Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Copper-catalyzed Highly Selective Approach to 2-Boroallylic Silanes from Allenylsilanes

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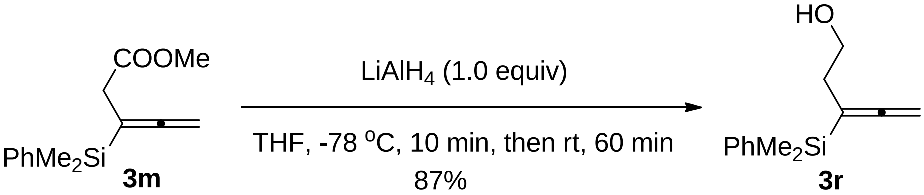
General Information. All reactions were carried out in oven dried Schlenk tubes under argon atmosphere. THF was distilled over sodium wire using benzophenone as the indicator under argon atmosphere. $LiAlH_4$ (1 M in THF) was purchased from Energy Chemical. *i*-PrOH was distilled using magnesium turnings as drying agent under argon.[1] The starting materials **3a-3l**,[2] **3p-3q,**[2] **3m**,[3] **3x,**[3] **3z,**[4] **3o,**[4] and **3n**[5] were prepared according to the literature.

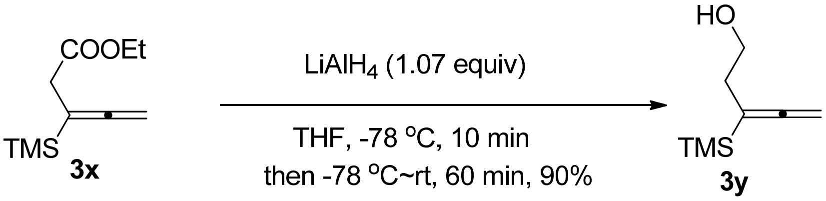
1. Synthesis of 3-(dimethyl(phenyl)silyl)penta-3,4-dien-1-ol[4] (3r) (sl-6-3)



To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially **3m**[3] (739.0 mg, 3 mmol) and THF (6 mL) under argon at rt. The resulting mixture was placed with a bath pre-set at -78 °C and stirred. $LiAlH_4$ (3 mL, 3 mmol, 1 M in THF) was then slowly added dropwise over 10 minutes, followed by removing the cool bath, and the resulting mixture was stirred at rt for another 60 minutes as monitored by TLC. Upon completion, the resulting mixture was slowly quenched with a saturated aqueous solution of NH_4Cl (0.5 mL), filtered through a short column of silica gel eluted with Et_2O (10 mL × 3), and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford **3r** (546.1 mg, 87%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.50 (m, 2 H, Ar-H), 7.41-7.33 (m, 3 H, Ar-H), 4.49 (t, *J* = 3.0 Hz, 2 H, $=CH_2$), 3.69 (q, *J* = 6.3 Hz, 2 H, OCH_2), 2.21-2.14 (m, 2 H, $=CCH_2$), 1.59 (t, *J* = 5.6 Hz, 1 H, OH), 0.40 (s, 6 H, $SiMe_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 137.4, 133.8, 129.3, 127.9, 90.5, 69.9, 62.0, 32.0, -3.3; IR (neat, cm^{-1}): 1926, 1427, 1249, 1111, 1040; MS (70 ev, EI) m/z (%) 218 (M^+, 1.02), 135 (100); HRMS Calcd for $C_{13}H_{18}OSi$ (M^+): 218.1127, Found: 218.1125.

2. Synthesis of 4-trimethylsilyl-4,5-dienenitrile[5] (3n)

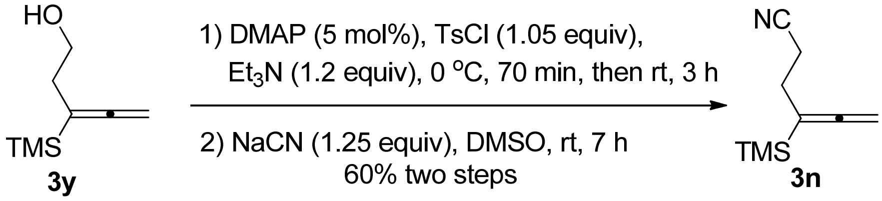
(1) Synthesis of 3-trimethysilyl-3,4-dien-1-ol (3y) (sl-6-22)



To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially **3x**[3] (1382.1 mg, 7.0 mmol) and THF (15 mL) under argon at rt. The resulting mixture was placed with a bath pre-set at -78 °C and stirred. $LiAlH_4$ (7.5

mL, 7.5 mmol, 1 M in THF) was then slowly added dropwise over 10 minutes, followed by removing the cool bath, stirred at rt for another 60 minutes as monitored by TLC. Upon completion, the resulting mixture was slowly quenched with a saturated aqueous solution of NH_4Cl (0.5 mL), the mixture was dried over $MgSO_4$, filtered through a short column of silica gel eluting with Et_2O (10 mL × 3), and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford **3y** (989.1 mg, 90%) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 4.42 (t, J = 3.2 Hz, 2 H, $=CH_2$), 3.78 (t, J = 6.4 Hz, 2 H, OCH_2), 2.27-2.15 (m, 2 H, $=CCH_2$), 1.83 (brs, 1 H, OH), 0.12 (s, 9 H, $SiMe_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 91.5, 69.3, 62.0, 31.7, -1.9; IR (neat, cm^{-1}): 2956, 1927, 1248, 1041; MS (70 ev, EI) m/z (%) 156 (M^+, 1.63), 73 (100); HRMS Calcd for $C_8H_{16}OSi$ (M^+): 156.0970, Found: 156.0969.

(2) Synthesis of 4-trimethylsilyl-4,5-pentadienenitrile (3n) (sl-6-23)

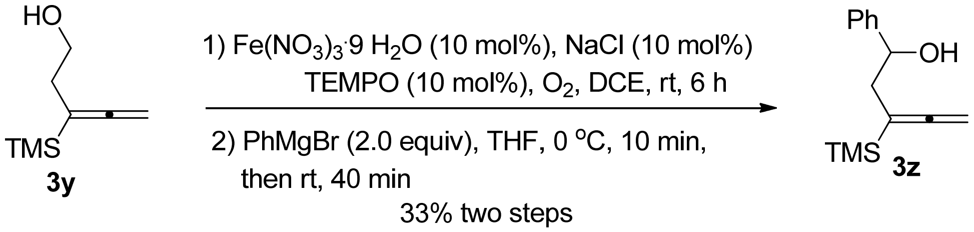


To an ice-cooled solution of **3y** (625.7 mg, 4 mmol), DMAP (24.5 mg, 0.2 mmol), Et_3N (0.67 mL, d = 0.726 g/cm^3, 486.4 mg, 4.8 mmol) in dry DCM (10 mL) was dropwised a solution of *p*-TsCl (799.9 mg, 4.2 mmol) in dry DCM (10 mL) over 70 minutes under argon atmosphere. Then the resulting mixture was warmed up to rt for another 3 h followed by the addition of 30 mL of DCM. The organic layer was separated and washed with water (10 mL × 3), dried over $MgSO_4$, filtrated, and concentrated under vacuum. The crude product was then used in the next step without further purification.

To a solution of the tosylate prepared above and anhydrous DMSO (4 mL) was added NaCN (251.1 mg, 5 mmol) at rt. The resulting mixture was stirred for 7 h at rt, quenched with H_2O (5 mL), and extracted with AcOEt (10 mL × 3). The combined organic layer was dried over $MgSO_4$, filtrated, and concentrated in vacuum. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 100/1) to afford **3n** (394.8 mg, 60%) as a liquid: H NMR (400 MHz, $CDCl_3$) δ 4.54 (t, *J* = 3.6 Hz, 2 H, $=CH_2$), 2.50 (t, *J* = 7.4 Hz, 2 H, $NCCH_2$), 2.32-2.23 (m, 2 H, $=CCH_2$), 0.12 (s, 9 H, $SiMe_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 119.7, 92.8, 71.9, 24.0, 16.2, -2.0; IR (neat, cm^{-1}): 2957, 1928, 1422, 1250, 1061; MS (70 ev, EI) m/z (%) 165 (M^+, 11.72), 73 (100); HRMS Calcd for $C_9H_{15}NSi$ (M^+): 165.0974, Found: 165.0975.

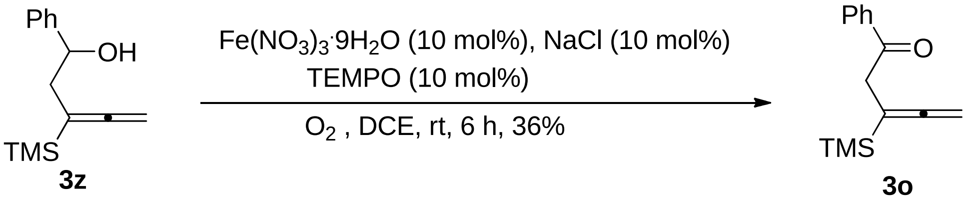
3. Synthesis of 3-trimethylsilyl-1-phenyl-3,4-dien-1-one[6]

(1) Synthesis of 3-trimethylsilyl-1-phenyl-3,4-pentadien-1-ol (3z) (sl-6-118)



To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially $Fe(NO_3)_3 \cdot 9H_2O$ (403.1 mg, 1 mmol), NaCl (58.6 mg, 1 mmol), TEMPO (156.5 mg, 1.0 mmol)/DCE (8 mL) under the atmosphere of oxygen. A solution of **3y** (1564.1 mg, 10 mmol) in DCE (2 mL) was added. The resulting mixture was stirred at rt for 6 h with oxygen from a balloon until the reaction was complete as monitored by TLC. Then THF (10 mL) was added. The resulting mixture was cooled with an ice bath, PhMgBr (20 mL, 20 mmol, 1 M in THF) was slowly added dropwise over 10 minutes. Then the resulting mixture was warmed up to rt for another 40 min as monitored by TLC. Upon completion, the resulting mixture was slowly quenched with a saturated aqueous of NH_4Cl (1 mL), filtered through a short column of silica gel eluted with DCM (20 mL × 3), and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 80/1) to afford **3z** (756.4 mg, 33%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.32 (m, 4 H, Ar-H), 7.31-7.24 (m, 1 H, Ar-H), 4.91-4.84 (m, 1 H, OCH), 4.52-4.41 (m, 2 H, $=CH_2$), 2.45-2.41 (m, 1 H, OH), 2.40-2.28 (m, 2 H, $=CCH_2$), 0.11 (s, 9 H, $SiMe_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 143.9, 128.3, 127.4, 125.8, 92.0, 73.4, 69.7, 39.1, -1.8; IR (neat, cm^{-1}): 3380, 3064, 3031, 2897, 1925, 1494, 1453, 1405, 1248, 1023; MS (70 ev, EI) m/z (%) 232 (M^+, 1.26), 73 (100); HRMS Calcd for $C_{14}H_{20}OSi$ (M^+): 232.1283, Found: 232.1285.

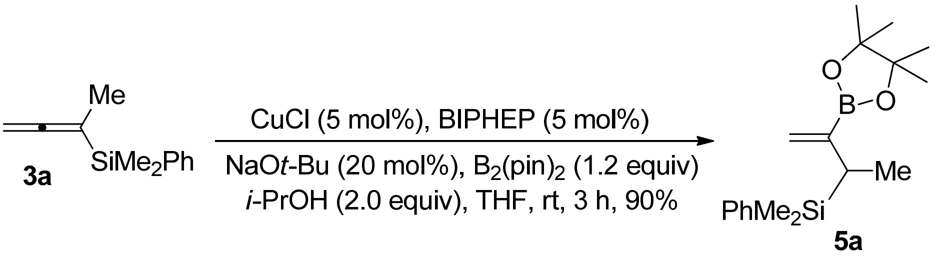
(2) Synehesis of 3-trimethylsilyl-1-phenyl-3,4-pentadien-1-one (3o) (sl-6-119)



To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially $Fe(NO_3)_3\cdot 9H_2O$ (121.3 mg, 0.3 mmol), NaCl (17.9 mg, 0.3 mmol), TEMPO (46.6 mg, 0.3 mmol)/DCE (4 mL) under the atmosphere of oxygen. Then a solution of **3z** (697.0 mg, 3 mmol) in DCE (1 mL) was added. The resulting mixture was stirred at rt for 6 h with oxygen from a balloon until the reaction was complete as monitored by TLC. After filtration through a short column of silica gel eluted with DCM (10 mL × 3) and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether) to afford **3o** (334.8 mg, 36%) as a liquid: δ 7.98-7.92 (m, 2 H, Ar-H), 7.59-7.52 (m, 1 H, Ar-H), 7.49-7.41 (m, 2 H, Ar-H), 4.34 (t, *J* = 2.8 Hz, 2 H, $=CH_2$), 3.63 (m, *J* = 2.8 Hz, 2 H, $=CCH_2$), 0.14 (s, 9 H, $SiMe_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 198.2, 136.6, 132.9, 128.55, 128.47, 89.6, 69.5, 39.9, -1.6; IR (neat, cm^{-1}): 2956, 1930, 1681, 1598, 1580, 1449, 1407, 1329, 1317, 1280, 1248, 1206, 1181, 1066, 1001; MS (70 ev, EI) m/z (%) 230 (M^+, 9.76), 73 (100); HRMS Calcd for $C_{14}H_{18}OSi$ (M^+): 230.1127, Found: 230.1126.

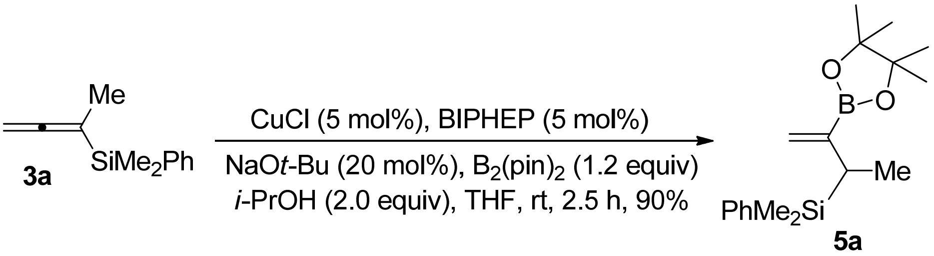
4. Synthesis of 2-Borylallylic silanes 5

(1) Synthesis of (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl) dimethyl(phenyl)silane (5a) (ywm-11-99)



Typical Procedure: To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaO*t*-Bu (19.4 mg, 0.2 mmol), bis(pinacolato)diboron (306.3 mg, 1.2 mmol)/THF (2 mL), **3a** (189.4 mg, 1.0 mmol)/THF (1 mL), and *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) under argon. The resulting mixture was stirred at rt for 3 h as monitored by TLC. Upon completion, the resulting mixture was filtered through a short column of silica gel eluted with Et_2O (20 mL × 3) and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl ether = 70/1) to afford **5a** (286.8 mg, 90%) as a liquid[7]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.47 (m, 2 H, Ar-H), 7.37-7.29 (m, 3 H, Ar-H), 5.78 (d, *J* = 2.7 Hz, 1 H, one proton of $=CH_2$), 5.35 (brs, 1 H, one proton of $=CH_2$), 2.19 (q, *J* = 7.3 Hz, 1 H, =CCH), 1.20 (s, 6 H, B(pin)), 1.18 (s, 6 H, B(pin)), 1.08 (d, *J* = 7.5 Hz, 3 H, CH_3), 0.25 (s, 6 H, $SiMe_2$); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 138.2, 134.2, 128.7, 127.4, 125.5, 83.2, 26.2, 24.8, 24.7, 14.4, -4.1, -5.6; IR (neat, cm^{-1}): 2978, 1600, 1426, 1388, 1372, 1358, 1305, 1270, 1247, 1136, 1111; MS (ESI) m/z 340 [$M^+(^{11}B)$+Na+H], 339 [$M^+(^{11}B)$+Na] or [$M^+(^{10}B)$+Na+H], 338 [$M^+(^{10}B)$+Na]; HRMS Calcd for $C_{18}H_{29}O_2Si^{11}B$ (M^+): 316.2030, Found: 316.2027.

Synthesis of 5a on one gram scale (ywm-13-188)

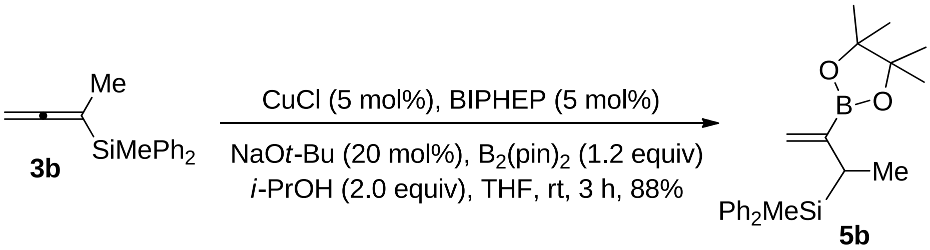


The reaction of CuCl (26.8 mg, 0.27 mmol), BIPHEP (141.3 mg, 0.27 mmol), NaO*t*-Bu (101.7 mg, 1.06 mmol), bis(pinacolato)diboron (1.6179 g, 6.37 mmol)/THF (8 mL), **3a** (1.0003 g, 5.31 mmol)/THF (2 mL), and *i*-PrOH (0.8 mL, d = 0.784 g/cm^3, 638.3 mg, 10.62 mmol) afforded **5a** (1.5065 g, 90%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.47 (m, 2 H, Ar-H), 7.36-7.29 (m, 3 H, Ar-H), 5.78 (d, *J* = 3.3 Hz, 1 H, one proton of $=CH_2$), 5.36 (d, *J* =

2.1 Hz, 1 H, one proton of $=CH_2$), 2.19 (q, *J* = 7.5 Hz, 1 H, =CCH), 1.20 (s, 6 H, B(pin)), 1.19 (s, 6 H, B(pin)), 1.09 (d, *J* = 7.5 Hz, 3 H, CH_3), 0.25 (s, 6 H, $SiMe_2$); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 138.2, 134.2, 128.7, 127.4, 125.5, 83.2, 26.2, 24.8, 24.7, 14.5, -4.1, -5.6.

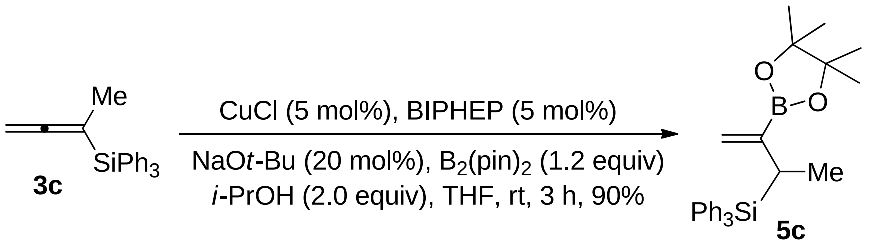
The following compounds were prepared according to this **Typical Procedure**.

(2) Synthesis of (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl) methyldiphenylsilane (5b) (ywm-13-178)



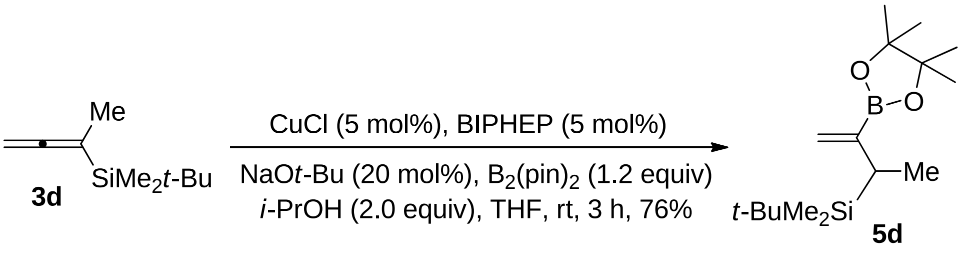
The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO*t*-Bu (19.2 mg, 0.2 mmol), bis(pinacolato)diboron (304.6 mg, 1.2 mmol)/THF (2 mL), **3b** (250.5 mg, 1.0 mmol)/THF (1 mL), and *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5b** (333.1 mg, 88%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.61-7.48 (m, 4 H, Ar-H), 7.41-7.22 (m, 6 H, Ar-H), 5.82 (d, *J* = 3.0 Hz, 1 H, one proton of $=CH_2$), 5.37 (d, *J* = 2.1 Hz, 1 H, one proton of $=CH_2$), 2.65 (q, *J* = 7.4 Hz, 1 H, =CCH), 1.17 (d, *J* = 7.2 Hz, 3 H, CH_3), 1.11 (s, 6 H, B(pin)), 1.07 (s, 6 H, B(pin)), 0.51 (s, 3 H, SiMe); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 136.7, 135.7, 135.2, 129.0, 128.9, 127.5, 126.5, 83.2, 24.7, 24.3, 15.3, -6.0; IR (neat, cm^{-1}): 2977, 1600, 1427, 1358, 1307, 1136, 1108; MS (ESI) m/z 402 [$M^+(^{11}B)$+Na+H], 401 [$M^+(^{11}B)$+Na] or [$M^+(^{10}B)$+Na+H], 400 [$M^+(^{10}B)$+Na]; HRMS Calcd for $C_{23}H_{31}O_2Si^{10}B$ (M^+): 377.2223, Found: 377.2220.

(3) Synthesis of (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl) triphenylsilane (5c) (ywm-13-179)



The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.0 mg, 0.05 mmol), NaO*t*-Bu (19.3 mg, 0.2 mmol), bis(pinacolato)diboron (304.8 mg, 1.2 mmol)/THF (2 mL), **3c** (312.4 mg, 1.0 mmol)/THF (1 mL), and *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5c** (396.3 mg, 90%) (eluent: petroleum ether/ethyl ether = 70/1) as a white solid: m.p. 99-100 ^{o}C (ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.55 (m, 6 H, Ar-H), 7.42-7.27 (m, 9 H, Ar-H), 5.82 (d, *J* = 2.4 Hz, 1 H, one proton of =CH_2), 5.22 (d, *J* = 2.4 Hz, 1 H, one proton of =CH_2), 2.96 (q, *J* = 7.5 Hz, 1 H, CH), 1.29 (d, *J* = 7.5 Hz, 3 H, CH_3), 1.11 (s, 6 H, B(pin)), 1.05 (s, 6 H, B(pin)); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 136.5, 134.5, 129.1, 128.6, 127.5, 83.2, 24.7, 23.3, 17.2; IR (neat, cm^{-1}): 2978, 1598, 1485, 1427, 1371, 1307, 1130, 1107; MS (ESI) m/z 464 [$M^+(^{11}B)$+Na+H], 463 [$M^+(^{11}B)$+Na] or [$M^+(^{10}B)$+Na+H], 462 [$M^+(^{10}B)$+Na]; Anal. Calcd. for $C_{28}H_{33}BO_2Si$ (%): C 76.35, H 7.55; Found: C 76.28, H 7.55.

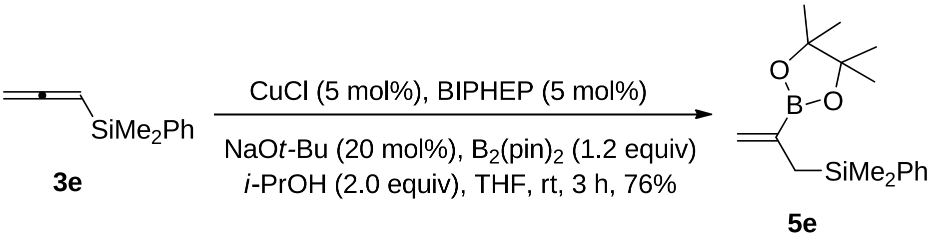
(4) Synthesis of (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl) *tert*-butyldimethylsilane (5d) (ywm-13-174)



The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO*t*-Bu (19.2 mg, 0.2 mmol), bis(pinacolato)diboron (304.6 mg, 1.2 mmol)/THF (2 mL), **3d** (168.5 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5d** (224.3 mg, 76%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (d, *J* = 3.3 Hz, 1 H, one proton of =CH_2), 5.43 (d, *J* = 2.4 Hz, 1 H, one proton of =CH_2), 2.09 (q, *J* = 7.4 Hz, 1 H,

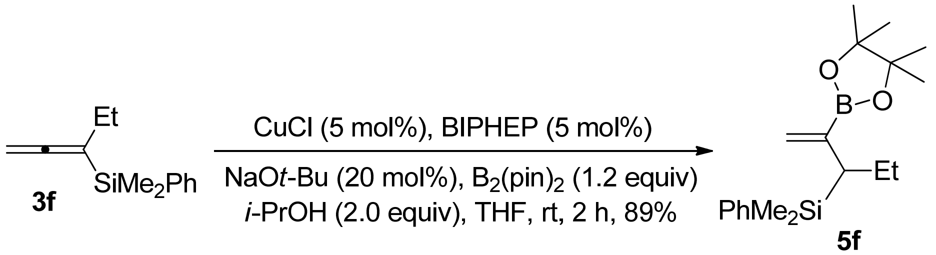
=CCH), 1.26 (s, 6 H, B(pin)), 1.25 (s, 6 H, B(pin)), 1.16 (d, *J* = 7.2 Hz, 3 H, CH_3), 0.91 (s, 9 H, 3 × CH_3), -0.09 (s, 3 H, SiMe), -0.11 (s, 3 H, SiMe); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 125.1, 83.2, 27.2, 24.9, 24.7, 24.0, 17.6, 16.1, -6.1, -8.4; IR (neat, cm^{-1}): 2978, 2955, 2857, 1600, 1470, 1358, 1305, 1248, 1138; MS (ESI) m/z 315 [M$^+$(^{11}B)+NH_4], 297 [M$^+$(^{11}B)+H]; HRMS Calcd for $C_{16}H_{33}{}^{11}BO_2Si$ (M$^+$): 296.2343, Found: 296.2344.

(5) Synthesis of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)dimethyl-(phenyl)silane (5e) (sl-4-68)



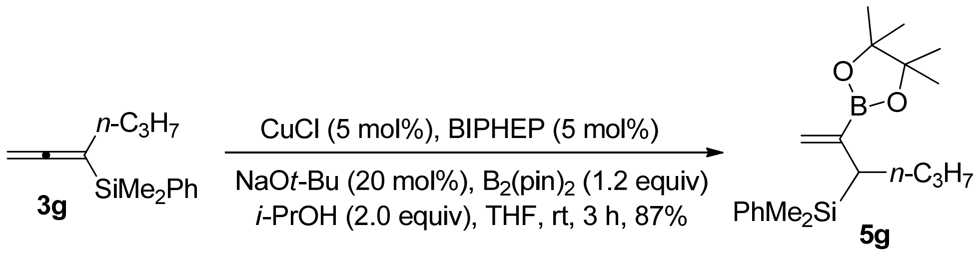
The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaO*t*-Bu (19.3 mg, 0.2 mmol), bis(pinacolato)diboron (304.9 mg, 1.2 mmol)/THF (2 mL), **3e** (174.6 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5e**[8] (230.0 mg, 76%) (eluent: petroleum ether/ethyl ether = 100/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.49 (m, 2 H, Ar-H), 7.36-7.29 (m, 3 H, Ar-H), 5.67 (d, *J* = 2.8 Hz, 1 H, one proton of =CH_2), 5.38 (d, *J* = 2.8 Hz, 1 H, one proton of =CH_2), 1.91 (s, 2 H, =CCH_2), 1.20 (s, 12 H, B(pin)), 0.26 (s, 6 H, $SiMe_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 133.8, 128.8, 127.6, 83.4, 24.7, 24.2, -3.3; IR (neat, cm^{-1}): 2978, 1605, 1425, 1358, 1308, 1247, 1192, 1142, 1113, 1092; MS (ESI) m/z 326 [M$^+$(^{11}B)+Na+H], 325 [M$^+$(^{11}B)+Na] or [M$^+$(^{10}B)+Na+H], 324 [M$^+$(^{10}B)+Na].

(6) Synthesis of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-3-yl) dimethyl(phenyl)silane (5f) (ywm-12-9)



The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.4 mg, 0.05 mmol), NaO*t*-Bu (19.6 mg, 0.2 mmol), bis(pinacolato)diboron (305.8 mg, 1.2 mmol)/THF (2 mL), **3f** (201.3 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5f** (293.6 mg, 89%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.47 (m, 2 H, Ar-H), 7.36-7.28 (m, 3 H, Ar-H), 5.82 (d, J = 3.0 Hz, 1 H, one proton of =CH_2), 5.36 (d, J = 3.0 Hz, 1 H, one proton of =CH_2), 1.97 (dd, J_1 = 10.8 Hz, J_2 = 4.5 Hz, 1 H, CH), 1.70-1.47 (m, 2 H, CH_2), 1.199 (s, 6 H, B(pin)), 1.195 (s, 6 H, B(pin)), 0.81 (t, J = 7.4 Hz, 3 H, CH_3), 0.26 (s, 3 H, SiMe), 0.23 (s, 3 H, SiMe); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 138.7, 134.2, 128.6, 127.4, 126.7, 83.1, 35.8, 24.8, 24.7, 21.8, 13.9, -3.7, -5.2; IR (neat, cm^{-1}): 2977, 2959, 1601, 1463, 1427, 1389, 1370, 1360, 1335, 1305, 1247, 1214, 1166, 1140, 1111, 1060, 1026; MS (ESI) m/z 369 [M^+(^{11}B)+K], 353 [M^+(^{11}B)+Na], 352 [M^+(^{10}B)+Na]; HRMS Calcd for $C_{19}H_{31}O_2Si^{11}B$ (M^+): 330.2186, Found: 330.2188.

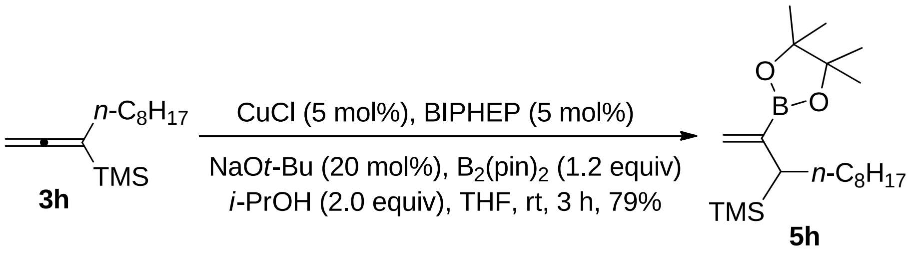
(7) Synthesis of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-3-yl) dimethyl(phenyl)silane (5g) (ywm-12-8)



The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.7 mg, 0.05 mmol), NaO*t*-Bu (19.4 mg, 0.2 mmol), bis(pinacolato)diboron (306.2 mg, 1.2 mmol)/THF (2 mL), **3g** (215.8 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5g** (300.1 mg, 87%) (eluent: petroleum ether/ethyl ether =

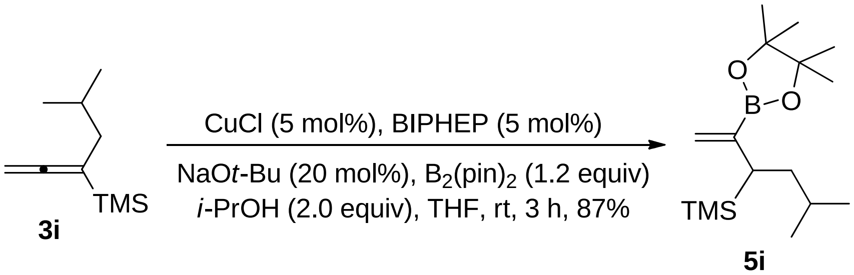
70/1) as a liquid: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.54-7.47 (m, 2 H, Ar-H), 7.36-7.28 (m, 3 H, Ar-H), 5.81 (d, *J* = 3.3 Hz, 1 H, one proton of =CH$_2$), 5.35 (d, *J* = 3.0 Hz, 1 H, one proton of =CH$_2$), 2.10 (dd, J_1 = 11.9 Hz, J_2 = 3.2 Hz, 1 H, CH), 1.72-1.54 (m, 1 H, one proton of CH$_2$), 1.48-1.27 (m, 2 H, CH$_2$), 1.21-1.02 (m, 13 H, one proton of CH$_2$ and B(pin)), 0.78 (t, *J* = 7.1 Hz, 3 H, CH$_3$), 0.26 (s, 3 H, SiMe), 0.23 (s, 3 H, SiMe); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 138.6, 134.2, 128.6, 127.4, 126.7, 83.1, 33.1, 30.8, 24.70, 24.67, 21.9, 13.8, -3.8, -5.1; IR (neat, cm^{-1}): 2977, 2956, 1601, 1465, 1426, 1418, 1388, 1361, 1344, 1305, 1273, 1246, 1226, 1165, 1141, 1111, 1067; MS (ESI) m/z 368 [M$^+$(^{11}B)+Na+H], 367 [M$^+$(^{11}B)+Na] or [M$^+$(^{10}B)+Na+H], 366 [M$^+$(^{10}B)+Na]; HRMS Calcd for $C_{20}H_{33}O_2Si^{11}B$ (M$^+$): 344.2343, Found: 344.2340.

(8) Synthesis of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-1-en-3-yl) trimethylsilane (5h) (ywm-13-161)



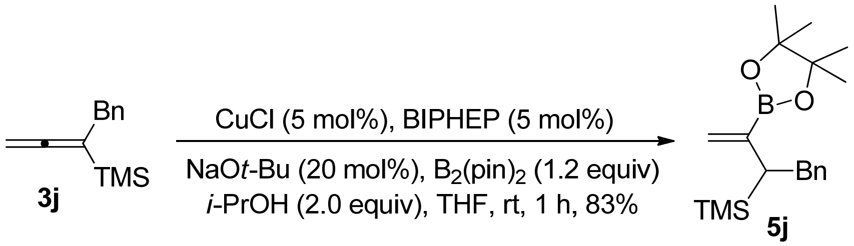
The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO*t*-Bu (19.1 mg, 0.2 mmol), bis(pinacolato)diboron (304.6 mg, 1.2 mmol)/THF (2 mL), **3h** (224.6 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5h** (279.4 mg, 79%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.79 (d, *J* = 3.3 Hz, 1 H, one proton of =CH$_2$), 5.40 (d, *J* = 3.0 Hz, 1 H, one proton of =CH$_2$), 1.80 (dd, J_1 = 11.6 Hz, J_2 = 3.2 Hz, 1 H, =CCH), 1.72-1.04 (m, 26 H, 7 × CH$_2$ and B(pin)), 0.87 (t, *J* = 6.8 Hz, 3 H, CH$_3$), -0.06 (s, 9 H, SiMe$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 126.0, 83.1, 34.2, 31.9, 29.60, 29.56, 29.4, 29.0, 28.3, 24.8, 24.7, 22.7, 14.1, -2.8; IR (neat, cm^{-1}): 2924, 2854, 1600, 1466, 1418, 1360, 1304, 1246, 1142; MS (70 ev, EI) m/z 352 [M$^+$(^{11}B), 1.09], 73 (100); HRMS Calcd for $C_{20}H_{41}O_2Si^{10}B$ (M$^+$): 351.3005, Found: 351.2999.

(9) Synthesis of (5-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-3-yl)trimethylsilane (5i) (ywm-13-158)



The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaO*t*-Bu (19.3 mg, 0.2 mmol), bis(pinacolato)diboron (304.9 mg, 1.2 mmol)/THF (2 mL), **3i** (168.4 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5i** (257.3 mg, 87%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 (d, J = 3.3 Hz, 1 H, one proton of =CH_2), 5.39 (d, J = 3.3 Hz, 1 H, one proton of =CH_2), 1.93 (dd, J_1 = 12.8 Hz, J_2 = 3.2 Hz, 1 H, =CCH), 1.81-1.67 (m, 1 H, one proton of CH_2), 1.65-1.49 (m, 1 H, CH), 1.24 (s, 12 H, B(pin)), 1.13-1.02 (m, 1 H, one proton of CH_2), 0.84 (d, J = 6.6 Hz, 3 H, CH_3), 0.77 (d, J = 6.6 Hz, 3 H, CH_3), -0.06 (s, 9 H, $SiMe_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 126.3, 83.1, 37.4, 32.0, 26.0, 24.7, 23.9, 20.8, -2.9; IR (neat, cm^{-1}): 2953, 2901, 1602, 1468, 1418, 1361, 1304, 1246, 1142; MS (70 ev, EI) m/z (%) 296 [$M^+(^{11}B)$, 1.78], 295 [$M^+(^{10}B)$, 0.47], 73 (100); HRMS Calcd for $C_{16}H_{33}O_2Si^{10}B$ (M^+): 295.2379, Found: 295.2378.

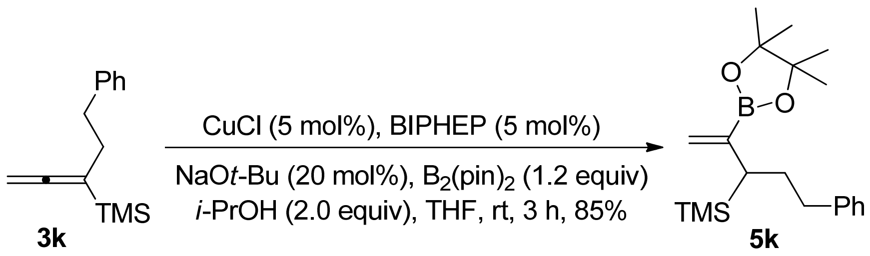
(10) Synthesis of (1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)trimethylsilane (5j) (ywm-13-138)



The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO*t*-Bu (19.1 mg, 0.2 mmol), bis(pinacolato)diboron (304.3 mg, 1.2 mmol)/THF (2 mL), **3j** (202.5 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2

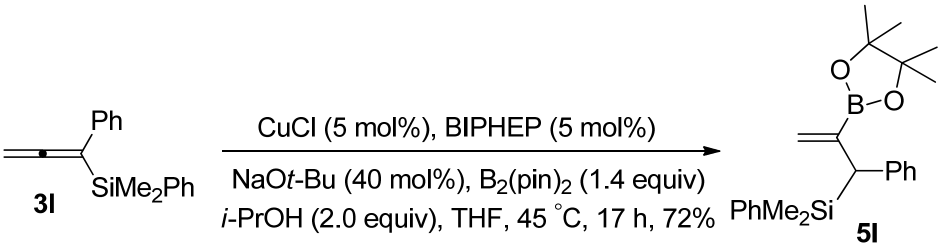
mg, 2.0 mmol) afforded **5j** (275.5 mg, 83%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.25-7.07 (m, 5 H, Ar-H), 5.75 (d, J = 3.3 Hz, 1 H, one proton of =CH$_2$), 5.42 (d, J = 2.4 Hz, 1 H, one proton of =CH$_2$), 2.99 (dd, J_1 = 14.6 Hz, J_2 = 11.0 Hz, 1 H, one proton of Ar-CH$_2$), 2.88 (dd, J_1 = 14.4 Hz, J_2 = 5.1 Hz, 1 H, one proton of Ar-CH$_2$), 2.30 (dd, J_1 = 11.1 Hz, J_2 = 5.1 Hz, 1 H, =CCH), 1.24 (s, 6 H, B(pin)), 1.22 (s, 6 H, B(pin)), 0.004 (s, 9 H, SiMe$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 142.6, 128.6, 127.8, 127.3, 125.2, 83.1, 35.3, 34.6, 24.8, 24.6, -2.7; IR (neat, cm^{-1}): 2978, 2956, 1602, 1495, 1417, 1361, 1304, 1247, 1212, 1139; MS (70 ev, EI) m/z (%) 330 [M$^+$(^{11}B), 2.45], 329 [M$^+$(^{10}B), 0.53], 73 (100); HRMS Calcd for $C_{19}H_{31}{}^{10}BO_2Si$ (M$^+$): 329.2223, Found: 329.2226.

(11) Synthesis of (5-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-3-yl)trimethylsilane (5k) (ywm-13-160)



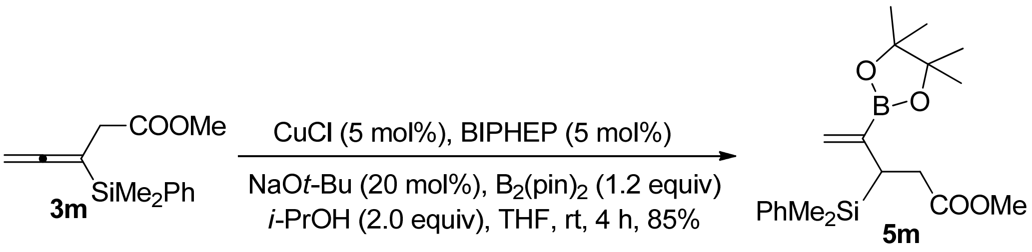
The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO*t*-Bu (19.3 mg, 0.2 mmol), bis(pinacolato)diboron (304.5 mg, 1.2 mmol)/THF (2 mL), **3k** (216.5 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5k** (292.5 mg, 85%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.31-7.22 (m, 2 H, Ar-H), 7.20-7.11 (m, 3 H, Ar-H), 5.89 (d, J = 3.3 Hz, 1 H, one proton of =CH$_2$), 5.50 (d, J = 2.7 Hz, 1 H, one proton of =CH$_2$), 2.80-2.67 (m, 1 H, =CCH), 2.47-2.34 (m, 1 H, one proton of CH$_2$), 2.08-1.67 (m, 3 H, one proton of CH$_2$ and Ar-CH$_2$), 1.27 (s, 12 H, B(pin)), -0.06 (s, 9 H, SiMe$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 143.2, 128.4, 128.1, 126.5, 125.4, 83.1, 35.3, 34.3, 30.7, 24.8, -2.9; IR (neat, cm^{-1}): 2978, 2955, 1601, 1496, 1418, 1359, 1305, 1246, 1134; MS (70 ev, EI) m/z (%) 344 [M$^+$(^{11}B), 1.82], 73 (100); HRMS Calcd for $C_{20}H_{33}O_2Si^{10}B$ (M$^+$): 343.2379, Found: 343.2382.

(12) Synthesis of (1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)-dimethyl(phenyl)silane (5l) (sl-2-175)



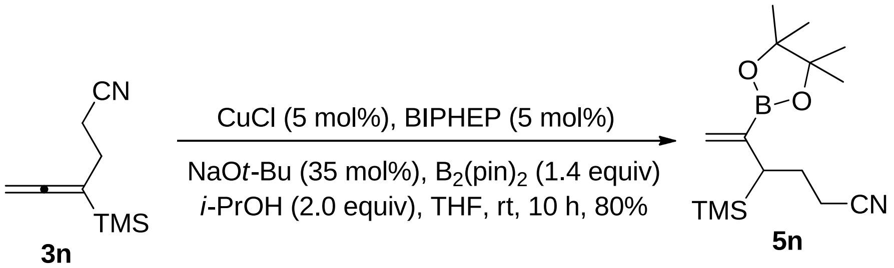
The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaO*t*-Bu (38.4 mg, 0.4 mmol), bis(pinacolato)diboron (355.9 mg, 1.4 mmol)/THF (2 mL), **3l** (250.7 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5l**[8] (273.0 mg, 72%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.47 (m, 2 H, Ar-H), 7.43-7.33 (m, 3 H, Ar-H), 7.30-7.22 (m, 2 H, Ar-H), 7.21-7.14 (m, 3 H, Ar-H), 5.99 (d, *J* = 2.8 Hz, 1 H, one proton of $=CH_2$), 5.76 (d, *J* = 2.0 Hz, 1 H, one proton of $=CH_2$), 3.65 (s, 1 H, =CCH), 1.25 (s, 6 H, B(pin)), 1.23 (s, 6 H, B(pin)), 0.41 (s, 3 H, SiMe), 0.37 (s, 3 H, SiMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 138.1, 134.4, 129.0, 128.8, 127.8, 127.3, 124.7, 83.4, 42.2, 24.7, 24.6, -3.0, -3.5; IR (neat, cm^{-1}): 2978, 1597, 1492, 1426, 1357, 1310, 1251, 1141, 1074; MS (ESI) m/z 402 [M^+(^{11}B)+Na+H], 401 [M^+(^{11}B)+Na] or [(^{10}B)+Na+H], 400 [M^+(^{10}B)+Na].

(13) Synthesis of methyl 3-(dimethyl(phenyl)silyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (5m) (sl-4-93)



The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaO*t*-Bu (19.3 mg, 0.2 mmol), bis(pinacolato)diboron (304.9 mg, 1.2 mmol)/THF (2 mL), **3m** (246.7 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5m** (320.1 mg, 85%) (eluent: petroleum ether/ethyl ether = 50/1) as a liquid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52-7.43 (m, 2 H, Ar-H), 7.36-7.30 (m, 3 H, Ar-H), 5.79 (d, *J* = 2.8 Hz, 1 H, one proton of =CH$_2$), 5.36 (d, *J* = 2.4 Hz, 1 H, one proton of =CH$_2$), 3.52 (s, 3 H, OCH$_3$), 2.72-2.56 (m, 2 H, CH$_2$), 2.41 (dd, J_1 = 14.6 Hz, J_2 = 3.4 Hz, 1 H, =CCH), 1.22 (s, 6 H, B(pin)), 1.21 (s, 6 H, B(pin)), 0.29 (s, 3H, SiMe), 0.27 (s, 3 H, SiMe); ^{13}C NMR (100 MHz, CDCl$_3$) δ 173.8, 137.2, 134.2, 129.0, 127.6, 127.2, 83.3, 51.3, 34.3, 29.8, 24.71, 24.68, -3.9, -5.4; IR (neat, cm^{-1}): 2977, 1737, 1428, 1363, 1308, 1249, 1137, 1112; MS (ESI) m/z (%) 398 [M$^+$(^{11}B) + Na+H], 397 [M$^+$(^{11}B)+Na]or [M$^+$(^{10}B) + Na+H], 396 [M$^+$(^{10}B)+Na]; HRMS Calcd for $C_{20}H_{31}O_4Si^{11}B$ (M$^+$): 374.2085, Found: 374.2083.

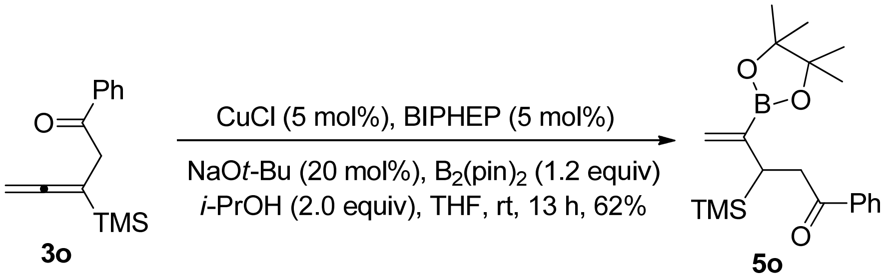
(14) Synthesis of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trimethylsilyl)hex-5-enenitrile (5n) (sl-6-54)



The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO*t*-Bu (33.6 mg, 0.35 mmol), bis(pinacolato)diboron (355.6 mg, 1.4 mmol)/THF (8 mL), **3n** (165.6 mg, 1.0 mmol)/THF (2 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5n** (232.7 mg, 80%) (eluent: petroleum ether/ethyl ether = 40/1) as an oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.86 (d, *J* = 2.4 Hz, 1 H, one proton of =CH$_2$), 5.45 (d, *J* = 2.8 Hz, 1 H, one proton of =CH$_2$), 2.45-2.35 (m, 1 H, =CCH), 2.24-2.12 (m, 1 H, one proton of CH$_2$), 2.12-2.00 (m, 1 H, one proton of CH$_2$), 1.94-1.79 (m, 2 H, CH$_2$), 1.24 (s, 12 H, B(Pin)), -0.02 (s, 9 H, SiMe$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 128.0, 120.2, 83.5, 34.5, 24.8, 24.7, 24.6, 16.6, -3.0; IR (neat, cm^{-1}): 2978, 2959, 2245, 1600, 1420, 1380, 1371, 1659, 1309, 1248, 1213, 1202, 1165, 1138;

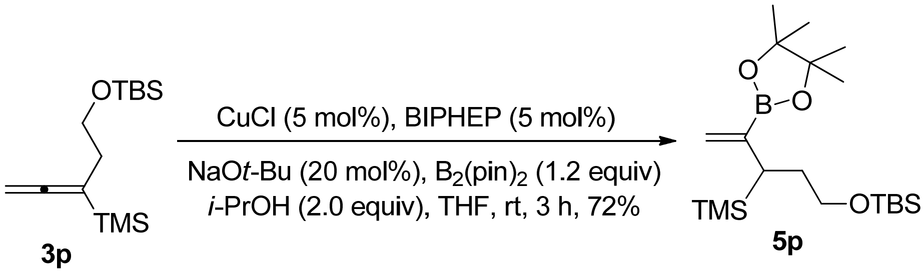
MS (70 ev, EI) m/z (%): 293 [M$^+$(^{11}B), 9.57], 292 [M$^+$(^{10}B), 2.48], 113 (100). HRMS Calcd for $C_{15}H_{28}NO_2Si^{11}B$ (M$^+$): 293.1982, Found: 293.1981.

(15) Synthesis of 1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)pent-4-en-1-one (5o) (sl-6-117)



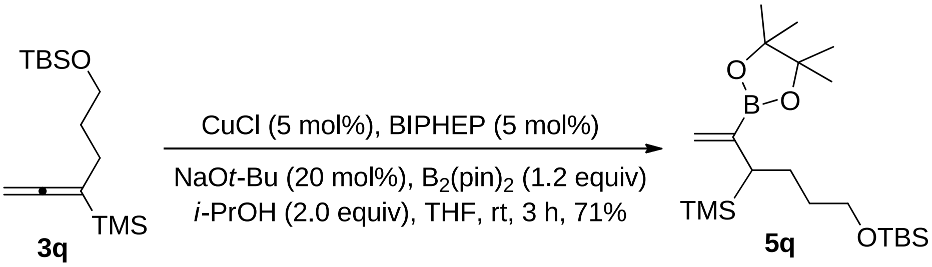
The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO*t*-Bu (19.3 mg, 0.2 mmol), bis(pinacolato)diboron (305.1 mg, 1.2 mmol)/THF (2 mL), **3o** (230.5 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5o** (222.8 mg, 62%) (eluent: petroleum ether/ethyl ether = 40/1) as a liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.90 (m, 2 H, Ar-H), 7.58-7.49 (m, 1 H, Ar-H), 7.47-7.40 (m, 2 H, Ar-H), 5.76 (d, J = 2.8 Hz, 1 H, one proton of =CH_2), 5.44 (d, J = 2.4 Hz, 1 H, one proton of =CH_2), 3.50 (dd, J_1 = 16.8 Hz, J_2 = 10.4 Hz, 1 H, one proton of $COCH_2$), 3.01 (dd, J_1 = 16.8 Hz, J_2 = 4.8 Hz, 1 H, one proton of $COCH_2$), 2.57 (dd, J_1 = 10.8 Hz, J_2 = 4.8 Hz 1 H, =CCH), 1.21 (s, 6 H, B(Pin)), 1.20 (s, 6 H, B(Pin)), 0.03 (s, 9 H, $SiMe_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 137.6, 132.5, 128.3, 128.0, 126.8, 83.3, 38.3, 29.9, 24.72, 24.70 , -2.8; IR (neat, cm^{-1}): 2978, 1687, 1598, 1580, 1447, 1421, 1359, 1306, 1247, 1216, 1165, 1139; MS (70 ev, EI) m/z (%): 358 [M$^+$(^{11}B), 4.70], 357 [M$^+$(^{10}B), 2.39], 73 (100). HRMS Calcd for $C_{20}H_{32}O_3Si^{11}B$ [M$^+$(^{11}B)+H]: 359.2214, Found: 359.2219.

(16) Synthesis of ((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)pent-4-en-1-yl)oxy)*tert*-butyldimethylsilane (5p) (ywm-12-26)



The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.7 mg, 0.05 mmol), NaO*t*-Bu (19.1 mg, 0.2 mmol), bis(pinacolato)diboron (305.0 mg, 1.2 mmol)/THF (2 mL), **3p** (271.3 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5p** (287.7 mg, 72%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (d, *J* = 3.3 Hz, 1 H, one proton of =CH_2), 5.43 (d, *J* = 2.7 Hz, 1 H, one proton of =CH_2), 3.67-3.56 (m, 1 H, =CCH), 3.49-3.38 (m, 1 H, one proton of CH_2), 1.93-1.82 (m, 2 H, CH_2), 1.76-1.64 (m, 1 H, one proton of CH_2), 1.24 (s, 12 H, B(pin)), 0.88 (s, 9 H, $(CH_3)_3$), 0.02 (s, 6 H, $(CH_3)_2$), -0.04 (s, 9 H, $SiMe_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 126.1, 83.2, 62.8, 31.5, 30.3, 26.0, 24.9, 24.7, 18.4, -2.9, -5.2; IR (neat, cm^{-1}): 2955, 2930, 2858, 1600, 1469, 1418, 1361, 1306, 1249, 1142, 1098; MS (ESI) m/z 422 [$M^+(^{11}B)$+Na+H], 421 [$M^+(^{11}B)$+Na] or [$M^+(^{10}B)$+Na+H], 420 [$M^+(^{10}B)$+Na]; HRMS Calcd for $C_{20}H_{43}O_3Si_2{}^{11}B$ (M^+): 398.2844, Found: 398.2849.

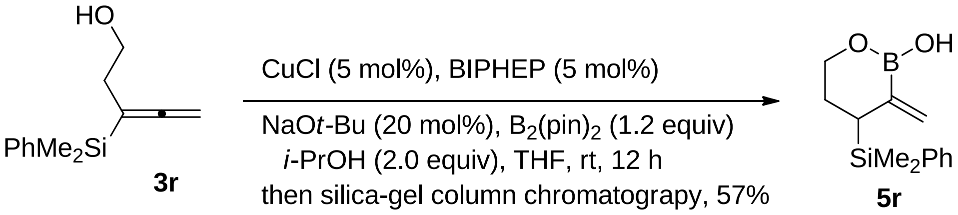
(17) Synthesis of ((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trimethylsilyl)hex-5-en-1-yl)oxy)*tert*-butyldimethylsilane (5q) (ywm-13-175)



The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaO*t*-Bu (19.1 mg, 0.2 mmol), bis(pinacolato)diboron (304.8 mg, 1.2 mmol)/THF (2 mL), **3q** (284.4 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5q** (291.4 mg, 71%) (eluent: petroleum ether/ethyl ether =

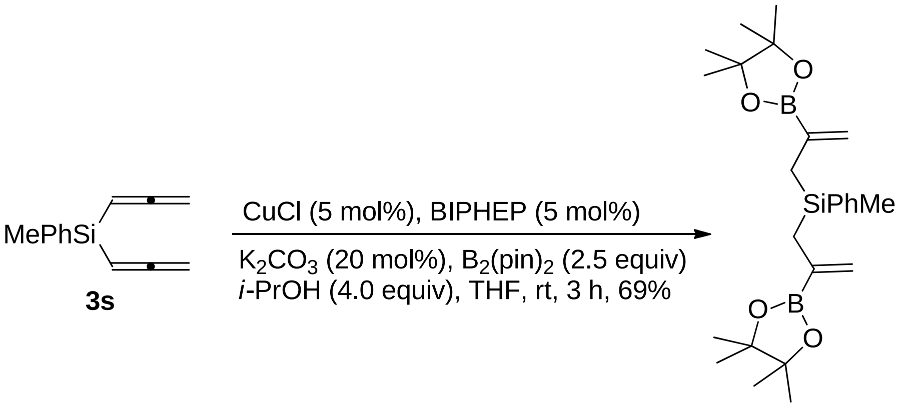
70/1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (d, *J* = 3.3 Hz, 1 H, one proton of $=CH_2$), 5.40 (d, *J* = 2.7 Hz, 1 H, one proton of $=CH_2$), 3.56 (t, *J* = 6.2 Hz, 2 H, CH_2OTBS), 1.84-1.77 (m, 1 H, =CCH), 1.71-1.49 (m, 3 H, one proton of CH_2 and CH_2), 1.47-1.33 (m, 1 H, one proton of CH_2), 1.24 (s, 12 H, B(pin)), 0.89 (s, 9 H, $(CH_3)_3$), 0.04 (s, 6 H, $(CH_3)_2$), -0.05 (s, 9 H, $SiMe_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 126.1, 83.1, 63.1, 33.7, 32.0, 26.0, 24.8, 24.7, 24.3, 18.3, -2.9, -5.3; IR (neat, cm^{-1}): 2954, 2858, 1601, 1471, 1361, 1305, 1247, 1142, 1100; MS (ESI) m/z 451 $[M^{+}(^{11}B)+K]$, 436 $[M^{+}(^{11}B)+Na+H]$, 435 $[M^{+}(^{11}B)+Na]$ or $[M^{+}(^{10}B)+Na+H]$, 434 $[M^{+}(^{10}B)+Na]$; HRMS Calcd for $C_{21}H_{45}O_3Si_2{}^{11}B$ (M^{+}): 412.3000, Found: 412.3003.

(18) Synthesis of 4-(dimethyl(phenyl)silyl)-3-methylene-2-hydroxy-1,2-oxaborinane (5r) (sl-6-5)



The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.1 mg, 0.05 mmol), NaO*t*-Bu (19.4 mg, 0.2 mmol), bis(pinacolato)diboron (304.9 mg, 1.2 mmol)/THF (2 mL), **3r** (218.7 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (120.2 mg, d = 0.784 g/cm^3, 2.0 mmol) afforded **5r** (140.2 mg, 57%, the desired hydroboration product was instable on silica gel.) (eluent: petroleum ether/ethyl acetate = 20/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.47 (m, 2 H, Ar-H), 7.40-7.30 (m, 3 H, Ar-H), 5.75 (dd, J_1 = 2.4 Hz, J_2 = 1.6 Hz, 1 H, one proton of $=CH_2$), 5.34 (s, 1 H, one proton of $=CH_2$), 4.29 (brs, 1 H, OH), 4.05-3.85 (m, 2 H, OCH_2), 2.23 (t, *J* = 5.2 Hz, =CCH), 2.02-1.85 (m, 1 H, one proton of CH_2), 1.82-1.72 (m, 1 H, one proton of CH_2), 0.33 (s, 3 H, SiMe), 0.32 (s, 3 H, SiMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 134.0, 129.1, 127.8, 125.0, 65.0, 31.6, 28.9, -3.96, -4.04; IR (neat, cm^{-1}): 3384, 2901, 1483, 1425, 1411, 1365, 1339, 1296, 1248, 1187, 1146, 1111, 1034; MS (70 ev, EI) m/z (%): 246 $(M^{+}(^{11}B)$, 1.89], 245 $[M^{+}(^{10}B)$, 0.67], 135 (100). HRMS Calcd for $C_{13}H_{19}O_2Si^{11}B$ (M^{+}): 246.1247, Found: 246.1249.

(19) Synthesis of bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)methyl (phenyl)silane (5s) (sl-4-83)

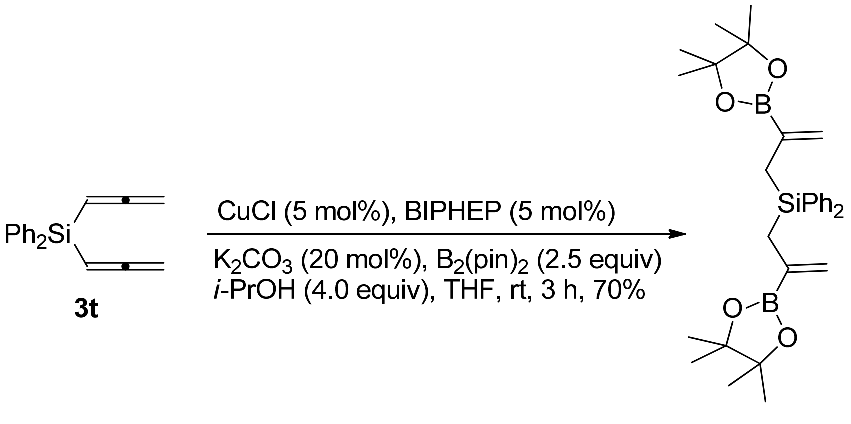


3s

5s

The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.4 mg, 0.05 mmol), K_2CO_3 (27.7 mg, 0.2 mmol), bis(pinacolato)diboron (635.2 mg, 2.5 mmol), THF (2 mL), **3s** (198.2 mg, 1.0 mmol), THF (1 mL), *i*-PrOH (306 *u*L, d = 0.784 g/mL, 240.4 mg, 4.0 mmol) afforded **5s** (311.7 mg, 69%) (eluent: petroleum ether/ethyl ether = 50/1) as a white solid: m.p. 42.1- 43.1 °C (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.47 (m, 2 H, Ar-H), 7.32-7.24 (m, 3 H, Ar-H), 5.64 (d, *J* = 4.0 Hz, 2 H, =CH_2), 5.39 (d, *J* = 3.2 Hz, 2 H, =CH_2), 1.96 (s, 4 H, 2 × =CCH_2), 1.15 (s, 24 H, 2 × B(pin)), 0.26 (s, 3 H, SiMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 134.5, 128.6, 127.8, 127.3, 83.3, 24.7, 24.6, 22.3, -5.8; IR (neat, cm^{-1}): 2984, 1603, 1469, 1423, 1372, 1356, 1316, 1248, 1193, 1111, 1083; MS (ESI) m/z 478 [M^+(^{11}B)+Na+H], 477 [M^+(^{11}B)+Na] or [M^+(^{10}B)+Na+H], 476 [M^+(^{10}B)+Na]; Anal. Calcd. for $C_{25}H_{40}B_2O_4Si$ (%): C 66.10, H 8.87; Found: C 66.04, H 8.93.

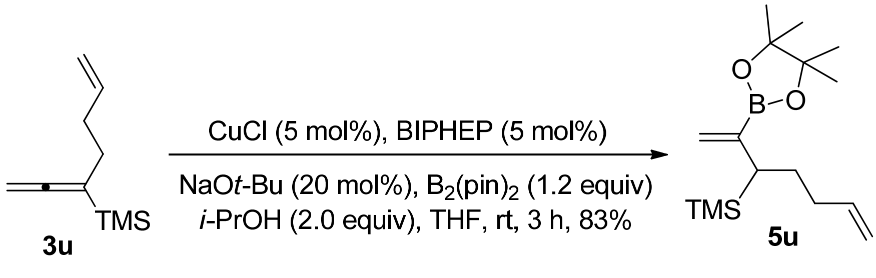
(20) Synthesis of bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)diphenyl silane (5t) (sl-4-82)



3t **5t**

The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), K_2CO_3 (27.8 mg, 0.2 mmol), bis(pinacolato)diboron (635.3 mg, 2.5 mmol), THF (2 mL), **3t** (260.8 mg, 1.0 mmol), THF (1 mL), *i*-PrOH (306 uL, d = 0.784 g/ml, 240.2 mg, 4.0 mmol) afforded **5t** (351.9 mg, 70%) (eluent: petroleum ether/ethyl ether = 50/1) as a white solid: m.p. 78.1-78.8 °C (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.49 (m, 4 H, Ar-H), 7.36-7.24 (m, 6 H, Ar-H), 5.65 (d, *J* = 4.0 Hz, 2 H, $=CH_2$), 5.41 (d, *J* = 3.2 Hz, 2 H, $=CH_2$), 2.27 (s, 4 H, 2 × $=CCH_2$), 1.06 (s, 24 H, 2 × B(pin)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 135.3, 128.9, 128.7, 127.3, 83.2, 24.6, 20.1; IR (neat, cm^{-1}): 2979, 2931, 2894, 1606, 1428, 1380, 1370, 1356, 1215, 1192, 1138, 1110, 1082; MS (ESI) m/z 555 [M^+(^{11}B)+K], 540 [M^+(^{11}B)+Na+H], 539 [M^+(^{11}B)+Na] or [M^+(^{10}B)+Na+H], 538 [M^+(^{10}B)+Na]; Anal. Calcd. for $C_{30}H_{42}O_4SiB_2$ (%): C 69.78, H 8.20; Found: C 69.96, H 8.19.

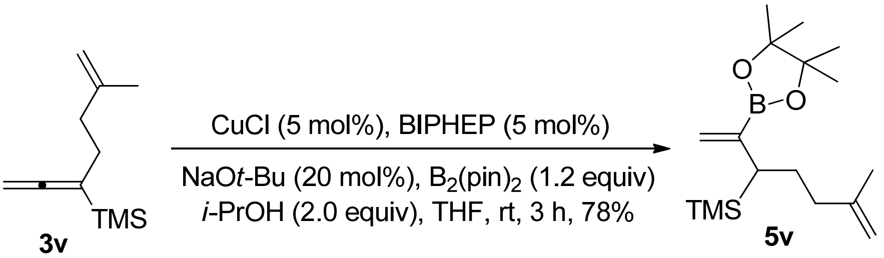
(21) Synthesis of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,6-dien-3-yl)trimethylsilane (5u) (ywm-13-159)



3u **5u**

The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO*t*-Bu (19.1 mg, 0.2 mmol), bis(pinacolato)diboron (304.5 mg, 1.2 mmol)/THF (2 mL), **3u** (166.4 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5u** (243.2 mg, 83%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86-5.70 (m, 2 H, one proton of $=CH_2$ and =CH), 5.42 (d, *J* = 2.7 Hz, 1 H, one proton of $=CH_2$), 5.00-4.88 (m, 2 H, $=CH_2$), 2.21-2.06 (m, 1 H, =CCH), 1.99-1.68 (m, 3 H, one proton of CH_2 and CH_2), 1.59-1.44 (m, 1 H, one proton of CH_2), 1.25 (s, 12 H, B(pin)), -0.05 (s, 9 H, $SiMe_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 139.2, 126.3, 114.2, 83.1, 33.7, 33.1, 27.8, 24.8, 24.7, -2.9; IR (neat, cm^{-1}): 2979, 1640, 1601, 1418, 1360, 1305, 1246, 1142; MS (70 ev, EI) m/z (%) 294 (M^+, 1.21), 73 (100); HRMS Calcd for $C_{16}H_{31}{}^{11}BO_2Si$ (M^+): 294.2186, Found: 294.2191.

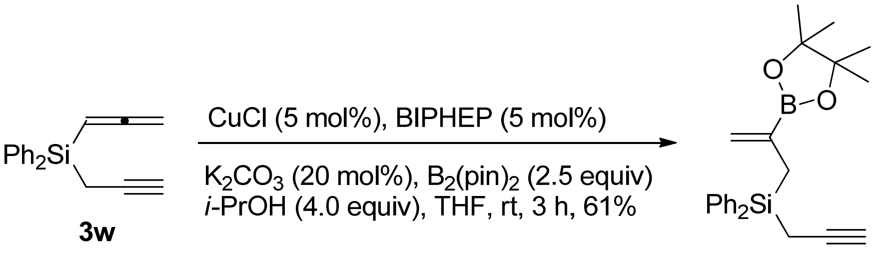
(22) Synthesis of (6-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,6-dien-3-yl)trimethylsilane (5v) (ywm-13-180)



The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaO*t*-Bu (19.1 mg, 0.2 mmol), bis(pinacolato)diboron (304.5 mg, 1.2 mmol)/THF (2 mL), **3v** (180.5 mg, 1.0 mmol)/THF (1 mL), *i*-PrOH (153 μL, d = 0.784 g/cm^3, 120.2 mg, 2.0 mmol) afforded **5v** (240.7 mg, 78%) (eluent: petroleum ether/ethyl ether = 50/1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82 (d, *J* = 3.0 Hz, 1 H, one proton of $=CH_2$), 5.42 (d, *J* = 3.0 Hz, 1 H, one proton of $=CH_2$), 4.67 (s, 1 H, one proton of $=CH_2$), 4.63 (s, 1 H, one proton of $=CH_2$), 2.13-2.01 (m, 1 H, =CCH), 1.94-1.72 (m, 3 H, one proton of CH_2 and CH_2), 1.69 (s, 3 H, CH_3), 1.67-1.53 (m, 1 H, one proton of CH_2), 1.25 (s, 12 H, B(pin)), -0.04 (s, 9 H, $SiMe_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 146.3, 126.2, 109.8, 83.1, 37.2, 34.0, 26.6, 24.7, 22.3, -2.9; IR (neat, cm^{-1}): 2979, 1648, 1600, 1418, 1360, 1304, 1246, 1138; MS (ESI) m/z 347 [M^+(^{11}B)+K], 332 [M^+(^{11}B)+Na+H], 331 [M^+(^{11}B)+Na] or [M^+(^{10}B)+Na+H], 330 [M^+(^{10}B)+Na]; HRMS

Calcd for $C_{17}H_{33}O_2Si^{10}B$ (M^+): 307.2379, Found: 307.2383.

(23) Synthesis of (prop-1-yn-3-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) allyldiphenylsilane (5w) (sl-4-106)

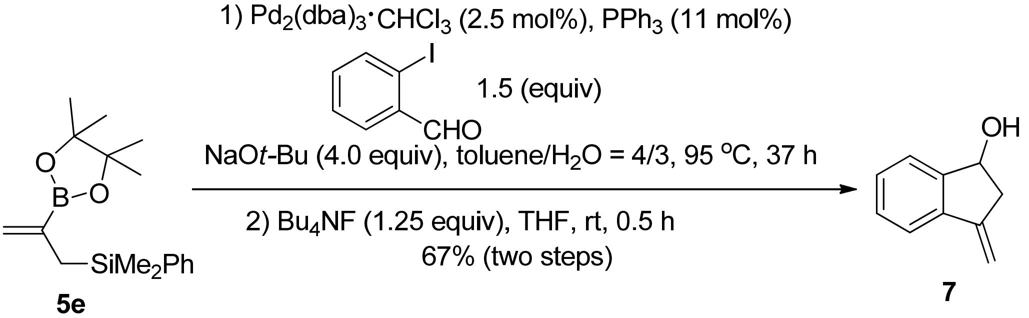


5w

The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), K_2CO_3 (27.8 mg, 0.2 mmol), bis(pinacolato)diboron (635.1 mg, 2.5 mmol), THF (2 mL), **3w** (260.7 mg, 1.0 mmol), THF (1 mL), *i*-PrOH (306 μL, d = 0.784 g/cm^3, 240.4 mg, 4.0 mmol) afforded **5w** (236.1 mg, 61%) (eluent: petroleum ether/ethyl ether = 150/1) as a white solid: m.p. 71.1-71.7 °C (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.55 (m, 4 H, Ar-H), 7.43-7.30 (m, 6 H, Ar-H), 5.73 (d, *J* = 3.2 Hz, 1 H, one proton of =CH_2), 5.52 (d, *J* = 2.8 Hz, 1 H, one proton of =CH_2), 2.37 (s, 2 H, =CCH_2), 2.09 (d, *J* = 2.8 Hz, 2 H, ≡CCH_2), 1.85 (t, *J* = 2.8 Hz, 1 H, ≡CH), 1.08 (s, 12 H, B(pin)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 134.0, 129.6, 129.2, 127.7, 83.4, 81.7, 68.6, 24.6, 19.9, 2.9; IR (neat, cm^{-1}): 1608, 1428, 1391, 1380, 1373, 1359, 1310, 1273, 1198, 1160, 1140, 1111, 1092; MS (70 ev, EI) m/z (%): 388 (M^+(^{11}B), 1.29), 221 (100); Anal. Calcd. for $C_{24}H_{29}BO_2Si$ (%): C 74.22, H 7.53; Found: C 74.07, H 7.54.

5. Synthetic applications

(1) Synthesis of 2,3-dihydro-3-methylene-1*H*-inden-1-ol (7) (sl-5-38)

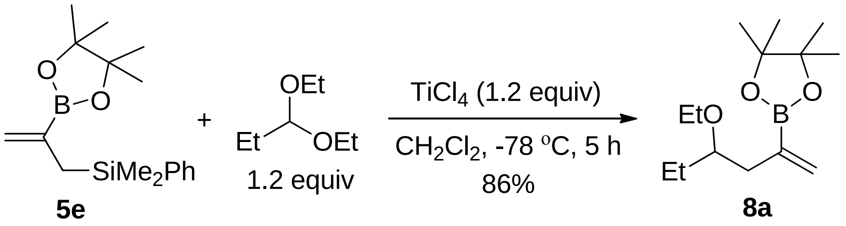


5e

7

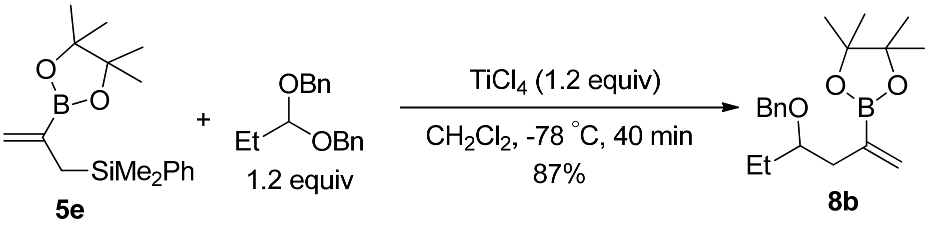
To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially $Pd_2(dba)_3{\cdot}CHCl_3$ (10.4 mg, 0.01 mmol), Ph_3P (11.9 mg, 0.044 mmol), NaO*t*-Bu (153.7 mg, 1.6 mmol), 2-iodobenzaldehyde (139.0 mg, 0.6 mmol), **5e** (120.7 mg, 0.4 mmol)/toluene (2 mL), and H_2O (1.5 mL) under argon. The mixture was stirred at rt for 10 min and then at 95 °C with a preheated oil bath for 37 h. Upon completion, the resulting mixture was cooled to rt, filtered through a short column of silica gel eluted with Et_2O (10 mL × 3), and concentrated. The residue was dissolved in 3 mL of THF followed by the addition of *n*-Bu_4NF (0.5 mL, 1 M in THF, 0.5 mmol). The resulting mixture was stirred at rt for 0.5 h. Upon completion, the resulting mixture was filtered through a short column of silica gel eluting with Et_2O (10 mL × 3) and concentrated. The reside was purified by chromatography on silica gel to afford **7**[9] (39.3 mg, 67%) (eluent: petroleum ether/ethyl acetate = 10/1) as a white solid: m.p. 69.5-70.6 °C (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.49 (m, 1 H, Ar-H), 7.48-7.42 (m, 1 H, Ar-H), 7.36-7.27 (m, 2 H, Ar-H), 5.52 (t, J = 2.4 Hz, 1 H, one proton of $=CH_2$), 5.25 (brs, 1 H, OCH), 5.09 (t, J = 1.8 Hz, 1 H, one proton of $=CH_2$), 3.19 (ddt, J_1 = 16.8 Hz, J_2 = 2.0 Hz, J_3 = 1.9 Hz, 1 H, one proton of CH_2), 2.69-2.60 (m, 1 H, one proton of CH_2), 2.00 (s, 1 H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 146.3, 140.1, 128.9, 128.7, 125.0, 120.6, 104.3, 73.3, 42.5; IR (neat, cm^{-1}): 3303, 3217, 1641, 1470, 1422, 1333, 1094, 1040, 1002; MS (70 ev, EI) m/z (%) 146 (M^+, 97.0), 131 (100).

(2) Synthesis of 4-ethoxyhexen-2-yl 4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8a (sl-4-74)



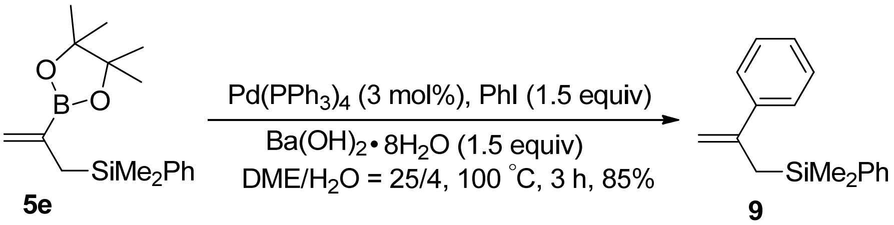
To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially **5e** (151.2 mg, 0.5 mmol), CH_2Cl_2 (1.25 mL), 1,1-diethoxypropane (95μL, d = 0.83 g/cm^3, 79.3 mg, 0.6 mmol), and CH_2Cl_2 (1.25 mL) under argon at rt. The mixture was cooled to -78 °C and $TiCl_4$ (0.6 mL, 1 M in CH_2Cl_2, 0.6 mmol) was added dropwise over 10 minutes. Upon completion as monitored by TLC, the resulting mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (10 mL) at -78 °C. After warming up to room temperature, the organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by chromatography on silica gel to afford **8a**[10] (108.7 mg, 86%) (eluent: petroleum ether/ethyl ether = 50/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (d, J = 3.6 Hz, 1 H, one proton of $=CH_2$), 5.65 (d, J = 3.6 Hz, 1 H, one proton of $=CH_2$), 3.60-3.40 (m, 2 H, OCH_2), 3.35-3.26 (m, 1 H, OCH), 2.41 (dd, J_1 = 13.4 Hz, J_2 = 6.2 Hz, 1 H, one proton of $=CCH_2$), 2.24 (dd, J_1 = 13.2 Hz, J_2 = 6.8 Hz, 1 H, one proton of $=CCH_2$), 1.57-1.44 (m, 1 H, one proton of CH_2), 1.43-1.34 (m, 1 H, one proton of CH_2), 1.27 (s, 12 H, B(pin)), 1.17 (t, J = 7.0 Hz, 3 H, CH_3), 0.91 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.2, 83.3, 80.1, 64.3, 40.2, 26.7, 24.8, 24.7, 15.5, 9.8; IR (neat, cm^{-1}): 2975, 2930, 2874, 1615, 1430, 1367, 1344, 1307, 1214, 1166, 1142, 1108, 1081; MS (ESI) m/z 278 [M^+(^{11}B)+Na+H], 277 [M^+(^{11}B)+Na] or [M^+(^{10}B)+Na+H], 276 [M^+(^{10}B)+Na], 255 [M^+(^{11}B)+H], 254 [M^+(^{11}B)].

(3) Synthesis of 4-benzyloxyhexen-2-yl 4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (8b) (sl-5-119)



To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially **5e** (151.4 mg, 0.5 mmol), CH_2Cl_2 (1.5 mL), propionaldehyde dibenzyl acetal (152.3 mg, 0.6 mmol), and CH_2Cl_2 (1.5 mL) under argon. The mixture was cooled to -78 °C and $TiCl_4$ (0.6 mL, 1 M in CH_2Cl_2, 0.6 mmol) was added dropwise over 10 minutes. Upon completion, the resulting mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (10 mL) at -78 °C. After warming up to room temperature, the organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by chromatography on silica gel to afford **8b** (137.6 mg, 87%) (eluent: petroleum ether/ethyl ether = 80/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 4 H, Ar-H), 7.28-7.21 (m, 1 H, Ar-H), 5.86 (d, J = 3.6 Hz, 1 H, one proton of =CH_2), 5.68 (d, J = 3.2 Hz, 1 H, one proton of =CH_2), 4.59 (d, 1 H, J = 11.6 Hz, one proton of Ar-CH_2), 4.49 (d, 1 H, J = 12.0 Hz, one proton of Ar-CH_2), 3.51-3.43 (m, 1 H, OCH), 2.53 (dd, J_1 = 13.2 Hz, J_2 = 6.0 Hz, 1 H, one proton of =CCH_2), 2.31 (dd, J_1 = 13.2 Hz, J_2 = 6.8 Hz, 1 H, one proton of =CCH_2), 1.61-1.34 (m, 2 H, CH_2), 1.24 (s, 6 H, B(pin)), 1.23 (s, 6 H, B(pin)), 0.91 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 131.5, 128.1, 127.7, 127.2, 83.3, 79.8, 70.8, 39.9, 26.4, 24.7, 24.6, 9.7; IR (neat, cm^{-1}): 2874, 1614, 1496, 1454, 1428, 1368, 1368, 1307, 1213, 1166, 1141, 1109, 1096, 1066, 1028; MS (70 ev, EI) m/z (%) 316 [M^+(^{11}B), 1.07], 315 [M^+(^{10}B), 0.27], 91 (100); HRMS Calcd for $C_{19}H_{29}O_3{}^{11}B$ (M^+): 316.2210, Found: 316.2208.

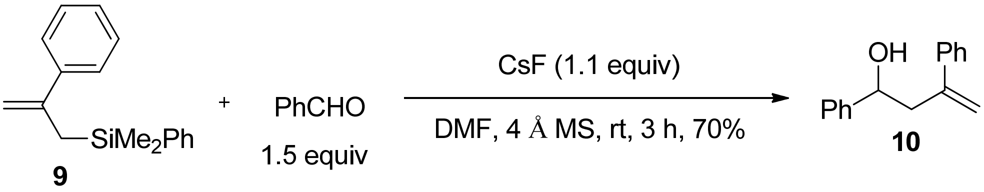
(4). Synthesis of 2-phenyl-2-propenyl dimethylphenylsilane (9) (sl-4-73)



To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially $Pd(PPh_3)_4$ (17.3 mg, 0.015 mmol), $Ba(OH)_2{\cdot}8H_2O$ (236.8 mg, 0.75 mmol), PhI (153.2 mg, 0.75 mmol)/DME (1.5 mL), **5e** (151.4 mg, 0.5 mmol)/DME (1.0 mL), and H_2O (0.4 mL) under argon. The mixture was stirred under reflux with an oil bath preheated at 100 °C for 3 h as monitored by TLC. Upon completion, the resulting mixture was cooled to rt, filtered through a short column of silica gel eluted with Et_2O (10 mL × 3), and concentrated. The residue was purified by chromatography on silica gel to afford **9**[10] (101.8 mg, 85%) (eluent: petroleum ether) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.42 (m, 2 H, Ar-H), 7.39-7.29 (m, 5

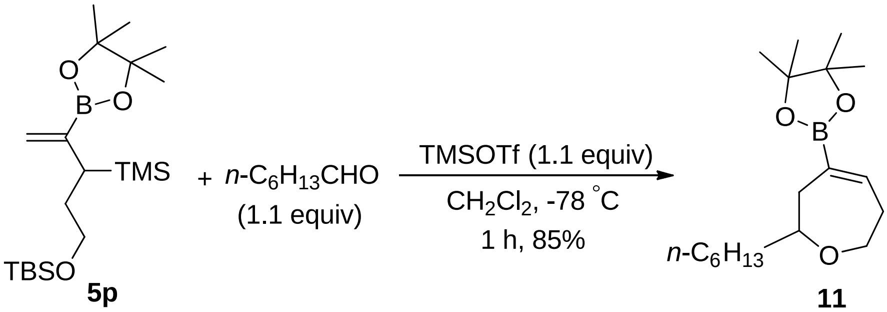
H, Ar-H), 7.29-7.18 (m, 3 H, Ar-H), 5.13 (d, *J* = 1.6 Hz, 1 H, one proton of =CH_2), 4.84 (d, *J* = 1.2 Hz, 1 H, one proton of =CH_2), 2.25 (d, *J* = 1.2 Hz, 2 H, CH_2), 0.14 (s, 6 H, $SiMe_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 142.6, 138.9, 133.5, 128.9, 128.0, 127.6, 127.2, 126.3, 110.9, 25.2, -3.0; IR (neat, cm^{-1}): 1615, 1493, 1426, 1299, 1248, 1160, 1112, 1028; MS (70 ev, EI) m/z (%): 252 (M^+, 10.42), 135 (100).

(5) Synthesis of 1,3-diphenylbut-3-en-1-ol (10) (sl-5-196)



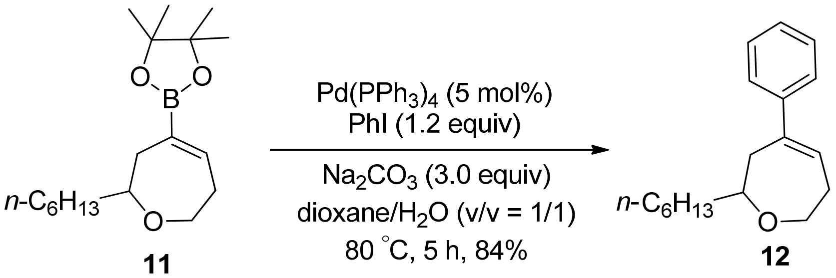
To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially CsF (33.6 mg, 0.22 mmol), 4 Å MS (50.1 mg,), PhCHO (30 uL, d = 1.048 g/cm^3, 41.8 mg, 0.3 mmol, fresh distilled)/DMF (0.5 mL), and **9** (50.5 mg, 0.2 mmol)/DMF (0.5 mL) under argon. The mixture was stirred at rt for 3 h as monitored by TLC. Upon completion, the resulting mixture was quenched with HCl (1 M, 5 mL), extracted with DCM (20 mL × 3), dried over $NaSO_4$, filtered, and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford **10**[11] (31.3 mg, 70%) as a solid: m.p. 50.2-51.2 °C (Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 2 H, Ar-H), 7.40-7.22 (m, 8 H, Ar-H), 5.41 (d, *J* = 0.4 Hz, 1 H, one proton of =CH_2), 5.16 (s, 1 H, one proton of =CH_2), 4.75-4.68 (m, 1 H, OCH), 3.00 (dd, J_1 = 14.2 Hz, J_2 = 3.4 Hz, 1 H, one proton of =CCH_2), 2.85 (dd, J_1 = 14.2 Hz, J_2 = 9.0 Hz , 1 H, one proton of =CCH_2), 2.07 (q, *J* = 2.1 Hz, 1 H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 143.9, 140.2, 128.5, 128.4, 127.8, 127.5, 126.3, 125.8, 115.8, 72.0, 45.9; IR (neat, cm^{-1}): 3280, 1629, 1494, 1447, 1354, 1322, 1199, 1050, 1029, 1009; MS (ESI) 207 (M^+-OH).

(6) Synthesis of 2-hexyl-2,3,6,7-tetrahydro 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) oxepine (11) (ywm-12-176)



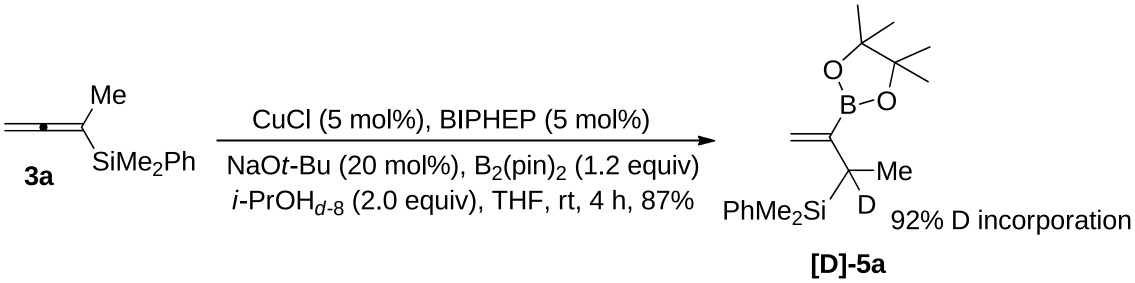
To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially **5p** (76.7 mg, 0.2 mmol), CH_2Cl_2 (2 mL), n-$C_6H_{13}CHO$ (25.9 mg, 0.22 mmol), and CH_2Cl_2 (2 mL) under argon. The resulting mixture was cooled to -78 °C and TMSOTf (43 μL, d = 1.15 g/cm^3, 48.9 mg, 0.22 mmol) was added dropwise for 5 min. The resulting mixture was stirred for an additional 55 min at -78 °C and quenched with a saturated aqueous solution of $NaHCO_3$ (3 mL). The organic phase was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1 to 30/1) to afford **11**[10] (50.4 mg, 85%) as a liquid[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79-6.73 (m, 1 H, =CH), 4.10-3.90 (dt, J_1 = 12.4 Hz, J_2 = 3.8 Hz, 1 H, OCH), 3.44-3.35 (m, 1 H, one proton of CH_2), 3.33-3.24 (m, 1 H, one proton of CH_2), 2.58-2.44 (m, 2 H, OCH_2), 2.36-2.25 (m, 2 H, CH_2), 1.57-1.39 (m, 3 H, one proton of CH_2 and =CCH_2), 1.36-1.19 (m, 19 H, one proton of CH_2 and 3 × CH_2 and B(pin)), 0.88 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 83.4, 80.2, 68.5, 38.1, 36.9, 34.1, 31.8, 29.3, 25.9, 24.8, 22.6, 14.1; IR (neat, cm^{-1}): 2930, 2856, 1632, 1467, 1326, 1304, 1147, 1052; MS (70 ev, EI) m/z (%): 308 (M^+(^{11}B), 12.83), 307 [M^+(^{10}B), 3.45], 194 (100).

(7) Synthesis of 2-hexyl-4-phenyl-2,3,6,7-tetrahydrooxepine (12) (ywm-12-194)



To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially $Pd(PPh_3)_4$ (11.9 mg, 0.01 mmol), Na_2CO_3 (64.5 mg, 0.6 mmol), **11** (61.5 mg, 0.2 mmol), 1,4-dioxane (1 mL), PhI (48.6 mg, 0.24 mmol), and H_2O (1 mL). The resulting mixture was stirred at 80 °C for 5 h as monitored by TLC. Upon completion, Et_2O (5 mL) was added. The organic phase was separated and the aqueous layer was extracted with Et_2O (5 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) to afford **12** (43.3 mg, 84%) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.19 (m, 5 H, Ar-H), 6.14-6.06 (m, 1 H, =CH), 4.09-4.00 (m, 1 H, OCH), 3.59-3.43 (m, 2 H, OCH_2), 2.89-2.78 (m, 1 H, one proton of CH_2), 2.69-2.54 (m, 2 H, CH_2), 2.39-2.25 (m, 1 H, one proton of CH_2), 1.66-1.54 (m, 1 H, one proton of CH_2), 1.52-1.20 (m, 9 H, one proton of CH_2 and 4 × CH_2), 0.88 (t, J = 6.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 142.8, 128.9, 128.2, 126.6, 125.7, 79.0, 69.1, 41.5, 37.1, 31.9, 31.8, 29.3, 25.9, 22.6, 14.1; IR (neat, cm^{-1}): 2928, 2855, 1598, 1492, 1456, 1377, 1110; MS (70 ev, EI) m/z (%): 258 (M^+, 7.44), 129 (100); HRMS Calcd for $C_{18}H_{26}O$ (M^+): 258.1984, Found: 258.1981.

5. Synthesis of (2-Deutero-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-but-3-en-2-yl) dimethyl(phenyl)silane ([D]-5a) (sl-6-144)



To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.1 mg, 0.05 mmol), NaO*t*-Bu (19.3 mg, 0.2 mmol), bis(pinacolato)diboron (304.9 mg, 1.2 mmol)/THF (2 mL), **3a** (188.4 mg, 1.0 mmol)/THF (1 mL), and *i*-PrOH$_{d\text{-}8}$ (136.3 mg, 2.0 mmol) under argon. The resulting mixture was stirred at rt for 4 h as monitored by TLC. Upon completion, the resulting mixture was filtered through a short column of silica gel eluted with Et$_2$O (10 mL × 3) and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl ether = 70/1) to afford **[D]-5a** (275.5 mg, 87%) as a liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53-7.46 (m, 2 H, Ar-H), 7.36-7.28 (m, 3 H, Ar-H), 5.78 (d, *J* = 2.4 Hz, 1 H, one proton of =CH$_2$), 5.36 (d, *J* = 2.8 Hz, 1 H, one proton of =CH$_2$), 1.20 (s, 6 H, B(pin)), 1.18 (s, 6 H, B(pin)), 1.08 (s, 3 H, CH$_3$), 0.24 (s, 6 H, SiMe$_2$), the following signal is discernible for **5a**: 2.19 (q, *J* = 7.5 Hz, 0.08 H, =CCH); ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.3, 134.2, 128.7, 127.4, 125.5, 83.3, 25.7 (t, *J* = 18.8 Hz), 24.9, 24.7, 14.4, -4.1, -5.6, the following signal is discernible for **5a:** 26.2, 14.5; IR (neat, cm^{-1}): 1596, 1426, 1388, 1372, 1356, 1306, 1247, 1213, 1187, 1165, 1143, 1110; MS (ESI) m/z 341 [M$^+$(^{11}B)+Na+H], 340 [M$^+$(^{11}B)+Na] or [M$^+$(^{10}B)+Na+H], 319 [M$^+$(^{11}B)+H], 318 [M$^+$(^{11}B)] or 318 [M$^+$(^{10}B)+H], 317 [M$^+$(^{10}B)]; HRMS Calcd for C$_{18}$H$_{32}$D^{11}BNO$_2$Si (M$^+$+NH$_4$): 335.2436, Found: 335.2432.

References:

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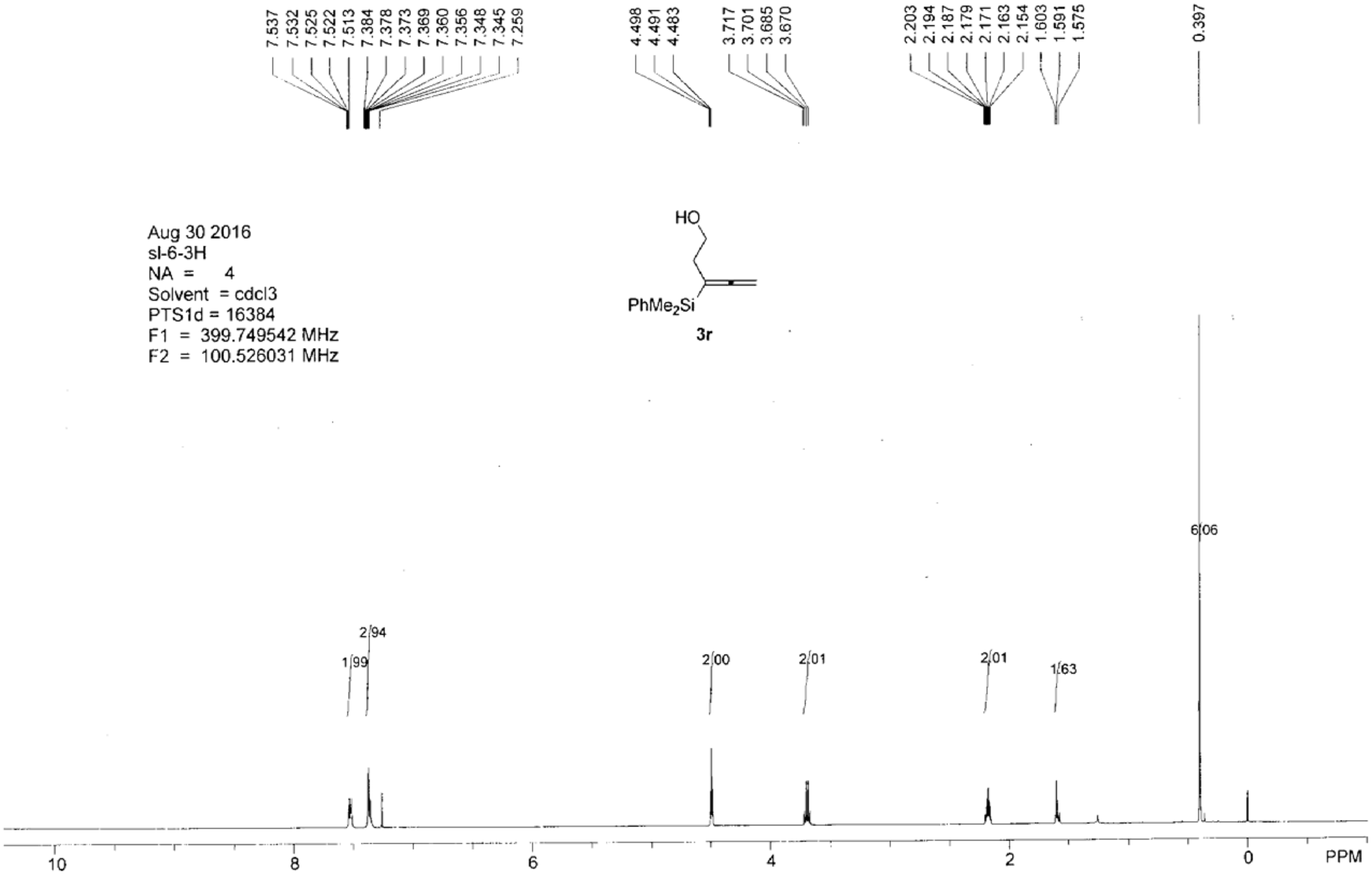

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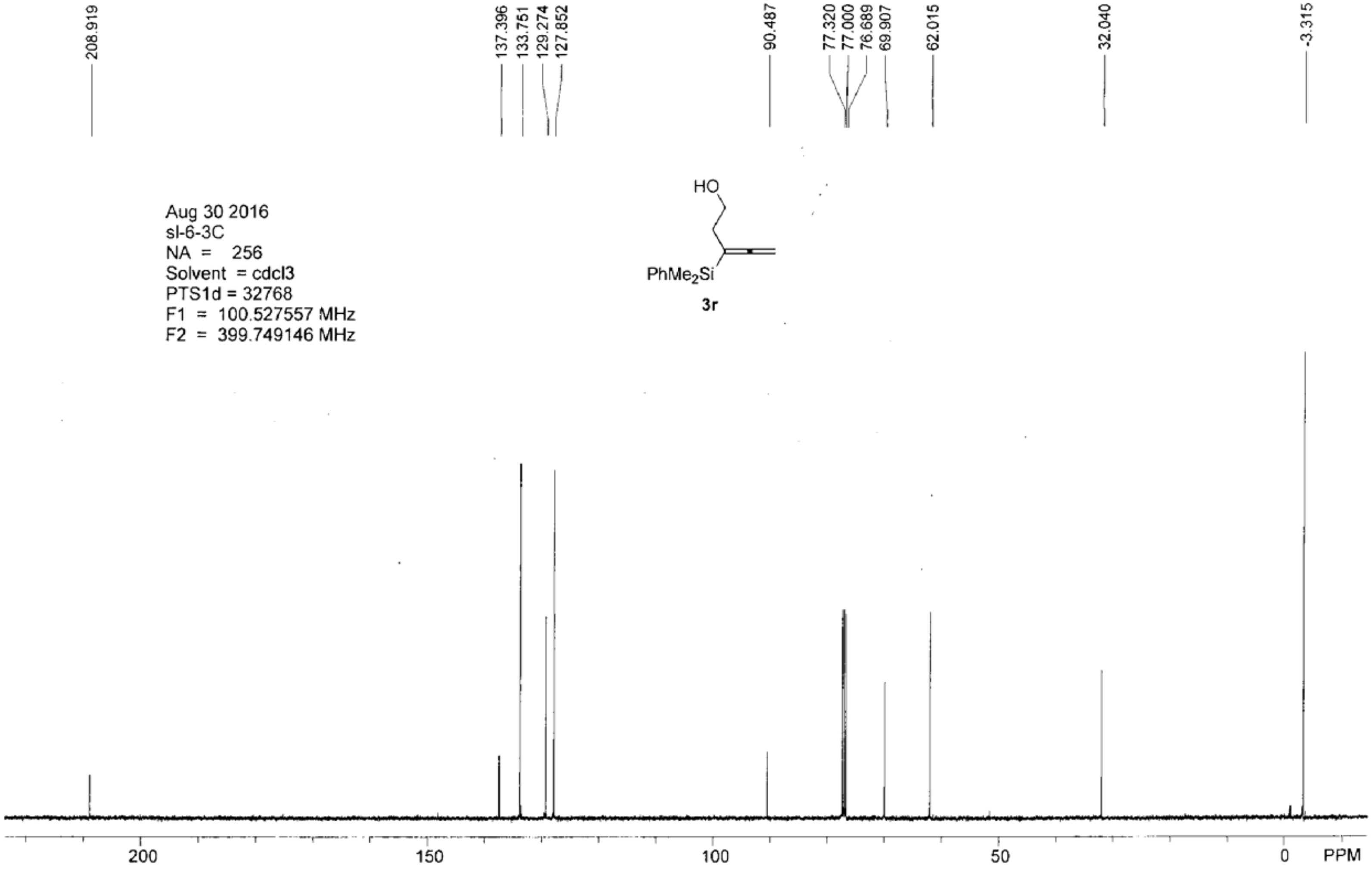

3r

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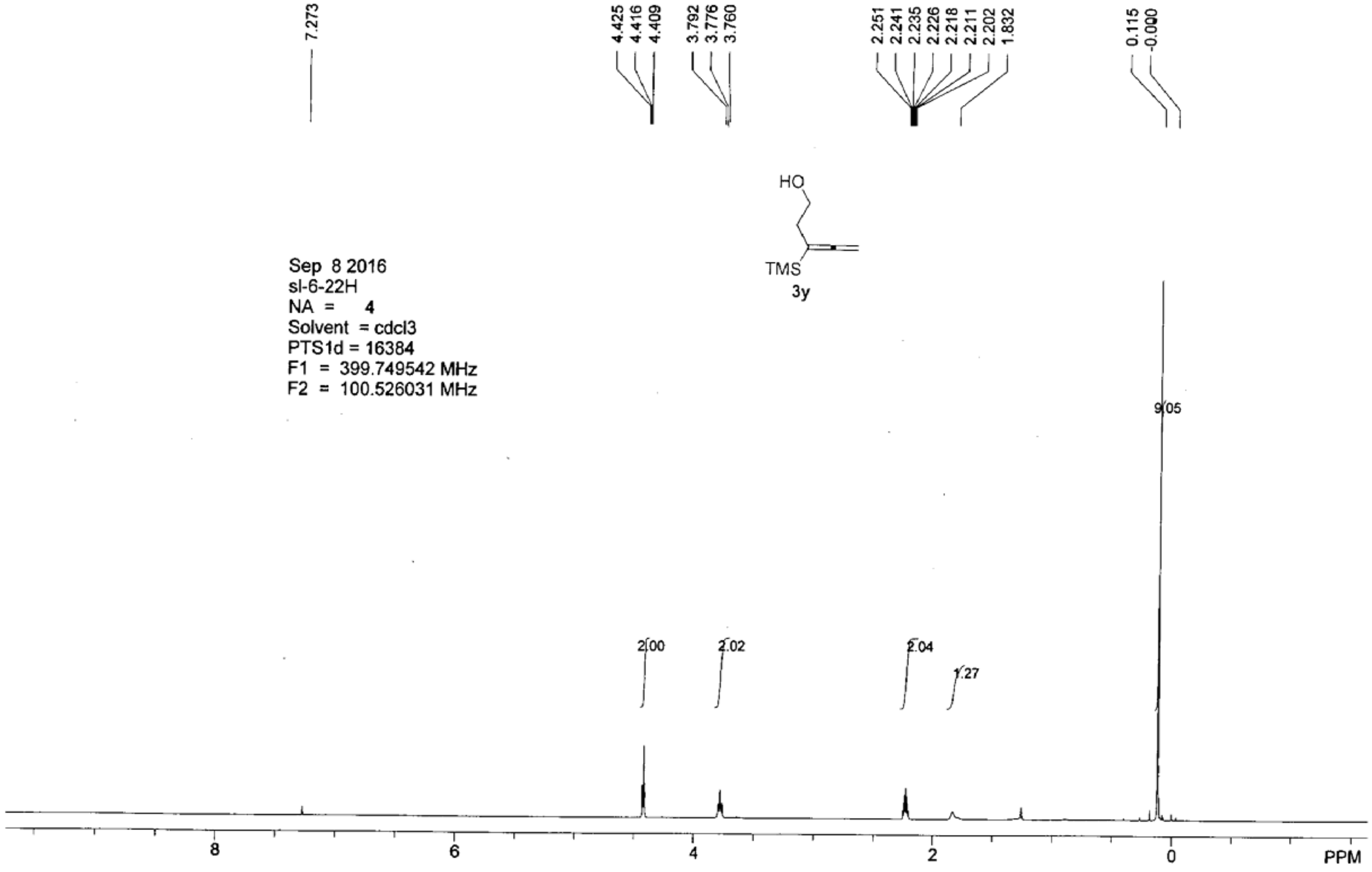
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Sep 8 2016
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4
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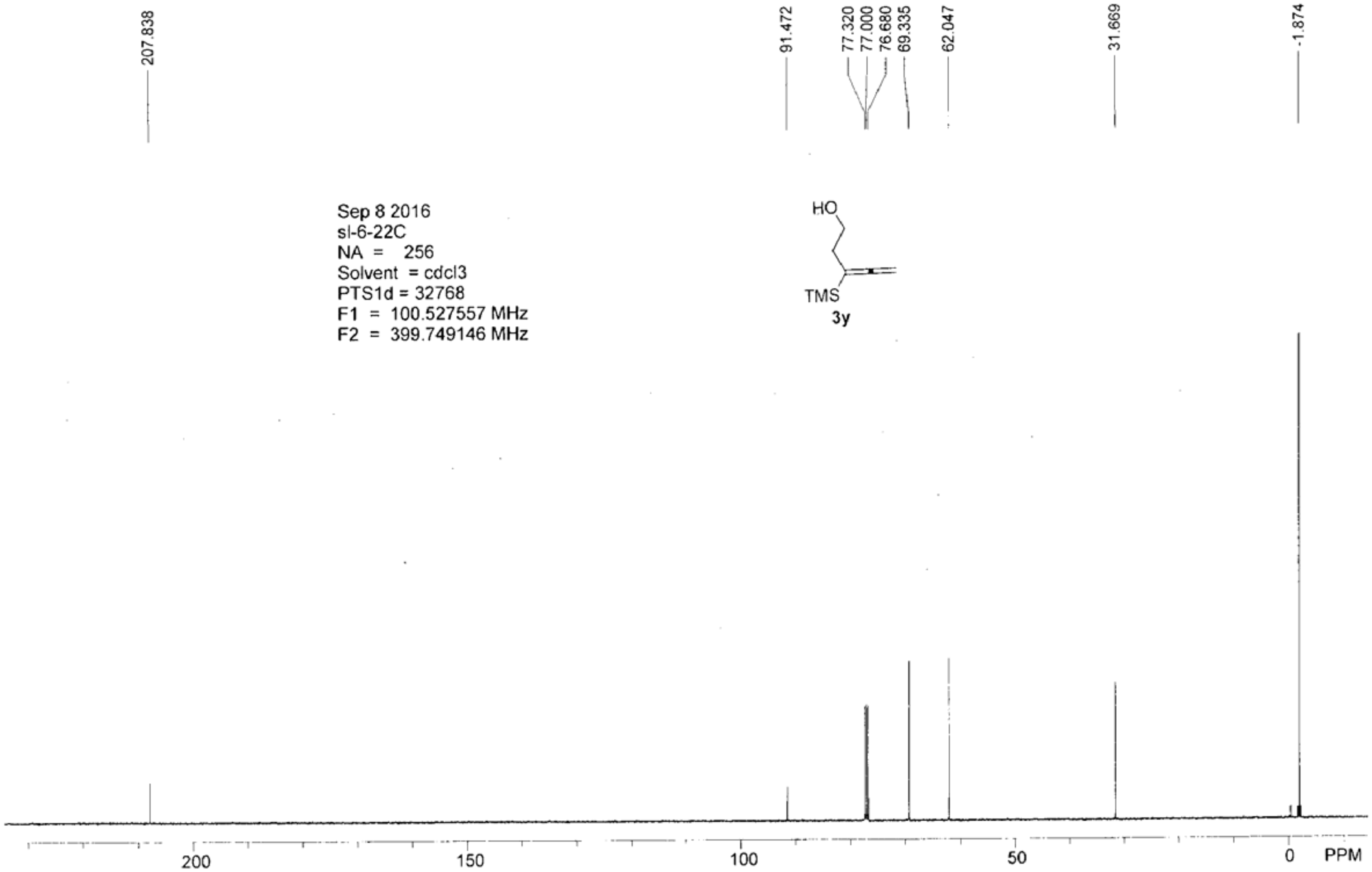
PPM



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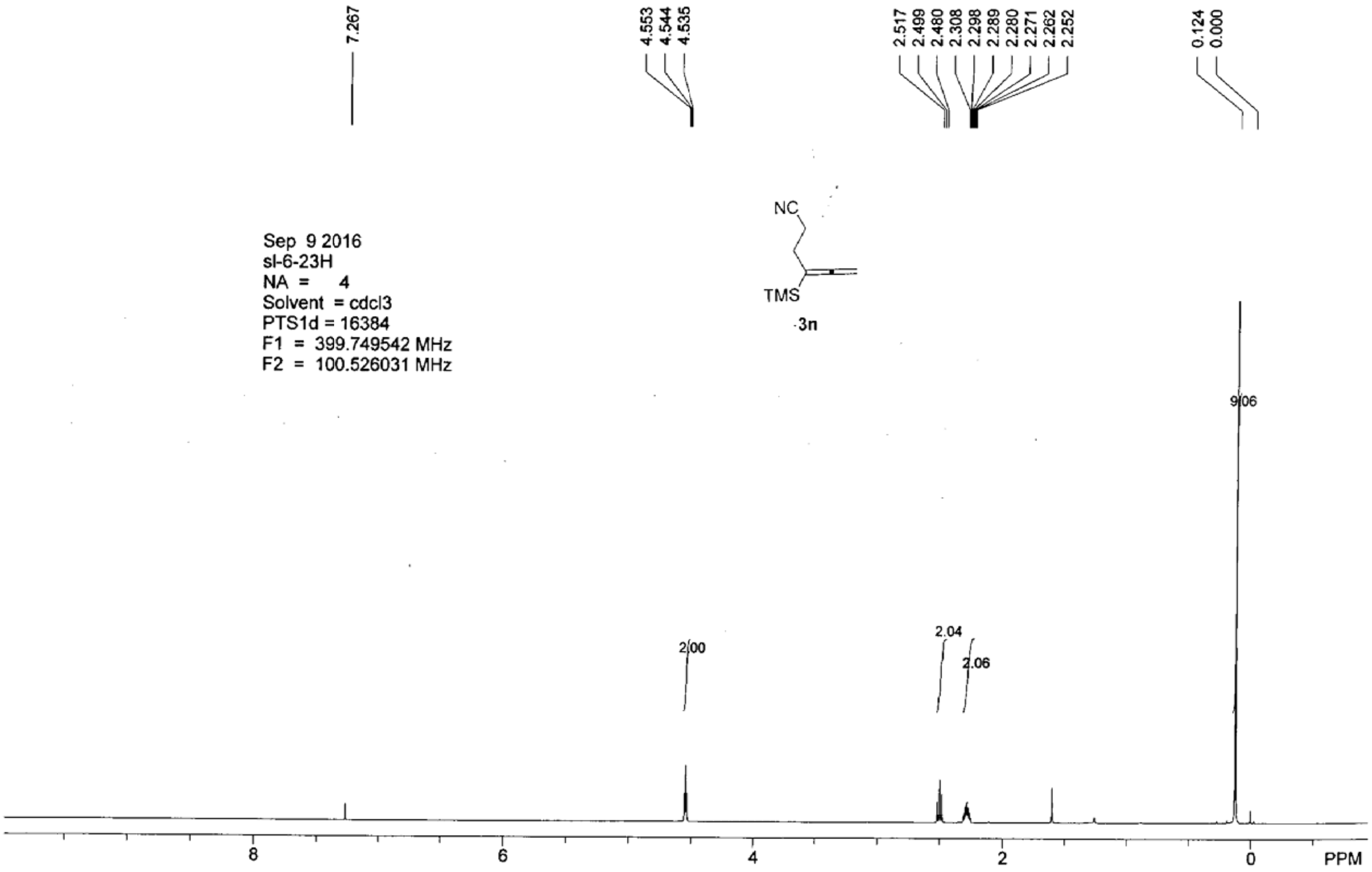
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Sep 9 2016
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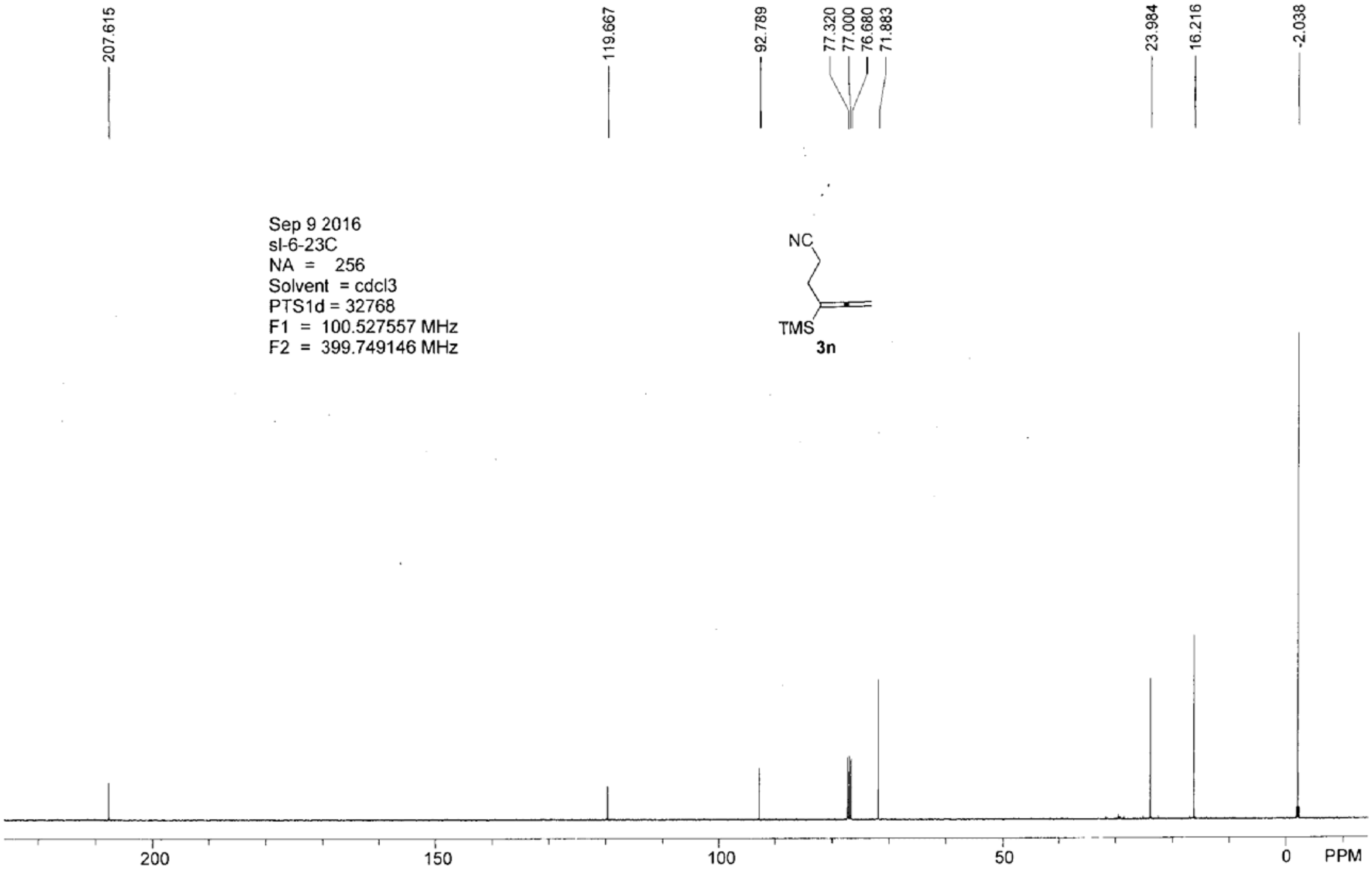
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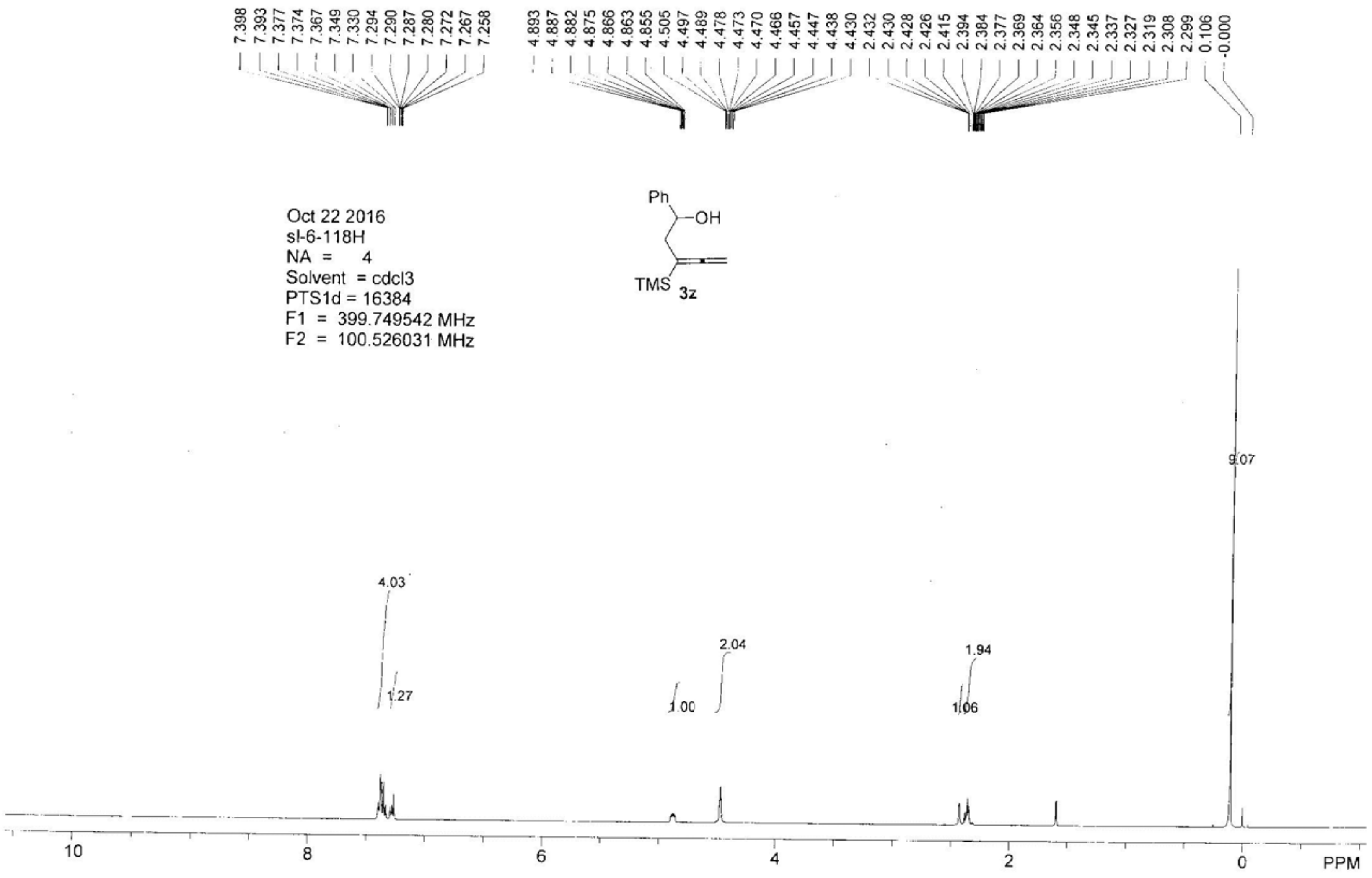

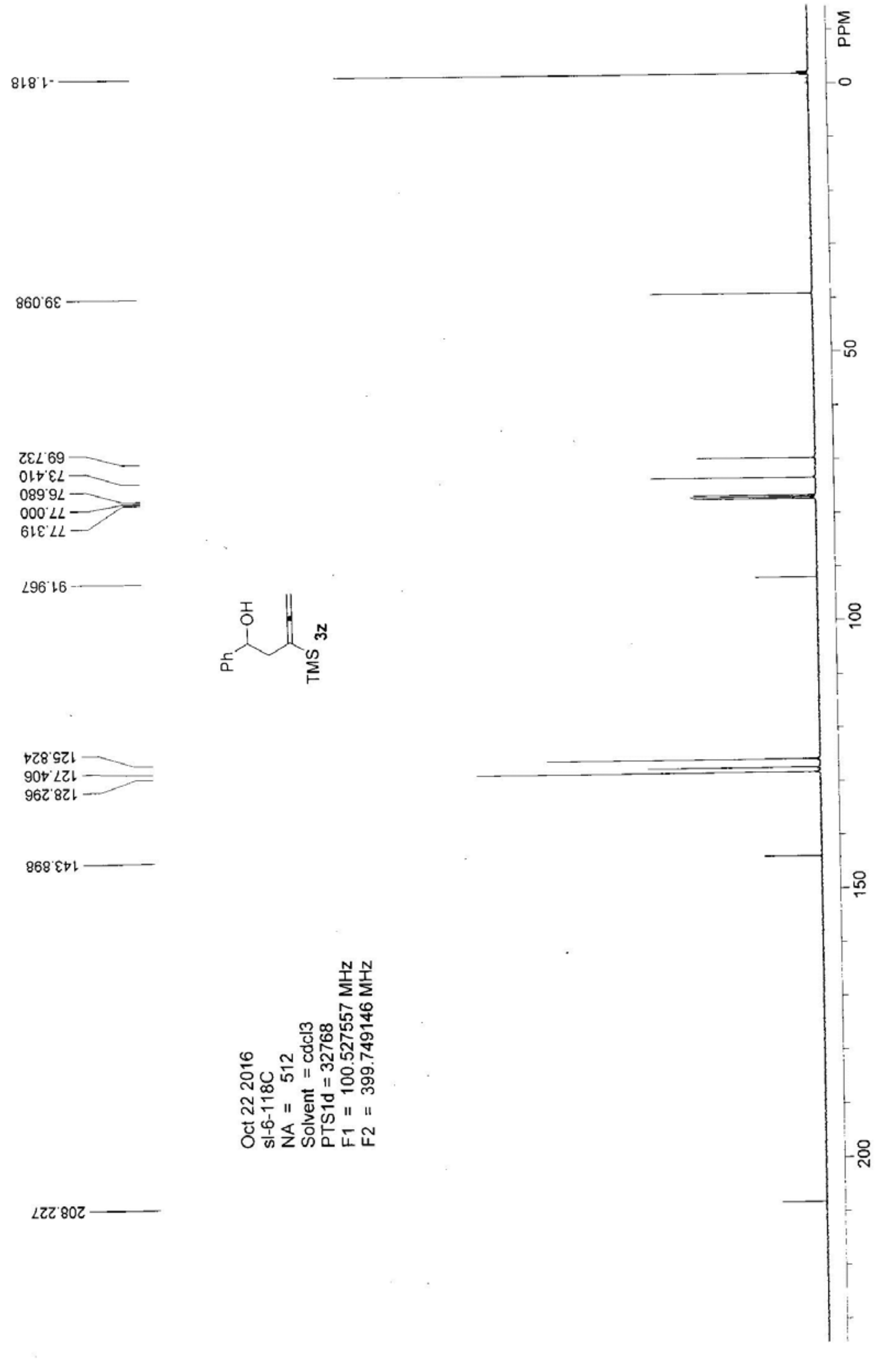
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Oct 22 2016
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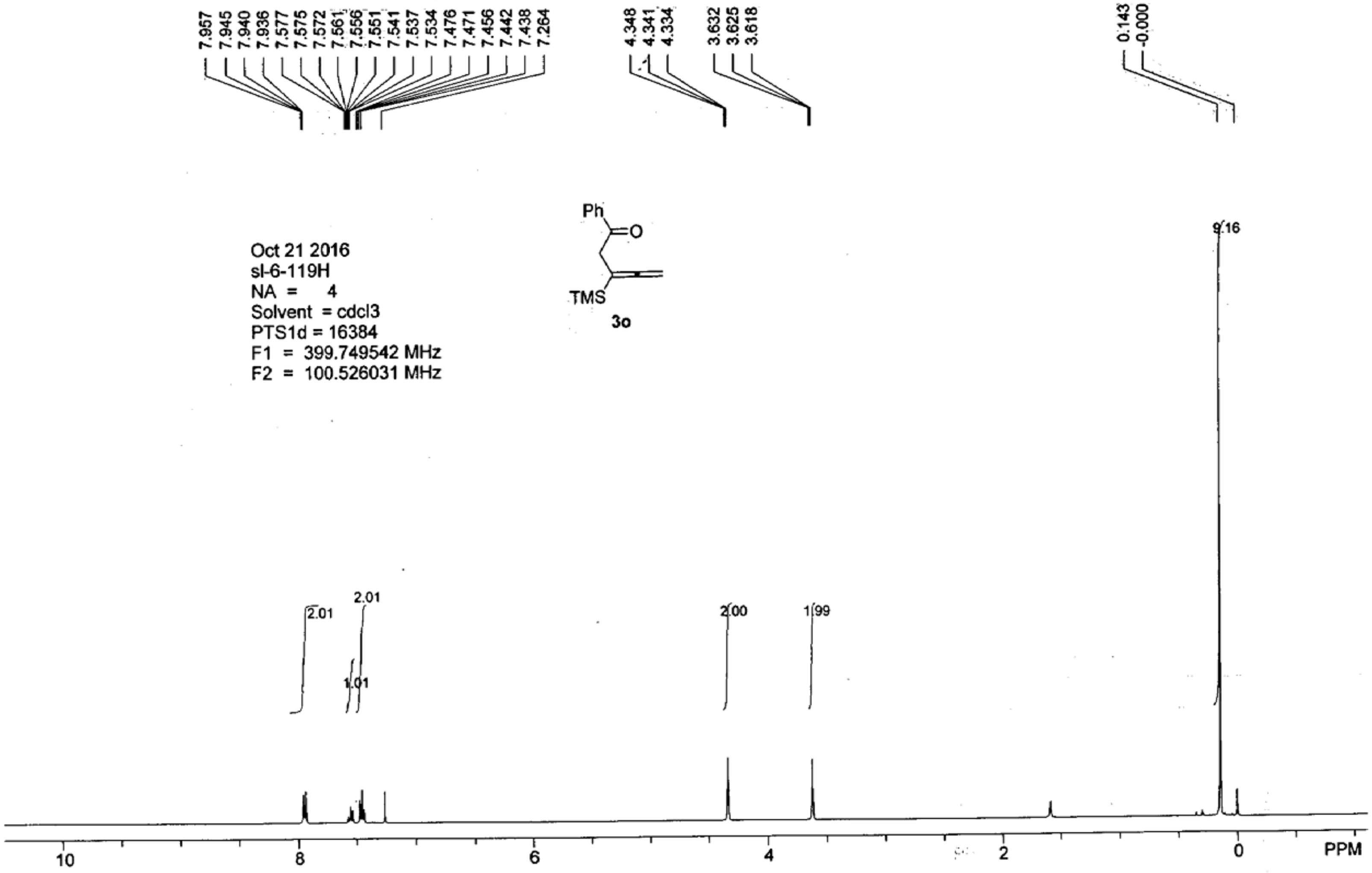
150
200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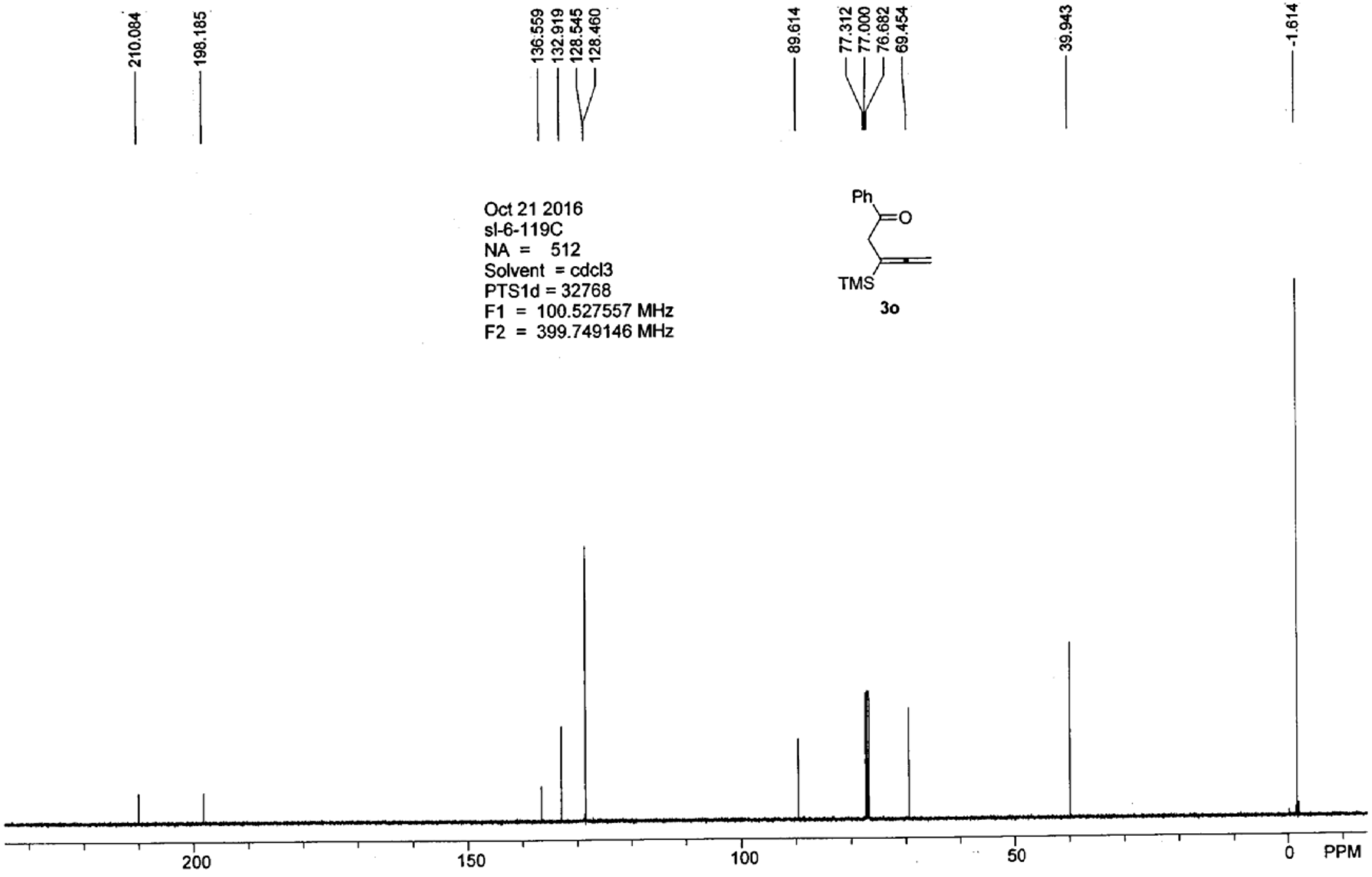

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Oct 21 2016
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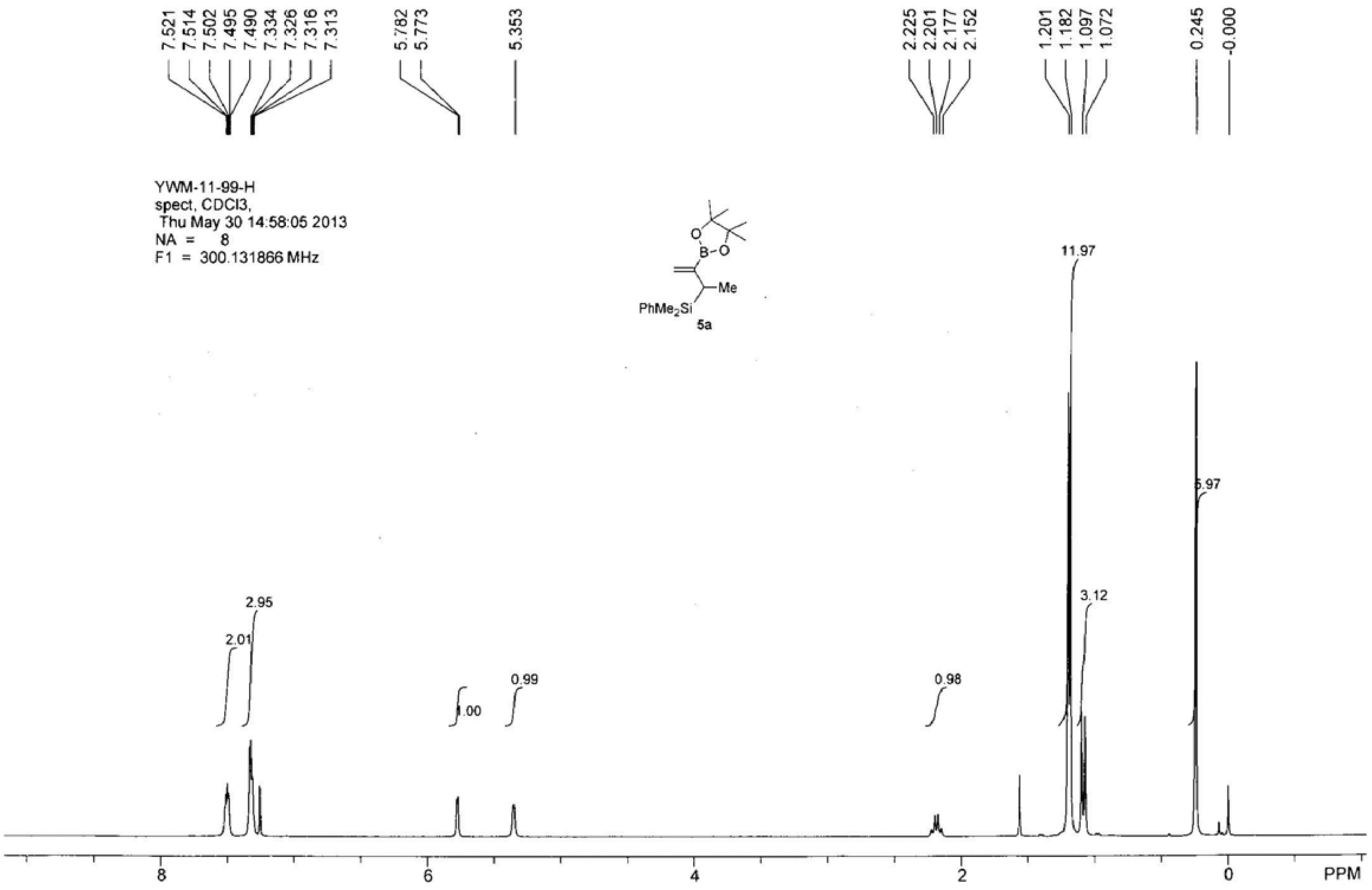
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Thu May 30 14:58:05 2013
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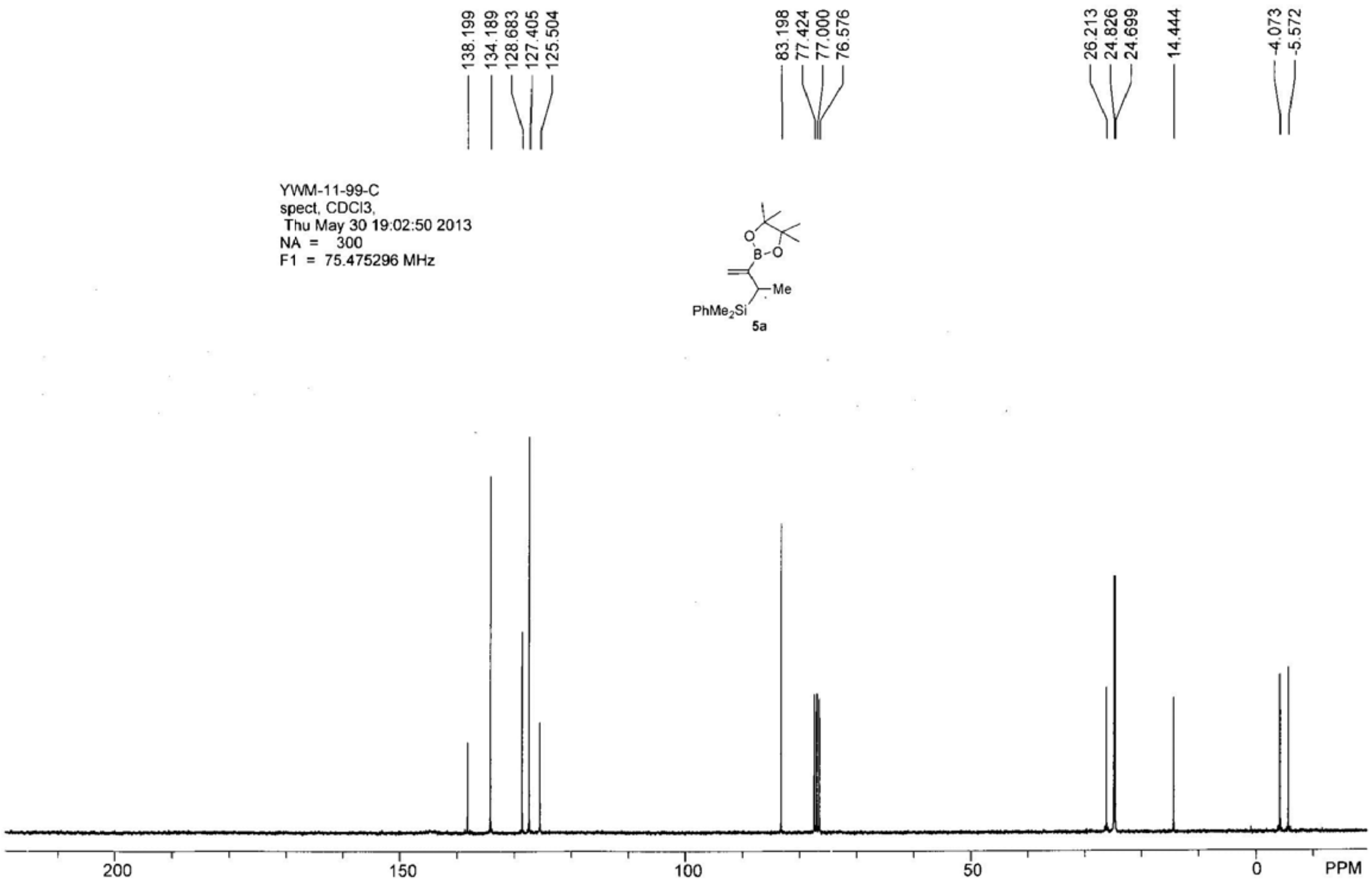
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Thu May 30 19:02:50 2013
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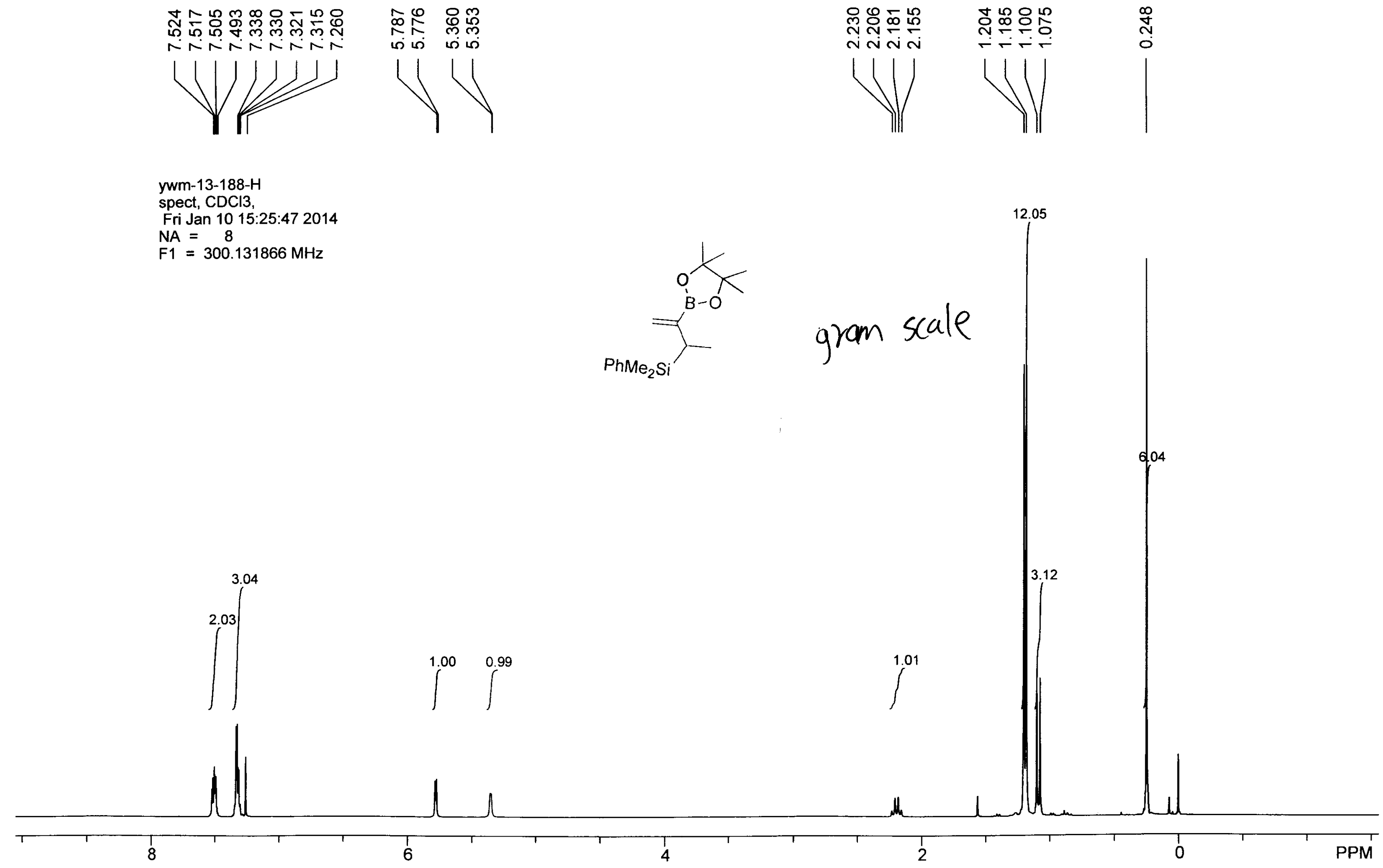

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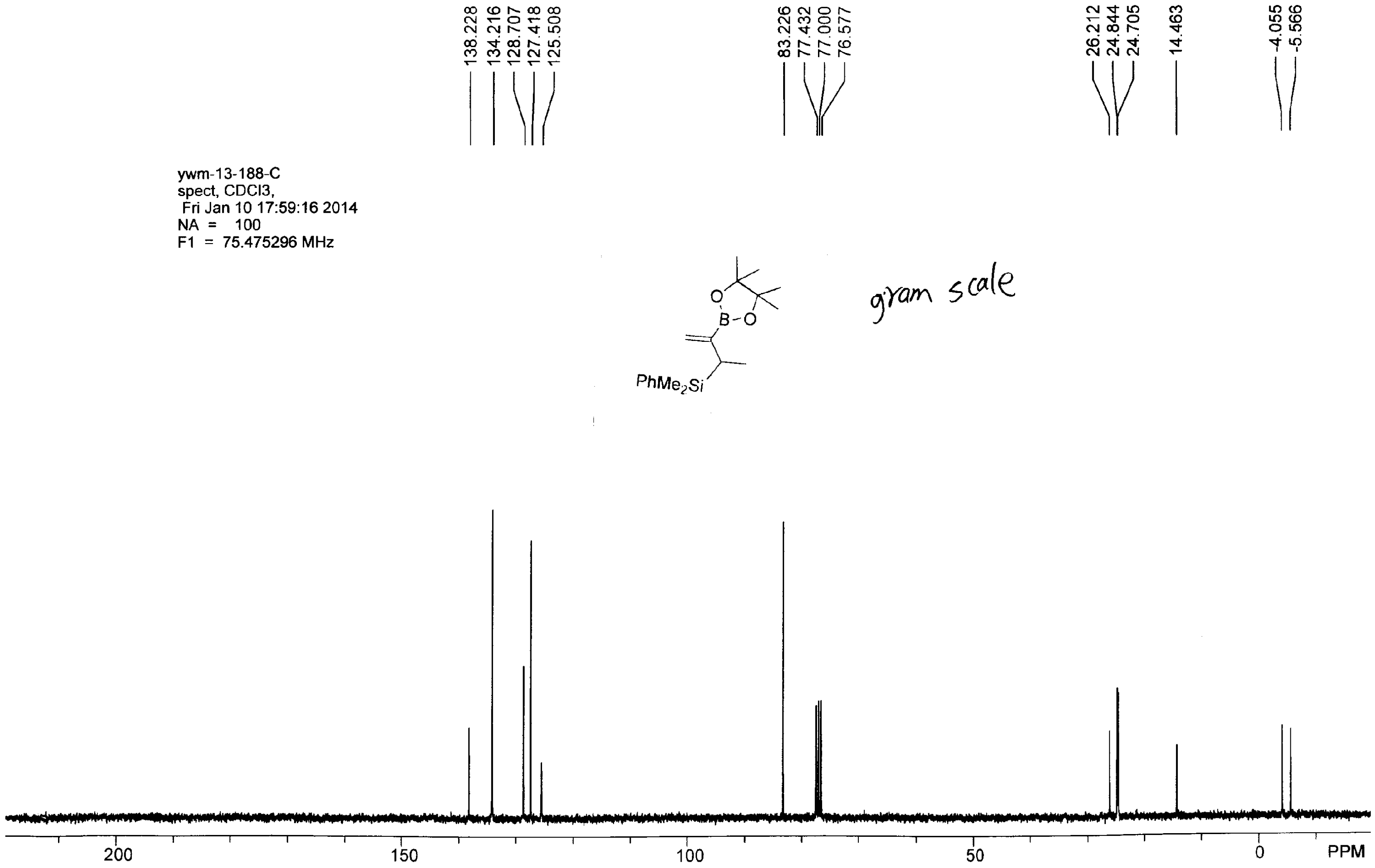
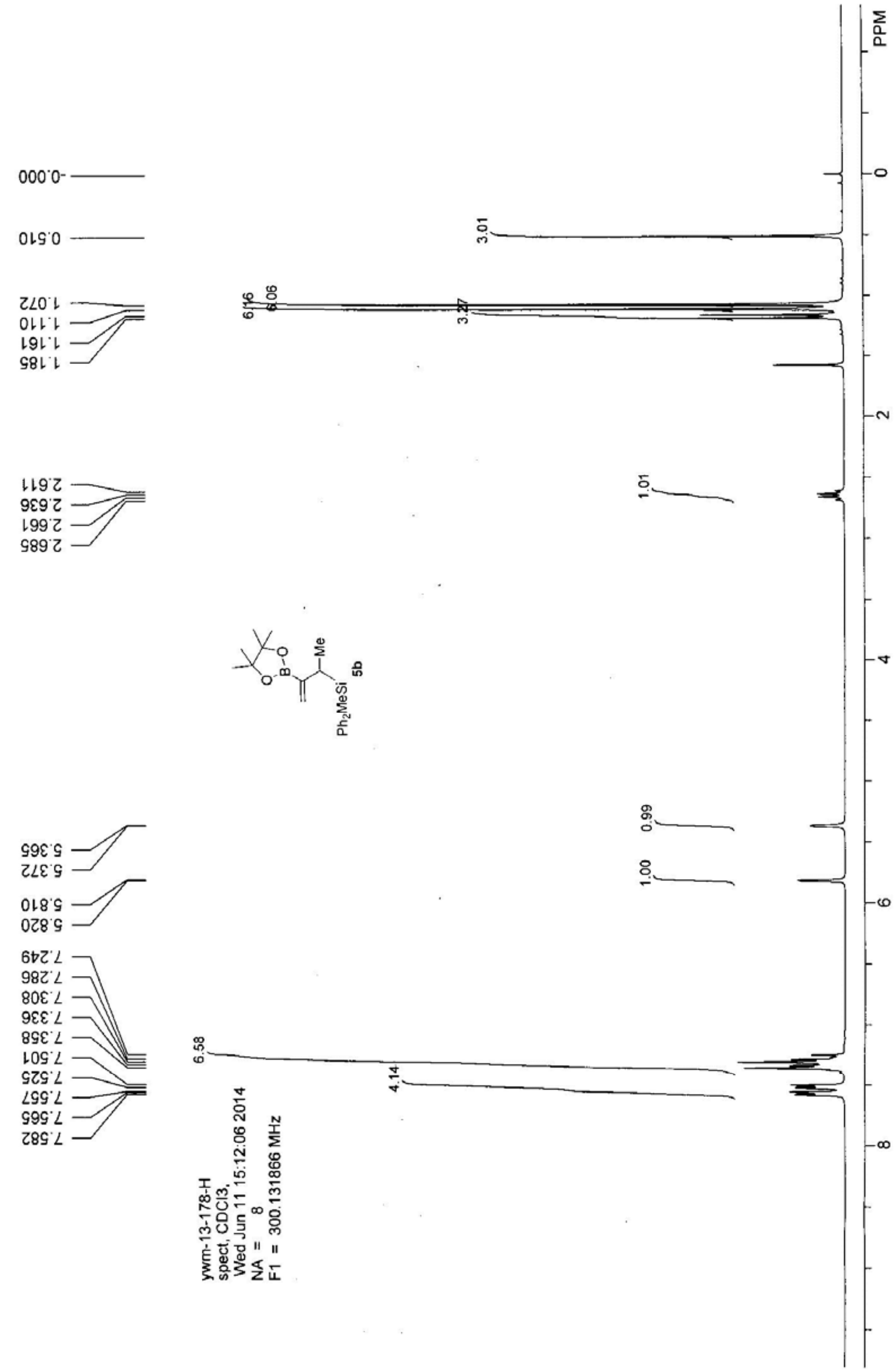
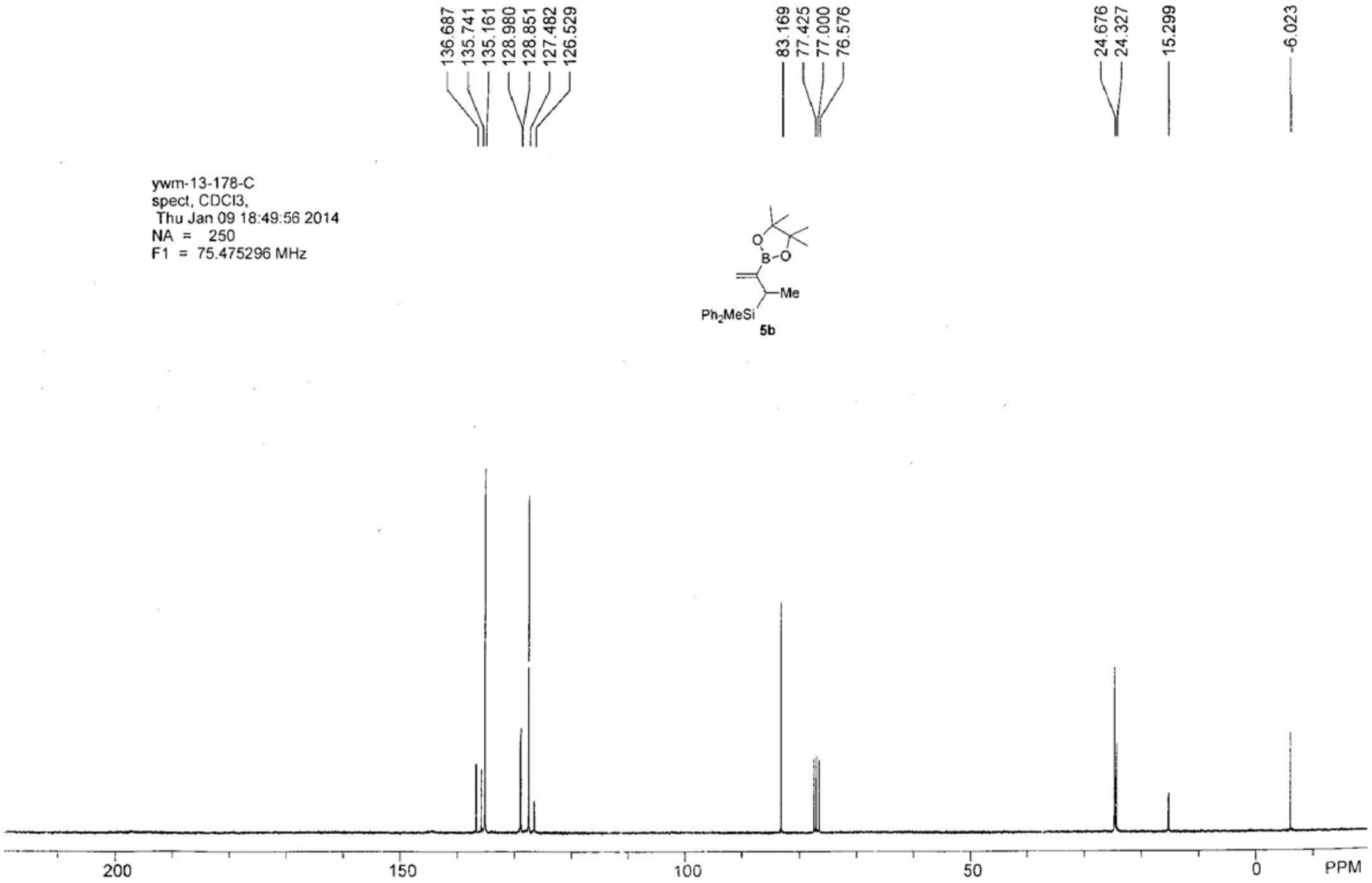
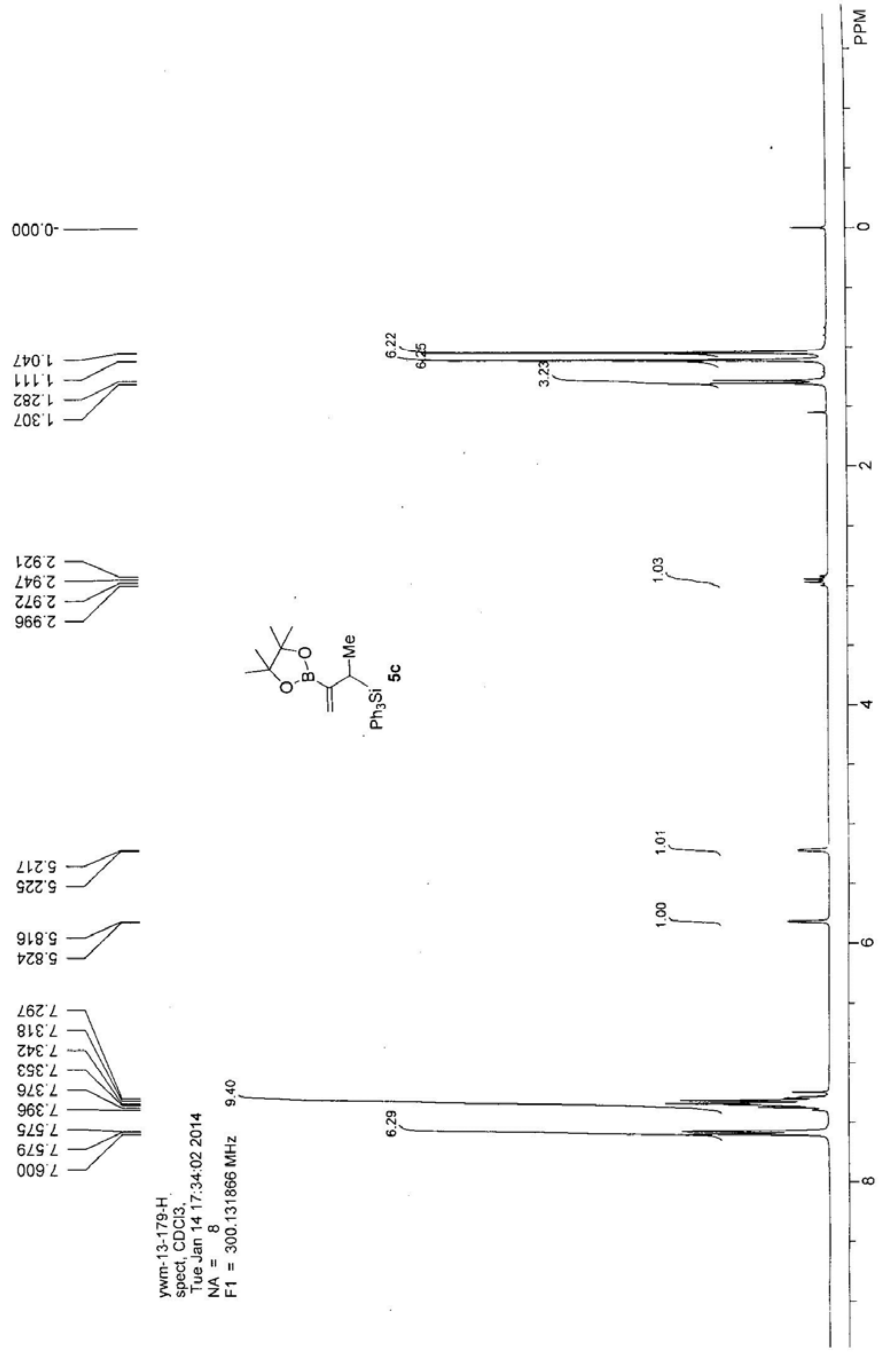
F1 = 300.131866 MHz

gram scale

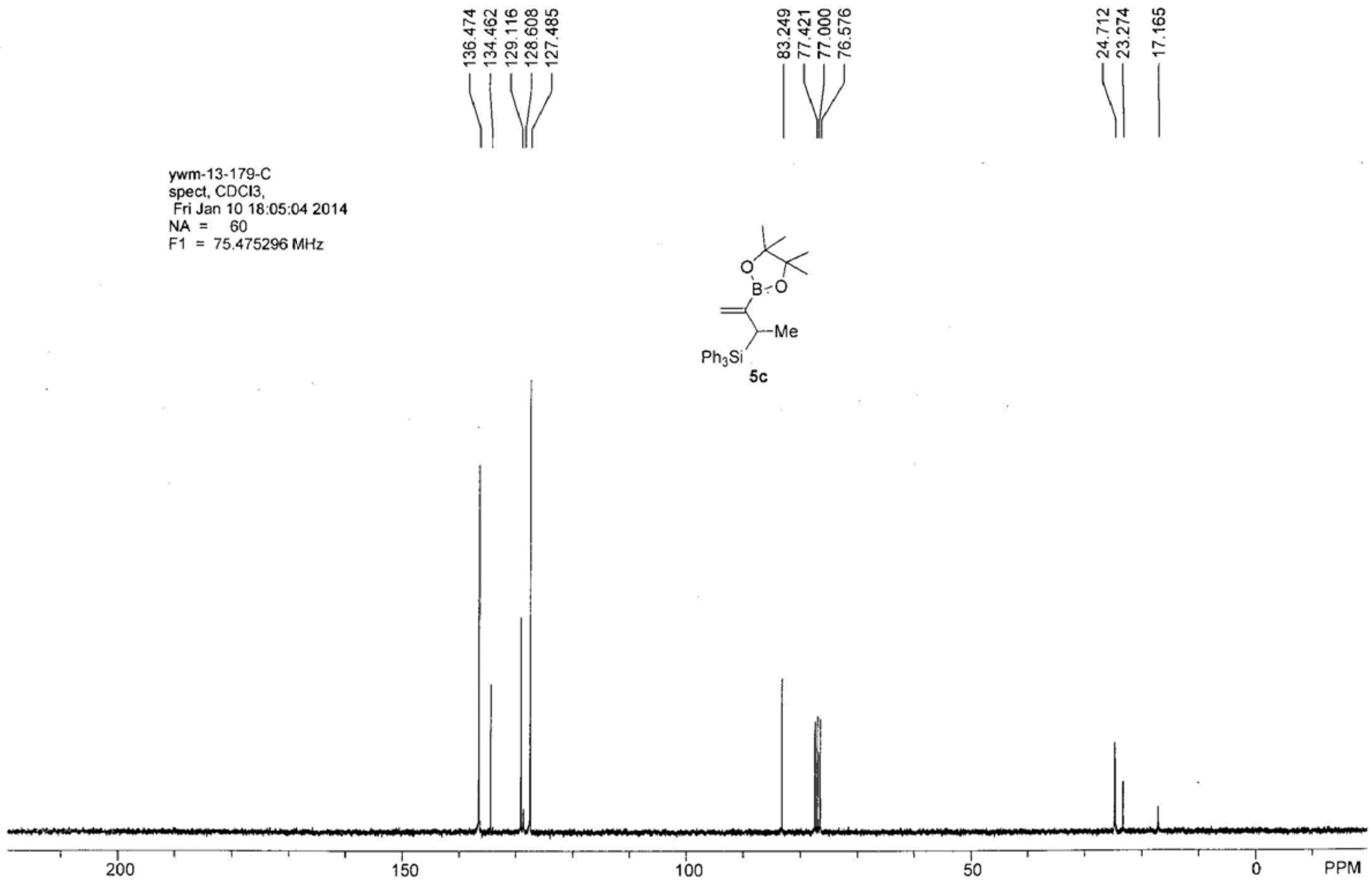

138.228
134.216
128.707
127.418
125.508
83.226
77.432
77.000
76.577
26.212
24.844
24.705
14.463
-4.055
-5.566
ywm-13-188-C
spect, CDCl3,
Fri Jan 10 17:59:16 2014
NA = 100
F1 = 75.475296 MHz
O
B
O
PhMe$_2$Si
gram scale
200
150
100
50
0
PPM

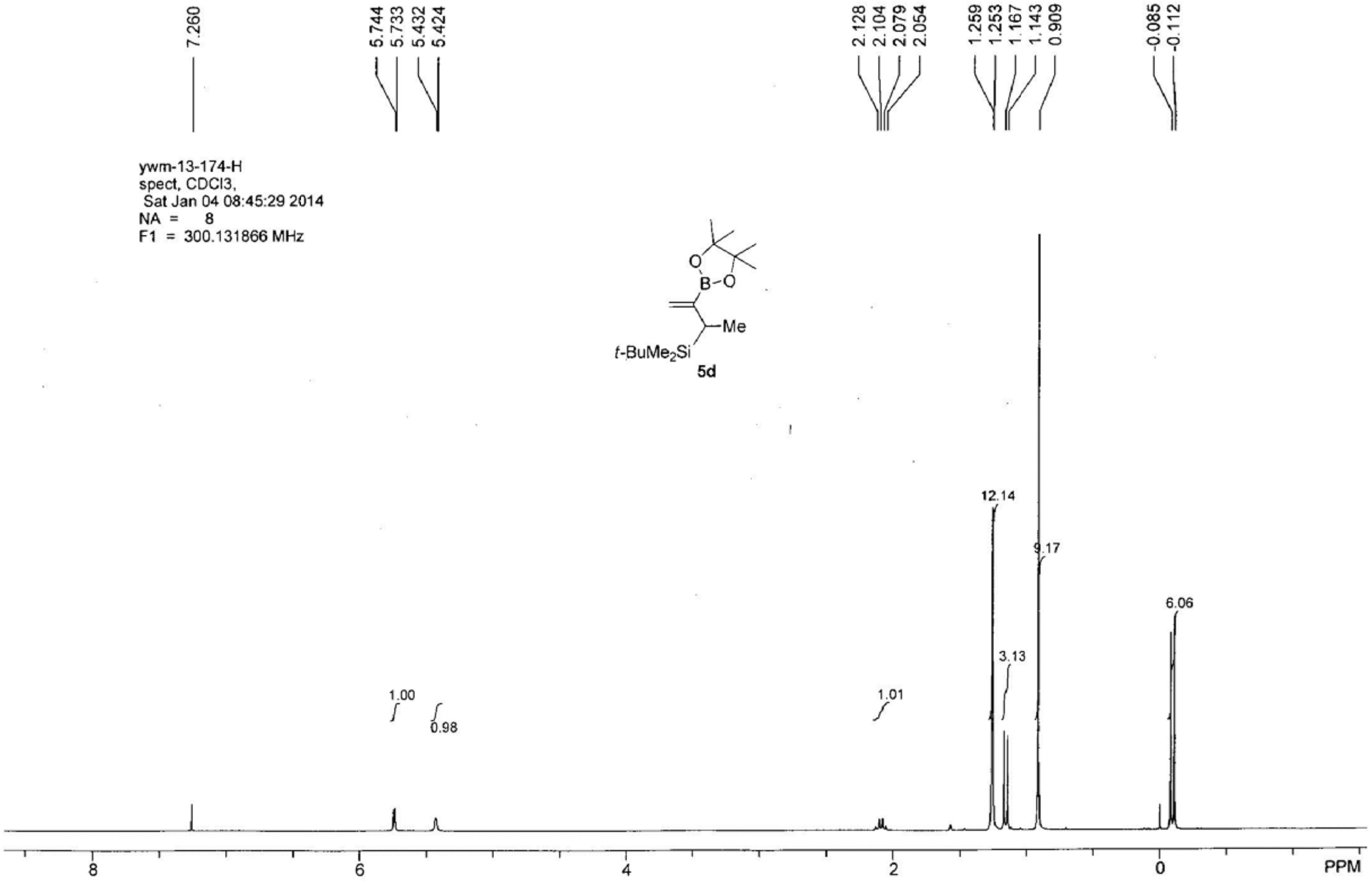
ywm-13-178-H
spect, CDCl3,
Wed Jun 11 15:12:06 2014
NA = 8
F1 = 300.131866 MHz
7.582
7.566
7.557
7.525
7.501
7.358
7.336
7.308
7.286
7.249
5.820
5.810
5.372
5.365
2.685
2.661
2.636
2.611
1.185
1.161
1.110
1.072
0.510
-0.000
6.58
4.14
1.00
0.99
1.01
6.16
6.06
3.27
3.01
Ph2MeSi
Me
B
O
O
5b
8
6
4
2
0
PPM

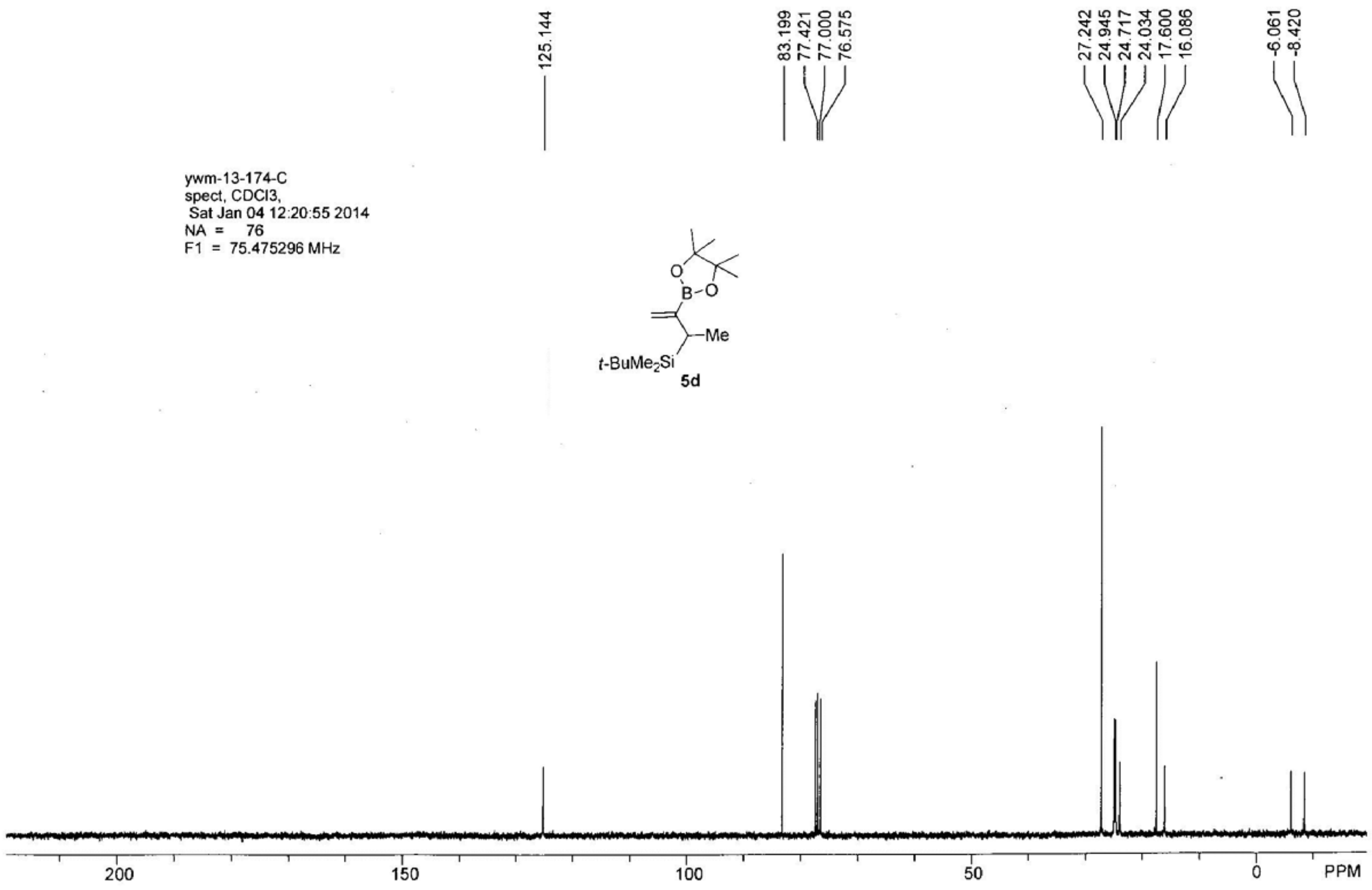

136.687
135.741
135.161
128.980
128.851
127.482
126.529
83.169
77.425
77.000
76.576
24.676
24.327
15.299
-6.023
ywm-13-178-C
spect, CDCl3,
Thu Jan 09 18:49:56 2014
NA = 250
F1 = 75.475296 MHz
Ph$_2$MeSi
Me
B
O
O
5b
200
150
100
50
0
PPM


-0.000
1.047
1.111
1.282
1.307
2.921
2.947
2.972
2.996
5.217
5.225
5.816
5.824
7.297
7.318
7.342
7.353
7.376
7.396
7.575
7.579
7.600
6.22
6.25
3.23
1.03
1.01
1.00
9.40
6.29
Me
O
B
O
Ph3Si
ywm-13-179-H
spect, CDCl3,
Tue Jan 14 17:34:02 2014
NA = 8
F1 = 300.131866 MHz
PPM
0
2
4
6
8

5c

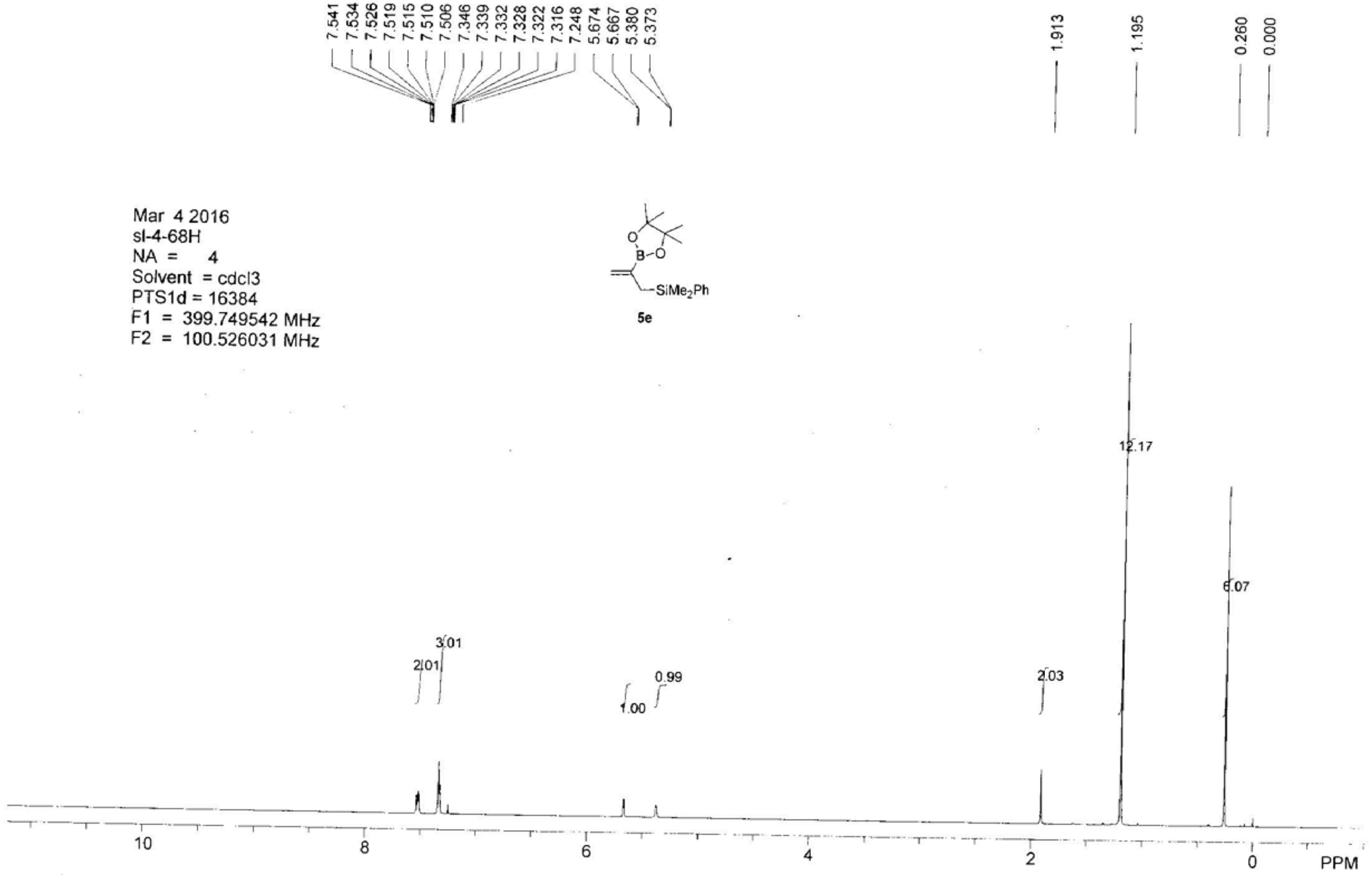

136.474
134.462
129.116
128.608
127.485
83.249
77.421
77.000
76.576
24.712
23.274
17.165
ywm-13-179-C
spect, CDCl3,
Fri Jan 10 18:05:04 2014
NA = 60
F1 = 75.475296 MHz
O
B
O
Me
Ph3Si
5c
200
150
100
50
0
PPM

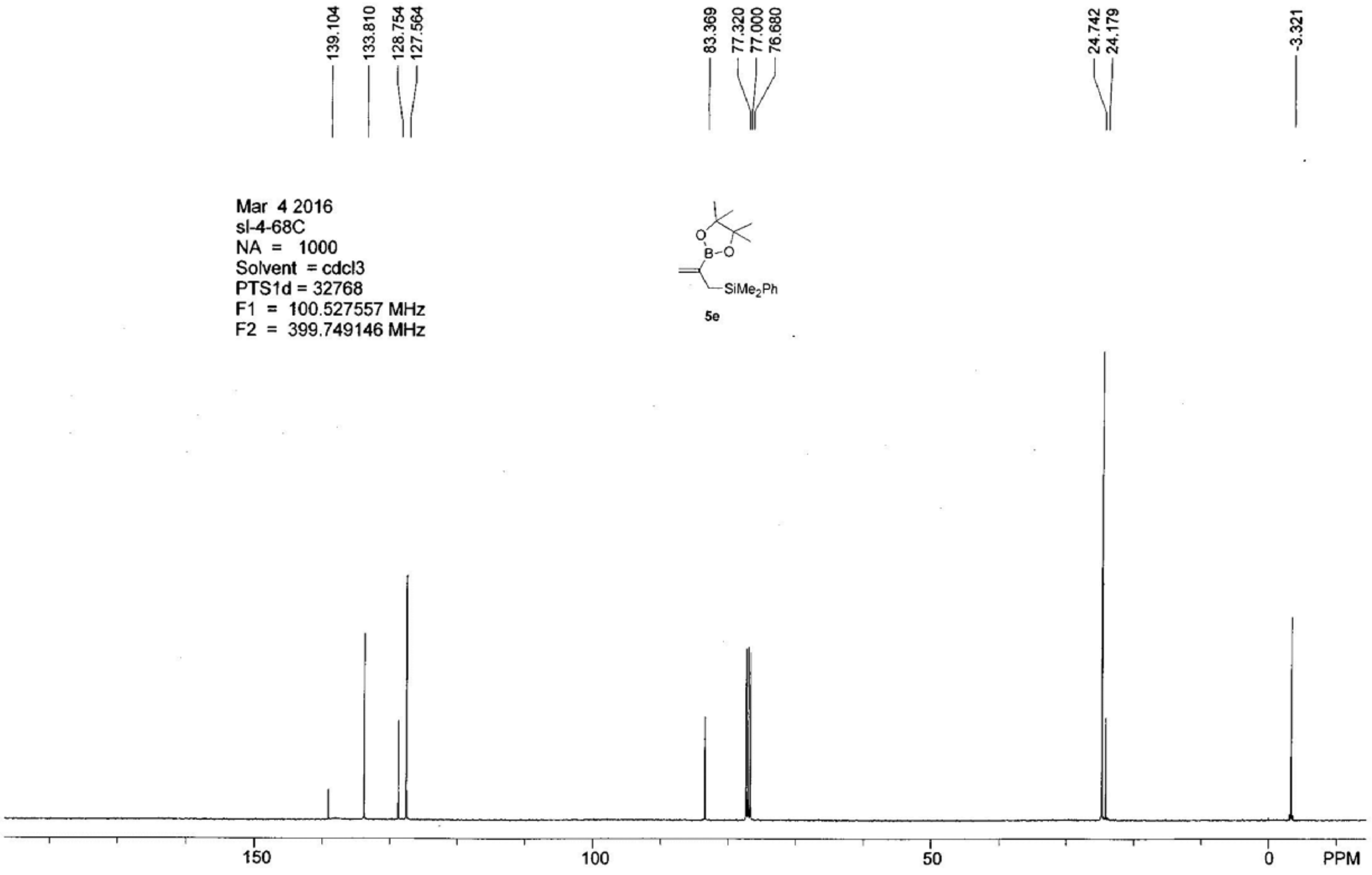

7.260
5.744
5.733
5.432
5.424
2.128
2.104
2.079
2.054
1.259
1.253
1.167
1.143
0.909
-0.085
-0.112
ywm-13-174-H
spect, CDCl3,
Sat Jan 04 08:45:29 2014
NA = 8
F1 = 300.131866 MHz
O
B-O
Me
t-BuMe2Si
5d
12.14
9.17
6.06
3.13
1.00
0.98
1.01
8
6
4
2
0
PPM



ywm-13-174-C
spect, CDCl3,
Sat Jan 04 12:20:55 2014
NA = 76
F1 = 75.475296 MHz

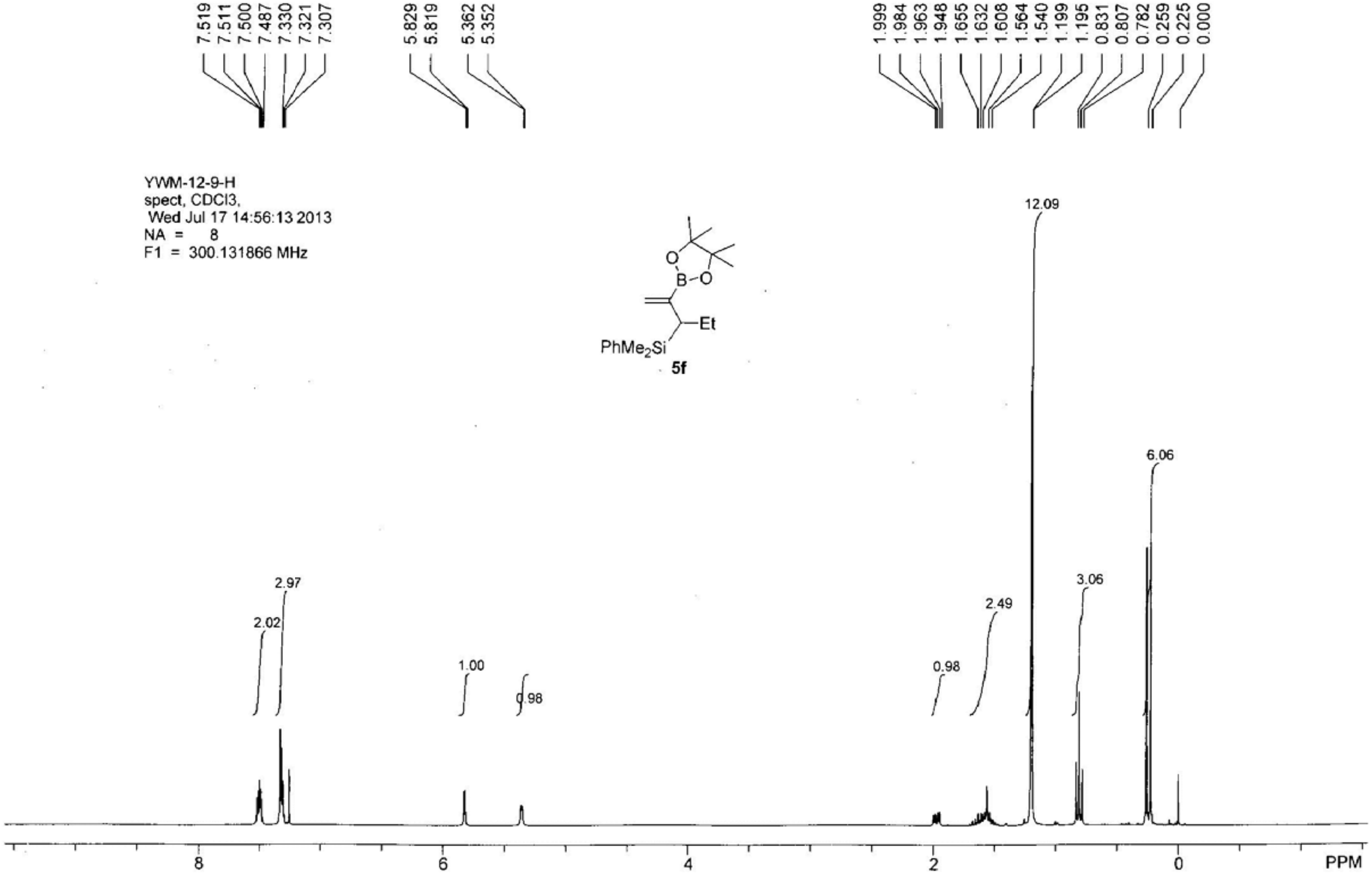
5d

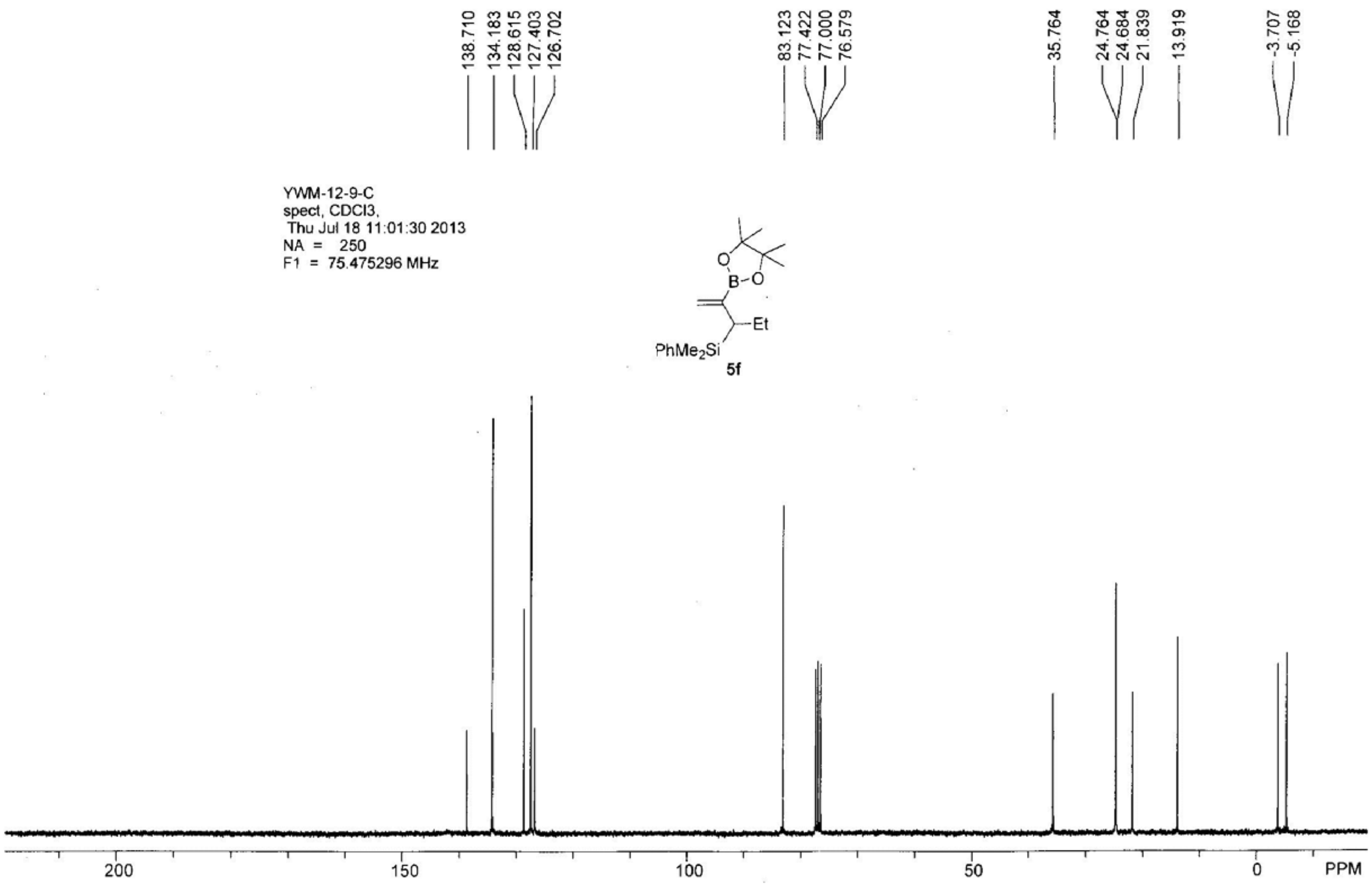

7.541
7.534
7.526
7.519
7.515
7.510
7.506
7.346
7.339
7.332
7.328
7.322
7.316
7.248
5.674
5.667
5.380
5.373
1.913
1.195
0.260
0.000
Mar 4 2016
sl-4-68H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
SiMe2Ph
5e
3.01
2.01
1.00
0.99
2.03
12.17
6.07
10
8
6
4
2
0
PPM

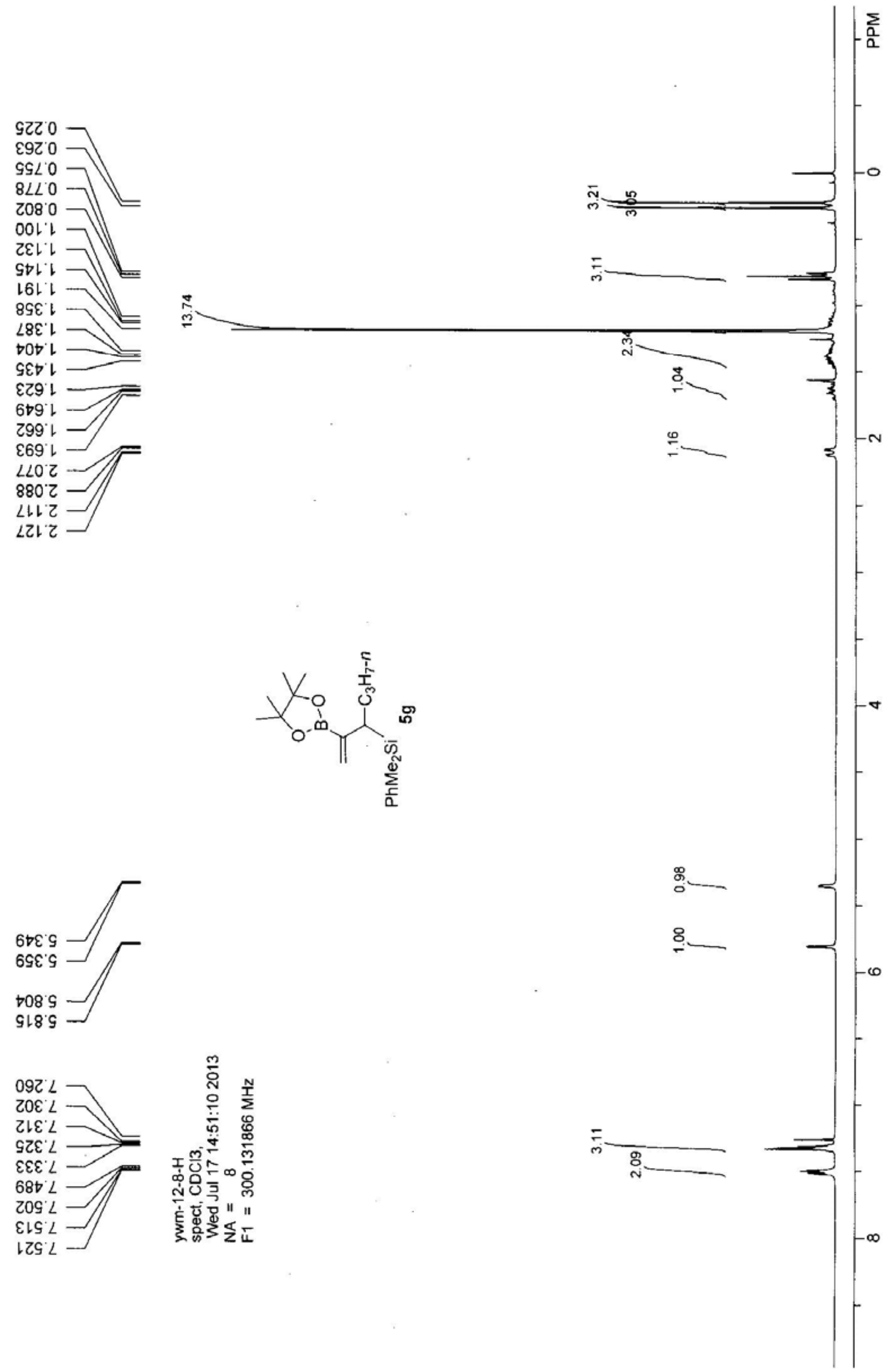


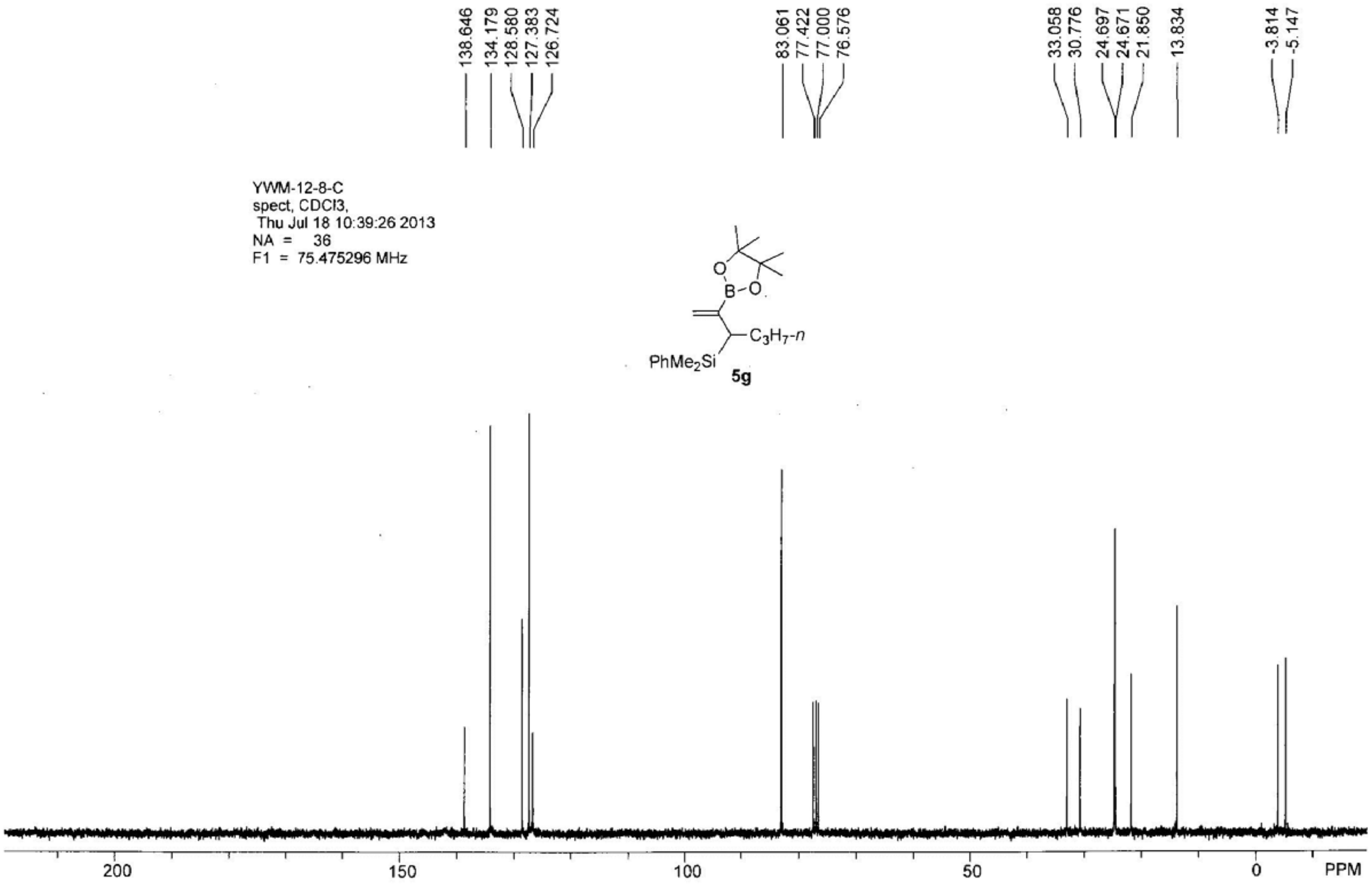
Mar 4 2016
sl-4-68C
NA = 1000
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz

5e

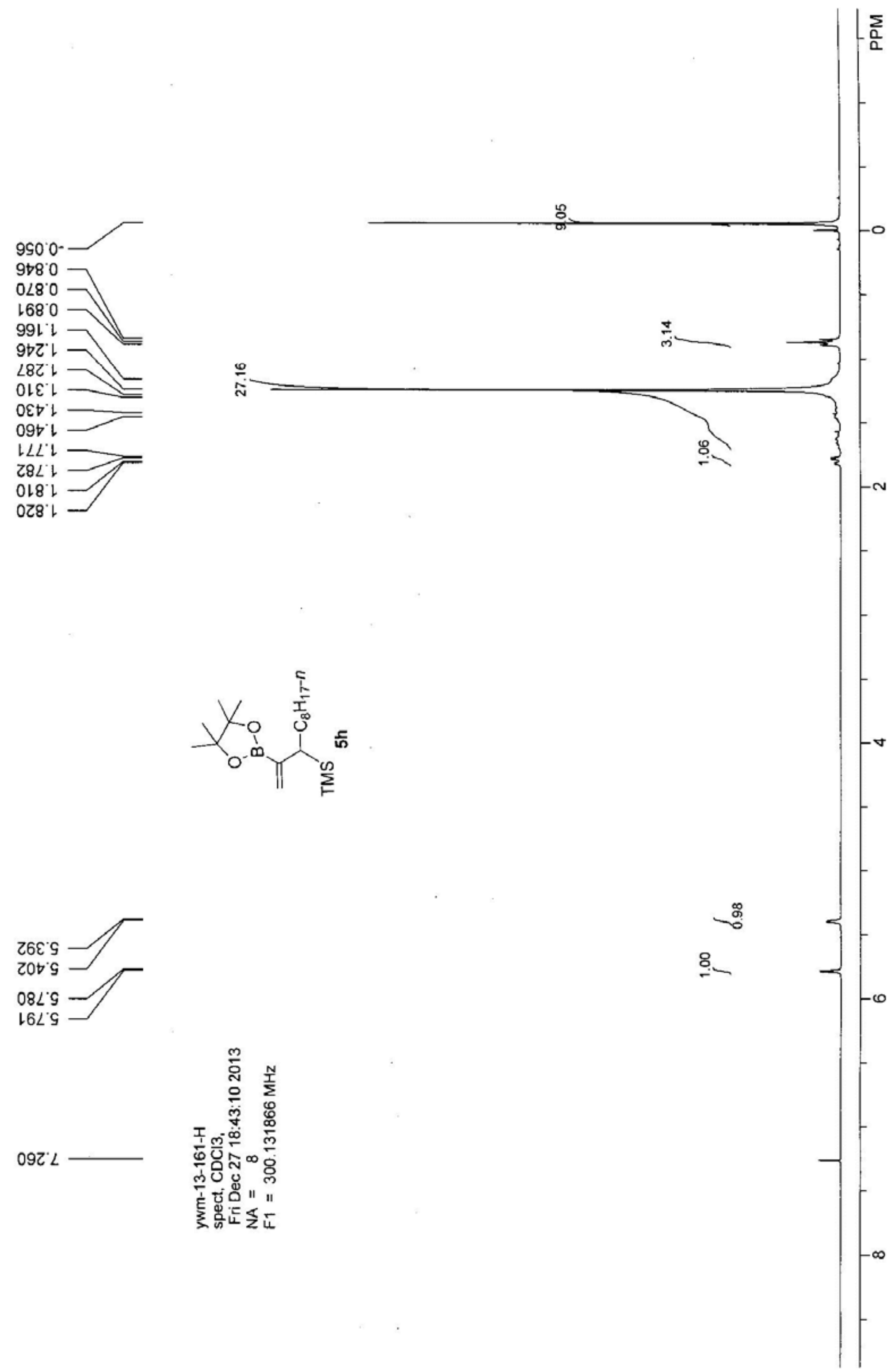

7.519
7.511
7.500
7.487
7.330
7.321
7.307
5.829
5.819
5.362
5.352
1.999
1.984
1.963
1.948
1.655
1.632
1.608
1.564
1.540
1.199
1.195
0.831
0.807
0.782
0.259
0.225
0.000
YWM-12-9-H
spect, CDCl3,
Wed Jul 17 14:56:13 2013
NA = 8
F1 = 300.131866 MHz
O
B
O
Et
PhMe2Si
5f
12.09
6.06
3.06
2.49
0.98
1.00
0.98
2.97
2.02
8
6
4
2
0
PPM


138.710
134.183
128.615
127.403
126.702
83.123
77.422
77.000
76.579
35.764
24.764
24.684
21.839
13.919
-3.707
-5.168
YWM-12-9-C
spect, CDCl3,
Thu Jul 18 11:01:30 2013
NA = 250
F1 = 75.475296 MHz
O
B
O
Et
PhMe$_2$Si
5f
200
150
100
50
0
PPM

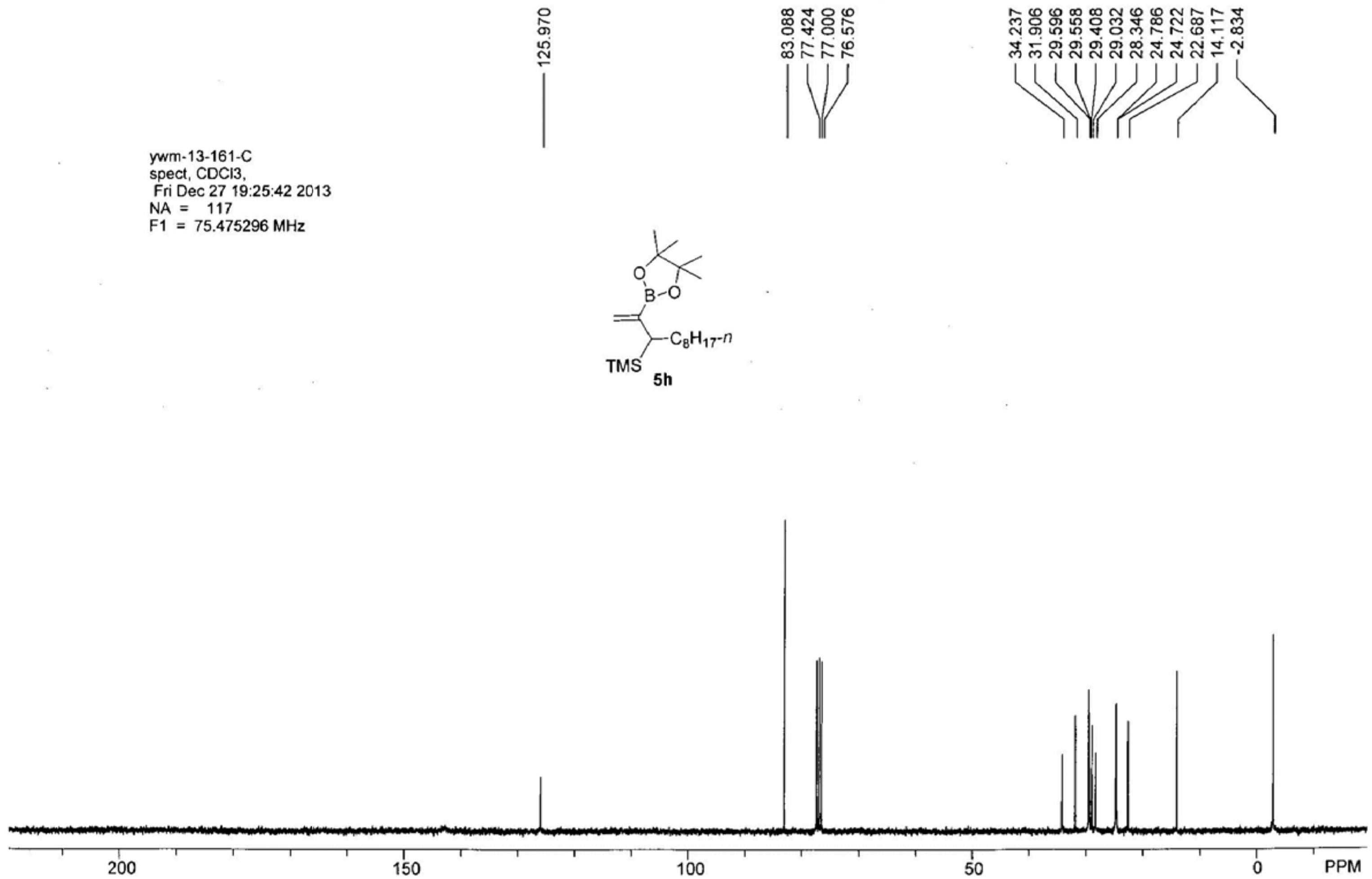

0.225
0.263
0.755
0.778
0.802
1.100
1.132
1.145
1.191
1.358
1.387
1.404
1.435
1.623
1.649
1.662
1.693
2.077
2.088
2.117
2.127
5.349
5.359
5.804
5.815
7.260
7.302
7.312
7.325
7.333
7.489
7.502
7.513
7.521
ywm-12-8-H
spect, CDCl3,
Wed Jul 17 14:51:10 2013
NA = 8
F1 = 300.131866 MHz
PhMe2Si
C3H7-n
O
B
O
5g
3.21
3.05
3.11
13.74
2.34
1.04
1.16
0.98
1.00
3.11
2.09
PPM
0
2
4
6
8


138.646
134.179
128.580
127.383
126.724
83.061
77.422
77.000
76.576
33.058
30.776
24.697
24.671
21.850
13.834
-3.814
-5.147
YWM-12-8-C
spect, CDCl3,
Thu Jul 18 10:39:26 2013
NA = 36
F1 = 75.475296 MHz
O
B
O
C_3H_7-n
$PhMe_2Si$
200
150
100
50
0
PPM

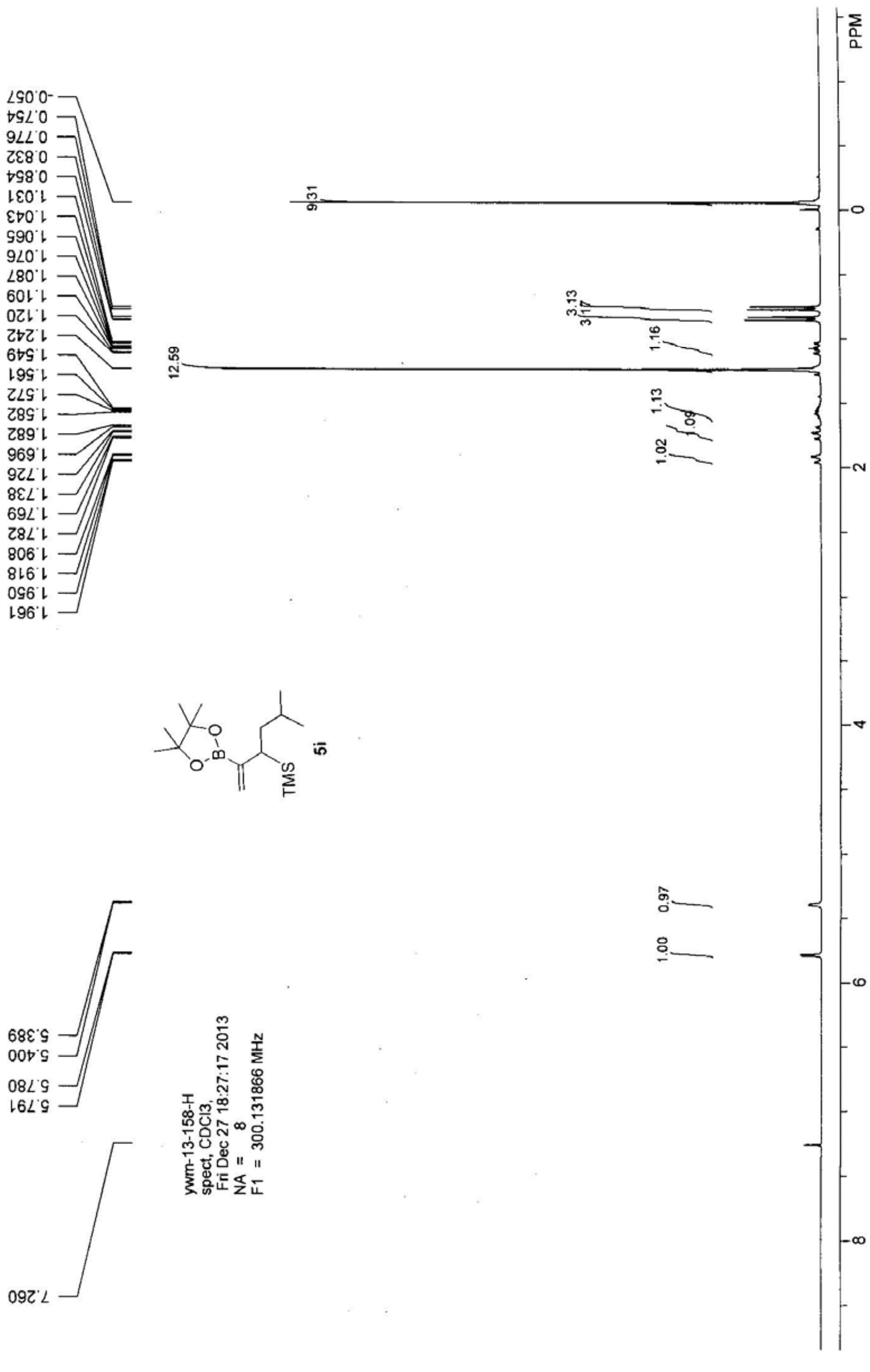
5g



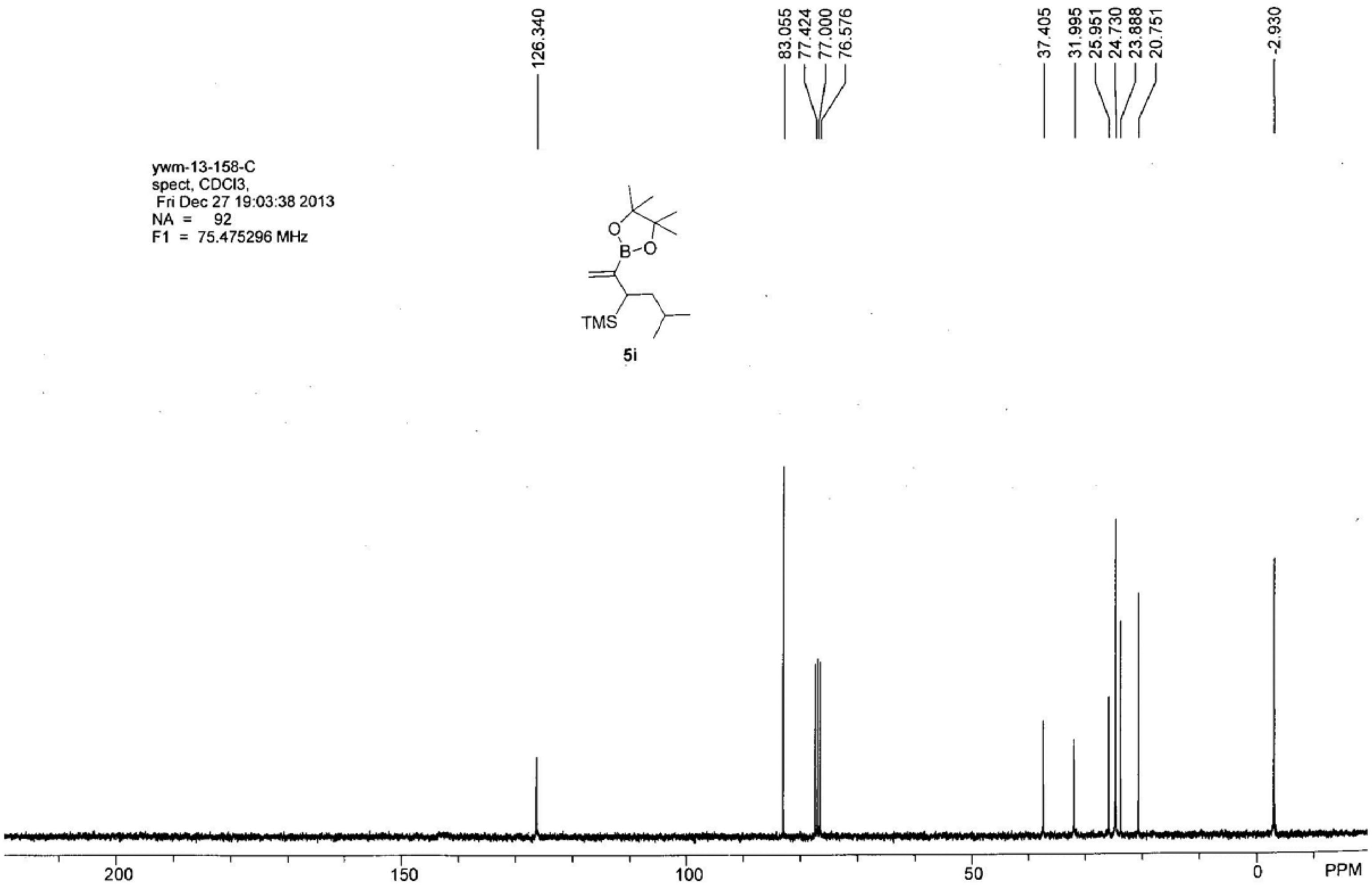
```
ywm-13-161-H
spect, CDCl3,
 Fri Dec 27 18:43:10 2013
 NA =    8
 F1 = 300.131866 MHz
```

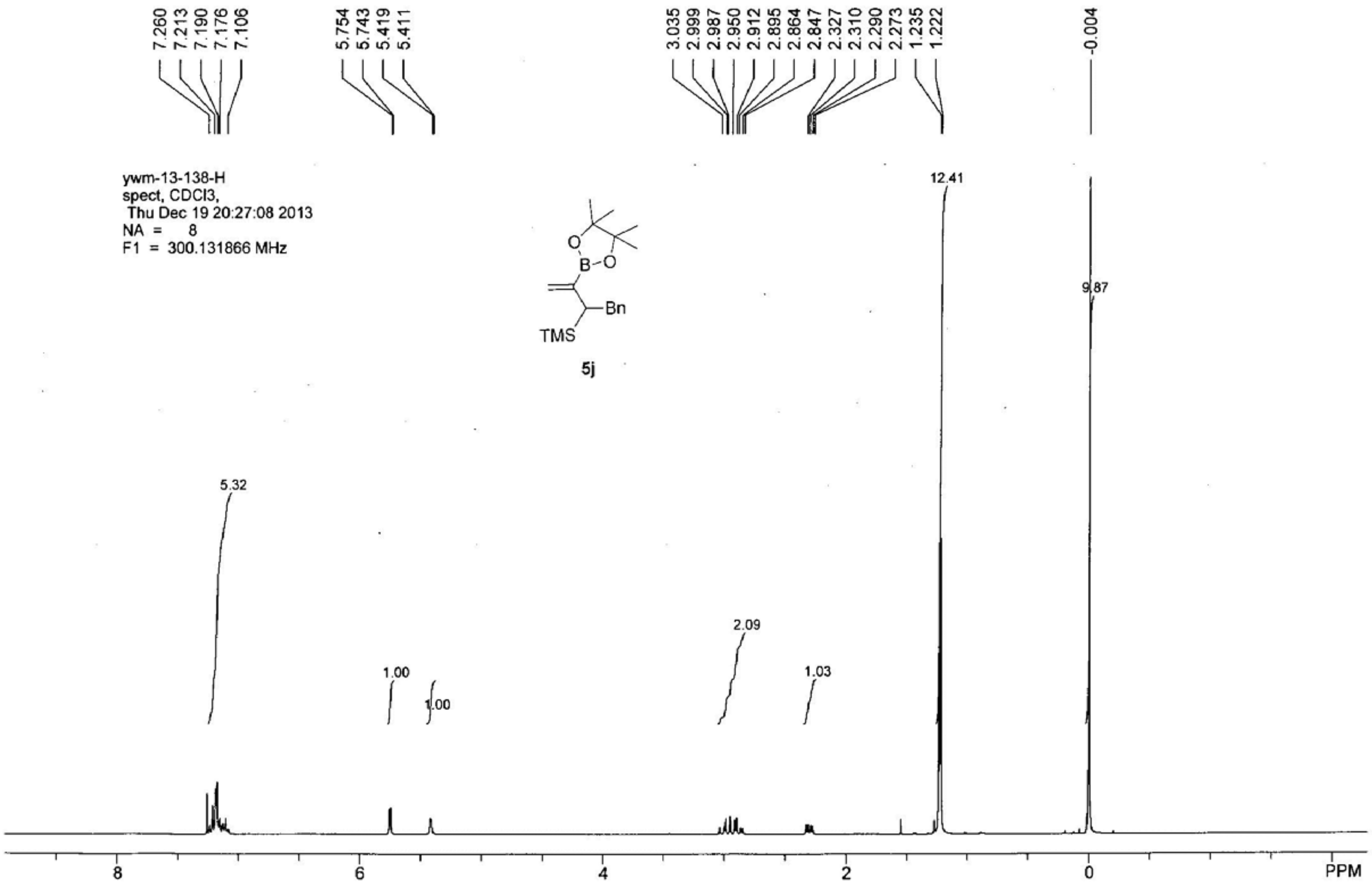

ywm-13-161-C
spect, CDCl3,
Fri Dec 27 19:25:42 2013
NA = 117
F1 = 75.475296 MHz

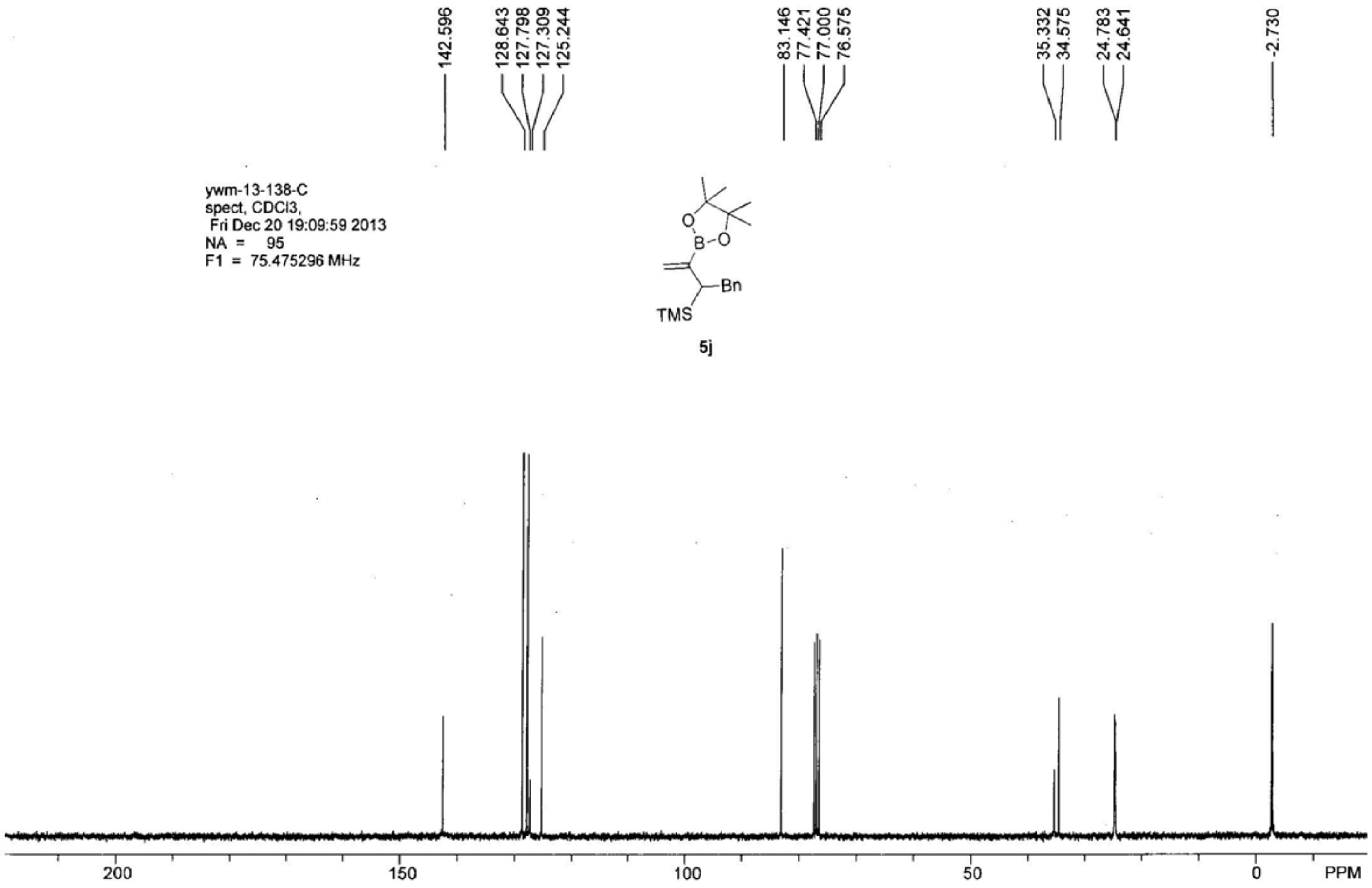
5h



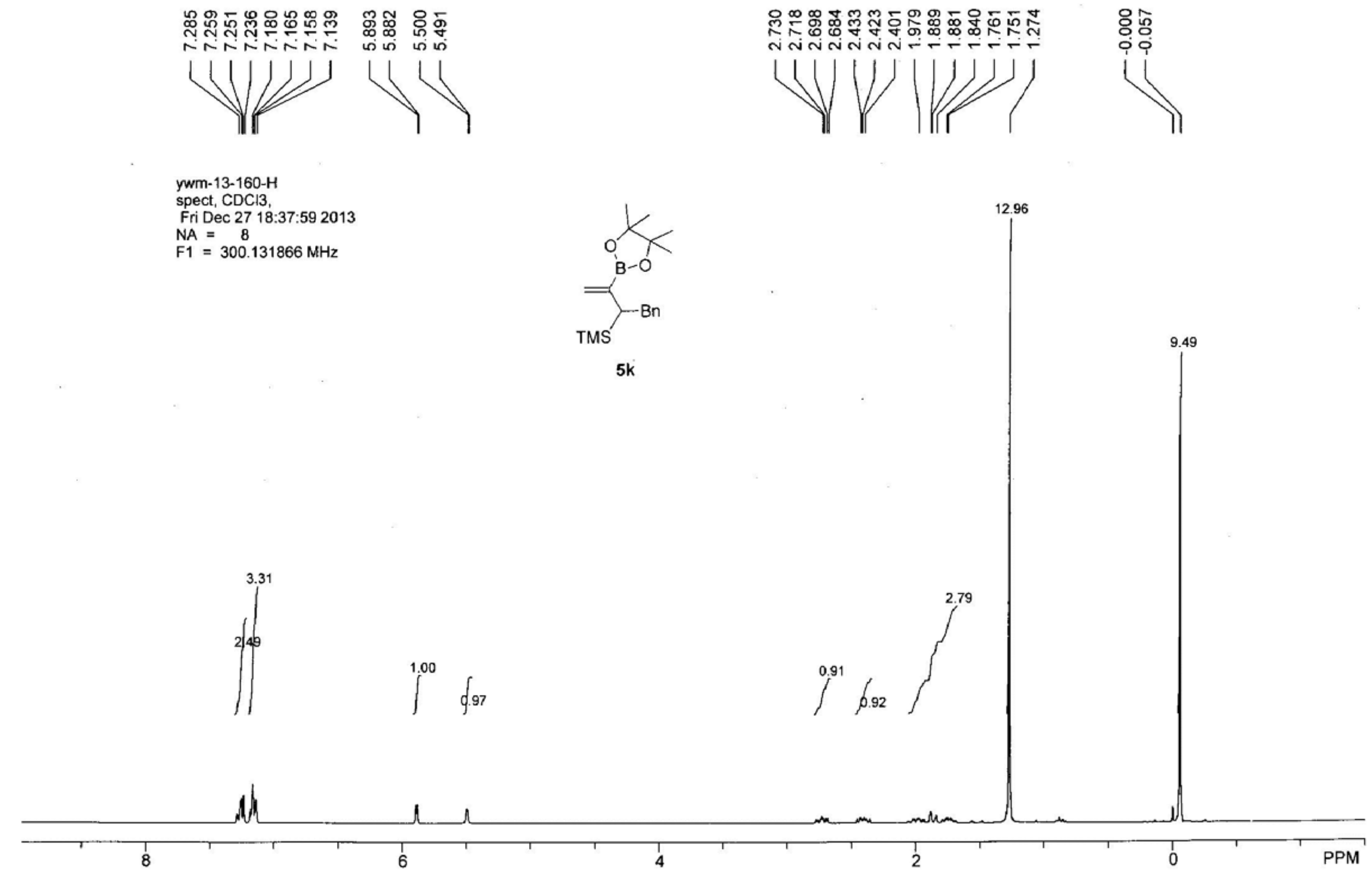
-0.057
0.754
0.776
0.832
0.854
1.031
1.043
1.065
1.076
1.087
1.109
1.120
1.242
1.549
1.561
1.572
1.582
1.682
1.696
1.726
1.738
1.769
1.782
1.908
1.918
1.950
1.961
5.389
5.400
5.780
5.791
7.260
O
B
O
TMS
5i
ywm-13-158-H
spect, CDCl3,
Fri Dec 27 18:27:17 2013
NA = 8
F1 = 300.131866 MHz
9.31
12.59
3.13
3.17
1.16
1.13
1.09
1.02
0.97
1.00
8
6
4
2
0
PPM


ywm-13-158-C
spect, CDCl3,
Fri Dec 27 19:03:38 2013
NA = 92
F1 = 75.475296 MHz
126.340
83.055
77.424
77.000
76.576
37.405
31.995
25.951
24.730
23.888
20.751
-2.930
O
B
O
TMS
5i
200
150
100
50
0
PPM

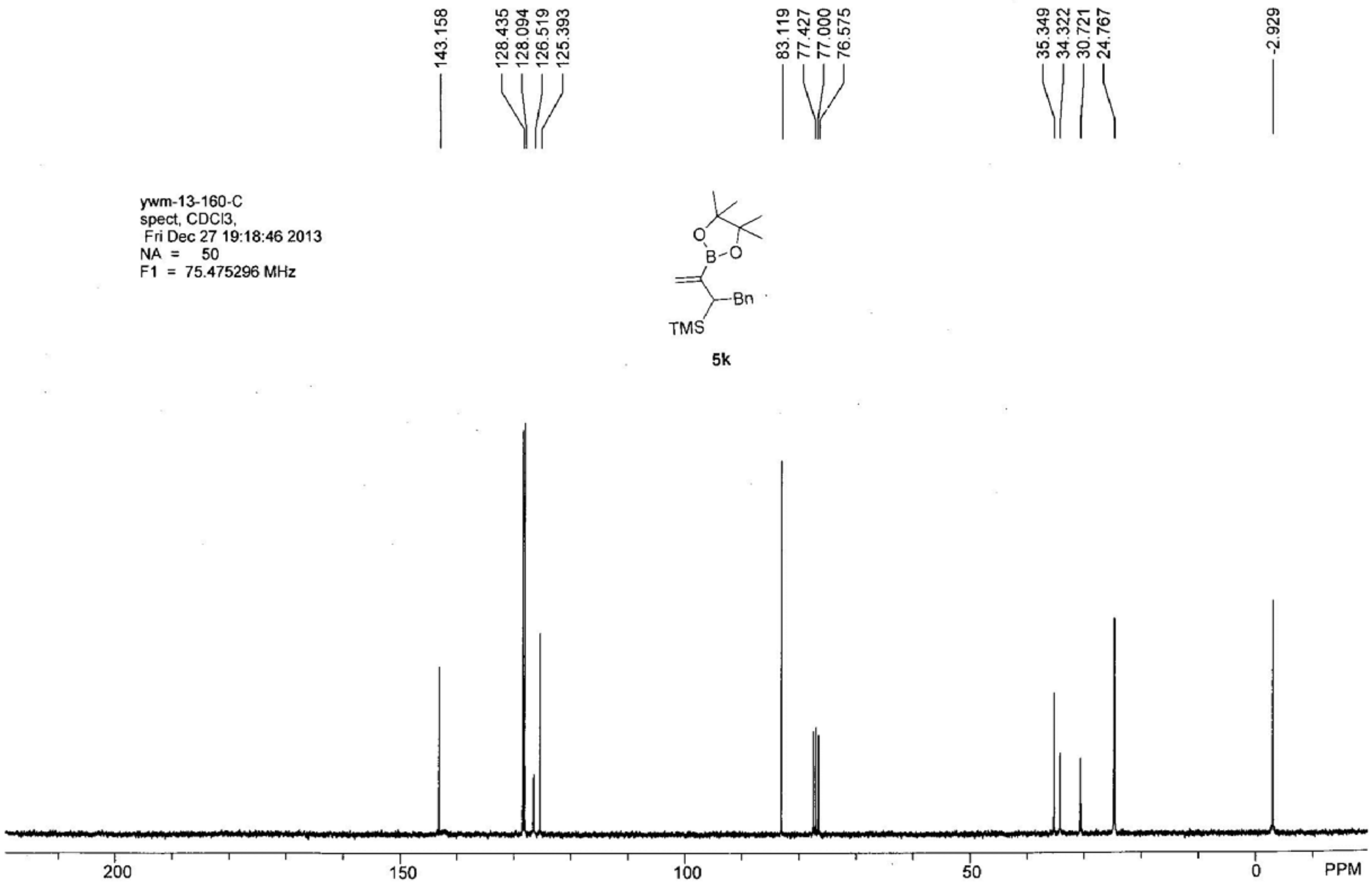

7.260
7.213
7.190
7.176
7.106
5.754
5.743
5.419
5.411
3.035
2.999
2.987
2.950
2.912
2.895
2.864
2.847
2.327
2.310
2.290
2.273
1.235
1.222
-0.004
ywm-13-138-H
spect, CDCl3,
Thu Dec 19 20:27:08 2013
NA = 8
F1 = 300.131866 MHz
O
B
O
Bn
TMS
5j
12.41
9.87
5.32
2.09
1.00
1.00
1.03
8
6
4
2
0
PPM

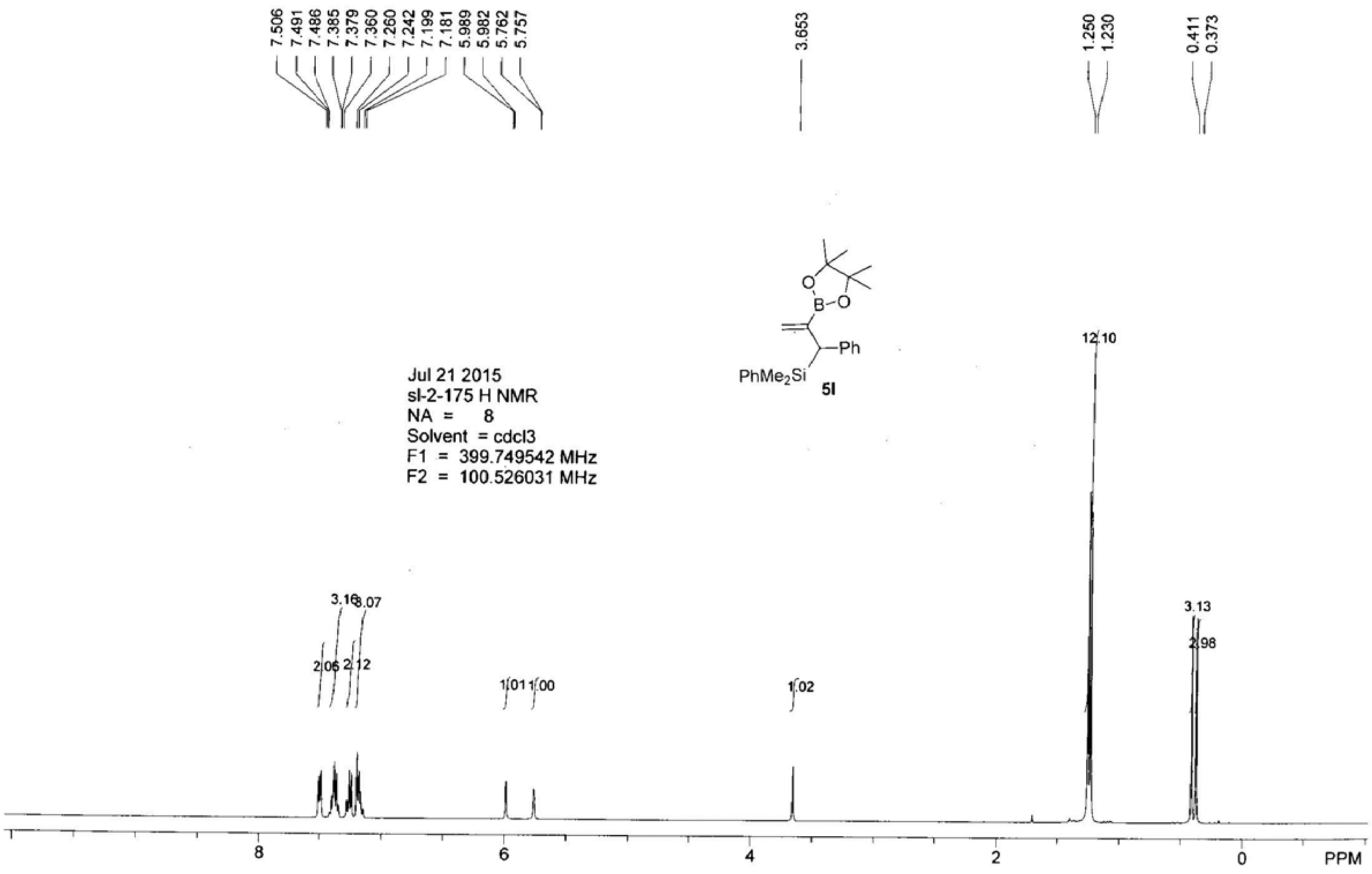

142.596
128.643
127.798
127.309
125.244
83.146
77.421
77.000
76.575
35.332
34.575
24.783
24.641
-2.730
ywm-13-138-C
spect, CDCl3,
Fri Dec 20 19:09:59 2013
NA = 95
F1 = 75.475296 MHz
O
B
O
Bn
TMS
200
150
100
50
0
PPM

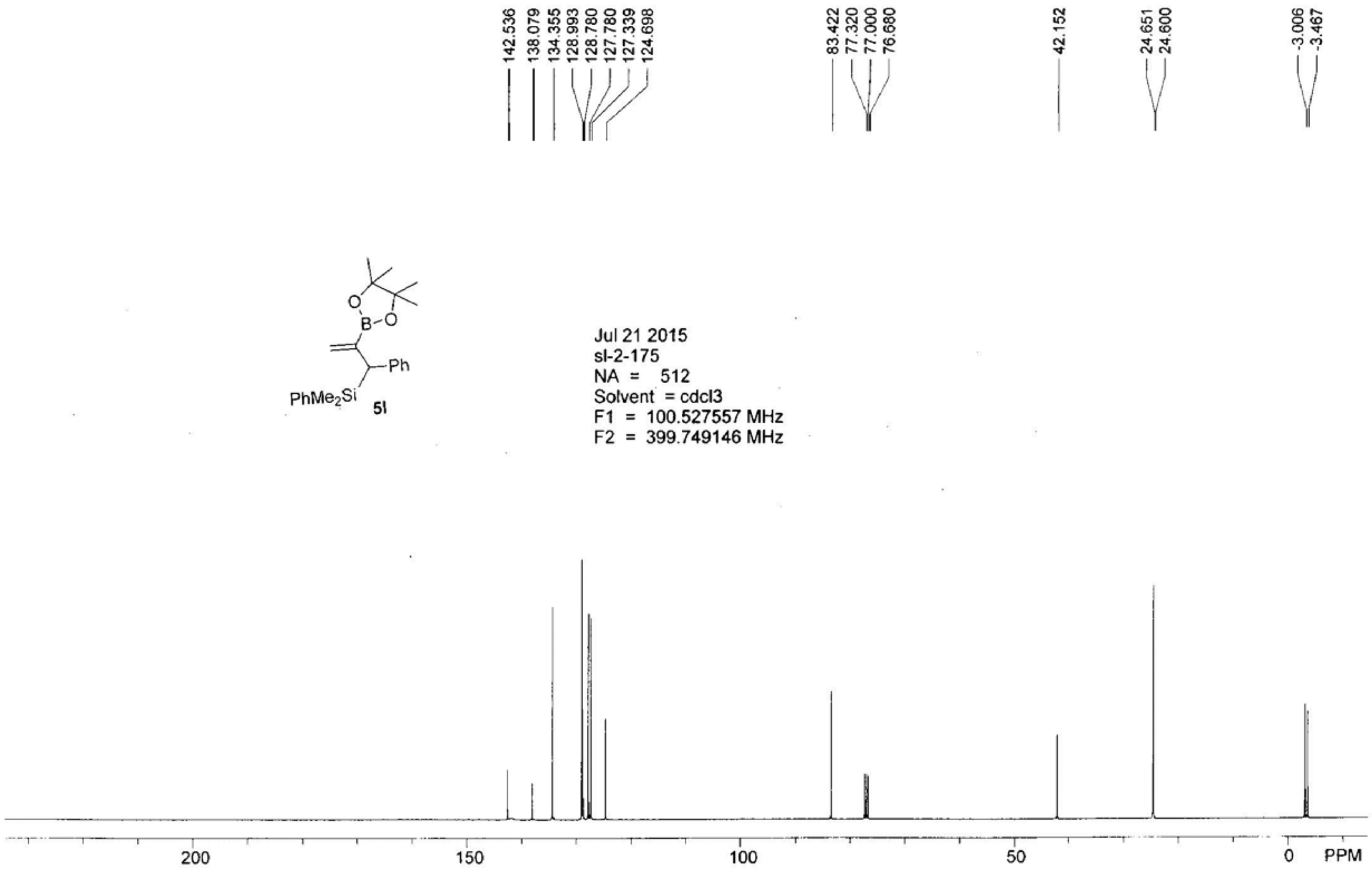
5j

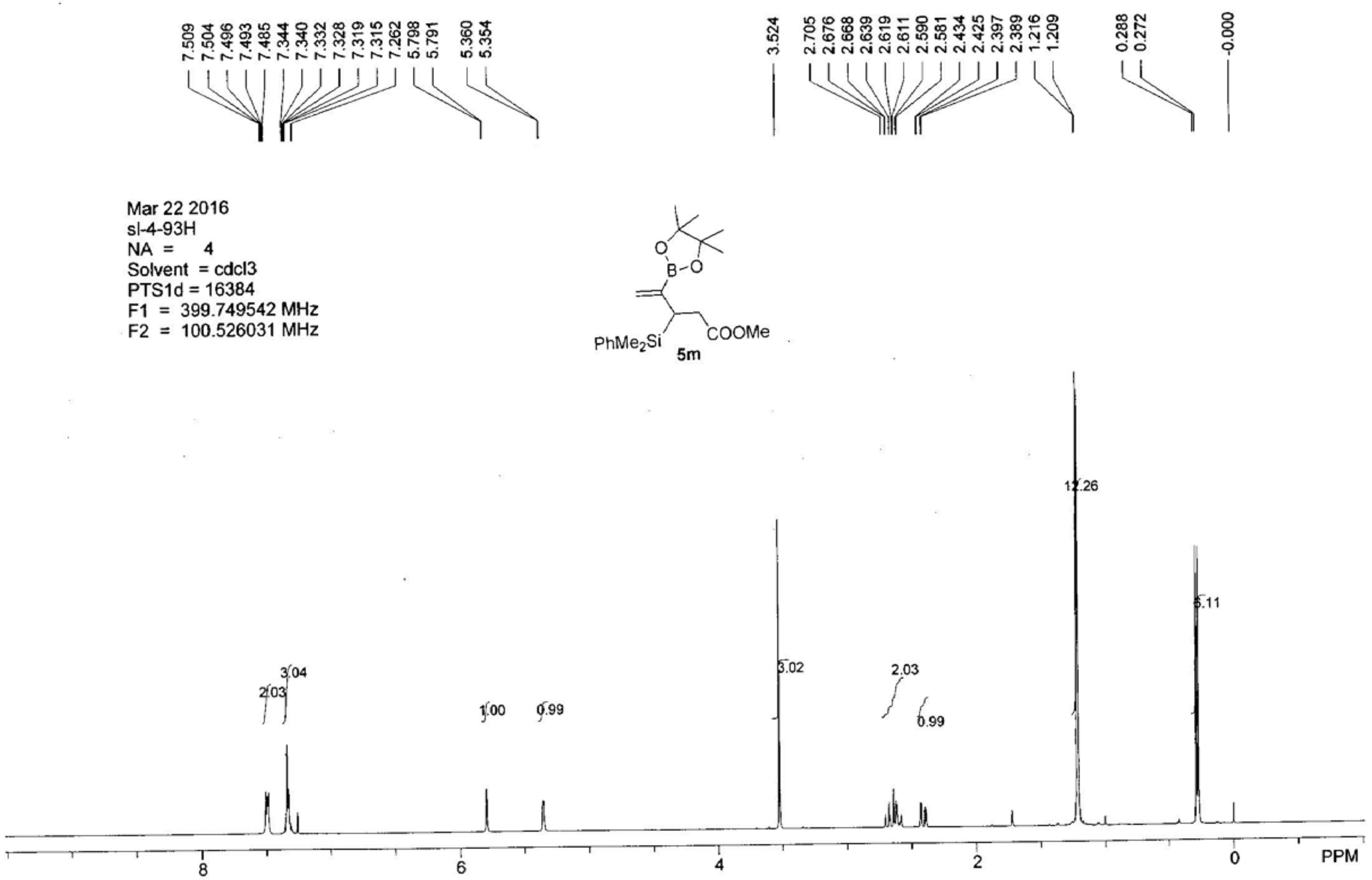

5k

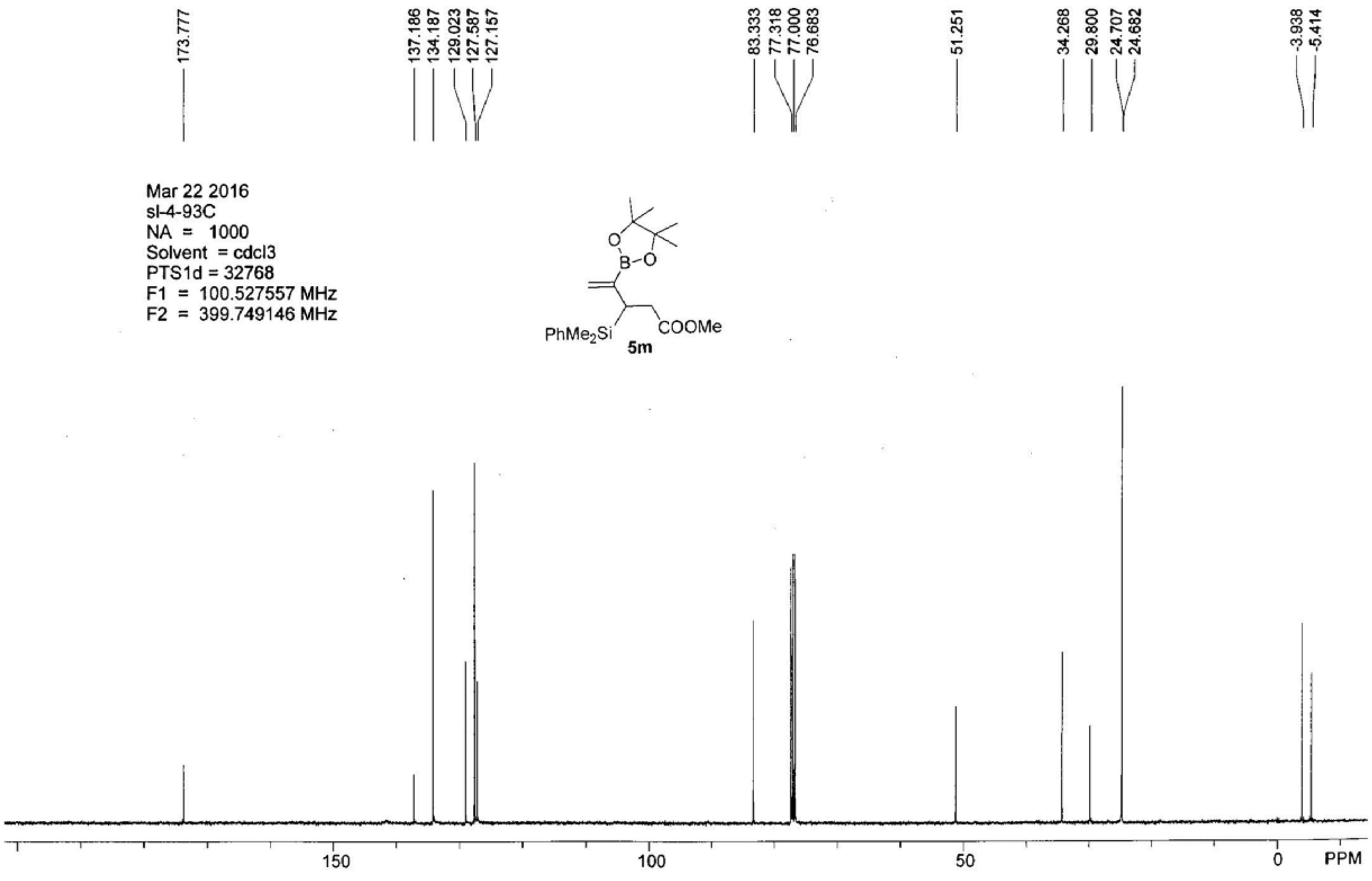
7.285
7.259
7.251
7.236
7.180
7.165
7.158
7.139
5.893
5.882
5.500
5.491
2.730
2.718
2.698
2.684
2.433
2.423
2.401
1.979
1.889
1.881
1.840
1.761
1.751
1.274
-0.000
-0.057
ywm-13-160-H
spect, CDCl3,
Fri Dec 27 18:37:59 2013
NA = 8
F1 = 300.131866 MHz
O
B
O
Bn
TMS
12.96
9.49
3.31
2.49
1.00
0.97
0.91
0.92
2.79
8
6
4
2
0
PPM

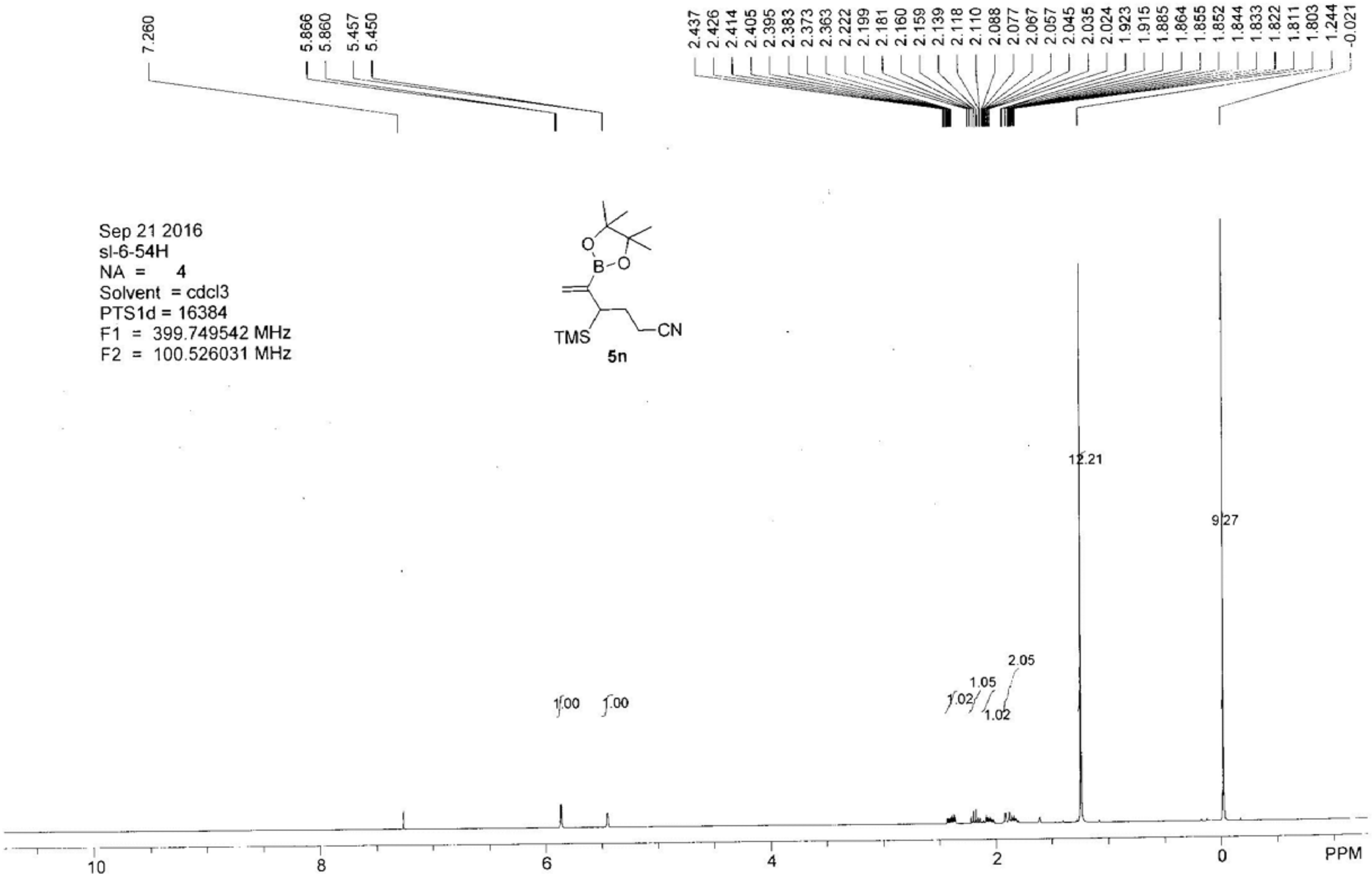

143.158
128.435
128.094
126.519
125.393
83.119
77.427
77.000
76.575
35.349
34.322
30.721
24.767
-2.929
ywm-13-160-C
spect, CDCl3,
Fri Dec 27 19:18:46 2013
NA = 50
F1 = 75.475296 MHz
O
B
O
Bn
TMS
5k
200
150
100
50
0
PPM


7.506
7.491
7.486
7.385
7.379
7.360
7.260
7.242
7.199
7.181
5.989
5.982
5.762
5.757
3.653
1.250
1.230
0.411
0.373
PhMe$_2$Si
Ph
B
O
O
5l
Jul 21 2015
sl-2-175 H NMR
NA = 8
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
3.16
3.07
2.06
2.12
1.01
1.00
1.02
12.10
3.13
2.98
8
6
4
2
0
PPM


142.536
138.079
134.355
128.993
128.780
127.780
127.339
124.698
83.422
77.320
77.000
76.680
42.152
24.651
24.600
-3.006
-3.467
O
B
O
Ph
PhMe$_2$Si
5l
Jul 21 2015
sl-2-175
NA = 512
Solvent = cdcl3
F1 = 100.527557 MHz
F2 = 399.749146 MHz
200
150
100
50
0
PPM

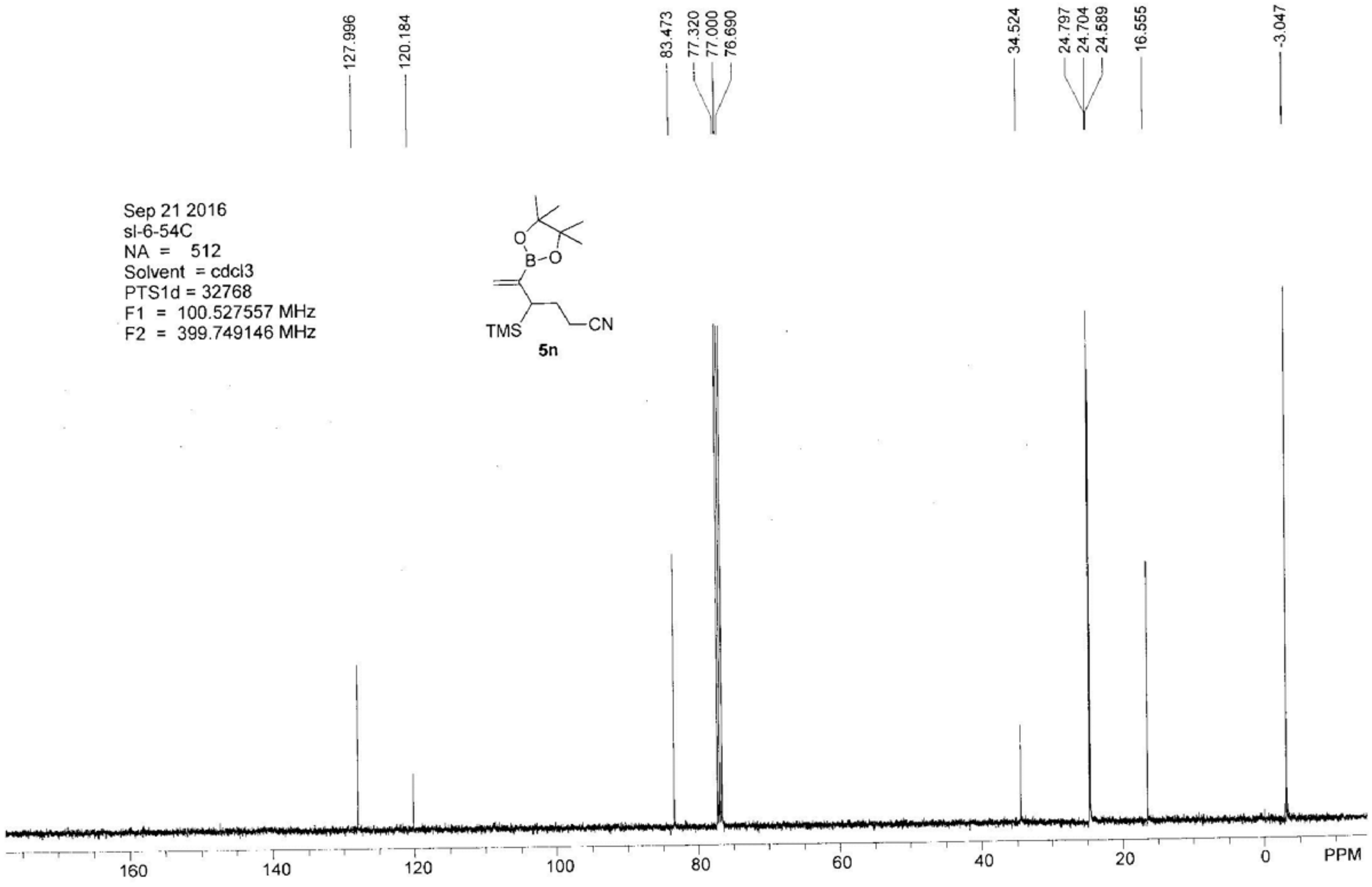

7.509
7.504
7.496
7.493
7.485
7.344
7.340
7.332
7.328
7.319
7.315
7.262
5.798
5.791
5.360
5.354
3.524
2.705
2.676
2.668
2.639
2.619
2.611
2.590
2.581
2.434
2.425
2.397
2.389
1.216
1.209
0.288
0.272
-0.000
Mar 22 2016
sl-4-93H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
PhMe2Si
COOMe
5m
2.03
3.04
1.00
0.99
3.02
2.03
0.99
12.26
6.11
8
6
4
2
0
PPM


173.777
137.186
134.187
129.023
127.587
127.157
83.333
77.318
77.000
76.683
51.251
34.268
29.800
24.707
24.682
-3.938
-5.414
Mar 22 2016
sl-4-93C
NA = 1000
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
B
O
PhMe2Si
COOMe
5m
150
100
50
0
PPM



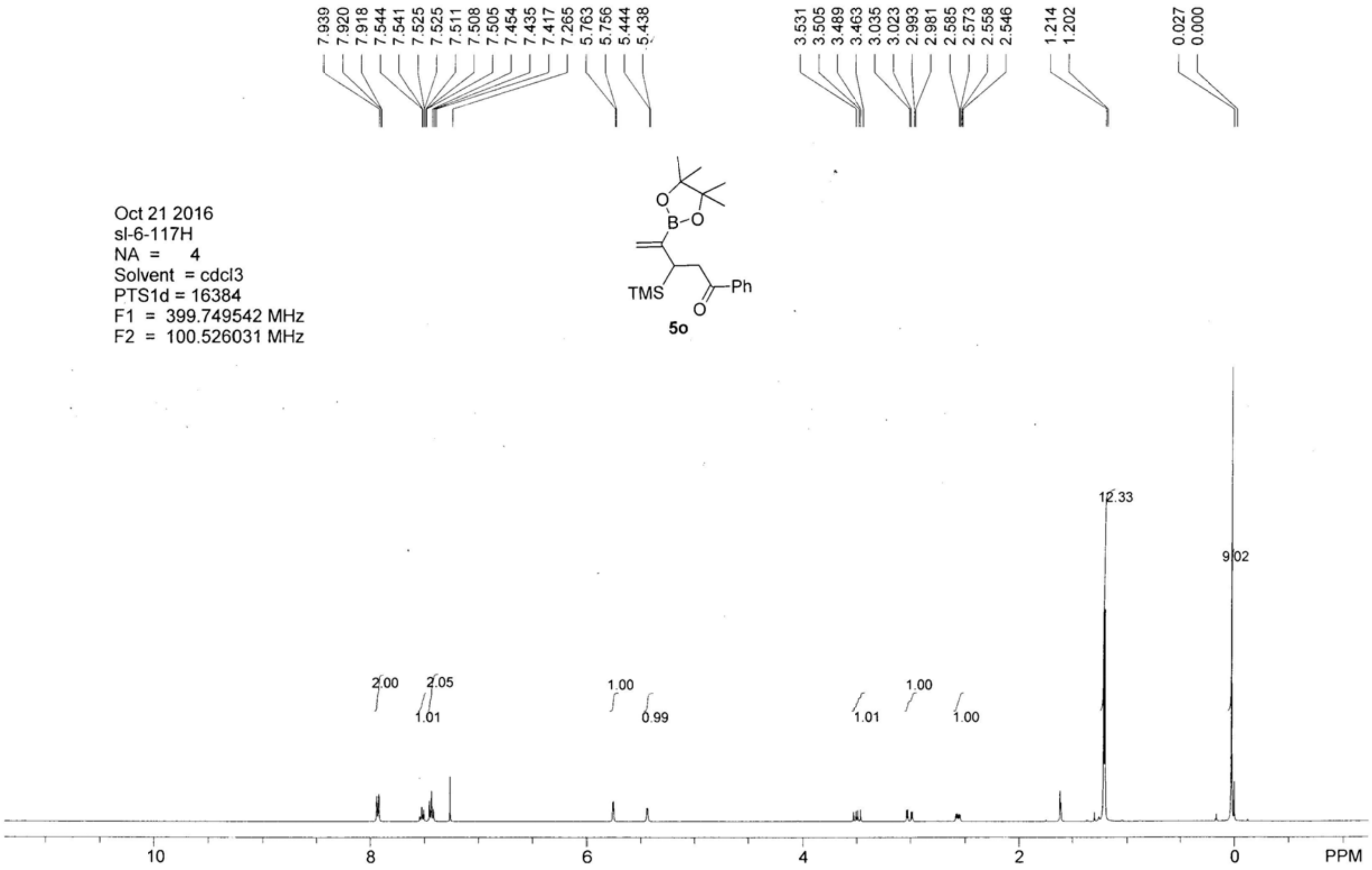
Sep 21 2016
sl-6-54H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz

5n

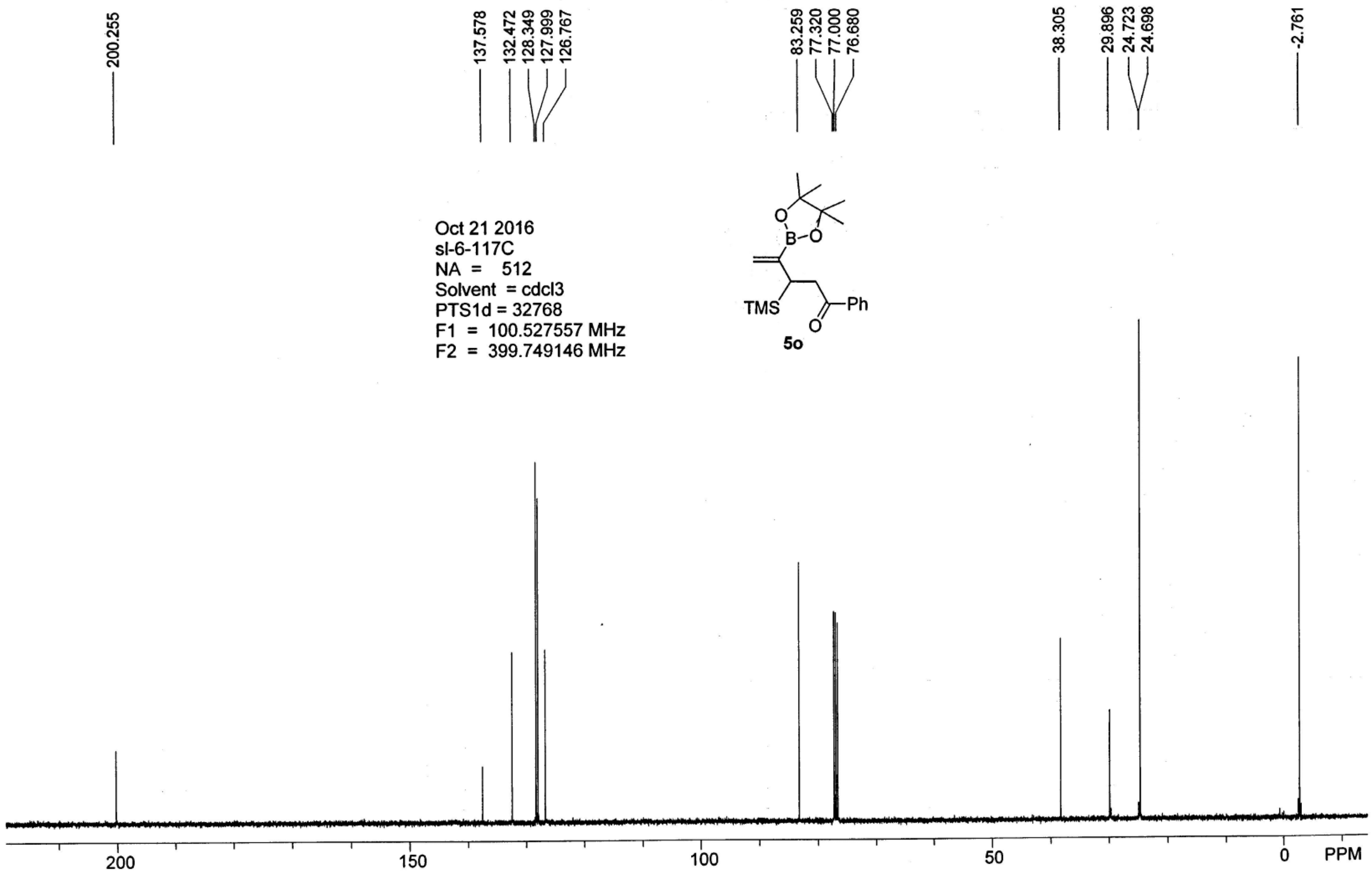


Sep 21 2016
sl-6-54C
NA = 512
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz

5n

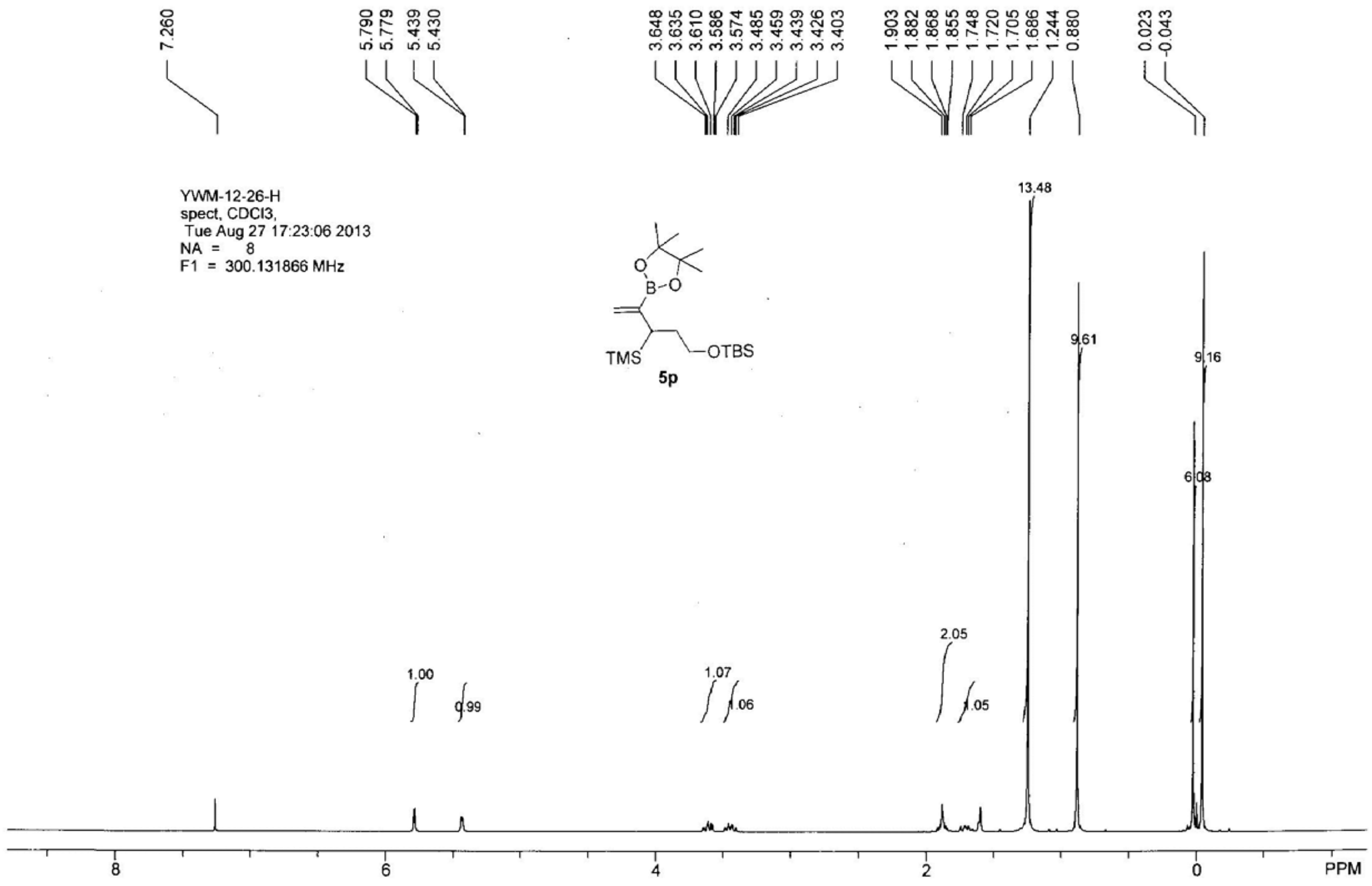

7.939
7.920
7.918
7.544
7.541
7.525
7.525
7.511
7.508
7.505
7.454
7.435
7.417
7.265
5.763
5.756
5.444
5.438
3.531
3.505
3.489
3.463
3.035
3.023
2.993
2.981
2.585
2.573
2.558
2.546
1.214
1.202
0.027
0.000
Oct 21 2016
sl-6-117H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
O
B
O
TMS
Ph
O
12.33
9.02
2.00
2.05
1.01
1.00
0.99
1.01
1.00
1.00
10
8
6
4
2
0
PPM

5o

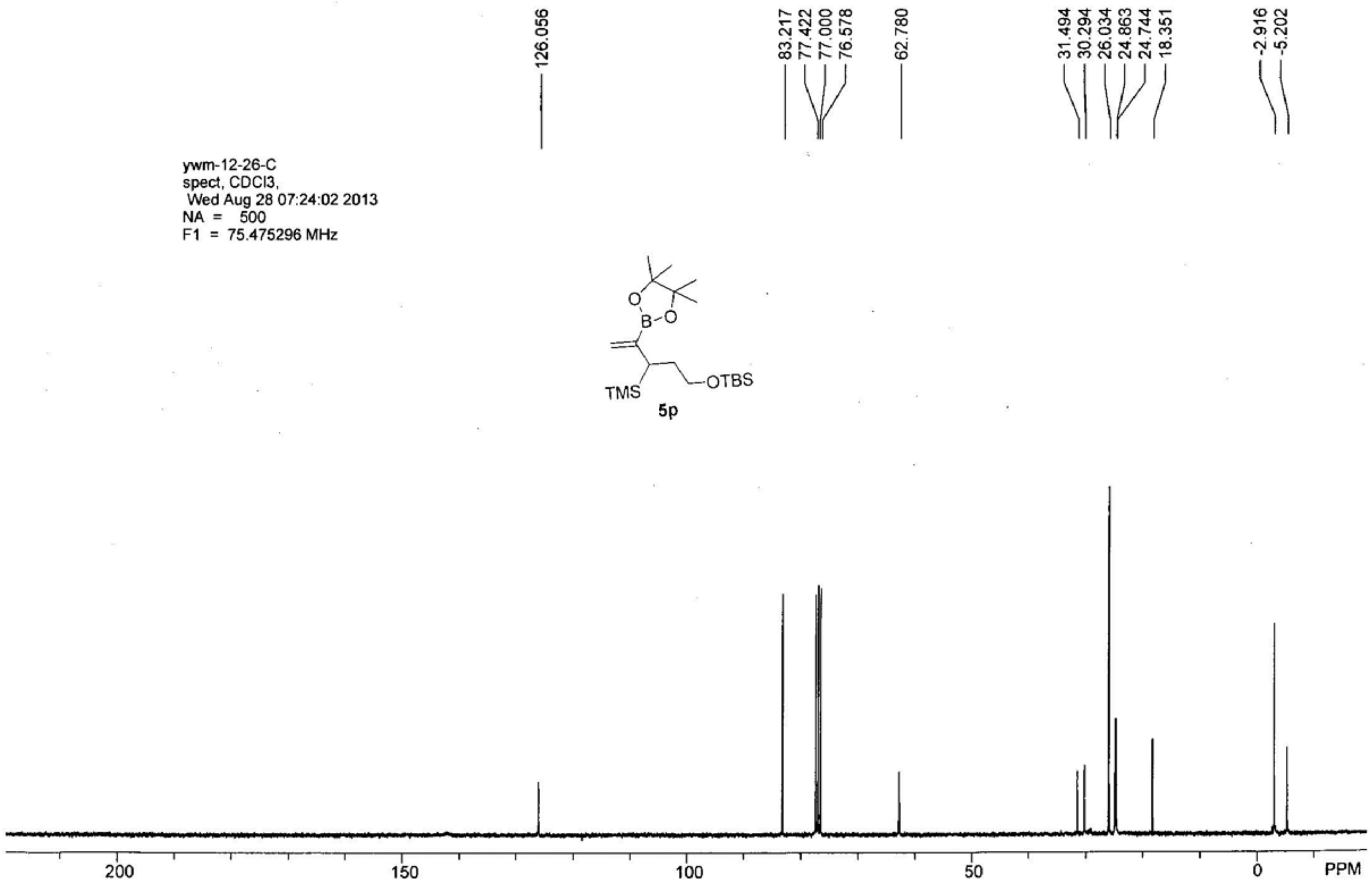


5o

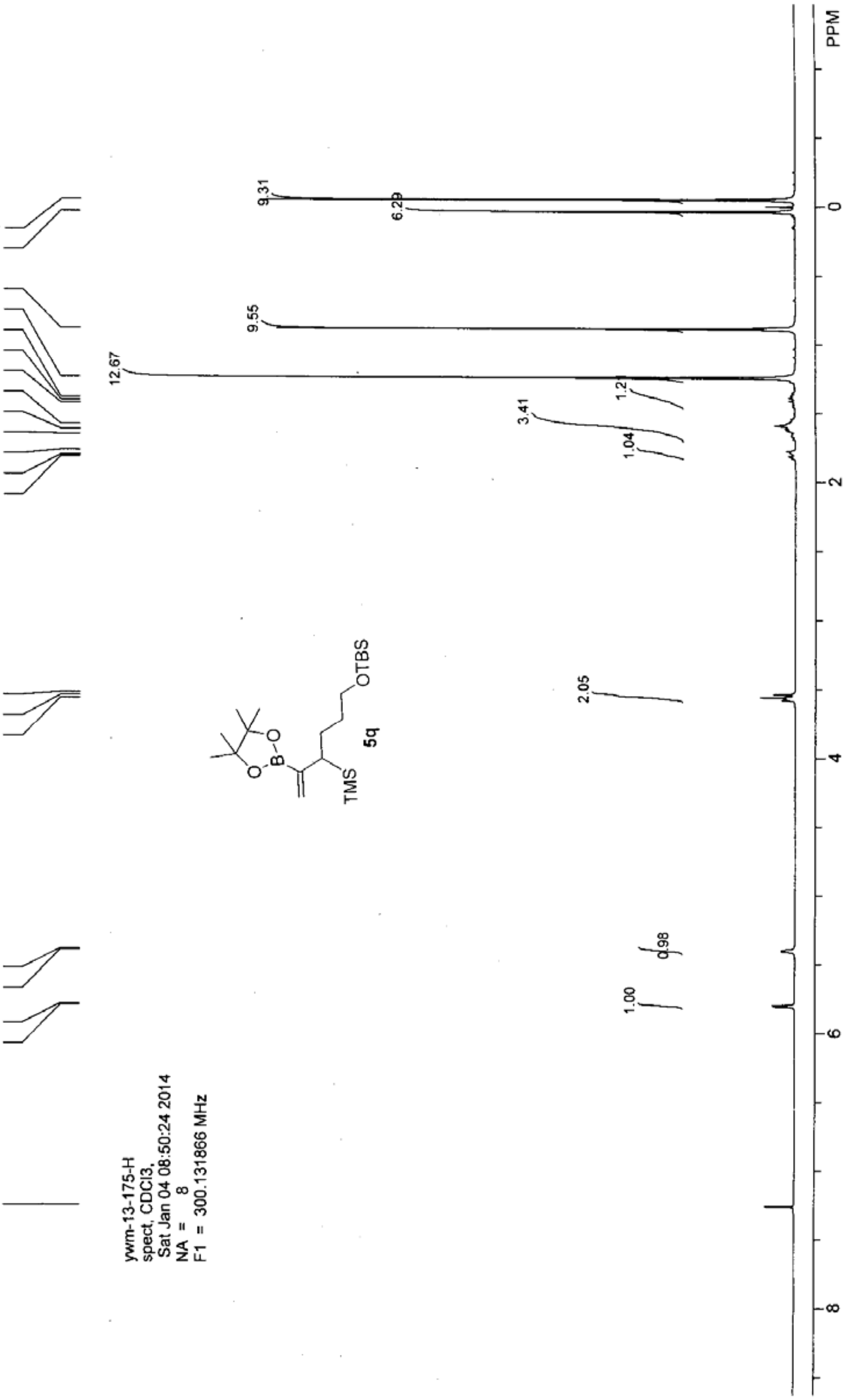
Oct 21 2016
sl-6-117C
NA = 512
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz

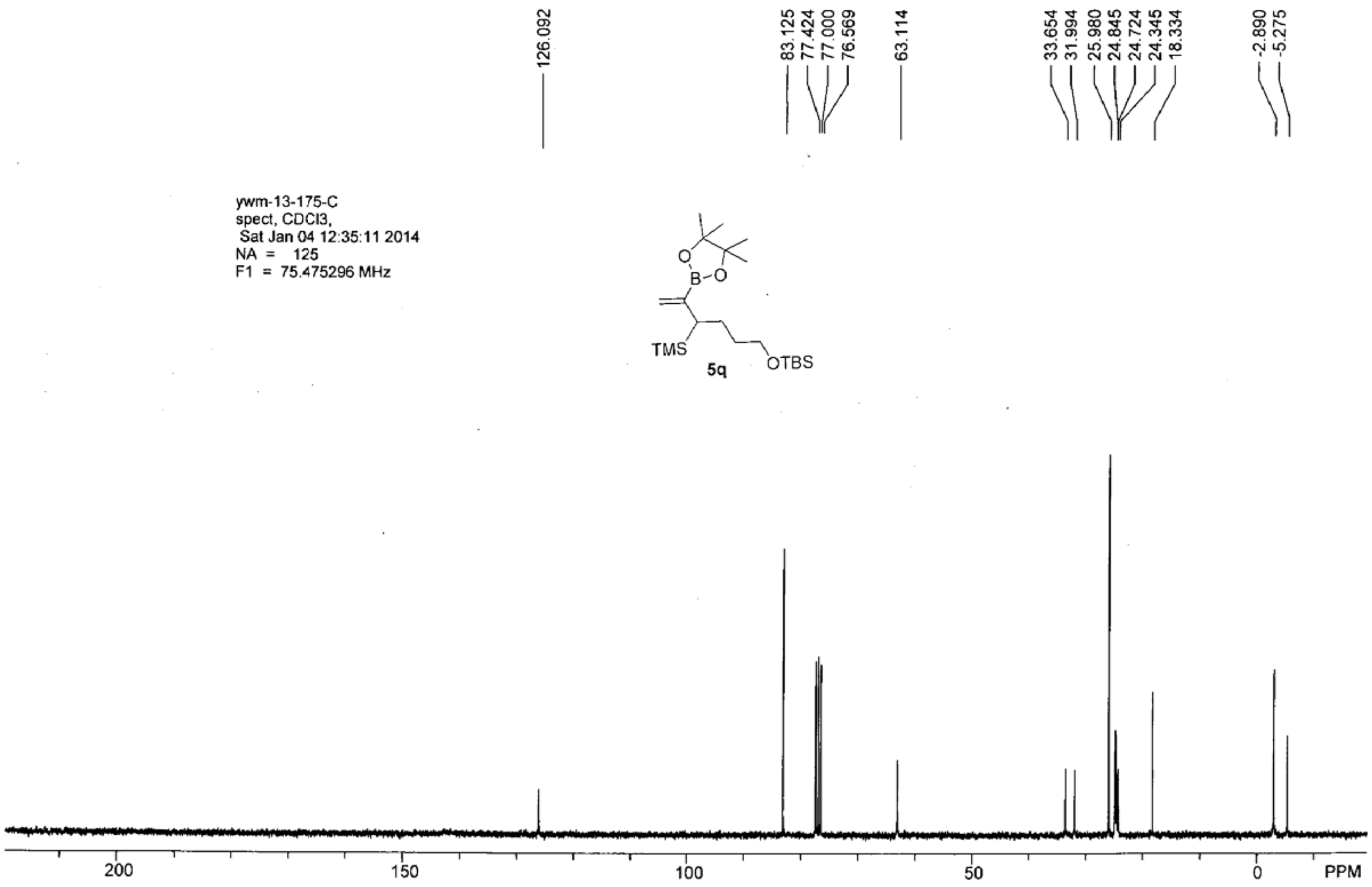

7.260
5.790
5.779
5.439
5.430
3.648
3.635
3.610
3.586
3.574
3.485
3.459
3.439
3.426
3.403
1.903
1.882
1.868
1.855
1.748
1.720
1.705
1.686
1.244
0.880
0.023
-0.043
YWM-12-26-H
spect, CDCl3,
Tue Aug 27 17:23:06 2013
NA = 8
F1 = 300.131866 MHz
TMS
OTBS
O
B
O
13.48
9.61
9.16
6.08
2.05
1.07
1.06
1.05
1.00
0.99
8
6
4
2
0
PPM

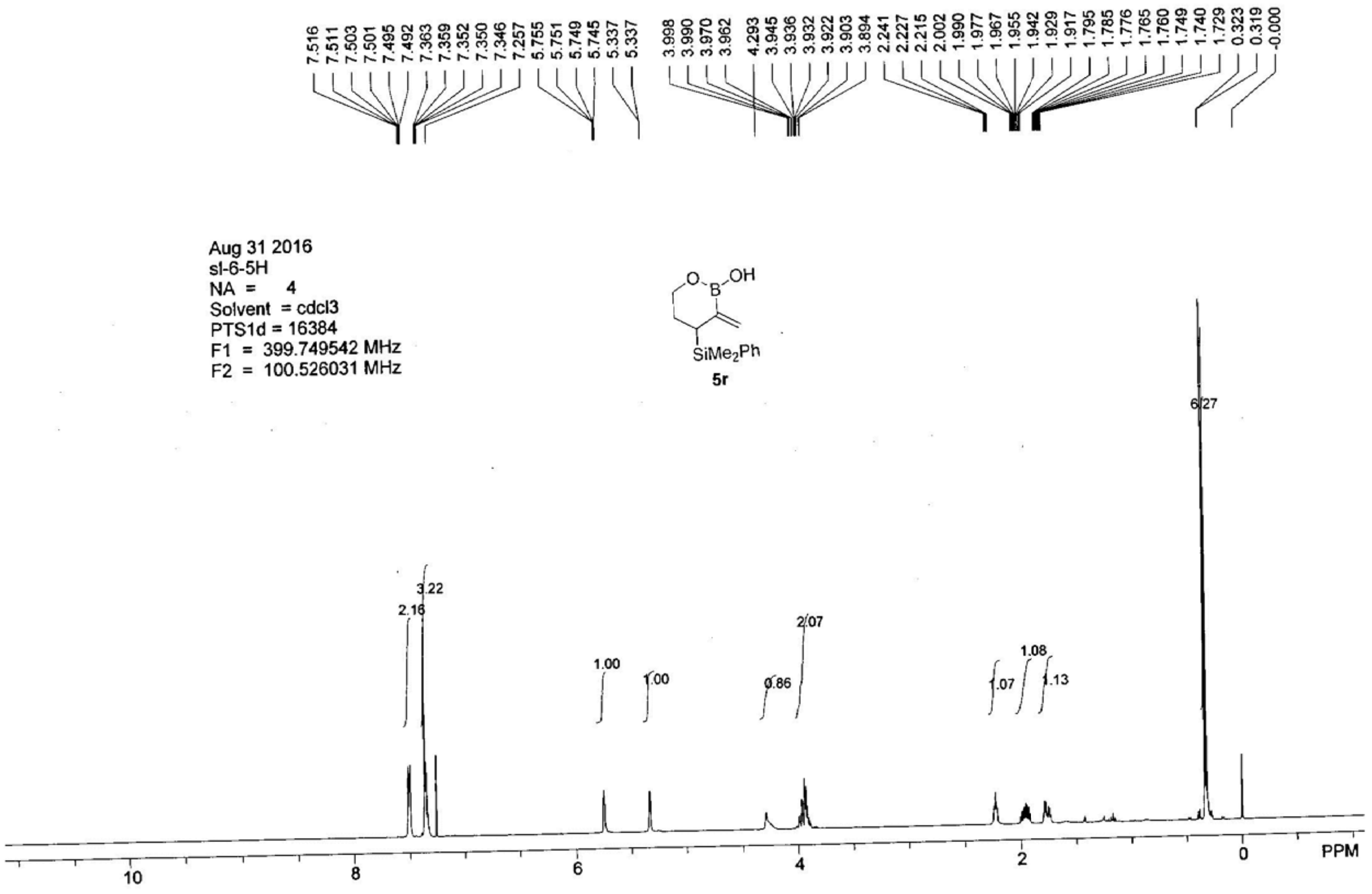
5p


126.056
83.217
77.422
77.000
76.578
62.780
31.494
30.294
26.034
24.863
24.744
18.351
-2.916
-5.202
ywm-12-26-C
spect, CDCl3,
Wed Aug 28 07:24:02 2013
NA = 500
F1 = 75.475296 MHz
O
B
O
TMS
OTBS
200
150
100
50
0
PPM

5p

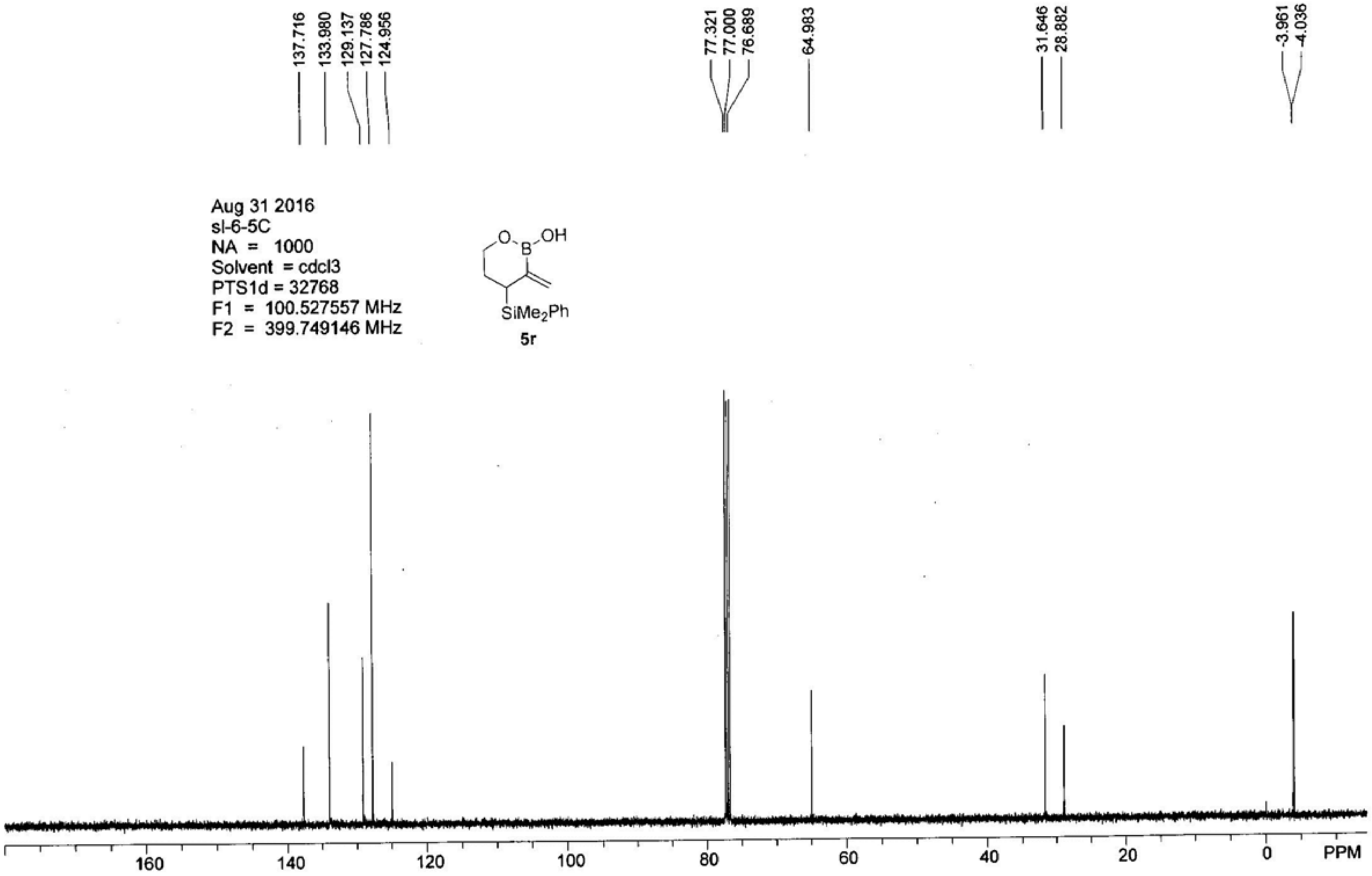

-0.052
0.035
0.886
1.244
1.390
1.412
1.434
1.590
1.625
1.663
1.778
1.814
1.827
3.536
3.557
3.577
5.398
5.407
5.795
5.806
7.260
ywm-13-175-H
spect, CDCl3,
Sat Jan 04 08:50:24 2014
NA = 8
F1 = 300.131866 MHz
9.31
6.29
9.55
12.67
3.41
1.2
1.04
2.05
0.98
1.00
TMS
OTBS
O
B
O
5q
PPM
0
2
4
6
8


126.092
83.125
77.424
77.000
76.569
63.114
33.654
31.994
25.980
24.845
24.724
24.345
18.334
-2.890
-5.275
ywm-13-175-C
spect, CDCl3,
Sat Jan 04 12:35:11 2014
NA = 125
F1 = 75.475296 MHz
O
B
O
TMS
OTBS
5q
200
150
100
50
0
PPM

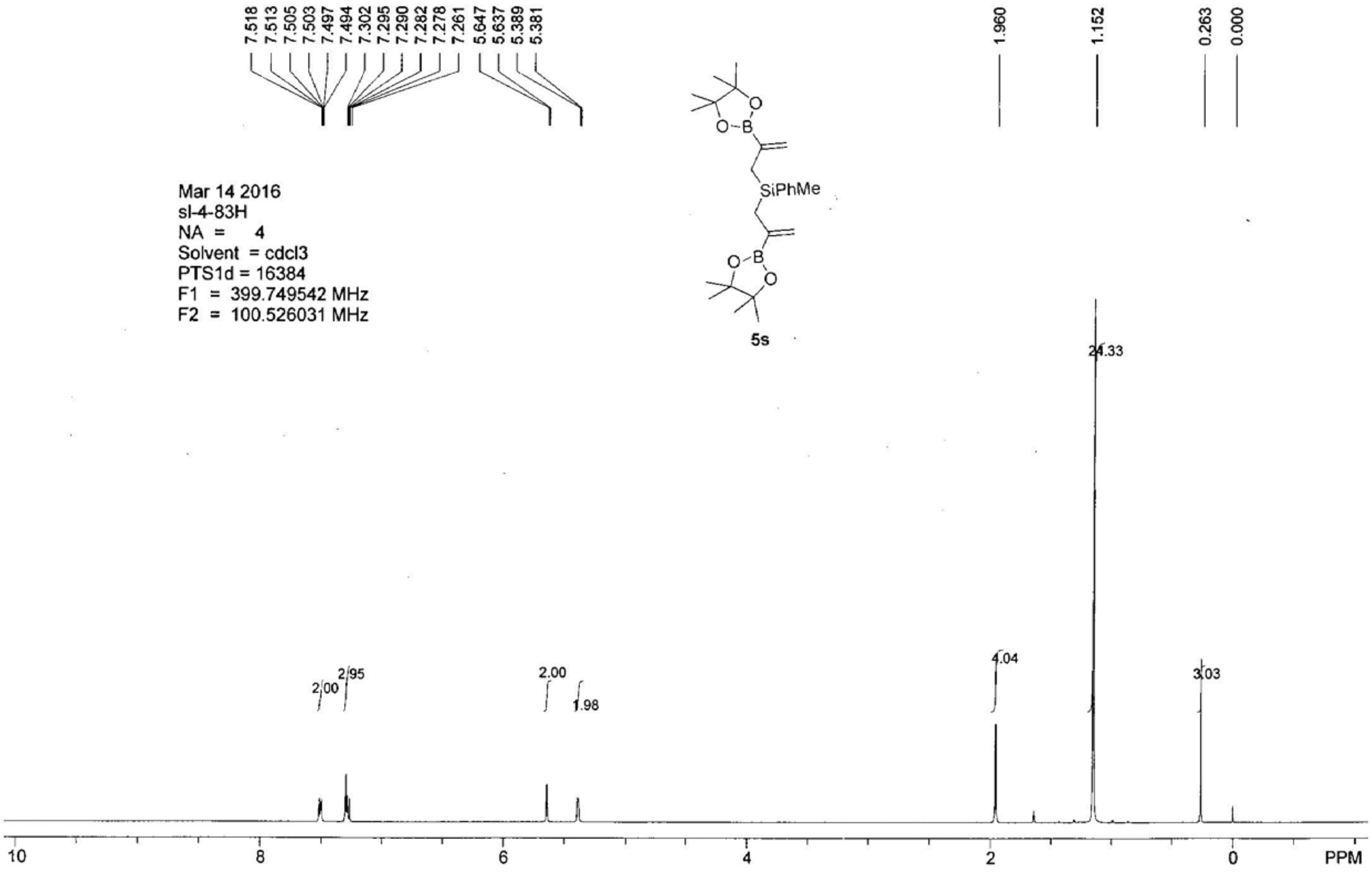


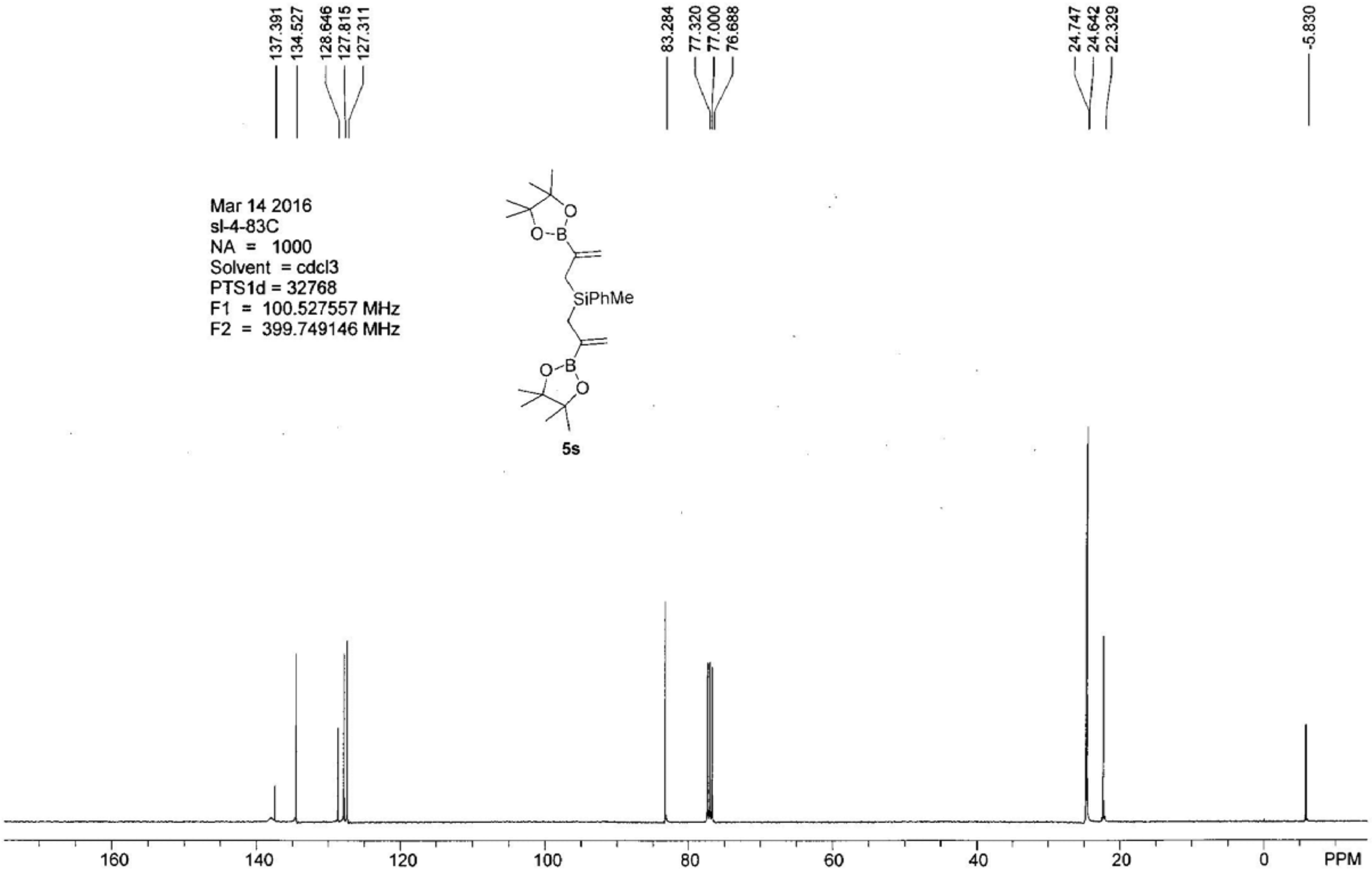
Aug 31 2016
sl-6-5H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz

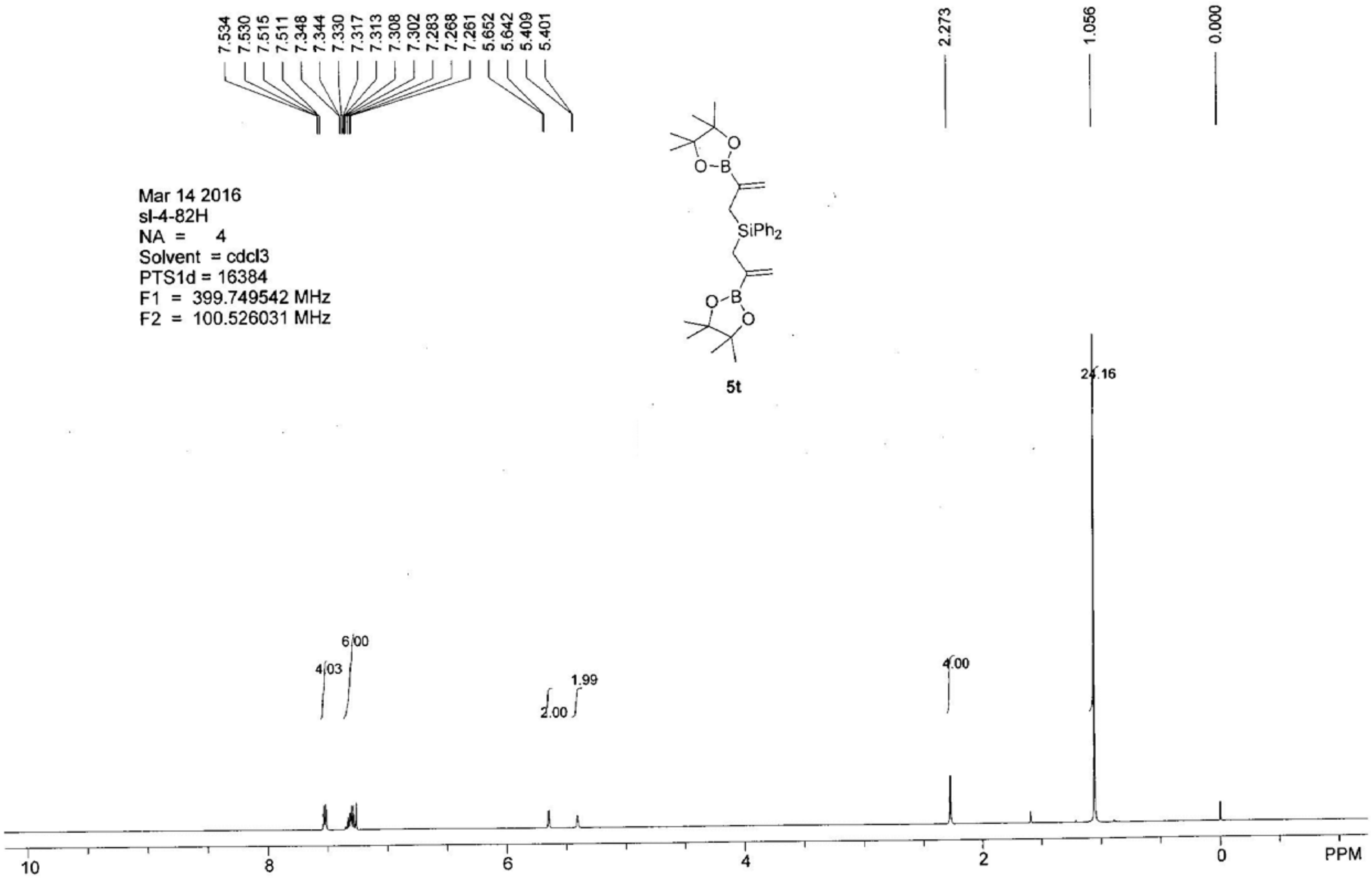
5r


137.716
133.980
129.137
127.786
124.956
77.321
77.000
76.689
64.983
31.646
28.882
-3.961
-4.036
Aug 31 2016
sl-6-5C
NA = 1000
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
B
OH
SiMe$_2$Ph
160
140
120
100
80
60
40
20
0
PPM

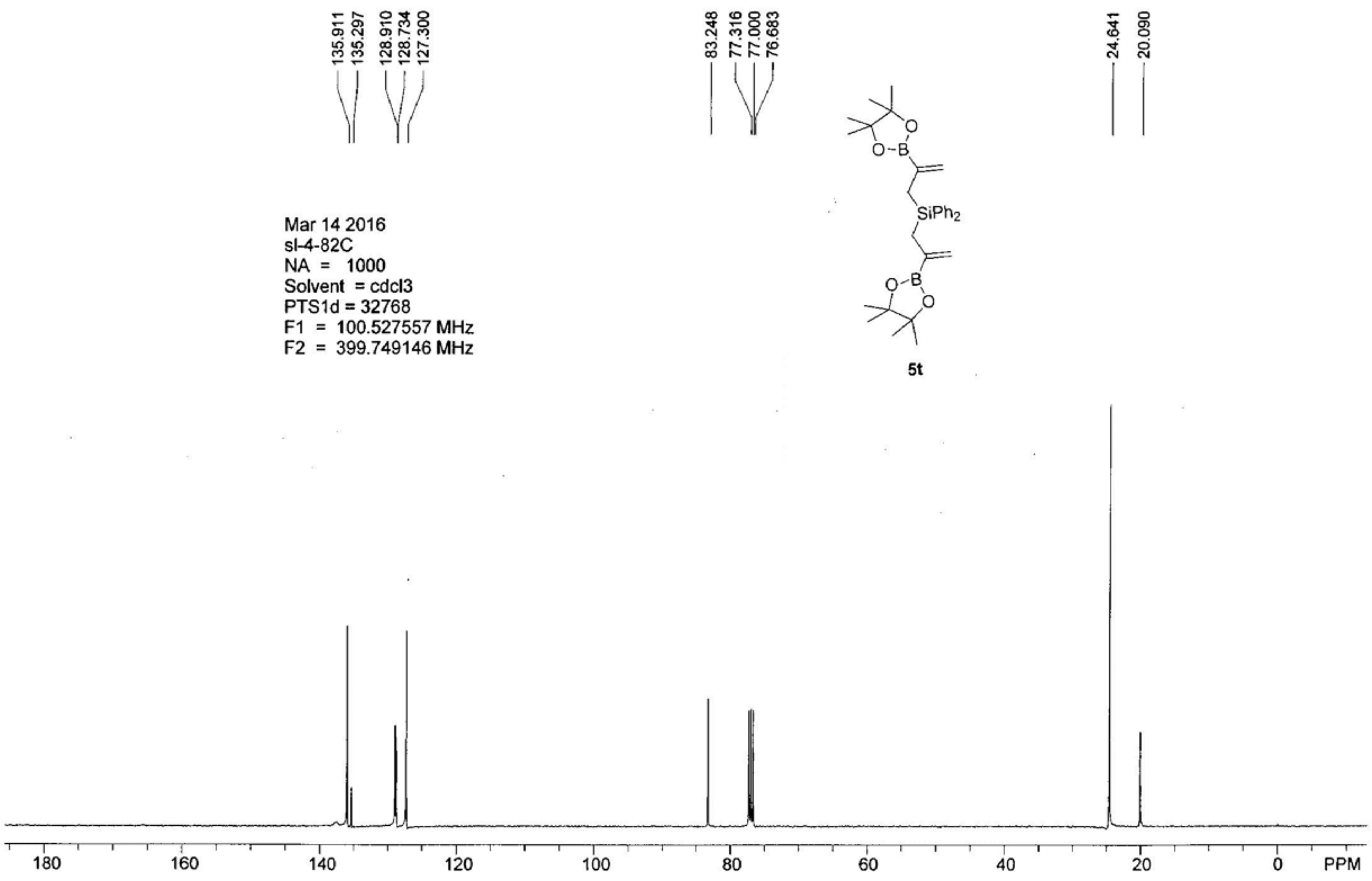
5r


7.518
7.513
7.505
7.503
7.497
7.494
7.302
7.295
7.290
7.282
7.278
7.261
5.647
5.637
5.389
5.381
1.960
1.152
0.263
0.000
Mar 14 2016
sl-4-83H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
SiPhMe
O
B
O
5s
2.00
2.95
2.00
1.98
4.04
24.33
3.03
10
8
6
4
2
0
PPM

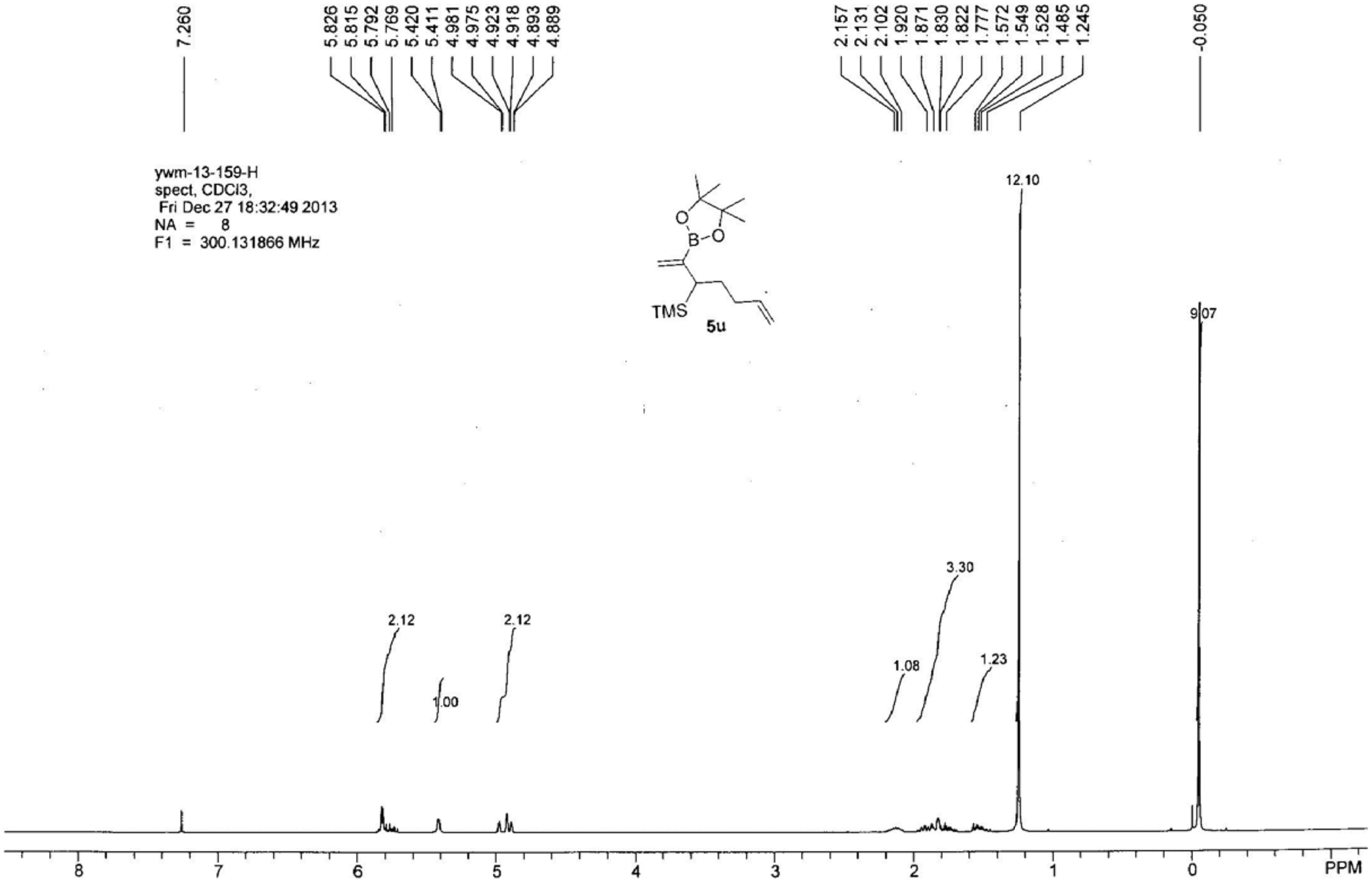

137.391
134.527
128.646
127.815
127.311
83.284
77.320
77.000
76.688
24.747
24.642
22.329
-5.830
Mar 14 2016
sl-4-83C
NA = 1000
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
O
B
SiPhMe
5s
160
140
120
100
80
60
40
20
0
PPM



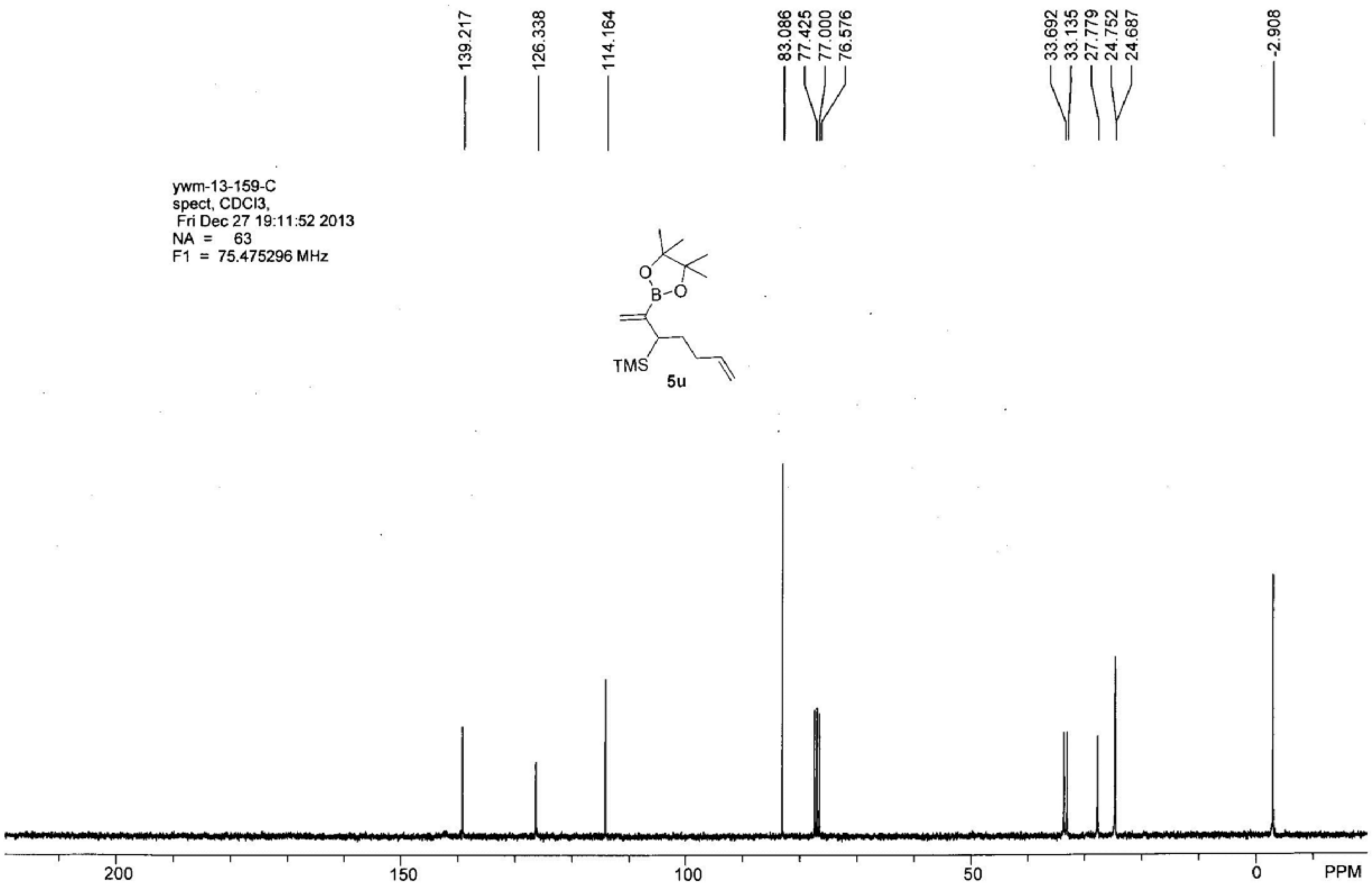
Mar 14 2016
sl-4-82H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz

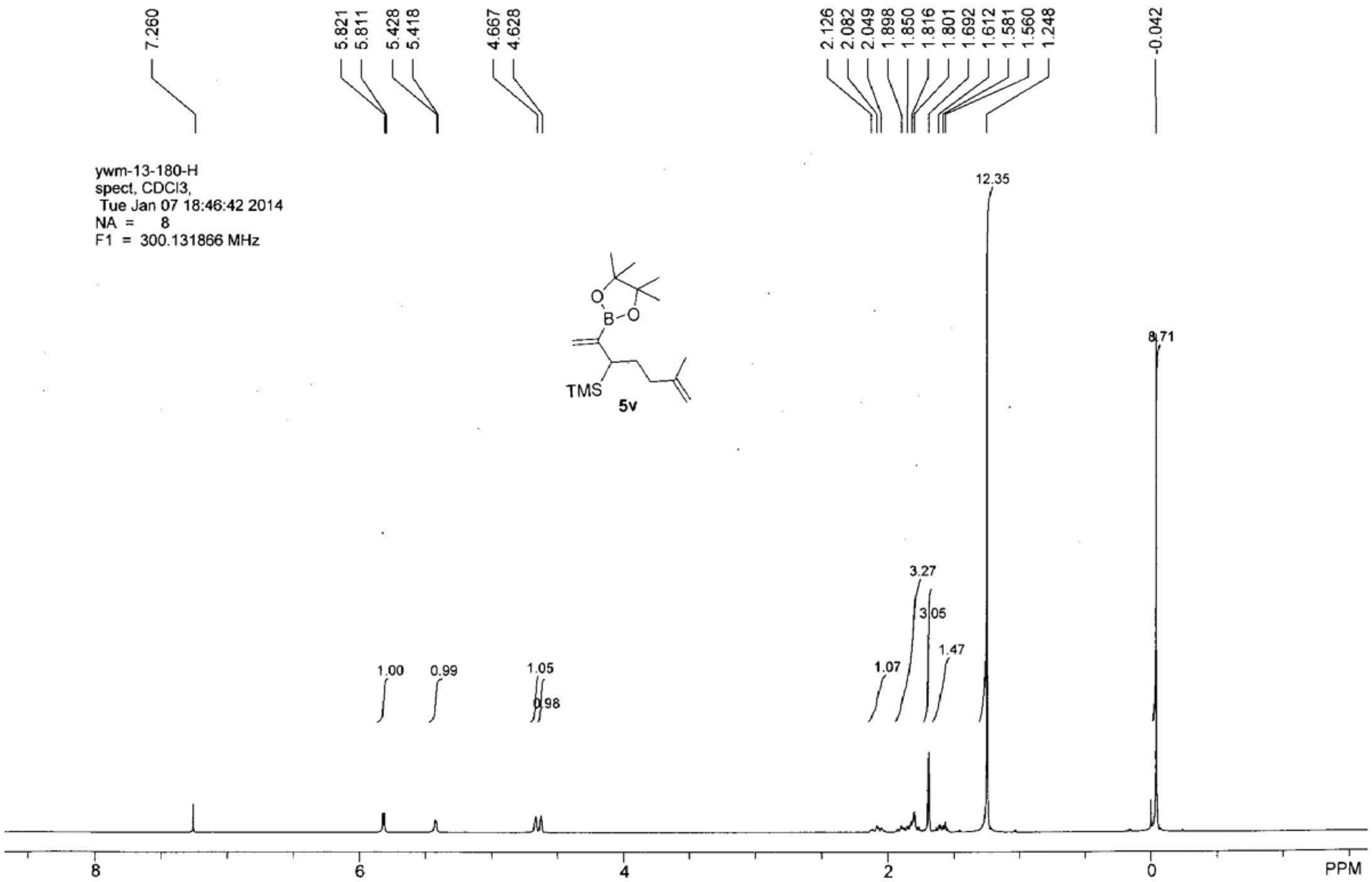

135.911
135.297
128.910
128.734
127.300
83.248
77.316
77.000
76.683
24.641
20.090
Mar 14 2016
sl-4-82C
NA = 1000
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
SiPh2
O
B
180
160
140
120
100
80
60
40
20
0
PPM

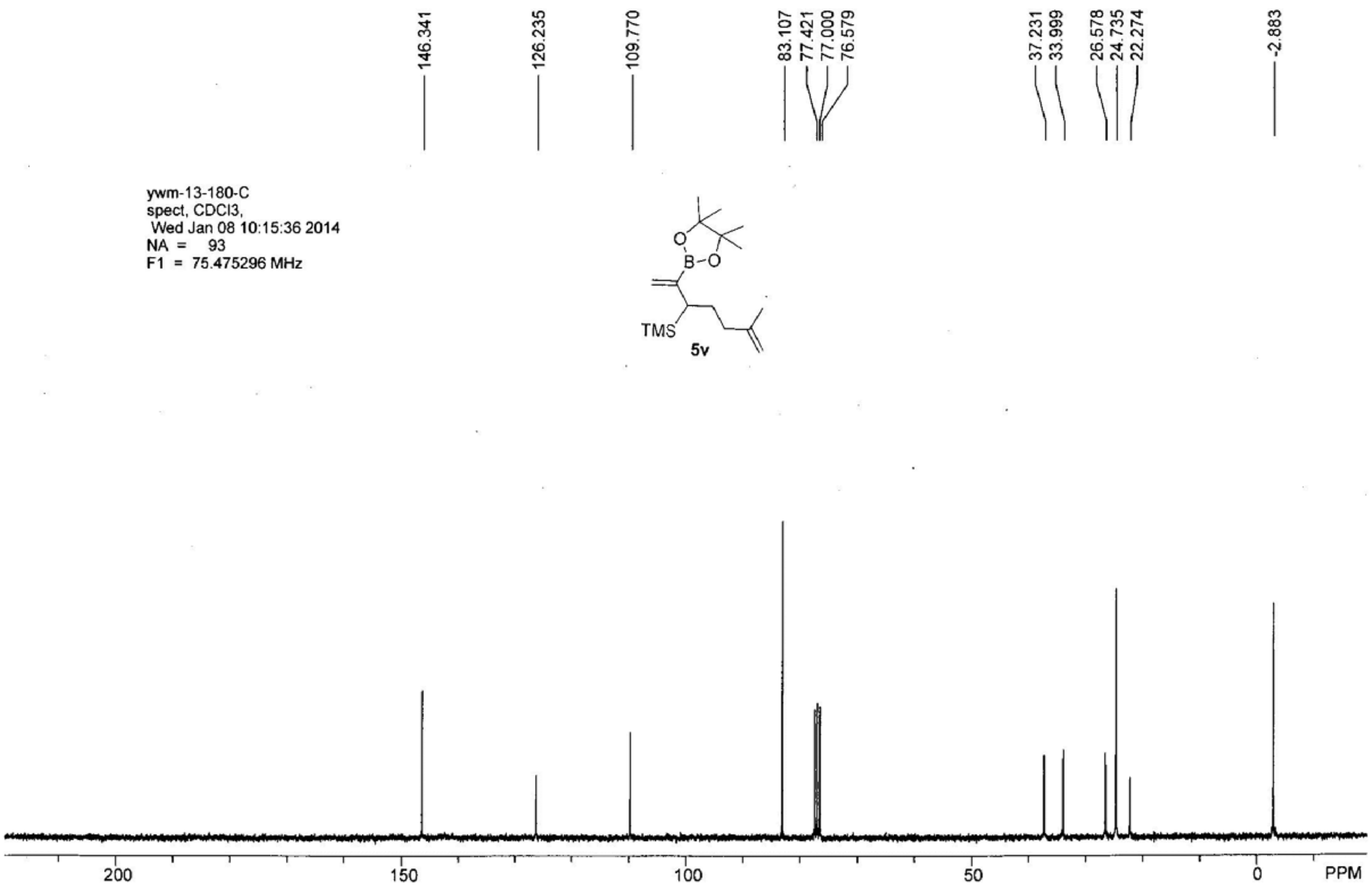
5t



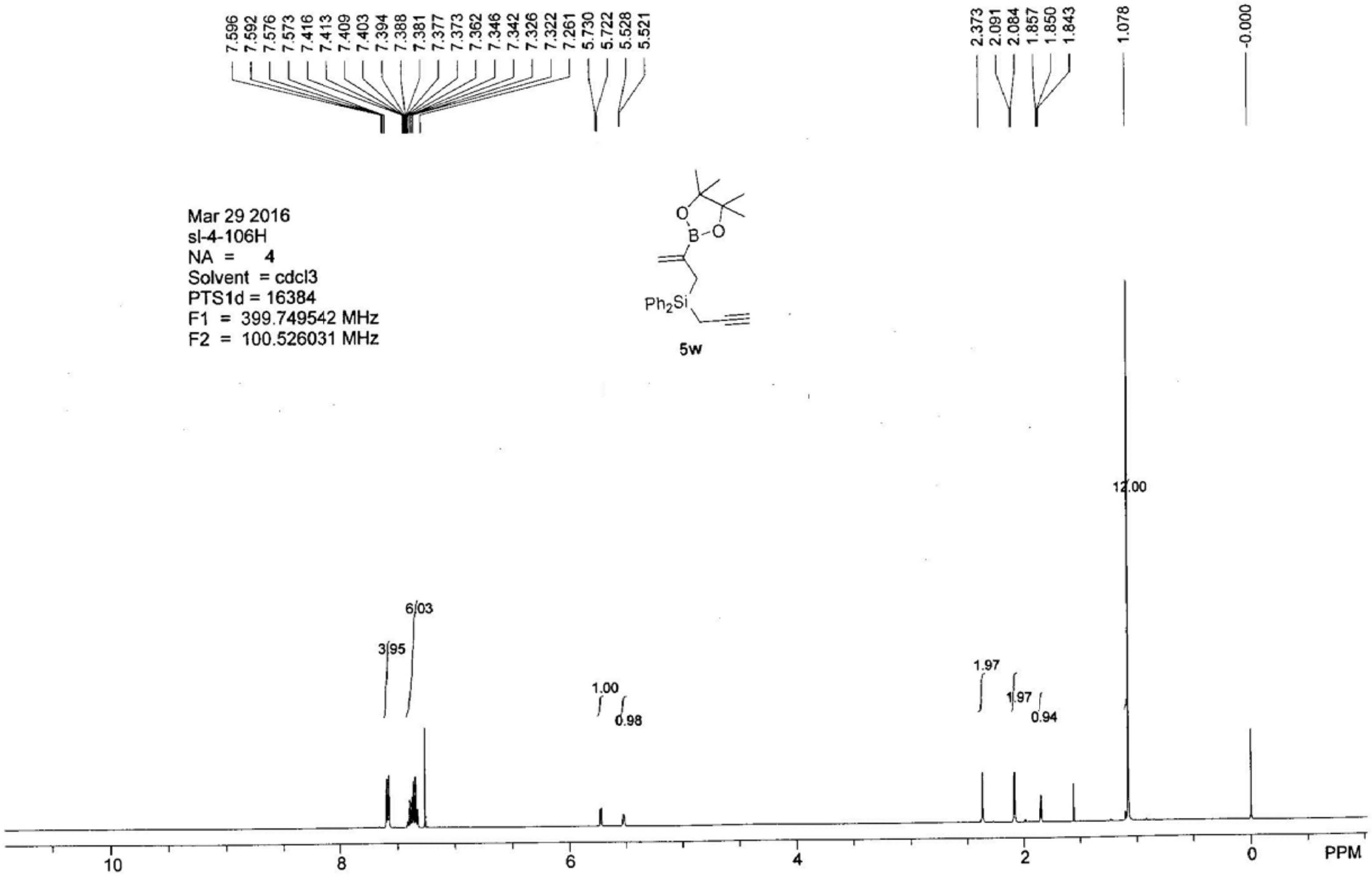
7.260
5.826
5.815
5.792
5.769
5.420
5.411
4.981
4.975
4.923
4.918
4.893
4.889
2.157
2.131
2.102
1.920
1.871
1.830
1.822
1.777
1.572
1.549
1.528
1.485
1.245
-0.050
ywm-13-159-H
spect, CDCl3,
Fri Dec 27 18:32:49 2013
NA = 8
F1 = 300.131866 MHz
O
B
O
TMS
5u
12.10
9.07
3.30
2.12
2.12
1.00
1.08
1.23
8
7
6
5
4
3
2
1
0
PPM

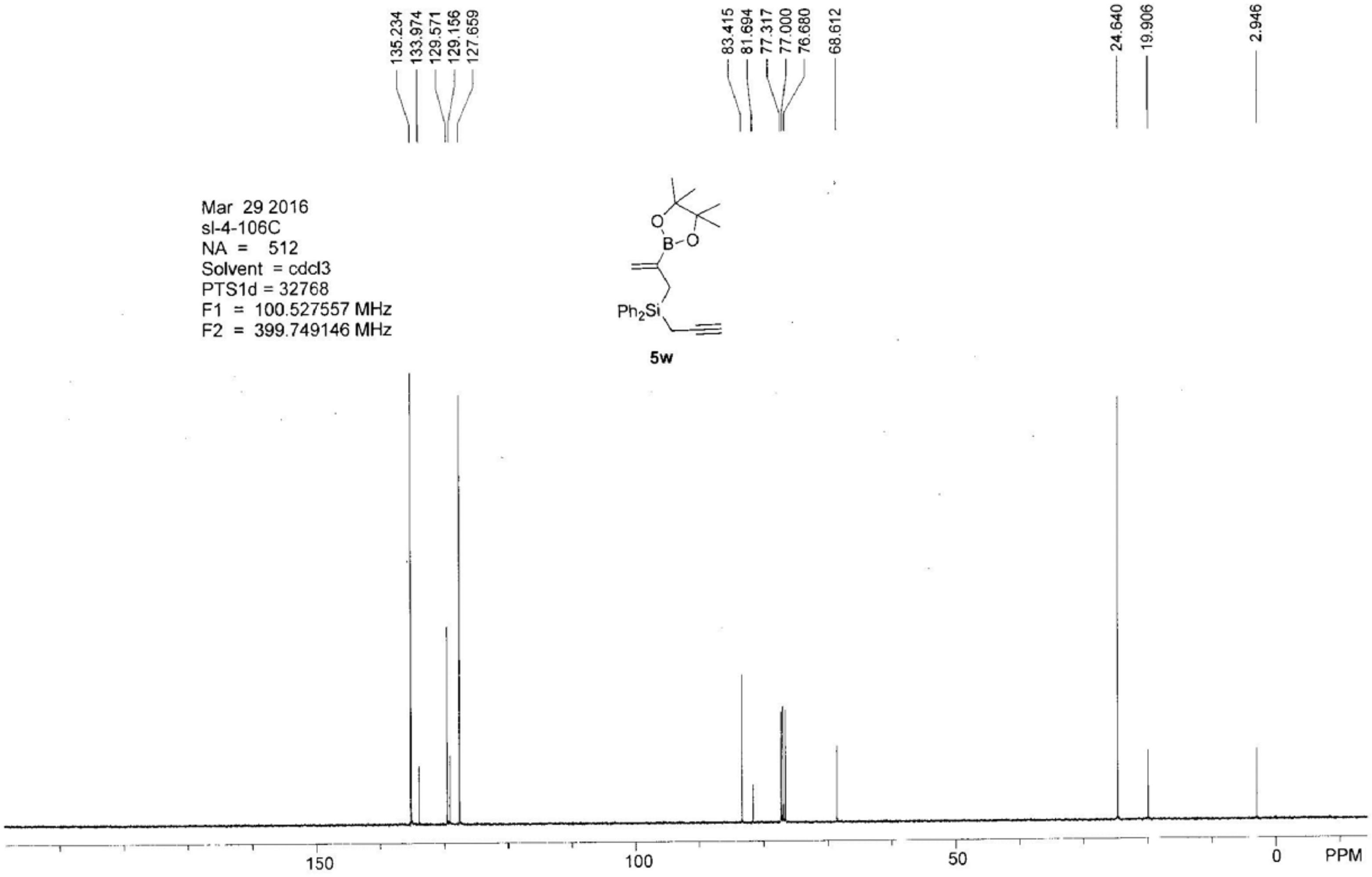

139.217
126.338
114.164
83.086
77.425
77.000
76.576
33.692
33.135
27.779
24.752
24.687
-2.908
ywm-13-159-C
spect, CDCl3,
Fri Dec 27 19:11:52 2013
NA = 63
F1 = 75.475296 MHz
O
B
O
TMS
5u
200
150
100
50
0
PPM

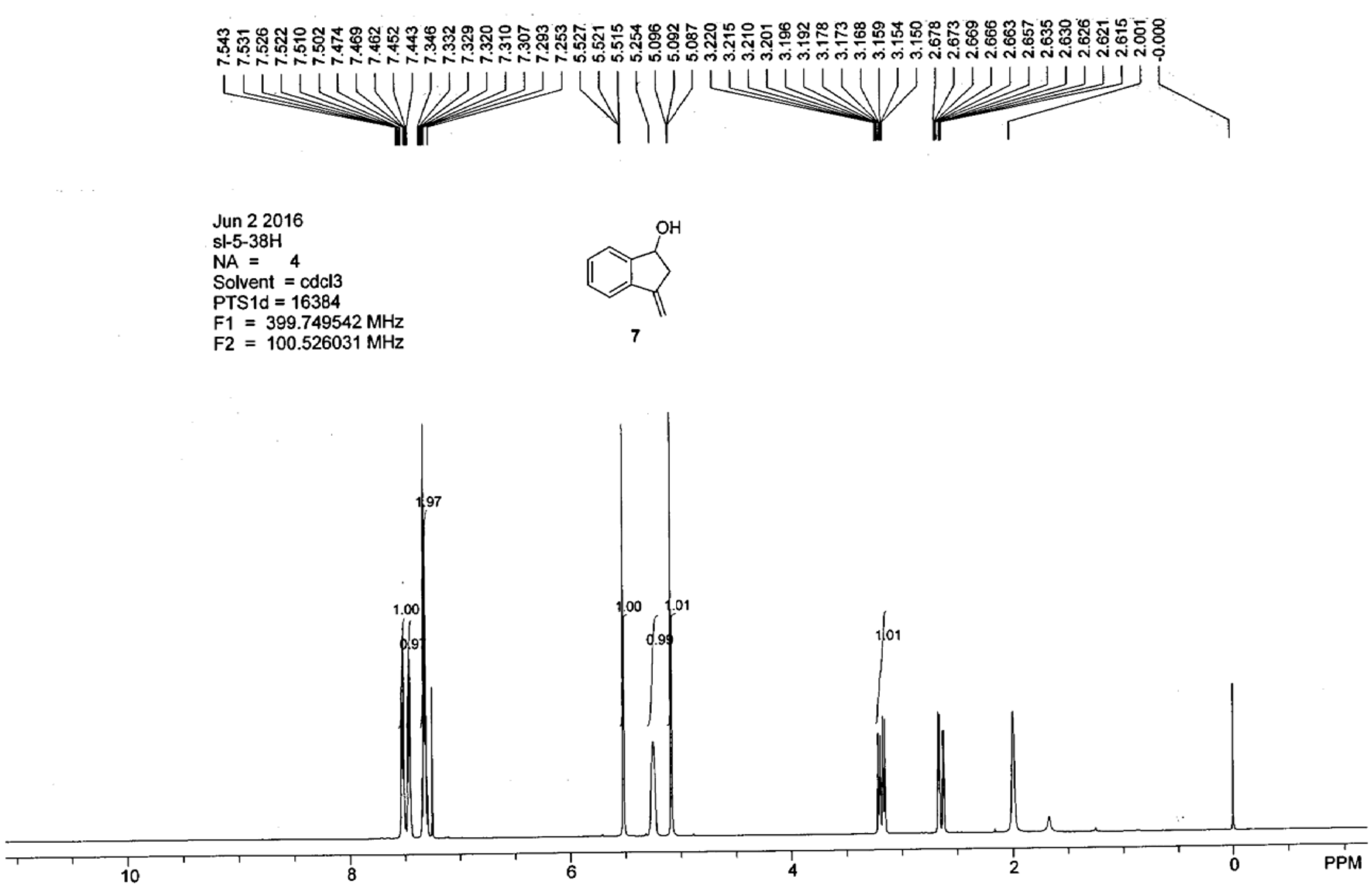

7.260
5.821
5.811
5.428
5.418
4.667
4.628
2.126
2.082
2.049
1.898
1.850
1.816
1.801
1.692
1.612
1.581
1.560
1.248
-0.042
ywm-13-180-H
spect, CDCl3,
Tue Jan 07 18:46:42 2014
NA = 8
F1 = 300.131866 MHz
O
B
O
TMS
5v
12.35
8.71
3.27
3.05
1.47
1.07
1.00
0.99
1.05
0.98
8
6
4
2
0
PPM

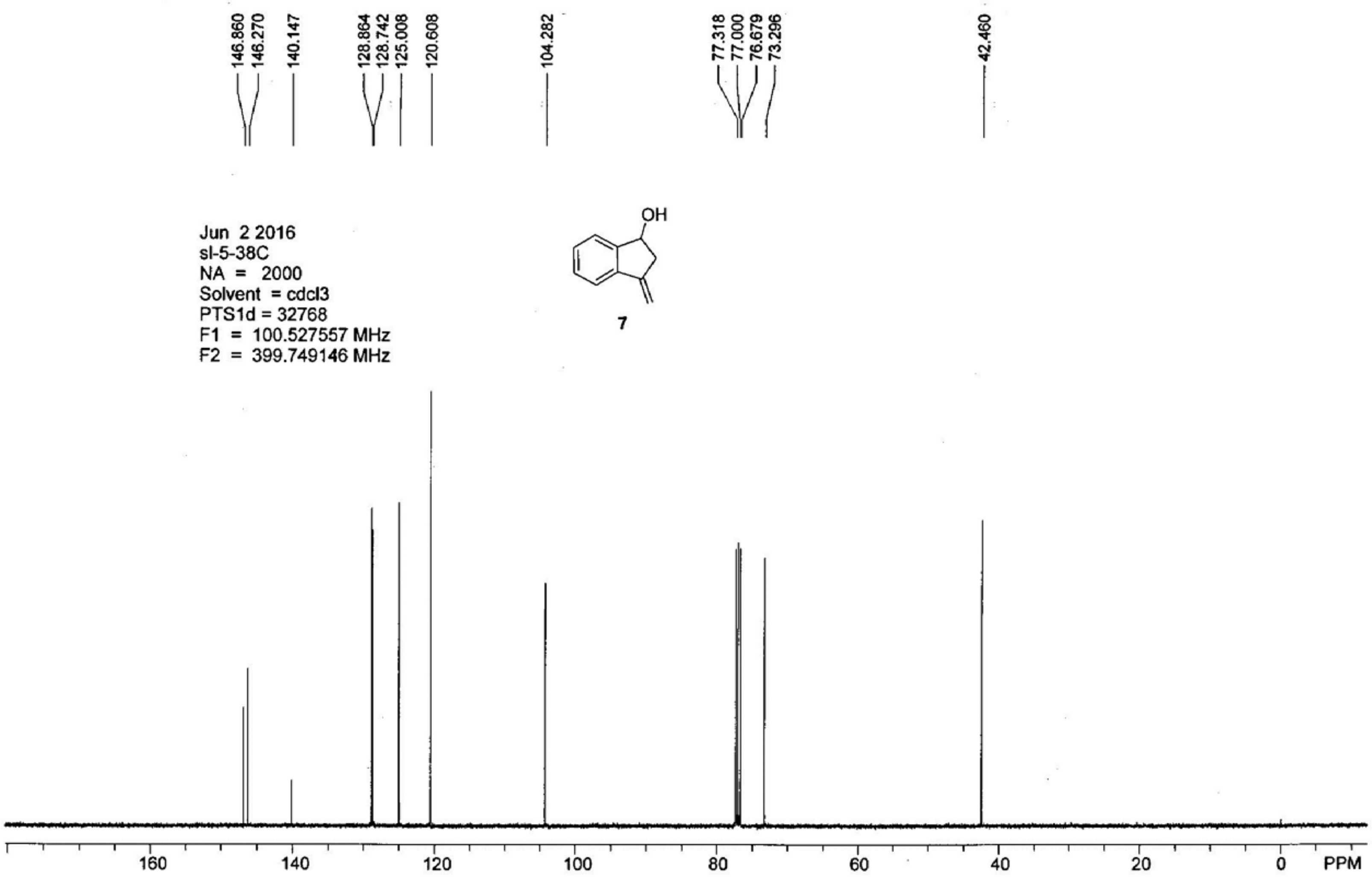


ywm-13-180-C
spect, CDCl3,
Wed Jan 08 10:15:36 2014
NA = 93
F1 = 75.475296 MHz

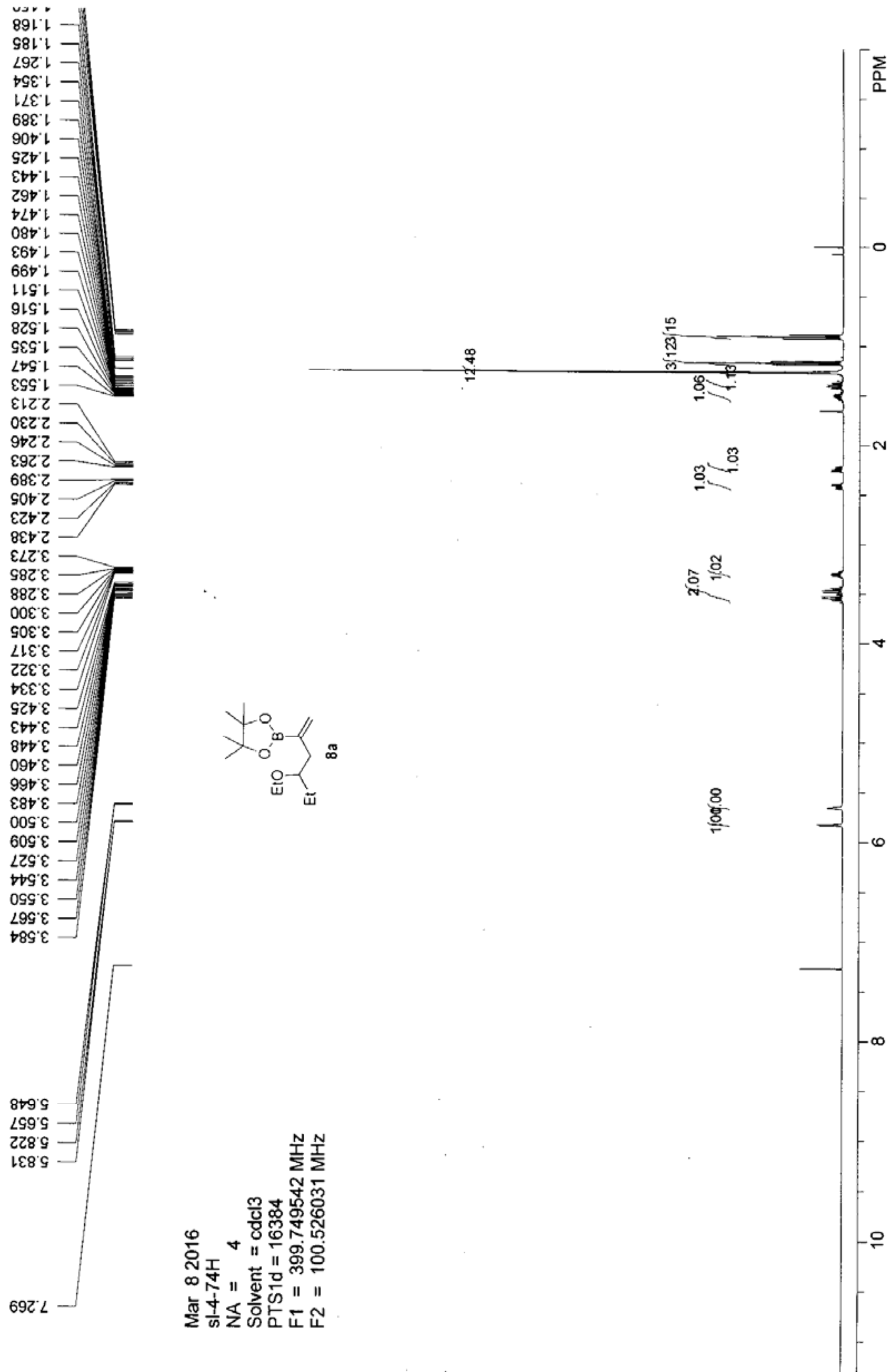

7.596
7.592
7.576
7.573
7.416
7.413
7.409
7.403
7.394
7.388
7.381
7.377
7.373
7.362
7.346
7.342
7.326
7.322
7.261
5.730
5.722
5.528
5.521
2.373
2.091
2.084
1.857
1.850
1.843
1.078
-0.000
Mar 29 2016
sl-4-106H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
O
B
O
Ph2Si
5w
6.03
3.95
1.00
0.98
1.97
1.97
0.94
12.00
10
8
6
4
2
0
PPM


135.234
133.974
129.571
129.156
127.659
83.415
81.694
77.317
77.000
76.680
68.612
24.640
19.906
2.946
Mar 29 2016
sl-4-106C
NA = 512
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
Ph2Si
B
O
O
5w
150
100
50
0
PPM


7.543
7.531
7.526
7.522
7.510
7.502
7.474
7.469
7.462
7.452
7.443
7.346
7.332
7.329
7.320
7.310
7.307
7.293
7.253
5.527
5.521
5.515
5.254
5.096
5.092
5.087
3.220
3.215
3.210
3.201
3.196
3.192
3.178
3.173
3.168
3.159
3.154
3.150
2.678
2.673
2.669
2.666
2.663
2.657
2.635
2.630
2.626
2.621
2.615
2.001
-0.000
Jun 2 2016
sl-5-38H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
OH
7
1.97
1.00
0.97
1.00
0.99
1.01
1.01
10
8
6
4
2
0
PPM

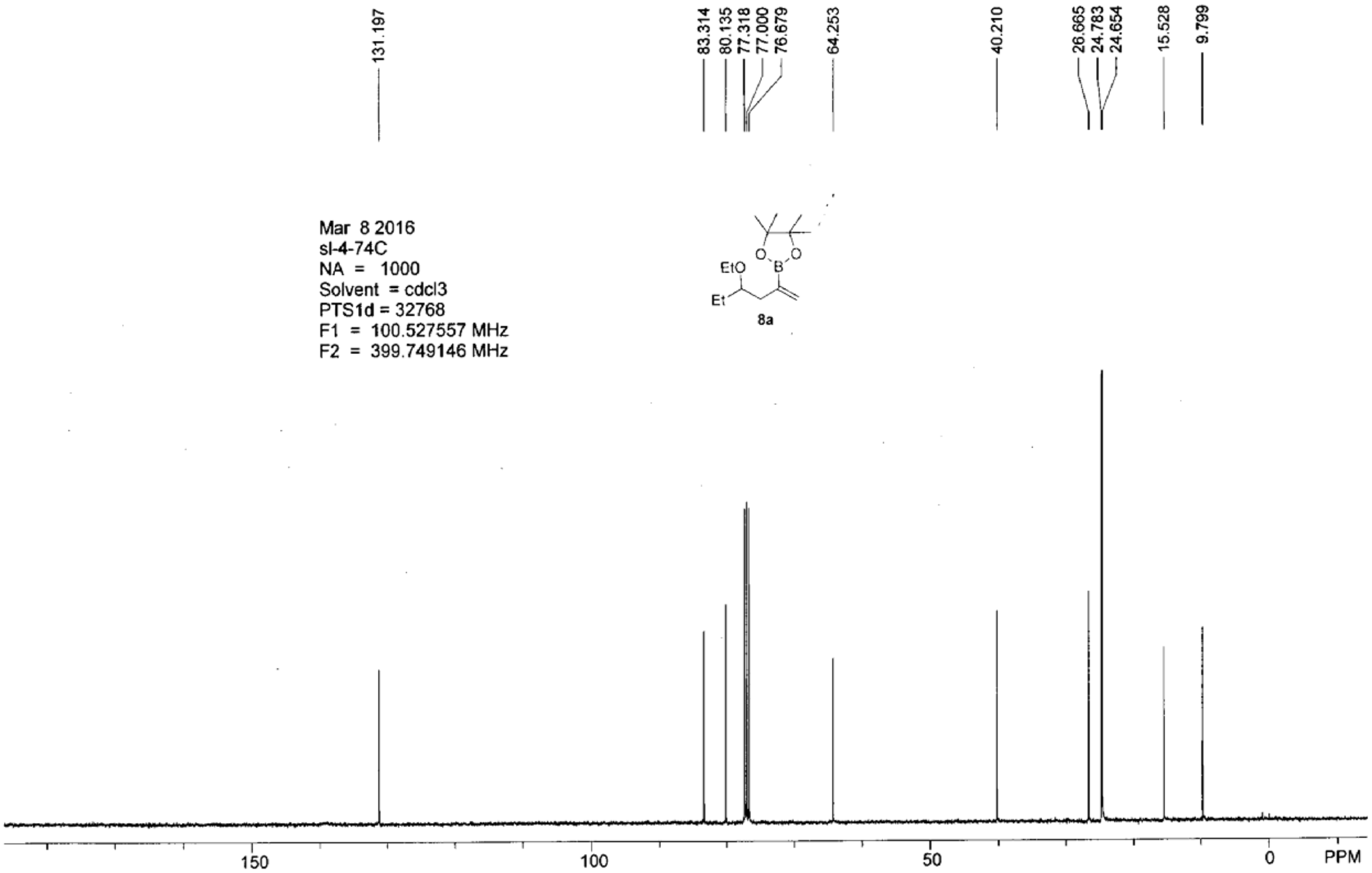

146.860
146.270
140.147
128.864
128.742
125.008
120.608
104.282
77.318
77.000
76.679
73.296
42.460
Jun 2 2016
sl-5-38C
NA = 2000
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
OH
160
140
120
100
80
60
40
20
0
PPM

7



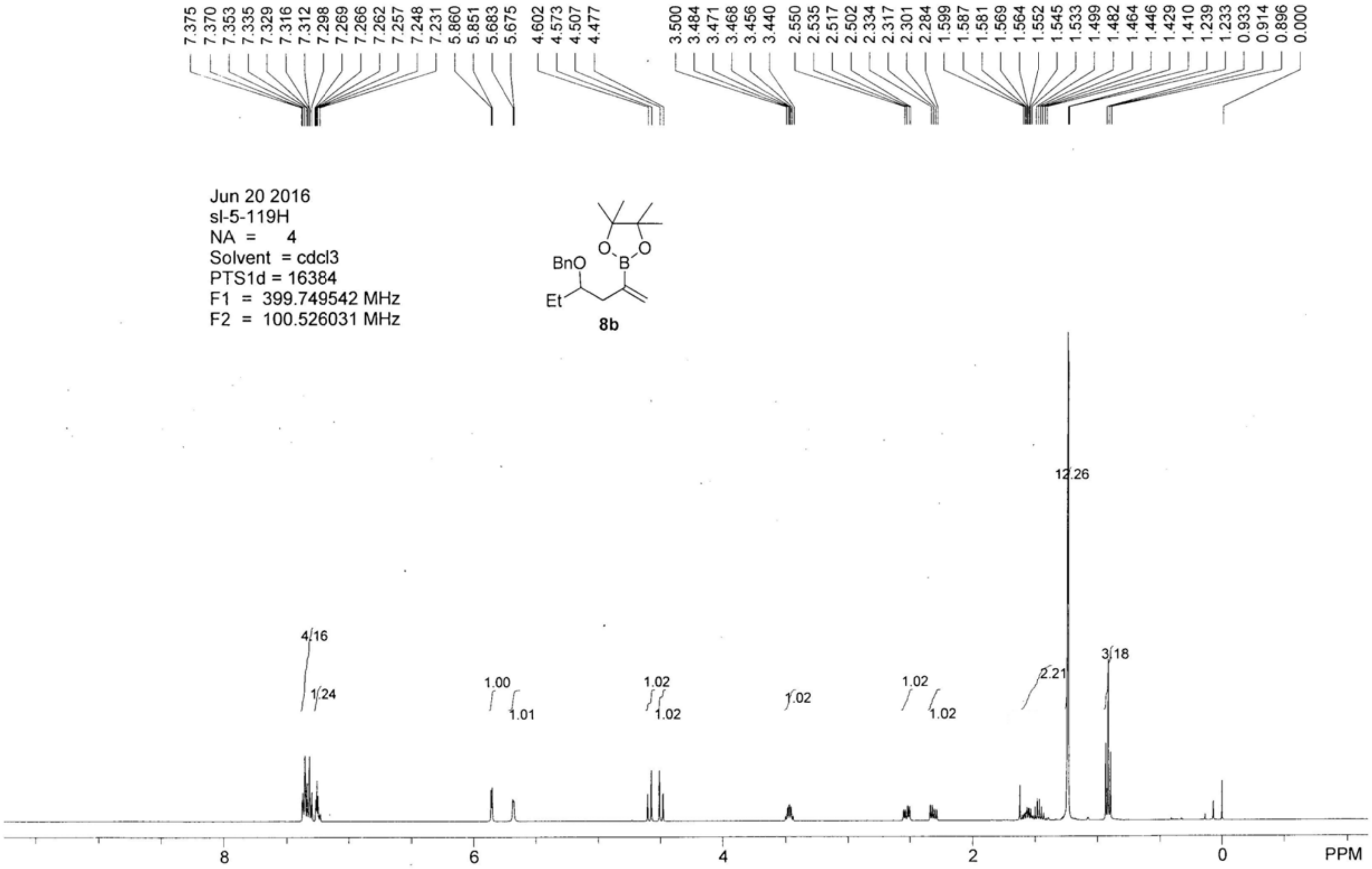
8a

Mar 8 2016
sl-4-74H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz



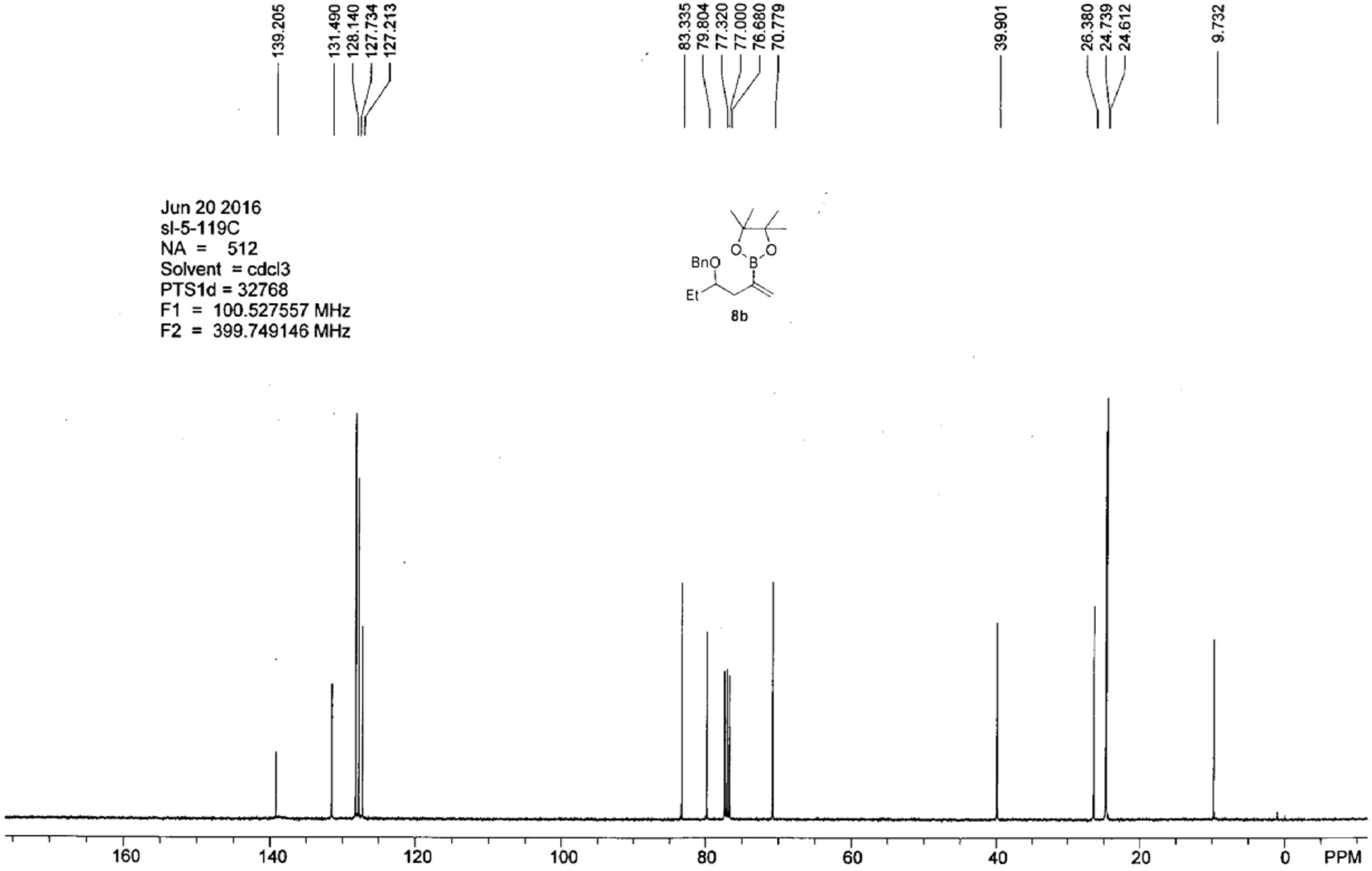
Mar 8 2016
sl-4-74C
NA = 1000
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz

8a



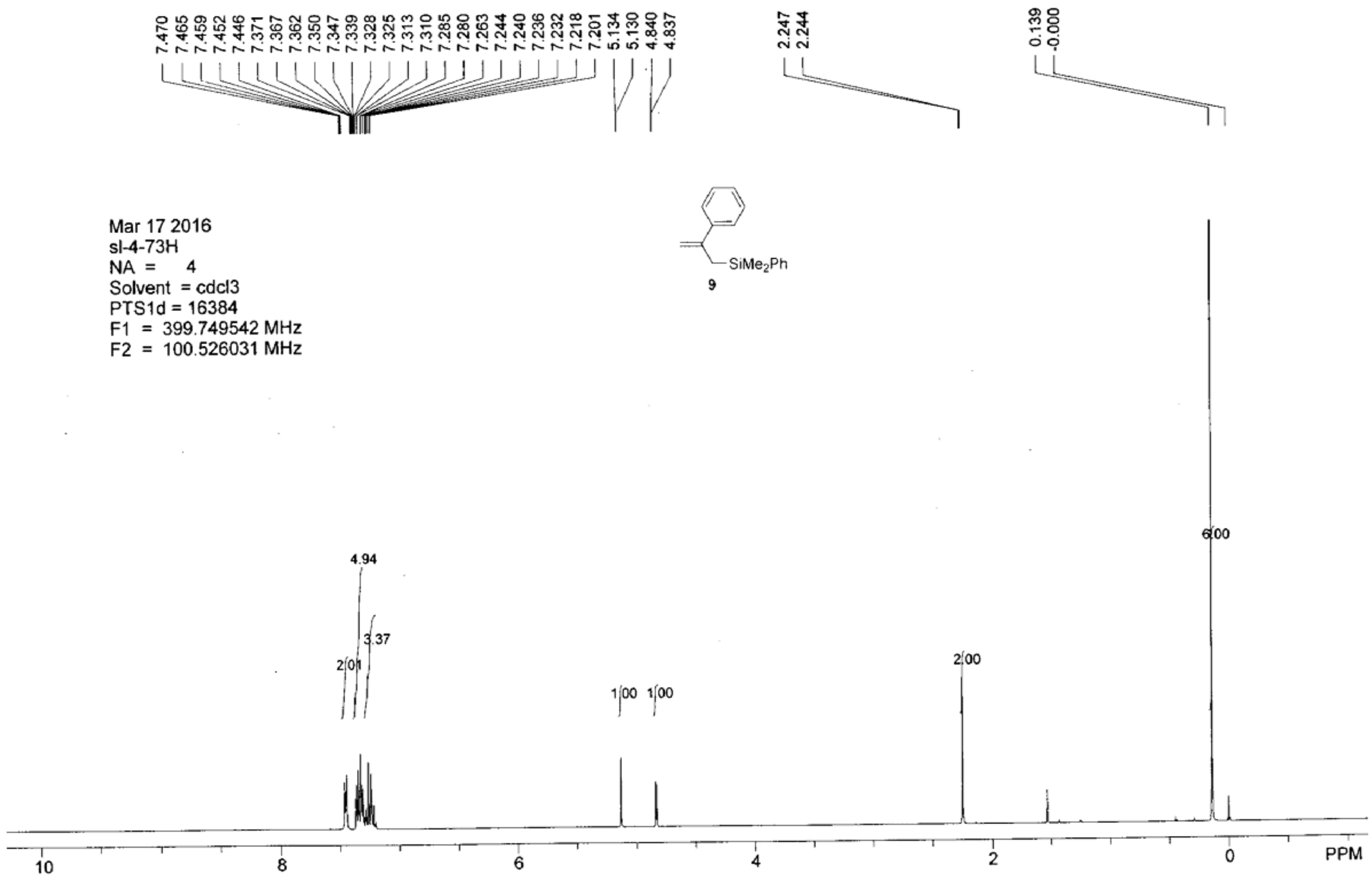
Jun 20 2016
sl-5-119H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz

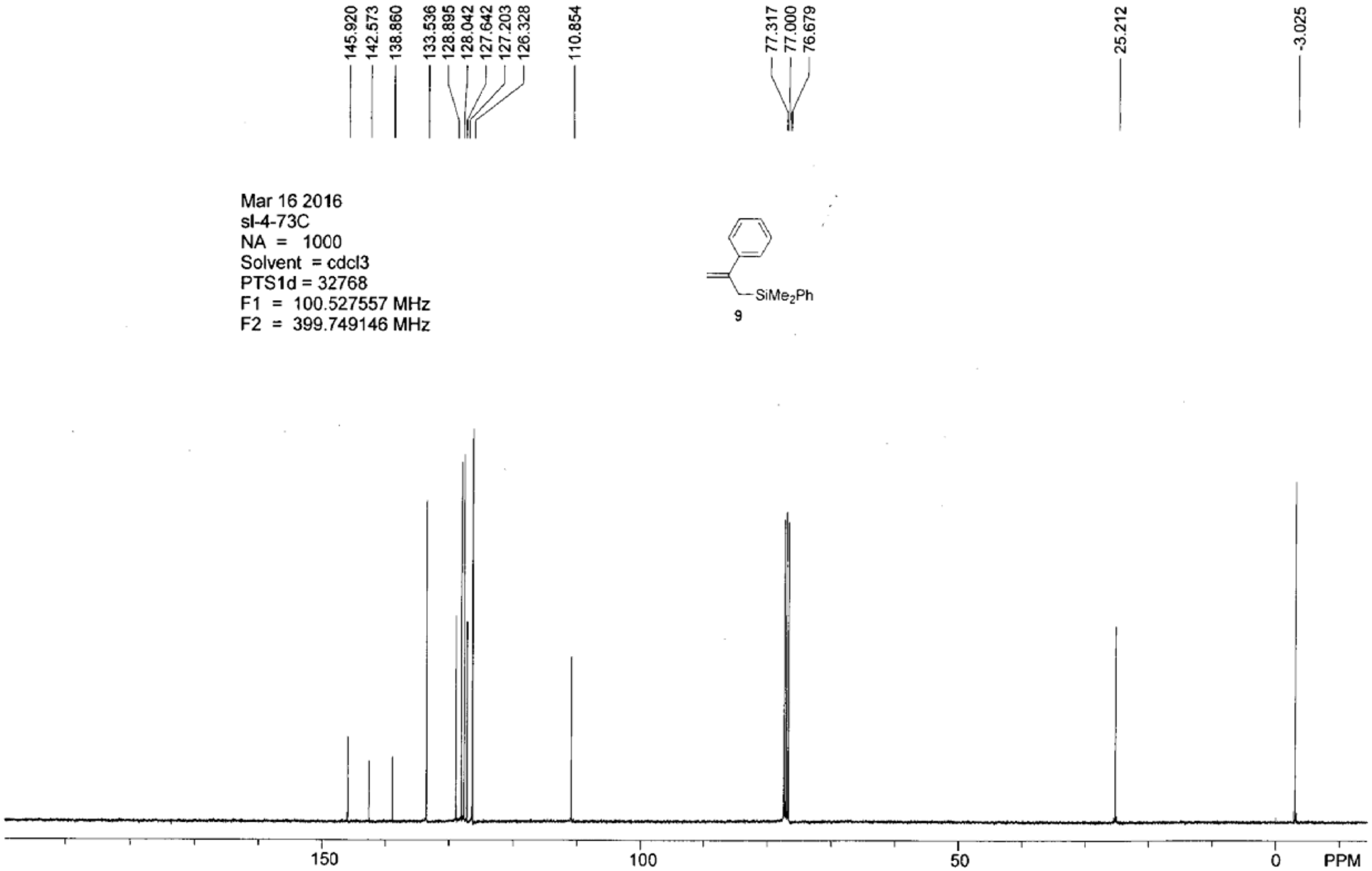
8b



8b

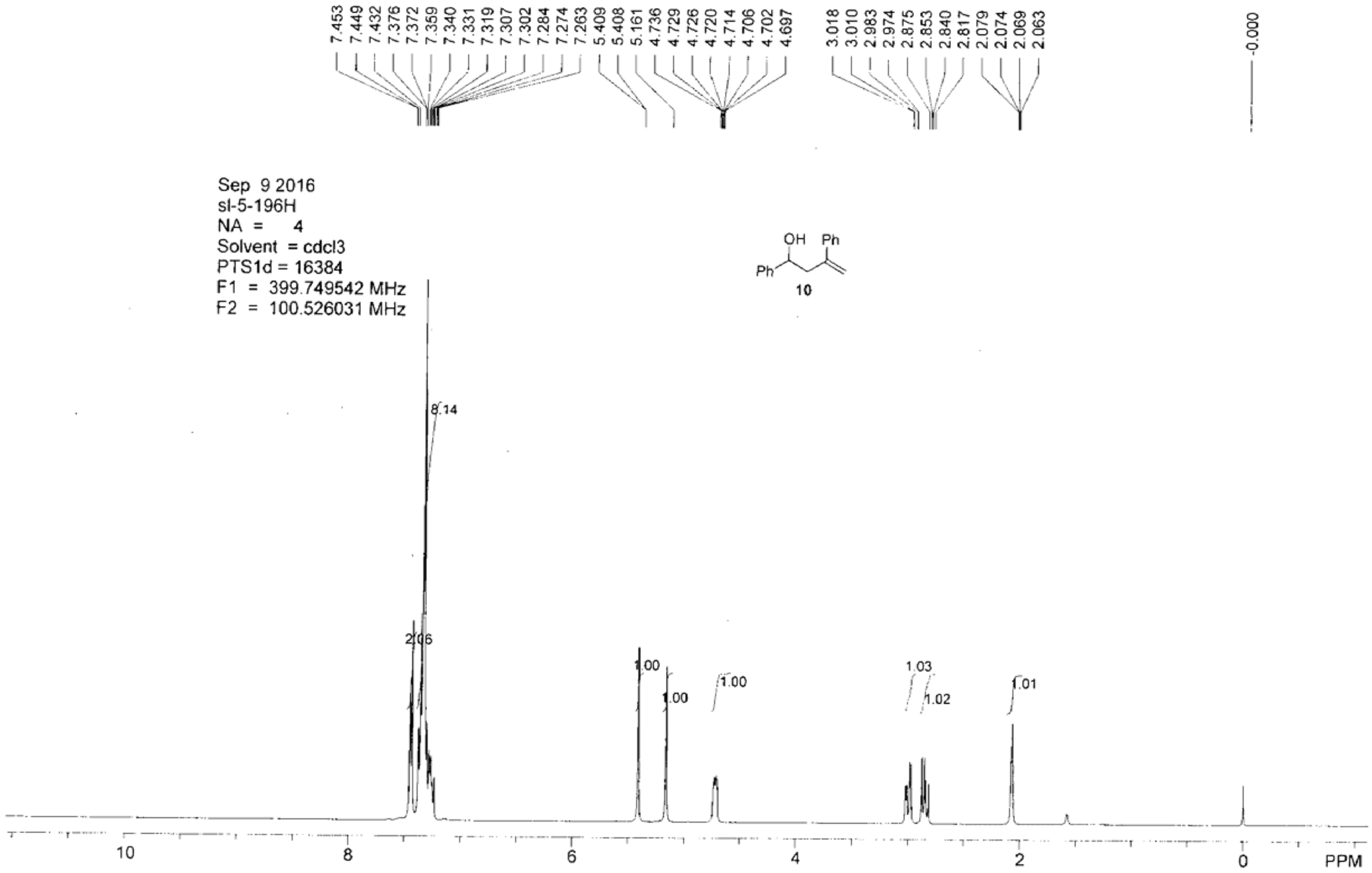
Jun 20 2016
sl-5-119C
NA = 512
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz

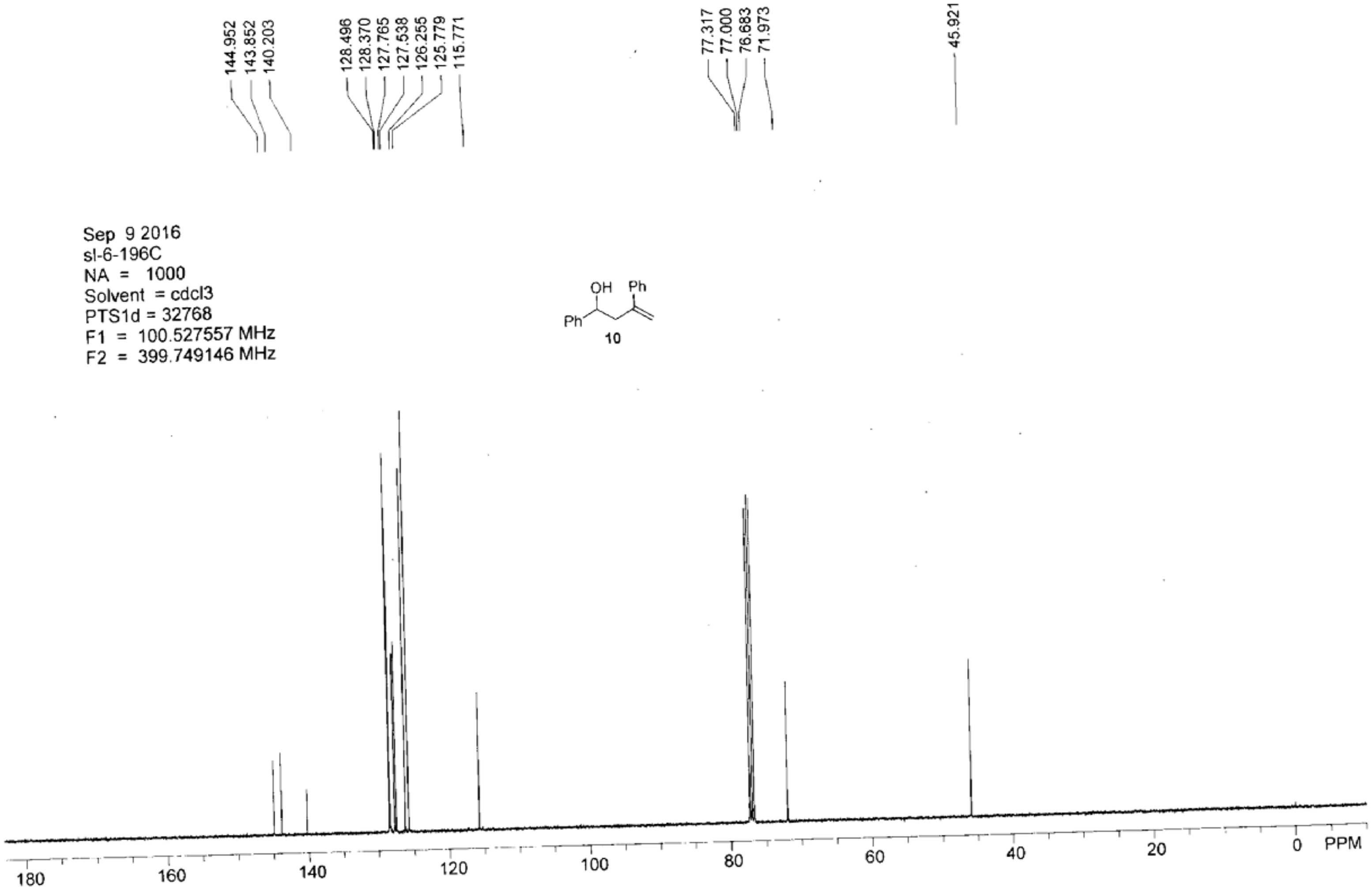

7.470
7.465
7.459
7.452
7.446
7.371
7.367
7.362
7.350
7.347
7.339
7.328
7.325
7.313
7.310
7.285
7.280
7.263
7.244
7.240
7.236
7.232
7.218
7.201
5.134
5.130
4.840
4.837
2.247
2.244
0.139
-0.000
Mar 17 2016
sl-4-73H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
SiMe2Ph
9
4.94
3.37
2.01
1.00
1.00
2.00
6.00
10
8
6
4
2
0
PPM



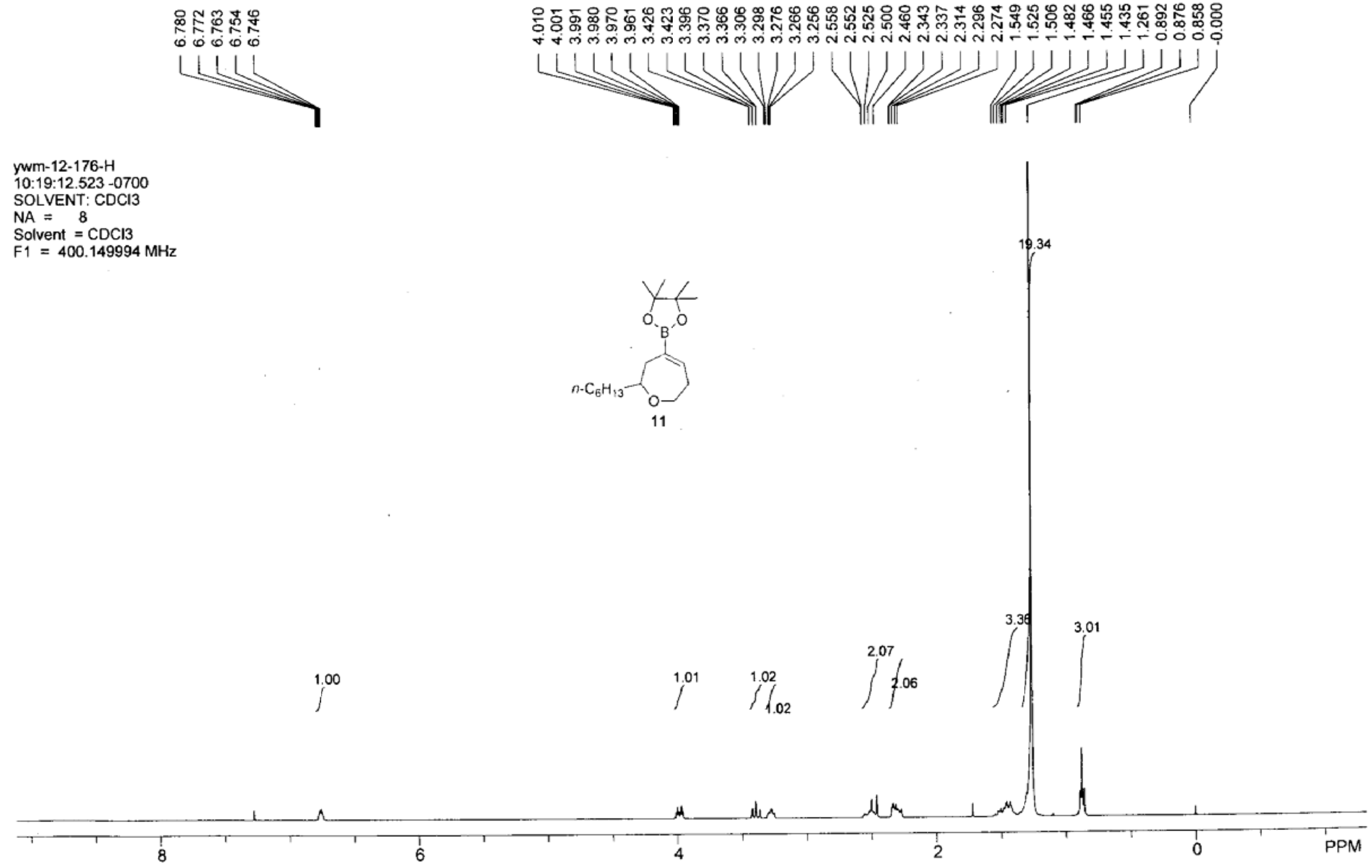
9

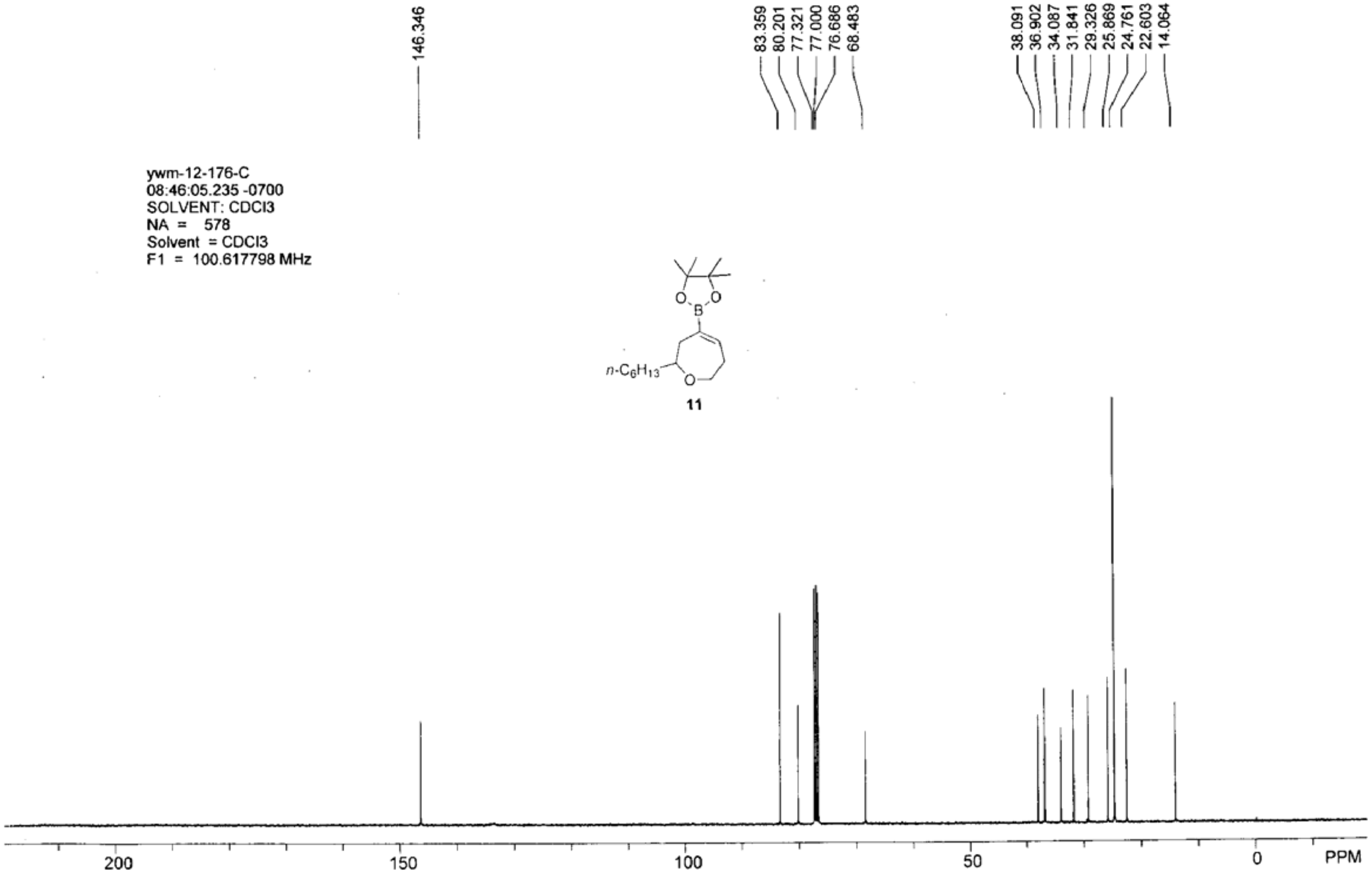
Mar 16 2016
sl-4-73C
NA = 1000
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz

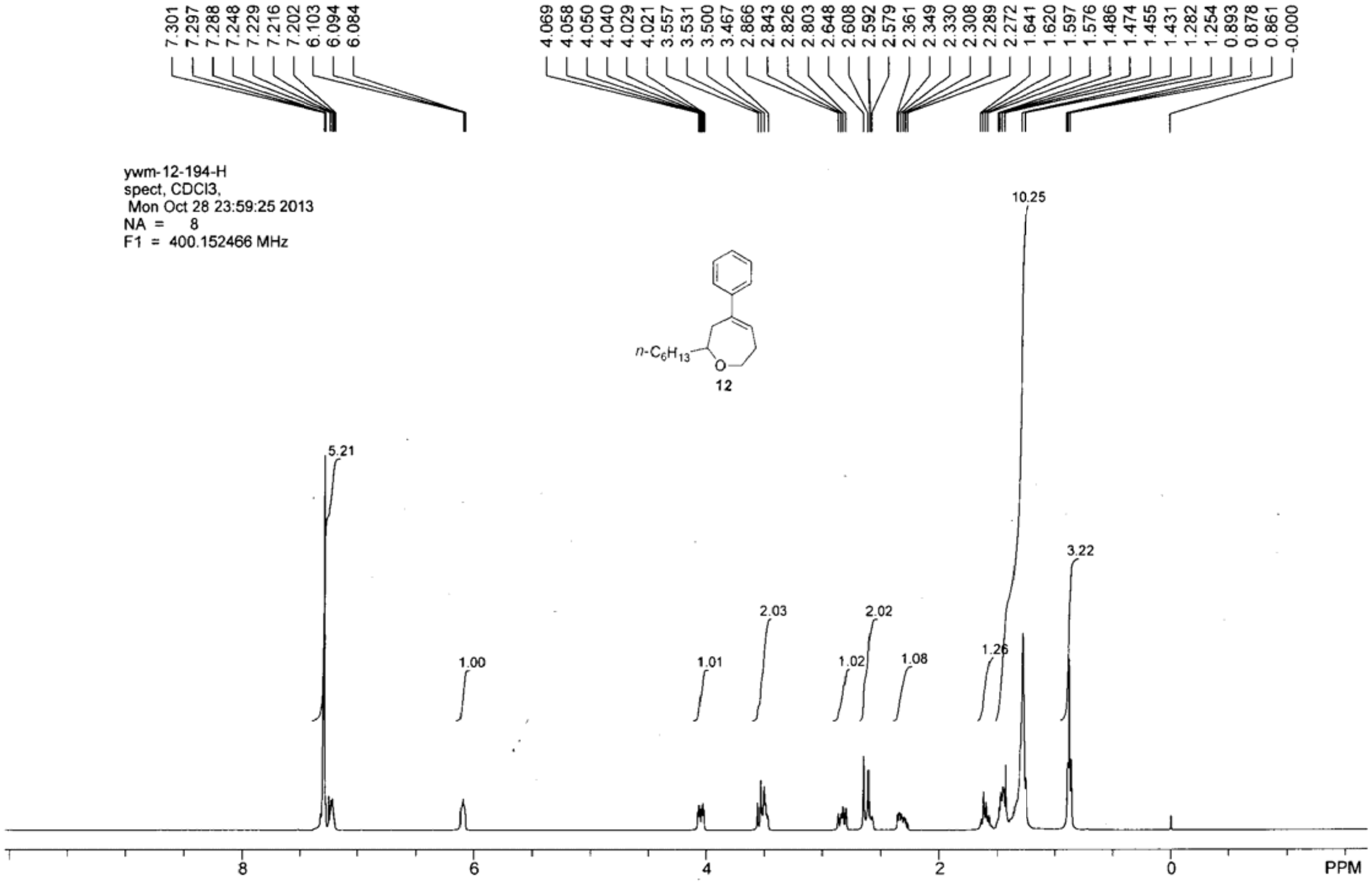

7.453
7.449
7.432
7.376
7.372
7.359
7.340
7.331
7.319
7.307
7.302
7.284
7.274
7.263
5.409
5.408
5.161
4.736
4.729
4.726
4.720
4.714
4.706
4.702
4.697
3.018
3.010
2.983
2.974
2.875
2.853
2.840
2.817
2.079
2.074
2.069
2.063
-0.000
Sep 9 2016
sl-5-196H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
OH
Ph
Ph
10
8.14
2.06
1.00
1.00
1.00
1.03
1.02
1.01
10
8
6
4
2
0
PPM

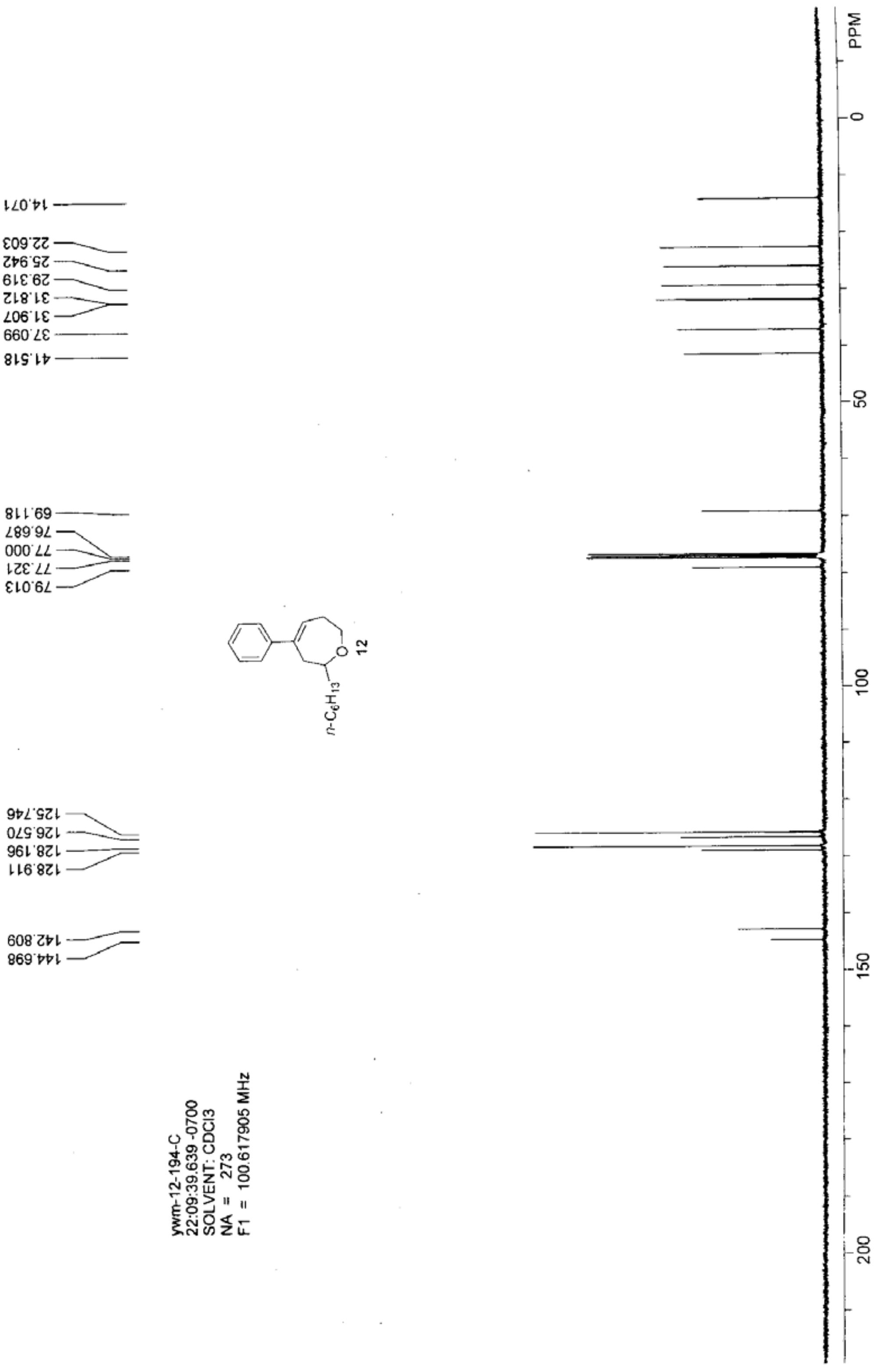

Sep 9 2016
sl-6-196C
NA = 1000
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz

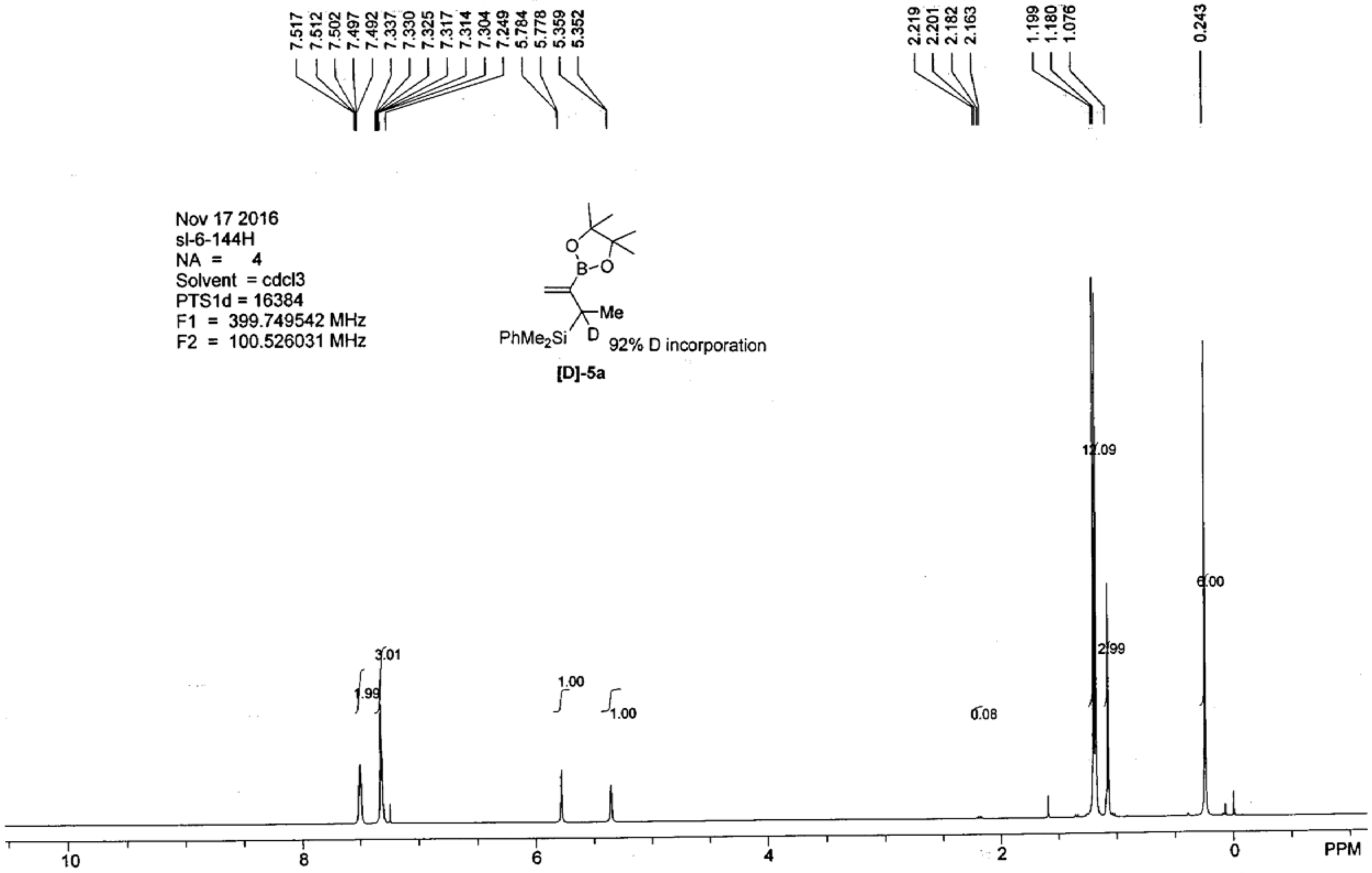
10


6.780
6.772
6.763
6.754
6.746
4.010
4.001
3.991
3.980
3.970
3.961
3.426
3.423
3.396
3.370
3.366
3.306
3.298
3.276
3.266
3.256
2.558
2.552
2.525
2.500
2.460
2.343
2.337
2.314
2.296
2.274
1.549
1.525
1.506
1.482
1.466
1.455
1.435
1.261
0.892
0.876
0.858
-0.000
ywm-12-176-H
10:19:12.523 -0700
SOLVENT: CDCl3
NA = 8
Solvent = CDCl3
F1 = 400.149994 MHz
O
B
O
n-C6H13
O
11
19.34
3.36
3.01
2.07
2.06
1.02
1.02
1.01
1.00
8
6
4
2
0
PPM

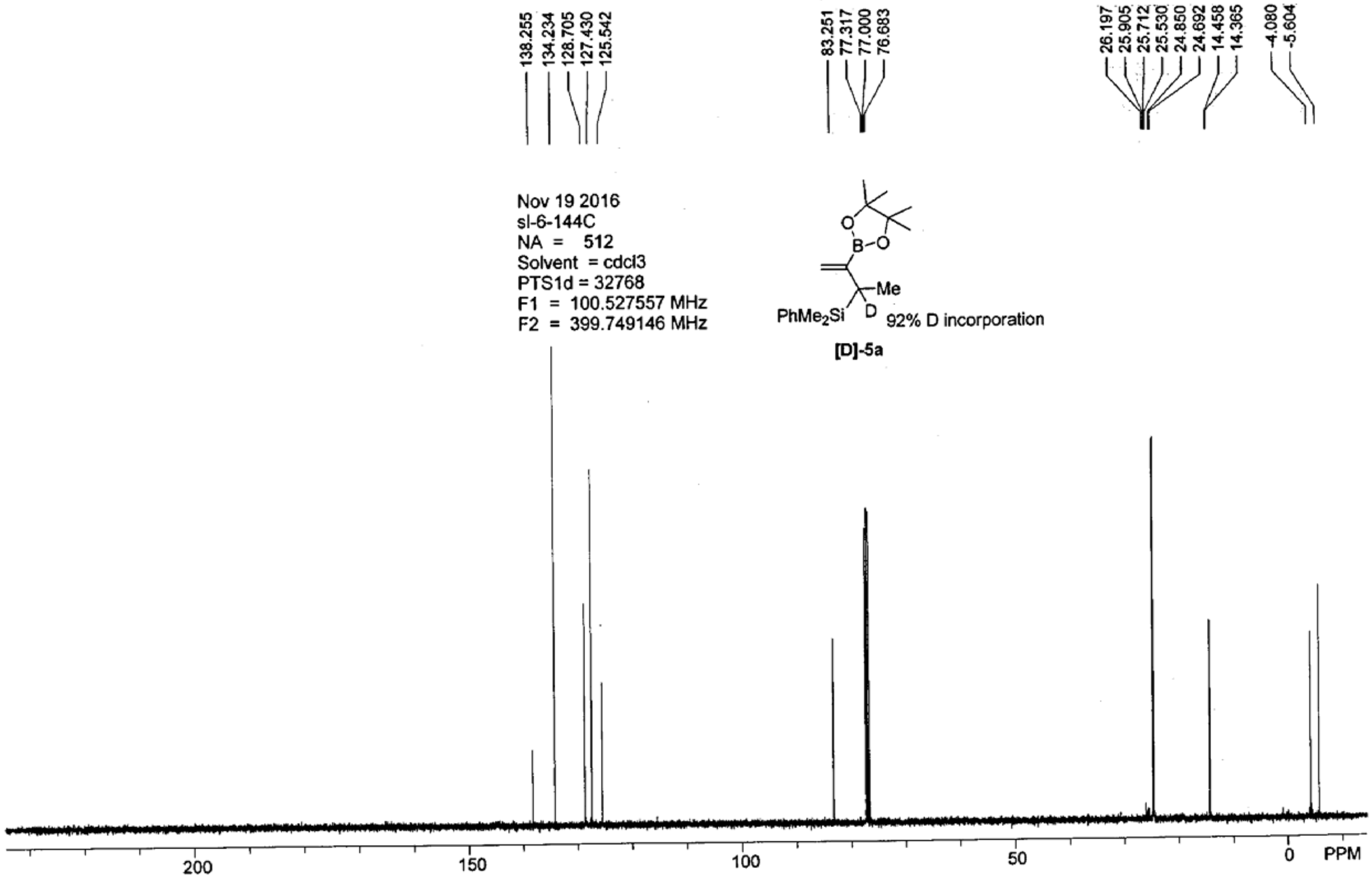

146.346
83.359
80.201
77.321
77.000
76.686
68.483
38.091
36.902
34.087
31.841
29.326
25.869
24.761
22.603
14.064
ywm-12-176-C
08:46:05.235 -0700
SOLVENT: CDCl3
NA = 578
Solvent = CDCl3
F1 = 100.617798 MHz
n-C6H13
O
B
O
O
11
200
150
100
50
0
PPM


7.301
7.297
7.288
7.248
7.229
7.216
7.202
6.103
6.094
6.084
4.069
4.058
4.050
4.040
4.029
4.021
3.557
3.531
3.500
3.467
2.866
2.843
2.826
2.803
2.648
2.608
2.592
2.579
2.361
2.349
2.330
2.308
2.289
2.272
1.641
1.620
1.597
1.576
1.486
1.474
1.455
1.431
1.282
1.254
0.893
0.878
0.861
-0.000
ywm-12-194-H
spect, CDCl3,
Mon Oct 28 23:59:25 2013
NA = 8
F1 = 400.152466 MHz
n-C6H13
O
12
5.21
1.00
1.01
2.03
1.02
2.02
1.08
1.26
10.25
3.22
8
6
4
2
0
PPM

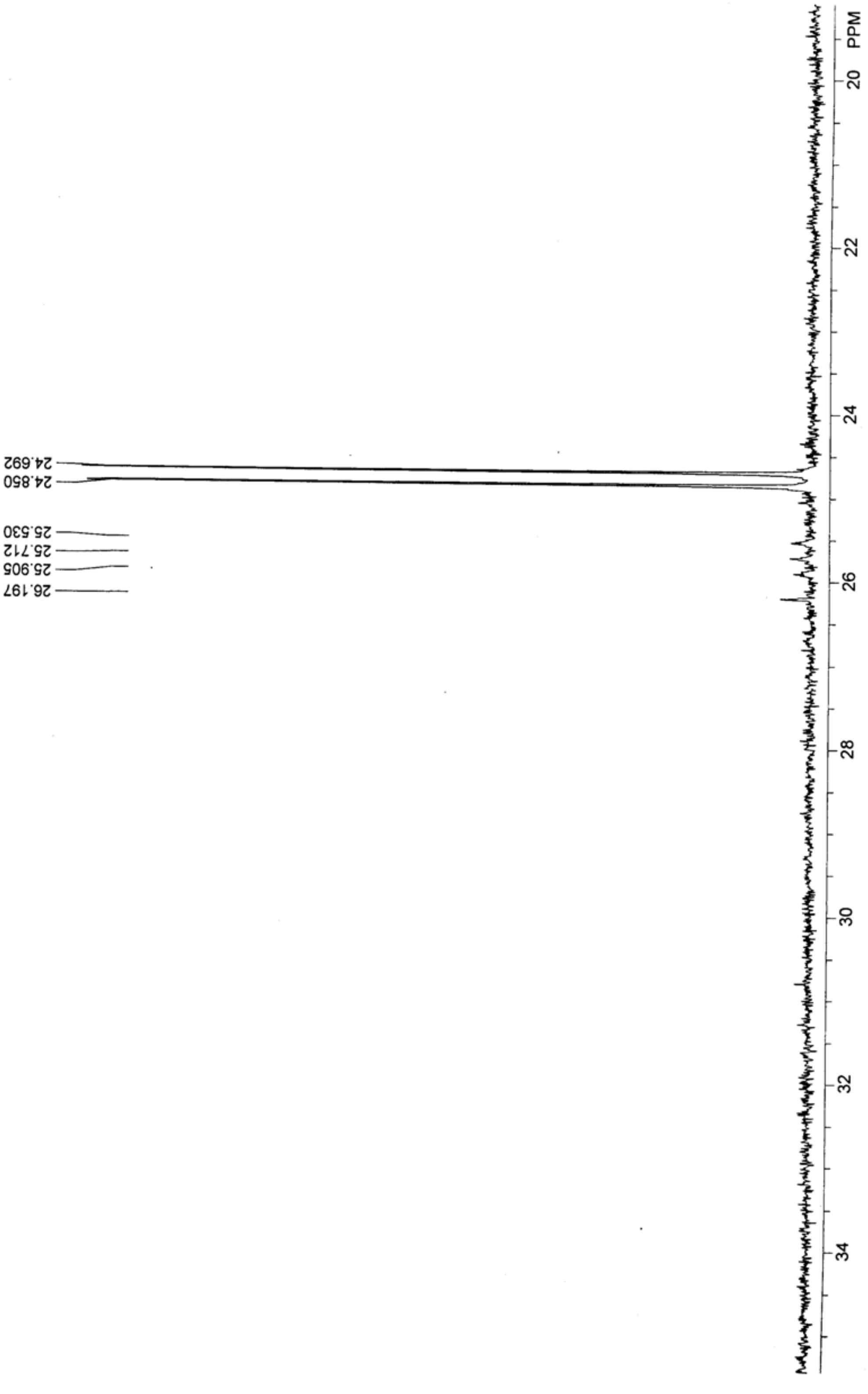

14.071
22.603
25.942
29.319
31.812
31.907
37.099
41.518
69.118
76.687
77.000
77.321
79.013
125.746
126.570
128.196
128.911
142.809
144.698
n-C_6H_{13}
O
12
ywm-12-194-C
22:09:39.639 -0700
SOLVENT: CDCl3
NA = 273
F1 = 100.617905 MHz
PPM
0
50
100
150
200


7.517
7.512
7.502
7.497
7.492
7.337
7.330
7.325
7.317
7.314
7.304
7.249
5.784
5.778
5.359
5.352
2.219
2.201
2.182
2.163
1.199
1.180
1.076
0.243
Nov 17 2016
sl-6-144H
NA = 4
Solvent = cdcl3
PTS1d = 16384
F1 = 399.749542 MHz
F2 = 100.526031 MHz
B
O
O
Me
D
PhMe2Si
92% D incorporation
1.99
3.01
1.00
1.00
0.08
12.09
2.99
6.00
10
8
6
4
2
0
PPM

[D]-5a


138.255
134.234
128.705
127.430
125.542
83.251
77.317
77.000
76.683
26.197
25.905
25.712
25.530
24.850
24.692
14.458
14.365
-4.080
-5.604
Nov 19 2016
sl-6-144C
NA = 512
Solvent = cdcl3
PTS1d = 32768
F1 = 100.527557 MHz
F2 = 399.749146 MHz
PhMe2Si
D
Me
B
O
O
92% D incorporation
200
150
100
50
0
PPM

[D]-5a


24.692
24.850
25.530
25.712
25.905
26.197
20
22
24
26
28
30
32
34
PPM