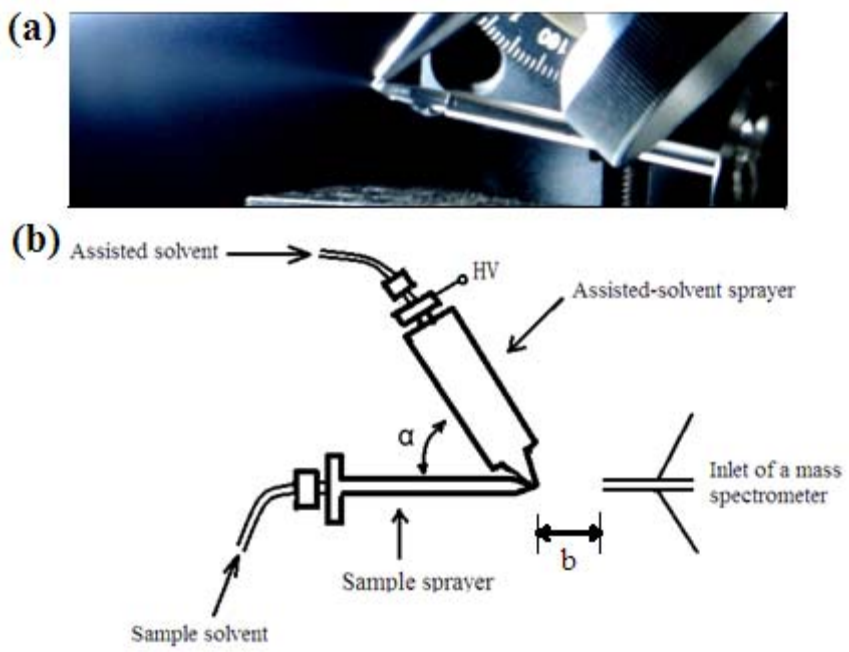


Figure S1. (a) Photographic image of SAESI apparatus. (b) Schematic representation of the SAESI. The angle (α) between the two sprayers is 45° and the distance (b) between the tip of sprayers and the inlet to the mass is 6 mm.

Mass spectrometric experiment results

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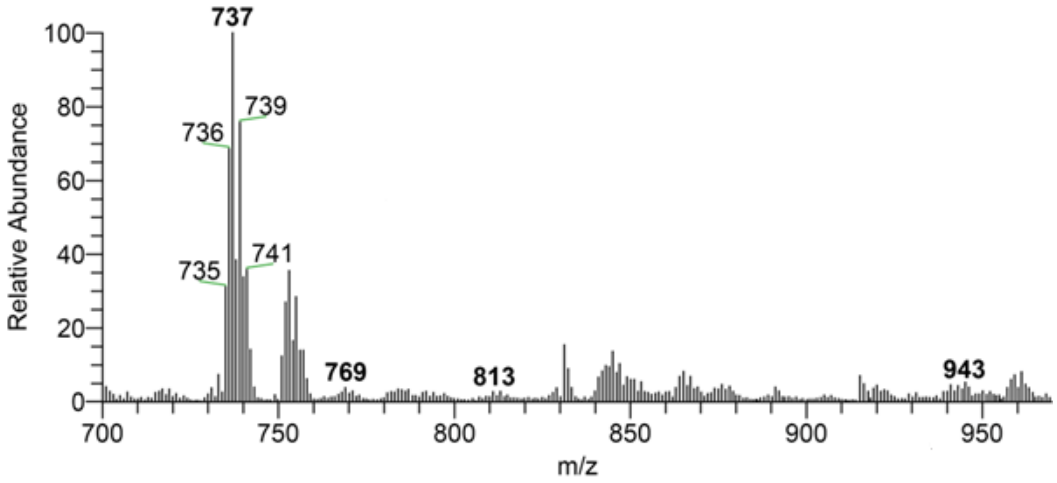
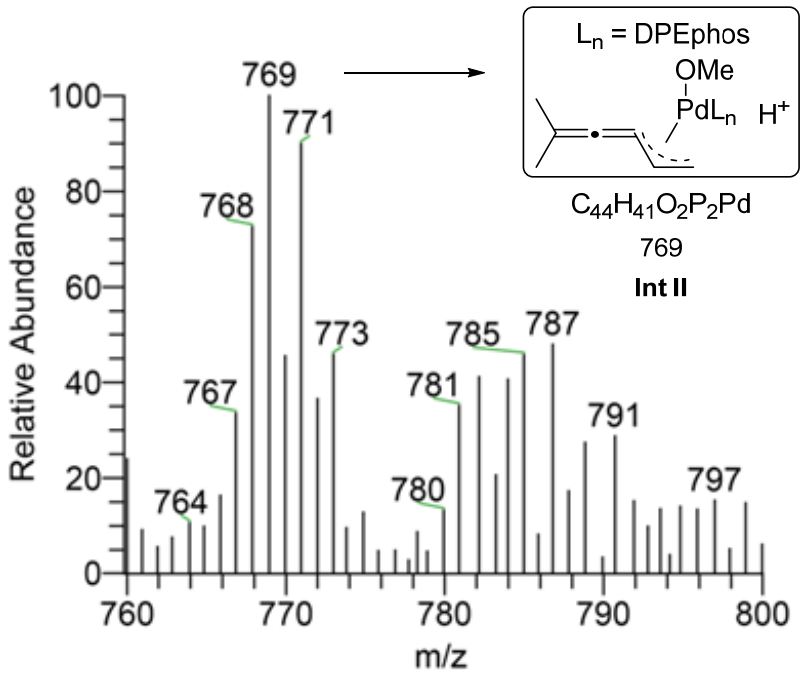


(b)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H+
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769
Int II
Relative Abundance
m/z
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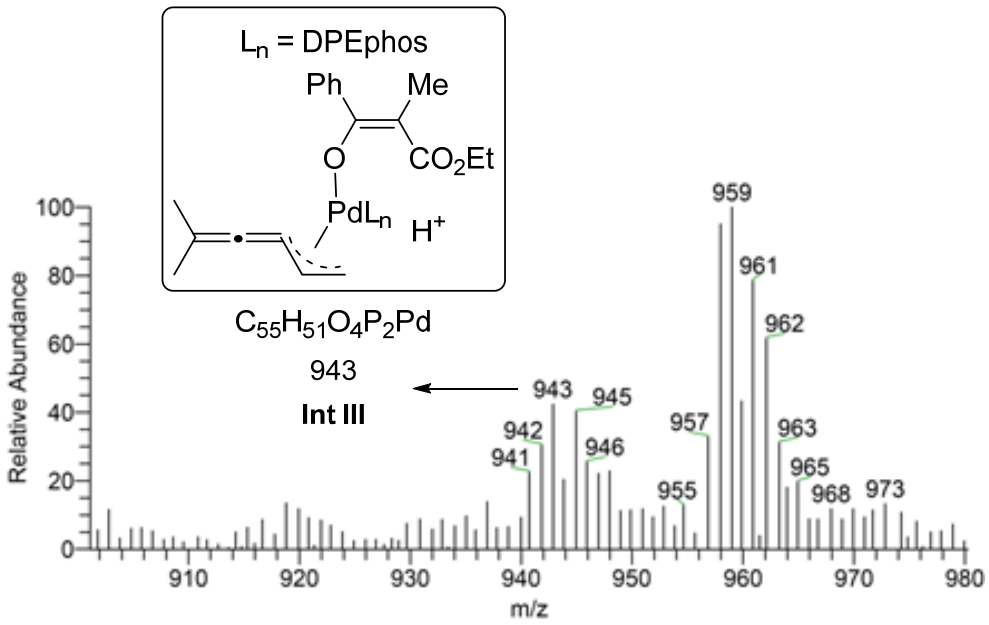
771
768
773
785
787
767
781
791
764
780
797
100
80
60
40
20
0
760
770
780
790
800

(c)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O
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PdLn
H+
C55H51O4P2Pd
943
Int III
Relative Abundance
m/z
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961
962
943
945
957
942
963
941
946
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955
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80
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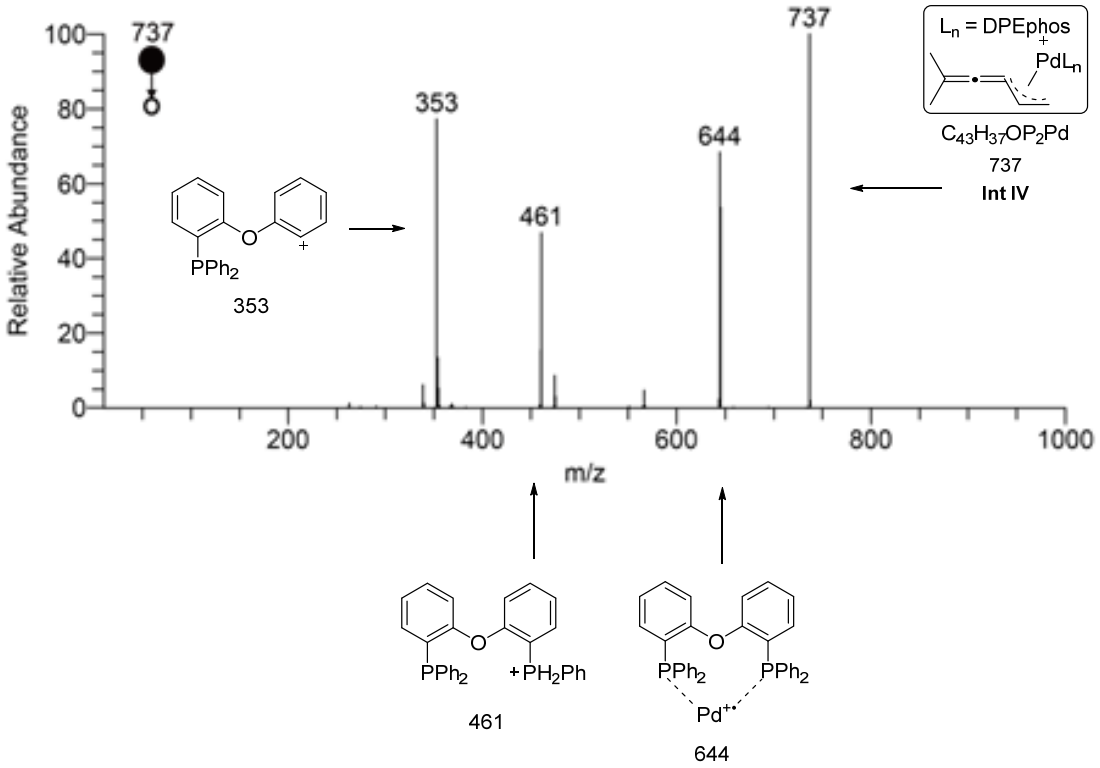
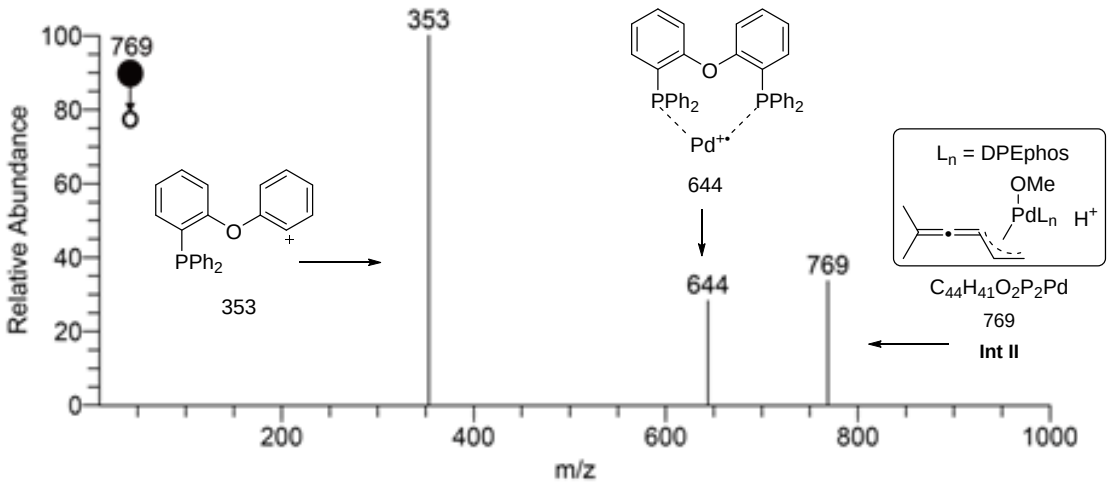
920
930
940
950
960
970
980

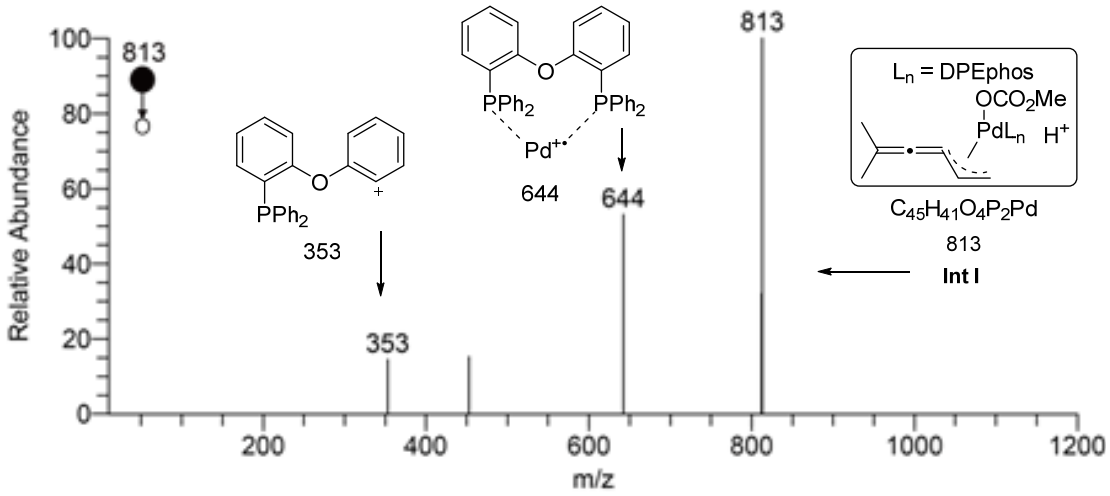
(d)


737
353
461
644
737
Relative Abundance
m/z
100
80
60
40
20
0
200
400
600
800
1000
PPh2
353
Ln = DPEphos
PdLn
C43H37OP2Pd
737
Int IV
PPh2
+PH2Ph
461
PPh2
PPh2
Pd+•
644

(e)


769
353
644
769
Relative Abundance
m/z
100
80
60
40
20
0
200
400
600
800
1000
PPh2
353
PPh2
PPh2
Pd+•
644
Ln = DPEphos
OMe
PdLn
H+
C44H41O2P2Pd
769
Int II

(f)



(g)

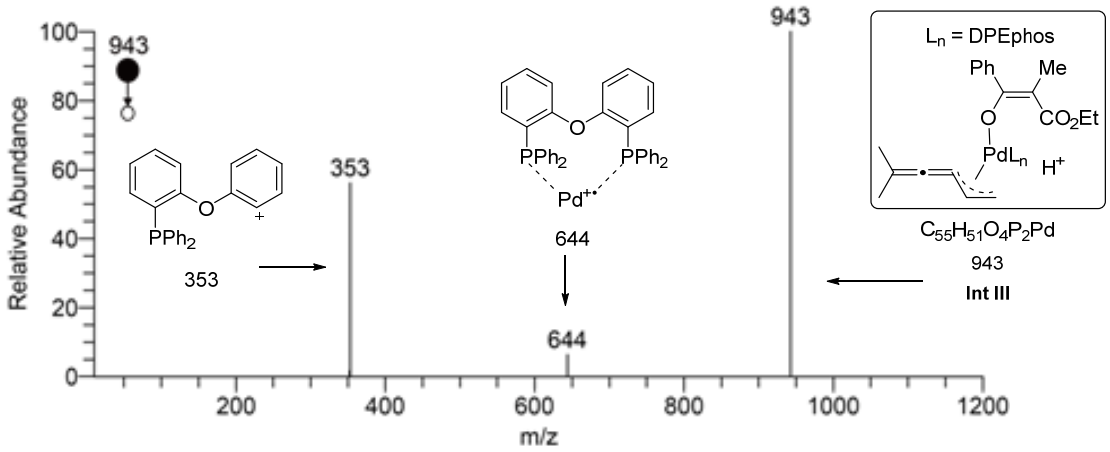


Figure S2. (a) SAESI-MS spectrum of the solution. (b) Expanded SAESI-MS spectrum, showing the major signal of **Int II** at m/z 769. (c) Expanded SAESI-MS spectrum, showing the major signal of **Int III** at m/z 943. (d) SAESI- MS/MS spectrum of complex ion **Int IV** at m/z 737. (e) SAESI- MS/MS spectrum of complex ion **Int II** at m/z 769. (f) SAESI- MS/MS spectrum of complex ion **Int I** at m/z 813. (g) SAESI- MS/MS spectrum of complex ion **Int III** at m/z 943.

References:

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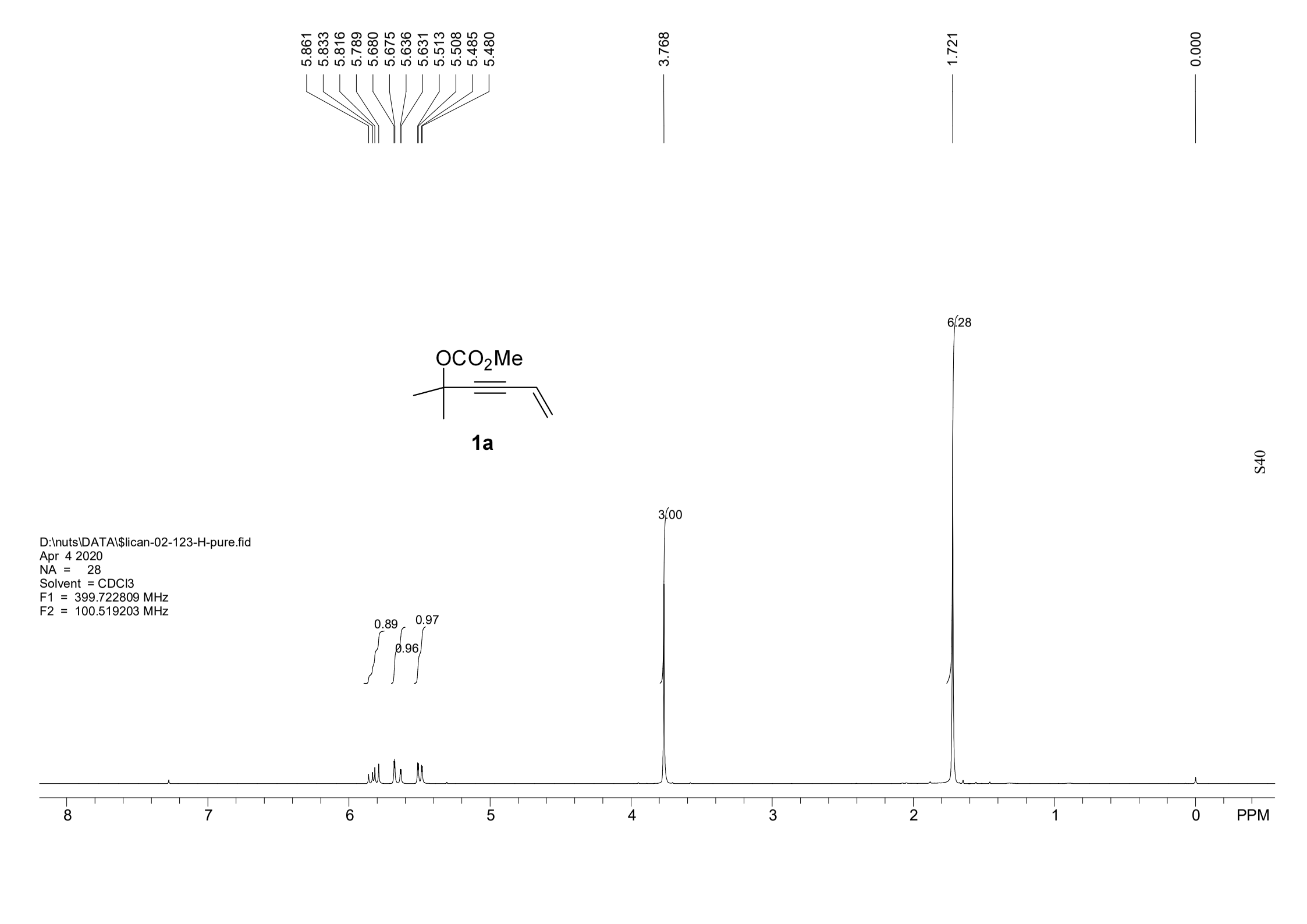
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5.631
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5.480
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1.721
0.000
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3.00
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0.97
0.96
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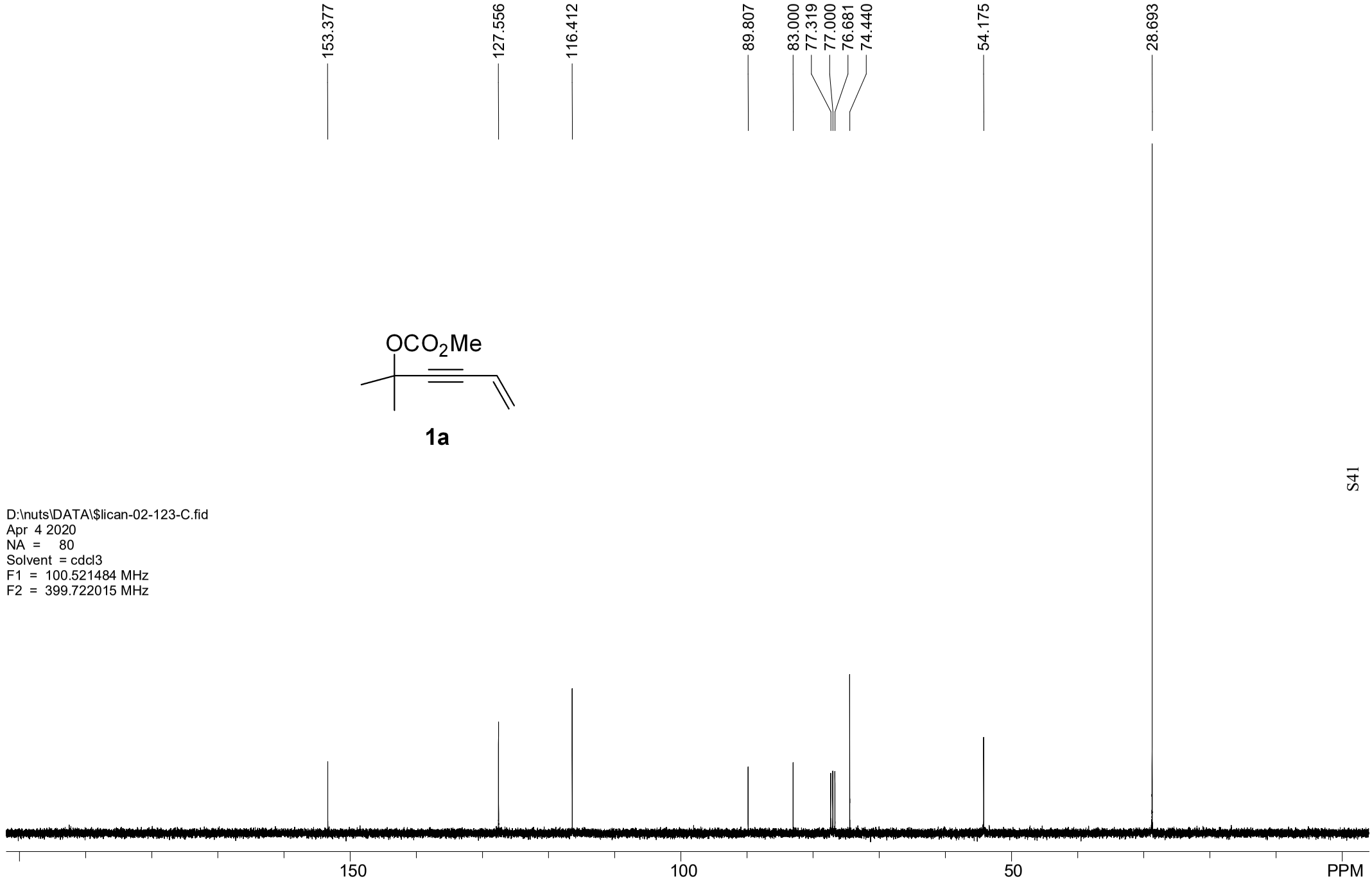
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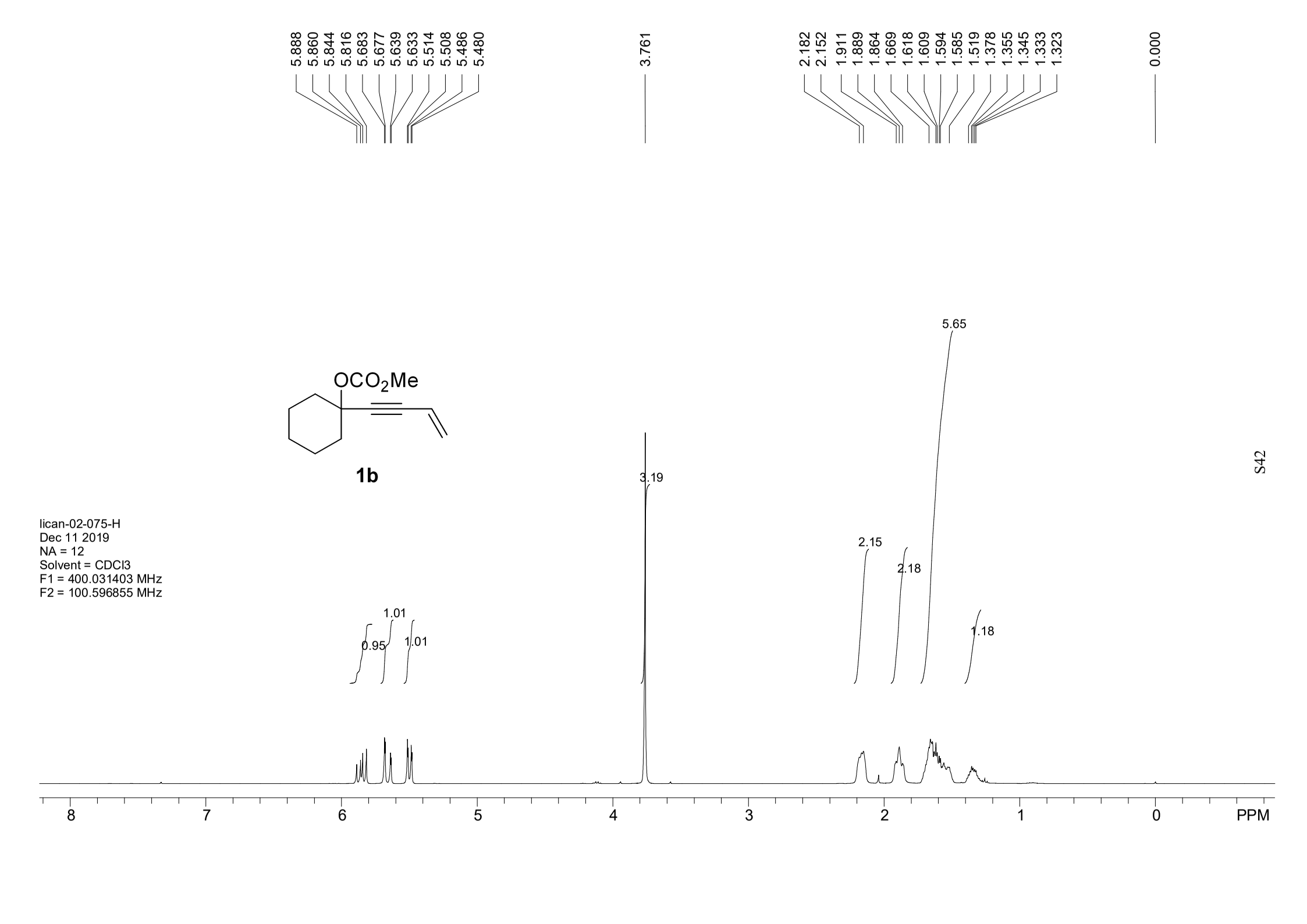
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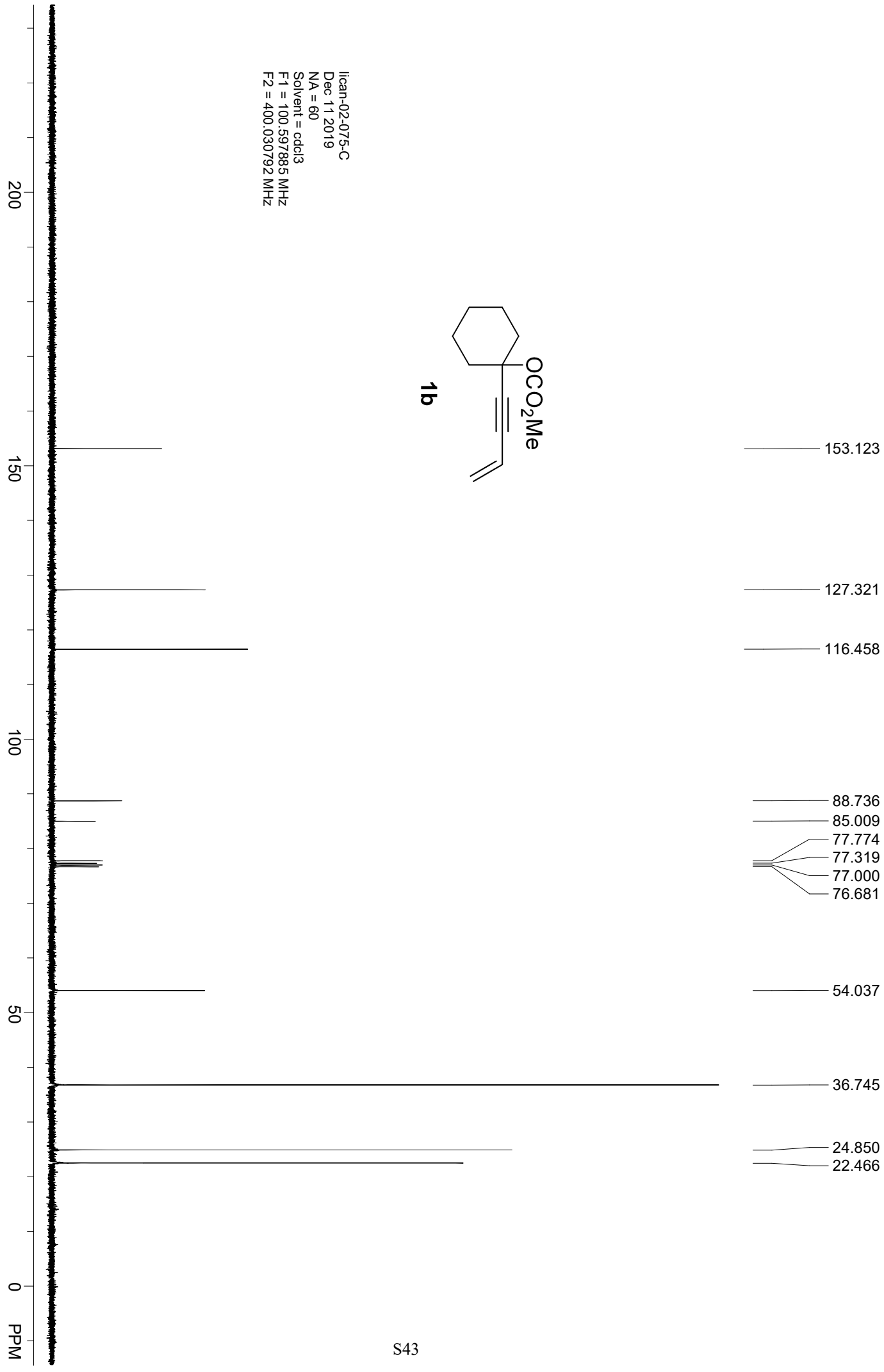
PPM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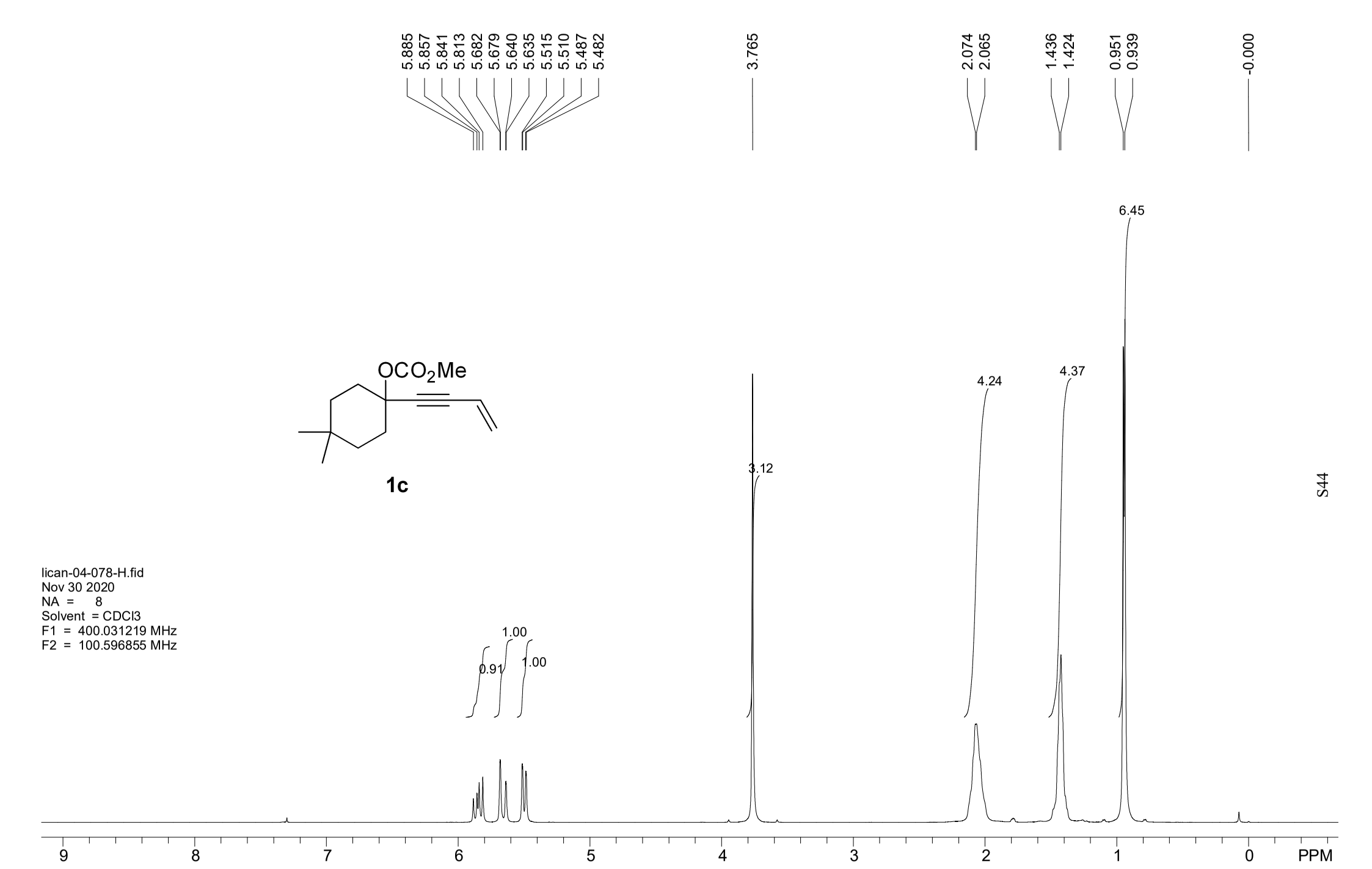
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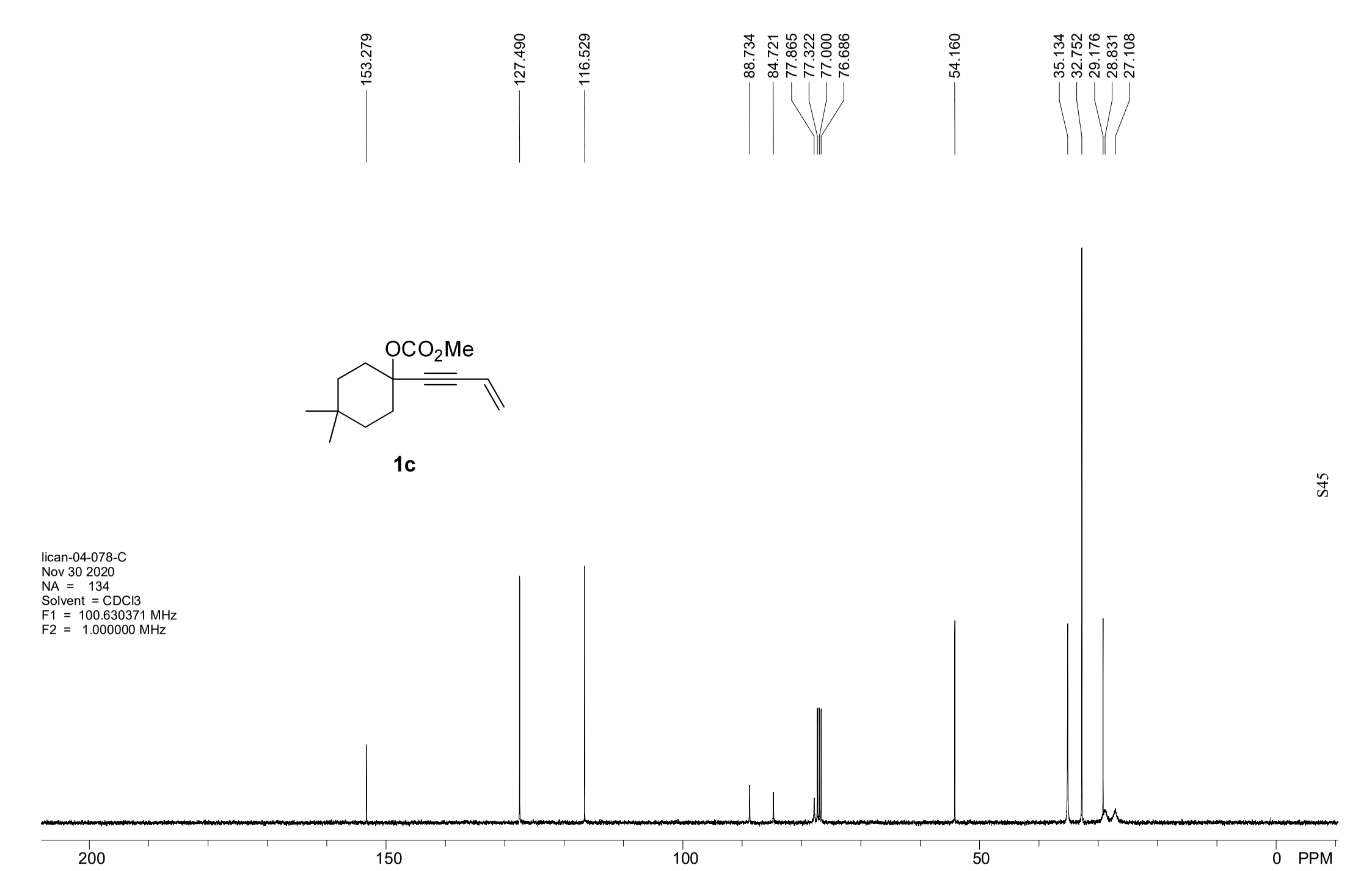
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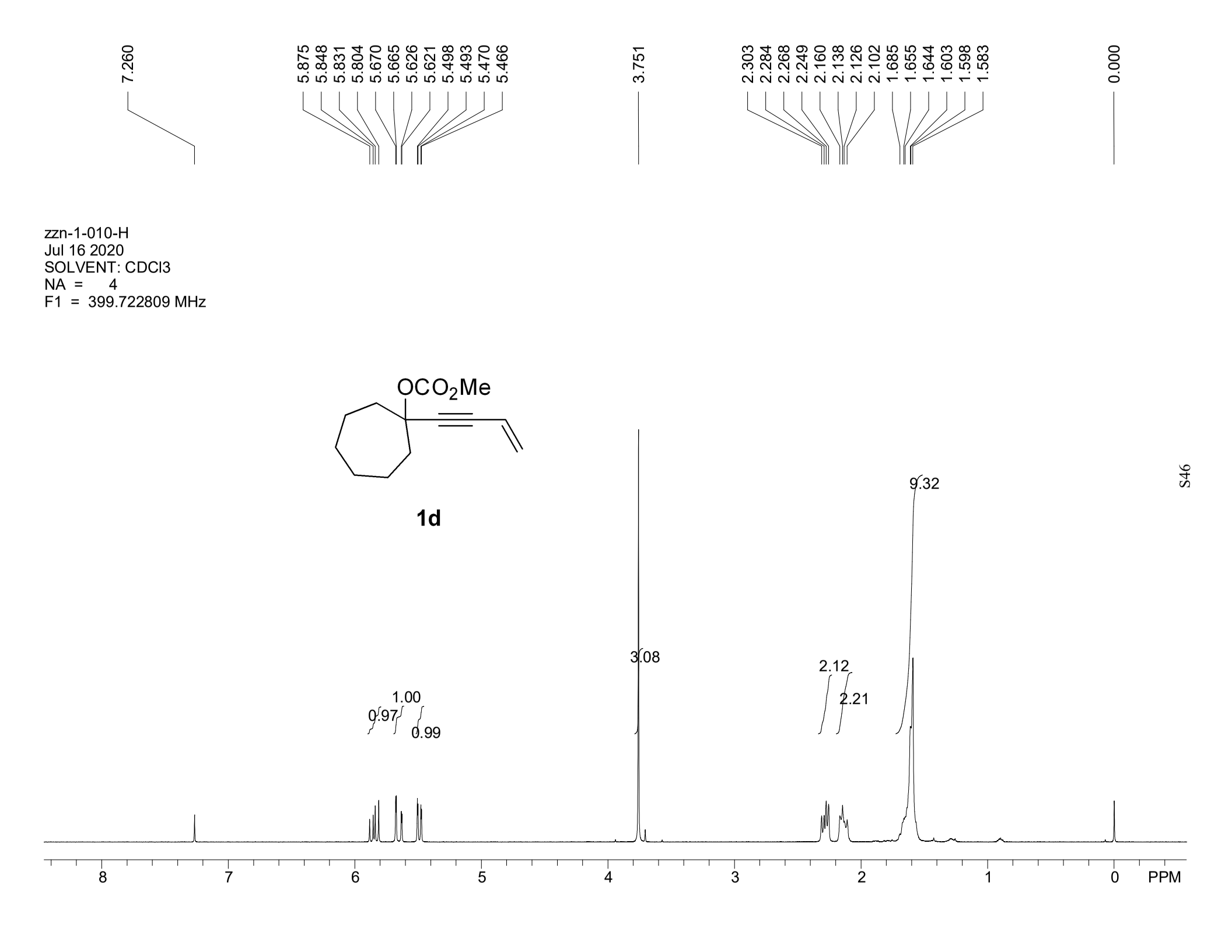
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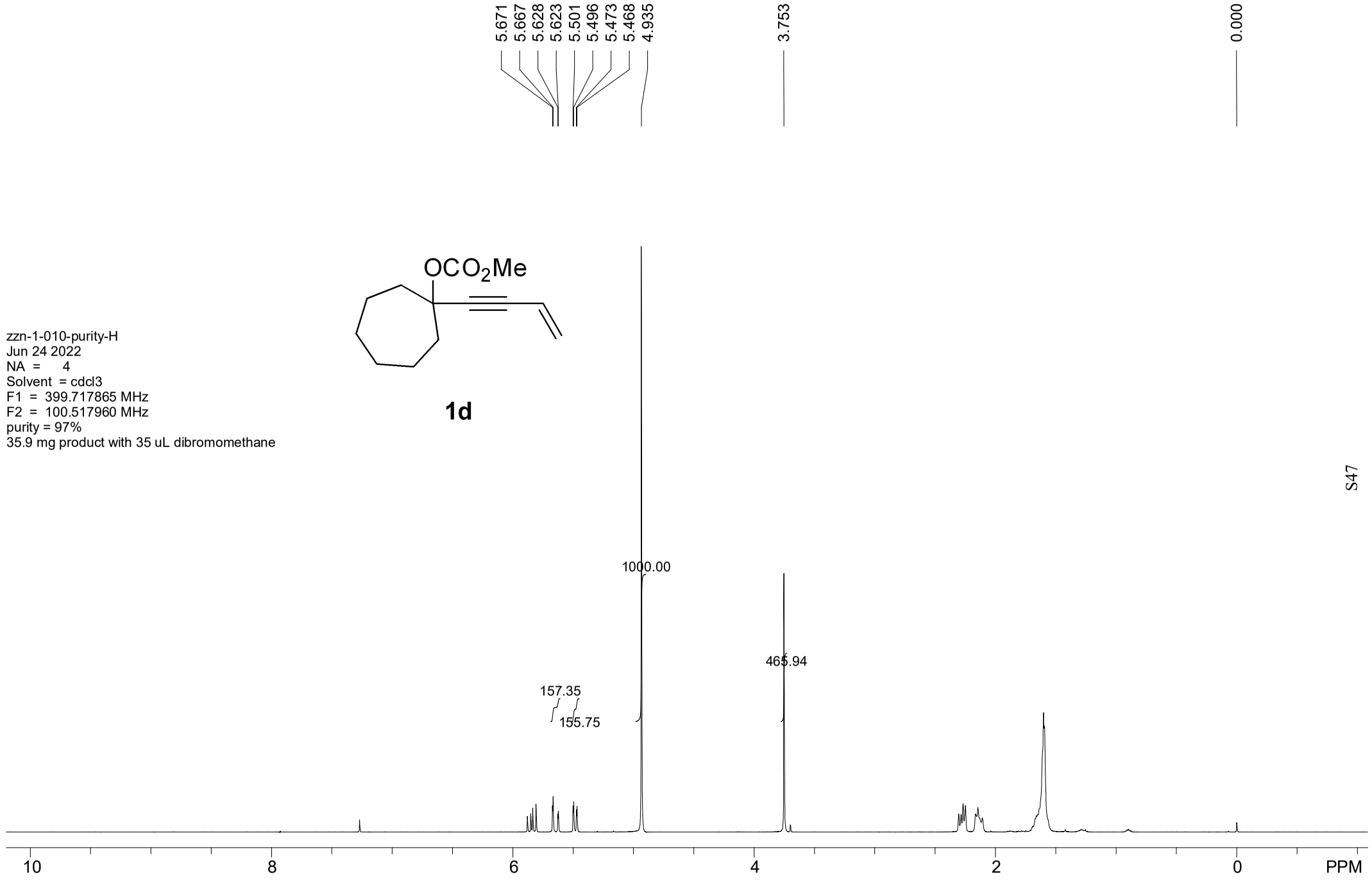
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Jun 24 2022
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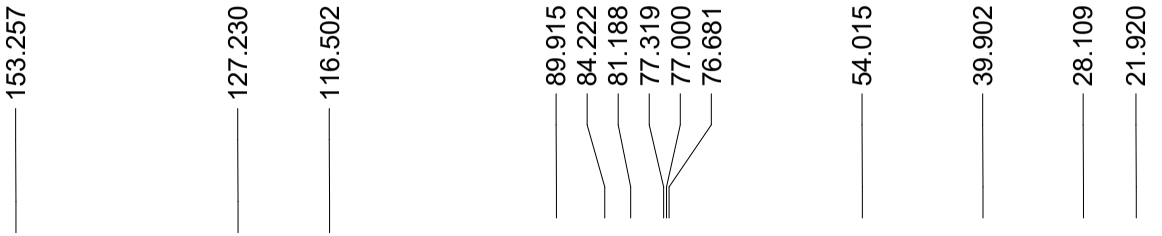

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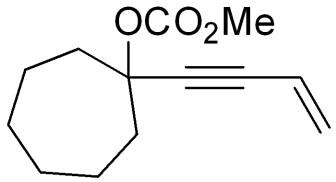

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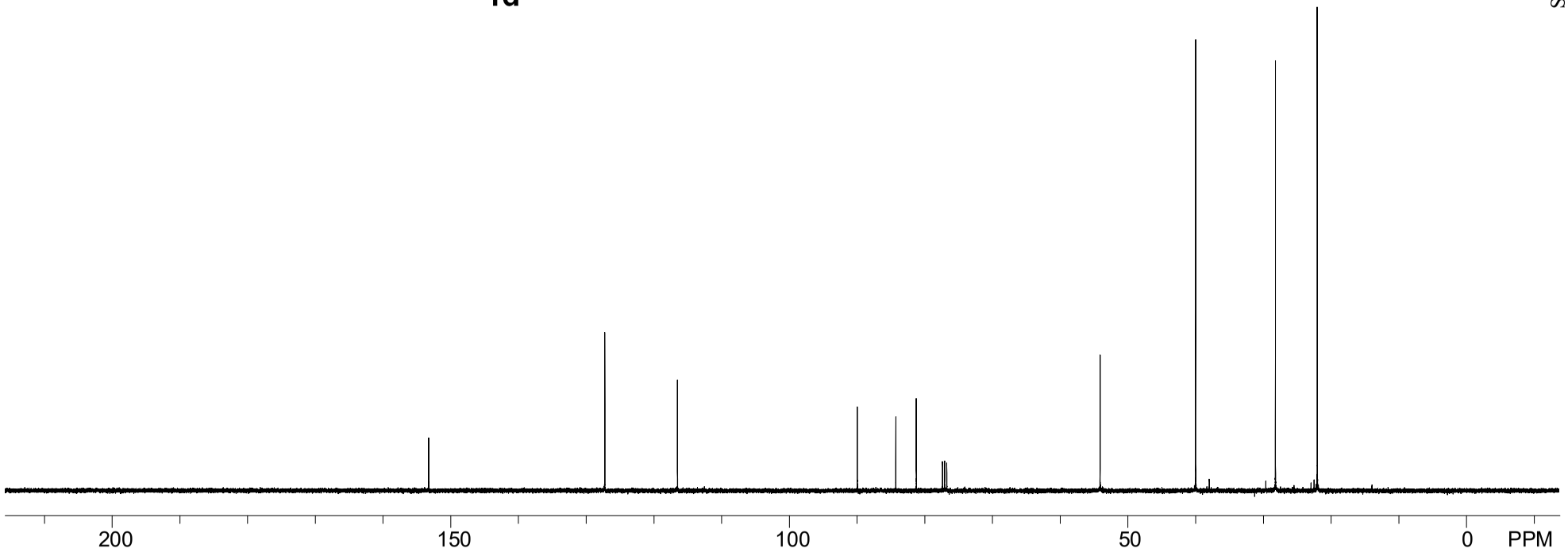

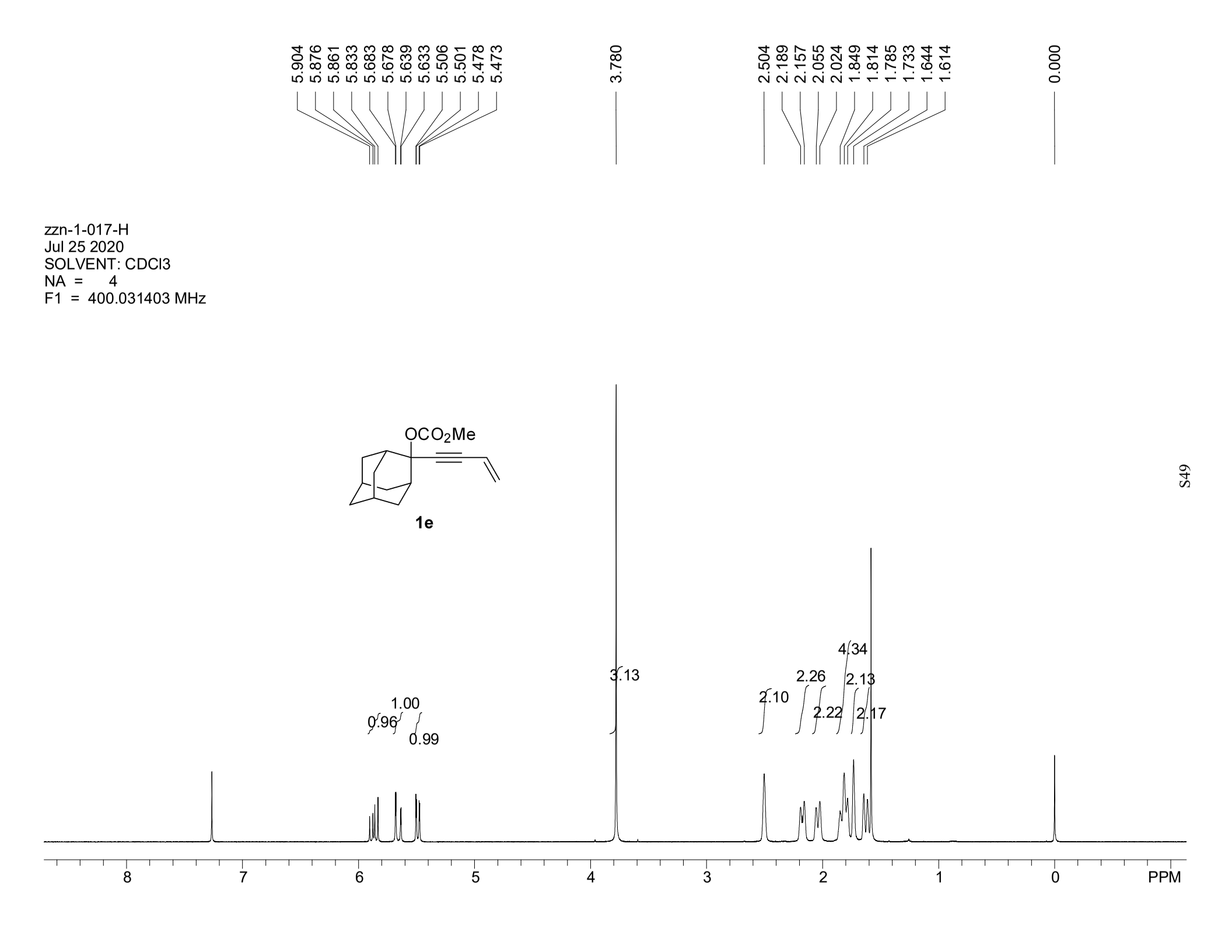
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Jul 25 2020
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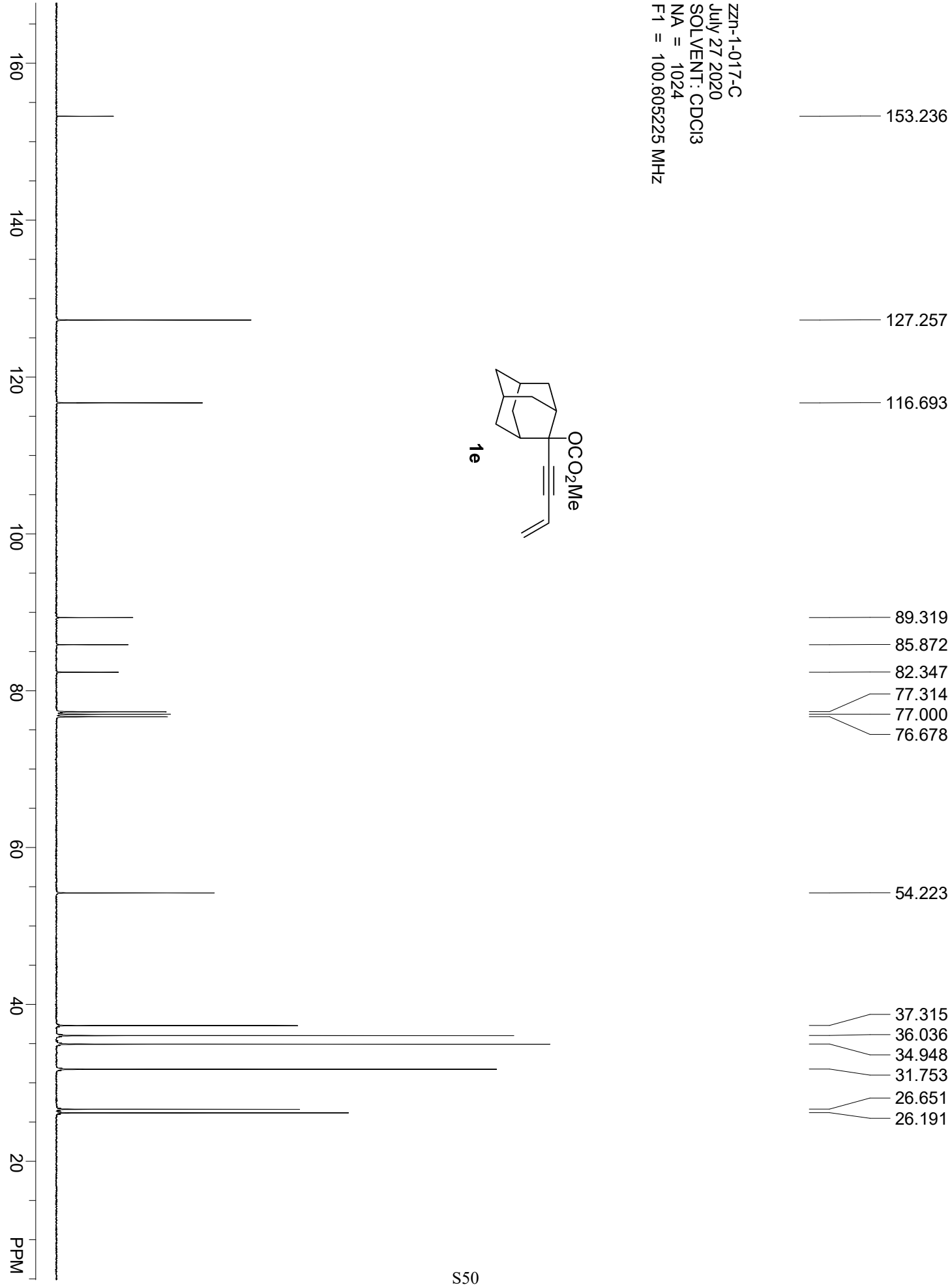
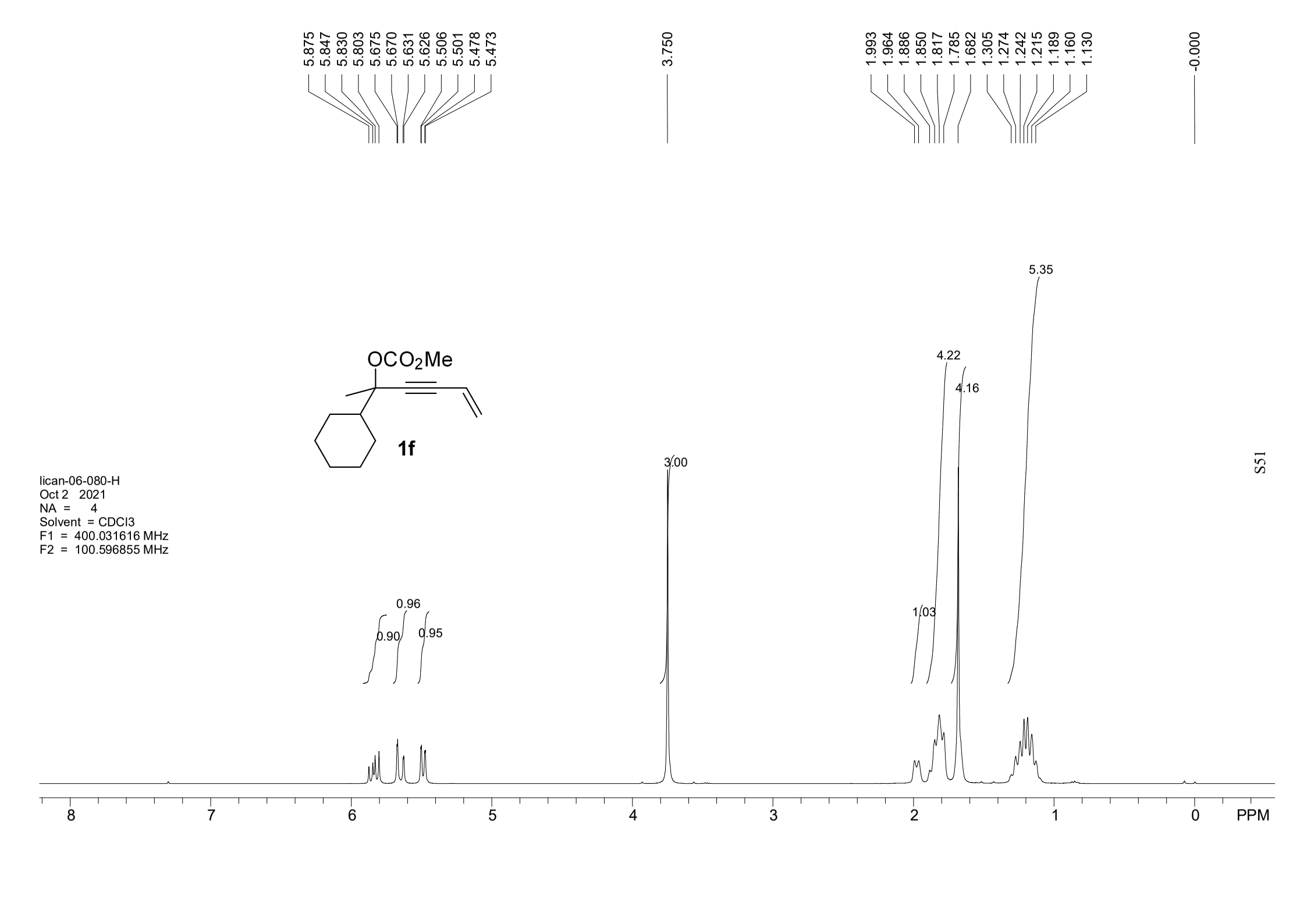
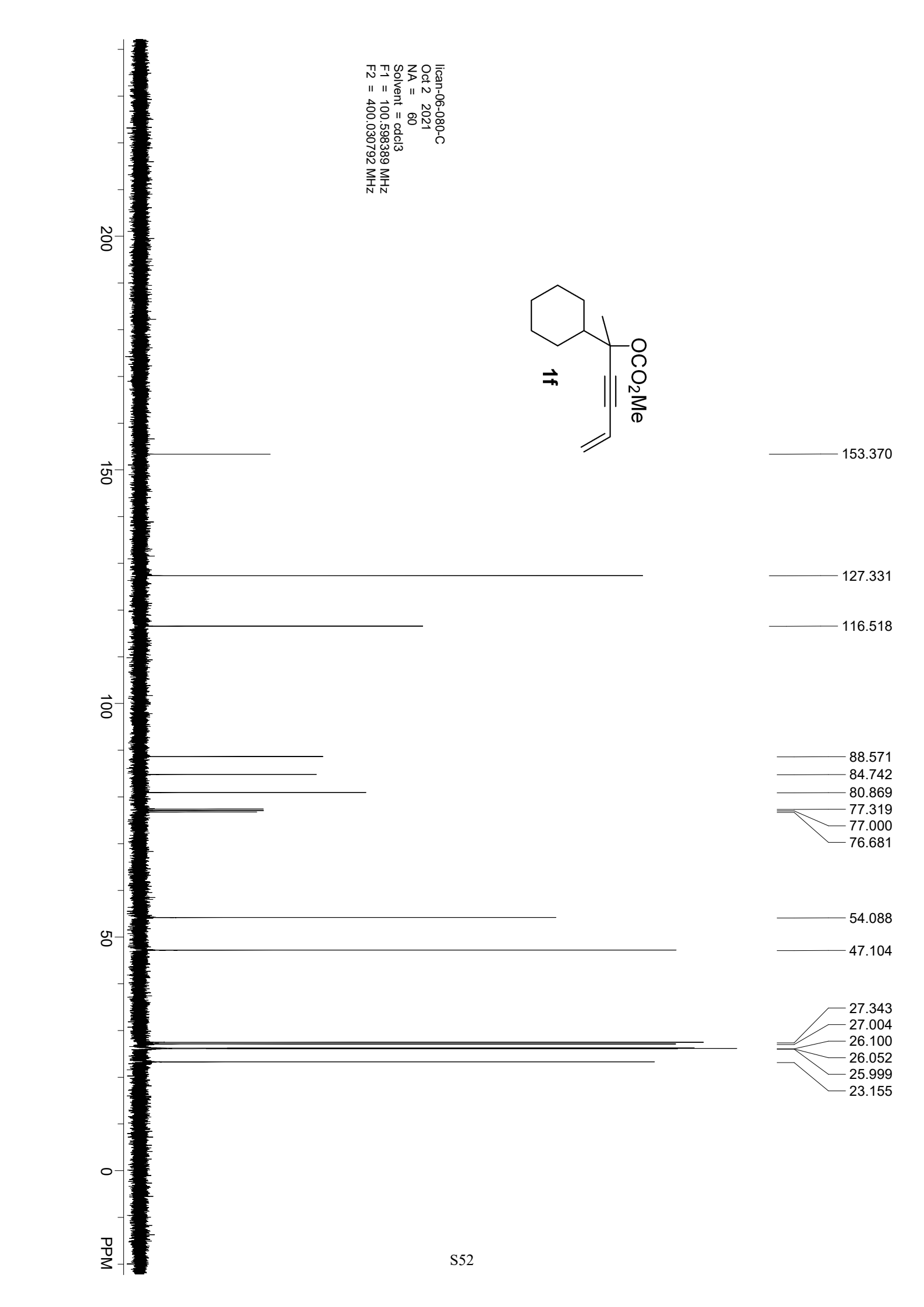
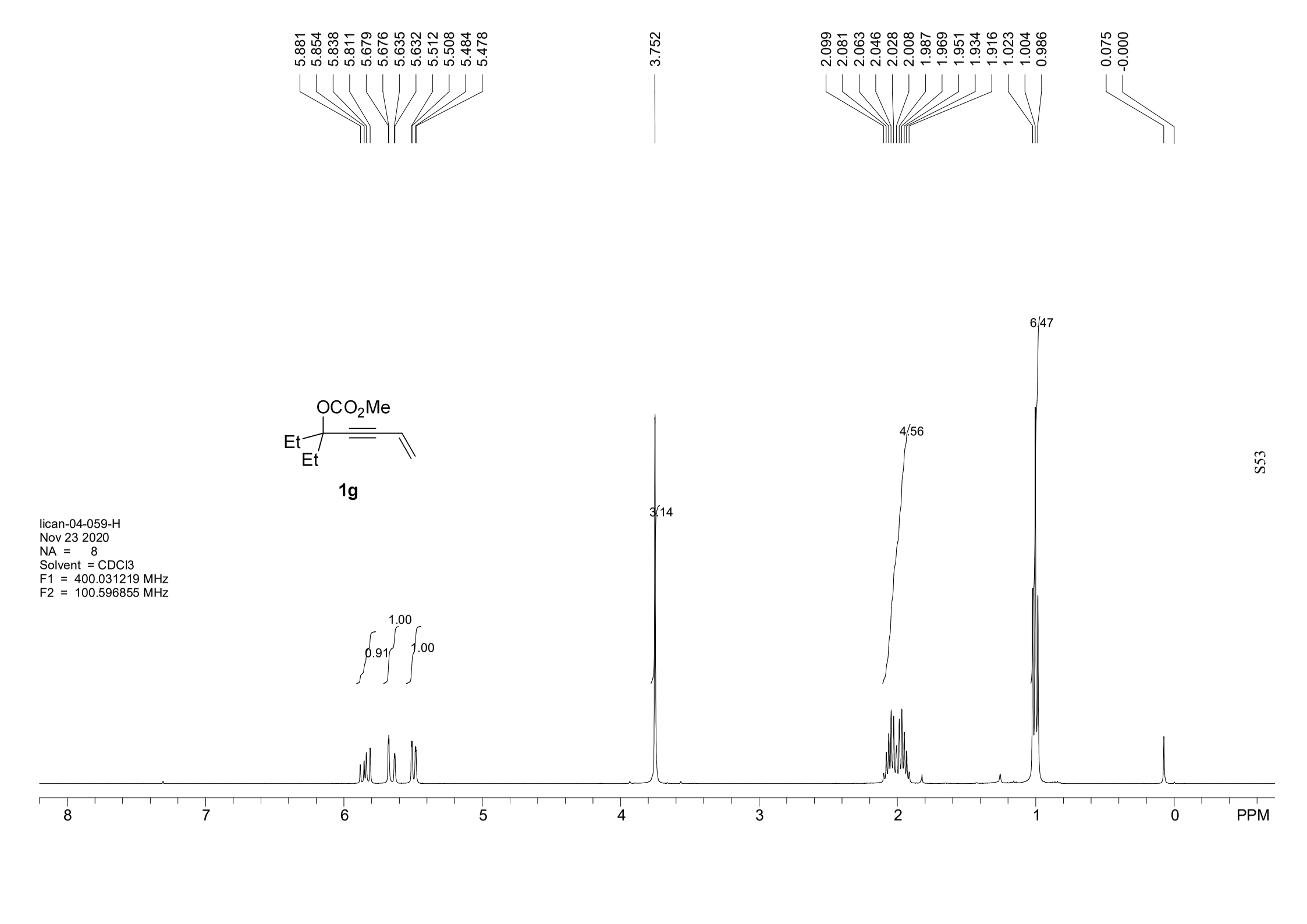
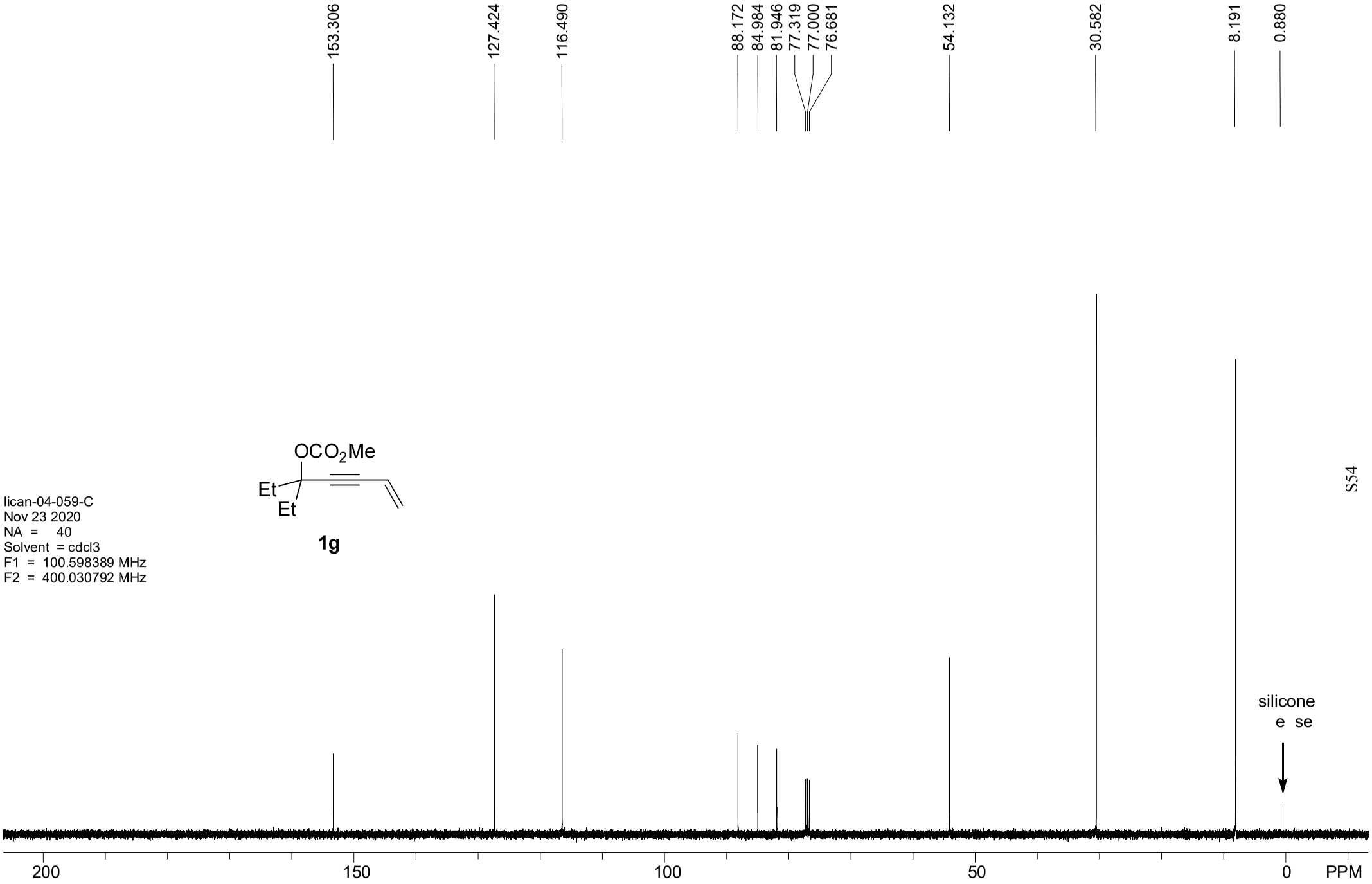
0
PPM

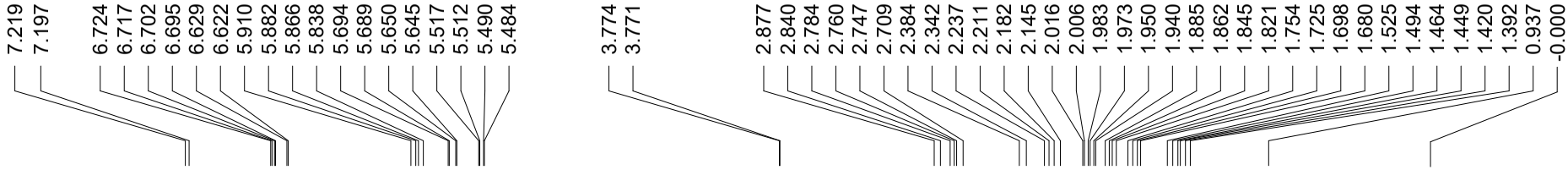

zzn-1-017-C
July 27 2020
SOLVENT: CDCl3
NA = 1024
F1 = 100.605225 MHz
153.236
127.257
116.693
89.319
85.872
82.347
77.314
77.000
76.678
54.223
37.315
36.036
34.948
31.753
26.651
26.191
OCO2Me
1e
160
140
120
100
80
60
40
20
PPM

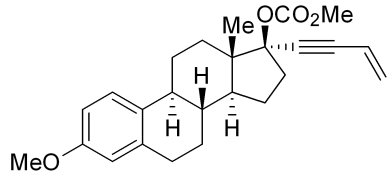

5.875
5.847
5.830
5.803
5.675
5.670
5.631
5.626
5.506
5.501
5.478
5.473
3.750
1.993
1.964
1.886
1.850
1.817
1.785
1.682
1.305
1.274
1.242
1.215
1.189
1.160
1.130
-0.000
OCO2Me
1f
5.35
4.22
4.16
3.00
0.96
0.90
0.95
1.03
lican-06-080-H
Oct 2 2021
NA = 4
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
S51
8
7
6
5
4
3
2
1
0
PPM


lican-06-080-C
Oct 2 2021
NA = 60
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
OCO2Me
1f
153.370
127.331
116.518
88.571
84.742
80.869
77.319
77.000
76.681
54.088
47.104
27.343
27.004
26.100
26.052
25.999
23.155
200
150
100
50
0
PPM


5.881
5.854
5.838
5.811
5.679
5.676
5.635
5.632
5.512
5.508
5.484
5.478
3.752
2.099
2.081
2.063
2.046
2.028
2.008
1.987
1.969
1.951
1.934
1.916
1.023
1.004
0.986
0.075
-0.000
OCO2Me
Et
Et
1g
lican-04-059-H
Nov 23 2020
NA = 8
Solvent = CDCl3
F1 = 400.031219 MHz
F2 = 100.596855 MHz
1.00
0.91
1.00
3.14
4.56
6.47
S53
8
7
6
5
4
3
2
1
0
PPM


153.306
127.424
116.490
88.172
84.984
81.946
77.319
77.000
76.681
54.132
30.582
8.191
0.880
OCO2Me
Et
Et
1g
lican-04-059-C
Nov 23 2020
NA = 40
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
silicone
e se
200
150
100
50
0
PPM

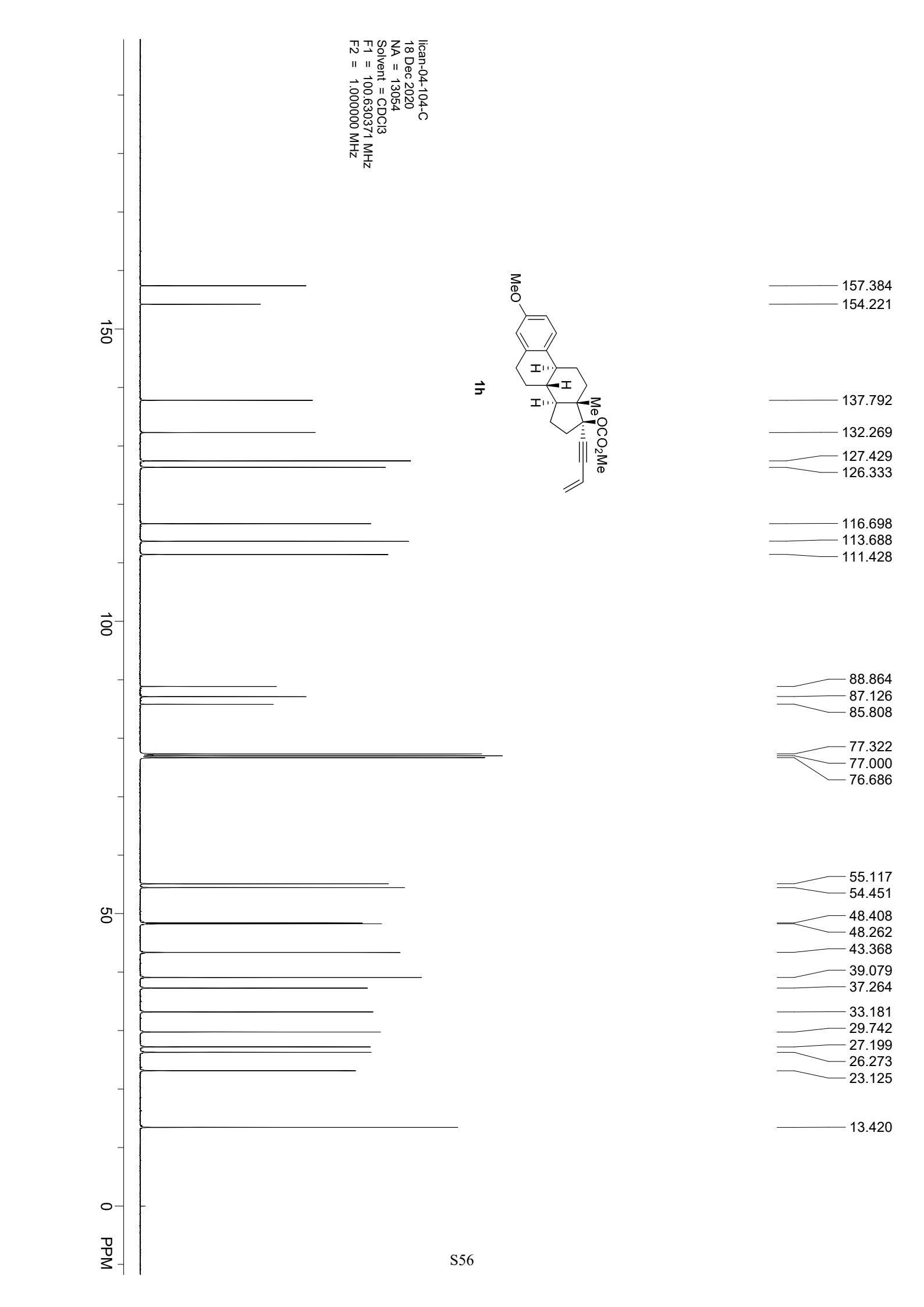


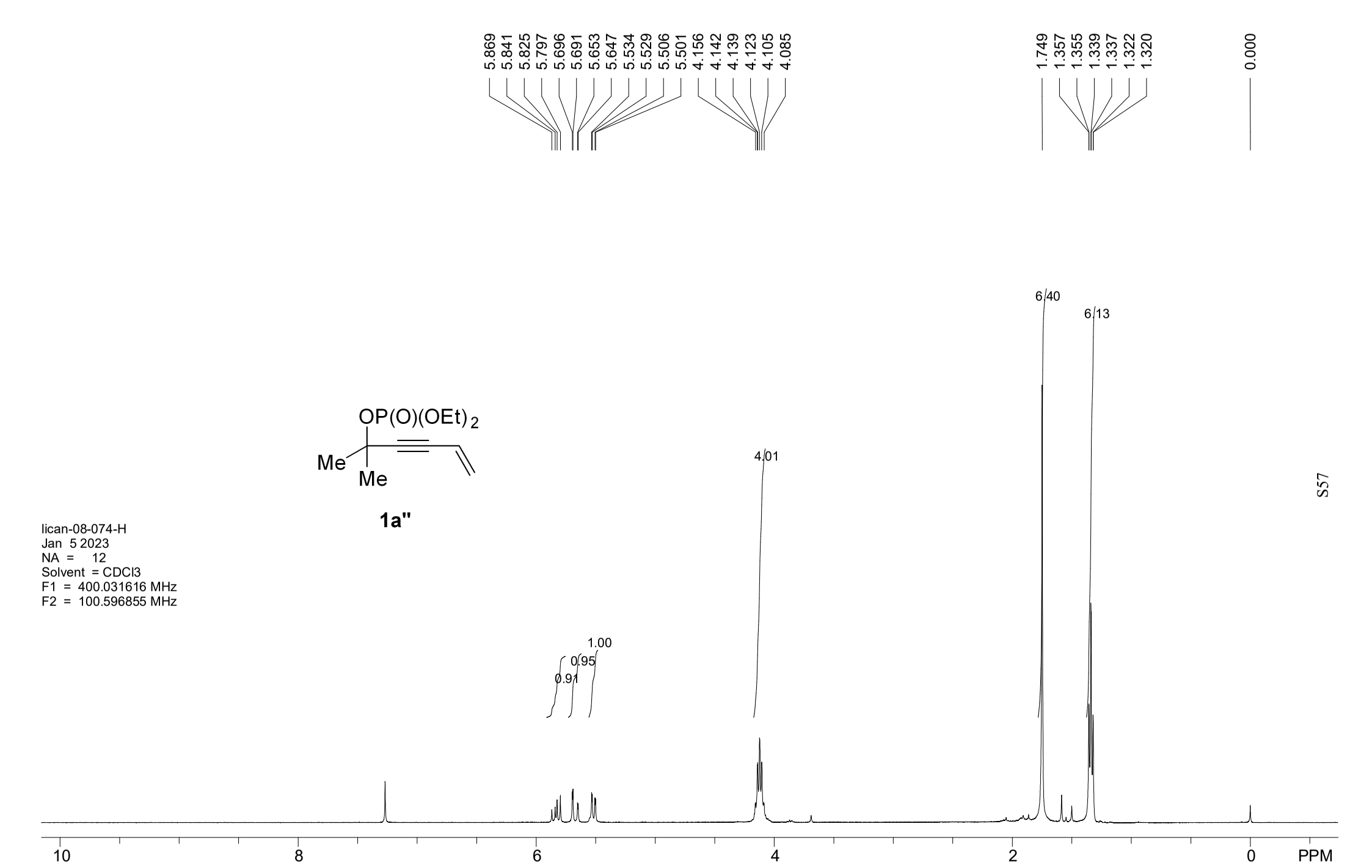


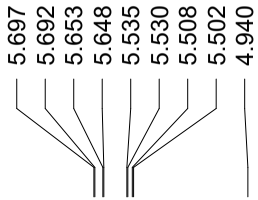
1h

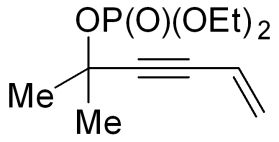
lican-04-104-H
18 Dec 2020
NA = 18
Solvent = CDCl3
F1 = 400.200012 MHz
F2 = 1.000000 MHz

S55


lican-04-104-C
18 Dec 2020
NA = 13054
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
1h
MeO
H
H
H
Me
OCO2Me
157.384
154.221
137.792
132.269
127.429
126.333
116.698
113.688
111.428
88.864
87.126
85.808
77.322
77.000
76.686
55.117
54.451
48.408
48.262
43.368
39.079
37.264
33.181
29.742
27.199
26.273
23.125
13.420
150
100
50
0
PPM

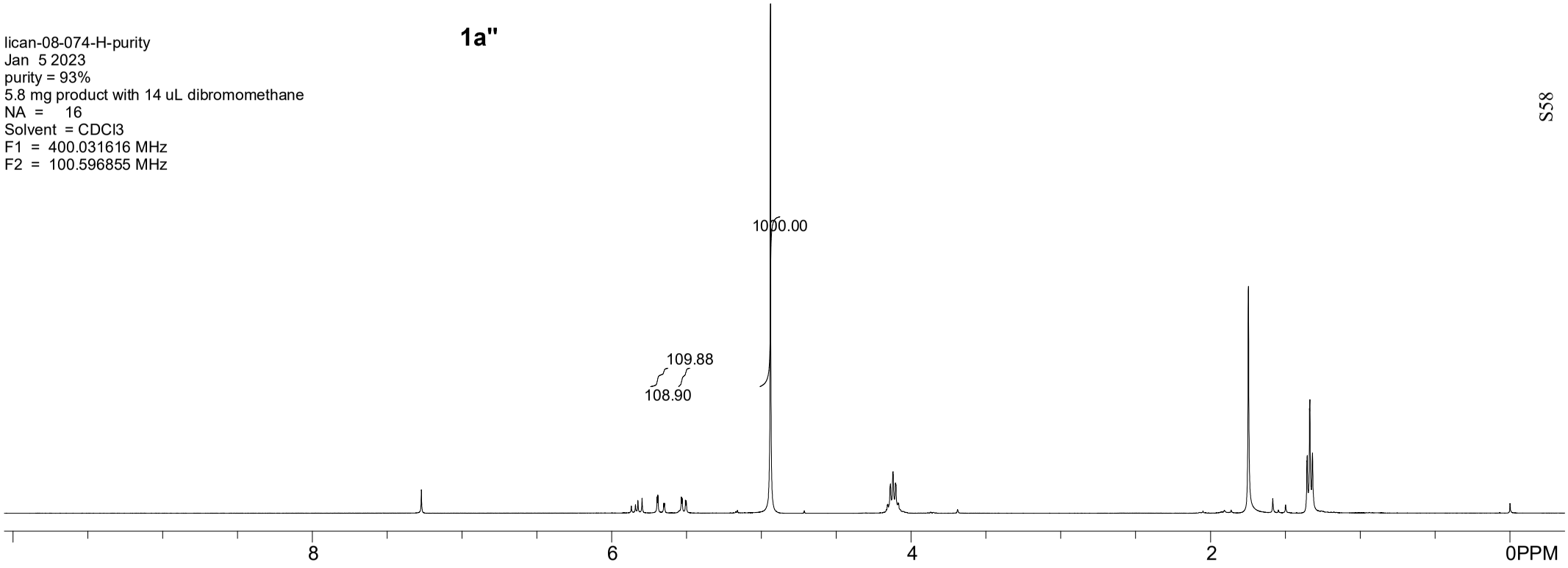

5.869
5.841
5.825
5.797
5.696
5.691
5.653
5.647
5.534
5.529
5.506
5.501
4.156
4.142
4.139
4.123
4.105
4.085
1.749
1.357
1.355
1.339
1.337
1.322
1.320
0.000
OP(O)(OEt)2
Me
Me
1a"
lican-08-074-H
Jan 5 2023
NA = 12
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
6.40
6.13
4.01
1.00
0.95
0.91
S57
10
8
6
4
2
0
PPM

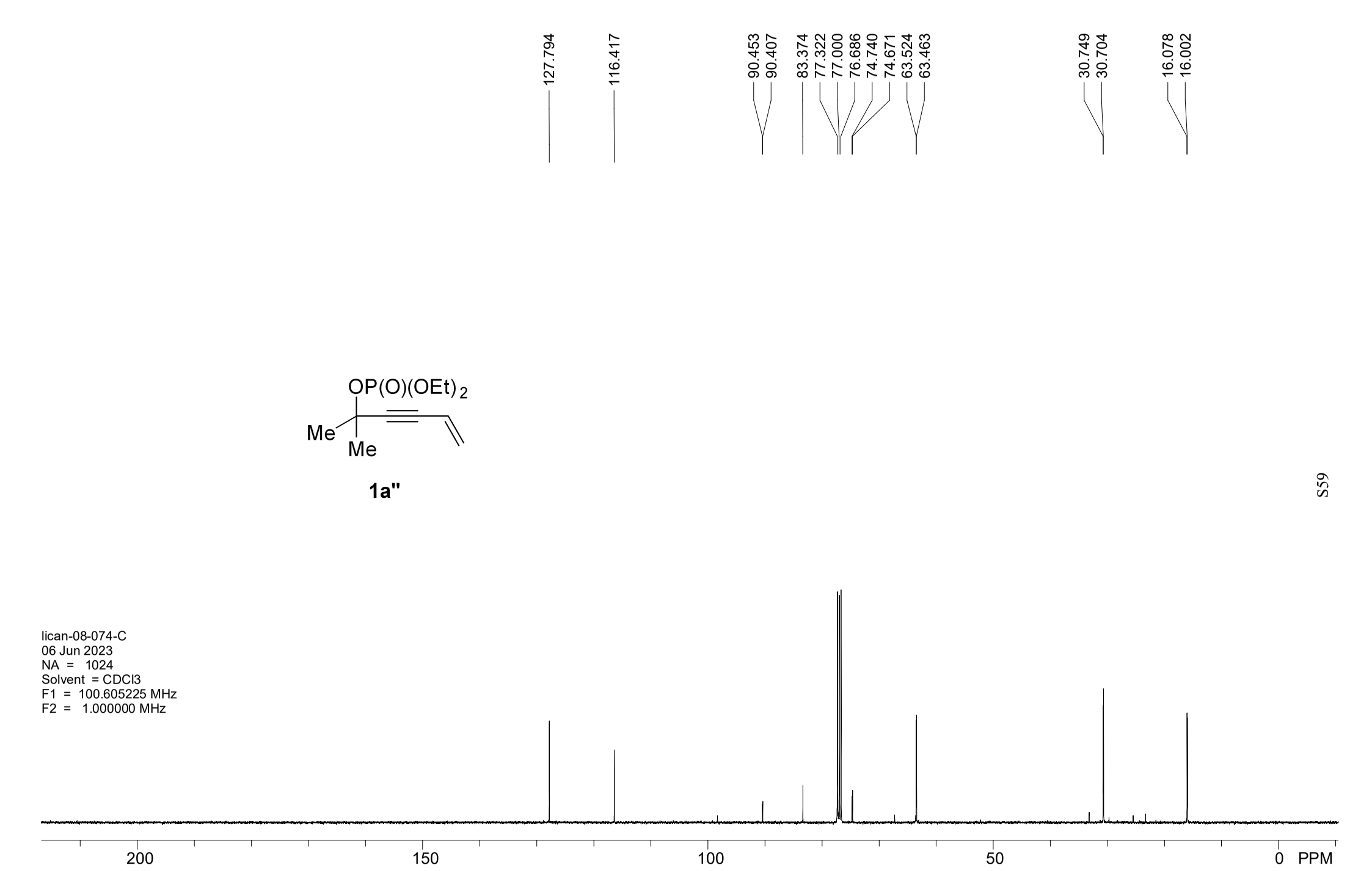


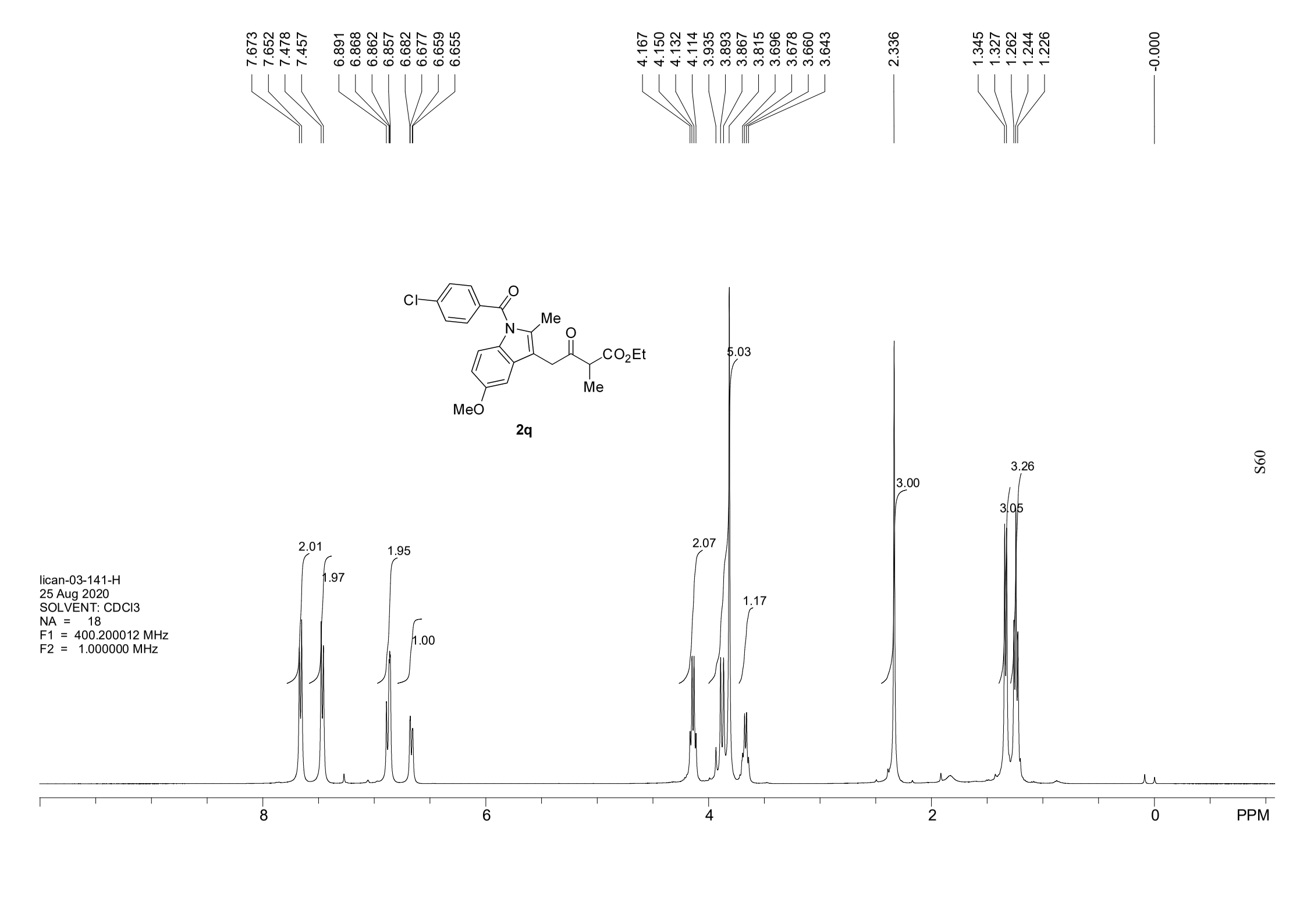


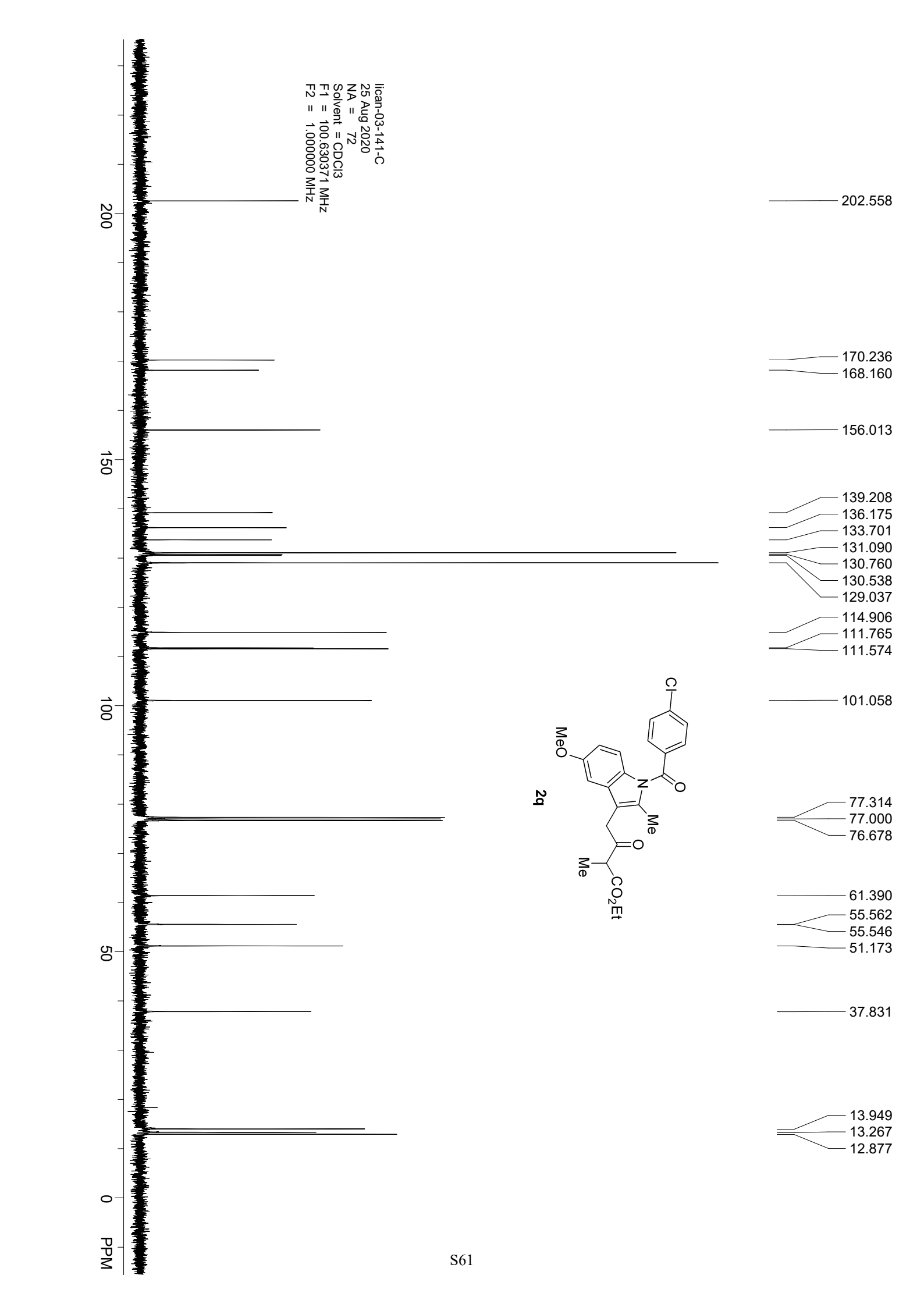
1a"

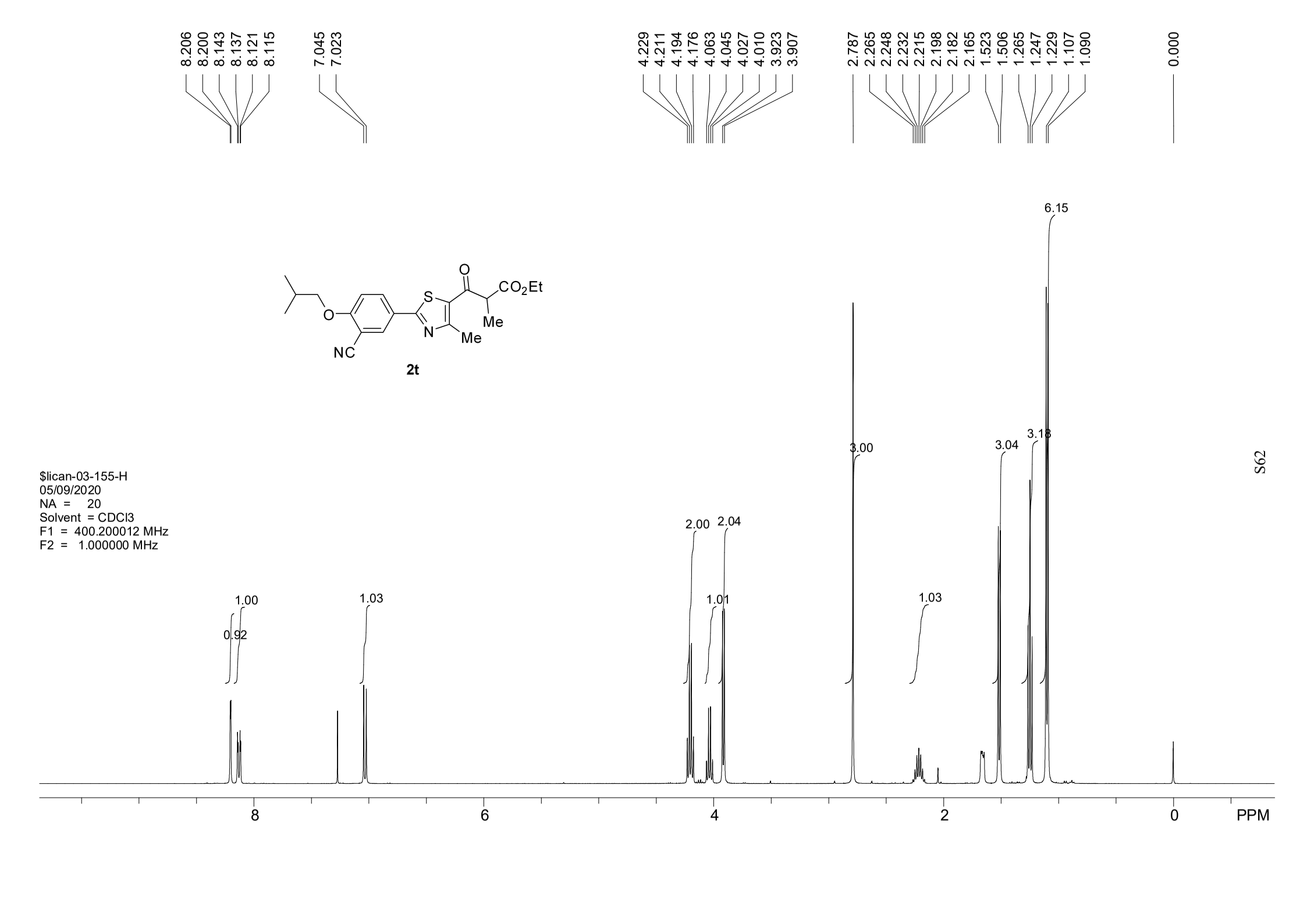
lican-08-074-H-purity
Jan 5 2023
purity = 93%
5.8 mg product with 14 uL dibromomethane
NA = 16
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz

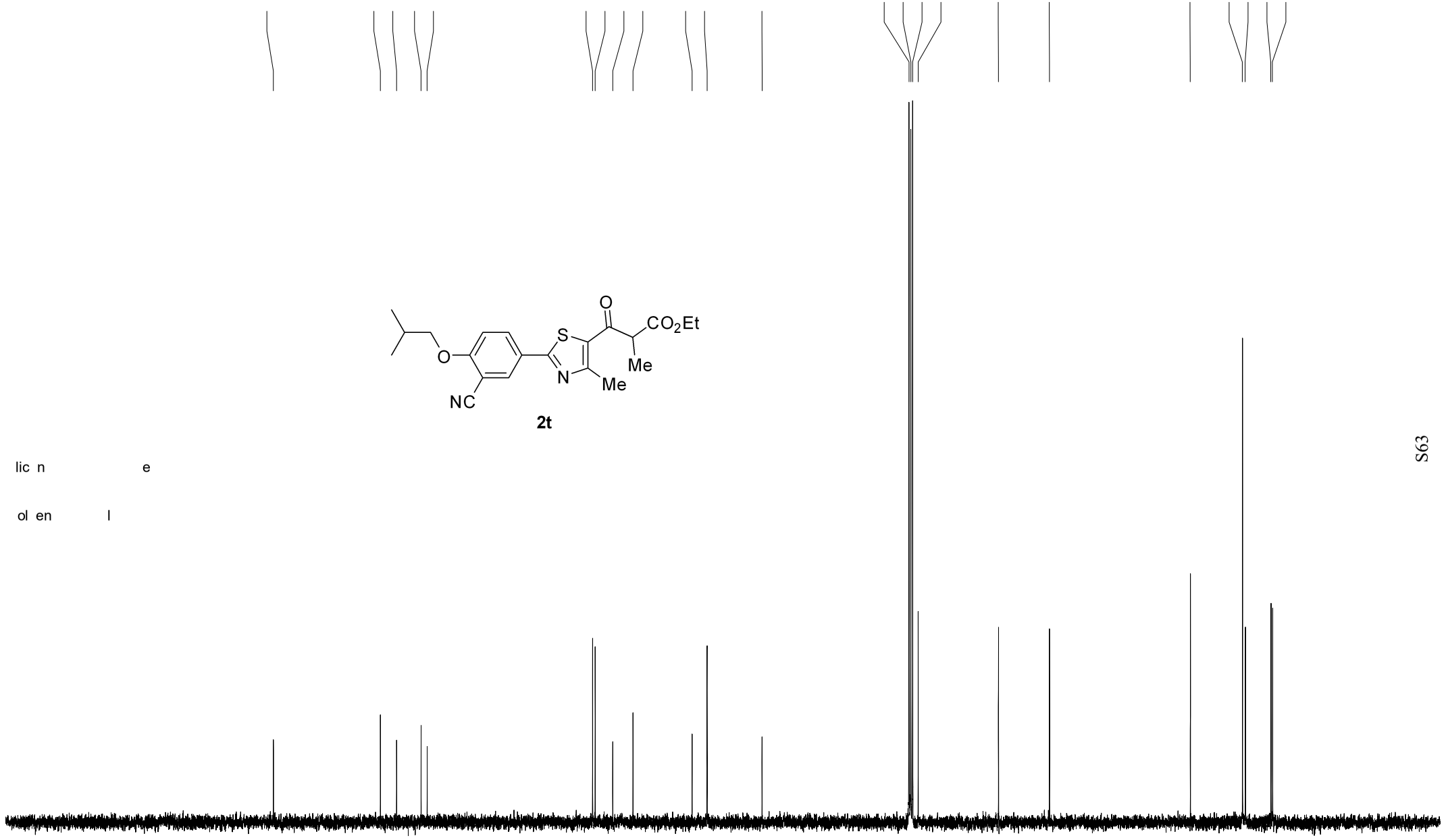



127.794
116.417
90.453
90.407
83.374
77.322
77.000
76.686
74.740
74.671
63.524
63.463
30.749
30.704
16.078
16.002
OP(O)(OEt)2
Me
Me
1a"
lican-08-074-C
06 Jun 2023
NA = 1024
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
200
150
100
50
0
PPM


7.673
7.652
7.478
7.457
6.891
6.868
6.862
6.857
6.682
6.677
6.659
6.655
4.167
4.150
4.132
4.114
3.935
3.893
3.867
3.815
3.696
3.678
3.660
3.643
2.336
1.345
1.327
1.262
1.244
1.226
-0.000
Cl
O
N
Me
O
CO2Et
Me
MeO
2q
lican-03-141-H
25 Aug 2020
SOLVENT: CDCl3
NA = 18
F1 = 400.200012 MHz
F2 = 1.000000 MHz
2.01
1.97
1.95
1.00
2.07
5.03
1.17
3.00
3.05
3.26
S60
8
6
4
2
0
PPM


lican-03-141-C
25 Aug 2020
NA = 72
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
202.558
170.236
168.160
156.013
139.208
136.175
133.701
131.090
130.760
130.538
129.037
114.906
111.765
111.574
101.058
77.314
77.000
76.678
61.390
55.562
55.546
51.173
37.831
13.949
13.267
12.877
200
150
100
50
0
PPM
Cl
MeO
N
O
Me
O
Me
CO2Et
2q

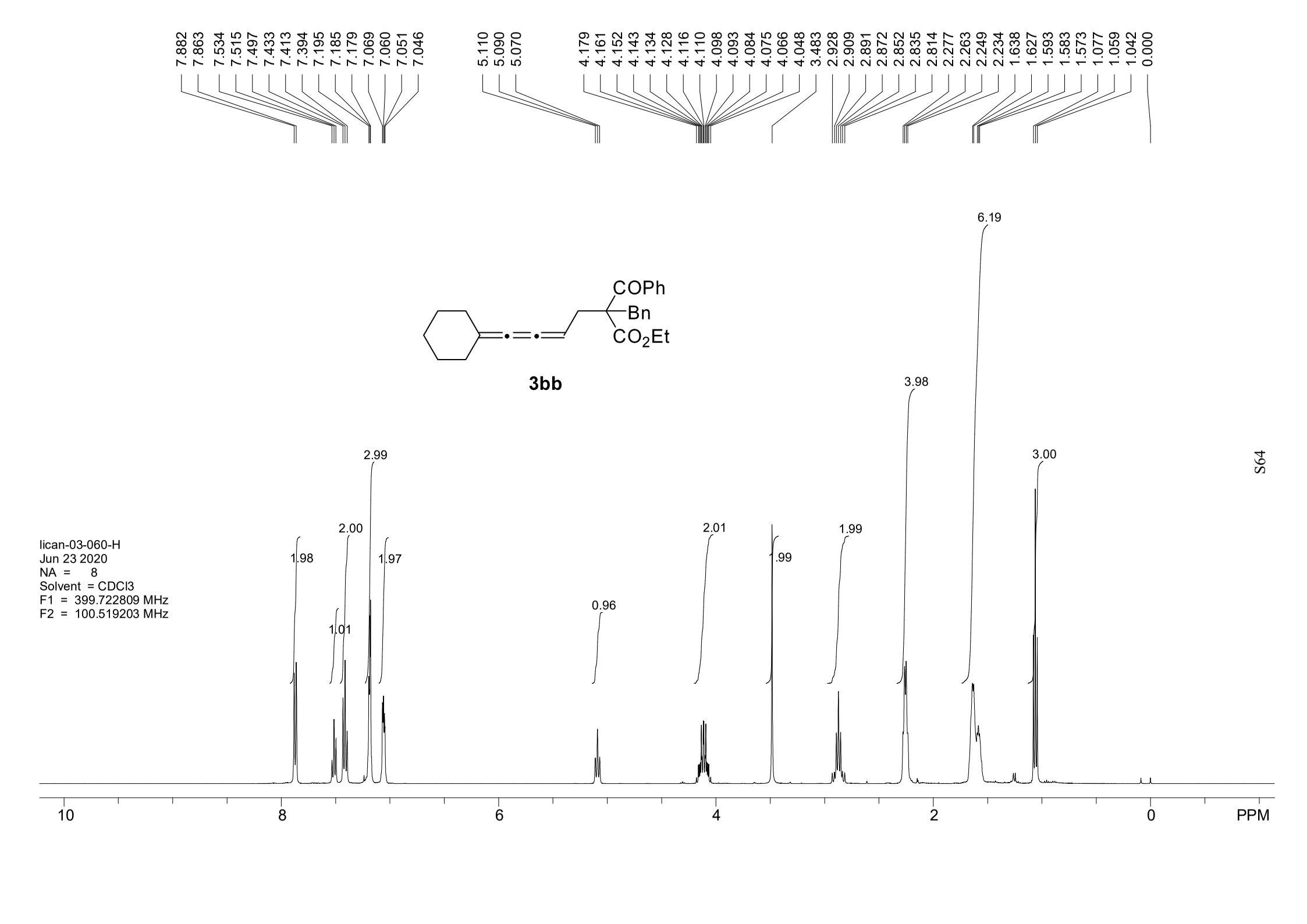

8.206
8.200
8.143
8.137
8.121
8.115
7.045
7.023
4.229
4.211
4.194
4.176
4.063
4.045
4.027
4.010
3.923
3.907
2.787
2.265
2.248
2.232
2.215
2.198
2.182
2.165
1.523
1.506
1.265
1.247
1.229
1.107
1.090
0.000
O
CO2Et
S
O
N
Me
Me
NC
2t
$lican-03-155-H
05/09/2020
NA = 20
Solvent = CDCl3
F1 = 400.200012 MHz
F2 = 1.000000 MHz
6.15
3.00
3.04
3.18
2.00
2.04
1.01
1.03
1.03
1.00
0.92
S62
8
6
4
2
0
PPM

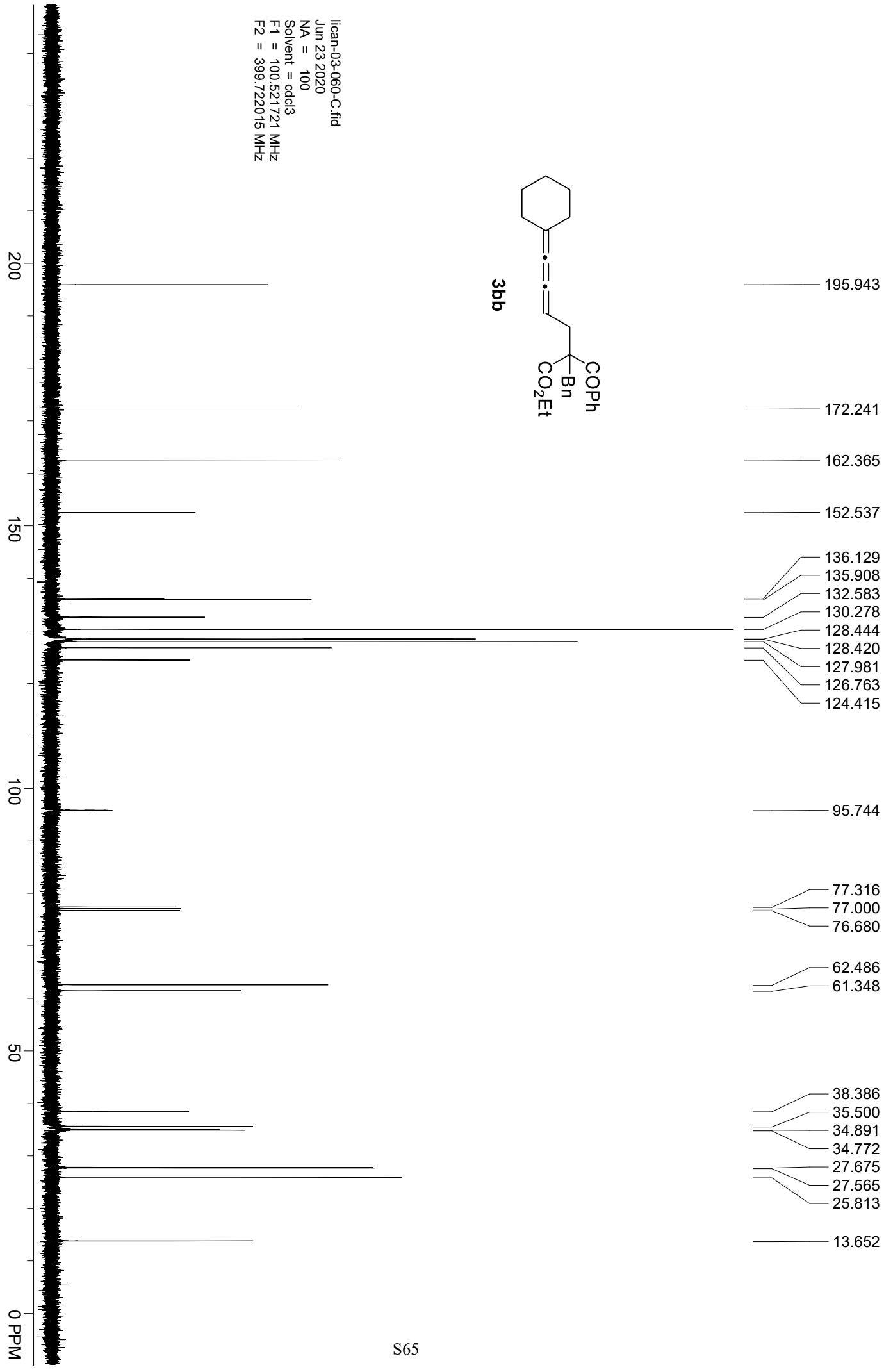


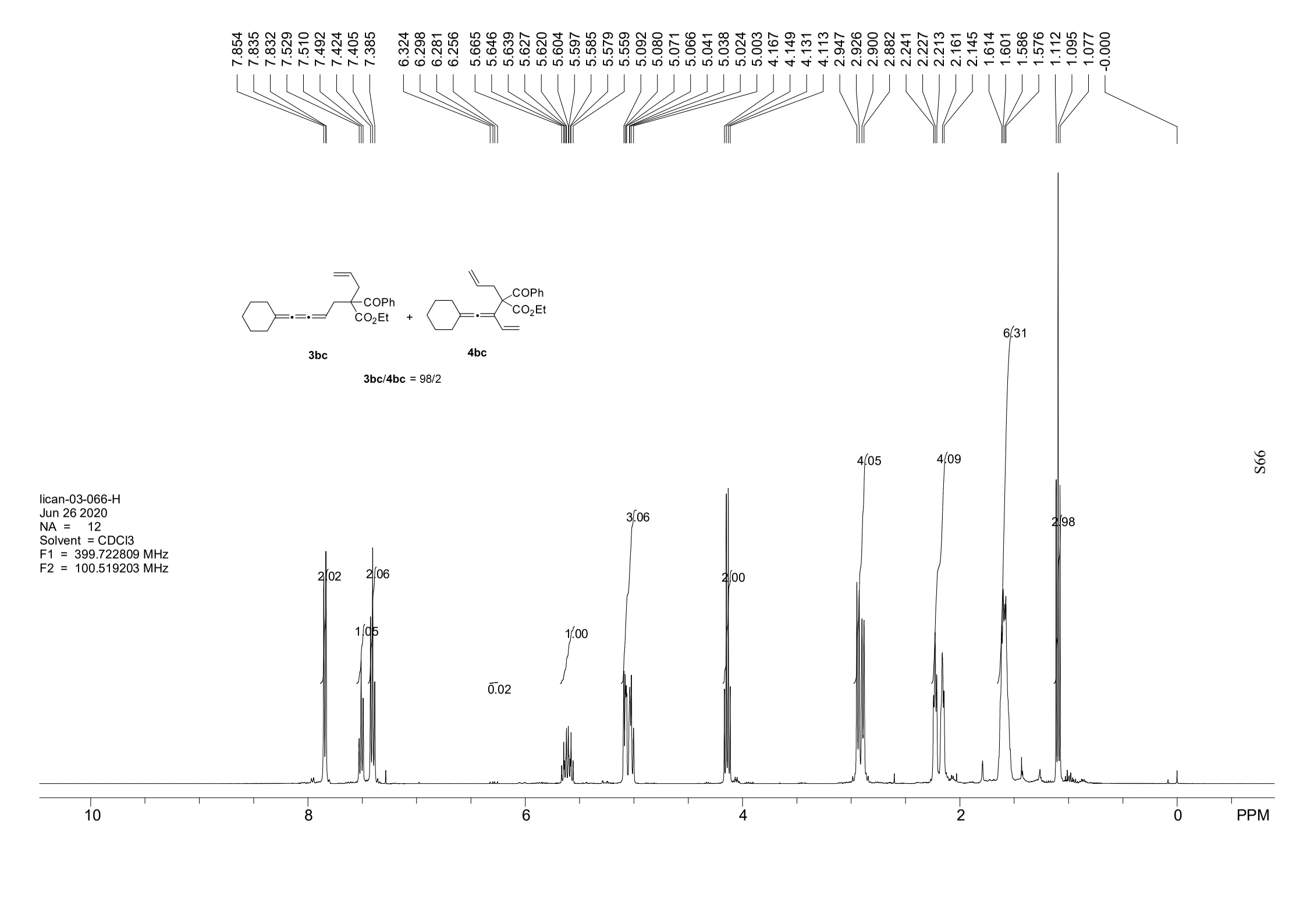
2t

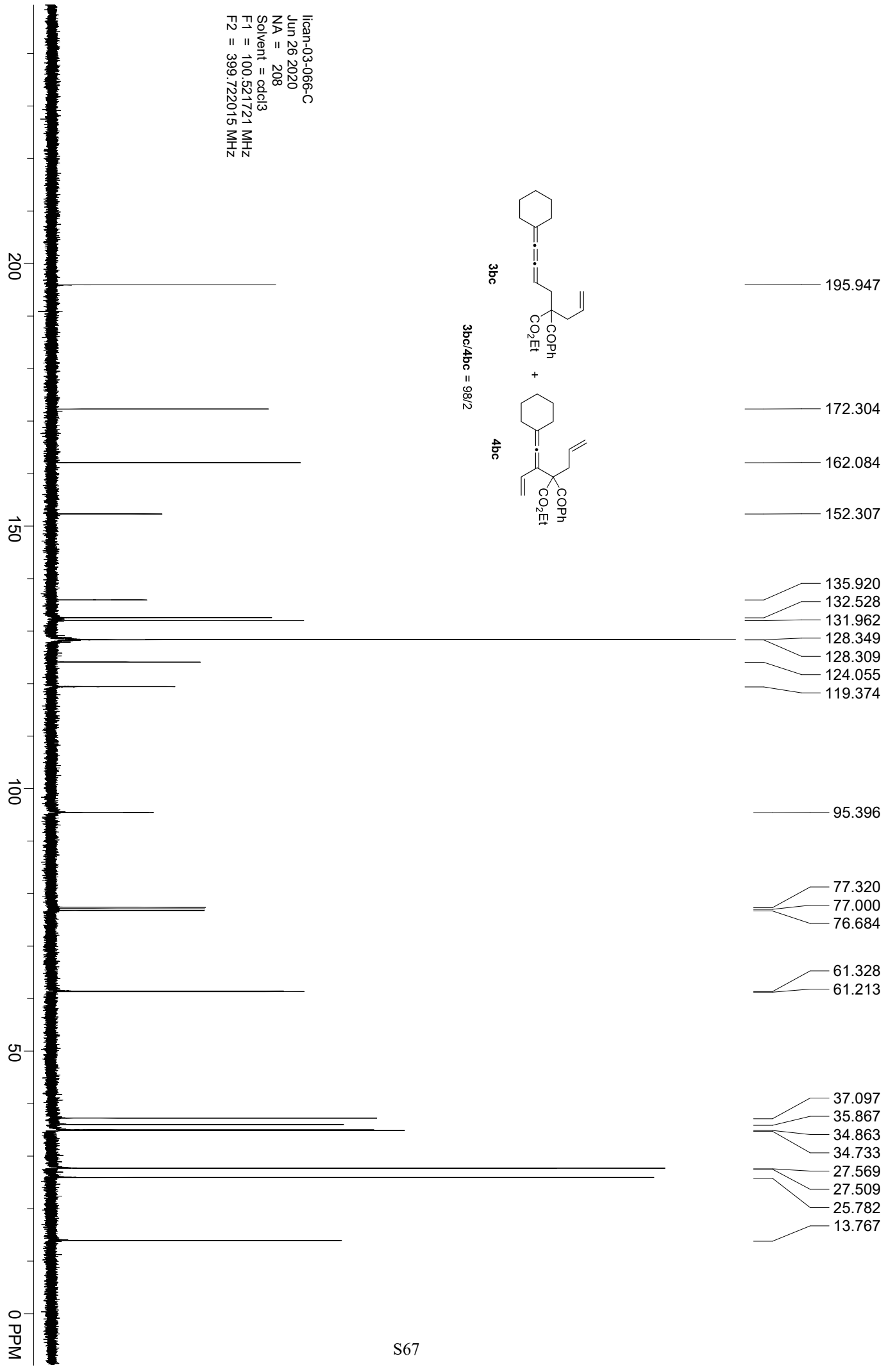
lic n e

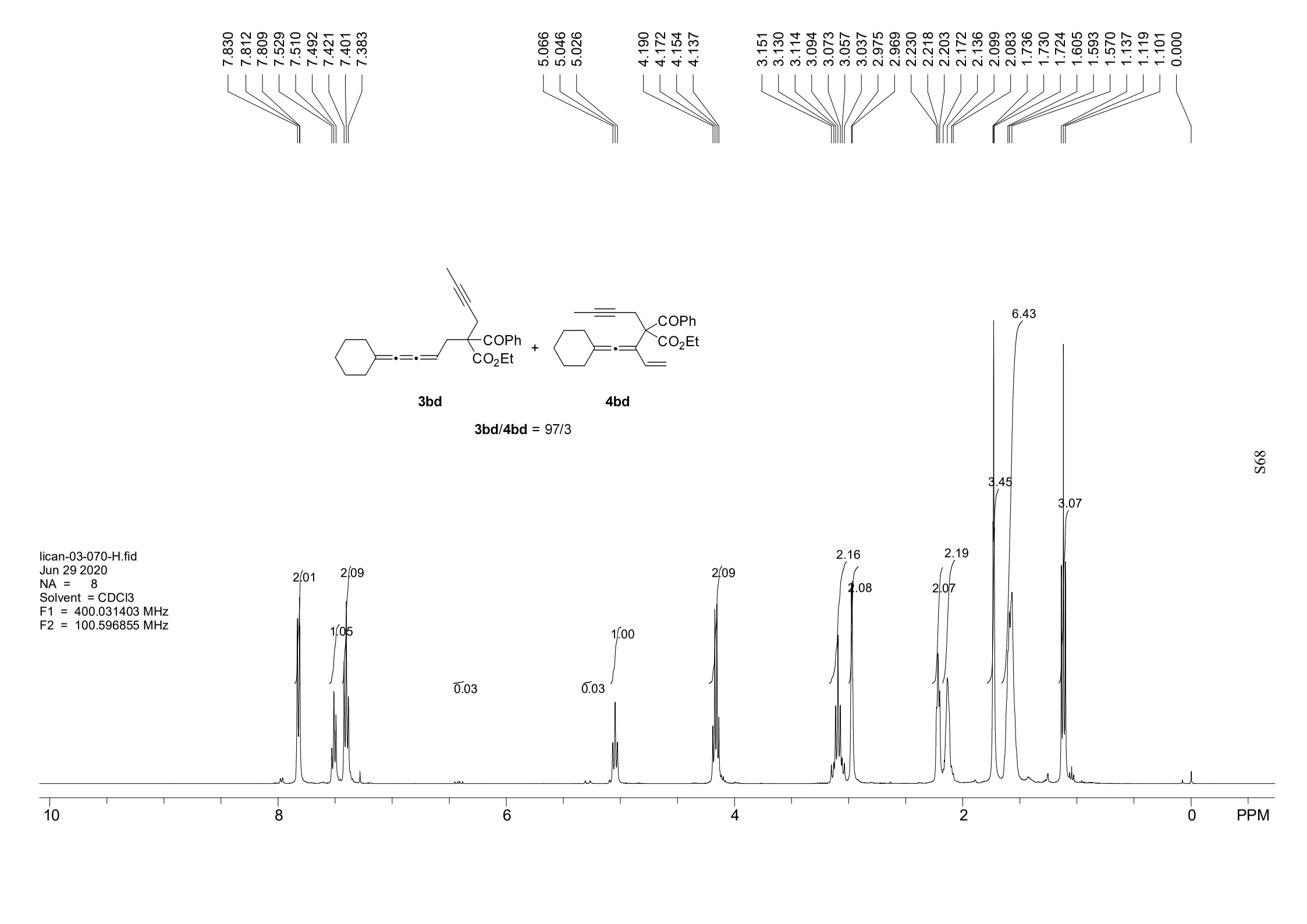
ol en l

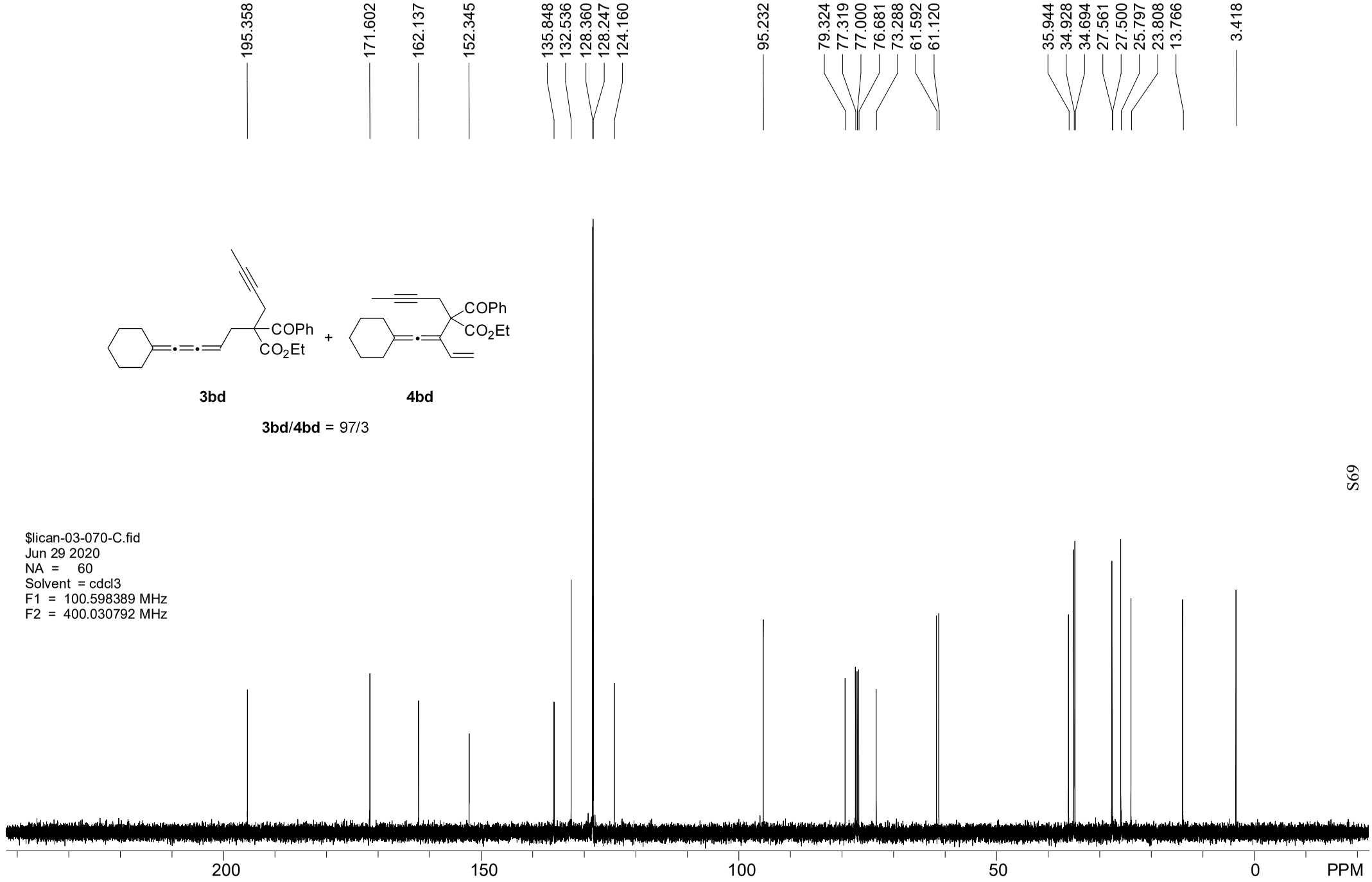

7.882
7.863
7.534
7.515
7.497
7.433
7.413
7.394
7.195
7.185
7.179
7.069
7.060
7.051
7.046
5.110
5.090
5.070
4.179
4.161
4.152
4.143
4.134
4.128
4.116
4.110
4.098
4.093
4.084
4.075
4.066
4.048
3.483
2.928
2.909
2.891
2.872
2.852
2.835
2.814
2.277
2.263
2.249
2.234
1.638
1.627
1.593
1.583
1.573
1.077
1.059
1.042
0.000
COPh
Bn
CO2Et
3bb
6.19
3.98
3.00
2.99
2.00
2.01
1.99
1.98
1.97
1.01
0.96
.99
lican-03-060-H
Jun 23 2020
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
10
8
6
4
2
0
PPM

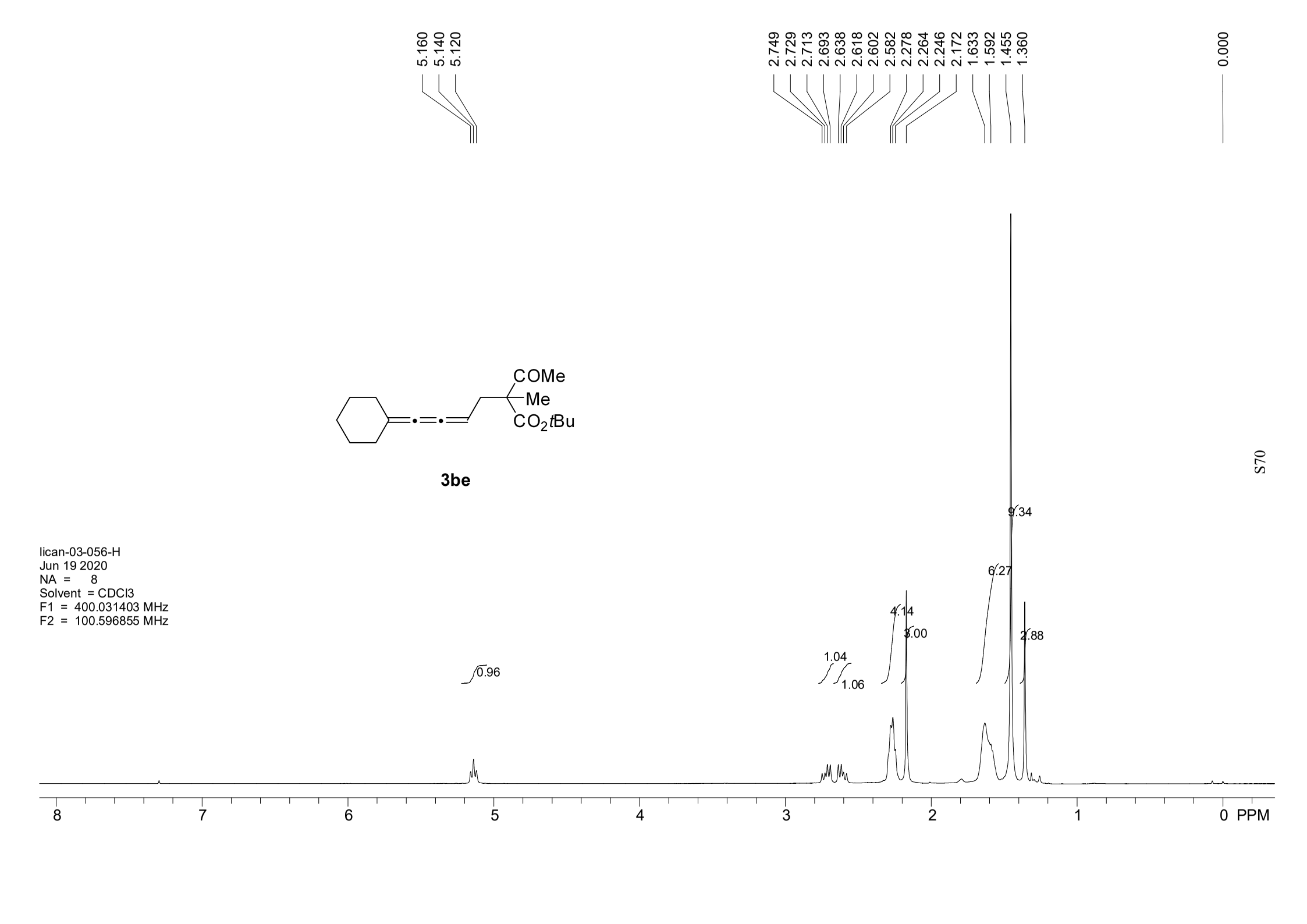

lican-03-060-C.fid
Jun 23 2020
NA = 100
Solvent = cdcl3
F1 = 100.521721 MHz
F2 = 399.722015 MHz
3bb
COPh
Bn
CO2Et
195.943
172.241
162.365
152.537
136.129
135.908
132.583
130.278
128.444
128.420
127.981
126.763
124.415
95.744
77.316
77.000
76.680
62.486
61.348
38.386
35.500
34.891
34.772
27.675
27.565
25.813
13.652
200
150
100
50
0 PPM

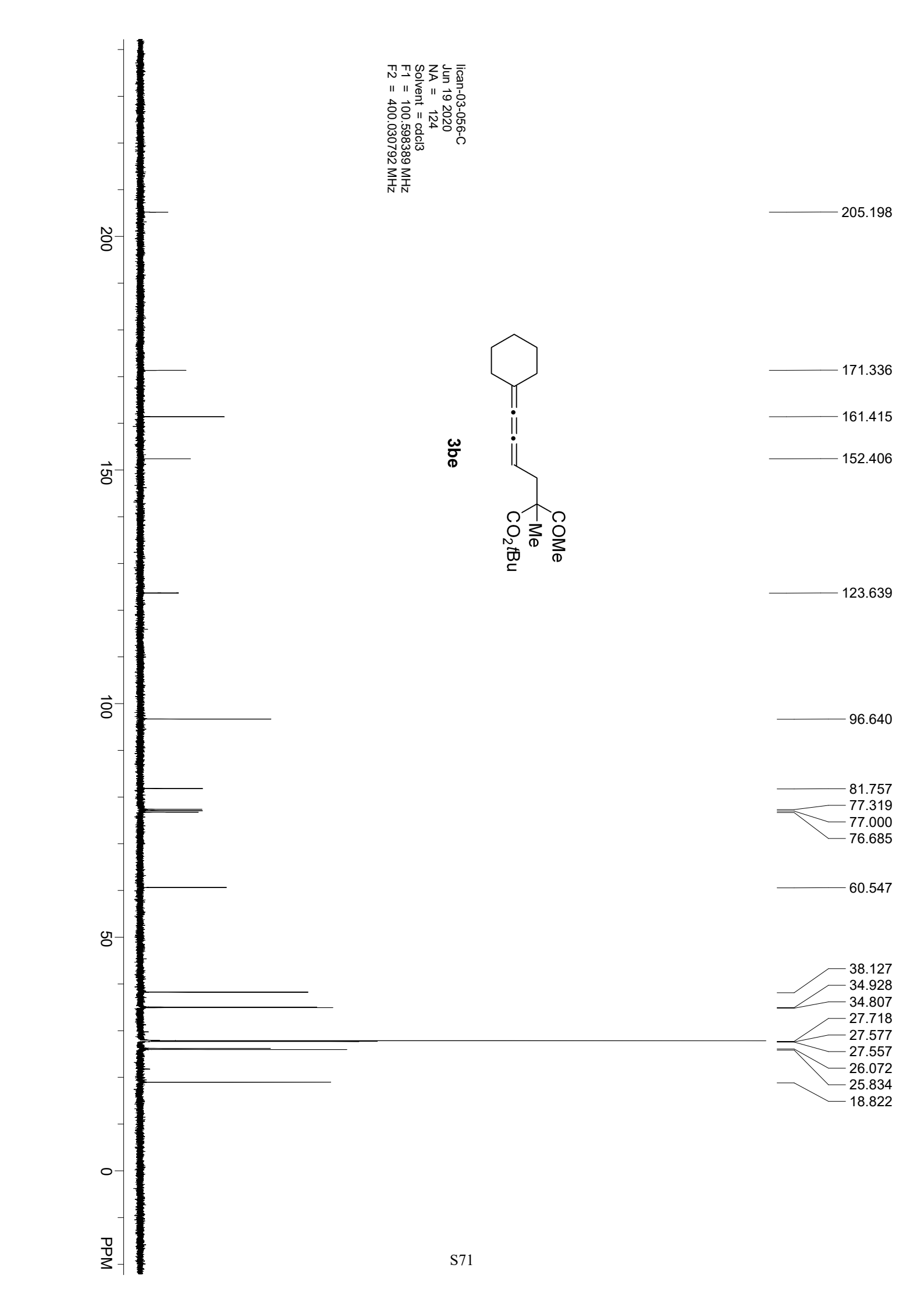

7.854
7.835
7.832
7.529
7.510
7.492
7.424
7.405
7.385
6.324
6.298
6.281
6.256
5.665
5.646
5.639
5.627
5.620
5.604
5.597
5.585
5.579
5.559
5.092
5.080
5.071
5.066
5.041
5.038
5.024
5.003
4.167
4.149
4.131
4.113
2.947
2.926
2.900
2.882
2.241
2.227
2.213
2.161
2.145
1.614
1.601
1.586
1.576
1.112
1.095
1.077
-0.000
COPh
CO2Et
+
COPh
CO2Et
3bc
4bc
3bc/4bc = 98/2
lican-03-066-H
Jun 26 2020
NA = 12
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
2.02
2.06
1.05
0.02
1.00
3.06
2.00
4.05
4.09
6.31
2.98
S66
10
8
6
4
2
0
PPM

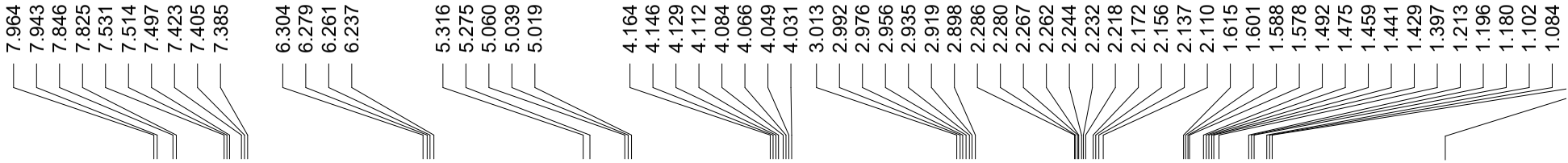

lican-03-066-C
Jun 26 2020
NA = 208
Solvent = cdcl3
F1 = 100.521721 MHz
F2 = 399.722015 MHz
3bc
3bc/4bc = 98/2
4bc
COPh
CO2Et
+
195.947
172.304
162.084
152.307
135.920
132.528
131.962
128.349
128.309
124.055
119.374
95.396
77.320
77.000
76.684
61.328
61.213
37.097
35.867
34.863
34.733
27.569
27.509
25.782
13.767
200
150
100
50
0 PPM

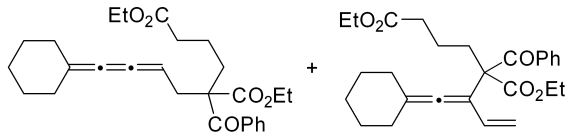

7.830
7.812
7.809
7.529
7.510
7.492
7.421
7.401
7.383
5.066
5.046
5.026
4.190
4.172
4.154
4.137
3.151
3.130
3.114
3.094
3.073
3.057
3.037
2.975
2.969
2.230
2.218
2.203
2.172
2.136
2.099
2.083
1.736
1.730
1.724
1.605
1.593
1.570
1.137
1.119
1.101
0.000
COPh
CO2Et
+
COPh
CO2Et
3bd
4bd
3bd/4bd = 97/3
S68
lican-03-070-H.fid
Jun 29 2020
NA = 8
Solvent = CDCl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz
2.01
2.09
1.05
0.03
0.03
1.00
2.09
2.16
2.08
2.19
2.07
6.43
3.45
3.07
10
8
6
4
2
0
PPM


195.358
171.602
162.137
152.345
135.848
132.536
128.360
128.247
124.160
95.232
79.324
77.319
77.000
76.681
73.288
61.592
61.120
35.944
34.928
34.694
27.561
27.500
25.797
23.808
13.766
3.418
COPh
CO2Et
+
COPh
CO2Et
3bd
4bd
3bd/4bd = 97/3
$lican-03-070-C.fid
Jun 29 2020
NA = 60
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
200
150
100
50
0
PPM


5.160
5.140
5.120
2.749
2.729
2.713
2.693
2.638
2.618
2.602
2.582
2.278
2.264
2.246
2.172
1.633
1.592
1.455
1.360
0.000
COMe
Me
CO2tBu
3be
S70
lican-03-056-H
Jun 19 2020
NA = 8
Solvent = CDCl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz
0.96
1.04
1.06
4.14
3.00
6.27
9.34
2.88
8
7
6
5
4
3
2
1
0 PPM

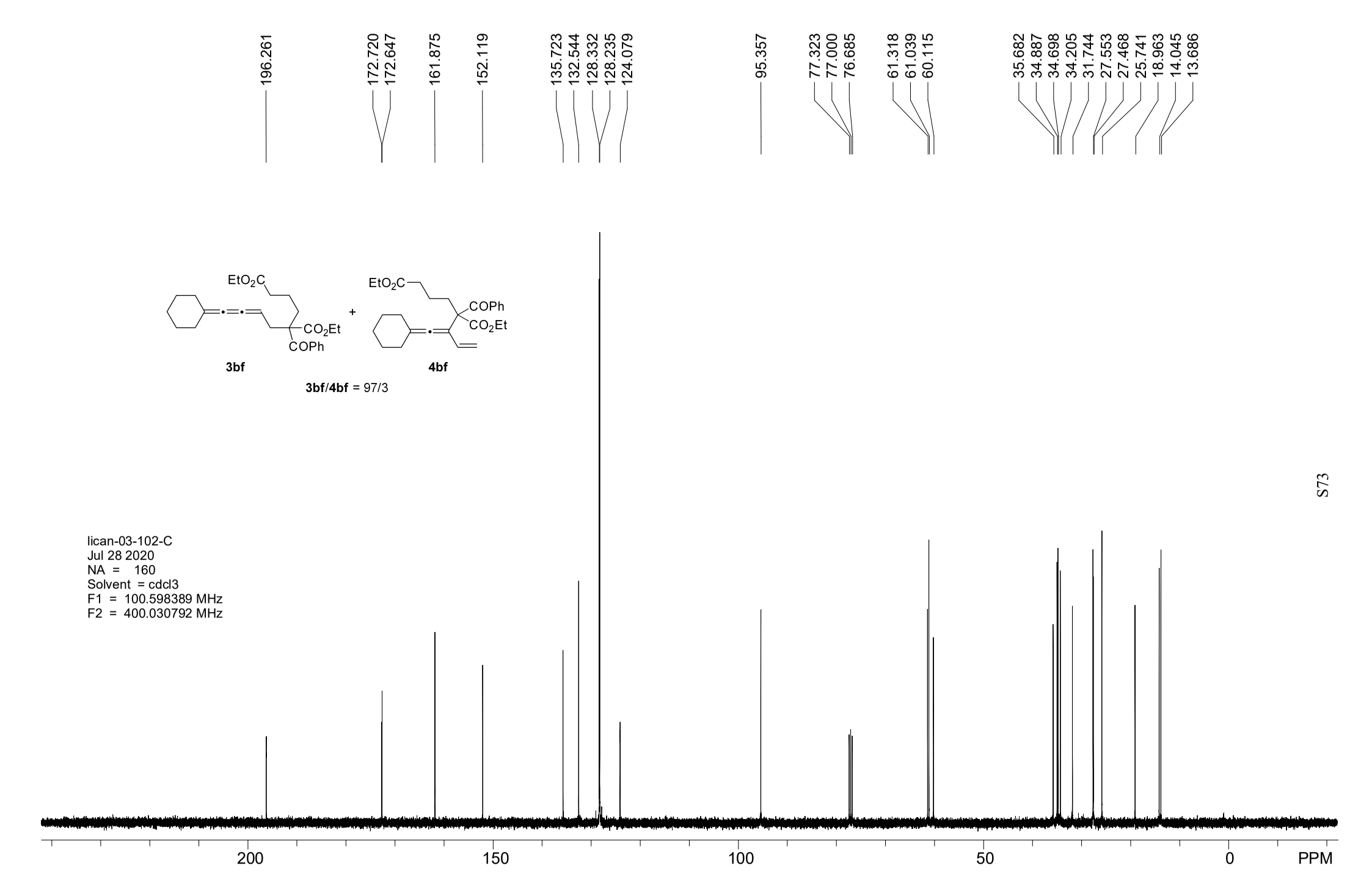

lican-03-056-C
Jun 19 2020
NA = 124
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
3be
COMe
Me
CO2tBu
205.198
171.336
161.415
152.406
123.639
96.640
81.757
77.319
77.000
76.685
60.547
38.127
34.928
34.807
27.718
27.577
27.557
26.072
25.834
18.822
200
150
100
50
0
PPM

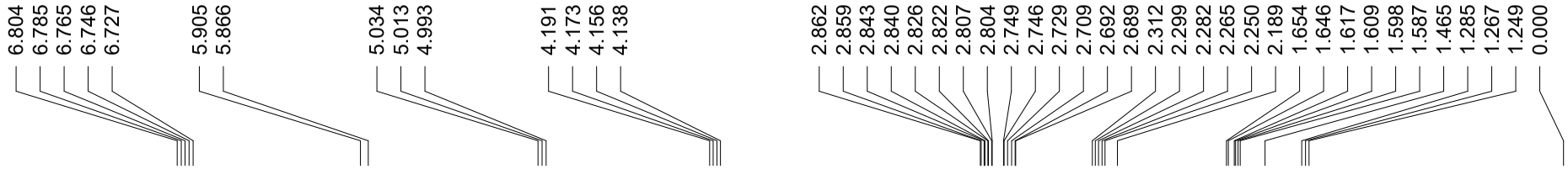


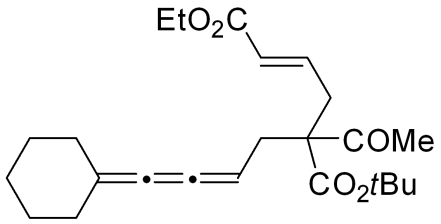


3bf **4bf**

3bf/**4bf** = 97/3

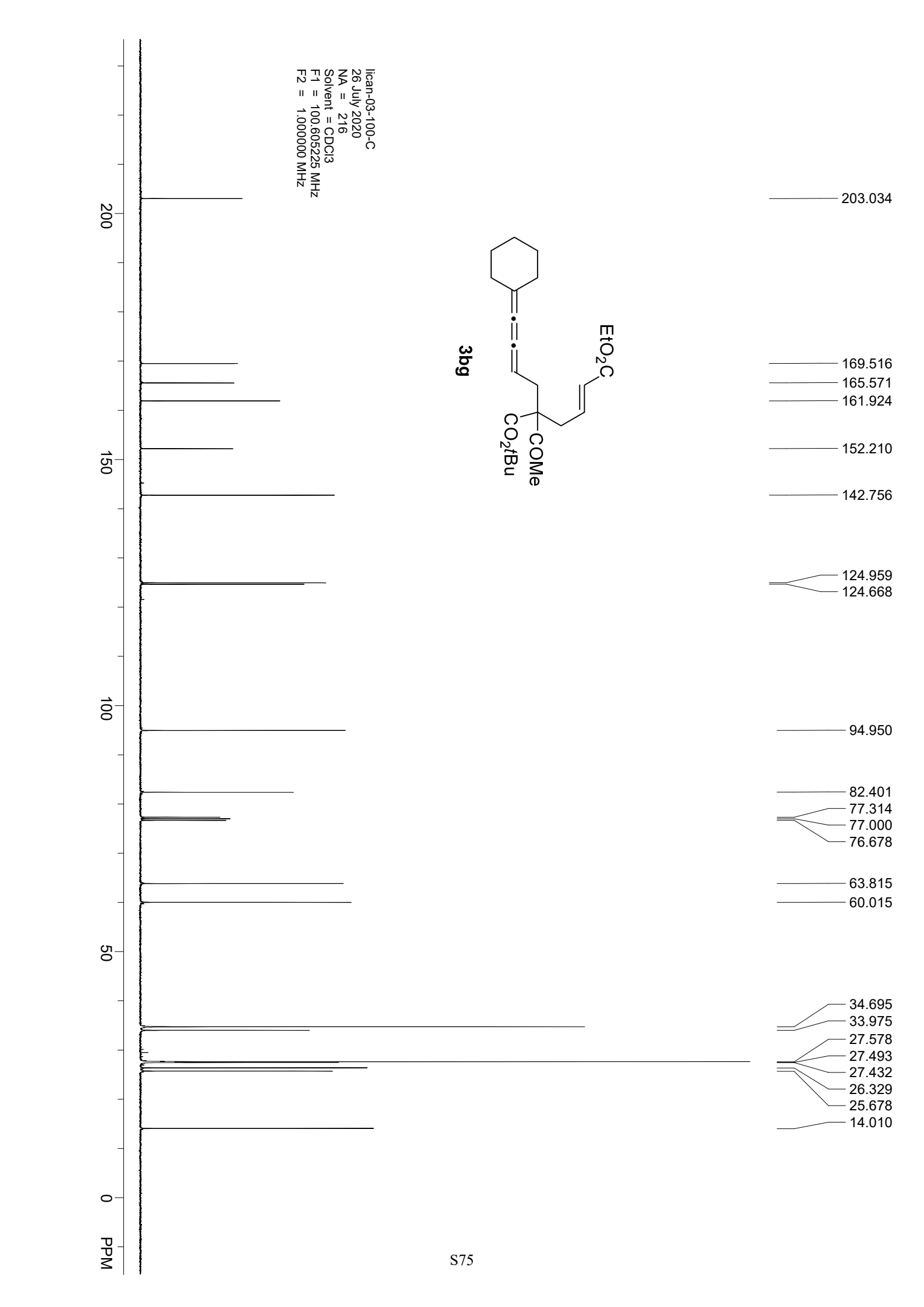

196.261
172.720
172.647
161.875
152.119
135.723
132.544
128.332
128.235
124.079
95.357
77.323
77.000
76.685
61.318
61.039
60.115
35.682
34.887
34.698
34.205
31.744
27.553
27.468
25.741
18.963
14.045
13.686
EtO2C
CO2Et
COPh
3bf
+
EtO2C
COPh
CO2Et
4bf
3bf/4bf = 97/3
lican-03-102-C
Jul 28 2020
NA = 160
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
200
150
100
50
0
PPM

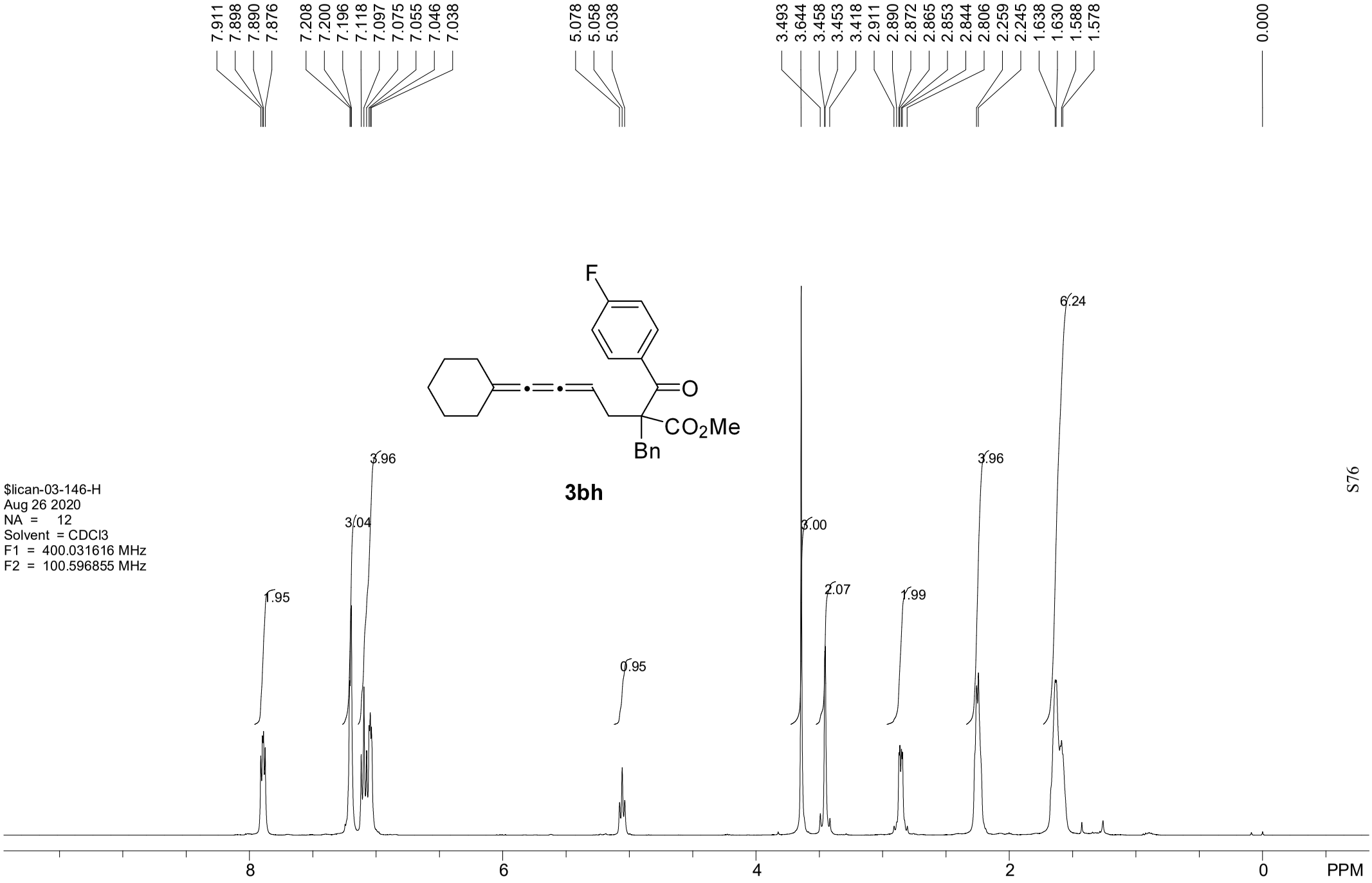


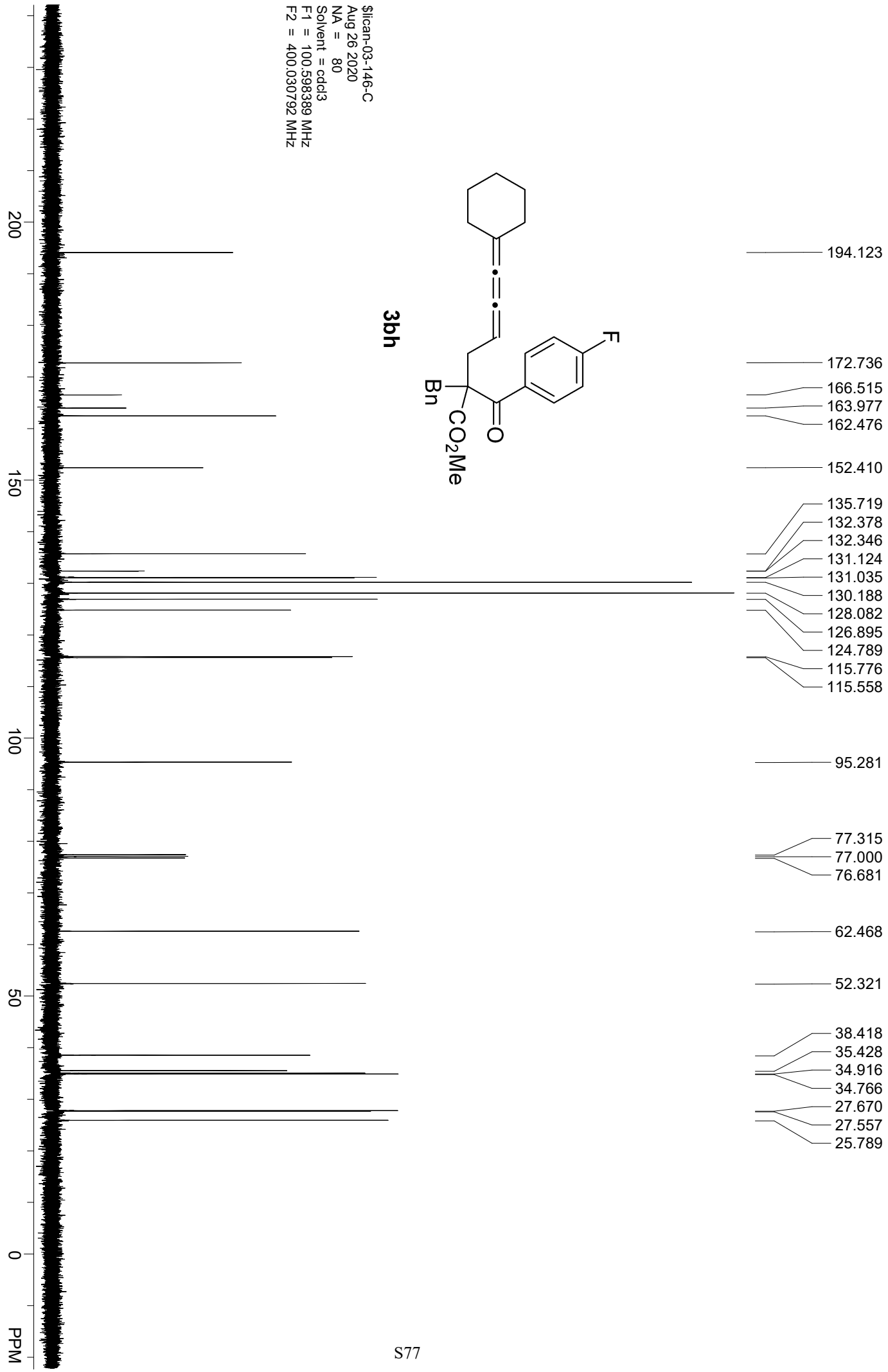


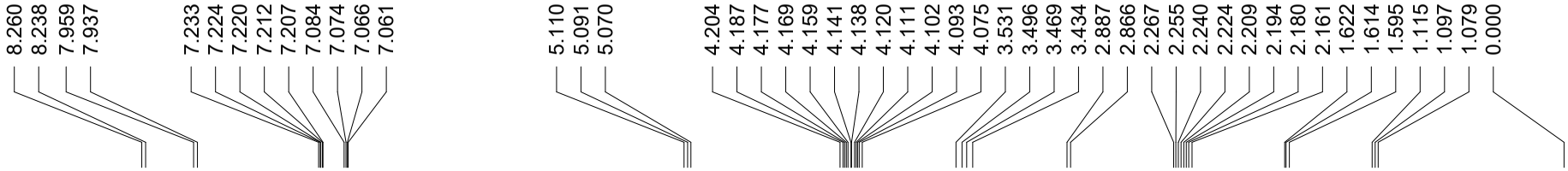
3bg

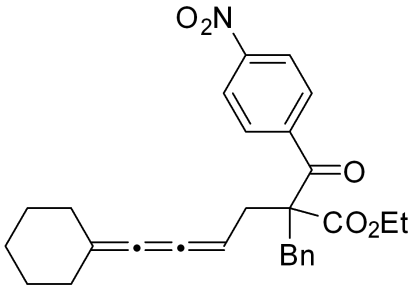
lican-03-100-H
26 July 2020
NA = 16
Solvent = CDCl3
F1 = 400.100006 MHz
F2 = 1.000000 MHz


lican-03-100-C
26 July 2020
NA = 216
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
3bg
EtO2C
COMe
CO2tBu
203.034
169.516
165.571
161.924
152.210
142.756
124.959
124.668
94.950
82.401
77.314
77.000
76.678
63.815
60.015
34.695
33.975
27.578
27.493
27.432
26.329
25.678
14.010
200
150
100
50
0
PPM

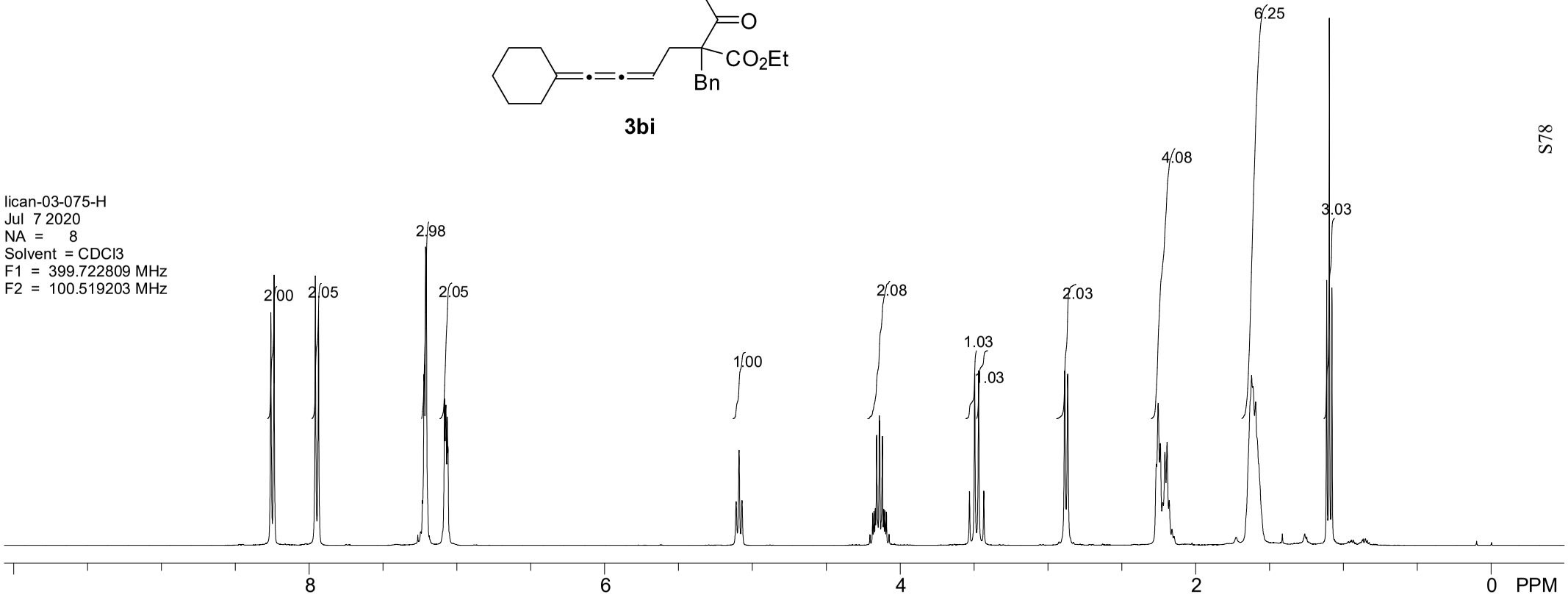

7.911
7.898
7.890
7.876
7.208
7.200
7.196
7.118
7.097
7.075
7.055
7.046
7.038
5.078
5.058
5.038
3.493
3.644
3.458
3.453
3.418
2.911
2.890
2.872
2.865
2.853
2.844
2.806
2.259
2.245
1.638
1.630
1.588
1.578
0.000
F
O
CO2Me
Bn
3bh
$lican-03-146-H
Aug 26 2020
NA = 12
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
1.95
3.04
3.96
0.95
3.00
2.07
1.99
3.96
6.24
8
6
4
2
0
PPM

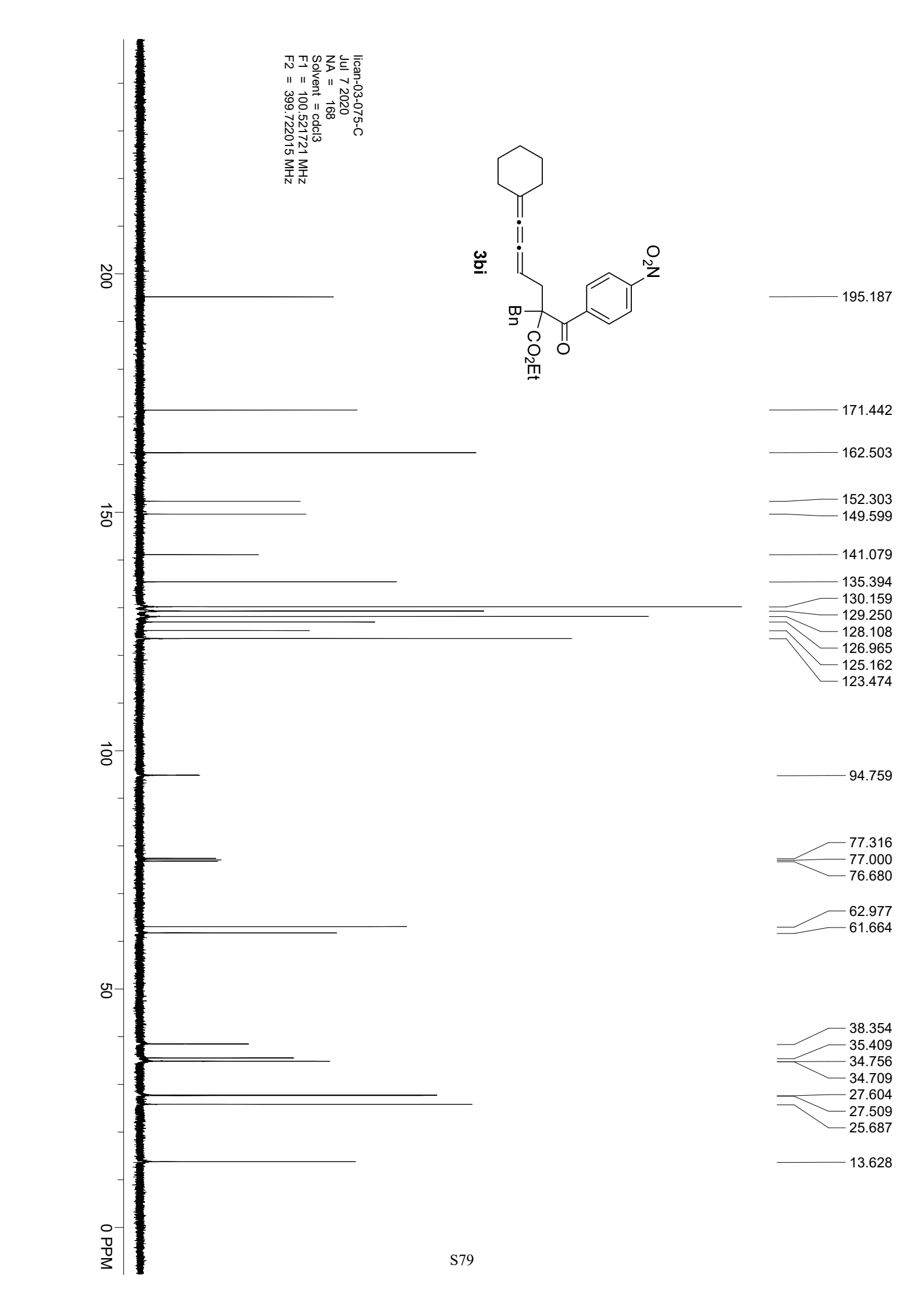

$lican-03-146-C
Aug 26 2020
NA = 80
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
3bh
Bn
CO2Me
O
F
194.123
172.736
166.515
163.977
162.476
152.410
135.719
132.378
132.346
131.124
131.035
130.188
128.082
126.895
124.789
115.776
115.558
95.281
77.315
77.000
76.681
62.468
52.321
38.418
35.428
34.916
34.766
27.670
27.557
25.789
200
150
100
50
0
PPM

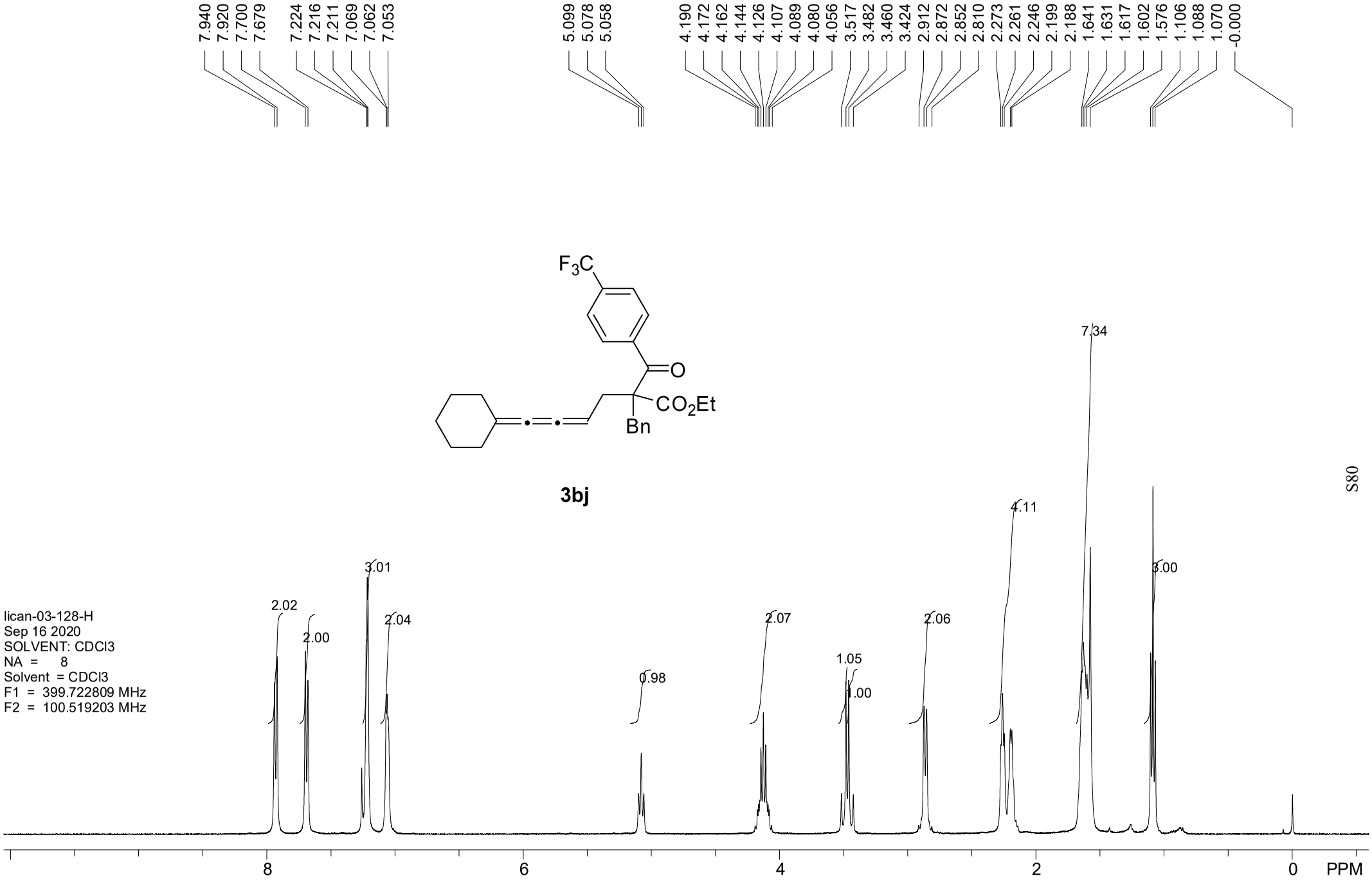

8.260
8.238
7.959
7.937
7.233
7.224
7.220
7.212
7.207
7.084
7.074
7.066
7.061
5.110
5.091
5.070
4.204
4.187
4.177
4.169
4.159
4.141
4.138
4.120
4.111
4.102
4.093
4.075
3.531
3.496
3.469
3.434
2.887
2.866
2.267
2.255
2.240
2.224
2.209
2.194
2.180
2.161
1.622
1.614
1.595
1.115
1.097
1.079
0.000

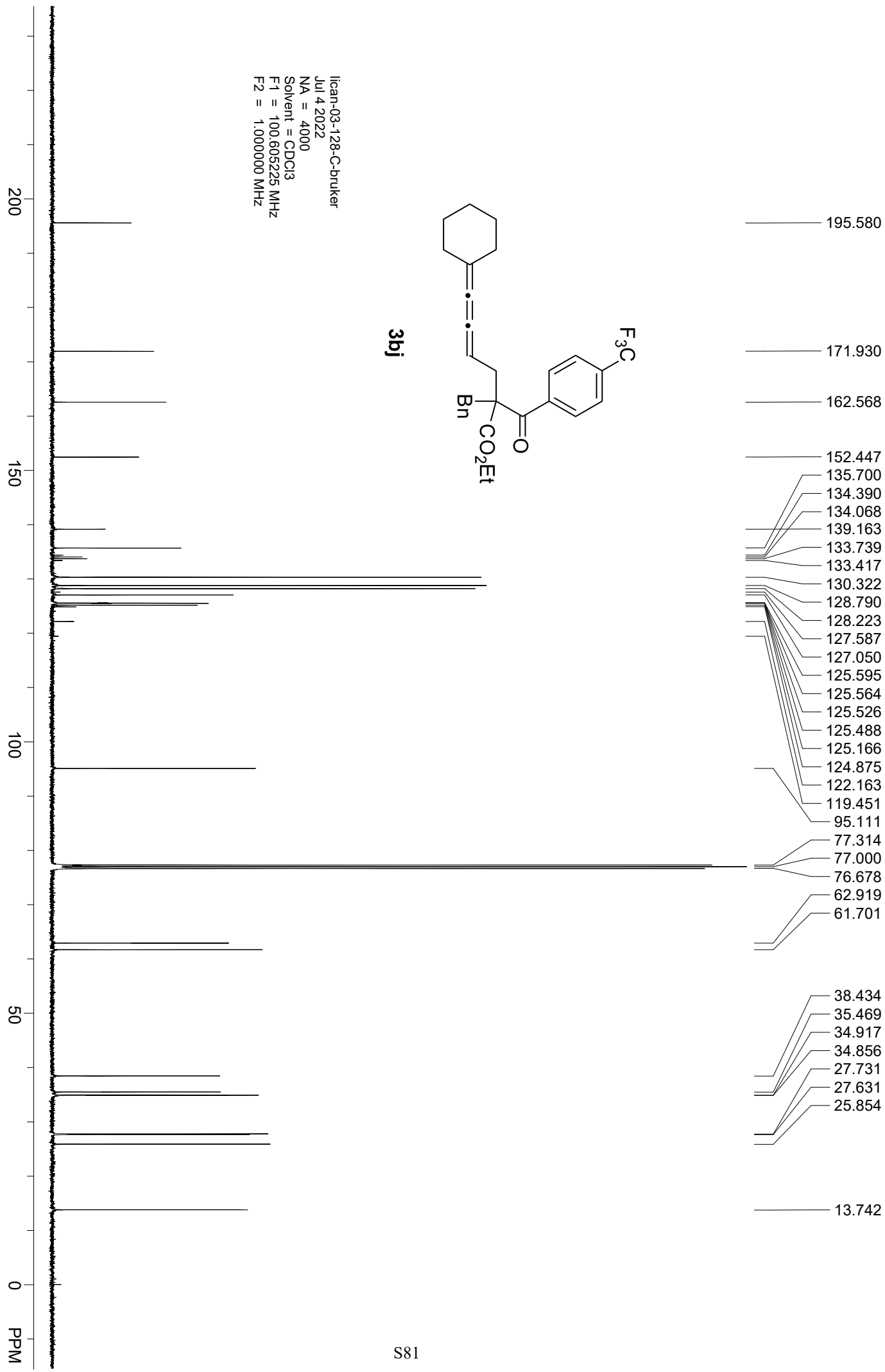

O2N
O
CO2Et
Bn

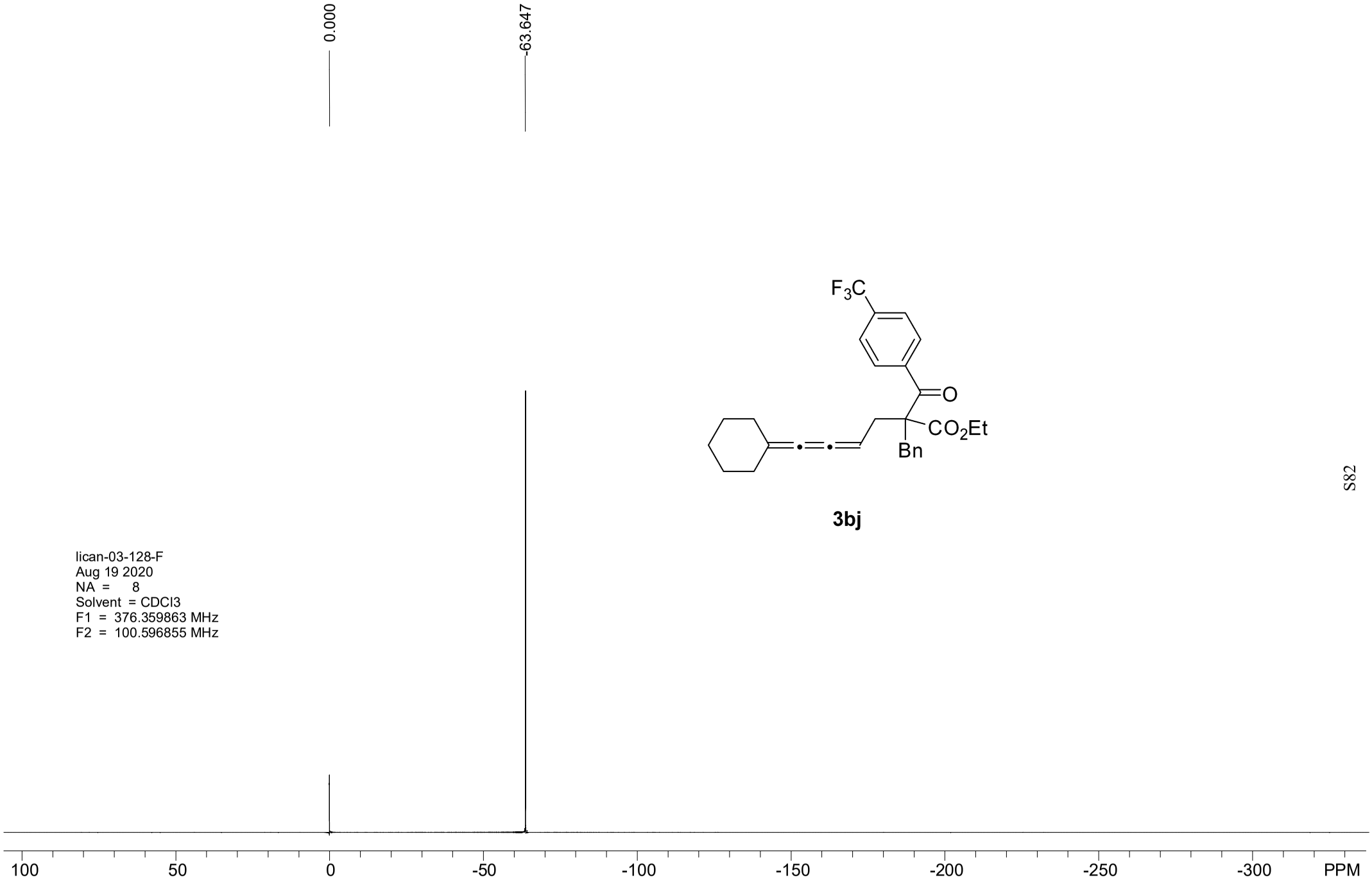
3bi

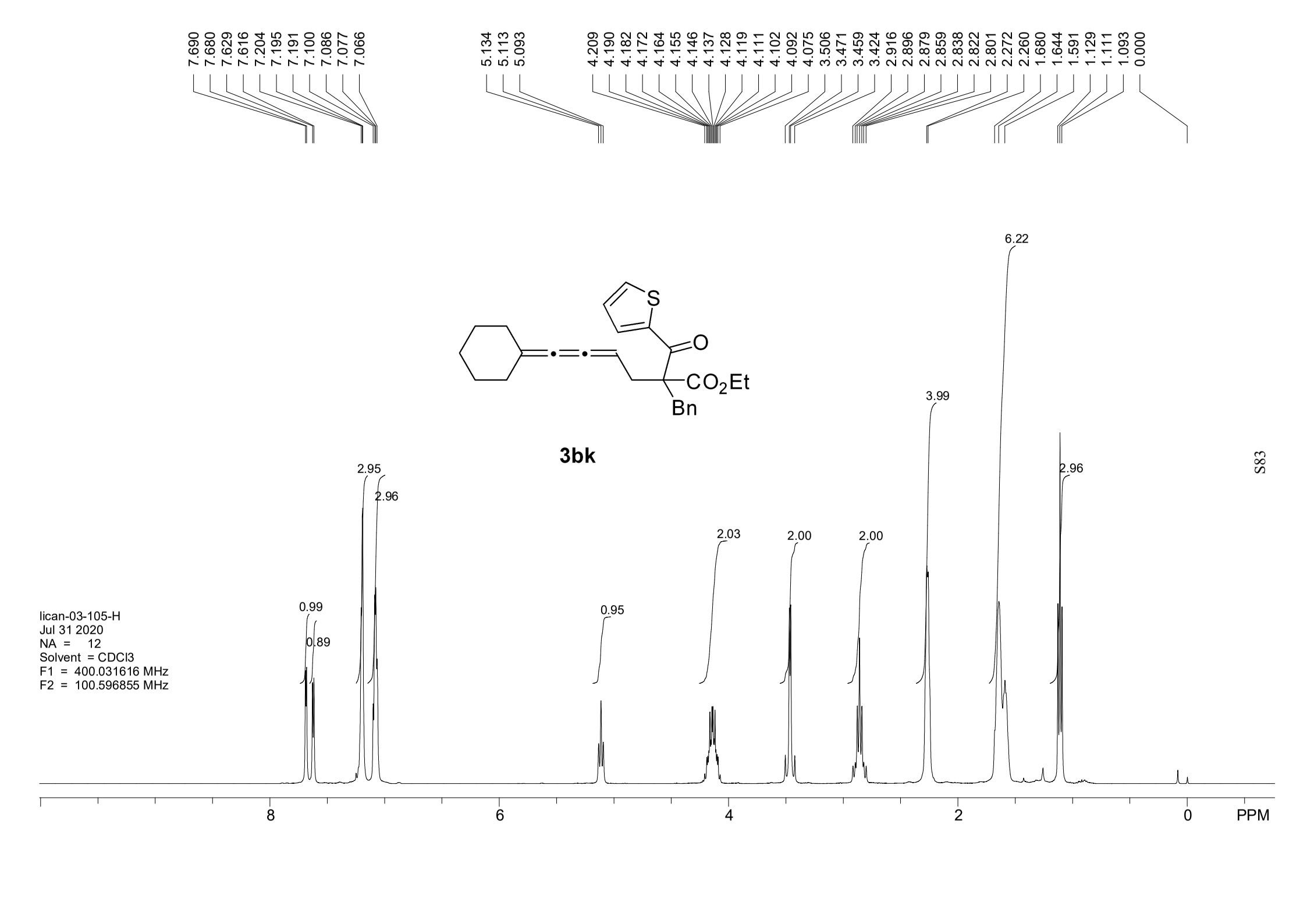

lican-03-075-H
Jul 7 2020
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
2.00
2.05
2.98
2.05
1.00
2.08
1.03
1.03
2.03
4.08
6.25
3.03
8
6
4
2
0
PPM

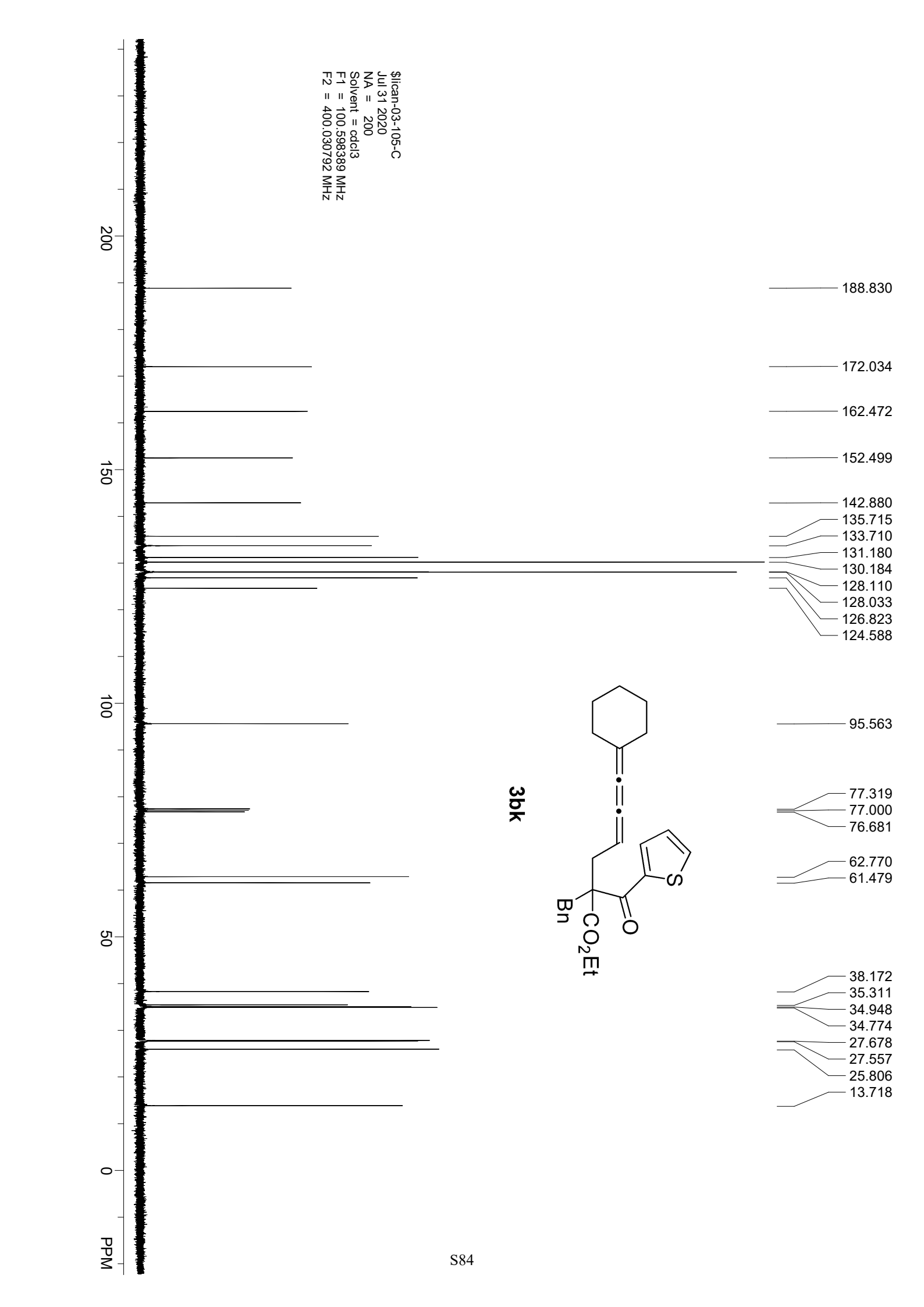

lican-03-075-C
Jul 7 2020
NA = 168
Solvent = cdcl3
F1 = 100.521721 MHz
F2 = 399.722015 MHz
3bi
Bn
CO2Et
O
O2N
195.187
171.442
162.503
152.303
149.599
141.079
135.394
130.159
129.250
128.108
126.965
125.162
123.474
94.759
77.316
77.000
76.680
62.977
61.664
38.354
35.409
34.756
34.709
27.604
27.509
25.687
13.628
200
150
100
50
0 PPM

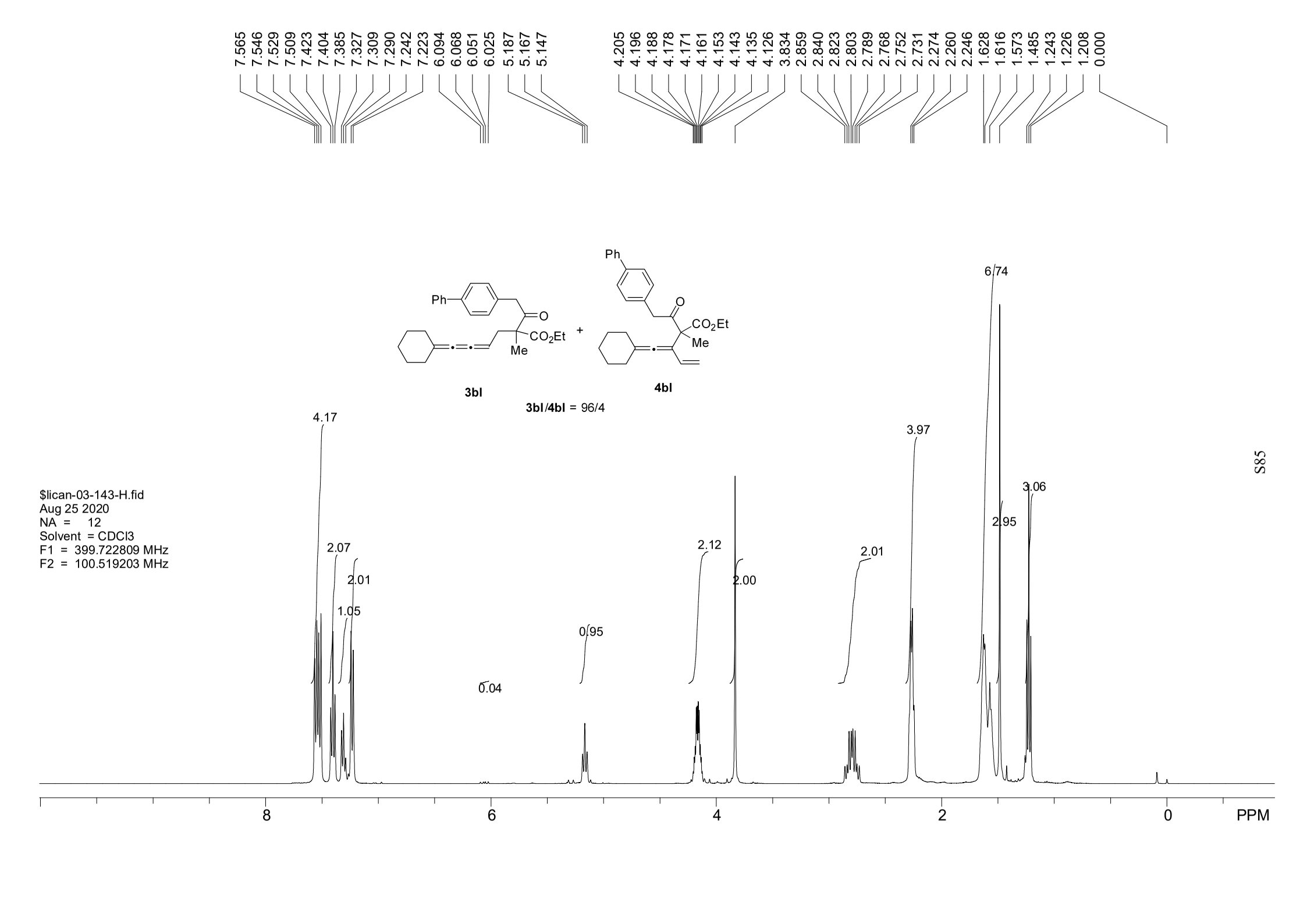

7.940
7.920
7.700
7.679
7.224
7.216
7.211
7.069
7.062
7.053
5.099
5.078
5.058
4.190
4.172
4.162
4.144
4.126
4.107
4.089
4.080
4.056
3.517
3.482
3.460
3.424
2.912
2.872
2.852
2.810
2.273
2.261
2.246
2.199
2.188
1.641
1.631
1.617
1.602
1.576
1.106
1.088
1.070
-0.000
F3C
O
CO2Et
Bn
3bj
S80
lican-03-128-H
Sep 16 2020
SOLVENT: CDCl3
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
2.02
2.00
3.01
2.04
0.98
2.07
1.05
1.00
2.06
4.11
7.34
3.00
8
6
4
2
0
PPM

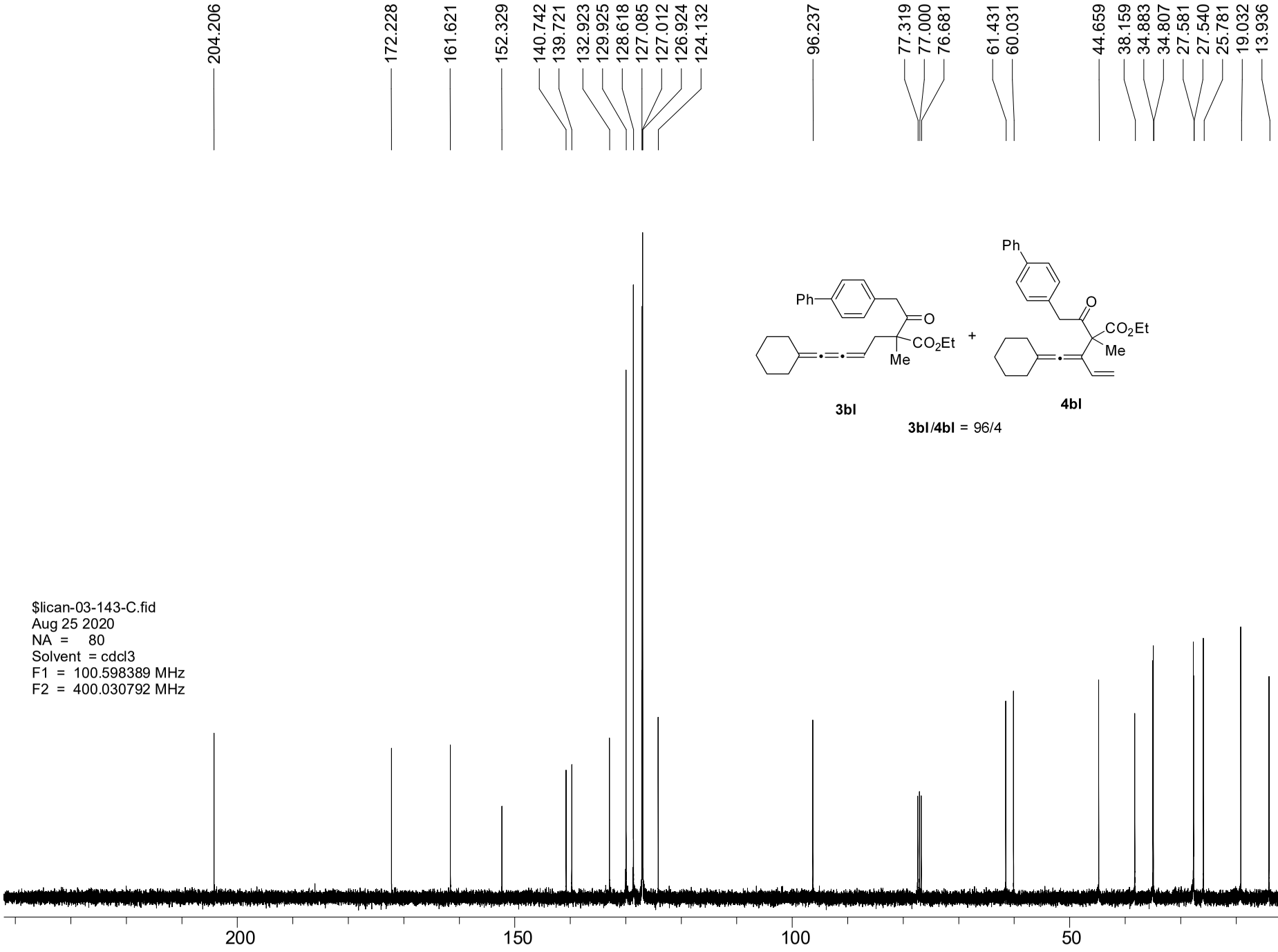

lican-03-128-C-bruker
Jul 4 2022
NA = 4000
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
3bj
Bn
CO2Et
O
F3C
195.580
171.930
162.568
152.447
135.700
134.390
134.068
139.163
133.739
133.417
130.322
128.790
128.223
127.587
127.050
125.595
125.564
125.526
125.488
125.166
124.875
122.163
119.451
95.111
77.314
77.000
76.678
62.919
61.701
38.434
35.469
34.917
34.856
27.731
27.631
25.854
13.742
200
150
100
50
0
PPM

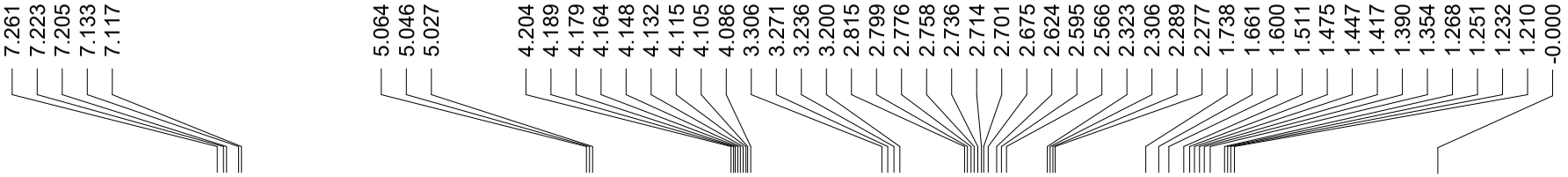

0.000
-63.647
F3C
O
CO2Et
Bn
3bj
lican-03-128-F
Aug 19 2020
NA = 8
Solvent = CDCl3
F1 = 376.359863 MHz
F2 = 100.596855 MHz
100
50
0
-50
-100
-150
-200
-250
-300
PPM

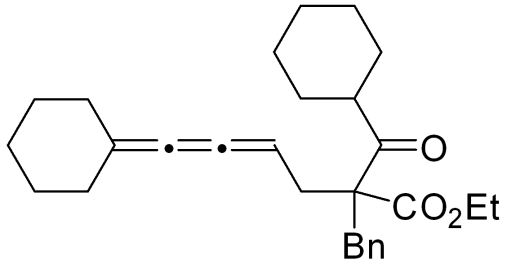

7.690
7.680
7.629
7.616
7.204
7.195
7.191
7.100
7.086
7.077
7.066
5.134
5.113
5.093
4.209
4.190
4.182
4.172
4.164
4.155
4.146
4.137
4.128
4.119
4.111
4.102
4.092
4.075
3.506
3.471
3.459
3.424
2.916
2.896
2.879
2.859
2.838
2.822
2.801
2.272
2.260
1.680
1.644
1.591
1.129
1.111
1.093
0.000
S
O
CO2Et
Bn
3bk
6.22
3.99
2.96
2.95
2.96
2.03
2.00
2.00
0.99
0.89
0.95
S83
lican-03-105-H
Jul 31 2020
NA = 12
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
8
6
4
2
0
PPM


$lican-03-105-C
Jul 31 2020
NA = 200
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
200
150
100
50
0
PPM
188.830
172.034
162.472
152.499
142.880
135.715
133.710
131.180
130.184
128.110
128.033
126.823
124.588
95.563
77.319
77.000
76.681
62.770
61.479
38.172
35.311
34.948
34.774
27.678
27.557
25.806
13.718
3bk
Bn
CO2Et
O
S


7.565
7.546
7.529
7.509
7.423
7.404
7.385
7.327
7.309
7.290
7.242
7.223
6.094
6.068
6.051
6.025
5.187
5.167
5.147
4.205
4.196
4.188
4.178
4.171
4.161
4.153
4.143
4.135
4.126
3.834
2.859
2.840
2.823
2.803
2.789
2.768
2.752
2.731
2.274
2.260
2.246
1.628
1.616
1.573
1.485
1.243
1.226
1.208
0.000
Ph
O
CO2Et
Me
+
Ph
O
CO2Et
Me
3bl
4bl
3bl/4bl = 96/4
$lican-03-143-H.fid
Aug 25 2020
NA = 12
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
4.17
2.07
2.01
1.05
0.04
0.95
2.12
2.00
2.01
3.97
6.74
2.95
3.06
S85
8
6
4
2
0
PPM


204.206
172.228
161.621
152.329
140.742
139.721
132.923
129.925
128.618
127.085
127.012
126.924
124.132
96.237
77.319
77.000
76.681
61.431
60.031
44.659
38.159
34.883
34.807
27.581
27.540
25.781
19.032
13.936
Ph
O
CO2Et
Me
+
Ph
O
CO2Et
Me
3bl
4bl
3bl/4bl = 96/4
$lican-03-143-C.fid
Aug 25 2020
NA = 80
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
200
150
100
50
0
PPM

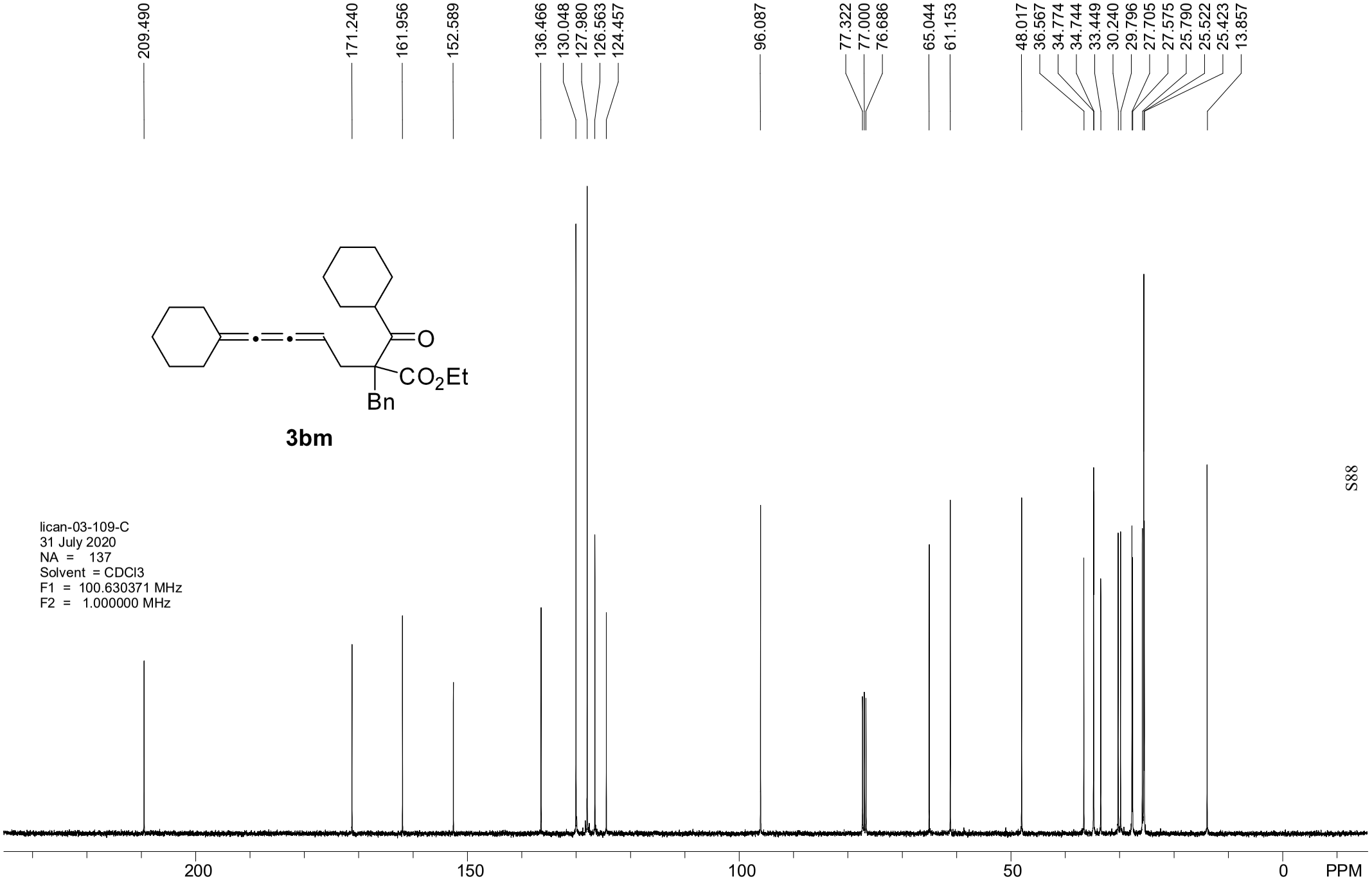


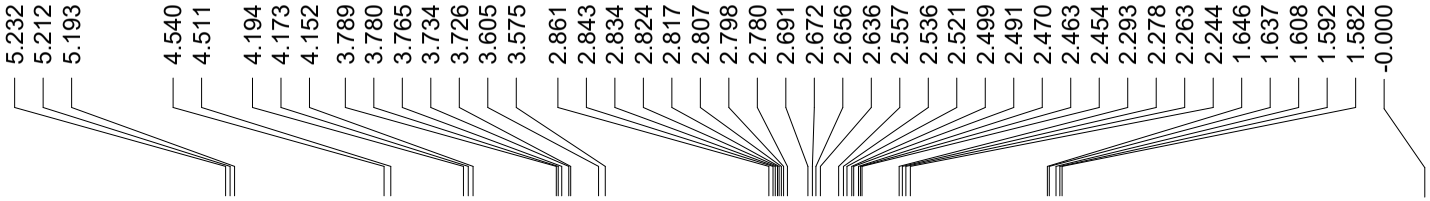


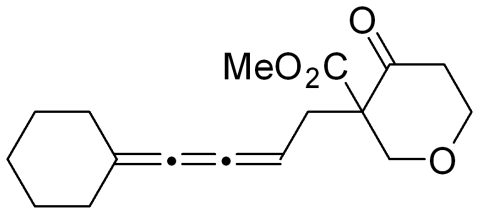
3bm

lican-03-109-H
Sep 16 2020
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz

S87

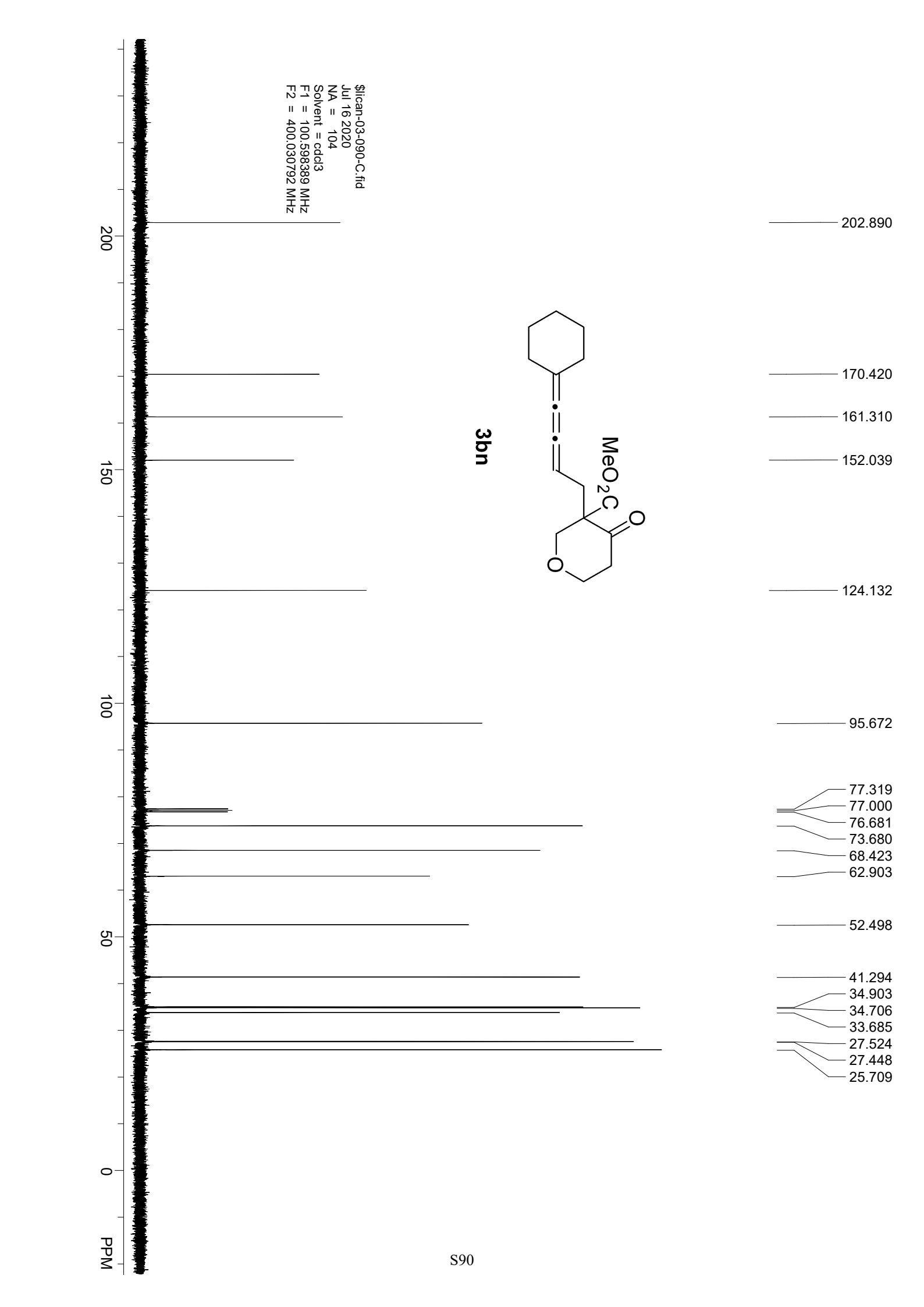

209.490
171.240
161.956
152.589
136.466
130.048
127.980
126.563
124.457
96.087
77.322
77.000
76.686
65.044
61.153
48.017
36.567
34.774
34.744
33.449
30.240
29.796
27.705
27.575
25.790
25.522
25.423
13.857
O
CO2Et
Bn
3bm
lican-03-109-C
31 July 2020
NA = 137
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
S88
200
150
100
50
0
PPM

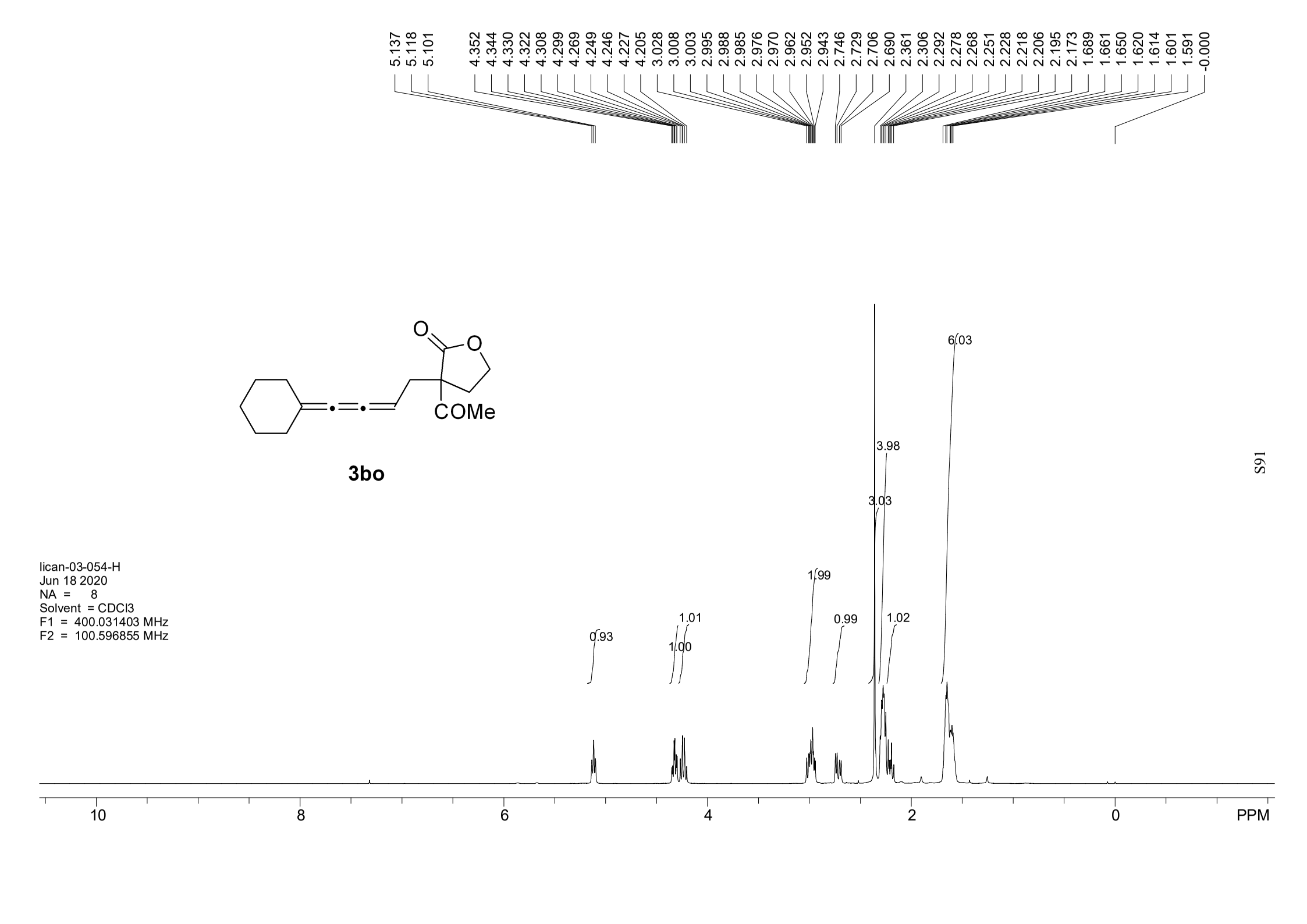


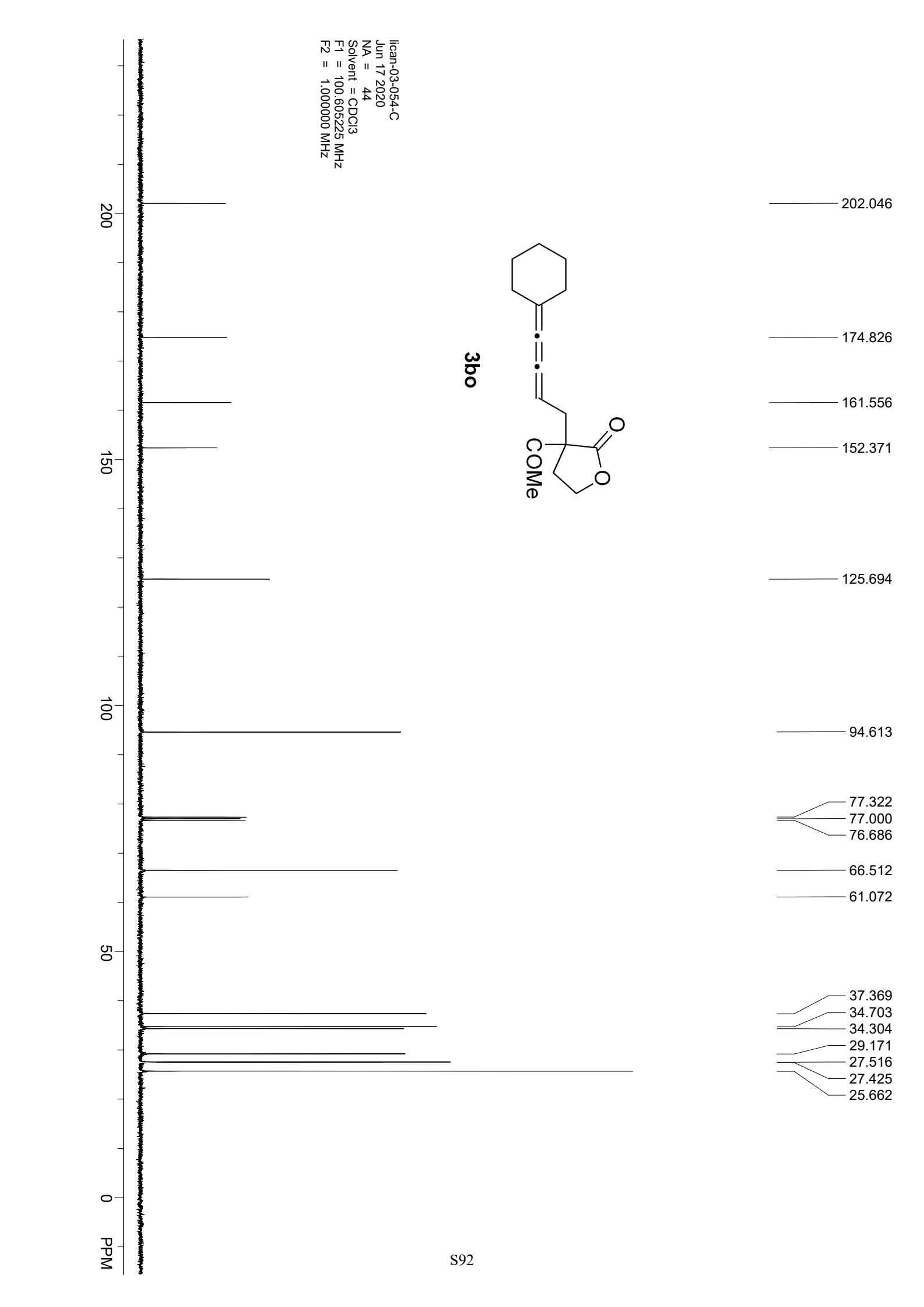


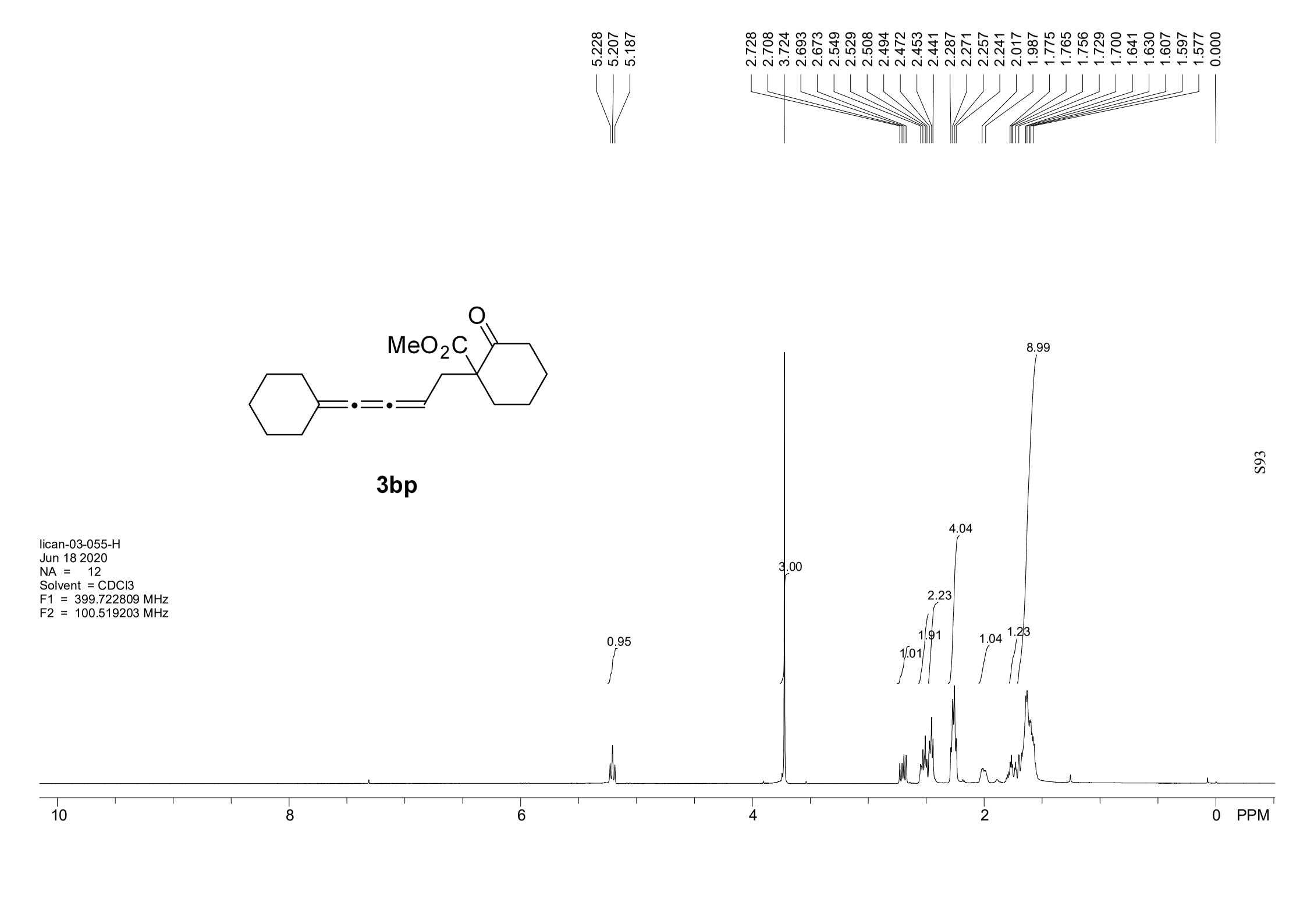
3bn

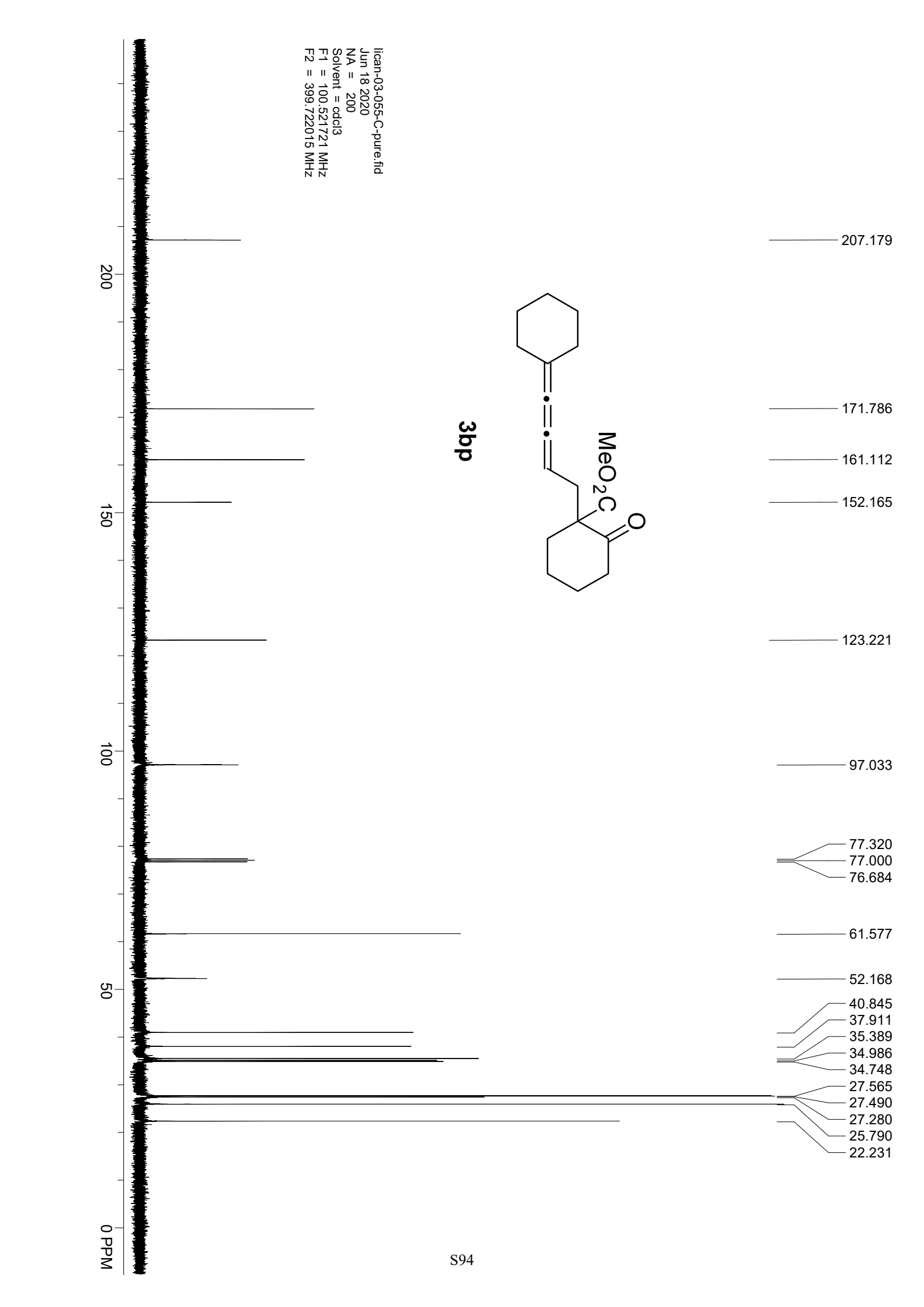
$lican-03-090-H.fid
Jul 16 2020
NA = 12
Solvent = CDCl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz

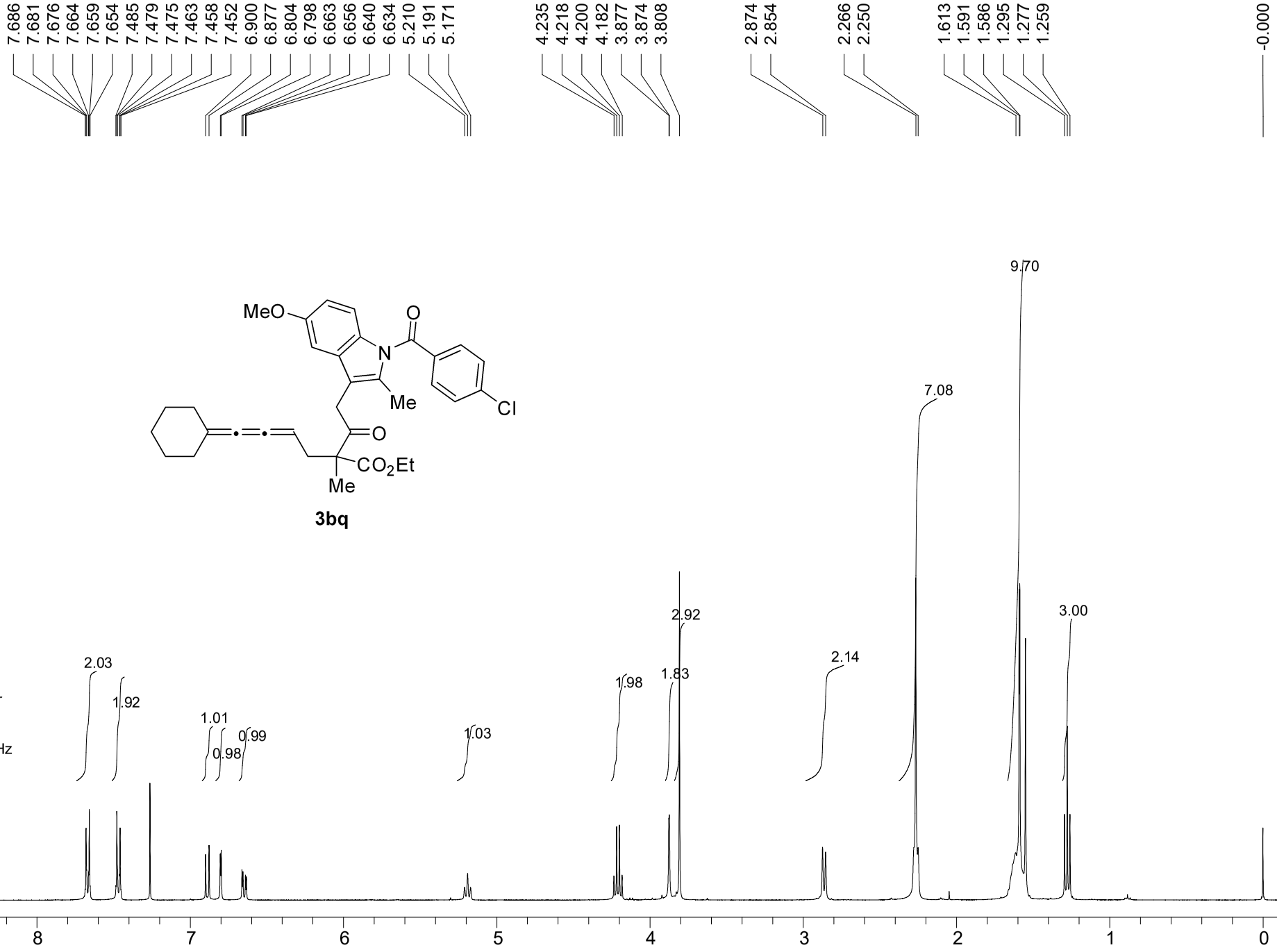

$lican-03-090-C.fid
Jul 16 2020
NA = 104
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
3bn
MeO2C
O
O
202.890
170.420
161.310
152.039
124.132
95.672
77.319
77.000
76.681
73.680
68.423
62.903
52.498
41.294
34.903
34.706
33.685
27.524
27.448
25.709
200
150
100
50
0
PPM

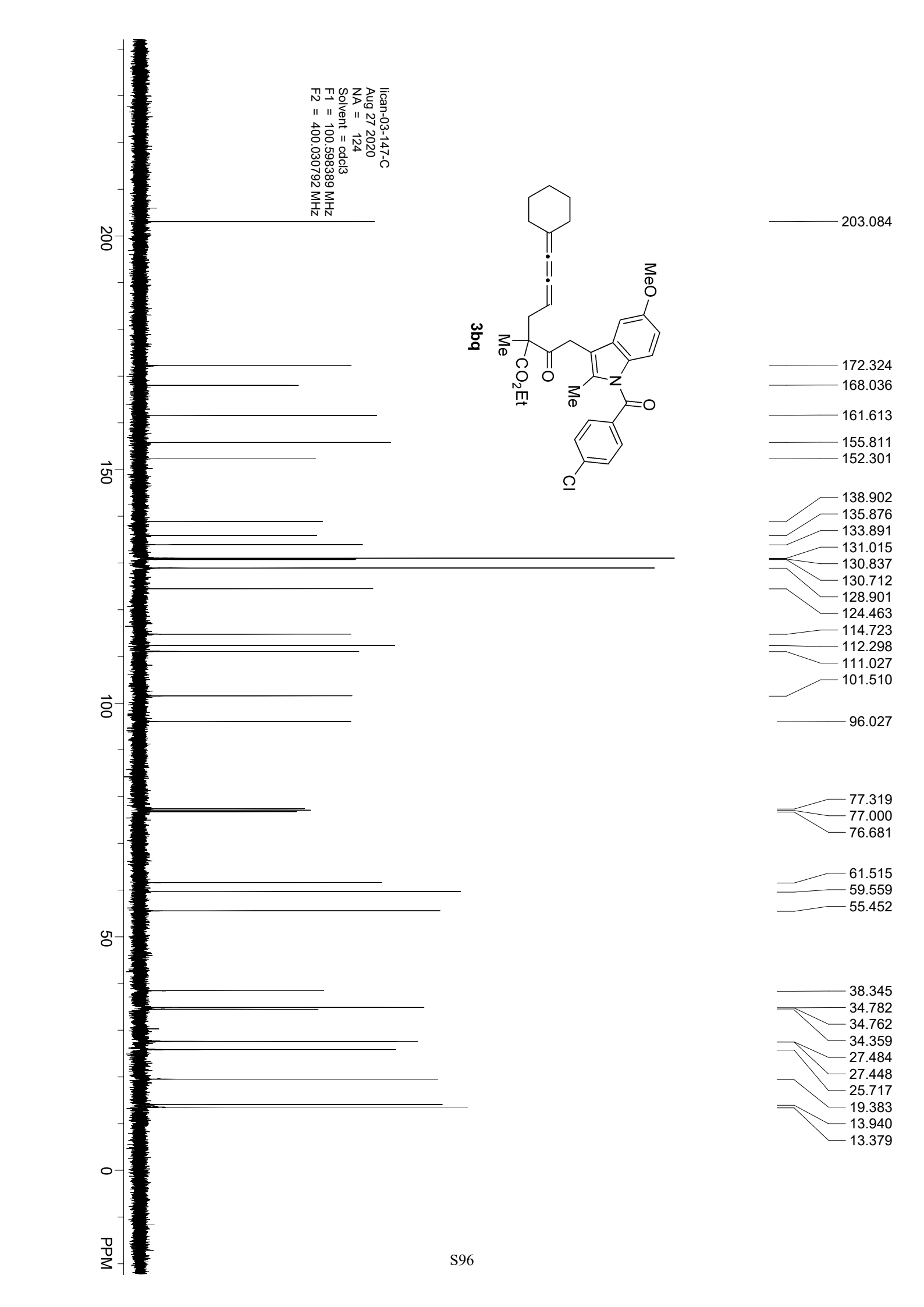

5.137
5.118
5.101
4.352
4.344
4.330
4.322
4.308
4.299
4.269
4.249
4.246
4.227
4.205
3.028
3.008
3.003
2.995
2.988
2.985
2.976
2.970
2.962
2.952
2.943
2.746
2.729
2.706
2.690
2.361
2.306
2.292
2.278
2.268
2.251
2.228
2.218
2.206
2.195
2.173
1.689
1.661
1.650
1.620
1.614
1.601
1.591
-0.000
O
O
COMe
3bo
6.03
3.98
3.03
1.99
1.01
1.02
0.99
0.93
1.00
lican-03-054-H
Jun 18 2020
NA = 8
Solvent = CDCl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz
10
8
6
4
2
0
PPM
S91

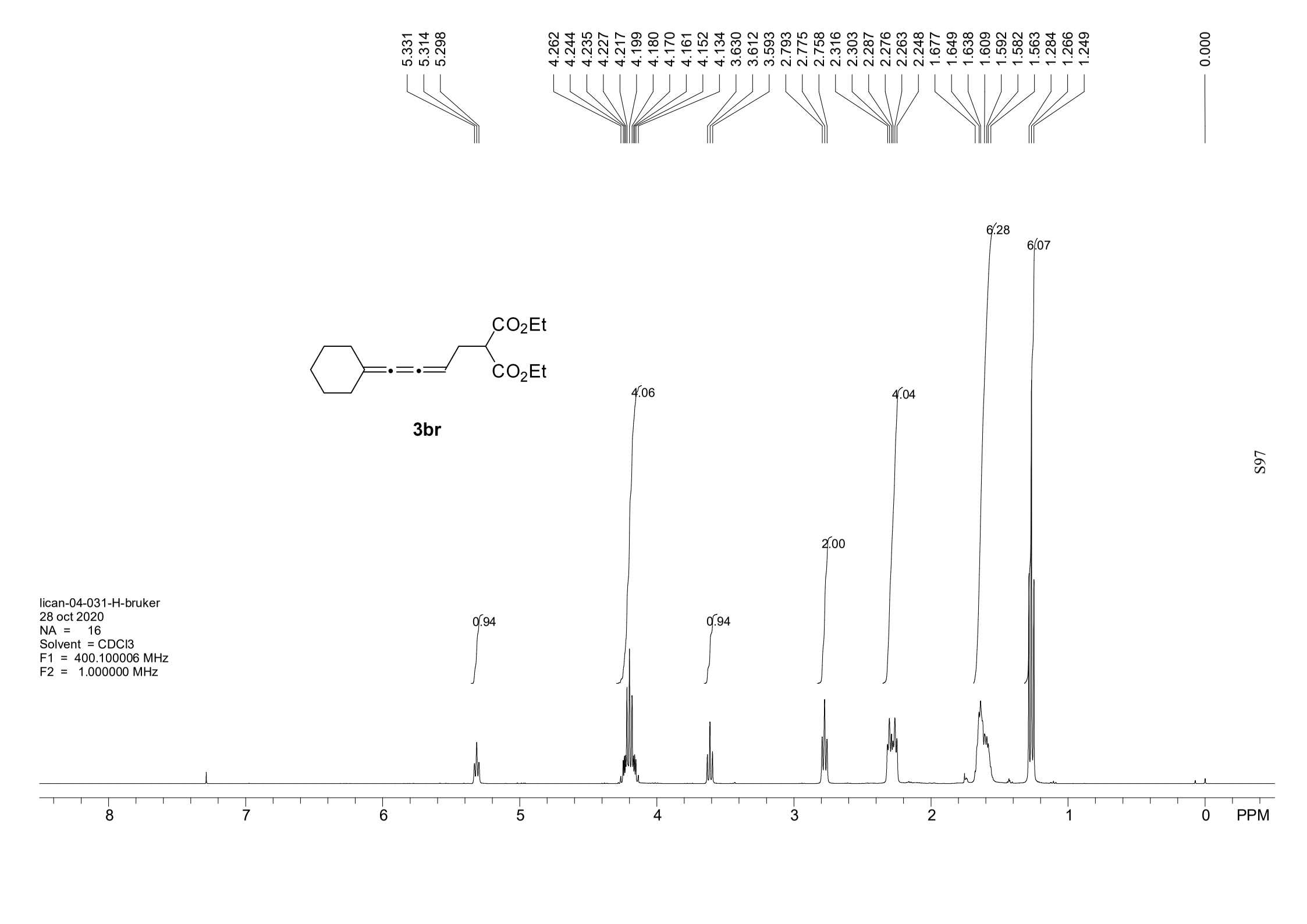

lican-03-054-C
Jun 17 2020
NA = 44
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
3bo
COMe
O
O
202.046
174.826
161.556
152.371
125.694
94.613
77.322
77.000
76.686
66.512
61.072
37.369
34.703
34.304
29.171
27.516
27.425
25.662
200
150
100
50
0
PPM

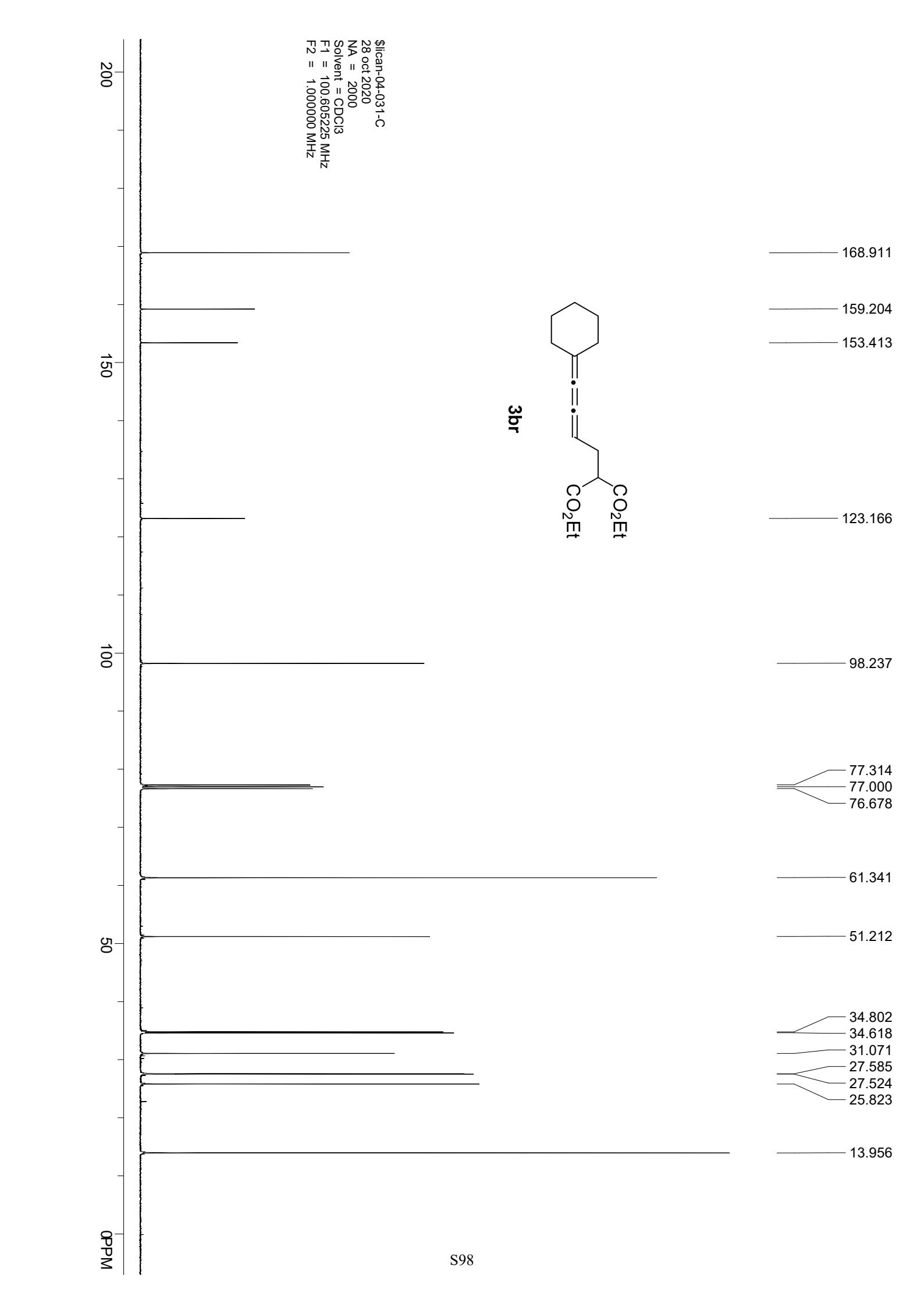

5.228
5.207
5.187
2.728
2.708
3.724
2.693
2.673
2.549
2.529
2.508
2.494
2.472
2.453
2.441
2.287
2.271
2.257
2.241
2.017
1.987
1.775
1.765
1.756
1.729
1.700
1.641
1.630
1.607
1.597
1.577
0.000
O
MeO2C
3bp
lican-03-055-H
Jun 18 2020
NA = 12
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
0.95
3.00
1.01
1.91
2.23
4.04
1.04
1.23
8.99
10
8
6
4
2
0
PPM
S93


lican-03-055-C-pure.fid
Jun 18 2020
NA = 200
Solvent = cdcl3
F1 = 100.521721 MHz
F2 = 399.722015 MHz
3bp
MeO2C
O
207.179
171.786
161.112
152.165
123.221
97.033
77.320
77.000
76.684
61.577
52.168
40.845
37.911
35.389
34.986
34.748
27.565
27.490
27.280
25.790
22.231
200
150
100
50
0 PPM

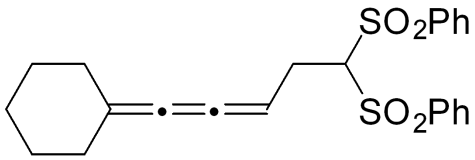

7.686
7.681
7.676
7.664
7.659
7.654
7.485
7.479
7.475
7.463
7.458
7.452
6.900
6.877
6.804
6.798
6.663
6.656
6.640
6.634
5.210
5.191
5.171
4.235
4.218
4.200
4.182
3.877
3.874
3.808
2.874
2.854
2.266
2.250
1.613
1.591
1.586
1.295
1.277
1.259
-0.000
MeO
O
N
Me
Cl
O
CO2Et
Me
3bq
lican-03-147-H-bruker
NA = 17
Solvent = CDCl3
F1 = 400.200012 MHz
F2 = 1.000000 MHz
2.03
1.92
1.01
0.98
0.99
1.03
1.98
1.83
2.92
2.14
7.08
9.70
3.00
9
8
7
6
5
4
3
2
1
0
PPM


lican-03-147-C
Aug 27 2020
NA = 124
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
3bq
MeO
Me
CO2Et
O
N
Me
O
Cl
203.084
172.324
168.036
161.613
155.811
152.301
138.902
135.876
133.891
131.015
130.837
130.712
128.901
124.463
114.723
112.298
111.027
101.510
96.027
77.319
77.000
76.681
61.515
59.559
55.452
38.345
34.782
34.762
34.359
27.484
27.448
25.717
19.383
13.940
13.379
200
150
100
50
0
PPM

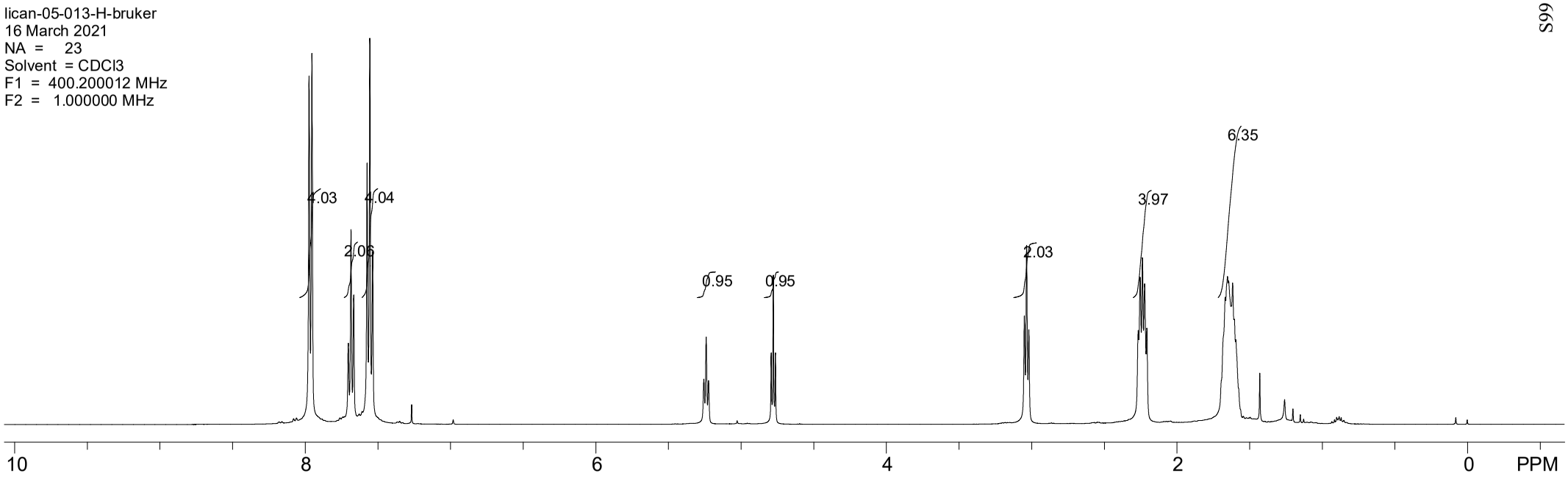

5.331
5.314
5.298
4.262
4.244
4.235
4.227
4.217
4.199
4.180
4.170
4.161
4.152
4.134
3.630
3.612
3.593
2.793
2.775
2.758
2.316
2.303
2.287
2.276
2.263
2.248
1.677
1.649
1.638
1.609
1.592
1.582
1.563
1.284
1.266
1.249
0.000
CO2Et
CO2Et
3br
6.28
6.07
4.06
4.04
2.00
0.94
0.94
lican-04-031-H-bruker
28 oct 2020
NA = 16
Solvent = CDCl3
F1 = 400.100006 MHz
F2 = 1.000000 MHz
S97
8
7
6
5
4
3
2
1
0
PPM

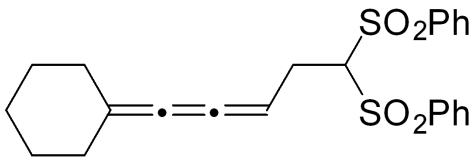

$lican-04-031-C
28 oct 2020
NA = 2000
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
3br
CO2Et
CO2Et
168.911
159.204
153.413
123.166
98.237
77.314
77.000
76.678
61.341
51.212
34.802
34.618
31.071
27.585
27.524
25.823
13.956
200
150
100
50
0PPM


7.974
7.954
7.703
7.685
7.666
7.574
7.555
7.536
5.257
5.241
5.224
4.794
4.779
4.764
3.051
3.036
3.020
2.267
2.254
2.238
2.223
2.207
1.667
1.644
1.616
1.595
-0.000


SO2Ph
SO2Ph

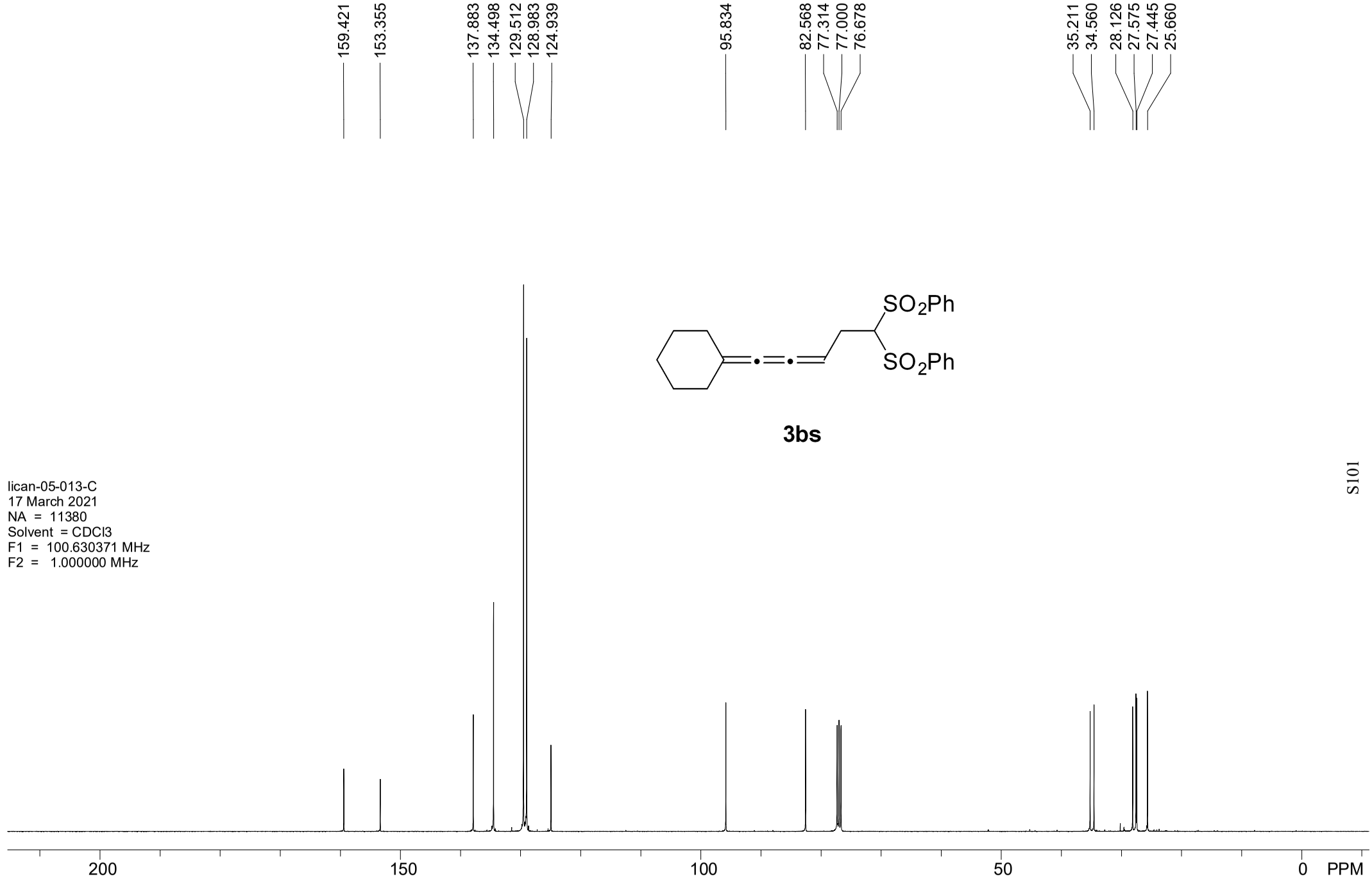
3bs

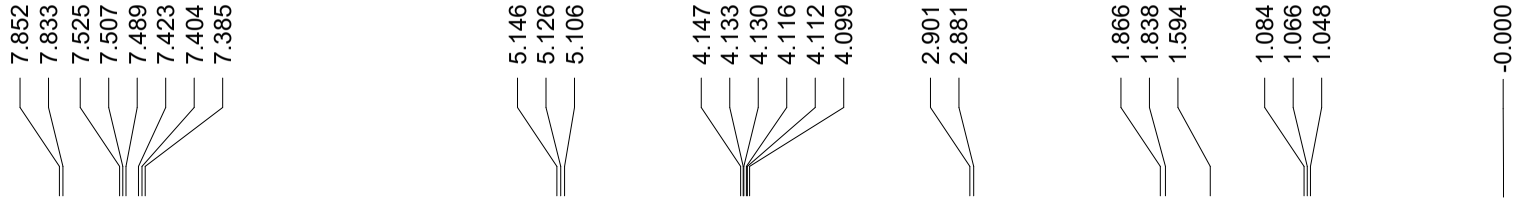

lican-05-013-H-bruker
16 March 2021
NA = 23
Solvent = CDCl3
F1 = 400.200012 MHz
F2 = 1.000000 MHz
4.03
4.04
2.06
0.95
0.95
2.03
3.97
6.35
10
8
6
4
2
0
PPM

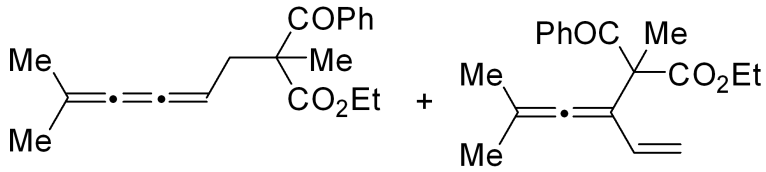


3bs

lican-05-013-purity
purity = 95%
Mar 18 2021
19.4 mg product with 35 uL dibromomethane
NA = 4
Solvent = CDCl3
F1 = 399.722626 MHz
F2 = 100.519203 MHz


159.421
153.355
137.883
134.498
129.512
128.983
124.939
95.834
82.568
77.314
77.000
76.678
35.211
34.560
28.126
27.575
27.445
25.660
SO2Ph
SO2Ph
3bs
lican-05-013-C
17 March 2021
NA = 11380
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
200
150
100
50
0
PPM





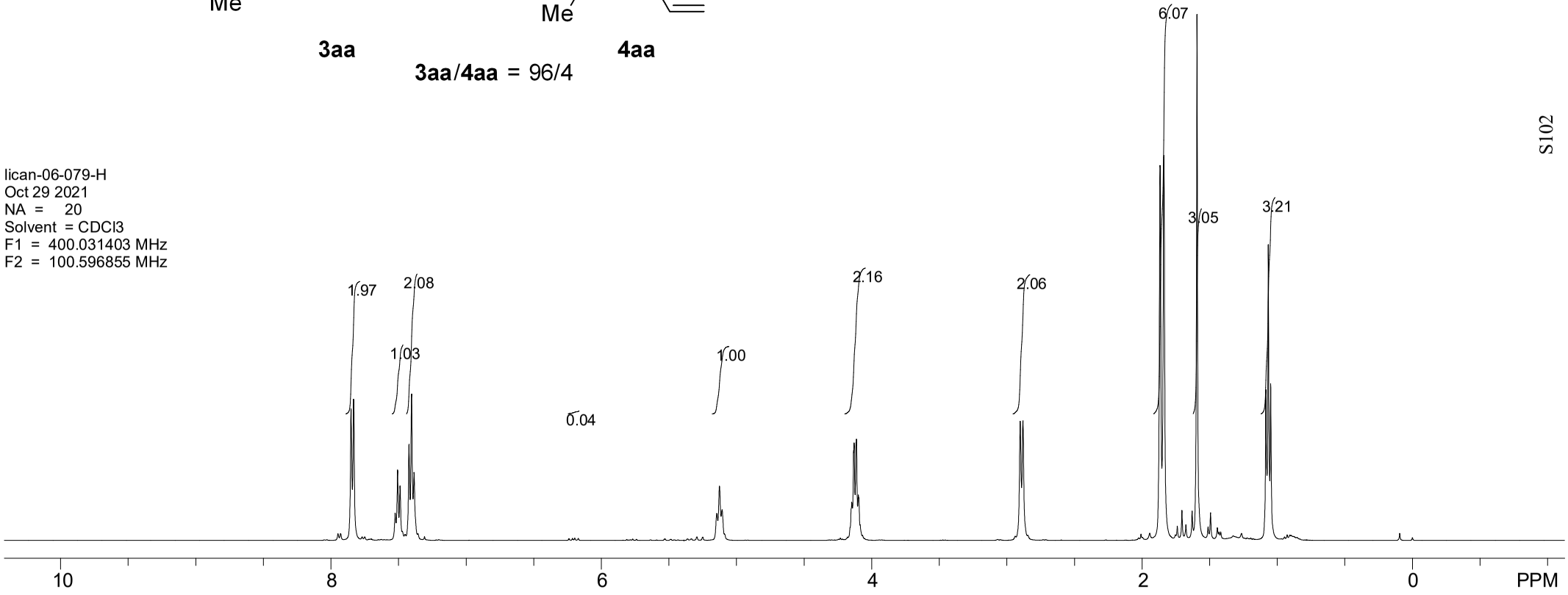
3aa

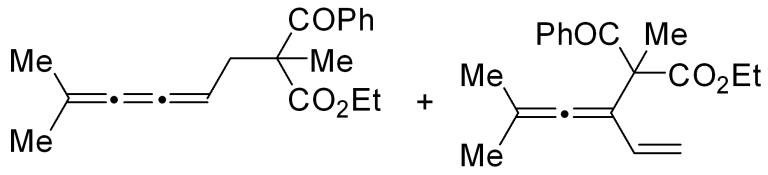
\+

4aa

3aa/**4aa** = 96/4

lican-06-079-H
Oct 29 2021
NA = 20
Solvent = CDCl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz





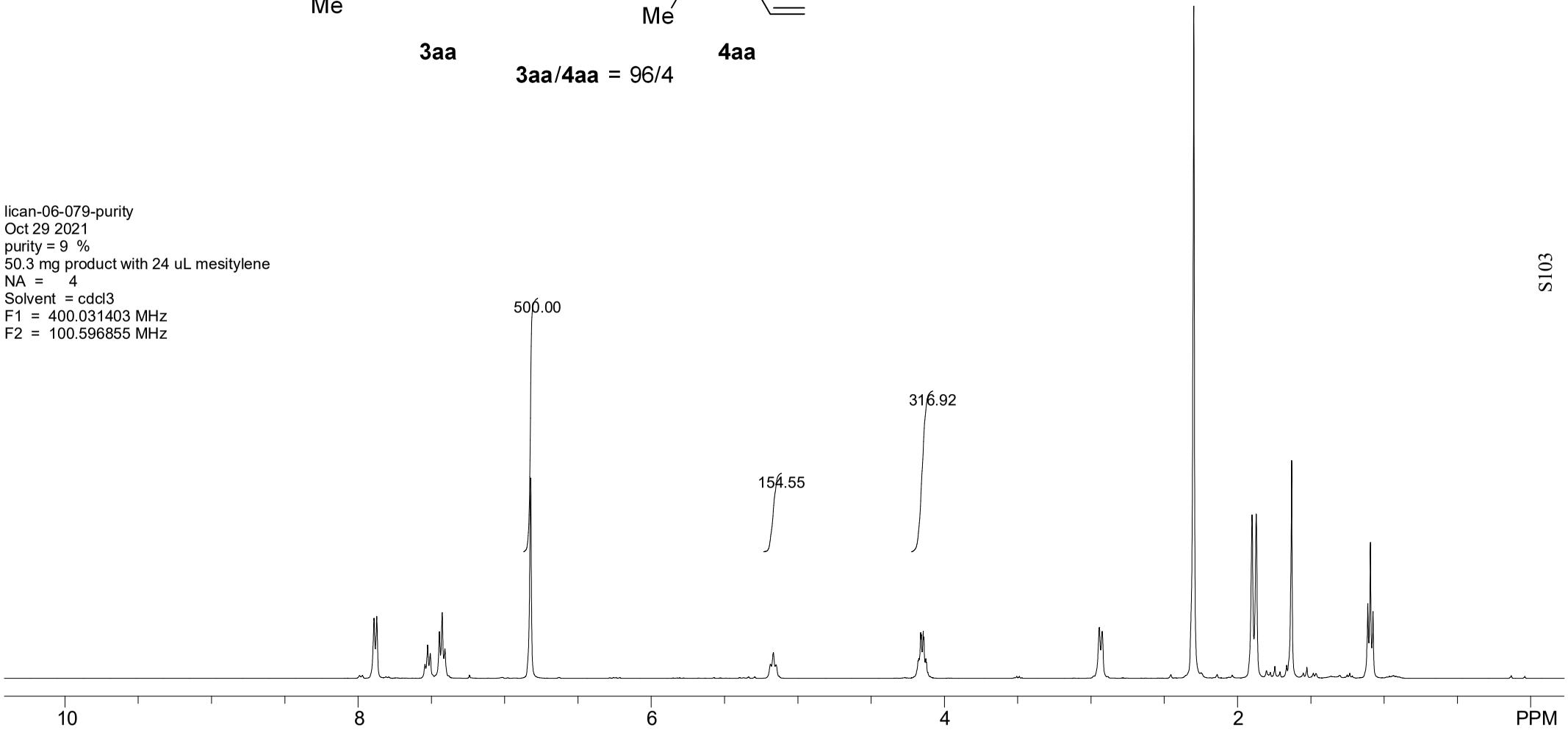
3aa

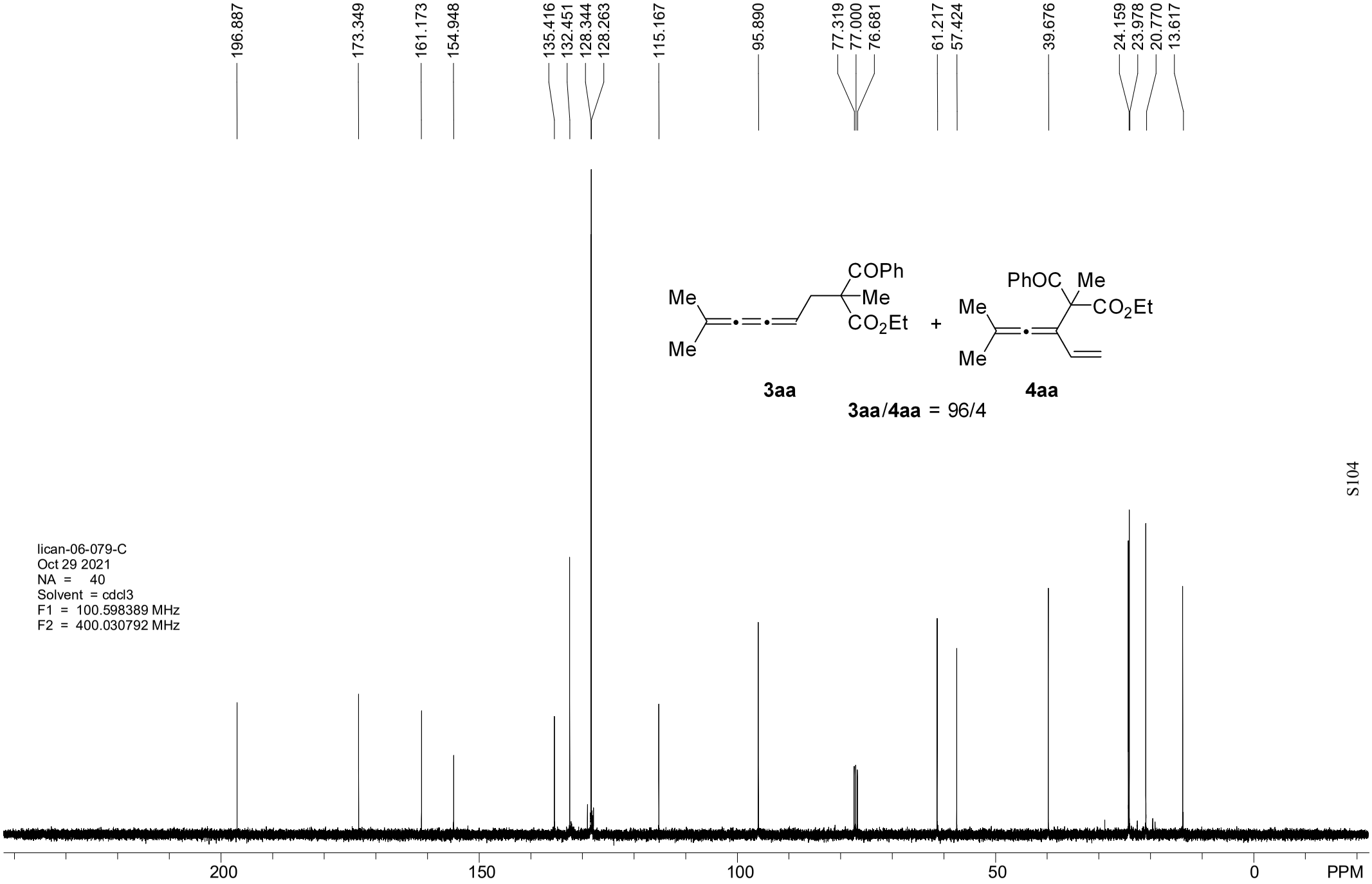
+

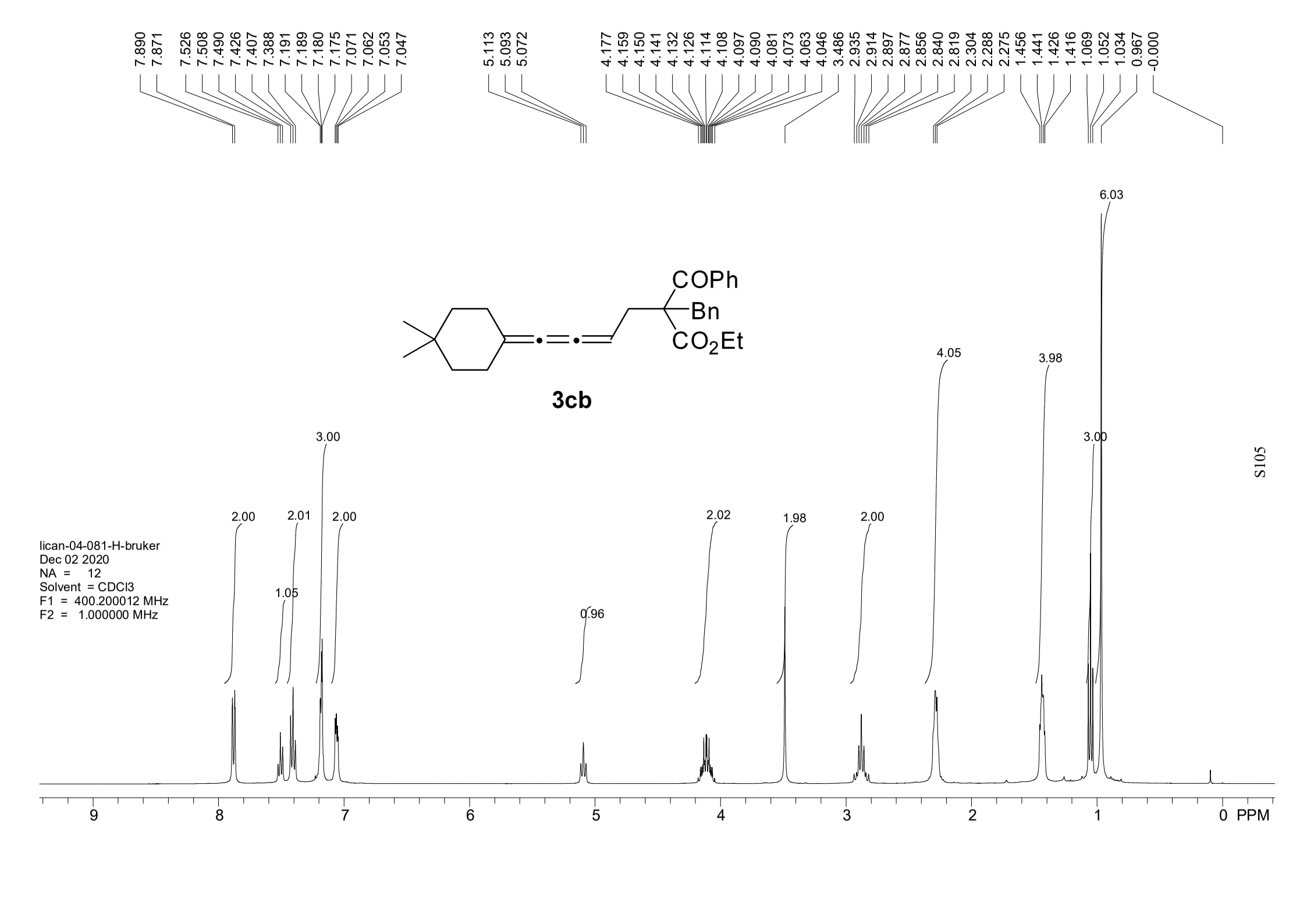
4aa

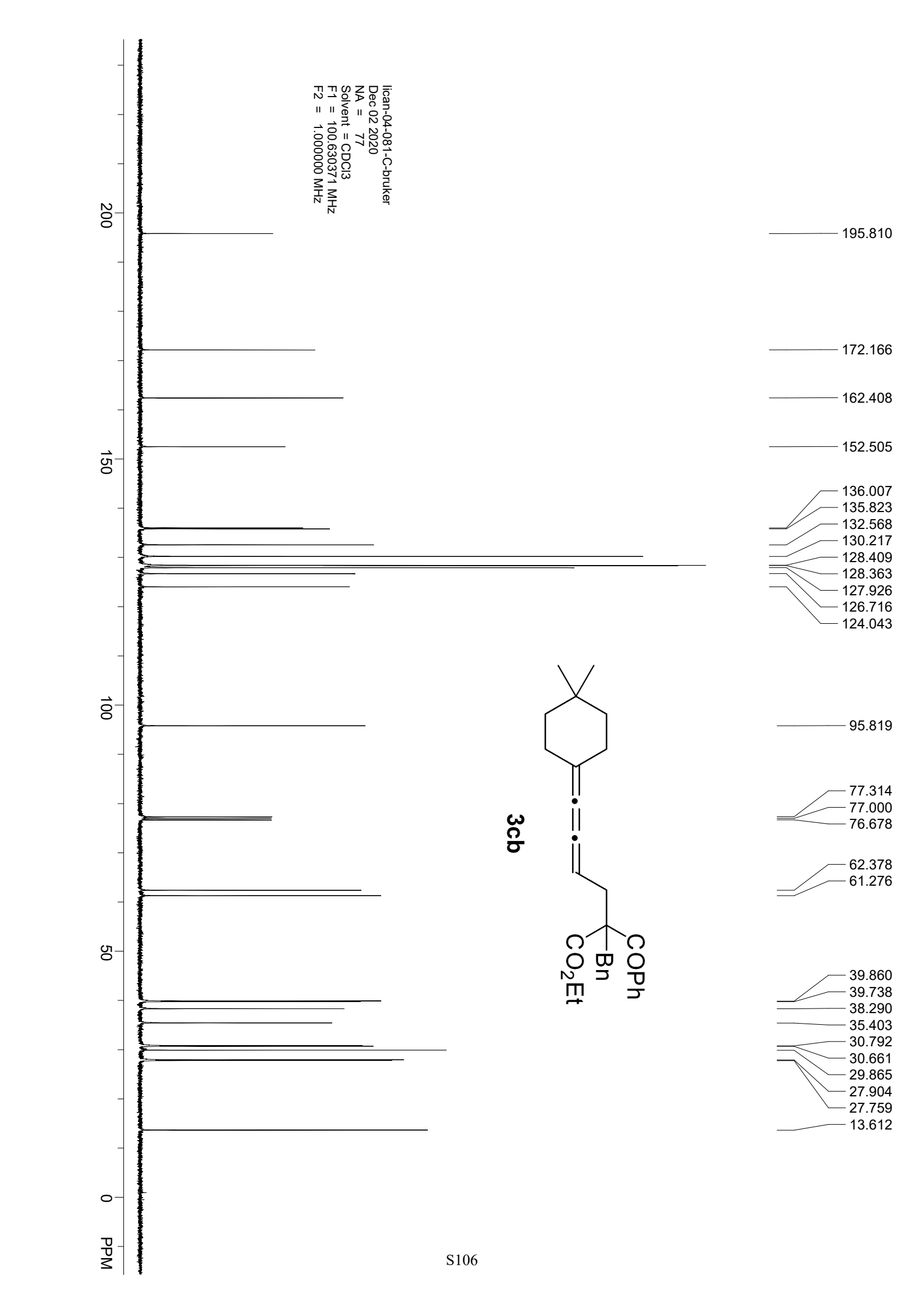
3aa/**4aa** = 96/4

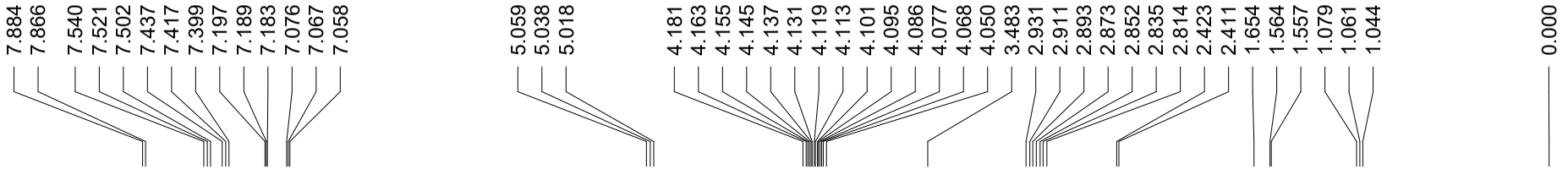
lican-06-079-purity
Oct 29 2021
purity = 9 %
50.3 mg product with 24 uL mesitylene
NA = 4
Solvent = cdcl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz

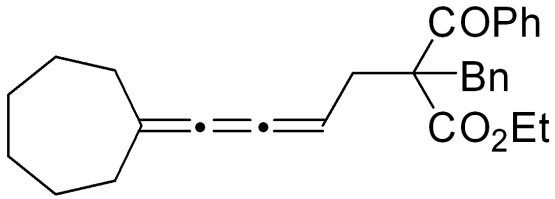



196.887
173.349
161.173
154.948
135.416
132.451
128.344
128.263
115.167
95.890
77.319
77.000
76.681
61.217
57.424
39.676
24.159
23.978
20.770
13.617
COPh
Me
Me
CO2Et
Me
Me
PhOC
Me
CO2Et
Me
Me
+
3aa
4aa
3aa/4aa = 96/4
lican-06-079-C
Oct 29 2021
NA = 40
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
200
150
100
50
0
PPM

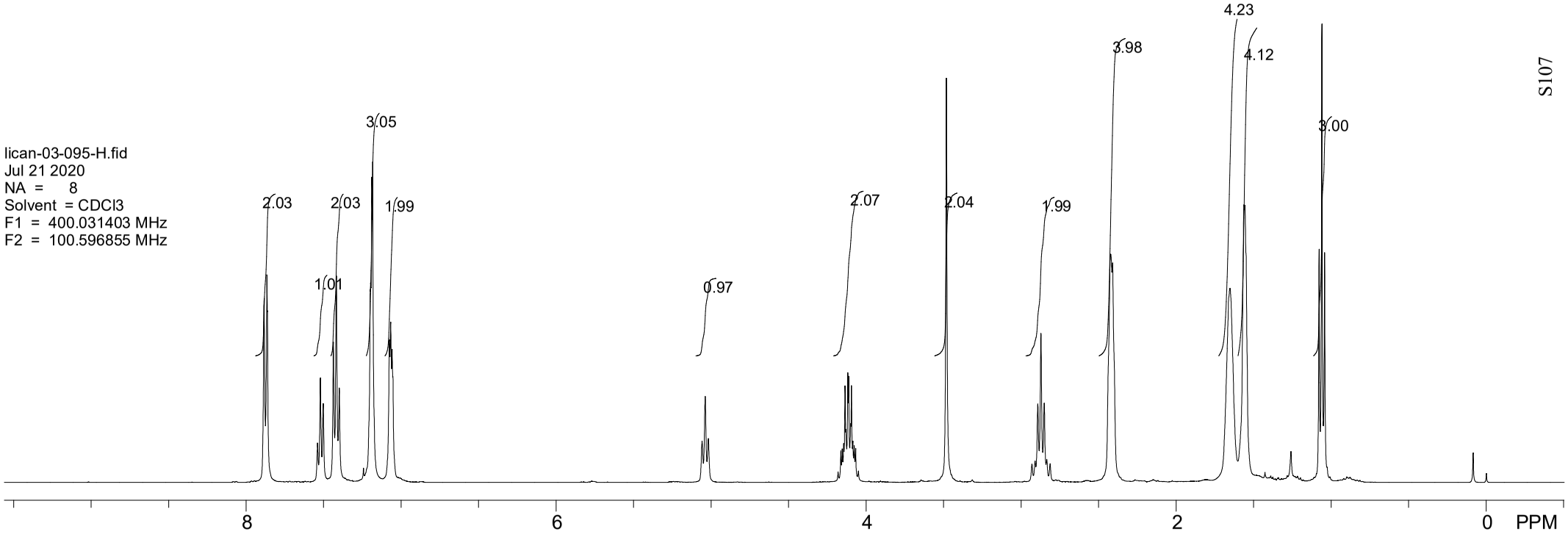

7.890
7.871
7.526
7.508
7.490
7.426
7.407
7.388
7.191
7.189
7.180
7.175
7.071
7.062
7.053
7.047
5.113
5.093
5.072
4.177
4.159
4.150
4.141
4.132
4.126
4.114
4.108
4.097
4.090
4.081
4.073
4.063
4.046
3.486
2.935
2.914
2.897
2.877
2.856
2.840
2.819
2.304
2.288
2.275
1.456
1.441
1.426
1.416
1.069
1.052
1.034
0.967
-0.000
COPh
Bn
CO2Et
3cb
6.03
4.05
3.98
3.00
3.00
2.00
2.01
2.00
2.02
1.98
2.00
1.05
0.96
lican-04-081-H-bruker
Dec 02 2020
NA = 12
Solvent = CDCl3
F1 = 400.200012 MHz
F2 = 1.000000 MHz
S105
9
8
7
6
5
4
3
2
1
0 PPM

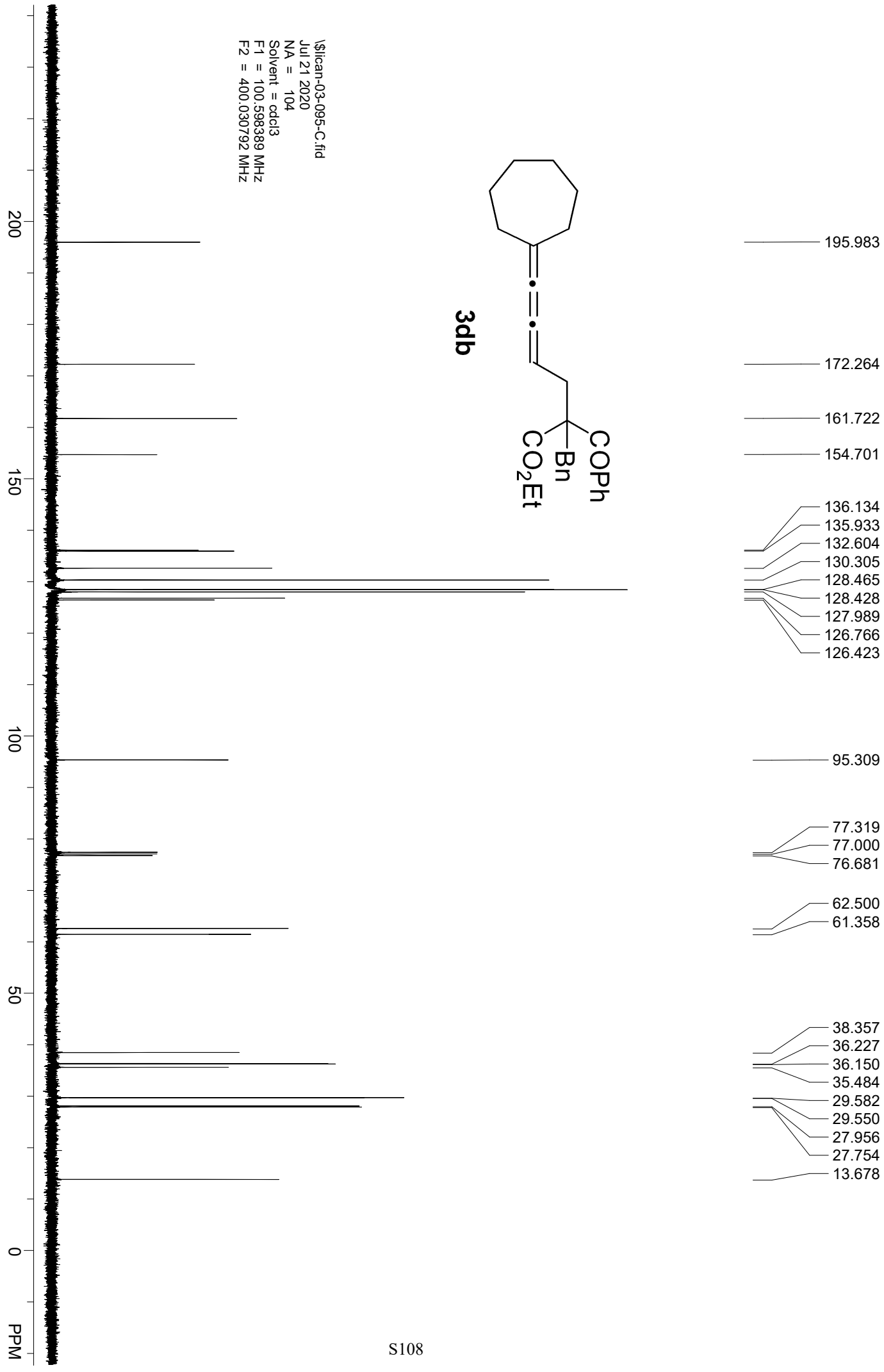

lican-04-081-C-bruker
Dec 02 2020
NA = 77
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
200
150
100
50
0
PPM
195.810
172.166
162.408
152.505
136.007
135.823
132.568
130.217
128.409
128.363
127.926
126.716
124.043
95.819
77.314
77.000
76.678
62.378
61.276
39.860
39.738
38.290
35.403
30.792
30.661
29.865
27.904
27.759
13.612
3cb
COPh
Bn
CO2Et

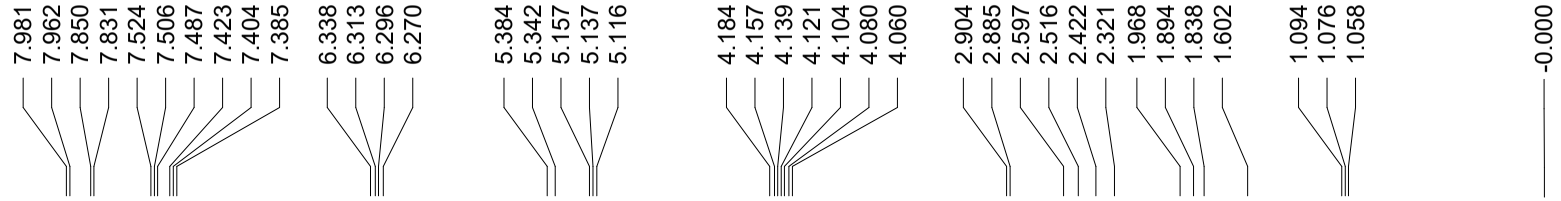

7.884
7.866
7.540
7.521
7.502
7.437
7.417
7.399
7.197
7.189
7.183
7.076
7.067
7.058
5.059
5.038
5.018
4.181
4.163
4.155
4.145
4.137
4.131
4.119
4.113
4.101
4.095
4.086
4.077
4.068
4.050
3.483
2.931
2.911
2.893
2.873
2.852
2.835
2.814
2.423
2.411
1.654
1.564
1.557
1.079
1.061
1.044
0.000

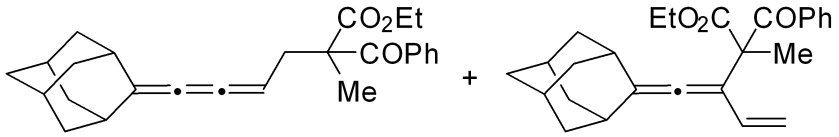

COPh
Bn
CO2Et

3db


lican-03-095-H.fid
Jul 21 2020
NA = 8
Solvent = CDCl3
F1 = 400.031403 MHz
F2 = 100.596855 MHz
2.03
2.03
1.99
3.05
1.01
0.97
2.07
2.04
1.99
3.98
4.23
4.12
3.00
S107
8
6
4
2
0
PPM


\$lican-03-095-C.fid
Jul 21 2020
NA = 104
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
3db
COPh
Bn
CO2Et
195.983
172.264
161.722
154.701
136.134
135.933
132.604
130.305
128.465
128.428
127.989
126.766
126.423
95.309
77.319
77.000
76.681
62.500
61.358
38.357
36.227
36.150
35.484
29.582
29.550
27.956
27.754
13.678
200
150
100
50
0
PPM

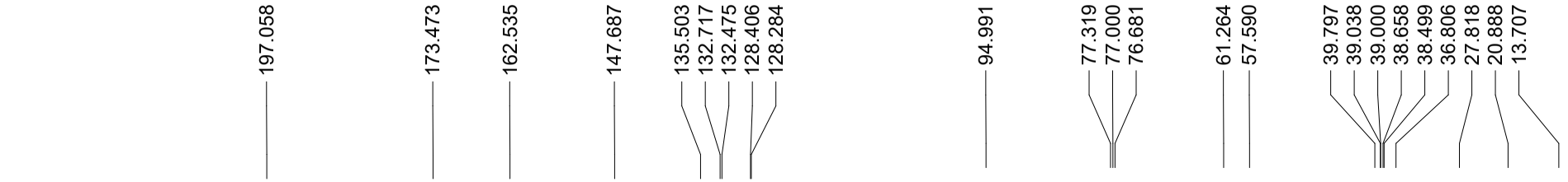


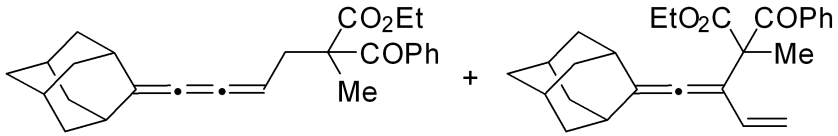


3ea **4ea**

3ea/**4ea** = 95/5

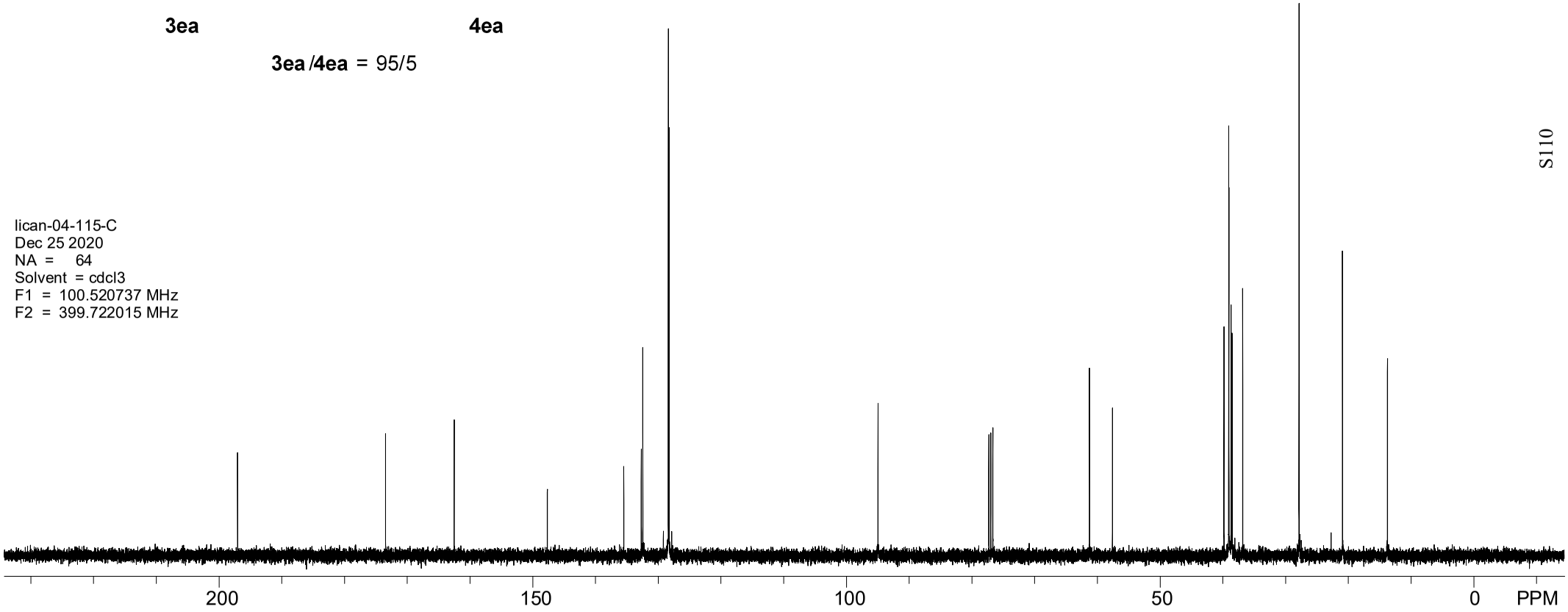
lican-04-115-H
Dec 25 2020
NA = 12
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz

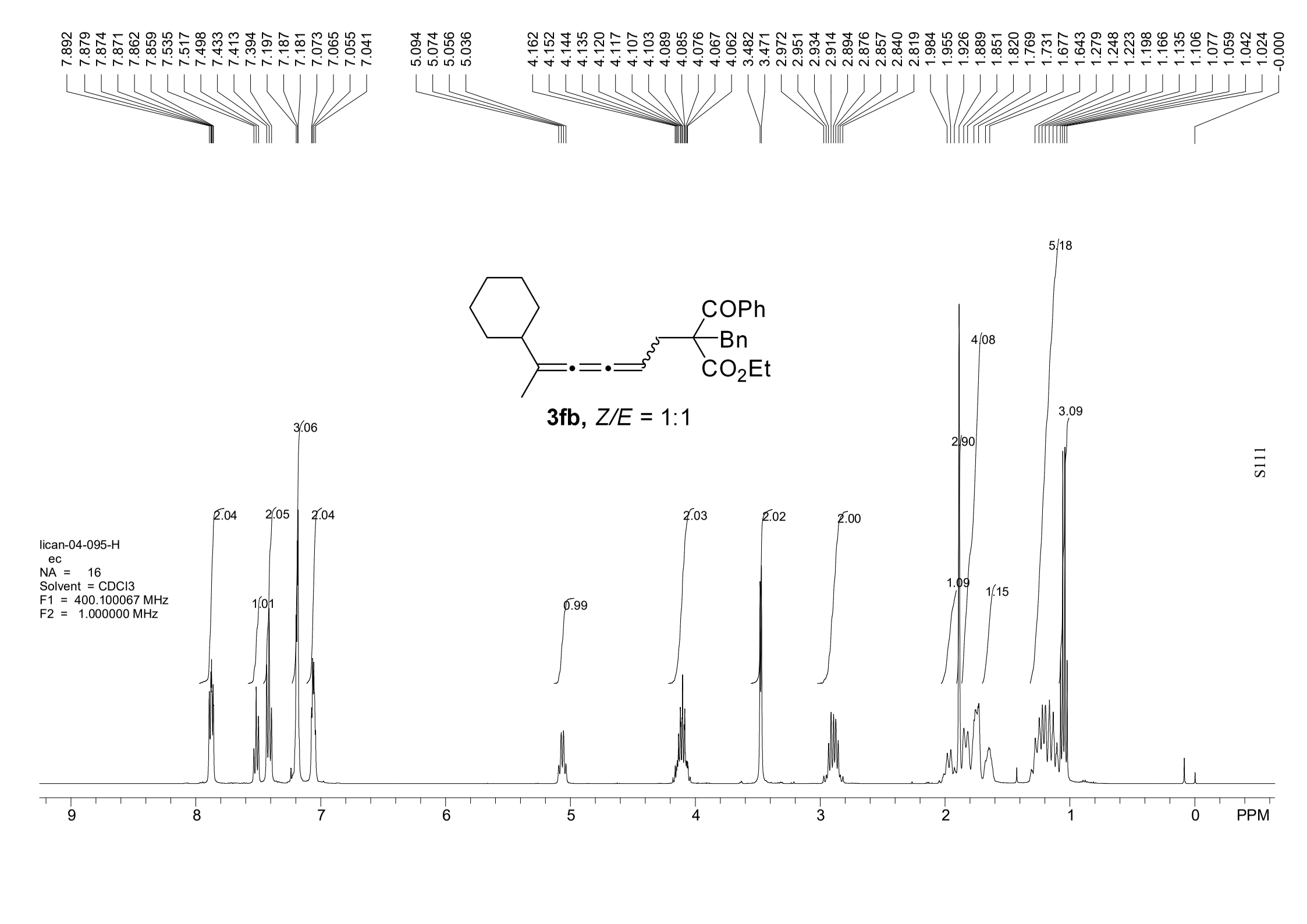


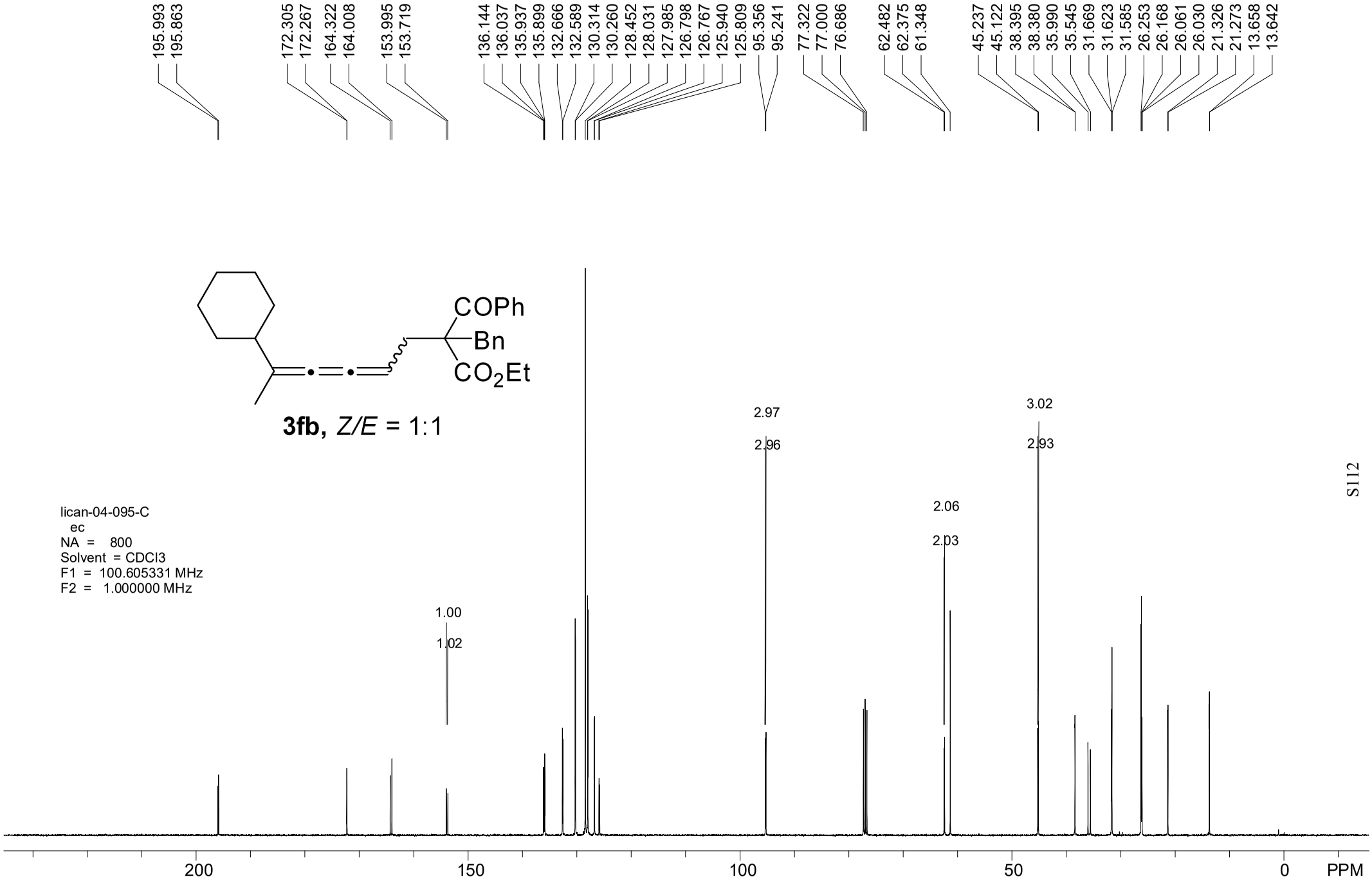


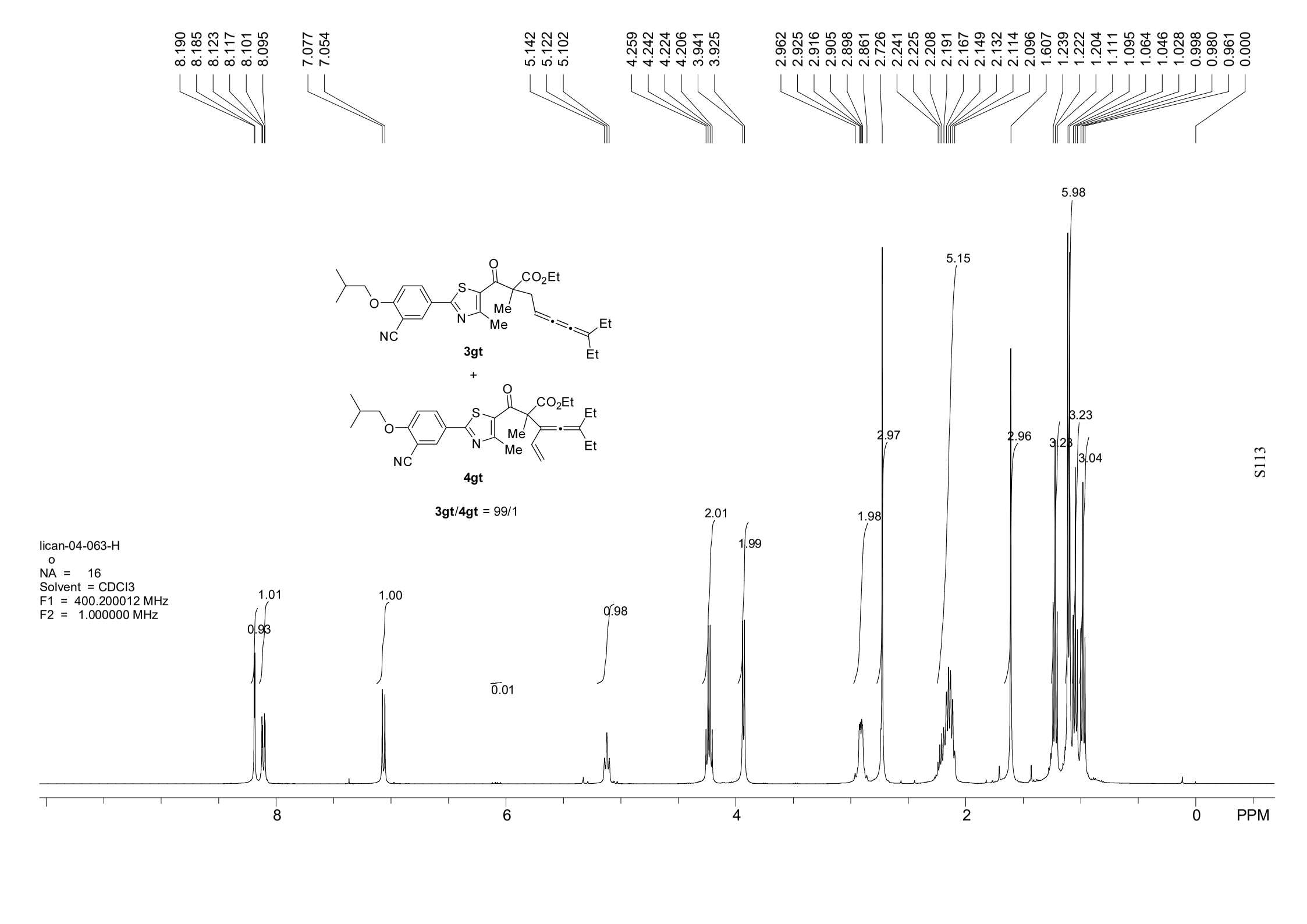
3ea **4ea**

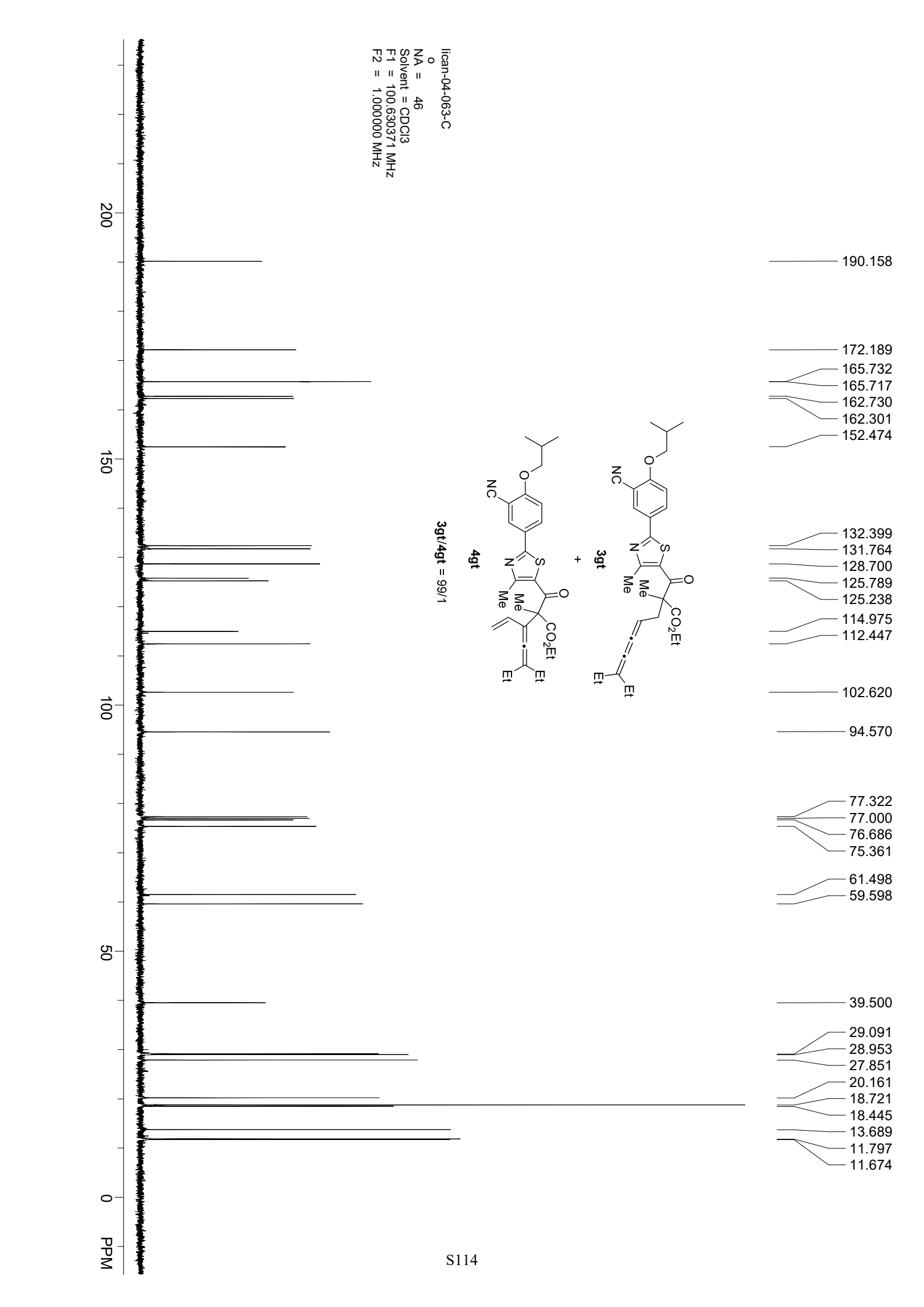
3ea/**4ea** = 95/5

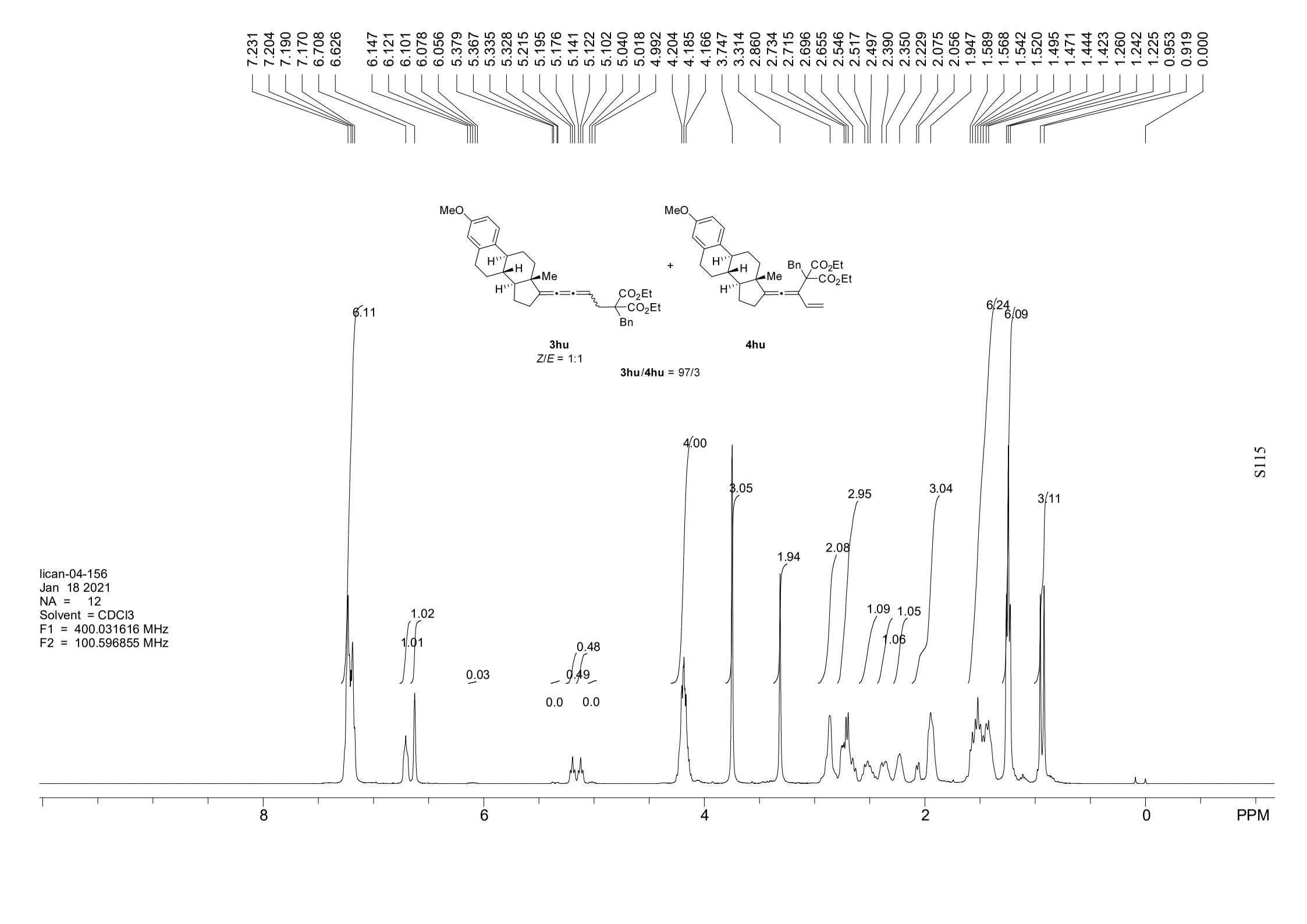


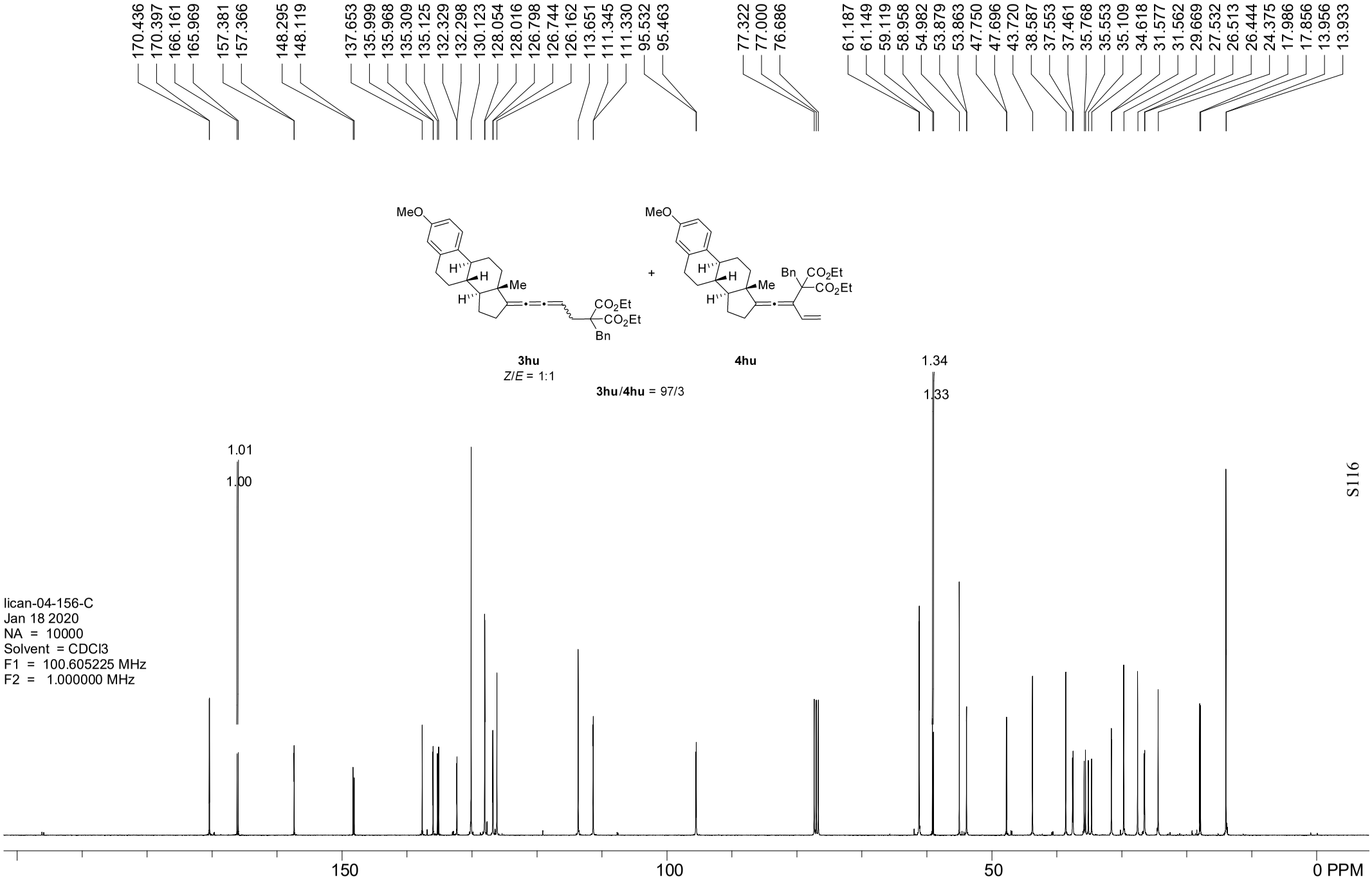

7.892 7.879 7.874 7.871 7.862 7.859 7.535 7.517 7.498 7.433 7.413 7.394 7.197 7.187 7.181 7.073 7.065 7.055 7.041
5.094 5.074 5.056 5.036
4.162 4.152 4.144 4.135 4.120 4.117 4.107 4.103 4.089 4.085 4.076 4.067 4.062
3.482 3.471
2.972 2.951 2.934 2.914 2.894 2.876 2.857 2.840 2.819
1.984 1.955 1.926 1.889 1.851 1.820 1.769 1.731 1.677 1.643 1.279 1.248 1.223 1.198 1.166 1.135 1.106 1.077 1.059 1.042 1.024 -0.000
COPh
Bn
CO2Et
3fb, Z/E = 1:1
lican-04-095-H
ec
NA = 16
Solvent = CDCl3
F1 = 400.100067 MHz
F2 = 1.000000 MHz
2.04
2.05
2.04
3.06
1.01
0.99
2.03
2.02
2.00
1.09
4.08
2.90
1.15
5.18
3.09
S111
9
8
7
6
5
4
3
2
1
0
PPM

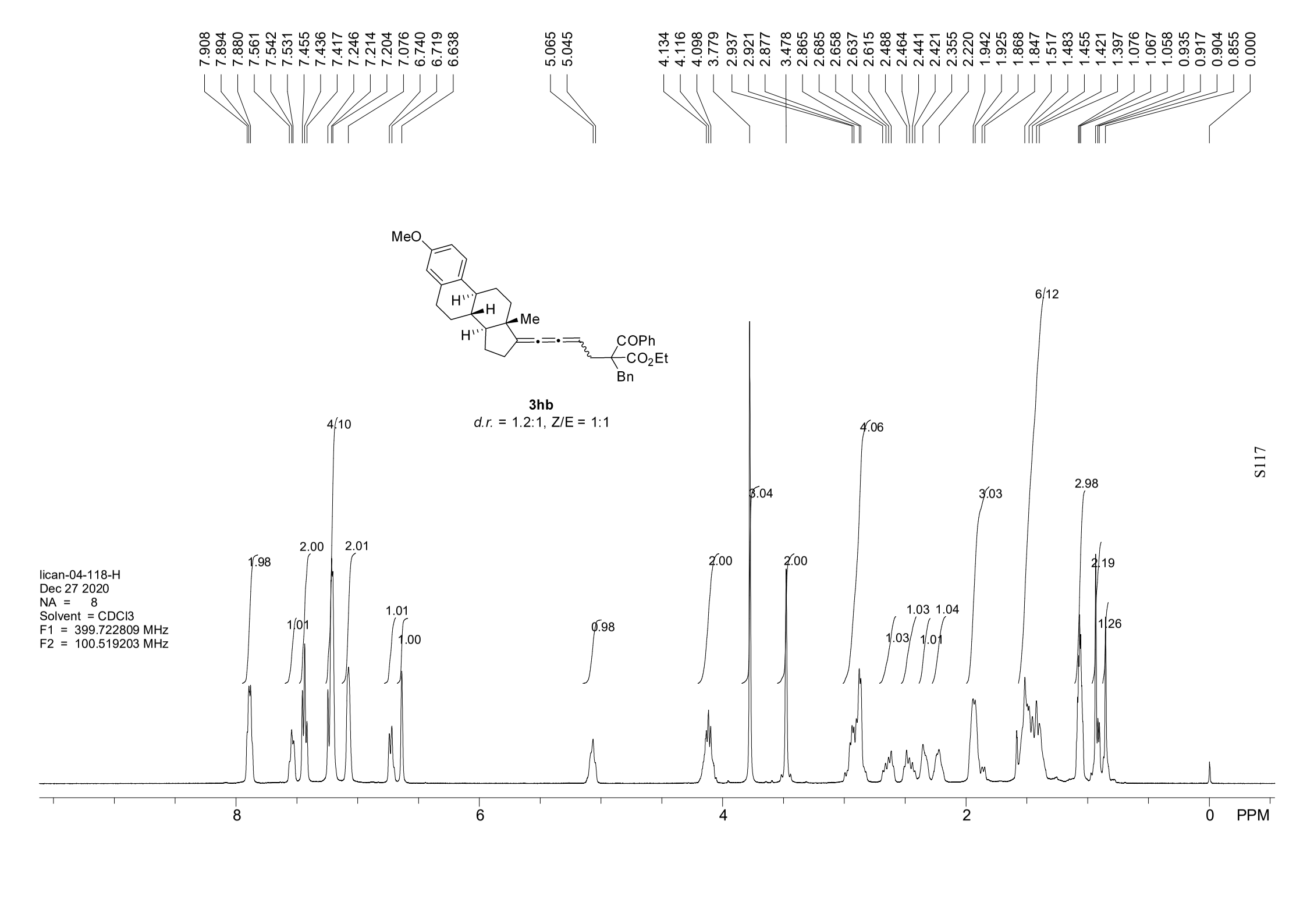

195.993
195.863
172.305
172.267
164.322
164.008
153.995
153.719
136.144
136.037
135.937
135.899
132.666
132.589
130.314
130.260
128.452
128.031
127.985
126.798
126.767
125.940
125.809
95.356
95.241
77.322
77.000
76.686
62.482
62.375
61.348
45.237
45.122
38.395
38.380
35.990
35.545
31.669
31.623
31.585
26.253
26.168
26.061
26.030
21.326
21.273
13.658
13.642
COPh
Bn
CO2Et
3fb, Z/E = 1:1
lican-04-095-C
ec
NA = 800
Solvent = CDCl3
F1 = 100.605331 MHz
F2 = 1.000000 MHz
1.00
1.02
2.97
2.96
2.06
2.03
3.02
2.93
S112
200
150
100
50
0
PPM

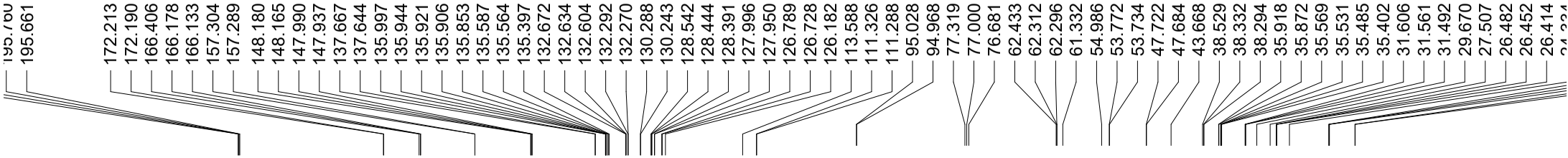

8.190
8.185
8.123
8.117
8.101
8.095
7.077
7.054
5.142
5.122
5.102
4.259
4.242
4.224
4.206
3.941
3.925
2.962
2.925
2.916
2.905
2.898
2.861
2.726
2.241
2.225
2.208
2.191
2.167
2.149
2.132
2.114
2.096
1.607
1.239
1.222
1.204
1.111
1.095
1.064
1.046
1.028
0.998
0.980
0.961
0.000
3gt
+
4gt
3gt/4gt = 99/1
lican-04-063-H
o
NA = 16
Solvent = CDCl3
F1 = 400.200012 MHz
F2 = 1.000000 MHz
0.93
1.01
1.00
0.01
0.98
2.01
1.99
1.98
2.97
5.15
2.96
3.23
3.23
3.04
5.98
S113
8
6
4
2
0
PPM

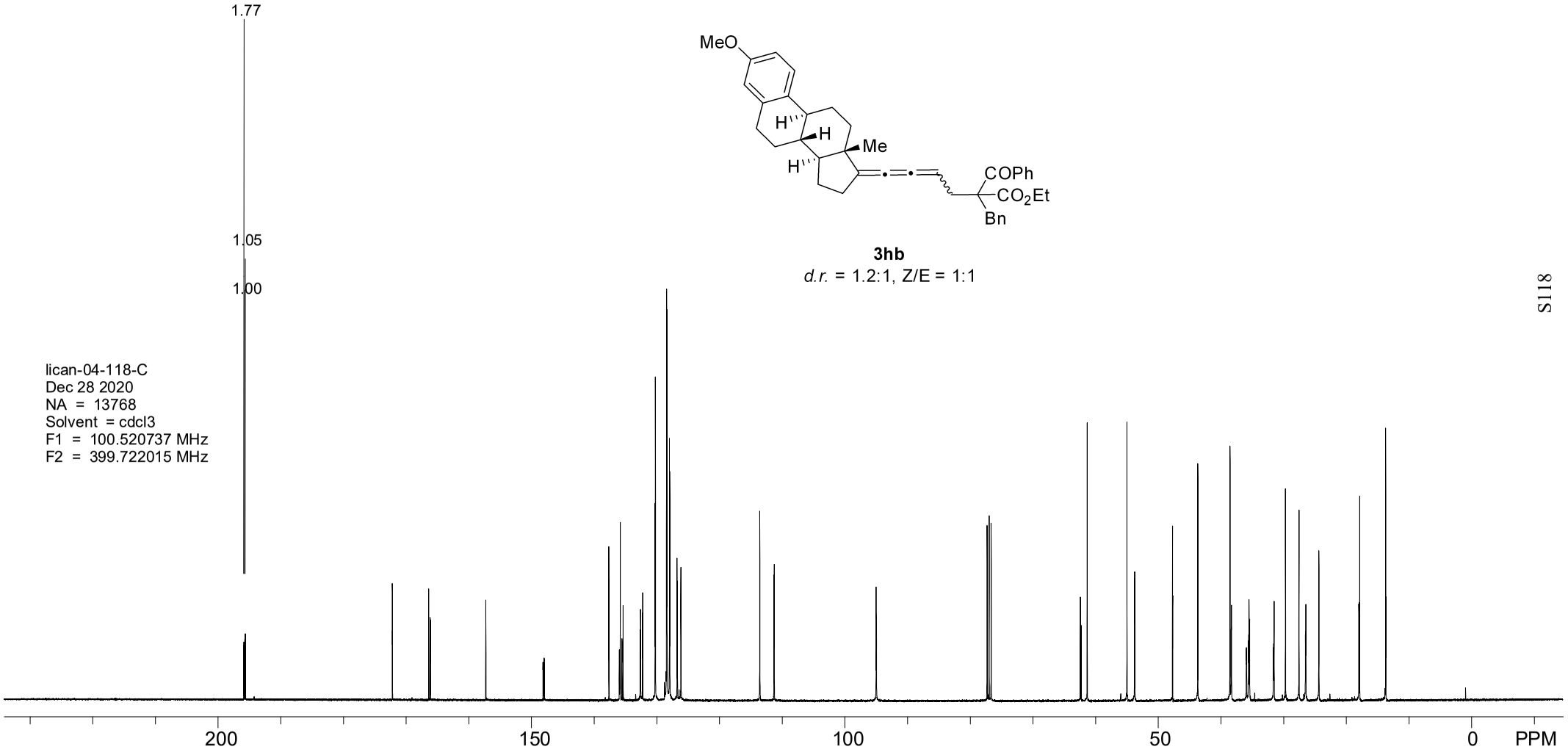

lican-04-063-C
o
NA = 46
Solvent = CDCl3
F1 = 100.630371 MHz
F2 = 1.000000 MHz
3gt/4gt = 99/1
4gt
+
3gt
190.158
172.189
165.732
165.717
162.730
162.301
152.474
132.399
131.764
128.700
125.789
125.238
114.975
112.447
102.620
94.570
77.322
77.000
76.686
75.361
61.498
59.598
39.500
29.091
28.953
27.851
20.161
18.721
18.445
13.689
11.797
11.674
200
150
100
50
0
PPM


7.231 7.204 7.190 7.170 6.708 6.626 6.147 6.121 6.101 6.078 6.056 5.379 5.367 5.335 5.328 5.215 5.195 5.176 5.141 5.122 5.102 5.040 5.018 4.992 4.204 4.185 4.166 3.747 3.314 2.860 2.734 2.715 2.696 2.655 2.546 2.517 2.497 2.390 2.350 2.229 2.075 2.056 1.947 1.589 1.568 1.542 1.520 1.495 1.471 1.444 1.423 1.260 1.242 1.225 0.953 0.919 0.000
MeO
H
H
Me
CO2Et
CO2Et
Bn
3hu
Z/E = 1:1
4hu
3hu/4hu = 97/3
6.11
1.02
1.01
0.03
0.48
0.49
0.0
0.0
4.00
3.05
1.94
2.08
2.95
1.09
1.06
1.05
3.04
6.24
6.09
3.11
lican-04-156
Jan 18 2021
NA = 12
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
8
6
4
2
0
PPM
S115


170.436
170.397
166.161
165.969
157.381
157.366
148.295
148.119
137.653
135.999
135.968
135.309
135.125
132.329
132.298
130.123
128.054
128.016
126.798
126.744
126.162
113.651
111.345
111.330
95.532
95.463
77.322
77.000
76.686
61.187
61.149
59.119
58.958
54.982
53.879
53.863
47.750
47.696
43.720
38.587
37.553
37.461
35.768
35.553
35.109
34.618
31.577
31.562
29.669
27.532
26.513
26.444
24.375
17.986
17.856
13.956
13.933
MeO
H
H
Me
H
CO2Et
CO2Et
Bn
+
MeO
H
H
Me
H
Bn
CO2Et
CO2Et
3hu
Z/E = 1:1
4hu
3hu/4hu = 97/3
1.34
1.33
1.01
1.00
lican-04-156-C
Jan 18 2020
NA = 10000
Solvent = CDCl3
F1 = 100.605225 MHz
F2 = 1.000000 MHz
150
100
50
0 PPM

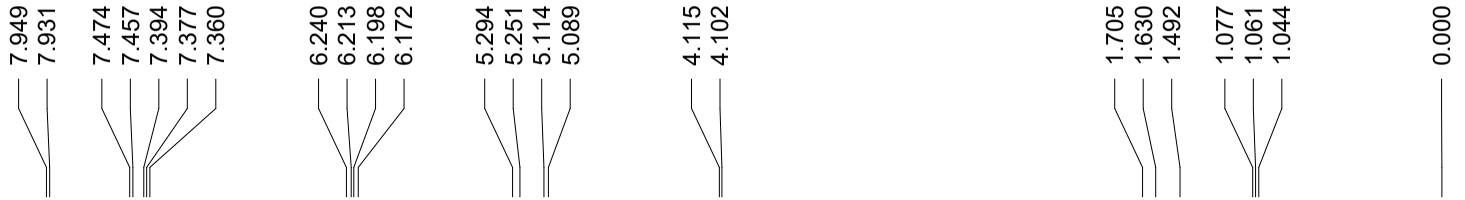

7.908
7.894
7.880
7.561
7.542
7.531
7.455
7.436
7.417
7.246
7.214
7.204
7.076
6.740
6.719
6.638
5.065
5.045
4.134
4.116
4.098
3.779
2.937
2.921
2.877
3.478
2.865
2.685
2.658
2.637
2.615
2.488
2.464
2.441
2.421
2.355
2.220
1.942
1.925
1.868
1.847
1.517
1.483
1.455
1.421
1.397
1.076
1.067
1.058
0.935
0.917
0.904
0.855
0.000
MeO
H
H
Me
H
COPh
CO2Et
Bn
3hb
d.r. = 1.2:1, Z/E = 1:1
lican-04-118-H
Dec 27 2020
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
1.98
1.01
2.00
4.10
2.01
1.01
1.00
0.98
2.00
3.04
2.00
4.06
1.03
1.03
1.04
1.01
3.03
6.12
2.98
2.19
1.26
S117
8
6
4
2
0
PPM

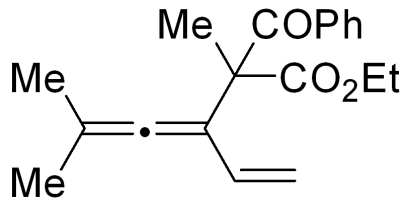




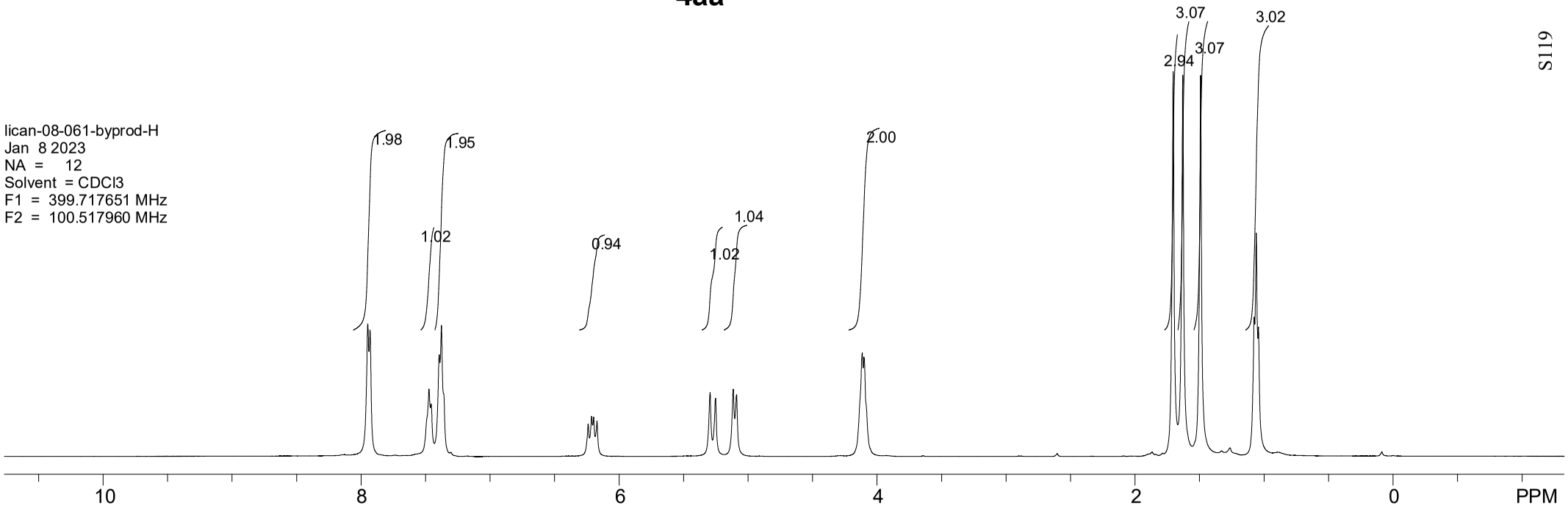
3hb

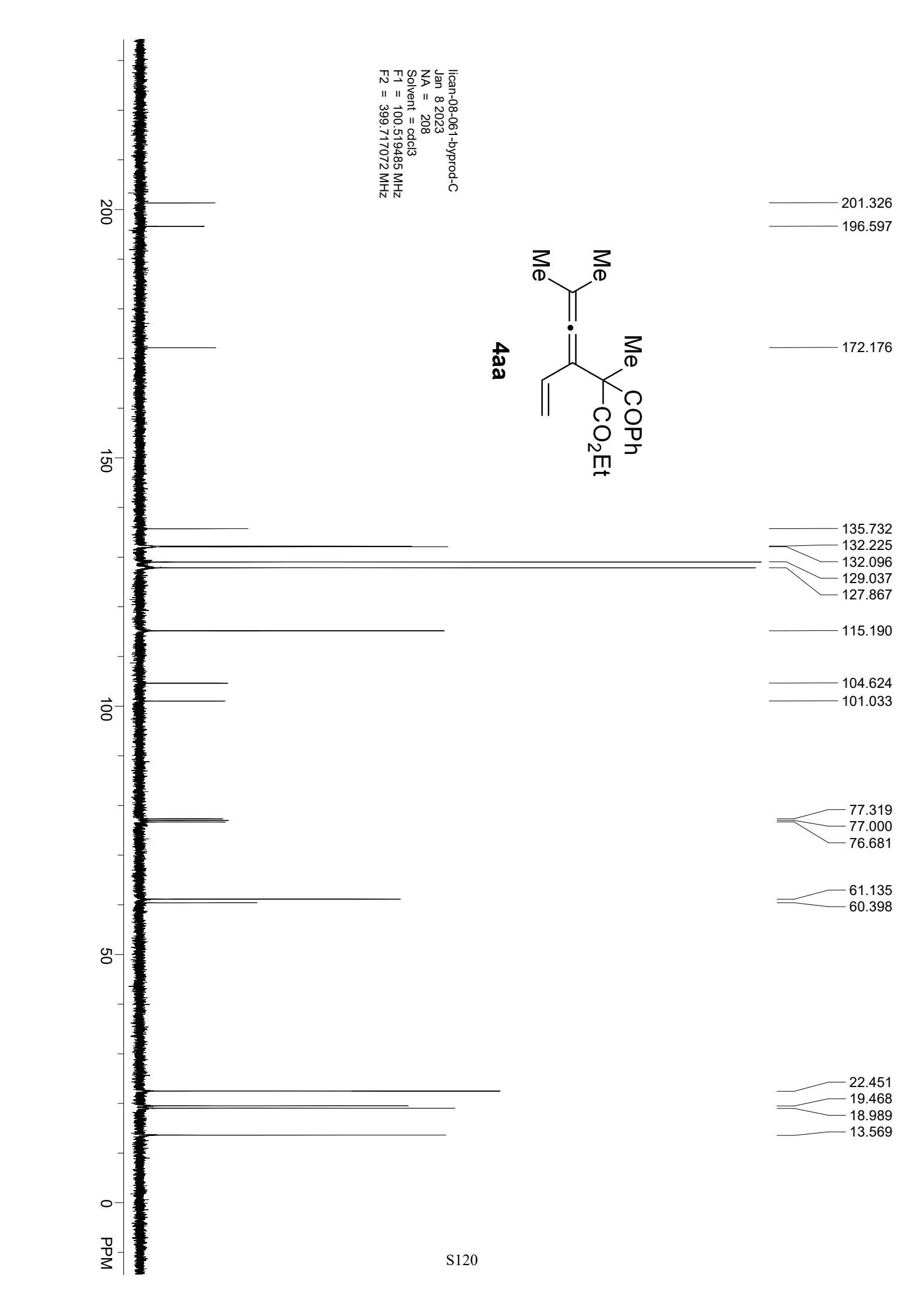
d.r. = 1.2:1, Z/E = 1:1


7.949
7.931
7.474
7.457
7.394
7.377
7.360
6.240
6.213
6.198
6.172
5.294
5.251
5.114
5.089
4.115
4.102
1.705
1.630
1.492
1.077
1.061
1.044
0.000


Me
COPh
Me
CO2Et
Me

4aa


lican-08-061-byprod-H
Jan 8 2023
NA = 12
Solvent = CDCl3
F1 = 399.717651 MHz
F2 = 100.517960 MHz
1.98
1.95
1.02
0.94
1.02
1.04
2.00
3.07
2.94
3.07
3.02
10
8
6
4
2
0
PPM


lican-08-061-byprod-C
Jan 8 2023
NA = 208
Solvent = cdcl3
F1 = 100.519485 MHz
F2 = 399.717072 MHz
Me
Me
Me
COPh
CO2Et
4aa
201.326
196.597
172.176
135.732
132.225
132.096
129.037
127.867
115.190
104.624
101.033
77.319
77.000
76.681
61.135
60.398
22.451
19.468
18.989
13.569
200
150
100
50
0
PPM