Supporting Information

Pd-catalyzed Ring Opening Coupling Reaction of 2,3-Allenylic Carbonates with Cyclopropanols

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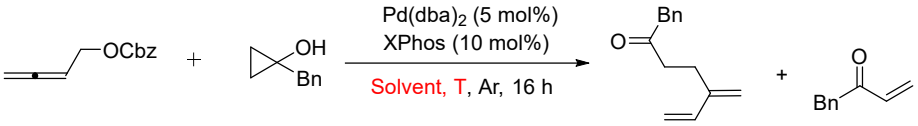
General Information. NMR spectra were taken with an Agilent-400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) or Bruker-400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR). Chemical shifts were recorded in ppm in relative to the TMS in $CDCl_3$ and coupling constants were reported in Hz. All reactions were carried out in flame-dried Schlenk tubes. $Pd(dba)_2$ was purchased from TCI Chemicals or J&K Chemicals; XPhos was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. or Energy (Shanghai) Chemical; Toluene, dioxane, tetrahydrofuran (THF), and methyl *tert*-butyl ether (MTBE) were dried over sodium wire with benzophenone as the indicator and distilled freshly before use; Dichloromethane, dichloroethane and acetonitrile were dried over calcium hydride and distilled before used. Petroleum ether (60 ^{o}C - 90 ^{o}C) was used for chromatography. All the temperatures are referred to the oil baths, acetone/dry ice bath, or ice/water bath used. NMR yields and recovery of starting material were determined by ^{1}H NMR analysis of the related reaction mixtures using dibromomethane or mesitylene as the internal standard. 2,3-Dienyl carbonate **1a'**,[1a] **1a**,[1b] **1d-1e**,[1b] **1g**,[1c] **1h**,[1d] were synthesized according to the reported procedures. Cyclopropanols **2a-2c**,[2a] **2d**,[2b] **2e**,[2a] **2f**,[2c] **2g**,[2d] **2h-2j**,[2e] **2k**,[2c,2f] **2l**,[2e] **2m**,[2a] **2n**,[2g] **2o**,[2h, 2i] **2p**,[2j] **2q**,[2a] were synthesized according to the reported procedures.

Experimental details and analytical data

I. Optimization of the reaction conditions.

Table S1. Optimization of solvent and temperature.[a]



1a' (0.20 mmol) **2a** (0.24 mmol) **3aa** **4**

Entry	Solvent	T (℃)	Yield (NMR, **3aa**, %)[b]	Yield (NMR, **4**, %)[b]
1	**Toluene**	**30**	**55**	**19**
2	dioxane	30	40	15
3	THF	30	41	15
4[c]	MTBE	30	44	2
5	DCM	30	34	19
6	DCE	30	29	26
7	CH_3CN	30	26	28
8	**Toluene**	**25**	**58**	**27**

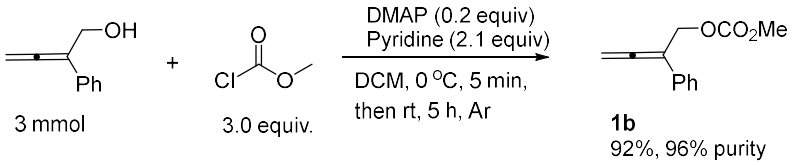
[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), $Pd(dba)_2$ (5 mol%), and XPhos (10 mol%) in solvent (1.0 mL) at T for 16 h.

[b] NMR yield with CH_2Br_2 as the internal standard.

[c] 15 h.

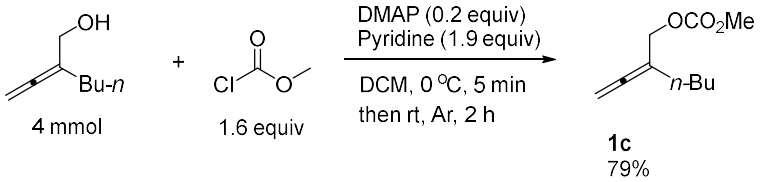
II. Synthesis of methyl carbonates

1) Synthesis of methyl 2-phenylbuta-2,3-dienyl carbonate (1b) (lj-1-168)



To a flame-dried Schlenk bottle were added 2-phenyl-2,3-butadienol (438.6 mg, 3.0 mmol), CH_2Cl_2 (30 mL), pyridine (0.5 mL, d = 0.983 g/mL, 491.5 mg, 6.2 mmol), and DMAP (73.7 mg, 0.6 mmol) under Ar. After being cooled to 0 °C with stirring, methyl chloroformate (0.7 mL, d = 1.223 g/mL, 856.1 mg, 9.1 mmol) was added dropwise within 5 minutes. After addition, the reaction was naturally warmed up to room temperature and stirred for 5 h. Then the reaction was cooled to 0 °C, hydrochloric acid (1 M, 30 mL) was added to quench the reaction. The organic phase was separated, the aqueous phase was extracted with DCM (30 mL × 3) and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by column chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 100/1 (0.9 L)] to afford **1b** (588.2 mg, 92%, 96% purity) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48-7.37 (m, 2 H, ArH), 7.37-7.29 (m, 2 H, ArH), 7.26-7.19 (m, 1 H, ArH), 5.23 (s, 2 H, OCH_2), 5.08 (t, *J* = 1.8 Hz, 2 H, $=CH_2$), 3.78 (s, 3 H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.8, 155.6, 133.3, 128.6, 127.2, 126.0, 101.1, 79.3, 66.6, 54.8; IR (neat, cm^{-1}): *v* = 3060, 2957, 1942, 1745, 1707, 1598, 1581, 1496, 1443, 1374, 1254, 1105, 1066, 1026, 1000; MS (70 eV, EI) *m/z* (%): 204 (M^+, 6.56), 105 (100); HRMS calcd for $C_{12}H_{12}O_3$ [M^+]: 204.0786; Found: 204.0789.

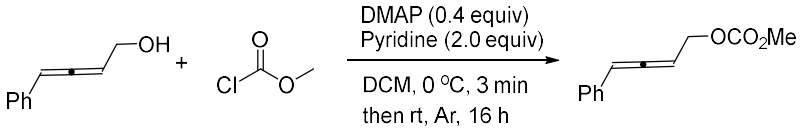
2) Synthesis of methyl 2-butylbuta-2,3-dienyl carbonate (1c) (lj-2-7)



To a flame-dried Schlenk bottle were added 2-butyl-2,3-butadienol (560.7 mg, 4 mmol), CH_2Cl_2 (30 mL), and DMAP (98.4 mg, 0.8 mmol) under Ar. After being

cooled to 0 °C with stirring, pyridine (0.6 mL, d = 0.983 g/mL, 589.8 mg, 7.5 mmol) was added, then methyl chloroformate (0.5 mL, d = 1.223 g/mL, 611.5 mg, 6.5 mmol) was added dropwise within 5 minutes. After addition, the reaction was naturally warmed up to room temperature and stirred for 2 h. Then the reaction was cooled to 0 °C, hydrochloric acid (1 M, 30 mL) was added to quench the reaction. The organic phase was separated, the aqueous phase was extracted with DCM (30 mL × 3), and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by column chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 100/1 (0.8 L)] to afford **1c** (581.7 mg, 79%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.87-4.78 (m, 2 H, =CH_2), 4.61 (t, *J* = 2.0 Hz, 2 H, OCH_2), 3.79 (s, 3 H, OCH_3), 2.07-1.96 (m, 2 H, CH_2), 1.52-1.26 (m, 4 H, CH_2×2), 0.91 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.9, 155.6, 99.1, 76.9, 68.4, 54.7, 29.4, 28.6, 22.2, 13.8; IR (neat, cm^{-1}): 2957, 2931, 2861, 1960, 1748, 1443, 1375, 1250, 1172, 1103; MS (ESI): *m/z* 202 $(M+NH_4)^+$, 185 $(M+H)^+$; HRMS Calcd for $C_{10}H_{17}O_3$ $(M+H)^+$: 185.1174; Found: 185.1172.

3) Synthesis of methyl 4-phenylbuta-2,3-dienyl carbonate (1f) (lj-3-106)



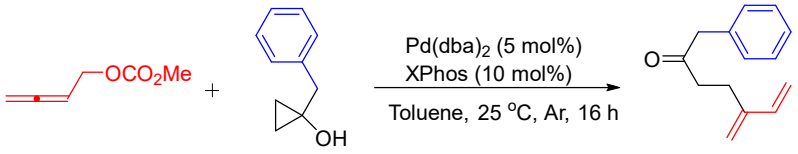
14 mmol　　1.5 equiv　　**1f** 49%

To a flame-dried Schlenk bottle were added DMAP (687.4 mg, 5.6 mmol), 4-phenyl-2,3-butadienol (2045.5 mg, 14 mmol), CH_2Cl_2 (30 mL), and pyridine (2.3 mL, d = 0.983 g/mL, 2260.9 mg, 28 mmol) sequentially under Ar. After being cooled to 0 °C with stirring, methyl chloroformate (1.6 mL, d = 1.223 g/mL, 1956.8 mg, 21 mmol) was added dropwise within 3 minutes. After addition, the reaction was naturally warmed up to room temperature and stirred for 16 h. Then the reaction was cooled to 0 °C, hydrochloric acid (1 M, 30 mL) was added to quench the reaction. The organic phase was separated, the aqueous phase was extracted with DCM (30 mL × 3), and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration and

evaporation, the residue was purified by column chromatography on silica gel [eluent: petroleum ether/dichloromethane = 5/1 (2.0 L)] to afford **1f** (1406.0 mg, 46%, 94% purity) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.15 (m, 5 H, ArH), 6.40-6.24 (m, 1 H, CH), 5.74 (q, *J* = 6.7 Hz, 1 H, CH), 4.80-4.67 (m, 2 H, CH_2), 3.77 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.6, 155.5, 133.1, 128.6, 127.4, 127.0, 96.7, 90.6, 65.3, 54.8; IR (neat, cm^{-1}): 3032, 3007, 2957, 1954, 1745, 1597, 1495, 1443, 1367, 1251, 1120, 1074; MS (70 eV, EI) *m/z* (%): 204 [M^+, 3.64], 128 (100); HRMS Calcd for $C_{12}H_{12}O_3$ (M^+): 204.0781; Found: 204.0785.

III. Synthesis of 1,3-dienes.

1) 5-Methylene-1-phenylhept-6-en-2-one (3aa) (lj-1-109, zth-7-100)

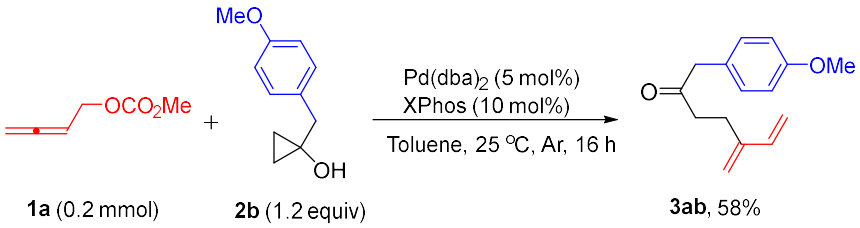


1a (0.2 mmol) **2a** (1.2 equiv) **3aa**, 64%

Typical Procedure I: To a flame-dried Schlenk tube were added $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1a** (25.8 mg, 0.20 mmol)/toluene (0.5 mL), and **2a** (35.8 mg, 0.24 mmol)/toluene (0.5 mL) sequentially under Ar atmosphere at room temperature. The resulting mixture was then stirred at 25 °C for 16 h. The crude reaction mixture was then filtrated through a short column of silica gel (height: 3 cm, *Φ*: 3.5 cm) eluted with diethyl ether (50 mL). After evaporation, the residue was purified by column chromatography on silica gel to afford **3aa** (25.9 mg, 64%) as an oil [eluent: petroleum ether/toluene = 4/1, 2.5 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37-7.29 (m, 2 H, ArH), 7.29-7.21 (m, 1 H, ArH), 7.21-7.16 (m, 2 H, ArH), 6.32 (dd, J_1 = 17.6 Hz, J_2 = 10.4 Hz, 1 H, =CH), 5.16 (d, *J* = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.04 (d, *J* = 11.2 Hz, 1 H, one proton of $=CH_2$), 4.99 (s, 1 H, one proton of $=CH_2$), 4.91 (s, 1 H, one proton of $=CH_2$), 3.69 (s, 2 H, $ArCH_2CO$), 2.65 (t, *J* = 7.6 Hz, 2 H, CH_2), 2.47 (t, *J* = 7.6 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.5, 144.9, 138.3, 134.1, 129.4, 128.7, 127.0, 116.0, 113.5, 50.2, 40.4, 25.2; IR (neat, cm^{-1}): 3087, 3029, 2924, 1711, 1595, 1495, 1454, 1409, 1091; MS (70 eV, EI) *m/z* (%): 200 [M^+,

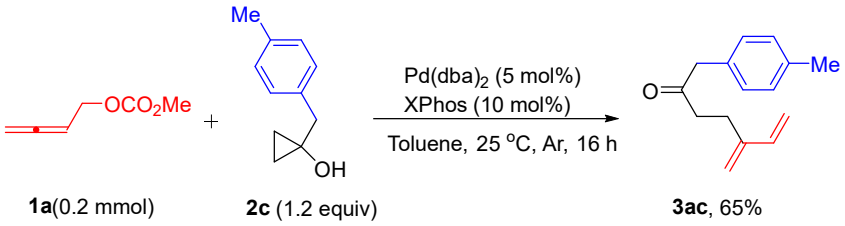
16.85], 91 (100); HRMS Calcd for $C_{14}H_{16}O$ (M^+): 200.1201; Found: 200.1198.

2) 1-(4-Methoxyphenyl)-5-methylenehept-6-en-2-one (3ab) (lj-1-132, lj-1-83)



Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.5 mg, 0.02 mmol), **1a** (25.7 mg, 0.20 mmol), **2b** (42.9 mg, 0.24 mmol) and toluene (1 mL) afforded **3ab** (26.8 mg, 58%) as an oil [eluent: petroleum ether/diethyl ether = 100/1, 2.0 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (d, J = 8.8 Hz, 2 H, ArH), 6.86 (d, J = 8.4 Hz, 2 H, ArH), 6.33 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1 H, =CH), 5.17 (d, J = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.05 (d, J = 10.4 Hz, 1 H, one proton of $=CH_2$), 4.99 (s, 1 H, one proton of $=CH_2$), 4.91 (s, 1 H, one proton of $=CH_2$), 3.80 (s, 3 H, OCH_3), 3.63 (s, 2 H, $ArCH_2CO$), 2.64 (t, J = 7.4 Hz, 2 H, CH_2), 2.47 (t, J = 7.4 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.1, 158.6, 144.9, 138.3, 130.4, 126.1, 116.1, 114.1, 113.5, 55.2, 49.3, 40.2, 25.2; IR (neat, cm^{-1}): 3087, 3034, 3002, 2954, 2934, 2906, 2835, 1710, 1611, 1595, 1510, 1462, 1441, 1421, 1355, 1322, 1300, 1245, 1177, 1113, 1082, 1033; MS (70 eV, EI) *m/z* (%): 230 [M^+, 13.09], 121 (100); HRMS Calcd for $C_{15}H_{18}O_2$ (M^+): 230.1307; Found: 230.1305.

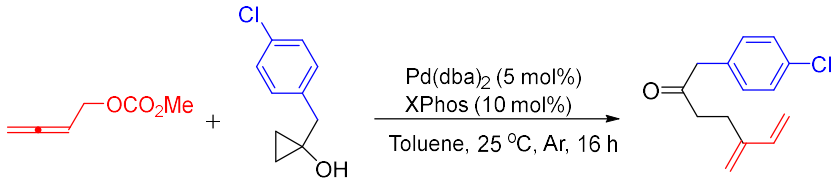
3) 5-Methylene-1-(*p*-tolyl)hept-6-en-2-one (3ac) (lj-1-146)



Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1a** (25.7 mg, 0.20 mmol), **2c** (39.0 mg, 0.24 mmol) and toluene (1 mL) afforded **3ac** (27.8 mg, 65%) as an oil [eluent: petroleum ether/toluene

= 4/1, 2.0 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.13 (d, *J* = 8.0 Hz, 2 H, ArH), 7.09 (d, *J* = 7.6 Hz, 2 H, ArH), 6.33 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1 H, =CH), 5.17 (d, *J* = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.04 (d, *J* = 10.8 Hz, 1 H, one proton of $=CH_2$), 4.99 (s, 1 H, one proton of $=CH_2$), 4.91 (s, 1 H, one proton of $=CH_2$), 3.65 (s, 2 H, $ArCH_2CO$), 2.64 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.46 (t, *J* = 7.6 Hz, 2 H, CH_2), 2.33 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.9, 144.9, 138.3, 136.6, 131.1, 129.4, 129.2, 116.1, 113.5, 49.9, 40.3, 25.2, 21.0; IR (neat, cm^{-1}): 3088, 3005, 2922, 1711, 1634, 1595, 1513, 1414, 1354, 1324, 1238, 1187, 1112, 1082, 1051, 1022; MS (70 eV, EI) *m/z* (%): 214 [M^+, 12.65], 105 (100); HRMS Calcd for $C_{15}H_{18}O$ (M^+): 214.1358; Found: 214.1362.

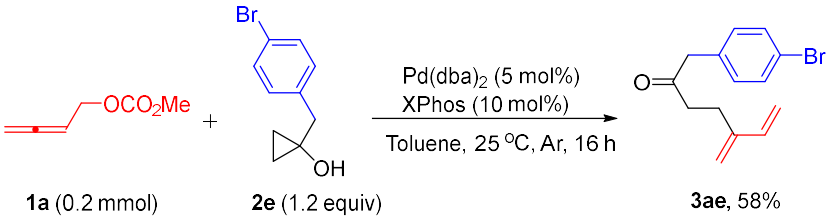
4) 1-(4-Chlorophenyl)-5-methylenehept-6-en-2-one (3ad) (lj-1-159, lj-1-71)



1a (0.2 mmol) **2d** (1.2 equiv) **3ad**, 56%

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1a** (25.7 mg, 0.20 mmol), **2d** (43.8 mg, 0.24 mmol) and toluene (1 mL) afforded **3ad** (26.3 mg, 56%) as an oil [eluent: petroleum ether/toluene = 4/1, 1.5 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 8.4 Hz, 2 H, ArH), 7.12 (d, *J* = 8.8 Hz, 2 H, ArH), 6.33 (dd, J_1 = 17.6 Hz, J_2 = 10.4 Hz, 1 H, =CH), 5.17 (d, *J* = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.06 (d, *J* = 10.8 Hz, 1 H, one proton of $=CH_2$), 5.00 (s, 1 H, one proton of $=CH_2$), 4.93 (s, 1 H, one proton of $=CH_2$), 3.67 (s, 2 H, $ArCH_2CO$), 2.73-2.58 (m, 2 H, CH_2), 2.48 (t, *J* = 7.6 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.9, 144.8, 138.3, 133.0, 132.5, 130.7, 128.8, 116.2, 113.6, 49.3, 40.6, 25.1; IR (neat, cm^{-1}): 3087, 2973, 1713, 1634, 1595, 1457, 1408, 1355, 1324, 1237, 1188, 1088, 1052, 1015; MS (70 eV, EI) *m/z* (%): 236 [M^+ (^{37}Cl), 4.59], 234 [M^+ (^{35}Cl), 13.90], 125 (100); HRMS Calcd for $C_{14}H_{15}{}^{35}ClO$ (M^+): 234.0811; Found: 234.0818.

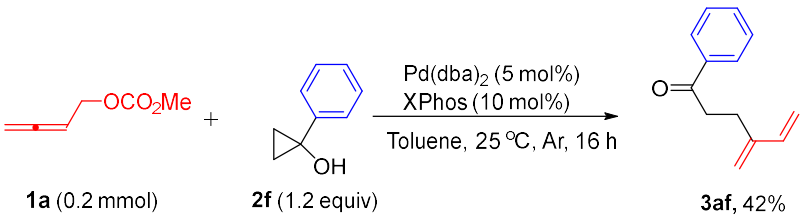
5) 1-(4-Bromophenyl)-5-methylenehept-6-en-2-one (3ae) (lj-1-122, lj-1-86)



1a (0.2 mmol) **2e** (1.2 equiv) **3ae**, 58%

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.7 mg, 0.02 mmol), **1a** (25.6 mg, 0.20 mmol), **2e** (54.6 mg, 0.24 mmol) and toluene (1 mL) afforded **3ae** (32.3 mg, 58%) as an oil [eluent: petroleum ether/toluene = 4/1, 2.0 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 8.4 Hz, 2 H, ArH), 7.07 (d, *J* = 8.4 Hz, 2 H, ArH), 6.33 (dd, J_1 = 17.6 Hz, J_2 = 10.4 Hz, 1 H, =CH), 5.17 (d, *J* = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.06 (d, *J* = 10.4 Hz, 1 H, one proton of $=CH_2$), 5.00 (s, 1 H, one proton of $=CH_2$), 4.93 (s, 1 H, one proton of $=CH_2$), 3.65 (s, 2 H, $ArCH_2CO$), 2.66 (t, *J* = 7.6 Hz, 2 H, CH_2), 2.48 (t, *J* = 7.6 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.8, 144.8, 138.3, 133.0, 131.8, 131.1, 121.1, 116.2, 113.6, 49.4, 40.7, 25.1; IR (neat, cm^{-1}): 3087, 2974, 1713, 1634, 1594, 1487, 1456, 1406, 1355, 1323, 1236, 1187, 1105, 1070, 1053, 1011; MS (70 eV, EI) *m/z* (%): 280 [M^+ (Br^{81}), 7.69], 278 [M^+ (Br^{79}), 7.92], 121 (100); HRMS Calcd for $C_{14}H_{15}{}^{79}BrO$ (M^+): 278.0306; Found: 278.0304.

6) 4-Methylene-1-phenylhex-5-en-1-one (3af) (lj-1-157, zth-7-141)

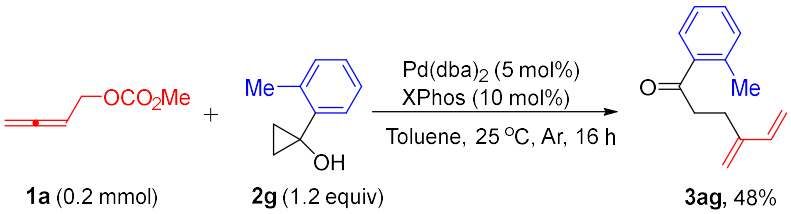


1a (0.2 mmol) **2f** (1.2 equiv) **3af**, 42%

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1a** (25.7 mg, 0.20 mmol), **2f** (32.2 mg, 0.24 mmol) and toluene (1 mL) afforded **3af** (15.6 mg, 42%) as an oil [eluent: petroleum ether/toluene = 4/1, 1.5 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 6.8 Hz, 2 H, ArH),

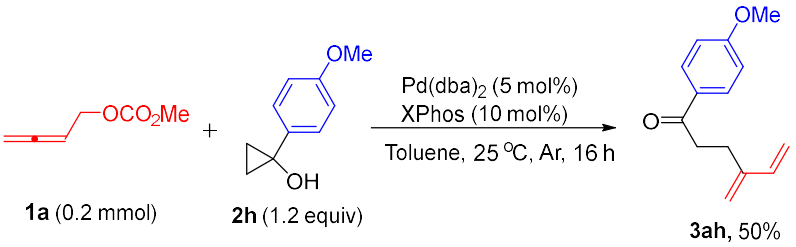
7.64-7.41 (m, 3 H, ArH), 6.41 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1 H, =CH), 5.29 (d, J = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.11 (d, J = 10.8 Hz, 1 H, one proton of $=CH_2$), 5.07 (s, 1 H, one proton of $=CH_2$), 5.06 (s, 1 H, one proton of $=CH_2$), 3.18 (t, J = 7.8 Hz, 2 H, CH_2), 2.68 (t, J = 7.8 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.5, 145.2, 138.4, 136.9, 133.0, 128.6, 128.0, 116.2, 113.6, 37.2, 25.6; IR (neat, cm^{-1}): 3087, 2924, 2854, 1683, 1595, 1580, 1448, 1357, 1323, 1283, 1249, 1202, 1180; MS (70 eV, EI) *m/z* (%): 186 [M^+, 2.25], 105 (100); HRMS Calcd for $C_{13}H_{14}O$ (M^+): 186.1045; Found: 186.1048.

7) 4-Methylene-1-(*o*-tolyl)hex-5-en-1-one (3ag) (lj-1-155, zth-7-130)



Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1a** (25.7 mg, 0.20 mmol), **2g** (35.5 mg, 0.24 mmol) and toluene (1 mL) afforded **3ag** (19.3 mg, 48%) as an oil [eluent: petroleum ether/toluene = 4/1, 1.5 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (d, J = 8.2 Hz, 1 H, ArH), 7.40-7.33 (m, 1 H, ArH), 7.28-7.20 (m, 2 H, ArH), 6.40 (dd, J_1 = 17.6 Hz, J_2 = 11.2 Hz, 1 H, =CH), 5.28 (d, J = 18.0 Hz, 1 H, one proton of $=CH_2$), 5.10 (d, J = 10.4 Hz, 1 H, one proton of $=CH_2$), 5.06 (s, 1 H, one proton of $=CH_2$), 5.03 (s, 1 H, one proton of $=CH_2$), 3.14-3.06 (m, 2 H, CH_2), 2.67-2.61 (m, 2 H, CH_2), 2.50 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.7, 145.2, 138.5, 138.0, 131.9, 131.2, 128.3, 125.6, 116.2, 113.6, 40.1, 25.8, 21.2; IR (neat, cm^{-1}): 3088, 2967, 2927, 1683, 1595, 1571, 1455, 1381, 1321, 1285, 1243, 1206, 1194; MS (70 eV, EI) *m/z* (%): 200 [M^+, 3.02], 119 (100); HRMS Calcd for $C_{14}H_{16}O_2$ (M^+): 200.1201; Found: 200.1199.

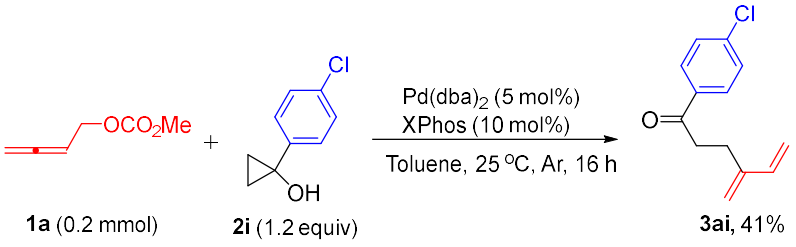
8) 1-(4-Methoxyphenyl)-4-methylenehex-5-en-1-one (3ah) (lj-1-142)



1a (0.2 mmol) **2h** (1.2 equiv) **3ah**, 50%

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.5 mg, 0.02 mmol), **1a** (25.7 mg, 0.20 mmol), **2h** (39.5 mg, 0.24 mmol) and toluene (1 mL) afforded **3ah** (21.5 mg, 50%) [eluent: petroleum ether/diethyl ether = 100/1, 1.6 L] as a white solid: m.p. = 52.3-53.1 °C (petroleum ether/dichloromethane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, J = 8.4 Hz, 2 H, ArH), 6.94 (d, J = 9.2 Hz, 2 H, ArH), 6.41 (dd, J_1 = 17.8 Hz, J_2 = 11.0 Hz, 1 H, =CH), 5.29 (d, J = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.11 (d, J = 10.4 Hz, 1 H, one proton of $=CH_2$), 5.06 (s, 1 H, one proton of $=CH_2$), 5.05 (s, 1 H, one proton of $=CH_2$), 3.87 (s, 3 H, OCH_3), 3.13 (t, J = 7.6 Hz, 2 H, CH_2), 2.66 (t, J = 7.6 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.2, 163.4, 145.4, 138.5, 130.3, 130.0, 116.1, 113.7, 113.6, 55.4, 36.9, 25.8; IR (neat, cm^{-1}): 3080, 2999, 2967, 2938, 2902, 2833, 1669, 1598, 1576, 1507, 1454, 1420, 1358, 1323, 1283, 1251, 1205, 1172, 1108, 1060, 1029; MS (70 eV, EI) *m/z* (%): 216 [M^+, 14.46], 135 (100); Anal. Calcd for $C_{14}H_{16}O_2$: C 77.75, H 7.46; Found: C 77.74, H 7.65.

9) 1-(4-Chlorophenyl)-4-methylenehex-5-en-1-one (3ai) (lj-1-134)

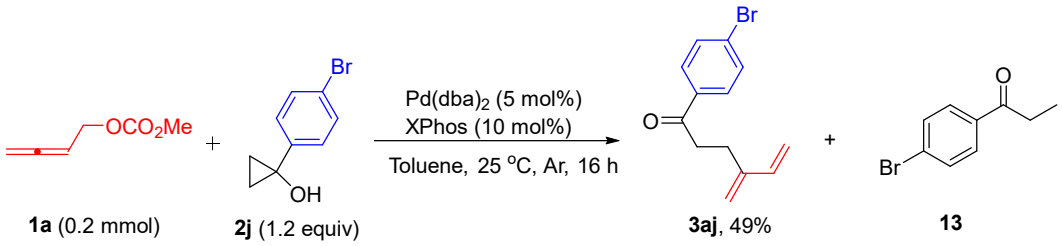


1a (0.2 mmol) **2i** (1.2 equiv) **3ai**, 41%

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1a** (25.7 mg, 0.20 mmol), **2i** (40.5 mg, 0.24 mmol) and toluene (1 mL) afforded **3ai** (18.2 mg, 41%) as an oil [eluent: petroleum ether/toluene = 4/1, 1.0 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, J = 8.8 Hz, 2 H, ArH), 7.44 (d, J = 8.8 Hz, 2 H, ArH), 6.40 (dd, J_1 = 17.6 Hz, J_2 = 11.2 Hz, 1 H, =CH), 5.28 (d, J =

18.0 Hz, 1 H, one proton of $=CH_2$), 5.12 (d, J = 10.8 Hz, 1 H, one proton of $=CH_2$), 5.07 (s, 1 H, one proton of $=CH_2$), 5.04 (s, 1 H, one proton of $=CH_2$), 3.15 (t, J = 7.6 Hz, 2 H, CH_2), 2.67 (t, J = 7.6 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.3, 145.1, 139.5, 138.4, 135.2, 129.4, 128.9, 116.3, 113.7, 37.2, 25.5; IR (neat, cm^{-1}): 3085, 3005, 2913, 1680, 1587, 1486, 1398, 1357, 1328, 1282, 1246, 1199, 1176, 1091, 1039, 1012; MS (70 eV, EI) *m/z* (%): 222 [M^+(^{37}Cl), 0.56], 220 [M^+(^{35}Cl), 1.61], 139 (100); HRMS Calcd for $C_{13}H_{13}{}^{35}ClO$ (M^+): 220.0655; Found: 220.0654.

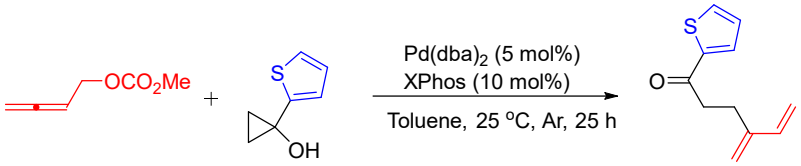
10) 1-(4-Bromophenyl)-4-methylenehex-5-en-1-one (3aj) (lj-1-129)



1a (0.2 mmol) **2j** (1.2 equiv) **3aj**, 49% **13**

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.5 mg, 0.02 mmol), **1a** (25.6 mg, 0.20 mmol), **2j** (54.6 mg, 0.24 mmol) and toluene (1 mL) afforded mixture include with **3aj** and **13** (28.0 mg, 49%, 92% purity) as an oil [eluent: petroleum ether/toluene = 4/1, 1.0 L]: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, J = 8.0 Hz, 2 H, ArH), 7.60 (d, J = 8.4 Hz, 2 H, ArH), 6.40 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1 H, =CH), 5.28 (d, J = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.12 (d, J = 10.8 Hz, 1 H, one proton of $=CH_2$), 5.07 (s, 1 H, one proton of $=CH_2$), 5.04 (s, 1 H, one proton of $=CH_2$), 3.14 (t, J = 8.0 Hz, 2 H, CH_2), 2.67 (t, J = 7.4 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.5, 145.0, 138.4, 135.6, 131.9, 129.5, 128.2, 116.3, 113.7, 37.2, 25.5; IR (neat, cm^{-1}): 3087, 2924, 2853, 1685, 1584, 1484, 1395, 1357, 1322, 1284, 1247, 1200, 1176, 1069, 1009; MS (70 eV, EI) *m/z* (%): 266 [M^+ (Br^{81}), 1.92], 264 [M^+ (Br^{79}), 1.89], 183 (100); HRMS Calcd for $C_{13}H_{14}{}^{79}BrO$ $(M+H)^+$: 265.0223; Found: 265.0222.

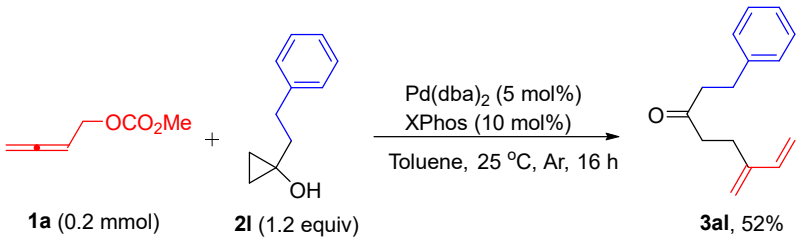
11) 4-Methylene-1-(thiophen-2-yl)hex-5-en-1-one (3ak) (lj-1-137, zth-7-111)



1a (0.2 mmol) **2k** (1.2 equiv) **3ak**, 50%

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1a** (25.7 mg, 0.20 mmol), **2k** (33.7 mg, 0.24 mmol) and toluene (1 mL) reacted for 25 h afforded **3ak** (19.1 mg, 50%) as an oil [eluent: petroleum ether/toluene = 4/1, 1.5 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 4.0 Hz, 1 H, ArH), 7.63 (d, *J* = 4.8 Hz, 1 H, ArH), 7.13 (t, *J* = 4.2 Hz, 1 H, ArH), 6.40 (dd, J_1 = 17.8 Hz, J_2 = 11.0 Hz, 1 H, =CH), 5.29 (d, *J* = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.12 (d, *J* = 10.8 Hz, 1 H, one proton of $=CH_2$), 5.06 (s, 2 H, one proton of $=CH_2$ +one proton of $=CH_2$), 3.11 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.68 (t, *J* = 7.8 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.6, 145.0, 144.2, 138.3, 133.5, 131.8, 128.1, 116.4, 113.7, 38.0, 25.9; IR (neat, cm^{-1}): 3088, 2924, 1658, 1594, 1518, 1414, 1355, 1248, 1235, 1205, 1055; MS (70 eV, EI) *m/z* (%): 192 [M^+, 9.47], 111 (100); HRMS Calcd for $C_{11}H_{12}OS$ (M^+): 192.0609; Found: 192.0603.

12) 6-Methylene-1-phenyloct-7-en-3-one (3al) (lj-1-125, zth-7-101)

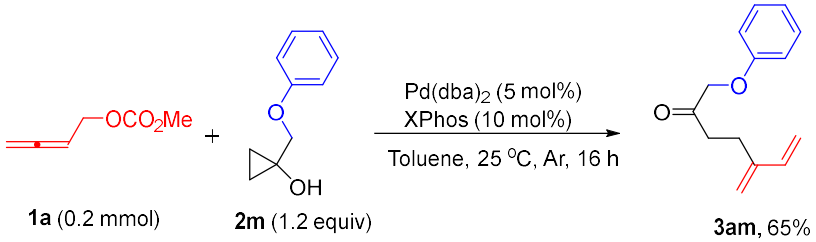


1a (0.2 mmol) **2l** (1.2 equiv) **3al**, 52%

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1a** (25.6 mg, 0.2 mmol), **2l** (39.1 mg, 0.24 mmol) and toluene (1 mL) afforded **3al** (22.1 mg, 52%) as an oil [eluent: petroleum ether/toluene = 4/1, 2.0 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34-7.23 (m, 2 H, ArH), 7.22-7.10 (m, 3 H, ArH), 6.34 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1 H, =CH), 5.20 (d, *J* = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.06 (d, *J* = 10.4 Hz, 1 H, one proton of $=CH_2$), 5.00 (s, 1 H, one proton of $=CH_2$), 4.94 (s, 1 H, one proton of $=CH_2$), 2.90 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.73 (t, *J* = 7.6 Hz, 2 H, CH_2), 2.63-2.54 (m, 2 H, CH_2), 2.54-2.42 (m, 2 H, CH_2); ^{13}C

NMR (100 MHz, $CDCl_3$) δ = 209.2, 145.0, 141.0, 138.3, 128.4, 128.3, 126.0, 116.0, 113.5, 44.3, 41.4, 29.7, 25.1; IR (neat, cm^{-1}): 3087, 3063, 3028, 2926, 1712, 1595, 1496, 1454, 1408, 1365, 1262, 1094; MS (70 eV, EI) *m/z* (%): 214 [M^+, 12.51], 105 (100); HRMS Calcd for $C_{15}H_{18}O$ (M^+): 214.1358; Found: 214.1359.

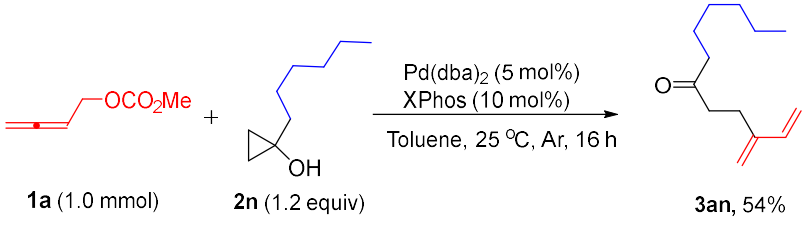
13) 5-Methylene-1-phenoxyhept-6-en-2-one (3am) (lj-1-149)



1a (0.2 mmol) **2m** (1.2 equiv) **3am**, 65%

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1a** (25.7 mg, 0.20 mmol), **2m** (39.6 mg, 0.24 mmol) and toluene (1 mL) afforded **3am** (28.1 mg, 65%) as an oil [eluent: petroleum ether/toluene = 4/1, 2.0 L]: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 8.0 Hz, 2 H, ArH), 7.00 (t, *J* = 7.4 Hz, 1 H, ArH), 6.89 (d, *J* = 8.0 Hz, 2 H, ArH), 6.36 (dd, J_1 = 17.6 Hz, J_2 = 10.4 Hz, 1 H, =CH), 5.23 (d, *J* = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.09 (d, *J* = 11.2 Hz, 1 H, one proton of $=CH_2$), 5.04 (s, 1 H, one proton of $=CH_2$), 5.00 (s, 1 H, one proton of $=CH_2$), 4.55 (s, 2 H, OCH_2), 2.82 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.56 (t, *J* = 7.4 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.2, 157.7, 144.7, 138.2, 129.7, 121.7, 116.3, 114.5, 113.7, 72.8, 37.7, 24.6; IR (neat, cm^{-1}): 3088, 2903, 1719, 1596, 1493, 1456, 1431, 1402, 1362, 1292, 1223, 1174, 1143, 1080, 1062; MS (70 eV, EI) *m/z* (%): 216 [M^+, 27.93], 77 (100); HRMS Calcd for $C_{14}H_{16}O_2$ (M^+): 216.1150; Found: 216.1153.

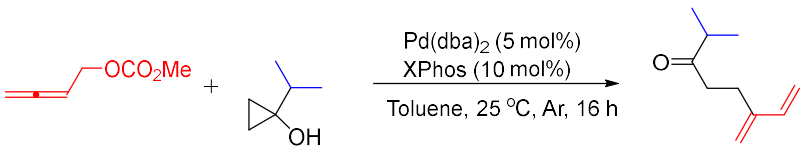
14) 3-Methylenedodec-1-en-6-one (3an) (lj-1-90, zth-7-116)



1a (1.0 mmol) **2n** (1.2 equiv) **3an**, 54%

To a flame-dried Schlenk tube were added $Pd(dba)_2$ (28.8 mg, 0.05 mmol), XPhos (47.6 mg, 0.10 mmol), **1a** (128.2 mg, 1.0 mmol)/toluene (1.0 mL), **2n** (170.4 mg, 1.2 mmol)/toluene (1.0 mL), and toluene (3.0 mL) sequentially under Ar atmosphere at room temperature. The reaction was then stirred at 25 °C for 16 h. The crude reaction mixture was then filtrated through a short column of silica gel (height: 3 cm, *Φ*: 3.5 cm) eluted with diethyl ether (50 mL). After evaporation, the residue was purified by column chromatography on silica gel to afford **3an** (105.1 mg, 54%) as an oil [eluent: petroleum ether/toluene = 4/1, 1.5 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.36 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1 H, =CH), 5.23 (d, J = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.08 (d, J = 11.2 Hz, 1 H, one proton of $=CH_2$), 5.02 (s, 1 H, one proton of $=CH_2$), 4.98 (s, 1 H, one proton of $=CH_2$), 2.61 (t, J = 7.2 Hz, 2 H, CH_2), 2.50 (t, J = 7.4 Hz, 2 H, CH_2), 2.41 (t, J = 7.4 Hz, 2 H, CH_2), 1.65-1.50 (m, 2 H, CH_2), 1.36-1.18 (m, 6 H, CH_2×3), 0.88 (t, J = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.5, 145.1, 138.4, 116.0, 113.4, 42.9, 41.1, 31.5, 28.8, 25.1, 23.7, 22.4, 14.0; IR (neat, cm^{-1}): 3090, 2955, 2927, 2857, 1713, 1595, 1458, 1411, 1369, 1319, 1234, 1196, 1127, 1081; MS (70 eV, EI) *m/z* (%): 194 [M^+, 8.46], 113 (100); HRMS Calcd for $C_{13}H_{22}O$ (M^+): 194.1671; Found: 194.1674.

15) 2-Methyl-6-methyleneoct-7-en-3-one (3ao) (lj-3-110, lj-3-115)

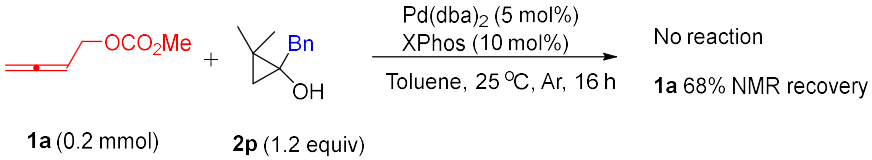


1a (0.2 mmol) **2o** (1.2 equiv) **3ao**, 50%

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1a** (25.7 mg, 0.20 mmol), **2o** (24.3 mg, 0.24 mmol) , and toluene (1 mL) afforded **3ao** (15.3 mg, 50%) as an oil [eluent: petroleum ether/diethyl ether = 100/1, 0.8 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.36 (dd, J_1 = 17.8 Hz, J_2 = 11.0 Hz, 1 H, =CH), 5.24 (d, J = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.08 (d, J = 11.2 Hz, 1 H, one proton of $=CH_2$), 5.02 (s, 1 H, one proton of $=CH_2$), 4.98 (s, 1 H, one proton of $=CH_2$), 2.74-2.54 (m, 3 H, CH_2 + CH), 2.50 (t, J = 7.6 Hz, 2 H, CH_2), 1.10

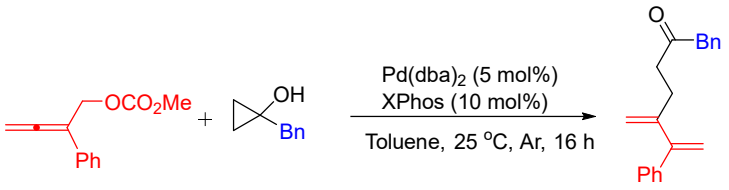
(d, J = 6.8 Hz, 6 H, CH_3×2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 214.1, 145.4, 138.5, 116.0, 113.5, 40.9, 38.9, 25.3, 18.2; IR (neat, cm^{-1}): 3088, 2969, 2931, 2884, 1808, 1710, 1594, 1461, 1376, 1262, 1189, 1081, 1044; MS (70 eV, EI) *m/z* (%): 152 [M^+, 8.92], 71 (100); HRMS Calcd for $C_{10}H_{16}O$ (M^+): 152.1196; Found: 152.1201.

16) 2-Methyl-6-methyleneoct-7-en-3-one (3ap) (lj-3-114)



To a flame-dried Schlenk tube were added $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1a** (25.7 mg, 0.2 mmol)/toluene (0.5 mL), and **2p** (43.4 mg, 0.24 mmol)/toluene (0.5 mL) sequentially under Ar atmosphere at room temperature. The reaction was then stirred at 25 °C for 16 h. The crude reaction mixture was then filtrated through a short column of silica gel (height: 3 cm, *Φ*: 3.5 cm) eluted with diethyl ether (50 mL). After evaporation, the residue was analyzed with ^1H NMR measurement in $CDCl_3$ with mesitylene (46 uL, d = 0.864 g/mL, 39.7 mg) as the internal standard: the recovery of **1a** and **2p** were determined to be 68% and 66%, respectively.

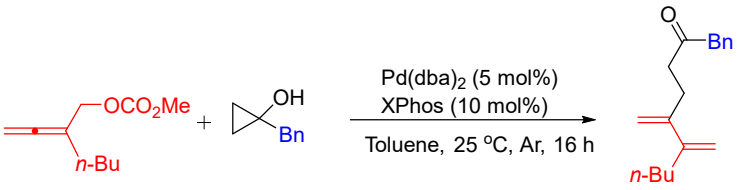
17) 5-Methylene-1,6-diphenylhept-6-en-2-one (3ba) (lj-1-184)



Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1b** (40.9 mg, 96% purity, 0.19 mmol), **2a** (35.5 mg, 0.24 mmol) and toluene (1 mL) afforded **3ba** (36.1 mg, 68%) as an oil [eluent: petroleum ether/toluene = 4/1, 2.0 L]: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.21 (m, 8 H, ArH), 7.21-7.13 (m, 2 H, ArH), 5.20 (s, 1 H, one proton of $=CH_2$), 5.16 (s, 1 H, one proton of $=CH_2$), 5.02 (s, 1 H, one proton of $=CH_2$), 4.94 (s, 1 H, one proton of $=CH_2$), 3.66

(s, 2 H, $ArCH_2CO$), 2.62 (t, J = 6.8 Hz, 2 H, CH_2), 2.52 (t, J = 6.8 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.5, 149.9, 147.3, 140.7, 134.1, 129.4, 128.7, 128.1, 128.0, 127.4, 127.0, 116.1, 113.9, 50.1, 40.6, 28.4; IR (neat, cm^{-1}): 3084, 3059, 3027, 2924, 1712, 1628, 1590, 1493, 1452, 1407, 1355, 1310, 1267, 1185, 1156, 1072, 1028, 1002; MS (70 eV, EI) *m/z* (%): 276 [M^+, 5.86], 55 (100); HRMS Calcd for $C_{20}H_{20}O$ (M^+): 276.1514; Found: 276.1518.

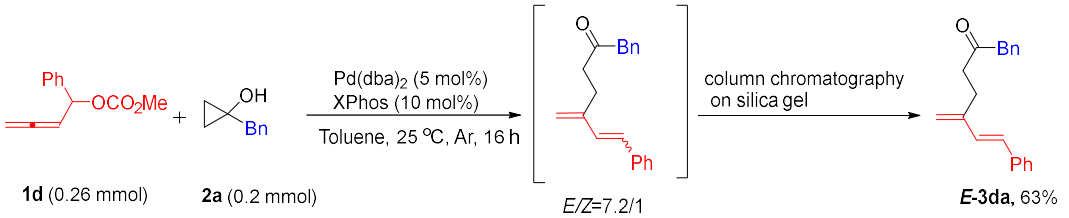
18) 6-*n*-Butyl-5-methylene-1-phenylhept-6-en-2-one (3ca) (lj-2-10)



1c (0.2 mmol) **2a** (1.2 equiv) **3ca,** 76%

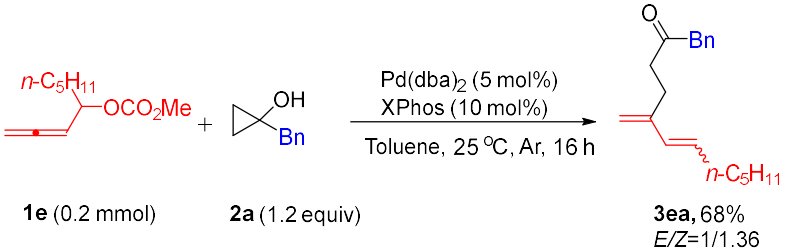
Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1c** (36.8 mg, 0.20 mmol), **2a** (35.6 mg, 0.24 mmol) and toluene (1 mL) afforded **3ca** (38.7 mg, 76%) as an oil [eluent: petroleum ether/toluene = 8/1, 1.8 L]: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.16 (m, 5 H, ArH), 5.05 (s, 1 H, one proton of $=CH_2$), 4.97 (s, 1 H, one proton of $=CH_2$), 4.91 (s, 1 H, one proton of $=CH_2$), 4.87 (s, 1 H, one proton of $=CH_2$), 3.68 (s, 2 H, $ArCH_2CO$), 2.61 (t, J = 7.2 Hz, 2 H, CH_2), 2.49 (t, J = 7.6 Hz, 2 H, CH_2), 2.19 (t, J = 7.4 Hz, 2 H, CH_2), 1.45-1.19 (m, 4 H, CH_2×2), 0.90 (t, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.7, 147.3, 146.3, 134.2, 129.4, 128.7, 127.0, 112.1, 111.7, 50.2, 41.2, 33.8, 30.8, 28.1, 22.5, 13.9; IR (neat, cm^{-1}): 3088, 3029, 2955, 2929, 2860, 1713, 1629, 1596, 1495, 1454, 1433, 1409, 1378, 1353, 1268, 1187, 1155, 1076, 1031, 1002; MS (70 eV, EI) *m/z* (%): 256 [M^+, 7.26], 91 (100); HRMS Calcd for $C_{18}H_{24}O$ (M^+): 256.1827; Found: 256.1833.

19) (*E*)-5-methylene-1,7-diphenylhept-6-en-2-one (3da) (lj-3-67)



Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1d** (53.2 mg, 0.26 mmol), **2a** (29.7 mg, 0.20 mmol) and toluene (1 mL) afforded ***E*-3da** (35.1 mg, 63%) as an oil. *Note*：*In the crude product, E/Z=7.2/1 was determined by* ^{1}*H NMR analysis using mesitylene as the internal standard. The Z-isomer was converted to the E-isomer after purification by column chromatography on silica gel.* [eluent: petroleum ether/diethyl ether = 100/1, 2.0 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70-7.10 (m, 10 H, ArH), 6.75 (d, *J* = 16.4 Hz, 1 H, one proton of $=CH_2$), 6.50 (d, *J* = 16.4 Hz, 1 H, one proton of $=CH_2$), 5.11 (s, 1 H, one proton of $=CH_2$), 4.98 (s, 1 H, one proton of $=CH_2$), 3.71 (s, 2 H, $ArCH_2CO$), 2.72 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.59 (t, *J* = 7.4 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.6, 144.7, 137.1, 134.1, 130.4, 129.4, 128.7, 128.6, 128.3, 127.5, 127.0, 126.4, 116.5, 50.3, 40.6, 25.8; IR (neat, cm^{-1}): 3083, 3060, 3027, 2922, 2900, 1712, 1602, 1494, 1450, 1410, 1332, 1264, 1186, 1157, 1078, 1030; MS (70 eV, EI) *m/z* (%): 276 (M^+, 9.39), 142 (100); HRMS Calcd for $C_{20}H_{20}O$ (M^+): 276.1514; Found: 276.1518.

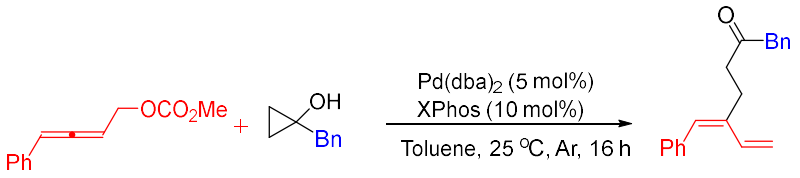
20) 5-Methylene-1-phenyldodec-6-en-2-one (3ea) (lj-1-176)



Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1e** (39.7 mg, 0.20 mmol), **2a** (35.6 mg, 0.24 mmol) and toluene (1 mL) afforded **3ea** (36.7 mg, 68%, *E/Z* = 1/1.36) as an oil [eluent: petroleum ether/toluene = 4/1, 1.5 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.27 (m, 2 H, ArH), 7.27-7.24 (m, 1 H, ArH), 7.24-7.16 (m, 2 H, ArH), [6.00 (d, *J* = 16.4 Hz, 0.42 H, for E

isomer), 5.69 (d, J = 11.6 Hz, 0.57 H, for Z isomer), =CH], [5.67-5.56 (m, 0.42 H, for *E* isomer), 5.53-5.40 (m, 0.57 H, for *Z* isomer), =CH], [4.92 (s, 0.56 H, for *Z* isomer), 4.86 (s, 0.42 H, for *E* isomer), one proton of $=CH_2$], [4.82 (s, 0.57 H, for *Z* isomer), 4.77 (s, 0.42 H, for *E* isomer), one proton of $=CH_2$], [3.69 (s, 0.84 H, for *E* isomer), 3.68 (s, 1.14 H, for *Z* isomer), $ArCH_2CO$], 2.72-2.28 (m, 4 H, CH_2×2), 2.20-2.00 (m, 2 H, CH_2), 1.45-1.18 (m, 6 H, CH_2×3), 0.98-0.83 (m, 3 H, CH_3); IR (neat, cm^{-1}): 3085, 3064, 3029, 3002, 2956, 2924, 2855, 1713, 1635, 1604, 1495, 1454, 1354, 1276, 1188, 1083, 1031; MS (70 eV, EI) *m/z* (%): 271 [(M^++1), 4.33], 270 [M^+, 15.54], 91 (100); Anal. Calcd for $C_{19}H_{26}O$: C 84.39, H 9.69; Found: C 84.66, H 9.52.

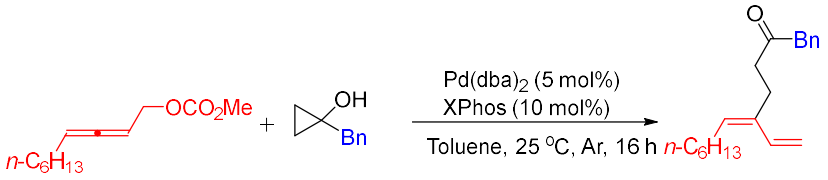
21) (*Z*)-5-benzylidene-1-phenylhept-6-en-2-one (3fa) (lj-3-107)



1f (0.19 mmol) **2a** (1.26 equiv) ***Z*-3fa**, 73%

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1f** (40.9 mg, 94% purity, 0.19 mmol), **2a** (35.7 mg, 0.24 mmol) and toluene (1 mL) afforded ***Z*-3fa** (38.3 mg, 73%) as an oil [eluent: petroleum ether/diethyl ether = 100/1, 2.0 L]: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.60-7.08 (m, 10 H, ArH), 6.72 (dd, J_1 = 17.8 Hz, J_2 = 11.0 Hz, 1 H, =CH), 6.42 (s, 1 H, =CH), 5.28 (d, J = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.14 (d, J = 11.2 Hz, 1 H, one proton of $=CH_2$), 3.70 (s, 2 H, $ArCH_2CO$), 2.72 (t, J = 7.2 Hz, 2 H, CH_2), 2.63 (t, J = 7.4 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.7, 137.5, 137.1, 134.1, 133.6, 129.9, 129.4, 129.3, 128.7, 128.0, 127.0, 126.7, 115.3, 50.4, 41.1, 27.8; IR (neat, cm^{-1}): 2927, 2899, 1711, 1601, 1494, 1453, 1410, 1355, 1187, 1076, 1029, 1003; MS (70 eV, EI) *m/z* (%): 276 [M^+, 7.55], 91 (100); HRMS Calcd for $C_{20}H_{20}O$ (M^+): 276.1509; Found: 276.1511.

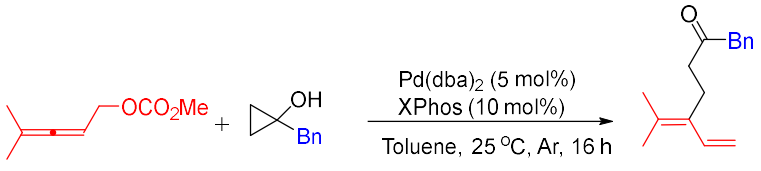
22) (*Z*)-1-phenyl-5-vinyldodec-5-en-2-one (3ga) (lj-3-112)



1g (0.2 mmol) **2a** (1.2 equiv) ***Z*-3ga**, 78%

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.6 mg, 0.02 mmol), **1g** (42.5 mg, 0.20 mmol), **2a** (35.8 mg, 0.24 mmol) and toluene (1 mL) afforded ***Z*-3ga** (44.3 mg, 78%) as an oil [eluent: petroleum ether/diethyl ether = 100/1, 1.2 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50-7.06 (m, 5 H, ArH), 6.60 (dd, J_1 = 17.6 Hz, J_2 = 11.2 Hz, 1 H, =CH), 5.33 (t, J = 7.4 Hz, 1 H, =CH), 5.11 (d, J = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.04 (d, J = 10.8 Hz, 1 H, one proton of $=CH_2$), 3.67 (s, 2 H, $ArCH_2CO$), 2.60 (t, J = 7.6 Hz, 2 H, CH_2), 2.44 (t, J = 7.4 Hz, 2 H, CH_2), 2.10 (q, J = 7.1 Hz, 2 H, CH_2), 1.50-1.18 (m, 8 H, CH_2×4), 0.88 (t, J = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.9, 134.8, 134.2, 132.3, 131.6, 129.4, 128.6, 126.9, 113.1, 50.3, 41.3, 31.6, 29.6, 28.9, 27.3, 22.5, 14.0; IR (neat, cm^{-1}): 2955, 2924, 2855, 1713, 1597, 1495, 1454, 1410, 1354, 1297, 1188, 1091, 1031; MS (70 eV, EI) *m/z* (%): 284 [M^+, 13.46], 91 (100); HRMS Calcd for $C_{20}H_{28}O$ (M^+): 284.2135; Found: 284.2139.

23) 6-Methyl-1-phenyl-5-vinylhept-5-en-2-one (3ha) (lj-2-17)

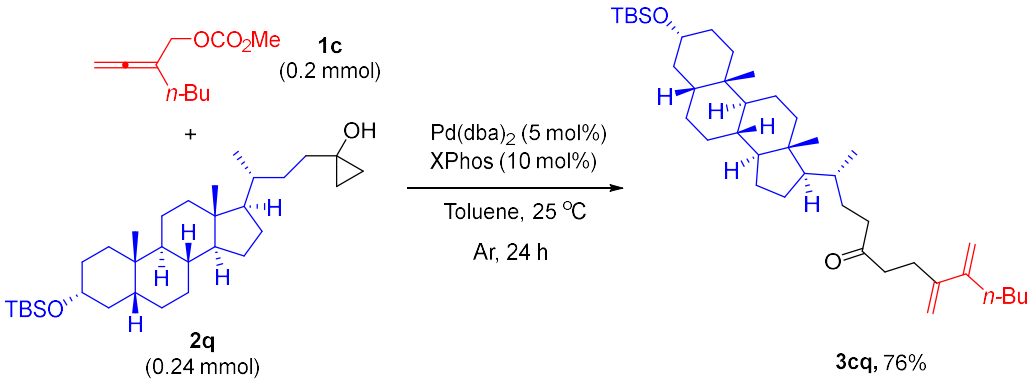


1h (0.4 mmol) **2a** (0.2 mmol) **3ha**, 33%

Following **Typical Procedure I**, the reaction of $Pd(dba)_2$ (5.8 mg, 0.01 mmol), XPhos (9.5 mg, 0.02 mmol), **1h** (62.5 mg, 0.40 mmol), **2a** (29.5 mg, 0.20 mmol) and toluene (1 mL) afforded **3ha** (15.8 mg, 33%, 94% purity) as an oil [eluent: petroleum ether/toluene = 5/1, 0.96 L, petroleum ether/toluene = 4/1, 1.0 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42-7.28 (m, 2 H, ArH), 7.28-7.23 (m, 1 H, ArH), 7.23-7.13 (m, 2 H, ArH), 6.66 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1 H, =CH), 4.97 (d, J = 17.6 Hz, 1 H, one

proton of =CH_2), 4.93 (d, J = 11.2 Hz, 1 H, one proton of =CH_2), 3.68 (s, 2 H, $ArCH_2CO$), 2.49 (s, 4 H, CH_2×2), 1.78 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.5, 134.2, 133.9, 132.6, 129.9, 129.4, 128.7, 127.0, 111.0, 50.3, 40.8, 21.9, 21.3, 20.2; IR (neat, cm^{-1}): 3086, 3062, 3028, 2979, 2922, 1710, 1632, 1602, 1495, 1454, 1409, 1358, 1254, 1203, 1188, 1146, 1077, 1030; MS (70 eV, EI) *m/z* (%): 228 [M^+, 4.32], 95 (100); HRMS Calcd for $C_{16}H_{20}O$ (M^+): 228.1514; Found: 228.1516.

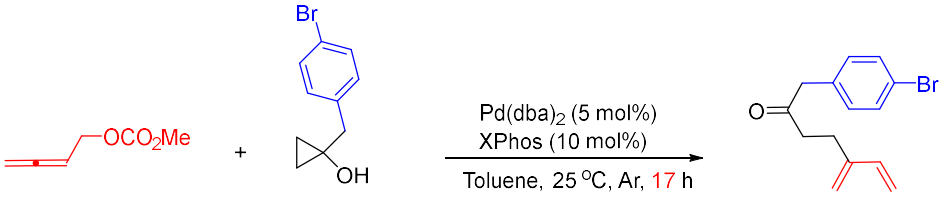
24) 3cq (lj-2-29)



To a flame-dried Schlenk tube were added XPhos (9.6 mg, 0.02 mmol), $Pd(dba)_2$ (5.8 mg, 0.01 mmol), **2q** (120.7 mg, 0.20 mmol), and **1c** (36.8 mg, 0.40 mmol)/toluene (1.0 mL) under Ar atmosphere at room temperature. The resulting mixture was stirred at 25 °C for 24 h. The crude reaction mixture was then filtrated through a short column of silica gel (height: 3 cm, *Φ*: 3.5 cm) eluted with diethyl ether (50 mL). After evaporation, the residue was purified by column chromatography on silica gel to afford **3cq** (92.8 mg, 76%) as an oil [eluent: petroleum ether/toluene = 8/1, 1.8 L, petroleum ether/toluene = 4/1, 1.0 L]: ^1H NMR (400 MHz, $CDCl_3$) δ = 5.08 (s, 1 H, one proton of =CH_2), 5.04 (s, 1 H, one proton of =CH_2), 4.95 (s, 1 H, one proton of =CH_2), 4.93 (s, 1 H, one proton of =CH_2), 3.62-3.52 (m, 1 H, OCH), 2.62-2.48 (m, 4 H), 2.46-2.37 (m, 1 H), 2.34-2.27 (m, 3 H), 2.00-0.98 (m, 32 H), 0.98-0.80 (m, 16 H), 0.62 (s, 3 H, CH_3), 0.06 (s, 6 H, CH_3×2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.2, 147.3, 146.5, 112.1, 111.7, 72.8, 56.4, 55.9, 42.7, 42.2, 41.9, 40.15, 40.10, 39.8, 36.9, 35.8, 35.5, 35.3, 34.5, 33.8, 31.0, 30.8, 29.8, 28.2, 27.3, 26.4, 25.9,

24.2, 23.4, 22.6, 20.8, 18.4, 18.3, 14.0, 12.0, -4.6; IR (neat, cm^{-1}): 3091, 2927, 2856, 1715, 1630, 1595, 1462, 1449, 1409, 1373, 1251, 1174, 1094, 1078, 1007; MS (ESI): *m/z* 611 $(M+H)^+$; HRMS Calcd for $C_{40}H_{71}O_2Si$ $(M+H)^+$: 611.5218; Found: 611.5218.

25) Gram scale reaction: 1-(4-bromophenyl)-5-methylenehept-6-en-2-one (3ae) (lj-2-12)

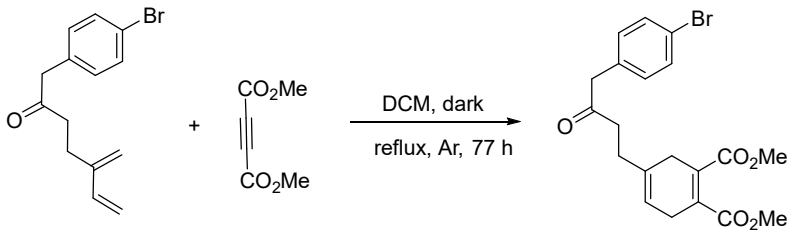


1a (10 mmol) **2e** (12 mmol) **3ae,** 1.4573 g 52% yield

To a flame-dried Schlenk tube were added $Pd(dba)_2$ (0.2877 g, 0.5 mmol) , XPhos (0.4768 g, 1.0 mmol), **1a** (1.2815 g, 10 mmol)/toluene (30 mL), **2e** (2.7256 g, 12 mmol)/toluene (10 mL), and toluene (10 mL) sequentially under Ar atmosphere at room temperature. The resulting mixture was then stirred at 25 °C for 17 h. The crude reaction mixture was filtrated through a short column of silica gel (height: 3 cm, *Φ*: 3.5 cm) eluted with diethyl ether (50 mL). After evaporation, the residue was purified by column chromatography on silica gel to afford **3ae** (1.4573 g, 52%) as an oil [eluent: petroleum ether/toluene = 4/1, 2.5 L]: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 8.4 Hz, 2 H, ArH), 7.07 (d, *J* = 8.4 Hz, 2 H, ArH), 6.34 (dd, J_1 = 17.6 Hz, J_2 = 10.4 Hz, 1 H, =CH), 5.18 (d, *J* = 17.6 Hz, 1 H, one proton of $=CH_2$), 5.07 (d, *J* = 10.4 Hz, 1 H, one proton of $=CH_2$), 5.01 (s, 1 H, one proton of $=CH_2$), 4.93 (s, 1 H, one proton of $=CH_2$), 3.65 (s, 2 H, $ArCH_2CO$), 2.66 (t, *J* = 7.6 Hz, 2 H, CH_2), 2.48 (t, *J* = 7.4 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.8, 144.7, 138.2, 133.0, 131.7, 131.1, 121.0, 116.2, 113.6, 49.3, 40.6, 25.1.

IV. Transformations of product 3ae.

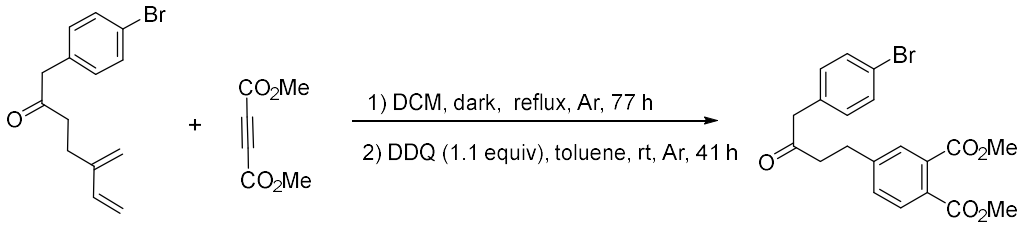
1) Intermolecular Diels-Alder reaction with 3ae and 5 (lj-2-64)



3ae (0.5 mmol) **5** (2.5 equiv) **6,** 88%

To a flame-dried Schlenk tube were added **5** (177.7 mg, 1.25 mmol), **3ae** (139.7 mg, 0.5 mmol), and DCM (2.5 mL) sequentially under Ar atmosphere. The Schlenk tube was then protected from light with an aluminum foil, then moved to a 60 ℃ oil bath to be stirred under reflux for 77 h. The reaction was allowed to cool to room temperature, transferred with 10 mL of DCM, evaporated to remove the solvent, and purified by chromatography on silica gel to afford **6** (185.4 mg, 88%) as an oil (eluent: petroleum ether/ethyl acetate = 10/1, 0.44 L; petroleum ether/ethyl acetate = 5/1, 0.96 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 8.4 Hz, 2 H, ArH), 7.07 (d, *J* = 8.4 Hz, 2 H, ArH), 5.35 (s, 1 H, =CH), 3.78 (s, 3 H, OCH_3), 3.775 (s, 3 H, OCH_3), 3.65 (s, 2 H, $ArCH_2CO$), 3.04-2.93 (m, 2 H, CH_2), 2.84 (t, *J* = 8.4 Hz, 2 H, CH_2), 2.59 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.26 (t, *J* = 7.4 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.5, 168.4, 168.1, 132.8, 132.0, 131.8, 131.1, 121.1, 117.0, 52.21, 52.19, 49.4, 39.6, 30.5, 30.0, 28.4; IR (neat, cm^{-1}): 3010, 2952, 2908, 1712, 1650, 1485, 1425, 1360, 1329, 1276, 1256, 1143, 1067, 1037, 1010; MS (ESI): *m/z* 440 $(M(Br^{81})+NH_4)^+$, 438 $(M(Br^{79})+NH_4)^+$, 423 $(M(Br^{81})+H)^+$, 421 $(M(Br^{79})+H)^+$; HRMS Calcd for $C_{20}H_{22}O_5{}^{79}Br$ $(M+H)^+$: 421.0645; Found: 421.0647.

2) Intermolecular Diels-Alder reaction with 3ae and 4 followed by oxidation with DDQ (lj-2-74)



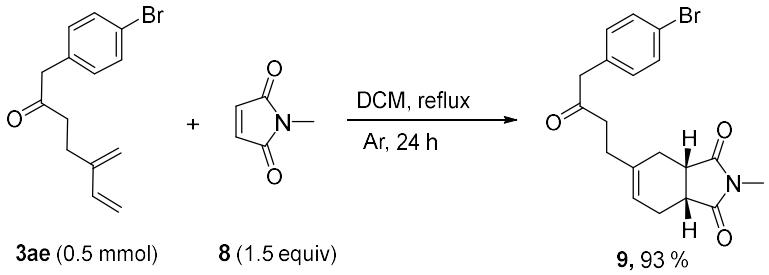
3ae (0.5 mmol) **5** (3.0 equiv) **7,** 83 %

To a flame-dried Schlenk tube were added **5** (213.2 mg, 1.5 mmol), **3ae** (140.1 mg,

0.5 mmol), and DCM (2.5 mL) sequentially under Ar atmosphere. The Schlenk tube was then protected from light with an aluminum foil and moved to a 60 ℃ oil bath to be stirred under reflux for 77 h. The reaction was allowed to cool to room temperature, transferred with 10 mL of DCM, and evaporated to remove the solvent.

The residue/toluene (5 mL) and DDQ (125.1 mg, 0.55 mmol) were added to a flame-dried Schlenk tube sequentially. The reaction was then stirred at room temperature for 41 h. After evaporation, the residue was purified by chromatography on silica gel to afford **7** (173.7 mg, 83%) (eluent: petroleum ether/ethyl acetate = 8/1, 0.96 L; petroleum ether/ethyl acetate = 5/1, 1.0 L] as white solid: m.p. = 48.8-49.5 ℃ (petroleum ether/dichloromethane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.0 Hz, 1 H, ArH), 7.48-7.38 (m, 3 H, ArH), 7.32-7.27 (m, 1 H, ArH), 7.01 (d, *J* = 8.4 Hz, 2 H, ArH), 3.90 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 3.62 (s, 2 H, $ArCH_2CO$), 2.93 (t, *J* = 7.2 Hz, 2 H, CH_2), 2.79 (t, *J* = 7.4 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.7, 168.2, 167.6, 144.7, 132.6, 132.5, 131.8, 131.0, 130.9, 129.3, 129.2, 128.5, 121.1, 52.6, 52.5, 49.3, 42.7, 29.1; IR (neat, cm^{-1}): 2954, 1713, 1609, 1569, 1487, 1438, 1414, 1365, 1289, 1249, 1194, 1127, 1070, 1011; MS (70 eV, EI) *m/z* (%): 420 [$M^+(Br^{81})$, 4.61], 418 [$M^+(Br^{79})$, 4.66], 217 (100); Anal. Calcd for $C_{20}H_{19}BrO_5$: C 57.29, H 4.57; Found: C 57.04, H 4.60.

3) Intermolecular Diels-Alder reaction with 3ae and 8 (lj-2-37)

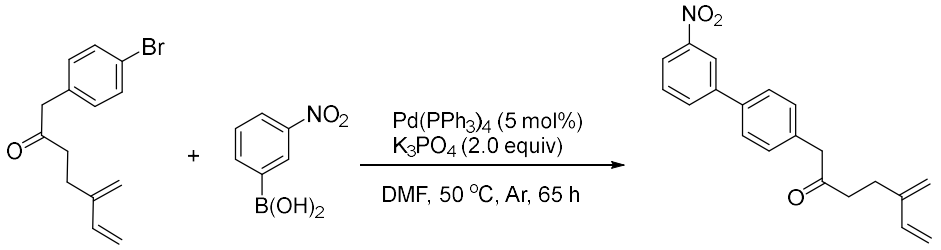


3ae (0.5 mmol) **8** (1.5 equiv) **9**, 93 %

To a flame-dried Schlenk tube were added **8** (83.4 mg, 0.75 mmol), **3ae** (139.6 mg, 0.5 mmol), and DCM (2.5 mL) sequentially under Ar atmosphere. The Schlenk tube was then moved to a 60 ºC oil bath and stirred for 24 h. The resulting mixture was allowed to cool to room temperature, transferred with 5 mL DCM, evaporated to remove the solvent, and purified by chromatography on silica gel to afford **9** (181.1

mg, 93%) as an oil (eluent: petroleum ether/ethyl acetate = 4/1, 0.5 L; petroleum ether/ethyl acetate = 3/1, 0.4 L; petroleum ether/ethyl acetate = 2/1, 0.3 L]. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 8.0 Hz, 2 H, ArH), 7.06 (d, *J* = 8.4 Hz, 2 H, ArH), 5.54-5.40 (m, 1 H, =CH), 3.63 (s, 2 H, $ArCH_2CO$), 3.14-2.98 (m, 2 H, CH_2), 2.90 (s, 3 H, CH_3), 2.63-2.37 (m, 4 H, CH_2×2), 2.30-2.07 (m, 4 H, CH_2×2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.3, 180.1, 180.0, 138.7, 132.9, 131.7, 131.1, 121.0, 120.7, 49.2, 39.6, 39.5, 39.1, 30.5, 27.1, 24.9, 24.1; IR (neat, cm^{-1}): 2945, 2898, 2847, 1774, 1689, 1487, 1432, 1382, 1315, 1282, 1192, 1118, 1069, 1044, 1010; MS (70 eV, EI) *m/z* (%): 391 [M^+ (Br^{81}), 10.88], 389 [M^+ (Br^{79}), 11.08], 220 (100); HRMS Calcd for $C_{19}H_{20}{}^{79}BrNO_3$ (M^+): 389.0627; Found: 389.0631.

4) Suzuki coupling reaction with 3ae and 10 (lj-2-70)



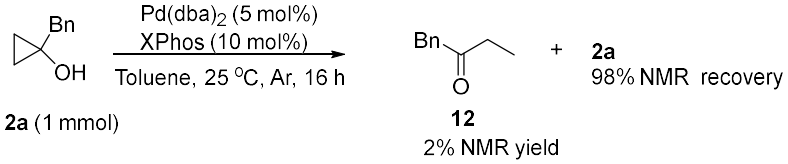
3ae (0.2 mmol) **10** (3 equiv) **11**, 71 %

To a flame-dried Schlenk tube were added $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol), K_3PO_4 (85.1 mg, 0.4 mmol), **10** (100.5 mg, 0.6 mmol), **3ae** (55.9 mg, 0.2 mmol), and DMF (2.0 mL) sequentially under Ar atmosphere at room temperature. The resulting mixture was then stirred at 50 °C for 65 h，cooled to room temperature, and diluted with ethyl acetate (4 mL), water (15 mL), and ethyl acetate (15 mL). The organic phase was separated, and aqueous phase was extracted with ethyl acetate (15 mL × 3). The organic phase was combined and washed with a saturated solution of NaCl (aq) (15 mL × 3), dried over anhydrous Na_2SO_4, filtrated through a short column of silica gel (height: 1 cm, *Φ*: 3.5 cm) eluted with ethyl acetate (50 mL), evaporated, and purified by chromatography on silica gel to afford **11** (45.7 mg, 71%) as an oil (eluent: petroleum ether/ethyl acetate = 40/1, 0.82 L; petroleum ether/ethyl acetate = 25/1, 0.83 L]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.43 (t, *J* = 2.0 Hz, 1 H, ArH), 8.26-8.18 (m,

1 H, ArH), 7.95-7.86 (m, 1 H, ArH), 7.68-7.54 (m, 3 H, ArH), 7.33 (d, J = 8.4 Hz, 2 H, ArH), 6.35 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1 H, =CH), 5.20 (d, J = 18.0 Hz, 1 H, one proton of $=CH_2$), 5.07 (d, J = 10.8 Hz, 1 H, one proton of $=CH_2$), 5.02 (s, 1 H, one proton of $=CH_2$), 4.96 (s, 1 H, one proton of $=CH_2$), 3.78 (s, 2 H, $ArCH_2CO$), 2.78-2.66 (m, 2 H, CH_2), 2.52 (t, J = 7.4 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.1, 148.7, 144.8, 142.3, 138.3, 137.3, 134.6, 132.9, 130.2, 129.7, 127.4, 122.0, 121.7, 116.2, 113.6, 49.6, 40.7, 25.2; IR (neat, cm^{-1}): 3078, 2898, 1710, 1598, 1528, 1515, 1475, 1440, 1412, 1345, 1303, 1263, 1234, 1213, 1112, 1083, 1047, 1017; MS (70 eV, EI) *m/z* (%): 321 [M^+, 16.36], 212 (100); HRMS Calcd for $C_{20}H_{19}NO_3$ (M^+): 321.1359; Found: 321.1360.

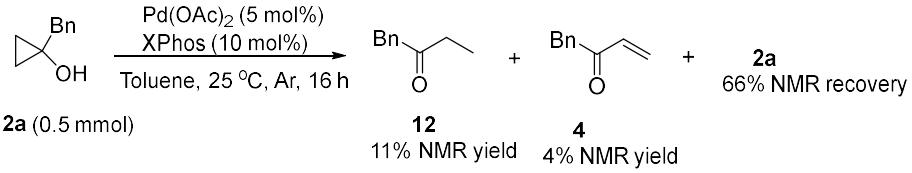
V. Mechanistic studies

1) Reaction of 2a under standard conditions (lj-2-20)



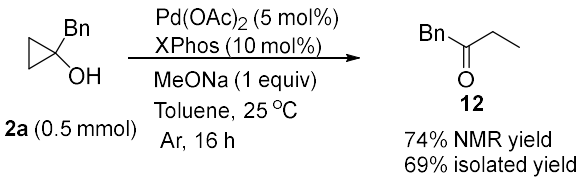
To a flame-dried Schlenk tube were added $Pd(dba)_2$ (28.8 mg, 0.05 mmol) and XPhos (47.6 mg, 0.10 mmol) under Ar atmosphere. A solution of **2a** (148.6 mg, 1.0 mmol) in toluene (2.0 mL) and toluene (3.0 mL) were added under Ar atmosphere at room temperature. The resulting mixture was stirred at 25 °C for 16 h and filtrated through a short column of silica gel eluted with diethyl ether (50 mL). After evaporation, the residue was analyzed with ^1H NMR measurement in $CDCl_3$ with mesitylene (46 uL, d = 0.864 g/mL, 39.7 mg) as the internal standard: the recovery of **2a**[2a] and NMR yield of compound **12**[3a,3b] were determined to be 98% and 2%, respectively.

2) Using $Pd(OAc)_2$ as catalyst for the reaction with cyclopropanol 2a (lj-2-97)



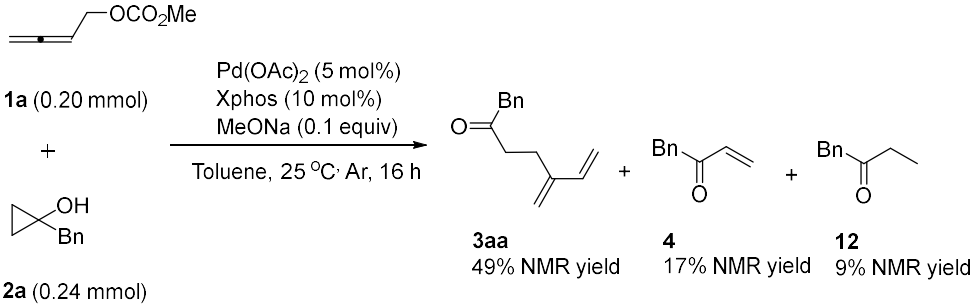
To a flame-dried Schlenk tube were added $Pd(OAc)_2$ (5.7 mg, 0.025 mmol) and XPhos (23.8 mg, 0.05 mmol) under Ar atmosphere. A solution of **2a** (74.1 mg, 0.5 mmol) in toluene (2.5 mL) was added under Ar atmosphere at room temperature. The resulting mixture was stirred at 25 °C for 16 h and filtrated through a short column of silica gel eluted with diethyl ether (50 mL). After evaporation, the residue was analyzed with NMR spectrum in $CDCl_3$ with mesitylene (46 uL, d = 0.864 g/mL, 39.7 mg) as the internal standard-the recovery of **2a**,[2a] NMR yield of compound **12**,[3a,3b] and NMR yield of compound **4**[3a,3c] were determined to be 66%, 11%, and 4%, respectively.

3) Using $Pd(OAc)_2$ as catalyst for the reaction of cyclopropanol 2a in the presence of MeONa (lj-2-98)



To a flame-dried Schlenk tube were added $Pd(OAc)_2$ (5.7 mg, 0.025 mmol), XPhos (23.8 mg, 0.05 mmol), and MeONa (27.1 mg, 0.5 mmol) under Ar atmosphere. A solution of **2a** (74.1 mg, 0.5 mmol) in toluene (2.5 mL) was added under Ar atmosphere at room temperature. The resulting mixture was stirred at 25 °C for 16 h and filtrated through a short column of silica gel eluted with diethyl ether (50 mL). After evaporation, the residue was analyzed with NMR measurement in $CDCl_3$ with mesitylene (46 uL, d = 0.864 g/mL, 39.7 mg) as the internal standard-the NMR yield of compound **12**[3a,3b] was determined to be 74%. Then the residue was purified by chromatography on silica gel to afford **12**[3a,3b] (50.3 mg, 69%) as an oil (eluent: petroleum ether/diethyl ether = 80/1, 1.2 L]. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.14 (m, 5 H, ArH), 3.67 (s, 2 H, CH_2), 2.46 (q, *J* = 7.3 Hz, 2 H, CH_2), 1.02 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.9, 134.4, 129.3, 128.6, 126.9, 49.7, 35.1, 7.7.

4) Using $Pd(OAc)_2$ as catalyst for the reaction of 1a and 2a in the presence of NaOMe (lj-3-94)



To a flame-dried Schlenk tube were added $Pd(OAc)_2$ (2.5 mg, 0.01 mmol) and XPhos (9.6 mg, 0.02 mmol), MeONa (2.2 mg, 0.02 mmol), **1a** (25.7 mg, 0.20 mmol)/toluene (0.5 mL), and **2a** (35.8 mg, 0.24 mmol)/toluene (0.5 mL) sequentially under Ar atmosphere at room temperature. The resulting mixture was stirred at 25 °C for 16 h and filtrated through a short column of silica gel eluted with diethyl ether (50 mL). After evaporation, the residue was analyzed with NMR spectrum in $CDCl_3$ with mesitylene (46 uL, d = 0.864 g/mL, 39.7 mg) as the internal standard-the NMR yield of compound **3aa,** NMR yield of compound **12**,[3a,3b] and NMR yield of compound **4**[3a,3c] were determined to be 49%, 17%, and 9%, respectively.

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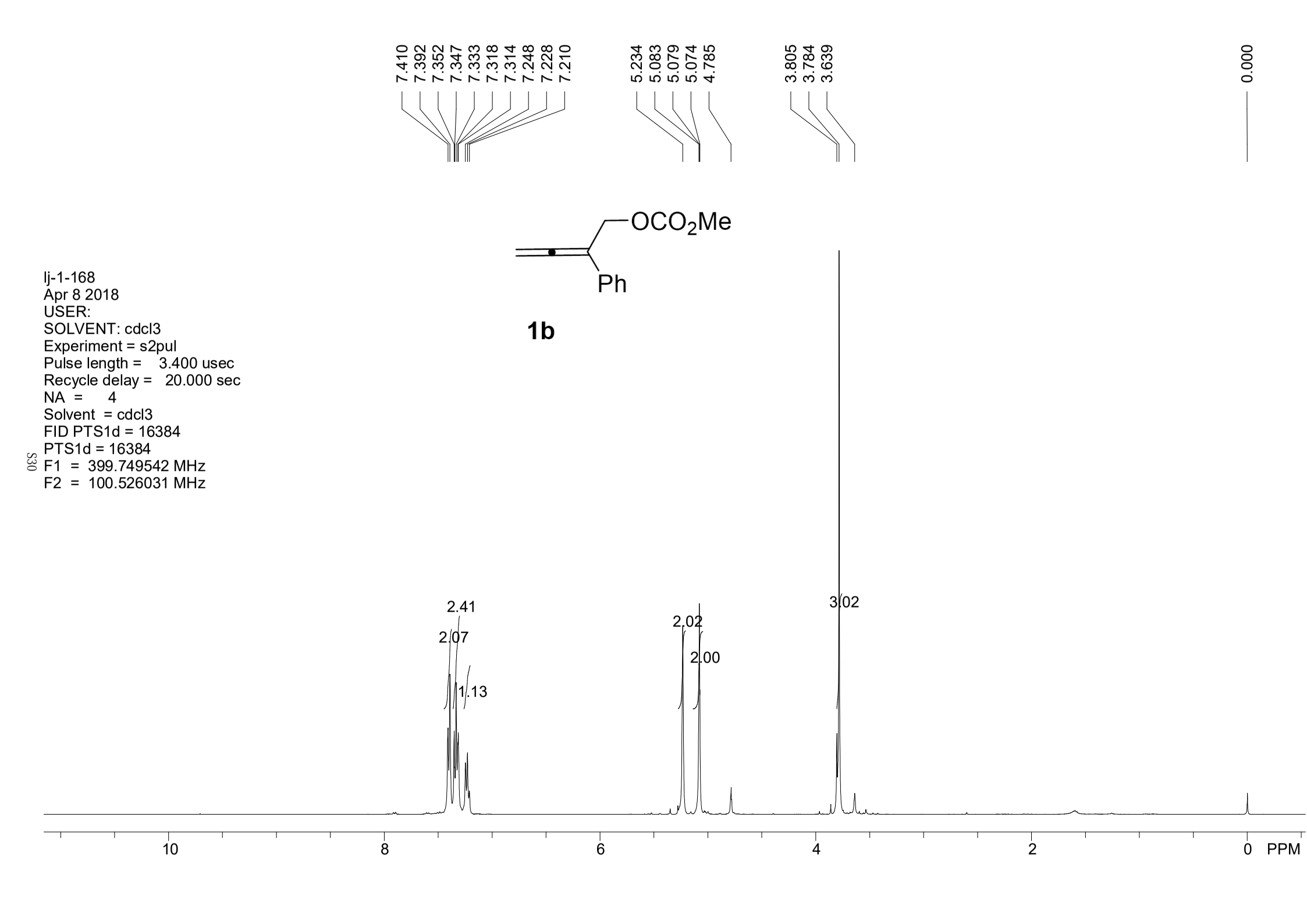
1. a) T. Zhu and S. Ma, *Chem. Commun.,* 2017, **53**, 6037; b) H. Wang, B. Beiring, D.-G. Yu, K. D. Collins and F. Glorius, *Angew. Chem. Int. Ed*., 2013, **52**, 12430; c) S. Song, J. Zhou, C. Fu and S. Ma, *Nat. Common.,* 2019, 10, 597; d) K. Semba, T. Fujihara, J. Terao and Y. Tsuji, *Angew. Chem. Int. Ed.,* 2013, **52**, 12400.
2. a) X. Zhou, S. Yu, L. Kong and X. Li, *ACS Catal.,* 2016, **6**, 647; b) H. Zhao, X. Fan, J. Yu and C. Zhu, *J. Am. Chem. Soc.,* 2015, **137**, 3490; c) K. Jia, F. Zhang , H. Huang and Y. Chen, *J. Am. Chem. Soc.,* 2016, **138**, 1514; d) S. Ren, C. Feng and T. P. Loh, *Org. Biomol. Chem.*, 2015, **13**, 5105; e) X.-P. He, Y.-J. Shu, J.-J. Dai, W.-M. Zhang, Y.-S. Feng and H.-J. Xu, *Org. Biomol. Chem.*, 2015, **13**, 7159; f) Z. Ye, X.

Cai, J. Li and M. Dai, *ACS Catal.,* 2018, **8**, 5907; g) K. N. Prokhorevich and O. G. Kulinkovich, *Tetrahedron Asymmetry*, 2006, **17**, 2976; h) S. Fukuzawa, Y. Miimoto and S. Sakai. *Tetrahedron Lett.,* 1991, **32**, 7691; i) A. M. Martinez, G. E. Cushmac and J. Rocek, *J. Am. Chem. Soc.,* 1975, 6502; j) Łukasz . Woz´niak, G. Magagnano and P. Melchiorre, *Angew. Chem. Int. Ed.,* **2018**, *57*, 1068.

3. a) P. Wu, M. Jia, W. Lin and S. Ma, *Org. Lett.,* 2018, **20**, 554; b) J. R. Lamb, M. Mulzer, A. M. LaPointe and G. W. Coates, *J. Am. Chem. Soc.,* 2015, **137**, 15049; c) S. Chanthamath, S. Takaki, K. Shibatomi and S. Iwasa, *Angew. Chem. Int. Ed.,* **2013**, *52*, 5818.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7.210
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5.079
5.074
4.785
3.805
3.784
3.639
0.000
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Ph
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2.02
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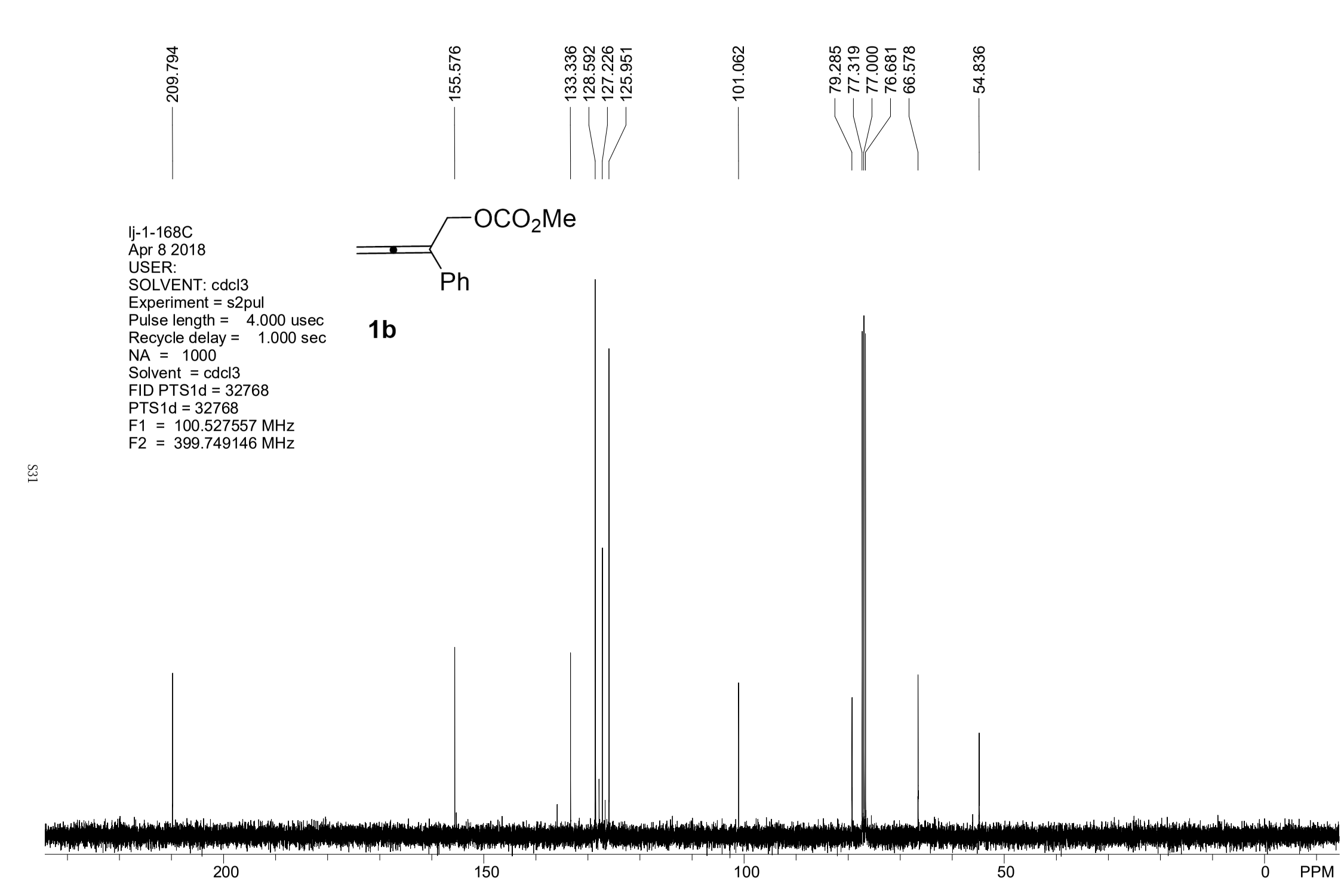
3.02
10
8
6
4
2
0
PPM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OCO2Me
Ph
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lj-1-168C
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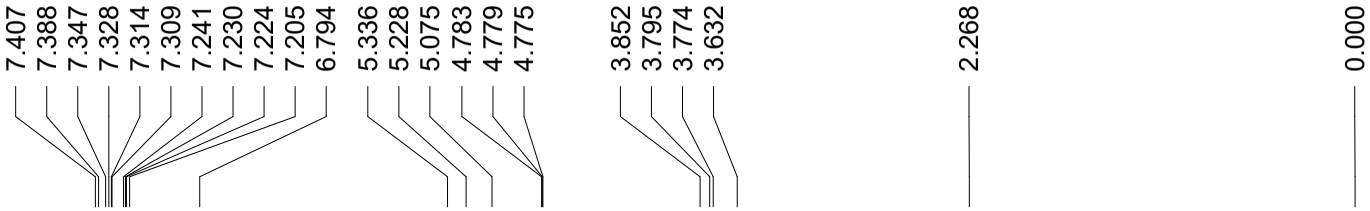

Purity was determined to be 96% by using 8 mg mesitylene as the internal standard in 60.5 mg sample.

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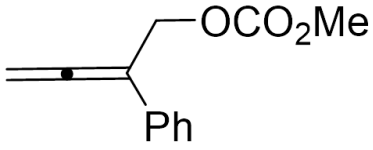
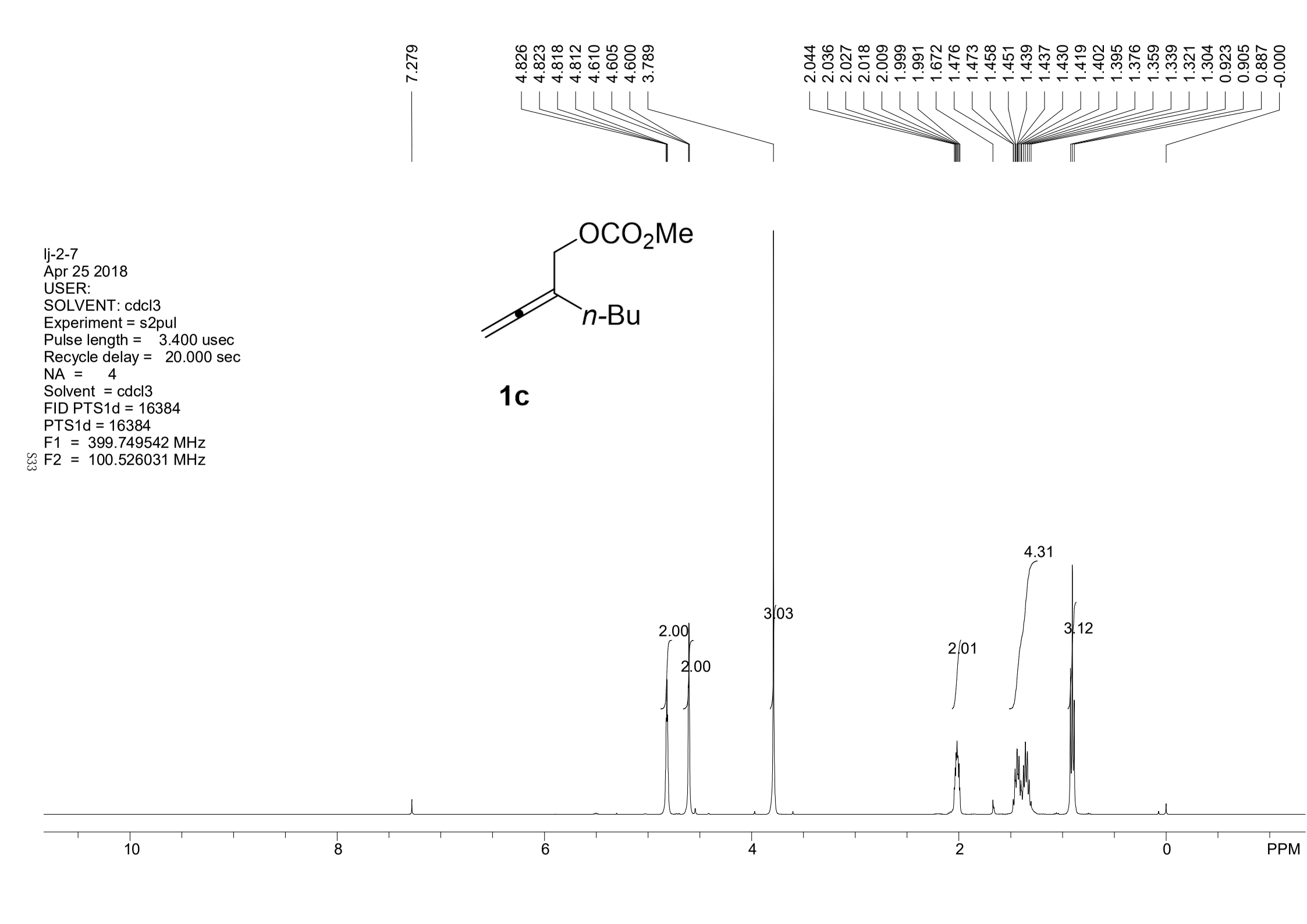


1b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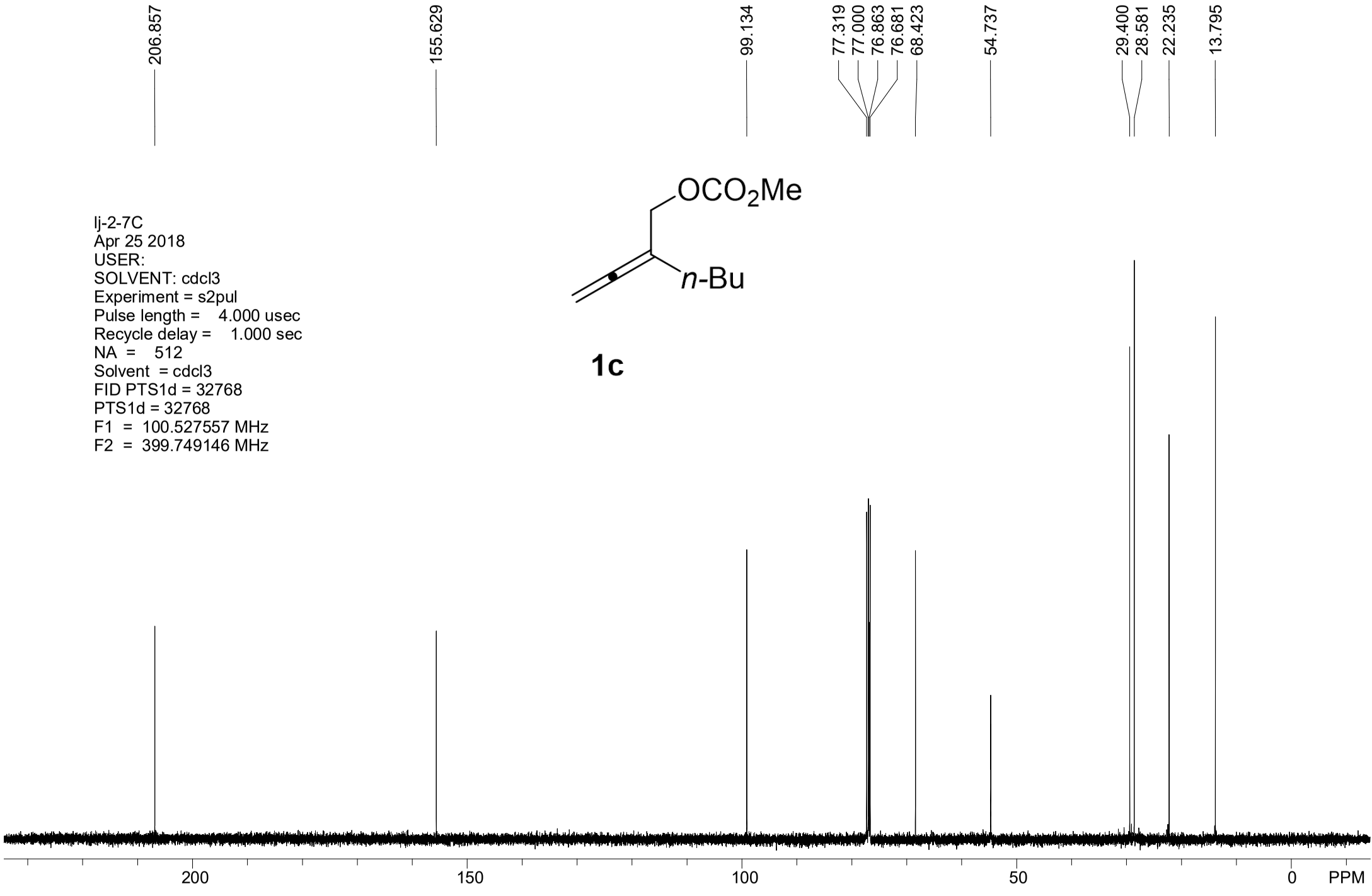
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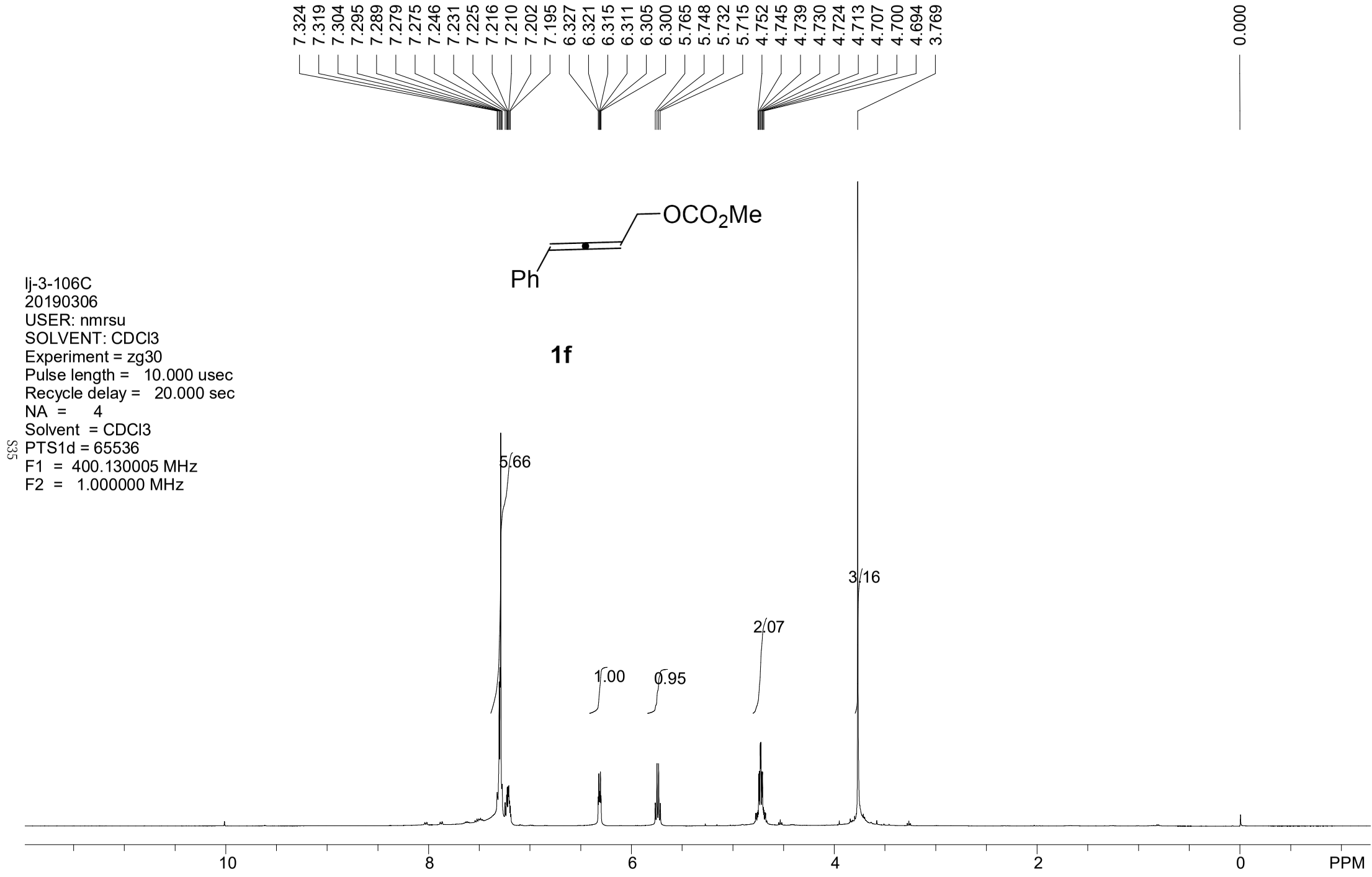
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6.321
6.315
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6.305
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5.715
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Ph
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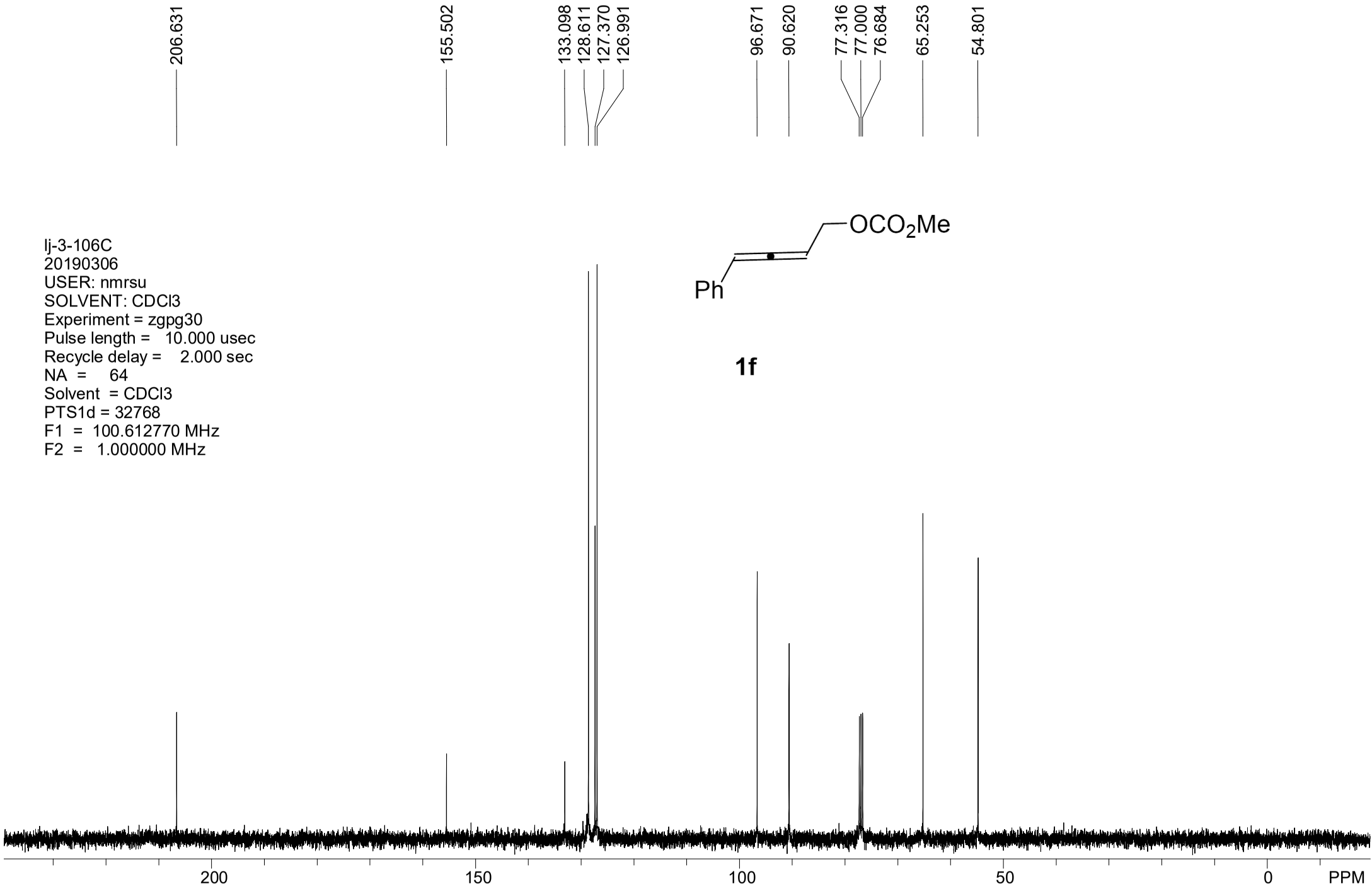
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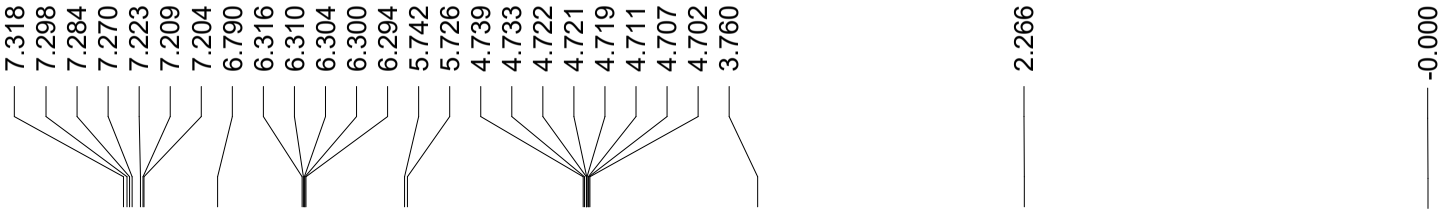
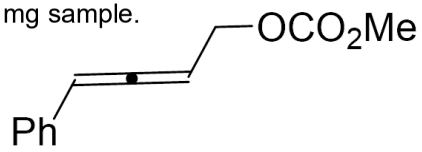


Purity was determined to be 94% by using 10.2 mg mesitylene as the internal standard in 40.9 mg sample.



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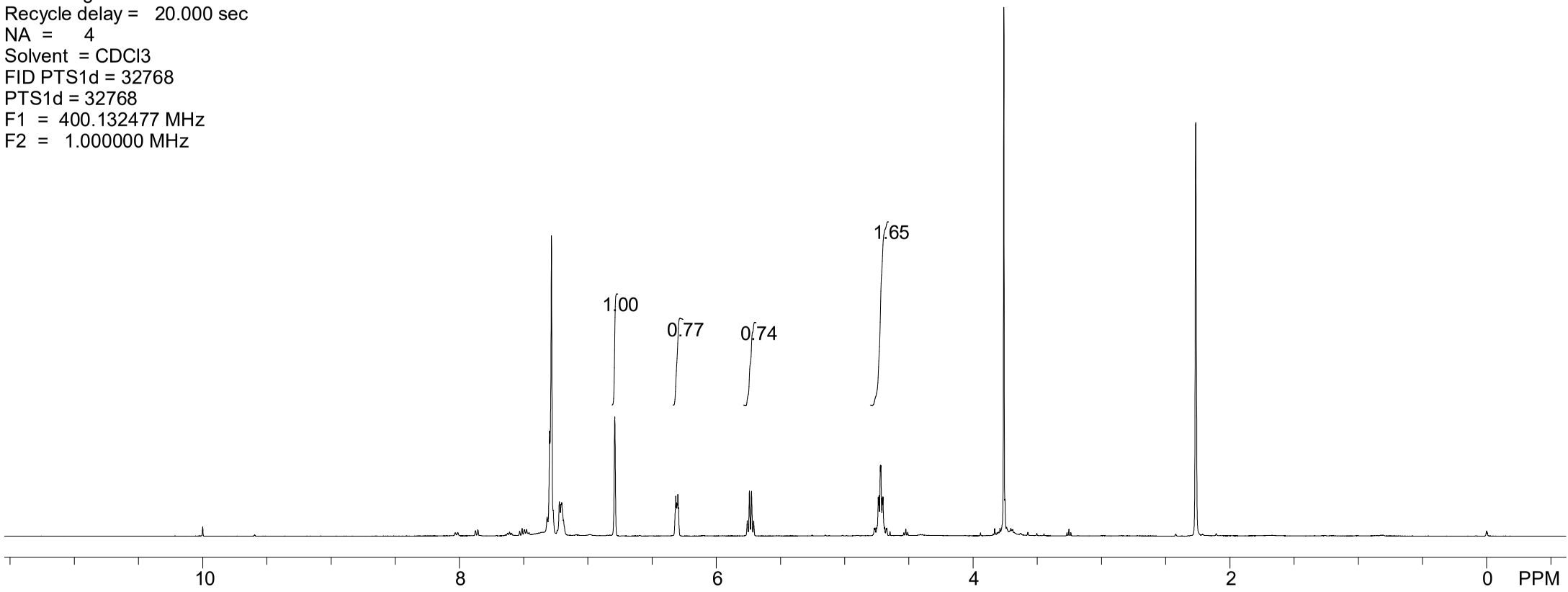

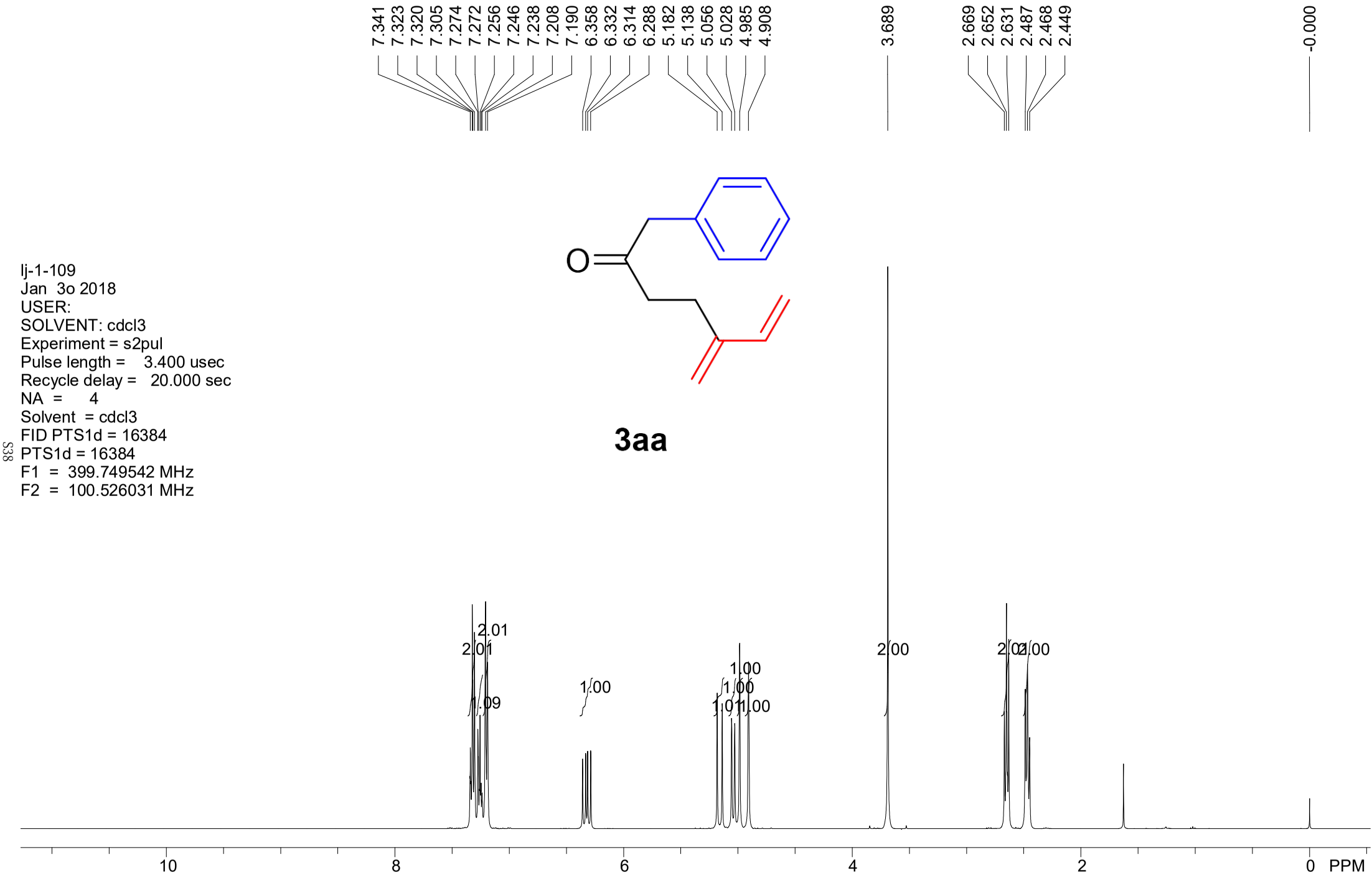
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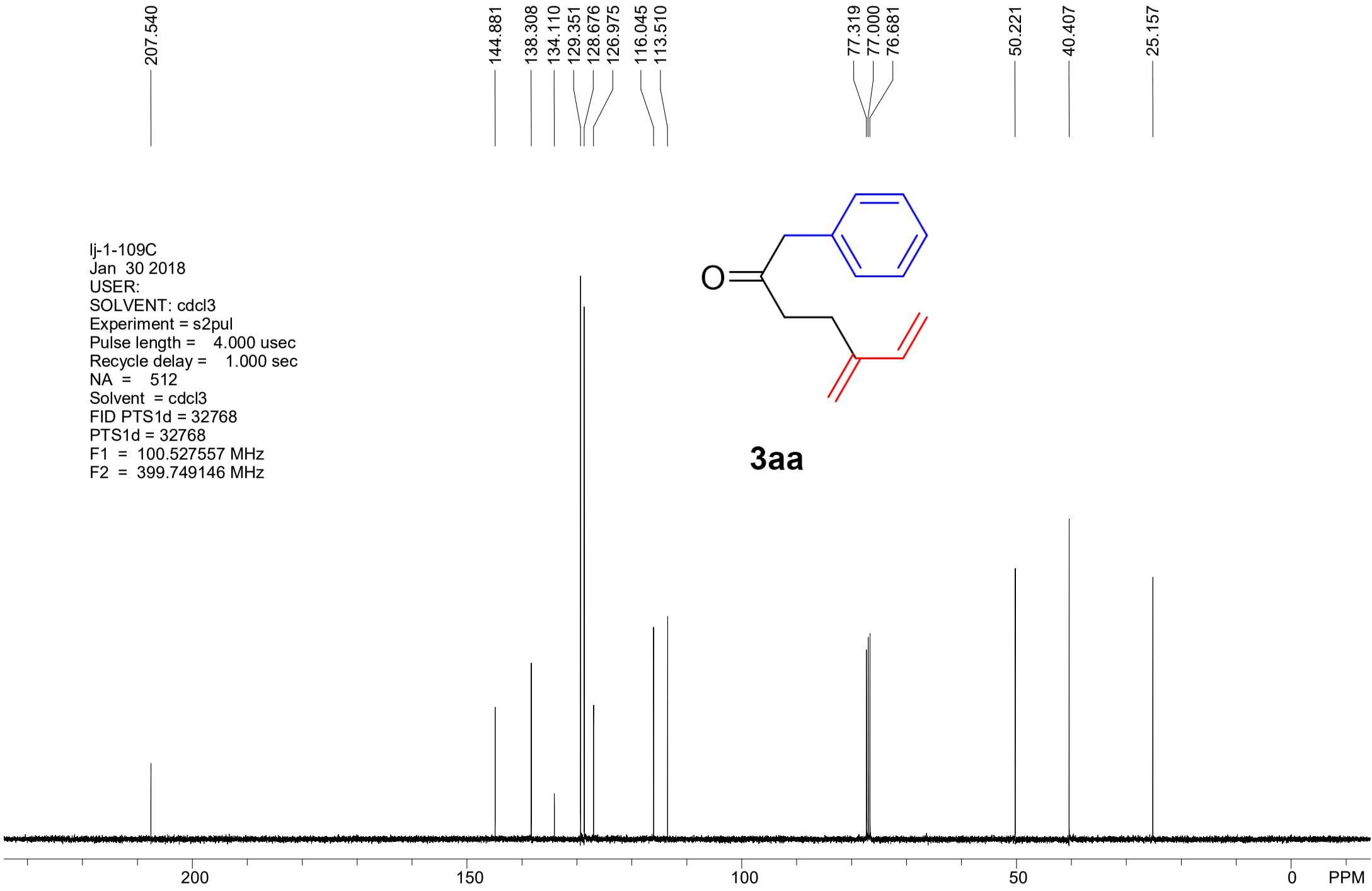
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lj-1-109C
Jan 30 2018
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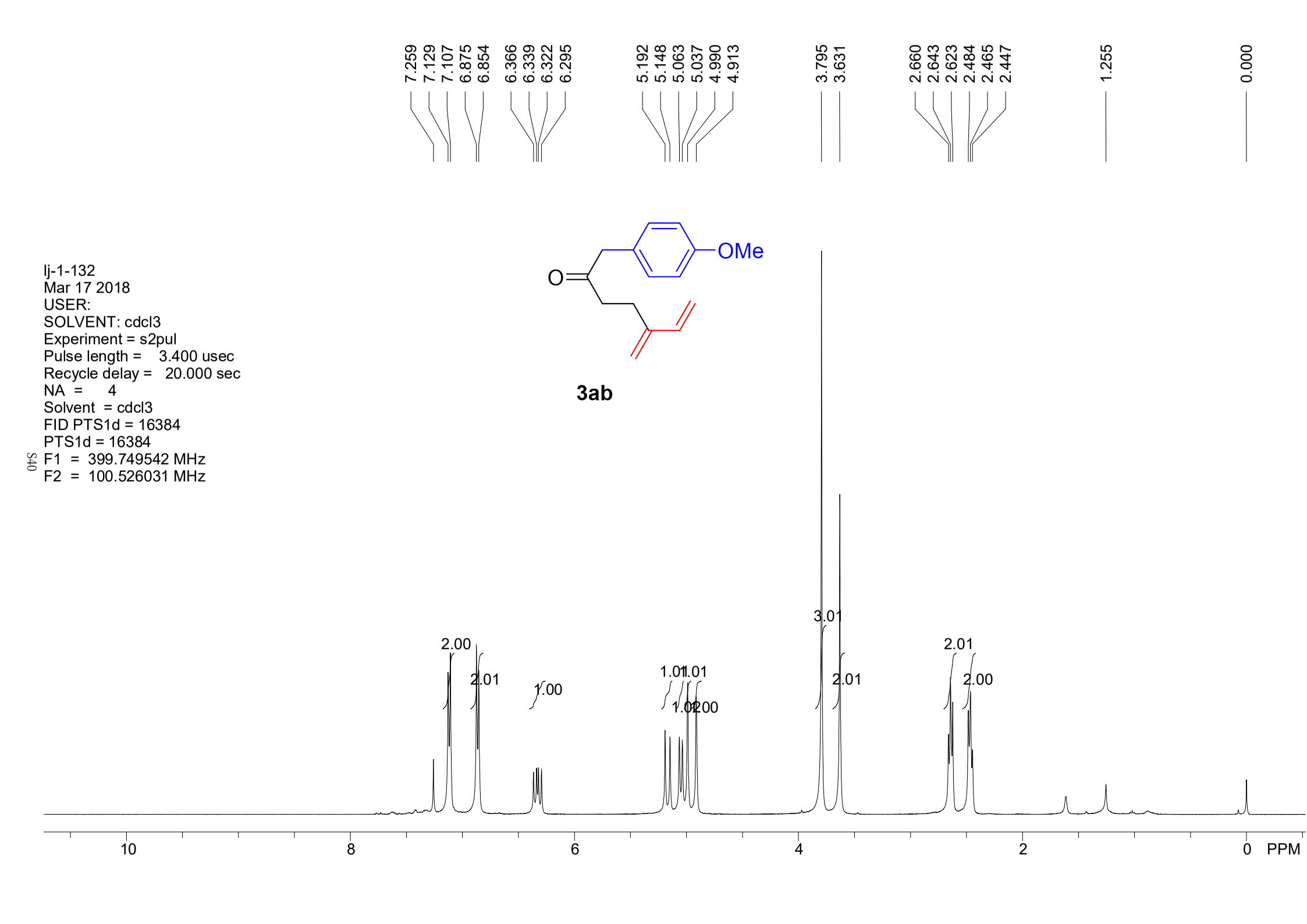
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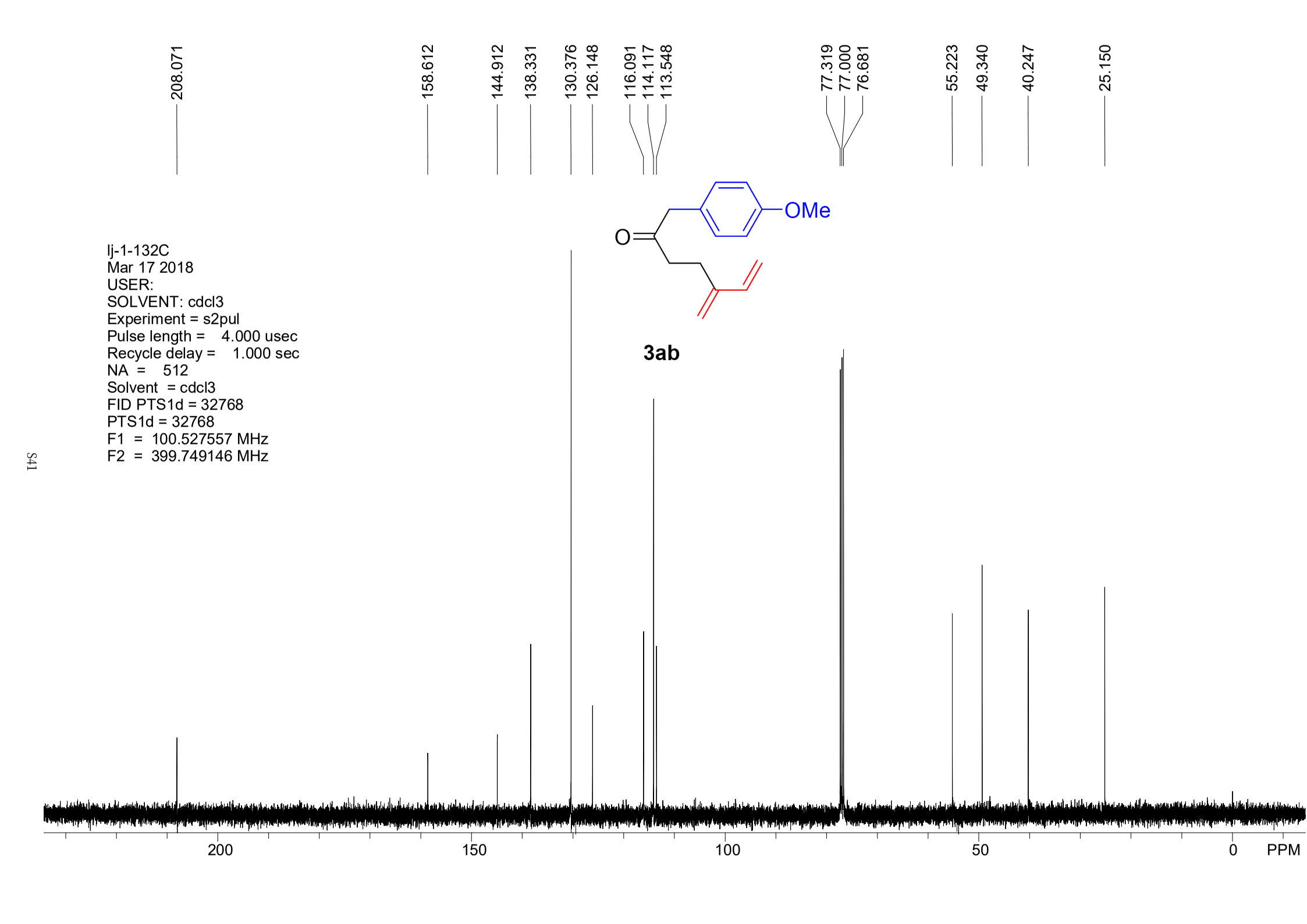
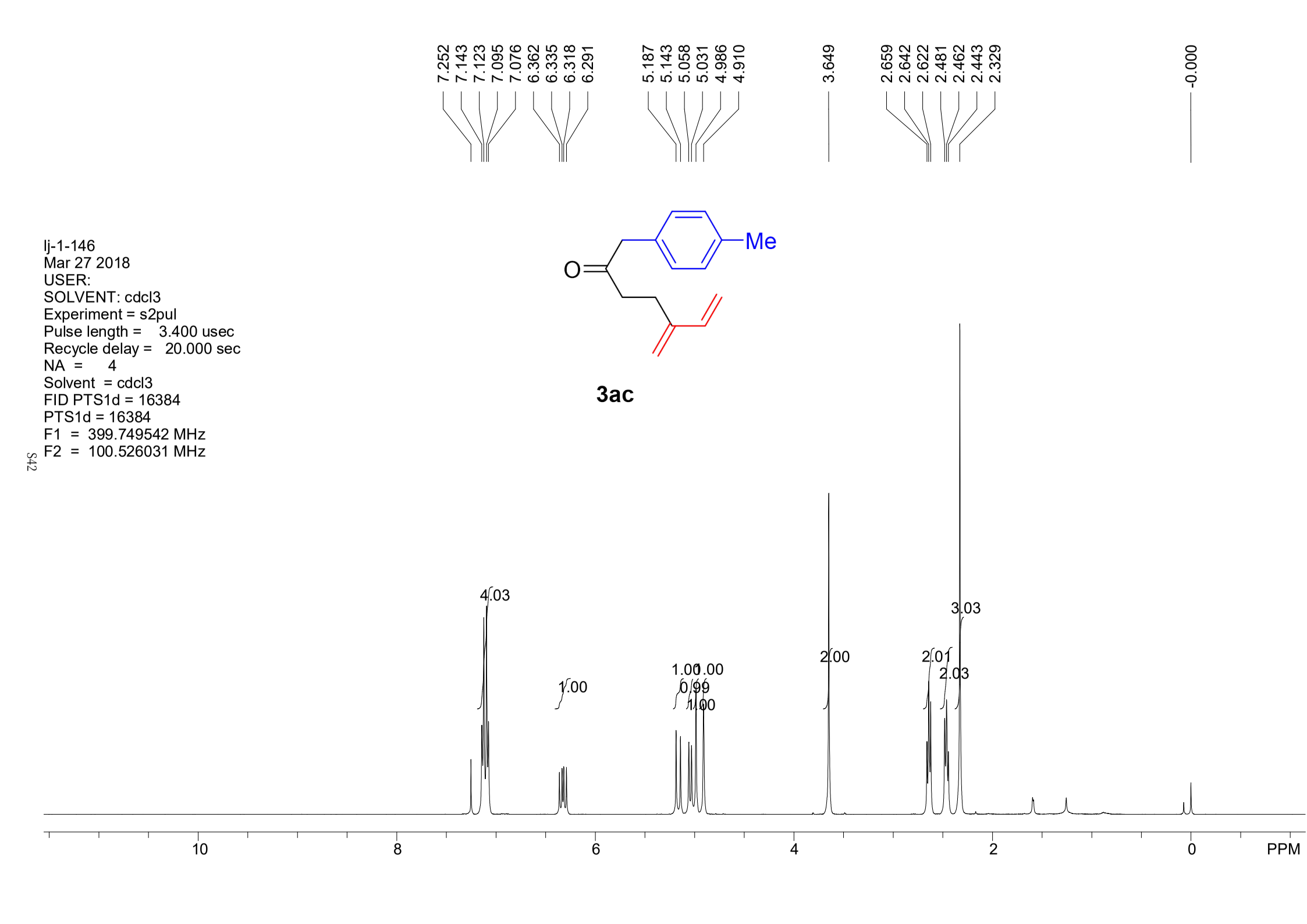
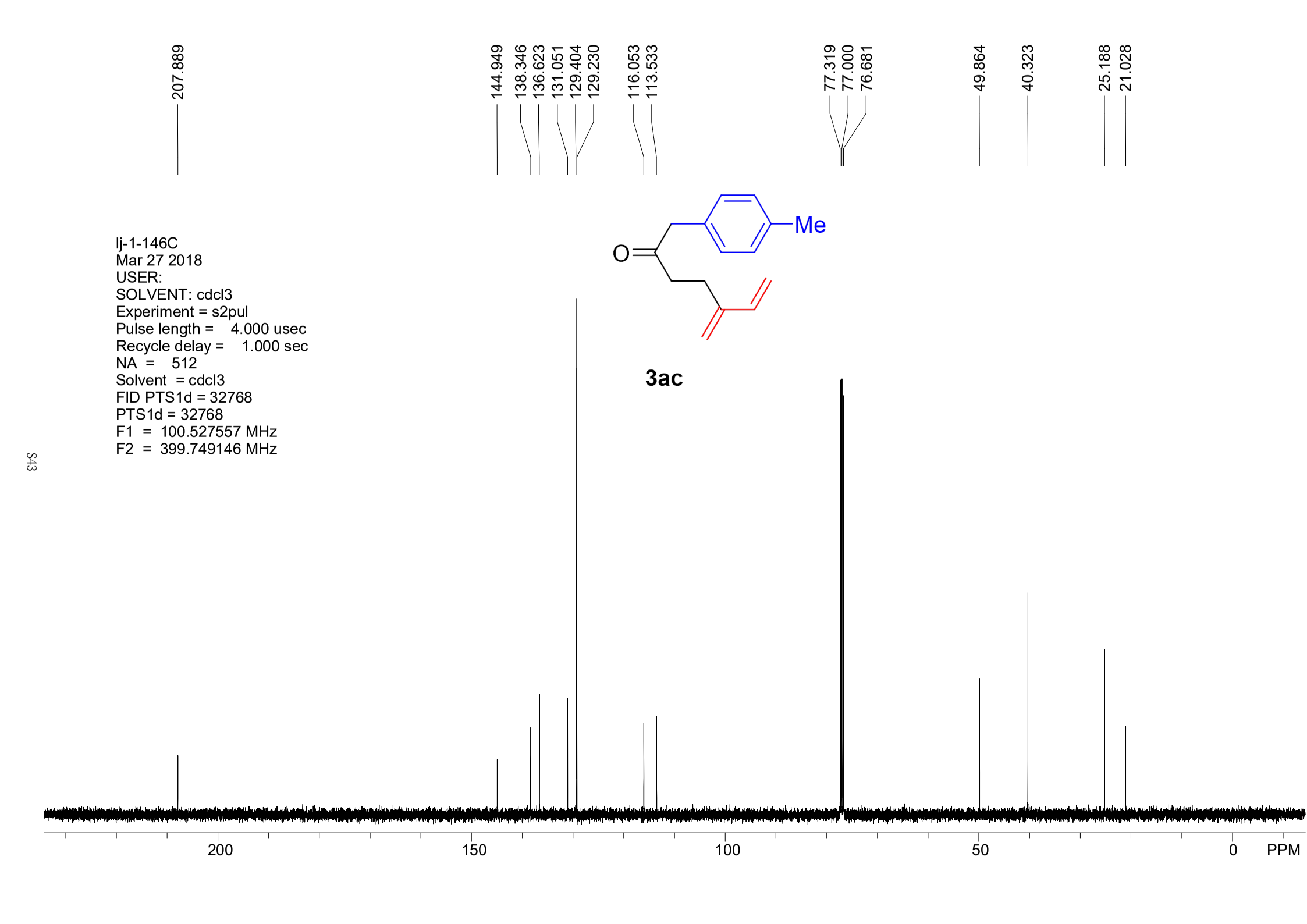
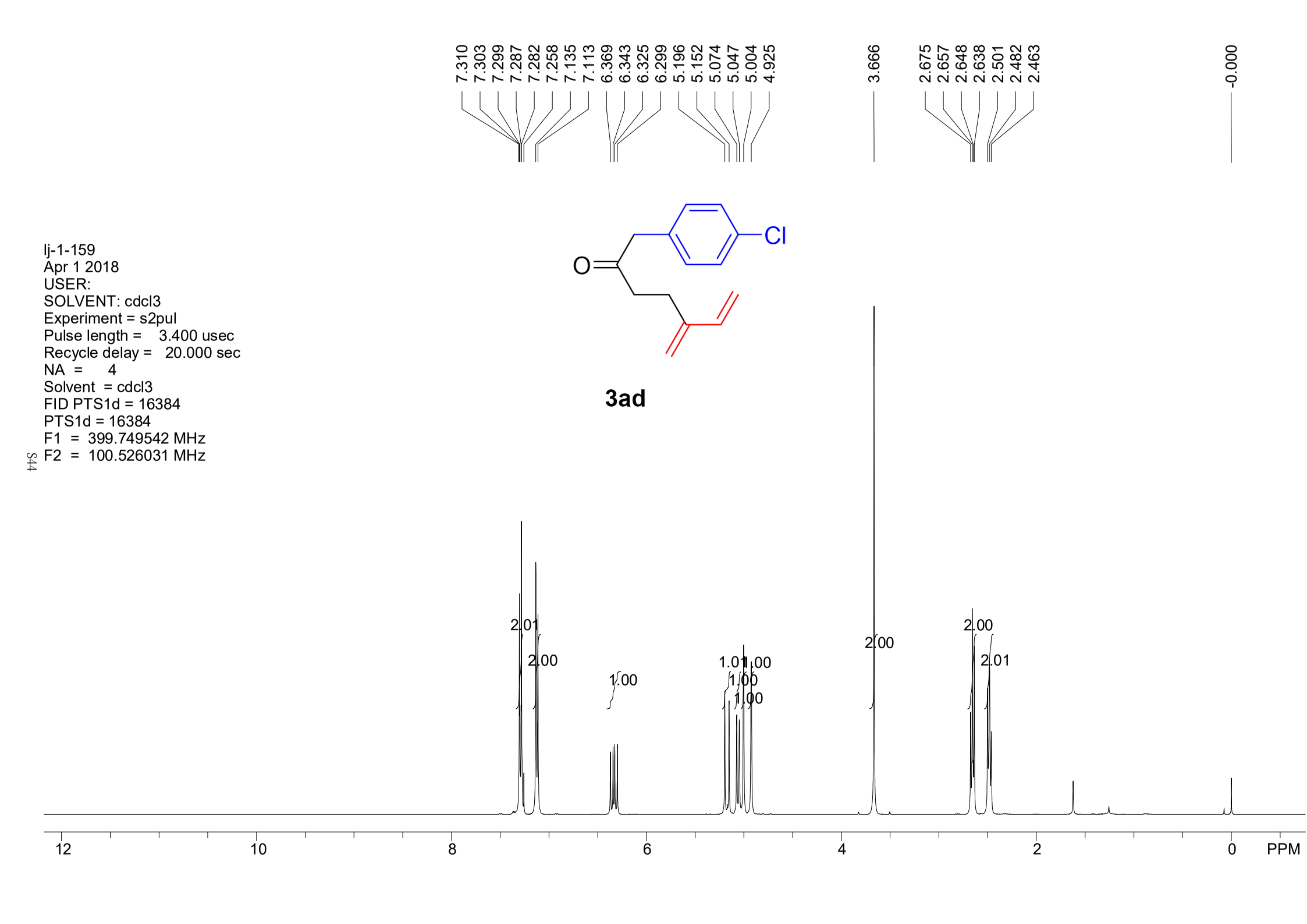
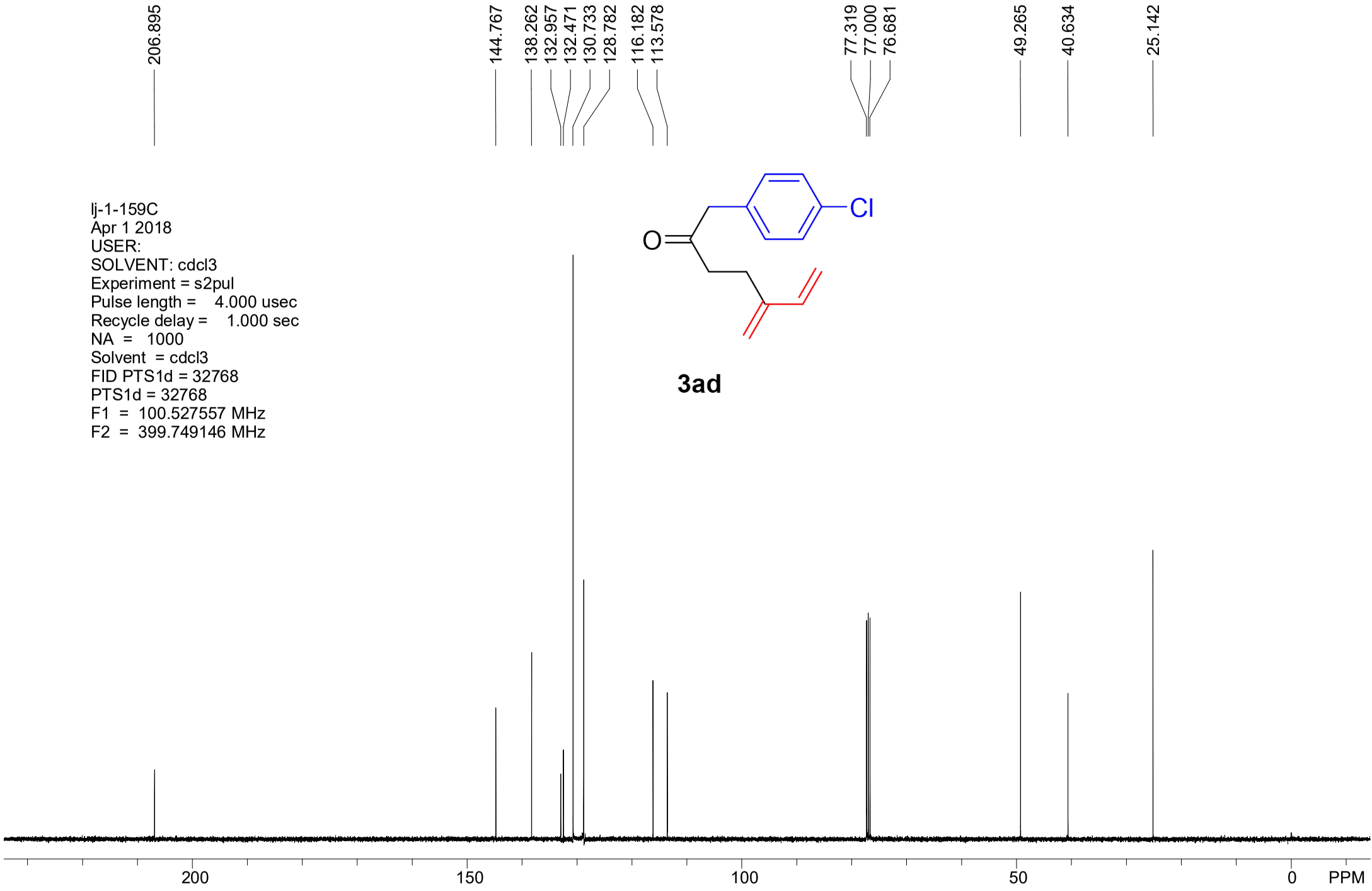
6.854
6.366
6.339
6.322
6.295
5.192
5.148
5.063
5.037
4.990
4.913
3.795
3.631
2.660
2.643
2.623
2.484
2.465
2.447
1.255
0.000
OMe
O
3ab
lj-1-132
Mar 17 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
2.00
2.01
1.00
1.01
1.01
1.02
2.00
3.01
2.01
2.01
2.00
10
8
6
4
2
0
PPM

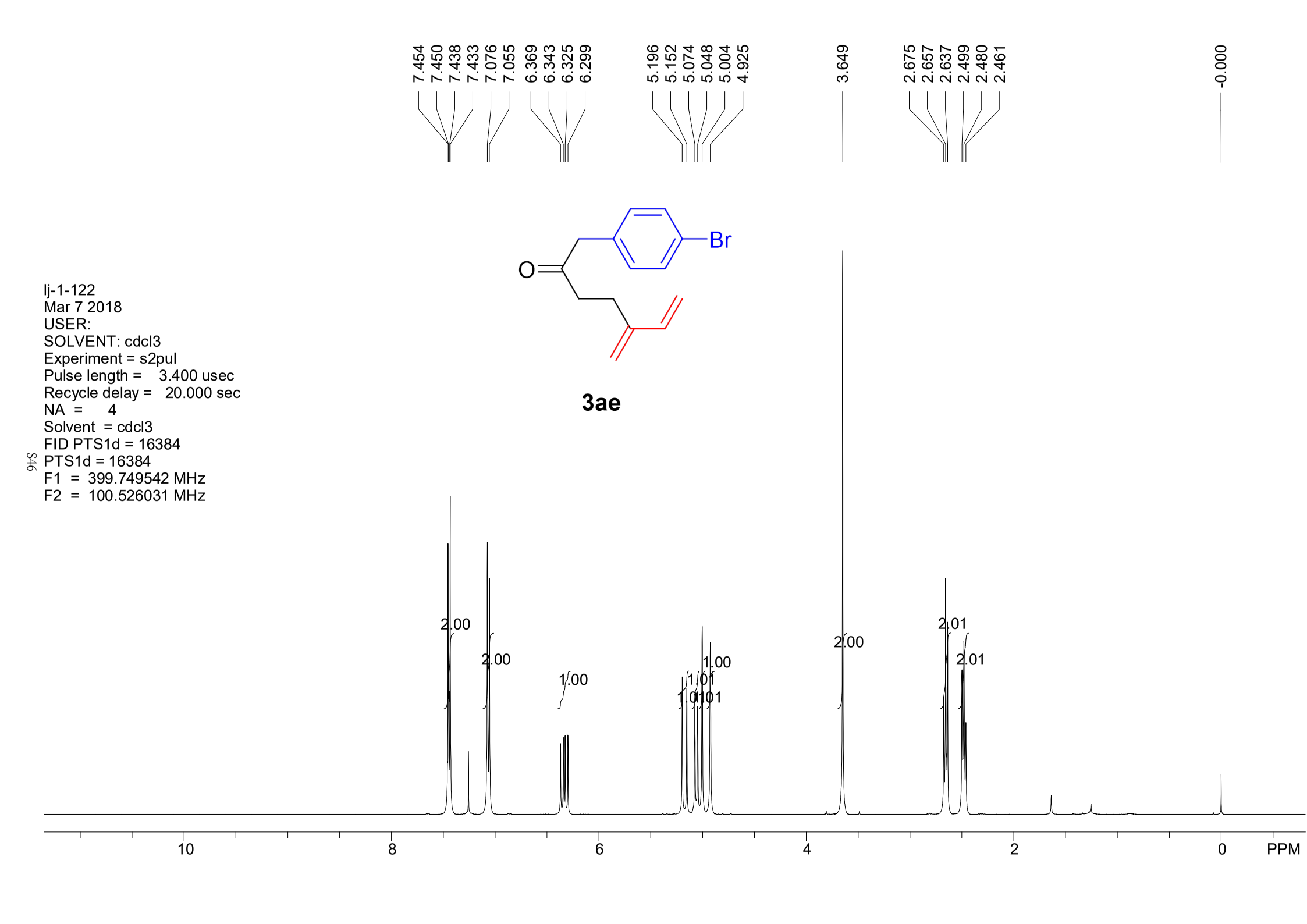

208.071
158.612
144.912
138.331
130.376
126.148
116.091
114.117
113.548
77.319
77.000
76.681
55.223
49.340
40.247
25.150
OMe
O
lj-1-132C
Mar 17 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 512
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
3ab
200
150
100
50
0
PPM

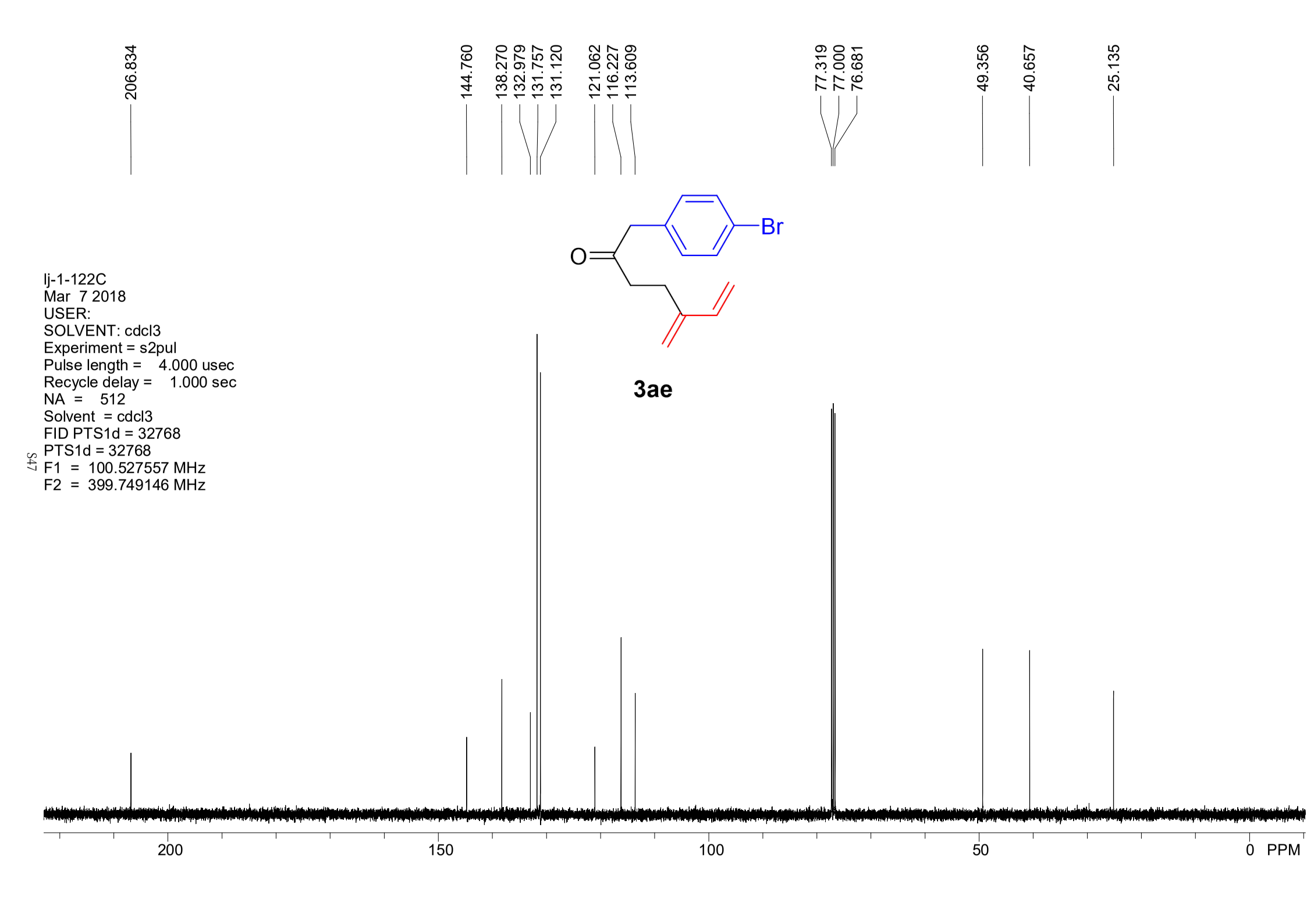

7.252
7.143
7.123
7.095
7.076
6.362
6.335
6.318
6.291
5.187
5.143
5.058
5.031
4.986
4.910
3.649
2.659
2.642
2.622
2.481
2.462
2.443
2.329
-0.000
lj-1-146
Mar 27 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
O
Me
3ac
4.03
1.00
1.00
0.99
1.00
2.00
2.01
2.03
3.03
10
8
6
4
2
0
PPM

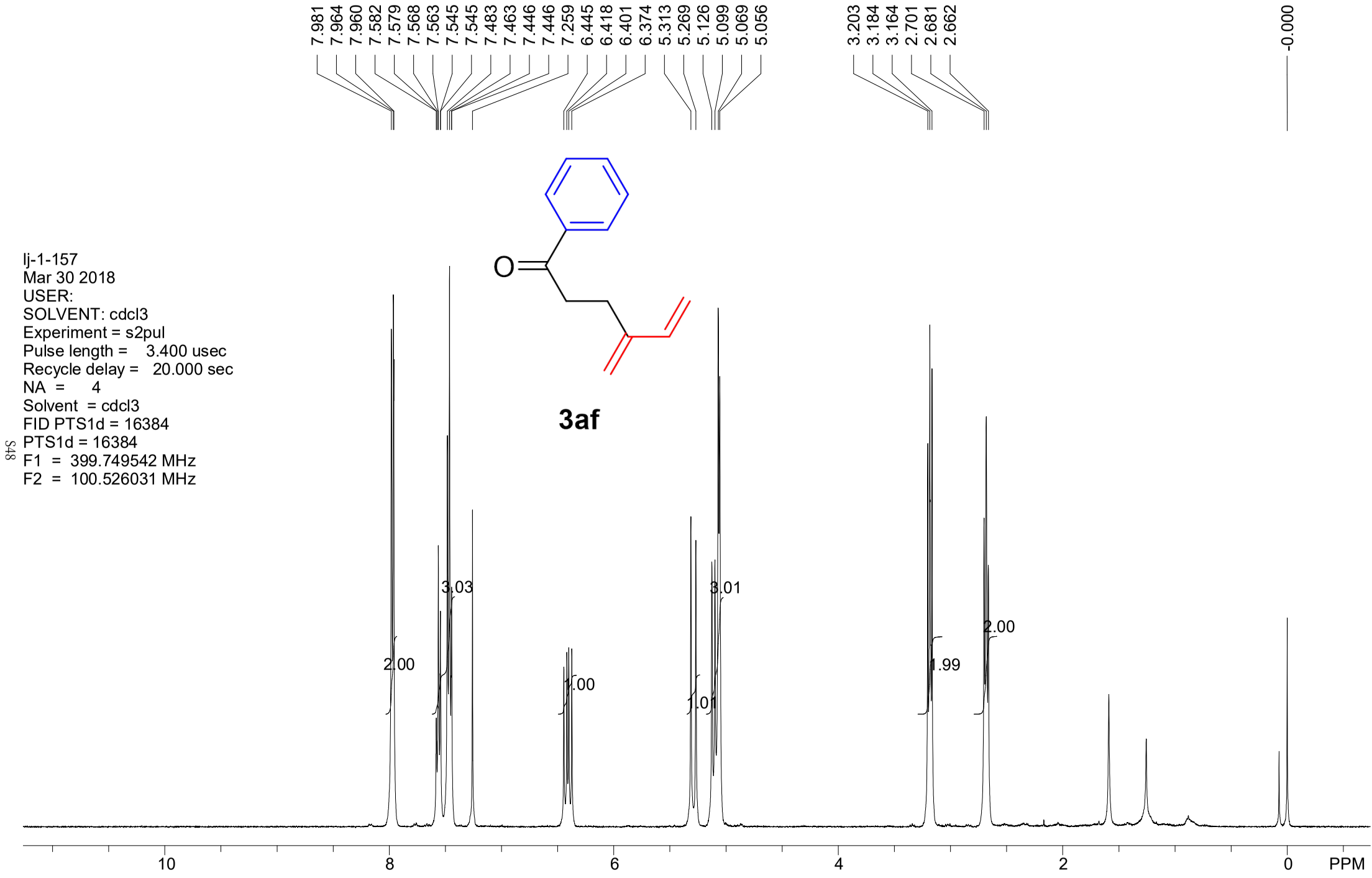

207.889
144.949
138.346
136.623
131.051
129.404
129.230
116.053
113.533
77.319
77.000
76.681
49.864
40.323
25.188
21.028
lj-1-146C
Mar 27 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 512
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
Me
3ac
200
150
100
50
0
PPM

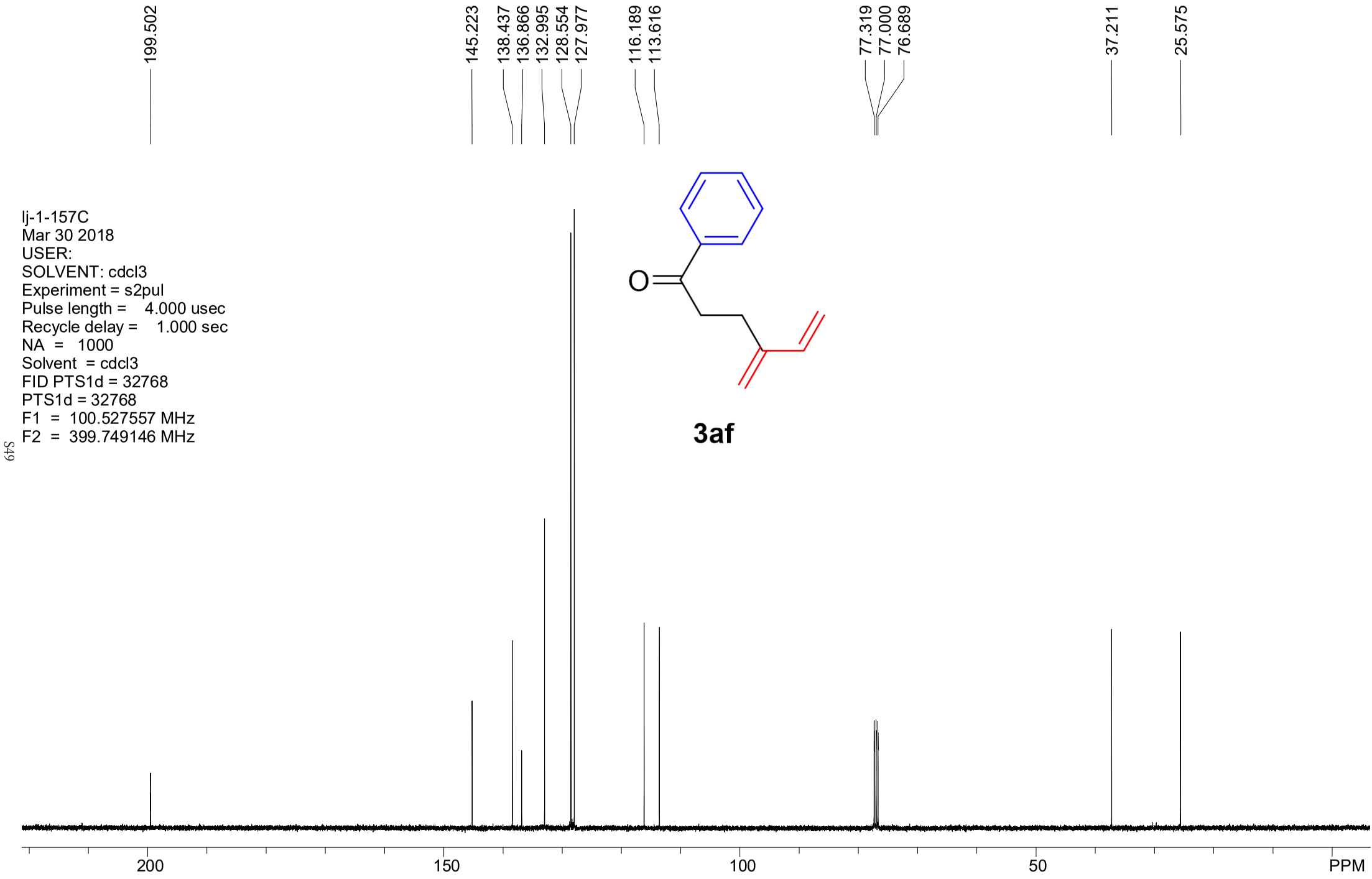

7.310
7.303
7.299
7.287
7.282
7.258
7.135
7.113
6.369
6.343
6.325
6.299
5.196
5.152
5.074
5.047
5.004
4.925
3.666
2.675
2.657
2.648
2.638
2.501
2.482
2.463
-0.000
lj-1-159
Apr 1 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Cl
O
3ad
2.01
2.00
1.00
1.01
1.00
1.00
1.00
2.00
2.00
2.01
12
10
8
6
4
2
0
PPM

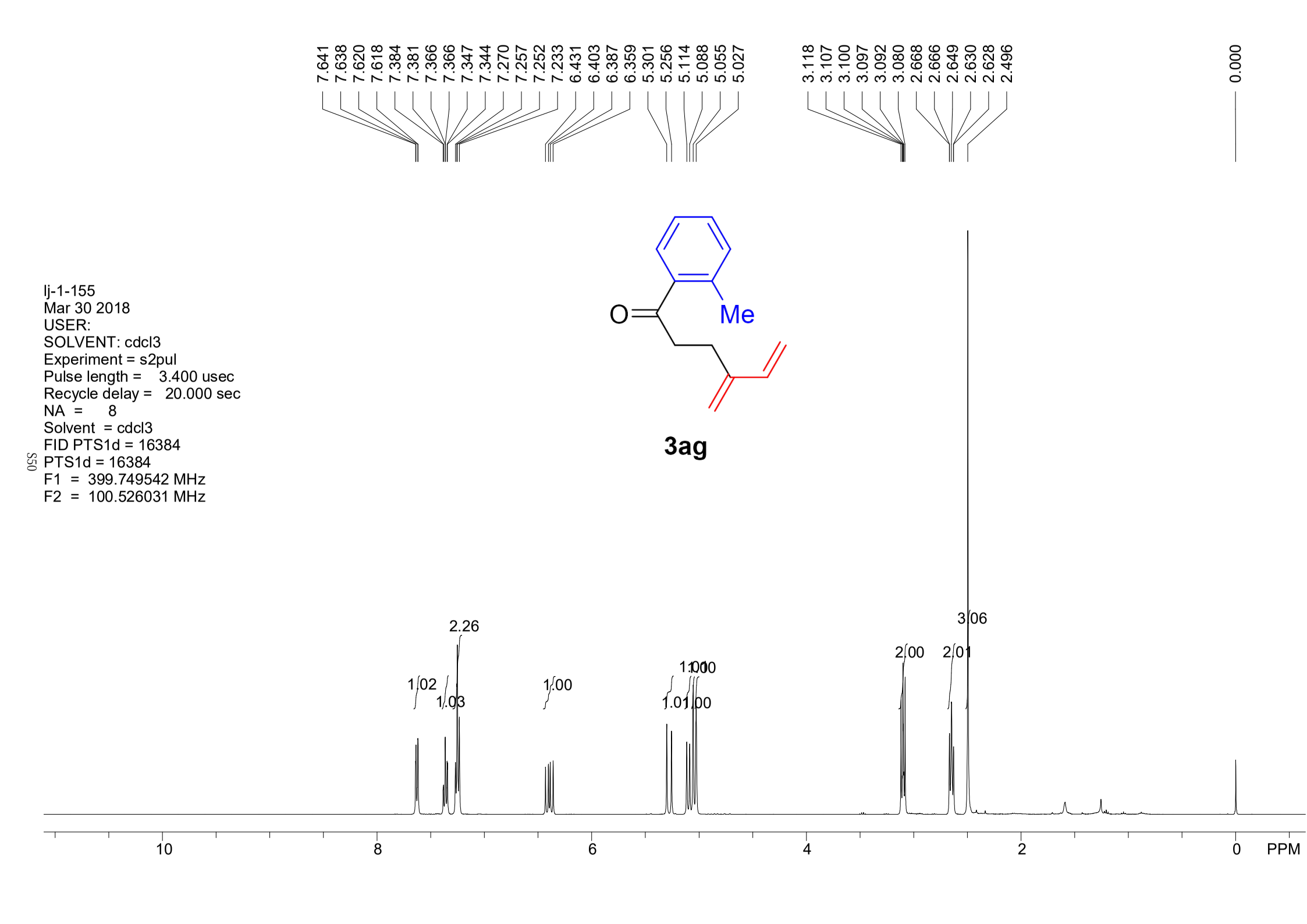

206.895
144.767
138.262
132.957
132.471
130.733
128.782
116.182
113.578
77.319
77.000
76.681
49.265
40.634
25.142
lj-1-159C
Apr 1 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 1000
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
Cl
3ad
200
150
100
50
0
PPM

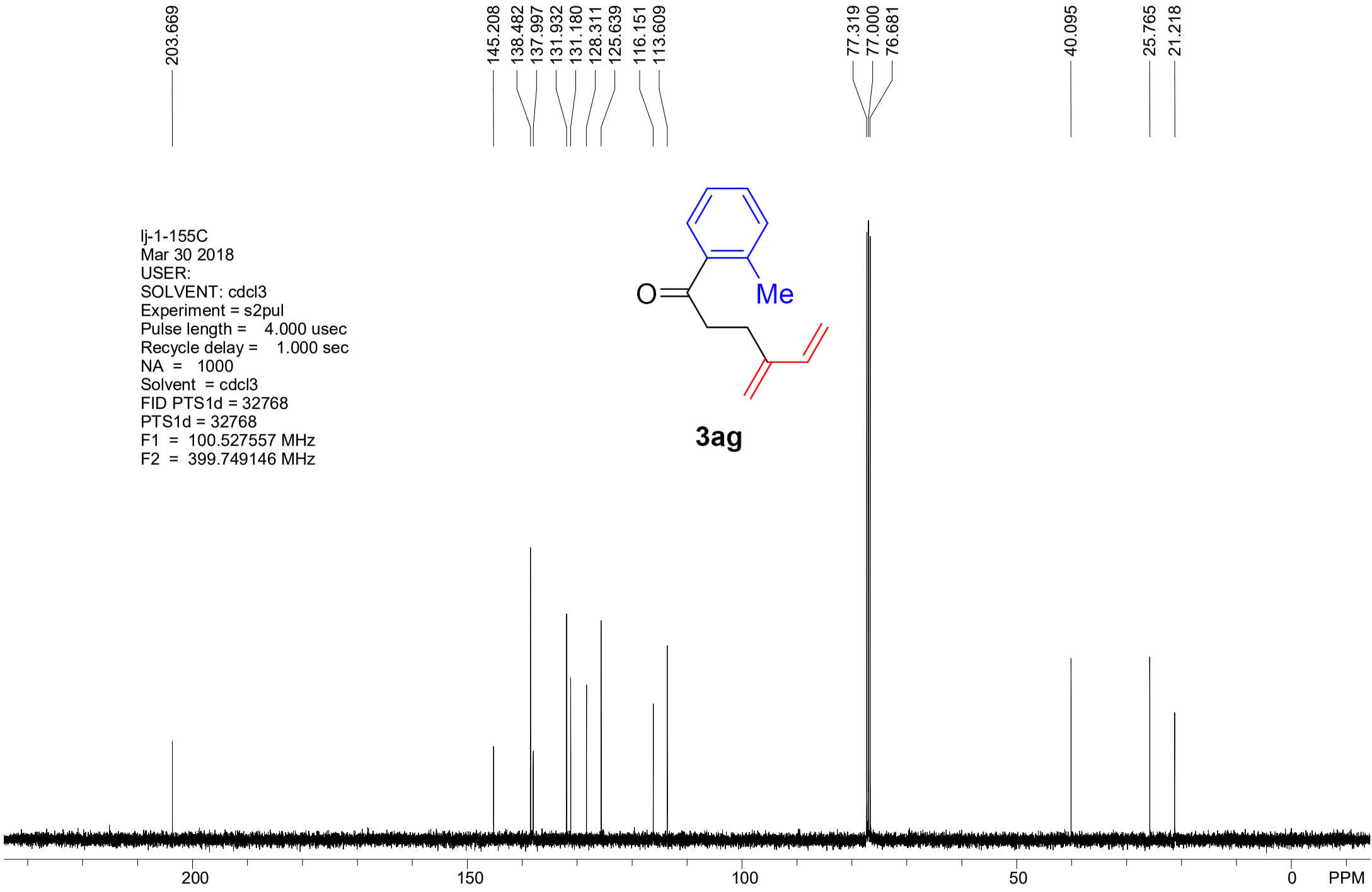

7.454
7.450
7.438
7.433
7.076
7.055
6.369
6.343
6.325
6.299
5.196
5.152
5.074
5.048
5.004
4.925
3.649
2.675
2.657
2.637
2.499
2.480
2.461
-0.000
Br
O
3ae
lj-1-122
Mar 7 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
2.00
2.00
1.00
1.00
1.01
1.01
1.01
2.00
2.01
2.01
10
8
6
4
2
0
PPM

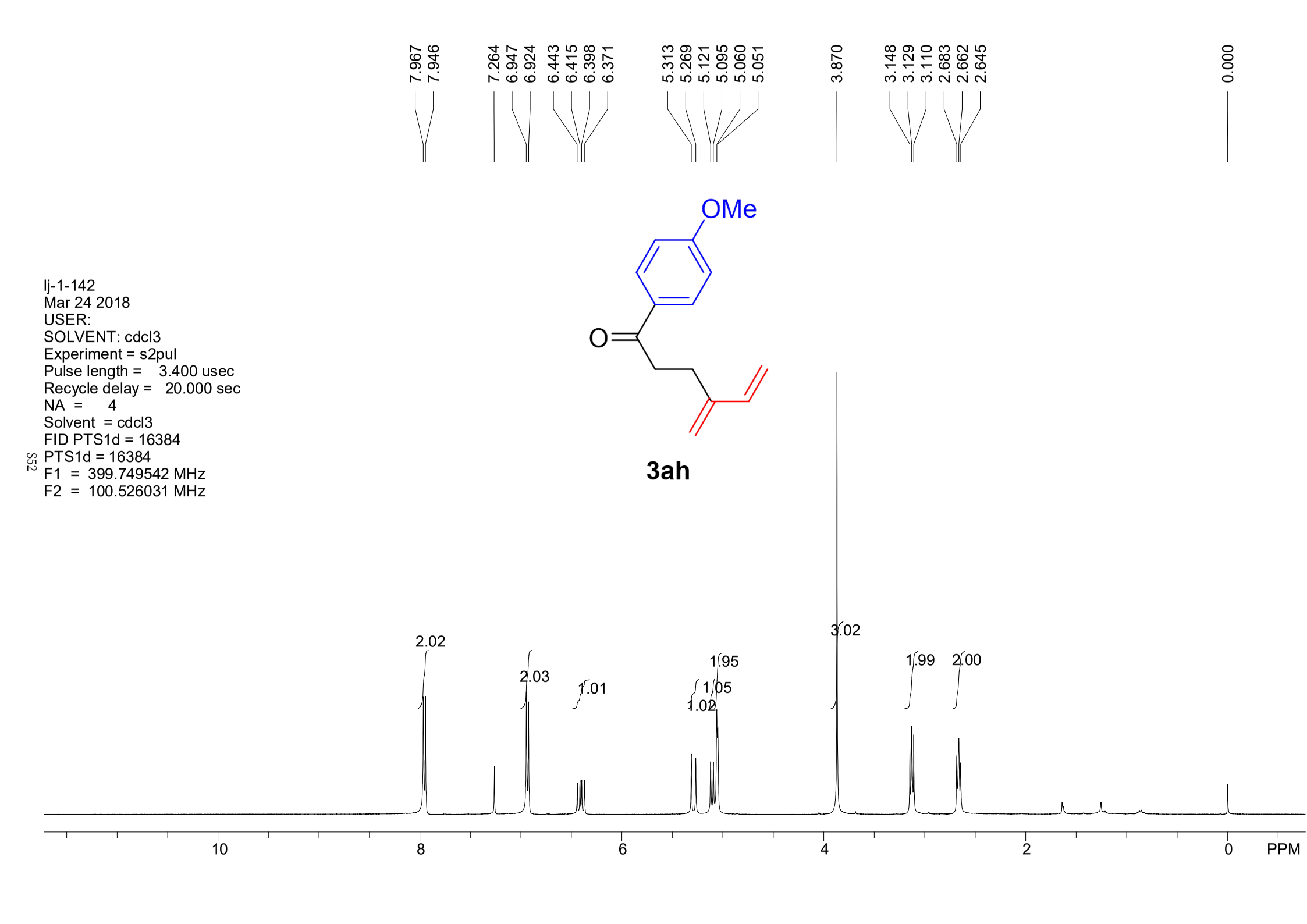

206.834
144.760
138.270
132.979
131.757
131.120
121.062
116.227
113.609
77.319
77.000
76.681
49.356
40.657
25.135
Br
O
3ae
lj-1-122C
Mar 7 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 512
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
200
150
100
50
0 PPM

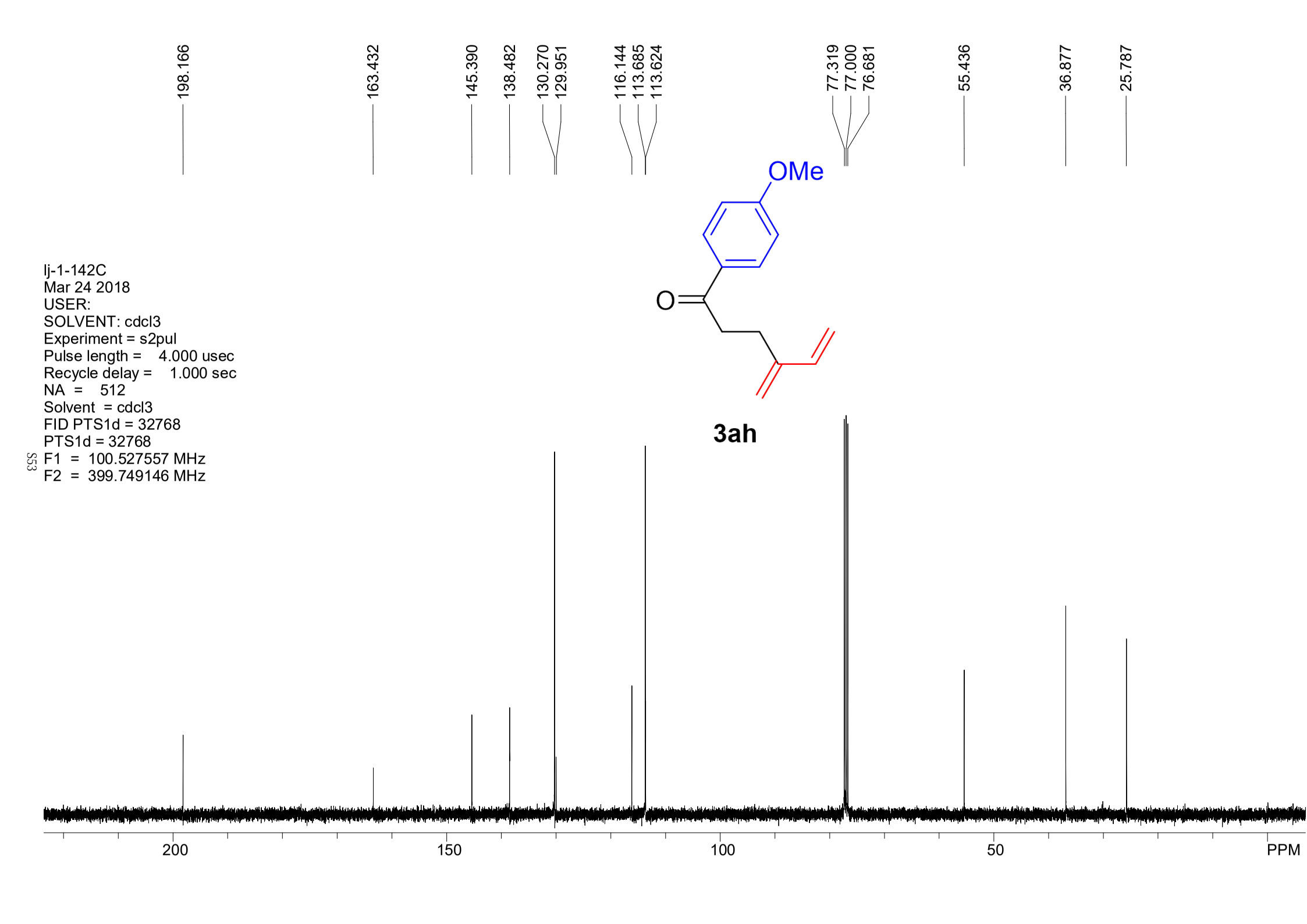

7.981
7.964
7.960
7.582
7.579
7.568
7.563
7.545
7.545
7.483
7.463
7.446
7.446
7.259
6.445
6.418
6.401
6.374
5.313
5.269
5.126
5.099
5.069
5.056
3.203
3.184
3.164
2.701
2.681
2.662
-0.000
O
3af
lj-1-157
Mar 30 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
2.00
3.03
2.00
1.01
3.01
1.99
2.00
10
8
6
4
2
0
PPM

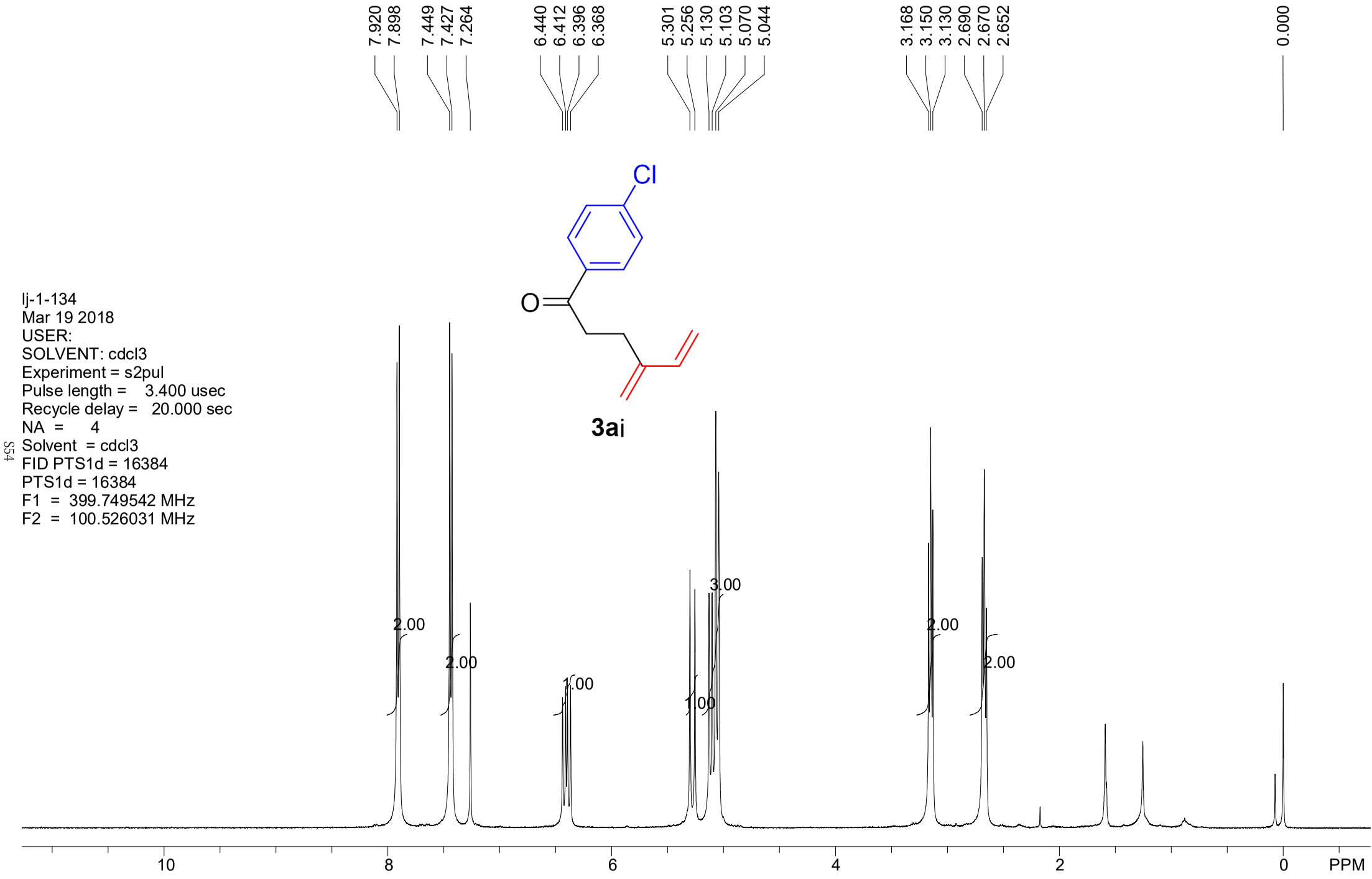

199.502
145.223
138.437
136.866
132.995
128.554
127.977
116.189
113.616
77.319
77.000
76.689
37.211
25.575
lj-1-157C
Mar 30 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 1000
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
3af
200
150
100
50
PPM

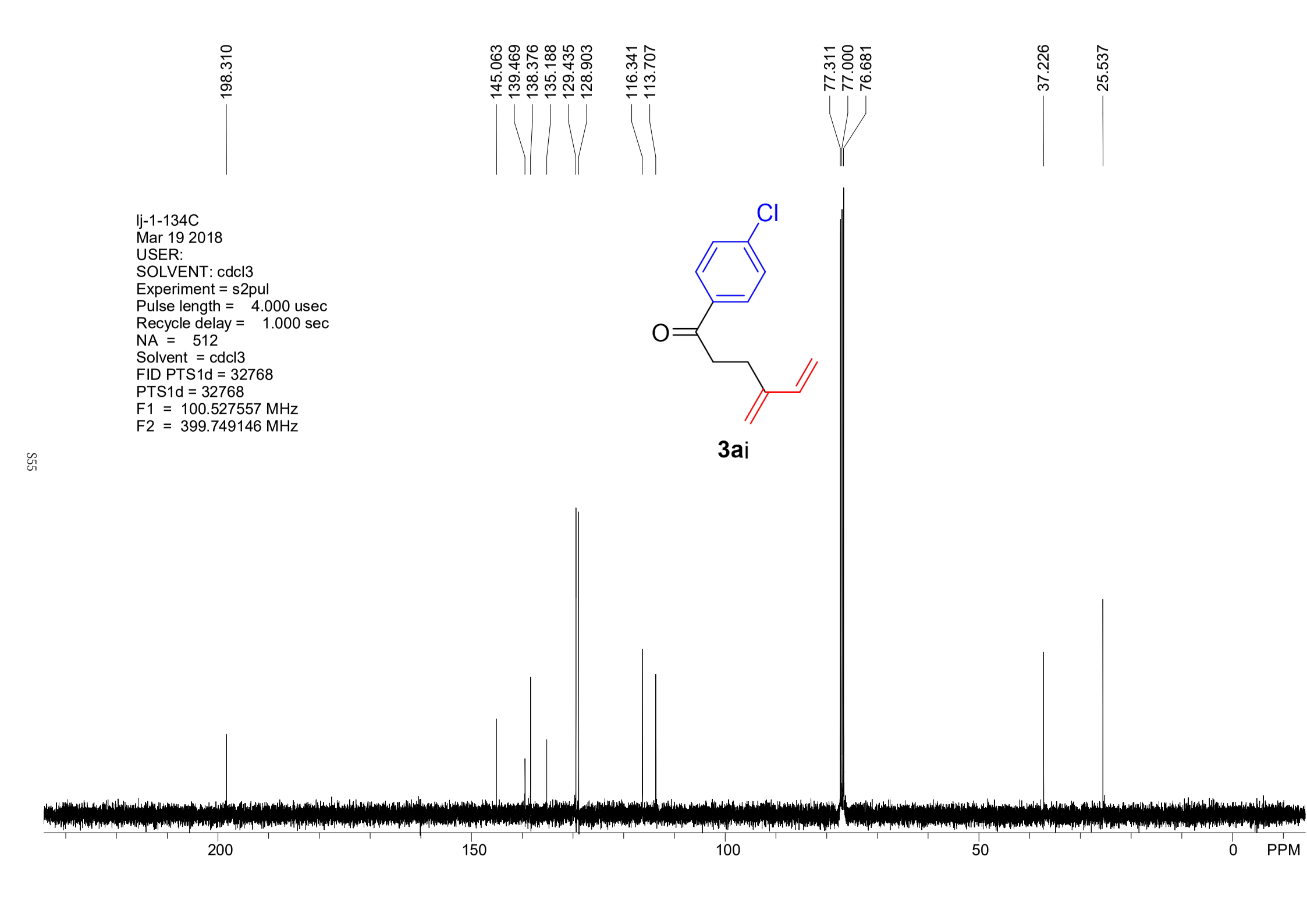

7.641
7.638
7.620
7.618
7.384
7.381
7.366
7.366
7.347
7.344
7.270
7.257
7.252
7.233
6.431
6.403
6.387
6.359
5.301
5.256
5.114
5.088
5.055
5.027
3.118
3.107
3.100
3.097
3.092
3.080
2.668
2.666
2.649
2.630
2.628
2.496
0.000
O
Me
3ag
lj-1-155
Mar 30 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 8
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
S50
2.26
1.02
1.03
1.00
1.01
1.00
2.00
2.01
3.06
10
8
6
4
2
0
PPM

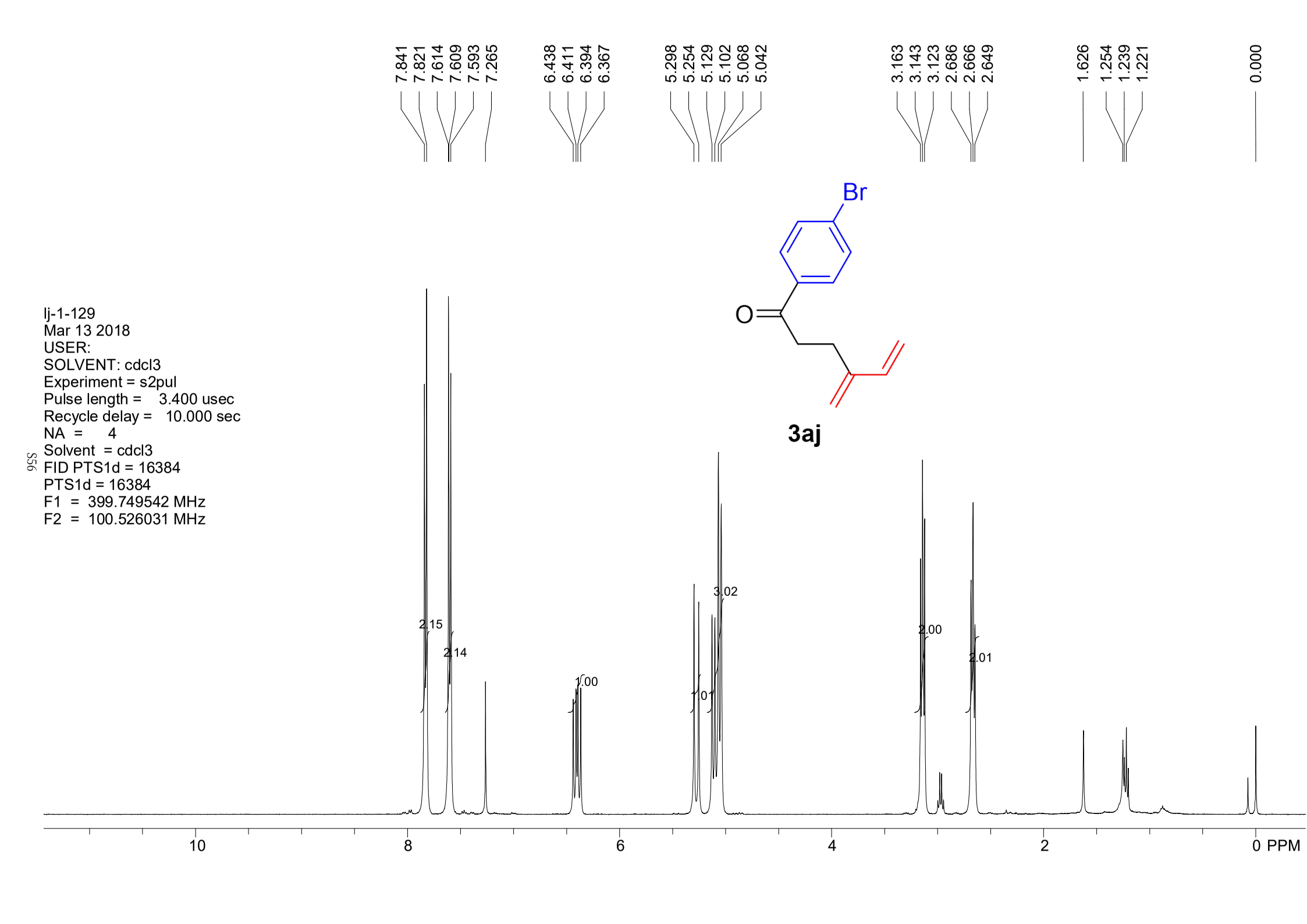

203.669
145.208
138.482
137.997
131.932
131.180
128.311
125.639
116.151
113.609
77.319
77.000
76.681
40.095
25.765
21.218
lj-1-155C
Mar 30 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 1000
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
Me
3ag
200
150
100
50
0
PPM

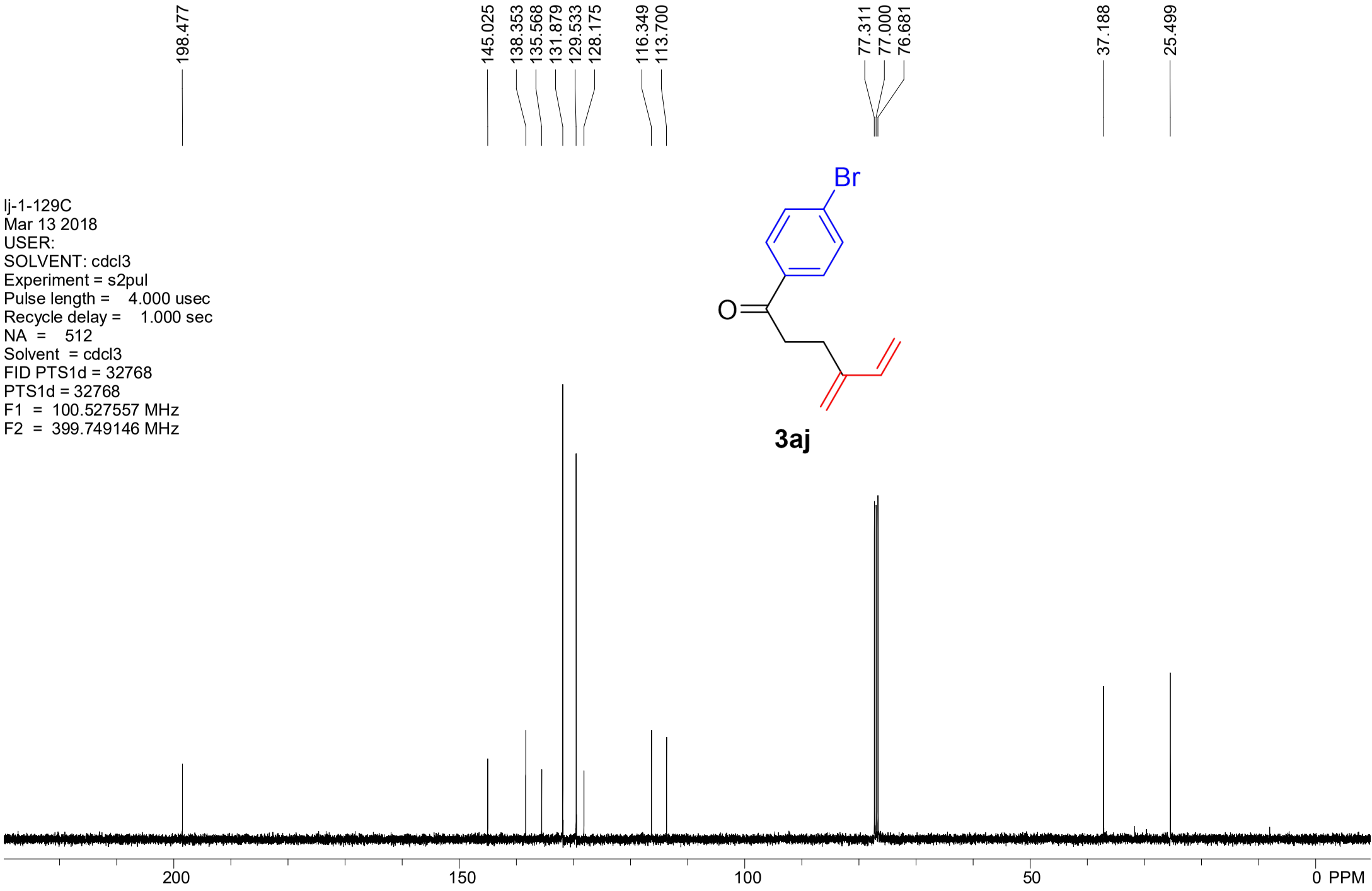

7.967
7.946
7.264
6.947
6.924
6.443
6.415
6.398
6.371
5.313
5.269
5.121
5.095
5.060
5.051
3.870
3.148
3.129
3.110
2.683
2.662
2.645
0.000
OMe
O
3ah
lj-1-142
Mar 24 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
2.02
2.03
1.01
1.95
1.05
1.02
3.02
1.99
2.00
10
8
6
4
2
0
PPM


198.166
163.432
145.390
138.482
130.270
129.951
116.144
113.685
113.624
77.319
77.000
76.681
55.436
36.877
25.787
OMe
O
lj-1-142C
Mar 24 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 512
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
3ah
200
150
100
50
PPM


7.920
7.898
7.449
7.427
7.264
6.440
6.412
6.396
6.368
5.301
5.256
5.130
5.103
5.070
5.044
3.168
3.150
3.130
2.690
2.670
2.652
0.000
Cl
O
3ai
lj-1-134
Mar 19 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
2.00
2.00
1.00
3.00
1.00
2.00
2.00
10
8
6
4
2
0
PPM

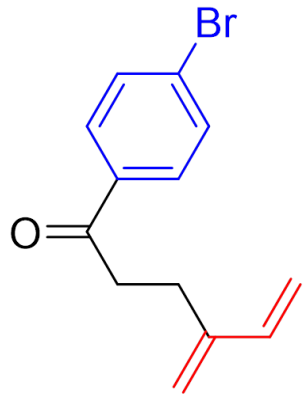

198.310
145.063
139.469
138.376
135.188
129.435
128.903
116.341
113.707
77.311
77.000
76.681
37.226
25.537
lj-1-134C
Mar 19 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 512
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
Cl
O
3ai
200
150
100
50
0
PPM


7.841
7.821
7.614
7.609
7.593
7.265
6.438
6.411
6.394
6.367
5.298
5.254
5.129
5.102
5.068
5.042
3.163
3.143
3.123
2.686
2.666
2.649
1.626
1.254
1.239
1.221
0.000
Br
O
3aj
lj-1-129
Mar 13 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 10.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
2.15
2.14
1.00
1.01
3.02
2.00
2.01
10
8
6
4
2
0 PPM

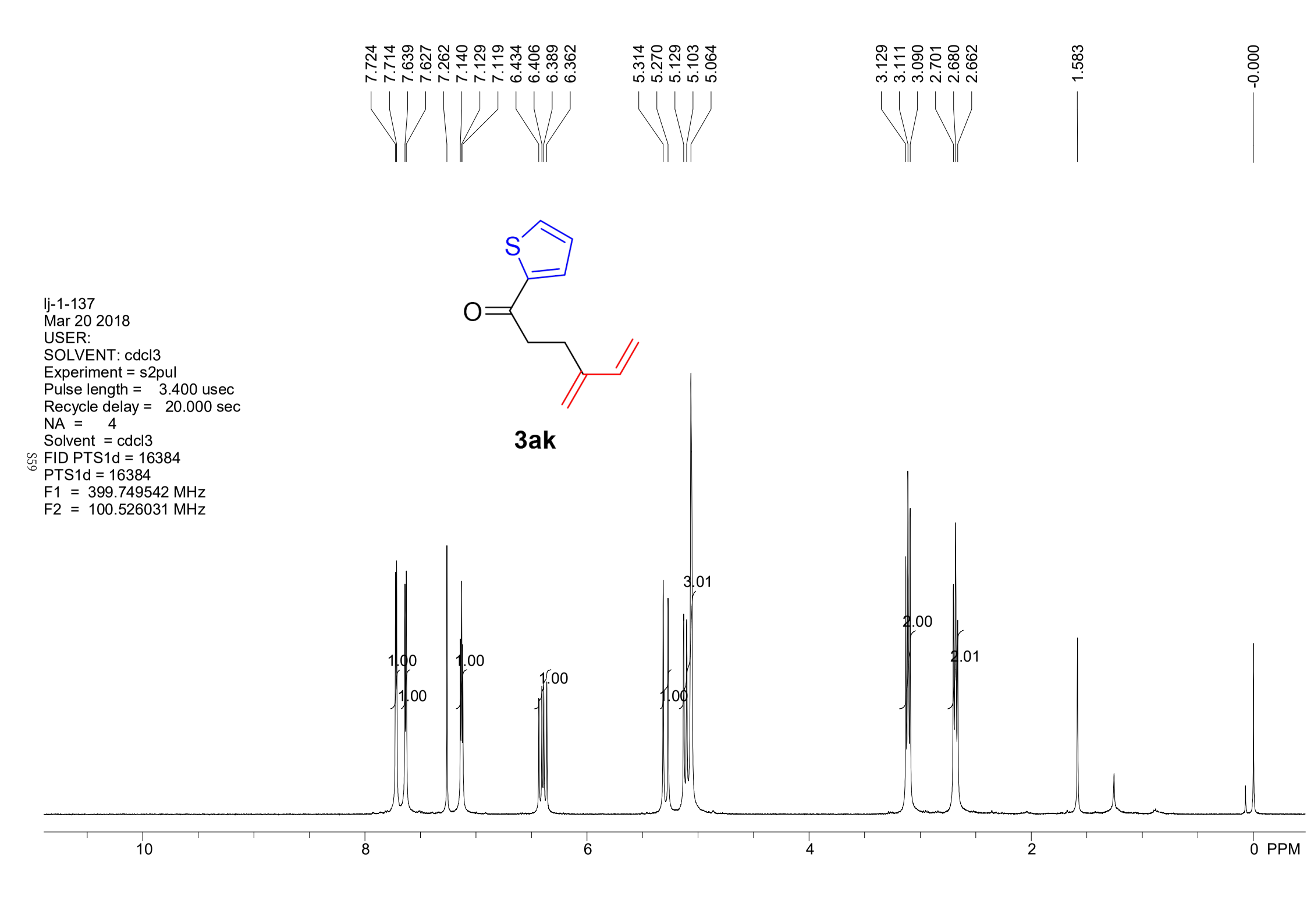

198.477
145.025
138.353
135.568
131.879
129.533
128.175
116.349
113.700
77.311
77.000
76.681
37.188
25.499
lj-1-129C
Mar 13 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 512
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
Br
O
3aj
S57
200
150
100
50
0 PPM

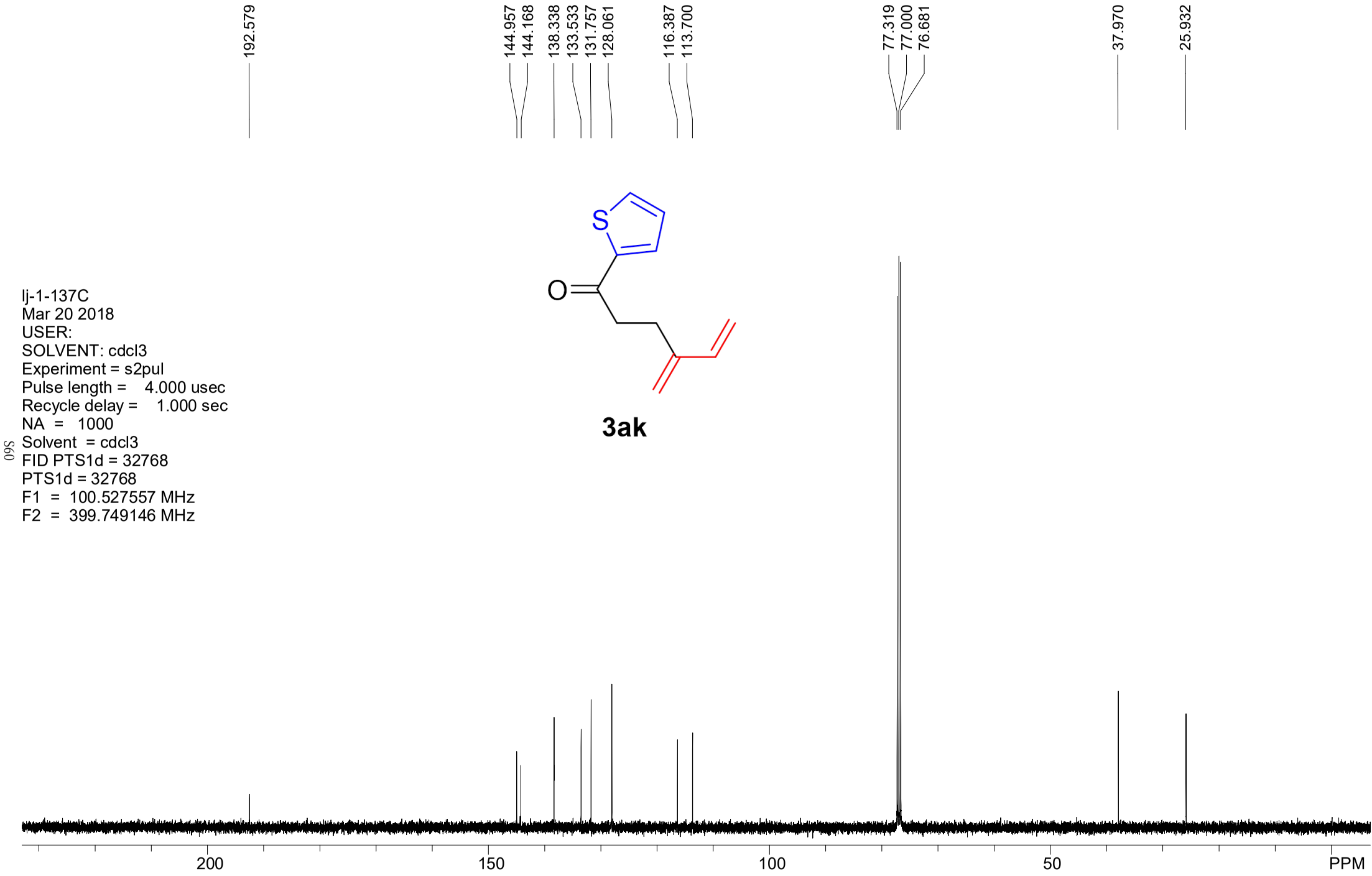
Purity was determined to be 92% by using 26.3 mg mesitylene as the internal standard in 9.1 mg sample.

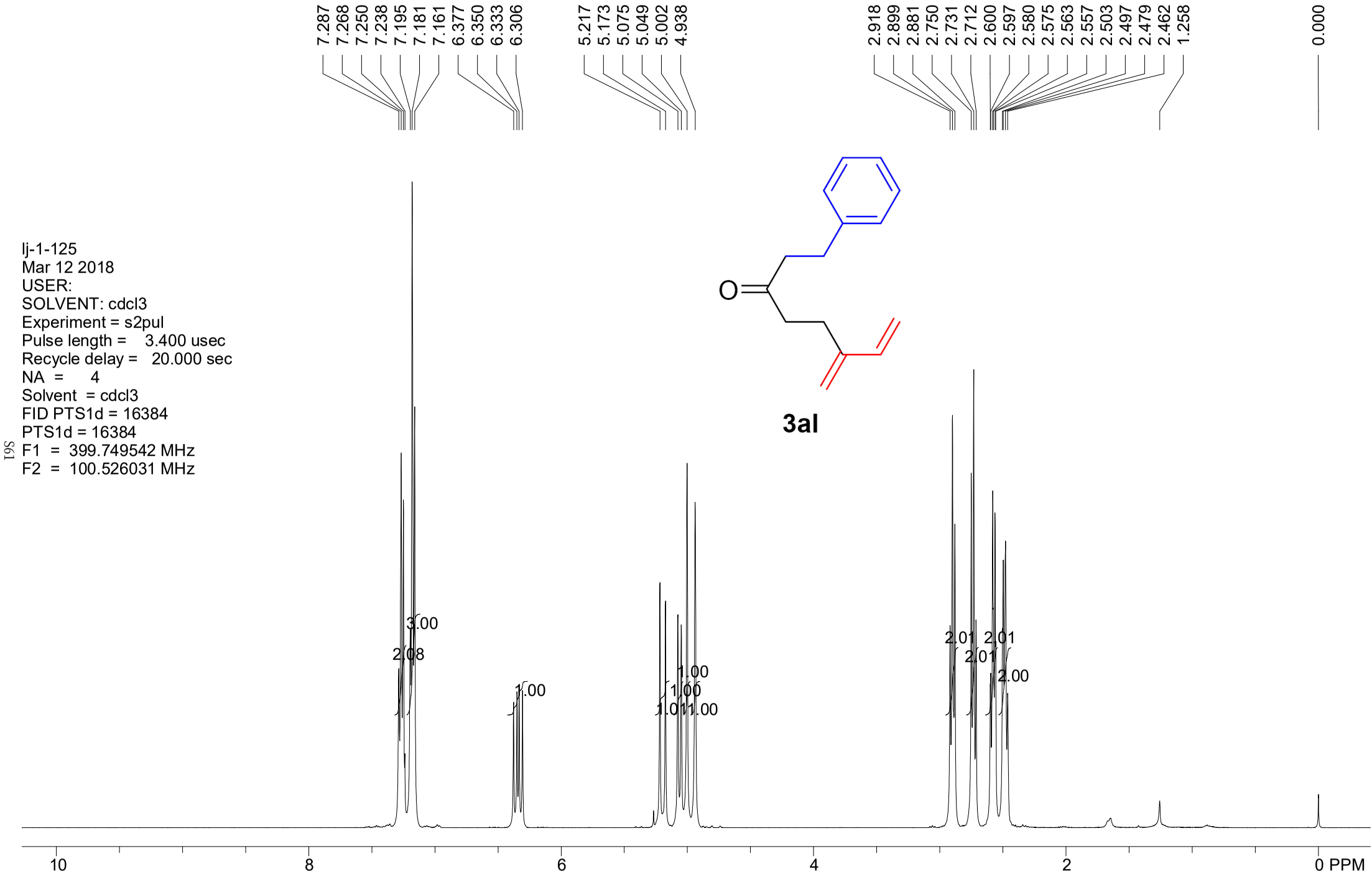
lj-1-129-purity
Mar 13 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz

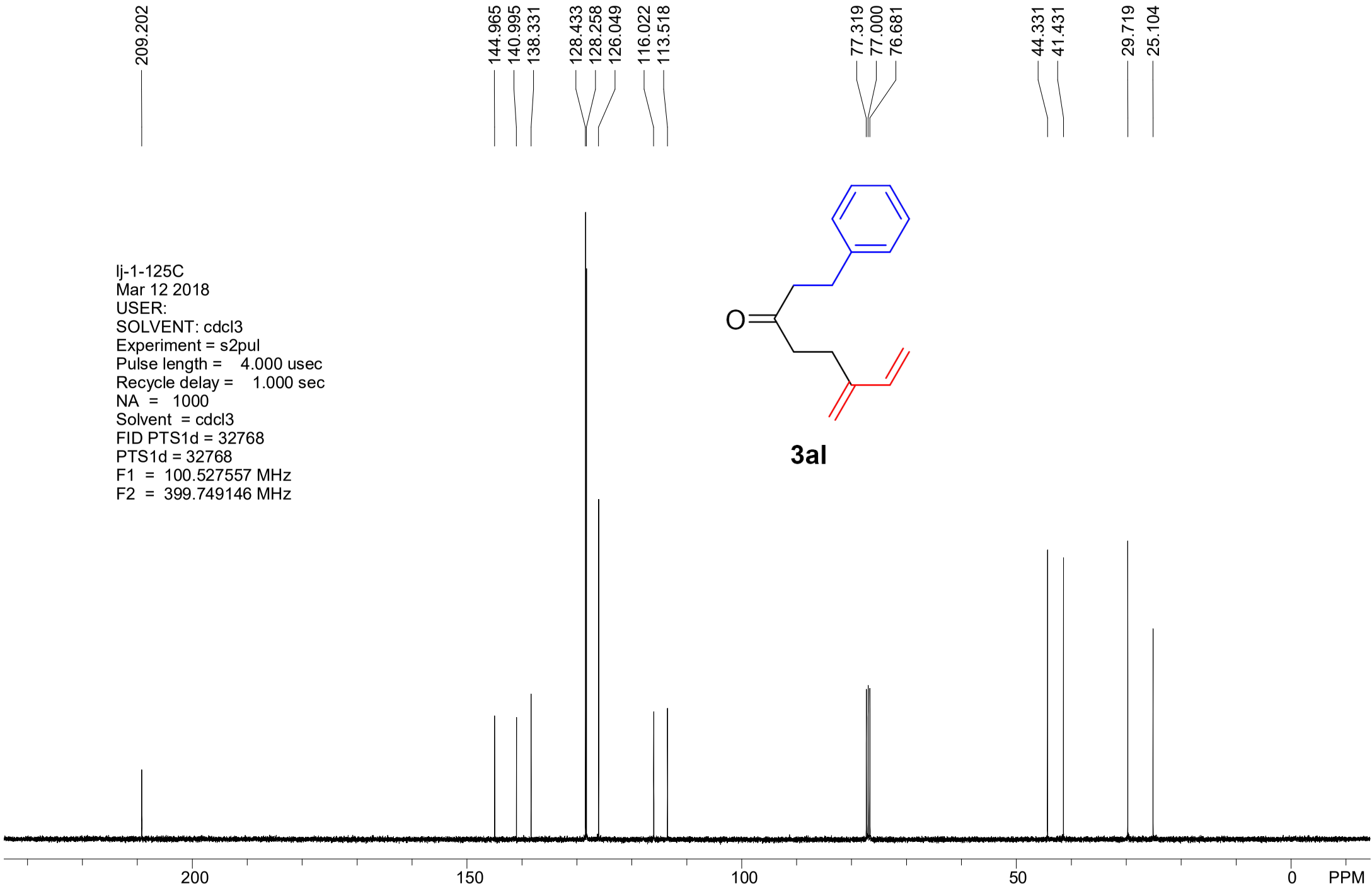


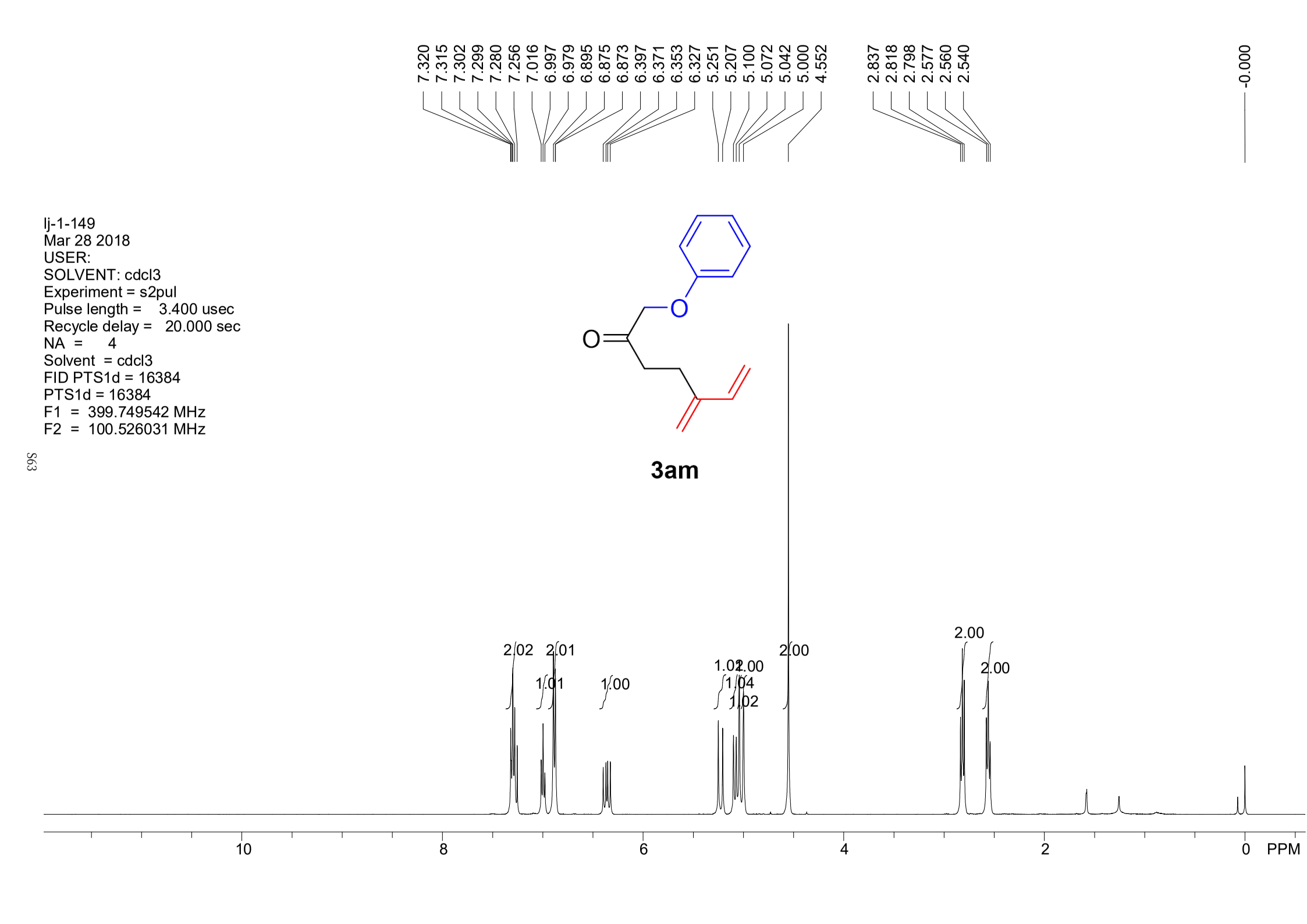
3aj

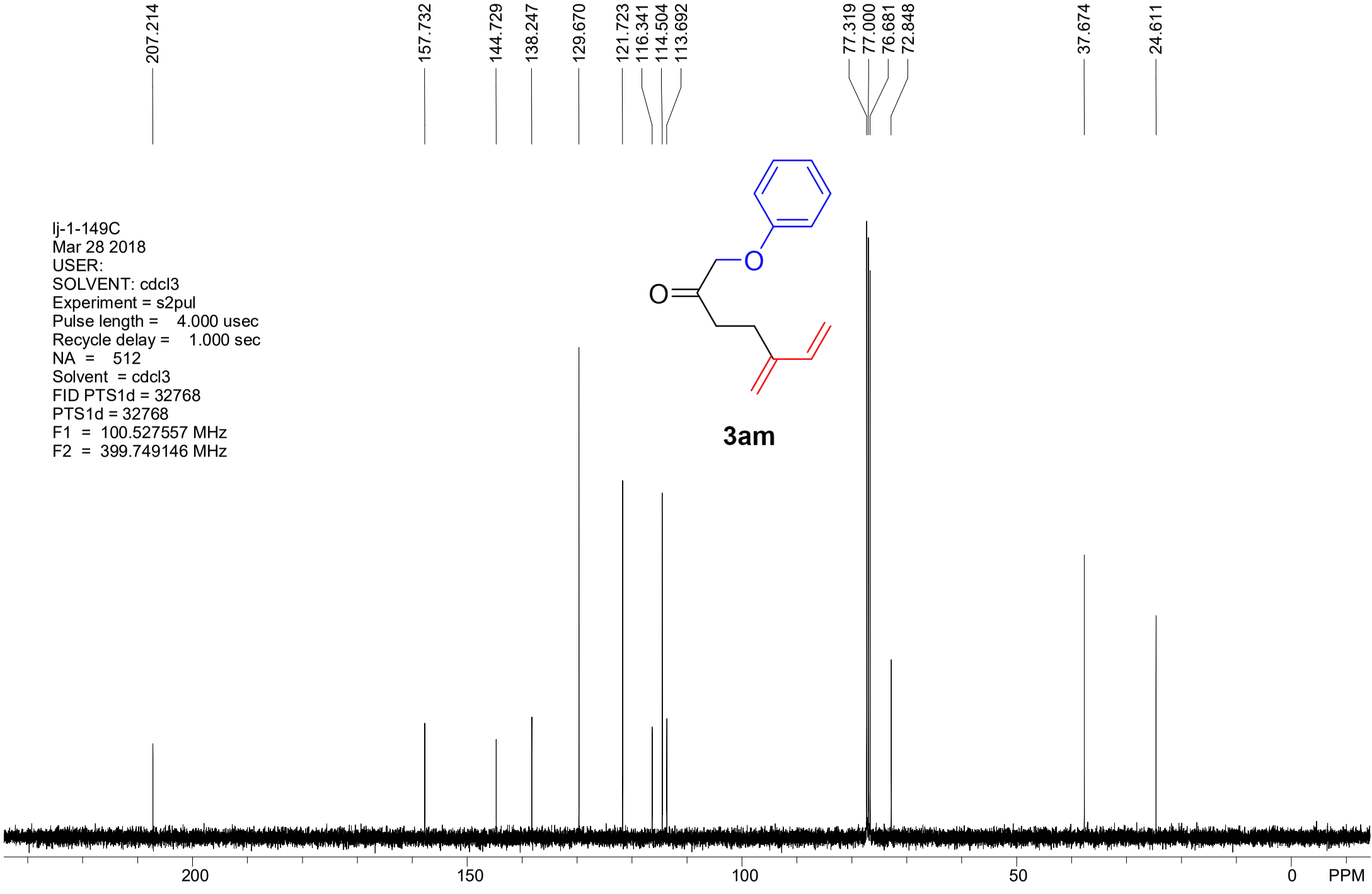

7.724
7.714
7.639
7.627
7.262
7.140
7.129
7.119
6.434
6.406
6.389
6.362
5.314
5.270
5.129
5.103
5.064
3.129
3.111
3.090
2.701
2.680
2.662
1.583
-0.000
S
O
3ak
lj-1-137
Mar 20 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
1.00
1.00
1.00
1.00
1.00
3.01
2.00
2.01
10
8
6
4
2
0 PPM

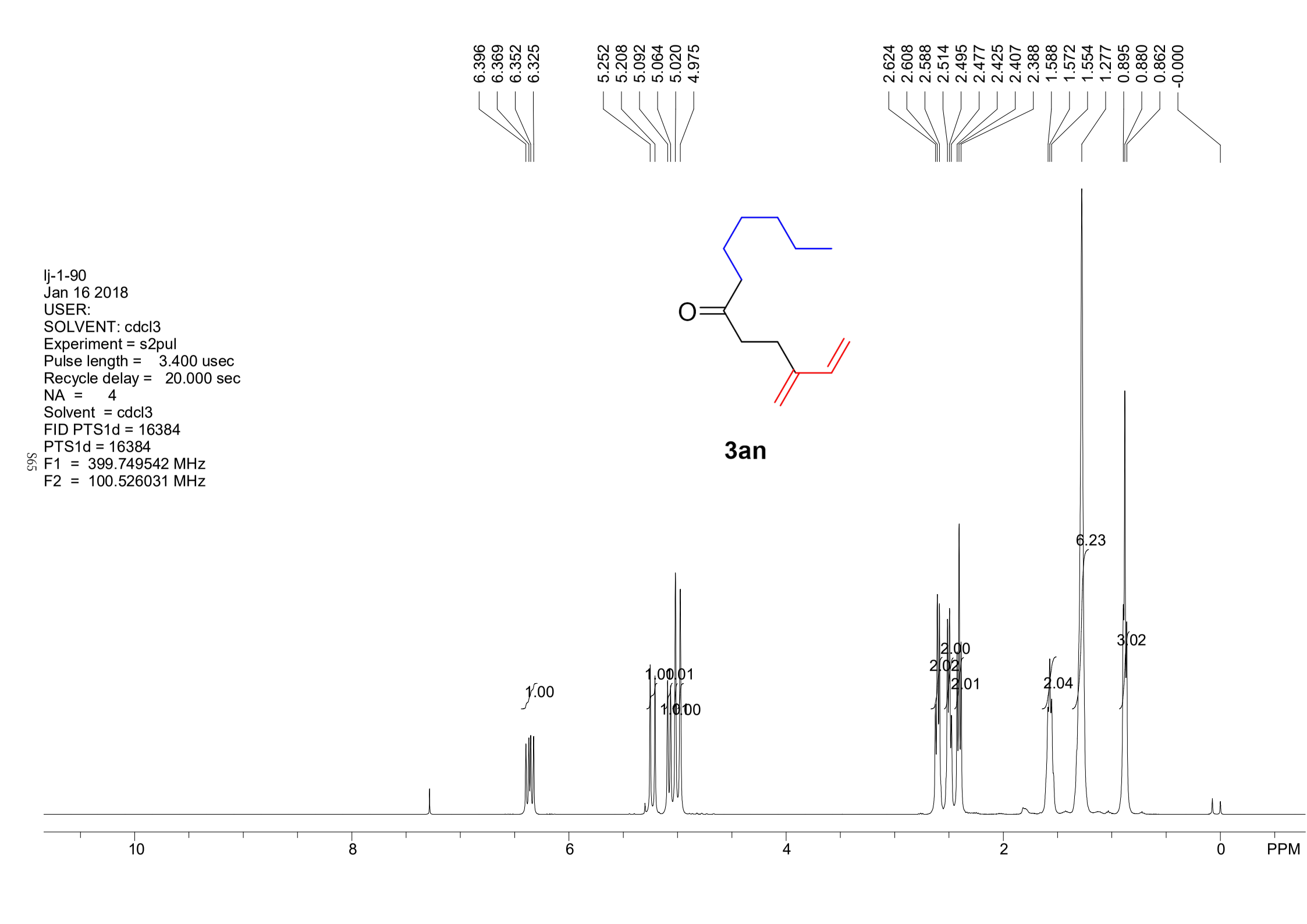

192.579
144.957
144.168
138.338
133.533
131.757
128.061
116.387
113.700
77.319
77.000
76.681
37.970
25.932
S
O
3ak
lj-1-137C
Mar 20 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 1000
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
S60
200
150
100
50
PPM

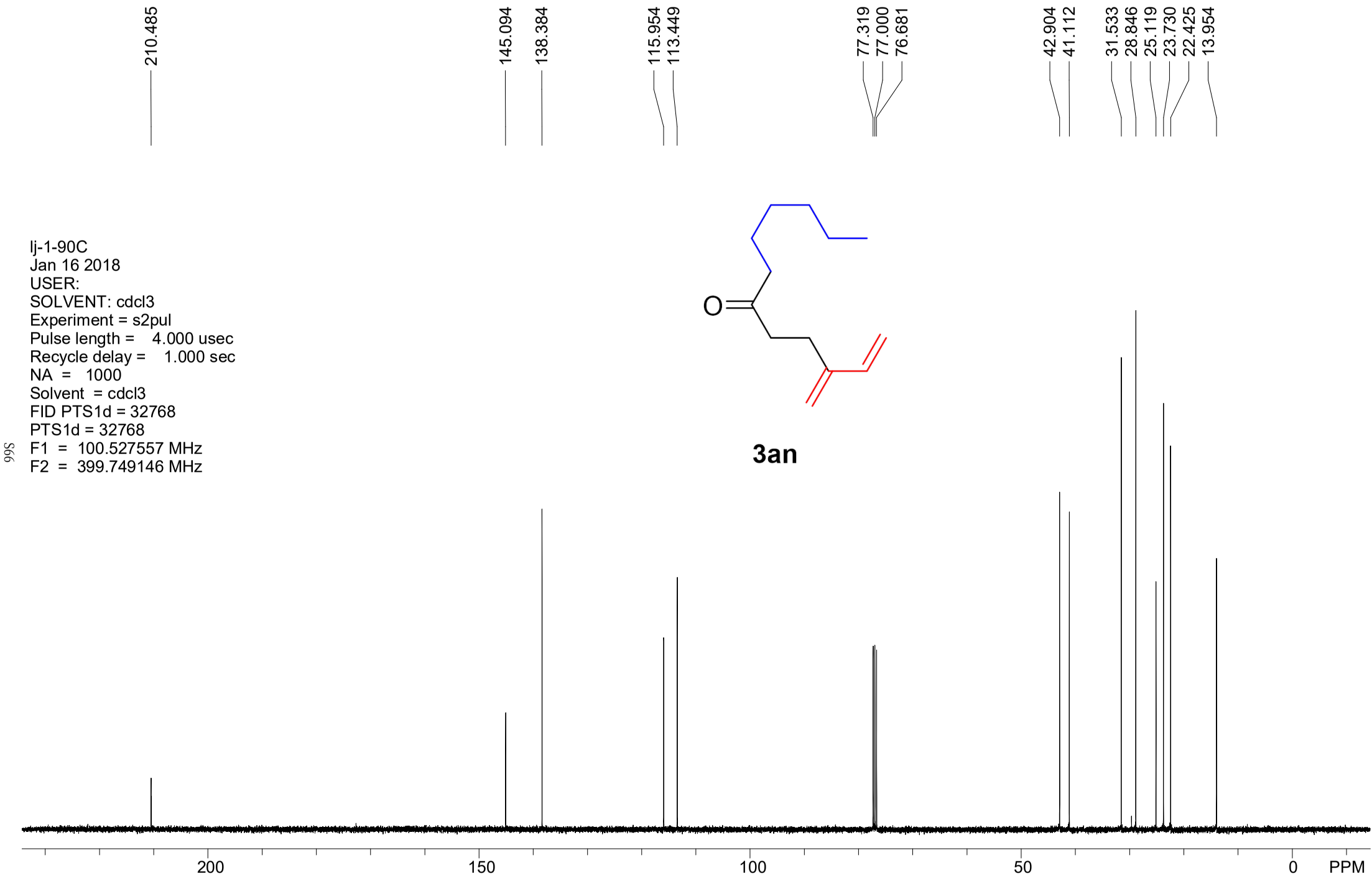

7.287
7.268
7.250
7.238
7.195
7.181
7.161
6.377
6.350
6.333
6.306
5.217
5.173
5.075
5.049
5.002
4.938
2.918
2.899
2.881
2.750
2.731
2.712
2.600
2.597
2.580
2.575
2.563
2.557
2.503
2.497
2.479
2.462
1.258
0.000
lj-1-125
Mar 12 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
S61
O
3al
3.00
2.08
1.00
1.00
1.00
1.00
1.00
2.01
2.01
2.01
2.00
10
8
6
4
2
0 PPM

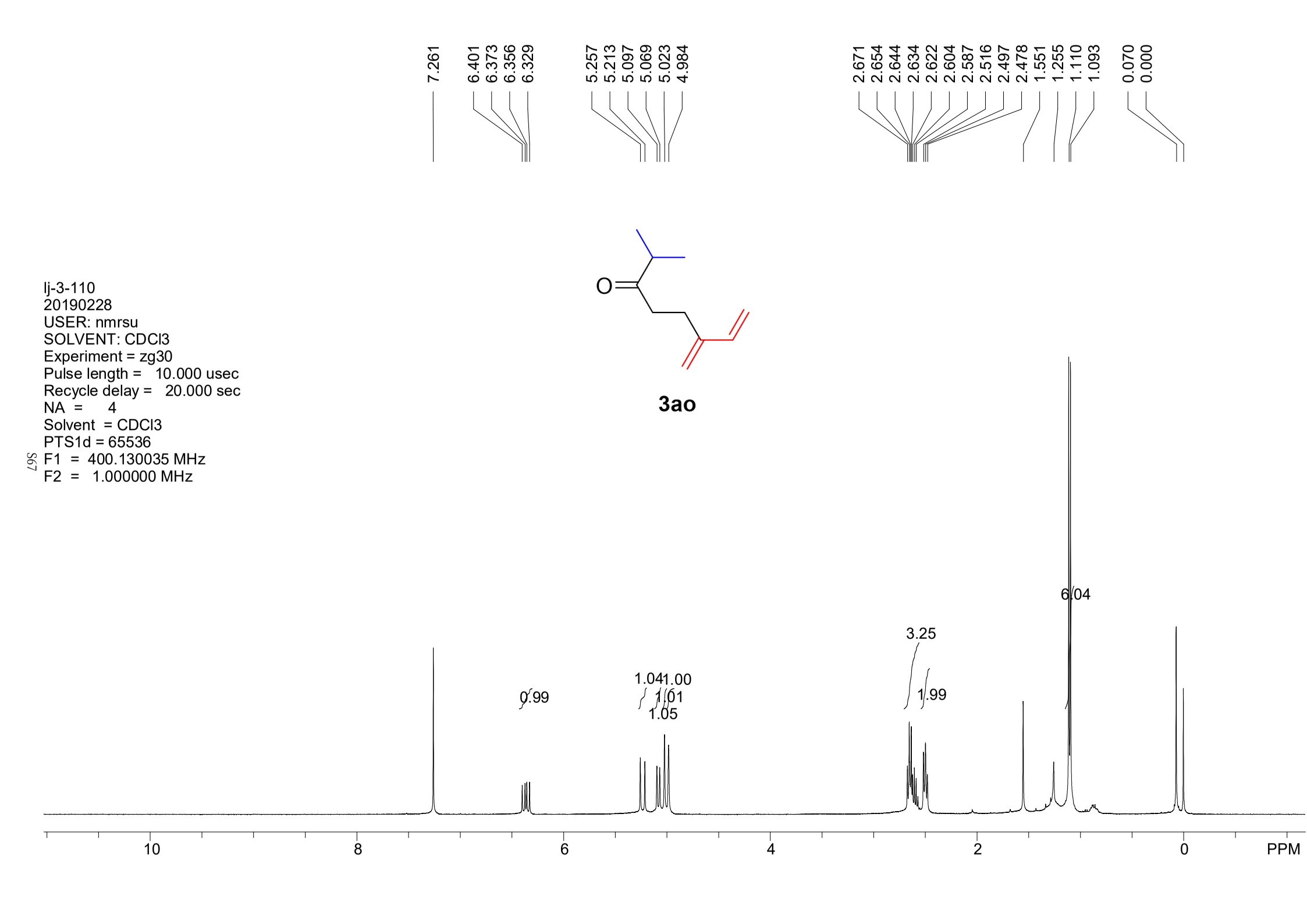

209.202
144.965
140.995
138.331
128.433
128.258
126.049
116.022
113.518
77.319
77.000
76.681
44.331
41.431
29.719
25.104
lj-1-125C
Mar 12 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 1000
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
3al
200
150
100
50
0
PPM

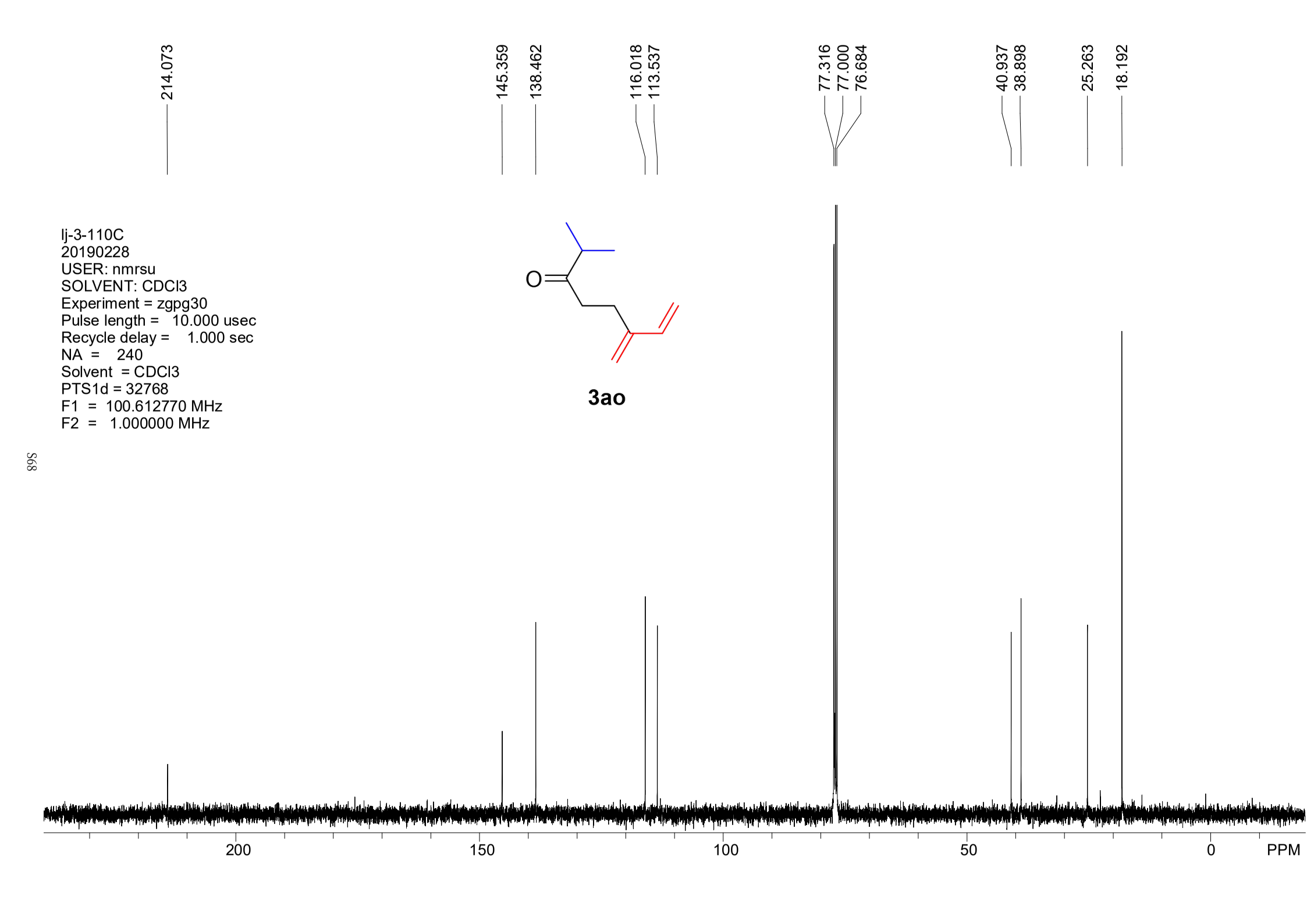

7.320
7.315
7.302
7.299
7.280
7.256
7.016
6.997
6.979
6.895
6.875
6.873
6.397
6.371
6.353
6.327
5.251
5.207
5.100
5.072
5.042
5.000
4.552
2.837
2.818
2.798
2.577
2.560
2.540
-0.000
lj-1-149
Mar 28 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
O
O
3am
2.02
2.01
1.01
1.00
1.02
2.00
1.04
1.02
2.00
2.00
2.00
10
8
6
4
2
0
PPM

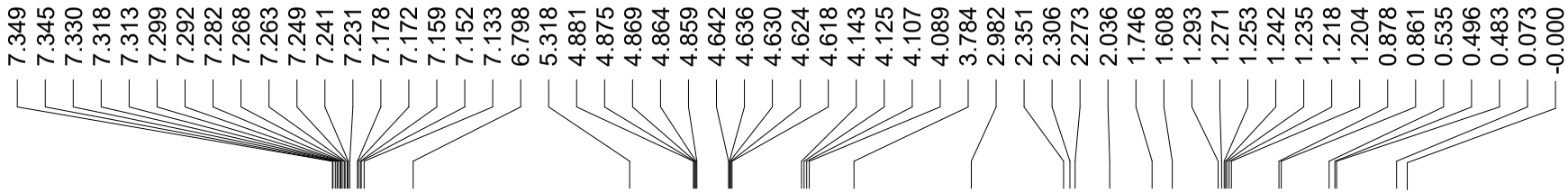

207.214
157.732
144.729
138.247
129.670
121.723
116.341
114.504
113.692
77.319
77.000
76.681
72.848
37.674
24.611
lj-1-149C
Mar 28 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 512
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
O
3am
200
150
100
50
0
PPM


6.396
6.369
6.352
6.325
5.252
5.208
5.092
5.064
5.020
4.975
2.624
2.608
2.588
2.514
2.495
2.477
2.425
2.407
2.388
1.588
1.572
1.554
1.277
0.895
0.880
0.862
-0.000
lj-1-90
Jan 16 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
S65
O
3an
1.00
1.00
1.01
1.00
2.00
2.02
2.01
2.04
6.23
3.02
10
8
6
4
2
0
PPM


210.485
145.094
138.384
115.954
113.449
77.319
77.000
76.681
42.904
41.112
31.533
28.846
25.119
23.730
22.425
13.954
lj-1-90C
Jan 16 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 1000
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
S66
O
3an
200
150
100
50
0
PPM

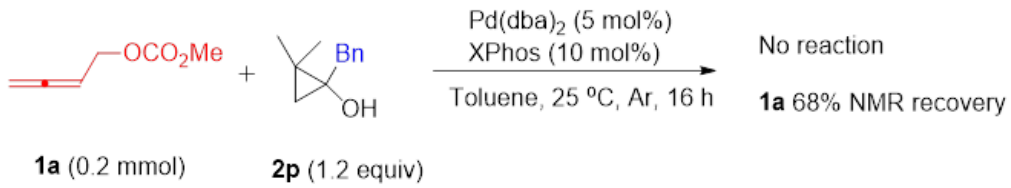

7.261
6.401
6.373
6.356
6.329
5.257
5.213
5.097
5.069
5.023
4.984
2.671
2.654
2.644
2.634
2.622
2.604
2.587
2.516
2.497
2.478
1.551
1.255
1.110
1.093
0.070
0.000
O
3ao
lj-3-110
20190228
USER: nmrsu
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130035 MHz
F2 = 1.000000 MHz
S67
0.99
1.04
1.00
1.01
1.05
3.25
1.99
6.04
10
8
6
4
2
0
PPM

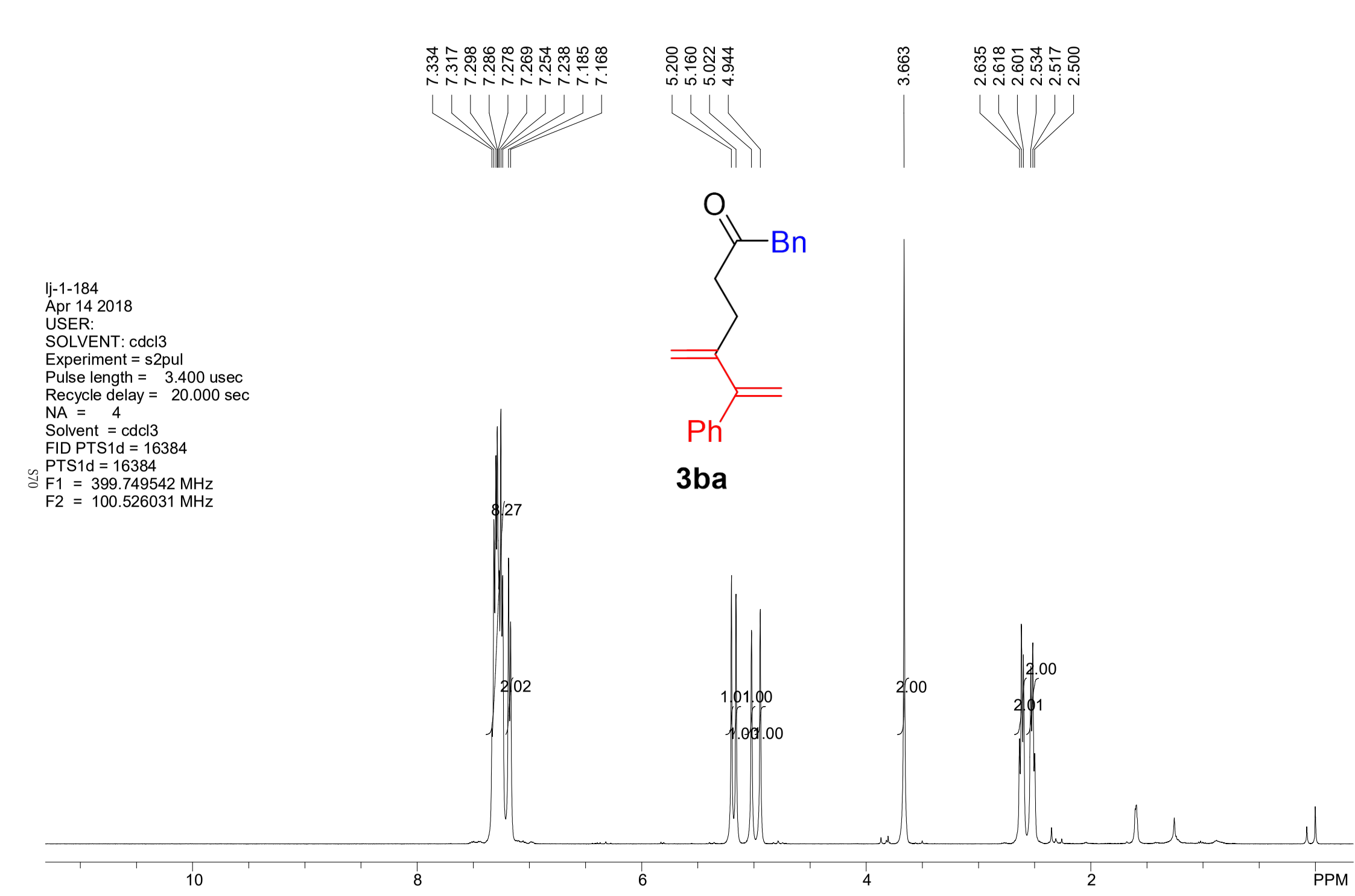

214.073
145.359
138.462
116.018
113.537
77.316
77.000
76.684
40.937
38.898
25.263
18.192
lj-3-110C
20190228
USER: nmrsu
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 240
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
O
3ao
200
150
100
50
0
PPM

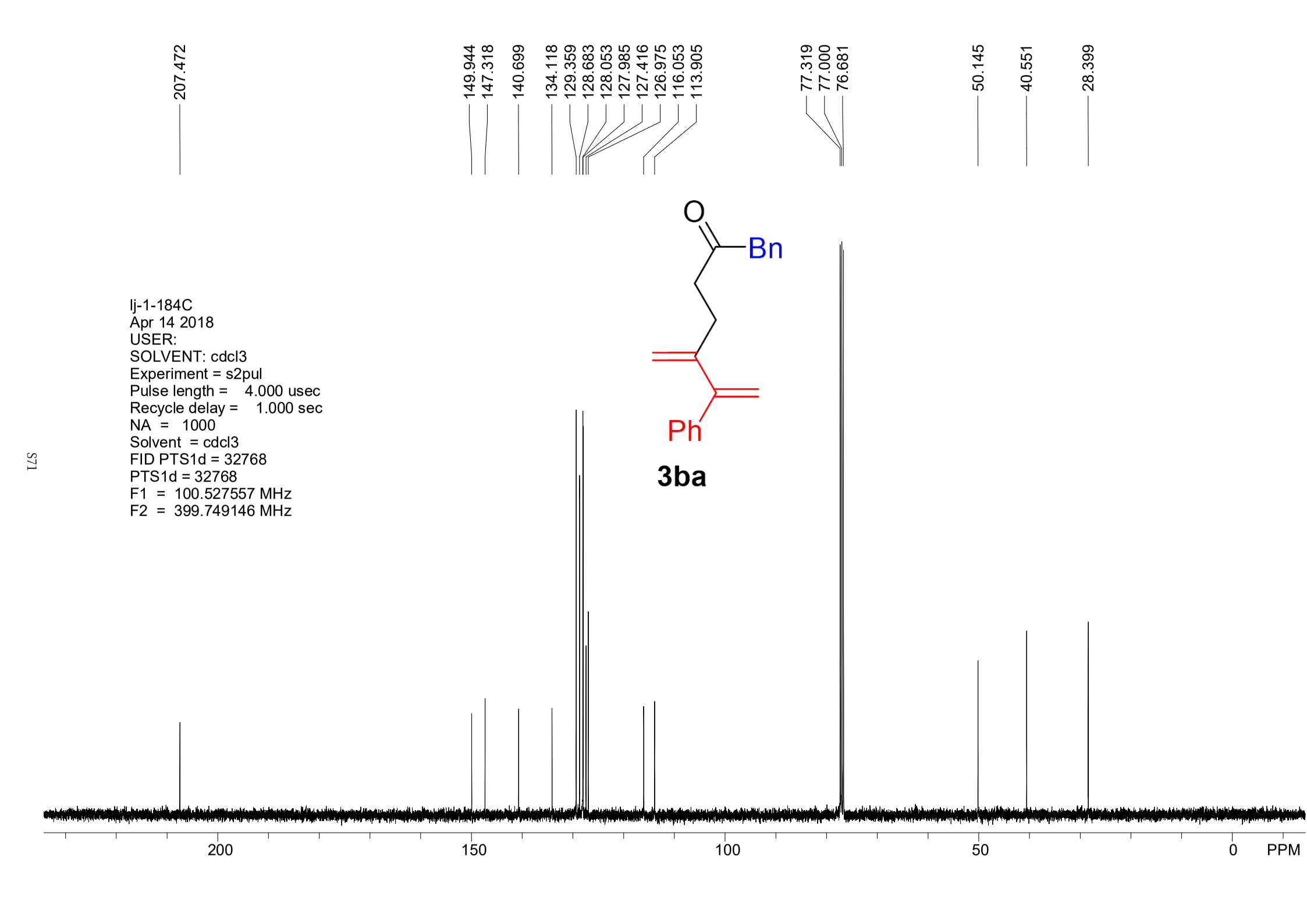


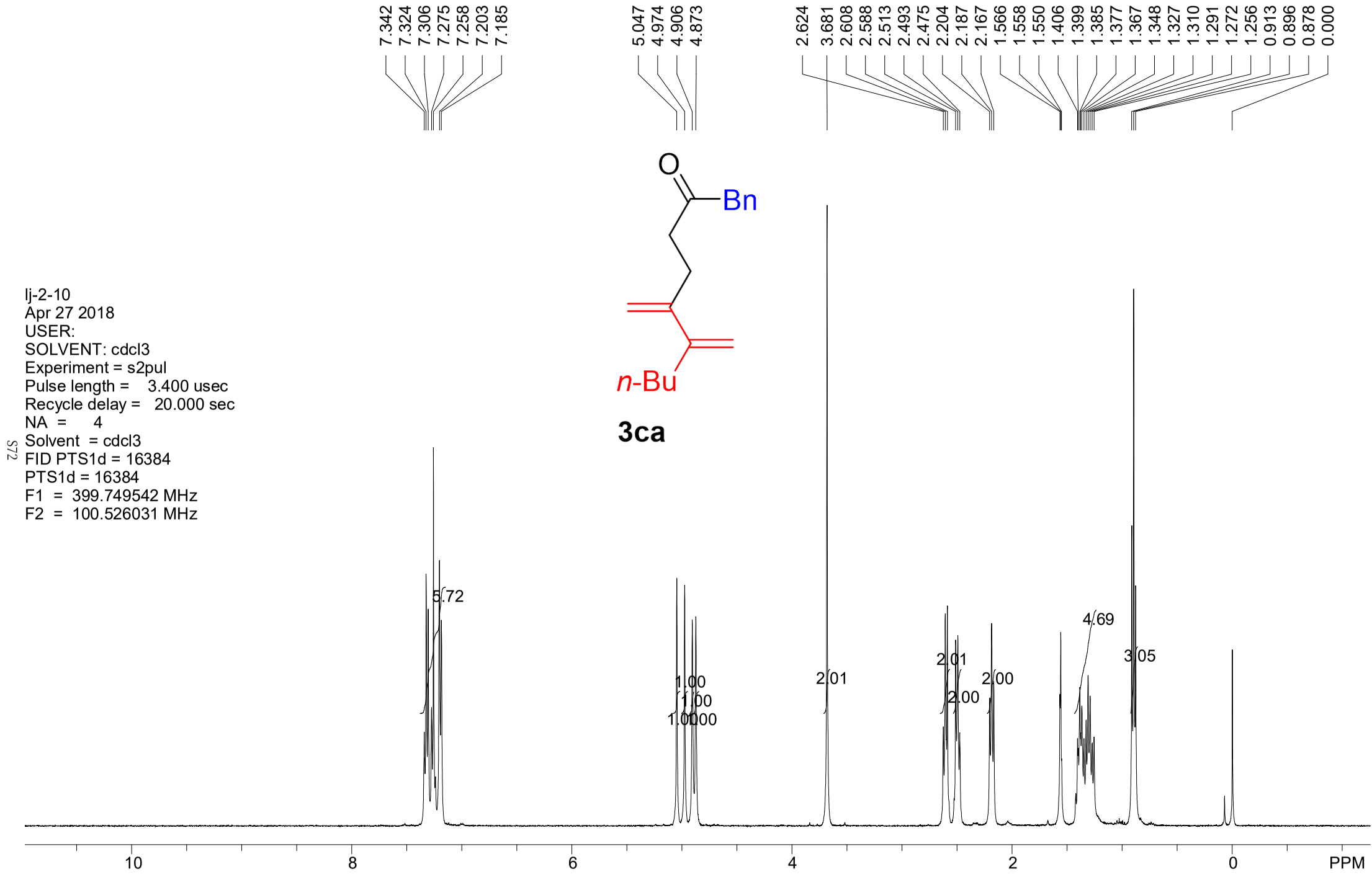
Analyzing with NMR measurement in CDCl3 with mesitylene (46 uL, d = 0.864 g/mL, 39.7 mg) as the internal standard.

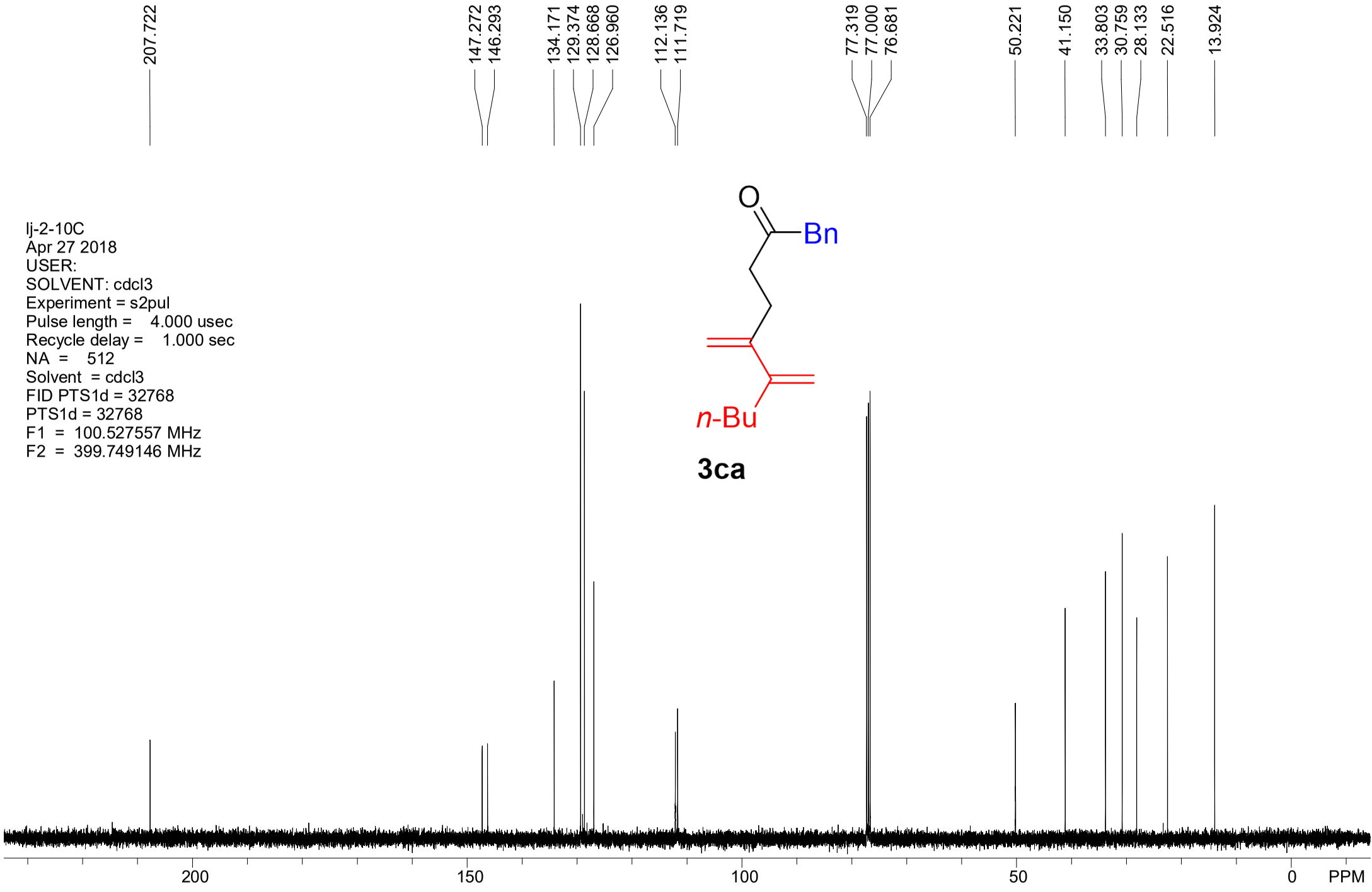
lj-3-114cr
20190301
USER: nmrsu
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz

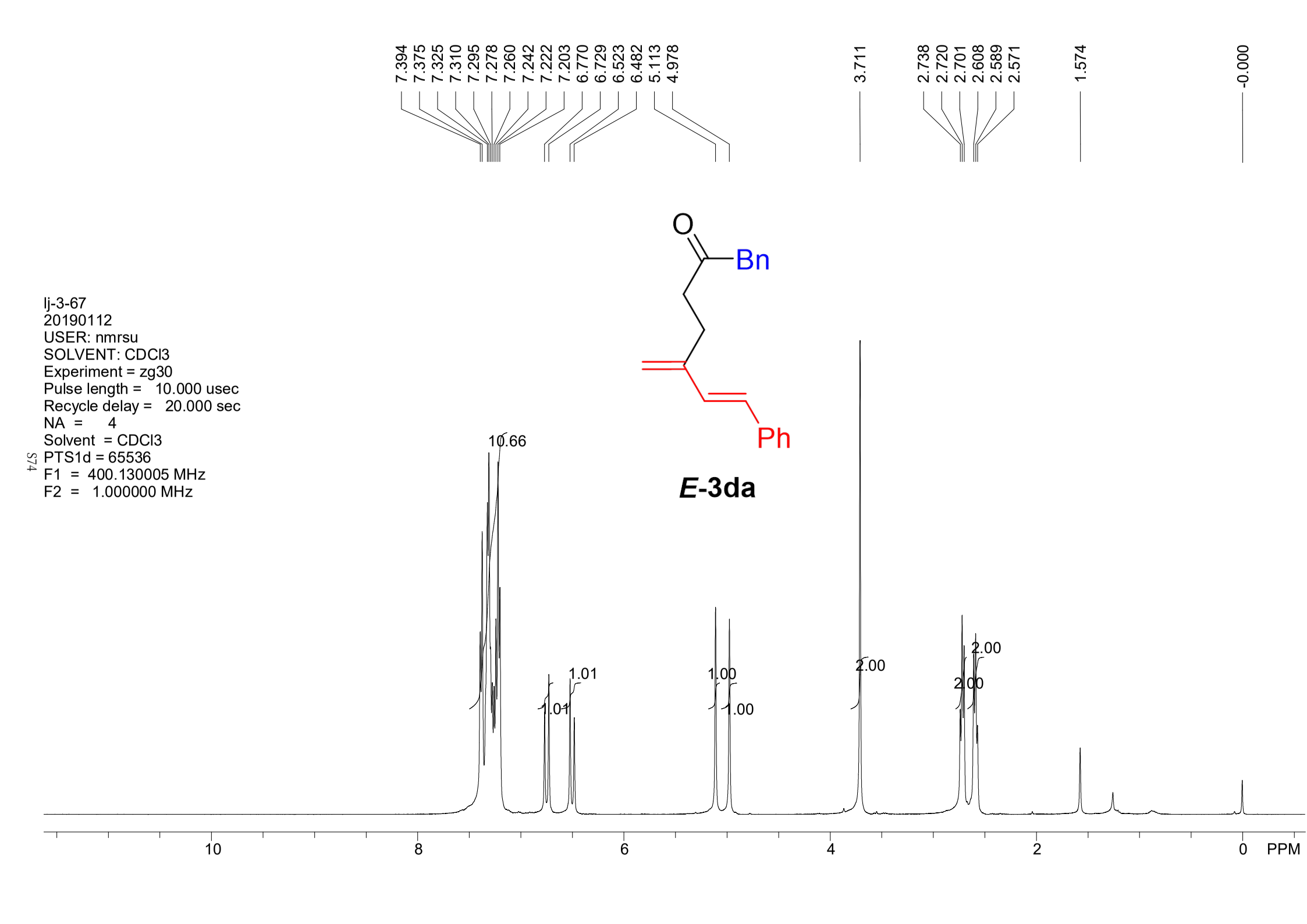


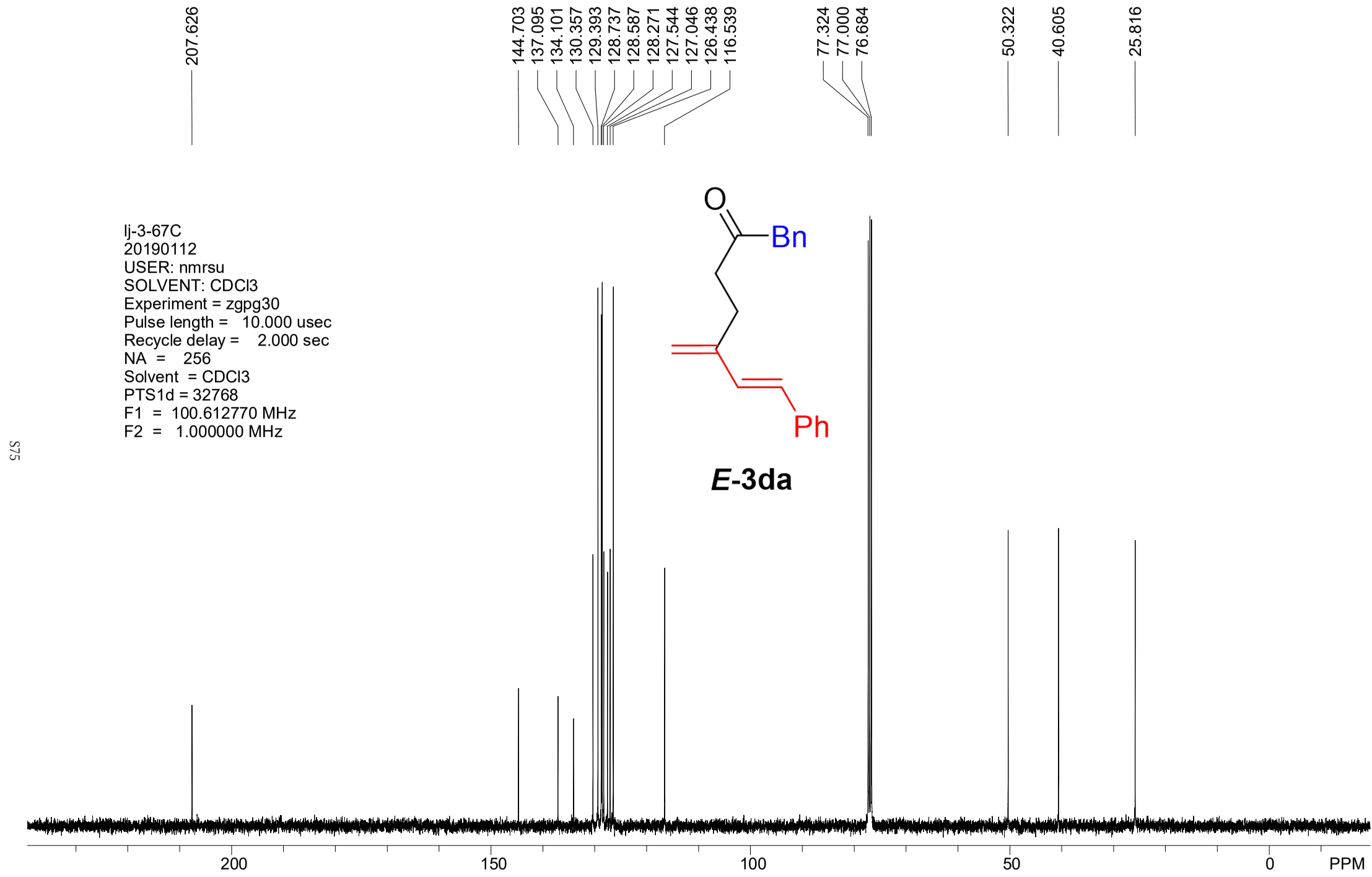

7.334
7.317
7.298
7.286
7.278
7.269
7.254
7.238
7.185
7.168
5.200
5.160
5.022
4.944
3.663
2.635
2.618
2.601
2.534
2.517
2.500
O
Bn
Ph
3ba
lj-1-184
Apr 14 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
S70
8.27
2.02
1.01
1.00
1.00
1.00
2.00
2.00
2.01
10
8
6
4
2
PPM

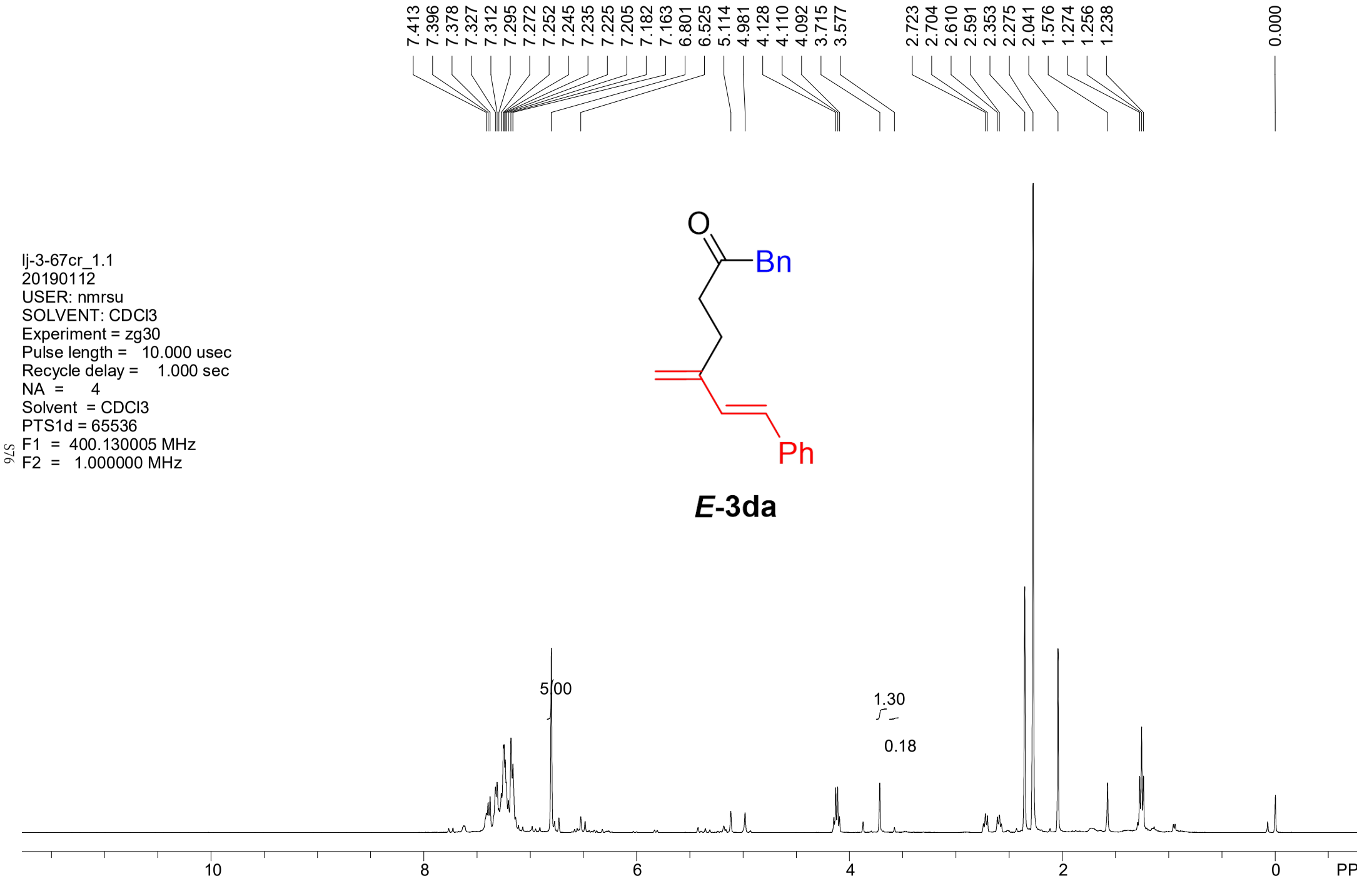

207.472
149.944
147.318
140.699
134.118
129.359
128.683
128.053
127.985
127.416
126.975
116.053
113.905
77.319
77.000
76.681
50.145
40.551
28.399
O
Bn
Ph
3ba
lj-1-184C
Apr 14 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 1000
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
200
150
100
50
0
PPM

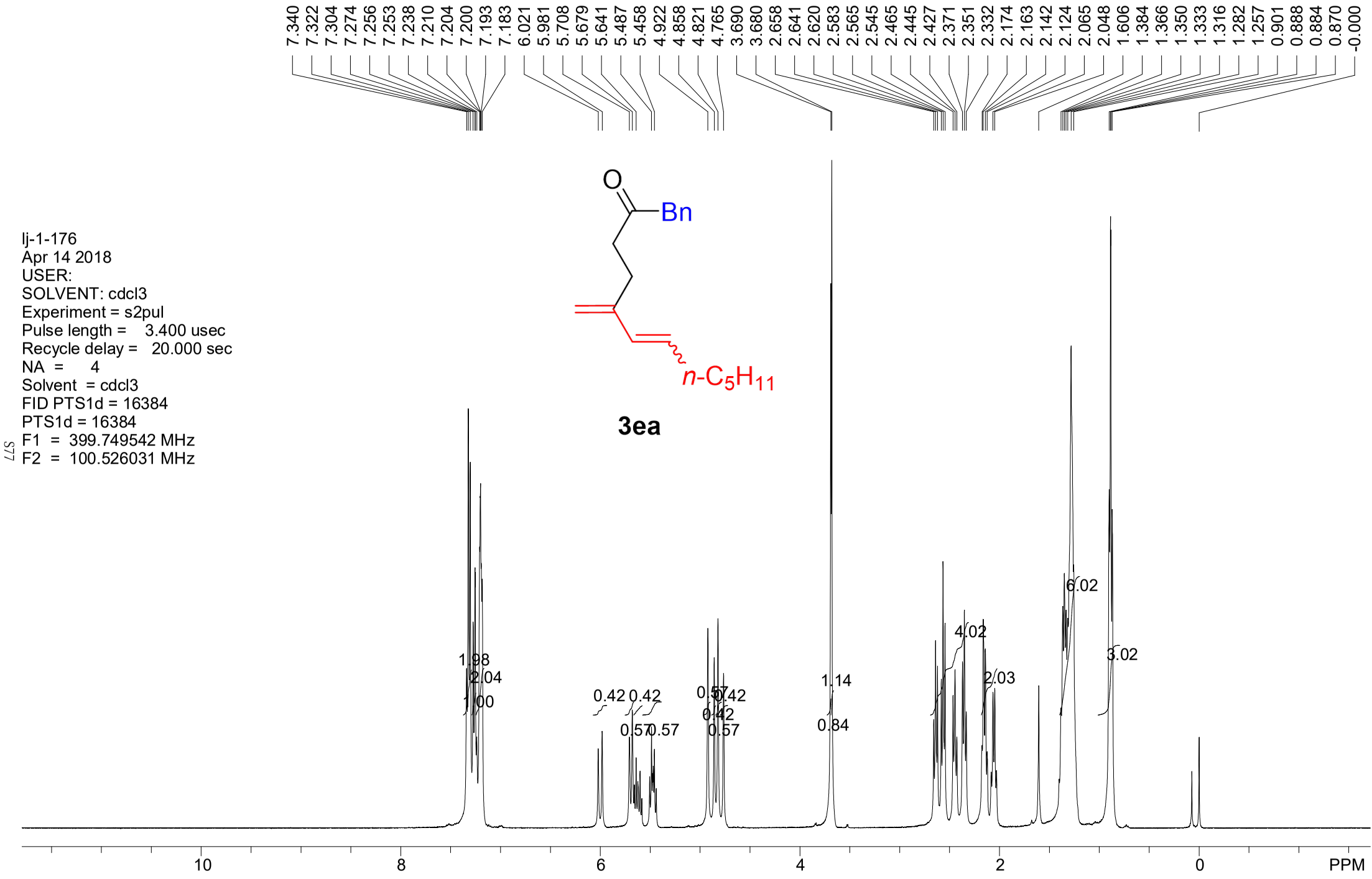

7.342
7.324
7.306
7.275
7.258
7.203
7.185
5.047
4.974
4.906
4.873
2.624
3.681
2.608
2.588
2.513
2.493
2.475
2.204
2.187
2.167
1.566
1.558
1.550
1.406
1.399
1.385
1.377
1.367
1.348
1.327
1.310
1.291
1.272
1.256
0.913
0.896
0.878
0.000
O
Bn
n-Bu
3ca
lj-2-10
Apr 27 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
5.72
1.00
1.00
1.0000
2.01
2.01
2.00
2.00
4.69
3.05
10
8
6
4
2
0
PPM

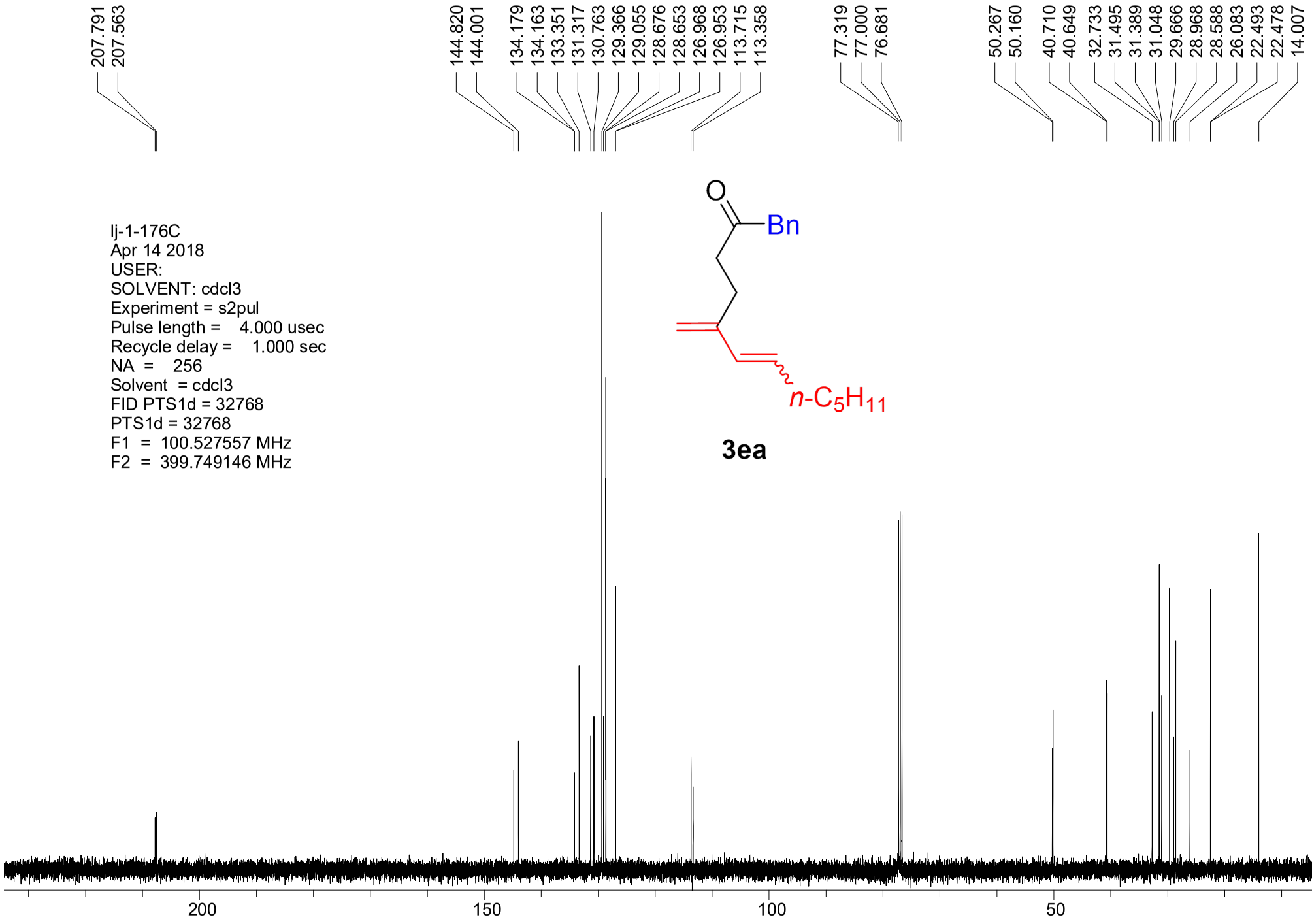

207.722
147.272
146.293
134.171
129.374
128.668
126.960
112.136
111.719
77.319
77.000
76.681
50.221
41.150
33.803
30.759
28.133
22.516
13.924
lj-2-10C
Apr 27 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 512
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
Bn
n-Bu
3ca
200
150
100
50
0
PPM

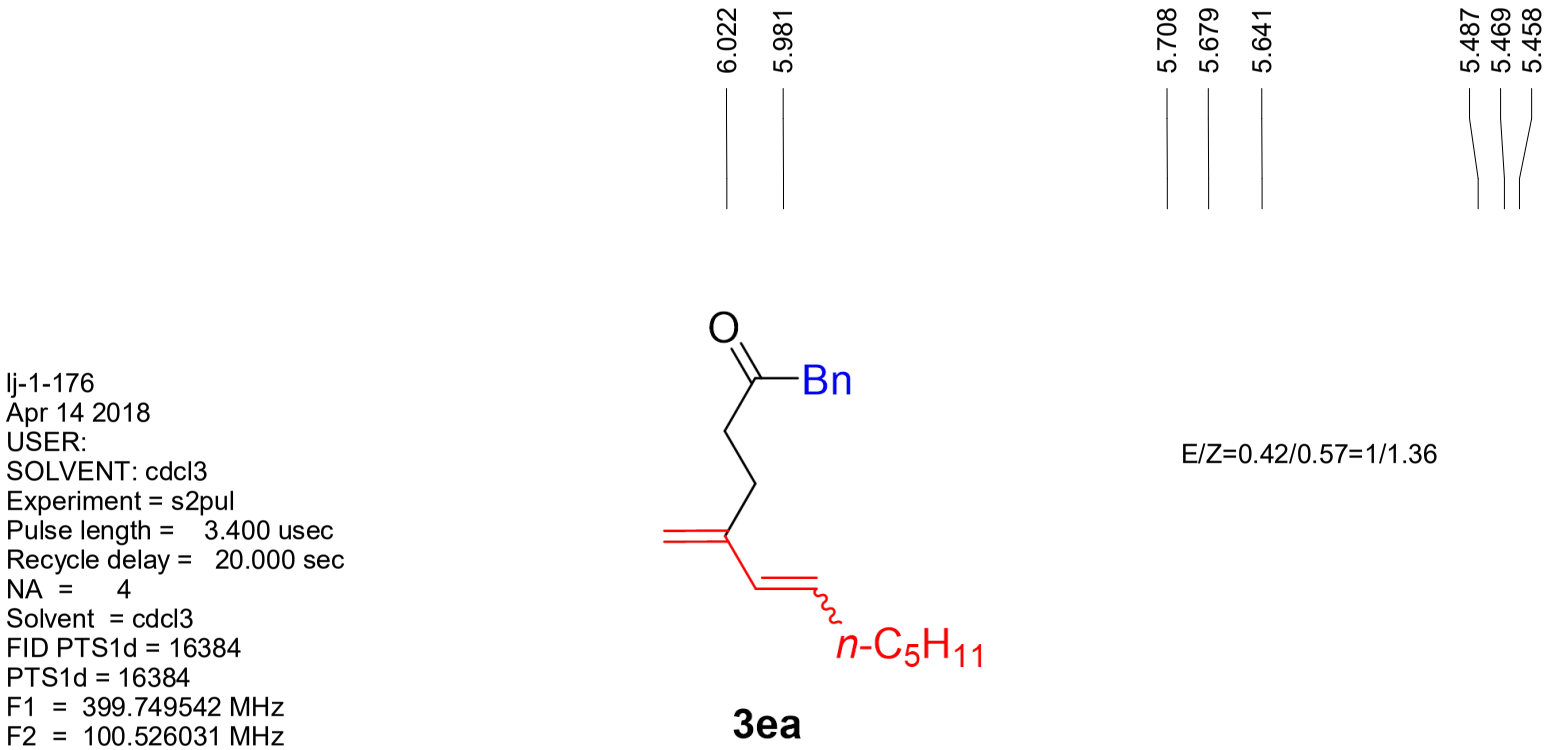

7.394
7.375
7.325
7.310
7.295
7.278
7.260
7.242
7.222
7.203
6.770
6.729
6.523
6.482
5.113
4.978
3.711
2.738
2.720
2.701
2.608
2.589
2.571
1.574
-0.000
lj-3-67
20190112
USER: nmrsu
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
S74
O
Bn
Ph
E-3da
10.66
1.01
1.01
1.00
1.00
2.00
2.00
2.00
10
8
6
4
2
0
PPM

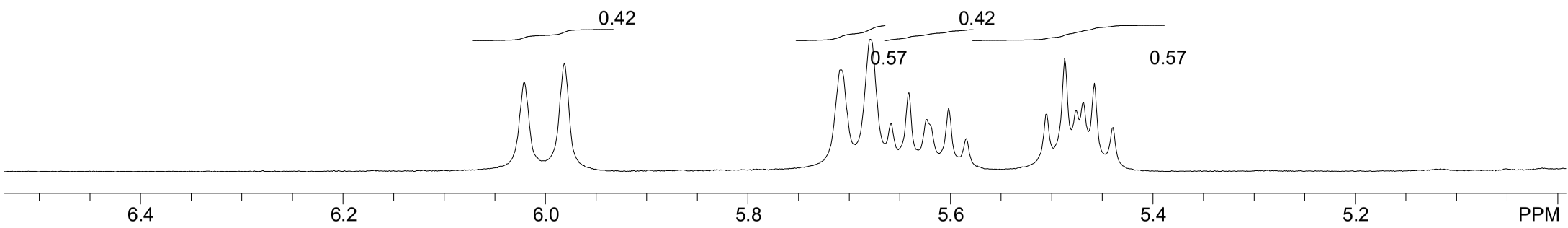

207.626
144.703
137.095
134.101
130.357
129.393
128.737
128.587
128.271
127.544
127.046
126.438
116.539
77.324
77.000
76.684
50.322
40.605
25.816
lj-3-67C
20190112
USER: nmrsu
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 10.000 usec
Recycle delay = 2.000 sec
NA = 256
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
O
Bn
Ph
E-3da
200
150
100
50
0
PPM

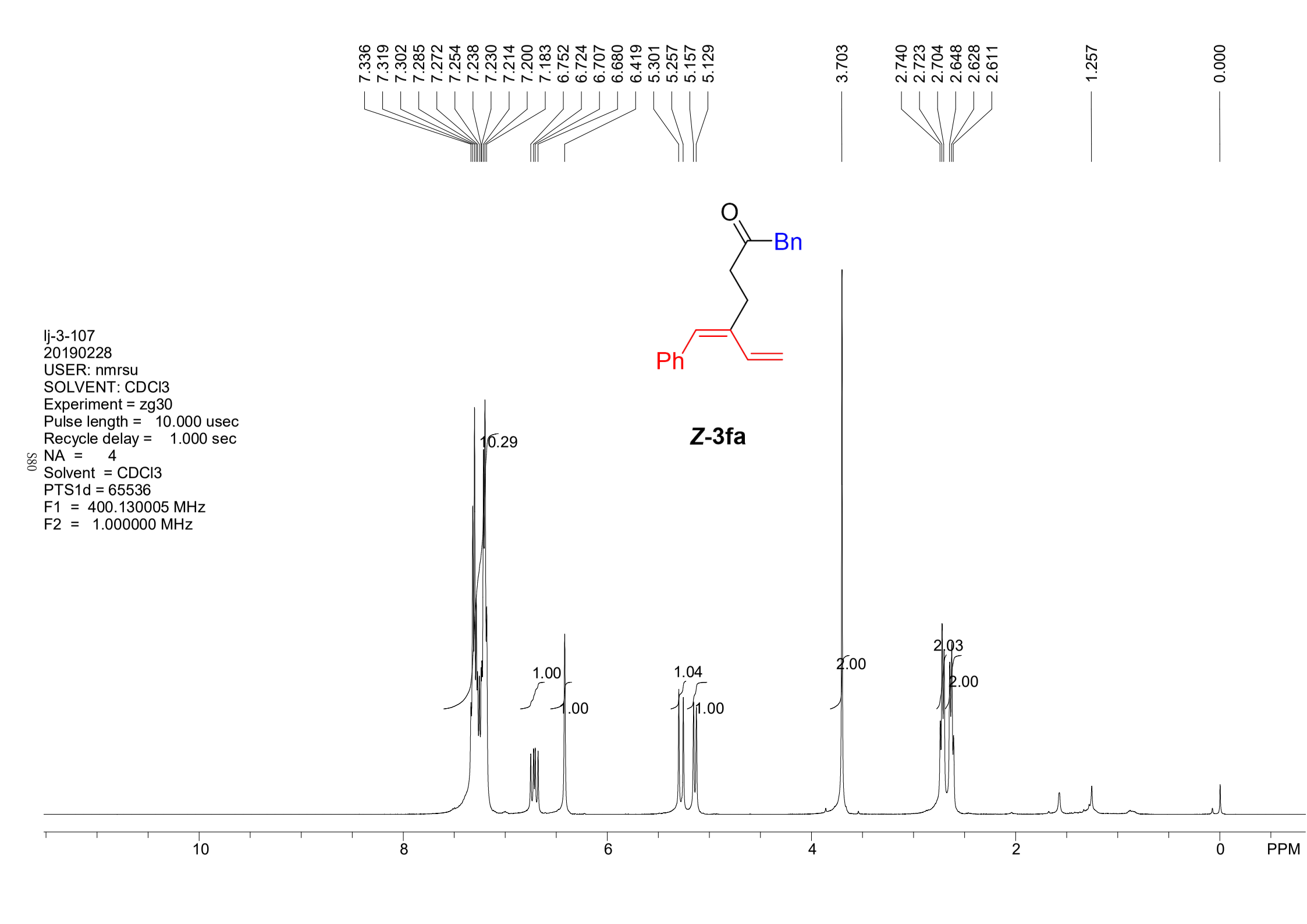

7.413
7.396
7.378
7.327
7.312
7.295
7.272
7.252
7.245
7.235
7.225
7.205
7.182
7.163
6.801
6.525
5.114
4.981
4.128
4.110
4.092
3.715
3.577
2.723
2.704
2.610
2.591
2.353
2.275
2.041
1.576
1.274
1.256
1.238
0.000
lj-3-67cr_1.1
20190112
USER: nmrsu
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
S76
O
Bn
Ph
E-3da
5.00
1.30
0.18
10
8
6
4
2
0
PPM

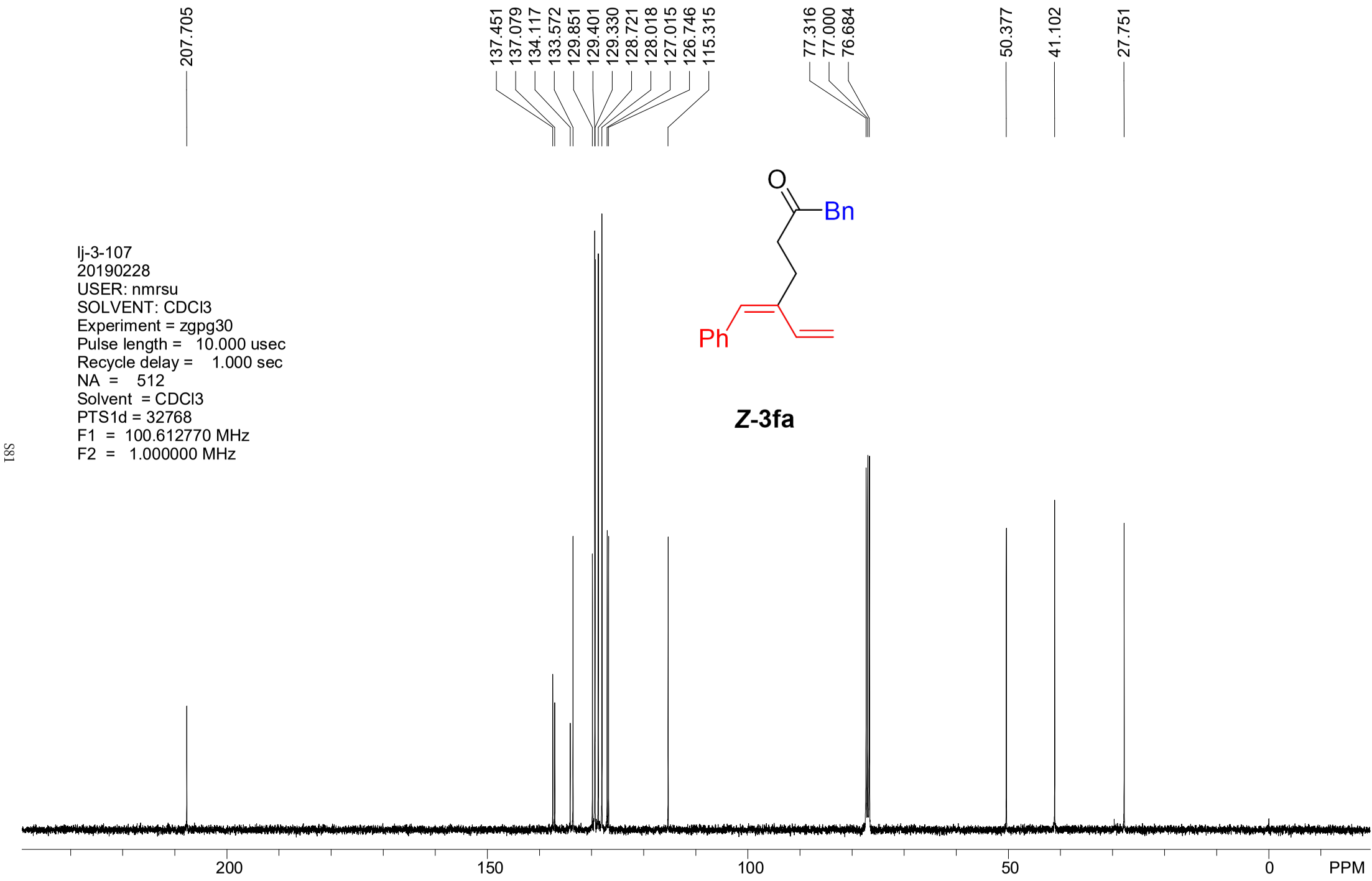

7.340
7.322
7.304
7.274
7.256
7.253
7.238
7.210
7.204
7.200
7.193
7.183
6.021
5.981
5.708
5.679
5.641
5.487
5.458
4.922
4.858
4.821
4.765
3.690
3.680
2.658
2.641
2.620
2.583
2.565
2.545
2.465
2.445
2.427
2.371
2.351
2.332
2.174
2.163
2.142
2.124
2.065
2.048
1.606
1.384
1.366
1.350
1.333
1.316
1.282
1.257
0.901
0.888
0.884
0.870
-0.000
lj-1-176
Apr 14 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
S77
O
Bn
n-C5H11
3ea
1.98
2.04
1.00
0.42
0.42
0.57
0.57
0.57
0.42
0.57
1.14
0.84
4.02
2.03
6.02
3.02
10
8
6
4
2
0
PPM

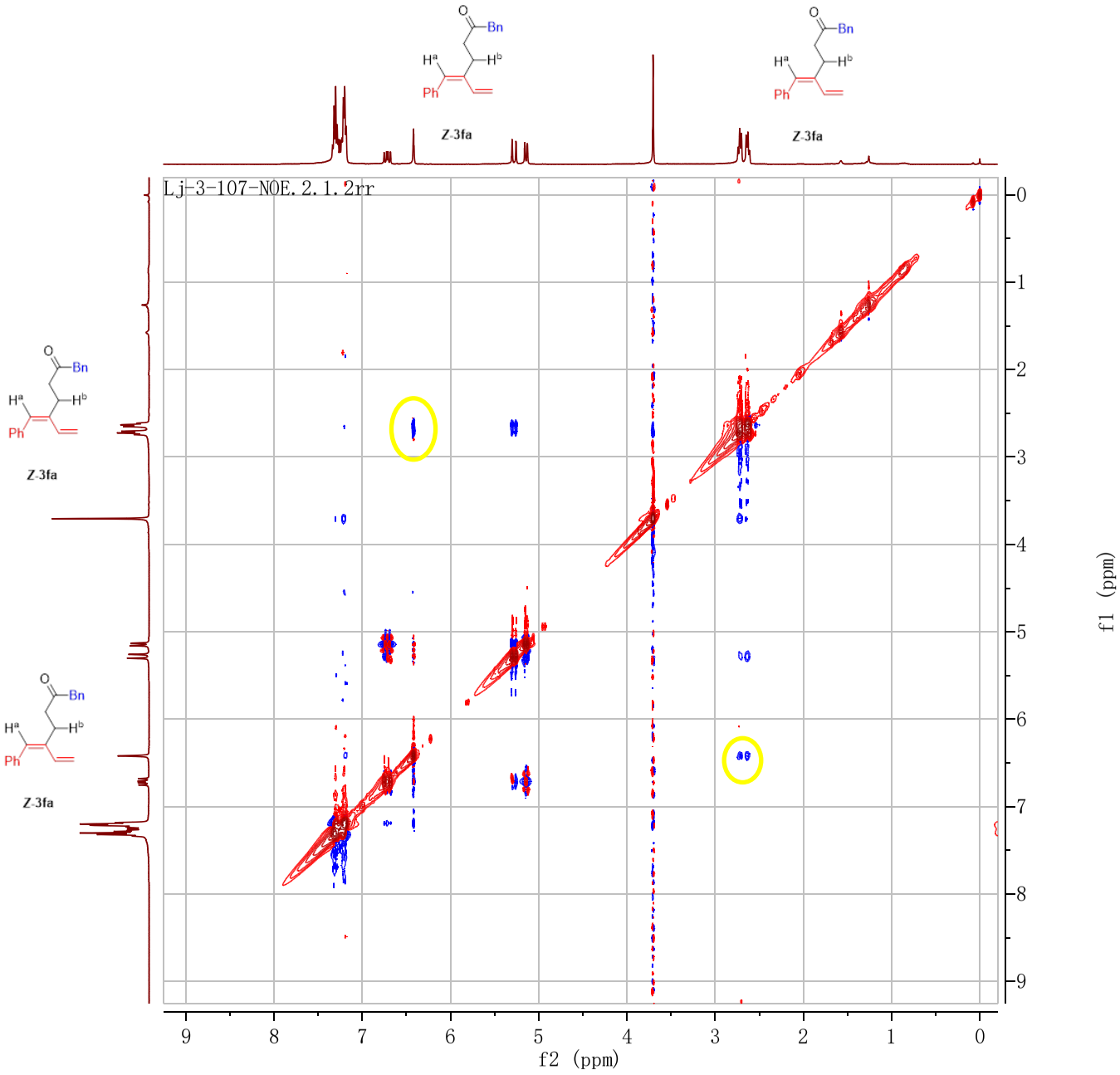

207.791
207.563
144.820
144.001
134.179
134.163
133.351
131.317
130.763
129.366
129.055
128.676
128.653
126.968
126.953
113.715
113.358
77.319
77.000
76.681
50.267
50.160
40.710
40.649
32.733
31.495
31.389
31.048
29.666
28.968
28.588
26.083
22.493
22.478
14.007
lj-1-176C
Apr 14 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 256
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
Bn
n-C5H11
3ea
200
150
100
50
0
PPM


6.022
5.981
5.708
5.679
5.641
5.487
5.469
5.458
lj-1-176
Apr 14 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
O
Bn
n-C5H11
3ea
E/Z=0.42/0.57=1/1.36

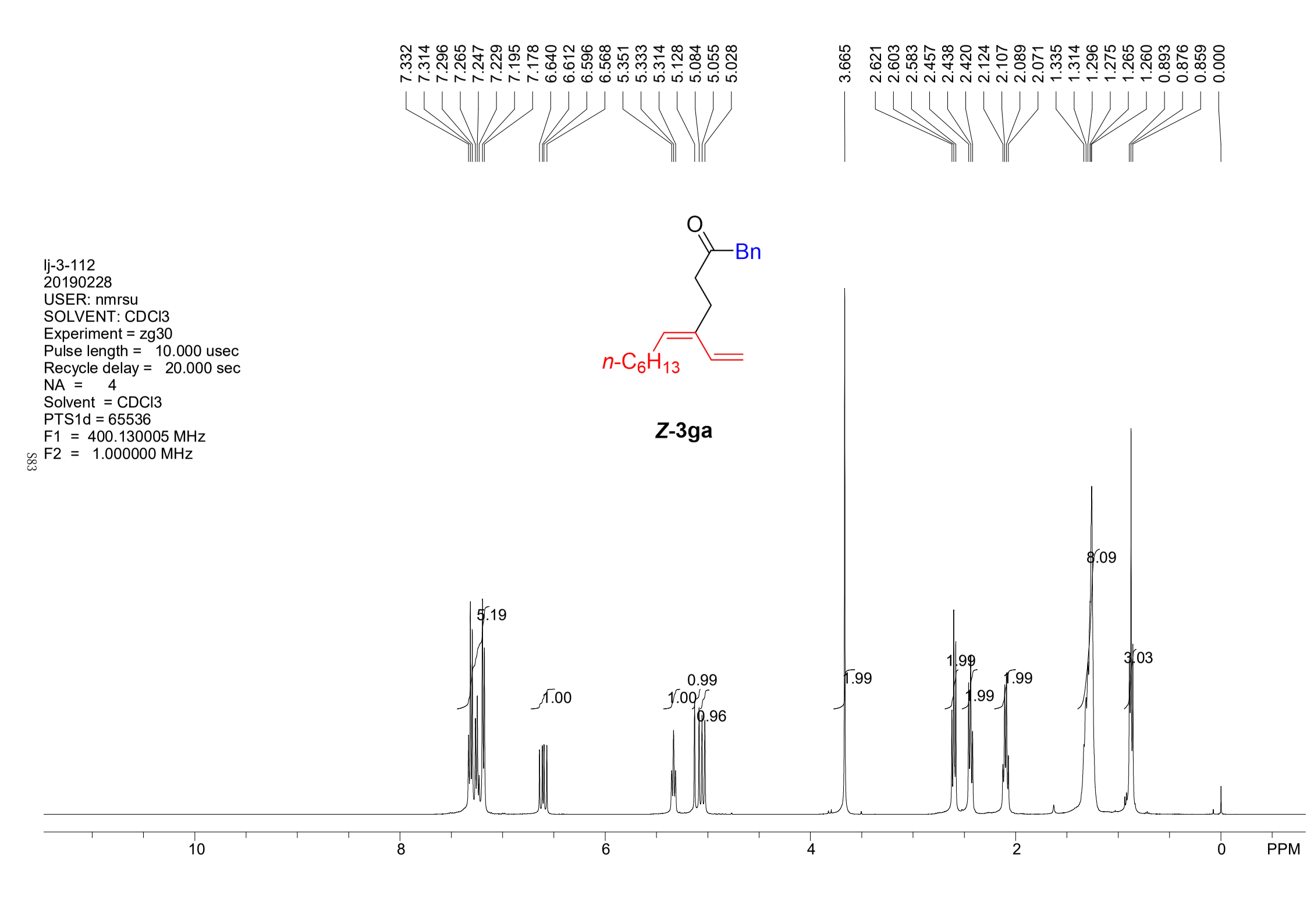

0.42
0.42
0.57
0.57
6.4
6.2
6.0
5.8
5.6
5.4
5.2
PPM

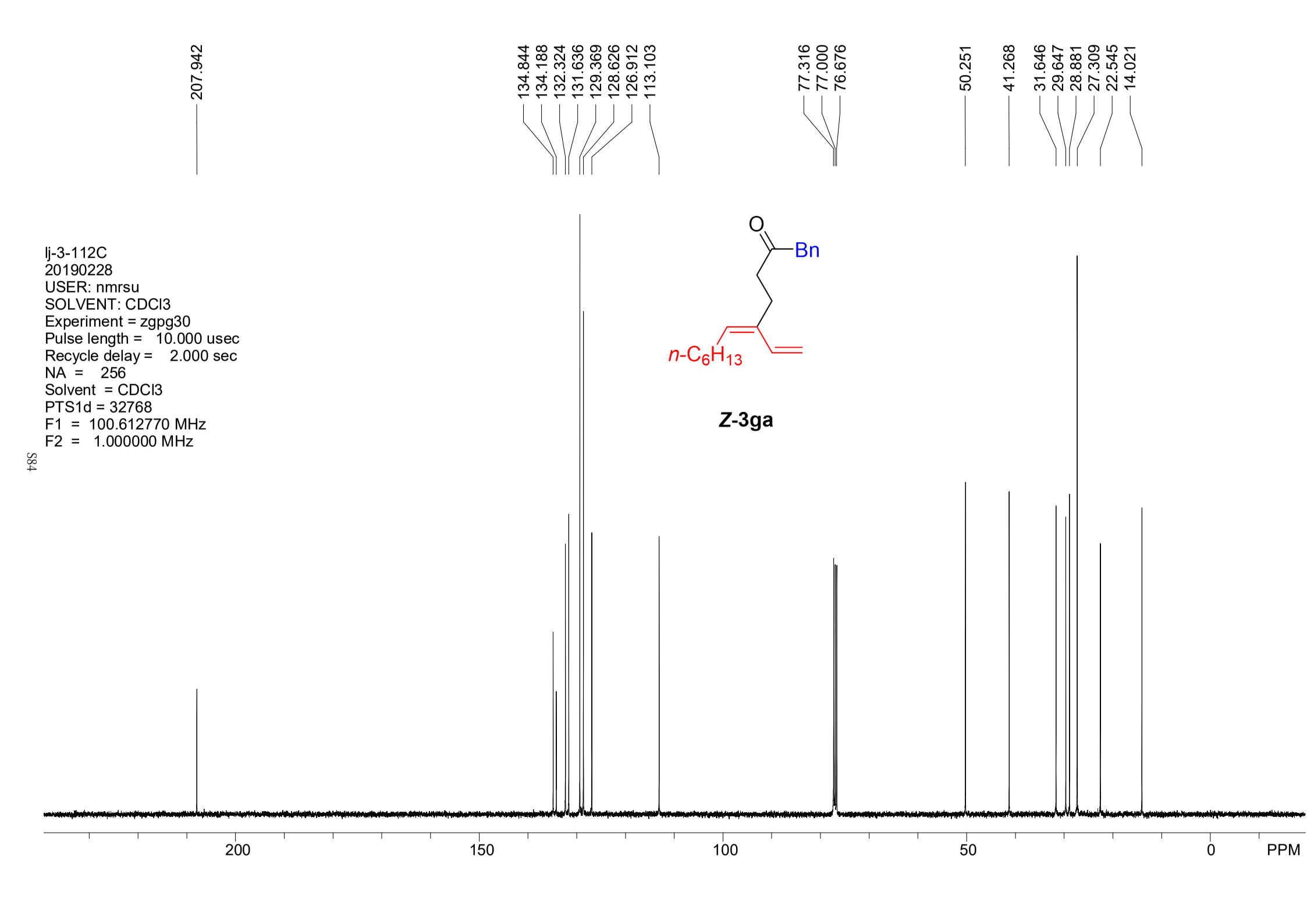

7.336
7.319
7.302
7.285
7.272
7.254
7.238
7.230
7.214
7.200
7.183
6.752
6.724
6.707
6.680
6.419
5.301
5.257
5.157
5.129
3.703
2.740
2.723
2.704
2.648
2.628
2.611
1.257
0.000
O
Bn
Ph
Z-3fa
lj-3-107
20190228
USER: nmrsu
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
S80
10.29
1.00
1.00
1.04
1.00
2.00
2.03
2.00
10
8
6
4
2
0
PPM

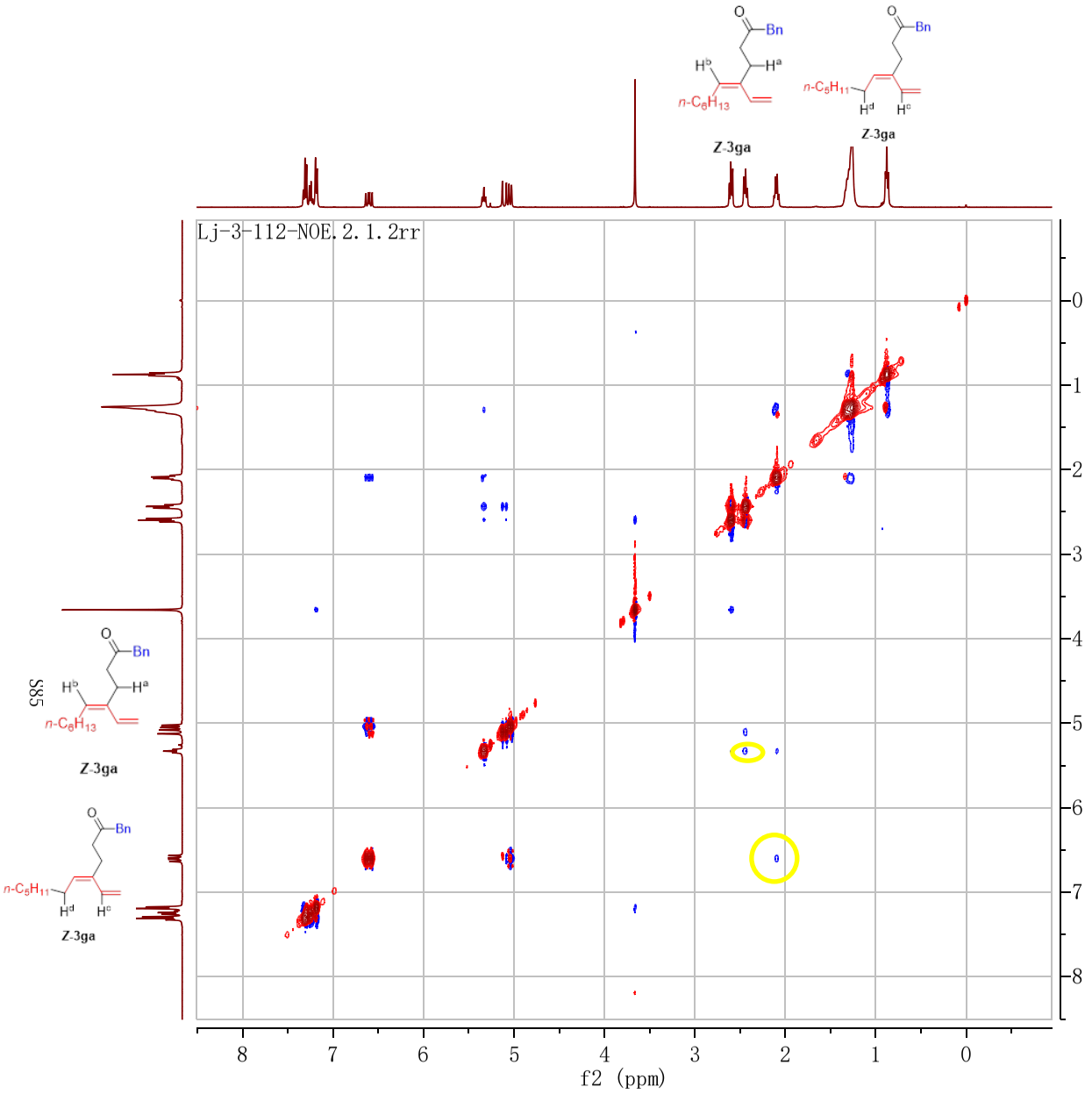

207.705
137.451
137.079
134.117
133.572
129.851
129.401
129.330
128.721
128.018
127.015
126.746
115.315
77.316
77.000
76.684
50.377
41.102
27.751
lj-3-107
20190228
USER: nmrsu
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
O
Bn
Ph
Z-3fa
200
150
100
50
0
PPM



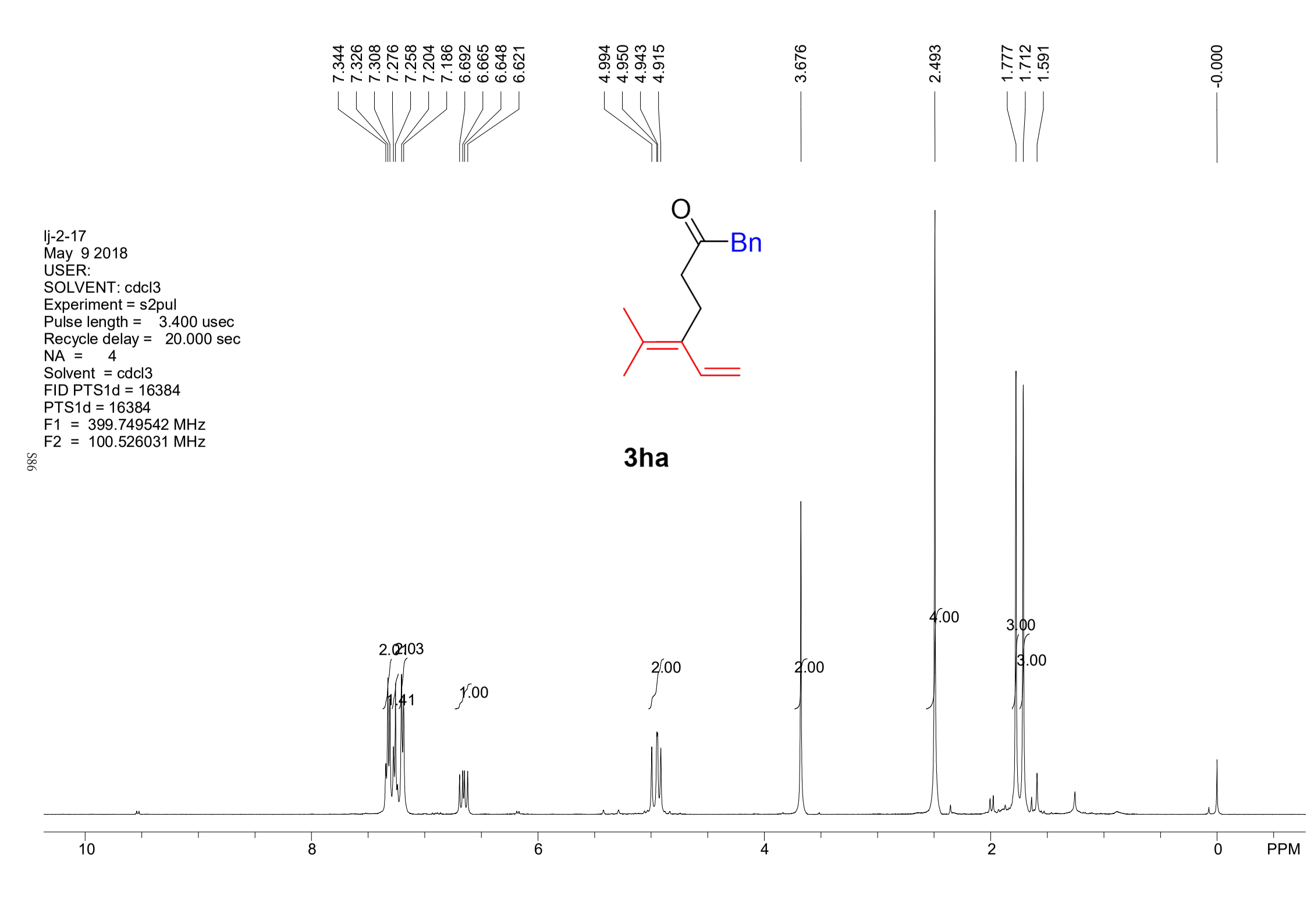
	Parameter	Value
1	Title	Lj-3-107-NOE.2.1.2rr
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Pulse Sequence	noesygpphpp
6	Experiment	NOESY
7	Number of Scans	4
8	Receiver Gain	32
9	Relaxation Delay	1.9857
10	Pulse Width	10.0000
11	Acquisition Time	0.2703
12	Spectrometer Frequency	(400.13, 400.13)
13	Spectral Width	(3787.9, 3787.9)
14	Lowest Frequency	(-84.4, -84.4)
15	Nucleus	(1H, 1H)
16	Acquired Size	(1024, 256)
17	Spectral Size	(1024, 1024)

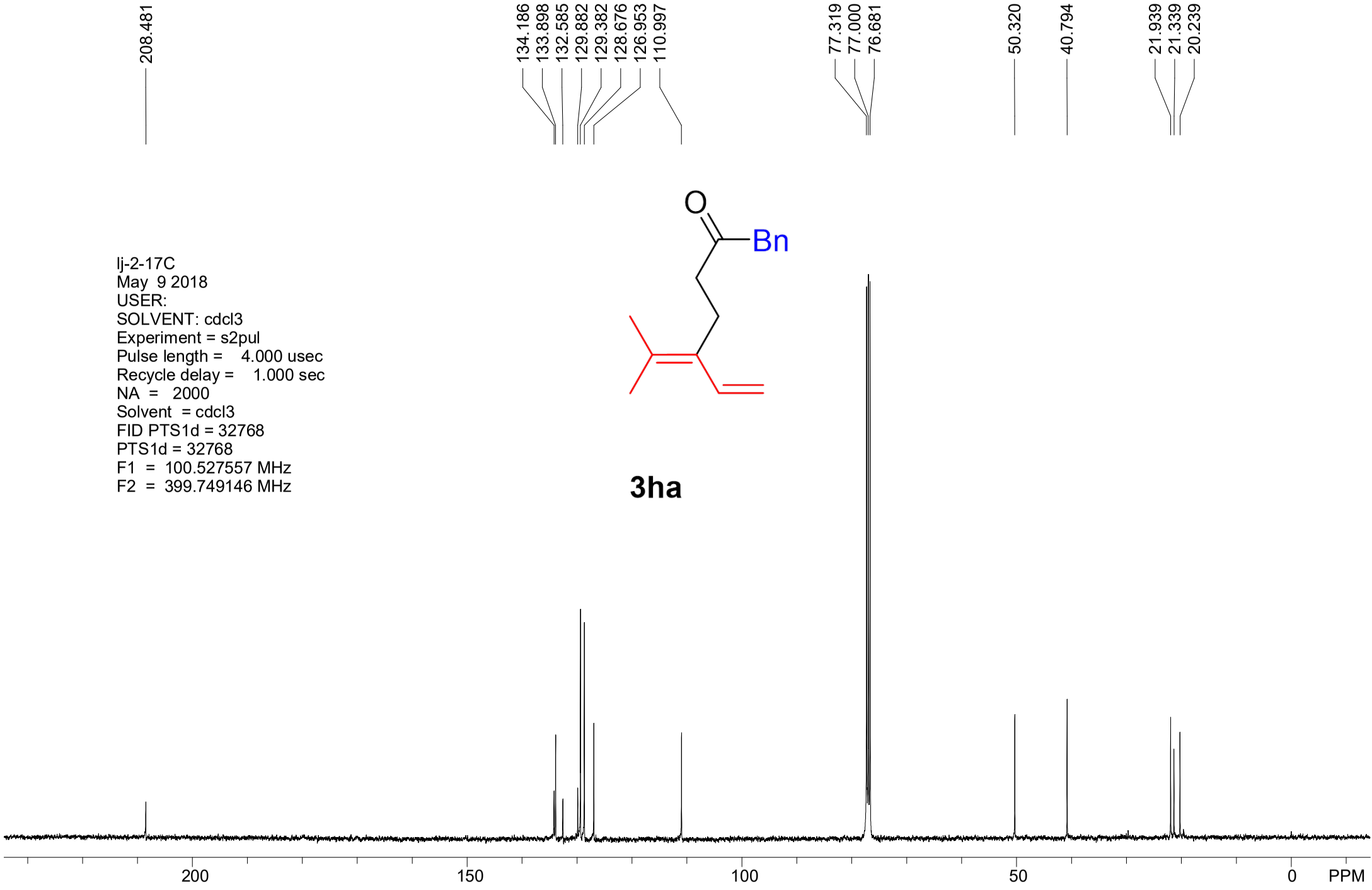

7.332
7.314
7.296
7.265
7.247
7.229
7.195
7.178
6.640
6.612
6.596
6.568
5.351
5.333
5.314
5.128
5.084
5.055
5.028
3.665
2.621
2.603
2.583
2.457
2.438
2.420
2.124
2.107
2.089
2.071
1.335
1.314
1.296
1.275
1.265
1.260
0.893
0.876
0.859
0.000
lj-3-112
20190228
USER: nmrsu
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
O
Bn
n-C6H13
Z-3ga
5.19
1.00
0.99
1.00
0.96
1.99
1.99
1.99
1.99
8.09
3.03
10
8
6
4
2
0
PPM

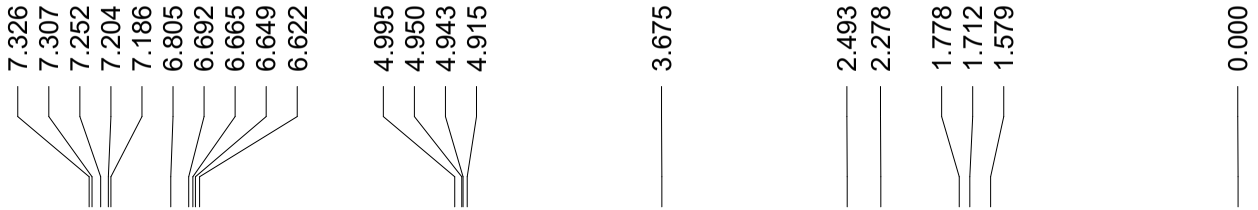

207.942
134.844
134.188
132.324
131.636
129.369
128.626
126.912
113.103
77.316
77.000
76.676
50.251
41.268
31.646
29.647
28.881
27.309
22.545
14.021
lj-3-112C
20190228
USER: nmrsu
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 10.000 usec
Recycle delay = 2.000 sec
NA = 256
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
O
Bn
n-C6H13
Z-3ga
200
150
100
50
0
PPM



	Parameter	Value
1	Title	Lj-3-112-NOE.2.1.2rr
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Pulse Sequence	noesygpphpp
6	Experiment	NOESY
7	Number of Scans	4
8	Receiver Gain	8
9	Relaxation Delay	1.9857
10	Pulse Width	10.0000
11	Acquisition Time	0.2703
12	Spectrometer Frequency	(400.13, 400.13)
13	Spectral Width	(3787.9, 3787.9)
14	Lowest Frequency	(-383.8, -383.8)
15	Nucleus	(1H, 1H)
16	Acquired Size	(1024, 256)
17	Spectral Size	(1024, 1024)

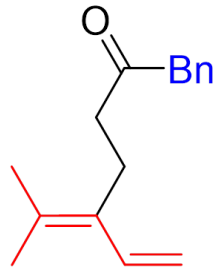

7.344
7.326
7.308
7.276
7.258
7.204
7.186
6.692
6.665
6.648
6.621
4.994
4.950
4.943
4.915
3.676
2.493
1.777
1.712
1.591
-0.000
lj-2-17
May 9 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
S86
O
Bn
3ha
2.03
1.41
1.00
2.00
2.00
4.00
3.00
3.00
10
8
6
4
2
0
PPM


208.481
134.186
133.898
132.585
129.882
129.382
128.676
126.953
110.997
77.319
77.000
76.681
50.320
40.794
21.939
21.339
20.239
lj-2-17C
May 9 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 2000
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
Bn
3ha
200
150
100
50
0
PPM

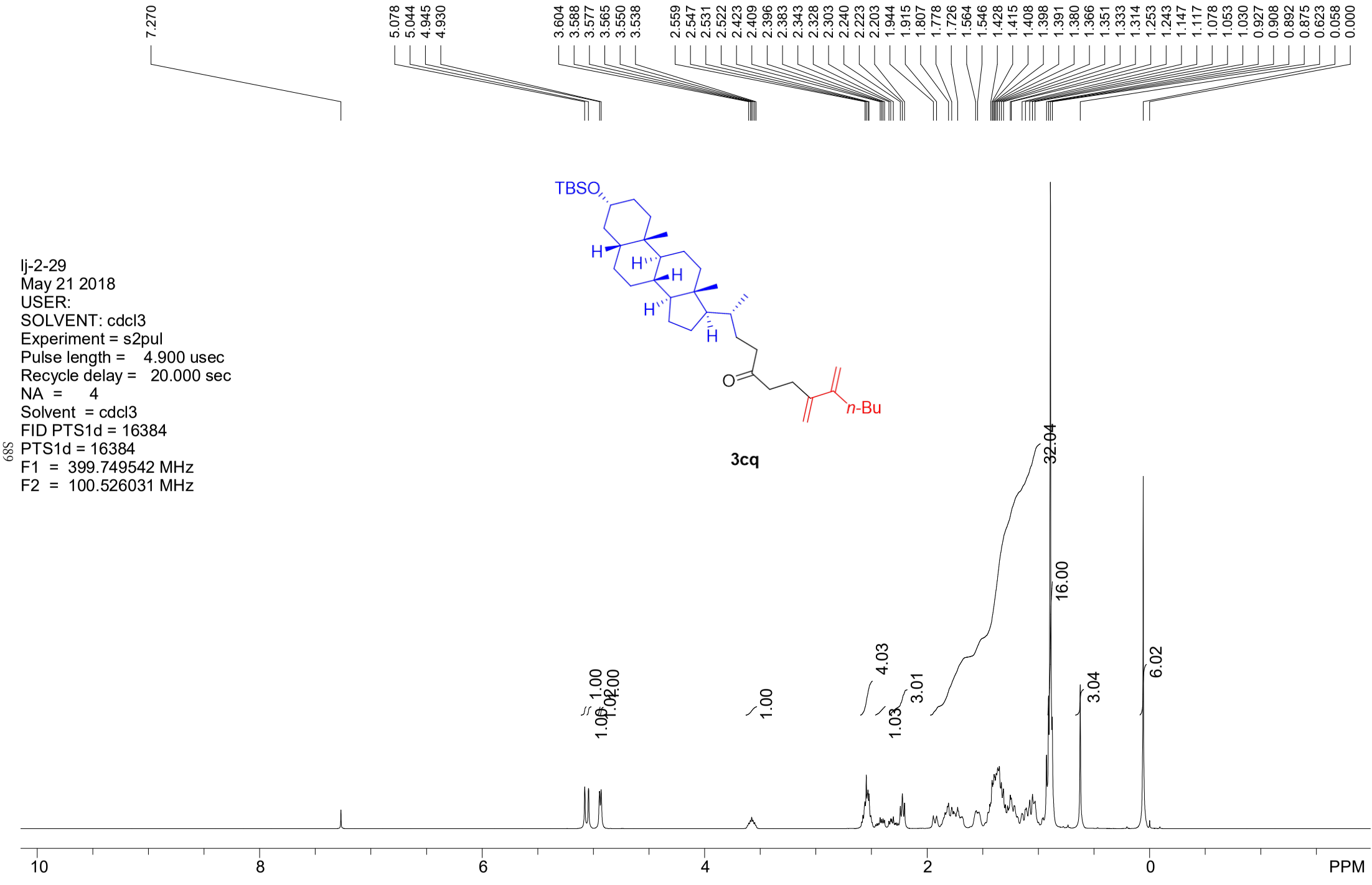


Purity was determined to be 94% by using 3.8 mg mesitylene as the internal standard in 8.3 mg sample.

lj-2-17-purity
May 9 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz

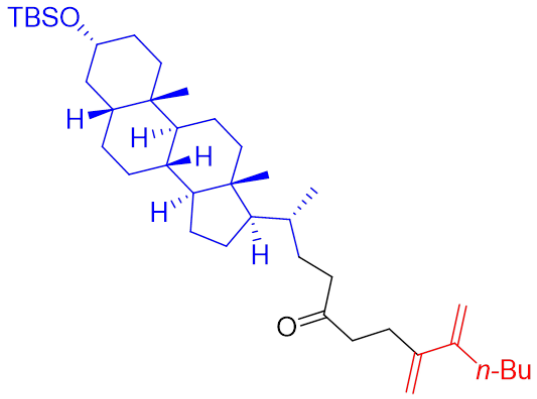


3ha

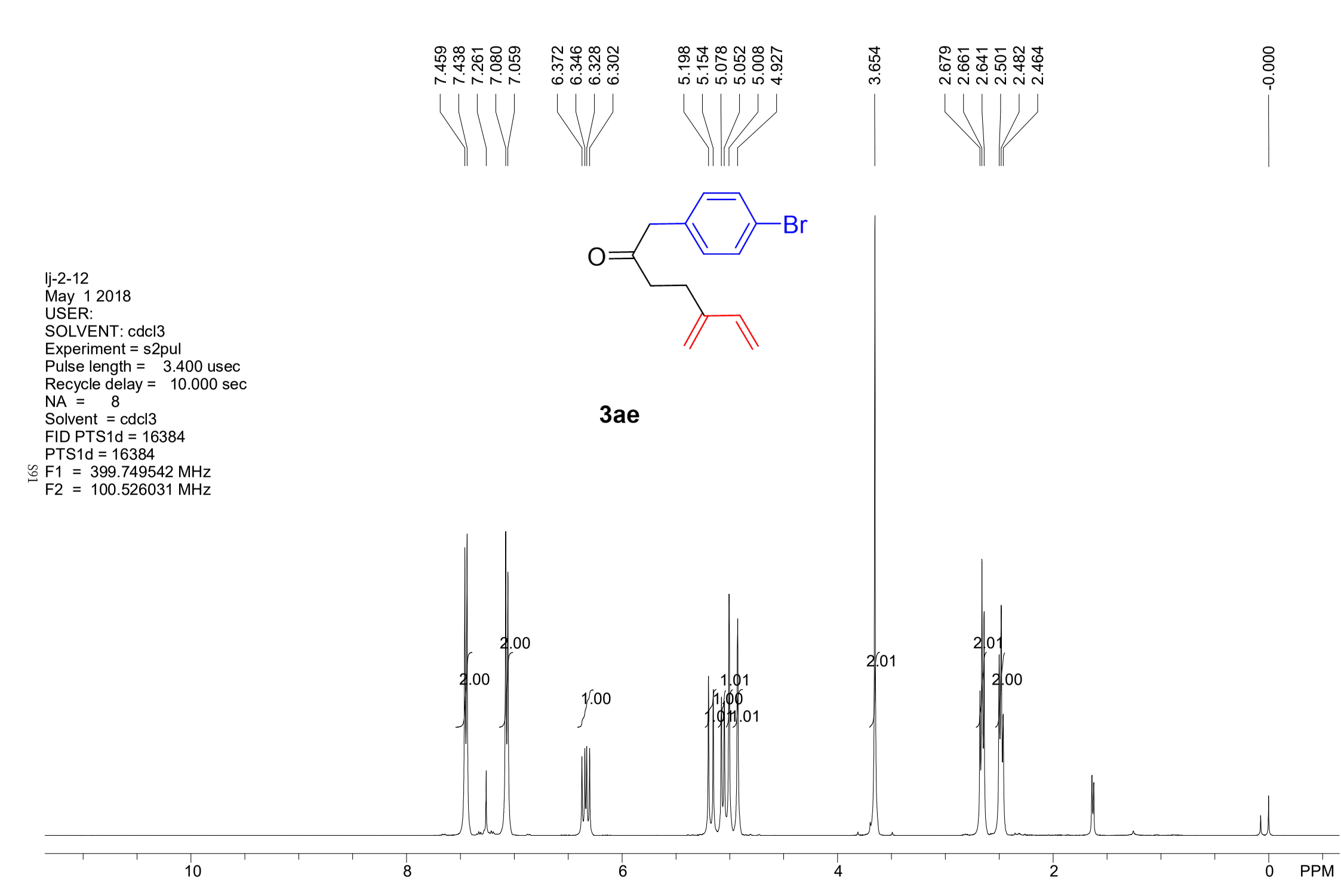

7.270
5.078
5.044
4.945
4.930
3.604
3.588
3.577
3.565
3.550
3.538
2.559
2.547
2.531
2.522
2.423
2.409
2.396
2.383
2.343
2.328
2.303
2.240
2.223
2.203
1.944
1.915
1.807
1.778
1.726
1.564
1.546
1.428
1.415
1.408
1.398
1.391
1.380
1.366
1.351
1.333
1.314
1.253
1.243
1.147
1.117
1.078
1.053
1.030
0.927
0.908
0.892
0.875
0.623
0.058
0.000
TBSO
H
H
H
H
H
O
n-Bu
3cq
lj-2-29
May 21 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.900 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
S89
1.00
1.00
1.00
1.00
1.03
4.03
3.01
32.04
16.00
3.04
6.02
10
8
6
4
2
0
PPM

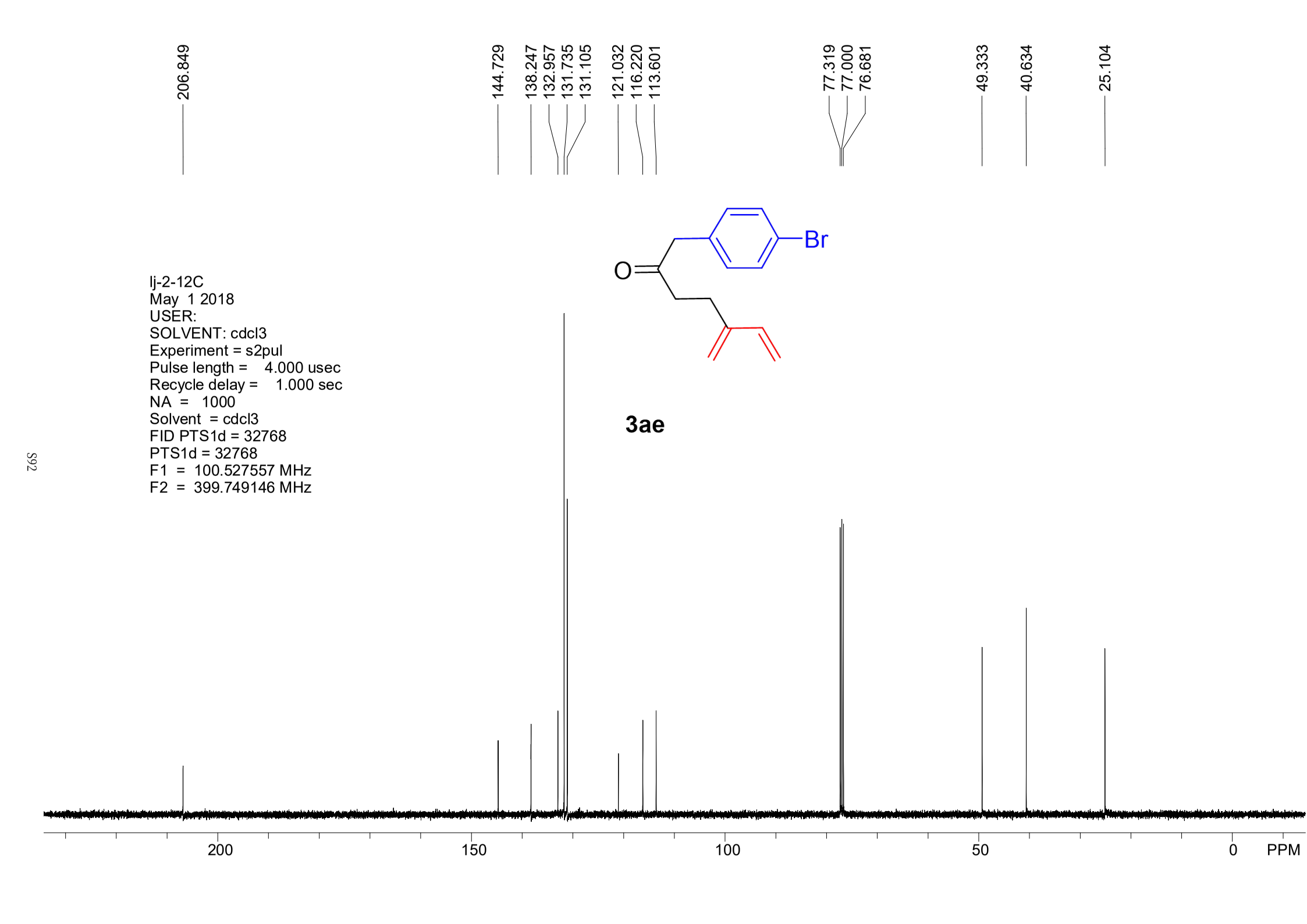
211.199
147.295
146.475
112.075
111.726
77.319
77.000
76.681
72.795
56.362
55.929
42.661
42.243
41.856
40.148
40.095
39.769
36.869
35.814
35.541
35.260
34.539
33.841
30.987
30.797
29.750
28.186
27.260
26.364
25.947
24.178
23.358
22.554
20.763
18.394
18.303
13.962
11.980
-4.635

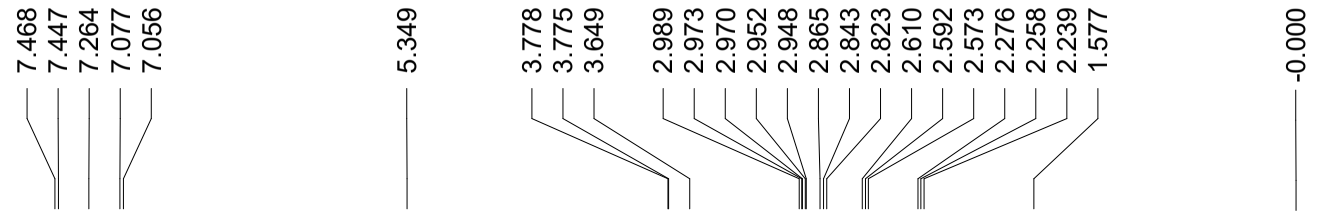
lj-2-29C
May 21 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 5.300 usec
Recycle delay = 1.000 sec
NA = 2000
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz

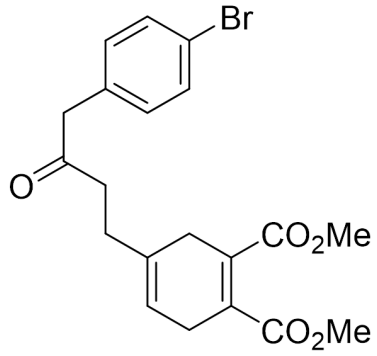


3cq


7.459
7.438
7.261
7.080
7.059
6.372
6.346
6.328
6.302
5.198
5.154
5.078
5.052
5.008
4.927
3.654
2.679
2.661
2.641
2.501
2.482
2.464
-0.000
Br
O
lj-2-12
May 1 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 10.000 sec
NA = 8
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
3ae
2.00
2.00
1.00
1.01
1.00
1.01
1.01
2.01
2.01
2.00
10
8
6
4
2
0
PPM


206.849
144.729
138.247
132.957
131.735
131.105
121.032
116.220
113.601
77.319
77.000
76.681
49.333
40.634
25.104
Br
O
lj-2-12C
May 1 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.000 usec
Recycle delay = 1.000 sec
NA = 1000
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
3ae
200
150
100
50
0
PPM





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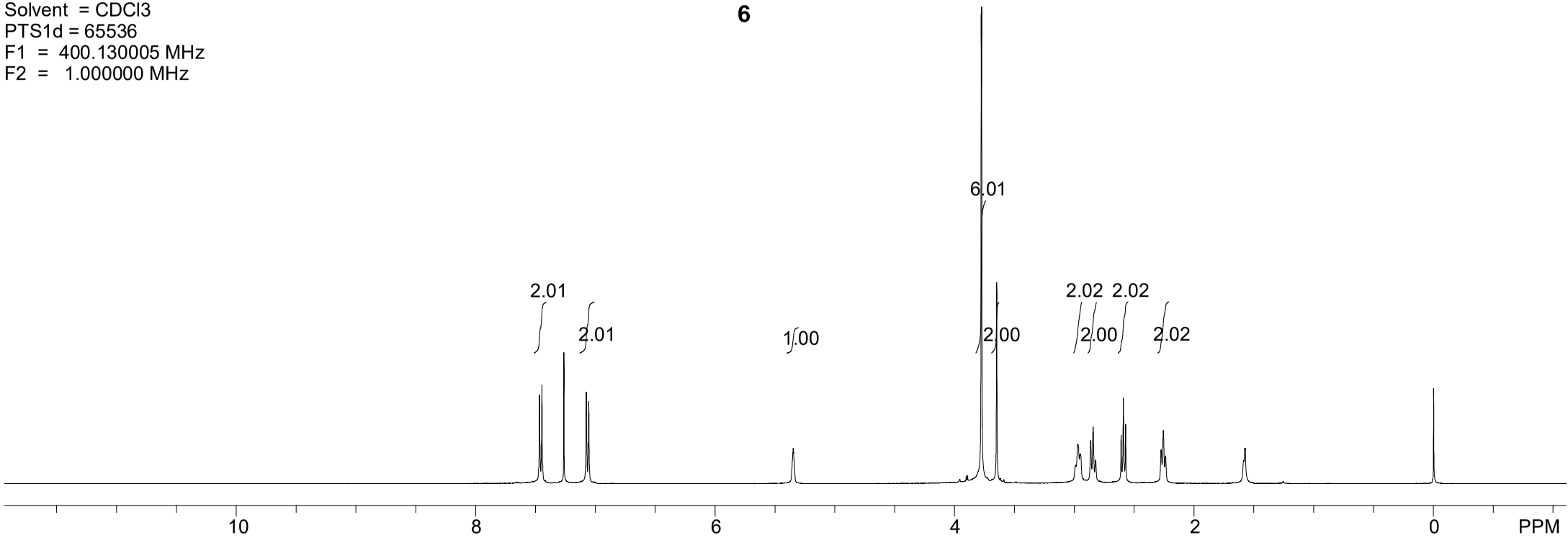
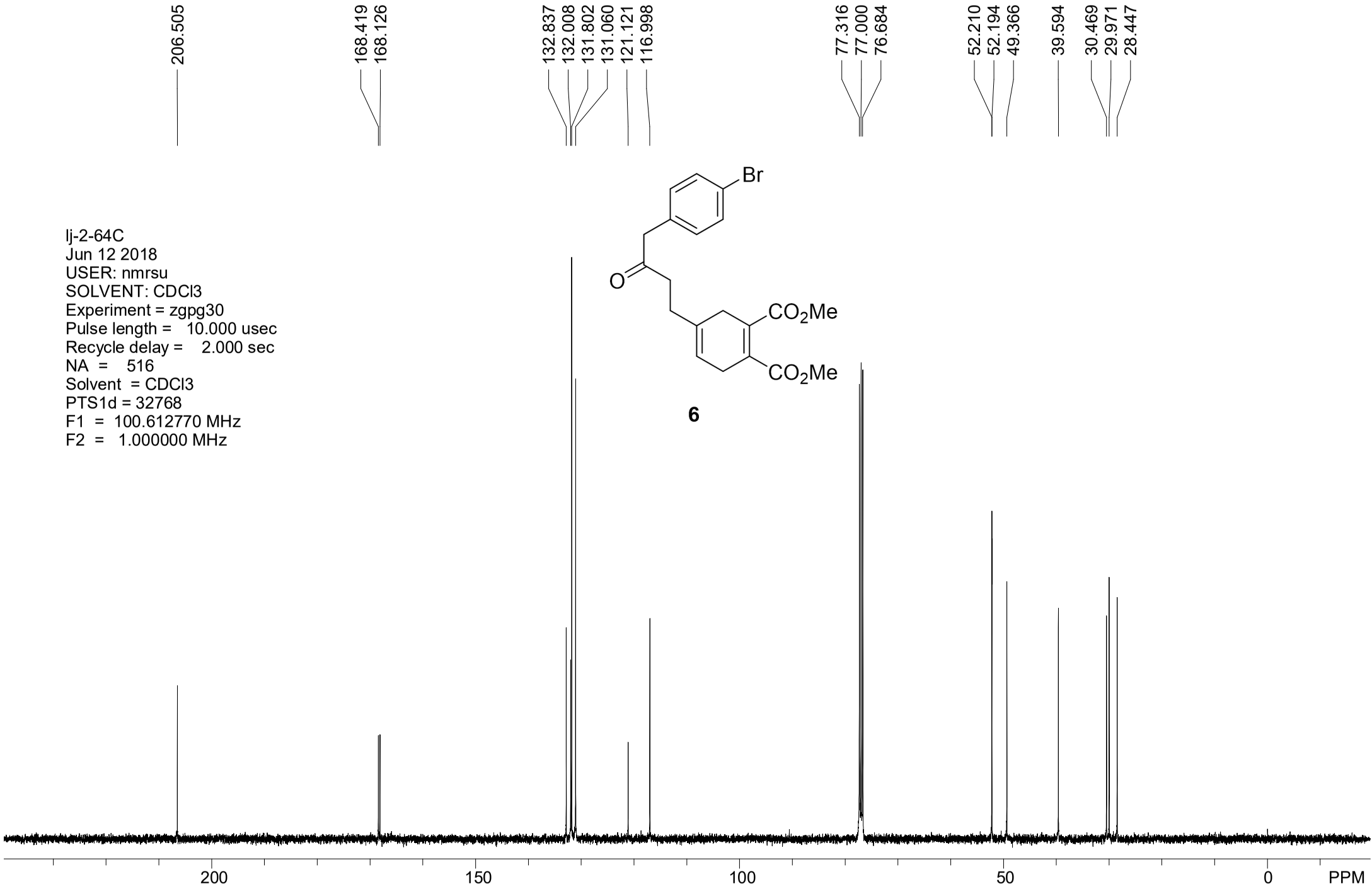
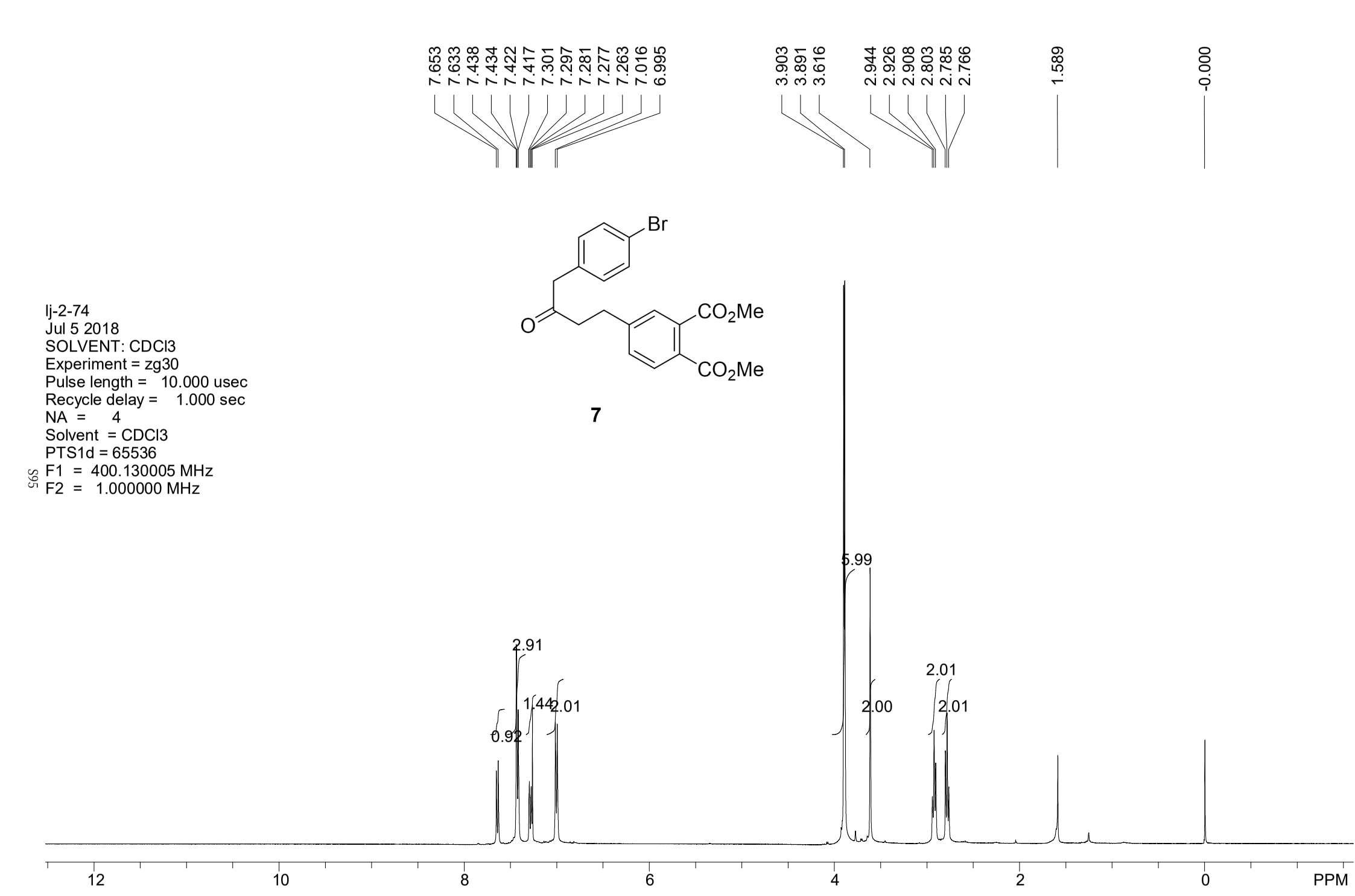
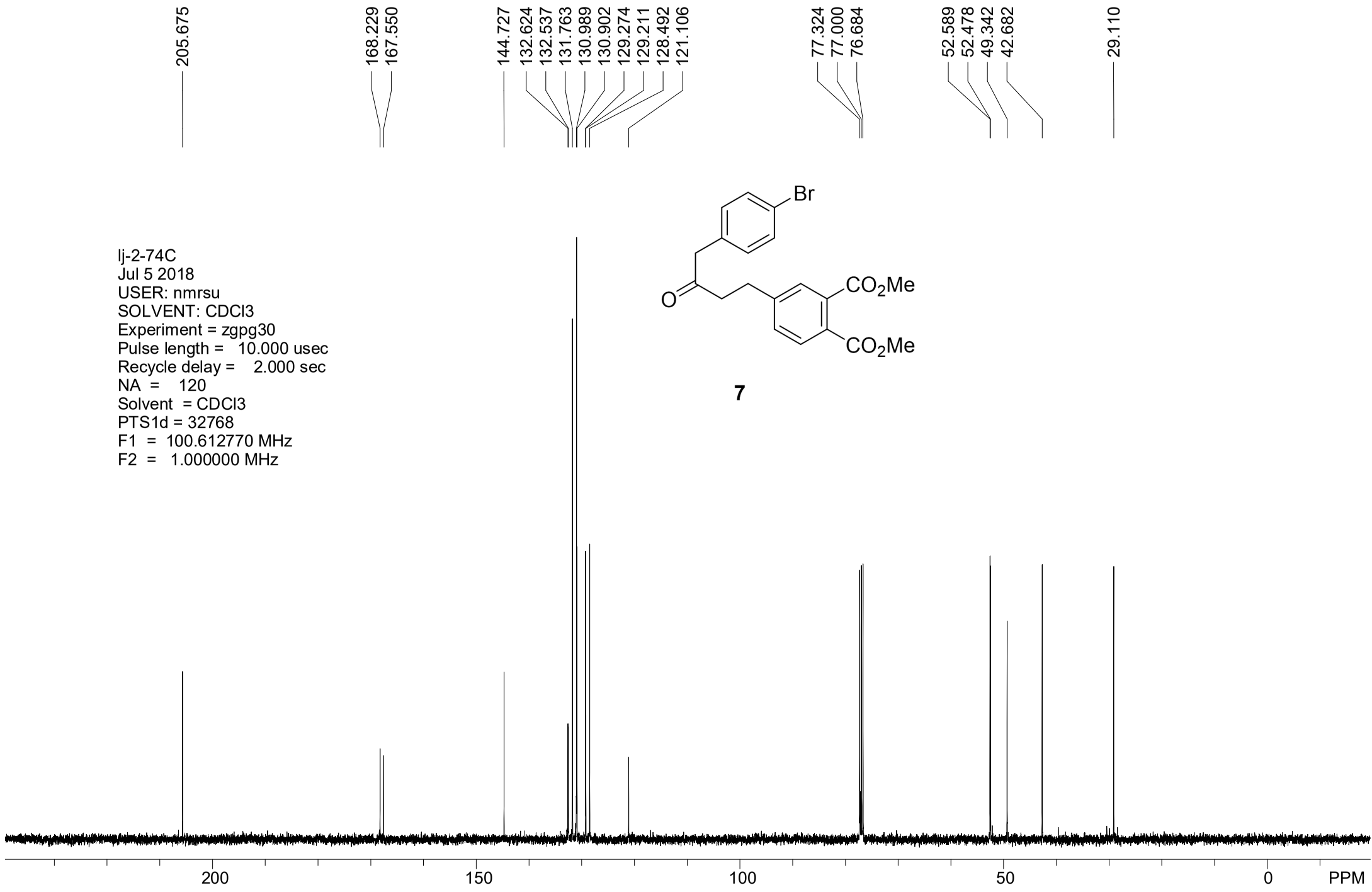
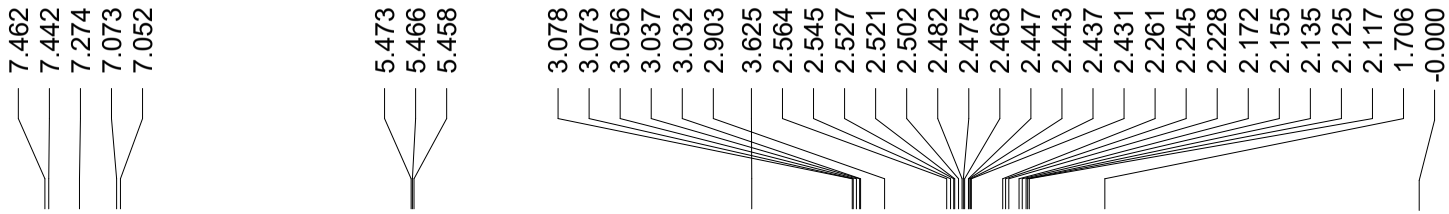
lj-2-64
Jun 12 2018
USER: nmrsu
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz

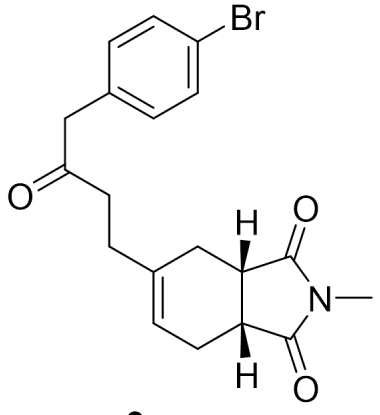



206.505
168.419
168.126
132.837
132.008
131.802
131.060
121.121
116.998
77.316
77.000
76.684
52.210
52.194
49.366
39.594
30.469
29.971
28.447
lj-2-64C
Jun 12 2018
USER: nmrsu
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 10.000 usec
Recycle delay = 2.000 sec
NA = 516
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
Br
O
CO2Me
CO2Me
6
200
150
100
50
0
PPM


7.653
7.633
7.438
7.434
7.422
7.417
7.301
7.297
7.281
7.277
7.263
7.016
6.995
3.903
3.891
3.616
2.944
2.926
2.908
2.803
2.785
2.766
1.589
-0.000
Br
O
CO2Me
CO2Me
7
lj-2-74
Jul 5 2018
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
5.99
2.91
2.01
2.00
2.01
1.44
2.01
0.92
12
10
8
6
4
2
0
PPM


205.675
168.229
167.550
144.727
132.624
132.537
131.763
130.989
130.902
129.274
129.211
128.492
121.106
77.324
77.000
76.684
52.589
52.478
49.342
42.682
29.110
lj-2-74C
Jul 5 2018
USER: nmrsu
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 10.000 usec
Recycle delay = 2.000 sec
NA = 120
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
Br
O
CO2Me
CO2Me
7
200
150
100
50
0
PPM





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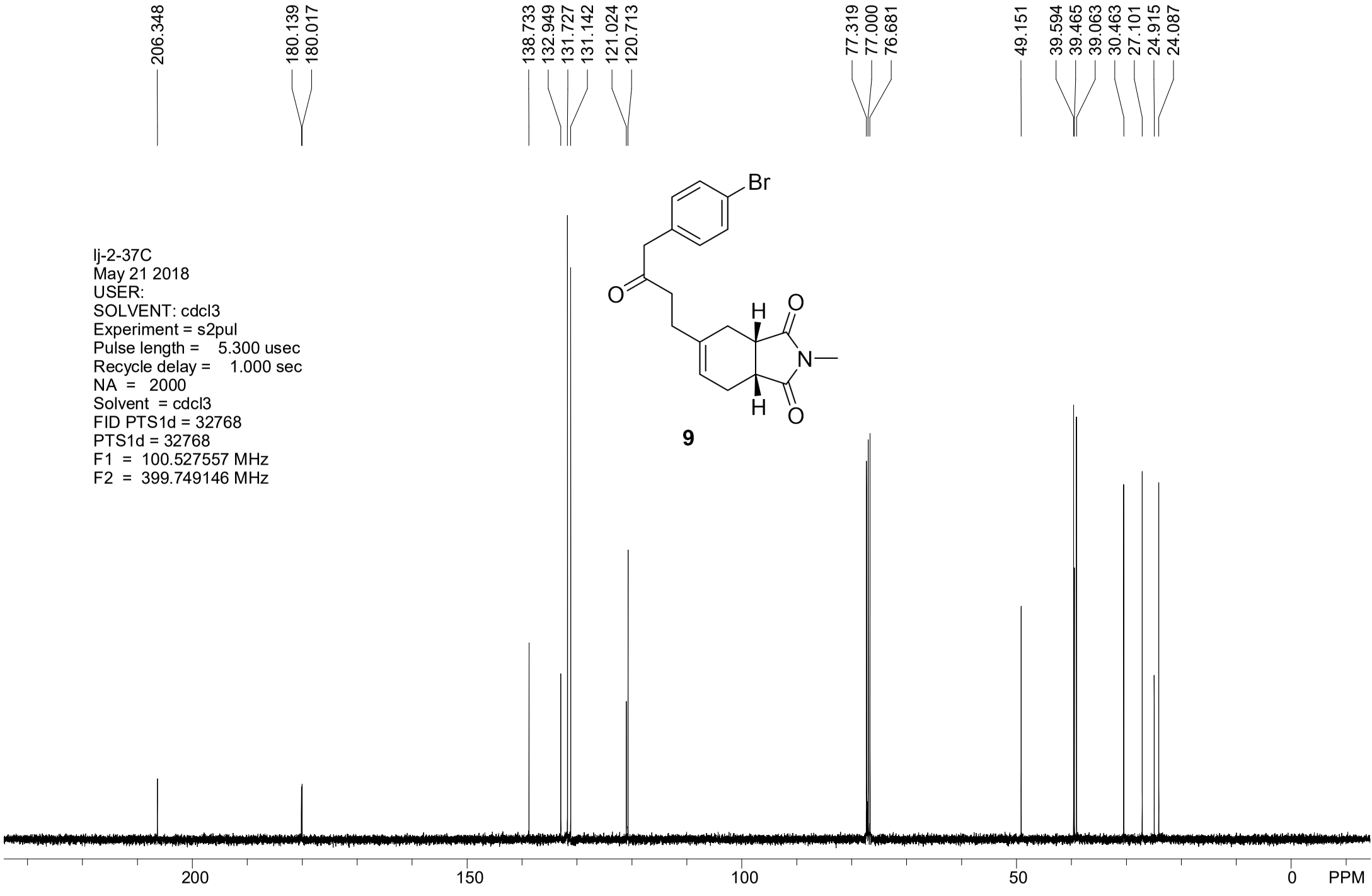
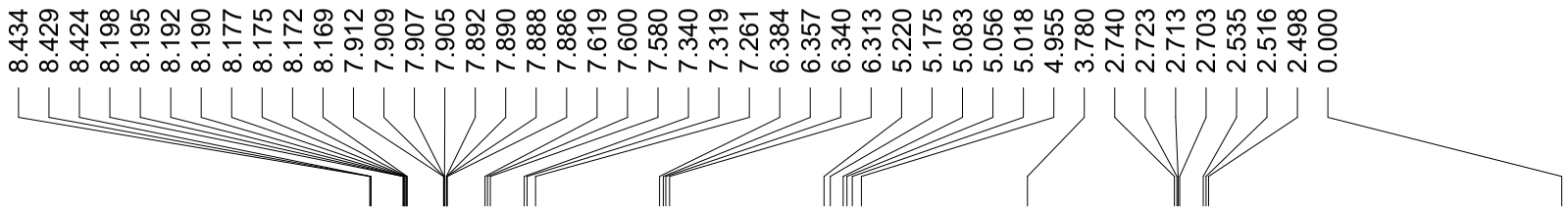
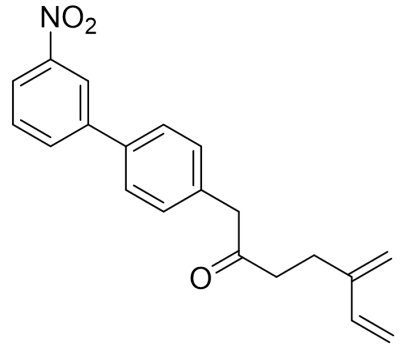
lj-2-37
May 21 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 4.900 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz


206.348
180.139
180.017
138.733
132.949
131.727
131.142
121.024
120.713
77.319
77.000
76.681
49.151
39.594
39.465
39.063
30.463
27.101
24.915
24.087
Br
O
H
O
N
H
O
9
lj-2-37C
May 21 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 5.300 usec
Recycle delay = 1.000 sec
NA = 2000
Solvent = cdcl3
FID PTS1d = 32768
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
200
150
100
50
0
PPM





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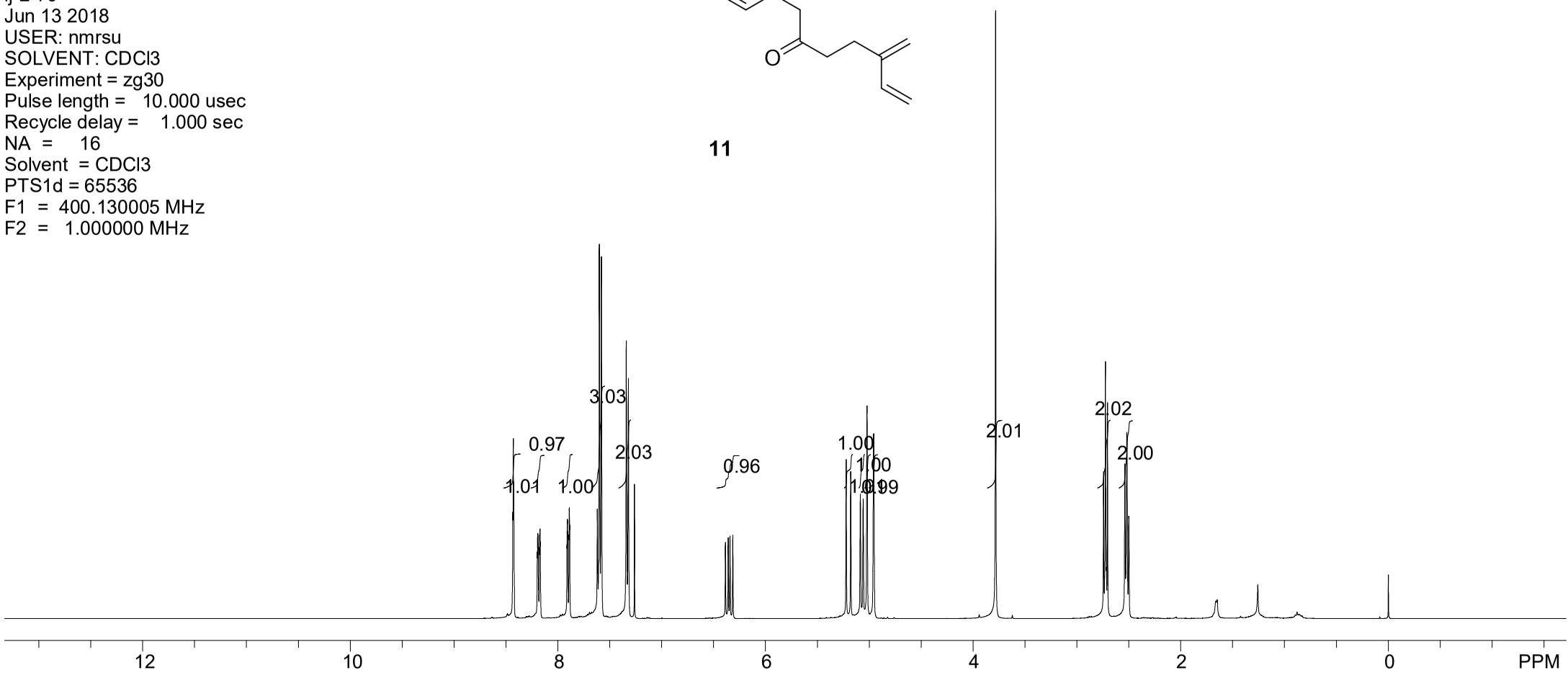
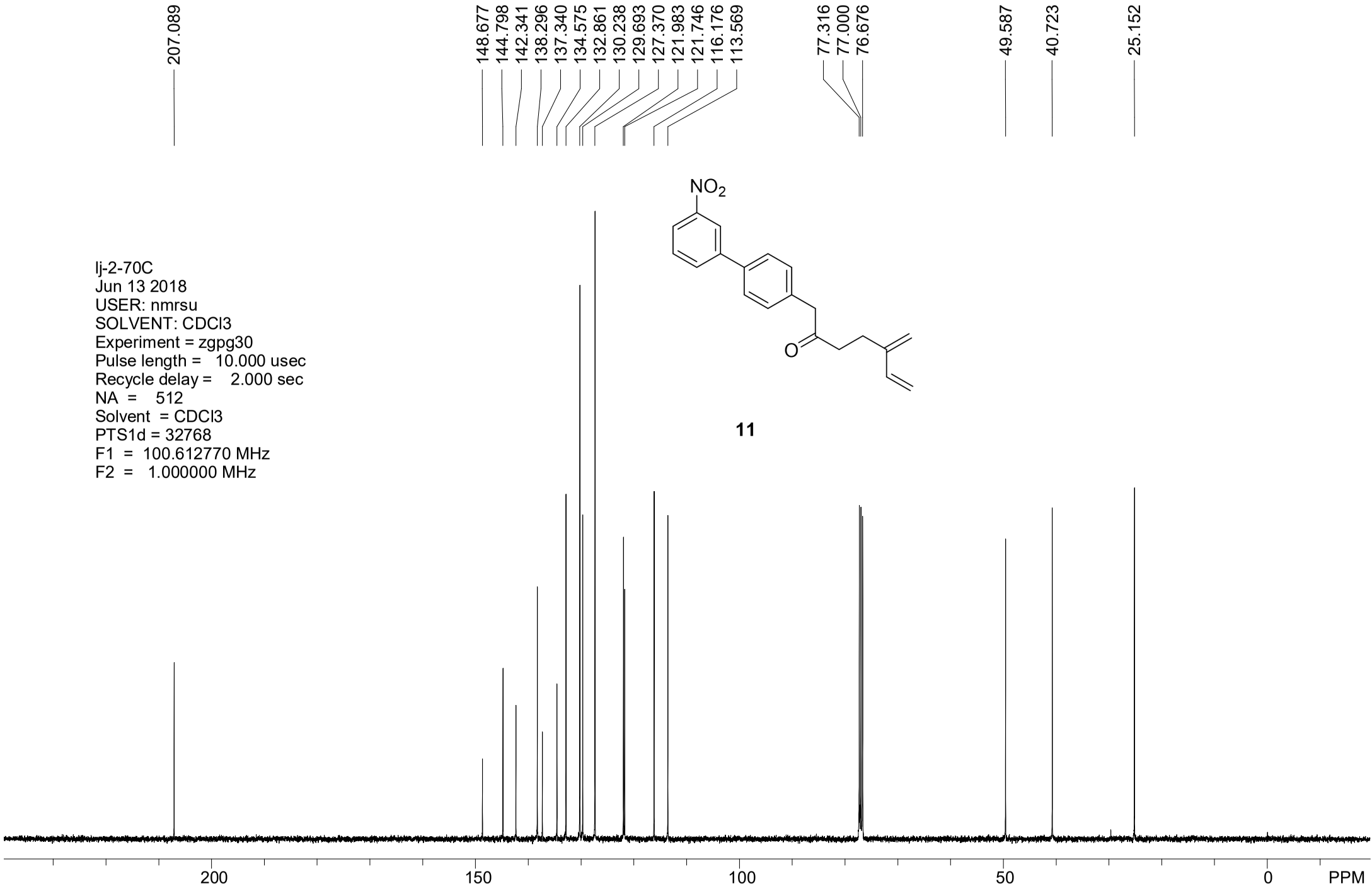
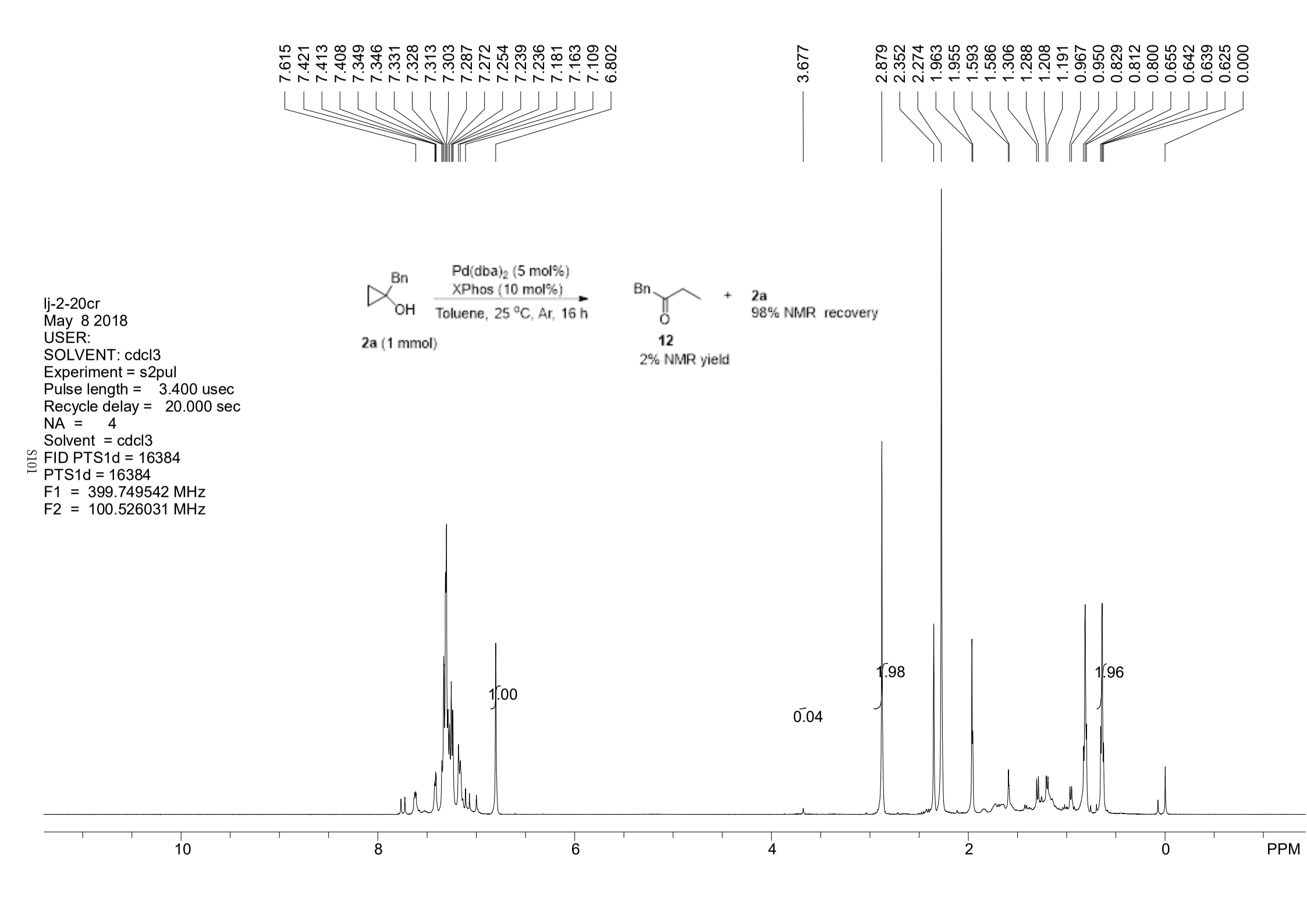
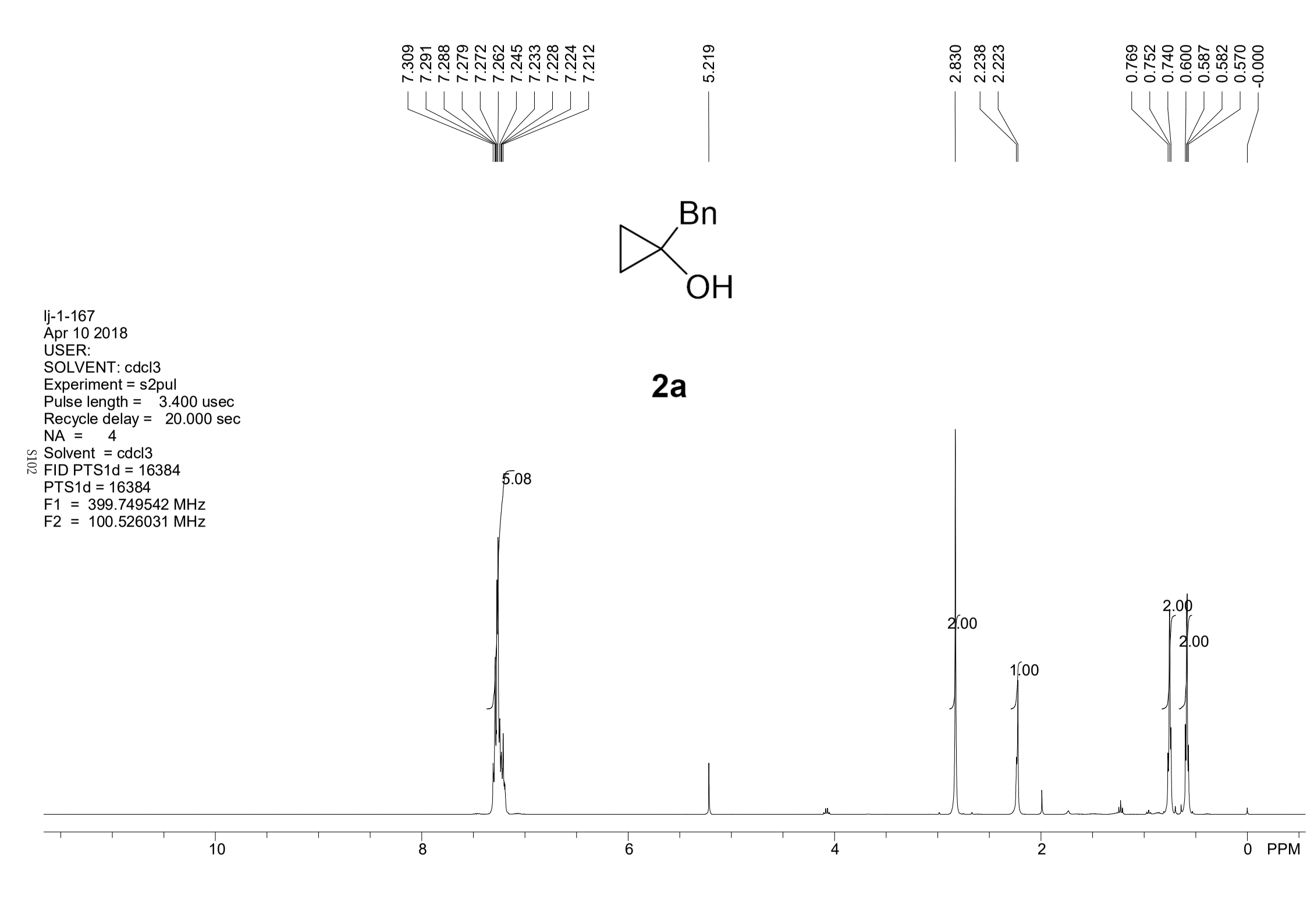
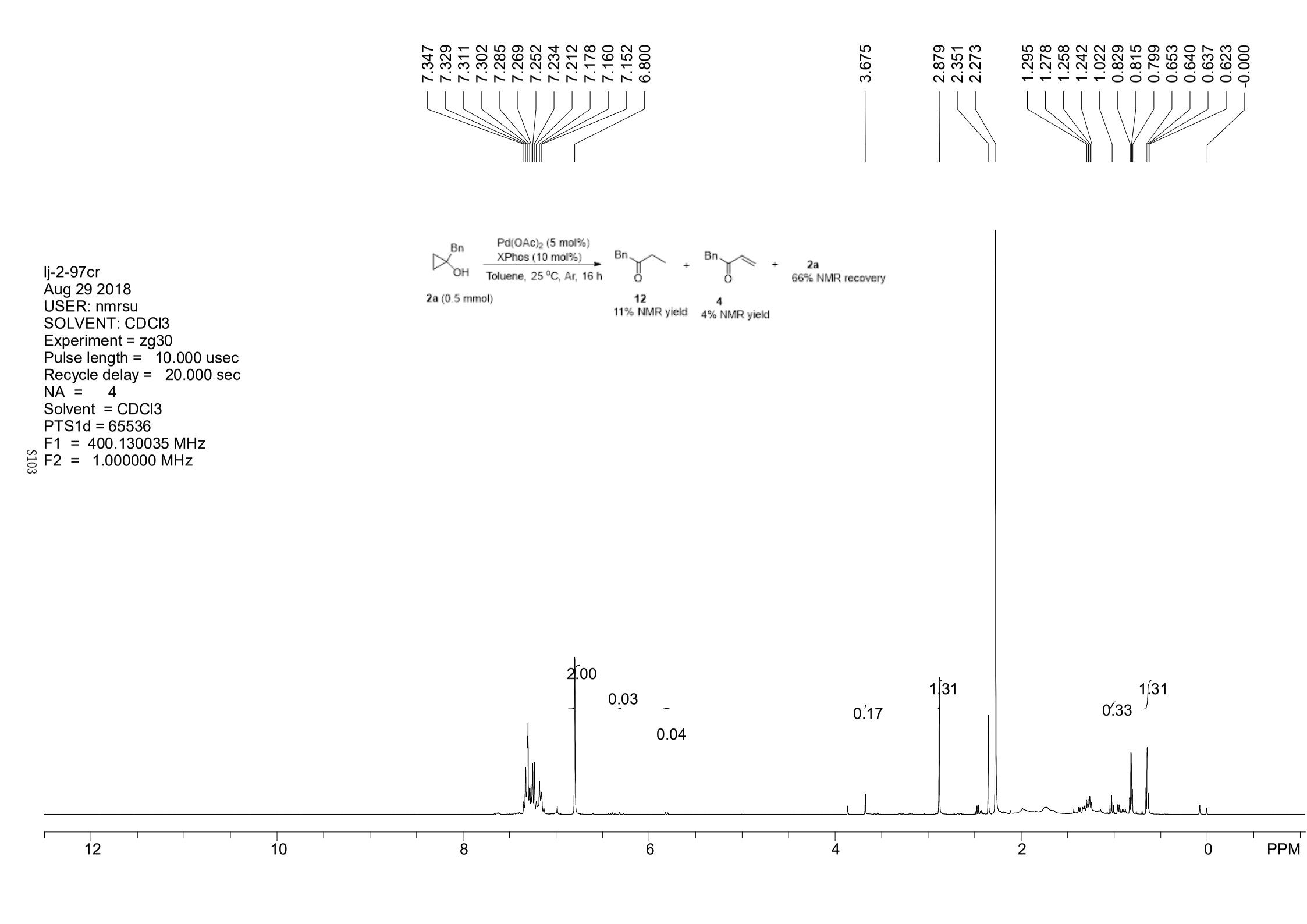
lj-2-70
Jun 13 2018
USER: nmrsu
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz

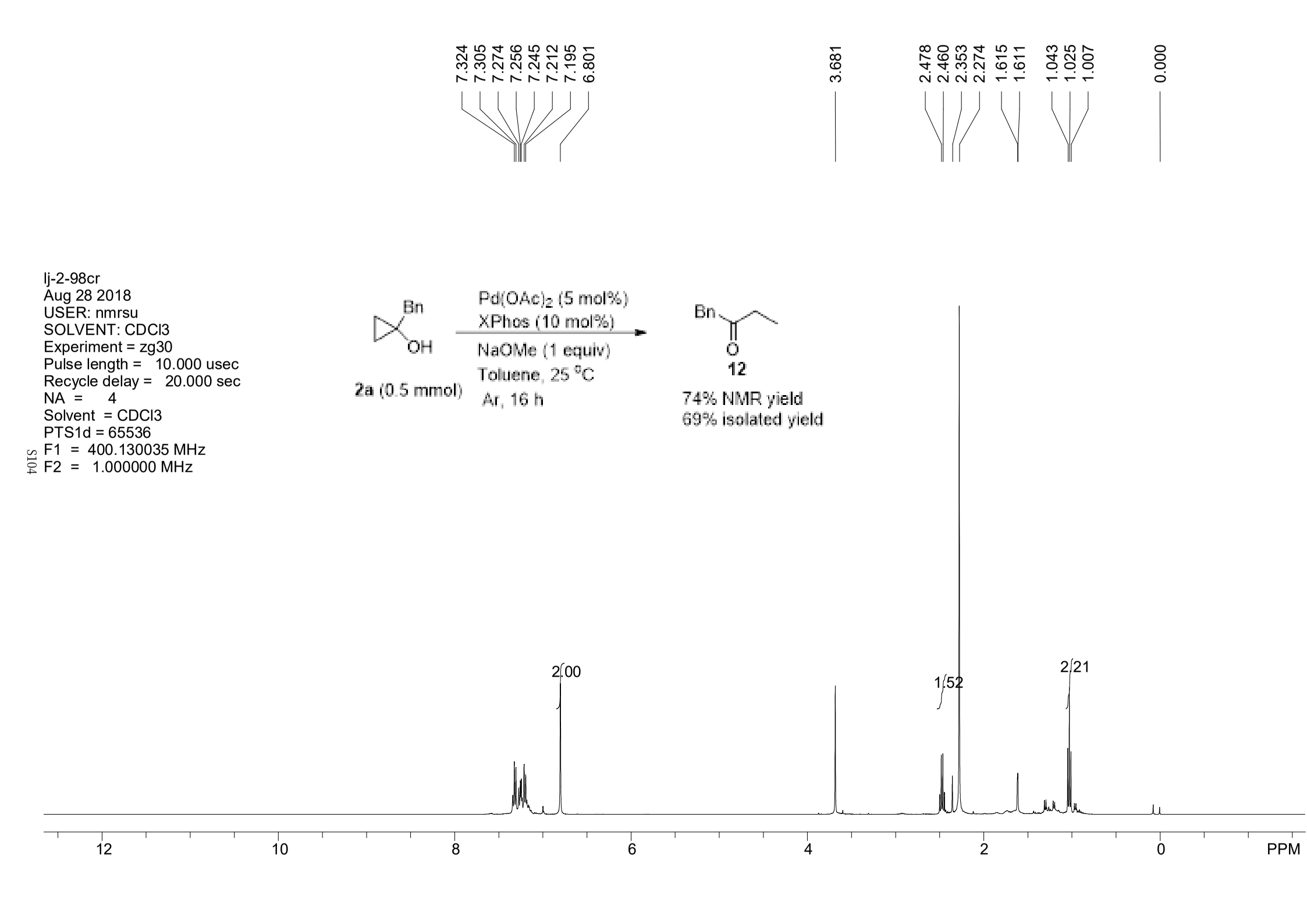


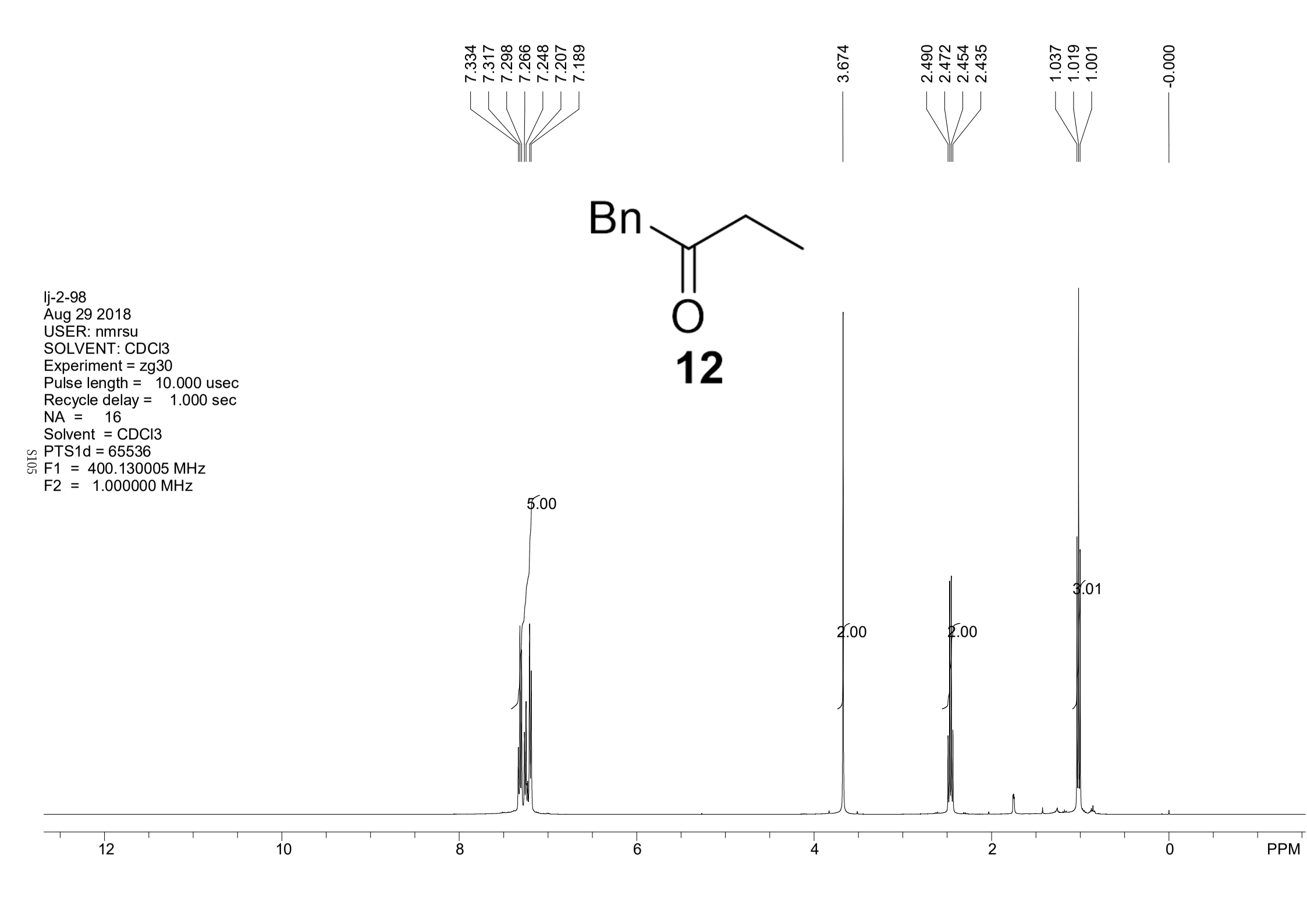

207.089
148.677
144.798
142.341
138.296
137.340
134.575
132.861
130.238
129.693
127.370
121.983
121.746
116.176
113.569
77.316
77.000
76.676
49.587
40.723
25.152
NO2
O
11
lj-2-70C
Jun 13 2018
USER: nmrsu
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 10.000 usec
Recycle delay = 2.000 sec
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
S100
200
150
100
50
0
PPM

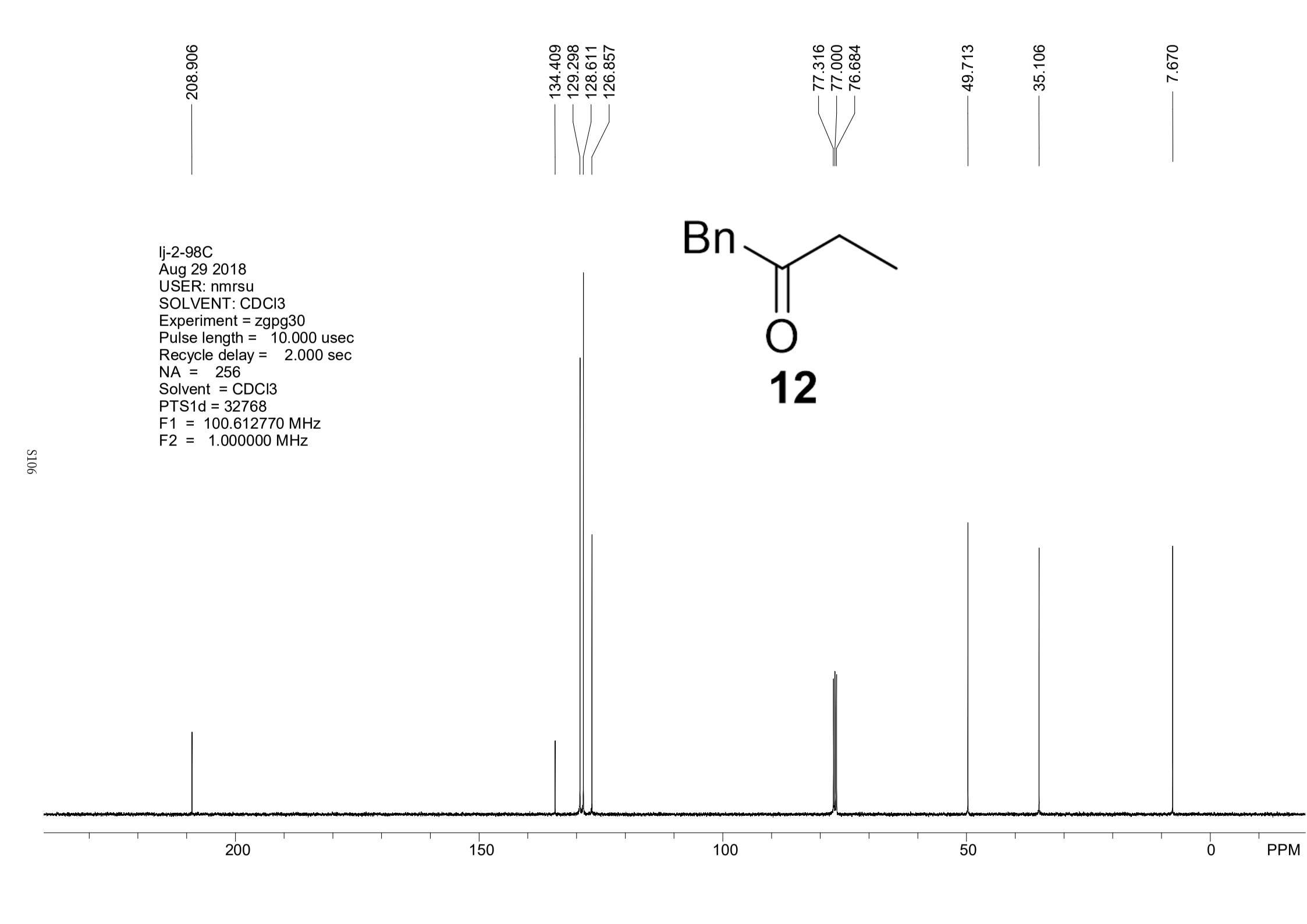

7.615
7.421
7.413
7.408
7.349
7.346
7.331
7.328
7.313
7.303
7.287
7.272
7.254
7.239
7.236
7.181
7.163
7.109
6.802
3.677
2.879
2.352
2.274
1.963
1.955
1.593
1.586
1.306
1.288
1.208
1.191
0.967
0.950
0.829
0.812
0.800
0.655
0.642
0.639
0.625
0.000
Bn
OH
Pd(dba)2 (5 mol%)
XPhos (10 mol%)
Toluene, 25 °C, Ar, 16 h
2a (1 mmol)
Bn
O
12
2% NMR yield
+
2a
98% NMR recovery
lj-2-20cr
May 8 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
SI01
1.00
0.04
1.98
1.96
10
8
6
4
2
0
PPM

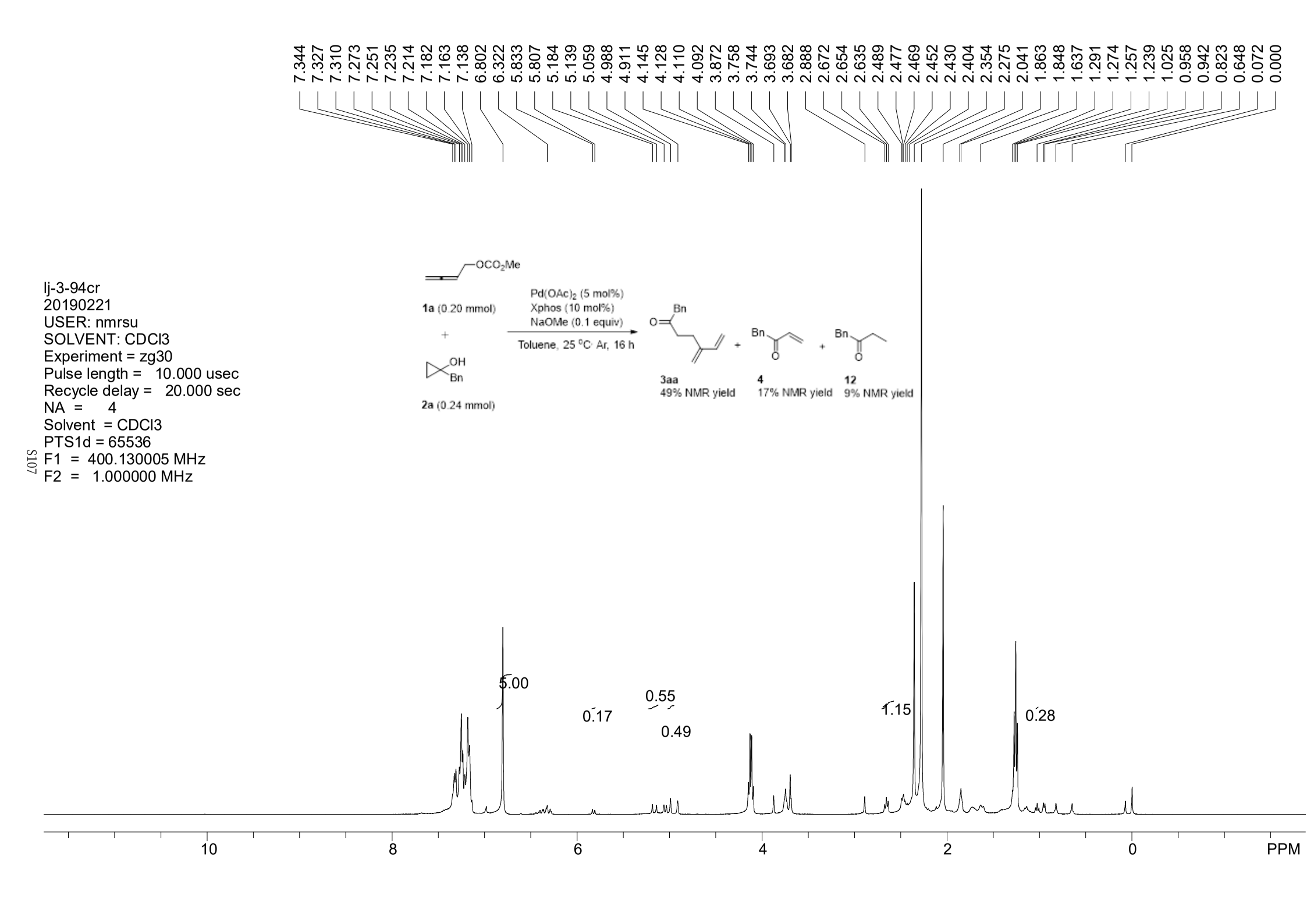

7.309
7.291
7.288
7.279
7.272
7.262
7.245
7.233
7.228
7.224
7.212
5.219
2.830
2.238
2.223
0.769
0.752
0.740
0.600
0.587
0.582
0.570
-0.000
Bn
OH
lj-1-167
Apr 10 2018
USER:
SOLVENT: cdcl3
Experiment = s2pul
Pulse length = 3.400 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = cdcl3
FID PTS1d = 16384
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
S102
2a
5.08
2.00
1.00
2.00
2.00
10
8
6
4
2
0
PPM


7.347
7.329
7.311
7.302
7.285
7.269
7.252
7.234
7.212
7.178
7.160
7.152
6.800
3.675
2.879
2.351
2.273
1.295
1.278
1.258
1.242
1.022
0.829
0.815
0.799
0.653
0.640
0.637
0.623
-0.000
Bn
OH
Pd(OAc)2 (5 mol%)
XPhos (10 mol%)
Toluene, 25 °C, Ar, 16 h
2a (0.5 mmol)
12
11% NMR yield
4
4% NMR yield
2a
66% NMR recovery
lj-2-97cr
Aug 29 2018
USER: nmrsu
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130035 MHz
F2 = 1.000000 MHz
2.00
0.03
0.04
0.17
1.31
0.33
1.31
12
10
8
6
4
2
0
PPM


7.324
7.305
7.274
7.256
7.245
7.212
7.195
6.801
3.681
2.478
2.460
2.353
2.274
1.615
1.611
1.043
1.025
1.007
0.000
lj-2-98cr
Aug 28 2018
USER: nmrsu
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130035 MHz
F2 = 1.000000 MHz
Bn
OH
2a (0.5 mmol)
Pd(OAc)2 (5 mol%)
XPhos (10 mol%)
NaOMe (1 equiv)
Toluene, 25 °C
Ar, 16 h
Bn
O
12
74% NMR yield
69% isolated yield
2.00
1.52
2.21
12
10
8
6
4
2
0
PPM


7.334
7.317
7.298
7.266
7.248
7.207
7.189
3.674
2.490
2.472
2.454
2.435
1.037
1.019
1.001
-0.000
Bn
O
12
lj-2-98
Aug 29 2018
USER: nmrsu
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
S105
5.00
2.00
2.00
3.01
12
10
8
6
4
2
0
PPM


208.906
134.409
129.298
128.611
126.857
77.316
77.000
76.684
49.713
35.106
7.670
lj-2-98C
Aug 29 2018
USER: nmrsu
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 10.000 usec
Recycle delay = 2.000 sec
NA = 256
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
Bn
O
12
S106
200
150
100
50
0
PPM


7.344 7.327 7.310 7.273 7.251 7.235 7.214 7.182 7.163 7.138 6.802 6.322 5.833 5.807 5.184 5.139 5.059 4.988 4.911 4.145 4.128 4.110 4.092 3.872 3.758 3.744 3.693 3.682 2.888 2.672 2.654 2.635 2.489 2.477 2.469 2.452 2.430 2.404 2.354 2.275 2.041 1.863 1.848 1.637 1.291 1.274 1.257 1.239 1.025 0.958 0.942 0.823 0.648 0.072 0.000
lj-3-94cr
20190221
USER: nmrsu
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 10.000 usec
Recycle delay = 20.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
S107
OCO2Me
1a (0.20 mmol)
OH
Bn
2a (0.24 mmol)
Pd(OAc)2 (5 mol%)
Xphos (10 mol%)
NaOMe (0.1 equiv)
Toluene, 25 °C Ar, 16 h
Bn
3aa
49% NMR yield
4
17% NMR yield
12
9% NMR yield
5.00
0.17
0.55
0.49
1.15
0.28
10
8
6
4
2
0
PPM