Supporting Information

Suzuki coupling for preparation of allenes-ligand effect and chirality transfer

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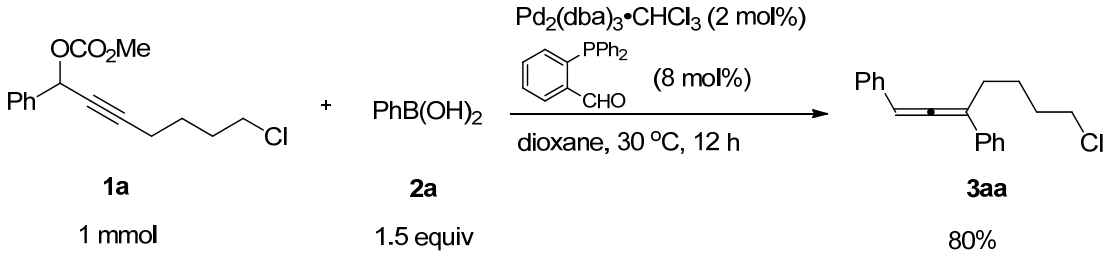
General Information. NMR spectra were taken with an Agilent-400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) in $CDCl_3$. Chemical shifts were recorded in ppm in relative to the TMS in $CDCl_3$ and coupling constants were reported in Hz. All reactions were carried out in flame-dried Schlenk tube under argon atmosphere. $Pd_2(dba)_3 \cdot CHCl_3$ and *N*-methylmaleimide was purchased from Alfa Aesar; *o*-(diphenylphosphino)benzaldehyde was purchased from Sun Chemical Technology Co., Ltd (Shanghai, China) and recrystallized from ethyl acetate before use. Organoboronic acids were all commercially available: phenylboronic acid was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and recrystallized from ethyl acetate before use; 1-pentenylboronic acid was purchased from Frontier Scientific; other arylboronic acids (98% purity) were purchased from Shanghai Boka Chemical Technology Co., Ltd (Shanghai, China) and used as received. 1,4-Dioxane were dried over sodium wire with benzophenone as the indicator and distilled freshly before use. DCM were dried over CaH_2 and distilled before use. All the temperatures are referred to the oil baths used. The starting racemic propargylic carbonates were synthesized from commercially or easily available propargylic alcohols[1] according to the reported procedures.[2] The optically active propargylic carbonates (*R*)-**1p** to (*R*)-**1s** were synthesized from optically active terminal propargylic alcohols[3] via coupling with allyl bromide according to the literature.[4]

Experimental details and analytical data

(1) 1,3-Diphenyl-7-chlorohepta-1,2-diene (3aa)(Table 2, entry 1)(lhw-11-109)



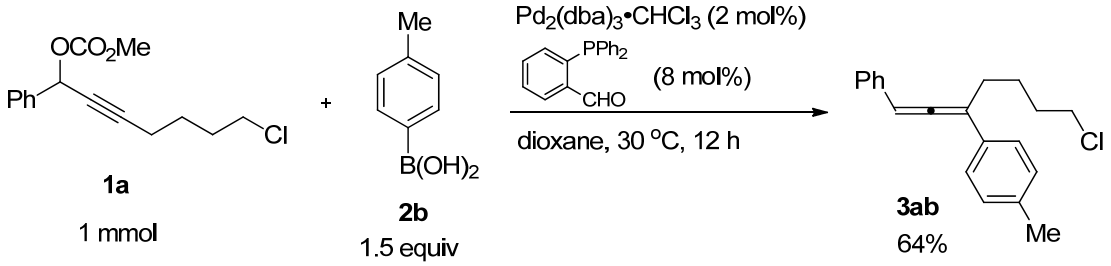
1a 1 mmol | **2a** 1.5 equiv | **3aa** 80%

Typical procedure A: To a flame-dried Schlenk tube were added $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.3 mg, 0.08 mmol), and **2a** (185.4 mg, 1.5 mmol) under argon atmosphere. After replacing air with argon for three times at rt under vacuum, **1a** (279.6 mg, 1.0 mmol)/dioxane (2.0 mL) was added. The resulting mixture was stirred for 12 h at 30 ^{o}C and then passed through a short pad of silica gel with Et_2O (~25 mL) as eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel to afford **3aa** (225.6 mg, 80%) (eluent: hexane) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.36-7.27 (m, 6 H, Ar-H), 7.25-7.17 (m, 2 H, Ar-H), 6.55 (t, *J* = 2.8 Hz, 1 H, =CH), 3.52 (t, *J* = 6.6 Hz, 2 H, $ClCH_2$), 2.67-2.52 (m, 2 H, $=CCH_2$), 1.95-1.84 (m, 2 H, CH_2), 1.84-1.66 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.3, 135.9, 134.4, 128.7, 128.5, 127.2, 127.1, 126.8, 126.1, 109.4, 98.2, 44.7, 32.3, 29.3, 25.1; IR (neat, cm^{-1}): 2934, 1933, 1596, 1492, 1446, 1329, 1074, 1028; MS (70 eV, EI) *m/z* (%): 284 (M^+(^{37}Cl), 4.14), 282 (M^+(^{35}Cl), 11.57), 206 (100); HRMS Calcd for $C_{19}H_{19}{}^{35}Cl$ (M^+): 282.1175, Found: 282.1177.

The following compounds **3ab-3ol** in Table 2 and Scheme 3 were prepared

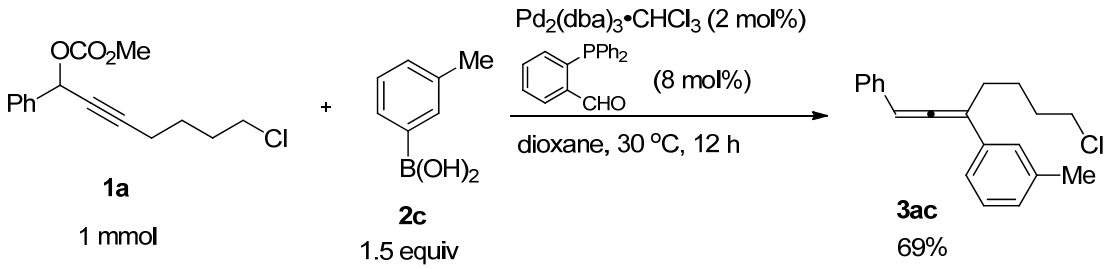
according to **Typical Procedure A**.

(2) 1-Phenyl-3-(4-methylphenyl)-7-chlorohepta-1,2-diene (3ab) (Table 2, entry 2) (lhw-11-145)



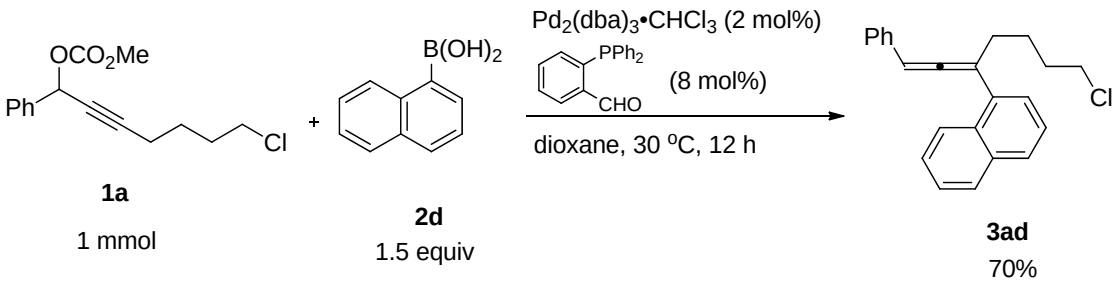
The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.6 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.4 mg, 0.08 mmol), **1a** (277.9 mg, 0.99 mmol), and **2b** (205.0 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3ab** (187.6 mg, 64%) (eluent: hexane to hexane/DCM = 50/1) as a solid: M.P. 52-55 °C (hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36-7.26 (m, 6 H, Ar-H), 7.24-7.17 (m, 1 H, Ar-H), 7.13 (d, *J* = 8.0 Hz, 2 H, Ar-H), 6.53 (t, *J* = 2.8 Hz, 1 H, =CH), 3.52 (t, *J* = 6.8 Hz, 2 H, $ClCH_2$), 2.66-2.51 (m, 2 H, $=CCH_2$), 2.33 (s, 3 H, CH_3), 1.94-1.84 (m, 2 H, CH_2), 1.84-1.67 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.1, 137.0, 134.6, 132.8, 129.3, 128.7, 127.0, 126.7, 125.9, 109.2, 98.1, 44.8, 32.3, 29.4, 25.1, 21.1; IR (neat, cm^{-1}): 2950, 1931, 1598, 1512, 1493, 1459, 1335, 1288; MS (70 eV, EI) *m/z* (%): 298 (M^+(^{37}Cl), 1.59), 296 (M^+(^{35}Cl), 3.89), 205 (100); Anal. Calcd for $C_{20}H_{21}Cl$: C 80.93, H 7.13; Found: C 80.94, H 7.24.

(3) 1-Phenyl-3-(3-methylphenyl)-7-chlorohepta-1,2-diene (3ac) (Table 2, entry 3) (lhw-11-158)



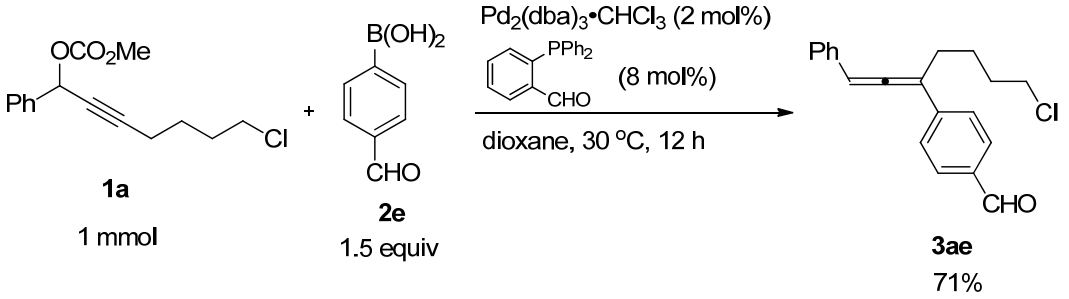
The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.5 mg, 0.08 mmol), **1a** (282.6 mg, 1.0 mmol), and **2c** (205.9 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3ac** (204.7 mg, 69%) (eluent: hexane to hexane/DCM = 40/1 to hexane/DCM = 20/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36-7.27 (m, 4 H, Ar-H), 7.27-7.17 (m, 4 H, Ar-H), 7.04 (d, *J* = 6.8 Hz, 1 H, Ar-H), 6.53 (t, *J* = 2.8 Hz, 1 H, =CH), 3.51 (t, *J* = 6.6 Hz, 2 H, $ClCH_2$), 2.66-2.50 (m, 2 H, $=CCH_2$), 2.33 (s, 3 H, CH_3), 1.93-1.83 (m, 2 H, CH_2), 1.83-1.65 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.3, 138.1, 135.7, 134.5, 128.7, 128.4, 128.0, 127.0, 126.7, 123.1, 109.3, 98.1, 44.7, 32.3, 29.4, 25.1, 21.5; IR (neat, cm^{-1}): 2939, 1932, 1599, 1493, 1457, 1310, 1092, 1027; MS (70 eV, EI) *m/z* (%): 298 (M^+(^{37}Cl), 8.16), 296 (M^+(^{35}Cl), 22.72), 220 (100); HRMS Calcd for $C_{20}H_{21}{}^{35}Cl$ (M^+): 296.1332, Found: 296.1333.

(4) 1-Phenyl-3-(1-naphthyl)-7-chlorohepta-1,2-diene (3ad) (Table 2, entry 4) (lhw-11-163)



The reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ (20.7 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.4 mg, 0.08 mmol), **1a** (281.8 mg, 1.0 mmol), and **2d** (256.2 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3ad** (232.5 mg, 70%) (eluent: hexane to hexane/DCM = 40/1 to hexane/DCM = 20/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21-8.15 (m, 1 H, Ar-H), 7.87-7.81 (m, 1 H, Ar-H), 7.76 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.53-7.41 (m, 4 H, Ar-H), 7.39-7.26 (m, 4 H, Ar-H), 7.21-7.15 (m, 1 H, Ar-H), 6.35 (t, *J* = 3.0 Hz, 1 H, =CH), 3.50 (t, *J* = 6.6 Hz, 2 H, $ClCH_2$), 2.71-2.55 (m, 2 H, $=CCH_2$), 1.93-1.84 (m, 2 H, CH_2), 1.82-1.65 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.5, 135.7, 134.7, 133.9, 131.2, 128.6, 128.5, 127.7, 126.9, 126.8, 126.1, 125.8, 125.5, 125.42, 125.36, 107.7, 95.5, 44.7, 34.0, 32.3, 25.4; IR (neat, cm^{-1}): 2939, 1944, 1594, 1495, 1457, 1386, 1334, 1310, 1072, 1015; MS (70 eV, EI) *m/z* (%): 334 (M^+(^{37}Cl), 6.06), 332 (M^+(^{35}Cl), 16.86), 241 (100); HRMS Calcd for $C_{23}H_{21}{}^{35}Cl$ (M^+): 332.1332, Found: 332.1330.

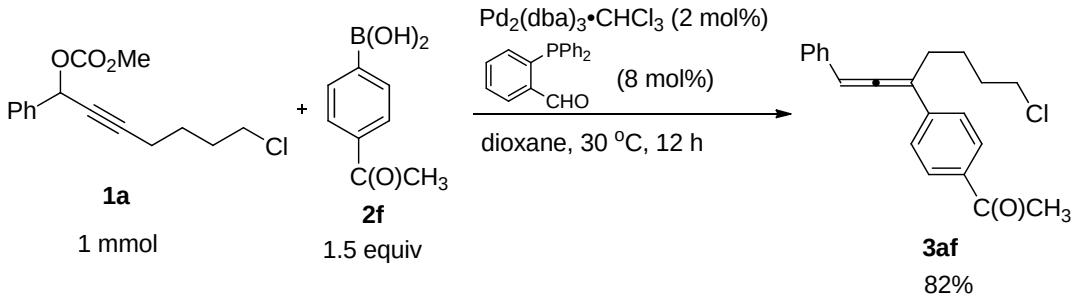
(5) 1-Phenyl-3-(4-formylphenyl)-7-chlorohepta-1,2-diene (3ae) (Table 2, entry 5) (lhw-11-146)



The reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ (20.8 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.4 mg, 0.08 mmol), **1a** (279.0 mg, 1.0 mmol),

and **2e** (230.5 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3ae** (218.0 mg, 71%) (eluent: hexane/DCM = 5/1 to 2/1 to 3/2) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.97 (s, 1 H, CHO), 7.82 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.59 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.36-7.29 (m, 4 H, Ar-H), 7.28-7.20 (m, 1 H, Ar-H), 6.64 (t, *J* = 3.0 Hz, 1 H, =CH), 3.53 (t, *J* = 6.6 Hz, 2 H, $ClCH_2$), 2.70-2.55 (m, 2 H, $=CCH_2$), 1.95-1.66 (m, 4 H, 2× CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.7, 191.6, 142.4, 135.0, 133.4, 129.9, 128.8, 127.5, 126.8, 126.4, 109.0, 98.9, 44.6, 32.2, 29.1, 25.0; IR (neat, cm^{-1}): 2937, 1930, 1697, 1599, 1568, 1494, 1458, 1307, 1213, 1169; MS (70 eV, EI) *m/z* (%): 312 (M^+(^{37}Cl), 3.60), 310 (M^+(^{35}Cl), 10.60), 234 (100); HRMS Calcd for $C_{20}H_{19}O^{35}Cl$ (M^+): 310.1124, Found: 310.1122.

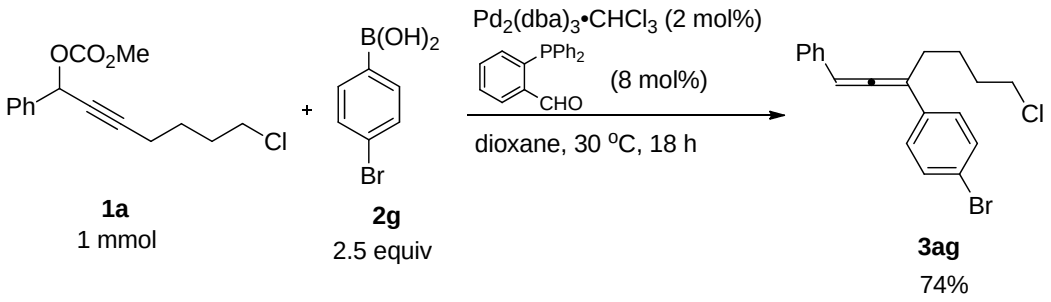
(6) 1-Phenyl-3-(4-acetylphenyl)-7-chlorohepta-1,2-diene (3af) (Table 2, entry 6) (lhw-13-73)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.6 mg, 0.08 mmol), **1a** (279.9 mg, 1.0 mmol), and **2f** (250.9 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3af** (264.6 mg, 82%) (eluent: hexane/DCM = 3/1 to 2/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93-7.88 (m, 2 H, Ar-H), 7.55-7.49 (m, 2 H, Ar-H), 7.35-7.29 (m, 4 H, Ar-H),

7.27-7.20 (m, 1 H, Ar-H), 6.62 (t, J = 3.0 Hz, 1 H, =CH), 3.53 (t, J = 6.4 Hz, 2 H, $ClCH_2$), 2.69-2.54 (m, 5 H, $=CCH_2$ and CH_3), 1.95-1.86 (m, 2 H, CH_2), 1.86-1.68 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.4, 197.5, 140.9, 135.7, 133.6, 128.8, 128.6, 127.4, 126.8, 126.0, 109.0, 98.7, 44.6, 32.2, 29.1, 26.5, 25.1; IR (neat, cm^{-1}): 2939, 1929, 1679, 1599, 1356, 1265, 1186; MS (70 eV, EI) *m/z* (%): 326 (M^+(^{37}Cl), 7.69), 324 (M^+(^{35}Cl), 21.94), 43 (100); HRMS Calcd for $C_{21}H_{21}O^{35}Cl$ (M^+): 324.1281, Found: 324.1277.

(7) 1-Phenyl-3-(4-bromophenyl)-7-chlorohepta-1,2-diene (3ag) (Table 2, entry 7) (lhw-13-74)



1a
1 mmol

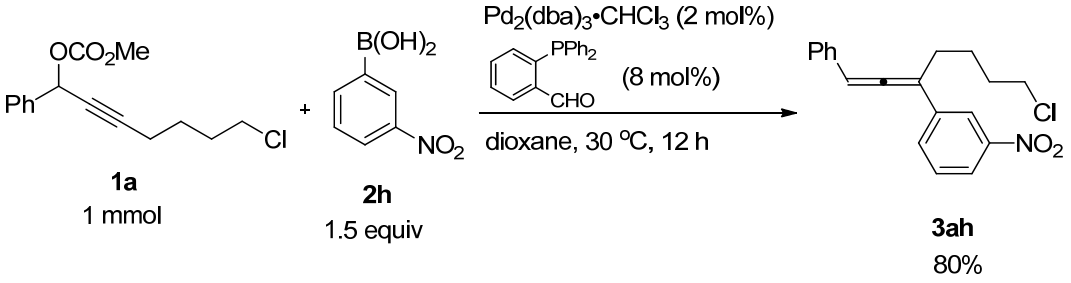
2g
2.5 equiv

3ag
74%

The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.5 mg, 0.08 mmol), **1a** (282.2 mg, 1.0 mmol), and **2g** (512.5 mg, 2.5 mmol) in dioxane (2.0 mL) afforded **3ag** (270.5 mg, 74%) (eluent: hexane to hexane/DCM = 50/1) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.45-7.39 (m, 2 H, Ar-H), 7.35-7.26 (m, 6 H, Ar-H), 7.26-7.18 (m, 1 H, Ar-H), 6.54 (t, J = 3.0 Hz, 1 H, =CH), 3.51 (t, J = 6.6 Hz, 2 H, $ClCH_2$), 2.63-2.47 (m, 2 H, $=CCH_2$), 1.92-1.83 (m, 2 H, CH_2), 1.83-1.64 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.3, 134.9, 133.9, 131.6, 128.8, 127.6, 127.3, 126.8, 121.0, 108.6, 98.6, 44.7, 32.2,

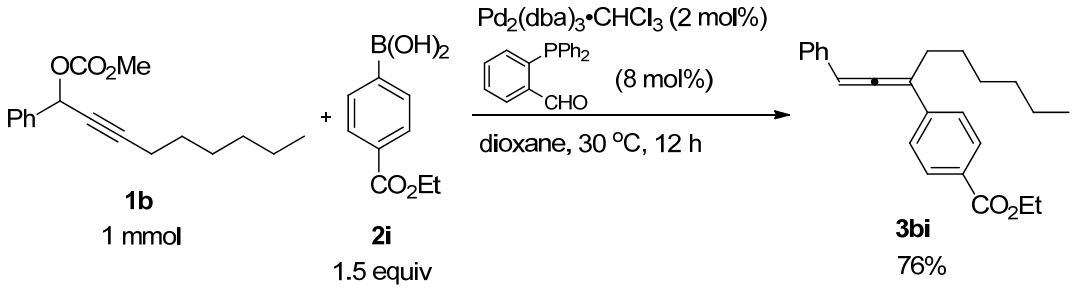
29.2, 25.0; IR (neat, cm^{-1}): 2940, 1933, 1597, 1485, 1458, 1073, 1007; MS (70 eV, EI) *m/z* (%): 364 (M^+(^{37}Cl, ^{81}Br), 1.89), 362 (M^+(^{35}Cl, ^{81}Br and ^{37}Cl, ^{79}Br), 7.17), 360 (M^+(^{35}Cl, ^{79}Br), 5.77), 204 (100); HRMS Calcd for $C_{19}H_{18}{}^{35}Cl\ {}^{79}Br(M^+)$: 360.0280, Found: 360.0281.

(8) 1-Phenyl-3-(3-nitrophenyl)-7-chlorohepta-1,2-diene (3ah) (Table 2, entry 8) (lhw-13-76)



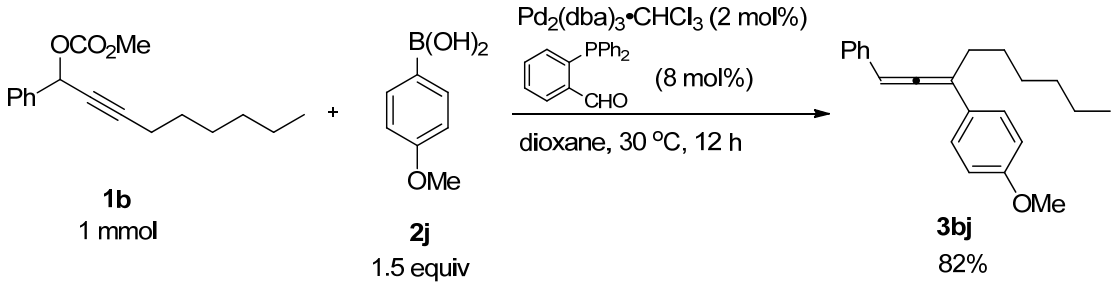
The reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ (20.6 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.3 mg, 0.08 mmol), **1a** (282.0 mg, 1.0 mmol), and **2h** (255.5 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3ah** (262.3 mg, 80%) (eluent: hexane/DCM = 50/1 to 20/1 to 10/1) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ = 8.25 (t, *J* = 2.2 Hz, 1 H, Ar-H), 8.09-8.04 (m, 1 H, Ar-H), 7.79-7.74 (m, 1 H, Ar-H), 7.46 (t, *J* = 8.0 Hz, 1 H, Ar-H), 7.37-7.30 (m, 4 H, Ar-H), 7.29-7.21 (m, 1 H, Ar-H), 6.67 (t, *J* = 3.2 Hz, 1 H, =CH), 3.54 (t, *J* = 6.2 Hz, 2 H, $ClCH_2$), 2.71-2.55 (m, 2 H, $=CCH_2$), 1.96-1.87 (m, 2 H, CH_2), 1.87-1.69 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.7, 148.6, 138.2, 133.3, 132.2, 129.3, 128.9, 127.6, 126.9, 121.9, 120.4, 108.1, 99.5, 44.6, 32.1, 29.2, 24.9; IR (neat, cm^{-1}): 2938, 2864, 1933, 1524, 1345, 1100, 1074; MS (70 eV, EI) *m/z* (%): 329 (M^+(^{37}Cl), 3.03), 327 (M^+(^{35}Cl), 9.42), 251 (100); HRMS Calcd for $C_{19}H_{18}NO_2{}^{35}Cl$ (M^+): 327.1026, Found: 327.1028.

(9) 1-Phenyl-3-(4-ethoxylcarbonylphenyl)nona-1,2-diene (3bi) (Table 2, entry 9) (lhw-13-77)



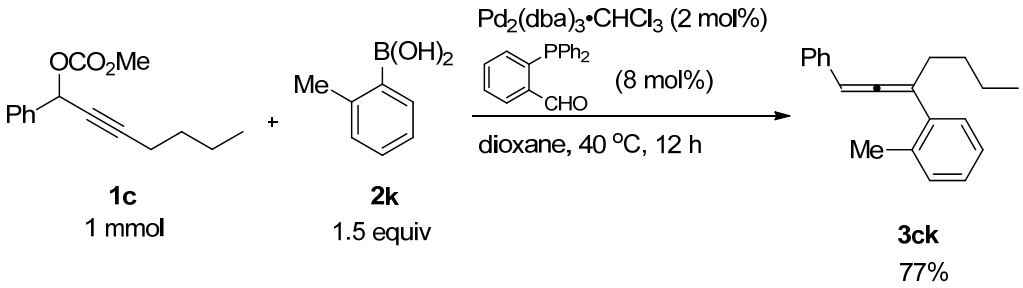
The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.6 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.5 mg, 0.08 mmol), **1b** (273.3 mg, 1.0 mmol), and **2i** (293.7 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3bi** (264.0 mg, 76%) (eluent: hexane/DCM = 10/1 to 5/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01-7.95 (m, 2 H, Ar-H), 7.53-7.47 (m, 2 H, Ar-H), 7.36-7.28 (m, 4 H, Ar-H), 7.26-7.18 (m, 1 H, Ar-H), 6.57 (t, *J* = 2.8 Hz, 1 H, =CH), 4.36 (q, *J* = 7.1 Hz, 2 H, OCH_2), 2.65-2.48 (m, 2 H, $=CCH_2$), 1.69-1.51 (m, 2 H, CH_2), 1.46-1.34 (m, 5 H, CH_2 and CH_3), 1.33-1.20 (m, 4 H, 2×CH_2), 0.85 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.4, 166.4, 141.0, 134.0, 129.7, 128.8, 128.7, 127.2, 126.8, 125.9, 109.6, 98.2, 60.8, 31.6, 30.0, 29.2, 27.8, 22.6, 14.3, 14.0; IR (neat, cm^{-1}): 2927, 2856, 1932, 1714, 1605, 1567, 1459, 1390, 1270, 1180, 1101, 1019; MS (70 eV, EI) *m/z* (%): 348 (M^+, 11.19), 278 (100); HRMS Calcd for $C_{24}H_{28}O_2$ (M^+): 348.2089, Found: 348.2093.

(10) 1-Phenyl-3-(4-methoxylphenyl)nona-1,2-diene (3bj) (Table 2, entry 10) (lhw-13-70)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.7 mg, 0.08 mmol), **1b** (274.4 mg, 1.0 mmol), and **2j** (233.2 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3bj**[5] (252.7 mg, 82%) (eluent: hexane/DCM = 50/1 to 20/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.26 (m, 6 H, Ar-H), 7.22-7.15 (m, 1 H, Ar-H), 6.89-6.82 (m, 2 H, Ar-H), 6.49 (t, *J* = 3.0 Hz, 1 H, =CH), 3.79 (s, 3 H, OCH_3), 2.60-2.45 (m, 2 H, $=CCH_2$), 1.68-1.50 (m, 2 H, CH_2), 1.45-1.33 (m, 2 H, CH_2), 1.33-1.20 (m, 4 H, 2×CH_2), 0.85 (t, *J* = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.1, 158.7, 135.0, 128.6, 128.4, 127.2, 126.8, 126.7, 113.9, 109.5, 97.7, 55.3, 31.7, 30.3, 29.3, 27.9, 22.6, 14.0; IR (neat, cm^{-1}): 2927, 2855, 1932, 1605, 1509, 1459, 1286, 1247, 1176, 1036; MS (70 eV, EI) *m/z* (%): 306 (M^+, 48.00), 135 (100).

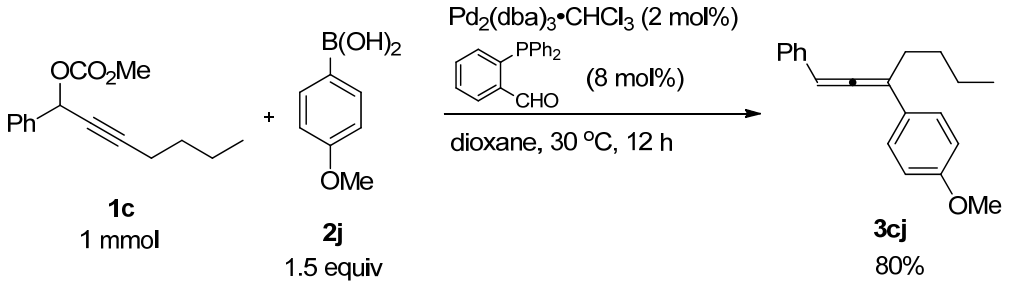
(11) 1-Phenyl-3-(2-methylphenyl)hepta-1,2-diene (3ck) (Table 2, entry 11) (lhw-11-92)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol),

o-(diphenylphosphino)benzaldehyde (23.7 mg, 0.08 mmol), **1c** (243.9 mg, 0.99 mmol), and **2k** (206.0 mg, 1.5 mmol) in dioxane (2.0 mL) at 40 °C afforded **3ck**[6] (200.0 mg, 77%) (eluent: hexane) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.25 (m, 5 H, Ar-H), 7.20-7.10 (m, 4 H, Ar-H), 6.24 (t, *J* = 2.8 Hz, 1 H, =CH), 2.53-2.37 (m, 2 H, =CCH_2), 2.36 (s, 3 H, $ArCH_3$), 1.57-1.47 (m, 2 H, CH_2), 1.46-1.34 (m, 2 H, CH_2), 0.89 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.9, 137.4, 135.9, 135.1, 130.5, 128.5, 128.0, 127.0, 126.8, 126.7, 125.8, 108.9, 95.1, 33.9, 30.0, 22.5, 20.6, 13.9; IR (neat, cm^{-1}): 3062, 3028, 2956, 2928, 2858, 1943, 1598, 1488, 1457, 1378, 1194, 1072, 1028; MS (70 eV, EI) *m/z* (%): 262 (M^+, 7.79), 205 (100).

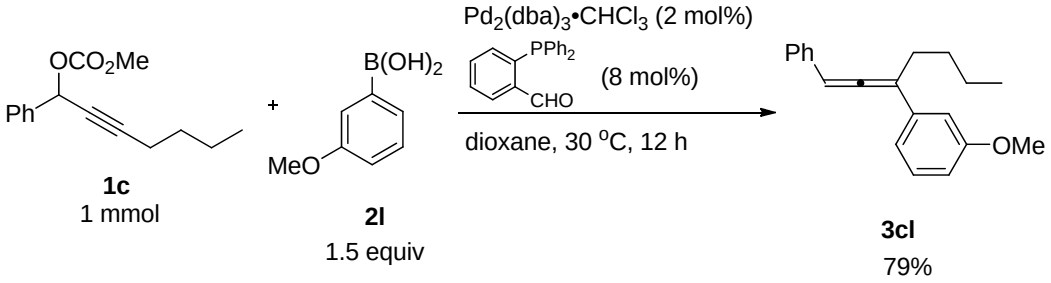
(12) 1-Phenyl-3-(4-methoxylphenyl)hepta-1,2-diene (3cj) (Table 2, entry 12) (lhw-11-75)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.6 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.5 mg, 0.08 mmol), **1c** (248.4 mg, 1.0 mmol), and **2j** (231.8 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3cj** (224.2 mg, 80%) (eluent: hexane/DCM = 20/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.26 (m, 6 H, Ar-H), 7.22-7.16 (m, 1 H, Ar-H), 6.88-6.82 (m, 2 H, Ar-H), 6.49 (t, *J* = 2.8 Hz, 1 H, =CH), 3.78 (s, 3 H, OCH_3), 2.60-2.45 (m, 2 H, =CCH_2), 1.66-1.52 (m, 2 H,

CH_2), 1.48-1.37 (m, 2 H, CH_2), 0.91 (t, J = 7.6 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.1, 158.8, 135.0, 128.6, 128.4, 127.2, 126.8, 126.7, 113.9, 109.5, 97.7, 55.3, 30.1, 30.0, 22.6, 13.9; IR (neat, cm^{-1}): 2955, 2929, 1930, 1605, 1509, 1459, 1294, 1246, 1176, 1110, 1035; MS (70 eV, EI) *m/z* (%): 278 (M^+, 4.27), 135 (100); HRMS Calcd for $C_{20}H_{22}O$ (M^+): 278.1671, Found: 278.1673.

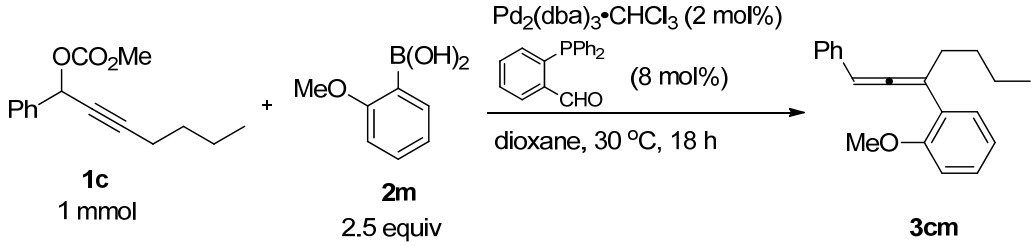
(13) 1-Phenyl-3-(3-methoxylphenyl)hepta-1,2-diene (3cl) (Table 2, entry 14) (lhw-11-103)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.6 mg, 0.08 mmol), **1c** (248.6 mg, 1.0 mmol), and **2l** (232.0 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3cl** (222.8 mg, 79%) (eluent: hexane to hexane/DCM = 50/1) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.26 (m, 4 H, Ar-H), 7.26-7.16 (m, 2 H, Ar-H), 7.08-7.03 (m, 1 H, Ar-H), 7.02-6.98 (m, 1 H, Ar-H), 6.79-6.74 (m, 1 H, Ar-H), 6.51 (t, J = 2.8 Hz, 1 H, =CH), 3.77 (s, 3 H, OCH_3), 2.62-2.47 (m, 2 H, $=CCH_2$), 1.65-1.52 (m, 2 H, CH_2), 1.48-1.37 (m, 2 H, CH_2), 0.91 (t, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.5, 159.8, 137.8, 134.6, 129.3, 128.7, 126.9, 126.7, 118.7, 112.13, 112.08, 109.9, 97.8, 55.2, 30.1, 29.9, 22.6, 13.9; IR (neat, cm^{-1}): 2956, 2930, 1933, 1597, 1580, 1486, 1462, 1432, 1286, 1267, 1166, 1050; MS (70 eV, EI) *m/z* (%): 278 (M^+, 19.84), 135

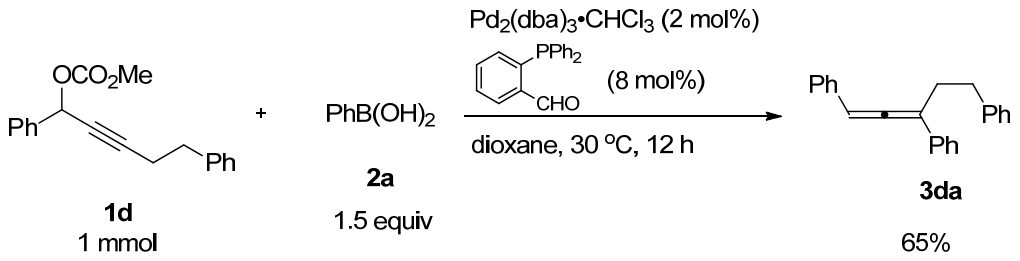
(100); HRMS Calcd for $C_{20}H_{22}O$ (M^+): 278.1671, Found: 278.1672.

(14) 1-Phenyl-3-(2-methoxylphenyl)hepta-1,2-diene (3cm) (Table 2, entry 15) (lhw-11-156)



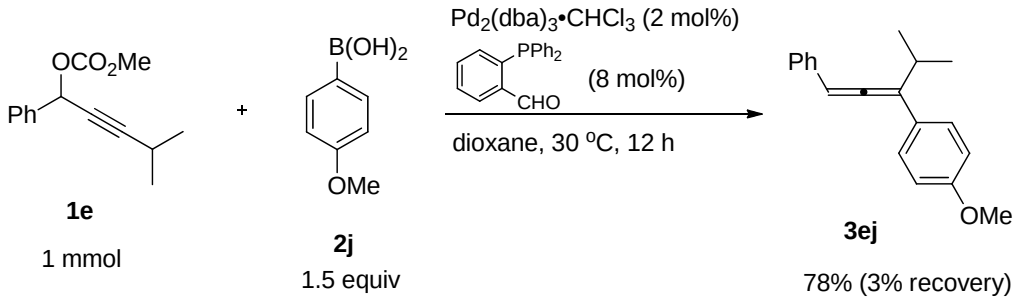
The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.4 mg, 0.08 mmol), **1c** (243.9 mg, 0.99 mmol), and **2m** (381.2 mg, 2.5 mmol) in dioxane (2.0 mL) afforded **3cm**[7] (199.6 mg, 72%) (eluent: hexane/DCM = 30/1 to 15/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42-7.37 (m, 2 H, Ar-H), 7.34-7.25 (m, 3 H, Ar-H), 7.25-7.15 (m, 2 H, Ar-H), 6.94-6.86 (m, 2 H, Ar-H), 6.25 (t, J = 3.0 Hz, 1 H, =CH), 3.78 (s, 3 H, OCH_3), 2.53 (td, J_1 = 7.6 Hz, J_2 = 2.8 Hz, 2 H, $=CCH_2$), 1.58-1.45 (m, 2 H, CH_2), 1.45-1.32 (m, 2 H, CH_2), 0.88 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.7, 156.9, 135.5, 129.4, 128.4, 128.3, 126.85, 126.78, 126.5, 120.5, 111.2, 107.3, 94.5, 55.5, 32.5, 30.2, 22.5, 13.9; IR (neat, cm^{-1}): 2955, 2930, 1940, 1596, 1579, 1491, 1459, 1434, 1280, 1247, 1028; MS (70 eV, EI) *m/z* (%): 278 (M^+, 22.02), 236 (100).

(15) 1,3,5-Triphenylpenta-1,2-diene (3da) (Table 2, entry 16)(lhw-11-113)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.5 mg, 0.08 mmol), **1d** (294.4 mg, 1.0 mmol), and **2a** (181.9 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3da** (191.3 mg, 65%) (eluent: hexane) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48-7.42 (m, 2 H, Ar-H), 7.36-7.16 (m, 13 H, Ar-H), 6.52 (t, *J* = 2.2 Hz, 1 H, =CH), 3.00-2.80 (m, 4 H, 2×CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.5, 141.8, 136.0, 134.4, 128.7, 128.6, 128.5, 128.4, 127.1, 127.0, 126.8, 126.1, 125.9, 109.3, 98.3, 34.1, 32.0; IR (neat, cm^{-1}): 3026, 2921, 1934, 1597, 1493, 1447, 1074, 1028; MS (70 eV, EI) *m/z* (%): 296 (M^+, 49.83), 205 (100); HRMS Calcd for $C_{23}H_{20}$ (M^+): 296.1565, Found: 296.1566.

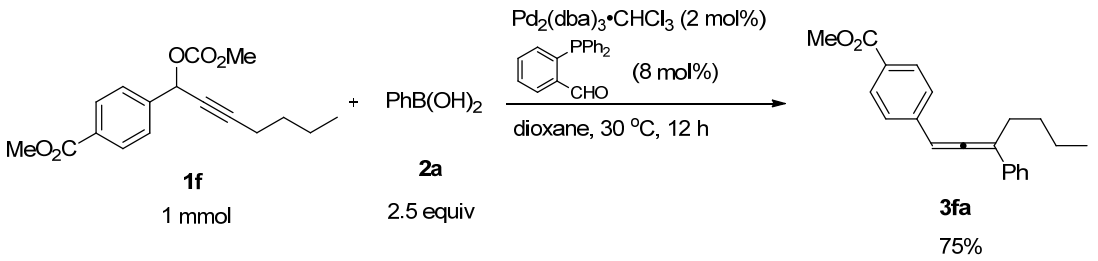
(16) 1-Phenyl-3-(4-methoxylphenyl)-4-methylpenta-1,2-diene (3ej) (Table 2, entry 17) (lhw-11-118)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.7 mg, 0.08 mmol), **1e** (231.9 mg, 1.0 mmol), and **2j** (231.2 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3ej** (206.0 mg, 78%)

(eluent: hexane to hexane/DCM = 20/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.26 (m, 6 H, Ar-H), 7.22-7.15 (m, 1 H, Ar-H), 6.89-6.82 (m, 2 H, Ar-H), 6.53 (d, *J* = 2.0 Hz, 1 H, =CH), 3.79 (s, 3 H, OCH_3), 2.99-2.86 (m, 1 H, CH), 1.21 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.18 (d, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.0, 158.7, 135.0, 128.7, 128.2, 127.7, 126.8, 126.5, 116.7, 113.9, 98.7, 55.3, 28.8, 22.6, 22.2; IR (neat, cm^{-1}): 2960, 1937, 1605, 1509, 1458, 1294, 1249, 1177, 1036; MS (70 eV, EI) *m/z* (%): 264 (M^+, 33.13), 221 (100); HRMS Calcd for $C_{19}H_{20}O$ (M^+): 264.1514, Found: 264.1516.

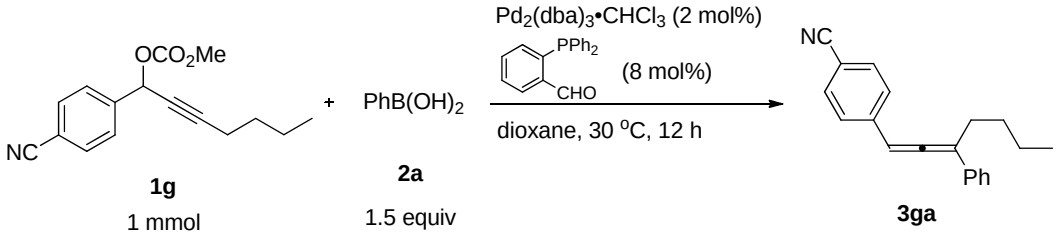
(17) 1-(Methoxylcarbonylphenyl)-3-phenylhepta-1,2-diene (3fa) (Table 2, entry 18) (lhw-11-180)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.8 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.8 mg, 0.08 mmol), **1f** (304.8 mg, 1.0 mmol), and **2a** (305.5 mg, 2.5 mmol) in dioxane (2.0 mL) afforded **3fa** (231.4 mg, 75%) (eluent: hexane/DCM = 5/1 to 3/1) as a solid: M.P. 66-67 °C (hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00-7.94 (m, 2 H, Ar-H), 7.45-7.41 (m, 2 H, Ar-H), 7.41-7.36 (m, 2 H, Ar-H), 7.36-7.29 (m, 2 H, Ar-H), 7.26-7.20 (m, 1 H, Ar-H), 6.55 (t, *J* = 3.4 Hz, 1 H, =CH), 3.90 (s, 3 H, OCH_3), 2.66-2.51 (m, 2 H, $=CCH_2$), 1.66-1.50 (m, 2 H, CH_2), 1.50-1.37 (m, 2 H, CH_2), 0.91 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100

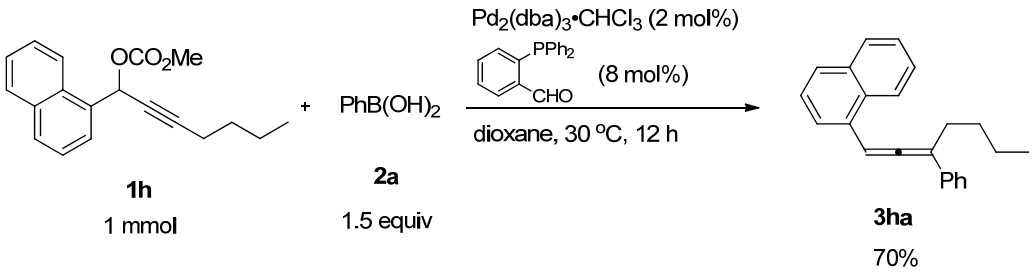
MHz, $CDCl_3$) δ = 207.8, 166.9, 139.7, 135.6, 130.0, 128.5, 128.4, 127.3, 126.5, 126.1, 110.5, 97.4, 52.0, 30.0, 29.8, 22.6, 13.9; IR (neat, cm^{-1}): 2951, 2923, 1931, 1718, 1605, 1491, 1452, 1431, 1297, 1270, 1174, 1098; MS (70 eV, EI) *m/z* (%): 306 (M^+, 9.77), 205 (100); Anal. Calcd for $C_{21}H_{22}O_2$: C 82.32, H 7.24; Found: C 82.32, H 7.18.

(18) 1-(4-Cyanophenyl)-3-phenylhepta-1,2-diene (3ga) (Table 2, entry 19) (lhw-11-105)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.6 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.3 mg, 0.08 mmol), **1g** (272.8 mg, 1.0 mmol), and **2a** (181.5 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3ga** (215.4 mg, 78%) (eluent: hexane/DCM = 5/1 to 4/1) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.59-7.54 (m, 2 H, Ar-H), 7.44-7.37 (m, 4 H, Ar-H), 7.36-7.30 (m, 2 H, Ar-H), 7.27-7.21 (m, 1 H, Ar-H), 6.53 (t, *J* = 3.0 Hz, 1 H, =CH), 2.66-2.51 (m, 2 H, $=CCH_2$), 1.66-1.50 (m, 2 H, CH_2), 1.50-1.36 (m, 2 H, CH_2), 0.92 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.1, 139.9, 135.1, 132.4, 128.6, 127.5, 127.1, 126.1, 119.0, 111.1, 110.1, 97.0, 30.0, 29.7, 22.5, 13.9; IR (neat, cm^{-1}): 2956, 2928, 2225, 1932, 1603, 1493, 1451, 1380, 1202, 1174, 1106, 1074; MS (70 eV, EI) *m/z* (%): 273 (M^+, 6.93), 231 (100); HRMS Calcd for $C_{20}H_{19}N$ (M^+): 273.1517, Found: 273.1515.

(19) 1-(1-Napthyl)-3-phenylhepta-1,2-diene (3ha) (Table 2, entry 20)(lhw-11-104)



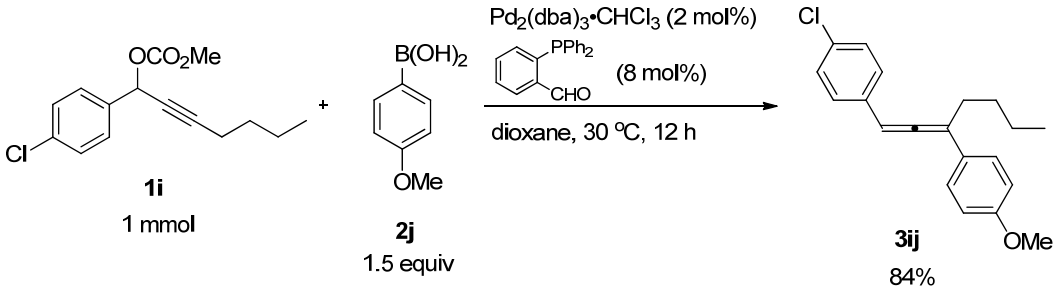
1h
1 mmol

2a
1.5 equiv

3ha
70%

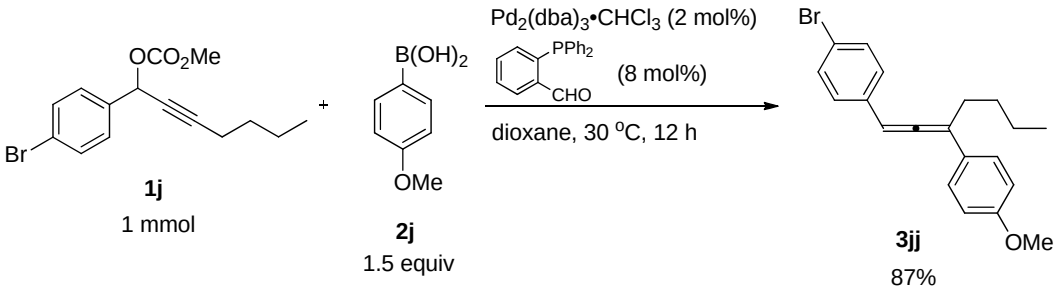
The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.3 mg, 0.08 mmol), **1h** (296.9 mg, 1.0 mmol), and **2a** (181.5 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3ha** (208.4 mg, 70%) (eluent: hexane) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.29 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.88-7.82 (m, 1 H, Ar-H), 7.73 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.60 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.55-7.45 (m, 4 H, Ar-H), 7.41 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.33 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.26-7.18 (m, 2 H, Ar-H and =CH), 2.69-2.53 (m, 2 H, $=CCH_2$), 1.73-1.55 (m, 2 H, CH_2), 1.51-1.38 (m, 2 H, CH_2), 0.91 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.8, 136.3, 134.0, 130.9, 130.7, 128.7, 128.5, 127.5, 126.9, 126.13, 126.07, 125.7, 125.2, 123.6, 108.9, 94.4, 30.1, 29.9, 22.7, 14.0; IR (neat, cm^{-1}): 2954, 1927, 1931, 1592, 1493, 1452; MS (70 eV, EI) *m/z* (%): 298 (M^+, 51.95), 241 (100); HRMS Calcd for $C_{23}H_{22}$ (M^+): 298.1722, Found: 298.1725.

(20) 1-(4-Chlorophenyl)-3-(4-methoxylphenyl)hepta-1,2-diene (3ij) (Table 2, entry 21) (lhw-11-116)



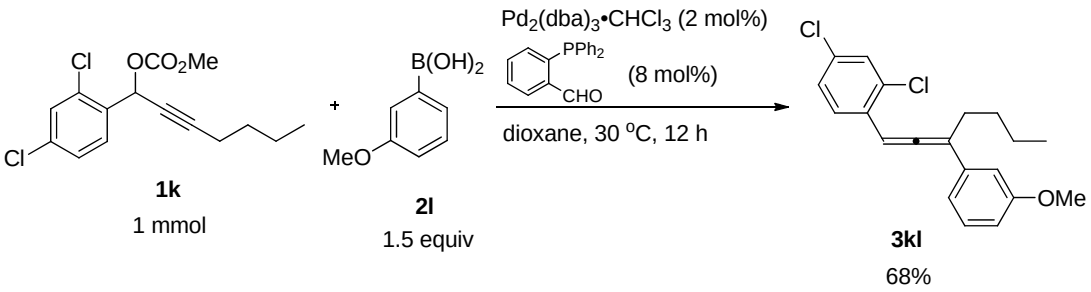
The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.6 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.2 mg, 0.08 mmol), **1i** (283.0 mg, 1.0 mmol), and **2j** (231.1 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3ij** (266.1 mg, 84%) (eluent: hexane to hexane/DCM = 20/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38-7.32 (m, 2 H, Ar-H), 7.29-7.22 (m, 4 H, Ar-H), 6.89-6.83 (m, 2 H, Ar-H), 6.45 (t, J = 3.2 Hz, 1 H, =CH), 3.80 (s, 3 H, OCH_3), 2.60-2.45 (m, 2 H, =CCH_2), 1.65-1.48 (m, 2 H, CH_2), 1.48-1.36 (m, 2 H, CH_2), 0.91 (t, J = 7.6 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.2, 158.9, 133.5, 132.4, 128.8, 128.0, 127.8, 127.2, 114.0, 109.9, 96.8, 55.3, 30.1, 30.0, 22.6, 13.9; IR (neat, cm^{-1}): 2955, 2928, 1930, 1606, 1576, 1509, 1488, 1462, 1441, 1379, 1291, 1246, 1176, 1089, 1036, 1012; MS (70 eV, EI) *m/z* (%): 314 (M^+(^{37}Cl), 17.52), 312 (M^+(^{35}Cl), 49.00), 235 (100); HRMS Calcd for $C_{20}H_{21}{}^{35}Cl$ (M^+): 312.1281, Found: 312.1283.

(21) 1-(4-Bromophenyl)-3-(4-methoxylphenyl)hepta-1,2-diene (3jj) (Table 2, entry 22) (lhw-13-71)



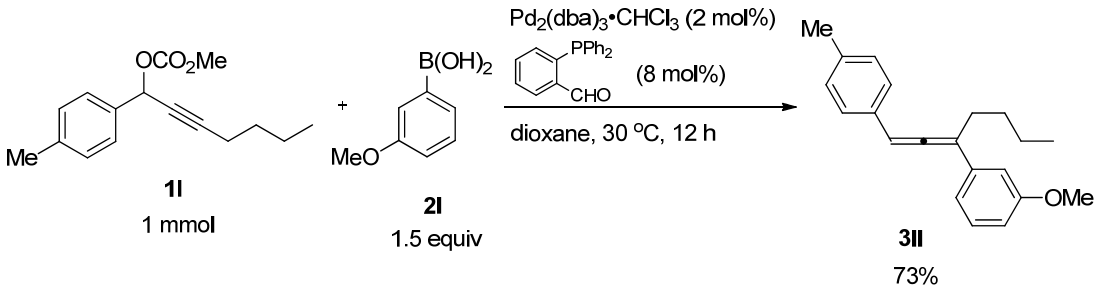
The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.6 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.3 mg, 0.08 mmol), **1j** (327.6 mg, 1.0 mmol), and **2j** (232.4 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3jj** (313.5 mg, 87%) (eluent: hexane/DCM = 50/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.38 (m, 2 H, Ar-H), 7.38-7.31 (m, 2 H, Ar-H), 7.22-7.15 (m, 2 H, Ar-H), 6.89-6.83 (m, 2 H, Ar-H), 6.44 (t, *J* = 3.2 Hz, 1 H, =CH), 3.79 (s, 3 H, OMe), 2.60-2.45 (m, 2 H, $=CCH_2$), 1.65-1.47 (m, 2 H, CH_2), 1.47-1.35 (m, 2 H, CH_2), 0.91 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.2, 158.9, 134.0, 131.7, 128.2, 128.0, 127.2, 120.4, 114.0, 110.0, 96.9, 55.3, 30.1, 29.9, 22.6, 13.9; IR (neat, cm^{-1}): 2955, 2929, 1930, 1606, 1576, 1509, 1486, 1462, 1291, 1246, 1176, 1110, 1070, 1036, 1008; MS (70 eV, EI) *m/z* (%): 358 (M^+(^{81}Br), 16.61), 356 (M^+(^{79}Br), 16.25), 135 (100); HRMS Calcd for $C_{20}H_{21}O\ ^{79}Br(M^+)$: 356.0776, Found: 356.0773.

(22) 1-(2,4-Dichlorophenyl)-3-(3-methoxylphenyl)hepta-1,2-diene (3kl)(Table 2, entry 23) (lhw-11-151)



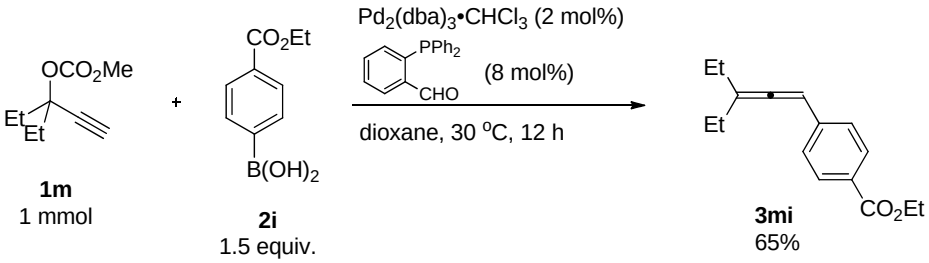
The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.6 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.8 mg, 0.08 mmol), **1k** (314.8 mg, 1.0 mmol), and **2l** (233.3 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3kl** (236.0 mg, 68%) (eluent: hexane to hexane/DCM = 20/1) as a solid: M.P. 62-64 ^oC (hexane/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.38-7.34 (m, 2 H, Ar-H), 7.26-7.22 (m, 1 H, Ar-H), 7.13 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H, Ar-H), 7.05-7.00 (m, 1 H, Ar-H), 6.97 (t, J = 2.0 Hz, 1 H, Ar-H), 6.89 (t, J = 3.4 Hz, 1 H, =CH), 6.79 (dd, J_1 = 7.8 Hz, J_2 = 2.2 Hz, 1 H, Ar-H), 3.79 (s, 3 H, OMe), 2.62-2.47 (m, 2 H, $=CCH_2$), 1.65-1.49 (m, 2 H, CH_2), 1.47-1.35 (m, 2 H, CH_2), 0.92 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.6, 159.8, 137.0, 132.8, 132.5, 131.0, 129.53, 129.48, 128.8, 127.3, 118.7, 112.4, 112.2, 110.6, 93.5, 55.2, 30.1, 29.8, 22.6, 13.9; IR (neat, cm^{-1}): 2954, 2927, 1928, 1604, 1581, 1556, 1472, 1449, 1435, 1366，1334, 1292, 1244, 1205, 1167, 1099, 1048; MS (70 eV, EI) *m/z* (%): 350 (M^+(^{37}Cl, ^{37}Cl), 3.50), 348 (M^+(^{35}Cl, ^{37}Cl), 18.58), 346 (M^+(^{35}Cl, ^{35}Cl), 27.18), 269 (100); Anal. Calcd for $C_{20}H_{20}Cl_2O_2$: C 69.17, H 5.80; Found: C 69.11, H 5.76.

(23) 1-(4-Methylphenyl)-3-(3-methoxylphenyl)hepta-1,2-diene (3ll) (Table 2, entry 24) (lhw-11-119)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.8 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.5 mg, 0.08 mmol), **1l** (261.4 mg, 1.0 mmol), and **2l** (234.4 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3ll** (214.6 mg, 73%) (eluent: hexane to hexane/DCM = 20/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26-7.19 (m, 3 H, Ar-H), 7.11 (d, J = 8.4 Hz, 2 H, Ar-H), 7.05 (d, J = 8.4 Hz, 1 H, Ar-H), 7.00 (t, J = 2.0 Hz, 1 H, Ar-H), 6.76 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H, Ar-H), 6.49 (t, J = 3.0 Hz, 1 H, =CH), 3.78 (s, 3 H, OMe), 2.61-2.46 (m, 2 H, $=CCH_2$), 2.33 (s, 3 H, $ArCH_3$), 1.65-1.49 (m, 2 H, CH_2), 1.48-1.35 (m, 2 H, CH_2), 0.91 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.3, 159.7, 138.0, 136.7, 131.6, 129.4, 129.3, 126.6, 118.7, 112.1, 112.0, 109.7, 97.6, 55.2, 30.1, 29.9, 22.6, 21.2, 13.9; IR (neat, cm^{-1}): 2955, 2927, 1932, 1597, 1579, 1512, 1485, 1463, 1454, 1432, 1287, 1266, 1197, 1165, 1106, 1049; MS (70 eV, EI) *m/z* (%): 292 (M^+, 37.88), 235 (100); HRMS Calcd for $C_{21}H_{24}O$ (M^+): 292.1827, Found: 292.1830.

(24) 1-(4-Ethoxycarbonylphenyl)-3-ethylpenta-1,2-diene (3mi) (Scheme 3a) (lhw-13-82)



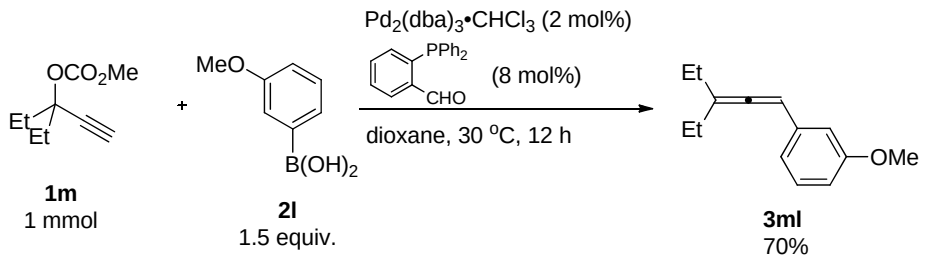
1m
1 mmol

2i
1.5 equiv.

3mi
65%

The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.6 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.2 mg, 0.08 mmol), **1m** (171.4 mg, 1.0 mmol), and **2i** (291.1 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3mi** (161.1 mg, 65%) (eluent: Hexane/DCM = 40:1 to 20:1 to 10:1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99-7.92 (m, 2 H, Ar-H), 7.35-7.29 (m, 2 H, Ar-H), 6.25-6.19 (m, 1 H, =CH), 4.36 (q, *J* = 7.2 Hz, 2 H, OCH_2), 2.21-2.04 (m, 4 H, 2×CH_2), 1.38 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.06 (t, *J* = 7.2 Hz, 6 H, 2×CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.1, 166.5, 141.3, 129.8, 128.2, 126.0, 112.9, 96.1, 60.7, 25.7, 14.3, 12.3; IR (neat, cm^{-1}): 2966, 2933, 1946, 1714, 1606, 1456, 1367, 1268, 1172, 1098, 1019; MS (70 eV, EI) *m/z* (%): 244 (M^+, 45.86), 143 (100); HRMS Calcd for $C_{16}H_{20}O_2$ (M^+): 244.1463, Found: 244.1465.

(25) 1-(3-Methoxylphenyl)-3-ethylpenta-1,2-diene (3ml) (Scheme 3b) (lhw-13-83)



1m
1 mmol

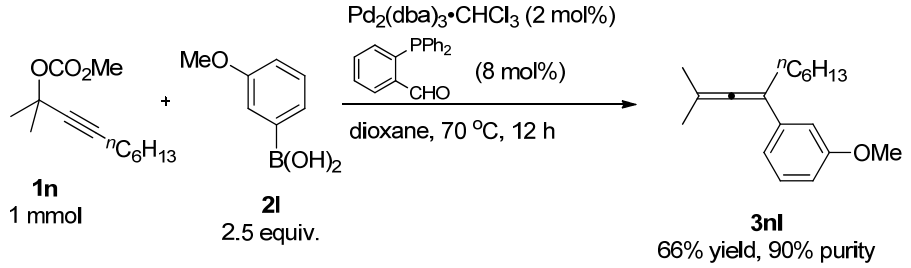
2l
1.5 equiv.

3ml
70%

The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.8 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.8 mg, 0.08 mmol), **1m** (171.2 mg, 1.0 mmol),

and **2l** (232.5 mg, 1.5 mmol) in dioxane (2.0 mL) afforded **3ml** (142.2 mg, 70%) (eluent: Hexane/DCM = 50:1 to 20:1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.19 (t, *J* = 8.0 Hz, 1 H, Ar-H), 6.90-6.82 (m, 2 H, Ar-H), 6.74-6.69 (m, 1 H, Ar-H), 6.18-6.12 (m, 1 H, =CH), 3.79 (s, 3 H, OCH_3), 2.18-2.01 (m, 4 H, 2×CH_2), 1.06 (t, *J* = 7.2 Hz, 6 H, 2×CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.8, 159.8, 137.9, 129.4, 119.0, 112.4, 111.9, 111.7, 96.4, 55.1, 25.8, 12.4; IR (neat, cm^{-1}): 2964, 2932, 2835, 1947, 1596, 1580, 1490, 1455, 1316, 1287, 1259, 1145, 1045; MS (70 eV, EI) *m/z* (%): 202 (M^+, 100); HRMS Calcd for $C_{14}H_{18}O$ (M^+): 202.1358, Found: 202.1359.

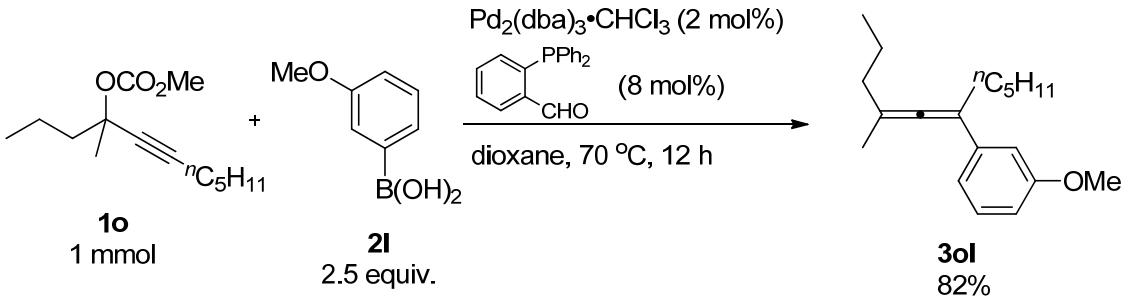
(26) 2-Methyl-4-(3-methoxylphenyl)deca-2,3-diene (3nl) (Scheme 3c)(lhw-13-106)



The reaction of $Pd_2(dba)_3$·$CHCl_3$ (20.8 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.3 mg, 0.08 mmol), **1n** (227.1 mg, 1.0 mmol), and **2l** (388.9 mg, 2.5 mmol) in dioxane (2.0 mL) at 70 °C afforded **3nl** (190.3 mg, 90% purity, 66%) (eluent: Hexane/DCM = 50:1 to 20:1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25-7.17 (m, 1 H, Ar-H), 6.99-6.94 (m, 1 H, Ar-H), 6.94-6.91 (m, 1 H, Ar-H), 6.74-6.69 (m, 1 H, Ar-H), 3.80 (s, 3 H, OCH_3), 2.36 (t, *J* = 7.0 Hz, 2 H, =CCH_2), 1.79 (s, 6 H, 2×=CCH_3), 1.55-1.45 (m, 2 H, CH_2), 1.42-1.22 (m, 6 H, 3×CH_2), 0.89 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.9, 159.6, 140.2, 129.0, 118.6, 112.2, 111.0, 103.3, 98.1, 55.1, 31.8, 30.2, 29.1, 27.9, 22.7, 20.4,

14.1; IR (neat, cm^{-1}): 2954, 2926, 2855, 1953, 1598, 1580, 1486, 1463, 1452, 1433, 1377, 1361, 1317, 1284, 1264, 1199, 1164, 1112, 1046; MS (70 eV, EI) *m/z* (%): 258 (M^+, 15.03), 173 (100); HRMS Calcd for $C_{18}H_{26}O$ (M^+): 258.1984, Found: 258.1983.

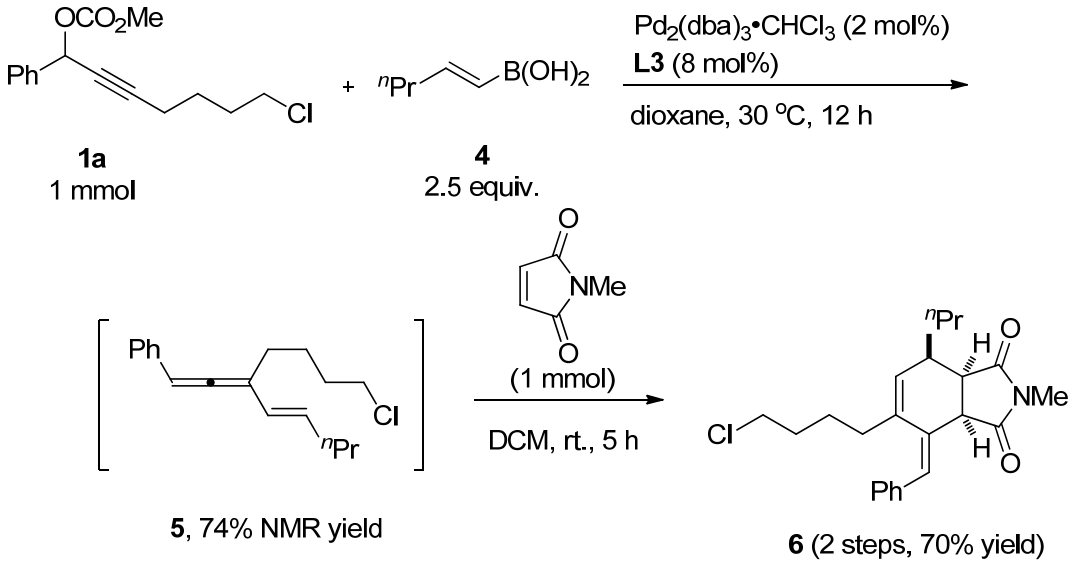
(27) 4-Methyl-6-(3-methoxylphenyl)undeca-4,5-diene (3ol) (Scheme 3d) (lhw-13-108)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.6 mg, 0.08 mmol), **1o** (240.3 mg, 1.0 mmol), and **2l** (386.4 mg, 2.5 mmol) in dioxane (2.0 mL) at 70 °C afforded **3ol** (223.2 mg, 82%) (eluent: Hexane/DCM = 50:1 to 20:1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.01-6.96 (m, 1 H, Ar-H), 6.96-6.92 (m, 1 H, Ar-H), 6.74-6.68 (m, 1 H, Ar-H), 3.80 (s, 3 H, OCH_3), 2.36 (t, *J* = 7.4 Hz, 2 H, $=CCH_2$), 2.05 (t, *J* = 7.8 Hz, 2 H, $=CCH_2$), 1.77 (s, 3 H, $=CCH_3$), 1.54-1.42 (m, 4 H, 2 $\times CH_2$), 1.41-1.28 (m, 4 H, 2$\times CH_2$), 0.96-0.82 (m, 6 H, 2$\times CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.5, 159.6, 140.2, 129.0, 118.5, 111.9, 111.1, 104.4, 102.6, 55.1, 36.5, 31.7, 30.3, 27.8, 22.6, 21.0, 18.8, 14.1, 14.0; IR (neat, cm^{-1}): 2955, 2928, 2871, 2858, 1949, 1598, 1580, 1486, 1463, 1433, 1284, 1262, 1199, 1165, 1051; MS (70 eV,

EI) *m/z* (%): 272 (M^+, 24.86), 187 (100); HRMS Calcd for $C_{19}H_{28}O$ (M^+): 272.2140, Found: 272.2137.

(28) (*Z*)-4-benzylidene-5-(4-chlorobutyl)-2-methyl-7-propyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (6) (Scheme 3e) (lhw-13-121)



The reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.6 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.3 mg, 0.08 mmol), **1a** (278.7 mg, 1.0 mmol), and **4** (290.4 mg, 2.5 mmol) in dioxane (2.0 mL) afforded **5** according the **Typical Procedure A**. After removal of the solvent, the crude product was submitted to next step directly without further purification.

To a flame-dried Schlenk tube were added *N*-methylmaleimide (113.4 mg, 1.0 mmol) and **5** / DCM (4.0 mL) under argon atmosphere. The resulting mixture was stirred for 5 h at room temperature and then removal of the solvent under vacuum. The residue was purified by flash chromatography on silica gel to afford **6** (269.0 mg, 70%) (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ^{1}H NMR (400 MHz,

$CDCl_3$) δ = 7.32-7.17 (m, 5 H, Ar-H), 6.64 (s, 1 H, =CH), 5.61 (d, *J* = 3.2 Hz, 1 H, =CH), 3.71 (d, *J* = 8.4 Hz, 1 H, CH), 3.29 (t, *J* = 6.8 Hz, 2 H, $ClCH_2$), 3.24-3.18 (m, 1 H, CH), 2.92 (s, 3 H, NCH_3), 2.40-2.30 (m, 1 H, CH), 2.01-1.76 (m, 4 H, 2×CH_2), 1.61-1.47 (m, 2 H, CH_2), 1.46-1.36 (m, 2 H, CH_2), 1.31-1.17 (m, 1 H, one proton of CH_2), 1.15-0.97 (m, 4 H, CH_3 and one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.6, 177.1, 140.7, 136.7, 132.0, 131.9, 130.4, 128.5, 128.0, 127.4, 51.7, 44.4, 43.5, 36.9, 33.4, 32.0, 31.9, 25.6, 24.8, 21.2, 14.1; IR (neat, cm^{-1}): 2954, 2931, 2861, 1772, 1697, 1430, 1379, 1283, 1152, 1108; MS (70 eV, EI) *m/z* (%): 387 (M^+(^{37}Cl), 29.10), 385 (M^+(^{35}Cl), 86.75), 84 (100); HRMS Calcd for $C_{23}H_{28}{}^{35}ClNO_2$ (M^+): 385.1809, Found: 385.1806.

We identified the peaks in the ^1H NMR spectrum according to the chemical shift, COSY, and HSQC spectrum (Figure S1). The NOESY spectrum showed that H^4 and H^{11}, H^{11} and H^{10} are close to each other. In addition, after checking the literature, we found that this is a known reaction, and similar compounds have reported.[8,9] Thus, we assigned the relative configuration based on the literature and our NMR analysis.

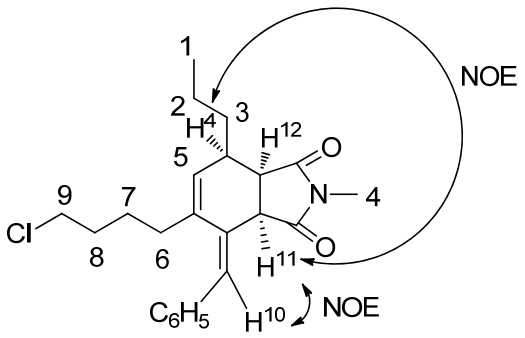
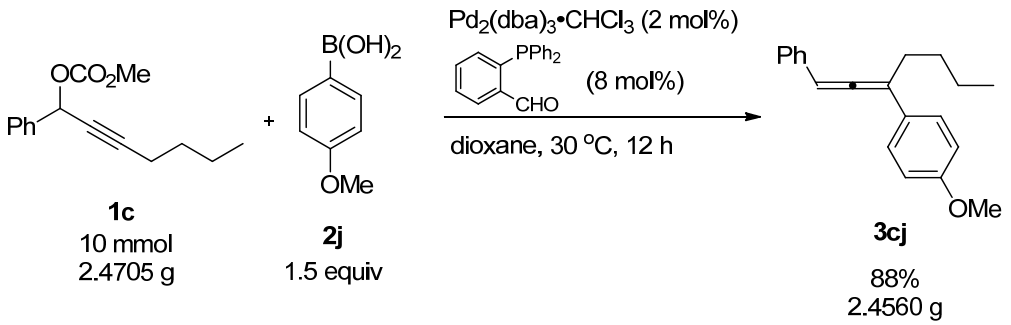


Figure S1

Gram-scale reaction

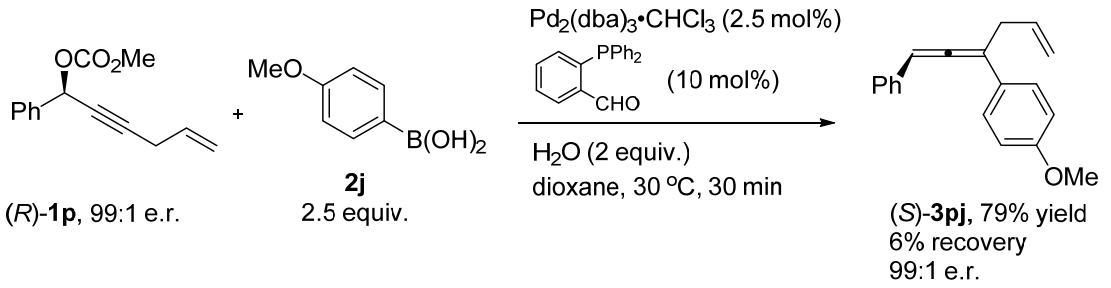
1-Phenyl-3-(4-methoxylphenyl)hepta-1,2-diene (3cj) (Table 2, entry 13) (lhw-13-90)



To a 100 mL flame-dried three-neck round-bottom flask equipped with a magnetic stirring bar were added $Pd_2(dba)_3{\cdot}CHCl_3$ (207.0 mg, 0.20 mmol), *o*-(diphenylphosphino)benzaldehyde (233.3 mg, 0.80 mmol), and **2j** (2.3235 g, 15.0 mmol) under argon atmosphere. After replacing air with argon for three times at rt under vacuum, **1c** (2.4705 g, 1.0 mmol) / dioxane (20 mL) was added. The resulting mixture was stirred for 12 h at 30 °C and then passed through a short pad of silica gel with Et_2O (25 mL) as eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel to afford **3cj** (2.4560 g, 88%) (eluent: hexane/DCM = 100/1 to 50/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.25 (m, 6 H, Ar-H), 7.21-7.15 (m, 1 H, Ar-H), 6.87-6.82 (m, 2 H, Ar-H), 6.49 (t, *J* = 2.8 Hz, 1 H, =CH), 3.77 (s, 3 H, OCH_3), 2.60-2.45 (m, 2 H, $=CCH_2$), 1.66-1.51 (m, 2 H, CH_2), 1.48-1.36 (m, 2 H, CH_2), 0.91 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.0, 158.7, 135.0, 128.6, 128.4, 127.2, 126.8, 126.7, 113.9, 109.4, 97.7, 55.2, 30.1, 30.0, 22.6, 13.9.

Chirality transfer

1. (*S*)-1-Phenyl-3-(4-methoxylphenyl)hexa-1,2,5-triene ((*S*)-3pj) (Scheme 5) (lhw-14-163)



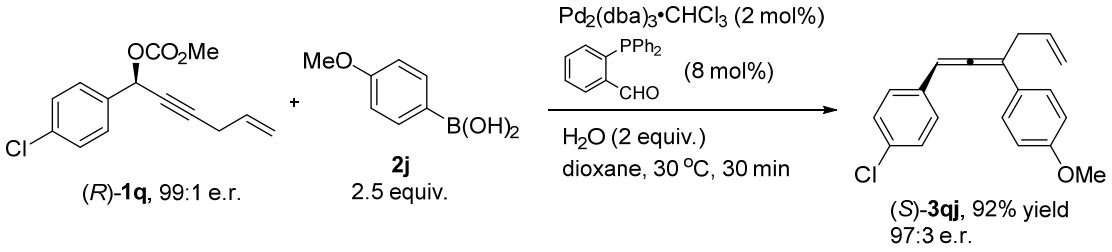
(*R*)-**1p**, 99:1 e.r.

(*S*)-**3pj,** 79% yield
6% recovery
99:1 e.r.

Typical Procedure B: To a flame-dried Schlenk tube were added $Pd_2(dba)_3 \cdot CHCl_3$ (26.0 mg, 0.025 mmol) and *o*-(diphenylphosphino)benzaldehyde (29.5 mg, 0.10 mmol) under argon atmosphere. After replacing air with argon for three times under vacuum, dioxane (2.0 mL) was added. The resulting mixture was stirred for 30 min at room temperature, which followed by addition of **2j** (380.8 mg, 2.5 mmol), (*R*)-**1p** (229.5 mg, 1.0 mmol, 99:1 e.r.)/dioxane (1.0 mL), and H_2O (36 μL, 2.0 mmol) sequentially. The resulting mixture was stirred for 30 min at 30 ^oC, and then passed through a short pad of silica gel with Et_2O (20 mL) as eluent. After removal of the solvent under vacuum, 6% of (*R*)-**1p** was detected by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as the internal standard. The residue was purified by flash chromatography on silica gel to afford (*S*)-**3pj** (206.2 mg, 79%) (eluent: petroleum ether (b.p. 30-60 ^oC) to petroleum ether (b.p. 30-60 ^oC)/ethyl ether = 200/1) as a liquid: 99:1 e.r. (HPLC conditions: OJ-H column, hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (minor) = 8.0 min, t_R (major) =11.3 min); $[\alpha]^{20}_D$ = +460.0^o (*c* = 1.01, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.27 (m, 6 H, Ar-H), 7.23-7.18 (m, 1 H, Ar-H), 6.89-6.83 (m, 2 H, Ar-H), 6.53 (t, *J* = 2.8 Hz, 1 H, C=C=CH), 6.04-5.92 (m, 1 H, =CH), 5.24-5.21 (m, 1 H, one proton from $=CH_2$), 5.10-5.05 (m, 1 H, one proton

from $=CH_2$), 3.79 (s, 3 H, CH_3), 3.39-3.25 (m, 2 H, $=CCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.4, 158.8, 135.6, 134.6, 128.7, 127.7, 127.3, 127.0, 126.8, 116.5, 113.9, 107.7, 97.9, 55.3, 35.0; IR (neat, cm^{-1}): 1932, 1604, 1509, 1460, 1288, 1246, 1176, 1035; MS (70 eV, EI) *m/z* (%): 262 (M^+, 66.06), 221 (100); HRMS Calcd for $C_{19}H_{18}O$ (M^+): 262.1358, Found: 262.1356.

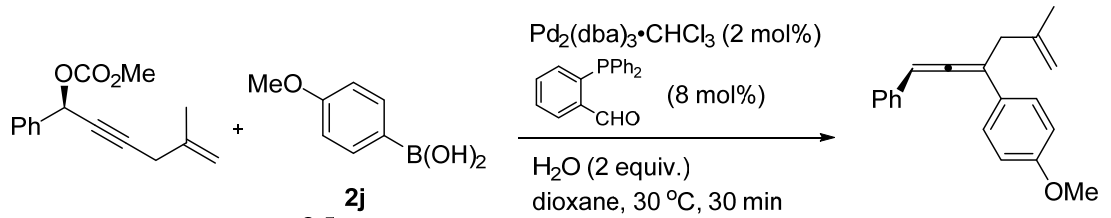
2. (*S*)-1-(4-Chlorophenyl)-3-(4-methoxylphenyl)hexa-1,2,5-triene ((*S*)-3qj) (Scheme 5) (lhw-14-176)



Following **Typical Procedure B**, the reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.8 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.9 mg, 0.08 mmol), (*R*)-**1q** (265.6 mg, 1.0 mmol, 99:1 e.r.), **2j** (380.1 mg, 2.5 mmol), and H_2O (36 μL, 2.0 mmol) in dioxane (3.0 mL) afforded (*S*)-**3qj** (273.1 mg, 92%) (eluent: petroleum ether (b.p. 30-60 °C) to petroleum ether (b.p. 30-60 °C)/ethyl ether = 150/1) as a solid: M.P. 73-74 °C (petroleum ether/DCM); 97:3 e.r. (HPLC conditions: OJ-H column, hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (minor) = 10.2 min, t_R (major) =17.0 min); $[\alpha]^{20}_D$ = +457.0° (*c* = 0.99, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.38-7.32 (m, 2 H, Ar-H), 7.29-7.22 (m, 4 H, Ar-H), 6.89-6.84 (m, 2 H, Ar-H), 6.48 (t, *J* = 3.0 Hz, 1 H, C=C=CH), 6.02-5.90 (m, 1 H, =CH), 5.23-5.16 (m, 1 H, one proton from $=CH_2$), 5.10-5.05 (m, 1 H, one proton from $=CH_2$), 3.80 (s, 3 H, CH_3), 3.38-3.24 (m, 2 H,

=CCH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.5, 158.9, 135.4, 133.1, 132.5, 128.8, 127.9, 127.4, 127.3, 116.6, 114.0, 108.2, 97.1, 55.3, 34.9; IR (neat, cm^{-1}): 1934, 1642, ,1604, 1511, 1488, 1291, 1249, 1200, 1084, 1031; MS (70 eV, EI) *m/z* (%): 298 (M^+(^{37}Cl), 20.91), 296 (M^+(^{35}Cl), 63.23), 255 (100); Anal. Calcd for $C_{19}H_{17}ClO$: C 76.89, H 5.77; Found: C 76.88, H 5.74.

3. (*S*)-1-Phenyl-3-(4-methoxylphenyl)-5-methylhexa-1,2,5-triene ((*S*)-3rj) (Scheme 5) (lhw-14-151)



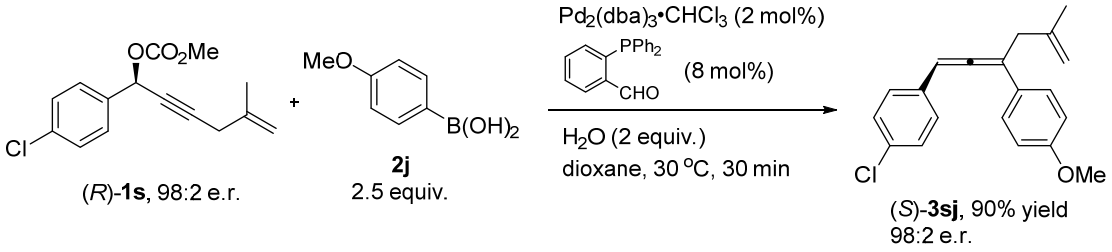
(*R*)-**1r**, 95:5 e.r.

(*S*)-**3rj**, 86% yield
8% recovery
95:5 e.r.

Following **Typical Procedure B**, the reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.8 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.8 mg, 0.08 mmol), (*R*)-**1r** (245.9 mg, 1.0 mmol, 95:5 e.r.), **2j** (379.3 mg, 2.5 mmol), and H_2O (36 μL, 2.0 mmol) in dioxane (3.0 mL) afforded (*S*)-**3rj** (238.4 mg, 86%) (eluent: petroleum ether (b.p. 30-60 °C) to petroleum ether (b.p. 30-60 °C)/ethyl ether = 100/1) as a liquid: 95:5 e.r. (HPLC conditions: OJ-H column, hexane/*i*-PrOH = 100/1, 1.0 mL/min, λ = 214 nm, t_R (minor) = 11.8 min, t_R (major) =13.3 min); $[\alpha]^{20}_D$ = +410.2° (*c* = 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41-7.27 (m, 6 H, Ar-H), 7.23-7.17 (m, 1 H, Ar-H), 6.87-6.82 (m, 2 H, Ar-H), 6.50 (t, *J* = 2.0 Hz, 1 H, C=C=CH), 4.90 (s, 1 H, one proton from =CH_2), 4.86 (s, 1 H, one proton from =CH_2), 3.78 (s, 3 H, OCH_3), 3.34-3.22 (m, 2 H,

=CCH_2) , 1.80 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.0, 158.7, 143.0, 134.6, 128.7, 127.8, 127.4, 126.9, 126.8, 113.8, 112.6, 106.8, 96.9, 55.2, 39.7, 22.5; IR (neat, cm^{-1}): 1932, 1650, 1603, 1577, 1509, 1245, 1176, 1033; MS (70 eV, EI) *m/z* (%): 276 (M^+, 7.30), 135 (100); HRMS Calcd for $C_{20}H_{20}O$ (M^+): 276.1514, Found: 276.1512.

4. (*S*)-1-(4-Chlorophenyl)-3-(4-methoxylphenyl)-5-methylhexa-1,2,5-triene ((*S*)-3sj) (Scheme 5) (lhw-14-149)

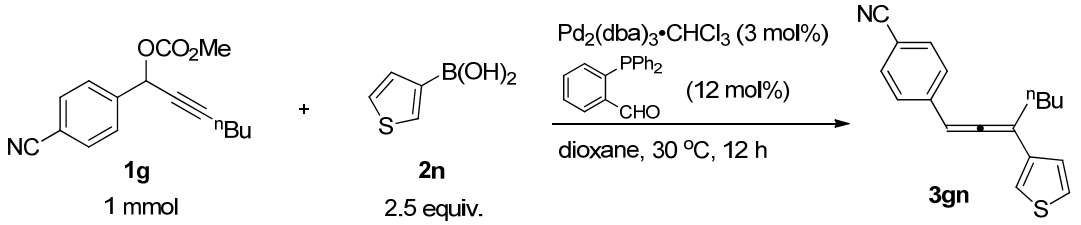


Following **Typical Procedure B**, the reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (20.8 mg, 0.02 mmol), *o*-(diphenylphosphino)benzaldehyde (23.4 mg, 0.08 mmol), (*R*)-**1s** (278.6 mg, 1.0 mmol, 98:2 e.r.), **2j** (379.0 mg, 2.5 mmol), and H_2O (36 μL, 2.0 mmol) in dioxane (3.0 mL) afforded (*S*)-**3sj** (280.3 mg, 90%) (eluent: petroleum ether (b.p. 30-60 °C) to petroleum ether (b.p. 30-60 °C)/ethyl ether = 100/1) as a liquid: 98:2 e.r. (HPLC conditions: OJ-H column, hexane/*i*-PrOH = 100/1, 1.0 mL/min, λ = 214 nm, t_R (minor) = 14.3 min, t_R (major) =16.7 min); $[\alpha]^{20}_D$ = +451.8° (*c* = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38-7.33 (m, 2 H, Ar-H), 7.29-7.23 (m, 4 H, Ar-H), 6.88-6.82 (m, 2 H, Ar-H), 6.46 (t, *J* = 2.6 Hz, 1 H, C=C=CH), 4.89 (s, 1 H, one proton from =CH_2), 4.86 (s, 1 H, one proton from =CH_2), 3.79 (s, 3 H, OCH_3), 3.33-3.21 (m, 2 H, =CCH_2) , 1.78 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.1, 158.8, 142.8,

133.1, 132.5, 128.8, 128.0, 127.5, 127.4, 113.9, 112.7, 107.3, 96.1, 55.2, 39.6, 22.5; IR (neat, cm^{-1}): 1931, 1650, 1605, 1509, 1489, 1246, 1176, 1089, 1034, 1012; MS (70 eV, EI) *m/z* (%): 312 (M^+(^{37}Cl), 6.82), 310 (M^+(^{35}Cl), 19.91), 135 (100); HRMS Calcd for $C_{20}H_{19}{}^{35}ClO$ (M^+): 310.1124, Found: 310.1118.

Coupling with heteroaryl boronic acids

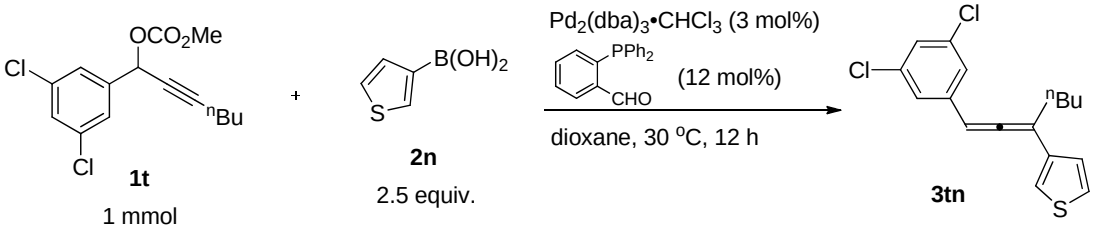
1. 1-(4-Cyanophenyl)-3-(thiophen-3-yl)hepta-1,2-diene (3gn) (Table 3, entry 1) (lhw-14-123)



According to **Typical Procedure A,** the reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (31.3 mg, 0.03 mmol), *o*-(diphenylphosphino)benzaldehyde (35.3 mg, 0.12 mmol), **1g** (271.5 mg, 1.0 mmol), and **2n** (326.0 mg, 2.5 mmol) in dioxane (2.0 mL) afforded **3gn** (146.9 mg, 52%) (eluent: petroleum ether (b.p. 30-60 °C)/ethyl ether = 100/1) as a solid: M.P. 89-91 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.39 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.29-7.24 (m, 1 H, Ar-H), 7.22-7.18 (m, 1 H, Ar-H), 7.07 (dd, J_1 = 5.0 Hz, J_2 = 1.0 Hz, 1 H, Ar-H), 6.50 (t, *J* = 3.0 Hz, 1 H, =CH), 2.62-2.47 (m, 2 H, =CCH_2), 1.67-1.48 (m, 2 H, CH_2), 1.48-1.36 (m, 2 H, CH_2), 0.92 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.3, 139.9, 136.6, 132.5, 127.2, 126.5, 125.8, 120.1, 119.1, 110.1, 107.1, 96.7, 30.4, 29.9, 22.6, 13.9; IR (neat, cm^{-1}): 2221, 1931, 1603, 1500, 1465, 1414, 1382,

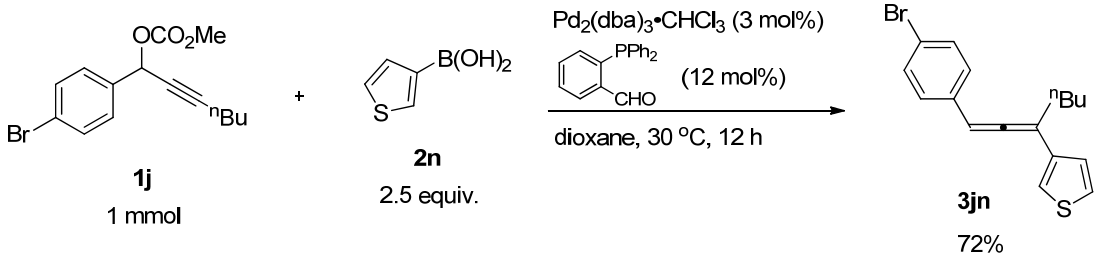
1234, 1204, 1173, 1108, 1083; MS (70 eV, EI) *m/z* (%): 279 (M^+, 31.40), 237 (100); Anal. Calcd for $C_{18}H_{17}NS$: C 77.38, H 6.13, N 5.01; Found: C 77.40, H 6.11, N 4.79.

2. 1-(3,5-Dichlorophenyl)-3-(thiophen-3-yl)hepta-1,2-diene (3tn) (Table 3, entry 2) (lhw-14-121)



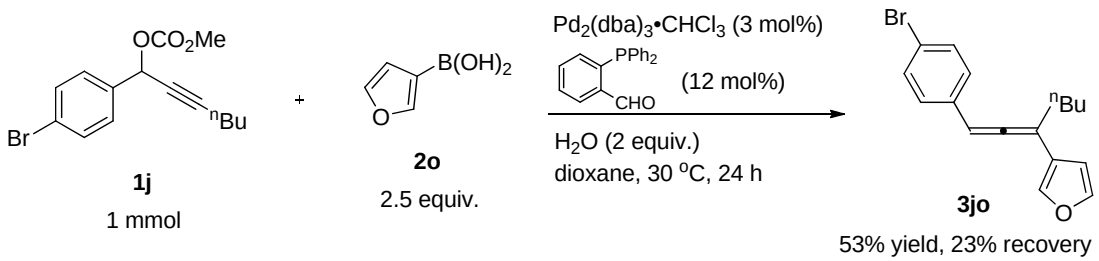
According to **Typical Procedure A,** the reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (31.0 mg, 0.03 mmol), *o*-(diphenylphosphino)benzaldehyde (35.0 mg, 0.12 mmol), **1t** (318.0 mg, 1.0 mmol), and **2n** (327.1 mg, 2.5 mmol) in dioxane (2.0 mL) afforded **3tn** (208.5 mg, 96% purity, 61%) (first round: petroleum ether (b.p. 30-60 °C), second round: petroleum ether (b.p. 30-60 °C)) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.25 (m, 1 H, Ar-H), 7.21-7.15 (m, 4 H, Ar-H), 7.09 (dd, J_1 = 5.0 Hz, J_2 = 1.0 Hz, 1 H, Ar-H), 6.37 (t, J = 2.8 Hz, 1 H, =CH), 2.61-2.46 (m, 2 H, =CCH_2), 1.66-1.49 (m, 2 H, CH_2), 1.48-1.37 (m, 2 H, CH_2), 0.93 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.3, 138.2, 136.9, 135.2, 126.8, 126.7, 125.7, 125.0, 120.1, 107.2, 95.8, 30.4, 29.9, 22.6, 13.9; IR (neat, cm^{-1}): 2956, 2927, 1933, 1582, 1562, 1430, 1377, 1232, 1199, 1112, 1101; MS (70 eV, EI) *m/z* (%): 326 (M^+(^{37}Cl, ^{37}Cl), 3.34), 324 (M^+(^{35}Cl, ^{37}Cl), 15.64), 322 (M^+(^{35}Cl, ^{35}Cl), 22.94), 245 (100); HRMS Calcd for $C_{17}H_{16}{}^{35}Cl_2S$ (M^+): 322.0350, Found: 322.0354.

3. 1-(4-Bromophenyl)-3-(thiophen-3-yl)hepta-1,2-diene (3jn) (Table 3, entry 3) (lhw-14-120)



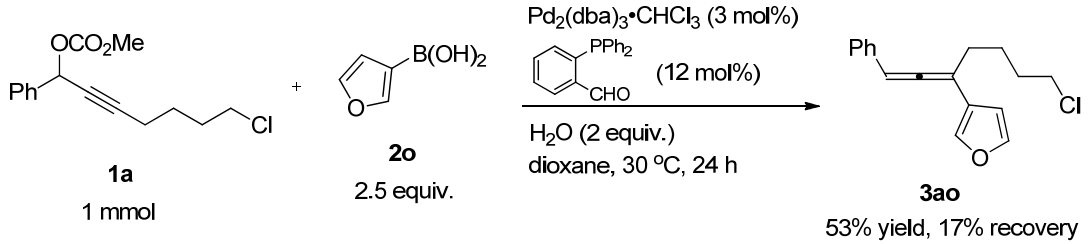
According to **Typical Procedure A,** the reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (31.2 mg, 0.03 mmol), *o*-(diphenylphosphino)benzaldehyde (35.1 mg, 0.12 mmol), **1j** (325.5 mg, 1.0 mmol), and **2n** (326.0 mg, 2.5 mmol) in dioxane (2.0 mL) afforded **3jn** (245.5 mg, 98% purity, 72%) (first round: petroleum ether (b.p. 30-60 °C), second round: petroleum ether (b.p. 30-60 °C)) as a solid: M.P. 50-52 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45-7.39 (m, 2 H, Ar-H), 7.27-7.22 (m, 1 H, Ar-H), 7.21-7.15 (m, 3 H, Ar-H), 7.07 (dd, J_1 = 5.0 Hz, J_2 = 1.0 Hz, 1 H, Ar-H), 6.43 (t, J = 2.8 Hz, 1 H, =CH), 2.59-2.44 (m, 2 H, =CCH_2), 1.66-1.49 (m, 2 H, CH_2), 1.47-1.36 (m, 2 H, CH_2), 0.91 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.7, 137.5, 133.7, 131.7, 128.3, 126.8, 125.5, 120.6, 119.6, 106.6, 96.7, 30.5, 30.0, 22.6, 13.9; IR (neat, cm^{-1}): 2957, 2923, 1931, 1485, 1464, 1228, 1200, 1068, 1011; MS (70 eV, EI) *m/z* (%): 334 (M^+(^{81}Br), 2.05), 332 (M^+(^{79}Br), 2.05), 237 (100); Anal. Calcd for $C_{17}H_{17}BrS$: C 61.26, H 5.14; Found: C 61.21, H 5.15.

4. 1-(4-Bromophenyl)-3-(furan-3-yl)hepta-1,2-diene (3jo) (Table 3, entry 4) (lhw-14-170)



Typical Procedure C: To a flame-dried Schlenk tube were added $Pd_2(dba)_3 \cdot CHCl_3$ (31.1 mg, 0.03 mmol), *o*-(diphenylphosphino)benzaldehyde (35.1 mg, 0.12 mmol), and **2o** (291.4 mg, 2.5 mmol) under argon atmosphere. After replacing air with argon for three times at rt under vacuum, **1j** (325.7 mg, 1.0 mmol)/dioxane (2.0 mL) and H_2O (36 μL, 2.0 mmol) was added sequentially. The resulting mixture was stirred for 24 h at 30 °C and then passed through a short pad of silica gel with Et_2O (20 mL) as eluent. After removal of the solvent under vacuum, 23% of **1j** was detected by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as the internal standard. The residue was purified by flash chromatography on silica gel to afford **3jo** (176.3 mg, 95% purity, 53%) (eluent: petroleum ether (b.p. 30-60 °C) to petroleum ether (b.p. 30-60 °C)/ethyl ether = 200/1) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.46-7.39 (m, 3 H, Ar-H), 7.35 (t, *J* = 1.8 Hz, 1 H, Ar-H), 7.20-7.14 (m, 2 H, Ar-H), 6.39 (t, *J* = 2.8 Hz, 1 H, =CH), 6.36-6.34 (m, 1 H, Ar-H), 2.46-2.32 (m, 2 H, $=CCH_2$), 1.65-1.48 (m, 2 H, CH_2), 1.46-1.34 (m, 2 H, CH_2), 0.90 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.4, 143.3, 138.5, 133.8, 131.7, 128.3, 122.4, 120.6, 109.2, 103.3, 96.6, 30.3, 29.9, 22.5, 13.9; IR (neat, cm^{-1}): 2956, 2927, 2859, 1934, 1486, 1154, 1070, 1036, 1009; MS (70 eV, EI) *m/z* (%): 318 (M^+(^{81}Br), 13.18), 316 (M^+(^{79}Br), 13.18), 165 (100); HRMS Calcd for $C_{17}H_{17}{}^{79}BrO$ (M^+): 316.0463, Found: 316.0461.

1-Phenyl-3-(furan-3-yl)-7-chlorohepta-1,2-diene (3jo) (Table 3, entry 5) (lhw-14-169)



According to **Typical Procedure C,** the reaction of $Pd_2(dba)_3 \cdot CHCl_3$ (31.0 mg, 0.03 mmol), *o*-(diphenylphosphino)benzaldehyde (35.2 mg, 0.12 mmol), **1a** (279.6 mg, 1.0 mmol), **2o** (291.0 mg, 2.5 mmol), and H_2O (36 μL, 2.0 mmol) in dioxane (2.0 mL) afforded **3ao** (149.0 mg, 97% purity, 53%) (eluent: petroleum ether (b.p. 30-60 ^oC) to petroleum ether (b.p. 30-60 ^oC)/ethyl ether = 200/1) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.46-7.43 (m, 1 H, Ar-H), 7.38-7.35 (m, 1 H, Ar-H), 7.34-7.28 (m, 4 H, Ar-H), 7.26-7.19 (m, 1 H, Ar-H), 6.48 (t, *J* = 2.6 Hz, 1 H, =CH), 6.40-6.37 (m, 1 H, Ar-H), 3.53 (t, *J* = 6.4 Hz, 2 H, $ClCH_2$), 2.51-2.36 (m, 2 H, $=CCH_2$), 1.96-1.65 (m, 4 H, $CH_2 \times 2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.0, 143.3, 138.4, 134.4, 128.7, 127.1, 126.8, 122.5, 109.2, 102.2, 97.8, 44.8, 32.2, 29.8, 24.9; IR (neat, cm^{-1}): 1936, 1597, 1494, 1457, 1155, 1068, 1027; MS (70 eV, EI) *m/z* (%): 274 ($M^+(^{37}Cl)$, 10.28), 272 ($M^+(^{35}Cl)$, 25.31), 152 (100); HRMS Calcd for $C_{17}H_{17}{}^{35}ClO$ (M^+): 272.0968, Found: 272.0971.

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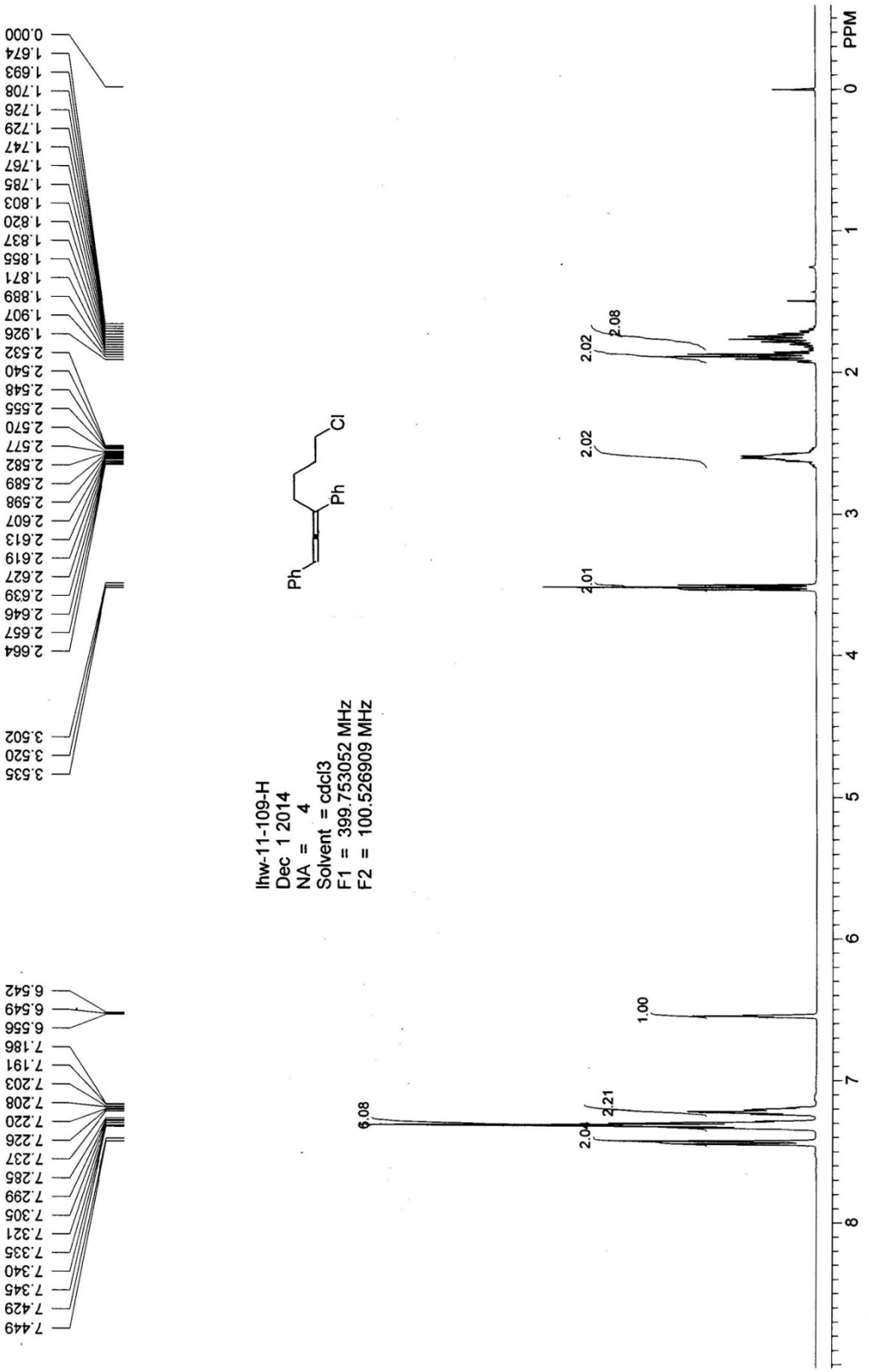
3aa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Dec 1 2014
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F2 = 100.526909 MHz
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Ph
Cl
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1.747
1.767
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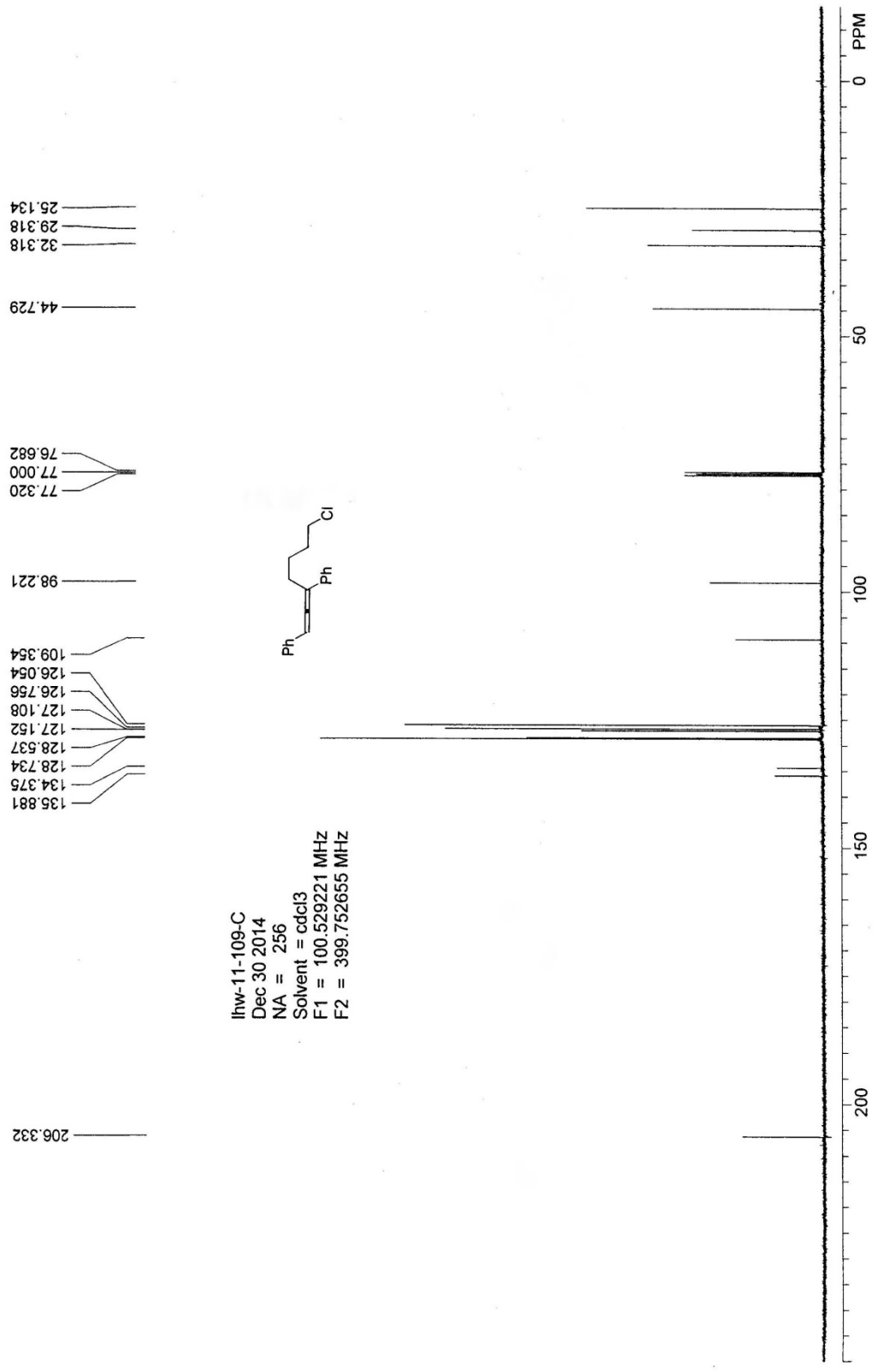
2.08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Dec 30 2014
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PPM

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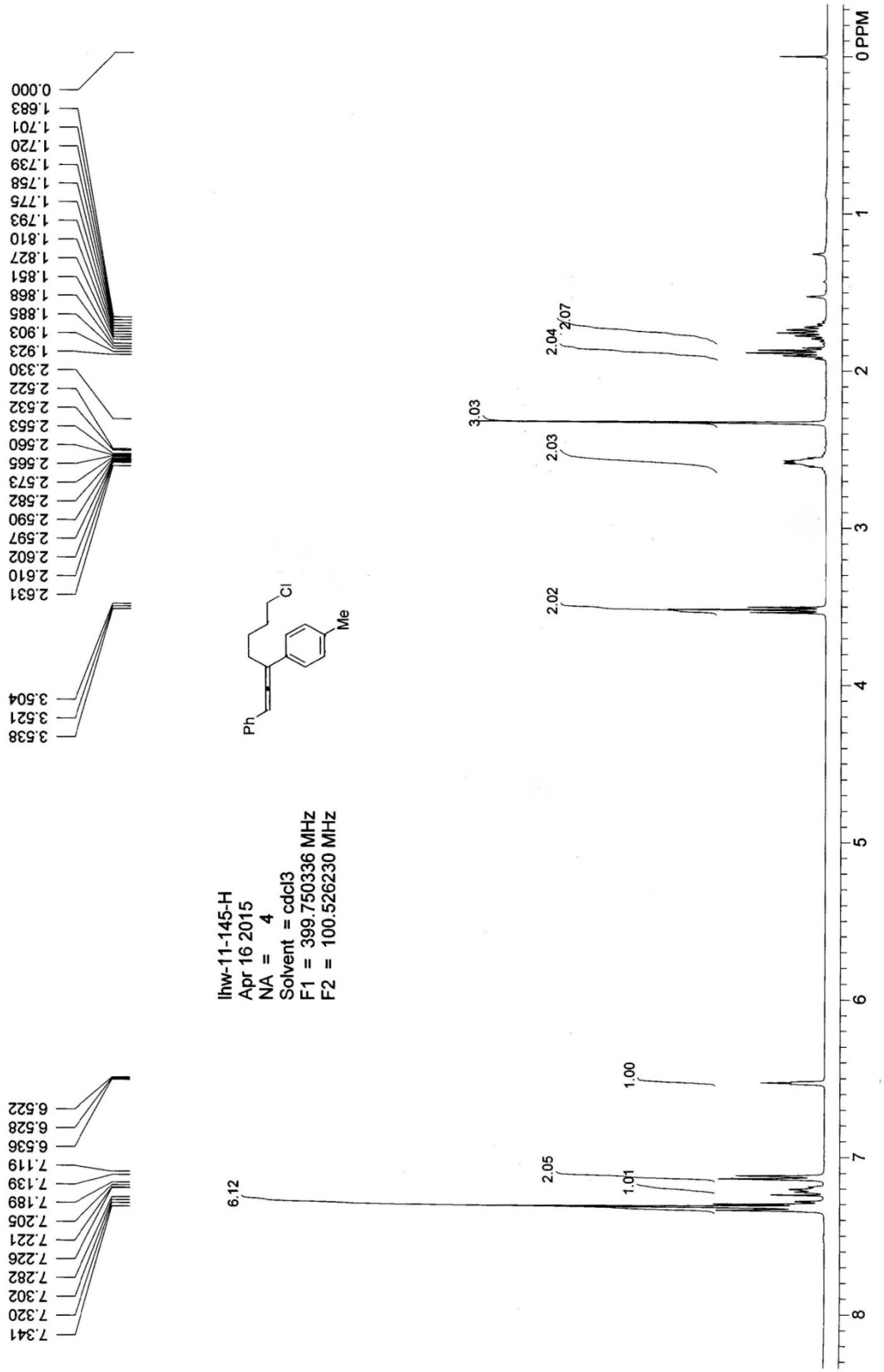
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Apr 16 2015
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Ph
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1.775
1.793
1.810
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7.139
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2.07
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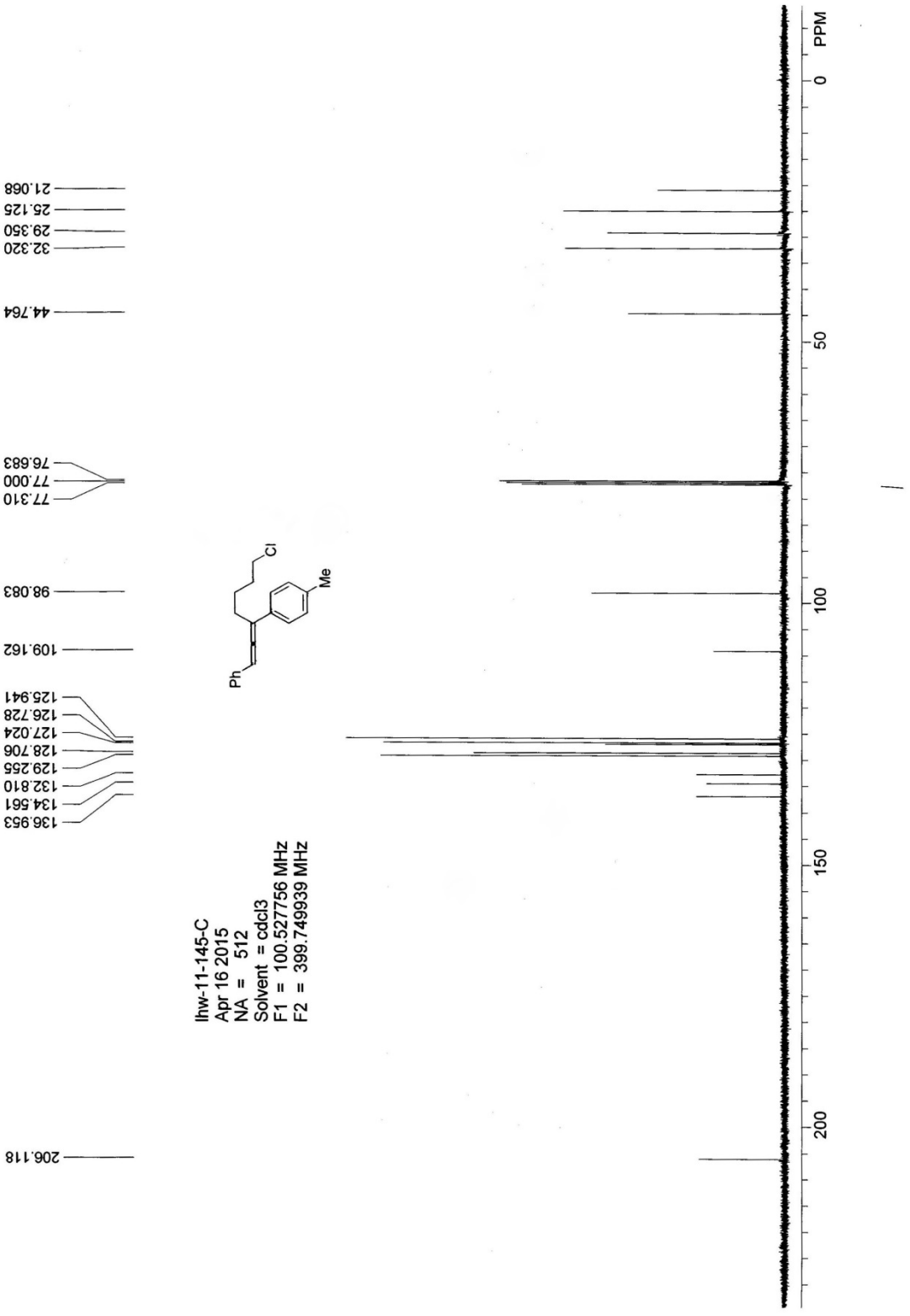
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Apr 16 2015
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127.024
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109.162
98.083
77.310
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150
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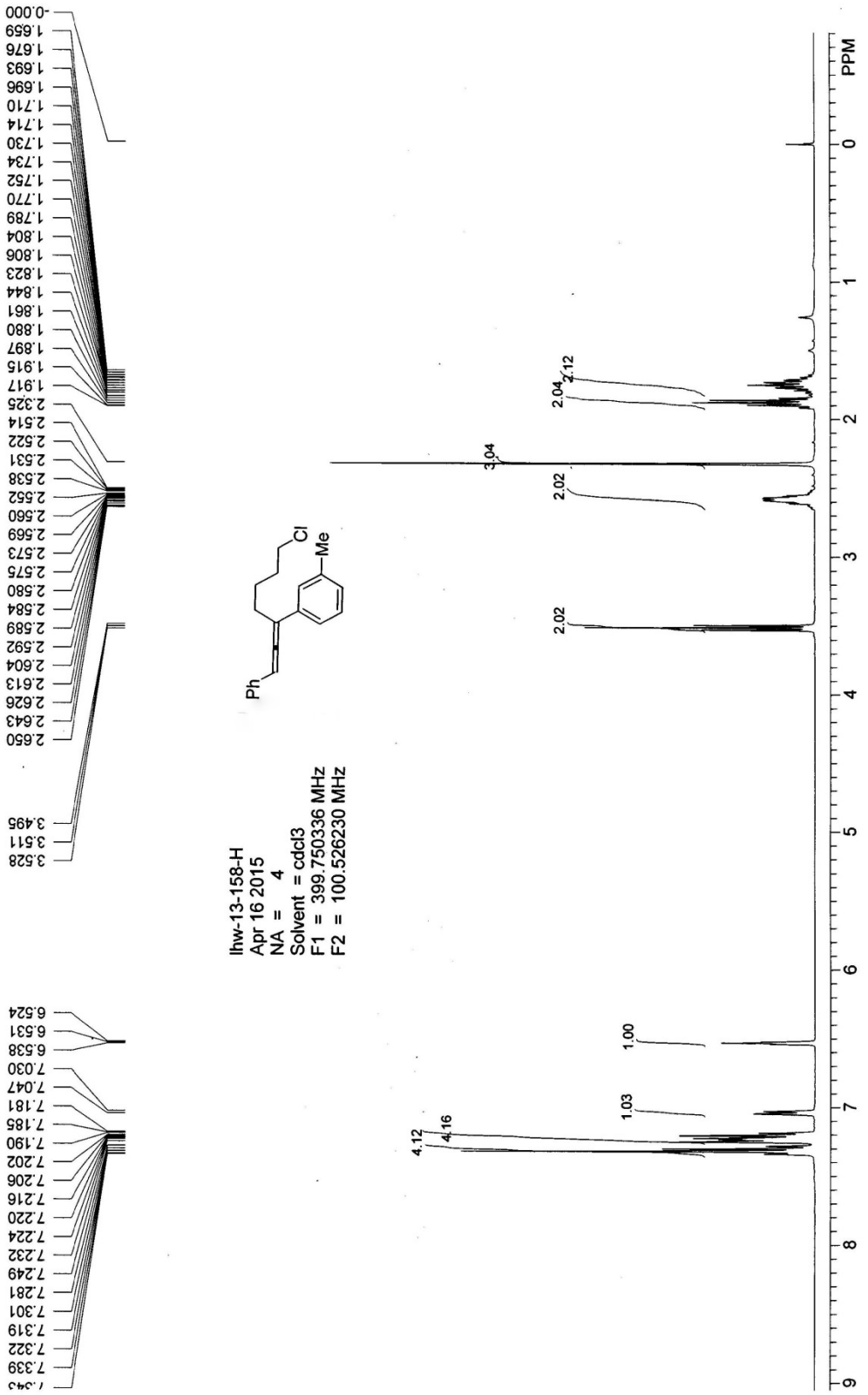
3ac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Apr 16 2015
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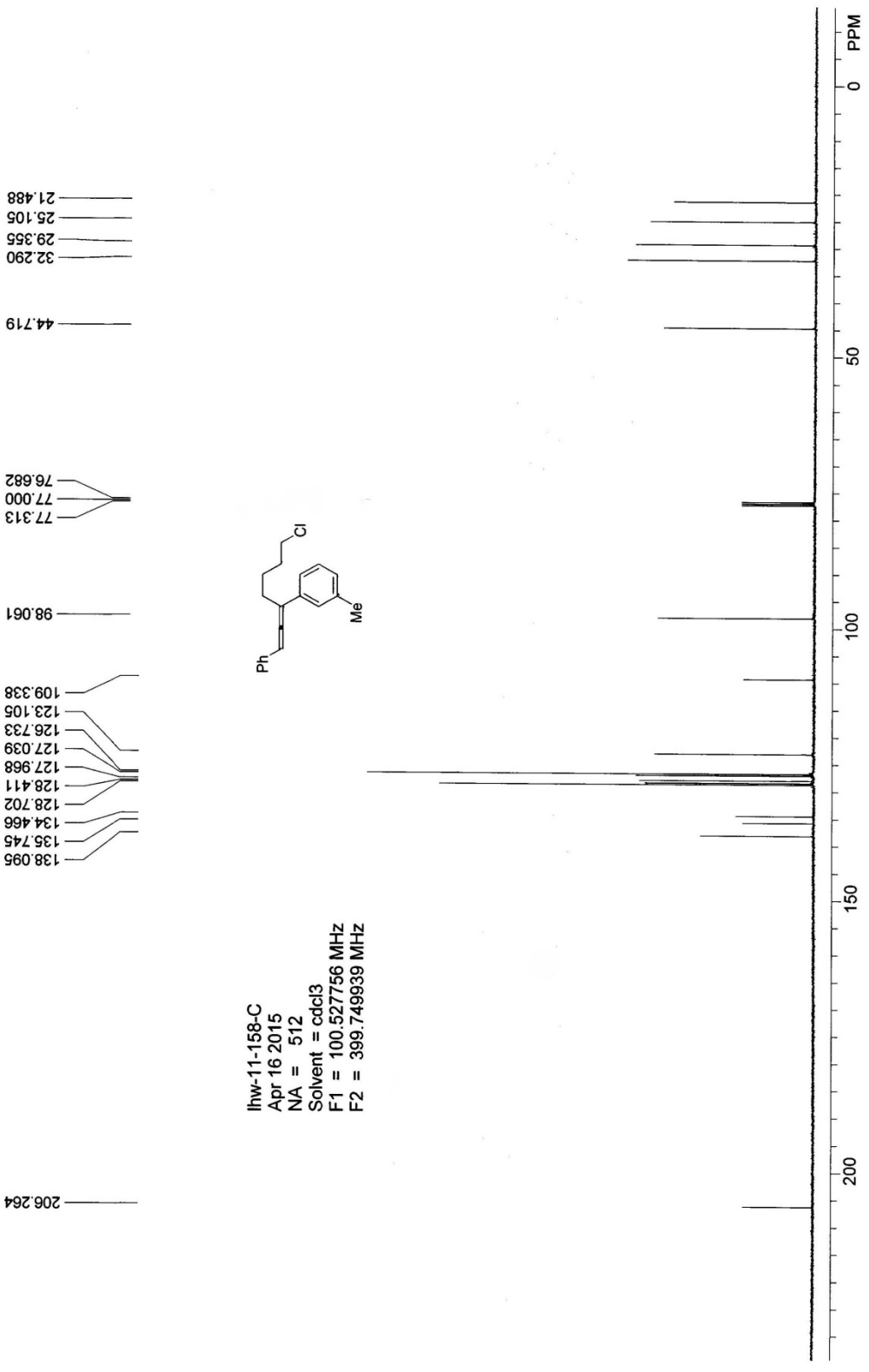
F1 = 399.750336 MHz
F2 = 100.526230 MHz
Cl
Me
Ph
PPM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Apr 16 2015
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F2 = 399.749939 MHz
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Ph
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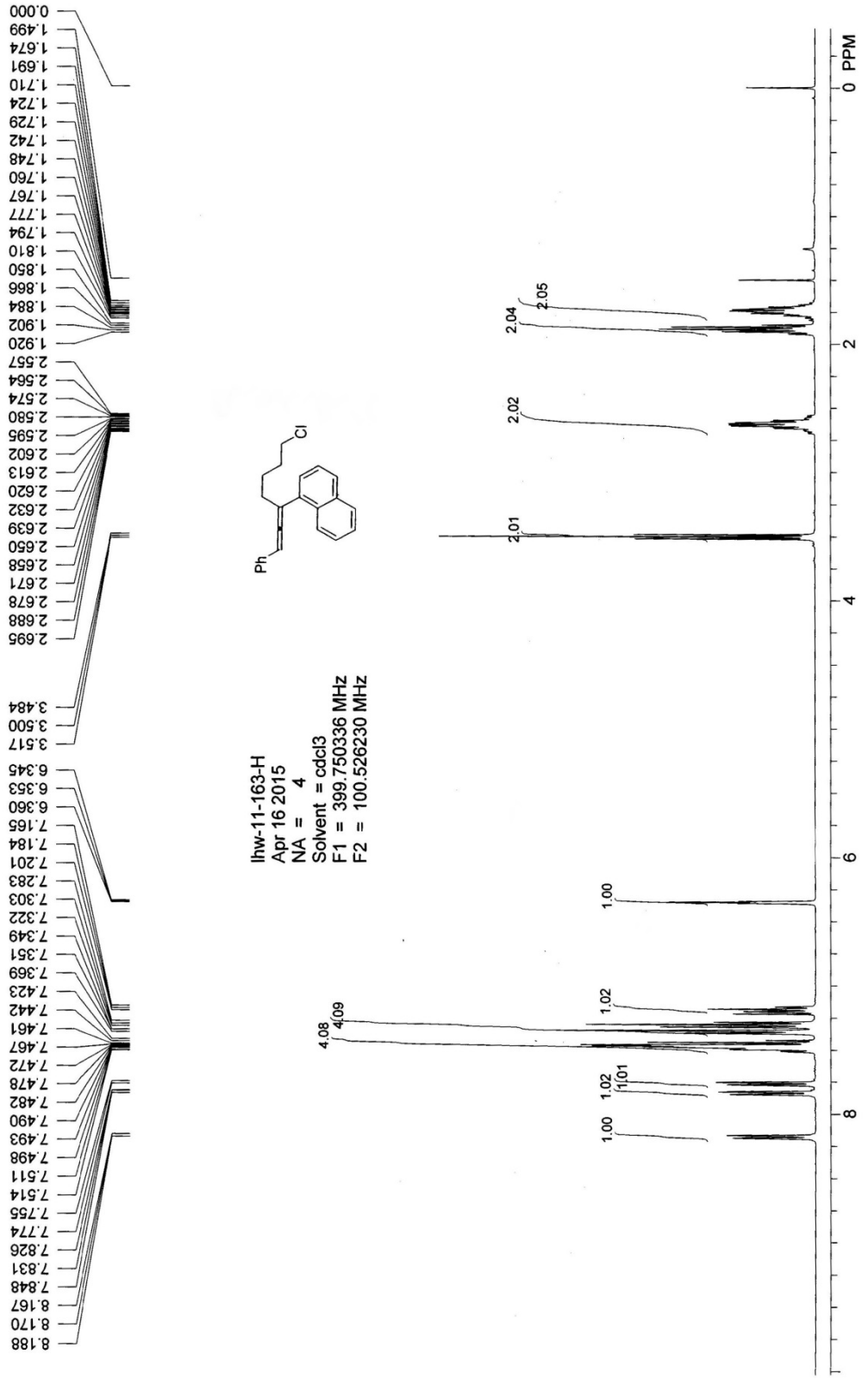
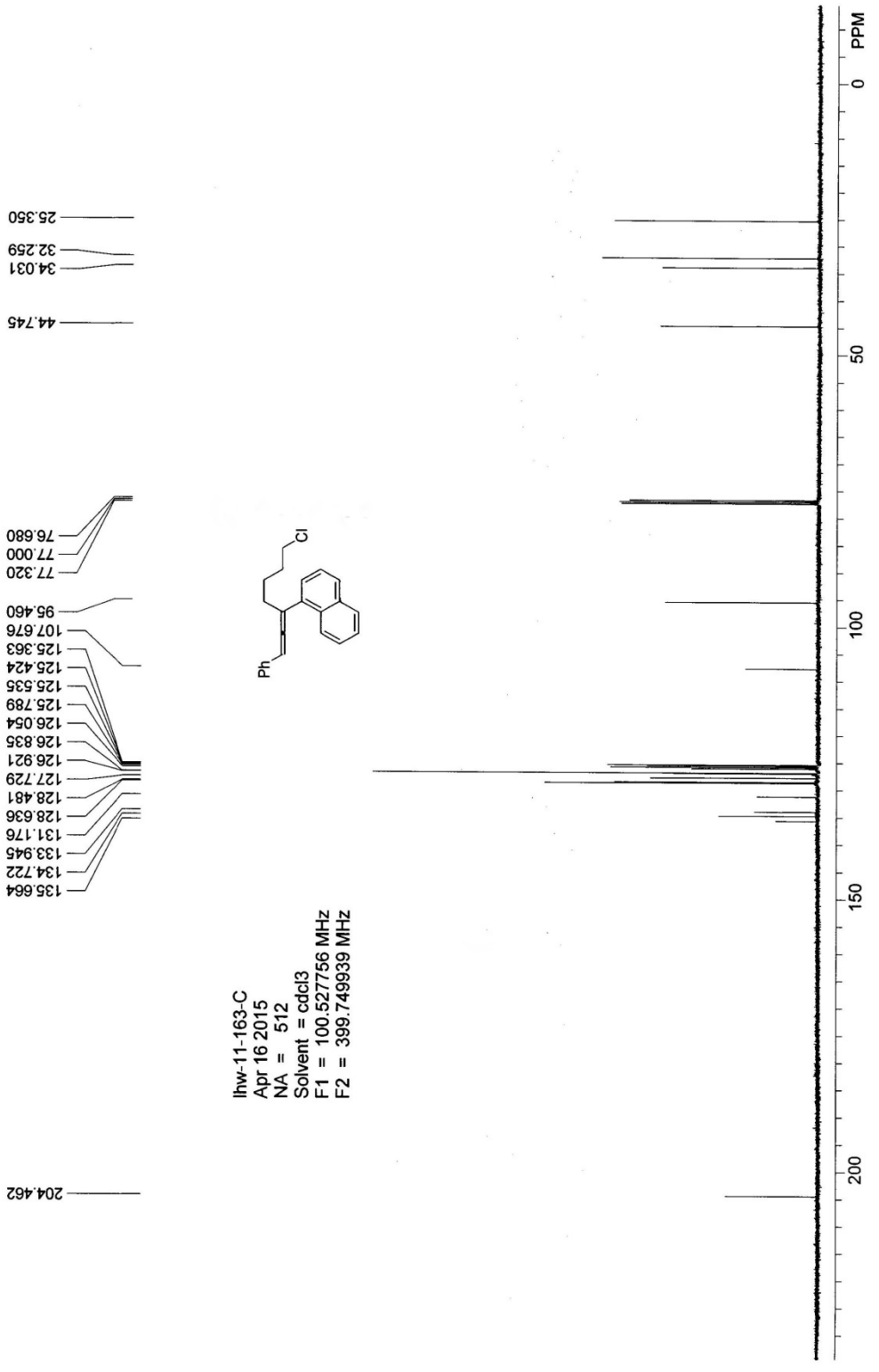
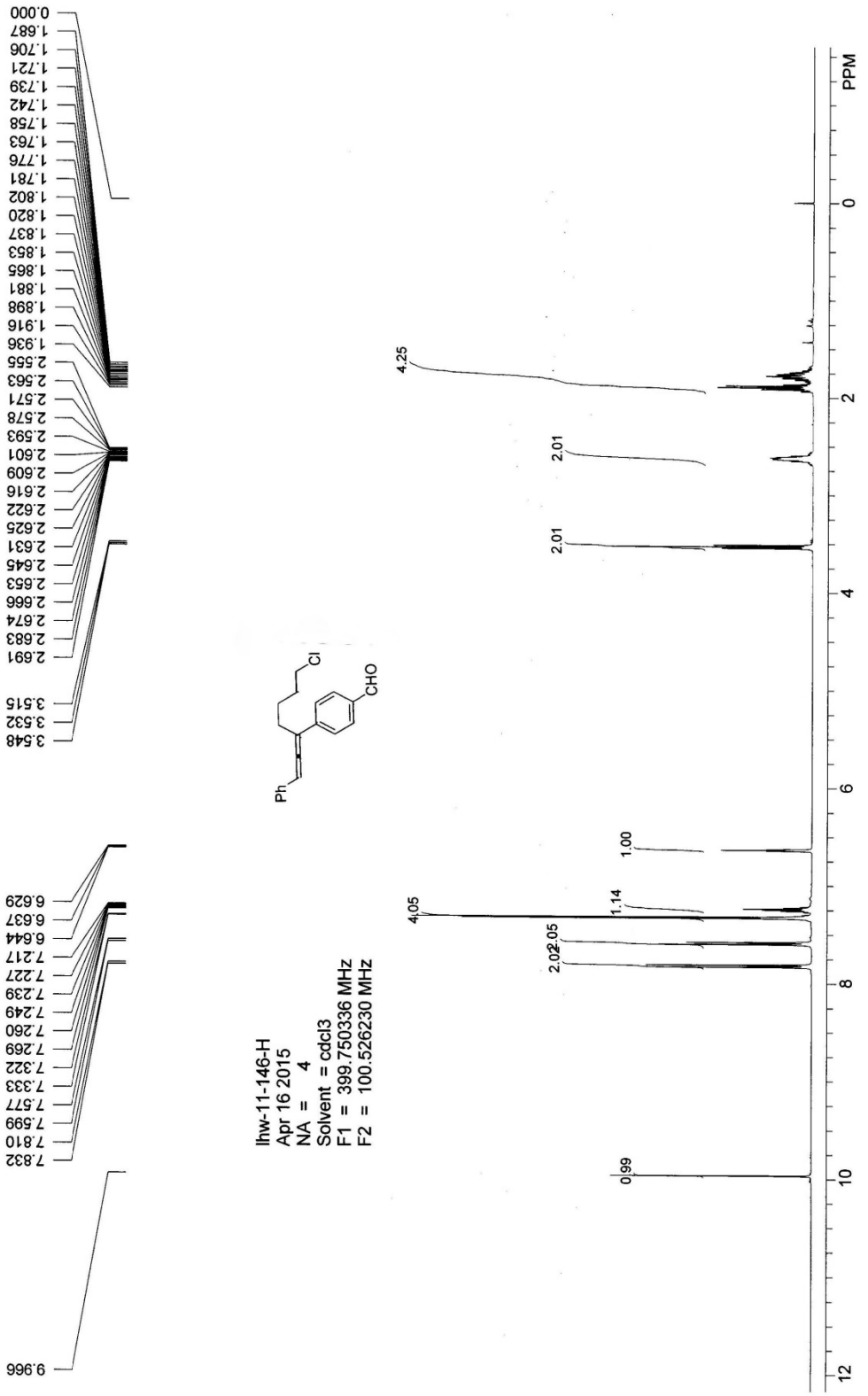
134.466
128.702
128.411
127.968
127.039
126.733
123.105
109.338
98.061
77.313
77.000
76.682
44.719
32.290
29.355
25.105
21.488
PPM
0
50
100
150
200

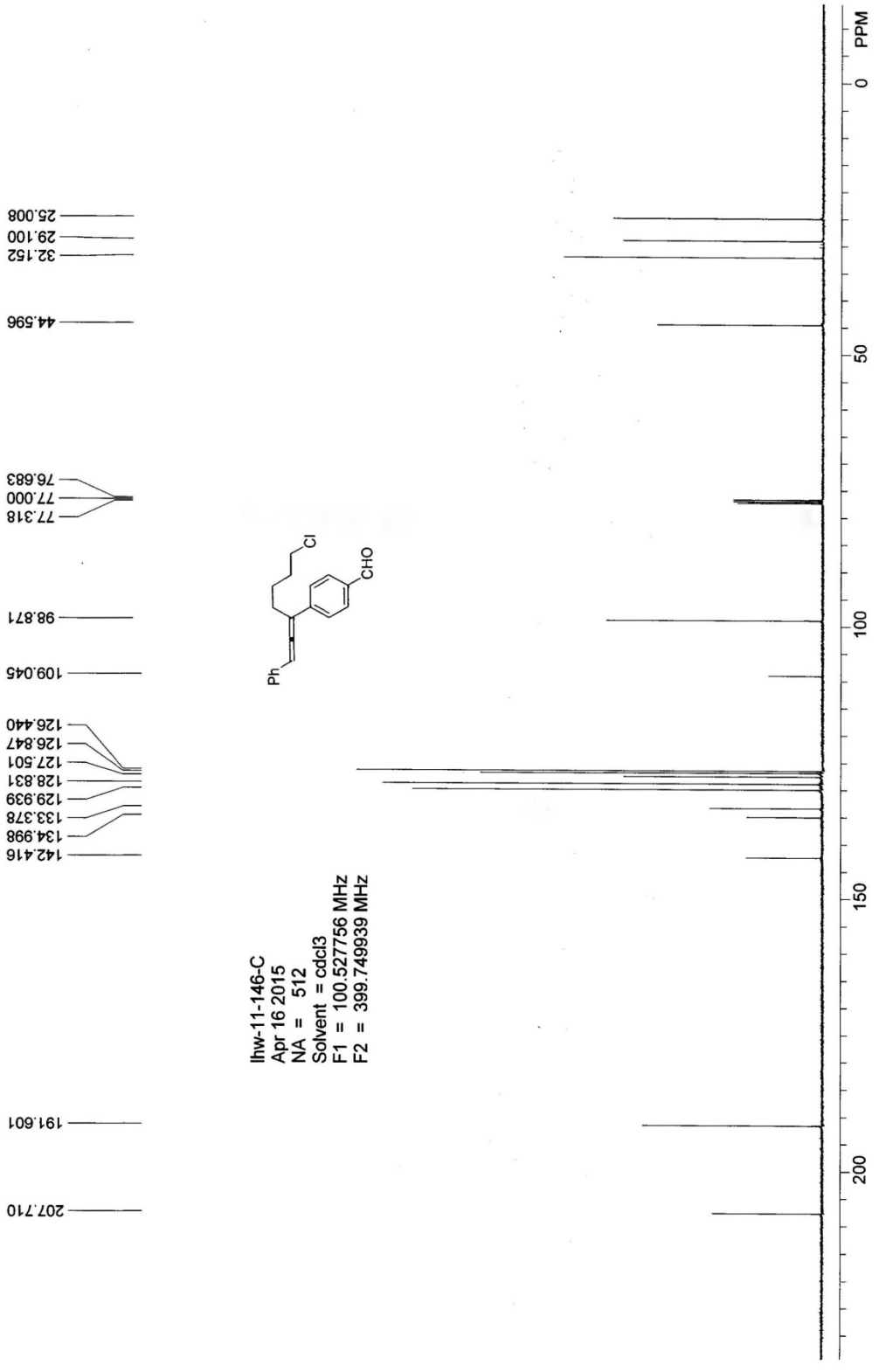
3ad


lhw-11-163-H
Apr 16 2015
NA = 4
Solvent = cdcl3
F1 = 399.750336 MHz
F2 = 100.526230 MHz
Cl
Ph
0 PPM
2
4
6
8

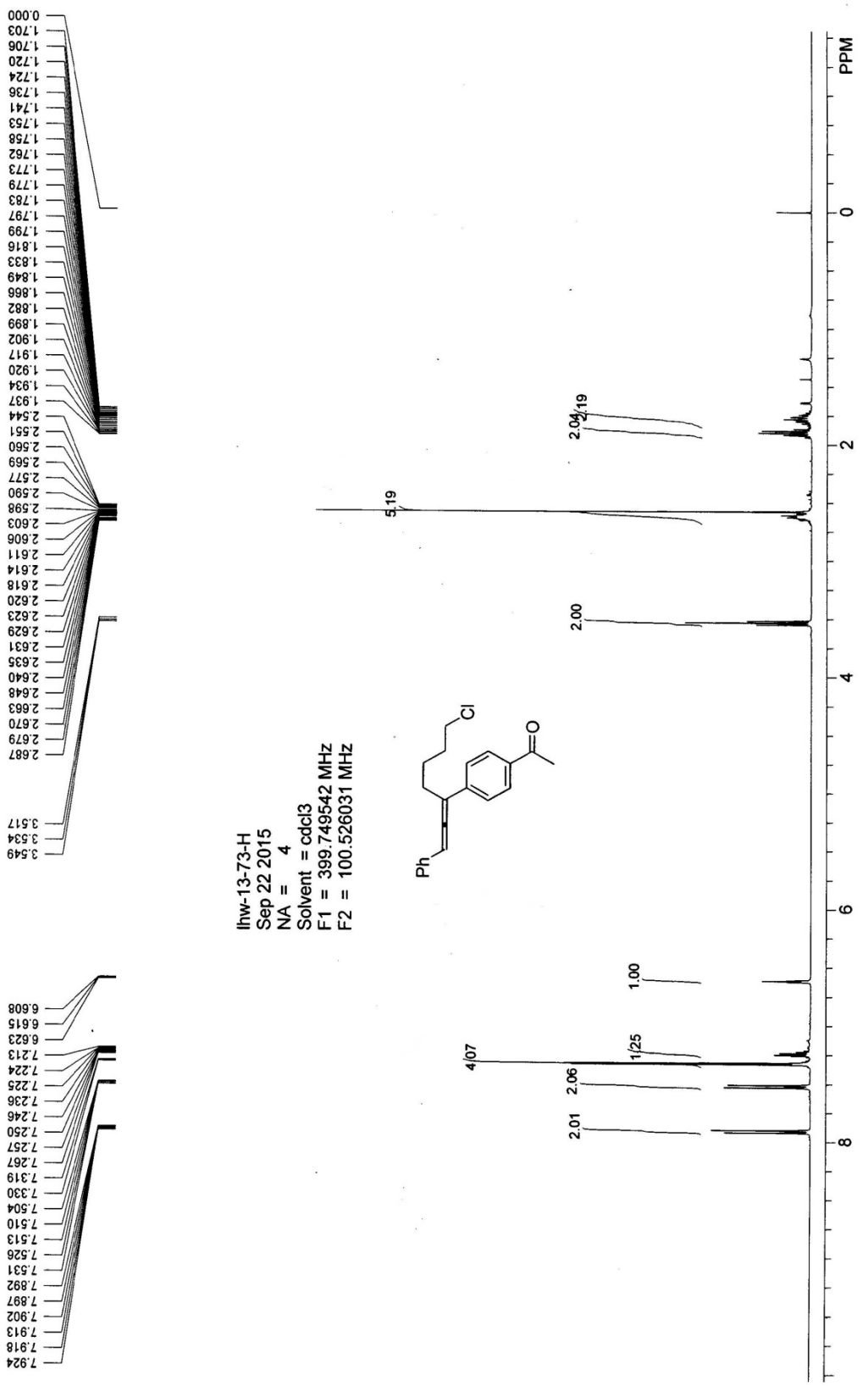

lhw-11-163-C
Apr 16 2015
NA = 512
Solvent = cdcl3
F1 = 100.527756 MHz
F2 = 399.749939 MHz
Cl
Ph
204.462
135.664
134.722
133.945
131.176
128.636
128.481
127.729
126.921
126.835
126.054
125.789
125.535
125.424
125.363
107.676
95.460
77.320
77.000
76.680
44.745
34.031
32.259
25.350
PPM
0
50
100
150
200

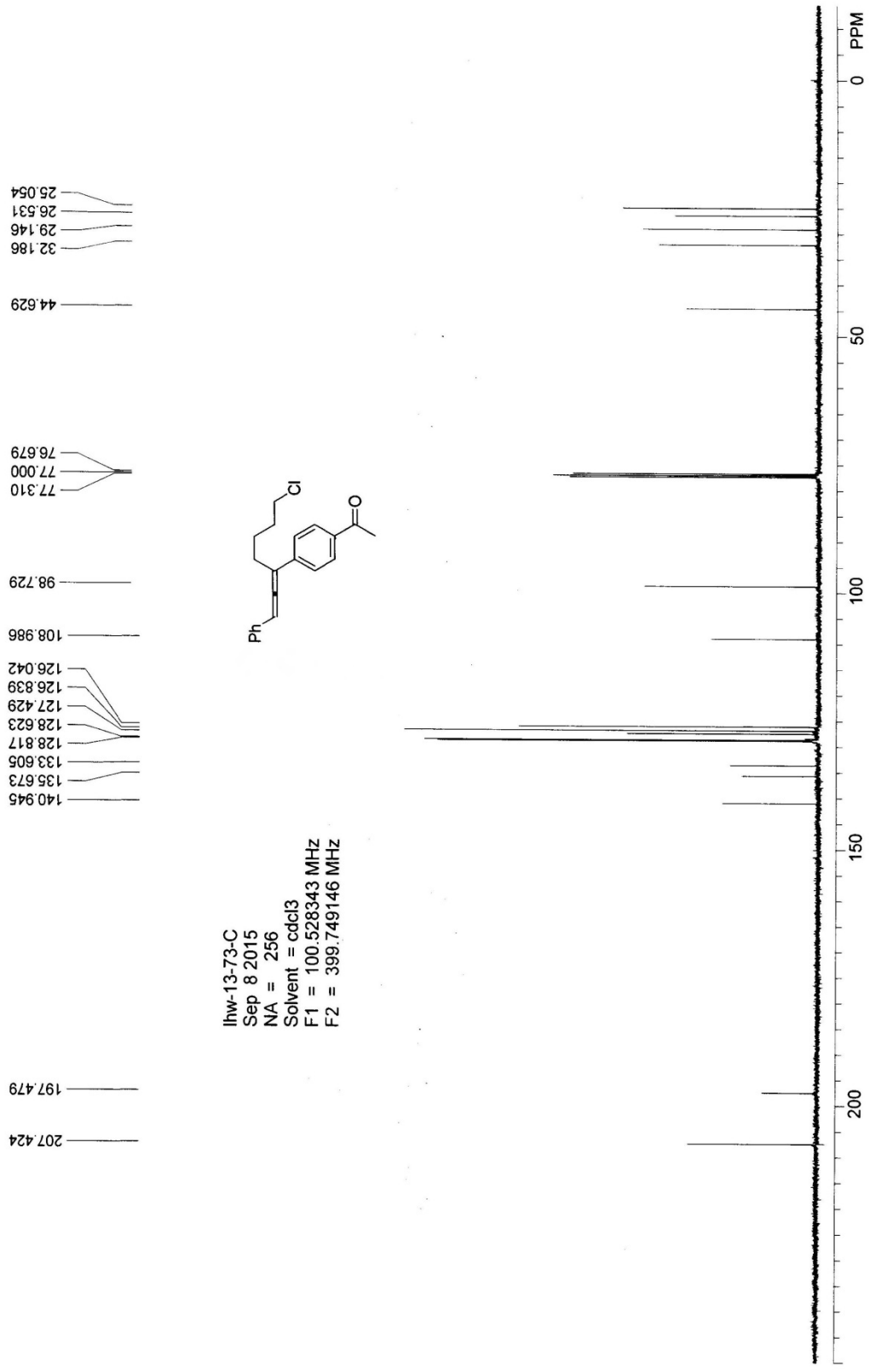
3ae


0.000
1.687
1.706
1.721
1.739
1.742
1.758
1.763
1.776
1.781
1.802
1.820
1.837
1.853
1.865
1.881
1.898
1.916
1.936
2.555
2.563
2.571
2.578
2.593
2.601
2.609
2.616
2.622
2.625
2.631
2.645
2.653
2.666
2.674
2.683
2.691
3.515
3.532
3.548
6.629
6.637
6.644
7.217
7.227
7.239
7.249
7.260
7.269
7.322
7.333
7.577
7.599
7.810
7.832
9.966
Cl
CHO
Ph
lhw-11-146-H
Apr 16 2015
NA = 4
Solvent = cdcl3
F1 = 399.750336 MHz
F2 = 100.526230 MHz
4.25
2.01
2.01
1.00
4.05
1.14
2.02
2.05
0.99
PPM
0
2
4
6
8
10
12

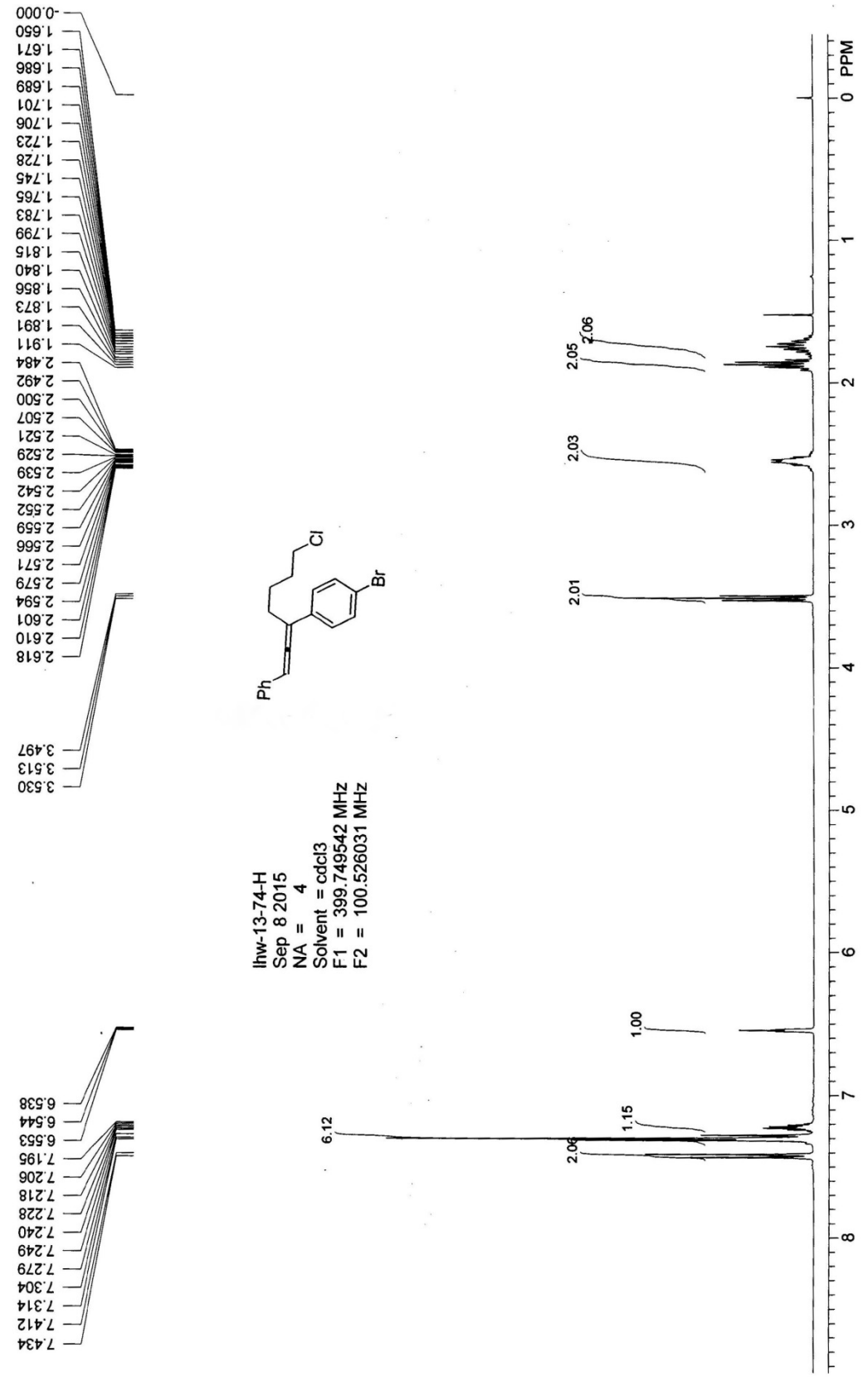

lhw-11-146-C
Apr 16 2015
NA = 512
Solvent = cdcl3
F1 = 100.527756 MHz
F2 = 399.749939 MHz
Cl
CHO
Ph
207.710
191.601
142.416
134.998
133.378
129.939
128.831
127.501
126.847
126.440
109.045
98.871
77.318
77.000
76.683
44.596
32.152
29.100
25.008
PPM
0
50
100
150
200

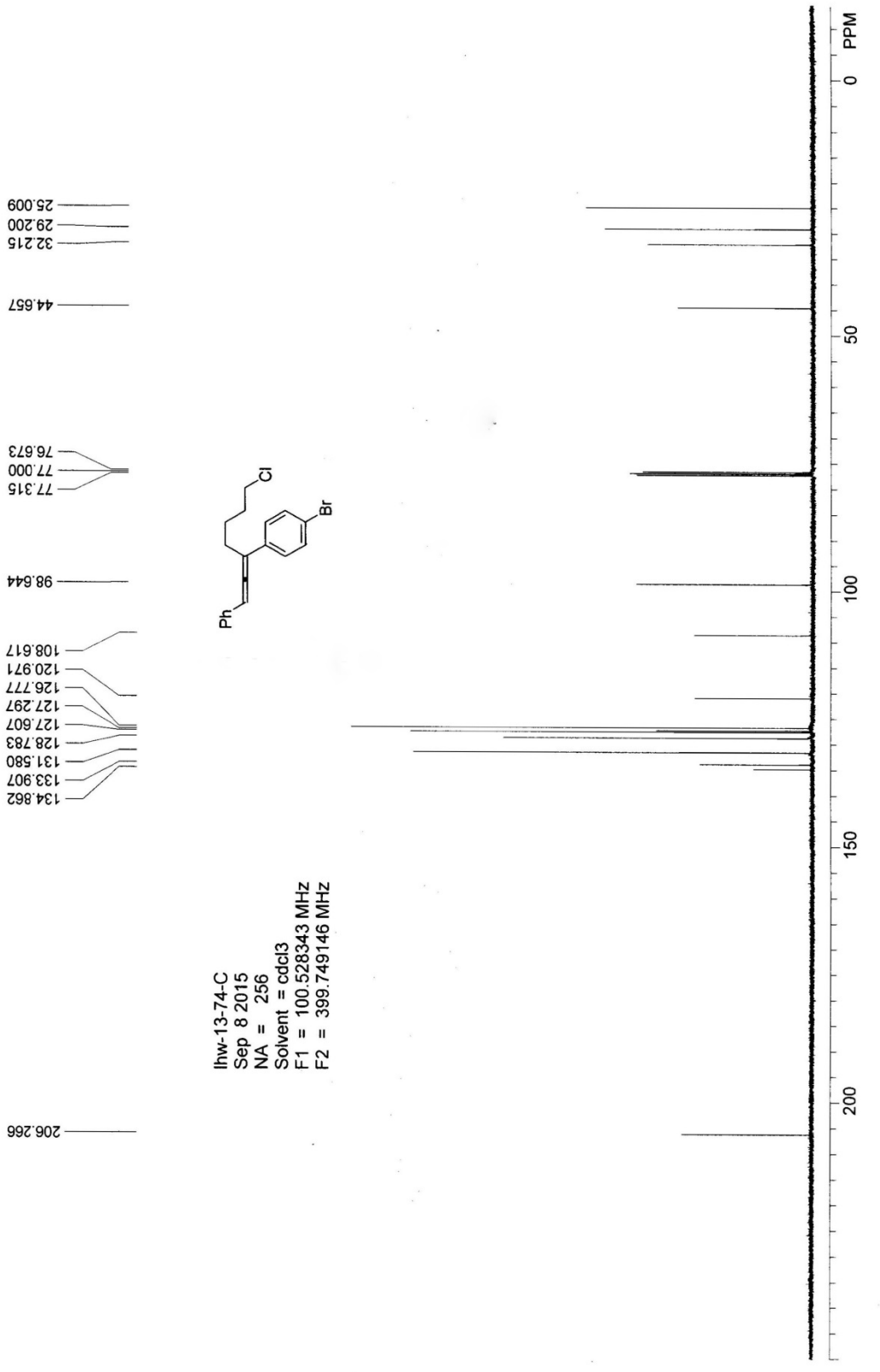
3af


lhw-13-73-H
Sep 22 2015
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Cl
O
Ph
5.19
2.04
2.19
2.00
1.00
1.25
4.07
2.06
2.01
PPM

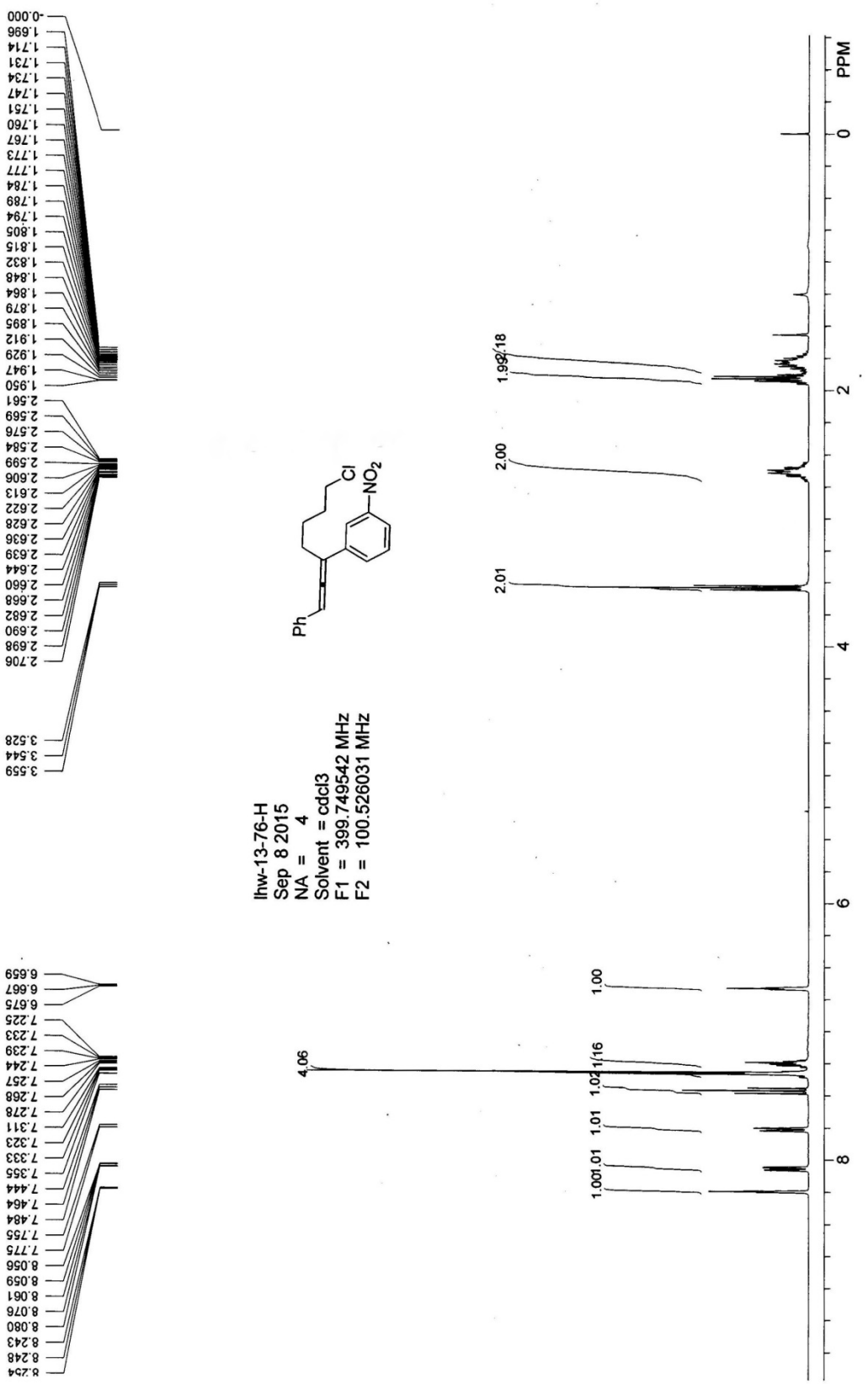

lhw-13-73-C
Sep 8 2015
NA = 256
Solvent = cdcl3
F1 = 100.528343 MHz
F2 = 399.749146 MHz
Cl
O
Ph
25.054
26.531
29.146
32.186
44.629
76.679
77.000
77.310
98.729
108.986
126.042
126.839
127.429
128.623
128.817
133.605
135.673
140.945
197.479
207.424
PPM
0
50
100
150
200

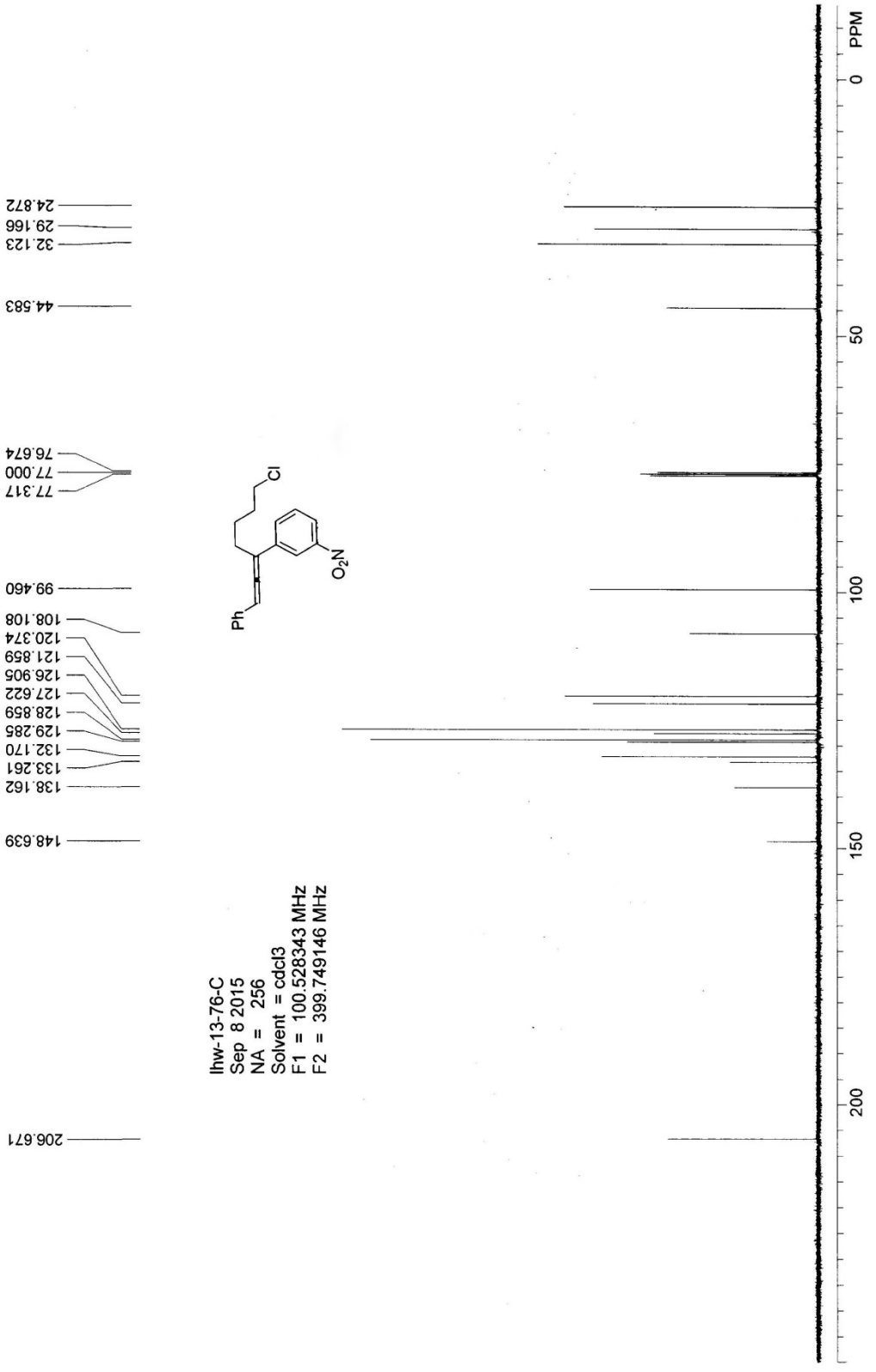
3ag


-0.000
1.650
1.671
1.686
1.689
1.701
1.706
1.723
1.728
1.745
1.765
1.783
1.799
1.815
1.840
1.856
1.873
1.891
1.911
2.484
2.492
2.500
2.507
2.521
2.529
2.539
2.542
2.552
2.559
2.566
2.571
2.579
2.594
2.601
2.610
2.618
3.497
3.513
3.530
6.538
6.544
6.553
7.195
7.206
7.218
7.228
7.240
7.249
7.279
7.304
7.314
7.412
7.434
Cl
Br
Ph
lhw-13-74-H
Sep 8 2015
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
6.12
2.06
1.15
1.00
2.01
2.03
2.05
2.06
0 PPM

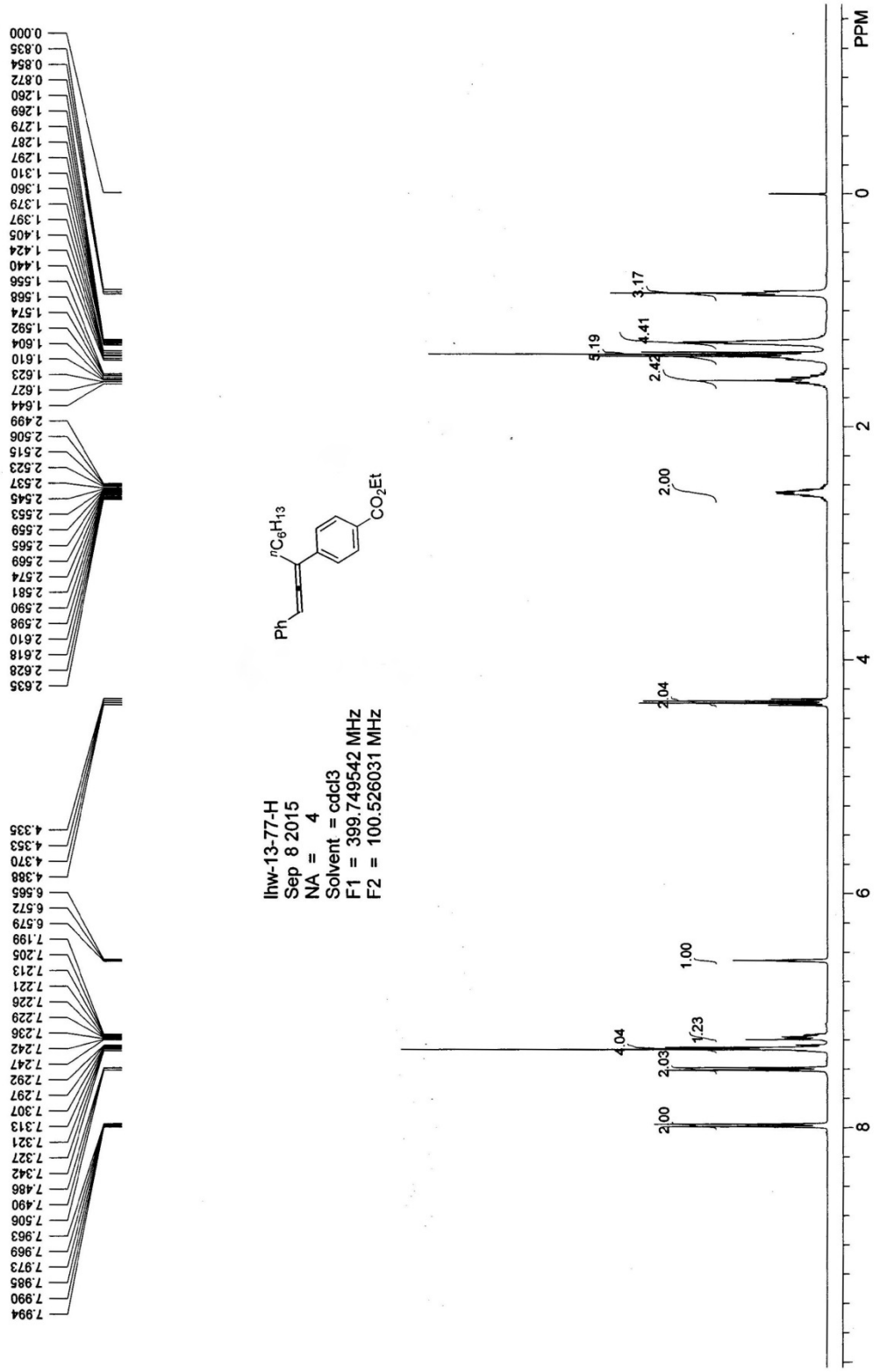

lhw-13-74-C
Sep 8 2015
NA = 256
Solvent = cdcl3
F1 = 100.528343 MHz
F2 = 399.749146 MHz
Cl
Br
Ph
206.266
134.862
133.907
131.580
128.783
127.607
127.297
126.777
120.971
108.617
98.644
77.315
77.000
76.673
44.657
32.215
29.200
25.009
PPM
0
50
100
150
200

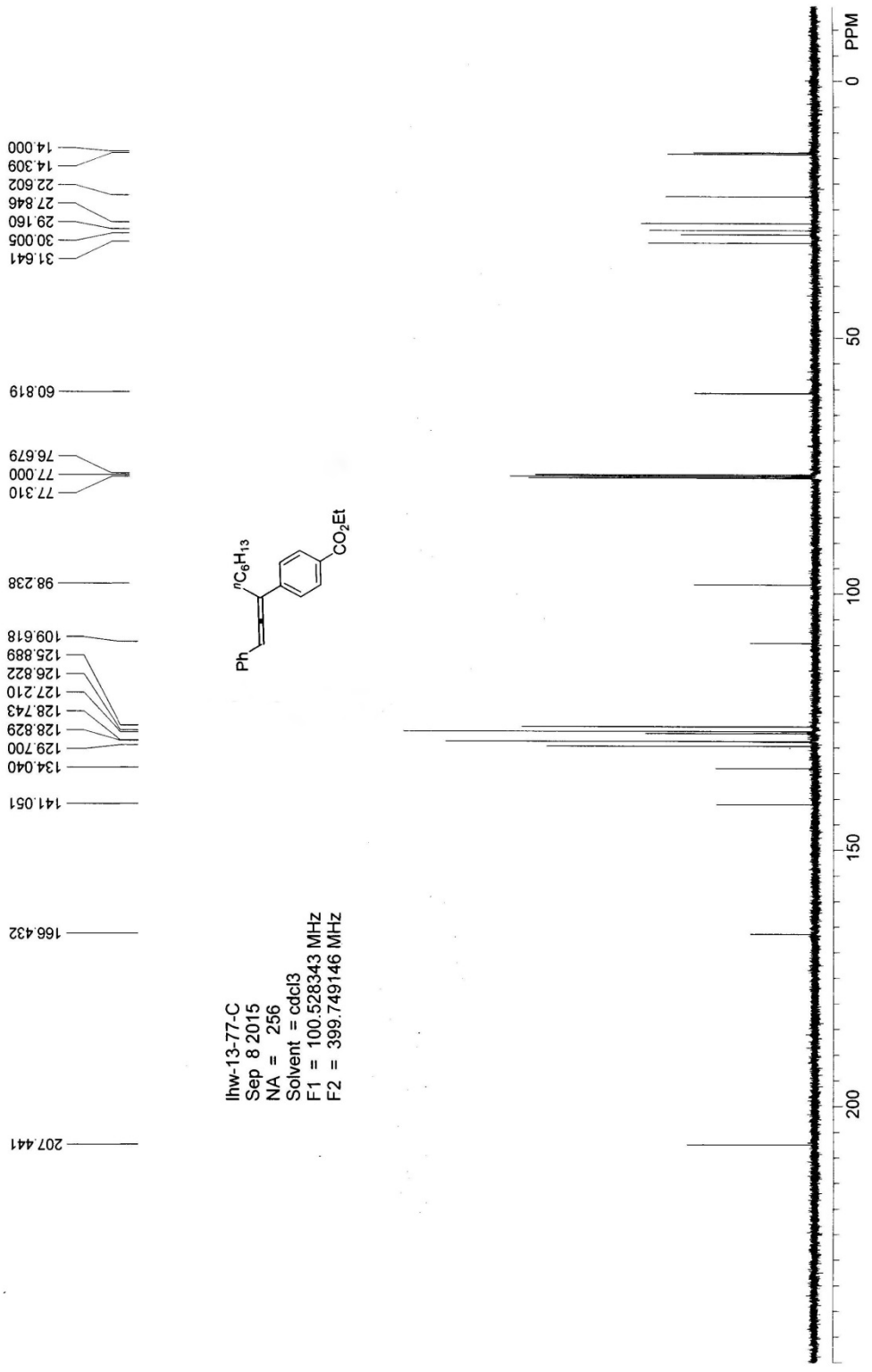
3ah


lhw-13-76-H
Sep 8 2015
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Cl
NO2
Ph
PPM

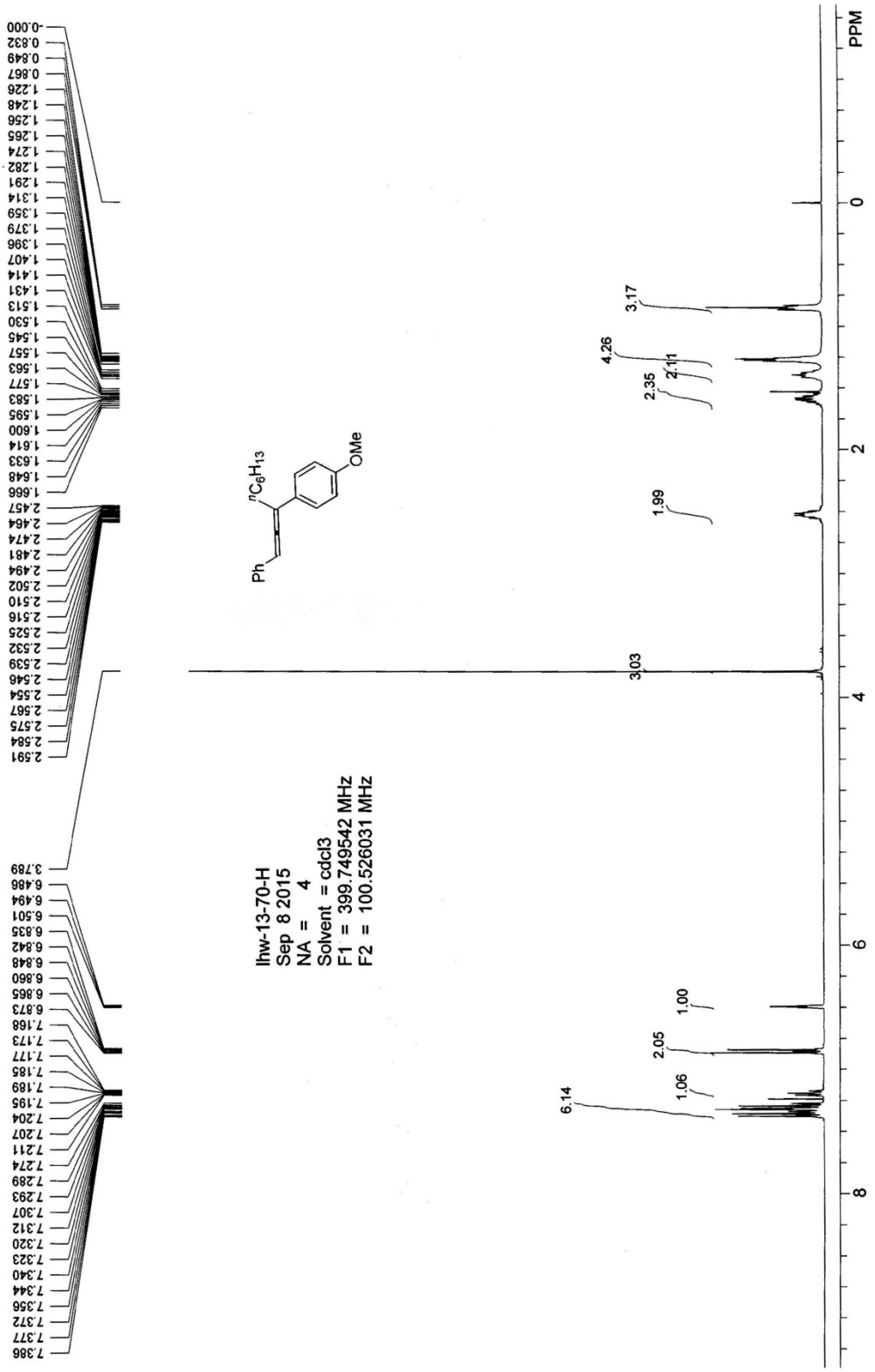

lhw-13-76-C
Sep 8 2015
NA = 256
Solvent = cdcl3
F1 = 100.528343 MHz
F2 = 399.749146 MHz
Cl
Ph
O2N
206.671
148.639
138.162
133.261
132.170
129.285
128.859
127.622
126.905
121.859
120.374
108.108
99.460
77.317
77.000
76.674
44.583
32.123
29.166
24.872
PPM
0
50
100
150
200

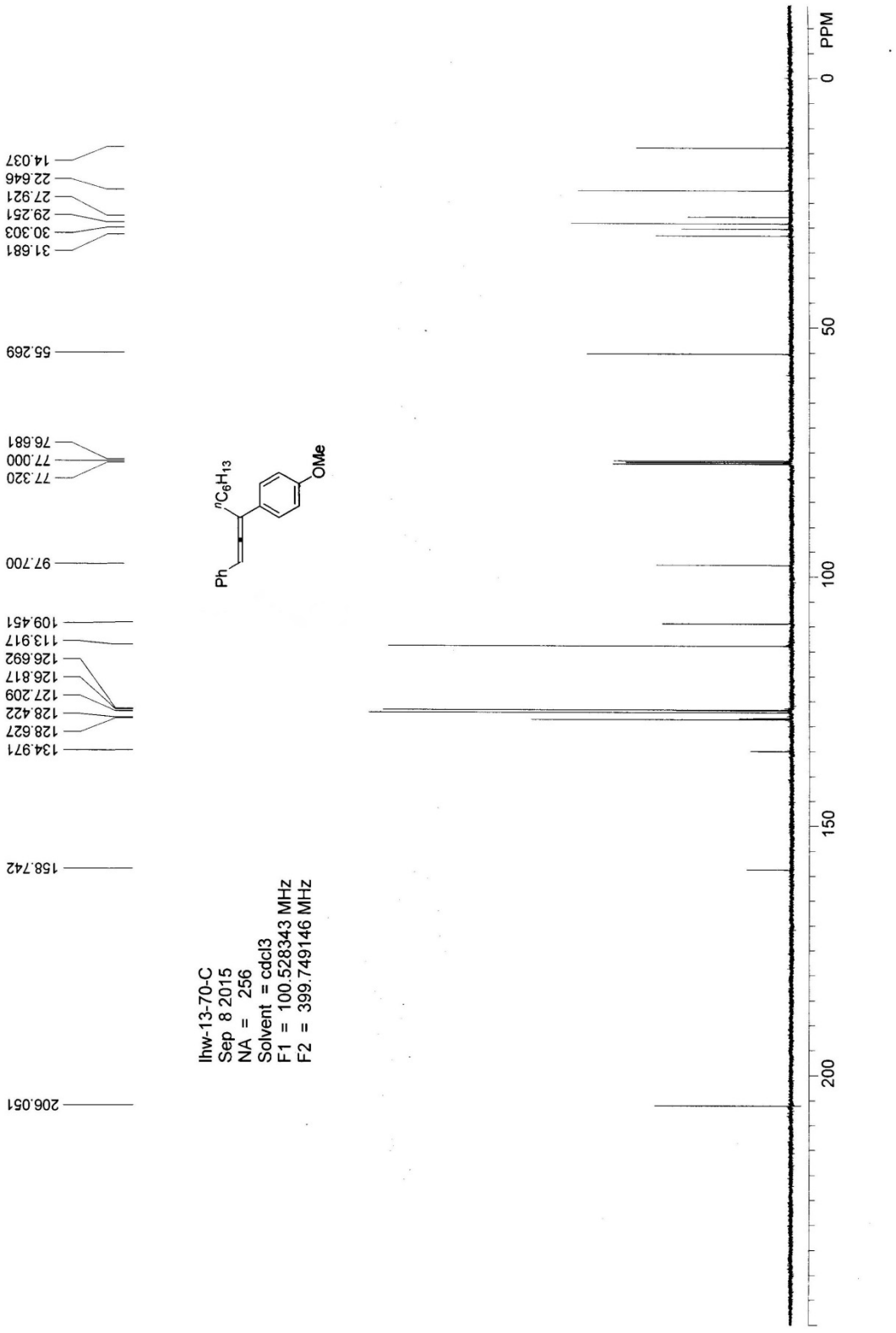
3bi


lhw-13-77-H
Sep 8 2015
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Ph
$^{n}C_6H_{13}$
CO_2Et
PPM

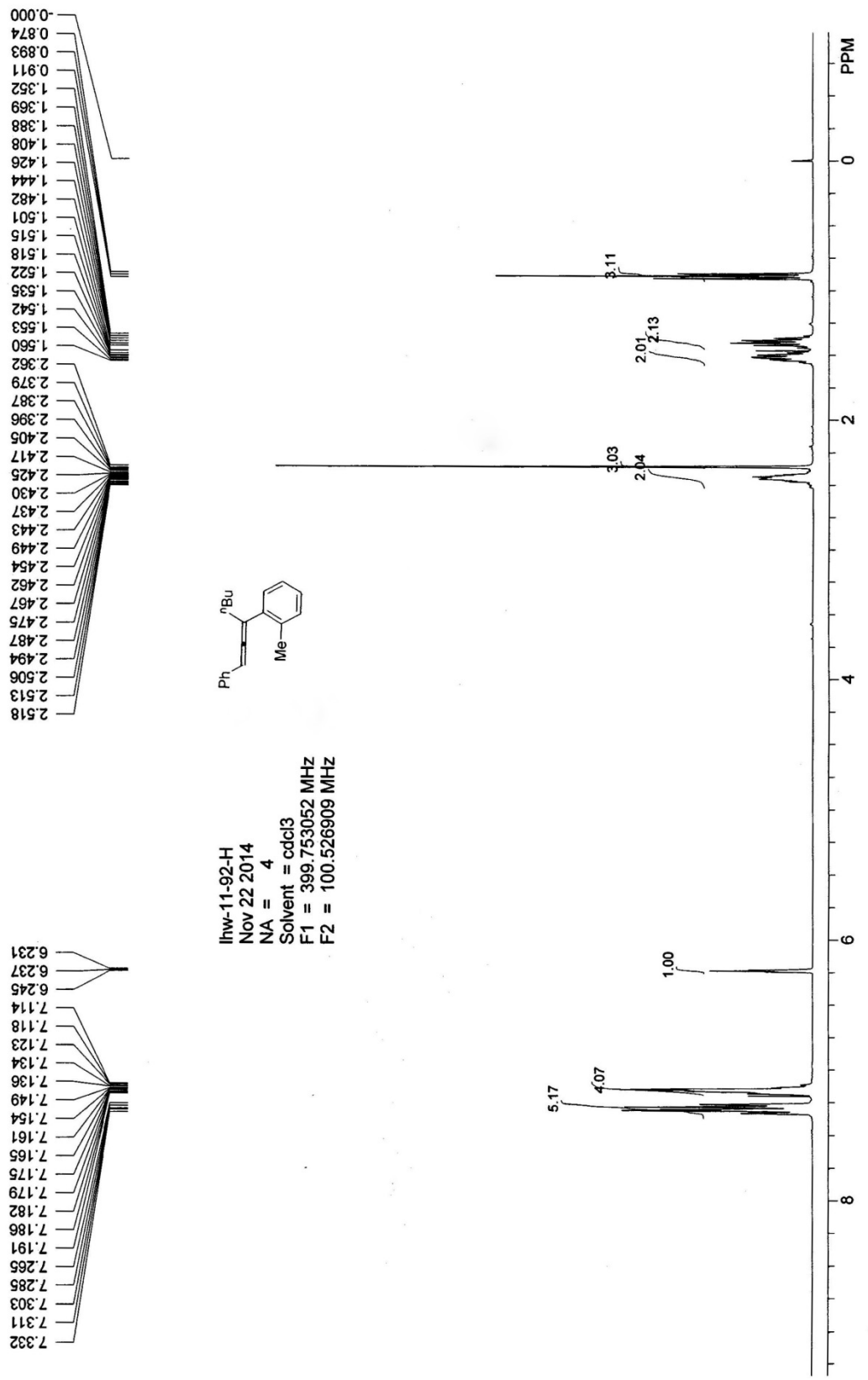

lhw-13-77-C
Sep 8 2015
NA = 256
Solvent = cdcl3
F1 = 100.528343 MHz
F2 = 399.749146 MHz
nC6H13
Ph
CO2Et
14.000
14.309
22.602
27.846
29.160
30.005
31.641
60.819
76.679
77.000
77.310
98.238
109.618
125.889
126.822
127.210
128.743
128.829
129.700
134.040
141.051
166.432
207.441
0
50
100
150
200
PPM

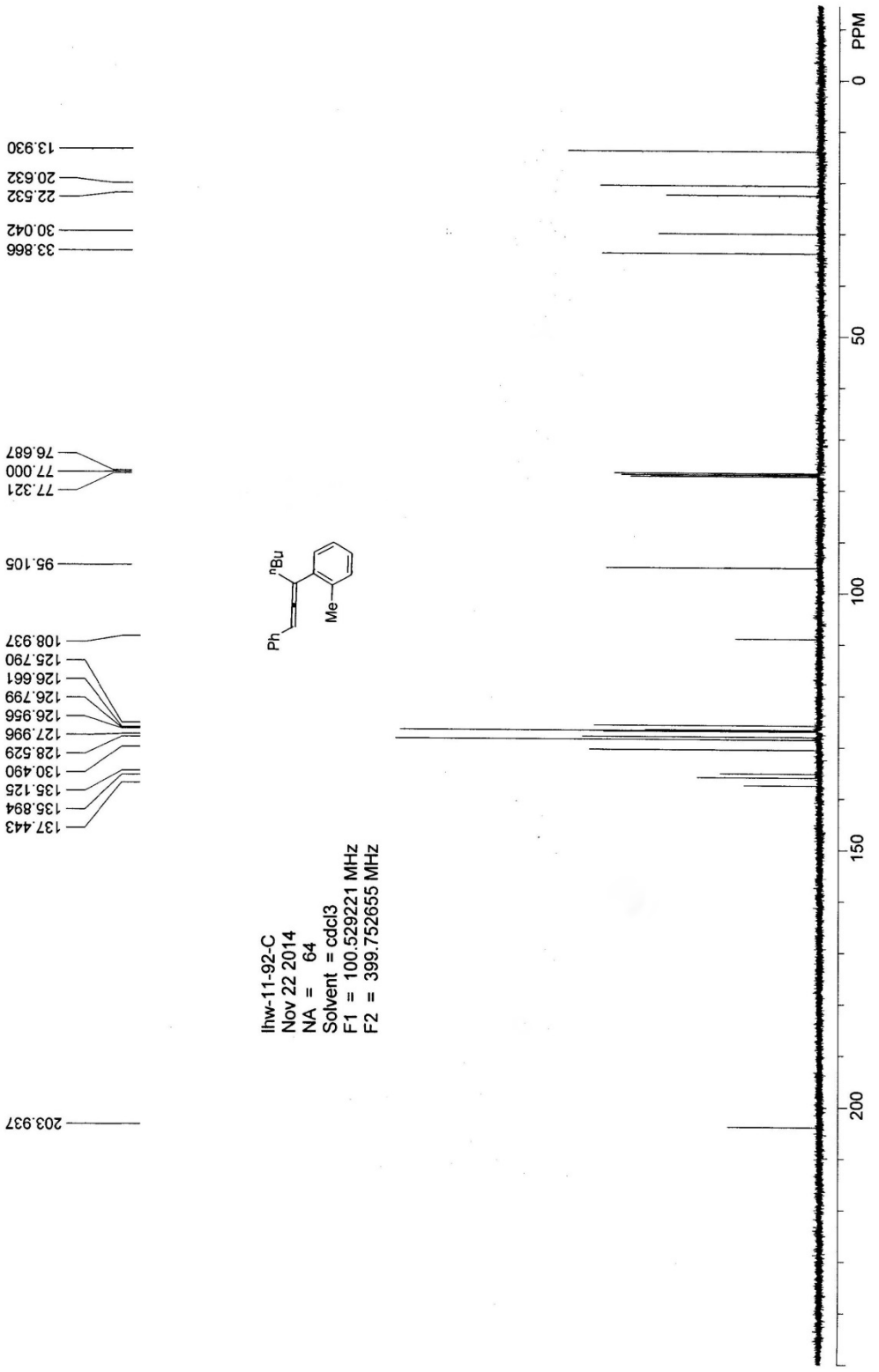
3bj


lhw-13-70-H
Sep 8 2015
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Ph
$^{n}C_6H_{13}$
OMe
6.14
1.06
2.05
1.00
3.03
1.99
2.35
2.11
4.26
3.17
PPM

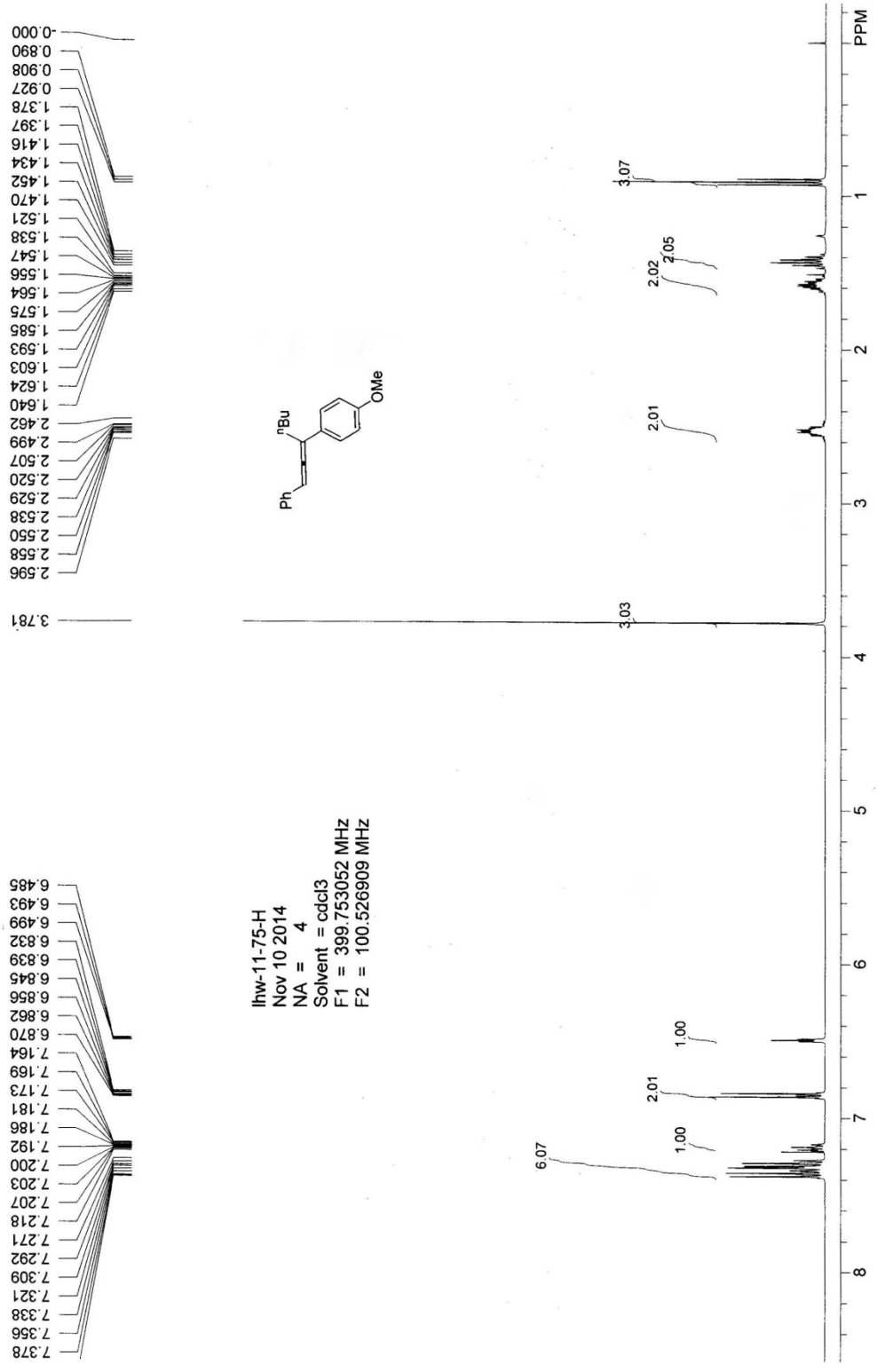

14.037
22.646
27.921
29.251
30.303
31.681
55.269
76.681
77.000
77.320
97.700
109.451
113.917
126.692
126.817
127.209
128.422
128.627
134.971
158.742
206.051
lhw-13-70-C
Sep 8 2015
NA = 256
Solvent = cdcl3
F1 = 100.528343 MHz
F2 = 399.749146 MHz
Ph
$^{n}C_6H_{13}$
OMe
PPM
0
50
100
150
200

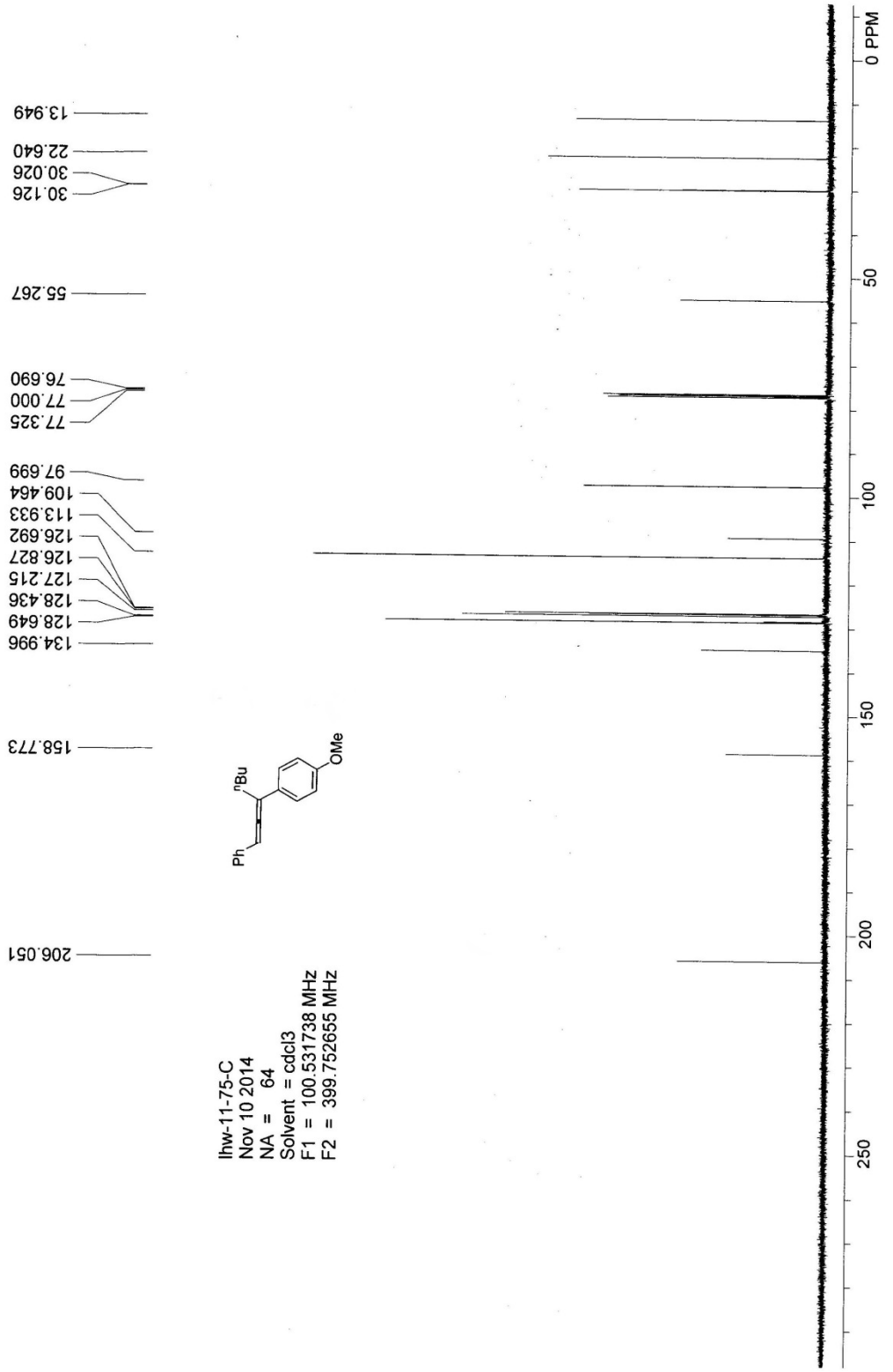
3ck


lhw-11-92-H
Nov 22 2014
NA = 4
Solvent = cdcl3
F1 = 399.753052 MHz
F2 = 100.526909 MHz
nBu
Ph
Me
PPM
0
2
4
6
8
3.11
2.01
2.13
3.03
2.04
1.00
4.07
5.17

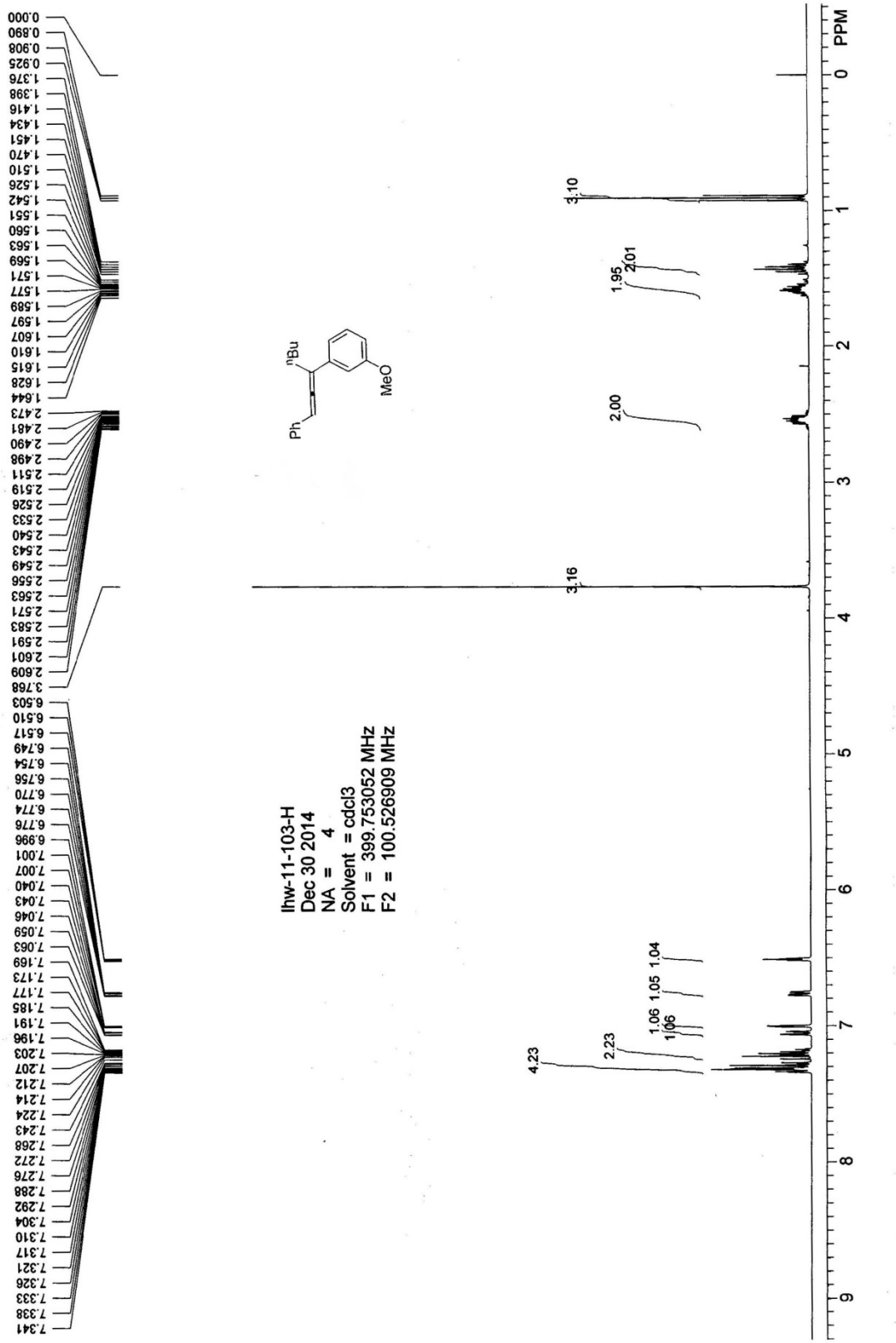

lhw-11-92-C
Nov 22 2014
NA = 64
Solvent = cdcl3
F1 = 100.529221 MHz
F2 = 399.752655 MHz
nBu
Ph
Me
13.930
20.632
22.532
30.042
33.866
76.687
77.000
77.321
95.105
108.937
125.790
126.661
126.799
126.956
127.996
128.529
130.490
135.125
135.894
137.443
203.937
PPM
0
50
100
150
200

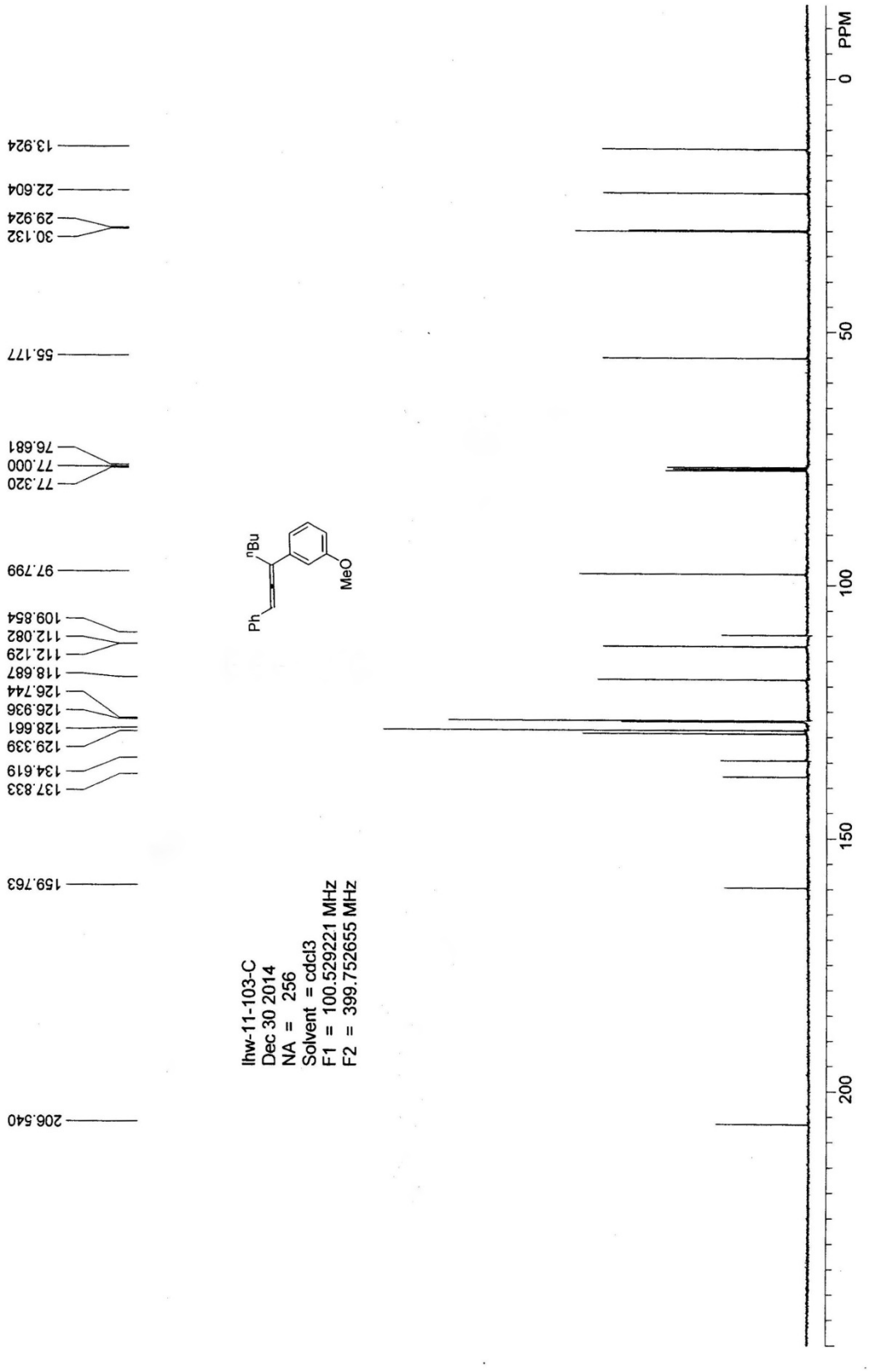
3cj


lhw-11-75-H
Nov 10 2014
NA = 4
Solvent = cdcl3
F1 = 399.753052 MHz
F2 = 100.526909 MHz
nBu
Ph
OMe
PPM

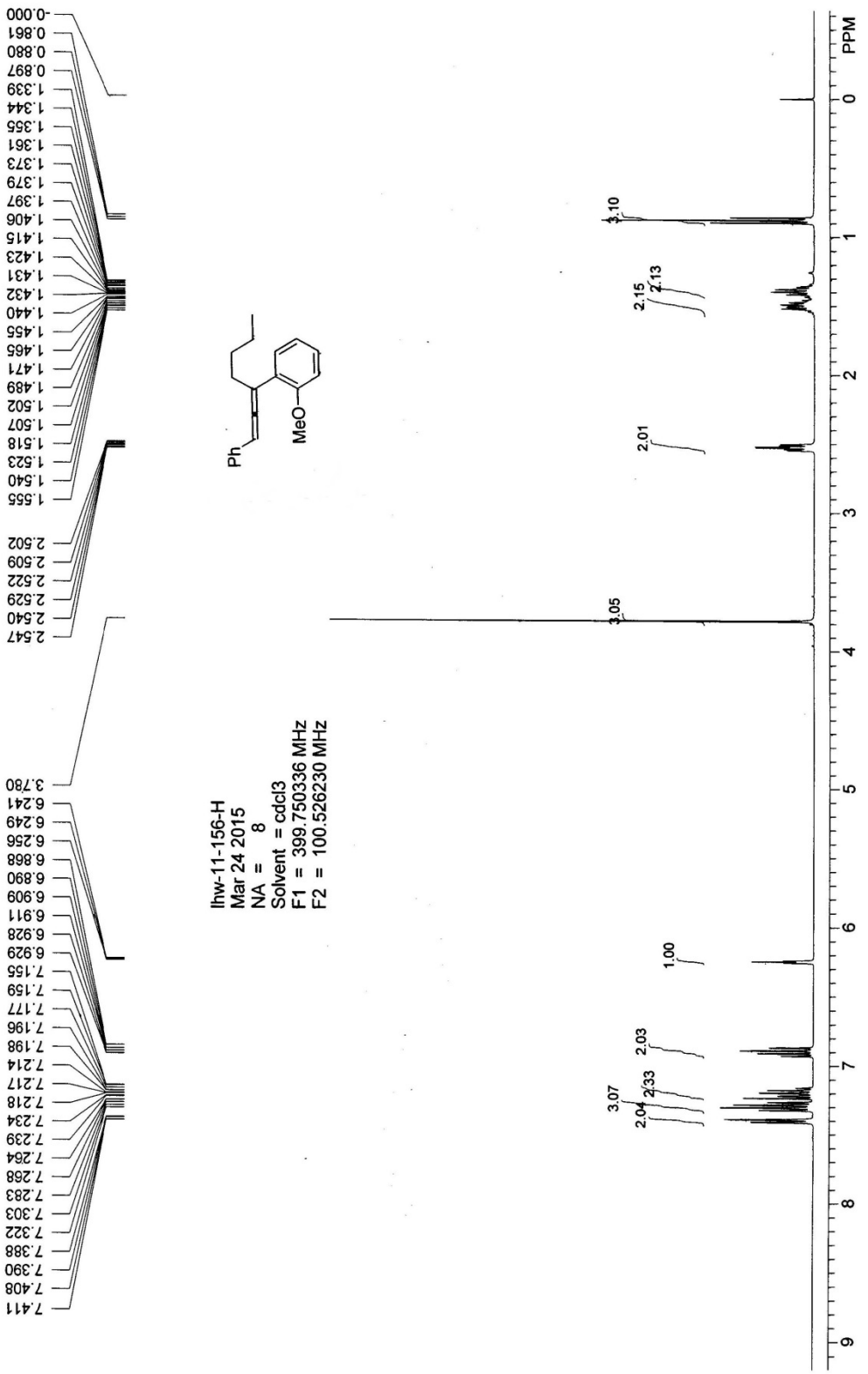

lhw-11-75-C
Nov 10 2014
NA = 64
Solvent = cdcl3
F1 = 100.531738 MHz
F2 = 399.752655 MHz
nBu
Ph
OMe
206.051
158.773
134.996
128.649
128.436
127.215
126.827
126.692
113.933
109.464
97.699
77.325
77.000
76.690
55.267
30.126
30.026
22.640
13.949
0 PPM
50
100
150
200
250

3cl


lhw-11-103-H
Dec 30 2014
NA = 4
Solvent = cdcl3
F1 = 399.753052 MHz
F2 = 100.526909 MHz
nBu
Ph
MeO
3.10
1.95
2.01
2.00
3.16
4.23
2.23
1.06
1.05
1.04
1.06
PPM

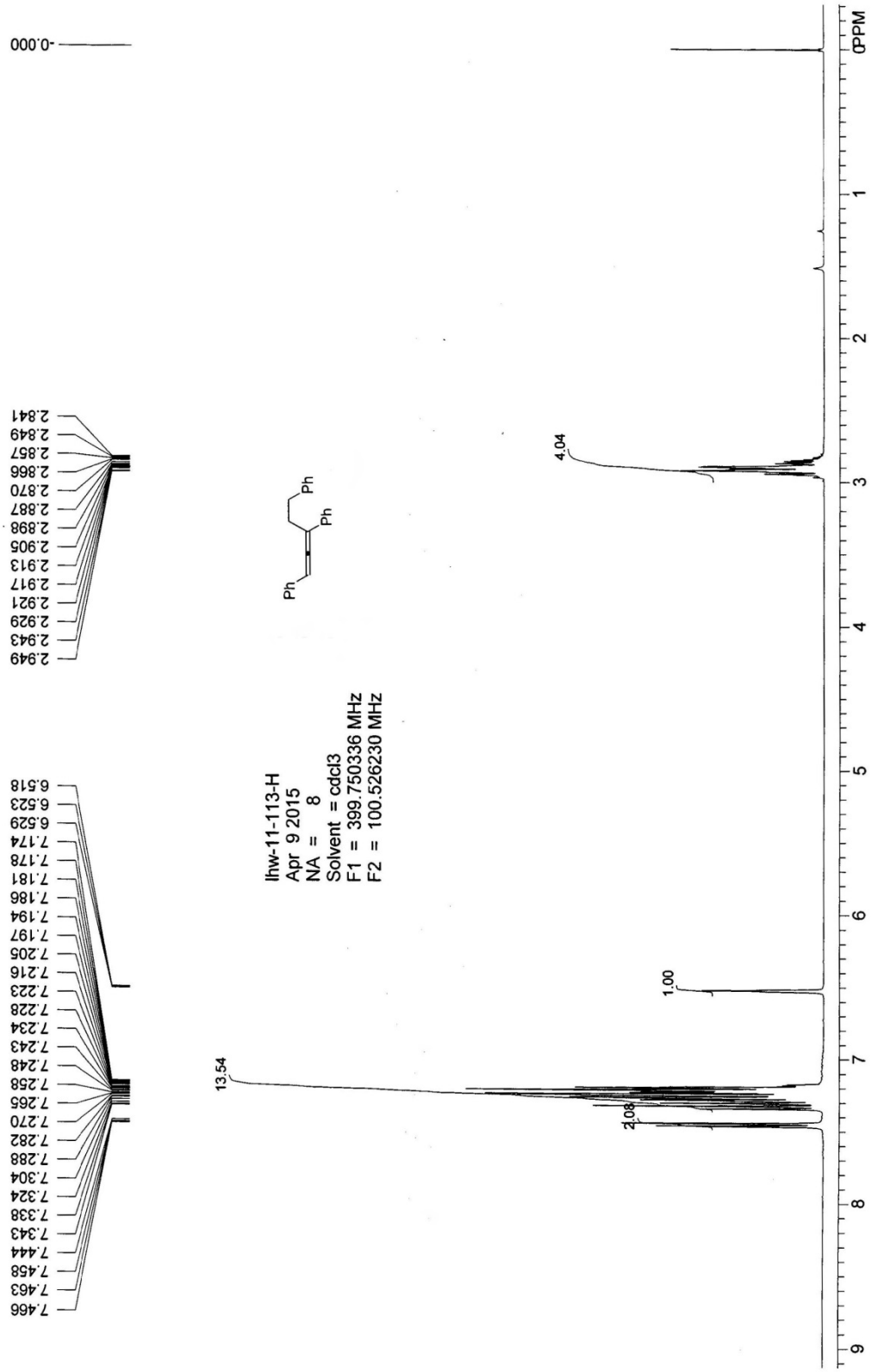

13.924
22.604
29.924
30.132
55.177
76.681
77.000
77.320
97.799
109.854
112.082
112.129
118.687
126.744
126.936
128.661
129.339
134.619
137.833
159.763
206.540
nBu
MeO
Ph
lhw-11-103-C
Dec 30 2014
NA = 256
Solvent = cdcl3
F1 = 100.529221 MHz
F2 = 399.752655 MHz
PPM
0
50
100
150
200

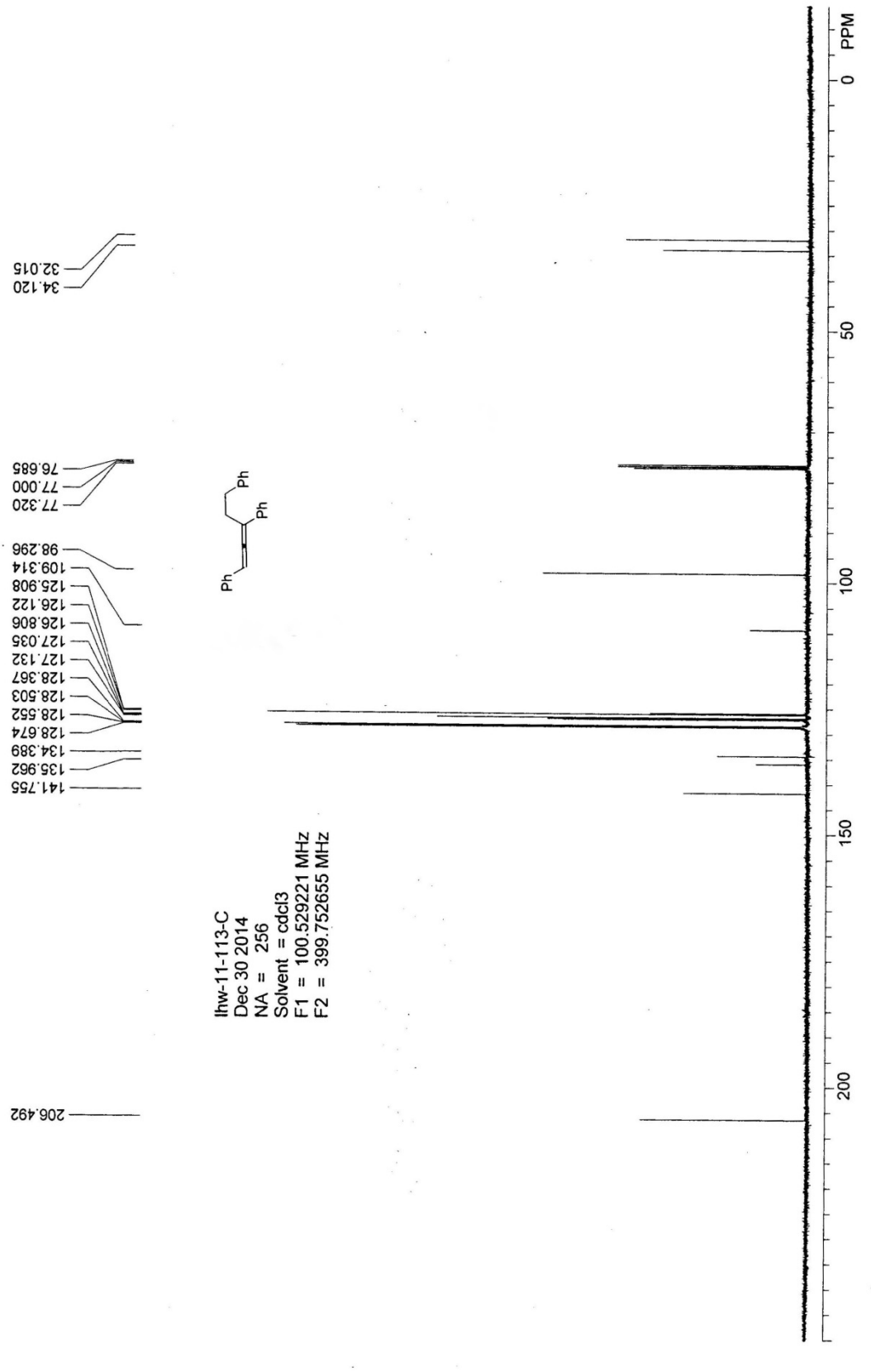
3cm


lhw-11-156-H
Mar 24 2015
NA = 8
Solvent = cdcl3
F1 = 399.750336 MHz
F2 = 100.526230 MHz
Ph
MeO
PPM

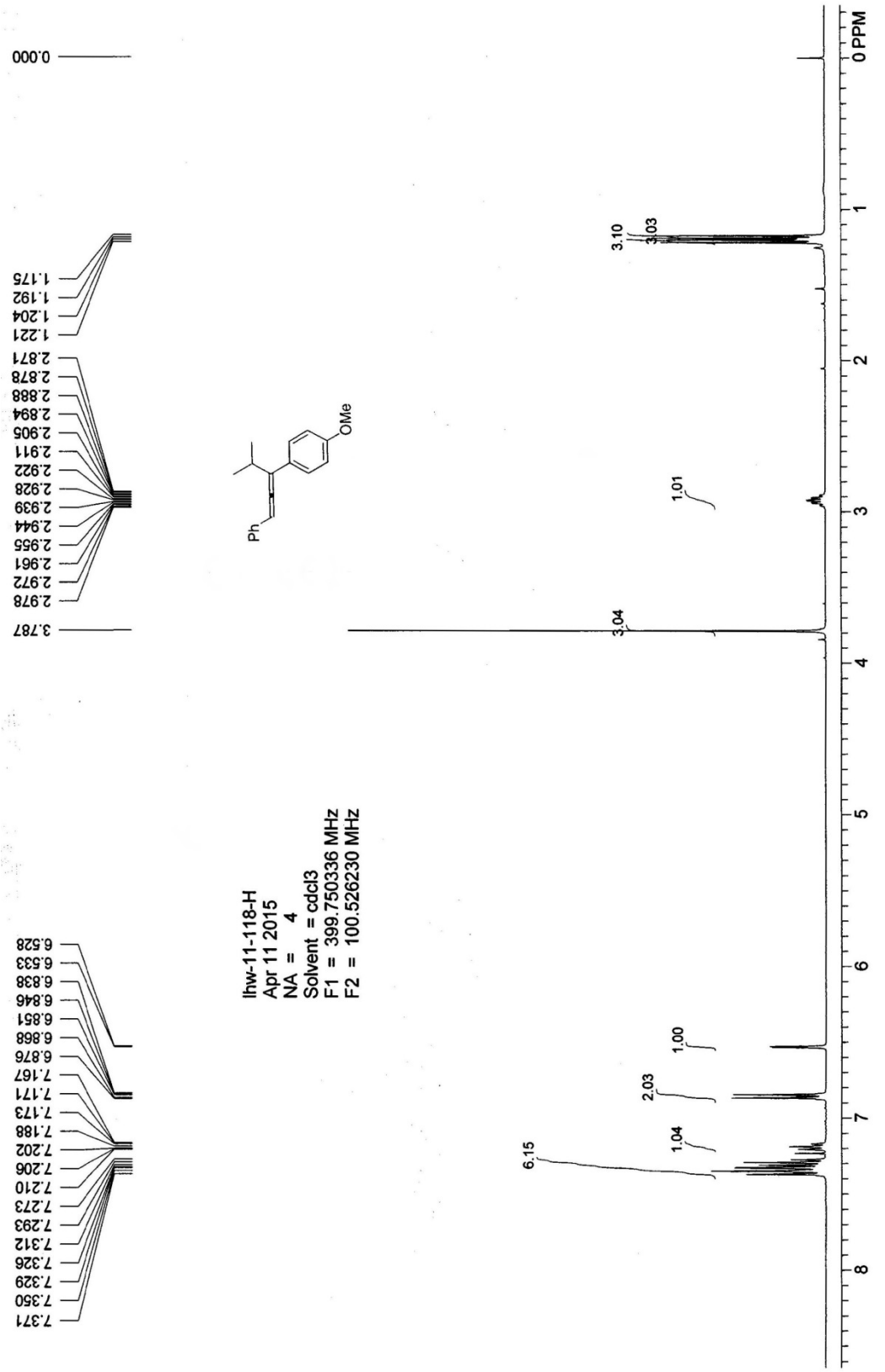
lhw-11-156-C
Mar 24 2015
NA = 64
Solvent = cdcl3
F1 = 100.528542 MHz
F2 = 399.749939 MHz
nBu
Ph
MeO
13.933
22.470
30.178
32.454
55.526
76.676
77.000
77.320
94.480
107.255
111.201
120.546
126.471
126.779
126.852
128.279
128.448
129.387
135.492
156.866
205.735
0
50
100
150
200
PPM

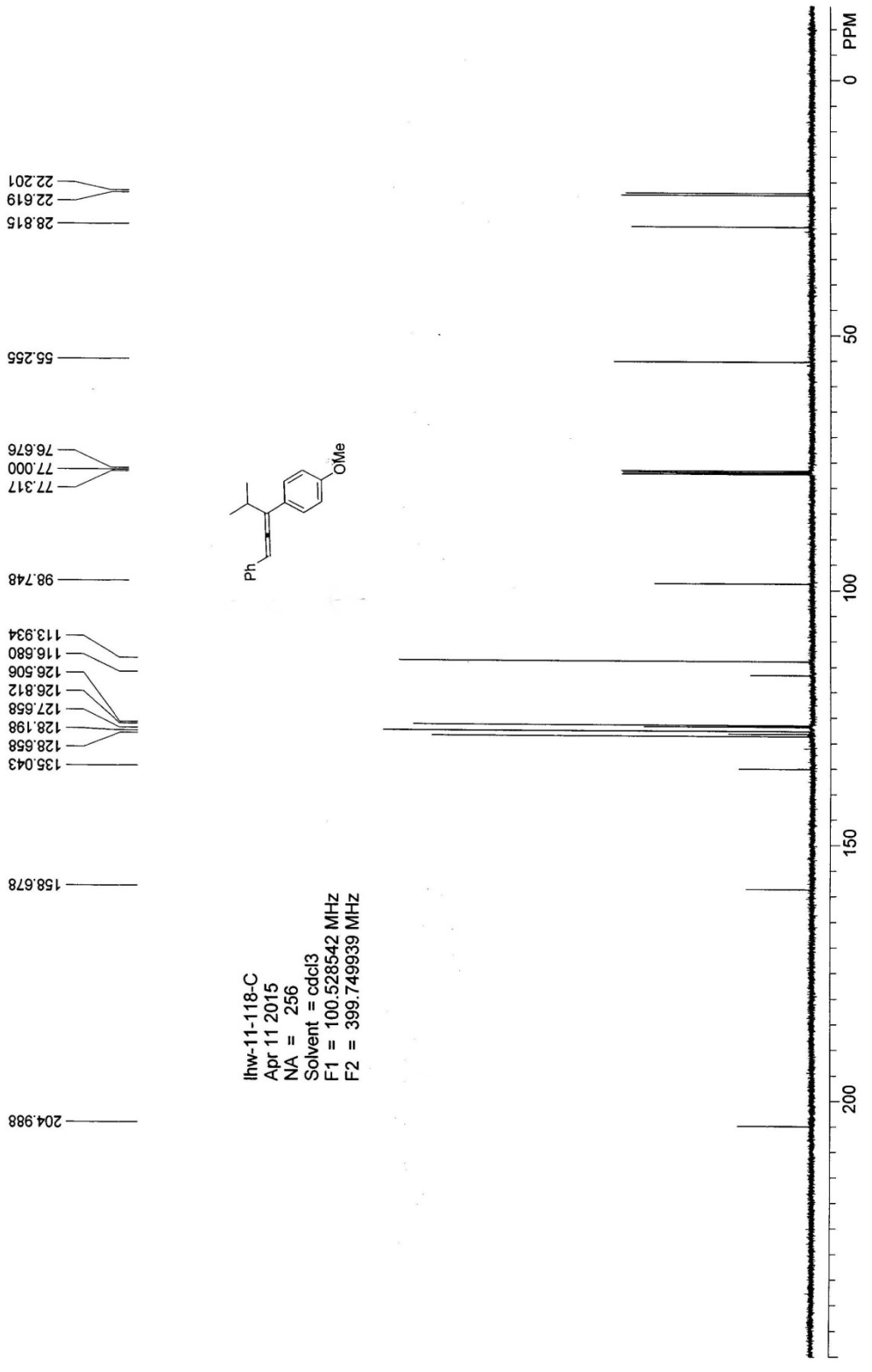
3da


lhw-11-113-H
Apr 9 2015
NA = 8
Solvent = cdcl3
F1 = 399.750336 MHz
F2 = 100.526230 MHz
Ph
Ph
Ph
13.54
2.08
1.00
4.04
PPM

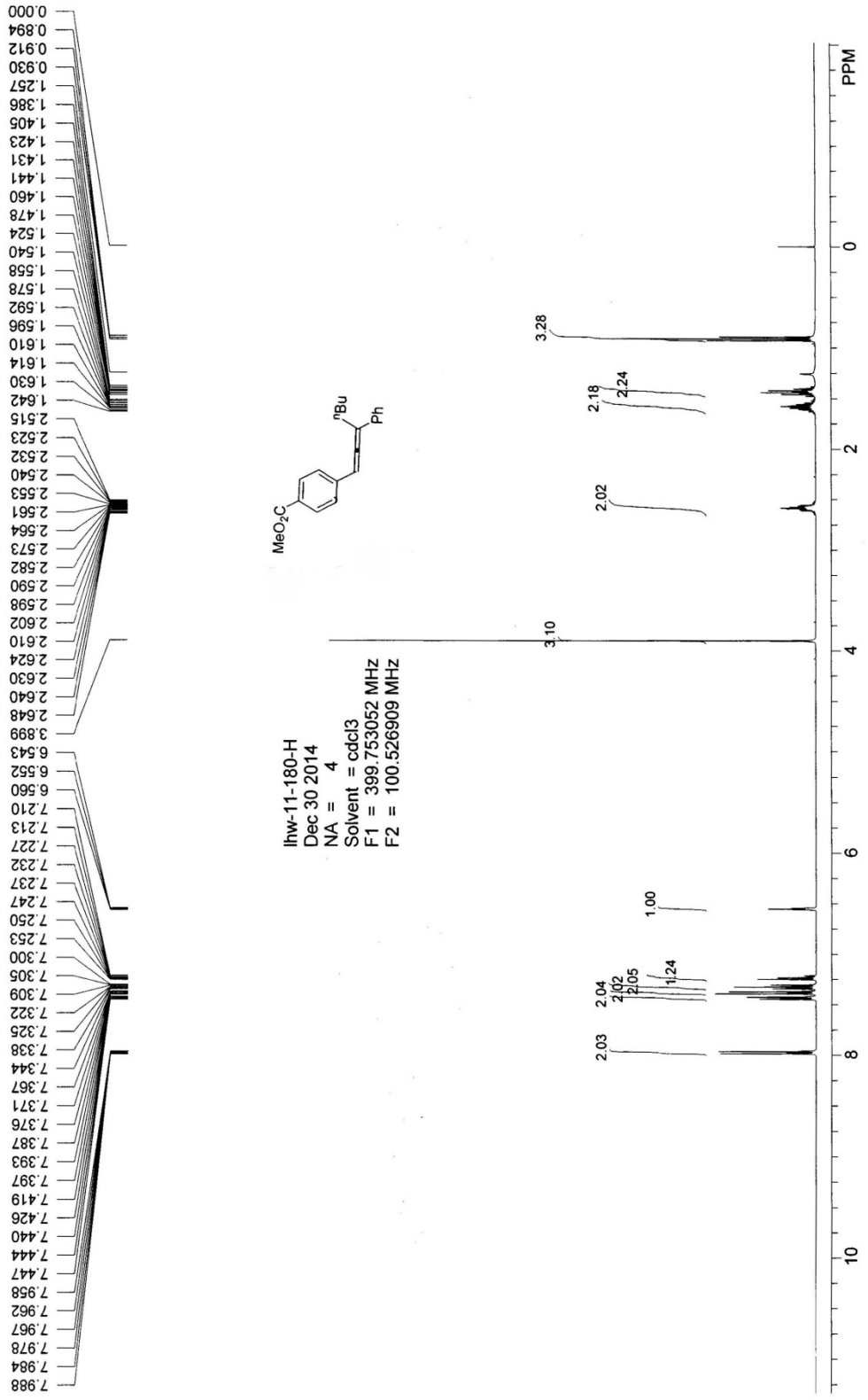

lhw-11-113-C
Dec 30 2014
NA = 256
Solvent = cdcl3
F1 = 100.529221 MHz
F2 = 399.752655 MHz
Ph
Ph
Ph
206.492
141.755
135.962
134.389
128.674
128.552
128.503
128.367
127.132
127.035
126.806
126.122
125.908
109.314
98.296
77.320
77.000
76.685
34.120
32.015
200
150
100
50
0
PPM

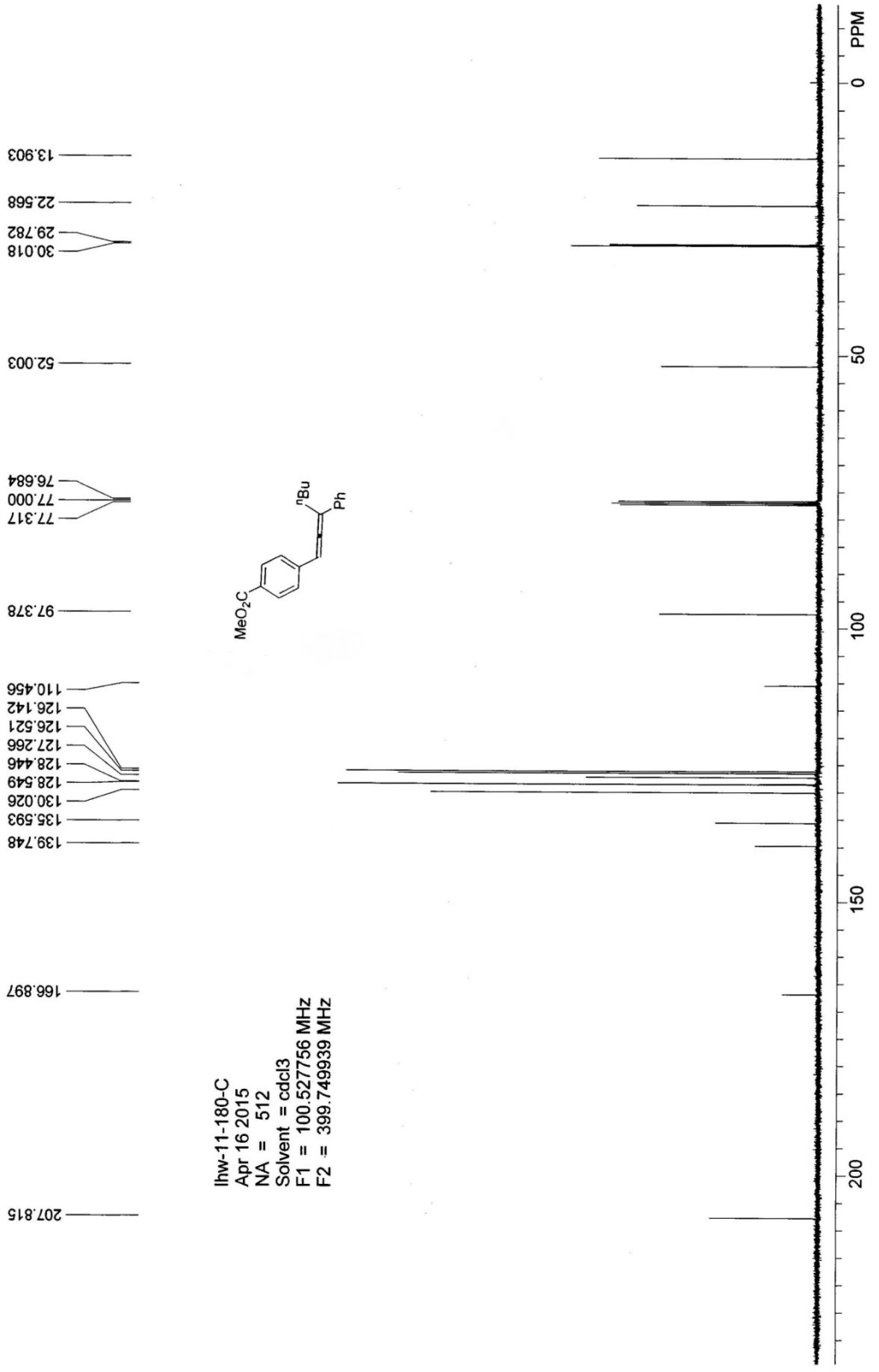
3ej


lhw-11-118-H
Apr 11 2015
NA = 4
Solvent = cdcl3
F1 = 399.750336 MHz
F2 = 100.526230 MHz
OMe
Ph
0.000
1.175
1.192
1.204
1.221
2.871
2.878
2.888
2.894
2.905
2.911
2.922
2.928
2.939
2.944
2.955
2.961
2.972
2.978
3.787
6.528
6.533
6.838
6.846
6.851
6.868
6.876
7.167
7.171
7.173
7.188
7.202
7.206
7.210
7.273
7.293
7.312
7.326
7.329
7.350
7.371
3.10
3.03
1.01
3.04
1.00
2.03
1.04
6.15
0 PPM

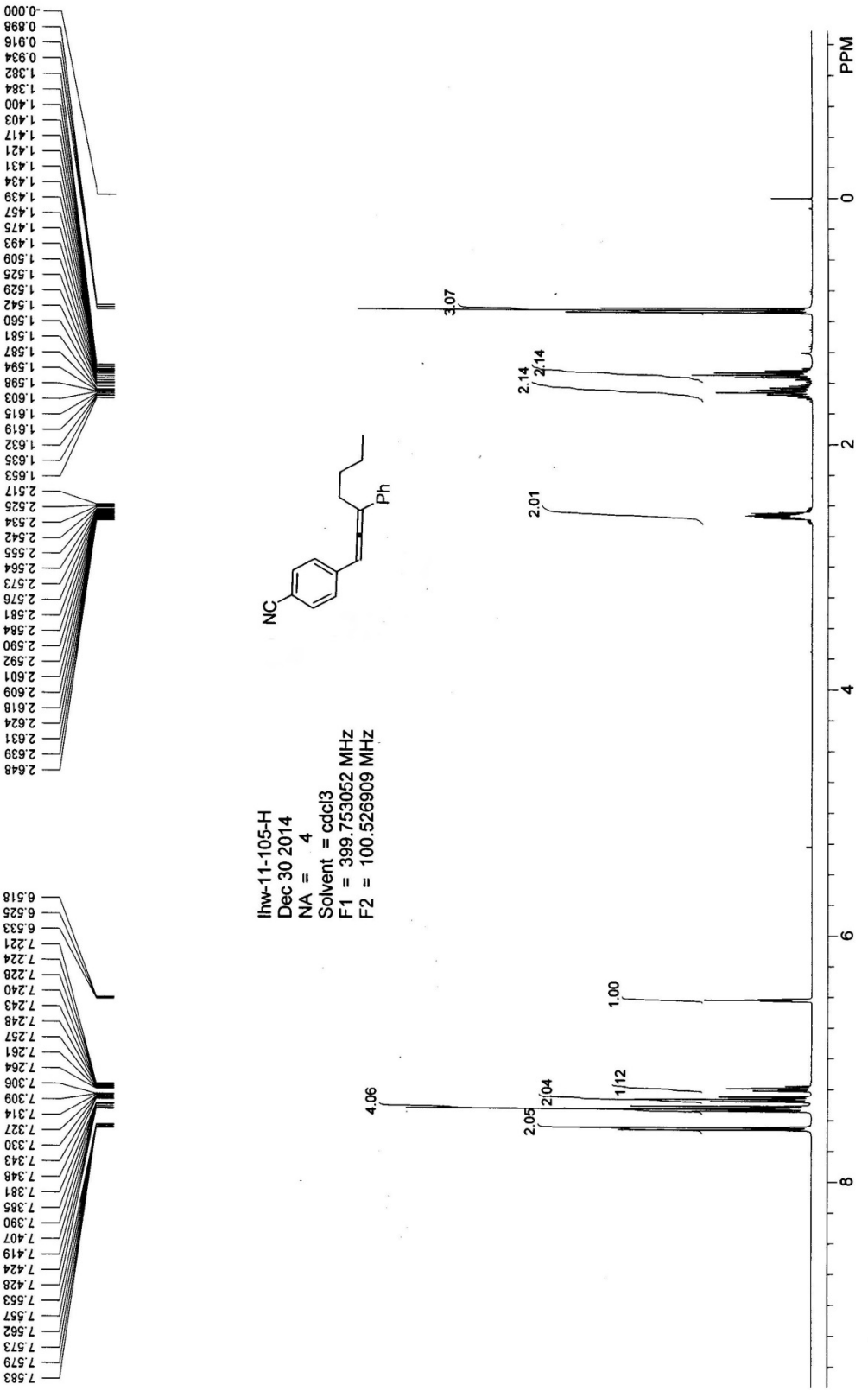

22.201
22.619
28.815
55.255
76.676
77.000
77.317
98.748
113.934
116.680
126.506
126.812
127.658
128.198
128.658
135.043
158.678
204.988
OMe
Ph
lhw-11-118-C
Apr 11 2015
NA = 256
Solvent = cdcl3
F1 = 100.528542 MHz
F2 = 399.749939 MHz
PPM
0
50
100
150
200

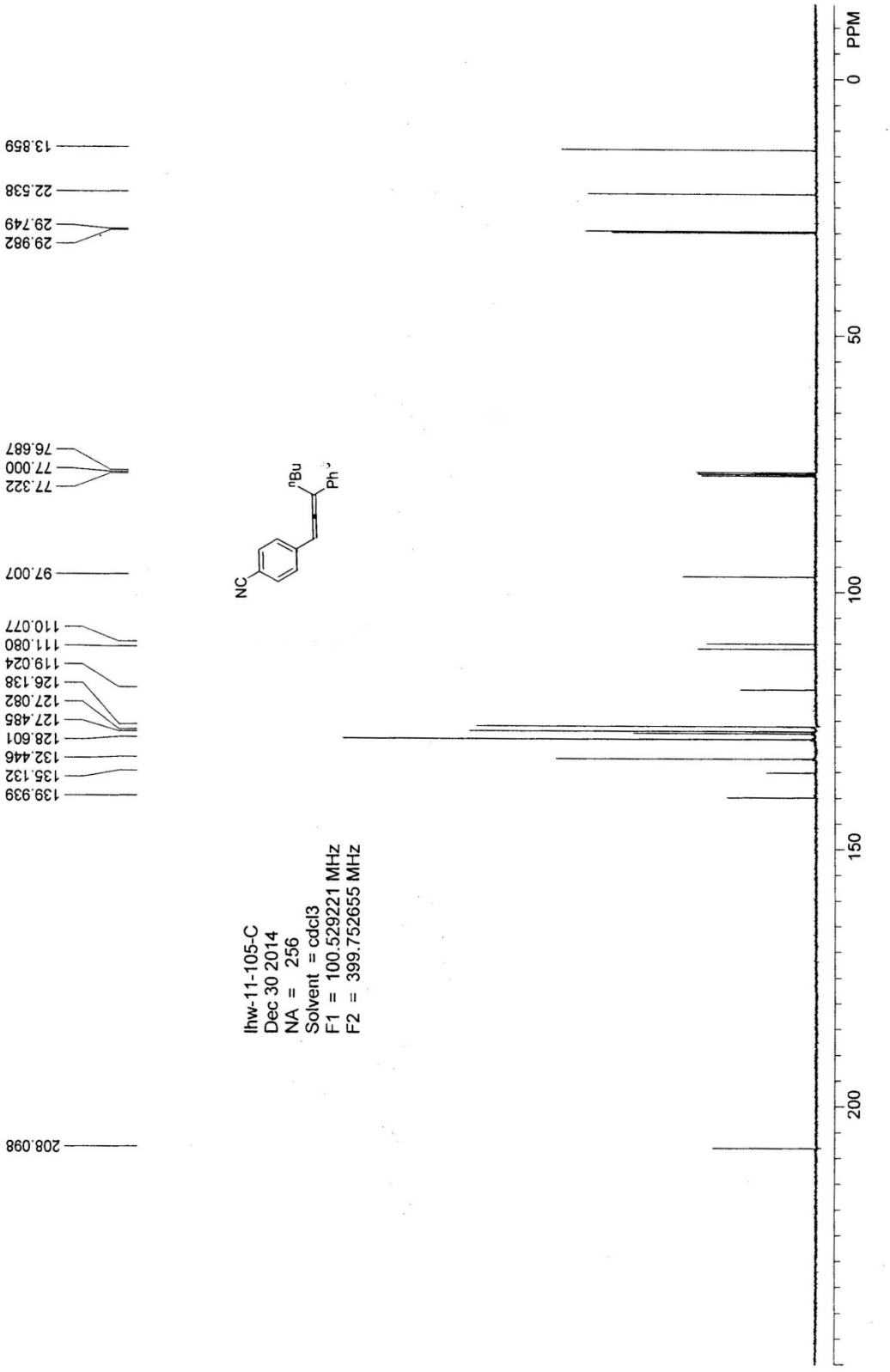
3fa


lhw-11-180-H
Dec 30 2014
NA = 4
Solvent = cdcl3
F1 = 399.753052 MHz
F2 = 100.526909 MHz
MeO2C
nBu
Ph
3.28
2.18
2.24
2.02
3.10
1.00
2.04
2.02
2.05
1.24
2.03
PPM

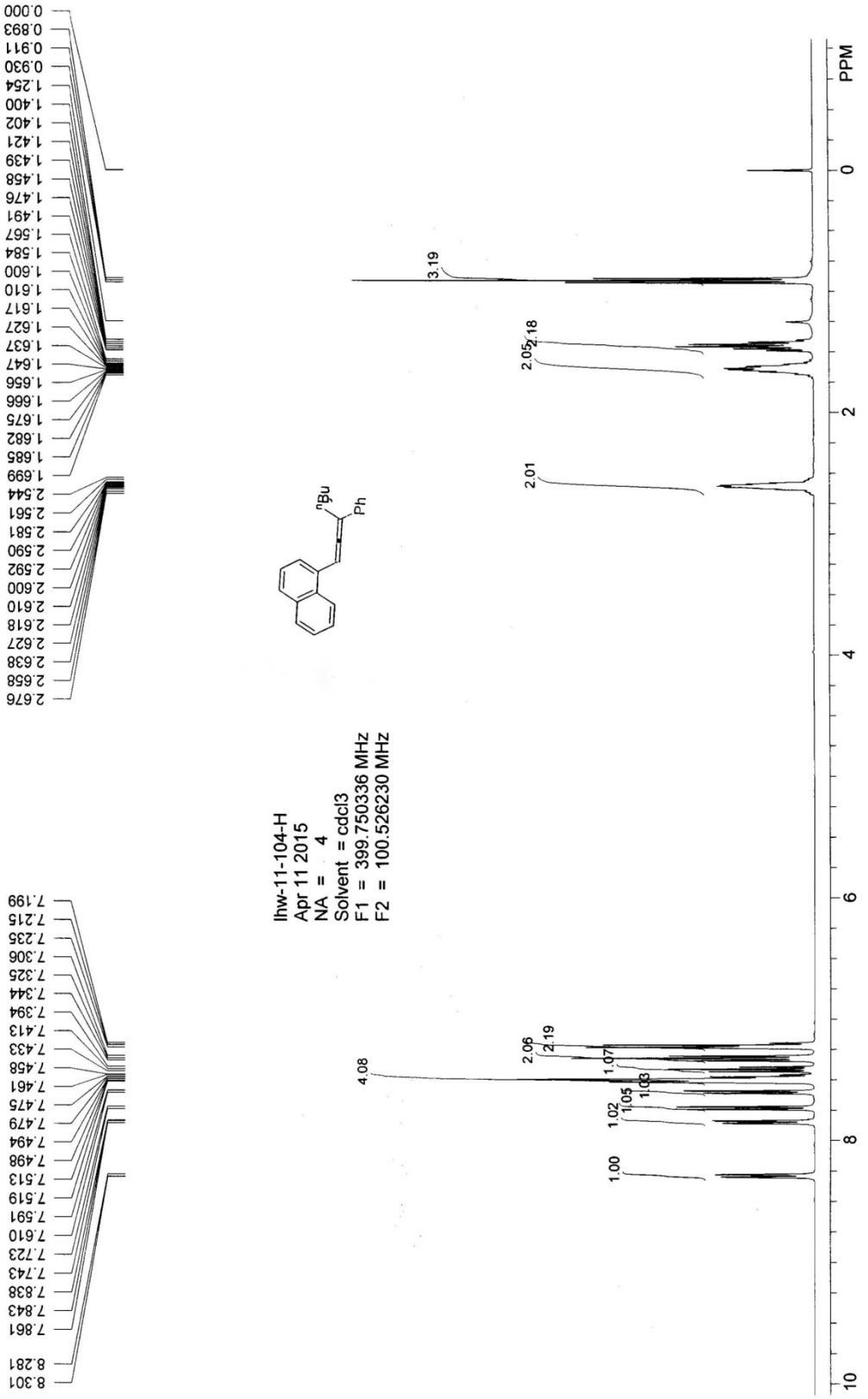

lhw-11-180-C
Apr 16 2015
NA = 512
Solvent = cdcl3
F1 = 100.527756 MHz
F2 = 399.749939 MHz
MeO2C
nBu
Ph
13.903
22.568
29.782
30.018
52.003
76.684
77.000
77.317
97.378
110.456
126.142
126.521
127.266
128.446
128.549
130.026
135.593
139.748
166.897
207.815
PPM
0
50
100
150
200

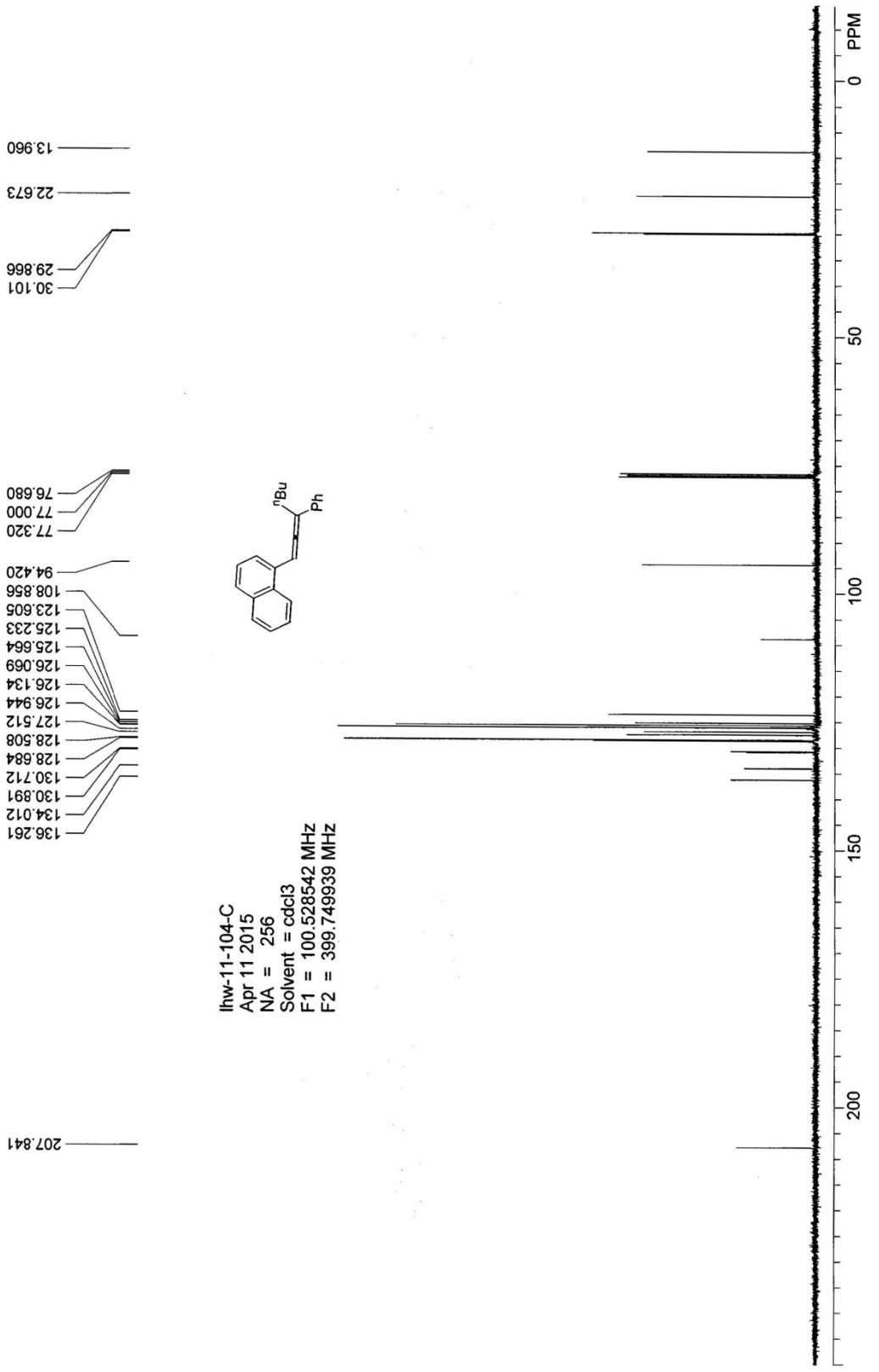
3ga


lhw-11-105-H
Dec 30 2014
NA = 4
Solvent = cdcl3
F1 = 399.753052 MHz
F2 = 100.526909 MHz
NC
Ph
PPM
3.07
2.14
2.14
2.01
1.00
4.06
2.04
1.12
2.05

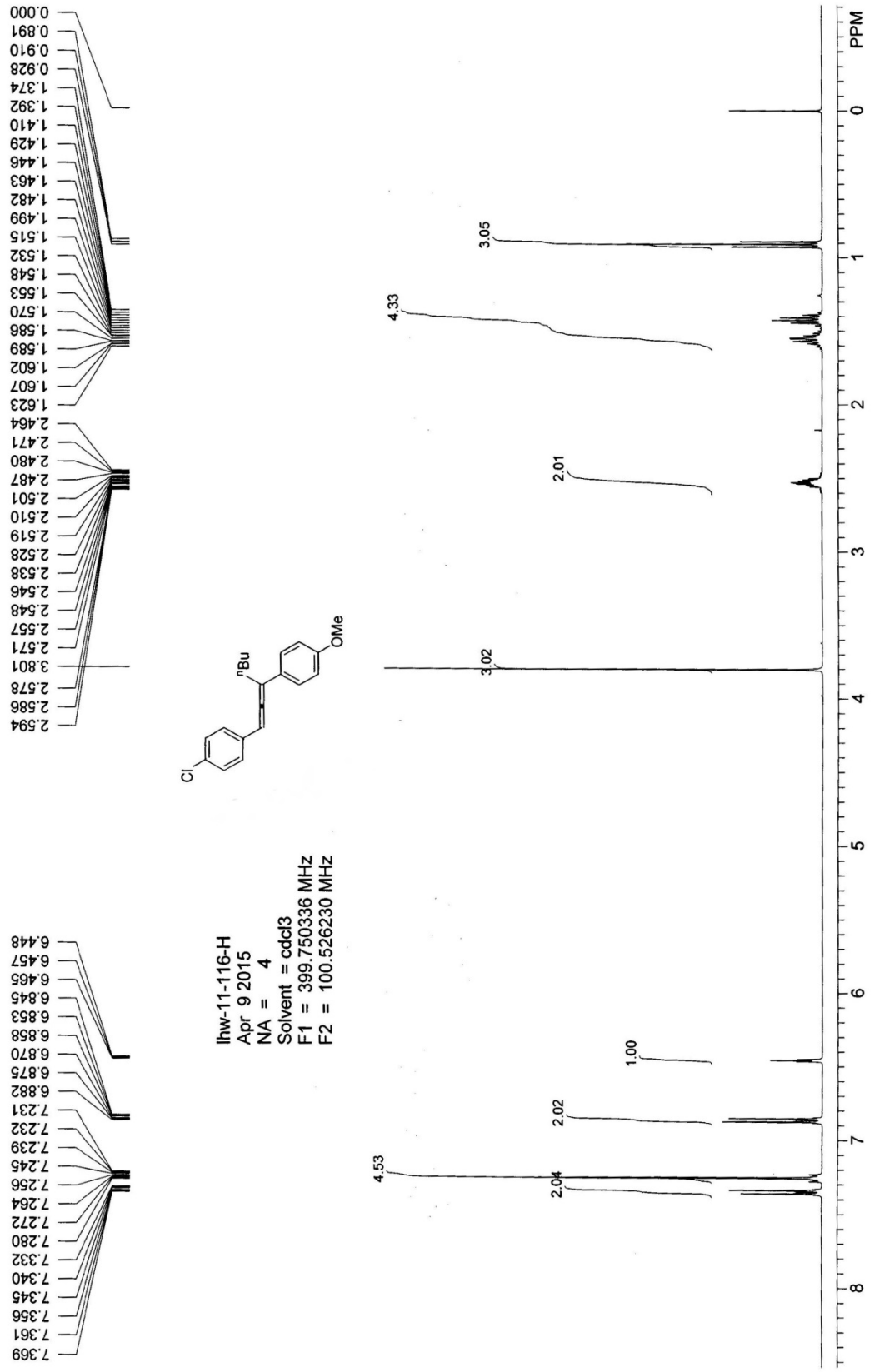

13.859
22.538
29.749
29.982
76.687
77.000
77.322
97.007
110.077
111.080
119.024
126.138
127.082
127.485
128.601
132.446
135.132
139.939
208.098
nBu
Ph
NC
lhw-11-105-C
Dec 30 2014
NA = 256
Solvent = cdcl3
F1 = 100.529221 MHz
F2 = 399.752655 MHz
PPM
0
50
100
150
200

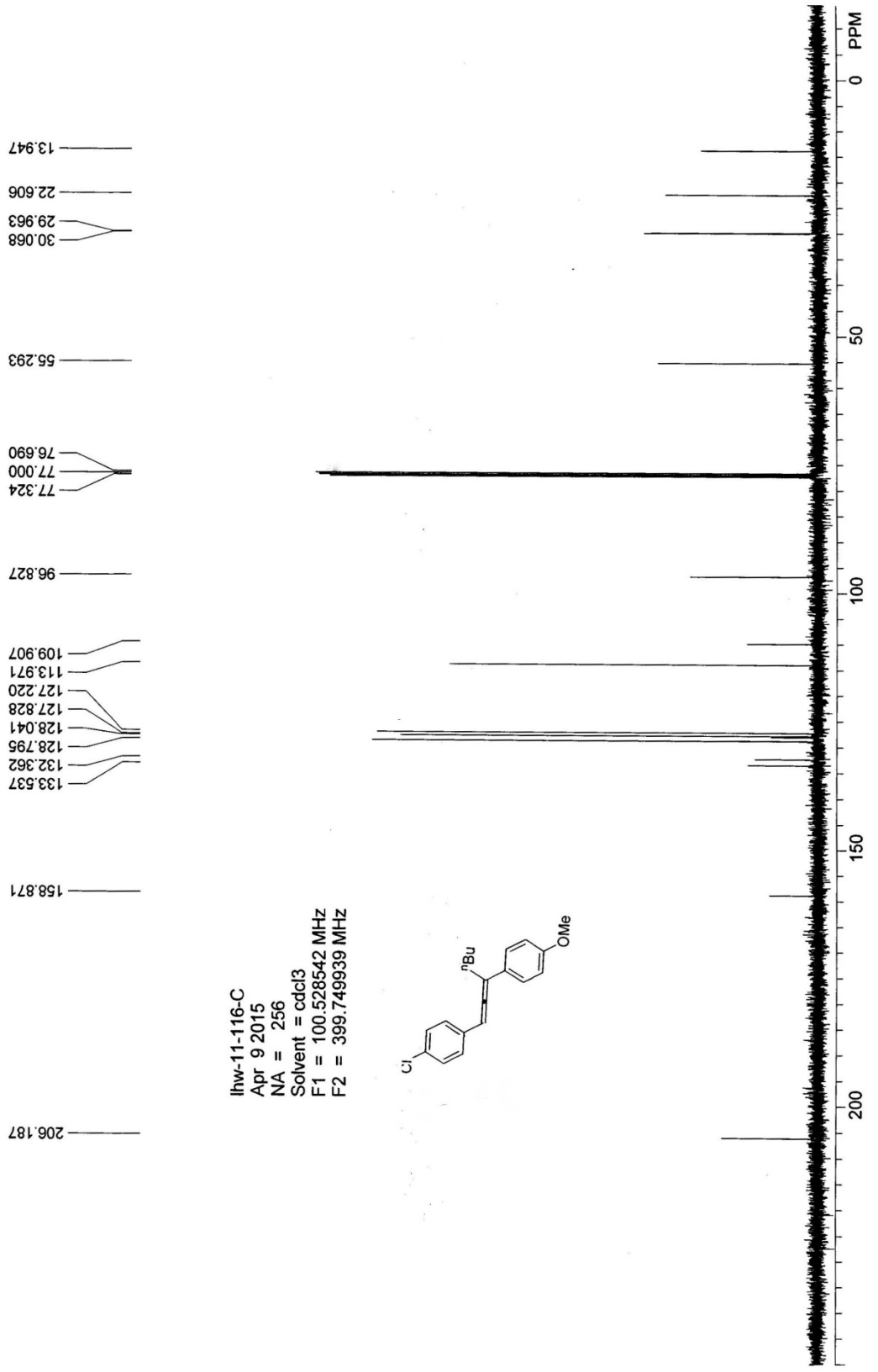
3ha


lhw-11-104-H
Apr 11 2015
NA = 4
Solvent = cdcl3
F1 = 399.750336 MHz
F2 = 100.526230 MHz
nBu
Ph
3.19
2.18
2.05
2.01
4.08
2.06
2.19
1.07
1.03
1.05
1.02
1.00
PPM

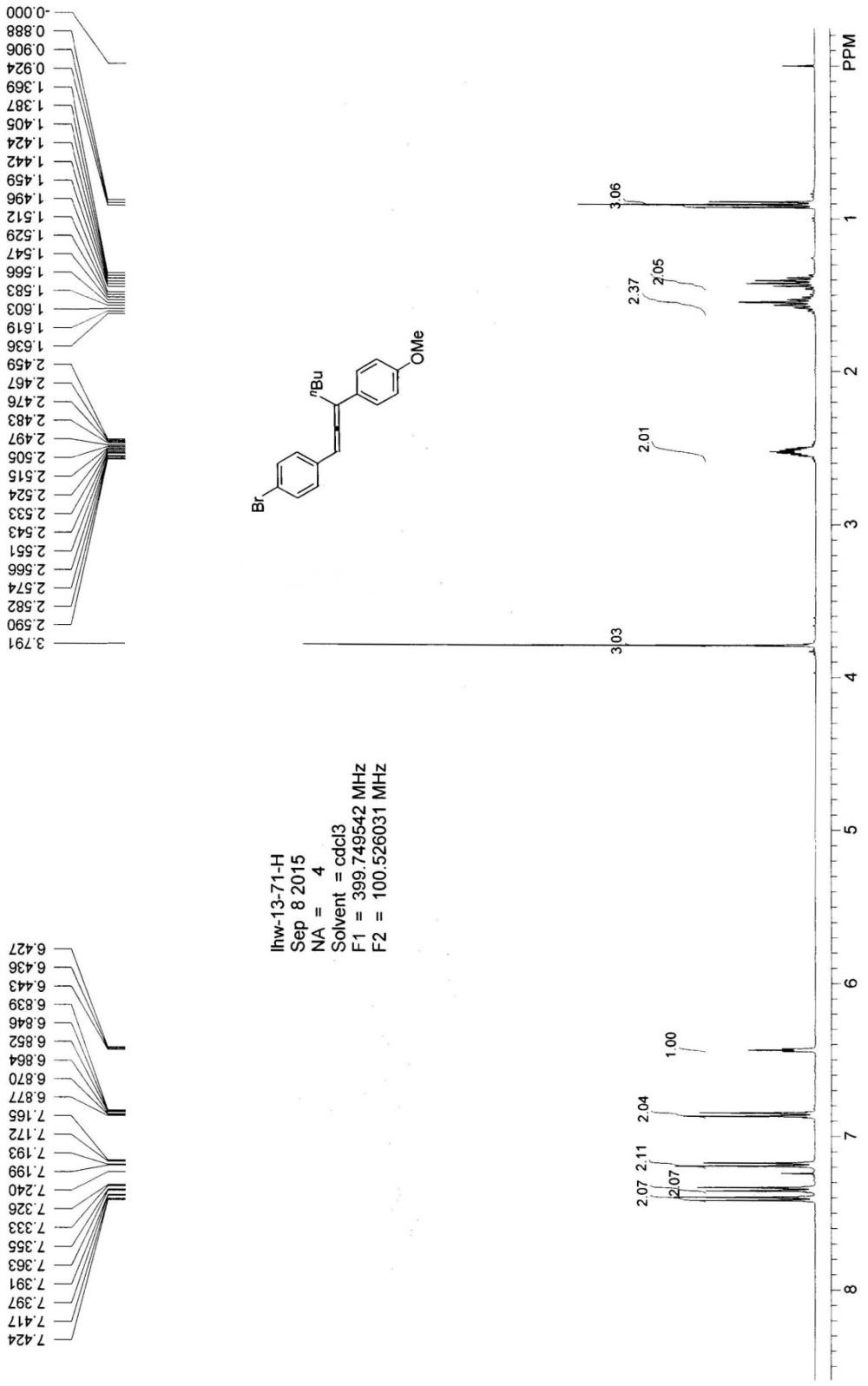

lhw-11-104-C
Apr 11 2015
NA = 256
Solvent = cdcl3
F1 = 100.528542 MHz
F2 = 399.749939 MHz
nBu
Ph
13.960
22.673
29.866
30.101
76.680
77.000
77.320
94.420
108.856
123.605
125.233
125.664
126.069
126.134
126.944
127.512
128.508
128.684
130.712
130.891
134.012
136.261
207.841
PPM
0
50
100
150
200

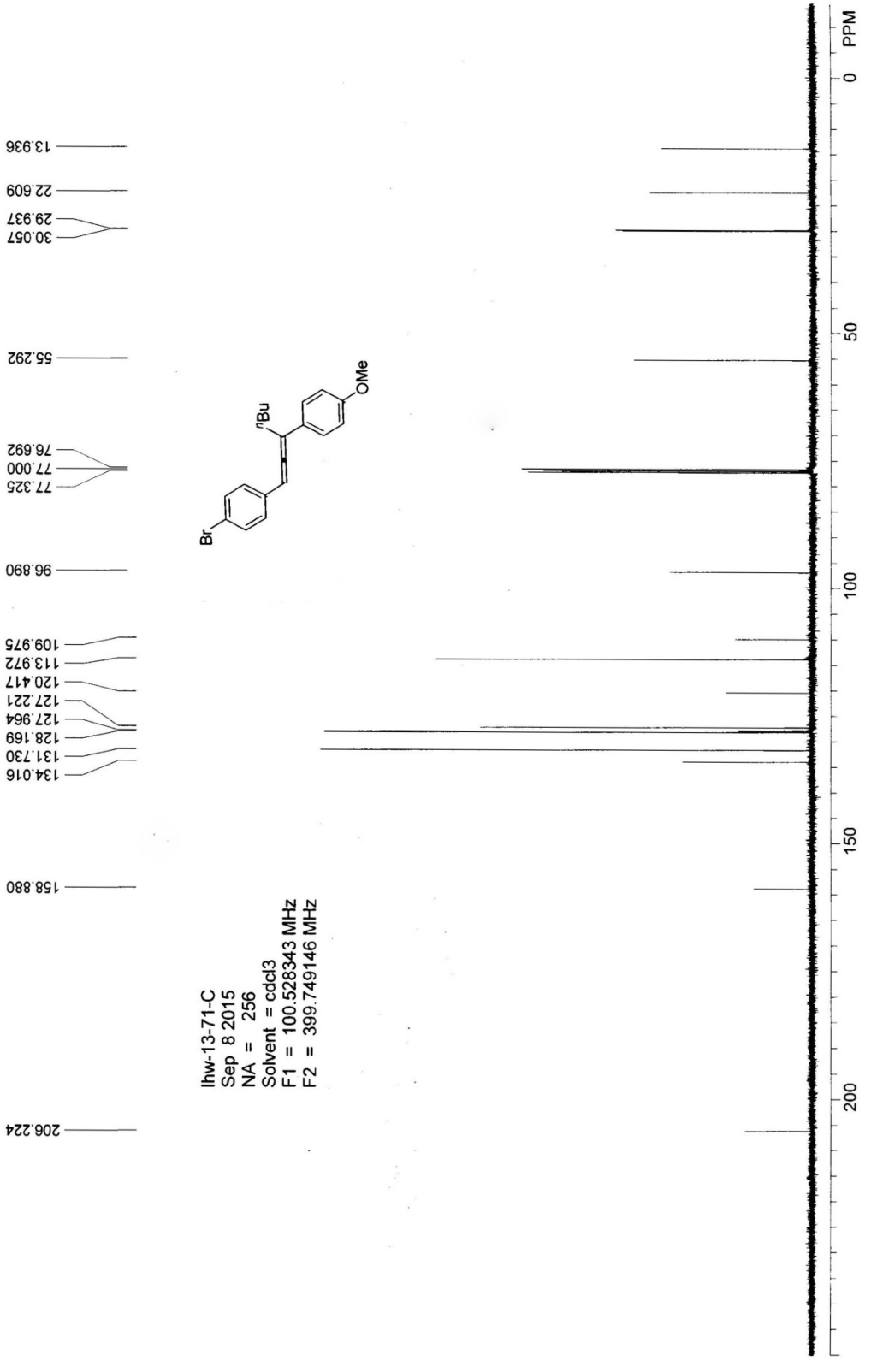
3ij


lhw-11-116-H
Apr 9 2015
NA = 4
Solvent = cdcl3
F1 = 399.750336 MHz
F2 = 100.526230 MHz
nBu
OMe
Cl
PPM

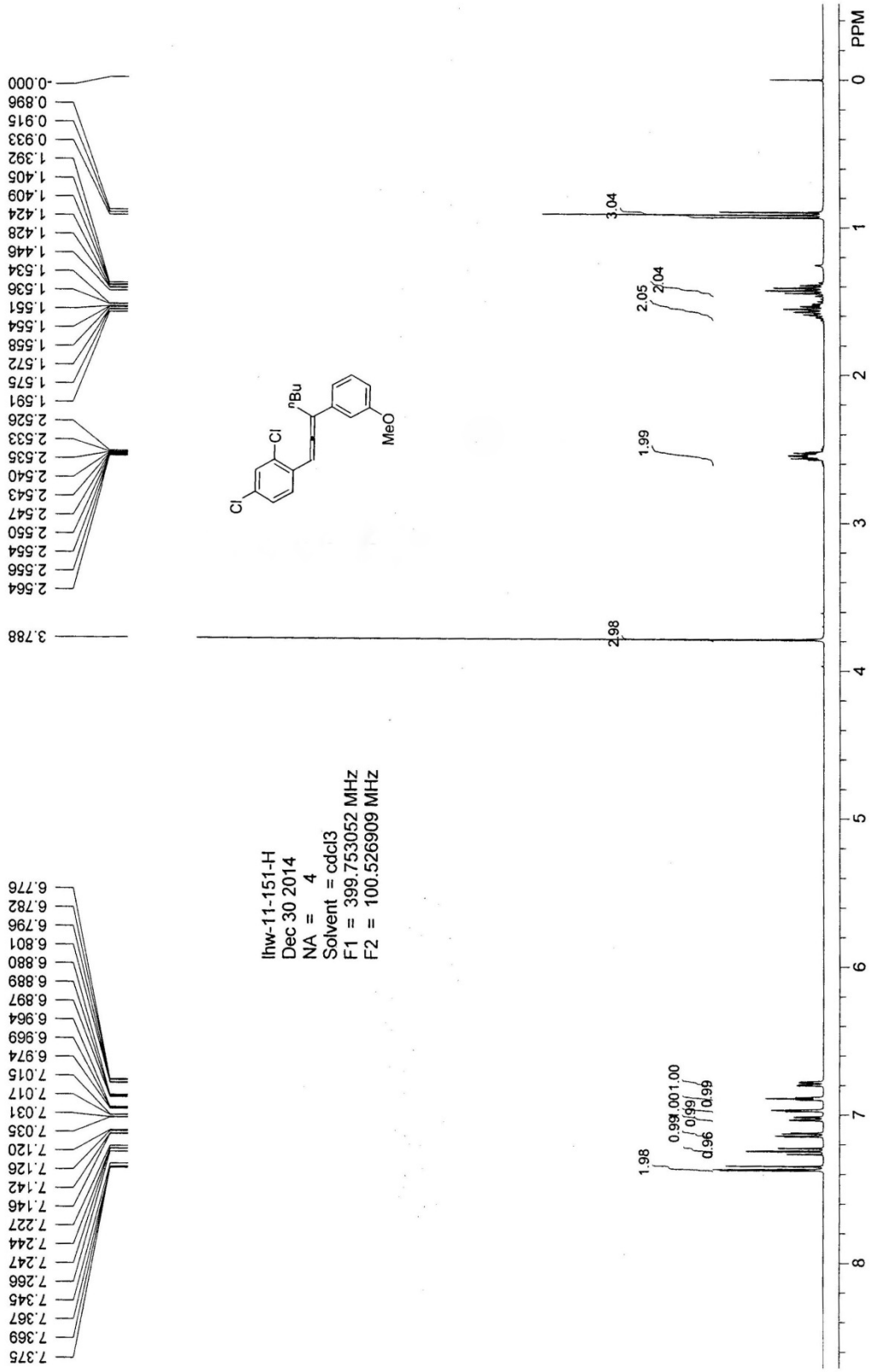

lhw-11-116-C
Apr 9 2015
NA = 256
Solvent = cdcl3
F1 = 100.528542 MHz
F2 = 399.749939 MHz
nBu
OMe
Cl
13.947
22.606
29.963
30.068
55.293
76.690
77.000
77.324
96.827
109.907
113.971
127.220
127.828
128.041
128.795
132.362
133.537
158.871
206.187
PPM
0
50
100
150
200

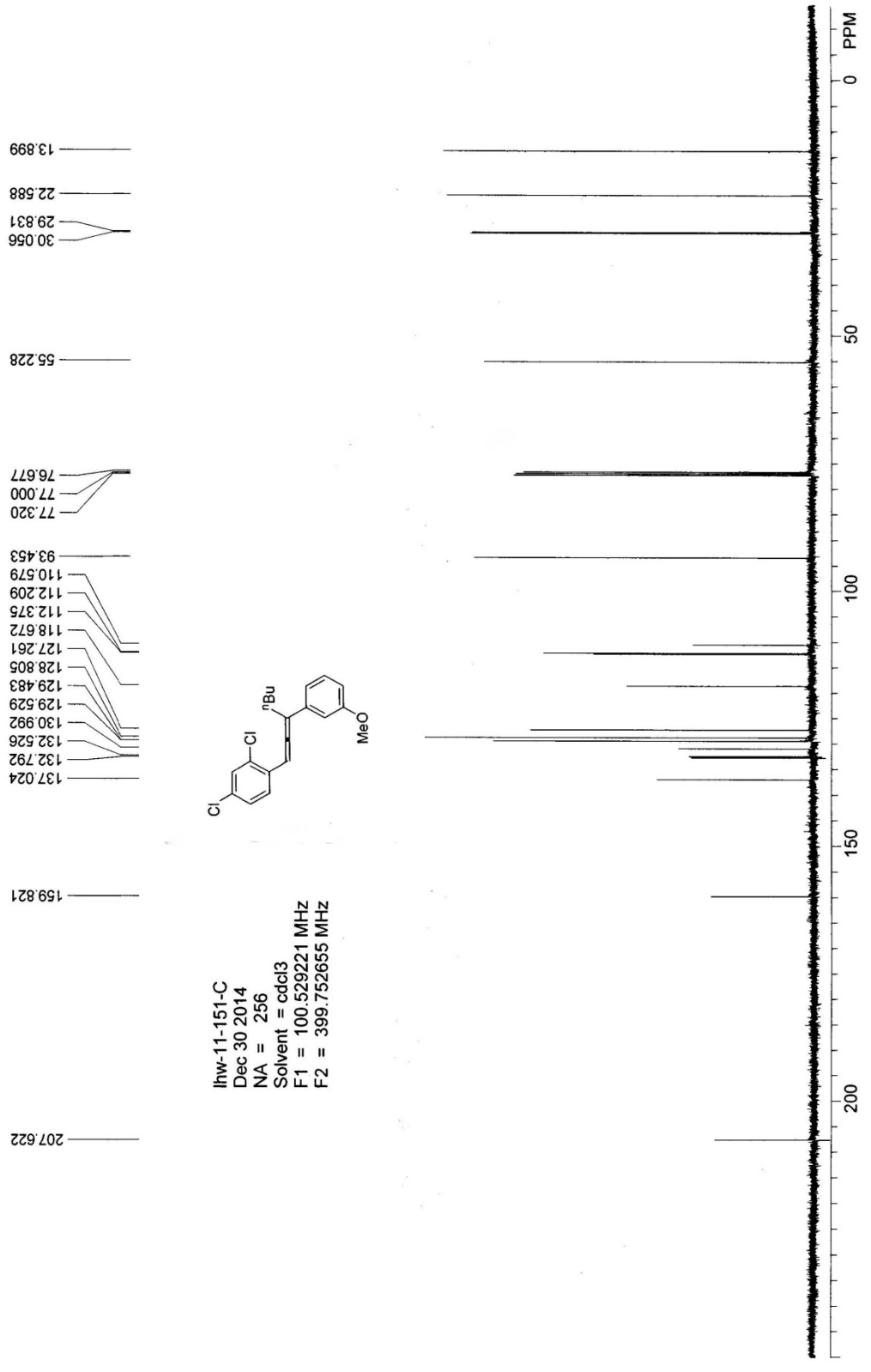
3jj


lhw-13-71-H
Sep 8 2015
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Br
nBu
OMe
PPM

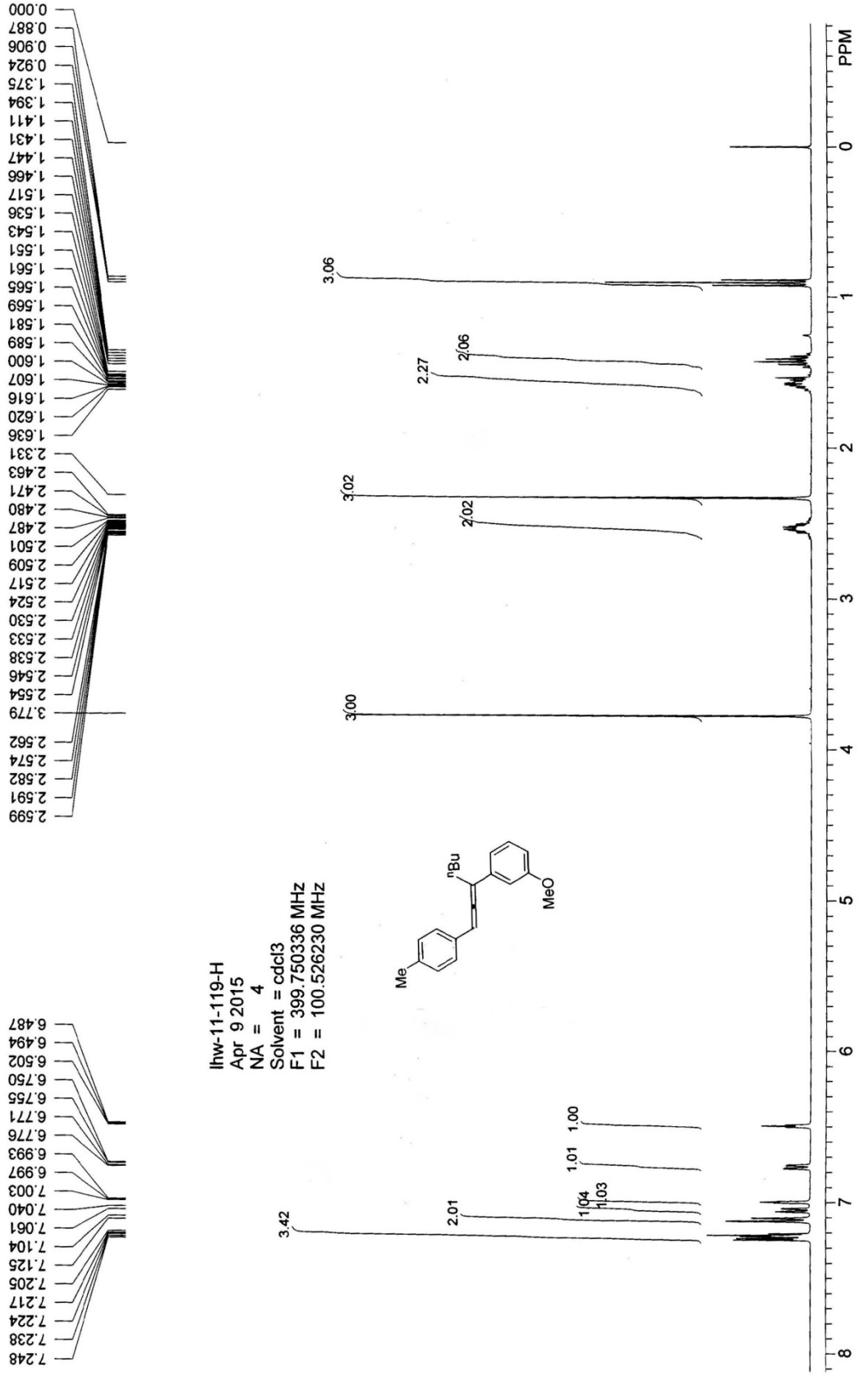

lhw-13-71-C
Sep 8 2015
NA = 256
Solvent = cdcl3
F1 = 100.528343 MHz
F2 = 399.749146 MHz
Br
nBu
OMe
13.936
22.609
29.937
30.057
55.292
76.692
77.000
77.325
96.890
109.975
113.972
120.417
127.221
127.964
128.169
131.730
134.016
158.880
206.224
PPM
0
50
100
150
200

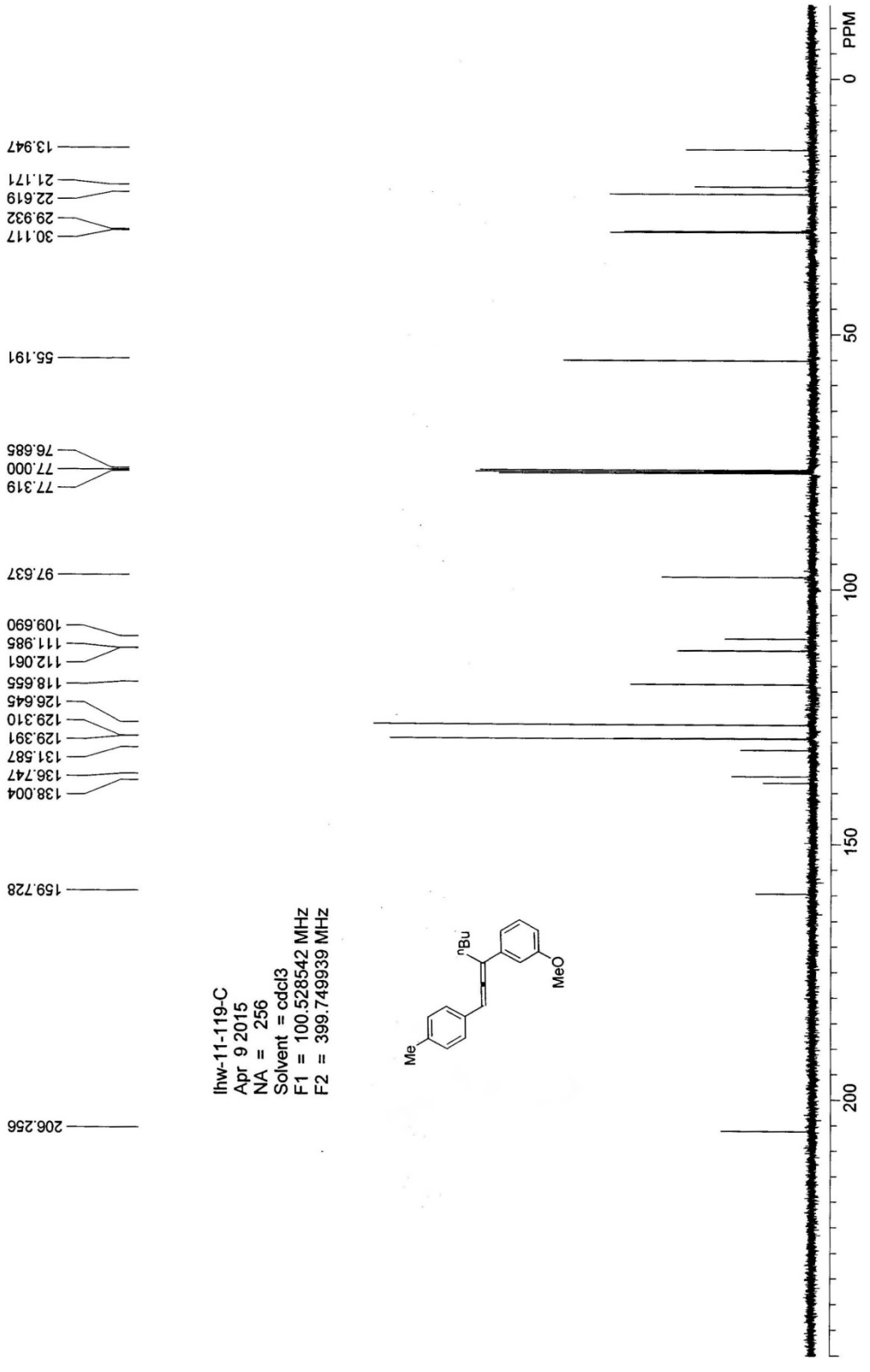
3kl


lhw-11-151-H
Dec 30 2014
NA = 4
Solvent = cdcl3
F1 = 399.753052 MHz
F2 = 100.526909 MHz
nBu
Cl
Cl
MeO
PPM

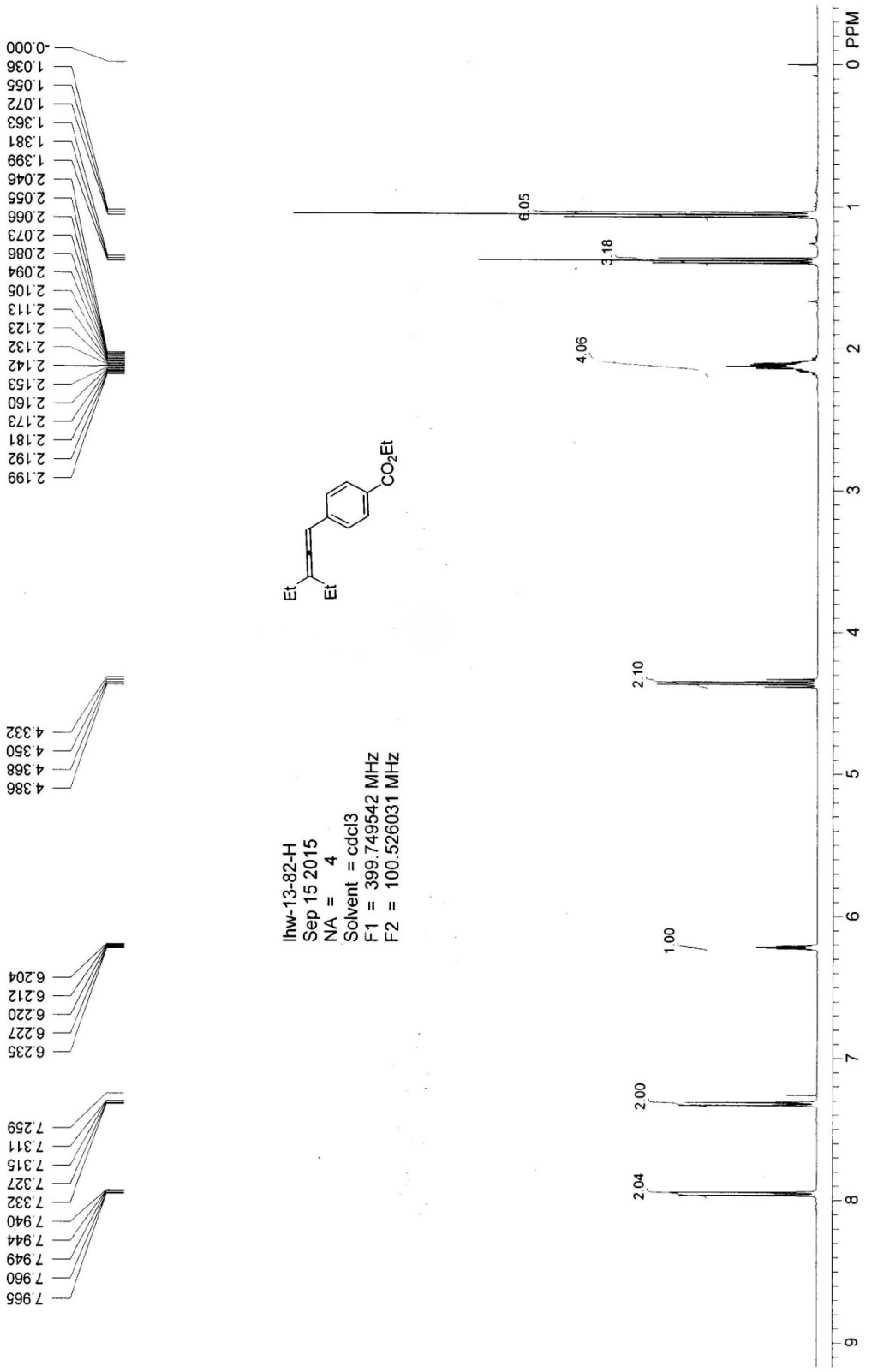

lhw-11-151-C
Dec 30 2014
NA = 256
Solvent = cdcl3
F1 = 100.529221 MHz
F2 = 399.752655 MHz
nBu
Cl
Cl
MeO
PPM
0
50
100
150
200
13.899
22.588
29.831
30.056
55.228
76.677
77.000
77.320
93.453
110.579
112.209
112.375
118.672
127.261
128.805
129.483
129.529
130.992
132.526
132.792
137.024
159.821
207.622

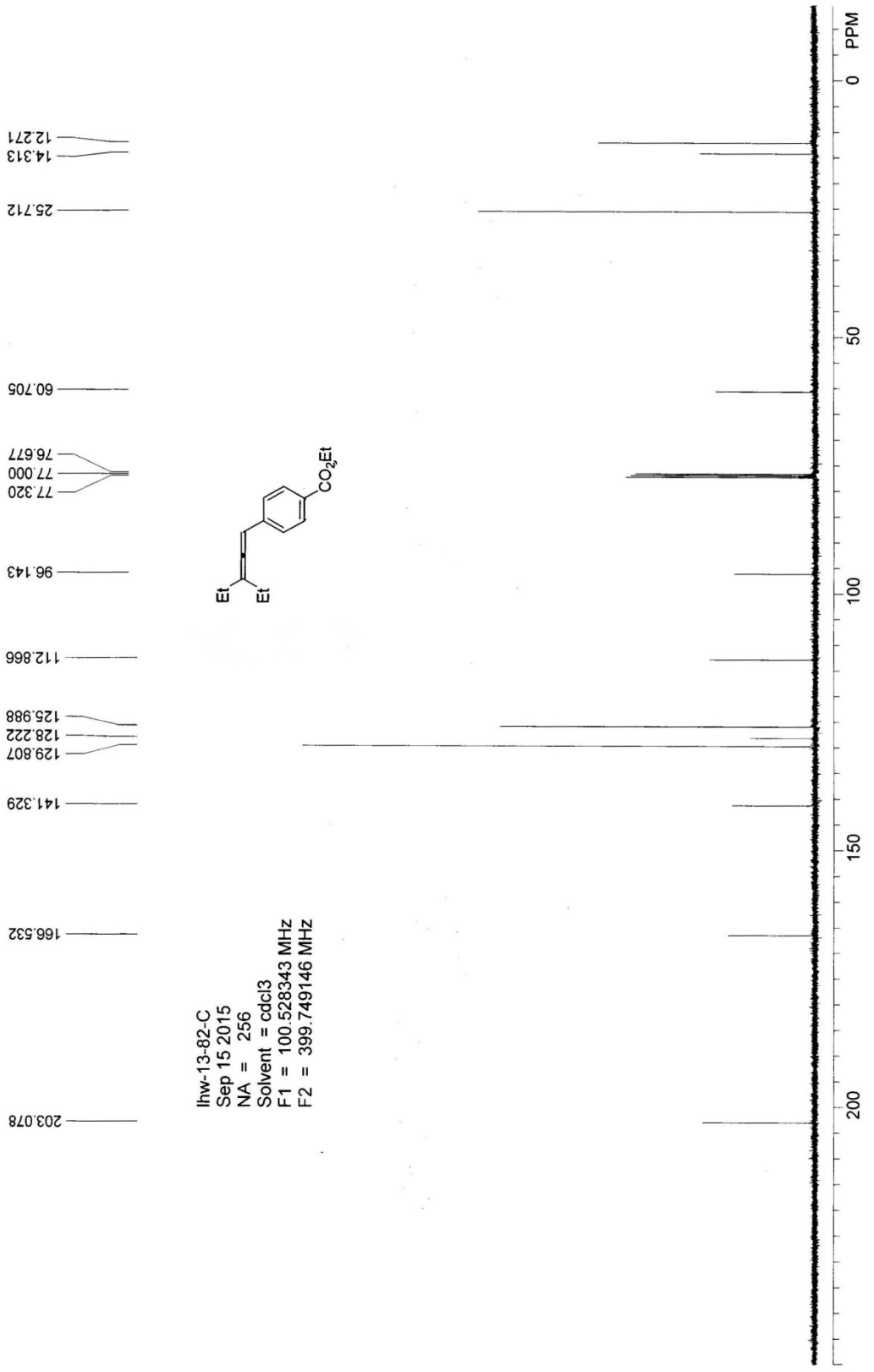
3ll


lhw-11-119-H
Apr 9 2015
NA = 4
Solvent = cdcl3
F1 = 399.750336 MHz
F2 = 100.526230 MHz
nBu
MeO
Me
3.42
2.01
1.04
1.03
1.01
1.00
3.00
3.02
2.02
2.27
2.06
3.06
PPM

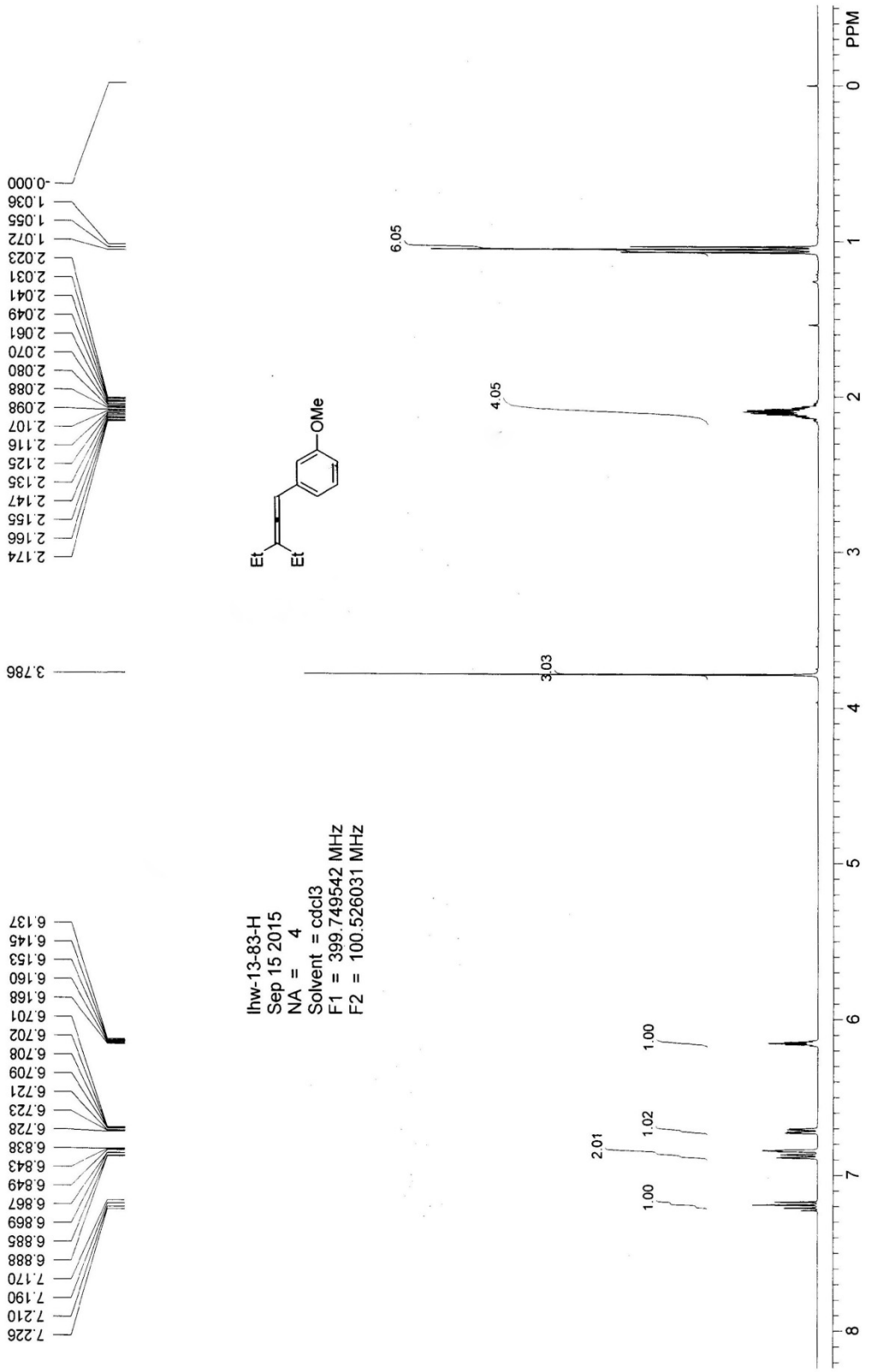

lhw-11-119-C
Apr 9 2015
NA = 256
Solvent = cdcl3
F1 = 100.528542 MHz
F2 = 399.749939 MHz
nBu
MeO
Me
PPM
0
50
100
150
200
13.947
21.171
22.619
29.932
30.117
55.191
76.685
77.000
77.319
97.637
109.690
111.985
112.061
118.655
126.645
129.310
129.391
131.587
136.747
138.004
159.728
206.256

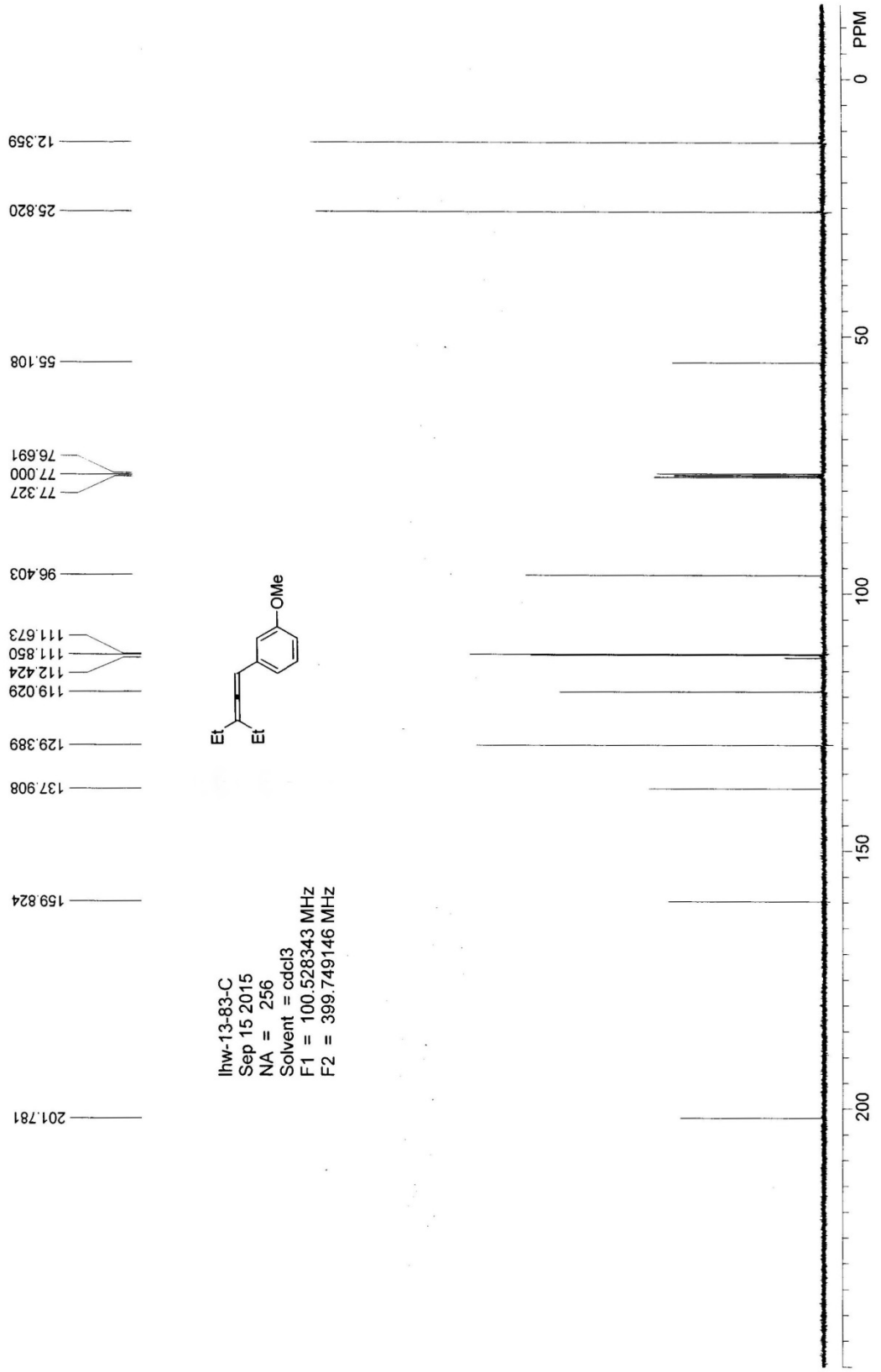
Eq.a-3mi


lhw-13-82-H
Sep 15 2015
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Et
Et
CO2Et
6.05
3.18
4.06
2.10
1.00
2.00
2.04
0 PPM
-0.000
1.036
1.055
1.072
1.363
1.381
1.399
2.046
2.055
2.066
2.073
2.086
2.094
2.105
2.113
2.123
2.132
2.142
2.153
2.160
2.173
2.181
2.192
2.199
4.332
4.350
4.368
4.386
6.204
6.212
6.220
6.227
6.235
7.259
7.311
7.315
7.327
7.332
7.940
7.944
7.949
7.960
7.965

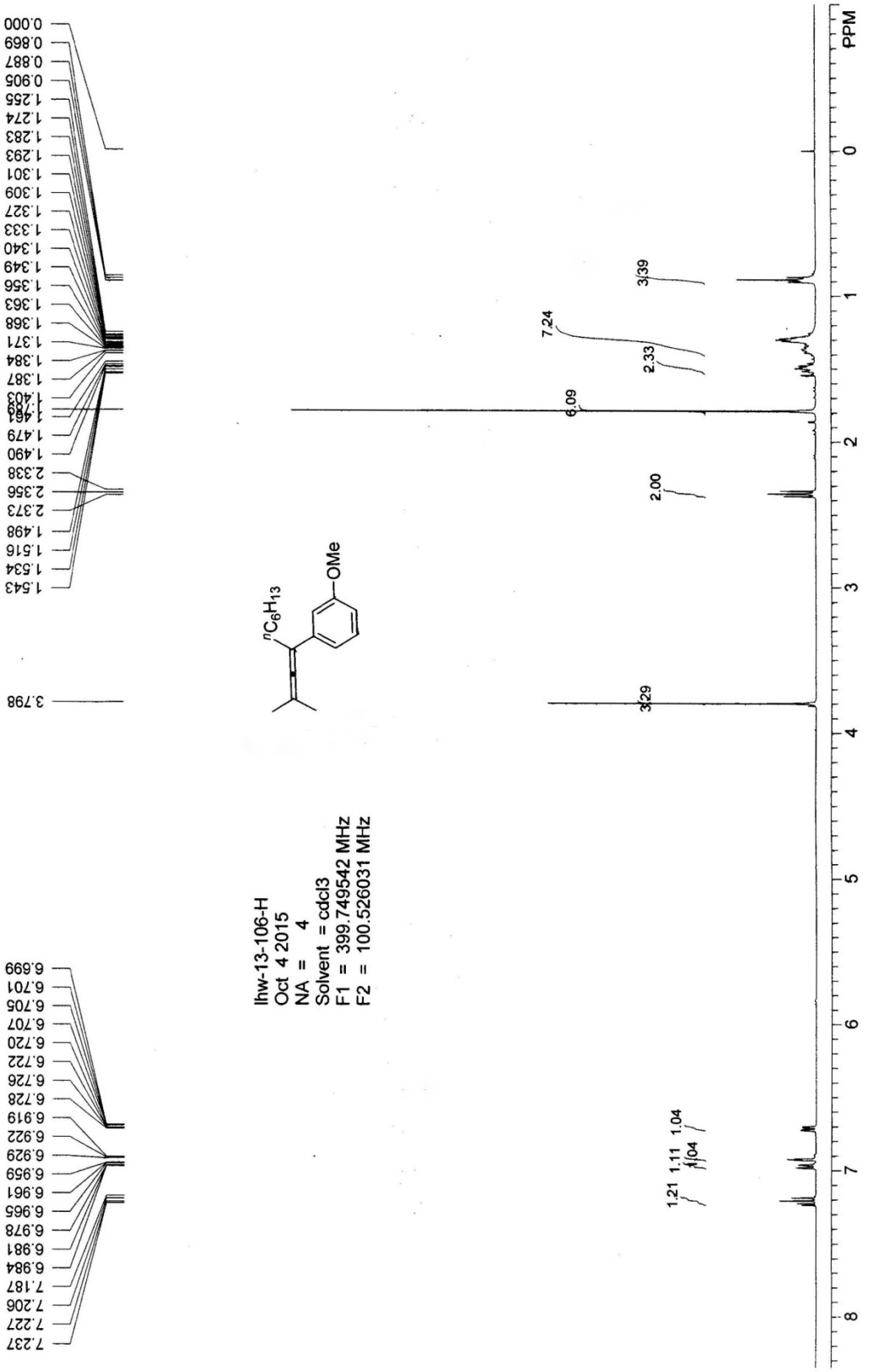

lhw-13-82-C
Sep 15 2015
NA = 256
Solvent = cdcl3
F1 = 100.528343 MHz
F2 = 399.749146 MHz
Et
Et
CO2Et
203.078
166.532
141.329
129.807
128.222
125.988
112.866
96.143
77.320
77.000
76.677
60.705
25.712
14.313
12.271
200
150
100
50
0
PPM

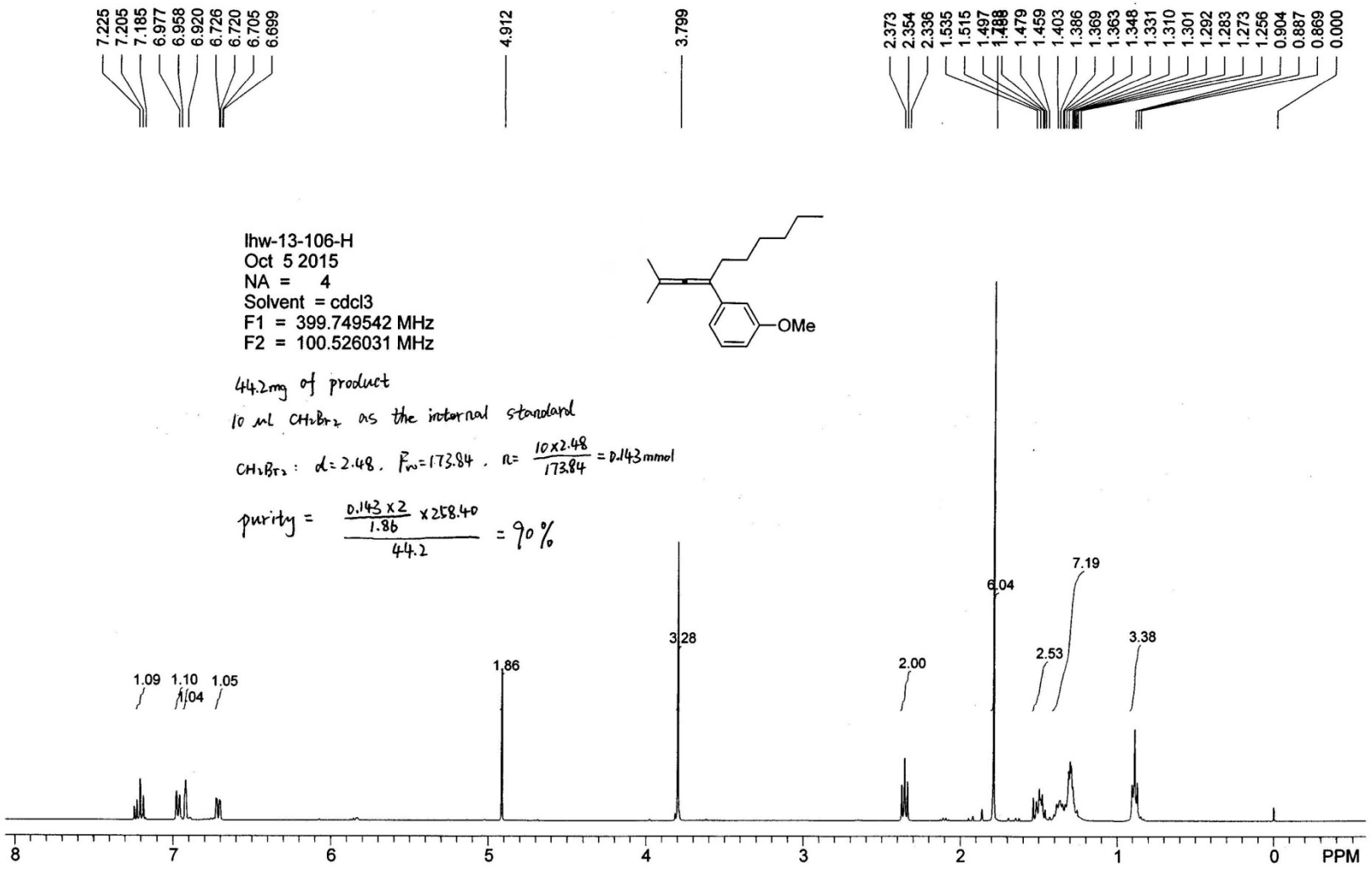
Eq.b-3ml

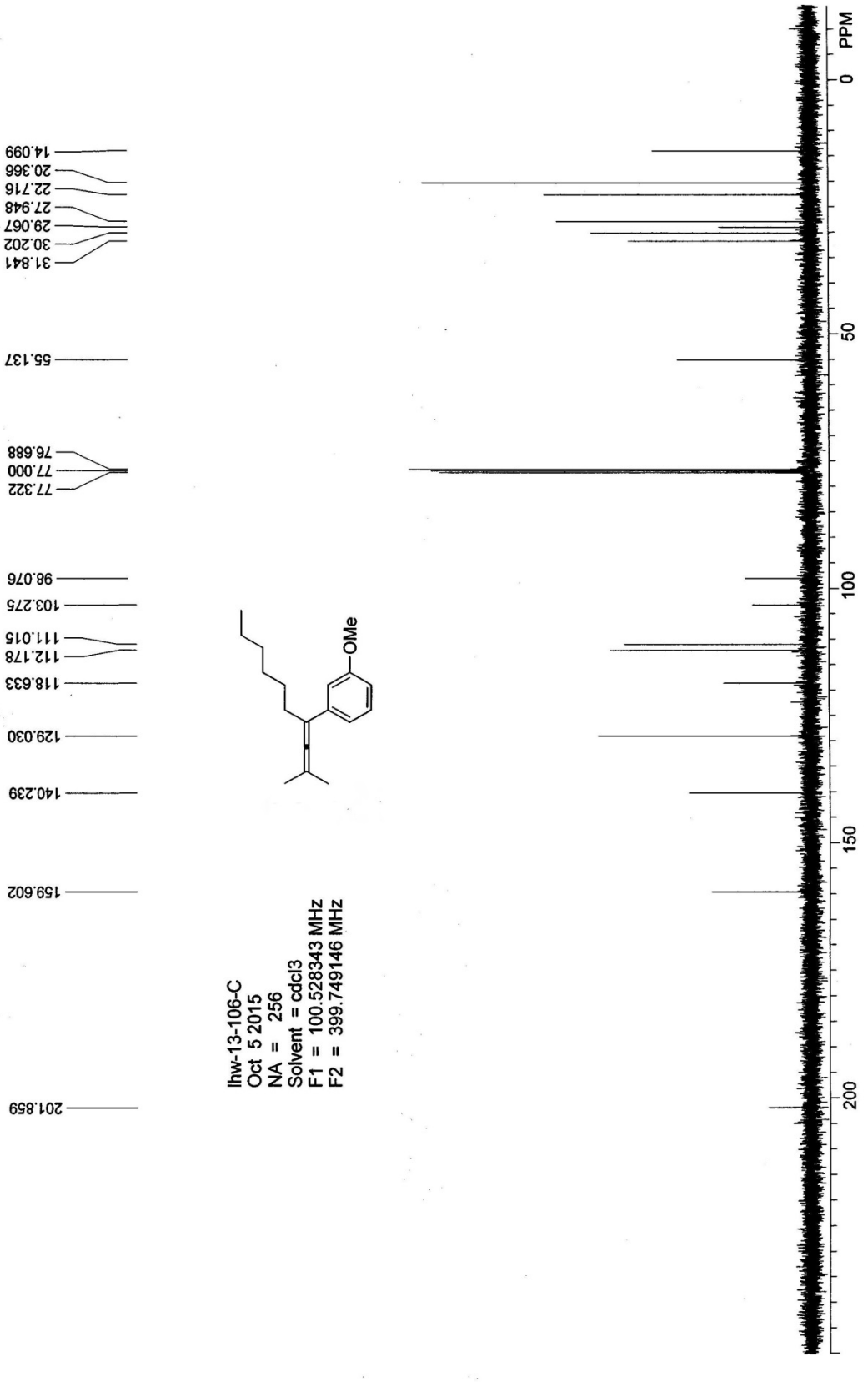

lhw-13-83-H
Sep 15 2015
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
Et
Et
OMe
6.05
4.05
3.03
2.01
1.02
1.00
1.00
PPM


lhw-13-83-C
Sep 15 2015
NA = 256
Solvent = cdcl3
F1 = 100.528343 MHz
F2 = 399.749146 MHz
OMe
Et
Et
12.359
25.820
55.108
76.691
77.000
77.327
96.403
111.673
111.850
112.424
119.029
129.389
137.908
159.824
201.781
0
50
100
150
200
PPM

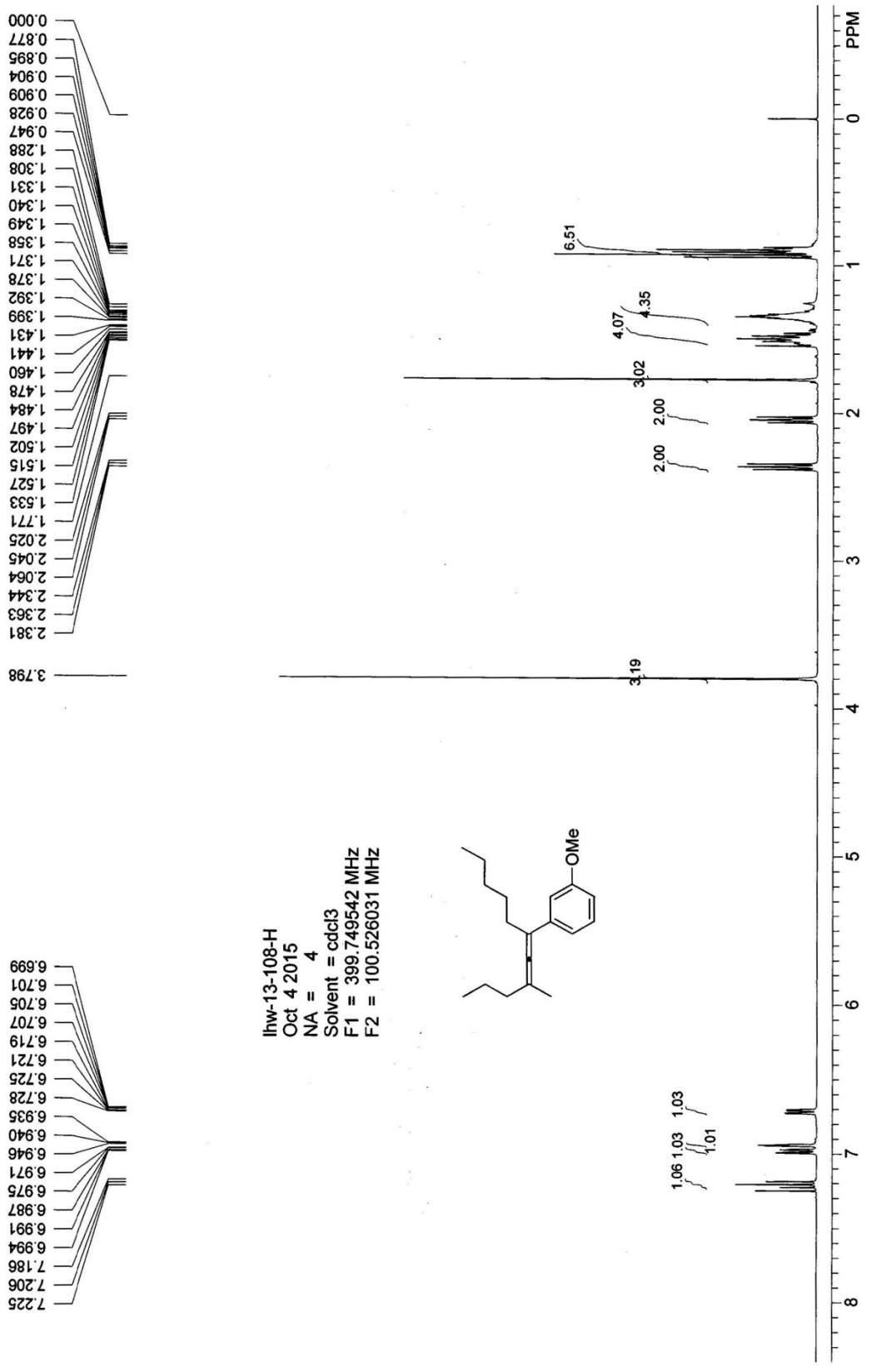
Eq.c-3nl

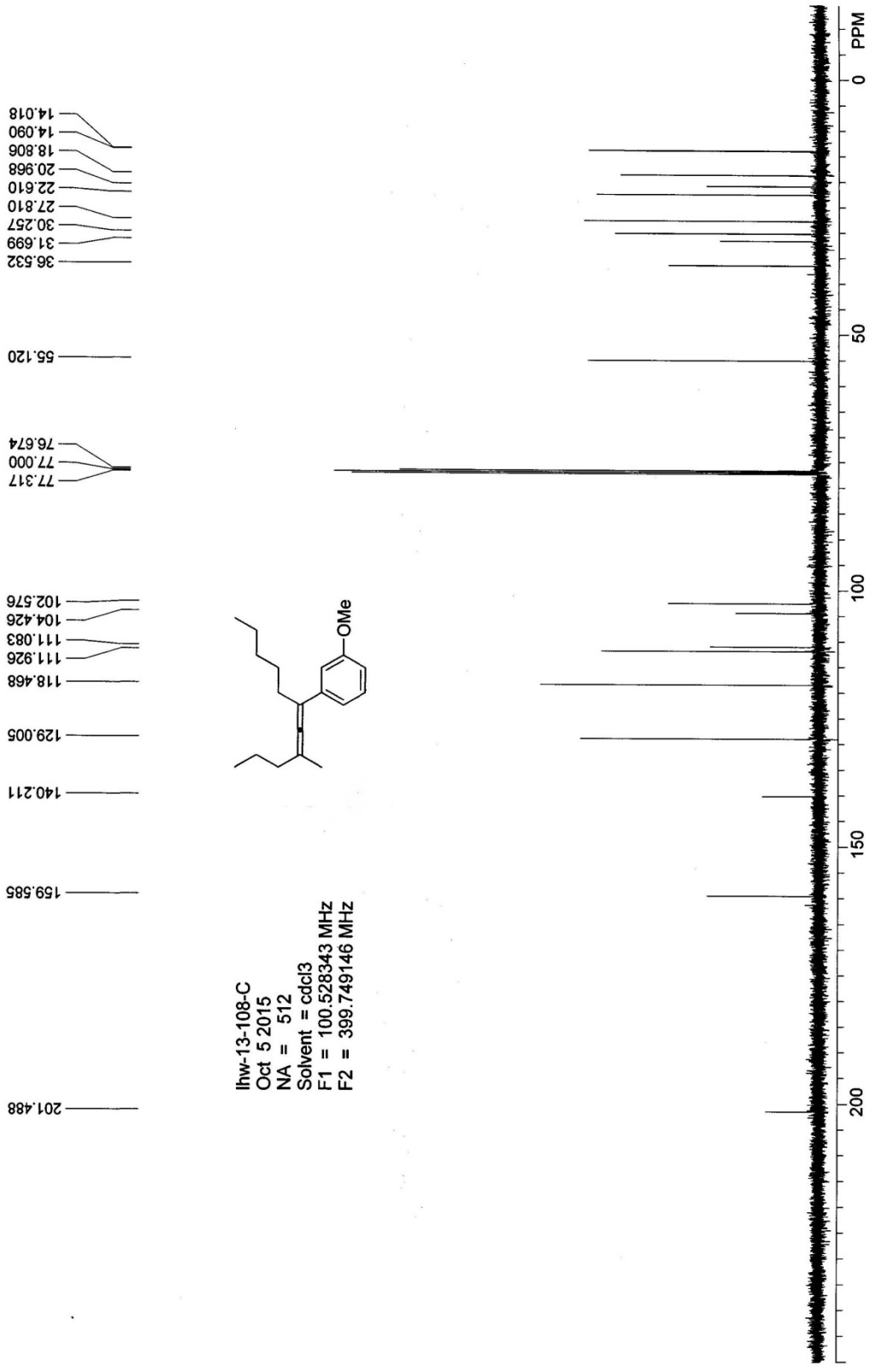

lhw-13-106-H
Oct 4 2015
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
OMe
PPM


7.225
7.205
7.185
6.977
6.958
6.920
6.726
6.720
6.705
6.699
4.912
3.799
2.373
2.354
2.336
1.535
1.515
1.497
1.479
1.459
1.403
1.386
1.369
1.363
1.348
1.331
1.310
1.301
1.292
1.283
1.273
1.256
0.904
0.887
0.869
0.000
lhw-13-106-H
Oct 5 2015
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
OMe
44.2mg of product
10 mL CH2Br2 as the internal standard
CH2Br2 : d = 2.48 , Mw = 173.84 , n = 10x2.48 / 173.84 = 0.143 mmol
purity = (0.143 x 2 / 1.86) x 258.40 / 44.2 = 90%
1.09
1.10
1.04
1.05
1.86
3.28
2.00
6.04
2.53
7.19
3.38
8
7
6
5
4
3
2
1
0
PPM

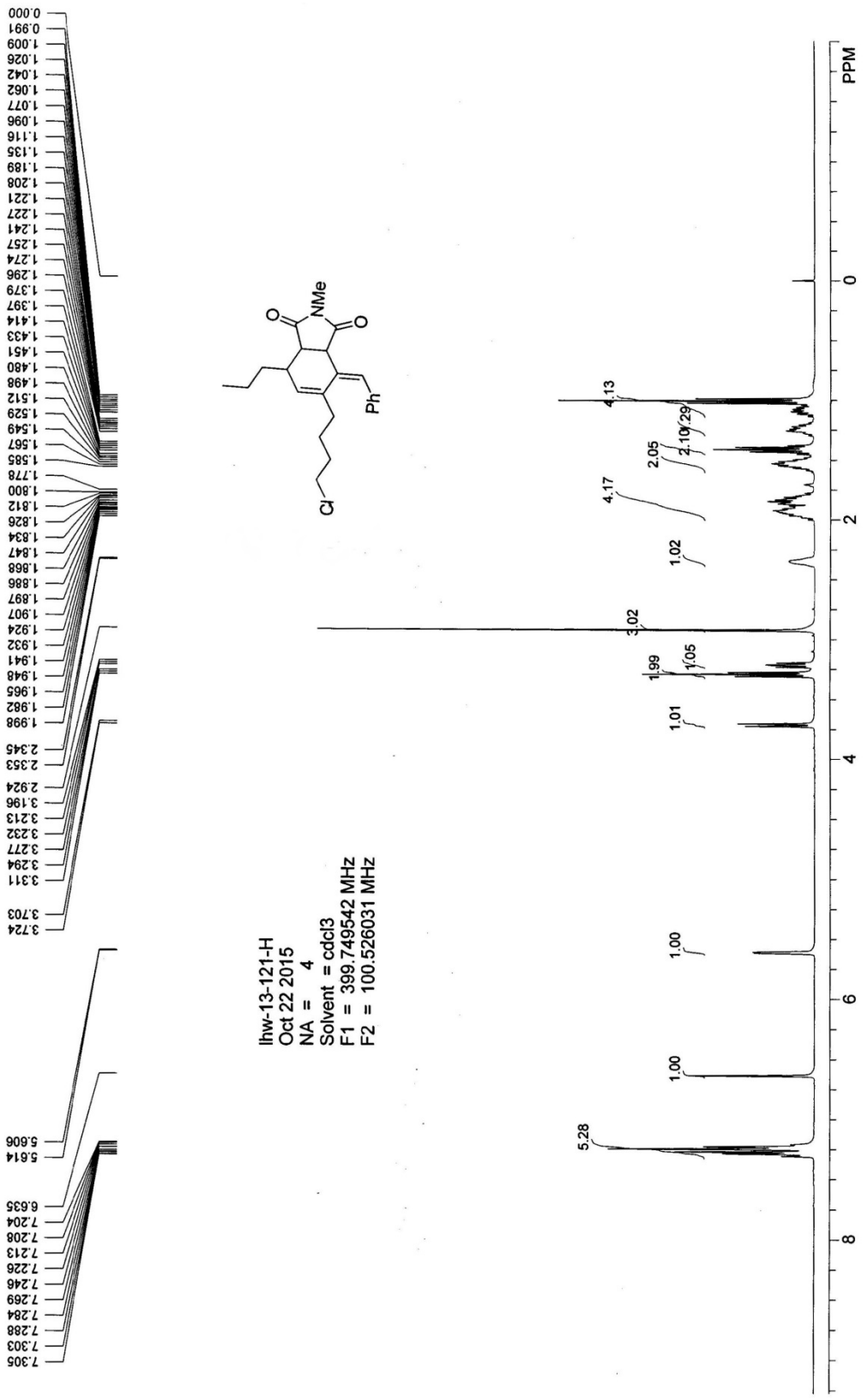

lhw-13-106-C
Oct 5 2015
NA = 256
Solvent = cdcl3
F1 = 100.528343 MHz
F2 = 399.749146 MHz
OMe
14.099
20.366
22.716
27.948
29.067
30.202
31.841
55.137
76.688
77.000
77.322
98.076
103.275
111.015
112.178
118.633
129.030
140.239
159.602
201.859
PPM
0
50
100
150
200

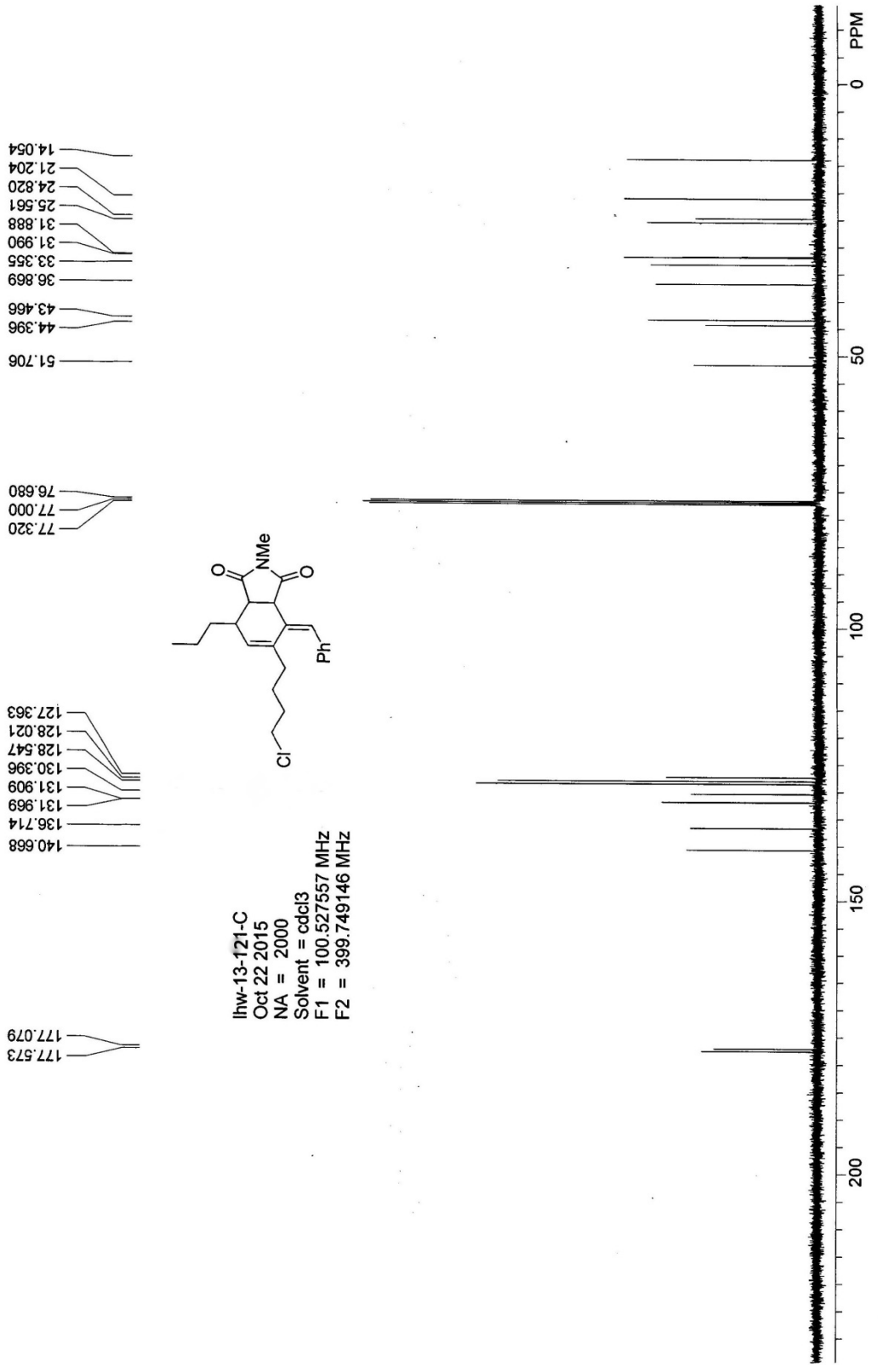
Eq.d-3ol

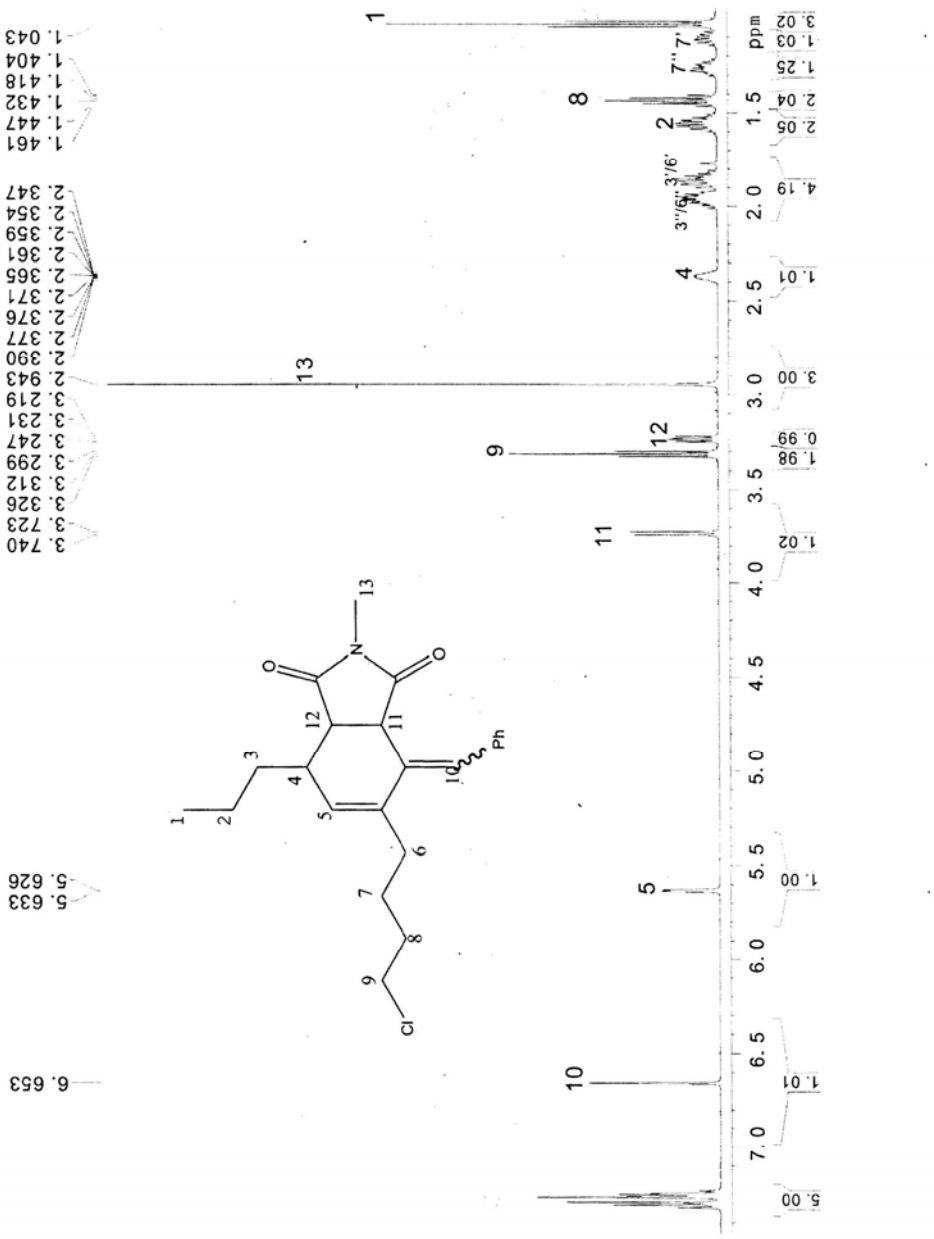

lhw-13-108-H
Oct 4 2015
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
OMe
PPM


14.018
14.090
18.806
20.968
22.610
27.810
30.257
31.699
36.532
55.120
76.674
77.000
77.317
102.576
104.426
111.083
111.926
118.468
129.005
140.211
159.585
201.488
OMe
lhw-13-108-C
Oct 5 2015
NA = 512
Solvent = cdcl3
F1 = 100.528343 MHz
F2 = 399.749146 MHz
PPM
0
50
100
150
200

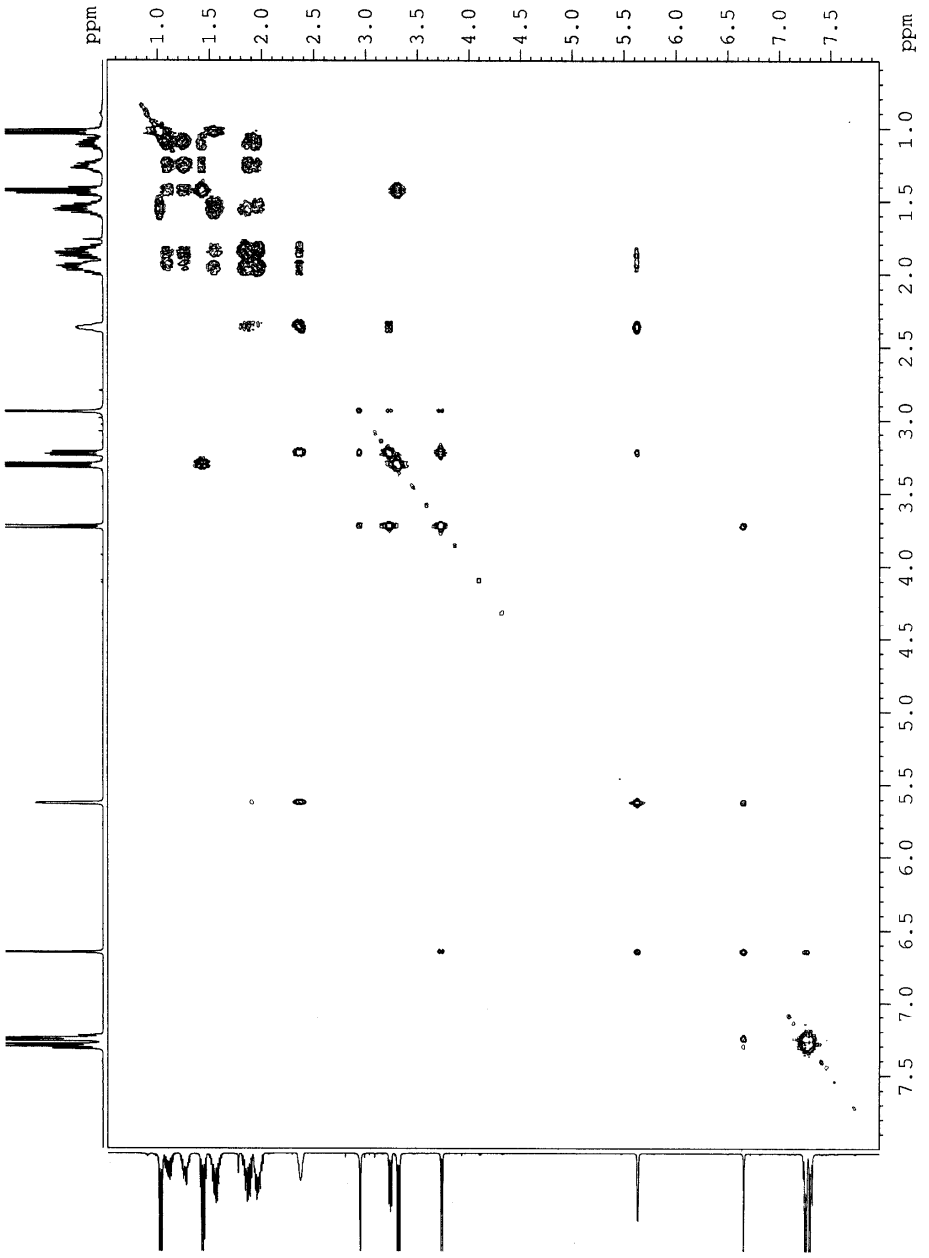
Eq.e-6


lhw-13-121-H
Oct 22 2015
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
NMe
Ph
Cl
PPM

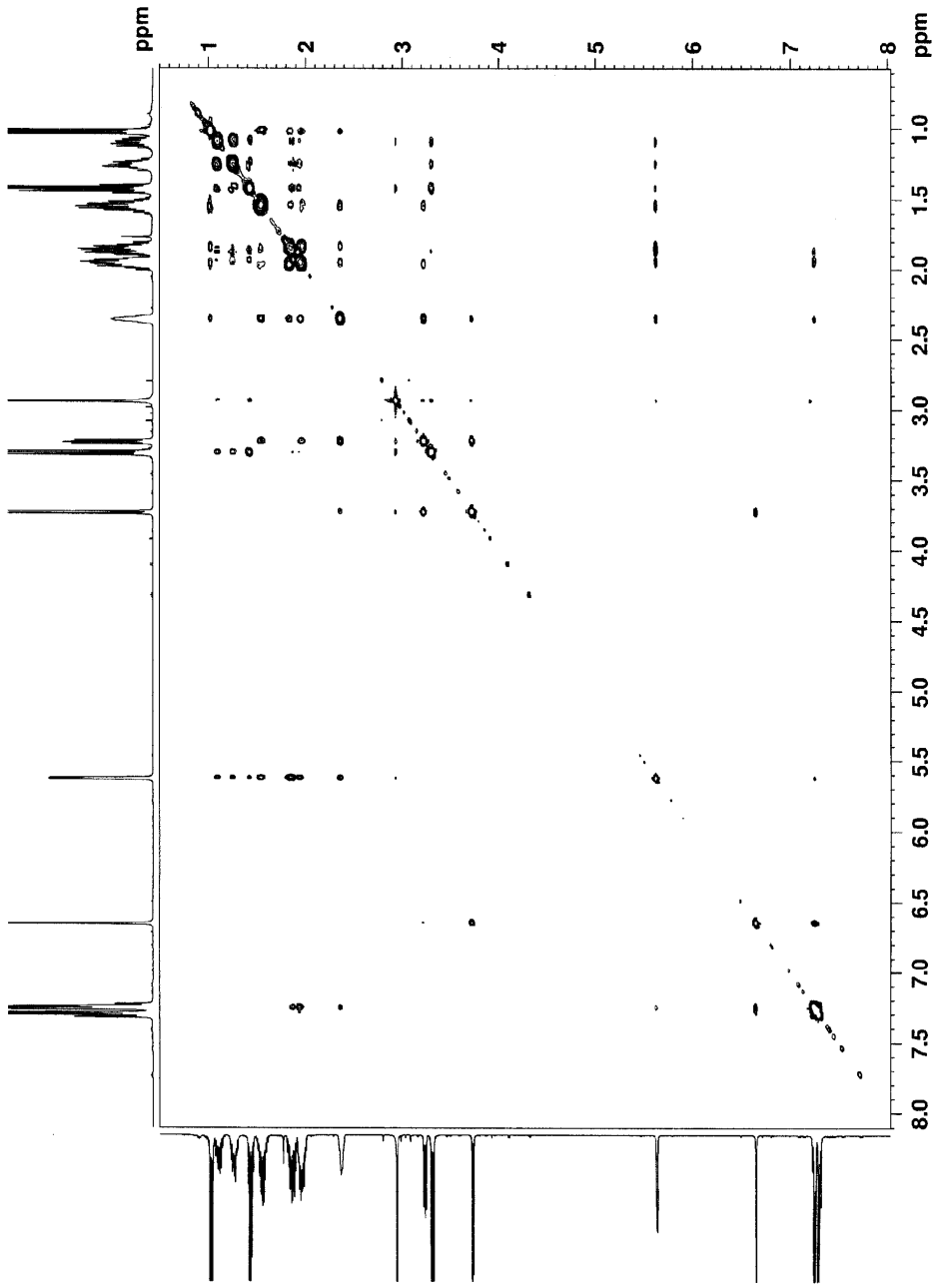

14.054
21.204
24.820
25.561
31.888
31.990
33.355
36.869
43.466
44.396
51.706
76.680
77.000
77.320
127.363
128.021
128.547
130.396
131.909
131.969
136.714
140.668
177.573
177.079
NMe
O
O
Ph
Cl
lhw-13-121-C
Oct 22 2015
NA = 2000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
PPM
0
50
100
150
200


1.043
1.404
1.418
1.432
1.447
1.461
2.347
2.354
2.359
2.361
2.365
2.371
2.376
2.377
2.390
2.943
3.219
3.231
3.247
3.299
3.312
3.326
3.723
3.740
5.626
5.633
6.653
ppm
O
N
O
Ph
Cl

COSY



NOESY



HSQC

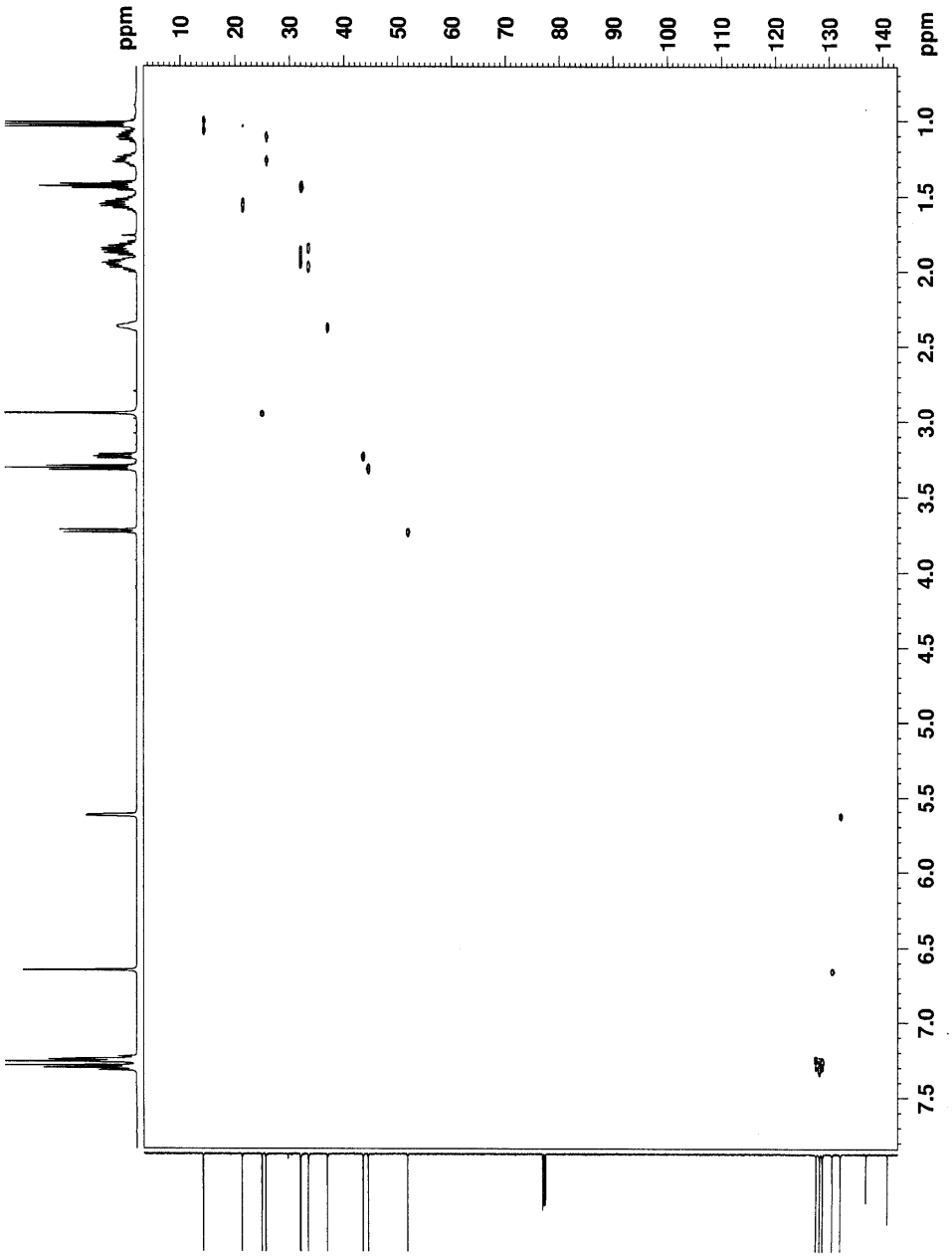
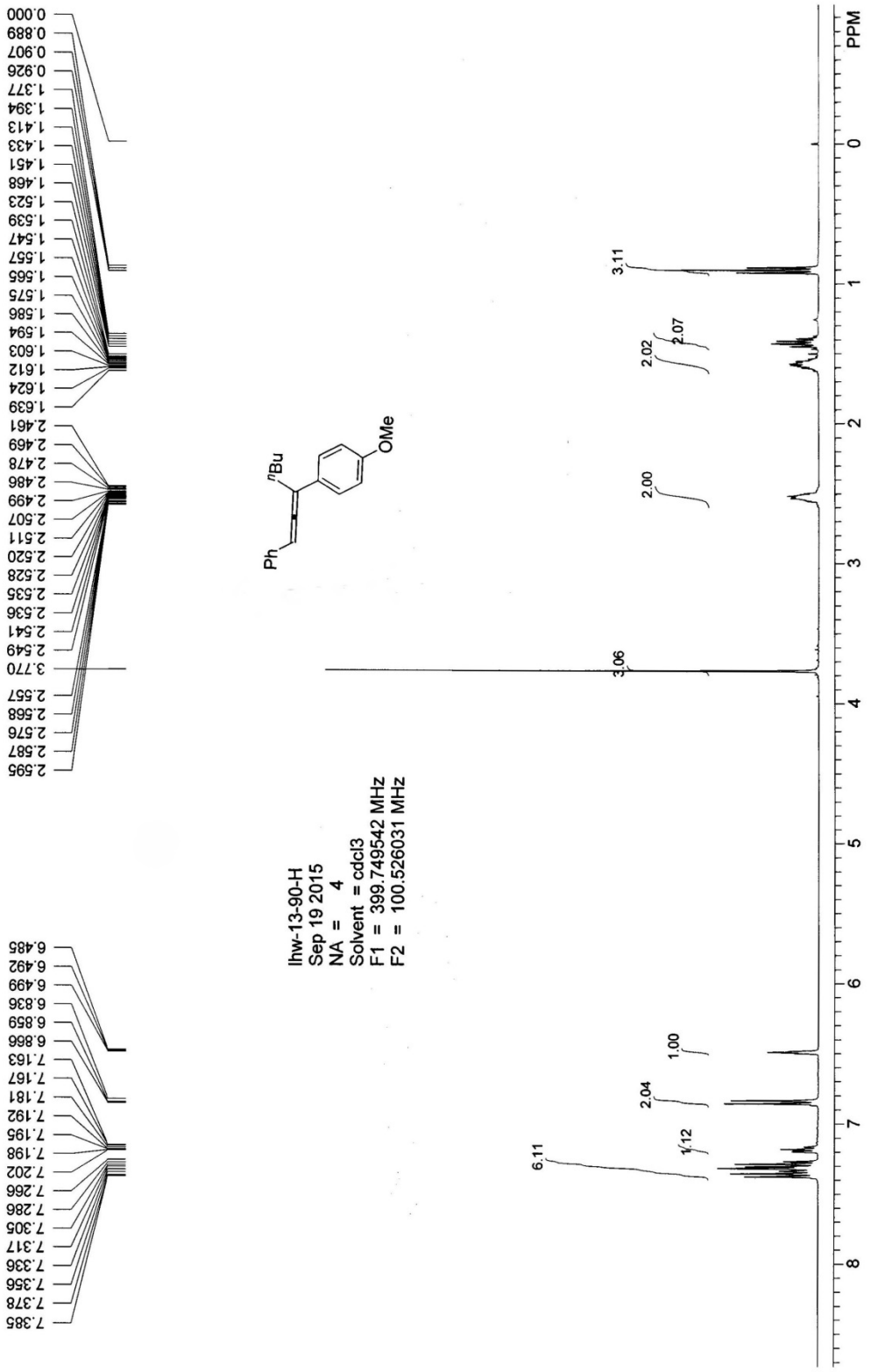
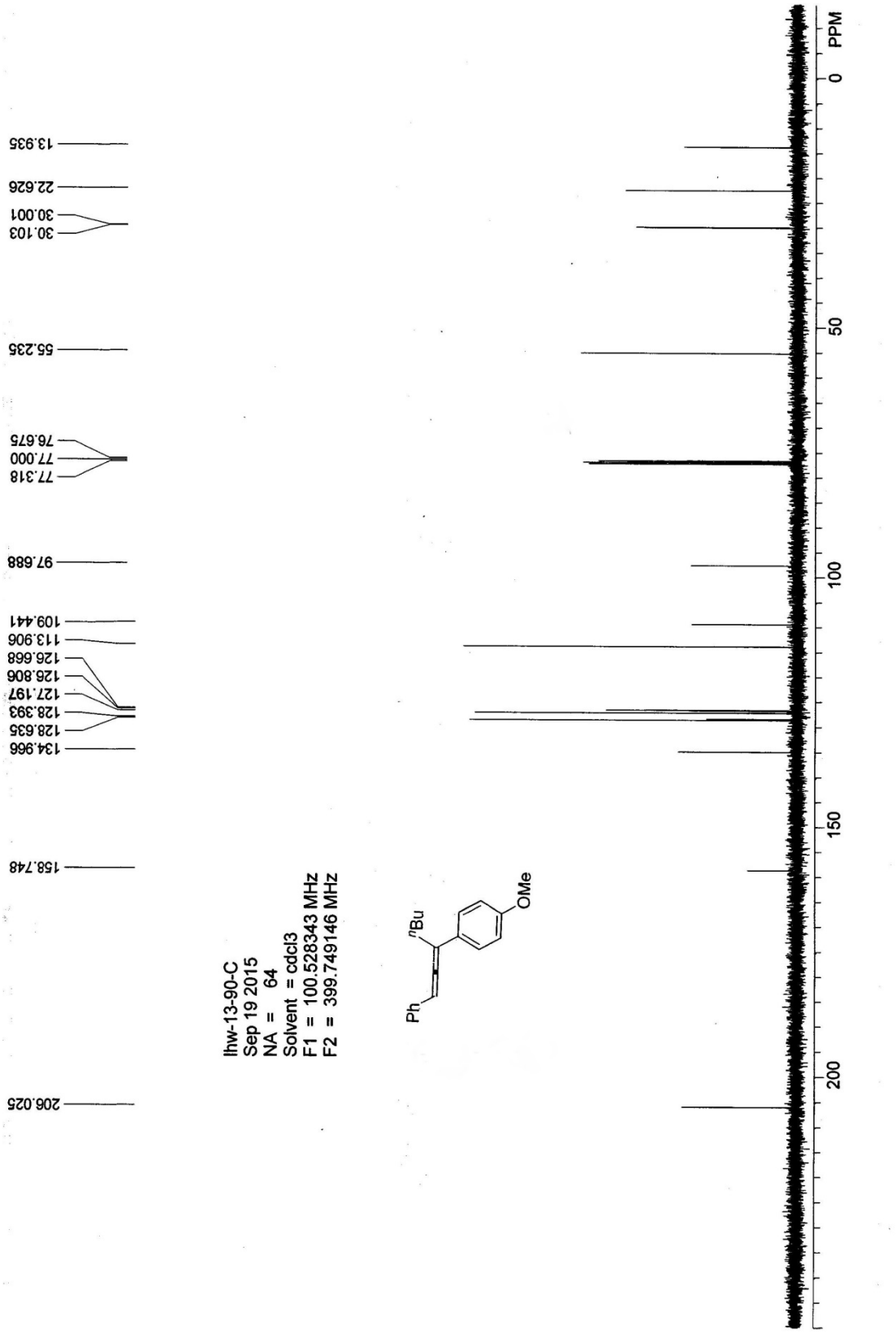
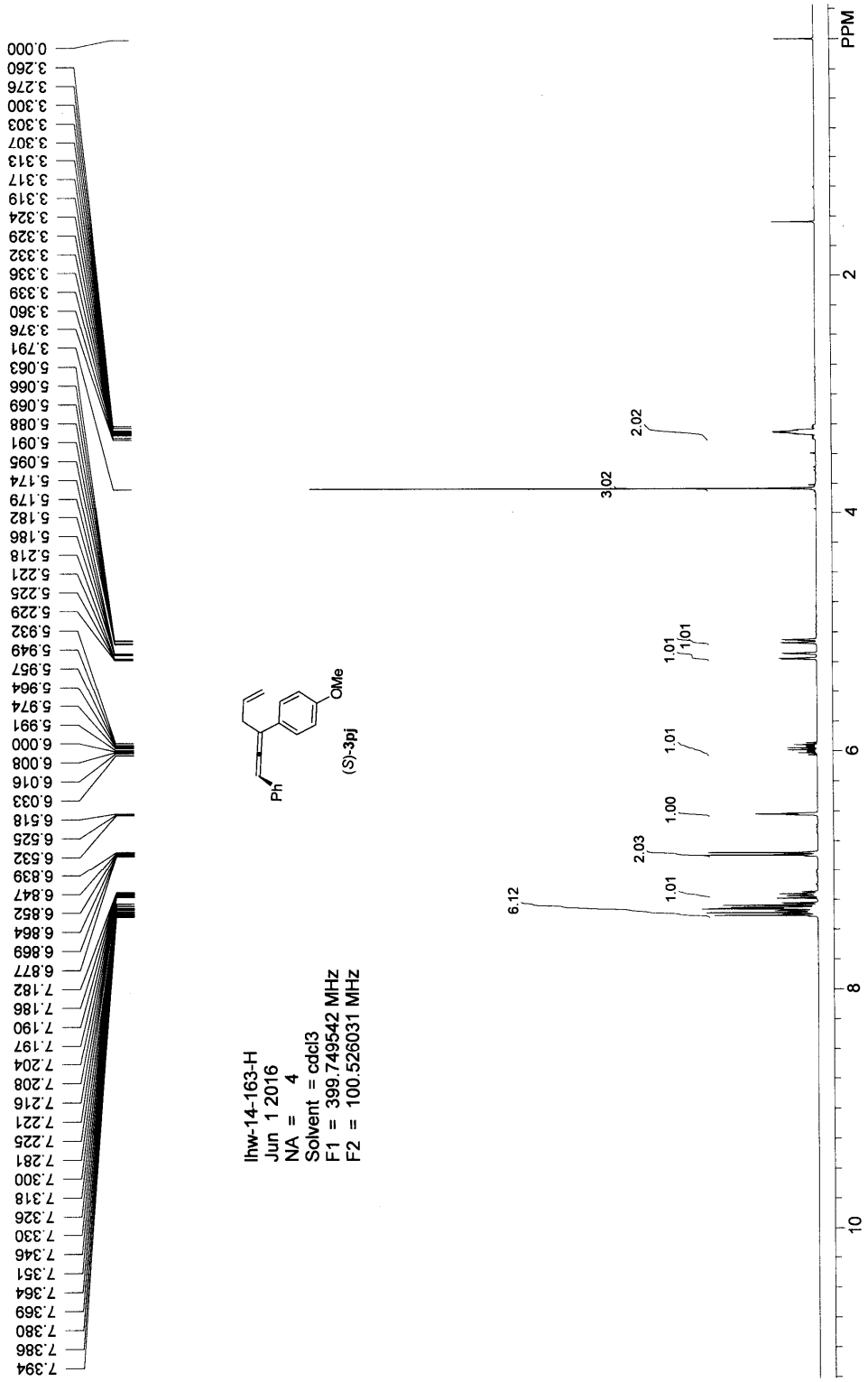

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

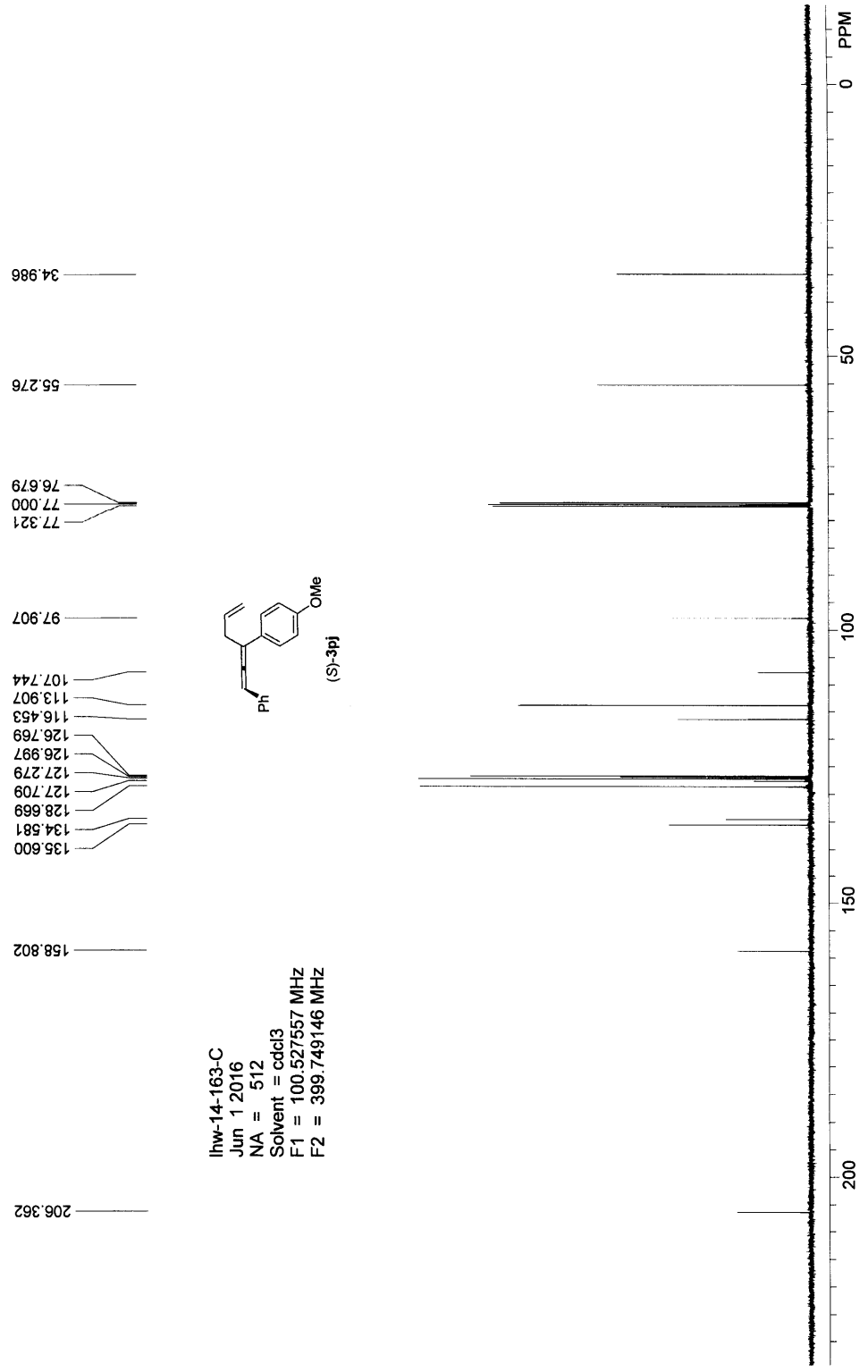
Table 2-entry 13-3cj




lhw-13-90-C
Sep 19 2015
NA = 64
Solvent = cdcl3
F1 = 100.528343 MHz
F2 = 399.749146 MHz
nBu
Ph
OMe
PPM
0
50
100
150
200
13.935
22.626
30.001
30.103
55.235
76.675
77.000
77.318
97.688
109.441
113.906
126.668
126.806
127.197
128.393
128.635
134.966
158.748
206.025

(*S*)-**3pj**

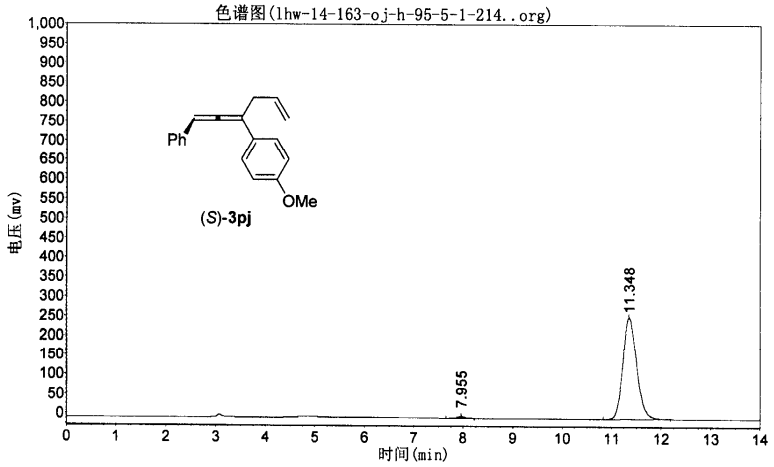

lhw-14-163-H
Jun 1 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
(S)-3pj
OMe
Ph
PPM
6.12
2.03
1.01
1.00
1.01
1.01
1.01
3.02
2.02


lhw-14-163-C
Jun 1 2016
NA = 512
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
OMe
Ph
(S)-3pj
206.362
158.802
135.600
134.581
128.669
127.709
127.279
126.997
126.769
116.453
113.907
107.744
97.907
77.321
77.000
76.679
55.276
34.986
PPM
0
50
100
150
200

lhw-14-163-oj-h-95-5-1-214

实验时间：2016-06-01,20:36:11　　报告时间：2016-06-01,20:37:11
谱图文件:F:\zhuguangjiong\lhw\20160601\lhw-14-163-oj-h-95-5-1-214..org

实验内容简介：



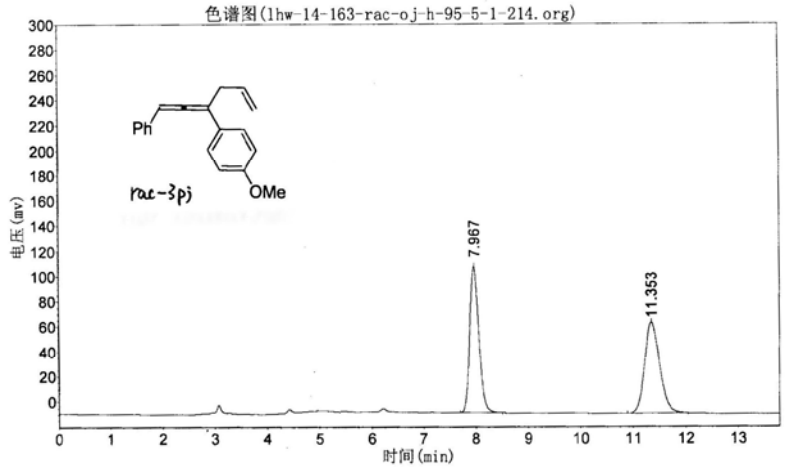
分析结果表

峰号	峰名	保留时间(Ret.Time)	峰高(Height)	峰面积(Area)	含量(Rel.Area)
1		7.955	2950.373	38983.629	0.7682
2		11.348	259498.234	5035580.000	99.2318
总计(Total)			262448.607	5074563.629	100.0000

lhw-14-163-rac-oj-h-95-5-1-214

实验时间：2016-06-01,20:07:04　　报告时间：2016-06-01,20:33:56
谱图文件:F:\zhuguangjiong\lhw\20160601\lhw-14-163-rac-oj-h-95-5-1-214.org

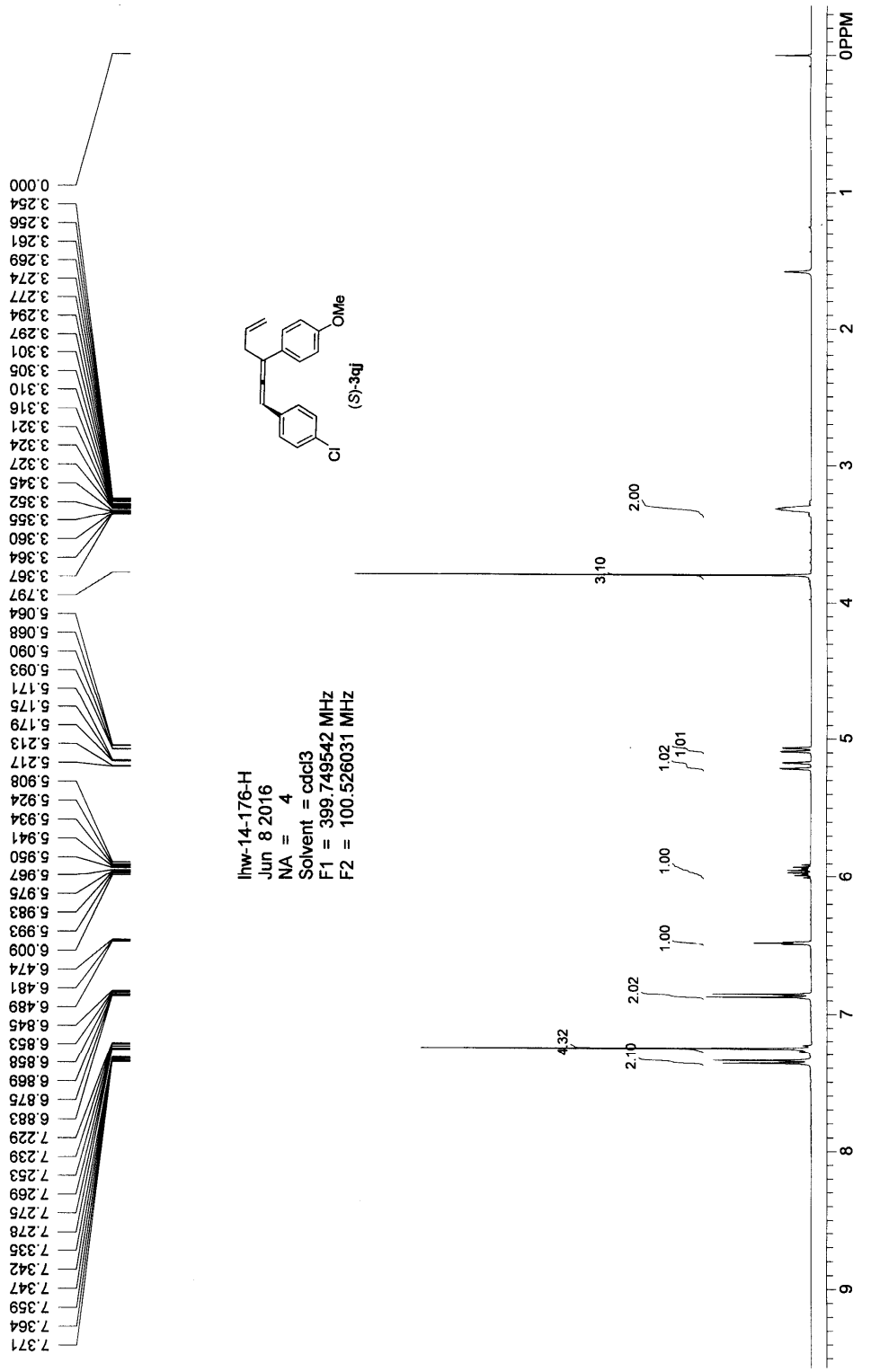
实验内容简介：

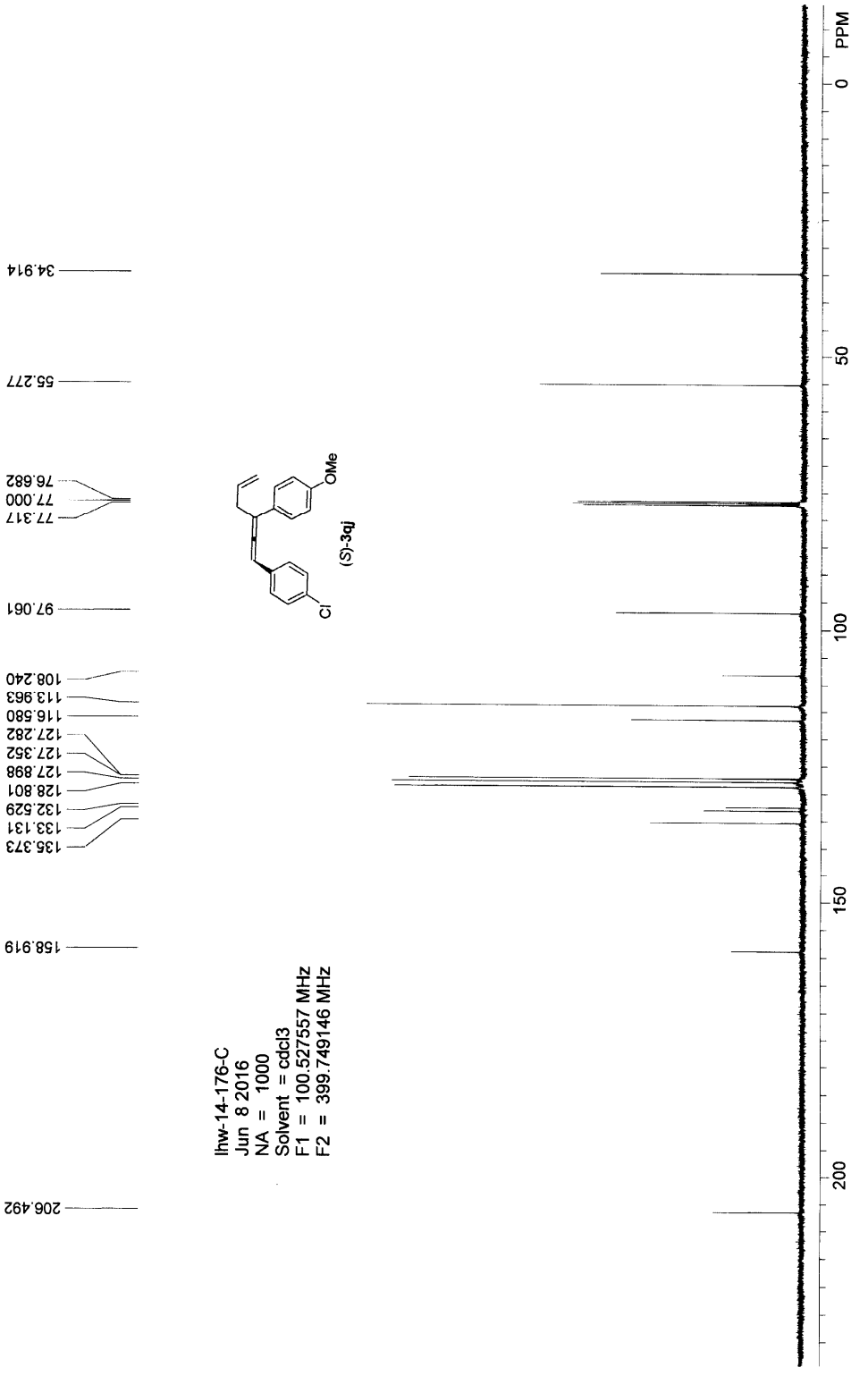


分析结果表

峰号	峰名	保留时间(Ret. Time)	峰高(Height)	峰面积(Area)	含量(Rel. Area)
1		7.967	116236.242	1404270.375	50.0722
2		11.353	72036.891	1400220.750	49.9278
总计(Total)			188273.133	2804491.125	100.0000

(*S*)-**3qj**


lhw-14-176-H
Jun 8 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
(S)-3qj
OMe
Cl
0.000
3.254
3.256
3.261
3.269
3.274
3.277
3.294
3.297
3.301
3.305
3.310
3.316
3.321
3.324
3.327
3.345
3.352
3.356
3.360
3.364
3.367
3.797
5.064
5.068
5.090
5.093
5.171
5.175
5.179
5.213
5.217
5.908
5.924
5.934
5.941
5.960
5.967
5.975
5.983
5.993
6.009
6.474
6.481
6.489
6.845
6.853
6.858
6.869
6.875
6.883
7.229
7.239
7.253
7.269
7.275
7.278
7.335
7.342
7.347
7.359
7.364
7.371
4.32
2.10
2.02
1.00
1.00
1.02
1.01
3.10
2.00
0PPM


lhw-14-176-C
Jun 8 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
OMe
Cl
(S)-3qj
34.914
55.277
76.682
77.000
77.317
97.061
108.240
113.963
116.580
127.282
127.352
127.898
128.801
132.529
133.131
135.373
158.919
206.492
PPM
0
50
100
150
200

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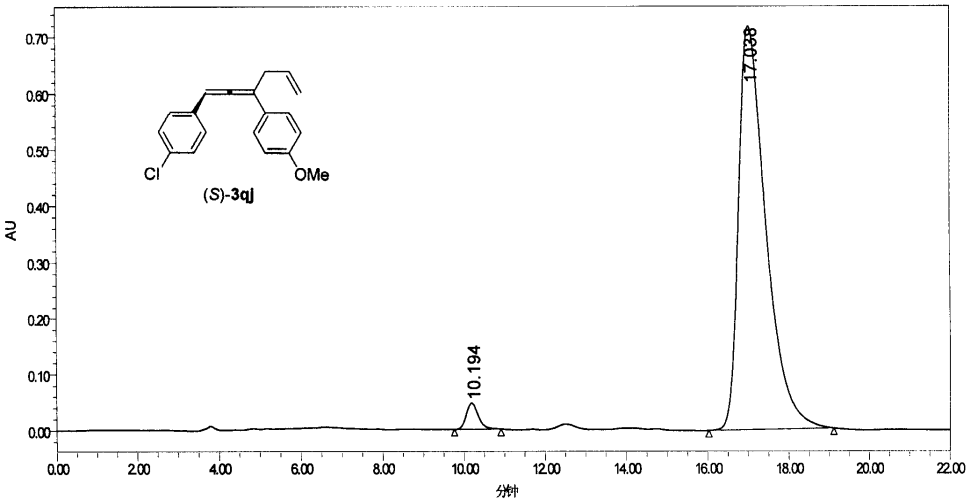
Project Name: defaults for copy

Reported by User: Breeze user (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	lhw-14-176-cj-h-95-5-1-214	Acquired By:	Breeze
Sample Type:	未知	Date Acquired:	2016/6/8 15:51:50 CST
Vial:	350	Acq. Method:	zcj95
Injection #:	1	Date Processed:	2016/6/8 17:43:32 CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	22.00 Minutes	Channel Desc.:	W2489 ChA 214nm
Column Type:		Sample Set Name:	



	RT (min)	Area (碘sec)	%Area	Height (碘	% Height
1	10.194	963502	2.79	46661	6.09
2	17.038	33568553	97.21	717516	93.91

Report Method: Individual Report ASC

Page: 1 (共计 1)

Printed: 2016/6/8 17:44:49 PRC

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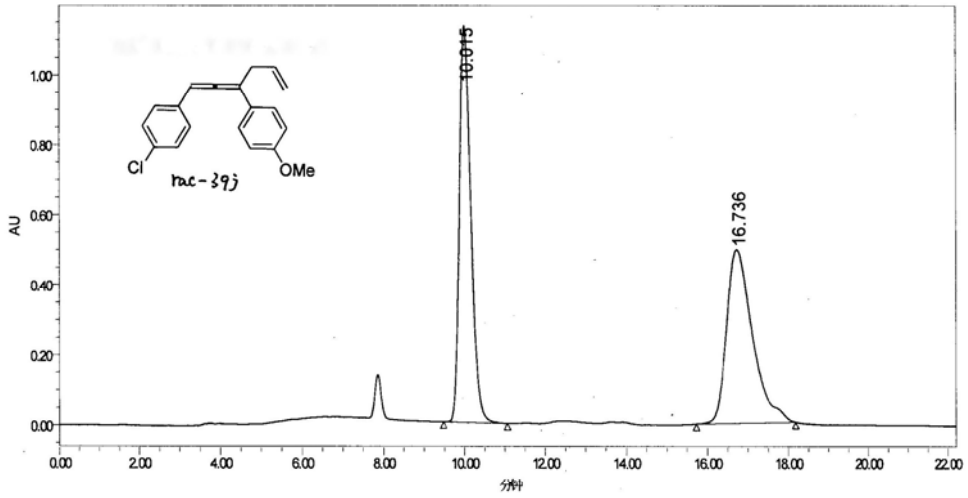
Project Name: defaults for copy

Reported by User: Breeze user (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	lhw-14-176-rac-cj-h-95-5-1-214	Acquired By:	Breeze
Sample Type:	未知	Date Acquired:	2016/6/8 15:02:00 CST
Vial:	348	Acq. Method:	zgj95
Injection #:	1	Date Processed:	2016/6/8 17:43:20 CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	200.00 Minutes	Channel Desc.:	W2489 ChA 214nm
Column Type:		Sample Set Name:	



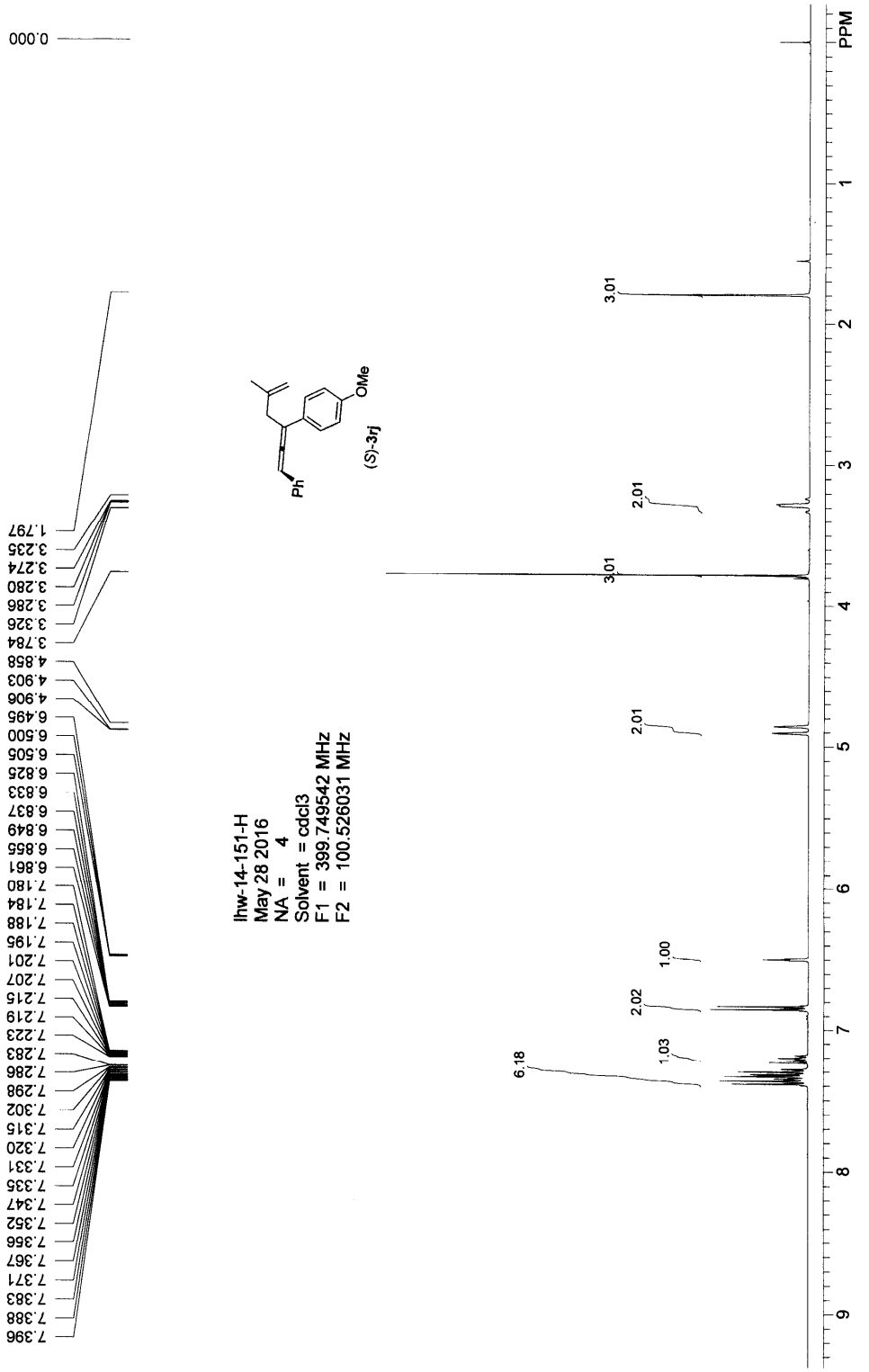
	RT (min)	Area (微sec)	% Area	Height (微	% Height
1	10.015	21965223	50.00	1132202	69.58
2	16.736	21956806	50.00	494919	30.42

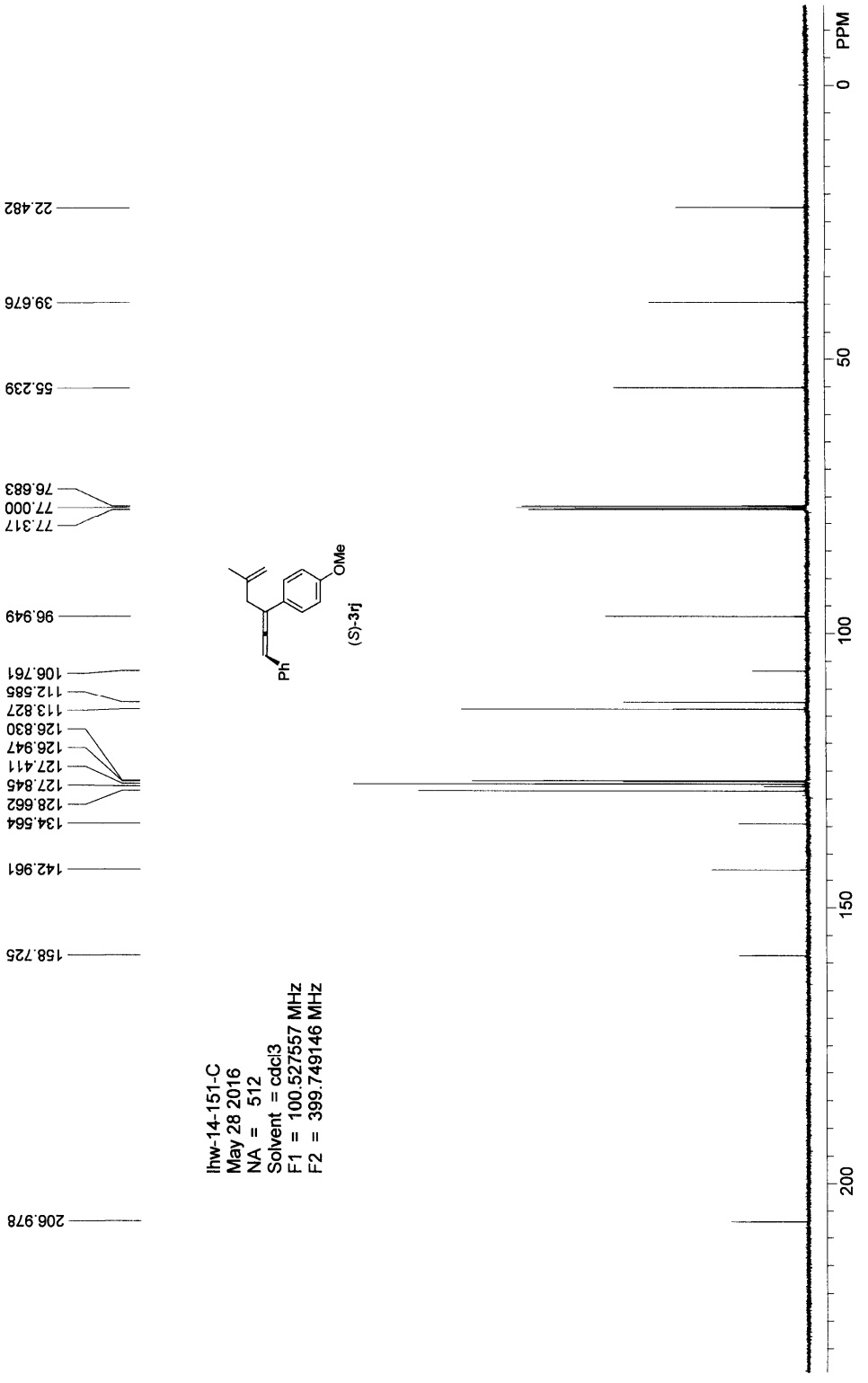
Report Method: Individual Report ASC

Page: 1 (共计 1)

Printed: 2016/6/8 17:43:59 PRC

(*S*)-**3rj**

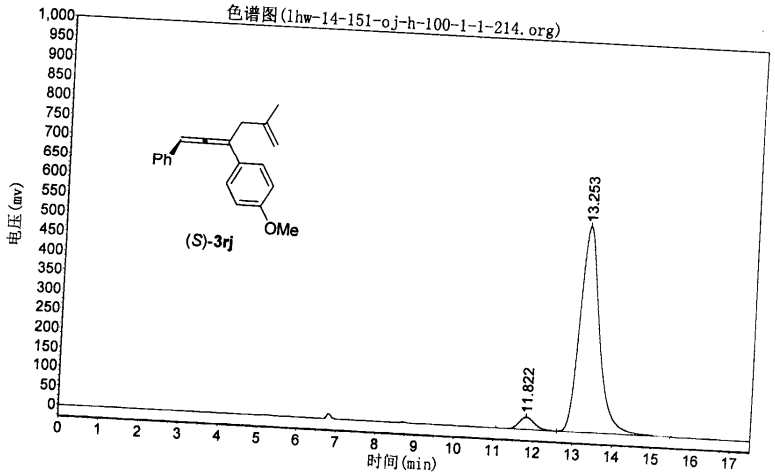

lhw-14-151-H
May 28 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
(S)-3rj
OMe
Ph
PPM
3.01
2.01
3.01
2.01
1.00
2.02
1.03
6.18


lhw-14-151-C
May 28 2016
NA = 512
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
(S)-3rj
OMe
Ph
22.482
39.676
55.239
76.683
77.000
77.317
96.949
106.761
112.585
113.827
126.830
126.947
127.411
127.845
128.662
134.564
142.961
158.725
206.978
PPM
0
50
100
150
200

lhw-14-151-oj-h-100-1-1-214

实验时间：2016/5/27,16:52:11
谱图文件:D:\zhuguangjiong\lhw\20160527\lhw-14-151-oj-h-100-1-1-214.org
报告时间：2016/5/27,18:15:24

实验内容简介：



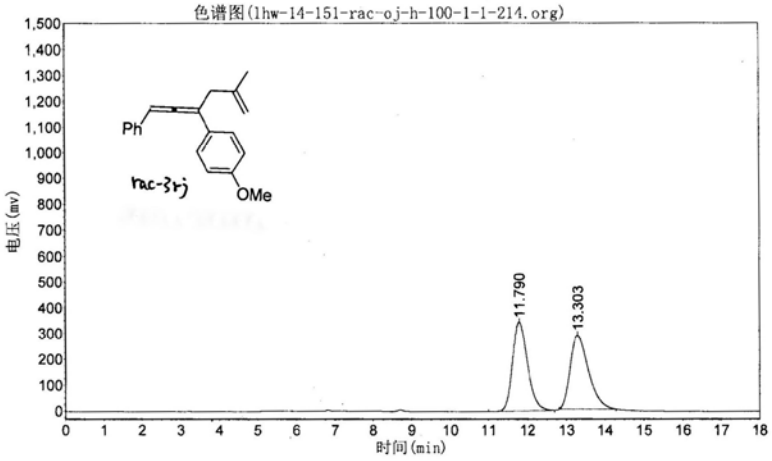
分析结果表

峰号	峰名	保留时间 (Ret. Time)	峰高 (Height)	峰面积 (Area)	含量 (Rel. Area)
1		11.822	32291.016	887061.375	4.6015
2		13.253	531038.750	18390612.000	95.3985
总计 (Total)			563329.766	19277673.375	100.0000

lhw-14-151-rac-oj-h-100-1-1-214

实验时间：2016/5/27,17:12:42　　报告时间：2016/5/27,17:33:14
谱图文件:D:\zhuguangjiong\lhw\20160527\lhw-14-151-rac-oj-h-100-1-1-214.org

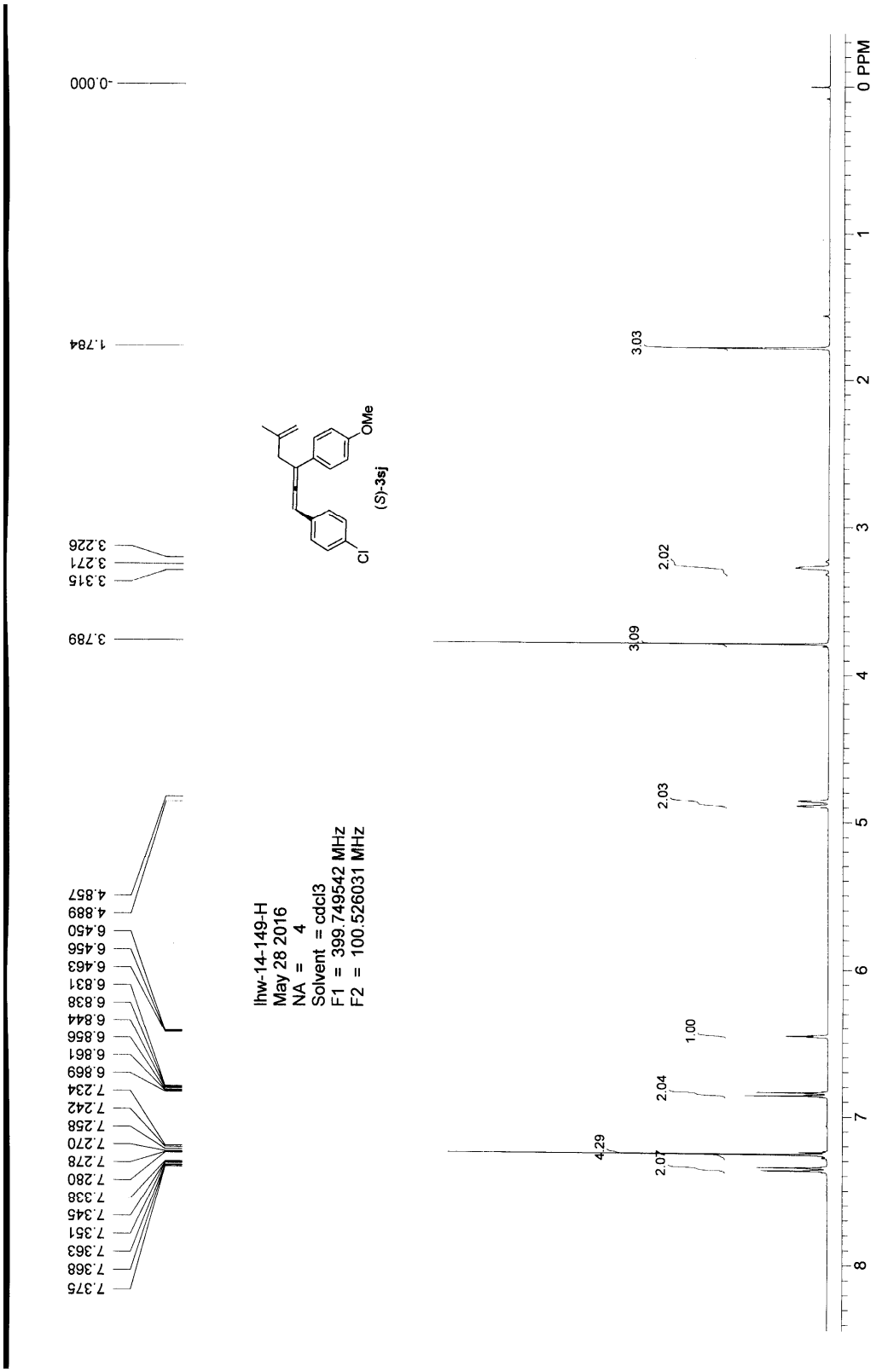
实验内容简介：

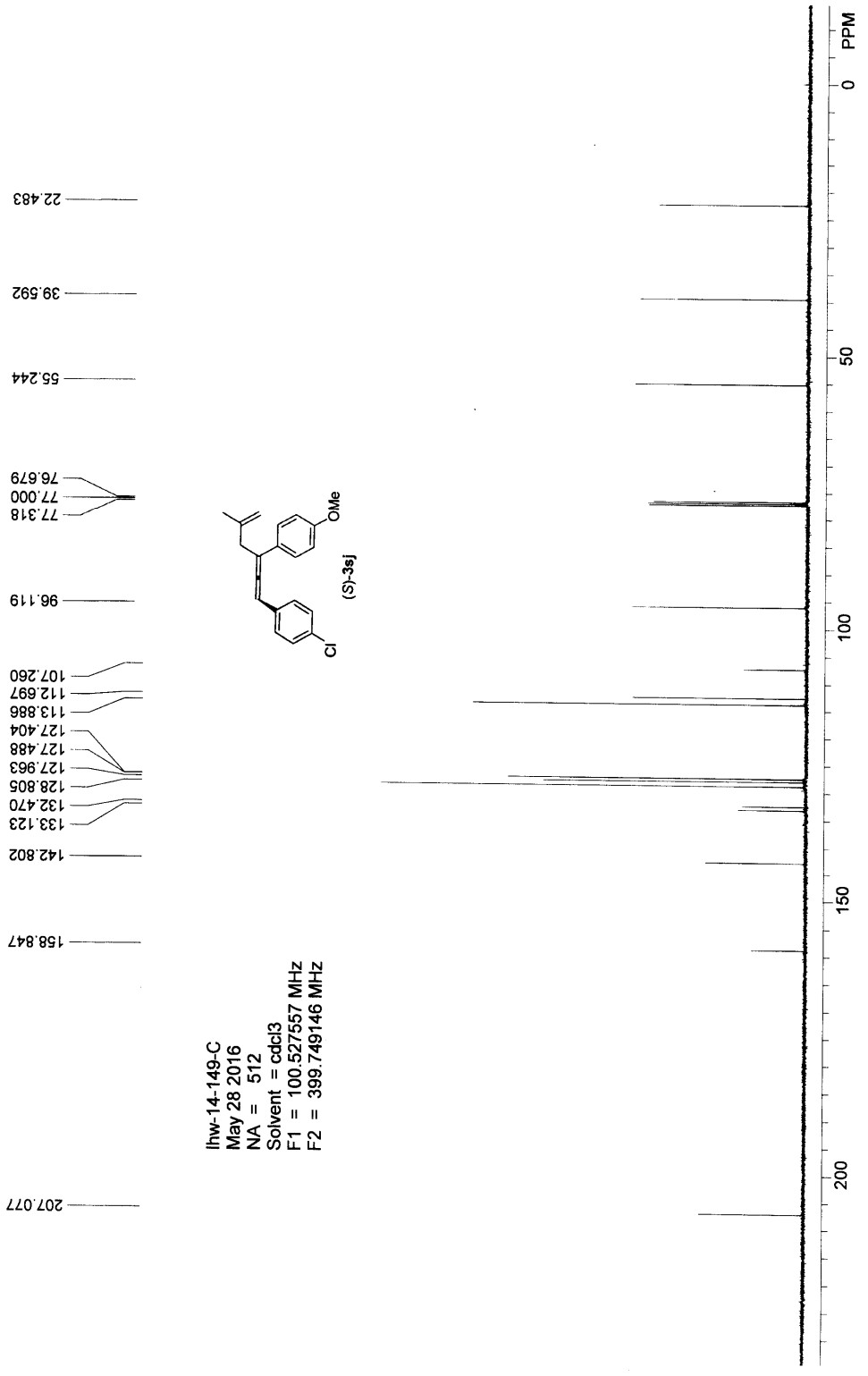


分析结果表

峰号	峰名	保留时间 (Ret. Time)	峰高 (Height)	峰面积 (Area)	含量 (Rel. Area)
1		11.790	343327.031	9216236.000	49.6075
2		13.303	284755.656	9362082.000	50.3925
总计 (Total)			628082.688	18578318.000	100.0000

(*S*)-**3sj**

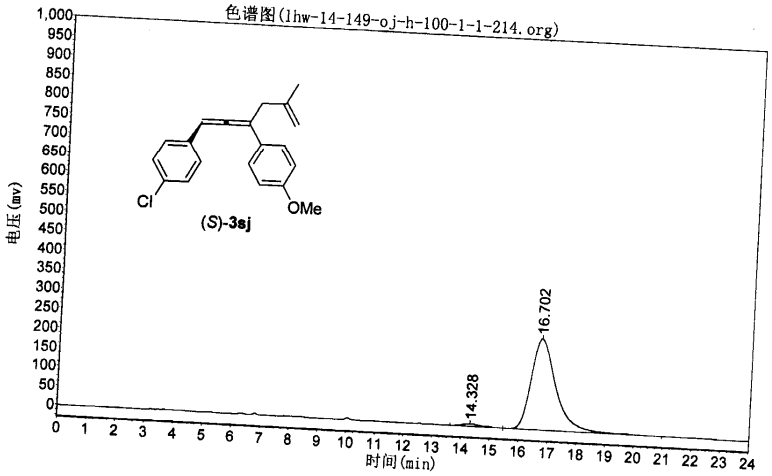

lhw-14-149-H
May 28 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
(S)-3sj
OMe
Cl
0 PPM
3.03
2.02
3.09
2.03
1.00
2.04
4.29
2.07
-0.000
1.784
3.226
3.271
3.315
3.789
4.857
4.889
6.450
6.456
6.463
6.831
6.838
6.844
6.856
6.861
6.869
7.234
7.242
7.258
7.270
7.278
7.280
7.338
7.345
7.351
7.363
7.368
7.375


lhw-14-149-C
May 28 2016
NA = 512
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
(S)-3sj
OMe
Cl
22.483
39.592
55.244
76.679
77.000
77.318
96.119
107.260
112.697
113.886
127.404
127.488
127.963
128.805
132.470
133.123
142.802
158.847
207.077
PPM
0
50
100
150
200

lhw-14-149-oj-h-100-1-1-214

实验时间：2016/5/27,15:15:09
谱图文件:D:\zhuguangjiong\lhw\20160527\lhw-14-149-oj-h-100-1-1-214.org
报告时间：2016/5/27,18:14:47

实验内容简介：



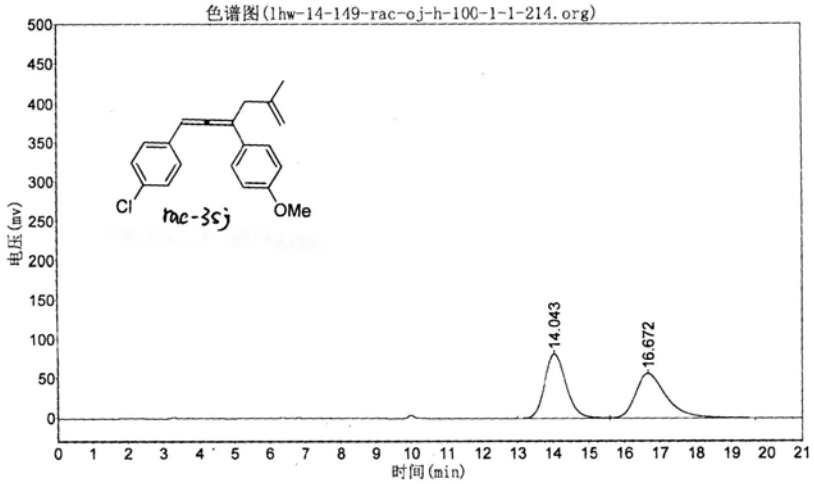
分析结果表

峰号	峰名	保留时间(Ret.Time)	峰高(Height)	峰面积(Area)	含量(Rel.Area)
1		14.328	6626.655	291921.781	2.0331
2		16.702	236117.828	14066513.000	97.9669
总计(Total)			242744.483	14358434.781	100.0000

lhw-14-149-rac-oj-h-100-1-1-214

实验时间：2016/5/27,14:52:58　　报告时间：2016/5/27,18:14:01
谱图文件:D:\zhuguangjiong\lhw\20160527\lhw-14-149-rac-oj-h-100-1-1-214.org

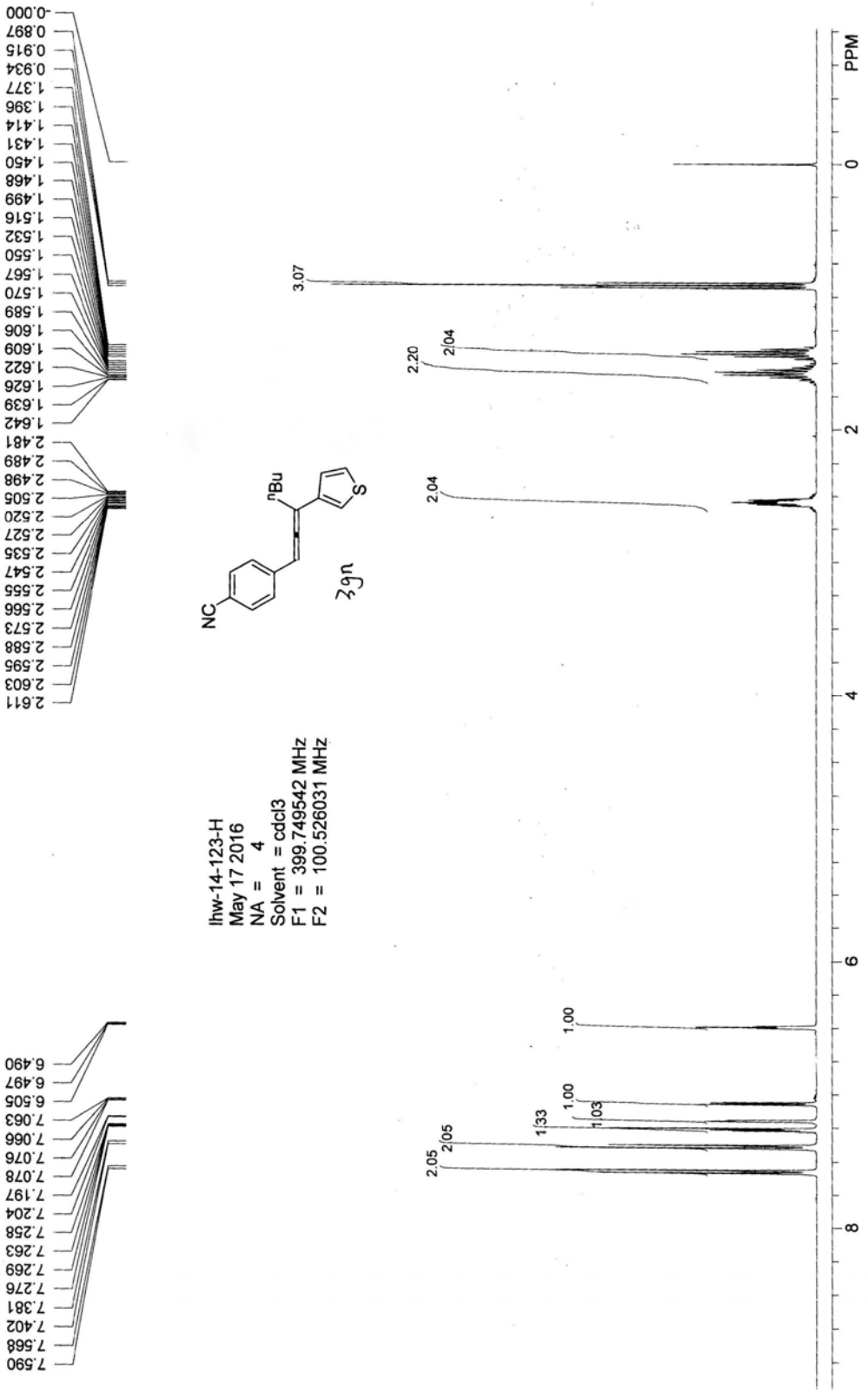
实验内容简介：



分析结果表

峰号	峰名	保留时间 (Ret.Time)	峰高 (Height)	峰面积 (Area)	含量 (Rel.Area)
1		14.043	81625.938	3392280.750	50.0757
2		16.672	56268.191	3382025.750	49.9243
总计 (Total)			137894.129	6774306.500	100.0000

Table 3-3gn


lhw-14-123-H
May 17 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
3gn
nBu
NC
S
PPM

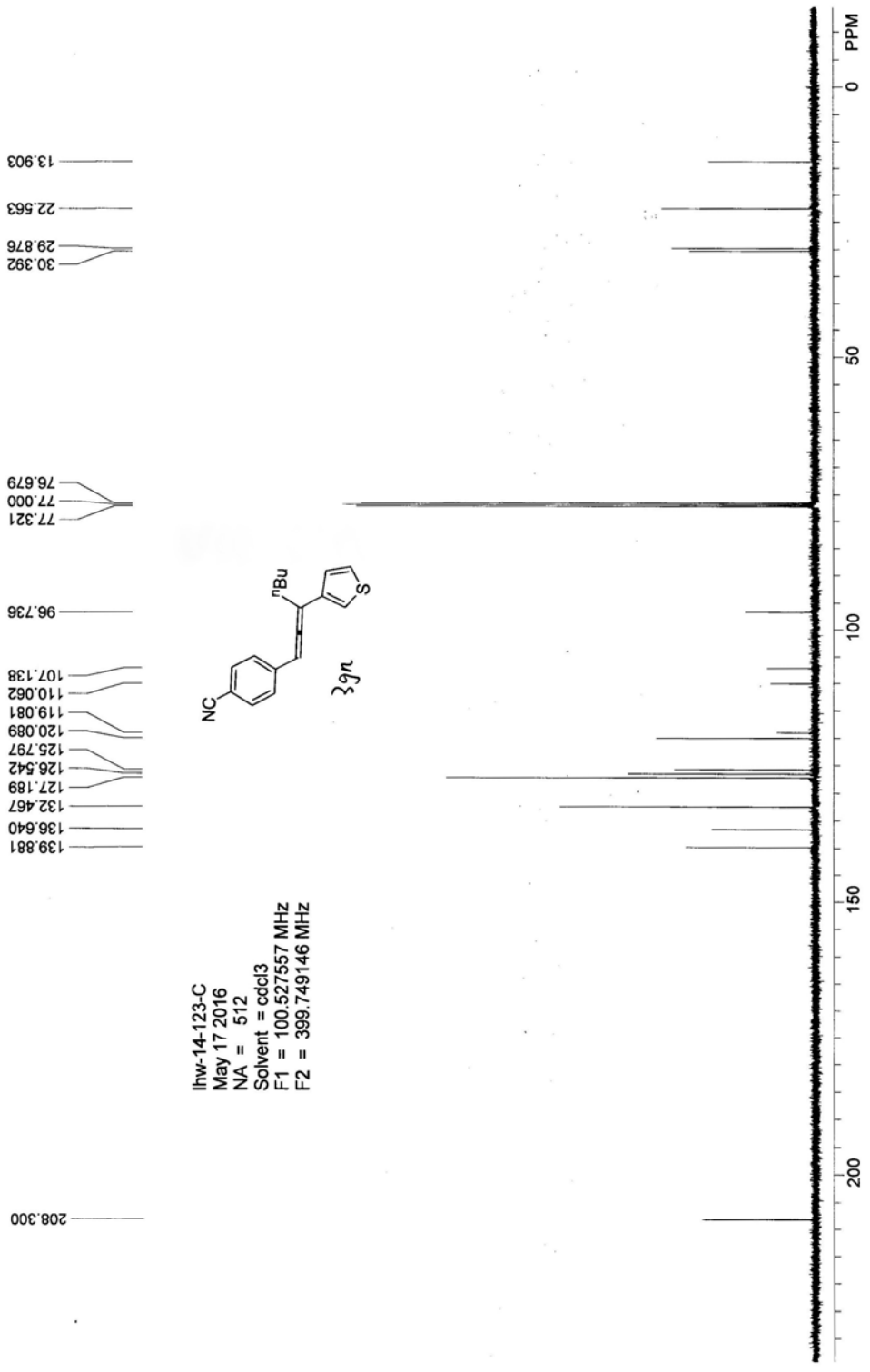
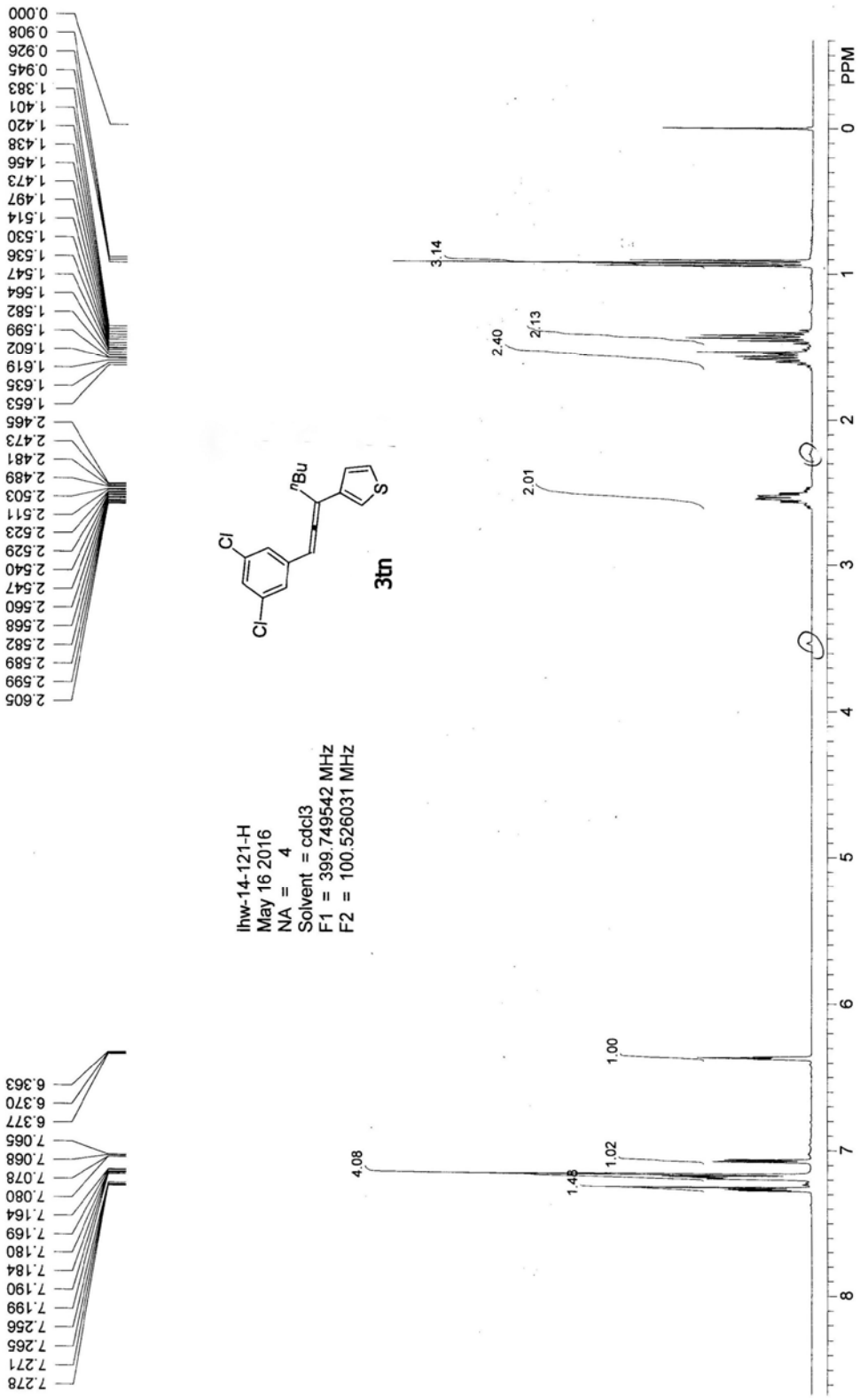
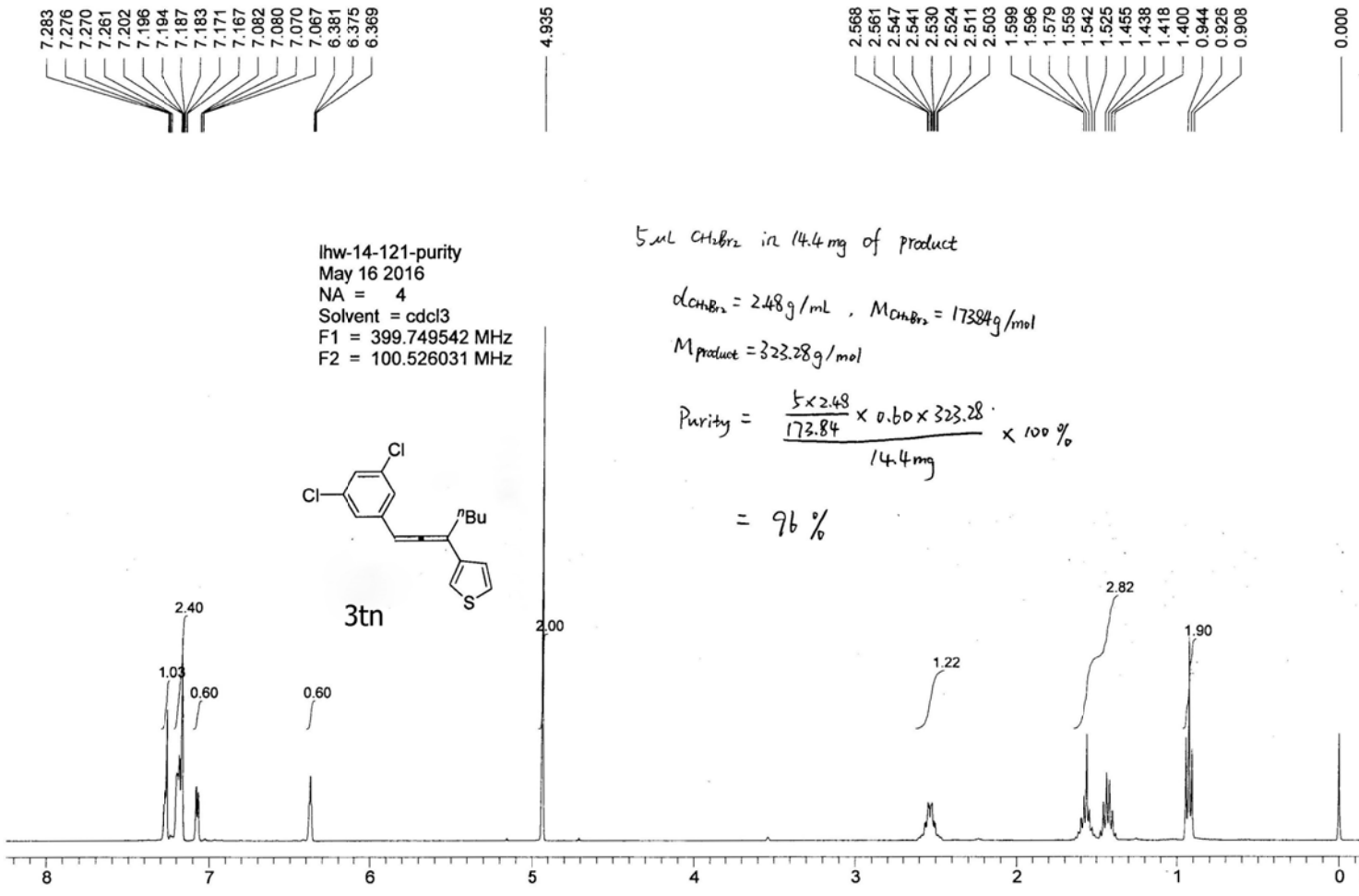

lhw-14-123-C
May 17 2016
NA = 512
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
3gn
nBu
S
NC
PPM
0
50
100
150
200
13.903
22.563
29.876
30.392
76.679
77.000
77.321
96.736
107.138
110.062
119.081
120.089
125.797
126.542
127.189
132.467
136.640
139.881
208.300

Table 3-3tn


lhw-14-121-H
May 16 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
3tn
PPM
3.14
2.40
2.13
2.01
1.00
1.02
1.48
4.08


7.283
7.276
7.270
7.261
7.202
7.196
7.194
7.187
7.183
7.171
7.167
7.082
7.080
7.070
7.067
6.381
6.375
6.369
4.935
2.568
2.561
2.547
2.541
2.530
2.524
2.511
2.503
1.599
1.596
1.579
1.559
1.542
1.525
1.455
1.438
1.418
1.400
0.944
0.926
0.908
0.000
lhw-14-121-purity
May 16 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
5 uL CH2Br2 in 14.4 mg of product
dCH2Br2 = 2.48 g/mL , MCH2Br2 = 173.84 g/mol
Mproduct = 323.28 g/mol
Purity = (5×2.48 / 173.84 × 0.60 × 323.28 / 14.4 mg) × 100 %
= 96 %
Cl
Cl
nBu
S
3tn
2.40
1.03
0.60
0.60
2.00
1.22
2.82
1.90
8
7
6
5
4
3
2
1
0
PPM

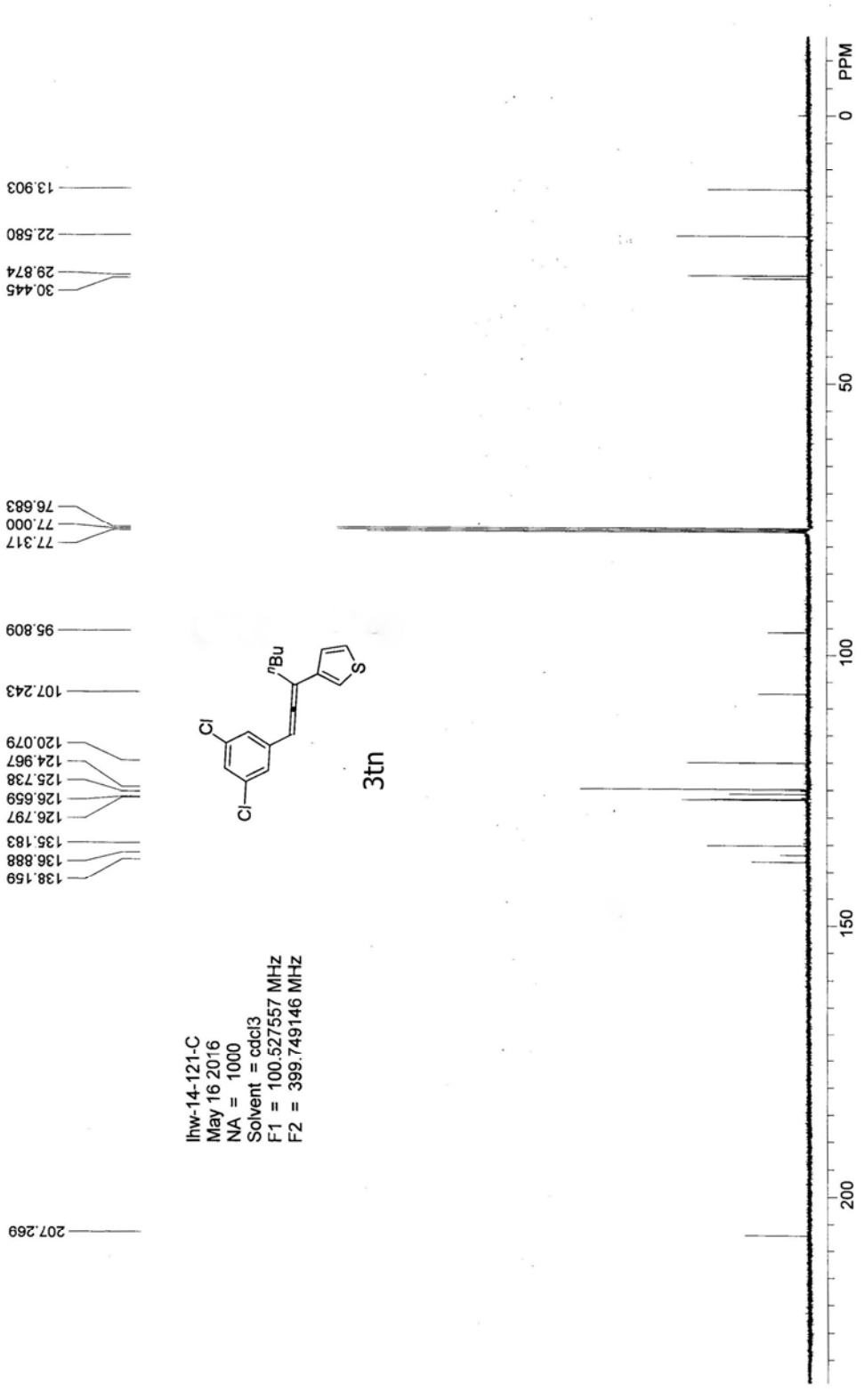
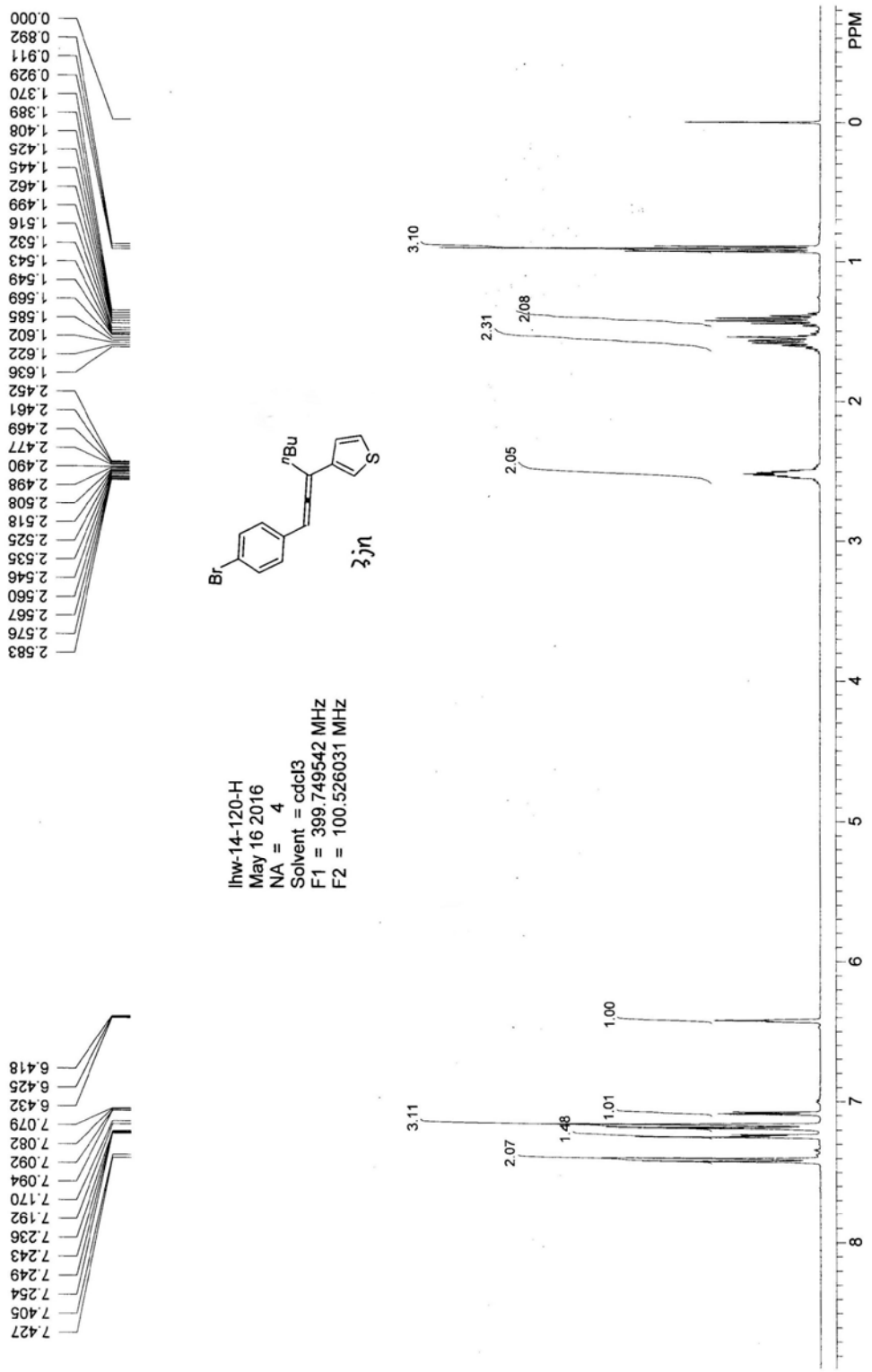
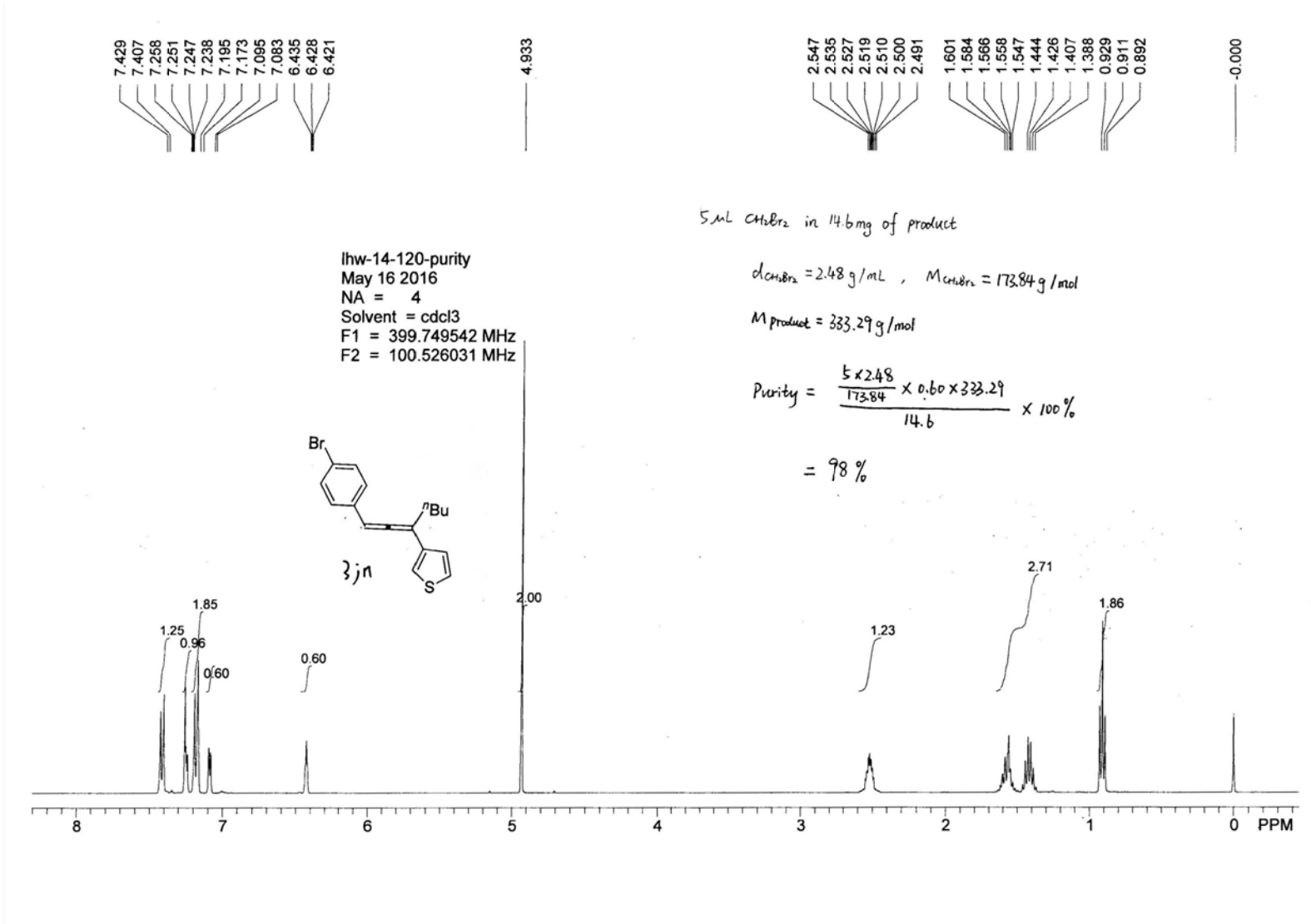

13.903
22.580
29.874
30.445
76.683
77.000
77.317
95.809
107.243
120.079
124.967
125.738
126.659
126.797
135.183
136.888
138.159
207.269
PPM
0
50
100
150
200
Cl
Cl
nBu
S
3tn
lhw-14-121-C
May 16 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz

Table 3-3jn


lhw-14-120-H
May 16 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
3jn
Br
nBu
S
PPM
3.10
2.31
2.08
2.05
1.00
3.11
1.01
1.48
2.07


7.429
7.407
7.258
7.251
7.247
7.238
7.195
7.173
7.095
7.083
6.435
6.428
6.421
4.933
2.547
2.535
2.527
2.519
2.510
2.500
2.491
1.601
1.584
1.566
1.558
1.547
1.444
1.426
1.407
1.388
0.929
0.911
0.892
-0.000
lhw-14-120-purity
May 16 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
5 mL CH2Br2 in 14.6 mg of product
dCH2Br2 = 2.48 g/mL , MCH2Br2 = 173.84 g/mol
M product = 333.29 g/mol
Purity = (5 × 2.48 / 173.84 × 0.60 × 333.29 / 14.6) × 100%
= 98 %
Br
nBu
S
3jn
1.25
1.85
0.96
0.60
0.60
2.00
1.23
2.71
1.86
8
7
6
5
4
3
2
1
0
PPM

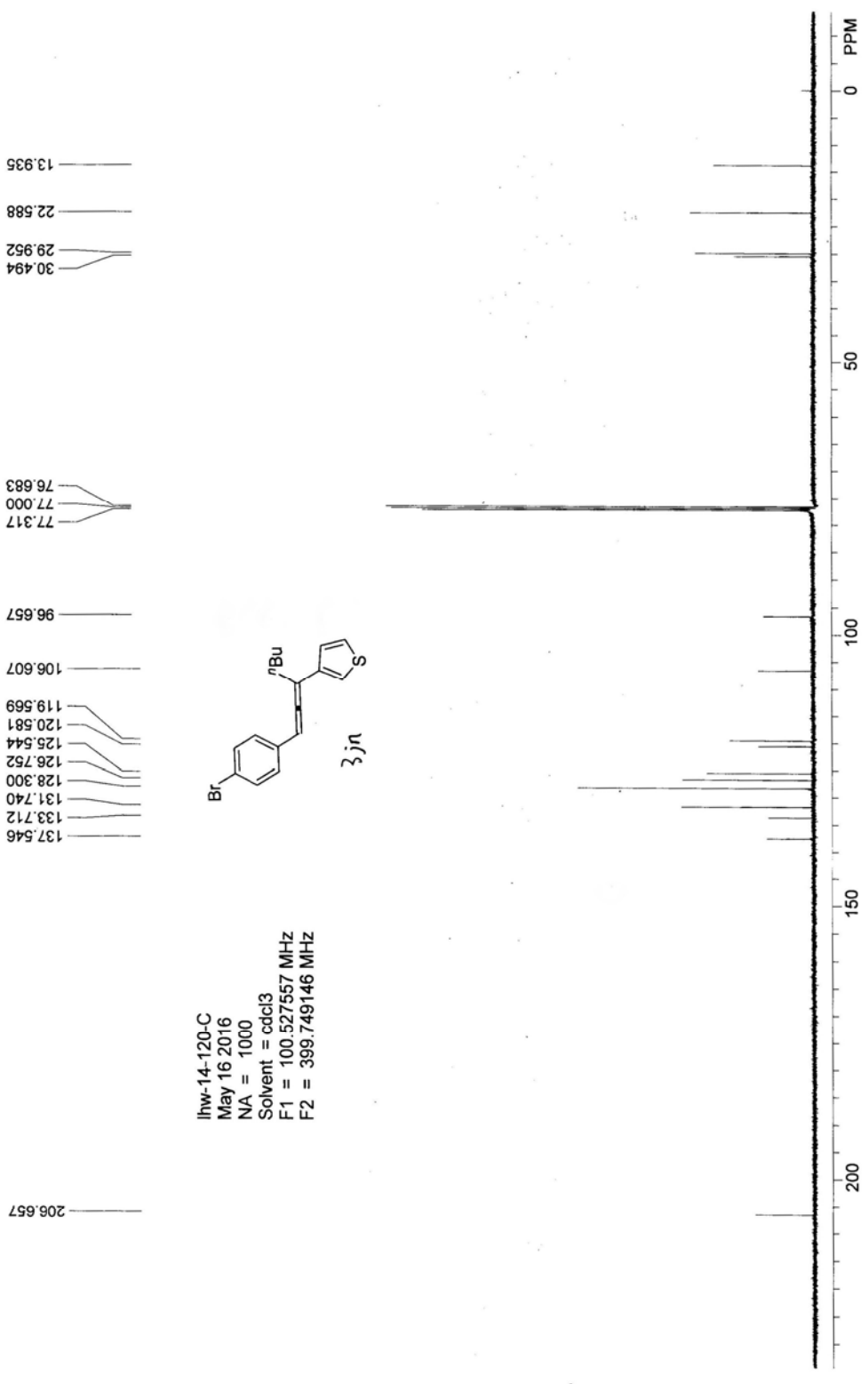
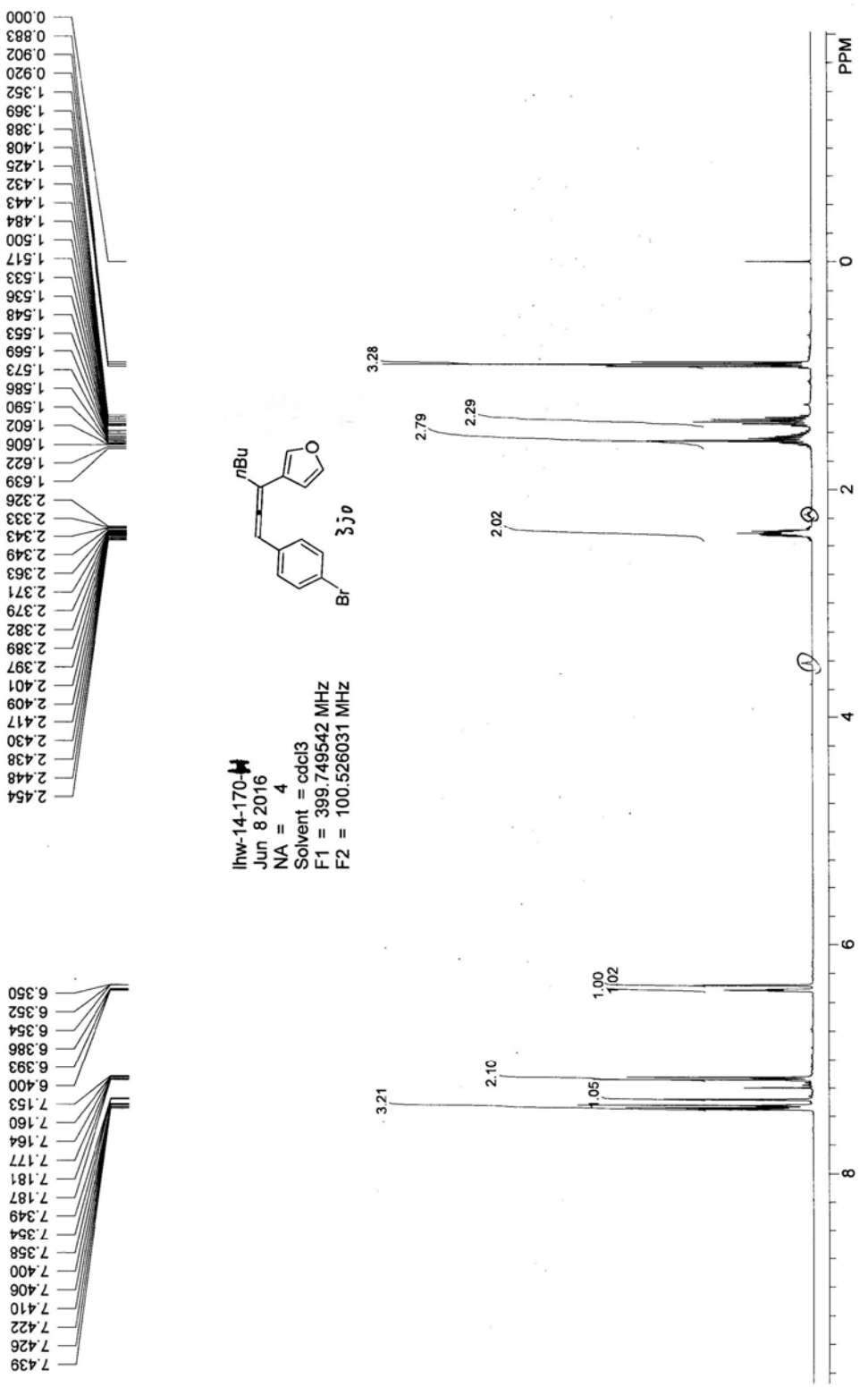
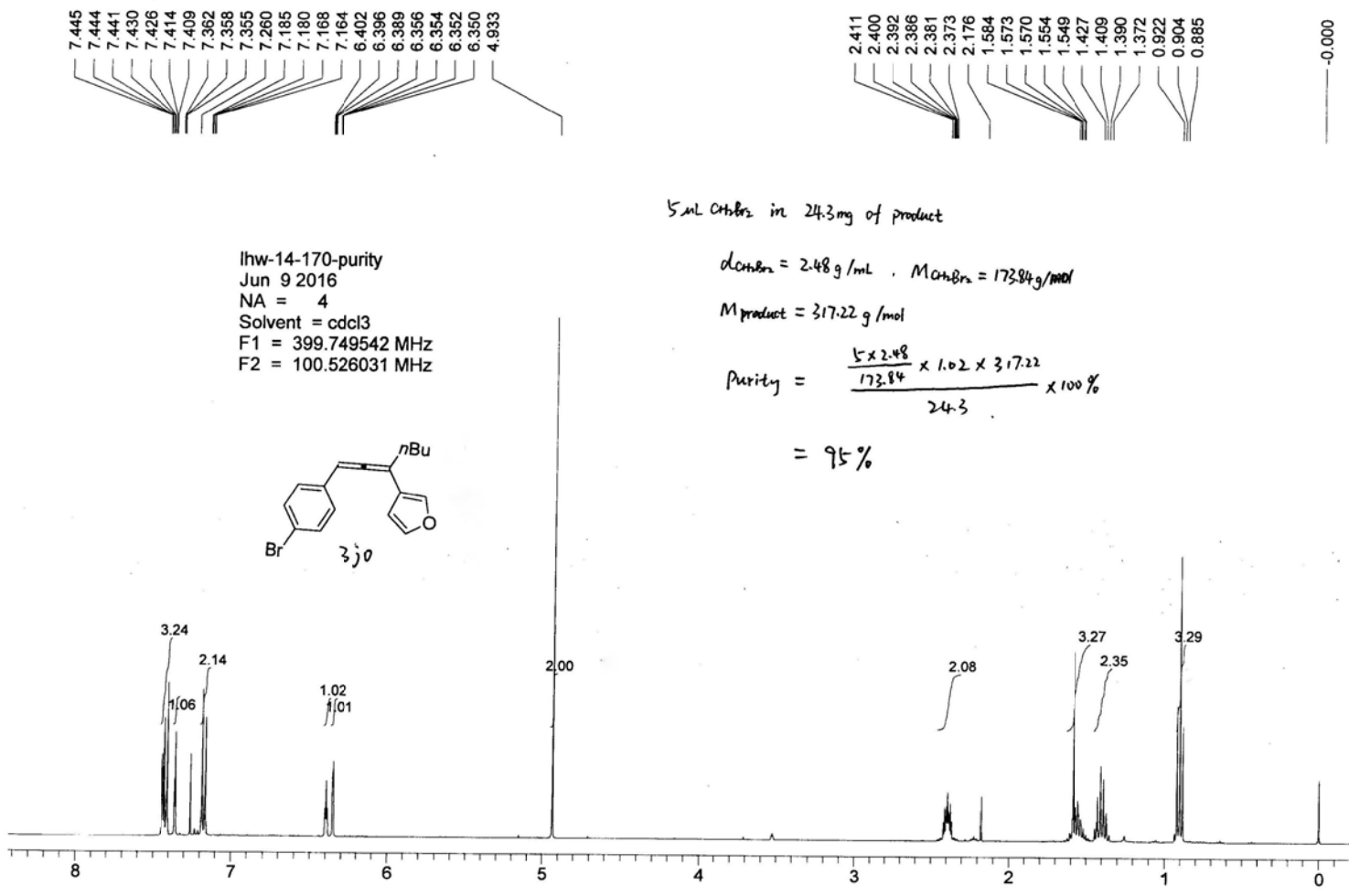

lhw-14-120-C
May 16 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
3jn
nBu
S
Br
13.935
22.588
29.952
30.494
76.683
77.000
77.317
96.657
106.607
119.569
120.581
125.544
126.752
128.300
131.740
133.712
137.546
206.657
PPM
0
50
100
150
200

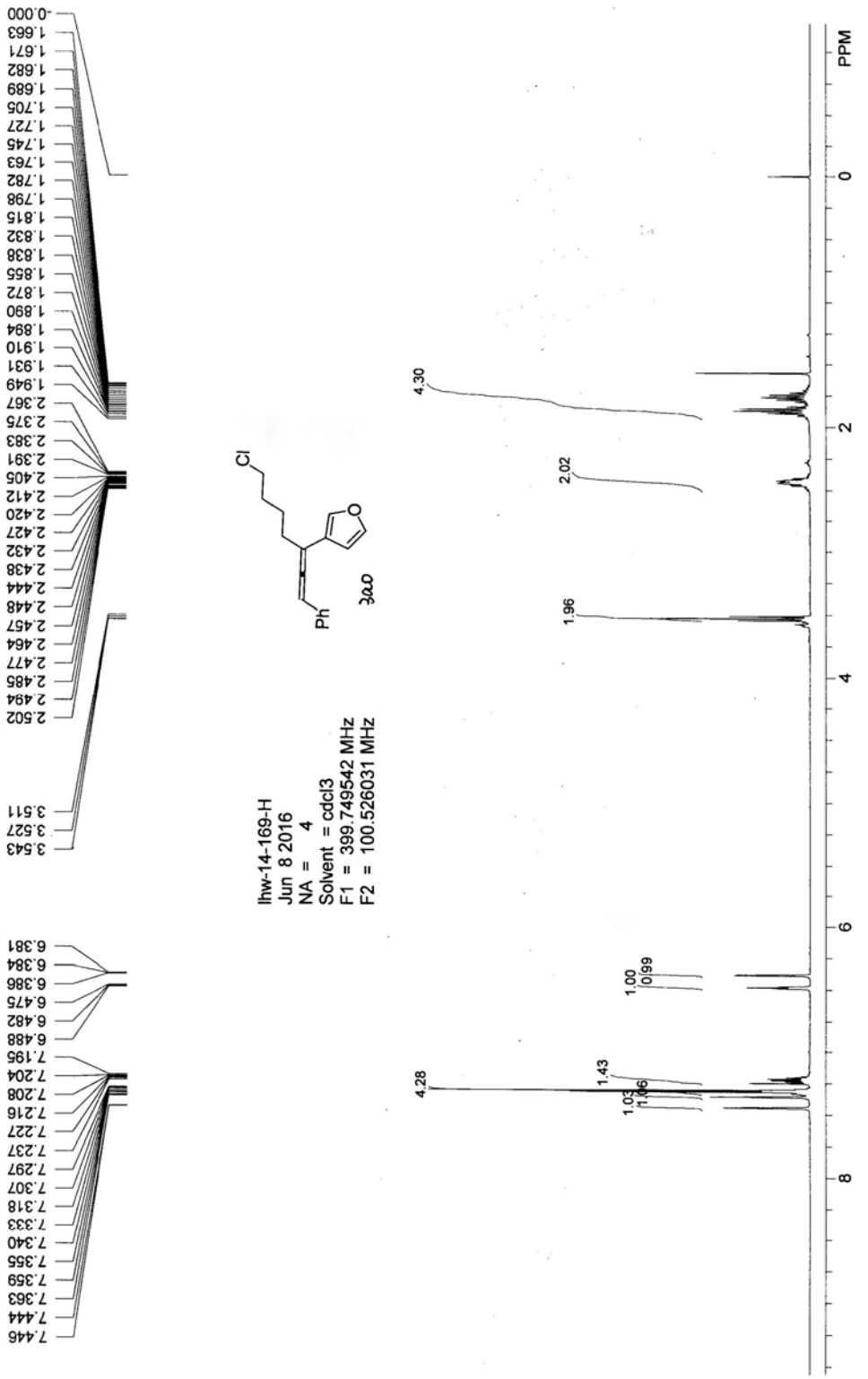
Table 3-3jo

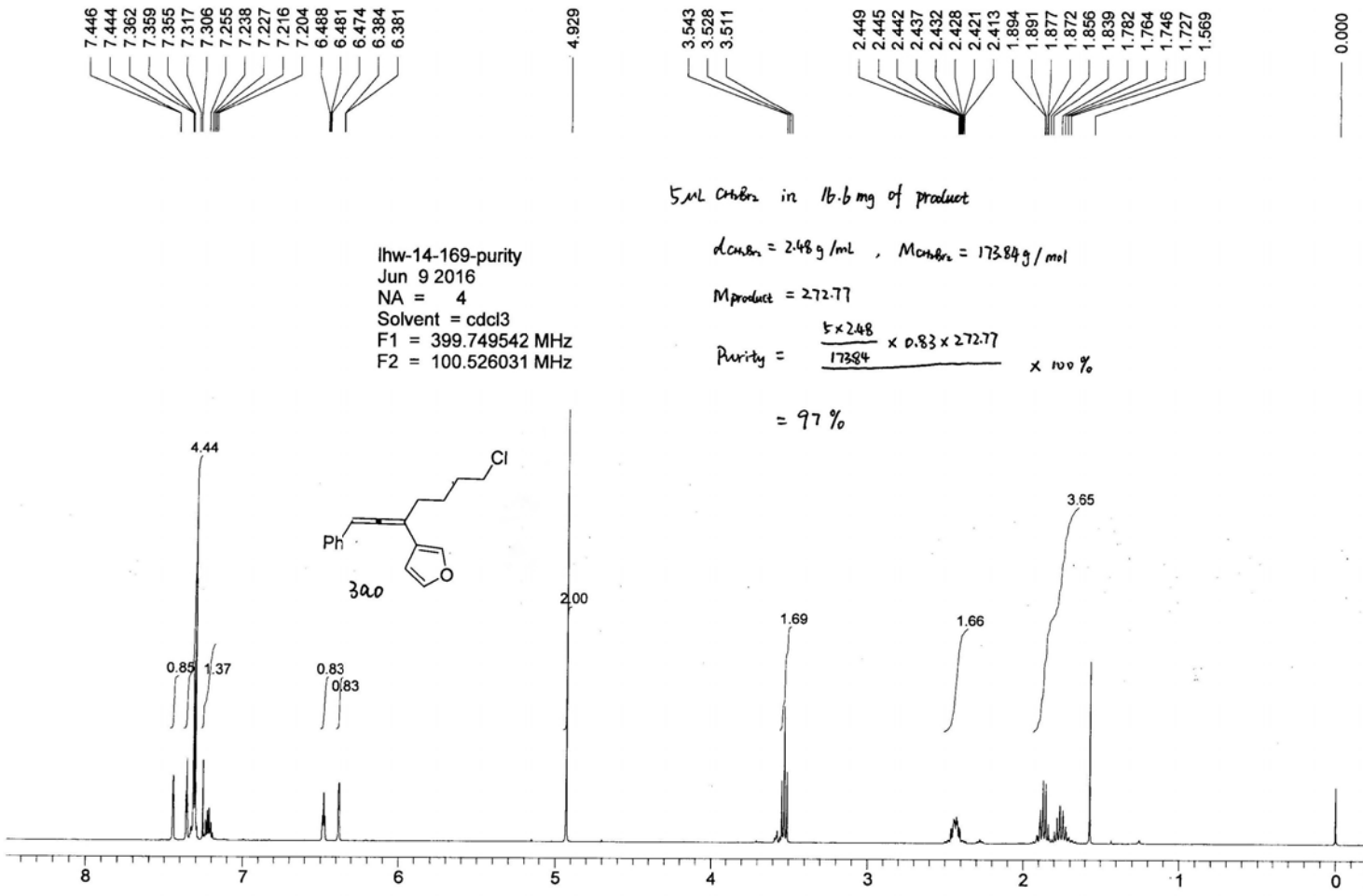

lhw-14-170-H
Jun 8 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
nBu
Br
3jo
PPM
3.28
2.79
2.29
2.02
1.00
1.02
2.10
1.05
3.21

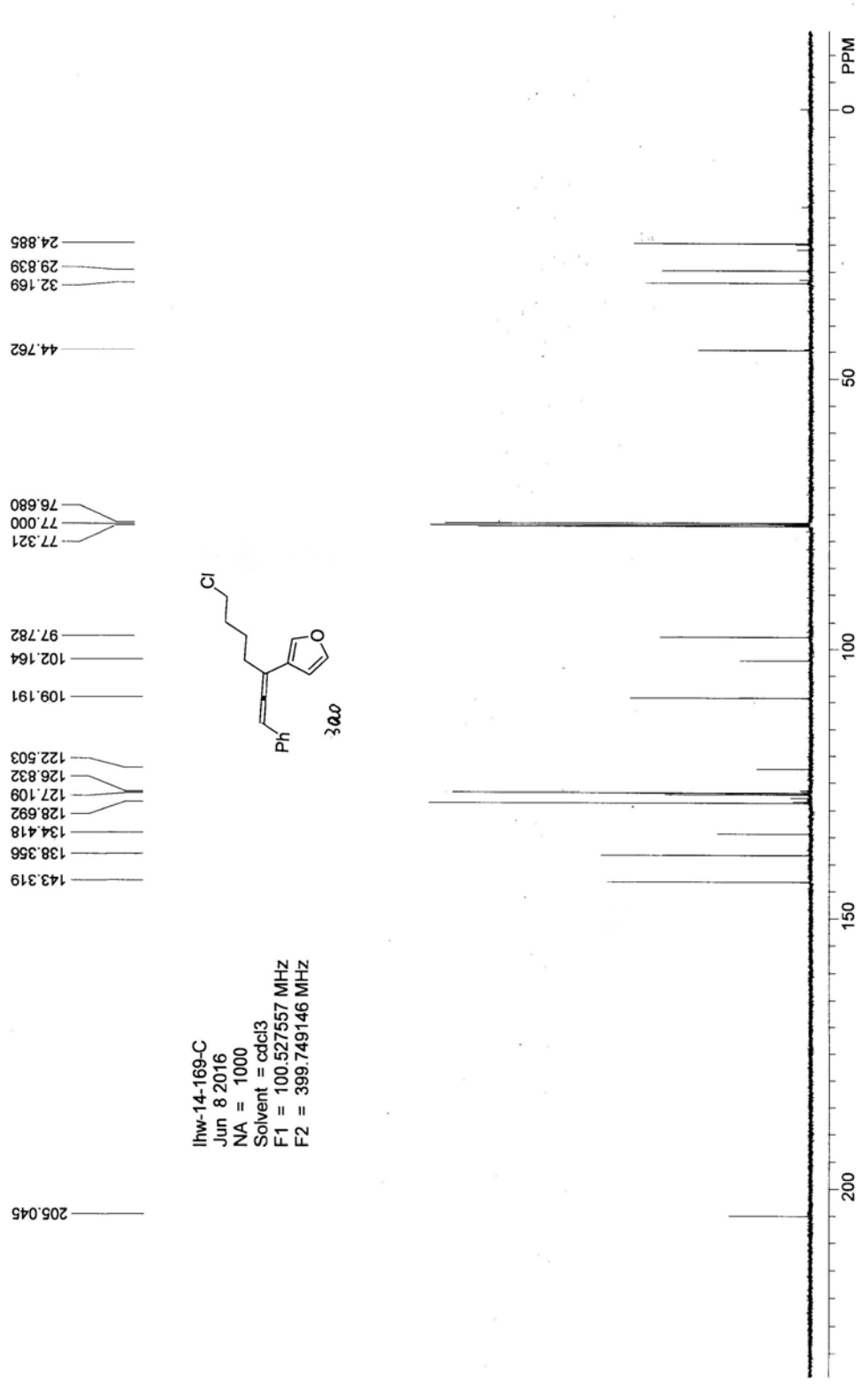

7.445
7.444
7.441
7.430
7.426
7.414
7.409
7.362
7.358
7.355
7.260
7.185
7.180
7.168
7.164
6.402
6.396
6.389
6.356
6.354
6.352
6.350
4.933
2.411
2.400
2.392
2.386
2.381
2.373
2.176
1.584
1.573
1.570
1.554
1.549
1.427
1.409
1.390
1.372
0.922
0.904
0.885
-0.000
5 mL CH2Br2 in 24.3 mg of product
dCH2Br2 = 2.48 g/mL . MCH2Br2 = 173.84 g/mol
Mproduct = 317.22 g/mol
Purity = (5 x 2.48 / 173.84 x 1.02 x 317.22 / 24.3) x 100%
= 95%
lhw-14-170-purity
Jun 9 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
nBu
Br
O
3j0
3.24
1.06
2.14
1.02
1.01
2.00
2.08
3.27
2.35
3.29
8
7
6
5
4
3
2
1
0
PPM

lhw-14-170-C
Jun 8 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
3jp
nBu
Br
O
13.924
22.536
29.866
30.317
76.690
77.000
77.207
77.320
96.565
103.287
109.153
120.566
122.393
128.289
131.716
133.767
138.526
143.290
205.399
PPM
0
50
100
150
200

Table 3-3ao


lhw-14-169-H
Jun 8 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
3ao
Cl
O
Ph
4.30
2.02
1.96
1.00
0.99
4.28
1.43
1.03
1.06
PPM


7.446
7.444
7.362
7.359
7.355
7.317
7.306
7.255
7.238
7.227
7.216
7.204
6.488
6.481
6.474
6.384
6.381
4.929
3.543
3.528
3.511
2.449
2.445
2.442
2.437
2.432
2.428
2.421
2.413
1.894
1.891
1.877
1.872
1.856
1.839
1.782
1.764
1.746
1.727
1.569
0.000
lhw-14-169-purity
Jun 9 2016
NA = 4
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
5 μL CH2Br2 in 16.6 mg of product
dCH2Br2 = 2.48 g/mL , MCH2Br2 = 173.84 g/mol
Mproduct = 272.77
Purity = (5×2.48)/173.84 × 0.83 × 272.77 × 100%
= 97 %
Cl
Ph
O
3ao
4.44
2.00
1.69
1.66
3.65
0.85
1.37
0.83
0.83
8
7
6
5
4
3
2
1
0
PPM


lhw-14-169-C
Jun 8 2016
NA = 1000
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
Cl
O
Ph
3aa
205.045
143.319
138.356
134.418
128.692
127.109
126.832
122.503
109.191
102.164
97.782
77.321
77.000
76.680
44.762
32.169
29.839
24.885
PPM
0
50
100
150
200