# Catalytic Transient Leaving Group for Atom-Economic Synthesis of Allenes from 2-Alkynols

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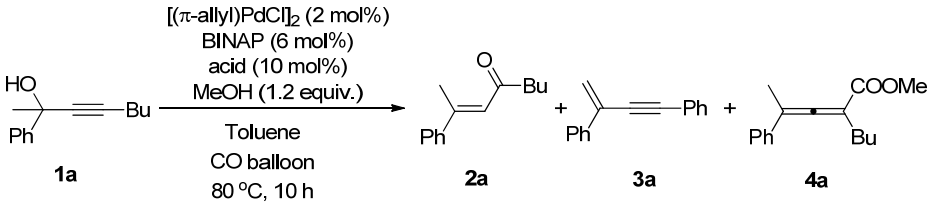
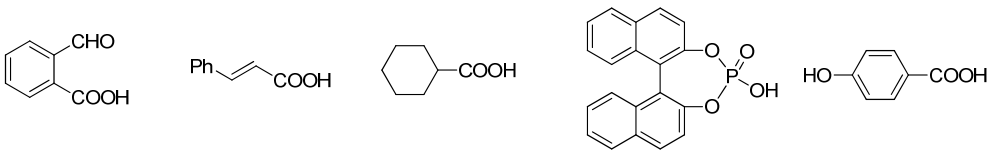
**General Information.** NMR spectra were taken with an Agilent-400 spectrometer (400 MHz for $^{1}H$ NMR, 100 MHz for $^{13}C$ NMR) in $CDCl_3$. Chemical shifts were recorded in ppm in relative to the TMS in $CDCl_3$ and coupling constants were reported in Hz. All reactions were carried out in flame-dried Schlenk tubes. $[PdCl(\pi\text{-allyl})]_2$ was purchased from J&K Chemicals; DPEphos was purchased from Acros Organics or Energy Chemical; $(PhO)_2POOH$ was purchased from Energy Chemical and purified through stirring with 1 N HCl, extracting with dichloromethane, and removing solvents under vacuum; MeOH was purchased from Sinopharm Chemical Reagent Co., Ltd; *n*-BuLi was purchased from Energy Chemical. Toluene was dried over sodium wire with benzophenone as the indicator and distilled freshly before use. THF was dried over sodium wire. The reaction should be conducted in a hood working efficiently due to the toxicity of CO gas. All the temperatures are referred to the oil baths used. Recovery of substrates were determined by $^{1}H$ NMR analysis using 1,3,5-trimethylbenzene or dibromomethane as the internal standard. The starting propargylic alcohols were synthesized according to the reported procedures. [1]

**Table S1 Screening of acids with BINAP as the ligand** [a]




| Entry | Acid | NMR yield (%) [b] | | | Recovery of 1a (%) [b] |
|---|---|---|---|---|---|
| | | 2a | 3a | 4a | |
| 1 | - | - | - | - | 71 |
| 2 | $CF_3COOH$ | 6 [c] | 8 | - | - |
| 3 | AgOTf | 27 [c] | - | - | - |
| 4 | $CH_3SO_2OH$ | 40 [c] | - | - | - |
| 5 | BnCOOH | - | - | - | 82 |
| 6 | Acid **1** | - | - | - | 80 |
| 7 | Acid **2** | - | - | - | 87 |
| 8 | Acid **3** | - | - | - | 96 |
| 9 | Acid **4** | - | 7 | 22 | 5 |
| 10 | Acid **5** | - | - | - | 100 |
| 11 | Acid **6** | - | - | - | 85 |
| 12 | Acid **7** | - | - | - | 87 |
| 13 | Acid **8** | - | - | - | 78 |
| 14 | Acid **9** | - | - | - | 61 |
| 15 | Acid **10** | - | - | - | 74 |
| 16 | $N(CH_2PO_3H)_3$ | - | - | - | 98 |
| 17 | $H_3PO_3$ | 26 [c] | 19 | - | - |
| 18 | $HPO_2 \cdot H_2O$ | - | 3 | 2 | - |
| 19 | $HPO_3$ | - | 40 | - | 15 |
| 20 | $H_3PO_4$ | 12 [d] | 56 | - | - |
| 21 | $Ph_2POOH$ | - | 1 | 2 | - |
| 22 | $(PhO)_2POOH$ | - | 2 | 27 | 5 |




acid **1**




acid **2**



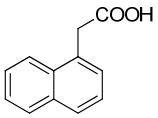

acid **3**



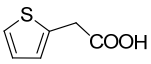

acid **4**



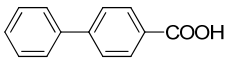

acid **5**



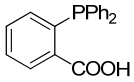

acid **6**



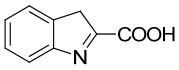

acid **7**




acid **8**



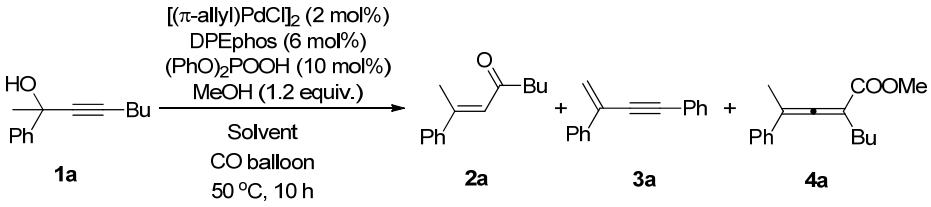

acid **9**




acid **10**

[a] Reaction conditions: **1a** (0.5 mmol), $[(\pi\text{-allyl})PdCl]_2$ (2 mol%), BINAP (6 mol%), acid (10 mol%) and MeOH (1.2 equiv.) at 80 $^{o}$C in toluene (2.0 mL) under 1 atm of CO unless otherwise noted; [b] Determined by $^{1}$H NMR analysis using 1,3,5-trimethylbenzene as the internal standard; [c] *E:Z* > 20:1; [d] *E:Z* = 3:1.

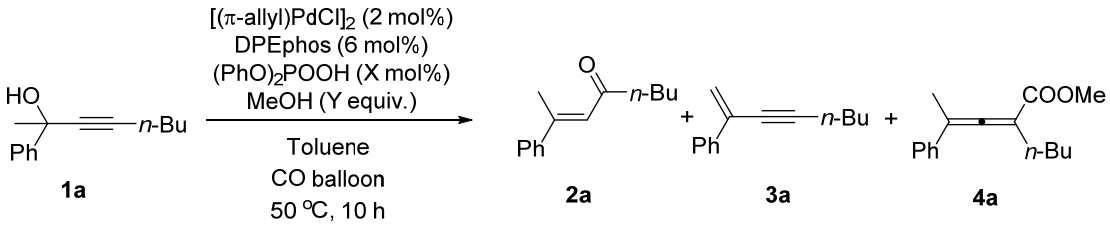
**Table S2 Screening of solvents**[a]




| Entry | Solvent | NMR yield (%) [b] | | | Recovery of 1a (%) [b] |
|---|---|---|---|---|---|
| | | 2a | 3a | 4a | |
| **1** | THF | - | - | 27 | 58 |
| **2** | toluene | - | - | 64 | 10 |
| **3** | DMF | - | - | 47 | - |
| **4** | DMSO | - | - | 42 | - |

[a] Reaction conditions: **1a** (0.5 mmol), $[(\pi\text{-allyl})PdCl]_2$ (2 mol%), DPEphos (6 mol%), $(PhO)_2POOH$ (10 mol%), and MeOH (1.2 equiv.) at 50 °C under 1 atm of CO unless otherwise noted; [b] Determined by $^1H$ NMR analysis using 1,3,5-trimethylbenzene as the internal standard.

**Table S3 Screening of loadings referring to $(PhO)_2POOH$ and MeOH [a]**



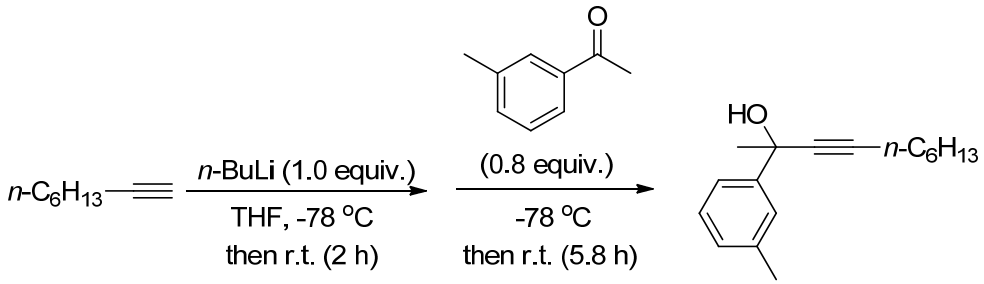

| Entry | $(PhO)_2POOH$ (mol%) | MeOH (equiv.) | NMR yield (%) [b] | | | Recovery of **1a** (%) [b] |
|---|---|---|---|---|---|---|
| | | | **2a** | **3a** | **4a** | |
| 1 | 10 | 1.2 | - | - | 64 | 10 |
| 2 | 5 | 1.2 | - | - | 64 | 23 |
| 3 | 5 | 2.0 | - | - | 68 | 13 |
| 4 | 5 | 4.0 | - | - | 72 | 7 |
| 5 | 5 | 8.0 | - | - | 86 | - |

[a] Reaction conditions: **1a** (0.5 mmol), $[(\pi\text{-allyl})PdCl]_2$ (2 mol%), DPEphos (6 mol%), $(PhO)_2POOH$, and MeOH in toluene (2.0 mL) at 50 $^{o}$C under 1 atm of CO unless otherwise noted;
[b] Determined by $^{1}$H NMR analysis using 1,3,5-trimethylbenzene as the internal standard.

**Experimental details and analytical data**

**1. Synthesis of propargylic alcohols**

**(1) Preparation of 2-(3-methylphenyl)dec-3-yn-2-ol (1b) (zwl-8-178)** [1]

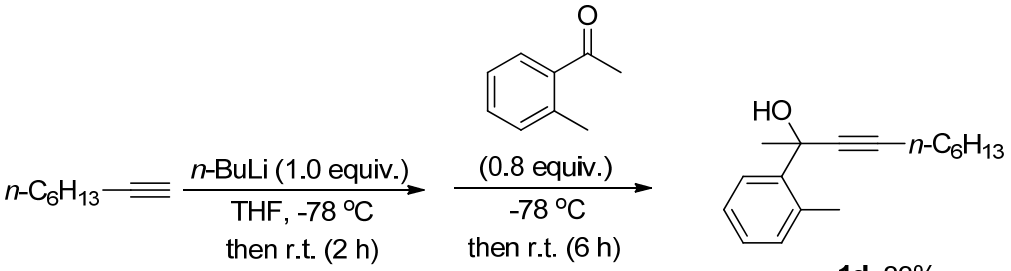



**1b**, 80%

**Typical Procedure I**: To a flame-dried three-neck flask were added 1-octyne (7.38 mL, d = 0.747 g/mL, 5.5129 g, 50 mmol) and THF (50 mL). Then a solution of *n*-BuLi (2.5 M in hexane, 20 mL, 50 mmol) was added dropwise at -78 $^{o}$C under argon. After stirring at room temperature for 2 h, the resulting mixture was cooled to -78 $^{o}$C, then a solution of 1-(3-methylphenyl)ethanone (5.44 mL, d = 0.986 g/mL, 5.3638 g, 40 mmol) in THF (30 mL) was added dropwise. The resulting mixture was then stirred at rt for 5.8 h, and quenched with a saturated aqueous solution of $NH_4Cl$ (20 mL). After extraction with ethyl acetate (20 mL x 3), the organic layer was washed with brine (50 mL) and dried over anhydrous $Na_2SO_4$. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel to afford **1b** (7.8198 g, 80%) as an oil (eluent: petroleum ether (b.p. 60-90 $^{o}$C)/ethyl acetate = 100/1): $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.38 (m, 2 H, Ar-H), 7.23 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.08 (d, *J* = 7.2 Hz, 1 H, Ar-H), 2.39 (bs, 1 H, OH), 2.36 (s, 3 H, $CH_3$), 2.26 (t, *J* = 7.2 Hz, 2 H, $CH_2$), 1.73 (s, 3 H, $CH_3$), 1.61-1.47 (m, 2 H, $CH_2$), 1.47-1.37 (m, 2 H, $CH_2$), 1.37-1.23 (m, 4 H, 2 x $CH_2$), 0.89 (t, *J* = 6.8 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 146.1, 137.8, 128.2, 128.1, 125.6, 122.0, 85.6, 83.8, 70.0, 33.5, 31.3, 28.6, 28.5, 22.5, 21.5, 18.7, 14.0 ; MS (70 eV, EI) *m/z* (%): 244 ($M^+$, 2.54), 229 (100); IR (neat): *v* = 3412, 2929, 2858, 2244, 1457, 1199, 1158, 1084, 1062 $cm^{-1}$; HRMS calcd for $C_{17}H_{24}O$ [$M^+$]: 244.1827, found: 244.1829.

The following compounds were prepared according to **Typical Procedure I**.

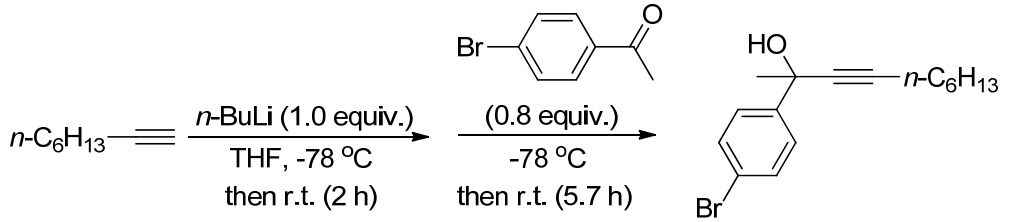
**(2) Preparation of 2-(2-methylphenyl)dec-3-yn-2-ol (1d) (zwl-8-177)** [1]




**1d**, 83%

The reaction of 1-octyne (7.38 mL, d = 0.747 g/mL, 5.5129 g, 50 mmol) in THF (50 mL), *n*-BuLi (2.5 M in hexane, 20 mL, 50 mmol), and 1-(2-methylphenyl)ethanone (5.23 mL, d = 1.026 g/mL, 5.3660 g, 40 mmol) in THF (30 mL) afforded **1d** (8.1131 g, 83%) as an oil [eluent: petroleum ether (b.p. 60-90 $^{o}$C)/ethyl acetate = 100/1]: $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 7.74-7.64 (m, 1 H, Ar-H), 7.22-7.13 (m, 3 H, Ar-H), 2.62 (s, 3 H, $CH_3$), 2.31 (s, 1 H, OH), 2.23 (t, *J* = 7.0 Hz, 2 H, $CH_2$), 1.81 (s, 3 H, $CH_3$), 1.57-1.46 (m, 2 H, $CH_2$), 1.45-1.20 (m, 6 H, 3 x $CH_2$), 0.88 (t, *J* = 7.2 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 142.8, 135.6, 132.1, 127.4, 125.6, 124.9, 85.3, 84.0, 69.6, 31.2, 31.1, 28.5, 28.4, 22.5, 21.2, 18.7, 14.0; MS (70 eV, EI) *m/z* (%): 244 ($M^+$, 2.58), 229 (100); IR (neat): *v* = 3413, 2930, 2858, 2243, 1456, 1367, 1328, 1079, 1047 cm$^{-1}$; HRMS calcd for $C_{17}H_{24}O$ [$M^+$]: 244.1827, found: 244.1825.

**(3) Preparation of 2-(4-bromophenyl)dec-3-yn-2-ol (1e) (zwl-8-179)** [1]

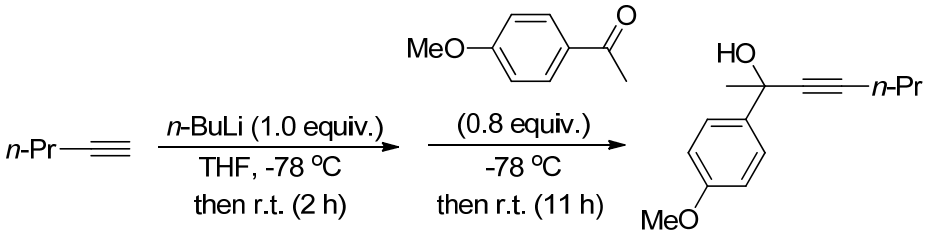



**1e**, 65%

The reaction of 1-octyne (7.38 mL, d = 0.747 g/mL, 5.5129 g, 50 mmol) in THF (50 mL), *n*-BuLi (2.5 M in hexane, 20 mL, 50 mmol), and 1-(4-bromophenyl)ethanone (7.9617 g, 40 mmol) in THF (30 mL) afforded **1e** (8.0401 g, 65%) as an oil [eluent: petroleum ether (b.p. 60-90 $^{o}$C)/ethyl acetate =

100/1]: $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.48 (m, 2 H, Ar-H), 7.48-7.42 (m, 2 H, Ar-H), 2.55-2.42 (m, 1 H, OH), 2.25 (t, *J* = 7.0 Hz, 2 H, $CH_2$), 1.70 (s, 3 H, $CH_3$), 1.59-1.47 (m, 2 H, $CH_2$), 1.46-1.20 (m, 6 H, 3 x $CH_2$), 0.89 (t, *J* = 6.8 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 145.3, 131.2, 126.9, 121.4, 86.1, 83.2, 69.6, 33.5, 31.2, 28.51, 28.49, 22.5, 18.6, 14.0; MS (70 eV, EI) *m/z* (%): 310 ($M^+$($^{81}$Br), 2.30), 308 ($M^+$($^{79}$Br), 2.34), 293 (100); IR (neat): *v* = 3403, 2929, 2858, 2241, 1681, 1589, 1074, 1010 cm$^{-1}$; HRMS calcd for $C_{16}H_{21}O^{79}Br$ [$M^+$]: 308.0776, found: 308.0771.

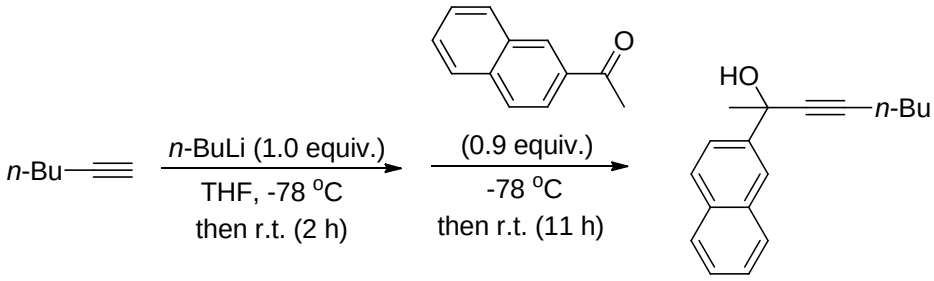
**(4) Preparation of 2-(4-methoxyphenyl)hept-3-yn-2-ol (1g) (zwl-8-18) [1]**




**1g**, 55%

The reaction of 1-pentyne (4.93 mL, d = 0.691 g/mL, 3.4066 g, 50 mmol) in THF (30 mL), *n*-BuLi (2.5 M in hexane, 20 mL, 50 mmol), and 1-(4-methoxyphenyl)ethanone (6.0069 g, 40 mmol) in THF (20 mL) afforded **1g** (4.8024 g, 55%) as an oil via distillation at 1 mmHg (b.p. 106-110 $^{o}$C/1 mmHg): $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 7.62-7.56 (m, 2 H, Ar-H), 6.92-6.85 (m, 2 H, Ar-H), 3.81 (s, 3 H, $CH_3$), 2.32-2.23 (m, 3 H, OH and $CH_2$), 1.74 (s, 3 H, $CH_3$), 1.64-1.53 (m, 2 H, $CH_2$), 1.01 (t, *J* = 7.4 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.9, 138.4, 126.2, 113.4, 85.4, 84.0, 69.7, 55.3, 33.4, 22.1, 20.7, 13.5; MS (70 eV, EI) *m/z* (%): 219 ($M^+$+1, 1.15), 218 ($M^+$, 6.81), 177 (100); IR (neat): *v* = 3430, 2963, 2933, 2243, 1609, 1508, 1463, 1300, 1245, 1174, 1089, 1031 cm$^{-1}$; HRMS calcd for $C_{14}H_{18}O_2$ [$M^+$]: 218.1307, found: 218.1306.

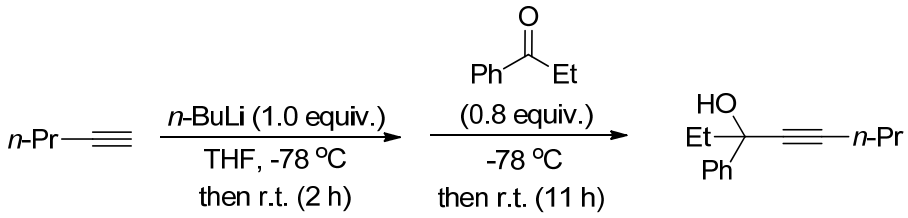
**(5) Preparation of 2-naphthyloct-3-yn-2-ol (1h) (zwl-8-41) [1]**




**1h**, 49%

The reaction of 1-hexyne (5.74 mL, d = 0.715 g/mL, 4.1046 g, 50 mmol) in THF (30 mL), *n*-BuLi (2.5 M in hexane, 20 mL, 50 mmol), and 1-(2-naphthyl)ethanone (7.6598 g, 45 mmol) in THF (20 mL) afforded **1h** (5.5643 g, 49%) as an oil via distillation at 1 mmHg (b.p. 140-145 °C/1 mmHg): $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 1 H, Ar-H), 7.90-7.78 (m, 3 H, Ar-H), 7.78-7.70 (m, 1 H, Ar-H), 7.56-7.43 (m, 2 H, Ar-H), 2.46-2.38 (m, 1 H, OH), 2.32 (t, *J* = 7.0 Hz, 2 H, $CH_2$), 1.83 (s, 3 H, $CH_3$), 1.63-1.52 (m, 2 H, $CH_2$), 1.52-1.39 (m, 2 H, $CH_2$), 0.94 (t, *J* = 7.2 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 143.5, 133.0, 132.8, 128.3, 128.0, 127.5, 126.1, 126.0, 123.6, 123.3, 85.9, 83.7, 70.1, 33.4, 30.7, 22.0, 18.4, 13.6 ; MS (70 eV, EI) *m/z* (%): 252 ($M^+$, 2.25), 127 (100); IR (neat): *v* = 3385, 2957, 2930, 2241, 1507, 1354, 1084 $cm^{-1}$; HRMS calcd for $C_{18}H_{20}O$ [$M^+$]: 252.1514, found: 252.1516.

**(6) Preparation of 3-phenyloct-4-yn-3-ol (1o) (zwl-8-16)** [1]

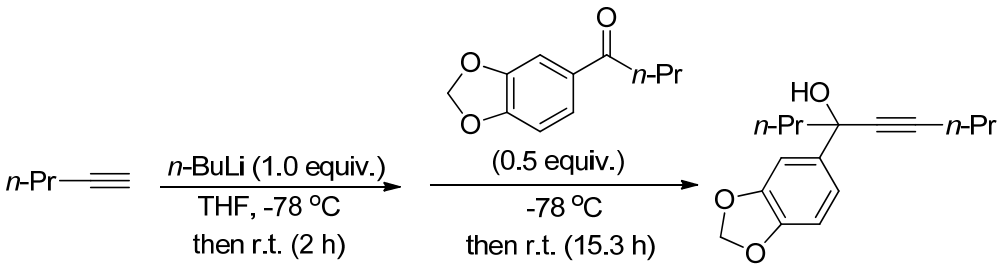



**1o**, 67%

The reaction of 1-pentyne (4.93 mL, d = 0.691 g/mL, 3.4066 g, 50 mmol) in THF (30 mL), *n*-BuLi (2.5 M in hexane, 20 mL, 50 mmol), and 1-phenylpropanone (5.32 mL, d = 1.009 g/mL, 5.3679 g, 40 mmol) in THF (20 mL) afforded **1o** (5.4241 g, 67%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl acetate = 10/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.56 (m, 2 H, Ar-H), 7.38-7.30 (m, 2 H, Ar-H), 7.30-7.22 (m, 1 H, Ar-H), 2.42-2.33 (m, 1 H, OH), 2.27 (t, *J* = 7.0 Hz, 2 H, $CH_2$), 2.02-1.80 (m, 2 H, $CH_2$), 1.68-1.52 (m, 2 H, $CH_2$), 1.02 (t, *J* = 7.4 Hz, 3 H, $CH_3$), 0.93 (t, *J* = 7.4 Hz, 3 H,

$CH_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 145.1, 127.9, 127.4, 125.5, 86.6, 82.6, 73.9, 38.5, 22.1, 20.7, 13.5, 9.1; MS (70 eV, EI) *m/z* (%): 202 ($M^+$, 1.73), 173 (100); IR (neat): *v* = 3422, 2966, 2934, 2242, 1600, 1448, 1328, 1051, 1017 $cm^{-1}$; HRMS calcd for $C_{14}H_{18}O$ [$M^+$]: 202.1358, found: 202.1361.

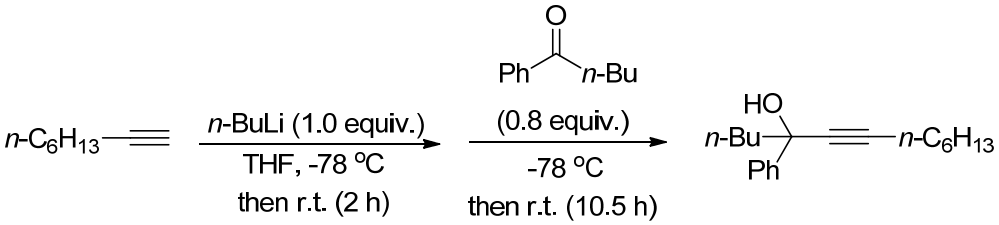
**(7) Preparation of 4-(3,4-methylenedioxy)phenylnon-5-yn-4-ol (1p) (hcf-1-104)** [1]




**1p**, 53%

The reaction of 1-pentyne (4.92 mL, d = 0.692 g/mL, 3.4046 g, 50 mmol) in THF (30 mL), *n*-BuLi (2.4 M in hexane, 20.8 mL, 50 mmol), and 1-(1,3-benzodioxol-5-yl)-1-butanone (4.8120 g, 25 mmol) in THF (20 mL) afforded **1p** (3.4494 g, 53%) via double chromatography on silica gel as an oil [first round eluent: petroleum ether (b.p. 60-90 °C)/ethyl acetate = 100/1 (5 L) to petroleum ether (b.p. 60-90 °C)/ethyl acetate = 10/1 (1 L); second round eluent: petroleum ether (b.p. 60-90 °C)/ethyl acetate = 100/1)]: $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.16-7.08 (m, 2 H, Ar-H), 6.76 (d, *J* = 8.0 Hz, 1 H, Ar-H), 5.95 (s, 2 H, $CH_2$), 2.33 (s, 1 H, OH), 2.27 (t, *J* = 7.2 Hz, 2 H, $CH_2$), 1.87 (td, $J_1$ = 12.6 Hz, $J_2$ = 4.7 Hz, 1 H, one proton of $CH_2$), 1.77 (td, $J_1$ = 12.5 Hz, $J_2$ = 4.8 Hz, 1 H, one proton of $CH_2$), 1.64-1.52 (m, 2 H, $CH_2$), 1.53-1.39 (m, 1 H, one proton of $CH_2$), 1.39-1.22 (m, 1 H, one proton of $CH_2$), 1.02 (t, *J* = 7.4 Hz, 3 H, $CH_3$), 0.88 (t, *J* = 7.6 Hz, 3 H, $CH_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 147.3, 146.8, 139.6, 118.9, 107.5, 106.5, 101.0, 86.5, 82.8, 73.3, 47.9, 22.1, 20.7, 18.2, 14.0, 13.6; MS (70 eV, EI) *m/z* (%): 261 ($M^+$+1, 1.12), 260 ($M^+$, 6.24), 217 (100); IR (neat): *v* = 3427, 2960, 2873, 1611, 1485, 1434, 1235, 1109, 1038 $cm^{-1}$; HRMS calcd for $C_{16}H_{20}O_3$ [$M^+$]: 260.1412, found: 260.1411.

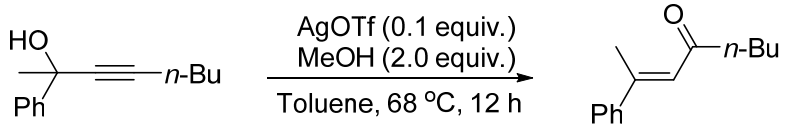
**(8) Preparation of 5-phenyltridec-6-yn-5-ol (1q) (hcf-1-98)** [1]




**1q**, 67%

The reaction of 1-octyne (14.7 mL, d = 0.746 g/mL, 11.04 g, 100 mmol) in THF (50 mL), *n*-BuLi (2.4 M in hexane, 41.6 mL, 100 mmol), and 1-phenyl-1-pentanone (12.9803 g, 80 mmol) in THF (50 mL) afforded the crude product via distillation at 1 mmHg (b.p. 84-110 $^{o}$C/1 mmHg), which was further purified by chromatography on silica gel to afford **1q** (10.0371 g, 67%) as an oil [eluent: petroleum ether (b.p. 60-90 $^{o}$C)/ethyl acetate = 100/1]: $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.58 (m, 2 H, Ar-H), 7.38-7.30 (m, 2 H, Ar-H), 7.30-7.23 (m, 1 H, Ar-H), 2.36 (s, 1 H, OH), 2.29 (t, *J* = 7.0 Hz, 2 H, $CH_2$), 1.97-1.78 (m, 2 H, $CH_2$), 1.61-1.51 (m, 2 H, $CH_2$), 1.50-1.20 (m, 10 H, 5 x $CH_2$), 0.95-0.81 (m, 6 H, 2 x $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 145.4, 128.0, 127.4, 125.5, 86.8, 82.7, 73.4, 45.4, 31.3, 28.7, 28.6, 27.0, 22.7, 22.6, 18.8, 14.05, 14.01; MS (ESI) *m/z* (%): 255 $(M\text{-}OH)^{+}$; IR (neat): *v* = 3422, 2956, 2930, 2860, 1466, 1331, 1033, 1000 $cm^{-1}$; HRMS calcd for $C_{19}H_{28}O$ $[M^{+}]$: 272.2140, found: 272.2141.

**2. Preparation of 2-phenyloct-2*(E)*-en-4-one (2a) (zwl-6-156)**

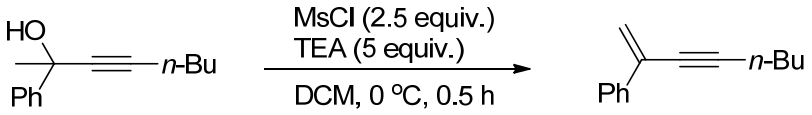



**2a**, 72%
*E:Z* > 20:1

To a flame-dried Schlenk tube was added AgOTf (25.6 mg, 0.12 mmol) in a glove box. After that, **1a** (202.2 mg, 1 mmol), MeOH (64.2 mg, 2.0 mmol), and toluene (5 mL) were added sequentially. Then the Schlenk tube was placed in an oil bath pre-heated at 68 $^{o}$C and stirred for 12 h. Then the resulting mixture was filtered through a short column silica gel (3.5 cm), eluted with ethyl acetate (20 mL), and concentrated under reduced pressure. The residue was purified by column

chromatography on silica gel to afford **2a**[2] (145.6 mg, 72%) (*E*/*Z* > 20:1) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.53-7.45 (m, 2 H, Ar-H), 7.42-7.35 (m, 3 H, Ar-H), 6.52-4.47 (m, 1 H, CH), 2.57-2.50 (m, 5 H, $CH_2$ and $CH_3$), 1.68-1.59 (m, 2 H, $CH_2$), 1.42-1.31 (m, 2 H, $CH_2$), 0.93 (t, *J* = 7.4 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 201.6, 153.5, 142.6, 128.9, 128.4, 126.4, 124.2, 44.6, 26.4, 22.4, 18.3, 13.9; MS (70 eV, EI) *m/z* (%): 203 ($M^+$+1, 1.96), 202 ($M^+$, 13.05), 145 (100); IR (neat): *v* = 2957, 2960, 1681, 1600, 1574, 1446, 1130 $cm^{-1}$.

**3. Preparation of 2-phenyl-3-yn-1-octene (3a) (zwl-9-187)** [3]

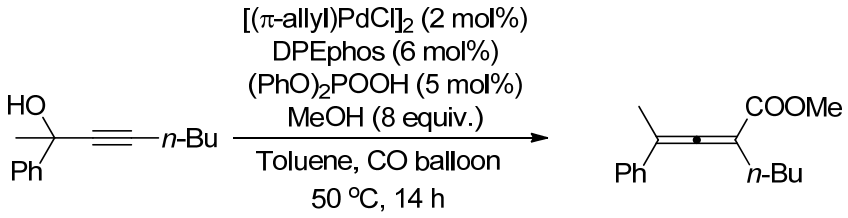



**3a**, 82%

To a flame-dried three-neck falsk were added **1a** (4.0457 g, 20 mmol) and DCM (20 mL) at 0 °C under argon. Then methanesulfonyl chloride (3.87 mL, d = 1.48 g/mL, 5.7276 g, 50 mmol) and triethylamine (13.90 mL, d = 0.728 g/mL, 10.1129 g, 100 mmol) were added sequentially. After stirring for 0.5 h at 0 °C, the reaction was quenched with a saturated aqueous solution of $NH_4Cl$ (20 mL). After extraction with ethyl ether (10 mL x 3), the organic layer was washed with brine (20 mL) and dried over anhydrous $Na_2SO_4$. The residue was then purified by column chromatography on aluminum oxide to afford **3a**[4] (3.1342 g, 82%, 97% purity) as an oil [eluent: petroleum ether (b.p. 60-90 °C)]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.69-7.60 (m, 2 H, Ar-H), 7.37-7.22 (m, 3 H, Ar-H), 5.82 (s, 1 H, one proton of =$CH_2$), 5.57 (s, 1 H, one proton of =$CH_2$), 2.40 (t, *J* = 7.0 Hz, 2 H, $CH_3$), 1.65-1.52 (m, 2 H, $CH_2$), 1.52-1.39 (m, 2 H, $CH_2$), 0.94 (t, *J* = 7.2 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 137.7, 130.9, 128.2, 128.0, 126.0, 119.3, 91.9, 79.7, 30.8, 22.0, 19.0, 13.6; MS (70 eV, EI) *m/z* (%): 185 ($M^+$+1, 10.64), 184 ($M^+$, 3.45), 129 (100); IR (neat): *v* = 2956, 2930, 2226, 1597, 1446, 1028.

**4. Synthesis of 2,3-allenoates**

**(1) Preparation of methyl 2-butyl-4-phenyl-2,3-pentadienoate (4a) (zwl-8-65)**

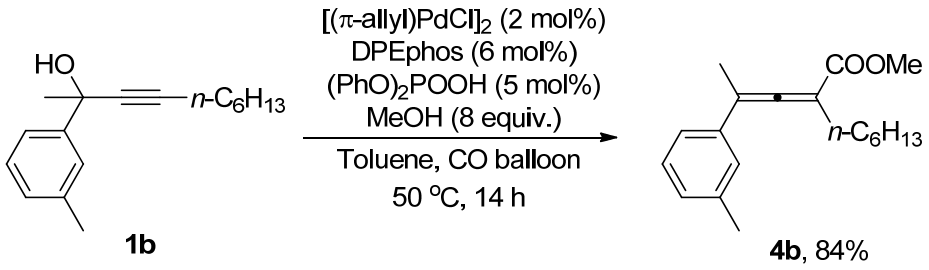



**1a** **4a**, 90%

**Typical Procedure II**: To a flame-dried Schlenk tube were added $[(\pi\text{-allyl})PdCl]_2$ (7.6 mg, 0.02 mmol), DPEphos (32.5 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1a** (202.1 mg, 1 mmol), MeOH (256.1 mg, 8.0 mmol), and toluene (5 mL) sequentially under argon. The resulting mixture was then frozen with a liquid nitrogen bath, degassed to remove the argon inside completely, and refilled with CO by a balloon of CO for three times. Then the resulting mixture was stirred at 50 $^{o}$C with a balloon of CO for 14 h. The resulting mixture was diluted with 5 mL of ethyl acetate, filtered through a short column silica gel (3.5 cm) eluted with ethyl acetate (20 mL), and concentrated. The residue was purified by column chromatography on silica gel to afford **4a** (219.6 mg, 90%) as an oil [eluent: petroleum ether (b.p. 60-90 $^{o}$C)/ethyl ether = 100/1]: $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.30 (m, 4 H, Ar-H), 7.28-7.21 (m, 1 H, Ar-H), 3.72 (s, 3 H, $OCH_3$), 2.35 (t, *J* = 7.6 Hz, 2 H, $CH_2$), 2.18 (s, 3 H, $CH_3$), 1.50-1.41 (m, 2 H, $CH_2$), 1.41-1.30 (m, 2 H, $CH_2$), 0.88 (t, *J* = 7.4 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 211.1, 167.8, 135.4, 128.5, 127.3, 125.9, 104.6, 102.0, 52.1, 30.2, 28.7, 22.3, 16.4, 13.8; MS (70 eV, EI) *m/z* (%): 244 ($M^+$, 1.99), 143 (100); IR (neat): *v* = 2954, 2928, 1943, 1712, 1494, 1434, 1262, 1087, 1067 $cm^{-1}$; HRMS calcd for $C_{16}H_{20}O_2$ [$M^+$]: 244.1463, found: 244.1465.

The following compounds were prepared according to **Typical Procedure II**.

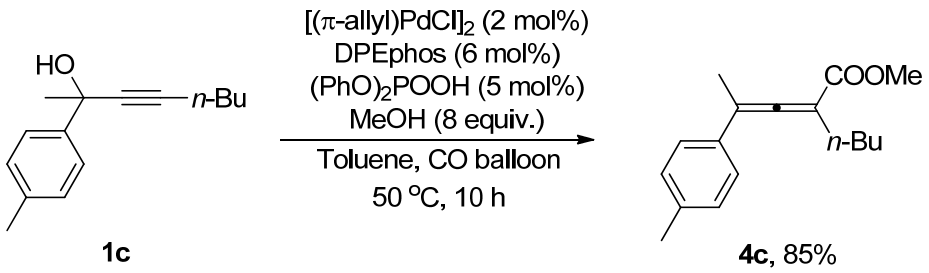
**(2) Preparation of methyl 2-(*n*-hexyl)-4-(3-methylphenyl)-2,3-pentadienoate (4b) (zwl-8-199)**




**1b** **4b**, 84%

The reaction of [(π-allyl)PdCl]$_2$ (7.6 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), (PhO)$_2$POOH (12.6 mg, 0.05 mmol), **1b** (244.4 mg, 1 mmol), MeOH (256.1 mg, 8 mmol), and toluene (5 mL) afforded **4b** (240.6 mg, 84%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.15 (m, 3 H, Ar-H), 7.06 (d, *J* = 7.2 Hz, 1 H, Ar-H), 3.72 (s, 3 H, $OCH_3$), 2.39-2.31 (m, 5 H, $CH_2$ and $CH_3$), 2.16 (s, 3 H, $CH_3$), 1.52-1.42 (m, 2 H, $CH_2$), 1.37-1.17 (m, 6 H, 3 x $CH_2$), 0.85 (t, *J* = 6.8 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 211.2, 167.9, 138.0, 135.3, 128.4, 128.1, 126.6, 123.1, 104.6, 101.8, 52.0, 31.6, 29.0, 28.9, 28.0, 22.6, 21.5, 16.5, 14.0; MS (70 eV, EI) *m/z* (%): 287 ($M^+$+1, 1.83), 286 ($M^+$, 7.45), 177 (100); IR (neat): *v* = 2924, 2856, 1943, 1713, 1604, 1434, 1249, 1087 cm$^{-1}$; HRMS calcd for $C_{19}H_{26}O_2$ [$M^+$]: 286.1933, found: 286.1935.

**(3) Preparation of methyl 2-butyl-4-(4-methylphenyl)-2,3-pentadienoate (4c) (zwl-8-74)**

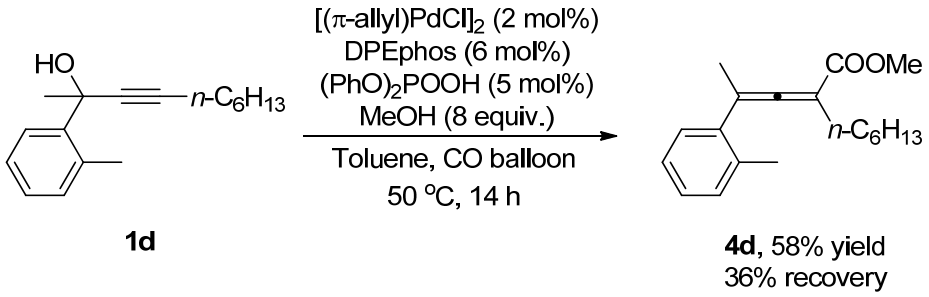



**1c** **4c**, 85%

The reaction of [(π-allyl)PdCl]$_2$ (7.6 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), (PhO)$_2$POOH (12.5 mg, 0.05 mmol), **1c** (216.4 mg, 1 mmol), MeOH (256.6 mg, 8 mmol), and toluene (5 mL) afforded **4c** (219.7 mg, 85%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.23 (m, 2 H, Ar-H), 7.15 (d, *J* = 8.0 Hz, 2 H, Ar-H), 3.71 (s, 3 H, $OCH_3$), 2.38-2.30 (m, 5 H, $CH_2$ and $CH_3$), 2.16 (s, 3 H, $CH_3$), 1.50-1.40 (m, 2 H, $CH_2$), 1.40-1.29 (m, 2 H, $CH_2$), 0.88 (t, *J* = 7.4 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$):

δ = 211.1, 167.9, 137.2, 132.4, 129.2, 125.8, 104.4, 101.8, 52.0, 30.2, 28.7, 22.3, 21.1, 16.4, 13.9; MS (70 eV, EI) *m/z* (%): 258 ($M^+$, 2.37), 157 (100); IR (neat): $\nu$ = 2947, 2926, 2866, 1942, 1713, 1509, 1435, 1235, 1117, 1082, 1059, 1018 $cm^{-1}$; HRMS calcd for $C_{17}H_{22}O_2$ [$M^+$]: 258.1620, found: 258.1621.

**(4) Preparation of methyl 2-(*n*-hexyl)-4-(2-methylphenyl)-2,3-pentadienoate (4d) (zwl-8-198)**

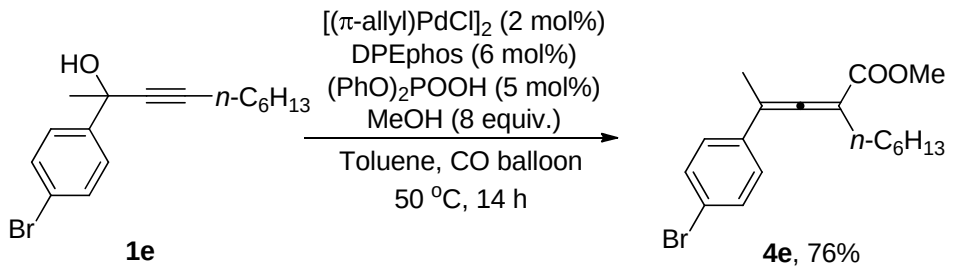



**1d**

**4d**, 58% yield
36% recovery

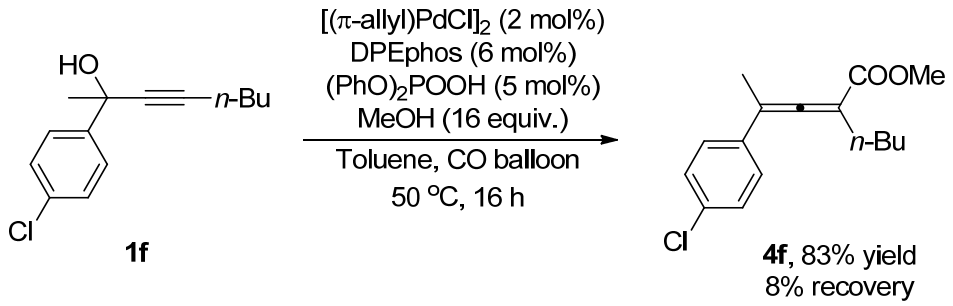
The reaction of [(π-allyl)PdCl]$_2$ (7.6 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1d** (244.6 mg, 1 mmol), MeOH (256.4 mg, 8 mmol), and toluene (5 mL) afforded **4d** (166.3 mg, 58%) (36% of **1d** remained based on $^1$H NMR analysis of the crude product) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.22 (m, 1 H, Ar-H), 7.22-7.15 (m, 3 H, Ar-H), 3.74 (s, 3 H, $OCH_3$), 2.38 (s, 3 H, $CH_3$), 2.37-2.15 (m, 2 H, $CH_2$), 2.11 (s, 3 H, $CH_3$), 1.51-1.41 (m, 2 H, $CH_2$), 1.35-1.20 (m, 6 H, 3 x $CH_2$), 0.86 (t, $J$ = 6.6 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 209.0, 168.3, 136.6, 135.9, 130.6, 127.8, 127.4, 125.9, 104.0, 99.1, 51.9, 31.7, 28.8, 28.7, 27.9, 22.6, 20.3, 20.1, 14.0; MS (70 eV, EI) *m/z* (%): 287 ($M^+$+1, 1.07), 286 ($M^+$, 4.38), 177 (100); IR (neat): $\nu$ = 2952, 2925, 2856, 1952, 1713, 1434, 1248, 1124, 1087, 1042 $cm^{-1}$; HRMS calcd for $C_{19}H_{26}O_2$ [$M^+$]: 286.1933, found: 286.1937.

**(5) Preparation of methyl 2-(*n*-hexyl)-4-(4-bromophenyl)-2,3-pentadienoate (4e) (zwl-8-200)**




The reaction of $[(\pi\text{-allyl})PdCl]_2$ (7.6 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1e** (309.4 mg, 1 mmol), MeOH (256.1 mg, 8 mmol), and toluene (5 mL) afforded **4e** (267.1 mg, 76%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.43 (dt, $J_1$ = 8.4 Hz, $J_2$ = 2.2 Hz, 2 H, Ar-H), 7.25-7.20 (m, 2 H, Ar-H), 3.73 (s, 3 H, $OCH_3$), 2.34 (t, $J$ = 7.4 Hz, 2 H, $CH_2$), 2.15 (s, 3 H, $CH_3$), 1.50-1.39 (m, 2 H, $CH_2$), 1.39-1.18 (m, 6 H, 3 x $CH_2$), 0.85 (t, $J$ = 6.8 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 211.0, 167.5, 134.5, 131.5, 127.5, 121.3, 103.9, 102.4, 52.1, 31.6, 29.0, 28.8, 27.9, 22.6, 16.3, 14.0; MS (70 eV, EI) *m/z* (%): 352 ($M^+$($^{81}$Br), 1.21), 350 ($M^+$($^{79}$Br), 1.37), 142 (100); IR (neat): $\nu$ = 2932, 2851, 1936, 1704, 1435, 1250, 1075, 1007 cm$^{-1}$; HRMS calcd for $C_{18}H_{23}O_2{}^{79}Br$ [$M^+$]: 350.0881, found: 350.0885.

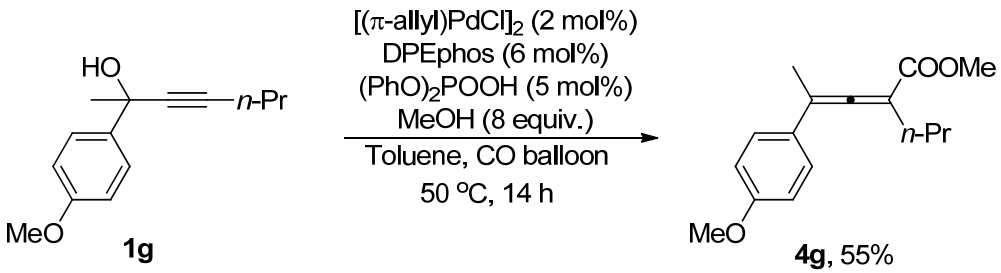
**(6) Preparation of methyl 2-butyl-4-(4-chlorophenyl)-2,3-pentadienoate (4f) (zwl-8-87)**




The reaction of $[(\pi\text{-allyl})PdCl]_2$ (7.6 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1f** (236.8 mg, 1 mmol), MeOH (512.7 mg, 16 mmol), and toluene (5 mL) afforded **4f** (231.4 mg, 83%) (8% of **1f** remained based $^1$H NMR analysis of the crude product) as a white solid [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: M.p. 47-48 °C (petroleum ether/ethyl acetate); $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.30 (s, 4 H, Ar-H), 3.73 (s, 3 H, $OCH_3$), 2.35 (t, $J$ =

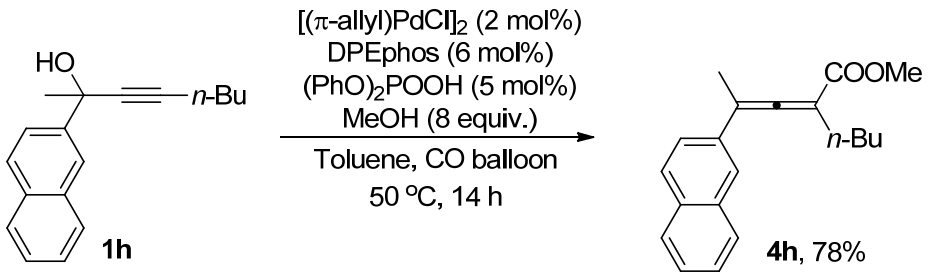
7.6 Hz, 2 H, $CH_2$), 2.15 (s, 3 H, $CH_3$), 1.50-1.29 (m, 4 H, 2 x $CH_2$), 0.88 (t, $J$ = 7.4 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 211.0, 167.5, 134.0, 133.1, 128.6, 127.2, 103.8, 102.3, 52.1, 30.1, 28.6, 22.2, 16.4, 13.8; MS (70 eV, EI) *m/z* (%): 280 ($M^+$($^{37}$Cl) , 0.88), 278 ($M^+$($^{35}$Cl) , 2.13), 177 (100); IR (neat): $\nu$ = 2935, 2859, 1937, 1703, 1435, 1264, 1237, 1081 cm$^{-1}$; Anal. Calcd. for $C_{16}H_{19}ClO_2$: C 68.93, H 6.87; found C 69.09, H 7.07.

**(7) Preparation of methyl 2-propyl-4-(4-methoxylphenyl)-2,3-pentadienoate (4g) (zwl-8-132)**



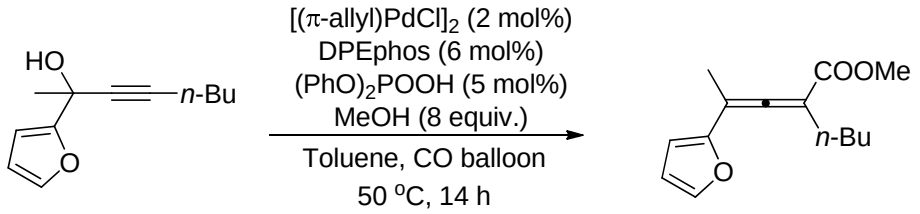

The reaction of [(π-allyl)PdCl]$_2$ (7.5 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1g** (218.4 mg, 1 mmol), MeOH (256.1 mg, 8 mmol), and toluene (5 mL) afforded **4g** (143.3 mg, 55%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.27 (m, 2 H, Ar-H), 6.92-6.84 (m, 2 H, Ar-H), 3.80 (s, 3 H, $OCH_3$), 3.72 (s, 3 H, $OCH_3$), 2.32 (t, $J$ = 7.4 Hz, 2 H, $CH_2$), 2.15 (s, 3 H, $CH_3$), 1.55-1.42 (m, 2 H, $CH_2$), 0.93 (t, $J$ = 7.6 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 210.9, 167.8, 159.0, 127.5, 127.1, 113.9, 104.1, 101.6, 55.2, 52.0, 31.1, 21.3, 16.5, 13.7; MS (70 eV, EI) *m/z* (%): 261 ($M^+$+1, 8.26), 260 ($M^+$, 37.48), 173 (100); IR (neat): $\nu$ = 2956, 2838, 1942, 1710, 1606, 1509, 1244, 1177, 1116, 1031 cm$^{-1}$; HRMS calcd for $C_{16}H_{20}O_3$ [$M^+$]: 260.1412, found: 260.1415.

**(8) Preparation of methyl 2-butyl-4-naphthyl-2,3-pentadienoate (4h) (zwl-8-97)**



The reaction of [(π-allyl)PdCl]$_2$ (7.5 mg, 0.02 mmol), DPEphos (32.5 mg, 0.06 mmol), (PhO)$_2$POOH (12.6 mg, 0.05 mmol), **1h** (252.1 mg, 1 mmol), MeOH (256.7 mg, 8 mmol), and toluene (5 mL) afforded **4h** (229.3 mg, 78%) as a white solid [eluent: petroleum ether (b.p. 60-90 $^{o}$C)/ethyl ether = 100/1]: M.p. 55-56 °C (petroleum ether/ethyl acetate); $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 7.85-7.71 (m, 4 H, Ar-H), 7.55-7.38 (m, 3 H, Ar-H), 3.73 (s, 3 H, $OCH_3$), 2.40 (t, *J* = 7.8 Hz, 2 H, $CH_2$), 2.29 (s, 3 H, $CH_3$), 1.54-1.43 (m, 2 H, $CH_2$), 1.43-1.31 (m, 2 H, $CH_2$), 0.89 (t, *J* = 7.2 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 211.8, 167.8, 133.5, 132.8, 132.6, 128.0, 127.9, 127.5, 126.2, 126.0, 124.8, 123.9, 104.9, 102.2, 52.1, 30.2, 28.8, 22.3, 16.4, 13.8; MS (70 eV, EI) *m/z* (%): 295 ($M^+$+1, 1.93), 294 ($M^+$, 8.46), 193 (100); IR (neat): *v* = 2950, 2925, 1940, 1713, 1432, 1237, 1117, 1086, 1059 cm$^{-1}$; Anal. Calcd. for $C_{20}H_{22}O_2$: C 81.60, H 7.53; found C 81.72, H 7.63.

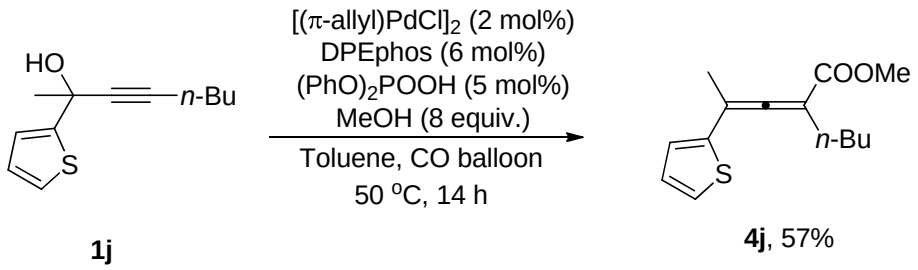
**(9) Preparation of methyl 2-butyl-4-furyl-2,3-pentadienoate (4i) (zwl-8-100)**




**1i** **4i**, 44%

The reaction of [(π-allyl)PdCl]$_2$ (7.6 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), (PhO)$_2$POOH (12.5 mg, 0.05 mmol), **1i** (192.1 mg, 1 mmol), MeOH (256.1 mg, 8 mmol), and toluene (5 mL) afforded **4i** (103.0 mg, 44%) as an oil [eluent: petroleum ether (b.p. 60-90 $^{o}$C)/ethyl ether = 100/1]: $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 1.6 Hz, 1 H, Ar-H), 6.41 (dd, $J_1$ = 3.2 Hz, $J_2$ = 2.0 Hz, 1 H, Ar-H), 6.28 (d, *J* = 3.2 Hz, 1 H, Ar-H), 3.72 (s, 3 H, $OCH_3$), 2.45-2.23 (m, 2 H, $CH_2$), 2.09 (s, 3 H, $CH_3$), 1.50-1.30 (m, 4 H, 2 x $CH_2$), 0.89 (t, *J* = 7.2 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 210.4, 167.3, 149.3, 142.5, 111.4, 107.3, 103.1, 97.2, 52.1, 30.0, 28.9, 22.2, 15.5, 13.8; MS (70 eV, EI) *m/z* (%): 235 ($M^+$+1, 3.78), 234 ($M^+$, 22.33), 192 (100); IR (neat): *v* = 2955, 2928, 1946, 1713, 1435, 1263, 1159, 1077 cm$^{-1}$; HRMS calcd for $C_{14}H_{18}O_3$ [$M^+$]: 234.1256, found: 234.1257.

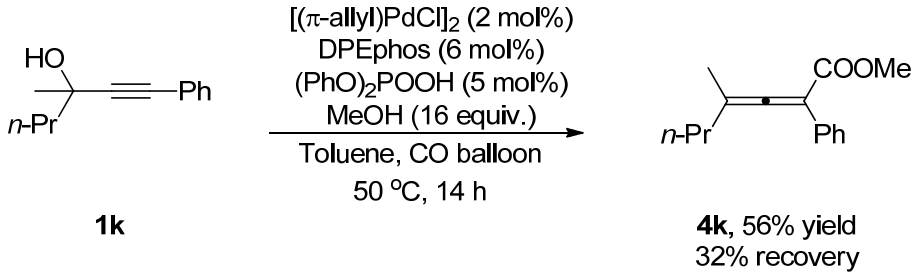
**(10) Preparation of methyl 2-butyl-4-thienyl-2,3-pentadienoate (4j) (zwl-8-101)**




**1j** **4j**, 57%

The reaction of $[(\pi\text{-allyl})PdCl]_2$ (7.5 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.5 mg, 0.05 mmol), **1j** (208.4 mg, 1 mmol), MeOH (256.1 mg, 8 mmol), and toluene (5 mL) afforded **4j** (142.7 mg, 57%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, *J* = 4.0 Hz, 1 H, Ar-H), 7.02-6.94 (m, 2 H, Ar-H), 3.72 (s, 3 H, $OCH_3$), 2.42-2.26 (m, 2 H, $CH_2$), 2.19 (s, 3 H, $CH_3$), 1.52-1.31 (m, 4 H, 2 x $CH_2$), 0.90 (t, *J* = 7.2 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 210.4, 167.3, 140.1, 127.5, 125.2, 123.9, 102.4, 100.6, 52.1, 30.1, 28.9, 22.3, 17.4, 13.9; MS (70 eV, EI) *m/z* (%): 250 ($M^+$, 6.02), 149 (100); IR (neat): *v* = 2955, 2928, 2860, 1944, 1713, 1434, 1263, 1242, 1119, 1081, 1051 $cm^{-1}$; HRMS calcd for $C_{14}H_{18}O_2S$ [$M^+$]: 250.1028, found: 250.1026.

**(11) Preparation of methyl 2-phenyl-4-methyl-2,3-heptadienoate (4k) (zwl-8-146)**

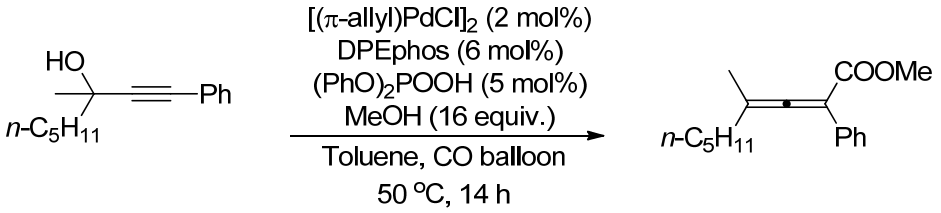



**1k** **4k**, 56% yield
32% recovery

The reaction of $[(\pi\text{-allyl})PdCl]_2$ (7.5 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1k** (188.4 mg, 1 mmol), MeOH (512.7 mg, 16 mmol), and toluene (5 mL) afforded **4k** (131.4 mg, 56%, 98% purity) (32% of **1f** was observed by $^1$H NMR analysis of crude product) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.41 (m, 2 H, Ar-H), 7.37-7.29 (m, 2 H, Ar-H), 7.28-7.18 (m, 1 H, Ar-H), 3.78 (s, 3 H, $OCH_3$), 2.20-2.07 (m, 2 H, $CH_2$), 1.87 (s, 3 H, $CH_3$), 1.60-1.46 (m, 2 H, $CH_2$), 0.93 (t, *J* = 7.4 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 209.4, 167.4, 134.0, 128.3,

128.1, 127.1, 105.0, 101.8, 52.0, 35.7, 20.5, 18.0, 13.7; MS (70 eV, EI) *m/z* (%): 231 ($M^+$+1, 5.20), 230 ($M^+$, 29.97), 128 (100); IR (neat): $\nu$ = 2956, 2873, 1949, 1715, 1434, 1274, 1196, 1175, 1040, 1022 $cm^{-1}$; HRMS calcd for $C_{15}H_{18}O_2$ [$M^+$]: 230.1307, found: 230.1313.

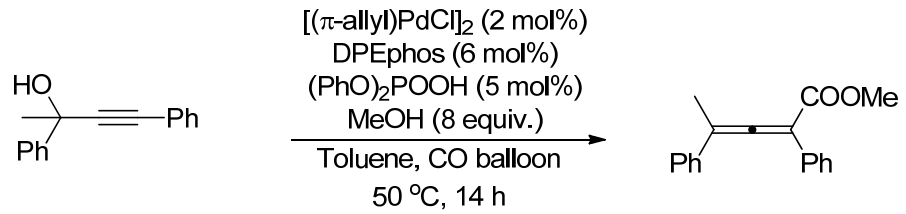
**(12) Preparation of methyl 2-phenyl-4-methyl-2,3-nonadienoate (4l) (zwl-8-147)**




**1l** **4l**, 53% yield
44% recovery

The reaction of [(π-allyl)PdCl]$_2$ (7.5 mg, 0.02 mmol), DPEphos (32.1 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1l** (216.1 mg, 1 mmol), MeOH (512.7 mg, 16 mmol), and toluene (5 mL) afforded **4l** (139.4 mg, 53%, 98% purity) (44% of **1f** remained based $^1$H NMR analysis of the crude product) as an oil [eluent: petroleum ether (b.p. 60-90 $^o$C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 6.8 Hz, 2 H, Ar-H), 7.32 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.28-7.17 (m, 1 H, Ar-H), 3.78 (s, 3 H, $OCH_3$), 2.23-2.07 (m, 2 H, $CH_2$), 1.87 (s, 3 H, $CH_3$), 1.58-1.45 (m, 2 H, $CH_2$), 1.39-1.21 (m, 4 H, 2 x $CH_2$), 0.85 (t, *J* = 7.0 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 209.4, 167.4, 134.0, 128.3, 128.1, 127.1, 105.1, 101.7, 52.0, 33.5, 31.3, 26.8, 22.4, 18.0, 14.0; MS (70 eV, EI) *m/z* (%): 259 ($M^+$+1, 2.80), 258 ($M^+$, 13.95), 143 (100); IR (neat): $\nu$ = 2926, 2858, 1949, 1716, 1434, 1273, 1195, 1175, 1023 $cm^{-1}$; HRMS calcd for $C_{17}H_{22}O_2$ [$M^+$]: 258.1620, found: 258.1618.

**(13) Preparation of methyl 2,4-diphenyl-2,3-pentadienoate (4m) (zwl-7-135)**

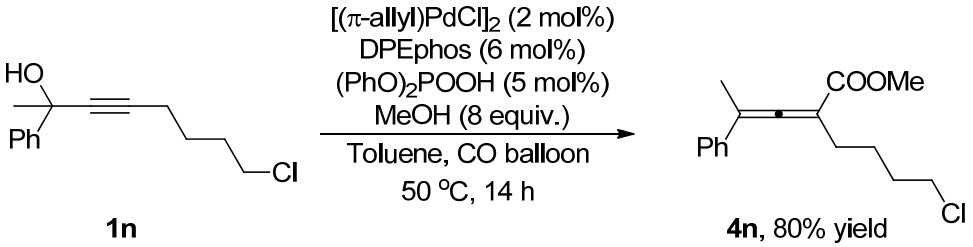



**1m** **4m**, 81%

The reaction of [(π-allyl)PdCl]$_2$ (7.6 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1m** (222.4 mg, 1 mmol), MeOH (256.1

mg, 8 mmol), and toluene (5 mL) afforded **4m** (214.6 mg, 81%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.45 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.38-7.22 (m, 6 H, Ar-H), 3.80 (s, 3 H, $OCH_3$), 2.28 (s, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 213.7, 166.5, 134.4, 132.8, 128.6, 128.3, 127.8, 127.6, 126.1, 106.0, 104.3, 52.3, 16.2; MS (70 eV, EI) *m/z* (%): 265 ($M^+$+1, 14.63), 264 ($M^+$, 78.23), 205 (100); IR (neat): *v* = 1935, 1712, 1492, 1434, 1369, 1278, 1199, 1175, 1018 cm$^{-1}$; HRMS calcd for $C_{18}H_{16}O_2$ [$M^+$]: 264.1150, found: 264.1152.

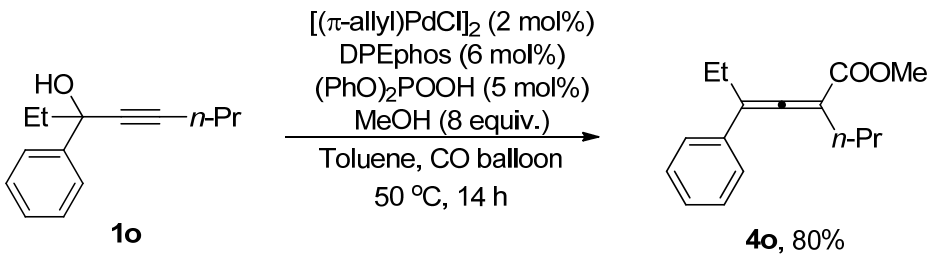
**(14) Preparation of methyl 2-(4-chlorobutyl)-4-phenyl-2,3-pentadienoate (4n) (zwl-8-145)**




**1n** **4n**, 80% yield

The reaction of [(π-allyl)PdCl]$_2$ (7.5 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1n** (236.7 mg, 1 mmol), MeOH (256.1 mg, 8 mmol), and toluene (5 mL) afforded **4n** (223.1 mg, 80%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.32 (m, 4 H, Ar-H), 7.28-7.22 (m, 1 H, Ar-H), 3.73 (s, 3 H, $OCH_3$), 3.50 (t, *J* = 6.6 Hz, 2 H, $CH_2$), 2.39 (t, *J* = 7.6 Hz, 2 H, $CH_2$), 2.19 (s, 3 H, $CH_3$), 1.87-1.75 (m, 2 H, $CH_2$), 1.68-1.57 (m, 2 H, $CH_2$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 211.1, 167.6, 135.1, 128.5, 127.5, 126.0, 105.1, 101.3, 52.2, 44.7, 32.0, 28.2, 25.2, 16.5; MS (70 eV, EI) *m/z* (%): 280 ($M^+$($^{37}$Cl) , 1.50), 278 ($M^+$($^{35}$Cl) , 4.70), 141 (100); IR (neat): *v* = 2950, 2864, 1943, 1710, 1494, 1434, 1252, 1098, 1066 cm$^{-1}$; HRMS calcd for $C_{16}H_{19}O_2{}^{35}Cl$ [$M^+$]: 278.1074, found: 278.1076.

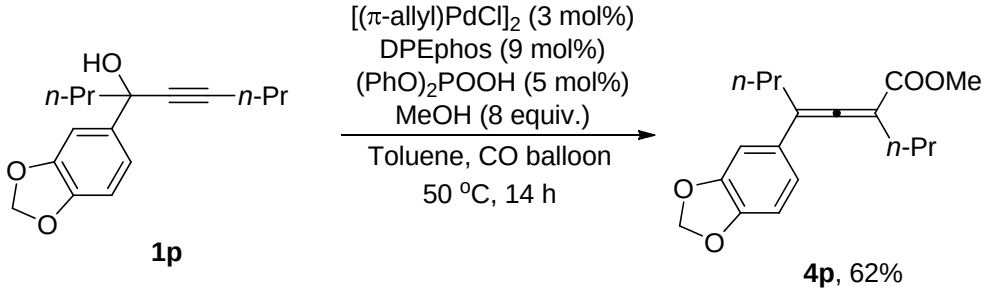
**(15) Preparation of methyl 2-propyl-4-phenyl-2,3-hexadienoate (4o) (zwl-8-25)**




**1o** **4o**, 80%

The reaction of $[(\pi\text{-allyl})PdCl]_2$ (7.5 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1o** (202.4 mg, 1 mmol), MeOH (256.1 mg, 8 mmol), and toluene (5 mL) afforded **4o** (195.6 mg, 80%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.42-7.28 (m, 4 H, Ar-H), 7.26-7.20 (m, 1 H, Ar-H), 3.72 (s, 3 H, $OCH_3$), 2.60-2.48 (m, 2 H, $CH_2$), 2.38-2.29 (m, 2 H, $CH_2$), 1.57-1.42 (m, 2 H, $CH_2$), 1.16 (t, $J$ = 7.4 Hz, 3 H, $CH_3$), 0.94 (t, $J$ = 7.2 Hz, 3 H, $CH_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 210.9, 168.0, 135.2, 128.5, 127.3, 126.2, 111.5, 103.8, 52.0, 31.1, 23.1, 21.5, 13.9, 12.3; MS (70 eV, EI) *m/z* (%): 245 ($M^+$+1, 10.55), 244 ($M^+$, 56.69), 91 (100); IR (neat): $\nu$ = 2962, 2931, 1937, 1712, 1493, 1434, 1251, 1129 $cm^{-1}$; HRMS calcd for $C_{16}H_{20}O_2$ [$M^+$]: 244.1463, found: 244.1465.

**(16) Preparation of methyl 2-propyl-4-(3,4-methylenedioxy)phenyl-2,3-hepta-dienoate (4p) (hcf-1-111)**

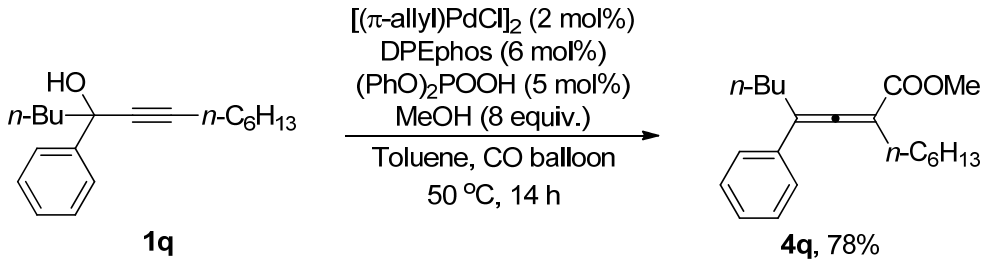



**1p** **4p**, 62%

The reaction of $[(\pi\text{-allyl})PdCl]_2$ (11.1 mg, 0.03 mmol), DPEPhos (48.5 mg, 0.09 mmol), $(PhO)_2POOH$ (12.5 mg, 0.05 mmol), **1p** (260.6 mg, 1 mmol), MeOH (257.1 mg, 8 mmol), and toluene (5 mL) afforded **4p** (187.3 mg, 62%) via double chromatography on silica gel as a white solid [first round eluent: petroleum ether (b.p. 60-90 °C)/ethyl acetate = 200/1 (1 L) to petroleum ether (b.p. 60-90 °C)/ethyl acetate = 150/1 (1.5 L) to petroleum ether (b.p. 60-90 °C)/ethyl acetate = 100/1 (0.5 L);

second round eluent: petroleum ether (b.p. 60-90 °C)/ethyl acetate = 150/1)]: M.p. 48-50 °C (petroleum ether/ethyl acetate); $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.90-6.83 (m, 2 H, Ar-H), 6.82-6.74 (m, 1 H, Ar-H), 5.95 (s, 2 H, $OCH_2$), 3.72 (s, 3 H, $OCH_3$), 2.44 (t, *J* = 7.4 Hz, 2 H, $CH_2$), 2.31 (t, *J* = 7.8 Hz, 2 H, $CH_2$), 1.63-1.40 (m, 4 H, 2 x $CH_2$), 1.05-0.85 (m, 6 H, 2 x $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 210.9, 167.9, 147.9, 146.9, 129.1, 119.5, 109.4, 108.2, 106.9, 102.9, 101.1, 52.0, 32.4, 31.2, 21.5, 20.9, 13.9, 13.8; MS (70 eV, EI) *m/z* (%): 303 ($M^+$+1, 15.22), 302 ($M^+$, 77.74), 273 (100); IR (neat): *v* = 2957, 2930, 1933, 1711, 1501, 1434, 1243, 1120, 1037 cm$^{-1}$; Anal. Calcd. for $C_{18}H_{22}O_4$: C 71.50, H 7.33; found C 71.61, H 7.34.

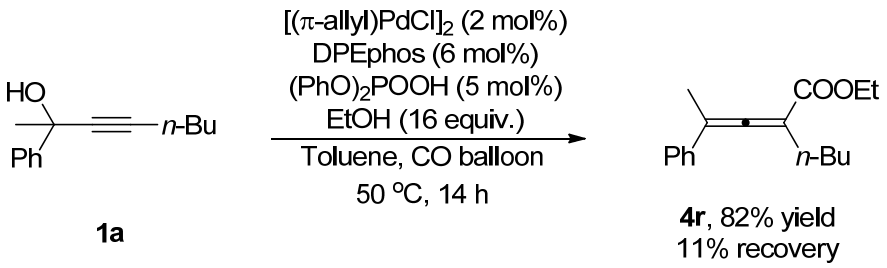
**(17) Preparation of methyl 2-(*n*-hexyl)-4-phenyl-2,3-octadienoate (4q) (hcf-1-103)**




**1q** **4q**, 78%

The reaction of [(π-allyl)PdCl]$_2$ (7.5 mg, 0.02 mmol), DPEPhos (32.3 mg, 0.06 mmol), $(PhO)_2POOH$ (12.5 mg, 0.05 mmol), **1q** (272.6 mg, 1 mmol), MeOH (257.0 mg, 8 mmol), and toluene (5 mL) afforded **4q** (245.3 mg, 78%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.28 (m, 4 H, Ar-H), 7.27-7.20 (m, 1 H, Ar-H), 3.72 (s, 3 H, $OCH_3$), 2.52 (t, *J* = 7.4 Hz, 2 H, $CH_2$), 2.34 (t, *J* = 7.6 Hz, 2 H, $CH_2$), 1.58-1.37 (m, 6 H, 3 x $CH_2$), 1.37-1.18 (m, 6 H, 3 x $CH_2$), 0.93 (t, *J* = 7.4 Hz, 3 H, $CH_3$), 0.84 (t, *J* = 7.0 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 211.1, 168.1, 135.3, 128.5, 127.3, 126.3, 109.8, 103.1, 52.0, 31.6, 29.9, 29.8, 29.1, 29.0, 28.2, 22.6, 22.4, 14.0, 13.9; MS (70 eV, EI) *m/z* (%): 315 ($M^+$+1, 2.94), 314 ($M^+$, 11.34), 129 (100); IR (neat): *v* = 2954, 2926, 2857, 1940, 1714, 1434, 1249, 1126 cm$^{-1}$; HRMS calcd for $C_{21}H_{30}O_2$ [$M^+$]: 314.2246, found: 314.2248.

**(18) Preparation of ethyl 2-butyl-4-phenyl-2,3-pentadienoate (4r) (zwl-8-113)**

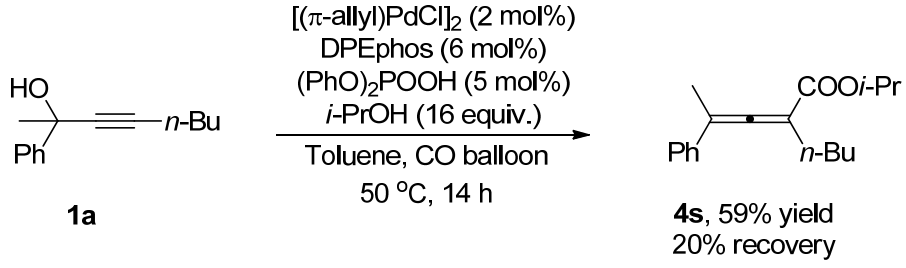



**1a**

**4r**, 82% yield
11% recovery

The reaction of $[(\pi\text{-allyl})PdCl]_2$ (7.6 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1a** (202.4 mg, 1 mmol), EtOH (737.5 mg, 16 mmol), and toluene (5 mL) afforded **4r** (212.0 mg, 82%) (11% of **1a** remained based $^1H$ NMR analysis of the crude product) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.42-7.29 (m, 4 H, Ar-H), 7.28-7.18 (m, 1 H, Ar-H), 4.19 (q, *J* = 7.1 Hz, 2 H, $OCH_2$), 2.35 (t, *J* = 7.4 Hz, 2 H, $CH_3$), 2.17 (s, 3 H, $CH_3$), 1.51-1.40 (m, 2 H, $CH_2$), 1.40-1.29 (m, 2 H, $CH_2$), 1.24 (t, *J* = 7.2 Hz, 3 H, $CH_3$), 0.88 (t, *J* = 7.4 Hz, 3 H, $CH_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 211.1, 167.4, 135.7, 128.4, 127.2, 125.9, 104.5, 102.3, 60.8, 30.2, 28.7, 22.3, 16.4, 14.3, 13.9; MS (70 eV, EI) *m/z* (%): 258 ($M^+$, 2.08), 143 (100); IR (neat): *v* = 2956, 2860, 1944, 1707, 1494, 1445, 1259, 1067, 1025 $cm^{-1}$; HRMS calcd for $C_{17}H_{22}O_2$ [$M^+$]: 258.1620, found: 258.1619.

**(19) Preparation of isopropyl 2-butyl-4-phenyl-2,3-pentadienoate (4s) (zwl-8-114)**



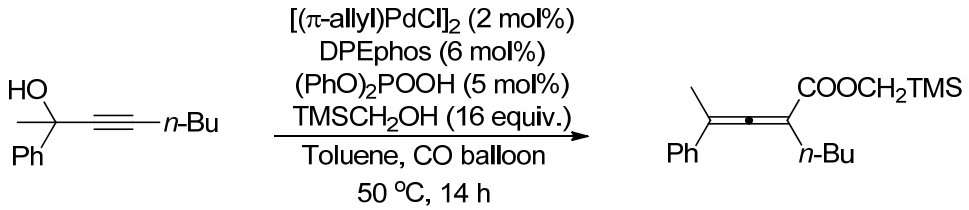

**1a**

**4s**, 59% yield
20% recovery

The reaction of $[(\pi\text{-allyl})PdCl]_2$ (7.6 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1a** (202.4 mg, 1 mmol), *i*-PrOH (961.6 mg, 16 mmol), and toluene (5 mL) afforded **4s** (166.2 mg, 59%, 96% purity) (20% of **1a** remained based $^1H$ NMR analysis of the crude product) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.42-7.29 (m, 4 H, Ar-H), 7.28-7.20 (m, 1 H, Ar-H), 5.15-4.99 (m, 1 H, OCH), 2.33 (t, *J* = 7.4 Hz, 2 H, $CH_2$), 2.17 (s, 3 H, $CH_3$), 1.49-1.28 (m, 4 H, 2 x $CH_2$), 1.28-1.18 (m,

6 H, 2 x $CH_3$), 0.88 (t, $J$ = 7.4 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 211.1, 166.9, 135.9, 128.4, 127.2, 126.0, 104.4, 102.7, 68.1, 30.2, 28.6, 22.3, 21.9, 21.8, 16.4, 13.9; MS (70 eV, EI) *m/z* (%): 272 ($M^+$, 1.63), 143 (100); IR (neat): $\nu$ = 2957, 2928, 2860, 1944, 1704, 1494, 1464, 1260, 1106, 1026 $cm^{-1}$; HRMS calcd for $C_{18}H_{24}O_2$ [$M^+$]: 272.1776, found: 272.1780.

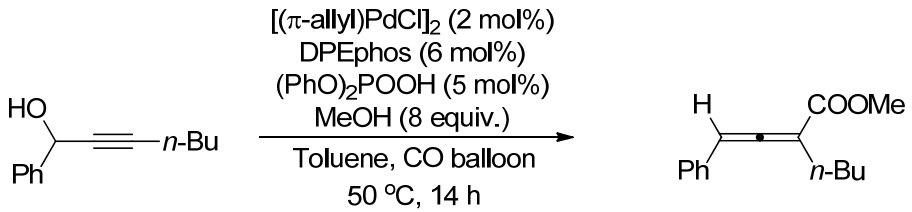
**(20) Preparation of trimethylsilylmethyl 2-butyl-4-phenyl-2,3-pentadienoate (4t) (zwl-8-115)**




**1a** **4t**, 82% yield

The reaction of [(π-allyl)PdCl]$_2$ (7.6 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1a** (202.4 mg, 1 mmol), $TMSCH_2OH$ (1.6676 g, 16 mmol), and toluene (5 mL) afforded **4t** (269.1 mg, 82%, 96% purity) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.16 (m, 4 H, Ar-H), 7.15-7.08 (m, 1 H, Ar-H), 3.70 (dd, $J_1$ = 15.6 Hz, $J_2$ = 14.0 Hz, 2 H, $OCH_2$), 2.23 (t, $J$ = 7.4 Hz, 2 H, $CH_2$), 2.05 (s, 3 H, $CH_3$), 1.40-1.30 (m, 2 H, $CH_2$), 1.30-1.19 (m, 2 H, $CH_2$), 0.76 (t, $J$ = 7.2 Hz, 3 H, $CH_3$), -0.11 (s, 9 H, 3 x $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 211.2, 168.1, 135.6, 128.3, 127.2, 125.9, 104.3, 102.2, 57.8, 30.2, 28.6, 22.3, 16.3, 13.8, -3.3; MS (70 eV, EI) *m/z* (%): 317 ($M^+$+1, 1.27), 316 ($M^+$, 6.18), 143 (100); IR (neat): $\nu$ = 2956, 2927, 1944, 1710, 1494, 1291, 1249, 1067 $cm^{-1}$; HRMS calcd for $C_{19}H_{28}O_2Si$ [$M^+$]: 316.1859, found: 316.1855.

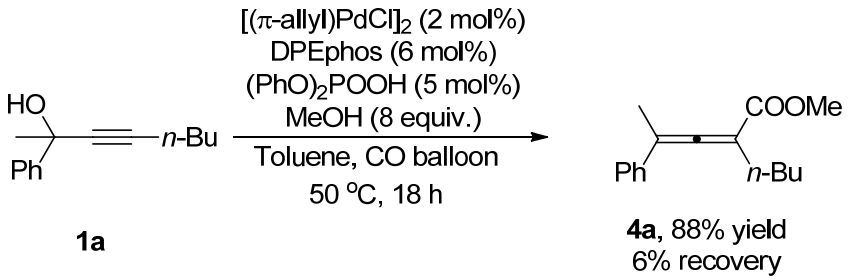
**(21) Preparation of methyl 2-butyl-4-phenyl-2,3-butadienoate (4u) (zwl-8-161)**




**1u** **4u**, 68% yield
9% recovery

The reaction of [(π-allyl)PdCl]$_2$ (7.5 mg, 0.02 mmol), DPEphos (32.5 mg, 0.06 mmol), (PhO)$_2$POOH (12.5 mg, 0.05 mmol), **1u** (188.4 mg, 1 mmol), MeOH (256.1 mg, 8 mmol), and toluene (5 mL) afforded **4u**[5] (156.7 mg, 68%) (9% of **1u** remained based $^1$H NMR analysis of the crude product) as an oil [eluent: petroleum ether (b.p. 60-90 $^o$C)/ethyl ether = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.21 (m, 5 H, Ar-H), 6.54 (t, *J* = 2.8 Hz, 1 H, =CH), 3.74 (s, 3 H, $OCH_3$), 2.46-2.29 (m, 2 H, $CH_2$), 1.54-1.43 (m, 2 H, $CH_2$), 1.43-1.32 (m, 2 H, $CH_2$), 0.89 (t, *J* = 7.2 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 212.1, 167.3, 132.5, 128.8, 127.7, 127.2, 104.3, 98.3, 52.3, 30.1, 28.6, 22.3, 13.9; MS (70 eV, EI) *m/z* (%): 230 ($M^+$, 2.54), 129 (100); IR (neat): *v* = 2955, 2929, 2860, 1943, 1714, 1434, 1263, 1243, 1119 cm$^{-1}$.

## 5. Gram scale synthesis of methyl 2-butyl-4-phenyl-2,3-pentadienoate (4a) (zwl-9-139)

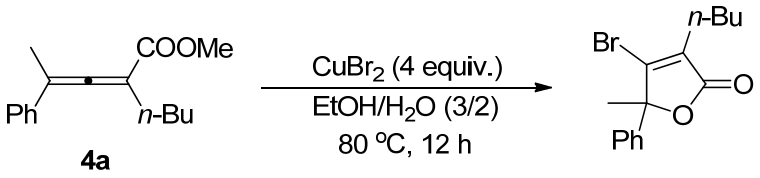



To a flame-dried Schlenk tube were added [(π-allyl)PdCl]$_2$ (37.4 mg, 0.1 mmol), DPEphos (161.7 mg, 0.3 mmol), (PhO)$_2$POOH (62.7 mg, 0.25 mmol), **1a** (1.0116 g, 5 mmol), MeOH (1.2817 g, 40 mmol), and toluene (20 mL) sequentially. The resulting mixture was then frozen with a liquid nitrogen bath, degassed to remove the argon inside completely, and refilled with CO with a balloon of CO for three times. Then the resulting mixture was stirred at 50 $^o$C with a balloon of CO for 18 h. After that, the resulting mixture was diluted with 10 mL of ethyl acetate, filtered through a short column silica gel (3.5 cm) eluted with ethyl acetate (50 mL), and concentrated. The residue was purified by column chromatography on silica gel to afford **4a** (1.0752 g, 88%) (6% of **1a** remained based $^1$H NMR analysis of the crude product) as an oil [eluent: petroleum ether (b.p. 60-90 $^o$C)/ethyl acetate = 100/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.31 (m, 4 H, Ar-H), 7.29-7.21 (m, 1 H, Ar-H), 3.73 (s, 3 H, $OCH_3$),

2.35 (t, $J$ = 7.6 Hz, 2 H, $CH_3$), 2.18 (s, 3 H, $CH_3$), 1.50-1.40 (m, 2 H, $CH_2$), 1.40-1.30 (m, 2 H, $CH_2$), 0.88 (t, $J$ = 7.4 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 211.1, 167.9, 135.4, 128.5, 127.3, 125.9, 104.6, 102.0, 52.1, 30.1, 28.7, 22.3, 16.4, 13.9.

## 6. Synthetic applications

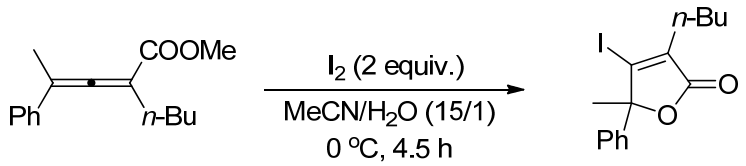
### (1) Preparation of 5-methyl-5-phenyl-4-bromo-3-butylfuran-2(*5H*)-one (5) (zwl-9-147) [6]




**4a** **5**, 83%

To a Schlenk tube were added $CuBr_2$ (446.8 mg, 2 mmol), **4a** (122.1 mg, 0.5 mmol), EtOH (3 mL), and $H_2O$ (2 mL) sequentially. Then the Schlenk tube was placed in an oil bath pre-heated at 80 °C and stirred for 12 h. To the mixture was added $H_2O$ (5 mL). After extraction with ethyl acetate (5 mL x 3), the organic layer was then washed with brine (10 mL) and dried over anhydrous $Na_2SO_4$. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel to afford **5** (128.2 mg, 83%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl ether = 50/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.31 (m, 5 H, Ar-H), 2.36 (t, $J$ = 7.6 Hz, 2 H, $CH_2$), 1.92 (s, 3 H, $CH_3$), 1.62-1.51 (m, 2 H, $CH_2$), 1.42-1.30 (m, 2 H, $CH_2$), 0.93 (t, $J$ = 7.4 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 170.5, 150.5, 137.2, 131.3, 128.8, 128.6, 125.5, 88.1, 29.0, 24.9, 23.9, 22.3, 13.7; MS (70 eV, EI) *m/z* (%): 310 ($M^+$($^{81}$Br), 5.74), 308 ($M^+$($^{79}$Br), 5.68), 229 (100); IR (neat): $\nu$ = 2957, 2930, 2862, 1757, 1651, 1448, 1312, 1142, 1079 $cm^{-1}$; HRMS calcd for $C_{15}H_{17}O_2{}^{79}Br$ [$M^+$]: 308.0412, found: 308.0416.

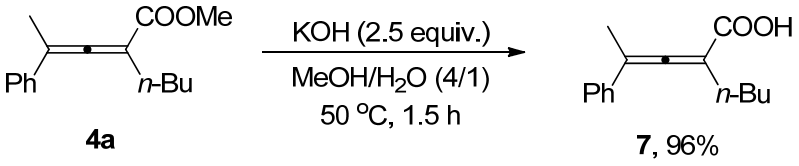
### (2) Preparation of 5-methyl-5-phenyl-4-iodo-3-butylfuran-2(*5H*)-one (6) (zwl-9-150) [7]




**4a** **6**, 93%

To a Schlenk tube were added iodine (253.9 mg, 1 mmol), **4a** (122.1 mg, 0.5 mmol), and MeCN/$H_2O$ (15:1) (2 mL) sequentially. Then the mixture was stirred at 0 $^oC$ for 4.5 h. After quenching with a saturated aqueous solution of $Na_2S_2O_3$ (5 mL) and extracted with diethyl ether (5 mL x 3), the organic layer was washed with brine (10 mL) and dried over 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** (165.6 mg, 93%) as a white solid [eluent: petroleum ether (b.p. 60-90 $^oC$)/ethyl ether = 100/1): M.p. 66-67 °C (petroleum ether/ethyl acetate); $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.43-7.27 (m, 5 H, Ar-H), 2.37 (t, *J* = 7.4 Hz, 2 H, $CH_2$), 1.89 (s, 3 H, $CH_3$), 1.65-1.48 (m, 2 H, $CH_2$), 1.45-1.30 (m, 2 H, $CH_2$), 0.94 (t, *J* = 7.2 Hz, 3 H, $CH_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 170.2, 137.9, 137.4, 130.6, 128.8, 128.6, 125.7, 89.3, 29.2, 27.4, 24.3, 22.4, 13.8; MS (70 eV, EI) *m/z* (%): 357 ($M^+$+1, 1.41), 356 ($M^+$, 8.06), 229 (100); IR (neat): *v* = 2950, 2926, 2866, 1732, 1630, 1448, 1303, 1222, 1146, 1039 $cm^{-1}$; Anal. Calcd. for $C_{15}H_{17}IO_2$: C 50.58, H 4.81; found C 50.59, H 4.76.

**(3) Preparation of 2-butyl-4-phenyl-2,3-pentadienoic acid (7) (zwl-9-145)** [8]

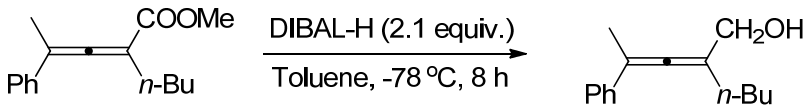



**4a** **7**, 96%

To a Schlenk tube were added KOH (70.3 mg, 1.25 mmol), **4a** (122.2 mg, 0.5 mmol), MeOH (1 mL), and $H_2O$ (0.25 mL) sequentially. Then the Schlenk tube was placed in an oil bath pre-heated at 50 $^oC$ and stirred for 1.5 h. To the mixture were added $H_2O$ (5 mL) and 3 N HCl (10 mL) sequentially. After extraction with ethyl acetate (5 mL x 3), the organic layer was washed with brine (10 mL) and dried over anhydrous $Na_2SO_4$. After filtration and concentration under reduced pressure, the

crude product was purified by column chromatography on silica gel to afford **7** (110.5 mg, 96%) as a white solid [eluent: DCM (200 mL) to DCM/MeOH = 20:1]: M.p. 123.7-124.4 °C (petroleum ether/ethyl acetate); $^1$H NMR (400 MHz, DMSO-$D_6$): δ = 12.41 (s, 1 H, COOH), 7.44-7.33 (m, 4 H, Ar-H), 7.33-7.23 (m, 1 H, Ar-H), 2.24 (t, *J* = 7.2 Hz, 2 H, $CH_2$), 2.12 (s, 3 H, $CH_3$), 1.45-1.24 (m, 4 H, 2 x $CH_2$), 0.84 (t, *J* = 7.0 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 212.6, 173.0, 135.0, 128.5, 127.6, 126.0, 105.2, 101.8, 30.2, 28.3, 22.3, 16.3, 13.8; MS (70 eV, EI) *m/z* (%): 230 ($M^+$, 3.96), 143 (100); IR (neat): *v* = 3500-2200 (br), 1935, 1675, 1466, 1420, 1280, 1249 $cm^{-1}$; Anal. Calcd. for $C_{15}H_{18}O_2$: C 78.23, H 7.88; found C 78.20, H 7.94.

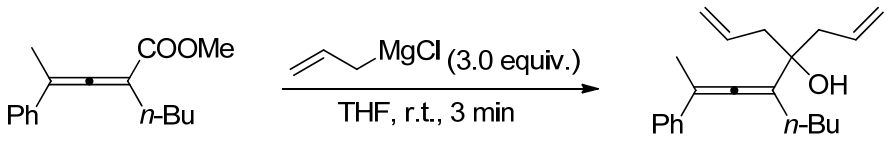
**(4) Preparation of 2-butyl-4-phenyl-2,3-pentadien-1-ol (8) (zwl-9-146)[5]**




**4a** **8**, 70%

To a flame-dried Schlenk tube were added **4a** (122.2 mg, 0.5 mmol), toluene (5 mL), and DIBAL-H (1.0 M in hexane, 1.05 mL, 1.05 mmol, 2.1 equiv.) at -78 °C. After stirring at -78 °C for 8 hours, the reaction was quenched with MeOH (5 mL) and the resulting mixture was warmed up to room temperature. Then $H_2O$ (10 mL) and 1 N HCl (10 mL) were added sequentially. After extraction with ethyl ether (10 mL x 3), the organic layer was washed with brine (10 mL) and dried over anhydrous $Na_2SO_4$. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel to afford **8** (75.7 mg, 70%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl acetate = 20/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.46-7.37 (m, 2 H, Ar-H), 7.36-7.28 (m, 2 H, Ar-H), 7.24-7.17 (m, 1 H, Ar-H), 4.21-4.05 (m, 2 H, $OCH_2$), 2.20-2.02 (m, 5 H, $CH_2$ and $CH_3$), 1.57-1.42 (m, 3 H, $CH_2$ and OH), 1.42-1.31 (m, 2 H, $CH_2$), 0.89 (t, *J* = 7.4 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 199.0, 137.5, 128.3, 126.7, 125.6, 108.0, 104.8, 63.2, 29.8, 29.4, 22.5, 17.4, 13.9; MS (70 eV, EI) *m/z* (%): 216 ($M^+$, 2.14), 143 (100); IR (neat): *v* = 3332, 2926, 2858, 1949, 1598, 1460, 1290, 1010 $cm^{-1}$; HRMS calcd for $C_{15}H_{20}O$ [$M^+$]: 216.1514, found: 216.1516.

**(5) Preparation of 7-phenyl-5-butyl-4-allyl-1,5,6-octatrien-4-ol (9) (zwl-9-155) [9]**

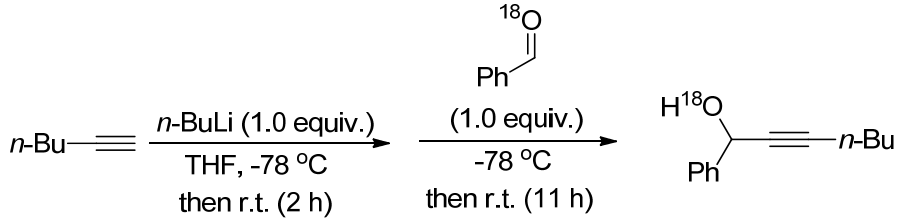



**4a** **9**, 85%

To a flame-dried Schlenk tube were added **4a** (122.1 mg, 0.5 mmol) and THF (5 mL). Then a solution of allyl magnesium chloride (1.0 M in THF, 1.5 mL, 1.5 mmol, 3 equiv.) was added dropwise at room temperature with vigorous stirring. After being stirred for 3 min at room temperature, the reaction mixture was quenched with a saturated aqueous solution of $NH_4Cl$ (2 mL) and extracted with ethyl ether (5 mL x 3). The organic layer was washed subsequently with 1 N HCl (5 mL), saturated $NaHCO_3$ (5 mL), brine (10 mL), and dried over anhydrous $Na_2SO_4$. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel to afford **9** (126.0 mg, 85%) as an oil [eluent: petroleum ether (b.p. 60-90 $^oC$)/ethyl ether = 60/1]: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.48-7.38 (m, 2 H, Ar-H), 7.37-7.26 (m, 2 H, Ar-H), 7.20 (t, *J* = 7.2 Hz, 1 H, Ar-H), 5.98-5.77 (m, 2 H, 2 x =CH), 5.20-5.06 (m, 4 H, 2 x $=CH_2$), 2.50-2.32 (m, 4 H, 2 x $CH_2$), 2.20-2.08 (m, 4 H, OH and $CH_3$), 2.08-1.98 (m, 2 H, $CH_2$), 1.48-1.28 (m, 4 H, 2 x $CH_2$), 0.87 (t, *J* = 7.0 Hz, 3 H, $CH_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 199.6, 137.3, 134.0, 133.8, 128.2, 126.6, 125.6, 118.2, 112.6, 105.4, 75.0, 44.1, 43.9, 29.9, 27.6, 22.7, 17.5, 14.0; MS (70 eV, EI) *m/z* (%): 296 ($M^+$, 2.91), 129 (100); IR (neat): *v* = 3552, 3074, 2955, 2927, 1944, 1639, 1493, 1026 $cm^{-1}$; HRMS calcd for $C_{21}H_{28}O$ [$M^+$]: 296.2140; found 296.2143.

## 7. Mechanistic studies:

### (1) Preparation of 1u-$^{18}$O (zwl-9-170) [1]




**1u-$^{18}$O**, 72% yield
83% $^{18}$O

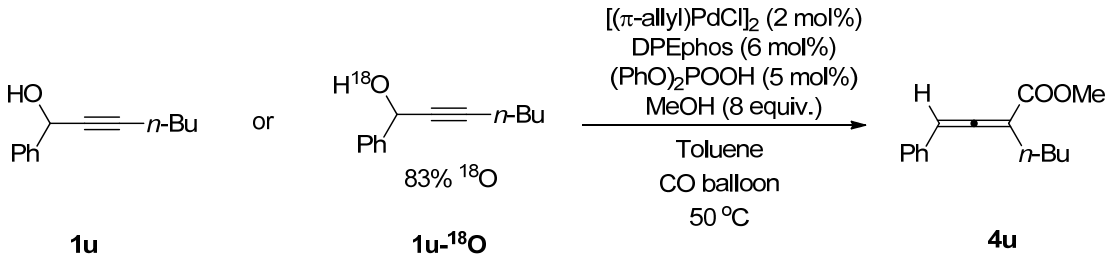
To a flame-dried three-neck flask were added 1-hexyne (0.57 mL, d = 0.715 g/mL, 407.5 mg, 5 mmol) and THF (20 mL). Then a solution of *n*-BuLi (2.5 M in hexane, 2 mL, 5 mmol) was added dropwise under argon at -78 °C. After stirring at room temperature for 2 h, the mixture was cooled to -78 °C, then a solution of $^{18}$O-benzaldehyde[10] (540.6 mg, 5 mmol) in THF (10 mL) was added dropwise. The resulting mixture was then stirred at room temperature for 11 h and quenched with a saturated aqueous solution of $NH_4Cl$ (10 mL). After extraction with ethyl acetate (5 mL x 3), the organic layer was washed with brine (10 mL) and dried over anhydrous $Na_2SO_4$. After filtration and evaporation, the crude product was purified by column chromatography on silica gel to afford **1u-$^{18}$O** (679.8 mg, 72%) as an oil [eluent: petroleum ether (b.p. 60-90 °C)/ethyl acetate = 10/1]: $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.49 (m, 2 H, Ar-H), 7.43-7.27 (m, 3 H, Ar-H), 5.44 (d, $J$ = 5.2 Hz, 1 H, CH), 2.27 (td, $J_1$ = 6.8 Hz, $J_2$ = 2.0 Hz, 2 H, $CH_2$), 2.23-2.12 (m, 1 H, OH), 1.58-1.48 (m, 2 H, $CH_2$), 1.48-1.34 (m, 2 H, $CH_2$), 0.92 (t, $J$ = 7.4 Hz, 3 H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 141.2, 128.5, 128.1, 126.6, 87.6, 79.9, 64.8, 30.6, 21.9, 18.5, 13.5; MS (70 eV, EI) *m/z* (%): 190 ($M^+$($^{18}$O), 100), 188 ($M^+$($^{16}$O), 18.53); IR (neat): $\nu$ = 3343, 2957, 2931, 2871, 2226, 1642, 1453, 1266, 1134 cm$^{-1}$; HRMS calcd for $C_{13}H_{16}{}^{18}O$ [$M^+$]: 190.1244, found: 190.1243.

The $^{18}$O% incorporation of **1u-$^{18}$O** was determined via the analysis of MS spectrum.[11] The $^{18}$O% of **1u-$^{18}$O** can be calculated as follows: [M($^{18}$O)$^+$] /([M($^{18}$O)$^+$] + [M($^{16}$O)$^+$]) = 100/(100+18.53) ≈ 84.37%. In addition, the contributions to the isotopic peak intensities from background peaks or from impurities in the sample

must be considered. The natural abundances of the stable isotopes of C, H, and O are known. According to the MS spectrum of **1u**, such contribution of **1u** to $[M(^{16}O)+2]^+$ is (1.13-100×0.002)% (≈ 0.93%).

So the $^{18}O$% of **1u-$^{18}$O** is 84.37% - 0.93% ≈ 83.4%.

**(2) Kinetic experiments**



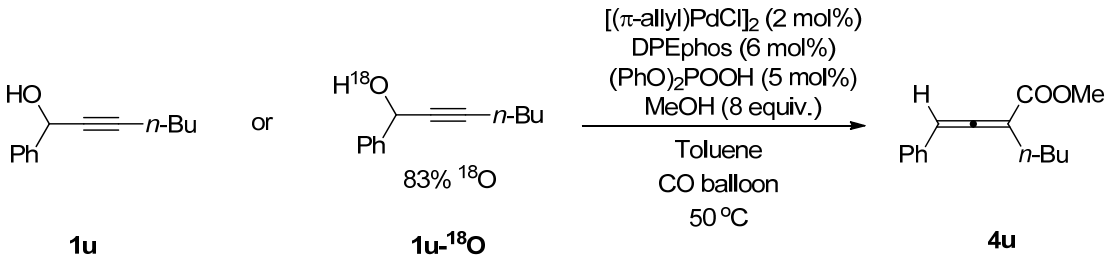

**1u** **1u-$^{18}$O** **4u**

To a flame-dried Schlenk tube were added $[(\pi\text{-allyl})PdCl]_2$ (7.5 mg, 0.02 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.5 mg, 0.05 mmol), **1u** (188.3 mg, 1 mmol), MeOH (256.7 mg, 8.0 mmol), toluene (5 mL), and 35.5 uL $CH_2Br_2$ sequentially. The resulting mixture was then frozen with a liquid nitrogen bath, degassed to remove the argon inside completely, and refilled with CO by a balloon of CO for three times. Then the resulting mixture was stirred at 50 $^oC$ with a balloon of CO. 0.1 mL each of the aliquot was taken with an Ar-purged syringes after 0.5 h, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 7 h, 8 h, 9 h. Each aliquot was immediately diluted with $CDCl_3$ and analyzed by $^1$H-NMR spectra directly to determine the recovery data of **1u** or **1u-$^{18}$O**. All the data acquired were analyzed by Microsoft Office Excel.

The reaction of $[(\pi\text{-allyl})PdCl]_2$ (7.5 mg, 0.05 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.5 mg, 0.05 mmol), **1u** (188.3 mg, 1 mmol), MeOH (256.7 mg, 8 mmol), and toluene (5 mL) contributed to data for **1u** in Table S4 **(zwl-9-177)**.

The reaction of $[(\pi\text{-allyl})PdCl]_2$ (7.5 mg, 0.05 mmol), DPEphos (32.4 mg, 0.06 mmol), $(PhO)_2POOH$ (12.6 mg, 0.05 mmol), **1u-$^{18}$O** (190.2 mg, 1 mmol), MeOH (256.4 mg, 8 mmol), and toluene (5 mL) contributed to data for **1u-$^{18}$O** in Table S4 **(zwl-9-176)**.

**Table S4 Recovery of substrate 1u or 1u-$^{18}$O with the standard catalytic formula**




**1u** **1u-$^{18}$O** **4u**

| Entry | time / h | Recovery of **1u** (%) | Recovery of **1u-$^{18}$O** (%) |
|---|---|---|---|
| 1 | 0.5 | 59 | 60 |
| 2 | 1 | 54 | 57 |
| 3 | 2 | 50 | 52 |
| 4 | 3 | 42 | 47 |
| 5 | 4 | 37 | 44 |
| 6 | 5 | 32 | 40 |
| 7 | 6 | 29 | 36 |
| 8 | 7 | 25 | 33 |
| 9 | 8 | 23 | 31 |
| 10 | 9 | 21 | 28 |

**Figure S1** Recovery of **1u** and **1u-$^{18}$O** vs. time

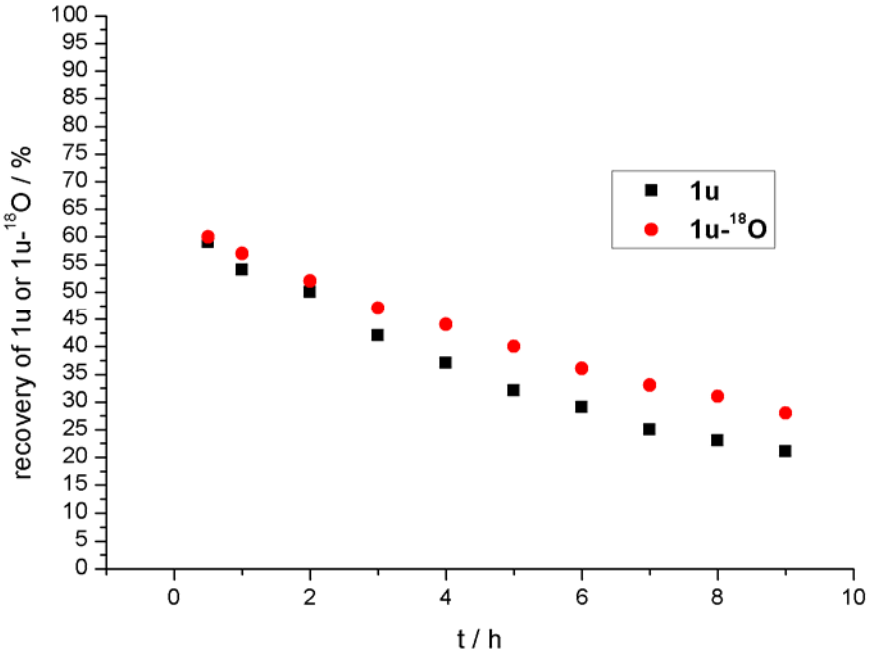
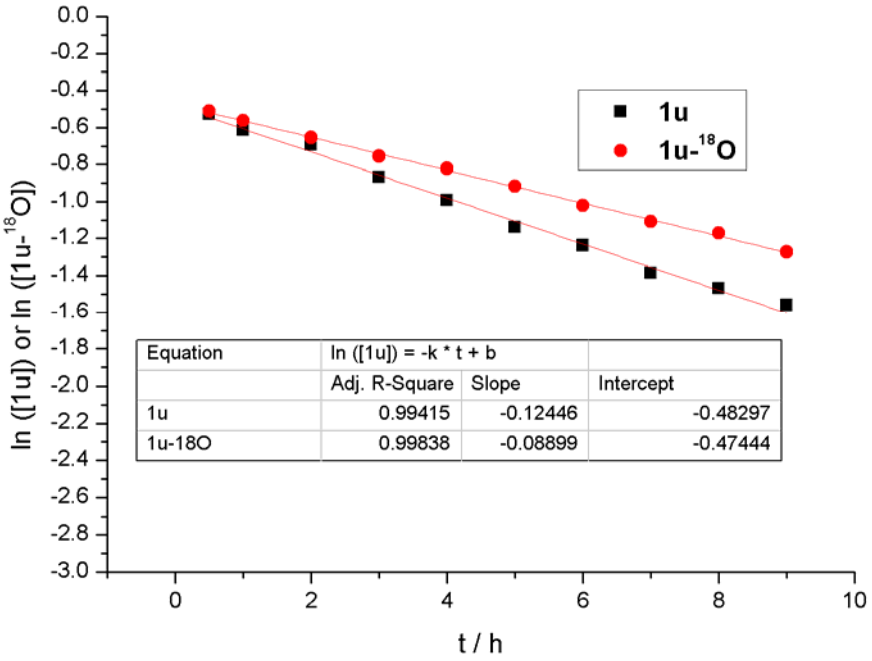



**Figure S2** Reaction order on the substrate **1u** and **1u-$^{18}$O**




| Equation | ln ([1u]) = -k * t + b | | |
|---|---|---|---|
| | Adj. R-Square | Slope | Intercept |
| 1u | 0.99415 | -0.12446 | -0.48297 |
| 1u-18O | 0.99838 | -0.08899 | -0.47444 |

The slopes of the lines correspond to the rate constant k (Figure S2), thus, the KIE = $k_{16O}/k_{18O}$ = 0.12446/0.08899 = 1.40.

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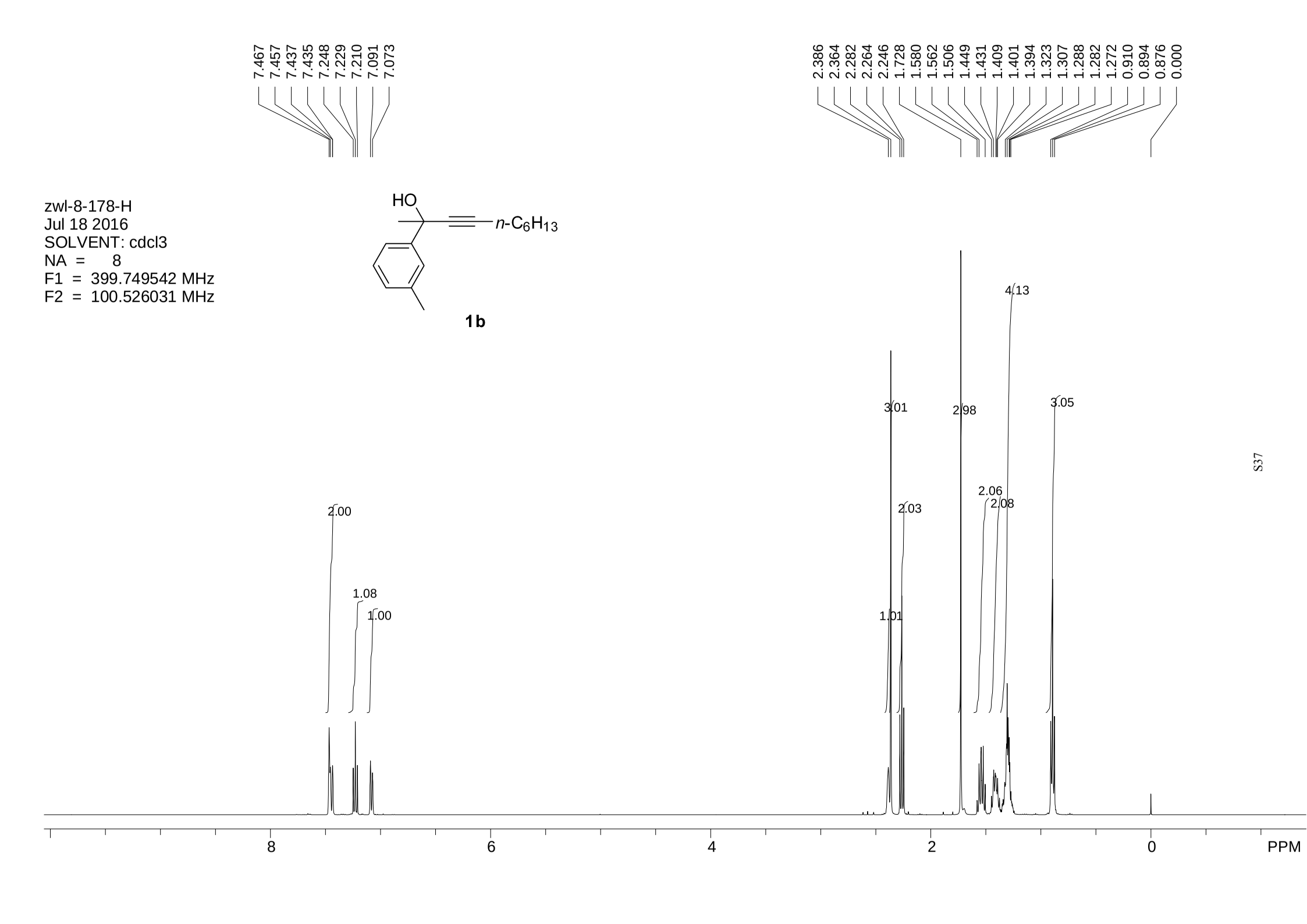
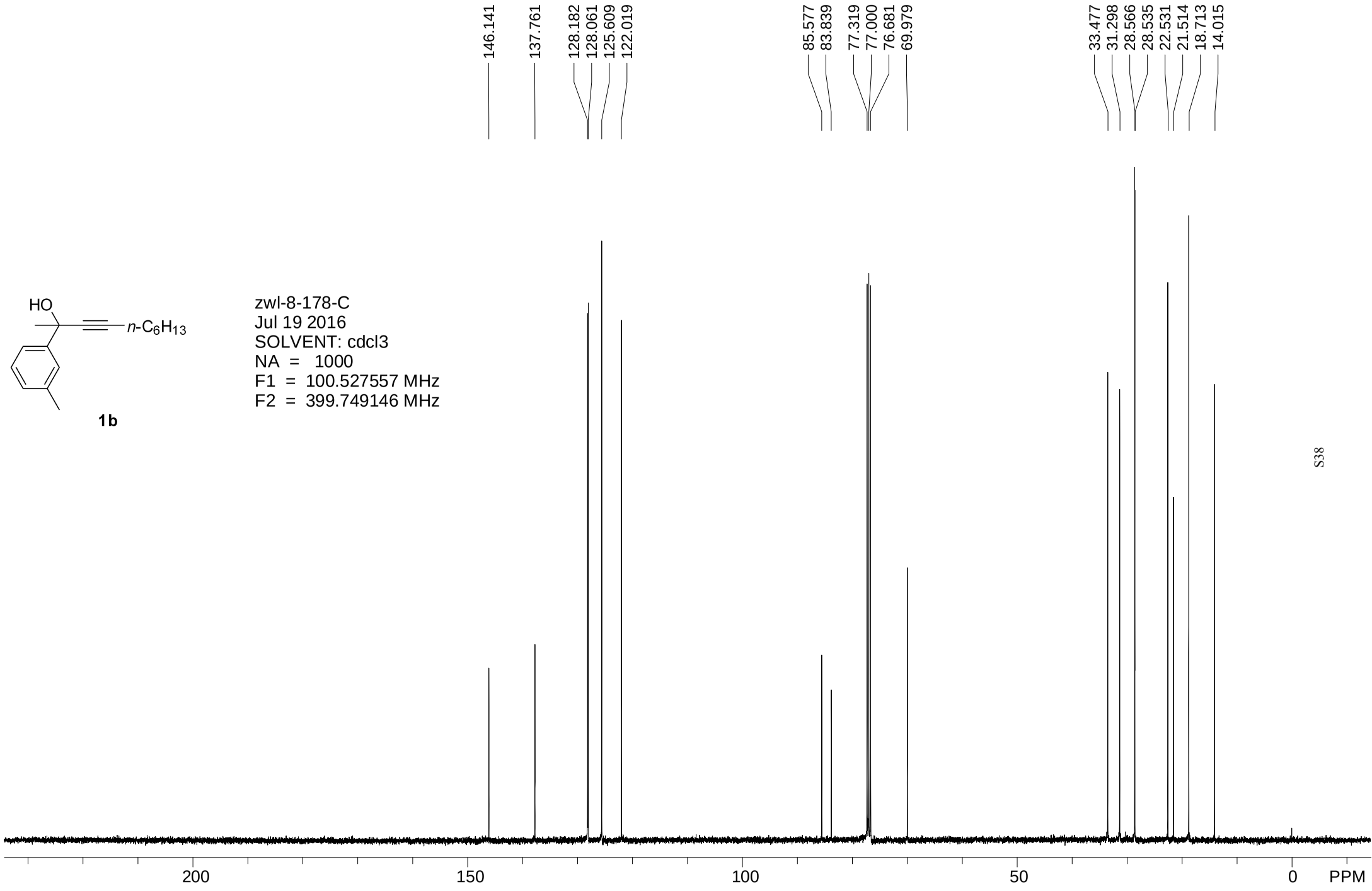
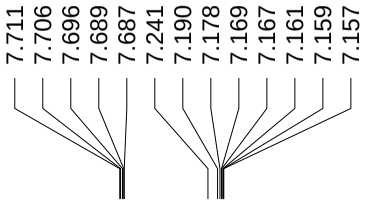
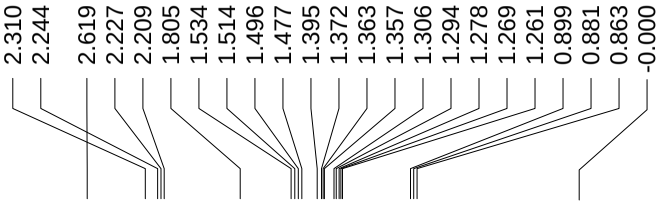
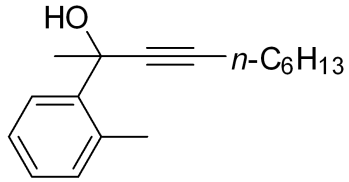

7.467
7.457
7.437
7.435
7.248
7.229
7.210
7.091
7.073
2.386
2.364
2.282
2.264
2.246
1.728
1.580
1.562
1.506
1.449
1.431
1.409
1.401
1.394
1.323
1.307
1.288
1.282
1.272
0.910
0.894
0.876
0.000
zwl-8-178-H
Jul 18 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
HO
n-C6H13
1b
4.13
3.01
2.98
3.05
2.06
2.08
2.03
2.00
1.08
1.00
1.01
S37
8
6
4
2
0
PPM


146.141
137.761
128.182
128.061
125.609
122.019
85.577
83.839
77.319
77.000
76.681
69.979
33.477
31.298
28.566
28.535
22.531
21.514
18.713
14.015
HO
n-C6H13
1b
zwl-8-178-C
Jul 19 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
200
150
100
50
0
PPM

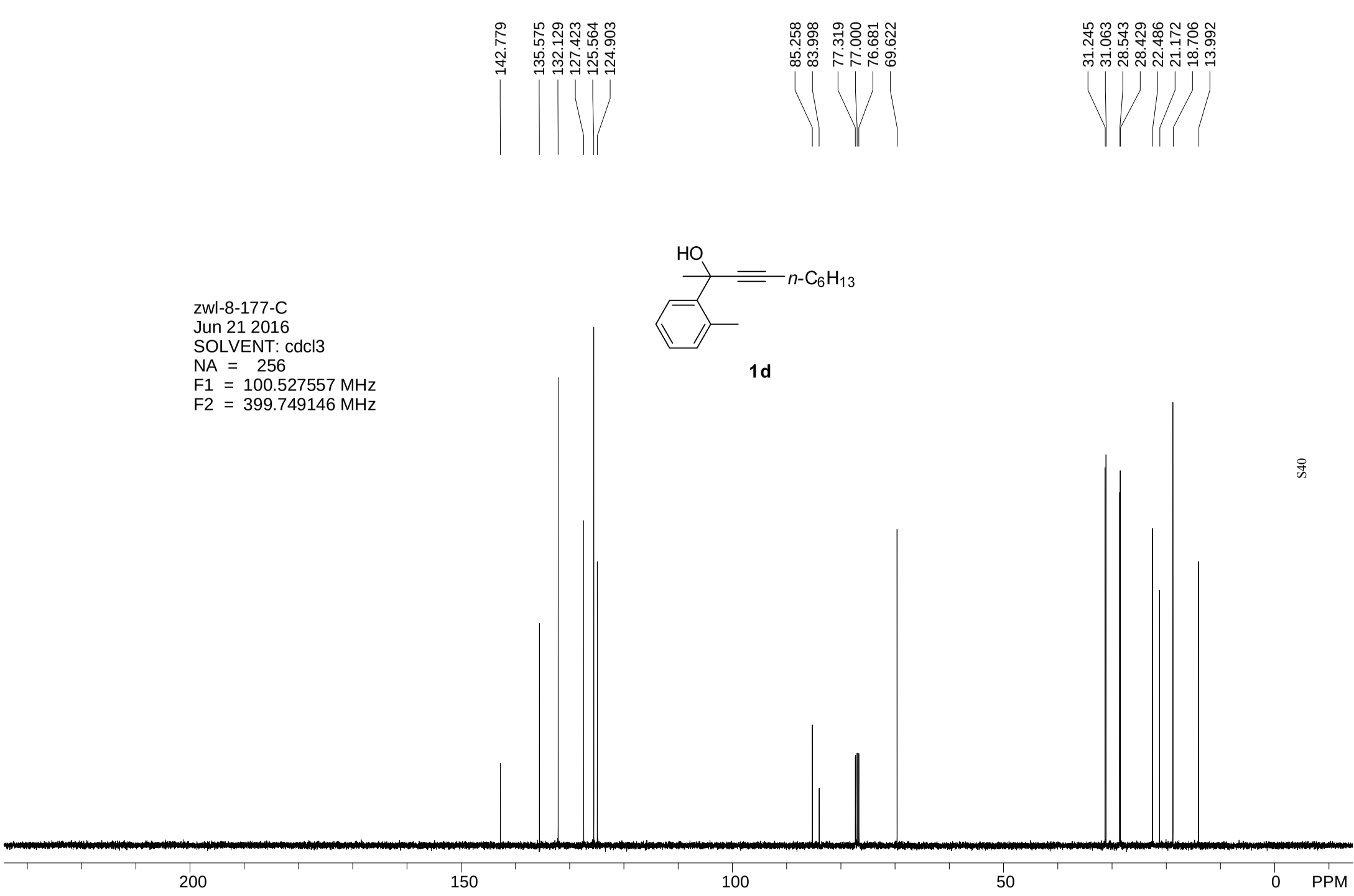


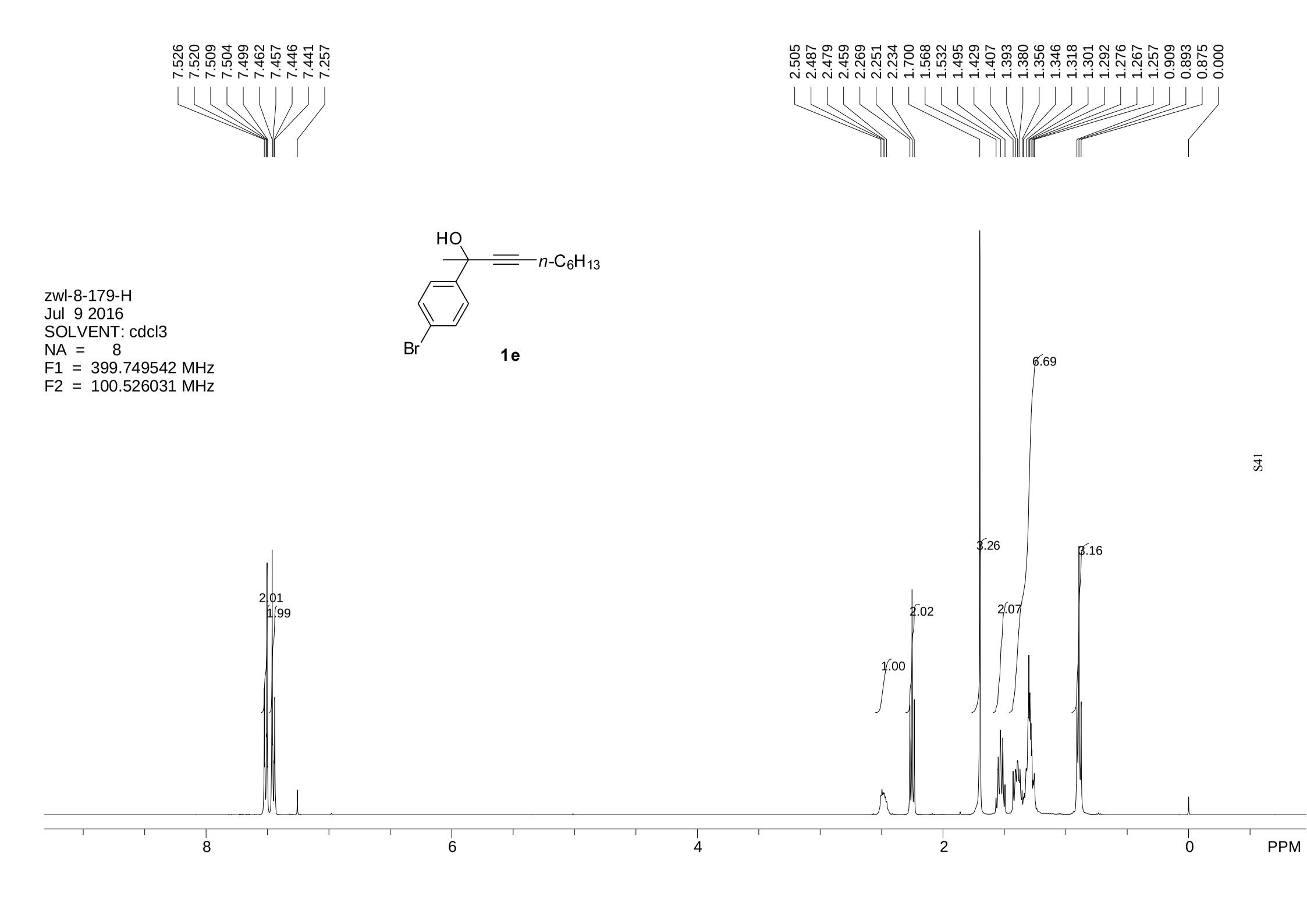



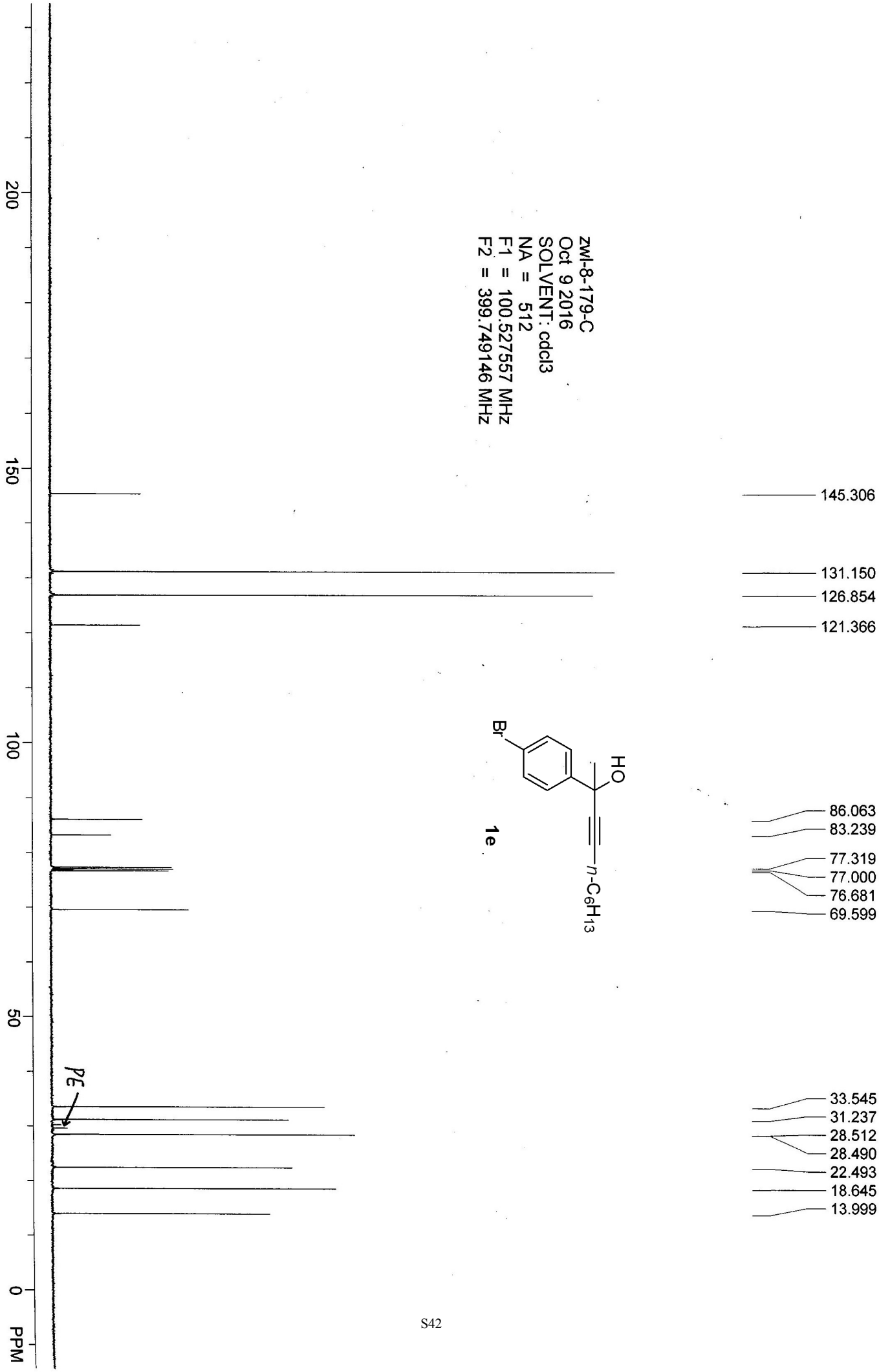

zwl-8-177-H
Jul 19 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz

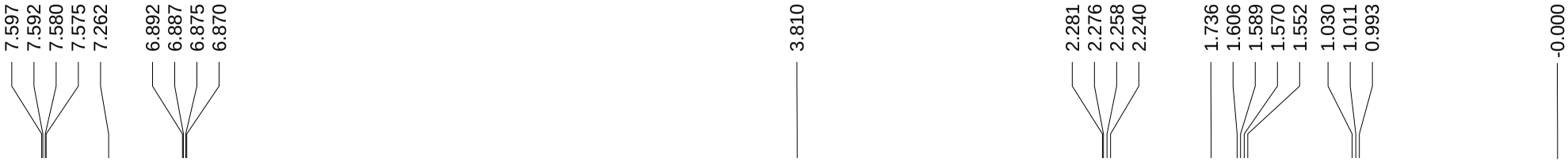



**1d**

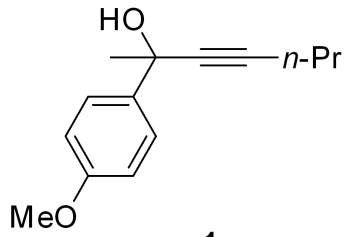

142.779
135.575
132.129
127.423
125.564
124.903
85.258
83.998
77.319
77.000
76.681
69.622
31.245
31.063
28.543
28.429
22.486
21.172
18.706
13.992
HO
n-C6H13
1d
zwl-8-177-C
Jun 21 2016
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
F2 = 399.749146 MHz
200
150
100
50
0
PPM


7.526
7.520
7.509
7.504
7.499
7.462
7.457
7.446
7.441
7.257
2.505
2.487
2.479
2.459
2.269
2.251
2.234
1.700
1.568
1.532
1.495
1.429
1.407
1.393
1.380
1.356
1.346
1.318
1.301
1.292
1.276
1.267
1.257
0.909
0.893
0.875
0.000
HO
n-C6H13
Br
1e
zwl-8-179-H
Jul 9 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
S41
2.01
1.99
1.00
2.02
3.26
2.07
6.69
3.16
8
6
4
2
0
PPM

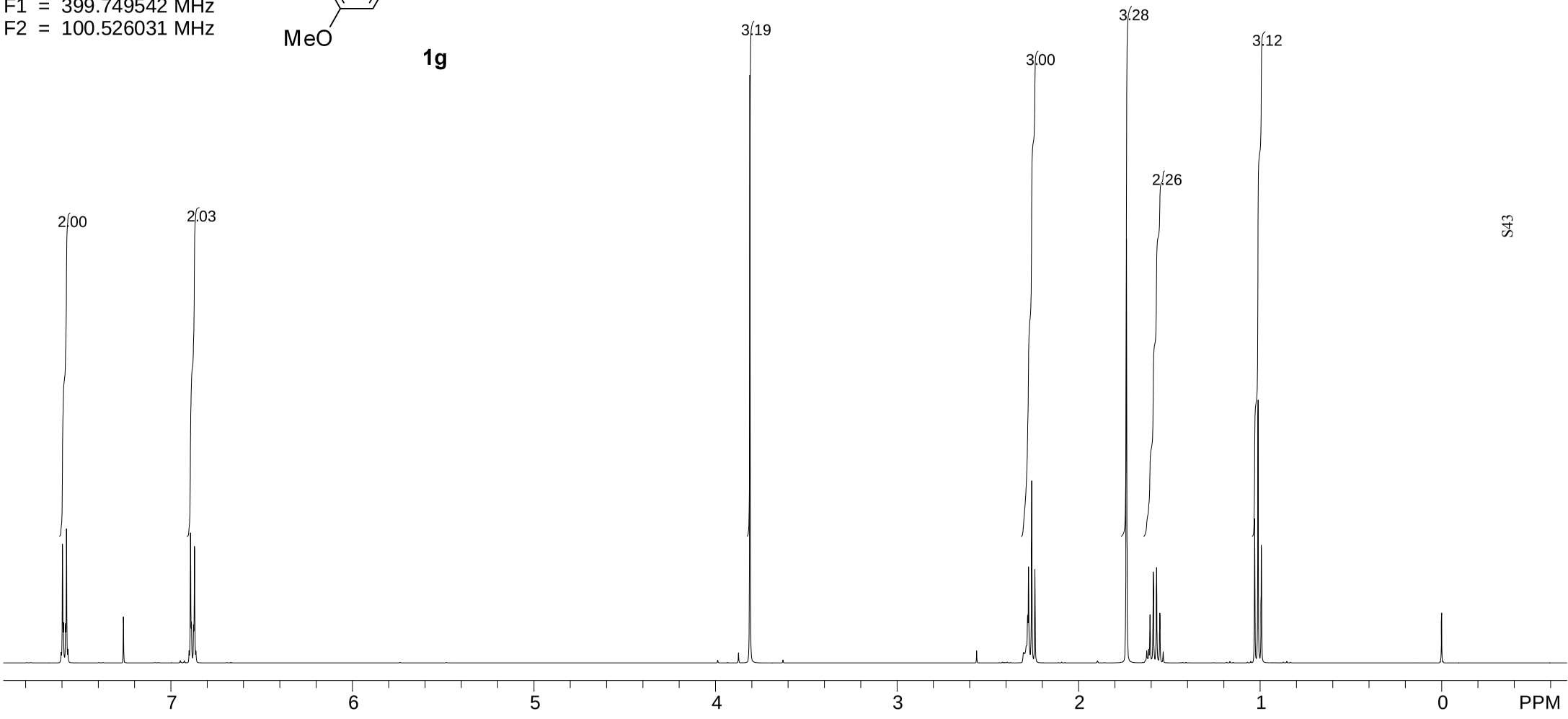

zwl-8-179-C
Oct 9 2016
SOLVENT: cdcl3
NA = 512
F1 = 100.527557 MHz
F2 = 399.749146 MHz
Br
HO
n-C6H13
1e
PE
145.306
131.150
126.854
121.366
86.063
83.239
77.319
77.000
76.681
69.599
33.545
31.237
28.512
28.490
22.493
18.645
13.999
200
150
100
50
0
PPM

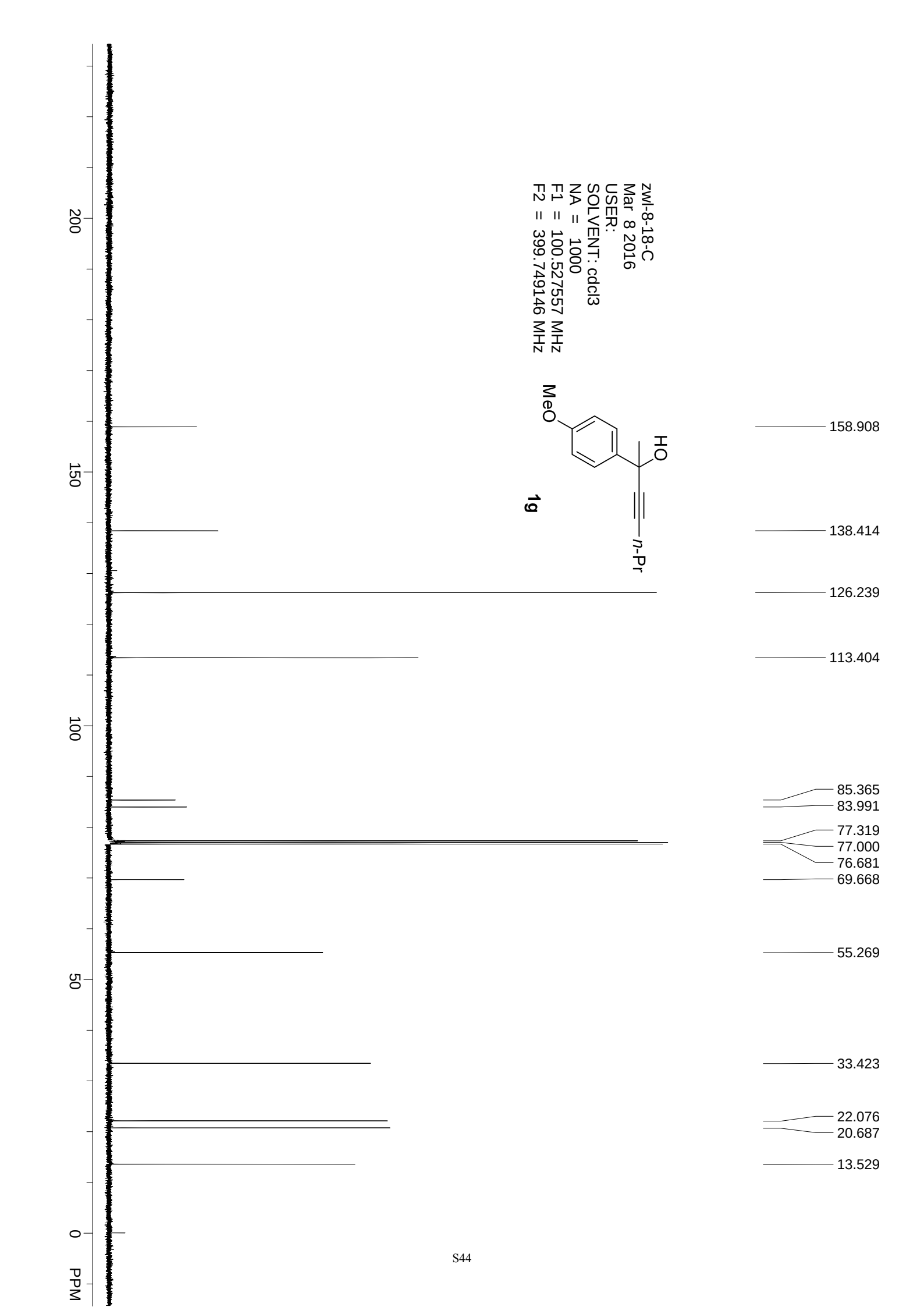


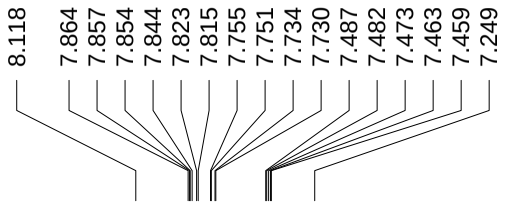

zwl-8-18-H
Mar 8 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz

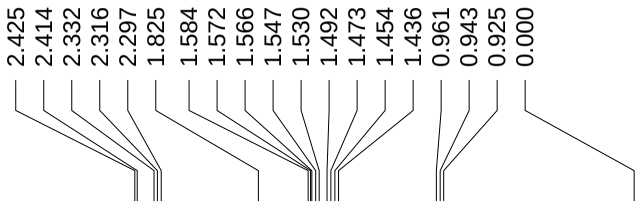



**1g**

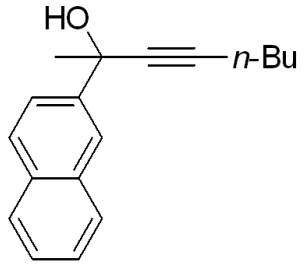



zwl-8-18-C
Mar 8 2016
USER:
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
MeO
HO
n-Pr
1g
158.908
138.414
126.239
113.404
85.365
83.991
77.319
77.000
76.681
69.668
55.269
33.423
22.076
20.687
13.529
200
150
100
50
0
PPM

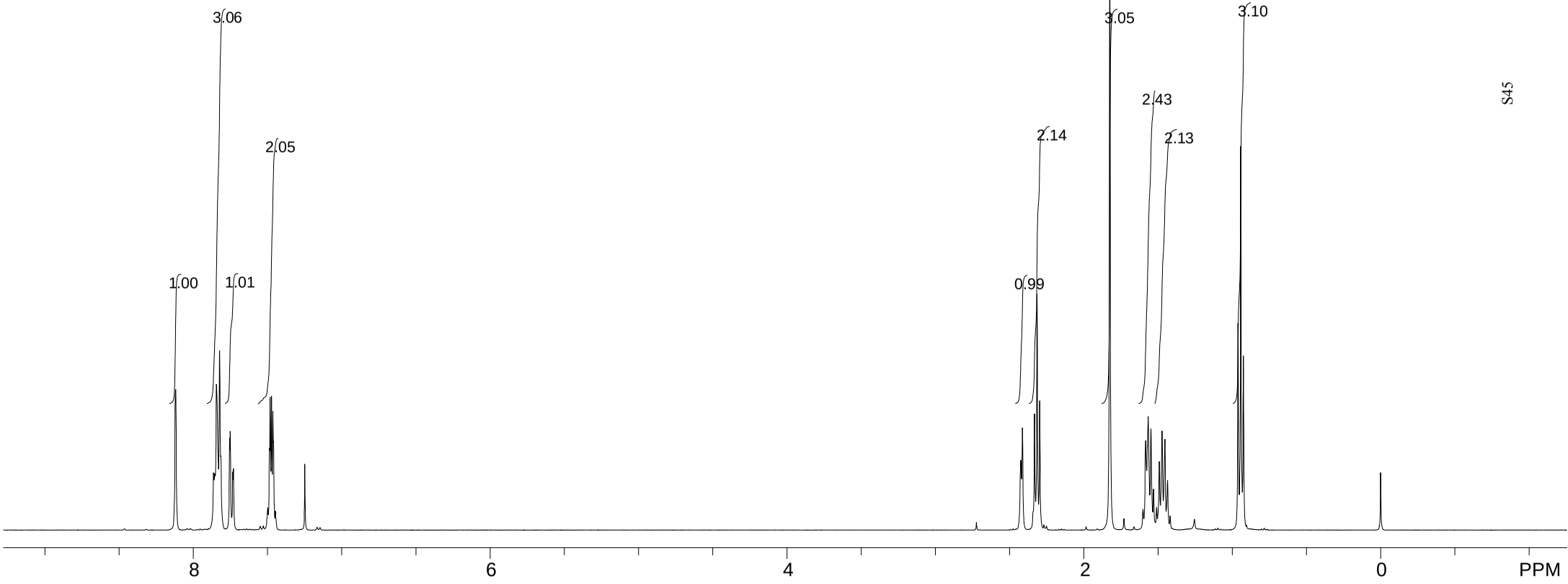


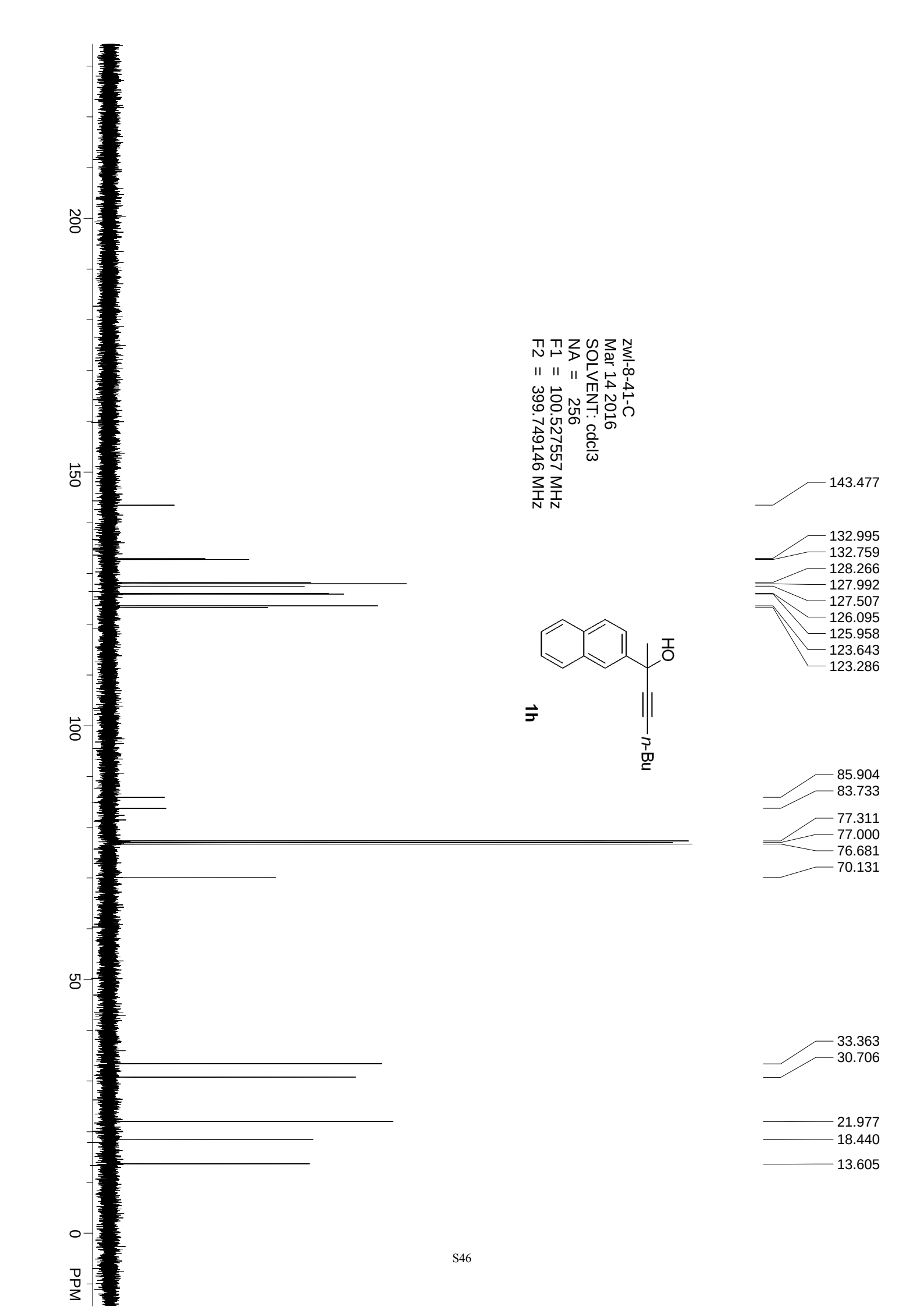



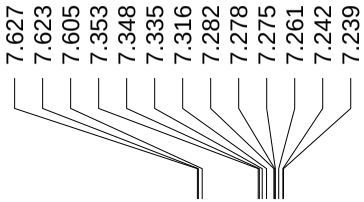

zwl-8-41-H
Mar 14 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz

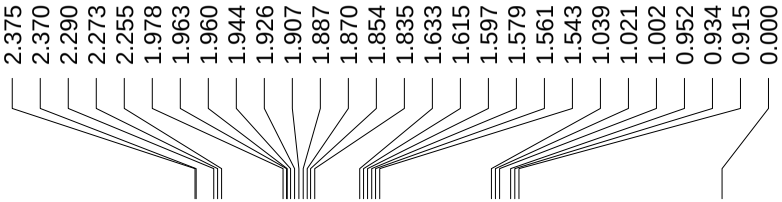



**1h**




zwl-8-41-C
Mar 14 2016
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
F2 = 399.749146 MHz
1h
HO
n-Bu
143.477
132.995
132.759
128.266
127.992
127.507
126.095
125.958
123.643
123.286
85.904
83.733
77.311
77.000
76.681
70.131
33.363
30.706
21.977
18.440
13.605
200
150
100
50
0
PPM




zwl-8-16-H
Apr 25 2016
SOLVENT: cdcl3
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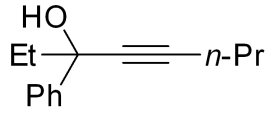
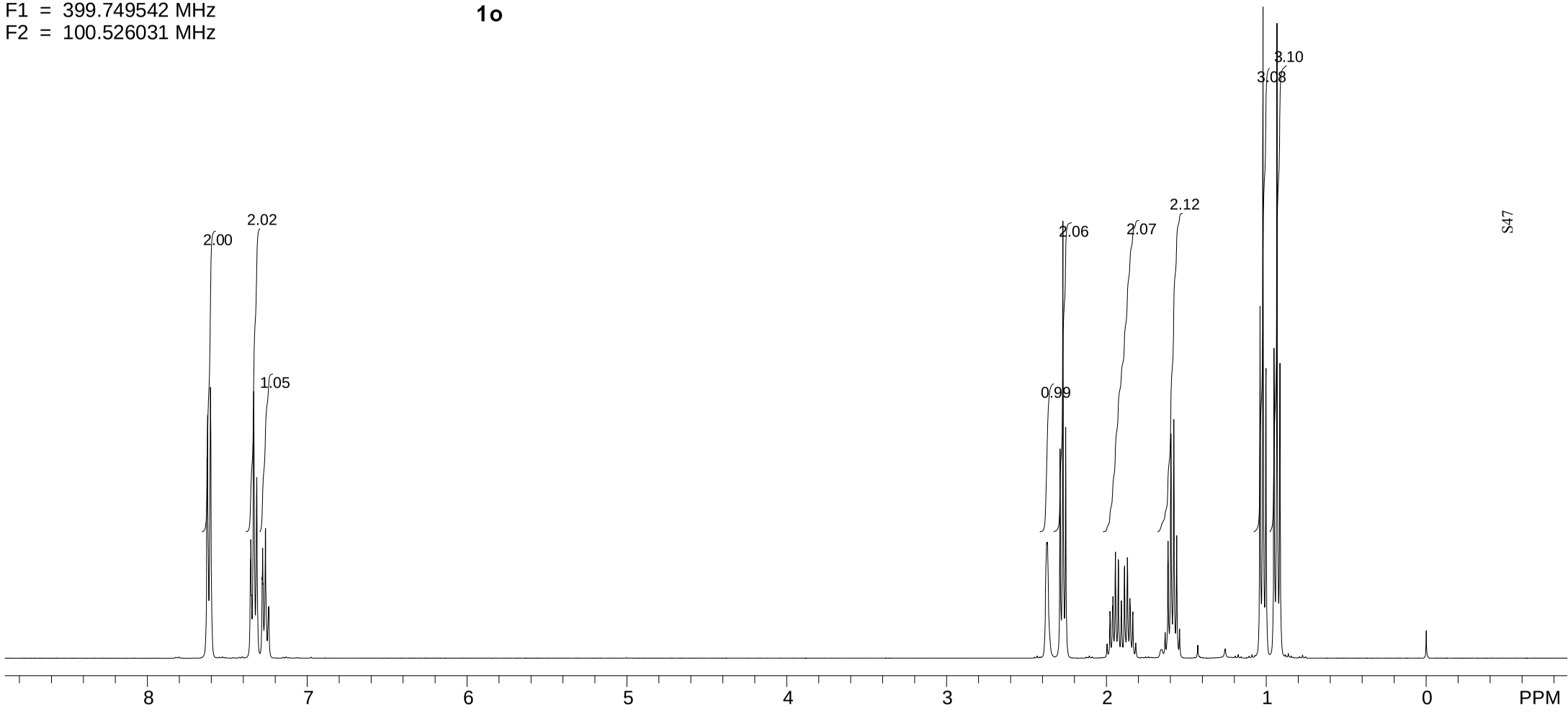
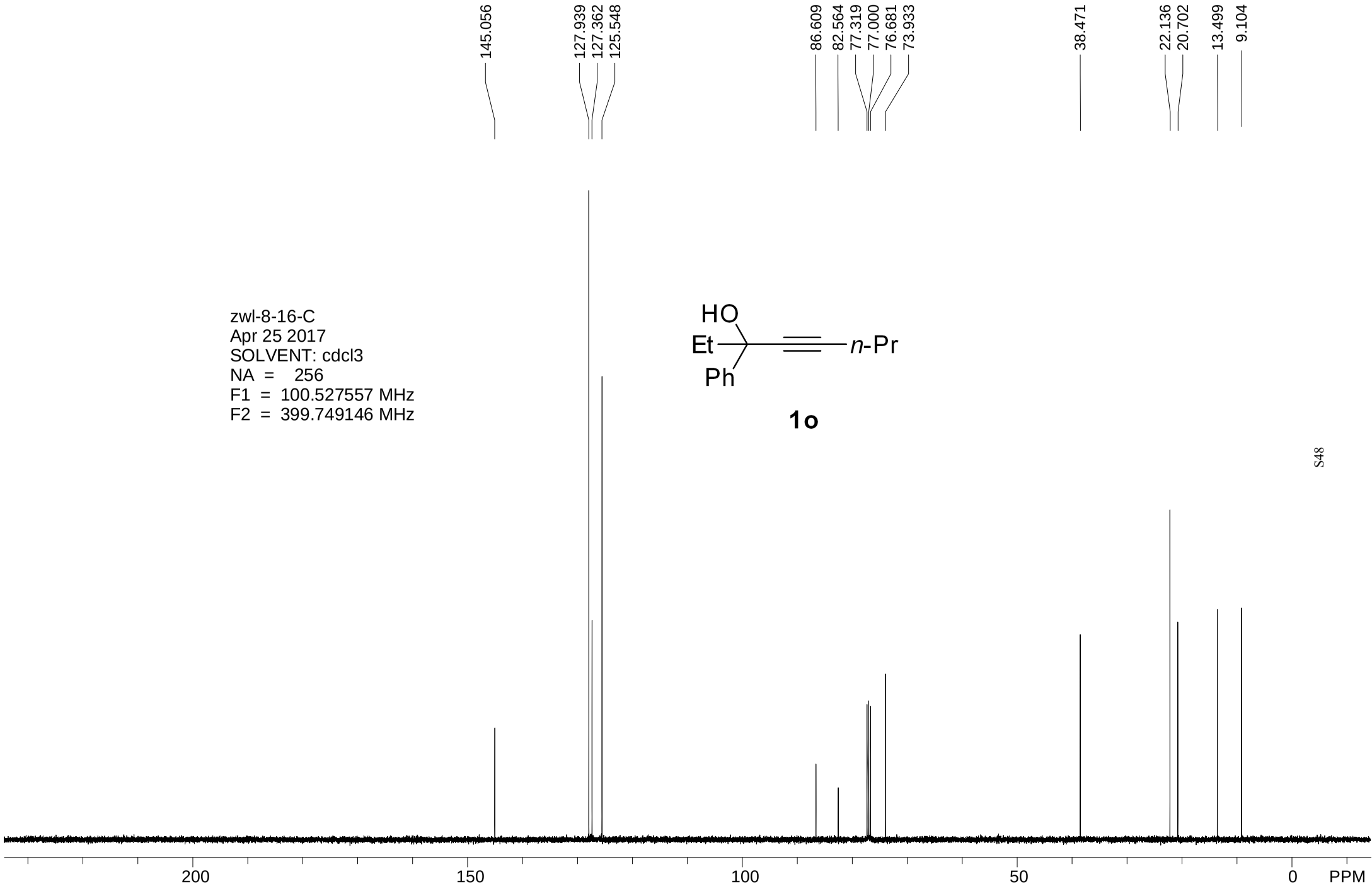
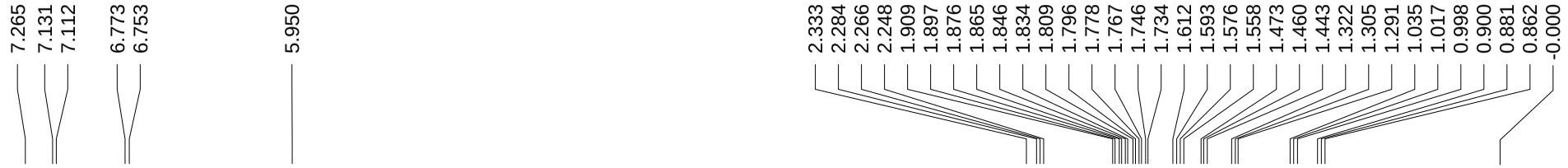
F1 = 399.749542 MHz
F2 = 100.526031 MHz



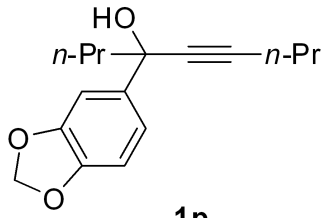

**1o**



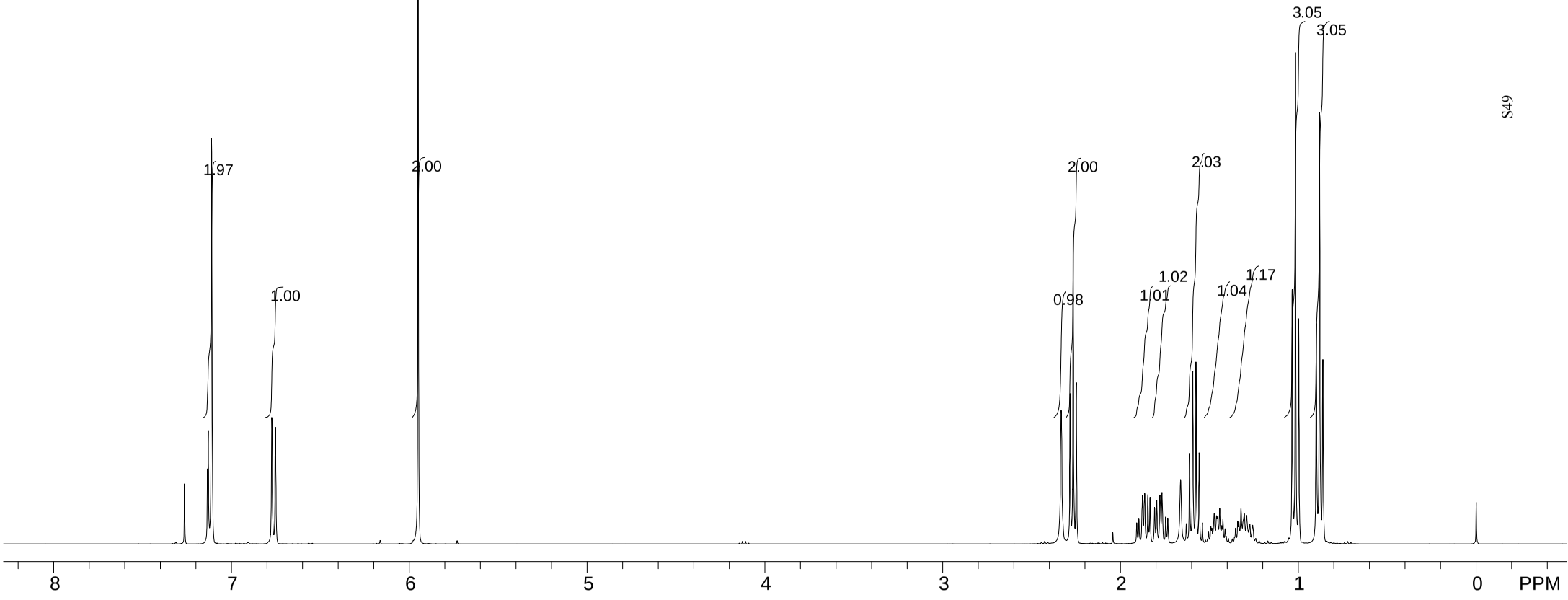

145.056
127.939
127.362
125.548
86.609
82.564
77.319
77.000
76.681
73.933
38.471
22.136
20.702
13.499
9.104
zwl-8-16-C
Apr 25 2017
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
F2 = 399.749146 MHz
HO
Et
Ph
n-Pr
1o
200
150
100
50
0
PPM

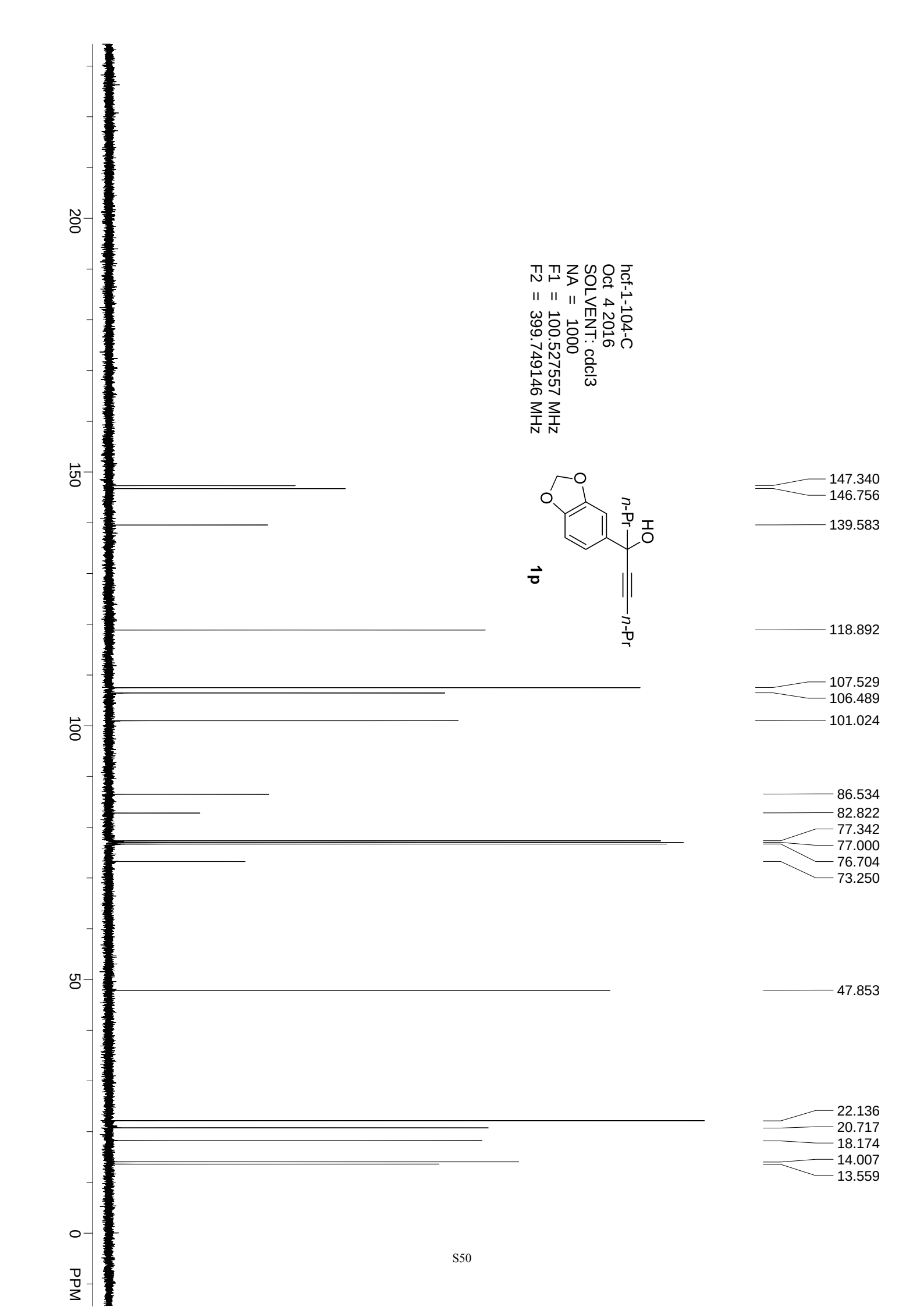


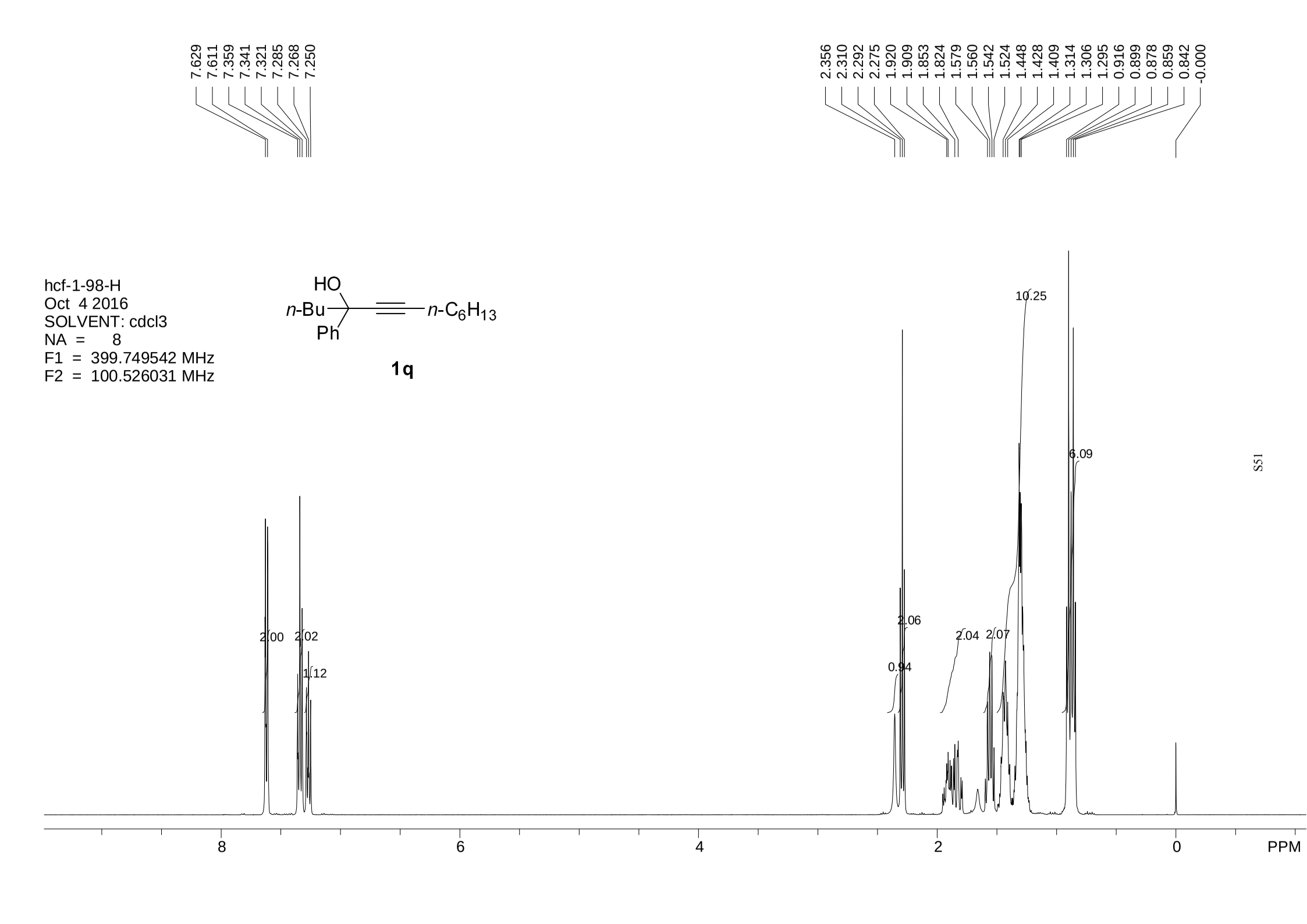

hcf-1-104-H
Oct 4 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz

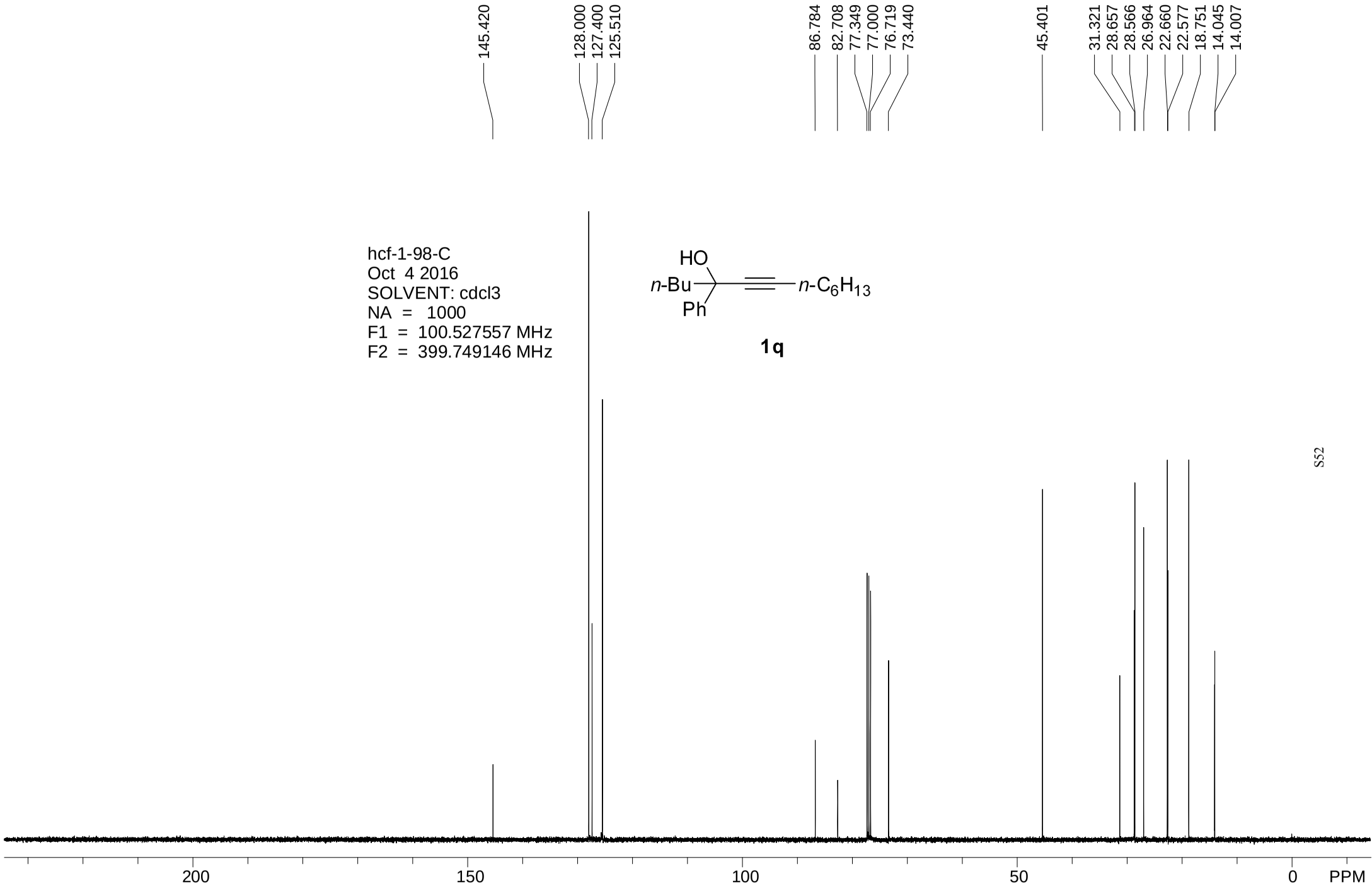


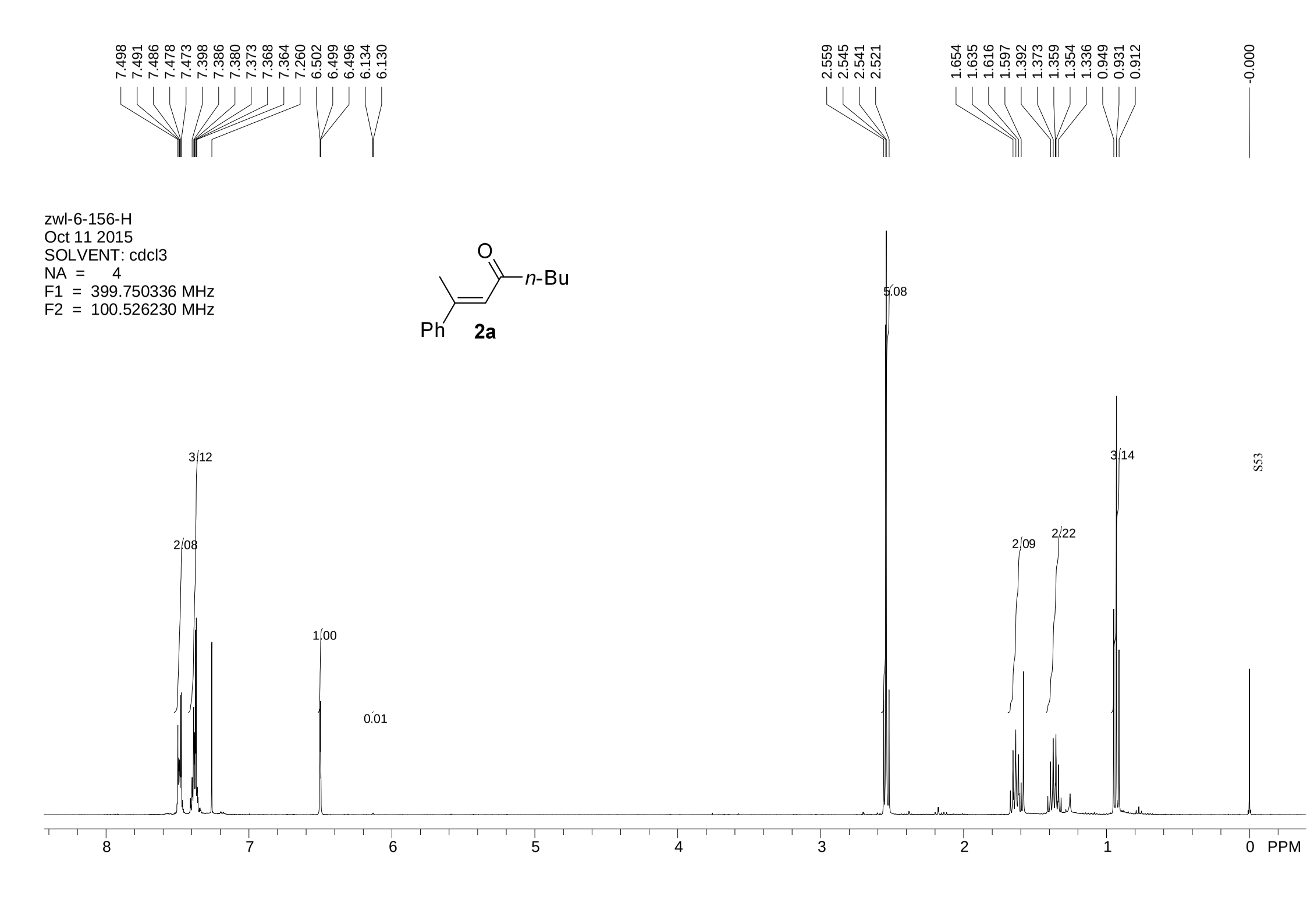

**1p**

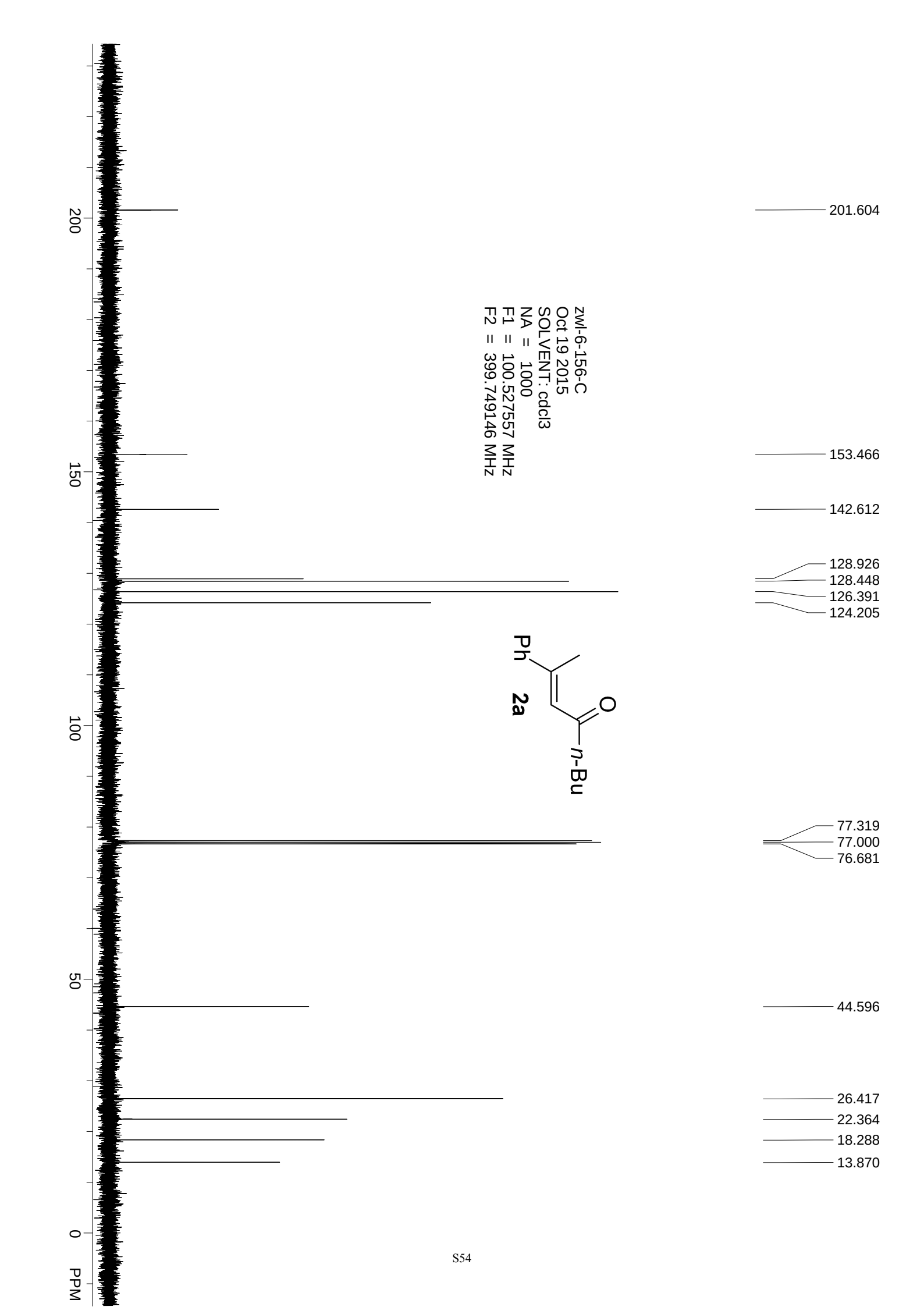


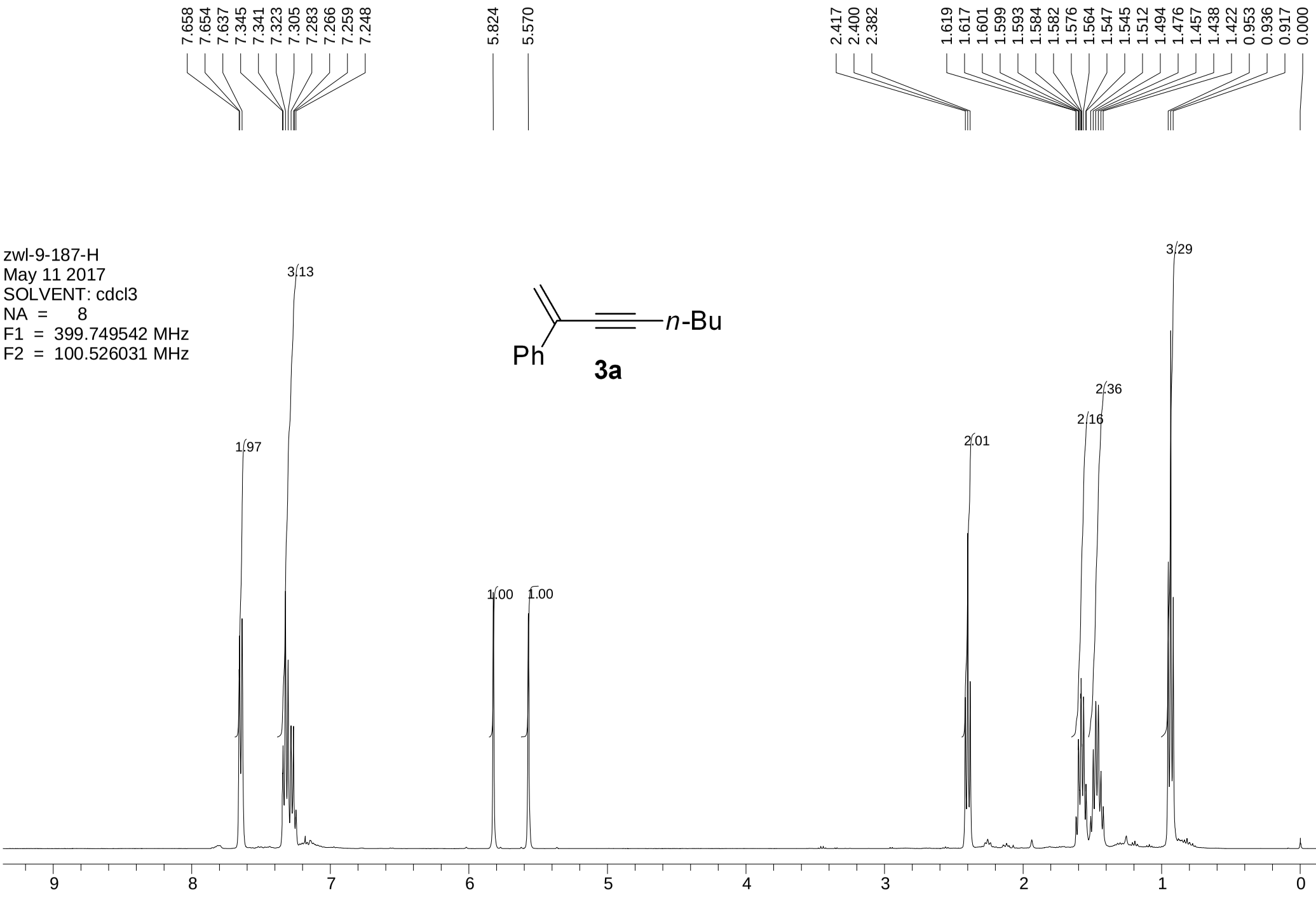

hcf-1-104-C
Oct 4 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
1p
HO
n-Pr
n-Pr
147.340
146.756
139.583
118.892
107.529
106.489
101.024
86.534
82.822
77.342
77.000
76.704
73.250
47.853
22.136
20.717
18.174
14.007
13.559
200
150
100
50
0
PPM

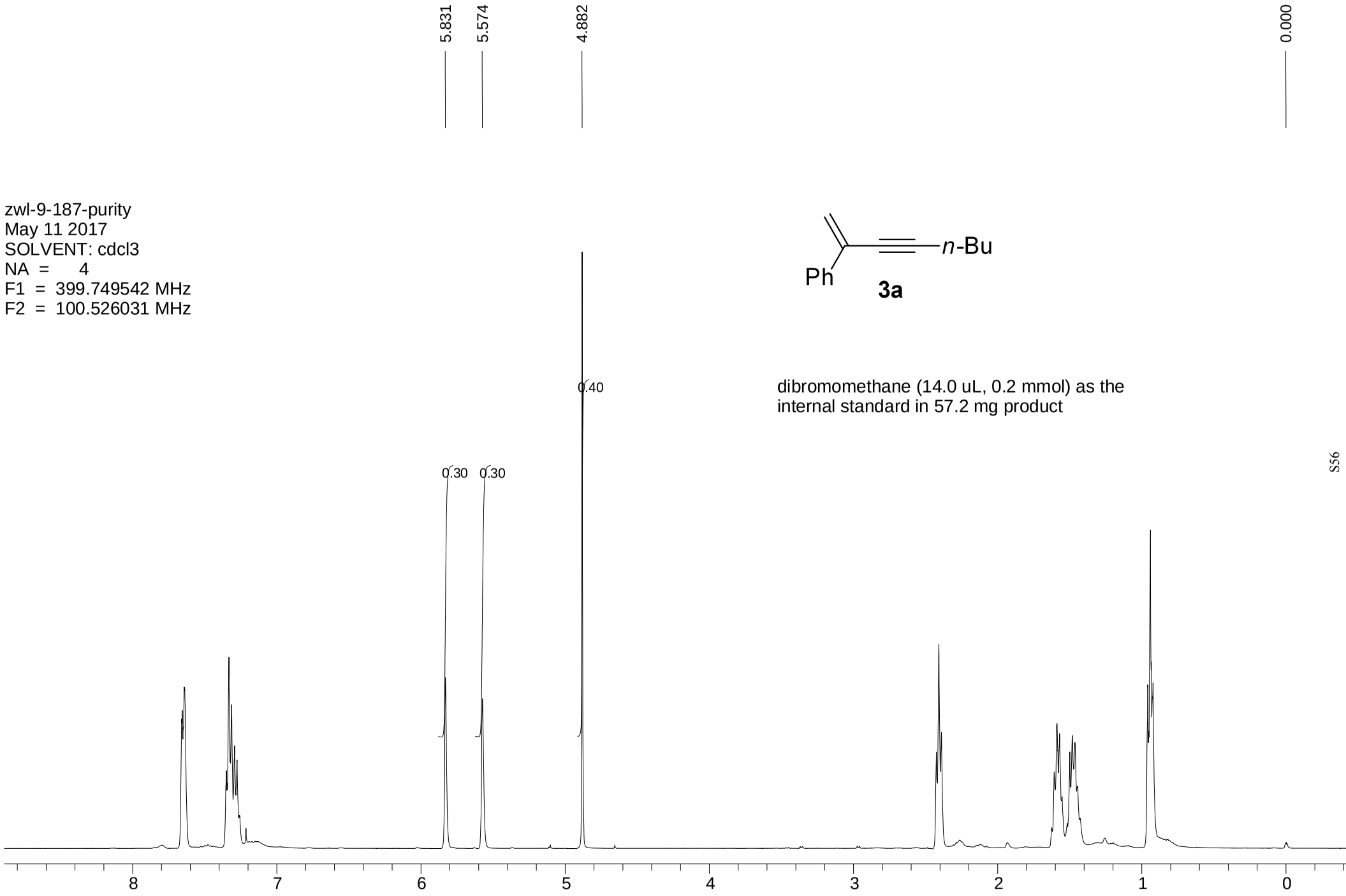

7.629
7.611
7.359
7.341
7.321
7.285
7.268
7.250
2.356
2.310
2.292
2.275
1.920
1.909
1.853
1.824
1.579
1.560
1.542
1.524
1.448
1.428
1.409
1.314
1.306
1.295
0.916
0.899
0.878
0.859
0.842
-0.000
hcf-1-98-H
Oct 4 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
HO
n-Bu
Ph
n-C6H13
1q
2.00
2.02
1.12
0.94
2.06
2.04
2.07
10.25
6.09
S51
8
6
4
2
0
PPM

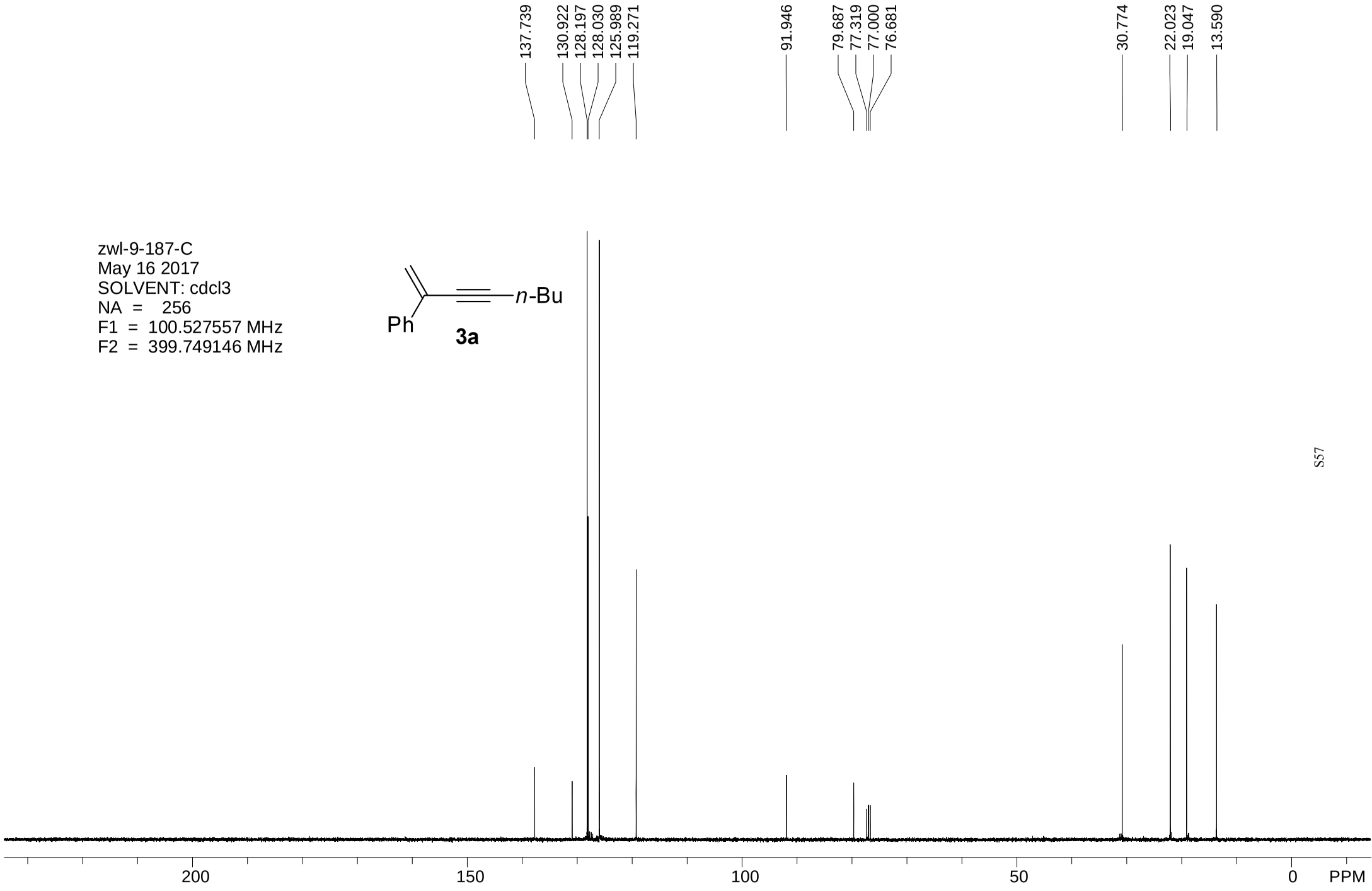

145.420
128.000
127.400
125.510
86.784
82.708
77.349
77.000
76.719
73.440
45.401
31.321
28.657
28.566
26.964
22.660
22.577
18.751
14.045
14.007
hcf-1-98-C
Oct 4 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
HO
n-Bu
Ph
n-C6H13
1q
S52
200
150
100
50
0
PPM

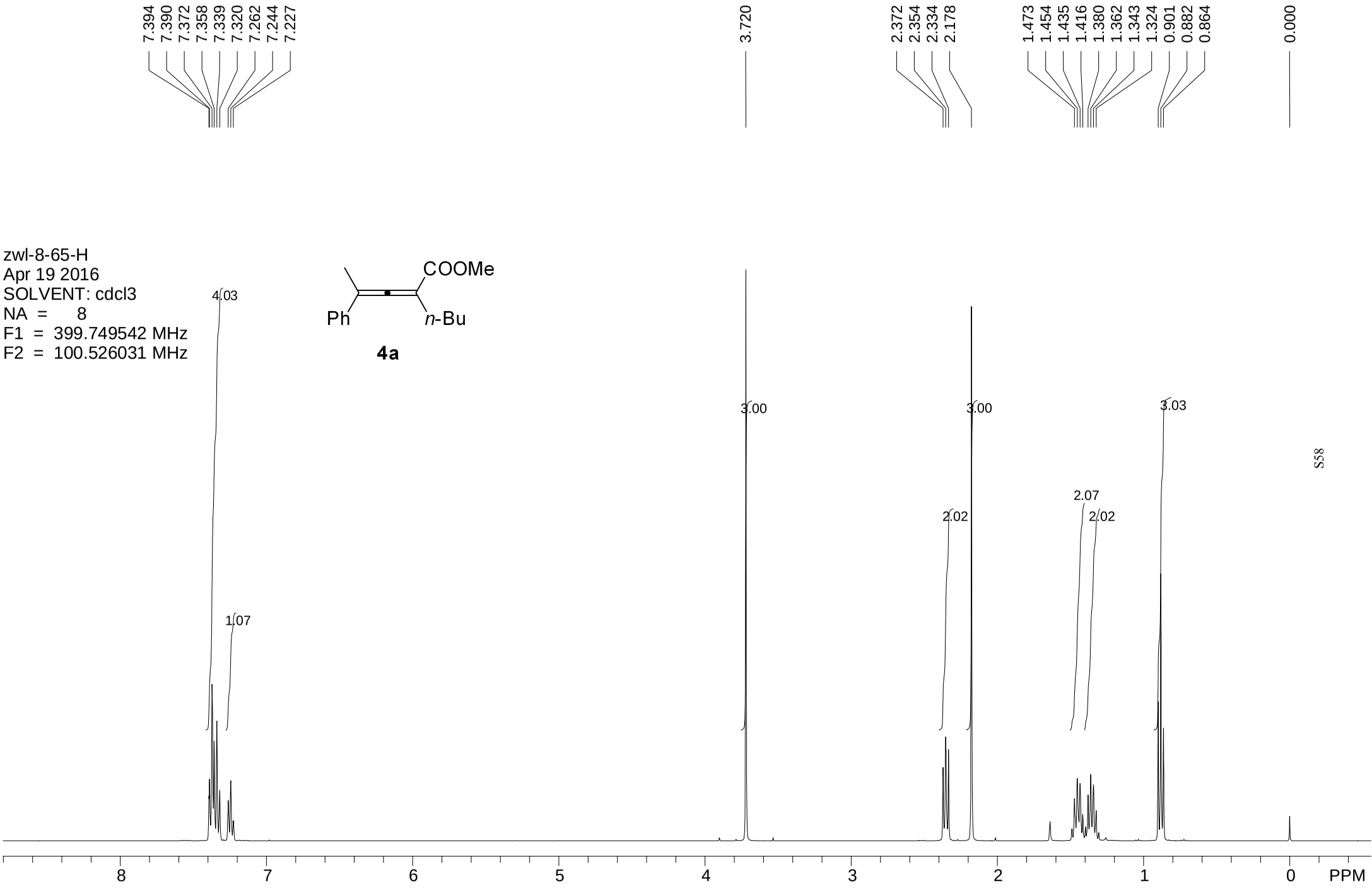

7.498
7.491
7.486
7.478
7.473
7.398
7.386
7.380
7.373
7.368
7.364
7.260
6.502
6.499
6.496
6.134
6.130
2.559
2.545
2.541
2.521
1.654
1.635
1.616
1.597
1.392
1.373
1.359
1.354
1.336
0.949
0.931
0.912
-0.000
zwl-6-156-H
Oct 11 2015
SOLVENT: cdcl3
NA = 4
F1 = 399.750336 MHz
F2 = 100.526230 MHz
O
n-Bu
Ph
2a
3.12
2.08
1.00
0.01
5.08
2.09
2.22
3.14
SS3
8
7
6
5
4
3
2
1
0
PPM

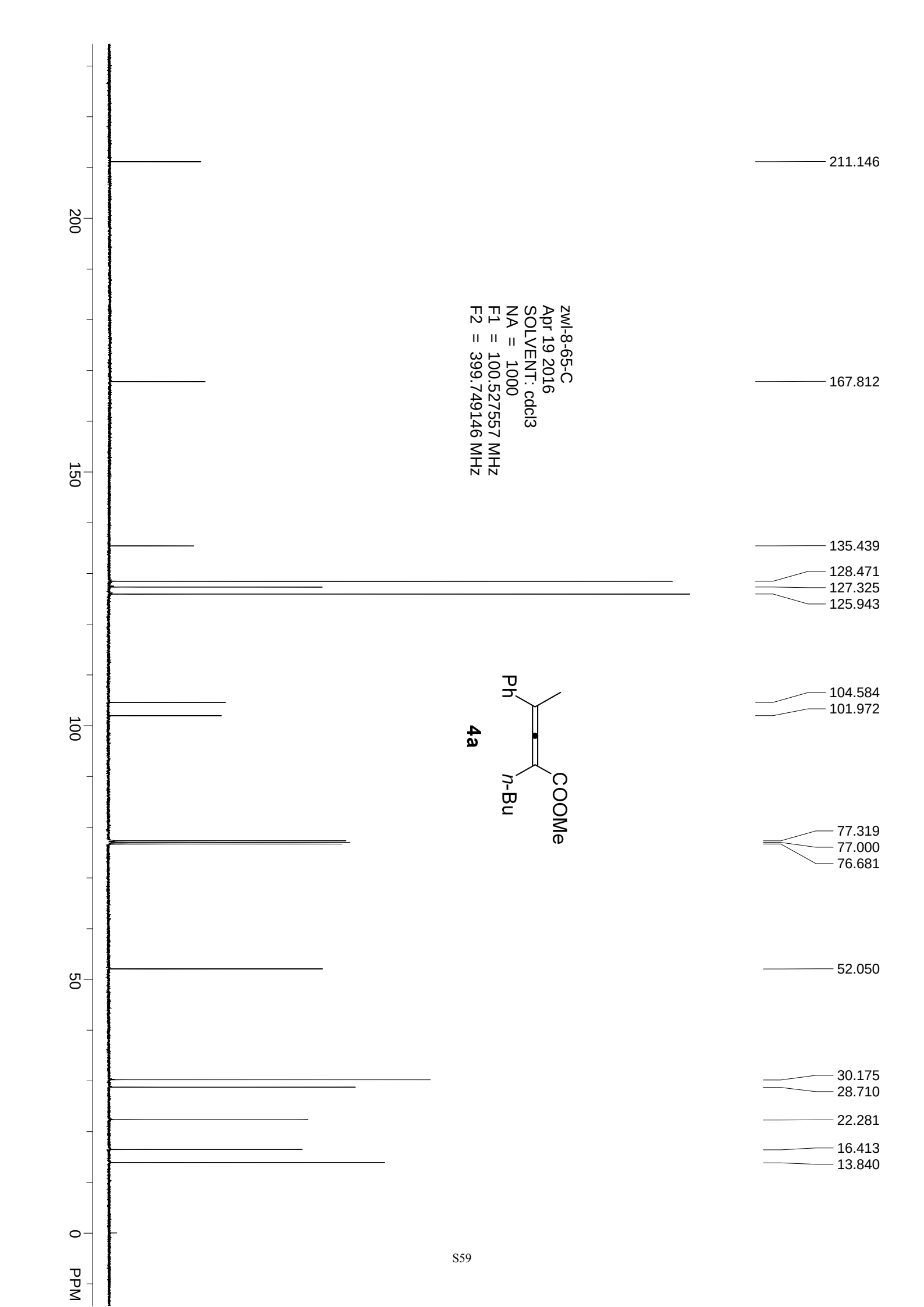

zwl-6-156-C
Oct 19 2015
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
Ph
O
n-Bu
2a
201.604
153.466
142.612
128.926
128.448
126.391
124.205
77.319
77.000
76.681
44.596
26.417
22.364
18.288
13.870
200
150
100
50
0
PPM

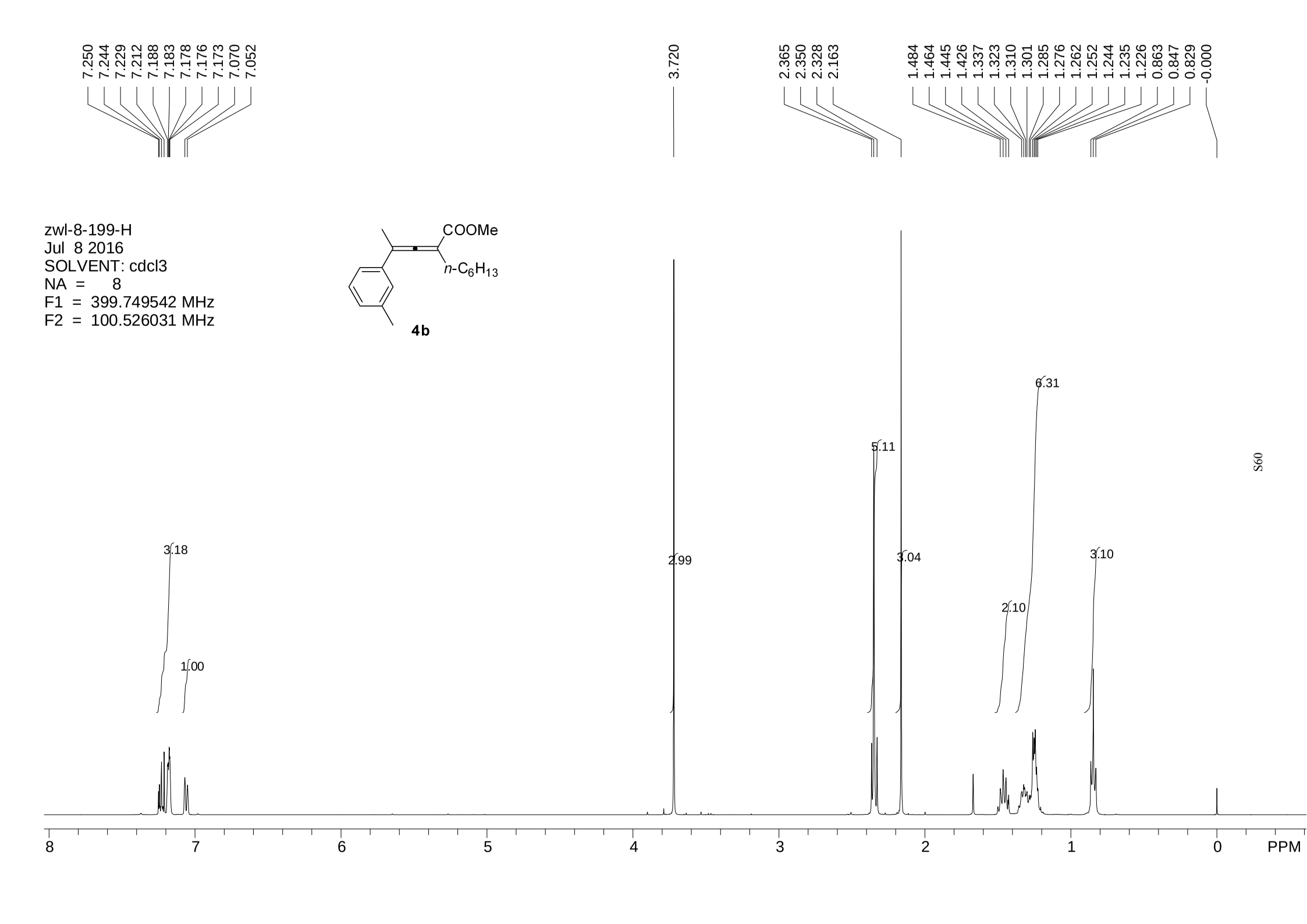

7.658
7.654
7.637
7.345
7.341
7.323
7.305
7.283
7.266
7.259
7.248
5.824
5.570
2.417
2.400
2.382
1.619
1.617
1.601
1.599
1.593
1.584
1.582
1.576
1.564
1.547
1.545
1.512
1.494
1.476
1.457
1.438
1.422
0.953
0.936
0.917
0.000
zwl-9-187-H
May 11 2017
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Ph
n-Bu
3a
1.97
3.13
1.00
1.00
2.01
2.16
2.36
3.29
S55
9
8
7
6
5
4
3
2
1
0
PPM

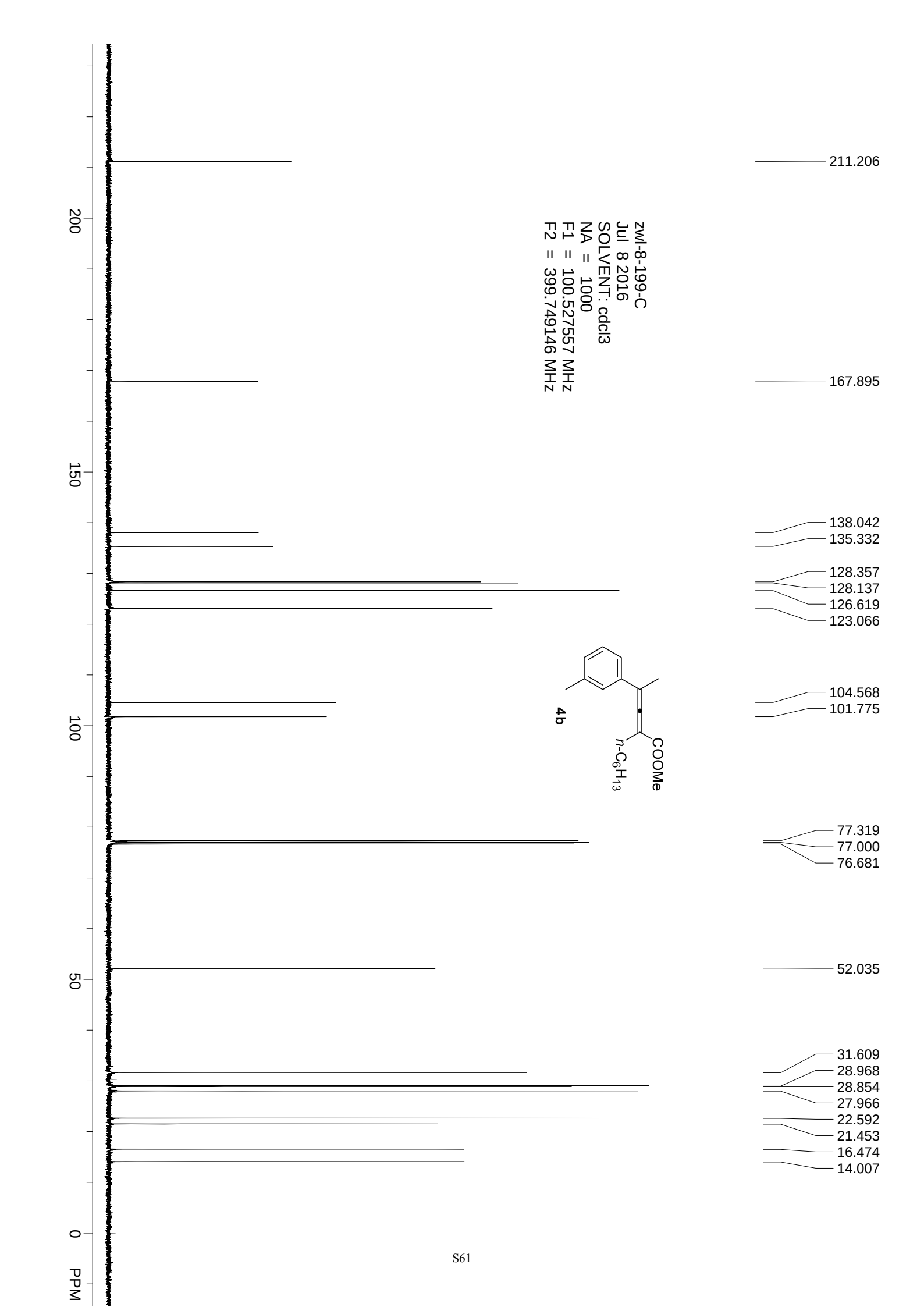

5.831
5.574
4.882
0.000
zwl-9-187-purity
May 11 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Ph
n-Bu
3a
dibromomethane (14.0 uL, 0.2 mmol) as the internal standard in 57.2 mg product
0.40
0.30
0.30
8
7
6
5
4
3
2
1
0
PPM

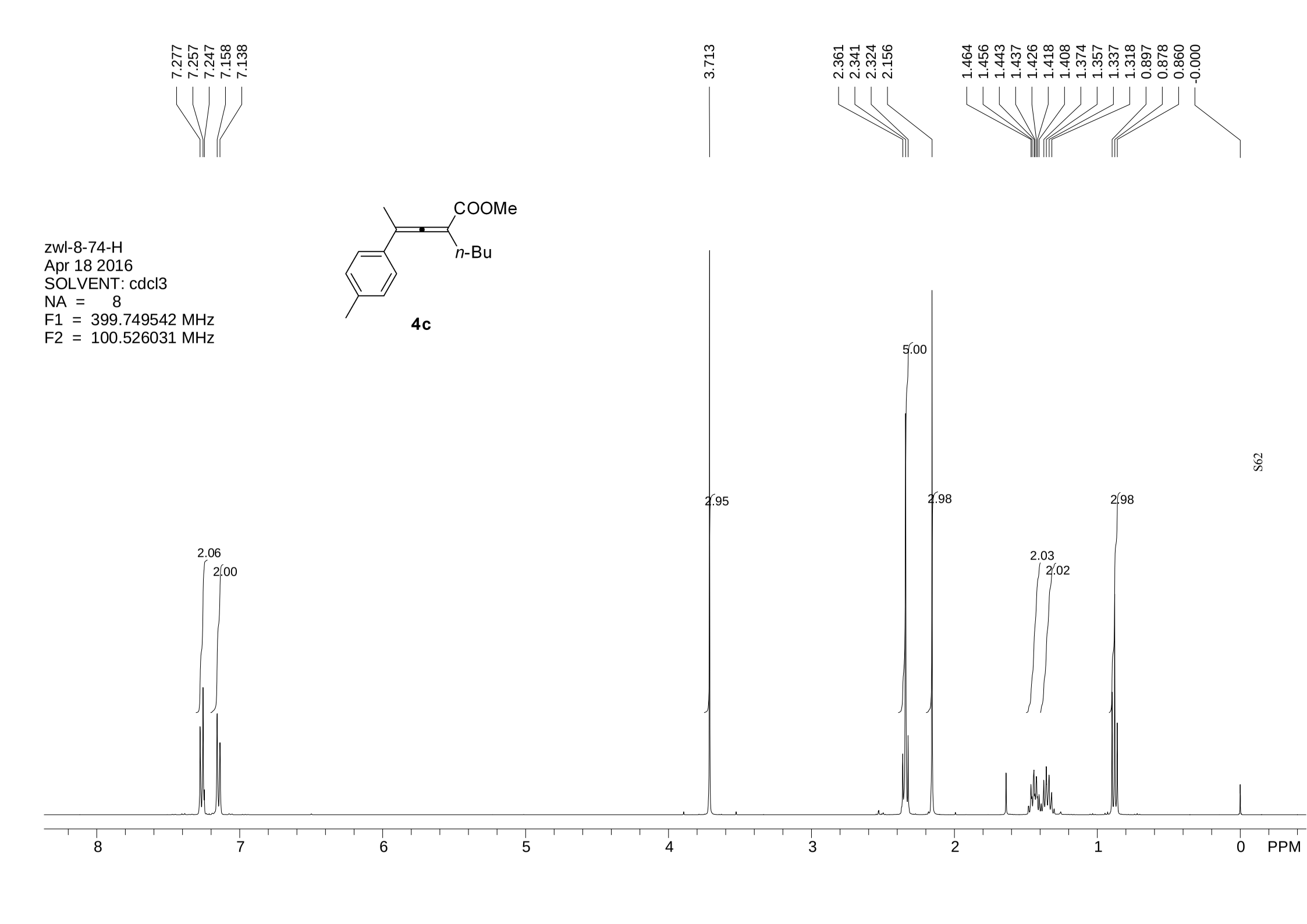

137.739
130.922
128.197
128.030
125.989
119.271
91.946
79.687
77.319
77.000
76.681
30.774
22.023
19.047
13.590
zwl-9-187-C
May 16 2017
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
F2 = 399.749146 MHz
Ph
n-Bu
3a
200
150
100
50
0
PPM

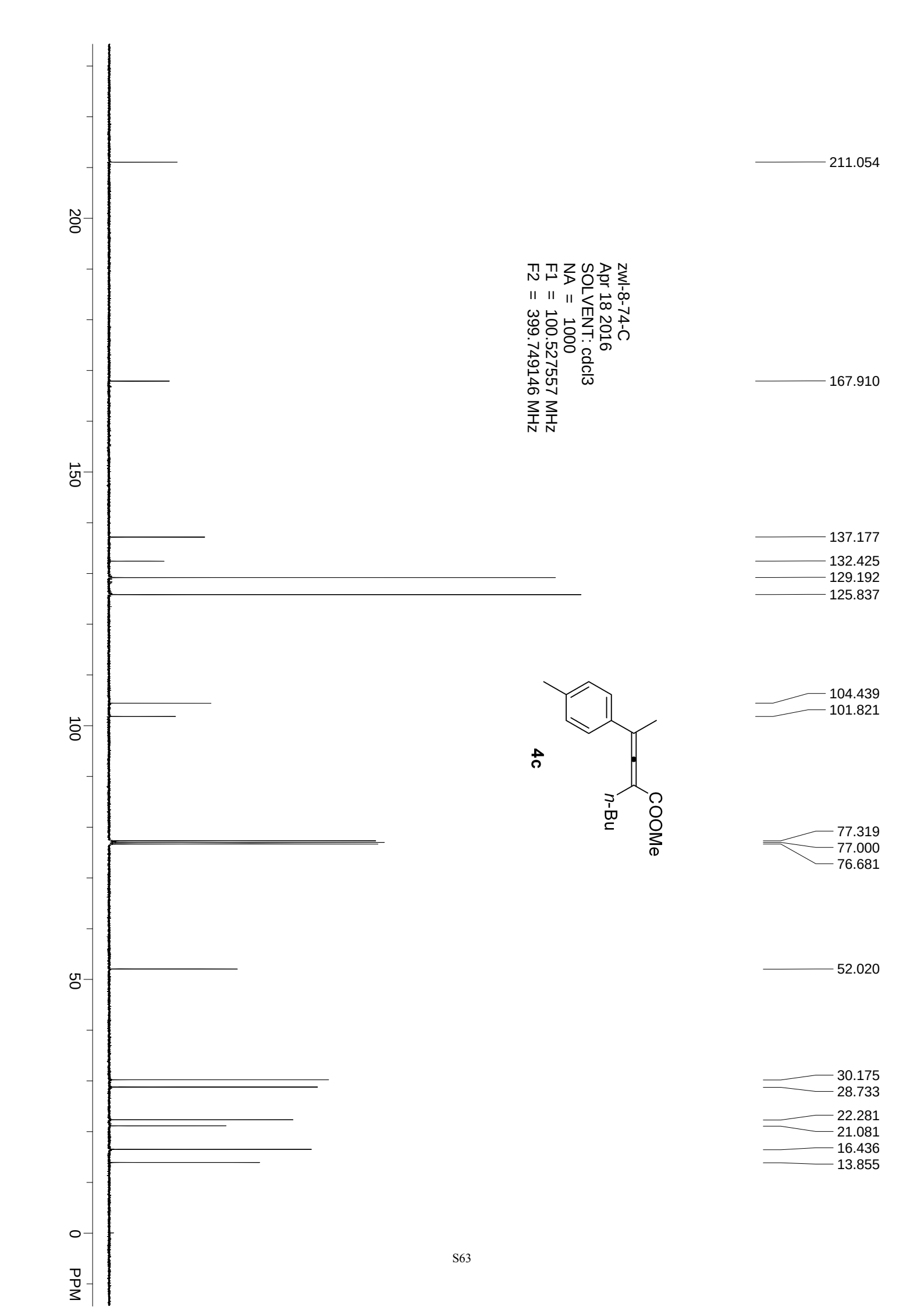

7.394
7.390
7.372
7.358
7.339
7.320
7.262
7.244
7.227
3.720
2.372
2.354
2.334
2.178
1.473
1.454
1.435
1.416
1.380
1.362
1.343
1.324
0.901
0.882
0.864
0.000
zwl-8-65-H
Apr 19 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
Ph
n-Bu
4a
4.03
1.07
3.00
2.02
3.00
2.07
2.02
3.03
S58
8
7
6
5
4
3
2
1
0
PPM

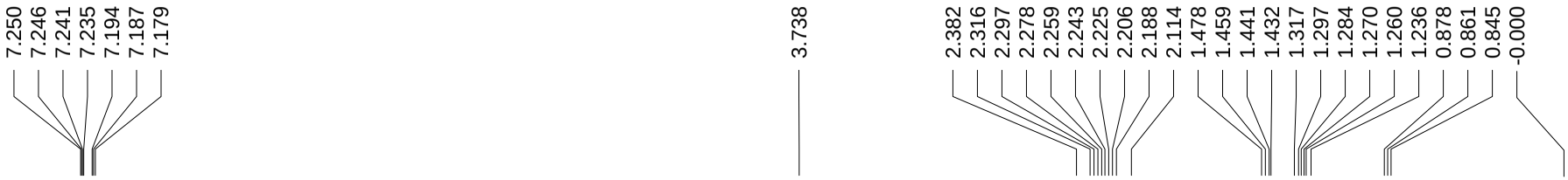

zwl-8-65-C
Apr 19 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
Ph
n-Bu
COOMe
4a
211.146
167.812
135.439
128.471
127.325
125.943
104.584
101.972
77.319
77.000
76.681
52.050
30.175
28.710
22.281
16.413
13.840
200
150
100
50
0
PPM


7.250
7.244
7.229
7.212
7.188
7.183
7.178
7.176
7.173
7.070
7.052
3.720
2.365
2.350
2.328
2.163
1.484
1.464
1.445
1.426
1.337
1.323
1.310
1.301
1.285
1.276
1.262
1.252
1.244
1.235
1.226
0.863
0.847
0.829
-0.000
zwl-8-199-H
Jul 8 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
n-C6H13
4b
3.18
1.00
2.99
5.11
3.04
6.31
2.10
3.10
S60
8
7
6
5
4
3
2
1
0
PPM

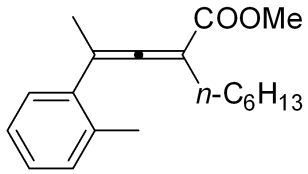

zwl-8-199-C
Jul 8 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4b
COOMe
n-C6H13
211.206
167.895
138.042
135.332
128.357
128.137
126.619
123.066
104.568
101.775
77.319
77.000
76.681
52.035
31.609
28.968
28.854
27.966
22.592
21.453
16.474
14.007
200
150
100
50
0
PPM


7.277
7.257
7.247
7.158
7.138
3.713
2.361
2.341
2.324
2.156
1.464
1.456
1.443
1.437
1.426
1.418
1.408
1.374
1.357
1.337
1.318
0.897
0.878
0.860
-0.000
COOMe
n-Bu
4c
zwl-8-74-H
Apr 18 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
2.06
2.00
2.95
5.00
2.98
2.03
2.02
2.98
S62
8
7
6
5
4
3
2
1
0
PPM

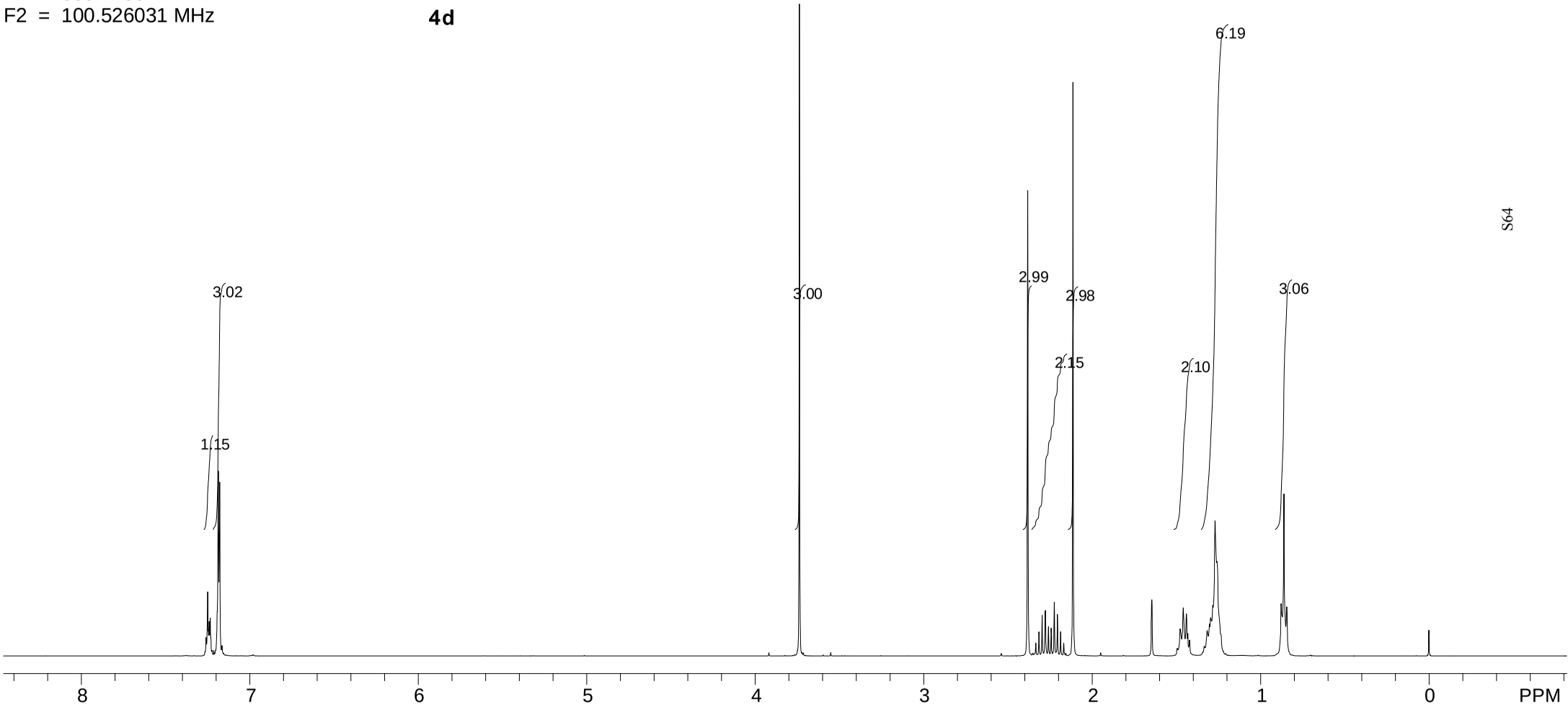

zwl-8-74-C
Apr 18 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4c
n-Bu
COOMe
211.054
167.910
137.177
132.425
129.192
125.837
104.439
101.821
77.319
77.000
76.681
52.020
30.175
28.733
22.281
21.081
16.436
13.855
200
150
100
50
0
PPM

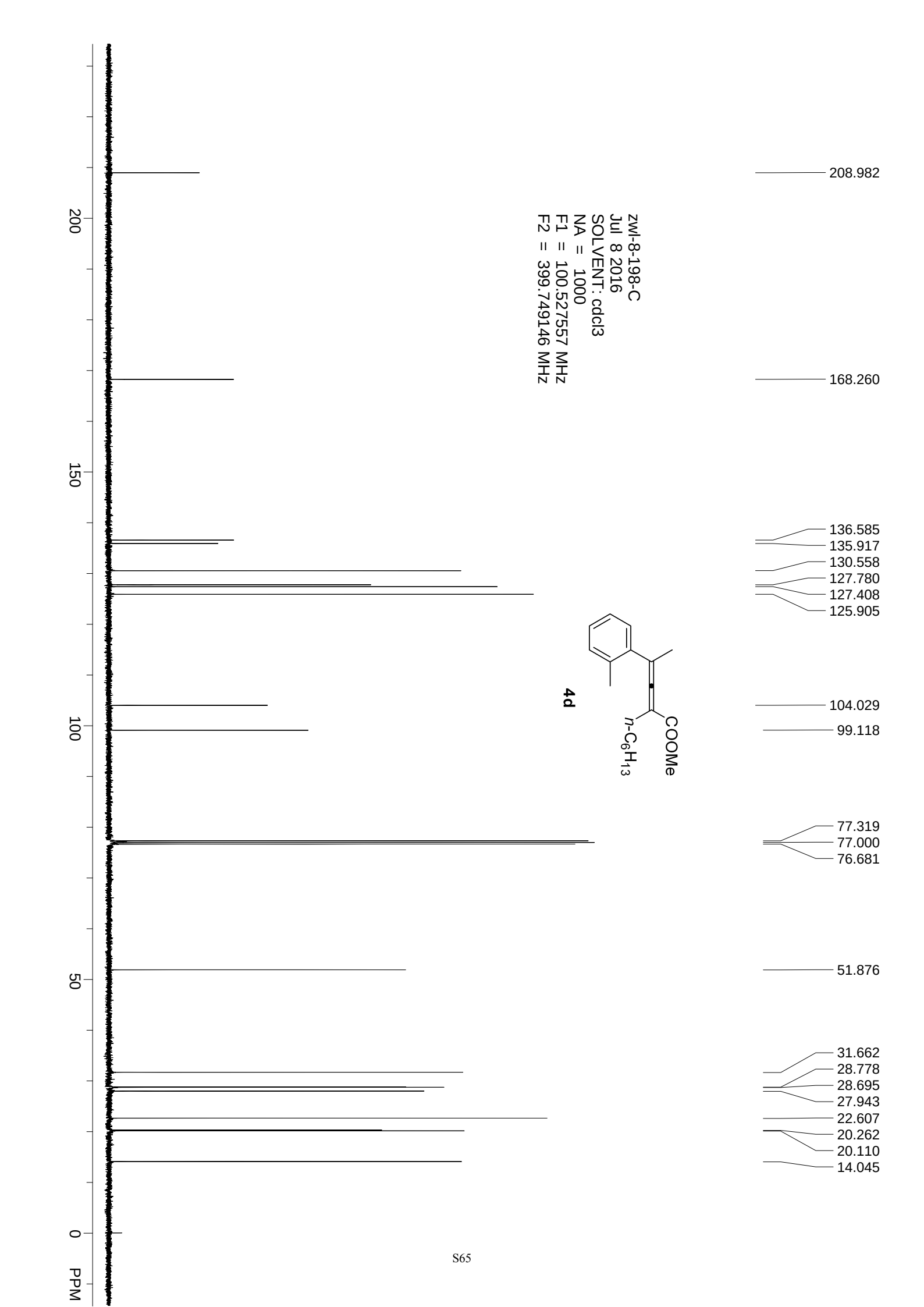


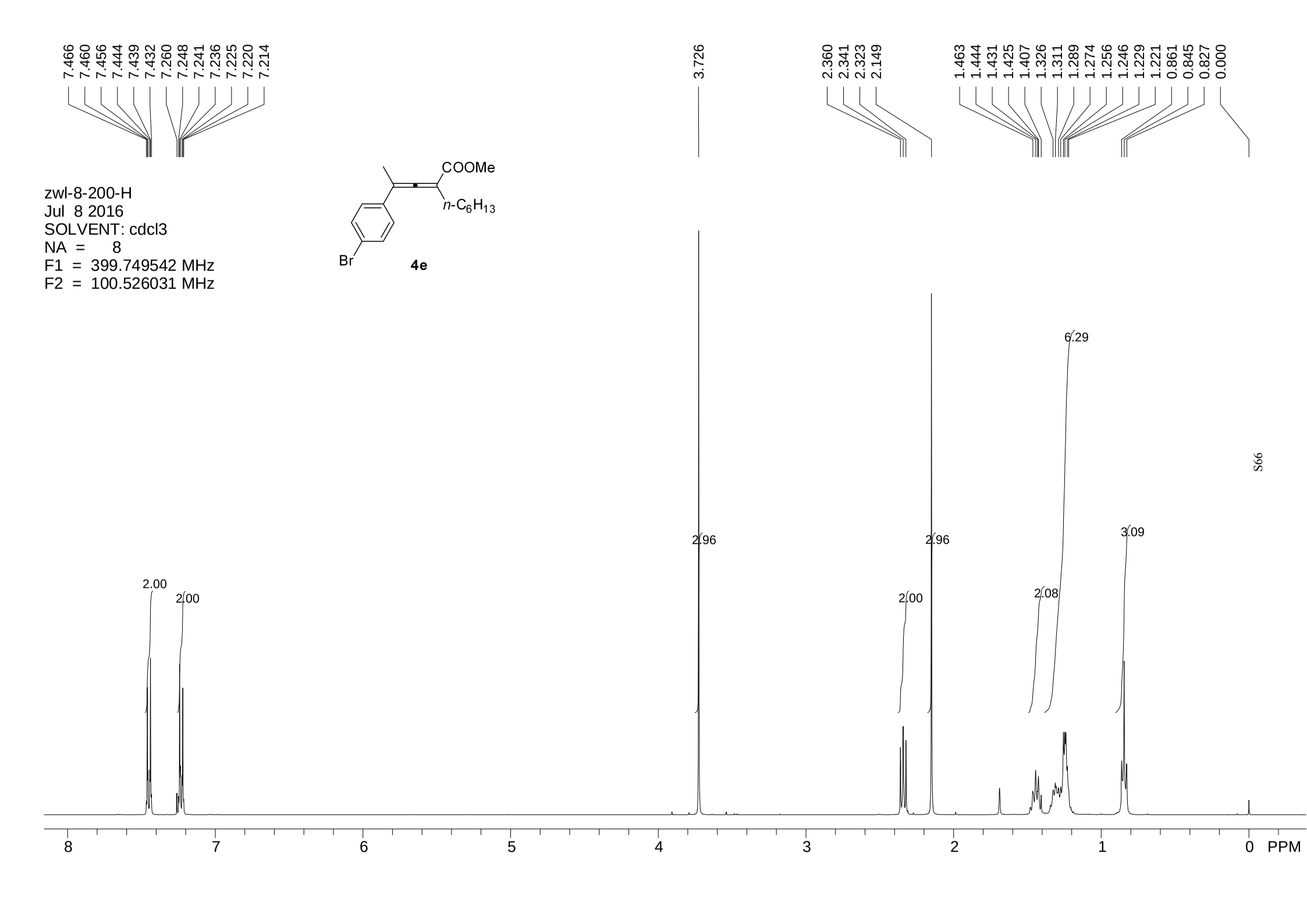

zwl-8-198-H
Jul 8 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz

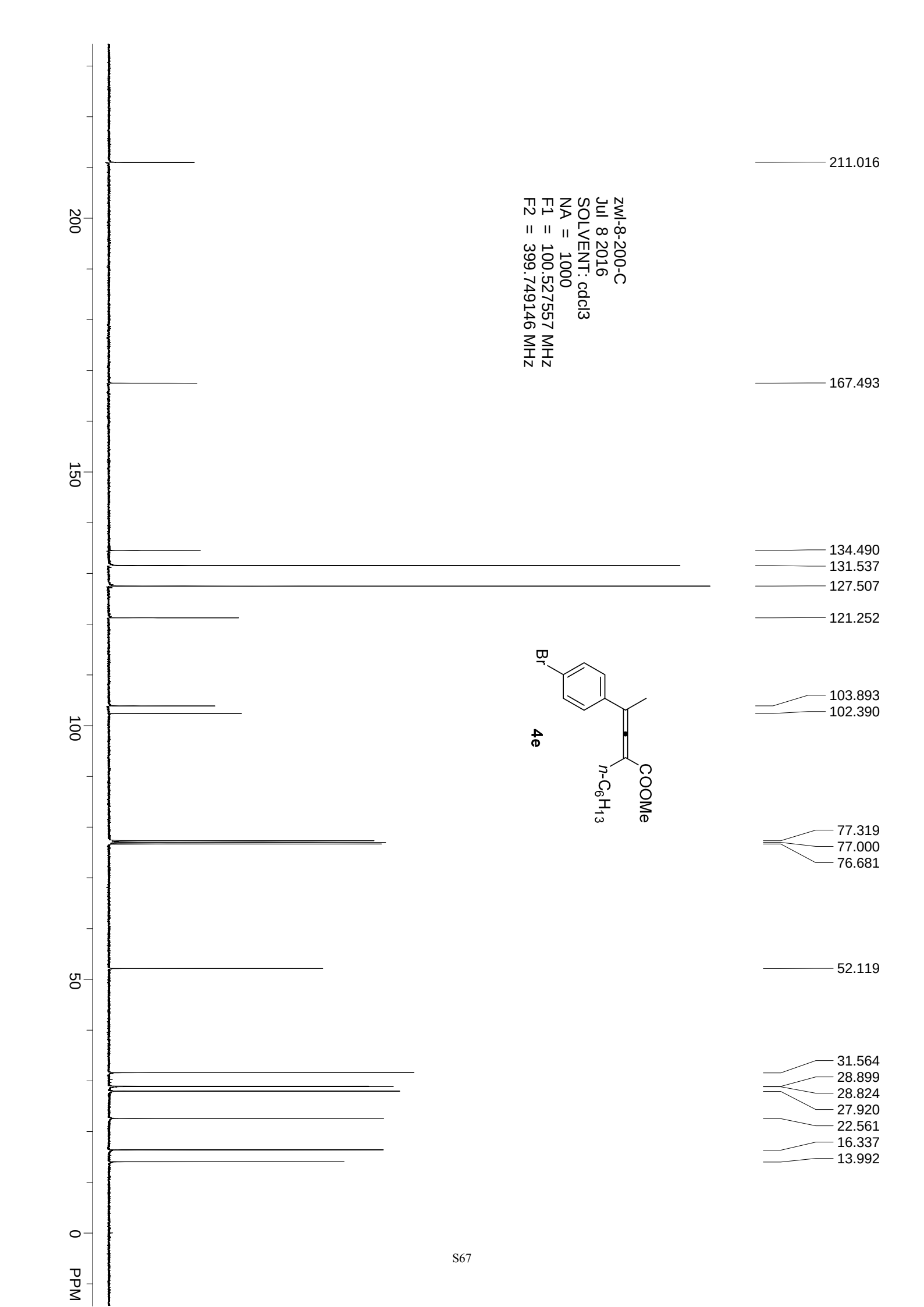


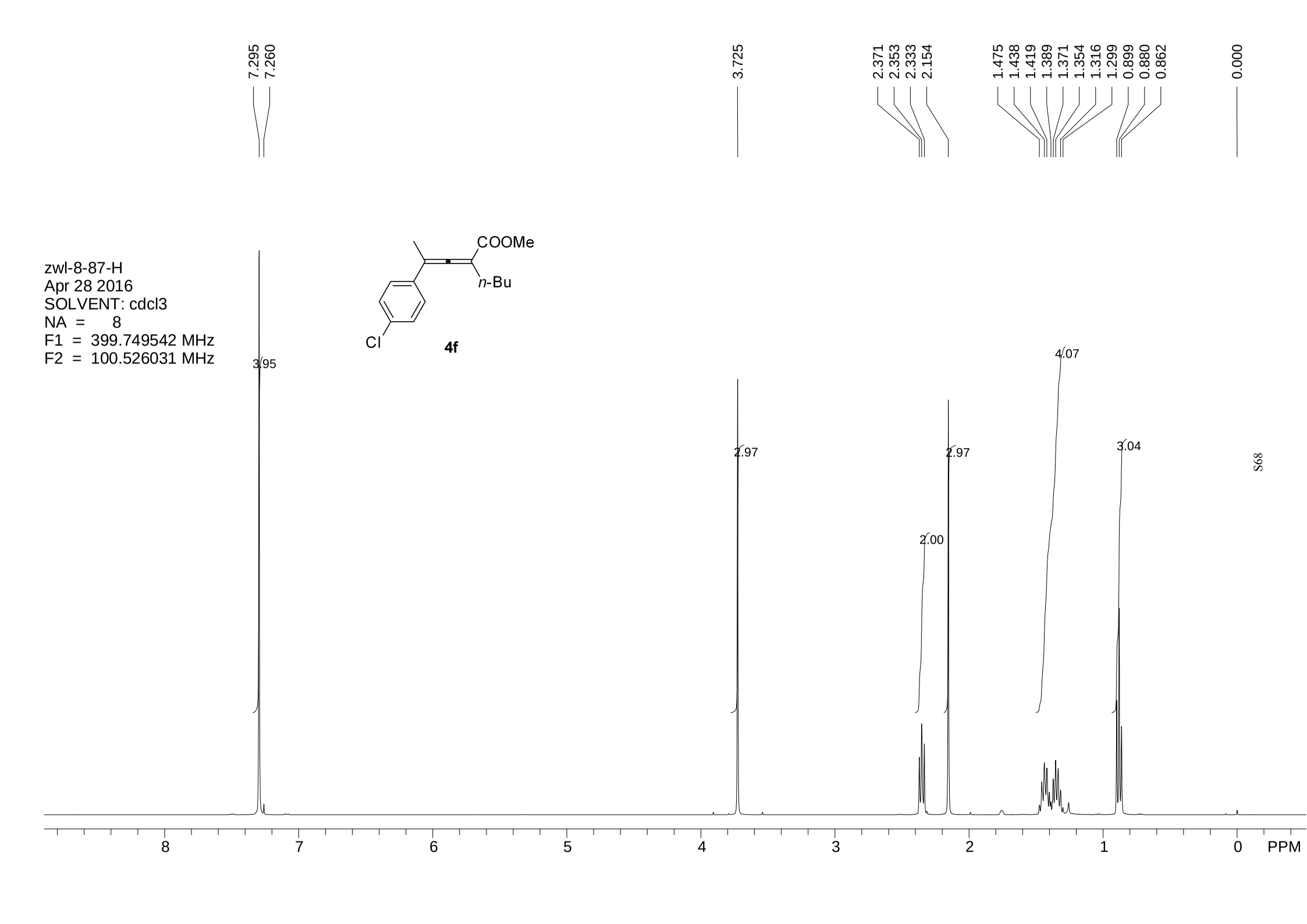

**4d**

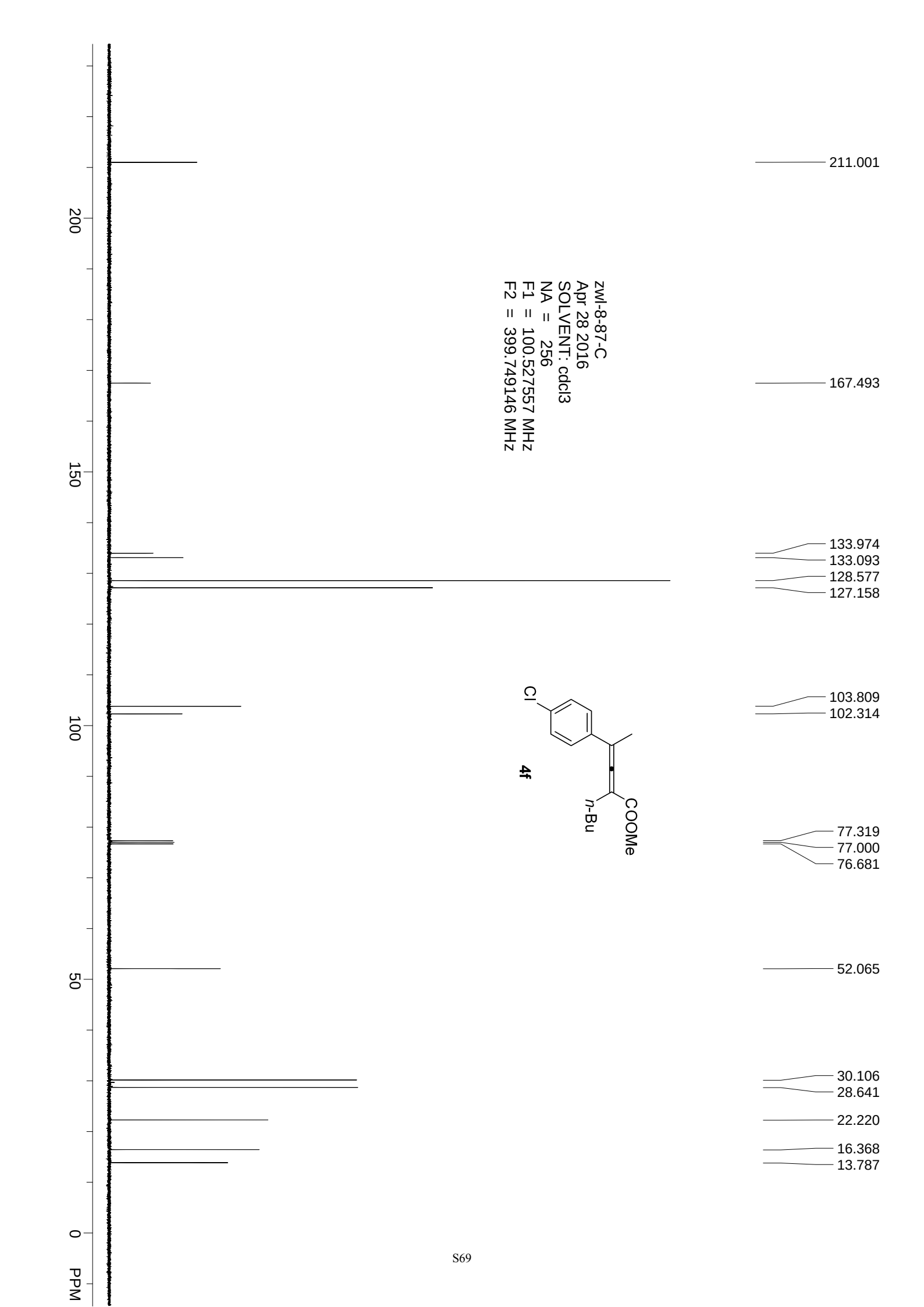


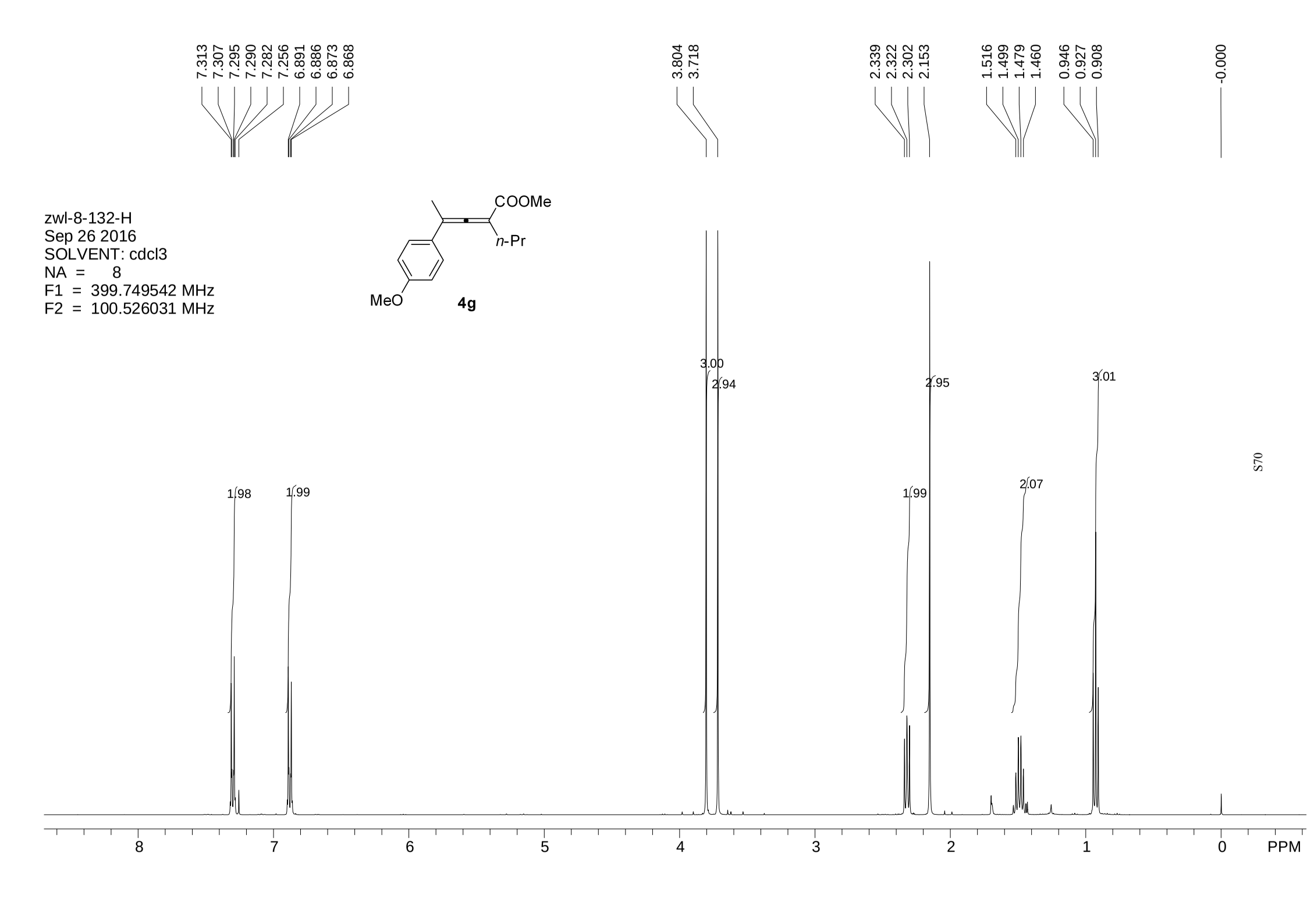

zwl-8-198-C
Jul 8 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4d
COOMe
n-C6H13
208.982
168.260
136.585
135.917
130.558
127.780
127.408
125.905
104.029
99.118
77.319
77.000
76.681
51.876
31.662
28.778
28.695
27.943
22.607
20.262
20.110
14.045
200
150
100
50
0
PPM

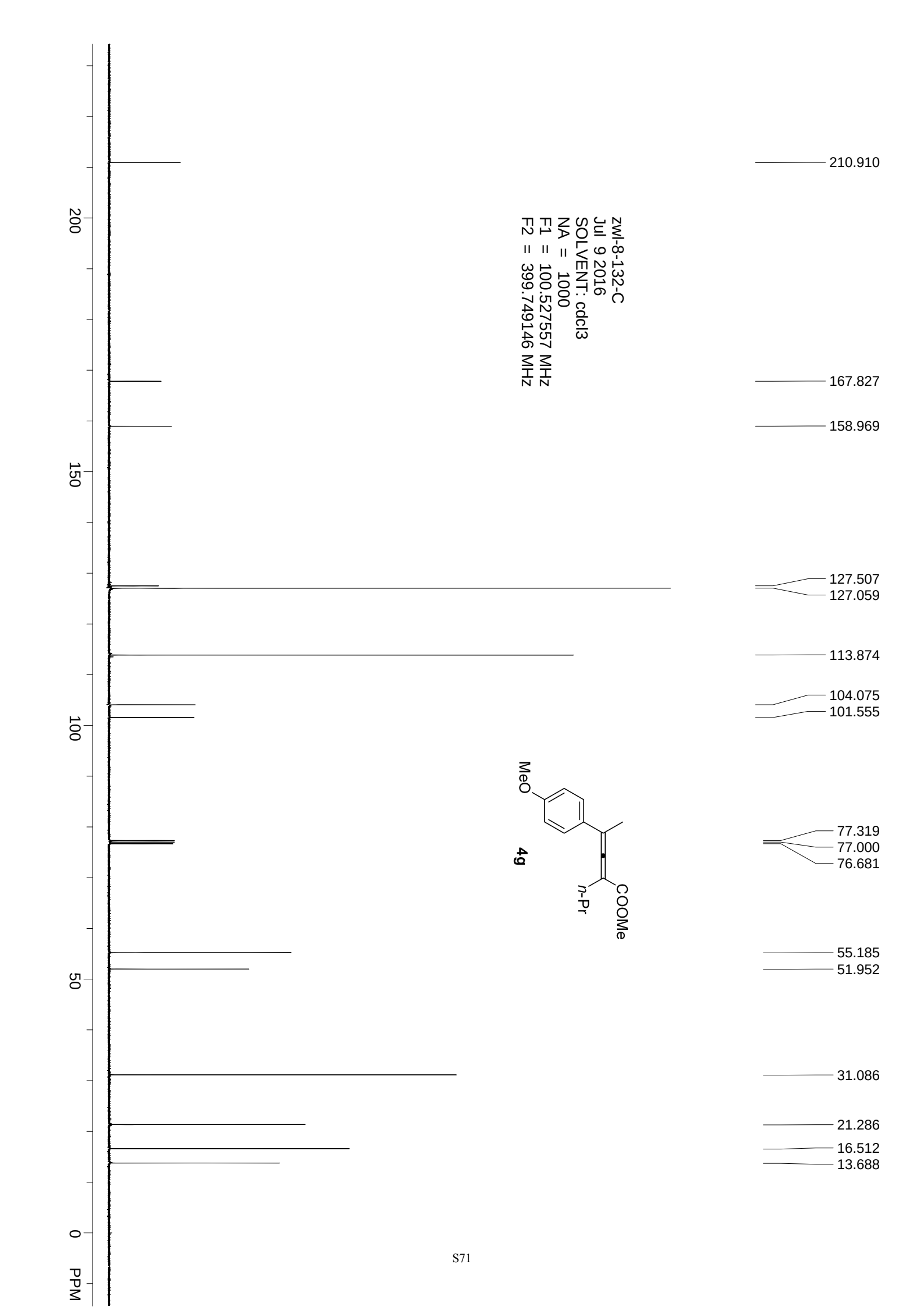

7.466
7.460
7.456
7.444
7.439
7.432
7.260
7.248
7.241
7.236
7.225
7.220
7.214
3.726
2.360
2.341
2.323
2.149
1.463
1.444
1.431
1.425
1.407
1.326
1.311
1.289
1.274
1.256
1.246
1.229
1.221
0.861
0.845
0.827
0.000
zwl-8-200-H
Jul 8 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
n-C6H13
Br
4e
2.00
2.00
2.96
2.00
2.96
2.08
6.29
3.09
S66
8
7
6
5
4
3
2
1
0
PPM

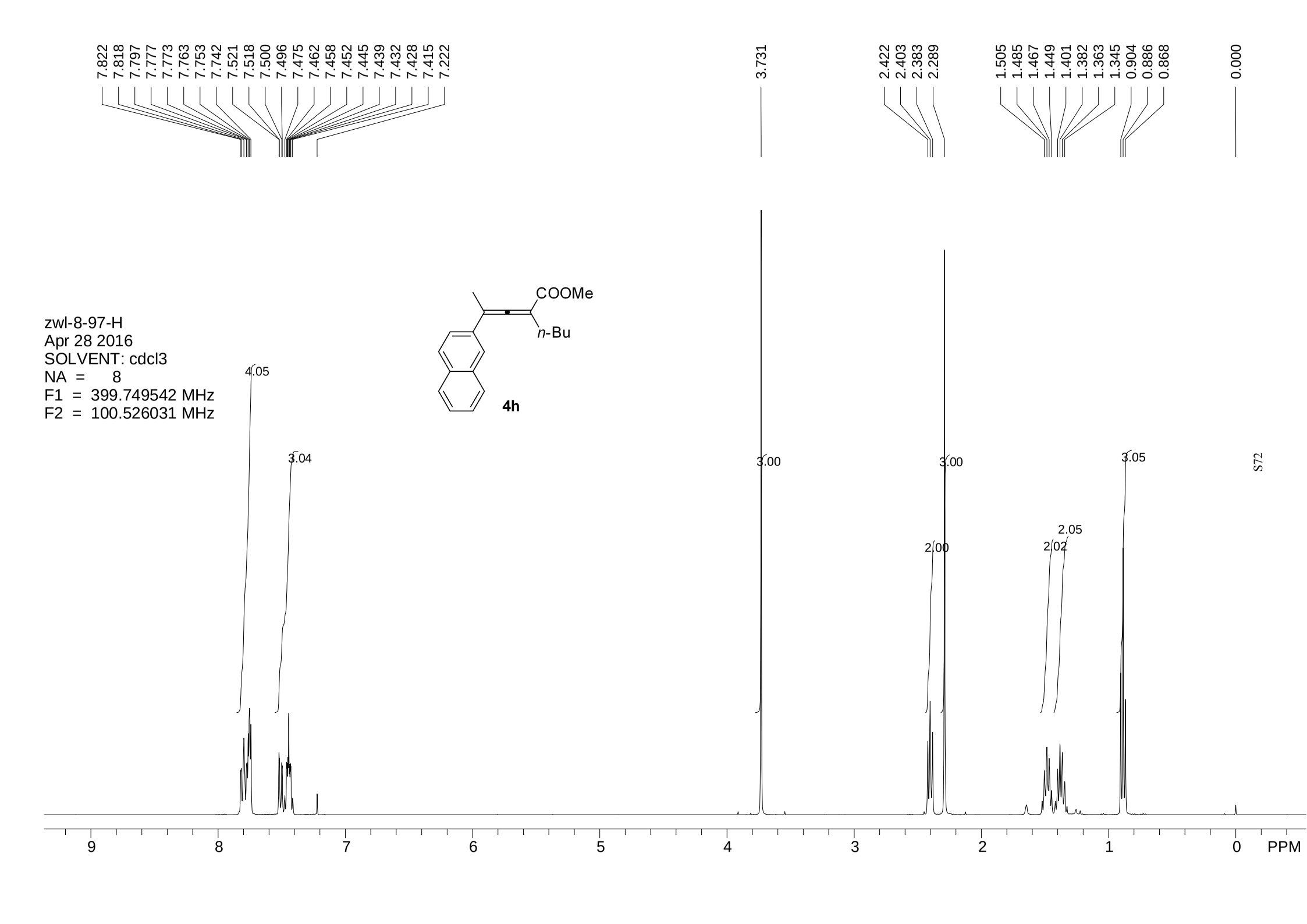

zwl-8-200-C
Jul 8 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
211.016
167.493
134.490
131.537
127.507
121.252
103.893
102.390
77.319
77.000
76.681
52.119
31.564
28.899
28.824
27.920
22.561
16.337
13.992
Br
COOMe
n-C6H13
4e
200
150
100
50
0
PPM

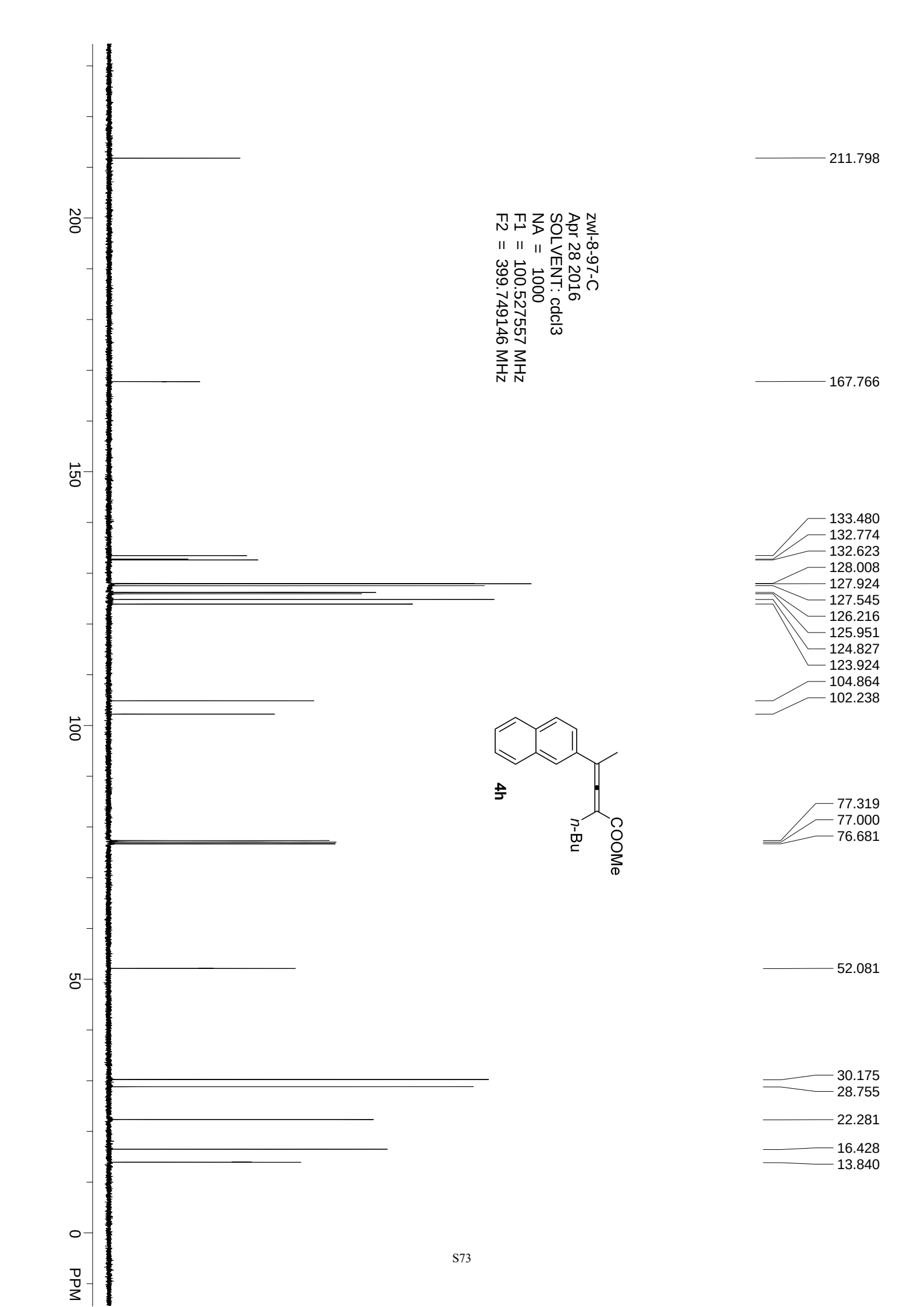

7.295
7.260
3.725
2.371
2.353
2.333
2.154
1.475
1.438
1.419
1.389
1.371
1.354
1.316
1.299
0.899
0.880
0.862
0.000
zwl-8-87-H
Apr 28 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
n-Bu
Cl
4f
3.95
2.97
2.00
2.97
4.07
3.04
S68
8
7
6
5
4
3
2
1
0
PPM

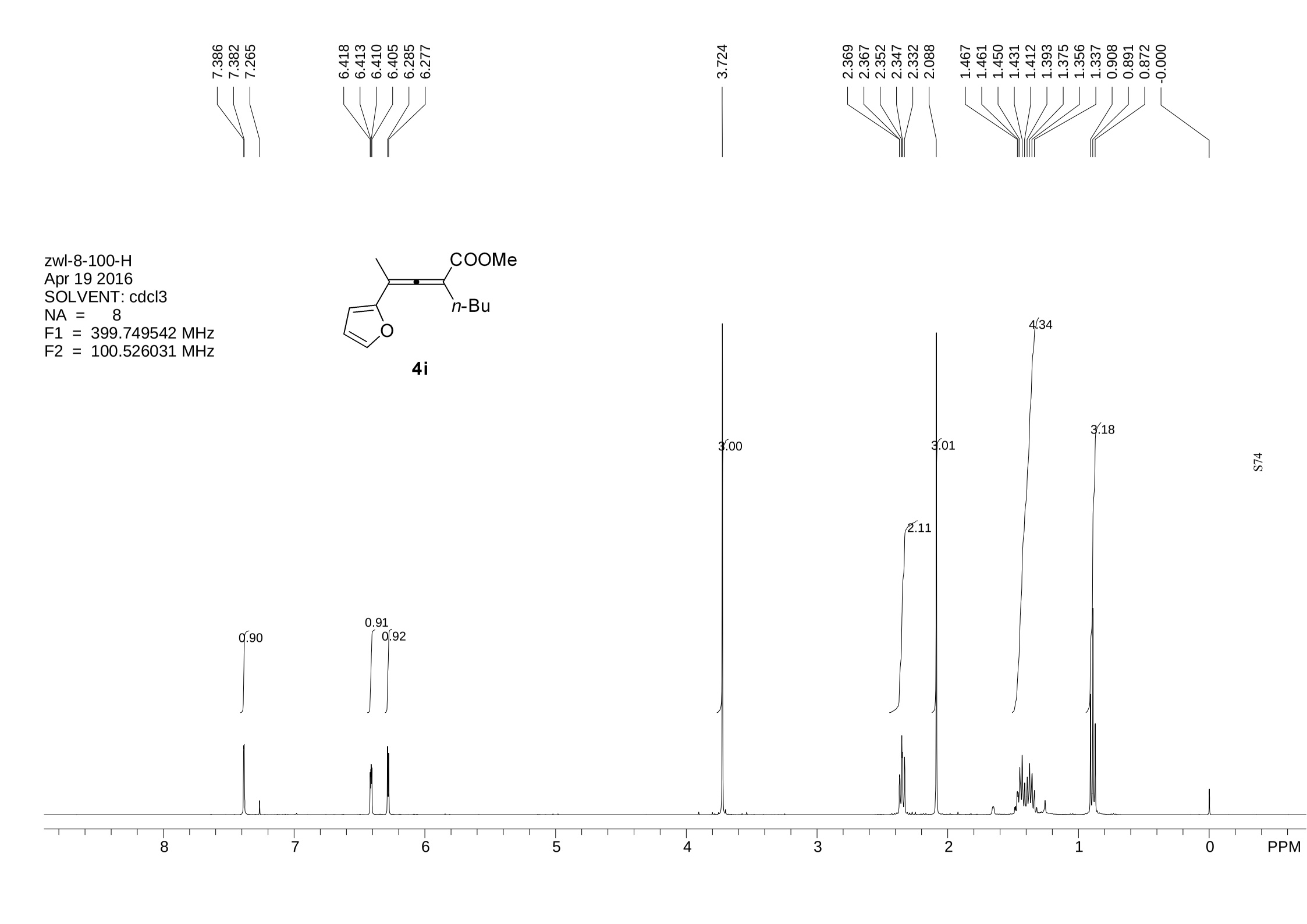

zwl-8-87-C
Apr 28 2016
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
F2 = 399.749146 MHz
Cl
COOMe
n-Bu
4f
211.001
167.493
133.974
133.093
128.577
127.158
103.809
102.314
77.319
77.000
76.681
52.065
30.106
28.641
22.220
16.368
13.787
200
150
100
50
0
PPM

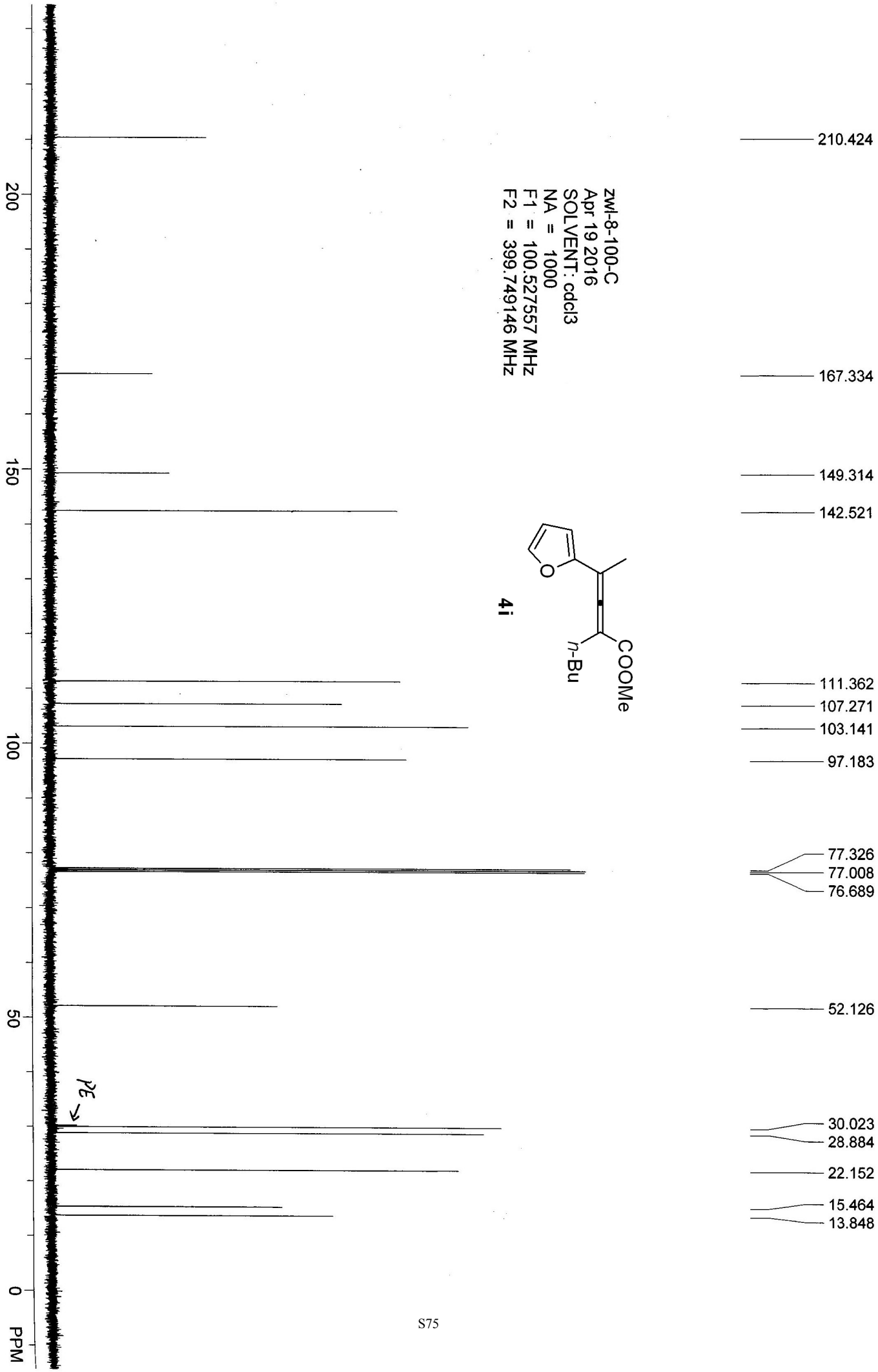

7.313
7.307
7.295
7.290
7.282
7.256
6.891
6.886
6.873
6.868
3.804
3.718
2.339
2.322
2.302
2.153
1.516
1.499
1.479
1.460
0.946
0.927
0.908
-0.000
zwl-8-132-H
Sep 26 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
n-Pr
MeO
4g
3.00
2.94
2.95
3.01
1.98
1.99
1.99
2.07
S70
8
7
6
5
4
3
2
1
0
PPM

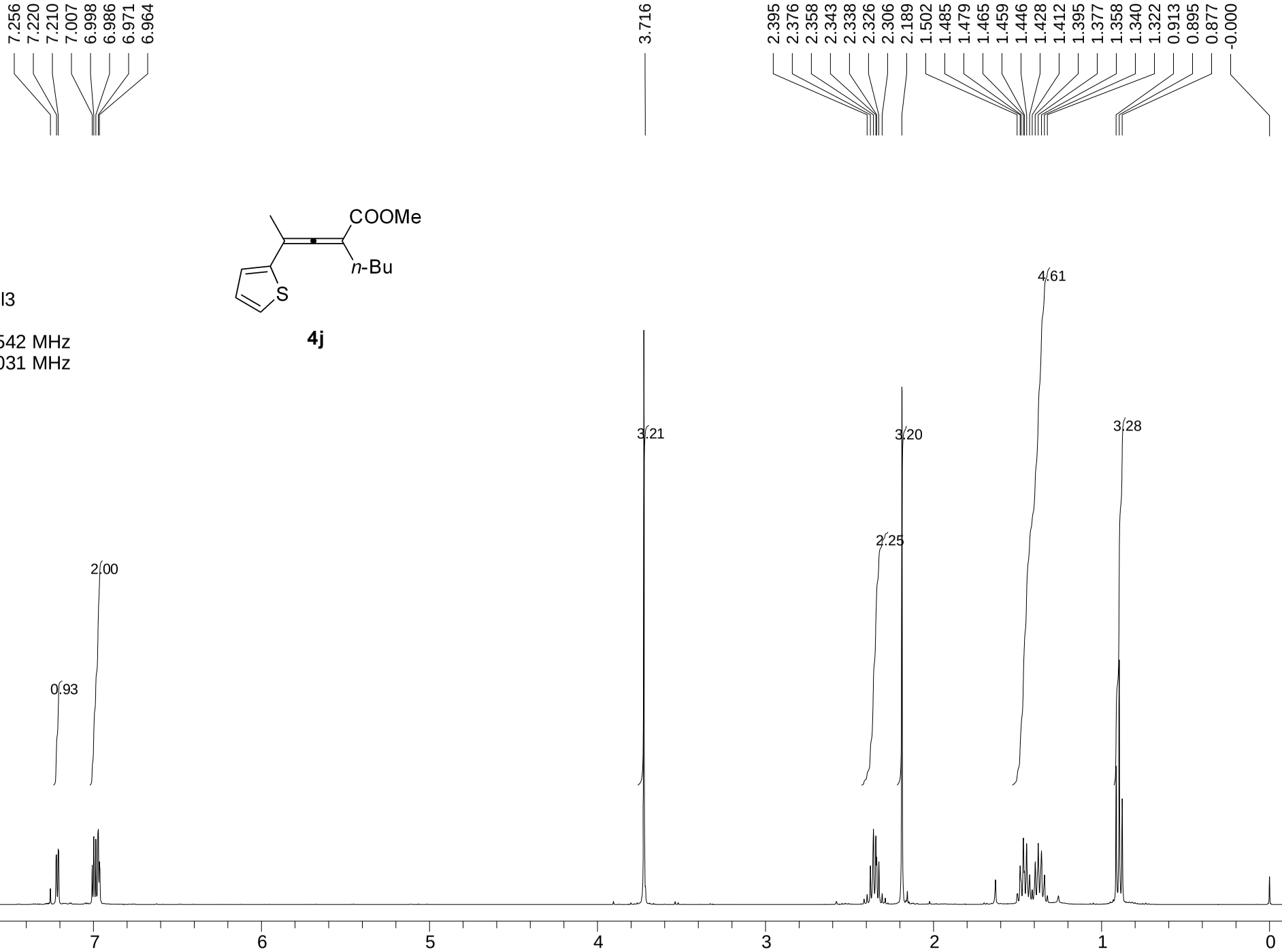

zwl-8-132-C
Jul 9 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
MeO
4g
n-Pr
COOMe
210.910
167.827
158.969
127.507
127.059
113.874
104.075
101.555
77.319
77.000
76.681
55.185
51.952
31.086
21.286
16.512
13.688
200
150
100
50
0
PPM

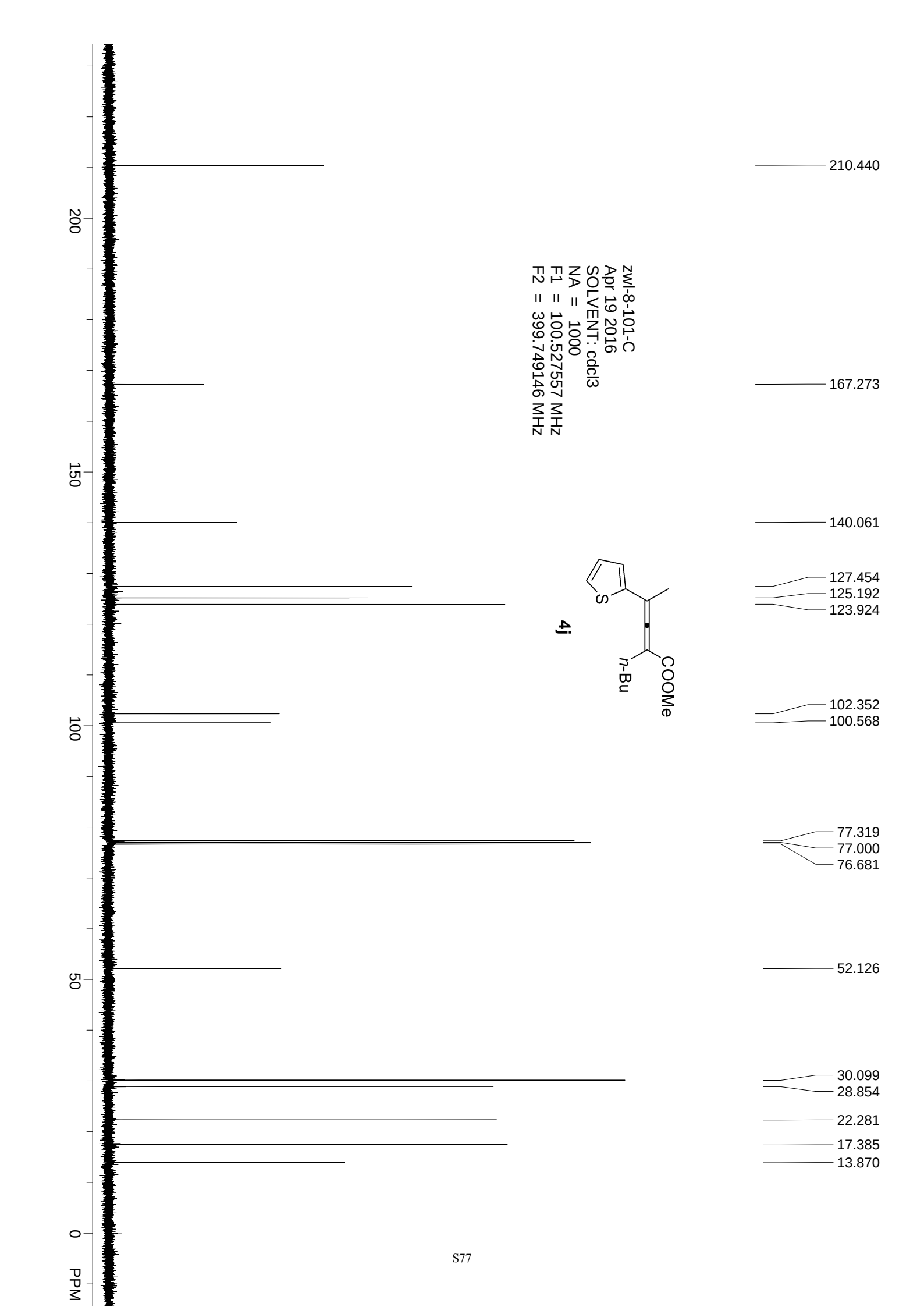

7.822
7.818
7.797
7.777
7.773
7.763
7.753
7.742
7.521
7.518
7.500
7.496
7.475
7.462
7.458
7.452
7.445
7.439
7.432
7.428
7.415
7.222
3.731
2.422
2.403
2.383
2.289
1.505
1.485
1.467
1.449
1.401
1.382
1.363
1.345
0.904
0.886
0.868
0.000
zwl-8-97-H
Apr 28 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
n-Bu
4h
4.05
3.04
3.00
2.00
3.00
2.02
2.05
3.05
S72
9
8
7
6
5
4
3
2
1
0
PPM

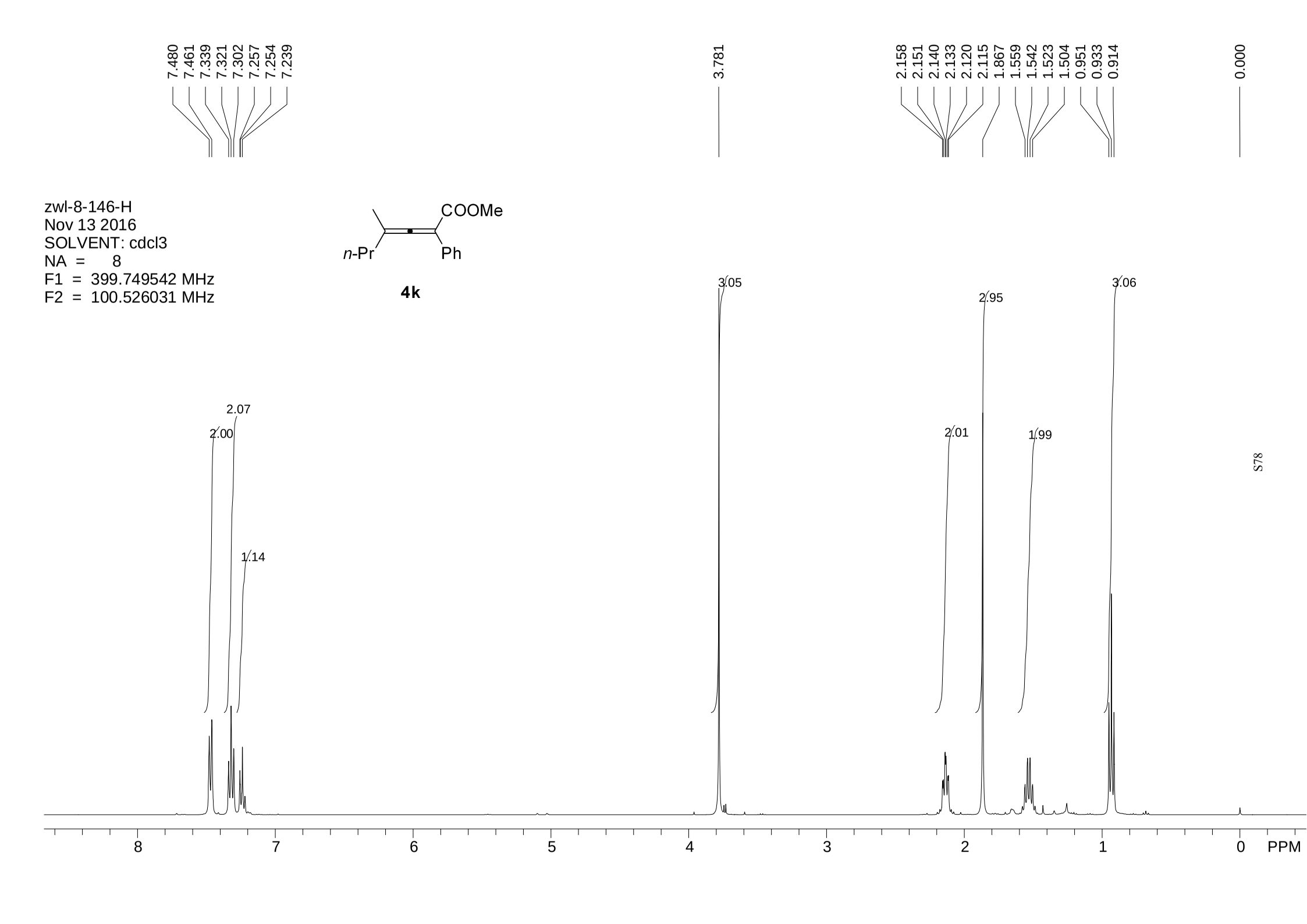

zwl-8-97-C
Apr 28 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4h
n-Bu
COOMe
211.798
167.766
133.480
132.774
132.623
128.008
127.924
127.545
126.216
125.951
124.827
123.924
104.864
102.238
77.319
77.000
76.681
52.081
30.175
28.755
22.281
16.428
13.840
200
150
100
50
0
PPM

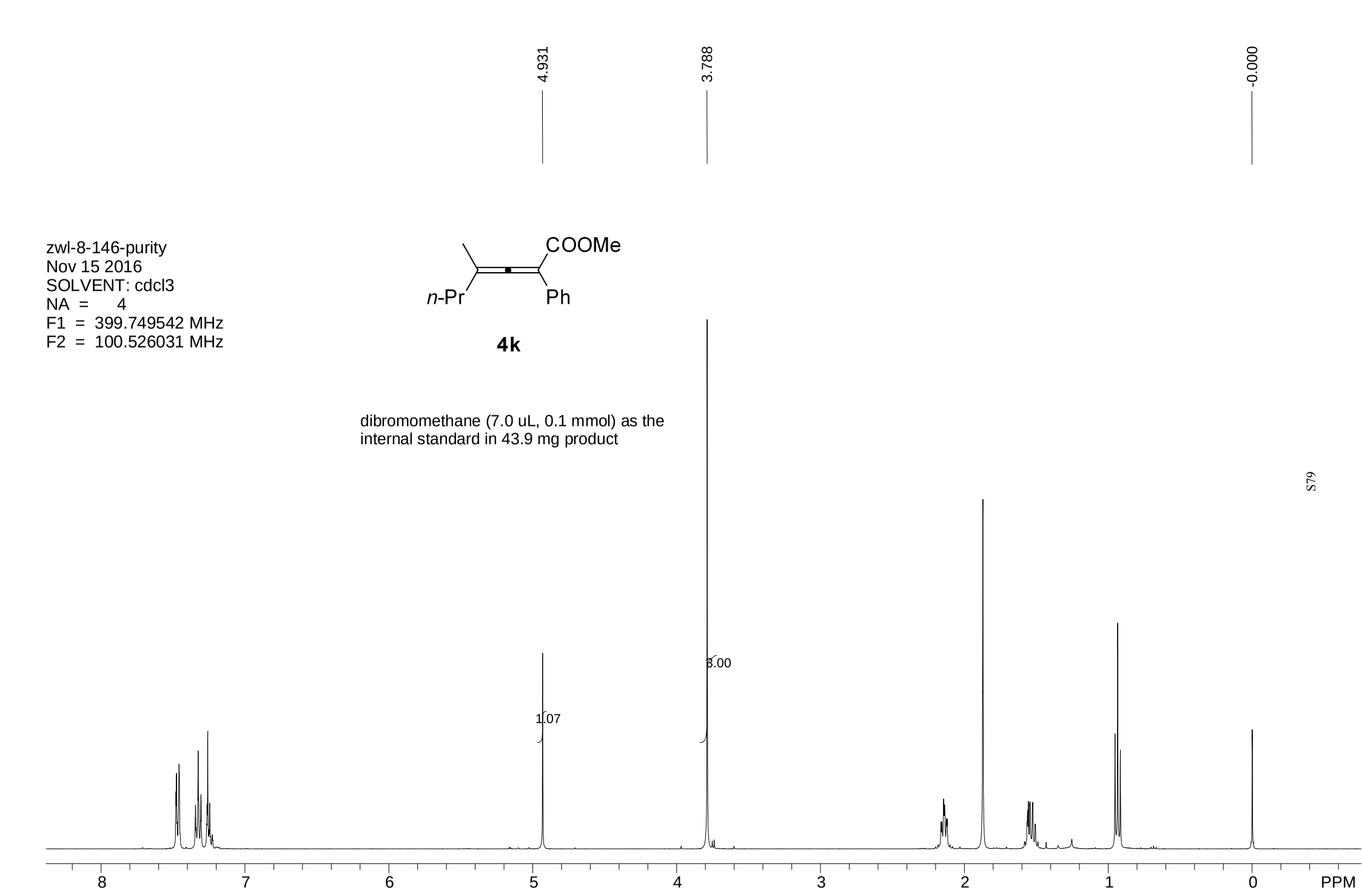

7.386
7.382
7.265
6.418
6.413
6.410
6.405
6.285
6.277
3.724
2.369
2.367
2.352
2.347
2.332
2.088
1.467
1.461
1.450
1.431
1.412
1.393
1.375
1.356
1.337
0.908
0.891
0.872
-0.000
zwl-8-100-H
Apr 19 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
n-Bu
O
4i
0.90
0.91
0.92
3.00
2.11
3.01
4.34
3.18
S74
8
7
6
5
4
3
2
1
0
PPM

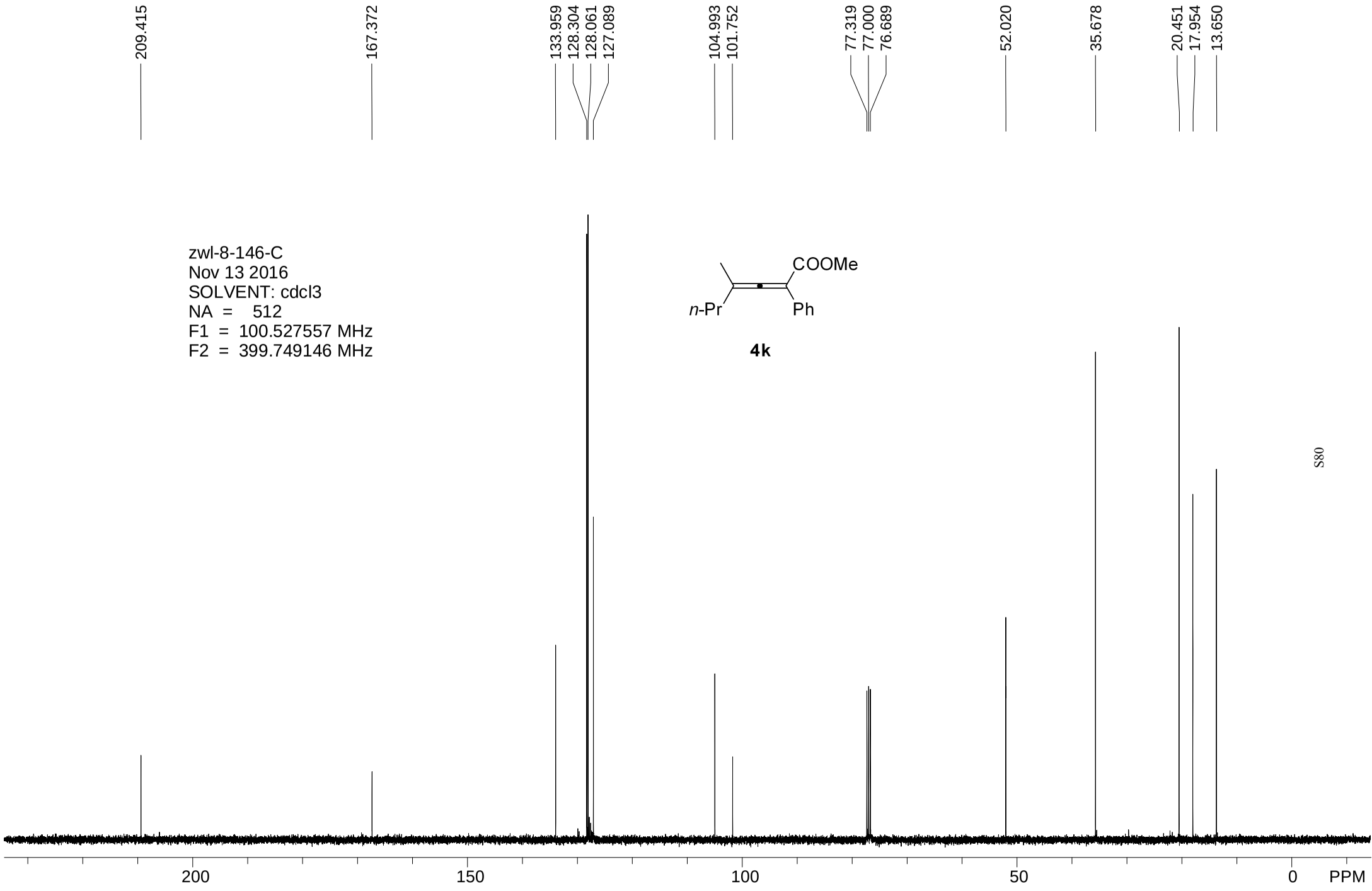

zwl-8-100-C
Apr 19 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4i
COOMe
n-Bu
210.424
167.334
149.314
142.521
111.362
107.271
103.141
97.183
77.326
77.008
76.689
52.126
30.023
28.884
22.152
15.464
13.848
200
150
100
50
0
PPM

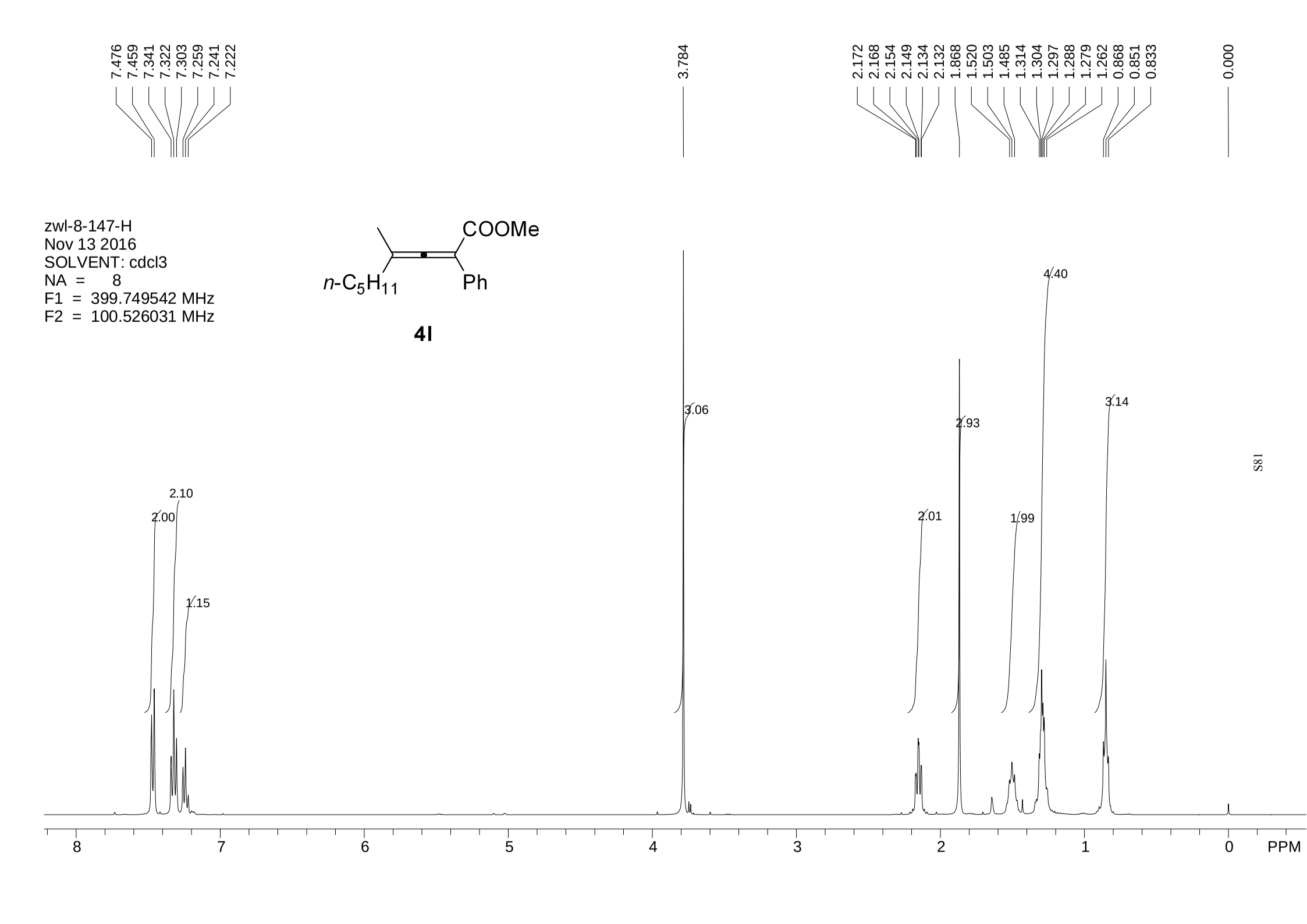

7.256
7.220
7.210
7.007
6.998
6.986
6.971
6.964
3.716
2.395
2.376
2.358
2.343
2.338
2.326
2.306
2.189
1.502
1.485
1.479
1.465
1.459
1.446
1.428
1.412
1.395
1.377
1.358
1.340
1.322
0.913
0.895
0.877
-0.000
COOMe
n-Bu
S
4j
zwl-8-101-H
Apr 19 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
0.93
2.00
3.21
2.25
3.20
4.61
3.28
S76
8
7
6
5
4
3
2
1
0
PPM

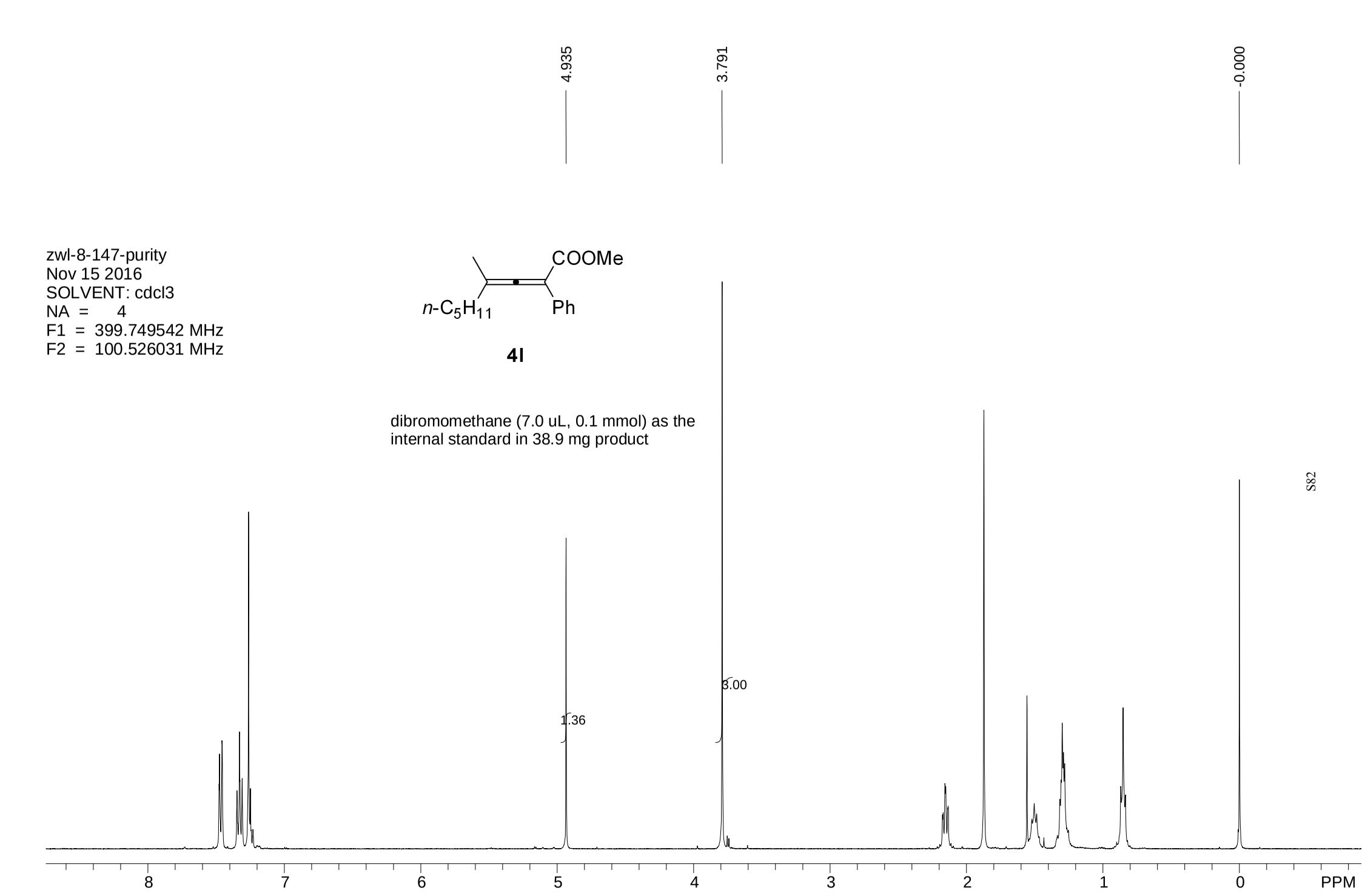

zwl-8-101-C
Apr 19 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4j
S
n-Bu
COOMe
210.440
167.273
140.061
127.454
125.192
123.924
102.352
100.568
77.319
77.000
76.681
52.126
30.099
28.854
22.281
17.385
13.870
200
150
100
50
0
PPM

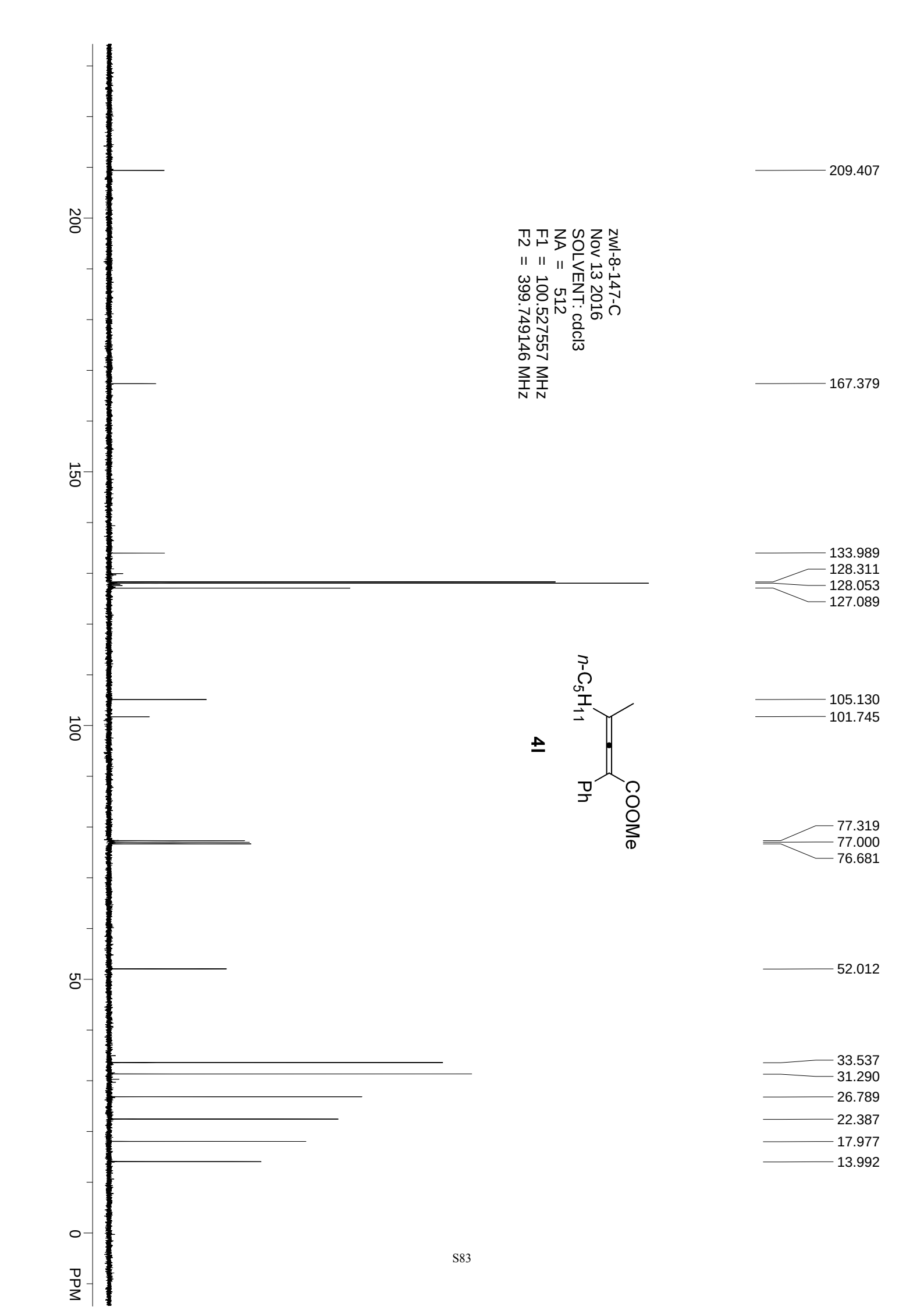

7.480
7.461
7.339
7.321
7.302
7.257
7.254
7.239
3.781
2.158
2.151
2.140
2.133
2.120
2.115
1.867
1.559
1.542
1.523
1.504
0.951
0.933
0.914
0.000
zwl-8-146-H
Nov 13 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
n-Pr
Ph
4k
3.05
2.95
3.06
2.07
2.00
2.01
1.99
1.14
S78
8
7
6
5
4
3
2
1
0
PPM

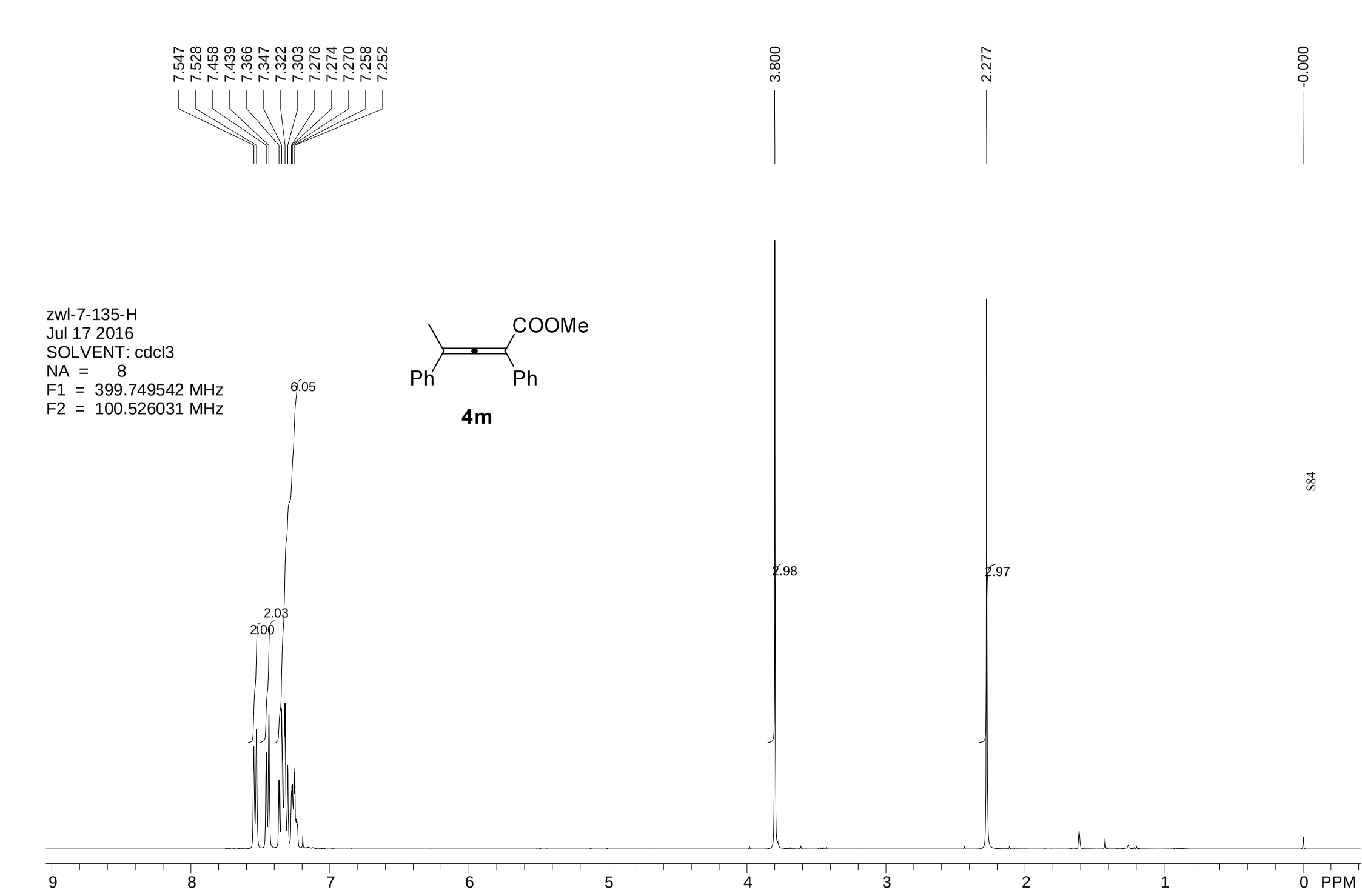

4.931
3.788
-0.000
zwl-8-146-purity
Nov 15 2016
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
n-Pr
Ph
4k
dibromomethane (7.0 uL, 0.1 mmol) as the internal standard in 43.9 mg product
1.07
3.00
S79
8
7
6
5
4
3
2
1
0
PPM

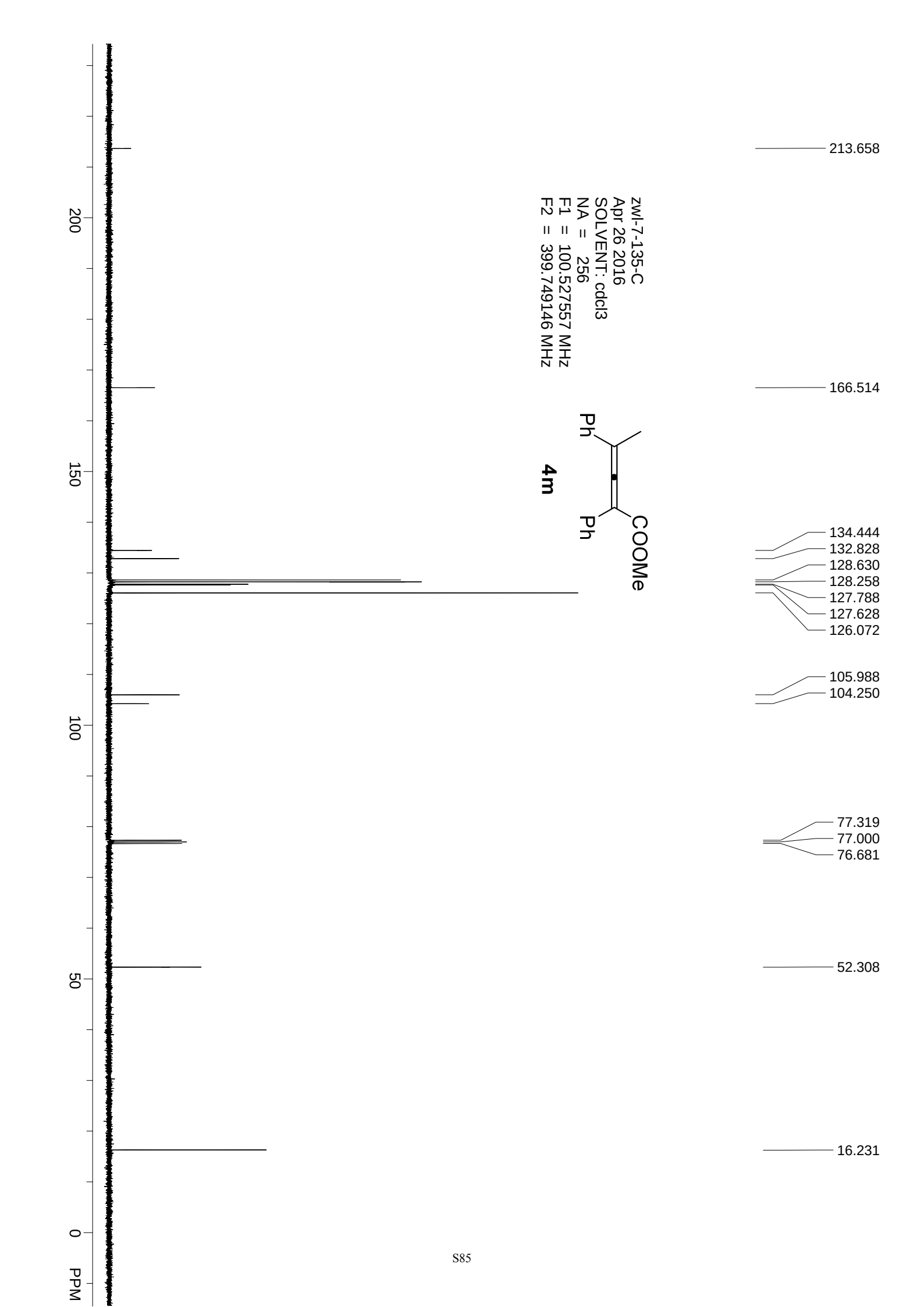

209.415
167.372
133.959
128.304
128.061
127.089
104.993
101.752
77.319
77.000
76.689
52.020
35.678
20.451
17.954
13.650
zwl-8-146-C
Nov 13 2016
SOLVENT: cdcl3
NA = 512
F1 = 100.527557 MHz
F2 = 399.749146 MHz
COOMe
n-Pr
Ph
4k
200
150
100
50
0
PPM

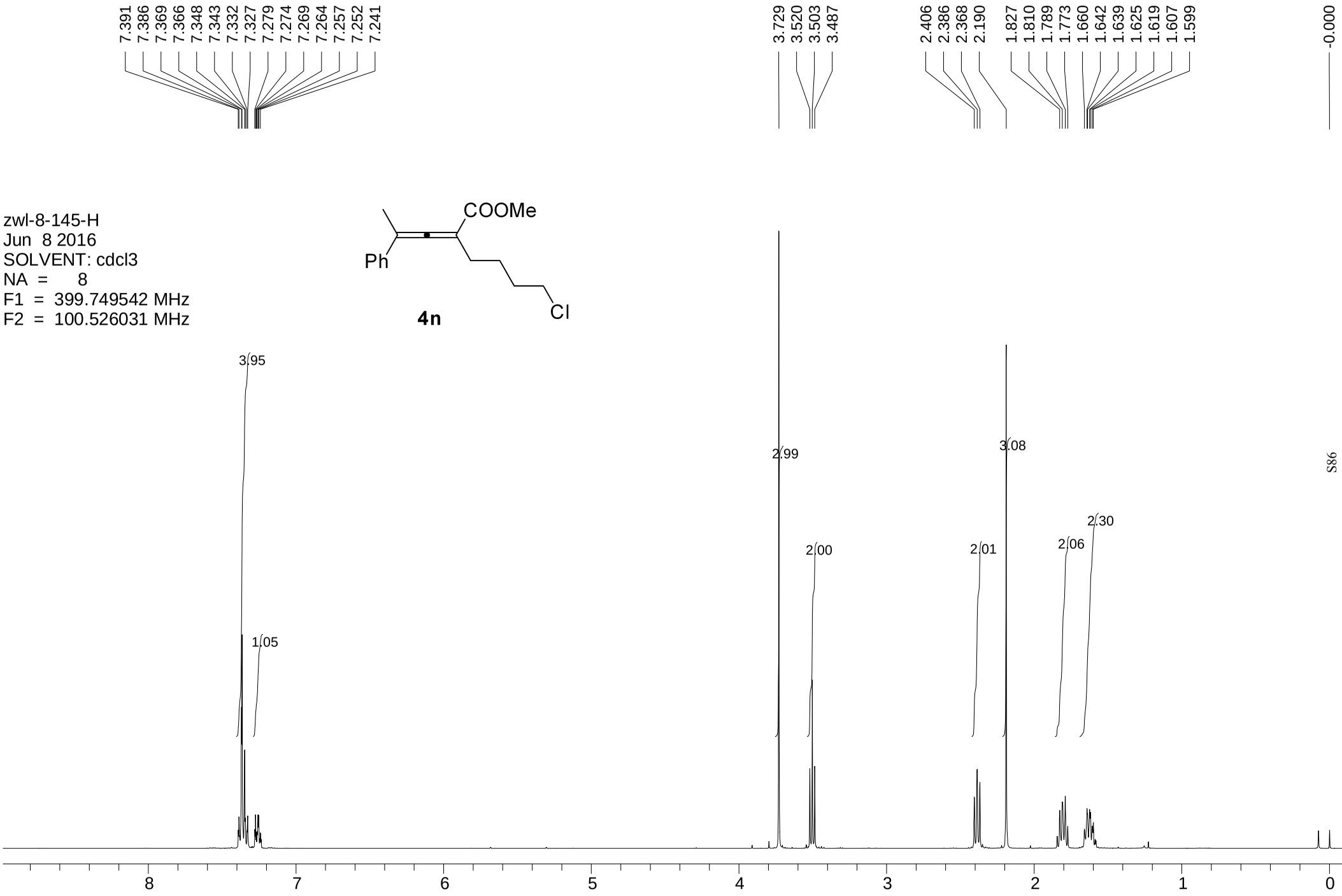

7.476
7.459
7.341
7.322
7.303
7.259
7.241
7.222
3.784
2.172
2.168
2.154
2.149
2.134
2.132
1.868
1.520
1.503
1.485
1.314
1.304
1.297
1.288
1.279
1.262
0.868
0.851
0.833
0.000
zwl-8-147-H
Nov 13 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
n-C5H11
Ph
4l
3.06
2.93
4.40
3.14
2.10
2.00
2.01
1.99
1.15
S81
8
7
6
5
4
3
2
1
0
PPM

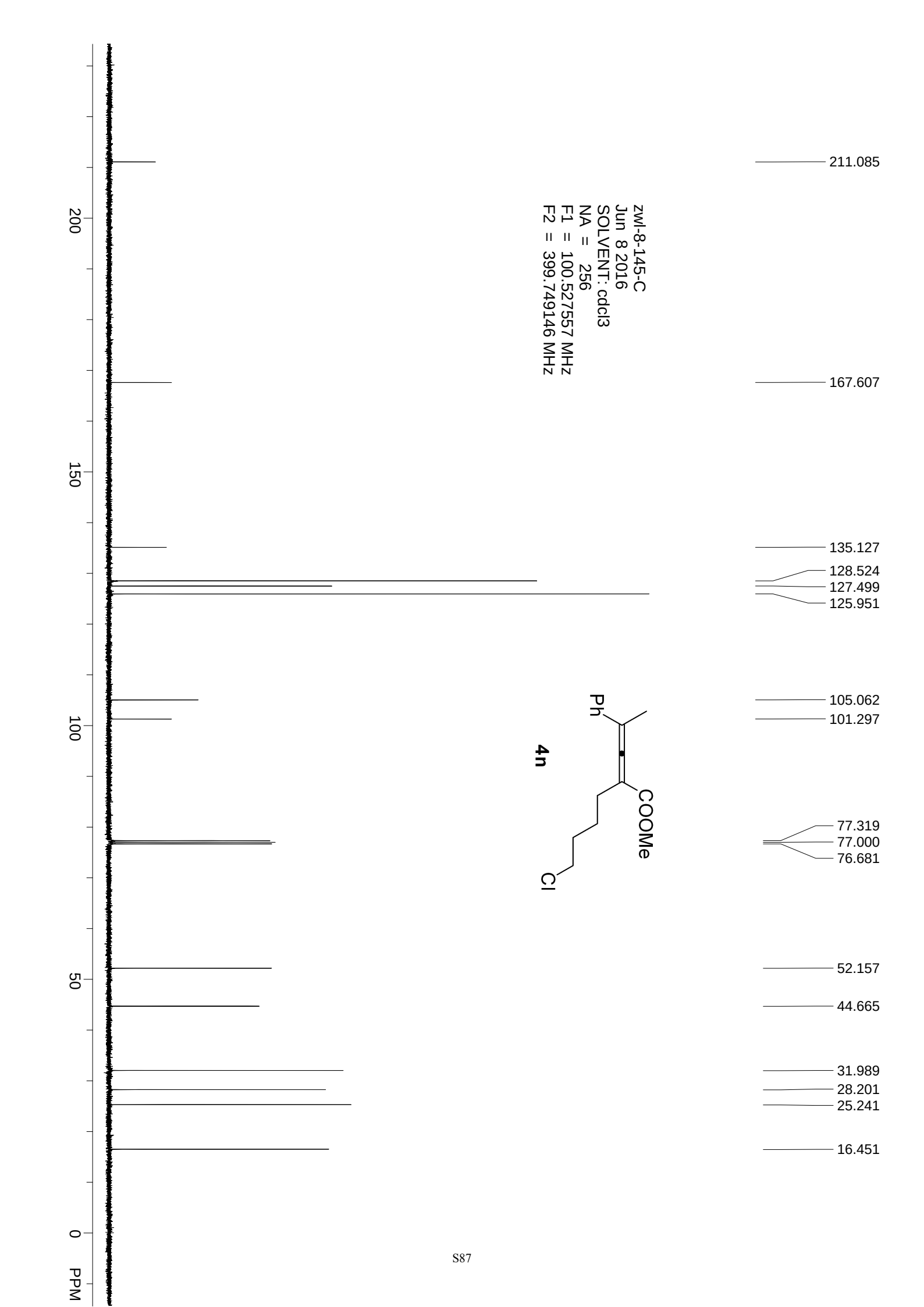

4.935
3.791
-0.000
zwl-8-147-purity
Nov 15 2016
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
n-C5H11
Ph
4l
dibromomethane (7.0 uL, 0.1 mmol) as the internal standard in 38.9 mg product
1.36
3.00
S82
8
7
6
5
4
3
2
1
0
PPM

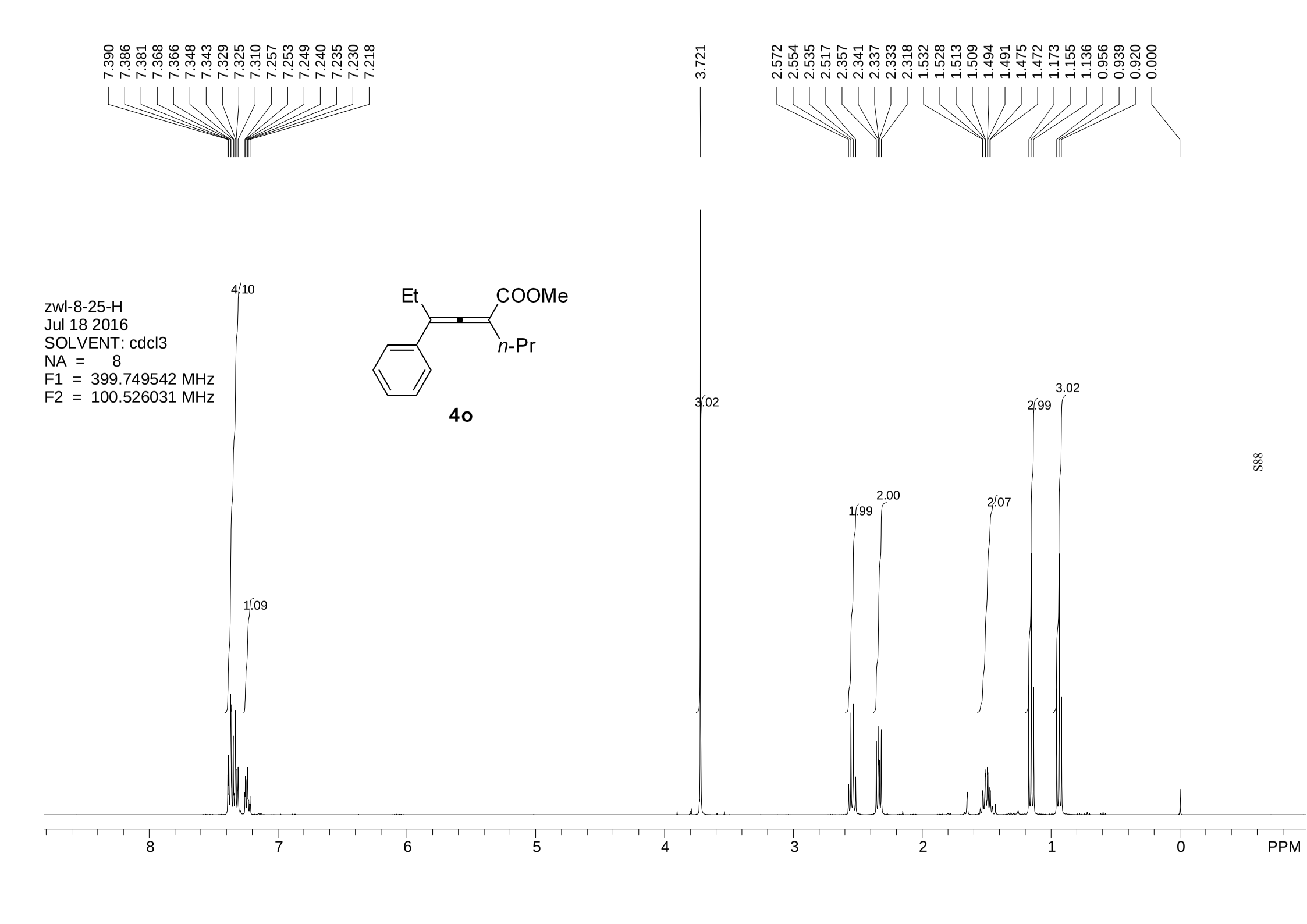

zwl-8-147-C
Nov 13 2016
SOLVENT: cdcl3
NA = 512
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4l
n-C5H11
Ph
COOMe
209.407
167.379
133.989
128.311
128.053
127.089
105.130
101.745
77.319
77.000
76.681
52.012
33.537
31.290
26.789
22.387
17.977
13.992
200
150
100
50
0
PPM

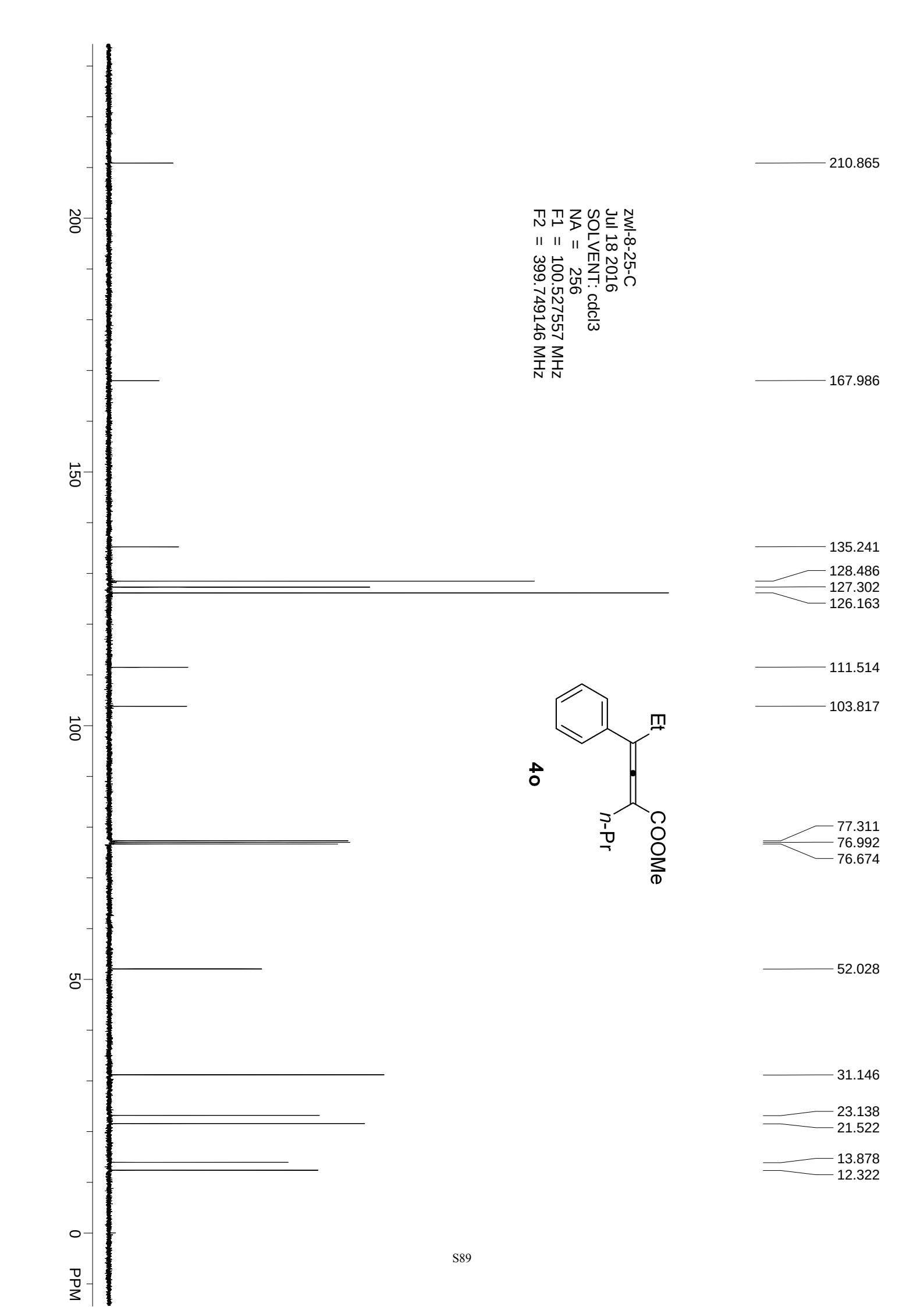

7.547
7.528
7.458
7.439
7.366
7.347
7.322
7.303
7.276
7.274
7.270
7.258
7.252
3.800
2.277
-0.000
zwl-7-135-H
Jul 17 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
Ph
Ph
4m
6.05
2.03
2.00
2.98
2.97
S84
9
8
7
6
5
4
3
2
1
0
PPM

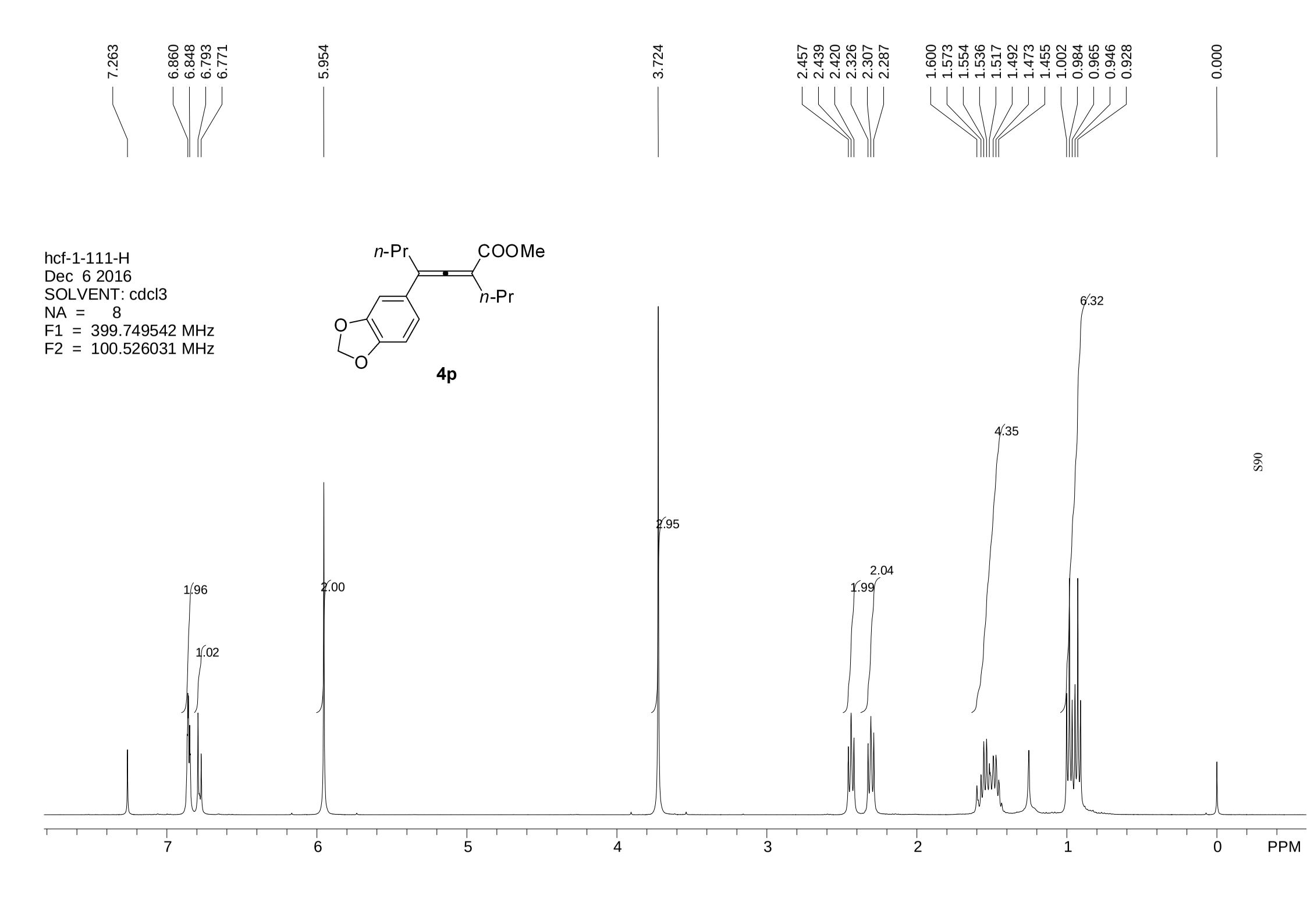

zwl-7-135-C
Apr 26 2016
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4m
Ph
Ph
COOMe
213.658
166.514
134.444
132.828
128.630
128.258
127.788
127.628
126.072
105.988
104.250
77.319
77.000
76.681
52.308
16.231
200
150
100
50
0
PPM

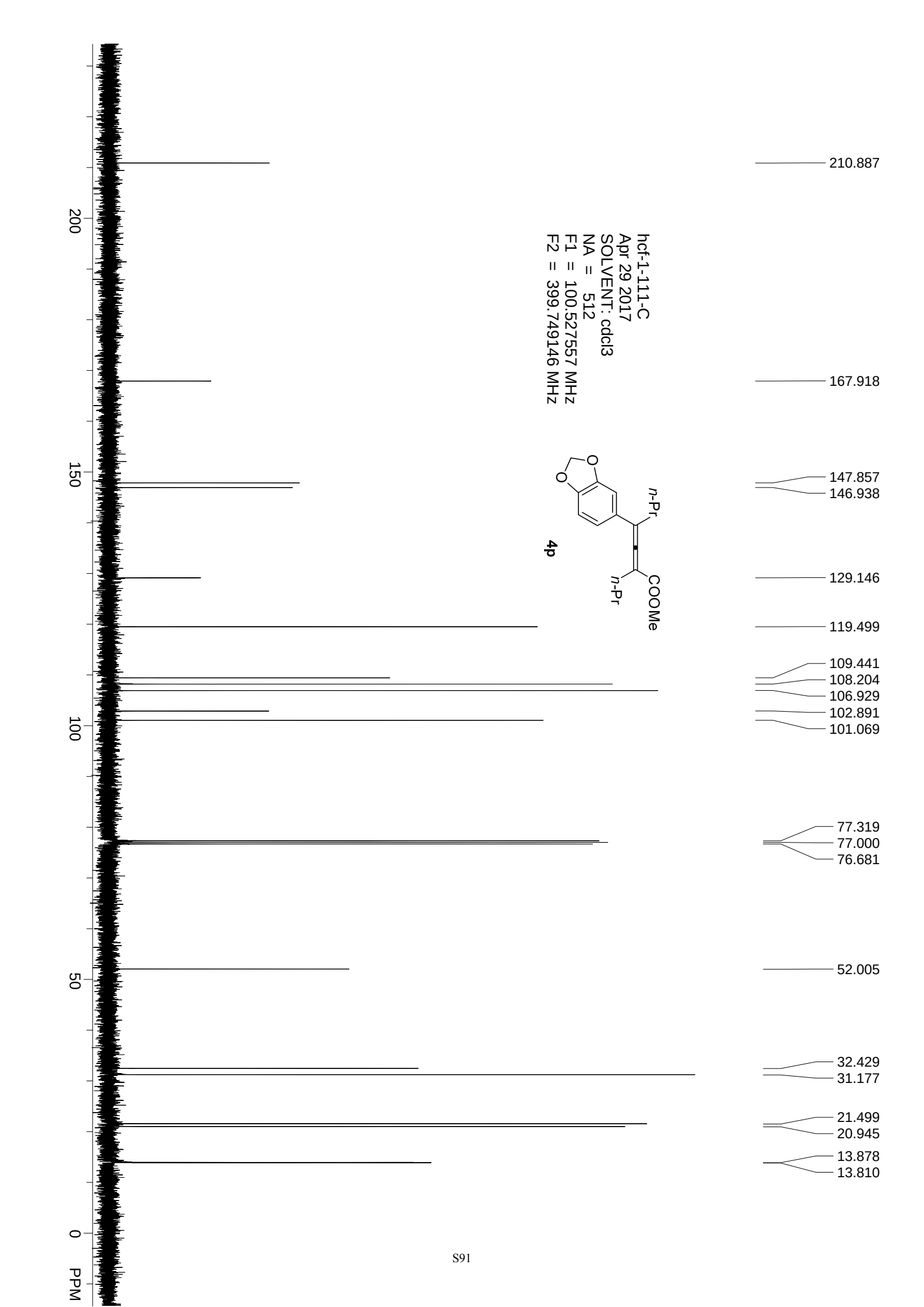

7.391
7.386
7.369
7.366
7.348
7.343
7.332
7.327
7.279
7.274
7.269
7.264
7.257
7.252
7.241
3.729
3.520
3.503
3.487
2.406
2.386
2.368
2.190
1.827
1.810
1.789
1.773
1.660
1.642
1.639
1.625
1.619
1.607
1.599
-0.000
zwl-8-145-H
Jun 8 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOMe
Ph
Cl
4n
3.95
1.05
2.99
2.00
3.08
2.01
2.06
2.30
S86
8
7
6
5
4
3
2
1
0 PPM

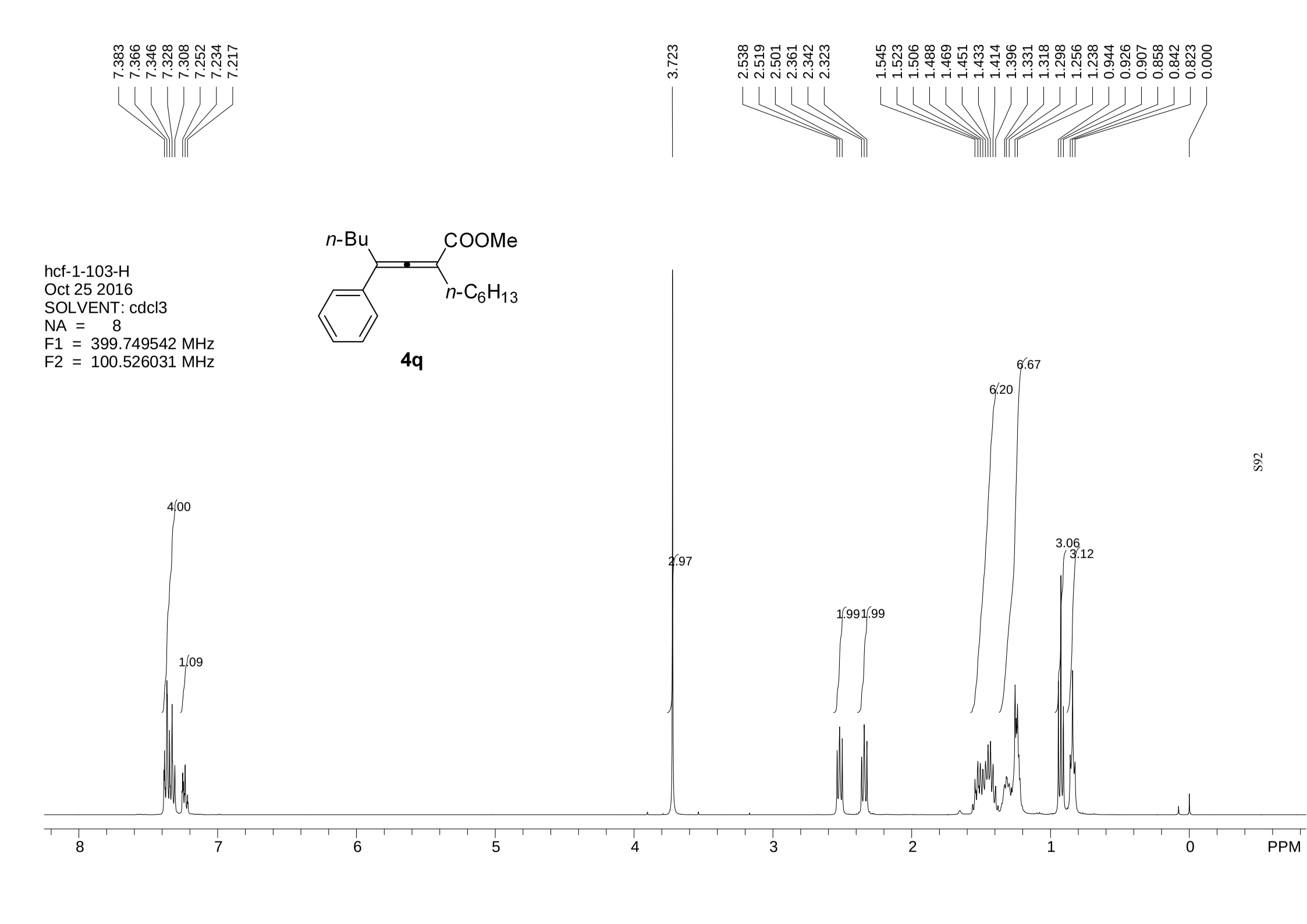

zwl-8-145-C
Jun 8 2016
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
F2 = 399.749146 MHz
Ph
COOMe
Cl
4n
211.085
167.607
135.127
128.524
127.499
125.951
105.062
101.297
77.319
77.000
76.681
52.157
44.665
31.989
28.201
25.241
16.451
200
150
100
50
0
PPM

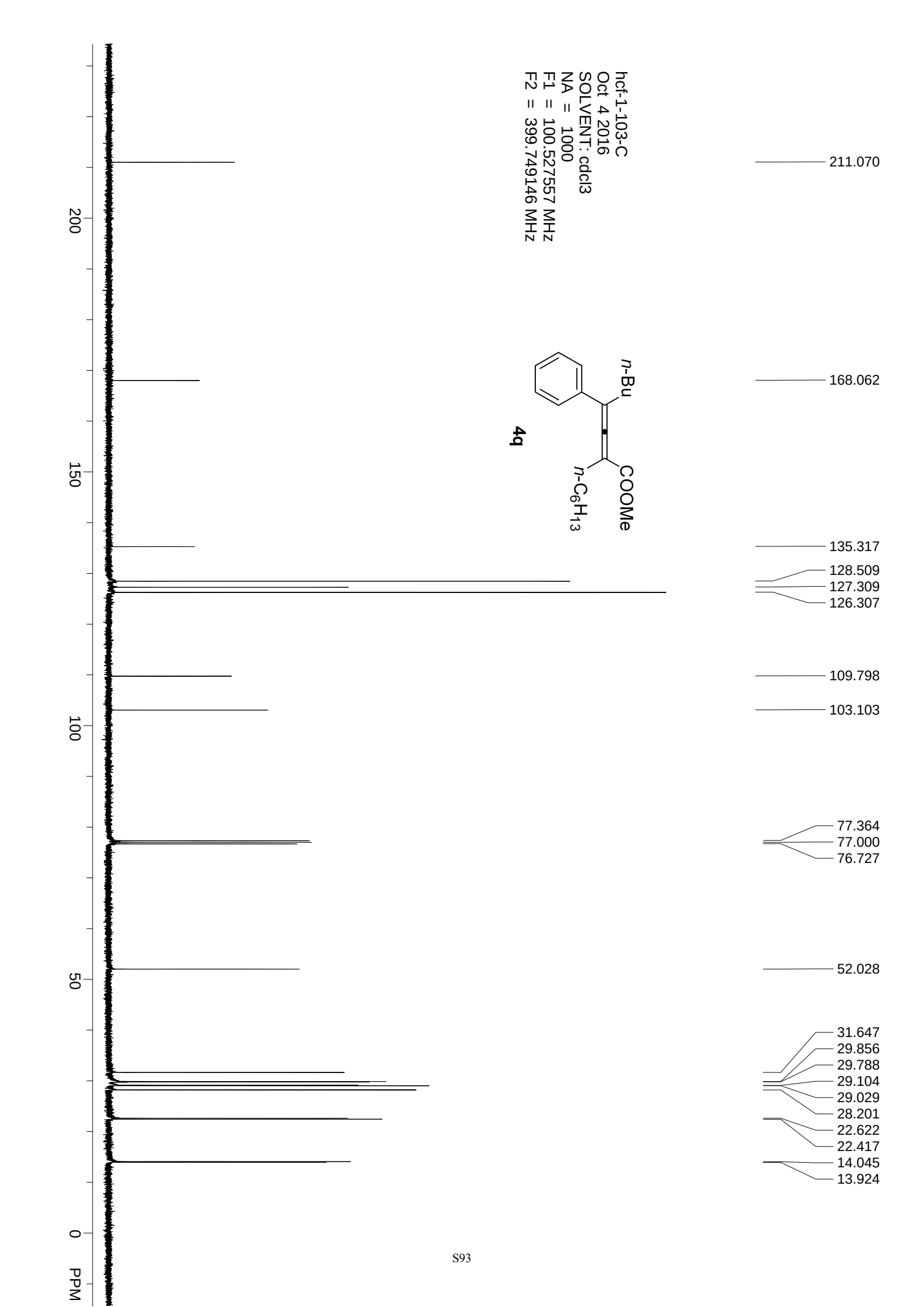

7.390
7.386
7.381
7.368
7.366
7.348
7.343
7.329
7.325
7.310
7.257
7.253
7.249
7.240
7.235
7.230
7.218
3.721
2.572
2.554
2.535
2.517
2.357
2.341
2.337
2.333
2.318
1.532
1.528
1.513
1.509
1.494
1.491
1.475
1.472
1.173
1.155
1.136
0.956
0.939
0.920
0.000
zwl-8-25-H
Jul 18 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Et
COOMe
n-Pr
4o
4.10
1.09
3.02
1.99
2.00
2.07
2.99
3.02
S88
8
7
6
5
4
3
2
1
0
PPM

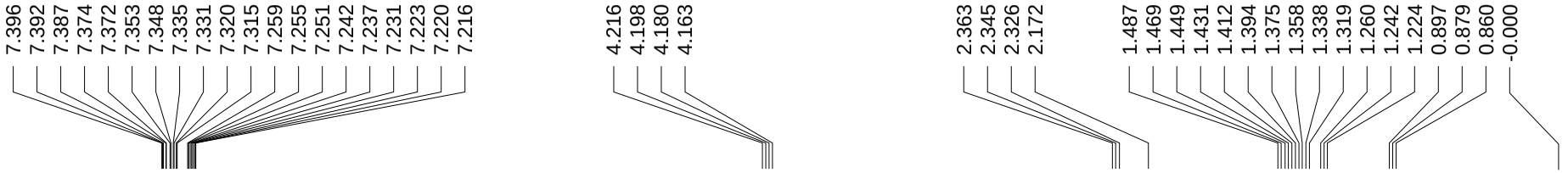

zwl-8-25-C
Jul 18 2016
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4o
Et
COOMe
n-Pr
210.865
167.986
135.241
128.486
127.302
126.163
111.514
103.817
77.311
76.992
76.674
52.028
31.146
23.138
21.522
13.878
12.322
200
150
100
50
0
PPM


7.263
6.860
6.848
6.793
6.771
5.954
3.724
2.457
2.439
2.420
2.326
2.307
2.287
1.600
1.573
1.554
1.536
1.517
1.492
1.473
1.455
1.002
0.984
0.965
0.946
0.928
0.000
hcf-1-111-H
Dec 6 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
n-Pr
COOMe
n-Pr
O
O
O
4p
6.32
4.35
2.95
2.04
1.99
1.96
2.00
1.02
S90
7
6
5
4
3
2
1
0
PPM

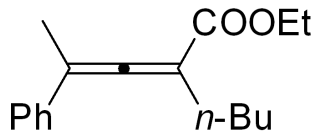

hcf-1-111-C
Apr 29 2017
SOLVENT: cdcl3
NA = 512
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4p
n-Pr
n-Pr
COOMe
210.887
167.918
147.857
146.938
129.146
119.499
109.441
108.204
106.929
102.891
101.069
77.319
77.000
76.681
52.005
32.429
31.177
21.499
20.945
13.878
13.810
200
150
100
50
0
PPM


7.383
7.366
7.346
7.328
7.308
7.252
7.234
7.217
3.723
2.538
2.519
2.501
2.361
2.342
2.323
1.545
1.523
1.506
1.488
1.469
1.451
1.433
1.414
1.396
1.331
1.318
1.298
1.256
1.238
0.944
0.926
0.907
0.858
0.842
0.823
0.000
n-Bu
COOMe
n-C6H13
4q
hcf-1-103-H
Oct 25 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
4.00
1.09
2.97
1.99
1.99
6.20
6.67
3.06
3.12
S92
8
7
6
5
4
3
2
1
0
PPM

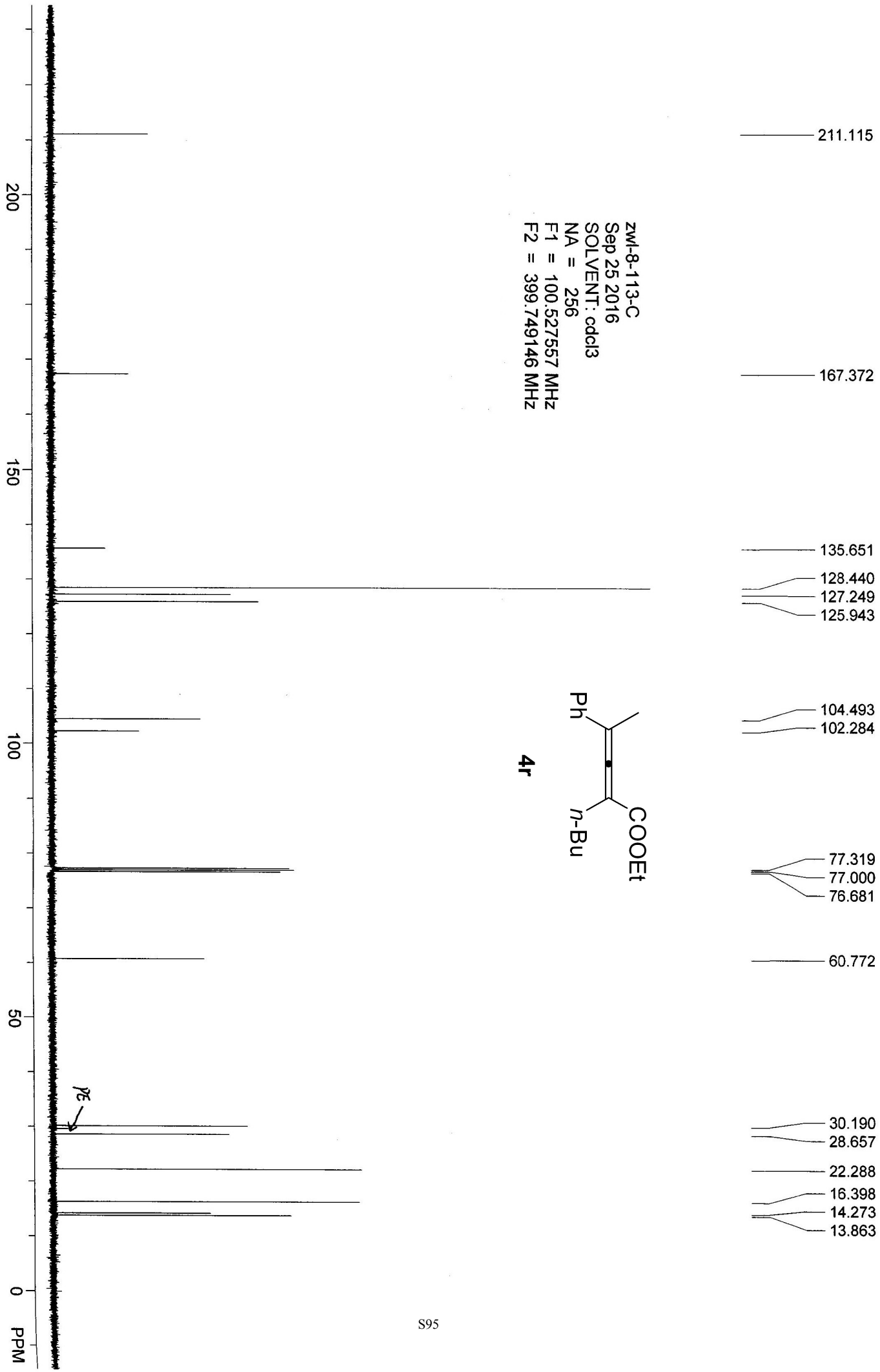

hcf-1-103-C
Oct 4 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4q
n-Bu
COOMe
n-C6H13
211.070
168.062
135.317
128.509
127.309
126.307
109.798
103.103
77.364
77.000
76.727
52.028
31.647
29.856
29.788
29.104
29.029
28.201
22.622
22.417
14.045
13.924
200
150
100
50
0
PPM

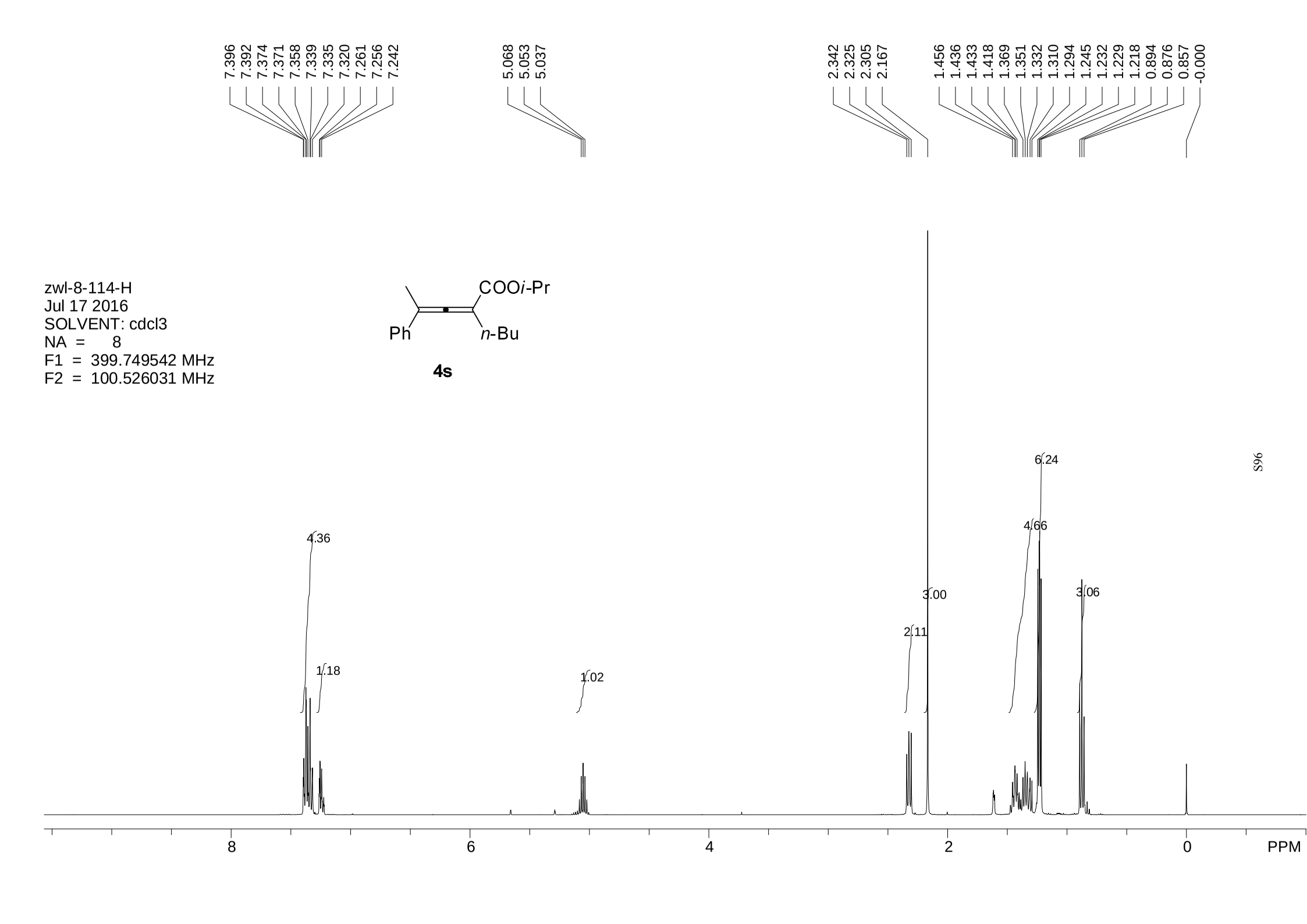


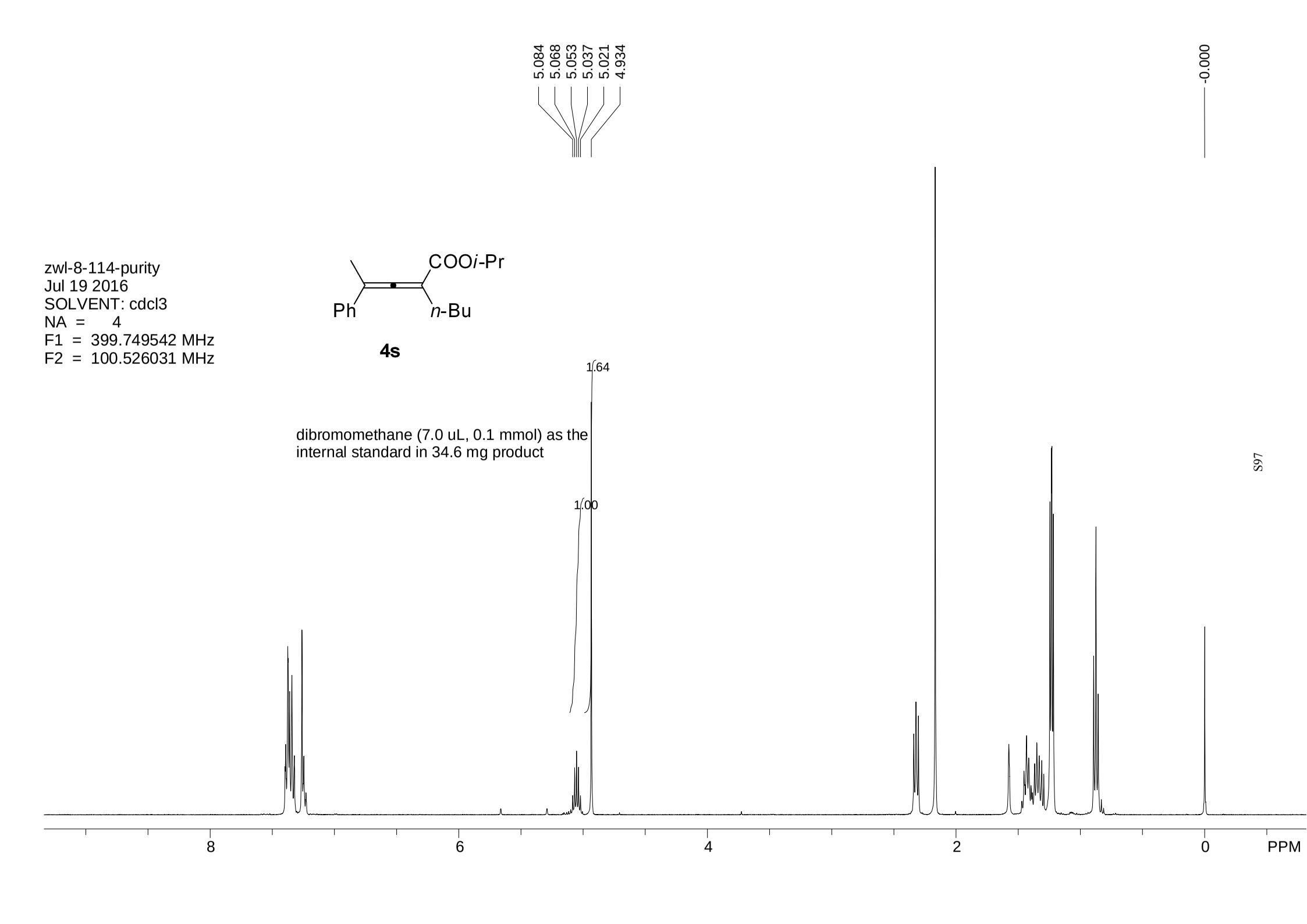

zwl-8-113-H
Jul 17 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz

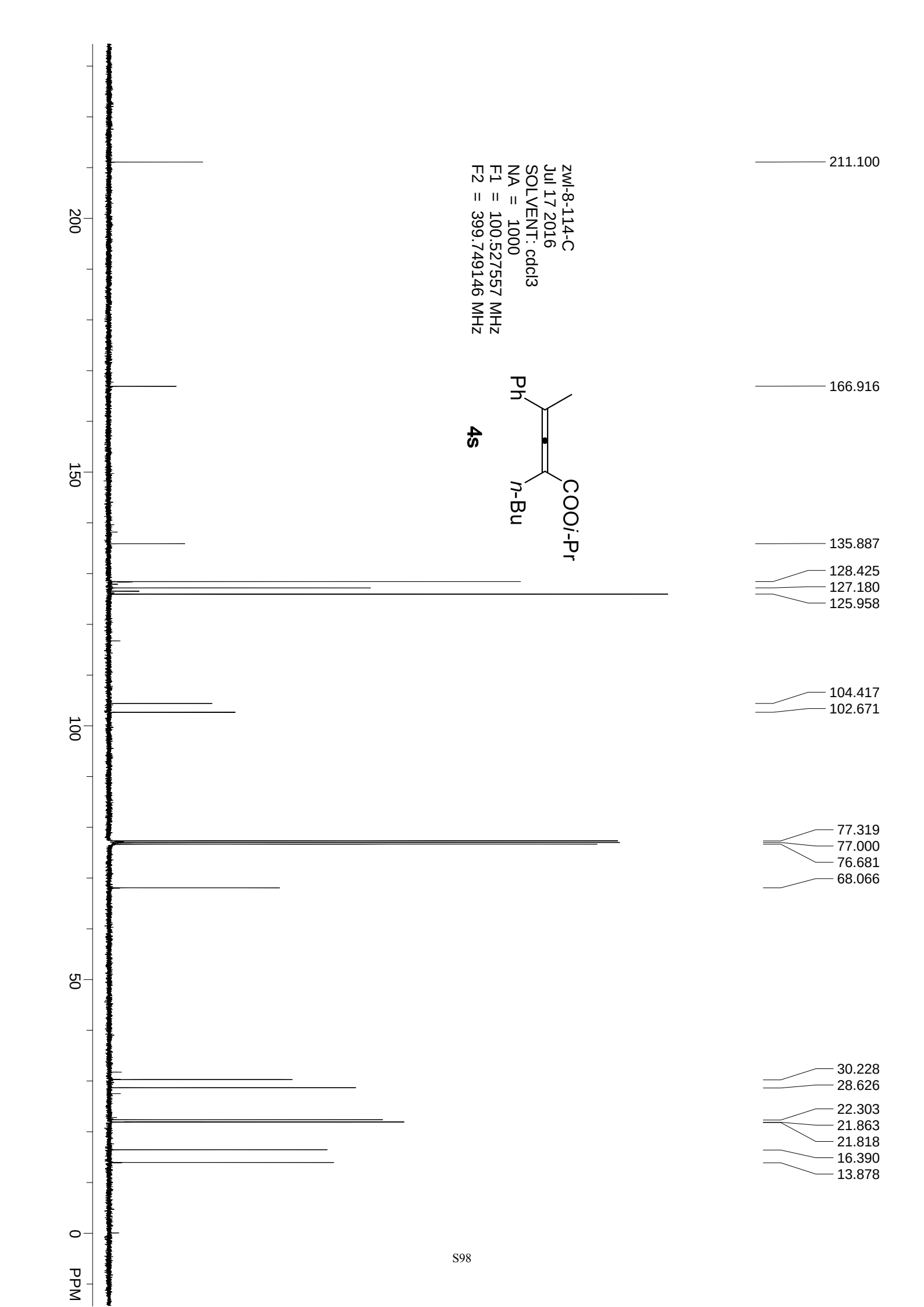


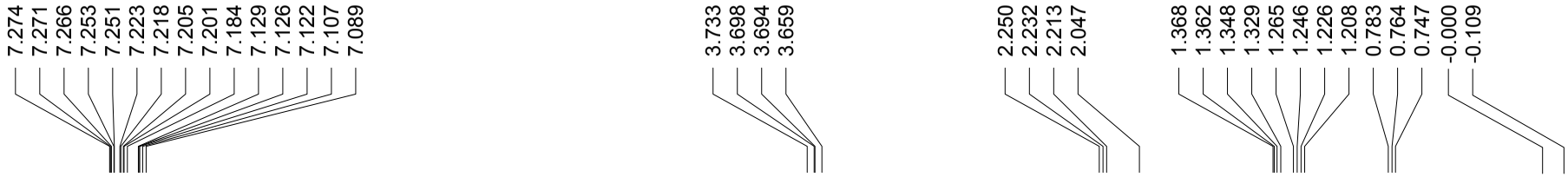

**4r**


zwl-8-113-C
Sep 25 2016
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4r
Ph
n-Bu
COOEt
211.115
167.372
135.651
128.440
127.249
125.943
104.493
102.284
77.319
77.000
76.681
60.772
30.190
28.657
22.288
16.398
14.273
13.863
200
150
100
50
0
PPM

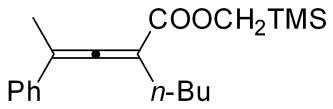

7.396
7.392
7.374
7.371
7.358
7.339
7.335
7.320
7.261
7.256
7.242
5.068
5.053
5.037
2.342
2.325
2.305
2.167
1.456
1.436
1.433
1.418
1.369
1.351
1.332
1.310
1.294
1.245
1.232
1.229
1.218
0.894
0.876
0.857
-0.000
zwl-8-114-H
Jul 17 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COO*i*-Pr
Ph
*n*-Bu
4s
6.24
4.66
4.36
3.06
3.00
2.11
1.18
1.02
S96
8
6
4
2
0
PPM


5.084
5.068
5.053
5.037
5.021
4.934
-0.000
zwl-8-114-purity
Jul 19 2016
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COO*i*-Pr
Ph
*n*-Bu
4s
1.64
1.00
dibromomethane (7.0 uL, 0.1 mmol) as the internal standard in 34.6 mg product
S97
8
6
4
2
0
PPM

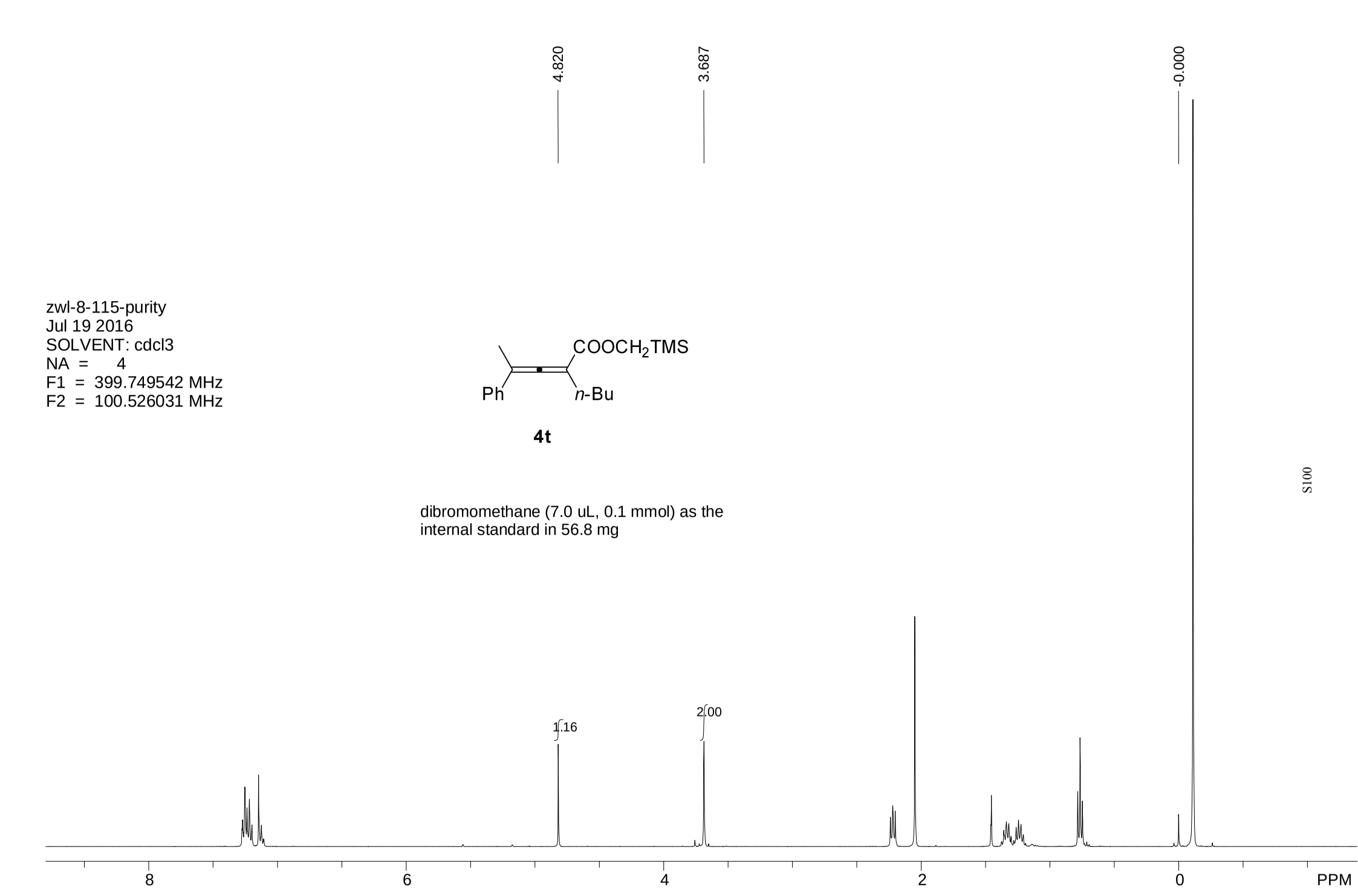

zwl-8-114-C
Jul 17 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4s
Ph
n-Bu
COOi-Pr
211.100
166.916
135.887
128.425
127.180
125.958
104.417
102.671
77.319
77.000
76.681
68.066
30.228
28.626
22.303
21.863
21.818
16.390
13.878
200
150
100
50
0
PPM

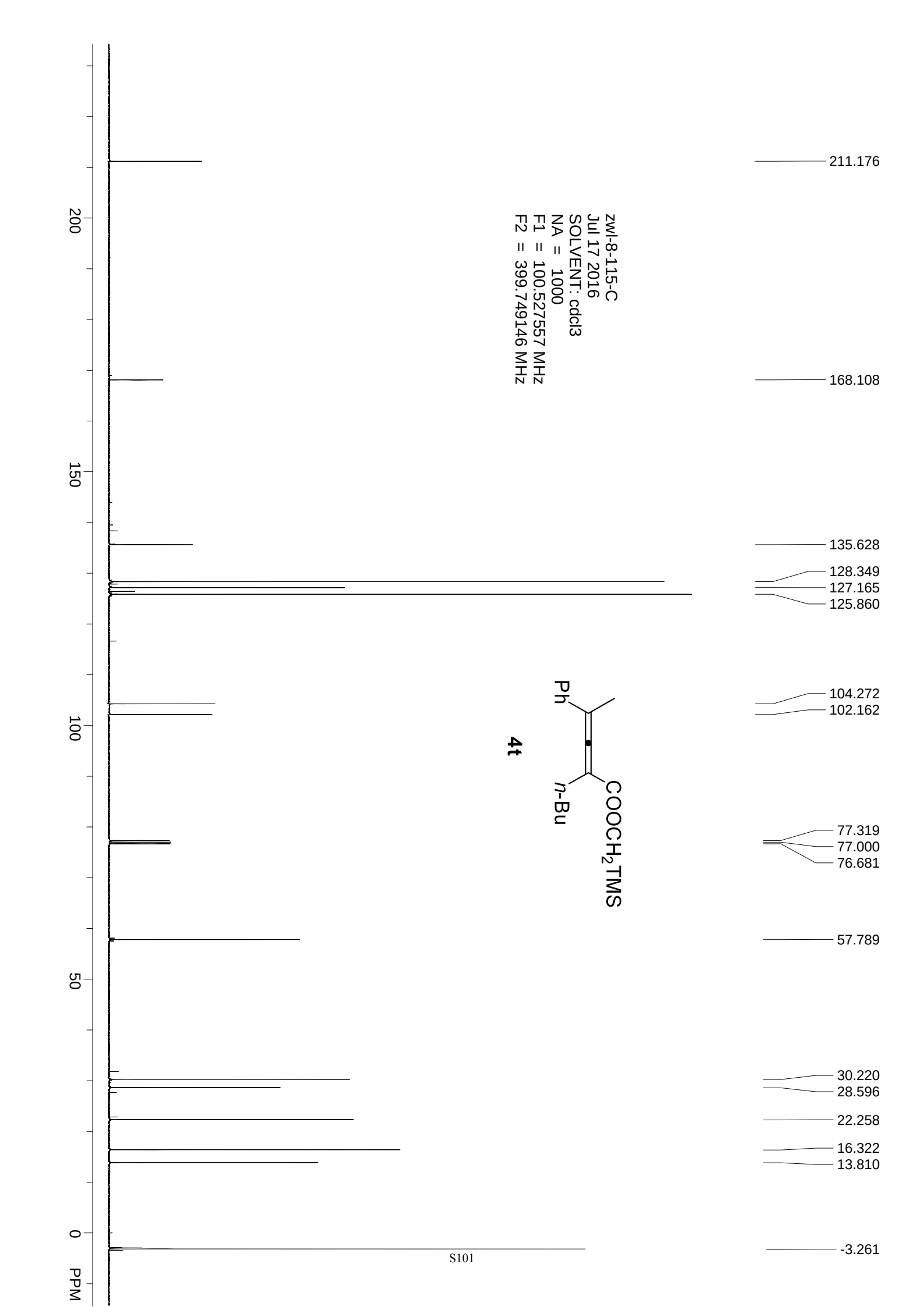


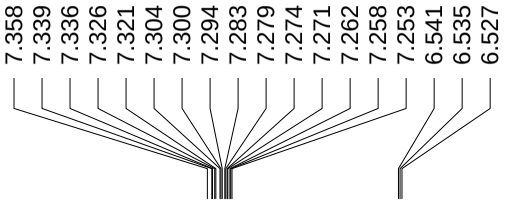

zwl-8-115-H
Jul 17 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz




**4t**

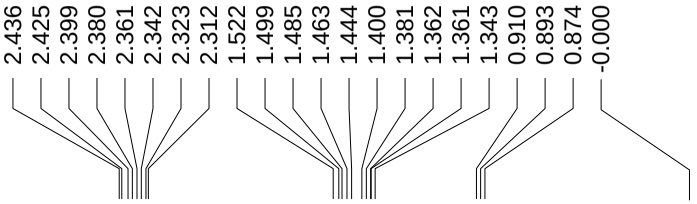

4.820
3.687
-0.000
zwl-8-115-purity
Jul 19 2016
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
F2 = 100.526031 MHz
COOCH2TMS
Ph
n-Bu
4t
S100
dibromomethane (7.0 uL, 0.1 mmol) as the
internal standard in 56.8 mg
1.16
2.00
8
6
4
2
0
PPM


zwl-8-115-C
Jul 17 2016
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4t
Ph
n-Bu
COOCH2TMS
211.176
168.108
135.628
128.349
127.165
125.860
104.272
102.162
77.319
77.000
76.681
57.789
30.220
28.596
22.258
16.322
13.810
-3.261
200
150
100
50
0
PPM

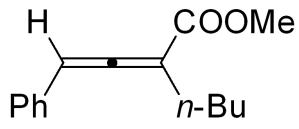




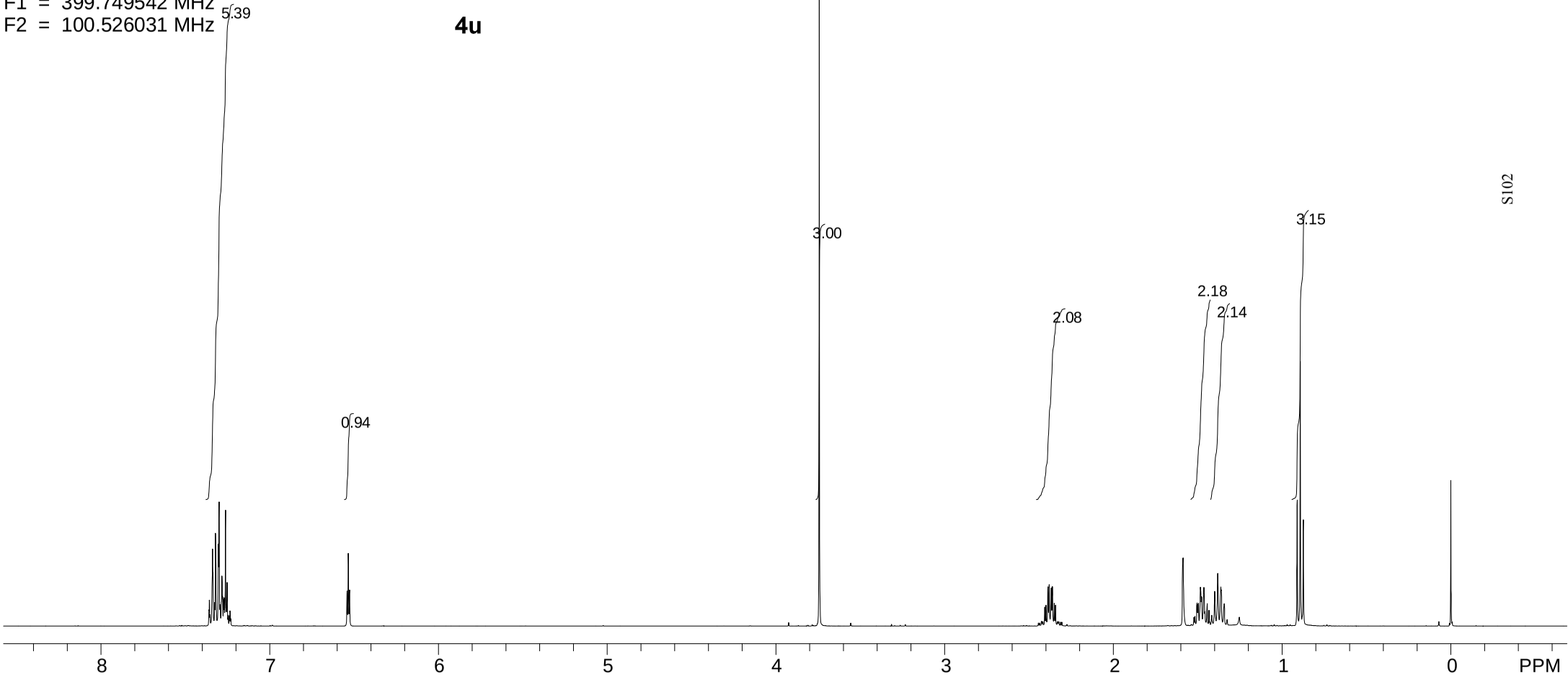


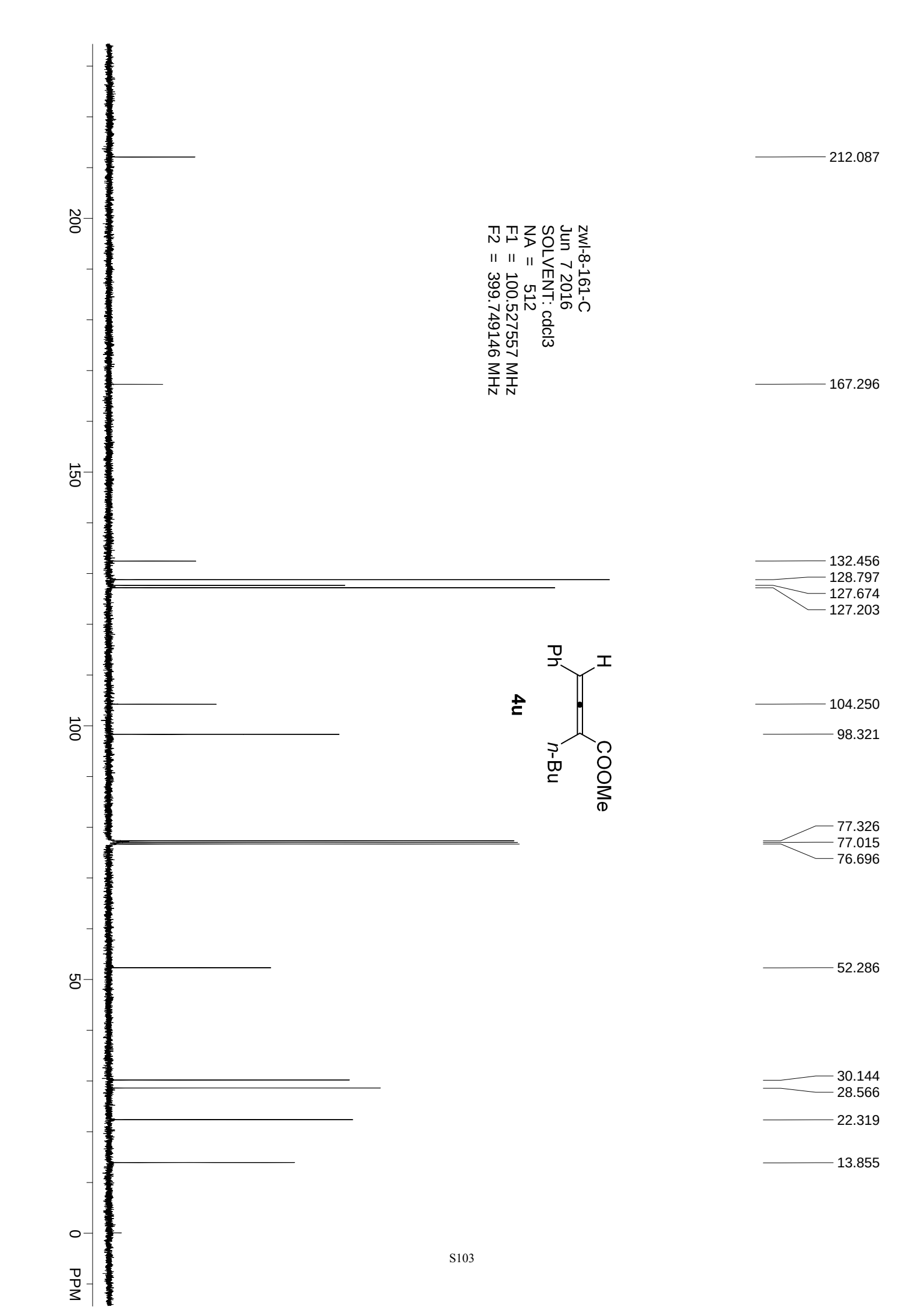


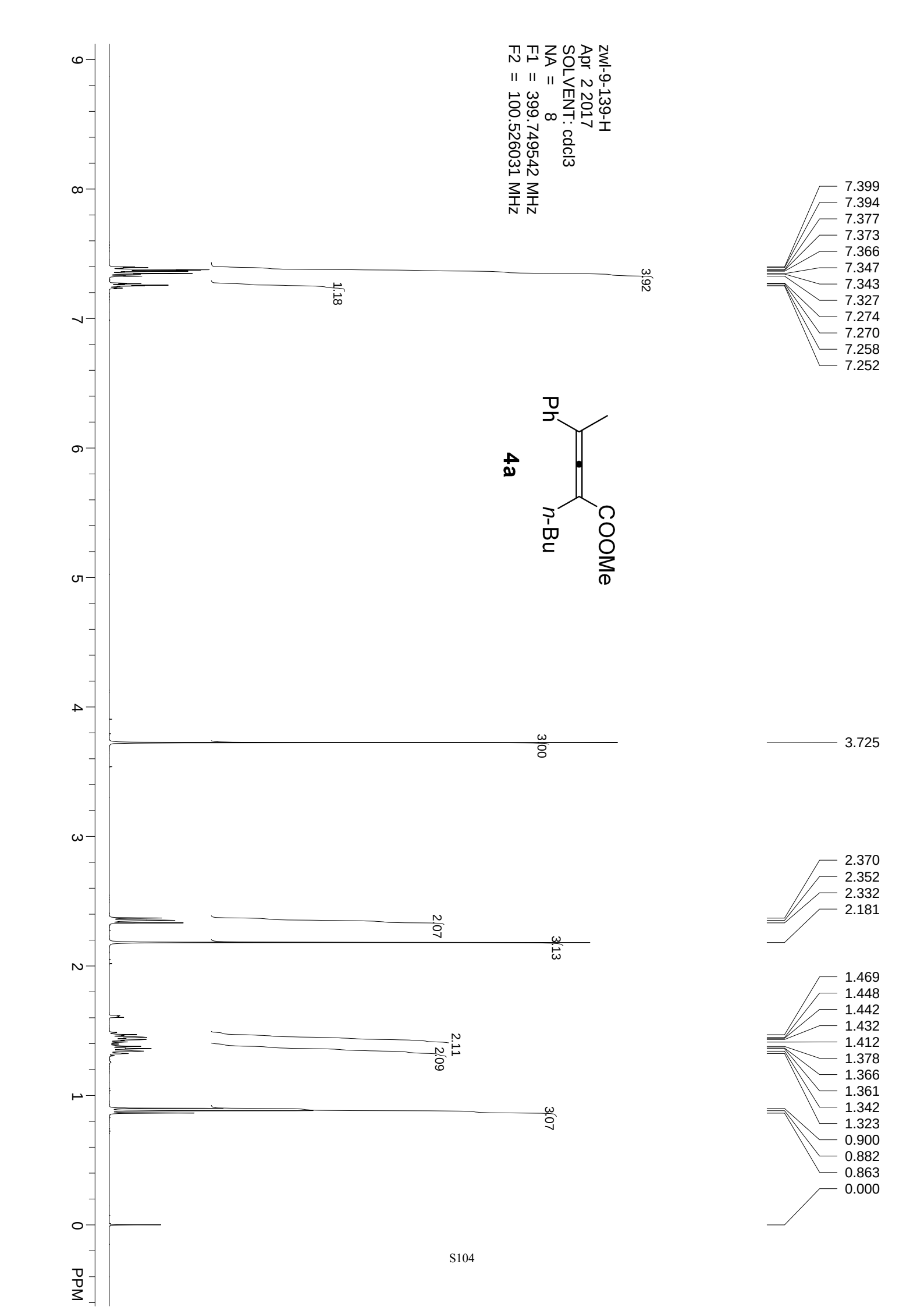

zwl-8-161-H
Jun 12 2016
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz

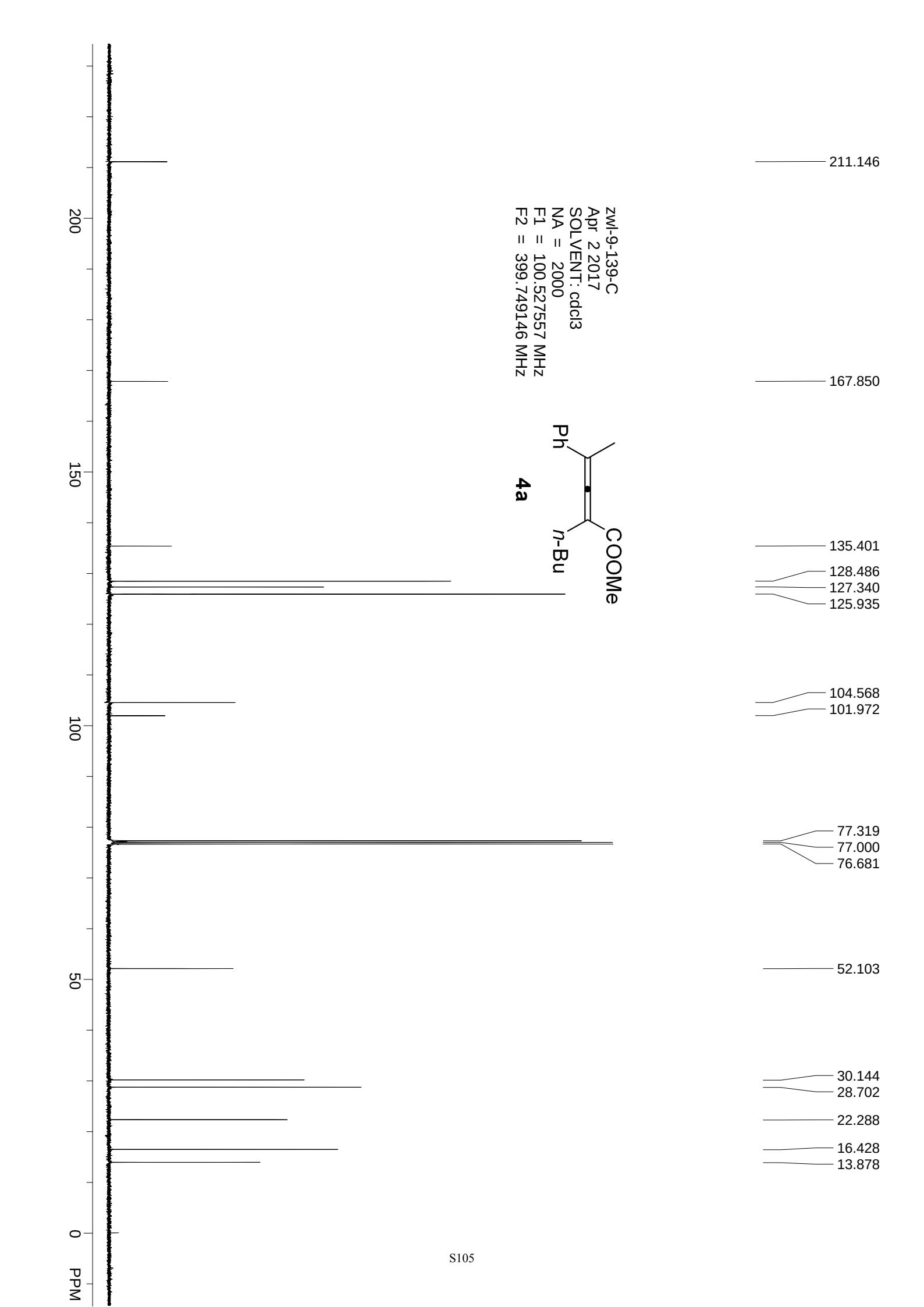


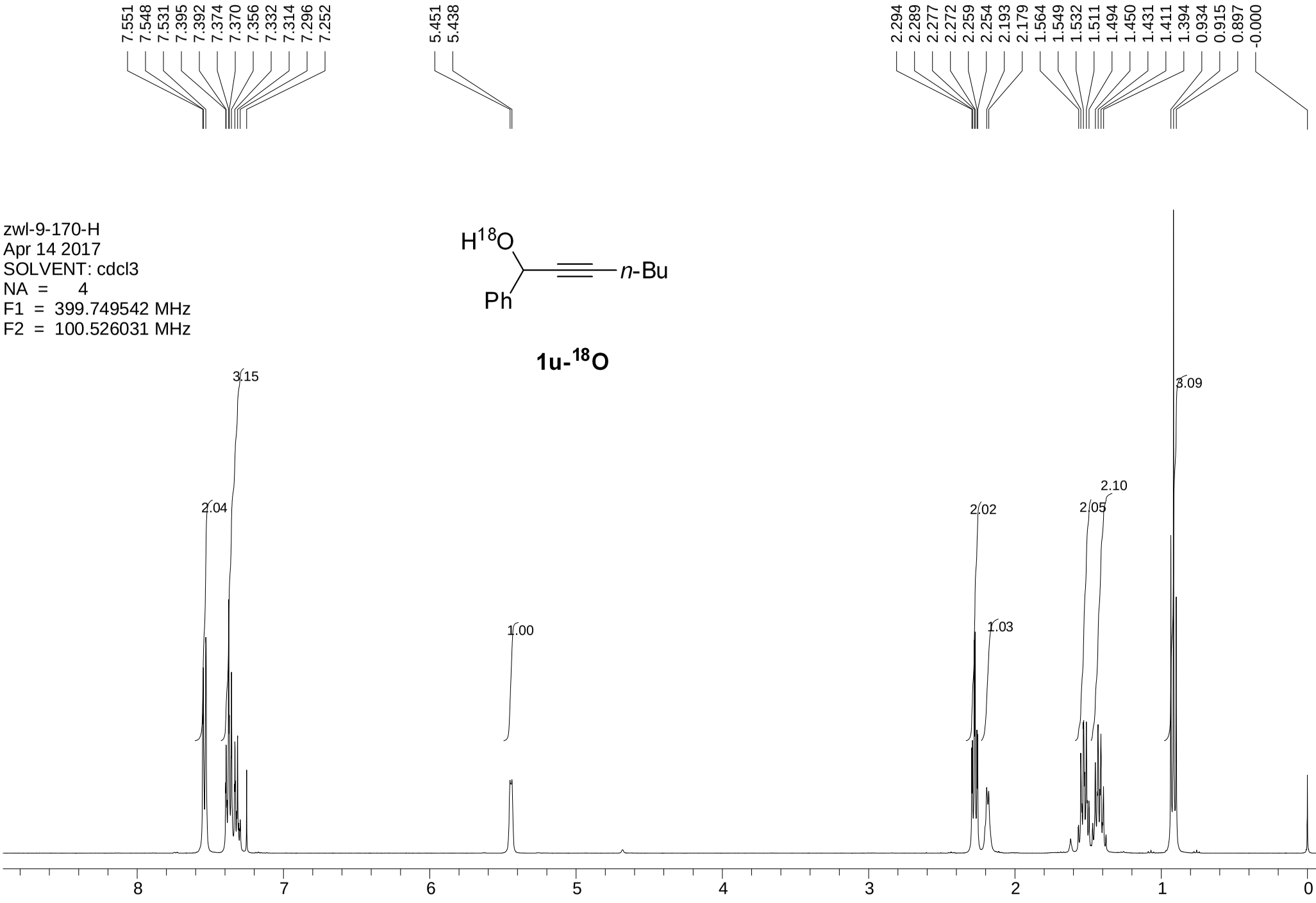

**4u**

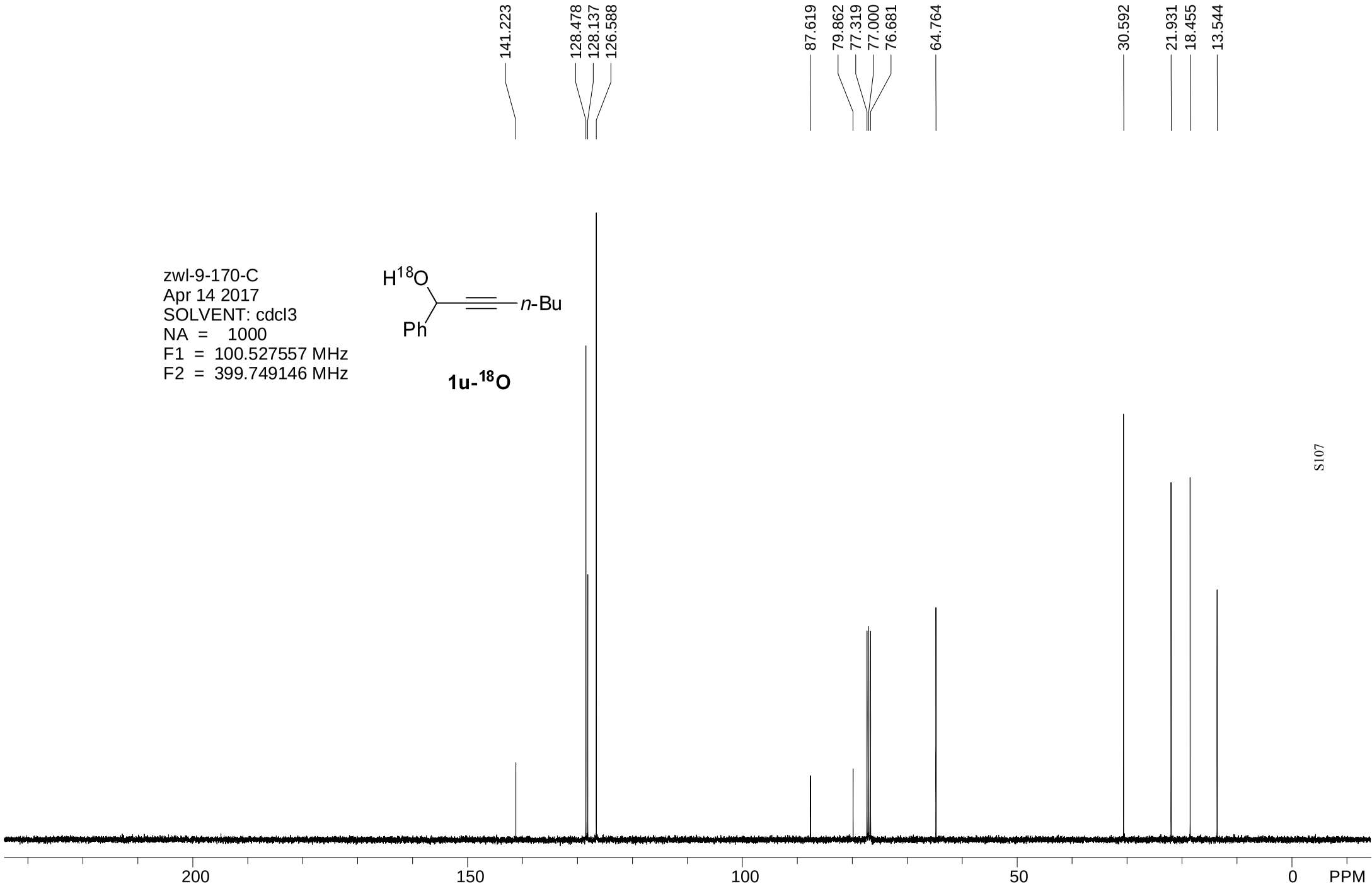


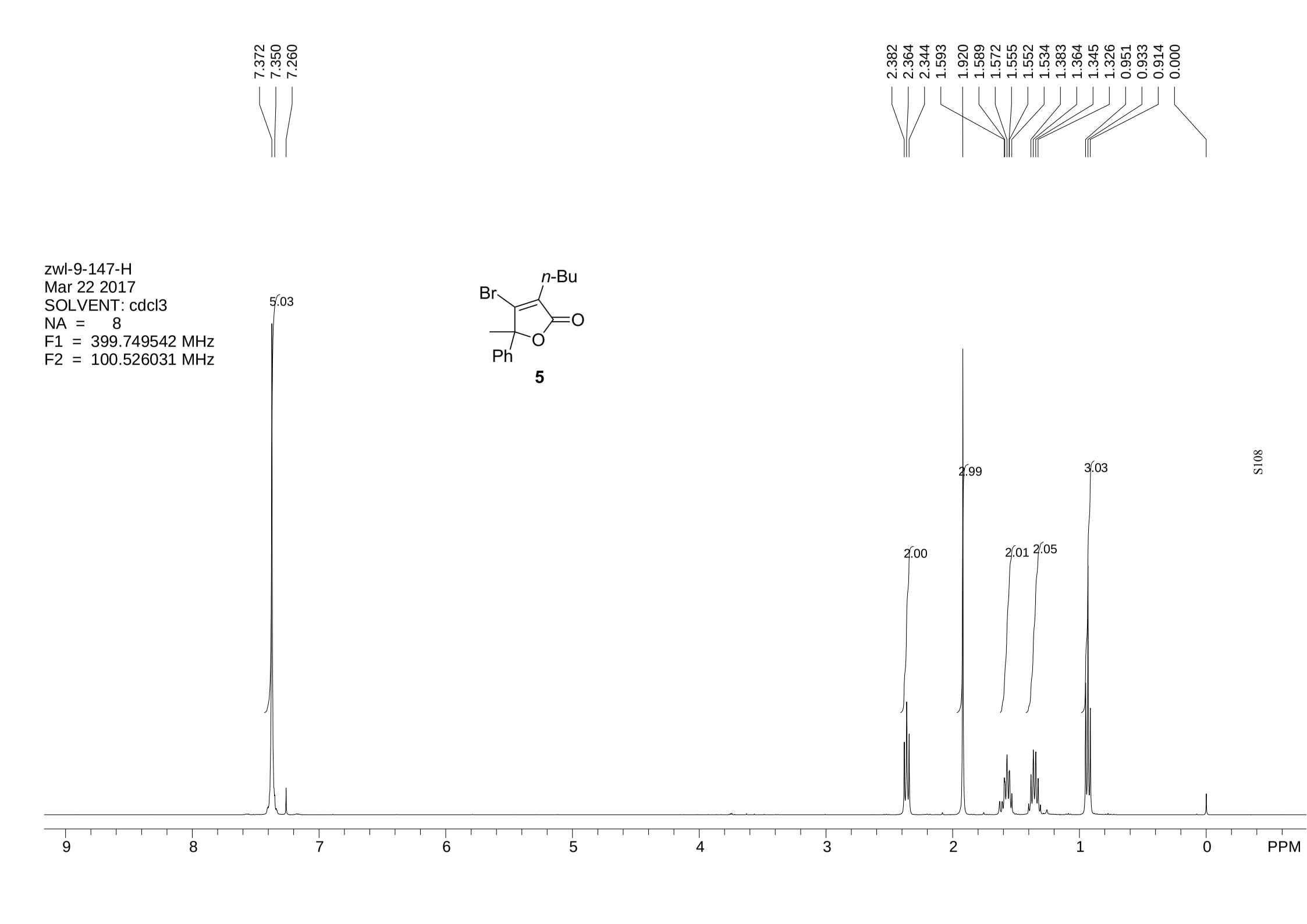

zwl-8-161-C
Jun 7 2016
SOLVENT: cdcl3
NA = 512
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4u
Ph
H
n-Bu
COOMe
212.087
167.296
132.456
128.797
127.674
127.203
104.250
98.321
77.326
77.015
76.696
52.286
30.144
28.566
22.319
13.855
200
150
100
50
0
PPM

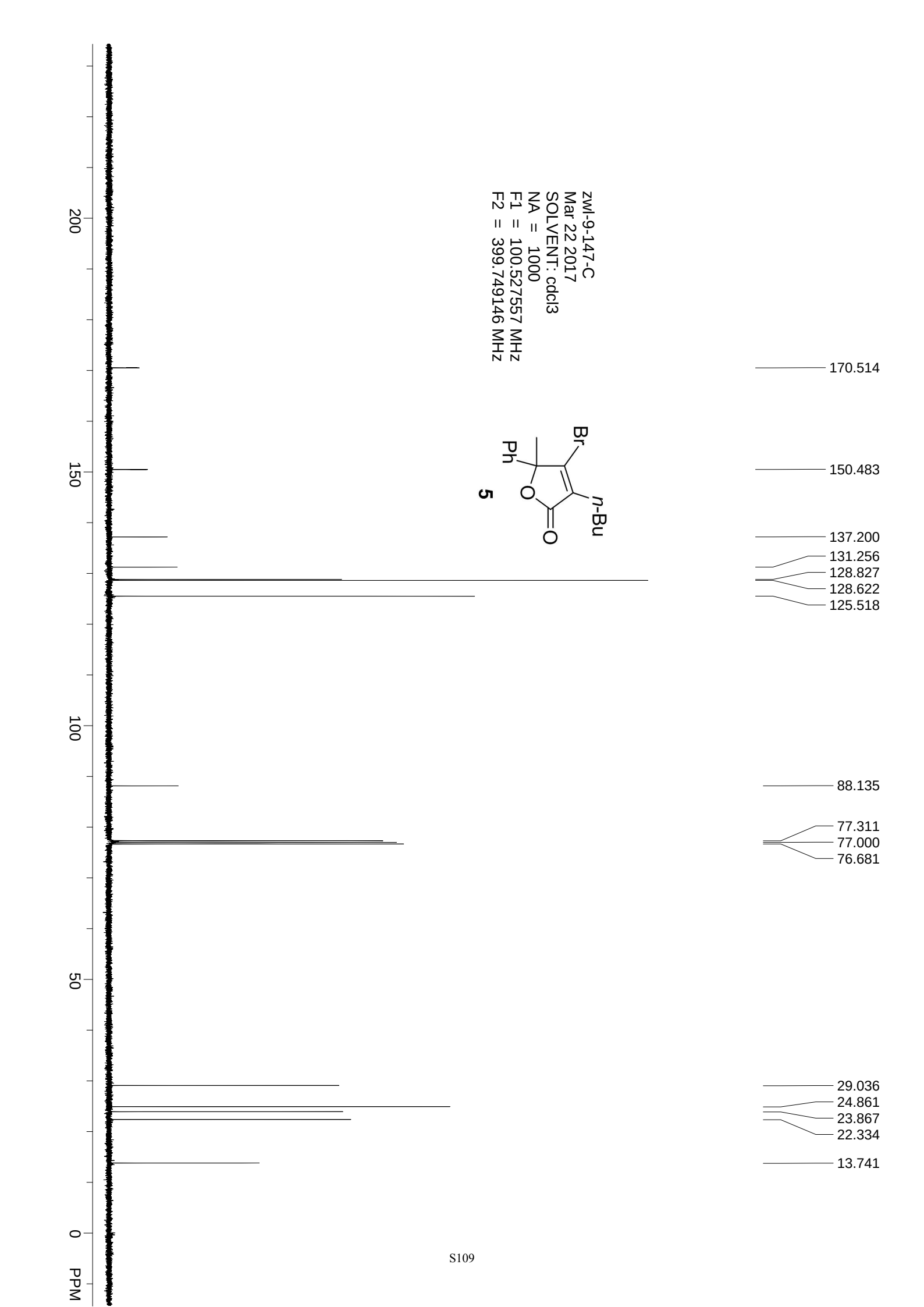

zwl-9-139-H
Apr 2 2017
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Ph
n-Bu
COOMe
4a
7.399
7.394
7.377
7.373
7.366
7.347
7.343
7.327
7.274
7.270
7.258
7.252
3.725
2.370
2.352
2.332
2.181
1.469
1.448
1.442
1.432
1.412
1.378
1.366
1.361
1.342
1.323
0.900
0.882
0.863
0.000
PPM

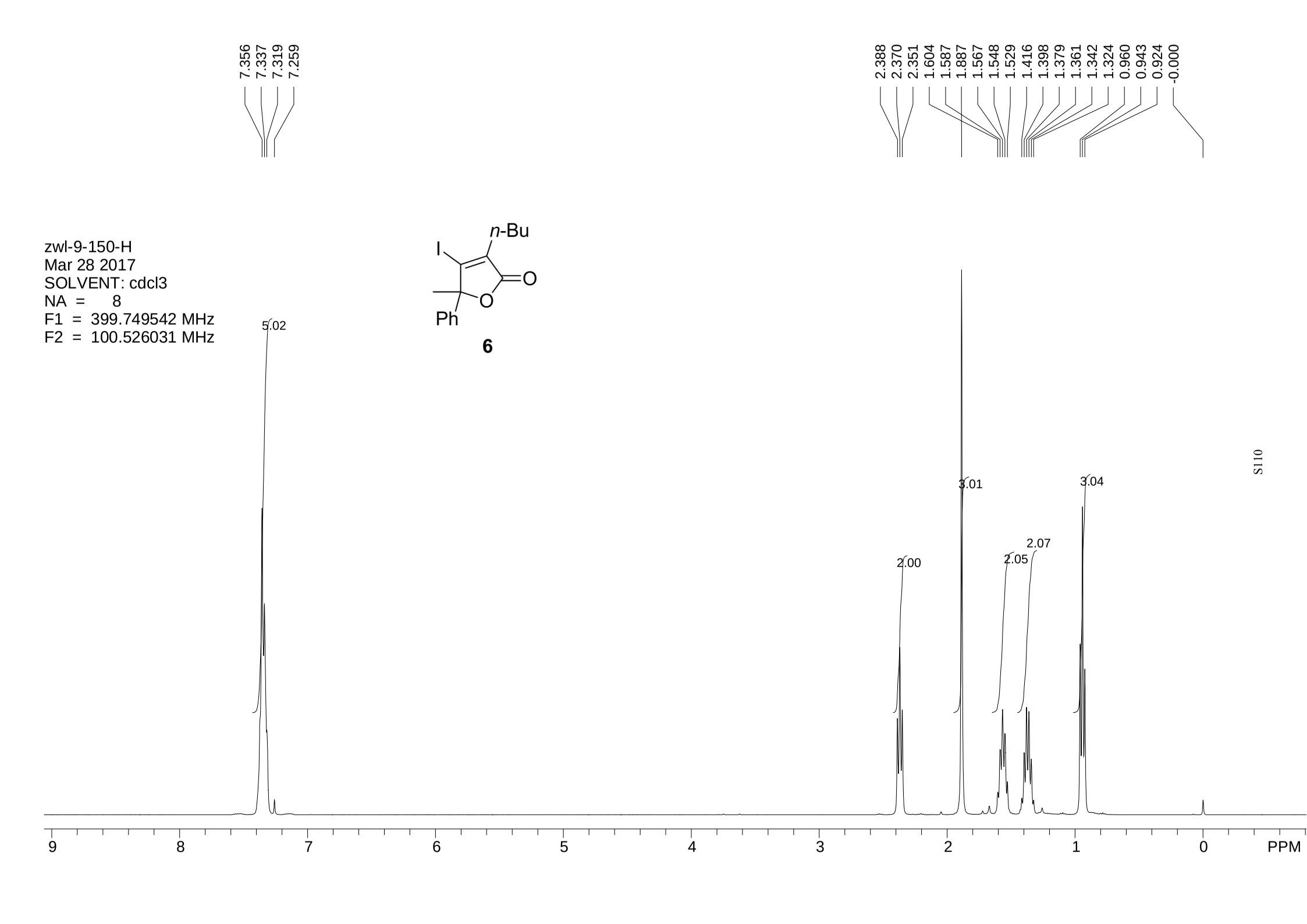

zwl-9-139-C
Apr 2 2017
SOLVENT: cdcl3
NA = 2000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
4a
Ph
n-Bu
COOMe
211.146
167.850
135.401
128.486
127.340
125.935
104.568
101.972
77.319
77.000
76.681
52.103
30.144
28.702
22.288
16.428
13.878
200
150
100
50
0
PPM

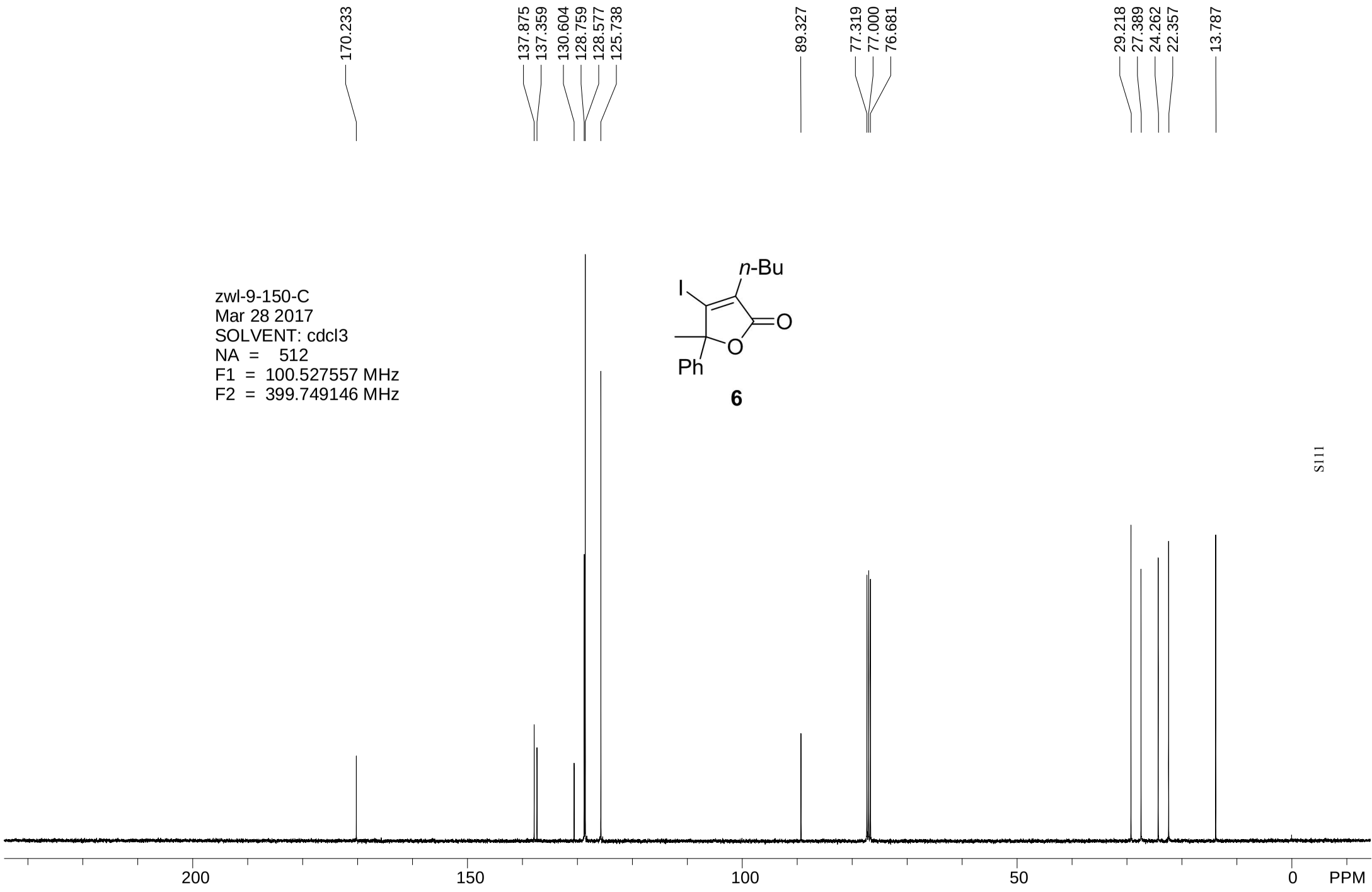

7.551
7.548
7.531
7.395
7.392
7.374
7.370
7.356
7.332
7.314
7.296
7.252
5.451
5.438
2.294
2.289
2.277
2.272
2.259
2.254
2.193
2.179
1.564
1.549
1.532
1.511
1.494
1.450
1.431
1.411
1.394
0.934
0.915
0.897
-0.000
zwl-9-170-H
Apr 14 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
F2 = 100.526031 MHz
H18O
Ph
n-Bu
1u-18O
3.15
2.04
1.00
2.02
1.03
2.05
2.10
3.09
S106
8
7
6
5
4
3
2
1
0
PPM

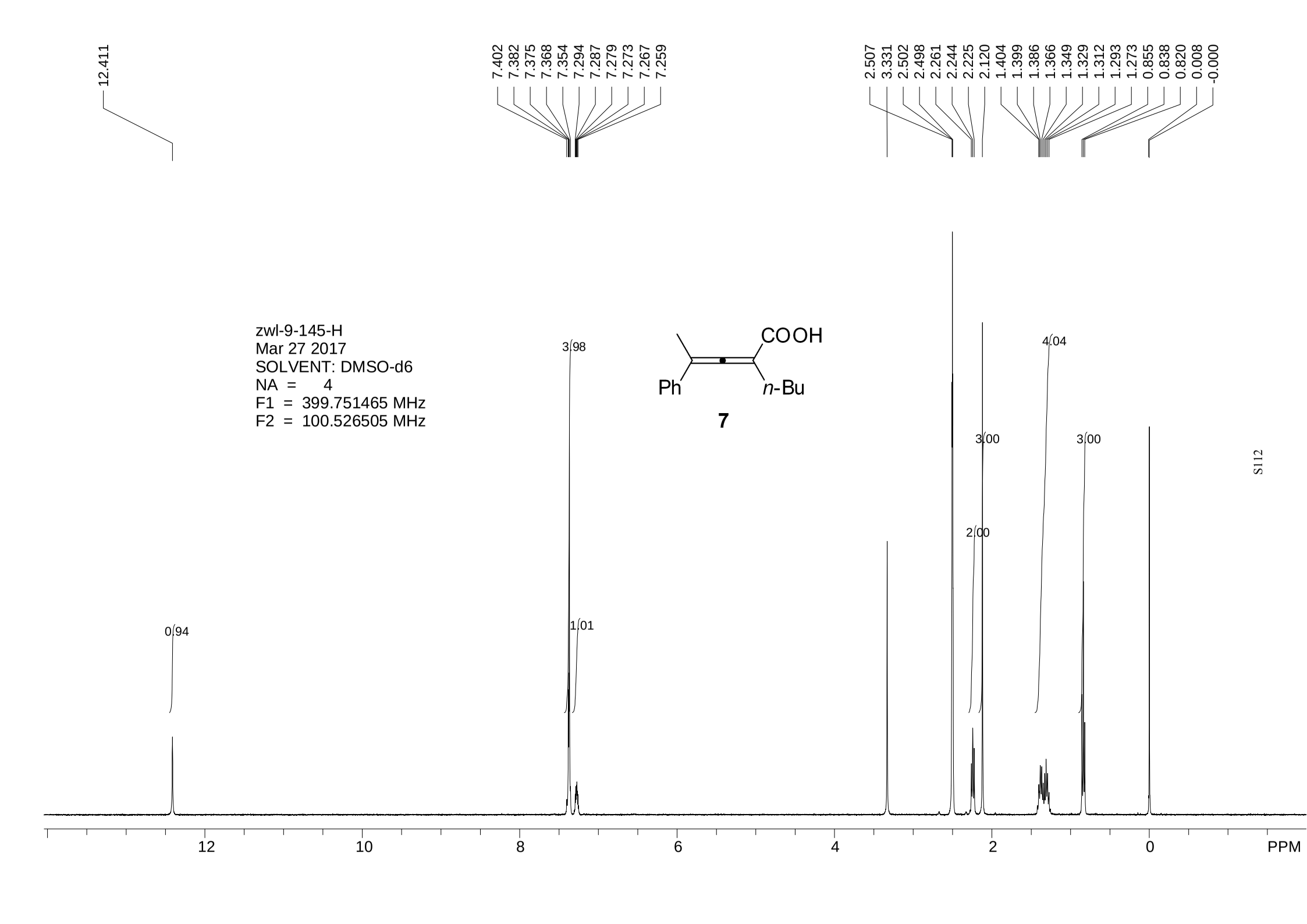

141.223
128.478
128.137
126.588
87.619
79.862
77.319
77.000
76.681
64.764
30.592
21.931
18.455
13.544
zwl-9-170-C
Apr 14 2017
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
H18O
n-Bu
Ph
1u-18O
S107
200
150
100
50
0
PPM

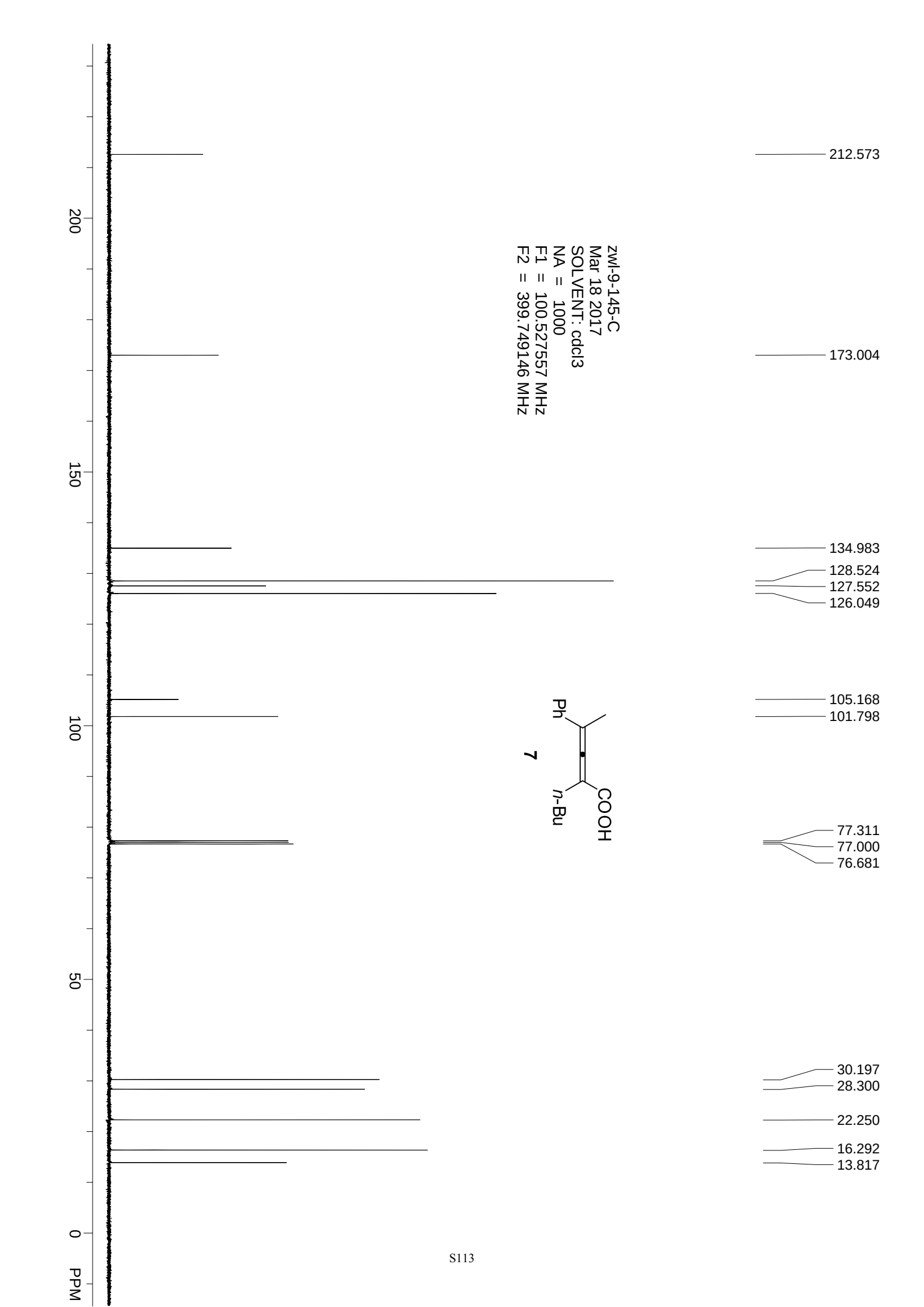

7.372
7.350
7.260
2.382
2.364
2.344
1.593
1.920
1.589
1.572
1.555
1.552
1.534
1.383
1.364
1.345
1.326
0.951
0.933
0.914
0.000
zwl-9-147-H
Mar 22 2017
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
n-Bu
Br
O
O
Ph
5
5.03
2.00
2.99
2.01
2.05
3.03
S108
9
8
7
6
5
4
3
2
1
0
PPM


zwl-9-147-C
Mar 22 2017
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
Br
Ph
O
O
n-Bu
5
170.514
150.483
137.200
131.256
128.827
128.622
125.518
88.135
77.311
77.000
76.681
29.036
24.861
23.867
22.334
13.741
200
150
100
50
0
PPM

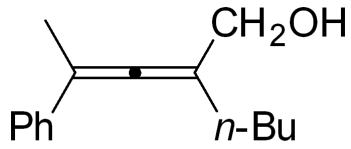

7.356
7.337
7.319
7.259
2.388
2.370
2.351
1.604
1.587
1.887
1.567
1.548
1.529
1.416
1.398
1.379
1.361
1.342
1.324
0.960
0.943
0.924
-0.000
zwl-9-150-H
Mar 28 2017
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz
n-Bu
I
O
O
Ph
6
5.02
2.00
3.01
2.05
2.07
3.04
S110
9
8
7
6
5
4
3
2
1
0
PPM


170.233
137.875
137.359
130.604
128.759
128.577
125.738
89.327
77.319
77.000
76.681
29.218
27.389
24.262
22.357
13.787
zwl-9-150-C
Mar 28 2017
SOLVENT: cdcl3
NA = 512
F1 = 100.527557 MHz
F2 = 399.749146 MHz
n-Bu
I
O
O
Ph
6
S111
200
150
100
50
0
PPM

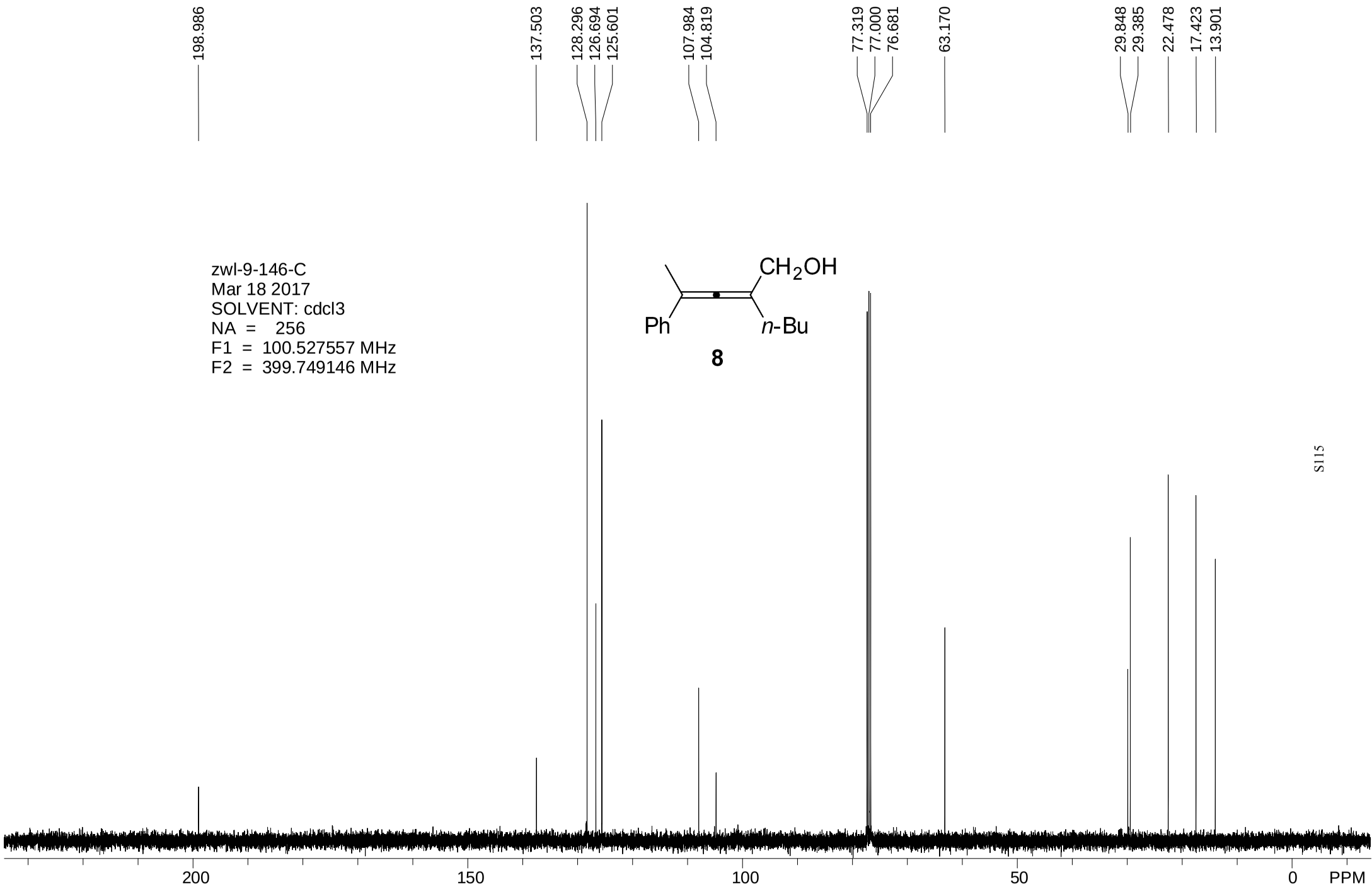

12.411
7.402
7.382
7.375
7.368
7.354
7.294
7.287
7.279
7.273
7.267
7.259
2.507
3.331
2.502
2.498
2.261
2.244
2.225
2.120
1.404
1.399
1.386
1.366
1.349
1.329
1.312
1.293
1.273
0.855
0.838
0.820
0.008
-0.000
zwl-9-145-H
Mar 27 2017
SOLVENT: DMSO-d6
NA = 4
F1 = 399.751465 MHz
F2 = 100.526505 MHz
COOH
Ph
n-Bu
7
0.94
3.98
1.01
2.00
3.00
4.04
3.00
S112
12
10
8
6
4
2
0
PPM


zwl-9-145-C
Mar 18 2017
SOLVENT: cdcl3
NA = 1000
F1 = 100.527557 MHz
F2 = 399.749146 MHz
212.573
173.004
134.983
128.524
127.552
126.049
105.168
101.798
77.311
77.000
76.681
30.197
28.300
22.250
16.292
13.817
Ph
n-Bu
COOH
7
200
150
100
50
0
PPM

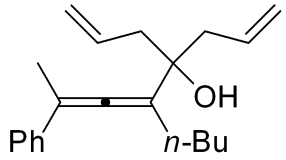

zwl-9-146-H
Mar 18 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.749542 MHz
F2 = 100.526031 MHz



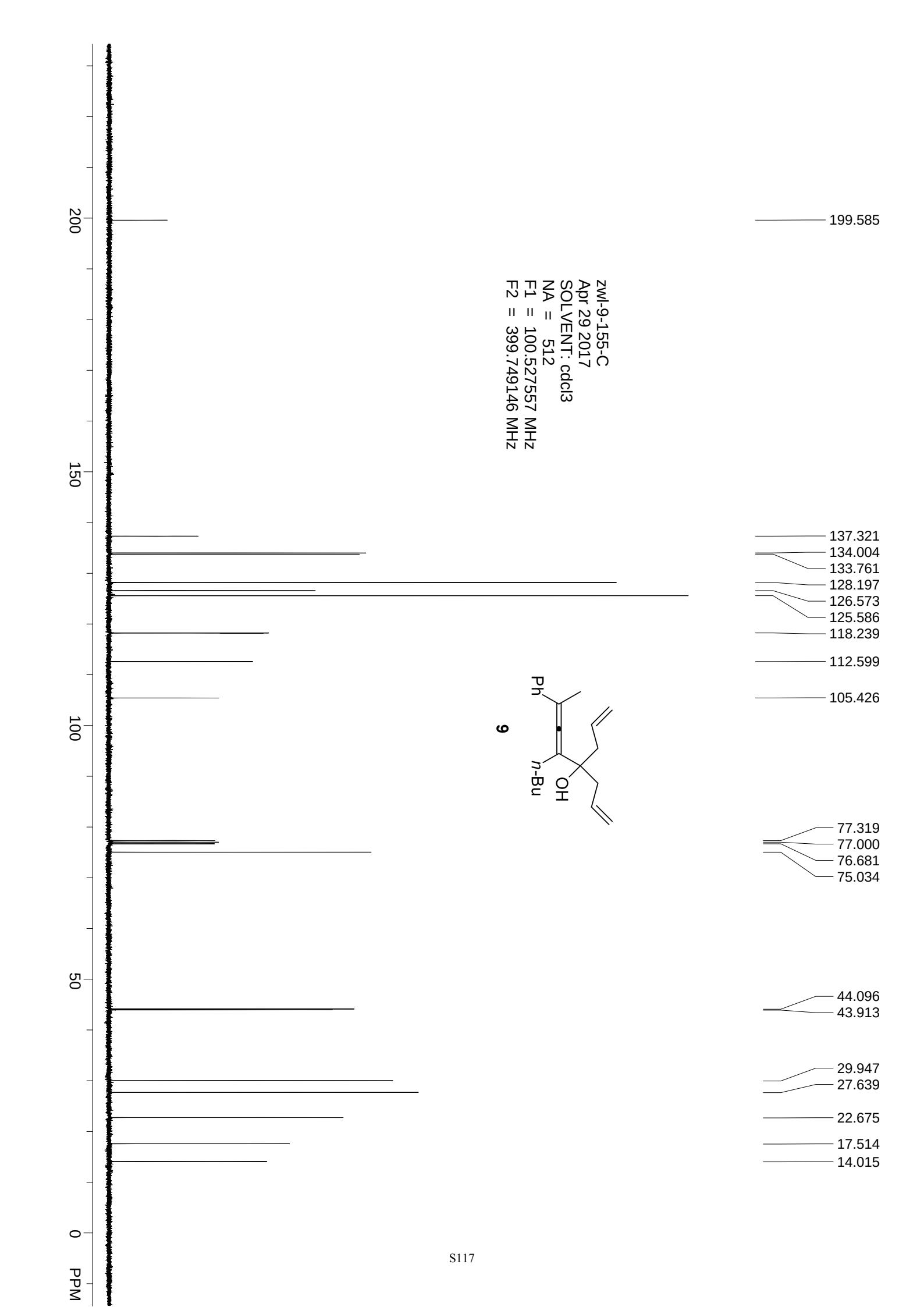

**8**


198.986
137.503
128.296
126.694
125.601
107.984
104.819
77.319
77.000
76.681
63.170
29.848
29.385
22.478
17.423
13.901
zwl-9-146-C
Mar 18 2017
SOLVENT: cdcl3
NA = 256
F1 = 100.527557 MHz
F2 = 399.749146 MHz
CH2OH
Ph
n-Bu
8
S115
200
150
100
50
0
PPM


zwl-9-155-H
Mar 28 2017
SOLVENT: cdcl3
NA = 8
F1 = 399.749542 MHz
F2 = 100.526031 MHz




**9**


zwl-9-155-C
Apr 29 2017
SOLVENT: cdcl3
NA = 512
F1 = 100.527557 MHz
F2 = 399.749146 MHz
9
Ph
n-Bu
OH
199.585
137.321
134.004
133.761
128.197
126.573
125.586
118.239
112.599
105.426
77.319
77.000
76.681
75.034
44.096
43.913
29.947
27.639
22.675
17.514
14.015
200
150
100
50
0
PPM