Supporting Information

Regioselective β-silylation of porphyrins via iridium-catalyzed C-H bond activation

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General Information

^{1}H and ^{13}C NMR spectra were recorded at rt on a JEOL JNM AL-300, a JEOL JNM AL-400, a JEOL JNM ECS-400, and a JEOL JNM LA-500 MHz spectrometers using perdeuterated solvents as internal standards. Chemical shifts of ^{1}H and ^{13}C spectra are given in ppm relative to residual protiated solvent and relative to the solvent respectively. $CHCl_3$ (δ = 7.24) for ^{1}H NMR and relative to the central resonance of $CDCl_3$ (δ = 77.0) for ^{13}C NMR. ^{19}F NMR spectra were recorded at rt on a JEOL JNM ECS-400 spectrometer using benzotrifluoride as an external standard. The chemical shift values are expressed as δ values (ppm) and the couple constants values (J) are in Hertz (Hz). The following abbreviations were used for signal multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. UV-visible spectra were recorded on a JASCO V-660 dual-beam grating spectrophotometer with a 1 cm quartz cell. IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. The mass spectroscopic data were obtained on JEOL JNM-DX302 spectrometer. The melting point data were not available for the porphyrin derivatives obtained because these compounds are infusible below 300 °C.

Reactions involving moisture sensitive reagents were carried out under an argon atmosphere using standard vacuum line techniques and glassware that was flame-dried and cooled under argon before use. Dry THF and dry dioxane were purchased for the reactions and used without further desiccation. Porphyrin derivatives, **H_2-1a**,[1] **Zn-1a**,[2] **H_2-1b**,[3] **H_2-1c**,[4,5] **Zn-1c**,[4] **Ni-1c**,[6] **H_2-1d**,[7] **Zn-1e**,[8] **H_2-1f**,[9] **H_2-1g**,[10] and **Zn-1h**,[11] were prepared according to the method described in the literature. Other chemicals were purchased from commercial sources and used as received unless stated otherwise.

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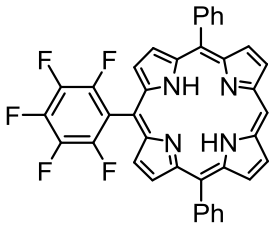
Experimental Section

Preparation of porphyrins H_2-1e and H_2-1h

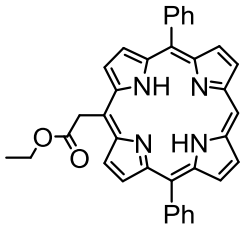
A mixture of THF (1.8 mL) and HCl (0.2 mL) was added dropwise to a solution of porphyrinate zinc **Zn-1** (0.5 mmol) in THF (10 mL) at rt. The mixture was stirred at rt for 20 min, diluted with THF/Et_2O (2:1, 50 mL), and then neutralized with saturated sodium bicarbonate. The solution was washed with water and brine, and the organic layer was dried over $MgSO_4$ and concentrated in vacuo. The resulting solid was purified by recrystallization from MeOH/CH_2Cl_2 to give the pure free base porphyrin.

5,15-Diphenyl-10-pentafluorophenylporphyrin **H_2-1e**



Prepared from porphyrin **Zn-1e** (345 mg, 500 μmol) following the general procedure; Purple solid; 307 mg, 98% yield; R_f = 0.72 (1/1 toluene/hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 10.28 (1H, s), 9.34 (2H, d, J = 4.6 Hz), 9.01 (2H, d, J = 4.6 Hz), 8.99 (2H, d, J = 4.6 Hz), 8.80 (2H, d, J = 4.6 Hz), 8.24-8.22 (4H, m), 7.80-7.77 (6H, m), -3.01 (2H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 148.0 (2C, br), 147.9 (2C, br), 146.5 (2C, d, J_{CF} = 246.2 Hz), 146.2 (2C, br), 146.0 (2C, br), 142.2 (1C, d, J_{CF} = 247.2 Hz), 141.6 (2C), 137.7 (2C, d, J_{CF} = 247.2 Hz), 134.9 (4C), 132.5 (2C), 132.1 (2C), 131.8 (2C), 129.5 (2C), 128.2 (2C), 127.2 (4C), 120.7 (2C), 117.5 (1C, t, J_{CF} = 18.1 Hz), 106.9, 100.9; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: -135.9 (2F, dd, J_{FF} = 24.7, 8.6 Hz), -152.0 (1F, t, J_{FF} = 21.3 Hz), -161.5 (2F, ddd, J_{FF} = 26.1, 18.1, 5.5 Hz); IR (KBr), 3297, 3116, 3077, 1496, 987, 790, 725 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 412.0 (5.5), 507.5 (4.2), 580.5 (3.7), 636.5 (3.2) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{38}H_{22}F_5N_4$ 629.1765, found 629.1757.

5,15-Diphenyl-10-(2-ethoxycarbonylethyl)porphyrin **H_2-1h**



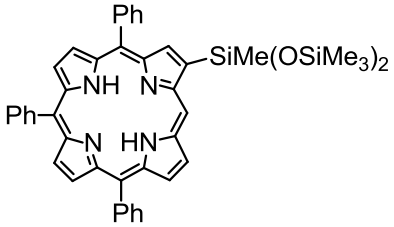
Prepared from porphyrin **Zn-1h** (306 mg, 500 μmol) following the general procedure; Purple solid; 270 mg, 98% yield; R_f = 0.80 (CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.14 (1H, s), 9.58 (2H, d, J = 4.9 Hz), 9.27 (2H, d, J = 4.9 Hz), 9.00 (2H, d, J = 4.9 Hz), 8.96 (2H, d, J = 4.9 Hz), 8.23-8.21 (4H, br m), 7.81-7.76 (6H, br m), 6.06 (2H, s), 4.16 (2H, q, J = 7.0 Hz), 1.12 (3H, t, J = 7.1 Hz), -3.04 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 172.5, 148.1 (2C, br), 147.1 (2C, br s), 145.9 (2C, br), 144.0 (2C, br), 141.8 (2C), 134.6 (4C), 131.7 (2C, br), 131.5 (2C, br), 131.2 (2C, br), 128.6 (2C),

127.7 (2C), 126.8 (4C), 119.5 (2C), 110.4, 105.0, 61.3, 41.2, 14.1; IR (KBr), 3301, 3054, 2985, 2938, 1727, 1157, 790, 740 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 413.5 (5.4), 509.0 (4.1), 544.5 (3.5), 584.0 (3.6), 640.5 (3.2) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{36}H_{29}N_4O_2$ 549.2291, found 549.2291.

General Procedure for the Iridium-Catalyzed *β*-Silylation of porphyrins

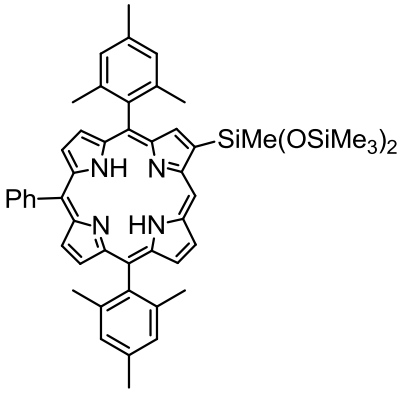
An oven-dried 50 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with porphyrin **1** (400 μmol), $[Ir(cod)OMe]_2$ (10.6 mg, 16 μmol, 4 mol%), and dtbpy (8.6 mg, 32 μmol, 8 mol%). The reaction vessel was evacuated and flushed with argon (three times), and then 1,1,1,3,5,5,5-heptamethyltrisiloxane (543 μL, 2 mmol, 5 equiv.) and dry dioxane (10 mL) were added. The mixture was stirred at 95 °C for 24-48 h, having been monitored by TLC (1/5 AcOEt/hexane). The solvent was evaporated to dryness. Column chromatography on silica gel (1/10 AcOEt/hexane) followed by recrystallization from $MeOH/CH_2Cl_2$ gave the pure product **2**.

2-(1,1,1,3,5,5,5-Heptamethyltrisiloxan-3-yl)-5,10,15-triphenylporphyrin **H_2-2a**



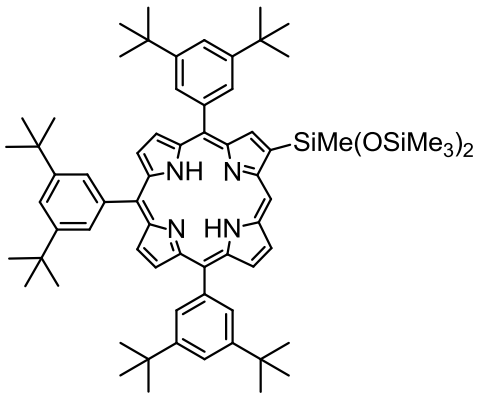
Prepared from triphenylporphyrin **H_2-1a** (215.5 mg, 400 μmol) following the general procedure; Purple solid; 216.5 mg, 71% yield; R_f = 0.75 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.56 (1H, s), 9.37 (1H, d, *J* = 4.4 Hz), 9.24 (1H, s), 9.06 (1H, d, *J* = 4.4 Hz), 8.95 (2H, d, *J* = 4.4 Hz), 8.90 (2H, d, *J* = 4.40 Hz), 8.36-8.20 (6H, m), 7.89-7.71 (9H, m), 0.92 (3H, s), 0.31 (18H, s), -2.81 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.6 (br), 148.1 (2C, br), 147.2 (2C, br), 146.1 (br), 145.4 (2C, br), 142.7, 142.0 (2C), 141.6, 140.3, 134.8 (2C), 134.7 (2C), 134.6 (2C), 131.9, 131.8, 131.7, 131.2, 131.0, 130.3, 127.7 (3C), 126.8 (2C), 126.7 (2C), 126.6 (2C), 120.4, 119.5, 119.4, 106.5, 2.5, 2.1 (6C); IR (KBr), 3309, 3055, 3024, 2958, 1589, 1396, 1257, 1053, 845, 791, 744 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 415.5 (5.6), 512.5 (4.2), 546.5 (3.6), 585.5 (3.7), 639.5 (3.1) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{45}H_{47}N_4O_2Si_3$ 759.3007, found 759.2999.

5,15-Bis(2,4,6-trimethylphenyl)-2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-10-phenylporphyrin **H_2-2b**



Prepared from porphyrin **H_2-1b** (259.1 mg, 400 μmol) following the general procedure; Purple solid; 259.4 mg, 77% yield; R_f = 0.67 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.50 (1H, s), 9.34 (1H, d, *J* = 4.4 Hz), 9.07 (1H, s), 8.92 (2H, d, *J* = 4.4 Hz), 8.89 (1H, d, *J* = 4.4 Hz), 8.84 (1H, d, *J* = 4.4 Hz), 8.82 (1H, d, *J* = 4.4 Hz), 8.36-8.26 (2H, m), 7.86-7.75 (3H, m), 7.39 (4H, s), 2.72 (6H, s), 1.96 (6H, s), 1.95 (6H, s), 0.95 (3H, s), 0.31 (18H, s), -2.63 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.9 (br), 147.5 (4C, br), 145.6 (3C, br), 142.6, 141.9, 139.6 (2C), 139.5 (2C), 139.4, 138.3 (2C), 137.81, 137.80, 134.6 (2C), 132.0 (2C), 131.3, 130.6, 130.1, 129.4, 127.9 (2C), 127.8 (2C), 127.7, 126.6 (2C), 119.7, 117.7, 117.6, 105.9, 21.7 (4C), 21.5, 21.4, 2.5, 2.0 (6C); IR (KBr) 3313, 2958, 2920, 2858, 1473, 1257, 1057, 845, 795, 748 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 415.5 (5.8), 510.5 (4.4), 542.5 (3.8), 585.0 (3.9), 640.5 (3.4) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{51}H_{59}N_4O_2Si_3$ 843.3946, found 843.3950.

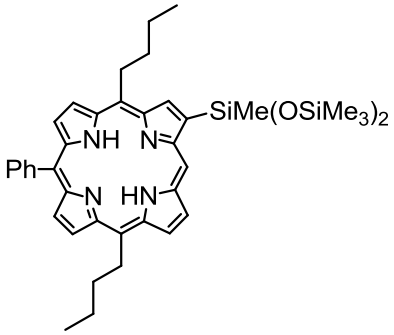
2-(1,1,1,3,5,5,5-Heptamethyltrisiloxan-3-yl)-5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrin **H_2-2c**



Prepared from porphyrin **H_2-1c** (350.1 mg, 400 μmol) following the general procedure; Purple solid; 314.6 mg, 72% yield; R_f = 0.72 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.44 (1H, s), 9.29 (1H, d, *J* = 4.4 Hz), 9.15 (1H, s), 9.02 (1H, d, *J* = 4.4 Hz), 8.93 (2H, d, *J* = 4.4 Hz), 8.87 (2H, d, *J* = 4.4 Hz), 8.10 (2H, d, *J* = 2.0 Hz), 8.08 (2H, d, *J* = 2.0 Hz), 8.05 (2H, d, *J* = 2.0 Hz), 7.79 (2H, t, *J* = 2.0 Hz), 7.77 (1H, t, *J* = 2.0 Hz), 1.53 (18H, s), 1.52 (18H, s), 1.50 (18H, s), 0.85 (3H, s), 0.20 (18H, s), -2.87 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.9 (2C), 148.7 (2C), 148.5 (2C), 148.0 (4C), 146.3 (4C), 141.7, 141.0 (2C), 140.6, 131.9 (2C), 131.6, 131.3 (2C), 130.5,

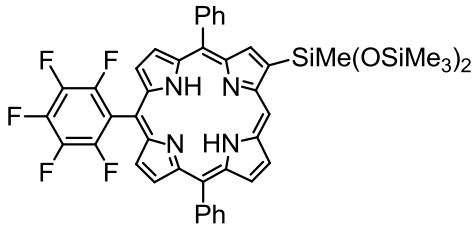
130.3, 129.9 (2C), 129.71 (2C), 129.67 (2C), 121.7, 121.1, 121.0 (2C), 120.7, 120.5, 106.1, 35.10 (2C), 35.07 (2C), 35.04 (2C), 31.8 (18C), 2.5, 2.1 (6C); IR (KBr) 3309, 2958, 2873, 1593, 1473, 1254, 1061, 845, 795 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 418.0 (5.7), 514.5 (4.3), 549.5 (3.8), 587.5 (3.7), 640.5 (3.5) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{69}H_{95}N_4O_2Si_3$ 1095.6763, found 1095.6768.

5,15-di(*n*-butyl)-2-(1,1,1,3,5,5,5-Heptamethyltrisiloxan-3-yl)-10-phenylporphyrin **H_2-2d**



Prepared from porphyrin **H_2-1d** (199.5 mg, 400 μmol) following the general procedure; Purple solid; 224.3 mg, 79% yield; R_f = 0.80 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.49 (1H, s), 9.88 (1H, s), 9.61 (1H, d, *J* = 4.4 Hz), 9.50 (1H, d, *J* = 4.40 Hz), 9.47 (1H, d, *J* = 4.4 Hz), 9.45 (1H, d, *J* = 4.4 Hz), 8.95 (2H, d, *J* = 4.4 Hz), 8.32-8.24 (2H, m), 7.90-7.75 (3H, m), 5.11 (2H, t, *J* = 8.0 Hz), 5.00 (2H, t, *J* = 8.0 Hz), 2.66 (2H, tt, *J* = 8.0, 7.6 Hz), 2.59 (2H, tt, *J* = 8.0, 7.6 Hz), 1.94 (2H, tq, *J* = 7.6, 7.3 Hz), 1.86 (2H, tq, *J* = 7.6, 7.3 Hz), 1.26 (3H, t, *J* = 7.3 Hz), 1.20 (3H, t, *J* = 7.3 Hz), 1.10 (3H, s), 0.46 (18H, s), -2.57 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.5, 148.2, 147.7, 146.5, 146.2, 146.0, 145.9, 144.4, 143.3, 141.7, 136.9, 134.5 (2C), 132.3, 132.2, 131.5, 128.3, 127.7, 127.6, 127.0, 126.5 (2C), 119.2, 119.1, 119.0, 105.6, 40.9, 40.7, 34.8, 34.6, 23.7, 23.6, 14.17, 14.15, 2.6, 2.2 (6C); IR (KBr) 3305, 3128, 3082, 3020, 2958, 2870, 1481, 1254, 1045, 841, 774 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 415.0 (5.6), 513.5 (4.3), 547.5 (3.8), 589.0 (3.8), 646.5 (3.5) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{41}H_{55}N_4O_2Si_3$ 719.3633, found 719.3624.

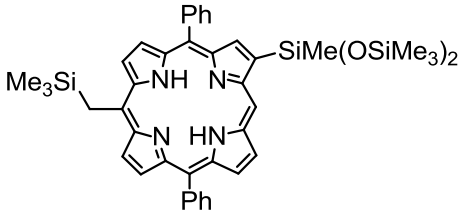
5,15-Diphenyl-2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-10-pentafluorophenylporphyrin **H_2-2e**



Prepared from porphyrin **H_2-1e** (251.4 mg, 400 μmol) following the general procedure; Purple solid; 197.2 mg, 58% yield; R_f = 0.86 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.67 (1H, s), 9.40 (1H, d, *J* = 4.6 Hz), 9.25 (1H, s), 9.07 (1H, d, *J* = 4.6 Hz), 9.06 (1H, d, *J* = 4.6 Hz), 9.05 (1H, d, *J* = 4.6 Hz), 8.86 (1H, d, *J* = 4.6 Hz), 8.85 (1H, d, *J* = 4.6 Hz), 8.34-8.27 (4H, m), 7.87-7.78 (6H, m), 0.93 (3H, s), 0.31 (18H, s), -2.80 (2H, br s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 148.7 (2C), 148.1, 146.9, 146.8 (2C, d, J_{CF} = 249.2 Hz), 146.3 (3C), 144.6, 142.4, 142.0 (1C, d, J_{CF}

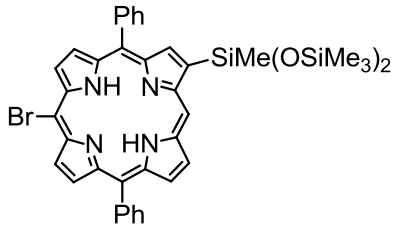
= 255.9 Hz), 141.59, 141.55, 140.4, 137.6 (2C, d, J_{CF} = 252.1 Hz), 134.8 (2C), 134.7 (2C), 132.7, 132.4, 131.9, 131.8, 129.5, 128.8, 128.0, 127.9, 126.94 (2C), 126.88 (2C), 120.3, 120.1, 117.4, 108.3, 100.5, 2.5, 2.1 (6C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ: -136.6 (2F, ddd, J_{FF} = 24.5, 8.6, 5.5 Hz), -153.1 (1F, tt, J_{FF} = 20.9, 5.5 Hz), -162.46 (2F, ddd, J_{FF} = 24.5, 20.9, 8.4 Hz); IR (KBr) 3309, 3059, 2958, 1493, 1257, 1061, 991, 845, 752 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 414.0 (5.5), 509.5 (4.3), 545.0 (3.5), 583.0 (3.8), 637.0 (3.3) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{45}H_{42}F_5N_4O_2Si_3$ 849.2536, found 849.2527.

5,15-Diphenyl-2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-10-(trimethylsilyl)methylporphyrin **H_2-2f**



Prepared from porphyrin **H_2-1f** (219.5 mg, 400 μmol) following the general procedure; Purple solid; 248.3 mg, 81% yield; R_f = 0.78 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.26 (1H, s), 9.39 (1H, d, J = 4.4 Hz), 9.38 (1H, d, J = 4.4 Hz), 9.20 (1H, d, J = 4.4 Hz), 9.09 (1H, s), 8.91 (1H, d, J = 4.4 Hz), 8.89 (2H, d, J = 4.4 Hz), 8.28-8.21 (4H, m), 7.83-7.74 (6H, m), 4.64 (2H, s), 0.85 (3H, s), 0.26 (18H, s), 0.07 (9H, s), -2.52 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.8 (8C), 142.4 (2C), 140.7 (2C), 134.7 (2C), 134.6 (2C), 132.0, 131.3, 130.9, 129.9, 128.9, 128.1, 127.59, 127.57, 126.7 (2C), 126.6 (2C), 121.3, 118.9, 118.8, 104.7, 27.2, 2.4, 2.1 (6C), -0.75 (3C); IR (KBr) 3313, 3059, 2954, 1597, 1477, 1254, 1049, 845, 748 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.0 (5.6), 519.0 (4.1), 554.5 (3.9), 593.0 (3.5), 650.5 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{43}H_{53}N_4O_2Si_4$ 769.3246, found 769.3253.

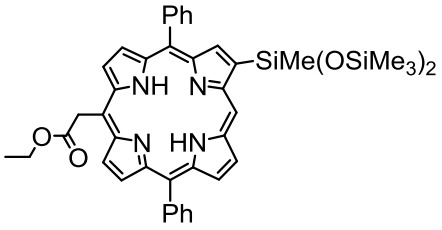
10-Bromo-5,15-diphenyl-2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)porphyrin **H_2-2g**



Prepared from porphyrin **H_2-1g** (216.6 mg, 400 μmol) following the general procedure; Purple solid; 146.2 mg, 48% yield; R_f = 0.69 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.55 (1H, s), 9.75 (2H, d, J = 4.9 Hz), 9.34 (1H, d, J = 4.9 Hz), 9.20 (1H, s), 9.01 (1H, d, J = 4.9 Hz), 9.00 (1H, d, J = 4.9 Hz), 8.98 (1H, d, J = 4.9 Hz), 8.33-8.21 (4H, m), 7.90-7.76 (6H, m), 0.92 (3H, s), 0.33 (18H, s), -2.77 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 149.1 (br), 148.4 (2C, br), 147.6 (br), 146.6 (2C, br), 145.9 (br), 144.6 (br), 142.1, 141.7, 141.6, 140.6, 134.8 (2C), 134.7 (2C), 132.8, 132.4, 132.2, 132.1 (2C), 131.5, 127.9 (2C), 126.9 (2C), 126.8 (2C), 120.2, 120.0, 107.3, 103.5, 2.5, 2.1 (6C); IR (KBr) 3313, 3051, 2958, 2900, 1477, 1257, 1053, 845, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max}

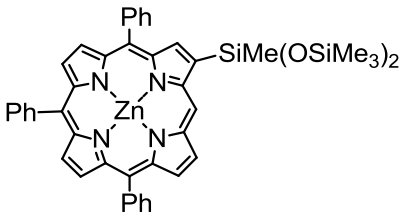
(log ε) 417.5 (5.5), 514.0 (4.2), 547.5 (3.8), 588.0 (3.7), 646.0 (3.5) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{39}H_{42}BrN_4O_2Si_3$ 761.1799, found 761.1805.

5,15-Diphenyl-10-(2-ethoxycarbonylethyl)-2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)porphyrin **H_2-2h**



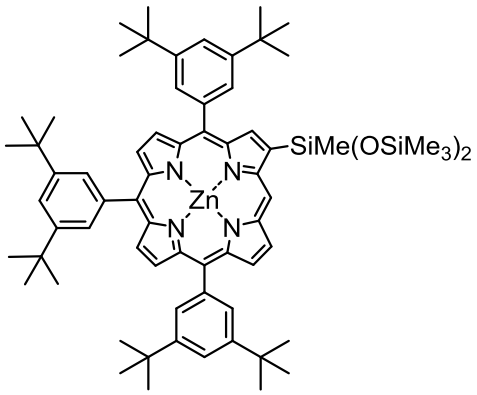
Prepared from porphyrin **H_2-1h** (75.4 mg, 137 μmol) following the general procedure; Purple solid; 68.6 mg, 65% yield; R_f = 0.75 (1/1 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 10.44 (1H, s), 9.57 (1H, d, *J* = 4.9 Hz), 9.56 (1H, d, *J* = 4.9 Hz), 9.27 (1H, d, *J* = 4.9 Hz), 9.12 (1H, s), 9.00 (1H, d, *J* = 4.9 Hz), 9.00 (1H, d, *J* = 4.9 Hz), 8.95 (1H, d, *J* = 4.9 Hz), 8.24-8.22 (4H, m), 7.81-7.75 (6H, m), 6.05 (2H, s), 4.17 (2H, q, *J* = 7.2 Hz), 1.13 (3H, t, *J* = 7.2 Hz), 0.83 (3H, s), 0.23 (18H, s), -2.96 (2H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 172.4, 149.1 (2C, br), 148.1 (3C, br), 145.8 (3C, br), 142.0 (2C), 140.2 (br), 134.7 (2C), 134.6 (2C), 132.2 (br), 132.0 br), 131.8 (2C, br), 131.2 (br), 128.9 (br), 128.1 (br), 127.8, 127.7, 126.8 (2C), 126.7 (2C), 119.4, 119.2, 110.3, 106.6, 61.3, 41.2, 14.1, 2.4, 2.1 (6C); IR (KBr), 3313, 3058, 2958, 1731, 1257, 1068, 844 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 416.0 (5.9), 512.5 (4.6), 545.5 (3.9), 586.0 (4.1), 642.5 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{43}H_{49}N_4O_4Si_3$ 769.3062, found 769.3069.

[2-(1,1,1,3,5,5,5-Heptamethyltrisiloxan-3-yl)-5,10,15-triphenylporphyrinato]zinc(II) **Zn-2a**



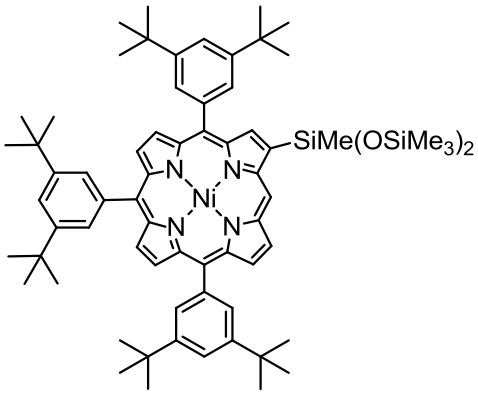
Prepared from porphyrin **Zn-1a** (240.8 mg, 400 μmol) following the general procedure; Purple solid; 223.6 mg, 68% yield; R_f = 0.74 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.55 (1H, s), 9.43 (1H, d, *J* = 4.6 Hz), 9.33 (1H, s), 9.06 (1H, d, *J* = 4.6 Hz), 8.97 (1H, d, *J* = 4.6 Hz), 8.95 (1H, d, *J* = 4.6 Hz), 8.92 (1H, d, *J* = 4.6 Hz), 8.91 (1H, d, *J* = 4.6 Hz), 8.35-8.20 (6H, m), 7.86-7.71 (9H, m), 0.95 (3H, s), 0.32 (18H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 156.8, 153.9, 153.8, 153.5, 153.43 (2C), 153.37, 153.1, 147.4, 147.2 (2C), 145.2, 145.0, 138.2 (2C), 138.1 (2C), 138.0 (2C), 135.4, 134.9, 134.8 (2C), 134.72, 134.68, 130.6 (3C), 129.8 (2C), 129.74 (2C), 129.66 (2C), 124.3, 123.5, 123.3, 110.5, 5.4, 4.9 (6C); IR (KBr) 3059, 3024, 2958, 1593, 1443, 1257, 1061, 845, 752 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.0 (5.7), 547.0 (4.3) nm; HRMS-FAB$^+$ ([M]$^+$) calcd for $C_{45}H_{44}N_4O_2Si_3Zn$ 820.2064, found 820.2064.

[2-(1,1,1,3,5,5,5-Heptamethyltrisiloxan-3-yl)-5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrinato]-znic (II) **Zn-2c**



Prepared from porphyrin **Zn-1c** (140 mg, 150 μmol) following the general procedure using 10 mol% of $[Ir(cod)OMe]_2$ and 20 mol% of dtbpy; Red solid; 72.0 mg, 42% yield; R_f = 0.78 (1/5 THF/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.51 (1H, s), 9.39 (1H, d, J = 4.6 Hz), 9.24 (1H, s), 9.13 (1H, d, J = 4.6 Hz), 9.04 (1H, d, J = 4.6 Hz), 9.03 (1H, d, J = 5.0 Hz), 9.01 (1H, d, J = 5.0 Hz), 9.00 (1H, d, J = 4.6 Hz), 8.10 (2H, d, J = 1.8 Hz), 8.08 (2H, d, J = 1.8 Hz), 8.06 (2H, d, J = 1.8 Hz), 7.80 (1H, t, J = 1.8 Hz), 7.79 (1H, t, J = 1.8 Hz), 7.76 (1H, t, J = 1.8 Hz), 1.53 (18H, s), 1.52 (18H, s), 1.50 (18H, s), 0.85 (3H, s), 0.21 (18H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.3, 150.5 (2C), 150.4 (2C), 150.2, 150.0, 149.9, 149.8, 149.7, 148.6 (2C), 148.4 (2C), 148.3 (2H, s), 142.3, 141.9, 141.8, 141.7, 141.6, 132.7, 132.2, 132.0, 131.9, 131.7, 129.7 (2C), 129.6 (2C), 129.4 (2C), 122.7, 121.8, 121.5, 120.9, 120.7, 107.3, 35.1 (2C), 35.0 (4C), 31.8 (6C), 31.7 (6C), 31.6 (6C), 2.6, 2.1 (6C); IR (KBr) 3066, 2958, 2869, 1592, 1253, 1064, 844 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 421.0 (5.5), 548.0 (4.1) nm; HRMS-FAB$^+$ ($[M]^+$) calcd for $C_{69}H_{92}N_4O_2Si_3Zn$ 1156.5820, found 1156.5815.

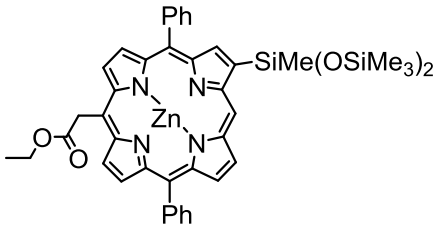
[2-(1,1,1,3,5,5,5-Heptamethyltrisiloxan-3-yl)-5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrinato]ni-ckel(II) **Ni-2c**



Prepared from porphyrin **Ni-1c** (372.8 mg, 400 μmol) following the general procedure; Red solid; 218.0 mg, 54% yield; R_f = 0.78 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.08 (1H, s), 9.13 (1H, d, J = 4.90 Hz), 9.06 (1H, s), 8.93 (1H, d, J = 4.9 Hz), 8.87 (1H, d, J = 4.9 Hz), 8.83 (3H, d, J = 4.9 Hz), 7.93 (2H, s), 7.92 (2H, s), 7.90 (2H, s), 7.78 (2H, s), 7.74 (1H, s), 1.52 (36H, s), 1.49

(18H, s), 0.78 (3H, s), 0.22 (18H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 149.1 (2C), 149.0 (3C), 146.2, 143.2, 143.1, 143.0, 142.9, 142.78, 142.75, 142.66, 142.5, 142.1 (2C), 140.4, 140.24, 140.23, 132.5, 132.2 (2C), 132.08, 132.05, 132.0, 128.9 (2C), 128.74 (2C), 128.68 (2C), 121.2, 121.11, 121.08, 120.5, 119.7, 119.5, 105.7, 35.1 (2C), 35.0 (4C), 31.7 (18C), 2.3, 2.1 (6C); IR (KBr) 3066, 2958, 2873, 1593, 1470, 1369, 1254, 1061, 845, 783 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 414.0 (5.4), 525.5 (4.3) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{69}H_{93}N_4NiO_2Si_3$ 1151.5960, found 1151.5957.

[5,15-Diphenyl-10-(2-ethoxycarbonylethyl)-2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)porphyrinato]znic(II) **Zn-2h**

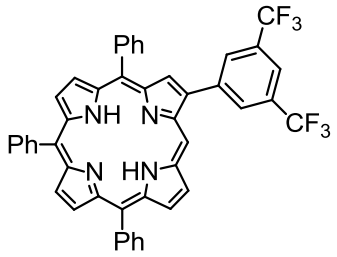


Prepared from porphyrin **Zn-1h** (102.0 mg, 166 μmol) following the general procedure; Purple solid; 112.7 mg, 82% yield; R_f = 0.63 (1/1 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 10.50 (1H, s), 9.55 (1H, d, J = 4.6 Hz), 9.54 (1H, d, J = 4.6 Hz), 9.36 (1H, d, J = 4.6 Hz), 9.21 (1H, s), 9.07 (1H, d, J = 4.6 Hz), 9.05 (1H, d, J = 4.6 Hz), 9.03 (1H, d, J = 4.6 Hz), 8.22-8.21 (4H, m), 7.81-7.74 (6H, m), 5.97 (2H, s), 4.15 (2H, q, J = 7.0 Hz), 1.17 (3H, t, J = 7.0 Hz), 0.83 (3H, s), 0.23 (18H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 172.9, 153.5, 150.3, 150.2, 150.1, 150.0, 149.9, 149.8, 149.7, 142.7, 142.6, 142.4, 142.0, 134.6 (2C), 134.5 (2C), 132.7, 132.6, 132.5, 132.0, 129.1, 129.0, 127.5, 127.4, 126.6 (2C), 126.5 (2C), 120.4, 120.2, 111.0, 107.8, 61.2, 41.0, 14.2, 2.6, 2.1 (6C); IR (KBr) 3058, 3023, 2958, 1689, 1257, 1052, 1006, 844 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 420.5 (5.6), 550.5 (4.2) nm; HRMS-FAB$^+$ ($[M]^+$) calcd for $C_{43}H_{46}N_4O_4Si_3Zn$ 830.2118, found 830.2116.

Preparation of *β*-Arylporphyrins 3

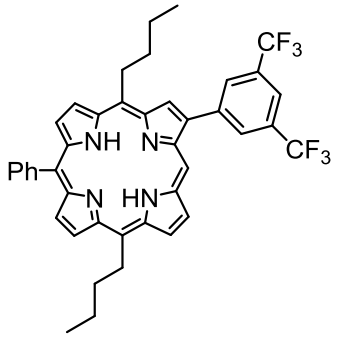
An oven-dried 50 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with *β*-silylporphyrin **2** (100 μmol), $Pd(PPh_3)_4$ (5.8 mg, 5 μmol, 5 mol%), and KO^{t}Bu (112.2 mg, 1 mmol, 10 equiv.). The reaction vessel was evacuated and flushed with argon (three times), and then 1-iodo-3,5-bis(trifluoromethyl)benzene (177 μL, 1 mmol, 10 equiv.) and dry THF (25 mL) were added. The mixture was stirred at 65 °C for 6-10 h, having been monitored by TLC (3/1 hexane/AcOEt). The reaction solution was diluted with CH_2Cl_2 (50 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (1/10 AcOEt/hexane) followed by recrystallization from MeOH/CH_2Cl_2 gave the pure product **3**.

2-[3,5-Bis(trifluoromethyl)phenyl-5,10,15-triphenylporphyrin **H_2-3a**



Prepared from porphyrin **H_2-2a** (75.9 mg, 100 μmol) following the general procedure; Purple solid; 46.6 mg, 62% yield; R_f = 0.65 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.12 (1H, s), 9.38 (1H, d, J = 4.8 Hz), 9.11 (1H, s), 9.09 (1H, d, J = 4.8 Hz), 8.99 (1H, d, J = 4.8 Hz), 8.97 (1H, d, J = 4.8 Hz), 8.91 (1H, d, J = 4.8 Hz), 8.88 (1H, d, J = 4.8 Hz), 8.76 (2H, s), 8.37-8.21 (7H, m), 7.91-7.71 (9H, m), -2.77 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 151.5 (br), 150.7 (br), 148.5 (br), 146.7 (br), 143.5 (br), 143.4 (br), 143.2, 142.9 (br), 142.4, 142.3 (br), 141.7 (2C), 139.2, 134.70 (2C), 134.68 (2C), 134.5 (2C), 133.3, 132.7, 132.4 (2C, q, J_{CF} = 33.2 Hz), 132.2, 131.2 (2C), 130.3 (2C), 130.2, 129.7, 128.0, 127.9 (2C), 127.0 (2C), 126.9 (2C), 126.7 (2C), 123.7 (2C, q, J_{CF} = 272.9 Hz), 121.4 (br), 121.1, 120.21, 120.18, 103.1; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: -63.34 (6F, s); IR (KBr) 3317, 3055, 2924, 2854, 1597, 1481, 1377, 1277, 1176, 1134, 980, 798, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 418.0 (5.6), 512.5 (4.3), 545.5 (3.5), 587.5 (3.7), 642.0 (3.1) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{46}H_{29}F_6N_4$ 751.2296 , found 751.2297.

2-[3,5-Bis(trifluoromethyl)phenyl-5,15-di(*n*-butyl)-10-phenylporphyrin **H_2-3d**



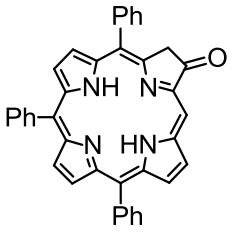
Prepared from porphyrin **H_2-2d** (78.0 mg, 108 μmol) following the general procedure; Purple solid; 64.8 mg, 84% yield; R_f = 0.62 (toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.89 (1H, s), 9.57 (1H, s), 9.54 (1H, d, J = 4.4 Hz), 9.46 (1H, d, J = 4.9 Hz), 9.39 (1H, d, J = 4.9 Hz), 9.33 (1H, d, J = 4.4 Hz), 8.92 (1H, d, J = 4.4 Hz), 8.83 (1H, d, J = 4.4 Hz), 8.75 (2H, s), 8.22 (1H, s), 8.19-8.17 (2H, m), 7.80-7.73 (3H, m), 4.97 (2H, t, J = 8.3 Hz), 4.95 (2H, t, J = 8.3 Hz), 2.57-2.49 (2H, m), 2.53-2.45 (2H, m), 1.86-1.80 (2H, m), 1.83-1.76 (2H, m), 1.12 (3H, t, J = 7.1 Hz), 1.11 (3H, t, J = 7.1 Hz), -2.76 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 151.8, 149.5, 148.7, 145.4, 143.9, 143.6, 143.5, 142.9 (2C), 141.9, 141.4, 139.5, 134.4 (2C), 133.8, 132.4 (2C, q, J_{CF} = 33.4 Hz), 131.2 (2C, q, J_{CF} = 7.0 Hz), 130.7, 130.6, 129.2, 129.0, 127.8, 126.9, 126.5 (2C), 126.2, 125.1, 122.4, 121.4-121.3 (1C, m), 119.9, 119.8, 102.1, 40.8, 40.7, 34.8, 34.7, 23.7, 23.6, 14.2, 14.1; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: -62.8 (6F, s); IR (KBr) 3289, 3085, 2958, 2931, 2865, 1276, 1130, 790 cm^{-1}; UV/vis ($CHCl_3$) λ_{max}

(log ε) 419.5 (5.6), 515.5 (4.3), 550.0 (3.8), 592.0 (3.8), 648.0 (3.7) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{42}H_{37}F_6N_4$ 711.2922, found 711.2919.

Preparation of *β*-Oxyporphyrins 4

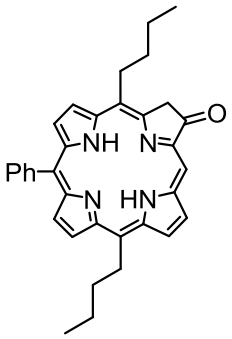
To a solution of *β*-silylporphyrin **2** (100 μmol) in a mixture of THF/acetone/H_2O (4 ml, 10/2/1, v/v), Oxone® (368.8 mg, 600 μmol, 6 equiv.) was added and stirred at 50 °C for 12 h. The reaction was quenched with aqueous $Na_2S_2O_3$, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude material was purified by column chromatography on silica gel (1/1 hexane/CH_2Cl_2) to give **4** as a brown-purple solid.

5,10,15-triphenylporphin-2(3*H*)-one **H_2-4a**



Prepared from porphyrin **H_2-2a** (75.9 mg, 100 μmol) following the general procedure; Brown-purple solid; 49.2 mg, 89% yield; R_f = 0.36 (1/5 AcOEt/hexane); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 9.70 (1H, s), 9.04 (1H, d, *J* = 4.4 Hz), 8.84 (1H, d, *J* = 4.4 Hz), 8.75 (1H, d, *J* = 4.4 Hz), 8.62 (1H, d, *J* = 4.4 Hz), 8.56 (1H, d, *J* = 4.4 Hz), 8.53 (1H, d, *J* = 4.4 Hz), 8.20-8.08 (4H, m), 7.98-7.87 (2H, m), 7.83-7.63 (9H, m), 4.63 (2H, s), -2.15 (1H, s), -2.33 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 204.6, 157.1, 154.6, 154.1, 149.6, 142.2, 141.4, 141.3, 140.2, 137.8, 136.8 (2C), 134.2 (2C), 134.1 (2C), 133.7, 133.6, 132.8 (2C), 129.0, 128.3, 128.1, 128.0, 127.9, 127.8 (2C), 126.9 (2C), 126.7 (2C), 126.2, 125.7, 123.2, 122.4, 113.3, 95.4, 45.5; IR (KBr) 3332, 3059, 2924, 2854, 1724, 1369, 1169, 968, 795, 710 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 417.5 (5.4), 518.0 (5.1), 553.5 (4.0), 591.0 (3.8), 646.0 (4.0) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{38}H_{27}N_4O$ 555.2185, found 555.2184.

5,15-di(*n*-butyl)-10-phenylporphin-2(3*H*)-one **H_2-4d**



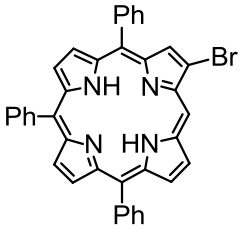
Prepared from porphyrin **H_2-2d** (72.0 mg, 100 μmol) following the general procedure; Brown-purple solid; 45.0 mg, 87% yield; R_f = 0.45 (1/1 CH_2Cl_2/hexane); ^{1}H-NMR ($CDCl_3$, 500

MHz) δ: 9.54 (1H, s), 9.35 (1H, d, *J* = 4.6 Hz), 9.20 (1H, d, *J* = 4.6 Hz), 9.07 (1H, d, *J* = 4.6 Hz), 8.99 (1H, dd, *J* = 4.9, 1.8 Hz), 8.75 (1H, dd, *J* = 4.9, 1.8 Hz), 8.58 (1H, d, *J* = 4.6 Hz), 8.13-8.12 (2H, m), 7.77-7.72 (3H, m), 4.78 (2H, t, *J* = 7.9 Hz), 4.65 (2H, s), 4.05 (2H, t, *J* = 7.9 Hz), 2.47-2.40 (2H, m), 2.15-2.09 (2H, m), 1.79-1.76 (2H, m), 1.72-1.68 (2H, m), 1.10 (3H, t, *J* = 7.3 Hz), 1.07 (3H, t, *J* = 7.3 Hz), -2.16 (1H, s), -2.58 (1H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 204.6, 156.8, 154.3, 153.2, 148.5, 142.6, 140.0, 136.9, 136.7, 135.7, 134.2, 134.0 (2C), 130.1, 129.4, 127.8, 126.6 (2C), 126.4, 124.9, 123.1, 122.6, 121.2, 111.7, 94.5, 43.5, 40.3, 37.9, 34.6, 34.0, 23.6, 23.5, 14.2, 14.1; IR (KBr) 3309, 3054, 2954, 2868, 1720, 1380, 971, 844, 786 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 415.0 (5.2), 429.0 (5.1), 524.0 (4.0), 558.5 (3.9), 594.5 (3.8), 650.0 (3.9) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{34}H_{35}N_4O$ 515.2811, found 515.2807.

Preparation of *β*-Bromoporphyrins 5

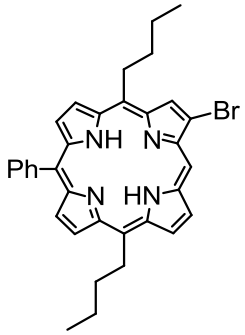
To a solution of silylpophyrin **2** (100 μmol) in $CHCl_3$ (10 mL) was added a solution of NBS (19.6 mg, 110 μmol, 1.1 equiv) in $CHCl_3$ (10 mL) at 0 °C. The reaction mixture was stirred for 30 min and quenched with acetone (1 mL). The solvent was evaporated to dryness. Column chromatography on silica gel (1/4 toluene/hexane) followed by recrystallization from CH_2Cl_2/hexane gave the pure compound **5**.

2-Bromo-5,10,15-triphenylporphyrin **H_2-5a**



Prepared from porphyrin **H_2-2a** (75.9 mg, 100 μmol) following the general procedure; Purple solid; 56.8 mg, 92% yield; R_f = 0.55 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.37 (1H, s), 9.42 (1H, d, *J* = 4.8 Hz), 9.06 (1H, d, *J* = 4.8 Hz), 8.94 (1H, s), 8.93 (1H, d, *J* = 4.8 Hz), 8.91 (1H, d, *J* = 4.8 Hz), 8.80 (1H, d, *J* = 4.8 Hz), 8.77 (1H, d, *J* = 4.8 Hz), 8.27-8.15 (6H, m), 7.83-7.68 (9H, m), -2.89 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 154.2, 153.4, 151.6, 148.8, 142.5, 141.7, 141.5, 140.7, 140.3, 139.9, 139.5, 134.7 (2C), 134.6 (2C), 134.5 (2C), 134.3, 134.0, 133.6, 129.1 (2C), 129.0, 128.5, 128.0, 127.9 (2C), 127.0 (2C), 126.9 (2C), 126.6 (2C), 123.4, 121.2, 120.2, 119.6, 102.4; IR (KBr) 3313, 3132, 3089, 3028, 1593, 1481, 1396, 1173, 1057, 972, 795, 741 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 416.5 (5.6), 512.0 (4.3), 545.5 (3.6), 585.5 (3.8), 640.0 (3.5) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{38}H_{26}BrN_4Br$ 617.1341, found 617.1343.

2-Bromo-5,15-di(*n*-butyl)-10-phenylporphyrin **H_2-5d**

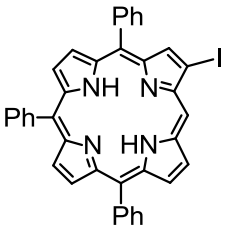


Prepared from porphyrin **H_2-2d** (143.8 mg, 200 μmol) following the general procedure; Purple solid; 109.0 mg, 94% yield; R_f = 0.76 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.11 (1H, s), 9.39 (1H, d, *J* = 4.9 Hz), 9.38 (1H, d, *J* = 4.9 Hz), 9.33 (1H, d, *J* = 4.9 Hz), 9.30 (2H, d, *J* = 4.9 Hz), 8.88 (1H, d, *J* = 4.9 Hz), 8.79 (1H, d, *J* = 4.9 Hz), 8.19 (2H, d, *J* = 6.8 Hz), 7.82 (1H, t, *J* = 7.3 Hz), 7.75 (2H, dd, *J* = 7.3, 6.8 Hz), 4.80 (2H, t, *J* = 8.0 Hz), 4.70 (2H, t, *J* = 8.0 Hz), 2.47 (2H, tt, *J* = 8.0, 7.7 Hz), 2.44 (2H, tt, *J* = 8.0, 7.7 Hz), 1.78 (2H, tq, *J* = 7.7, 7.3 Hz), 1.76 (2H, tq, *J* = 7.7, 7.3 Hz), 1.14 (3H, t, *J* = 7.3 Hz), 1.12 (3H, t, *J* = 7.3 Hz), -2.91 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 154.5, 152.1, 151.7, 147.32, 142.99, 140.8, 140.3, 138.9, 138.4, 134.8, 134.4 (2C), 130.9, 130.1, 129.3, 129.2, 127.7, 126.5, 125.6 (2C), 124.9, 123.8, 119.8, 119.6, 119.1, 101.2, 40.6, 40.5, 34.54, 34.49, 23.6 (2C), 14.1 (2C); IR (KBr) 3305, 3124, 3197, 2954, 2924, 2858, 1477, 1300, 1057, 1026, 980, 922, 791, 733 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 417.0 (5.6), 514.5 (4.3), 547.5 (3.7), 588.5 (3.8), 645.5 (3.7) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{34}H_{34}BrN_4$ 577.1967 , found 577.1965.

Preparation of *β*-Iodoporphyrins 6

To a solution of silylpophyrin **2** (100 μmol) in $CHCl_3$ (10 mL) was added a mixed solution of [bis(trifluoroacetoly)iodo]-benzene (64.5 mg, 150 μmol, 1.5 equiv) and Iodine (19 mg, 150 μmol, 1.5 equiv) in $CHCl_3$ (10 mL) at 0 °C. The reaction mixture was stirred for 3 h and quenched with acetone (1 mL). The reaction mixture was diluted with CH_2Cl_2 and washed with aqueous $Na_2S_2O_3$, water and brine. The organic layer was dried over anhydrous $MgSO_4$, and concentrated in vacuo. Column chromatography on silica gel (1/4 toluene/hexane) followed by recrystallization from MeOH/CH_2Cl_2 gave the pure compound **6**.

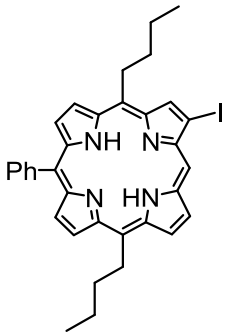
2-Iodo-5,10,15-triphenylporphyrin **H_2-6a**



Prepared from porphyrin **H_2-2a** (75.9 mg, 100 μmol) following the general procedure; Purple solid; 55.4 mg, 83% yield; R_f = 0.53 (1/5 AcOEt/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.30 (1H, s),

9.43 (1H, d, *J* = 4.9 Hz), 9.17 (1H, s), 9.07 (1H, d, *J* = 4.9 Hz), 8.96 (1H, d, *J* = 4.9 Hz), 8.94 (1H, d, *J* = 4.9 Hz), 8.83 (1H, d, *J* = 4.9 Hz), 8.80 (1H, d, *J* = 4.9 Hz), 8.33-8.14 (6H, m), 7.88-7.66 (9H, m), -2.85 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 154.0, 153.3 (2C), 150.8, 142.5, 141.7, 141.51 (2C), 141.49, 141.0, 140.4, 140.2, 139.8, 134.69 (2C), 134.65 (2C), 134.5 (2C), 134.2, 133.5, 129.23, 129.20, 129.1, 128.7, 128.0, 127.9 (2C), 127.0 (2C), 126.9 (2C), 126.6 (2C), 121.1, 120.1, 119.3, 104.8; IR (KBr) 3302, 3059, 3020, 1593, 1481, 972, 795, 752 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 418.0 (5.8), 513.0 (4.5), 546.5 (3.8), 585.5 (4.0), 640.5 (3.7) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{38}H_{26}IN_4$ 665.1202 , found 665.1201.

2-Iodo-5,15-di(*n*-butyl)-10-phenylporphyrin **H_2-6d**

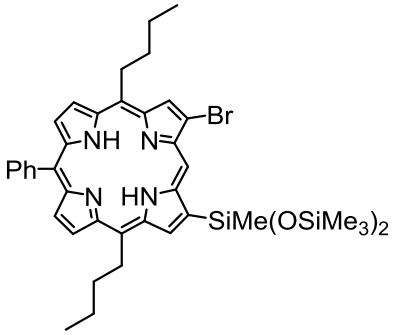


Prepared from porphyrin **H_2-2d** (74.0 mg, 102 μmol) following the general procedure; Purple solid; 41.4 mg, 65% yield; R_f = 0.58 (1/2 THF/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.09 (1H, s), 9.65 (1H, s), 9.50 (1H, d, *J* = 4.6 Hz), 9.40 (2H, d, *J* = 4.6 Hz), 9.32 (1H, d, *J* = 4.6 Hz), 8.89 (1H, d, *J* = 4.6 Hz), 8.77 (1H, d, *J* = 4.6 Hz), 8.16 (2H, d, *J* = 7.0 Hz), 7.79-7.71 (3H, m), 4.89 (2H, t, *J* = 7.9 Hz), 4.83 (2H, t, *J* = 7.9 Hz), 2.52-2.44 (2H, m), 2.50-2.42 (2H, m), 1.81-1.77 (2H, m), 1.80-1.75 (2H, m), 1.12 (3H, t, *J* = 7.2 Hz), 1.11 (3H, t, *J* = 7.2 Hz), -2.86 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 154.8, 154.0, 152.4, 149.9, 143.2, 143.1, 141.1, 140.5, 139.2, 138.8, 135.1, 134.7 (2C), 130.5, 129.7, 129.6, 128.0, 126.8 (2C), 126.0, 125.4, 120.1, 120.0, 119.2, 104.0, 95.8, 41.1, 41.0 (0H, s), 34.9, 34.8, 23.9, 23.8, 14.5 (2C); IR (KBr) 3305, 3120, 3050, 2954, 2927, 2861, 1481, 979, 790, 732 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 420.0 (5.5), 516.5 (4.2), 592.0 (3.7), 647.5 (3.5) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{34}H_{34}IN_4$ 625.1812 , found 625.1820.

Preparation of *β*-Bromo-*β*-silylporphyrins 7

An oven-dried 50 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with porphyrin **H_2-5d** (87 mg, 150 μmol), $[Ir(cod)OMe]_2$ (10 mg, 15 μmol, 10 mol%), and dtbpy (8.1 mg, 30 μmol, 20 mol%). The reaction vessel was evacuated and flushed with argon (three times), and then 1,1,1,3,5,5,5-heptamethyltrisiloxane (205 μL, 750 μmol, 5 equiv.) and dry dioxane (1 mL) were added. The mixture was stirred at 95 °C for 24 h, having been monitored by TLC (1/2 $CHCl_3$/hexane). The solvent was evaporated to dryness. Column chromatography on silica gel (1/10 AcOEt/hexane) followed by recrystallization from MeOH/CH_2Cl_2 gave the pure product **H_2-7d**.

2-Bromo-5,15-di(*n*-butyl)-18-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-10-phenylporphyrin **H_2-7d**

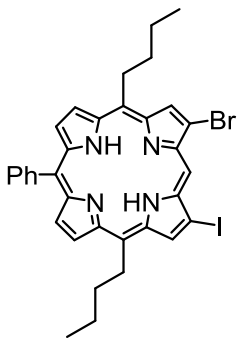


Purple solid; 100.7 mg, 84% yield; R_f = 0.50 (1/2 $CHCl_3$/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.46 (1H, s), 9.76 (1H, s), 9.49 (1H, s), 9.42 (1H, d, *J* = 4.8 Hz), 9.36 (1H, d, *J* = 4.8 Hz), 8.89 (1H, d, *J* = 4.9 Hz), 8.77 (1H, d, *J* = 4.8 Hz), 8.17-8.15 (2H, m), 7.74 (3H, dd, *J* = 14.4, 5.2 Hz), 4.98 (2H, t, *J* = 8.0 Hz), 4.86 (2H, t, *J* = 7.9 Hz), 2.57-2.47 (2H, m), 2.52-2.42 (2H, m), 1.88-1.79 (2H, m), 1.83-1.73 (2H, m), 1.14 (3H, t, *J* = 7.4 Hz), 1.11 (3H, t, *J* = 7.3 Hz), 1.03 (3H, s), 0.28 (18H, s), -2.79 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.2, 152.8, 152.6, 148.1, 143.1, 141.8, 140.2, 140.1, 140.0, 138.6, 135.2, 134.6 (2C), 134.5, 131.4, 130.6, 129.3, 127.9, 126.7 (2C), 125.1, 124.7, 120.0, 119.7, 119.2, 103.1, 41.1, 40.9, 35.0, 34.9, 23.9, 23.8, 14.4 (2C), 2.8, 2.4 (6C); IR (KBr) 3295, 3082, 3055, 2956, 2855, 1471, 1253, 1068, 919, 842, 790 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.5 (5.5), 517.5 (4.2), 554.0 (3.5), 590.0 (3.7), 647.0 (3.5) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{41}H_{54}BrN_4O_2Si_3$ 797.2738, found 797.2744.

Preparation of *β*-Bromo-*β*-Iodoporphyrins H_2-8d

To a solution of silylpophyrin **H_2-7d** (101 mg, 126 μmol) in $CHCl_3$ (10 mL) was added a mixed solution of [bis(trifluoroacetoly)iodo]-benzene (135 mg, 315 μmol, 2.5 equiv.) and Iodine (40 mg, 315 μmol, 2.5 equiv.) in $CHCl_3$ (10 mL) at 0 °C. The reaction mixture was stirred for 2 h and quenched with acetone (1 mL). The reaction mixture was diluted with CH_2Cl_2 and washed with aqueous $Na_2S_2O_3$ and brine. The organic layer was dried over anhydrous $MgSO_4$, and concentrated in vacuo. Column chromatography on silica gel (1/7 THF/hexane) followed by recrystallization from MeOH/CH_2Cl_2 gave the pure compound **H_2-8d**.

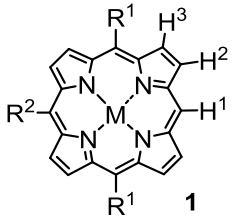
2-Bromo-5,15-di(*n*-butyl)-18-iodo-10-phenylporphyrin **H_2-8d**



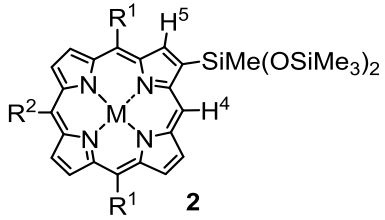
Purple solid; 67.4 mg, 76% yield; R_f = 0.76 (1/2 THF/hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ:

10.11 (1H, s), 9.58 (1H, s), 9.36 (1H, s), 9.28 (2H, d, *J* = 4.6 Hz), 9.27 (2H, d, *J* = 4.6 Hz), 8.79 (2H, d, *J* = 4.6 Hz), 8.78 (2H, d, *J* = 4.6 Hz), 8.15-8.13 (2H, m), 7.79 (1H, tt, *J* = 7.5, 1.7 Hz), 7.75-7.72 (2H, m), 4.72 (2H, t, *J* = 7.9 Hz), 4.69 (2H, t, *J* = 7.9 Hz), 2.43-2.40 (2H, m), 2.40-2.37 (2H, m), 1.78-1.76 (2H, m), 1.75-1.73 (2H, m), 1.10 (3H, t, *J* = 7.3 Hz), 1.09 (3H, t, *J* = 7.3 Hz), -2.95 (2H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 147.9, 147.2, 146.8, 146.2, 145.9, 145.3, 143.3, 142.6, 141.9, 135.9, 134.3 (2C), 132.5, 132.1, 128.8, 128.0, 127.8, 127.6, 126.5 (2C), 122.0, 120.3, 119.5, 119.2, 101.7, 92.9, 40.7, 40.6, 34.5, 29.7, 23.6, 23.5, 14.1 (2C); IR (KBr) 3293, 3050, 2954, 2923, 2861, 1473, 1442, 1014, 790 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 422.0 (5.7), 518.5 (4.5), 552.5 (3.8), 594.5 (4.0), 650.5 (3.7) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{34}H_{33}BrIN_4$ 703.0933, found 703.0931.

Table S1. Comparison of ^{1}H NMR spectra of *β*-silyated porphyrins 2 with the starting *meso*-unsubstituted porphyrins 1.



1



2

									Δδ (**2**-**1**)	
R^1	R^2	**1**	δ (*meso*-H^1)	δ (*β*-H^2)	δ (*β*-H^3)	**2**	δ (*meso*-H^4)	δ (*β*-H^5)	$\Delta\delta_{meso}$ = $\delta_H{}^4$-$\delta_H{}^1$	$\Delta\delta_{\beta}$ = $\delta_H{}^5$-$\delta_H{}^3$
Ph	Ph	**H_2-1a**	10.21 (s)	9.31 (d)	9.01 (d)	**H_2-2a**	10.56 (s)	9.24 (s)	0.35	0.23
2,4,6-Me_3Ph	Ph	**H_2-1b**	10.10 (s)	9.25 (d)	8.81 (d)	**H_2-2b**	10.50 (s)	9.07 (s)	0.40	0.26
3,5-(*t*-Bu)$_2$$C_6H_3$	3,5-(*t*-Bu)$_2$$C_6H_3$	**H_2-1c**	10.18 (s)	9.32 (d)	9.04 (d)	**H_2-2c**	10.44 (s)	9.15 (s)	0.26	0.11
n-Bu	Ph	**H_2-1d**	10.05 (s)	9.53 (d)	9.42 (d)	**H_2-2d**	10.49 (s)	9.88 (s)	0.44	0.46
Ph	C_6F_5	**H_2-1e**	10.28 (s)	9.34 (d)	9.01 (d)	**H_2-2e**	10.67 (s)	9.25 (s)	0.39	0.24
Ph	CH_2SiMe_3	**H_2-1f**	9.94 (s)	9.18 (d)	8.92 (d)	**H_2-2f**	10.26 (s)	9.10 (s)	0.32	0.18
Ph	Br	**H_2-1g**	10.16 (s)	9.27 (d)	8.94 (d)	**H_2-2g**	10.55 (s)	9.20 (s)	0.39	0.26
Ph	CH_2CO_2Et	**H_2-1h**	10.14 (s)	9.26 (d)	8.96 (d)	**H_2-2h**	10.44 (s)	9.12 (s)	0.30	0.16
Ph	Ph	**Zn-1a**	10.23 (s)	9.38 (d)	9.08 (d)	**Zn-2a**	10.55 (s)	9.33 (s)	0.32	0.25
3,5-(*t*-Bu)$_2$$C_6H_3$	3,5-(*t*-Bu)$_2$$C_6H_3$	**Zn-1c**	10.25 (s)	9.39 (d)	9.12 (d)	**Zn-2c**	10.51 (s)	9.21 (s)	0.26	0.09
3,5-(*t*-Bu)$_2$$C_6H_3$	3,5-(*t*-Bu)$_2$$C_6H_3$	**Ni-1c**	9.81 (s)	9.12 (d)	8.91 (d)	**Ni-2c**	10.08 (s)	9.06 (s)	0.27	0.15
Ph	CH_2CO_2Et	**Zn-1h**	10.12 (s)	9.29 (d)	9.01 (d)	**Zn-2h**	10.50 (s)	9.21 (s)	0.38	0.20

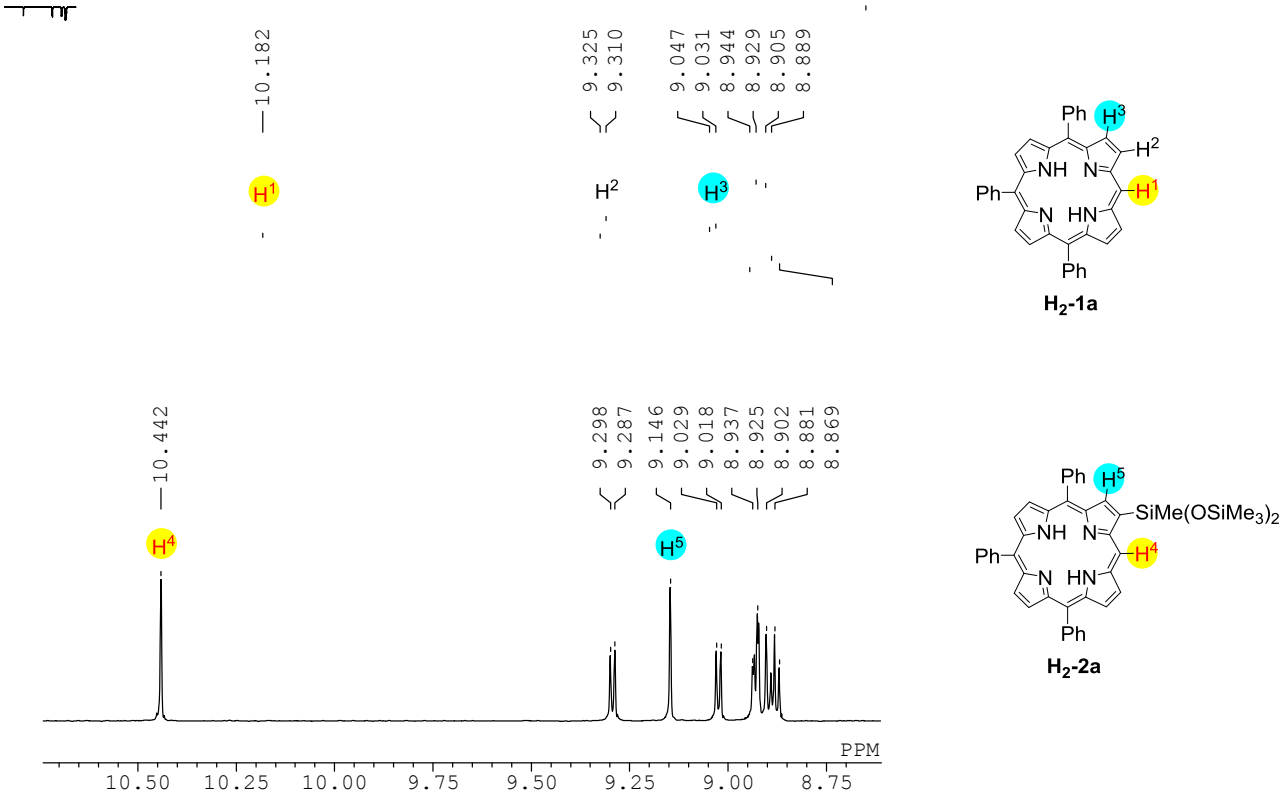


Fig. S1 Comparison of ^{1}H NMR spectra of *β*-silyated porphyrin **H_2-2a** with starting porphyrin **H_2-1a** (in $CDCl_3$).

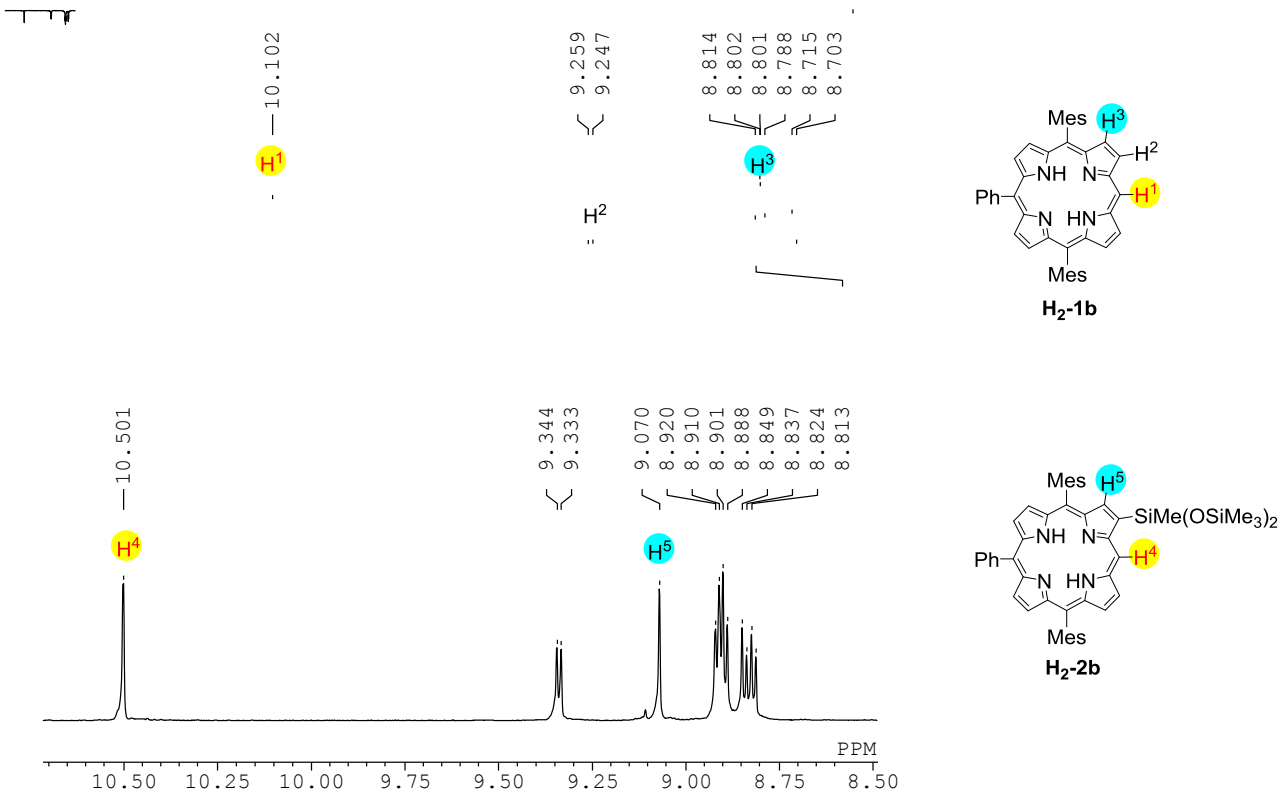


Fig. S2 Comparison of ^{1}H NMR spectra of *β*-silyated porphyrin **H_2-2b** with starting porphyrin **H_2-1b** (in $CDCl_3$).

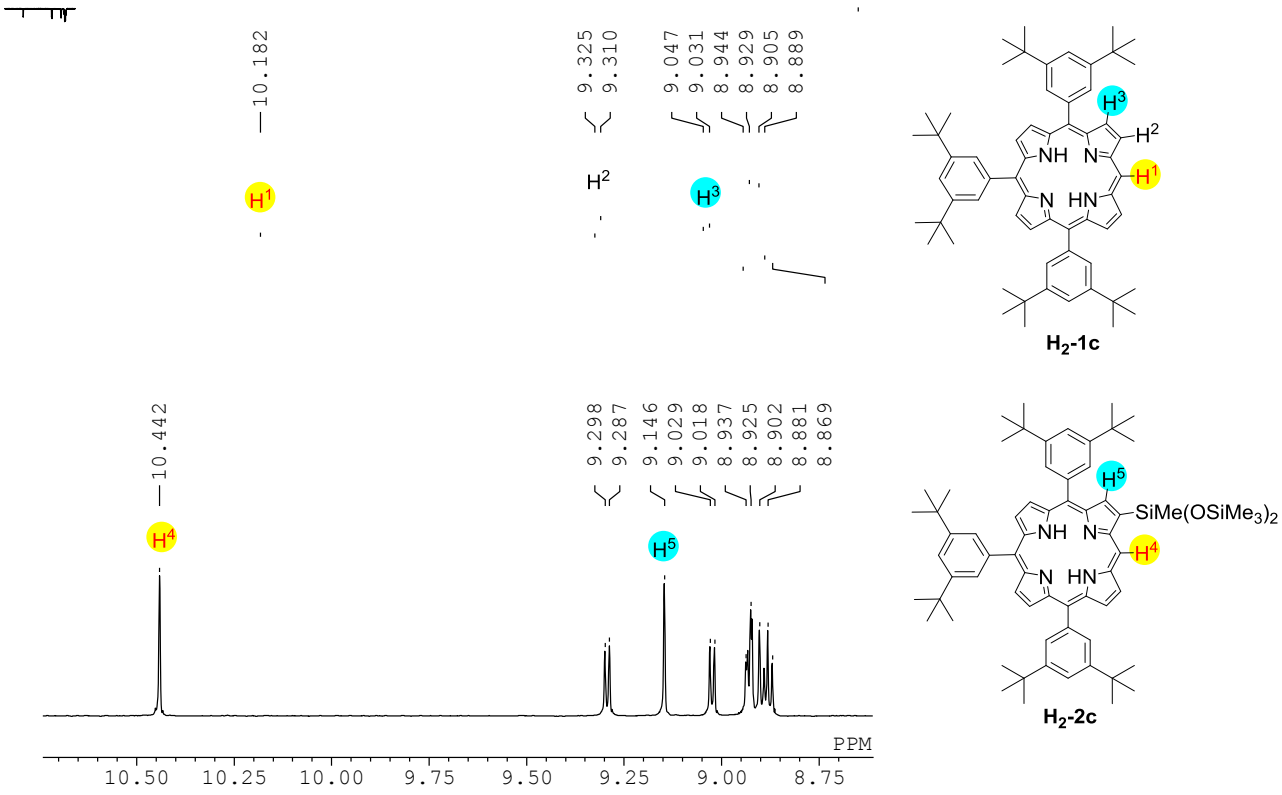


Fig. S3 Comparison of ^{1}H NMR spectra of *β*-silyated porphyrin **H_2-2c** with starting porphyrin **H_2-1c** (in $CDCl_3$).

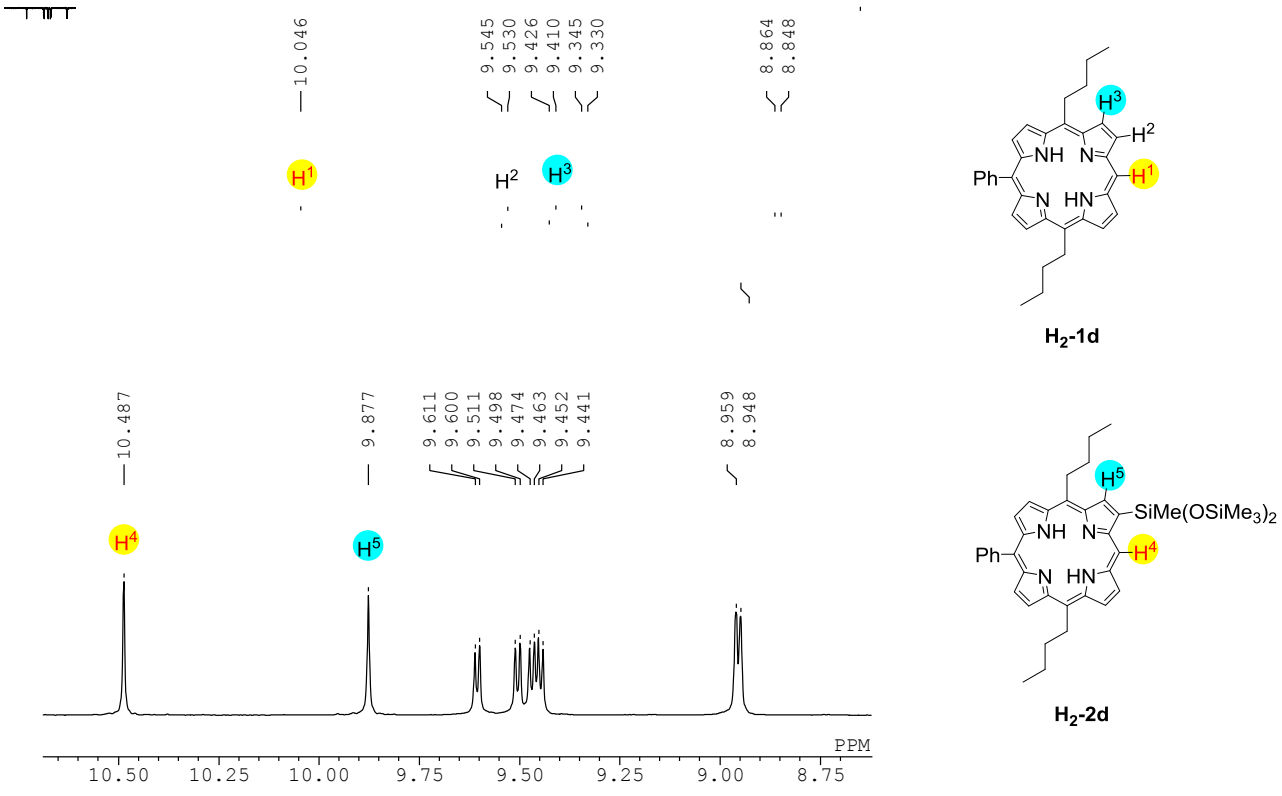


Fig. S4 Comparison of ^{1}H NMR spectra of *β*-silyated porphyrin **H_2-2d** with starting porphyrin **H_2-1d** (in $CDCl_3$).

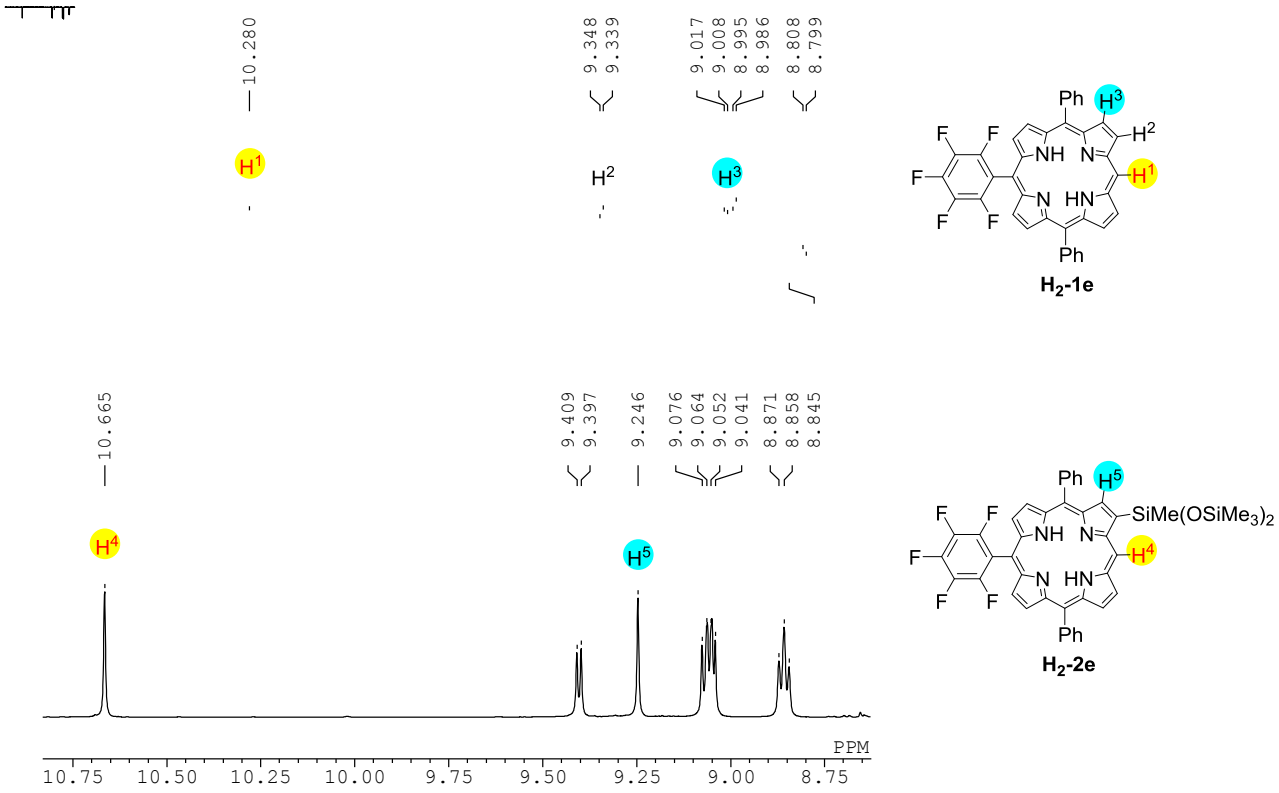


Fig. S5 Comparison of ^{1}H NMR spectra of *β*-silyated porphyrin **H$_2$-2e** with starting porphyrin **H$_2$-1e** (in $CDCl_3$).

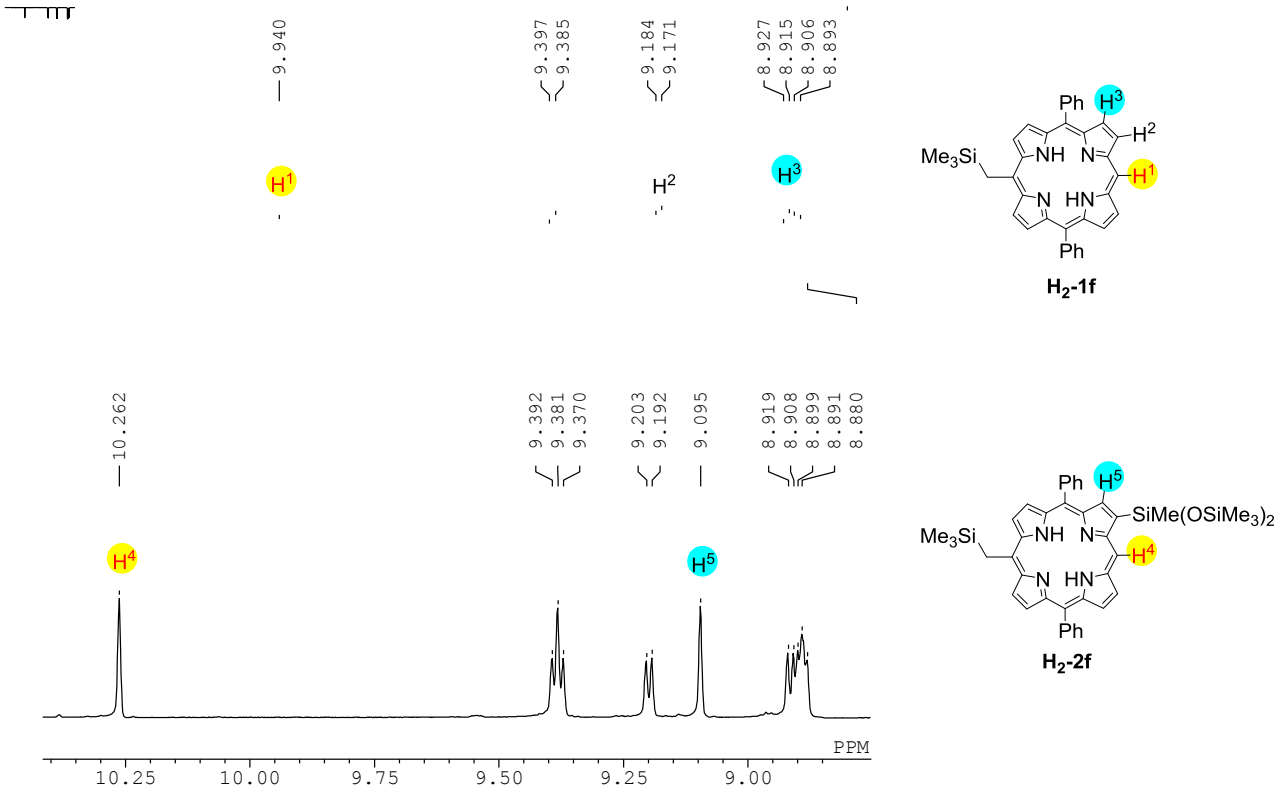


Fig. S6 Comparison of ^{1}H NMR spectra of *β*-silyated porphyrin **H$_2$-2f** with starting porphyrin **H$_2$-1f** (in $CDCl_3$).

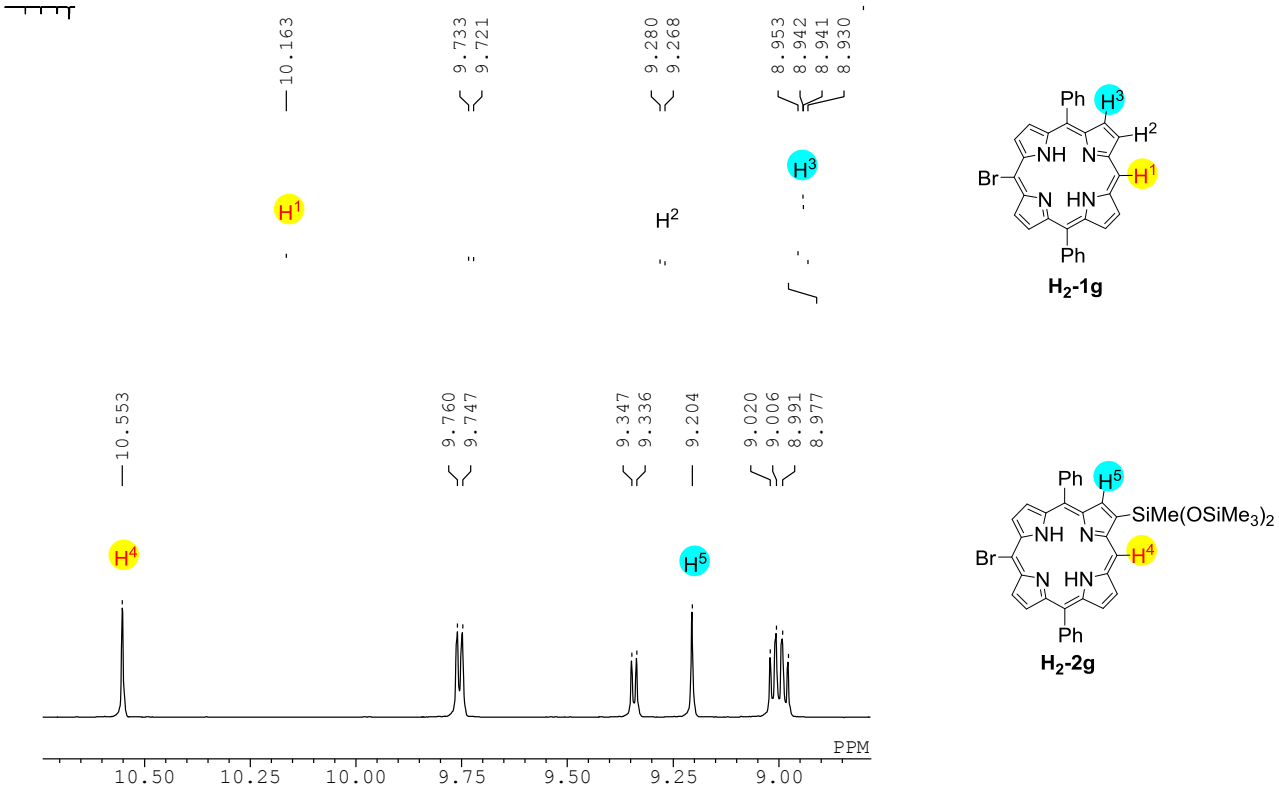


Fig. S7 Comparison of ^{1}H NMR spectra of *β*-silyated porphyrin **H_2-2g** with starting porphyrin **H_2-1g** (in $CDCl_3$).

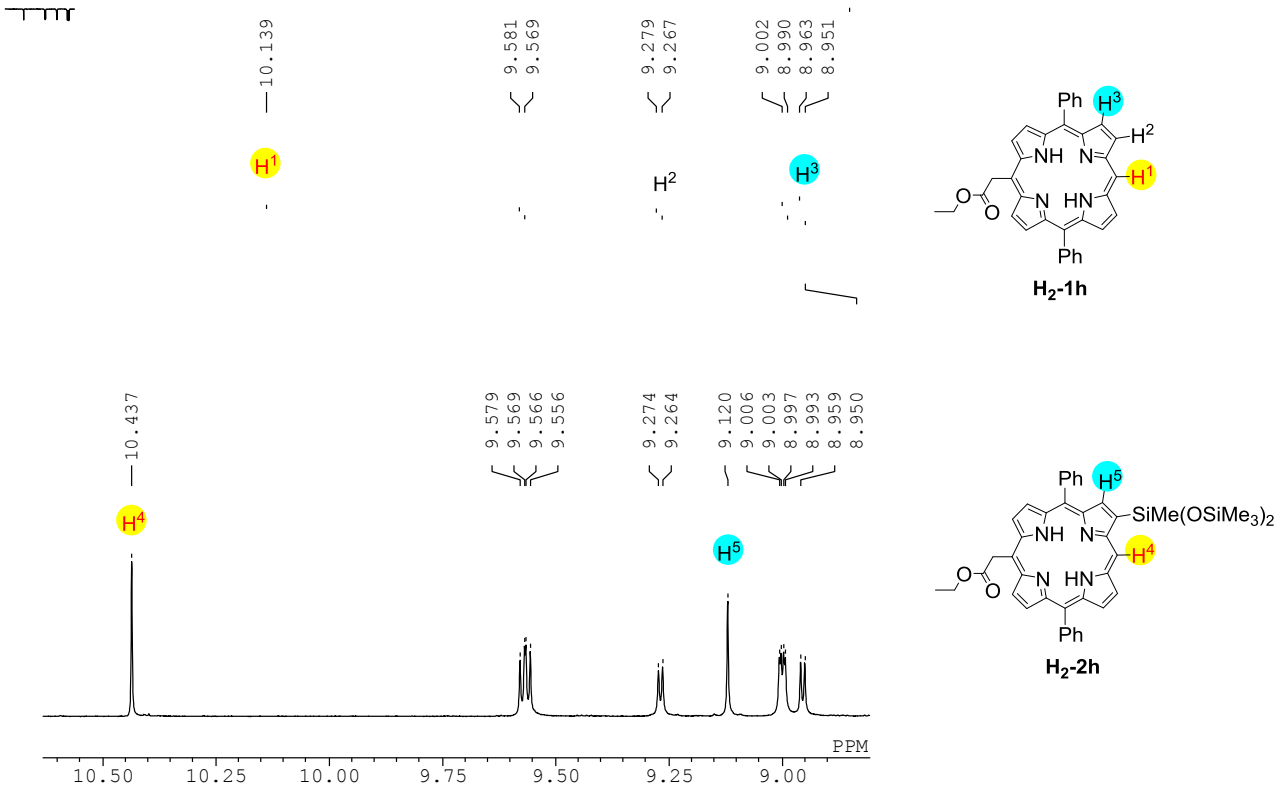


Fig. S8 Comparison of ^{1}H NMR spectra of *β*-silyated porphyrin **H_2-2h** with starting porphyrin **H_2-1h** (in $CDCl_3$).

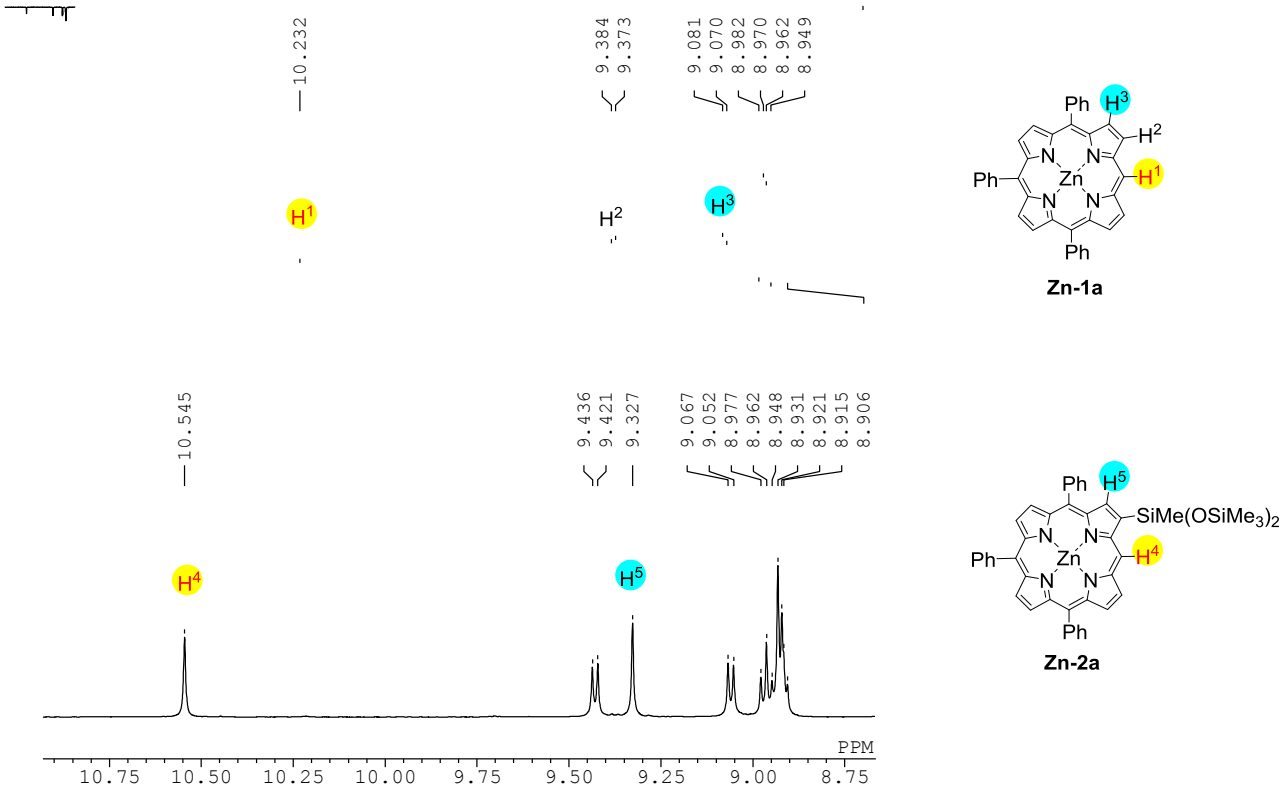


Fig. S9 Comparison of ^{1}H NMR spectra of *β*-silyated porphyrin **Zn-2a** with starting porphyrin **Zn-1a** (in $CDCl_3$).

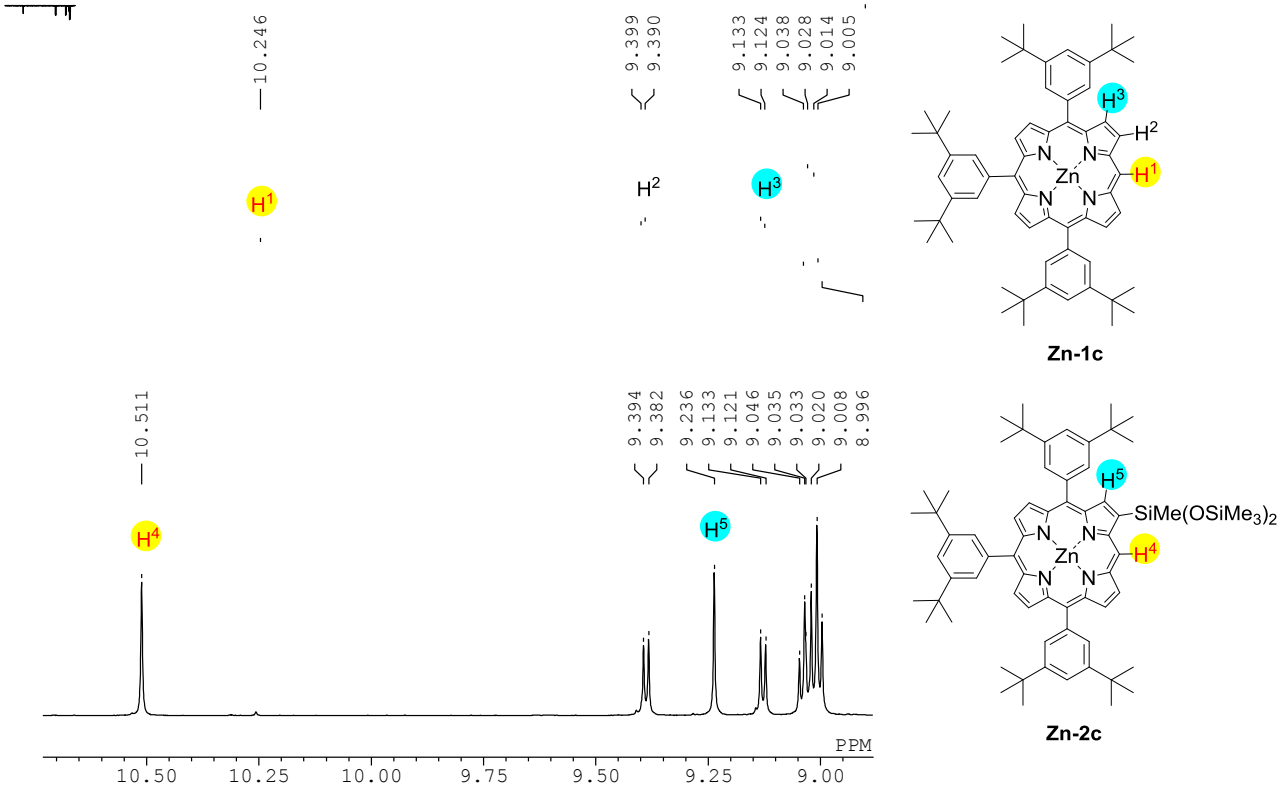


Fig. S10 Comparison of ^{1}H NMR spectra of *β*-silyated porphyrin **Zn-2c** with starting porphyrin **Zn-1c** (in $CDCl_3$).

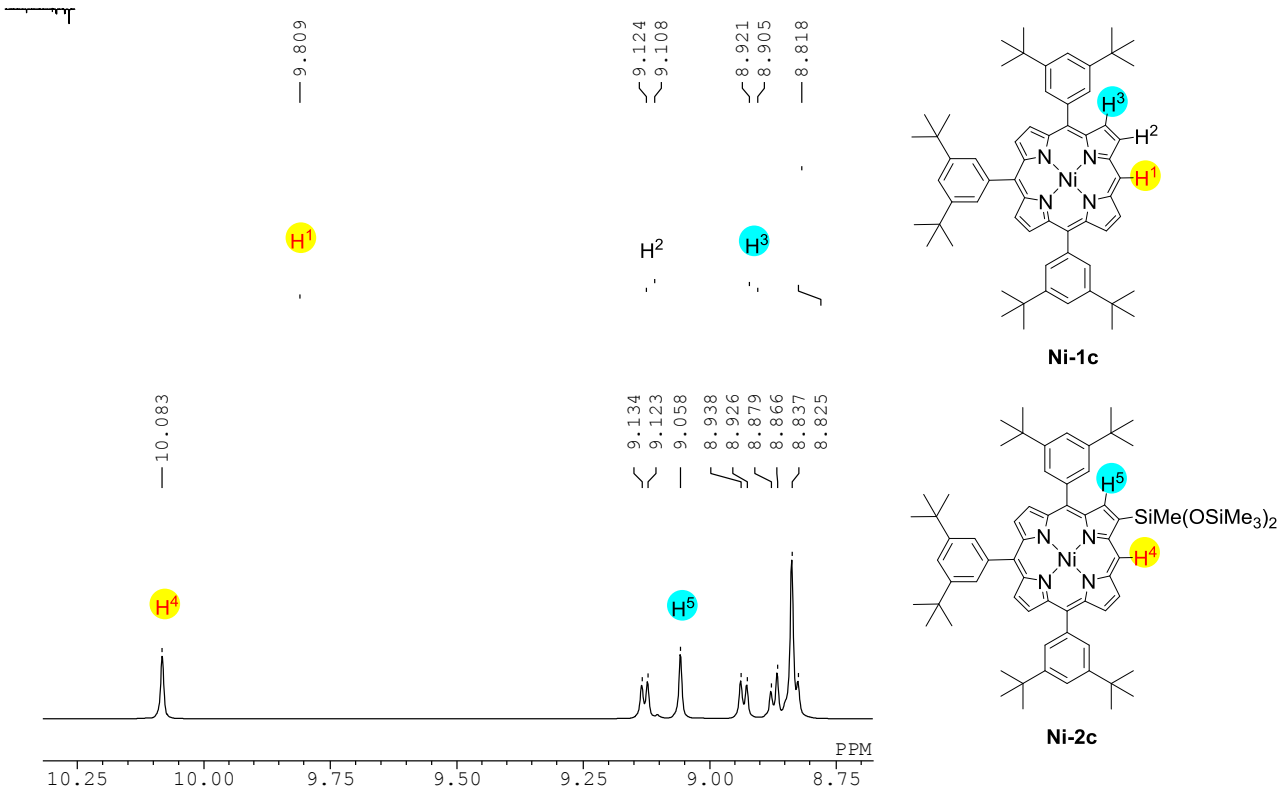


Fig. S11 Comparison of ^{1}H NMR spectra of *β*-silyated porphyrin **Ni-2c** with starting porphyrin **Ni-1c** (in $CDCl_3$).

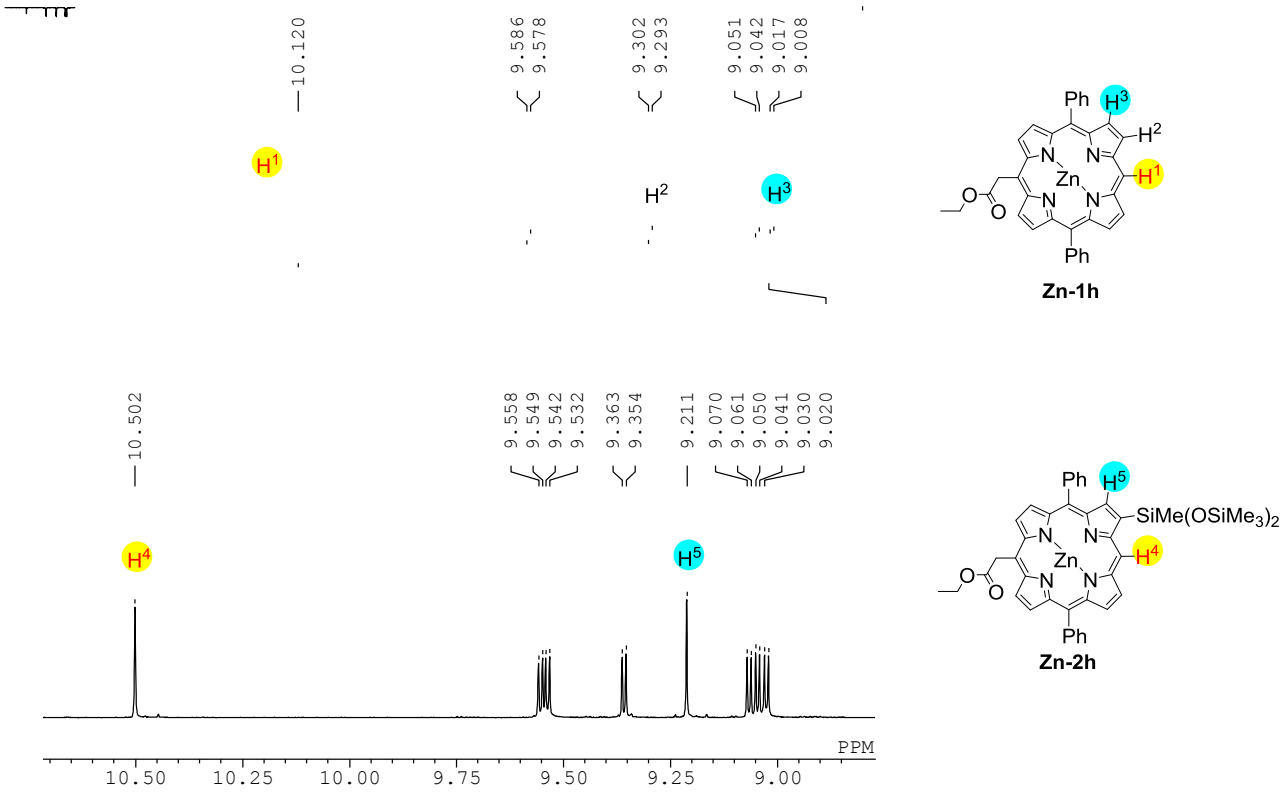


Fig. S12 Comparison of ^{1}H NMR spectra of *β*-silyated porphyrin **Zn-2h** with starting porphyrin **Zn-1h** (in $CDCl_3$).

X-ray crystallographic data of H_2-2a, H_2-5a, and H_2-6a

All measurements were made on a Rigaku R-AXIS RAPID imaging plate diffractometer using filtered Cu-Kα radiation. The data were corrected for Lorentz and polarization effects and numerical absorption. The structures were solved by direct methods[12] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[13] crystallographic software package except for refinement, which was performed using SHELX.[14]

Table S2. Experimental data for the X-ray crystallography of **H_2-2a**.

Compound	**H_2-2a**
formula	$C_{45}H_{46}N_4O_4Si_3$
Mw	759.14
crystal size/mm	0.110 × 0.088 × 0.024
crystal system	triclinic
a/Å	6.4848(2)
b/Å	10.6582(2)
c/Å	30.3573(6)
α/deg	85.3716(8)
β/deg	88.6754(7)
γ/deg	78.2900(7)
V/Å^3	2047.77(7)
space group	*P*-1 (#2)
Z	2
g/cm	1.231
μ (Cu Kα)/cm^{-1}	13.959
T/K	93
no. of measured reflections	37521
no. of unique reflections	7379
R_{int}	0.0364
goodness of fit	1.115
R_1	0.0552
wR_2	0.1694
CCDC	1503314

[12] SIR2008: Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Siliqi, D. Spagna, R. (2007). SHELX97: Sheldrick, G. M. *Acta Cryst*. **2008**, *A64*, 112. SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, *27*, 435.

[13] (a) CrystalStructure 4.0, CrystalStructure 4.1: Crystal Structure Analysis Package, Rigaku Corporation (2000-2014). Tokyo 196-8666, Japan. (b) CRYSTALS Issue 11: Carruthers, J. R., Rollett,J.S., Betteridge, P. W., Kinna, D., Pearce, L., Larsen, A., and Gabe, E. Chemical Crystallography Laboratory, Oxford, UK. (1999)

[14] SHELX97, SHELXL2013: Sheldrick, G. M. *Acta Cryst*. **2008**, *A64*, 112.

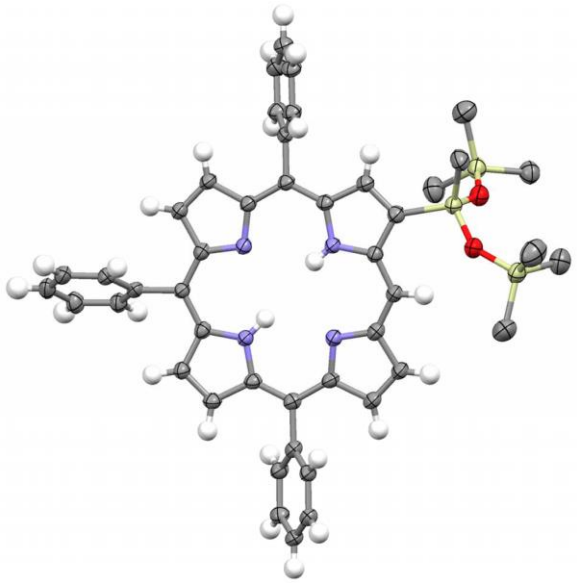
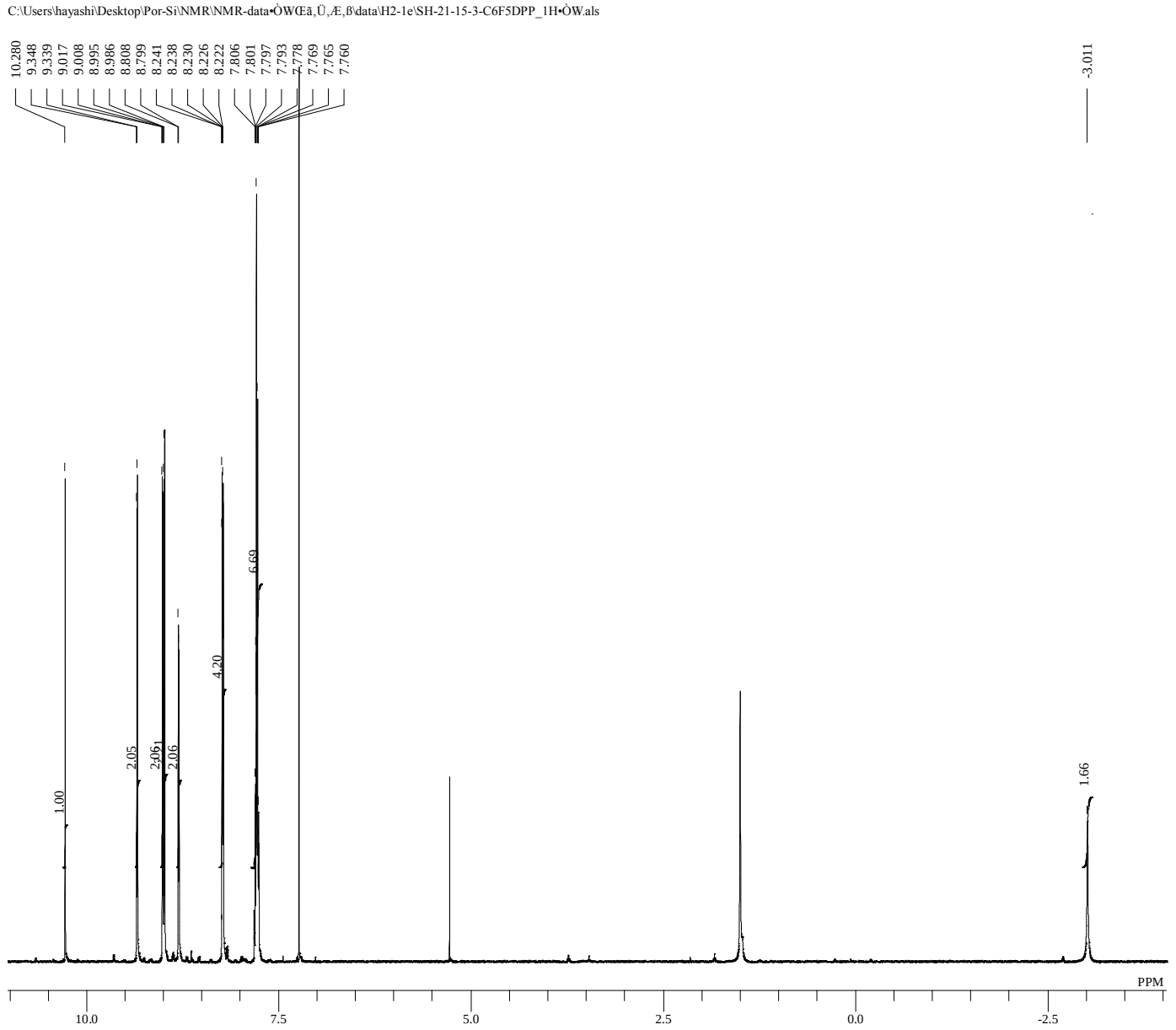


Fig. S13 Crystal structure of **H_2-2a**. Atomic thermal ellipsoids are drawn at the 50% probability level for non-hydrogen atoms. Hydrogen atoms on the silyl group were omitted for clarity.

NMR spectra of New Compounds

Fig. S14 ^{1}H NMR spectrum of compound **H_2-1e** (in $CDCl_3$)



DATIM Tue Aug 30 03:54:28 2016
DFILE SH-21-15-3-C6F5DPP_1H•ÒW.als
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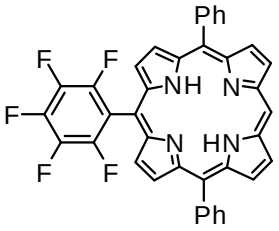
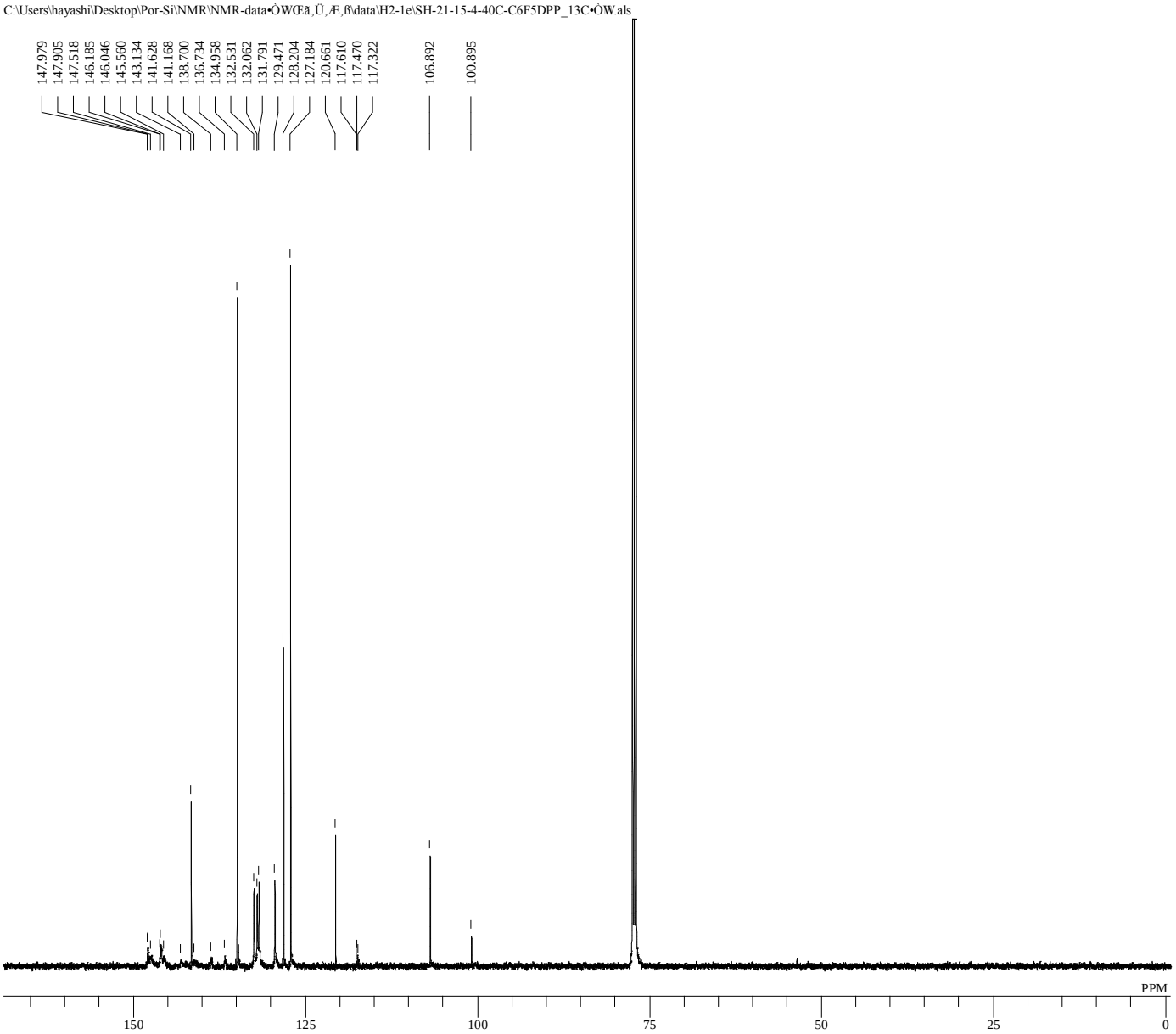
EXMOD non
OFR 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 8
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.00 usec
IRN
CTEMP 28.4 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 3.40 Hz
RGAIN 23

1H-NMR (CDCl3) δ :
10.28 (1H, s),
9.34 (2H, d, J = 4.6 Hz),
9.01 (2H, d, J = 4.6 Hz),
8.99 (2H, d, J = 4.6 Hz),
8.80 (2H, d, J = 4.6 Hz),
8.24−8.22 (4H, m),
7.80−7.77 (6H, m),
−3.01 (2H, s).



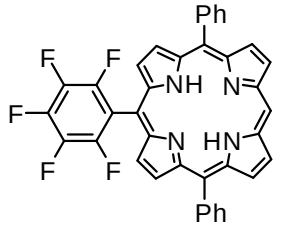
H_2-1e

Fig. S15 ^{13}C NMR spectrum of compound **H_2-1e** (in $CDCl_3$)



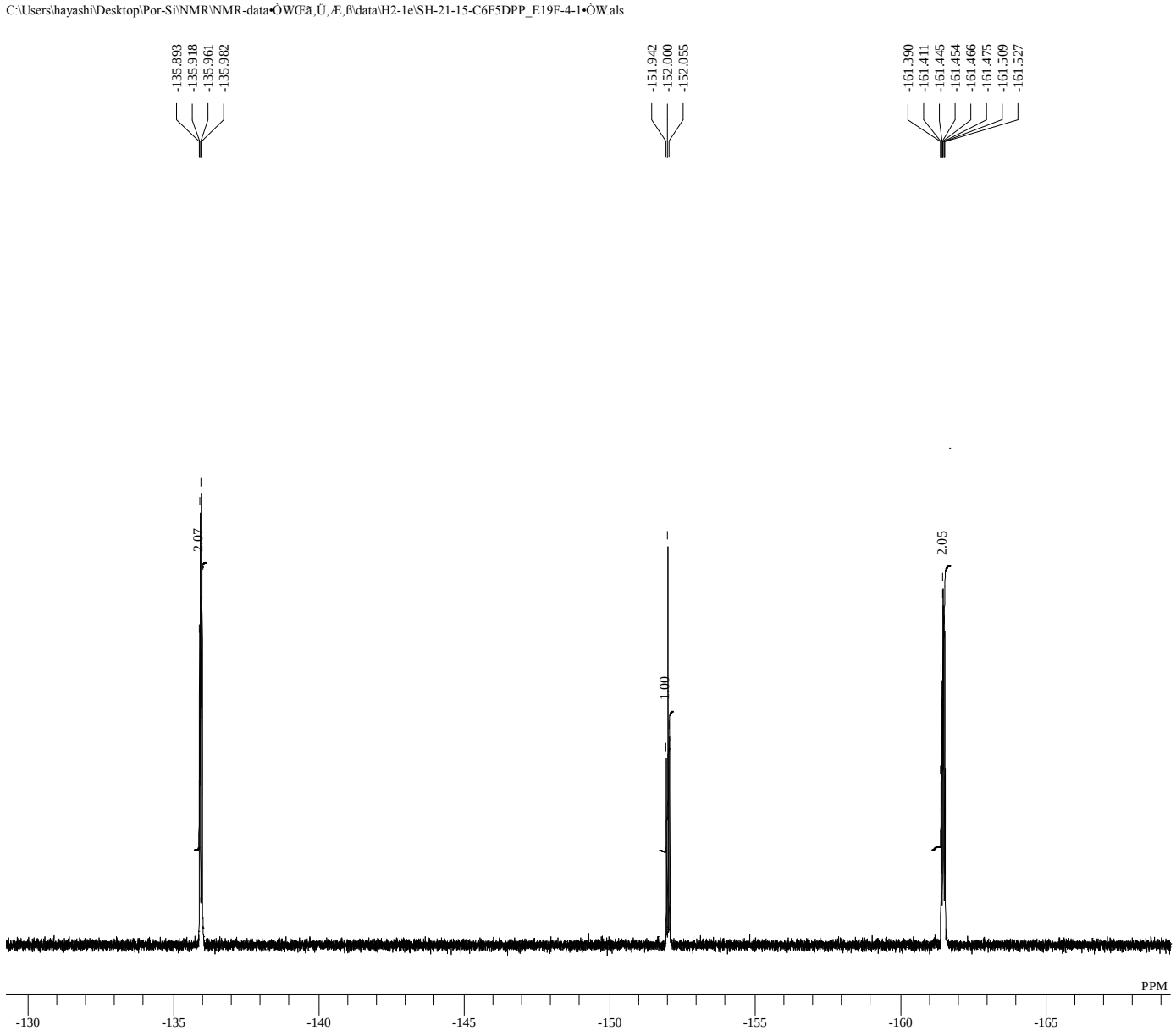
DATIM Tue Aug 30 19:17:33 2016
DFILE SH-21-15-4-40C-C6F5DPP_13C•ÒW.als
OBNUC 13C
EXMOD bcm
OFR 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 18000
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 4.40 usec
IRN
CTEMP 40.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.60 Hz
RGAIN 28

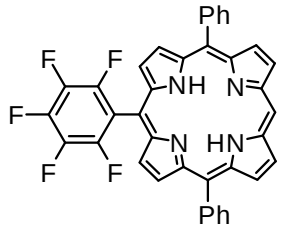
13C-NMR (CDCl3) δ :
147.98 (2H, br s),
147.90 (2H, br s),
146.54 (2H, d, J = 246.2 Hz),
146.18 (2H, br s),
146.04 (2H, br s),
142.15 (0H, d, J = 247.2 Hz),
141.63 (2H, s),
137.72 (2H, d, J = 247.2 Hz),
134.96 (4H, s),
132.53 (2H, s),
132.06 (2H, s),
131.79 (2H, s),
129.47 (2H, s),
128.20 (2H, s),
127.18 (4H, s),
120.66 (2H, s),
117.47 (0H, t, J = 18.1 Hz),
106.89 (0H, s),
100.90 (0H, s).



H_2-1e

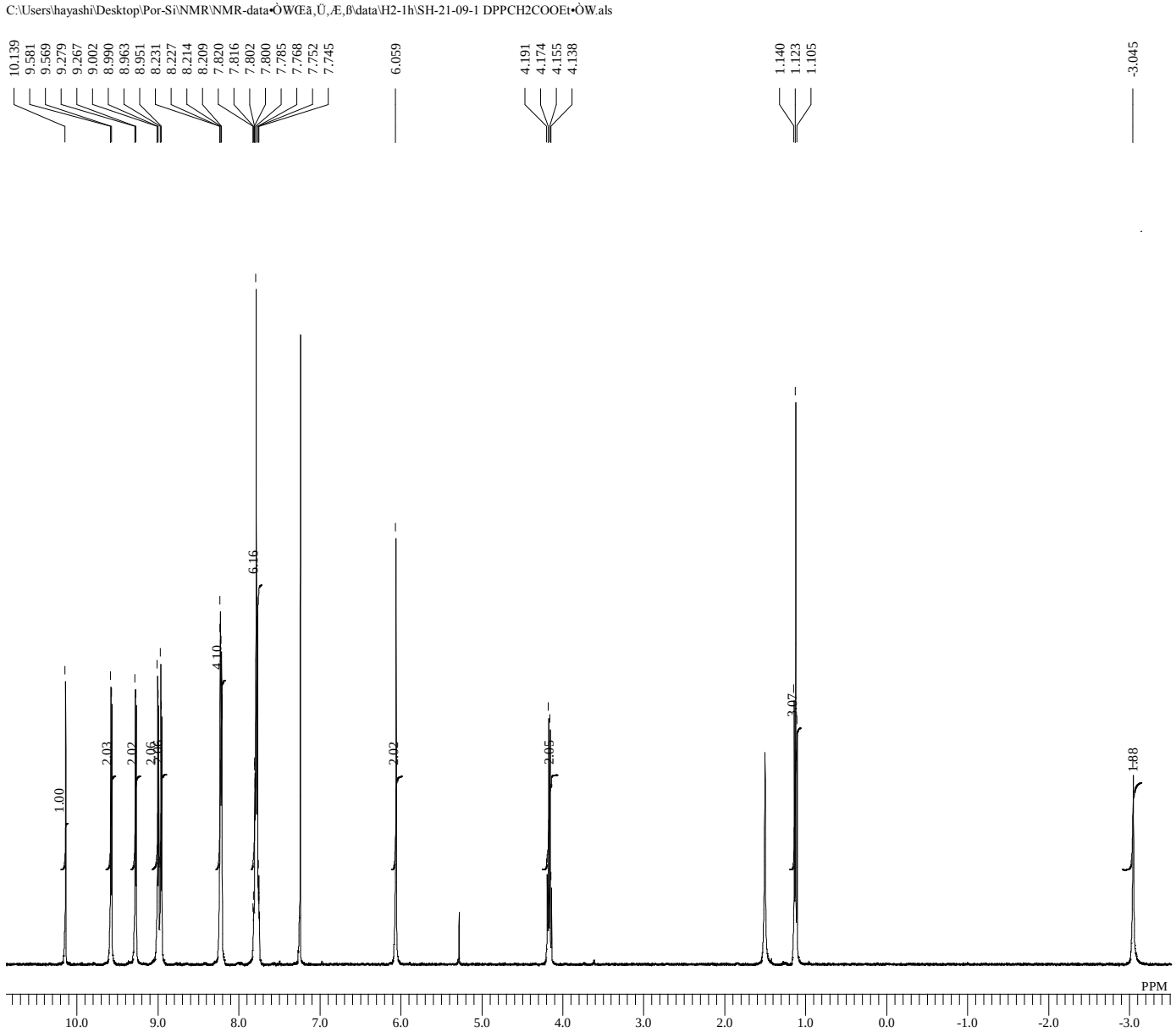
Fig. S16 ^{19}F NMR spectrum of compound **H_2-1e** (in $CDCl_3$)





H_2-1e

Fig. S17 ^{1}H NMR spectrum of compound **H_2-1h** (in $CDCl_3$)



DATIM Sat Aug 27 19:32:03 2016
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OBNUC 1H
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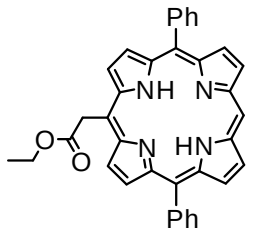
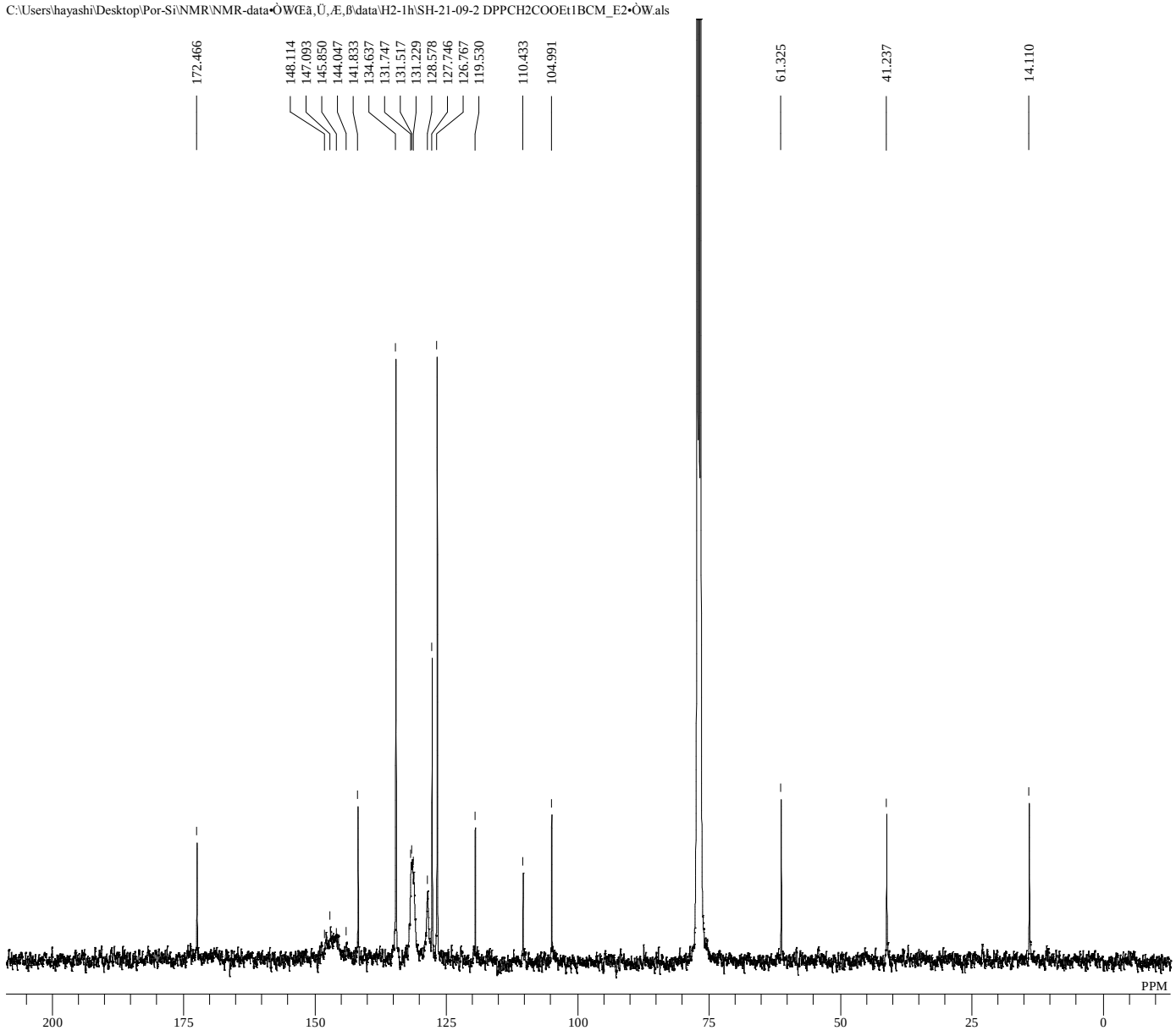
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 16
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 5.60 usec
IRN
CTEMP 25.1 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 22

1H-NMR (CDCl3) δ :
10.14 (1H, s),
9.58 (2H, d, J = 4.9 Hz),
9.27 (2H, d, J = 4.9 Hz),
9.00 (2H, d, J = 4.9 Hz),
8.96 (2H, d, J = 4.9 Hz),
8.23−8.21 (4H, br m),
7.81−7.76 (6H, br m),
6.06 (2H, s),
4.16 (2H, q, J = 7.0 Hz),
1.12 (3H, t, J = 7.1 Hz),
−3.04 (2H, s).



H_2-1h

Fig. S18 ^{13}C NMR spectrum of compound **H_2-1h** (in $CDCl_3$)



DATIM Sun Aug 28 20:56:53 2016
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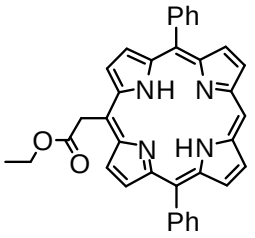
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 10000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.80 usec
IRN
CTEMP 24.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 6.00 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
172.47 (0H, s),
148.11 (2H, br s),
147.09 (2H, br s),
145.85 (2H, br s),
144.05 (2H, br s),
141.83 (2H, s),
134.64 (4H, s),
131.75 (2H, br s),
131.52 (2H, br s),
131.23 (2H, br s),
128.58 (2H, s),
127.75 (2H, s),
126.77 (4H, s),
119.53 (2H, s),
110.43 (0H, s),
104.99 (0H, s),
61.32 (0H, s),
41.24 (0H, s),
14.11 (0H, s).



H_2-1h

Fig. S19 ^{1}H NMR spectrum of compound **H_2-2a** (in $CDCl_3$)

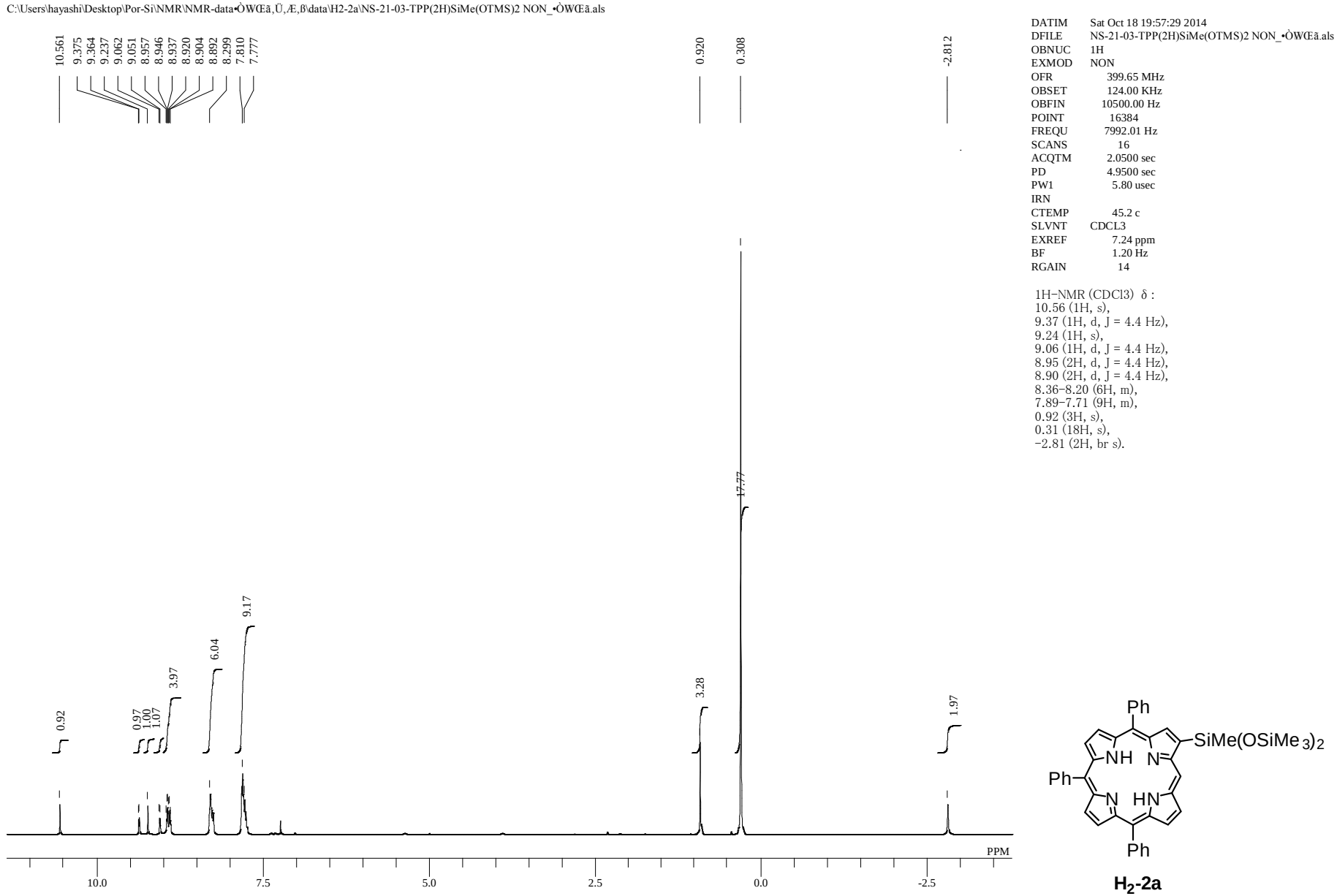
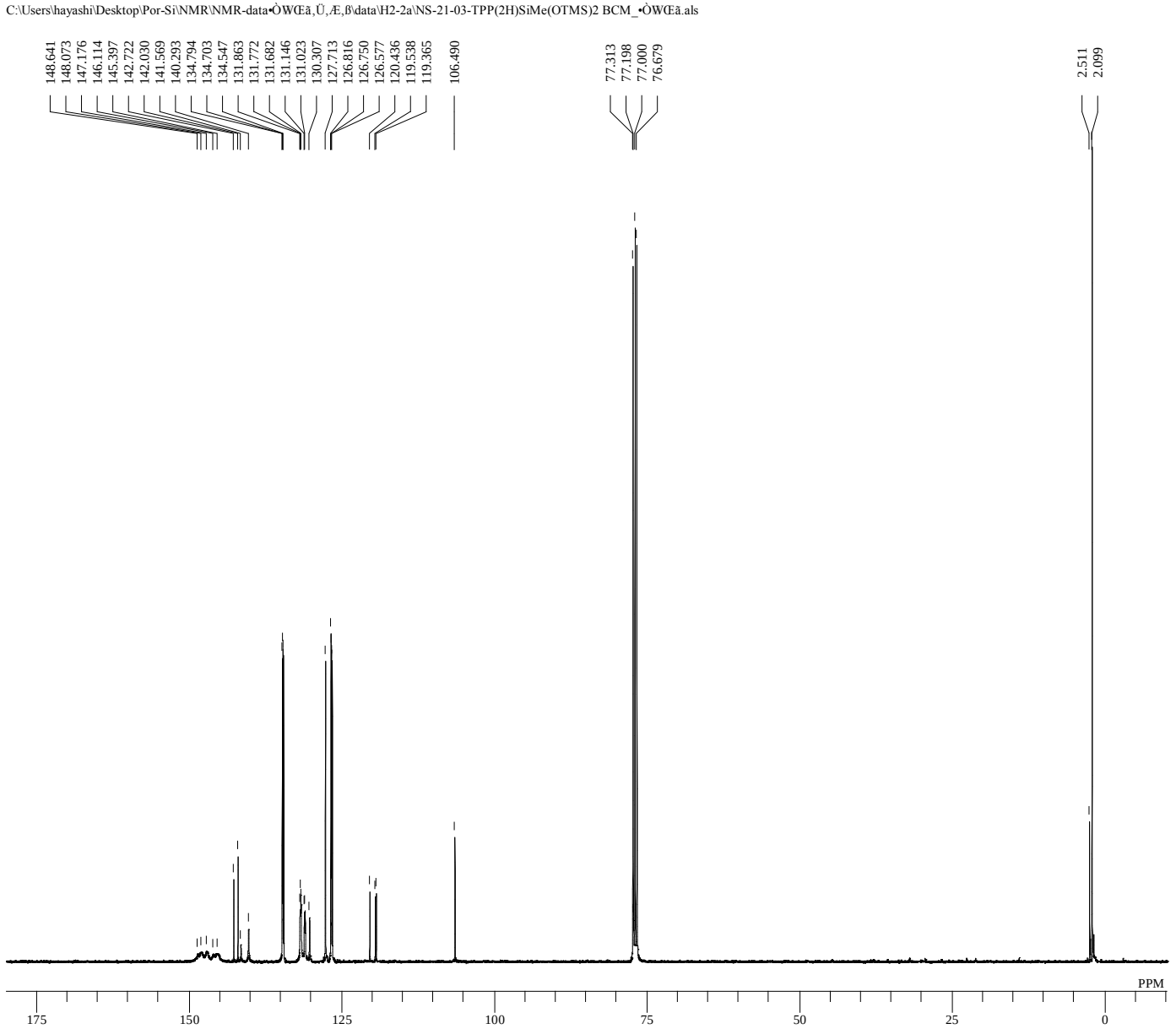


Fig. S20 ^{13}C NMR spectrum of compound **H_2-2a** (in $CDCl_3$)



DATIM Mon Oct 20 13:38:23 2014
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EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 50000
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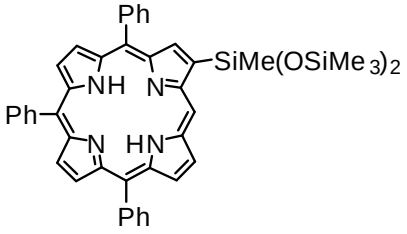
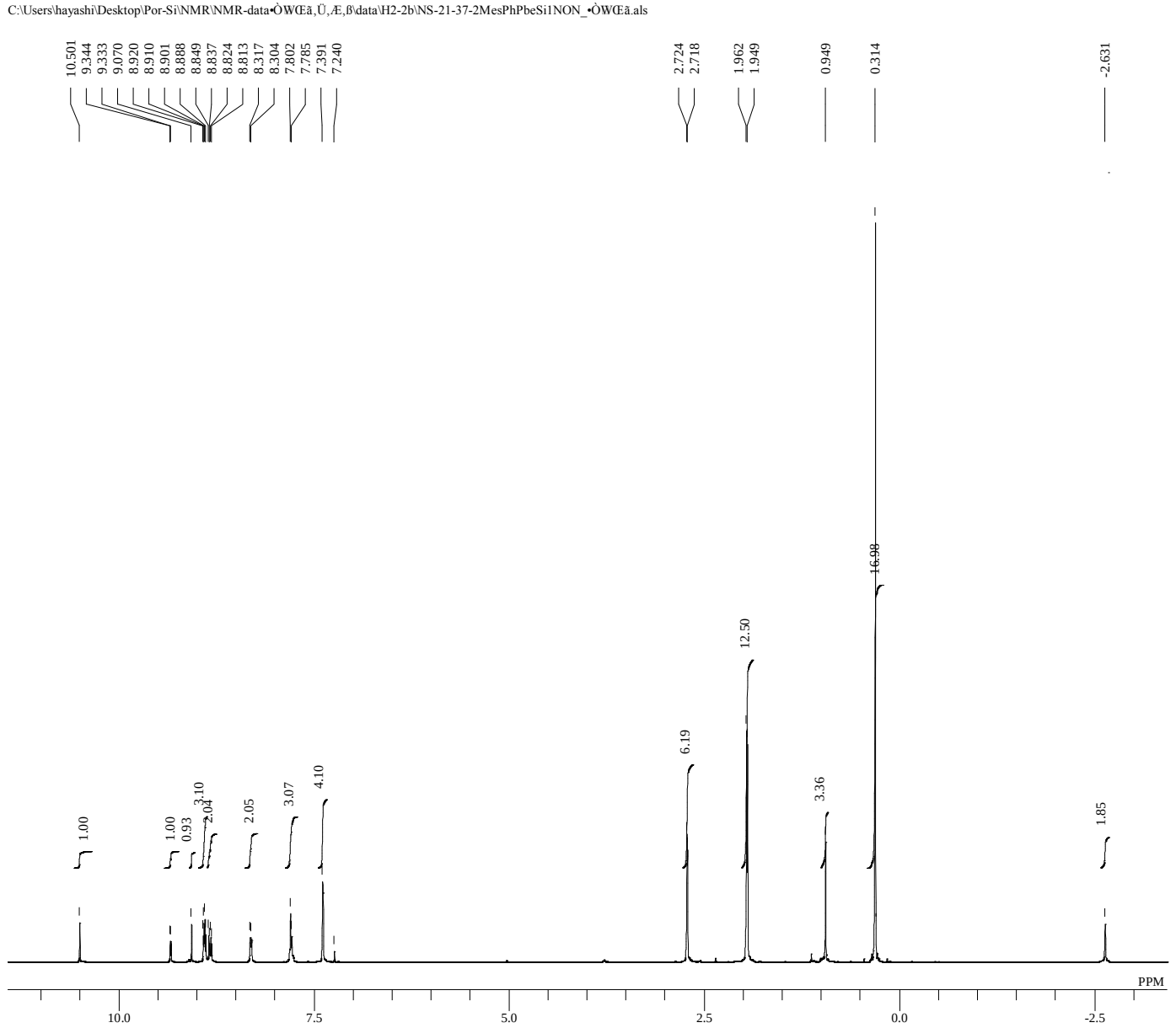
PD 1.7920 sec
PW1 6.00 usec
IRN
CTEMP 45.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
148.64 (1H, br s),
148.07 (2H, br s),
147.18 (2H, br s),
146.11 (1H, br s),
145.40 (2H, br s),
142.72 (1H, s),
142.03 (2H, s),
141.57 (1H, s),
140.29 (1H, s),
134.79 (2H, s),
134.70 (2H, s),
134.55 (2H, s),
131.86 (1H, s),
131.77 (1H, s),
131.68 (1H, s),
131.15 (1H, s),
131.02 (1H, s),
130.31 (1H, s),
127.71 (3H, s),
126.82 (2H, s),
126.75 (2H, s),
126.58 (2H, s),
120.44 (1H, s),
119.54 (1H, s),
119.37 (1H, s),
106.49 (1H, s),
2.51 (1H, s),
2.10 (6H, s).



H_2-2a

Fig. S21 ^{1}H NMR spectrum of compound **H_2-2b** (in $CDCl_3$)



DATIM Fri Dec 12 19:39:01 2014
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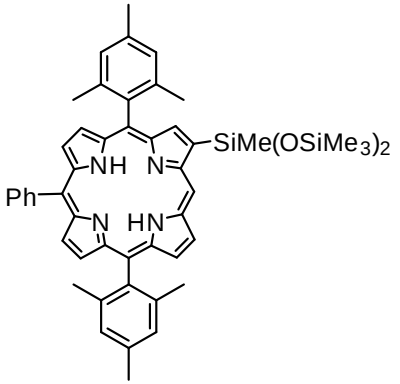
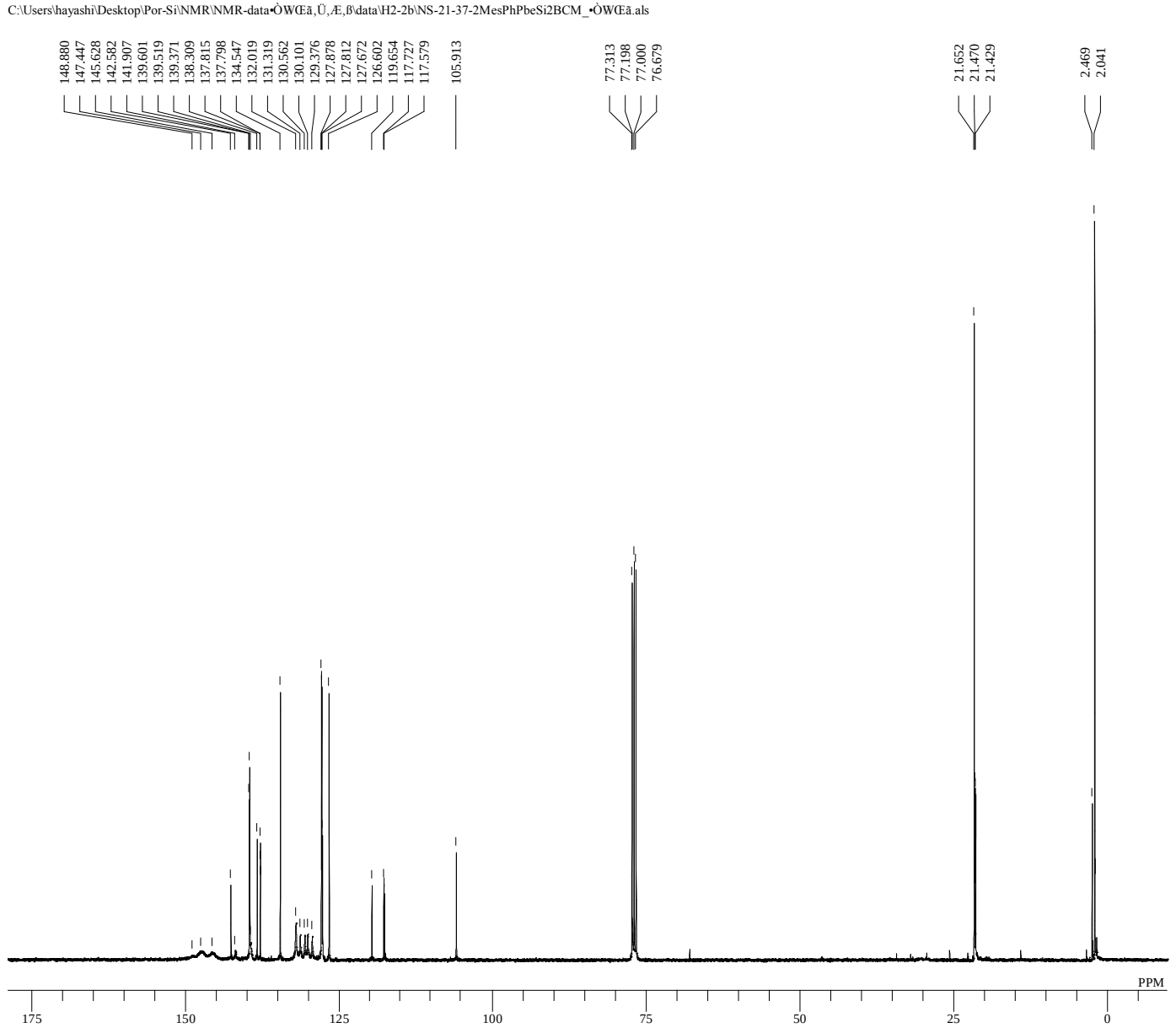
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 16
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 5.80 usec
IRN
CTEMP 50.3 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.09 Hz
RGAIN 11

1H-NMR (CDCl3) δ :
10.50 (1H, s),
9.34 (1H, d, J = 4.4 Hz),
9.07 (1H, s),
8.92 (2H, d, J = 4.4 Hz),
8.89 (1H, d, J = 4.4 Hz),
8.84 (1H, d, J = 4.4 Hz),
8.82 (1H, d, J = 4.4 Hz),
8.36−8.26 (2H, m),
7.86−7.75 (3H, m),
7.39 (4H, s),
2.72 (6H, s),
1.96 (6H, s),
1.95 (6H, s),
0.95 (3H, s),
0.31 (18H, s),
−2.63 (2H, br s).



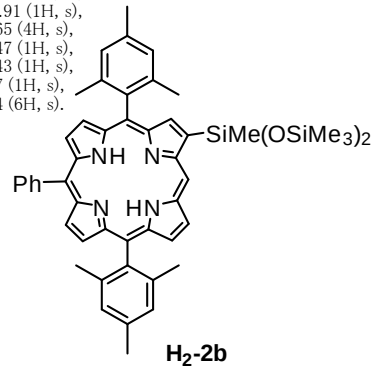
H_2-2b

Fig. S22 ^{13}C NMR spectrum of compound **H_2-2b** (in $CDCl_3$)



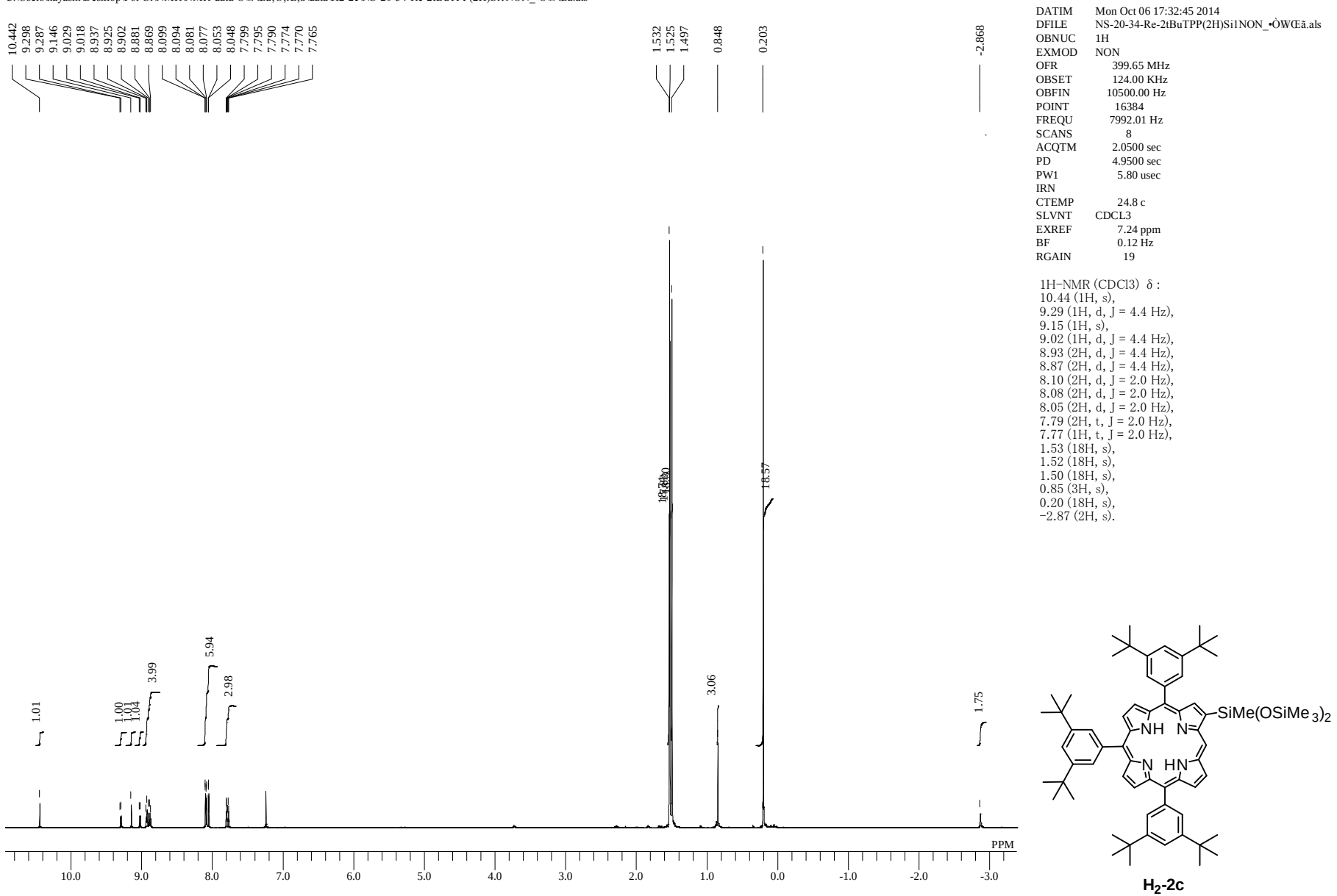
DATIM Sat Dec 13 05:39:34 2014
DFILE NS-21-37-2MesPhPbeSi2BCM_•ÒWŒÊã.als
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 12000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.00 usec
IRN
CTEMP 50.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
148.88 (1H, br s),
147.45 (4H, br s),
145.63 (3H, br s),
142.58 (1H, s),
141.91 (1H, s),
139.60 (2H, s),
139.52 (2H, s),
139.37 (1H, s),
138.31 (2H, s),
137.81 (1H, s),
137.80 (1H, s),
134.55 (2H, s),
132.02 (2H, s),
131.32 (1H, s),
130.56 (1H, s),
130.10 (1H, s),
129.38 (1H, s),
127.88 (2H, s),
127.81 (2H, s),
127.67 (1H, s),
126.60 (2H, s),
119.65 (1H, s),
117.73 (1H, s),
117.58 (1H, s),
105.91 (1H, s),
21.65 (4H, s),
21.47 (1H, s),
21.43 (1H, s),
2.47 (1H, s),
2.04 (6H, s).



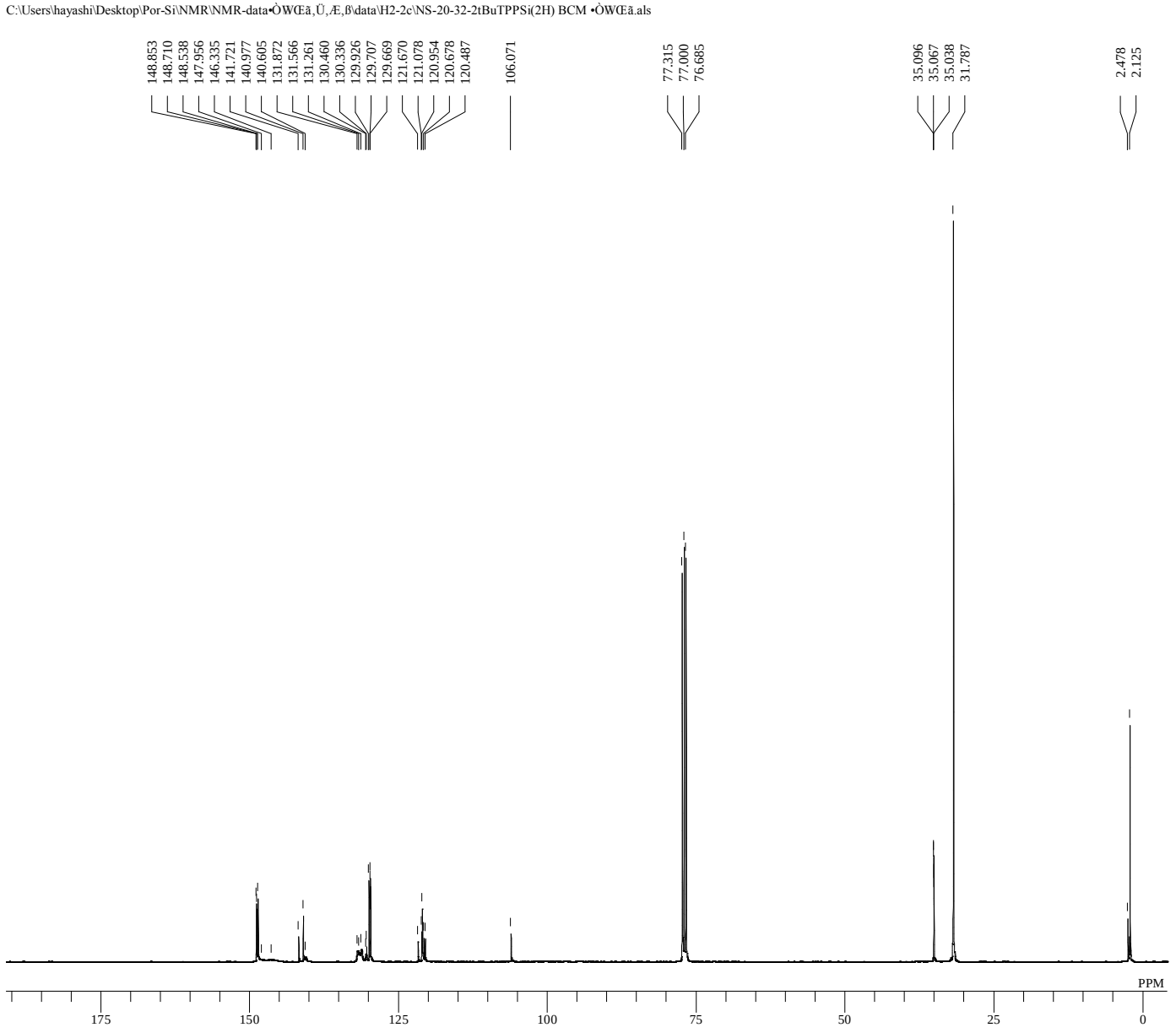
H_2-2b

Fig. S23 ^{1}H NMR spectrum of compound **H_2-2c** (in $CDCl_3$)



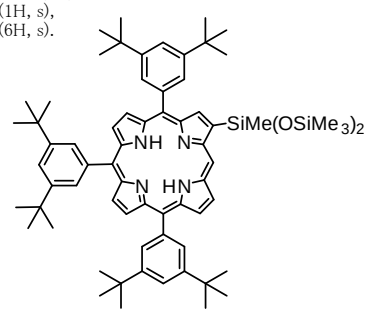
H_2-2c

Fig. S24 ^{13}C NMR spectrum of compound **H_2-2c** (in $CDCl_3$)



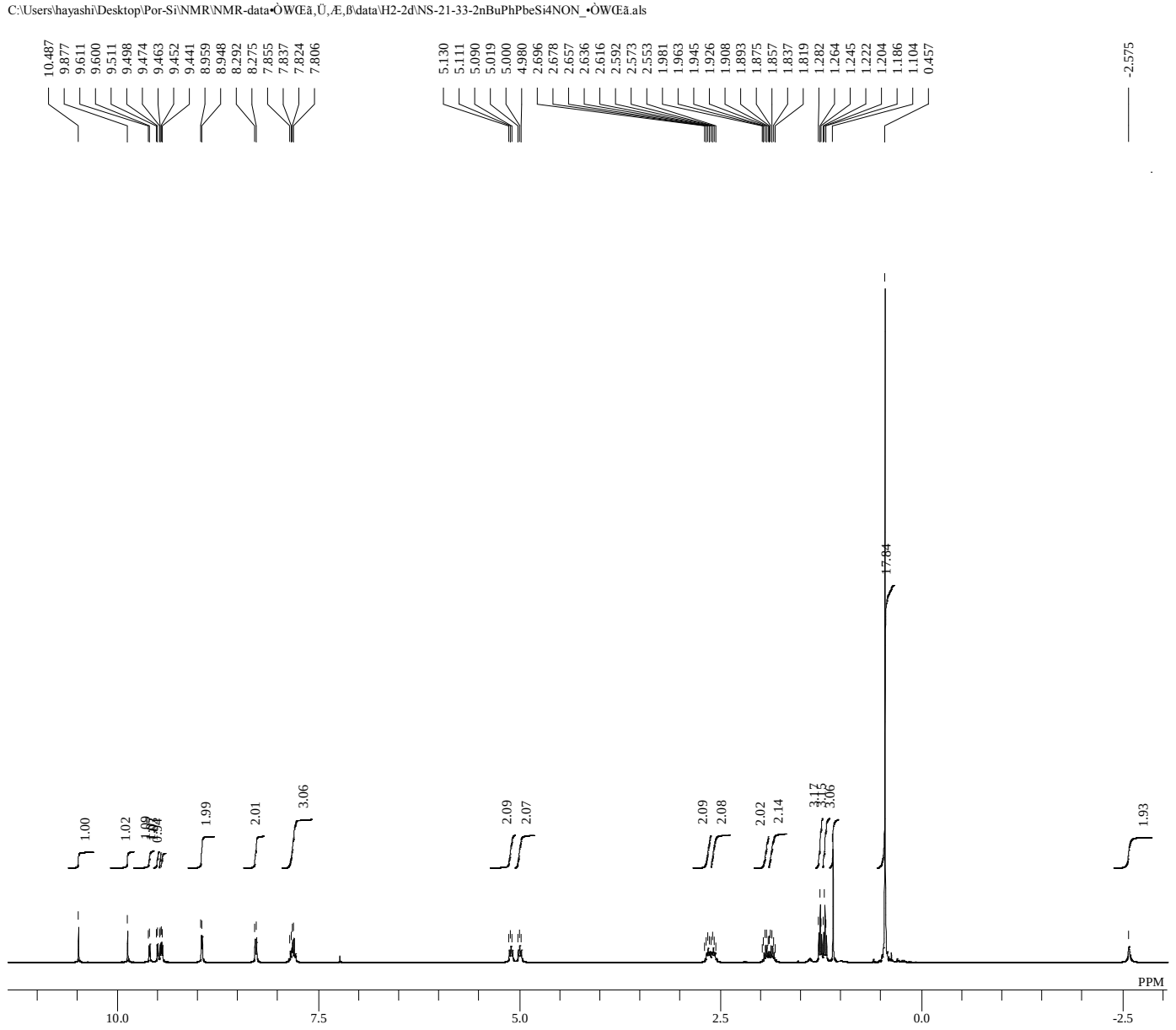
DATIM 2014-09-26 18:22:52
DFILE NS-20-32-2tBuTPPSi(2H) BCM •ÒWŒã.als
OBNUC 13C
EXMOD single_pulse_dec
OFR 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.04 Hz
SCANS 20000
ACQTM 1.0433 sec
PD 1.7000 sec
PW1 3.70 usec
IRN
CTEMP 22.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60

13C-NMR (CDCl3) δ :
148.85 (2H, s),
148.71 (2H, s),
148.54 (2H, s),
147.96 (4H, s),
146.34 (4H, s),
141.72 (1H, s),
140.98 (2H, s),
140.61 (1H, s),
131.87 (2H, s),
131.57 (1H, s),
131.26 (2H, s),
130.46 (1H, s),
130.34 (1H, s),
129.93 (2H, s),
129.71 (2H, s),
129.67 (2H, s),
121.67 (1H, s),
121.08 (1H, s),
120.95 (2H, s),
120.68 (1H, s),
120.49 (1H, s),
106.07 (1H, s),
35.10 (2H, s),
35.07 (2H, s),
35.04 (2H, s),
31.79 (18H, s),
2.48 (1H, s),
2.12 (6H, s).



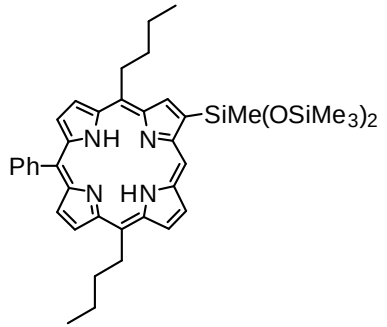
H_2-2c

Fig. S25 ^{1}H NMR spectrum of compound **H_2-2d** (in $CDCl_3$)



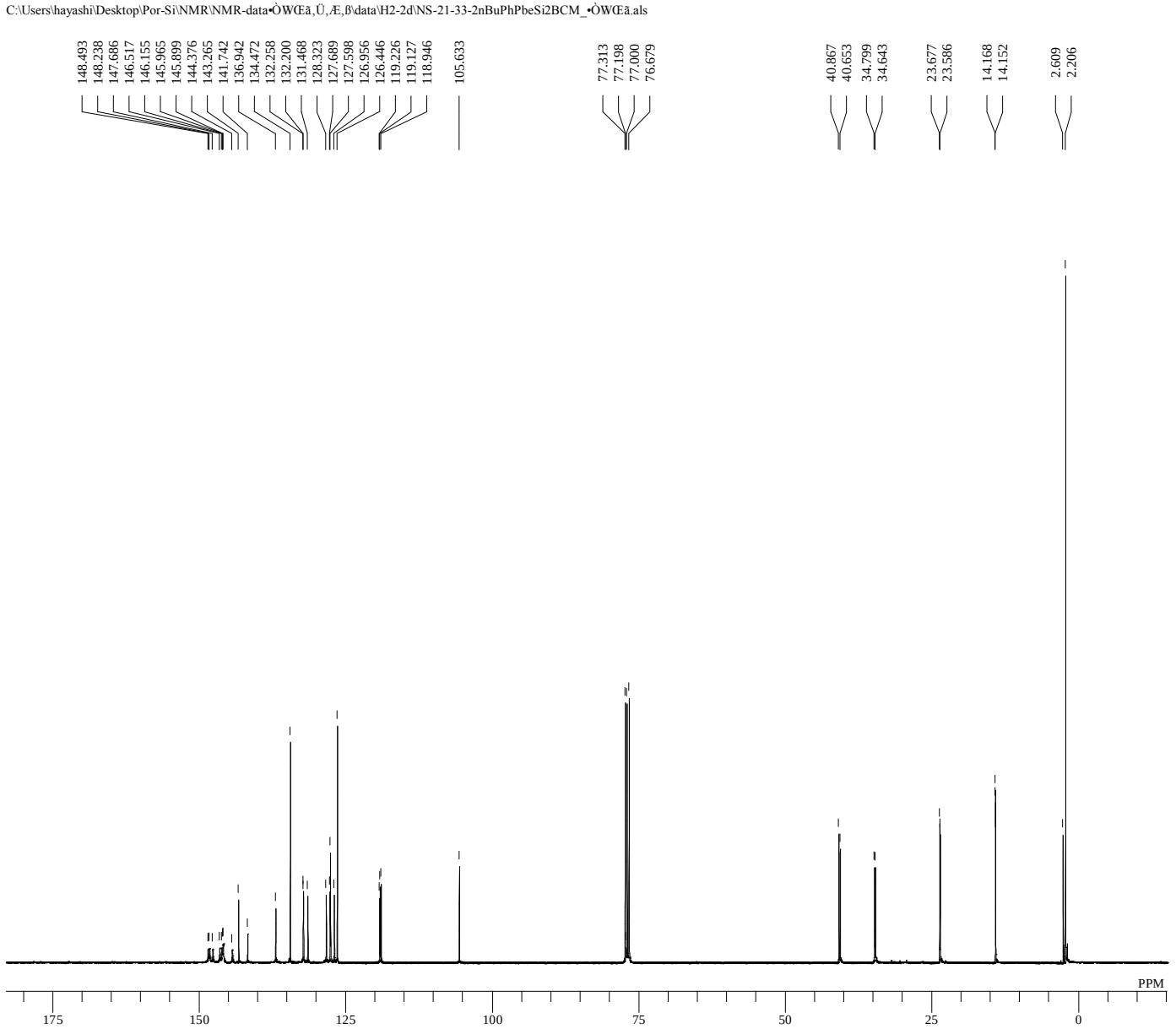
DATIM Fri Dec 19 10:48:23 2014
DFILE NS-21-33-2nBuPhPbeSi4NON_•ÒWŒã.als
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 5.80 usec
IRN
CTEMP 50.2 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 1.20 Hz
RGAIN 12

1H-NMR (CDCl3) δ :
10.49 (1H, s),
9.88 (1H, s),
9.61 (1H, d, J = 4.4 Hz),
9.50 (1H, d, J = 4.4 Hz),
9.47 (1H, d, J = 4.4 Hz),
9.45 (1H, d, J = 4.4 Hz),
8.95 (2H, d, J = 4.4 Hz),
8.32−8.24 (2H, m),
7.90−7.75 (3H, m),
5.11 (2H, t, J = 8.0 Hz),
5.00 (2H, t, J = 8.0 Hz),
2.66 (2H, tt, J = 8.0, 7.6 Hz),
2.59 (2H, tt, J = 8.0, 7.6 Hz),
1.94 (2H, tq, J = 7.6, 7.3 Hz),
1.86 (2H, tq, J = 7.6, 7.3 Hz),
1.26 (3H, t, J = 7.3 Hz),
1.20 (3H, t, J = 7.3 Hz),
1.10 (3H, s),
0.46 (18H, s),
−2.57 (2H, br s).



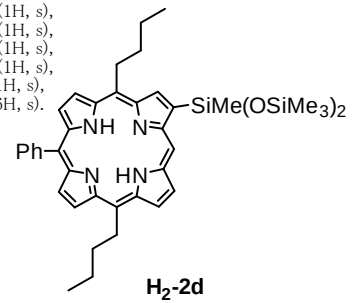
H_2-2d

Fig. S26 ^{13}C NMR spectrum of compound **H_2-2d** (in $CDCl_3$)



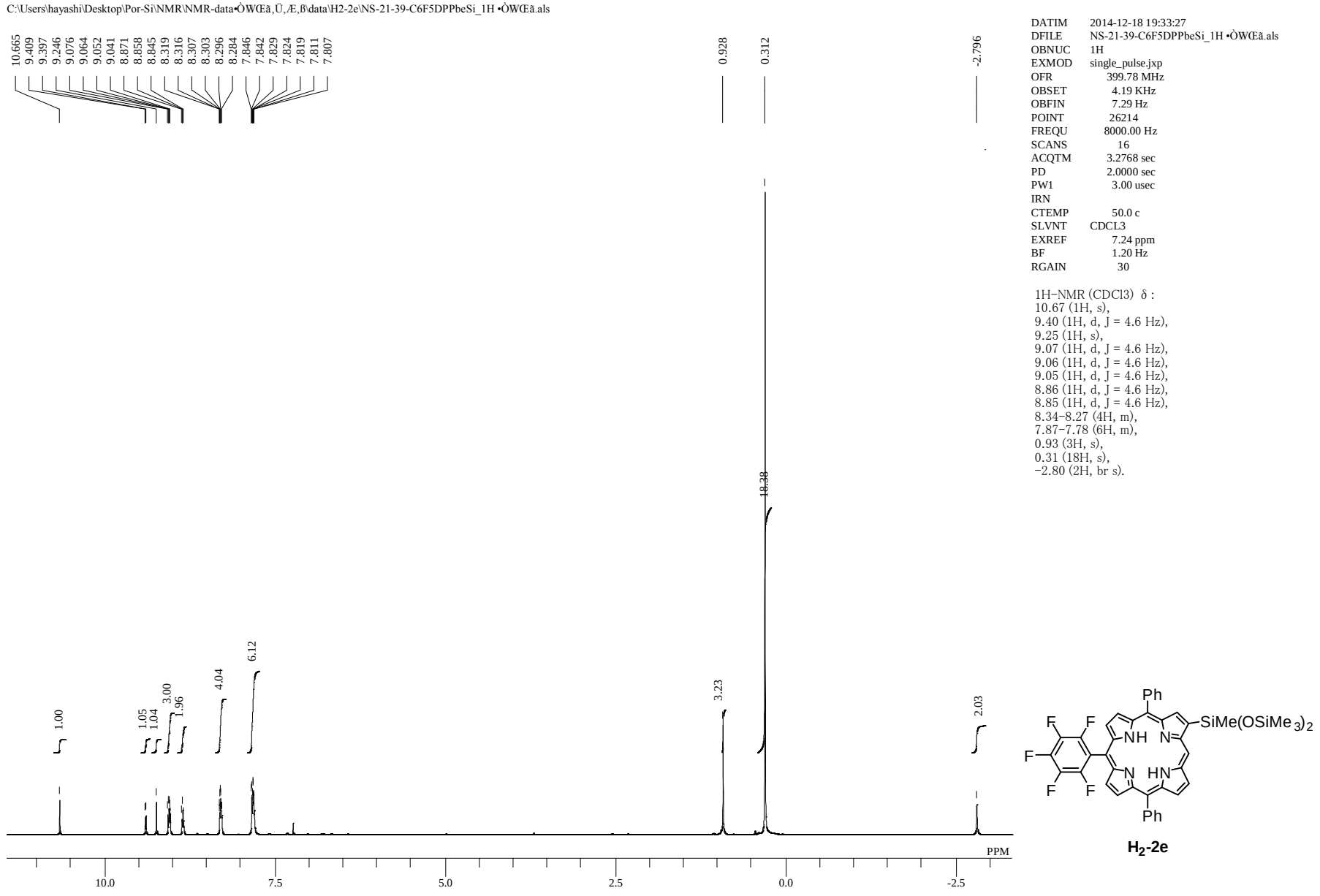
DATIM Fri Dec 19 08:58:59 2014
DFILE NS-21-33-2nBuPhPbeSi2BCM_•ÒWŒã.als
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 16000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.00 usec
IRN
CTEMP 50.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
148.49 (1H, s),
148.24 (1H, s),
147.69 (1H, s),
146.52 (1H, s),
146.15 (1H, s),
145.97 (1H, s),
145.90 (1H, s),
144.38 (1H, s),
143.26 (1H, s),
141.74 (1H, s),
136.94 (1H, s),
134.47 (2H, s),
132.26 (1H, s),
132.20 (1H, s),
131.47 (1H, s),
128.32 (1H, s),
127.69 (1H, s),
127.60 (1H, s),
126.96 (1H, s),
126.45 (2H, s),
119.23 (1H, s),
119.13 (1H, s),
118.95 (1H, s),
105.63 (1H, s),
40.87 (1H, s),
40.65 (1H, s),
34.80 (1H, s),
34.64 (1H, s),
23.68 (1H, s),
23.59 (1H, s),
14.17 (1H, s),
14.15 (1H, s),
2.61 (1H, s),
2.21 (6H, s).



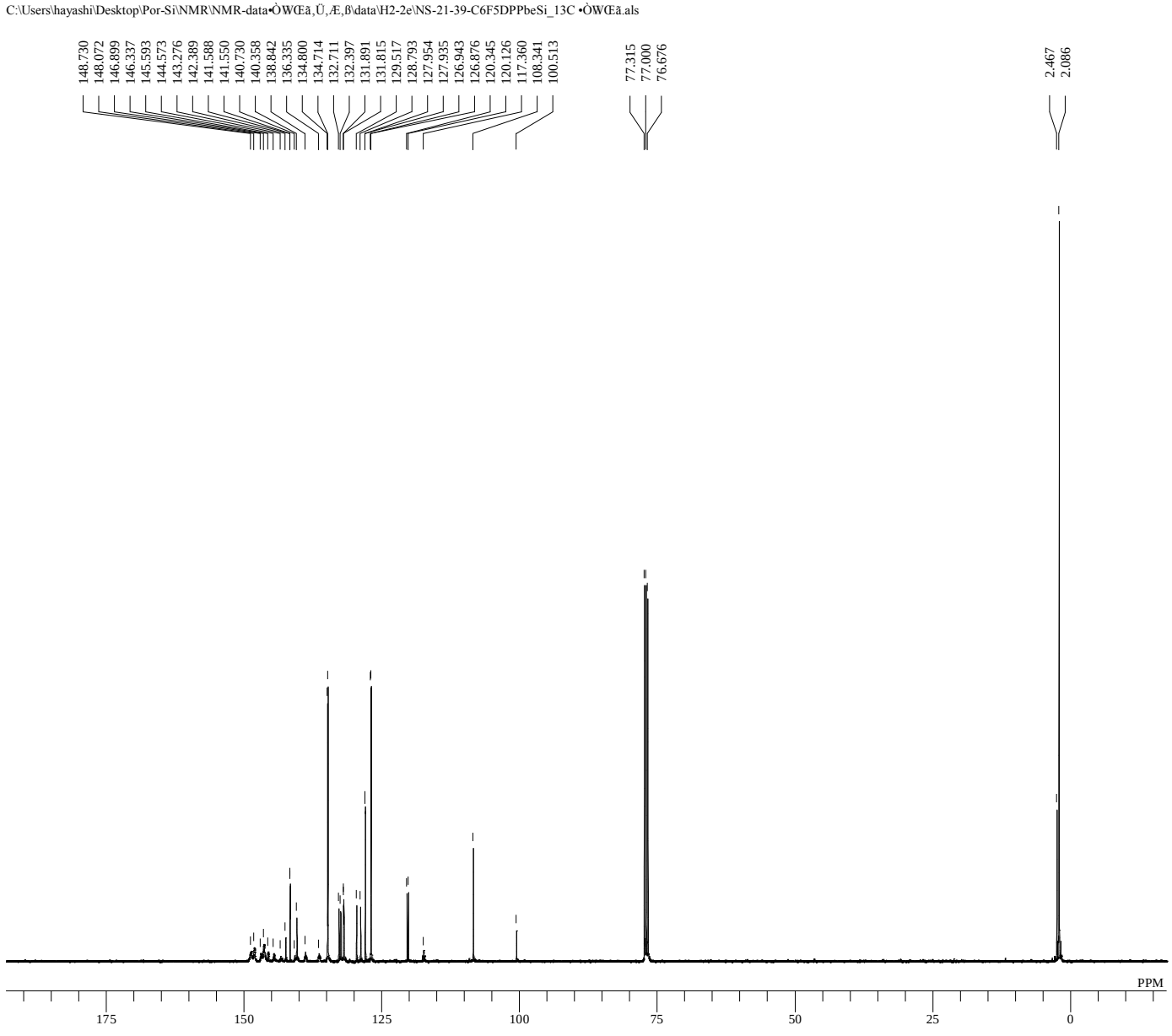
H_2-2d

Fig. S27 ^{1}H NMR spectrum of compound **H_2-2e** (in $CDCl_3$)



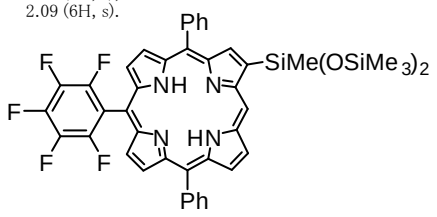
H_2-2e

Fig. S28 ^{13}C NMR spectrum of compound **H_2-2e** (in $CDCl_3$)



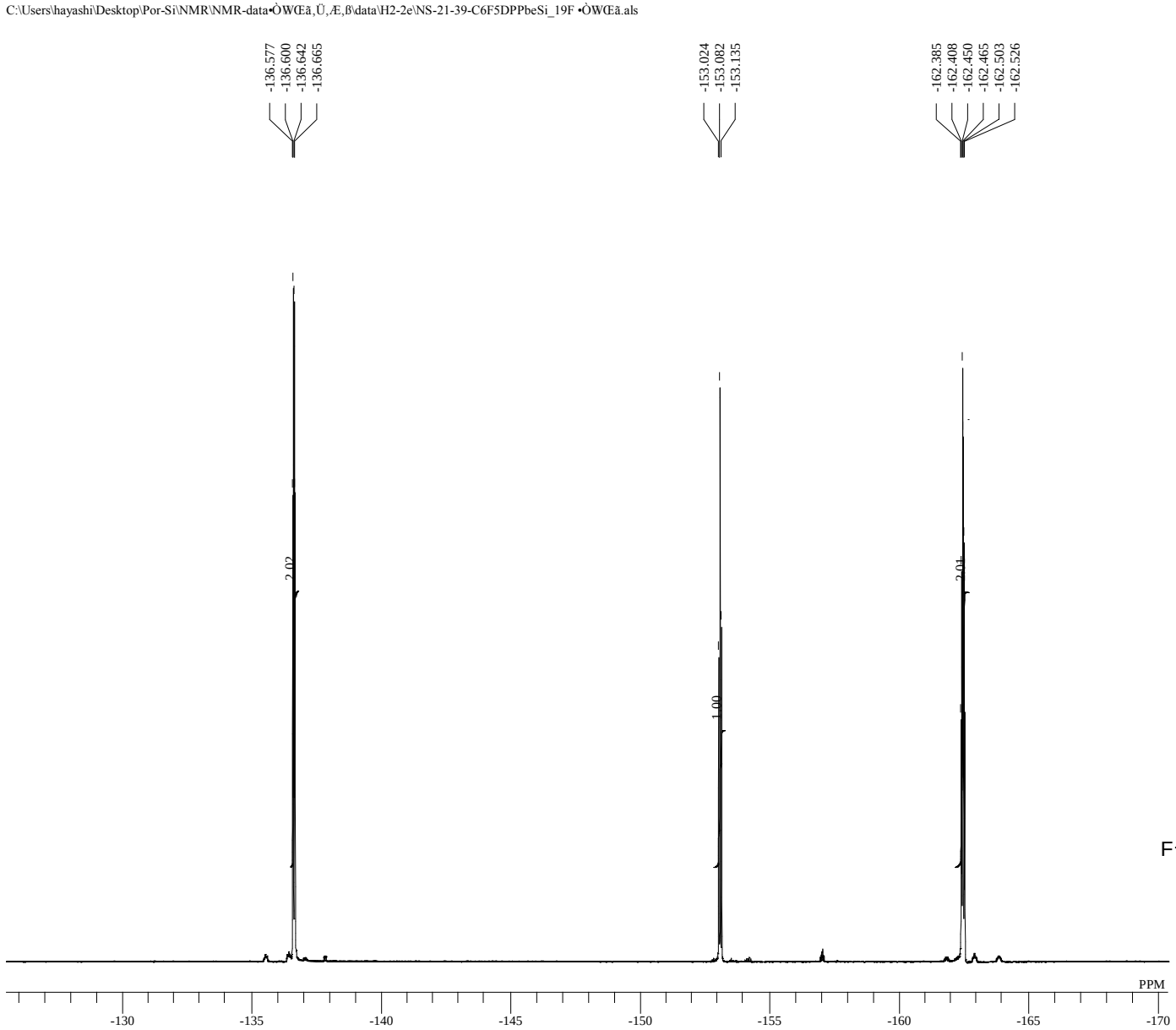
DATIM 2014-12-18 19:40:50
DFILE NS-21-39-C6F5DPPbeSi_13C •ÒWŒã.als
OBNUC 13C
EXMOD single_pulse_dec
OFR 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 20000
ACQTM 1.0433 sec
PD 1.7000 sec
PW1 3.70 usec
IRN
CTEMP 50.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60

13C-NMR (CDCl3) δ :
148.73 (2H, s),
148.07 (1H, s),
146.90 (1H, s),
146.83 (2H, d, J = 249.2 Hz),
146.34 (3H, s),
144.57 (1H, s),
142.39 (1H, s),
142.00 (1H, d, J = 255.9 Hz),
141.59 (1H, s),
141.55 (1H, s),
140.36 (1H, s),
137.59 (2H, d, J = 252.1 Hz),
134.80 (2H, s),
134.71 (2H, s),
132.71 (1H, s),
132.40 (1H, s),
131.89 (1H, s),
131.81 (1H, s),
129.52 (1H, s),
128.79 (1H, s),
127.95 (1H, s),
127.93 (1H, s),
126.94 (2H, s),
126.88 (2H, s),
120.34 (1H, s),
120.12 (1H, s),
117.36 (1H, s),
108.34 (1H, s),
100.51 (1H, s),
2.47 (1H, s),
2.09 (6H, s).



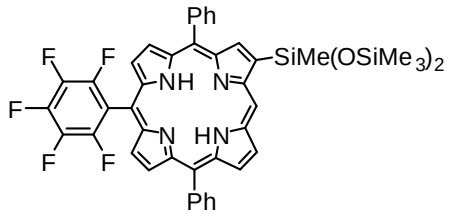
H_2-2e

Fig. S29 ^{19}F NMR spectrum of compound **H_2-2e** (in $CDCl_3$)



DATIM 2014-12-18 19:37:02
DFILE NS-21-39-C6F5DPPbeSi_19F •ÒWŒã.als
OBNUC 19F
EXMOD single_pulse.jxp
OFR 376.11 MHz
OBSET 4.62 KHz
OBFIN 8.27 Hz
POINT 16384
FREQU 23584.91 Hz
SCANS 16
ACQTM 0.6947 sec
PD 5.0000 sec
PW1 3.76 usec
IRN
CTEMP 50.0 c
SLVNT CDCL3
EXREF -136.60 ppm
BF 1.20 Hz
RGAIN 48

19F-NMR (CDCl3) δ :
−136.62 (2H, ddd, J = 24.5, 8.6, 5.5 Hz),
−153.08 (1H, tt, J = 20.9, 5.5 Hz),
−162.46 (2H, ddd, J = 24.5, 20.9, 8.4 Hz).



H_2-2e

Fig. S30 ^{1}H NMR spectrum of compound **H_2-2f** (in $CDCl_3$)

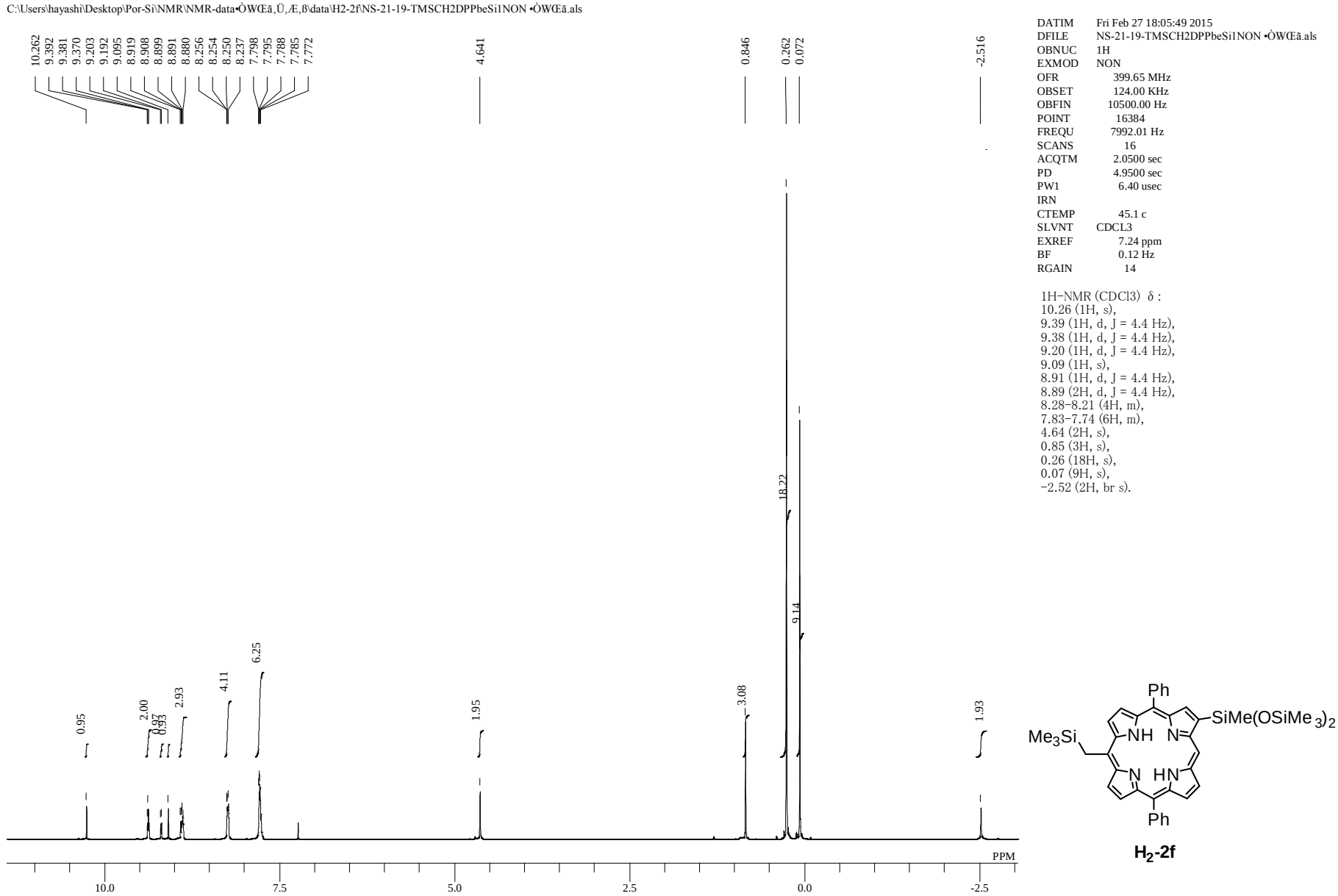
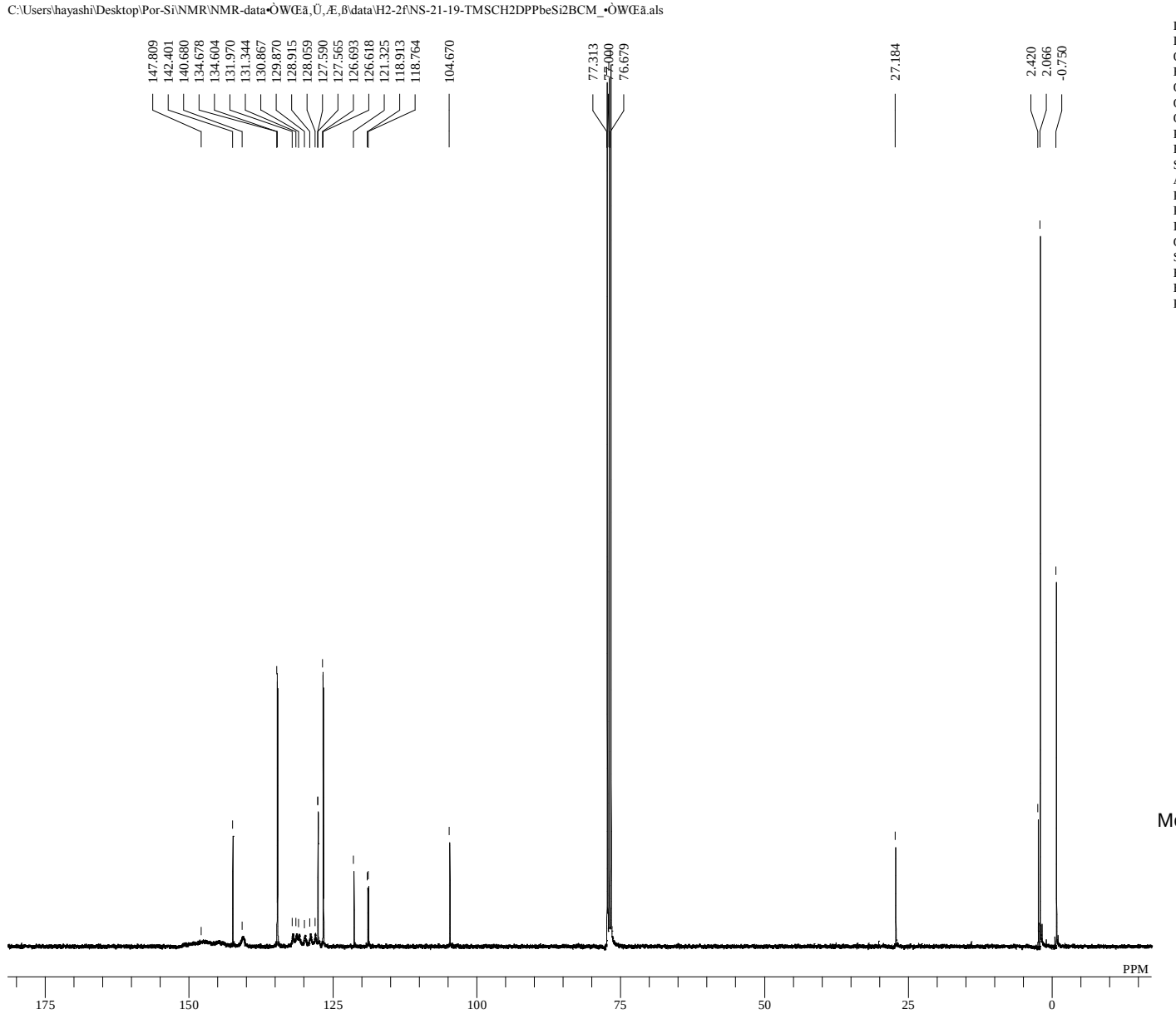
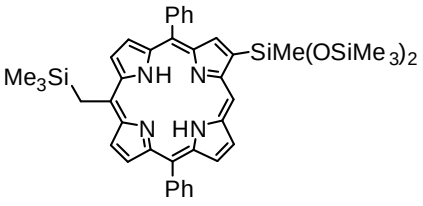


Fig. S31 ^{13}C NMR spectrum of compound **H_2-2f** (in $CDCl_3$)



DATIM Sat Feb 28 09:56:26 2015
DFILE NS-21-19-TMSCH2DPPbeSi2BCM_•ÒWŒã.als
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 19000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.10 usec
IRN
CTEMP 45.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
147.81 (8H, s),
142.40 (2H, s),
140.68 (2H, s),
134.68 (2H, s),
134.60 (2H, s),
131.97 (1H, s),
131.34 (1H, s),
130.87 (1H, s),
129.87 (1H, s),
128.92 (1H, s),
128.06 (1H, s),
127.59 (1H, s),
127.57 (1H, s),
126.69 (2H, s),
126.62 (2H, s),
121.32 (1H, s),
118.91 (1H, s),
118.76 (1H, s),
104.67 (1H, s),
27.18 (1H, s),
2.42 (1H, s),
2.07 (6H, s),
−0.75 (3H, s).



H_2-2f

Fig. S32 ^{1}H NMR spectrum of compound **H_2-2g** (in $CDCl_3$)

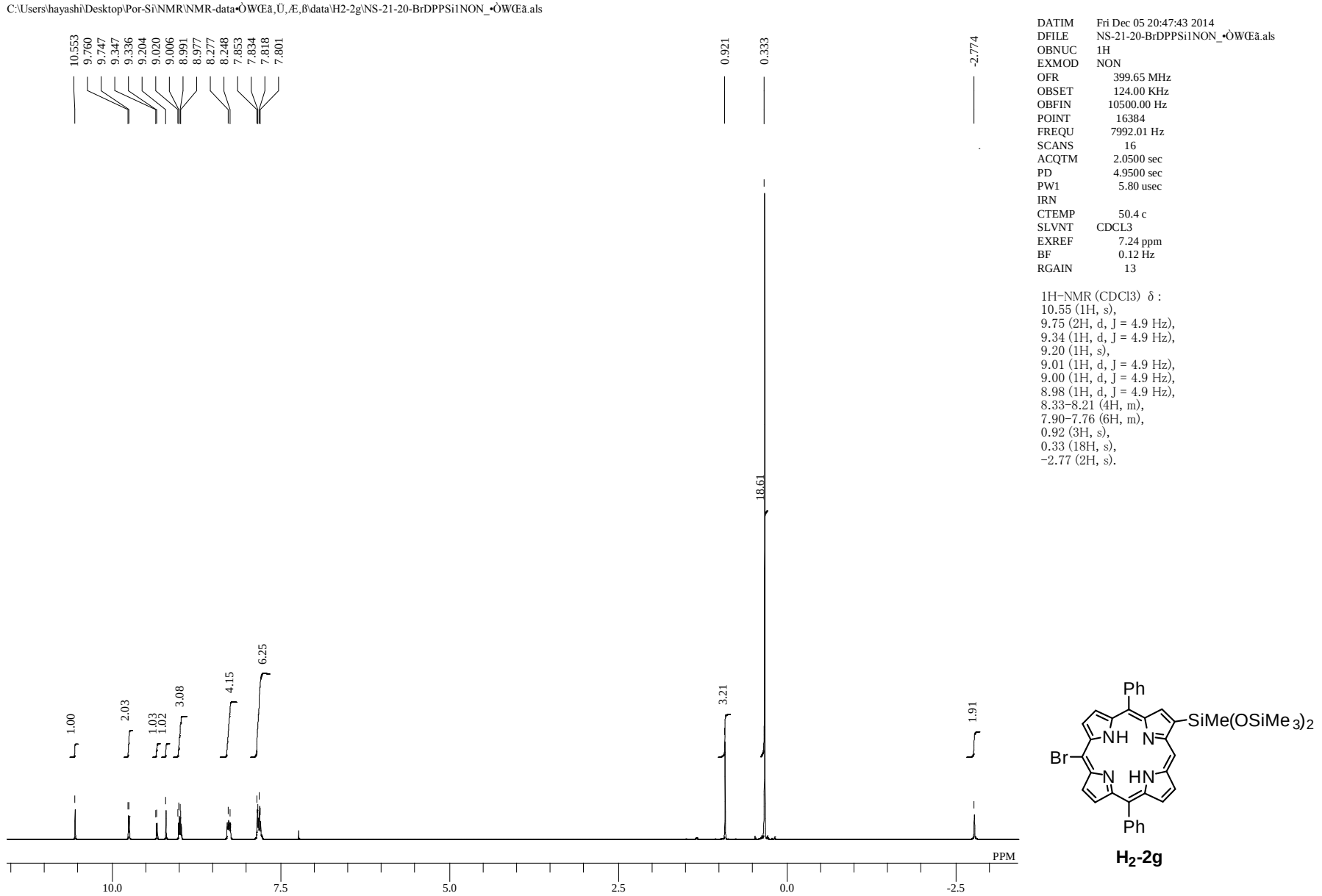
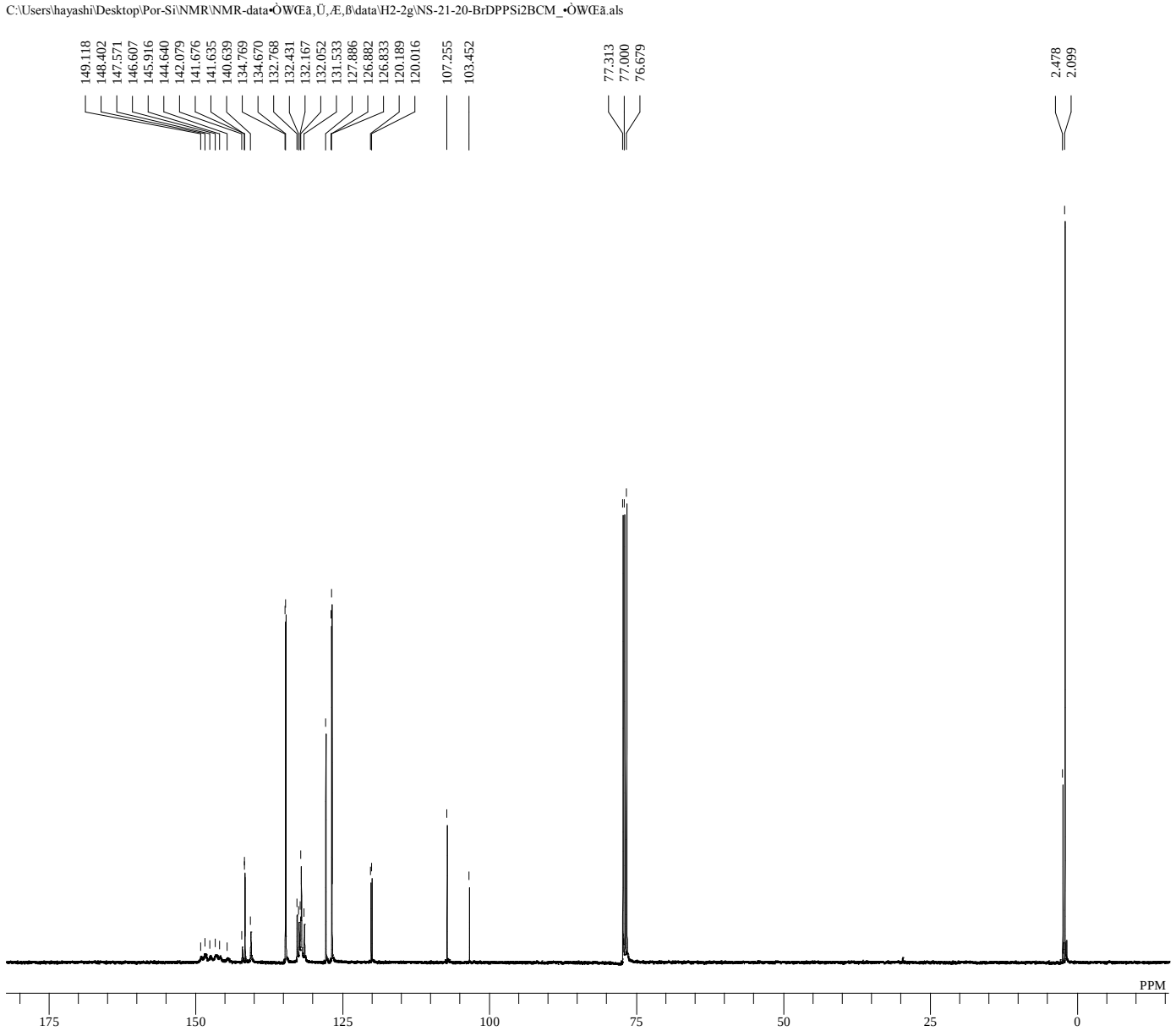
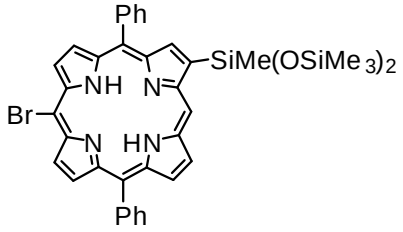


Fig. S33 ^{13}C NMR spectrum of compound **H_2-2g** (in $CDCl_3$)



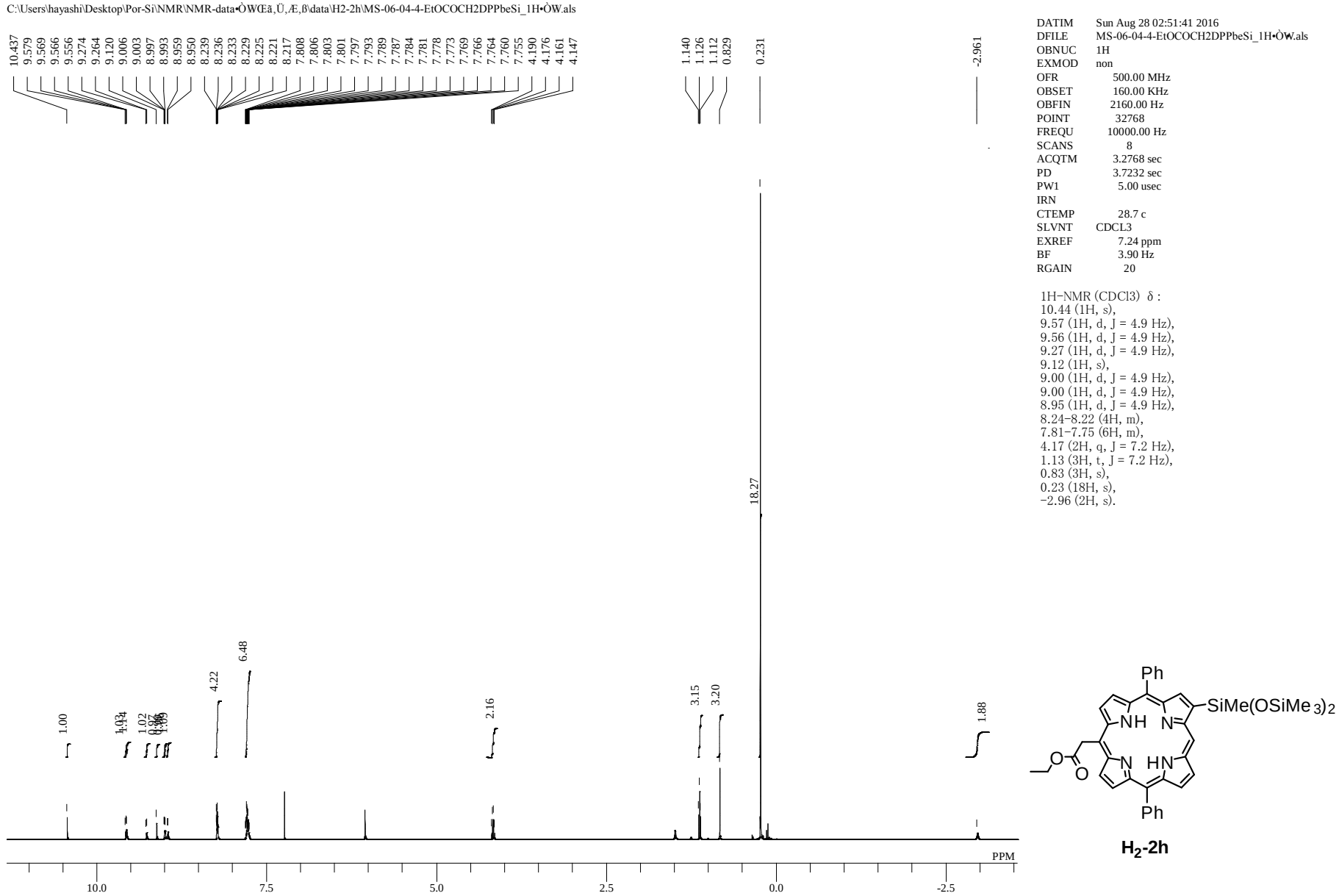
DATIM Sat Dec 06 05:08:15 2014
DFILE NS-21-20-BrDPPSi2BCM_•ÒWŒã.als
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 10000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.00 usec
IRN
CTEMP 50.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
149.12 (1H, br s),
148.40 (2H, br s),
147.57 (1H, br s),
146.61 (2H, br s),
145.92 (1H, br s),
144.64 (1H, br s),
142.08 (1H, s),
141.68 (1H, s),
141.63 (1H, s),
140.64 (1H, s),
134.77 (2H, s),
134.67 (2H, s),
132.77 (1H, s),
132.43 (1H, s),
132.17 (1H, s),
132.05 (2H, s),
131.53 (1H, s),
127.89 (2H, s),
126.88 (2H, s),
126.83 (2H, s),
120.19 (1H, s),
120.02 (1H, s),
107.26 (1H, s),
103.45 (1H, s),
2.48 (1H, s),
2.10 (6H, s).



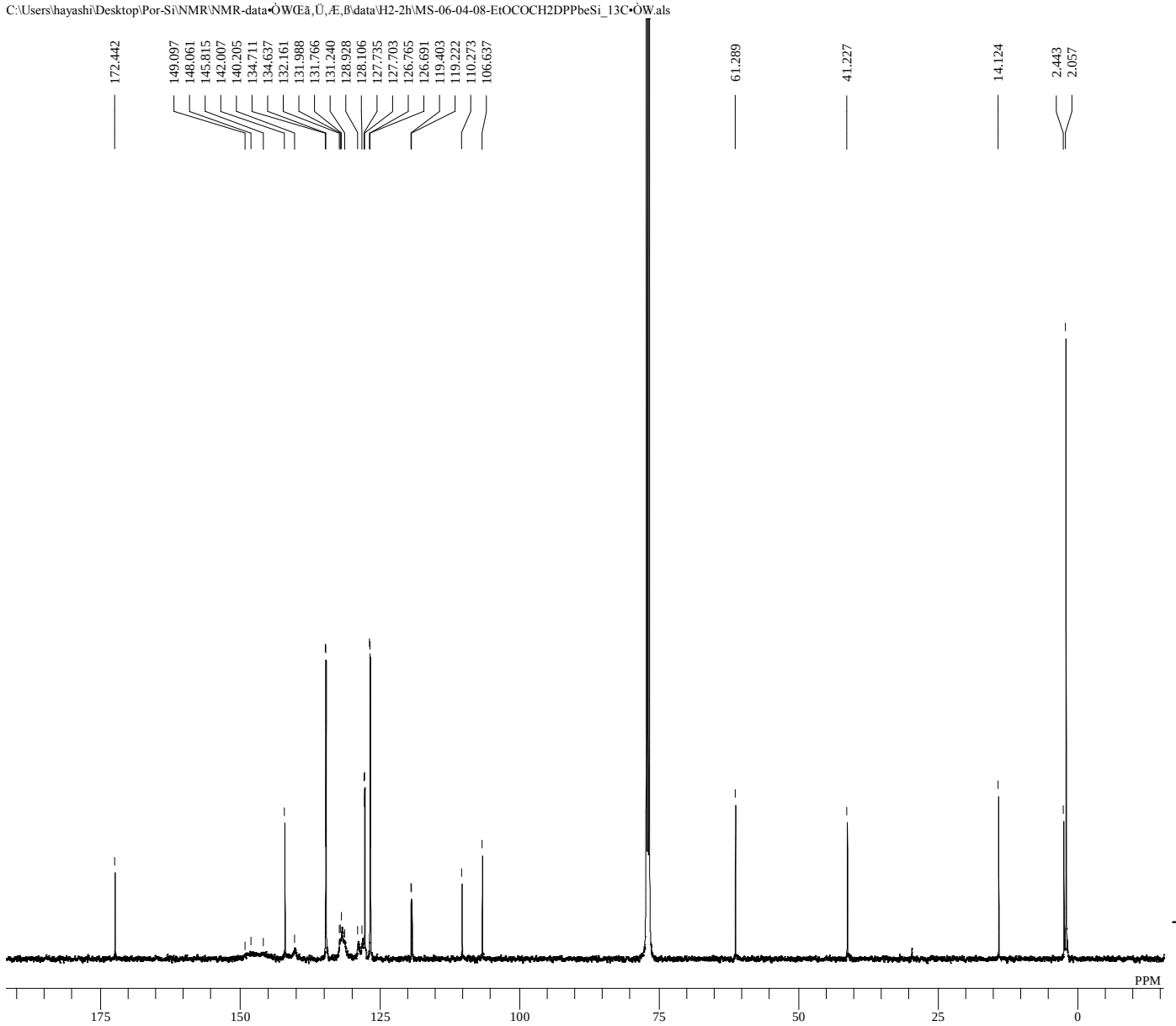
H_2-2g

Fig. S34 ^{1}H NMR spectrum of compound **H_2-2h** (in $CDCl_3$)



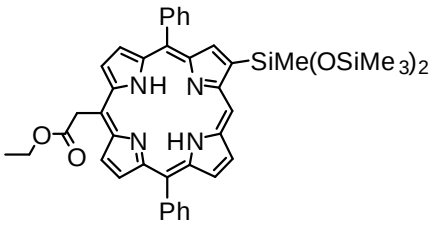
H_2-2h

Fig. S35 ^{13}C NMR spectrum of compound **H_2-2h** (in $CDCl_3$)



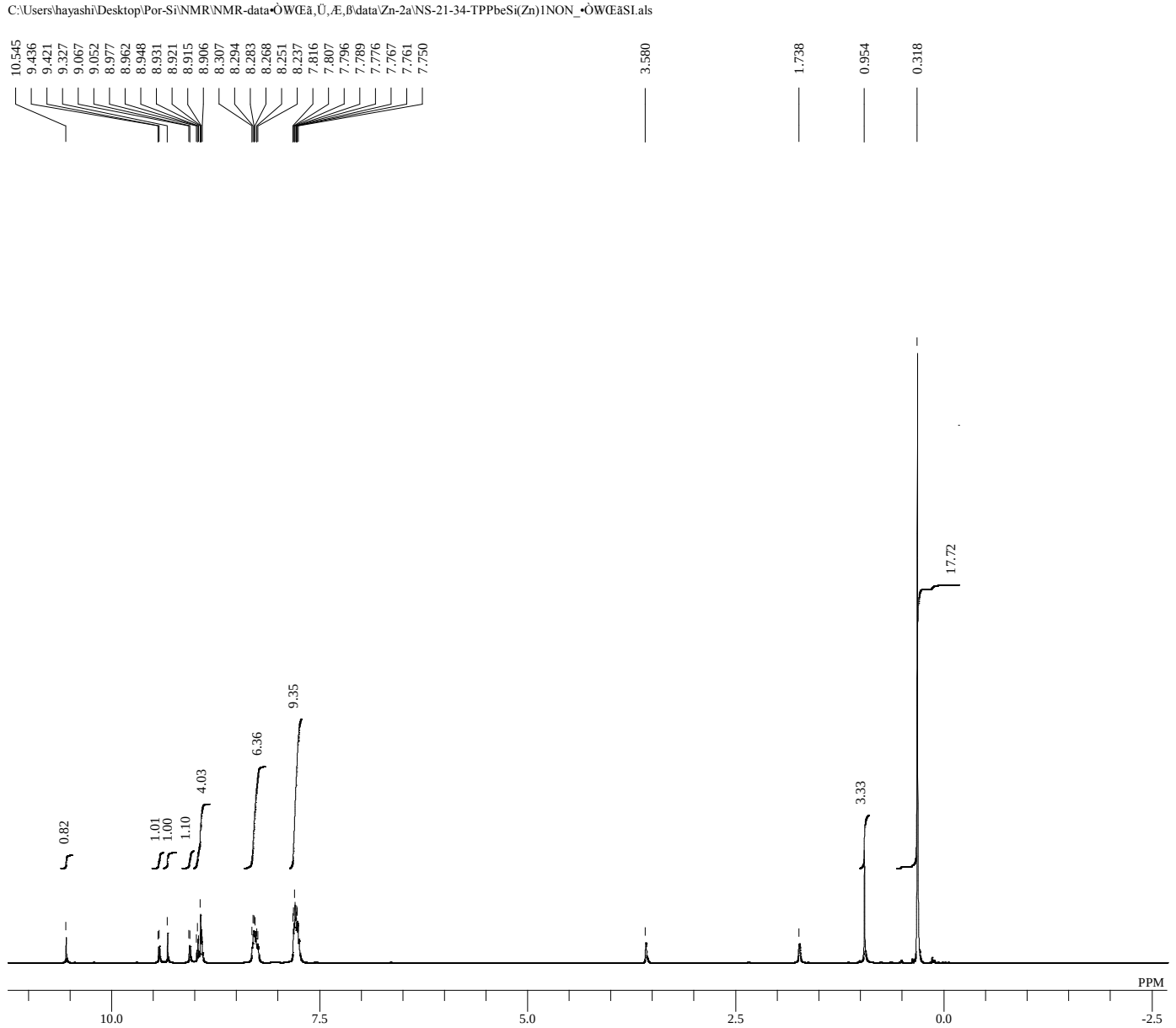
DATIM Sun Aug 28 19:56:10 2016
DFILE MS-06-04-08-EtOCOCH2DPPbeSi_13C•ÒW.als
OBNUC 13C
EXMOD bcm
OFR 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 19000
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 4.40 usec
IRN
CTEMP 40.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 3.90 Hz
RGAIN 29

13C-NMR (CDCl3) δ :
172.44 (0H, s),
149.10 (2H, br s),
148.06 (3H, br s),
145.82 (3H, br s),
142.01 (2H, s),
140.21 (1H, br s),
134.71 (2H, s),
134.64 (2H, s),
132.16 (0H, br s),
131.99 (0H, br s),
131.77 (2H, br s),
131.24 (0H, br s),
128.93 (0H, br s),
128.11 (0H, br s),
127.74 (0H, s),
127.70 (0H, s),
126.76 (2H, s),
126.69 (2H, s),
119.40 (0H, s),
119.22 (0H, s),
110.27 (0H, s),
106.64 (0H, s),
61.29 (0H, s),
41.23 (0H, s),
14.12 (0H, s),
2.44 (0H, s),
2.06 (6H, s).



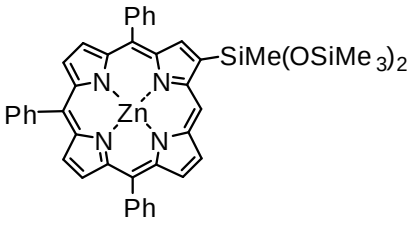
H_2-2h

Fig. S36 ^{1}H NMR spectrum of compound **Zn-2a** (in $CDCl_3$)



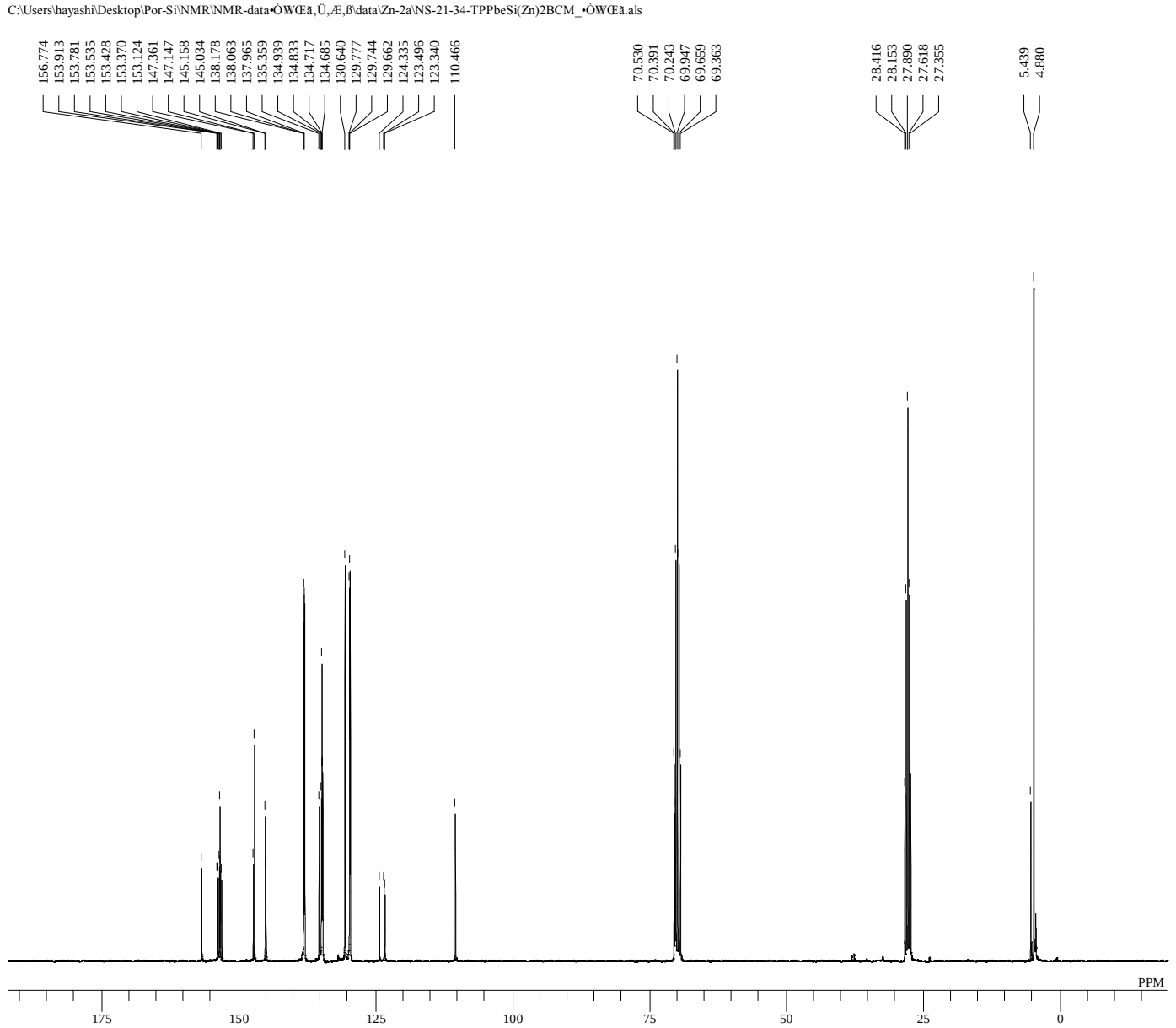
DATIM Thu Dec 18 22:18:40 2014
DFILE NS-21-34-TPPbeSi(Zn)1NON_•ÒWŒÈãSI.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 8
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.30 usec
IRN
CTEMP 50.8 c
SLVNT CDCL3
EXREF 3.58 ppm
BF 1.20 Hz
RGAIN 11

1H-NMR (CDCl3) δ :
10.55 (1H, s),
9.43 (1H, d, J = 4.4 Hz),
9.33 (1H, s),
9.06 (1H, d, J = 4.6 Hz),
8.97 (1H, d, J = 4.6 Hz),
8.95 (1H, d, J = 4.6 Hz),
8.92 (1H, d, J = 4.6 Hz),
8.91 (1H, d, J = 4.6 Hz),
8.35−8.20 (6H, m),
7.86−7.71 (9H, m),
0.95 (3H, s),
0.32 (18H, s).



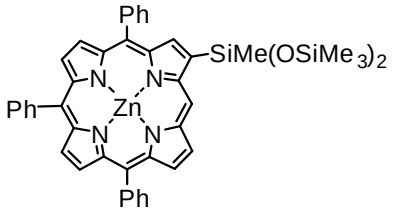
Zn-2a

Fig. S37 ^{13}C NMR spectrum of compound **Zn-2a** (in $CDCl_3$)



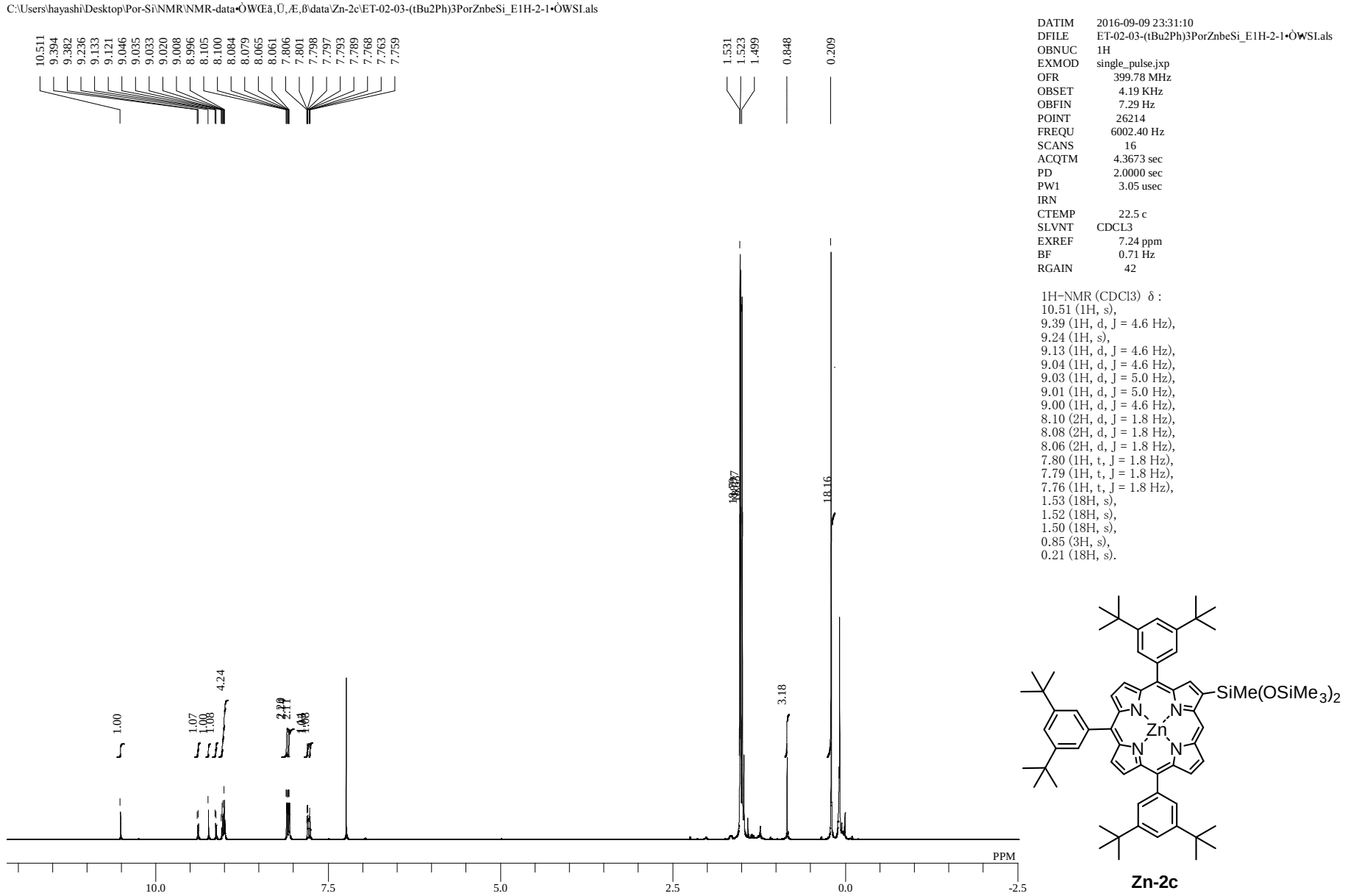
DATIM Fri Dec 19 06:39:03 2014
DFILE NS-21-34-TPPbeSi(Zn)2BCM_•ÒWŒÈã.als
OBNUC 13C
EXMOD BCM
OFR 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 10000
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.30 usec
IRN
CTEMP 50.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 22

13C-NMR (CDCl3) δ :
156.77 (1H, s),
153.91 (1H, s),
153.78 (1H, s),
153.53 (1H, s),
153.43 (2H, s),
153.37 (1H, s),
153.12 (1H, s),
147.36 (1H, s),
147.15 (2H, s),
145.16 (1H, s),
145.03 (1H, s),
138.18 (2H, s),
138.06 (2H, s),
137.96 (2H, s),
135.36 (1H, s),
134.94 (1H, s),
134.83 (2H, s),
134.72 (1H, s),
134.68 (1H, s),
130.64 (3H, s),
129.78 (2H, s),
129.74 (2H, s),
129.66 (2H, s),
124.33 (1H, s),
123.50 (1H, s),
123.34 (1H, s),
110.47 (1H, s),
5.44 (1H, s),
4.88 (6H, s).



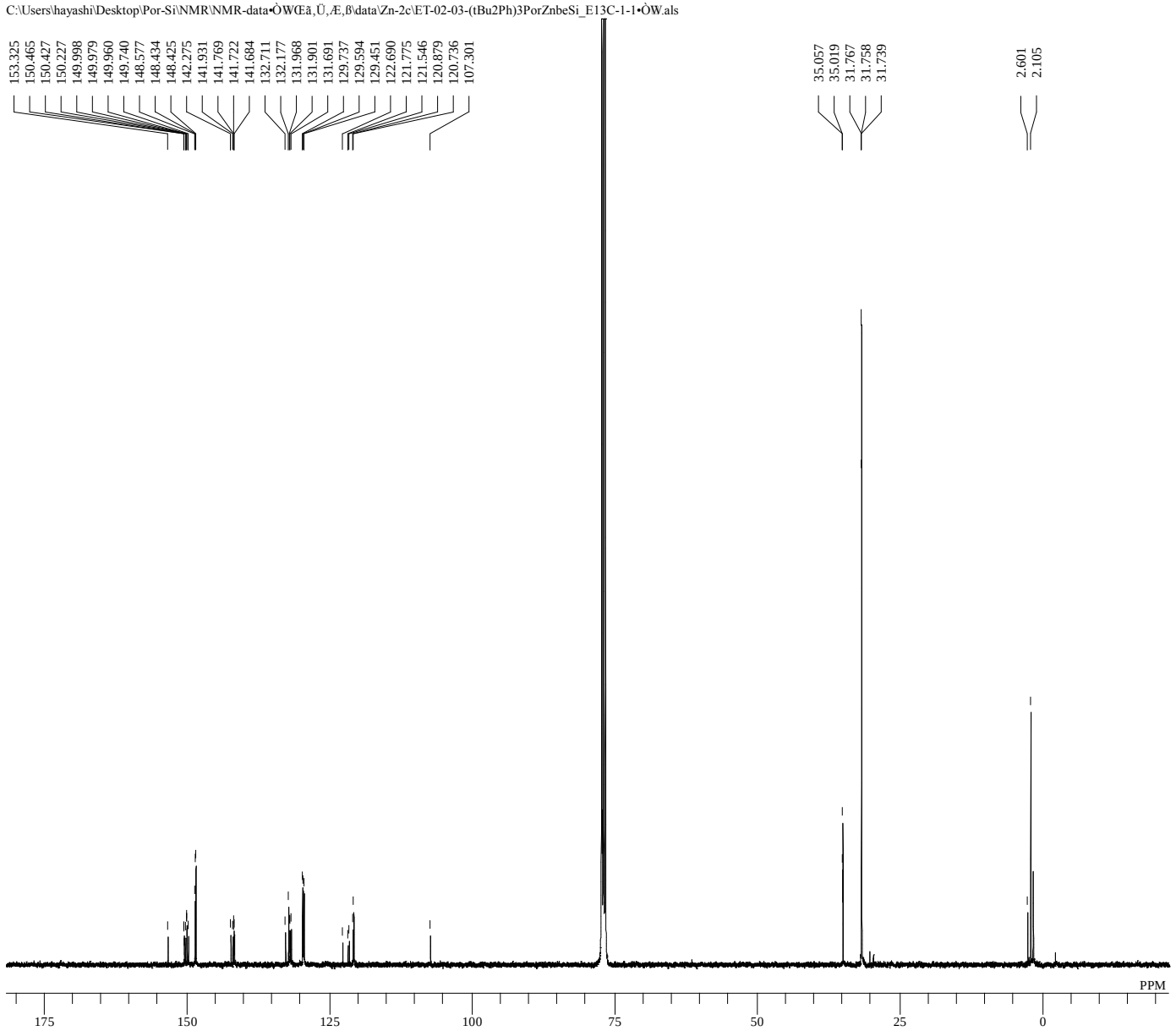
Zn-2a

Fig. S38 ^{1}H NMR spectrum of compound **Zn-2c** (in $CDCl_3$)



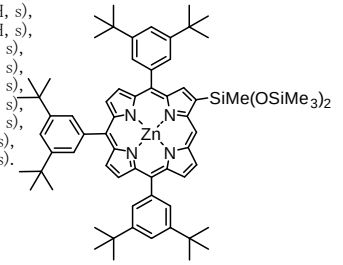
Zn-2c

Fig. S39 ^{13}C NMR spectrum of compound **Zn-2c** (in $CDCl_3$)



DATIM 2016-09-09 23:43:52
DFILE ET-02-03-(tBu2Ph)3PorZnbeSi_E13C-1-1•ÒW.als
OBNUC 13C
EXMOD single_pulse_dec
OFR 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 60000
ACQTM 1.0433 sec
PD 1.7000 sec
PW1 3.53 usec
IRN
CTEMP 21.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.41 Hz
RGAIN 60

13C-NMR (CDCl3) δ :
153.32 (0H, s),
150.47 (2H, s),
150.43 (2H, s),
150.23 (0H, s),
150.00 (0H, s),
149.98 (0H, s),
149.96 (0H, s),
149.74 (0H, s),
148.58 (2H, s),
148.43 (2H, s),
148.42 (2H, s),
142.27 (0H, s),
141.93 (0H, s),
141.77 (0H, s),
141.72 (0H, s),
141.68 (0H, s),
132.71 (0H, s),
132.18 (0H, s),
131.97 (0H, s),
131.90 (0H, s),
131.69 (0H, s),
129.74 (2H, s),
129.59 (2H, s),
129.45 (2H, s),
122.69 (0H, s),
121.77 (0H, s),
121.55 (0H, s),
120.88 (0H, s),
120.74 (0H, s),
107.30 (0H, s),
35.06 (2H, s),
35.02 (4H, s),
31.77 (6H, s),
31.76 (6H, s),
31.74 (6H, s),
2.60 (0H, s),
2.11 (6H, s).



Zn-2c

Fig. S40 ^{1}H NMR spectrum of compound **Ni-2c** (in $CDCl_3$)

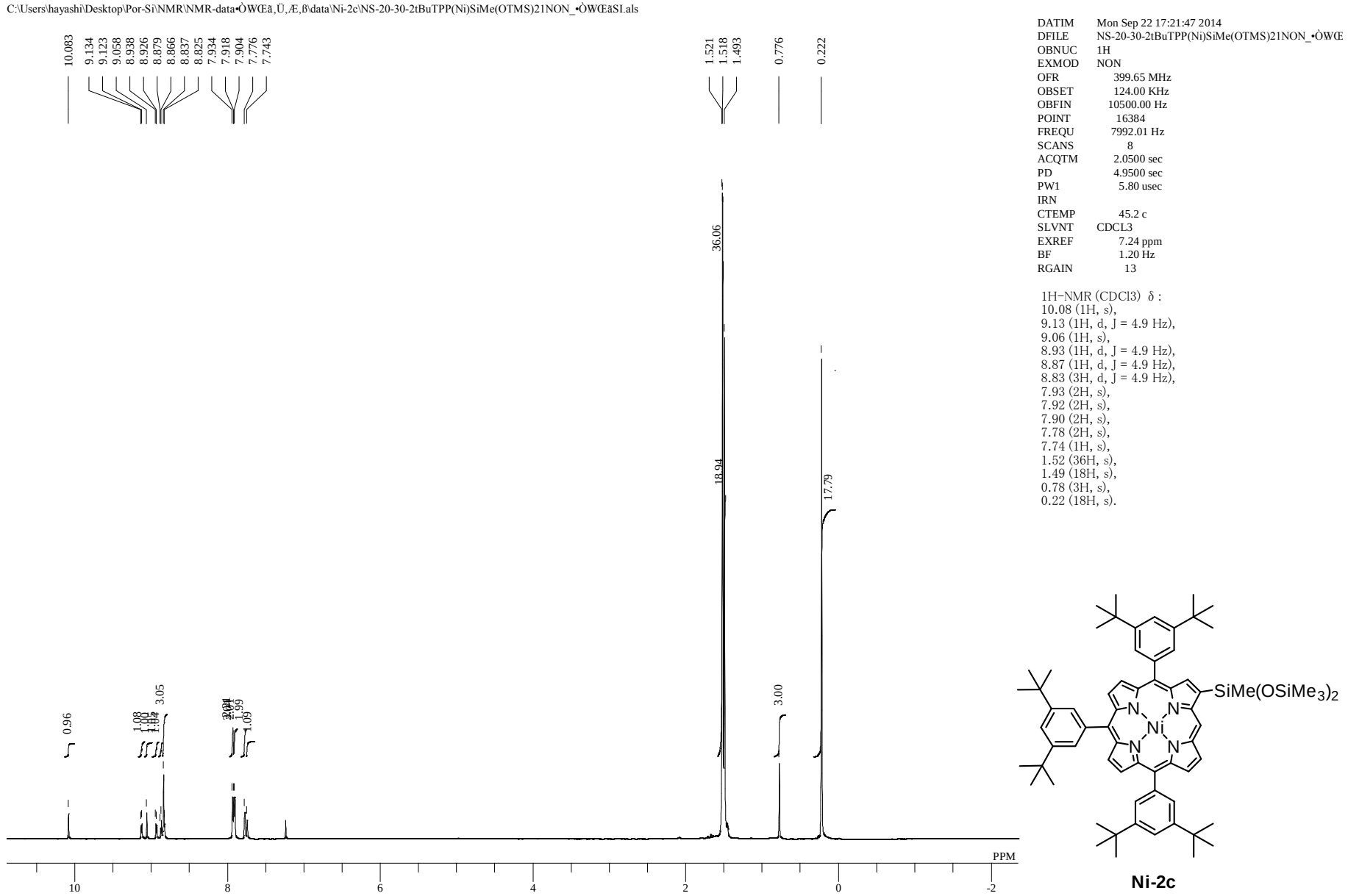
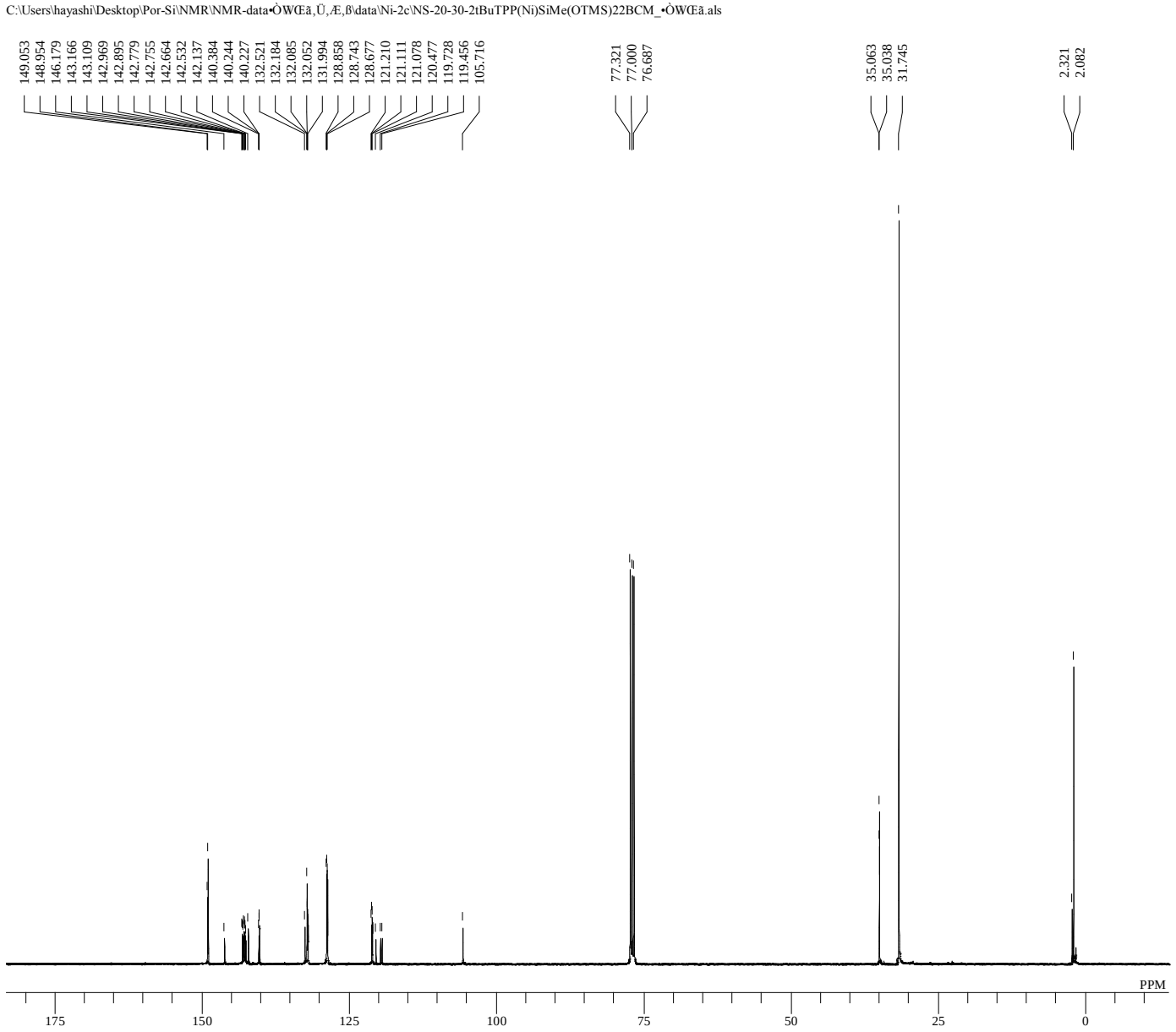
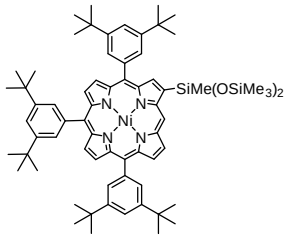


Fig. S41 ^{13}C NMR spectrum of compound **Ni-2c** (in $CDCl_3$)



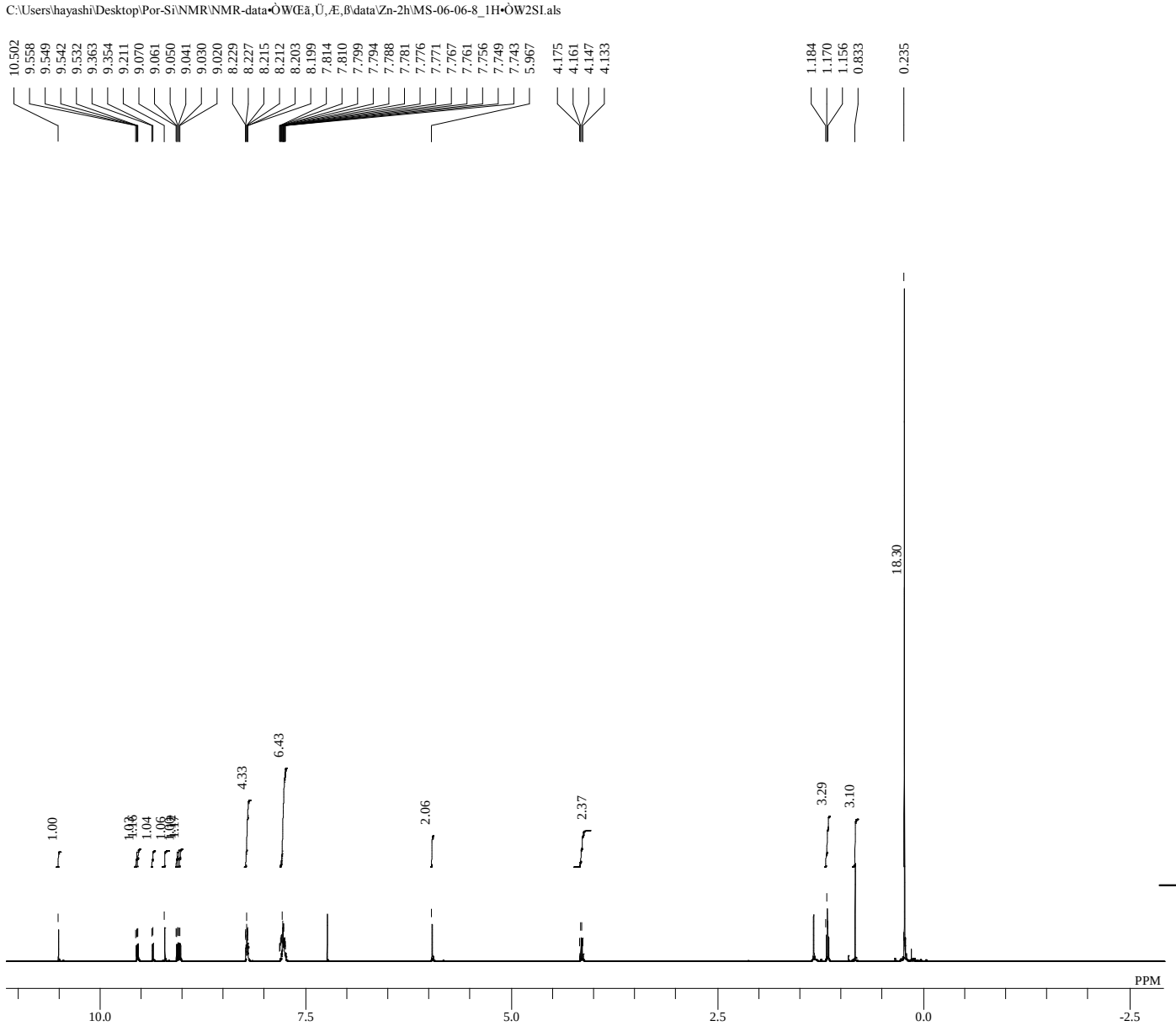
DATIM Wed Sep 24 06:02:39 2014
DFILE NS-20-30-2tBuTPP(Ni)SiMe(OTMS)22BCM_•ÒWŒ
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 44000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.00 usec
IRN
CTEMP 45.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
149.05 (2H, s),
148.95 (3H, s),
146.18 (1H, s),
143.17 (1H, s),
143.11 (1H, s),
142.97 (1H, s),
142.89 (1H, s),
142.78 (1H, s),
142.75 (1H, s),
142.66 (1H, s),
142.53 (1H, s),
142.14 (2H, s),
140.38 (1H, s),
140.24 (1H, s),
140.23 (1H, s),
132.52 (1H, s),
132.18 (2H, s),
132.08 (1H, s),
132.05 (1H, s),
131.99 (1H, s),
128.86 (2H, s),
128.74 (2H, s),
128.68 (2H, s),
121.21 (1H, s),
121.11 (1H, s),
121.08 (1H, s),
120.48 (1H, s),
119.73 (1H, s),
119.46 (1H, s),
105.72 (1H, s),
35.06 (2H, s),
35.04 (4H, s),
31.74 (18H, s),
2.32 (1H, s),
2.08 (6H, s).



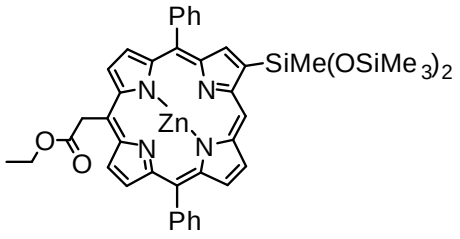
Ni-2c

Fig. S42 ^{1}H NMR spectrum of compound **Zn-2h** (in $CDCl_3$)



DATIM Sat Aug 27 03:44:27 2016
DFILE MS-06-06-8_1H•ÒW2SI.als
OBNUC 1H
EXMOD non
OFR 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 8
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.00 usec
IRN
CTEMP 28.4 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.40 Hz
RGAIN 21

1H-NMR (CDCl3) δ :
10.50 (1H, s),
9.55 (1H, d, J = 4.6 Hz),
9.54 (1H, d, J = 4.6 Hz),
9.36 (1H, d, J = 4.6 Hz),
9.21 (1H, s),
9.07 (1H, d, J = 4.6 Hz),
9.05 (1H, d, J = 4.6 Hz),
9.03 (1H, d, J = 4.6 Hz),
8.22-8.21 (4H, m),
7.81-7.74 (6H, m),
5.97 (2H, s),
4.15 (2H, q, J = 7.0 Hz),
1.17 (3H, t, J = 7.0 Hz),
0.83 (3H, s),
0.23 (18H, s).



Zn-2h

Fig. S43 ^{13}C NMR spectrum of compound **Zn-2h** (in $CDCl_3$)

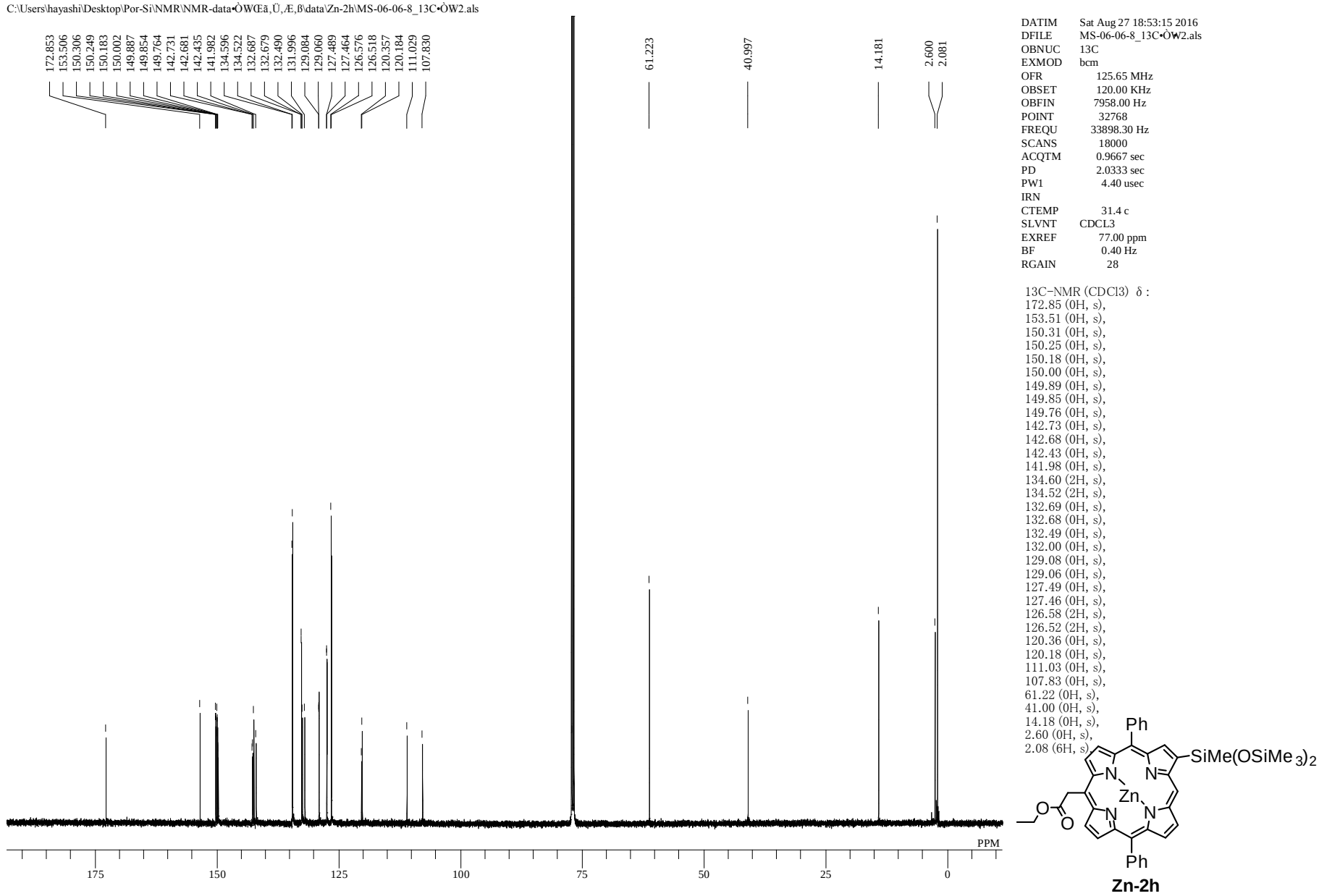
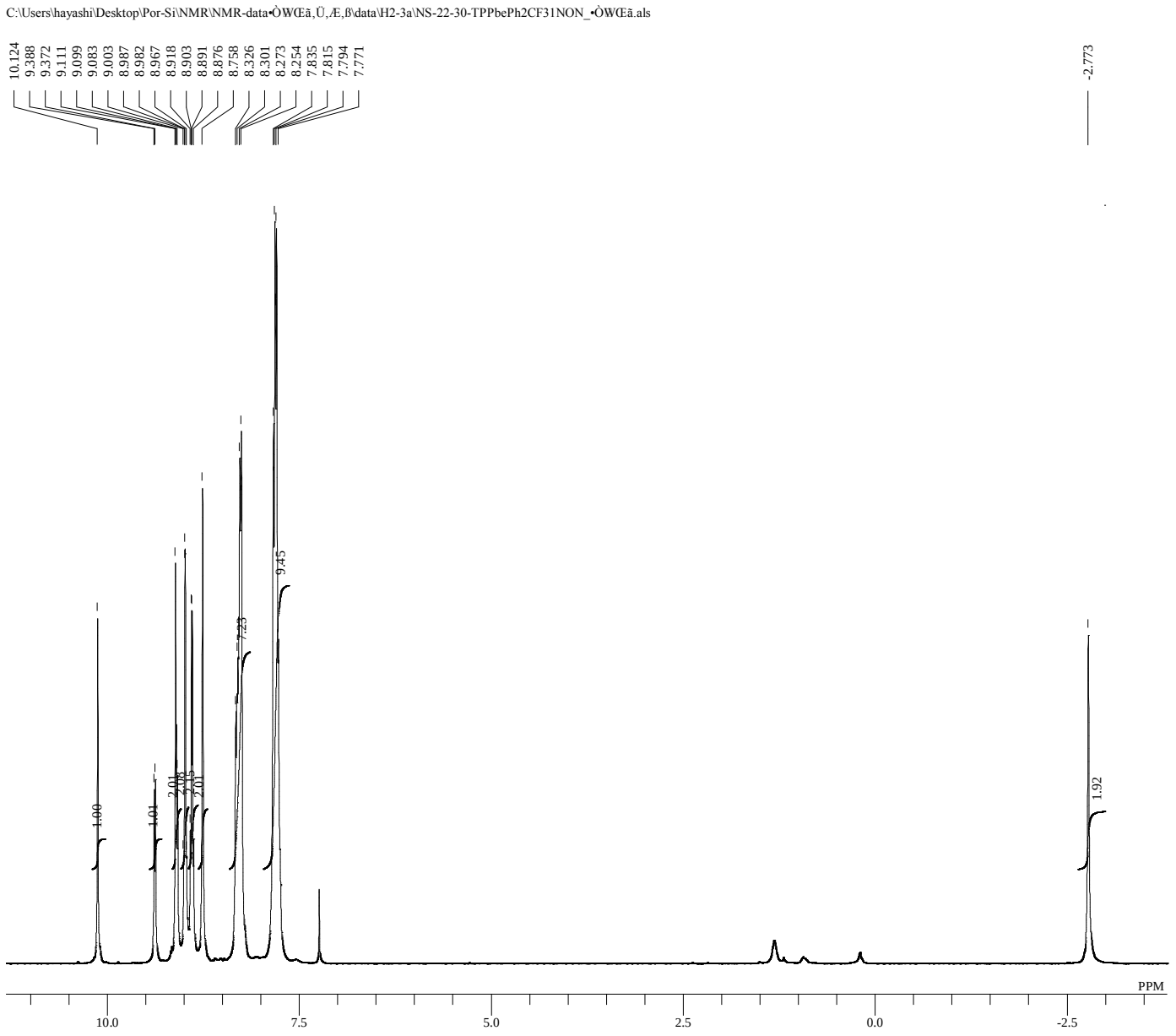
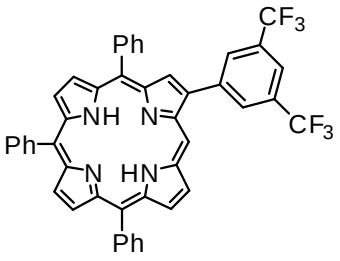


Fig. S44 ^{1}H NMR spectrum of compound **H_2-3a** (in $CDCl_3$)



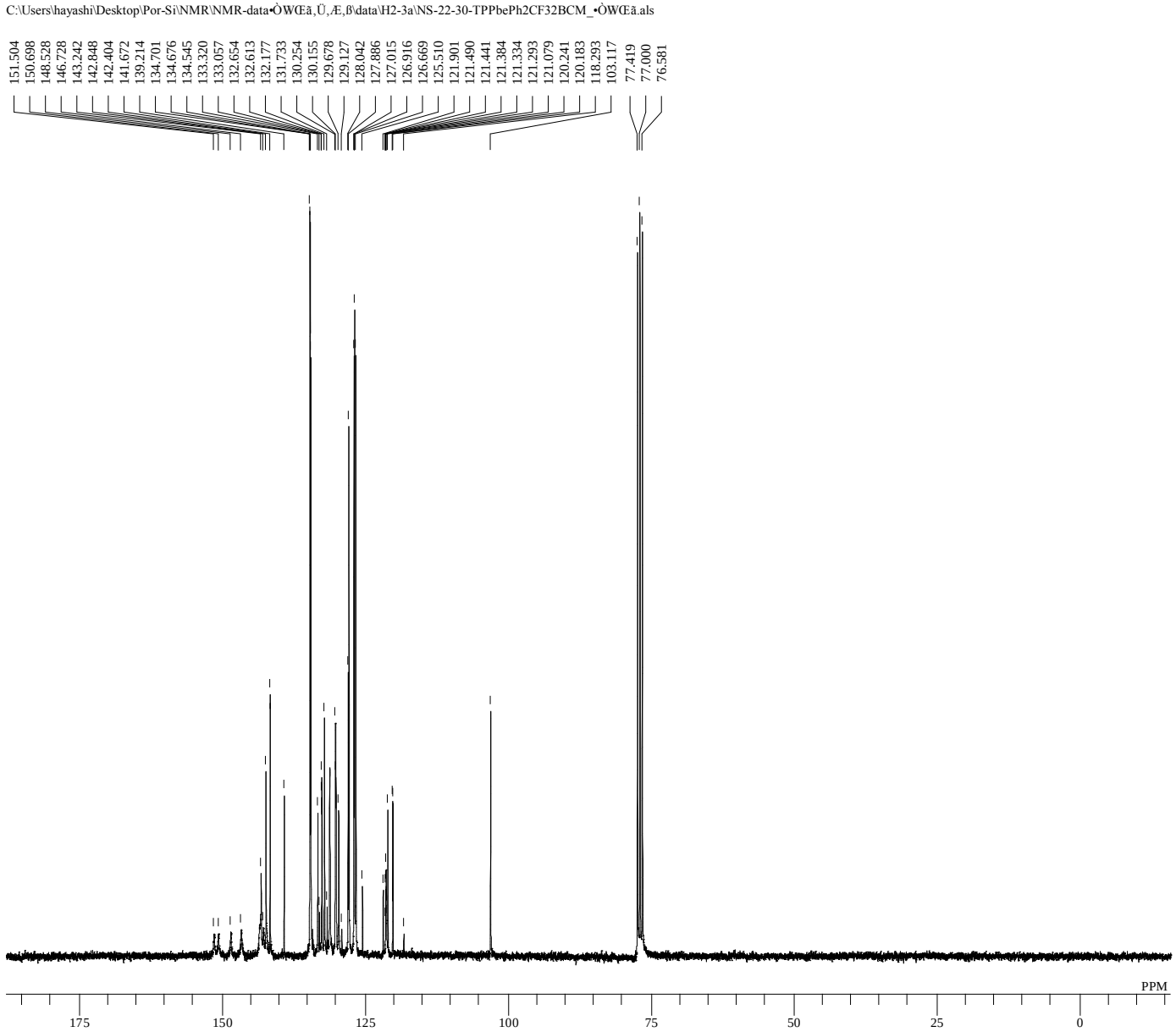
DATIM Fri Feb 20 22:04:16 2015
DFILE NS-22-30-TPPbePh2CF31NON_•ÒWŒã.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.30 usec
IRN
CTEMP 45.7 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 1.20 Hz
RGAIN 13

1H-NMR (CDCl3) δ :
10.12 (1H, s),
9.38 (1H, d, J = 4.8 Hz),
9.11 (1H, s),
9.09 (1H, d, J = 4.8 Hz),
8.99 (1H, d, J = 4.8 Hz),
8.97 (1H, d, J = 4.8 Hz),
8.91 (1H, d, J = 4.8 Hz),
8.88 (1H, d, J = 4.8 Hz),
8.76 (2H, s),
8.37−8.21 (7H, m),
7.91−7.71 (9H, m),
−2.77 (2H, br s).



H_2-3a

Fig. S45 ^{13}C NMR spectrum of compound **H_2-3a** (in $CDCl_3$)



DATIM Sat Feb 21 06:24:41 2015
DFILE NS-22-30-TPPbePh2CF32BCM_•ÒWŒã.als
OBNUC 13C
EXMOD BCM
OFR 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 10000
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.30 usec
IRN
CTEMP 45.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
151.50 (1H, br s),
150.70 (1H, br s),
148.53 (1H, br s),
146.73 (1H, br s),
143.51 (1H, br s),
143.37 (1H, br s),
143.24 (1H, s),
142.85 (1H, br s),
142.40 (1H, s),
142.31 (1H, br s),
141.67 (2H, s),
139.21 (1H, s),
134.70 (2H, s),
134.68 (2H, s),
134.54 (2H, s),
133.32 (1H, s),
132.65 (1H, s),
132.40 (2H, q, J = 33.2 Hz),
132.17 (1H, s),
131.24 (2H, s),
130.25 (2H, s),
130.15 (1H, s),
129.68 (1H, s),
128.04 (1H, s),
127.89 (2H, s),
127.01 (2H, s),
126.92 (2H, s),
126.67 (2H, s),
123.71 (2H, q, J = 272.9 Hz),
121.38 (1H, br s),
121.08 (1H, s),
120.24 (1H, s),
120.18 (1H, s),
103.12 (1H, s).

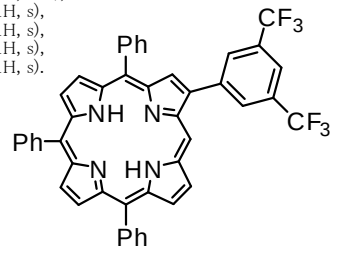
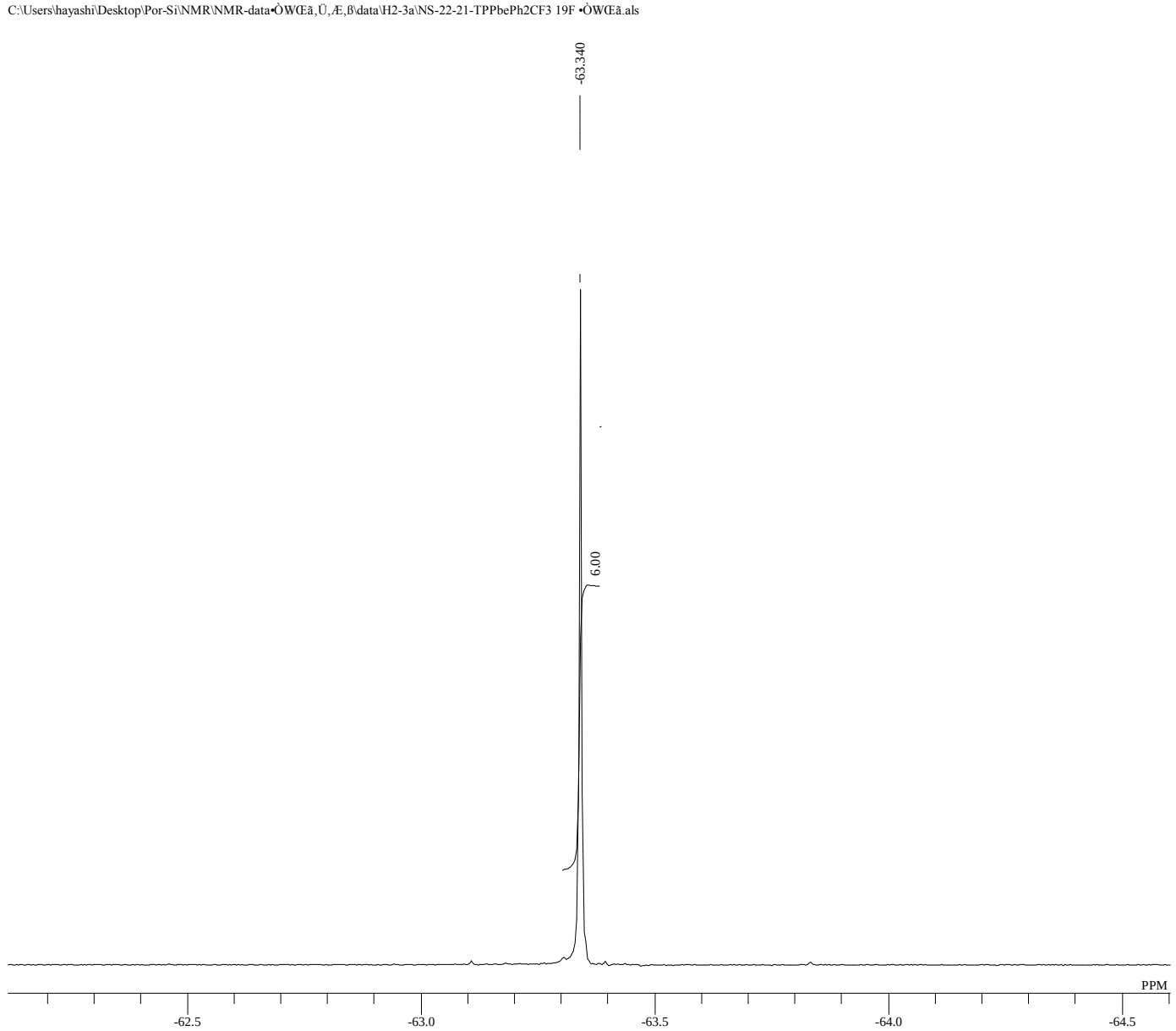
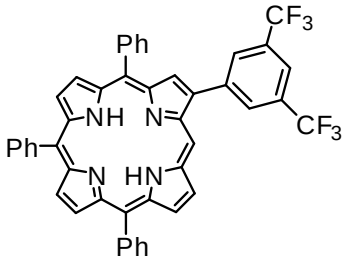


Fig. S46 ^{19}F NMR spectrum of compound **H_2-3a** (in $CDCl_3$)



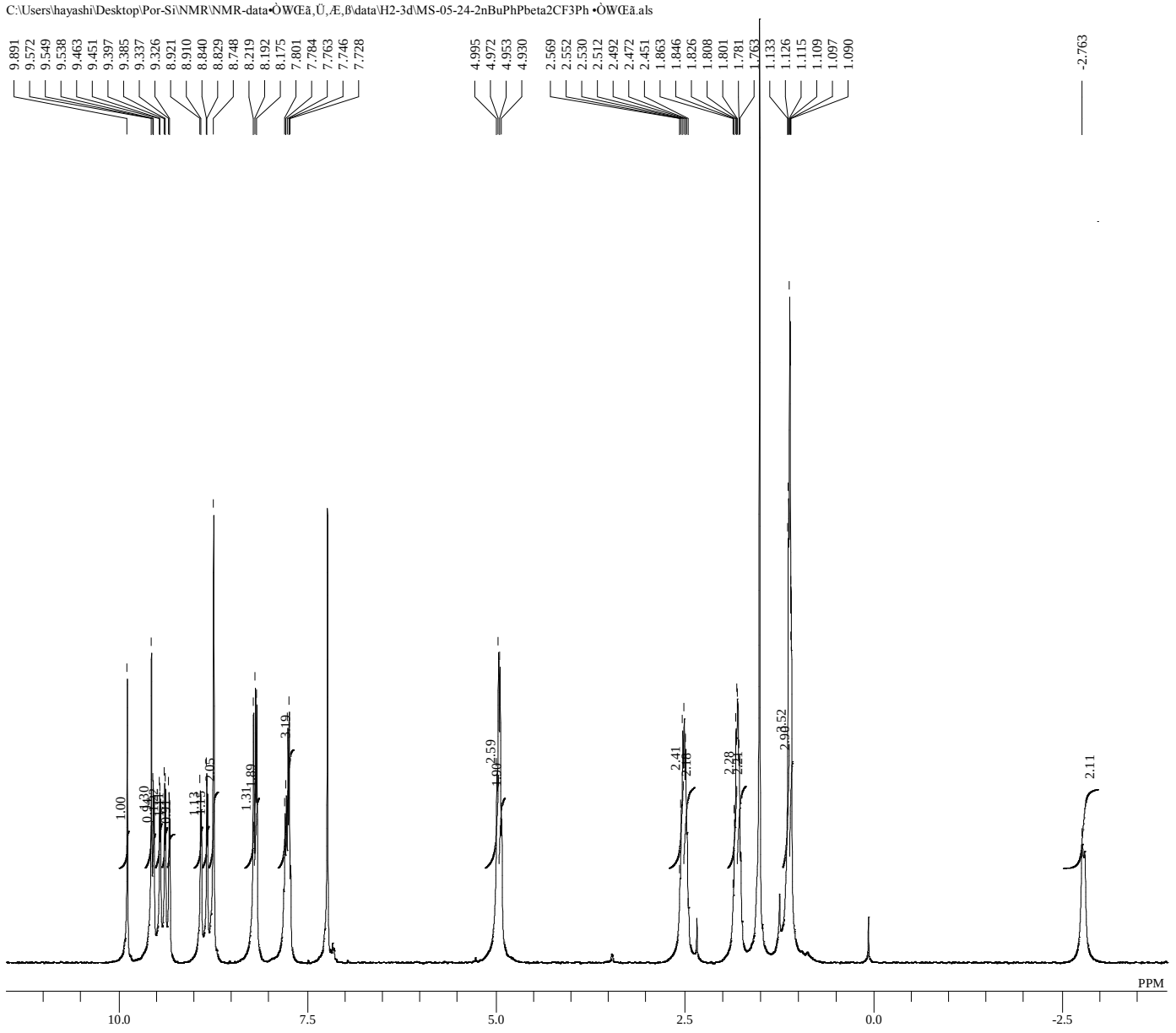
DATIM 2015-02-10 10:44:57
DFILE NS-22-21-TPPbePh2CF3 19F •ÒWŒã.als
OBNUC 19F
EXMOD single_pulse.jxp
OFR 376.14 MHz
OBSET 8.48 KHz
OBFIN 3.66 Hz
POINT 13107
FREQU 18867.93 Hz
SCANS 16
ACQTM 0.6947 sec
PD 5.0000 sec
PW1 3.76 usec
IRN
CTEMP 20.9 c
SLVNT CDCL3
EXREF -63.34 ppm
BF 0.10 Hz
RGAIN 46

19F-NMR (CDCl3) δ :
-63.34 (6H, s).



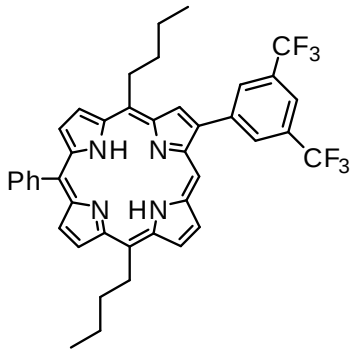
H_2-3a

Fig. S47 ^{1}H NMR spectrum of compound **H_2-3d** (in $CDCl_3$)



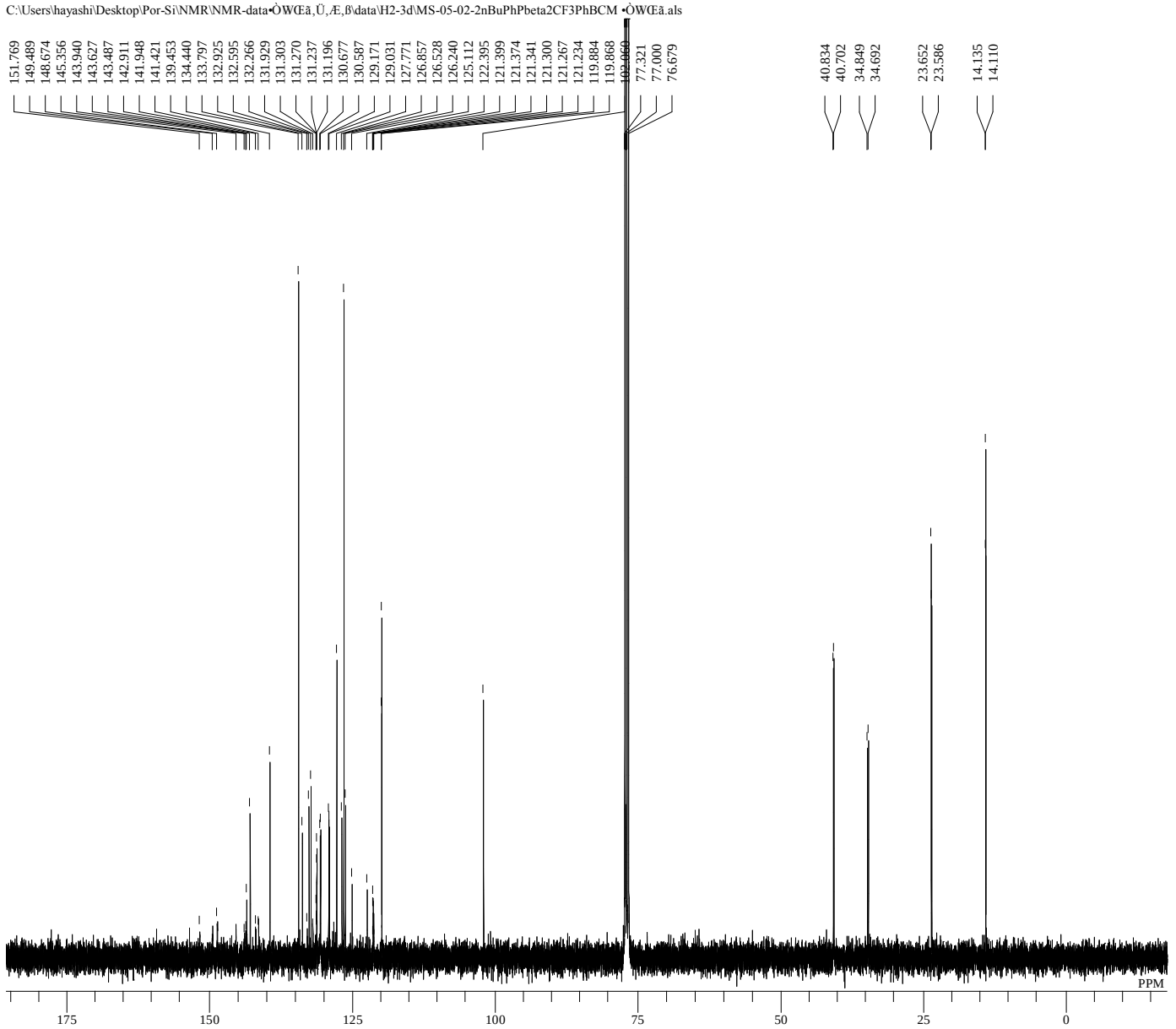
DATIM Thu Aug 25 18:24:25 2016
DFILE MS-05-24-2nBuPhPbeta2CF3Ph •ÒWŒã.als
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 16
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 5.75 usec
IRN
CTEMP 24.5 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 2.00 Hz
RGAIN 21

1H-NMR (CDCl3) δ :
9.89 (1H, s),
9.57 (1H, s),
9.54 (1H, d, J = 4.4 Hz),
9.46 (1H, d, J = 4.9 Hz),
9.39 (1H, d, J = 4.9 Hz),
9.33 (1H, d, J = 4.4 Hz),
8.92 (1H, d, J = 4.4 Hz),
8.83 (1H, d, J = 4.4 Hz),
8.75 (2H, s),
8.22 (1H, s),
8.19-8.17 (2H, m),
7.80-7.73 (3H, m),
4.97 (2H, t, J = 8.3 Hz),
4.95 (2H, t, J = 8.3 Hz),
2.57-2.49 (2H, m),
2.53-2.45 (2H, m),
1.86-1.80 (2H, m),
1.83-1.76 (2H, m),
1.12 (3H, t, J = 7.1 Hz),
1.11 (3H, t, J = 7.1 Hz),
-2.76 (2H, s).



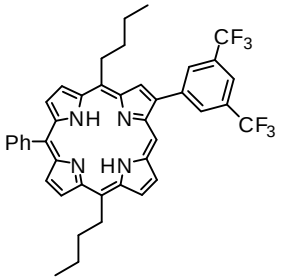
H_2-3d

Fig. S48 ^{13}C NMR spectrum of compound **H_2-3d** (in $CDCl_3$)



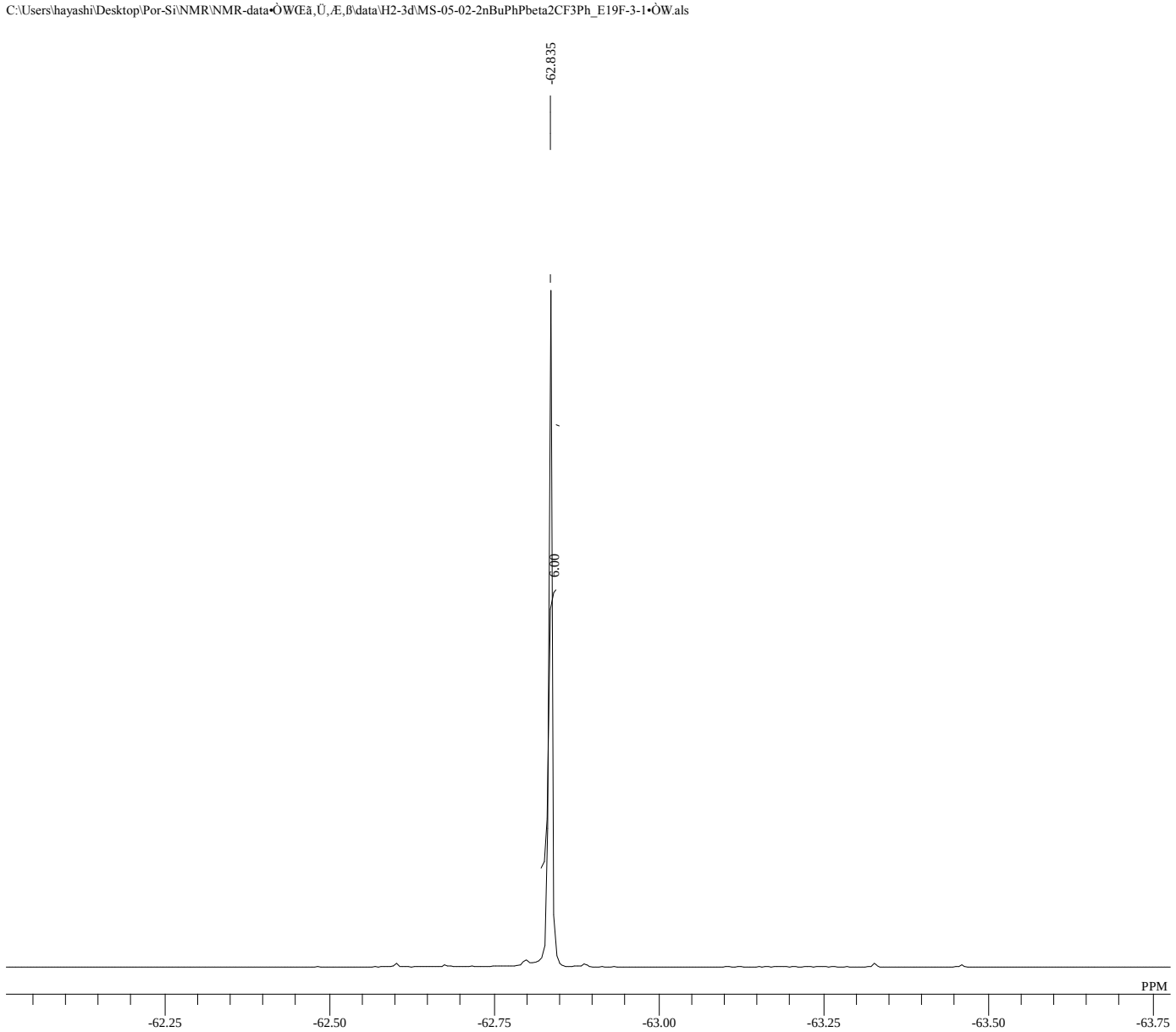
DATIM Fri Aug 26 09:02:56 2016
DFILE MS-05-02-2nBuPhPbeta2CF3PhBCM •ÒWŒã.als
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 14020
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.80 usec
IRN
CTEMP 50.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
151.77 (0H, s),
149.49 (0H, s),
148.67 (0H, s),
145.36 (0H, s),
143.94 (0H, s),
143.63 (0H, s),
143.49 (0H, s),
142.91 (2H, s),
141.95 (0H, s),
141.42 (0H, s),
139.45 (0H, s),
134.44 (2H, s),
133.80 (0H, s),
132.43 (2H, q, J = 33.4 Hz),
131.25 (2H, q, J = 7.0 Hz),
130.68 (0H, s),
130.59 (0H, s),
129.17 (0H, s),
129.03 (0H, s),
127.77 (0H, s),
126.86 (0H, s),
126.53 (2H, s),
126.24 (0H, s),
125.11 (0H, s),
122.40 (0H, s),
121.35-121.28 (0H, m),
119.88 (0H, s),
119.87 (0H, s),
102.06 (0H, s),
40.83 (0H, s),
40.70 (0H, s),
34.85 (0H, s),
34.69 (0H, s),
23.65 (0H, s),
23.59 (0H, s),
14.14 (0H, s),
14.11 (0H, s).



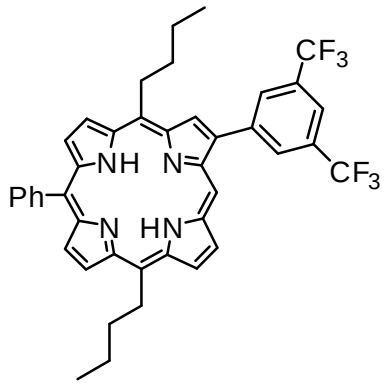
H_2-3d

Fig. S49 ^{19}F NMR spectrum of compound **H_2-3d** (in $CDCl_3$)



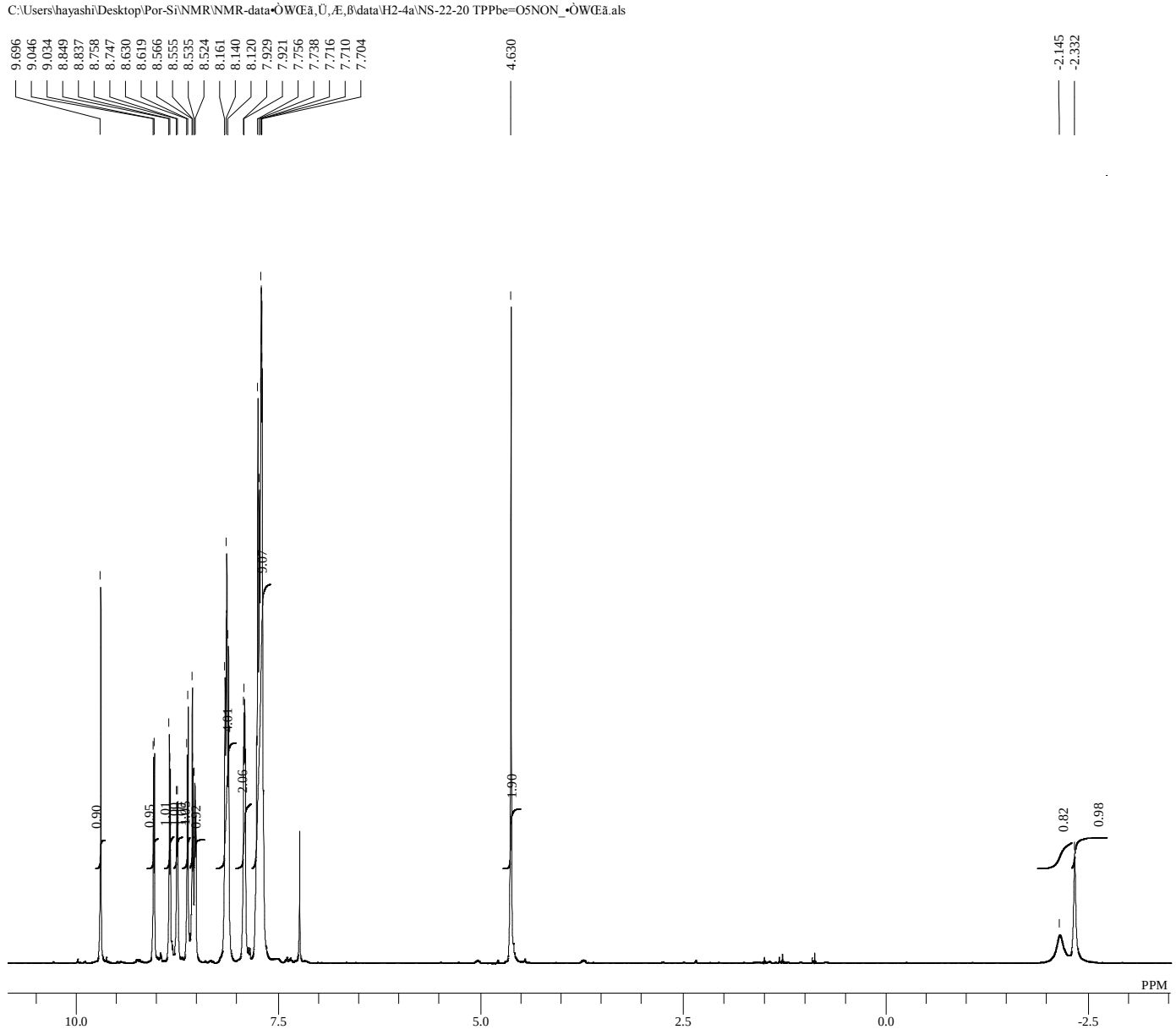
DATIM 2016-08-27 21:03:04
DFILE MS-05-02-2nBuPhPbeta2CF3Ph_E19F-3-1•ÒW.als
OBNUC 19F
EXMOD single_pulse.jxp
OFR 376.14 MHz
OBSET 8.48 KHz
OBFIN 3.66 Hz
POINT 13107
FREQU 22624.44 Hz
SCANS 16
ACQTM 0.5793 sec
PD 5.0000 sec
PW1 3.76 usec
IRN
CTEMP 21.7 c
SLVNT CDCL3
EXREF -63.34 ppm
BF 0.10 Hz
RGAIN 44

19F-NMR (CDCl3) δ :
-62.84 (6H, s).



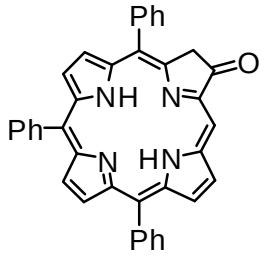
H_2-3d

Fig. S50 ^{1}H NMR spectrum of compound **H_2-4a** (in $CDCl_3$)



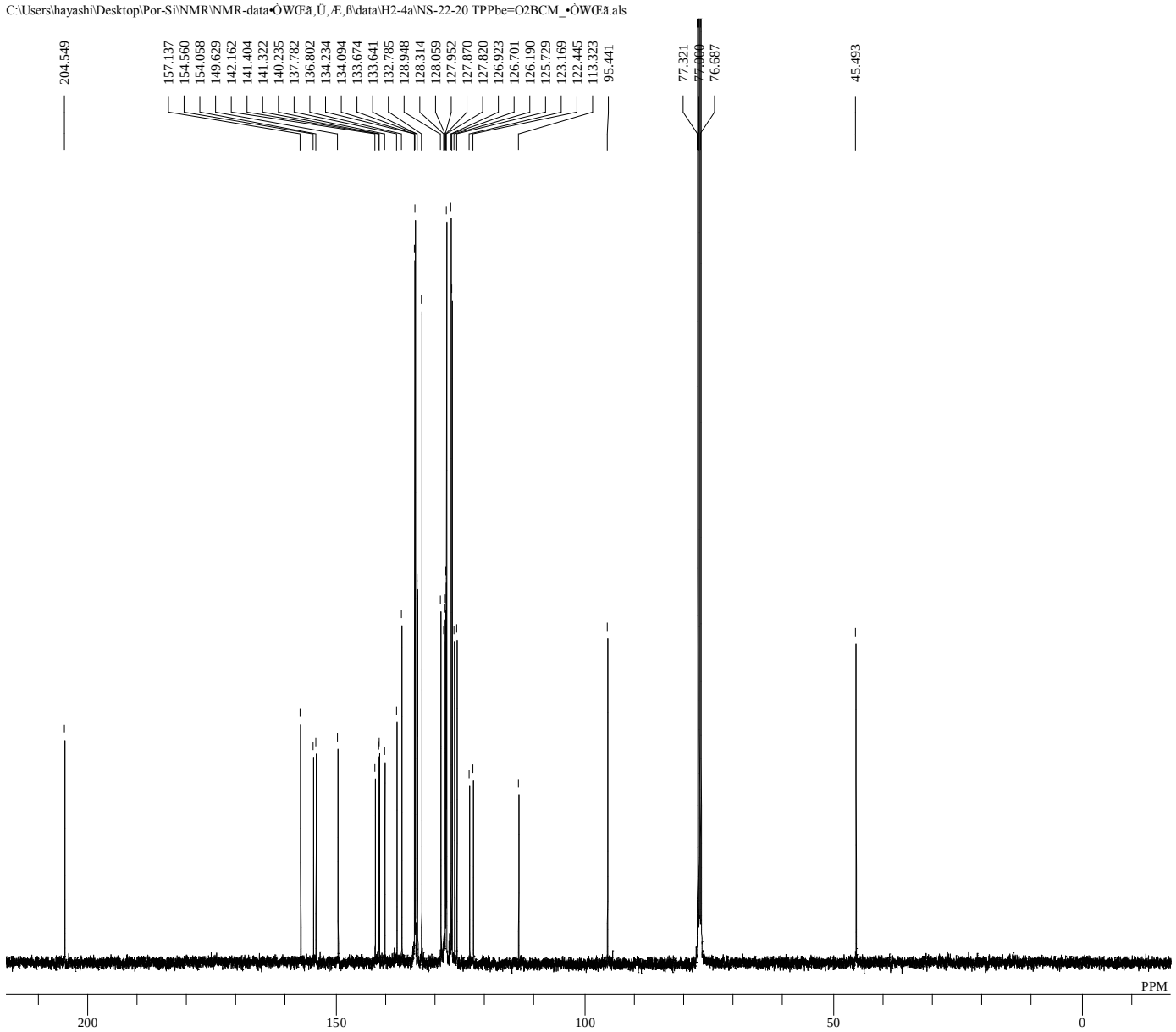
DATIM Fri Feb 06 09:36:12 2015
DFILE NS-22-20 TPPbe=O5NON_•ÒWŒã.als
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.40 usec
IRN
CTEMP 40.1 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 1.20 Hz
RGAIN 17

1H-NMR (CDCl3) δ :
9.70 (1H, s),
9.04 (1H, d, J = 4.4 Hz),
8.84 (1H, d, J = 4.4 Hz),
8.75 (1H, d, J = 4.4 Hz),
8.62 (1H, d, J = 4.4 Hz),
8.56 (1H, d, J = 4.4 Hz),
8.53 (1H, d, J = 4.4 Hz),
8.20−8.08 (4H, m),
7.98−7.87 (2H, m),
7.83−7.63 (9H, m),
4.63 (2H, s),
−2.15 (1H, s),
−2.33 (1H, s).



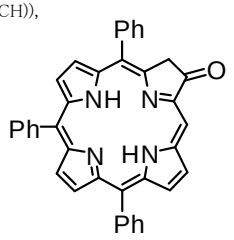
H_2-4a

Fig. S51 ^{13}C NMR spectrum of compound **H_2-4a** (in $CDCl_3$)



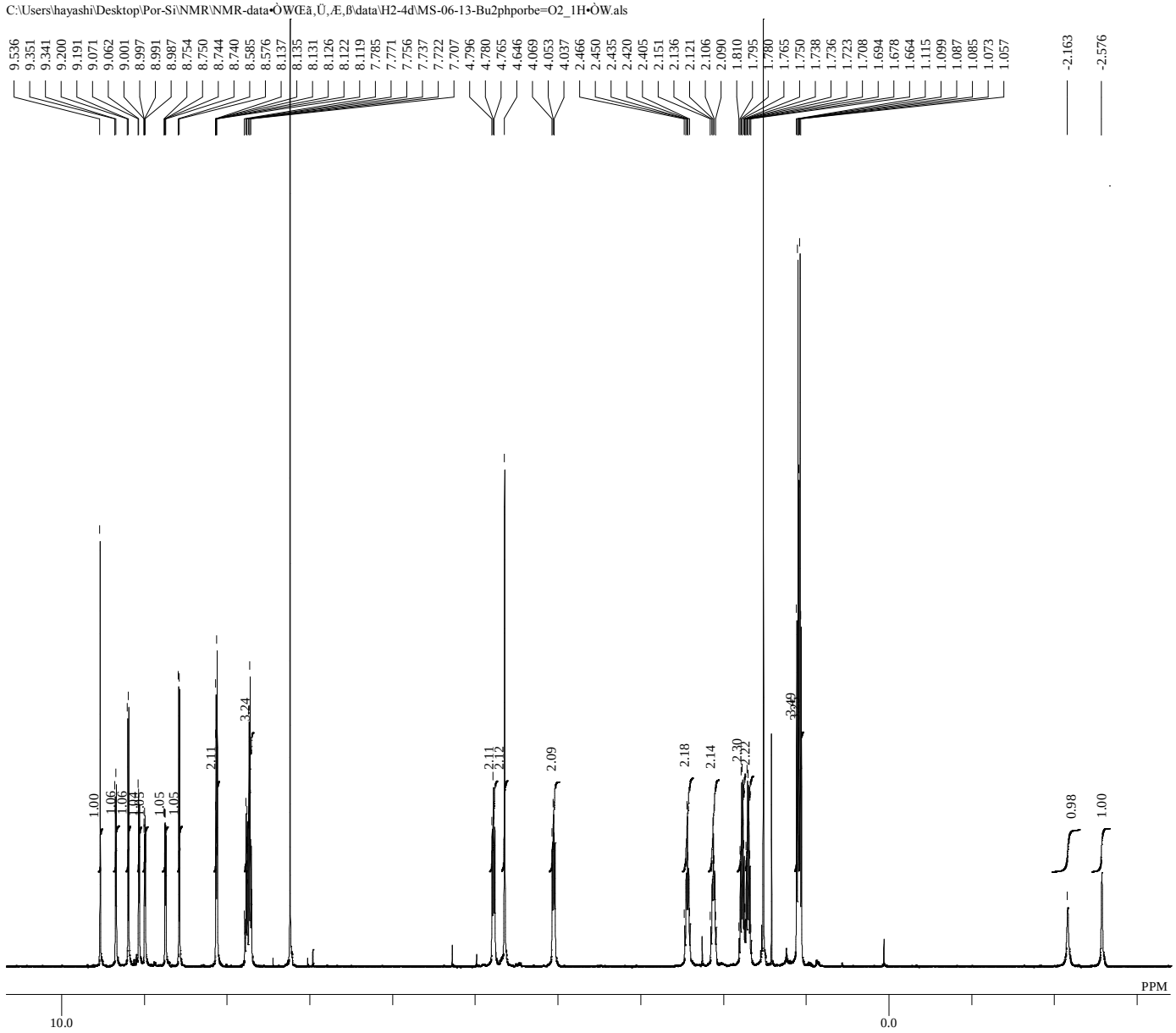
DATIM Fri Feb 06 03:44:15 2015
DFILE NS-22-20 TPPbe=O2BCM_•ÒWŒã.als
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 10000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.10 usec
IRN
CTEMP 40.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
204.55 (1H, s, C=O),
157.14 (1H, s, C-N),
154.56 (1H, s, C-N),
154.06 (1H, s, C-N),
149.63 (1H, s, C-N),
142.16 (1H, s, C-N),
141.40 (1H, s, C-N),
141.32 (1H, s, C-N),
140.24 (1H, s, C-N),
137.78 (1H, s, Ph(4)),
136.80 (2H, s, Ph(4)),
134.23 (2H, s, Ph(o)),
134.09 (2H, s, Ph(o)),
133.67 (1H, s, Beta),
133.64 (1H, s, Beta),
132.78 (2H, s, Ph(o)),
128.95 (1H, s, Beta),
128.31 (1H, s, Beta),
128.06 (1H, s, Ph(p)),
127.95 (1H, s, Ph(p)),
127.87 (1H, s, Ph(p)),
127.82 (2H, s, Ph(m)),
126.92 (2H, s, Ph(m)),
126.70 (2H, s, Ph(m)),
126.19 (1H, s, Beta),
125.73 (1H, s, Beta),
123.17 (1H, s, meso(4)),
122.44 (1H, s, meso(4)),
113.32 (1H, s, meso(4)),
95.44 (1H, s, meso(CH)),
45.49 (1H, s, CH2).



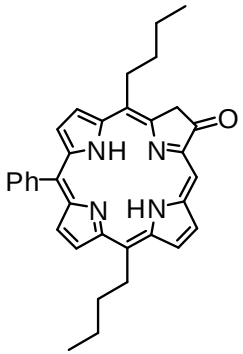
H_2-4a

Fig. S52 ^{1}H NMR spectrum of compound **H_2-4d** (in $CDCl_3$)



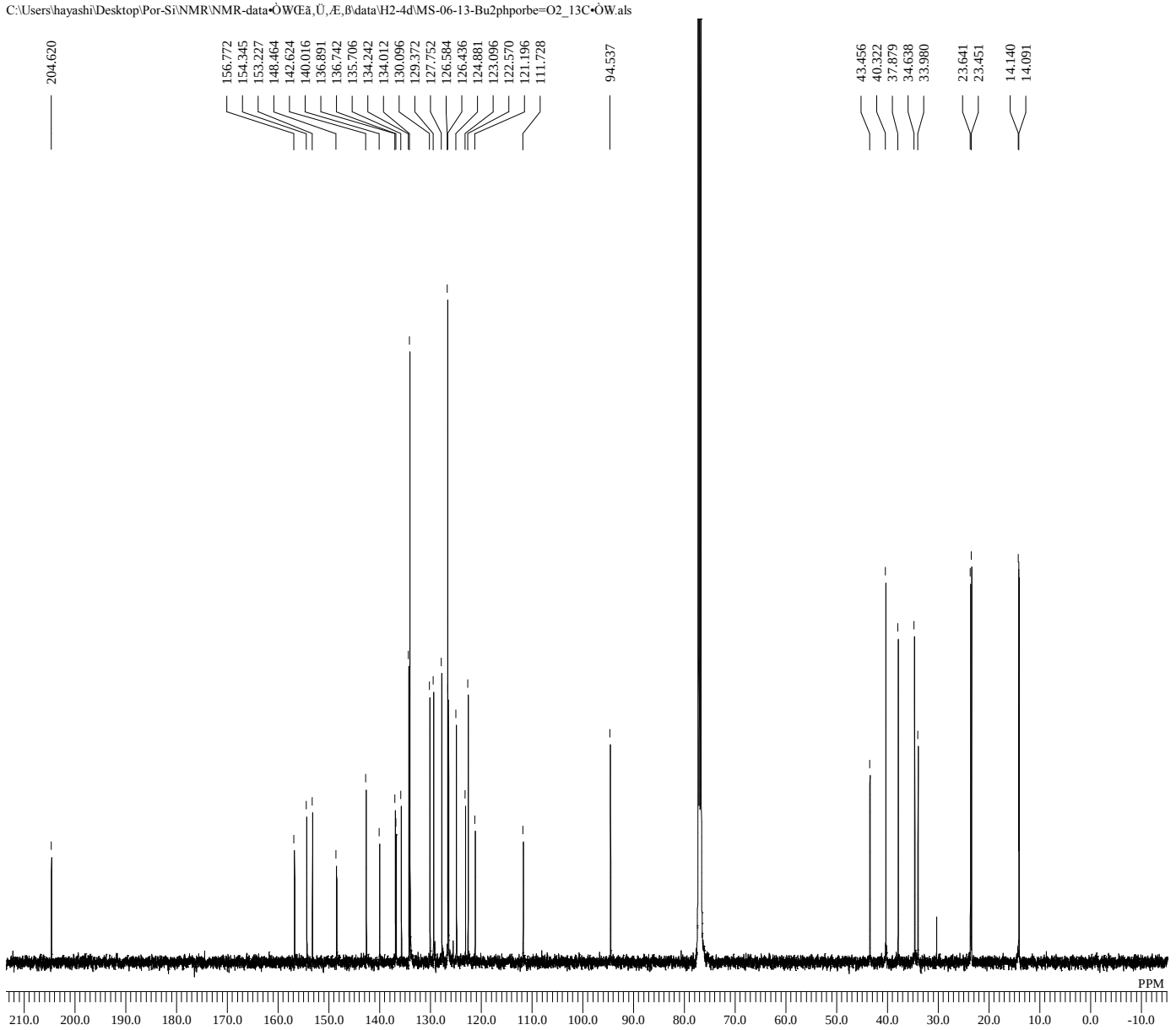
DATIM Wed Aug 31 09:07:17 2016
DFILE MS-06-13-Bu2phporbe=O2_1H•ÒW.als
OBNUC 1H
EXMOD non
OFR 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 8
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.00 usec
IRN
CTEMP 28.3 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.61 Hz
RGAIN 24

1H-NMR (CDCl3) δ :
9.54 (1H, s),
9.35 (1H, d, J = 4.6 Hz),
9.20 (1H, d, J = 4.6 Hz),
9.07 (1H, d, J = 4.6 Hz),
8.99 (1H, dd, J = 4.9, 1.8 Hz),
8.75 (1H, dd, J = 4.9, 1.8 Hz),
8.58 (1H, d, J = 4.6 Hz),
8.13−8.12 (2H, m),
7.77−7.72 (3H, m),
4.78 (2H, t, J = 7.9 Hz),
4.65 (2H, s),
4.05 (2H, t, J = 7.9 Hz),
2.47−2.40 (2H, m),
2.15−2.09 (2H, m),
1.79−1.76 (2H, m),
1.72−1.68 (2H, m),
1.10 (3H, t, J = 7.3 Hz),
1.07 (3H, t, J = 7.3 Hz),
−2.16 (1H, s),
−2.58 (1H, s).



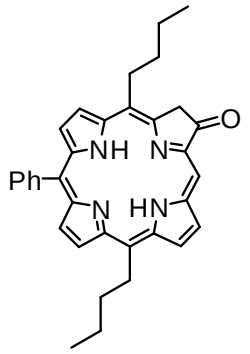
H_2-4d

Fig. S53 ^{13}C NMR spectrum of compound **H_2-4d** (in $CDCl_3$)



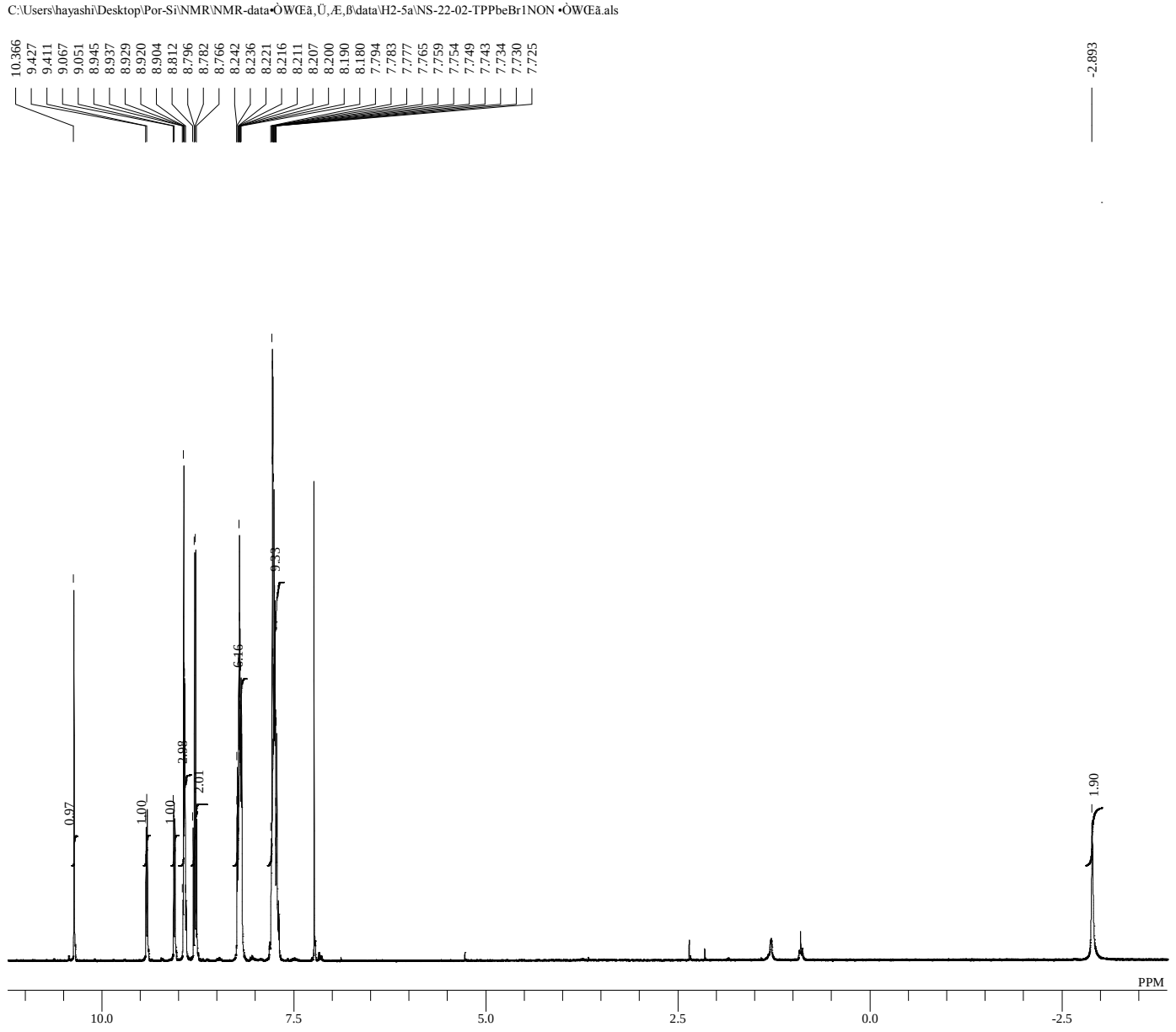
DATIM Thu Sep 1 22:46:20 2016
DFILE MS-06-13-Bu2phporbe=O2_13C•ÒW.als
OBNUC 13C
EXMOD bcm
OFR 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 45000
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 4.40 usec
IRN
CTEMP 31.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.81 Hz
RGAIN 28

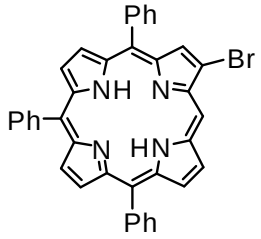
13C-NMR (CDCl3) δ :
204.62 (0H, s),
156.77 (0H, s),
154.35 (0H, s),
153.23 (0H, s),
148.46 (0H, s),
142.62 (0H, s),
140.02 (0H, s),
136.89 (0H, s),
136.74 (0H, s),
135.71 (0H, s),
134.24 (0H, s),
134.01 (2H, s),
130.10 (0H, s),
129.37 (0H, s),
127.75 (0H, s),
126.58 (2H, s),
126.44 (0H, s),
124.88 (0H, s),
123.10 (0H, s),
122.57 (0H, s),
121.20 (0H, s),
111.73 (0H, s),
94.54 (0H, s),
43.46 (0H, s),
40.32 (0H, s),
37.88 (0H, s),
34.64 (0H, s),
33.98 (0H, s),
23.64 (0H, s),
23.45 (0H, s),
14.14 (0H, s),
14.09 (0H, s).



H_2-4d

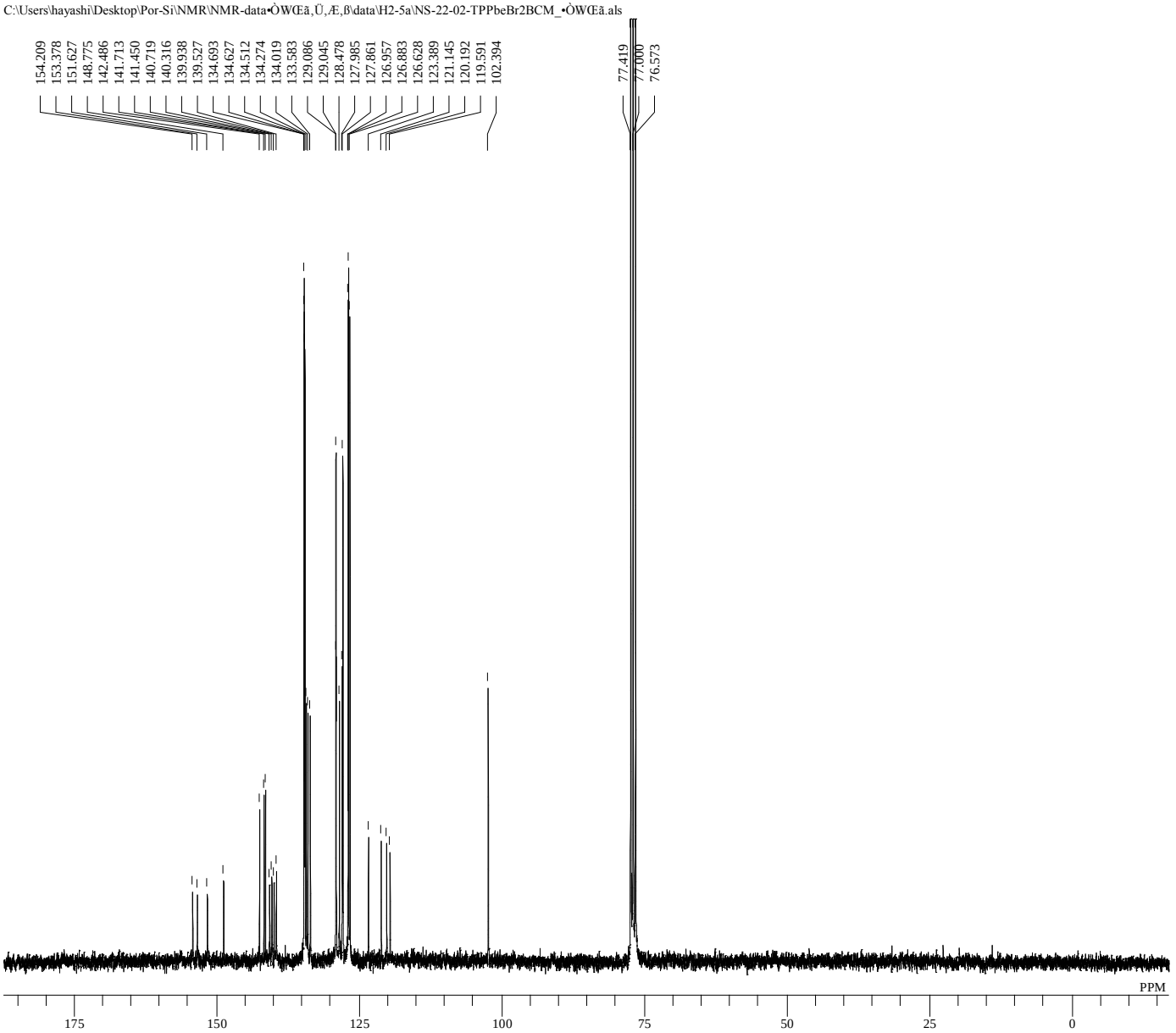
Fig. S54 ^{1}H NMR spectrum of compound **H_2-5a** (in $CDCl_3$)





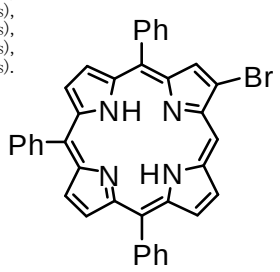
H_2-5a

Fig. S55 ^{13}C NMR spectrum of compound **H_2-5a** (in $CDCl_3$)



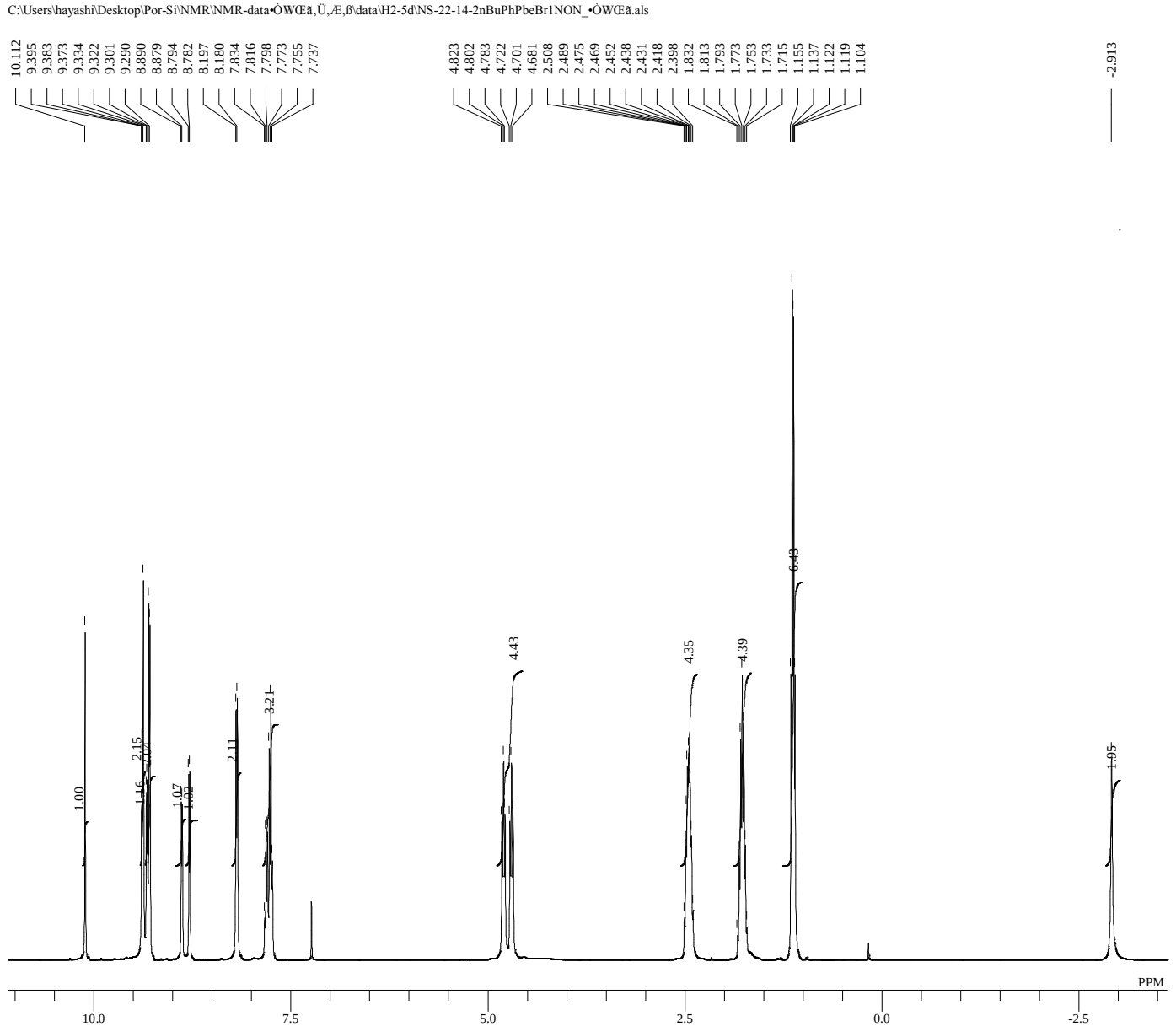
DATIM Wed Dec 17 07:46:40 2014
DFILE NS-22-02-TPPbeBr2BCM_•ÒWŒã.als
OBNUC 13C
EXMOD BCM
OFR 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 10000
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.30 usec
IRN
CTEMP 55.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
154.21 (1H, s),
153.38 (1H, s),
151.63 (1H, s),
148.77 (1H, s),
142.49 (1H, s),
141.71 (1H, s),
141.45 (1H, s),
140.72 (1H, s),
140.32 (1H, s),
139.94 (1H, s),
139.53 (1H, s),
134.69 (2H, s),
134.63 (2H, s),
134.51 (2H, s),
134.27 (1H, s),
134.02 (1H, s),
133.58 (1H, s),
129.09 (2H, s),
129.05 (1H, s),
128.48 (1H, s),
127.98 (1H, s),
127.86 (2H, s),
126.96 (2H, s),
126.88 (2H, s),
126.63 (2H, s),
123.39 (1H, s),
121.15 (1H, s),
120.19 (1H, s),
119.59 (1H, s),
102.39 (1H, s).



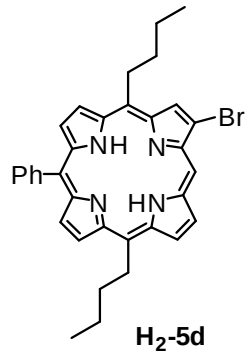
H_2-5a

Fig. S56 ^{1}H NMR spectrum of compound **H_2-5d** (in $CDCl_3$)



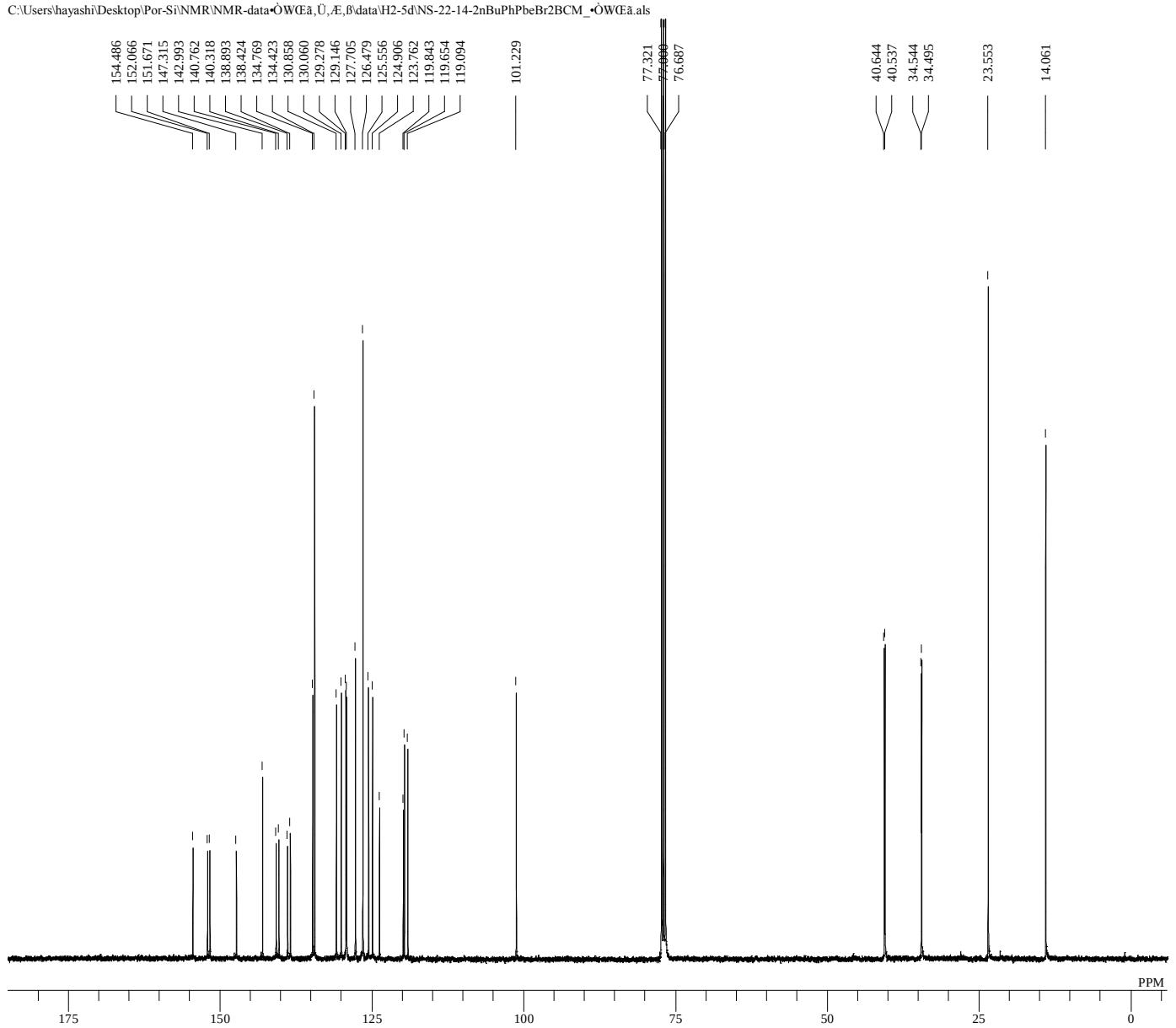
DATIM Fri Jan 23 20:47:27 2015
DFILE NS-22-14-2nBuPhPbeBr1NON_•ÒWŒã.als
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 16
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 5.80 usec
IRN
CTEMP 55.1 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 1.20 Hz
RGAIN 15

1H-NMR (CDCl3) δ :
10.11 (1H, s),
9.39 (1H, d, J = 4.9 Hz),
9.38 (1H, d, J = 4.9 Hz),
9.33 (1H, d, J = 4.9 Hz),
9.30 (2H, d, J = 4.9 Hz),
8.88 (1H, d, J = 4.9 Hz),
8.79 (1H, d, J = 4.9 Hz),
8.19 (2H, d, J = 6.8 Hz),
7.82 (1H, t, J = 7.3 Hz),
7.75 (2H, dd, J = 7.3, 6.8 Hz),
4.80 (2H, t, J = 8.0 Hz),
4.70 (2H, t, J = 8.0 Hz),
2.47 (2H, tt, J = 8.0, 7.7 Hz),
2.44 (2H, tt, J = 8.0, 7.7 Hz),
1.78 (2H, tq, J = 7.7, 7.3 Hz),
1.76 (2H, tq, J = 7.7, 7.3 Hz),
1.14 (3H, t, J = 7.3 Hz),
1.12 (3H, t, J = 7.3 Hz),
−2.91 (2H, br s).



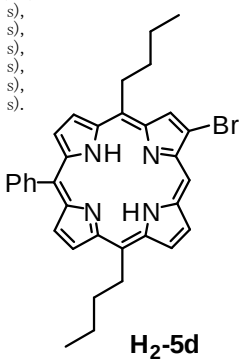
H_2-5d

Fig. S57 ^{13}C NMR spectrum of compound **H_2-5d** (in $CDCl_3$)



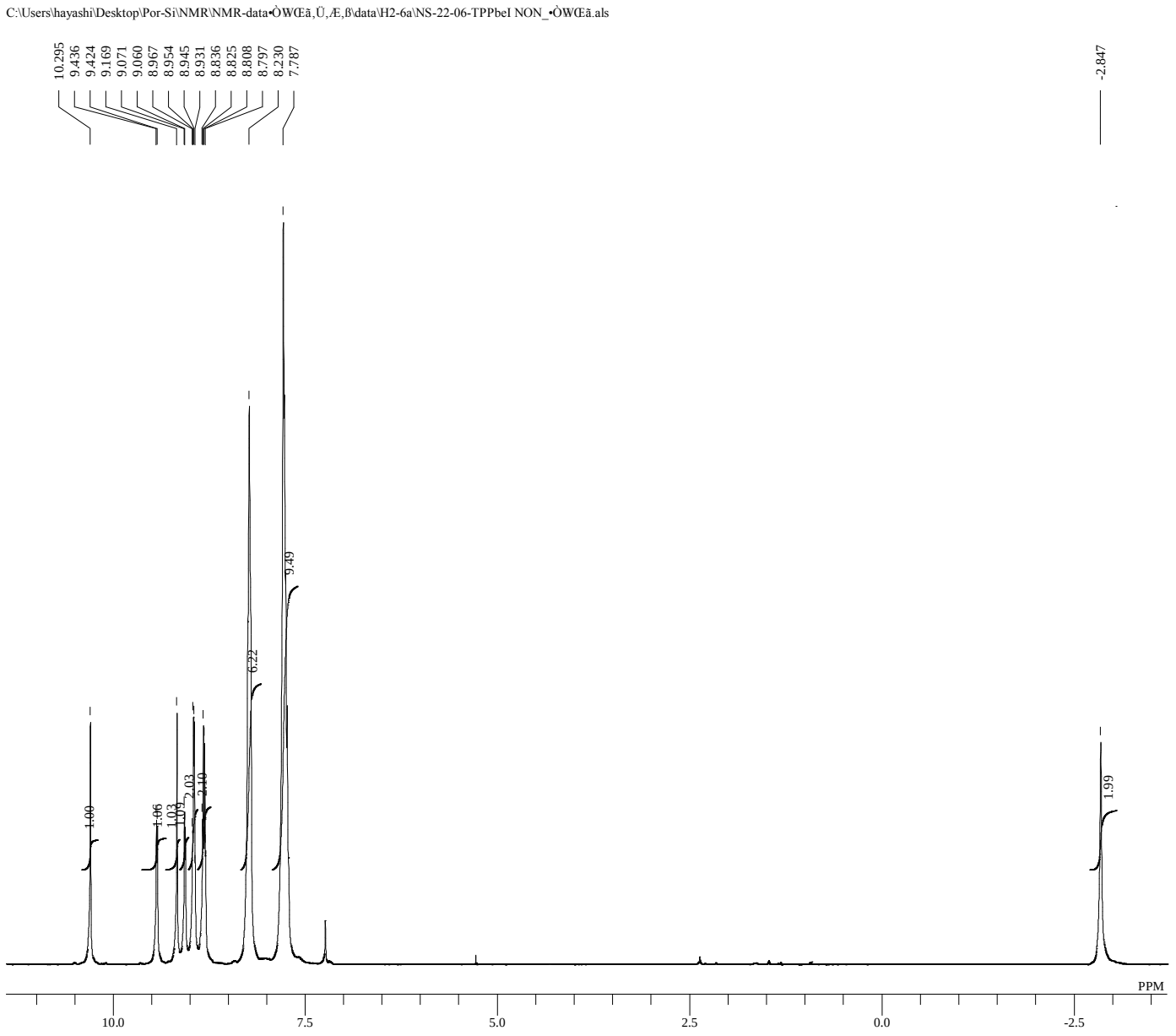
DATIM Sat Jan 24 08:28:01 2015
DFILE NS-22-14-2nBuPhPbeBr2BCM_•ÒWŒã.als
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 14000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.00 usec
IRN
CTEMP 55.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
154.49 (1H, s),
152.07 (1H, s),
151.67 (1H, s),
147.32 (1H, s),
142.99 (1H, s),
140.76 (1H, s),
140.32 (1H, s),
138.89 (1H, s),
138.42 (1H, s),
134.77 (1H, s),
134.42 (2H, s),
130.86 (1H, s),
130.06 (1H, s),
129.28 (1H, s),
129.15 (1H, s),
127.71 (1H, s),
126.48 (1H, s),
125.56 (2H, s),
124.91 (1H, s),
123.76 (1H, s),
119.84 (1H, s),
119.65 (1H, s),
119.09 (1H, s),
101.23 (1H, s),
40.64 (1H, s),
40.54 (1H, s),
34.54 (1H, s),
34.49 (1H, s),
23.55 (2H, s),
14.06 (2H, s).



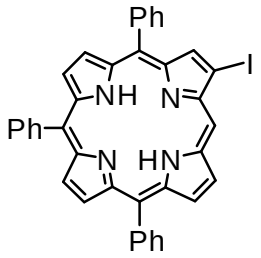
H_2-5d

Fig. S58 ^{1}H NMR spectrum of compound **H_2-6a** (in $CDCl_3$)



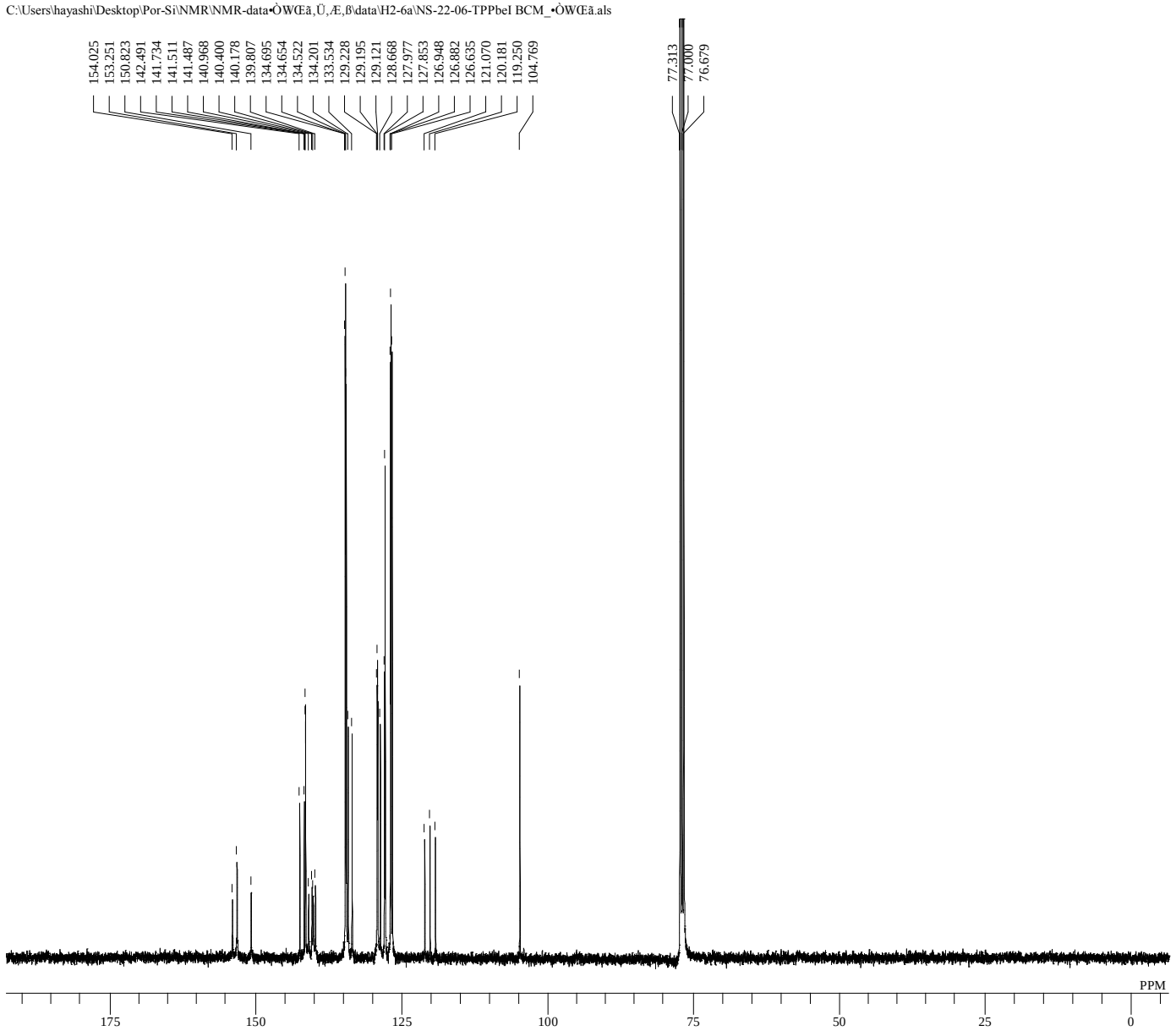
DATIM Wed Jan 21 05:49:11 2015
DFILE NS-22-06-TPPbeI NON_•ÒWŒã.als
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 5.80 usec
IRN
CTEMP 58.2 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 1.20 Hz
RGAIN 17

1H-NMR (CDCl3) δ :
10.30 (1H, s),
9.43 (1H, d, J = 4.9 Hz),
9.17 (1H, s),
9.07 (1H, d, J = 4.9 Hz),
8.96 (1H, d, J = 4.9 Hz),
8.94 (1H, d, J = 4.9 Hz),
8.83 (1H, d, J = 4.9 Hz),
8.80 (1H, d, J = 4.9 Hz),
8.33-8.14 (6H, m),
7.88-7.66 (9H, m),
-2.85 (2H, br s).



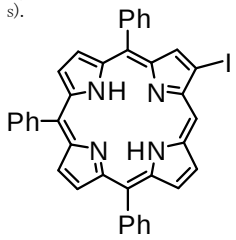
H_2-6a

Fig. S59 ^{13}C NMR spectrum of compound **H_2-6a** (in $CDCl_3$)



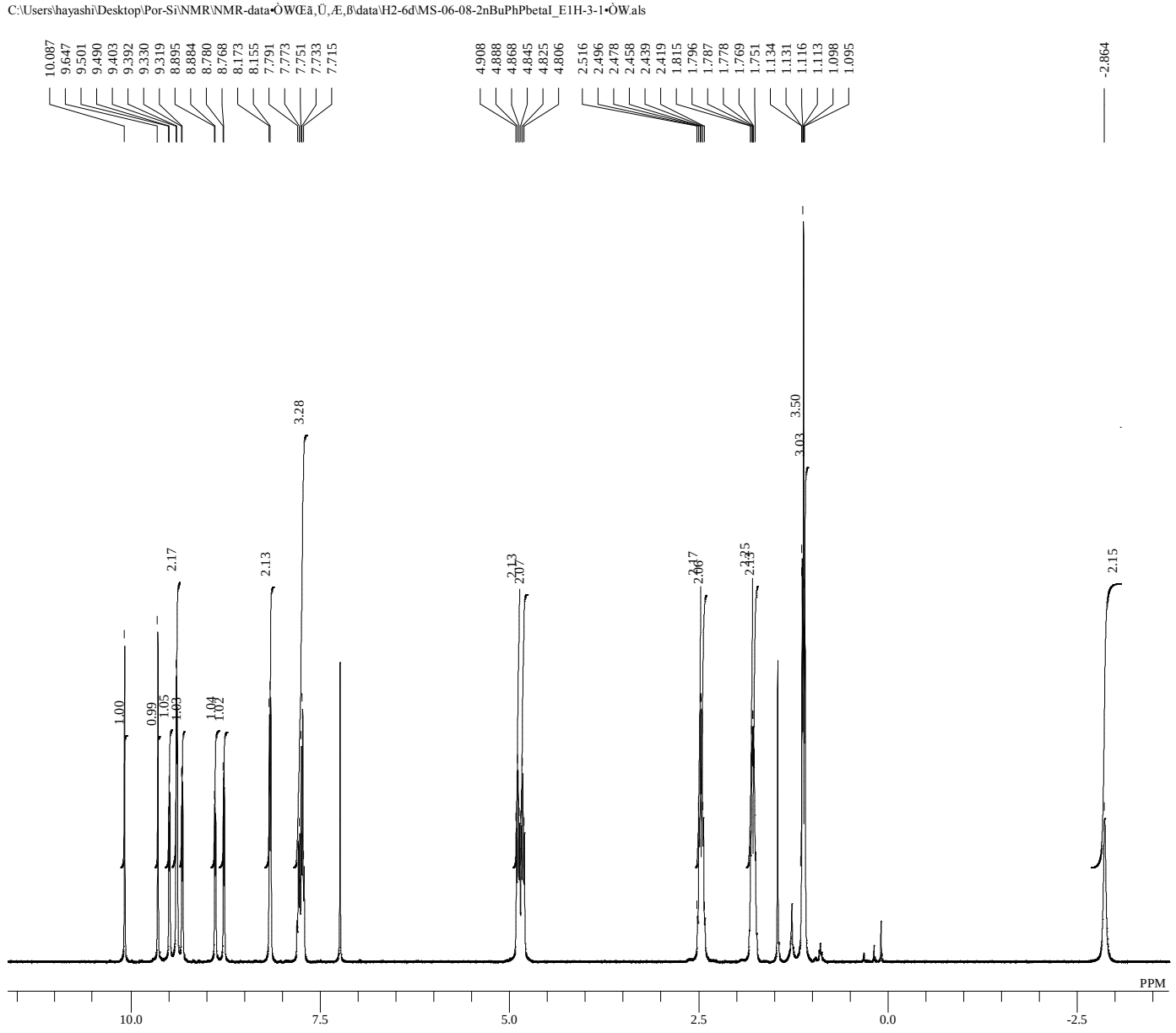
DATIM Wed Jan 21 05:47:41 2015
DFILE NS-22-06-TPPbeI BCM_•ÒWŒã.als
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 12000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.00 usec
IRN
CTEMP 58.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

13C-NMR (CDCl3) δ :
154.03 (1H, s),
153.25 (2H, s),
150.82 (1H, s),
142.49 (1H, s),
141.73 (1H, s),
141.51 (2H, s),
141.49 (1H, s),
140.97 (1H, s),
140.40 (1H, s),
140.18 (1H, s),
139.81 (1H, s),
134.69 (2H, s),
134.65 (2H, s),
134.52 (2H, s),
134.20 (1H, s),
133.53 (1H, s),
129.23 (1H, s),
129.20 (1H, s),
129.12 (1H, s),
128.67 (1H, s),
127.98 (1H, s),
127.85 (2H, s),
126.95 (2H, s),
126.88 (2H, s),
126.63 (2H, s),
121.07 (1H, s),
120.18 (1H, s),
119.25 (1H, s),
104.77 (1H, s).



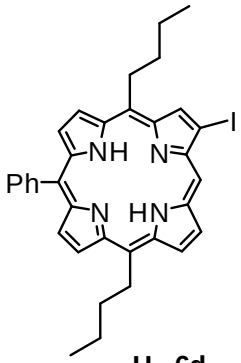
H_2-6a

Fig. S60 ^{1}H NMR spectrum of compound **H_2-6d** (in $CDCl_3$)



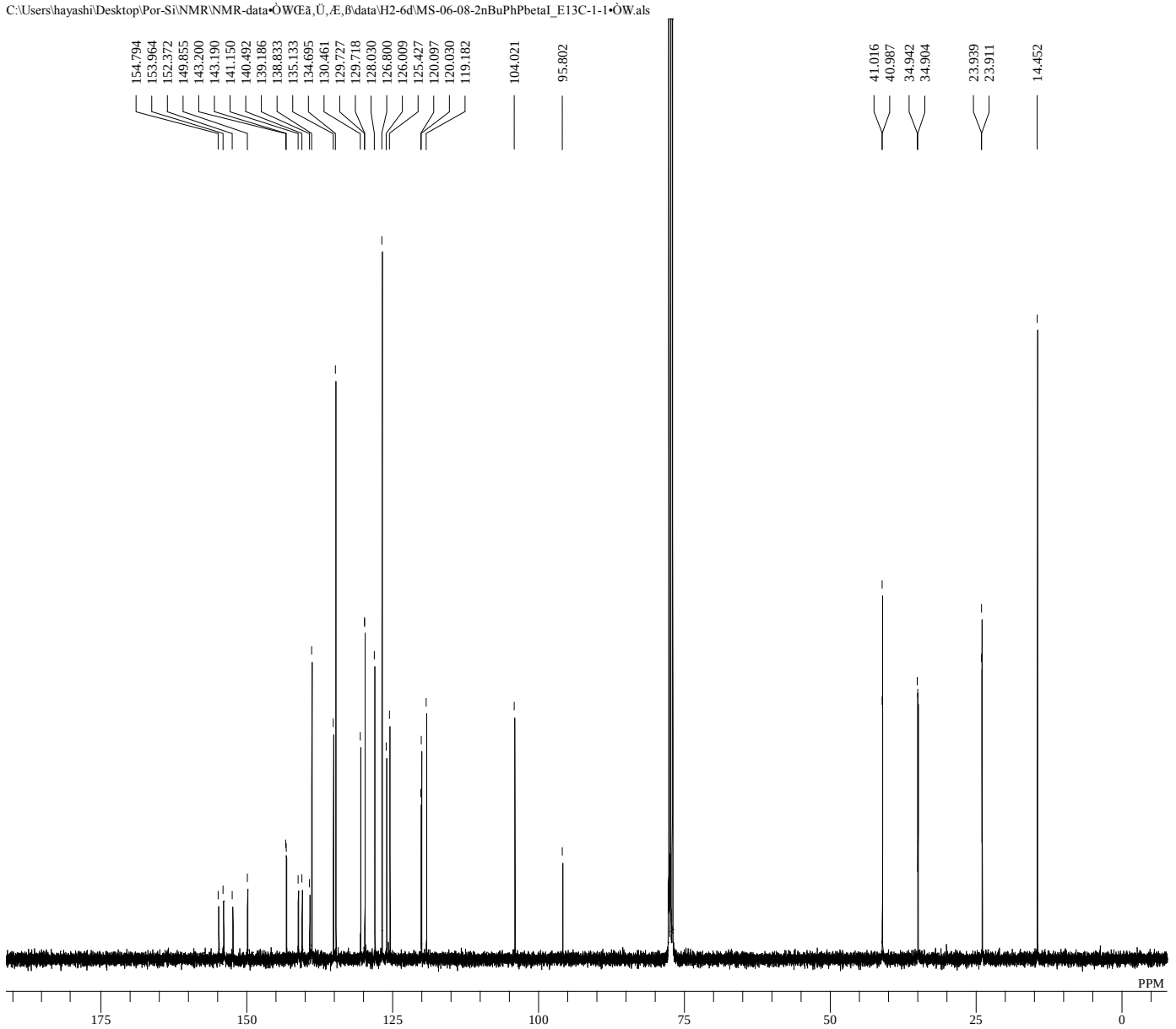
DATIM 03-09-2016 22:01:52
DFILE MS-06-08-2nBuPhPbetaI_E1H-3-1•ÒW.als
OBNUC 1H
EXMOD single_pulse.jxp
OFR 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 26214
FREQU 8000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 2.0000 sec
PW1 3.05 usec
IRN
CTEMP 40.0 c
SLVNT CDCL3
EXREF 7.24 ppm
BF -0.10 Hz
RGAIN 40

1H-NMR (CDCl3) δ :
10.09 (1H, s),
9.65 (1H, s),
9.50 (1H, d, J = 4.6 Hz),
9.40 (2H, d, J = 4.6 Hz),
9.32 (1H, d, J = 4.6 Hz),
8.89 (1H, d, J = 4.6 Hz),
8.77 (1H, d, J = 4.6 Hz),
8.16 (2H, d, J = 7.0 Hz),
7.79-7.71 (3H, m),
4.89 (2H, t, J = 7.9 Hz),
4.83 (2H, t, J = 7.9 Hz),
2.52-2.44 (2H, m),
2.50-2.42 (2H, m),
1.81-1.77 (2H, m),
1.80-1.75 (2H, m),
1.12 (3H, t, J = 7.2 Hz),
1.11 (3H, t, J = 7.2 Hz),
-2.86 (2H, s).



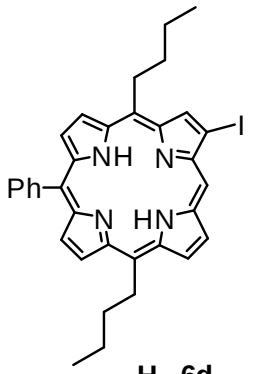
H_2-6d

Fig. S61 ^{13}C NMR spectrum of compound **H_2-6d** (in $CDCl_3$)



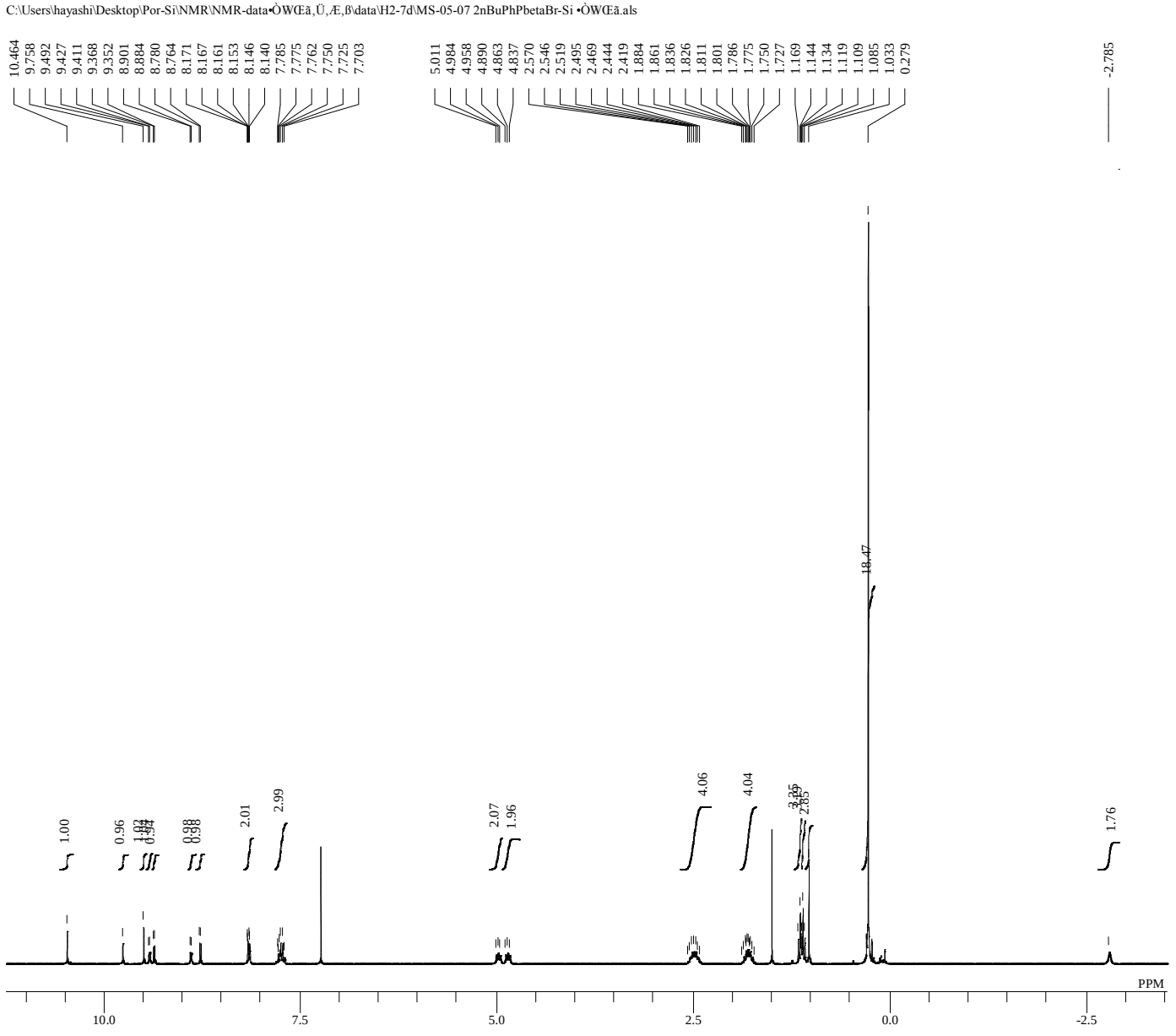
DATIM 03-09-2016 22:03:47
DFILE MS-06-08-2nBuPhPbetaI_E13C-1-1•ÒW.als
OBNUC 13C
EXMOD single_pulse_dec
OFR 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 42000
ACQTM 1.0433 sec
PD 1.7000 sec
PW1 3.53 usec
IRN
CTEMP 40.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF -0.10 Hz
RGAIN 60

13C-NMR (CDCl3) δ :
154.79 (0H, s),
153.96 (0H, s),
152.37 (0H, s),
149.85 (0H, s),
143.20 (0H, s),
143.19 (0H, s),
141.15 (0H, s),
140.49 (0H, s),
139.19 (0H, s),
138.83 (0H, s),
135.13 (0H, s),
134.69 (2H, s),
130.46 (0H, s),
129.73 (0H, s),
129.72 (0H, s),
128.03 (0H, s),
126.80 (2H, s),
126.01 (0H, s),
125.43 (0H, s),
120.10 (0H, s),
120.03 (0H, s),
119.18 (0H, s),
104.02 (0H, s),
95.80 (0H, s),
41.02 (0H, s),
40.99 (0H, s),
34.94 (0H, s),
34.90 (0H, s),
23.94 (0H, s),
23.91 (0H, s),
14.45 (2H, s).



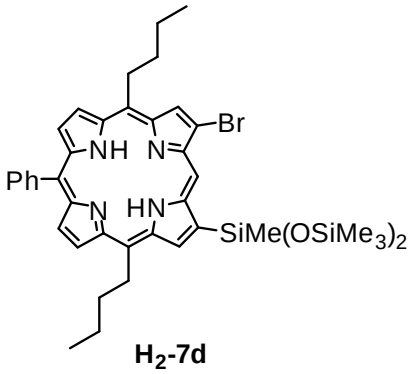
H_2-6d

Fig. S62 ^{1}H NMR spectrum of compound **H_2-7d** (in $CDCl_3$)



DATIM Tue Jul 19 15:14:53 2016
DFILE MS-05-07 2nBuPhPbetaBr-Si •ÒWŒã.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.60 usec
IRN
CTEMP 26.5 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.09 Hz
RGAIN 20

1H-NMR (CDCl3) δ :
10.46 (1H, s),
9.76 (1H, s),
9.49 (1H, s),
9.42 (1H, d, J = 4.8 Hz),
9.36 (1H, d, J = 4.8 Hz),
8.89 (1H, d, J = 4.9 Hz),
8.77 (1H, d, J = 4.8 Hz),
8.17−8.15 (2H, m),
7.74 (3H, dd, J = 14.4, 5.2 Hz),
4.98 (2H, t, J = 8.0 Hz),
4.86 (2H, t, J = 7.9 Hz),
2.57−2.47 (2H, m),
2.52−2.42 (2H, m),
1.88−1.79 (2H, m),
1.83−1.73 (2H, m),
1.14 (3H, t, J = 7.4 Hz),
1.11 (3H, t, J = 7.3 Hz),
1.03 (3H, s),
0.28 (18H, s),
−2.79 (2H, s).



H_2-7d

Fig. S63 ^{13}C NMR spectrum of compound **H_2-7d** (in $CDCl_3$)

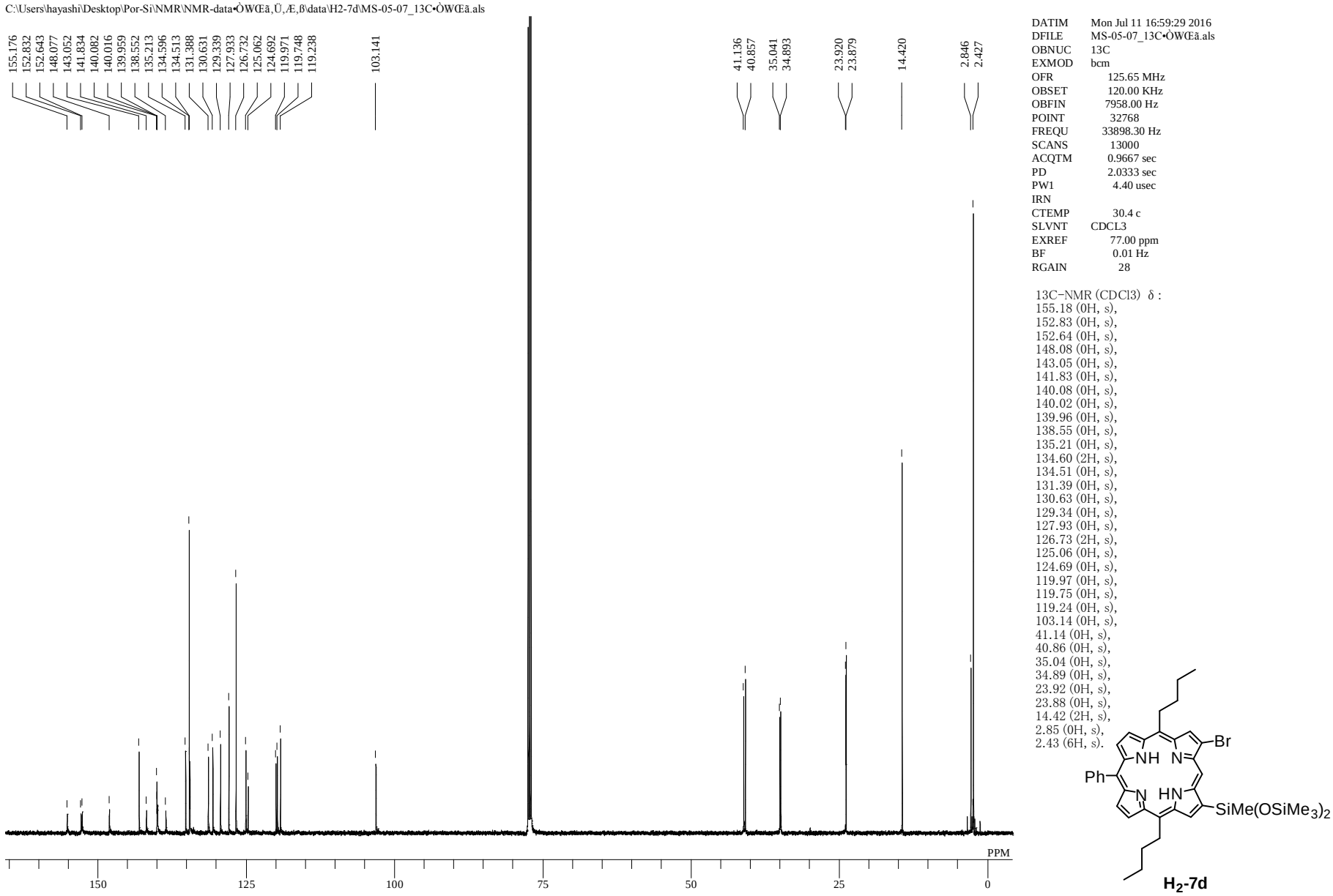
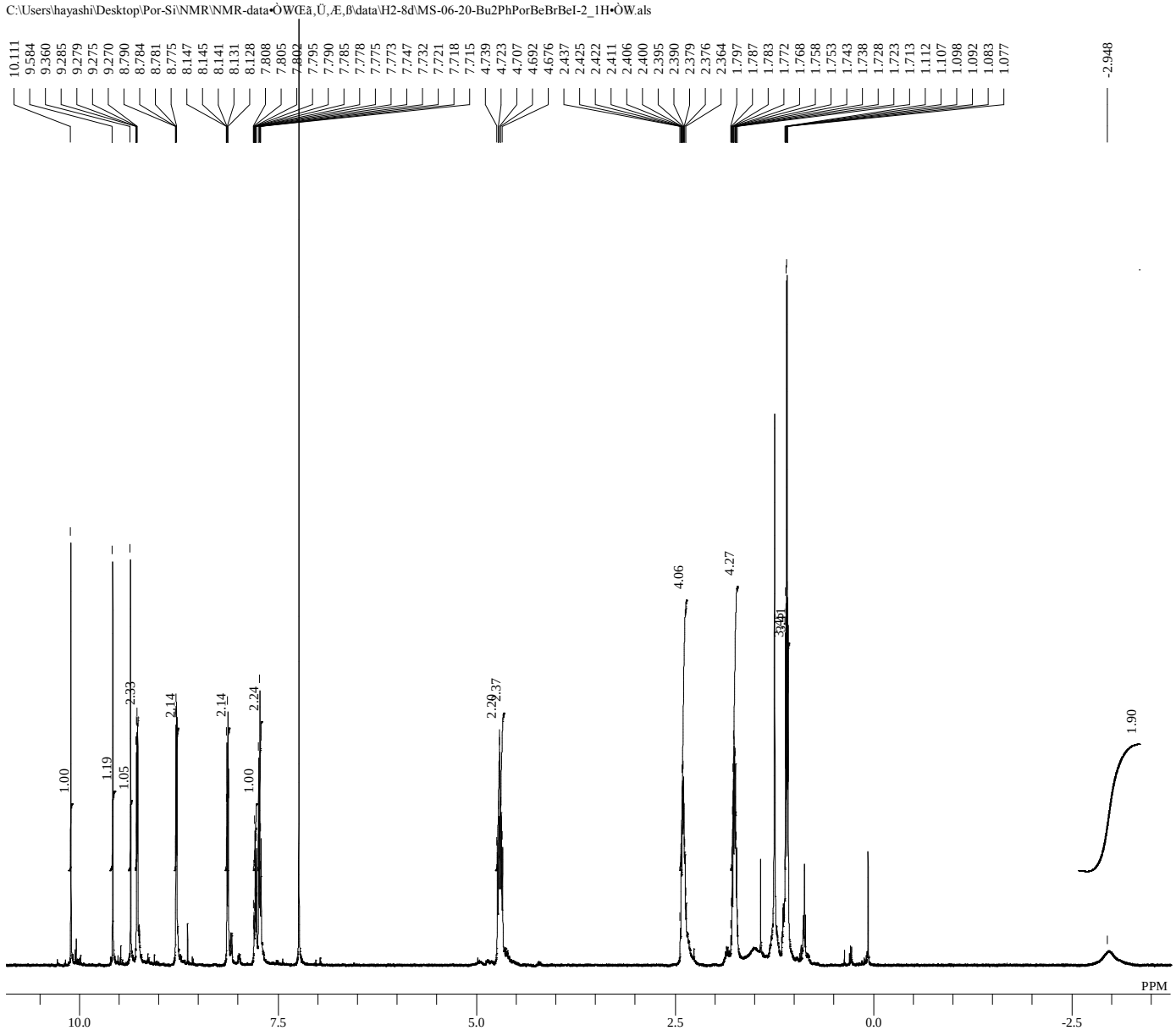
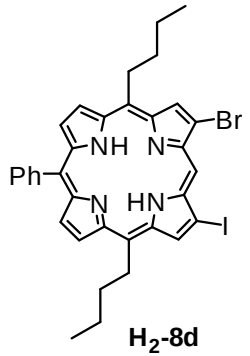


Fig. S64 ^{1}H NMR spectrum of compound **H_2-8d** (in $CDCl_3$)



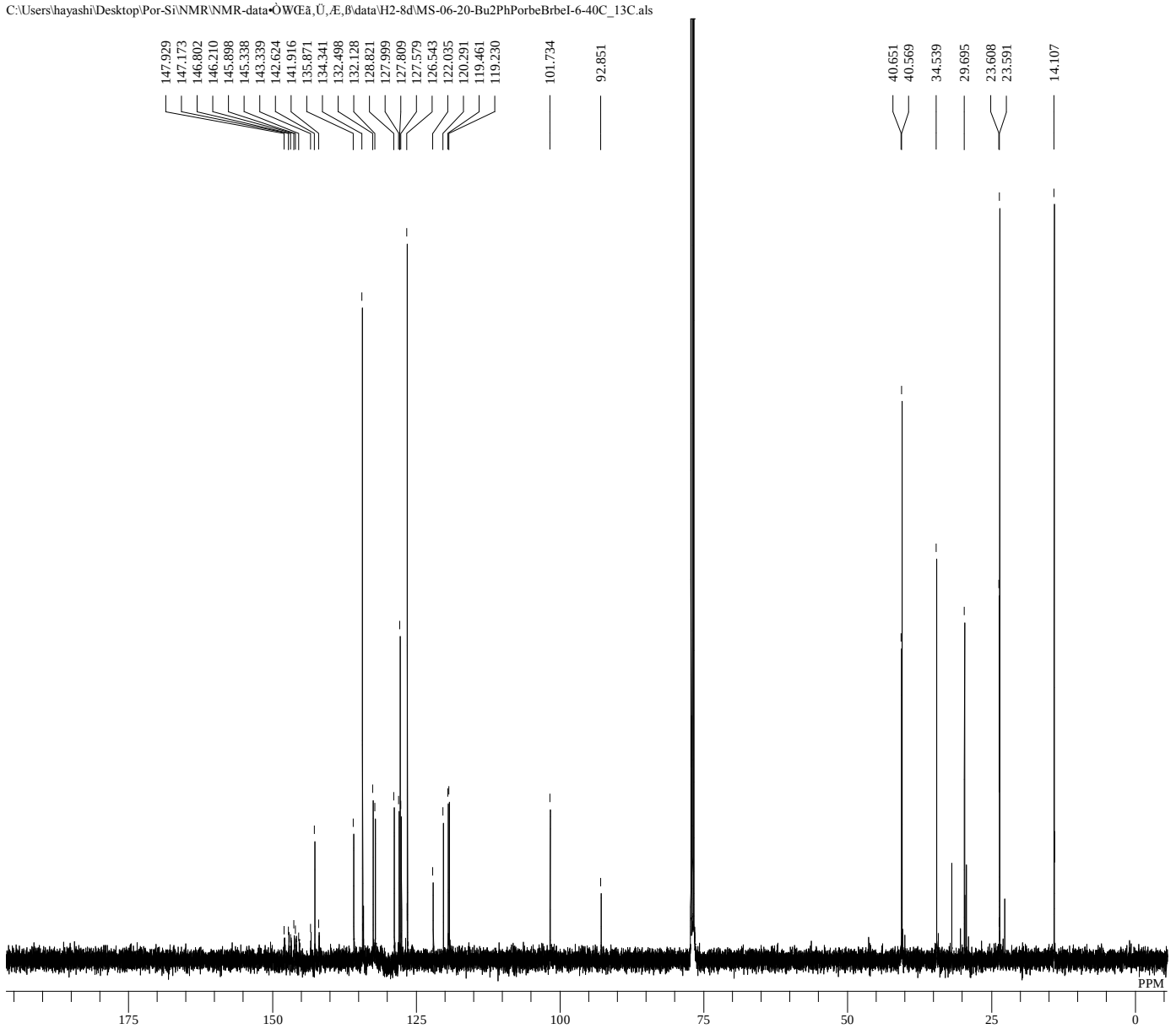
DATIM Sat Sep 3 18:45:36 2016
DFILE MS-06-20-Bu2PhPorBeBrBeI-2_1H•ÒW.als
OBNUC 1H
EXMOD non
OFR 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 8
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.00 usec
IRN
CTEMP 29.3 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.01 Hz
RGAIN 23

1H-NMR (CDCl3) δ :
10.11 (1H, s),
9.58 (1H, s),
9.36 (1H, s),
9.28 (2H, d, J = 4.6 Hz),
9.27 (2H, d, J = 4.6 Hz),
8.79 (2H, d, J = 4.6 Hz),
8.78 (2H, d, J = 4.6 Hz),
8.15−8.13 (2H, m),
7.79 (1H, tt, J = 7.5, 1.7 Hz),
7.75−7.72 (2H, m),
4.72 (2H, t, J = 7.9 Hz),
4.69 (2H, t, J = 7.9 Hz),
2.43−2.40 (2H, m),
2.40−2.37 (2H, m),
1.78−1.76 (2H, m),
1.75−1.73 (2H, m),
1.10 (3H, t, J = 7.3 Hz),
1.09 (3H, t, J = 7.3 Hz),
−2.95 (2H, s).



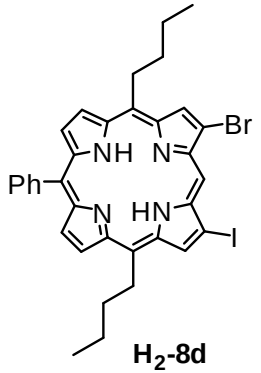
H_2-8d

Fig. S65 ^{13}C NMR spectrum of compound **H_2-8d** (in $CDCl_3$)



DATIM Sun Sep 4 20:08:38 2016
DFILE MS-06-20-Bu2PhPorbeBrbeI-6-40C_13C.als
OBNUC 13C
EXMOD bcm
OFR 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 24000
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 4.40 usec
IRN
CTEMP 40.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 28

13C-NMR (CDCl3) δ :
147.93 (0H, s),
147.17 (0H, s),
146.80 (0H, s),
146.21 (0H, s),
145.90 (0H, s),
145.34 (0H, s),
143.34 (0H, s),
142.62 (0H, s),
141.92 (0H, s),
135.87 (0H, s),
134.34 (2H, s),
132.50 (0H, s),
132.13 (0H, s),
128.82 (0H, s),
128.00 (0H, s),
127.81 (0H, s),
127.58 (0H, s),
126.54 (2H, s),
122.04 (0H, s),
120.29 (0H, s),
119.46 (0H, s),
119.23 (0H, s),
101.73 (0H, s),
92.85 (0H, s),
40.65 (0H, s),
40.57 (0H, s),
34.54 (0H, s),
29.69 (0H, s),
23.61 (0H, s),
23.59 (0H, s),
14.11 (2H, s).



H_2-8d