Electronic Supplementary Material (ESI) for Chemical Communications.

3,4-Alkadienyl Ketones *via* the Palladium-Catalyzed Decarboxylative Allenylation of 3-Oxocarboxylic acids

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Supporting Information

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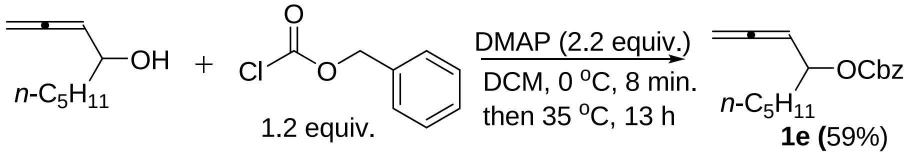
General Information. All reactions were carried out in oven dried Schlenk tubes under argon atmosphere. All of 2,3-dien-1-ols were prepared as reported in the reference.[1] The starting materials **1a-c** were prepared according to the reported method.[2] *Tert*-butyl 1-phenylbuta-2,3-dienyl carbonate **1m** were prepared according to the literature.[3] 3-Oxocarboxylic acids **2a-i** were freshly prepared according to the literature.[4] $Pd_2(dba)_3\cdot CHCl_3$ was purchased from Alfa Aesar. Binap was purchased from Boka. $LiOBu^t$ was purchased from Acros. THF, Et_2O, MTBE, Toluene, 1,4-dioxane, and DME were distilled over sodium wire using benzophenone as the indicator under argon atmosphere. MeCN, DCM, and DMSO were dried over CaH_2 and distilled right before use. All the temperatures are referred to the bath temperature. NMR spectra were taken using TMS (^1H, δ = 0), $CDCl_3$ (^1H, δ = 7.26), DMSO-d_6 (^{13}C CPD, δ = 39.5) and $CFCl_3$ (^{19}F CPD, δ = 0), and $CFCl_3$ (^{19}F CPD, δ = 0) as the internal standards, respectively.

Synthesis of benzyl carbonates of 2,3-dien-1-ols

1. **Synthesis of benzyl nona-1,2-dien-4-yl carbonate (1e, zth-5-144):**

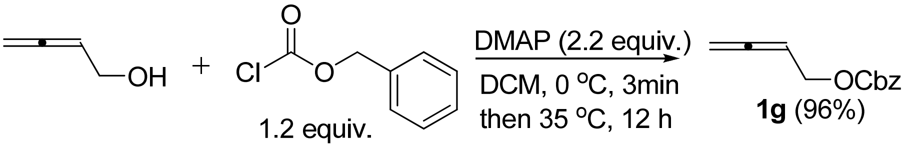


Typical Procedure I: DMAP (806.7 mg, 6.6 mmol), nona-1,2-dien-4-ol (420.9 mg, 3.0 mmol), and DCM (3 mL) were added sequentially into a flask under Argon. Then benzyl chloroformate (0.5 mL, d = 1.212 g/mL, 630.2 mg, 3.6 mmol) was added dropwise within 8 min at 0 °C. Then, the resulting mixture was allowed to stir at 35 °C in the oil bath for 13 hours as monitored by TLC. Upon completion, water (20 mL) and DCM (20 mL) were added and the organic phase was separated. The aqueous phase was extracted with DCM (10 mL × 3). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After filtration and evaporation, a ~ 5 mL residue was mixed with pre-treated silica gel (saturated with Et_3N then evaporated to dry). After complete evaporation, the silica gel loaded with the crude product was submitted to column chromatography on silica gel (eluent: petroleum ether / diethyl ether / triethylamine = 1000/1/1. It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) to afford **1e** (488.0 mg, 59%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H, ArH), 5.23 (q, *J* = 6.8 Hz, 1H, =CH), 5.16 (s, 2H, CH_2), 5.14 – 5.06 (m, 1H, CH), 4.94 – 4.77 (m, 2H, =CH_2), 1.84 – 1.60 (m, 2H, CH_2), 1.48 – 1.18 (m, 6H, CH_2), 0.88 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 154.5, 135.2, 128.4, 128.3, 128.1, 90.3, 77.1, 76.1, 69.3, 34.0, 31.3, 24.7, 22.4, 13.8; IR (neat, cm^{-1}): 2954, 2932, 2861, 1958, 1741, 1587, 1498, 1456, 1383, 1247; MS (ESI) m/z 297 $(M+Na)^+$; HRMS (ESI) Calcd for $C_{17}H_{26}NO_3$ $(M+NH_4)^+$: 292.1907, Found: 292.1909.

2. **Synthesis of benzyl deca-1,2-dien-4-yl carbonate (1f, zth-5-105):**

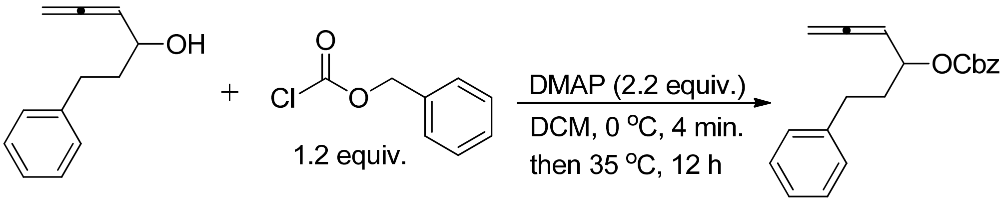
According to **Typical Procedure I**, the reaction of deca-1,2-dien-4-ol (1.5427 g, 10.0 mmol), DMAP (2.6897 g, 22.0 mmol), and benzyl chloroformate (1.70 mL, d = 1.212 g/mL, 2.0604 g, 12.0 mmol) in DCM (10 mL) afforded **1f** (2.3575 g, 82%) (eluent: petroleum ether / diethyl ether / triethylamine = 1000/1/1 to 1000/4/1. It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 5H, ArH), 5.23 (q, *J* = 6.7 Hz, 1H, =CH), 5.16 (s, 2H, CH_2), 5.14 – 5.05 (m, 1H, CH), 4.94 – 4.76 (m, 2H, =CH_2), 1.82 – 1.60 (m, 2H, CH_2), 1.46 – 1.18 (m, 8H, CH_2), 0.87 (t, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 154.6, 135.3, 128.5, 128.4, 128.2, 90.4, 77.2, 76.3, 69.4, 34.1, 31.6, 28.8, 25.0, 22.5, 14.0; IR (neat, cm^{-1}): 2931, 2859, 1958, 1741, 1587, 1498, 1456, 1384, 1246; MS (ESI) m/z 311 $(M+Na)^+$; HRMS (ESI) Calcd for $C_{18}H_{28}NO_3$ $(M+NH_4)^+$: 306.2064, Found: 306.2064.

3. **Synthesis of benzyl buta-2,3-dienyl carbonate (1g, zth-4-165)**



Typical Procedure II: buta-2,3-dien-1-ol (0.3506 g, 5.0 mmol)/DCM(4 mL), DMAP (1.3445 g, 11.0 mmol), and DCM (1 mL) were added sequentially into a flask under Argon. Then benzyl chloroformate (0.86 mL, d = 1.212 g/mL, 1.0908 g, 3.6 mmol) was added dropwise within 3 min at 0 °C. The resulting mixture was allowed to stir at 35 °C in the oil bath for 12 hours as monitored by TLC. Upon completion, water (20 mL) and DCM (50 mL) were added and the organic phase was separated. The aqueous phase was extracted with DCM (20 mL × 3), the combined organic phase was washed with brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation, a ~ 5 mL residue was mixed with pre-treated silica gel (saturated with Et_3N then evaporated to dry). After complete evaporation the silica gel loaded with the crude product was submitted to column chromatography on silica gel (eluent: petroleum ether / diethyl ether / triethylamine = 1000/1/1. It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) to afford **1g** (0.9816 g, 96%) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 5H, ArH), 5.32 (quint, J = 6.8 Hz, 1H, =CH), 5.17 (s, 2H, CH_2), 4.86 (dt, J = 6.7 Hz, 2.1 Hz, 2H, =CH_2), 4.64 (dt, J = 7.1 Hz, 2.3 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 154.8, 135.1, 128.44, 128.39, 128.2, 85.8, 76.7, 69.5, 65.5; IR (neat, cm^{-1}): 1958, 1742, 1498, 1455, 1390, 1370, 1323, 1239; MS (ESI) m/z 205 $(M+H)^+$, 227 $(M+Na)^+$, 237$(M+H+CH_3OH)^+$; HRMS (ESI) Calcd for $C_{12}H_{13}O_3$ $(M+H)^+$: 205.0859, Found: 205.0860.

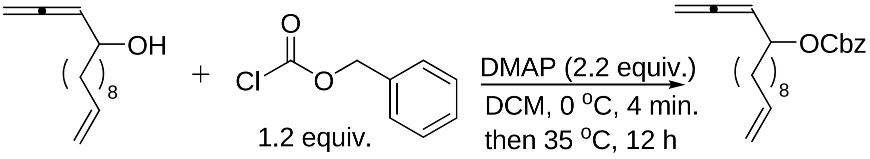
4. **Synthesis of benzyl 1-phenylhexa-4,5-dien-3-yl carbonate (1h, zth-5-013)**



1h (79%)

According to **Typical Procedure II**, the reaction of 1-phenylhexa-4,5-dien-3-ol (0.8714 g, 5.0 mmol), DMAP (1.3451 g, 11.0 mmol), and benzyl chloroformate (0.90 mL, d = 1.212 g/mL, 1.0908 g, 6.0 mmol) in DCM (5 mL) afforded **1h** (1.2116 g, 79%) (eluent: petroleum ether / diethyl ether / triethylamine = 1000/1/1 to 1000/2/1). It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.22 (m, 7H, ArH), 7.22 – 7.10 (m, 3H, ArH), 5.33 – 5.23 (m, 1H, =CH), 5.21 – 5.06 (m, 3H, CH_2+CH), 4.95 – 4.78 (m, 2H, =CH_2), 2.80 – 2.60 (m, 2H, CH_2), 2.15 – 1.90 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 154.5, 140.9, 135.2, 128.5, 128.44, 128.39, 128.31, 128.28, 126.0, 90.2, 77.6, 75.4, 69.5, 35.7, 31.4; IR (neat, cm^{-1}): 3086, 3064, 3030, 2953, 2863, 1957, 1739, 1603, 1586, 1497, 1455, 1384, 1318, 1245, 1180, 1129, 1081, 1015; MS (ESI) m/z 331 $(M+Na)^+$; HRMS (ESI) Calcd for $C_{20}H_{24}NO_3$ $(M+NH_4)^+$: 326.1751, Found: 326.1751.

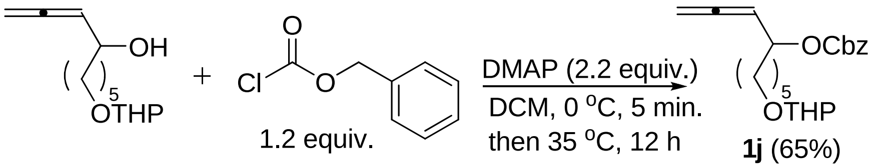
5. **Synthesis of benzyl tetradeca-1,2,13-trien-4-yl carbonate (1i, zth-5-007)**



1i (78%)

According to **Typical Procedure II**, the reaction of tetradeca-1,2,13-trien-4-ol (1.0418 g, 5.0 mmol), DMAP (1.3456 g, 11.0 mmol), and benzyl chloroformate (0.90 mL, d = 1.212 g/mL, 1.0908 g, 6.0 mmol) in DCM (5 mL) afforded **1i** (1.3412 g, 78%) (eluent: petroleum ether / diethyl ether / triethylamine = 1000/1/1 to 1000/4/1). It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) as a liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 – 7.30 (m, 5H, ArH), 5.87 – 5.75 (m, 1H, =CH), 5.23 (q, J = 6.7 Hz, 1H, =CH), 5.16 (s, 2H, CH$_2$), 5.14 – 5.06 (m, 1H, CH), 4.99 (dq, J = 17.2 Hz, 1.7 Hz, 1H, one proton of =CH$_2$), 4.95 – 4.90 (m, 1H, one proton of =CH$_2$), 4.90 – 4.78 (m, 2H, =CH$_2$), 2.08 – 1.98 (m, 2H, CH$_2$), 1.80 – 1.60 (m, 2H, CH$_2$) 1.44 – 1.18 (m, 12H, CH$_2$); ^{13}C NMR (100 MHz, DMSO-d_6) δ 207.6, 153.9, 138.6, 135.5, 128.3, 128.1, 127.9, 114.3, 90.2, 77.4, 75.3, 68.7, 33.6, 33.2, 28.9, 28.8, 28.6, 28.5, 28.3, 24.6; IR (neat, cm^{-1}): 3070, 3035, 2926, 2855, 1958, 1742, 1640, 1587, 1498, 1456, 1384, 1248; MS (ESI) m/z 365 (M+Na)$^+$; HRMS (ESI) Calcd for $C_{22}H_{34}NO_3$ (M+NH$_4$)$^+$: 360.2533, Found: 360.2534.

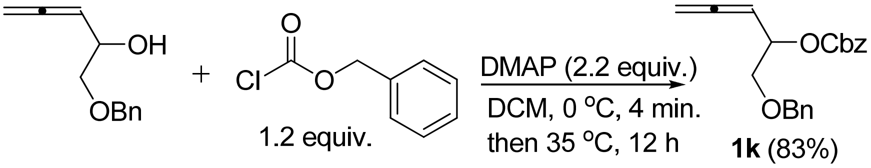
6. **Synthesis of benzyl 9-(tetrahydro-2*H*-pyran-2-yloxy)nona-1,2-dien-4-yl carbonate (1j, zth-5-045)**



According to **Typical Procedure I**, the reaction of 9-(tetrahydro-2*H*-pyran-2-yloxy)nona-1,2-dien-4-ol (1.2021 g, 5.0 mmol), DMAP (1.3441 g, 11.0 mmol), and benzyl chloroformate (0.86 mL, d = 1.212 g/mL, 1.0423 g, 6.0 mmol) in DCM (5 mL) afforded **1j** (1.2188 g, 65%) (eluent: petroleum ether / diethyl ether / triethylamine = 1000/1/1 to 1000/9/1). It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) as a liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.30 (m, 5H, ArH), 5.23 (q, J = 6.8 Hz, 1H, =CH), 5.16 (s, 2H, CH$_2$), 5.14 – 5.06 (m, 1H, CH), 4.90 – 4.78 (m, 2H, =CH$_2$), 4.60 – 4.54 (m, 1H, CH), 3.92 – 3.80 (m, 1H, one proton of OCH$_2$), 3.72 (dt, J = 12.3 Hz, 4.8 Hz, 1H, one proton of OCH$_2$), 3.56 – 3.44 (m, 1H, one proton of OCH$_2$), 3.37 (dt, J = 11.7 Hz, 4.9 Hz, 1H, one proton of OCH$_2$), 1.90 – 1.32 (m, 14H, 7 × CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 208.5, 154.6, 135.2, 128.53, 128.45, 128.3, 98.8, 90.3, 77.4, 76.2, 69.5, 67.4, 62.3, 34.1, 30.7, 29.5, 25.9, 25.4, 25.0, 19.7; IR (neat, cm^{-1}): 3034, 2940, 2864, 2793, 1958, 1741, 1498, 1455, 1384, 1352, 1322, 1248, 1201, 1120, 1077, 1025; MS (ESI) m/z

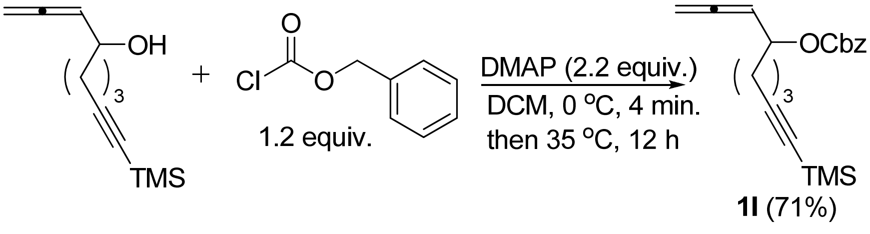
397 (M+Na)$^+$; HRMS (EI) Calcd for $C_{22}H_{30}O_5$ (M$^+$): 374.2093, Found: 374.2092.

7. **Synthesis of benzyl 1-(benzyloxy)penta-3,4-dien-2-yl carbonate (1k, zth-5-099)**



According to **Typical Procedure I**, the reaction of 1-(benzyloxy)penta-3,4-dien-2-ol (0.9517 g, 5.0 mmol), DMAP (1.3451 g, 11.0 mmol), and benzyl chloroformate (0.90 mL, d = 1.212 g/mL, 1.0908 g, 6.0 mmol) in DCM (5 mL) afforded **1k** (1.3525 g, 83%) (eluent: petroleum ether / diethyl ether / triethylamine = 1000/1/1 to 1000/4/1). It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) as a liquid: ^{1}H NMR (400 MHz, toluene-*d$_8$*) δ 7.24 – 6.94 (m, 10H, ArH), 5.54 – 5.44 (m, 1H, CH), 5.17 (q, *J* = 6.9 Hz, 1H, =CH), 4.91 (s, 2H, CH_2), 4.64 – 4.48 (m, 2H, =CH_2), 4.27 (d, *J* = 12.4 Hz, 1H, one proton of OCH_2Ph), 4.24 (d, *J* = 12.4 Hz, 1H, one proton of OCH_2Ph), 3.46 (dd, *J* = 10.4, 6.8 Hz, 1H, one proton of CH_2), 3.38 (dd, *J* = 11.2, 4.4 Hz, 1H, one proton of CH_2); ^{13}C NMR (100MHz, $CDCl_3$) δ 208.7, 154.4, 137.7, 135.1, 128.44, 128.37, 128.3, 128.2, 127.6, 127.5, 87.4, 77.7, 74.3, 73.1, 70.9, 69.5; IR (neat, cm^{-1}): 3089, 3065, 3033, 3008, 2947, 2898, 2863, 1958, 1744, 1606, 1587, 1497, 1455, 1384, 1248, 1104, 1029; MS (ESI) m/z 347 (M+Na)$^+$; HRMS (EI) Calcd for $C_{20}H_{20}O_4$ (M$^+$): 324.1362, Found: 324.1360.

8. **Synthesis of benzyl 1-(benzyloxy)penta-3,4-dien-2-yl carbonate (1l, zth-5-044)**

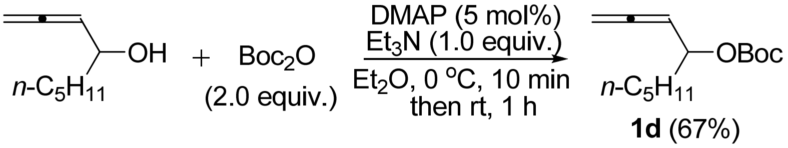


According to **Typical Procedure I**, the reaction of

9-(trimethylsilyl)nona-1,2-dien-8-yn-4-ol (1.0421 g, 5.0 mmol), DMAP (1.3453 g, 11.0 mmol), and benzyl chloroformate (0.86 mL, d = 1.212 g/mL, 1.0908 g, 6.0 mmol) in DCM (5 mL) afforded **1l** (1.2158 g, 71%) (eluent: petroleum ether / diethyl ether / triethylamine = 1000/1/1 to 1000/4/1). It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H, ArH), 5.24 (q, *J* = 6.7 Hz, 1H, =CH), 5.20 – 5.08 (m, 3H, CH_2+CH), 4.93 – 4.80 (m, 2H, =CH_2), 2.25 (t, *J* = 7.2 Hz, 2H, CH_2), 1.90 – 1.74 (m, 2H, CH_2), 1.70 – 1.50 (m, 2H, CH_2), 0.14 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 154.5, 135.2, 128.6, 128.5, 128.3, 106.5, 90.2, 85.1, 77.6, 75.7, 69.6, 33.2, 24.1, 19.5, 0.1; IR (neat, cm^{-1}): 2956, 2174, 1958, 1743, 1498, 1456, 1385, 1248, 1180, 1039; MS (ESI) m/z 365 $(M+Na)^+$; HRMS (EI) Calcd for $C_{20}H_{30}NO_3Si$ $(M+NH_4)^+$: 360.1989, Found: 360.1990.

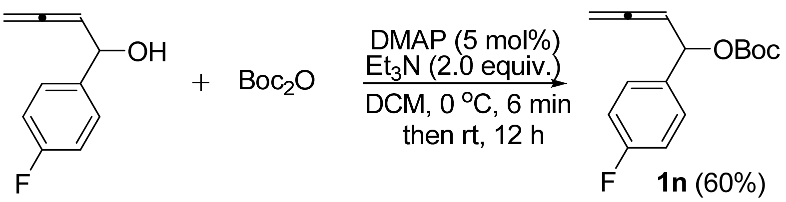
Synthesis of *tert*-butyl carbonates of 2,3-dien-1-ols

9. **Synthesis of *tert*-butyl nona-1,2-dien-4-yl carbonate (1d, zth-6-122):**



To a cooled (ice-water bath) solution of Boc_2O (4.7 mL, d = 0.949 g/mL, 4.4603 g, 20.0 mmol) in Et_2O (10 mL), a mixture of DMAP (60.9 mg, 0.5 mmol), nona-1,2-dien-4-ol (1.4022 g, 10.0 mmol), and triethylamine (1.4 mL, d = 0.726, 1.0164 g, 10.0 mmol), and Et_2O (10 mL) was added via dropping funnel within 10 min at 0 ^{o}C. Then, the resulting mixture was allowed to stir at rt for 1 hour as monitored by TLC. Upon completion, water (50 mL) and DCM (50 mL) were added and the organic phase was separated. The aqueous phase was extracted with DCM (30 mL × 3). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After filtration and evaporation, a ~ 5 mL residue was mixed with pre-treated silica gel (saturated with Et_3N then evaporated to dry). After complete evaporation the silica gel loaded with the crude product was submitted to column chromatography on silica gel (eluent: petroleum ether / diethyl ether / triethylamine = 1000/1/1. It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) afforded **1d** (1.6103 g, 67%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) 5.22 (q, *J* = 6.7 Hz, 1H, =CH), 5.08 – 4.98 (m, 1H, CH), 4.92 – 4.80 (m, 2H, =CH_2), 1.80 - 1.58 (m, 2H, CH_2), 1.49 (s, 9H, $C(CH_3)_3$), 1.44 – 1.23 (m, 6H, 3×CH_2), 0.89 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 153.0, 90.7, 81.9, 77.2, 74.9, 34.2, 31.4, 27.8, 24.9, 22.5, 14.0; IR (neat, cm^{-1}): 2955, 2932, 2861, 1959, 1739, 1459, 1435, 1393, 1275, 1251, 1166, 1086; MS (ESI) m/z 263 $(M+Na)^+$; HRMS (ESI) Calcd for $C_{14}H_{28}NO_3$ $(M+NH_4)^+$: 258.2064, Found: 258.2064.

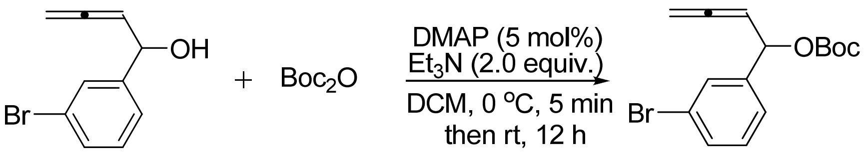
10. **Synthesis of *tert*-butyl 1-(4-fluorophenyl)buta-2,3-dienyl carbonate (1n, zth-5-091):**



Typical Procedure III: DMAP (31.0 mg, 0.25 mmol), 1-(4-fluorophenyl)buta-2,3-dien-1-ol (0.8212 g, 5.0 mmol), triethylamine (1.4 mL, d = 0.726, 1.0164 g, 10.0 mmol), and DCM (5 mL) were added sequentially into a flask under Argon. Then Boc_2O (1.2 mL, d = 0.949 g/mL, 1.1388 g, 5.0 mmol) was added dropwise within 6 min at 0 °C. Then, the resulting mixture was allowed to stir at rt for 1 hour as monitored by TLC. Upon completion, water (50 mL) and DCM (50 mL) were added and the organic phase was separated. The aqueous phase was extracted with DCM (30 mL × 3). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After complete evaporation the silica gel loaded with the crude product was submitted to column chromatography on silica gel (eluent: petroleum ether / diethyl ether / triethylamine = 1000/1/1 to 1000/3/1). It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) afforded **1n**

(915.9 mg, 60%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H, ArH), 7.08 – 7.00 (m, 2H, ArH), 6.04 (dt, *J* = 3.2 Hz, 2.2 Hz, 1H, CH), 5.44 (q, *J* = 6.7 Hz, 1H, =CH), 4.94 – 4.80 (m, 2H, $=CH_2$), 1.47 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 162.5 (d, $J_{C\text{-}F}$ = 245.5 Hz), 152.5, 134.7 (d, $J_{C\text{-}F}$ = 2.9 Hz), 128.6 (d, $J_{C\text{-}F}$ = 8.6 Hz), 115.2 (d, $J_{C\text{-}F}$ = 22.3 Hz), 91.4, 82.4, 77.9, 75.7, 27.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.1; IR (neat, cm^{-1}): 1958, 1739, 1606, 1510, 1370, 1273, 1252, 1226, 1155, 1126, 1081, 1035, 1015, 1004; MS (70 eV, EI) m/z (%) 264 (M^+, 1.05), 57 (100); HRMS (EI) Calcd for $C_{15}H_{17}FO_3$ (M^+): 264.1162, Found: 264.1159.

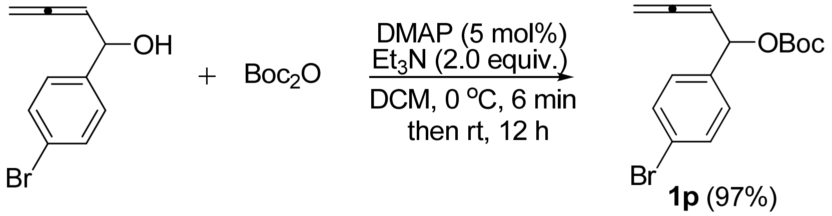
11. **Synthesis of *tert*-butyl 1-(3-bromophenyl)buta-2,3-dienyl carbonate (1o, zth-4-118):**



1o (99%)

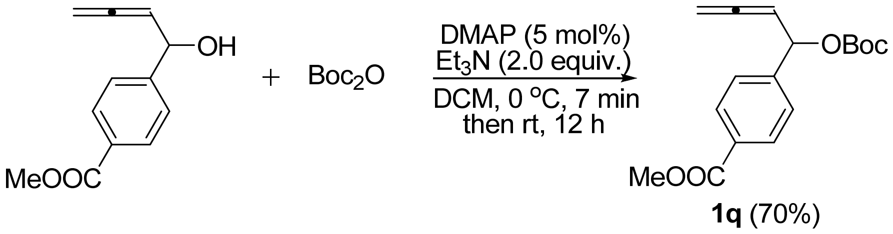
According to **Typical Procedure III**, the reaction of 1-(3-bromophenyl)buta-2,3-dien-1-ol (1.1263 g, 5.0 mmol), DMAP (30.7 mg, 0.25 mmol), triethylamine (1.4 mL, d = 0.726, 1.0164 g, 10.0 mmol), and Boc_2O (1.2 mL, d = 0.949 g/mL, 1.1388 g, 5.0 mmol) in DCM (5 mL) afforded **1o** (1.6158 g, 99%) (eluent: petroleum ether / diethyl ether / triethylamine = 1000/4/1). It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (t, *J* = 1.6 Hz, 1H, ArH), 7.44 (dt, *J* = 8.0 Hz, 1.6 Hz, 1H, ArH), 7.34 – 7.28 (m, 1H, ArH), 7.23 (t, *J* = 7.6 Hz, 1H, ArH), 6.01 (dt, *J* = 7.0 Hz, 1.8 Hz, 1H, CH), 5.41 (q, *J* = 6.8 Hz, 1H, =CH), 4.96 – 4.84 (m, 2H, $=CH_2$), 1.49 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.7, 152.4, 141.2, 131.3, 130.0, 129.8, 125.4, 122.5, 91.2, 82.8, 78.2, 75.6, 27.7; IR (neat, cm^{-1}): 3067, 2981, 2935, 2873, 1957, 1739, 1596, 1572, 1475, 1430, 1369, 1272, 1251, 1156, 1126, 1075, 1035; MS (ESI) m/z 349 $[M(^{81}Br)+Na]^+$, 347 $[M(^{79}Br)+Na]^+$; HRMS (EI) Calcd for $C_{15}H_{17}O_3{}^{79}Br$ (M^+): 324.0361, Found: 324.0352.

12. **Synthesis of *tert*-butyl 1-(4-bromophenyl)buta-2,3-dienyl carbonate (1p, zth-4-106):**



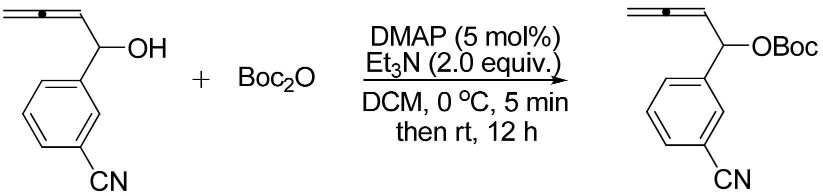
According to **Typical Procedure III**, the reaction of 1-(4-bromophenyl)buta-2,3-dien-1-ol (1.1259 g, 5.0 mmol), DMAP (30.7 mg, 0.25 mmol), triethylamine (1.4 mL, d = 0.726, 1.0164 g, 10.0 mmol), and Boc$_2$O (1.2 mL, d = 0.949 g/mL, 1.1388 g, 5.0 mmol) in DCM (5 mL) afforded **1p** (1.5735 g, 97%) (eluent: petroleum ether / diethyl ether / triethylamine = 1000/4/1).It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) as a liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 (dt, *J* = 8.4 Hz, 2.0 Hz, 2H, ArH), 7.26 (dt, *J* = 8.8 Hz, 2.2 Hz, 2H, ArH), 6.01 (dt, *J* = 6.4 Hz, 2.2 Hz, 1H, CH), 5.42 (q, *J* = 6.7 Hz, 1H, =CH), 4.94 – 4.81 (m, 2H, =CH$_2$), 1.47 (s, 9H, C(CH$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 208.7, 152.5, 138.0, 131.6, 128.5, 122.2, 91.2, 82.7, 78.1, 75.8, 27.7; IR (neat, cm^{-1}): 2981, 2934, 1958, 1740, 1595, 1488, 1458, 1434, 1395, 1369, 1273, 1252, 1159, 1126, 1072, 1036, 1012; MS (ESI) m/z 344 [M(^{81}Br)+NH$_4$]$^+$, 342 [M(^{79}Br)+NH$_4$]$^+$; HRMS (ESI) Calcd for $C_{15}H_{21}{}^{79}BrNO_3$ (M+NH$_4$)$^+$: 342.0699, Found: 342.0699.

13. **Synthesis of *tert*-butyl 1-(4-methoxycarbonylphenyl)buta-2,3-dienyl carbonate (1q, zth-4-120):**



According to **Typical Procedure III**, the reaction of 1-(4-methoxycarbonyl phenyl)buta-2,3-dien-1-ol (1.0223 g, 5.0 mmol), DMAP (30.7 mg, 0.25 mmol), triethylamine (1.4 mL, d = 0.726, 1.0164 g, 10.0 mmol), and Boc_2O (1.2 mL, d = 0.949 g/mL, 1.1388 g, 5.0 mmol) in DCM (5 mL) afforded **1q** (1.0587 g, 70%) (eluent: petroleum ether / diethyl ether / triethylamine = 1000/4/1 to 1000/9/1).It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (dt, *J* = 8.0 Hz, 1.8 Hz, 2H, ArH), 7.26 (d, *J* = 8.0 Hz, 2H, ArH), 6.10 (dt, *J* = 6.8 Hz, 2.0 Hz, 1H, CH), 5.44 (q, *J* = 6.8 Hz, 1H, =CH), 4.93 – 4.81 (m, 2H, $=CH_2$), 3.92 (s, 3H, CH_3), 1.48 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8, 166.6, 152.4, 143.9, 129.8, 129.7, 126.5, 91.1, 82.7, 78.0, 75.9, 52.1, 27.6; IR (neat, cm^{-1}): 1958, 1741, 1725, 1614, 1436, 1370, 1274, 1254, 1161, 1110, 1020; MS (ESI) m/z 327 $(M+Na)^+$; HRMS (ESI) Calcd for $C_{17}H_{24}NO_5$ $(M+NH_4)^+$: 322.1649, Found: 322.1652.

14. **Synthesis of *tert*-butyl 1-(3-cyanophenyl)buta-2,3-dienyl carbonate (1r, zth-4-121):**

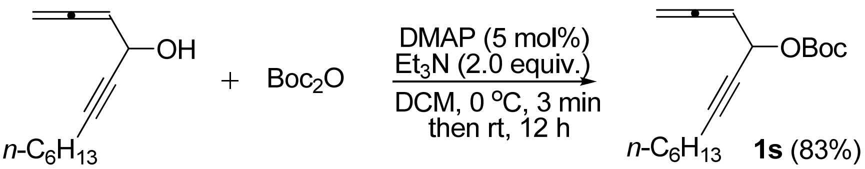


1r (82%)

According to **Typical Procedure III**, the reaction of 1-(3-cyanophenyl)buta-2,3-dien-1-ol (0.8566 g, 5.0 mmol), DMAP (30.7 mg, 0.25 mmol), triethylamine (1.4 mL, d = 0.726, 1.0164 g, 10.0 mmol), and Boc_2O (1.2 mL, d = 0.949 g/mL, 1.1388 g, 5.0 mmol) in DCM (5 mL) afforded **1r** (1.1176 g, 82%) (eluent: petroleum ether / diethyl ether / triethylamine = 1000/4/1 to 1000/9/1). It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H, ArH), 7.64 – 7.58 (m, 2H, ArH), 7.48 (t, *J* = 7.6 Hz, 1H, ArH), 6.07 (dt, *J* = 6.8 Hz, 2.2 Hz, 1H, CH), 5.43 (q, *J* = 6.7

Hz, 1H, =CH), 4.96 – 4.83 (m, 2H, =CH$_2$), 1.49 (s, 9H, C(CH$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 208.9, 152.3, 140.5, 131.8, 131.1, 130.3, 129.3, 118.6, 112.6, 90.9, 83.1, 78.5, 75.2, 27.7; IR (neat, cm^{-1}): 3069, 2982, 2935, 2232, 1958, 1740, 1605, 1586, 1482, 1460, 1435, 1395, 1370, 1353, 1272, 1251, 1156, 1126, 1082, 1036; MS (ESI) m/z 272 (M+H)$^+$; HRMS (EI) Calcd for $C_{16}H_{17}NO_3$ (M$^+$): 271.1208, Found: 271.1214.

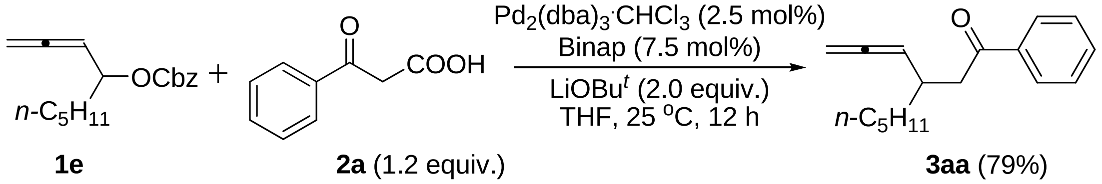
15. **Synthesis of *tert*-butyl dodeca-1,2-dien-5-yn-4-yl carbonate (1s, zth-5-089):**



According to **Typical Procedure III**, the reaction of dodeca-1,2-dien-5-yn-4-ol (0.8917 g, 5.0 mmol), DMAP (30.7 mg, 0.25 mmol), triethylamine (1.4 mL, d = 0.726, 1.0164 g, 10.0 mmol), and Boc$_2$O (1.2 mL, d = 0.949 g/mL, 1.1388 g, 5.0 mmol) in DCM (5 mL) afforded **1s** (1.1494 g, 83%) (eluent: petroleum ether / diethyl ether / triethylamine = 1000/1/1 to 1000/3/1). It should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether (200 mL) and triethylamine (0.8 mL) before loading the sample) as a liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.71 – 5.64 (m, 1H, CH), 5.36 (q, J = 6.7 Hz, 1H, =CH), 5.01 – 4.91 (m, 2H, =CH$_2$), 2.22 (td, J = 7.2 Hz, 2.0 Hz, 2H, CH$_2$), 1.54 – 1.44 (m, 11H, C(CH$_3$)$_3$+CH$_2$), 1.42 – 1.22 (m, 6H, 3×CH$_2$), 0.89 (t, J = 7.0 Hz, 3H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 209.0, 152.2, 89.8, 87.9, 82.4, 78.2, 75.5, 65.4, 31.2, 28.3, 28.2, 27.6, 22.4, 18.6, 13.9; IR (neat, cm^{-1}): 3069, 2932, 2860, 2239, 1959, 1743, 1459, 1433, 1370, 1351, 1321, 1272, 1251, 1157, 1117, 1077, 1035; MS (ESI) m/z 301 (M+Na)$^+$; HRMS (ESI) Calcd for $C_{17}H_{30}NO_3$ (M+NH$_4$)$^+$: 296.2220, Found: 296.2219.

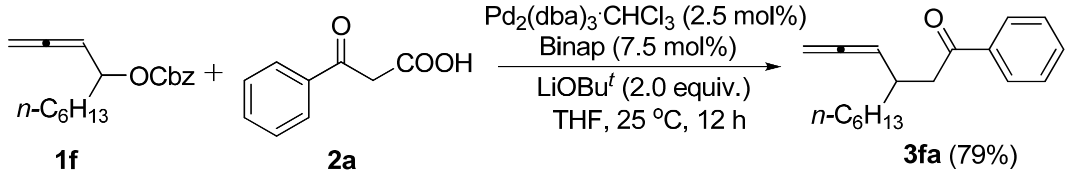
Synthesis of 3,4-alkadienyl ketones (Table 4)

1. **Synthesis of 1-phenyl-3-(propa-1,2-dienyl)octan-1-one (3aa, zth-3-157)**



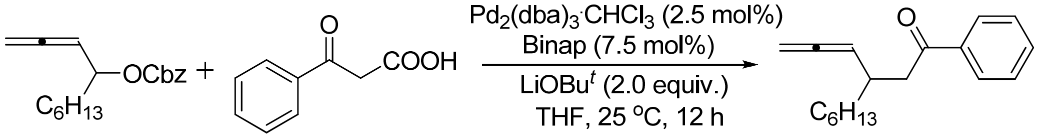
To an oven-dried Schlenk tube was added LiOBu^t (160.3 mg, 2.0 mmol) under argon. Then to the Schlenk tube equipped with a magnetic stirring bar were added sequentially **1e** (274.4 mg, 1.0 mmol)/THF (3 mL), $Pd_2(dba)_3 \cdot CHCl_3$ (25.8 mg, 0.025 mmol), binap (47.7 mg, 0.075 mmol), and **2a** (197.3 mg, 1.2 mmol)/THF (2 mL) under argon. The resulting mixture was stirred at 25 °C for 12 hours. Upon completion, the resulting mixture was filtered through a short column of silica gel eluted with Et_2O (20 mL) and concentrated. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 500/1) to afford **3aa** (191.9 mg, 79%) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.2 Hz, 2H, ArH), 7.55 (t, J = 7.6 Hz, 1H, ArH), 7.45 (t, J = 7.4 Hz, 2H, ArH), 5.18 (q, J = 6.7 Hz, 1H, =CH), 4.72 – 4.62 (m, 2H, $=CH_2$), 3.09 (dd, J = 16.6 Hz, 7.4 Hz, 1H, one proton of CH_2), 2.95 (dd, J = 16.6 Hz, 6.2 Hz, 1H, one proton of CH_2), 2.86 – 2.74 (m, 1H, CH), 1.54 – 1.20 (m, 8H, 4 × CH_2), 0.88 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 199.3, 137.4, 132.8, 128.5, 128.0, 93.8, 76.2, 43.6, 35.0, 34.0, 31.8, 26.7, 22.6, 14.0; IR (neat, cm^{-1}): 2955, 2927, 2856, 1954, 1685, 1597, 1580, 1448, 1406, 1357, 1274, 1210, 1179, 1001; MS (70 eV, EI) m/z (%) 242 (M^+, 1.23), 105 (100); HRMS (EI) calcd for $C_{17}H_{22}O$ (M^+): 242.1671, found 242.1672.

2. **Synthesis of 1-phenyl-3-(propa-1,2-dienyl)nonan-1-one (3fa, zth-3-158)**



To an oven-dried Schlenk tube was added LiOBu^t (160.4 mg, 2.0 mmol) under argon. Then to the Schlenk tube equipped with a magnetic stirring bar were added sequentially $Pd_2(dba)_3 \cdot CHCl_3$ (25.8 mg, 0.025 mmol), binap (47.7 mg, 0.075 mmol), **1f** (288.5 mg, 1.0 mmol)/THF (3 mL), and **2a** (197.4 mg, 1.2 mmol)/THF (2 mL) under argon. The mixture was stirred at 25 °C for 12 hours. Upon completion, the resulting mixture was filtered through a short column of silica gel eluted with Et_2O (20 mL) and concentrated. The crude product was purified by chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 500/1) to afford **3fa** (202.1 mg, 79%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H, ArH), 7.55 (t, *J* = 7.4 Hz, 1H, ArH), 7.45 (t, *J* = 7.6 Hz, 2H, ArH), 5.18 (q, *J* = 6.5 Hz, 1H, =CH), 4.71 – 4.61 (m, 2H, =CH_2), 3.09 (dd, *J* = 16.6 Hz, 7.4 Hz, 1H, one proton of CH_2), 2.95 (dd, *J* = 16.4, 6.0 Hz, 1H, one proton of CH_2), 2.86 – 2.74 (m, 1H, CH), 1.54 – 1.18 (m, 10H, 5 × CH_2), 0.88 (t, *J* = 6.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 199.4, 137.4, 132.8, 128.5, 128.0, 93.8, 76.2, 43.6, 35.1, 34.0, 31.8, 29.3, 27.0, 22.6, 14.0; IR (neat, cm^{-1}): 2955, 2925, 2855, 1955, 1685, 1598, 1580, 1448, 1406, 1358, 1279, 1266, 1208, 1179, 1001; MS (70 eV, EI) m/z (%) 256 (M^+, 1.59), 105 (100); HRMS calcd for $C_{18}H_{24}O$ (M^+): 256.1827, found 256.1831.

The gram scale synthesis of 1-phenyl-3-(propa-1,2-dienyl)nonan-1-one (3fa, zth-5-146)

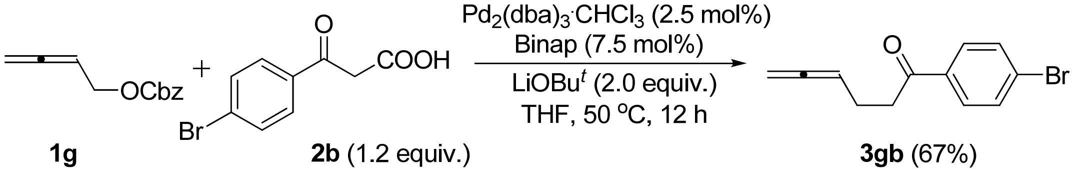


1f (7.5 mmol) **2a** (1.2 equiv.) **3fa** (65%)

To an oven-dried Schlenk tube was added LiOBu^t (1.2013 g, 15.0 mmol) under argon. Then, to the Schlenk tube equipped with a magnetic stirring bar were added sequentially $Pd_2(dba)_3{\cdot}CHCl_3$ (194.4 mg, 0.1875 mmol), binap (350.5 mg, 0.5625 mmol), **2a** (1477.0 mg, 1.2 mmol), and **1f** (2163.2 mg, 7.5 mmol), and THF (37.5 mL) under argon. The mixture was stirred at 25 °C for 12 hours. Upon completion, the resulting mixture was filtered through a short column of silica gel eluting with Et_2O (150 mL) and concentrated. The crude product was purified by chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 500/1) to afford **3fa** (1.2580 g, 65%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 2H, ArH), 7.60 - 7.52 (m, 1H, ArH), 7.46 (t, *J* = 7.6 Hz, 2H, ArH), 5.18 (q, *J* = 6.9 Hz, 1H, =CH), 4.72 – 4.60 (m, 2H, =CH_2), 3.09 (dd, *J* = 16.4, 7.6 Hz, 1H, one proton of CH_2), 2.95 (dd, *J* =

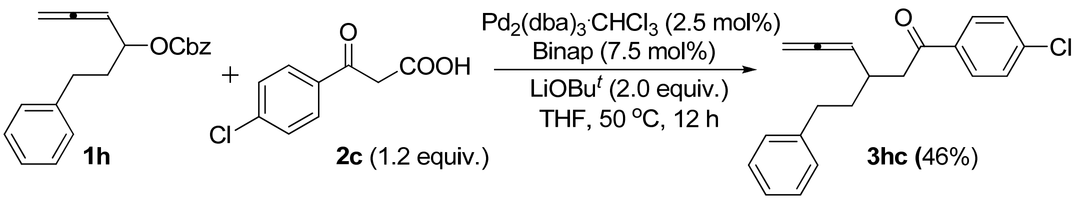
16.6 Hz, 6.2 Hz, 1H, one proton of CH_2), 2.86 – 2.74 (m, 1H, CH), 1.54 – 1.20 (m, 10H, 5 × CH_2), 0.88 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 199.4, 137.3, 132.9, 128.5, 128.0, 93.8, 76.2, 43.6, 35.1, 34.0, 31.8, 29.3, 27.0, 22.6, 14.1.

3. **Synthesis of 1-(4-bromophenyl)hexa-4,5-dien-1-one (3gb, zth-5-060)**



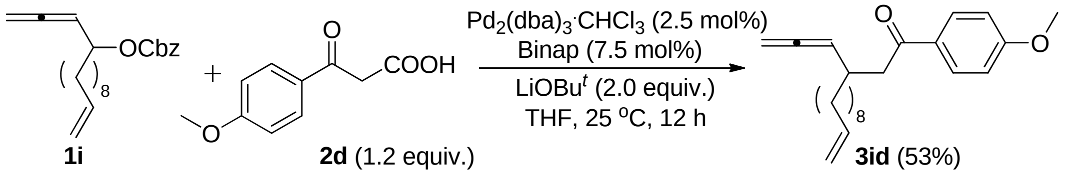
Typical Procedure IV: To an oven-dried Schlenk tube was added LiOBu^t (160.7 mg, 2.0 mmol) under argon. Then to the Schlenk tube equipped with a magnetic stirring bar were added sequentially $Pd_2(dba)_3 \cdot CHCl_3$ (26.0 mg, 0.025 mmol), binap (47.6 mg, 0.075 mmol), **2b** (291.9 mg, 1.2 mmol), **1g** (204.3 mg, 1.0 mmol), and THF (5 mL) under argon. The resulting mixture was stirred at 25 °C for 12 hours. Upon completion, the resulting mixture was filtered through a short column of silica gel eluting with Et_2O (50 mL) and concentrated. The crude product was purified by chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 500/1) to afford **3gb** (168.3 mg, 67%) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.4 Hz, 2H, ArH), 7.60 (d, J = 8.8 Hz, 2H, ArH), 5.25 (quintet, J = 6.5 Hz, 1H, =CH), 4.70 (quintet, J = 3.4 Hz, 2H, =CH_2), 3.07 (t, J = 7.0 Hz, 2H, CH_2), 2.50 – 2.35 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.3, 198.3, 135.6, 131.9, 129.5, 128.1, 89.1, 79.2, 37.3, 22.1; IR (neat, cm^{-1}): 2959, 2914, 2858, 1955, 1674, 1584, 1567, 1468, 1447, 1420, 1396, 1361, 1340, 1294, 1263, 1198, 1179, 1070, 1060, 1036, 1011; MS (70 eV, EI) m/z (%) 252 [M(^{81}Br)$^+$, 24.38], 250 [M(^{79}Br)$^+$, 24.00], 183 (100); HRMS calcd for $C_{12}H_{11}{}^{79}BrO$ (M^+): 249.9993, found 249.9995.

4. **Synthesis of 1-(4-chlorophenyl)-3-phenethylhexa-4,5-dien-1-one (3hc, zth-5-050)**



According to **Typical Procedure IV**, the reaction of **1h** (308.5 mg, 1.0 mmol), **2c** (239.0 mg, 1.2 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (25.9 mg, 0.025 mmol), binap (47.8 mg, 0.075 mmol), and $LiOBu^t$ (160.4 mg, 2.0 mmol) in THF (5 mL) at 50 ^{o}C afforded **3hc** (153.7 mg, 46%, purity = 93%) (eluent : petroleum ether / ethyl ether = 1000/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.81 (m, 2H, ArH), 7.48 – 7.39 (m, 2H, ArH), 7.30 – 7.22 (m, 2H, ArH), 7.22 – 7.12 (m, 3H, ArH), 5.23 (q, J = 6.5 Hz, 1H, =CH), 4.77 - 4.66 (m, 2H, $=CH_2$), 3.09 (dd, J = 16.2 Hz, 7.8 Hz, 1H, one proton of CH_2), 2.94 (dd, J = 16.4 Hz, 6.0 Hz, 1H, one proton of CH_2), 2.90 – 2.80 (m, 1H, CH), 2.80 – 2.58 (m, 2H, CH_2), 1.86 – 1.69 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 197.8, 142.0, 139.4, 135.5, 129.4, 128.8, 128.3, 125.8, 93.3, 76.6, 43.6, 36.7, 33.7, 33.4; IR (neat, cm^{-1}): 3085, 3062, 3026, 2924, 2856, 1954, 1684, 1588, 1571, 1496, 1488, 1454, 1400, 1360, 1261, 1251, 1210, 1091, 1030, 1012; MS (ESI) m/z 313 $[M(^{37}Cl)+H]^+$, 311 $[M(^{35}Cl)+H]^+$; HRMS calcd for $C_{20}H_{19}O^{35}Cl\,(M^+)$: 310.1124, found 310.1128.

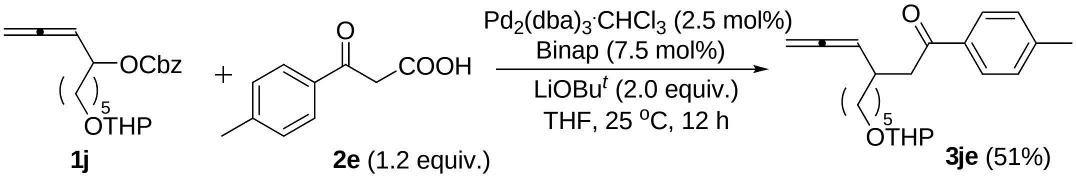
5. **Synthesis of 1-(4-methoxyphenyl)-3-(propa-1,2-dienyl)tridec-12-en-1-one (3id, zth-5-022)**



According to **Typical Procedure IV**, the reaction of **1i** (342.5 mg, 1.0 mmol), **2d** (233.4 mg, 1.2 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (25.9 mg, 0.025 mmol), binap (47.8 mg, 0.075 mmol), and $LiOBu^t$ (160.4 mg, 2.0 mmol) in THF (5 mL) afforded **3id** (180.3 mg, 53%) [eluent: petroleum ether / ethyl ether = 1000/1 (4 L) to 500/1 (2 L)] as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 9.2 Hz, 2H, ArH), 6.93 (d, J = 9.2 Hz, 2H, ArH), 5.86 – 5.75 (m, 1H, =CH), 5.17 (q, J = 6.8 Hz, 1H, =CH), 5.03 - 4.89

(m, 2H, =CH_2), 4.71 – 4.61 (m, 2H, =CH_2), 3.87 (s, 3H, CH_3), 3.03 (dd, J = 16.0, 7.6 Hz, 1H, one proton of CH_2), 2.89 (dd, J = 16.2, 6.2 Hz, 1H, one proton of CH_2), 2.81 – 2.71 (m, 1H, CH), 2.03 (q, J = 7.1 Hz, 2H, CH_2), 1.50 – 1.20 (m, 14H, 7 $\times$ CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 198.0, 163.3, 139.2, 130.5, 130.3, 114.1, 113.6, 93.9, 76.2, 55.4, 43.3, 35.1, 34.2, 33.8, 29.6, 29.5, 29.4, 29.1, 28.9, 27.0; IR (neat, cm^{-1}): 2924, 2853, 1955, 1677, 1640, 1600, 1576, 1509, 1462, 1441, 1418, 1359, 1307, 1256, 1168, 1112, 1031; MS(70 eV, EI) m/z (%) 340 (M^+, 3.76) 135 (100); HRMS calcd for $C_{23}H_{32}O_2$ (M^+): 340.2402, found 340.2404.

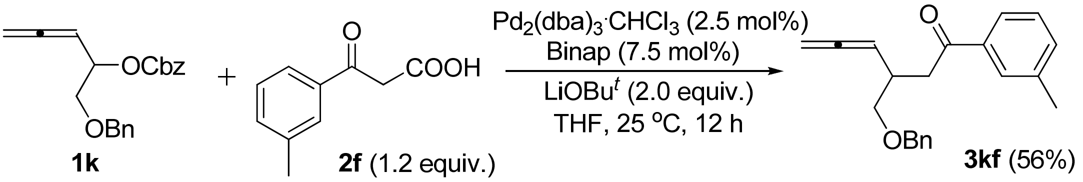
6. **Synthesis of 1-*p*-tolyl-3-(propa-1,2-dienyl)-8-(tetrahydro-2*H*-pyran-2-yloxy)-octan-1-one (3je, zth-5-104)**



According to **Typical Procedure IV**, the reaction of **1j** (374.5 mg, 1.0 mmol), **2e** (214.1 mg, 1.2 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (25.9 mg, 0.025 mmol), binap (47.8 mg, 0.075 mmol), and $LiOBu^t$ (160.7 mg, 2.0 mmol) in THF (5 mL) afforded **3je** (181.8 mg, 51%) [eluent: petroleum ether / ethyl acetate = 1000/1 (1 L) to 500/1 (4 L) to 250/1 for the first round afforded impure **3je**, which was further purified by eluent: petroleum ether / ethyl acetate = 100/1 (1 L) to 50/1 (3 L) to 20/1 (1 L) for the second round] as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H, ArH), 7.25 (d, J = 8.8 Hz, 2H, ArH), 5.17 (q, J = 6.7 Hz, 1H, =CH), 4.71 – 4.61 (m, 2H, =CH_2), 4.59 – 4.54 (m, 1H, CH), 3.91 – 3.80 (m, 1H, one proton of OCH_2), 3.72 (dt, J = 9.6 Hz, 4.6 Hz, 1H, one proton of OCH_2), 3.54 – 3.44 (m, 1H, one proton of OCH_2), 3.37 (dt, J = 9.6, 5.0 Hz, 1H, one proton of OCH_2), 3.06 (dd, J = 16.4, 7.6 Hz, 1H, one proton of CH_2), 2.92 (dd, J = 16.4, 6.0 Hz, 1H, one proton of CH_2), 2.84 – 2.72 (m, 1H, CH), 2.41 (s, 3H, CH_3), 1.88 – 1.64 (m, 2H, CH_2), 1.64 – 1.30 (m, 12H, $6 \times CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 199.0, 143.6, 134.8, 129.2, 128.1, 98.8, 93.7, 76.2, 67.5, 62.3, 43.5, 35.0, 34.0, 30.7, 29.6, 26.9, 26.2, 25.5, 21.6, 19.7; IR (neat,

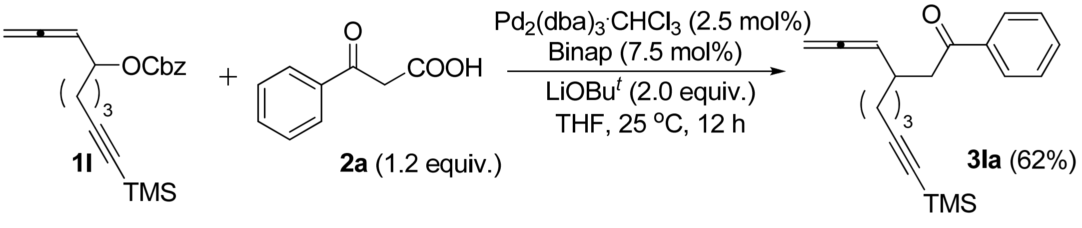
cm^{-1}): 2934, 2857, 1954, 1682, 1606, 1573, 1440, 1407, 1352, 1323, 1282, 1261, 1224, 1201, 1180, 1136, 1119, 1077, 1023; MS (70 eV, EI) m/z (%) 356 (M^+, 1.15), 119 (100); HRMS calcd for $C_{23}H_{32}O_3$ (M^+): 356.2351, found 356.2354.

7. **Synthesis of 1-*m*-tolyl-3-(benzyloxymethyl)hexa-4,5-dien-1-one (3kf, zth-5-129)**



According to **Typical Procedure IV**, the reaction of **1k** (324.5 mg, 1.0 mmol), **2f** (214.0 mg, 1.2 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (25.9 mg, 0.025 mmol), binap (47.8 mg, 0.075 mmol), and $LiOBu^t$ (160.5 mg, 2.0 mmol) in THF (5 mL) afforded **3kf** (171.7 mg, 56%) [eluent: petroleum ether / ethyl acetate = 1000/1 (5 L) to 500/1 (1 L)] as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.70 (m, 2H, ArH), 7.40 – 7.22 (m, 7H, ArH), 5.29 (q, J = 6.4 Hz, 1H, =CH), 4.76 – 4.65 (m, 2H, =CH_2), 4.51 (s, 2H, CH_2), 3.56 (dd, J = 9.2, 5.2 Hz, 1H, one proton of CH_2), 3.48 (dd, J = 9.2, 6.4 Hz, 1H, one proton of CH_2), 3.27 – 3.12 (m, 2H, one proton of CH_2+CH), 3.06 (dd, J = 15.8, 6.8 Hz, 1H, one proton of CH_2), 2.40 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 199.2, 138.3, 138.2, 137.2, 133.6, 128.6, 128.33, 128.29, 127.54, 127.51, 125.2, 91.2, 76.8, 72.9, 72.8, 40.2, 34.1, 21.3; IR (neat, cm^{-1}): 2854, 1954, 1684, 1596, 1580, 1487, 1448, 1404, 1359, 1245, 1203, 1180, 1072, 1010; MS (ESI) m/z 307 $(M+H)^+$; HRMS calcd for $C_{21}H_{22}O_2$ (M^+): 306.1620, found 306.1621.

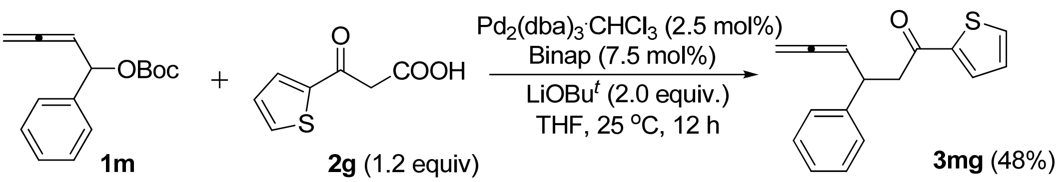
8. **Synthesis of 1-phenyl-3-(propa-1,2-dienyl)-8-(trimethylsilyl)oct-7-yn-1-one (3la, zth-5-131)**



According to **Typical Procedure IV**, the reaction of **1l** (342.6 mg, 1.0 mmol), **2a**

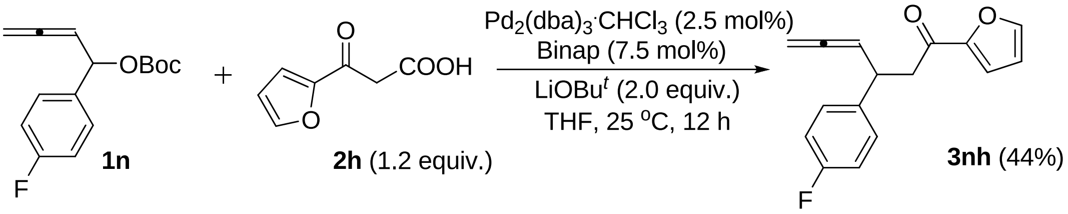
(197.2 mg, 1.2 mmol), $Pd_2(dba)_3\cdot CHCl_3$ (25.9 mg, 0.025 mmol), binap (47.7 mg, 0.075 mmol), and LiOBu^t (160.4 mg, 2.0 mmol) in THF (5 mL) afforded **3la** (198.5 mg, 62%, purity = 97%) (eluent: petroleum ether / ethyl acetate = 1000/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H, ArH), 7.60 – 7.52 (m, 1H, ArH), 7.46 (t, J = 7.6 Hz, 2H, ArH), 5.18 (q, J = 6.7 Hz, 1H, =CH), 4.74 – 4.62 (m, 2H, $=CH_2$), 3.11 (dd, J = 16.8, 7.6 Hz, 1H, one proton of CH_2), 2.96 (dd, J = 16.6, 6.2 Hz, 1H, one proton of CH_2), 2.88 – 2.76 (m, 1H, CH), 2.30 -2.15 (m, 2H, CH_2), 1.75 – 1.45 (m, 4H, 2×CH_2), 0.14 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 199.1, 137.2, 132.9, 128.5, 128.0, 107.2, 93.4, 84.6, 76.5, 43.6, 34.1, 33.5, 26.1, 19.8, 0.13; IR (neat, cm^{-1}) 3087, 3061, 3030, 2956, 2929, 2900, 2861, 2173, 1955, 1686, 1598, 1580, 1448, 1407, 1360, 1328, 1248, 1217, 1180, 1159, 1002; MS (70 eV, EI) m/z (%) 310 (M$^+$, 1.32), 105 (100); HRMS calcd for $C_{20}H_{26}OSi$ (M$^+$): 310.1753, found 310.1750.

9. **Synthesis of 3-phenyl-1-(thien-2-yl)hexa-4,5-dien-1-one (3mg, zth-5-069)**



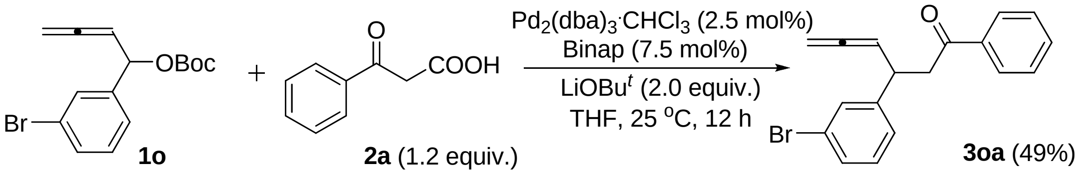
According to **Typical Procedure IV**, the reaction of **1m** (246.5 mg, 1.0 mmol), **2g** (204.0 mg, 1.2 mmol), $Pd_2(dba)_3\cdot CHCl_3$ (25.9 mg, 0.025 mmol), binap (47.6 mg, 0.075 mmol), and LiOBu^t (159.9 mg, 2.0 mmol) in THF (5 mL) afforded **3mg** (122.7 mg, 48%) [eluent: petroleum ether / ethyl acetate = 1000/1 (4 L) to 500/1 for the first round afforded impure **3mg**, which was further purified by eluent: petroleum ether / diethyl ether = 500/1 (2 L) to 250/1 (2 L) to 100/1 (1 L) for the second round] as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 3.4 Hz, 1.0 Hz, 1H, ArH), 7.59 (dd, J = 5.0 Hz, 0.6 Hz, 1H, ArH), 7.34 – 7.27 (m, 4H, ArH), 7.26 – 7.16 (m, 1H, ArH), 7.11 – 7.05 (m, 1H, ArH), 5.42 (q, J = 6.3 Hz, 1H, =CH), 4.85 – 4.71 (m, 2H, $=CH_2$), 4.19 – 4.09 (m, 1H, CH), 3.44 (dd, J = 16.4, 8.0 Hz, 1H, one proton of CH_2), 3.17 (dd, J = 16.6, 6.2 Hz, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 191.0, 144.4, 143.3, 133.5, 131.7, 128.5, 128.0, 127.7, 126.7, 93.9, 77.7, 45.2, 39.4; IR (neat, cm^{-1}) 3101, 3061, 3027, 2924, 2898, 2853, 1954, 1659, 1601, 1518, 1492, 1452, 1414, 1355, 1246, 1205, 1079, 1063; MS (70 eV, EI) m/z (%) 254 (M$^+$, 6.92), 111 (100); HRMS calcd for $C_{16}H_{14}OS$ (M$^+$): 254.0765, found 254.0767.

10. **Synthesis of 3-(4-fluorophenyl)-1-(furan-2-yl)hexa-4,5-dien-1-one (3nh, zth-5-095)**



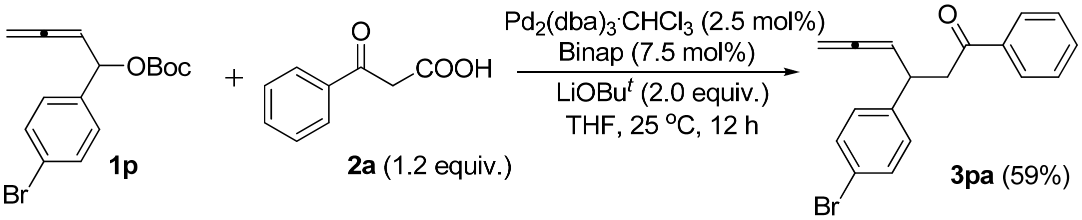
According to **Typical Procedure IV**, the reaction of **1n** (264.3 mg, 1.0 mmol), **2h** (185.2 mg, 1.2 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (25.9 mg, 0.025 mmol), binap (48.1 mg, 0.075 mmol), and LiOBu^t (160.7 mg, 2.0 mmol) in THF (5 mL) afforded **3nh** (124.4 mg, 44%, purity = 91%) [eluent: petroleum ether / ethyl acetate = 1000/1 (5 L) to 500/1 (2 L)] as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 1H, ArH), 7.30 – 7.22 (m, 2H, ArH), 7.13 (d, J = 3.6 Hz, 1H, ArH), 6.97 (t, J = 8.8 Hz, 2H, ArH), 6.50 (q, J = 1.9 Hz, 1H, ArH), 5.38 (q, J = 6.5 Hz, 1H, =CH), 4.86 – 4.72 (m, 2H, =CH_2), 4.16 – 4.06 (m, 1H, CH), 3.33 (dd, J = 16.4 Hz, 7.2 Hz, 1H, one proton of CH_2), 3.09 (dd, J = 16.4, 7.2 Hz, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 187.2, 161.6 (d, J = 243.0 Hz), 152.8, 146.3, 138.9 (d, J = 3.2 Hz), 129.2 (d, J = 7.6 Hz), 117.1, 115.2 (d, J = 21.4 Hz), 112.2, 93.9, 77.8, 44.3, 38.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -116.7; IR (neat, cm^{-1}): 1955, 1672, 1603, 1568, 1508, 1467, 1394, 1358, 1295, 1280, 1263, 1220, 1158, 1085, 1059, 1016; MS (70 ev, EI) m/z (%) 256 (M$^+$, 10.31), 95 (100); HRMS calcd for $C_{16}H_{13}FO_2$ (M$^+$): 256.0900, found 256.0904.

11. **Synthesis of 3-(3-bromophenyl)-1-phenylhexa-4,5-dien-1-one (3oa, zth-4-130)**



According to **Typical Procedure IV**, the reaction of **1o** (325.4 mg, 1.0 mmol), **2a** (197.1 mg, 1.2 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (25.7 mg, 0.025 mmol), binap (47.7 mg, 0.075 mmol), and LiOBu^t (160.1 mg, 2.0 mmol) in THF (5 mL) afforded **3oa** (163.6 mg, 49%, purity = 98%) [eluent: petroleum ether / ethyl acetate = 1000/1 (4 L) to 500/1 (0.5 L)] as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H, ArH), 7.59 – 7.51 (m, 1H, ArH), 7.50 - 7.40 (m, 3H, ArH), 7.38 – 7.30 (m, 1H, ArH), 7.29 – 7.22 (m, 1H, ArH), 7.16 (t, J = 7.8 Hz, 1H, ArH), 5.39 (q, J = 6.1 Hz, 1H, =CH), 4.87 - 4.71 (m, 2H, $=CH_2$), 4.20 - 4.08 (m, 1H, CH), 3.52 (dd, J = 17.0, 7.8 Hz, 1H, one proton of CH_2), 3.21 (dd, J = 17.4, 6.2 Hz, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 197.6, 146.0, 136.9, 133.1, 130.8, 130.1, 129.8 128.5, 127.9, 126.6, 122.5, 93.6, 78.0, 44.2, 38.8; IR (neat, cm^{-1}) 3084, 3037, 2985, 2895, 2855, 1955, 1684, 1595, 1580, 1567, 1474, 1448, 1426, 1406, 1359, 1299, 1285, 1243, 1202, 1181, 1092, 1073; MS (70 eV, EI) m/z (%) 328 [$M^+(^{81}Br)$, 3.42], 326 [$M^+(^{79}Br)$, 3.40], 105 (100); HRMS calcd for $C_{18}H_{15}{}^{79}BrO$ (M^+): 326.0306, found 326.0308.

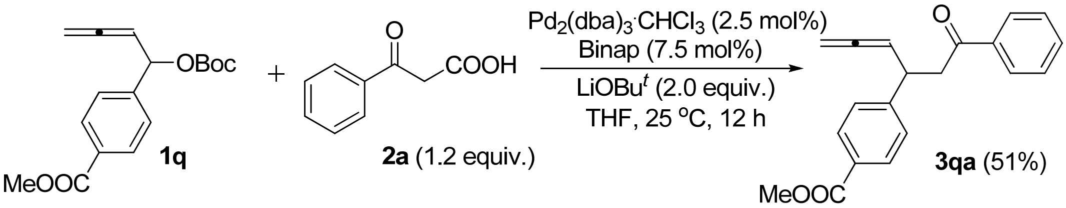
12. **Synthesis of 3-(4-bromophenyl)-1-phenylhexa-4,5-dien-1-one (3pa, zth-4-129)**



According to **Typical Procedure IV**, the reaction of **1p** (325.4 mg, 1.0 mmol), **2a** (197.2 mg, 1.2 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (25.8 mg, 0.025 mmol), binap (47.7 mg, 0.075 mmol), and LiOBu^t (160.7 mg, 2.0 mmol) in THF (5 mL) afforded **3pa** (193.1 mg, 59%) (eluent : petroleum ether / ethyl acetate = 1000/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H, ArH), 7.55 (t, J = 7.6 Hz, 1H, ArH), 7.48 - 7.38 (m, 4H, ArH), 7.19 (d, J = 8.4 Hz, 2H, ArH), 5.39 (q, J = 6.1 Hz, 1H, =CH), 4.85 -

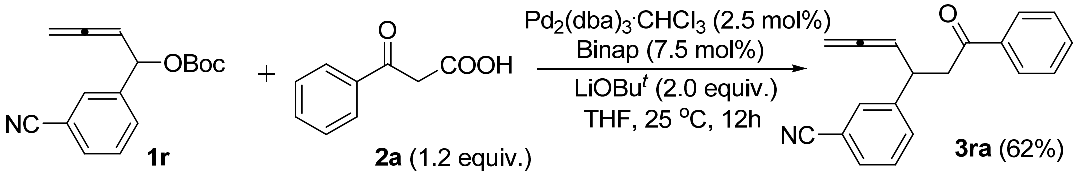
4.70 (m, 2H, $=CH_2$), 4.18 - 4.07 (m, 1H, CH), 3.50 (dd, *J* = 17.6, 7.6 Hz, 1H, one proton of CH_2), 3.21 (dd, *J* = 17.6, 6.8 Hz, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 197.8, 142.6, 136.9, 133.1, 131.5, 129.5, 128.5, 127.9, 120.4, 93.7, 77.9, 44.3, 38.7; IR (neat, cm^{-1}): 1955, 1685, 1596, 1580, 1487, 1448, 1434, 1404, 1359, 1319, 1298, 1280, 1245, 1203, 1181, 1159, 1102, 1073, 1010; MS (70 eV, EI) m/z (%) 328 [M$^+$ (^{81}Br), 3.95], 326 [M$^+$ (^{79}Br), 3.82], 105 (100); HRMS calcd for $C_{18}H_{15}{}^{79}BrO$ (M$^+$): 326.0306, found 326.0308.

13. **Synthesis of 3-(4-(methoxycarbonylphenyl)-1-phenylhexa-4,5-dien-1-one (3qa, zth-4-136)**



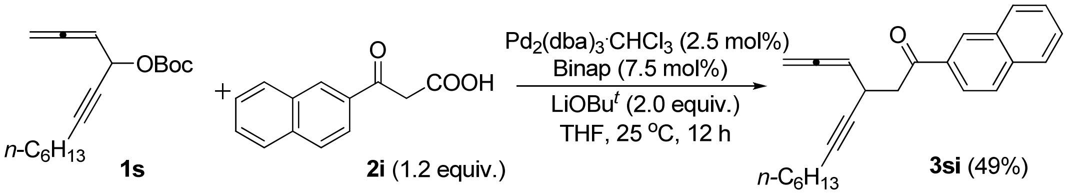
According to **Typical Procedure IV**, the reaction of **1q** (304.6 mg, 1.0 mmol), **2a** (197.1 mg, 1.2 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (25.9 mg, 0.025 mmol), binap (47.7 mg, 0.075 mmol), and LiOBu^t (160.4 mg, 2.0 mmol) in THF (5 mL) afforded **3qa** (156.2 mg, 51%) [eluent: petroleum ether (60–90 °C) / ethyl acetate = 1000/1(2 L) to 500/1 (2 L) to 250/1(1 L)] as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H, ArH), 7.94 - 7.89 (m, 2H, ArH), 7.55 (tt, *J* = 7.4, 1.5 Hz, 1H, ArH), 7.47 – 7.41 m, 2H, ArH), 7.41 – 7.35 (m, 2H, ArH), 5.42 (q, *J* = 6.4 Hz, 1H, =CH), 4.86 - 4.71 (m, 2H, $=CH_2$), 4.27 – 4.18 (m, 1H, CH), 3.90 (s, 3H, CH_3), 3.54 (dd, *J* = 17.4, 7.4 Hz, 1H, one proton of CH_2), 3.26 (dd, *J* = 17.2, 6.4 Hz, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 197.7, 166.9, 148.9, 136.9, 133.1, 129.8, 128.58, 128.56, 127.9, 127.8, 93.6, 78.0, 52.0, 44.1, 39.2; IR (neat, cm^{-1}): 1955, 1718, 1684, 1609, 1434, 1276, 1180, 1103, 1019, 1001; MS (70 eV, EI) m/z (%) 306 (M$^+$, 8.84), 105 (100); HRMS calcd for $C_{20}H_{18}O_3$ (M$^+$): 306.1256, found 306.1254.

14. **Synthesis of 3-(3-cyanophenyl)-1-phenylhexa-4,5-dien-1-one (3ra, zth-4-137)**



According to **Typical Procedure IV**, the reaction of **1r** (271.4 mg, 1.0 mmol), **2a** (197.1 mg, 1.2 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (25.8 mg, 0.025 mmol), binap (47.7 mg, 0.075 mmol), and $LiOBu^t$ (160.3 mg, 2.0 mmol) in THF (5 mL) afforded **3ra** (168.3, 62%) [eluent : petroleum ether / ethyl acetate = 1000/1 (2 L) to 500/1 (2 L) to 250/1(1 L)] as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H, ArH), 7.64 - 7.60 (m, 1H, ArH), 7.60 – 7.54 (m, 2H, ArH), 7.50 (dt, J = 7.9 Hz, 1.4 Hz, 1H, ArH), 7.49 - 7.38 (m, 3H, ArH), 5.40 (q, J = 6.4 Hz, 1H, =CH), 4.90 – 4.76 (m, 2H, $=CH_2$), 4.25 - 4.15 (m, 1H, CH), 3.53 (dd, J = 17.8, 7.0 Hz, 1H, one proton of CH_2), 3.26 (dd, J = 17.6, 6.8 Hz, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 197.3, 145.1, 136.7, 133.3, 132.6, 131.5, 130.4, 129.2, 128.6, 127.9, 118.9, 112.5 93.3, 78.3, 44.0, 38.7; IR (neat, cm^{-1}) 3085, 3063, 3030, 2999, 2966, 2902, 2854, 2229, 1956, 1686, 1598, 1581, 1482, 1449, 1360, 1258, 1204, 1002; MS (70 eV, EI) m/z (%) 273 (M^+, 8.96), 105 (100); HRMS calcd for $C_{19}H_{15}NO$ (M^+): 273.1154, found 273.1152.

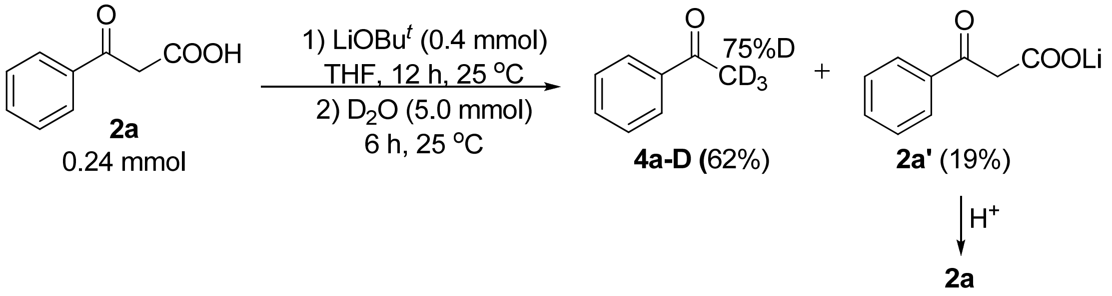
15. **Synthesis of 1-(naphthalen-2-yl)-3-(propa-1,2-dienyl)undec-4-yn-1-one (3si, zth-5-096)**



According to **Typical Procedure IV**, the reaction of **1s** (278.4 mg, 1.0 mmol), **2i** (257.4 mg, 1.2 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (25.9 mg, 0.025 mmol), binap (47.8 mg, 0.075 mmol), and $LiOBu^t$ (160.1 mg, 2.0 mmol) in THF (5 mL) afforded **3si** (161.7 mg, 49%) [eluent: petroleum ether / ethyl acetate = 1000/1 (4 L) to 500/1 (1 L) for the first round afforded impure **3si**, which was further purified by eluent: petroleum ether / ethyl acetate = 1000/0 (1 L) to 1000/1 (1 L) to 500/1 (4 L) for the second round] as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H, ArH), 8.04 (dd, J = 8.8 Hz, 1.6 Hz, 1H, ArH), 7.97 (d, *J* = 7.6 Hz, 1H, ArH), 7.88 (t, *J* = 7.6 Hz, 2H, ArH), 7.64 – 7.50 (m, 2H, ArH), 5.35 (q, *J* = 6.4 Hz, 1H, =CH), 4.87 – 4.74 (m, 2H, $=CH_2$), 3.92 – 3.80 (m, 1H, CH), 3.48 – 3.30 (m, 2H, CH_2), 2.13 (td, *J* = 7.0, 2.7 Hz, 2H, CH_2), 1.48 – 1.36 (m, 2H, CH_2), 1.36 – 1.14 (m, 6H, $3\times CH_2$), 0.85 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 197.5, 135.6, 134.3, 132.5, 129.9, 129.6, 128.5, 128.4, 127.8, 126.8, 123.9, 92.2, 82.7, 80.3, 78.0, 43.9, 31.3, 28.8, 28.4, 26.7, 22.5, 18.7, 14.0. IR (neat, cm^{-1}) 3059, 2954, 2928, 2856, 1957, 1681, 1627, 1596, 1468, 1434, 1405, 1357, 1276, 1233, 1208, 1182, 1171, 1123, 1048, 1020; MS (70 eV, EI) m/z (%) 330 (M^+, 7.51), 155 (100); HRMS calcd for $C_{24}H_{26}O$ (M^+): 330.1984, found 330.1982.

Mechanistic studies

1. The reaction of 2a with LiO*t*-Bu quenching with D_2O-Synthesis of acetophenone-D (4a-D, zth-6-094)

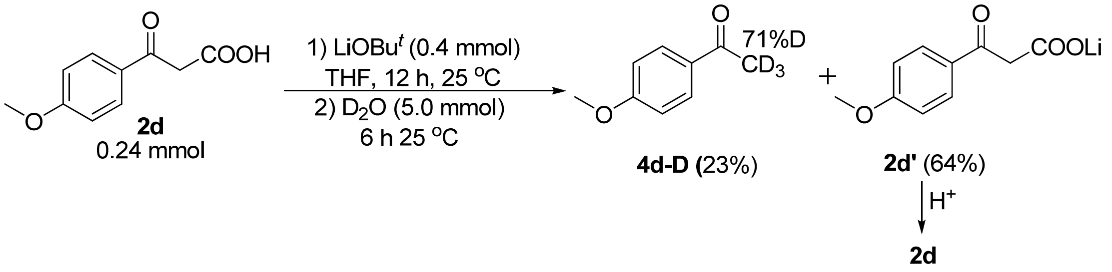


Typical Procedure V: To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added **2a** (39.5 mg, 0.24 mmol), LiOBu^t (32.0 mg, 0.40 mmol), and THF (1 mL) sequentially under argon. The mixture was stirred at 25 °C for 12 hours. After that, D_2O (90 uL, d = 1.107 g/mL, 99.6 mg, 5.00 mmol) was added under argon. Then, the mixture was stirred for at 25 °C for 6 hours. The resulting mixture was filtered and washed with Et_2O (10 mL × 3). The solid containing **2a’** was collected and treated with an aqueous HCl solution (3 N, 20 mL). Then to the resulting mixture were added sequentially water (20 mL) and DCM (20 mL). The organic phase was separated and the aqueous phase was extracted with DCM (20 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and evaporated to afford **2a**[5] (7.5 mg, 19%, ketone : enol = 2.6 : 1) as a solid. The filtrate was concentrated and purified by chromatography on silica gel [eluent: petroleum ether (30 - 60 °C) / ethyl ether = 10/1] to afford **4a-D**[6] (18.3 mg, 62% , D% = 75%) as a liquid.

2a: ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.92 (m, 2H, ArH), 7.66 (t, *J* = 7.4 Hz, 1H, ArH), 7.58 – 7.50 (m, 2H, ArH), 4.09 (s, 2H, CH_2); the following signals are discernible for Enol-**2a**: 12.30 (s, 1H, OH), 7.84 – 7.78 (m, 2H, ArH), 7.50 – 7.40 (m, 3H, ArH), 5.73 (s, 1H, =CH); MS (70 eV, EI) m/z (%) 164 (M^+, 9.00), 105 (100).

4a-D: ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.90 (m, 2H, ArH), 7.57 (tt, *J* = 7.5 Hz, 1.5 Hz, 1H, ArH), 7.52 – 7.42 (m, 2H, ArH), the following signal is discernible for **4a**: 2.64 – 2.55 (m, 0.75 H); IR (neat, cm^{-1}): 1677, 1597, 1580, 1449, 1317, 1265, 1219, 1180, 1160, 1074, 1027, 1001; MS (70 eV, EI) m/z (%) 123 [$M^+(CD_3)$, 15.67], 122 [$M^+(CHD_2)$, 14.26], 121 [$M^+(CH_2D)$, 8.86], 120 [$M^+(CH_3)$, 4.80].

2. **The reaction of 2d with LiO*t*-Bu quenching with D_2O-Synthesis of 4'-methoxyacetophenone-D (4d-D, zth-6-092)**

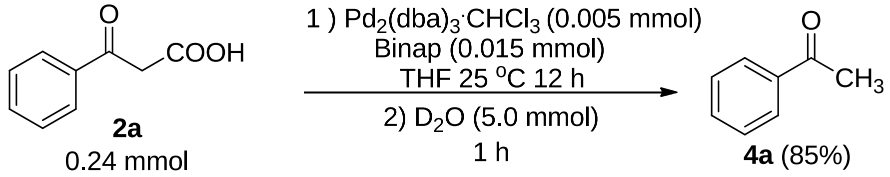


According to **Typical Procedure V**, the reaction of **2d** (46.7 mg, 0.24 mmol), $LiOBu^t$ (32.2 mg, 0.40 mmol), and D_2O (90 uL, 99.6 mg, 5.00 mmol) in THF (1 mL) afforded **4d-D**[7] (8.4 mg, 23%, D% = 71%) as a solid and afforded **2d**[8] (29.9 mg, 64%, ketone : enol = 7.1 : 1) by acidification of **2d’** as a solid.

4d-D: ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (dt, *J* = 9.8 Hz, 2.3 Hz, 2H, ArH), 6.94 (dt, *J* = 9.5 Hz, 2.4 Hz, 2H, ArH), 3.87 (s, 3H, CH_3), the following signal is discernible for **4d**: 2.56 – 2.50 (m, 0.86H); IR (neat, cm^{-1}): 1663, 1598, 1576, 1507, 1462, 1444, 1416, 1306, 1275, 1252, 1170, 1109, 1078, 1022; MS(ESI) m/z 154 $[M(CD_3)+H]^+$, 153 $[M(CHD_2)+H]^+$, 152 $[M(CH_2D)+H]^+$, 151 $[M(CH_3)+H]^+$; HRMS calcd for $C_9H_7D_3O_2$ [M(CD_3)]$^+$: 153.0869, found 153.0867.

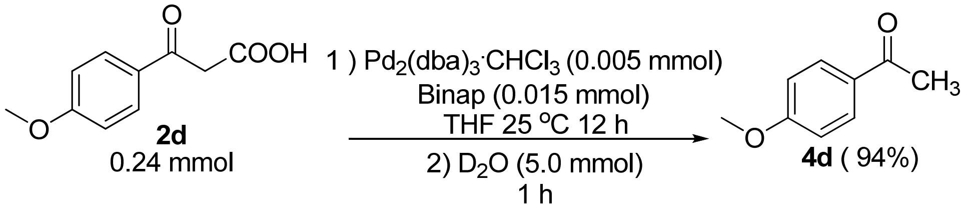
2d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.2 Hz, 2H, ArH), 6.98 (d, *J* = 8.4 Hz, 2H, ArH), 4.03 (s, 2H, CH_2), 3.90 (s, 3H, CH_3); the following signals are discernible for Enol-**2d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.38 (s, 1H, OH), 7.77 (d, *J* = 9.2 Hz, 2H, ArH), 6.94 (d, *J* = 9.2 Hz, 2H, ArH), 5.63 (s, 1H, =CH), 3.86 (s, 3H, CH_2); MS (70 eV, EI) m/z (%) 194 (M$^+$, 5.71), 135 (100).

3. **The reaction of 2a with $Pd_2(dba)_3$·$CHCl_3$ and binap quenching with D_2O (zth-6-097)**



Typical Procedure VI: To an oven-dried Schlenk tube equipped with a magnetic stirring bar was added $Pd_2(dba)_3$·$CHCl_3$ (5.1 mg, 0.005 mmol) and binap (9.6 mg, 0.015 mmol) under argon. Then **2a** (39.7 mg, 0.24 mmol) and THF (1 mL) were added sequentially under argon. The mixture was stirred at 25 °C for 12 hours. After that, D_2O (90 uL, d = 1.107 g/mL, 99.6 mg, 5.0 mmol) was added under argon. The resulting mixture was stirred for at 25 °C for 1 hours. Evaporation, and column chromatography on silica gel (eluent: petroleum ether (30 – 60 °C) / diethyl ether = 50/1) afforded **4a**[9] (24.5 mg, 85%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H, ArH), 7.61 – 7.54 (m, 1H, ArH), 7.52 – 7.41 (m, 2H, ArH), 2.61 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 137.0, 133.1, 128.5, 128.3, 26.6; IR (neat, cm^{-1}): 1681, 1598, 1582, 1448, 1358, 1302, 1263, 1179, 1078, 1023; MS (70 eV, EI) m/z (%) 120 (M$^+$, 40.54), 105 (100).

4. **The reaction of 2d with $Pd_2(dba)_3$·$CHCl_3$ and binap quenching with D_2O (zth-6-098)**



According to **Typical Procedure VI**, the reaction of **2d** (46.6 mg, 0.24 mmol), $Pd_2(dba)_3\cdot CHCl_3$ (5.1 mg, 0.005 mmol), binap (9.6 mg, 0.015 mmol), and D_2O (90 uL, d = 1.107 g/mL, 99.6 mg, 5.0 mmol) in THF (1 mL) afforded **4d**[9] (33.9 mg, 94%) (eluent: petroleum ether (30–60 °C) / diethyl ether = 20/1): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (dt, J = 9.6 Hz, 2.5 Hz, 2H, ArH), 6.94 (dt, J = 9.3 Hz, 2.4 Hz, 2H, ArH), 3.87 (s, 3H, CH_3), 2.56 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.8, 163.4, 130.5, 130.3, 113.6, 55.4, 26.3; IR (neat, cm^{-1}): 1665, 1596, 1573, 1506, 1461, 1416, 1357, 1276, 1245, 1174, 1111, 1075, 1019; MS(EI) *m/z* (%) 150 (M$^+$, 37.02), 135 (100).

References:

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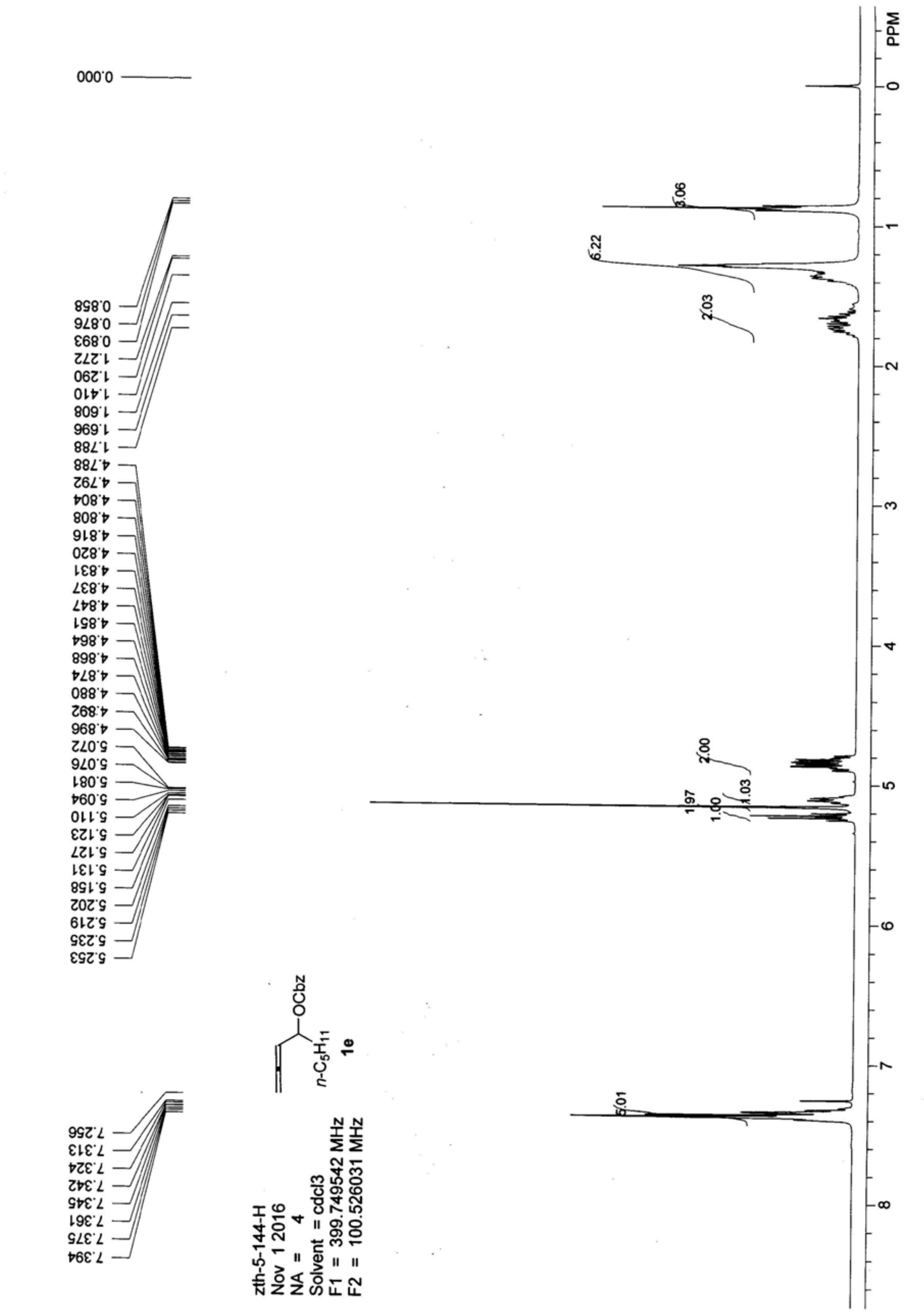
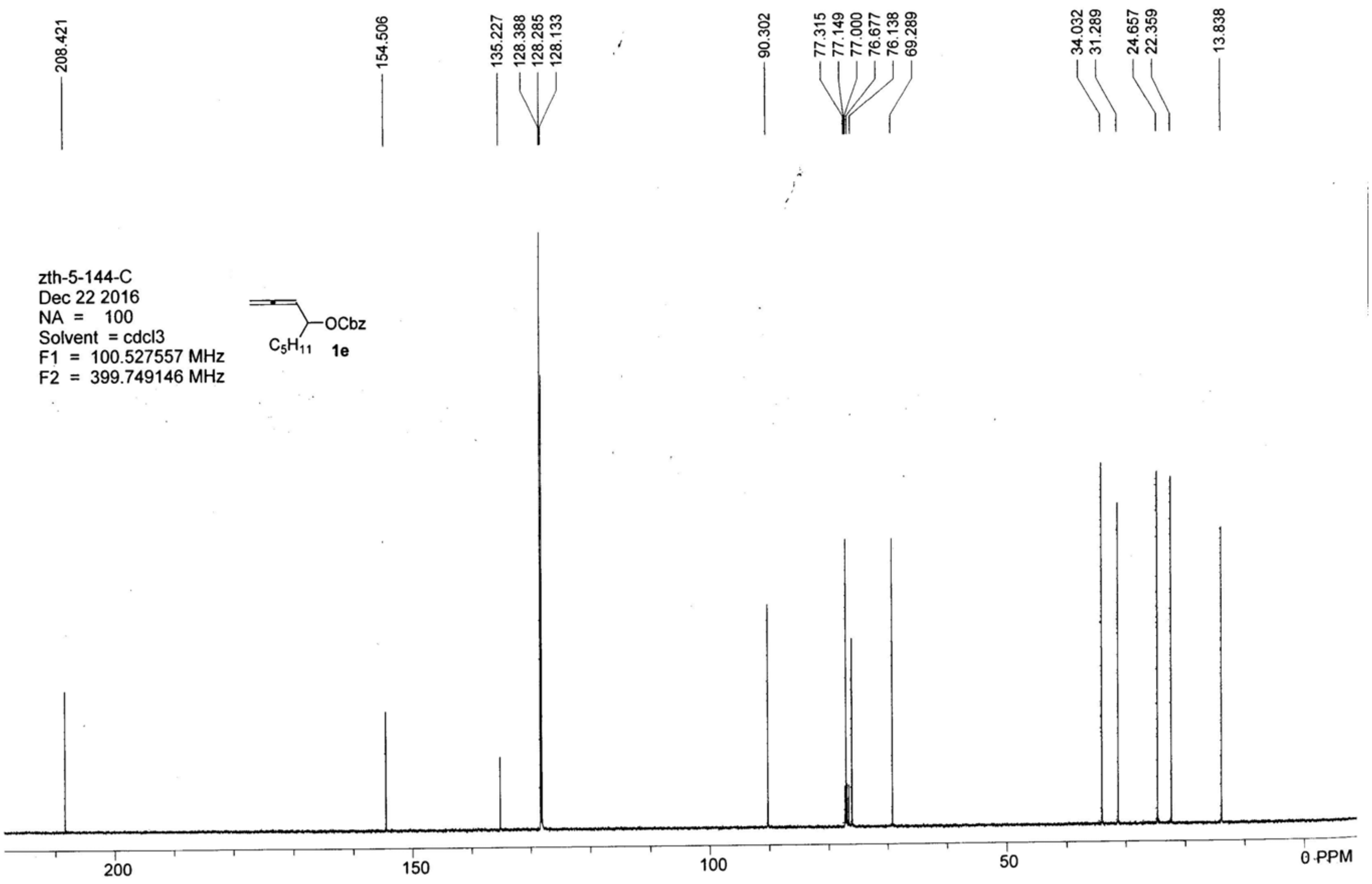
benzyl nona-1,2-dien-4-yl carbonate (1e, zth-5-144)

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77.000
76.677
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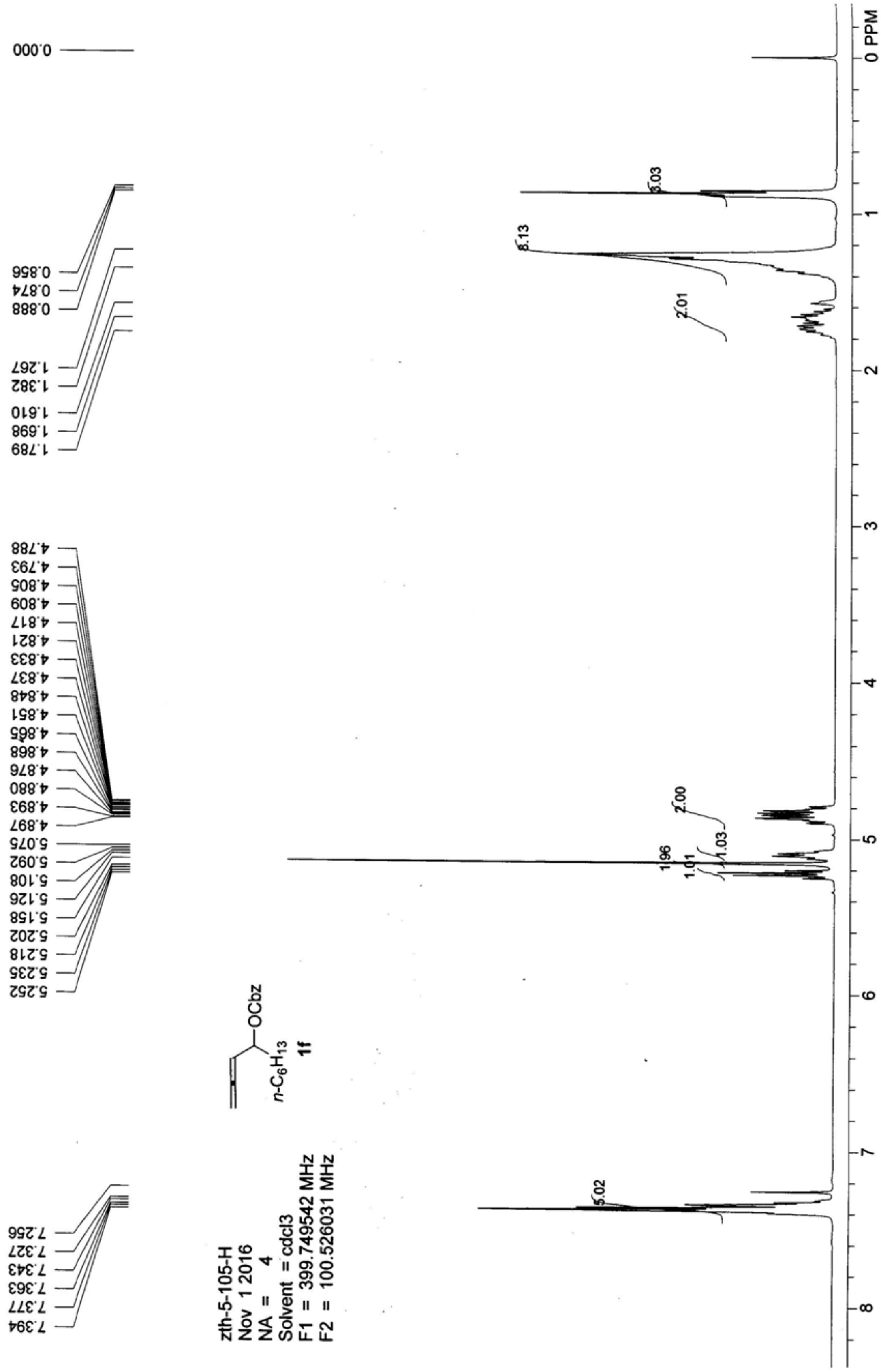
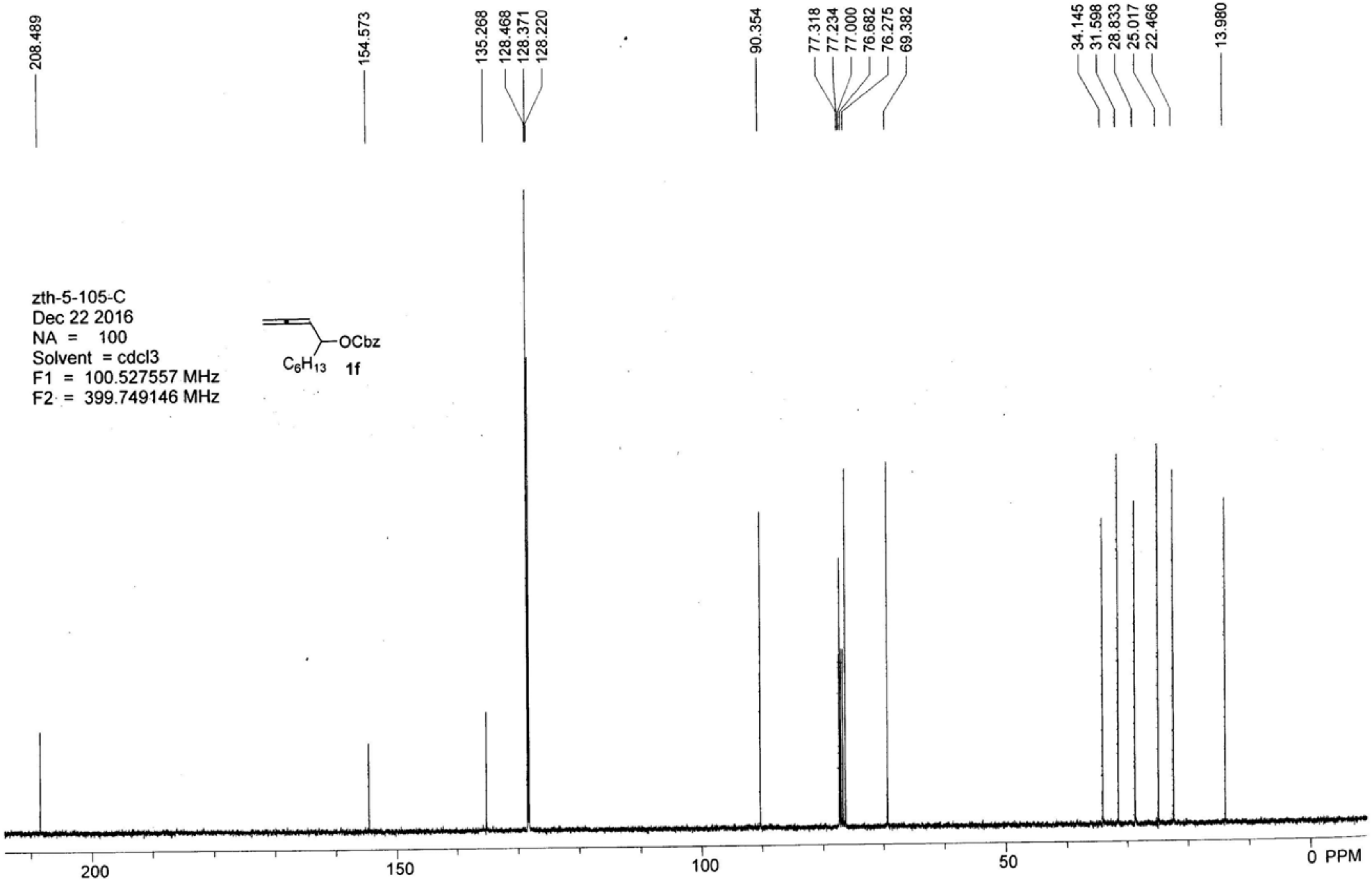
69.289
34.032
31.289
24.657
22.359
13.838
zth-5-144-C
Dec 22 2016
NA = 100
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
OCbz
C_5H_{11}
1e
200
150
100
50
0 PPM

benzyl deca-1,2-dien-4-yl carbonate (1f, zth-5-105)





zth-5-105-C
Dec 22 2016
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F2 = 399.749146 MHz

1f

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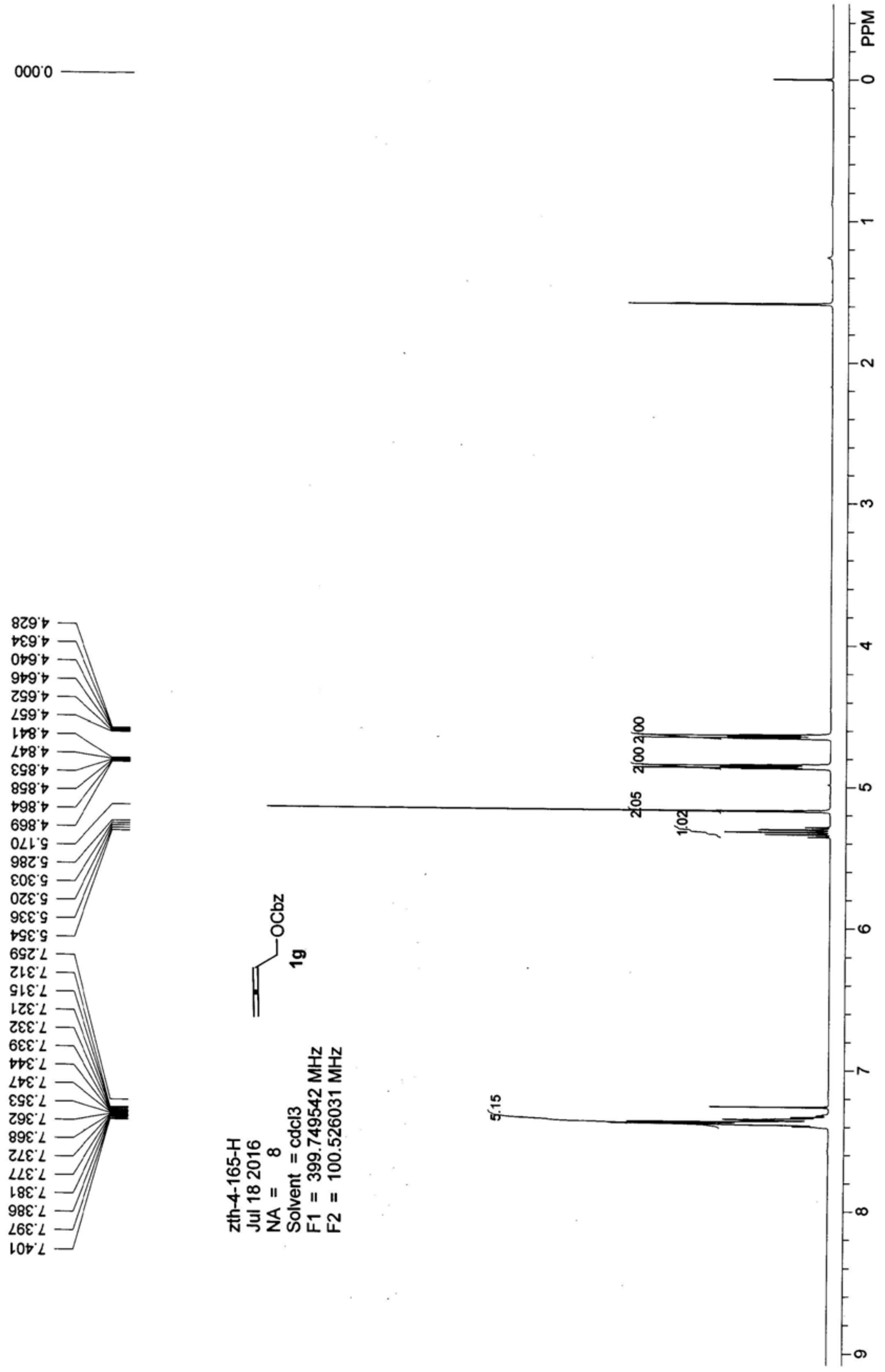

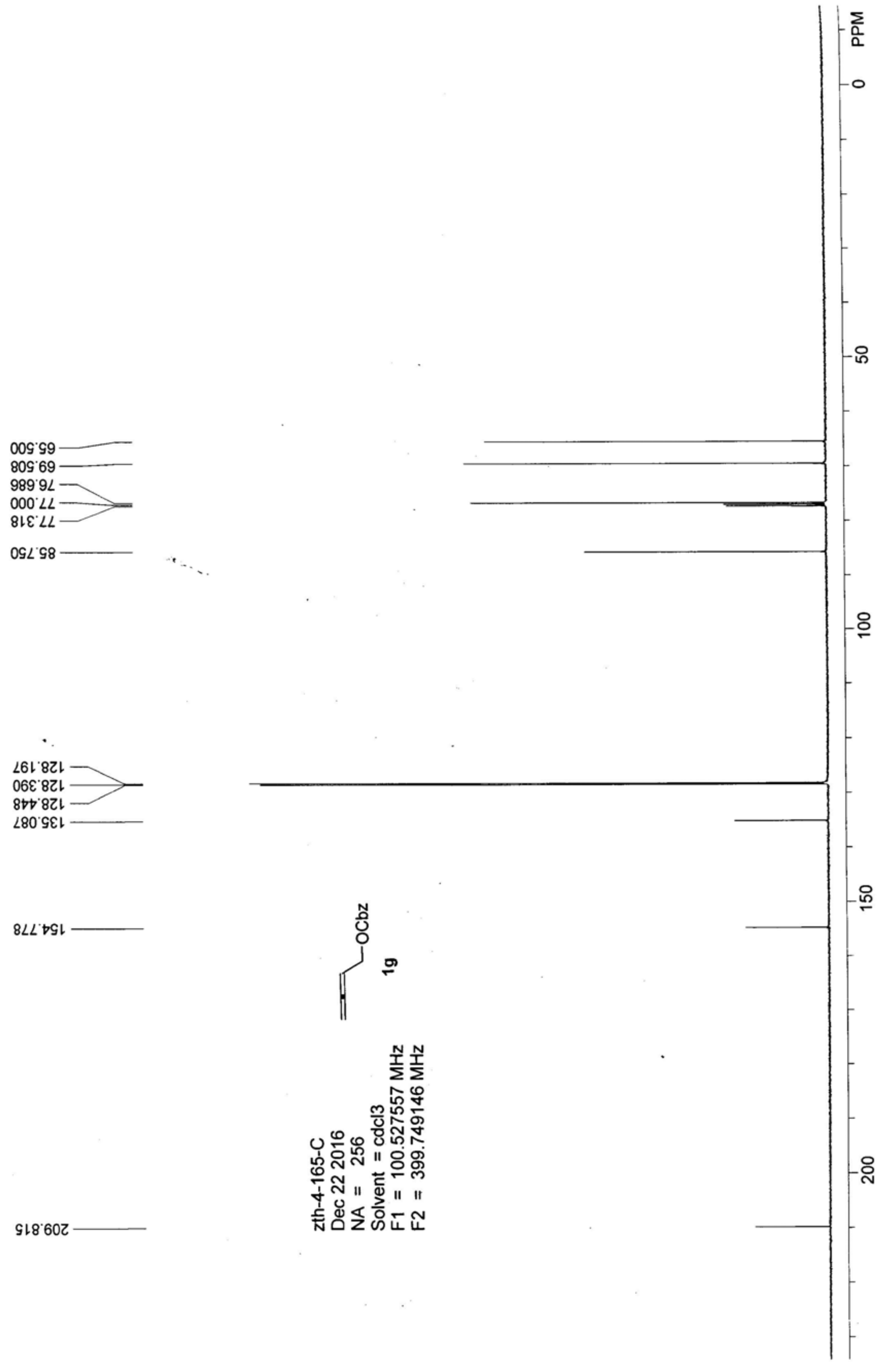

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77.000
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85.750
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128.390
128.448
135.087
154.778
209.815
OCbz
1g
zth-4-165-C
Dec 22 2016
NA = 256
Solvent = cdcl3
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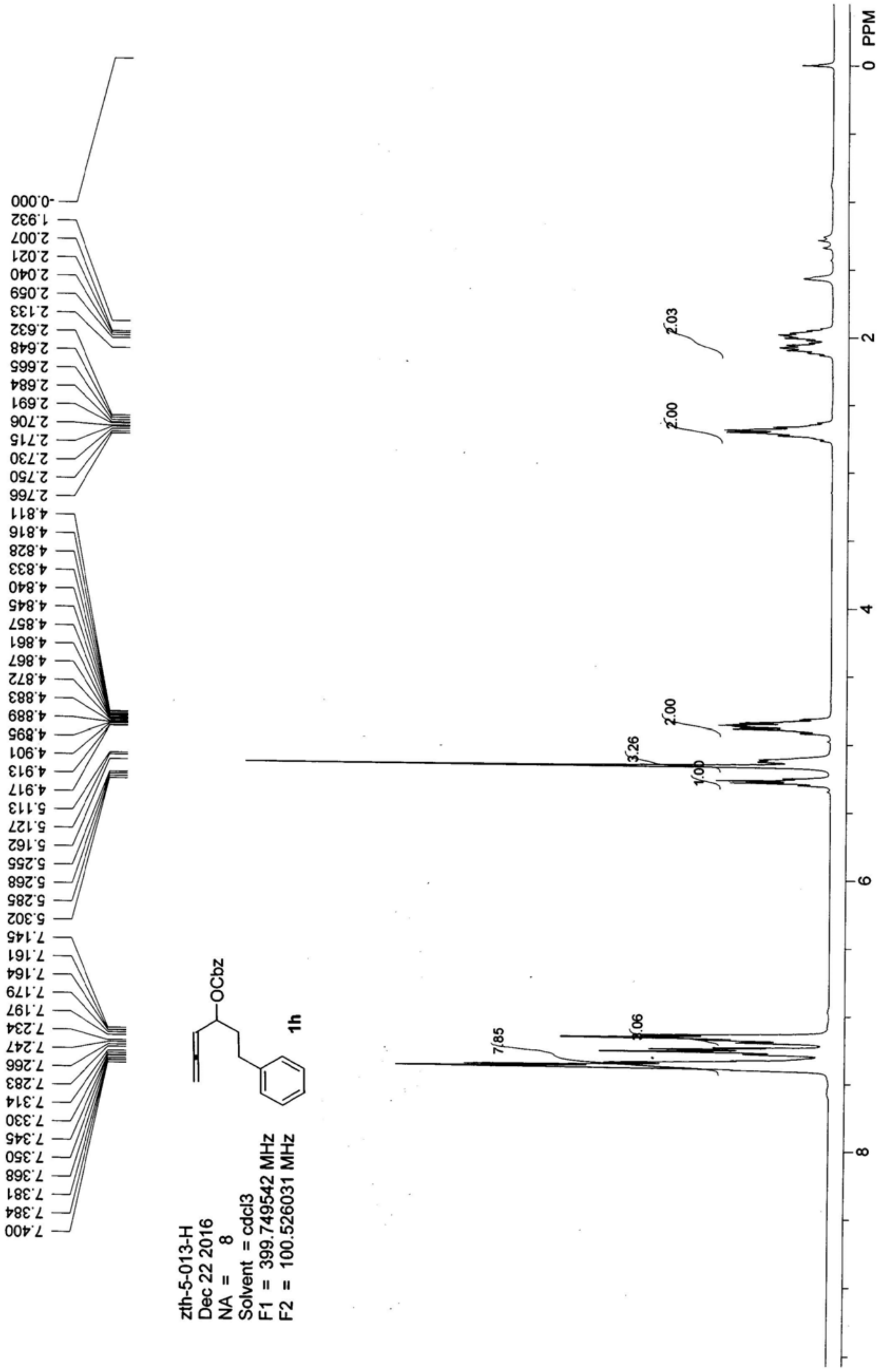
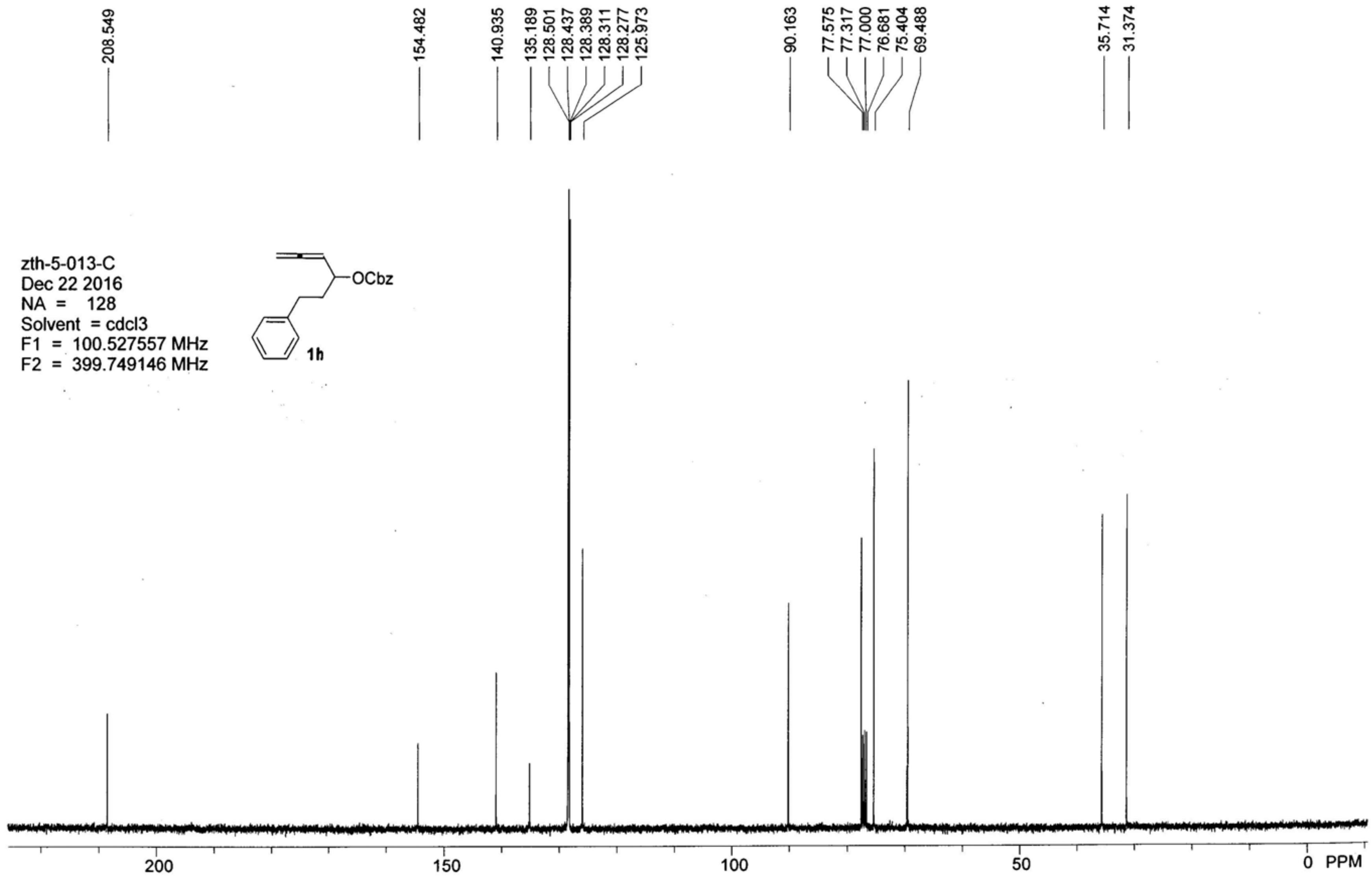
F2 = 399.749146 MHz
PPM
0
50
100
150
200

benzyl 1-phenylhexa-4,5-dien-3-yl carbonate (1h, zth-5-013)

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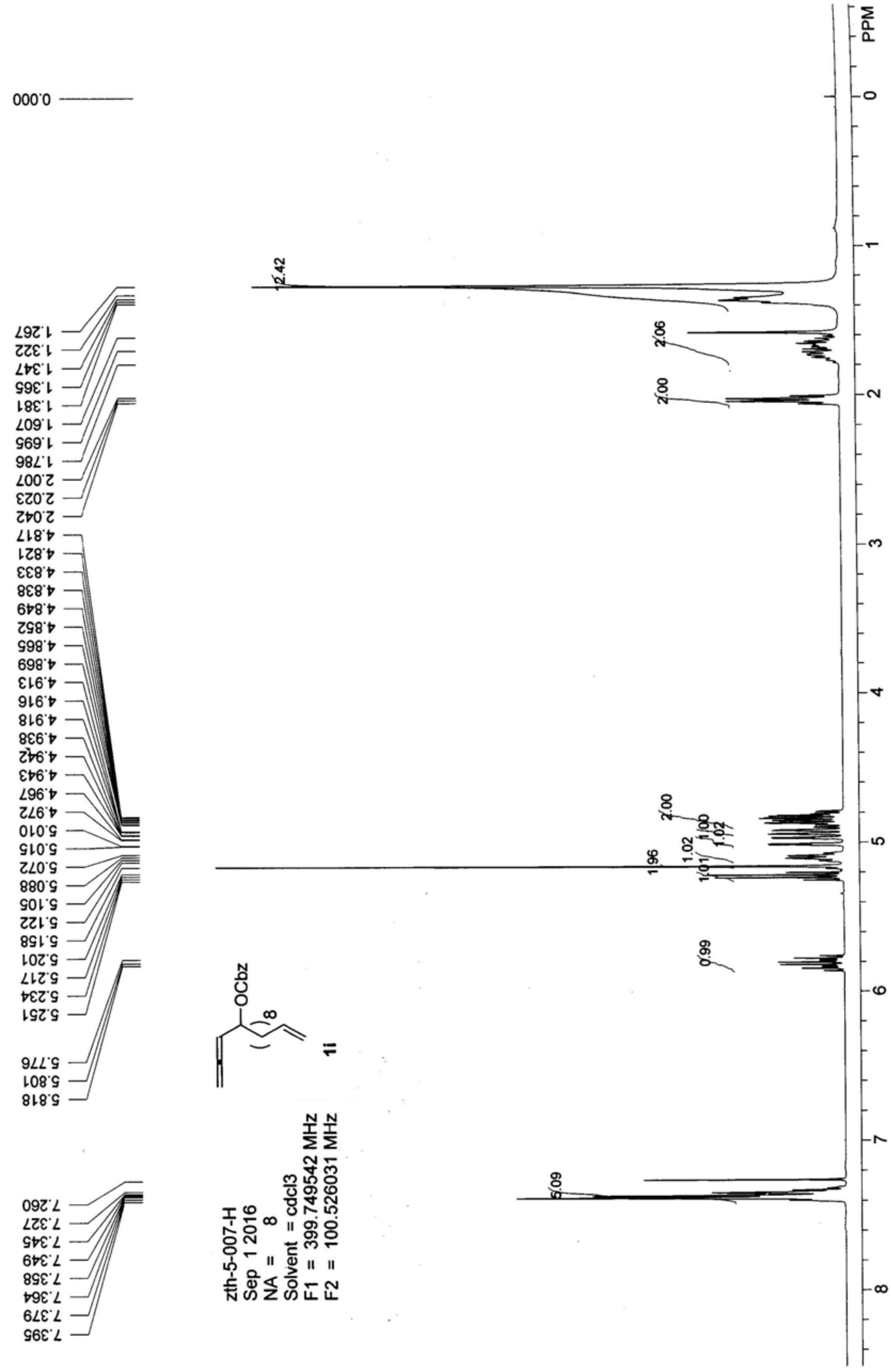
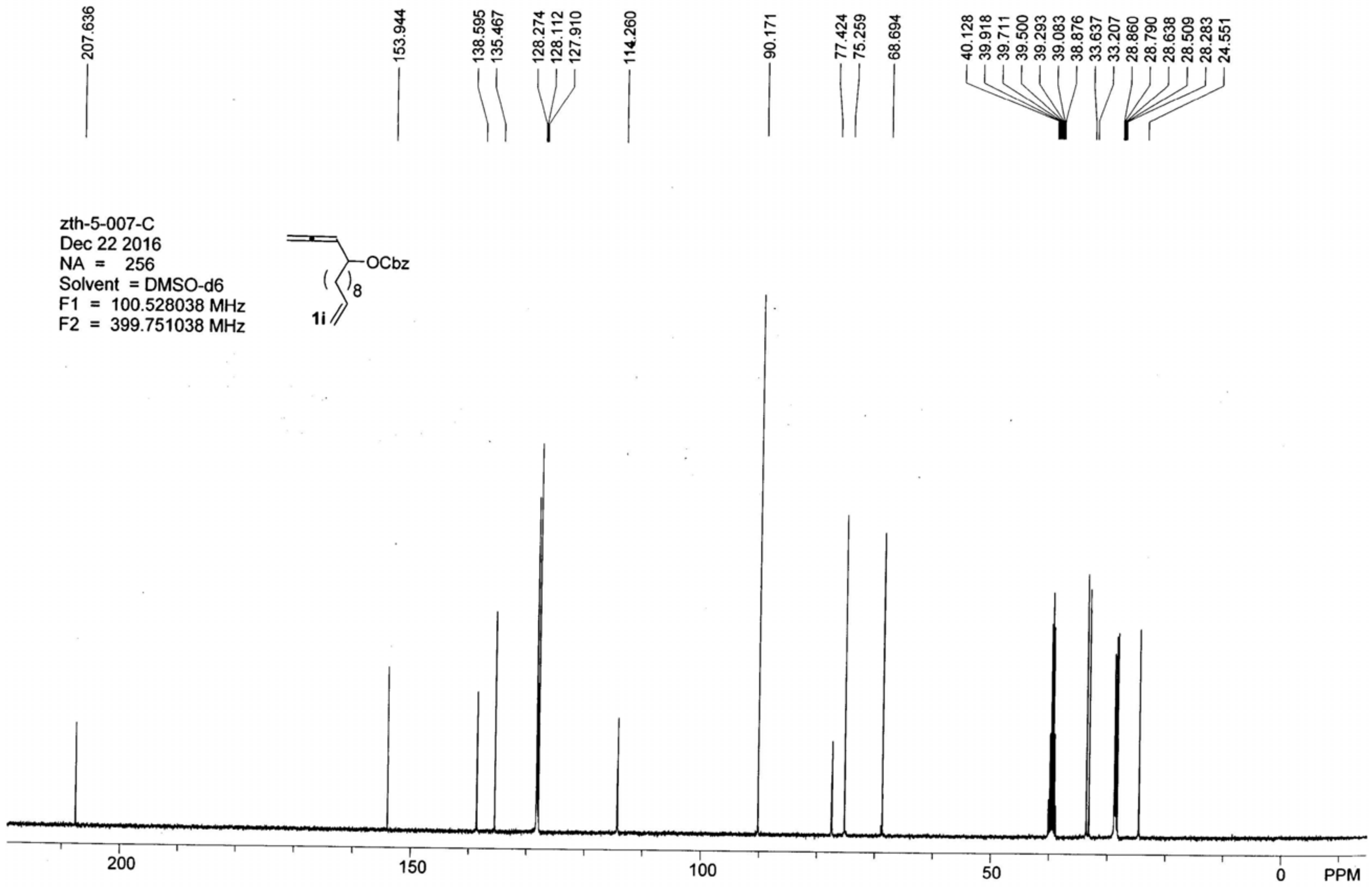
77.317
77.000
76.681
75.404
69.488
35.714
31.374
zth-5-013-C
Dec 22 2016
NA = 128
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
OCbz
1h
200
150
100
50
0 PPM

benzyl tetradeca-1,2,13-trien-4-yl carbonate (1i, zth-5-007)




1i

207.636
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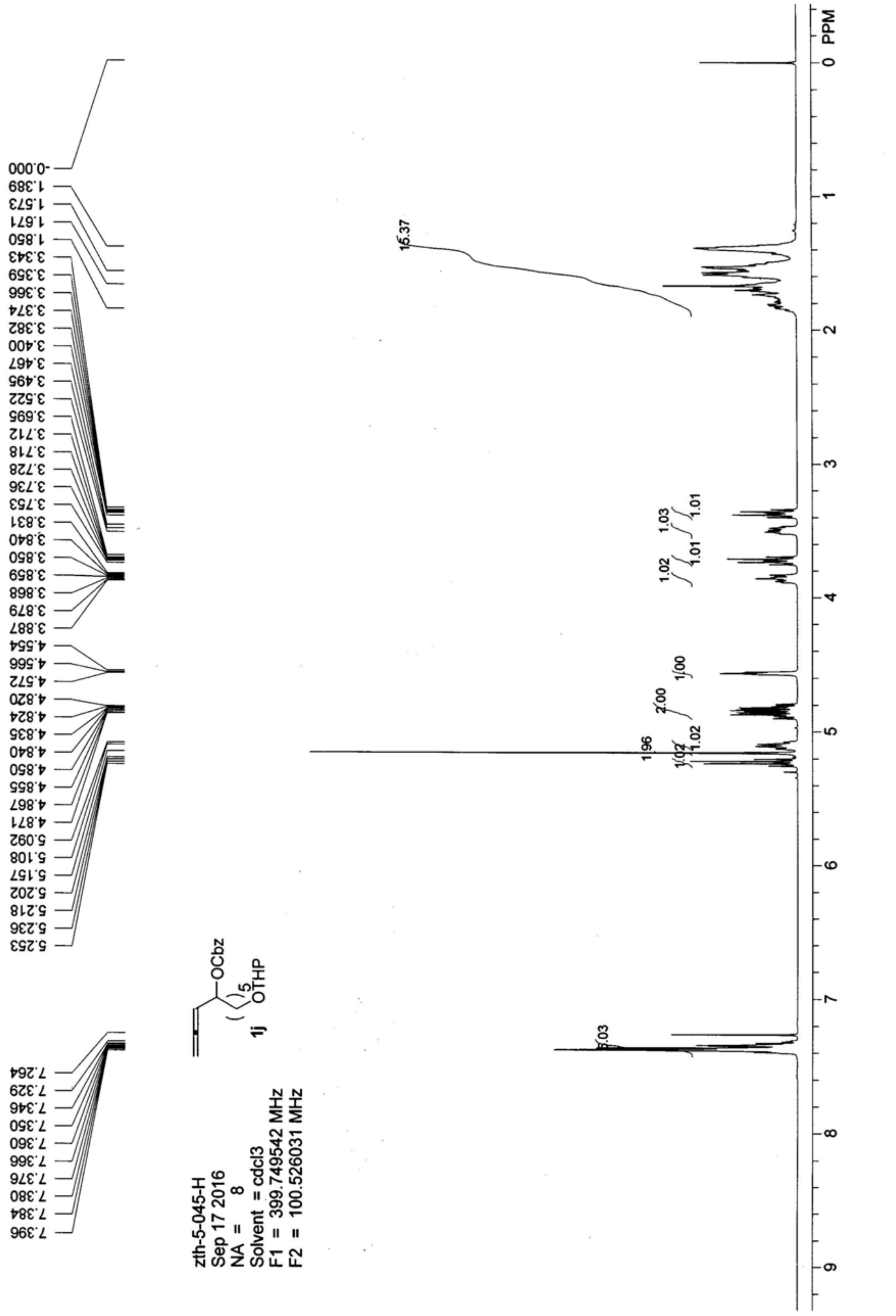
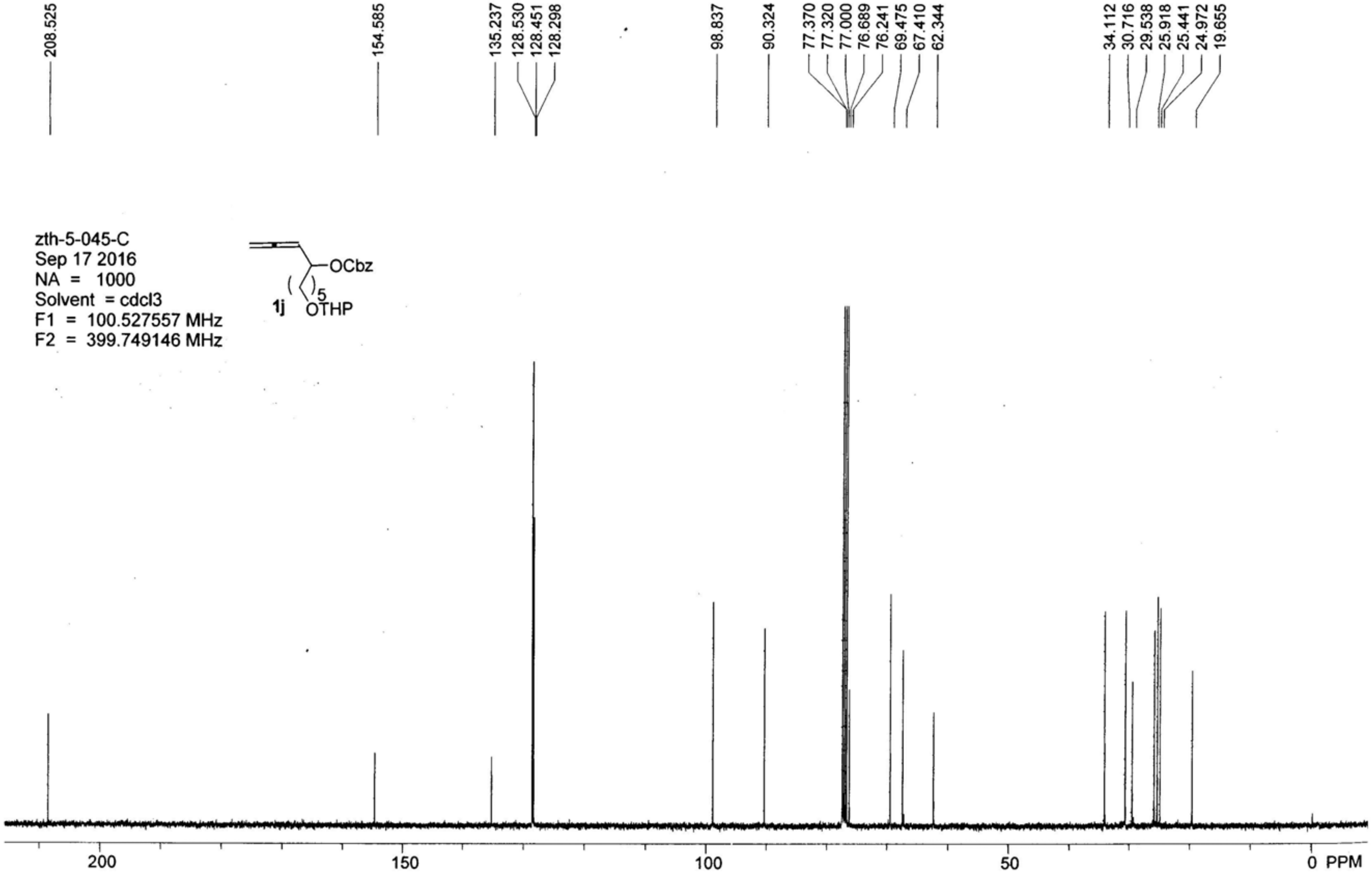
39.711
39.500
39.293
39.083
38.876
33.637
33.207
28.860
28.790
28.638
28.509
28.283
24.551
zth-5-007-C
Dec 22 2016
NA = 256
Solvent = DMSO-d6
F1 = 100.528038 MHz
F2 = 399.751038 MHz
OCbz
8
200
150
100
50
0
PPM

benzyl 9-(tetrahydro-2*H*-pyran-2-yloxy)nona-1,2-dien-4-yl carbonate (1j, zth-5-045)





zth-5-045-C
Sep 17 2016
NA = 1000
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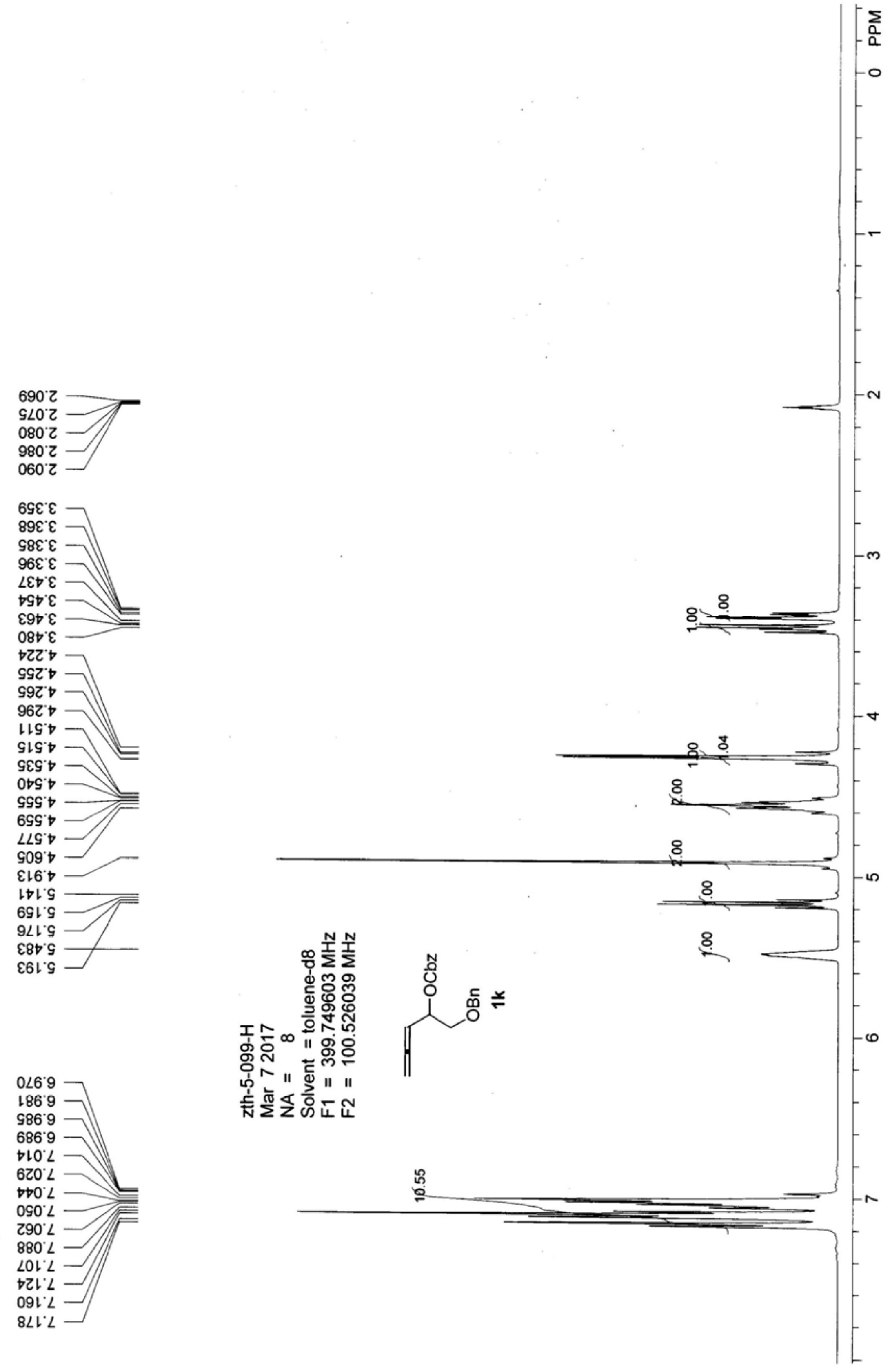
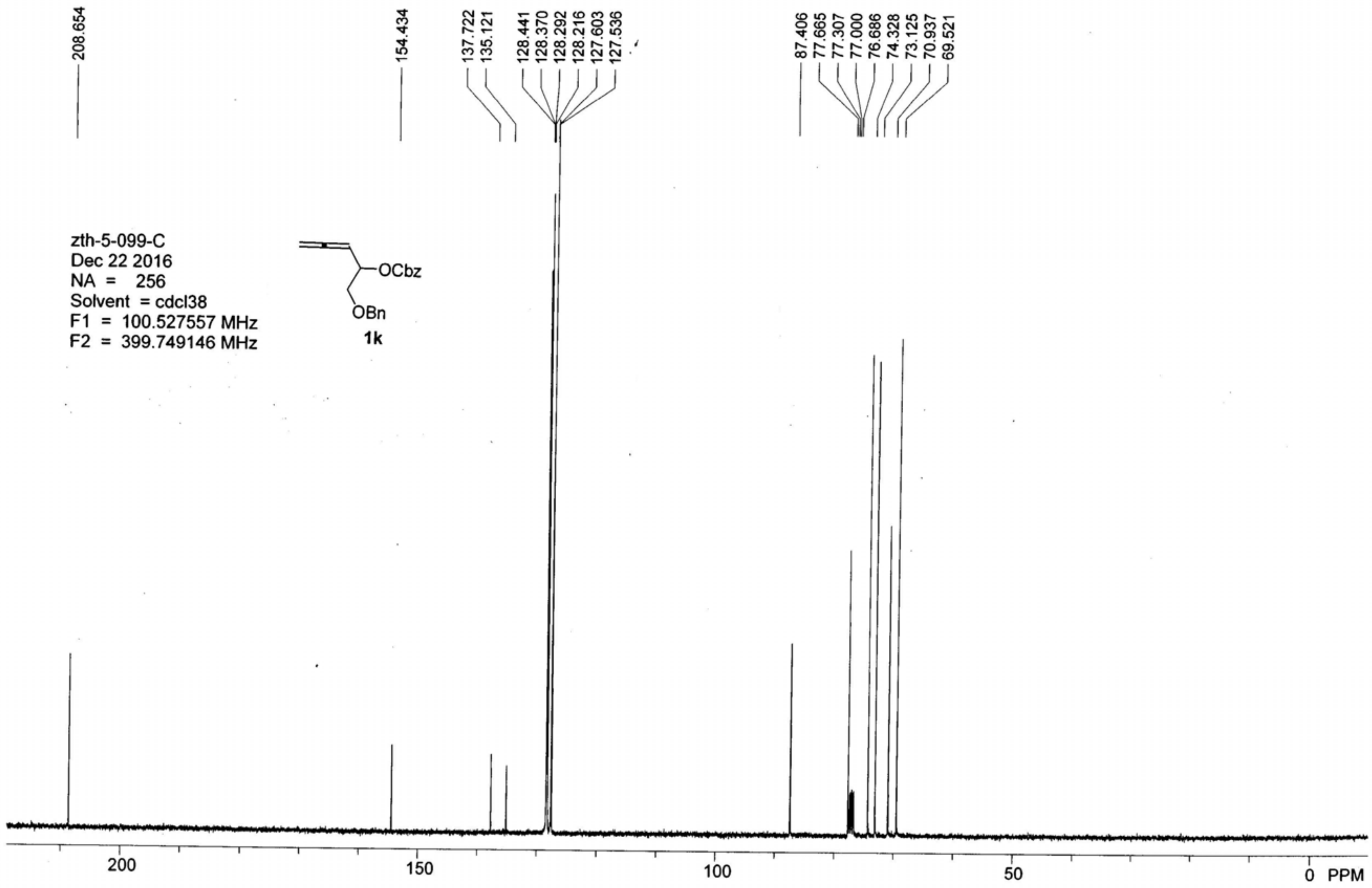
F2 = 399.749146 MHz

1j

benzyl 1-(benzyloxy)penta-3,4-dien-2-yl carbonate (1k, zth-5-099)

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70.937
69.521
zth-5-099-C
Dec 22 2016
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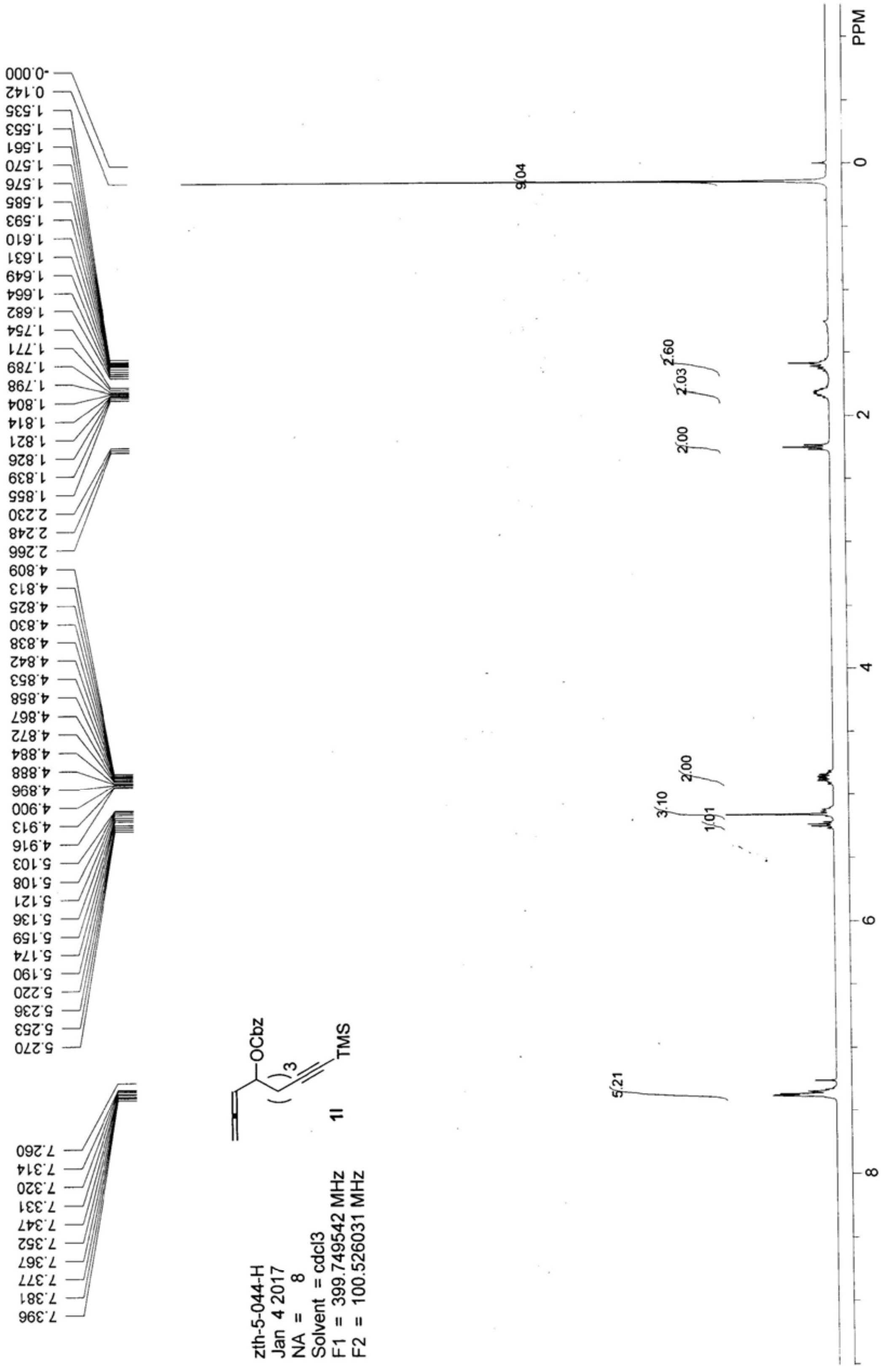
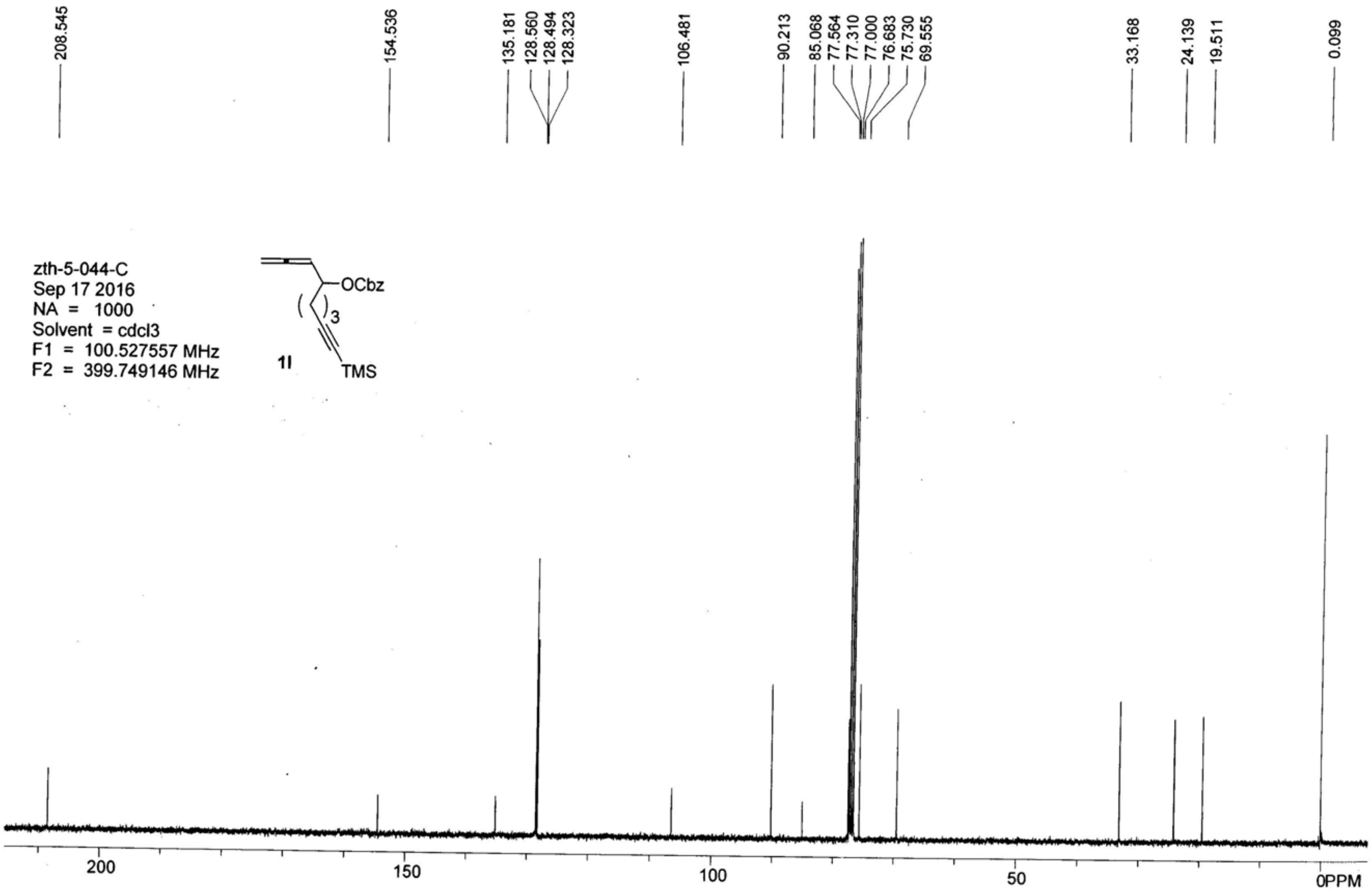
Solvent = cdcl38
F1 = 100.527557 MHz
F2 = 399.749146 MHz
OCbz
OBn
200
150
100
50
0 PPM

1k

benzyl 1-(benzyloxy)penta-3,4-dien-2-yl carbonate (1l, zth-5-044)





zth-5-044-C
Sep 17 2016
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Solvent = cdcl3
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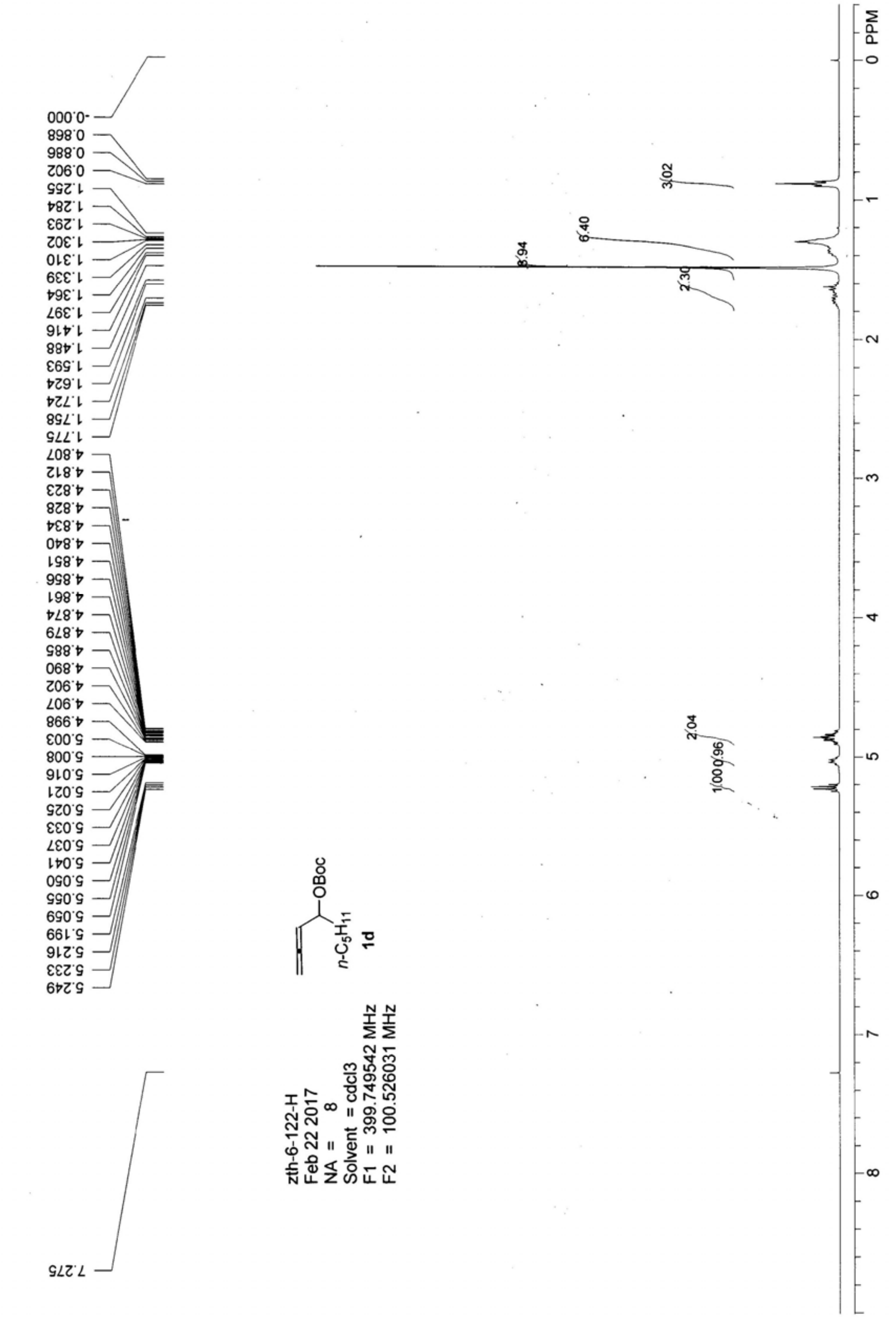
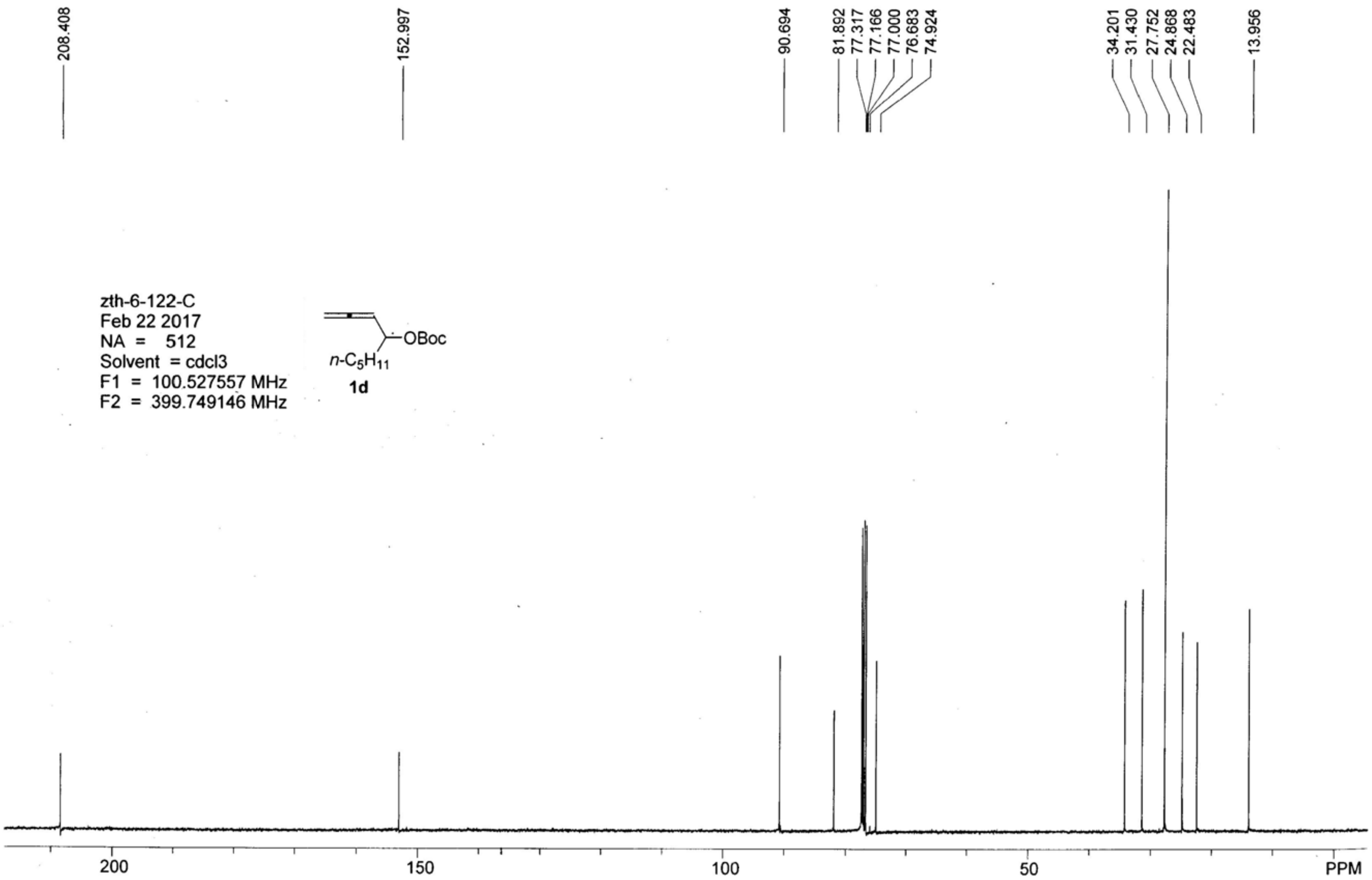
F2 = 399.749146 MHz

1l

tert-butyl nona-1,2-dien-4-yl carbonate (1d, zth-6-122)

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13.956
zth-6-122-C
Feb 22 2017
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100
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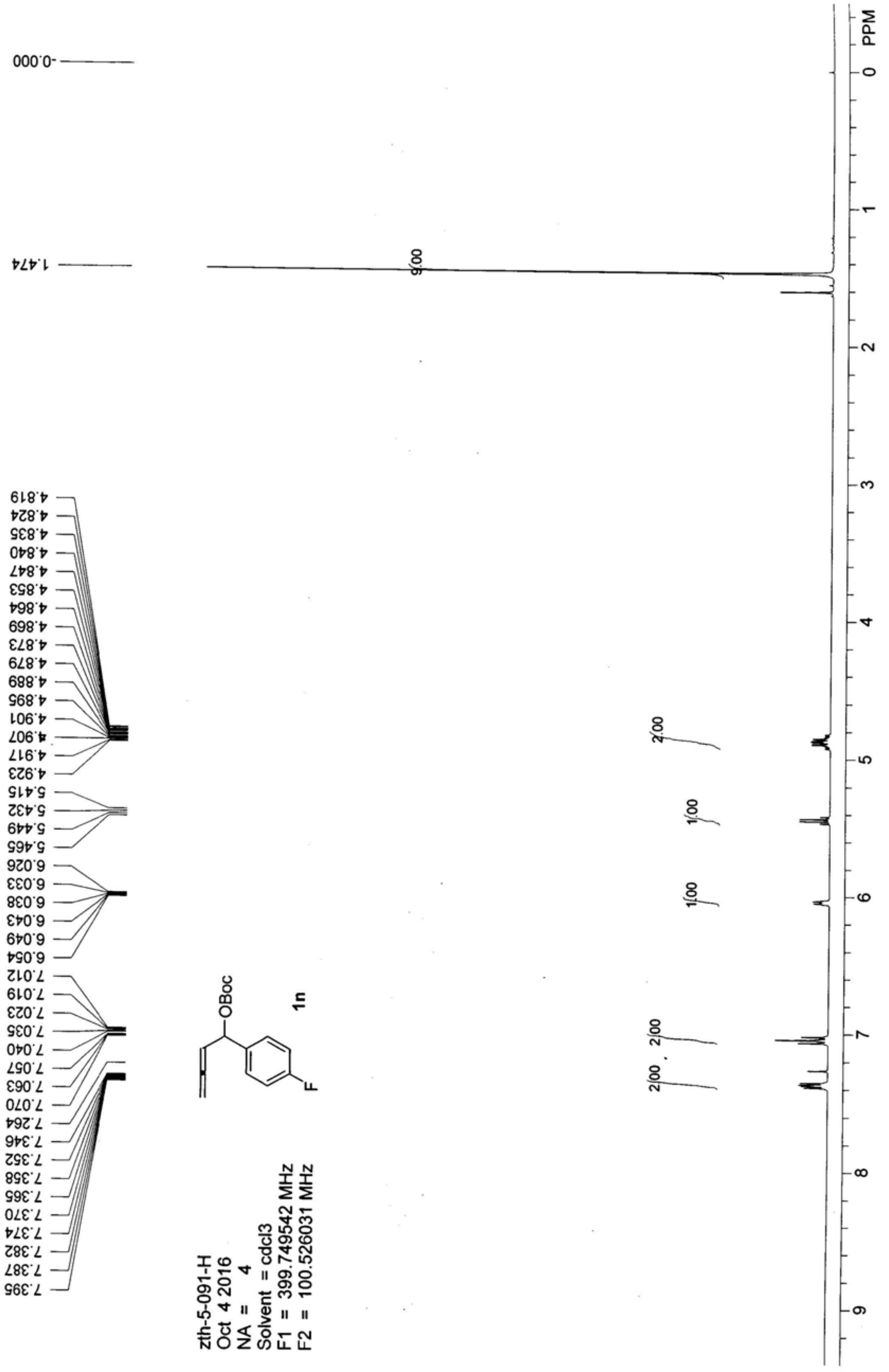
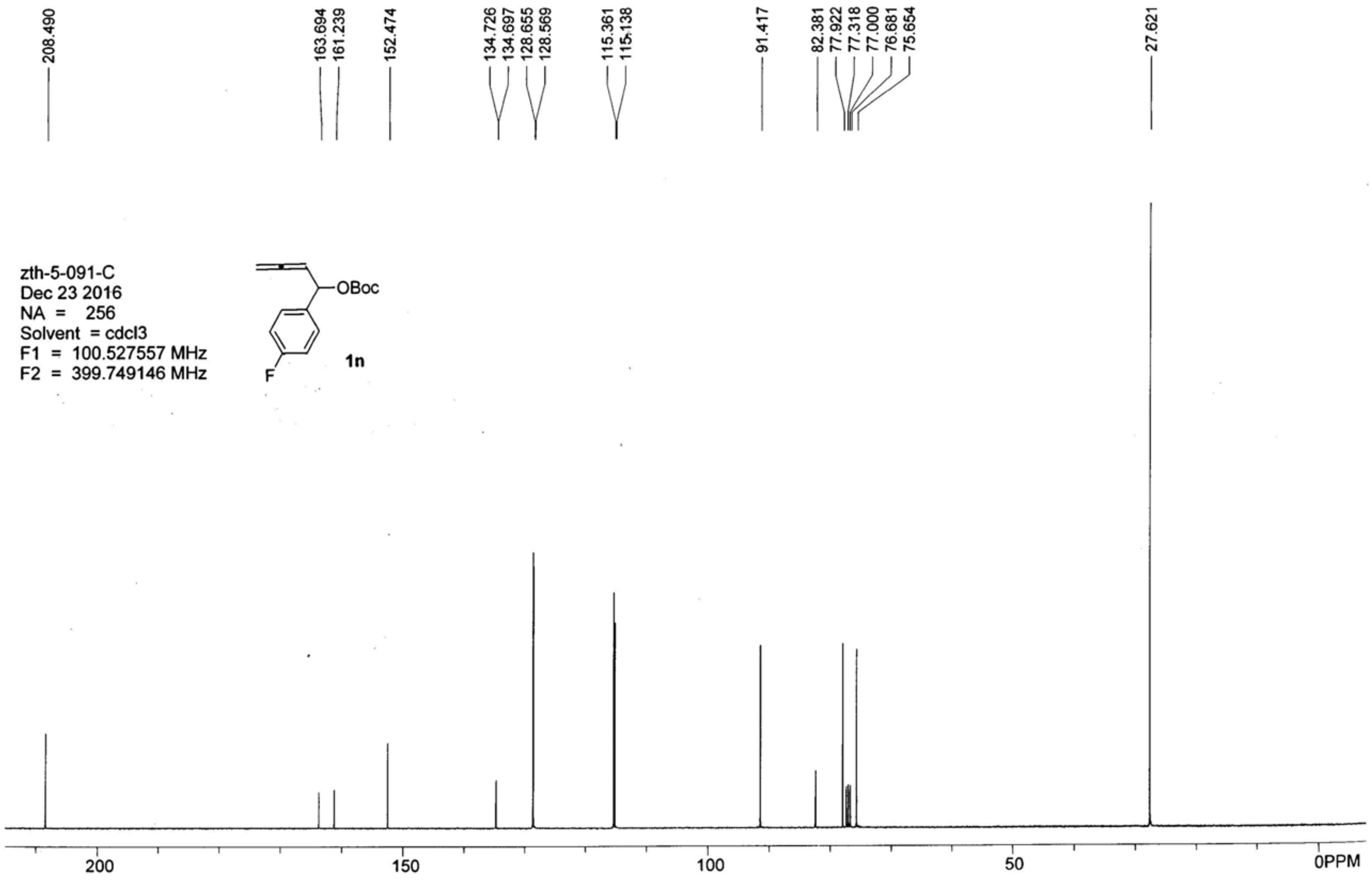
PPM

tert-butyl 1-(4-fluorophenyl)buta-2,3-dienyl carbonate (1n, zth-5-091)

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77.000
76.681
75.654
27.621
zth-5-091-C
Dec 23 2016
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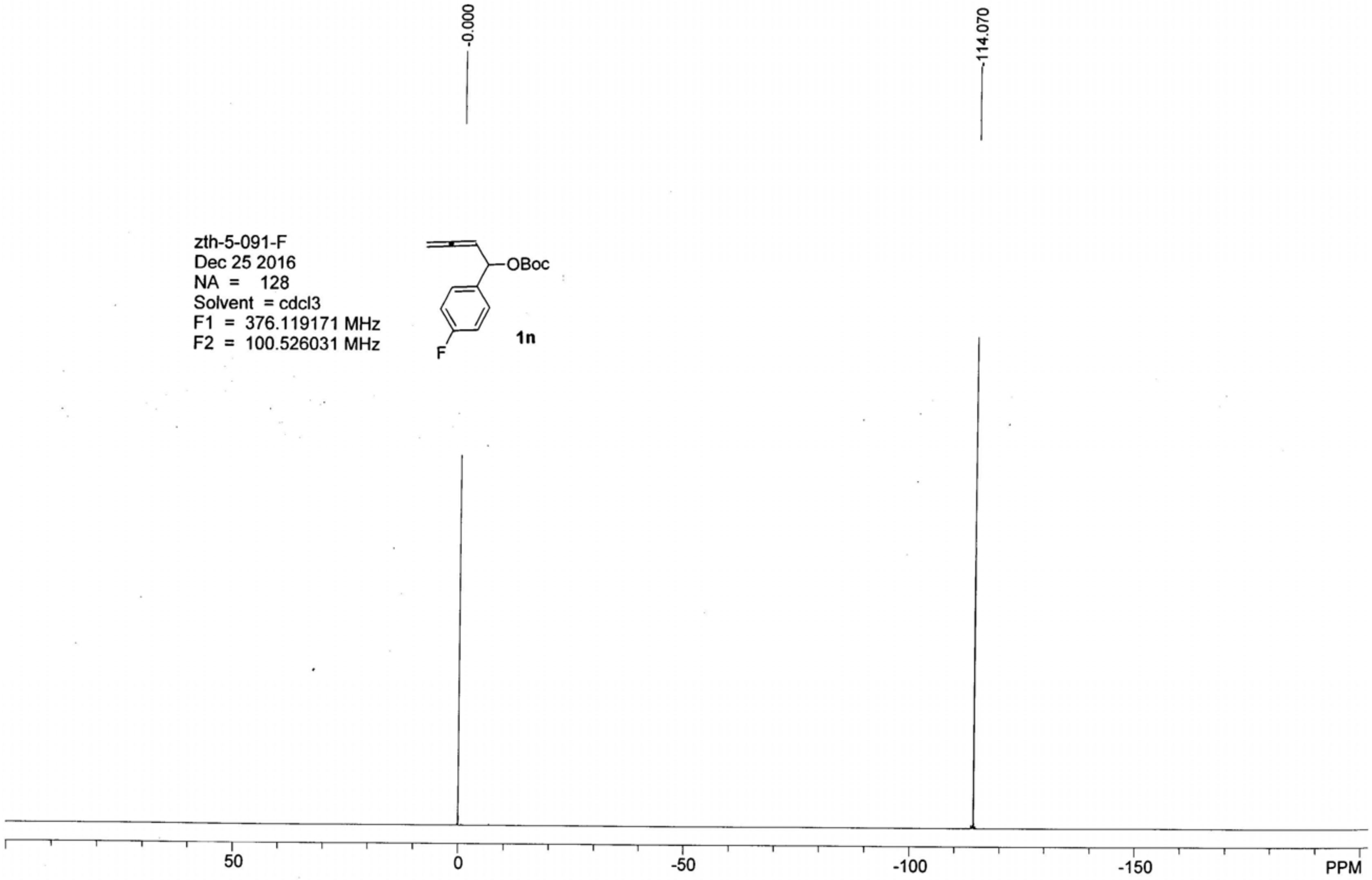
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Dec 25 2016
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F
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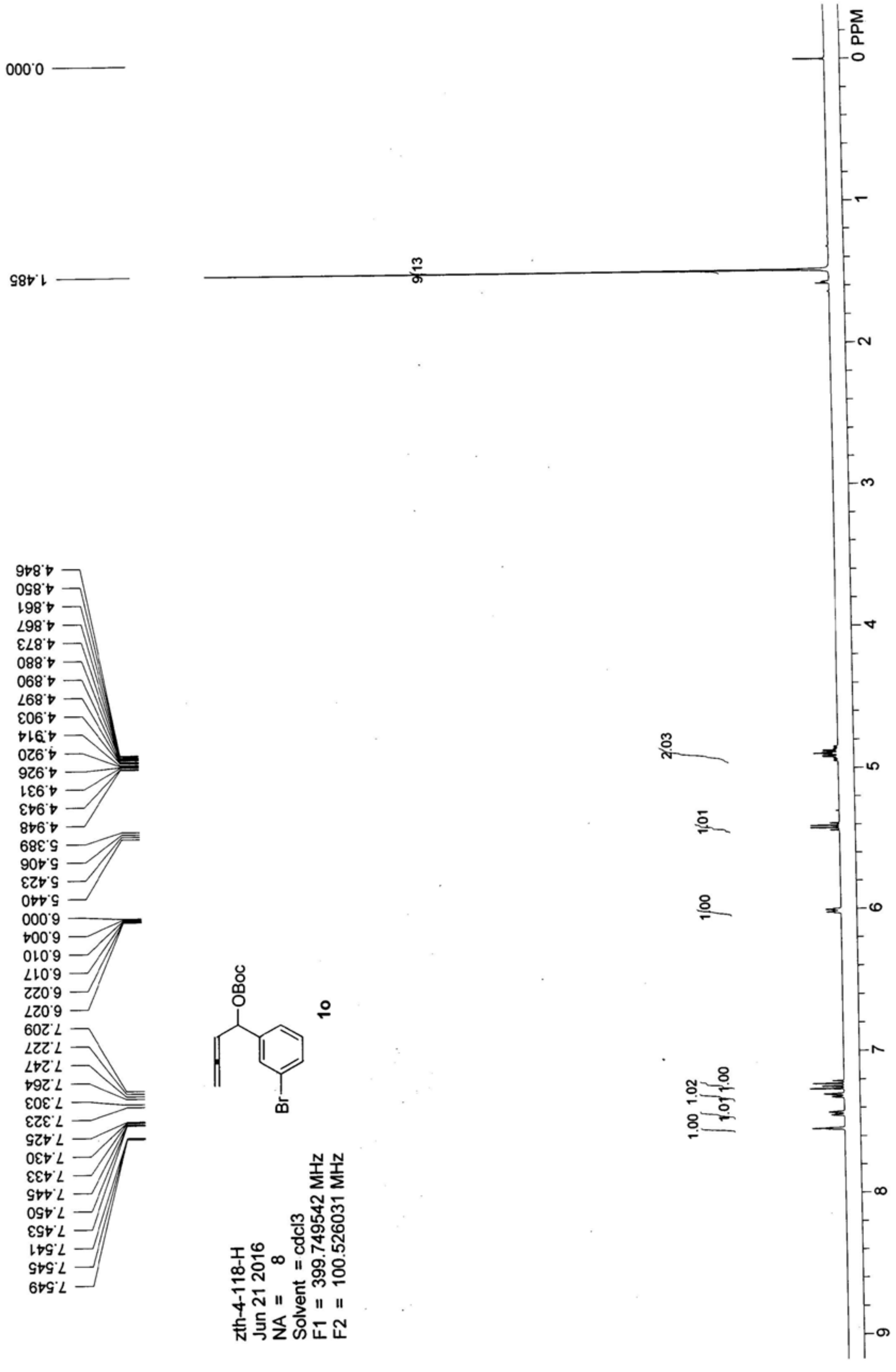
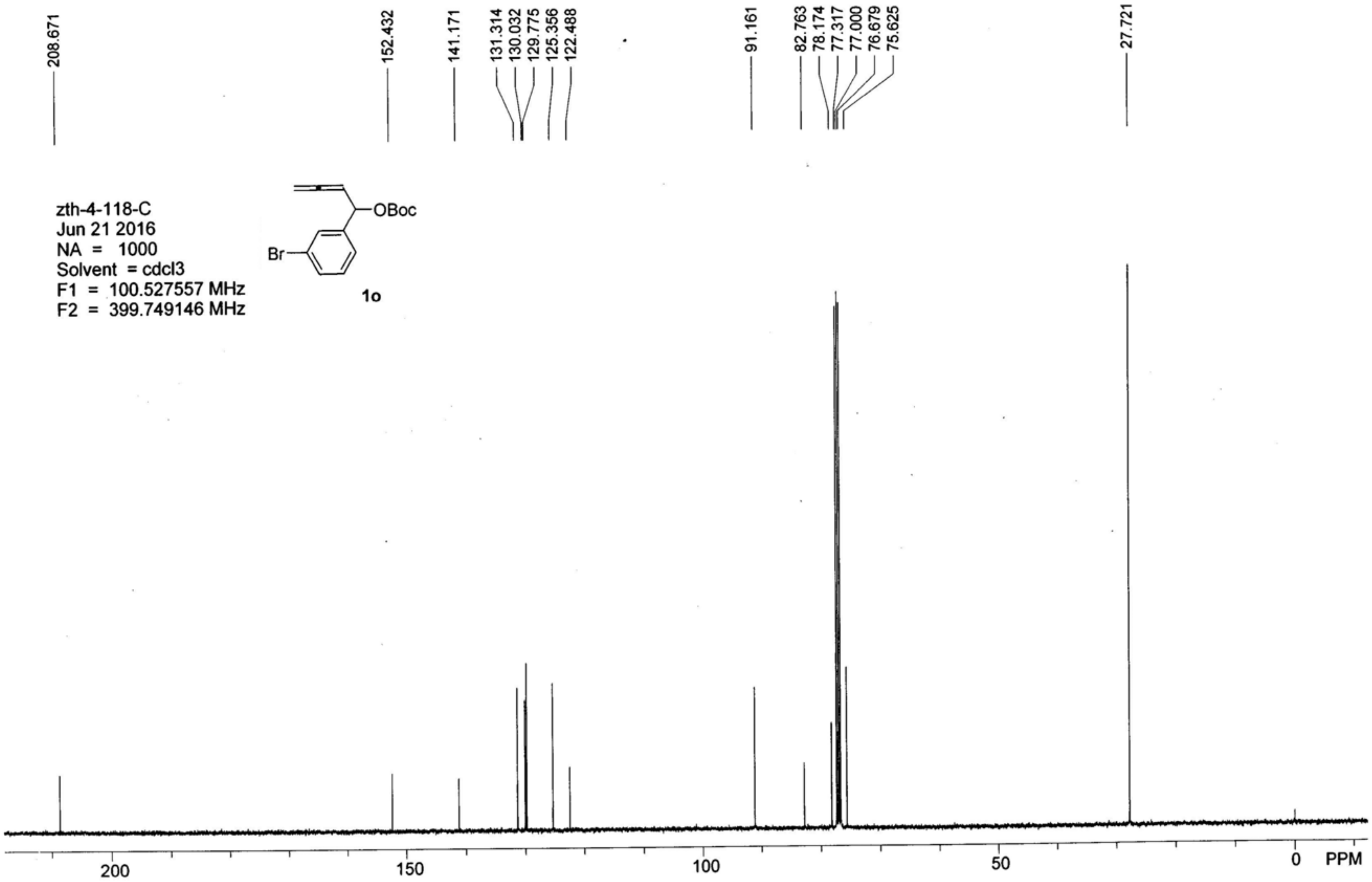
PPM

tert-butyl 1-(4-fluorophenyl)buta-2,3-dienyl carbonate (1o, zth-4-118)





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75.625
27.721
zth-4-118-C
Jun 21 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
OBoc
Br
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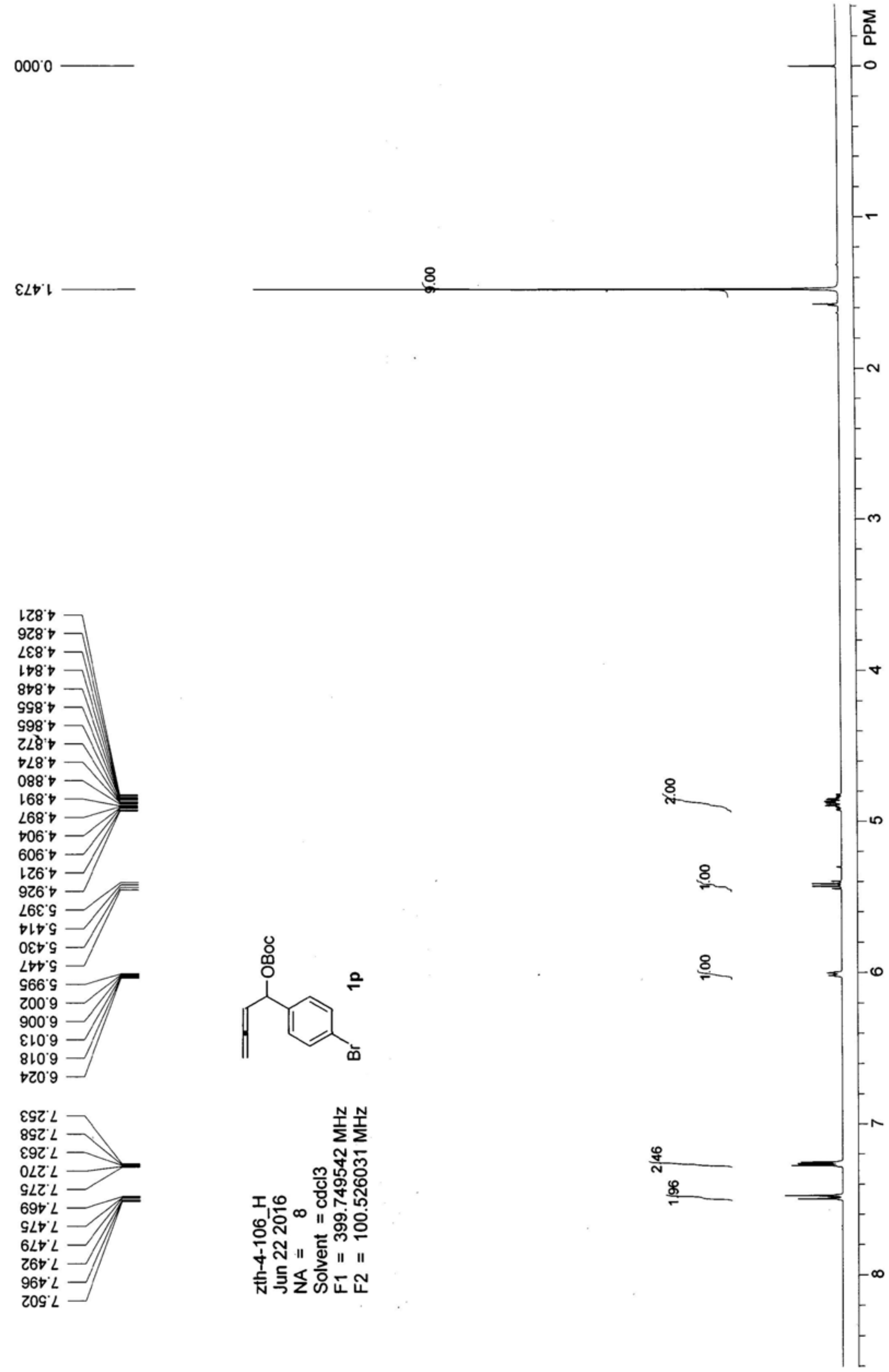
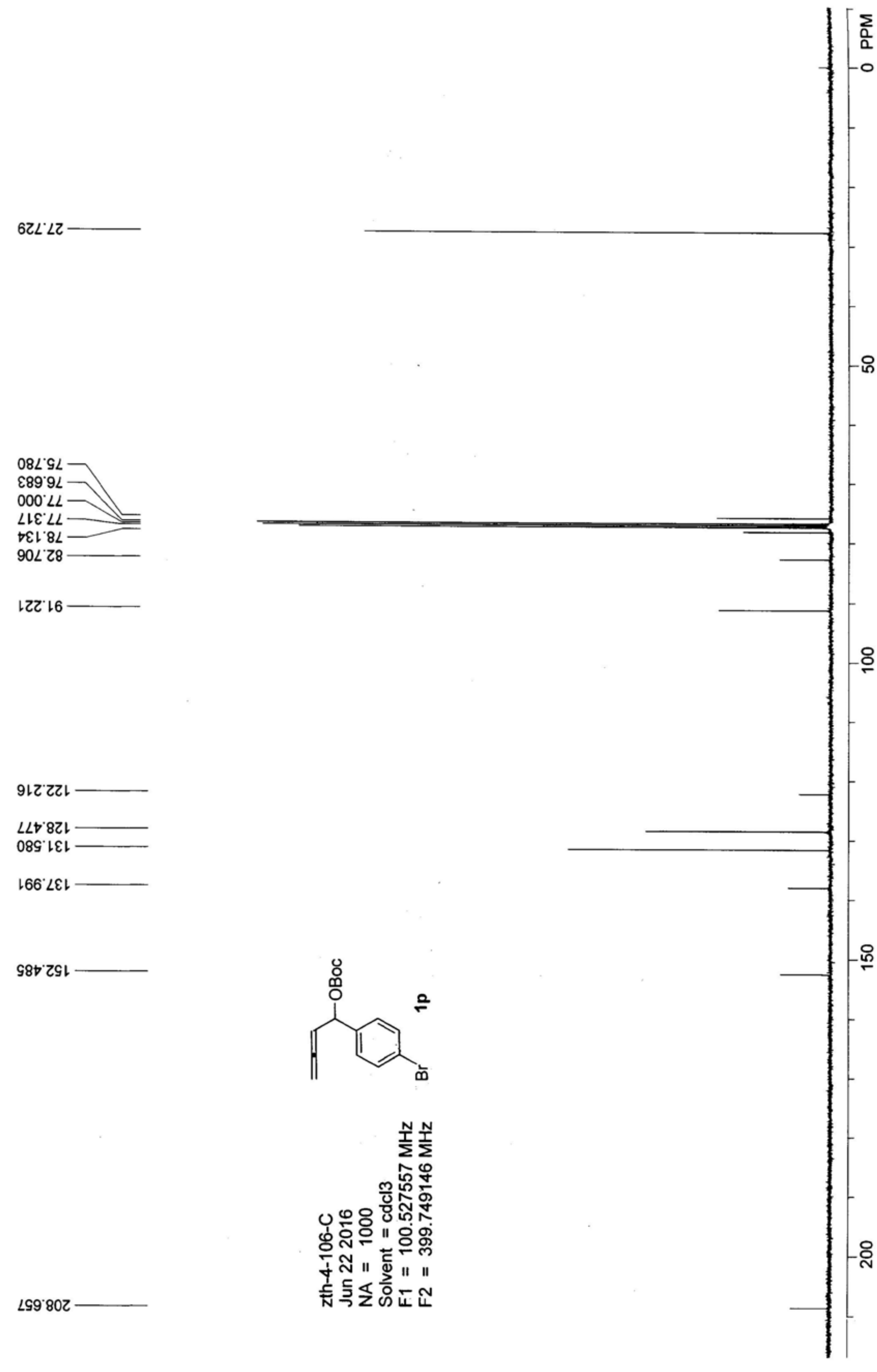
200
150
100
50
0
PPM

tert-butyl 1-(4-bromophenyl)buta-2,3-dienyl carbonate (1p, zth-4-106)

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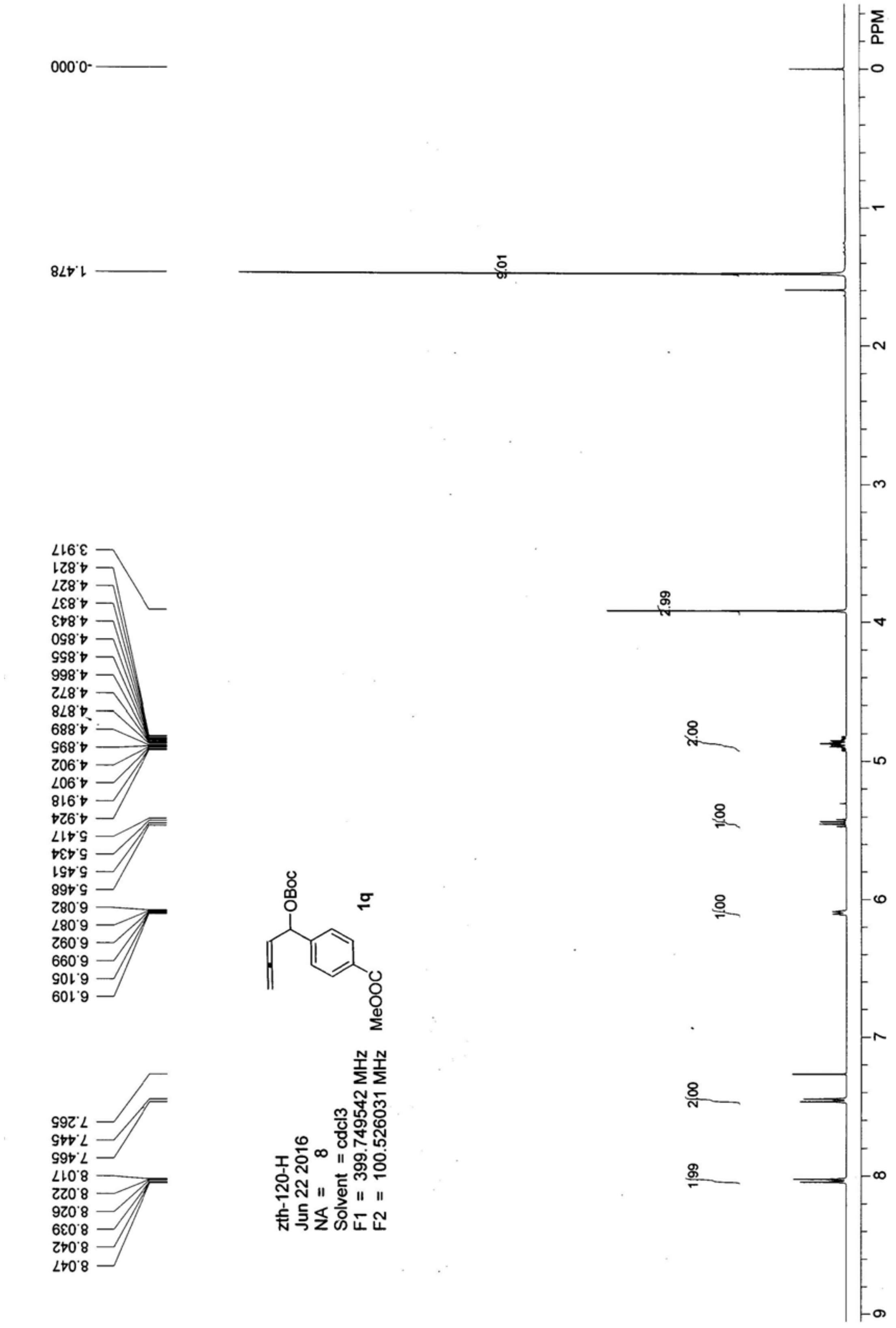
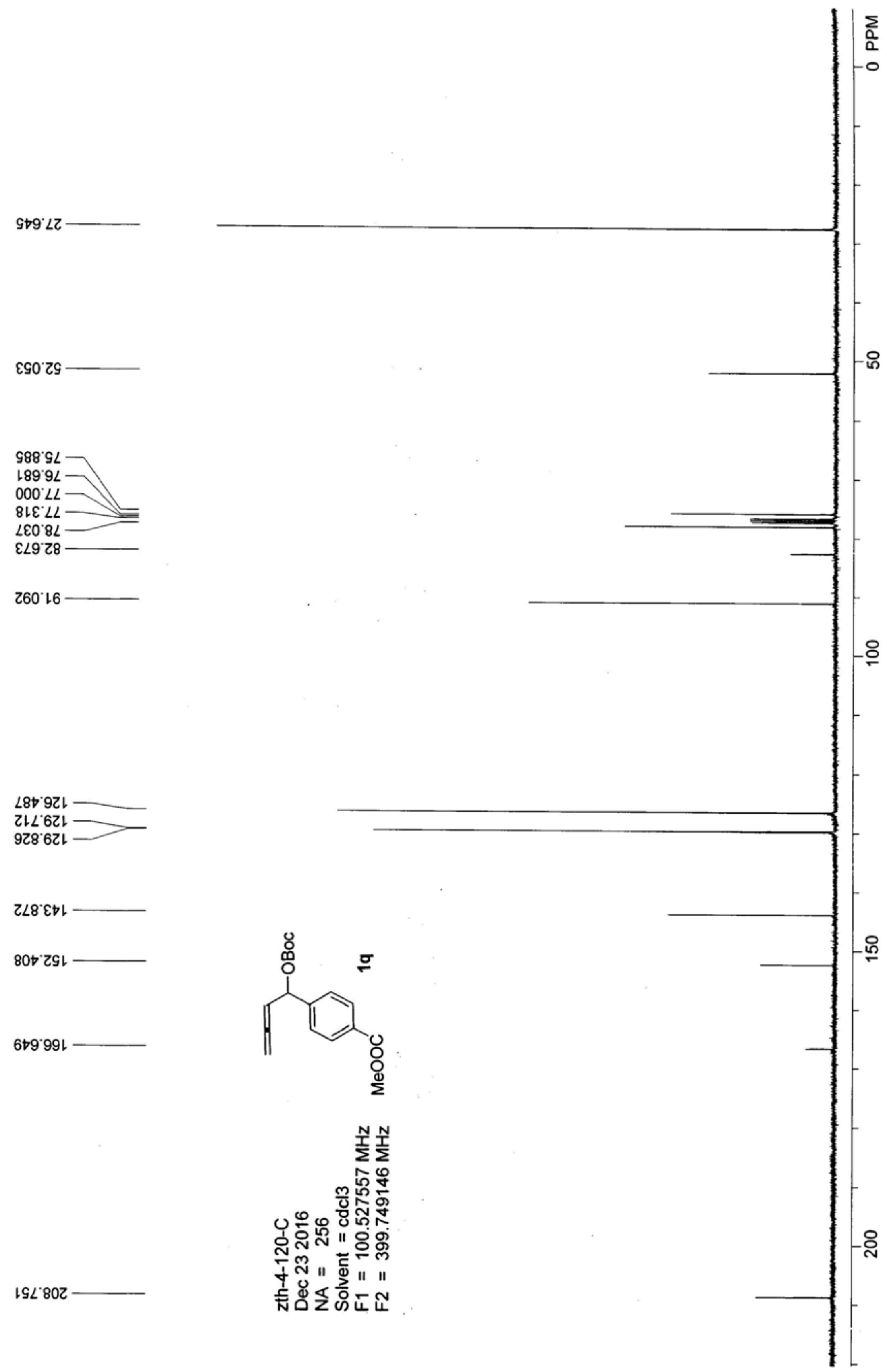
OBoc
Br
1p
zth-4-106-C
Jun 22 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
0 PPM
50
100
150
200

tert-butyl 1-(4-methoxycarbonylphenyl)buta-2,3-dienyl carbonate (1q, zth-4-120)

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91.092
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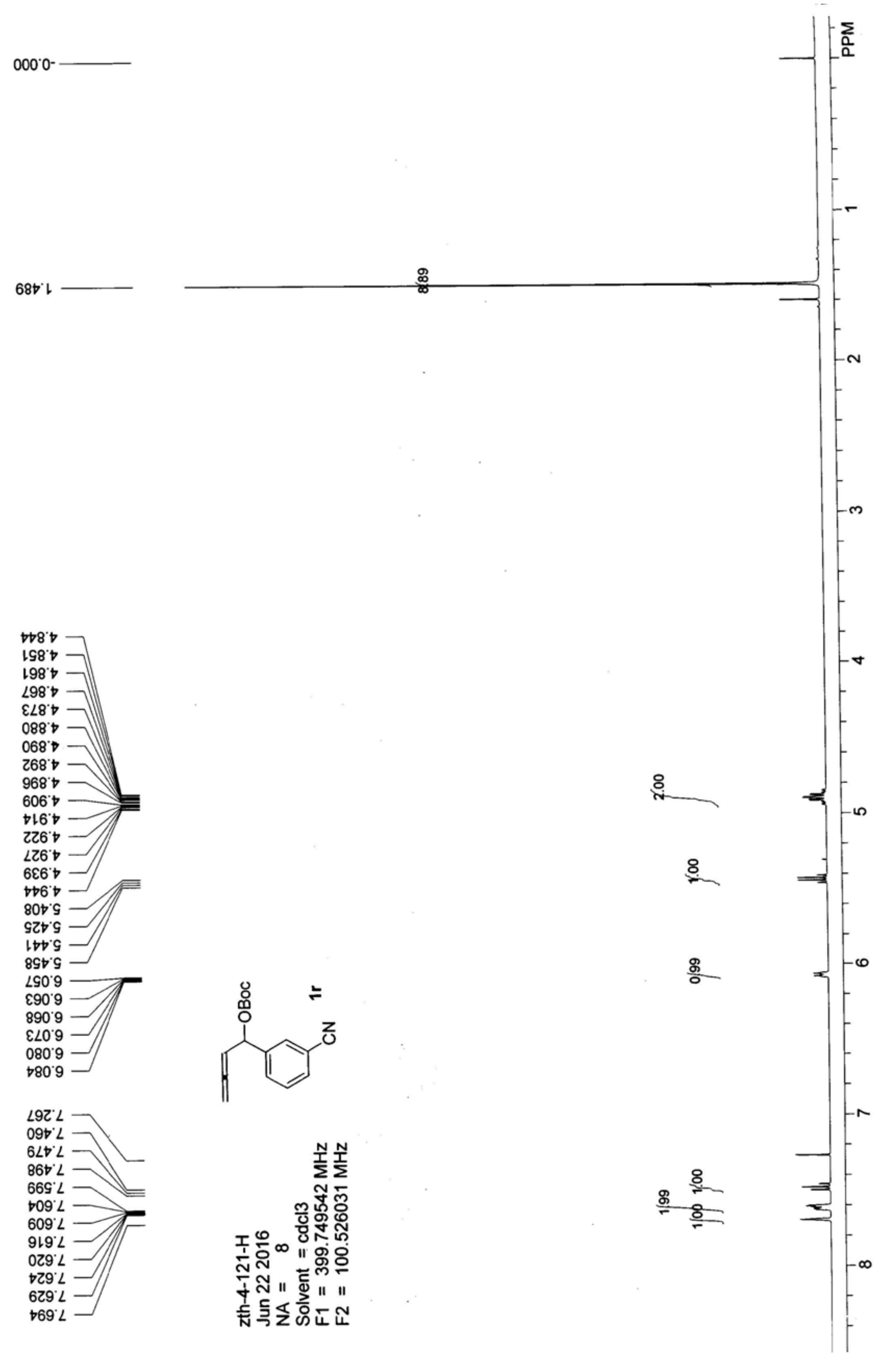
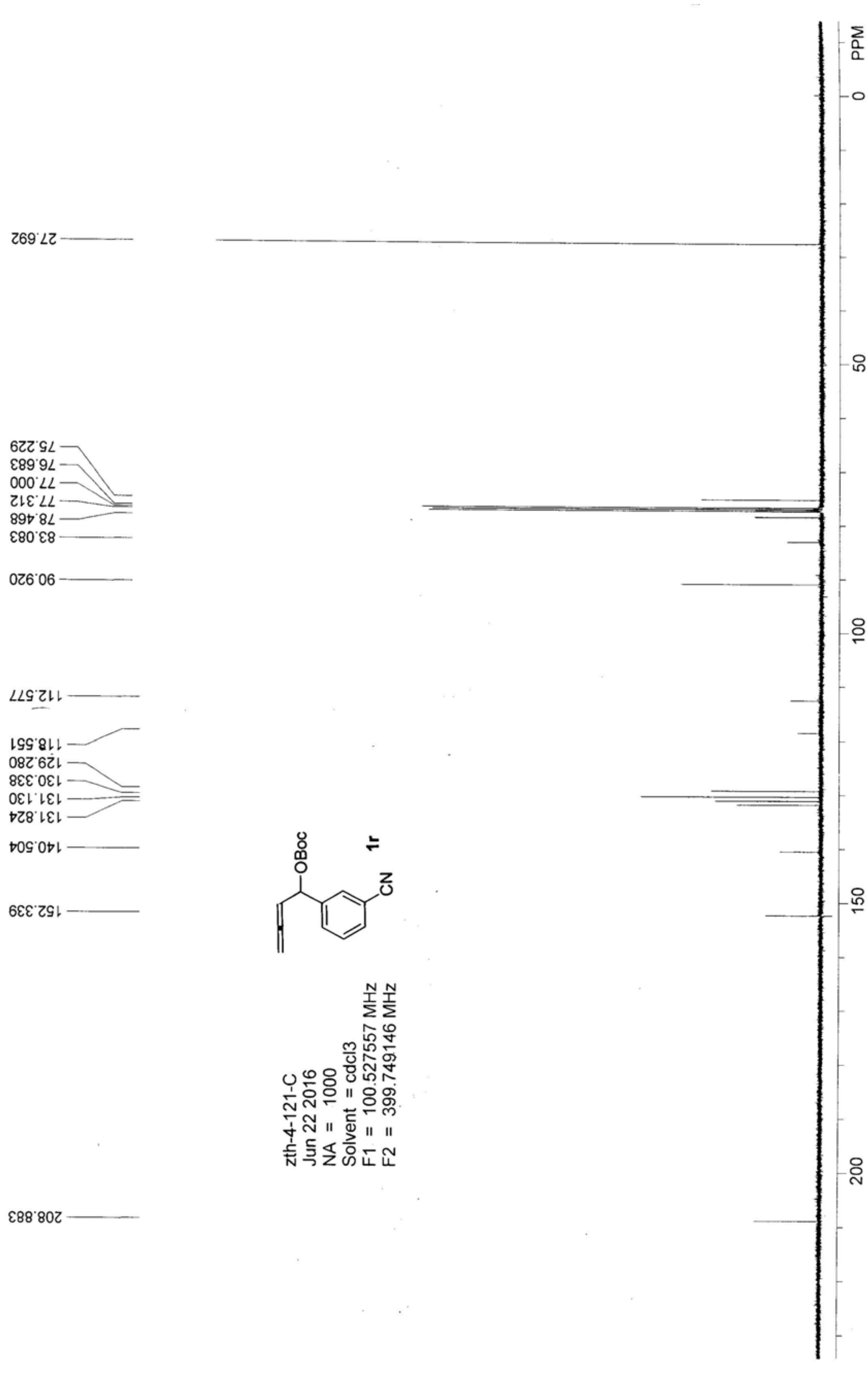
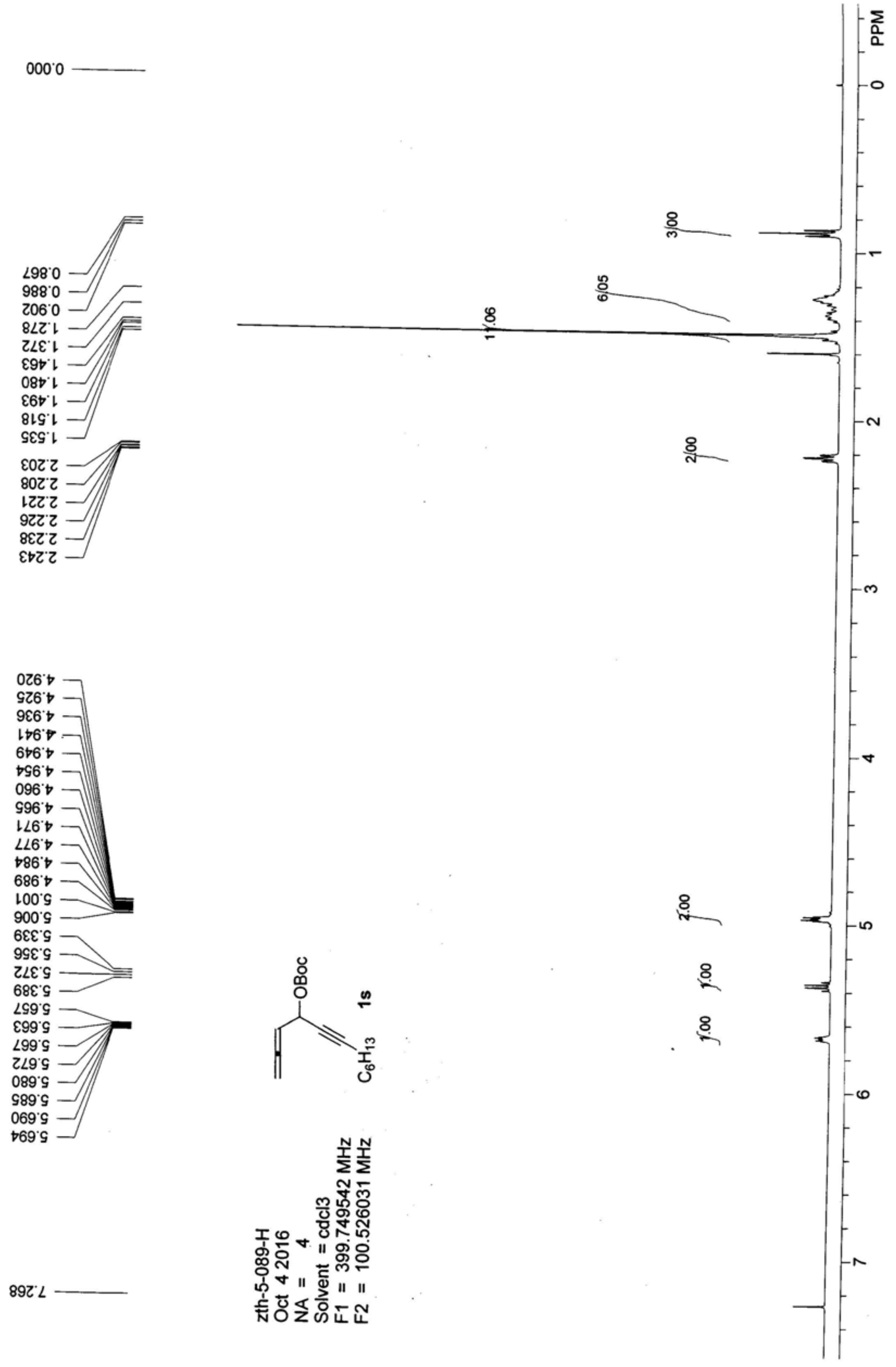
129.712
129.826
143.872
152.408
166.649
208.751
OBoc
MeOOC
1q
zth-4-120-C
Dec 23 2016
NA = 256
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
0 PPM
50
100
150
200

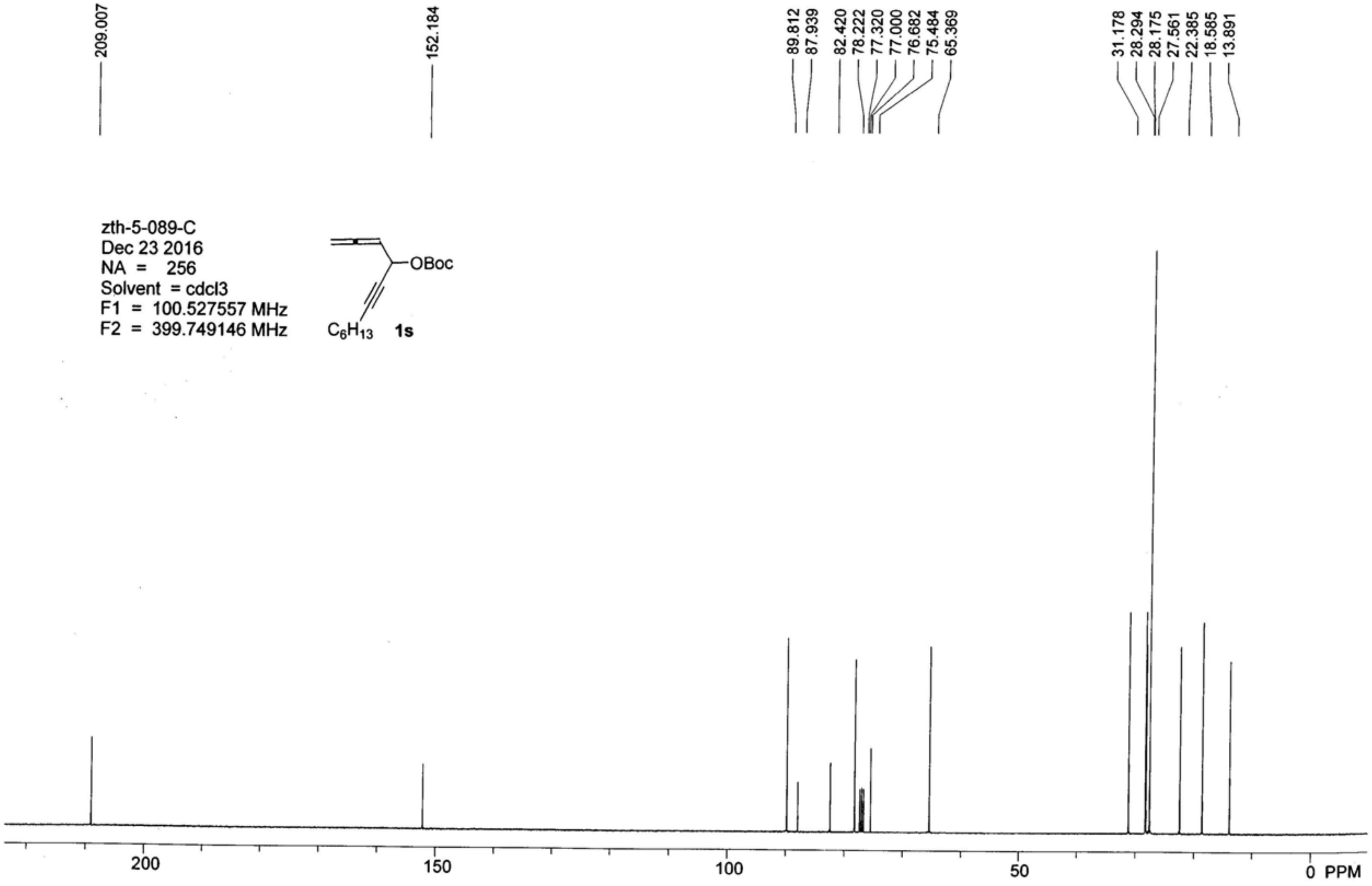
***tert*-butyl 1-(3-cyanophenyl)buta-2,3-dienyl carbonate (1r, zth-4-121)**



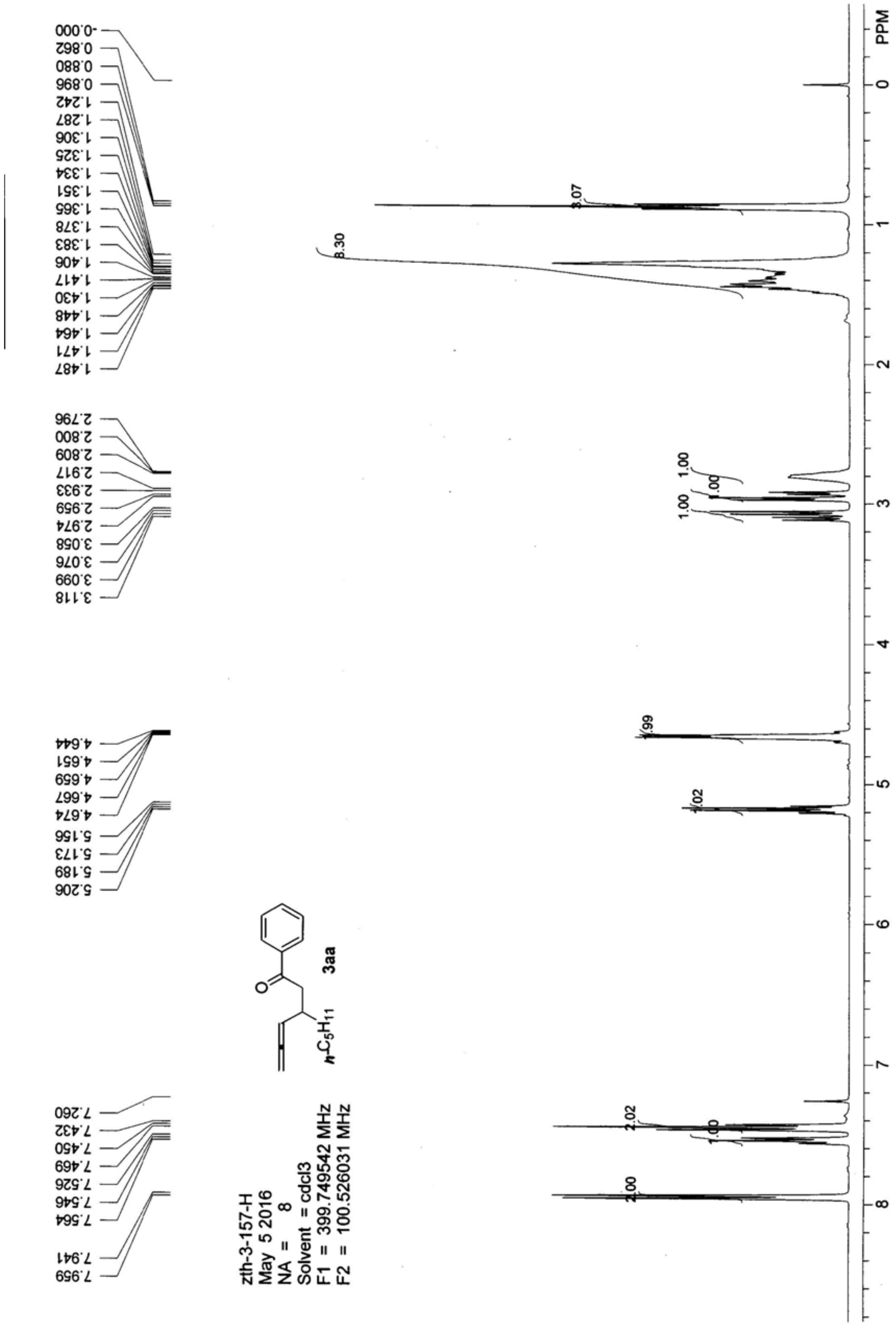

27.692
75.229
76.683
77.000
77.312
78.468
83.083
90.920
112.577
118.551
129.280
130.338
131.130
131.824
140.504
152.339
208.883
OBoc
CN
1r
zth-4-121-C
Jun 22 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
PPM
0
50
100
150
200

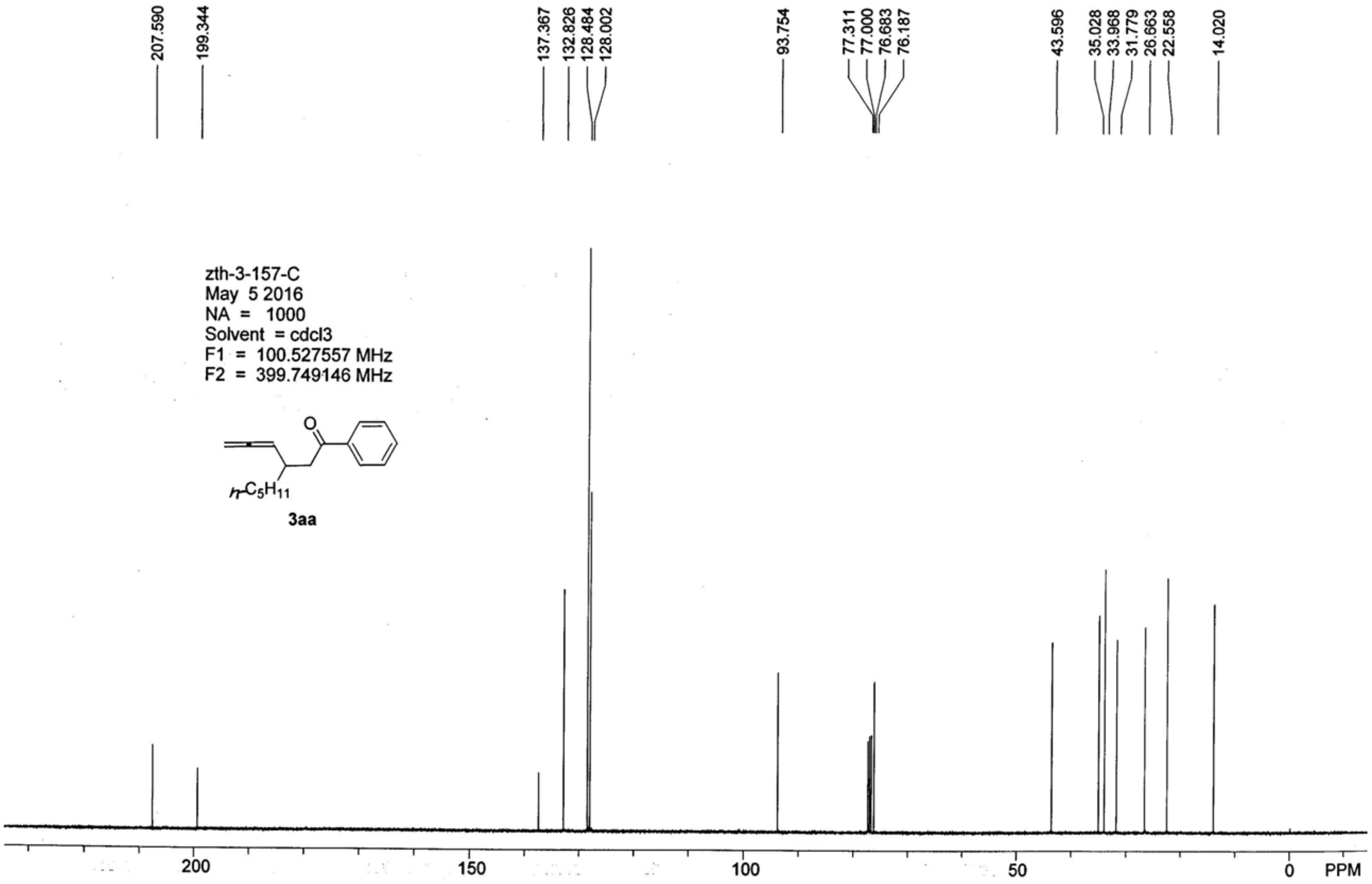
tert-butyl dodeca-1,2-dien-5-yn-4-yl carbonate (1s, zth-5-089)



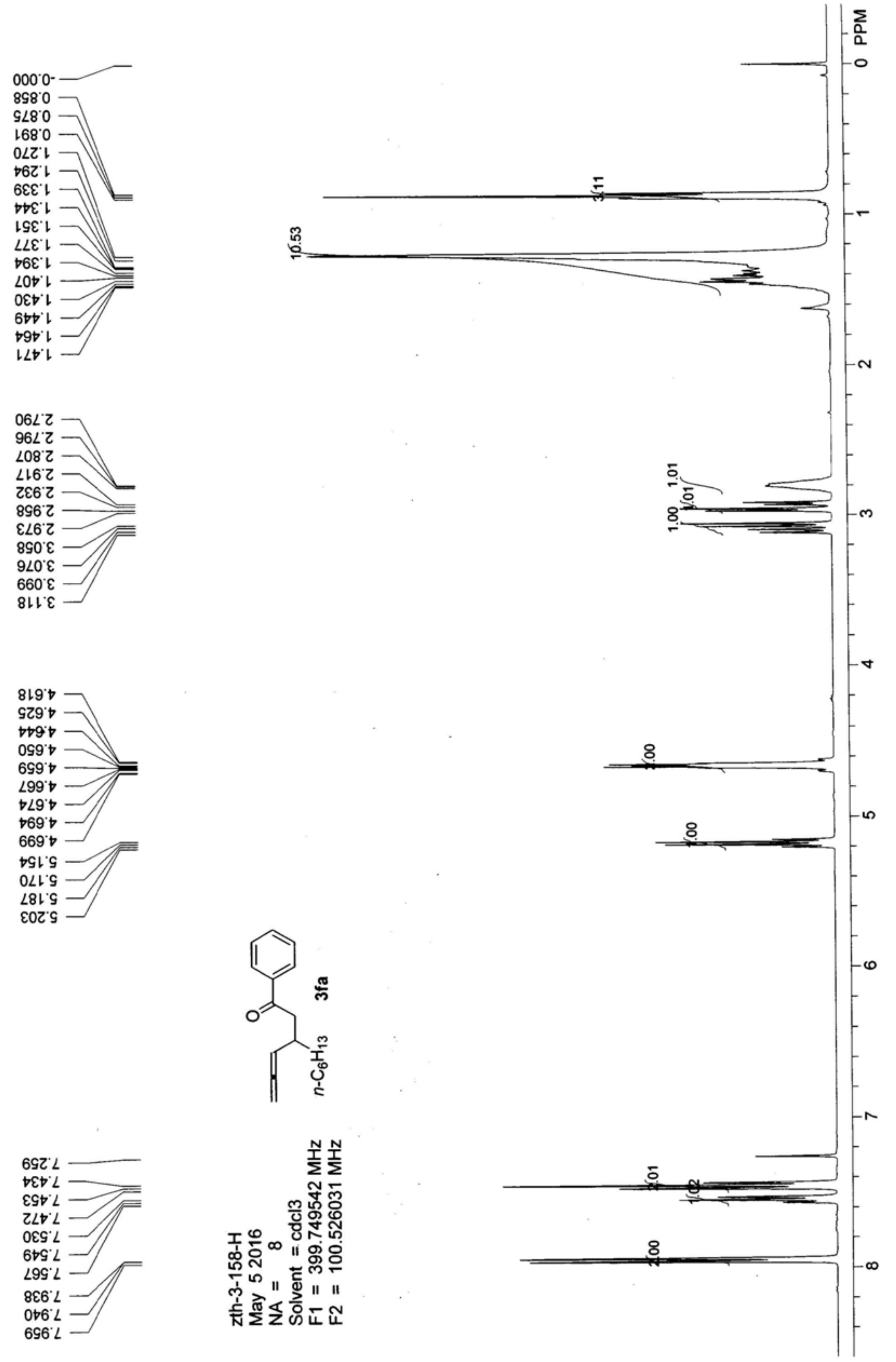

209.007
152.184
89.812
87.939
82.420
78.222
77.320
77.000
76.682
75.484
65.369
31.178
28.294
28.175
27.561
22.385
18.585
13.891
zth-5-089-C
Dec 23 2016
NA = 256
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
OBoc
C6H13
1s
200
150
100
50
0 PPM

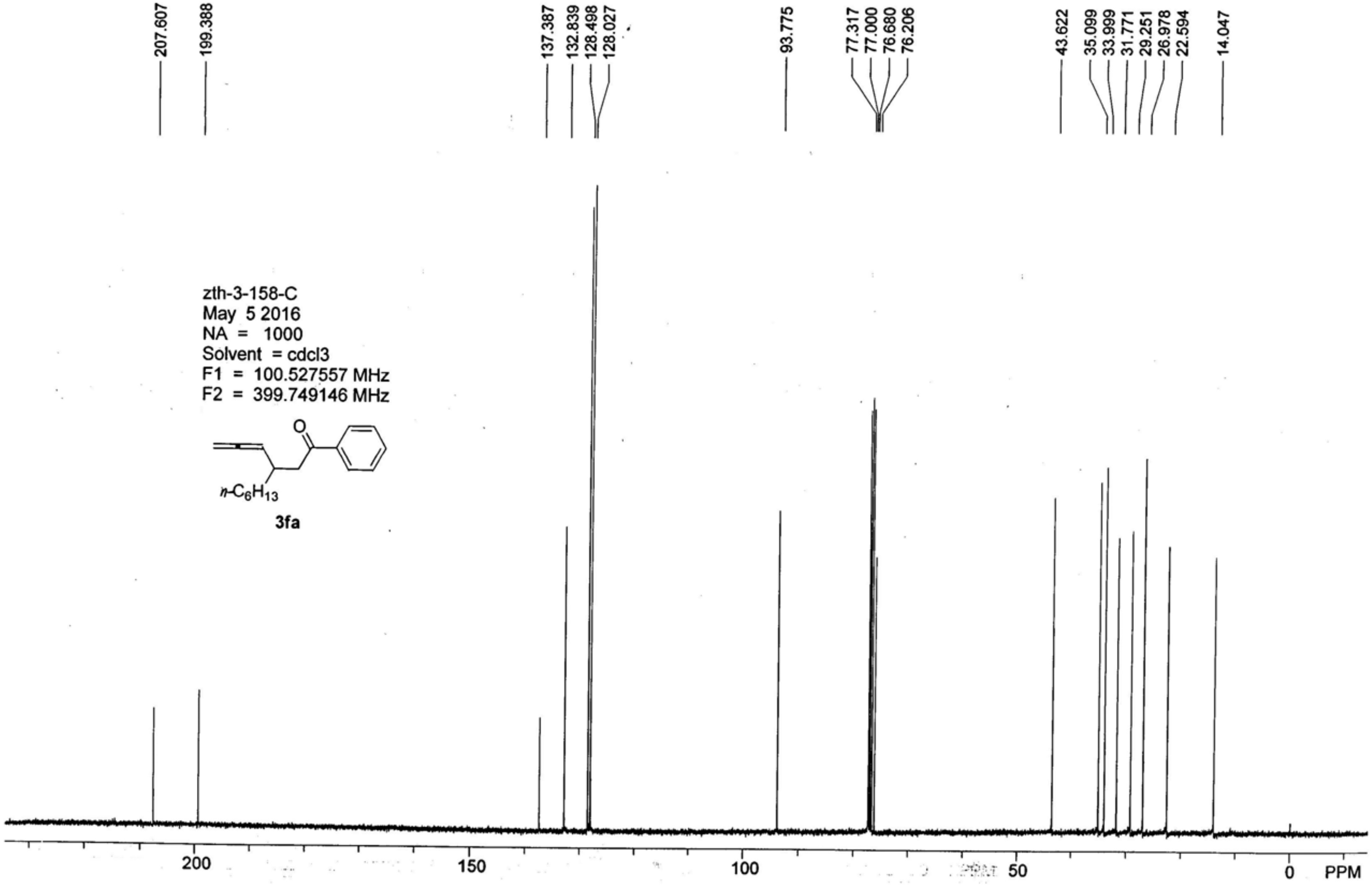
1-phenyl-3-(propa-1,2-dienyl)octan-1-one (3aa, zth-3-157)



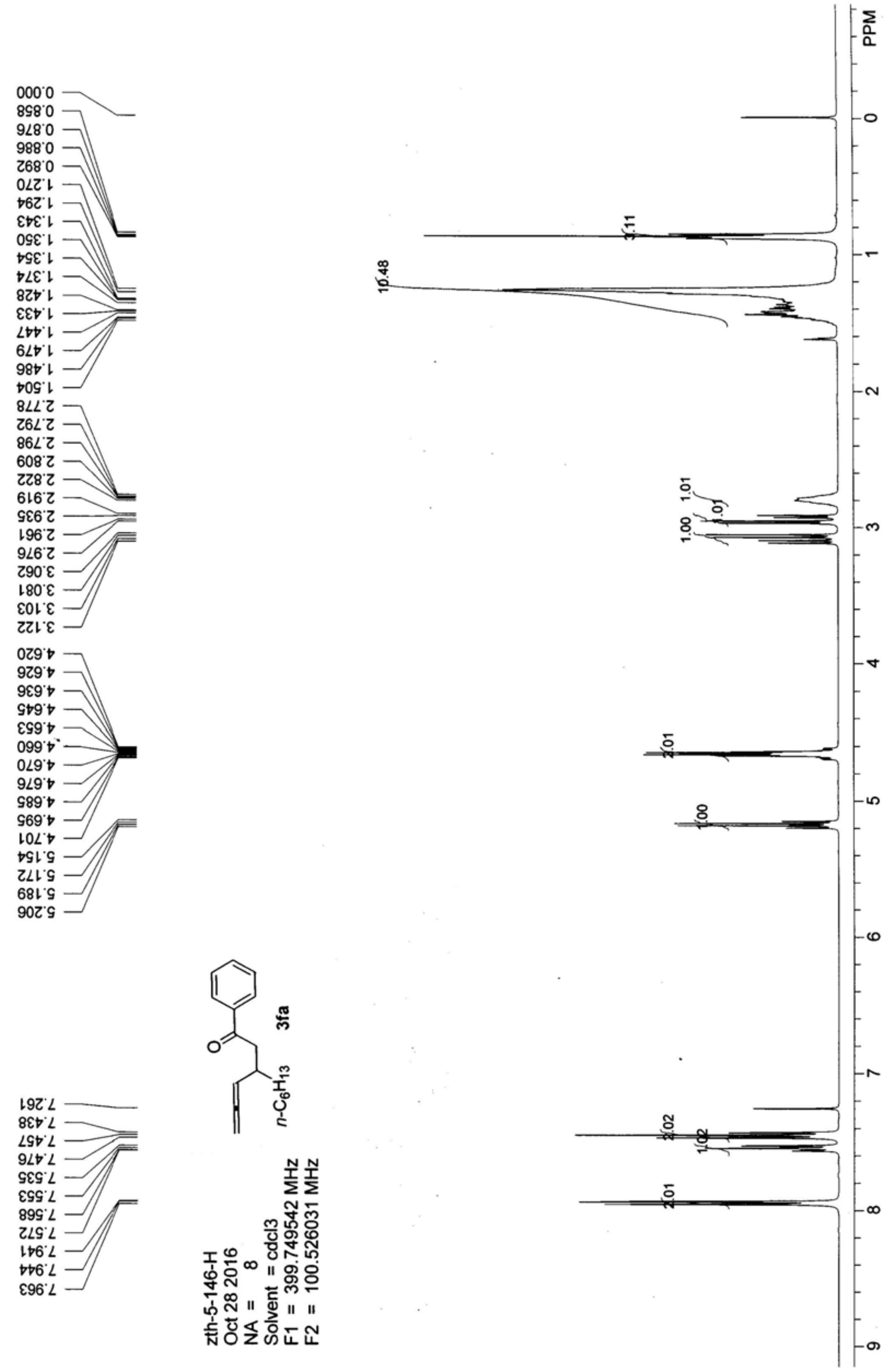

207.590
199.344
137.367
132.826
128.484
128.002
93.754
77.311
77.000
76.683
76.187
43.596
35.028
33.968
31.779
26.663
22.558
14.020
zth-3-157-C
May 5 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
n-C5H11
3aa
200
150
100
50
0
PPM

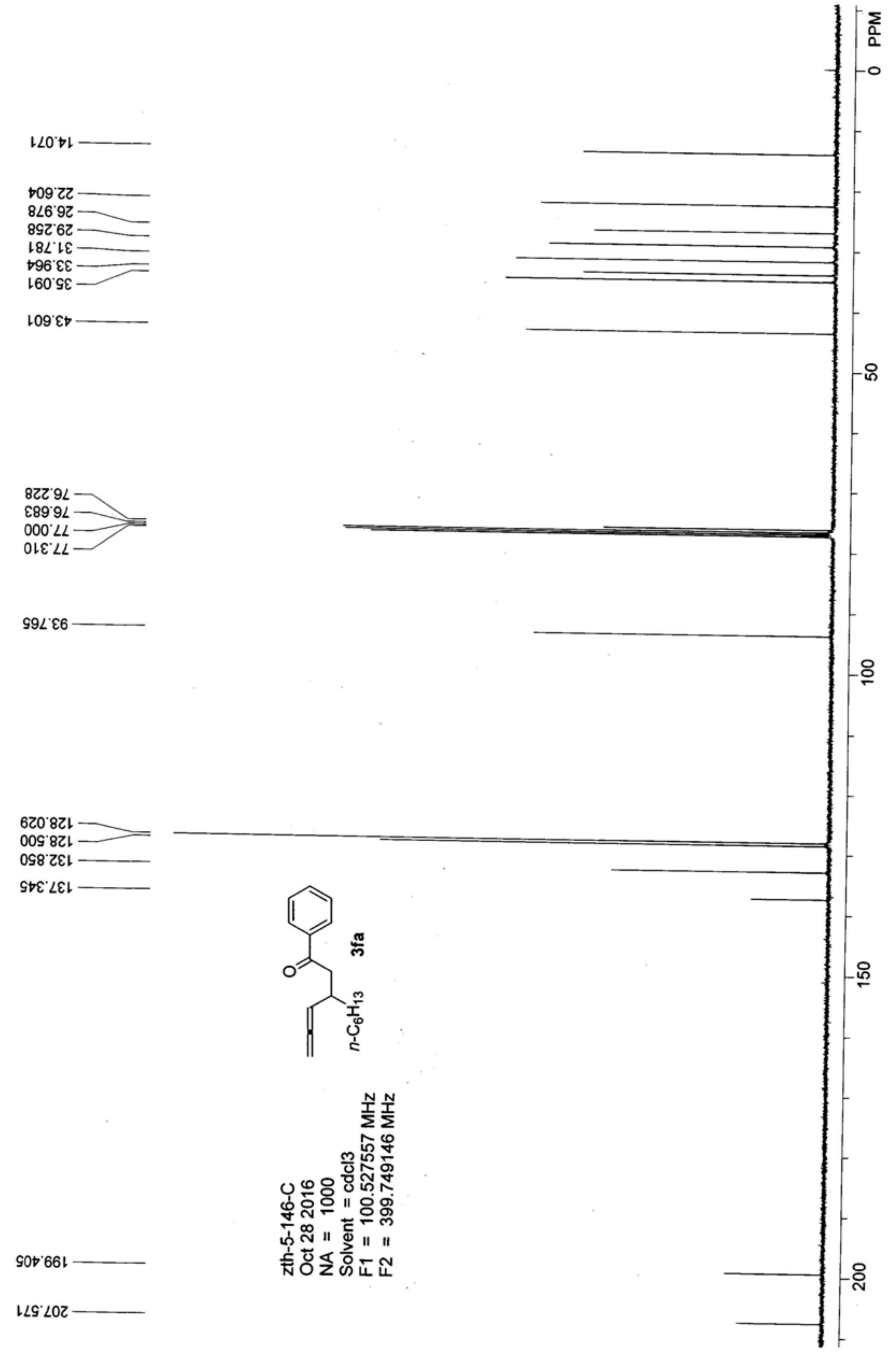
1-phenyl-3-(propa-1,2-dienyl)nonan-1-one (3fa, zth-3-158)



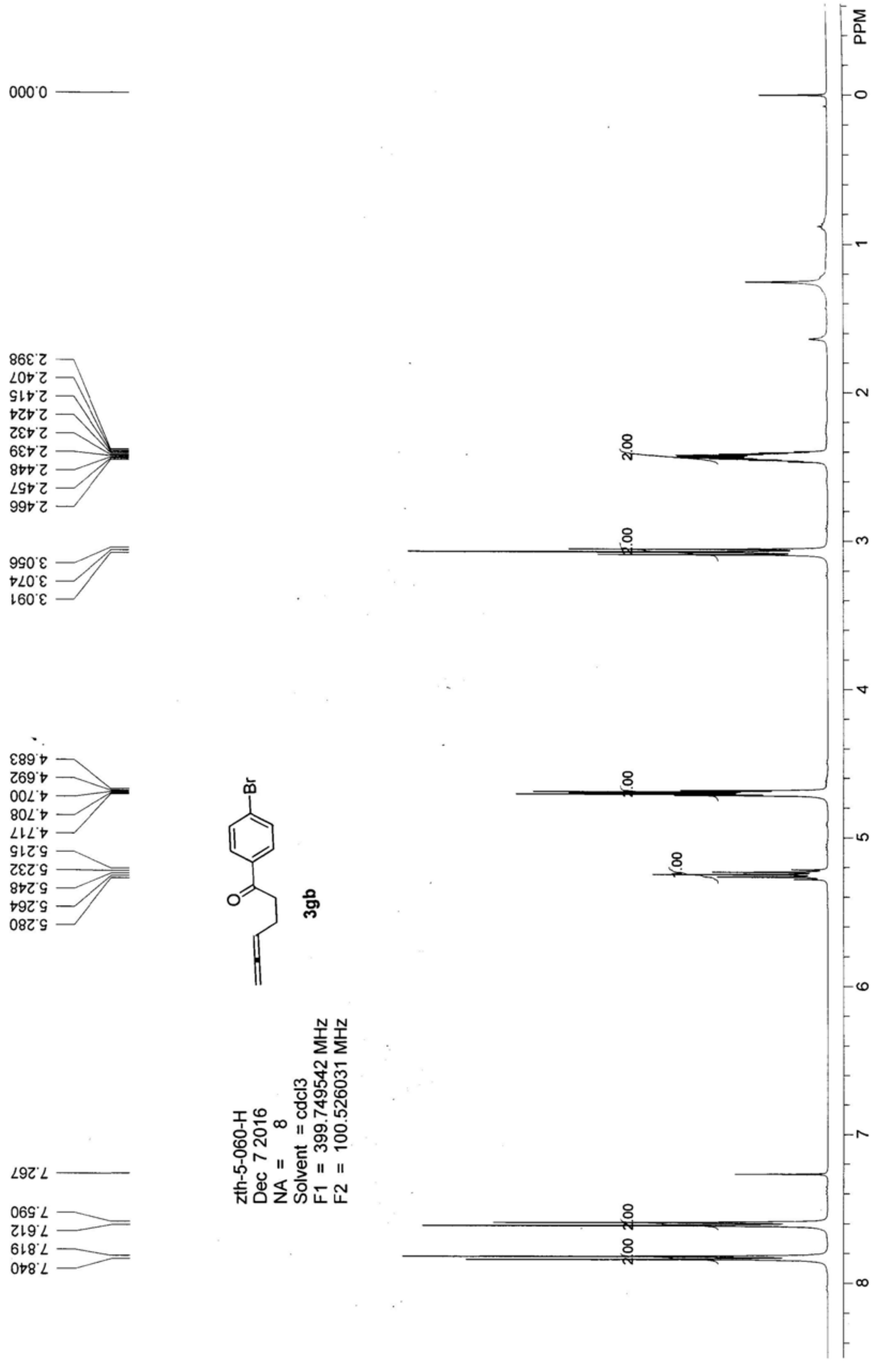

207.607
199.388
137.387
132.839
128.498
128.027
93.775
77.317
77.000
76.680
76.206
43.622
35.099
33.999
31.771
29.251
26.978
22.594
14.047
zth-3-158-C
May 5 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
n-C6H13
3fa
200
150
100
50
0
PPM

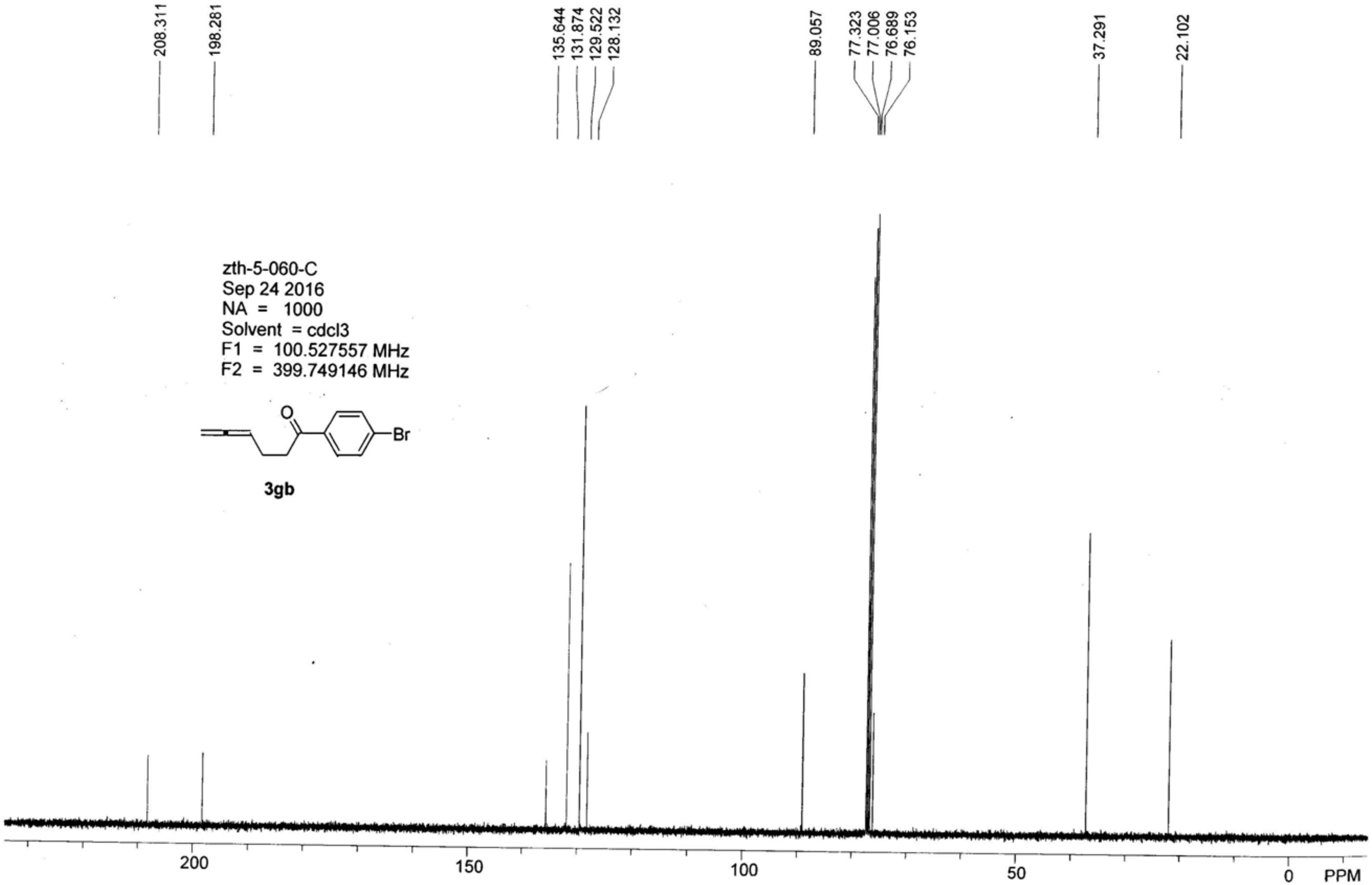
1-phenyl-3-(propa-1,2-dienyl)nonan-1-one (3fa, zth-5-146)



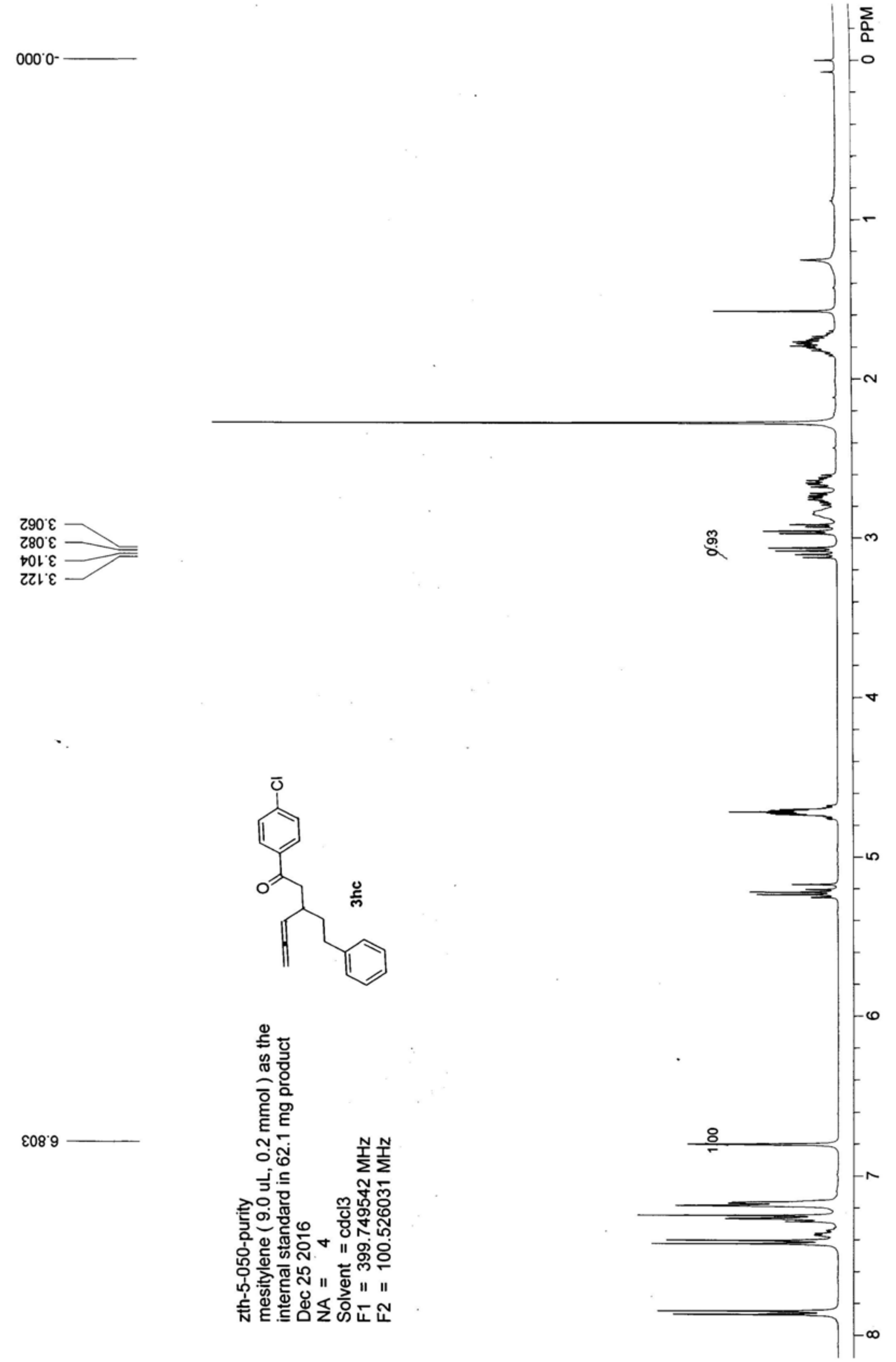

14.071
22.604
26.978
29.258
31.781
33.964
35.091
43.601
76.228
76.683
77.000
77.310
93.765
128.029
128.500
132.850
137.345
199.405
207.571
3fa
O
n-C_6H_{13}
zth-5-146-C
Oct 28 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
0
PPM
50
100
150
200

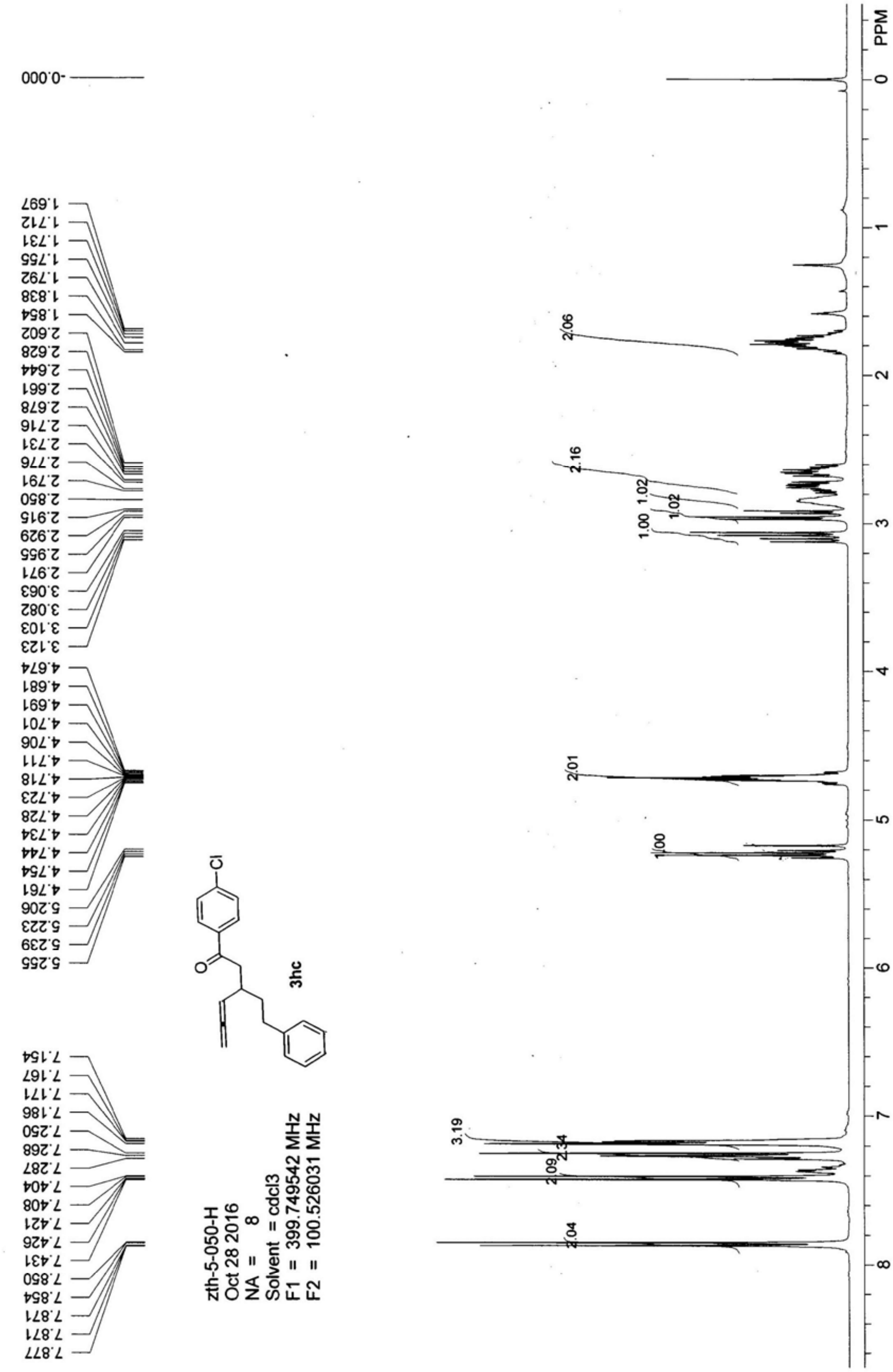
1-(4-bromophenyl)hexa-4,5-dien-1-one (3gb, zth-5-060)

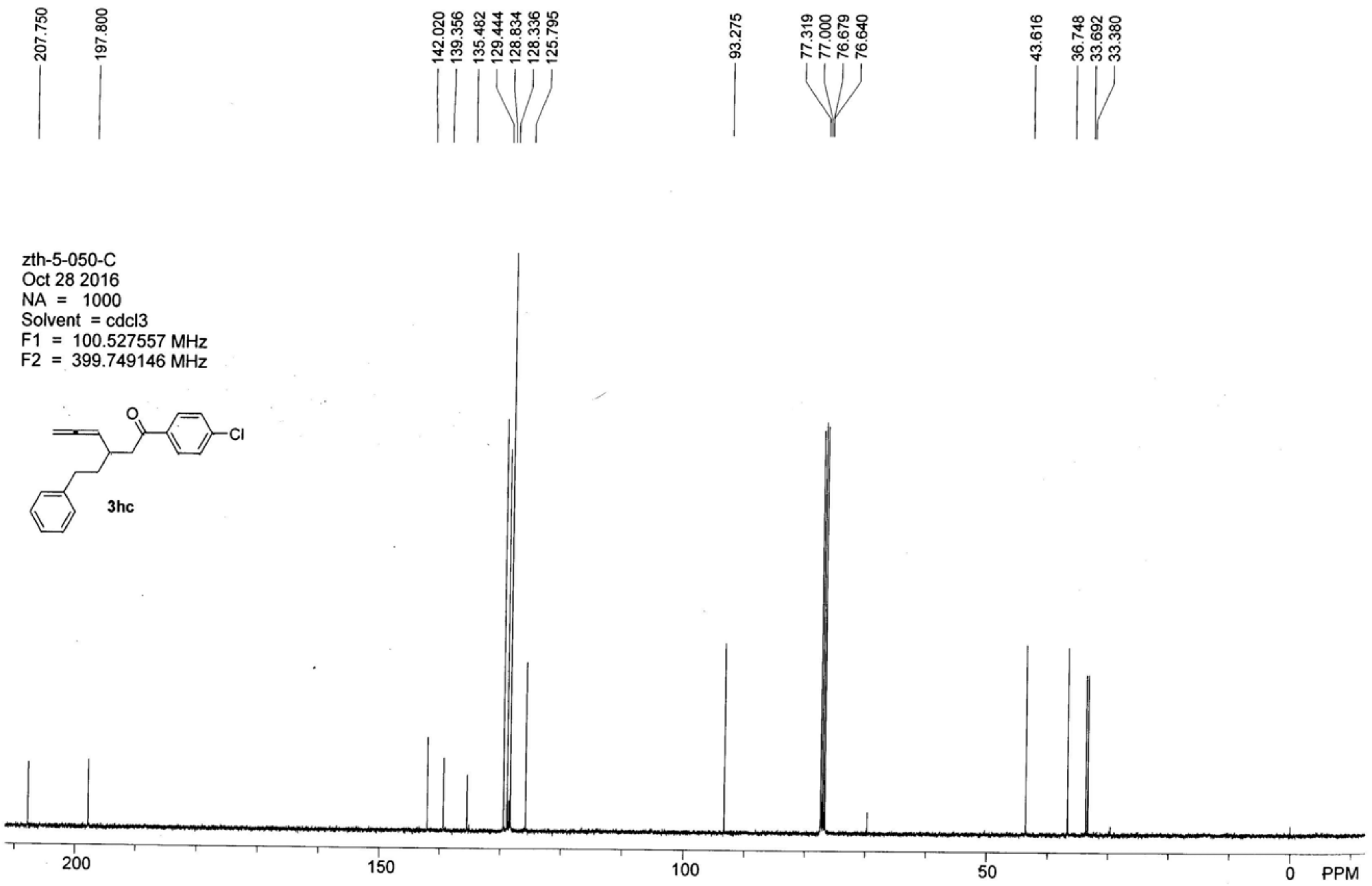



208.311
198.281
135.644
131.874
129.522
128.132
89.057
77.323
77.006
76.689
76.153
37.291
22.102
zth-5-060-C
Sep 24 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
Br
3gb
200
150
100
50
0
PPM

1-(4-chlorophenyl)-3-phenethylhexa-4,5-dien-1-one (3hc, zth-5-050)



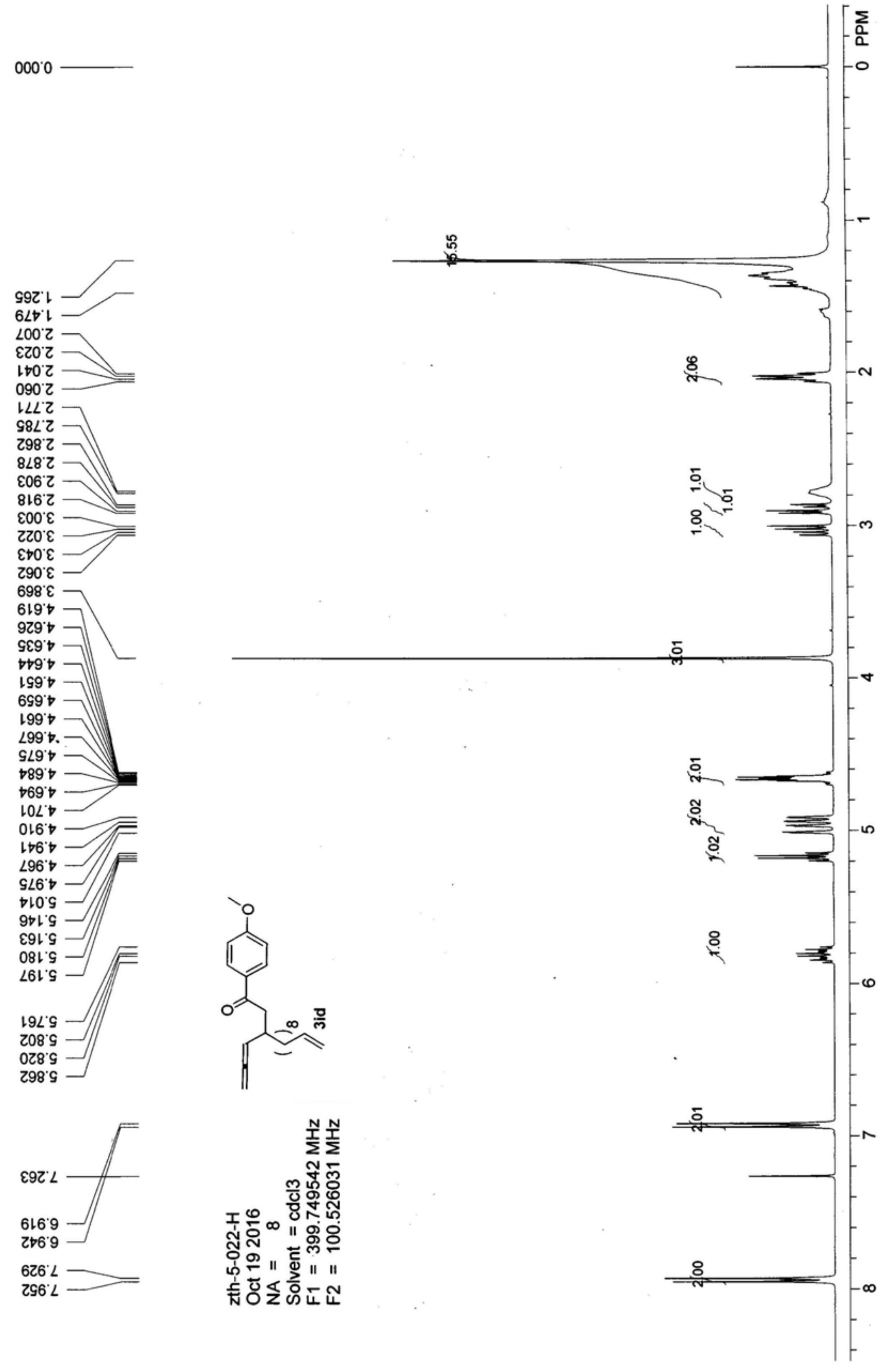

zth-5-050-H
Oct 28 2016
NA = 8
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
3hc
O
Cl
7.877
7.871
7.871
7.854
7.850
7.431
7.426
7.421
7.408
7.404
7.287
7.268
7.250
7.186
7.171
7.167
7.154
5.255
5.239
5.223
5.206
4.761
4.754
4.744
4.734
4.728
4.723
4.718
4.711
4.706
4.701
4.691
4.681
4.674
3.123
3.103
3.082
3.063
2.971
2.955
2.929
2.915
2.850
2.791
2.776
2.731
2.716
2.678
2.661
2.644
2.628
2.602
1.854
1.838
1.792
1.755
1.731
1.712
1.697
-0.000
2.04
2.09
2.34
3.19
1.00
2.01
1.00
1.02
1.02
2.16
2.06
8
7
6
5
4
3
2
1
0
PPM

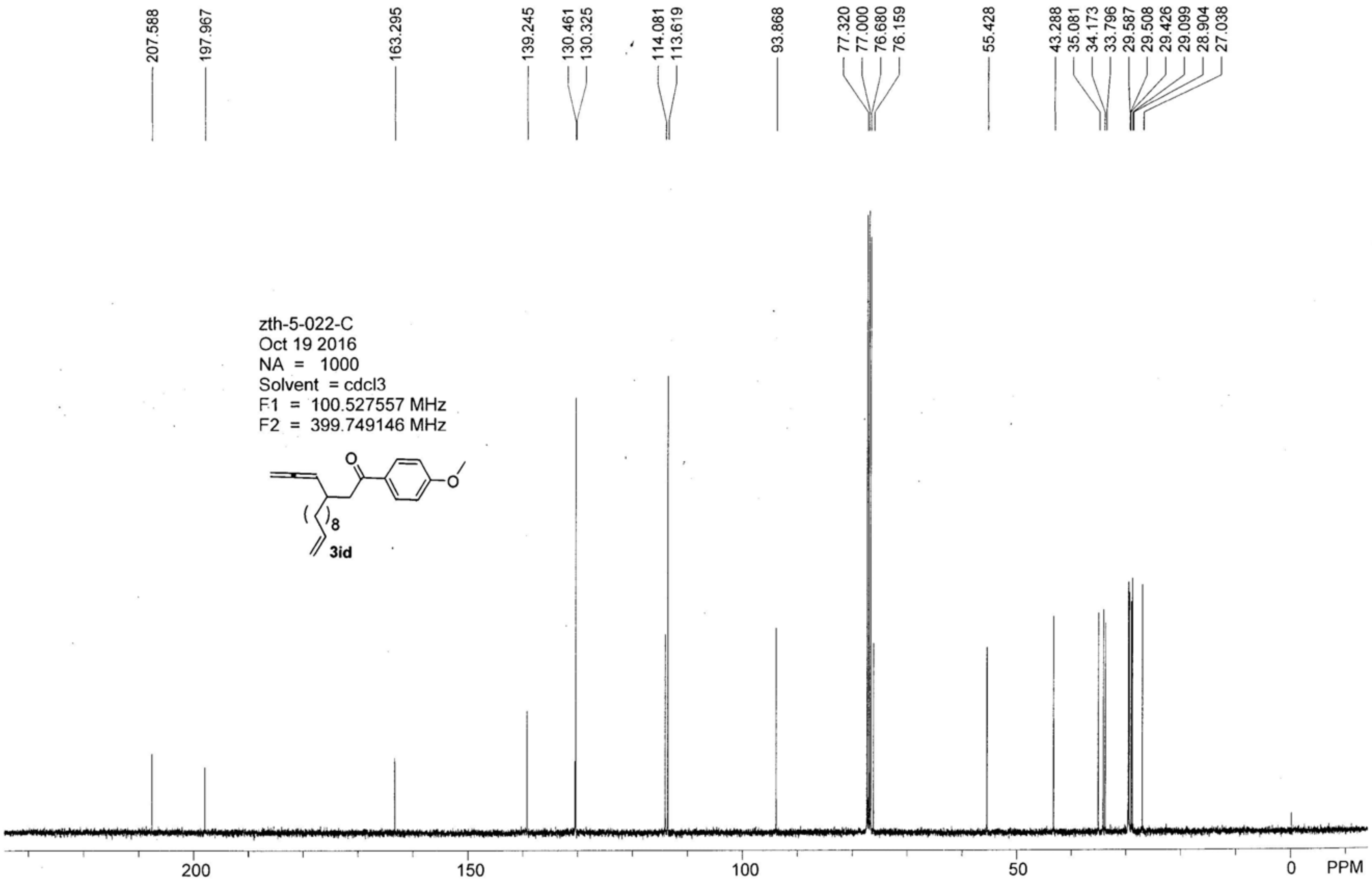


zth-5-050-C
Oct 28 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz

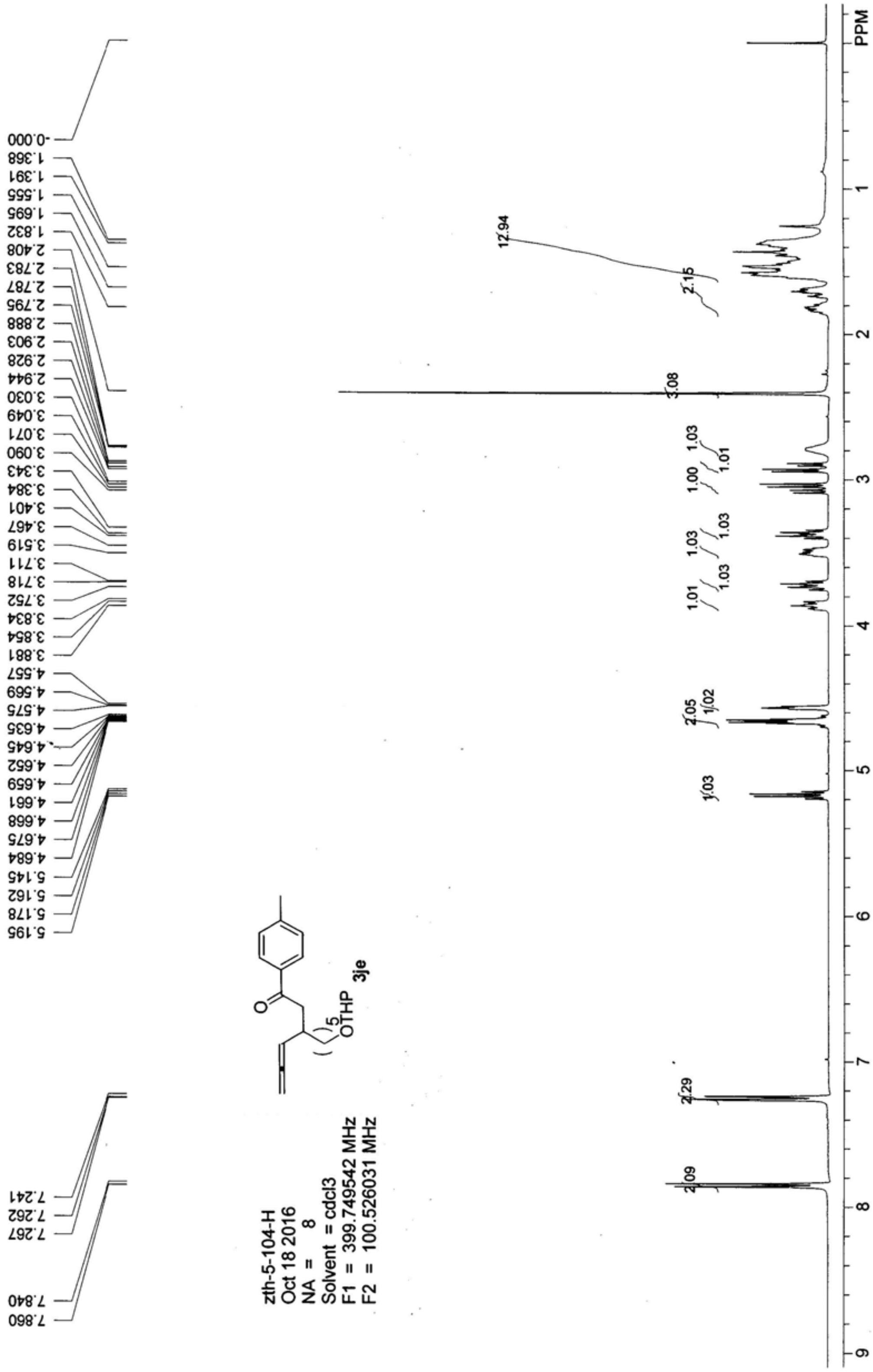
3hc

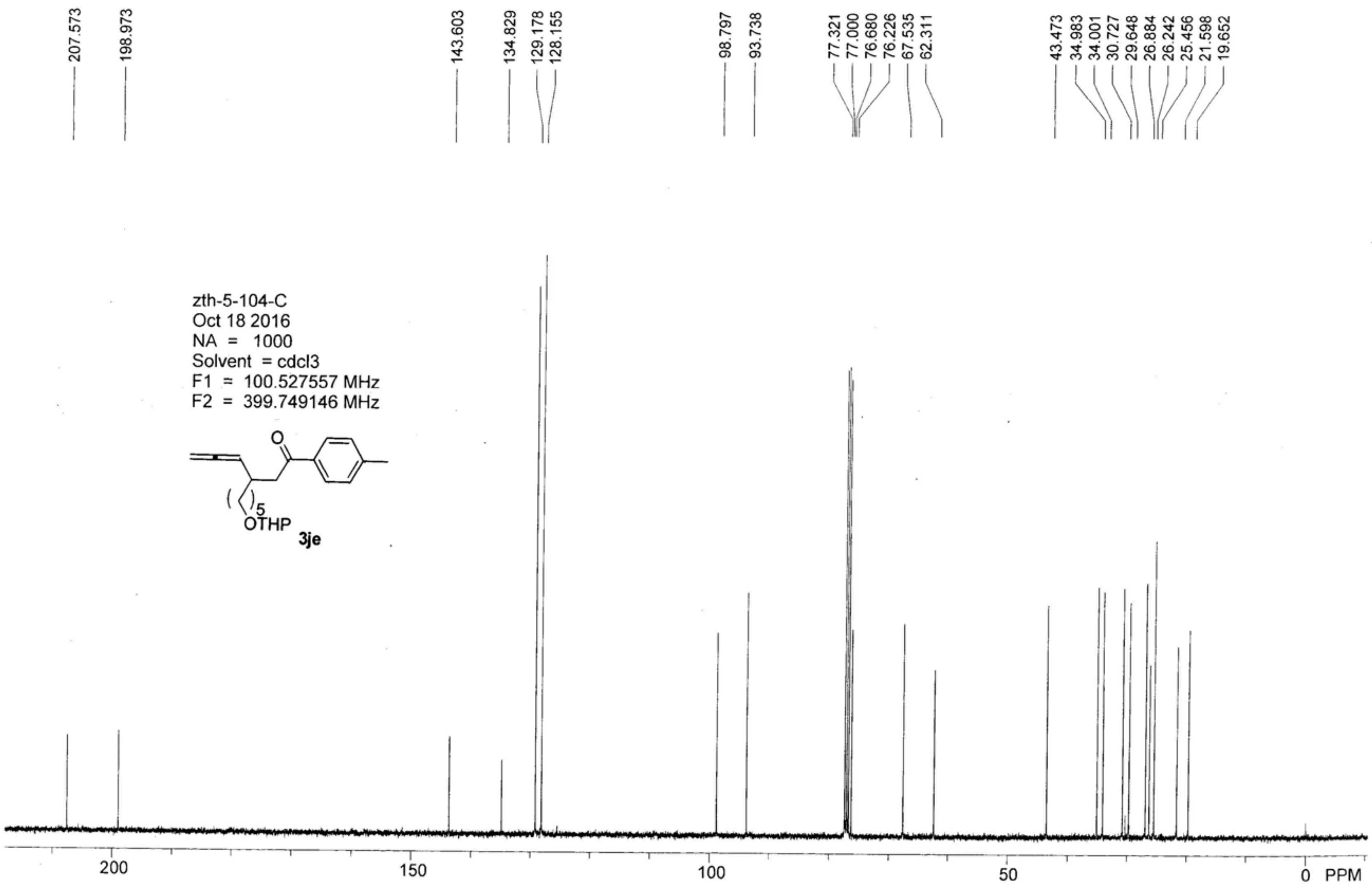
1-(4-methoxyphenyl)-3-(propa-1,2-dienyl)tridec-12-en-1-one (3id, zth-5-022)




207.588
197.967
163.295
139.245
130.461
130.325
114.081
113.619
93.868
77.320
77.000
76.680
76.159
55.428
43.288
35.081
34.173
33.796
29.587
29.508
29.426
29.099
28.904
27.038
zth-5-022-C
Oct 19 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
8
3id
200
150
100
50
0
PPM

1-*p*-tolyl-3-(propa-1,2-dienyl)-8-(tetrahydro-2*H*-pyran-2-yloxy)- octan-1-one (3je, zth-5-104)

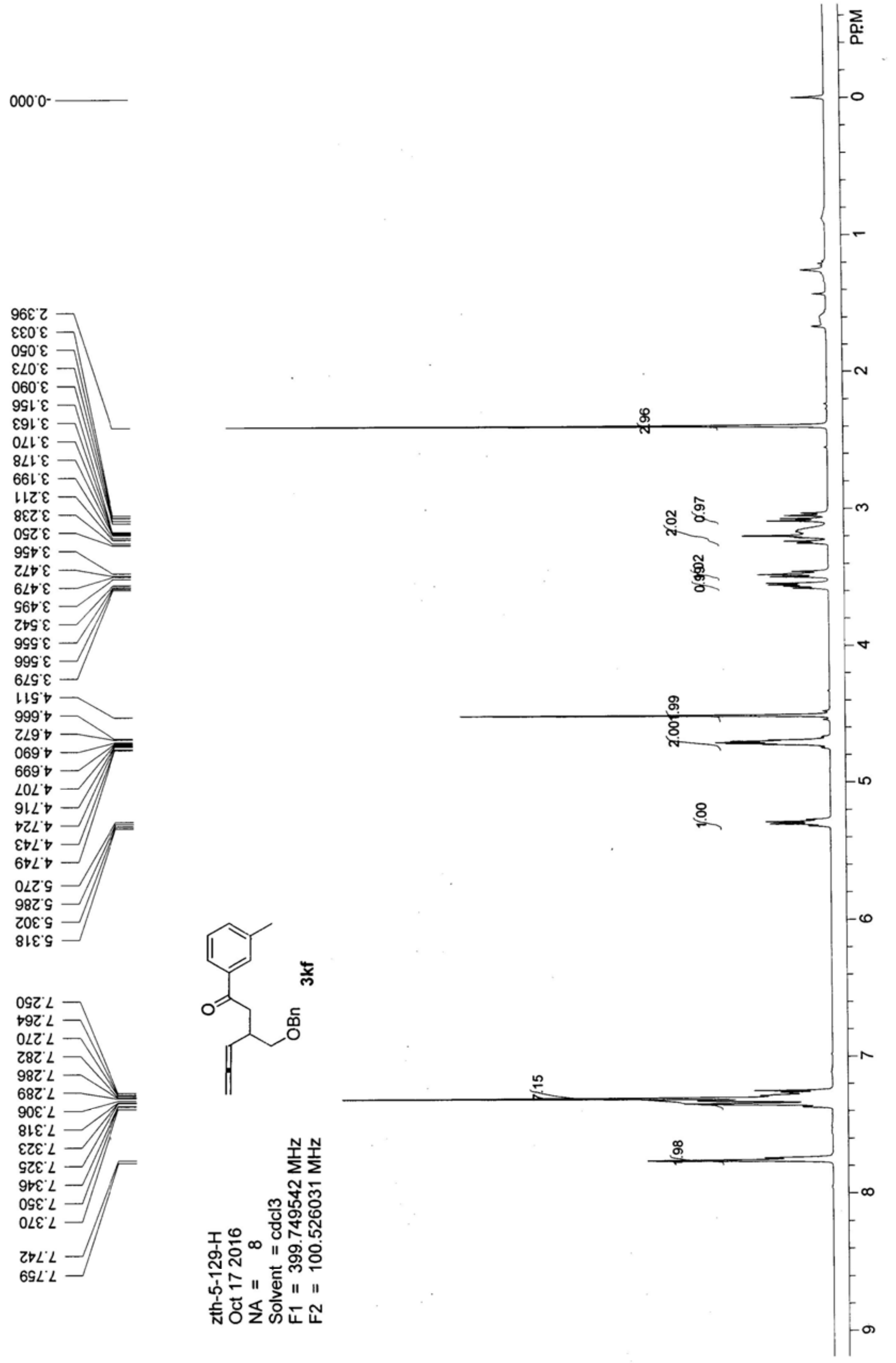


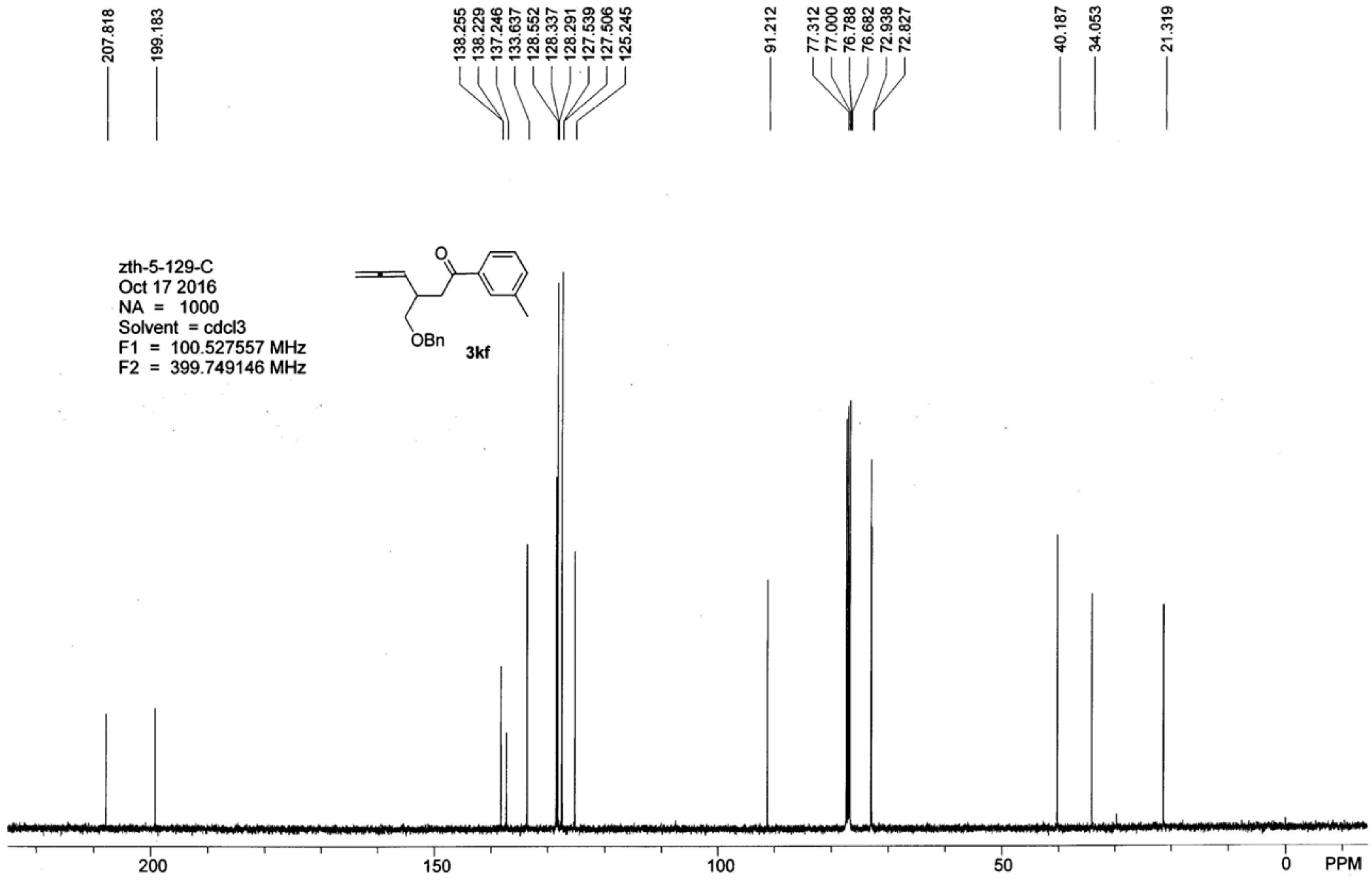


zth-5-104-C
Oct 18 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz

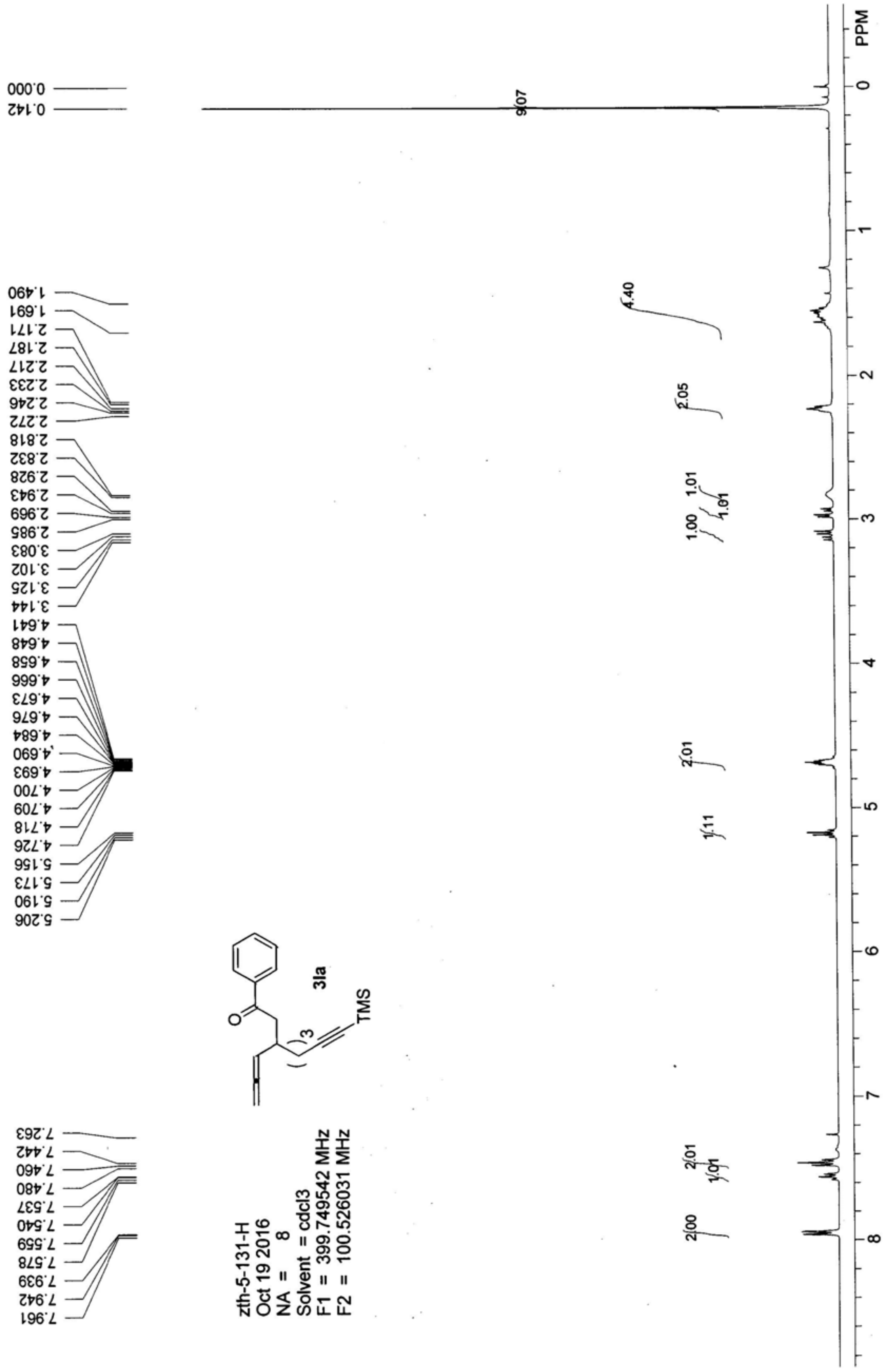
3je

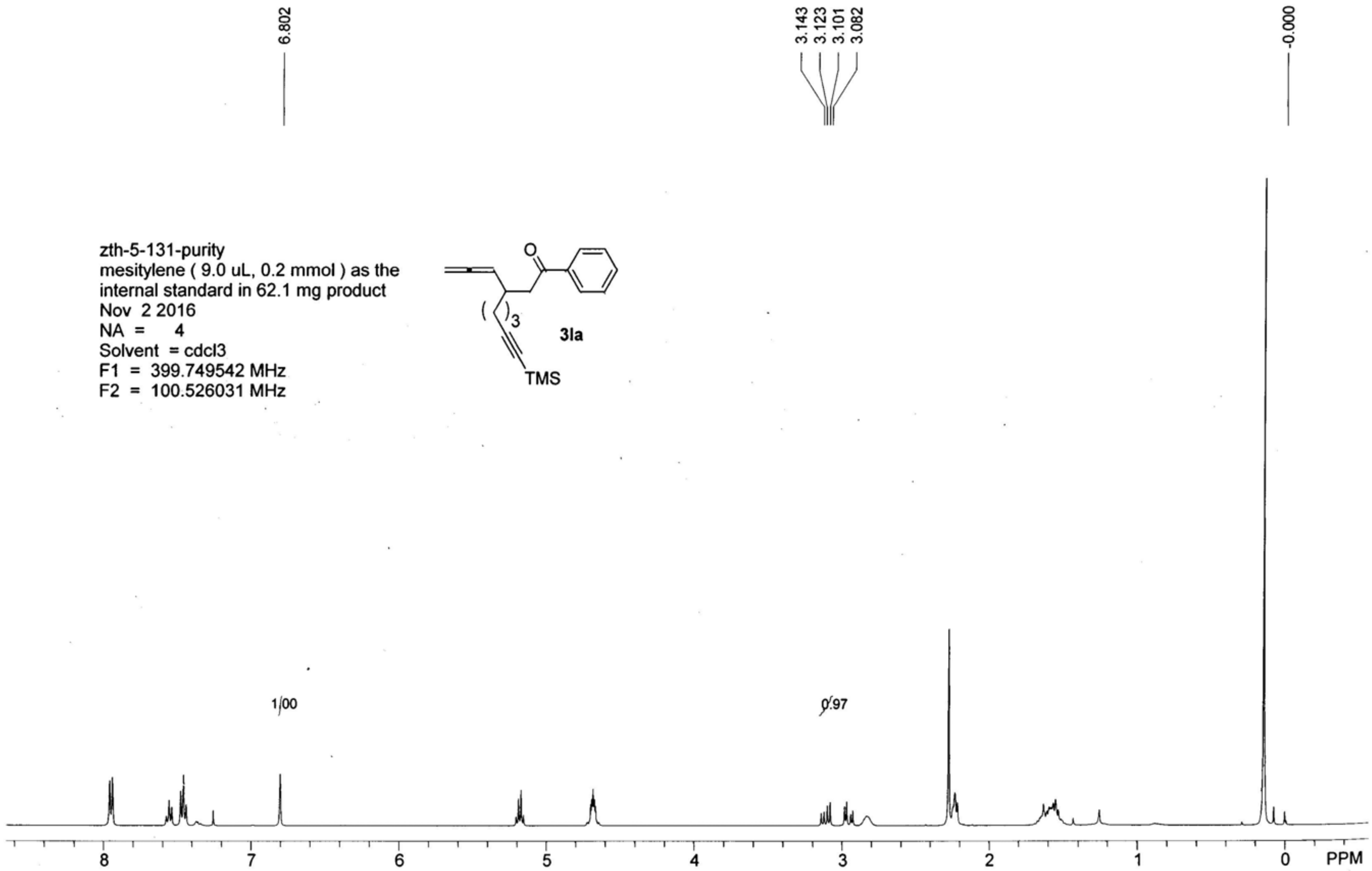
3-(4-bromophenyl)-1-phenylhexa-4,5-dien-1-one (3pa, zth-4-129)




207.818
199.183
138.255
138.229
137.246
133.637
128.552
128.337
128.291
127.539
127.506
125.245
91.212
77.312
77.000
76.788
76.682
72.938
72.827
40.187
34.053
21.319
zth-5-129-C
Oct 17 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
OBn
3kf
200
150
100
50
0
PPM

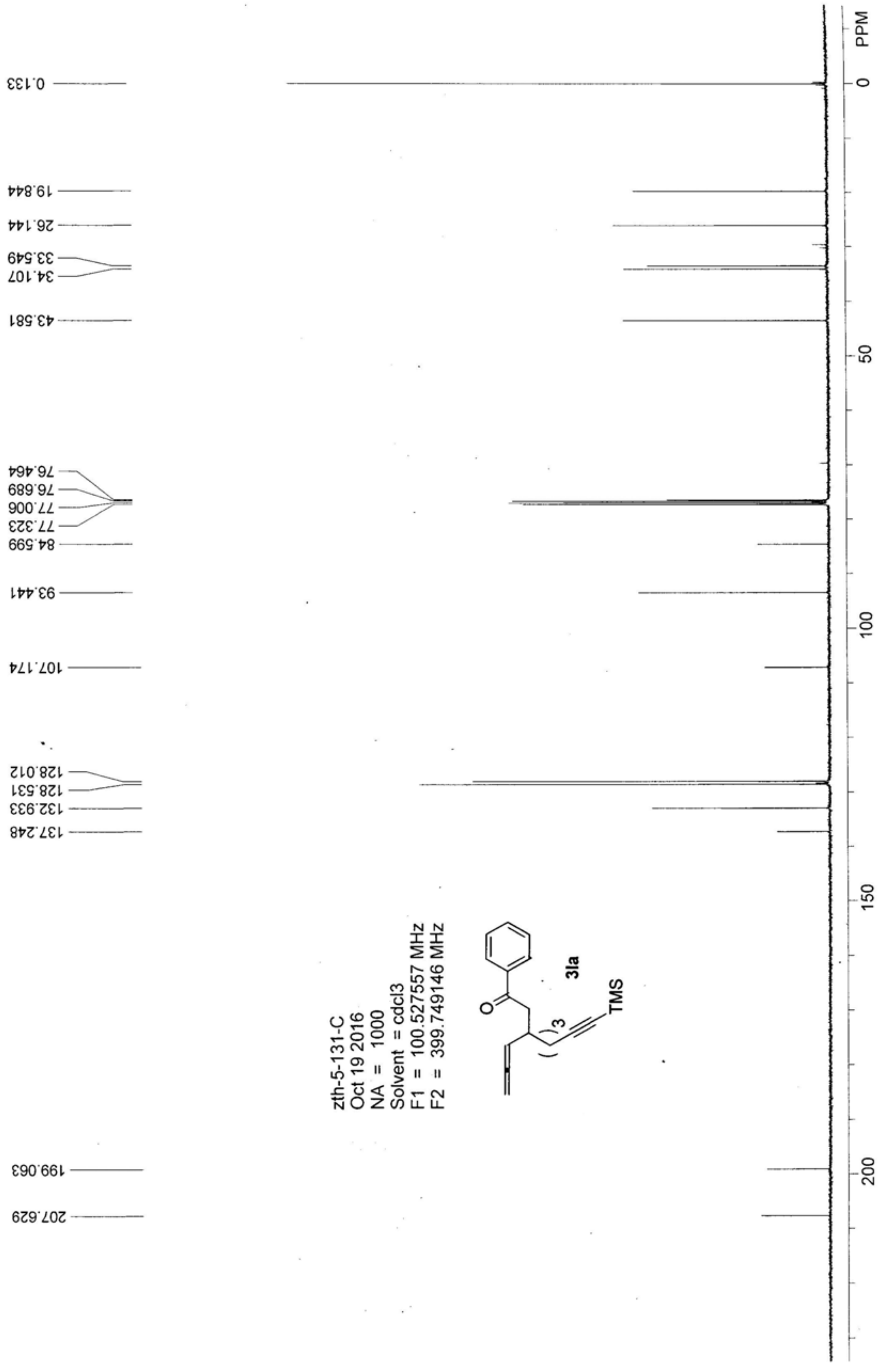
1-phenyl-3-(propa-1,2-dienyl)-8-(trimethylsilyl)oct-7-yn-1-one (3la, zth-5-131)



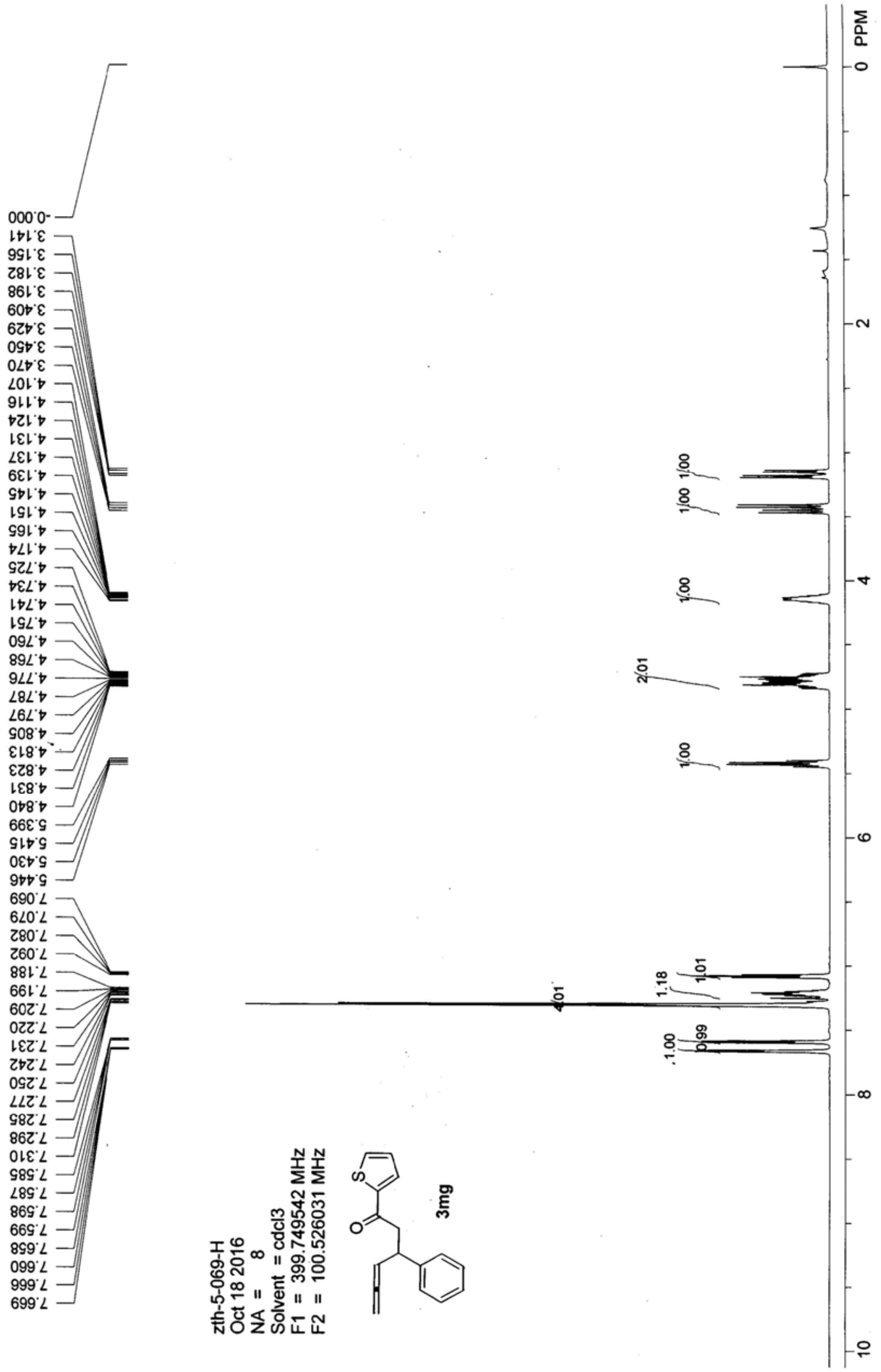


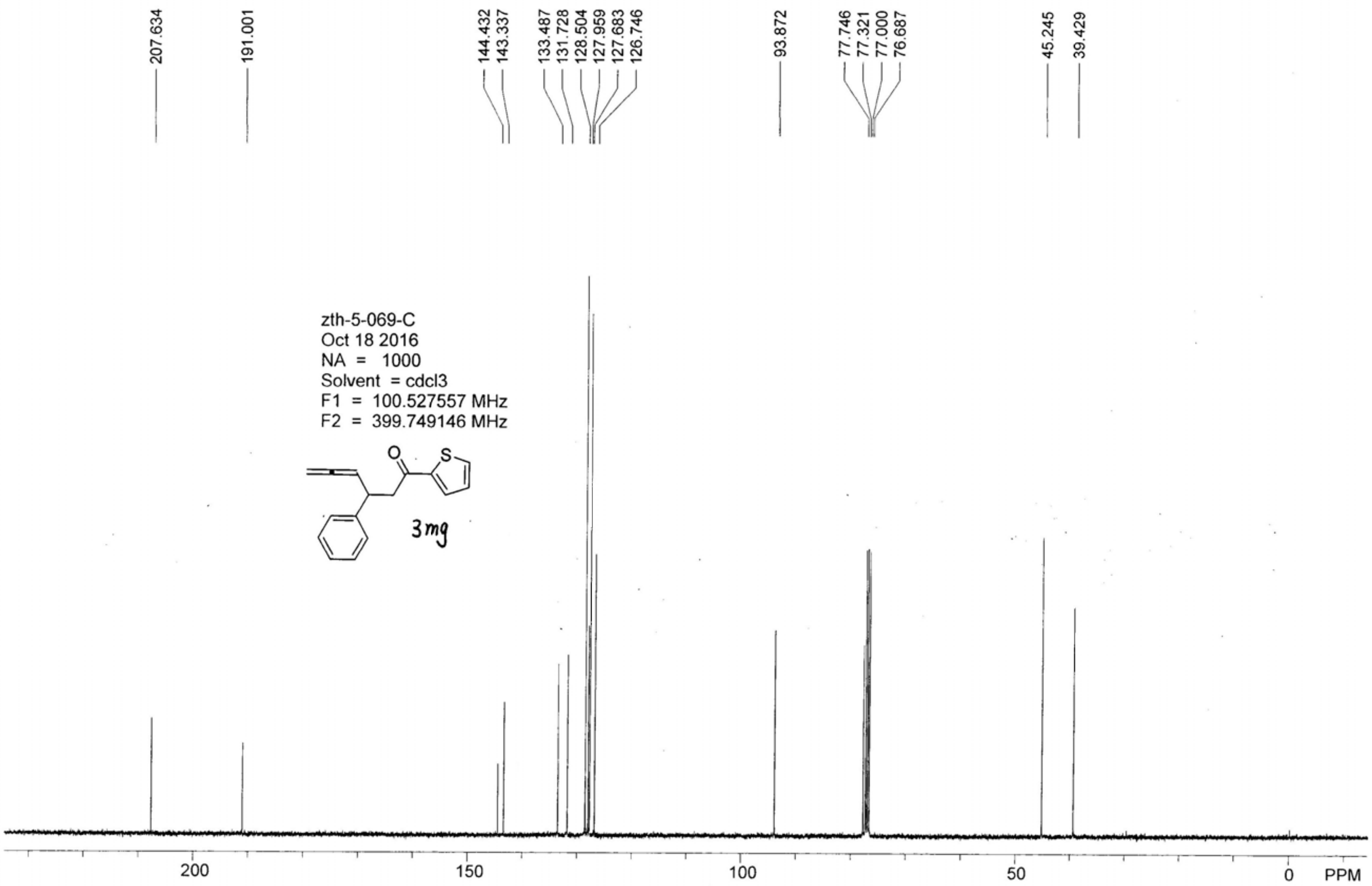
zth-5-131-purity
mesitylene (9.0 uL, 0.2 mmol) as the
internal standard in 62.1 mg product
Nov 2 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz

3la

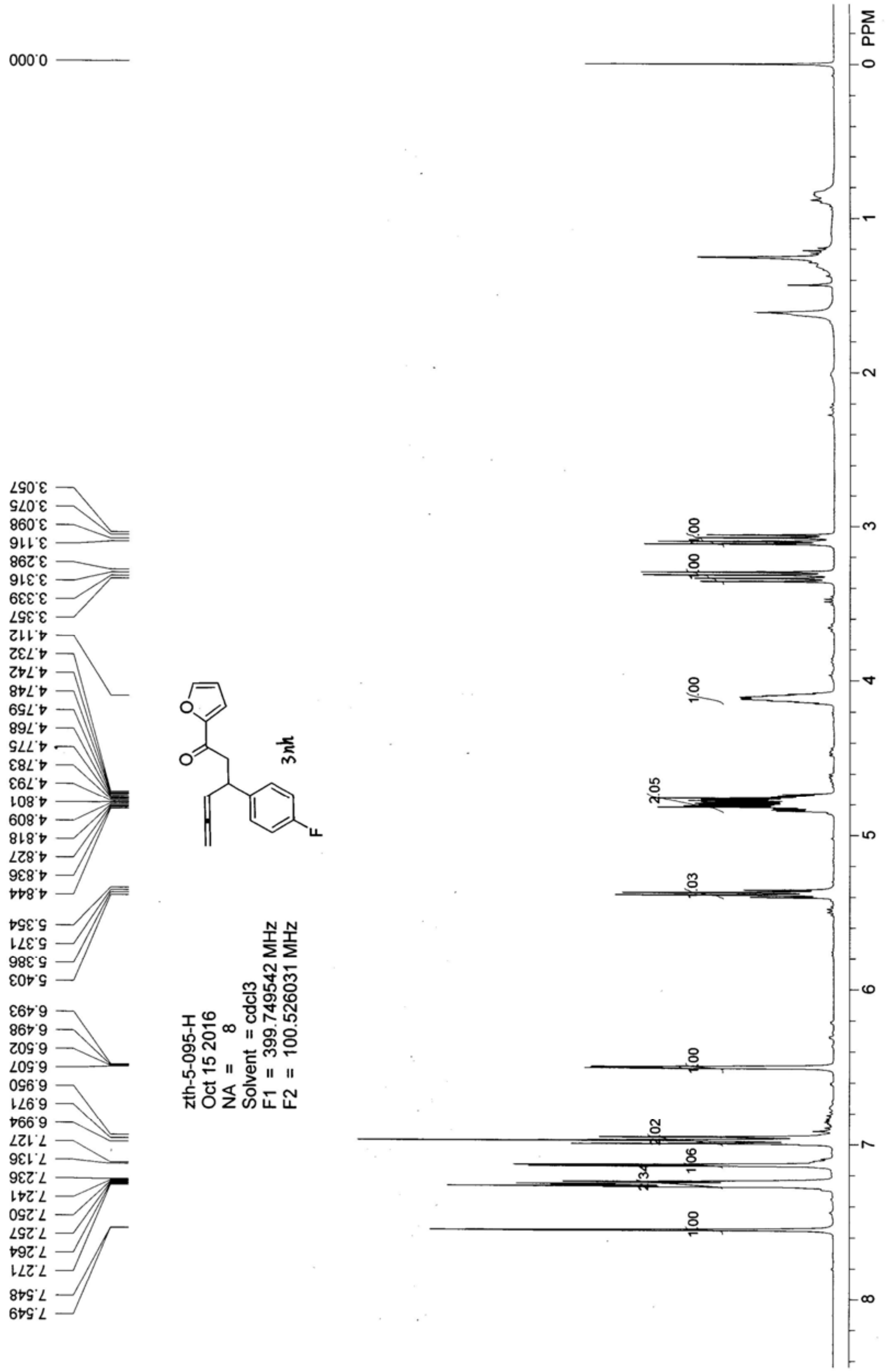

0.133
19.844
26.144
33.549
34.107
43.581
76.464
76.689
77.006
77.323
84.599
93.441
107.174
128.012
128.531
132.933
137.248
199.063
207.629
zth-5-131-C
Oct 19 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
3
TMS
3la
PPM
0
50
100
150
200

3-phenyl-1-(thiophen-2-yl)hexa-4,5-dien-1-one (3mg, zth-5-069)

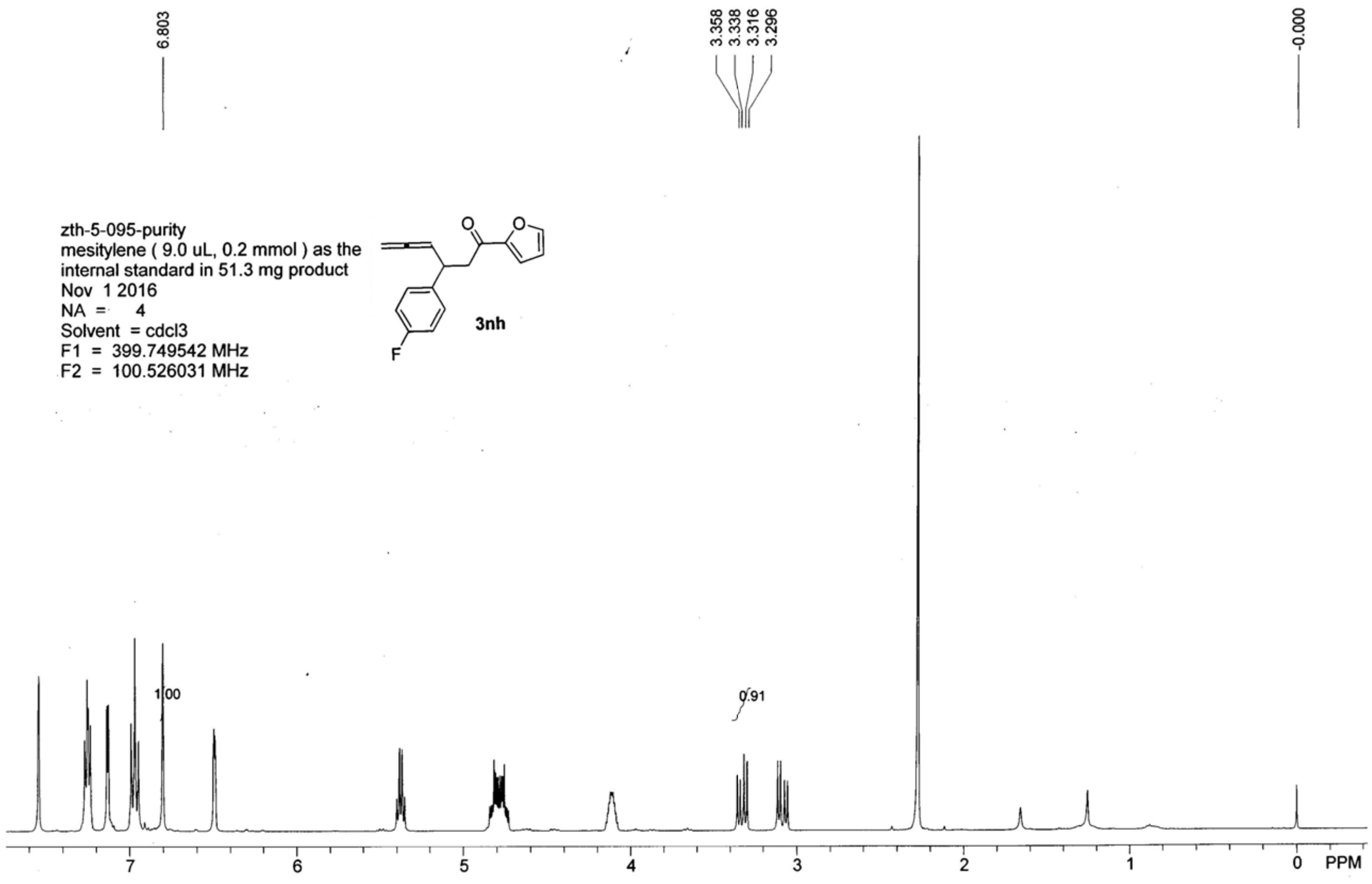



207.634
191.001
144.432
143.337
133.487
131.728
128.504
127.959
127.683
126.746
93.872
77.746
77.321
77.000
76.687
45.245
39.429
zth-5-069-C
Oct 18 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
S
3mg
200
150
100
50
0
PPM

3-(4-fluorophenyl)-1-(furan-2-yl)hexa-4,5-dien-1-one (3nh, zth-5-095)

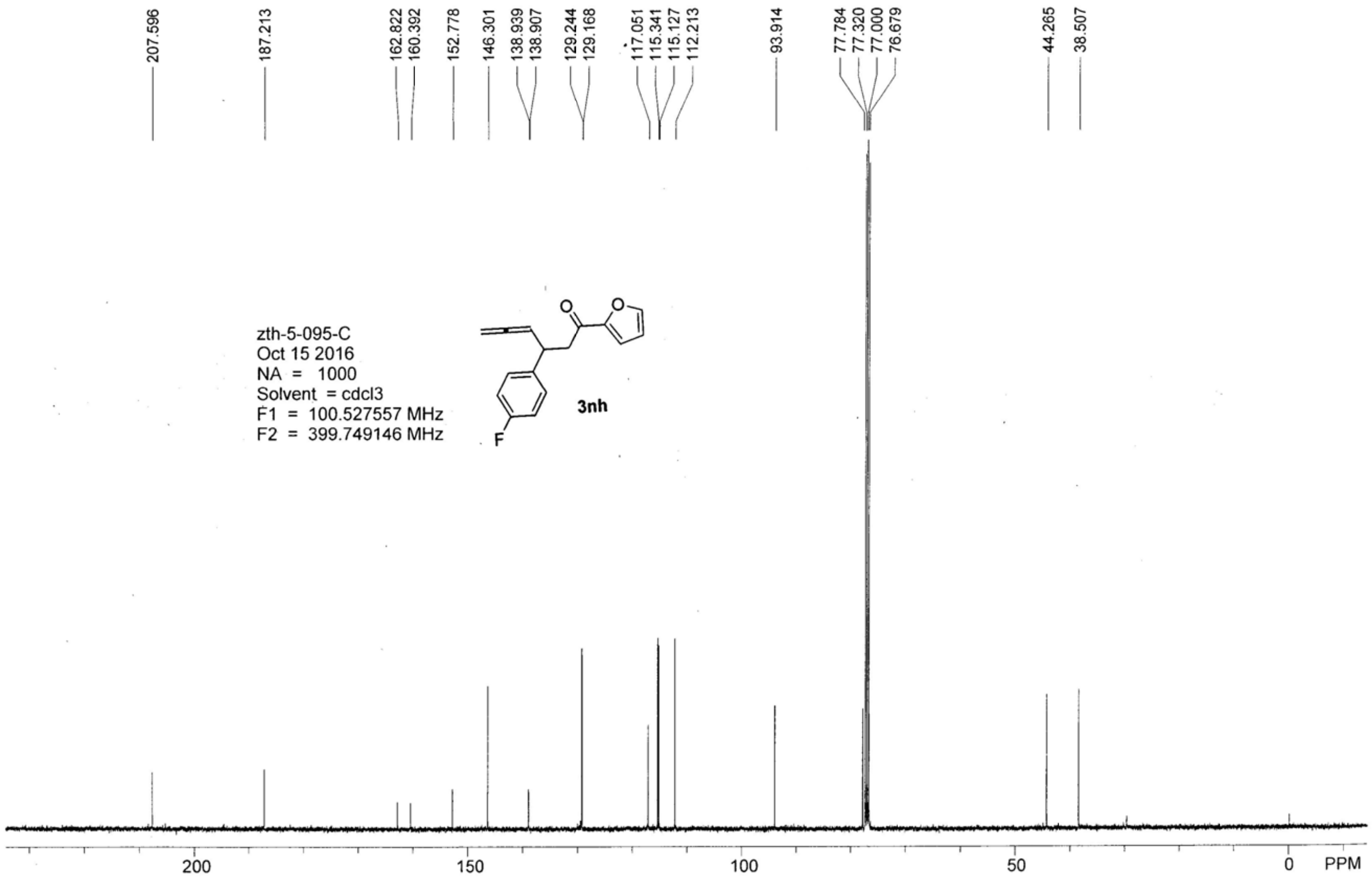


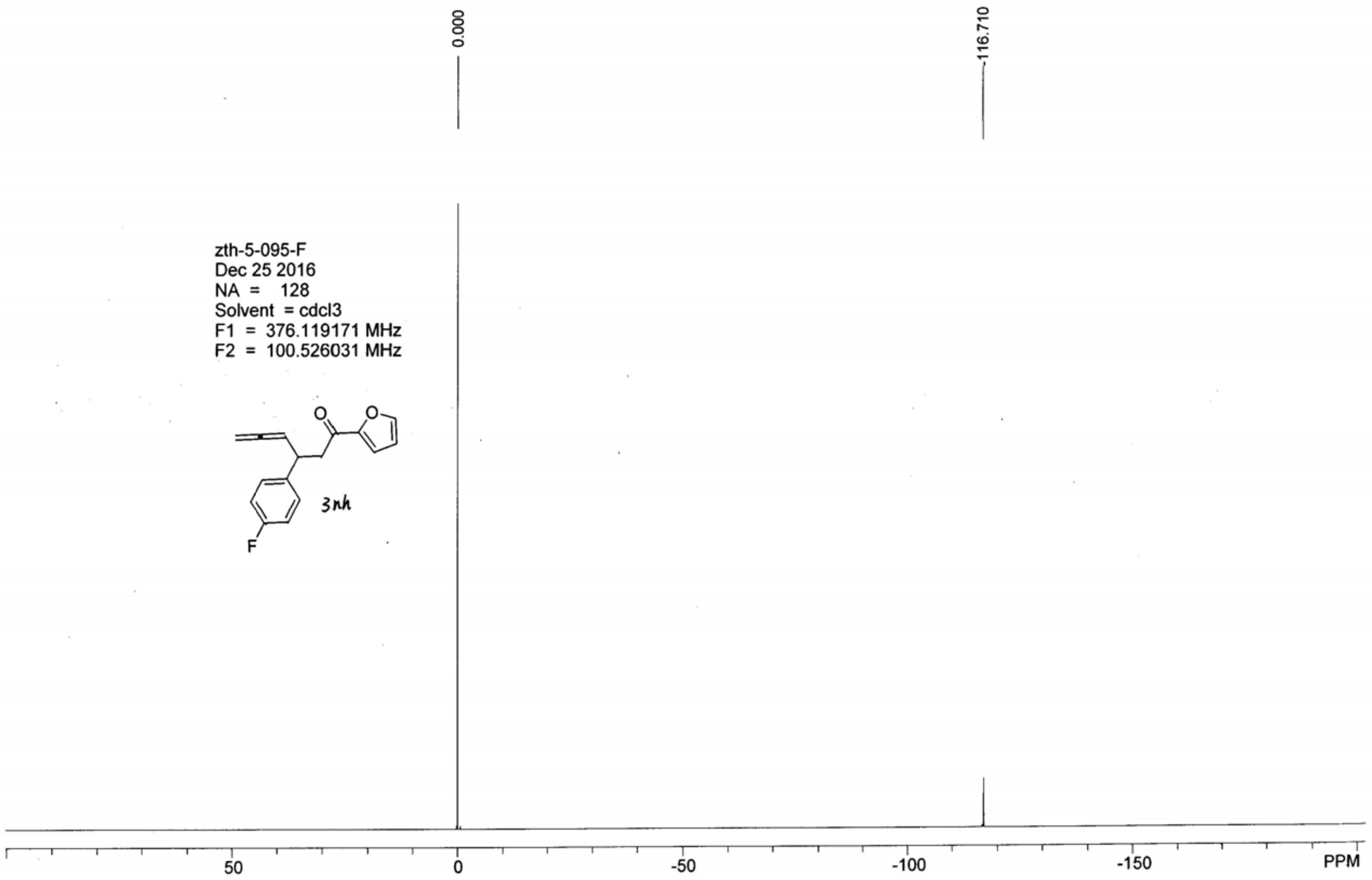
zth-5-095-H
Oct 15 2016
NA = 8
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz



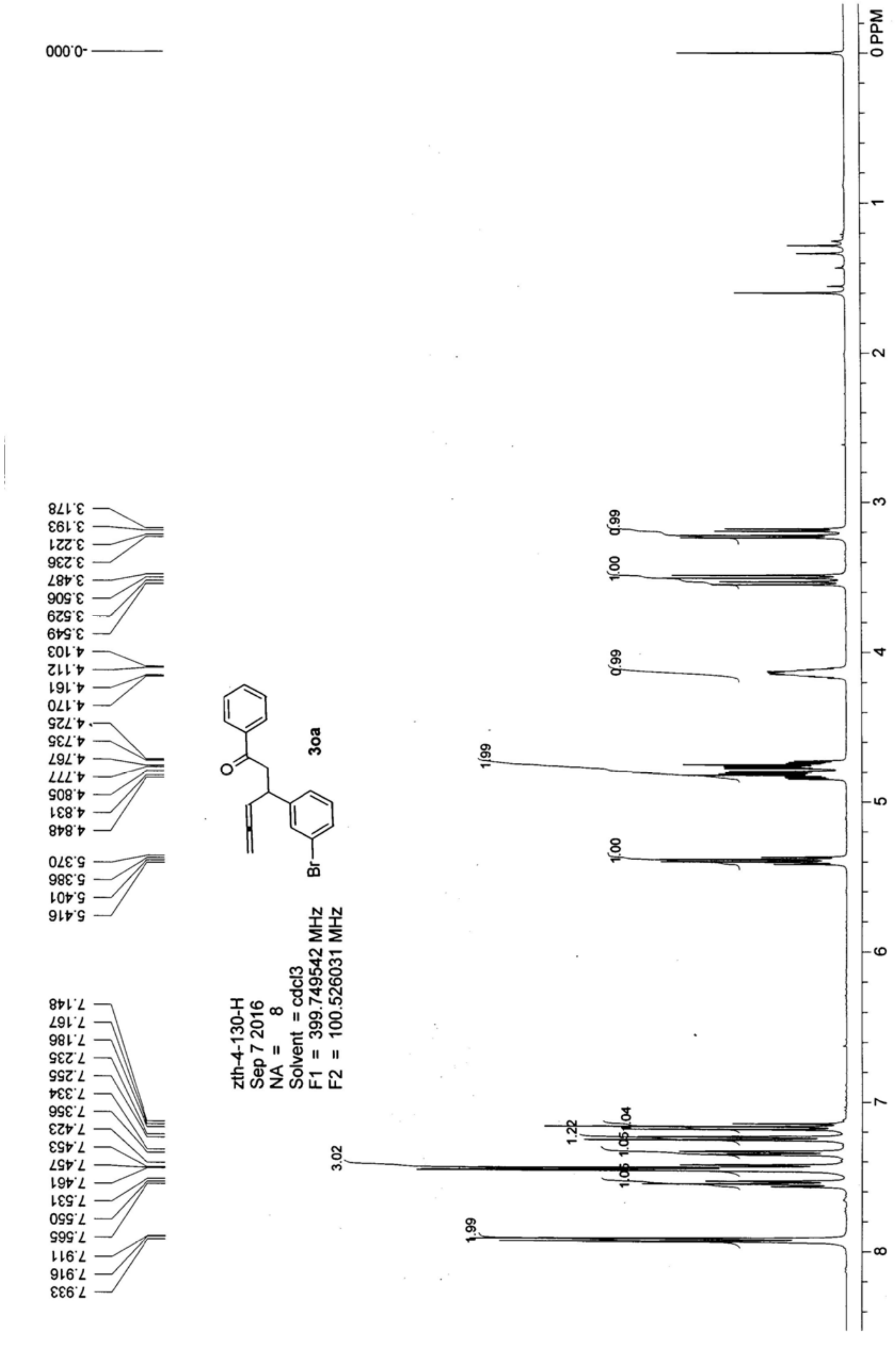
3nh

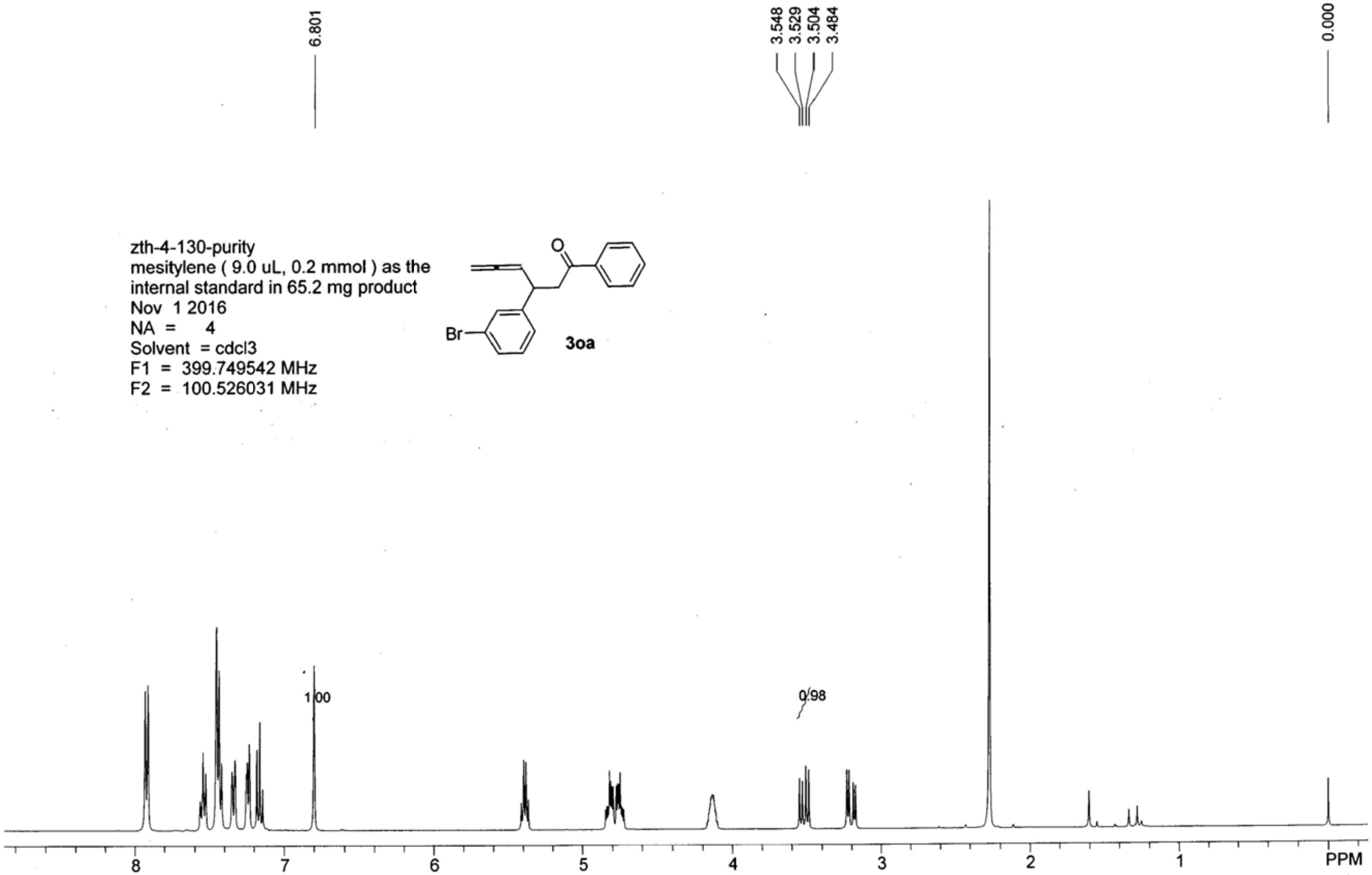
zth-5-095-purity
mesitylene (9.0 uL, 0.2 mmol) as the
internal standard in 51.3 mg product
Nov 1 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz


207.596
187.213
162.822
160.392
152.778
146.301
138.939
138.907
129.244
129.168
117.051
115.341
115.127
112.213
93.914
77.784
77.320
77.000
76.679
44.265
38.507
zth-5-095-C
Oct 15 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
O
F
3nh
200
150
100
50
0
PPM

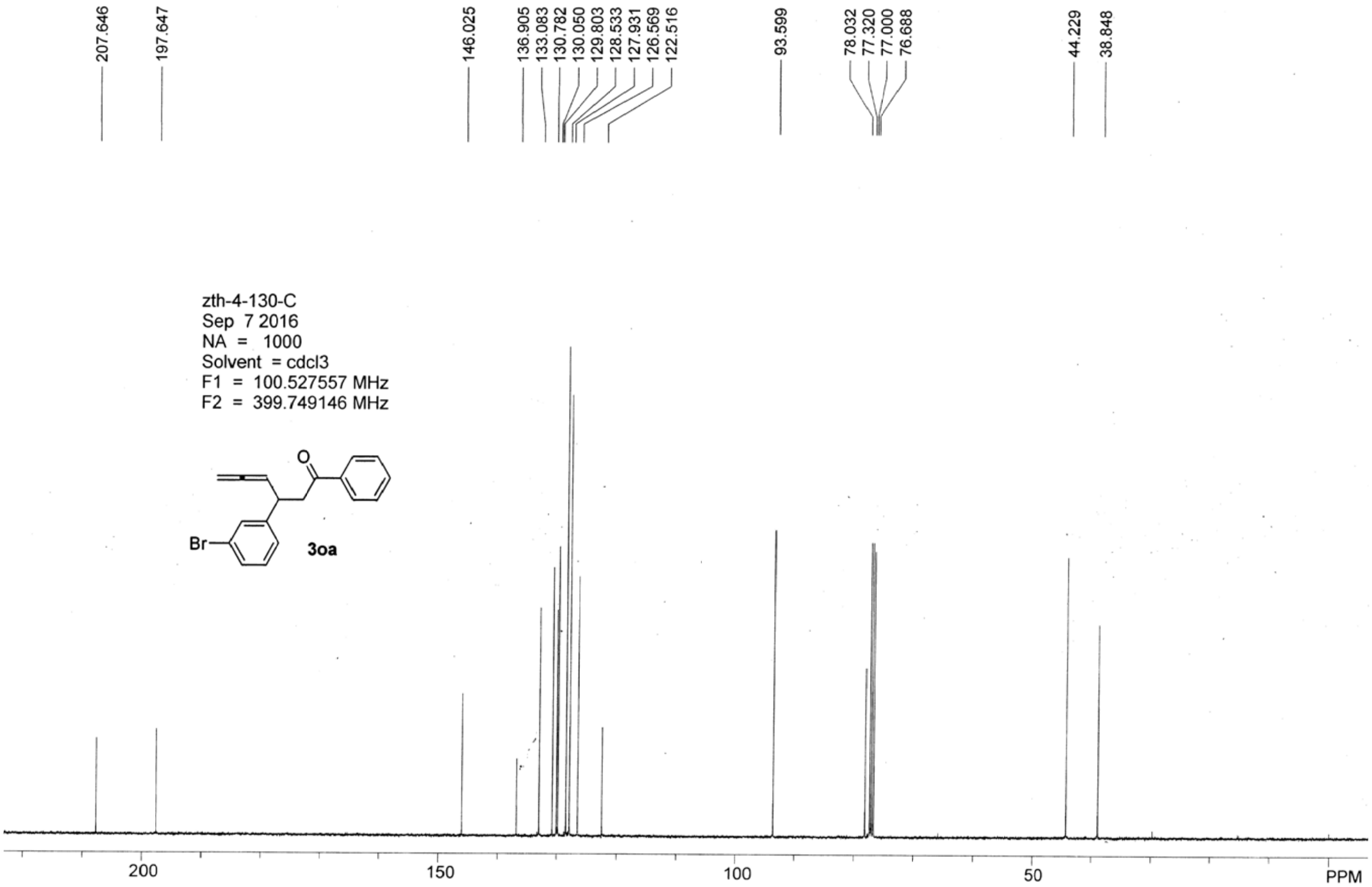

0.000
-116.710
zth-5-095-F
Dec 25 2016
NA = 128
Solvent = cdcl3
F1 = 376.119171 MHz
F2 = 100.526031 MHz
O
O
F
3nh
50
0
-50
-100
-150
PPM

3-(3-bromophenyl)-1-phenylhexa-4,5-dien-1-one (3oa, zth-4-130)

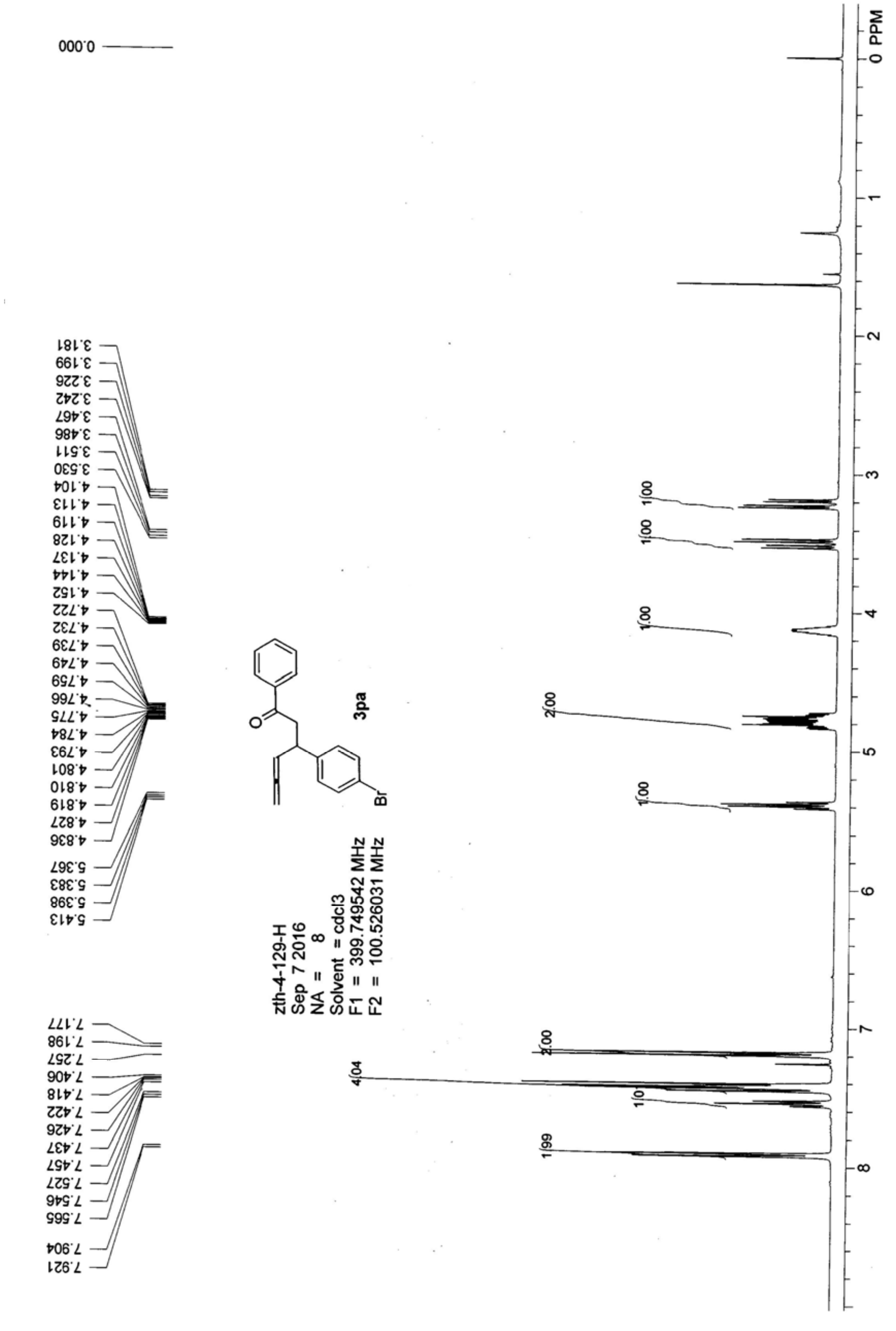


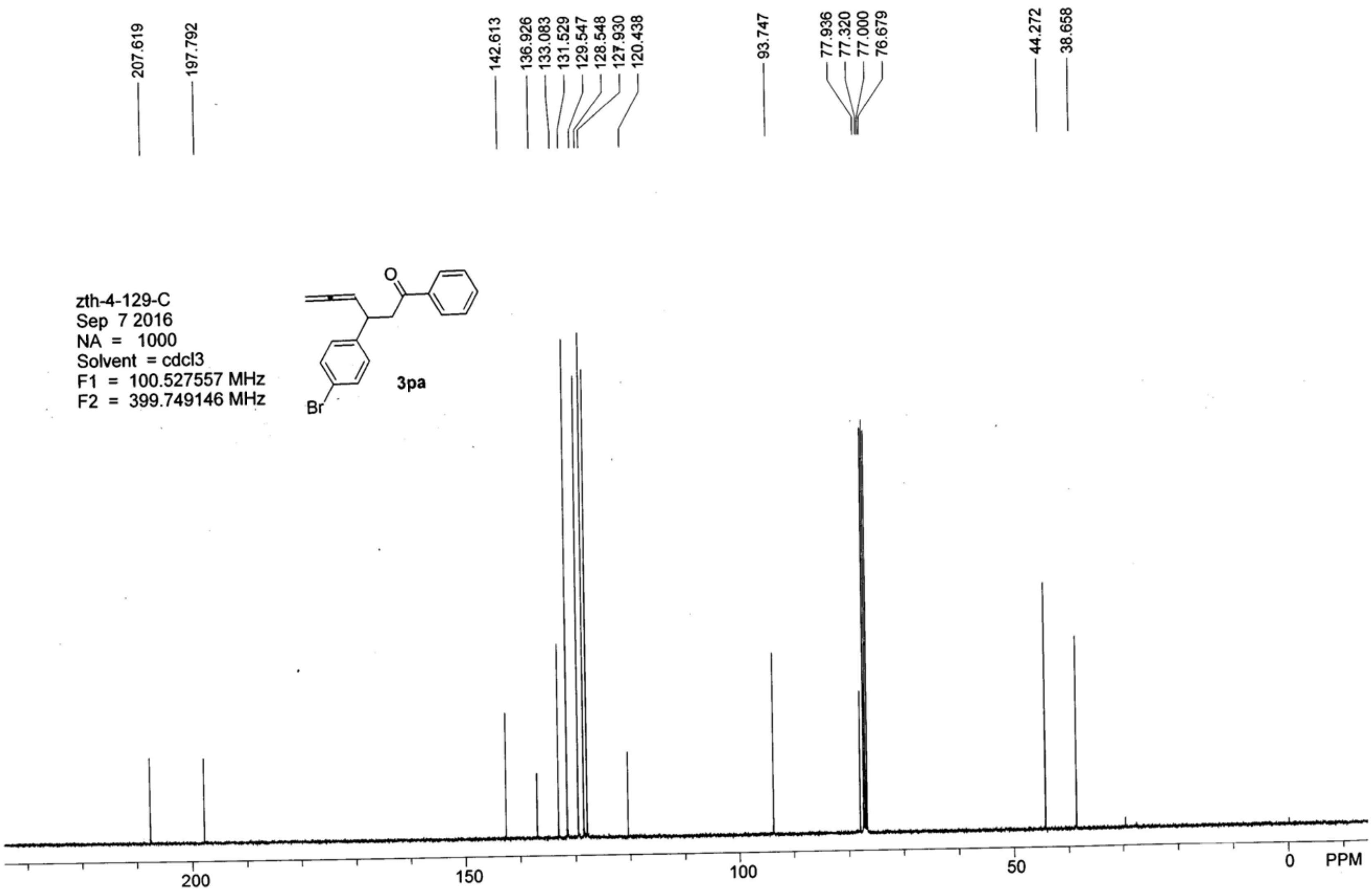

zth-4-130-purity
mesitylene (9.0 uL, 0.2 mmol) as the
internal standard in 65.2 mg product
Nov 1 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz

3oa

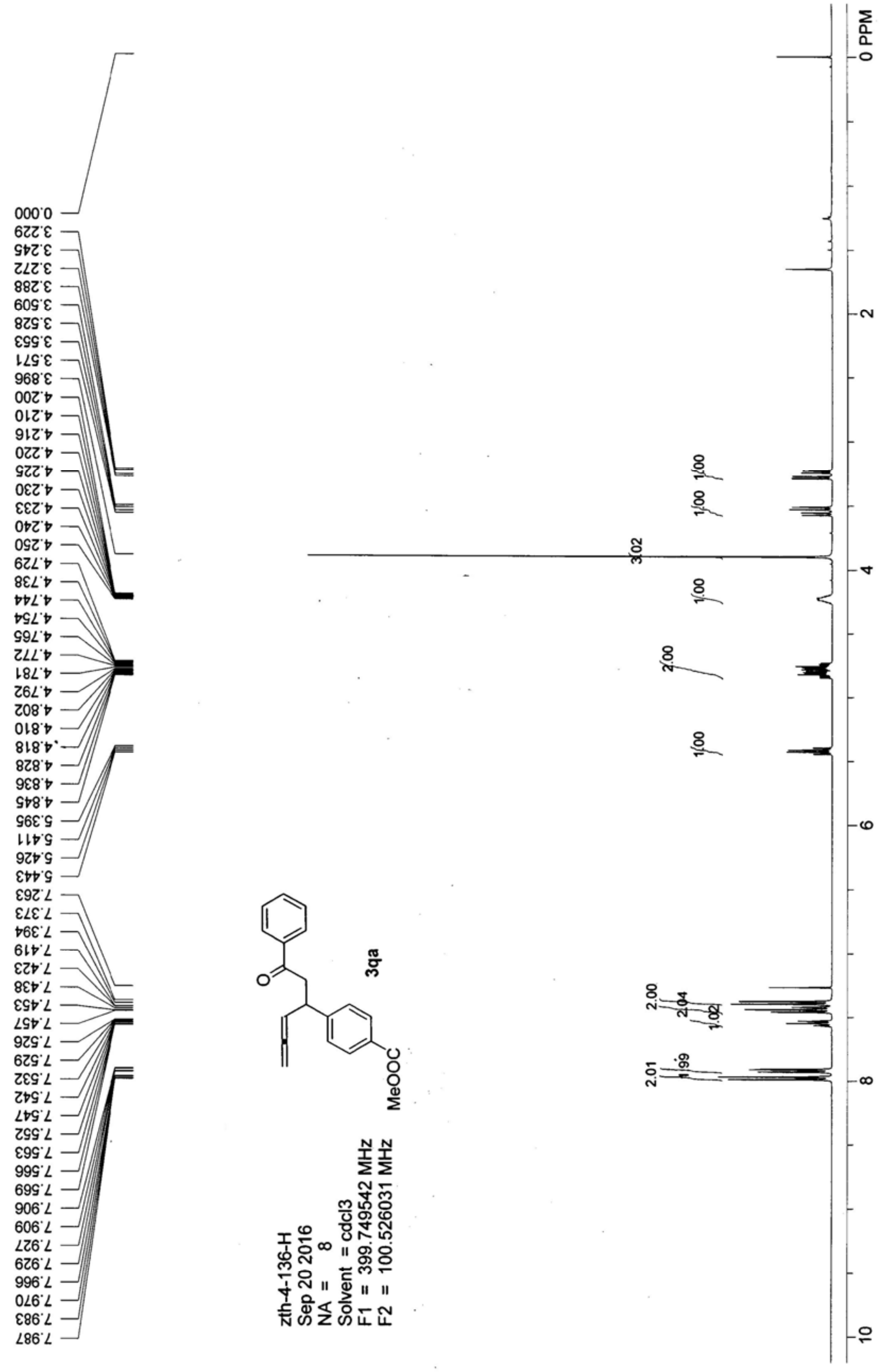

207.646
197.647
146.025
136.905
133.083
130.782
130.050
129.803
128.533
127.931
126.569
122.516
93.599
78.032
77.320
77.000
76.688
44.229
38.848
zth-4-130-C
Sep 7 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
Br
3oa
200
150
100
50
PPM

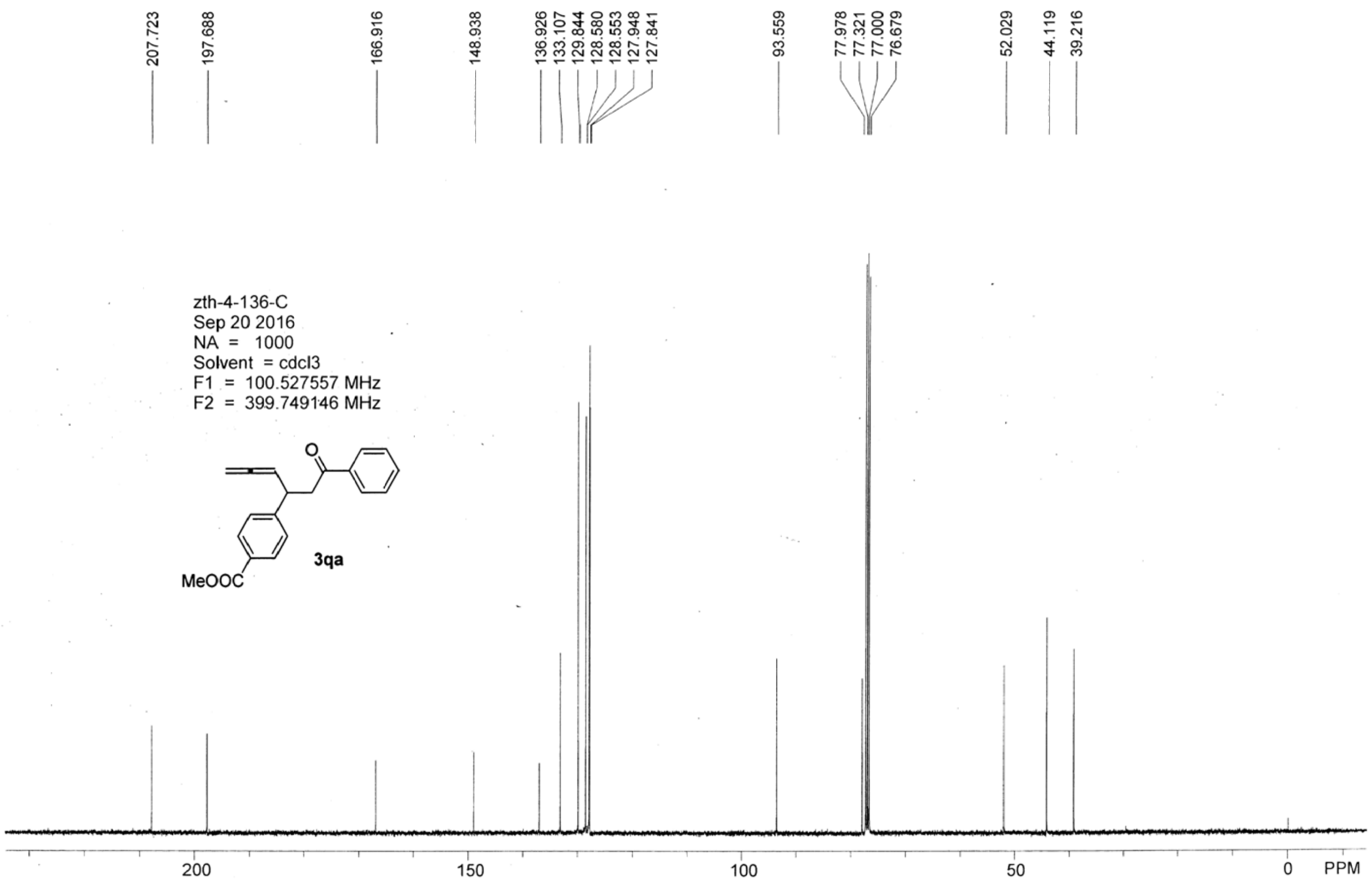
3-(4-bromophenyl)-1-phenylhexa-4,5-dien-1-one (3pa, zth-4-129)



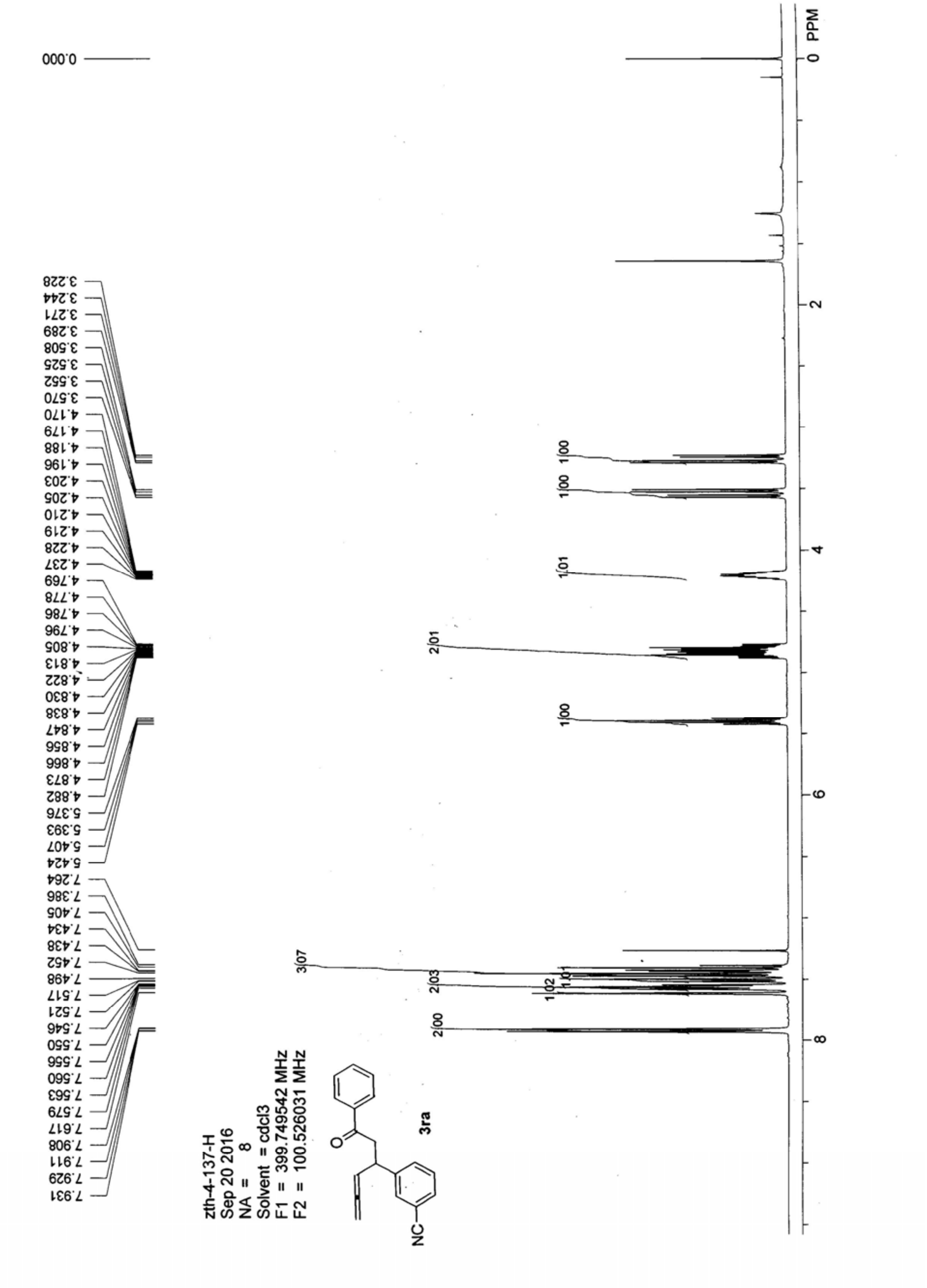

207.619
197.792
142.613
136.926
133.083
131.529
129.547
128.548
127.930
120.438
93.747
77.936
77.320
77.000
76.679
44.272
38.658
zth-4-129-C
Sep 7 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
Br
3pa
200
150
100
50
0
PPM

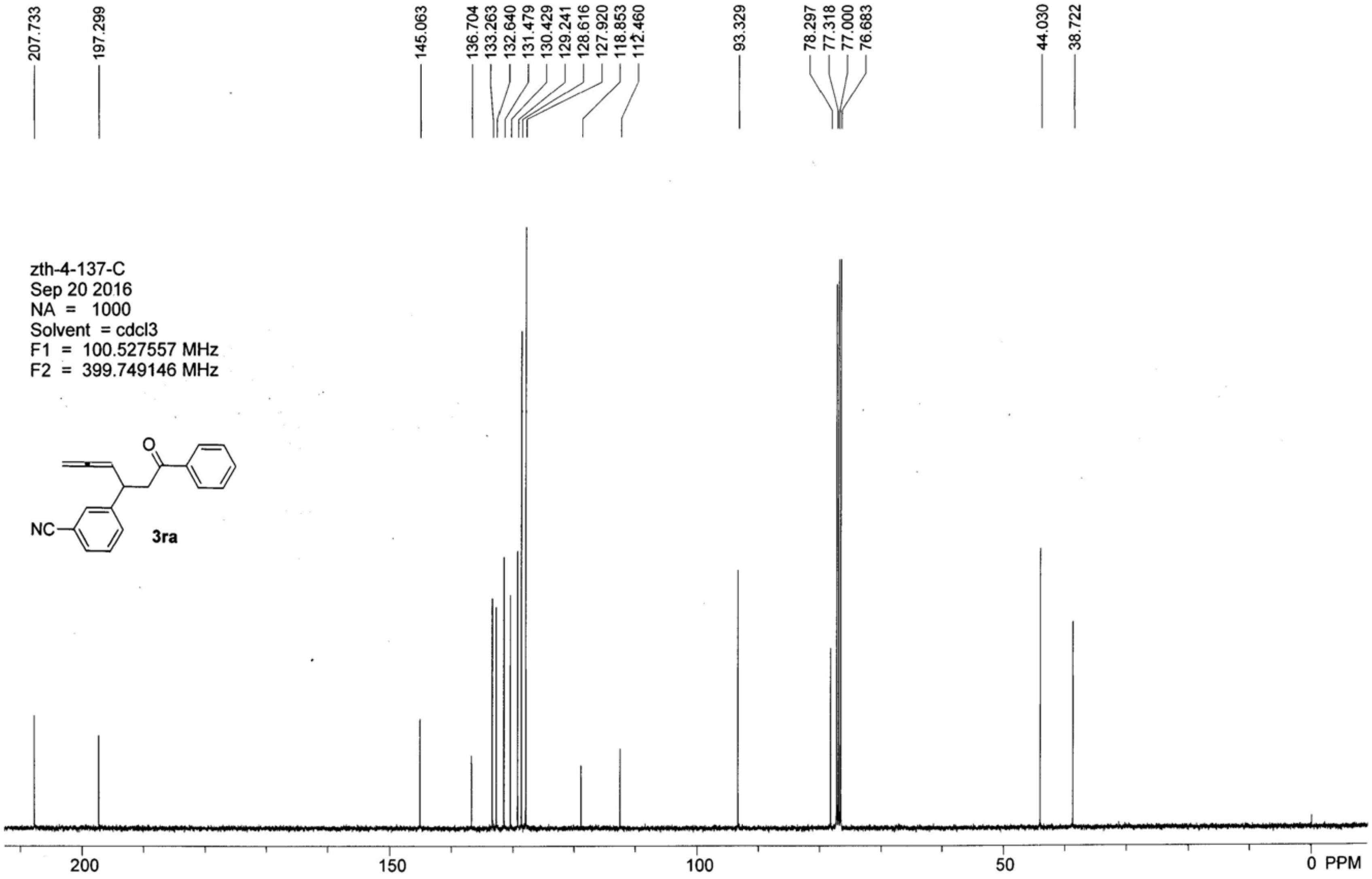
3-(4-(methoxycarbonylphenyl)-1-phenylhexa-4,5-dien-1-one (3pa, zth-4-136)



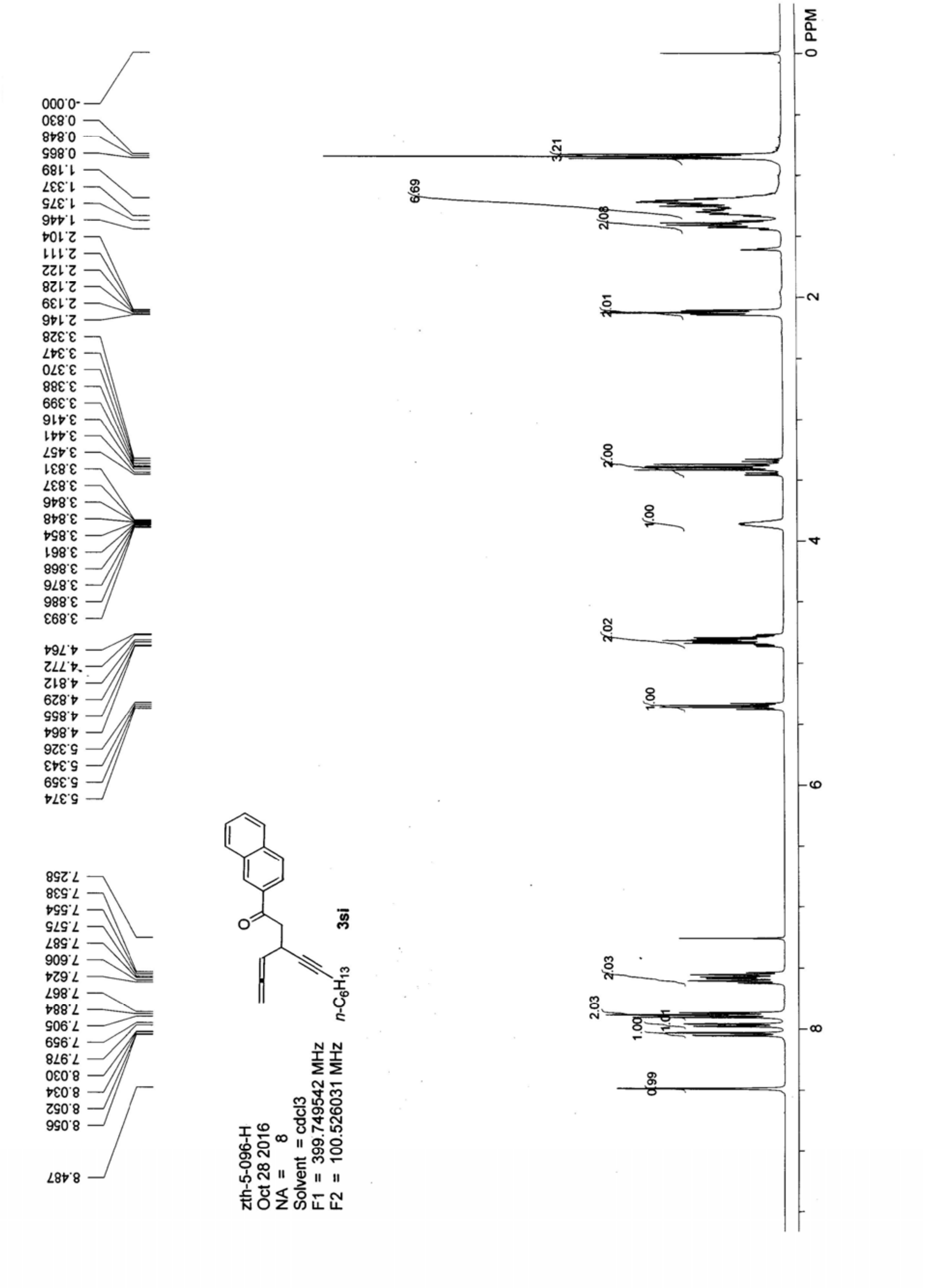

207.723
197.688
166.916
148.938
136.926
133.107
129.844
128.580
128.553
127.948
127.841
93.559
77.978
77.321
77.000
76.679
52.029
44.119
39.216
zth-4-136-C
Sep 20 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
MeOOC
3qa
200
150
100
50
0
PPM

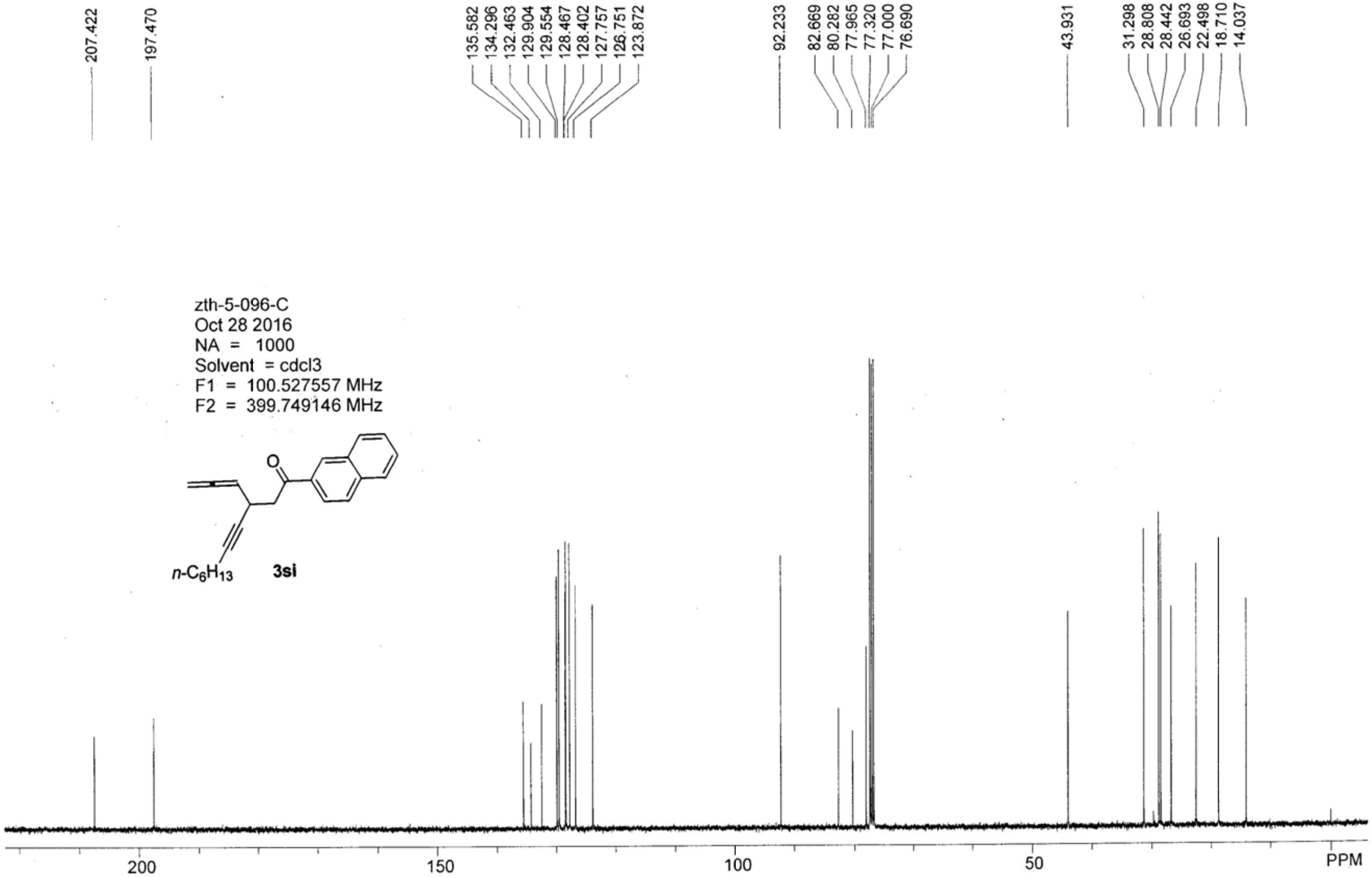
3-(3-cyanophenyl)-1-phenylhexa-4,5-dien-1-one (3ra, zth-4-137)



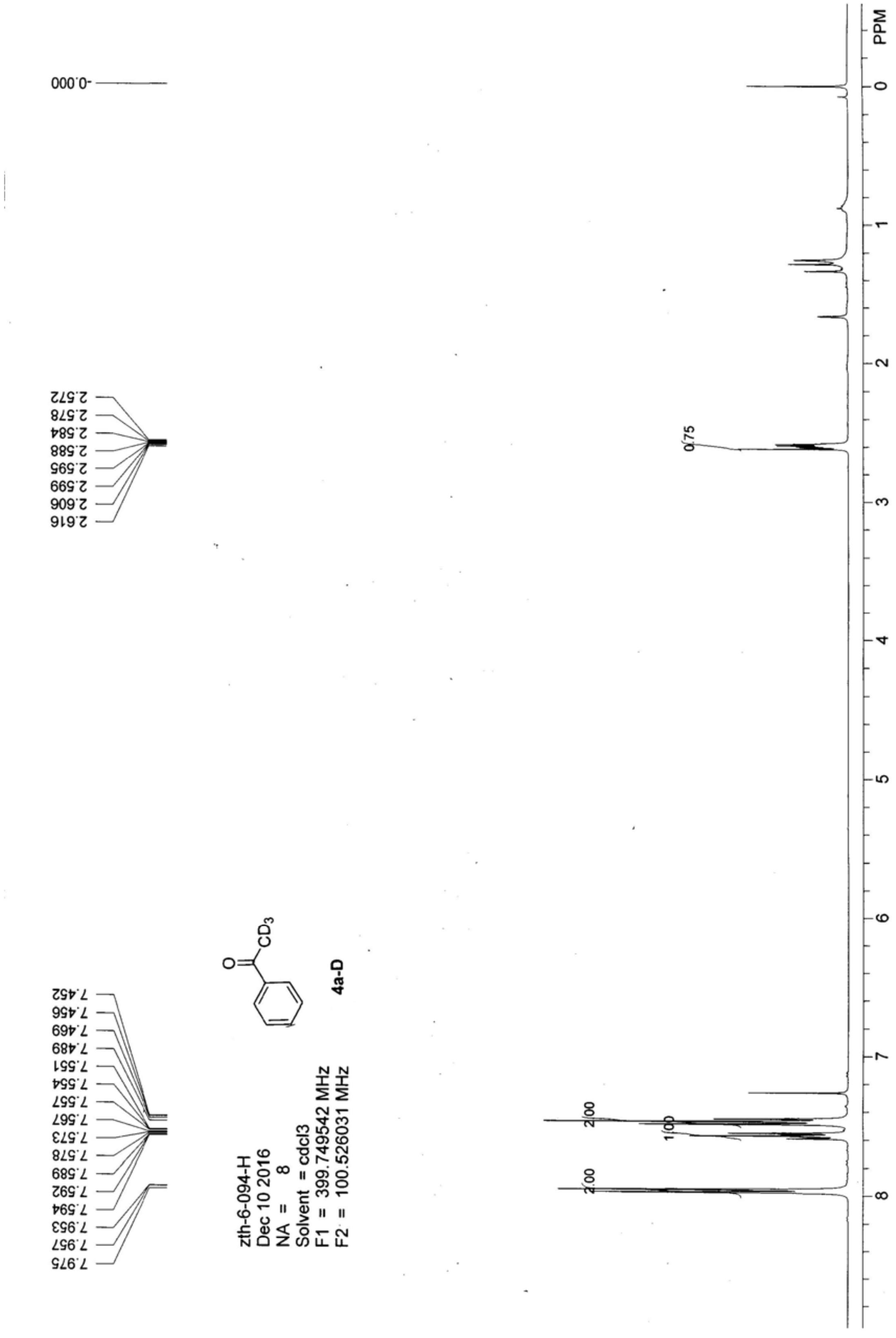

207.733
197.299
145.063
136.704
133.263
132.640
131.479
130.429
129.241
128.616
127.920
118.853
112.460
93.329
78.297
77.318
77.000
76.683
44.030
38.722
zth-4-137-C
Sep 20 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
NC
3ra
200
150
100
50
0 PPM

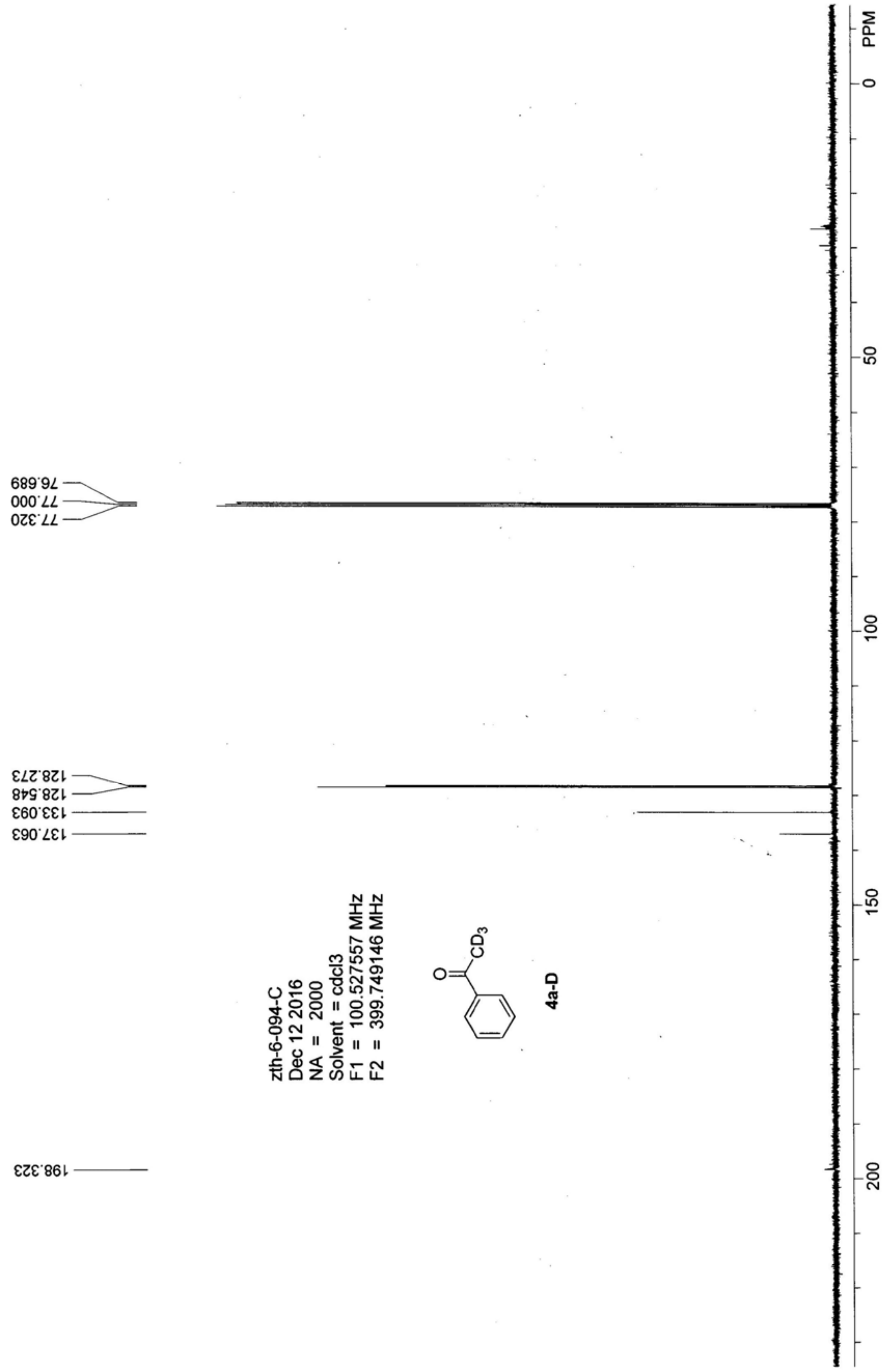
1-(naphthalen-2-yl)-3-(propa-1,2-dienyl)undec-4-yn-1-one (3si, zth-5-096)



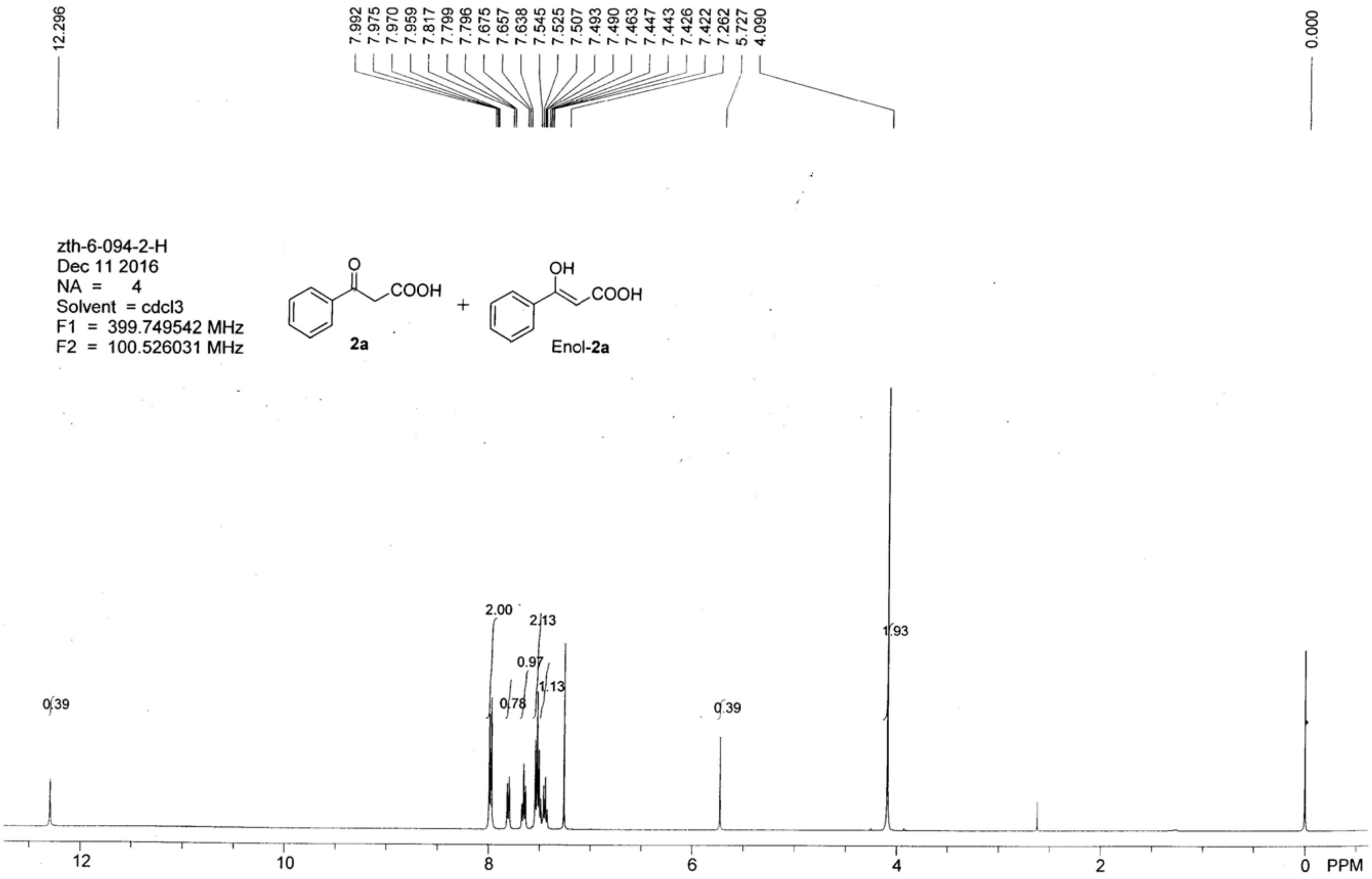
207.422
197.470
135.582
134.296
132.463
129.904
129.554
128.467
128.402
127.757
126.751
123.872
92.233
82.669
80.282
77.965
77.320
77.000
76.690
43.931
31.298
28.808
28.442
26.693
22.498
18.710
14.037
zth-5-096-C
Oct 28 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
n-C6H13
3si
200
150
100
50
PPM

acetophenone-D (4a-D, zth-6-094)

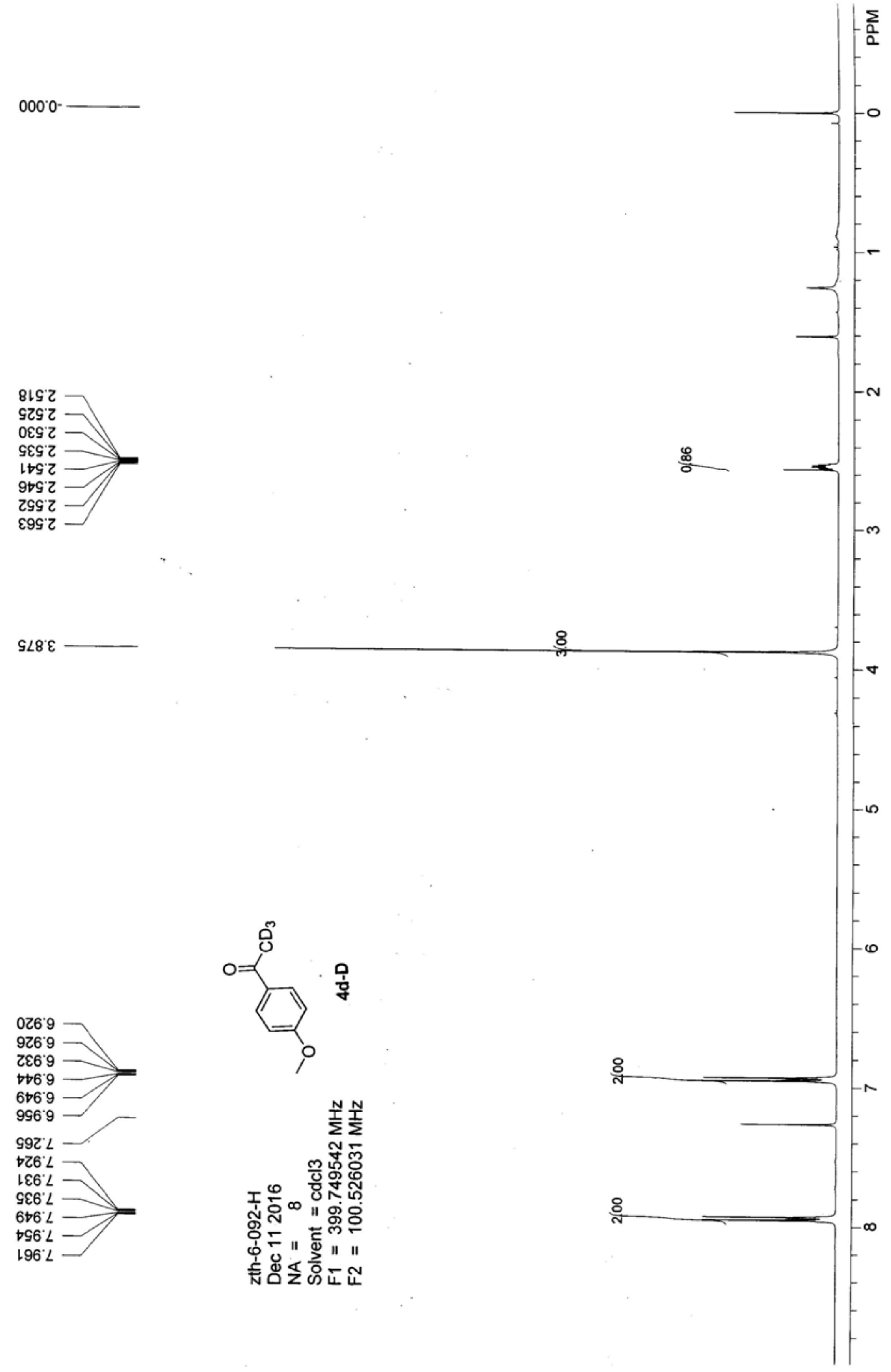


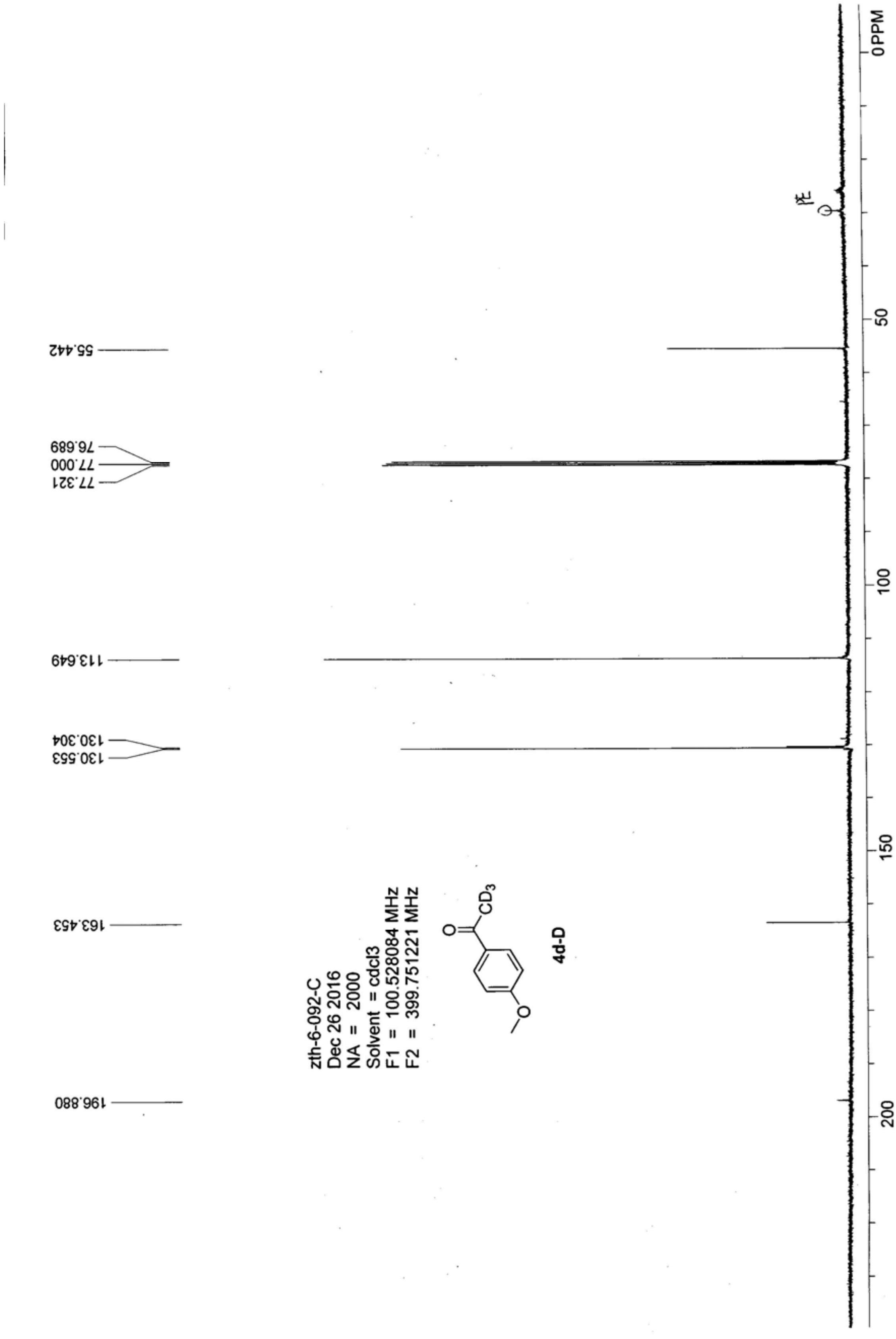

76.689
77.000
77.320
128.273
128.548
133.093
137.063
198.323
zth-6-094-C
Dec 12 2016
NA = 2000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
CD3
PPM
0
50
100
150
200

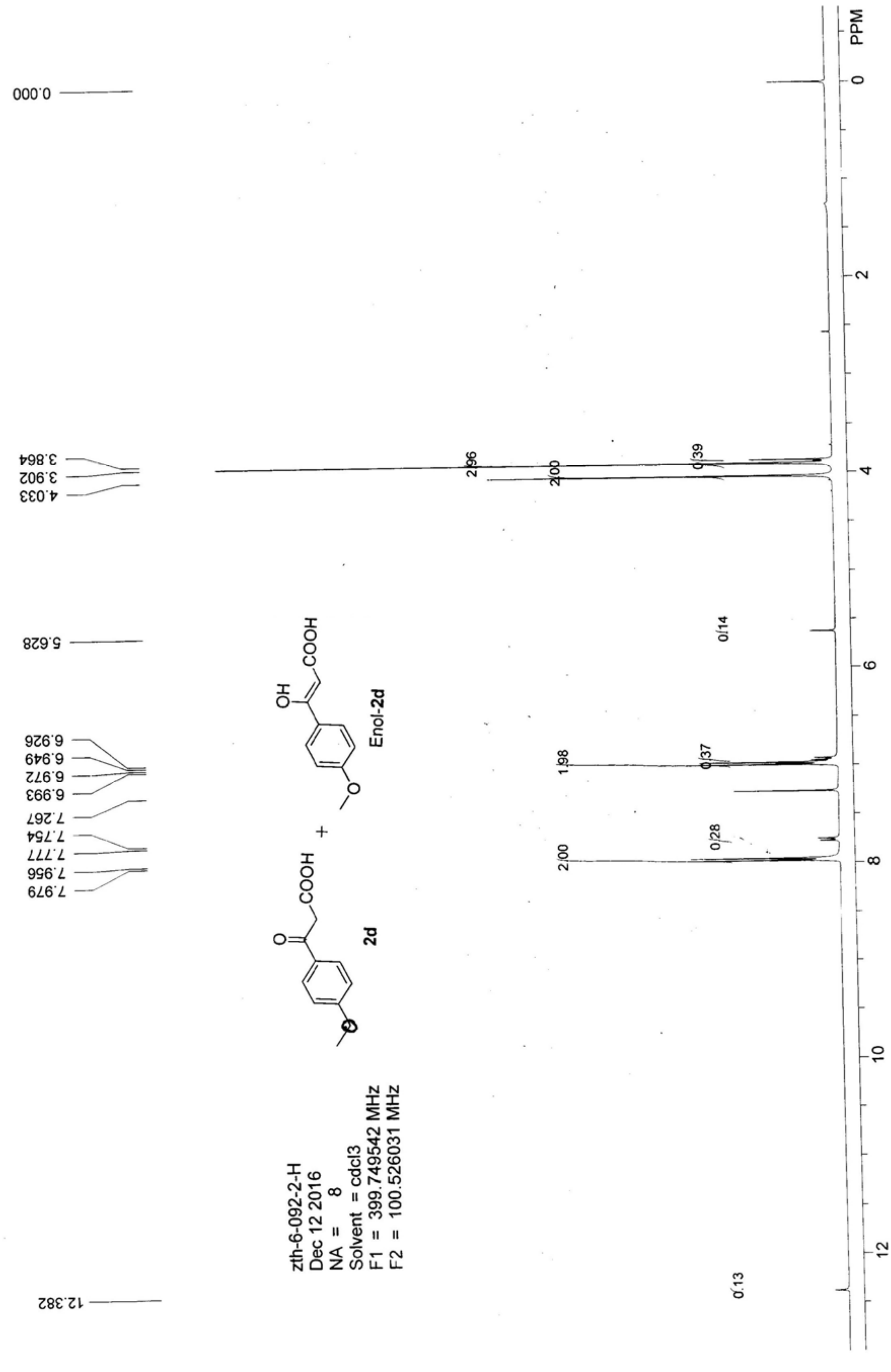
4a-D


zth-6-094-2-H
Dec 11 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz

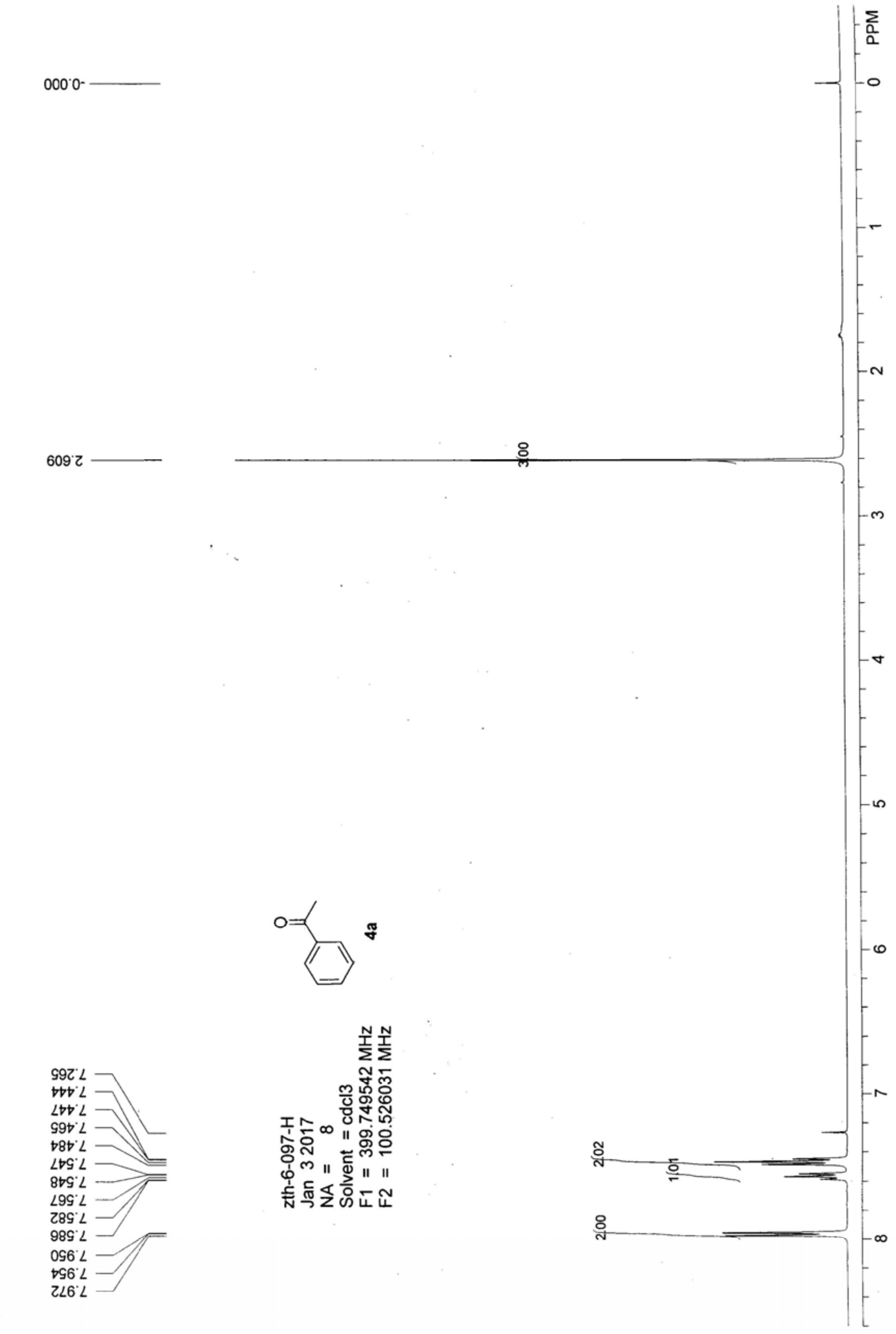
4'-methoxyacetophenone-D (4d-D, zth-6-092)

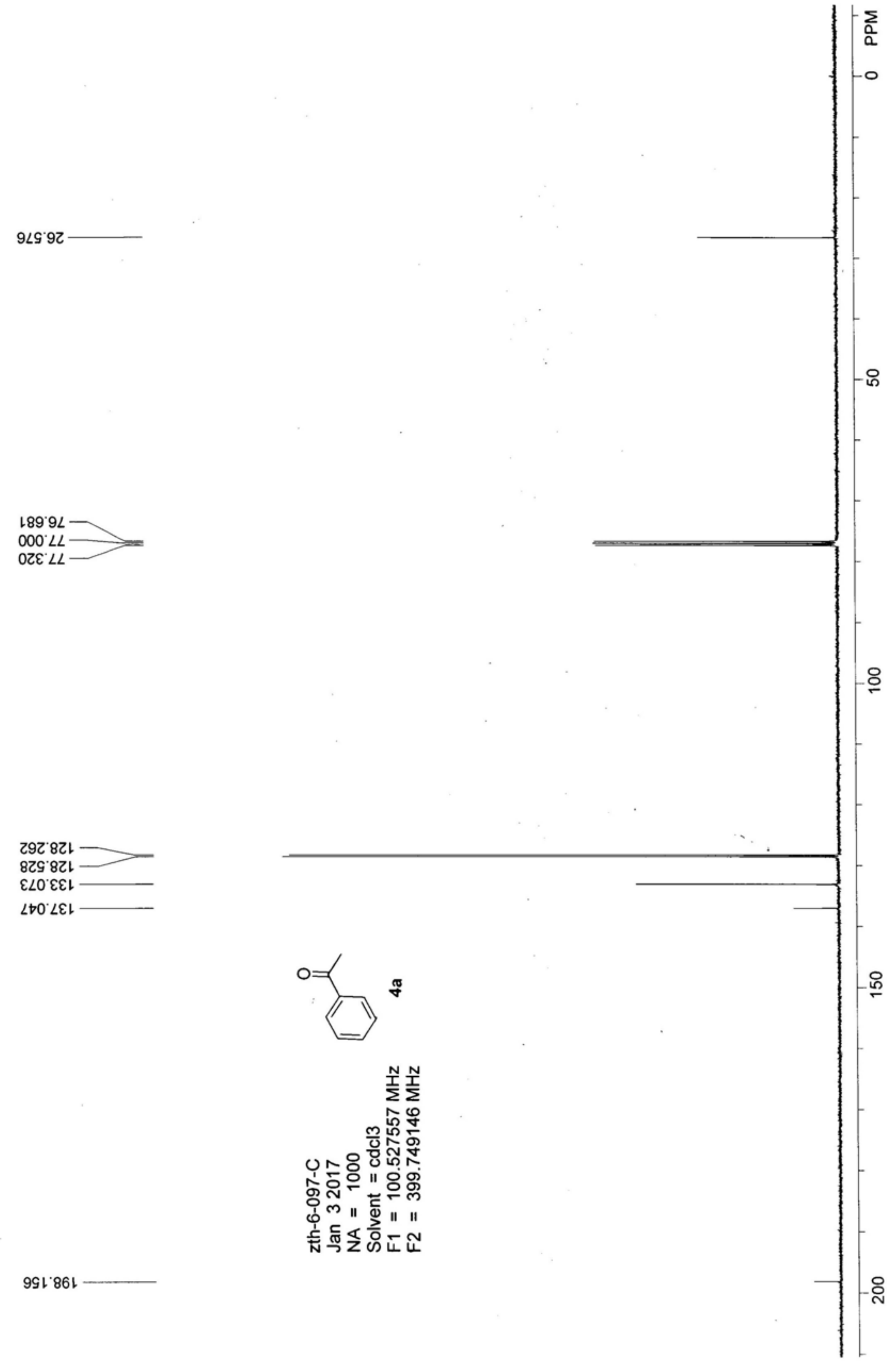



55.442
76.689
77.000
77.321
113.649
130.304
130.553
163.453
196.880
zth-6-092-C
Dec 26 2016
NA = 2000
Solvent = cdcl3
F1 = 100.528084 MHz
F2 = 399.751221 MHz
O
CD3
4d-D
0PPM
50
100
150
200


zth-6-092-2-H
Dec 12 2016
NA = 8
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
2d
Enol-2d
COOH
OH
O
0.000
3.864
3.902
4.033
5.628
6.926
6.949
6.972
6.993
7.267
7.754
7.777
7.956
7.979
12.382
2.96
2.00
0.39
0.14
1.98
0.37
2.00
0.28
0.13
PPM
0
2
4
6
8
10
12

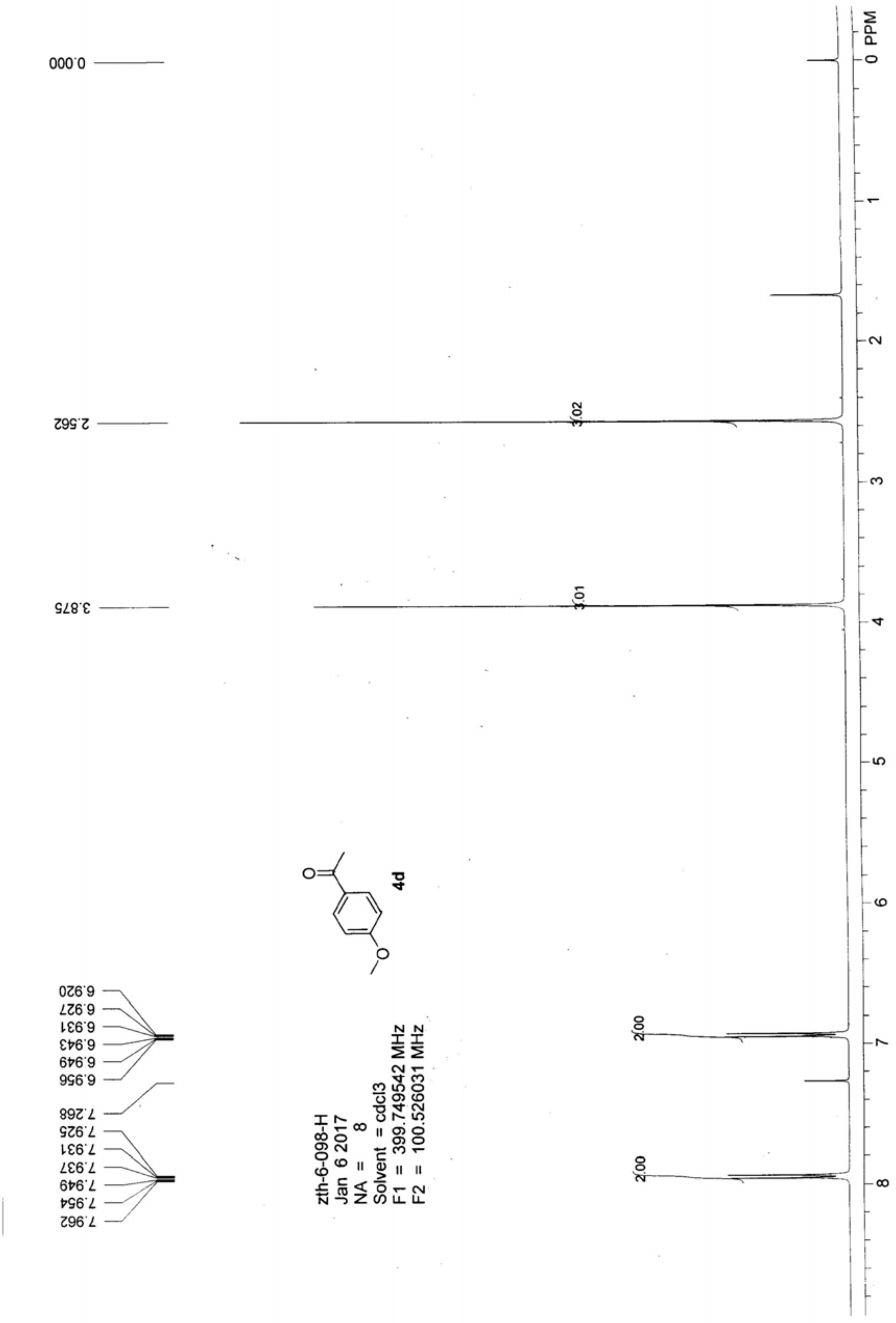
acetophenone 4a (zth-6-097)

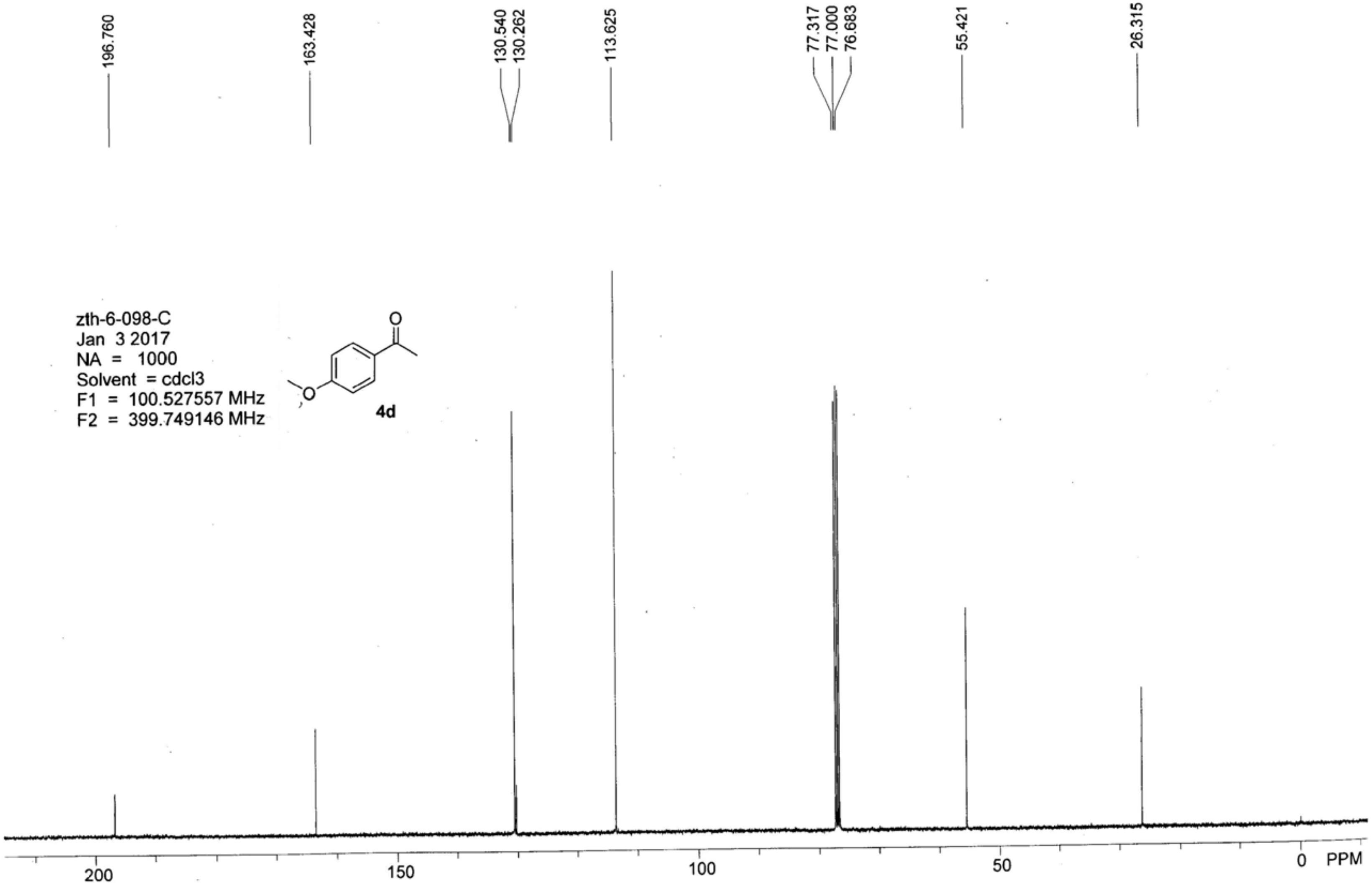




198.156
137.047
133.073
128.528
128.262
77.320
77.000
76.681
26.576
4a
zth-6-097-C
Jan 3 2017
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
200
150
100
50
0
PPM

4'-methoxyacetophenone 4d (zth-6-098)




196.760
163.428
130.540
130.262
113.625
77.317
77.000
76.683
55.421
26.315
zth-6-098-C
Jan 3 2017
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
O
4d
200
150
100
50
0
PPM