# Palladium-Catalyzed Approach to Allenic Aromatic Ethers and First Total Syntheses of Terricollene A

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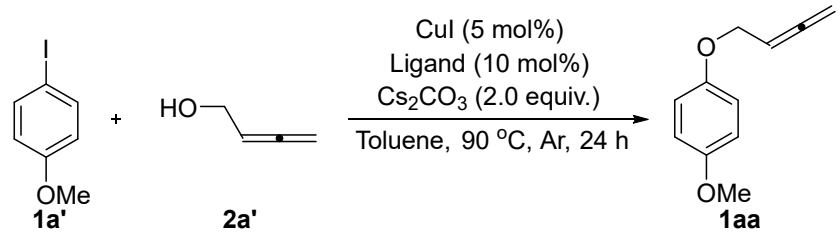
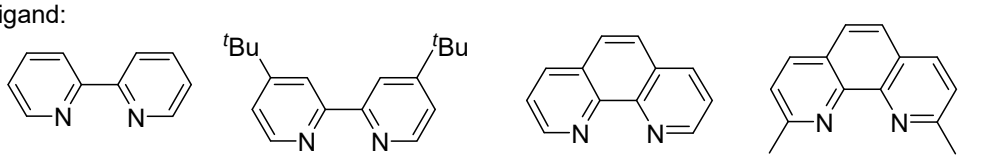
**General Information.** NMR spectra were taken with a Bruker-400 spectrometer (400 MHz for $^{1}H$ NMR; 100 MHz for $^{13}C$ NMR; 376 MHz for $^{19}F$ NMR) in $CDCl_3$. All $^{1}H$ NMR experiments were measured with tetramethylsilane (0 ppm) in $CDCl_3$ as the internal reference; $^{13}C$ NMR experiments were measured in relative to the signal of $CDCl_3$ (77.0 ppm); $^{19}F$ NMR experiments were measured in relative to the signal of $CFCl_3$ (0 ppm) in $CDCl_3$. All reactions were carried out in flame-dried Schlenk tubes. $Pd_2(dba)_3$ was purchased from Alfa Aesar (China) Chemical Co. Ltd.; Xantphos was purchased from J&K Chemicals; methyl (*E*)-3-(4-hydroxyphenyl)acrylate was purchased from Energy Chemical; Diethyl ether ($Et_2O$), ethyl *tert*-butyl ether (MTBE), and 1,4-dixoane were dried over sodium wire with benzophenone as the indicator and distilled freshly before use. Petroleum ether (60 ºC - 90 ºC) was used for chromatography. Recoveries of substrates were determined by $^{1}H$ NMR analysis using nitromethane as the internal standard.

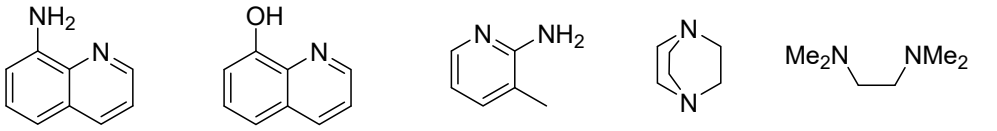
**Table S1. Optimization of the reaction condition** [a]




Ligand:



yield = 2%, recovery = 97% | yield = 2%, recovery = 98% | yield = 9%, recovery = 85% | yield = 2%, recovery = 87%

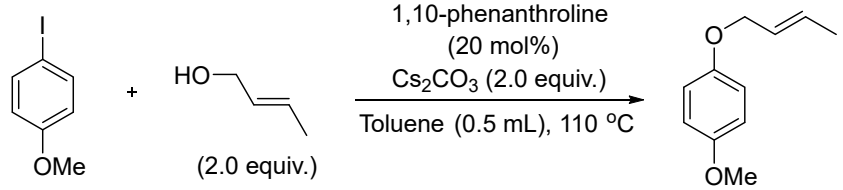


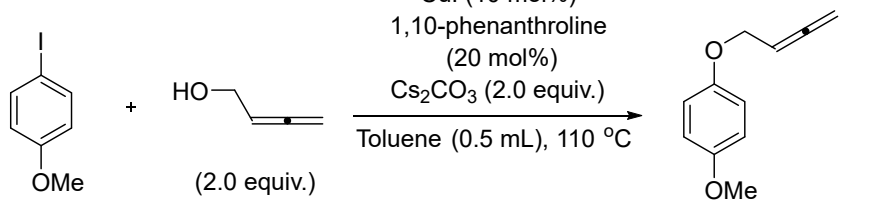
yield = 2%, recovery = 71% | yield = 7%, recovery = 84% | recovery = 100% | recovery = 98% | recovery = 99%

[a] Reaction condition: **1a** (0.2 mmol), **2a** (0.4 mmol), CuI (5 mol%), ligand (10 mol %), $Cs_2CO_3$ (2.0 equiv.), toluene (0.2 mL), 90 °C, 24 h; Yield and recovery of **1a'** were determined by $^1$H-NMR analysis using $CH_2Br_2$ as internal standard.

Buchwald's condition 1:[1]

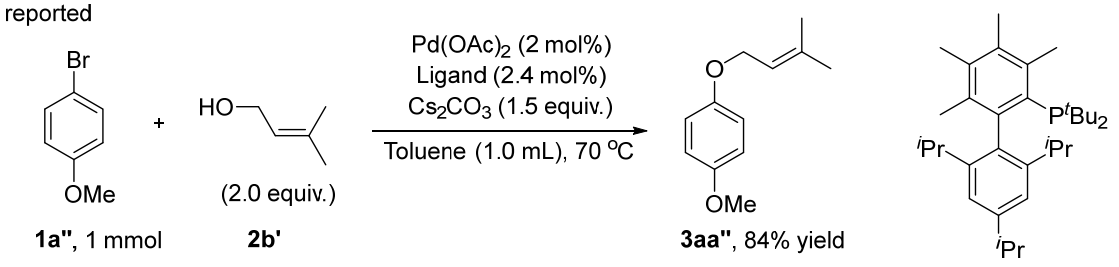
reported



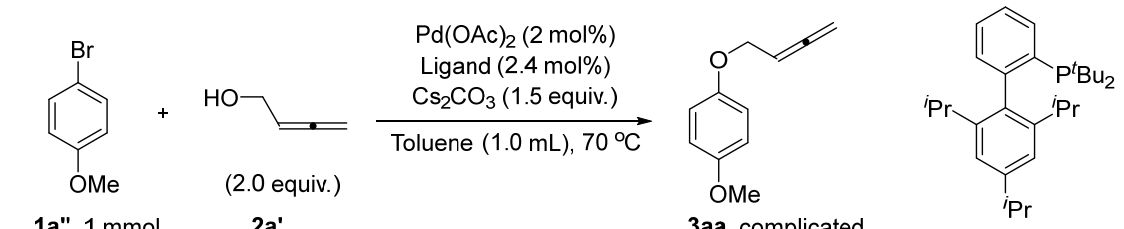



Buchwald's condition 2:[2]

reported



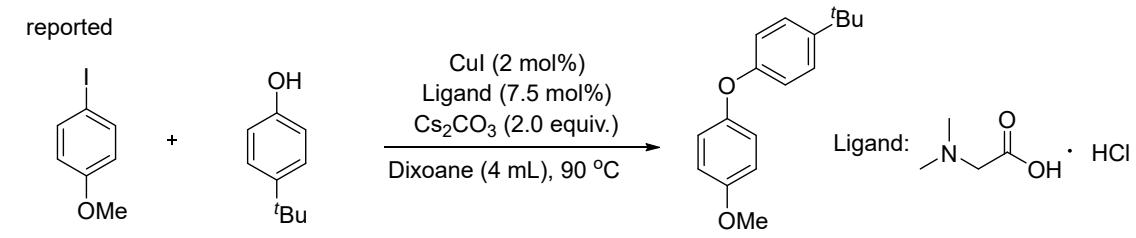

**1a''**, 1 mmol **2b'** **3aa''**, 84% yield Ligand:



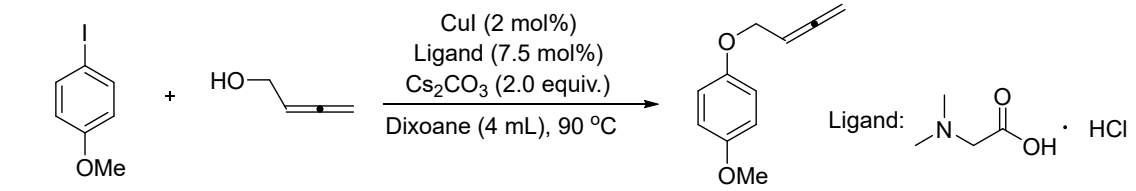

**1a''**, 1 mmol **2a'** **3aa**, complicated Ligand:

Ma's condition:[3]

reported




**1a'**, 2 mmol **1a'''** (1.5 equiv.) **3aa'''**, 82% yield

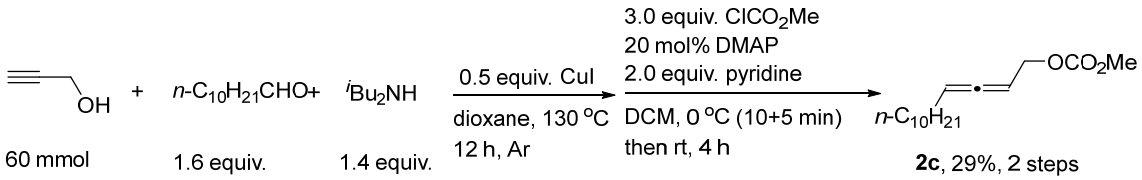



**1a',** 1 mmol **2a'** (1.5 equiv.) **3aa,** 2% yield recovery of **1a'** = 98%

**Experimental details and analytical data**

**1. Synthesis of allenylic carbonates**

**(1) Preparation of methyl 2,3-tetradecadienyl carbonate (2c) (hcf-4-139) [4]**

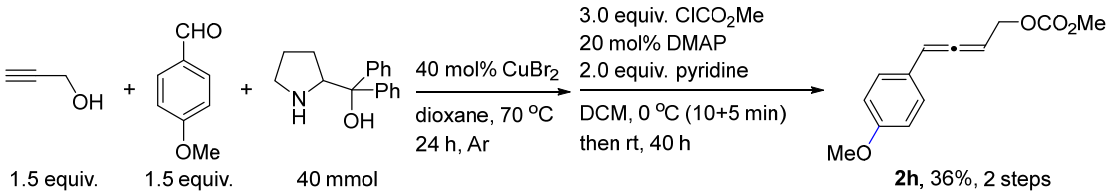



**Typical Procedure I**: To an oven-dried Schlenk tube with a reflux condenser, CuI (5.714 g, 30 mmol), 1-undecanal (19.8 mL, d = 0.825 g/mL, 16.335 g, 96 mmol), diisobutylamine (15.0 mL, d = 0.74 g/mL, 11.1 g, 84 mmol), 2-propyn-1-ol (3.50 mL, d = 0.963 g/mL, 3.3705 g, 60 mmol), and dioxane (30 mL) were sequentially added under argon atmosphere. After being stirred in an oil bath preheated at 130 °C for 12 h, the reaction was complete as monitored by TLC. After cooling to room temperature, the resulting mixture was filtrated through a short pad of celite eluted with $Et_2O$ (20 mL × 3). The filtrate was washed with an aqueous solution of hydrochloric acid (2 M, 40 mL × 3). The organic layer was washed with brine (40 mL) and dried over anhydrous $Na_2SO_4$. After filtration and evaporation, the residue was purified by chromatography on silica gel to afford tetradeca-2,3-dien-1-ol (5.7272 g) as an oil [eluent: petroleum ether/ethyl acetate = 80:1 (400 mL), 60/1 (1800 mL)], which was used in the next step without further purification.

**Typical Procedure II**: To a round bottom flask were added DMAP (662.9 mg, 5.4 mmol), tetradeca-2,3-dien-1-ol (5.7272 mg, 27 mmol), pyridine (4.3 mL, d = 0.983 g/mL, 4.2269 g, 54 mmol), and DCM (100 mL) sequentially. After the resulting mixture was stirred at 0 °C with an ice-water bath for 10 min, methyl chloroformate (6.3 mL, d = 1.22 g/mL, 7.686 g, 81 mmol) was added dropwise over 5 min. After the addition, the resulting mixture was removed from the cooling bath and allowed to warm up to room temperature gradually. The reaction was complete after being stirred at room temperature for 4 h as monitored by TLC. The resulting mixture was quenched with an aqueous solution of hydrochloric acid (1 M, 60 mL). The organic layer was separated and the aqueous layer was extracted with DCM (30 mL) for three

times. The combined organic layer was washed with brine (40 mL) and dried over anhydrous $Na_2SO_4$. After filtration and evaporation, the residue was purified by flash chromatography on silica gel to afford **2c** (4.6373 g, overall yield of two steps: 29%) as an oil [eluent: petroleum ether/DCM = 20:1 (2000 mL)]: **$^1$H NMR** (400 MHz, CDCl3): δ = 5.34-5.19 (m, 2 H, 2 x =CH), 4.67-4.52 (m, 2 H, $OCH_2$), 3.78 (s, 3 H, $OCH_3$), 2.07-1.94 (m, 2 H, $CH_2$), 1.48-1.06 (m, 16 H, 8 x $CH_2$), 0.88 (t, *J* = 6.6 Hz, 3 H, $CH_3$); **$^{13}$C NMR** (100 MHz, CDCl3): δ = 205.7, 155.6, 93.1, 86.4, 66.4, 54.7, 31.9, 29.6, 29.4, 29.3, 29.0, 28.9, 28.2, 22.6, 14.0; **MS** (ESI) *m/z* : 291 $(M+Na)^+$, 286 $(M+NH_4)^+$; **IR** (neat): ν = 2955, 2923, 2854, 1966, 1749, 1444 $cm^{-1}$; **HRMS** calcd for $C_{16}H_{29}O_3$ $[M+H]^+$: 269.2111, found: 269.2111.

**(2) Preparation of methyl 4-(4-methoxyphenyl)buta-2,3-dienyl carbonate (2h) (lj-4-176)** [5]

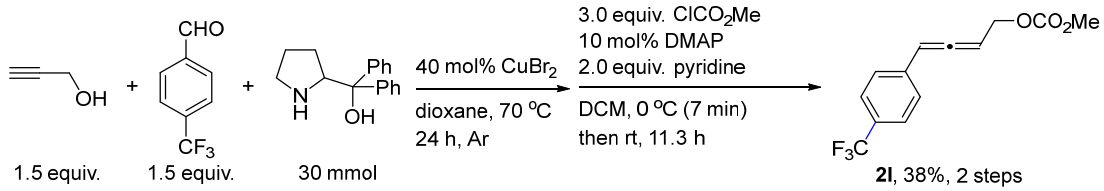



**Typical Procedure III**: To an oven-dried Schlenk tube with a polytetrafluoroethylene plug were added diphenylprolinol (10.1342 g, 40 mmol) and $CuBr_2$ (3.5736 g, 16 mmol, in glove box). After replacing air with argon for three times at rt under vacuum, 4-methoxybenzaldehyde (7.3 mL, d = 1.121 g/mL, 8.1833 g, 60 mmol), 2-propyn-1-ol (3.5 mL, d = 0.963 g/mL, 3.3705 g, 60 mmol), and dioxane (15.0 mL) were added sequentially. The Schlenk tube was then sealed by screwing the polytetrafluoroethylene plug tightly. After being vigorously stirred in an oil bath preheated at 70 °C for 24 h, the reaction was complete as monitored by TLC and the resulting mixture was diluted with $Et_2O$ (100.0 mL) and washed with an aqueous solution of hydrochloric acid (2 M, 100.0 mL). The organic layer was separated and the aqueous layer was extracted with $Et_2O$ (100.0 mL) for three times. The combined organic layer was washed with brine (100 mL) and dried over anhydrous $Na_2SO_4$. After removal of the solvent under vacuum, the residue was purified by flash

chromatography on silica gel to afford 4-(4-methoxyphenyl)-2,3-butadien-1-ol (4.4054 g) [eluent: petroleum ether/ethyl acetate = 40:1 (820 mL), 5/1 (960 mL)] as an oil, which was used in the next step without further purification.

**Following Typical Procedure II**, the reaction of DMAP (611.2 mg, 5.0 mmol), pyridine (4.0 mL, d = 0.983 g/mL, 3.9550 g, 50 mmol), DCM (80 mL), and methyl chloroformate (5.8 mL, d = 1.223 g/mL, 7.0871 g, 75 mmol) afforded **2h** (2.1803 g, overall yield of two steps: 36%) as an oil [eluent: petroleum ether/DCM = 20:1 (420 mL), 10/1 (1760 mL), 5/1 (480 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.8 Hz, 2 H, Ar-H), 6.85 (d, *J* = 8.8 Hz, 2 H, Ar-H), 6.32-6.24 (m, 2 H, =CH), 5.71 (q, *J* = 6.5 Hz, 1 H, =CH), 4.80-4.60 (m, 2 H, $OCH_2$), 3.86-3.70 (m, 6 H, 2 x $OCH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 206.2, 159.1, 155.5, 128.1, 125.3, 114.2, 96.1, 90.5, 65.5, 55.3, 54.8; **IR** (neat): ν = 3003, 2955, 2840, 1952, 1746, 1695, 1604, 1510, 1447, 1367, 1244, 1171, 1109, 1028 $cm^{-1}$; **MS** (70 eV, EI) *m/z* (%): 234 ($M^+$, 58.07), 115 (100); **HRMS** calcd. for $C_{13}H_{14}O_4$ [$M^+$]: 234.0887, found 234.0882.

**(3) Preparation of methyl 4-(4-trifluoromethylphenyl)buta-2,3-dienyl carbonate (2l) (whn-2-192)** [5]

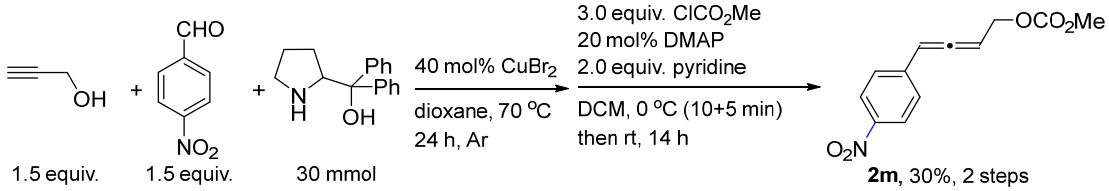



Following **Typical Procedure III**, the reaction of diphenylprolinol (10.1351 g, 40 mmol), $CuBr_2$ (3.5644 g, 16 mmol), 4-trifluoromethylbenzaldehyde (10.6746 g, 60 mmol), 2-propyn-1-ol (3.5217 g, 45 mmol), and dioxane (120 mL) afforded 4-(4-trifluoromethylphenyl)-2,3-butadien-1-ol (3.4391 g) [eluent: petroleum ether/ethyl acetate = 10:1 (440 mL), 5:1 (960 mL), 2:1 (300 mL),] as a yellow solid, which was used in the next step without further purification.

Following **Typical Procedure II**, the reaction of 4-(4-(trifluoromethyl)phenyl)buta-2,3-dien-1-ol (2.1680 g, 10 mmol), DMAP (0.2462 g, 2.0 mmol), pyridine (1.6 mL, d = 0.983 g/mL, 1.5728 g, 20 mmol), DCM (20 mL),

and methyl chloroformate (2.5 mL, d = 1.223 g/mL, 2.8350 g, 30 mmol) afforded **2l** (2.208 g, overall yield of two steps: 38%) as an oil [eluent: petroleum ether/ethyl acetate = 10/1 (550 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.39 (d, *J* = 8.0 Hz, 2 H, Ar-H), 6.25-6.75 (m, 1 H, =CH), 5.81 (q, *J* = 6.5 Hz, 1 H, =CH), 4.65-4.85 (m, 2 H, $CH_2$), 3.78 (s, 3 H, $OCH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 207.2, 155.5, 137.1, 129.3 (q, *J* = 32.4 Hz), 127.2, 125.6 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 270.2 Hz), 96.0, 91.3, 64.7, 54.9; **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ = -63.0; **MS** (70eV, EI) *m/z* (%): 272 ($M^+$, 15.7), 59 (100); **IR** (neat): ν = 3007, 2960, 1956, 1747, 1616, 1441, 1323, 1255, 1107, 1065 $cm^{-1}$; **HRMS** calcd *m/z* for $C_{13}H_{11}F_3O_3$ [$M^+$]: 272.0655, found 272.0657.

**(4) Preparation of methyl 4-(4-nitrophenyl)buta-2,3-dienyl carbonate (2m) (hcf-4-135)** [5]

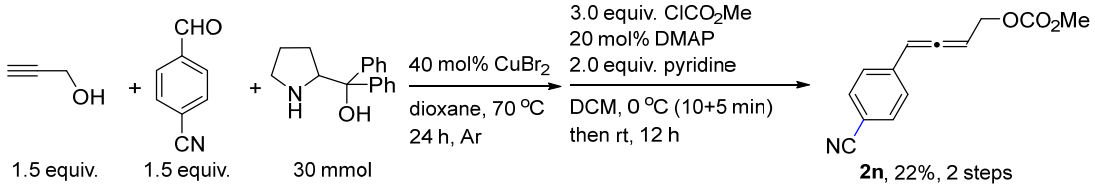



Following **Typical Procedure III**, the reaction of diphenylprolinol (7.6021 g, 30 mmol), $CuBr_2$ (2.6807 g, 12 mmol), 4-nitrobenzaldehyde (6.8032 g, 45 mmol), 2-propyn-1-ol (2.6 mL, d = 0.963 g/mL, 2.5038 g, 45 mmol), and dioxane (90 mL) afforded 4-(4-nitrophenyl)-2,3-butadien-1-ol (3.0856 g) [eluent: petroleum ether/ethyl acetate = 5:1 (1 L), 2:1 (1 L)] as an oil, which was used in the next step without further purification.

Following **Typical Procedure II**, the reaction of 4-(4-(nitromethyl)phenyl)buta-2,3-dien-1-ol (3.0856 g, 16 mmol), DMAP (0.3929 g, 3.2 mmol), pyridine (2.6 mL, d = 0.983 g/mL, 2.5558 g, 32 mmol), DCM (20 mL), and methyl chloroformate (3.7 mL, d = 1.223 g/mL, 4.514 g, 48 mmol) afforded **2m** (2.2435 g, overall yield of two steps: 30%) as a white solid [eluent: petroleum ether/ethyl acetate = 10/1 (550 mL)]: m.p. 63.9-64.3 °C (petroleum ether/DCM); **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.43 (d, *J* = 8.8 Hz, 2 H, Ar-H), 6.44-6.35 (m, 1 H, =CH), 5.87 (t, *J* = 6.5 Hz, 1 H, =CH), 4.85-4.67 (m, 2 H,

$OCH_2$), 3.79 (s, 3 H, $OCH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 207.9, 155.4, 146.8, 140.4, 127.4, 124.0, 95.7, 91.7, 64.3, 54.9; **MS** (70 eV, EI) *m/z* (%): 250 ($M^+$+1, 1.95), 249 ($M^+$, 13.51), 115 (100); **IR** (neat): *ν* = 3077, 3011, 2960, 1950, 1741, 1593, 1508, 1446, 1248, 1105 $cm^{-1}$; **Anal. Calcd.** for $C_{12}H_{11}NO_5$: C 57.83, H 4.45; found C 57.93, H 4.28.

**(5) Preparation of methyl 4-(4-cyanophenyl)buta-2,3-dienyl carbonate (2n) (zy-5-79)** [5]

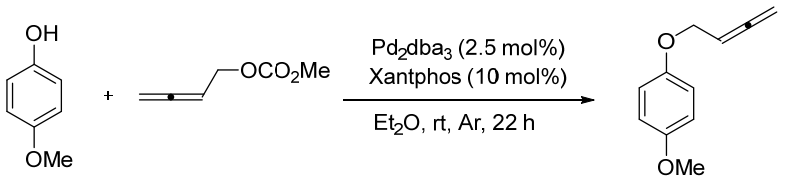



Following **Typical Procedure III**, the reaction of diphenylprolinol (7.7537 g, 30 mmol), $CuBr_2$ (2.6802 g, 12 mmol), 4-cyanobenzaldehyde (6.0217 g, 45 mmol), 2-propyn-1-ol (2.7 mL, d = 0.963 g/mL, 2.6001 g, 45 mmol), and dioxane (60 mL) afforded 4-(4-cyanophenyl)-2,3-butadien-1-ol (2.0390 g) [eluent: petroleum ether/ethyl acetate = 6:1 (980 mL), 2:1 (1.2 L)] as an oil, which was used in the next step without further purification.

Following **Typical Procedure II**, the reaction of 4-(4-cyanophenyl)buta-2,3-dien-1-ol (2.0289 g, 12.0 mmol), DMAP (0.2931 mg, 2.4 mmol), pyridine (1.9 mL, d = 0.983 g/mL, 1.8677 g, 24 mmol), DCM (24 mL), and methyl chloroformate (2.8 mL, d = 1.223 g/mL, 3.4244 g, 36 mmol) afforded **2n** (1.4969 g, overall yield of two steps: 22%) as an oil [eluent: petroleum ether/ethyl acetate = 10/1 (2750 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.39 (d, *J* = 8.0 Hz, 2 H, Ar-H), 6.39-6.31 (m, 1 H, =CH), 5.71 (q, *J* = 6.5 Hz, 1 H, =CH), 4.83-4.67 (m, 2 H, $CH_2$), 3.78 (s, 3 H, $OCH_3$), **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 207.2, 155.2, 138.2, 132.2, 127.3, 118.6, 110.4, 95.8, 91.5, 64.2, 54.7; **IR** (neat): ν = 2958, 2358, 2225, 1952, 1745, 1604, 1504, 1446, 1366, 1253, 1175, 1110 $cm^{-1}$; **MS** (70 eV, EI) *m/z* (%): 229 ($M^+$, 32.32), 154 (100); **HRMS** Calc *m/z* for $C_{13}H_{11}NO_3$ $[M]^+$: 229.0733, found 229.0736.

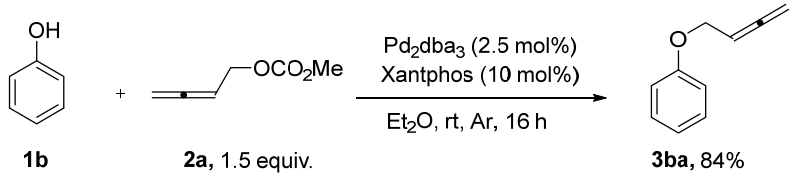
## 2. Synthesis of allenic aromatic ethers

### (1) Preparation of buta-2,3-dienyl 4-methoxyphenyl ether (3aa) (hcf-4-102)




**Typical Procedure IV**: To a flame-dried Schlenk tube were added $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1a** (124.1 mg, 1.0 mmol), **2a** (193.1 mg, 1.5 mmol), and $Et_2O$ (5 mL) sequentially under argon atmosphere. The resulting mixture was stirred at room temperature for 22 h. After the completion of the reaction as monitored by TLC, the resulting mixture was diluted with 3 mL of ethyl acetate, filtered through a short column of silica gel (3 cm), eluted with ethyl acetate (20 x 2 mL), and concentrated. The residue was purified by column chromatography on silica gel to afford **3aa**[6] (166.8 mg, 95%) as a white solid [eluent: petroleum ether/DCM = 200/1 (600 mL), 150/1 (300mL)]: m. p. 43.8-44.4 °C (petroleum ether/DCM); **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 6.91-6.77 (m, 4 H, Ar-H), 5.37 (quint, $J$ = 6.7 Hz, 1 H, =CH), 4.84 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.6 Hz, 2 H, $=CH_2$), 4.51 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.6 Hz, 2 H, $CH_2$), 3.76 (s, 3 H, $OCH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.4, 154.0, 152.4, 116.0, 114.6, 87.2, 76.3, 66.6, 55.7; **MS** (70 eV, EI) *m/z* (%): 177 ($M^+$+1, 2.79), 176 ($M^+$, 22.92), 109 (100); **IR** (neat): $\nu$ = 2954, 2923, 1957, 1506, 1381, 1223, 1179, 1033, 1014 $cm^{-1}$.

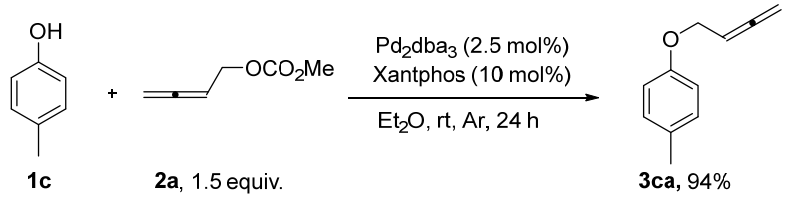
### (2) Preparation of buta-2,3-dienyl phenyl ether (3ba) (hcf-4-71)




Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1b** (94.1 mg, 1 mmol), **2a** (192.9 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3ba**[6] (122.4 mg, 84%) as an oil [eluent: petroleum ether/DCM = 150/1 (450 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.32-7.18 (m, 2 H, Ar-H), 6.99-6.77 (m, 3 H, Ar-H), 5.39 (quint, $J$ = 6.7 Hz, 1 H, =CH), 4.85 (dt, $J_1$ = 6.8 Hz, $J_2$

= 2.4 Hz, 2 H, =$CH_2$), 4.55 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.4, 158.3, 129.4, 120.9, 114.8, 87.1, 76.4, 65.7; **MS** (70 eV, EI) *m/z* (%): 147 ($M^+$+1, 1.15), 146 ($M^+$, 11.36), 94 (100); **IR** (neat): *ν* = 3062, 3040, 2930, 2871, 1957, 1598, 1494, 1238, 1213, 1030, 1011 $cm^{-1}$.

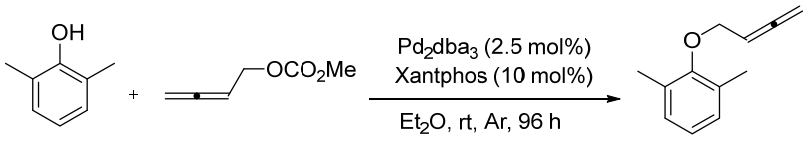
**(3) Preparation of buta-2,3-dienyl 4-methylphenyl ether (3ca) (hcf-4-107)**




**1c** **2a**, 1.5 equiv. **3ca,** 94%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1c** (108.2 mg, 1 mmol), **2a** (193.3 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3ca**[6] (150.5 mg, 94%) as an oil [eluent: petroleum ether/DCM = 200/1 (600 mL), 150/1 (150 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.07 (d, *J* = 8.4 Hz, 2 H, Ar-H), 6.81 (d, *J* = 8.4 Hz, 2 H, Ar-H), 5.38 (quint, *J* = 6.7 Hz, 1 H, =CH), 4.85 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 2 H, =$CH_2$), 4.54 (dt, $J_1$ = 7.2 Hz, $J_2$ = 2.6 Hz, 2 H, $CH_2$), 2.28 (s, 3 H, $CH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.4, 156.2, 130.2, 129.9, 114.8, 87.2, 76.4, 65.9, 20.4; **MS** (70 eV, EI) *m/z* (%): 161 ($M^+$+1, 2.3), 160 ($M^+$, 18.4), 108 (100); **IR** (neat): *ν* = 3030, 2922, 2865, 1956, 1508, 1235, 1212, 1175, 1016 $cm^{-1}$.

**(4) Preparation of buta-2,3-dienyl 2,6-dimethylphenyl ether (3da) (xjz-3-154)**

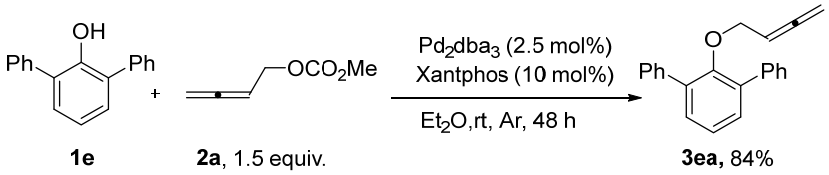



**1d** **2a**, 1.5 equiv. **3da,** 71%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (23.0 mg, 0.025 mmol), Xantphos (57.5 mg, 0.1 mmol), **1d** (122.0 mg, 1 mmol), **2a** (192.1 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3da** (123.7 mg, 71%) as an oil [eluent: petroleum ether (800 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 6.99 (d, *J* = 7.6 Hz, 2 H, Ar-H), 6.91 (dd, $J_1$ = 8.0 Hz, $J_2$ = 6.8 Hz, 1 H, Ar-H), 5.45 (quint, *J* = 6.8 Hz, 1 H, =CH), 4.82 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.5 Hz, 2 H, =$CH_2$), 4.33 (dt, $J_1$ = 7.2 Hz, $J_2$ = 2.4 Hz, 2 H, $CH_2$), 2.28 (s, 6 H, 2 x $CH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.4, 155.7, 131.0, 128.7, 123.9,

87.7, 76.0, 70.0, 16.4; **IR** (neat): $\nu$ = 2921, 1956, 1474, 1369, 1263, 1192, 1091 $cm^{-1}$; **MS** (70 eV, EI) *m/z* (%): 174 ($M^+$, 12.7), 122 (100); **HRMS** calcd for $C_{12}H_{14}O$ [$M^+$]: 174.1045, found: 174.1051.

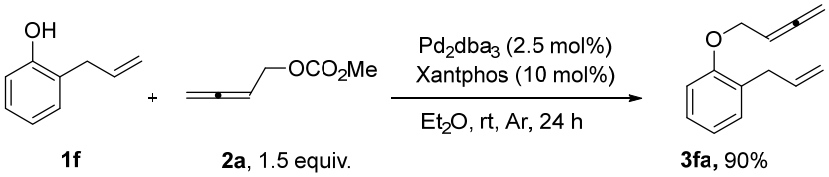
**(5) Preparation of buta-2,3-dienyl 2,6-diphenylphenyl ether (3ea) (cyf-3-90)**




**1e** **2a**, 1.5 equiv. **3ea,** 84%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (23.0 mg, 0.025 mmol), Xantphos (58.2 mg, 0.1 mmol), **1e** (168.3 mg, 1 mmol), **2a** (192.8 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3ea** (250.6 mg, 84%) as an oil [eluent: petroleum ether (800 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.64-7.58 (m, 4 H, Ar-H), 7.45-7.38 (m, 4 H, Ar-H), 7.37-7.30 (m, 4 H, Ar-H), 7.27-7.20 (m, 1 H, Ar-H), 4.69 (quint, $J$ = 6.9 Hz, 1 H, =CH), 4.48 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.2 Hz, 2 H, $=CH_2$), 3.77 (dt, $J_1$ = 6.4 Hz, $J_2$ = 2.2 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, CDCl3): δ = 209.1, 153.3, 138.7, 136.2, 130.1, 129.5, 128.1, 127.1, 124.4, 87.0, 75.2, 70.8; **MS** (70 eV, EI) *m/z* (%): 298 ($M^+$, 37.30), 246 (100); **IR** (neat) $\nu$ = 3056, 3027, 2931, 2866, 1954, 1737, 1598, 1573, 1496, 1460, 1440, 1416, 1367, 1313, 1275, 1199, 1157, 1119, 1072, 1029, 1012 $cm^{-1}$; **HRMS** calcd for $C_{22}H$ O ($M^+$): 298.1358. Found: 298.1366.

**(6) Preparation of buta-2,3-dienyl 2-allylphenyl ether (3fa) (hcf-4-85)**

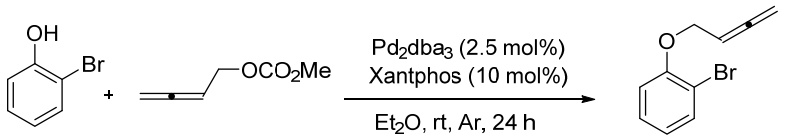



**1f** **2a**, 1.5 equiv. **3fa,** 90%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1f** (134.3 mg, 1 mmol), **2a** (193.2 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3fa** (167.8 mg, 90%) as an oil [eluent: petroleum ether /dichloromethane = 200/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.21-7.06 (m, 2 H, Ar-H), 6.96-6.78 (m, 2 H, Ar-H), 6.07-5.86 (m, 1 H, =CH), 5.38 (quint, $J$ = 6.6 Hz, 1 H, C=CH), 5.12-4.94 (m, 2 H, $CH_2$), 4.90-4.72 (m, 2 H, $=CH_2$), 4.62-4.46 (m, 2 H, $CH_2$), 3.40 (d, $J$ = 6.8 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.2,

156.0, 137.0, 129.9, 129.2, 127.2, 120.8, 115.3, 112.0, 87.4, 76.5, 65.9, 34.3; **MS** (70 eV, EI) *m/z* (%): 186 ($M^+$, 5.57), 145 (100); **IR** (neat): $\nu$ = 3076, 2978, 2915, 1957, 1600, 1588, 1490, 1453, 1236, 1218, 1014 $cm^{-1}$; **HRMS** calcd for $C_{13}H_{14}O$ [$M^+$]: 186.1039, found: 186.1043.

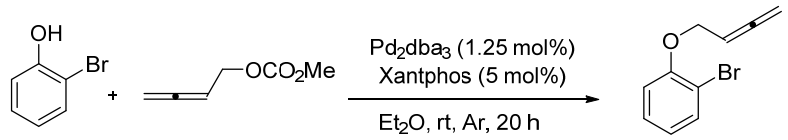
**(7) Preparation of buta-2,3-dienyl 2-bromophenyl ether (3ga) (hcf-4-89)**




**1g** **2a**, 1.5 equiv. **3ga**, 86%, 98% purity

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1g** (173.0 mg, 1 mmol), **2a** (193.1 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3ga** (197.7 mg, 86%, 98% purity) as an oil [eluent: petroleum ether/DCM = 200/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.53 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.4 Hz, 1 H, Ar-H), 7.29-7.18 (m, 1 H, Ar-H), 6.96-6.88 (m, 1 H, Ar-H), 6.84 (dt, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1 H, Ar-H), 5.41 (quint, $J$ = 6.7 Hz, 1 H, =CH), 4.87 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 2 H, $=CH_2$), 4.65 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.6 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.5, 154.8, 133.5, 128.3, 122.1, 114.0, 112.5, 86.8, 76.7, 67.0; **MS** (70 eV, EI) *m/z* (%): 226 ($M(^{81}Br)^+$, 3.31), 224 ($M(^{79}Br)^+$, 4.04), 53 (100); **IR** (neat): $\nu$ = 2988, 2883, 1956, 1587, 1572, 1474, 1281, 1215, 1009 $cm^{-1}$; **HRMS** calcd for $C_{10}H_9{}^{79}BrO$ [$M^+$]: 223.9831, found: 223.9830.

**Gram-scale synthesis of buta-2,3-dienyl 2-bromophenyl ether (3ga) (hcf-4-127)**

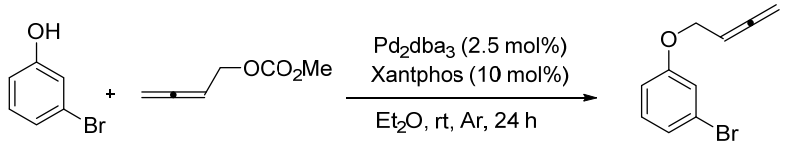



**1g**, 5 mmol **2a**, 1.25 equiv. **3ga**, 93%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (57.2 mg, 0.0625 mmol), Xantphos (144.8 mg, 0.25 mmol), **1g** (865.1 mg, 5 mmol), **2a** (800.9 mg, 6.25 mmol), and $Et_2O$ (20.0 mL) afforded **3ga** (1.0465 g, 93%) as an oil [eluent: petroleum ether/DCM = 80/1 (1000 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.53 (d, $J$ = 7.6 Hz, 1 H, Ar-H), 7.31-7.16 (m, 1 H, Ar-H), 6.92 (d, $J$ = 8.0 Hz, 1 H, Ar-H), 6.84 (t, $J$ = 7.6 Hz, 1 H, Ar-H), 5.41 (quint, $J$ = 6.5 Hz, 1 H, =CH), 4.93-4.75 (m, 2 H, $=CH_2$),

4.70-4.51 (m, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.5, 154.8, 133.5, 128.3, 122.1, 114.0, 112.5, 86.8, 76.7, 67.0.

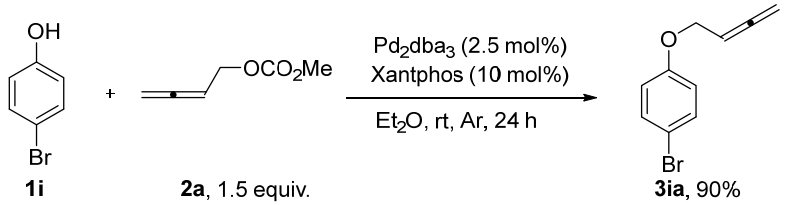
**(8) Preparation of buta-2,3-dienyl 3-bromophenyl ether (3ha) (hcf-4-88)**




**1h** **2a**, 1.5 equiv. **3ha,** 92%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1h** (173.1 mg, 1 mmol), **2a** (193.1 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3ha**[6] (206.8 mg, 90%) as an oil [eluent: petroleum ether/DCM = 200/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.18-6.96 (m, 3 H, Ar-H), 6.89-6.72 (m, 1 H, Ar-H), 5.36 (quint, $J$ = 6.7 Hz, 1 H, =CH), 4.87 (dt, $J_1$ = 6.4 Hz, $J_2$ = 2.4 Hz, 2 H, =$CH_2$), 4.54 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.6, 159.1, 130.5, 124.0, 122.7, 118.2, 113.9, 86.6, 76.7, 66.0; **MS** (70 eV, EI) *m/z* (%): 226 (M($^{81}$Br)$^+$, 1.78), 224 (M($^{79}$Br)$^+$, 1.88), 172 (100); **IR** (neat): $\nu$ = 3064, 2988, 2873, 1956, 1586, 1573, 1475, 1459, 1274, 1244, 1225, 1030 $cm^{-1}$.

**(9) Preparation of buta-2,3-dienyl 4-bromophenyl ether (3ia) (hcf-4-81)**

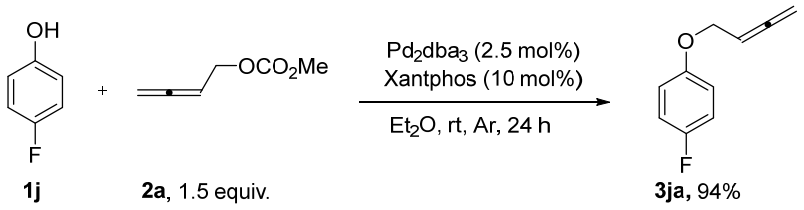



**1i** **2a**, 1.5 equiv. **3ia**, 90%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1i** (173.1 mg, 1 mmol), **2a** (193.1 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3ia** (202.7 mg, 90%) as an oil [eluent: petroleum ether /dichloromethane = 200/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.41-7.28 (m, 2 H, Ar-H), 6.83-6.66 (m, 2 H, Ar-H), 5.36 (quint, $J$ = 6.7 Hz, 1 H, =CH), 4.86 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.6 Hz, 2 H, =$CH_2$), 4.53 (dt, $J_1$ = 6.4 Hz, $J_2$ = 2.6 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.5, 157.4, 132.2, 116.7, 113.1, 86.8, 76.7, 66.0; **MS** (70 eV, EI) *m/z* (%): 226 (M($^{81}$Br)$^+$, 3.5), 224 (M($^{79}$Br)$^+$, 3.75), 53 (100); **IR** (neat): $\nu$ = 2930, 2873, 1956, 1589, 1578, 1461, 1284, 1235, 1219, 1171, 1072 $cm^{-1}$; **HRMS**

calcd for $C_{10}H_9{}^{79}BrO$ [$M^+$]: 223.9831, found: 223.9827.

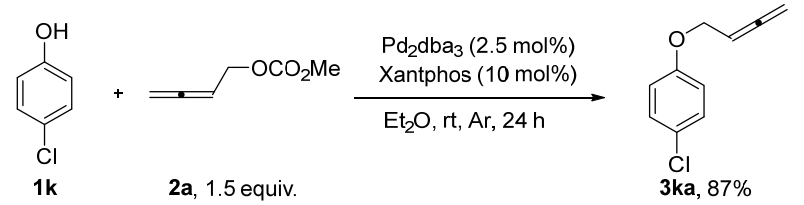
**(10) Preparation of buta-2,3-dienyl 4-fluorophenyl ether (3ja) (hcf-4-111)**




**1j** **2a**, 1.5 equiv. **3ja,** 94%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1j** (112.1 mg, 1 mmol), **2a** (193.4 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3ja** (154.3 mg, 94%) as an oil [eluent: petroleum ether /ethyl acetate = 200/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.02-6.88 (m, 2 H, Ar-H), 6.88-6.74 (m, 2 H, Ar-H), 5.36 (quint, *J* = 6.7 Hz, 1 H, =CH), 4.92-4.75 (m, 2 H, $=CH_2$), 4.60-4.39 (m, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.5, 157.4 (d, *J* = 237.0 Hz), 154.4 (d, *J* = 1.6 Hz), 116.0 (d, *J* = 7.9 Hz), 115.8 (d, *J* = 22.9 Hz), 87.0, 76.5, 66.5; **$^{19}$F NMR** (376 MHz, CDCl3): δ = -124.2; **MS** (70 eV, EI) *m/z* (%): 164 ($M^+$, 8.54), 112 (100); **IR** (neat): *v* = 2927, 1956, 1502, 1244, 1196, 1097, 1008 $cm^{-1}$; **HRMS** calcd for $C_{10}H_9OF$ [$M^+$]: 164.0632, found: 164.0634.

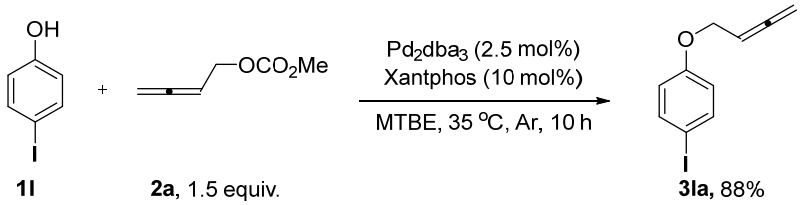
**(11) Preparation of buta-2,3-dienyl 4-chlorophenyl ether (3ka) (hcf-4-77)**




**1k** **2a**, 1.5 equiv. **3ka**, 87%

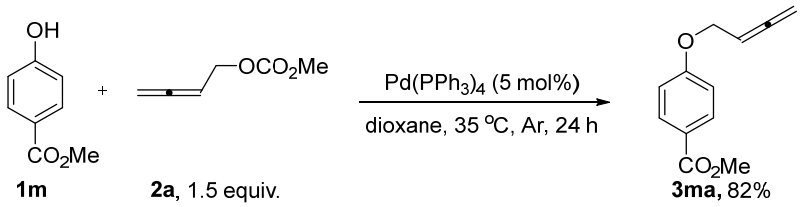
Following **Typical Procedure Iv**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1k** (128.4 mg, 1 mmol), **2a** (193.2 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3ka**[6] (156.9 mg, 87%) as an oil [eluent: petroleum ether /DCM = 150/1 (450 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.26-7.10 (m, 2 H, Ar-H), 6.87-6.74 (m, 2 H, Ar-H), 5.35 (quint, *J* = 6.7 Hz, 1 H, =CH), 4.86 (dt, $J_1$ = 6.4 Hz, $J_2$ = 2.6 Hz, 2 H, $=CH_2$), 4.52 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.5, 156.9, 129.3, 125.8, 116.2, 86.8, 76.6, 66.1; **MS** (70 eV, EI) *m/z* (%): 182 ($M(^{37}Cl)^+$, 1.17), 180 ($M(^{35}Cl)^+$, 3.56), 128 (100); **IR** (neat): *v* = 2930, 2874, 1956, 1596, 1581, 1488, 1237, 1218, 1170, 1091, 1004 $cm^{-1}$.

**(12) Preparation of buta-2,3-dienyl 4-iodophenyl ether (3la) (hcf-4-116)**



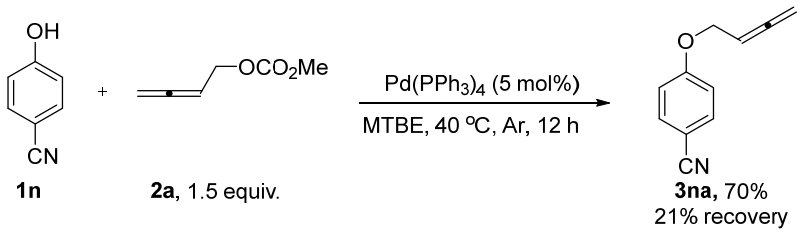

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1l** (220.1 mg, 1 mmol), **2a** (193.3 mg, 1.5 mmol), and MTBE (5.0 mL) at 35°C afforded **3la**[6] (239.2 mg, 88%) as an oil [eluent: petroleum ether/ethyl acetate = 200/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.8 Hz, 2 H, Ar-H), 6.69 (d, *J* = 8.8 Hz, 2 H, Ar-H), 5.35 (quint, *J* = 6.7 Hz, 1 H, =CH), 4.93-4.73 (m, 2 H, $=CH_2$), 4.57-4.40 (m, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.5, 158.2, 138.2, 117.3, 86.7, 83.0, 65.9; **MS** (70 eV, EI) *m/z* (%): 272 ($M^+$, 12.18), 220 (100); **IR** (neat): *v* = 3064, 2927, 2871, 1955, 1584, 1482, 1280, 1235, 1217, 1173 $cm^{-1}$.

**(13) Preparation of methyl 4-((buta-2,3-dienyl)oxy)benzoate (3ma) (hcf-5-77)**



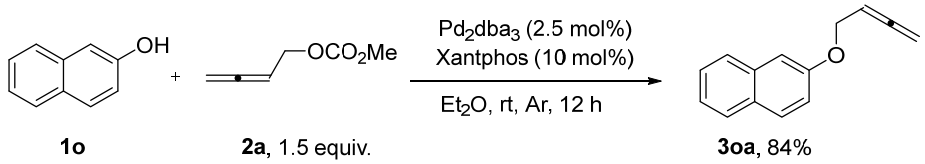

Following **Typical Procedure IV**, the reaction of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), **1m** (152.1 mg, 1 mmol), **2a** (193.0 mg, 1.5 mmol), and dioxane (5.0 mL) at 35°C afforded **3ma**[7] (167.4 mg, 82%) as a white solid [eluent: petroleum ether/ethyl acetate = 15/1 (500 mL)]: m. p. 42.1-42.7 °C (petroleum ether/ethyl acetate); **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.02-7.95 (m, 2 H, Ar-H), 6.96-6.89 (m, 2 H, Ar-H), 5.38 (quint, *J* = 6.7 Hz, 1 H, =CH), 4.92-4.84 (m, 2 H, $=CH_2$), 4.65-4.58 (m, 2 H, $CH_2$), 3.88 (s, 3 H, $OCH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.6, 166.8, 162.1, 131.5, 122.7, 114.4, 86.6, 76.8, 65.9, 51.8; **MS** (70 eV, EI) *m/z* (%): 204 ($M^+$, 4.33), 121 (100); **IR** (neat): *v* = 2958, 2876, 1958, 1719, 1603, 1507, 1430, 1280, 1247, 1231, 1169, 1106, 1010 $cm^{-1}$.

**(14) Preparation of buta-2,3-dienyl 4-cyanophenyl ether (3na) (hcf-6-65)**



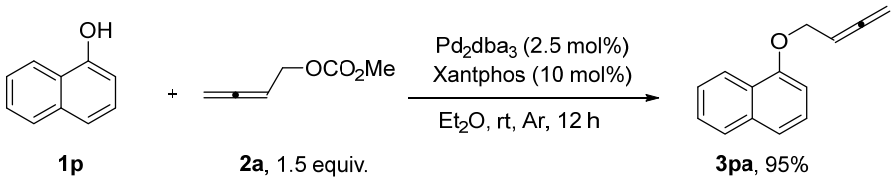

Following **Typical Procedure IV**, the reaction of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), **1n** (119.1 mg, 1 mmol), **2a** (192.3 mg, 1.5 mmol), and MTBE (5.0 mL) at 40°C afforded **3na** (119.8 mg, 70%) as an oil [eluent: petroleum ether/ethyl acetate = 15/1 (500 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.58 (dt, $J_1$ = 8.8 Hz, $J_2$ = 2.4 Hz, 2 H, Ar-H), 6.96 (dt, $J_1$ = 8.8 Hz, $J_2$ = 2.4 Hz, 2 H, Ar-H), 5.37 (quint, $J$ = 6.7 Hz, 1 H, =CH), 4.90 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.6 Hz, 2 H, $=CH_2$), 4.62 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.6, 161.6, 133.9, 119.1, 115.5, 104.1, 86.2, 77.0, 66.0; **MS** (70 eV, EI) *m/z* (%): 172 ($M^+$+1, 1.39), 171 ($M^+$, 12.52), 119 (100); **IR** (neat): $\nu$ = 3074, 2931, 2874, 2224, 1956, 1604, 1506, 1251, 1228, 1171 $cm^{-1}$; **HRMS** calcd for $C_{11}H_9NO$ [$M^+$]: 171.0679, found: 171.0675.

**(15) Preparation of buta-2,3-dienyl 2-naphthyl ether (3oa) (hcf-4-73)**




Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1o** (144.2 mg, 1 mmol), **2a** (193.2 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3oa** (164.7 mg, 84%) as a white solid [eluent: petroleum ether/DCM = 150/1 (450 mL)]: m. p. 60.6-61.4 °C (petroleum ether/DCM); **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.72 (q, $J$ = 8.7 Hz, 3 H, Ar-H), 7.41 (t, $J$ = 7.4 Hz, 1 H, Ar-H), 7.32 (t, $J$ = 7.4 Hz, 1 H, Ar-H), 7.19-7.01 (m, 2 H, Ar-H), 5.44 (quint, $J$ = 6.7 Hz, 1 H, =CH), 4.87 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 2 H, $=CH_2$), 4.66 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.6, 156.2, 134.4, 129.4, 129.0, 127.6, 126.8, 126.3, 123.7, 119.0, 107.3, 87.0, 76.5, 65.8; **MS** (70 eV, EI) *m/z* (%): 197 ($M^+$+1, 6.06), 196 ($M^+$, 38.8), 144 (100); **IR** (neat): $\nu$ = 3055, 2931, 1955, 1626, 1597, 1382, 1255, 1212, 1177 $cm^{-1}$; **Anal**. Calcd. for $C_{14}H_{12}O$: C 85.68, H 6.16; found C 85.67, H 6.06.

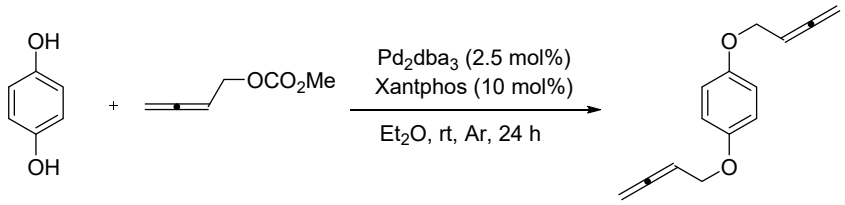
**(16) Preparation of buta-2,3-dienyl 1-naphthyl ether (3pa) (hcf-4-92)**




**1p** **2a**, 1.5 equiv. **3pa**, 95%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1p** (144.2 mg, 1 mmol), **2a** (193.4 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3pa** (187.4 mg, 95%) as an oil [eluent: petroleum ether /dichloromethane = 200/1 (400 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.34-8.17 (m, 1 H, Ar-H), 7.82-7.70 (m, 1 H, Ar-H), 7.52-7.26 (m, 4 H, Ar-H), 6.80 (d, $J$ = 7.6 Hz, 1 H, Ar-H), 5.50 (quint, $J$ = 6.6 Hz, 1 H, =CH), 4.89 (dt, $J_1$ = 6.4 Hz, $J_2$ = 2.8 Hz, 2 H, =$CH_2$), 4.73 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.6 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.4, 154.1, 134.5, 127.4, 126.4, 125.8, 125.7, 125.2, 122.1, 120.5, 105.2, 87.2, 76.6, 66.0; **MS** (70 eV, EI) *m/z* (%): 197 ($M^+$+1, 5.65), 196 ($M^+$, 24.78), 115 (100); **IR** (neat): $\nu$ = 3052, 2930, 2870, 1956, 1578, 1507, 1399, 1371, 1265, 1238, 1095 $cm^{-1}$; **HRMS** calcd for $C_{14}H_{12}O$ [$M^+$]: 196.0883, found: 196.0881.

**(17) Preparation of di(buta-2,3-dienyl) 1,4-phenylene ether (3qa) (hcf-4-93)**

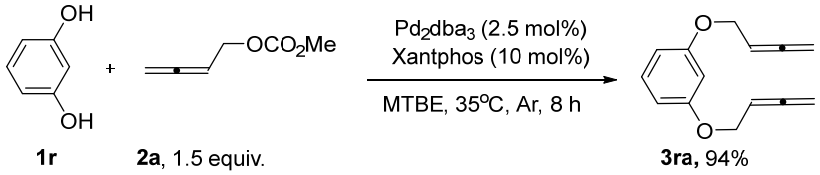



**1q** **2a**, 2.5 equiv. **3qa**, 91%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1q** (110.2 mg, 1 mmol), **2a** (320.9 mg, 2.5 mmol), and $Et_2O$ (5.0 mL) afforded **3qa** (195.7 mg, 91%) as a white solid [eluent: petroleum ether/DCM = 200/1 (400 mL), 150/1 (150 mL)]: m. p. 72.0-72.8 ℃ (petroleum ether/DCM); **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 6.84 (s, 4 H, Ar-H), 5.37 (quint, $J$ = 6.7 Hz, 2 H, =CH), 4.84 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 4 H, =$CH_2$), 4.52 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.6 Hz, 4 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.4, 152.7, 115.9, 87.2, 76.4, 66.5; **MS** (70 eV, EI) *m/z* (%): 215 ($M^+$+1, 1.48), 214 ($M^+$, 8.77), 53 (100); **IR** (neat): $\nu$ = 2923, 2871, 1956, 1505, 1462, 1382, 1219, 1016, 1002 $cm^{-1}$; **Anal**.

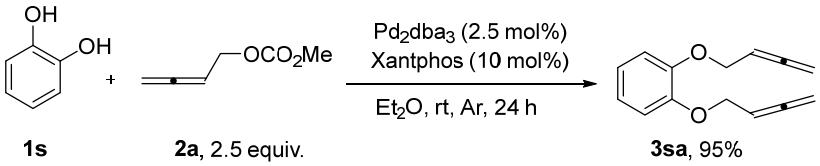
Calcd. for $C_{14}H_{12}O_2$: C 78.48, H 6.59; found C 78.25, H 6.36.

**(18) Preparation of di(buta-2,3-dienyl) 1,3-phenylene ether (3ra) (hcf-4-117)**



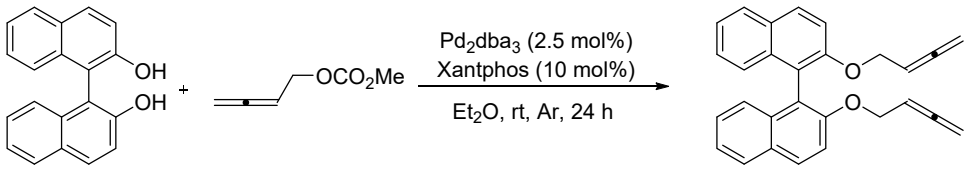

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1r** (110.1 mg, 1 mmol), **2a** (320.9 mg, 2.5 mmol), and MTBE (5.0 mL) at 35°C afforded **3ra** (201.2 mg, 94%) as an oil [eluent: petroleum ether/ethyl acetate = 150/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.15 (t, *J* = 8.0 Hz, 1 H, Ar-H), 6.62-6.37 (m, 3 H, Ar-H), 5.38 (quint, *J* = 6.6 Hz, 2 H, 2 x =CH), 4.98-4.75 (m, 4 H, 2 x =$CH_2$), 4.62-4.37 (m, 4 H, 2 x $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.4, 159.5, 129.8, 107.4, 102.2, 87.0, 76.4, 65.8; **MS** (70 eV, EI) *m/z* (%): 214 ($M^+$, 9.93), 53 (100); **IR** (neat): *v* = 2939, 2874, 1956, 1589, 1489, 1175, 1144, 1033 $cm^{-1}$; **HRMS** calcd for $C_{14}H_{14}O_2$ [$M^+$]: 214.0988, found: 214.0987.

**(19) Preparation of di(buta-2,3-dienyl) 1,2-phenylene ether (3sa) (hcf-4-96)**




Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1s** (110.1 mg, 1 mmol), **2a** (320.5 mg, 2.5 mmol), and $Et_2O$ (5.0 mL) afforded **3sa**[8] (202.8 mg, 95%) as an oil [eluent: petroleum ether/DCM = 150/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 6.99-6.80 (m, 4 H, Ar-H), 5.42 (quint, *J* = 6.7 Hz, 2 H, 2 x =CH), 4.83 (dt, $J_1$ = 6.4 Hz, $J_2$ = 2.4 Hz, 4 H, 2 x =$CH_2$), 4.64 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.6 Hz, 4 H, 2 x $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.5, 148.3, 121.4, 114.6, 87.3, 76.3, 66.9; **MS** (70 eV, EI) *m/z* (%): 214 ($M^+$, 4.7), 110 (100); **IR** (neat): *v* = 3064, 2933, 2868, 1956, 1592, 1498, 1246, 1203, 1122, 1006 $cm^{-1}$.

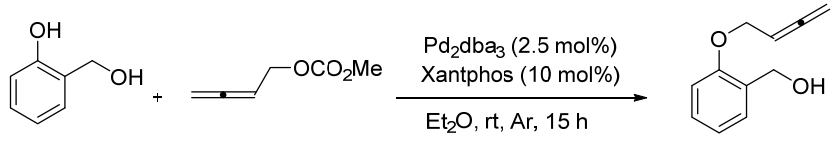
**(20) Preparation of di(buta-2,3-dienyl) 2,2'-[1,1'-binaphthalene]diyl ether (3ta) (hcf-4-110)**




**1t** **2a**, 2.5 equiv. **3ta,** 90%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1t** (286.3 mg, 1 mmol), **2a** (320.9 mg, 2.5 mmol), and $Et_2O$ (5.0 mL) afforded **3ta**[9] (351.2 mg, 90%) as an oil [eluent: petroleum ether/ethyl acetate = 150/1 (900 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.86 (dd, $J_1$ = 6.6 Hz, $J_2$ = 1.8 Hz, 4 H, Ar-H), 7.52-7.01 (m, 8 H, Ar-H), 5.03 (quint, $J$ = 6.6 Hz, 2 H, 2 x =CH), 4.77-4.38 (m, 8 H, 2 x $CH_2$ and 2 x =$CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.0, 153.7, 134.1, 129.4, 129.1, 127.8, 126.2, 125.5, 123.7, 120.8, 116.2, 87.6, 76.1, 67.3; **MS** (70 eV, EI) *m/z* (%): 391 ($M^+$+1, 20.78), 390 ($M^+$, 58.54), 268 (100); **IR** (neat): $\nu$ = 3056, 2988, 1954, 1590, 1505, 1259, 1212, 1015 $cm^{-1}$.

**(21) Preparation of buta-2,3-dienyl 2-(hydroxymethyl)phenyl ether (3ua) (hcf-4-72)**

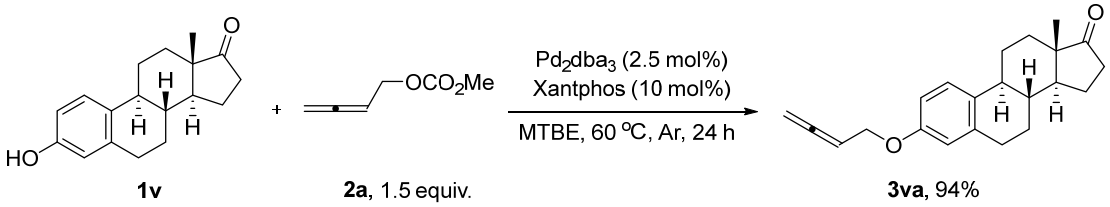



**1u** **2a**, 1.5 equiv. **3ua**, 93%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1u** (124.1 mg, 1 mmol), **2a** (192.9 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3ua** (163.3 mg, 93%) as an oil [eluent: petroleum ether /DCM = 10/1 (1000 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.33-7.13 (m, 2 H, Ar-H), 6.93 (t, $J$ = 7.4 Hz, 1 H, Ar-H), 6.86 (d, $J$ = 8.0 Hz, 1 H, Ar-H), 5.38 (quint, $J$ = 6.5 Hz, 1 H, =CH), 4.96-4.76 (m, 2 H, =$CH_2$), 4.67 (s, 2 H, $CH_2$), 4.63-4.48 (m, 2 H, $CH_2$), 2.61 (br, 1 H, OH); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.1, 156.2, 129.5, 128.72, 128.69, 120.9, 111.5, 87.0, 76.7, 65.3, 62.0; **MS** (70 eV, EI) *m/z* (%): 176 ($M^+$, 1.16), 78 (100); **IR** (neat): $\nu$ = 3372, 2929, 2874, 1956, 1602, 1589, 1489, 1454, 1232, 1217, 1005 $cm^{-1}$; **HRMS** calcd for $C_{11}H_{12}O_2Na$ [M+$Na^+$]: 199.0730, found: 199.0732.

**(22) Preparation of buta-2,3-dienyl**

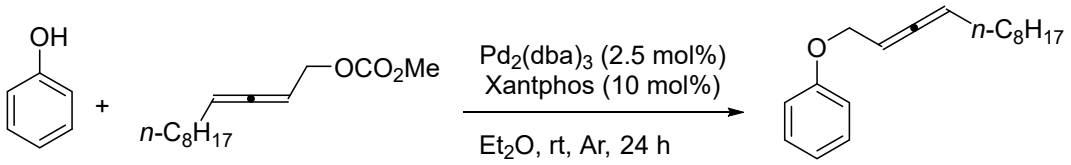
**(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl ether (3va) (hcf-4-101)**




**1v** **2a**, 1.5 equiv. **3va**, 94%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1v** (270.4 mg, 1 mmol), **2a** (193.4 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3va** (303.1 mg, 94%) as a white solid [eluent: petroleum ether/DCM = 150/1 (450 mL), 100/1 (600 mL)]: m. p. 86.7-87.2 °C (petroleum ether/DCM); **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.19 (d, $J$ = 8.8 Hz, 1 H, Ar-H), 6.72 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.4 Hz, 1 H, Ar-H), 6.68-6.61 (m, 1 H, Ar-H), 5.38 (quint, $J$ = 6.7 Hz, 1 H, =CH), 4.90-4.79 (m, 2 H, =$CH_2$), 4.58-4.48 (m, 2 H, $CH_2$), 2.93-2.81 (m, 2 H, $CH_2$), 2.55-2.45 (m, 1 H, CH), 2.43-2.32 (m, 1 H, CH), 2.30-1.80 (m, 5 H, 2 x $CH_2$ and CH), 1.75-1.34 (m, 6 H, 3 x $CH_2$), 0.90 (s, 3 H, $CH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 220.8, 209.4, 156.3, 137.7, 132.3, 126.2, 114.9, 112.4, 87.2, 76.3, 65.8, 50.4, 47.9, 43.9, 38.3, 35.8, 31.5, 29.6, 26.5, 25.8, 21.5, 13.8; **MS** (70 eV, EI) *m/z* (%): 323 ($M^+$+1, 12.01), 322 ($M^+$, 45.1), 158 (100); **IR** (neat): $\nu$ = 2930, 2914, 2876, 1975, 1950, 1732, 1494, 1248, 1052, 1026 $cm^{-1}$; **Anal**. Calcd. for $C_{22}H_{26}O_2$: C 81.95, H 8.13; found C 82.29, H 8.62.

**(23) Preparation of dodeca-2,3-dienyl phenyl ether (3bb) (zyz-5-65)**

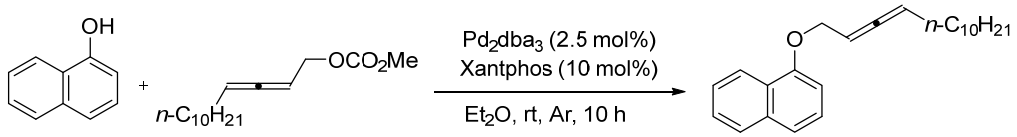



**1b** **2b**, 1.5 equiv. **3bb**, 88%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.8 mg, 0.1 mmol), **1b** (94.2 mg, 1 mmol), **2b** (361.3 mg, 2.5 mmol), and $Et_2O$ (5.0 mL) afforded **3bb** (226.7 mg, 88%) as an oil [eluent: petroleum ether/ethyl acetate = 150/1 (900 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.30-7.23 (m, 2 H, Ar-H), 6.96-6.89 (m, 3 H, Ar-H), 5.38-5.20 (m, 2 H, 2 x =CH), 4.57-4.50 (m, 2 H, $CH_2$),

2.05-1.96 (m, 2 H, $CH_2$), 1.43-1.20 (m, 12 H, 6 x $CH_2$), 0.88 (t, $J$ = 6.8 Hz, 3 H, $CH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 205.1, 158.4, 129.3, 120.7, 114.9, 92.9, 87.6, 66.4, 31.9, 29.4, 29.3, 29.08, 29.06, 28.4, 22.7, 14.1; **MS** (EI, 70 eV) *m/z* (%): 259 ($M^+$+1, 4.42), 258 ($M^+$, 21.95), 94 (100); **IR** (neat): 2955, 2923, 2853, 1965, 1599, 1587, 1494, 1462, 1365, 1301, 1238, 1213, 1171, 1153, 1078, 1030, 1011 $cm^{-1}$; **HRMS** (ESI) Calcd for $C_{18}H_{26}O$ $[M]^+$: 258.1984, Found: 258.1991.

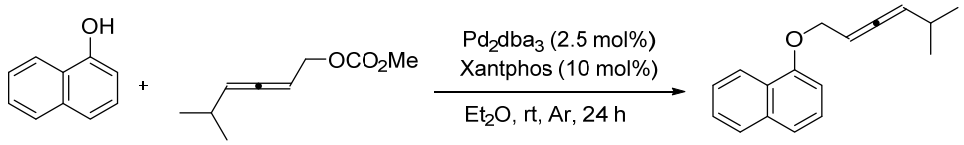
**(24) Preparation of tetradeca-2,3-dienyl 1-naphthyl ether (3pc) (hcf-4-140)**




**1p** **2c**, 1.5 equiv. **3pc,** 95%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1p** (144.2 mg, 1 mmol), **2c** (402.6 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3pc** (319.7 mg, 95%) as an oil [eluent: petroleum ether/DCM = 100/1 (500 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.29 (d, $J$ = 8.0 Hz, 1 H, Ar-H), 7.78 (d, $J$ = 6.8 Hz, 1 H, Ar-H), 7.51-7.38 (m, 3 H, Ar-H), 7.35 (t, $J$ = 7.8 Hz, 1 H, Ar-H), 6.83 (d, $J$ = 7.2 Hz, 1 H, Ar-H), 5.51-5.40 (m, 1 H, =CH), 5.35-5.24 (m, 1 H, =CH), 4.72 (dd, $J_1$ = 6.6 Hz, $J_2$ = 1.8 Hz, 2 H, $CH_2$), 2.08-1.94 (m, 2 H, $CH_2$), 1.46-1.35 (m, 2 H, $CH_2$), 1.35-1.00 (m, 14 H, 7 x $CH_2$), 0.88 (t, $J$ = 6.4 Hz, 3 H, $CH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 205.1, 154.3, 134.6, 127.4, 126.3, 125.9, 125.7, 125.1, 122.2, 120.3, 105.4, 93.0, 87.7, 66.7, 31.9, 29.6, 29.4, 29.3, 29.1, 28.4, 22.7, 14.1; **MS** (70 eV, EI) *m/z* (%): 337 ($M^+$+1, 5.37), 336 ($M^+$, 21.3), 144 (100); **IR** (neat): $\nu$ = 3053, 2922, 2852, 1965, 1581, 1400, 1266, 1066 $cm^{-1}$; **HRMS** calcd for $C_{24}H_{32}O$ [$M^+$]: 336.2448, found: 336.2448.

**(25) Preparation of 5-methyl-hexa-2,3-dienyl 1-naphthyl ether (3pd) (wpl-5-101)**

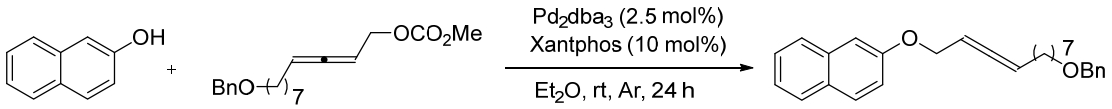



**1p** **2d**, 1.5 equiv. **3pd,** 98%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.8 mg, 0.1 mmol), **1p** (144.4 mg, 1 mmol), **2d** (255.6 mg, 1.5 mmol),

and $Et_2O$ (5.0 mL) afforded **3pd** (234.5 mg, 98%) as an oil [eluent: petroleum ether/ethyl acetate = 150/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.33-8.27 (m, 1 H, Ar-H), 7.82-7.75 (m, 1 H, Ar-H), 7.51-7.32 (m, 4 H, Ar-H), 6.83 (d, $J$ = 7.6 Hz, 1 H, Ar-H), 5.55-5.48 (m, 1 H, =CH), 5.35-5.29 (m, 1 H, =CH), 4.72 (dd, $J_1$ = 6.4 Hz, $J_2$ = 2.0 Hz, 2 H, $CH_2$), 2.40-2.28 (m, 1 H, CH), 1.02 (dd, $J_1$ = 6.8 Hz, $J_2$ = 1.6 Hz, 6 H, 2 x $CH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 203.6, 154.3, 134.5, 127.4, 126.3, 125.9, 125.7, 125.1, 122.2, 120.3, 105.4, 100.4, 89.0, 66.7, 27.8, 22.5, 22.4; **MS** (70 eV, EI) *m/z* (%): 238 ($M^+$, 15.16), 144 (100); **IR** (neat): $\nu$ = 3053, 2959, 2925, 2867, 1963, 1595, 1399, 1267, 1238, 1066 $cm^{-1}$; **HRMS** calcd for $C_{17}H_{18}O$ [$M^+$]: 238.1352, found: 238.1355.

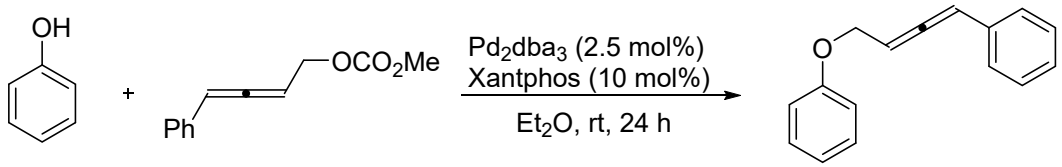
**(26) Preparation of 11-(benzyloxy)-undeca-2,3-dienyl 2-naphthyl ether (3oe) (hcf-4-109)**




**1o** **2e**, 1.5 equiv. **3oe**, 96%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1o** (144.3 mg, 1 mmol), **2e** (499.1 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3oe** (384.8 mg, 96%) as an oil [eluent: petroleum ether/ethyl acetate = 200/1 (600 mL), 150/1 (300 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.80-7.60 (m, 3 H, Ar-H), 7.41 (t, $J$ = 7.6 Hz, 1 H, Ar-H), 7.37-7.20 (m, 6 H, Ar-H), 7.19-7.04 (m, 2 H, Ar-H), 5.44-5.32 (m, 1 H, =CH), 5.32-5.22 (m, 1 H, =CH), 4.65 (dd, $J_1$ = 6.6 Hz, $J_2$ = 1.8 Hz, 2 H, $CH_2$), 4.48 (s, 2 H, $CH_2$), 3.43 (t, $J$ = 6.6 Hz, 2 H, $CH_2$), 2.07-1.95 (m, 2 H, $CH_2$), 1.64-1.52 (m, 2 H, $CH_2$), 1.45-1.08 (m, 8 H, 4 x $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 205.3, 156.4, 138.7, 134.5, 129.3, 129.0, 128.3, 127.62, 127.58, 127.4, 126.7, 126.3, 123.6, 119.1, 107.4, 92.9, 87.6, 72.8, 70.5, 66.5, 29.7, 29.2, 29.00, 28.97, 28.4, 26.1; **MS** (70 eV, EI) *m/z* (%): 400 ($M^+$, 9.32), 144 (100); **IR** (neat): $\nu$ = 3060, 3028, 2928, 2853, 1965, 1629, 1600, 1363, 1255, 1213, 1175, 1007 $cm^{-1}$; **HRMS** calcd for $C_{28}H_{32}O_2$ [$M^+$]: 400.2397, found: 400.2399.

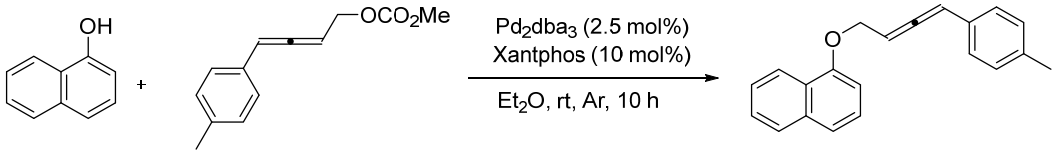
**(27) Preparation of 4-phenyl-buta-2,3-dienyl phenyl ether (3bf) (XHB-2-130)**




**1b** **2f**, 1.5 equiv **3bf**, 99%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1b** (94.2 mg, 1 mmol), **2f** (306.7 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3bf** (220.1 mg, 99%) as an oil [eluent: petroleum ether/ethyl acetate = 200:1 (200 mL), 100:1 (200 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.32-7.18 (m, 7 H, Ar-H), 6.98-6.91 (m, 3 H, Ar-H), 6.29 (dt, $J_1$ = 6.4 Hz, $J_2$ = 2.6 Hz, 1 H, =CH), 5.80 (q, $J$ = 6.5 Hz, 1 H, =CH), 4.68 (dd, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 206.2, 158.1, 133.4, 129.4, 128.6, 127.2, 127.0, 121.0, 115.0, 96.2, 91.8, 65.7; **MS** (70 eV, EI) *m/z* (%): 222 ($M^+$, 27.33), 128 (100); **IR** (neat): $\nu$ = 3061, 3030, 1952, 1729, 1701, 1597, 1586, 1493, 1458, 1363, 1301, 1237, 1213, 1171, 1154, 1076, 1029 $cm^{-1}$; **HRMS** calcd for $C_{16}H_{14}O$ [$M^+$]: 222.1045, Found: 222.1055.

**(28) Preparation of *p*-tolyl-buta-2,3-dienyl 1-naphthyl ether (3pg) (hcf-4-119)**

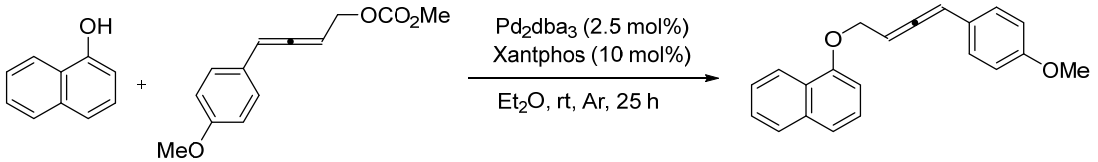



**1p** **2g**, 1.5 equiv. **3pg,** 96%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1p** (144.2 mg, 1 mmol), **2g** (327.5 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3pg** (274.3 mg, 96%) as an oil [eluent: petroleum ether/DCM = 80/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.30 (d, $J$ = 7.6 Hz, 1 H, Ar-H), 7.78 (d, $J$ = 7.2 Hz, 1 H, Ar-H), 7.54-7.39 (m, 3 H, Ar-H), 7.33 (t, $J$ = 8.0 Hz, 1 H, Ar-H), 7.21-7.14 (m, 2 H, Ar-H), 7.14-7.02 (m, 2 H, Ar-H), 6.84 (d, $J$ = 7.6 Hz, 1 H, Ar-H), 6.35-6.24 (m, 1 H, =CH), 5.90 (q, $J$ = 6.5 Hz, 1 H, =CH), 4.84 (dd, $J_1$ = 6.4 Hz, $J_2$ = 2.4 Hz, 2 H, $CH_2$), 2.32 (s, 3 H, $CH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 206.1, 154.1, 137.1, 134.6, 130.5, 129.4, 127.4, ,126.9, 126.4, 125.9, 125.8, 125.2, 122.1, 120.5, 105.6, 96.2, 91.8, 66.2, 21.2; **MS** (70 eV, EI) *m/z* (%): 287 ($M^+$+1, 8.1), 286 ($M^+$, 37.44), 128 (100); **IR** (neat): $\nu$ = 3050, 2987, 2918, 1952, 1579, 1509, 1266,

1095 $cm^{-1}$; **HRMS** calcd for $C_{21}H_{18}O$ [$M^+$]: 286.1352, found: 286.1350.

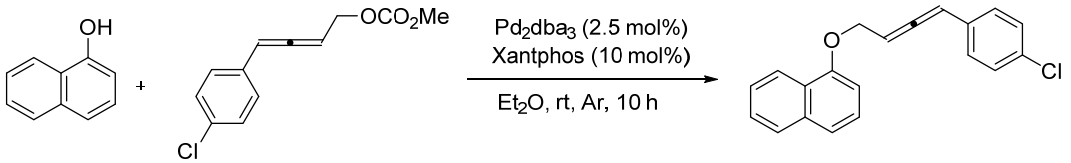
**(29) Preparation of 4-methoxyphenyl-buta-2,3-dienyl 1-naphthyl ether (3ph) (lj-4-178)**




**1p** **2h**, 1.5 equiv. **3ph,** 98%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (23.0 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1p** (144.3 mg, 1 mmol), **2h** (351.4 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3ph** (296.9 mg, 84%) as an oil [eluent: petroleum ether/ethyl acetate = 200/1 (600 mL]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.79 (d, *J* = 7.2 Hz, 1 H, Ar-H), 7.53-7.37 (m, 3 H, Ar-H), 7.34 (t, *J* = 8.0 Hz, 1 H, Ar-H), 7.26-7.16 (m, 2 H, Ar-H), 6.91-6.79 (m, 3 H, Ar-H), 6.34-6.25 (m, 1 H, =CH), 5.90 (q, *J* = 6.4 Hz, 1 H, $=CH_2$), 4.90-4.80 (m, 2 H, $CH_2$), 3.80 (s, 3 H, $OCH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 205.9, 159.0, 154.0, 134.6, 132.4, 130.0, 128.1, 127.4, 126.4, 125.9, 125.8, 125.7, 125.2, 122.1, 120.5, 114.1, 105.6, 95.8, 91.2, 66.2, 55.3; **MS** (70 eV, EI) *m/z* (%): 302 ($M^+$, 35.7), 115 (100); **IR** (neat): *ν* = 3054, 3002, 2945, 2837, 1950, 1581, 1508, 1453, 1396, 1359, 1239, 1169, 1097, 1027 $cm^{-1}$; **HRMS** calcd for $C_{21}H_{18}O_2$ [$M^+$]: 302.1301, found: 302.1298.

**(30) Preparation of 4-chlorophenyl-buta-2,3-dienyl 1-naphthyl ether (3pi) (hcf-4-114)**

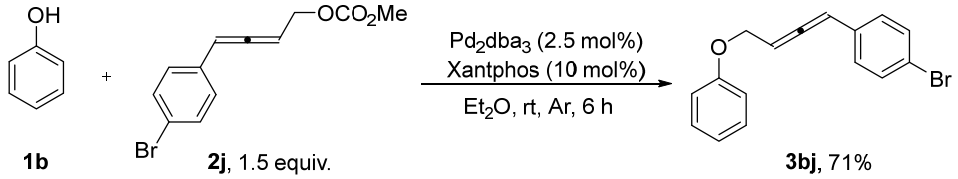



**1p** **2i**, 1.5 equiv. **3pi,** 88%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1p** (144.2 mg, 1 mmol), **2i** (358.3 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3pi** (269.9 mg, 88%) as an oil [eluent: petroleum ether/ethyl acetate = 200/1 (800 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.79 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.55-7.39 (m, 3 H, Ar-H), 7.33 (t, *J* = 8.0 Hz, 1 H, Ar-H), 7.29-7.08 (m, 4 H, Ar-H), 6.84 (d, *J* = 7.6 Hz, 1 H, Ar-H), 6.35-6.18 (m, 1

H, =CH), 5.93 (q, $J$ = 6.4 Hz, 1 H, =CH), 4.86 (dd, $J_1$ = 6.6 Hz, $J_2$ = 2.2 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 206.4, 153.9, 134.6, 132.9, 132.0, 128.8, 128.2, 127.5, 126.4, 125.9, 125.7, 125.3, 122.0, 120.7, 105.6, 95.6, 92.3, 65.8; **MS** (70 eV, EI) *m/z* (%): 308 (M ($^{37}$Cl)$^+$, 13.09), 306 (M ($^{35}$Cl)$^+$, 39.44), 144 (100); **IR** (neat): $\nu$ = 3051, 2925, 2864, 1954, 1490, 1266, 1093, 1013 cm$^{-1}$; **HRMS** calcd for $C_{20}H_{15}O^{35}Cl$ [$M^+$]: 306.0806, found: 306.0803.

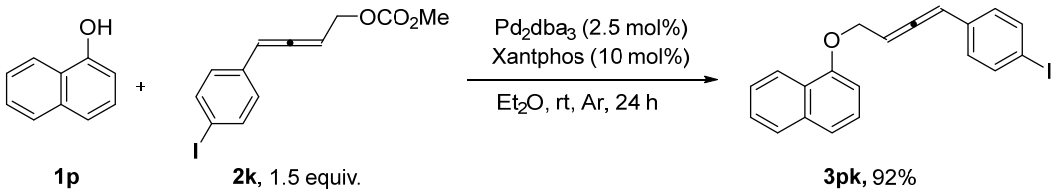
**(31) Preparation of 4-bromophenyl-buta-2,3-dienyl phenyl ether (3bj) (lc-1-55)**




**1b** **2j**, 1.5 equiv. **3bj**, 71%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (23.0 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1b** (94.3 mg, 1 mmol), **2j** (424.9 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3bj** (213.9 mg, 71%) as an oil [eluent: petroleum ether/ethyl acetate = 200/1 (500 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.43-7.36 (m, 2 H, Ar-H), 7.30-7.23 (m, 2 H, Ar-H), 7.12-7.06 (m, 2 H, Ar-H), 6.99-6.89 (m, 3 H, Ar-H), 6.22 (dt, $J_1$ = 6.4 Hz, $J_2$ = 2.4 Hz, 1 H, =CH), 5.79 (q, $J$ = 6.8 Hz, 1 H, =CH), 6.22 (dd, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 206.3, 158.1, 132.4, 131.7, 129.5, 128.5, 121.1, 120.9, 115.1, 95.5, 92.3, 65.4; **IR** (neat) $\nu$ = 3039, 2930, 1952, 1586, 1488, 1236, 1213, 1008 cm$^{-1}$; **MS** (70 eV, EI) *m/z* (%): 300 (M($^{79}$Br)$^+$, 2.62), 302 (M($^{81}$Br)$^+$, 1.82), 101 (100); **HRMS** Calcd. for $C_{16}H_{13}O^{79}Br$ [$M^+$]: 300.1044, found: 300.0143.

**(32) Preparation of 4-iodophenyl-buta-2,3-dienyl 1-naphthyl ether (3pk) (wpl-5-107)**

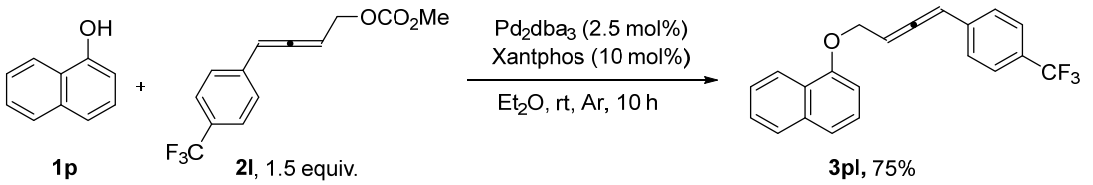



**1p** **2k**, 1.5 equiv. **3pk**, 92%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (58.0 mg, 0.1 mmol), **1p** (144.3 mg, 1 mmol), **2k** (495.4 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3pk** (366.7 mg, 92%) as an oil [eluent: petroleum

ether/ethyl acetate = 150/1 (800 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.38-8.26 (m, 1 H, Ar-H), 7.79-7.73 (m, 1 H, Ar-H), 7.56 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.48-7.38 (m, 3 H, Ar-H), 7.30 (t, *J* = 8.0 Hz, 1 H, Ar-H), 6.95 (d, *J* = 8.4 Hz, 2 H, Ar-H), 6.78 (d, *J* = 7.6 Hz, 1 H, Ar-H), 6.23-6.18 (m, 1 H, =CH), 5.87 (q, *J* = 6.4 Hz, 1 H, =CH), 4.80 (dd, $J_1$ = 6.4 Hz, $J_2$ = 2.4 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 206.3, 153.9, 137.6, 134.5, 133.1, 128.7, 127.4, 126.4, 125.8, 125.7, 125.2, 122.0, 120.7, 105.5, 95.7, 92.3, 65.6; **MS** (70 eV, EI) *m/z* (%): 398 ($M^+$, 30.56), 128 (100); **IR** (neat): *v* = 2963, 2907, 1260, 1091, 1019 $cm^{-1}$; **HRMS** calcd for $C_{20}H_{15}OI$ [$M^+$]: 398.0162, found: 398.0169.

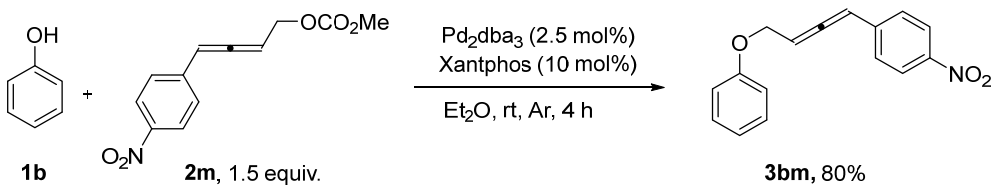
**(33) Preparation of 4-(trifluoromethyl)phenyl-buta-2,3-dienyl 1-naphthyl ether (3pl) (hcf-4-122)**




**1p** **2l**, 1.5 equiv. **3pl,** 75%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1p** (144.2 mg, 1 mmol), **2l** (408.5 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3pl** (306.1 mg, 90%) as an oil [eluent: petroleum ether/DCM = 80/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.77 (d, *J* = 7.2 Hz, 1 H, Ar-H), 7.60-7.38 (m, 5 H, Ar-H), 7.38-7.24 (m, 3 H, Ar-H), 6.82 (d, *J* = 7.6 Hz, 1 H, Ar-H), 6.40-6.24 (m, 1 H, =CH), 5.96 (q, *J* = 6.4 Hz, 1 H, =CH), 4.85 (dd, $J_1$ = 6.4 Hz, $J_2$ = 2.4 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 207.0, 153.9, 137.4, 134.6, 129.1 (q, *J* = 32.1 Hz), 127.5, 127.1, 126.5, 125.9, 125.7, 125.5 (q, *J* = 3.9 Hz), 125.3, 124.2 (q, *J* = 270.4 Hz), 122.0, 120.8, 105.6, 95.7, 92.5, 65.5; **$^{19}$F NMR** (376 MHz, CDCl3): δ = -63.0; **MS** (70 eV, EI) *m/z* (%): 341 ($M^+$+1, 9.88), 340 ($M^+$, 45.17), 144 (100); **IR** (neat): *v* = 3054, 2938, 2874, 1955, 1579, 1396, 1322, 1267, 1096, 1064, 1016 $cm^{-1}$; **HRMS** calcd for $C_{21}H_{15}OF_3$ [$M^+$]: 340.1070, found: 340.1069.

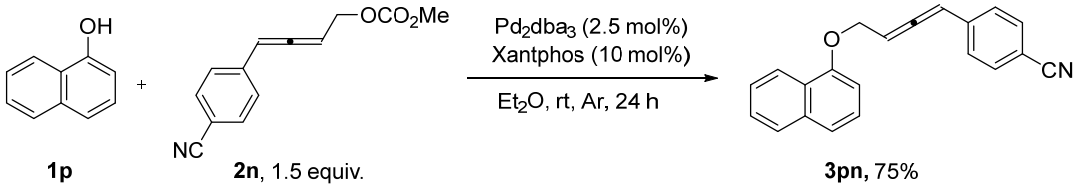
**(34) Preparation of 4-nitrophenyl-buta-2,3-dienyl phenyl ether (3bm) (hcf-4-138)**




**1b** **2m**, 1.5 equiv. **3bm,** 80%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1b** (94.1 mg, 1 mmol), **2m** (373.9 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3bm** (213.5 mg, 80%) as an oil [eluent: petroleum ether/DCM = 5/1 (500 mL), 2/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.41-7.18 (m, 4 H, Ar-H), 7.02-6.82 (m, 3 H, Ar-H), 6.42-6.26 (m, 1 H, =CH), 5.92 (q, *J* = 6.3 Hz, 1 H, =CH), 4.72 (d, *J* = 6.0 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 207.7, 157.9, 146.7, 140.8, 129.5, 127.4, 123.9, 121.3, 115.1, 95.4, 92.9, 64.9; **MS** (70 eV, EI) *m/z* (%): 268 ($M^+$+1, 7.36), 267 ($M^+$, 40.01), 94 (100); **IR** (neat): *v* = 3075, 2930, 2850, 1952, 1594, 1512, 1493, 1335, 1236, 1012 $cm^{-1}$; **HRMS** calcd for $C_{16}H_{13}NO_3$ [$M^+$]: 267.0890, found: 267.0891.

**(35) Preparation of 4-cyanophenyl-buta-2,3-dienyl 1-naphthyl ether (3pn) (hcf-4-121)**

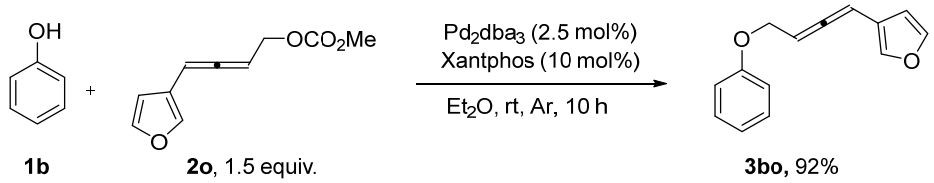



**1p** **2n**, 1.5 equiv. **3pn,** 75%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1p** (144.2 mg, 1 mmol), **2n** (344.1 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3pn** (223.3 mg, 75%) as an oil [eluent: petroleum ether/DCM = 20/1 (200 mL), 10/1 (500 mL), 50/1 (200 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.80 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.61-7.38 (m, 5 H, Ar-H), 7.38-7.27 (m, 3 H, Ar-H), 6.84 (d, *J* = 7.6 Hz, 1 H, Ar-H), 6.39-6.25 (m, 1 H, =CH), 6.01 (q, *J* = 6.4 Hz, 1 H, =CH), 4.89 (dd, $J_1$ = 6.2 Hz, $J_2$ = 2.2 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 207.4, 153.8, 138.7, 134.6, 132.3, 127.5, 127.4, 126.5, 125.8, 125.6, 125.3, 121.9, 120.9, 118.9, 110.4, 105.6, 95.8, 92.8, 65.3; **MS** (70 eV, EI) *m/z* (%): 298 ($M^+$+1, 12.94), 297 ($M^+$, 60.93), 144 (100); **IR** (neat): *v* = 3052, 2929, 2877, 2224, 1951, 1579, 1395, 1267, 1095 $cm^{-1}$; **HRMS** calcd for

$C_{21}H_{15}ON$ [$M^+$]: 297.1148, found: 297.1148.

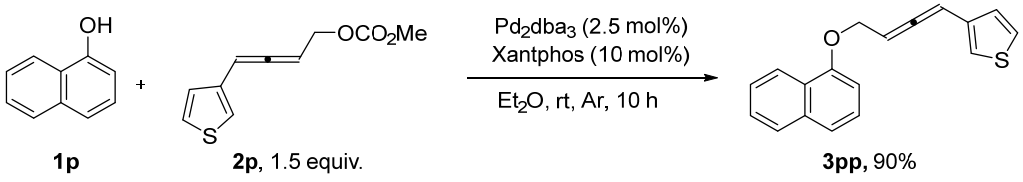
**(36) Preparation of 3-furyl-buta-2,3-dienyl phenyl ether (3bo) (hcf-4-132)**




**1b** **2o**, 1.5 equiv. **3bo,** 92%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1b** (94.2 mg, 1 mmol), **2o** (291.9 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3bo** (195.4 mg, 92%) as an oil [eluent: petroleum ether/DCM = 80/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.35 (d, $J$ = 12.8 Hz, 2 H, Ar-H), 7.27 (t, $J$ = 8.0 Hz, 2 H, Ar-H), 7.01-6.81 (m, 3 H, Ar-H), 6.31 (s, 1 H, Ar-H), 6.23-6.12 (m, 1 H, =CH), 5.70 (q, $J$ = 6.5 Hz, 1 H, =CH), 4.63 (dd, $J_1$ = 6.6 Hz, $J_2$ = 2.2 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 206.2, 158.2, 143.5, 139.7, 129.4, 121.0, 119.2, 115.0, 108.9, 91.0, 86.4, 65.7; **MS** (70 eV, EI) *m/z* (%): 213 ($M^+$+1, 6.92), 212 ($M^+$, 43.04), 91 (100); **IR** (neat): $\nu$ = 3062, 3031, 2930, 2874, 1954, 1598, 1494, 1238, 1212, 1155, 1014 $cm^{-1}$; **HRMS** calcd for $C_{14}H_{12}O_2$ [$M^+$]: 212.0832, found: 212.0829.

**(37) Preparation of 3-thienyl-buta-2,3-dienyl 1-naphthyl ether (3pp) (hcf-4-120)**



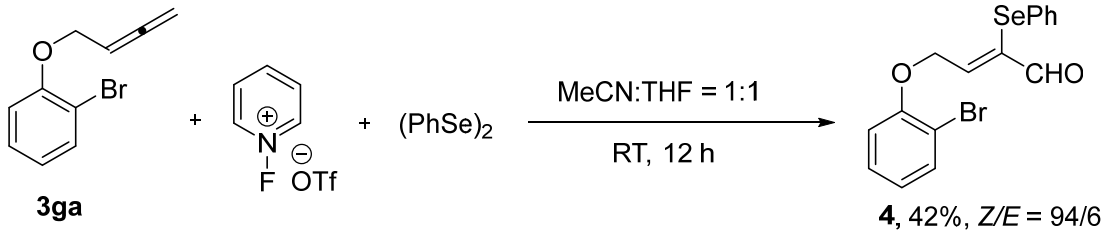

**1p** **2p**, 1.5 equiv. **3pp,** 90%

Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), **1p** (144.2 mg, 1 mmol), **2p** (315.6 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **3pp** (250.5 mg, 90%) as an oil [eluent: petroleum ether/DCM = 80/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 8.29 (dd, $J_1$ = 6.6 Hz, $J_2$ = 2.6 Hz, 1 H, Ar-H), 7.78 (d, $J$ = 7.2 Hz, 1 H, Ar-H), 7.54-7.37 (m, 3 H, Ar-H), 7.37-7.29 (m, 1 H, Ar-H), 7.28-7.17 (m, 1 H, Ar-H), 7.13-6.95 (m, 2 H, Ar-H), 6.83 (d, $J$ = 7.6 Hz, 1 H, Ar-H), 6.45-6.26 (m, 1 H, =CH), 5.85 (q, $J$ = 6.4 Hz, 1 H, =CH), 4.83 (dd, $J_1$ = 6.6 Hz, $J_2$ = 2.2 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 206.7, 154.0, 134.63, 134.56, 127.4, 126.4, 126.0, 125.9, 125.7, 125.2, 122.1, 121.4, 120.6,

105.5, 91.1, 90.9, 66.1; **MS** (70 eV, EI) *m/z* (%): 279 ($M^+$+1, 15.14), 278 ($M^+$, 59.4), 144 (100); **IR** (neat): $\nu$ = 3098, 3051, 2988, 1953, 1578, 1401, 1265, 1236, 1094 $cm^{-1}$; **HRMS** calcd for $C_{18}H_{14}OS$ [$M^+$]: 278.0760, found: 278.0756.

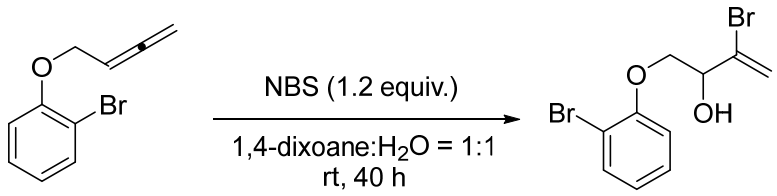
## 3. Synthetic applications

### (1) Preparation of (Z)-2-bromophenyl 4-oxo-3-(phenylselanyl)but-2-enyl ether (4) (hcf-4-186)[10]




To a Schlenk tube equipped with a stirring bar were added $[PyF]^+[OTf]^-$ (59.3 mg, 0.24 mmol), $(PhSe)_2$ (62.4 mg, 0.2 mmol), and a solution of the allenic ether **3ga** in MeCN/THF (1:1, v/v, 4 mL) sequentially in the glove box. Then the resulting mixture was removed from the glove box and stirred at room temperature until disappearance of the starting material as monitored by TLC and extracted with ethyl acetate (3 x 5 mL). The organic extract was washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. Chromatography of the residue gave analytically pure compound **4** as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (600 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 9.44 (s, 1 H, CHO), 7.65-7.37 (m, 4 H, Ar-H), 7.37-7.16 (m, 4 H, Ar-H), 6.87 (t, *J* = 7.8 Hz, 1 H, Ar-H), 6.71 (d, *J* = 8.4 Hz, 1 H, =CH), 4.89 (d, *J* = 4.8 Hz, 2 H, $CH_2$), the following signal is discernible for (*E*)-**4**: δ = 9.92 (s, 1 H, CHO), 5.06 (d, *J* = 5.6 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 189.5, 154.2, 153.4, 136.4, 133.7, 132.9, 129.5, 128.5, 128.0, 122.8, 113.3, 112.2, 68.2; **MS** (70 eV, EI) *m/z* (%): 398 ($M(^{81}Br)^+$, 7.2), 396 ($M(^{79}Br)^+$, 8.86), 133 (100); **IR** (neat): $\nu$ = 3061, 2819, 2718, 1697, 1575, 1475, 1438, 1244, 1225, 1141, 1051, 1031 $cm^{-1}$.

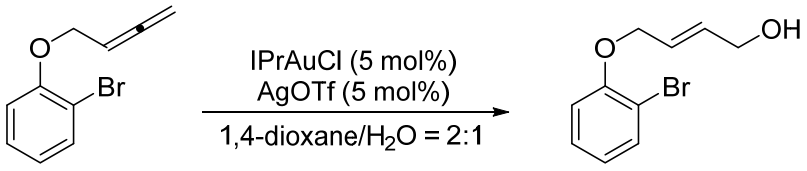
### (2) Preparation of 2-bromophenyl 3-bromo-2-hydroxybut-3-enyl ether (5) (hcf-4-200)[11]




**3ga** **5**, 72%

To a Schlenk tube equipped with a stirring bar, NBS (42.7 mg, 0.24 mmol), a solution of the allenic ether **3ga** (45.0 mg, 0.2 mmol) in 1,4-dixoane (1.5 mL), and water (1.5 mL) were added sequentially. The resulting mixture was stirred at room temperature until disappearance of the starting material as determined by TLC, quenched with 5 mL of sat. aq. $Na_2S_2O_3$, extracted with ethyl acetate (5 mL×3), washed with brine, and dried over anhydrous $Na_2SO_4$. After filtration and concentration, column chromatography of the residue afforded compound **5** as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (400 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.54 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1 H, Ar-H), 7.34-7.20 (m, 1 H, Ar-H), 7.01-6.80 (m, 2 H, Ar-H), 6.17 (dd, $J_1$ = 2.0 Hz, $J_2$ = 1.2 Hz, 1 H, one proton of $=CH_2$), 5.74 (dd, $J_1$ = 2.2 Hz, $J_2$ = 0.6 Hz, 1 H, one proton of $=CH_2$), 4.62 (q, $J$ = 5.1 Hz, 1 H, CH), 4.27 (dd, $J_1$ = 9.4 Hz, $J_2$ = 3.8 Hz, 1 H, one proton of $OCH_2$), 4.13 (dd, $J_1$ = 9.4 Hz, $J_2$ = 2.6 Hz, 1 H, one proton of $OCH_2$), 3.02-2.86 (m, 1 H, OH); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 154.5, 133.4, 130.6, 128.6, 122.8, 119.0, 114.1, 112.6, 74.0, 71.3; **MS** (70 eV, EI) *m/z* (%): 324 (M ($^{81}$Br x 2)$^+$, 11.4), 322 (M ($^{81}$Br + $^{79}$Br)$^+$, 22.4), 320 (M ($^{79}$Br x 2)$^+$, 10.65), 172 (100); **IR** (neat): $\nu$ = 3416, 2938, 2878, 1627, 1585, 1479, 1442, 1277, 1247, 1053, 1030 cm$^{-1}$; **HRMS** calcd for $C_{10}H_{10}{}^{79}Br^{81}BrO_2$ [M$^+$]: 321.9022, found: 321.9025.

**(3) Preparation of (*E*)-2-bromophenyl but-2-en-1,4-diol ether (6) (hcf-5-57)**[12]

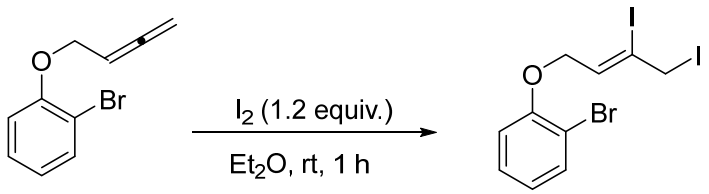



**3ga** **6**, 70%, *E*/*Z* = 98/2

To a Schlenk tube were added IPrAuCl (6.2 mg, 0.01 mmol), AgOTf (2.6 mg, 0.01 mmol), **3ga** (45.0 mg, 0.2 mmol) in 1,4-dixoane (0.6 mL), and $H_2O$ (0.3 mL) sequentially under argon. The resulting mixture was stirred at room temperature for

24 h until disappearance of the starting material as monitored by TLC, quenched with 5 mL of $H_2O$, and extracted with $Et_2O$ (3 x 5 mL). The combined organic layer was washed with brine (5 mL) and dried with anhydrous $Na_2SO_4$. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel to afford **6** (34.0 mg, 70%) as an oil [eluent: DCM (300 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.55 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.4 Hz, 1 H, Ar-H), 7.26-7.21 (m, 1 H, Ar-H), 6.95-6.80 (m, 2 H, Ar-H), 6.17-5.92 (m, 2 H, 2 x =CH), 4.68-4.58 (m, 2 H, $CH_2$), 4.23 (d, $J$ = 4.4 Hz, 2 H, $CH_2$), 1.57 (br, 1 H, OH), the following signal is discernible for (*Z*)-**6**: δ = 4.70 (d, $J$ = 4.8 Hz, 2 H, $CH_2$), 4.31 (d, $J$ = 6.0 Hz, 2 H, $CH_2$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 154.8, 133.4, 132.7, 128.4, 125.4, 122.0, 113.5, 112.2, 68.7, 62.8; **MS** (70 eV, EI) *m/z* (%): 244 (M ($^{81}$Br)$^+$, 3.61), 242 (M ($^{79}$Br)$^+$, 3.58), 172 (100); **IR** (neat): $\nu$ = 3328, 2918, 2865, 1585, 1476, 1442, 1275, 1242, 1030 cm$^{-1}$; **HRMS** calcd for $C_{10}H_{11}{}^{79}BrO_2$ [$M^+$]: 241.9937, found: 241.9937.

**(4) Preparation of (*Z*)-2-bromophenyl 3,4-diiodobut-2-enyl ether ((*Z*)-7) (hcf-5-62)**[13]



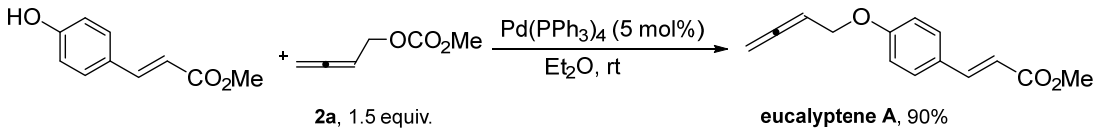

**3ga** (*Z*)-**7**, 69%

To a flame-dried Schlenk tube were added $I_2$ (60.8 mg, 0.24 mmol), **3ga** (45.0 mg, 0.2 mmol), and $Et_2O$ (2 mL) sequentially under argon. The resulting mixture was stirred at room temperature for 1 h until disappearance of the starting material as monitored by TLC, quenched with 5 mL of sat. aq. $Na_2S_2O_3$, extracted with $Et_2O$ (5 mL×3), and dried over anhydrous $Na_2SO_4$. After filtration and concentration, column chromatography of the residue afforded compounds (*Z*)-**7** as an oil [eluent: petroleum ether/DCM = 80/1 (500 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.54 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1 H, Ar-H), 7.27 (dt, $J_1$ = 7.8 Hz, $J_2$ = 1.5 Hz, 1 H, Ar-H), 6.92-6.80 (m, 2 H, Ar-H), 6.42 (t, $J$ = 5.0 Hz, 1 H, =CH), 4.59 (d, $J$ = 5.2 Hz, 2 H, $CH_2$), 4.42 (s, 2 H, $CH_2I$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 154.4, 134.7, 133.5, 128.5, 122.5, 113.7,

112.2, 104.6, 73.5, 16.5; **MS** (70 eV, EI) *m/z* (%): 480 (M ($^{81}$Br)$^+$, 2.85), 478 (M ($^{79}$Br)$^+$, 2.72), 53 (100); **IR** (neat): $\nu$ = 3003, 2948, 2917, 2848, 1584, 1569, 1479, 1438, 1283, 1245, 1155, 1017 cm$^{-1}$; **HRMS** calcd for $C_{10}H_9{}^{79}BrI_2O$ [M$^+$]: 477.7921, found: 477.7928.

**(5) Synthesis of naturally occurring allenes**

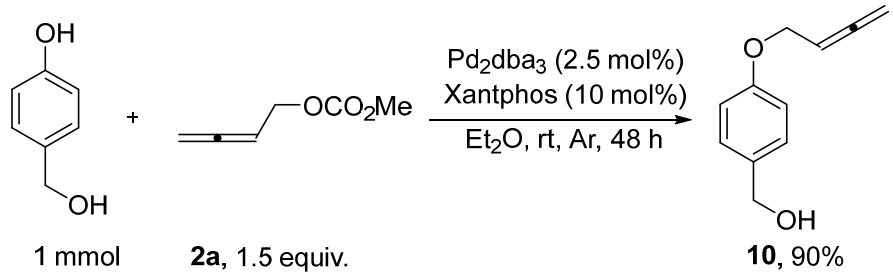
**(5.1) Eucalyptene A (hcf-5-67)**




Following **Typical Procedure IV**, the reaction of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), methyl (*E*)-3-(4-hydroxyphenyl)acrylate (178.2 mg, 1 mmol), **2a** (192.2 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **eucalyptene A**[7] (207.1 mg, 90%) as a white solid [eluent: petroleum ether/ethyl acetate = 10/1 (600 mL)]: m. p. 65.1-65.9 ℃ (petroleum ether/DCM); **$^1$H NMR** (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 16.4 Hz, 1 H, =CH), 7.46 (d, *J* = 8.4 Hz, 2 H, Ar-H), 6.91 (d, *J* = 8.8 Hz, 2 H, Ar-H), 6.31 (d, *J* = 16.0 Hz, 1 H, =CH), 5.38 (quint, *J* = 6.7 Hz, 1 H, =CH), 4.92-4.84 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.7 Hz, 2 H, =$CH_2$), 4.67-4.53 (m, 2 H, O$CH_2$), 3.79 (s, 3 H, O$CH_3$); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ = 209.5, 167.7, 160.1, 144.4, 129.6, 127.3, 115.3, 115.1, 86.7, 76.7, 65.8, 51.5; **MS** (70 eV, EI) *m/z* (%): 231 (M$^+$+1, 2.43), 230 (M$^+$, 11.69), 147 (100); **IR** (neat): $\nu$ = 2956, 2932, 2874, 2842, 1958, 1720, 1509, 1283, 1167, 1010 cm$^{-1}$.

**(5.2) Terricollene A**

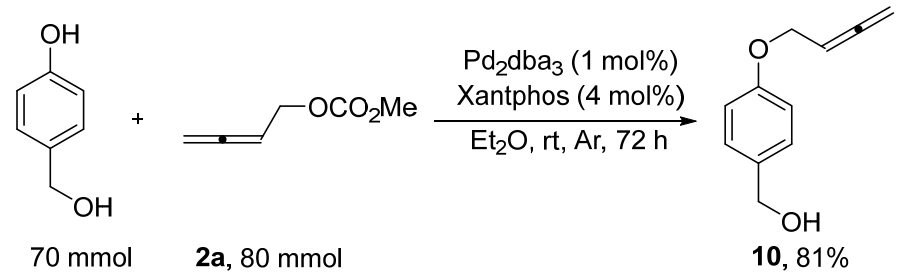
**Preparation of buta-2,3-dienyl 4-(hydroxymethyl)phenyl ether (hcf-5-68)**




Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), *p*-hydroxylmethylphenol (124.1 mg, 1 mmol), **2a**

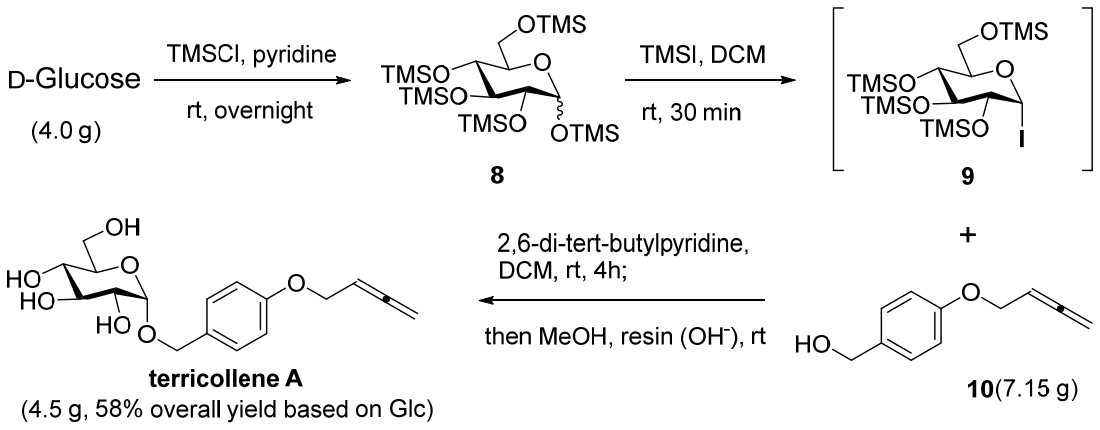
(192.1 mg, 1.5 mmol), and $Et_2O$ (5.0 mL) afforded **10**[7] (158.4 mg, 90%) as a white solid [eluent: petroleum ether/ethyl acetate = 5/1 (600 mL)]: m.p. 46.2-46.9 ℃ (petroleum ether/ethyl acetate); **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.26 (d, *J* = 8.4 Hz, 2 H, Ar-H), 6.94-6.84 (m, 2 H, Ar-H), 5.38 (quint, *J* = 6.7 Hz, 1 H, =CH), 4.86 (dt, $J_1$ = 6.5 Hz, $J_2$ = 2.4 Hz, 2 H, C=$CH_2$), 4.63-4.50 (m, 4 H, 2 x $CH_2$), 1.91 (br, 1 H, OH); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 209.4, 157.9, 133.4, 128.5, 114.9, 87.0, 76.5, 65.8, 64.9; **MS** (70 eV, EI) *m/z* (%): 176 ($M^+$, 4.75), 95 (100); **IR** (neat): *v* = 3341, 3256, 2930, 2864, 1958, 1509, 1381, 1241, 1230, 1044, 1011 $cm^{-1}$.

**70 mmol scale preparation of buta-2,3-dienyl 4-(hydroxymethyl)phenyl ether (hcf-6-75)**




Following **Typical Procedure IV**, the reaction of $Pd_2dba_3$ (641.9 mg, 0.7 mmol), Xantphos (1.6213 g, 2.8 mmol), *p*-hydroxylmethylphenol (8.6895 g, 70 mmol), **2a** (10.2517 g, 80 mmol), and $Et_2O$ (250.0 mL) afforded **10**[7] (9.9913 g, 81%) as a white solid [eluent: petroleum ether/ethyl acetate = 5/1 (1500 mL)]: **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.25 (d, *J* = 8.4 Hz, 2 H, Ar-H), 6.88 (d, *J* = 8.4 Hz, 2 H, Ar-H), 5.38 (quint, *J* = 6.8 Hz, 1 H, =CH), 4.86 (dt, $J_1$ = 6.4 Hz, $J_2$ = 2.4 Hz, 2 H, C=$CH_2$), 4.69-4.46 (m, 4 H, 2 x $CH_2$), 2.07 (br, 1 H, OH); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 209.4, 157.8, 133.3, 128.5, 114.8, 86.9, 76.5, 65.8, 64.8.

**4.5 Gram-scale synthesis of terricollene A**




To a solution of D-glucose (4 g, 22.2 mmol) in anhydrous pyridine (40 mL) at room temperature under argon atmosphere was slowly added TMSCl (16.9 mL, 133.2 mmol). The resulting mixture was stirred overnight. $CH_2Cl_2$ (150 mL) was added to dilute the reaction mixture, which was then washed with ice-cold $H_2O$, hydrochloric acid (1 M, 30 mL×2), saturated sodium bicarbonate solution (30 mL×2), and a saturated sodium chloride solution (50 mL), respectively. The aqueous phase was extracted with $CH_2Cl_2$ (30 mL×2). The organic phases were combined, dried over anhydrous $Na_2SO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatograph (petroleum ether/ethyl acetate = 9:1) to afford compound **8** (11.1 g, 92.4% yield) as a colorless oil [eluent: petroleum ether/ethyl acetate = 9:1]: **$^1$H NMR** (400 MHz, $CDCl_3$) δ = [5.00 (d, *J* = 2.8 Hz, 0.79 H), 4.45 (d, *J* = 7.2 Hz, 0.21 H), 1 H, anomer CH], [3.82-3.56 (m, 3.86 H), 3.26-3.19 (m, 0.47 H), 4 H, 4 x CH], 3.47-3.30 (m, 2 H, $CH_2$), 0.21-0.08 (m, 45 H).

To a solution of **8** (10.96 g, 20.29 mmol) in dry $CH_2Cl_2$ (70 mL) at room temperature under argon atmosphere was added iodotrimethylsilane (2.92 mL, 20.29 mmol). The resulting mixture was stirred for 30 min. Then a solution of **10** (7.15 g, 40.58 mmol) and 2,6-di-*tert*-butylpyridine (4.9 mL, 40.6 mmol) in dry $CH_2Cl_2$ (48 mL) was added. After being stirred for 4 h at room temperature, MeOH (90 mL) was added to the mixture, and the stirring was continued for 15 min. Resin($OH^-$) was added to neutralize the reaction mixture, which was then filtered. The filtrates were concentrated to give a residue, which was purified by silica gel column chromatograph to afford target compound **terricollene A** (4.5 g, 58% yield, α only,

96% purity) as a white solid [eluent: $CH_2Cl_2$/MeOH = 10:1]: m.p. 84.2-84.9 °C (dichloromethane/methanol); **$^1$H NMR** (500 MHz, $CD_3OD$) δ = 7.33 (d, *J* = 9.0 Hz, 2 H, Ar-H), 6.89 (d, *J* = 9.0 Hz, 2 H, Ar-H), 5.37 (quint, *J* = 6.7 Hz, 1 H, =CH), 4.85 – 4.82 (m, 1 H, CH), 4.68 (d, *J* = 11.5 Hz, 1 H, CH), 4.54 (dt, $J_1$ = 6.5 Hz, $J_2$ = 2.4 Hz, 2 H, C=$CH_2$), 4.48 (d, *J* = 12.0 Hz, 1 H, CH), 3.80 (dd, $J_1$ = 12.0 Hz, $J_2$ = 2.5 Hz, 1 H, CH), 3.71 – 3.59 (m, 3 H, $CH_2$ and CH), 3.40 (dd, $J_1$ = 9.5 Hz, $J_2$ = 3.5 Hz, 1 H, CH), 3.36-3.28 (m, 1 H, CH); **$^{13}$C NMR** (126 MHz, $CD_3OD$) δ = 209.3, 158.1, 129.9, 129.5, 114.3, 97.6, 86.6, 75.1, 73.7, 72.4, 72.1, 70.4, 68.5, 65.4, 61.2; **MS** (ESI) m/z : 361 $(M+Na)^+$; **IR** (neat): *ν* = 3346, 2924, 1958, 1611, 1511, 1234, 1034, 1005 $cm^{-1}$.

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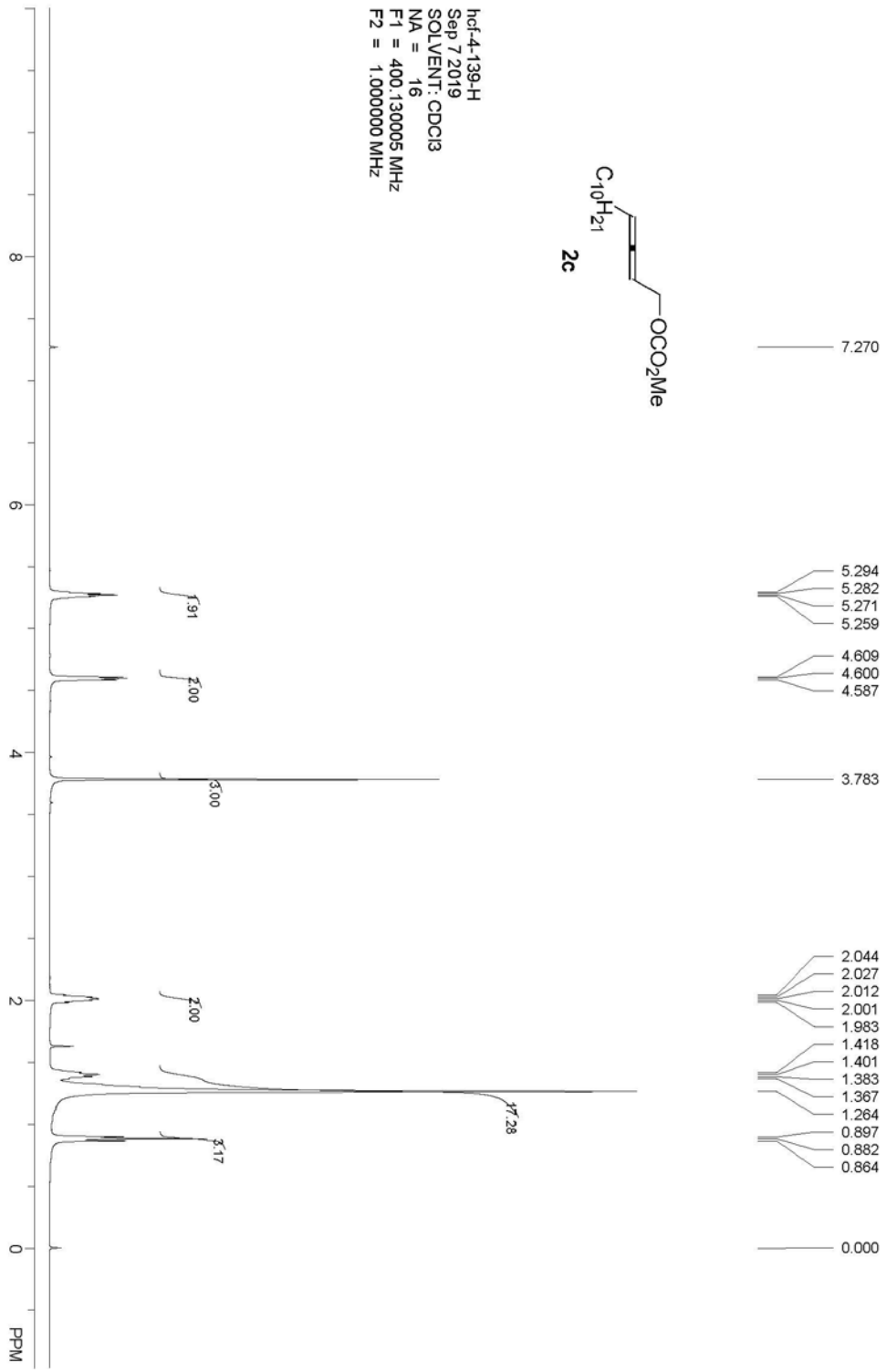
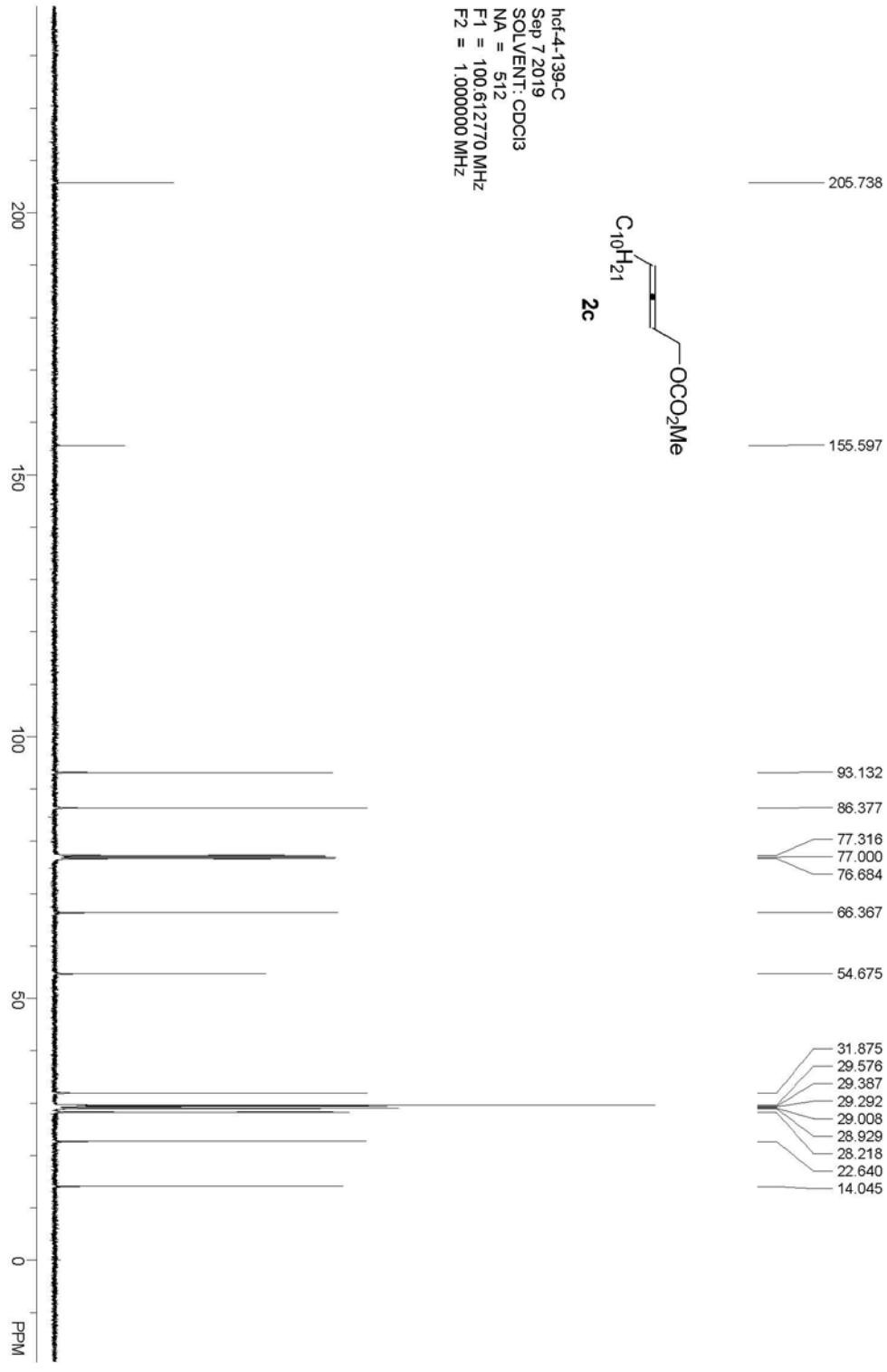
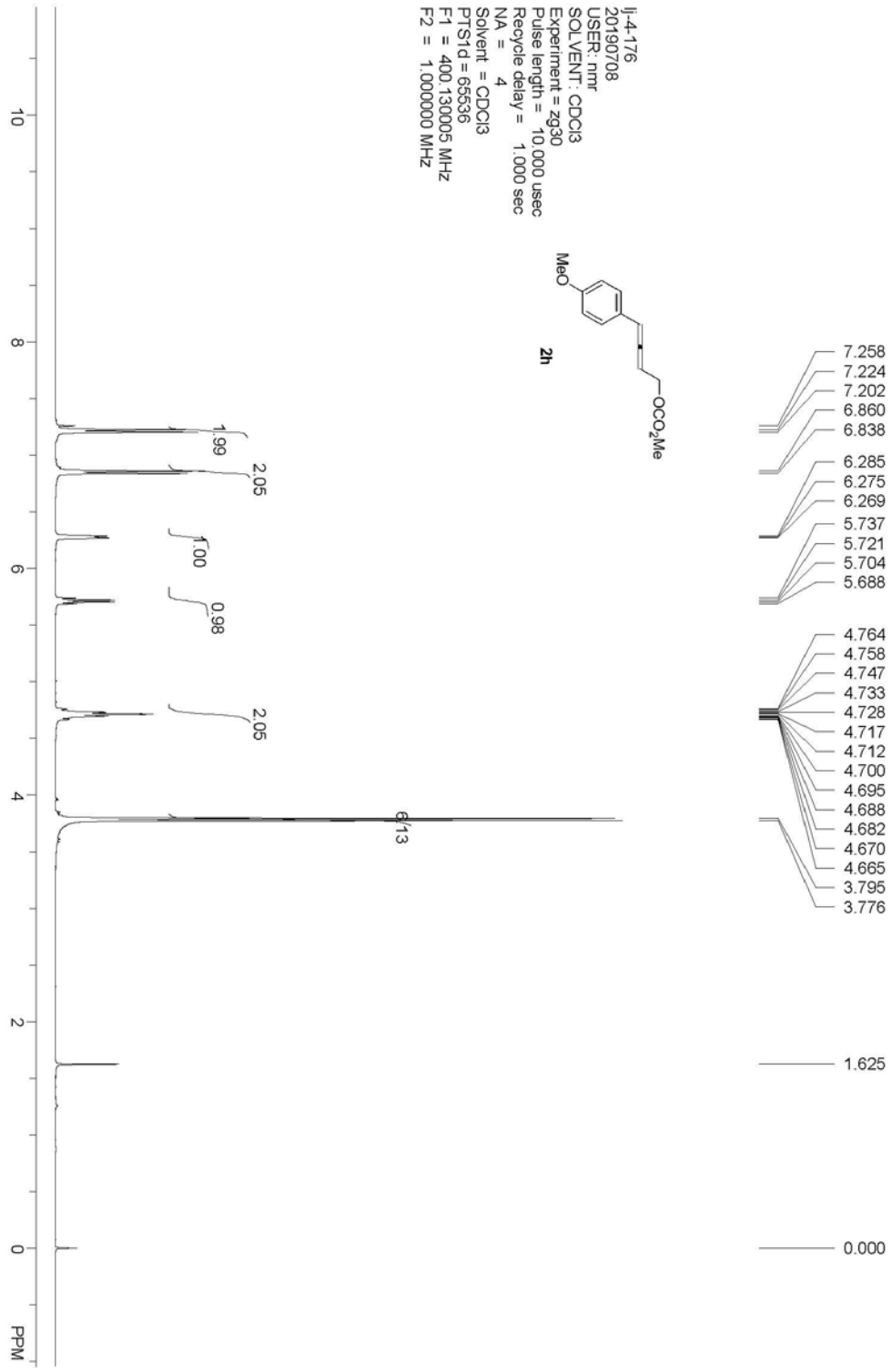
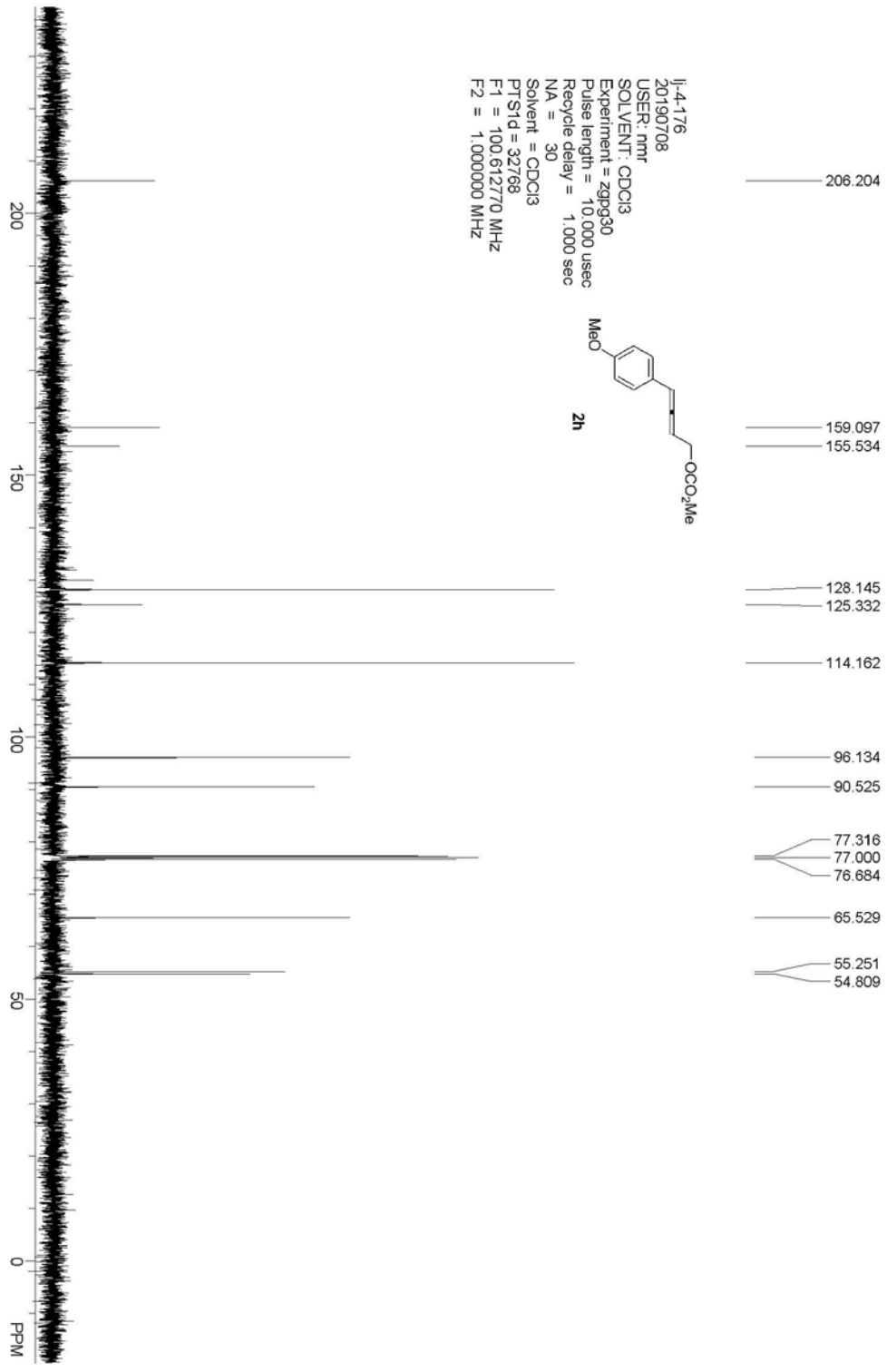
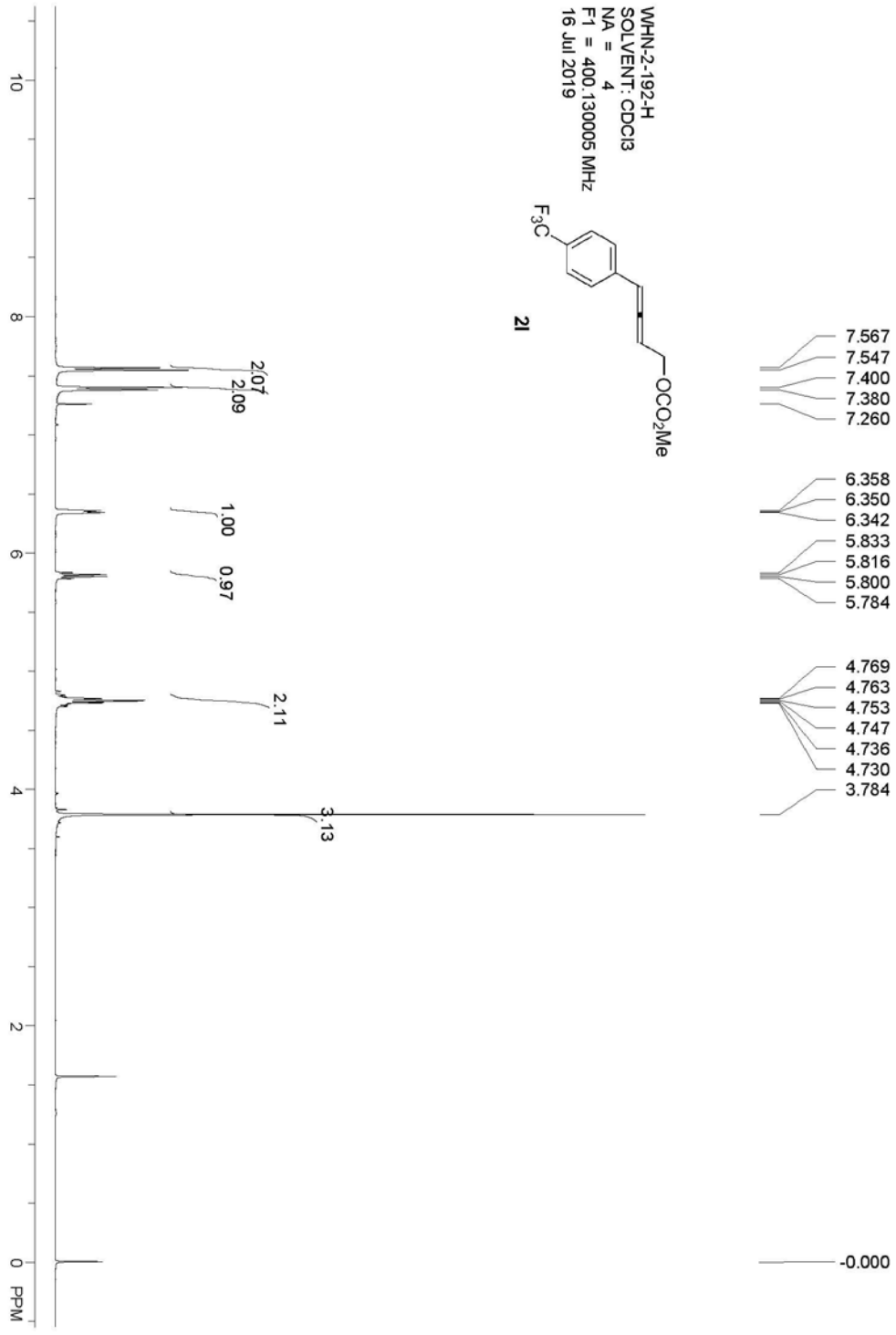
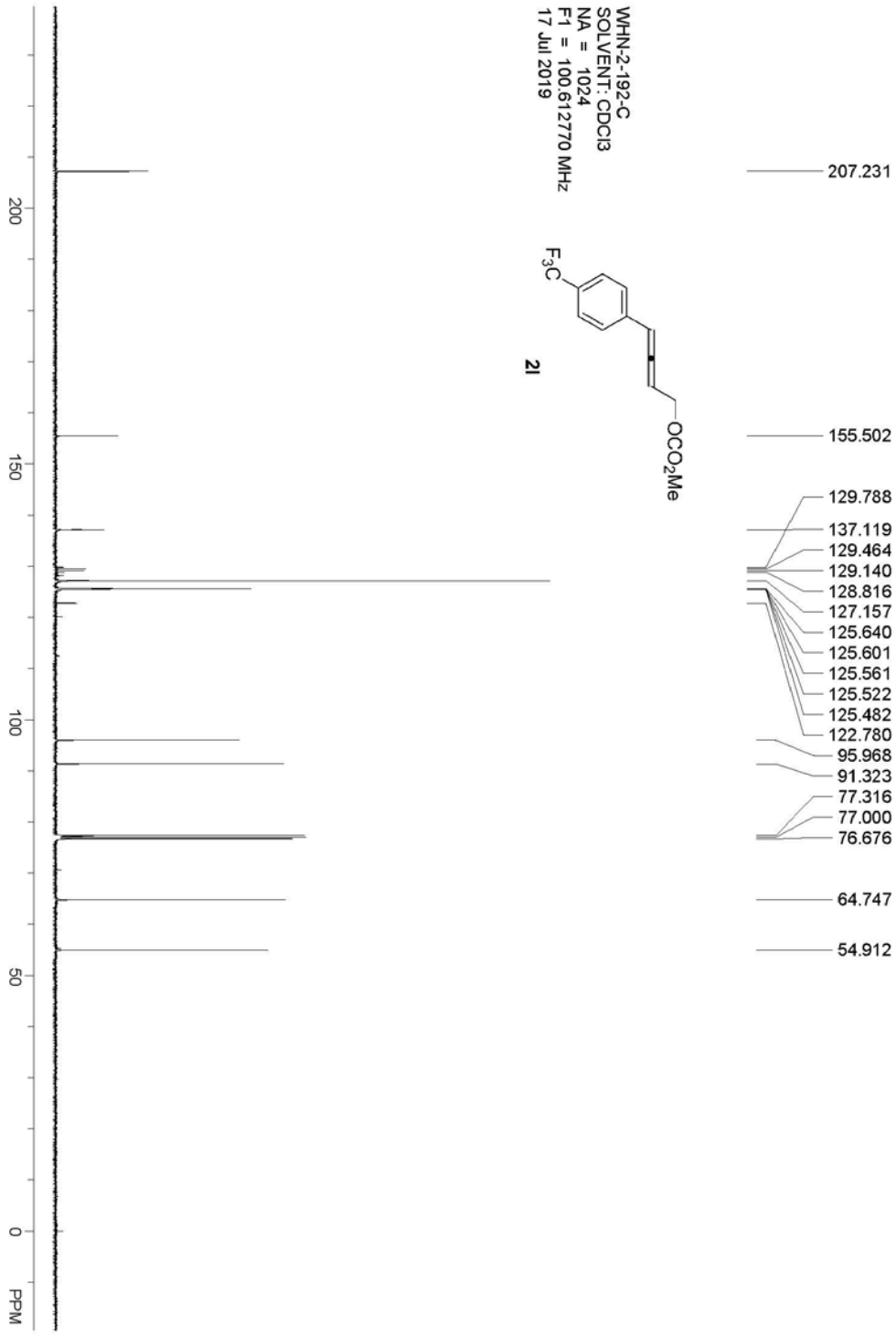

hcf-4-139-H
Sep 7 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
C10H21
OCO2Me
2c
7.270
5.294
5.282
5.271
5.259
4.609
4.600
4.587
3.783
2.044
2.027
2.012
2.001
1.983
1.418
1.401
1.383
1.367
1.264
0.897
0.882
0.864
0.000
1.91
2.00
3.00
2.00
17.28
3.17
PPM

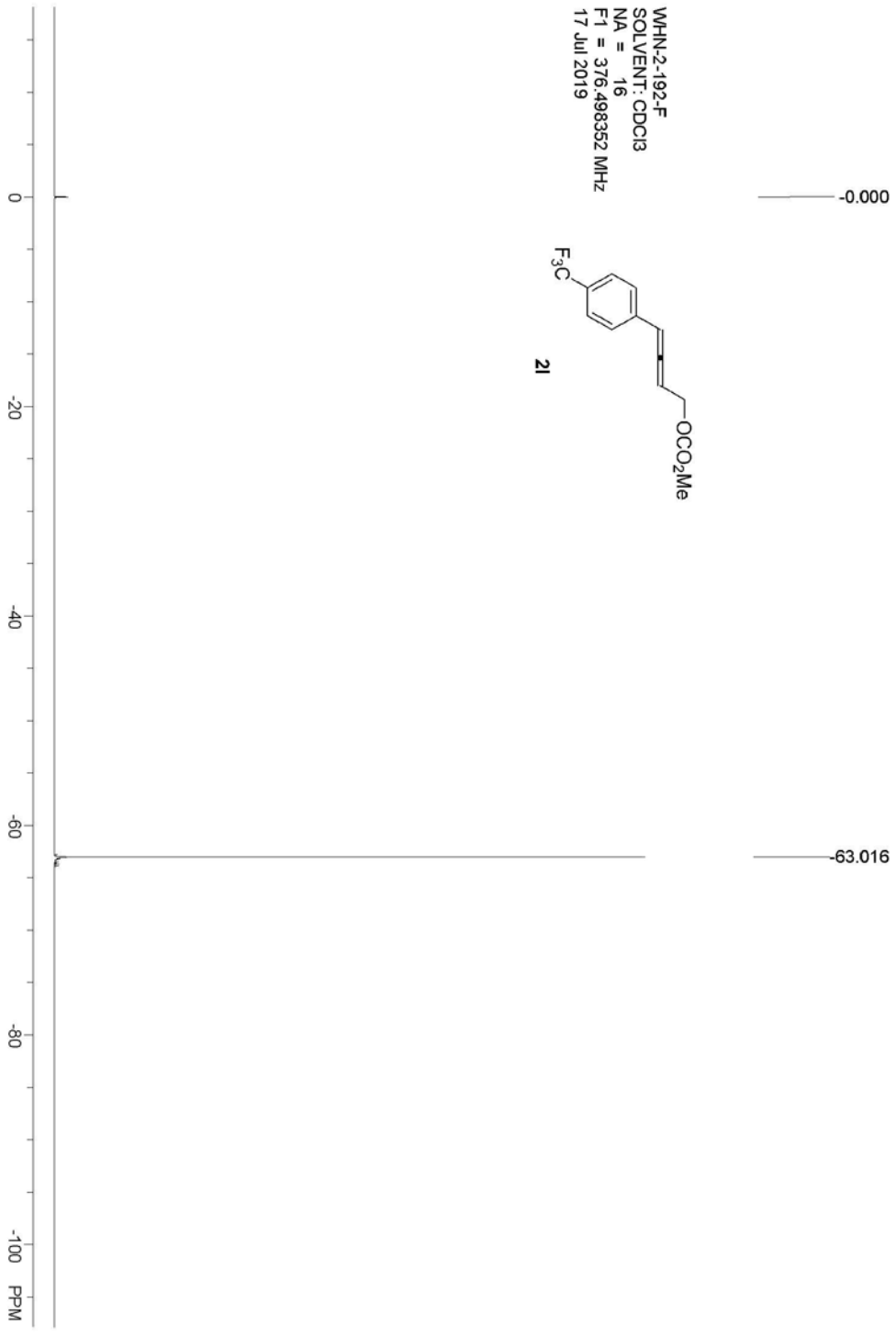

hcf-4-139-C
Sep 7 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
$C_{10}H_{21}$
2c
$OCO_2Me$
205.738
155.597
93.132
86.377
77.316
77.000
76.684
66.367
54.675
31.875
29.576
29.387
29.292
29.008
28.929
28.218
22.640
14.045
200
150
100
50
0
PPM

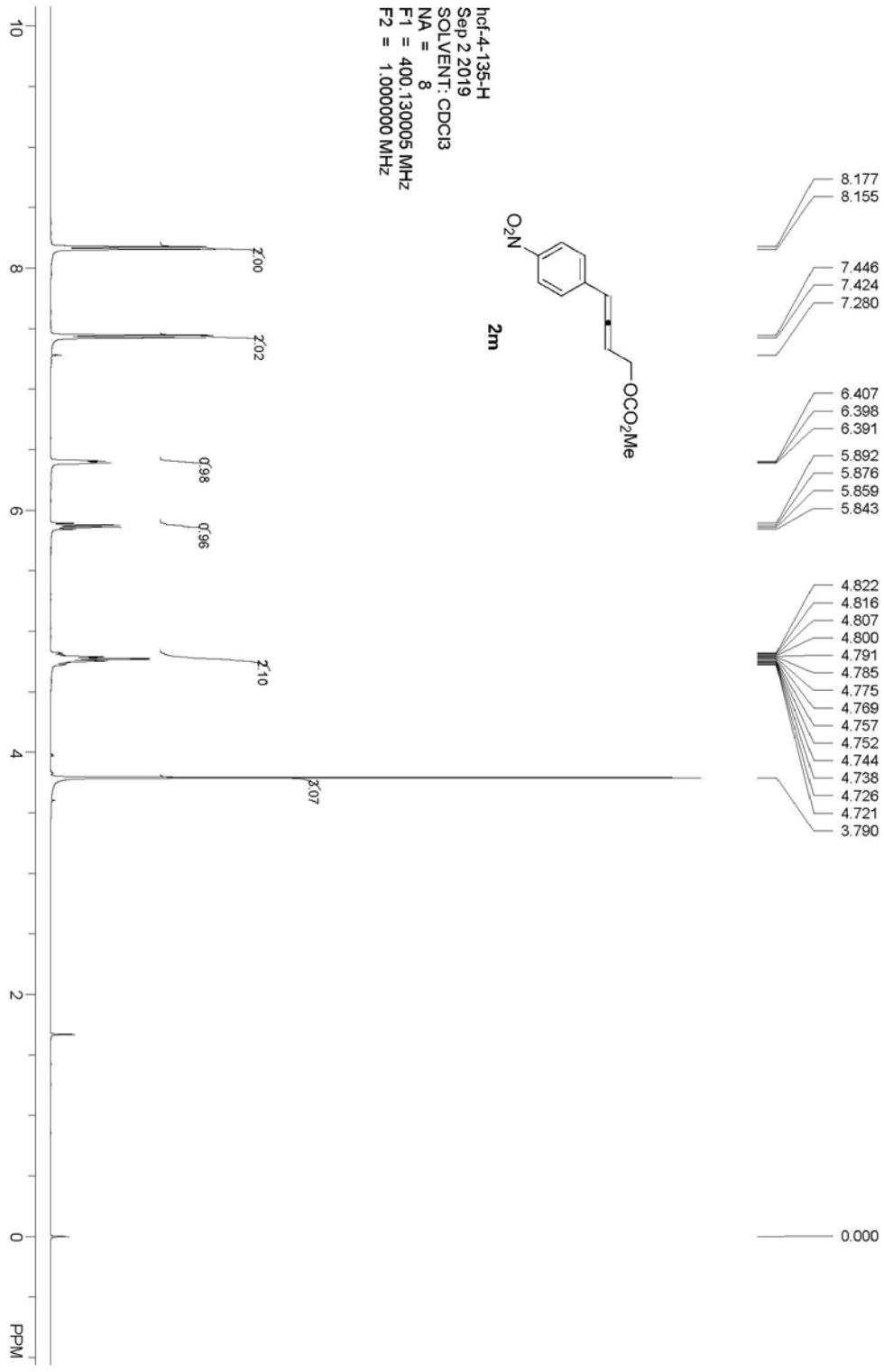

lj-4-176
20190708
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
MeO
OCO2Me
2h
7.258
7.224
7.202
6.860
6.838
6.285
6.275
6.269
5.737
5.721
5.704
5.688
4.764
4.758
4.747
4.733
4.728
4.717
4.712
4.700
4.695
4.688
4.682
4.670
4.665
3.795
3.776
1.625
0.000
1.99
2.05
1.00
0.98
2.05
6.13
10
8
6
4
2
0
PPM

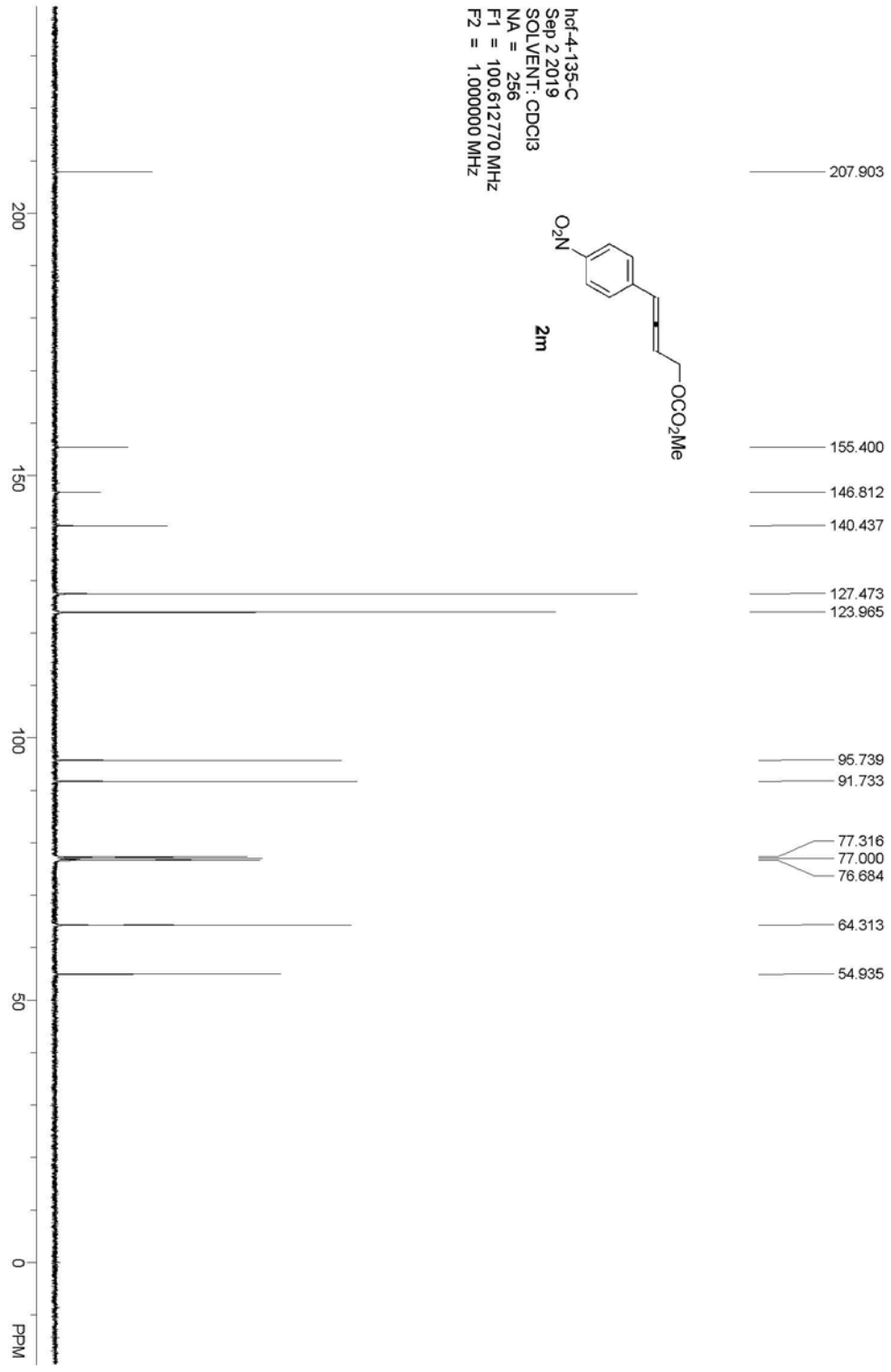

lj-4-176
20190708
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 30
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
MeO
2h
OCO2Me
206.204
159.097
155.534
128.145
125.332
114.162
96.134
90.525
77.316
77.000
76.684
65.529
55.251
54.809
200
150
100
50
0
PPM


WHN-2-192-H
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
16 Jul 2019
F3C
OCO2Me
2l
7.567
7.547
7.400
7.380
7.260
6.358
6.350
6.342
5.833
5.816
5.800
5.784
4.769
4.763
4.753
4.747
4.736
4.730
3.784
-0.000
2.07
2.09
1.00
0.97
2.11
3.13
10
8
6
4
2
0
PPM

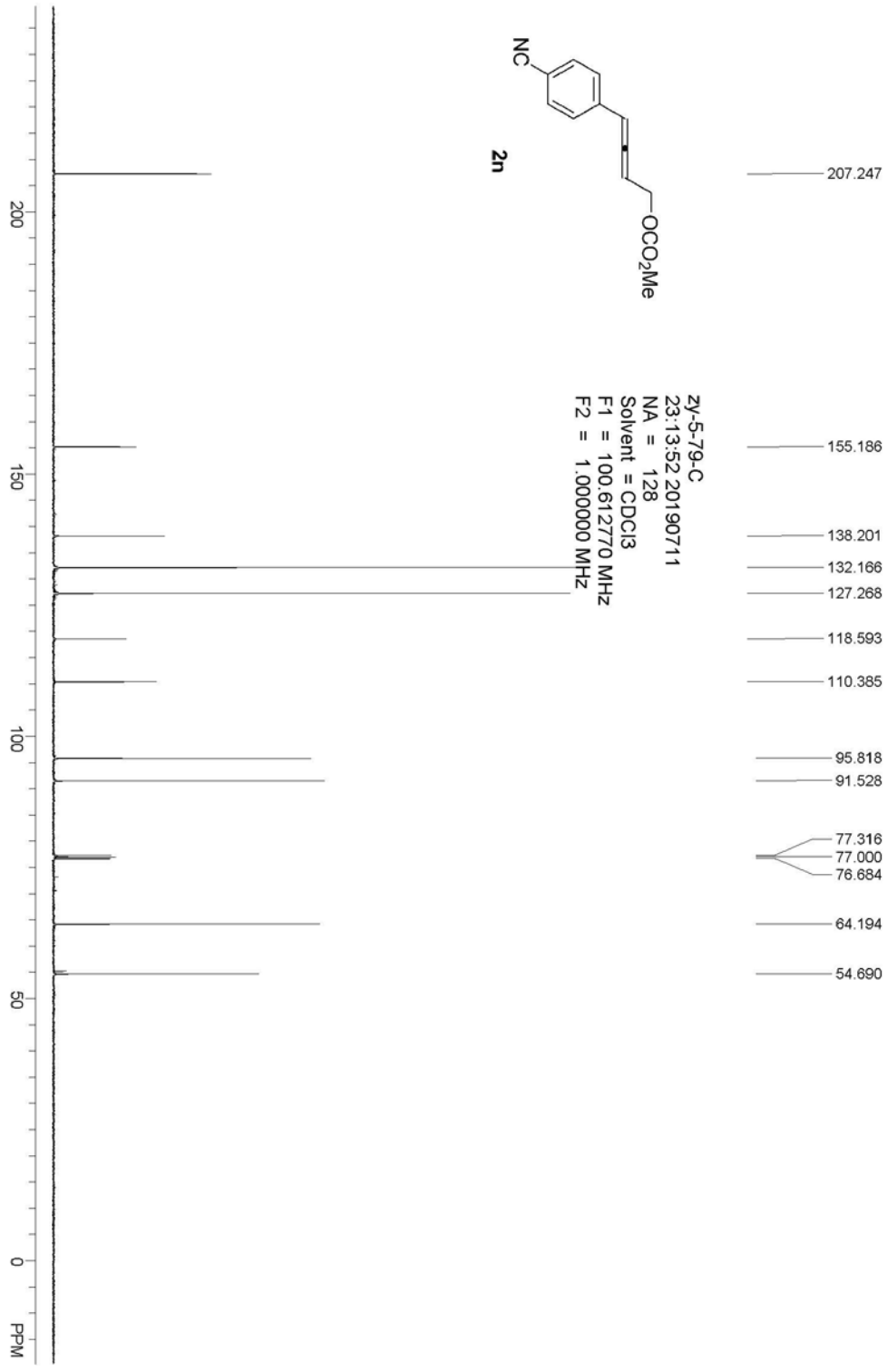

WHN-2-192-C
SOLVENT: CDCl3
NA = 1024
F1 = 100.612770 MHz
17 Jul 2019
F3C
OCO2Me
2l
207.231
155.502
129.788
137.119
129.464
129.140
128.816
127.157
125.640
125.601
125.561
125.522
125.482
122.780
95.968
91.323
77.316
77.000
76.676
64.747
54.912
200
150
100
50
0
PPM

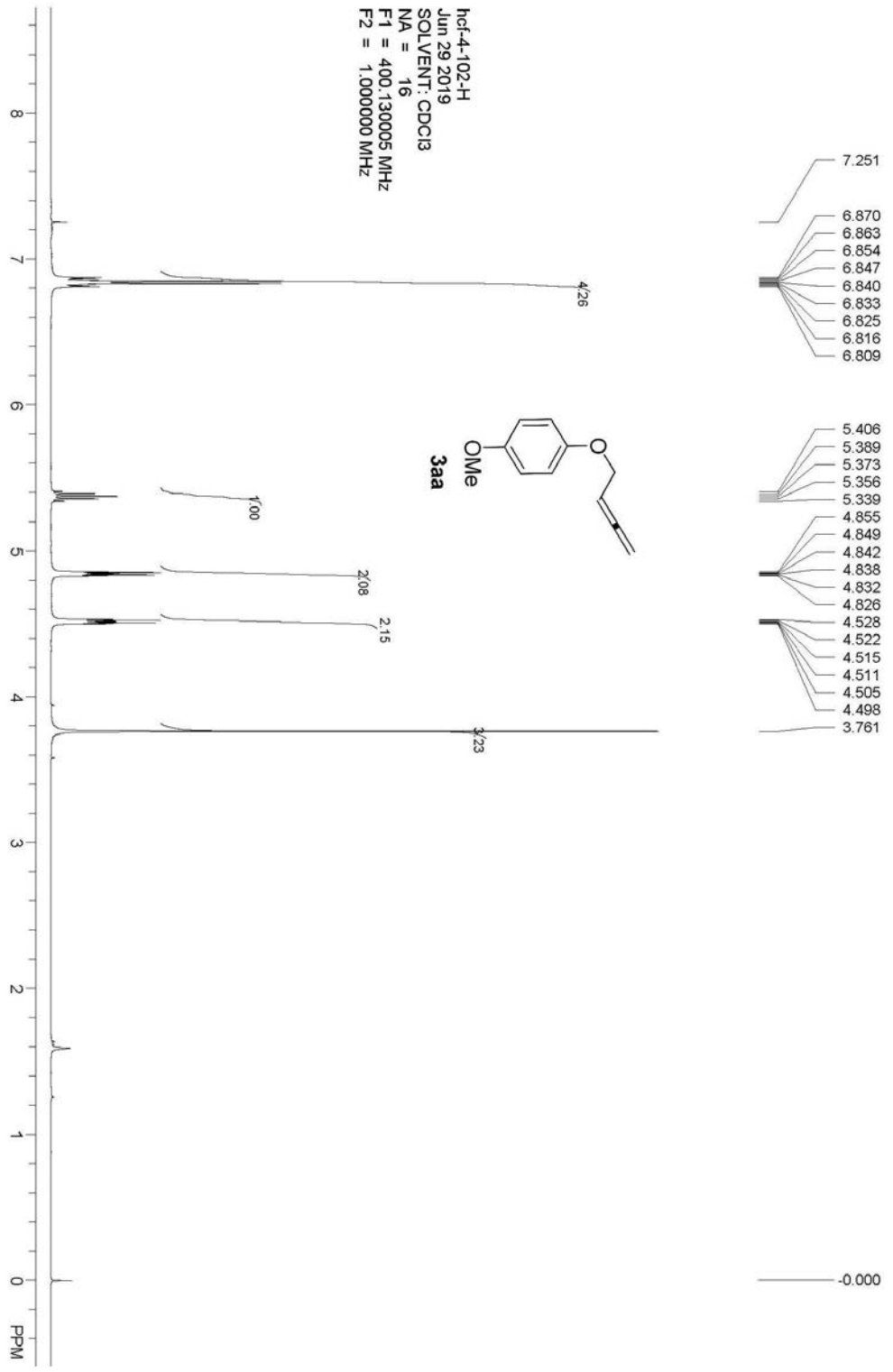

WHN-2-192-F
SOLVENT: CDCl3
NA = 16
F1 = 376.498352 MHz
17 Jul 2019
F3C
OCO2Me
2l
-0.000
-63.016
0
-20
-40
-60
-80
-100
PPM

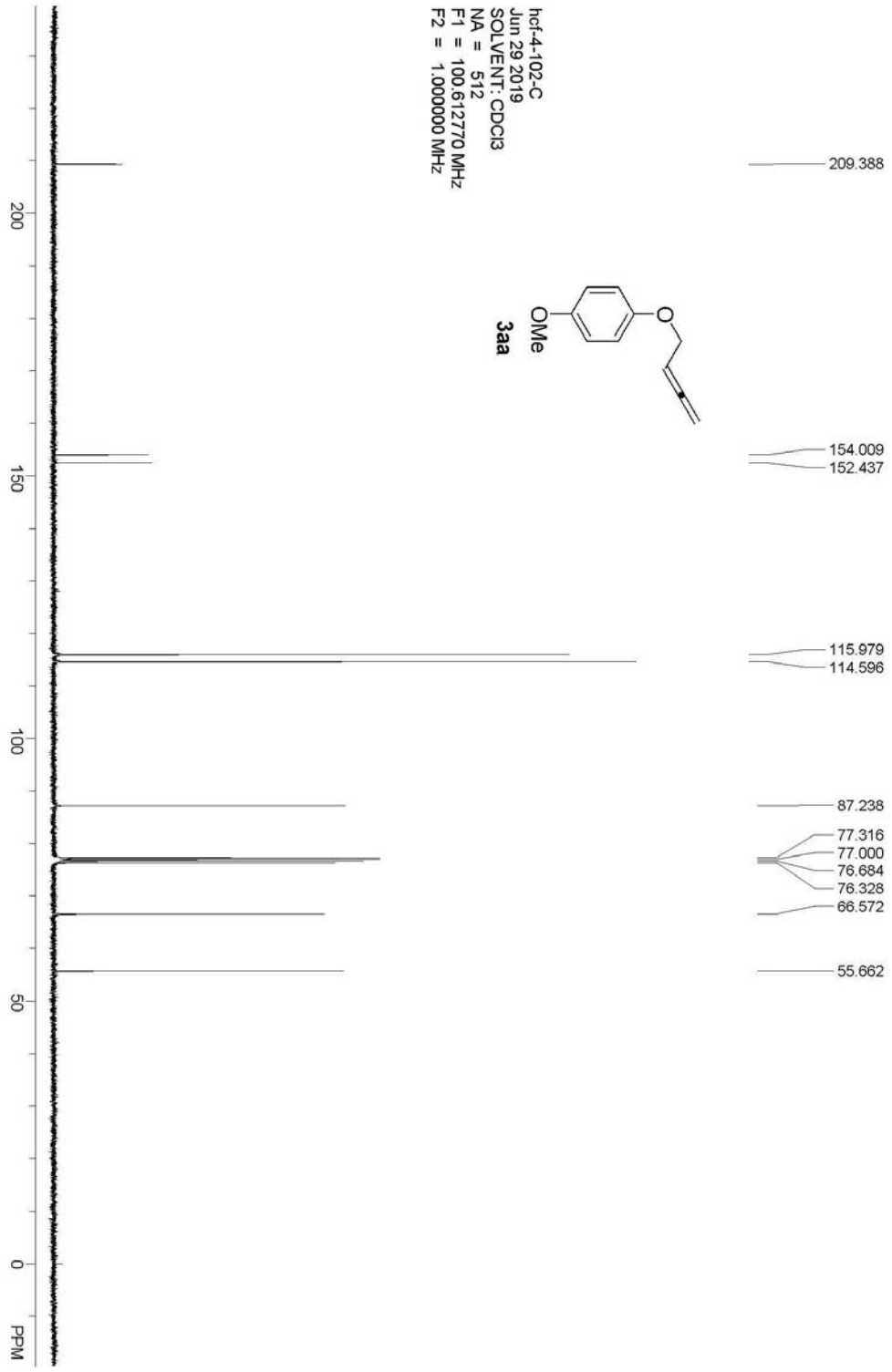

hcf-4-135-H
Sep 2 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
O2N
OCO2Me
2m
8.177
8.155
7.446
7.424
7.280
6.407
6.398
6.391
5.892
5.876
5.859
5.843
4.822
4.816
4.807
4.800
4.791
4.785
4.775
4.769
4.757
4.752
4.744
4.738
4.726
4.721
3.790
0.000
2.00
2.02
0.98
0.96
2.10
2.07
10
8
6
4
2
0
PPM

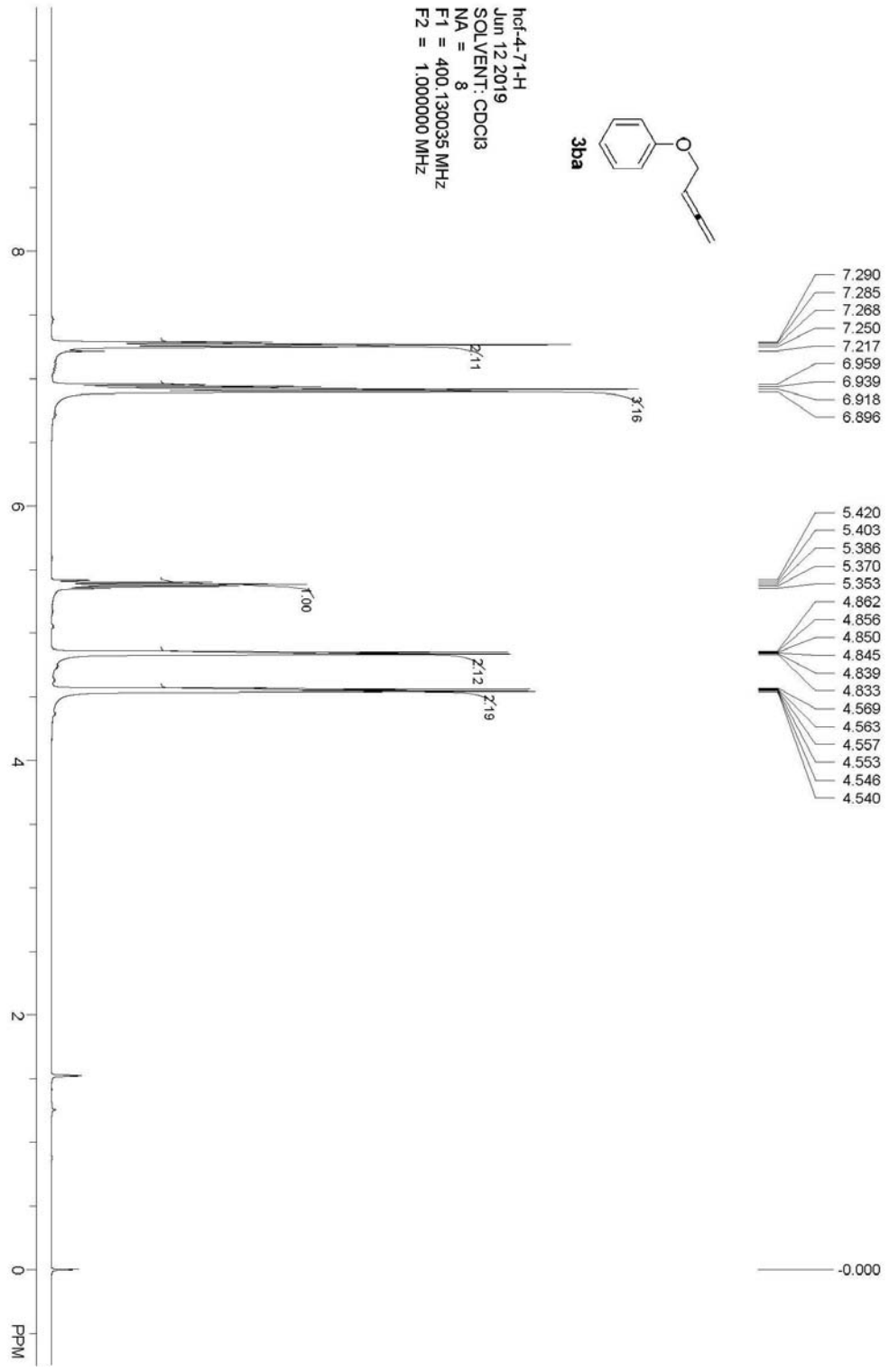

hcf-4-135-C
Sep 2 2019
SOLVENT: CDCl3
NA = 256
F1 = 100.612770 MHz
F2 = 1.000000 MHz
O2N
OCO2Me
2m
207.903
155.400
146.812
140.437
127.473
123.965
95.739
91.733
77.316
77.000
76.684
64.313
54.935
200
150
100
50
0
PPM

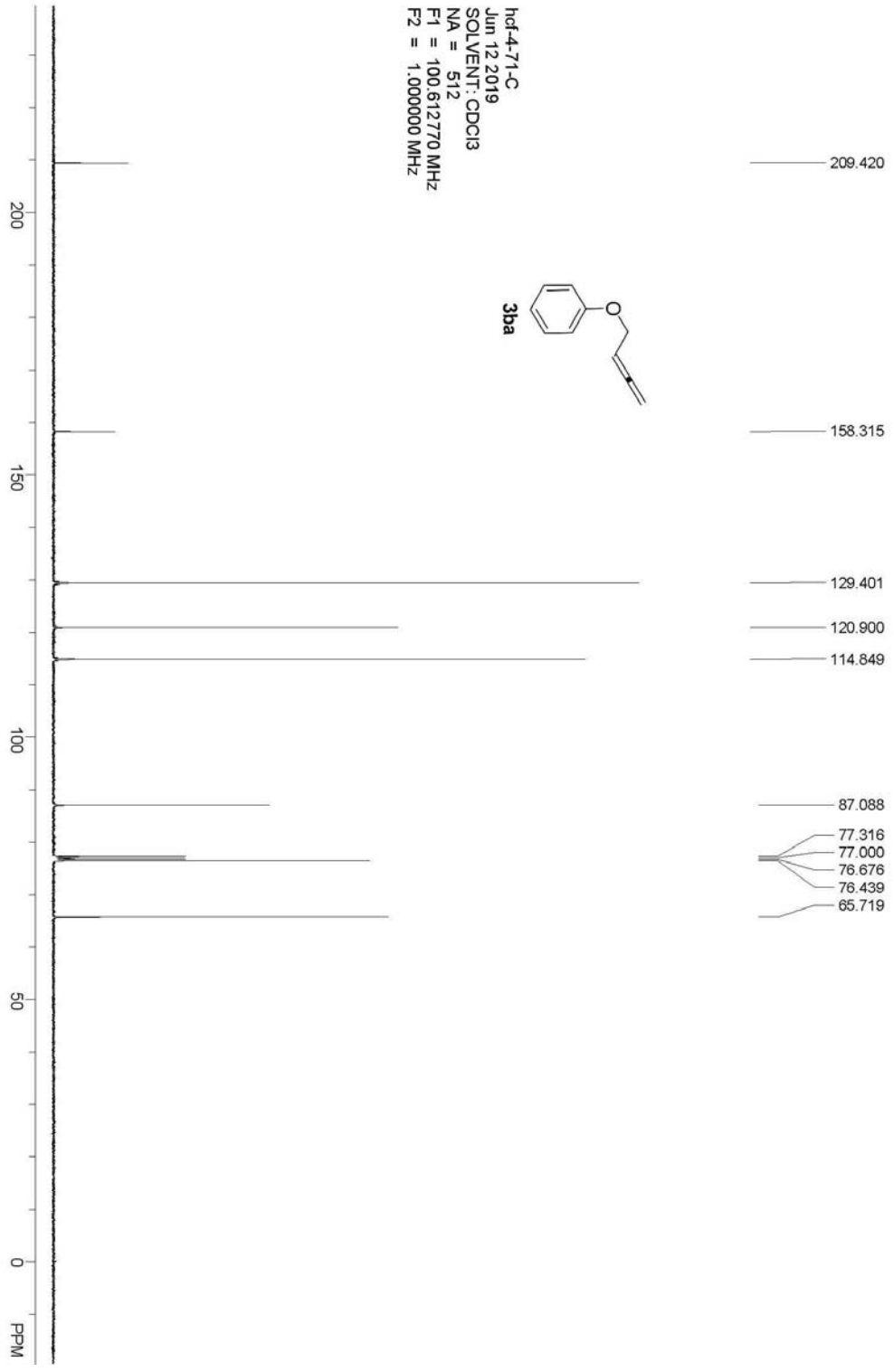

zy-5-79-H
23:05:55 20190711
NA = 4
Solvent = CDCl3
F1 = 400.129974 MHz
F2 = 1.000000 MHz
NC
OCO2Me
2n
7.594
7.573
7.395
7.375
6.358
6.350
6.342
5.868
5.852
5.836
5.819
4.796
4.788
4.781
4.772
4.766
4.755
4.750
4.738
4.732
4.724
4.718
4.707
4.701
3.776
-0.000
2.05
2.20
1.00
0.96
2.20
3.00
8
6
4
2
0
PPM

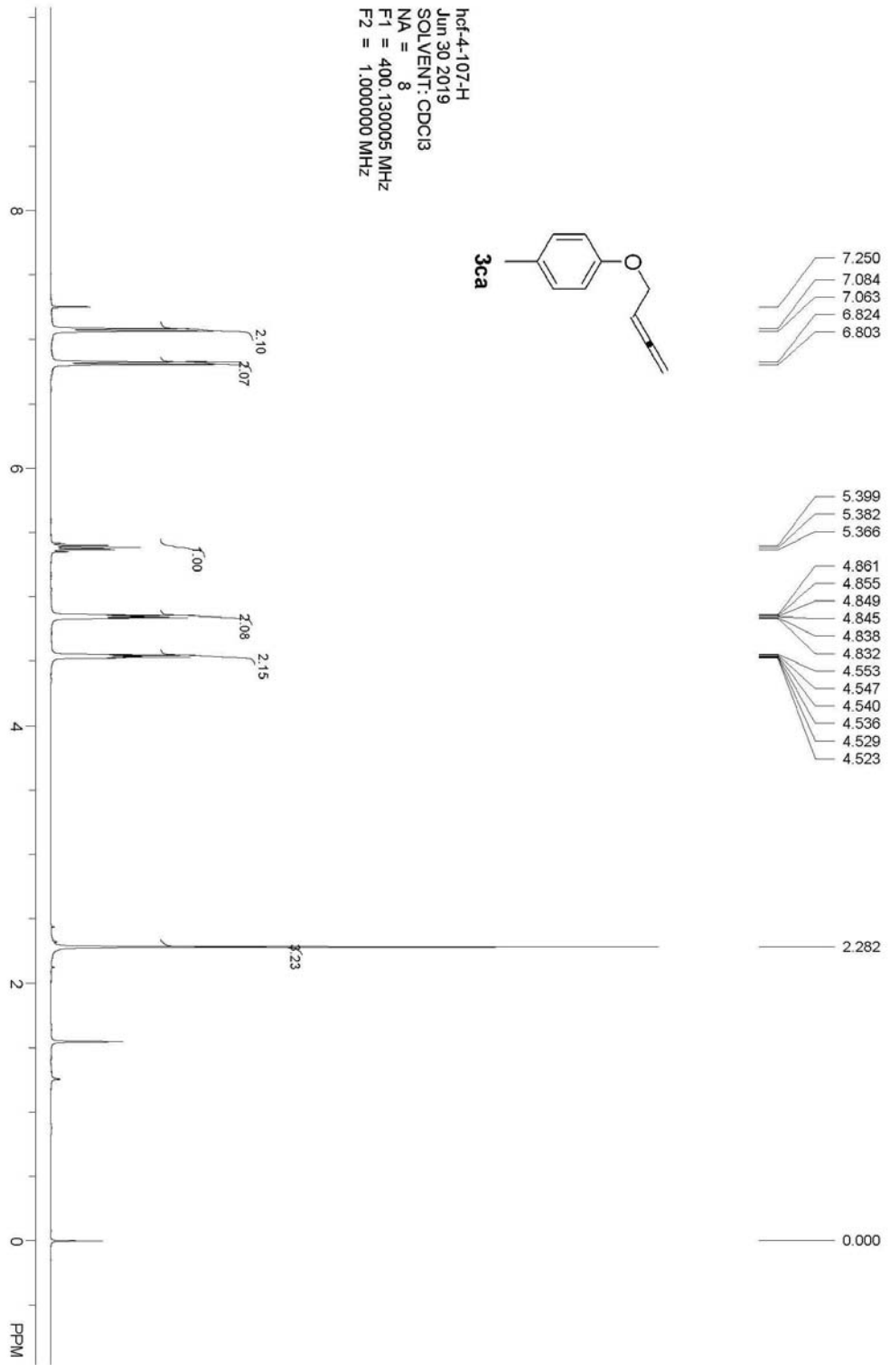

NC
OCO2Me
2n
zy-5-79-C
23:13:52 20190711
NA = 128
Solvent = CDCl3
F1 = 100.612770 MHz
F2 = 1.000000 MHz
207.247
155.186
138.201
132.166
127.268
118.593
110.385
95.818
91.528
77.316
77.000
76.684
64.194
54.690
200
150
100
50
0
PPM

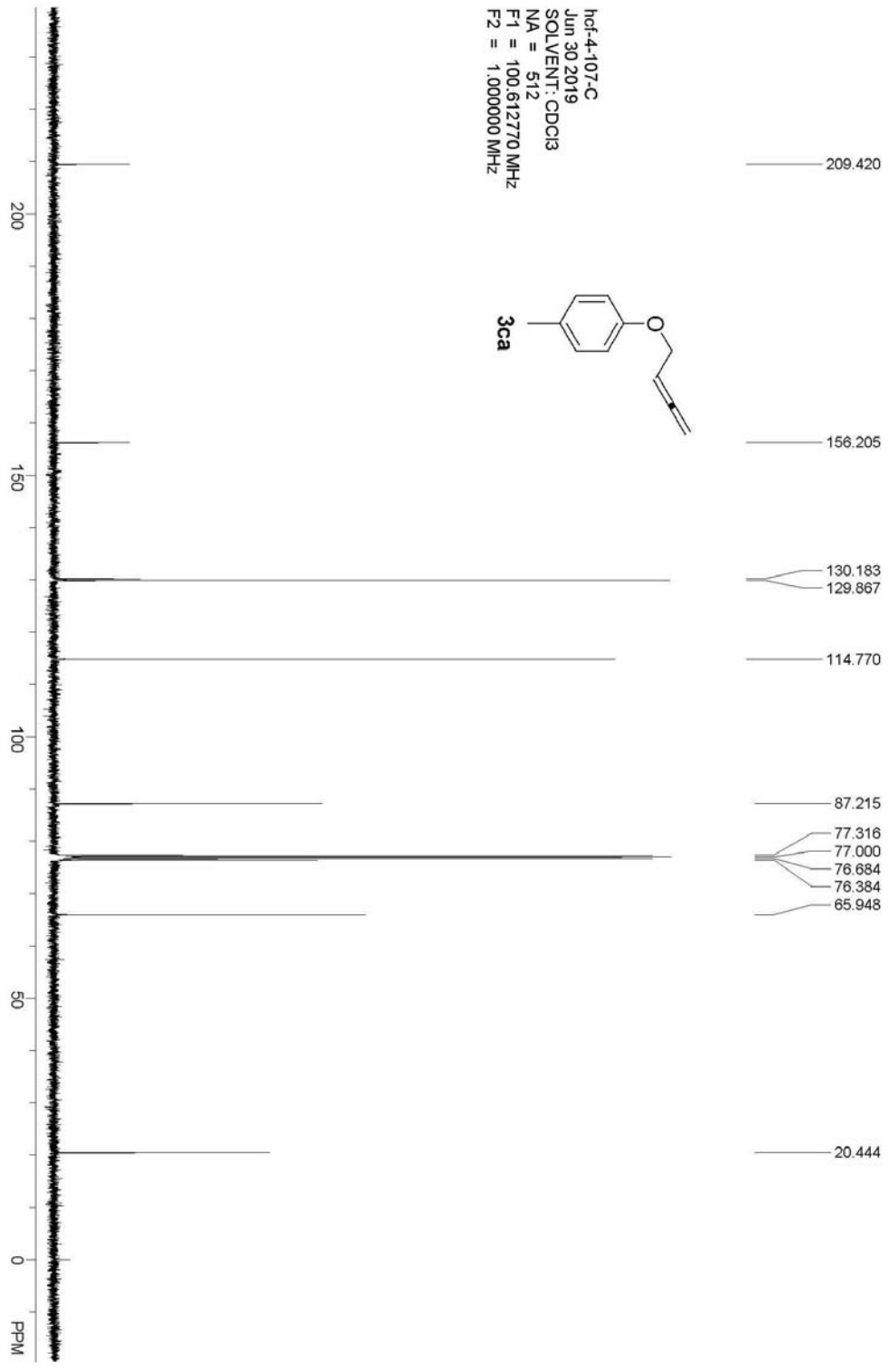

hcf-4-102-H
Jun 29 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
4.26
1.00
2.08
2.15
3.23
OMe
3aa
7.251
6.870
6.863
6.854
6.847
6.840
6.833
6.825
6.816
6.809
5.406
5.389
5.373
5.356
5.339
4.855
4.849
4.842
4.838
4.832
4.826
4.528
4.522
4.515
4.511
4.505
4.498
3.761
-0.000
PPM

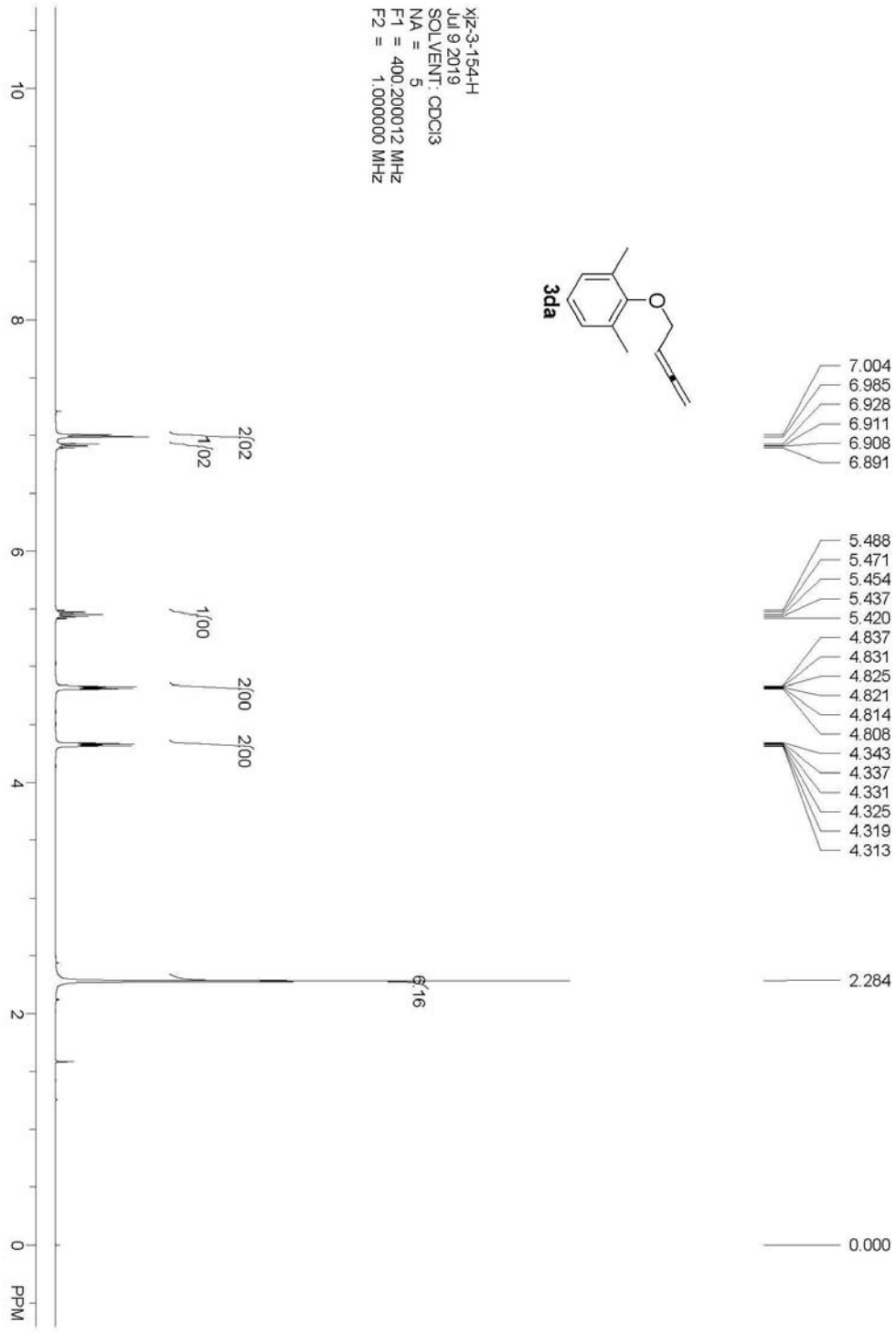

hcf-4-102-C
Jun 29 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
OMe
3aa
209.388
154.009
152.437
115.979
114.596
87.238
77.316
77.000
76.684
76.328
66.572
55.662
200
150
100
50
0
PPM

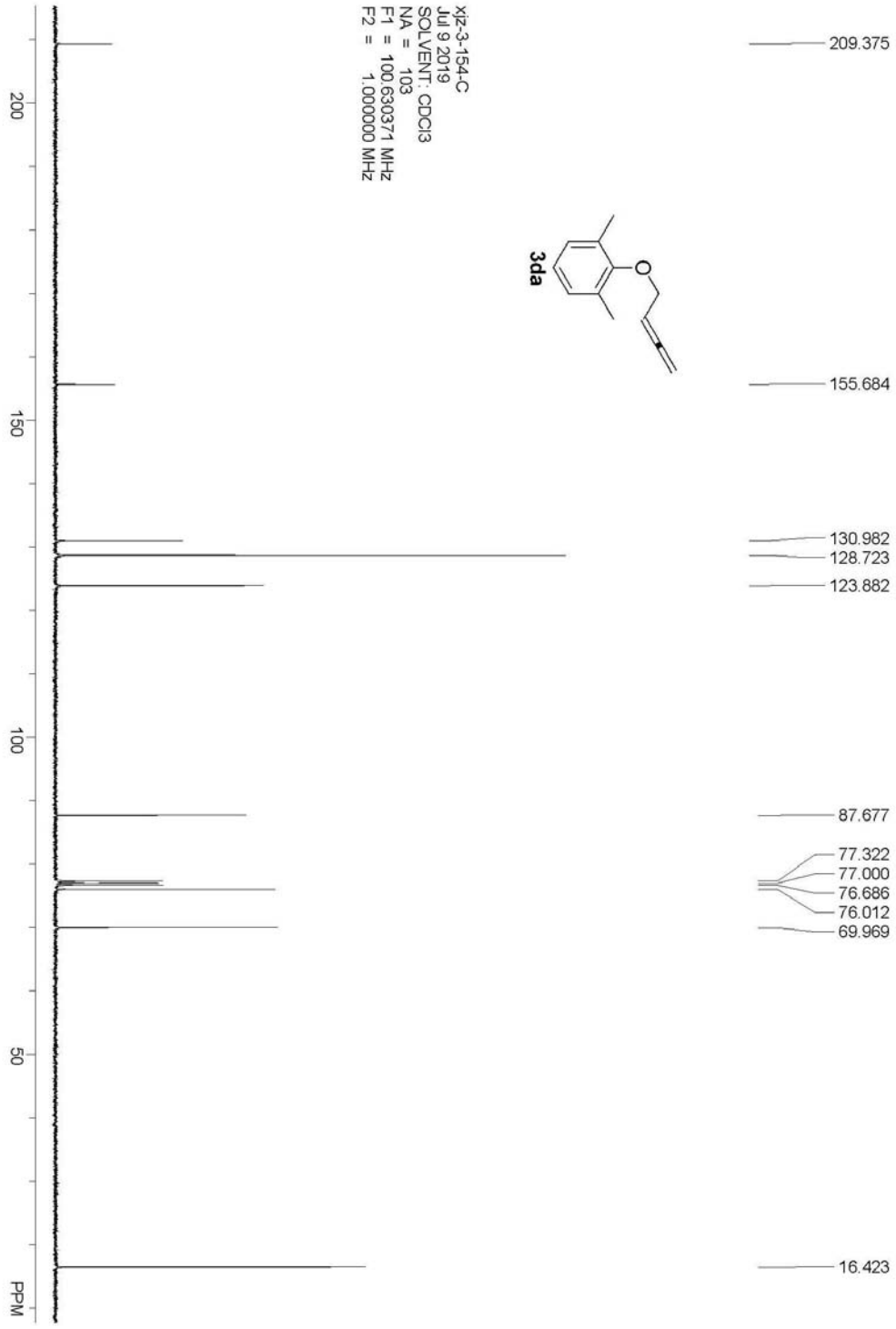

hcf-4-71-H
Jun 12 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130035 MHz
F2 = 1.000000 MHz
3ba
7.290
7.285
7.268
7.250
7.217
6.959
6.939
6.918
6.896
5.420
5.403
5.386
5.370
5.353
4.862
4.856
4.850
4.845
4.839
4.833
4.569
4.563
4.557
4.553
4.546
4.540
-0.000
2.11
3.16
1.00
2.12
2.19
8
6
4
2
0
PPM

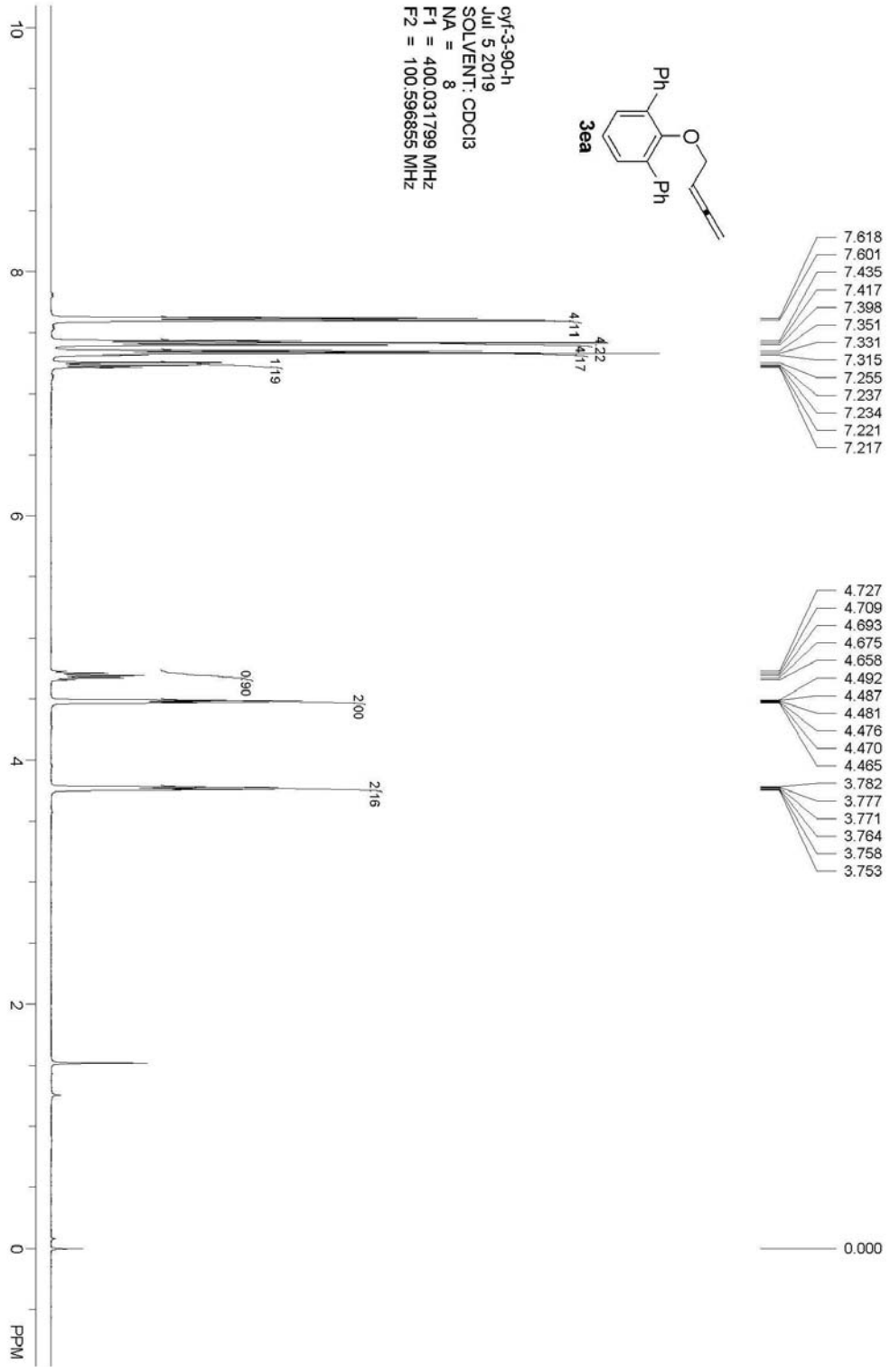

hcf-4-71-C
Jun 12 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3ba
209.420
158.315
129.401
120.900
114.849
87.088
77.316
77.000
76.676
76.439
65.719
200
150
100
50
0
PPM

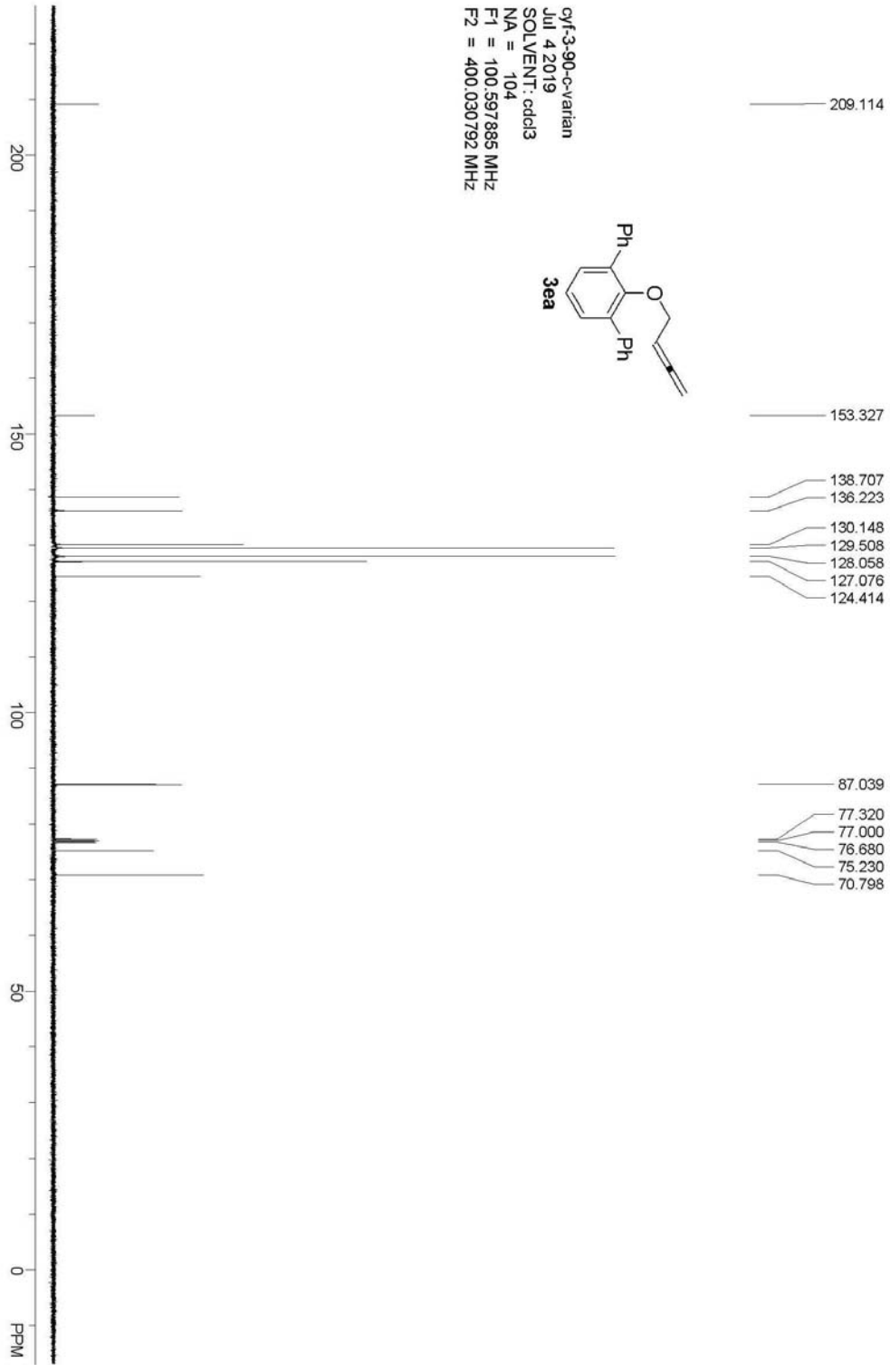

hcf-4-107-H
Jun 30 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3ca
7.250
7.084
7.063
6.824
6.803
5.399
5.382
5.366
4.861
4.855
4.849
4.845
4.838
4.832
4.553
4.547
4.540
4.536
4.529
4.523
2.282
0.000
2.10
2.07
1.00
2.08
2.15
7.23
8
6
4
2
0
PPM

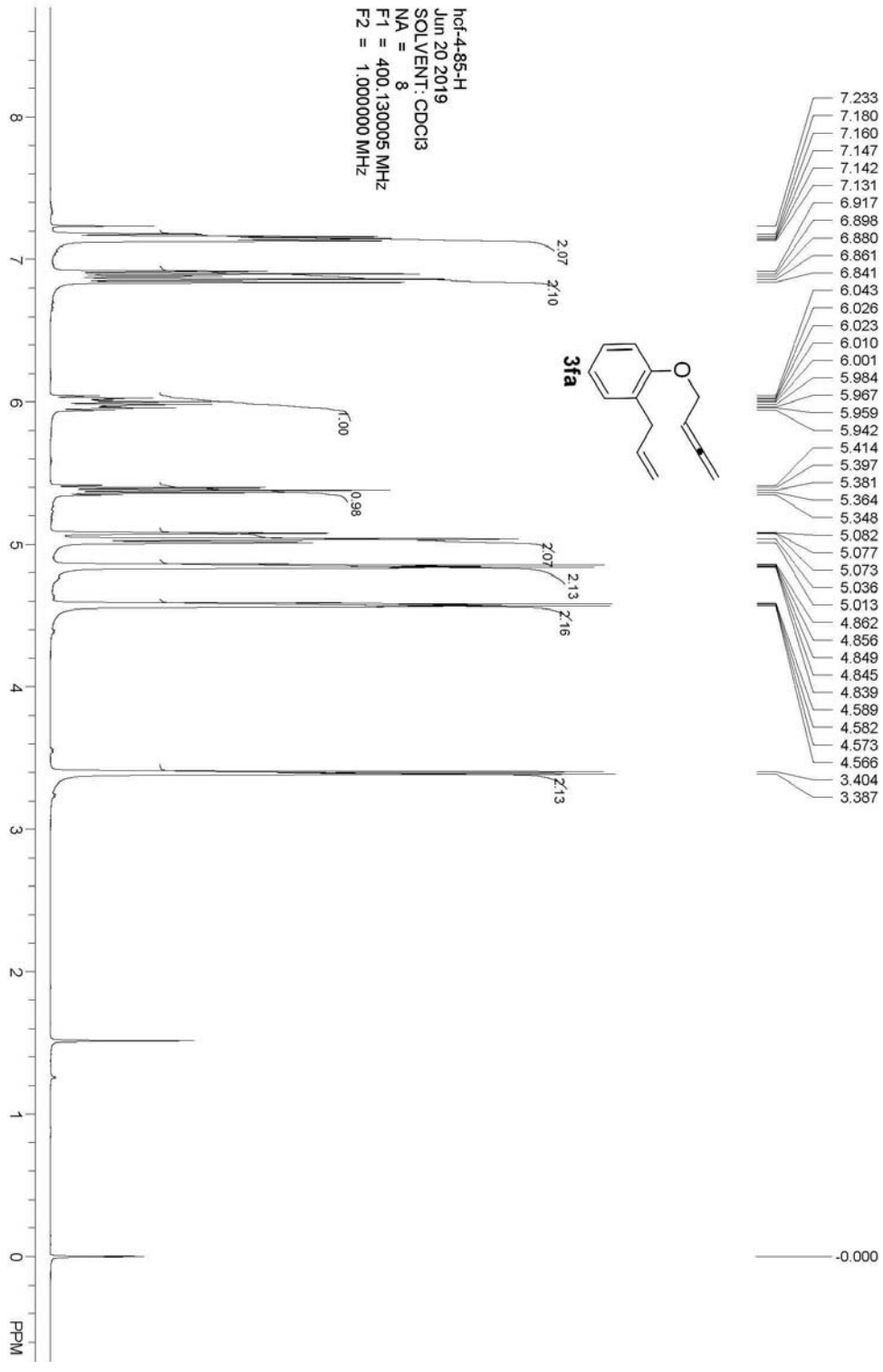

hcf-4-107-C
Jun 30 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3ca
209.420
156.205
130.183
129.867
114.770
87.215
77.316
77.000
76.684
76.384
65.948
20.444
200
150
100
50
0
PPM

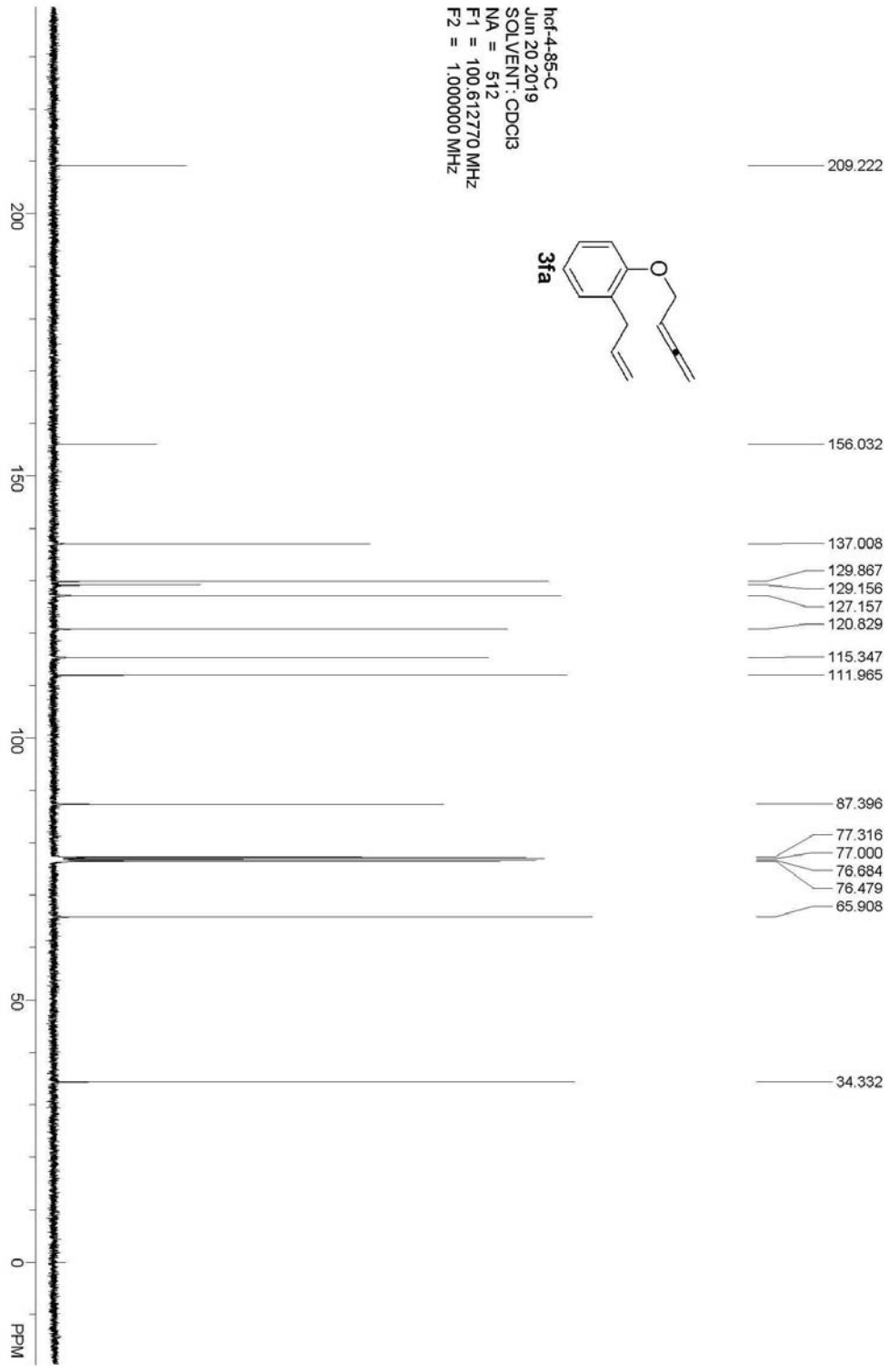

xjz-3-154-H
Jul 9 2019
SOLVENT: CDCl3
NA = 5
F1 = 400.200012 MHz
F2 = 1.000000 MHz
3da
7.004
6.985
6.928
6.911
6.908
6.891
5.488
5.471
5.454
5.437
5.420
4.837
4.831
4.825
4.821
4.814
4.808
4.343
4.337
4.331
4.325
4.319
4.313
2.284
0.000
2.02
1.02
1.00
2.00
2.00
6.16
10
8
6
4
2
0
PPM

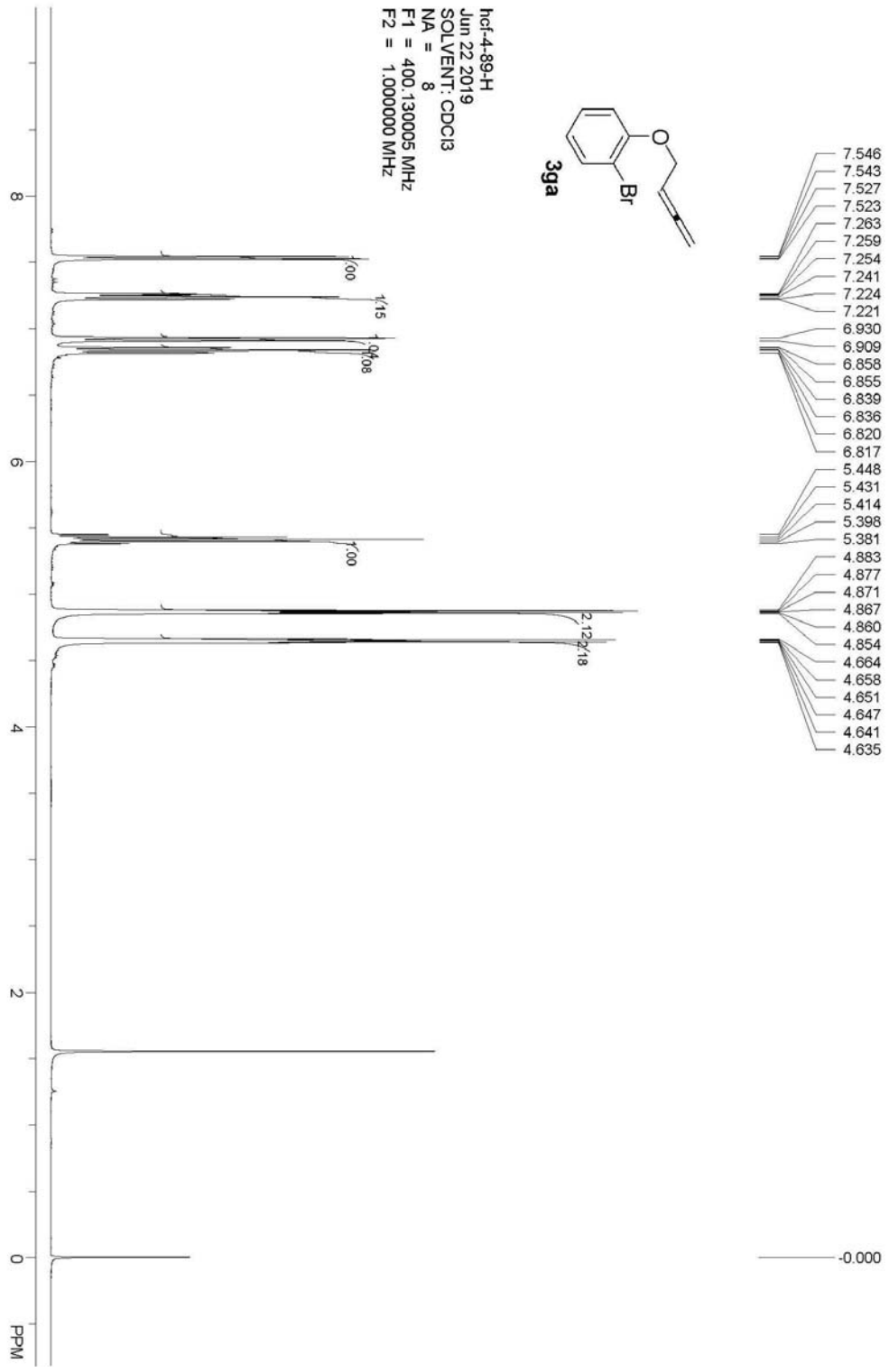

xjz-3-154-C
Jul 9 2019
SOLVENT: CDCl3
NA = 103
F1 = 100.630371 MHz
F2 = 1.000000 MHz
3da
209.375
155.684
130.982
128.723
123.882
87.677
77.322
77.000
76.686
76.012
69.969
16.423
200
150
100
50
PPM

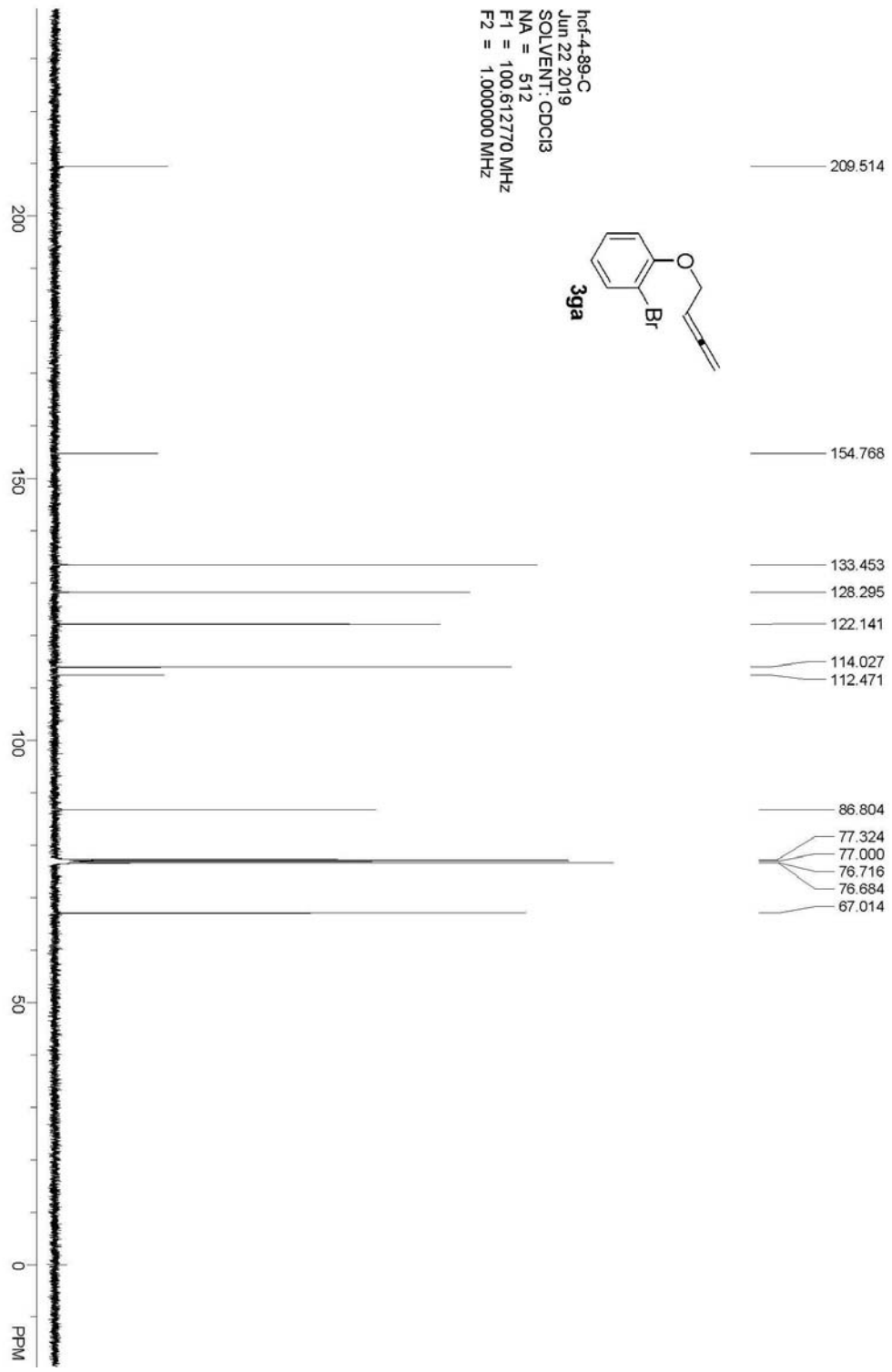

cyf-3-90-h
Jul 5 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.031799 MHz
F2 = 100.596855 MHz
3ea
Ph
Ph
O
7.618
7.601
7.435
7.417
7.398
7.351
7.331
7.315
7.255
7.237
7.234
7.221
7.217
4.727
4.709
4.693
4.675
4.658
4.492
4.487
4.481
4.476
4.470
4.465
3.782
3.777
3.771
3.764
3.758
3.753
0.000
4.11
4.22
4.17
1.19
0.90
2.00
2.16
10
8
6
4
2
0
PPM

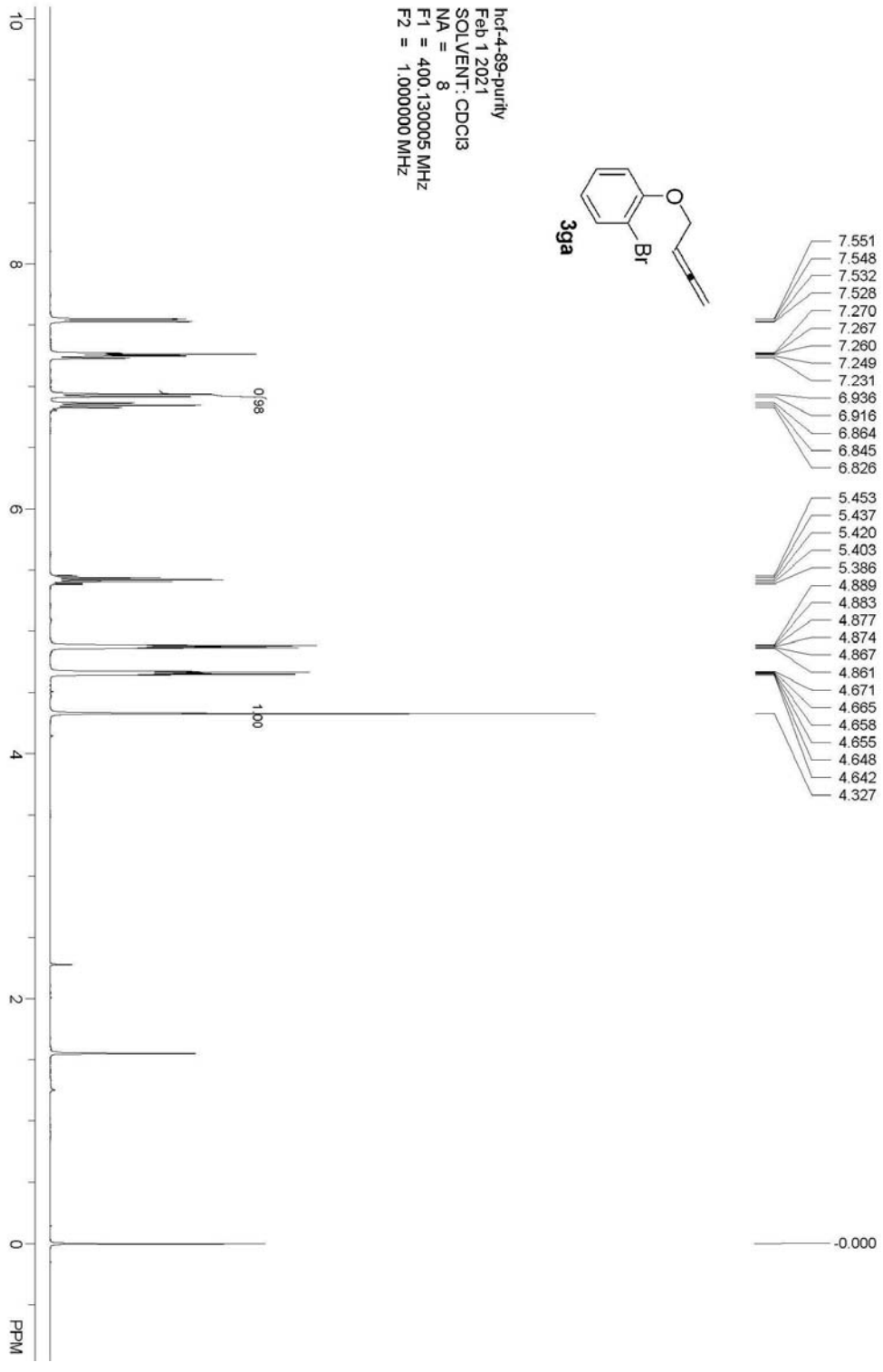

cyf-3-90-c-varian
Jul 4 2019
SOLVENT: cdcl3
NA = 104
F1 = 100.597885 MHz
F2 = 400.030792 MHz
3ea
Ph
Ph
O
209.114
153.327
138.707
136.223
130.148
129.508
128.058
127.076
124.414
87.039
77.320
77.000
76.680
75.230
70.798
200
150
100
50
0
PPM

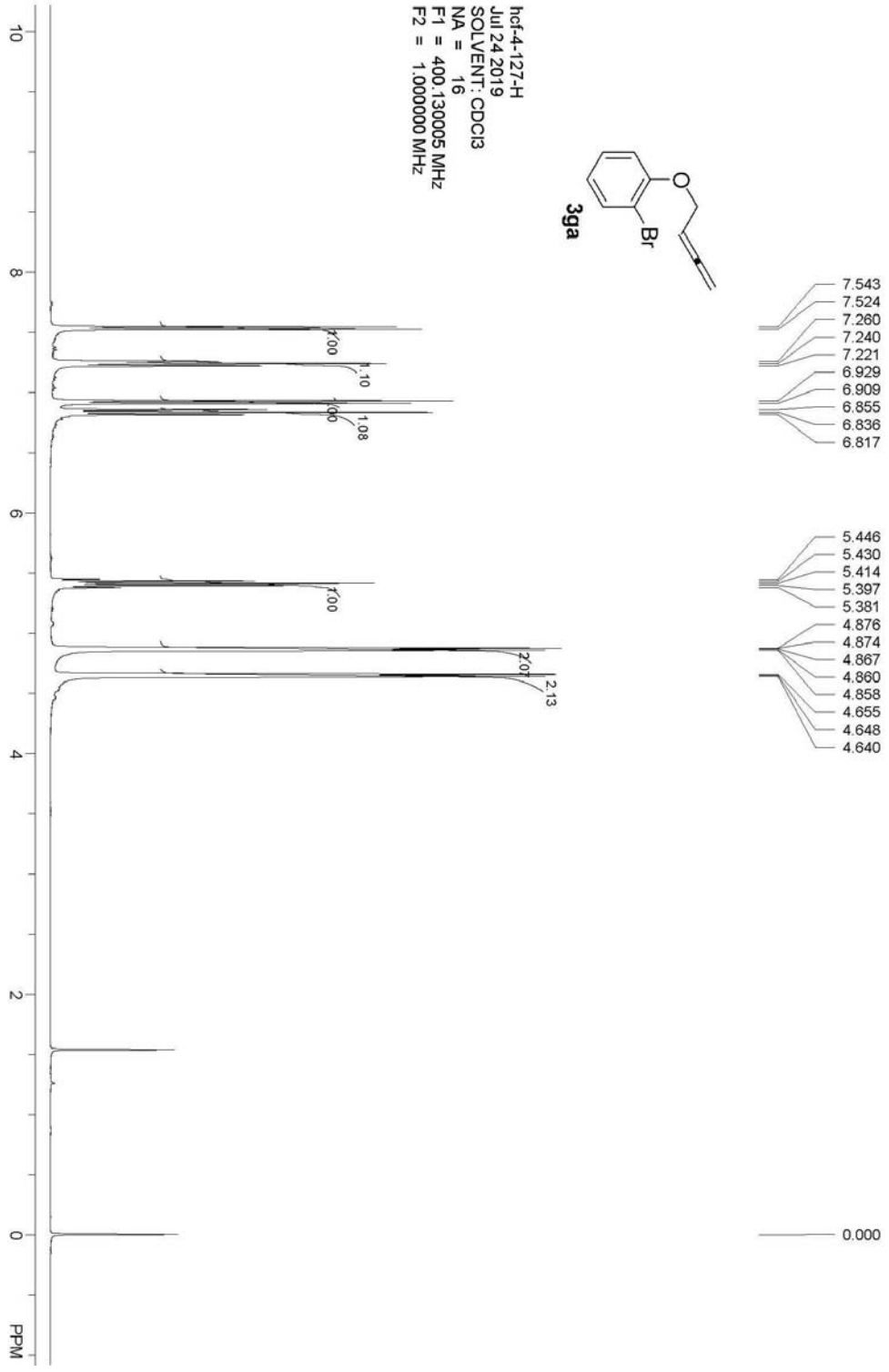

hcf-4-85-H
Jun 20 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
2.07
2.10
1.00
0.98
2.07
2.13
2.16
2.13
3fa
7.233
7.180
7.160
7.147
7.142
7.131
6.917
6.898
6.880
6.861
6.841
6.043
6.026
6.023
6.010
6.001
5.984
5.967
5.959
5.942
5.414
5.397
5.381
5.364
5.348
5.082
5.077
5.073
5.036
5.013
4.862
4.856
4.849
4.845
4.839
4.589
4.582
4.573
4.566
3.404
3.387
-0.000
PPM

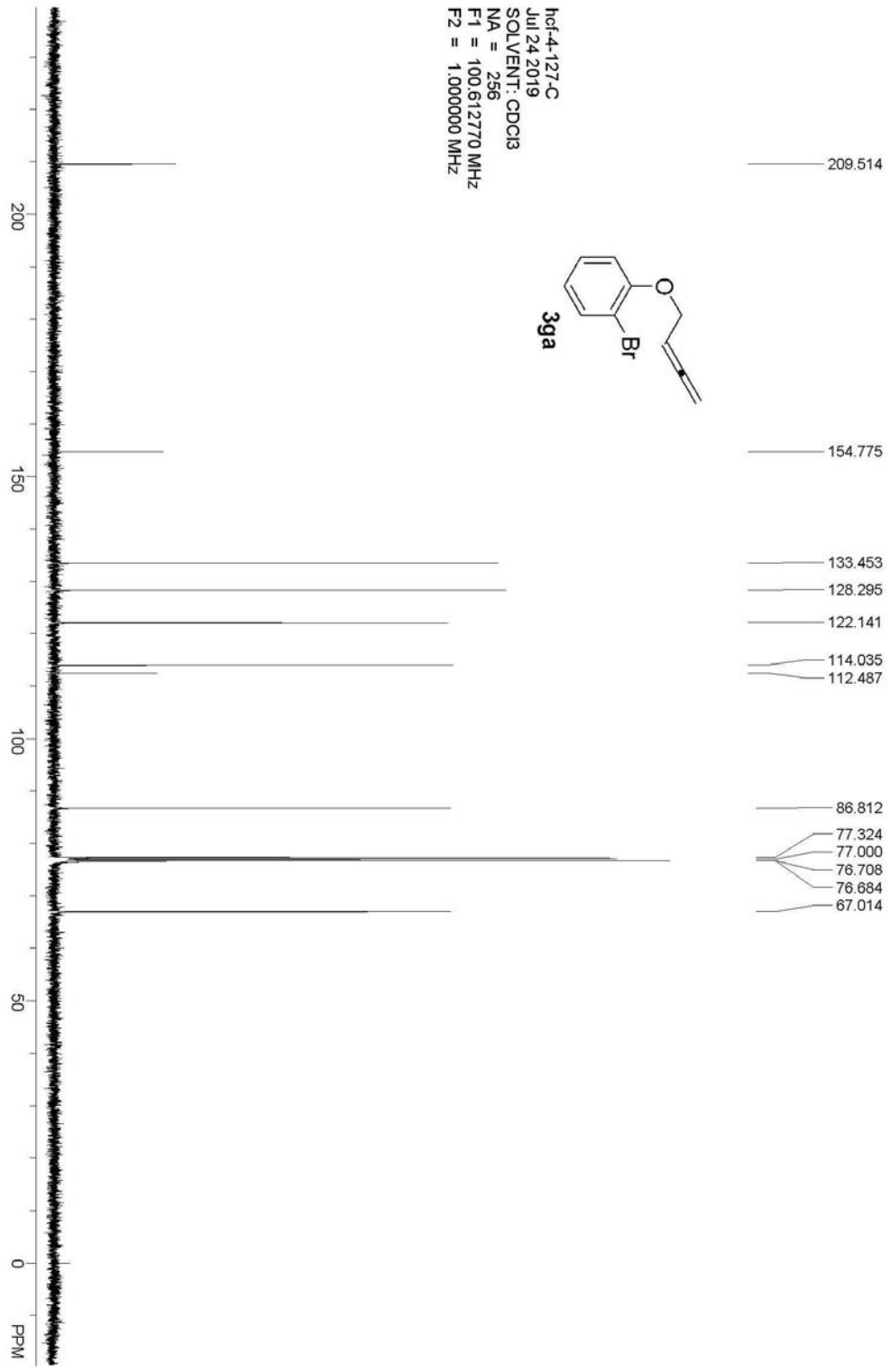

hcf-4-85-C
Jun 20 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3fa
209.222
156.032
137.008
129.867
129.156
127.157
120.829
115.347
111.965
87.396
77.316
77.000
76.684
76.479
65.908
34.332
200
150
100
50
0
PPM

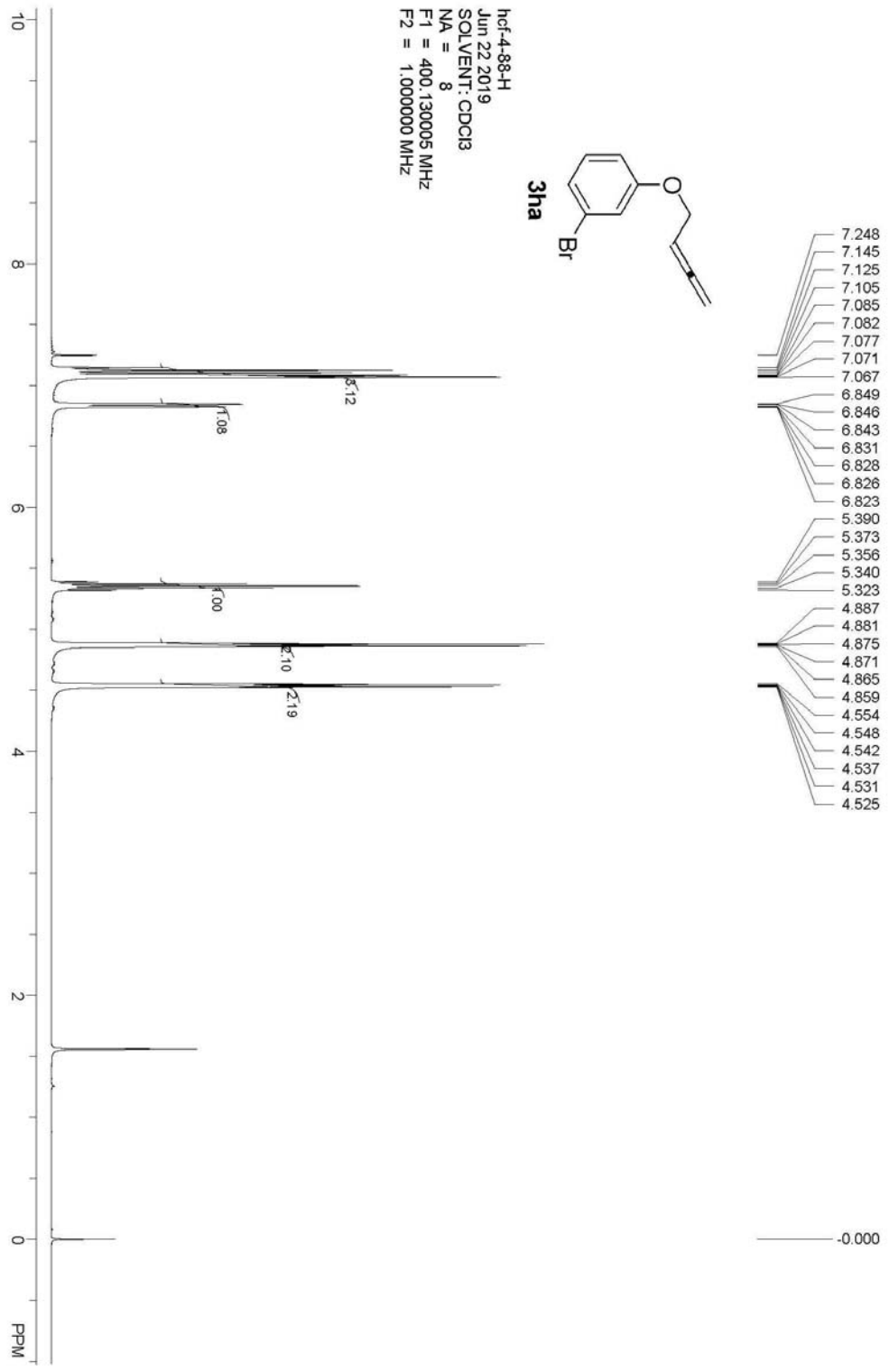

hcf-4-89-H
Jun 22 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3ga
Br
O
7.546
7.543
7.527
7.523
7.263
7.259
7.254
7.241
7.224
7.221
6.930
6.909
6.858
6.855
6.839
6.836
6.820
6.817
5.448
5.431
5.414
5.398
5.381
4.883
4.877
4.871
4.867
4.860
4.854
4.664
4.658
4.651
4.647
4.641
4.635
-0.000
1.00
1.15
1.04
1.08
1.00
2.12
2.18
8
6
4
2
0
PPM

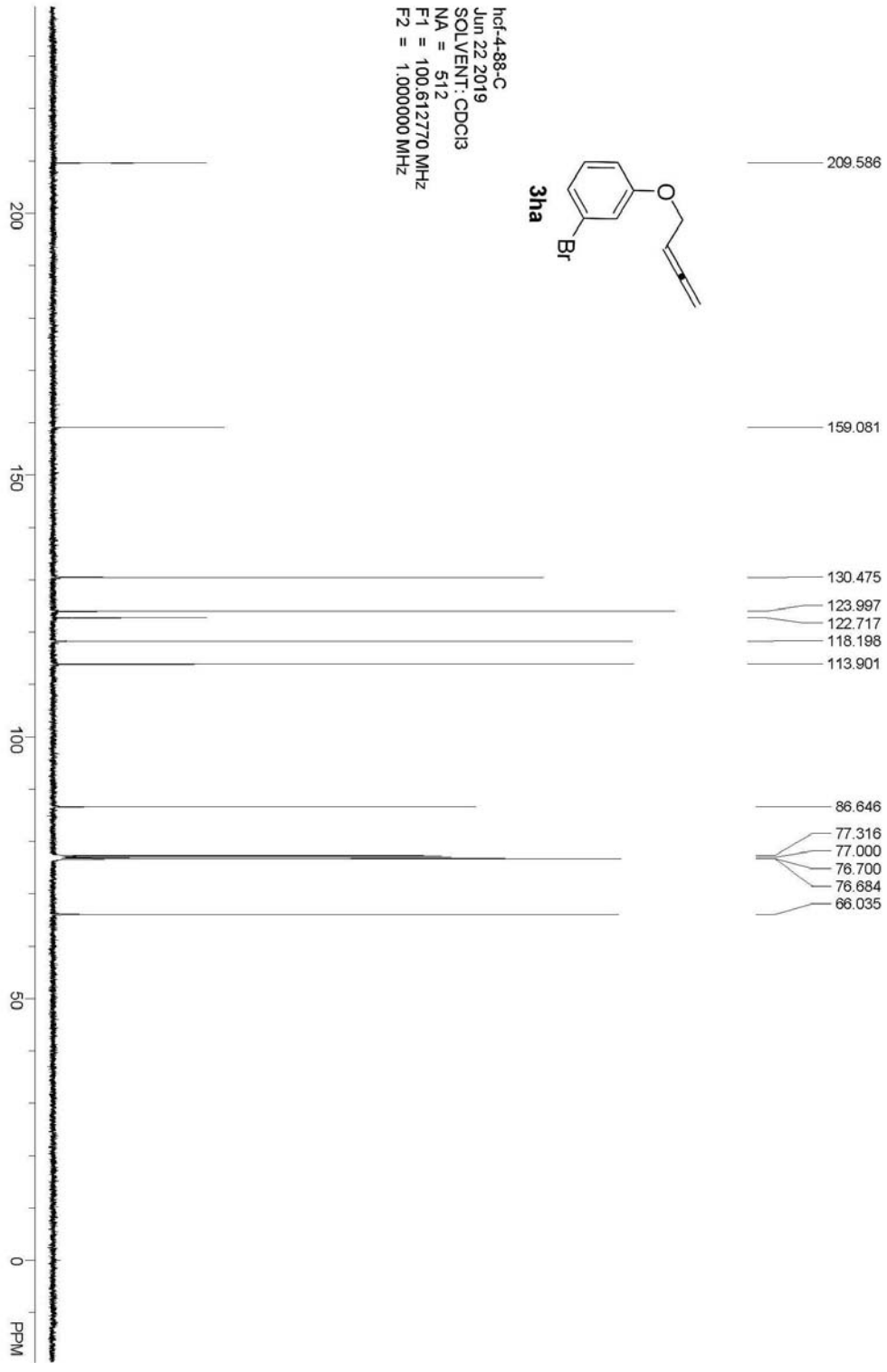

hcf-4-89-C
Jun 22 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3ga
Br
209.514
154.768
133.453
128.295
122.141
114.027
112.471
86.804
77.324
77.000
76.716
76.684
67.014
200
150
100
50
0
PPM

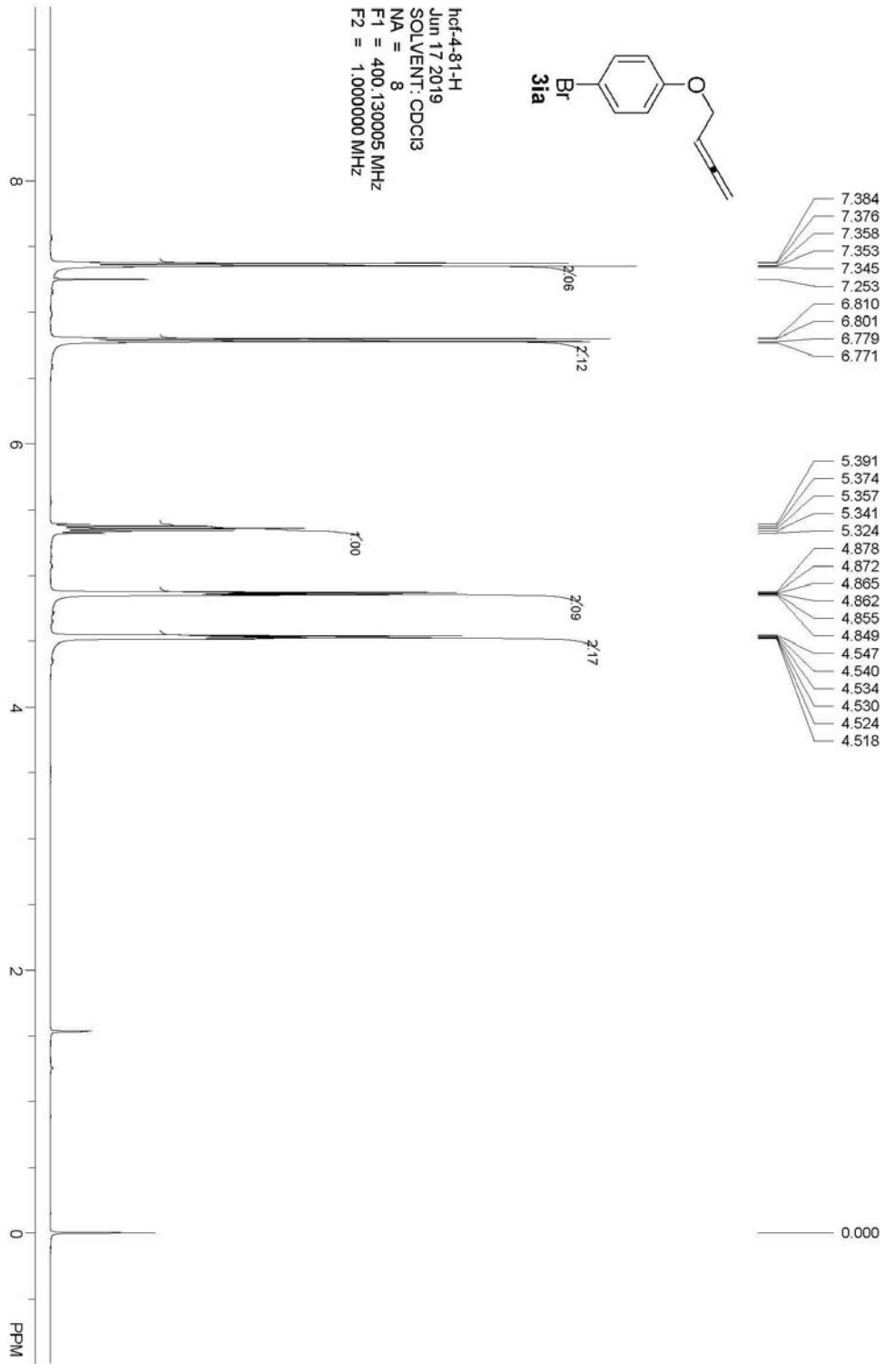

hcf-4-89-purity
Feb 1 2021
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3ga
Br
O
7.551
7.548
7.532
7.528
7.270
7.267
7.260
7.249
7.231
6.936
6.916
6.864
6.845
6.826
5.453
5.437
5.420
5.403
5.386
4.889
4.883
4.877
4.874
4.867
4.861
4.671
4.665
4.658
4.655
4.648
4.642
4.327
-0.000
0.98
1.00
10
8
6
4
2
0
PPM

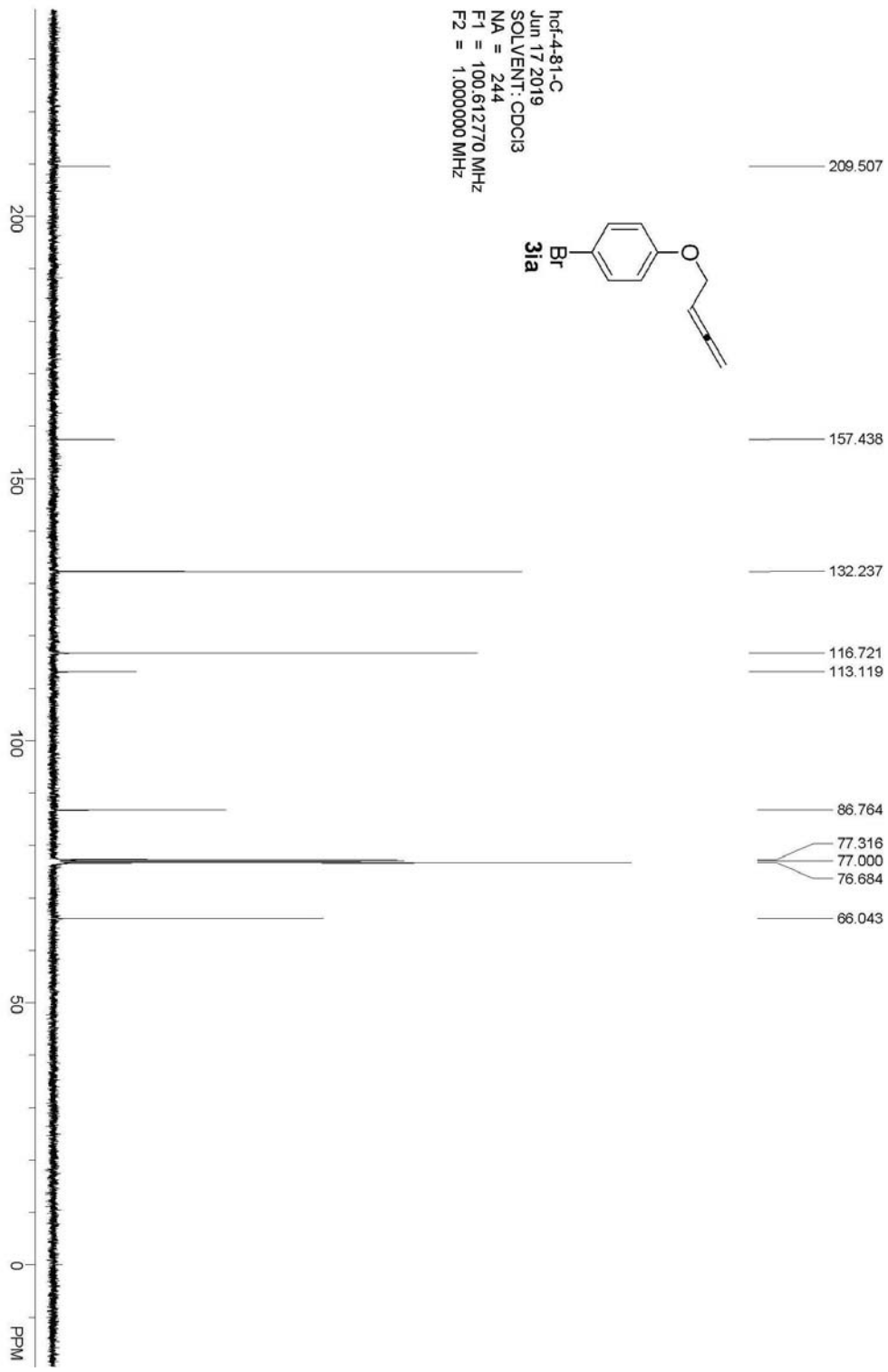

hcf-4-127-H
Jul 24 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3ga
Br
7.543
7.524
7.260
7.240
7.221
6.929
6.909
6.855
6.836
6.817
5.446
5.430
5.414
5.397
5.381
4.876
4.874
4.867
4.860
4.858
4.655
4.648
4.640
0.000
1.00
1.10
1.00
1.08
1.00
2.07
2.13
10
8
6
4
2
0
PPM

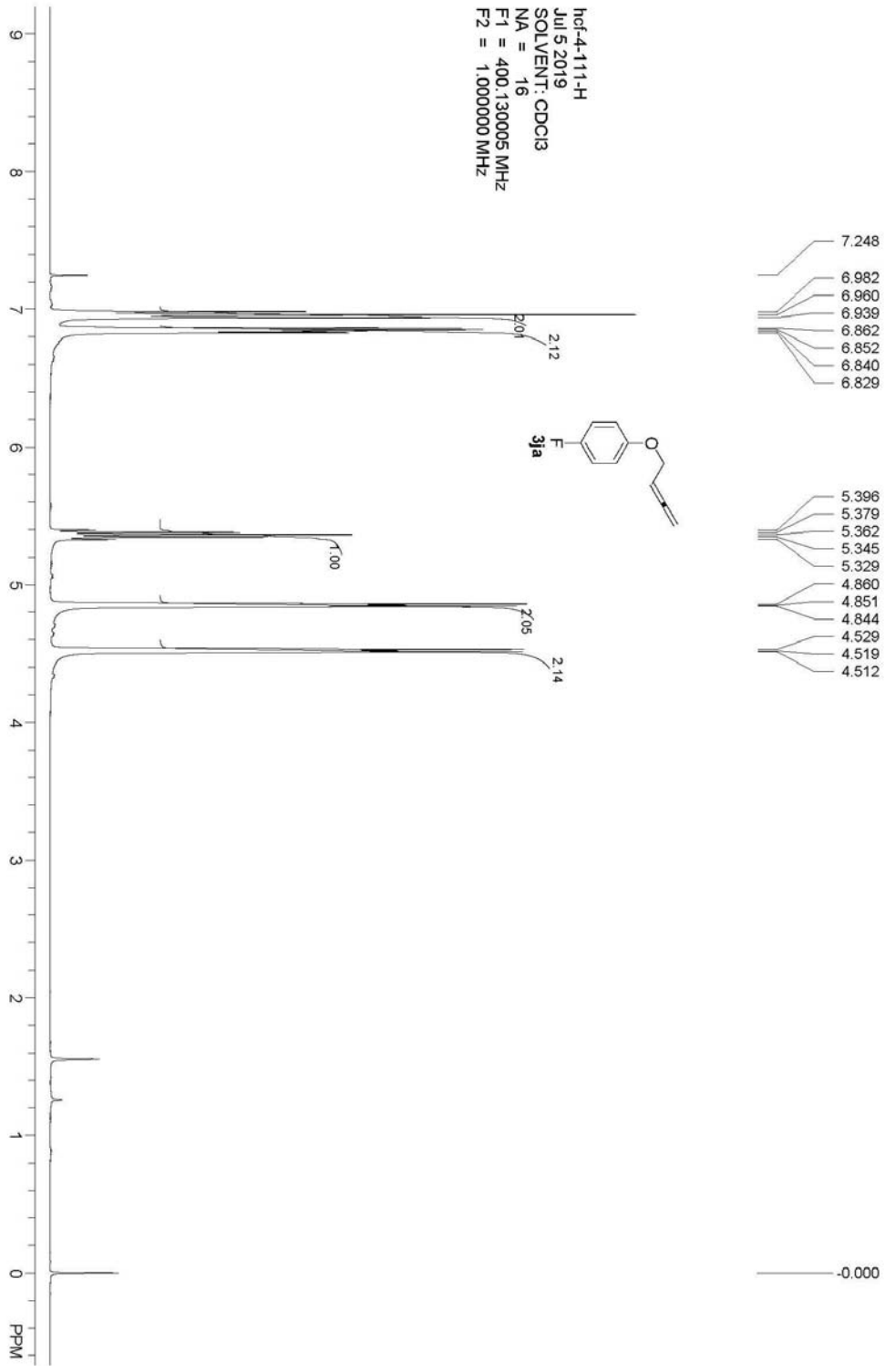

hcf-4-127-C
Jul 24 2019
SOLVENT: CDCl3
NA = 256
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3ga
Br
O
209.514
154.775
133.453
128.295
122.141
114.035
112.487
86.812
77.324
77.000
76.708
76.684
67.014
200
150
100
50
0
PPM

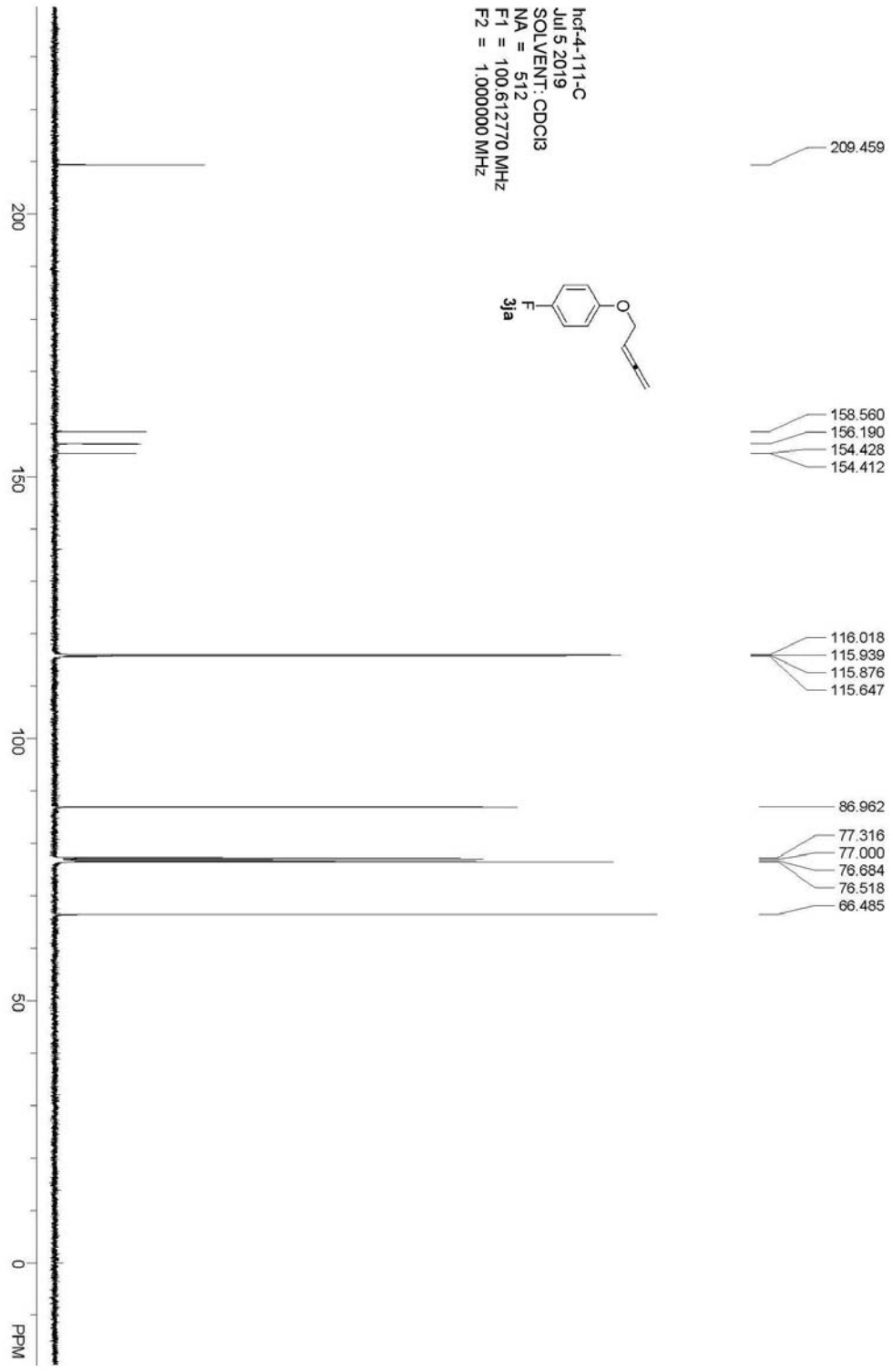

hcf-4-88-H
Jun 22 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3ha
Br
O
7.248
7.145
7.125
7.105
7.085
7.082
7.077
7.071
7.067
6.849
6.846
6.843
6.831
6.828
6.826
6.823
5.390
5.373
5.356
5.340
5.323
4.887
4.881
4.875
4.871
4.865
4.859
4.554
4.548
4.542
4.537
4.531
4.525
-0.000
3.12
1.08
1.00
2.10
2.19
10
8
6
4
2
0
PPM

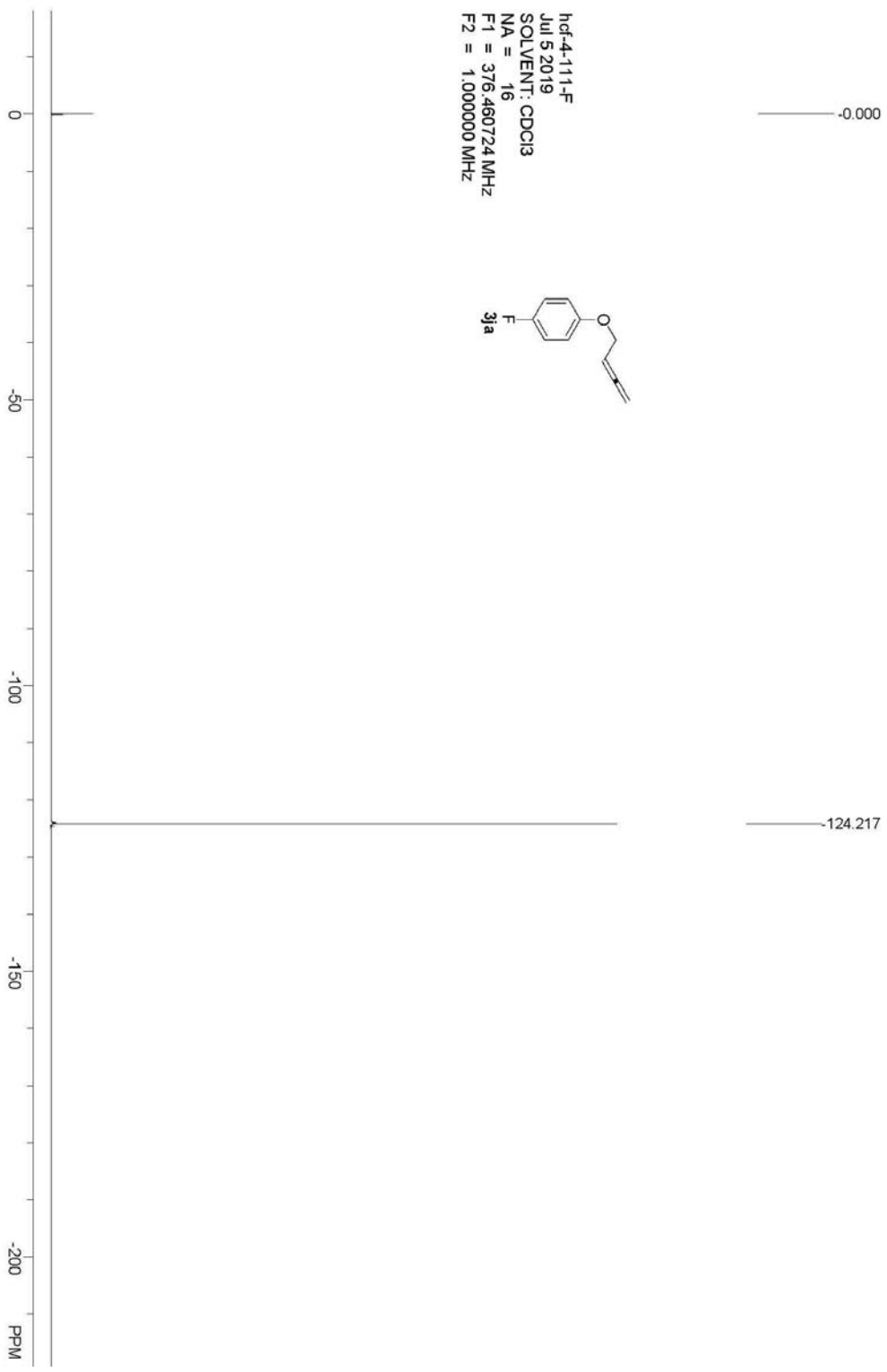

hcf-4-88-C
Jun 22 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3ha
Br
O
209.586
159.081
130.475
123.997
122.717
118.198
113.901
86.646
77.316
77.000
76.700
76.684
66.035
200
150
100
50
0
PPM

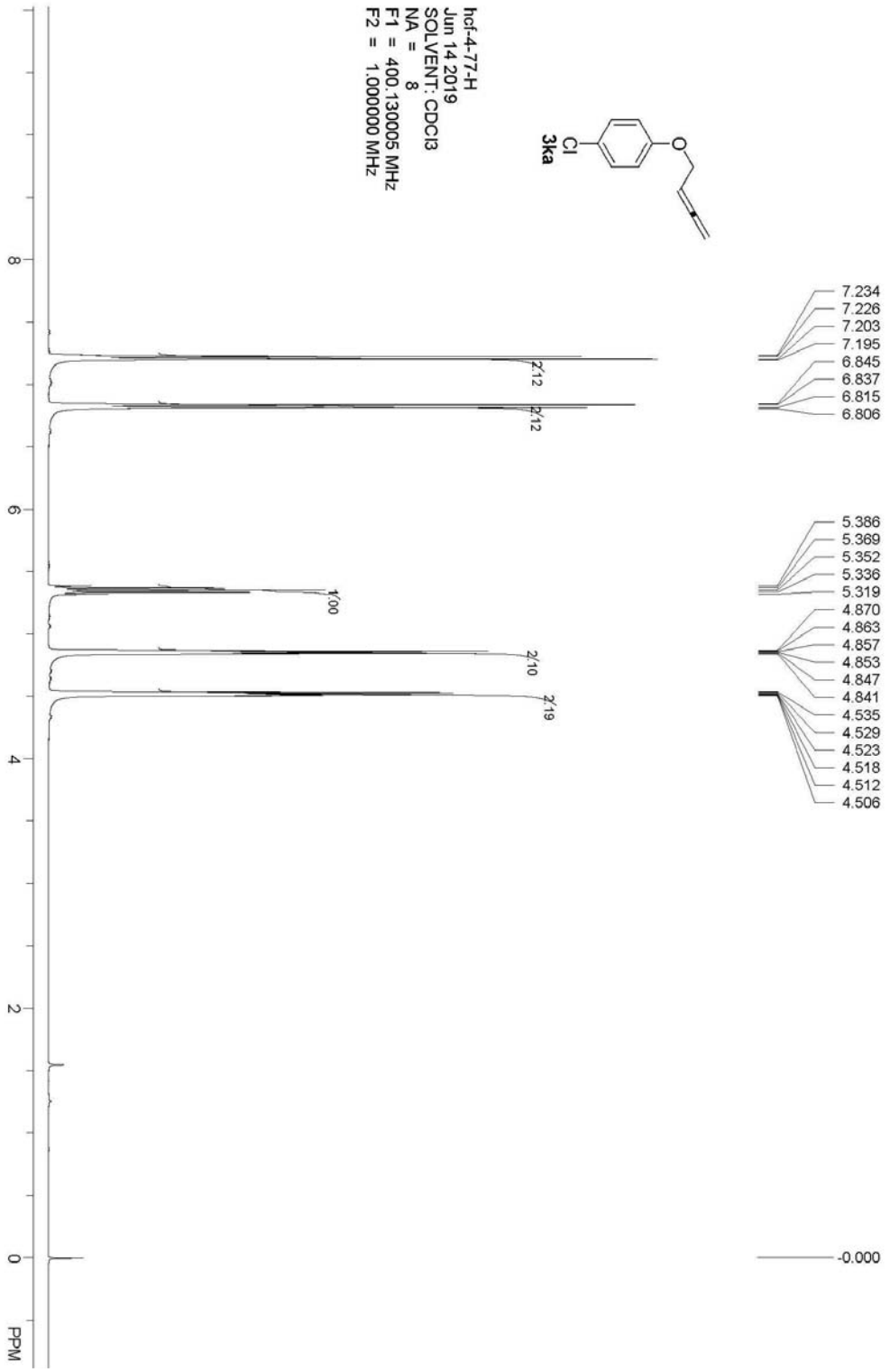

hcf-4-81-H
Jun 17 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
Br
3ia
O
7.384
7.376
7.358
7.353
7.345
7.253
6.810
6.801
6.779
6.771
5.391
5.374
5.357
5.341
5.324
4.878
4.872
4.865
4.862
4.855
4.849
4.547
4.540
4.534
4.530
4.524
4.518
0.000
2.06
2.12
1.00
2.09
2.17
8
6
4
2
0
PPM

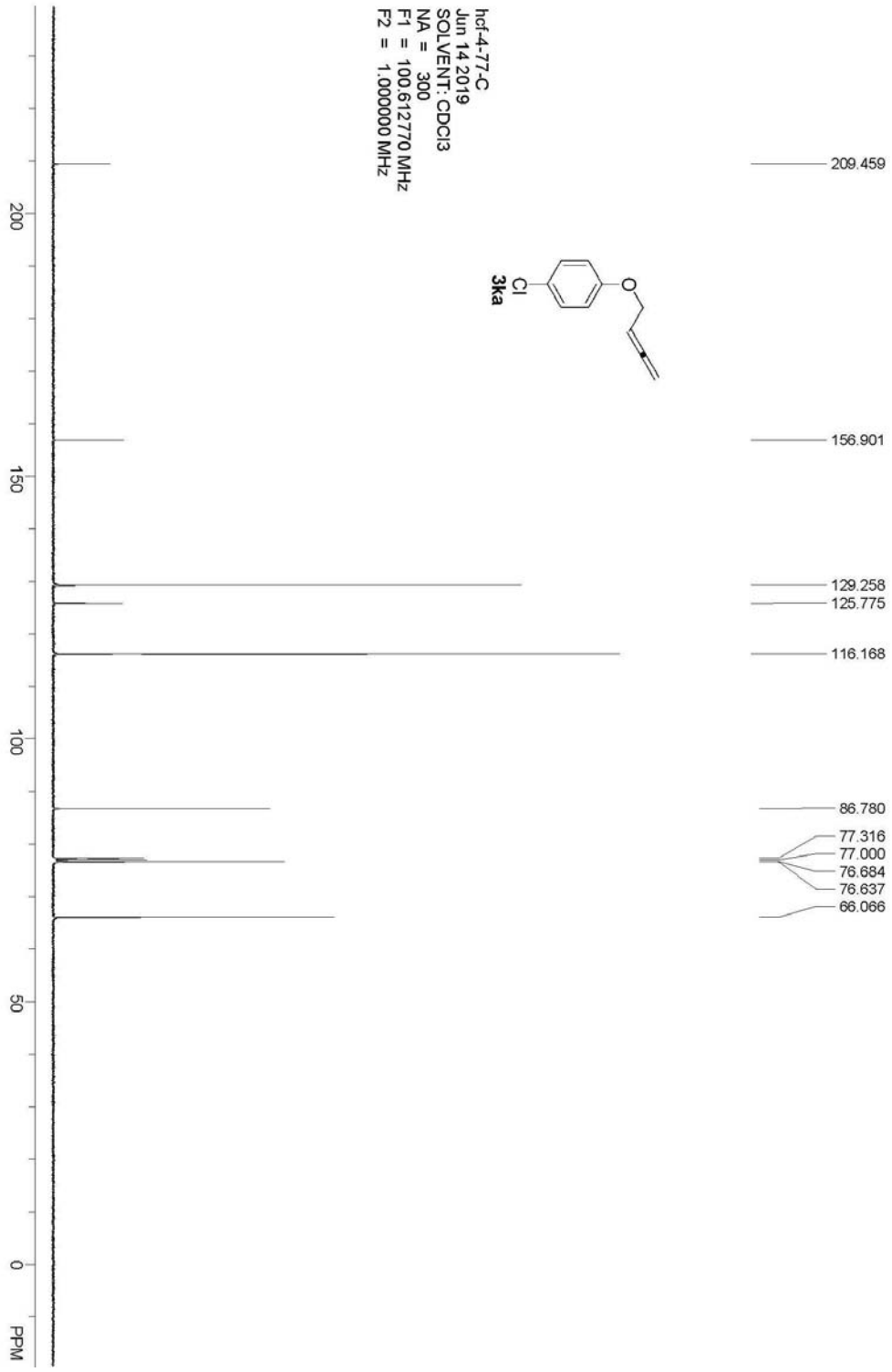

hcf-4-81-C
Jun 17 2019
SOLVENT: CDCl3
NA = 244
F1 = 100.612770 MHz
F2 = 1.000000 MHz
Br
3ia
209.507
157.438
132.237
116.721
113.119
86.764
77.316
77.000
76.684
66.043
200
150
100
50
0
PPM

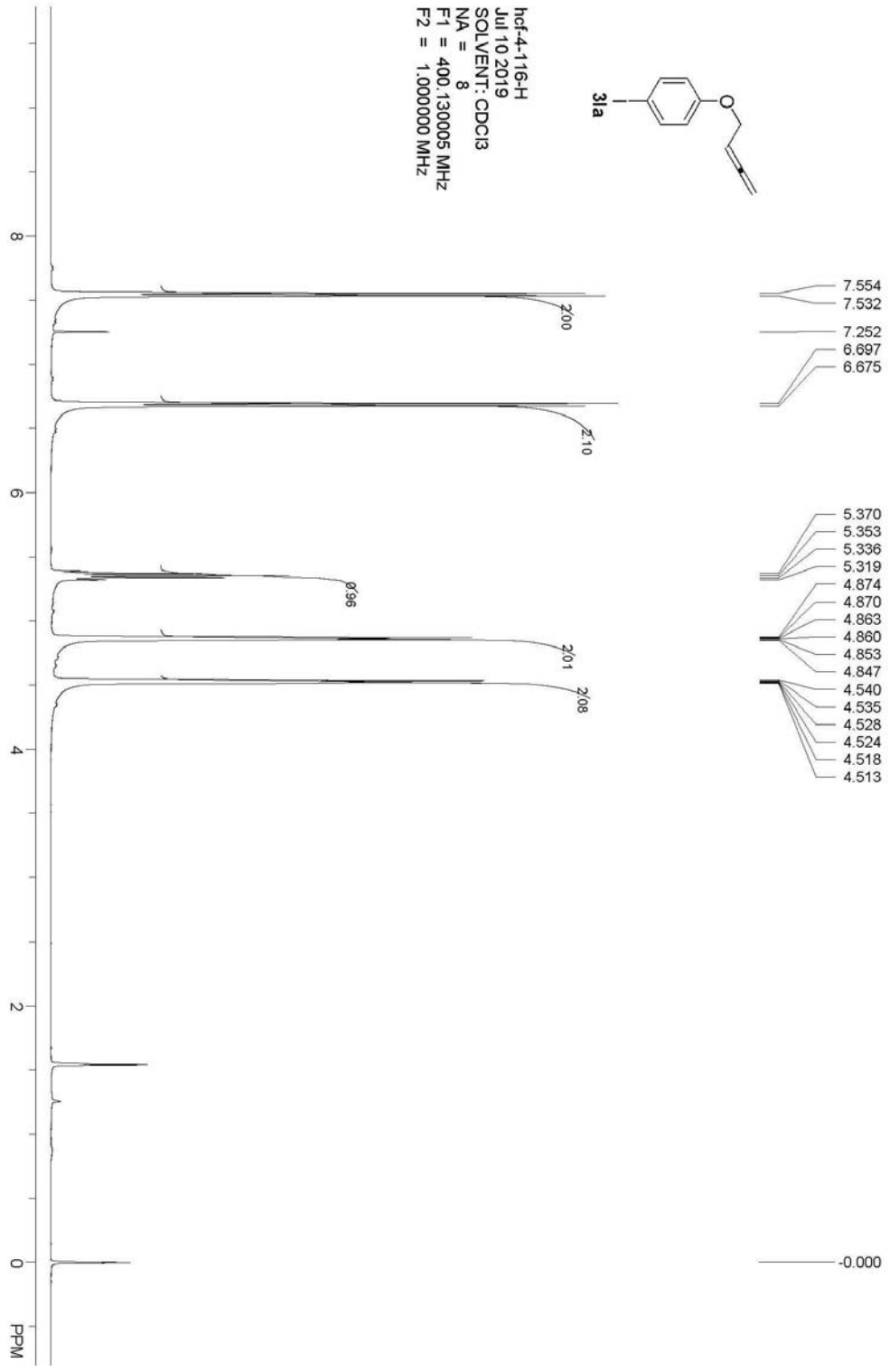

hcf-4-111-H
Jul 5 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3ja
F
O
2.01
2.12
1.00
2.05
2.14
7.248
6.982
6.960
6.939
6.862
6.852
6.840
6.829
5.396
5.379
5.362
5.345
5.329
4.860
4.851
4.844
4.529
4.519
4.512
-0.000
PPM

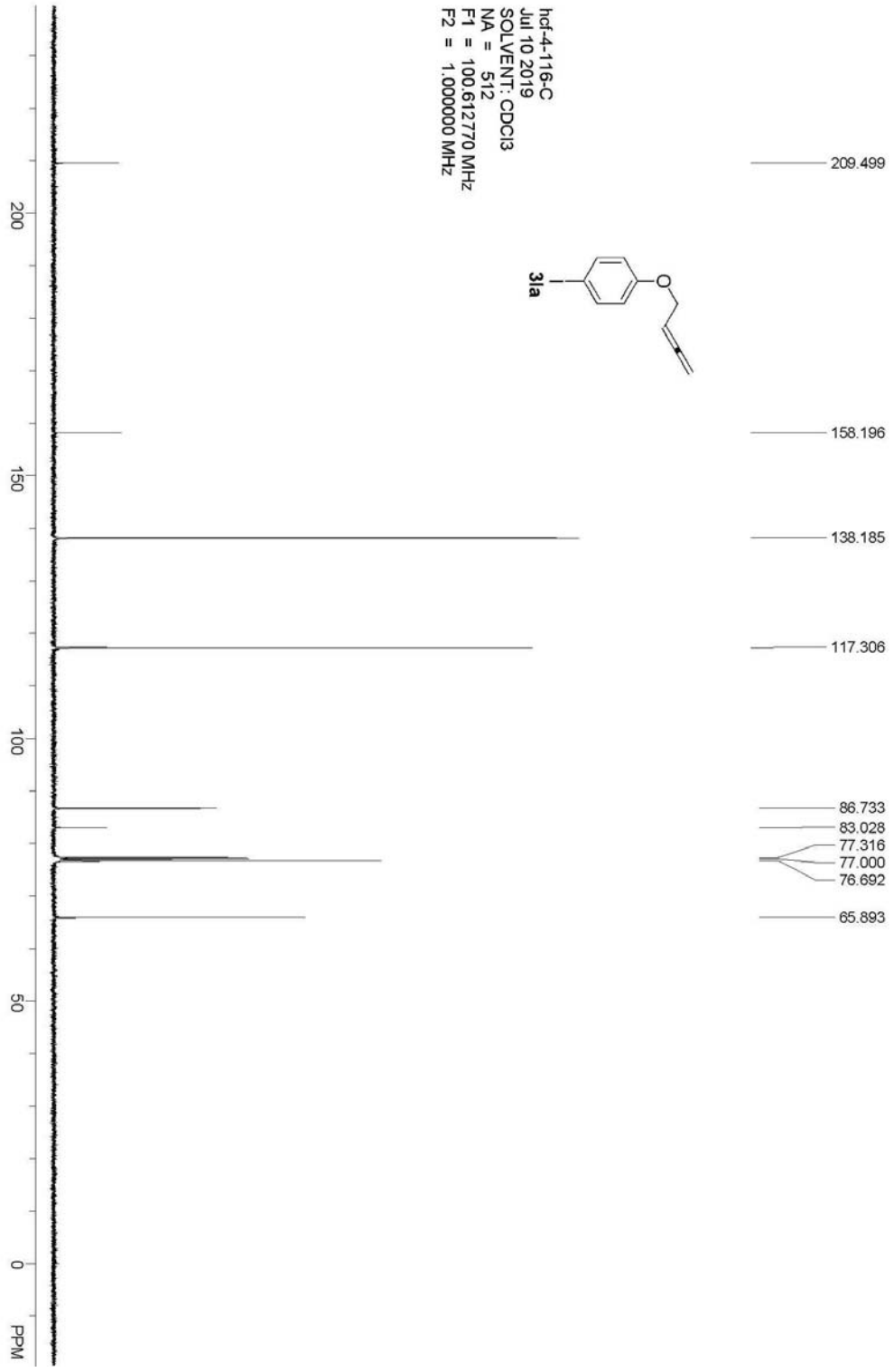

hcf-4-111-C
Jul 5 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3ja
F
O
209.459
158.560
156.190
154.428
154.412
116.018
115.939
115.876
115.647
86.962
77.316
77.000
76.684
76.518
66.485
200
150
100
50
0
PPM

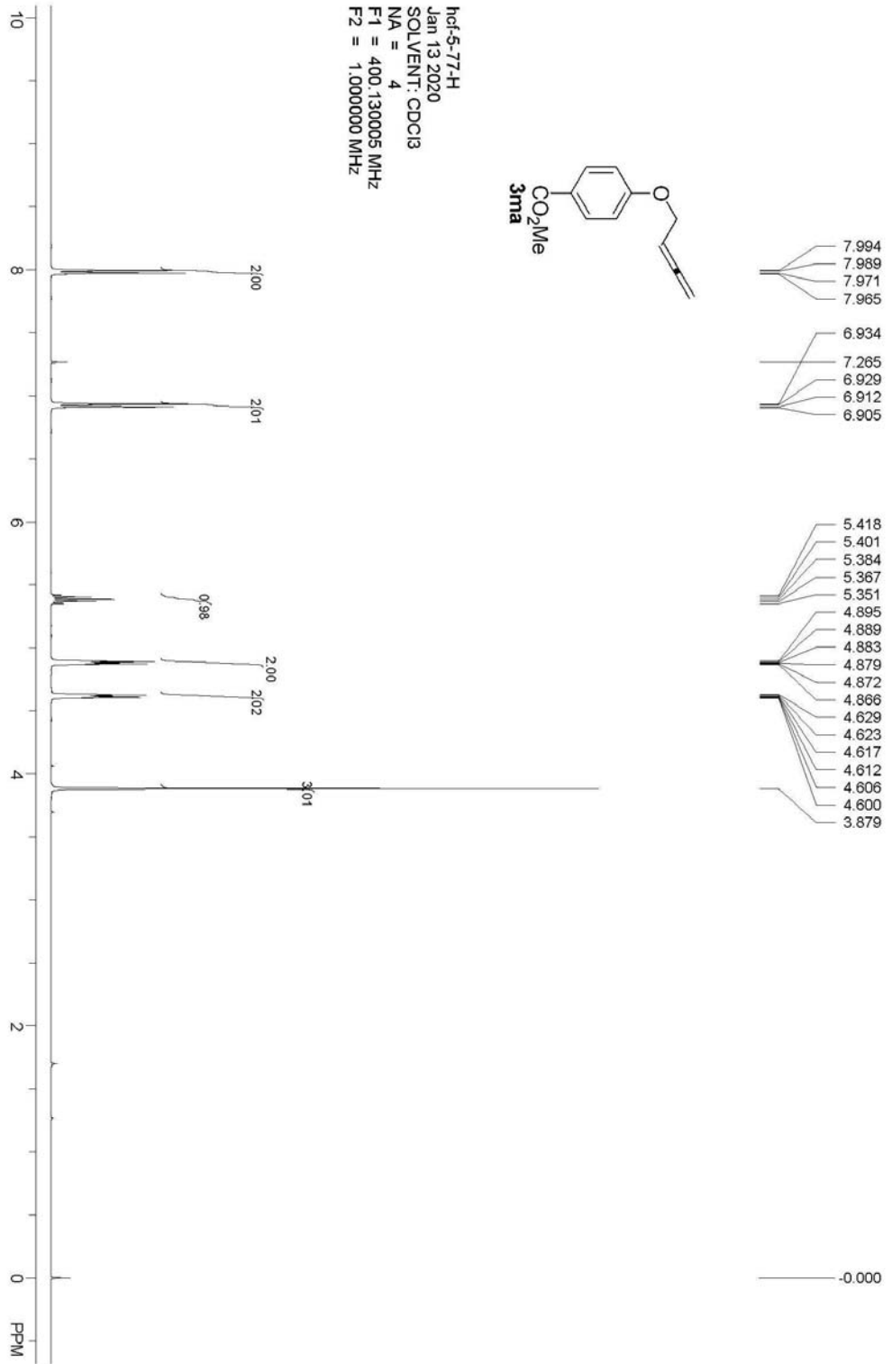

hcf-4-111-F
Jul 5 2019
SOLVENT: CDCl3
NA = 16
F1 = 376.460724 MHz
F2 = 1.000000 MHz
F
3ja
-0.000
-124.217
0
-50
-100
-150
-200
PPM

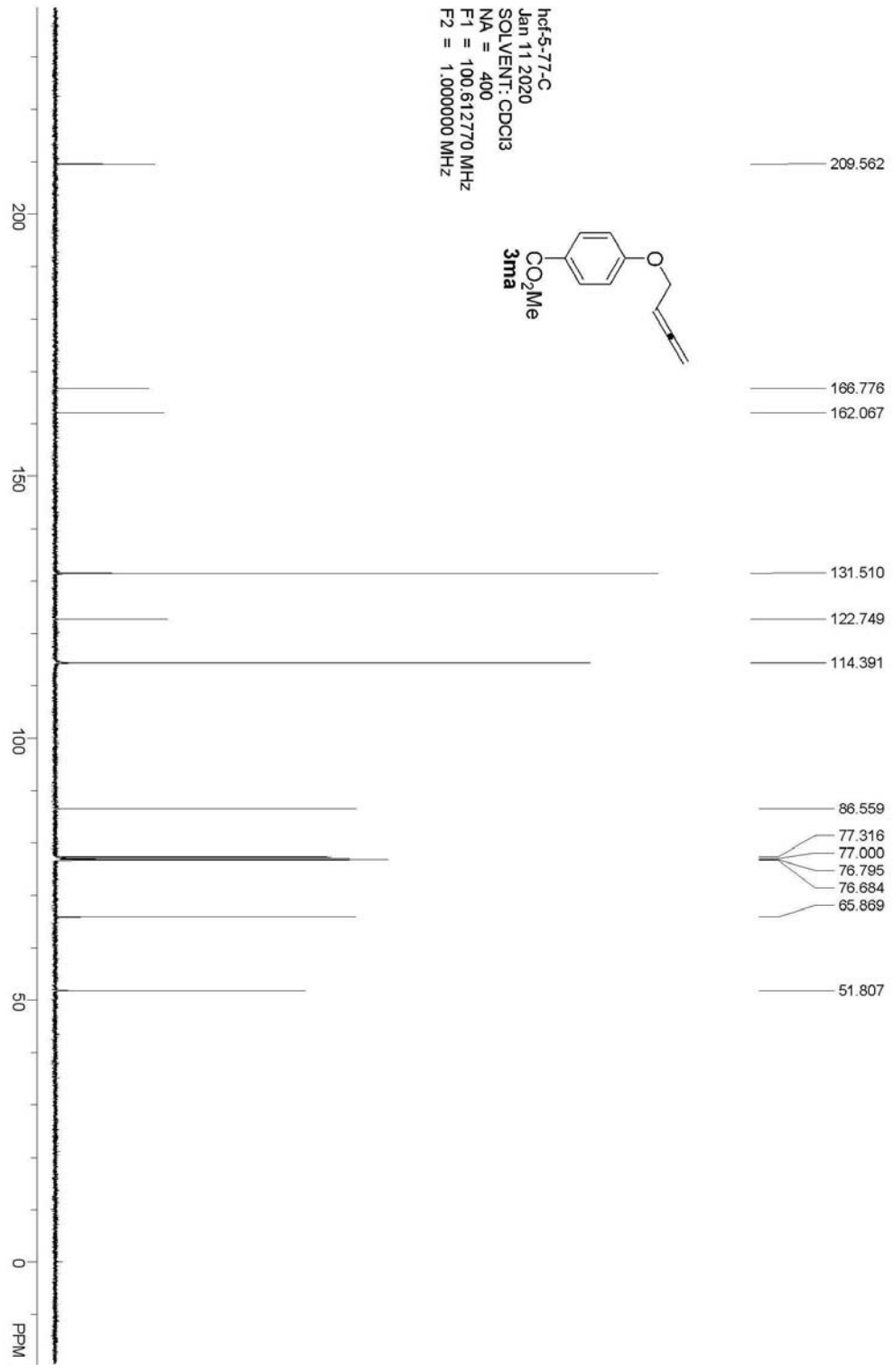

hcf-4-77-H
Jun 14 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
Cl
3ka
7.234
7.226
7.203
7.195
6.845
6.837
6.815
6.806
5.386
5.369
5.352
5.336
5.319
4.870
4.863
4.857
4.853
4.847
4.841
4.535
4.529
4.523
4.518
4.512
4.506
-0.000
2.12
2.12
1.00
2.10
2.19
8
6
4
2
0
PPM

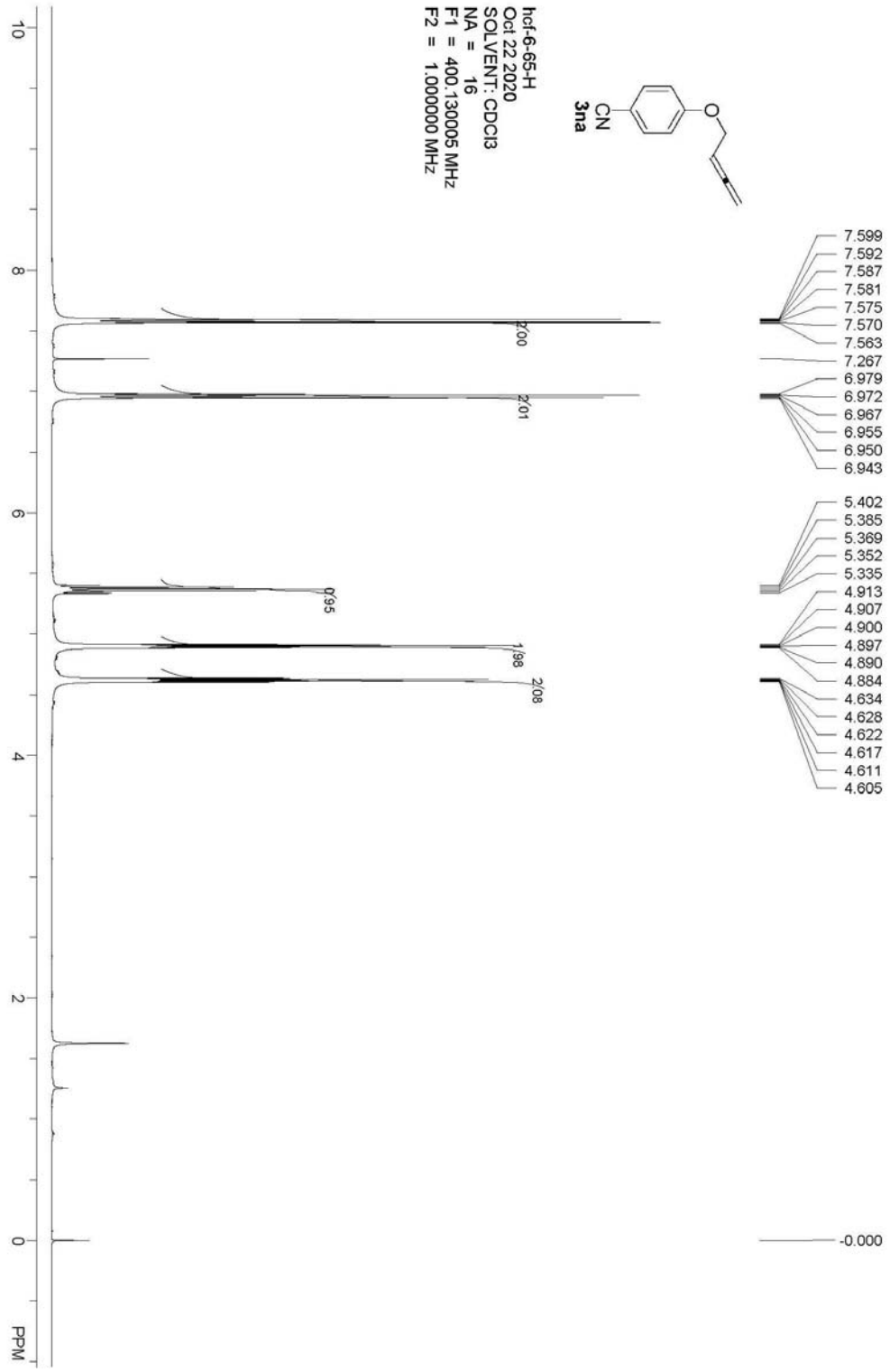

hcf-4-77-C
Jun 14 2019
SOLVENT: CDCl3
NA = 300
F1 = 100.612770 MHz
F2 = 1.000000 MHz
Cl
3ka
209.459
156.901
129.258
125.775
116.168
86.780
77.316
77.000
76.684
76.637
66.066
200
150
100
50
0
PPM

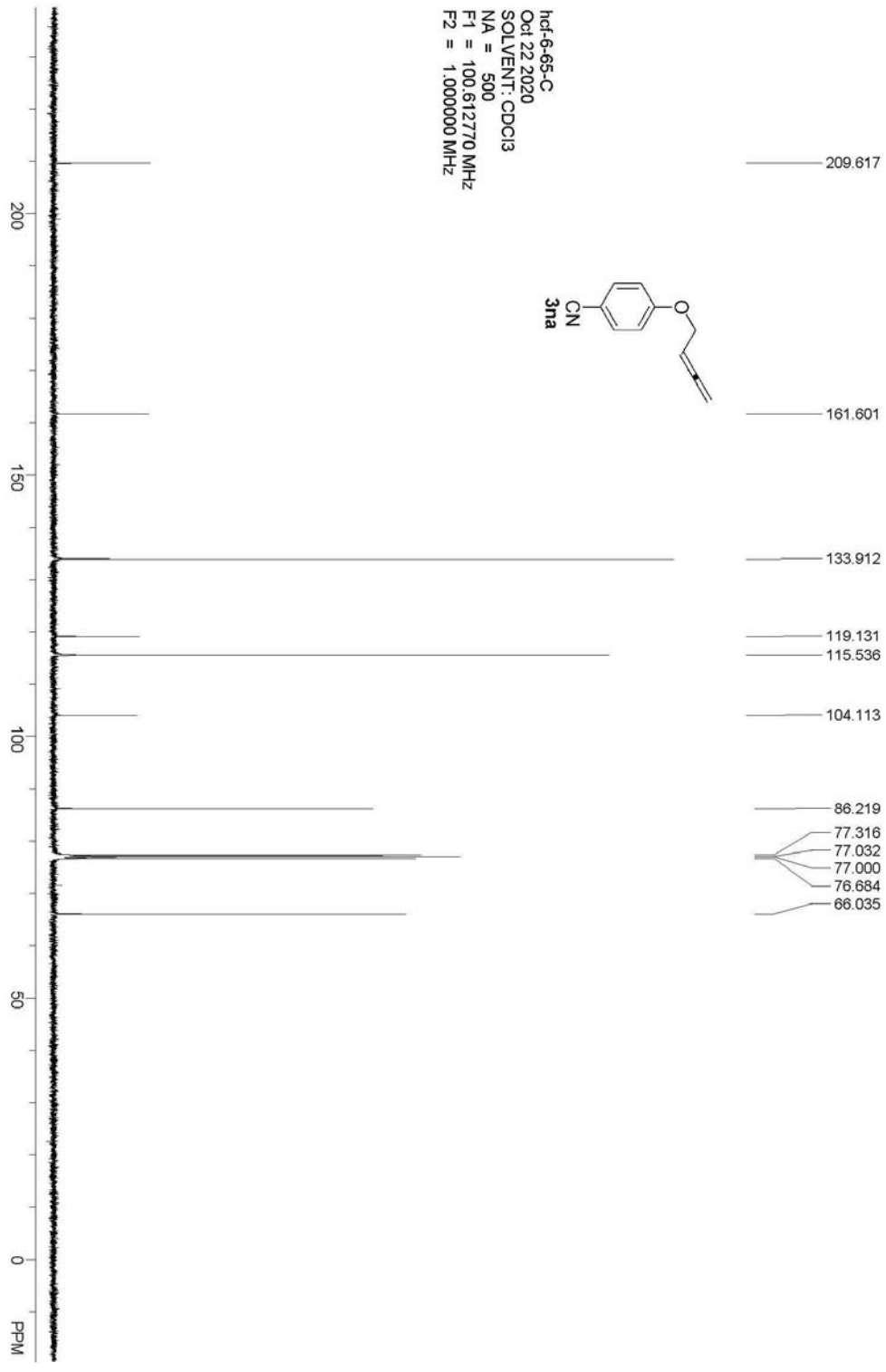

hcf-4-116-H
Jul 10 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3la
7.554
7.532
7.252
6.697
6.675
5.370
5.353
5.336
5.319
4.874
4.870
4.863
4.860
4.853
4.847
4.540
4.535
4.528
4.524
4.518
4.513
-0.000
2.00
2.10
0.96
2.01
2.08
8
6
4
2
0
PPM

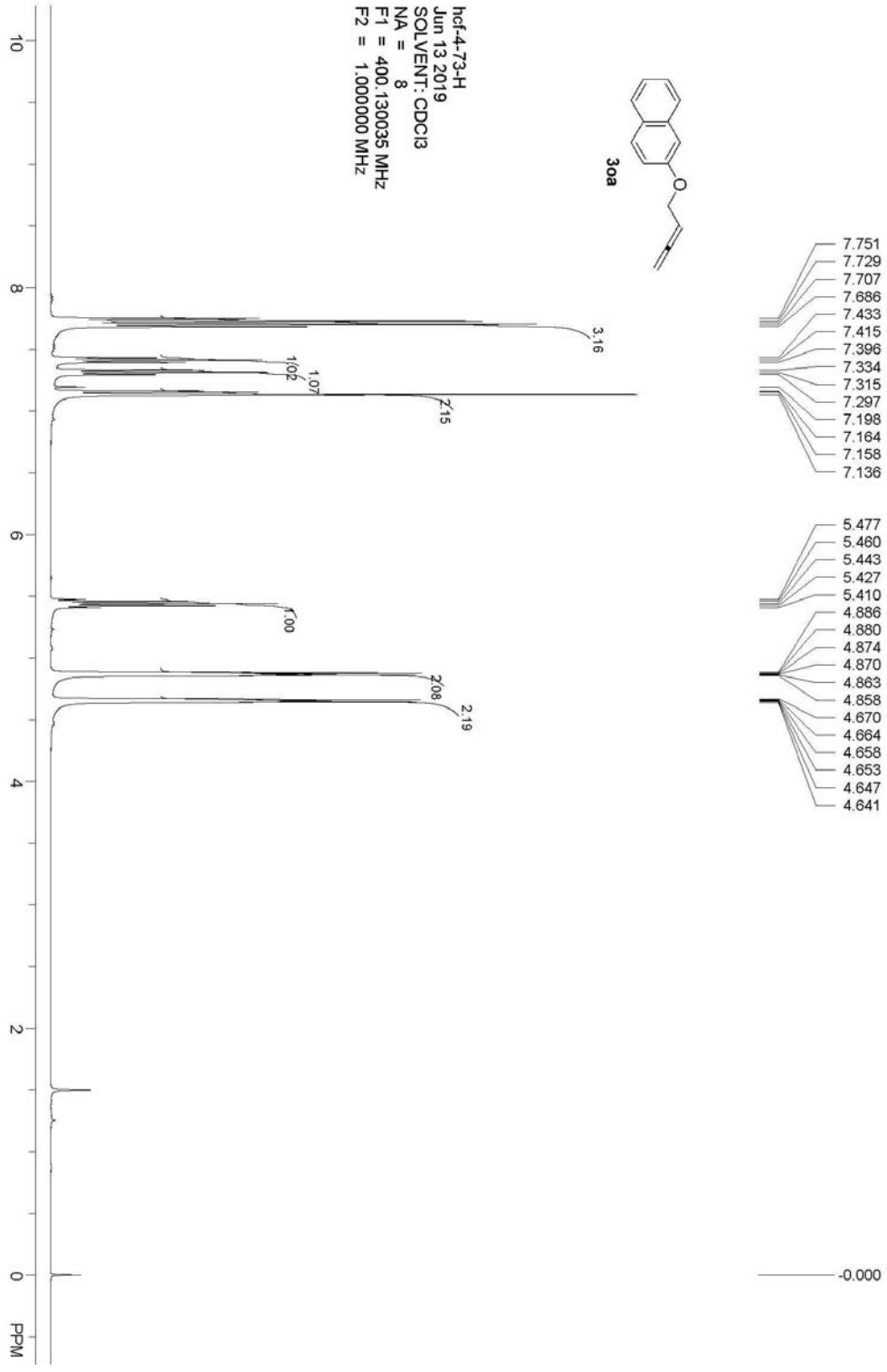

hcf-4-116-C
Jul 10 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3la
209.499
158.196
138.185
117.306
86.733
83.028
77.316
77.000
76.692
65.893
200
150
100
50
0
PPM

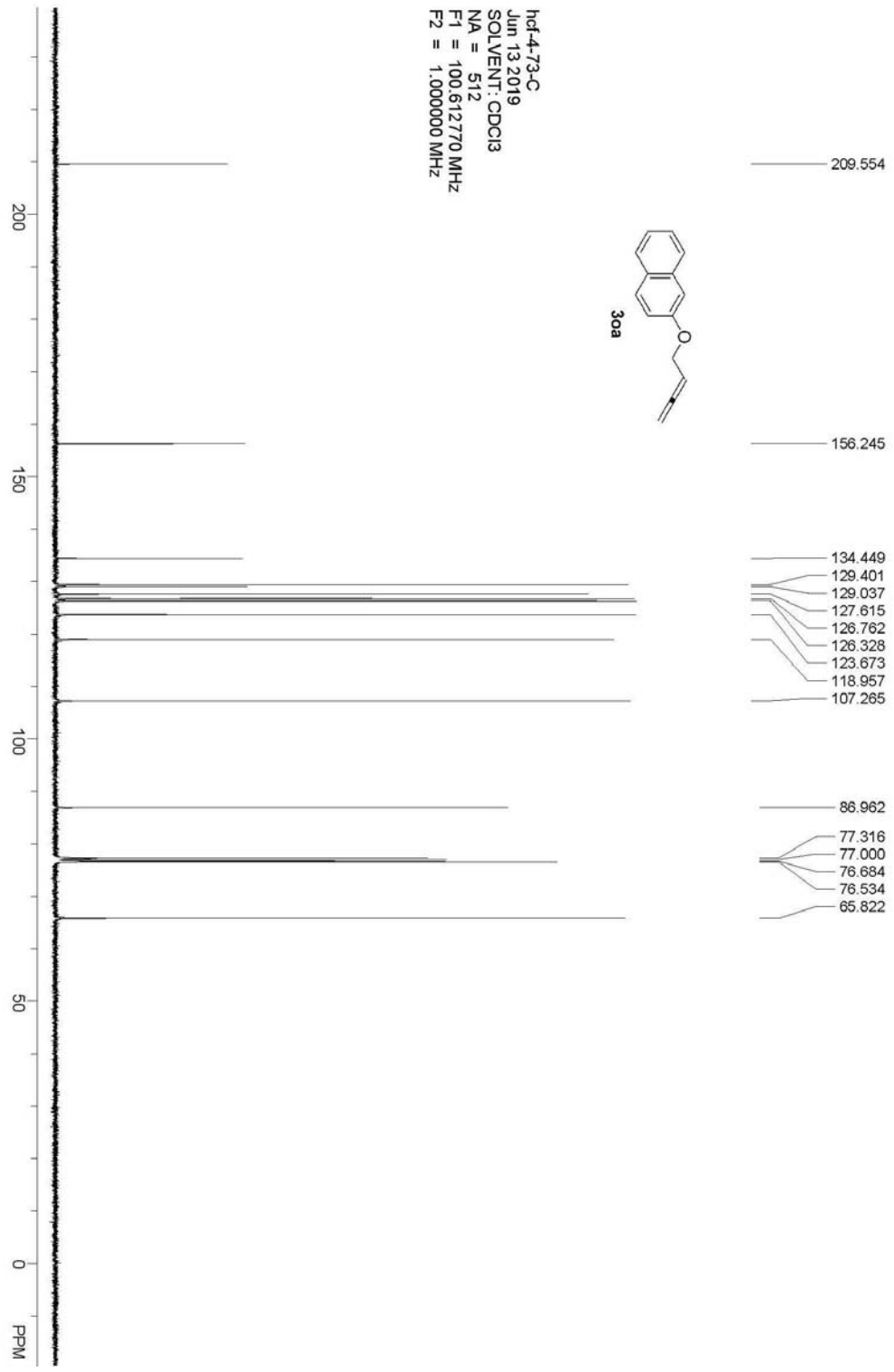

hcf-5-77-H
Jan 13 2020
SOLVENT: CDCl3
NA = 4
F1 = 400.130005 MHz
F2 = 1.000000 MHz
CO2Me
3ma
7.994
7.989
7.971
7.965
6.934
7.265
6.929
6.912
6.905
5.418
5.401
5.384
5.367
5.351
4.895
4.889
4.883
4.879
4.872
4.866
4.629
4.623
4.617
4.612
4.606
4.600
3.879
-0.000
2.00
0.98
2.00
2.02
3.01
10
8
6
4
2
0
PPM

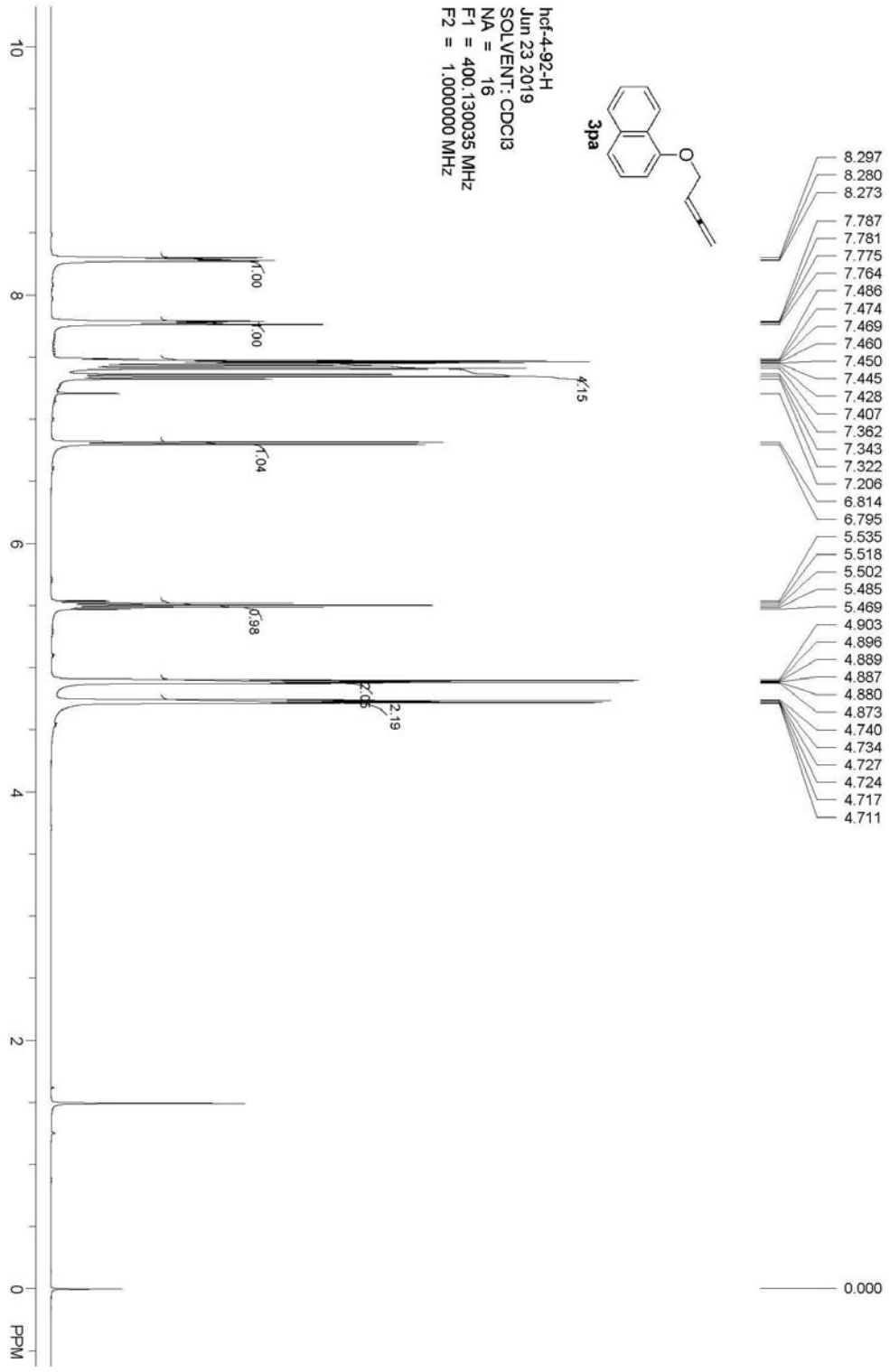

hcf-5-77-C
Jan 11 2020
SOLVENT: CDCl3
NA = 400
F1 = 100.612770 MHz
F2 = 1.000000 MHz
CO2Me
3ma
209.562
166.776
162.067
131.510
122.749
114.391
86.559
77.316
77.000
76.795
76.684
65.869
51.807
200
150
100
50
0
PPM

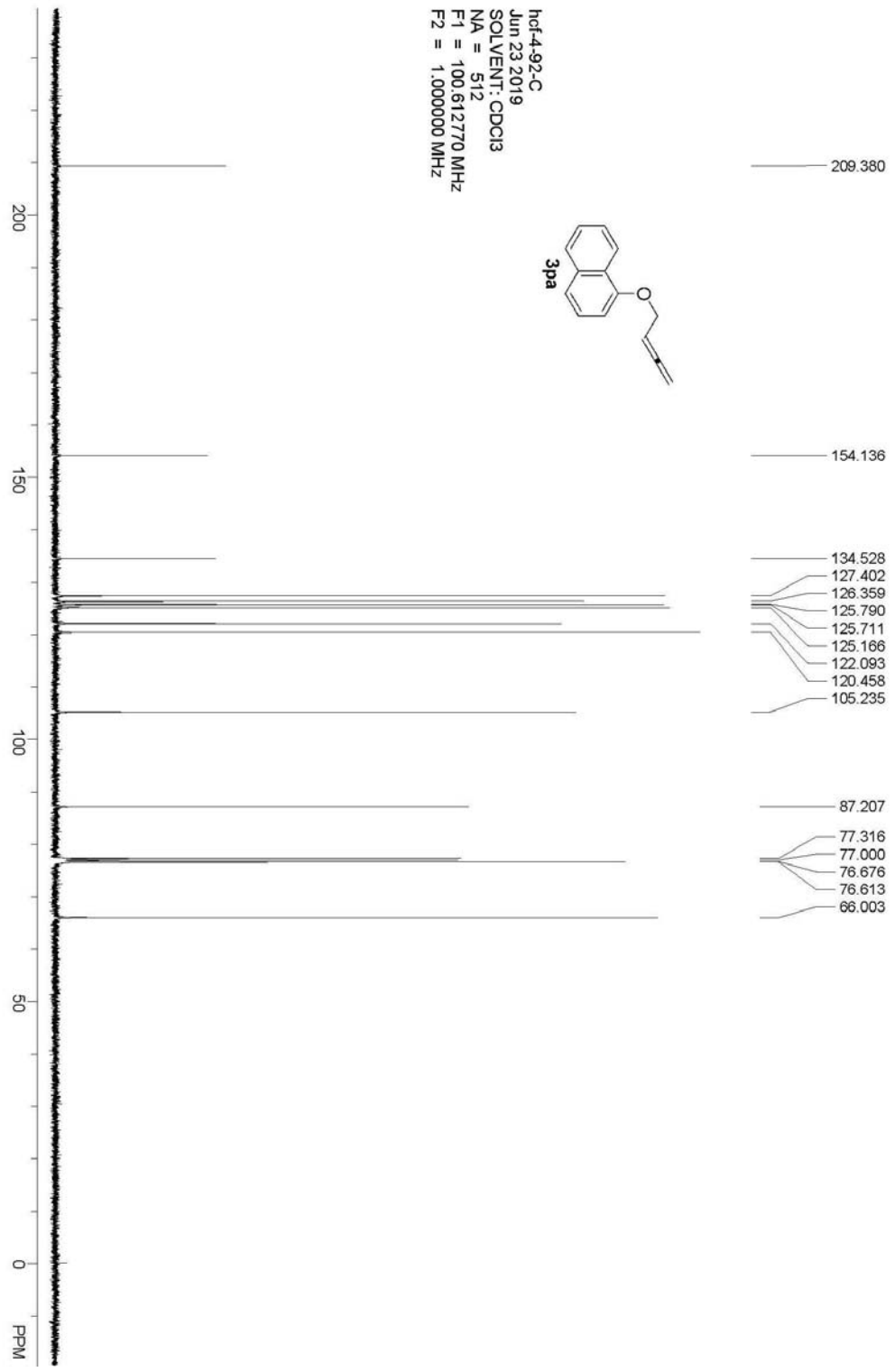

hcf-6-65-H
Oct 22 2020
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
CN
3na
7.599
7.592
7.587
7.581
7.575
7.570
7.563
7.267
6.979
6.972
6.967
6.955
6.950
6.943
5.402
5.385
5.369
5.352
5.335
4.913
4.907
4.900
4.897
4.890
4.884
4.634
4.628
4.622
4.617
4.611
4.605
-0.000
2.00
2.01
0.95
1.98
2.08
10
8
6
4
2
0
PPM

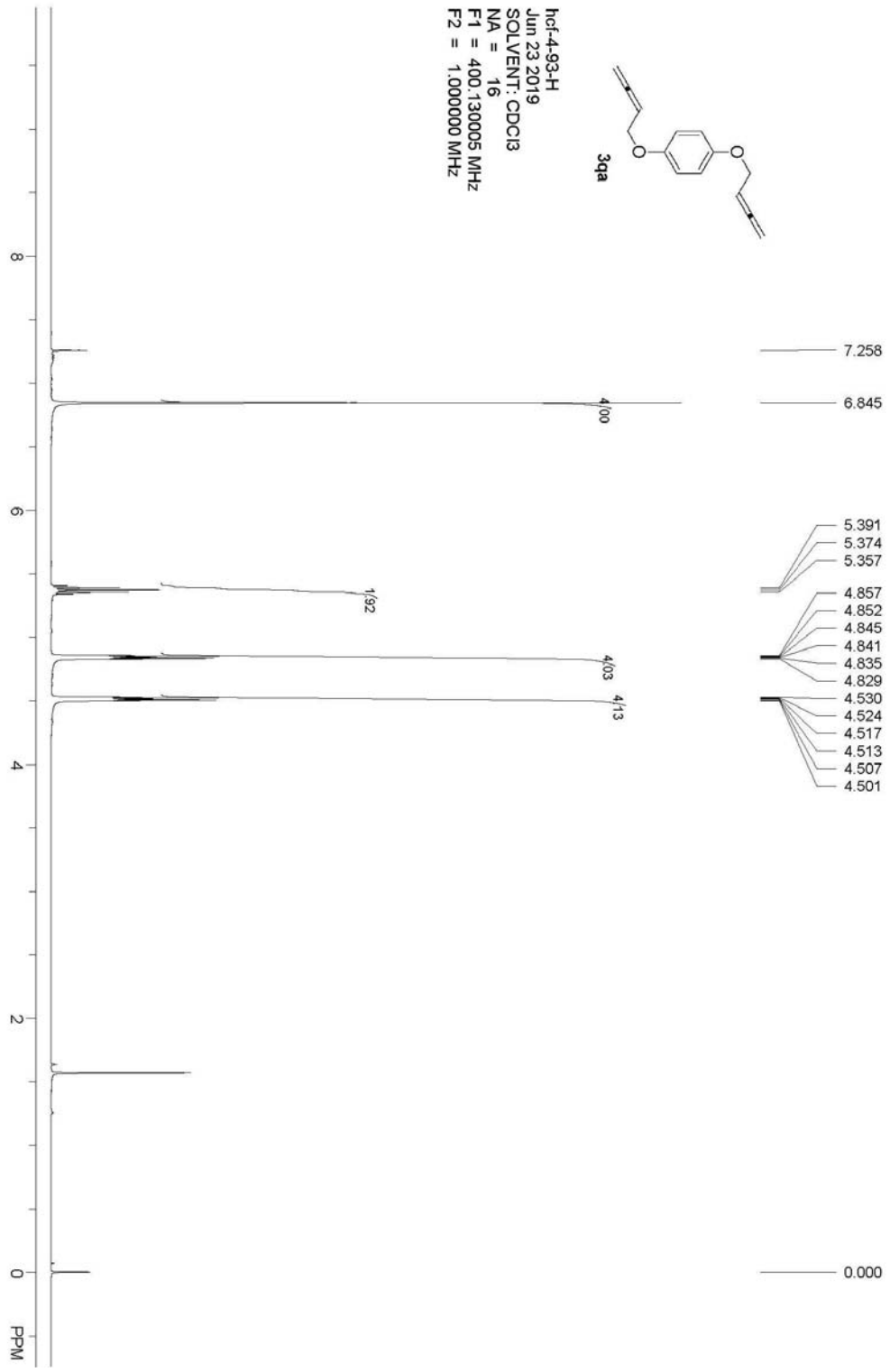

hcf-6-65-C
Oct 22 2020
SOLVENT: CDCl3
NA = 500
F1 = 100.612770 MHz
F2 = 1.000000 MHz
CN
3na
209.617
161.601
133.912
119.131
115.536
104.113
86.219
77.316
77.032
77.000
76.684
66.035
200
150
100
50
0
PPM

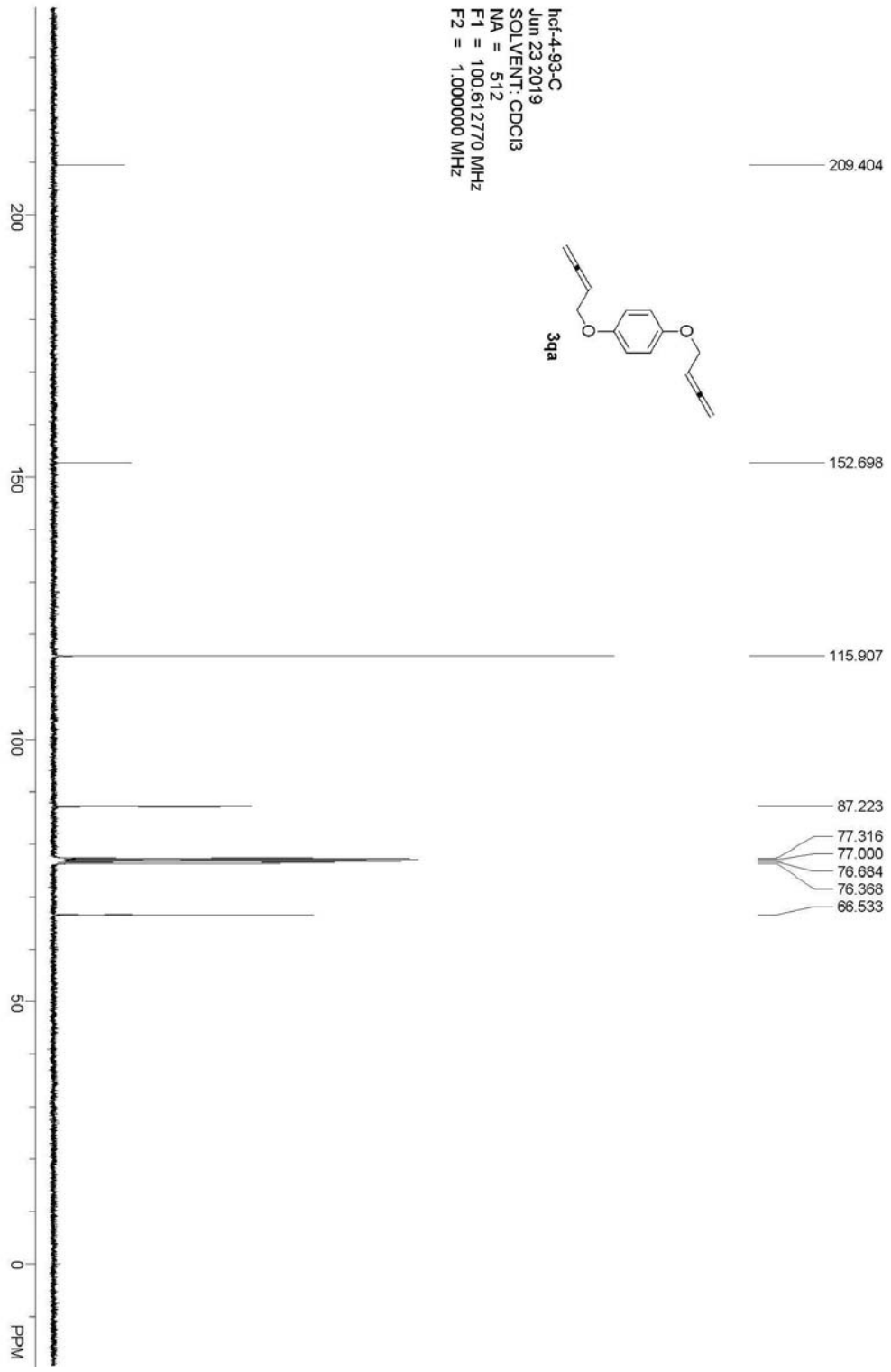

hcf-4-73-H
Jun 13 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130035 MHz
F2 = 1.000000 MHz
3oa
7.751
7.729
7.707
7.686
7.433
7.415
7.396
7.334
7.315
7.297
7.198
7.164
7.158
7.136
5.477
5.460
5.443
5.427
5.410
4.886
4.880
4.874
4.870
4.863
4.858
4.670
4.664
4.658
4.653
4.647
4.641
-0.000
3.16
1.02
1.07
2.15
1.00
2.08
2.19
PPM

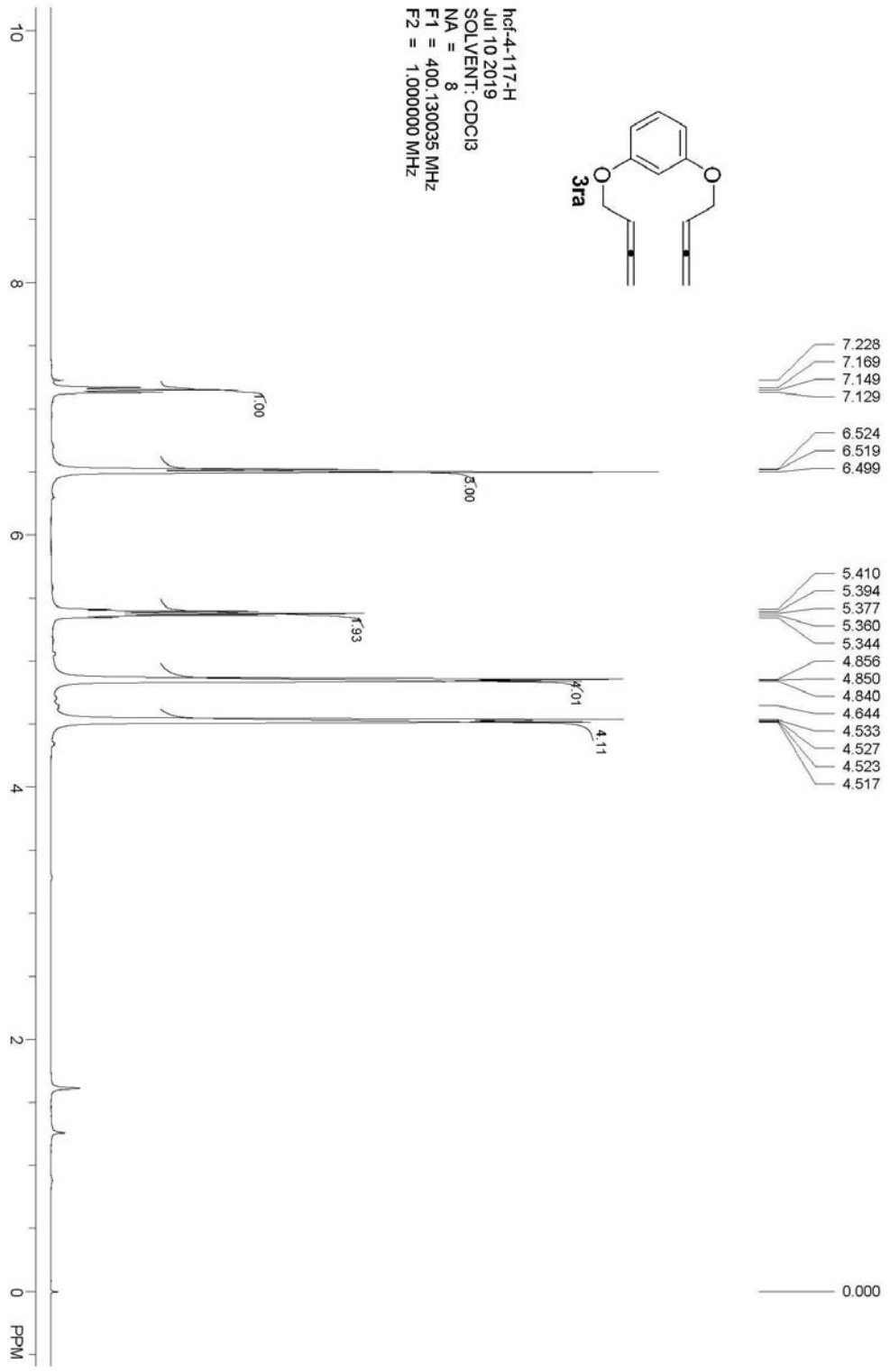

hdf-4-73-C
Jun 13 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3oa
209.554
156.245
134.449
129.401
129.037
127.615
126.762
126.328
123.673
118.957
107.265
86.962
77.316
77.000
76.684
76.534
65.822
200
150
100
50
0
PPM

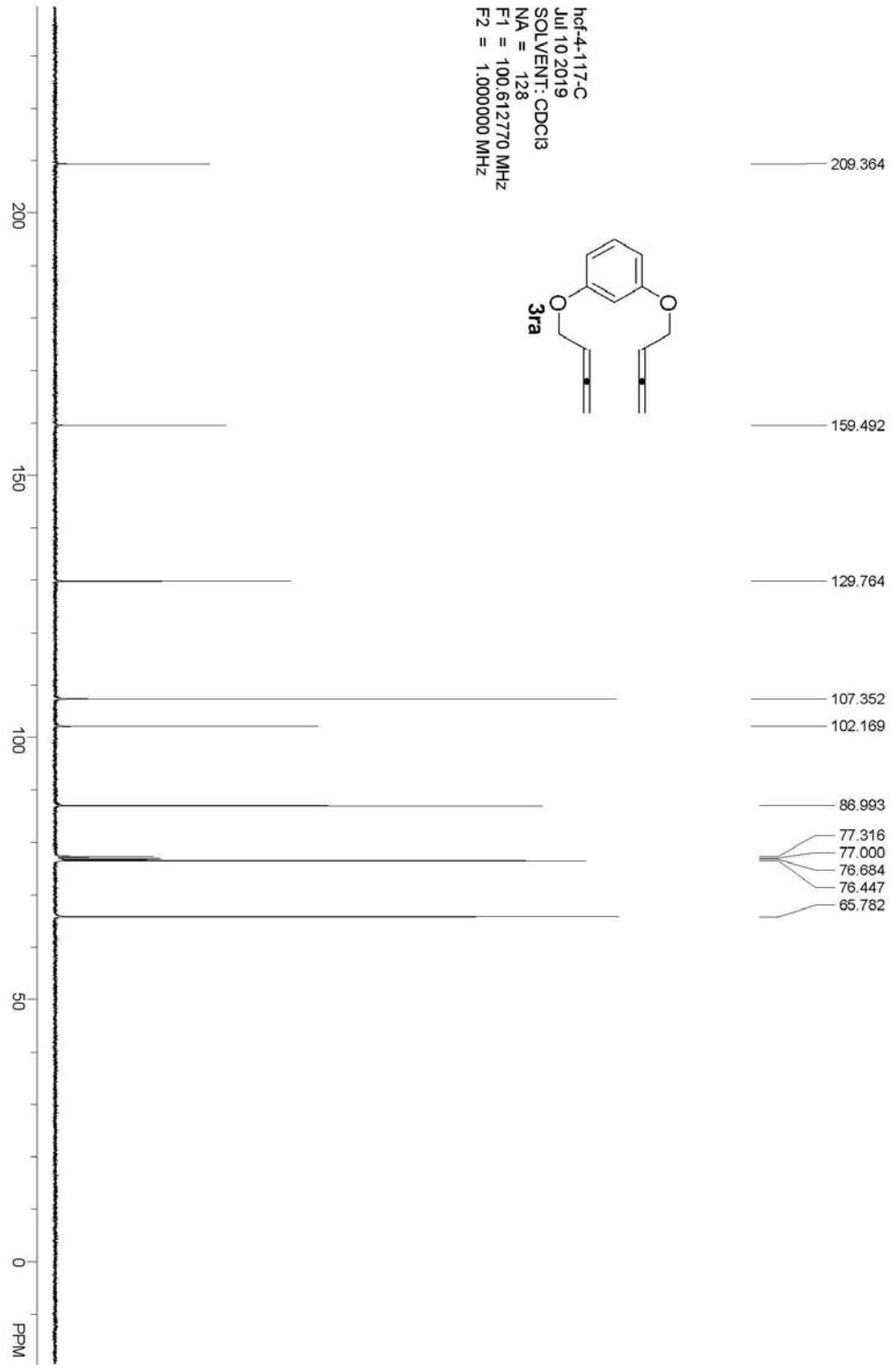

hcf-4-92-H
Jun 23 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130035 MHz
F2 = 1.000000 MHz
3pa
8.297
8.280
8.273
7.787
7.781
7.775
7.764
7.486
7.474
7.469
7.460
7.450
7.445
7.428
7.407
7.362
7.343
7.322
7.206
6.814
6.795
5.535
5.518
5.502
5.485
5.469
4.903
4.896
4.889
4.887
4.880
4.873
4.740
4.734
4.727
4.724
4.717
4.711
0.000
1.00
1.00
4.15
1.04
0.98
2.05
2.19
10
8
6
4
2
0
PPM

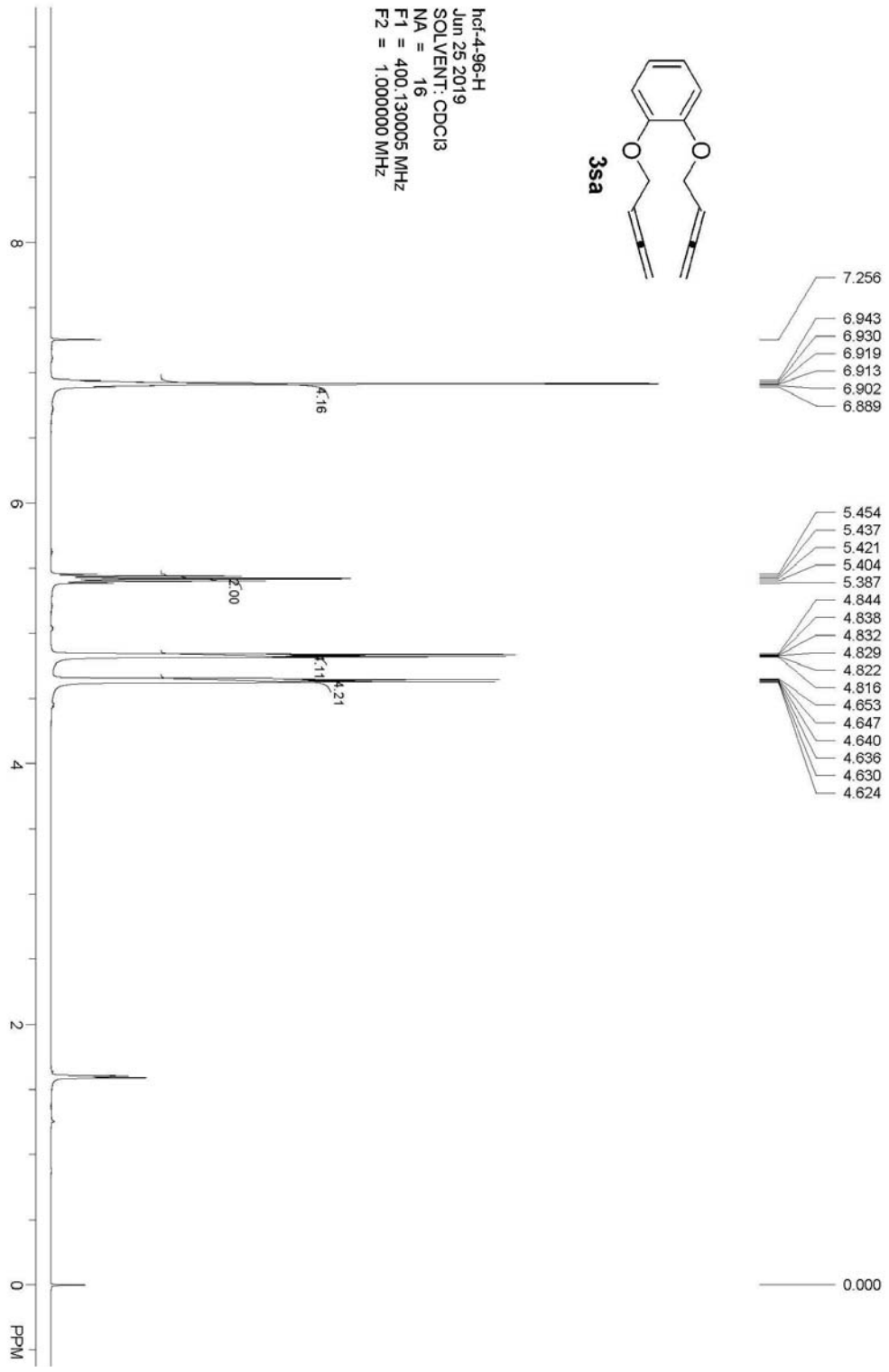

hcf-4-92-C
Jun 23 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3pa
209.380
154.136
134.528
127.402
126.359
125.790
125.711
125.166
122.093
120.458
105.235
87.207
77.316
77.000
76.676
76.613
66.003
200
150
100
50
0
PPM

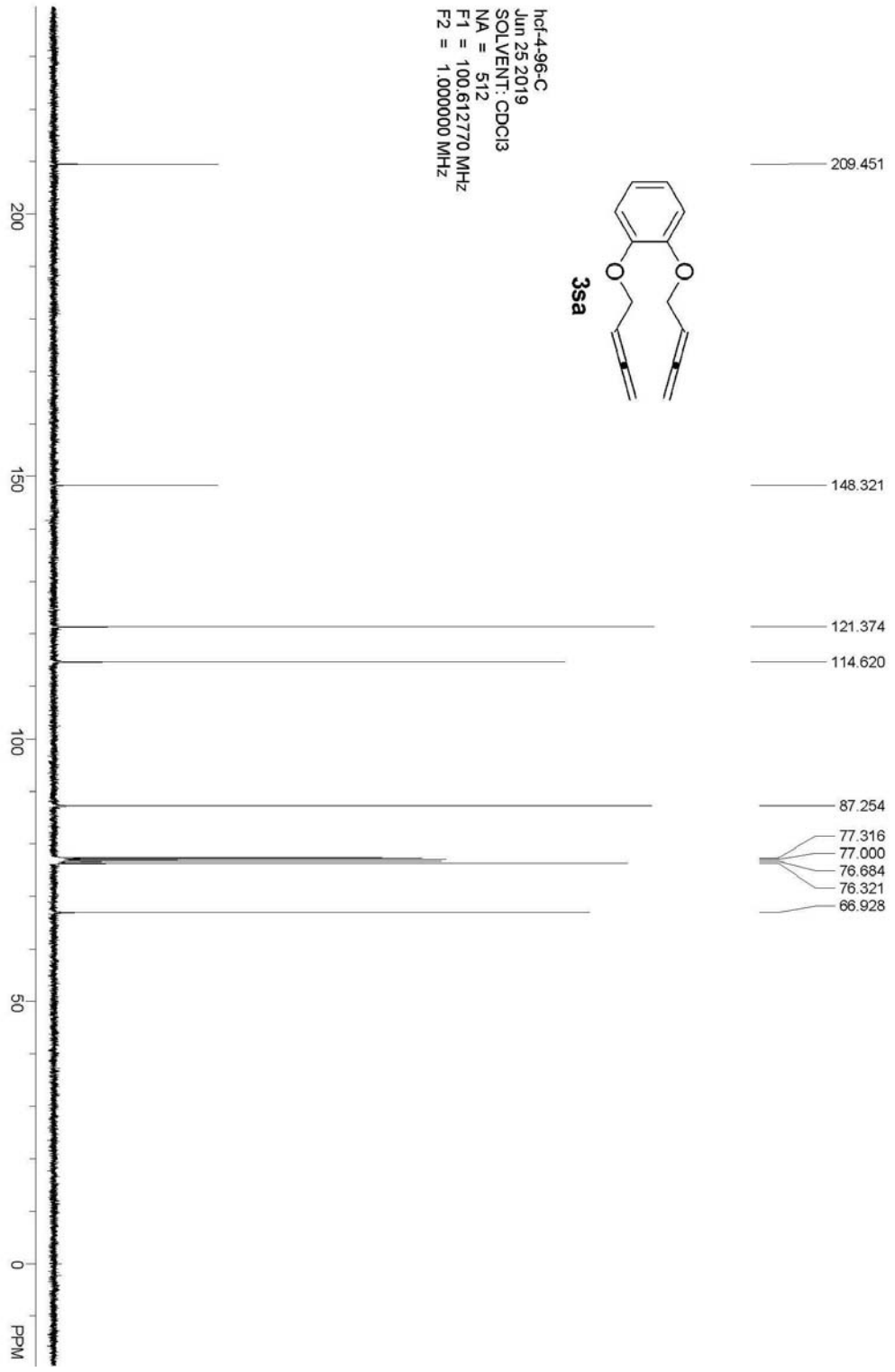

hcf-4-93-H
Jun 23 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3qa
7.258
6.845
5.391
5.374
5.357
4.857
4.852
4.845
4.841
4.835
4.829
4.530
4.524
4.517
4.513
4.507
4.501
0.000
4.00
1.92
4.03
4.13
8
6
4
2
0
PPM

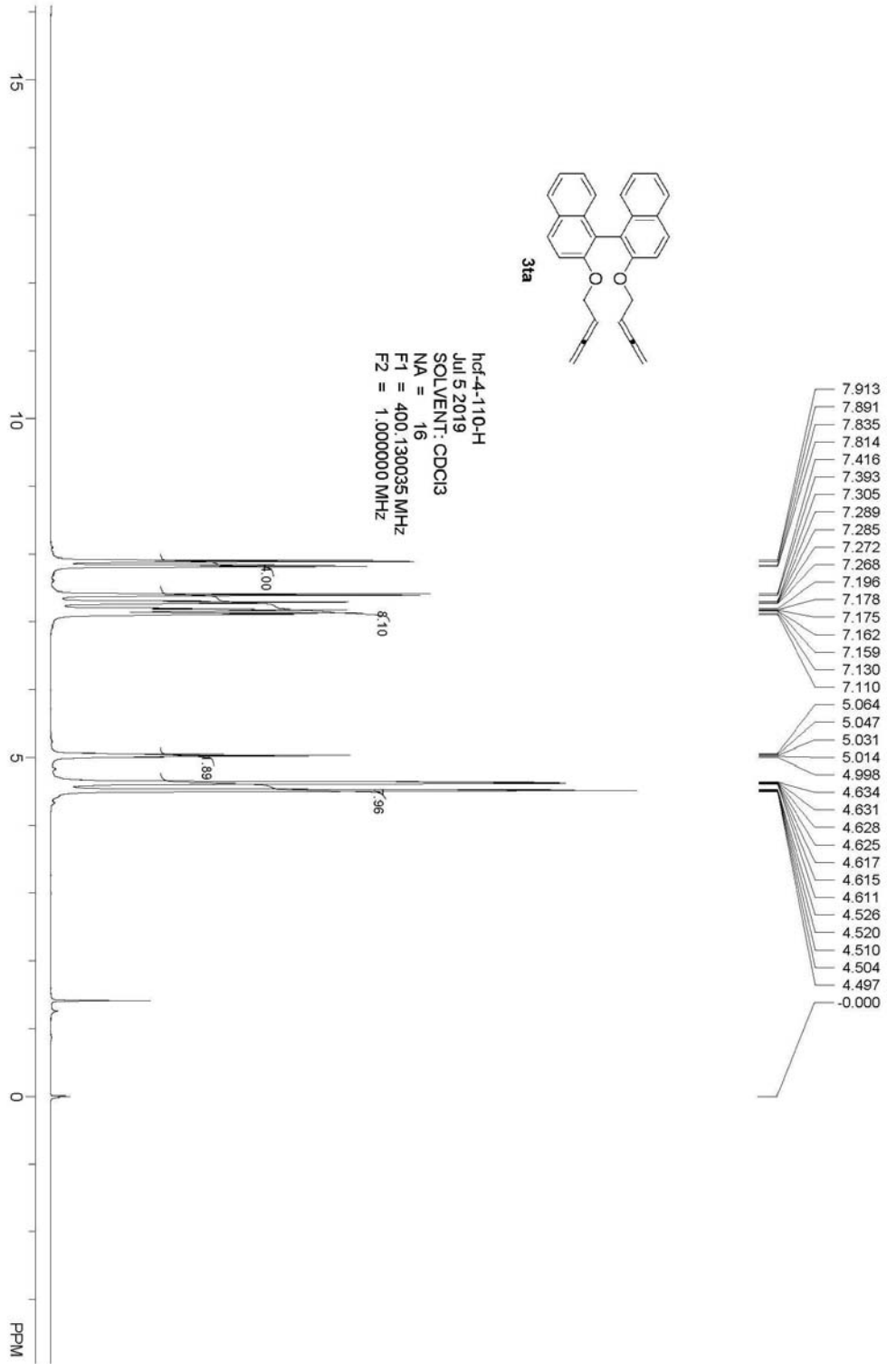

hcf-4-93-C
Jun 23 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3qa
209.404
152.698
115.907
87.223
77.316
77.000
76.684
76.368
66.533
200
150
100
50
0
PPM

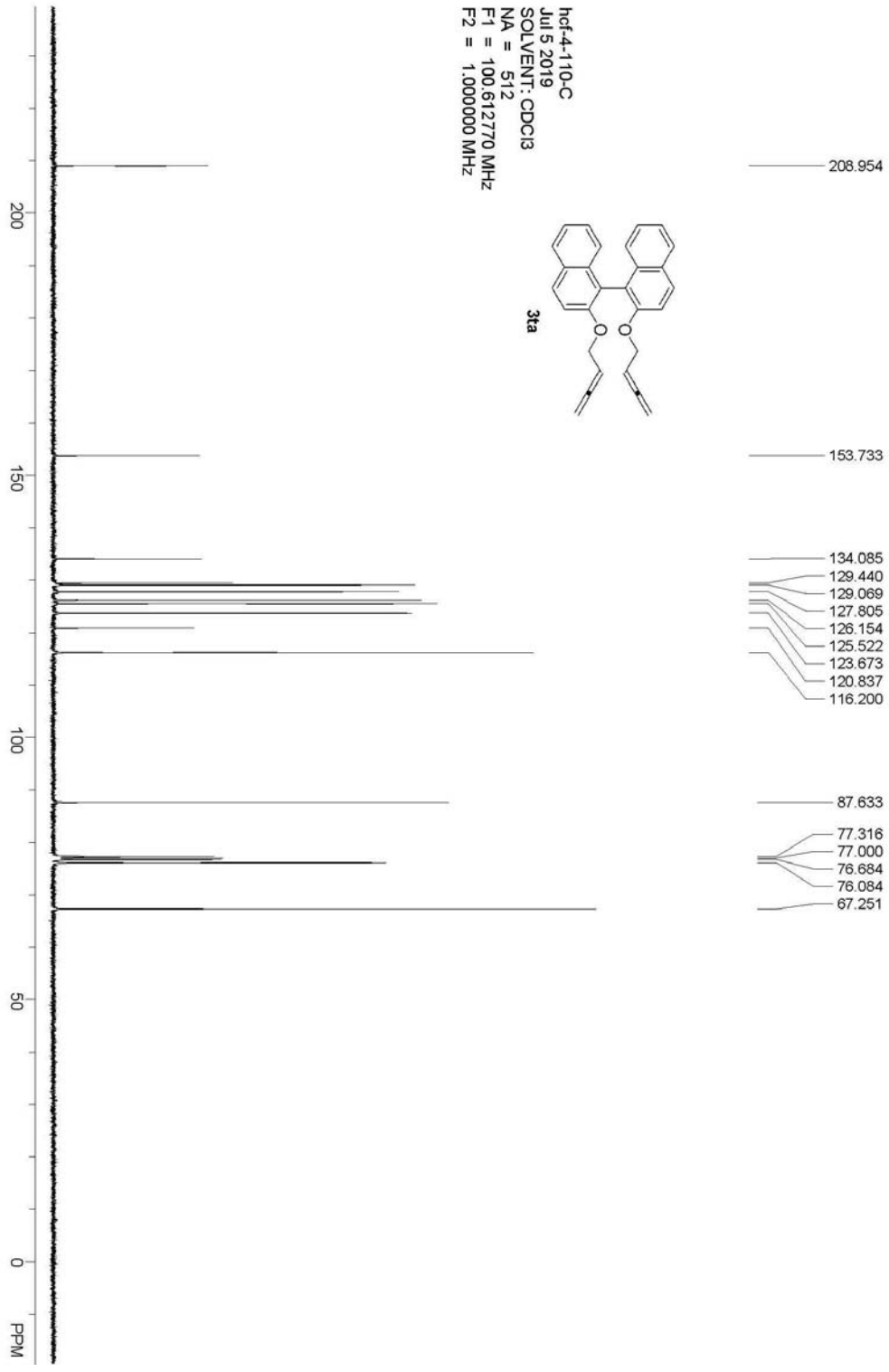

hcf-4-117-H
Jul 10 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130035 MHz
F2 = 1.000000 MHz
3ra
7.228
7.169
7.149
7.129
6.524
6.519
6.499
5.410
5.394
5.377
5.360
5.344
4.856
4.850
4.840
4.644
4.533
4.527
4.523
4.517
0.000
1.00
5.00
1.93
4.01
4.11
10
8
6
4
2
0
PPM

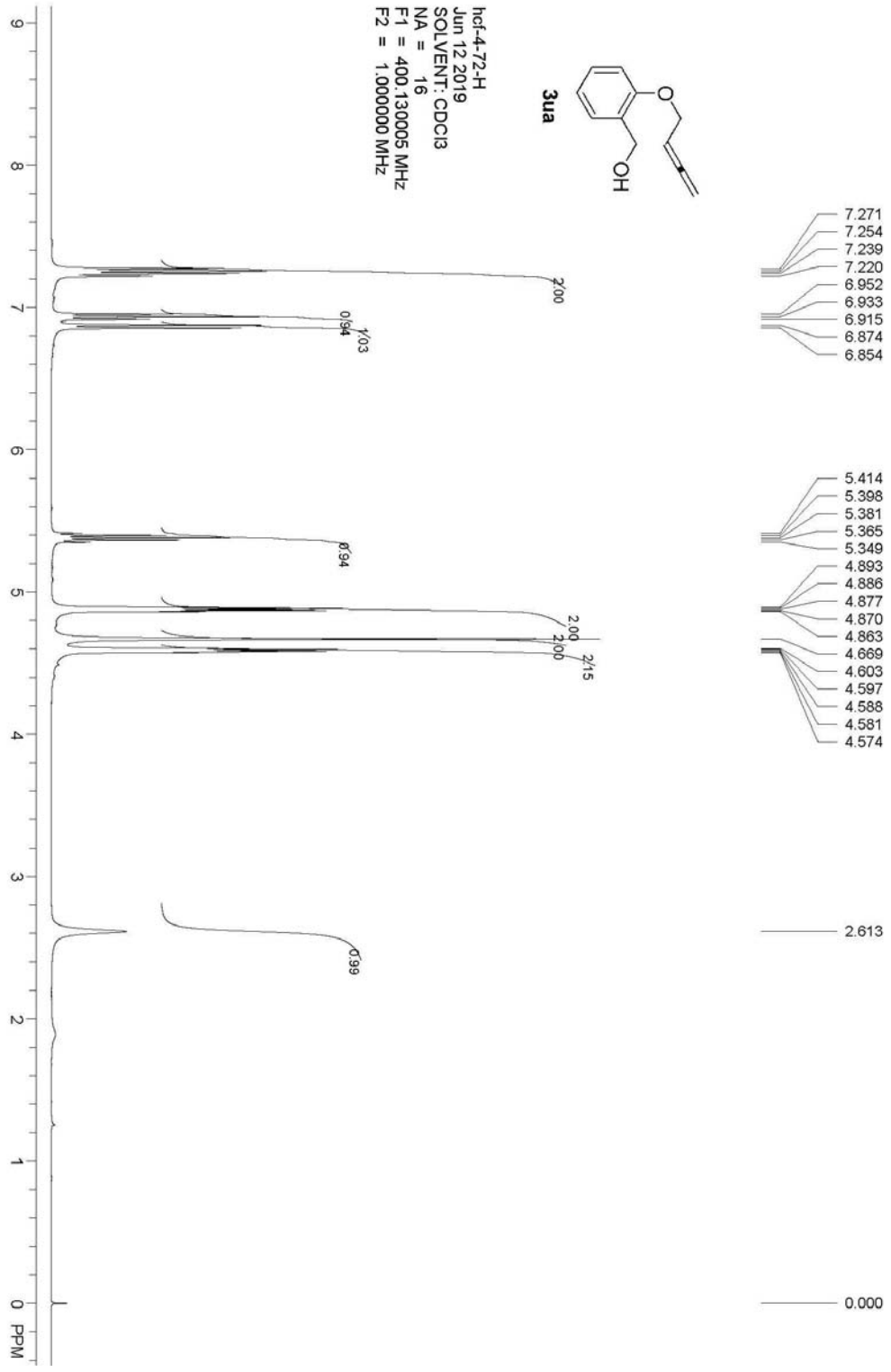

hcf-4-117-C
Jul 10 2019
SOLVENT: CDCl3
NA = 128
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3ra
209.364
159.492
129.764
107.352
102.169
86.993
77.316
77.000
76.684
76.447
65.782
200
150
100
50
0
PPM

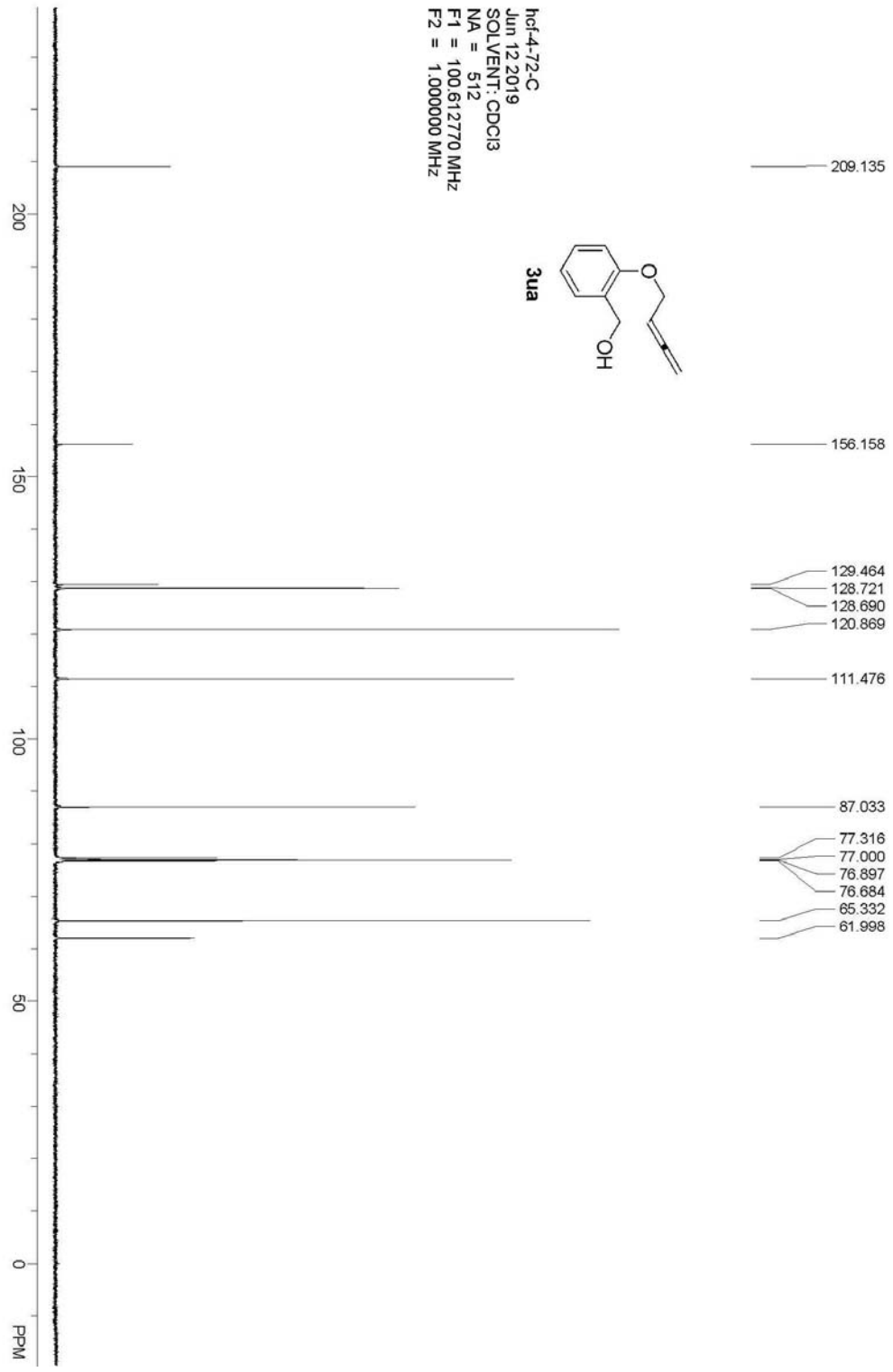

hcf-4-96-H
Jun 25 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3sa
7.256
6.943
6.930
6.919
6.913
6.902
6.889
5.454
5.437
5.421
5.404
5.387
4.844
4.838
4.832
4.829
4.822
4.816
4.653
4.647
4.640
4.636
4.630
4.624
0.000
4.16
2.00
4.11
4.21
8
6
4
2
0
PPM

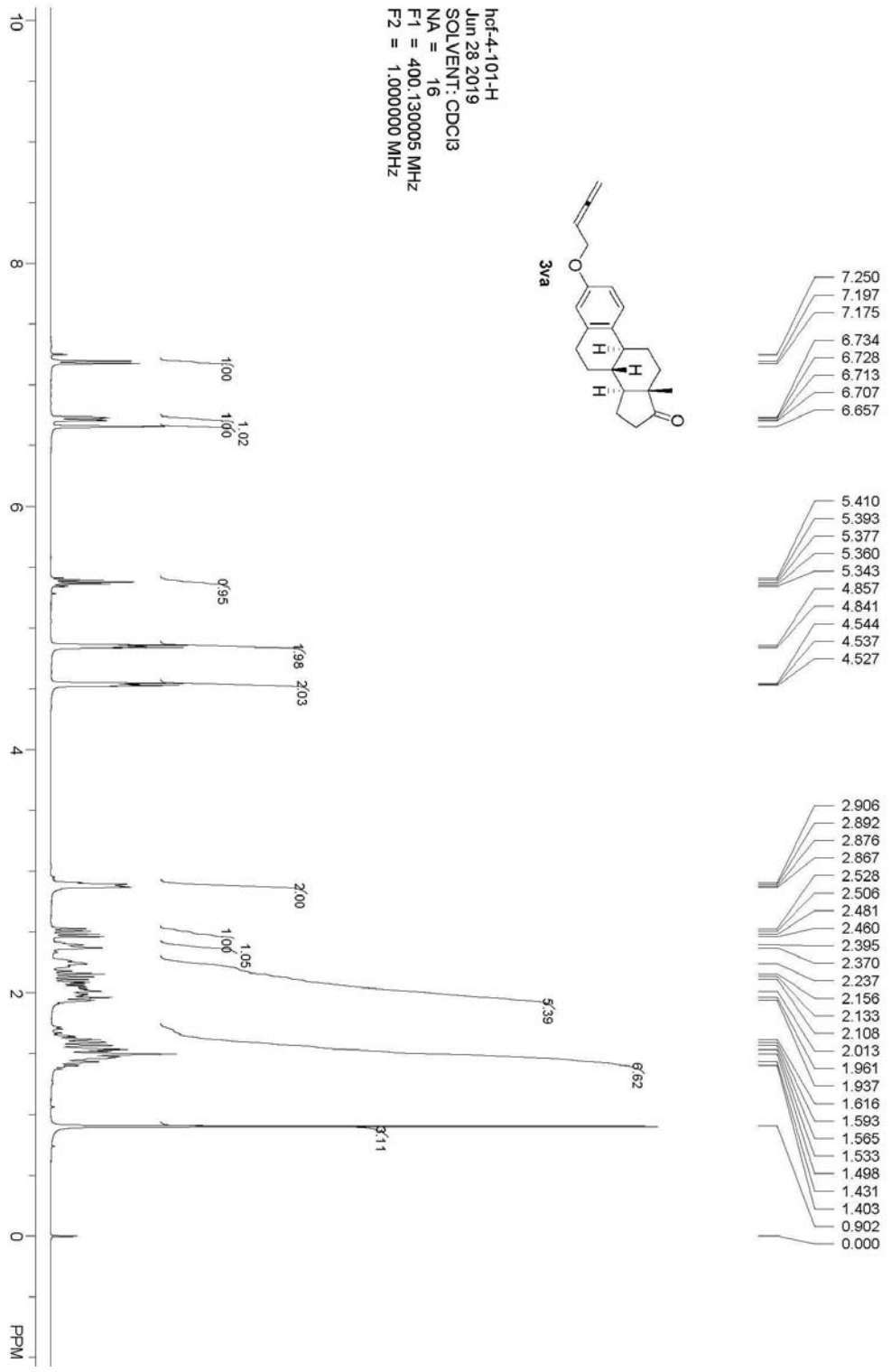

hcf-4-96-C
Jun 25 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3sa
209.451
148.321
121.374
114.620
87.254
77.316
77.000
76.684
76.321
66.928
200
150
100
50
0
PPM

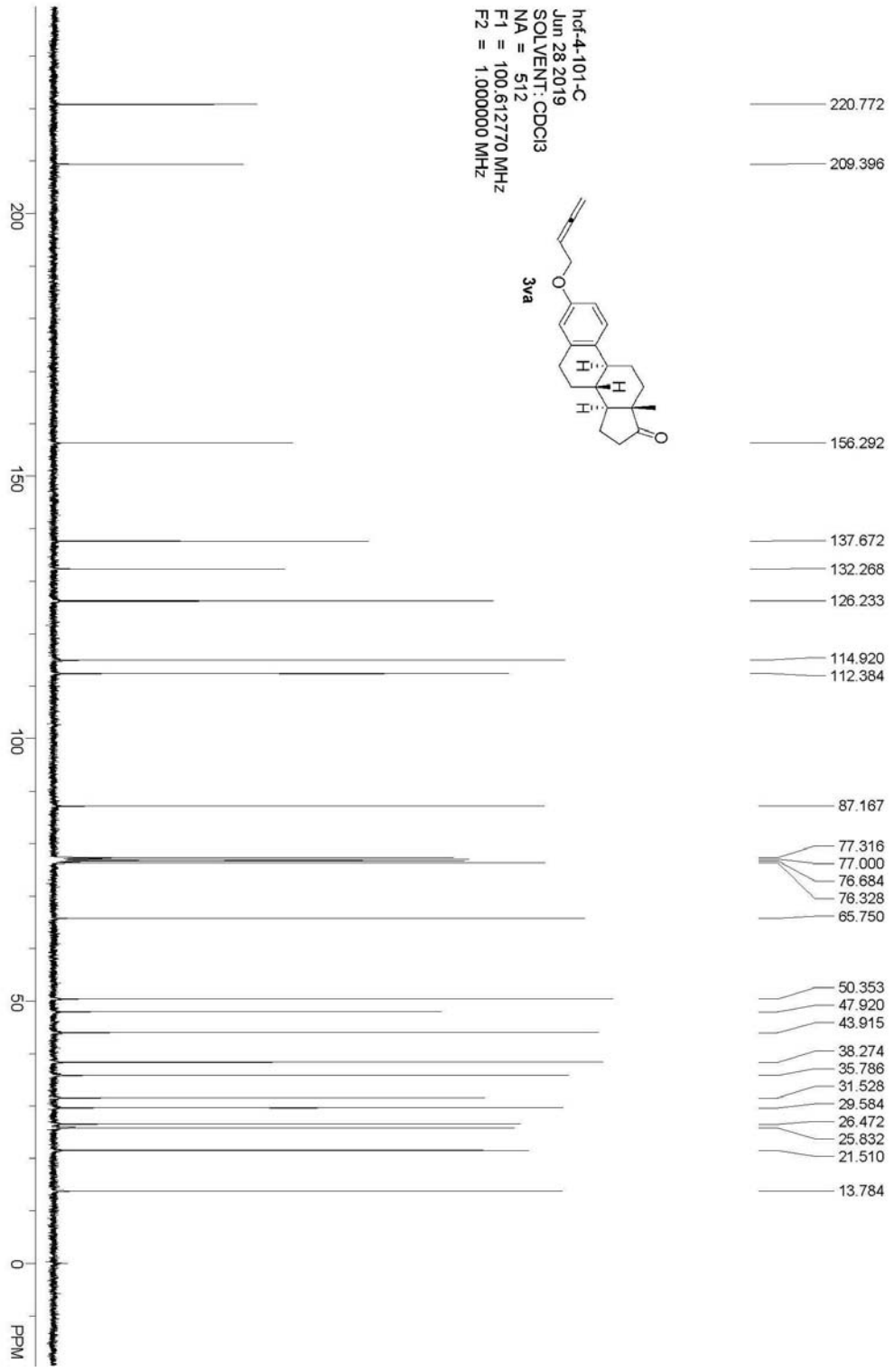

hcf-4-110-H
Jul 5 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130035 MHz
F2 = 1.000000 MHz
4.00
8.10
1.89
7.96
3ta
7.913
7.891
7.835
7.814
7.416
7.393
7.305
7.289
7.285
7.272
7.268
7.196
7.178
7.175
7.162
7.159
7.130
7.110
5.064
5.047
5.031
5.014
4.998
4.634
4.631
4.628
4.625
4.617
4.615
4.611
4.526
4.520
4.510
4.504
4.497
-0.000
15
10
5
0
PPM

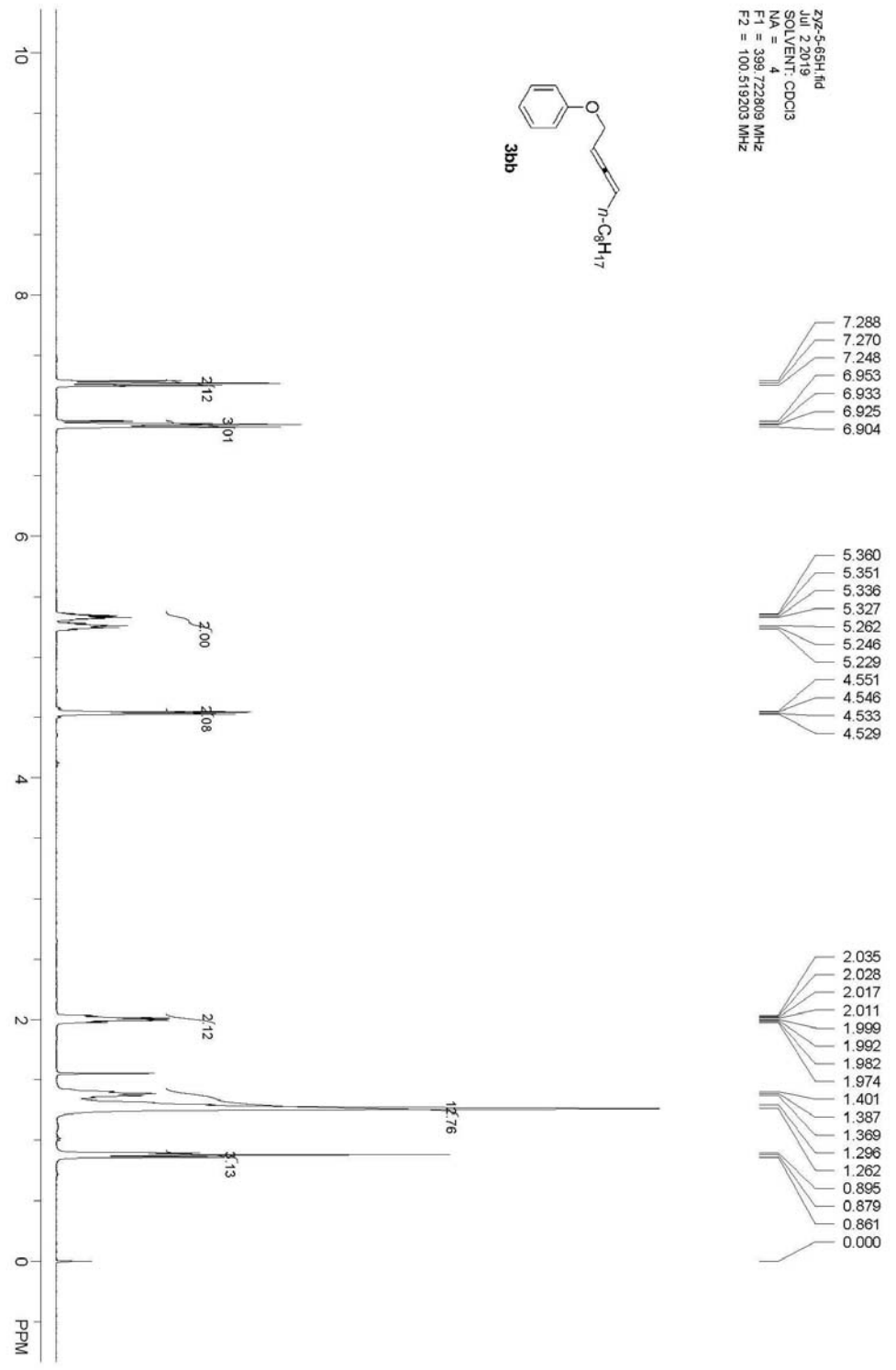

hcf-4-110-C
Jul 5 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3ta
208.954
153.733
134.085
129.440
129.069
127.805
126.154
125.522
123.673
120.837
116.200
87.633
77.316
77.000
76.684
76.084
67.251
200
150
100
50
0
PPM

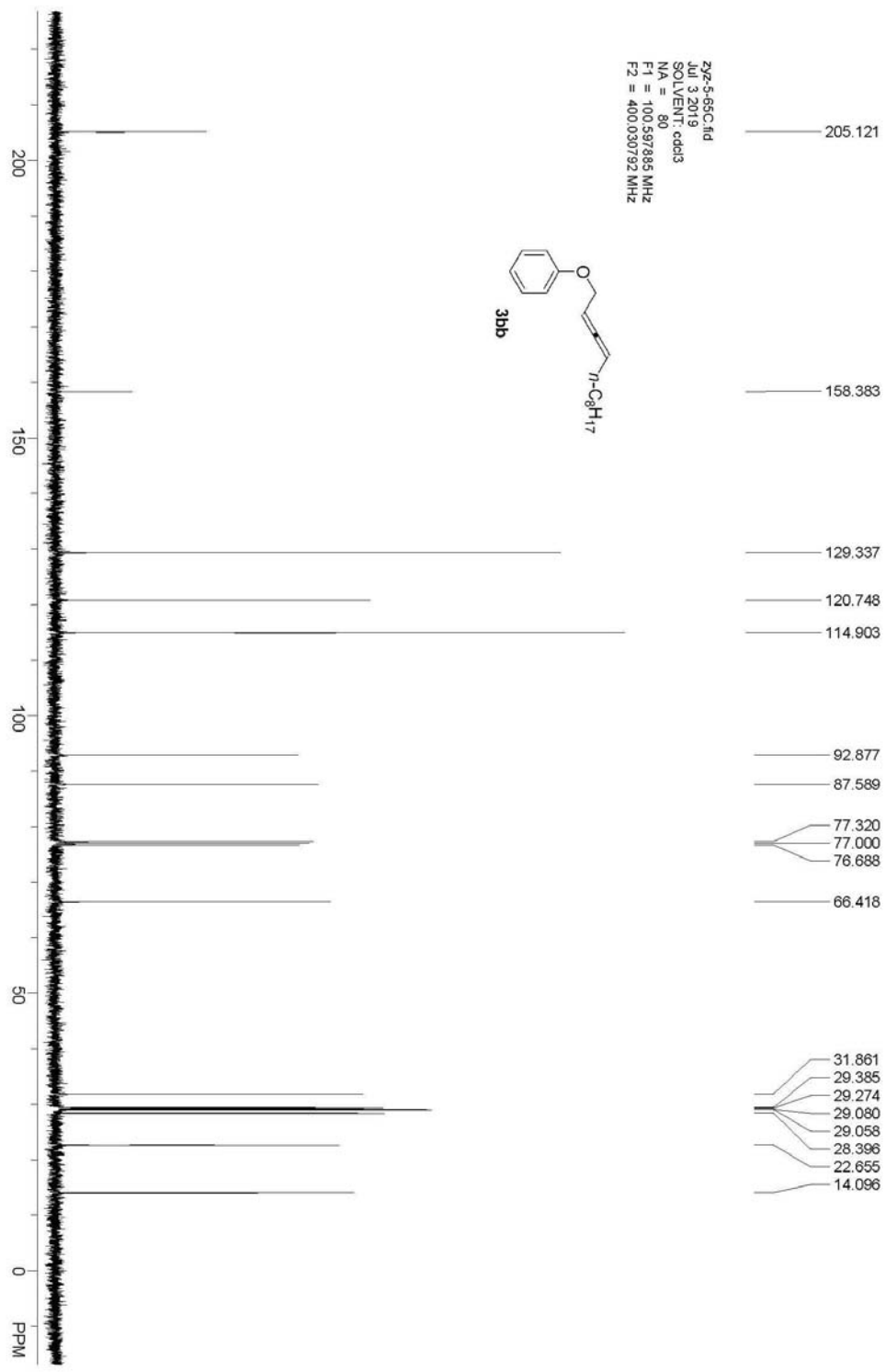

hcf-4-72-H
Jun 12 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3ua
OH
7.271
7.254
7.239
7.220
6.952
6.933
6.915
6.874
6.854
5.414
5.398
5.381
5.365
5.349
4.893
4.886
4.877
4.870
4.863
4.669
4.603
4.597
4.588
4.581
4.574
2.613
0.000
2.00
0.94
1.03
0.94
2.00
2.00
2.15
0.99
PPM

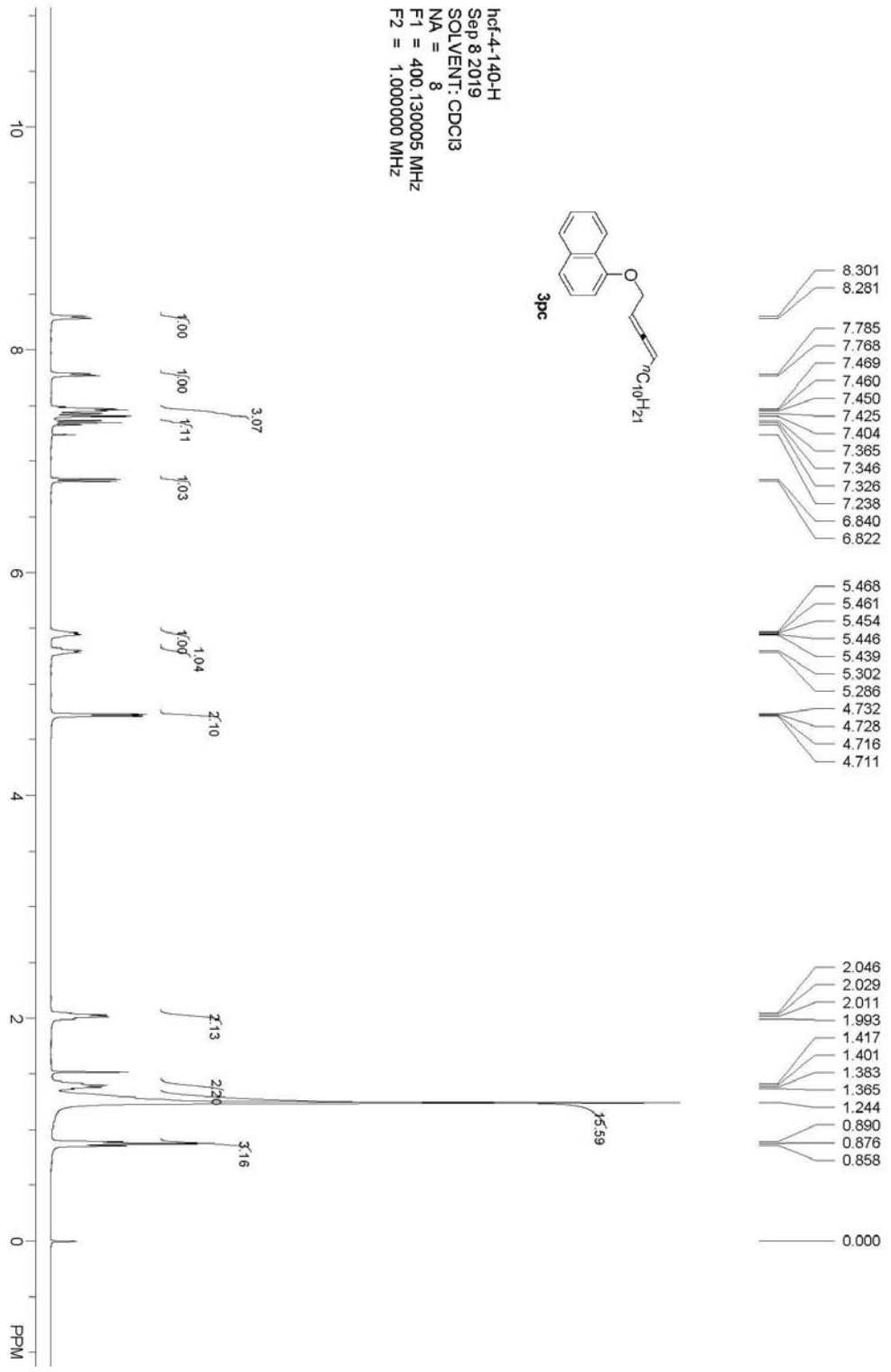

hcf-4-72-C
Jun 12 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3ua
OH
209.135
156.158
129.464
128.721
128.690
120.869
111.476
87.033
77.316
77.000
76.897
76.684
65.332
61.998
200
150
100
50
0
PPM

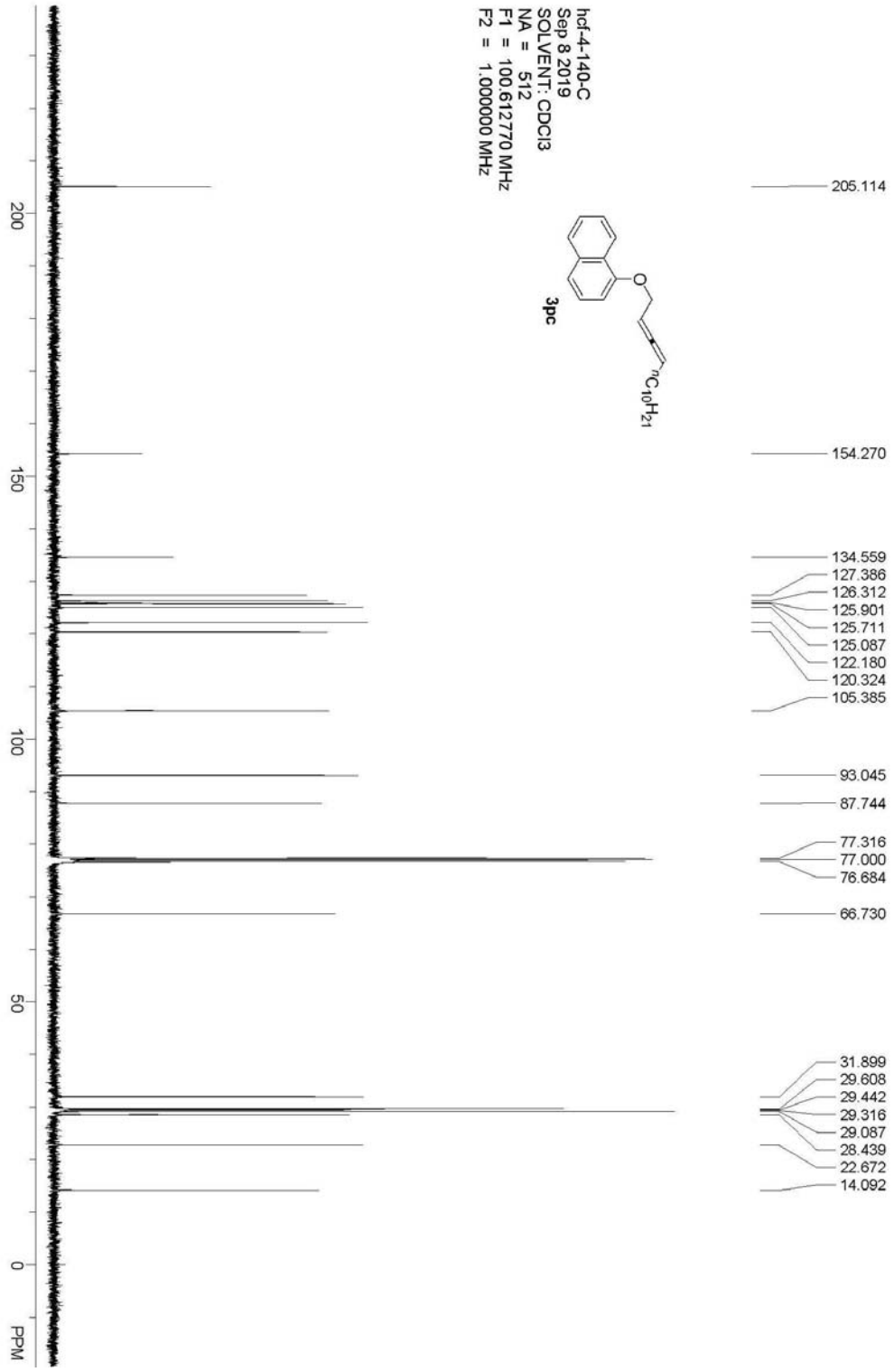

hcf-4-101-H
Jun 28 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3va
7.250
7.197
7.175
6.734
6.728
6.713
6.707
6.657
5.410
5.393
5.377
5.360
5.343
4.857
4.841
4.544
4.537
4.527
2.906
2.892
2.876
2.867
2.528
2.506
2.481
2.460
2.395
2.370
2.237
2.156
2.133
2.108
2.013
1.961
1.937
1.616
1.593
1.565
1.533
1.498
1.431
1.403
0.902
0.000
1.00
1.02
1.00
0.95
1.98
2.03
2.00
1.00
1.05
5.39
6.62
3.11
PPM

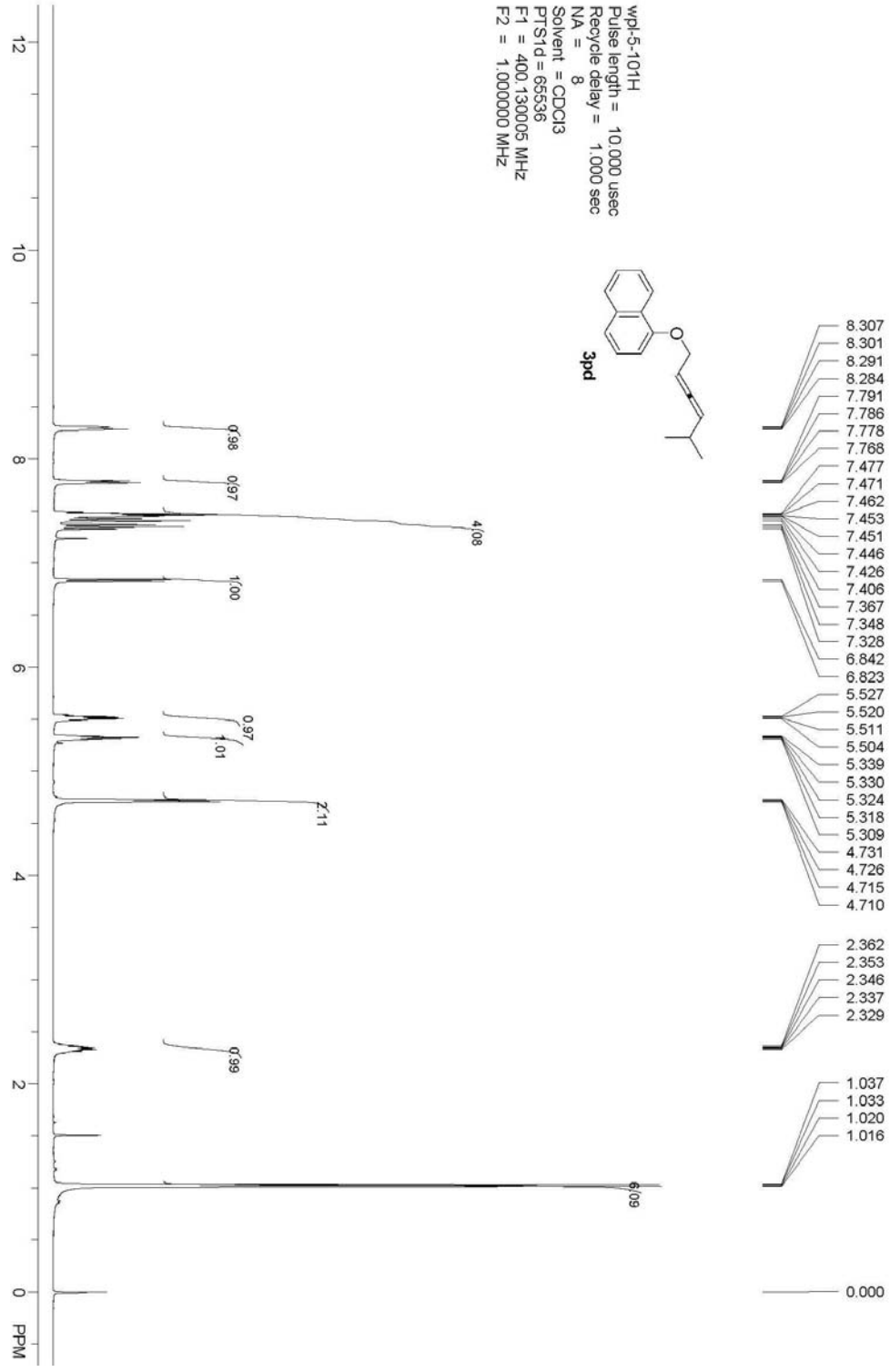

hcf-4-101-C
Jun 28 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3va
220.772
209.396
156.292
137.672
132.268
126.233
114.920
112.384
87.167
77.316
77.000
76.684
76.328
65.750
50.353
47.920
43.915
38.274
35.786
31.528
29.584
26.472
25.832
21.510
13.784
200
150
100
50
0
PPM

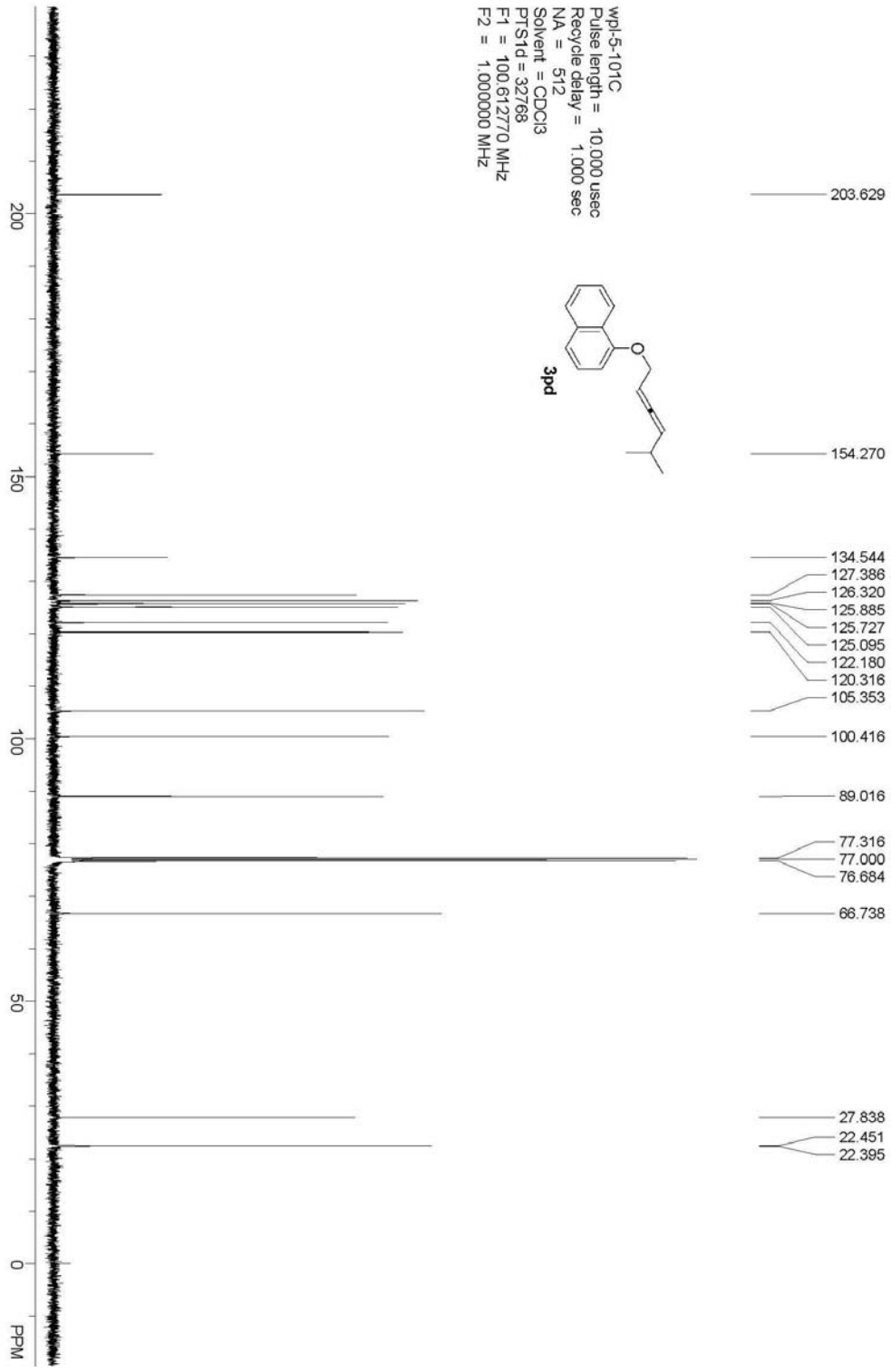

zyz-5-65H.fid
Jul 2 2019
SOLVENT: CDCl3
NA = 4
F1 = 399.722809 MHz
F2 = 100.519203 MHz
3bb
n-C8H17
7.288
7.270
7.248
6.953
6.933
6.925
6.904
5.360
5.351
5.336
5.327
5.262
5.246
5.229
4.551
4.546
4.533
4.529
2.035
2.028
2.017
2.011
1.999
1.992
1.982
1.974
1.401
1.387
1.369
1.296
1.262
0.895
0.879
0.861
0.000
2.12
3.01
2.00
2.08
2.12
12.76
3.13
10
8
6
4
2
0
PPM

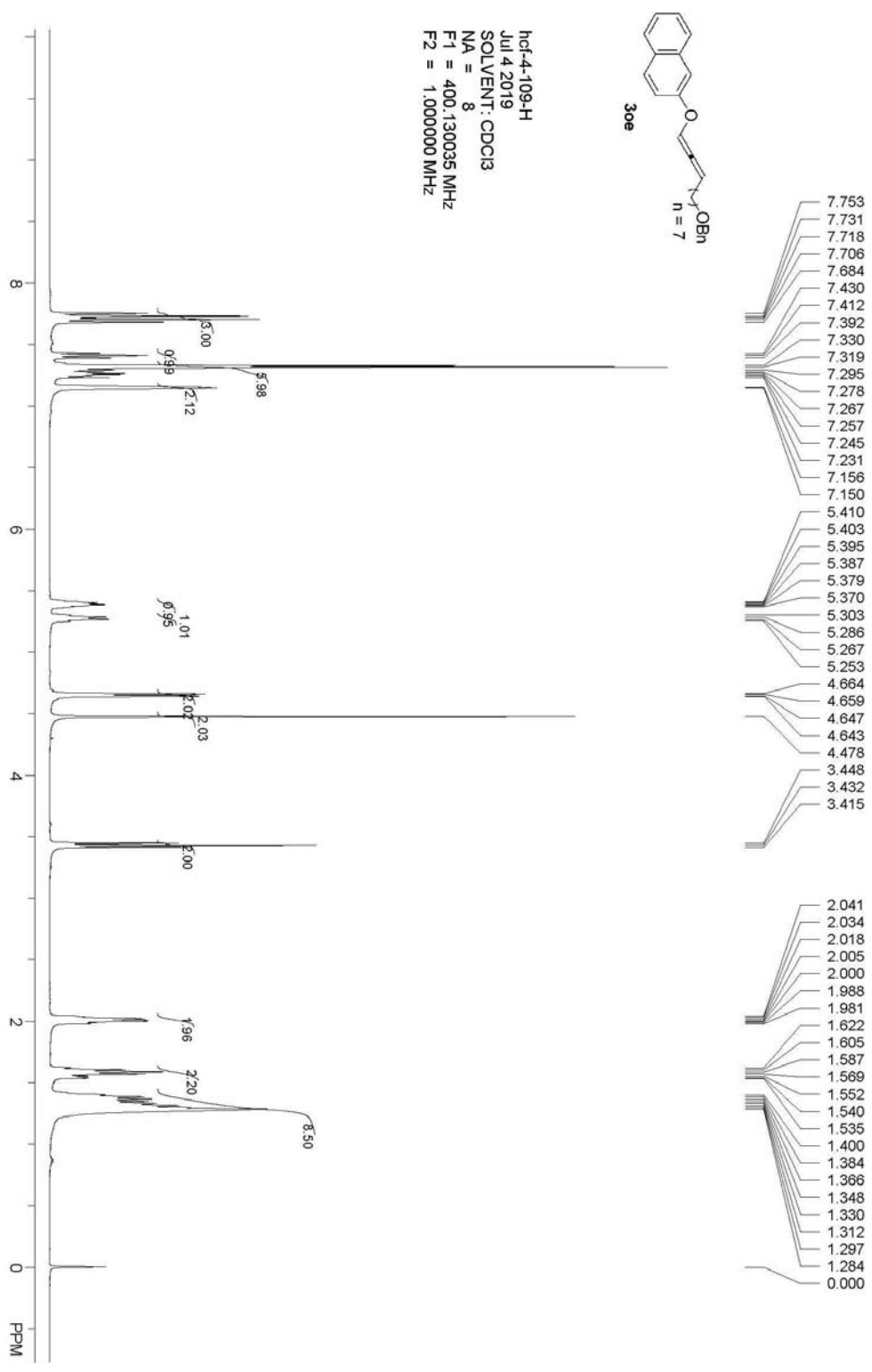

zyz-5-65C.fid
Jul 3 2019
SOLVENT: cdcl3
NA = 80
F1 = 100.597885 MHz
F2 = 400.030792 MHz
3bb
n-C8H17
205.121
158.383
129.337
120.748
114.903
92.877
87.589
77.320
77.000
76.688
66.418
31.861
29.385
29.274
29.080
29.058
28.396
22.655
14.096
200
150
100
50
0
PPM

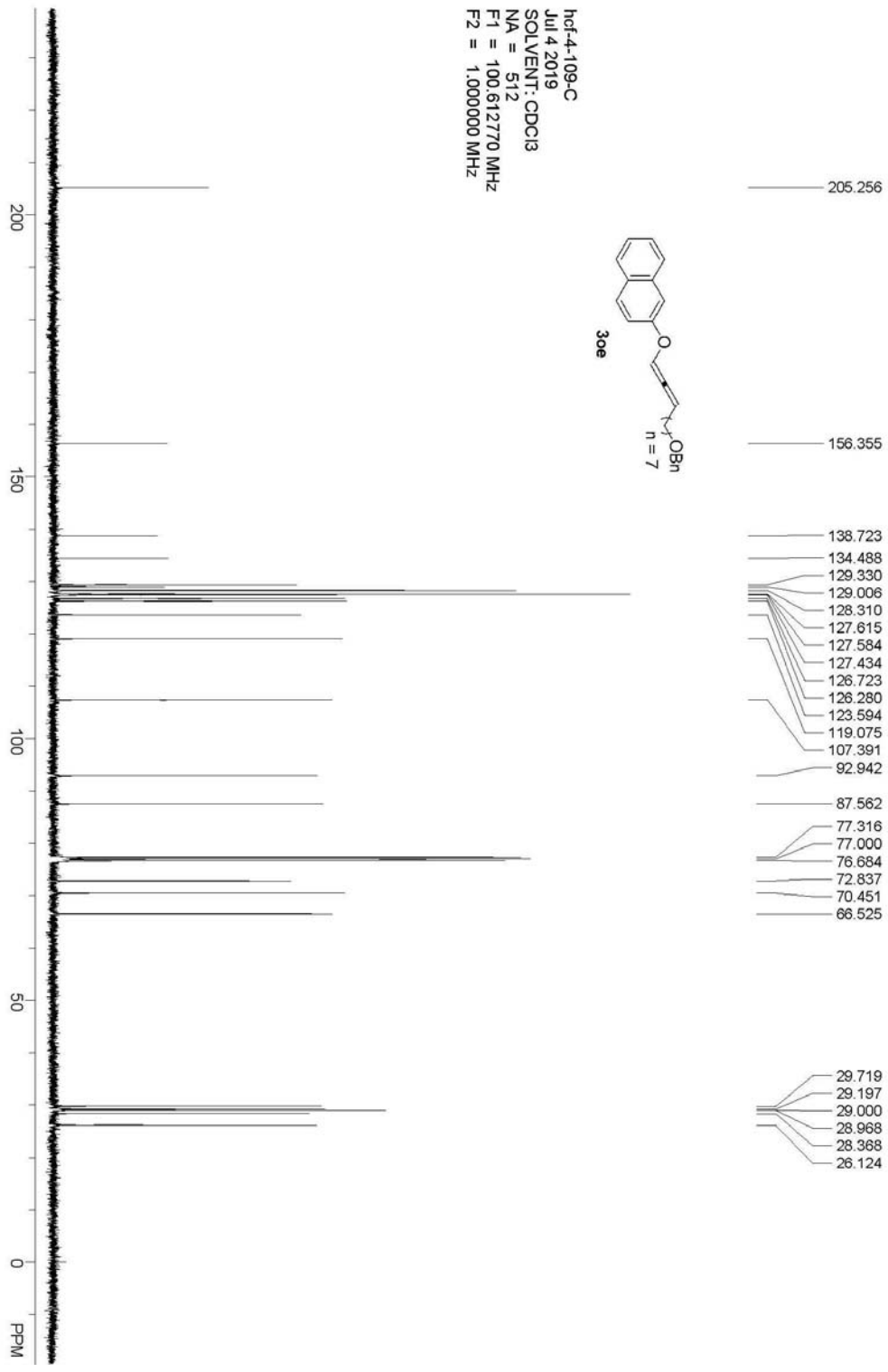

hcf-4-140-H
Sep 8 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3pc
nC10H21
8.301
8.281
7.785
7.768
7.469
7.460
7.450
7.425
7.404
7.365
7.346
7.326
7.238
6.840
6.822
5.468
5.461
5.454
5.446
5.439
5.302
5.286
4.732
4.728
4.716
4.711
2.046
2.029
2.011
1.993
1.417
1.401
1.383
1.365
1.244
0.890
0.876
0.858
0.000
3.07
1.00
1.00
1.11
1.03
1.04
1.00
2.10
2.13
2.20
15.59
3.16
10
8
6
4
2
0
PPM

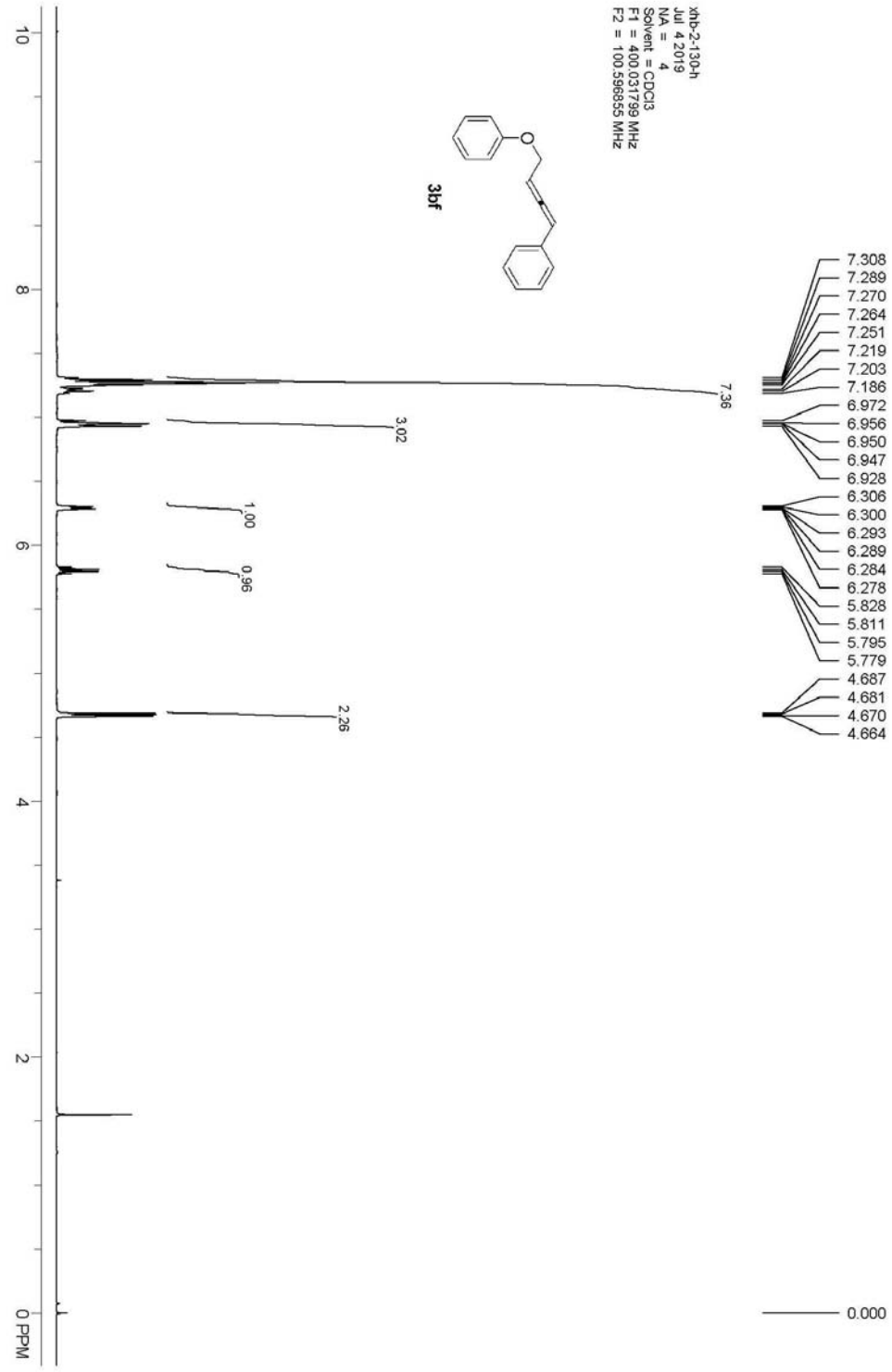

hcf-4-140-C
Sep 8 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3pc
$^{n}C_{10}H_{21}$
205.114
154.270
134.559
127.386
126.312
125.901
125.711
125.087
122.180
120.324
105.385
93.045
87.744
77.316
77.000
76.684
66.730
31.899
29.608
29.442
29.316
29.087
28.439
22.672
14.092
200
150
100
50
0
PPM

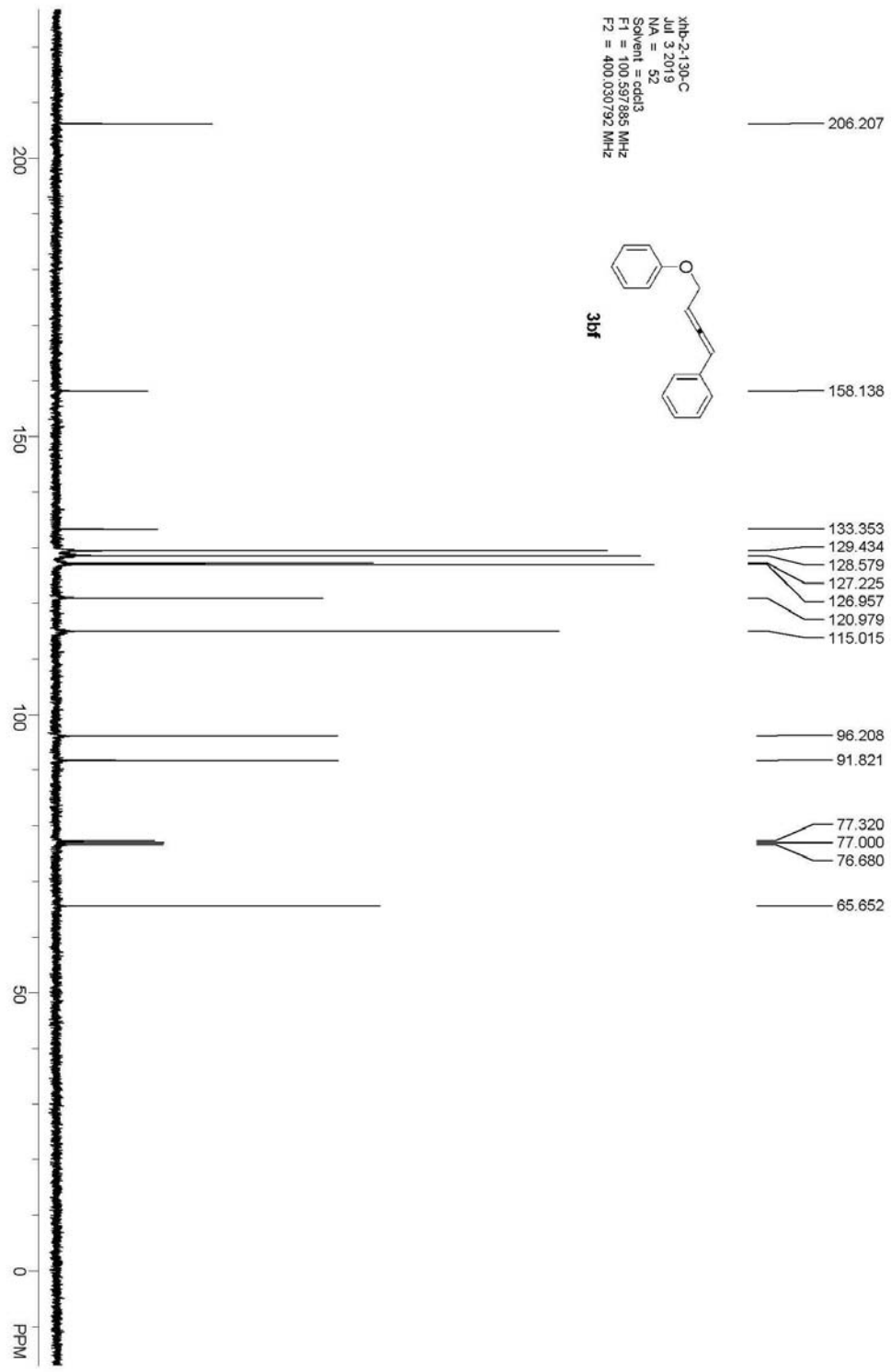

wpl-5-101H
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 8
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3pd
0.98
0.97
4.08
1.00
0.97
1.01
2.11
0.99
6.09
8.307
8.301
8.291
8.284
7.791
7.786
7.778
7.768
7.477
7.471
7.462
7.453
7.451
7.446
7.426
7.406
7.367
7.348
7.328
6.842
6.823
5.527
5.520
5.511
5.504
5.339
5.330
5.324
5.318
5.309
4.731
4.726
4.715
4.710
2.362
2.353
2.346
2.337
2.329
1.037
1.033
1.020
1.016
0.000
12
10
8
6
4
2
0
PPM

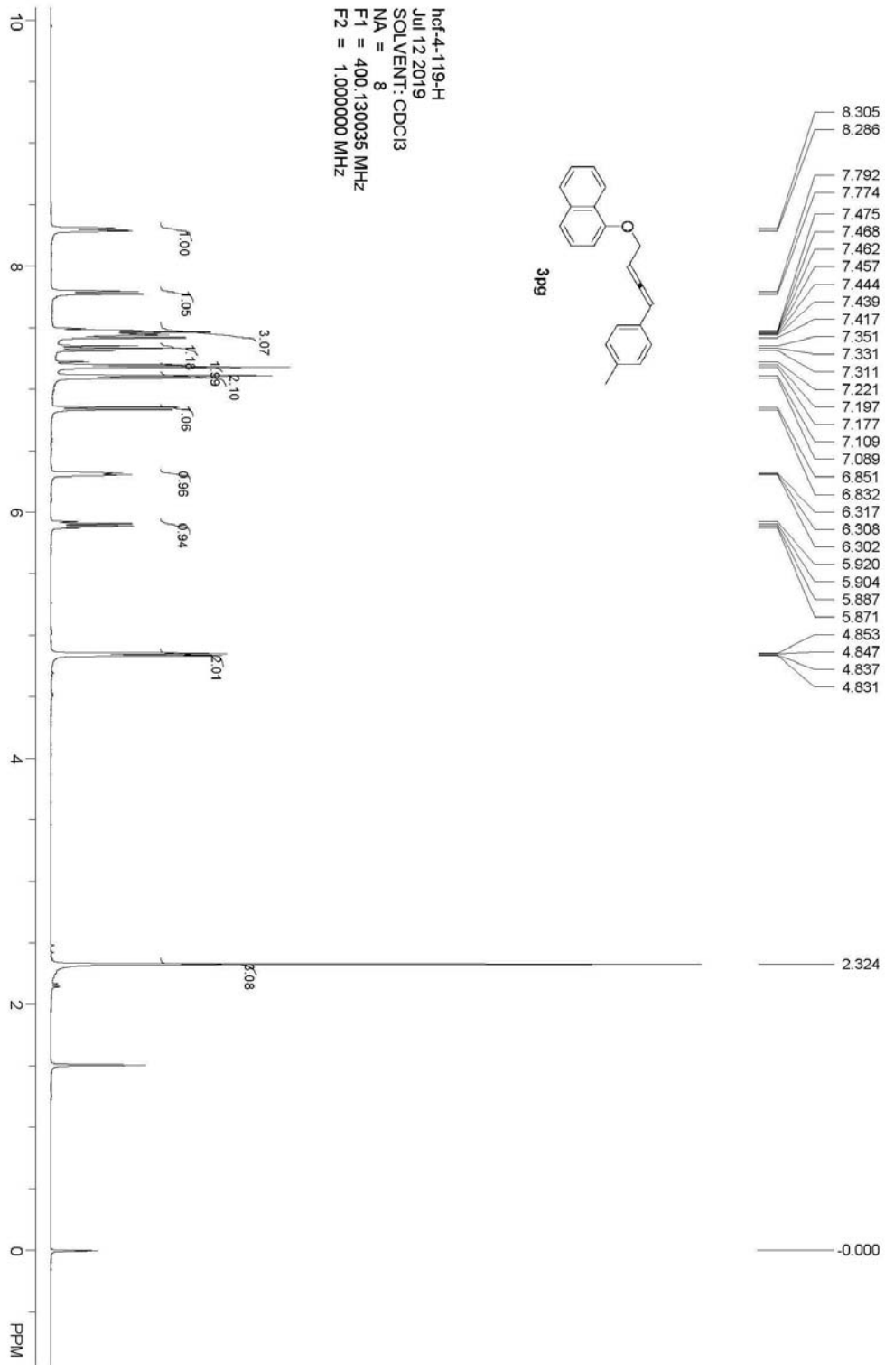

wpl-5-101C
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3pd
203.629
154.270
134.544
127.386
126.320
125.885
125.727
125.095
122.180
120.316
105.353
100.416
89.016
77.316
77.000
76.684
66.738
27.838
22.451
22.395
200
150
100
50
0
PPM

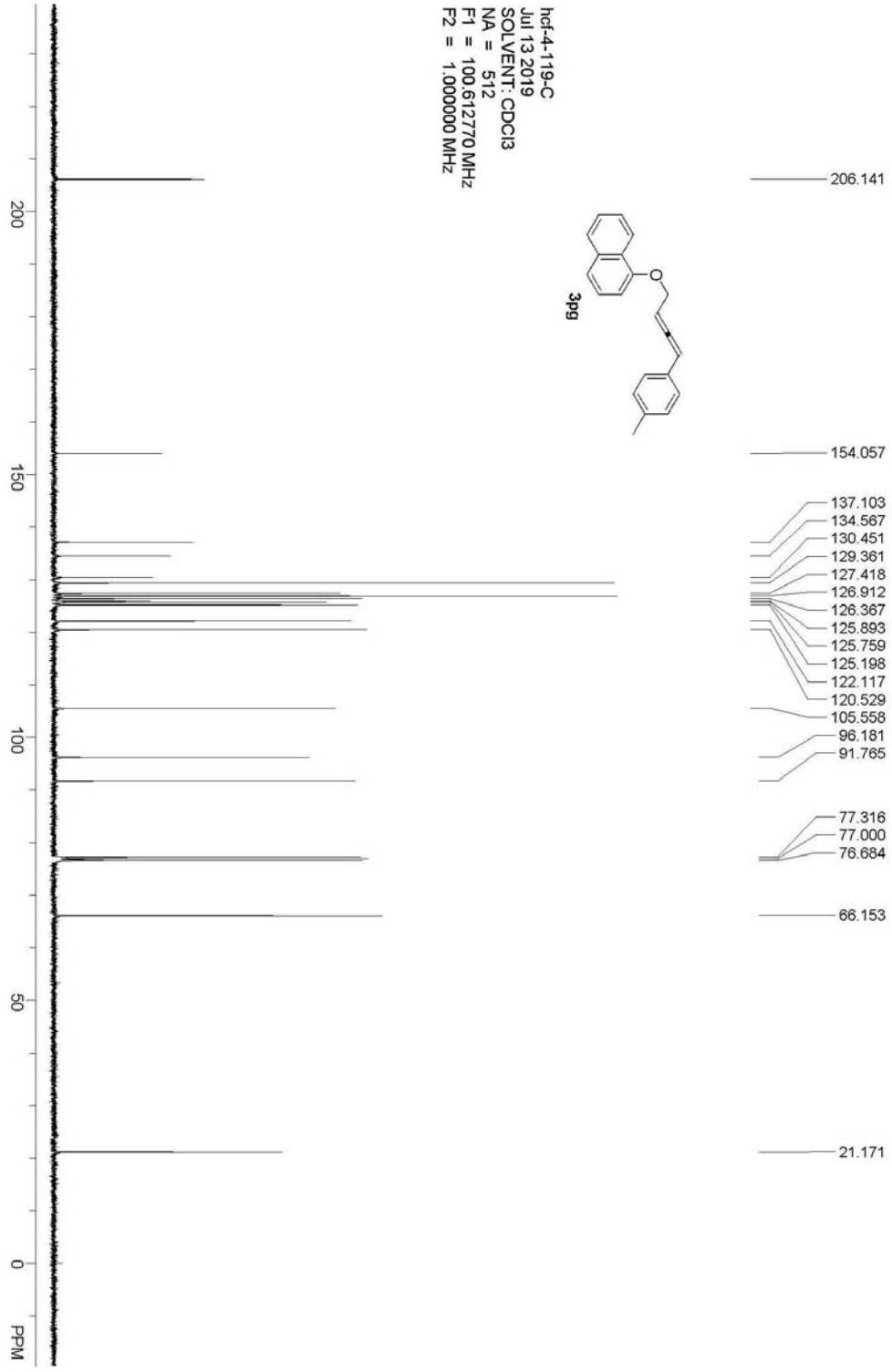

hcf-4-109-H
Jul 4 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130035 MHz
F2 = 1.000000 MHz
3oe
OBn
n = 7
7.753
7.731
7.718
7.706
7.684
7.430
7.412
7.392
7.330
7.319
7.295
7.278
7.267
7.257
7.245
7.231
7.156
7.150
5.410
5.403
5.395
5.387
5.379
5.370
5.303
5.286
5.267
5.253
4.664
4.659
4.647
4.643
4.478
3.448
3.432
3.415
2.041
2.034
2.018
2.005
2.000
1.988
1.981
1.622
1.605
1.587
1.569
1.552
1.540
1.535
1.400
1.384
1.366
1.348
1.330
1.312
1.297
1.284
0.000
3.00
0.99
5.98
2.12
1.01
0.95
2.02
2.03
2.00
1.96
2.20
8.50
8
6
4
2
0
PPM

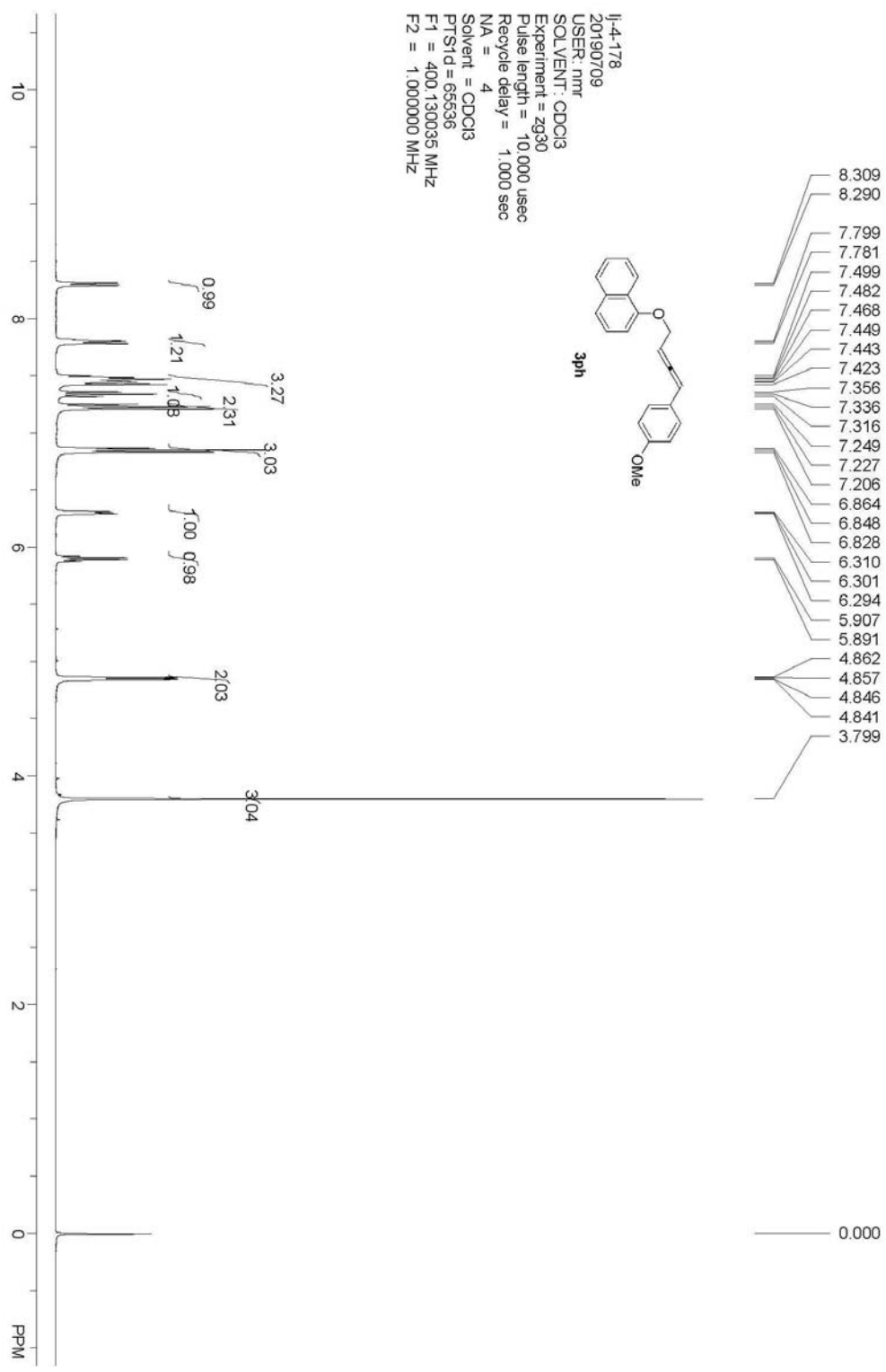

hcf-4-109-C
Jul 4 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3oe
n = 7
OBn
205.256
156.355
138.723
134.488
129.330
129.006
128.310
127.615
127.584
127.434
126.723
126.280
123.594
119.075
107.391
92.942
87.562
77.316
77.000
76.684
72.837
70.451
66.525
29.719
29.197
29.000
28.968
28.368
26.124
200
150
100
50
0
PPM

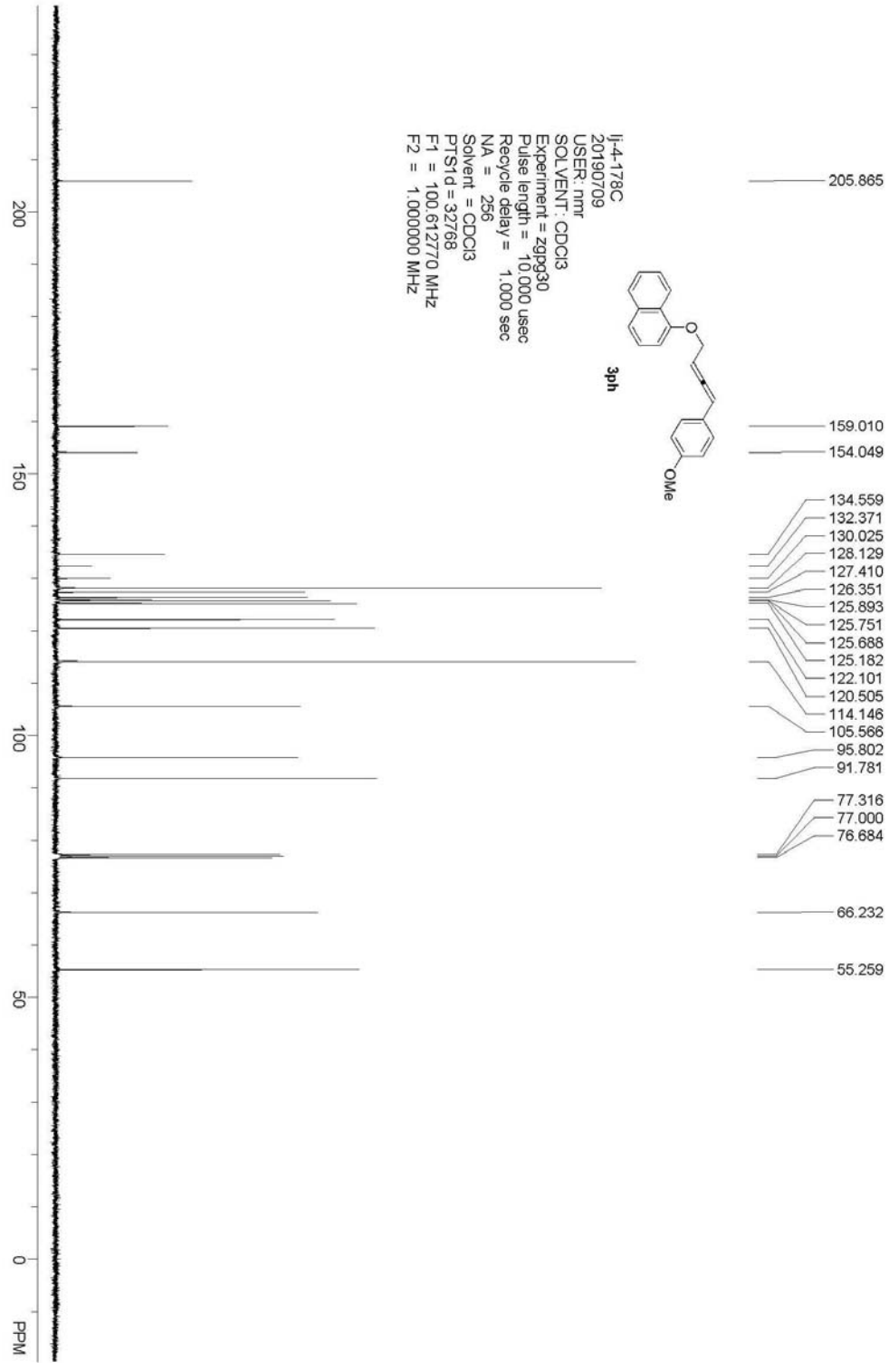

xhb-2-130-h
Jul 4 2019
NA = 4
Solvent = CDCl3
F1 = 400.031799 MHz
F2 = 100.596855 MHz
3bf
7.308
7.289
7.270
7.264
7.251
7.219
7.203
7.186
6.972
6.956
6.950
6.947
6.928
6.306
6.300
6.293
6.289
6.284
6.278
5.828
5.811
5.795
5.779
4.687
4.681
4.670
4.664
7.36
3.02
1.00
0.96
2.26
0.000
10
8
6
4
2
0 PPM

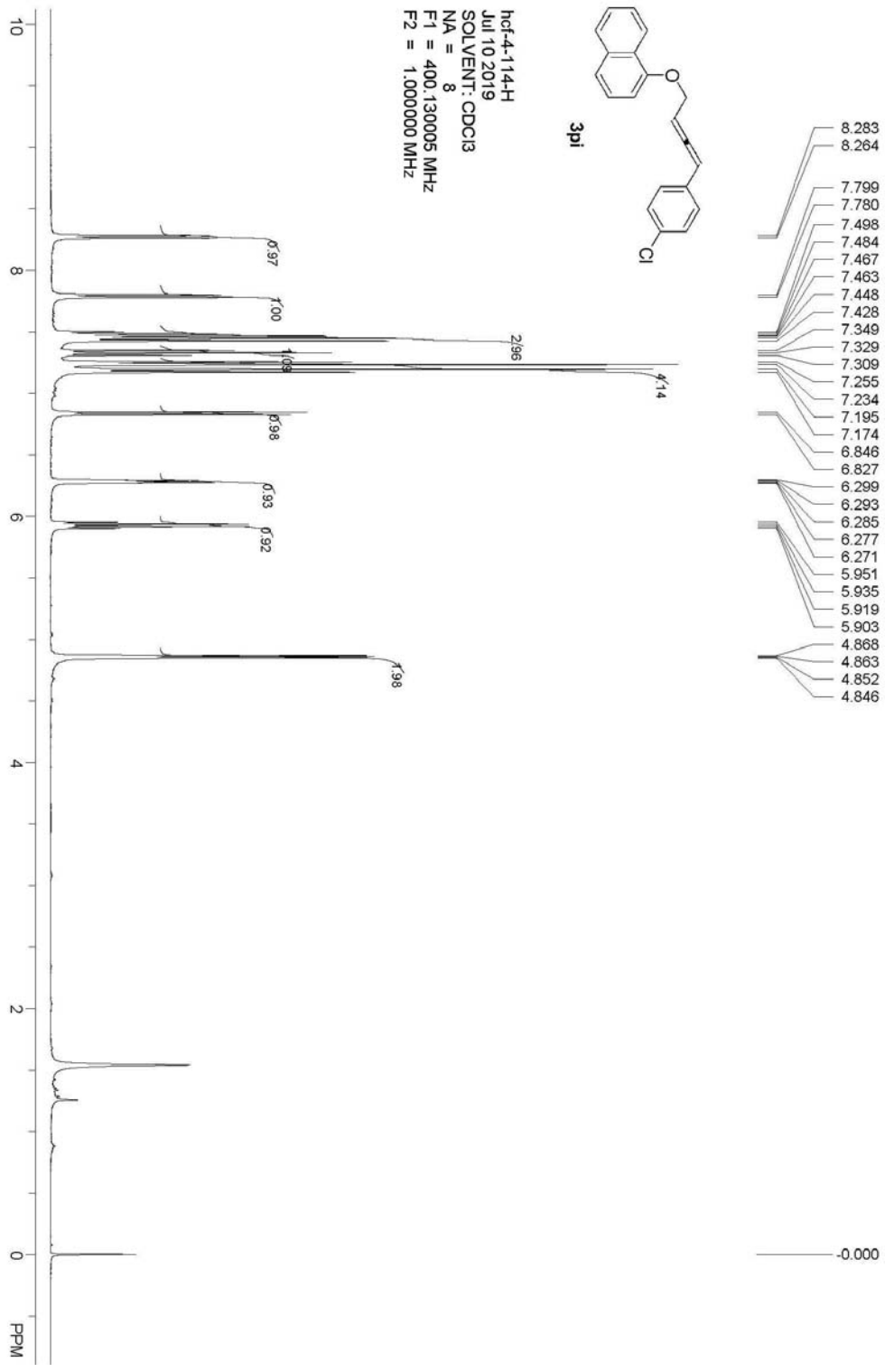

xhb-2-130-C
Jul 3 2019
NA = 52
Solvent = cdcl3
F1 = 100.597885 MHz
F2 = 400.030792 MHz
3bf
206.207
158.138
133.353
129.434
128.579
127.225
126.957
120.979
115.015
96.208
91.821
77.320
77.000
76.680
65.652
200
150
100
50
0
PPM

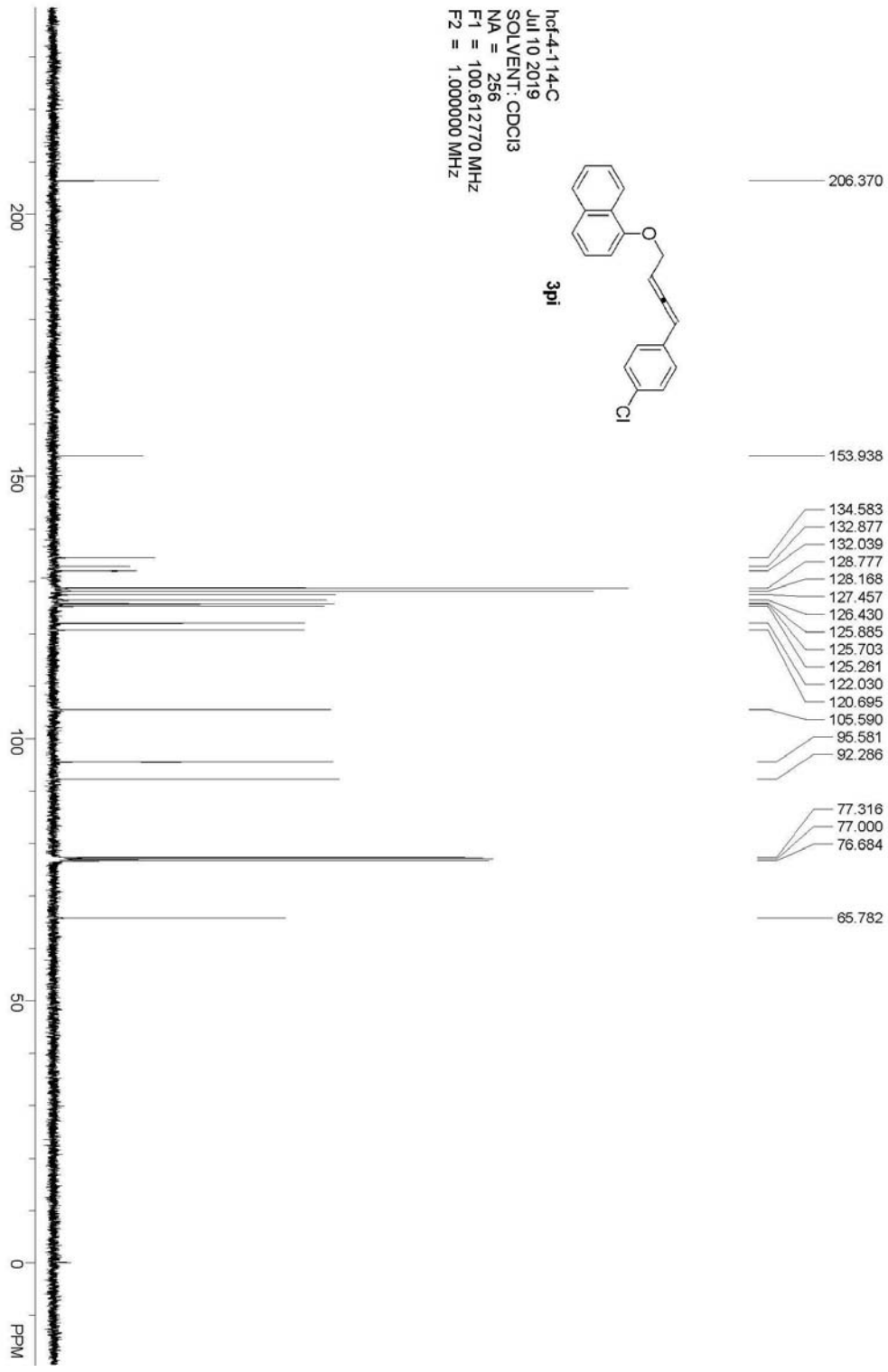

hcf-4-119-H
Jul 12 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130035 MHz
F2 = 1.000000 MHz
3pg
8.305
8.286
7.792
7.774
7.475
7.468
7.462
7.457
7.444
7.439
7.417
7.351
7.331
7.311
7.221
7.197
7.177
7.109
7.089
6.851
6.832
6.317
6.308
6.302
5.920
5.904
5.887
5.871
4.853
4.847
4.837
4.831
2.324
-0.000
1.00
1.05
3.07
1.18
1.99
2.10
1.06
0.96
0.94
2.01
9.08
10
8
6
4
2
0
PPM

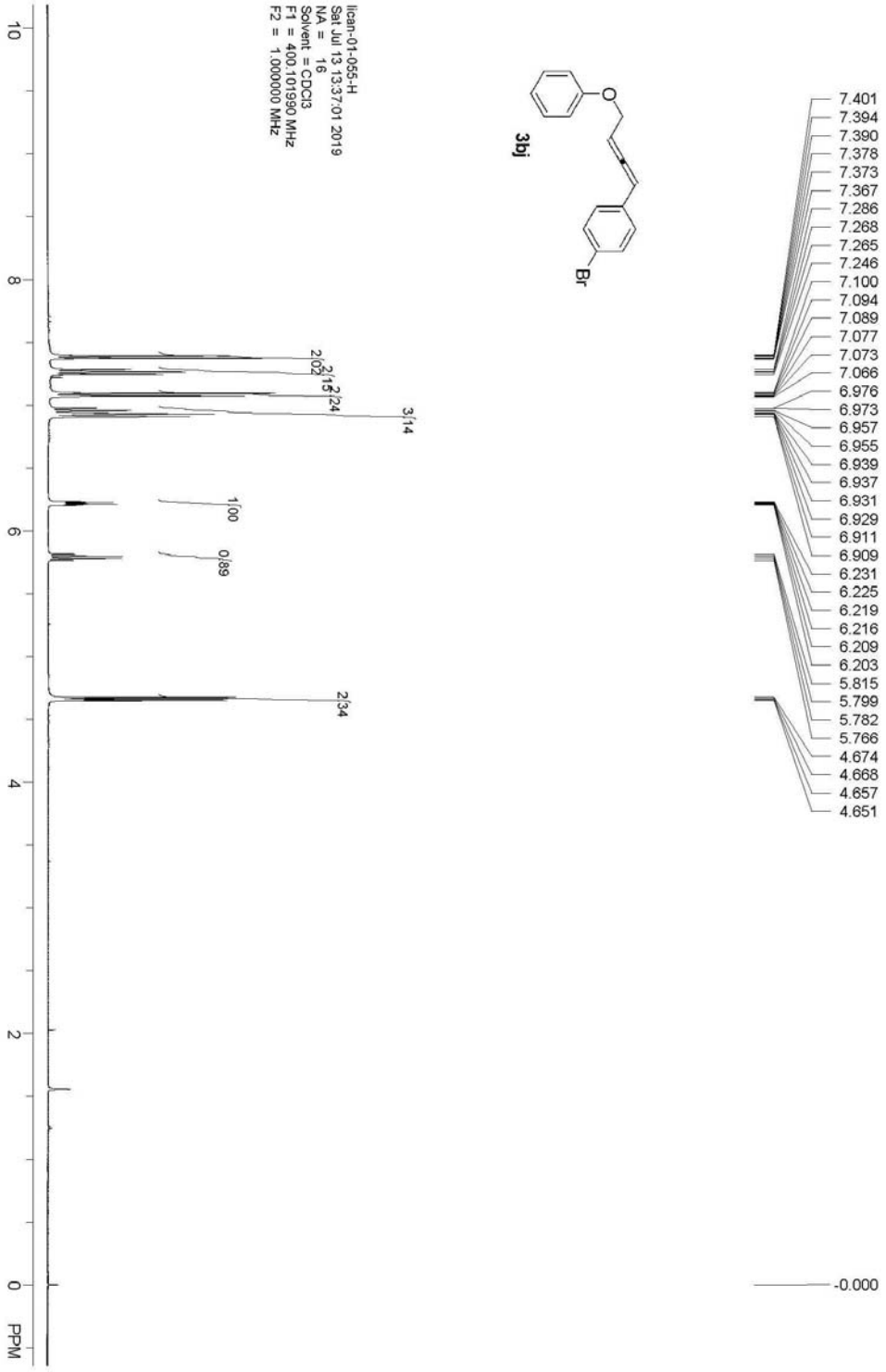

hcf-4-119-C
Jul 13 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3pg
206.141
154.057
137.103
134.567
130.451
129.361
127.418
126.912
126.367
125.893
125.759
125.198
122.117
120.529
105.558
96.181
91.765
77.316
77.000
76.684
66.153
21.171
200
150
100
50
0
PPM

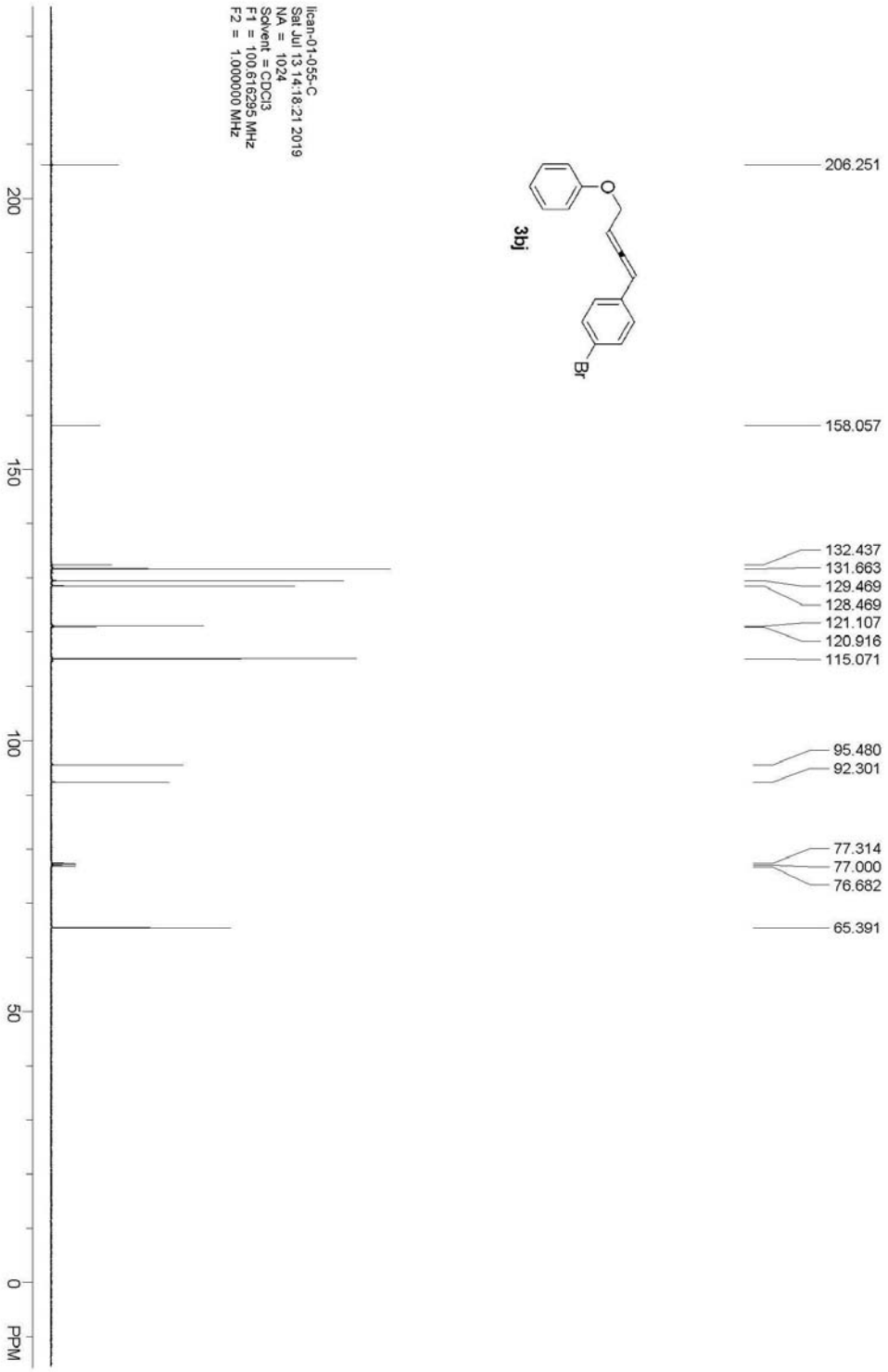

lj-4-178
20190709
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130035 MHz
F2 = 1.000000 MHz
3ph
OMe
8.309
8.290
7.799
7.781
7.499
7.482
7.468
7.449
7.443
7.423
7.356
7.336
7.316
7.249
7.227
7.206
6.864
6.848
6.828
6.310
6.301
6.294
5.907
5.891
4.862
4.857
4.846
4.841
3.799
0.000
0.99
1.21
1.08
3.27
2.31
3.03
1.00
0.98
2.03
3.04
10
8
6
4
2
0
PPM

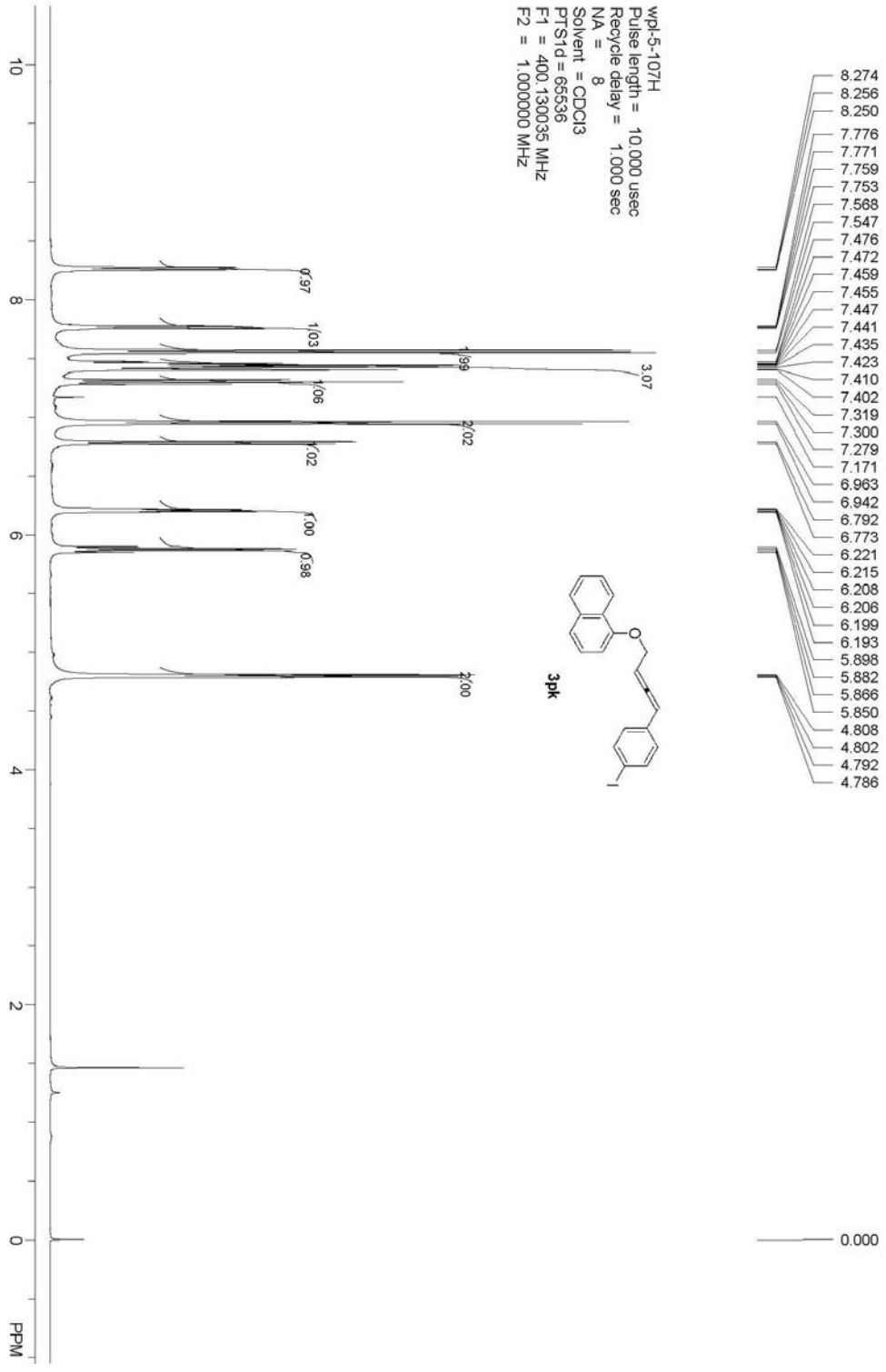

lj-4-178C
20190709
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 256
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3ph
OMe
205.865
159.010
154.049
134.559
132.371
130.025
128.129
127.410
126.351
125.893
125.751
125.688
125.182
122.101
120.505
114.146
105.566
95.802
91.781
77.316
77.000
76.684
66.232
55.259
200
150
100
50
0
PPM

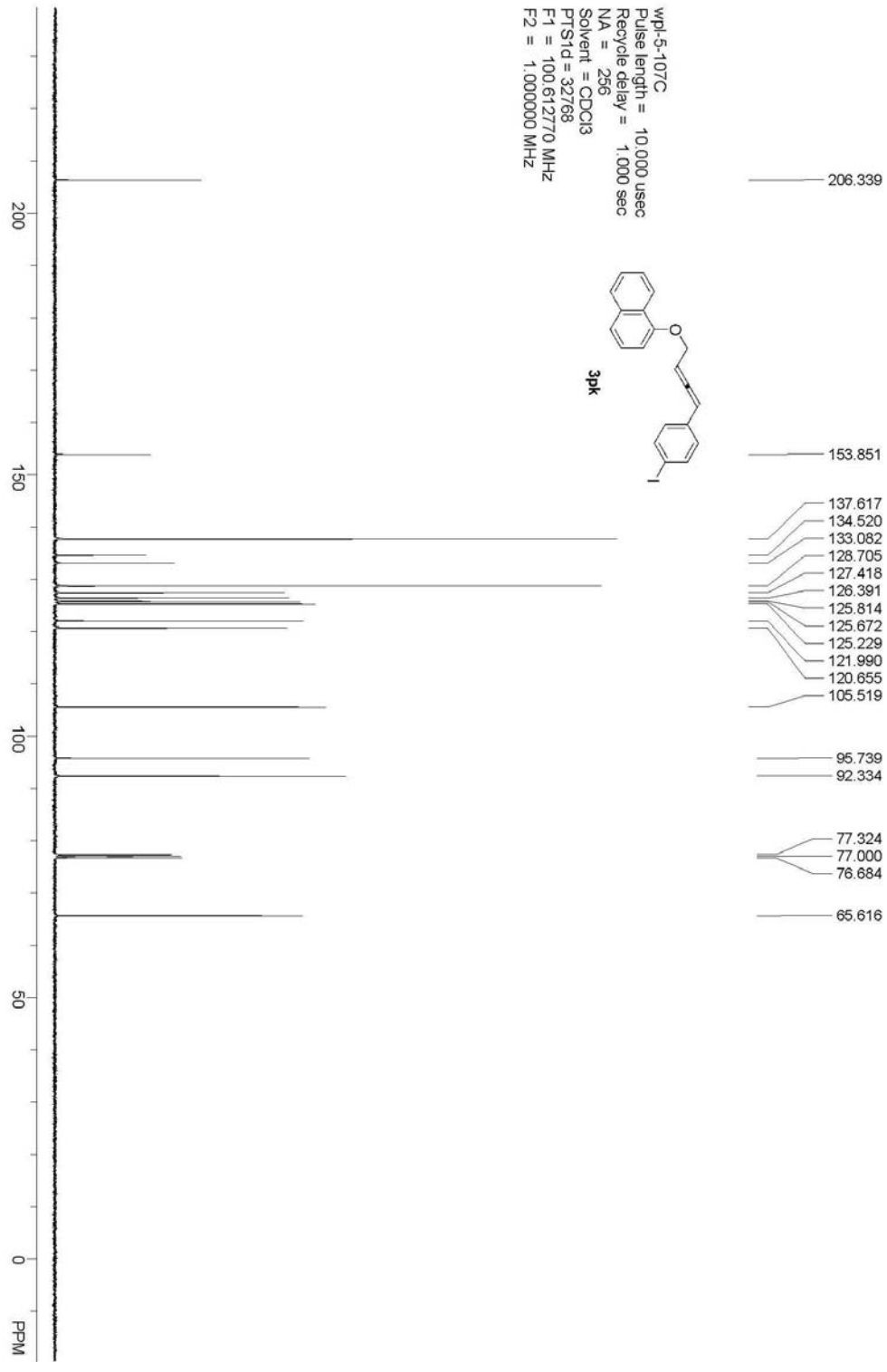

hcf-4-114-H
Jul 10 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3pi
Cl
8.283
8.264
7.799
7.780
7.498
7.484
7.467
7.463
7.448
7.428
7.349
7.329
7.309
7.255
7.234
7.195
7.174
6.846
6.827
6.299
6.293
6.285
6.277
6.271
5.951
5.935
5.919
5.903
4.868
4.863
4.852
4.846
-0.000
0.97
1.00
2.96
1.09
4.14
0.98
0.93
0.92
1.98
10
8
6
4
2
0
PPM

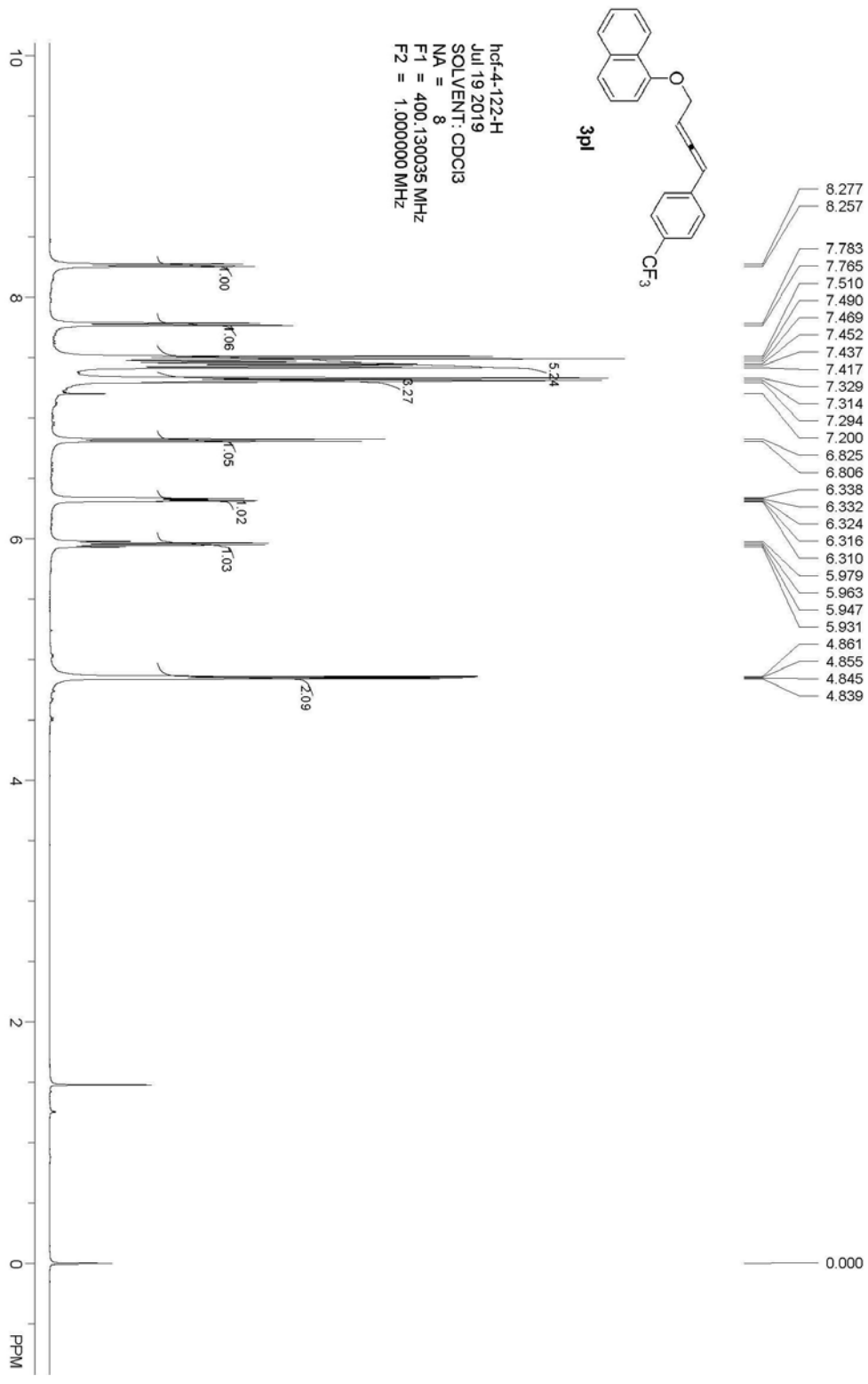

hcf-4-114-C
Jul 10 2019
SOLVENT: CDCl3
NA = 256
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3pi
Cl
206.370
153.938
134.583
132.877
132.039
128.777
128.168
127.457
126.430
125.885
125.703
125.261
122.030
120.695
105.590
95.581
92.286
77.316
77.000
76.684
65.782
200
150
100
50
0
PPM

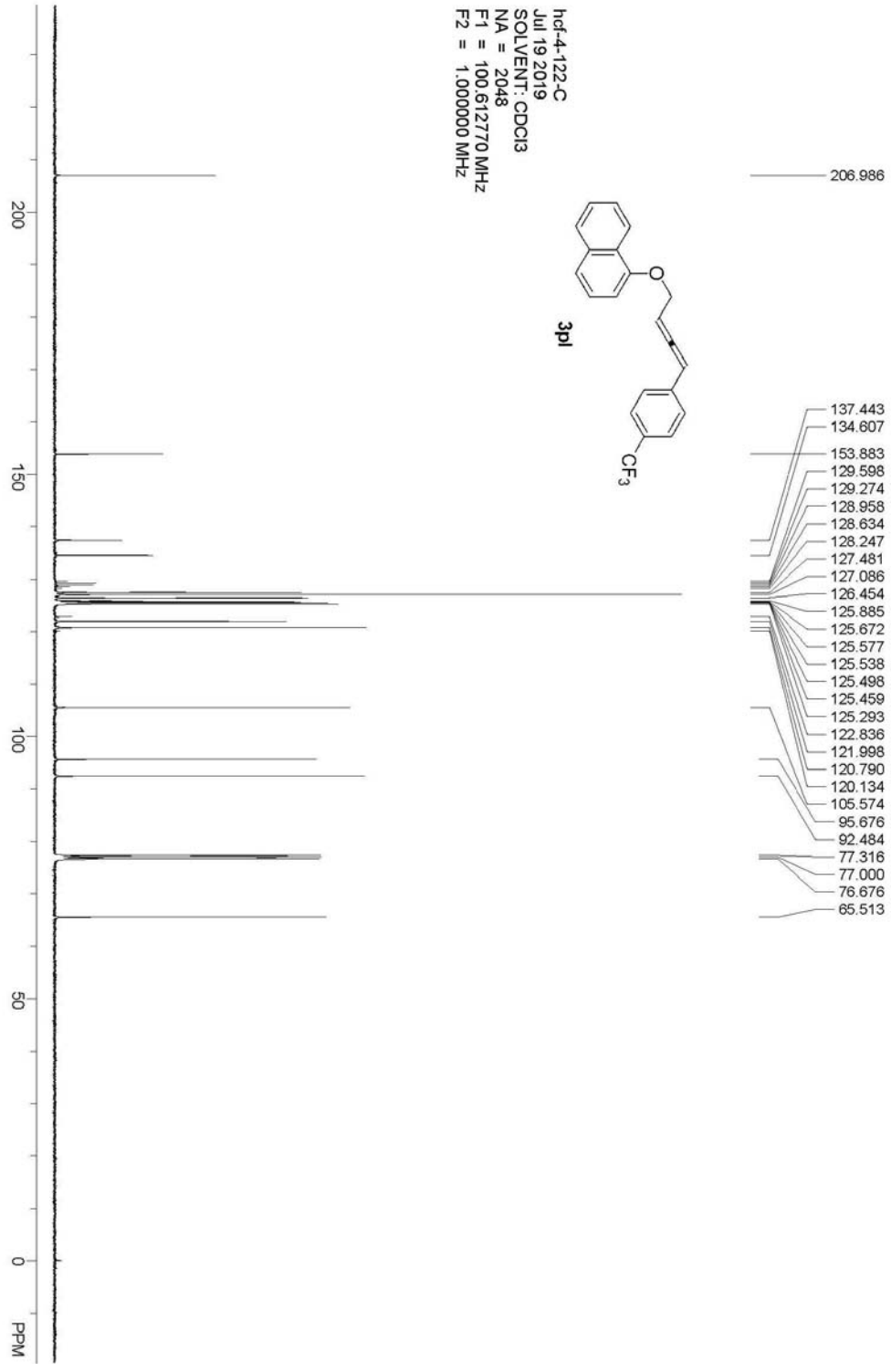

Ilcan-01-055-H
Sat Jul 13 13:37:01 2019
NA = 16
Solvent = CDCl3
F1 = 400.101990 MHz
F2 = 1.000000 MHz
2.02
2.15
2.24
3.14
1.00
0.89
2.34
10
8
6
4
2
0
PPM
3bj
Br
7.401
7.394
7.390
7.378
7.373
7.367
7.286
7.268
7.265
7.246
7.100
7.094
7.089
7.077
7.073
7.066
6.976
6.973
6.957
6.955
6.939
6.937
6.931
6.929
6.911
6.909
6.231
6.225
6.219
6.216
6.209
6.203
5.815
5.799
5.782
5.766
4.674
4.668
4.657
4.651
-0.000

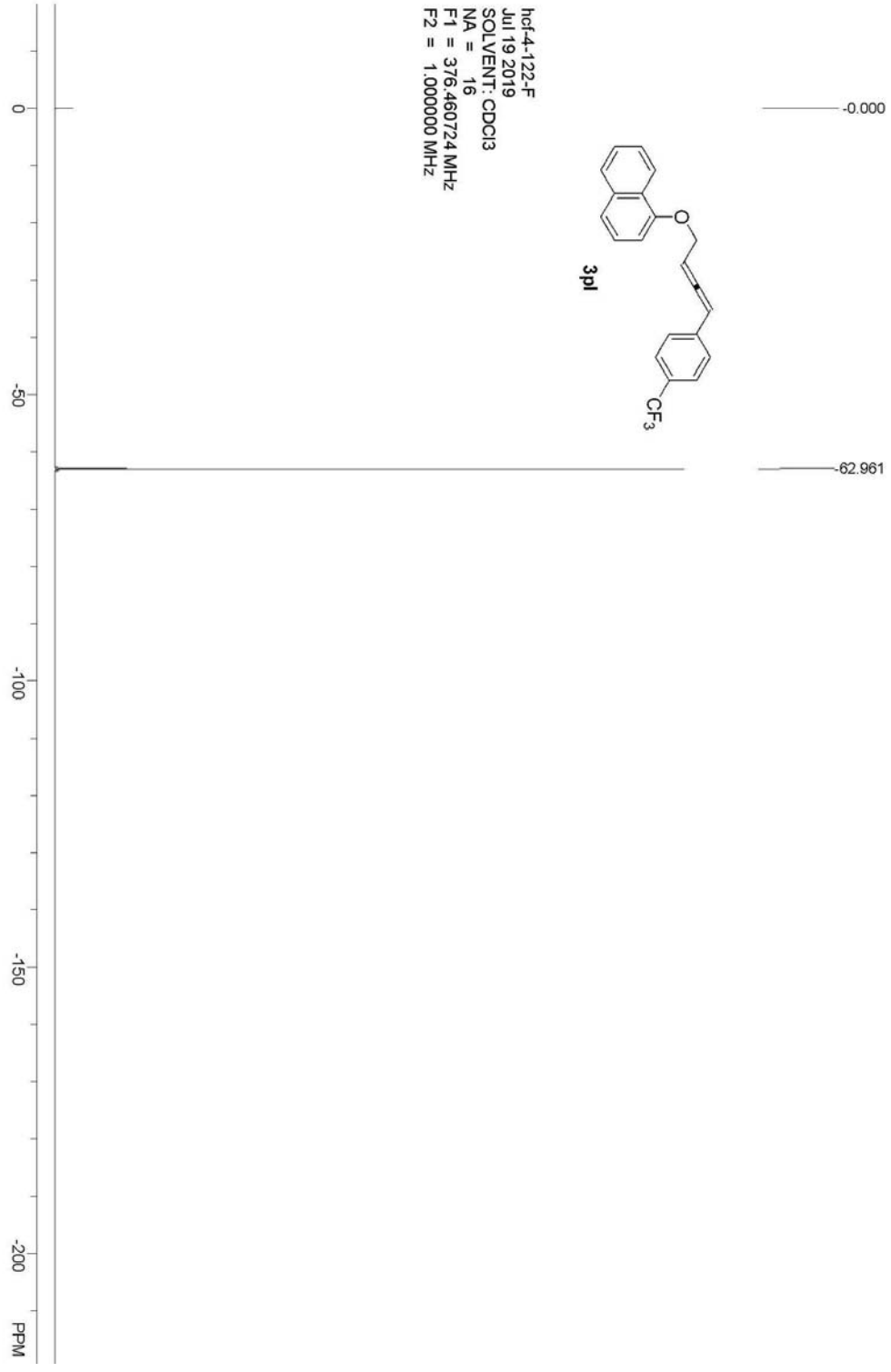

lican-01-055-C
Sat Jul 13 14:18:21 2019
NA = 1024
Solvent = CDCl3
F1 = 100.616295 MHz
F2 = 1.000000 MHz
3bj
Br
206.251
158.057
132.437
131.663
129.469
128.469
121.107
120.916
115.071
95.480
92.301
77.314
77.000
76.682
65.391
200
150
100
50
0
PPM

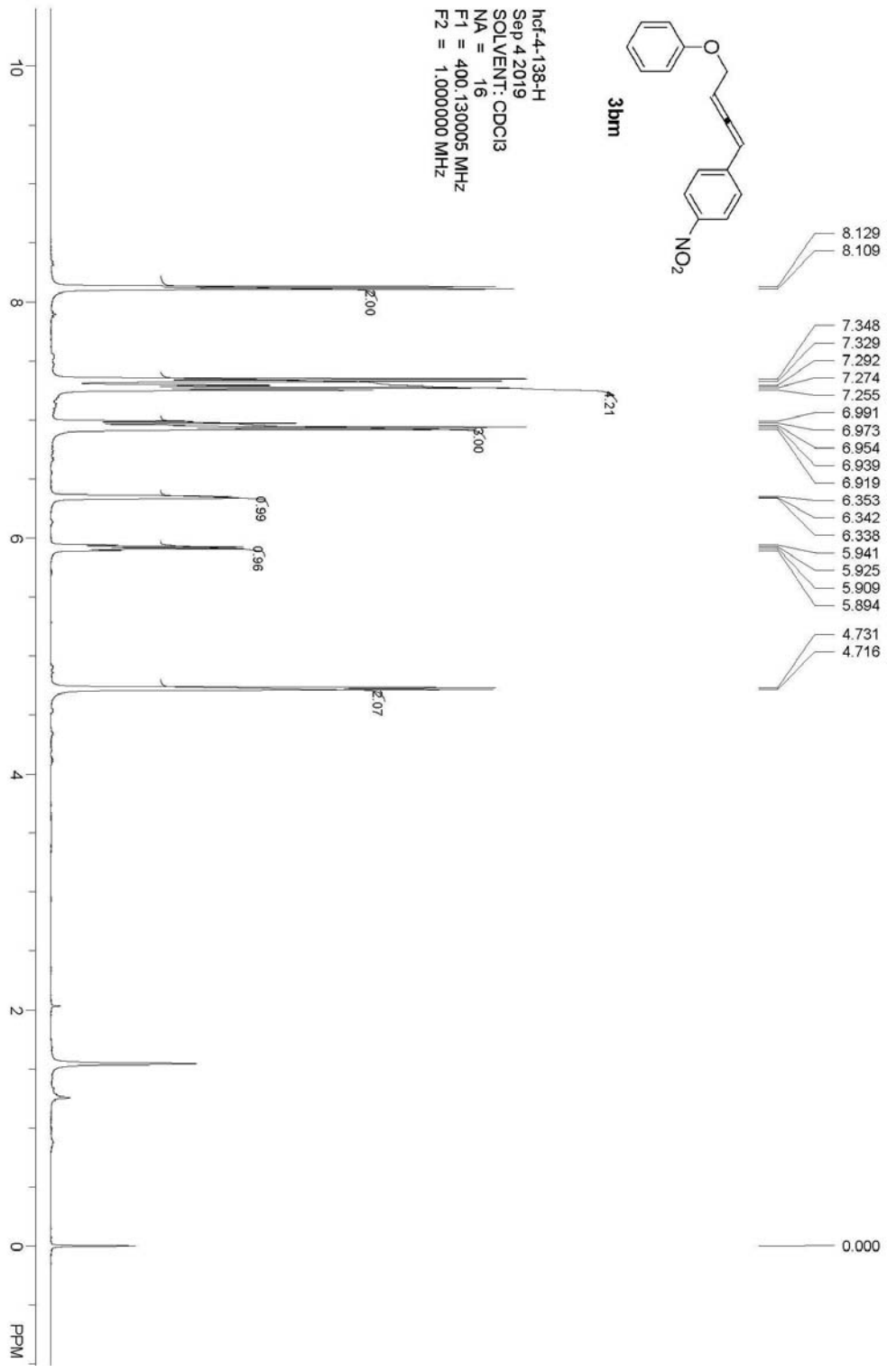

wpl-5-107H
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 8
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130035 MHz
F2 = 1.000000 MHz
0.97
1.03
1.99
3.07
1.06
2.02
1.02
1.00
0.98
2.00
3pk
8.274
8.256
8.250
7.776
7.771
7.759
7.753
7.568
7.547
7.476
7.472
7.459
7.455
7.447
7.441
7.435
7.423
7.410
7.402
7.319
7.300
7.279
7.171
6.963
6.942
6.792
6.773
6.221
6.215
6.208
6.206
6.199
6.193
5.898
5.882
5.866
5.850
4.808
4.802
4.792
4.786
0.000
10
8
6
4
2
0
PPM

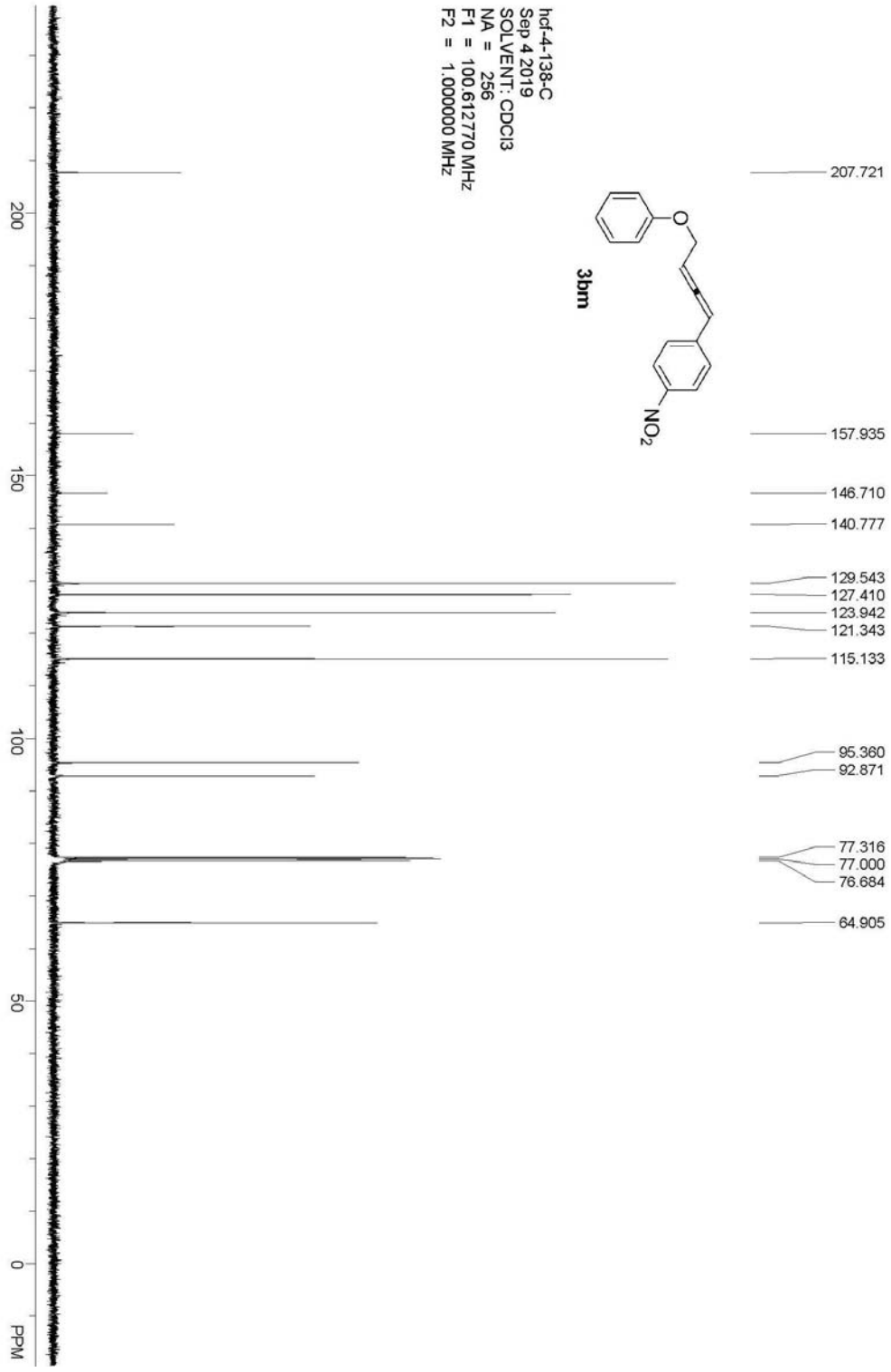

wpl-5-107C
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 256
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3pk
206.339
153.851
137.617
134.520
133.082
128.705
127.418
126.391
125.814
125.672
125.229
121.990
120.655
105.519
95.739
92.334
77.324
77.000
76.684
65.616
200
150
100
50
0
PPM

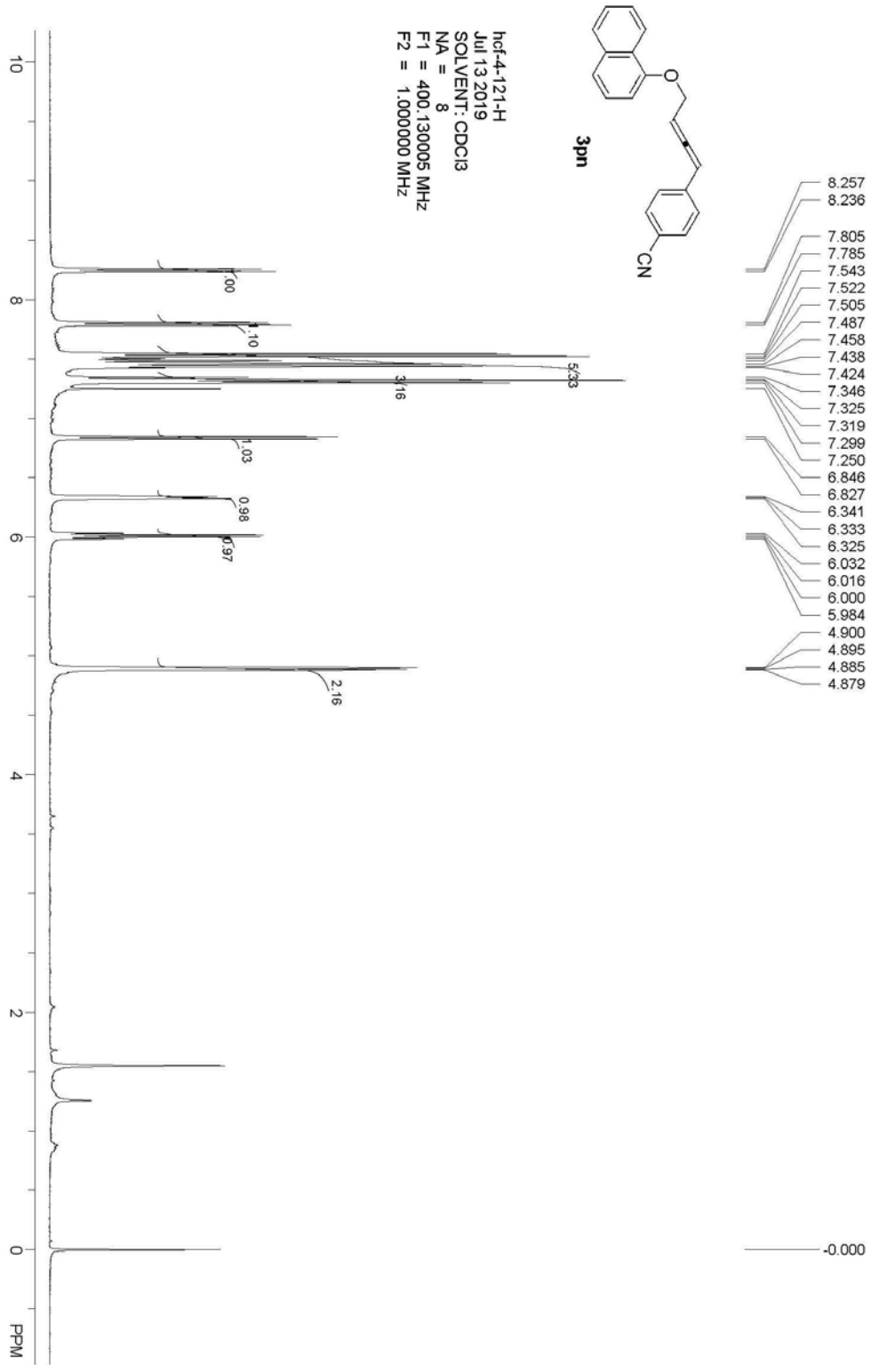

hcf-4-122-H
Jul 19 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130035 MHz
F2 = 1.000000 MHz
3pl
CF3
8.277
8.257
7.783
7.765
7.510
7.490
7.469
7.452
7.437
7.417
7.329
7.314
7.294
7.200
6.825
6.806
6.338
6.332
6.324
6.316
6.310
5.979
5.963
5.947
5.931
4.861
4.855
4.845
4.839
0.000
1.00
1.06
5.24
3.27
1.05
1.02
1.03
2.09
10
8
6
4
2
0
PPM

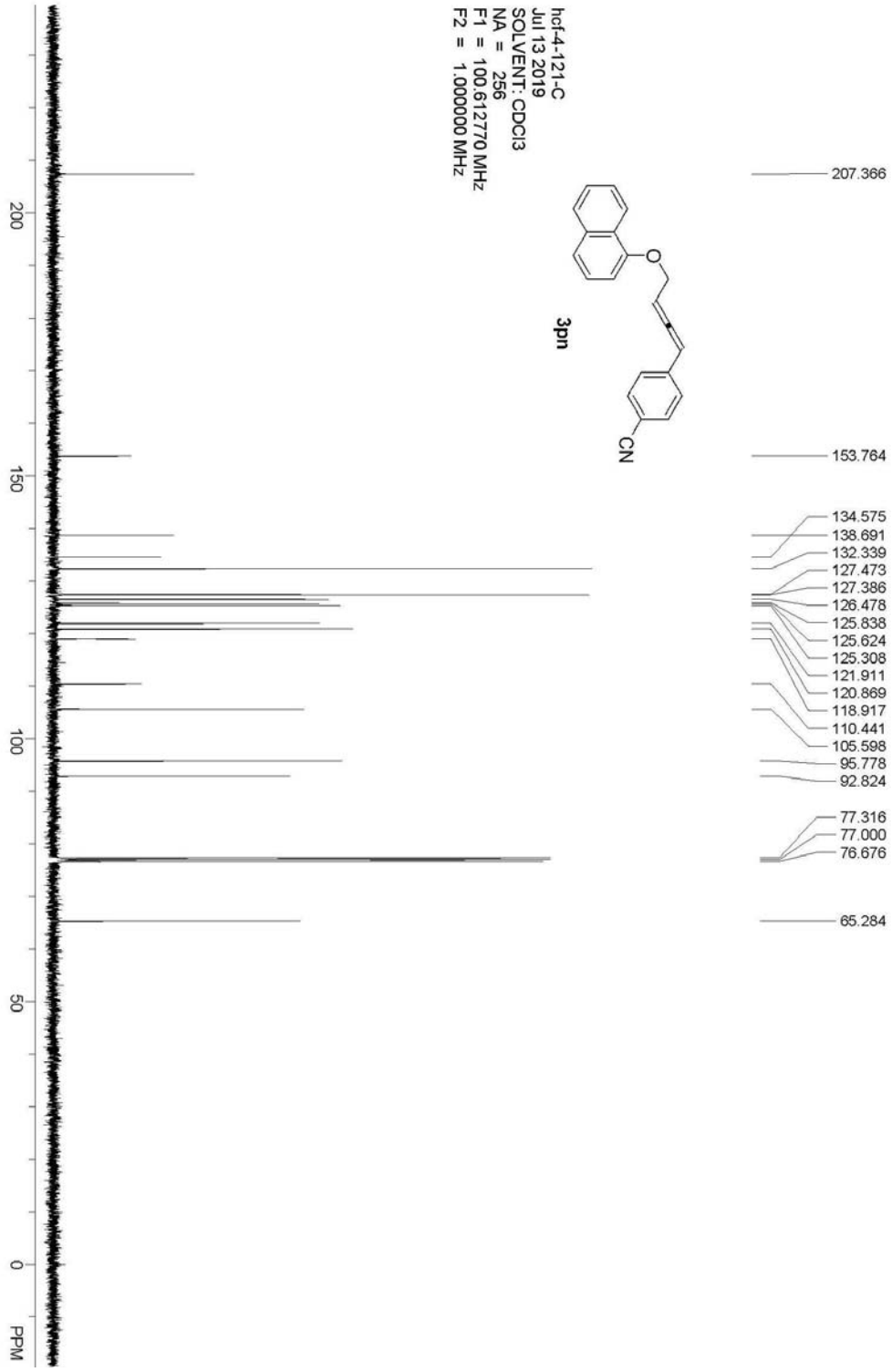

hcf-4-122-C
Jul 19 2019
SOLVENT: CDCl3
NA = 2048
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3pl
CF3
206.986
137.443
134.607
153.883
129.598
129.274
128.958
128.634
128.247
127.481
127.086
126.454
125.885
125.672
125.577
125.538
125.498
125.459
125.293
122.836
121.998
120.790
120.134
105.574
95.676
92.484
77.316
77.000
76.676
65.513
200
150
100
50
0
PPM

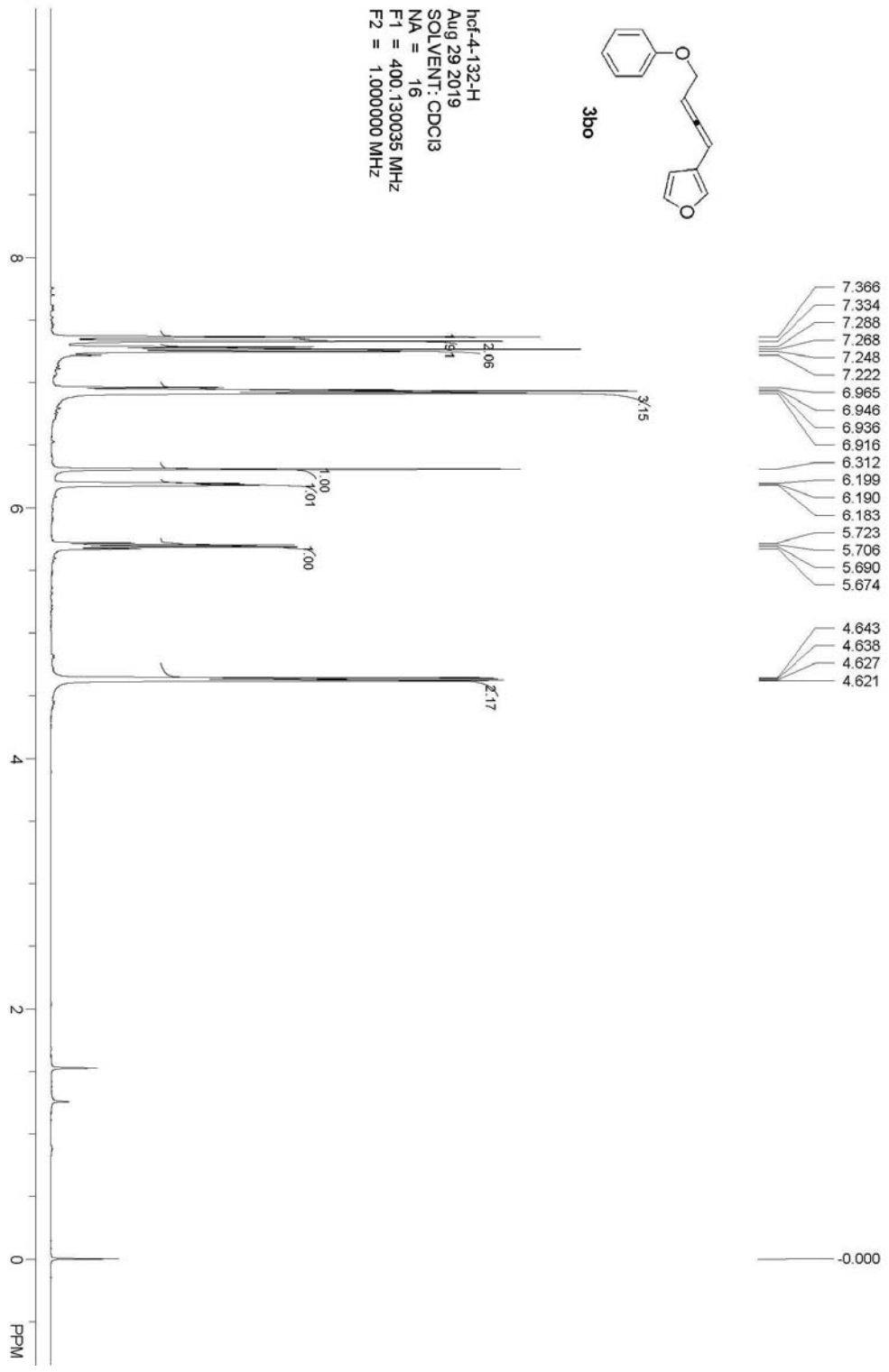

hcf-4-122-F
Jul 19 2019
SOLVENT: CDCl3
NA = 16
F1 = 376.460724 MHz
F2 = 1.000000 MHz
3pl
CF3
-0.000
-62.961
0
-50
-100
-150
-200
PPM

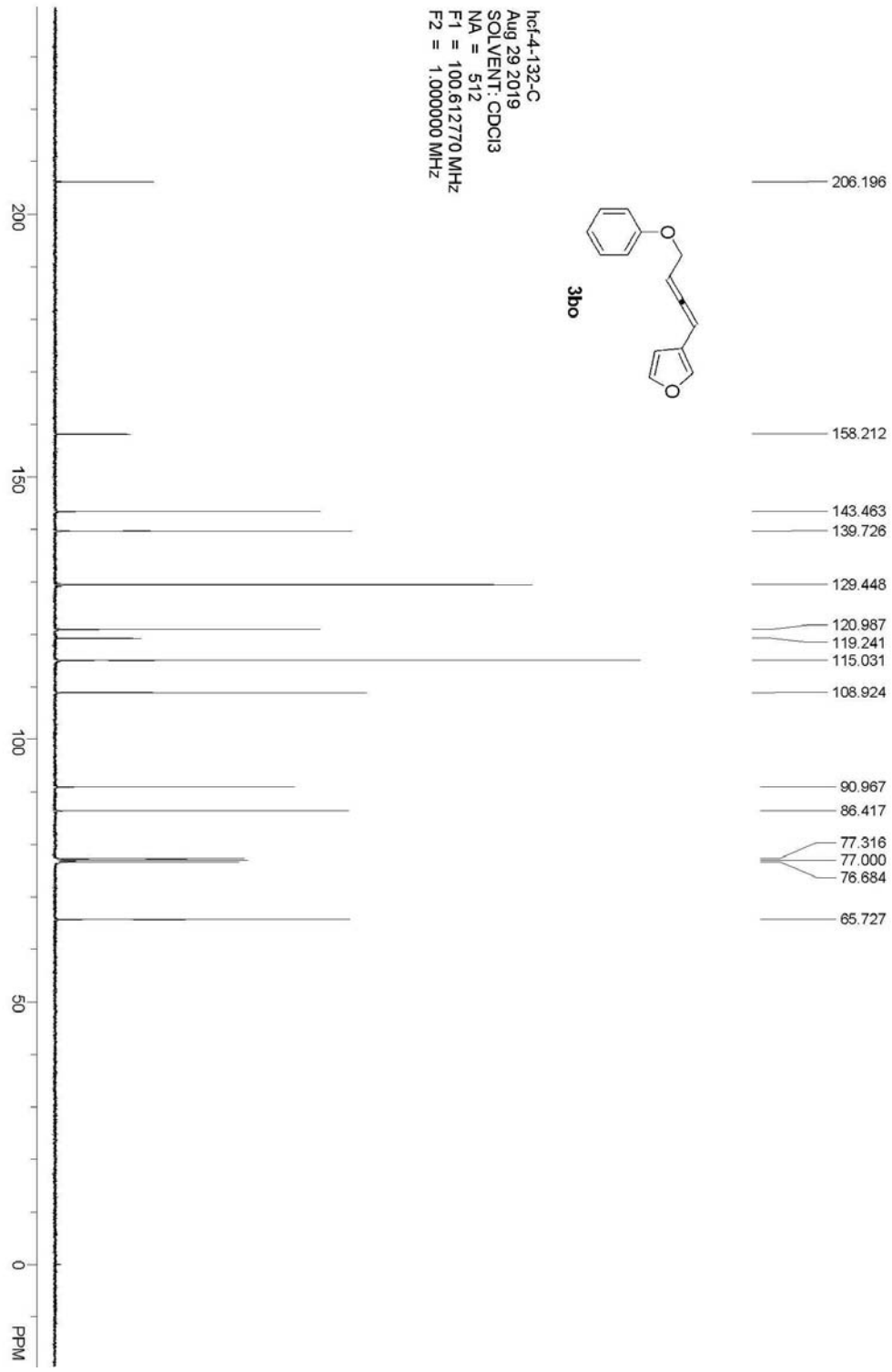

hcf-4-138-H
Sep 4 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3bm
NO2
8.129
8.109
7.348
7.329
7.292
7.274
7.255
6.991
6.973
6.954
6.939
6.919
6.353
6.342
6.338
5.941
5.925
5.909
5.894
4.731
4.716
0.000
2.00
4.21
2.00
0.99
0.96
2.07
10
8
6
4
2
0
PPM

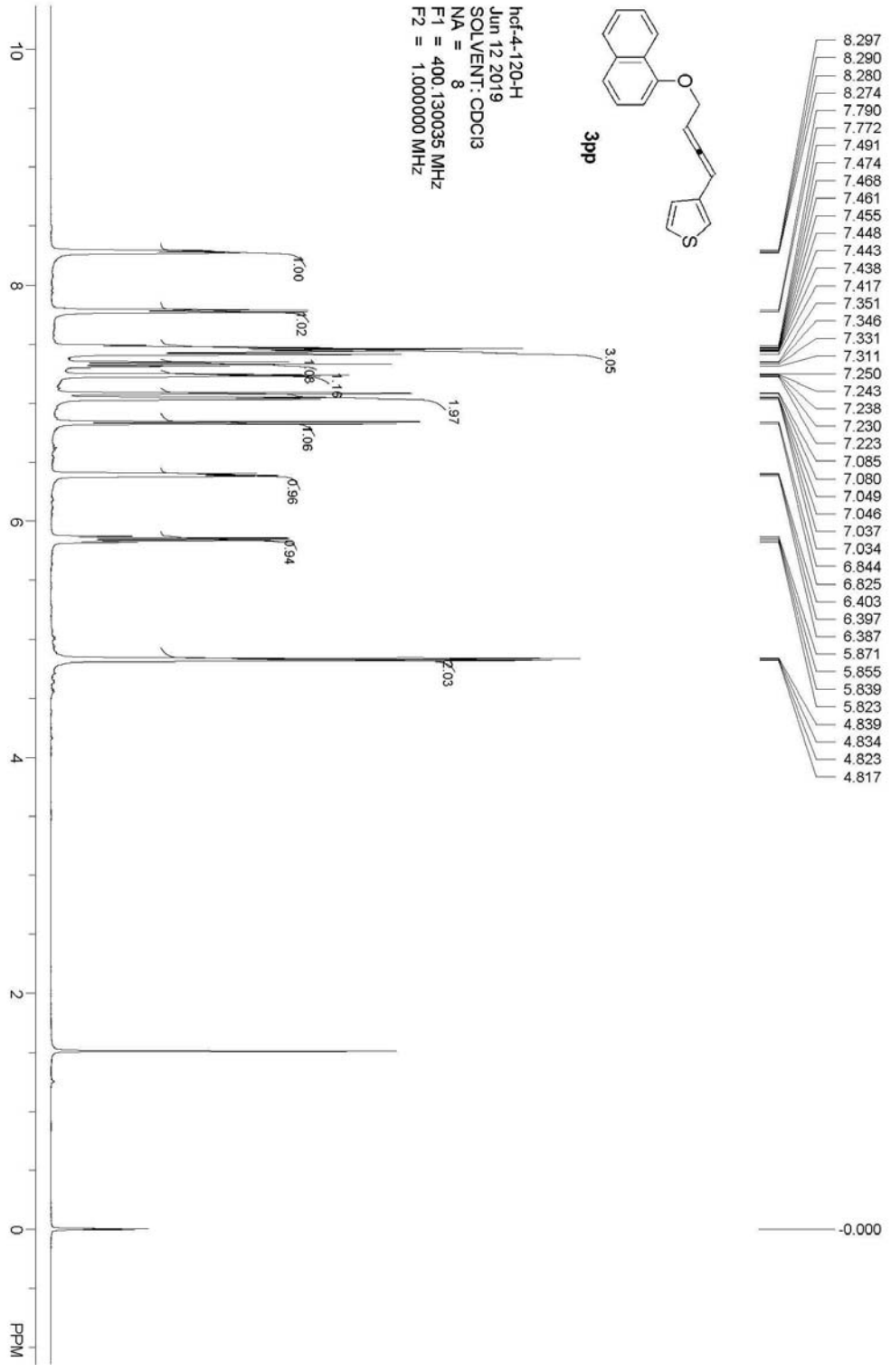

hcf-4-138-C
Sep 4 2019
SOLVENT: CDCl3
NA = 256
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3bm
NO2
207.721
157.935
146.710
140.777
129.543
127.410
123.942
121.343
115.133
95.360
92.871
77.316
77.000
76.684
64.905
200
150
100
50
0
PPM

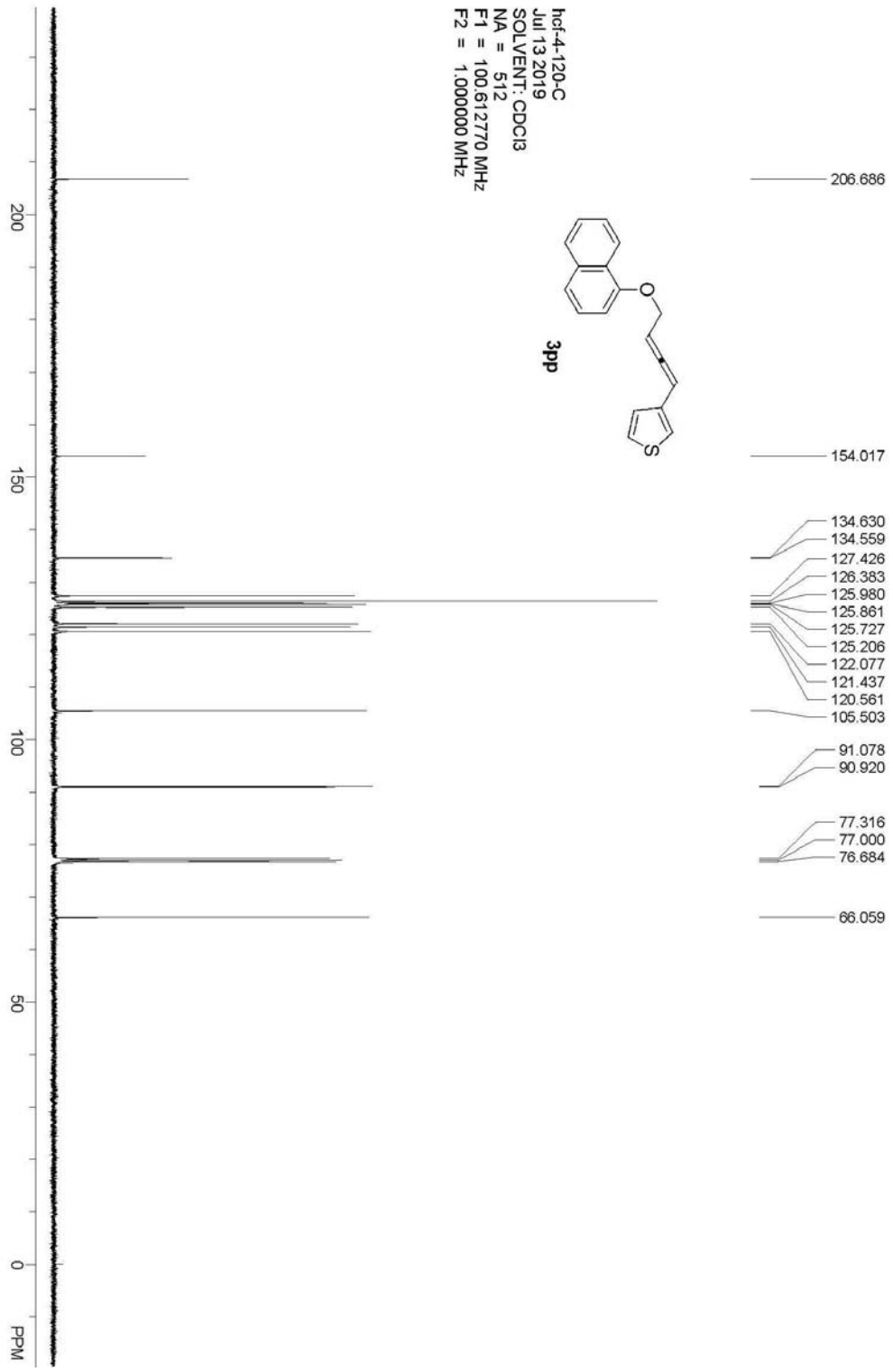

hcf-4-121-H
Jul 13 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
3pn
CN
8.257
8.236
7.805
7.785
7.543
7.522
7.505
7.487
7.458
7.438
7.424
7.346
7.325
7.319
7.299
7.250
6.846
6.827
6.341
6.333
6.325
6.032
6.016
6.000
5.984
4.900
4.895
4.885
4.879
-0.000
1.00
1.10
5.33
3.16
1.03
0.98
0.97
2.16
PPM

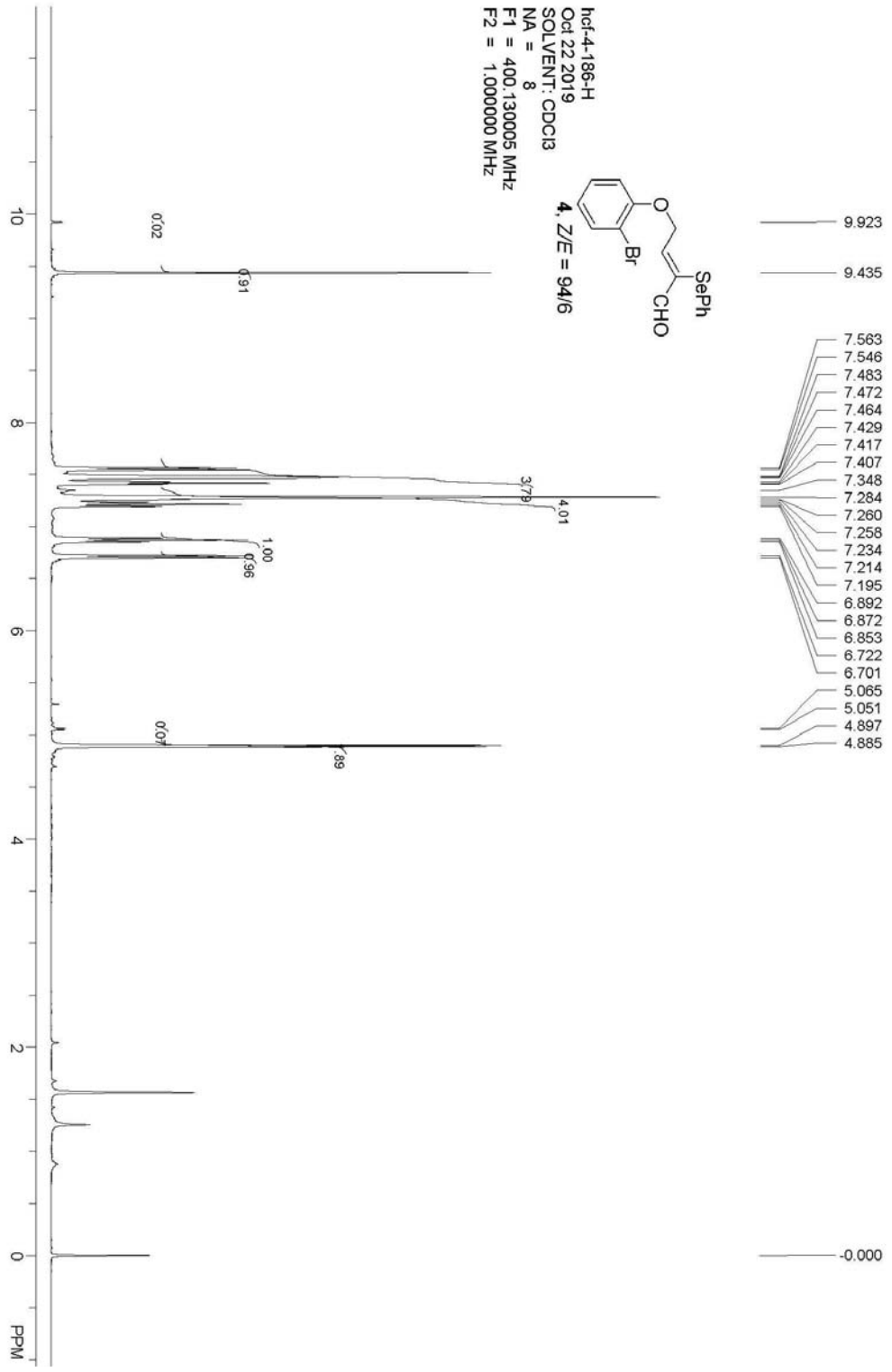

hcf-4-121-C
Jul 13 2019
SOLVENT: CDCl3
NA = 256
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3pn
O
CN
207.366
153.764
134.575
138.691
132.339
127.473
127.386
126.478
125.838
125.624
125.308
121.911
120.869
118.917
110.441
105.598
95.778
92.824
77.316
77.000
76.676
65.284
200
150
100
50
0
PPM

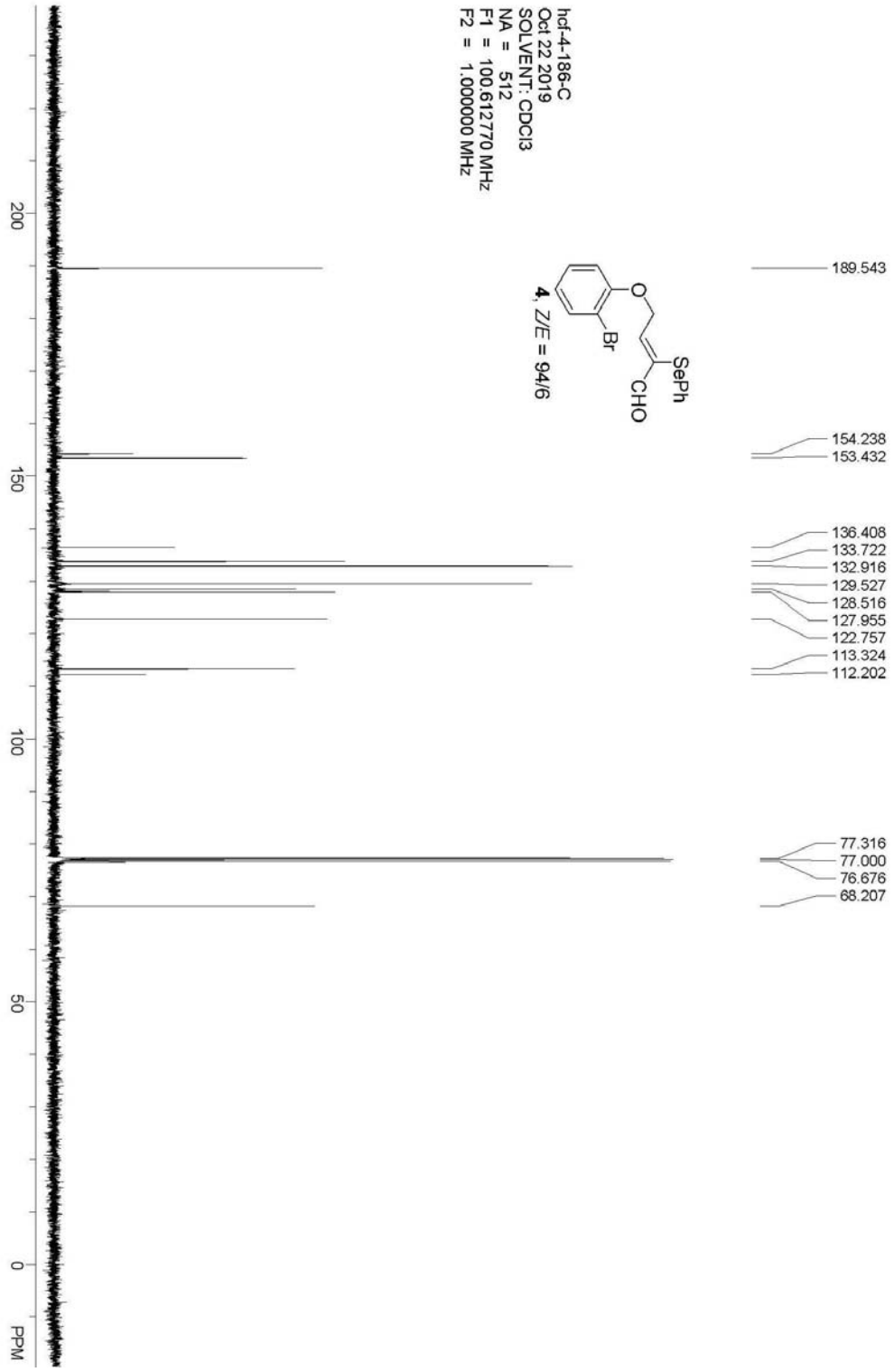

hcf-4-132-H
Aug 29 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130035 MHz
F2 = 1.000000 MHz
3bo
1.91
2.06
3.15
1.00
1.01
1.00
2.17
7.366
7.334
7.288
7.268
7.248
7.222
6.965
6.946
6.936
6.916
6.312
6.199
6.190
6.183
5.723
5.706
5.690
5.674
4.643
4.638
4.627
4.621
-0.000
8
6
4
2
0
PPM

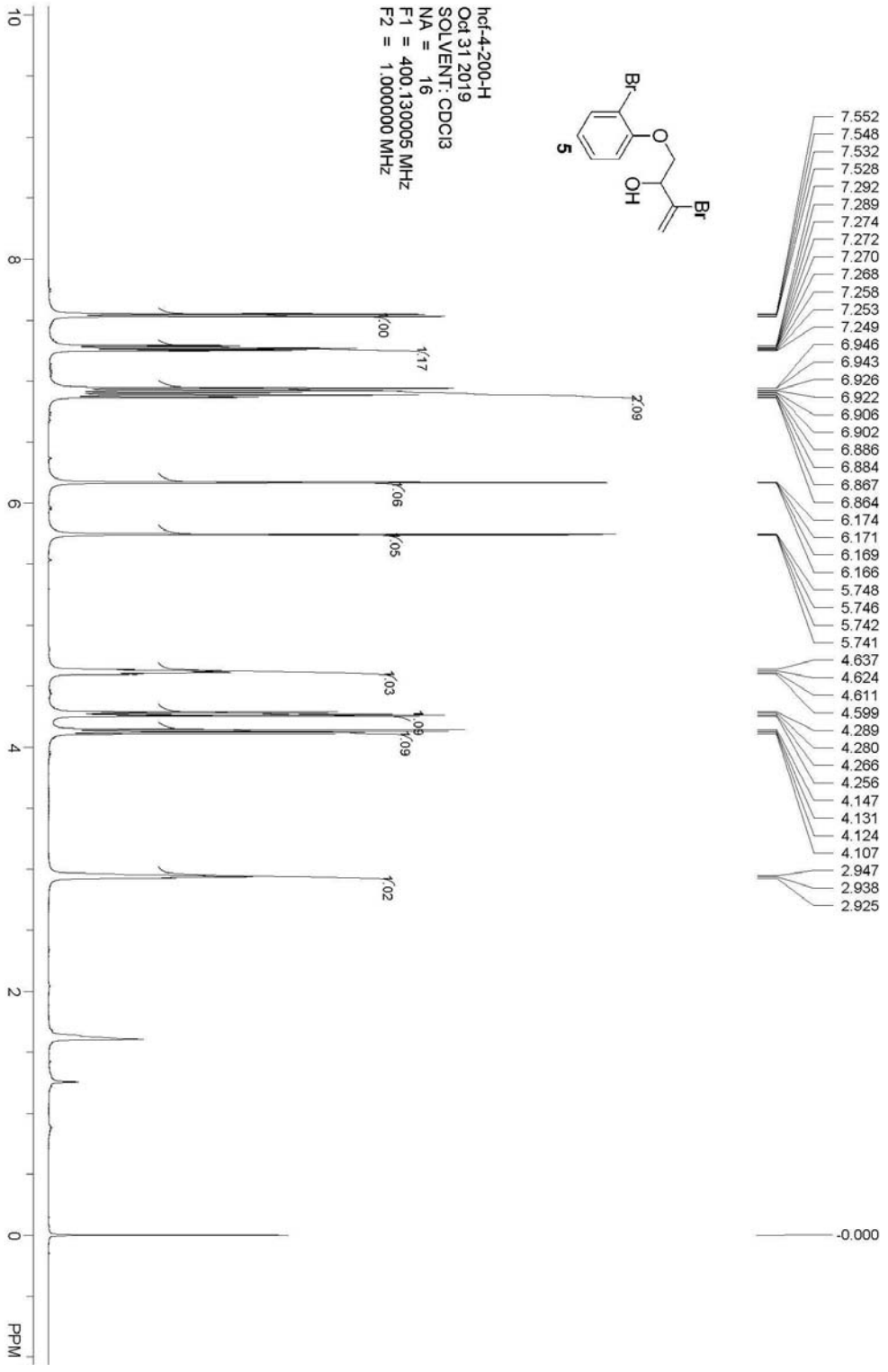

hcf-4-132-C
Aug 29 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3bo
206.196
158.212
143.463
139.726
129.448
120.987
119.241
115.031
108.924
90.967
86.417
77.316
77.000
76.684
65.727
200
150
100
50
0
PPM

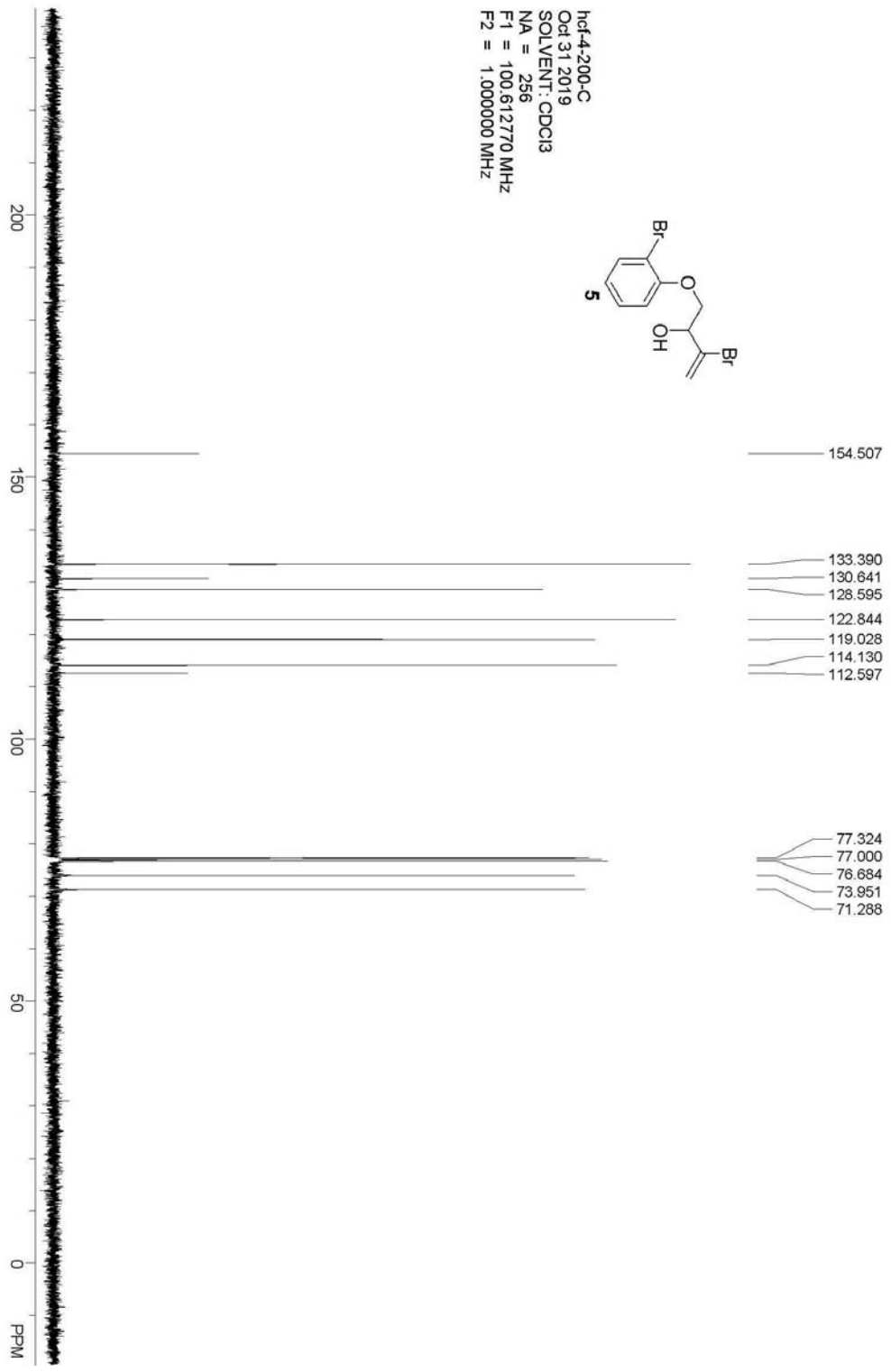

hcf-4-120-H
Jun 12 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130035 MHz
F2 = 1.000000 MHz
3pp
8.297
8.290
8.280
8.274
7.790
7.772
7.491
7.474
7.468
7.461
7.455
7.448
7.443
7.438
7.417
7.351
7.346
7.331
7.311
7.250
7.243
7.238
7.230
7.223
7.085
7.080
7.049
7.046
7.037
7.034
6.844
6.825
6.403
6.397
6.387
5.871
5.855
5.839
5.823
4.839
4.834
4.823
4.817
-0.000
1.00
1.02
3.05
1.08
1.16
1.97
1.06
0.96
0.94
2.03
10
8
6
4
2
0
PPM

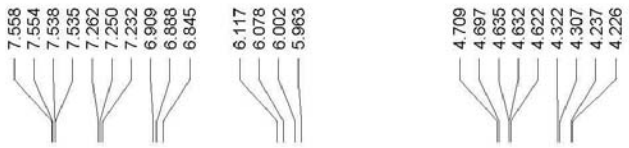

hcf-4-120-C
Jul 13 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
3pp
206.686
154.017
134.630
134.559
127.426
126.383
125.980
125.861
125.727
125.206
122.077
121.437
120.561
105.503
91.078
90.920
77.316
77.000
76.684
66.059
200
150
100
50
0
PPM

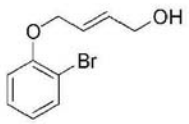

hcf-4-186-H
Oct 22 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
4, Z/E = 94/6
Br
O
SePh
CHO
9.923
9.435
7.563
7.546
7.483
7.472
7.464
7.429
7.417
7.407
7.348
7.284
7.260
7.258
7.234
7.214
7.195
6.892
6.872
6.853
6.722
6.701
5.065
5.051
4.897
4.885
-0.000
0.02
0.91
3.79
4.01
1.00
0.96
0.07
1.89
10
8
6
4
2
0
PPM


hcf-4-186-C
Oct 22 2019
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
4, Z/E = 94/6
Br
O
SePh
CHO
189.543
154.238
153.432
136.408
133.722
132.916
129.527
128.516
127.955
122.757
113.324
112.202
77.316
77.000
76.676
68.207
200
150
100
50
0
PPM

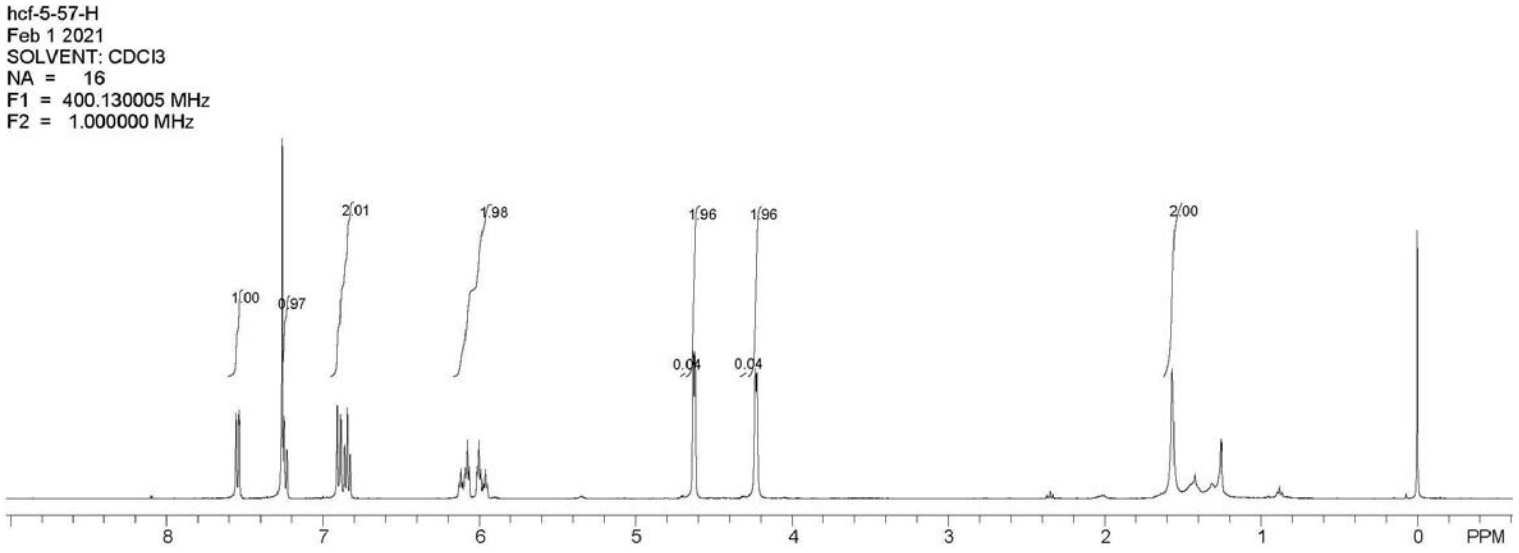

hcf-4-200-H
Oct 31 2019
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
5
Br
O
OH
Br
7.552
7.548
7.532
7.528
7.292
7.289
7.274
7.272
7.270
7.268
7.258
7.253
7.249
6.946
6.943
6.926
6.922
6.906
6.902
6.886
6.884
6.867
6.864
6.174
6.171
6.169
6.166
5.748
5.746
5.742
5.741
4.637
4.624
4.611
4.599
4.289
4.280
4.266
4.256
4.147
4.131
4.124
4.107
2.947
2.938
2.925
-0.000
1.00
1.17
2.09
1.06
1.05
1.03
1.08
1.09
1.02
10
8
6
4
2
0
PPM

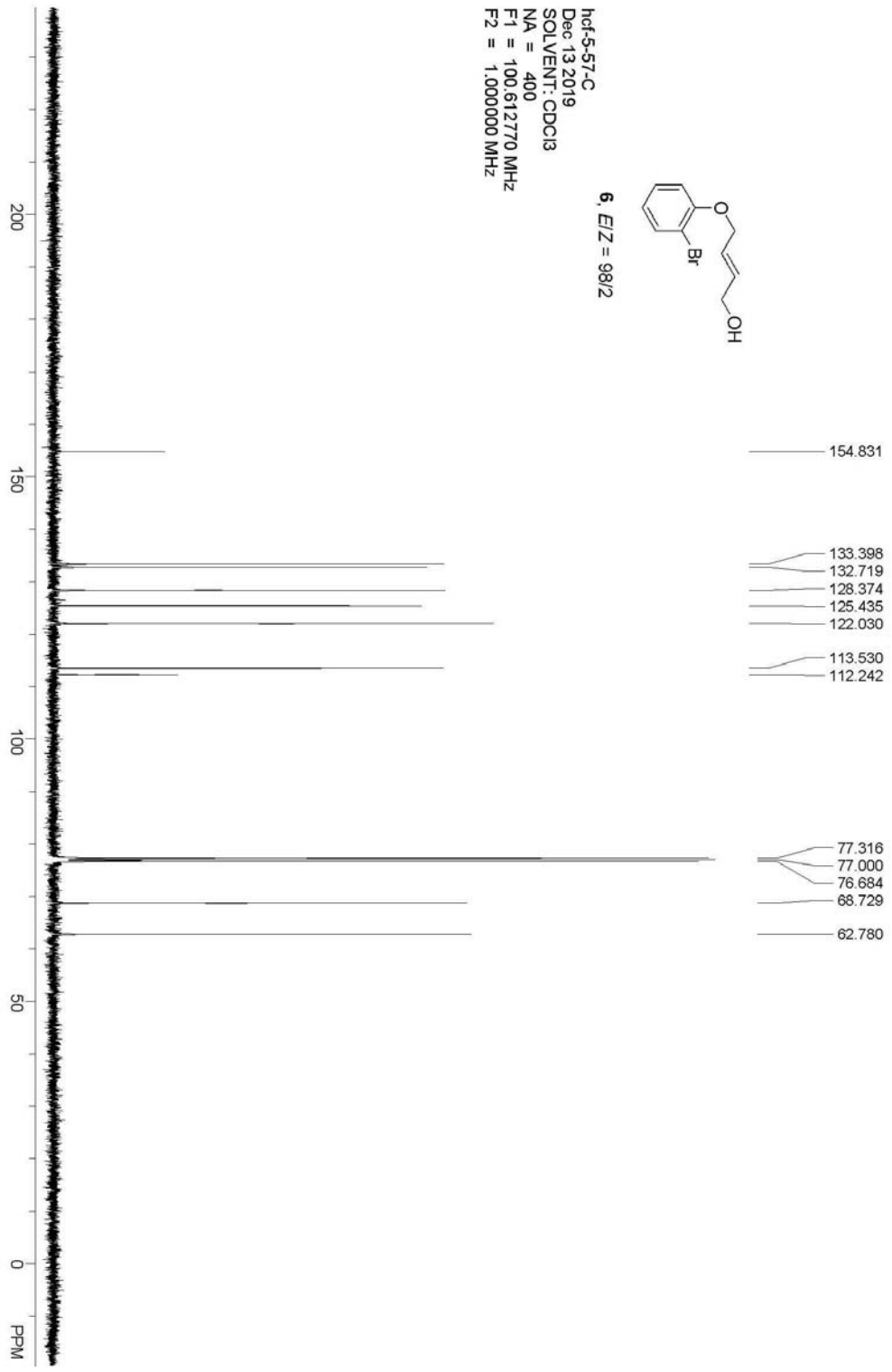

hcf-4-200-C
Oct 31 2019
SOLVENT: CDCl3
NA = 256
F1 = 100.612770 MHz
F2 = 1.000000 MHz
Br
O
OH
Br
5
154.507
133.390
130.641
128.595
122.844
119.028
114.130
112.597
77.324
77.000
76.684
73.951
71.288
200
150
100
50
0
PPM

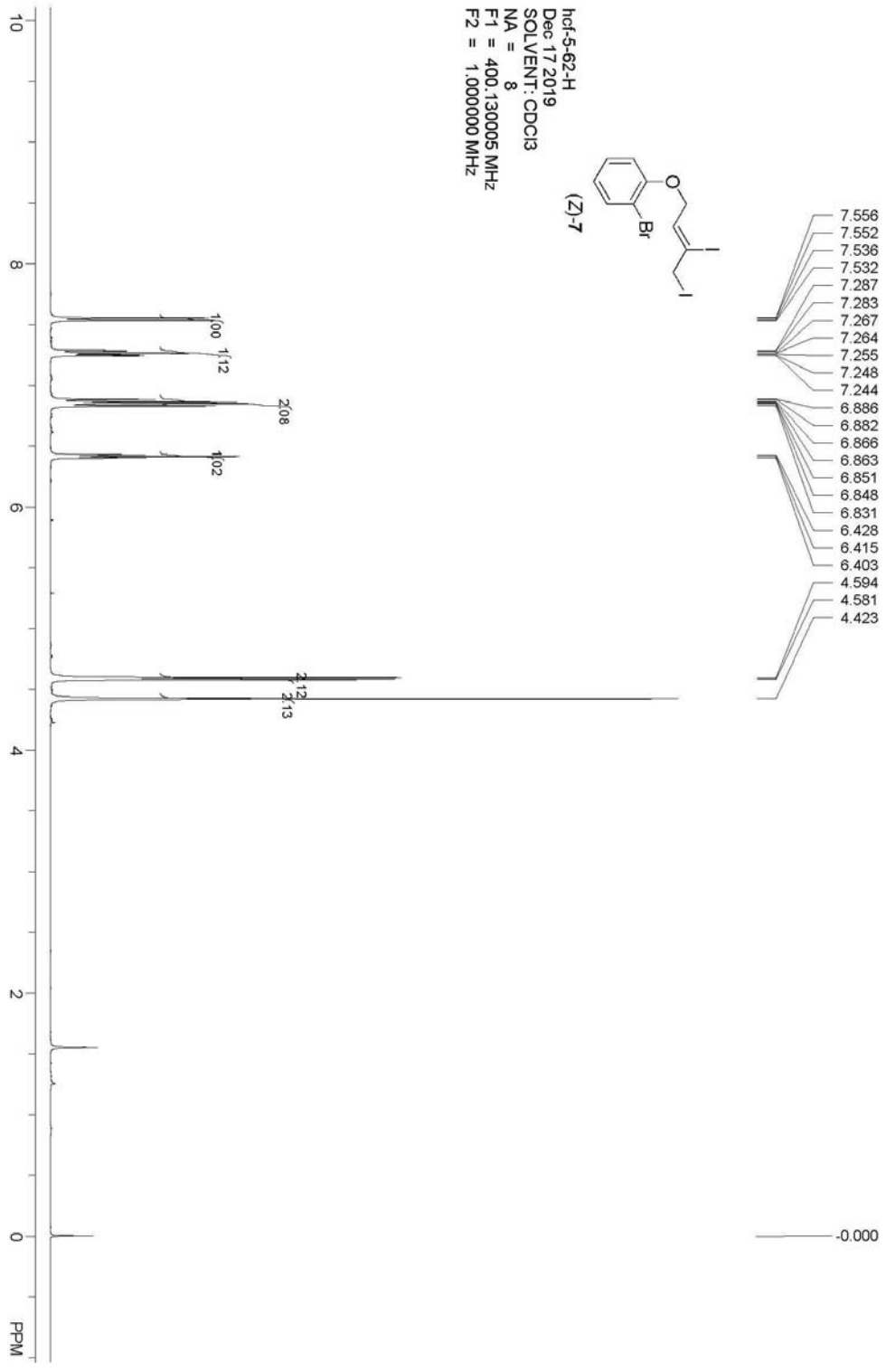

7.558
7.554
7.538
7.535
7.262
7.250
7.232
6.909
6.888
6.845
6.117
6.078
6.002
5.963
4.709
4.697
4.635
4.632
4.622
4.322
4.307
4.237
4.226
1.568
0.000

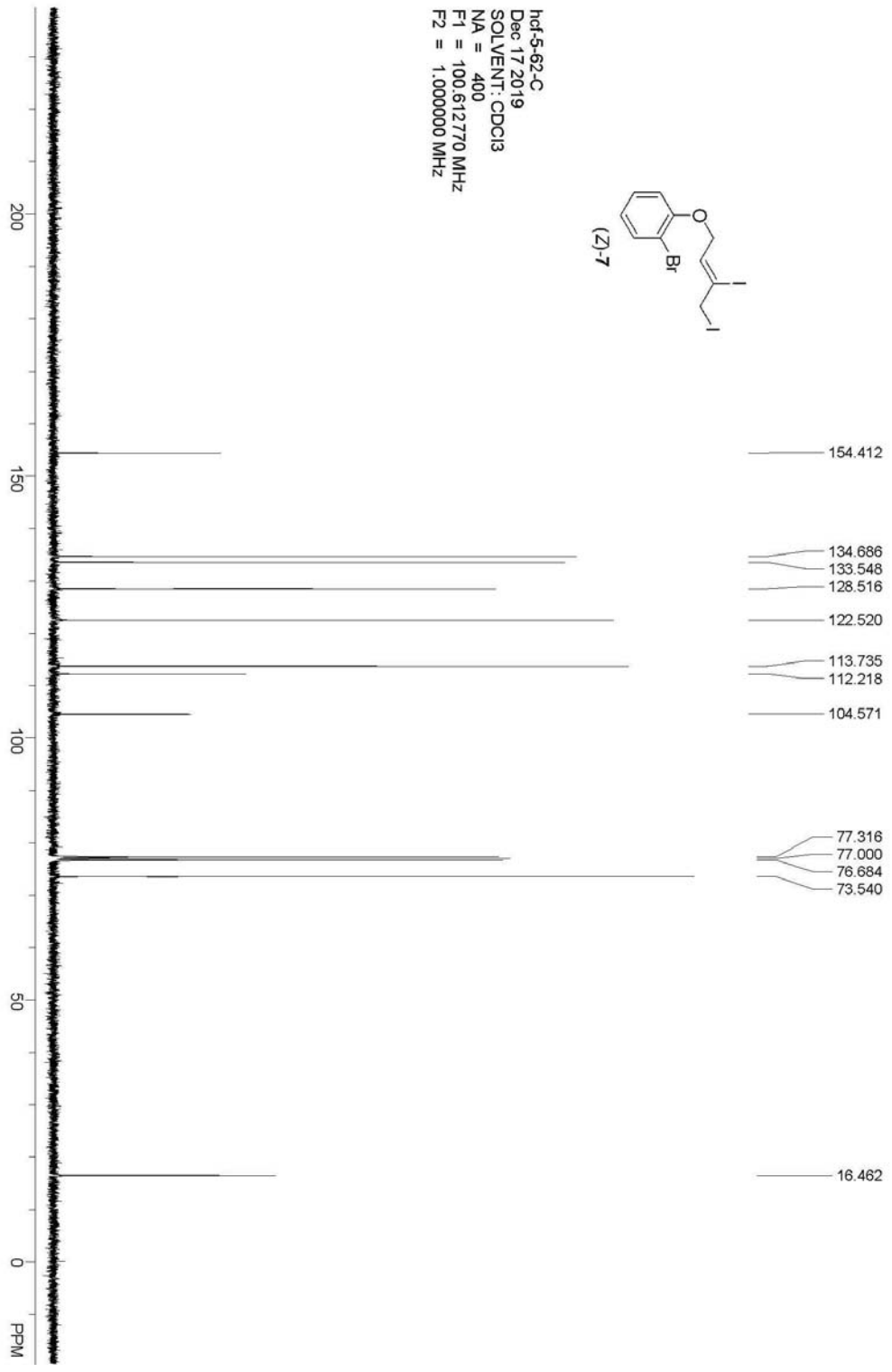

O
OH
Br

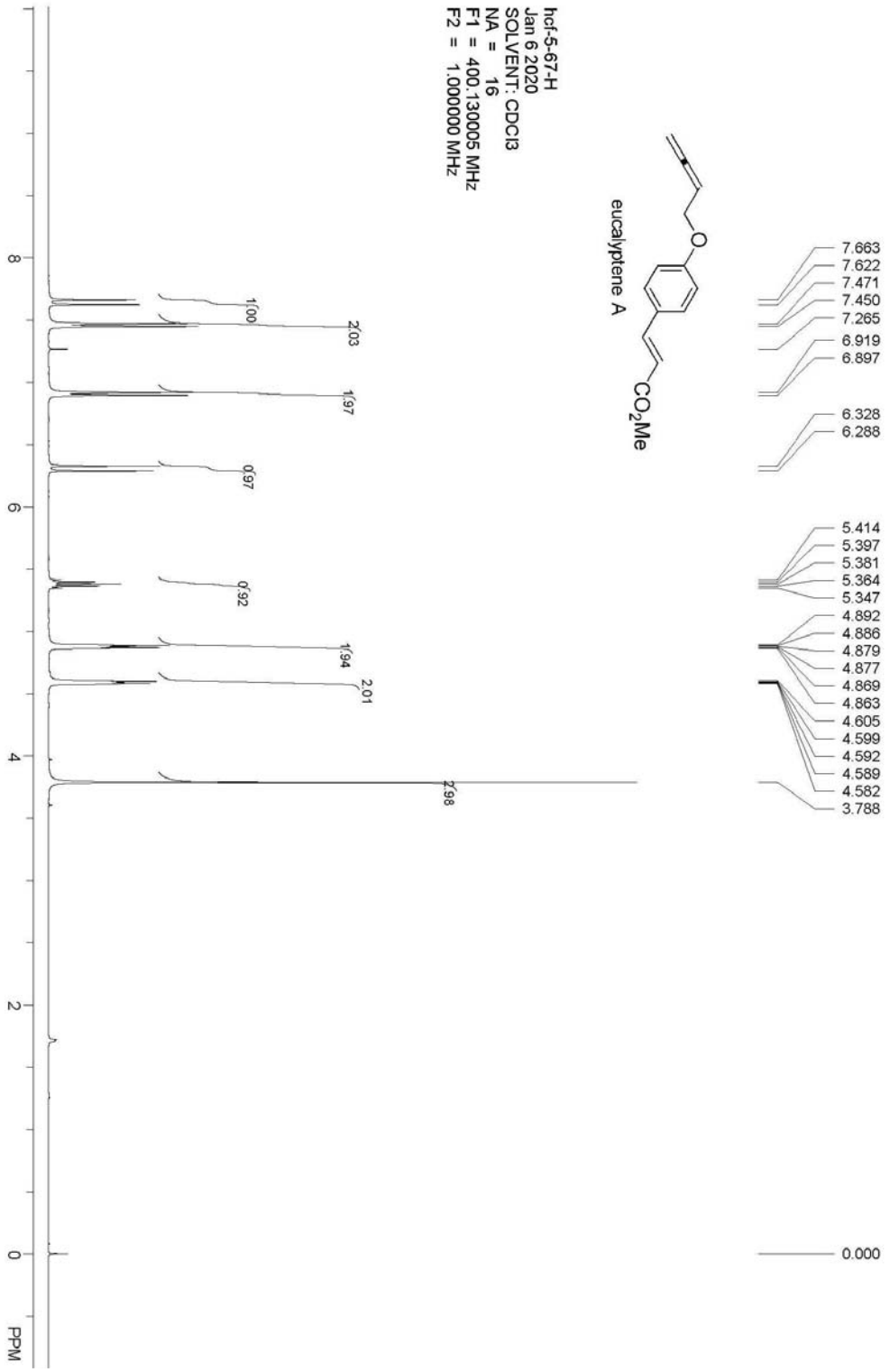
**6**, *E*/*Z* = 98/2

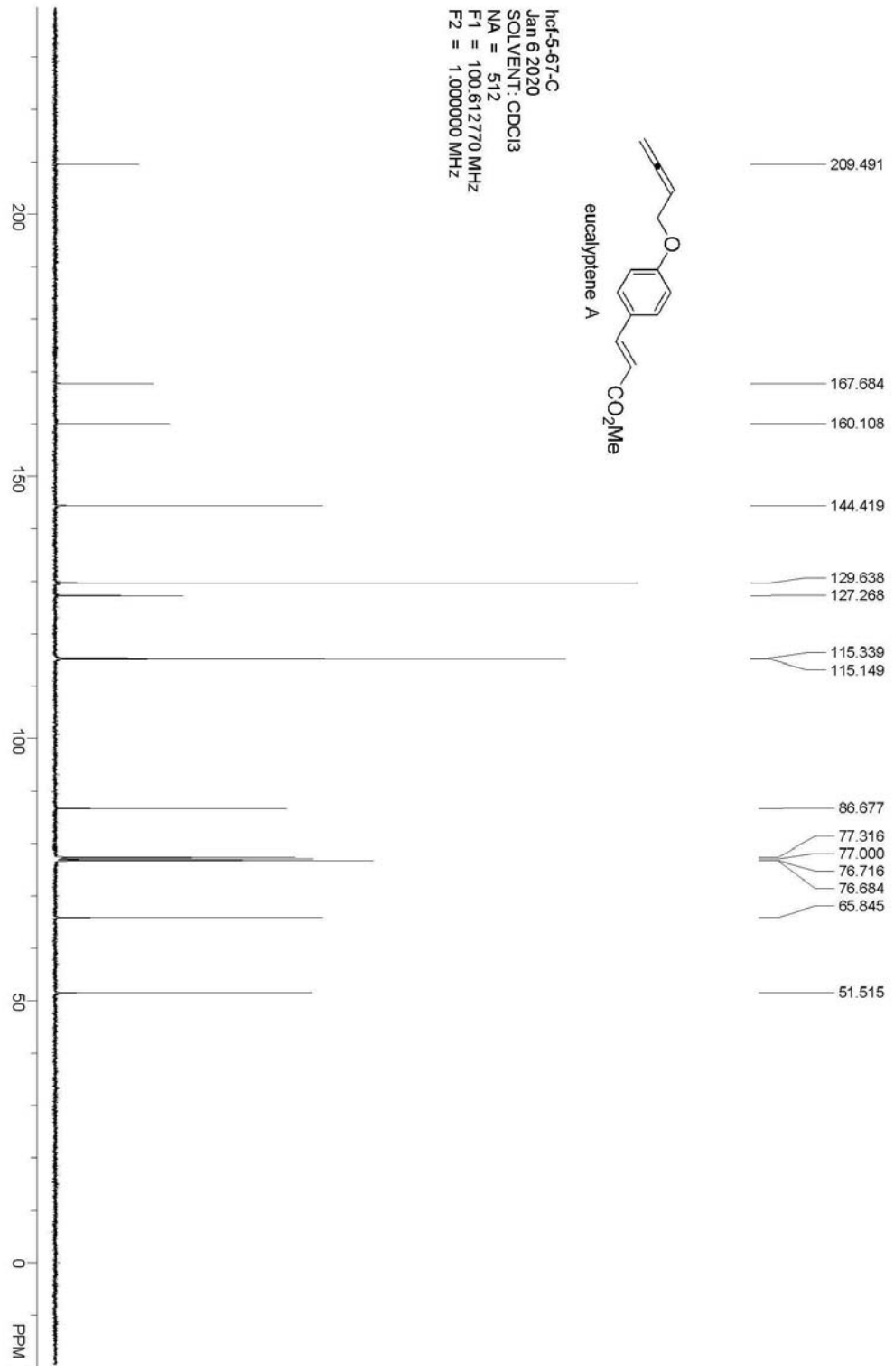

hcf-5-57-H
Feb 1 2021
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
1.00
0.97
2.01
1.98
1.96
1.96
2.00
0.04
0.04
8
7
6
5
4
3
2
1
0
PPM

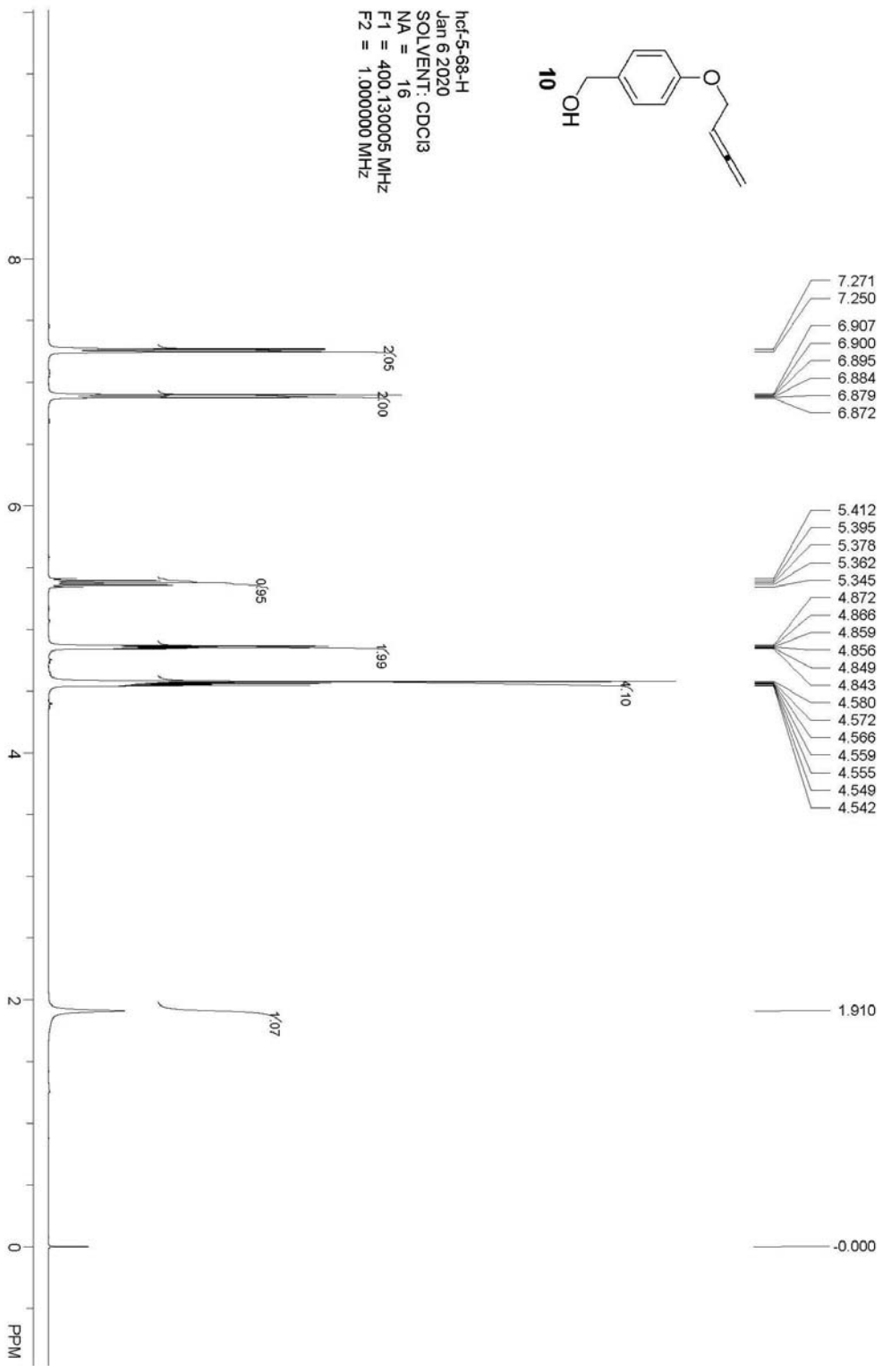

hcf-5-57-C
Dec 13 2019
SOLVENT: CDCl3
NA = 400
F1 = 100.612770 MHz
F2 = 1.000000 MHz
6, E/Z = 98/2
Br
O
OH
154.831
133.398
132.719
128.374
125.435
122.030
113.530
112.242
77.316
77.000
76.684
68.729
62.780
200
150
100
50
0
PPM

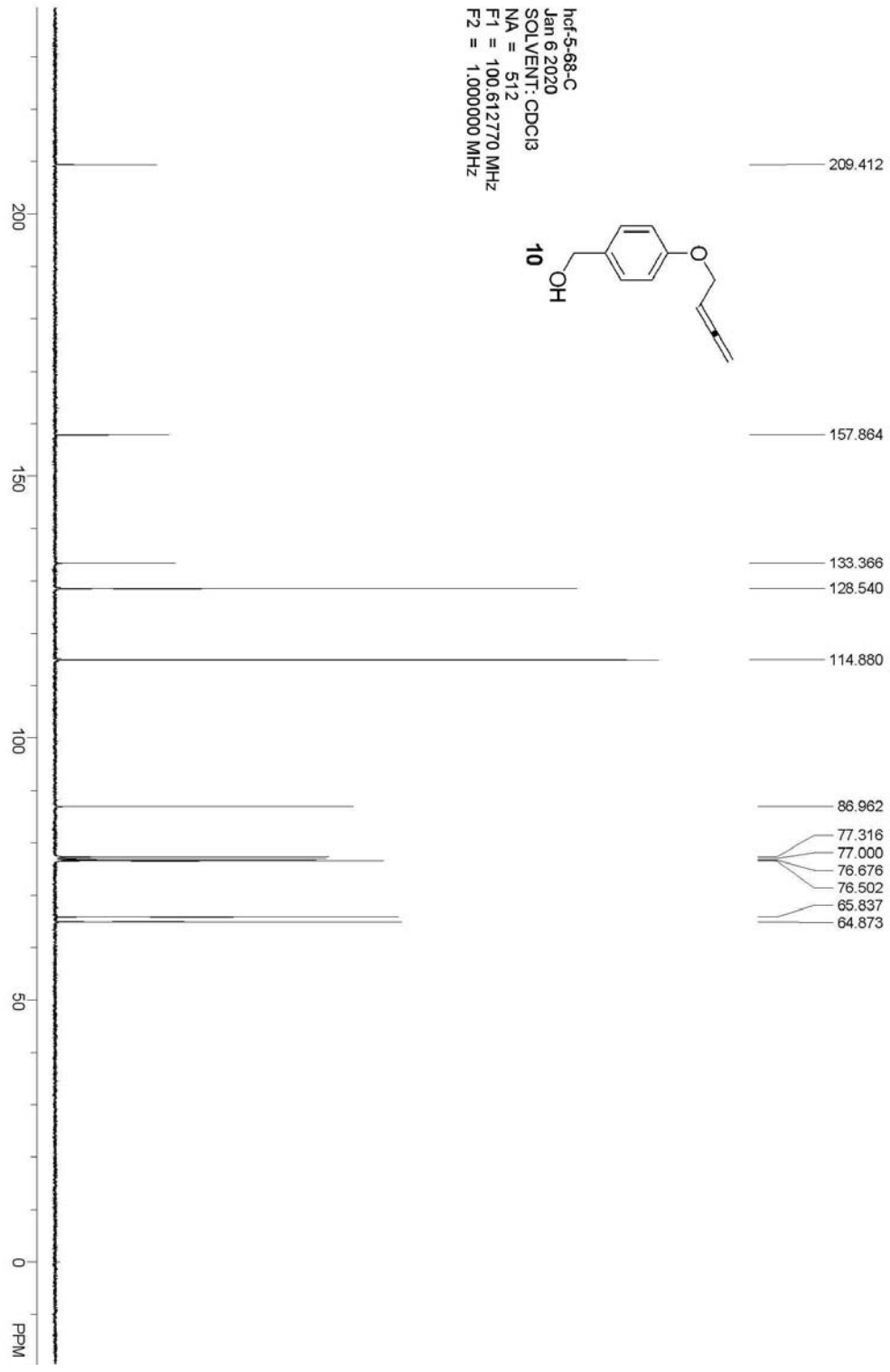

hcf-5-62-H
Dec 17 2019
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
(Z)-7
Br
I
I
7.556
7.552
7.536
7.532
7.287
7.283
7.267
7.264
7.255
7.248
7.244
6.886
6.882
6.866
6.863
6.851
6.848
6.831
6.428
6.415
6.403
4.594
4.581
4.423
1.00
1.12
2.08
1.02
2.12
2.13
-0.000
10
8
6
4
2
0
PPM

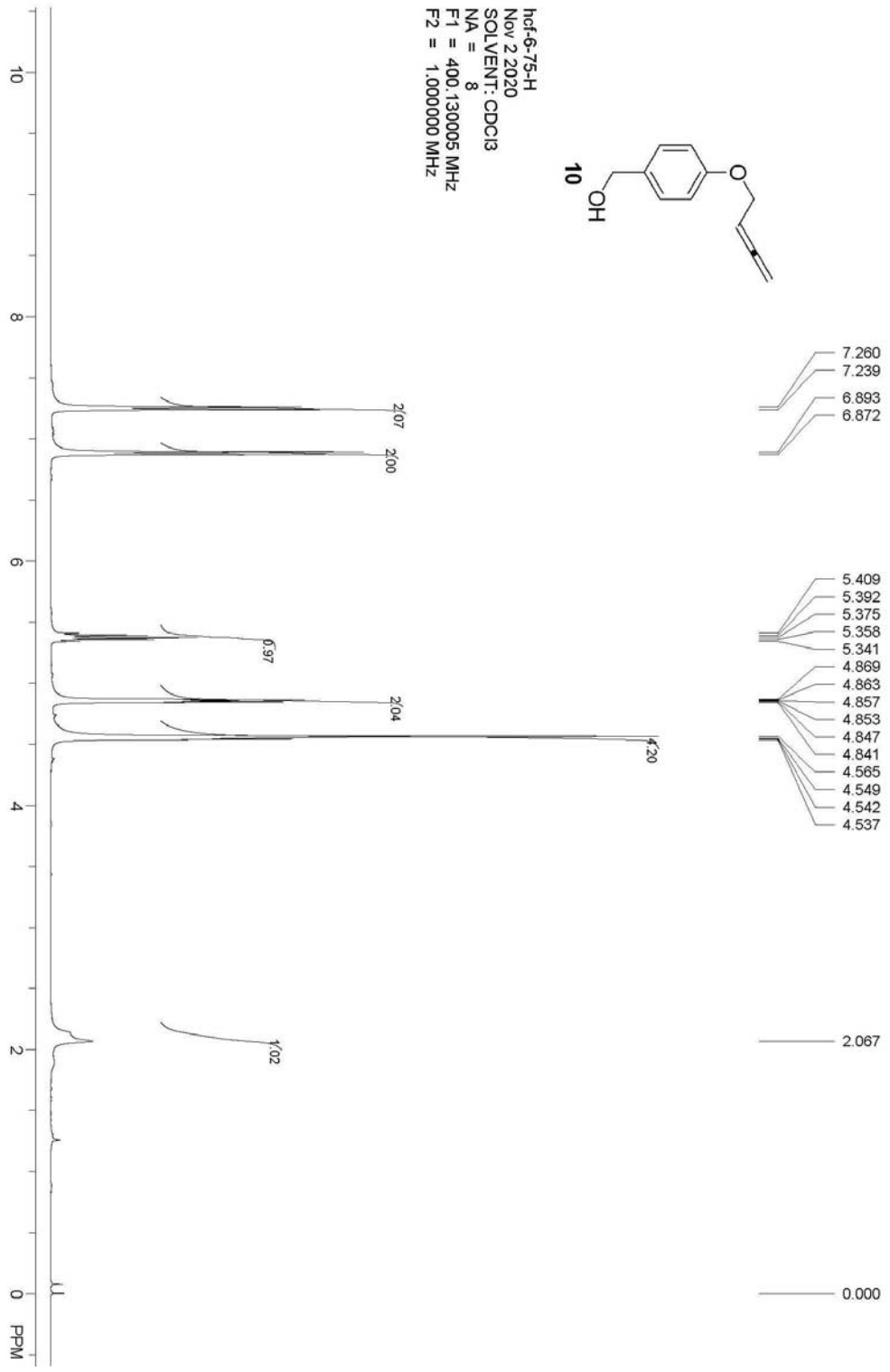

hcf-5-62-C
Dec 17 2019
SOLVENT: CDCl3
NA = 400
F1 = 100.612770 MHz
F2 = 1.000000 MHz
(Z)-7
Br
O
I
I
154.412
134.686
133.548
128.516
122.520
113.735
112.218
104.571
77.316
77.000
76.684
73.540
16.462
200
150
100
50
0
PPM

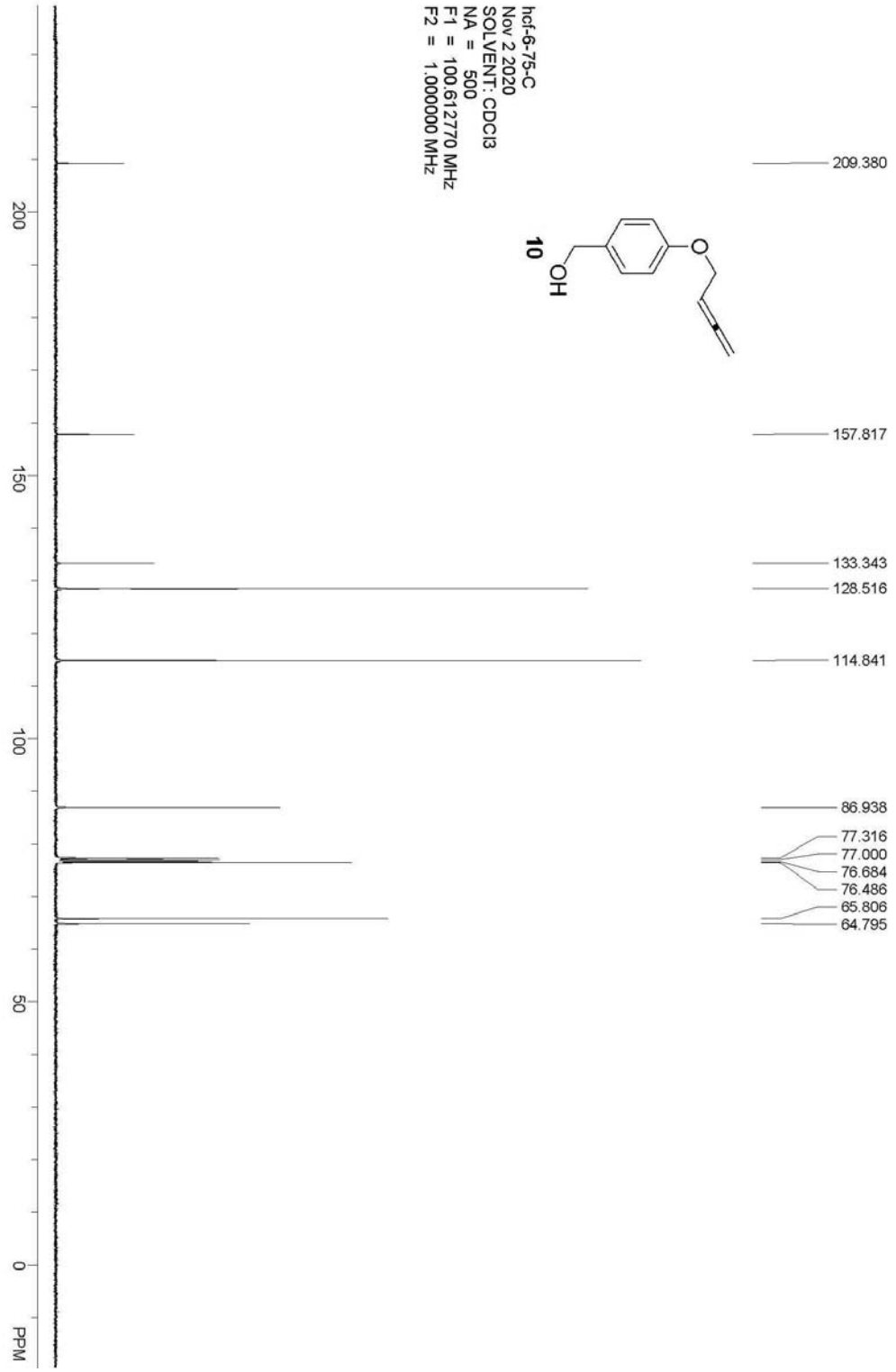

hcf-5-67-H
Jan 6 2020
SOLVENT: CDCl3
NA = 16
F1 = 400.130005 MHz
F2 = 1.000000 MHz
eucalyptene A
CO2Me
7.663
7.622
7.471
7.450
7.265
6.919
6.897
6.328
6.288
5.414
5.397
5.381
5.364
5.347
4.892
4.886
4.879
4.877
4.869
4.863
4.605
4.599
4.592
4.589
4.582
3.788
0.000
1.00
2.03
1.97
0.97
0.92
1.94
2.01
2.98
8
6
4
2
0
PPM

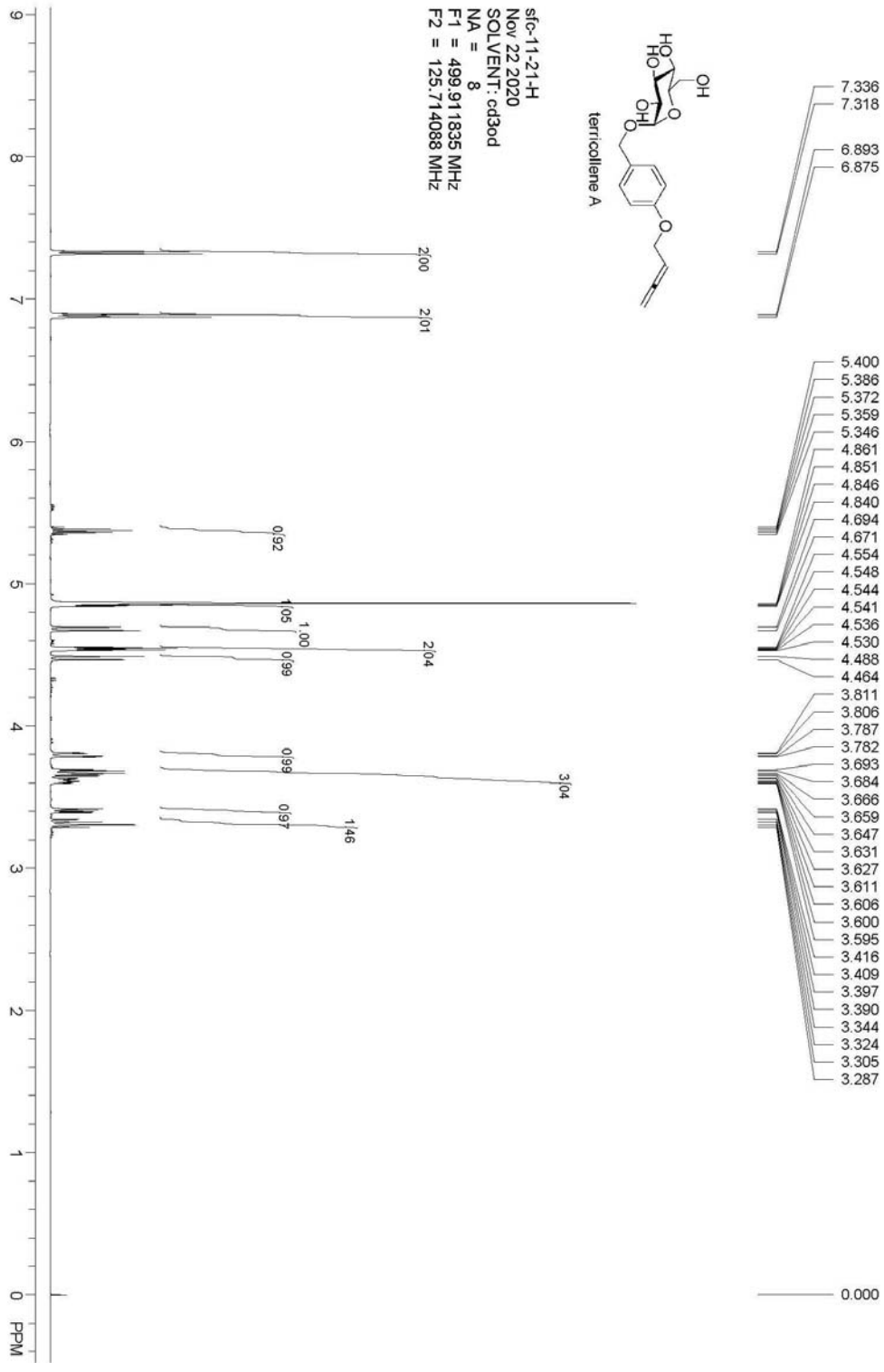

hcf-5-67-C
Jan 6 2020
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
eucalyptene A
O
CO2Me
209.491
167.684
160.108
144.419
129.638
127.268
115.339
115.149
86.677
77.316
77.000
76.716
76.684
65.845
51.515
200
150
100
50
0
PPM

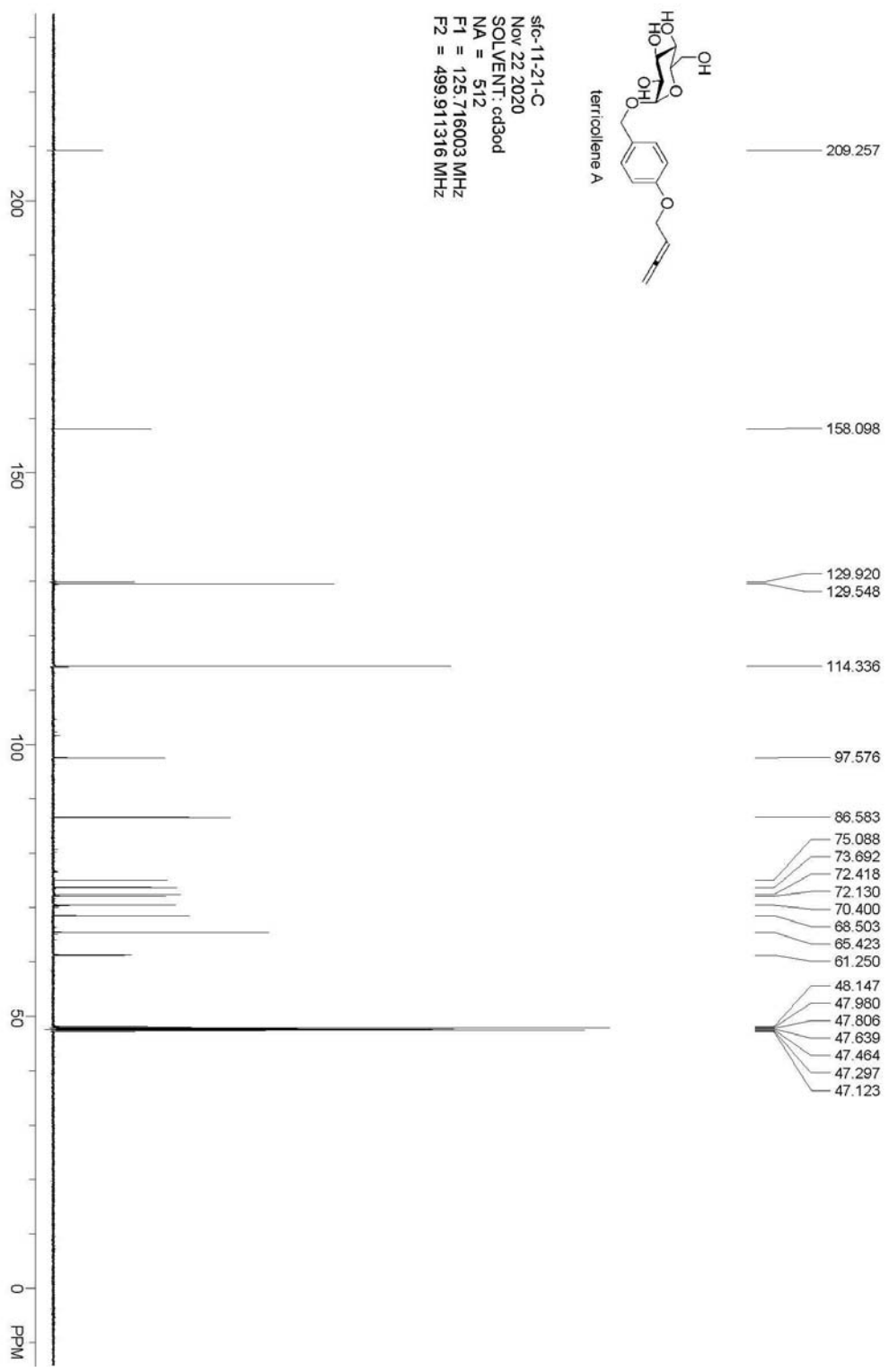

hcf-5-68-H
Jan 6 2020
SOLVENT: CDCl3
NA = 16
F1 = 400.13005 MHz
F2 = 1.000000 MHz
10
OH
O
7.271
7.250
6.907
6.900
6.895
6.884
6.879
6.872
5.412
5.395
5.378
5.362
5.345
4.872
4.866
4.859
4.856
4.849
4.843
4.580
4.572
4.566
4.559
4.555
4.549
4.542
1.910
-0.000
2.05
2.00
0.95
1.99
4.10
1.07
8
6
4
2
0
PPM

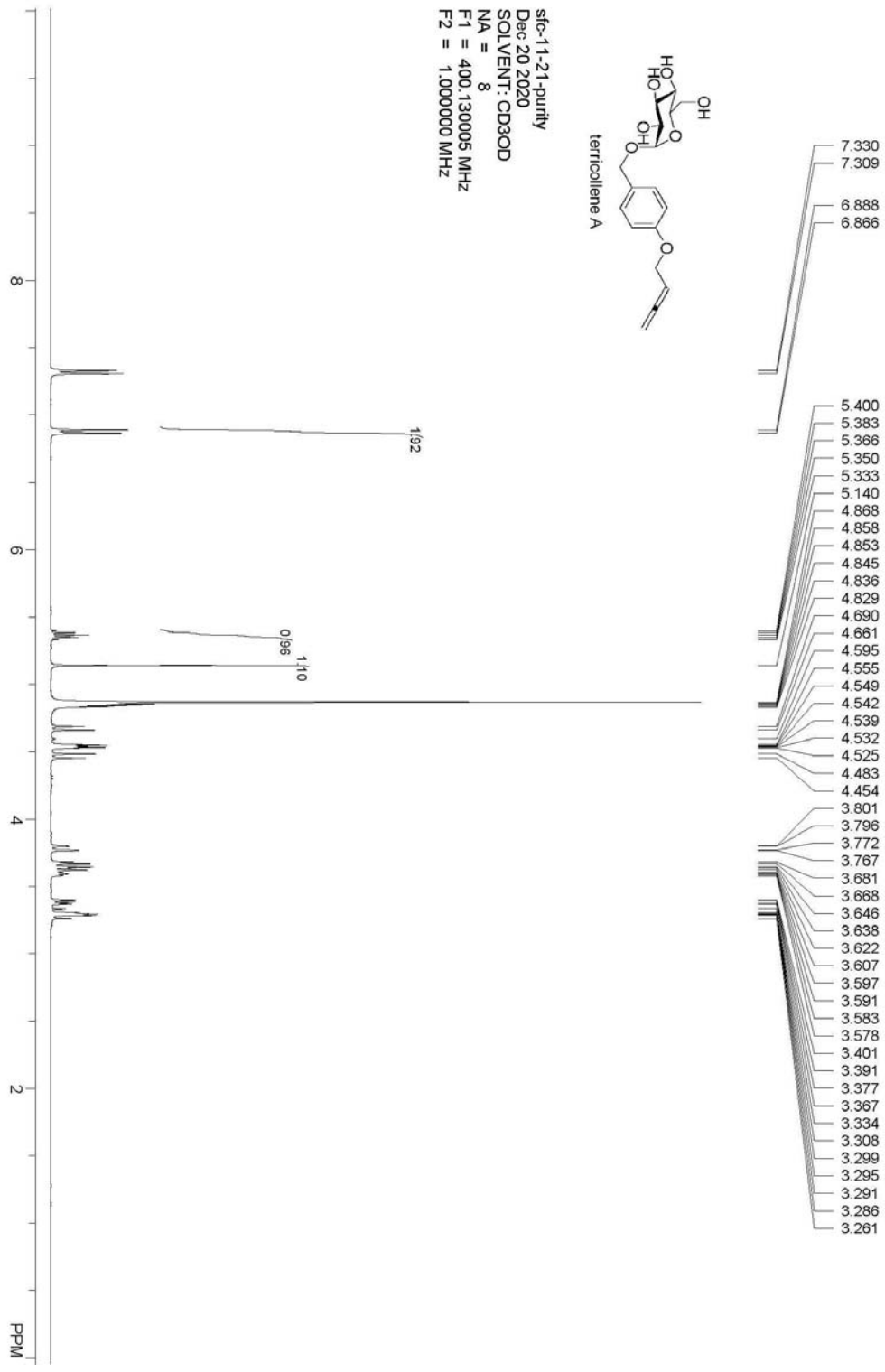

hcf-5-68-C
Jan 6 2020
SOLVENT: CDCl3
NA = 512
F1 = 100.612770 MHz
F2 = 1.000000 MHz
10
OH
O
209.412
157.864
133.366
128.540
114.880
86.962
77.316
77.000
76.676
76.502
65.837
64.873
200
150
100
50
0
PPM


hcf-6-75-H
Nov 2 2020
SOLVENT: CDCl3
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
10
OH
O
7.260
7.239
6.893
6.872
5.409
5.392
5.375
5.358
5.341
4.869
4.863
4.857
4.853
4.847
4.841
4.565
4.549
4.542
4.537
2.067
0.000
2.07
2.00
0.97
2.04
4.20
1.02
10
8
6
4
2
0
PPM


hcf-6-75-C
Nov 2 2020
SOLVENT: CDCl3
NA = 500
F1 = 100.612770 MHz
F2 = 1.000000 MHz
10
OH
O
209.380
157.817
133.343
128.516
114.841
86.938
77.316
77.000
76.684
76.486
65.806
64.795
200
150
100
50
0
PPM


sfc-11-21-H
Nov 22 2020
SOLVENT: cd3od
NA = 8
F1 = 499.911835 MHz
F2 = 125.714088 MHz
terricollene A
7.336
7.318
6.893
6.875
5.400
5.386
5.372
5.359
5.346
4.861
4.851
4.846
4.840
4.694
4.671
4.554
4.548
4.544
4.541
4.536
4.530
4.488
4.464
3.811
3.806
3.787
3.782
3.693
3.684
3.666
3.659
3.647
3.631
3.627
3.611
3.606
3.600
3.595
3.416
3.409
3.397
3.390
3.344
3.324
3.305
3.287
0.000
2.00
2.01
0.92
1.05
1.00
2.04
0.99
0.99
3.04
0.97
1.46
PPM


sfc-11-21-C
Nov 22 2020
SOLVENT: cd3od
NA = 512
F1 = 125.716003 MHz
F2 = 499.911316 MHz
terricollene A
209.257
158.098
129.920
129.548
114.336
97.576
86.583
75.088
73.692
72.418
72.130
70.400
68.503
65.423
61.250
48.147
47.980
47.806
47.639
47.464
47.297
47.123
200
150
100
50
0
PPM


sfc-11-21-purity
Dec 20 2020
SOLVENT: CD3OD
NA = 8
F1 = 400.130005 MHz
F2 = 1.000000 MHz
terricollene A
1.92
0.96
1.10
7.330
7.309
6.888
6.866
5.400
5.383
5.366
5.350
5.333
5.140
4.868
4.858
4.853
4.845
4.836
4.829
4.690
4.661
4.595
4.555
4.549
4.542
4.539
4.532
4.525
4.483
4.454
3.801
3.796
3.772
3.767
3.681
3.668
3.646
3.638
3.622
3.607
3.597
3.591
3.583
3.578
3.401
3.391
3.377
3.367
3.334
3.308
3.299
3.295
3.291
3.286
3.261
8
6
4
2
PPM