Supporting Information

Oxidation of *gem*-Borylsilylalkylcoppers to Acylsilanes with Air

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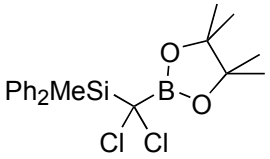
Instrumentation and Materials

^{1}H NMR (300 MHz), ^{13}C NMR (75.3 MHz) were taken on a Varian GEMINI 300 spectrometer in $CDCl_3$ as a solvent, and chemical shifts of ^{1}H and ^{13}C nuclides were given in δ value with tetramethylsilane as an internal standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL JMS-700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merck Silica gel $60F_{254}$. Column chromatography was done with silica gel (Wakogel 200 mesh). The analyses were carried out at the Elemental Analysis Center of Kyoto University. Tetrahydrofuran (THF) sealed and stored under argon without stabilizer was commercially available from KANTO Chemical, INC. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

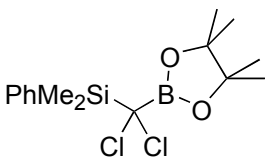
Experimental and Compound Data

Procedure for the Synthesis of [(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dichloromethyl]methyldiphenylsilane (2a)



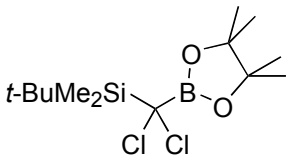
n-BuLi (0.31 mL, 1.6 M solution in hexane, 0.50 mmol) was added to a solution of $Ph_2MeSiCHCl_2$ (**1a**, 140.6 mg, 0.50 mmol) in THF (5 mL) at –78 °C, and the mixture was stirred for 30 min. Addition of methoxypinacolatoborane (95 mg, 0.6 mmol, MW=158.00) in THF solution to the resulting solution at –78 °C was followed by stirring for 1.5 h at the same temperature. The reaction was quenched with dilute HCl aq. The mixture was extracted with ethyl acetate (10 mL × 3), and the organic layers were dried over anhydrous Na_2SO_4 and were concentrated in vacuo. Purification by silicagel flash column chromatography provided [(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dichloromethyl]methyldiphenylsilane (**2a**, 187.3 mg, 0.46 mmol) in 92% yield as a white solid: R_f = 0.62 (hexane/ethyl acetate = 10/1); IR (KBr) 3072, 2984, 1428, 1353, 1320, 1274, 1254, 1138, 1107, 971, 846, 800, 732, 697, 629 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (s, 3H), 1.14 (s, 12H), 7.34-7.48 (m, 6H), 7.74-7.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ –4.38, 24.45, 85.45, 127.57, 130.02, 132.41, 135.77; Found: C, 59.07; H, 6.09%. Calcd for $C_{20}H_{25}BCl_2O_2Si$: C, 58.99; H, 6.19%.

[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dichloromethyl]dimethylphenylsilane (2b)



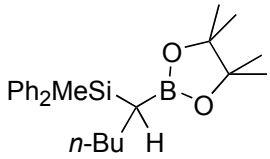
R_f = 0.68 (hexane/ethyl acetate = 10/1), as a white solid; IR (KBr) 2980, 1428, 1374, 1353, 1321, 1252, 1138, 1113, 971, 847, 784, 742, 705, 629 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.61 (s, 6H), 1.23 (s, 12H), 7.33-7.45 (m, 3H), 7.71 (d, *J*= 8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –5.10, 24.44, 85.35, 127.57, 130.05, 133.66, 135.11; HRMS (FAB^+, Matrix: NBA/acetone) (*m*/*z*) Observed: 345.1080 (Δ = +0.8 ppm). Calcd for $C_{15}H_{24}BCl_2O_2Si$ [MH^+]: 345.1016.

[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dichloromethyl](*tert*-butyl)dimethylsilane (2c)



R_f = 0.73 (hexane/ethyl acetate = 10/1), as a white solid; IR (KBr) 2932, 2861, 1472, 1323, 1325, 1261, 1142, 975, 848, 780, 708, 673, 624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.25 (s, 6H), 1.01 (s, 9H), 1.30 (s, 12H); ^{13}C NMR ($CDCl_3$) δ –6.91, 18.60, 24.55, 27.81, 85.26; HRMS (FAB^+, Matrix: NBA/acetone) (*m*/*z*) Observed: 325.1325 (Δ = –1.2 ppm). Calcd for $C_{13}H_{28}BCl_2O_2Si$ [MH^+]: 325.1329.

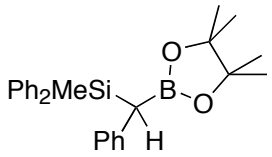
1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(methyldiphenylsilyl)pentane (5aa)



R_f = 0.53 (hexane/ethyl acetate = 10/1), as colorless oil; IR (neat) 3069, 2930, 2854, 1428, 1261, 1104, 989, 808, 733, 699, 640, 486, 472 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.63 (s, 3H), 0.82 (t, *J*= 7 Hz, 3H), 1.01 (s, 6H), 1.10 (s, 6H), 1.19-1.33 (m, 4H), 1.33-1.50 (m, 2H), 1.58-1.74 (m, 1H), 7.30-7.36 (m, 6H), 7.54-7.60 (m, 4H); ^{13}C NMR ($CDCl_3$) δ –4.21, 14.11, 22.47, 24.63, 24.99, 25.90, 35.64, 82.71, 127.42, 127.49, 128.83, 134.58, 134.71, 137.04, 137.11. HRMS (DI-EI^+) (*m*/*z*) Observed: 394.2500 (Δ = +0.2 ppm). Calcd for

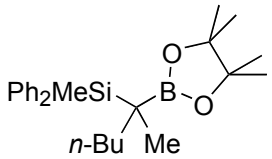
$C_{24}H_{35}B0_2Si$ [M^+]: 394.2499.

1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-1-(methyldiphenylsilyl)methane (5ab)



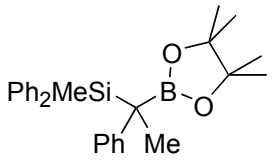
R_f = 0.26 (hexane/ethyl acetate = 20/1), as colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.59 (s, 3H), 0.98 (s, 6H), 1.07 (s, 6H), 2.60 (s, 1H), 6.99-7.03 (m, 1H), 7.05-7.13 (m, 4H), 7.20-7.25 (m, 2H), 7.27-7.39 (m, 6H), 7.60-7.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –4.80, 24.47, 24.91, 83.17, 123.74, 127.34, 127.51, 127.75, 128.95, 129.21, 129.30, 134.80, 135.17, 136.00, 136.57, 139.13. HRMS (DI-EI$^+$) (*m*/*z*) Observed: 414.2182 (Δ = –1.1 ppm). Calcd for $C_{26}H_{31}B0_2Si$ [M^+]: 414.2186.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(methyldiphenylsilyl)hexane (6aa)



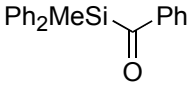
R_f = 0.61 (hexane/ethyl acetate = 10/1), as colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.62 (s, 3H), 0.85 (t, *J*= 8 Hz, 3H), 1.11 (s, 6H), 1.13 (s, 6H), 1.17 (s, 3H), 1.18-1.34 (m, 4H), 1.35-1.44 (m, 1H), 1.85-1.92 (m, 1H), 7.29-7.39 (m, 6H), 7.59 (d, *J*= 7 Hz, 2H), 7.68 (d, *J*= 7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –4.59, 14.17, 16.55, 23.48, 24.91, 24.99, 29.54, 33.85, 82.92, 127.29, 127.34, 128.76, 128.85, 135.74, 136.57, 136.67. HRMS (DI-EI$^+$) (*m*/*z*) Observed: 408.2655 (Δ = –0.1 ppm). Calcd for $C_{25}H_{37}B0_2Si$ [M^+]: 408.2656.

1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-1-(methyldiphenylsilyl)ethane (6ab)



R_f = 0.69 (hexane/ethyl acetate = 10/1), as colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.61 (s, 3H), 1.13 (s, 6H), 1.15 (s, 6H), 1.56 (s, 3H), 7.05-7.13 (m, 1H), 7.16-7.25 (m, 6H), 7.28-7.42 (m, 6H), 7.50-7.56 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –3.76, –0.59, 17.45, 24.65, 24.91, 83.24, 123.96, 127.05, 127.24, 127.37, 127.71, 127.96, 128.81, 129.00, 133.97, 135.78, 135.93, 143.63. HRMS (DI-EI$^+$) (*m*/*z*) Observed: 428.2343 (Δ = –0.1 ppm). Calcd for $C_{27}H_{33}B0_2Si$ [M^+]: 428.2343.

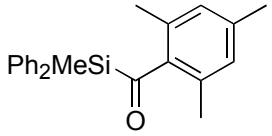
General Procedure for the Synthesis of acylsilane (7ab) via Aerobic Oxidation



n-BuLi (0.31 mL, 1.6 M solution in hexane, 0.50 mmol) was added to a solution of **2a** (204 mg, 0.50 mmol) in THF (5 mL) dropwise at –78 ˚C, and the mixture was stirred for 5 min. To the resulting yellow solution at –78 ˚C were sequentially added CuCN•2LiCl (0.55 mL, 1.0 M solution in THF, 0.55 mmol) and PhMgBr (0.55 mL, 1.0 M solution in THF, 0.55 mmol). After stirring for 5 min, the mixture was allowed to warm gradually to 0 ˚C. Pyridine (0.13 mL, 2.0 mmol) was added to the mixture, which was vigorously stirred under air for 1 h at 0 ˚C. After quenching by aqueos NH_4Cl, the mixture was extracted with ethyl acetate, and the organic layers were dried over anhydrous Na_2SO_4. Concentration and purification provided benzoyl(methyl)diphenylsilane (**7ab**, 130 mg, 0.43 mmol) in 86% yield as clear, yellow oil.

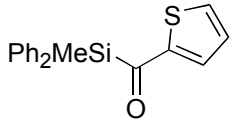
R_f = 0.44 (hexane/ethyl acetate = 10/1); IR (neat) 1612, 1589, 1576, 1447, 1429, 1252, 1209, 1173, 1111, 794, 729, 698 cm^{-1}; ^{1}H NMR (CDCl3) δ 0.87 (s, 3H), 7.31-7.50 (m, 9H), 7.60 (dd, *J* = 1.5, 7.5 Hz, 4H), 7.77 (dd, *J* = 1.5, 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –3.3, 128.2, 128.2, 128.5, 130.0, 132.9, 133.7, 135.1, 141.7, 232.0. Found: C, 79.68; H, 6.06%. Calcd for $C_{20}H_{18}OSi$: C, 79.43; H, 6.00%.

(2,4,6-trimethylbenzoyl)methyldiphenylsilane (7ac)



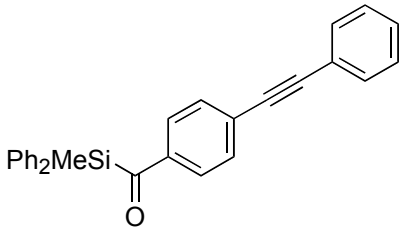
R_f = 0.38 (hexane/ethylacetate = 10/1), as pale yellow oil; IR (neat) 2978, 1612, 1591, 1578, 1340, 1250, 1142, 1113, 838, 785, 734, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80 (s, 3H), 1.85 (s, 6H), 2.26 (s, 3H), 6.73 (s, 2H), 7.34-7.39 (m, 6H), 7.41-7.46 (m, 4H); ^{13}C NMR ($CDCl_3$) δ –5.20, 19.01, 20.72, 128.00, 128.52, 129.97, 132.02, 132.69, 134.96, 138.16, 143.20, 249.48. HRMS (DI-EI$^+$) (*m/z*) Observed: 344.1590 (Δ = –1.7 ppm). Calcd for $C_{23}H_{24}0Si$ [M^+]: 344.1596.

Methyldiphenylsilyl 2-thienyl ketone (7ad)



R_f = 0.53 (hexane/ethyl acetate = 5/1); yellow oil; IR (KBr) 3068, 1570, 1512, 1428, 1406, 1230, 1113, 1051, 788, 731, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (s, 3H), 6.97 (t, *J*= 4.5 Hz, 1H), 7.34 (d, *J*= 4.5 Hz, 1H), 7.38–7.48 (m, 6H), 7.59 (d, *J*= 4.5 Hz, 1H), 7.61–7.65 (m, 4H); ^{13}C NMR ($CDCl_3$) δ –3.8, 128.2, 130.2, 133.2, 133.6, 134.6, 135.2, 151.2, 221.0. Found: C, 70.10; H, 5.33%. Calcd for $C_{18}H_{16}OSSi$: C, 70.09; H, 5.23%.

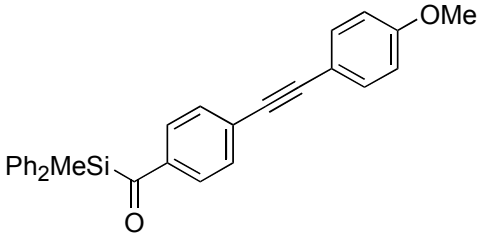
[4-(Phenylethynyl)benzoyl]diphenylsilane (7ae)



R_f = 0.35 (hexane/ethyl acetate = 10/1); yellow oil; IR (neat) 3071, 2957, 1589, 1427, 1209, 1111, 756, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (s, 3H), 7.19–7.33 (m, 9H), 7.35–7.42 (m,

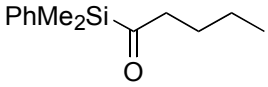
4H), 7.59–7.64 (m, 4H), 7.76 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –3.3, 128.2, 128.2, 128.5, 130.0, 132.9, 133.7, 135.1, 141.7, 232.0. Found: C, 83.70; H, 5.41%. Calcd for $C_{28}H_{22}OSi$: C, 83.54; H, 5.51%.

[4-(4-Methoxyphenylethynyl)benzoyl]methyldiphenylsilane (7af)



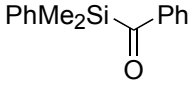
R_f = 0.22 (hexane/ethylacetate = 10/1), as yellow oil; IR (neat) 3071, 2959, 2214, 1587, 1514, 1429, 1288, 1250, 1211, 1174, 1136, 1111, 1030, 833, 793, 727, 698, 486 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 3H), 3.83 (s, 3H), 6.88 (d, J = 9 Hz, 2H), 7.37-7.42 (m, 4H), 7.43-7.48 (m, 6H), 7.58-7.62 (m, 4H), 7.74 (d, J = 9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –3.36, 55.31, 87.65, 92.97, 114.06, 114.72, 128.12, 128.26, 128.32, 130.09, 131.46, 133.23, 133.60, 135.12, 140.29, 159.99, 231.12. HRMS (DI-EI$^+$) (m/z) Observed: 432.1538 (Δ = –1.8 ppm). Calcd for $C_{29}H_{24}O_2Si$ [M$^+$]: 432.1546.

Dimethylphenylpentanoylsilane (7ba)



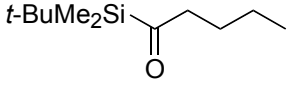
R_f = 0.62 (hexane/ethylacetate = 20/1), as colorless oil; IR (neat) 2959, 1643, 1429, 1340, 1250, 1111, 837, 820, 782, 735, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.50 (s, 6H), 0.83 (t, J= 8 Hz, 3H), 1.16-1.24 (m, 6H), 1.44 (quint, J= 8 Hz, 2H), 2.57 (t, J= 8 Hz, 2H), 7.36-7.46 (m, 3H), 7.54-7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –4.73, 13.84, 22.29, 24.21, 48.54, 128.11, 129.81, 133.94, 134.59, 246.62.

Benzoyldimethylphenylsilane (7bb)



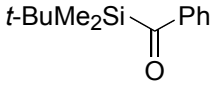
R_f = 0.57 (hexane/ethyl acetate = 10/1), as yellow oil; IR (neat) 2978, 1612, 1591, 1578, 1340, 1250, 1142, 1113, 838, 785, 734, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.63 (s, 6H), 7.35-7.43 (m, 5H), 7.46-7.51 (m, 1H), 7.59-7.63 (m, 2H), 7.74-7.78 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –2.94, 127.81, 128.24, 128.53, 129.80, 132.74, 133.96, 135.61, 141.25, 233.79.

***tert*-Butyldimethylpentanoylsilane (7ca)**

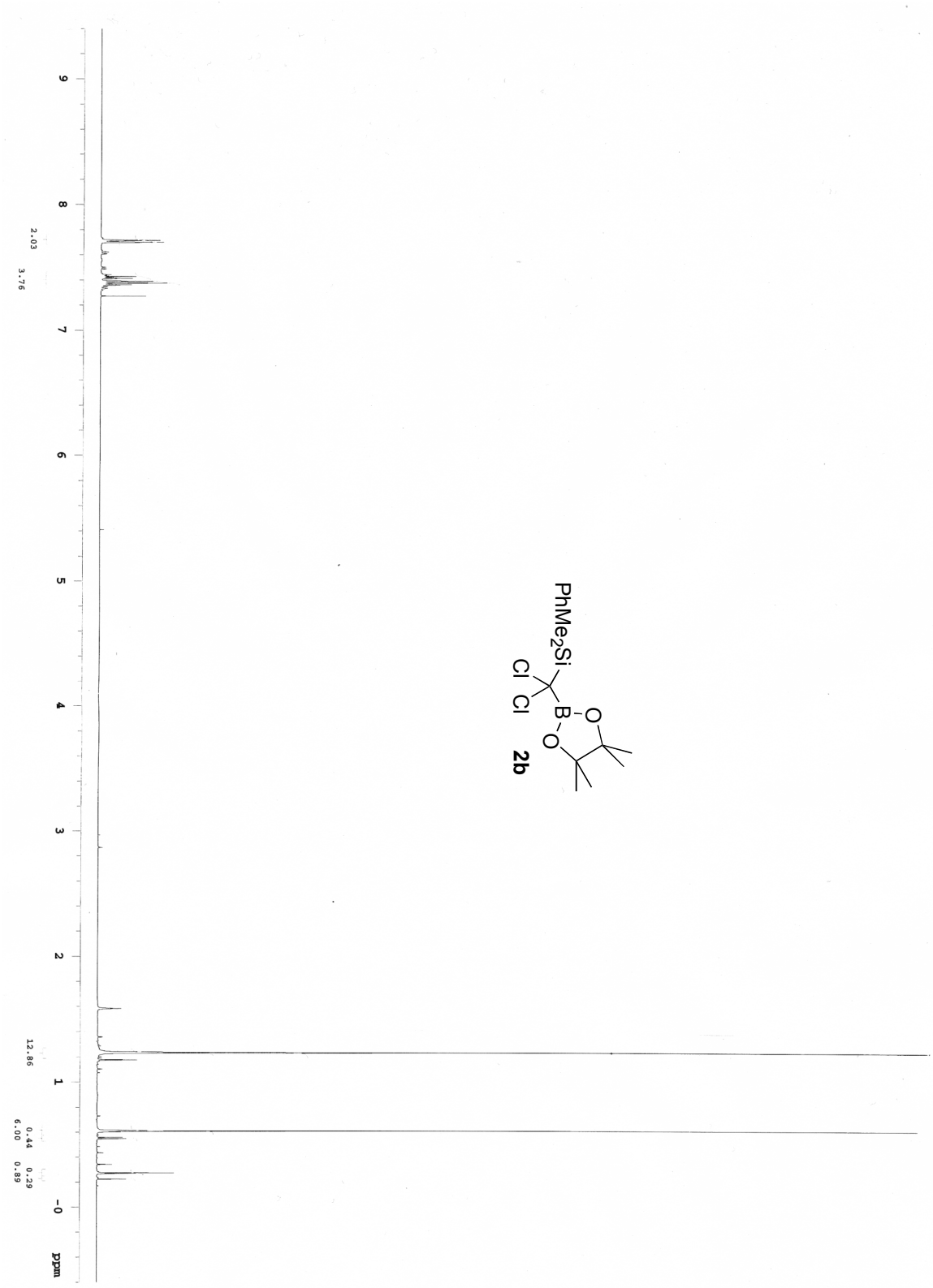


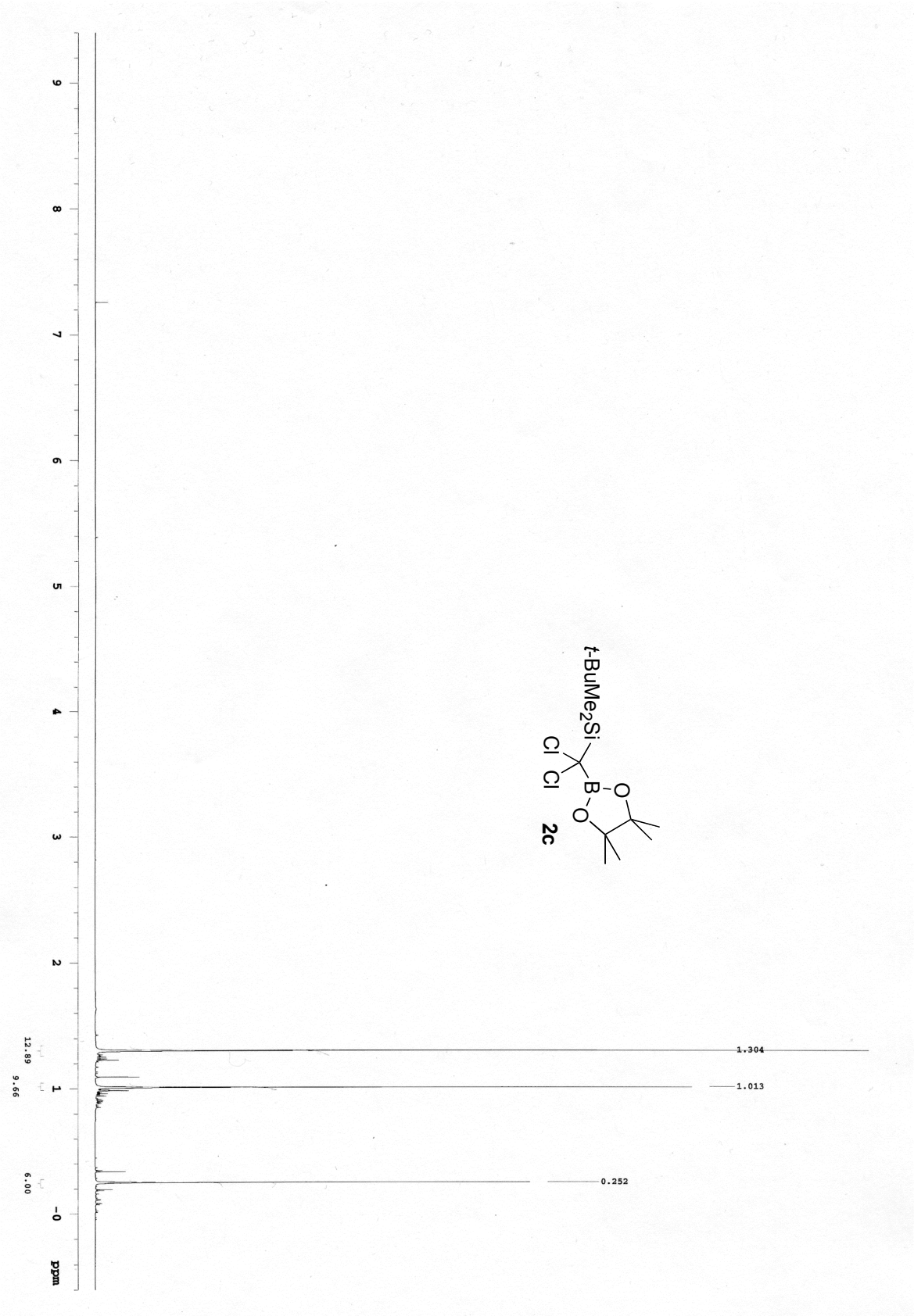
R_f = 0.67 (hexane/ethylacetate = 20/1), as colorless oil; IR (neat) 2957, 2860, 1641, 1466, 1340, 1250, 1144, 837, 775, 671 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 6H), 0.88 (t, *J*= 8 Hz, 3H), 0.92 (s, 9H), 1.23-1.31 (m, 4H), 1.48 (quint, *J*= 8 Hz, 2H), 2.58 (t, *J*= 8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –6.96, 13.96, 22.42, 24.01, 26.43, 50.00, 247.98.

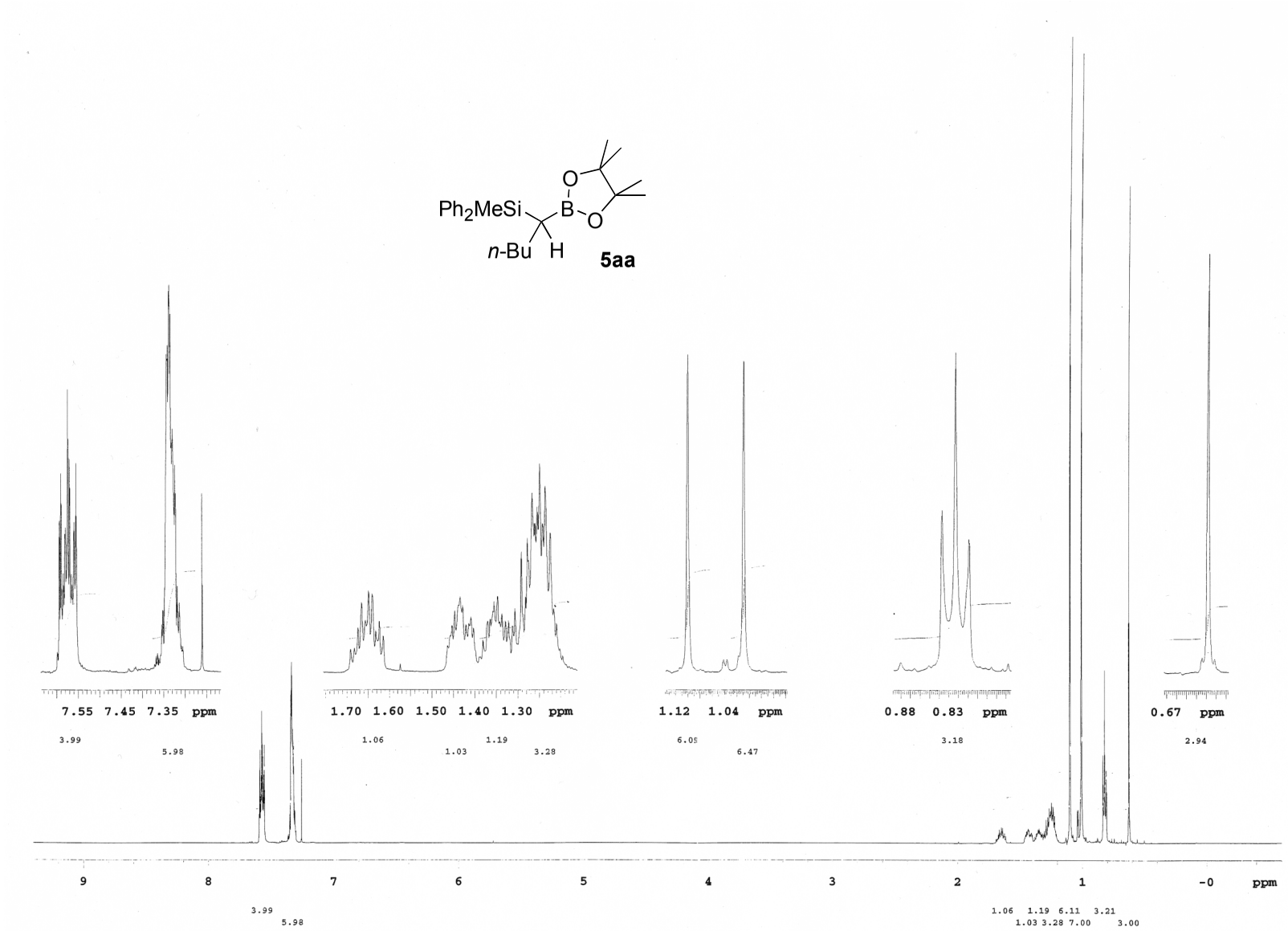
Benzoyl-*tert*-butyldimethylsilane (7cb)

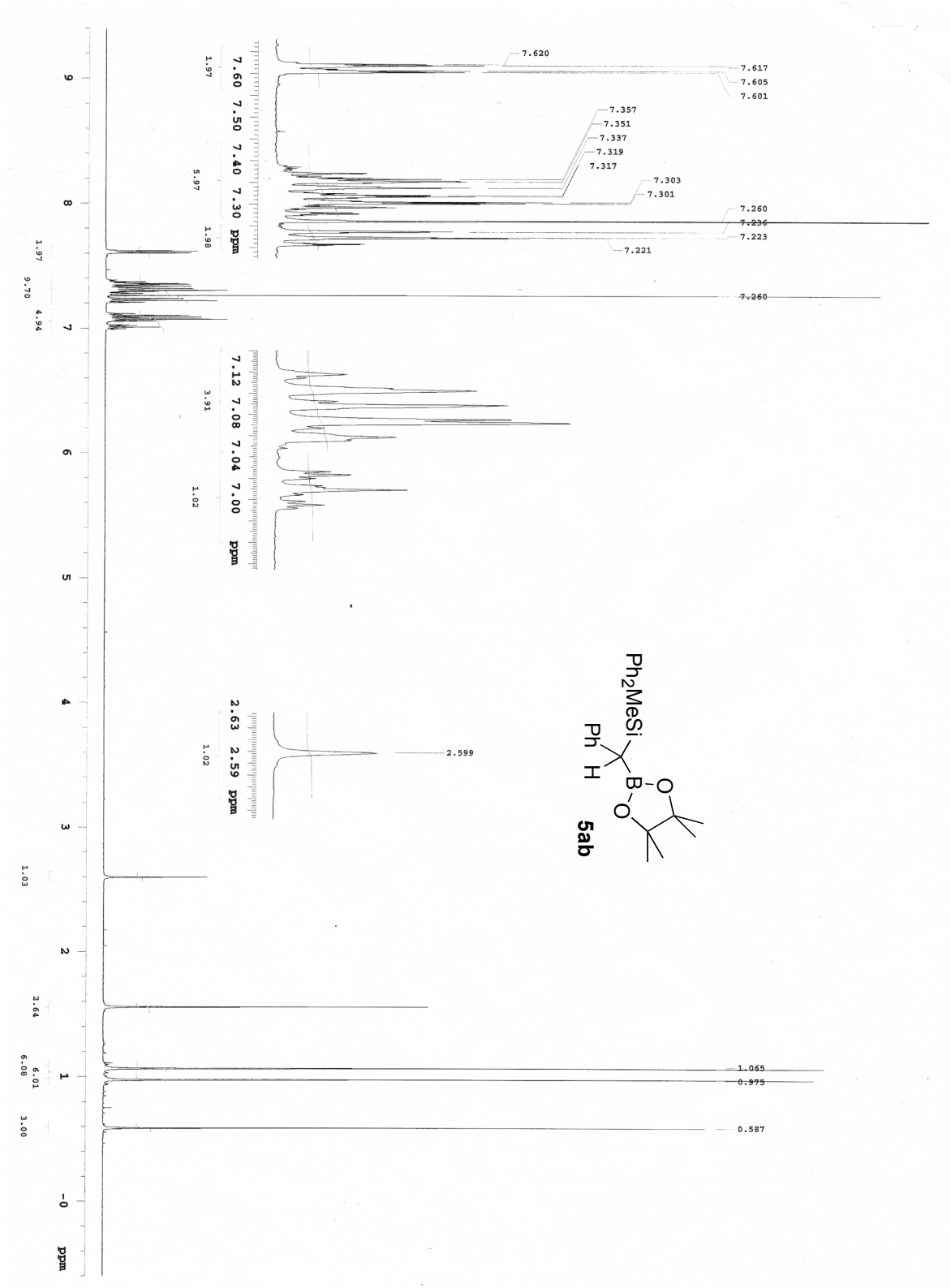


R_f = 0.67 (hexane/ethyl acetate = 10/1), as yellow oil; IR (neat) 2955, 2930, 2858, 1612, 1576, 1472, 1339, 1250, 1210, 1144, 839, 810, 777, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.37 (s, 6H), 0.96 (s, 9H), 7.44-7.54 (m, 3H), 7.78-7.82 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –4.72, 16.91, 26.72, 127.55, 128.52, 132.49, 142.71, 235.89.


PhMe2Si
Cl Cl
B
O
O
2b
9
8
7
6
5
4
3
2
1
0
ppm
2.03
3.76
12.86
0.44
6.00
0.29
0.89


t-BuMe2Si
Cl Cl
B
O
O
2c
1.304
1.013
0.252
12.89
9.66
6.00
ppm


Ph2MeSi
B
O
O
n-Bu
H
5aa
7.55 7.45 7.35 ppm
3.99
5.98
1.70 1.60 1.50 1.40 1.30 ppm
1.06
1.03
1.19
3.28
1.12 1.04 ppm
6.05
6.47
0.88 0.83 ppm
3.18
0.67 ppm
2.94
9 8 7 6 5 4 3 2 1 -0 ppm
3.99
5.98
1.06 1.19 6.11 3.21
1.03 3.28 7.00 3.00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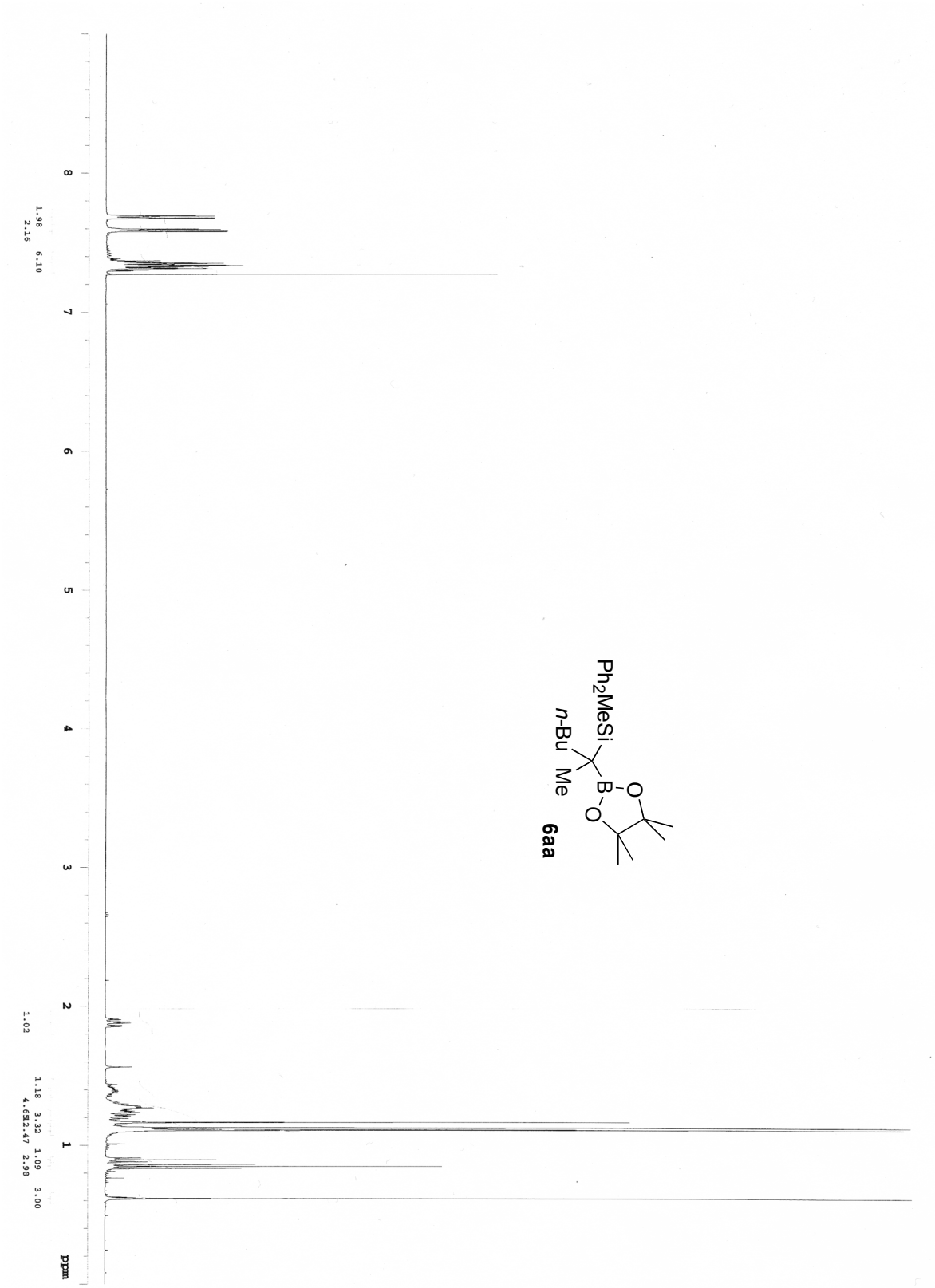
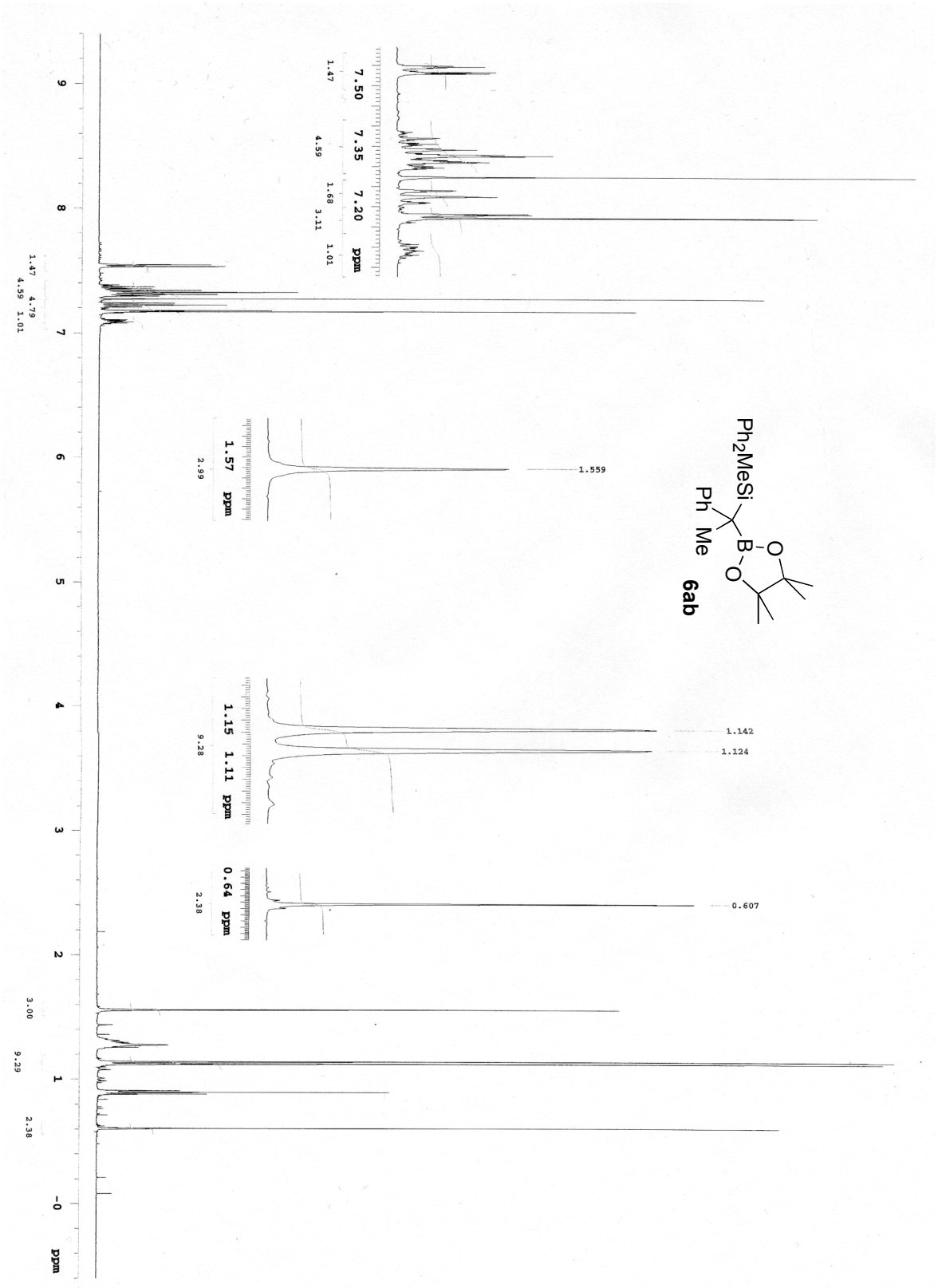
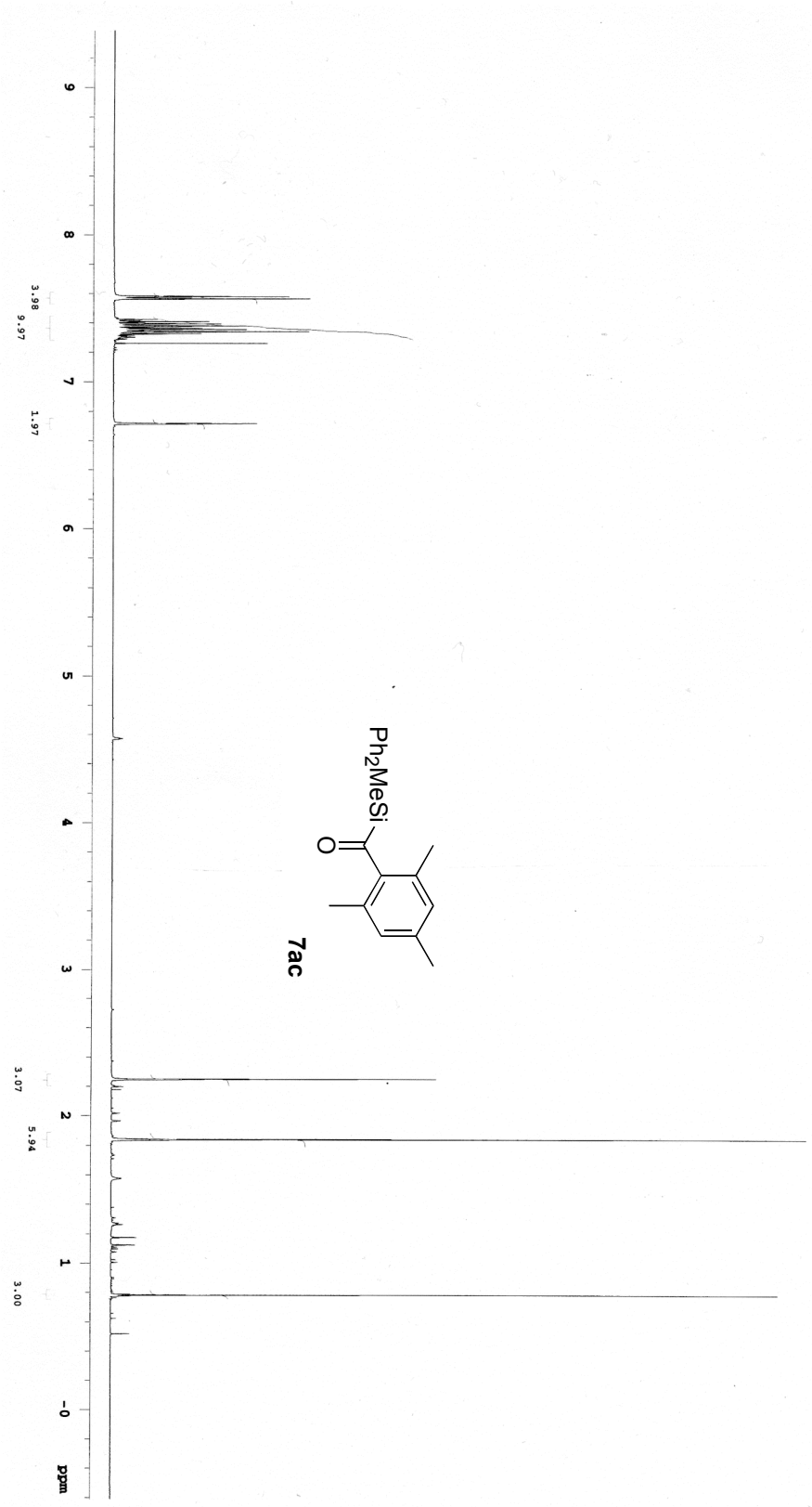
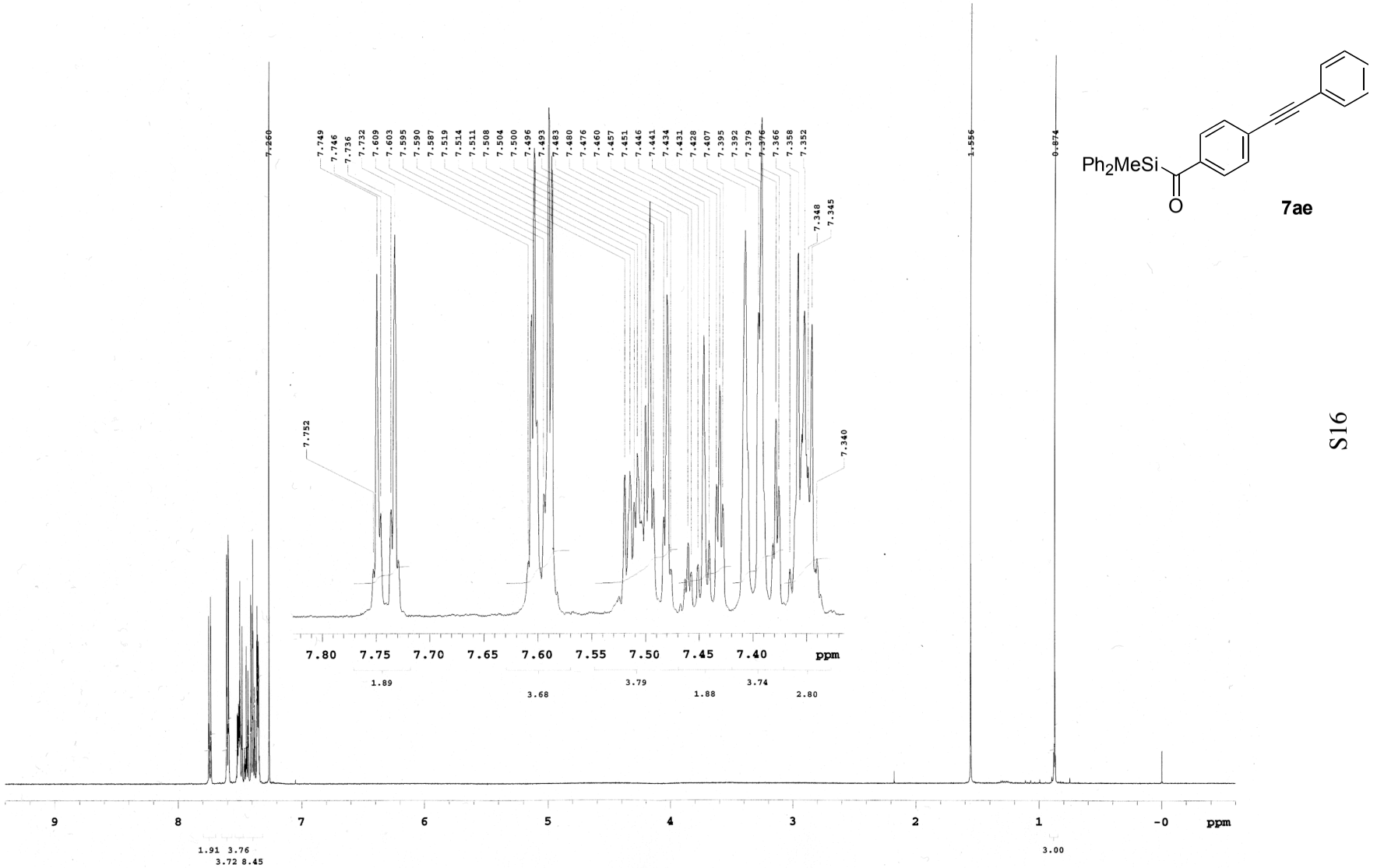
7.617
7.605
7.601
7.357
7.351
7.337
7.319
7.317
7.303
7.301
7.260
7.236
7.223
7.221
7.260
2.599
1.065
0.975
0.587
Ph2MeSi
Ph
H
B
O
O
5ab
7.60 7.50 7.40 7.30 ppm
7.12 7.08 7.04 7.00 ppm
2.63 2.59 ppm
ppm


Ph2MeSi
n-Bu
Me
B
O
O
6aa
8
7
6
5
4
3
2
1
ppm
1.98
6.10
2.16
1.02
1.18
3.32
1.09
3.00
4.65
2.47
2.98


Ph2MeSi
Ph
Me
B
O
O
6ab
1.559
1.142
1.124
0.607
1.57 ppm
1.15 1.11 ppm
0.64 ppm
7.50 7.35 7.20 ppm
ppm


Ph2MeSi
O
7ac
9
8
7
6
5
4
3
2
1
-0
ppm
3.98
9.97
1.97
3.07
5.94
3.00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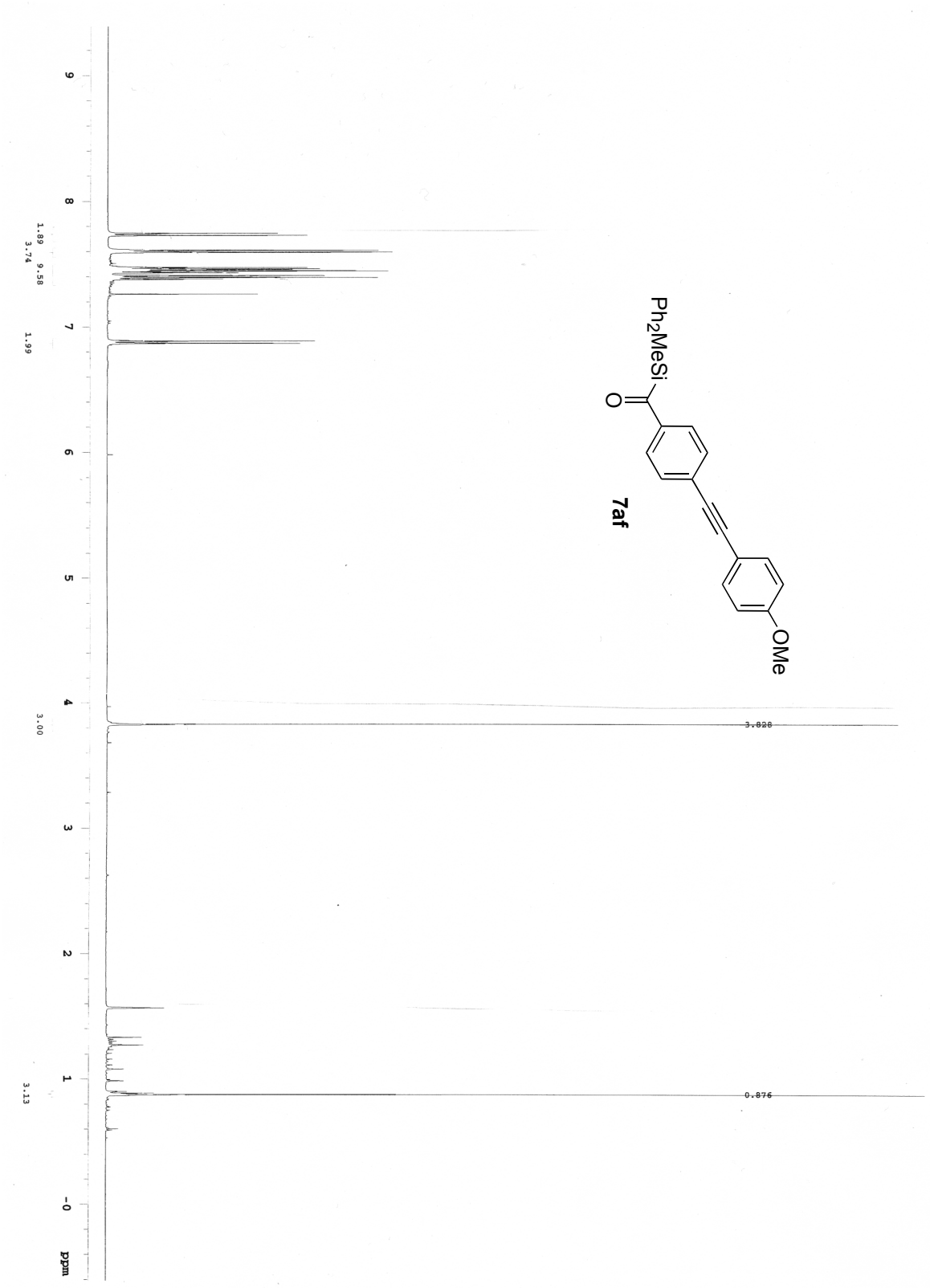
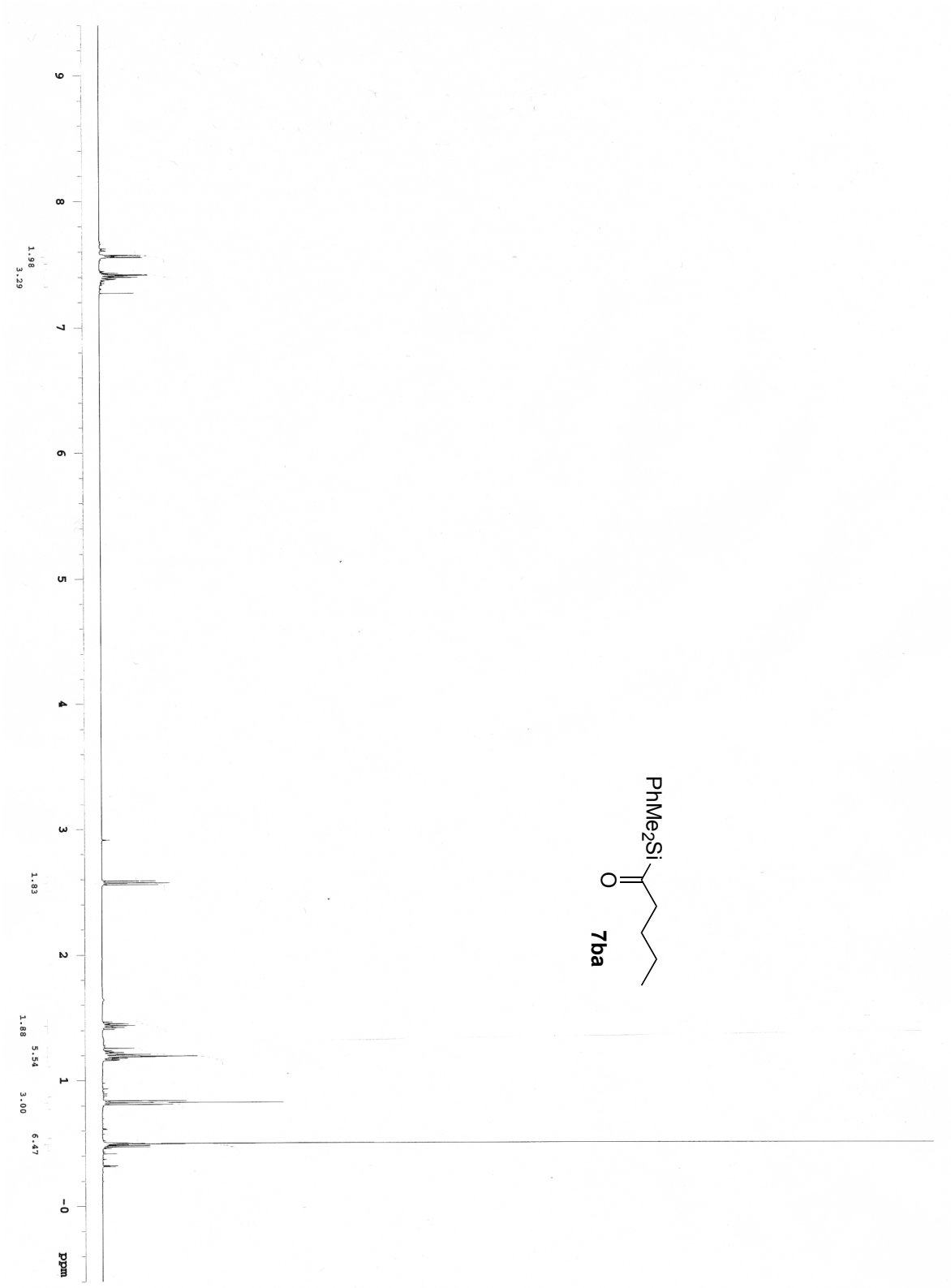
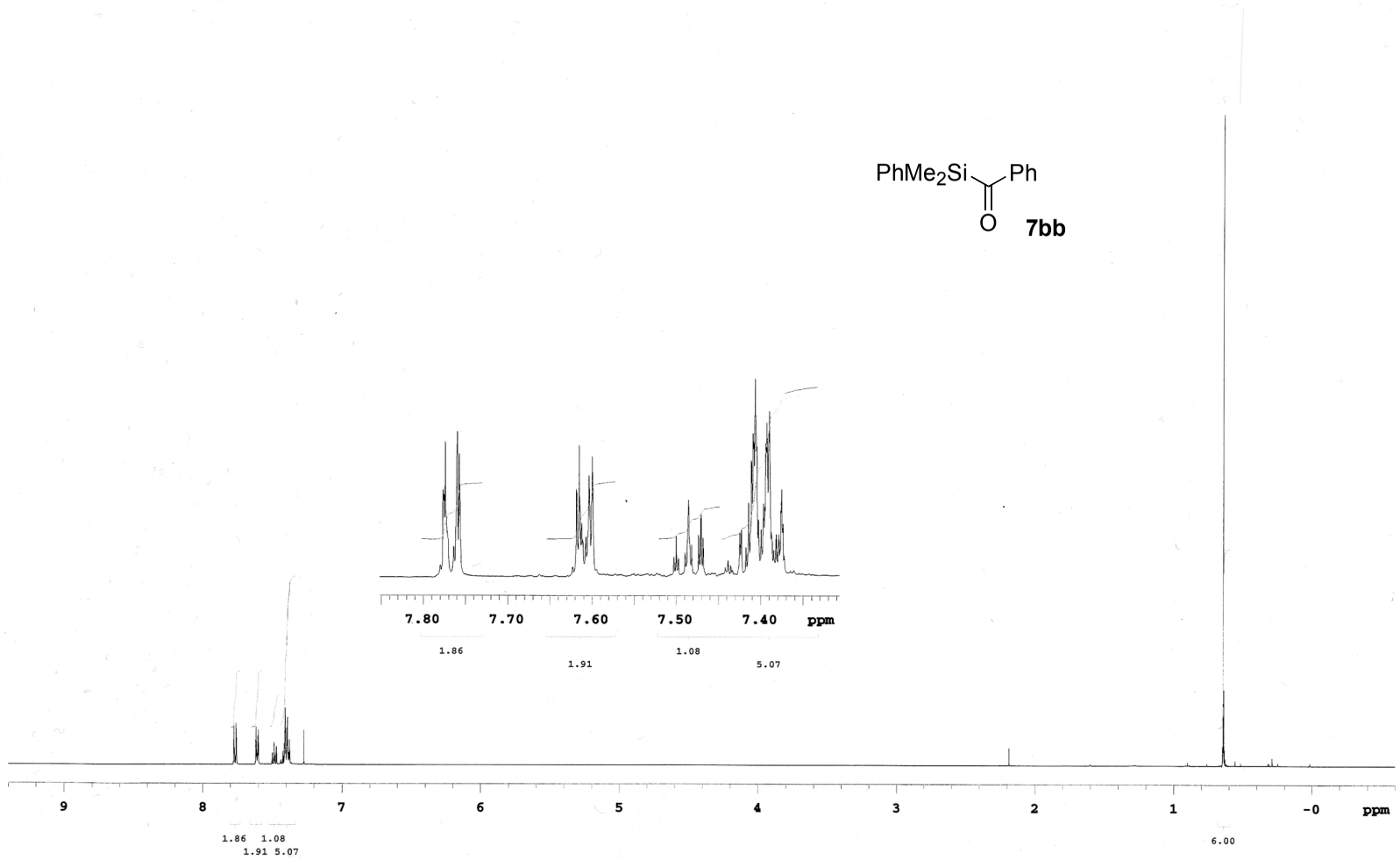
7.749
7.746
7.736
7.732
7.609
7.603
7.595
7.590
7.587
7.519
7.514
7.511
7.508
7.504
7.500
7.496
7.493
7.483
7.480
7.476
7.460
7.457
7.451
7.446
7.441
7.434
7.431
7.428
7.407
7.395
7.392
7.379
7.376
7.366
7.358
7.352
7.348
7.345
7.752
7.340
7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 ppm
1.89
3.68
3.79
1.88
3.74
2.80
1.556
0.874
9 8 7 6 5 4 3 2 1 -0 ppm
1.91 3.76
3.72 8.45
3.00

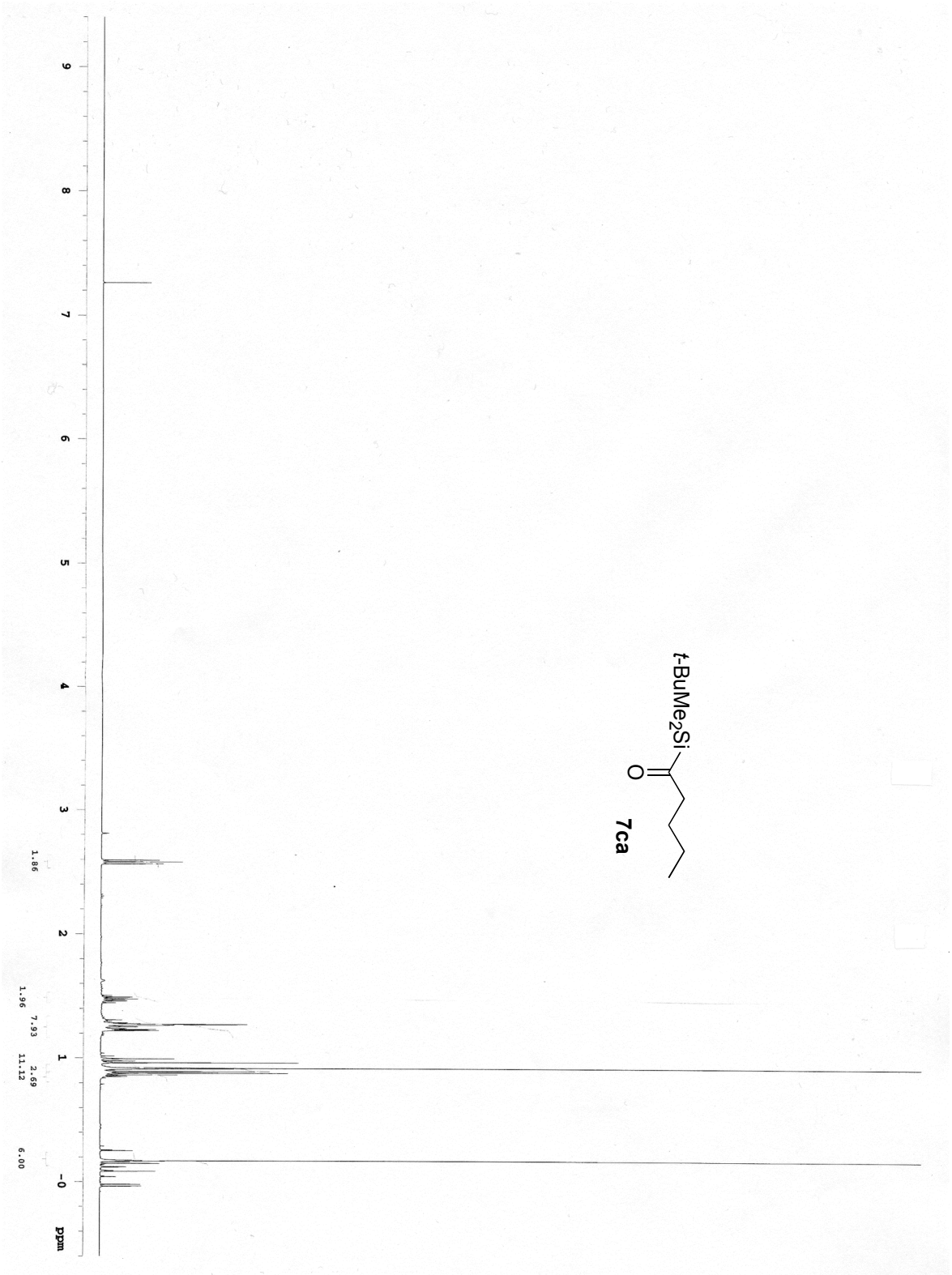
Ph2MeSi
O

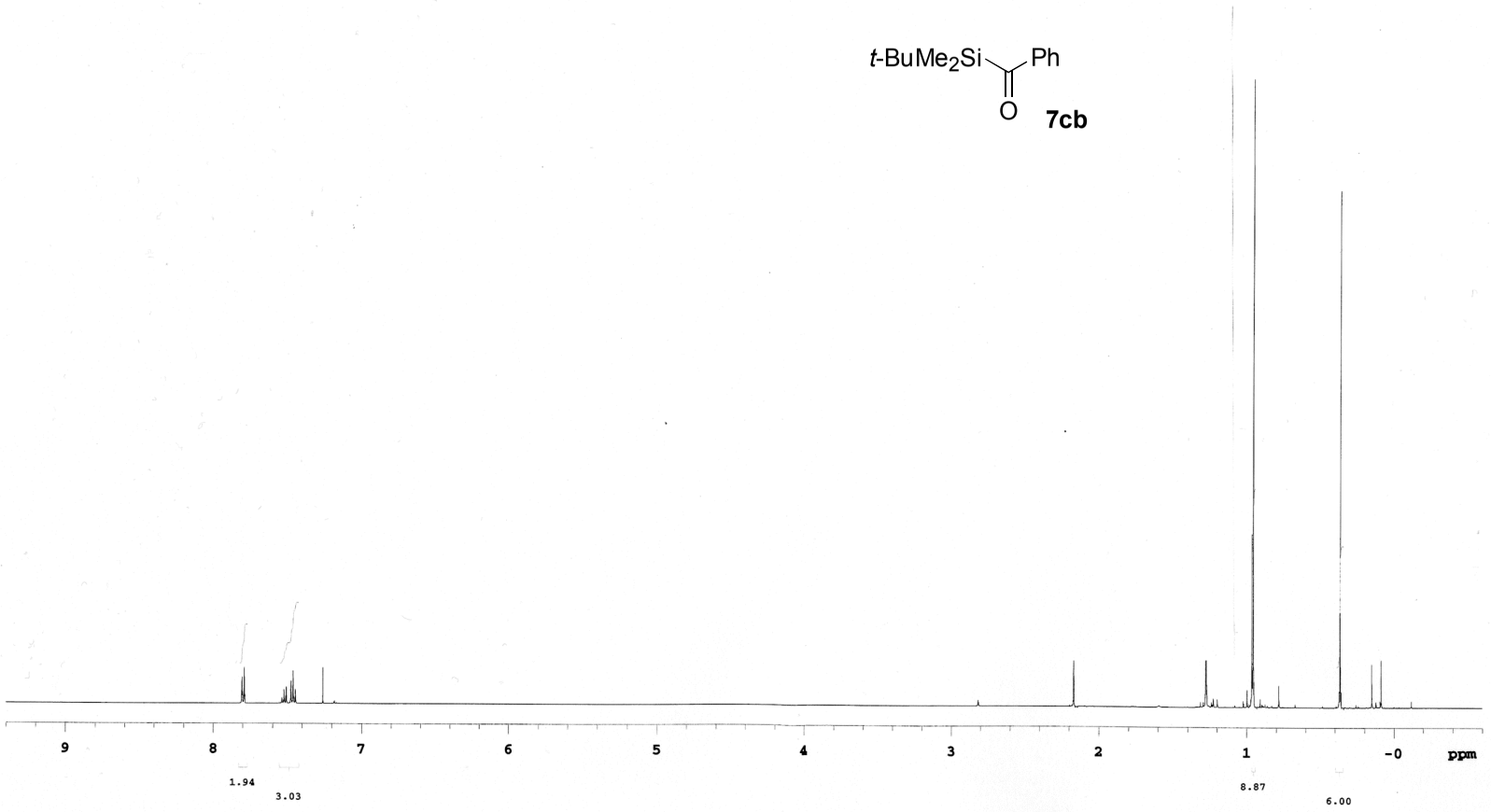
7ae


Ph2MeSi
O
OMe
7af
1.89
9.58
3.74
1.99
3.00
3.828
0.876
3.13
9
8
7
6
5
4
3
2
1
-0
ppm


PhMe2Si
O
7ba
9
8
7
6
5
4
3
2
1
-0
ppm
1.98
3.29
1.83
1.88
5.54
3.00
6.47


PhMe2Si
Ph
O
7bb
7.80
7.70
7.60
7.50
7.40
ppm
1.86
1.91
1.08
5.07
9
8
7
6
5
4
3
2
1
-0
ppm
1.86 1.08
1.91 5.07
6.00


t-BuMe2Si
O
7ca
9
8
7
6
5
4
3
2
1
-0
ppm
1.86
1.96
7.93
2.69
11.12
6.00


t-BuMe2Si
Ph
O
7cb
9
8
7
6
5
4
3
2
1
-0
ppm
1.94
3.03
8.87
6.00