Supporting Information

C2-Selective Silylation of Pyridines by a Rhodium–Aluminum Complex

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General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere or in a glove box under a nitrogen atmosphere. Medium pressure liquid chromatography (MPLC) was performed using Kanto Chemical silica gel 60 (spherical, 40–50 μm), Wakogel® 50NH2, or activated basic alumina (purchased from FUJIFILM Wako Pure Chemical Corporation). Analytical thin layer chromatography (TLC) was performed on Merck TLC silica gel 60 F_{254} (0.25 mm) plate, NH2 Silica Gel 60 F_{254} Plate-Wako (0.25 mm), or Merck TLC Aluminum oxide 60 F_{254} (0.25 mm) basic plate. Visualization was accomplished with UV light (254 nm).

Apparatus. Proton, carbon, and phosphorus nuclear magnetic resonance spectra (^{1}H, ^{13}C, and ^{31}P NMR) were recorded on a JEOL ECS-400 (^{1}H NMR, 400MHz; ^{13}C NMR 101 MHz; ^{31}P NMR 162 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm, C_6D_6 at 7.16 ppm, $(CD_3)_2SO$ at 2.50 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm, C_6D_6 at 128.0 ppm, $(CD_3)_2SO$ at 39.5 ppm). NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet, vt = virtual triplet), coupling constants (Hz), and integration. High-resolution mass spectra were obtained with Thermo Fisher Scientific MS: Exactive Plus HPLC: UltiMate 3000 (ESI) and with Bruker Daltonics micrOTOF II (CSI). Medium pressure liquid chromatography (MPLC) was performed with a Yamazen EPLC-W-Prep 2XY. GC analysis was performed on a Shimadzu GC-2014 equipped with a BP1 column (SGE Analytical Science, 0.25 mm x 30 m, pressure = 149.0 kPa, detector = FID, 290 °C) with helium gas as a carrier. Elemental analyses were performed on a MICRO CORDER MT-5 (YANACO CO.,Ltd.).

Chemicals. Unless otherwise noted, commercially available chemicals were distilled over CaH_2 and degassed before use. When commercially available chemicals are solids, the chemicals are used without purification. 2-Norbornene was used after distillation over CaH_2. 4-Methyltetrahydropyran (MTHP) was provided by KURARAY and used after distillation over NaH and CaH_2. Pentane (Super Dehydrated) was purchased from FUJIFILM Wako Pure Chemical Corporation. Rh–Al complexes **3, 5,** and **6** were prepared according to literature procedures.[1,2] Anhydrous hexane, toluene, and THF were purchased from Kanto Chemical and purified by passage through activated alumina under positive argon pressure as described by Grubbs *et al*.[3] All other commercially available reagents were purchased from common sources (*e.g.* Tokyo Chemical Industry Co., Ltd., FUJIFILM Wako Pure Chemical Corporation, Sigma-Aldrich, Alfa-Aesar, Nacalai Tesque INC. etc.).

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[1] I. Fujii, K. Semba, Q.-Z. Li, S. Sakaki, Y. Nakao, *J. Am. Chem. Soc.* **2020**, *142*, 11647–11652.
[2] N. Hara, T. Saito, K. Semba, N. Kuriakose, H. Zheng, S. Sakaki, Y. Nakao, *J. Am. Chem. Soc.* **2018**, *140*, 7070–7073.
[3] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518–1520.

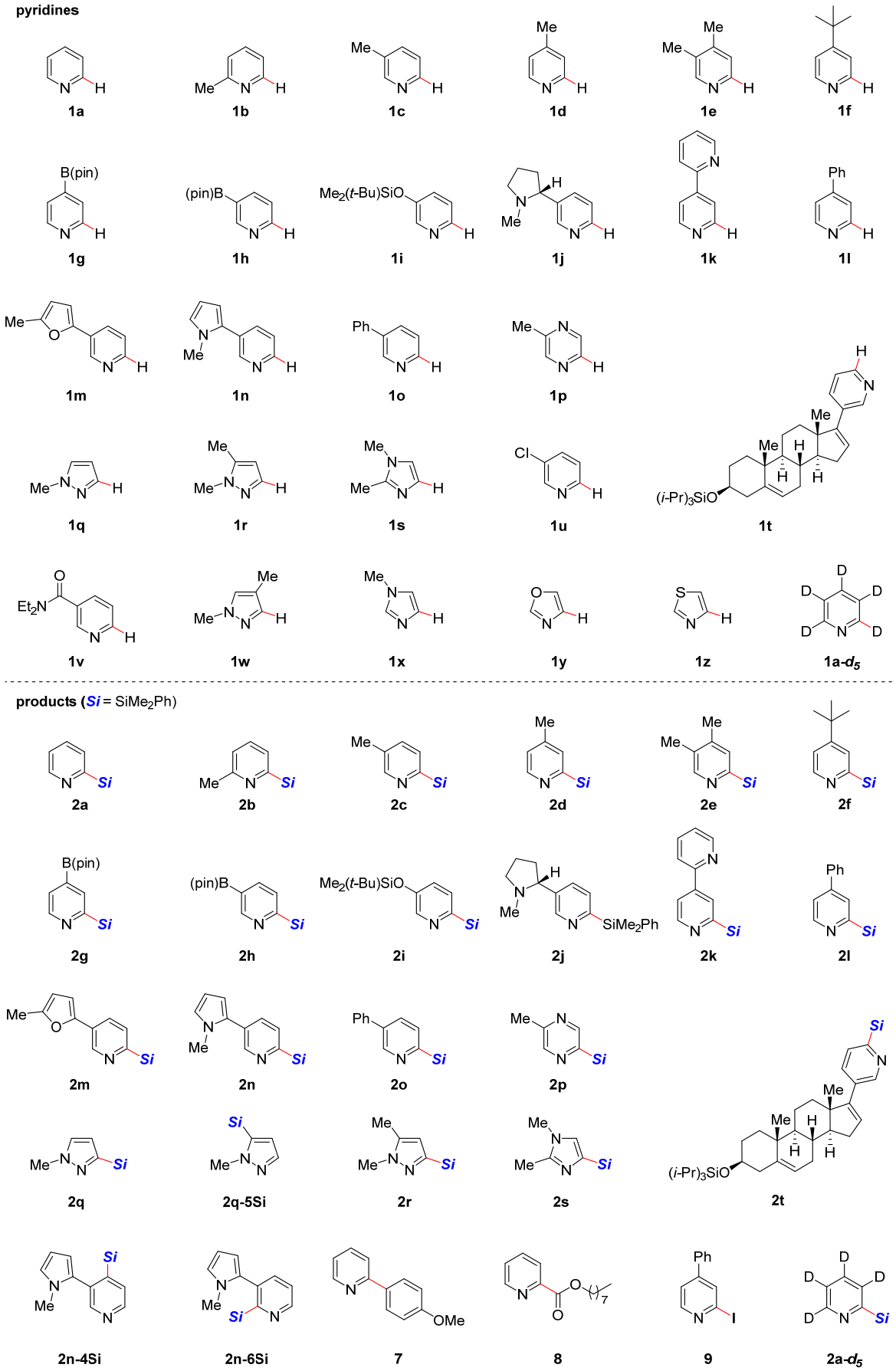
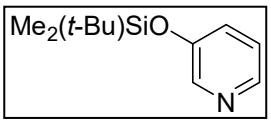
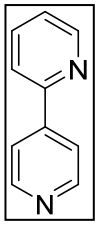


Figure S1. A list of pyridines in this study

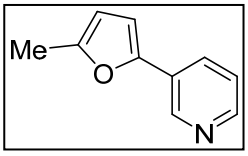
Synthesis of Substrates.



3-(*tert*-butyldimethylsilyloxy)pyridine (1i): To a solution of 3-hydroxypyridine (2.9 g, 30 mmol) in DMF (25 mL), imidazole (4.1 g, 60 mmol), and chloro(1,1-dimethylethyl)dimethylsilane (5.4 g, 36 mmol) were added. The resulting mixture was stirred at room temperature for 7 h. The reaction mixture was poured into water (50 mL) and extracted with EtOAc (100 mL x 3). The combined organic layers were washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by MPLC (Kanto Chemical silica gel 60, *n*-hexane/EtOAc = 100:0 to 90:10) and distillation (120 ºC, 8.0 Torr) to give the title compound (4.0 g, 19 mmol, 64%) as a colorless oil. R_f 0.25 [*n*-hexane/EtOAc (90:10)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23–8.17 (m, 2H), 7.16–7.08 (m, 2H), 0.96 (s, 9H), 0.19 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 152.1, 142.6, 142.5, 126.7, 123.8, 25.5, 18.1, –4.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{11}H_{20}NOSi$ 210.1309; Found, 210.1303.



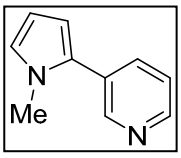
2,4'-bipyridine (1k): The mixture of 2-bromopyridine (0.78 mL, 8.0 mmol), 4-pyridylboronic acid (1.1 g, 8.8 mmol), $Pd(PPh_3)_4$ (0.46 g, 0.40 mmol), and Cs_2CO_3 (5.2 g, 16 mmol) were dissolved in a mixed degassed solvent composed of 1,4-dioxane/H_2O = 4/1 (30 mL) and stirred at 80 °C for 3 days. The reaction mixture was poured into water (20 mL) and extracted with EtOAc (15 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by MPLC (Kanto Chemical silica gel 60, *n*-hexane/EtOAc = 50:50 to 29:71 to 10:90) and the obtained compound was recrystallized by layering *n*-hexane on a concentrated methyl *tert*-butyl ether solution to afford the title compound (150 mg, 0.96 mmol, 12%) as a white powder. R_f 0.42 [*n*-hexane/EtOAc (50:50)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77–8.68 (m, 3H), 7.89 (d, *J* = 4.6 Hz, 2H), 7.85–7.77 (m, 2H), 7.38–7.30 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.6, 150.4, 150.1, 146.4, 137.1, 123.8, 121.0, 120.9. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[4]



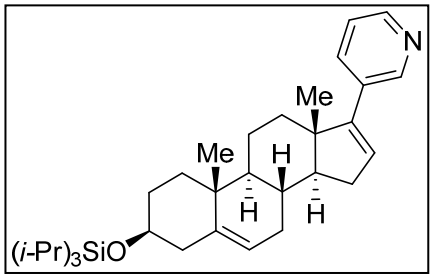
3-(5-methylfuran-2-yl)pyridine (1m): To a solution of 2-methylfuran (5.4 mL, 61 mmol) in THF (100 mL) was added *n*-butyllithium (43 mL, 68 mmol, 1.6 M solution in *n*-hexane) at –78 °C. The mixture was stirred for 30 min at –78 °C and additionally for 30 min at room temperature. A solution of vacuum- and flame-dried $ZnCl_2$ (8.3 g, 61 mmol) in THF (60 mL) was transferred to the mixture at –78 °C. The resulting mixture was stirred for 30 min at –78 °C and additionally for 30 min at room temperature. The mixture was transferred to a solution of 3-bromopyridine (5.6 mL, 58 mmol) and $Pd(PPh_3)_4$ (3.5 g, 3.0 mmol) in THF (50 mL) at room temperature. The resulting mixture was stirred for 11 h. The reaction mixture was quenched with $NaHCO_3$ aq. and the aqueous phase was extracted with

[4] A. J. De Koning, P. H. M. Budzelaar, J. Boersma, G. J. M. Van Der Kerk, **1980**, *199*, 153–169.

dichloromethane (20 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by MPLC (Kanto Chemical silica gel 60, *n*-hexane/EtOAc = 66:34 to 55:45) to afford the title compound (2.0 g, 15 mmol, 25%) as a yellowish oil. R_f 0.42 [*n*-hexane/EtOAc (50:50)]. The title compound was degassed by freeze-pump-thaw cycle (three times) and then used for the silylation. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 1H), 8.41 (d, *J* = 4.6 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.25–7.21 (m, 1H), 6.62–6.58 (m, 1H), 6.06 (s, 1H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.1, 149.3, 147.6, 145.0, 130.2, 127.1, 123.4, 107.9, 107.4, 13.7. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[5]



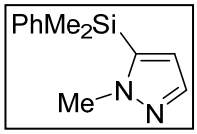
3-(1-Methyl-1*H*-pyrrol-2-yl)pyridine (1n): To a solution of 1-methylpyrrole (1.8 mL, 20 mmol) in THF (50 mL) was added *n*-butyllithium (14 mL, 22 mmol, 1.6 M solution in *n*-hexane) at –78 °C. The mixture was stirred for 30 min at –78 °C and additionally for 30 min at room temperature. The lithiation was not fully completed, *tert*-butyllithium (6.2 mL, 10 mmol, 1.6 M solution in pentane) was added at –78 °C and stirred for 60 min. A solution of vacuum- and flame-dried $ZnCl_2$ (3.3 g, 24 mmol) in THF (25 mL) was transferred to the mixture at –78 °C. The mixture was stirred for 30 min –78 °C and additionally for 60 min at room temperature. The resulting mixture was transferred to a solution of 3-bromopyridine (1.9 mL, 19 mmol) and $Pd(PPh_3)_4$ (1.2 g, 1.0 mmol) in THF (25 mL) at room temperature. The resulting mixture was stirred for 36 h. The reaction mixture was quenched with $NaHCO_3$ aq. and the aqueous phase was extracted with dichloromethane (20 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by MPLC (Kanto Chemical silica gel 60, *n*-hexane/EtOAc/NEt_3 = 85:15:1 to 50:50:1) to afford the title compound (1.7 g, 11 mmol, 56%) as a yellowish oil. R_f 0.42 [*n*-hexane/EtOAc/NEt_3 (50:50:1)]. The title compound was degassed by freeze-pump-thaw cycle (three times) and then used for the silylation. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.53 (d, *J* = 4.7 Hz, 1H), 7.70 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.36–7.28 (m, 1H), 6.77 (d, *J* = 1.8 Hz, 1H), 6.32–6.27 (m, 1H), 6.25–6.20 (m, 1H), 3.68 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 149.2, 147.7, 135.5, 130.8, 129.2, 124.7, 123.2, 109.8, 108.2, 35.1. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[6]



3-((3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-Dimethyl-3-((triisopropylsilyl)oxy)-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pyridine (1t): A 100 mL round-bottom flask containing a stirring bar was charged with a solution of abiraterone (0.80 g, 2.3 mmol) in dichloromethane (40 mL). To the solution was added imidazole (0.93 g, 14 mmol) at 0 °C. After stirred for 10 min, to the mixture were added chloro(triisopropyl)silane (1.3 g, 6.9 mmol) and N,N-dimethyl-4-aminopyridine (42 mg, 0.34 mmol)

[5] F.-M. Chen, F.-D. Huang, X.-Y. Yao, T. Li, F.-S. Liu, *Org. Chem. Front.* **2017**, *4*, 2536–2542.
[6] Ghosh, B. König, *Angew. Chem., Int. Ed.* **2016**, *55*, 7676–7679.

and the resulting mixture was stirred for 44 h at room temperature. The reaction mixture was quenched with NH_4Cl aq. and the aqueous phase was extracted with dichloromethane (30 mL x 4). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was washed with *n*-hexane (5.0 mL x 3) and EtOAc (5.0 mL x 3). After removal of all the volatiles, the title compound (0.93 g, 1.8 mmol, 80%) was obtained as a white powder. R_f 0.11 [*n*-hexane/EtOAc (90:10)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 8.45 (d, *J* = 4.1 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 6.2 Hz, 1H), 5.99 (s, 1H), 5.35 (d, *J* = 2.8 Hz, 1H), 3.62–3.50 (m, 1H), 2.36–2.22 (m, 3H), 2.11–2.00 (m, 3H), 1.85–1.40 (m, 9H), 1.12–0.99 (m, *J* = 6.4 Hz, 29H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 151.7, 147.9, 147.8, 142.0, 133.6, 133.0, 129.2, 123.0, 120.7, 72.4, 57.6, 50.4, 47.3, 43.1, 37.3, 36.8, 35.2, 32.3, 31.8, 31.5, 30.4, 20.8, 19.4, 18.1, 16.5, 12.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{33}H_{52}NOSi$, 506.3813; Found, 506.3820. m.p. 172 ºC.

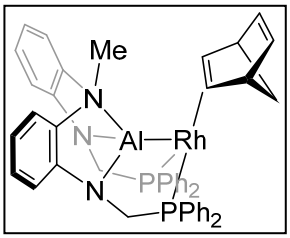


5-(Dimethylphenylsilyl)-1-methyl-1*H*-pyrazole (2q-5Si): *We followed the reported procedure for by Durandetti and Maddaluno.*[7]

A 20 mL Schlenk containing a stirring bar was charged with 1-methyl-1*H*-pyrazole (0.41 g, 5.0 mmol) and Et_2O (5.0 mL). The solution was cooled to – 35 °C and then *n*-butyllithium (3.8 mL, 6.0 mmol, 1.6 M solution in *n*-hexane) was added to it. After stirred for 1 h, to the mixture was added chloro(dimethylphenyl)silane (0.94 g, 5.5 mmol) and the resulting mixture was stirred for 21 h at room temperature. The reaction mixture was quenched with NH_4Cl aq. and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by MPLC (Kanto Chemical silica gel 60, *n*-hexane/EtOAc/NEt_3 = 100:0:1 to 10:90:1) to afford the title compound (38 mg, 0.18 mmol, 4%) as a yellowish oil. R_f 0.57 [*n*-hexane/EtOAc (80:20)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.50–7.45 (m, 2H), 7.43–7.33 (m, 3H), 6.44 (s, 1H), 3.75 (s, 3H), 0.59 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 140.2, 138.3, 136.2, 133.9, 129.7, 128.1, 115.8, 39.7, –2.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{12}H_{17}N_2Si$, 217.1156; Found, 217.1154.

[7] L. Mistico, O. Querolle, L. Meerpoel, P. Angibaud, M. Durandetti, J. Maddaluno, *Chem. Eur. J.* **2016**, *22*, 9687–9692.

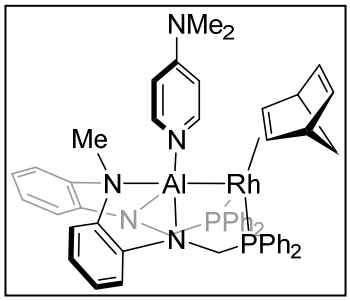
Synthesis of Rhodium–Aluminum Complexes.



7(nbd): The mixture of complex **3** (0.50 g, 0.31 mmol) and norbornadiene (0.17 g, 1.9 mmol) in THF (8.0 mL) was cooled to –35 °C. Then, KC_8 (0.18 g, 1.3 mmol) was added to the solution all at once and transferred with THF (2.0 mL) quantitatively. The resulting mixture was stirred at room temperature for 10 h. After graphite powders were filtered through a glass filter paper, the resulting solution was concentrated in vacuo. To remove THF completely, the residue was washed with pentane (4.0 mL, 2.0 mL x 2) and dried under reduced pressure. After the addition of toluene (6.0 mL), the solution was left for 1.5 h, filtered through a glass filter paper, and concentrated in vacuo. The precipitate was washed with pentane (2.0 mL x 3) and then dried under reduced pressure to afford complex **7(nbd)** (0.34 g, 0.41 mmol, 67%) as a light brown powder.

*Note: Toluene and pentane were not removed completely because complex **7(nbd)** was quite unstable under long-time vacuum even at room temperature. Then, we prepared **7(nbd)** with benzene instead of toluene. We determined the NMR resonances of **7(nbd)** compared with that of prepared **7(nbd)**.*

^{1}H NMR (400 MHz, C_6D_6): δ 7.76–7.69 (m br, 4H), 7.36–7.29 (m br, 4H), 7.25 (d, *J* = 7.3 Hz, 2H), 7.13 (d, *J* = 7.3 Hz, 4H), 7.10–7.04 (m, 4H), 6.92 (t, *J* = 7.1 Hz, 2H), 6.83 (t, *J* = 7.3 Hz, 4H), 6.51 (t, *J* = 7.6 Hz, 2H), 6.46 (d, *J* = 7.8 Hz, 2H), 5.06 (br, 2H, C*H*=C*H*), 3.62 (dt, *J* = 12, 3.6 Hz, 2H, NC*H*$_2$P), 3.26 (d, *J* = 12 Hz, 2H, NC*H*$_2$P), 3.10 (br, 2H, C*H*=C*H*), 2.99 (s, 2H, C*H*CH$_2$C*H*), 2.78 (s, 3H, NC*H*$_3$), 1.15 (s, 2H, CHC*H*$_2$CH). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 150.0 (t, $J_{P\text{-}C}$ = 9.8 Hz), 146.3 (t, $J_{P\text{-}C}$ = 15 Hz), 140.2 (t, $J_{P\text{-}C}$ = 12 Hz), 138.5, 133.3 (t, $J_{P\text{-}C}$ = 6.4 Hz), 130.8 (t, $J_{P\text{-}C}$ = 5.8 Hz), 129.50, 128.53, 128.48, 128.1, 122.5, 114.1, 111.8, 79.8–78.8 (m), 63.6, 50.3 (t, $J_{P\text{-}C}$ = 19 Hz), 49.1, 46.1, 33.0–31.0 (m), one signal probably overlaps the signal of C_6D_6. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 49.5 (d, $J_{Rh–P}$ = 161 Hz). HRMS (CSI) at –20 °C *m/z*: $[M + H]^+$ Calcd. for $C_{46}H_{44}N_3P_2AlRh$ 830.1875; Found, 830.1851. m.p. 190 ºC (decomp.).



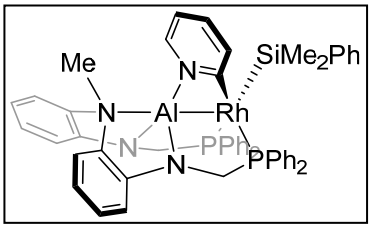
8(nbd)-DMAP: The mixture of **7(nbd)** (0.42 mg, 50 μmol) and *N*,*N*-dimethyl-4-aminopyridine (DMAP; 6.1 mg, 50 μmol) in benzene (2.0 mL) was stirred at room temperature for 5 min. After removal of all the volatiles, the residue was washed with a mixed solvent composed of benzene/pentane = 1/1 (1.0 mL x 5) followed by pentane (1.0 mL x 1) and then dried in vacuo to afford **8(nbd)-DMAP** (30 mg, 32 μmol, 63%) as a brown powder. Yellow crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion of hexane into a toluene solution of **8(nbd)-DMAP** at room temperature.

*Note: The removal of pentane was impossible because **8(nbd)-DMAP** is quite unstable toward vacuum, i.e., even 10 minutes vacuum at room temperature decomposed a part of **8(nbd)-DMAP**, probably due to easy desorption of norbornadiene ligand showing low boiling point (90 °C). Then,*

8(nbd)-DMAP *was azeotropically dried with benzene (1.0 mL), which was then removed in vacuo (five times).*

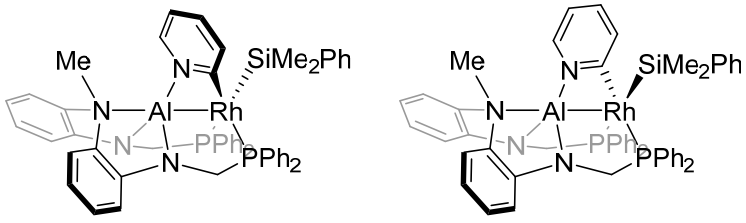
^{1}H NMR (400 MHz, C_6D_6) δ 8.18 (br, 4H), 7.53 (br, 4H), 7.38 (d, *J* = 6.5 Hz, 2H, C(2)–*H* of DMAP), 7.31 (t, *J* = 7.5 Hz, 4H), 7.23–7.18 (m, 2H), 7.15–7.07 (m, 4H), 7.03–6.96 (m, 2H), 6.91 (t, *J* = 7.5 Hz, 4H), 6.64 (t, *J* = 7.5 Hz, 2H), 6.50 (d, *J* = 8.0 Hz, 2H), 5.45 (d, *J* = 6.4 Hz, 2H, C(3)–*H* of DMAP), 5.29 (s, 2H, C*H*=C*H* of nbd), 3.88 (d, *J* = 12.1 Hz, 2H, P–CH_2–N), 3.58 (s, 2H, C*H*=C*H* of nbd), 2.95 (d, *J* = 11.9 Hz, 2H, P–CH_2–N), 2.31 (s, 2H, C*H* of nbd), 1.97 (s, 3H, NCH_3), 1.60 (s, 6H, N(CH_3)$_2$ of DMAP), 1.37 (d, *J* = 7.2 Hz, 1H, CH–CH_2–CH of nbd), 1.27 (d, *J* = 7.3 Hz, 1H, CH–CH_2–CH of nbd). ^{13}C NMR (101 MHz, C_6D_6) δ 152.4, 150.1–149.7 (m), 146.0 (t, *J* = 13.1 Hz), 143.4, 140.8–140.1 (m), 138.5, 132.3 (t, *J* = 6.2 Hz), 130.8 (t, *J* = 6.1 Hz), 127.7–127.4 (m), 126.9, 126.39, 126.36, 121.2, 113.2, 110.8, 104.4, 83.2, 62.2, 51.5–50.1 (m), 47.1, 43.6, 37.0–36.7 (m), 36.6. ^{31}P NMR (162 MHz, C_6D_6) δ 40.2 (d, *J* = 170 Hz). HRMS (CSI) at –20 °C *m/z*: $[M + H]^+$ Calcd. for $C_{53}H_{53}N_5P_2AlRh$ 952.2719; Found, 952.2672.

Note: Though the norbornadiene coordinates to the Rh atom in a bidentate manner judged from XRD study, ^{1}H NMR spectrum shows two kinds of olefinic protons of the norbornadiene at δ 5.29 and 3.58 ppm, suggesting that the norbornadiene coordinates to the Rh atom in a monodentate manner in solution state.



11: To a solution of complex **7(nbd)** (0.30 g, 0.36 mmol) in THF (5.0 mL) were added pyridine (29 μL, 0.36 mmol) and dimethylphenylsilane (55 μL, 0.36 mmol). The resulting mixture was stirred at 60 °C for 3 h. After removal of all the volatiles, the residue was washed with a mixed solvent composed of pentane/THF = 5/1 (2.0 mL x 3) and pentane (2.0 mL x 3). The residue was dried under reduced pressure to afford complex **11** (243 mg, 0.26 mmol, 71%) as a brown powder. Yellow crystals suitable for X-ray diffraction analysis were obtained by layering pentane on a concentrated dichloromethane solution at –35 °C.

*Note: THF and pentane were not removed completely because complex **11** is quite unstable under long-time vacuum even at room temperature. There are numerous signals on ^{1}H and ^{13}C NMR because the complex contains one isomer as shown below. These two isomers were also detected by X-ray diffraction analysis.*



11

^{1}H NMR (400 MHz, C_6D_6):δ 8.02 (t, *J* = 7.8 Hz, 2H). 7.87–7.80 (m, 2H), 7.69 (d, *J* = 5.5 Hz, 1H), 7.54–7.49 (m, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.32–7.19 (m, 7H), 7.19–7.12

(m, 3H), 6.98 (t, J = 8.0 Hz, 2H), 6.94–6.73 (m, 9H), 6.71 (t, J = 7.6 Hz, 1H), 6.55 (t, J = 7.1 Hz, 2H), 6.47 (d, J = 7.8 Hz, 1H), 6.27 (t, J = 7.6 Hz, 1H), 5.96 (t, J = 6.4 Hz, 1H), 4.24 (d, J = 12 Hz, 1H, NCH_2P), 4.10 (t, J = 11 Hz, 1H, NCH_2P), 3.77 (t, J = 11 Hz, 1H, NCH_2P), 3.00 (s, 3H, NCH_3), 2.47 (dd, J = 12, 4.1 Hz, 1H, NCH_2P), 0.56 (s, 3H, SiCH_3), 0.04 (s, 3H, SiCH_3). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 220.9 (dd, $J_{Rh\text{-}C}$ = 39 Hz, $J_{P\text{-}C}$ = 13 Hz), 220.8 (dd, $J_{Rh\text{-}C}$ = 39 Hz, $J_{P\text{-}C}$ = 13 Hz), 152.1 (d, J = 4.6 Hz), 150.6, 150.4, 150.3, 150.1, 144.5 (d, J = 9.3 Hz), 144.2 (d, J = 9.3 Hz), 143.6 (d, J = 4.6 Hz), 143.2 (d, J = 5.8 Hz), 142.94, 142.92, 139.8 (s br, one peak may overlap), 139.6, 137.83, 137.80, 137.4, 137.1, 136.8, 134.7 (d, J = 14 Hz), 134.1, 134.0, 132.8, 130.7 (d, J = 10 Hz), 130.0 (d, J = 6.9 Hz), 128.92 (d, J = 4.6 Hz), 128.85, 128.53 (d, J = 6.9 Hz), 128.47, 127.9, 127.5, 127.1, 126.9, 126.7, 126.0, 122.1, 119.7, 115.1, 114.2, 113.6, 111.9, 110.4, 50.9, 50.4, 48.1, 47.6, 47.2, 4.4–4.2 (m), 4.2–4.1 (m), two signals probably overlaps other signals. ^{31}P NMR (162 MHz, C_6D_6): δ 30.5 (dd, $J_{Rh–P}$ = 117 Hz, $J_{P–P}$ = 22 Hz), 26.4 (dd, $J_{Rh–P}$ = 100 Hz, $J_{P–P}$ = 22 Hz). HRMS (CSI) at −20 °C *m/z*: [M − $C_8H_{11}Si]^+$ Calcd. for $C_{44}H_{39}N_3P_2AlRh$, 815.1515; Found, 815.1517. Anal. Calcd. for $C_{52}H_{50}N_4SiP_2AlRh$: C, 65.68; H, 5.30; N, 5.89. Found: C, 64.57; H, 5.64; N, 5.65. The experimental values did not agree with calculated values because complex **11** is quite unstable toward air and moisture. m.p. 104 °C (decomp.).

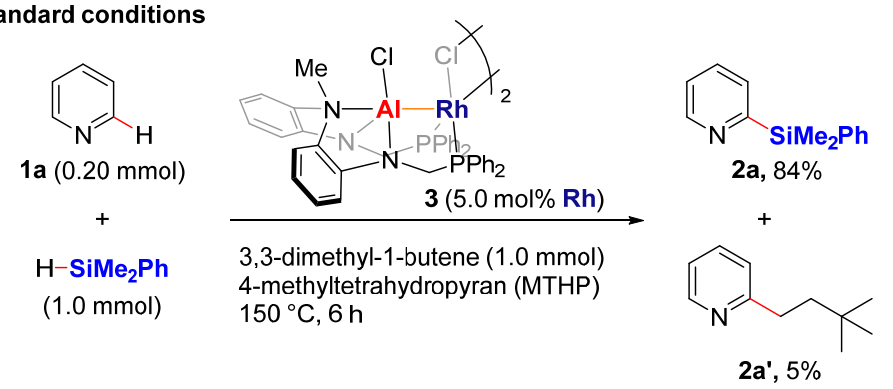
Optimization of the Reaction Conditions.

Our study started with the optimization of the reaction conditions (Table S1). We found that the reaction of pyridine (**1a**) with H–$SiMe_2Ph$ in the presence of 3,3-dimethyl-1-butene and Rh–Al complex **3** at 150 °C afforded 2-(dimethylphenylsilyl)pyridine (**2a**) in 84% yield and 2-alkylpyridine as a side product in 5% yield. Notably, other silylpyridines such as 3- or 4-silylpyridine or 2,6-disilylpyridine were not observed, indicating that this system is exclusively C2-selective. Employing Rh–Al complex **7(nbd)**, obtained from the reduction of **3**, gave **2a** in 83% yield, suggesting that the active catalyst could be a rhodium complex bearing an X-type aluminyl ligand. These results also implied that **3** is reduced by the hydrosilane *in situ* to generate an active Rh–Al complex. The silylation did not proceed in the presence of **12**, which is a complex that bears isopropyl instead of phenyl groups on the phosphorus atoms. Complex **13**, synthesized by the reduction of **12**, catalyzed the silylation, albeit in low yield.[2] These results show that the P-substituent dramatically affects the reaction efficiency, but the detail effects of of the substituent on the P atoms are still unclear. The reaction did not take place in the absence of a Rh–Al complex. The combination of $[RhCl(nbd)]_2$ (nbd = norbornadiene) and PPh_3, 1,5-bis(diphenylphosphino)pentane or Xantphos with or without $AlEt_3$ did not yield **2a**, clearly supporting the notion that the silylation is catalyzed by the Rh–Al complexes. Norbornene provided **2a** in good yield, albeit that the amount of the 2-alkylpyridine product was increased, whereas cyclohexene furnished **2a** in only 9% yield. The reaction in the absence of hydrogen-accepting olefins was unsuccessful, presumably due to the endergonic C–H silylation with a hydrosilane.[8] Employing H–$SiEt_3$ afforded 2-(triethylsilyl)pyridine in low yield, while $(SiMe_2Ph)_2$, $HSi(OEt)_3$, and $PhMe_2Si$–B(pin) did not. The use of smaller amounts of H–$SiMe_2Ph$ and 3,3-dimethyl-1-butene than the standard conditions or that of toluene as a solvent gave **2a** in good yield. **2a** was obtained in low yield at 100 °C, whereas it was not observed at 60 °C.

[8] M. Tobisu, Y. Ano, N. Chatani, *Chem. Asian J.* **2008**, *3*, 1585–1591.

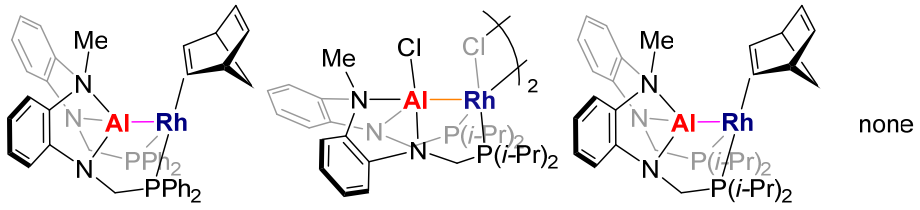
Table S1. Optimization of the reaction conditions.

standard conditions



deviation from the standard conditions

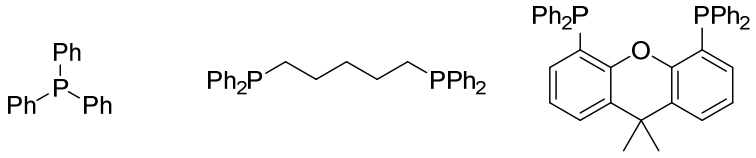
Rh–Al complexes (5.0 mol% Rh) instead of 3



7(nbd)	**12**	**13**	none
yield of **2a**/**2a'** = 83%/6%	trace/trace	18%/9%	<5%/<5%

rhodium/phosphine catalysts instead of 3

$[RhCl(nbd)]_2$ (5.0 mol% **Rh**)/P ligand (10 mol% P)/$AlEt_3$ (0 or 5 mol%)



<5%/<5%	<5%/<5%	<5%/<5%

alkenes instead of 3,3-dimethyl-1-butene

72%/17%	9%/<5%	none 4%/--

silanes instead of H–SiMe2Ph

H–SiEt3	(PhMe2Si)2	H–Si(OEt)3	PhMe2Si–B(pin)
10%/8%	<5%/<5%	<5%/<5%	<5%/<5%

others

H–SiMe2Ph (0.50 mmol) 3,3-dimethyl-1-butene (0.50 mmol)	toluene	100 °C	60 °C w/ **3** or **7(nbd)**
74%/9%	78%/7%	39%/7%	<5%/<5%

Yield determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard. nbd = norbornadiene

General procedures for Table S1.

Rh–Al complexes: In a glove box, a 4 mL vial containing a stirring bar was charged with Rh–Al complex (5.0 mol% Rh), **1a** (16 mg, 0.20 mmol), dimethylphenylsilane (0.14 g, 1.0 mmol), 3,3-dimethyl-1-butene (84 mg, 1.0 mmol), MTHP (1.0 mL), and *n*-dodecane (8.6 mg, 25 mol%) as an internal standard. The resulting mixture was stirred for 6 h at 150 ºC. The generation of the product was confirmed by GC analysis of the reaction mixture. The reaction mixture was cooled to room temperature and filtered through a celite plug with EtOAc. All the volatiles were removed in vacuo and the NMR yields were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

other Rh catalysts: In a glove box, a 4 mL vial containing a stirring bar was charged with [RhCl(nbd)]$_2$ (nbd = norbornadiene; 2.3 mg, 5.0 mol% Rh), PPh_3 (5.2 mg, 10 mol% P) or 1,5-Bis(diphenylphosphino)pentane (4.4 mg, 10 mol% P) or Xantphos (5.8 mg, 10 mol% P), **1a** (16 mg, 0.20 mmol), dimethylphenylsilane (0.14 g, 1.0 mmol), 3,3-dimethyl-1-butene (84 mg, 1.0 mmol), MTHP (1.0 mL), $AlEt_3$ (0 or 11 μL, 0 or 5 mol%, 0.94 M solution in toluene), and *n*-dodecane (8.6 mg, 25 mol%) as an internal standard. The resulting mixture was stirred for 6 h at 150 ºC. The generation of the product was confirmed by GC analysis of the reaction mixture.

alkenes: In a glove box, a 4 mL vial containing a stirring bar was charged with Rh–Al complex **3** (8.1 mg, 5.0 mol% Rh), **1a** (16 mg, 0.20 mmol), dimethylphenylsilane (0.14 g, 1.0 mmol), norbornene (94 mg, 1.0 mmol) or cyclohexene (82 mg, 1.0 mmol), MTHP (1.0 mL), and *n*-dodecane (8.6 mg, 25 mol%) as an internal standard. The resulting mixture was stirred for 6 h at 150 ºC. The generation of the product was confirmed by GC analysis of the reaction mixture. The reaction mixture was cooled to room temperature and filtered through a celite plug with EtOAc. All the volatiles were removed in vacuo and the NMR yields were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

silanes: In a glove box, a 4 mL vial containing a stirring bar was charged with **3** (8.1 mg, 5.0 mol% Rh), **1a** (16 mg, 0.20 mmol), silanes (1.0 mmol), 3,3-dimethyl-1-butene (84 mg, 1.0 mmol), MTHP (1.0 mL), and *n*-dodecane (8.6 mg, 25 mol%) as an internal standard. The resulting mixture was stirred for 6 h at 150 ºC. The generation of the product was confirmed by GC analysis of the reaction mixture. The reaction mixture was cooled to room temperature and filtered through a celite plug with EtOAc. All the volatiles were removed in vacuo and the NMR yields were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

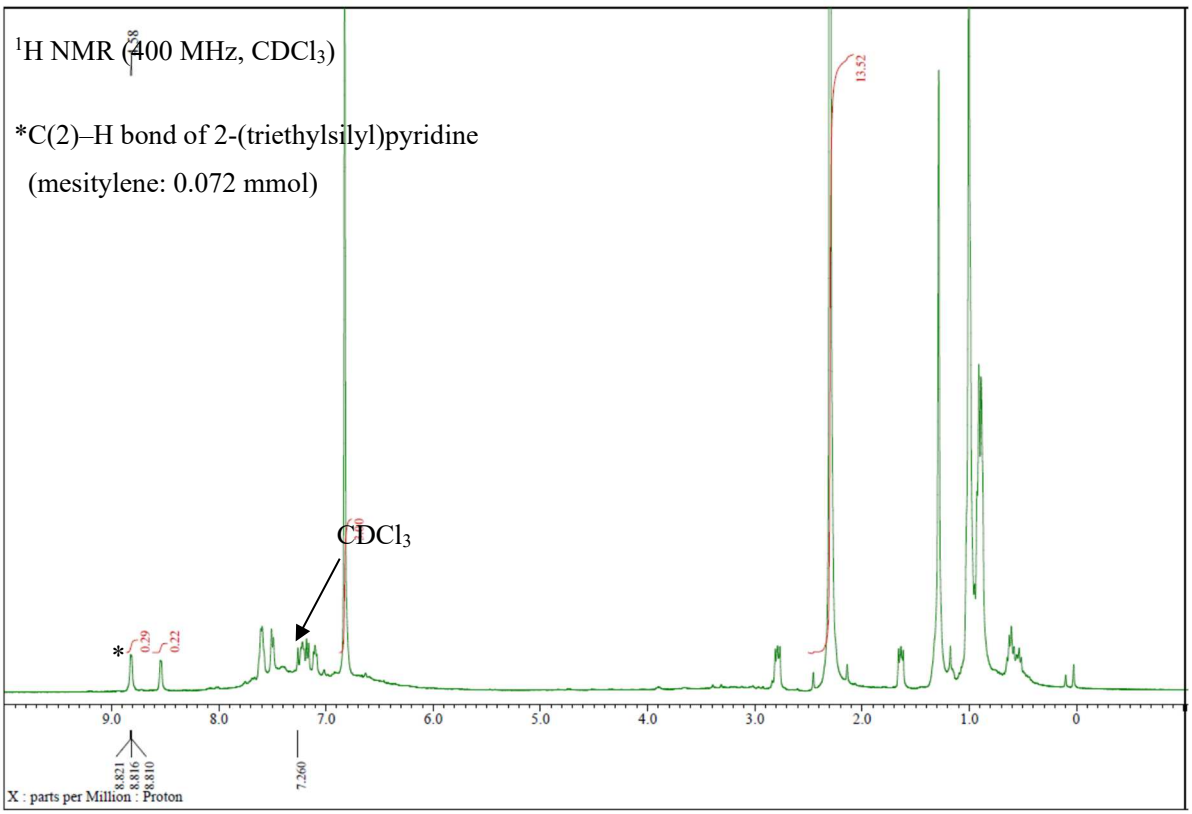


Figure S2. ^{1}H NMR spectra of the crude product in the case of H–$SiEt_3$.

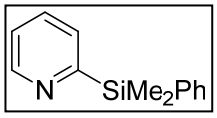
others: In a glove box, a 4 mL vial containing a stirring bar was charged with Rh–Al complex **3** or **7(nbd)** (5.0 mol% Rh), **1a** (16 mg, 0.20 mmol), dimethylphenylsilane (0.14 g, 1.0 mmol), 3,3-dimethyl-1-butene (84 mg, 1.0 mmol), MTHP (1.0 mL) or toluene (1.0 mL), and *n*-dodecane (8.6 mg, 25 mol%). The resulting mixture was stirred for 6 h at 150 ºC or 100 or 60 ºC. The generation of the product was confirmed by GC analysis of the reaction mixture. The reaction mixture was cooled to room temperature and filtered through a celite plug with EtOAc. All the volatiles were removed in vacuo and the NMR yields were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

*Note: On the reaction with complex **3** at 60 °C, the reduction of complex **3** was not observed.*

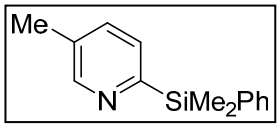
General Procedure of C2-Selective Silylation of Pyridines for Table 1.

In a glove box, a 15 mL vial containing a stirring bar was charged with complex **3** (20 mg, 5.0 mol% Rh), **1** (0.50 mmol), dimethylphenylsilane (0.34 g, 2.5 mmol), 3,3-dimethyl-1-butene (0.21 g, 2.5 mmol), MTHP (2.5 mL), and *n*-dodecane (21 mg, 25 mol%) as an internal standard. The resulting mixture was vigorously stirred for 6 h at 150 ºC. The generation of the target compound was determined by GC and GC-MS analysis of the reaction mixture. The reaction mixture was cooled to room temperature and filtered through a celite plug with EtOAc. All the volatiles were removed in vacuo and the NMR yield of the target compound was determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard. After MPLC purification (Wakogel® 50NH2 or basic alumina), the target compound was obtained.

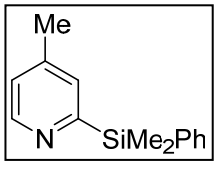
Note: A small amount of 2-alkylpyridine was also generated. Although the purification by MPLC removed it, isolated yield often decreased because 2-alkylpyridine shows quite similar Rf value to 2-silylpyridine.



2-(Dimethylphenylsilyl)pyridine (2a): The reaction of **1a** (40 mg, 0.50 mmol) gave **2a** in 83% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc = 99:1 to 96:4), **2a** was obtained as a slight yellowish oil (61 mg, 0.28 mmol, 57%). R_f 0.14 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc (99:1)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 4.6 Hz, 1H) 7.62–7.58 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.39–7.34 (m, 3H), 7.19 (t, *J* = 6.2 Hz, 1H), 0.62 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.7, 150.3, 137.3, 134.2, 133.9, 129.7, 129.3, 127.9, 122.8, –3.2. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[9]



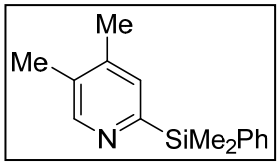
2-(Dimethylphenylsilyl)-5-methylpyridine (2c): The reaction of **1c** (47 mg, 0.50 mmol) gave **2c** in 94% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc = 100:0 to 95:5), **2c** was obtained as a slight yellowish oil (97 mg, 0.43 mmol, 86%). R_f 0.23 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc (98:2)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 7.61–7.55 (m, 2H), 7.40–7.32 (m, 5H), 2.32 (s, 3H), 0.61 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 162.7, 151.0, 137.6, 134.6, 134.2, 132.4, 129.4, 129.2, 127.8, 18.6, –3.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{14}H_{18}NSi$, 228.1203; Found, 228.1200.



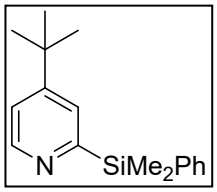
2-(Dimethylphenylsilyl)-4-methylpyridine (2d): The reaction of **1d** (47 mg, 0.50 mmol) gave **2d** in 89% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc = 100:0 to 99:1 to 96:4), **2d** was obtained as a slight yellowish oil (71 mg, 0.31 mmol, 63%). R_f 0.18 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc (97:3)]. ^{1}H NMR (400 MHz, C_6D_6): δ 8.66 (d, *J* = 5.0 Hz, 1H), 7.68 (d, *J* = 7.3 Hz,

[9] N. Chernyak, A. S. Dudnik, C. Huang, V. Gevorgyan, *J. Am. Chem. Soc.* **2010**, *132*, 8270–8272.

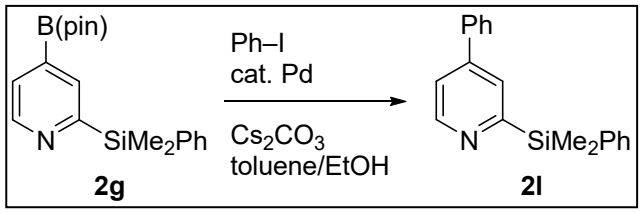
2H), 7.26–7.18 (m, 4H), 6.54 (d, J = 4.6 Hz, 1H), 1.76 (s, 3H), 0.67 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6): δ 166.4, 150.4, 144.4, 138.0, 134.7, 130.6, 129.4, 128.1, 123.8, 20.6, –2.8. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[10]



2-(Dimethylphenylsilyl)-4,5-dimethylpyridine (2e): The reaction of **1e** (54 mg, 0.50 mmol) for 8 h gave **2e** in 91% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 100:0:1 to 95:5:1), **2e** was obtained as a slight yellowish oil (0.10 g, 0.42 mmol, 84%). R_f 0.40 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc/NEt_3 (95:5:1)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.61–7.55 (m, 2H), 7.40–7.32 (m, 3H), 7.20 (s, 1H), 2.23 (s, 3H), 2.21 (s, 3H), 0.59 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 162.9, 151.0, 143.4, 137.8, 134.2, 131.5, 130.9, 129.1, 127.8, 19.0, 16.4, –3.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{15}H_{20}NSi$, 242.1360; Found, 242.1355.

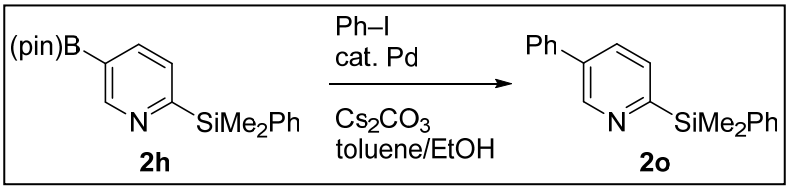


2-(Dimethylphenylsilyl)-4-*tert*-butylpyridine (2f): The reaction of **1f** (68 mg, 0.50 mmol) for 10 h gave **2f** in 89% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 100:0:1 to 95:5:1) and drying at 80 ºC under vacuum to remove volatiles, **2f** was obtained as a colorless oil (85 mg, 0.32 mmol, 63%). R_f 0.33 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc (95:5)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, J = 5.0 Hz, 1H) 7.63–7.58 (m, 2H), 7.45 (s, 1H), 7.39–7.33 (m, 3H), 7.19 (d, J = 5.0 Hz, 1H), 1.26 (s, 9H), 0.62 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 165.7, 157.5, 150.2, 137.6, 134.2, 129.2, 127.8, 126.6, 119.9, 34.5, 30.5, –3.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{17}H_{24}NSi$, 270.1673; Found, 270.1668.

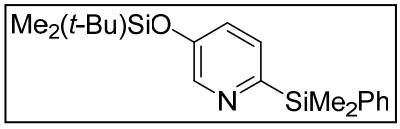


2-(Dimethylphenylsilyl)pyridine-4-boronic acid pinacol ester (2g): The reaction of **1g** (0.10 g, 0.50 mmol) for 10 h gave **2g** in 88% NMR yield. Then, a 15 mL vial containing a stirring bar was charged with the crude product, iodobenzene (0.11 g, 0.55 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol), Cs_2CO_3 (0.49 g, 1.5 mmol), toluene (4.0 mL), and EtOH (1.0 mL), and the mixture was stirred at 80 ºC for 1 h. The reaction mixture was cooled to room temperature, filtered through celite and Wakogel® 50NH2 plugs with EtOAc, and concentrated in vacuo. The residue was purified by MPLC (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 100:0:3 to 92:8:3) and dried at 110 ºC under vacuum to afford 2-(dimethylphenylsilyl)-4-phenylpyridine (**2l**) as a yellowish oil (90 mg, 0.31 mmol, 62%). R_f 0.20 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc (95:5)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 4.6 Hz, 1H), 7.68–7.60 (m, 3H), 7.57 (d, J = 7.3 Hz, 2H), 7.49–7.35 (m, 7H), 0.66 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 166.9, 150.7, 146.2, 138.7, 137.2, 134.2, 129.3, 129.0, 128.8, 127.9, 127.7, 127.1, 120.9, –3.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{19}H_{20}NSi$, 290.1360; Found, 290.1356.

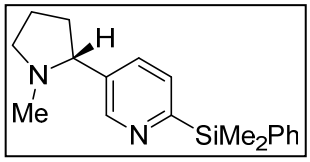
[10] K. Oshima, T. Ohmura, M. Suginome, *J. Am. Chem. Soc.* **2011**, *133*, 7324–7327.



2-(Dimethylphenylsilyl)pyridine-5-boronic acid pinacol ester (2h): The reaction of **1h** (0.10 g, 0.50 mmol) for 10 h gave **2h** in 80% NMR yield. Then, a 15 mL vial containing a stirring bar was charged with the crude product, iodobenzene (0.11 g, 0.55 mmol), $Pd(PPh_3)_4$ (58 mg, 50 μmol), Cs_2CO_3 (0.49 g, 1.5 mmol), toluene (4.0 mL), and EtOH (1.0 mL), and the mixture was stirred at 80 ºC for 1.5 h. The reaction mixture was cooled to room temperature, filtered through celite and Wakogel® 50NH2 plugs with EtOAc, and concentrated in vacuo. The residue was purified by MPLC (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 100:0:3 to 92:8:3) and dried at 110 ºC under vacuum to afford 2-(dimethylphenylsilyl)-5-phenylpyridine (**2o**) as an off-white powder (91 mg, 0.31 mmol, 63%). R_f 0.43 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc/NEt_3 (95:5:1)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.66–7.61 (m, 2H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.55–7.44 (m, 3H), 7.42–7.37 (m, 4H), 0.66 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.0, 148.8, 138.1, 137.3, 135.5, 134.2, 132.2, 129.6, 129.3, 129.0, 128.0, 127.9, 127.1, –3.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{19}H_{20}NSi$, 290.1360; Found, 290.1356. m.p. 47 ºC.

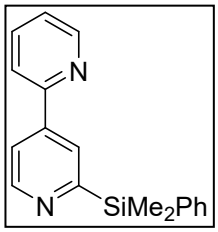


2-(Dimethylphenylsilyl)-5-(*tert*-butyldimethylsilyloxy)pyridine (2i): The reaction of **1i** (0.10 g, 0.50 mmol) gave **2i** in 85% NMR yield. After MPLC purification (basic alumina, addition of 7% of water, *n*-hexane/EtOAc = 100:0 to 80:20), **2i** was obtained as a slight yellowish oil (0.11 g, 0.31 mmol, 62%). R_f 0.66 [basic alumina, *n*-hexane/EtOAc (90:10)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.60–7.54 (m, 2H), 7.39–7.28 (m, 4H), 7.01 (d, *J* = 8.2 Hz, 1H), 0.98 (s, 9H), 0.59 (s, 6H), 0.22 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 157.6, 151.8, 143.5, 137.8, 134.2, 130.3, 129.1, 127.8, 124.7, 25.6, 18.2, –2.9, –4.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{19}H_{30}NOSi_2$, 344.1860; Found, 344.1859.

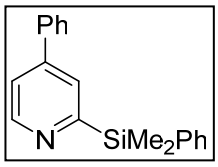


2-(Dimethylphenylsilyl)-(*S*)-5-(1-methylpyrrolidin-2-yl)pyridine (2j): The reaction of **1j** (87 mg, 0.53 mmol) gave **2j** in 84% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 100:0:1 to 90:10:1), **2j** was obtained as a slight yellowish oil (98 mg, 0.33 mmol, 62%). R_f 0.23 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc (90:10)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.63–7.55 (m, 3H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.39–7.34 (m, 3H), 3.23 (t, *J* = 8.5 Hz, 1H), 3.06 (t, *J* = 8.2 Hz, 1H), 2.30 (q, *J* = 9.0 Hz, 1H), 2.23–2.13 (m, 4H), 2.01–1.88 (m, 1H), 1.87–1.77 (m, 1H), 1.77–1.65 (m, 1H), 0.61 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 164.9, 150.4, 137.9, 137.5, 134.2, 132.7, 129.7, 129.2, 127.8, 69.0, 57.1, 40.5, 35.2, 22.6, –3.1. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[11]

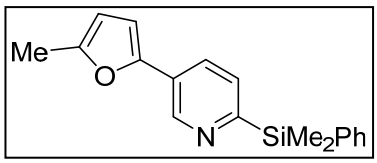
[11] F. C. Février, E. D. Smith, D. L. Comins, *Org. Lett.* **2005**, *7*, 5457–5460.



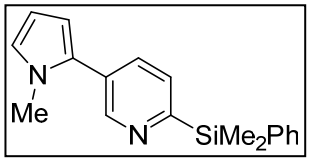
2'-(Dimethylphenylsilyl)-2,4'-bipyridine (2k): The reaction of **1k** (78 mg, 0.50 mmol) for 1 h gave **2k** in 80% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 95:5:1 to 80:20:1) and drying at 100 ºC under vacuum to remove volatiles, **2k** was obtained as a light brown powder (93 mg, 0.32 mmol, 64%). R_f 0.71 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc/NEt_3 (50:50:1)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (d, *J* = 4.6 Hz, 1H), 8.73 (m, 1H), 8.05 (s, 1H), 7.81–7.75 (m, 2H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.67–7.60 (m, 2H), 7.40–7.34 (m, 3H), 7.31 (t, *J* = 5.7 Hz, 1H), 0.68 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 167.2, 155.3, 150.9, 150.1, 144.3, 137.3, 137.0, 134.3, 129.3, 127.9, 126.8, 123.5, 121.0, 120.3, –3.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{18}H_{19}N_2Si$, 291.1312; Found, 291.1307. m.p. 65 ºC.



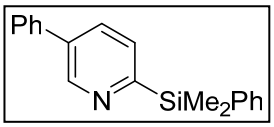
2-(Dimethylphenylsilyl)-4-phenylpyridine (2l): The reaction of **1l** (78 mg, 0.50 mmol) for 9 h gave **2l** in 83% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 100:0:1 to 95:5:1), **2l** was obtained as a yellowish oil (0.11 g, 0.37 mmol, 74%). R_f 0.20 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc (95:5)]. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with the values of **2g**.



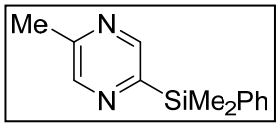
2-(Dimethylphenylsilyl)-5-(5-methylfuran-2-yl)pyridine (2m): The reaction of **1m** (80 mg, 0.50 mmol) for 8 h gave **2m** in 70% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 98:2:1 to 85:15:1) and drying at 110 ºC under vacuum to remove volatiles, **2m** was obtained as a white powder (96 mg, 0.33 mmol, 65%). R_f 0.57 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc/NEt_3 (75:25:1)]. ^{1}H NMR (400 MHz, $(CD_3)_2SO$):δ 9.05 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.59–7.52 (m, 3H), 7.41–7.32 (m, 3H), 6.98 (d, J = 2.7 Hz, 1H), 6.25 (s, 1H), 2.35 (s, 3H), 0.56 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2SO$): δ 163.4, 152.9, 148.8, 144.8, 137.2, 133.9, 129.4, 129.2, 127.8, 127.7, 125.5, 108.7, 108.5, 13.5, –3.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{18}H_{20}NOSi$, 294.1309; Found, 294.1304. m.p. 73 ºC.



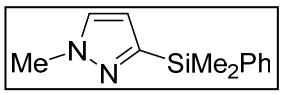
2-(Dimethylphenylsilyl)-5-(1-methyl-1*H*-pyrrol-2-yl)pyridine (2n): The reaction of **1n** (81 mg, 0.51 mmol) for 8 h gave **2n** in 86% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 98:2:1 to 85:15:1) and drying at 110 ºC under vacuum to remove volatiles, **2n** was obtained as a yellowish oil (0.11 g, 0.39 mmol, 75%). R_f 0.71 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc/NEt_3 (75:25:1)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 7.67–7.60 (m, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.43–7.35 (m, 3H), 6.78–6.74 (m, 1H), 6.32–6.27 (m, 1H), 6.24–6.20 (m, 1H), 3.69 (s, 3H), 0.65 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 164.1, 149.6, 137.2, 134.2, 133.2, 131.2, 129.32, 129.28, 128.1, 127.9, 124.8, 109.9, 108.2, 35.2, –3.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{18}H_{21}N_2Si$, 293.1469; Found, 293.1465.



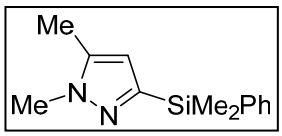
2-(Dimethylphenylsilyl)-5-phenylpyridine (2o): The reaction of **1o** (78 mg, 0.50 mmol) for 9 h gave **2o** in 84% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 100:0:1 to 95:1:1) and drying at 60 ºC under vacuum to remove volatiles, **2o** was obtained as an off-white powder (0.12 g, 0.41 mmol, 82%). R_f 0.43 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc/NEt_3 (95:5:1)]. All the resonances of ^1H and ^{13}C NMR spectra were consistent with the values of **2h**.



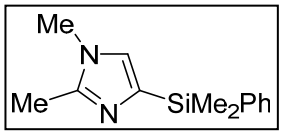
2-(Dimethylphenylsilyl)-5-methylpyradine (2p): The reaction of **1p** (47 mg, 0.50 mmol) gave **2p** in 86% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 100:0:1 to 96:4:1), **2p** was obtained a slight yellowish oil (91 mg, 0.40 mmol, 80%). R_f 0.30 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc/NEt_3 (95:5:1)]. ^1H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.49 (s, 1H), 7.61–7.56 (m, 2H), 7.42–7.34 (m, 3H), 2.53 (s, 3H), 0.63 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 157.1, 152.9, 148.5, 145.8, 136.3, 134.1, 129.6, 128.0, 21.7, –3.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{13}H_{17}N_2Si$, 229.1156; Found, 229.1151.



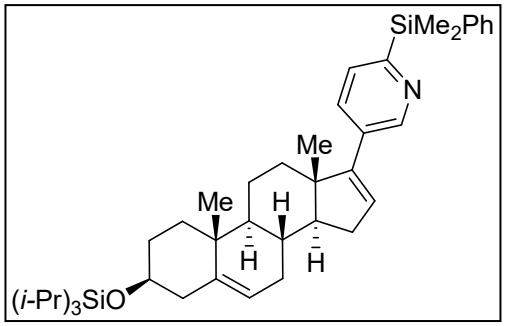
3-(Dimethylphenylsilyl)-1-methyl-1*H*-pyrazole (2q): The reaction of **1q** (41 mg, 0.50 mmol) with norbornene (0.35 g, 3.8 mmol) under neat conditions in a 4 mL vial for 24 h gave **2q** in 81% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 100:0:1 to 0:100:1), **2q** was obtained as a light brown oil (75 mg, 0.35 mmol, 69%). R_f 0.55 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc (80:20)]. ^1H NMR (400 MHz, $CDCl_3$): δ7.62–7.56 (m, 2H), 7.39 (s, 1H), 7.37–7.32 (m, 3H), 6.36 (s, 1H), 3.97 (s, 3H), 0.57 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 151.1, 138.3, 134.0, 130.0, 129.0, 127.7, 113.0, 38.7, –2.2. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{12}H_{16}N_2SiNa$, 239.0975; Found, 239.0969.



3-(Dimethylphenylsilyl)-1,5-dimethyl-1*H*-pyrazole (2r): The reaction of **1r** (48 mg, 0.50 mmol) with 3,3-dimethyl-1-butene (0.32 g, 3.8 mmol) under neat conditions in a 4 mL vial for 24 h gave **2r** in 87% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 100:0:1 to 75:25:1), **2r** was obtained as a light brown powder (94 mg, 0.41 mmol, 82%). R_f 0.55 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc (80:20)]. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63–7.57 (m, 2H), 7.38–7.32 (m, 3H), 6.12 (s, 1H), 3.83 (s, 3H), 2.25 (s, 3H), 0.55 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 149.5, 138.4, 138.3, 134.0, 129.0, 127.7, 112.7, 36.2, 11.0, –2.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{13}H_{18}N_2SiNa$, 253.1131; Found, 253.1127.

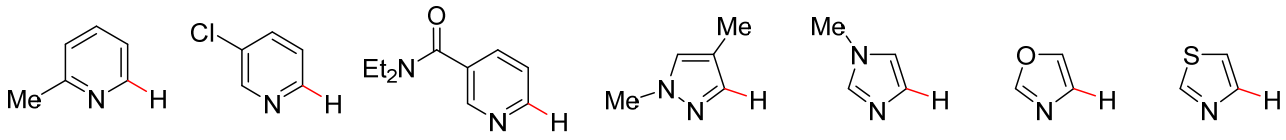


4-(Dimethylphenylsilyl)-1,2-dimethyl-1*H*-imidazole (2s): The reaction of **1s** (48 mg, 0.50 mmol) with 3,3-dimethyl-1-butene (0.32 g, 3.8 mmol) under neat conditions in a 4 mL vial for 24 h gave **2s** in 90% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 100:0:1 to 20:80:1 to 0:100:1), **2s** was obtained as a yellow powder (101 mg, 0.44 mmol, 87%). R_f 0.11 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc (80:20)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.57 (m, 2H), 7.38–7.30 (m, 3H), 6.81 (s, 1H), 3.51 (s, 3H), 2.40 (s, 3H), 0.52 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 147.6, 138.7, 137.0, 134.0, 129.3, 128.9, 127.6, 32.6, 13.0, –2.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{13}H_{19}N_2Si$, 231.1312; Found, 231.1307.



2-(Dimethylphenylsilyl)-5-((3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-3-((triisopropylsilyl)oxy)-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pyridine (2t): The reaction of **1t** (0.10 g, 0.20 mmol) with complex **3** (8.1 mg, 5.0 mol% Rh), dimethylphenylsilane (0.14 g, 1.0 mmol), norbornene (94 mg, 1.0 mmol), MTHP (0.20 mL), and *n*-dodecane (8.6 mg, 25 mol%) as an internal standard in a 4 mL vial for 24 h gave **2t** in 66% NMR yield. After MPLC purification (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 99:1:1 to 97:3:1), **2t** was obtained as a colorless viscous liquid (79 mg, 0.12 mmol, 62%). R_f 0.23 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc (99:1)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 1H), 7.59–7.64 (m, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.40–7.35 (m, 4H), 6.02 (s, 1H), 5.36 (d, *J* = 2.8 Hz, 1H), 3.63–3.53 (m, 1H), 2.37–2.22 (m, 3H), 2.12–1.96 (m, 3H), 1.87–1.42 (m, 9H), 1.12–1.02 (m, 29H), 0.62 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 164.0, 151.9, 148.3, 142.0, 137.4, 134.2, 131.9, 131.4, 129.3, 129.22, 129.16, 127.8, 120.7, 72.4, 57.5, 50.4, 47.2, 43.1, 37.3, 36.7, 35.3, 32.3, 31.8, 31.5, 30.4, 20.8, 19.4, 18.1, 16.6, 12.3, –3.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{41}H_{62}NOSi_2$, 640.4364; Found, 640.4373.

Unsuccessful substrates.



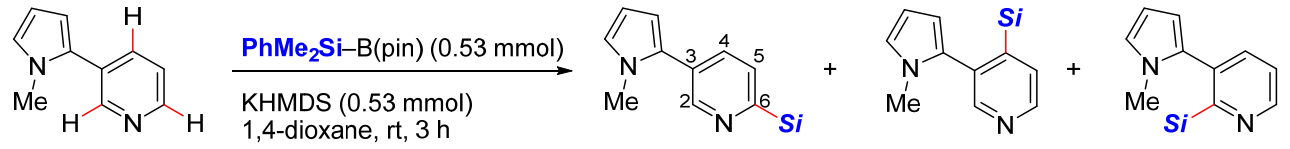
1b **1u** **1v** **1w** **1x** **1y** **1z**

*Procedure for **1b, 1u,** and **1v***: In a glove box, a 4 mL vial containing a stirring bar was charged with complex **3** (8.1 mg, 5.0 mol% Rh), **1b**, **1u**, or **1v** (0.20 mmol), dimethylphenylsilane (0.14 g, 1.0 mmol), 3,3-dimethyl-1-butene (84 mg, 1.0 mmol), MTHP (1.0 mL), and *n*-dodecane (8.6 mg, 25 mol%) as an internal standard. The resulting mixture was vigorously stirred for 6 h at 150 ºC. The target compounds were not detected by GC and GC-MS analysis of the reaction mixture.
Discussion: The rhodium and aluminum centers in a Rh–Al complex may activate chloro and carbonyl groups cooperatively, supported by our previous work[1], resulting in the deactivation or decomposition of the complex. Thus, the silylation with pyridines bearing Lewis basic Chloro or amido groups dose not proceed.

*Procedure for **1w** and **1x**:* In a glove box, a 4 mL vial containing a stirring bar was charged with complex **3** (20 mg, 5.0 mol% Rh), **1w** or **1x** (0.50 mmol), dimethylphenylsilane (0.34 g, 2.5 mmol), 3,3-dimethyl-1-butene (0.32 g, 3.8 mmol) and *n*-dodecane (21 mg, 25 mol%) as an internal standard under neat conditions. The resulting mixture was vigorously stirred for 24 h at 150 ºC. The target compounds were not detected by GC and GC-MS analysis of the reaction mixture.

*Procedure for **1y** and **1z**:* In a glove box, a 4 mL vial containing a stirring bar was charged with complex **3** (8.1 mg, 5.0 mol% Rh), **1y** or **1z** (0.20 mmol), dimethylphenylsilane (0.14 g, 1.0 mmol), 3,3-dimethyl-1-butene (0.13 g, 1.5 mmol) and *n*-dodecane (8.6 mg, 25 mol%) as an internal standard under neat conditions. The resulting mixture was vigorously stirred for 24 h at 150 ºC. The target compounds were not detected by GC and GC-MS analysis of the reaction mixture.

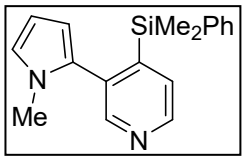
Selectivity Study.



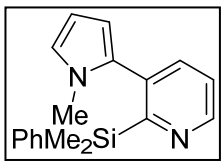
1n (0.53 mmol) (***Si*** = **SiMe$_2$Ph**) **2n** 16% **2n-4Si** 7% **2n-2Si** 5%

We followed the reported procedure for C2-selective silylation by Martin.[12]

In a glove box, a 15 mL vial containing a stirring bar was charged with **1n** (84 mg, 0.53 mmol), PhMe$_2$Si–B(pin) (0.14 g, 0.53 mmol), KHMDS (0.11 g, 0.53 mmol), and 1,4-dioxane (2.5 mL). The resulting mixture was stirred for 1 min and taken out of the glove box. The mixture was vigorously stirred at room temperature for 3 h, and then diluted with EtOAc (6.0 mL) and filtered through a celite plug. The filtrate was concentrated in vacuo. The NMR yields of **2n**, 3-(1-methyl-1*H*-pyrrol-2-yl)-4-(dimethylphenylsilyl)pyridine (**2n-4Si**), and 2-dimethylphenylsilyl-3-(1-methyl-1*H*-pyrrol-2-yl)pyridine (**2n-2Si**) were determined by ^{1}H NMR spectroscopy of the crude product using mesitylene as an internal standard. To identify **2n-4Si** and **2n-2Si**, the crude product was purified by MPLC (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt$_3$ = 98:2:1 to 85:15:1 to 80:20:1) to isolate **2n-2Si** and afford a mixture of **2n-4Si** and impurities. Then, the mixture was again purified by MPLC (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt$_3$ = 100:0:1 to 80:20:1) to isolate **2n-4Si**. Obtained **2n-4Si** and **2n-2Si** were determined by ^{1}H and ^{13}C NMR spectroscopy and HRMS analysis.



3-(1-Methyl-1*H*-pyrrol-2-yl)-4-(dimethylphenylsilyl)pyridine (2n-4Si): The target compound was obtained as a yellowish oil. R_f 0.43 [NH2 Silica Gel 60 F_{254} Plate-Wako, *n*-hexane/EtOAc (80:20)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 4.6 Hz, 1H), 8.43 (s, 1H), 7.44 (d, *J* = 4.6 Hz, 1H), 7.38–7.27 (m, 5H), 6.58–6.54 (m, 1H), 6.14–6.09 (m, 1H), 5.93–5.89 (m, 1H), 3.01 (s, 3H), 0.32 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.1, 150.3, 147.8, 137.1, 135.3, 133.9, 130.4, 129.3, 129.2, 127.7, 121.9, 111.4, 107.3, 33.8, –2.5. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd. for $C_{18}H_{21}N_2Si$, 293.1469; Found, 293.1474.



2-(Dimethylphenylsilyl)-3-(1-methyl-1*H*-pyrrol-2-yl)pyridine (2n-2Si): The target compound was obtained as a white powder. R_f 0.57 [NH2 Silica Gel 60 F_{254} Plate-Wako, *n*-hexane/EtOAc (80:20)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 4.6 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.35–7.21 (m, 6H), 6.55–6.50 (m, 1H), 6.13–6.07 (m, 1H), 5.89–5.83 (m, 1H), 2.97 (s, 3H), 0.36 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 167.3, 149.0, 138.3, 137.3, 136.4, 133.9, 130.9, 128.7, 127.4, 122.0, 121.9, 111.0, 107.2, 33.8, –2.3. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd. for $C_{18}H_{21}N_2Si$, 293.1469; Found, 293.1475.

[12] Y. Gu, Y. Shen, C. Zarate, R. Martin, *J. Am. Chem. Soc.* **2019**, *141*, 127–132.

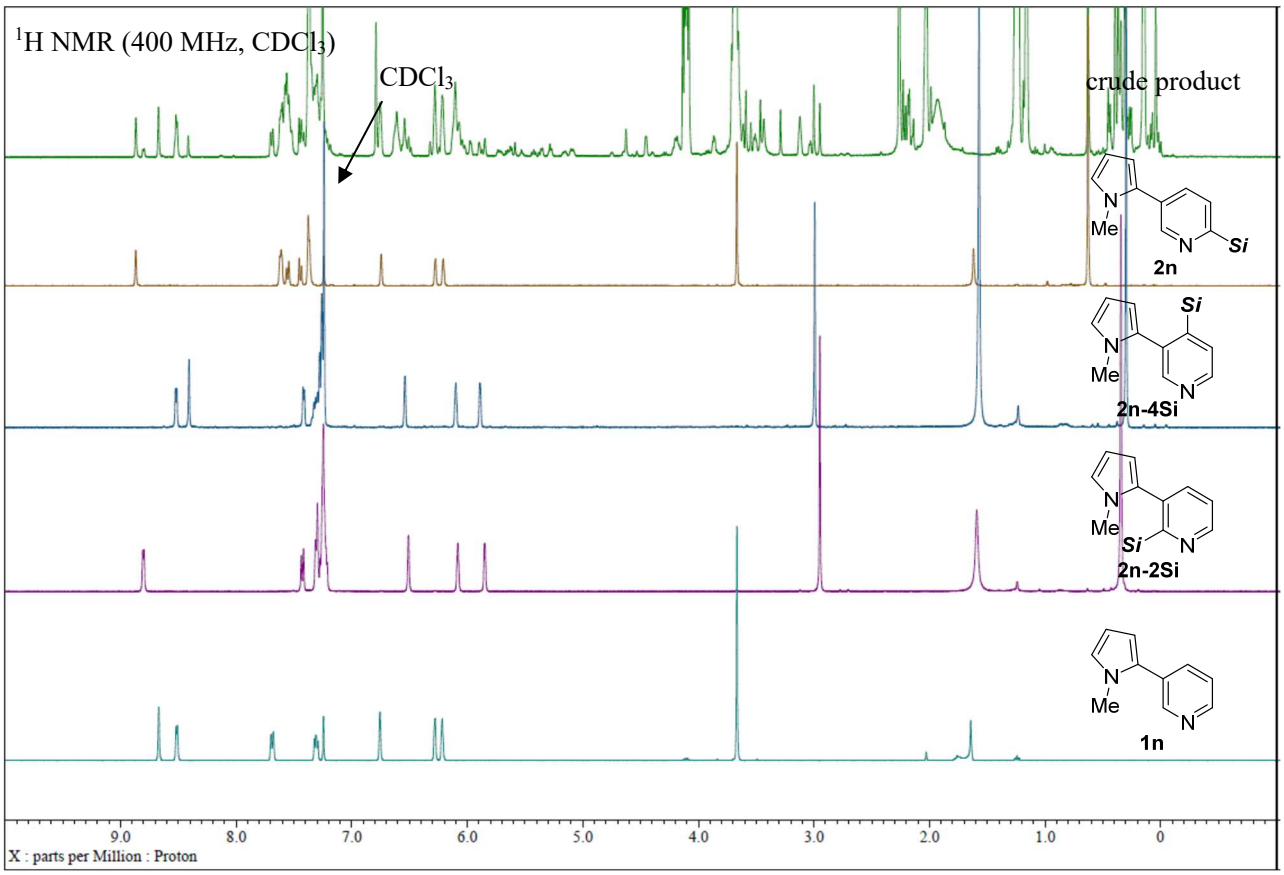
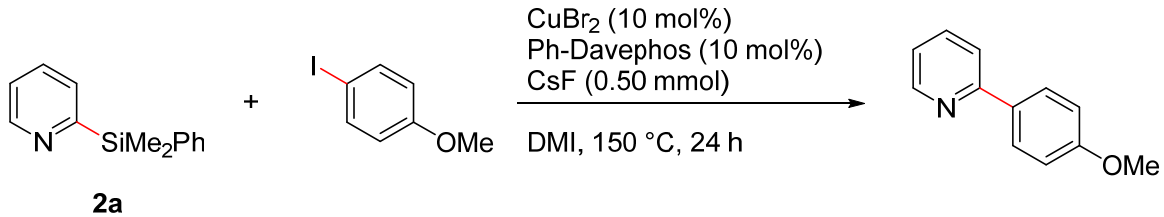


Figure S3. ^{1}H NMR spectra of the crude product, **2n**, **2n-4Si**, **2n-2Si**, and **1n**.

Transformations of 2-Silylpyridines for Scheme 2.

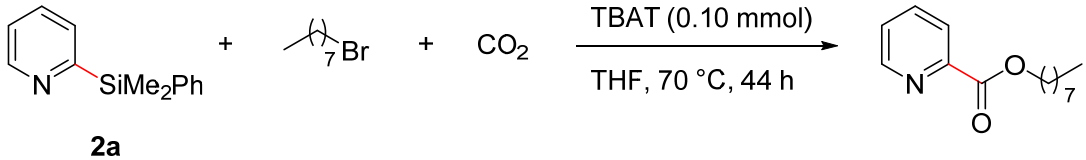
Hiyama coupling of 2-dimethylphenylsilylpyridine.



2a (0.20 mmol) (0.42 mmol) **4**, 55%

We followed the reported procedure for a copper-catalyzed Hiyama coupling.[13]
A 4 mL vial containing a stirring bar charged with copper(ll) bromide (4.5 mg, 20 μmol) and Ph-Davephos (7.6 mg, 20 μmol), was brought into a glove box. To the vial were added 4-iodoanisole (98 mg, 0.42 mmol), **2a** (43 mg, 0.20 mmol), CsF (76 mg, 0.50 mmol) and 1,3-dimethyl-2-imidazolidinone (DMI; 50 μL). The resulting mixture was taken out of the glove box and stirred at 150 ºC for 24 h. The reaction mixture was cooled to room temperature, filtered through a silica pad with dichloromethane (6.0 mL), and concentrated in vacuo. The residue was purified by MPLC (Kanto Chemical silica gel 60, *n*-hexane/EtOAc = 99:1 to 85:15 to 60:40) to afford **4** (20 mg, 0.11 mmol, 55%) as an off-white powder. R_f 0.29 [*n*-hexane/EtOAc (90:10)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 4.1 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.74–7.64 (m, 2H), 7.17 (t, *J* = 6.0 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 2H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 160.4, 157.1, 149.5, 136.6, 132.0, 128.1, 121.4, 119.8, 114.1, 55.3. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[14]

Esterification of 2-dimethylphenylsilylpyridine.



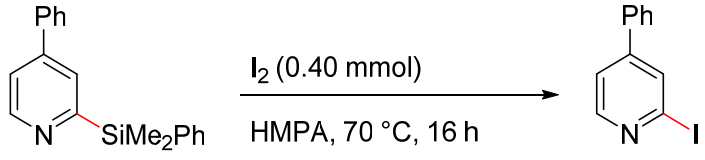
2a (0.10 mmol) (0.10 mmol) (1 atm) **5**, 71%

We followed the reported procedure for an esterification of 2-(dimethyphenylsilyl)pyridine.[15]
A 20 mL Schlenk with a J. Young valve and a stirring bar was charged with **2a** (21 mg, 0.10 mmol), *n*-octylbromide (19 mg, 0.10 mmol), tetrabutylammonium difluorotriphenylsilicate (TBAT; 54 mg, 0.10 mmol), and THF (0.60 mL). The mixture was degassed by a freeze-pump-thaw cycle (three times) and exposed to a CO_2 atmosphere (1 atm). The resulting mixture was stirred at 70 °C for 44 h. The reaction mixture was quenched with water and extracted with Et_2O (8.0 mL x 3) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue

[13] T. Komiyama, Y. Minami, T. Hiyama, *Angew. Chem., Int. Ed.* **2016**, *55*, 15787–15791.
[14] G. Adjabeng, T. Brenstrum, J. Wilson, C. Frampton, A. Robertson, J. Hillhouse, J. McNulty, A. Capretta, *Org. Lett.* **2003**, *5*, 953–955.
[15] X. Frogneux, N. Von Wolff, P. Thuéry, G. Lefèvre, T. Cantat, *Chem. Eur. J.* **2016**, *22*, 2930–2934.

was purified by MPLC (Kanto Chemical silica gel 60, *n*-hexane/EtOAc = 90:10 to 60:40) to afford **5** (17 mg, 71 µmol, 71%) as a slight yellowish oil. R_f 0.68 [*n*-hexane/EtOAc (50:50)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 4.6 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.84 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 6.2 Hz, 1H), 4.41 (t, *J* = 6.9 Hz, 2H), 1.83 (q, *J* = 7.2 Hz, 2H), 1.48–1.20 (m, 10H), 0.87 (t, *J* = 6.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.3, 149.9, 148.3, 136.9, 126.8, 125.1, 66.1, 31.8, 29.2, 29.1, 28.7, 25.9, 22.6, 14.1. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[16]

Iodation of 2-dimethylphenylsilylpyridine.



2l
(0.10 mmol)

6, 82%

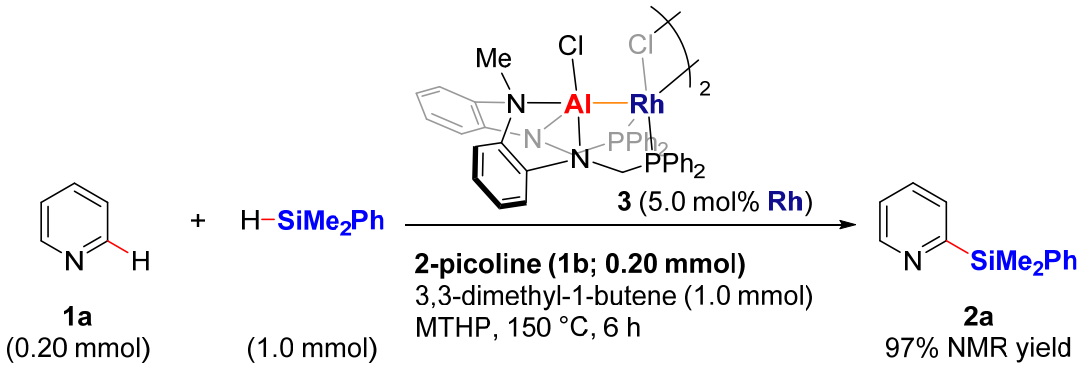
We followed the reported procedure for an iodation of 2-silylisoquinoline.[17]

A 4 mL vial containing a stirring bar was charged with **2l** (21 mg, 0.10 mmol), iodine (0.10 g, 0.40 mmol), and HMPA (0.10 mL) and the resulting mixture was stirred at 70 °C for 16 h. To the reaction mixture was added a 1:1 mixture of NH_4Cl aq./brine (=1/1, 20 mL), and $Na_2S_2O_3$ aq. (20 mL). The mixture was extracted with EtOAc (15 mL x 3) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by MPLC (Kanto Chemical silica gel 60, *n*-hexane/EtOAc = 99:1 to 55:45) to afford **6** (23 mg, 82 µmol, 82%) as a white powder. R_f 0.43 [*n*-hexane/EtOAc (90:10)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 5.0 Hz, 1H), 7.95 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.52–7.44 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 150.8, 150.3, 136.5, 132.7, 129.6, 129.2, 127.0, 121.2, 118.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{11}H_9IN$, 281.9774; Found, 281.9780.

[16] M. Hosseini-Sarvari, E. Sodagar, *Comptes Rendus Chim.* **2013**, *16*, 229–238.
[17] T. Ikawa, H. Urata, Y. Fukumoto, Y. Sumii, T. Nishiyama, S. Akai, *Chem. - A Eur. J.* **2014**, *20*, 16228–16232.

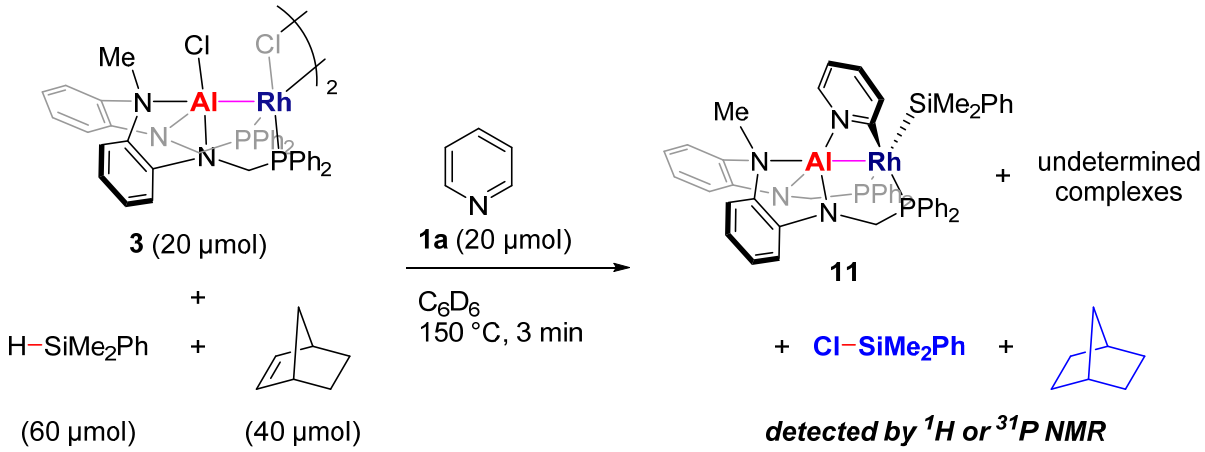
Mechanistic Study.

C2-selective silylation of 1a in the presence of 1b.



In a glove box, a 4 mL vial containing a stirring bar was charged with complex **3** (8.1 mg, 10 μmol), **1a** (16 mg, 0.20 mmol), **1b** (19 mg, 0.20 mmol), dimethylphenylsilane (0.14 g, 1.0 mmol), 3,3-dimethyl-1-butene (84 mg, 1.0 mmol), MTHP (1.0 mL), and *n*-dodecane (8.6 mg, 25 mol%) as an internal standard. The resulting mixture was stirred for 6 h at 150 ºC. The generation of **2a** was confirmed by GC analysis of the reaction mixture. The reaction mixture was cooled to room temperature and filtered through a celite plug with EtOAc. All the volatiles were removed in vacuo and the NMR yield of **2a** was determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

Identification of byproducts.



In a glove box, a 4 mL vial containing a stirring bar was charged with complex **3** (16 mg, 20 μmol), **1a** (1.6 mg, 20 μmol), dimethylphenylsilane (8.2 mg, 60 μmol), norbornene (3.8 mg, 40 μmol), and C_6D_6 (0.60 mL). The resulting mixture was stirred for 3 min at 150 ºC and then analyzed by ^{1}H and ^{31}P NMR spectroscopy (Figure S4 and S5). After removal of all the volatiles, the residue was extracted with hexane (0.50 mL x 3) and dried under reduced pressure and analyzed again by ^{1}H NMR spectroscopy (Figure S6).

After the reaction, norbornane, Cl–SiMe$_2$Ph, and complex **11** were detected by ^{1}H and ^{31}P NMR spectroscopies (Figure S4 to S6), suggesting that complex **3** is reduced by norbornene and H–SiMe$_2$Ph to afford complex **7**, which rapidly reacts with **1a**, H–SiMe$_2$Ph, and norbornene to afford complex **11**. Although we tried to identify other detected complexes by the reaction of complex **3** with the reaction reagents, we cannot find the same resonances on ^{31}P NMR spectroscopy.

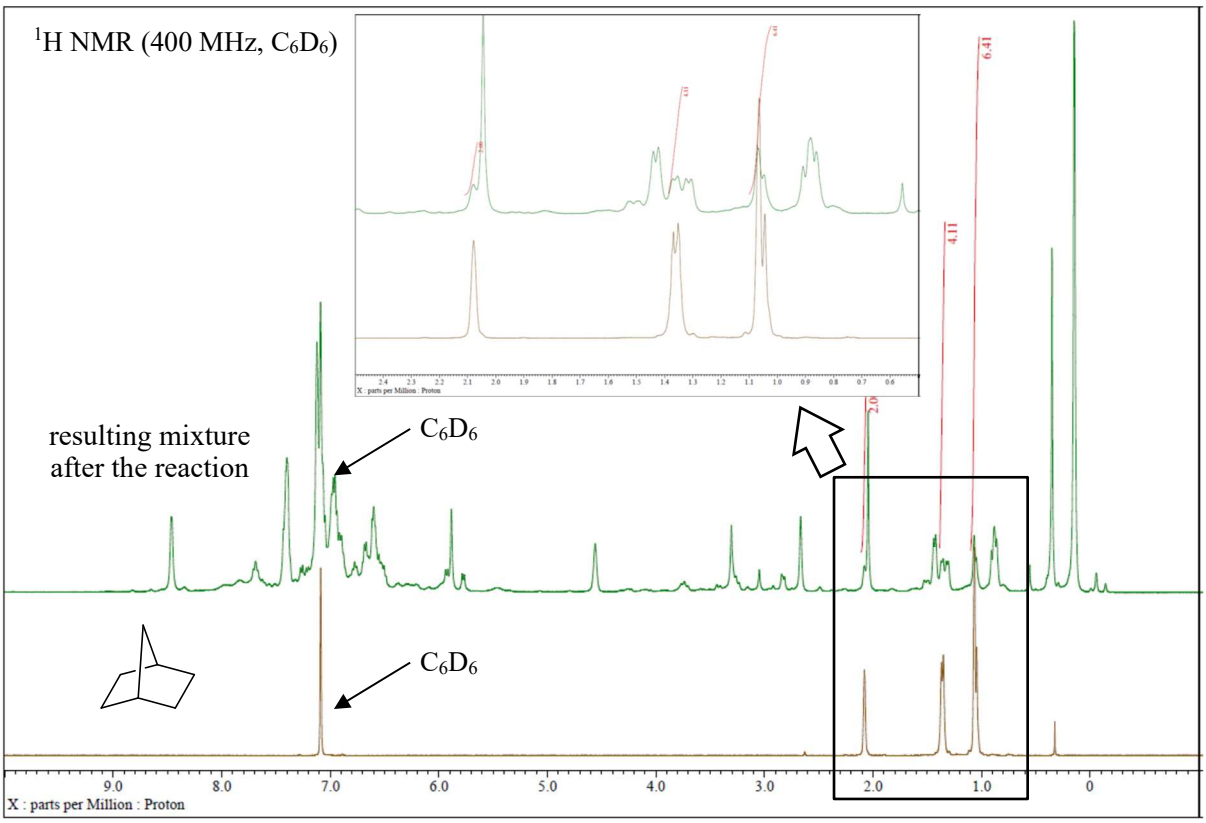


Figure S4. Top: ^{1}H NMR spectra of the resulting mixture after the reaction. Bottom: ^{1}H NMR spectra of norbornane.

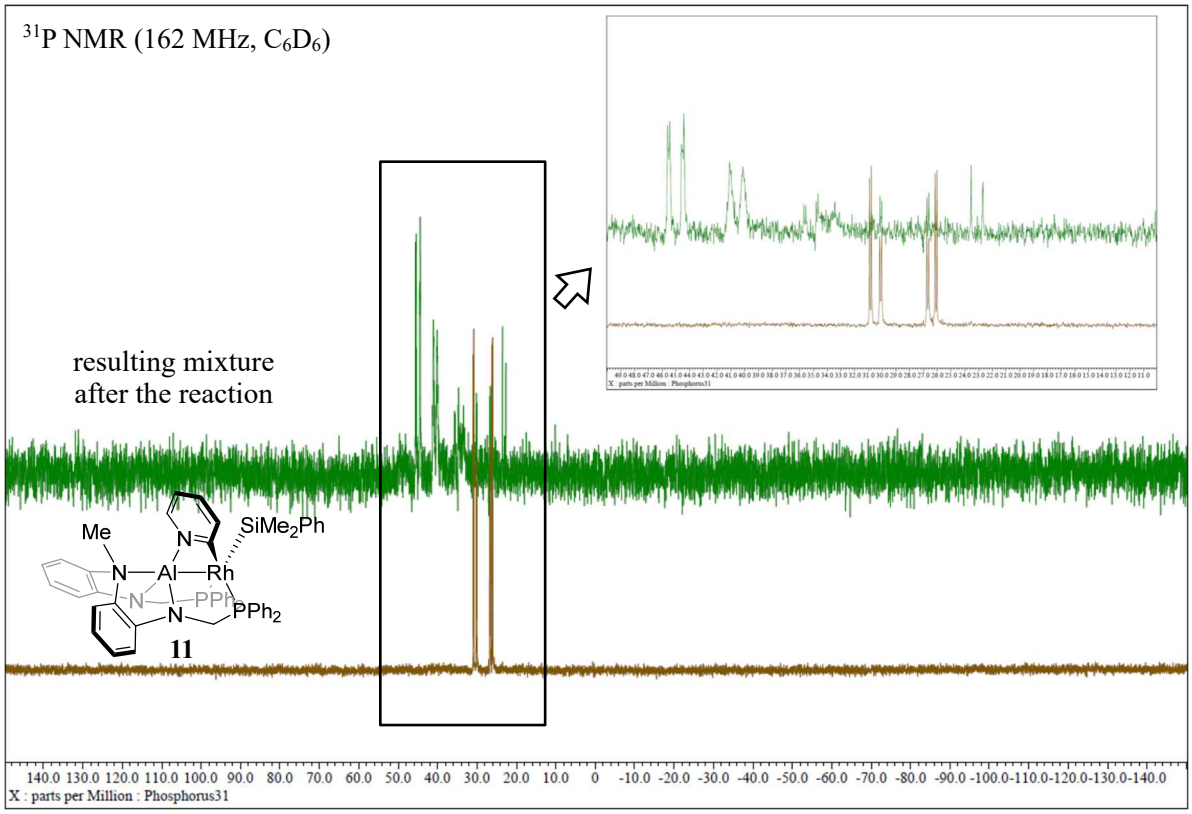


Figure S5. Top: ^{31}P NMR spectrum of the resulting mixture after the reaction. Bottom: ^{31}P NMR spectrum of complex **11**.

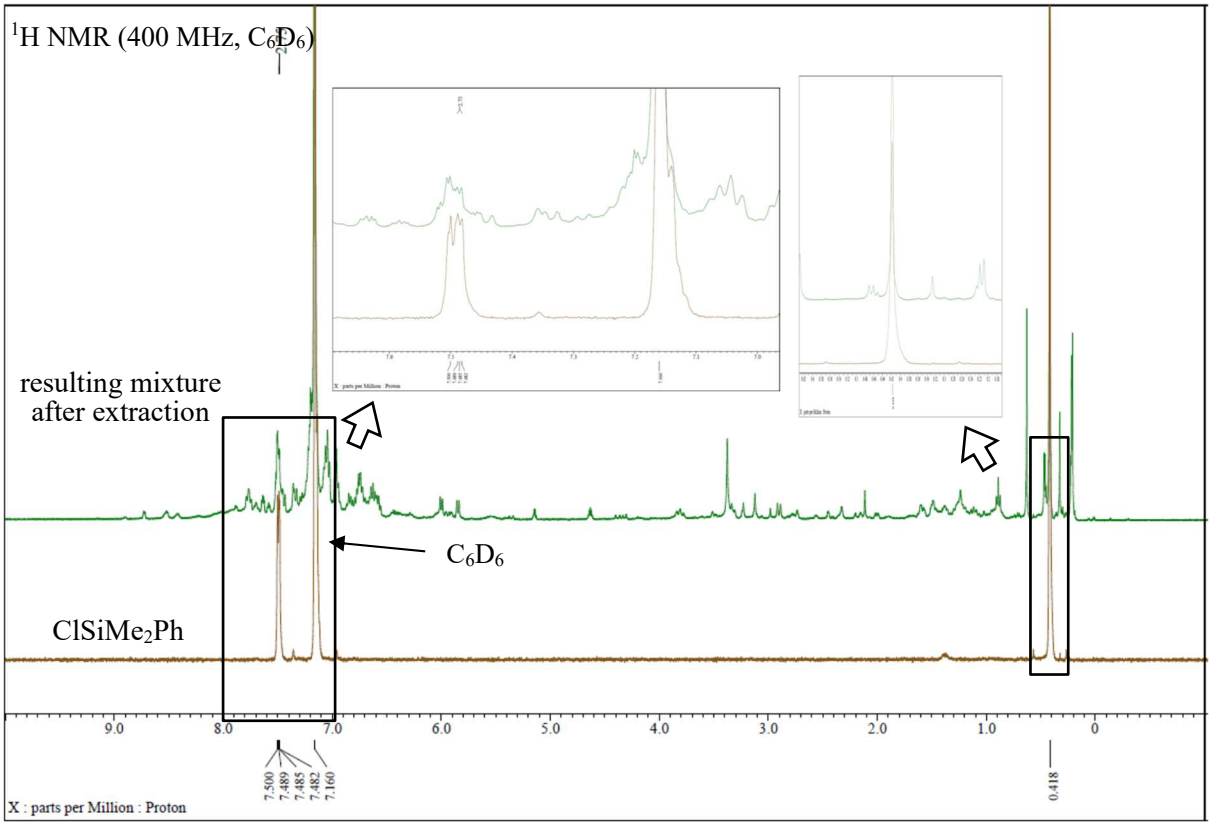
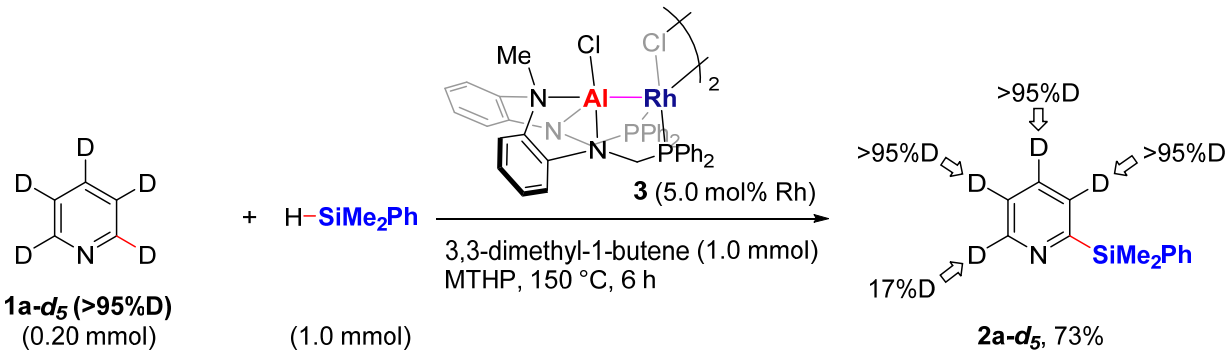


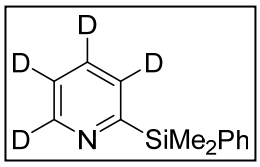
Figure S6. Top: ^{1}H NMR spectrum of the resulting mixture after extraction. Bottom: ^{1}H NMR spectrum of $ClSiMe_2Ph$.

Deuterium-labeling experiment.



In a glove box, a 4 mL vial containing a stirring bar was charged with complex **3** (8.1 mg, 5.0 mol% Rh), pyridine-d_5 (**1a-*d*$_5$**; 17 mg, 0.20 mmol), dimethylphenylsilane (0.14 g, 1.0 mmol), 3,3-dimethyl-1-butene (84 mg, 1.0 mmol), MTHP (1.0 mL), and *n*-dodecane (8.6 mg, 25 mol%) as an internal standard. The resulting mixture was stirred for 6 h at 150 ºC. The reaction mixture was cooled to room temperature, filtered through a celite plug with EtOAc, and concentrated in vacuo. The residue was purified by MPLC (Wakogel® 50NH2, *n*-hexane/EtOAc/NEt_3 = 99:1:1 to 95:5:1) to afford **2a-*d*$_5$** as a slight yellowish oil (32 mg, 0.15 mmol, 73%).

Deuteriums of **2a-*d*$_5$** at the C3-, C4-, and C5-positions remained, while H/D exchange took place at the C6-position and decreased the deuterium ratio to 17% based on Figure S7. These results suggest a Rh–Al complex activates the C(2)–H bond of pyridine exclusively and the oxidative addition step and alkene insertion step are reversible, consistent with the mechanistic study in our previous work.[2]



R_f 0.14 [NH2 Silica Gel 60 F254 Plate-Wako, *n*-hexane/EtOAc (99:1)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 0.83H), 7.63–7.57 (m, 2H), 7.41–7.33 (m, 3H), 0.62 (s, 6H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.5, 150.2, 137.2, 134.2, 133.5 (t, $J_{D–C}$ = 25 Hz), 129.2 (t, $J_{D–C}$ = 25 Hz), 129.2, 127.8, 122.4 (t, $J_{D–C}$ = 25 Hz), –3.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{13}H_{12}D_3NSi$, 217.1235; Found, 217.1234.

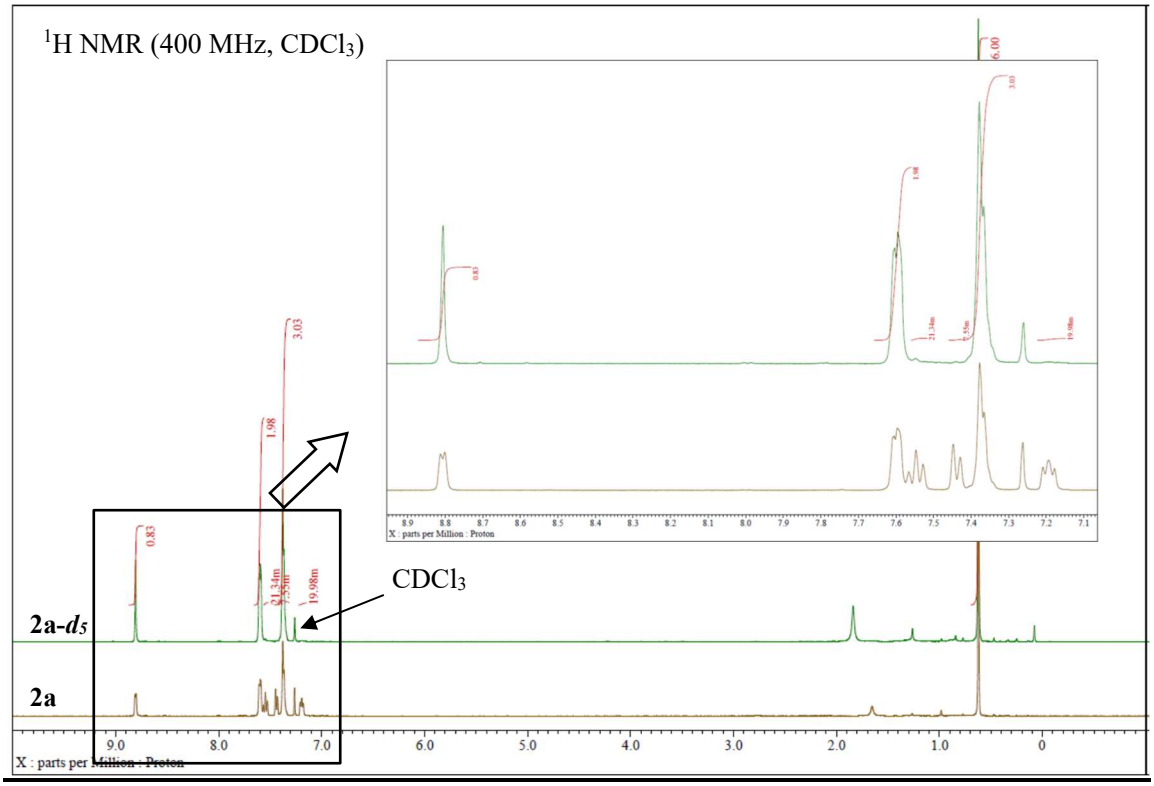
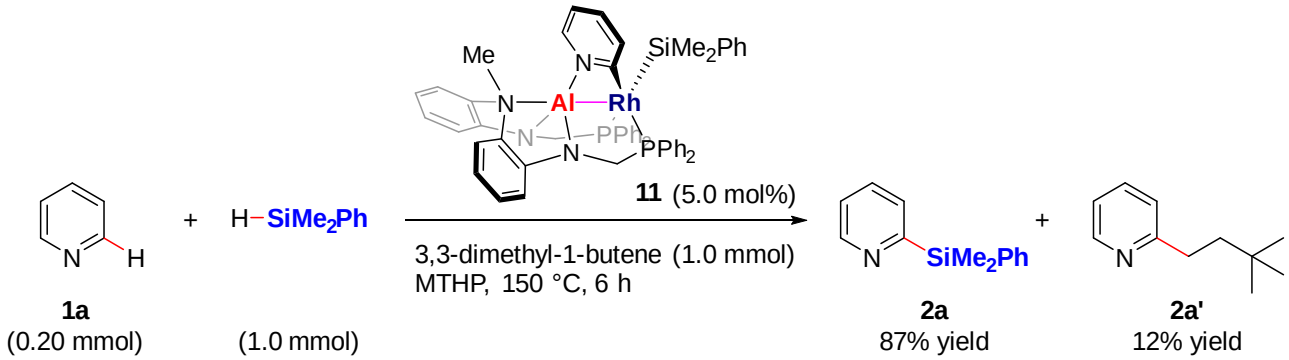


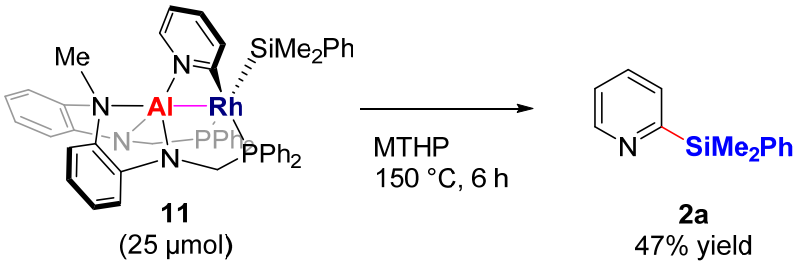
Figure S7. Top: ^{1}H NMR spectra of **2a**-d_5. Bottom: ^{1}H NMR spectra of **2a**.

C2-Selective silylation of pyridine catalyzed by complex 11.



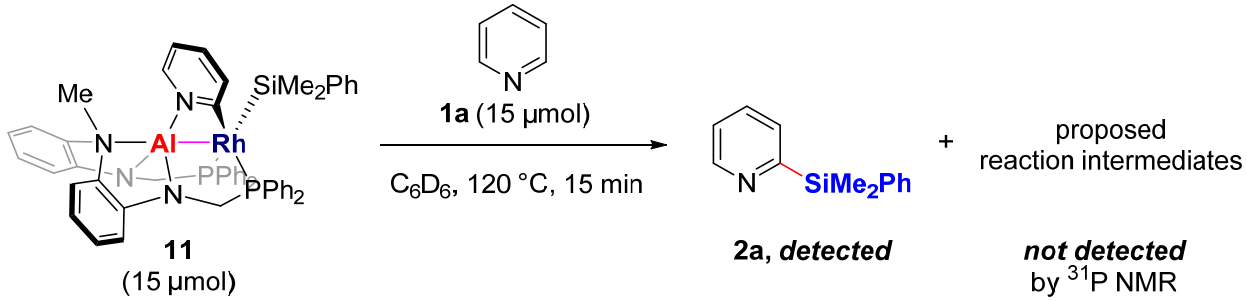
In a glove box, a 4 mL vial containing a stirring bar was charged with complex **11** (10 mg, 10 μmol), **1a** (16 mg, 0.20 mmol), dimethylphenylsilane (0.14 g, 1.0 mmol), 3,3-dimethyl-1-butene (84 mg, 1.0 mmol), MTHP (1.0 mL), and *n*-dodecane (8.6 mg, 25 mol%) as an internal standard. The resulting mixture was stirred for 6 h at 150 ºC. The generation of **2a** was confirmed by GC analysis of the reaction mixture. The reaction mixture was cooled to room temperature and filtered through a celite plug with EtOAc. All the volatiles were removed in vacuo and the NMR yield of **2a** and **2a'** were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Reductive elimination from complex 11.



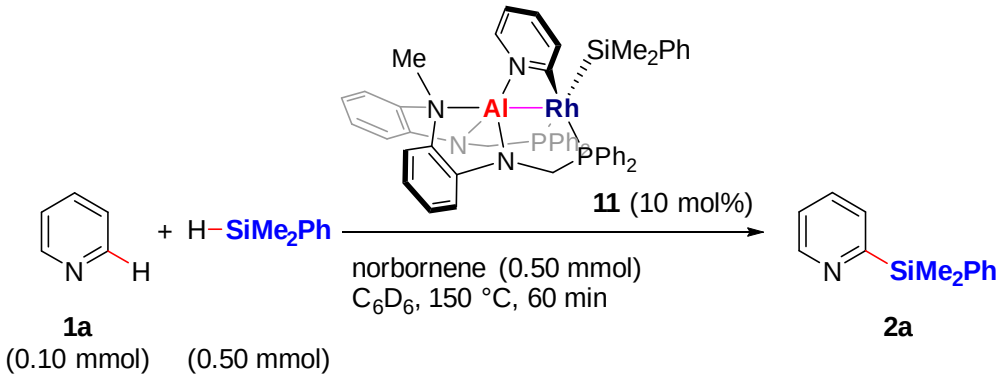
In a glove box, a 4 mL vial containing a stirring bar was charged with complex **11** (24 mg, 25 μmol), MTHP (1.0 mL), and *n*-dodecane (8.6 mg, 50 μmol) as an internal standard. The resulting mixture was stirred for 6 h at 150 ºC. The generation of **2a** was confirmed by GC analysis of the reaction mixture. The reaction mixture was cooled to room temperature, filtered through a celite plug with EtOAc, and concentrated in vacuo. The NMR yield of **2a** was determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

Reaction of complex 11 with 1a.



In a glove box, a 4 mL vial containing a stirring bar was charged with complex **11** (14 mg, 15 μmol), **1a** (1.2 mg, 15 μmol), and C_6D_6 (0.60 mL). The resulting mixture was transferred to a J. Young NMR tube, heated for 15 min at 120 ºC, and then analyzed by ^{1}H and ^{31}P NMR spectroscopies. The generation of **2a** was detected, but proposed reaction intermediates were not. This is probably because the intermediates except for complex **11** could be unstable to observe, supported by the fact that the reaction of complex **7(nbd)** with **1a** and H–$SiMe_2Ph$ only afforded complex **11,** as shown in Scheme 3.

NMR time-course study of the silylation catalyzed by complex 11.



In a glove box, a 4 mL vial containing a stirring bar was charged with **11** (10 mg, 10 mol%), **1a** (7.9 mg, 0.10 mmol), dimethylphenylsilane (68 mg, 0.50 mmol), norbornene (47 mg, 0.50 mmol), C_6D_6 (0.60 mL), and *n*-dodecane (8.6 mg, 50 mol%) as an internal standard. The resulting mixture was stirred at 150 ºC, and analyzed at 0, 10, 30, and 60 min by GC and ^{1}H and ^{31}P NMR spectroscopy.

While the reaction was proceeding, complex **11** was always observed though it was being decomposed gradually (Figure S8 and S9). These results support that complex **11** would be a resting state of the reaction.

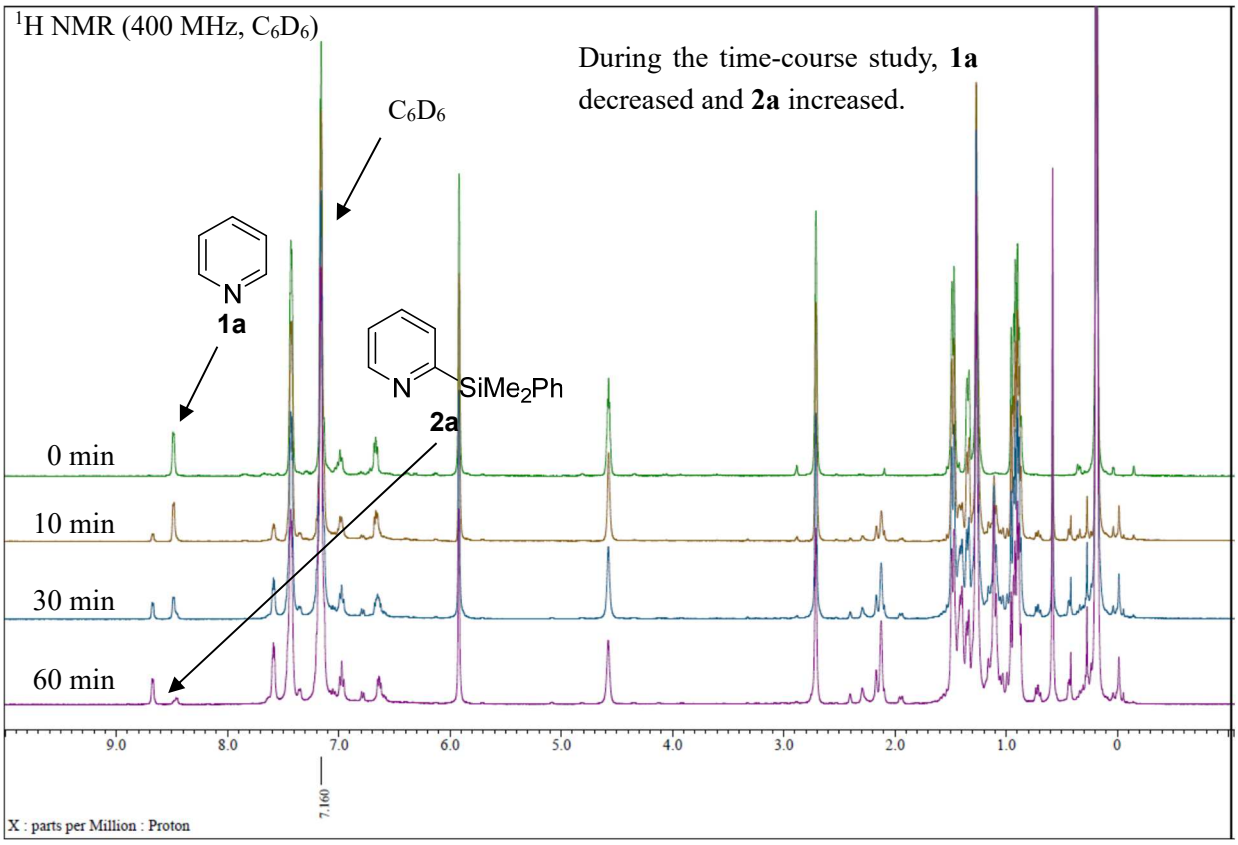


Figure S8. ^{1}H NMR spectra during the silylation catalyzed by complex **11**.

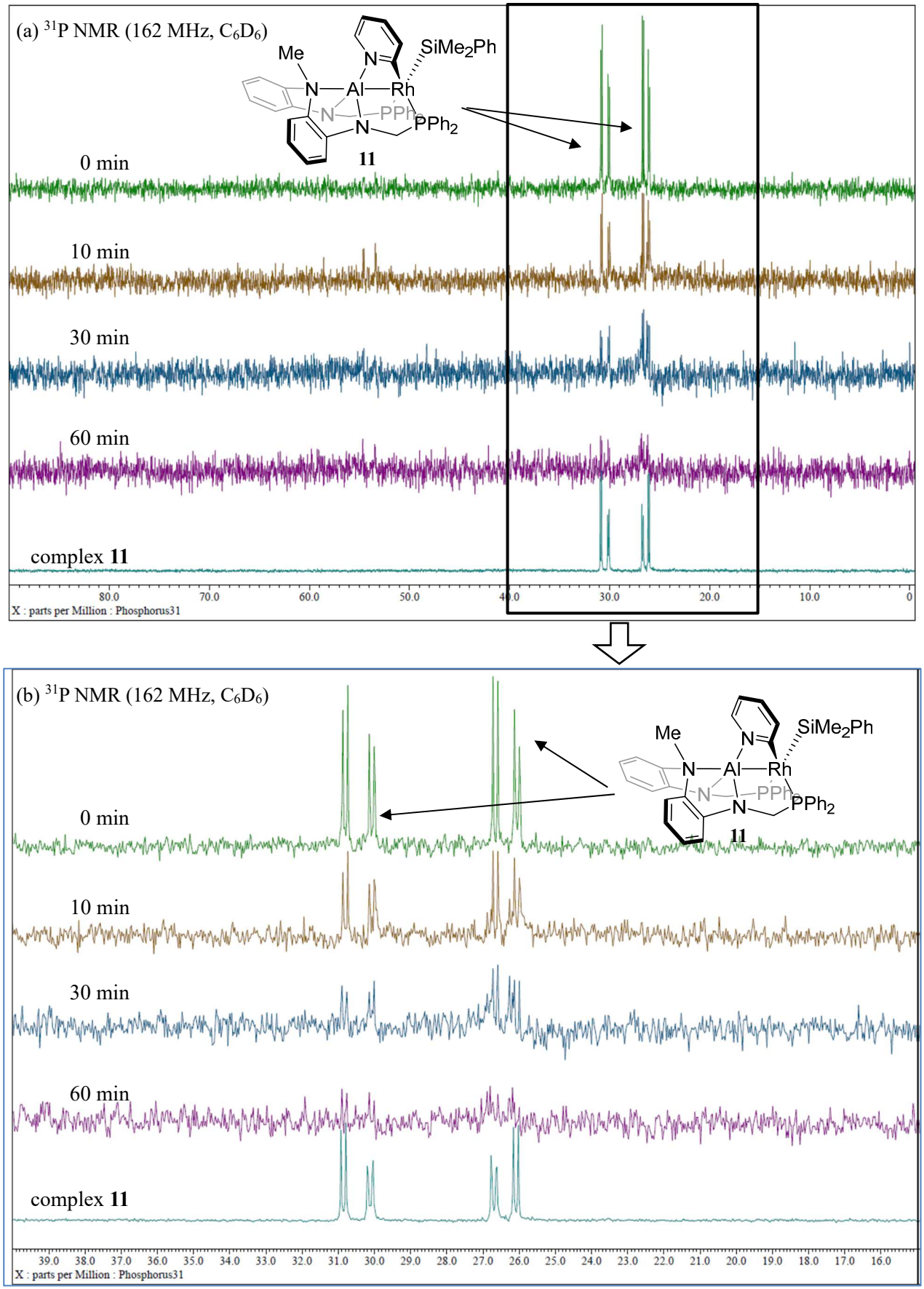
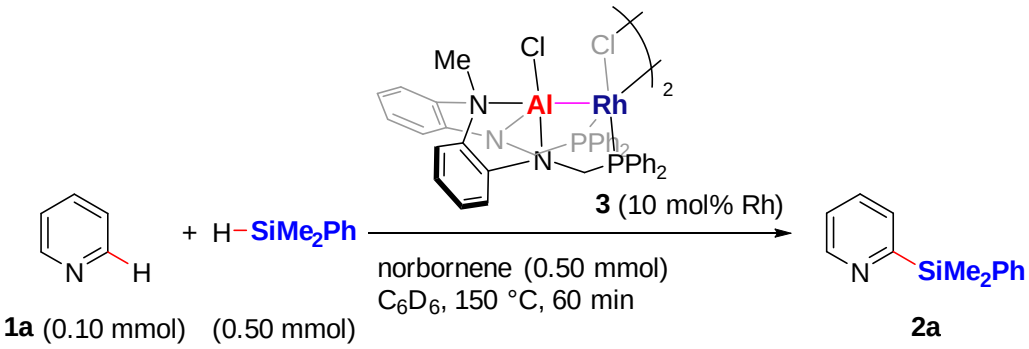


Figure S9. (a) ^{31}P NMR spectra during the silylation catalyzed by complex **11**. (b) Enlarged ^{31}P NMR spectra of (a).

NMR time-course study of the silylation catalyzed by complex 3.



In a glove box, a 4 mL vial containing a stirring bar was charged with complex **3** (8.1 mg, 10 mol% Rh), **1a** (7.9 mg, 0.10 mmol), dimethylphenylsilane (68 mg, 0.50 mmol), norbornene (47 mg, 0.50 mmol), C_6D_6 (0.70 mL), and *n*-dodecane (8.6 mg, 50 mol%) as an internal standard. The resulting mixture was stirred at 150 ºC, and analyzed at 0 min, 5 min, 15 min, and 60 min by ^{1}H and ^{31}P NMR spectroscopy and GC.

While the reaction was proceeding, complex **11** and two new complexes at 16.0 ppm (dd, J_{Rh-P} = 98 Hz, J_{P-P} = 20 Hz) and 60.8 ppm (dd, J_{Rh-P} = 174 Hz, J_{P-P} = 22 Hz), respectively, were mainly detected (Figure S10 and S11). Although we tried to synthesize and identify these complexes by the reaction of complex **3** with the reaction reagents, we cannot find the same resonances. Considering that these complexes were not detected on the silylation catalyzed by **11** (Figure S9), they may be formed from the reduction of **3** to the formation of **11**.

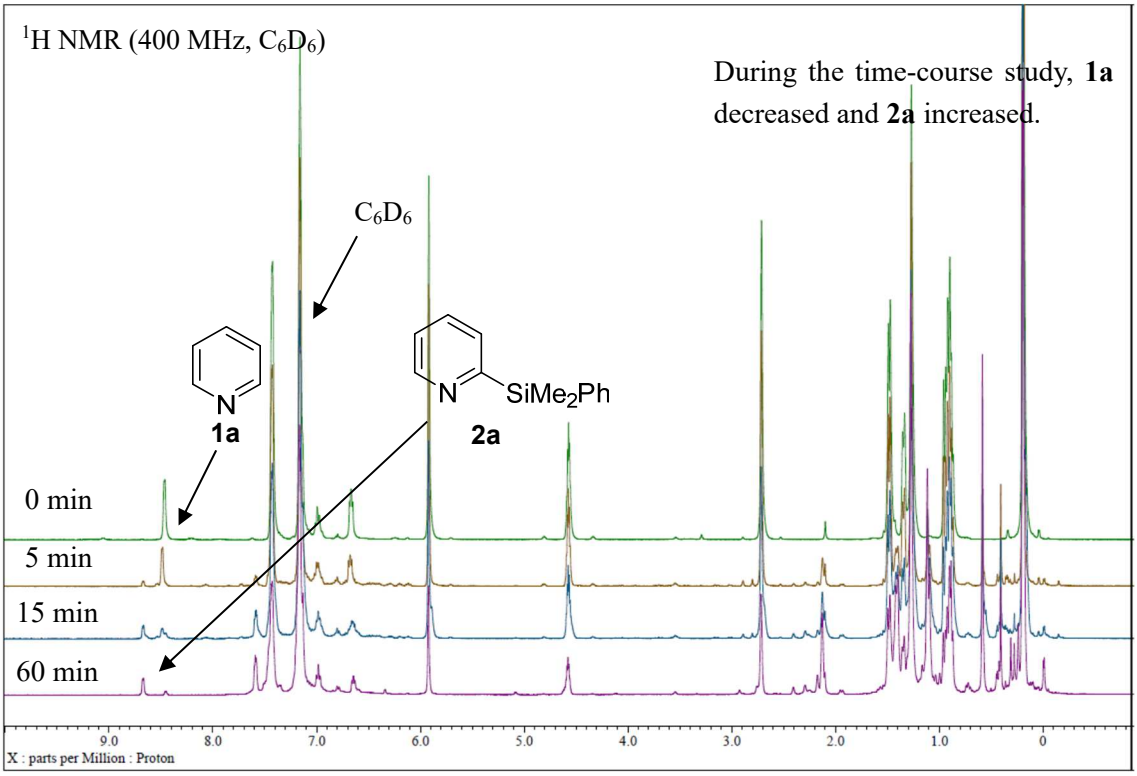


Figure S10. ^{1}H NMR spectra during the silylation catalyzed by complex **3**.

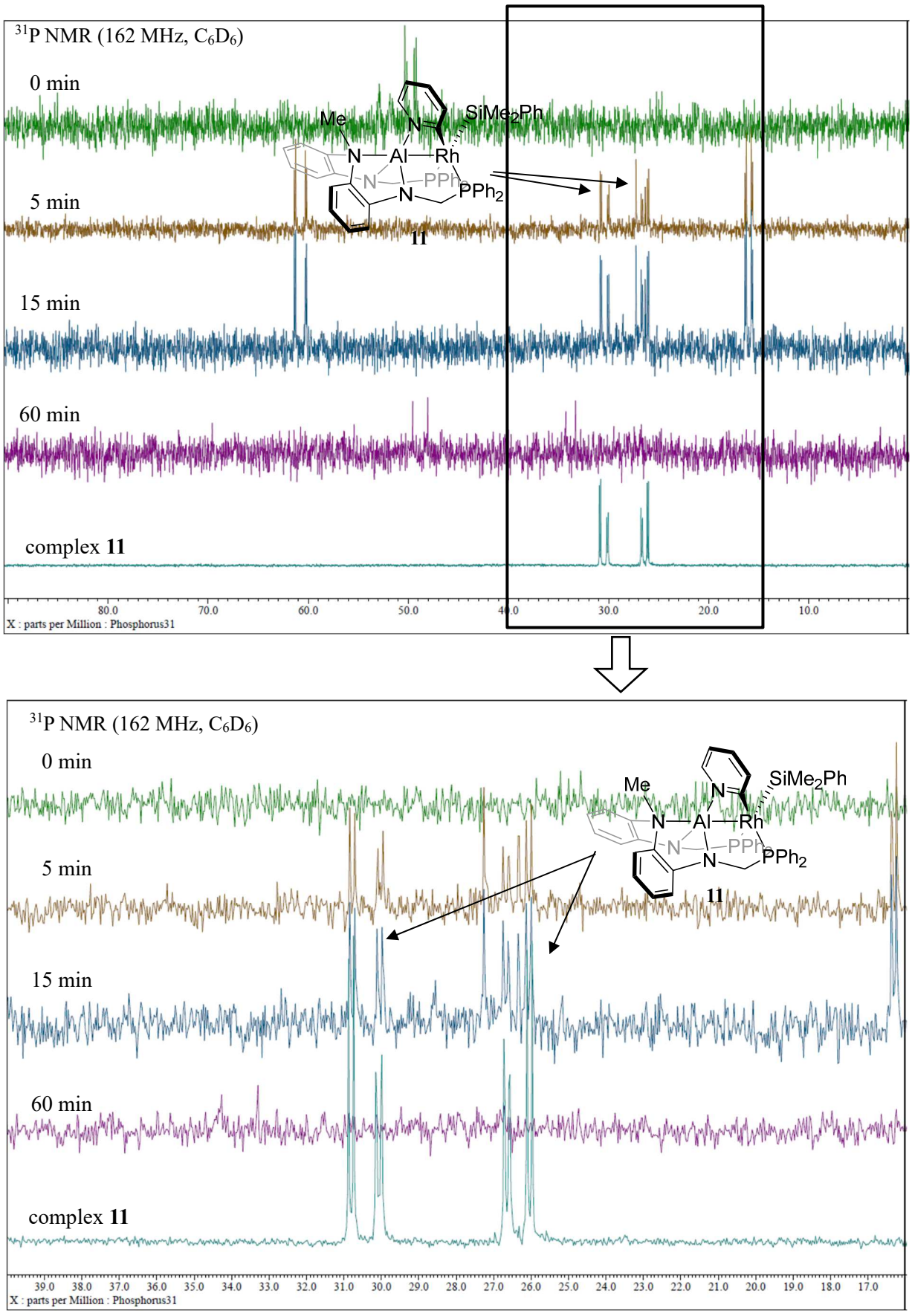


Figure S11. (a) ^{31}P NMR spectra during the silylation catalyzed by complex **3**. (b) Enlarged ^{31}P NMR spectra of (a).

X-ray Diffraction Study and X-Ray Crystallographic Analysis.

The crystal of **8(nbd)-DMAP** and **11** were mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 143(1) K. The X-ray structural determination was performed on a Rigaku Saturn724+ CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) at 143 K, and processed using CrystalClear (Rigaku).[18] All calculations were performed using OLEX2 (Rigaku).[19] The structure was solved by direct methods using SHELXT[20] and refined by full-matrix least-square refinement on *F*2 with SHELXL.[21] The non-hydrogen atoms were refined anisotropically except for the disordered atoms. All hydrogen atoms were located at the calculated positions. Solvent mask was applied to remove the disordered cocrystallized solvent. The function minimized was $[\Sigma w(F_o^2 - F_c^2)^2]$ (w = 1 / $[\sigma^2(F_o^2) + (aP)^2 + bP]$), where P = (Max($F_o^2$,0) + 2$F_c^2$) / 3 with $\sigma^2(F_o^2)$ from counting statistics. The function *R*1 and *wR*2 were $(\Sigma||F_o| - |F_c||) / \Sigma|F_o|$ and $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma(wF_o^4)]^{1/2}$, respectively. CCDC 2024383 and 2056314 (Depositions Number) contains the supplementary crystallographic data. These data can be obtained from The Cambridge Crystallographic Data Centre.

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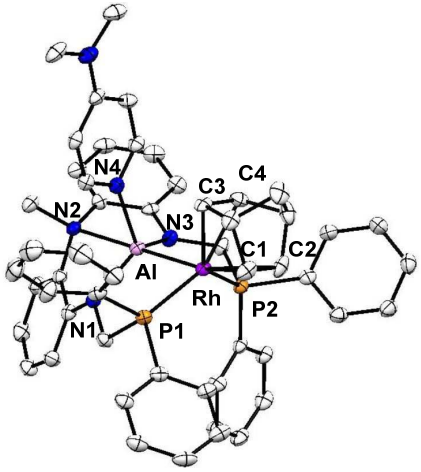
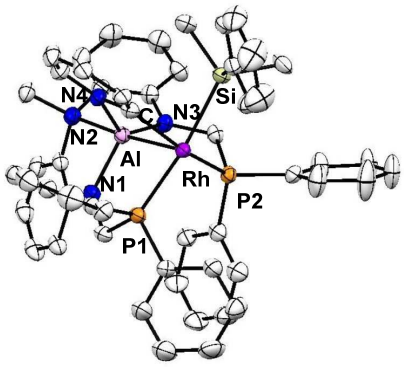
[18] (a) Rigaku Corporation, **1999**, and CrystalClear Software User's Guide, Molecular Structure Corporation, **2000**; (b) Pflugrath, J. W. Acta Cryst. **1999**, *D55*, 1718.
[19] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.
[20] Sheldrick, G. M. *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3.
[21] Sheldrick, G. M. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3.

Table S2. Crystal structure and crystallographic data of **8(nbd)-DMAP** and **11.**



8(nbd)-DMAP



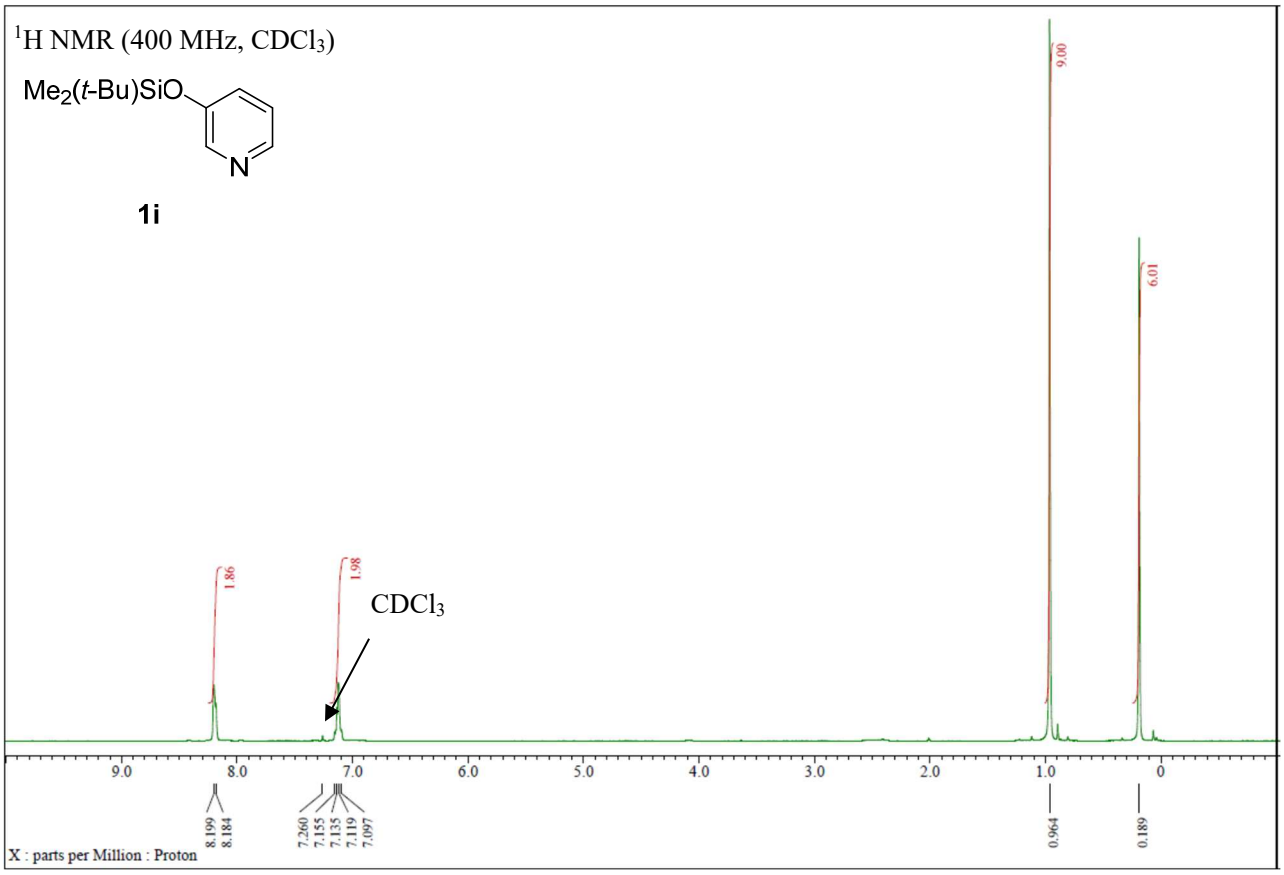
11

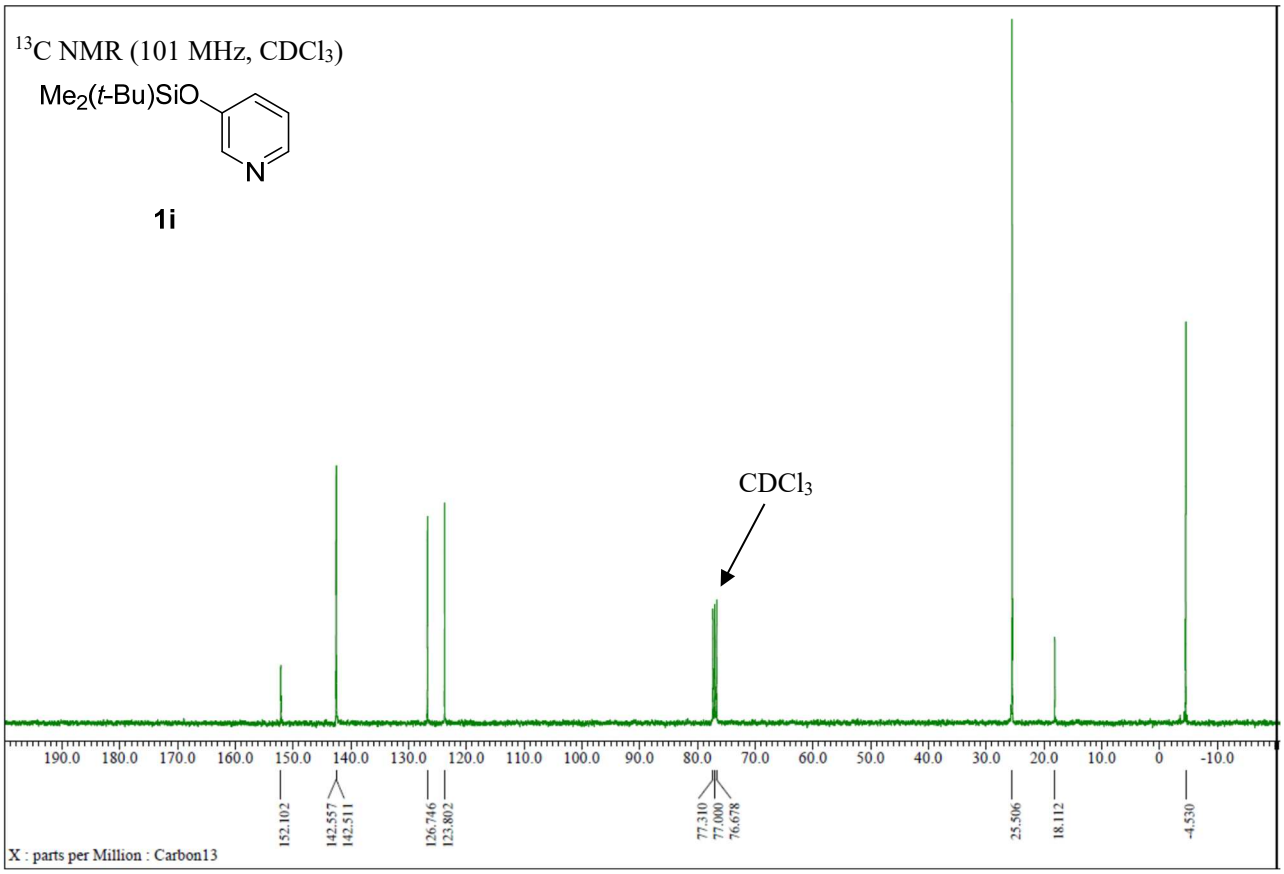
Crystal structure of **14** (atomic displacement parameters set at 30% probability; all hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: **8(nbd)-DMAP**. Rh–Al, 2.488(4); Rh–P1, 2.247(4); Rh–P2, 2.255(5); Rh–C1, 2.463(5); Rh–C2, 2.440(4); Rh–C3, 2.188(6); Rh–C4, 2.185(5); Al–N1, 1.894(4); Al–N2, 2.427(4); Al–N3, 1.887(4); Al–N4, 1.993(5); C1–C2, 1.527(6); C3–C4, 1.424(5); P1–Rh–P2, 118.22(8); Rh–Al–N4, 99.63(11); Rh–Al–N2, 179.50(8); N1–Al–N3, 116.96(17); N1–Al–N4, 118.35(13); N3–Al–N4, 109.45(19); **11**. Rh–Al, 2.4717(12); Rh–P1, 2.3092(10); Rh–P2, 2.2523(9); Rh–Si, 2.4095(11); Rh–C, 2.034(4); Al–N1, 1.875(3); Al–N2, 2.183(3); Al–N3, 1.872(3); Al–N4, 1.975(3); P1–Rh–P2, 101.97(3); P2–Rh–Si, 91.51(3); Si–Rh–C, 79.78(10); C–Rh–P1, 88.94(10); Rh–Al–N2, 174.64(10); N1–Al–N3, 114.18(14); N3–Al–N4, 133.54(14); N1–Al–N4, 112.07(13).

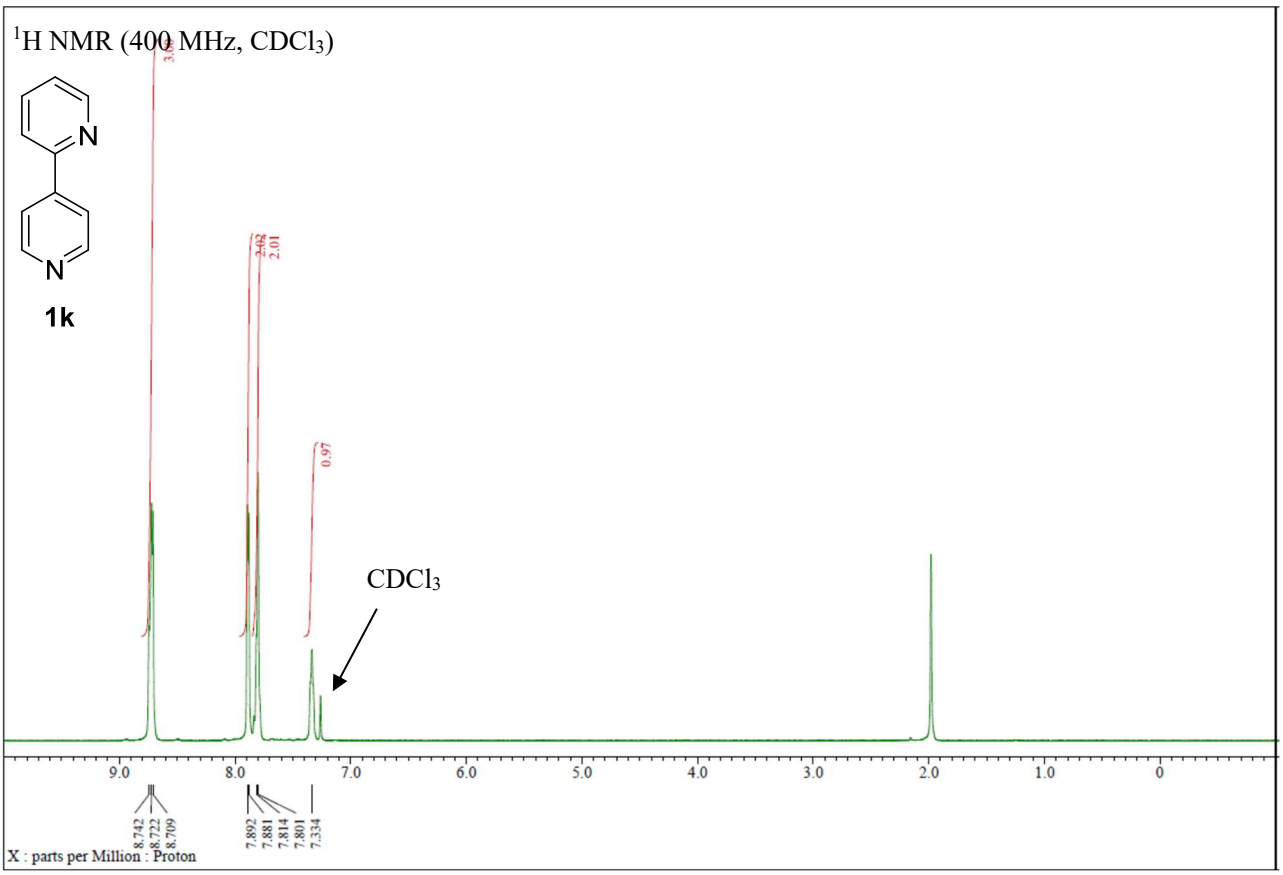
compound	**8(nbd)-DMAP**	**11**
empirical formula	$C_{53}H_{53}AlN_5P_2Rh$	$C_{52}H_{50}AlN_4P_2RhSi$
formula weight	951.83	950.88
crystal system	triclinic	orthorhombic
space group	*P* –1 (#2)	*P b c a* (#61)
a, Å	10.528(18)	29.694(5)
b, Å	11.89(3)	10.5922(16)
c, Å	20.18(3)	32.967(5)
α, deg.	90.03(5)	90
β, deg.	97.48(5)	90
γ, deg.	105.32(5)	90
V, $Å^3$	2414(8)	10369(3)
Z	2	8
*D*calcd, g/cm^{-3}	1.309	1.218
μ [Mo-*K*α], mm^{-1}	0.479	0.467
T, K	143	143
crystal size, mm	0.12 x 0.12 x 0.090	0.111 x 0.070 x 0.050
θ range for data collection (deg.)	3.03 to 27.5	3.00 to 27.50
no. of reflections measured	19679	72398
unique data	10587	11716
data / restraints / parameters	10587 / 0/ 562	11716 / 0 / 553
*R*1 ($I > 2.0\sigma(I)$)	0.0464	0.0611
*wR*2 ($I > 2.0\sigma(I)$)	0.0915	0.1147
*R*1 (all data)	0.0562	0.0797
*wR*2 (all data)	0.0969	0.1239
GOF on F^2	1.073	1.094

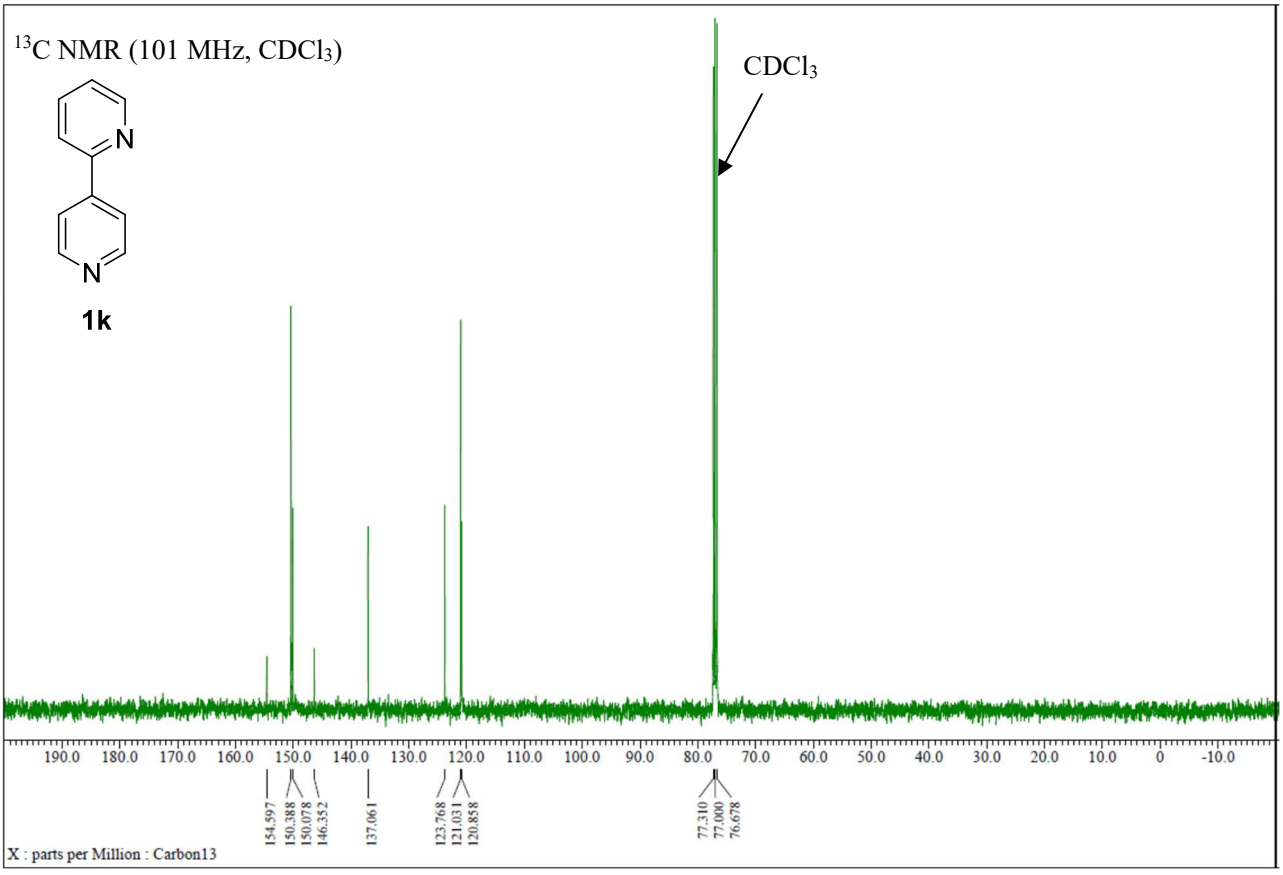
a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

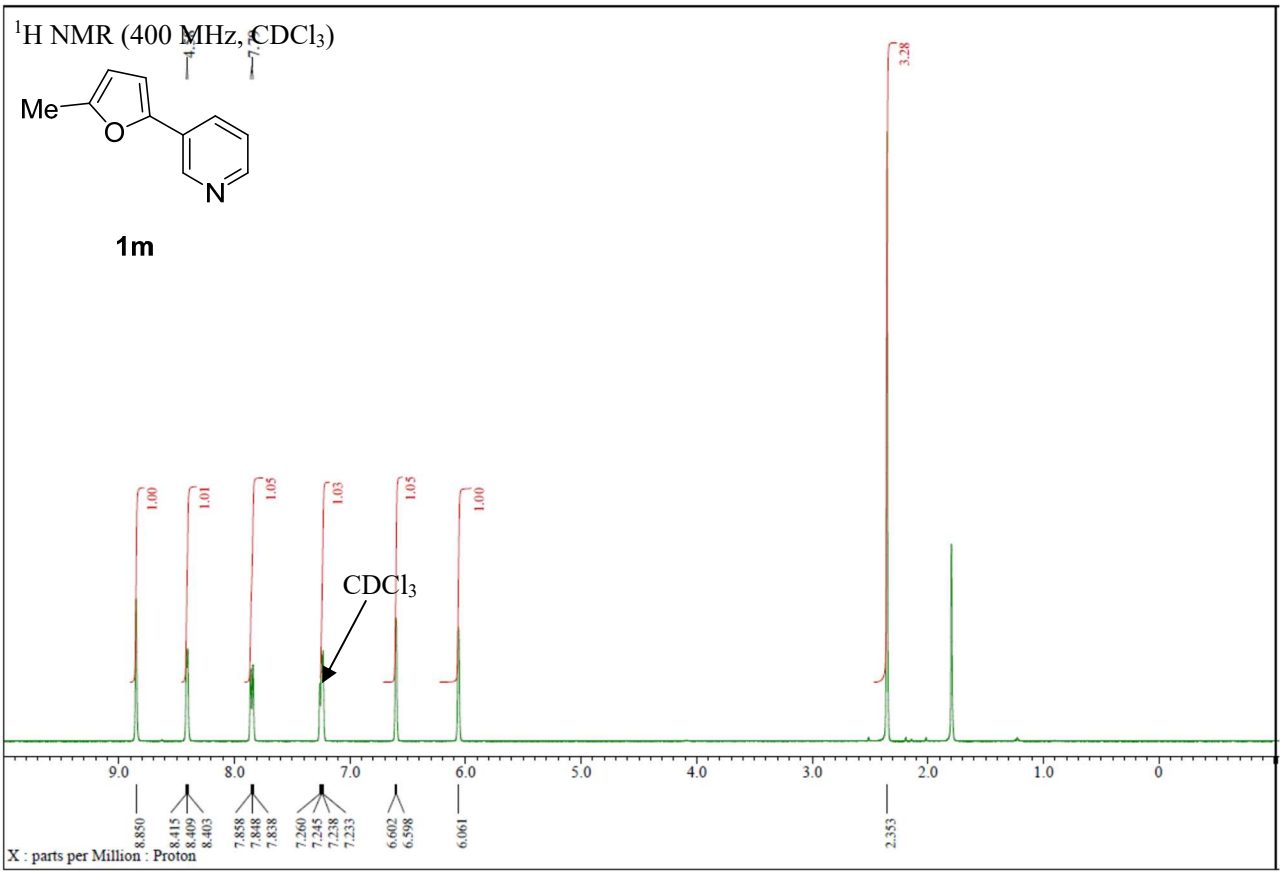
NMR Spectra.

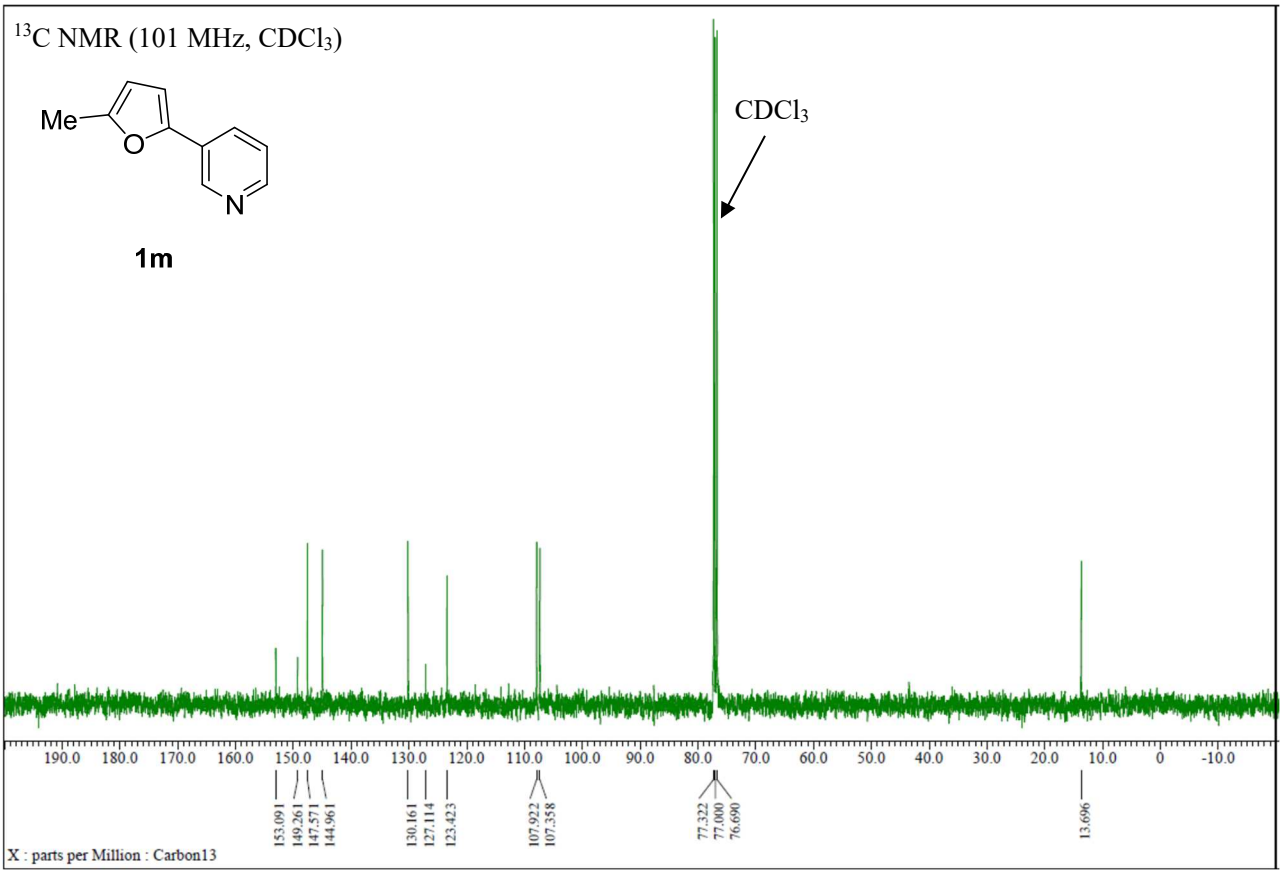

^{1}H NMR (400 MHz, $CDCl_3$)
$Me_2(t\text{-}Bu)SiO$
N
1i
9.00
6.01
1.86
1.98
$CDCl_3$
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.199
8.184
7.260
7.155
7.135
7.119
7.097
0.964
0.189
X : parts per Million : Proton


^{13}C NMR (101 MHz, $CDCl_3$)
$Me_2(t\text{-}Bu)SiO$
N
1i
$CDCl_3$
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
152.102
142.557
142.511
126.746
123.802
77.310
77.000
76.678
25.506
18.112
-4.530
X : parts per Million : Carbon13

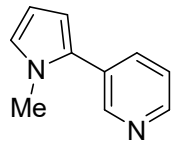

1H NMR (400 MHz, CDCl3)
1k
CDCl3
X : parts per Million : Proton


13C NMR (101 MHz, CDCl3)
1k
CDCl3
X : parts per Million : Carbon13


^{1}H NMR (400 MHz, $CDCl_3$)
Me
O
N
1m
3.28
1.00
1.01
1.05
1.03
1.05
1.00
$CDCl_3$
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.850
8.415
8.409
8.403
7.858
7.848
7.838
7.260
7.245
7.238
7.233
6.602
6.598
6.061
2.353
X : parts per Million : Proton

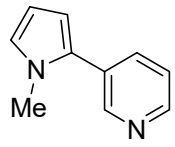

^{13}C NMR (101 MHz, $CDCl_3$)
Me
O
N
1m
$CDCl_3$
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
153.091
149.261
147.571
144.961
130.161
127.114
123.423
107.922
107.358
77.322
77.000
76.690
13.696
X : parts per Million : Carbon13

^{1}H NMR (400 MHz, $CDCl_3$)



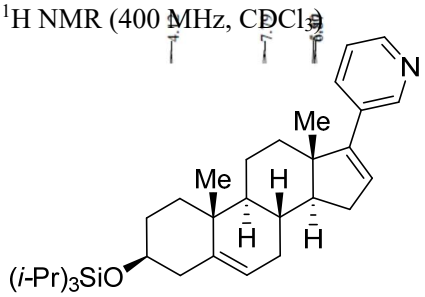
1n

^{13}C NMR (101 MHz, $CDCl_3$)



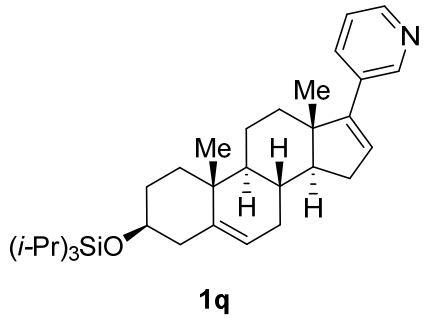
1n

^{1}H NMR (400 MHz, $CDCl_3$)



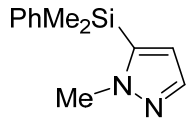
1q

^{13}C NMR (101 MHz, $CDCl_3$)



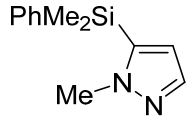
1q

^{1}H NMR (400 MHz, $CDCl_3$)

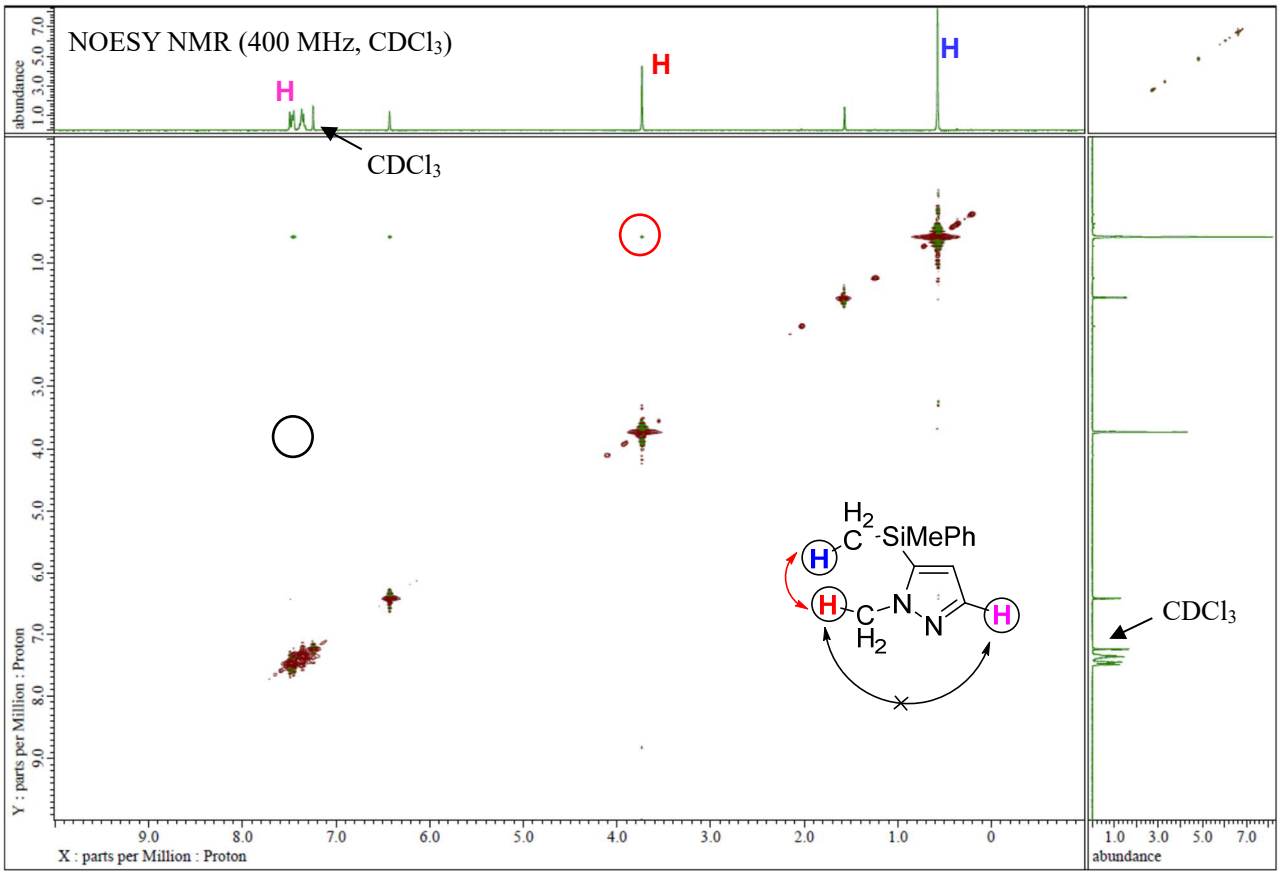


2q-5Si

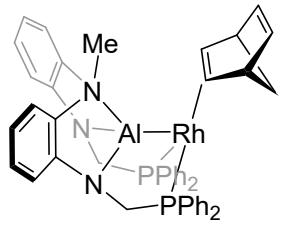
^{13}C NMR (101 MHz, $CDCl_3$)



2q-5Si


NOESY NMR (400 MHz, CDCl3)
H
H
H
CDCl3
CDCl3
H2C-SiMePh
H
H
C-N
N
H2
H
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

^{1}H NMR (400 MHz, C_6D_6)



7(nbd)

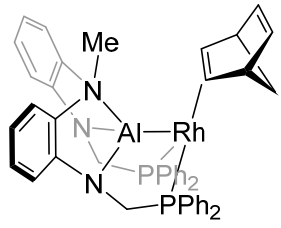
*pentane

**toluene

C_6D_6

X : parts per Million : Proton

^{1}H NMR (400 MHz, C_6D_6)



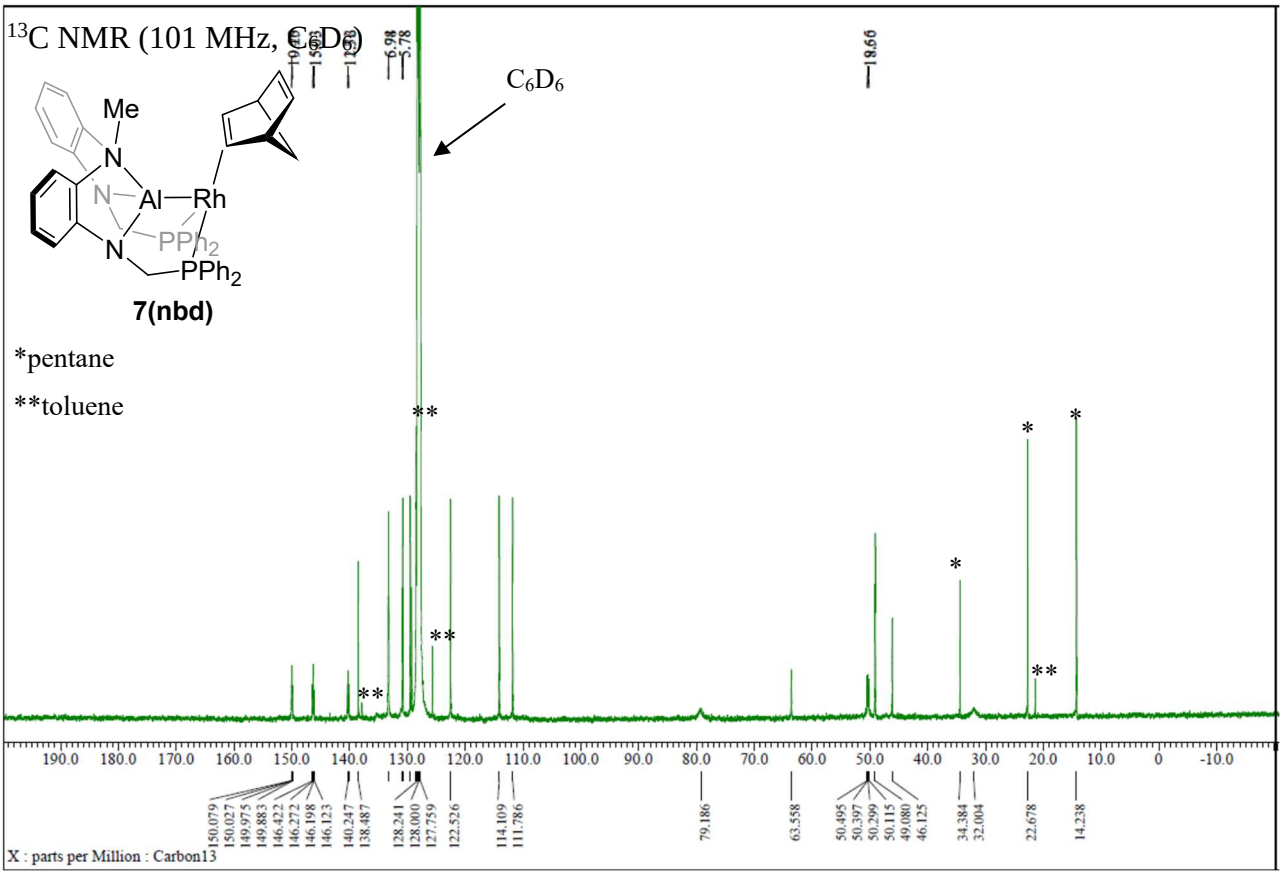
7(nbd)

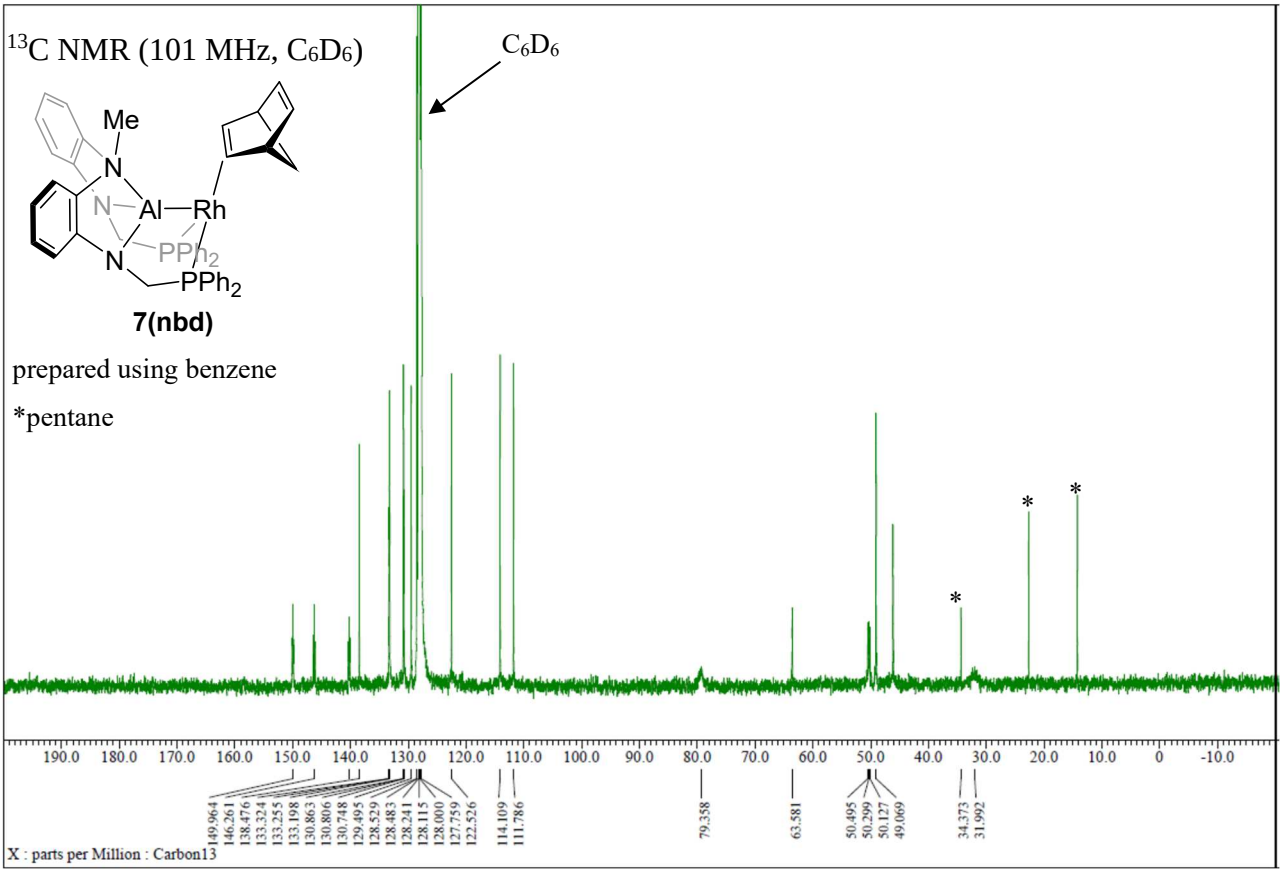
prepared using benzene

*pentane

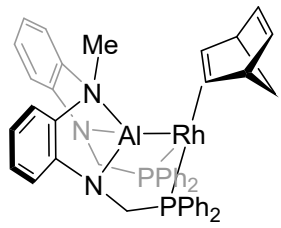
C_6D_6

X : parts per Million : Proton


^{13}C NMR (101 MHz, C$_6$D$_6$)
C$_6$D$_6$
Me
N
N
Al
Rh
PPh$_2$
N
PPh$_2$
7(nbd)
*pentane
**toluene
X : parts per Million : Carbon13

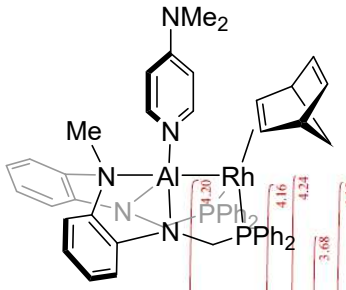

^{13}C NMR (101 MHz, C$_6$D$_6$)
C$_6$D$_6$
Me
N
N
Al
Rh
PPh$_2$
N
PPh$_2$
7(nbd)
prepared using benzene
*pentane
X : parts per Million : Carbon13

^{31}P NMR (162 MHz, C_6D_6)



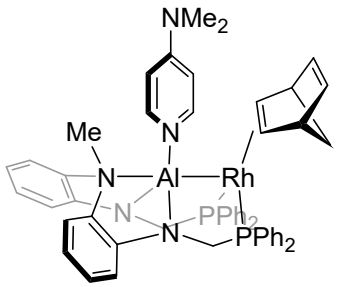
7(nbd)

^{1}H NMR (400 MHz, C_6D_6)



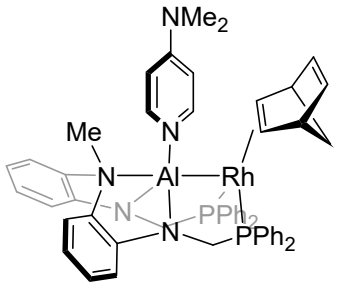
8(nbd)-DMAP

^{13}C NMR (101 MHz, C_6D_6)

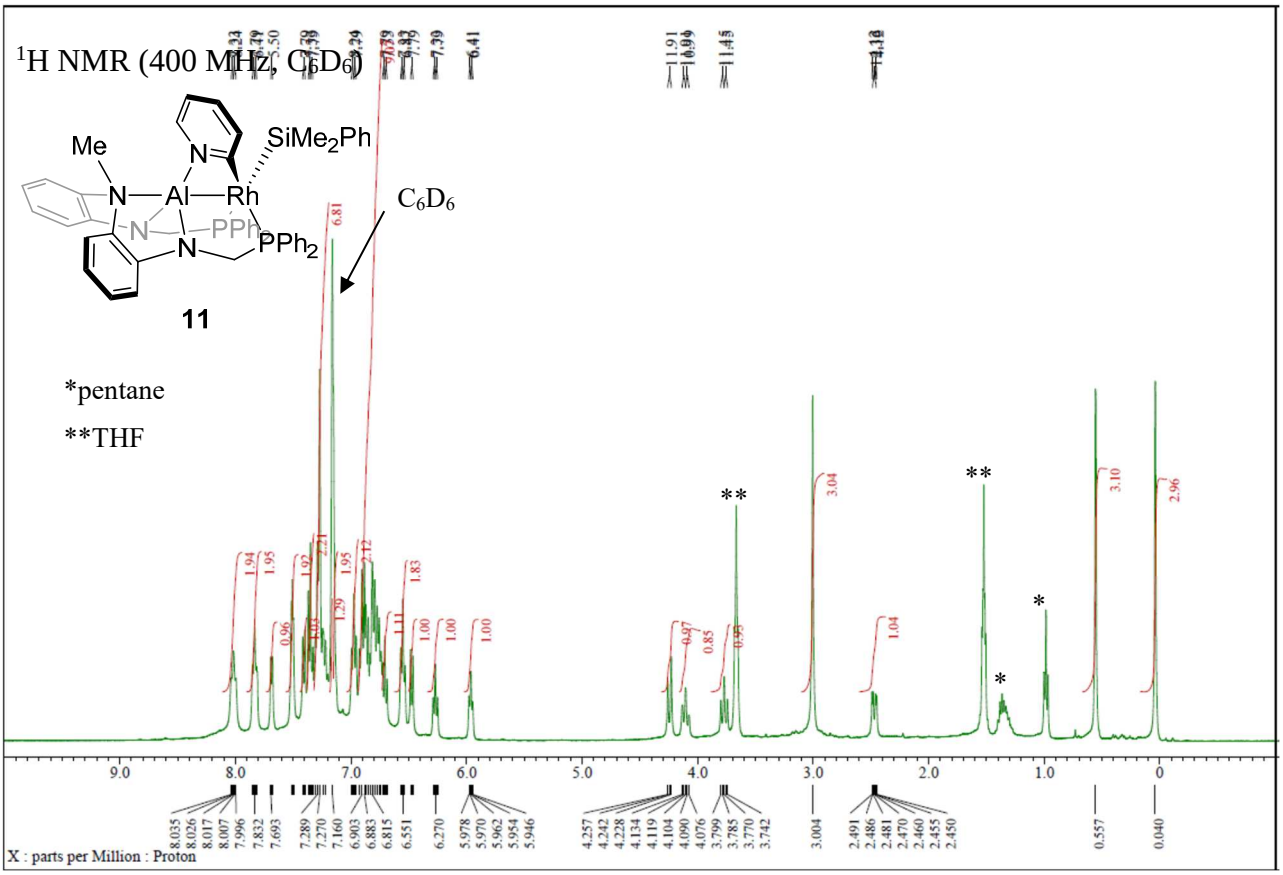


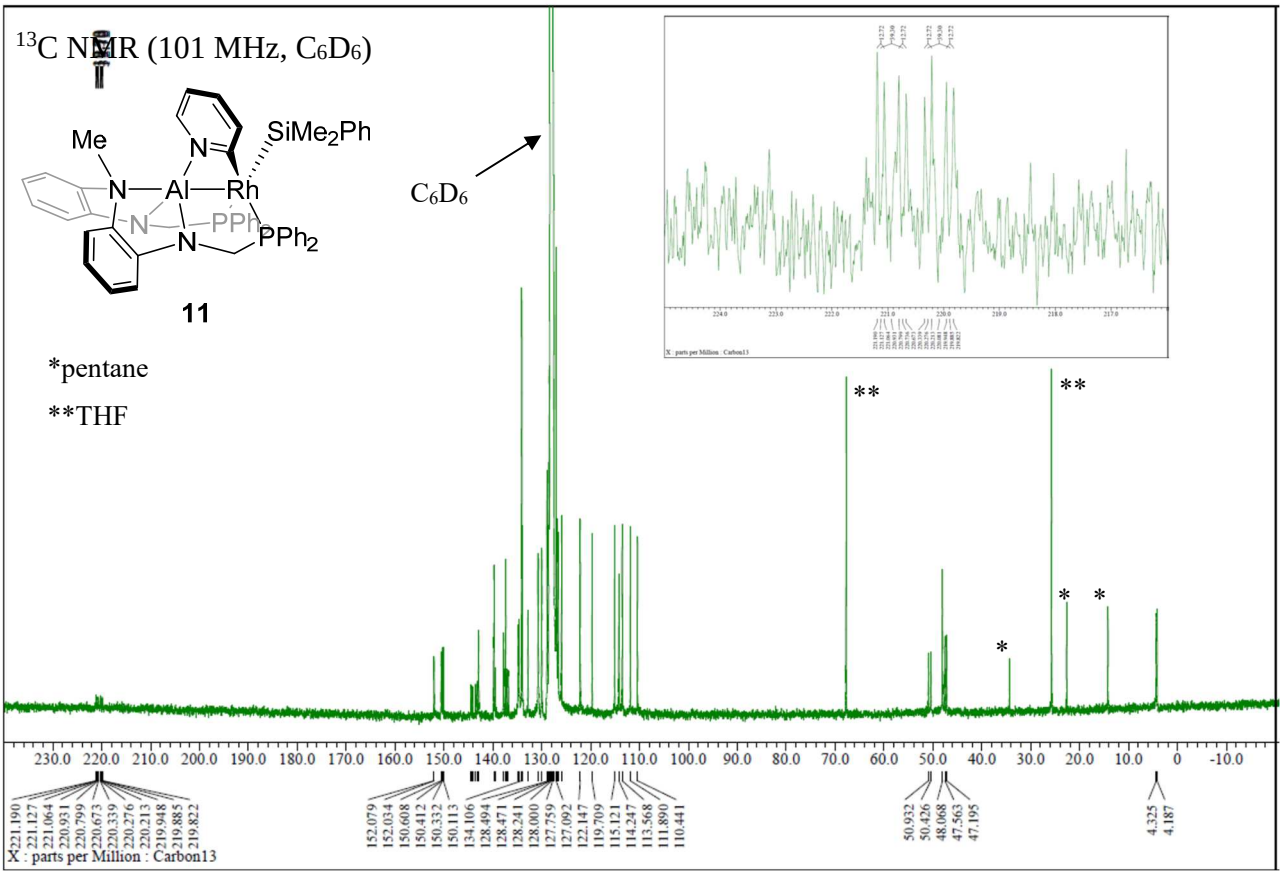
8(nbd)-DMAP

^{31}P NMR (162 MHz, C_6D_6)

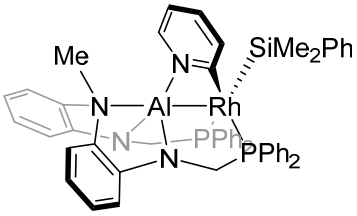


8(nbd)-DMAP


^{1}H NMR (400 MHz, C_6D_6)
Me
N
Al
Rh
SiMe$_2$Ph
PPh$_2$
11
C_6D_6
*pentane
**THF
X : parts per Million : Proton

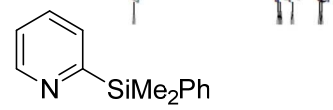

^{13}C NMR (101 MHz, C_6D_6)
Me
N
Al
Rh
SiMe$_2$Ph
PPh$_2$
11
C_6D_6
*pentane
**THF
X : parts per Million : Carbon13

^{31}P NMR (162 MHz, C_6D_6)



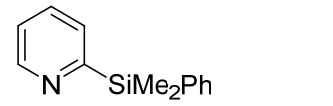
11

^{1}H NMR (400 MHz, $CDCl_3$)



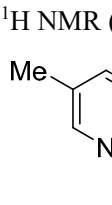
2a

^{13}C NMR (101 MHz, $CDCl_3$)



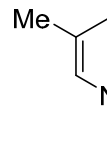
2a

^{1}H NMR (400 MHz, $CDCl_3$)

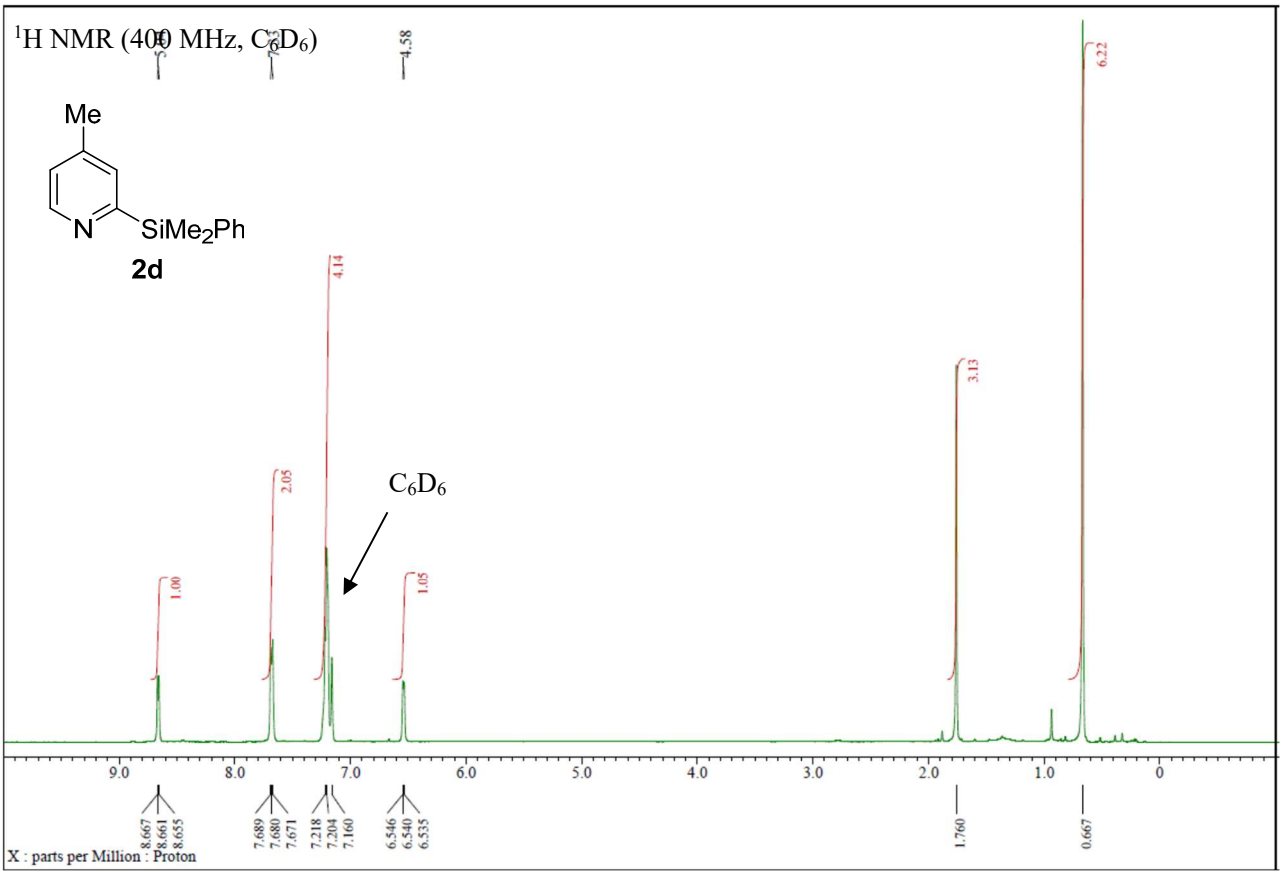


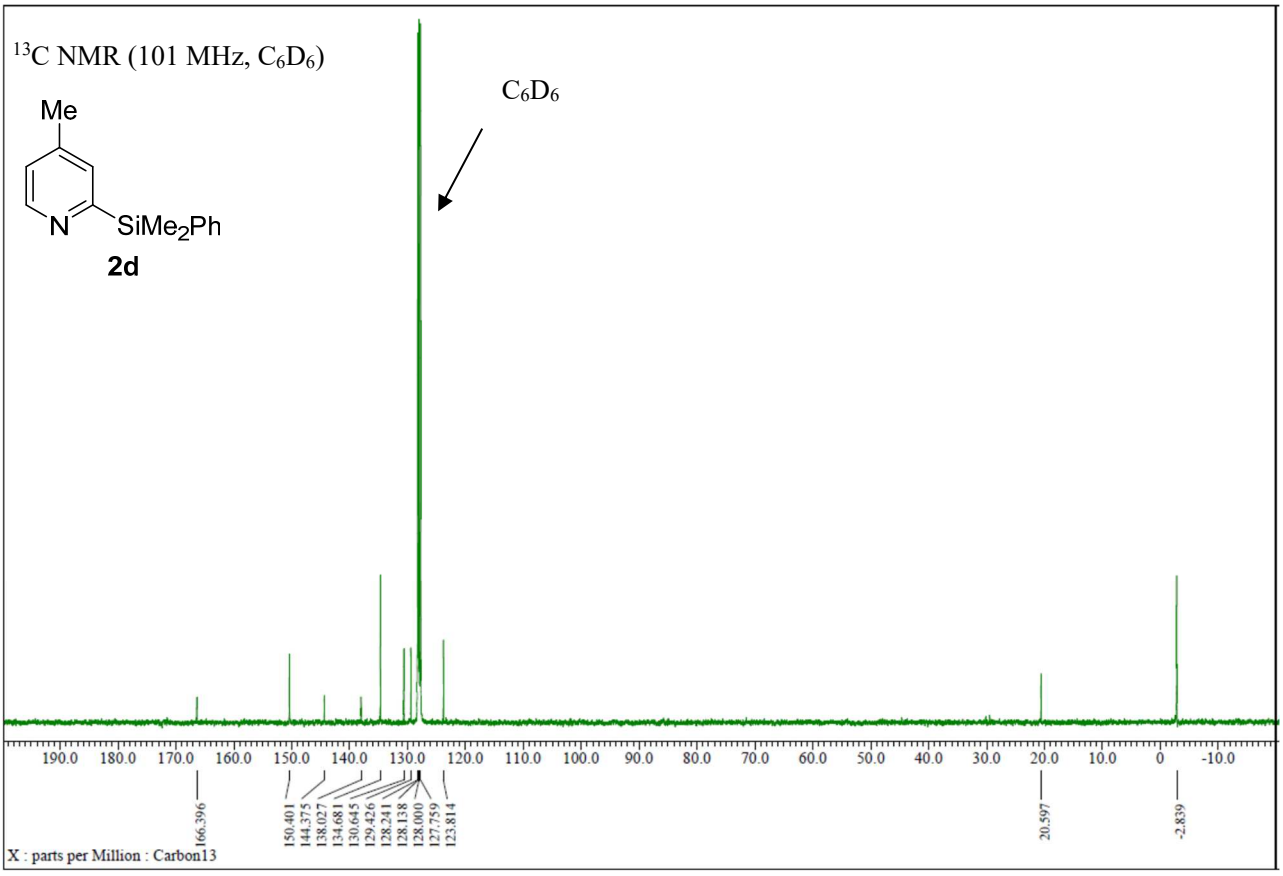
2c

^{13}C NMR (101 MHz, $CDCl_3$)

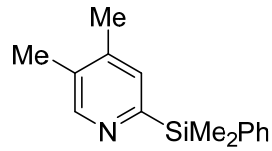


2c


^{1}H NMR (400 MHz, C_6D_6)
Me
N
SiMe$_2$Ph
2d
C_6D_6
X : parts per Million : Proton

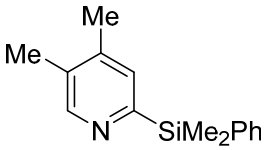

^{13}C NMR (101 MHz, C_6D_6)
Me
N
SiMe$_2$Ph
2d
C_6D_6
X : parts per Million : Carbon13

^{1}H NMR (400 MHz, $CDCl_3$)



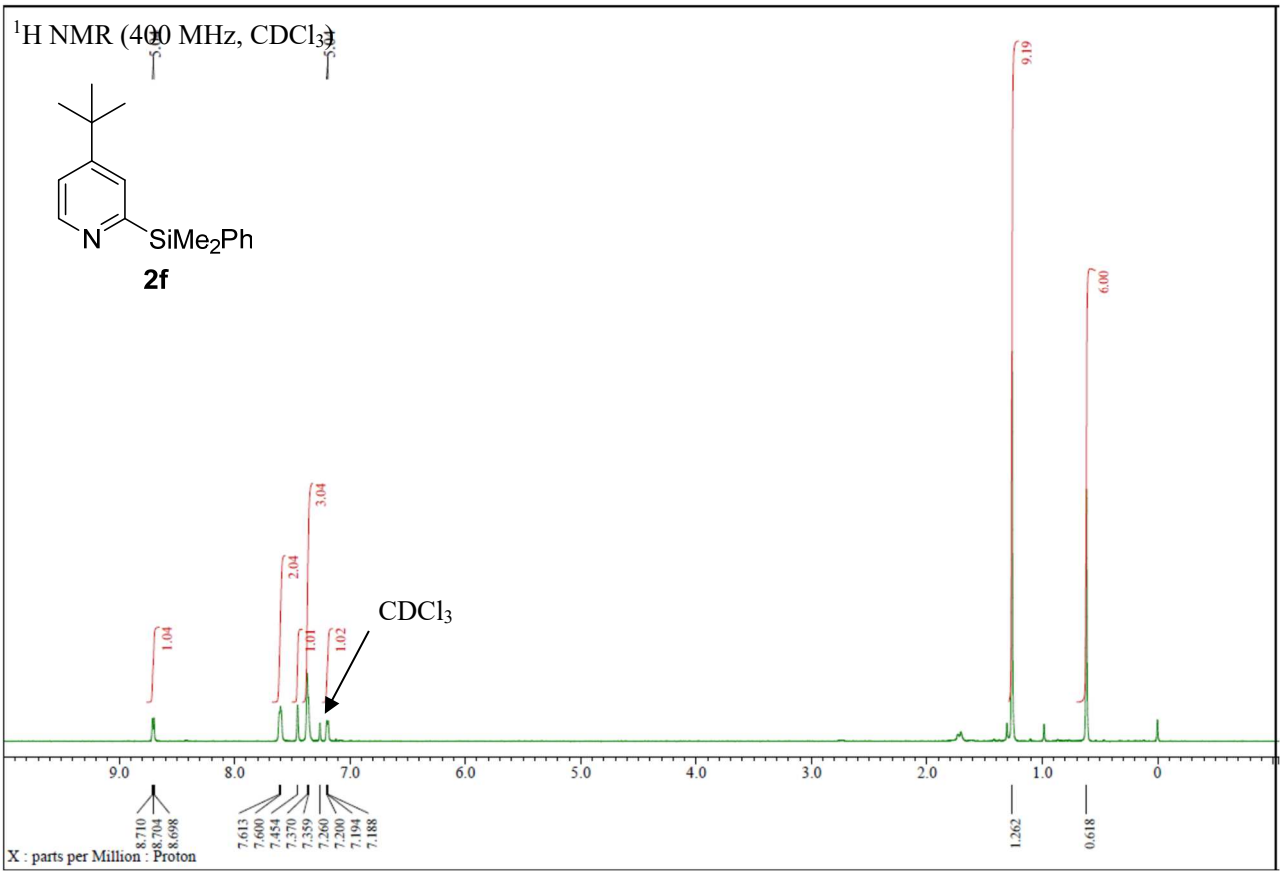
2e

^{13}C NMR (101 MHz, $CDCl_3$)

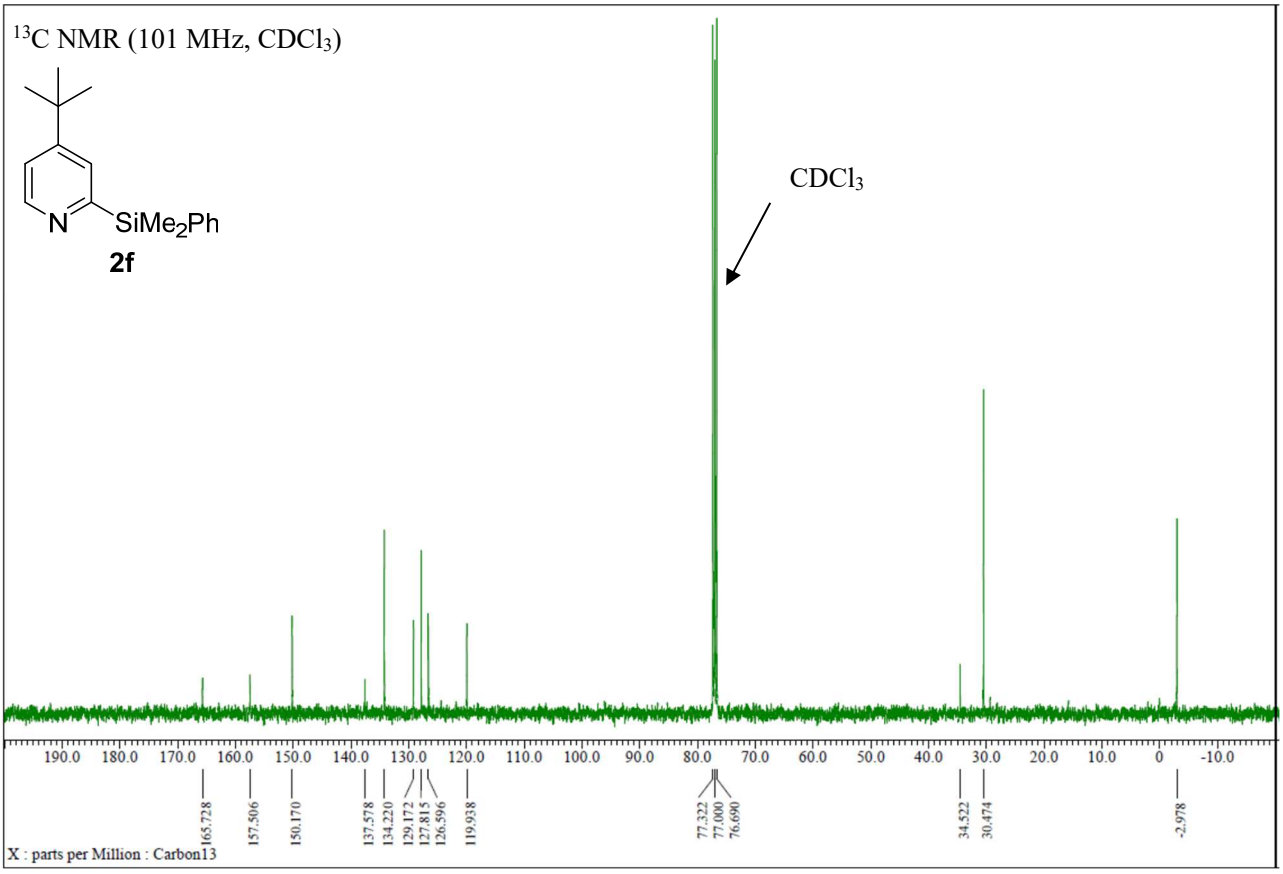


2e

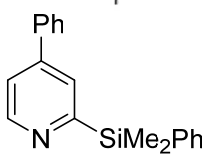
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

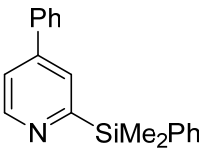


^{1}H NMR (400 MHz, $CDCl_3$)



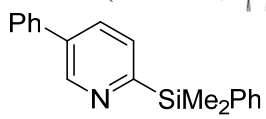
2l (from **2g**)

^{13}C NMR (101 MHz, $CDCl_3$)



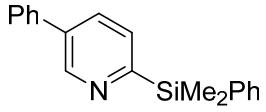
2l (from **2g**)

^{1}H NMR (400 MHz, $CDCl_3$)



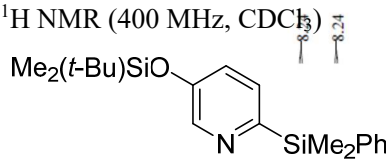
2o (from **2h**)

^{13}C NMR (101 MHz, $CDCl_3$)



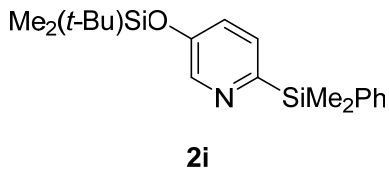
2o (from **2h**)

^{1}H NMR (400 MHz, $CDCl_3$)



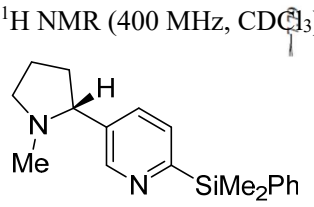
2i

^{13}C NMR (101 MHz, $CDCl_3$)



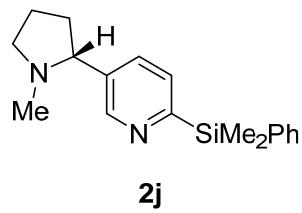
2i

^{1}H NMR (400 MHz, $CDCl_3$)

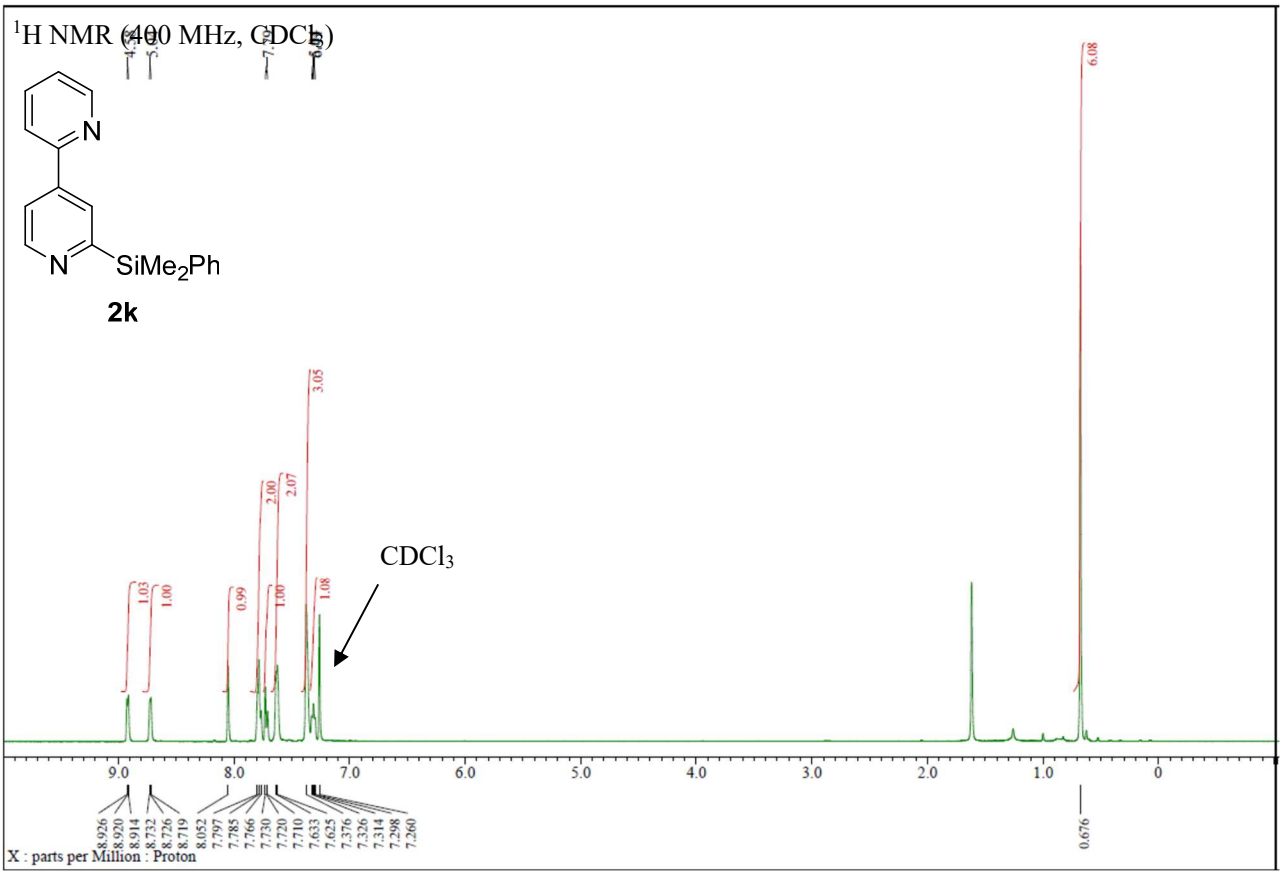


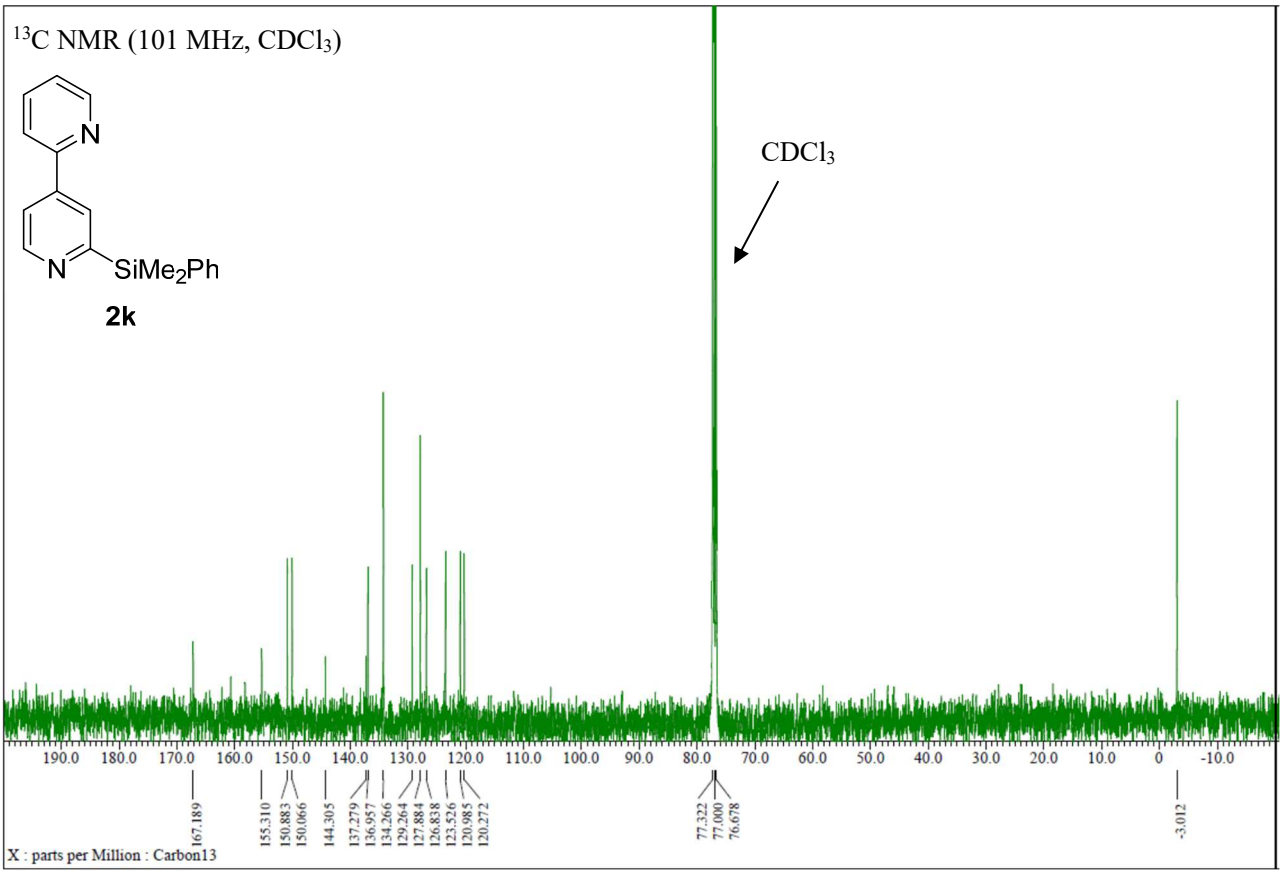
2j

^{13}C NMR (101 MHz, $CDCl_3$)

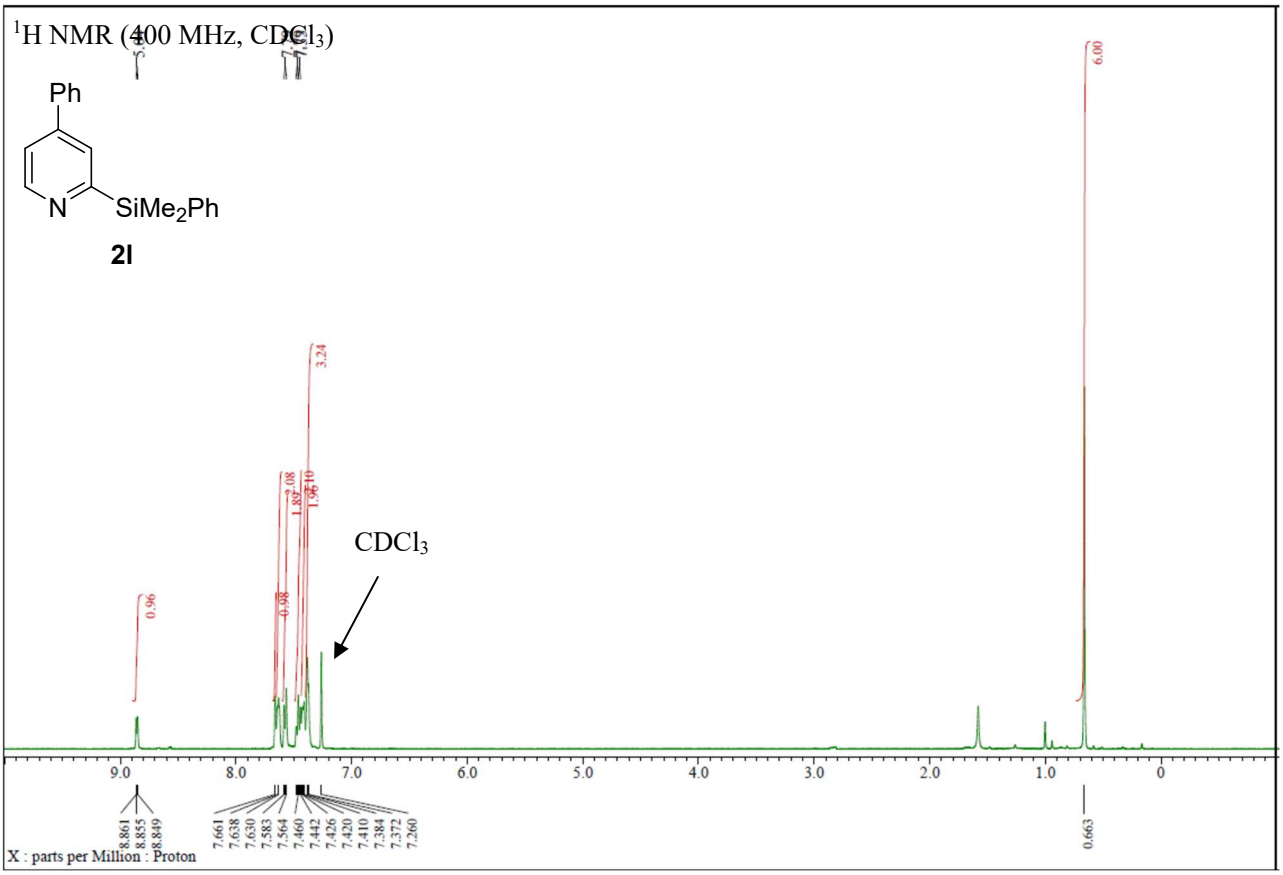


2j

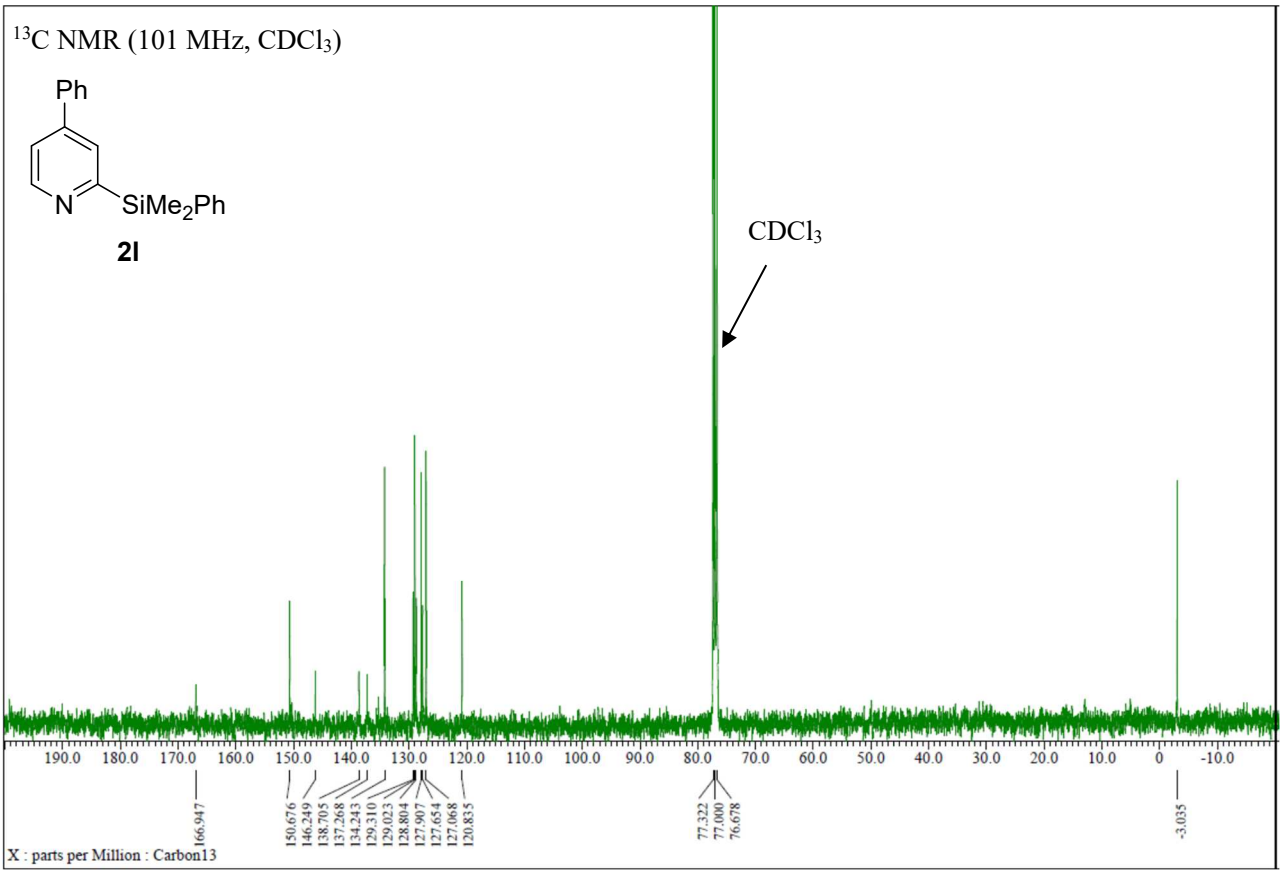

^{1}H NMR (400 MHz, CDCl$_3$)
N
N
SiMe$_2$Ph
2k
CDCl$_3$
X : parts per Million : Proton

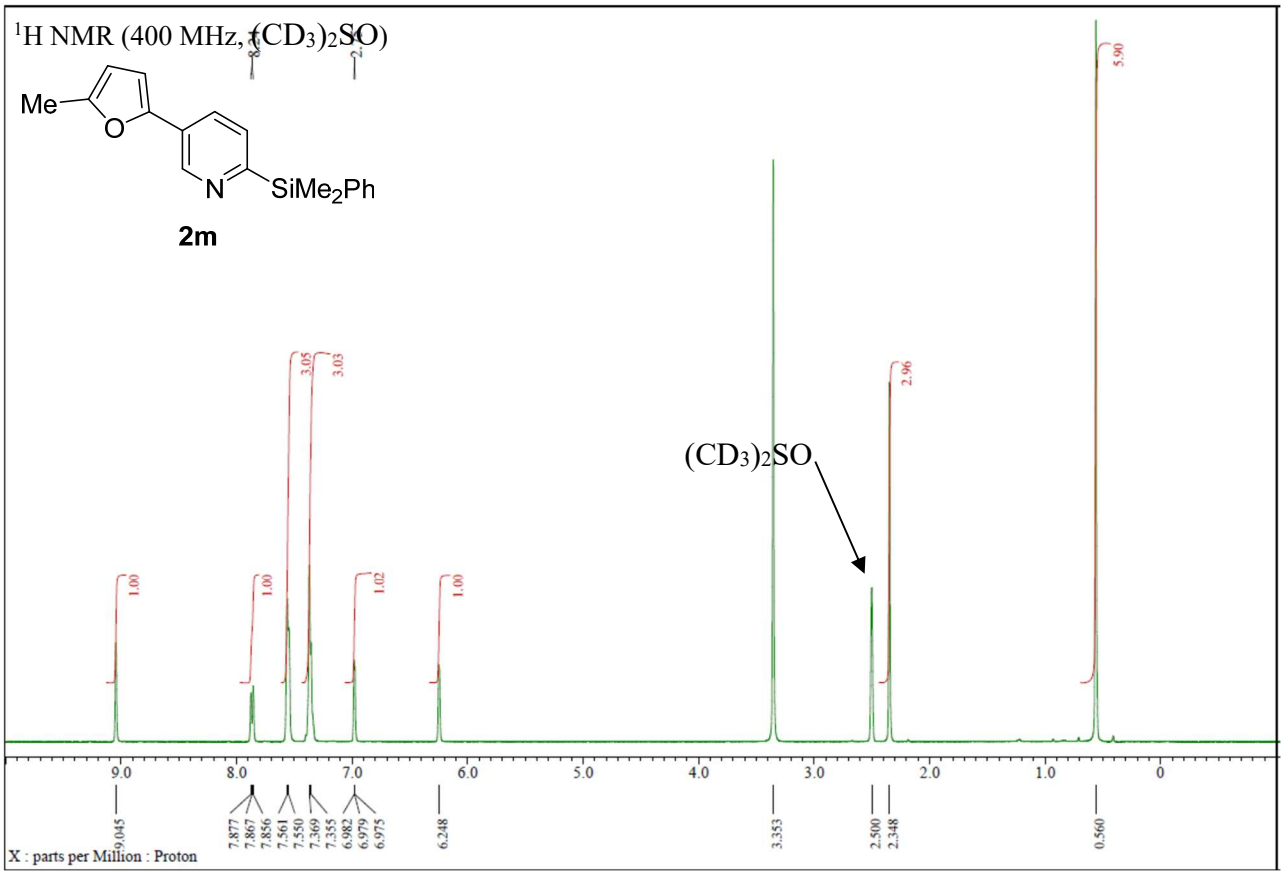

^{13}C NMR (101 MHz, CDCl$_3$)
N
N
SiMe$_2$Ph
2k
CDCl$_3$
X : parts per Million : Carbon13

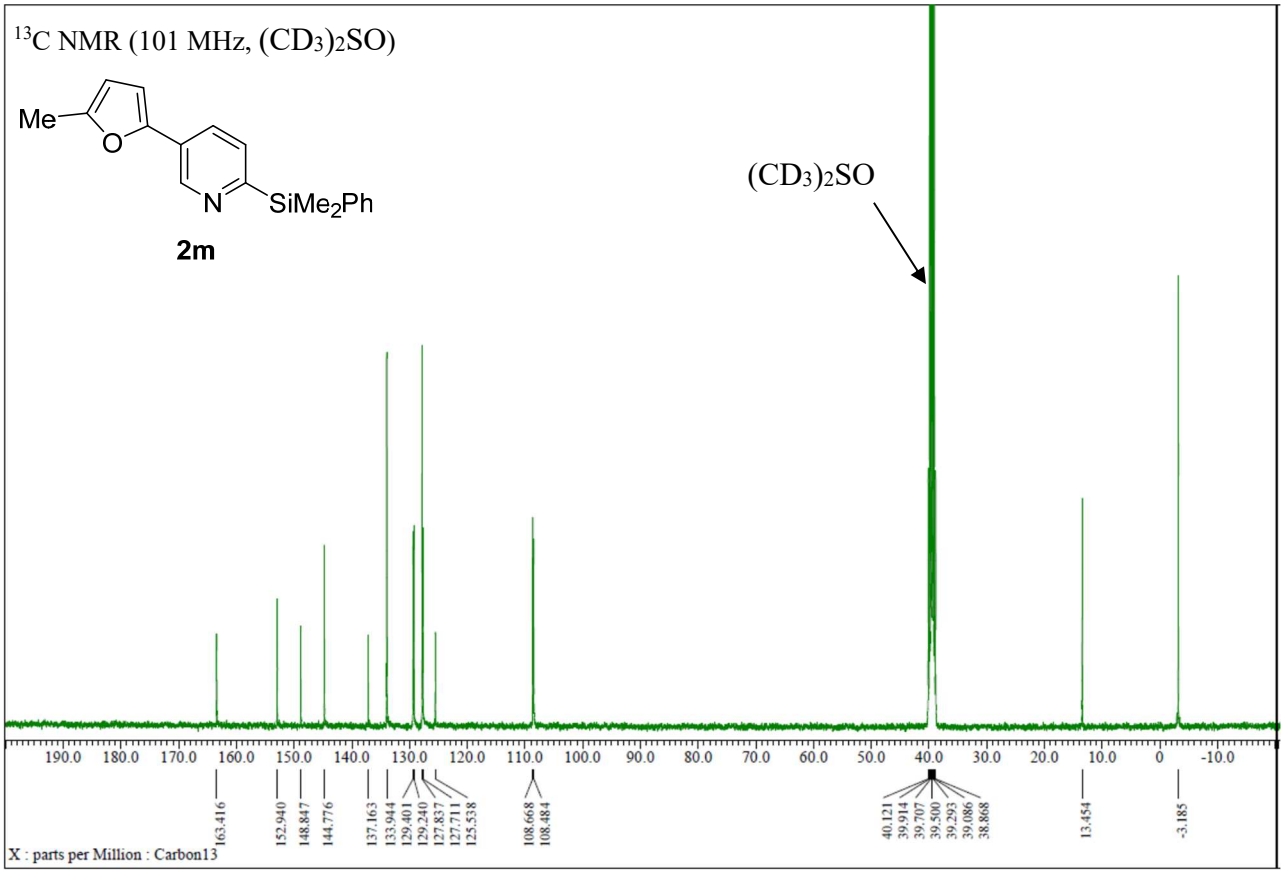
^{1}H NMR (400 MHz, $CDCl_3$)

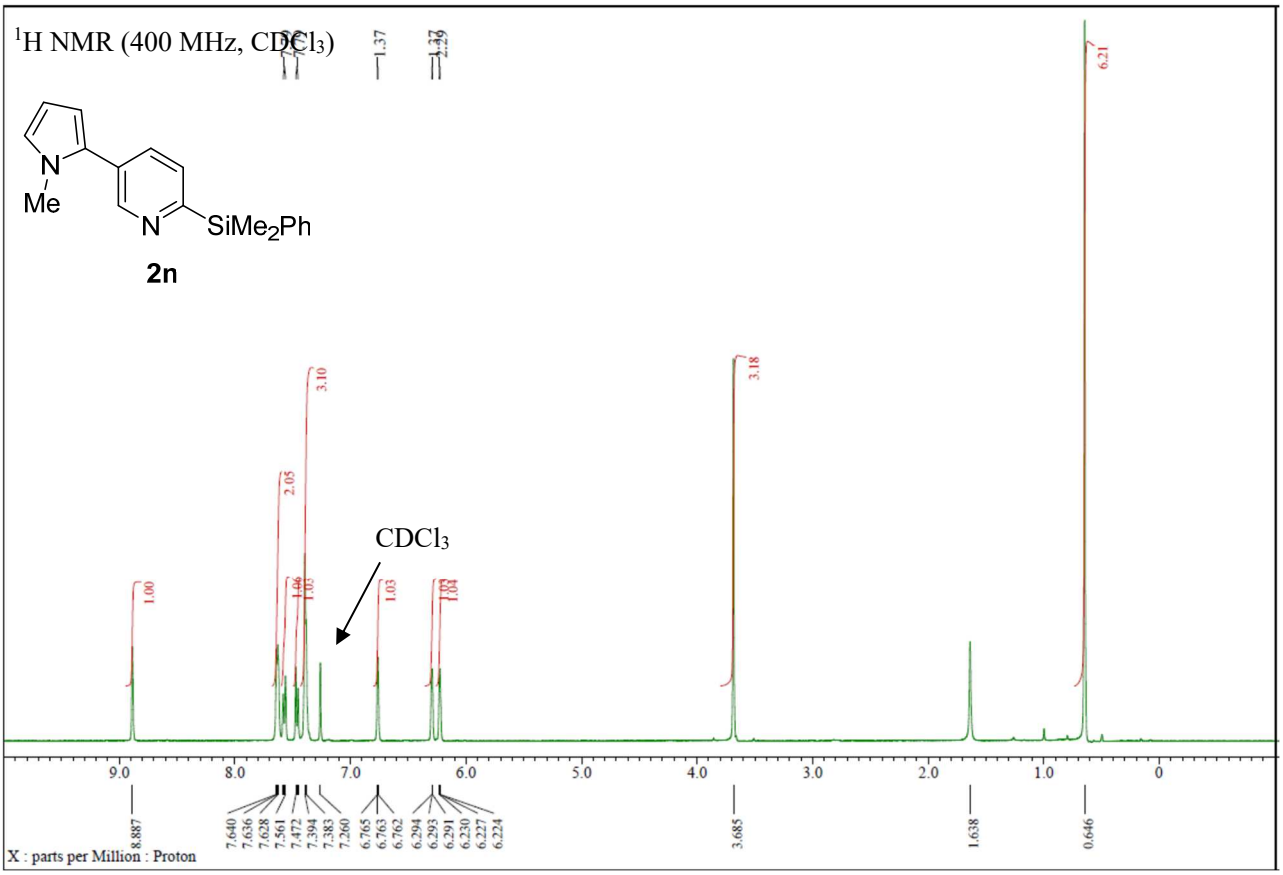


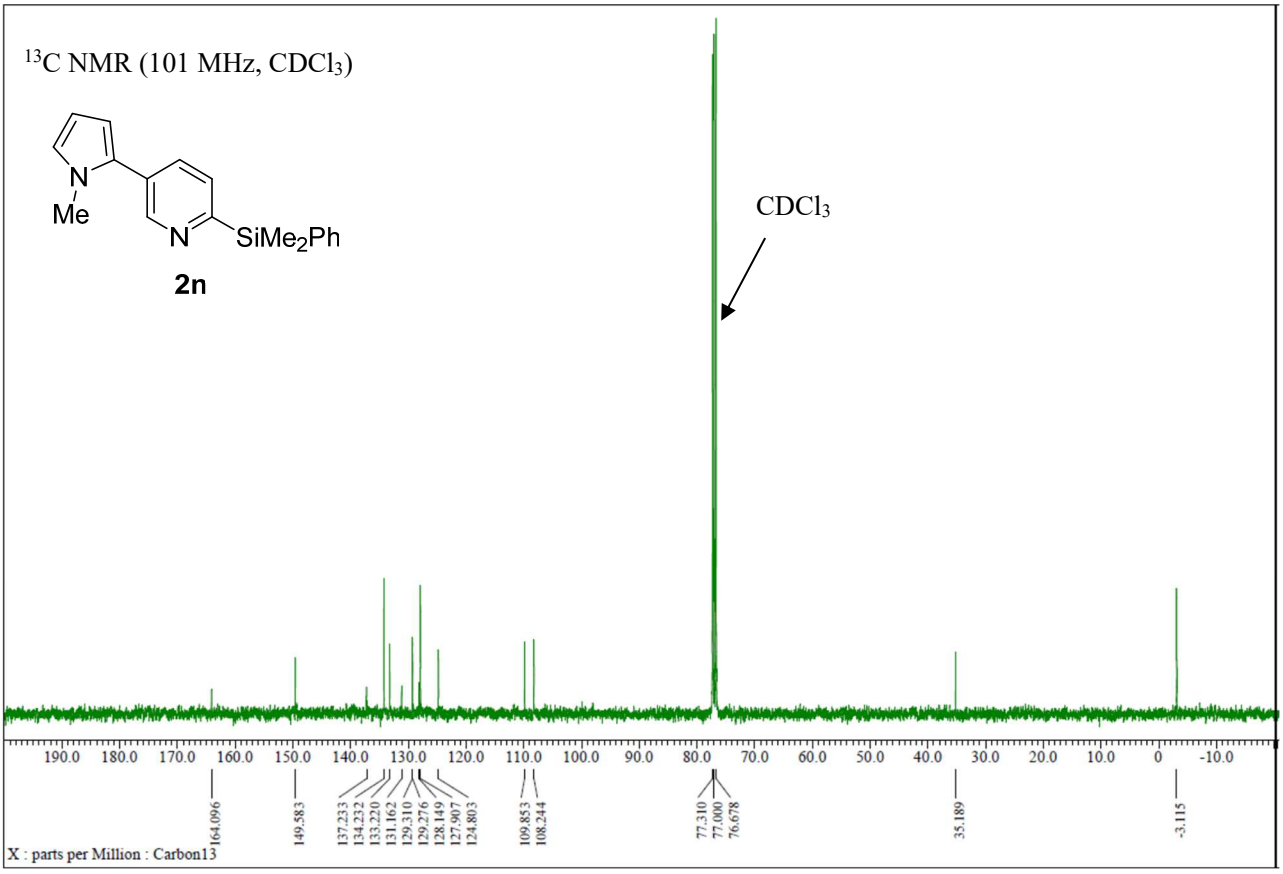
^{13}C NMR (101 MHz, $CDCl_3$)



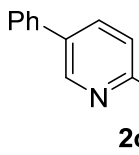

^{1}H NMR (400 MHz, (CD$_3$)$_2$SO)
Me
O
N
SiMe$_2$Ph
2m
(CD$_3$)$_2$SO
X : parts per Million : Proton


^{13}C NMR (101 MHz, (CD$_3$)$_2$SO)
Me
O
N
SiMe$_2$Ph
2m
(CD$_3$)$_2$SO
X : parts per Million : Carbon13


^{1}H NMR (400 MHz, CDCl$_3$)
N
Me
N
SiMe$_2$Ph
2n
CDCl$_3$
X : parts per Million : Proton

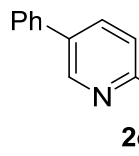

^{13}C NMR (101 MHz, CDCl$_3$)
N
Me
N
SiMe$_2$Ph
2n
CDCl$_3$
X : parts per Million : Carbon13

^{1}H NMR (400 MHz, $CDCl_3$)



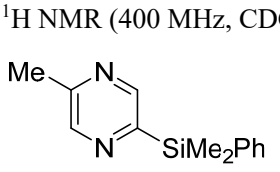
2o

^{13}C NMR (101 MHz, $CDCl_3$)



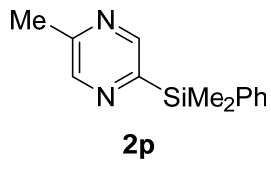
2o

^{1}H NMR (400 MHz, $CDCl_3$)



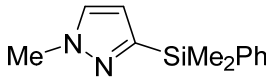
2p

^{13}C NMR (101 MHz, $CDCl_3$)



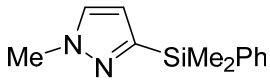
2p

^{1}H NMR (400 MHz, $CDCl_3$)

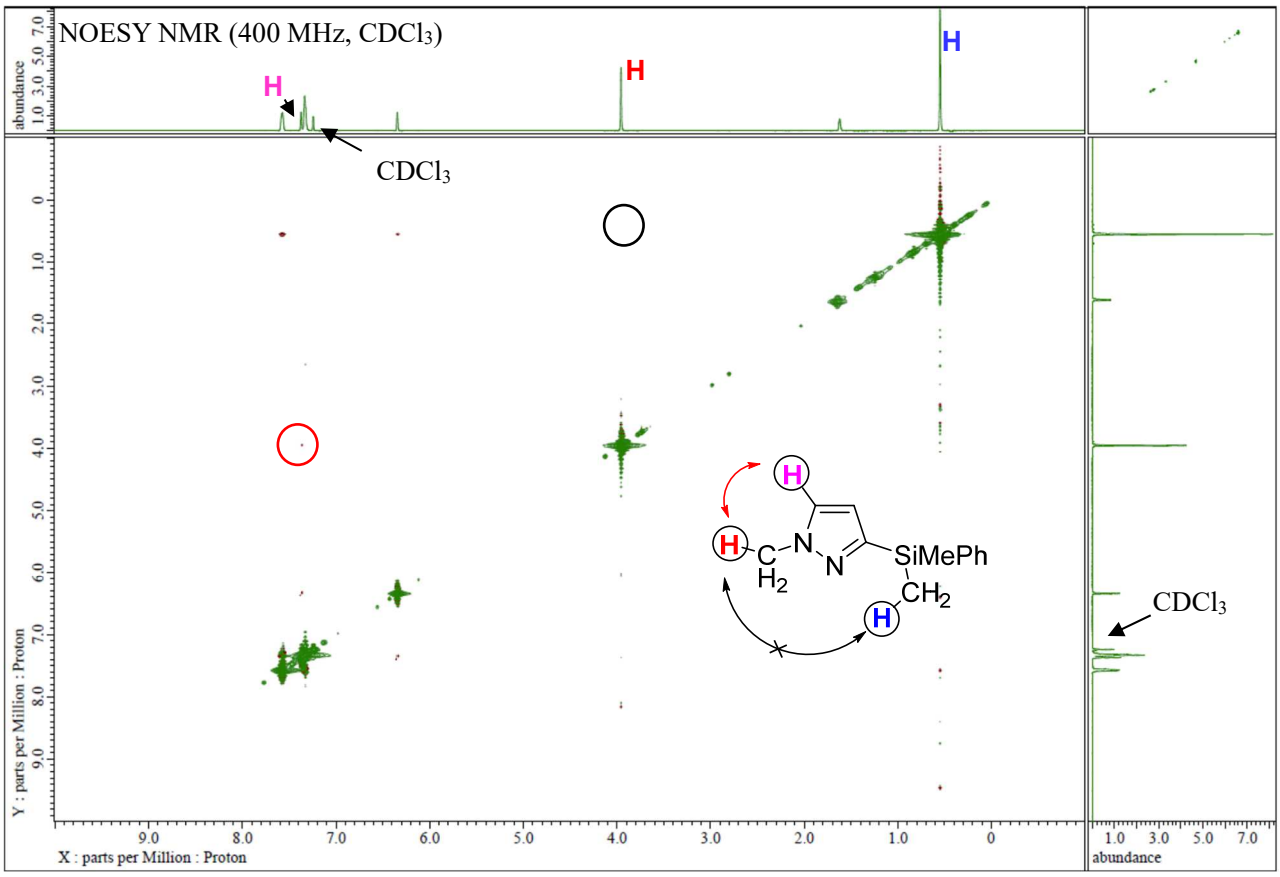


2q

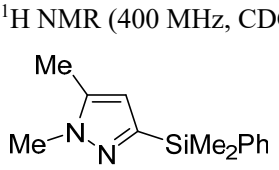
^{13}C NMR (101 MHz, $CDCl_3$)



2q

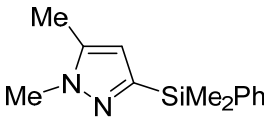

NOESY NMR (400 MHz, CDCl3)
H
H
H
CDCl3
CDCl3
SiMePh
CH2
CH2
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

^{1}H NMR (400 MHz, $CDCl_3$)



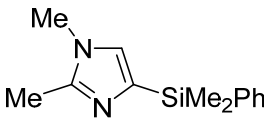
2r

^{13}C NMR (101 MHz, $CDCl_3$)



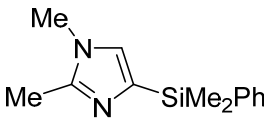
2r

^{1}H NMR (400 MHz, $CDCl_3$)

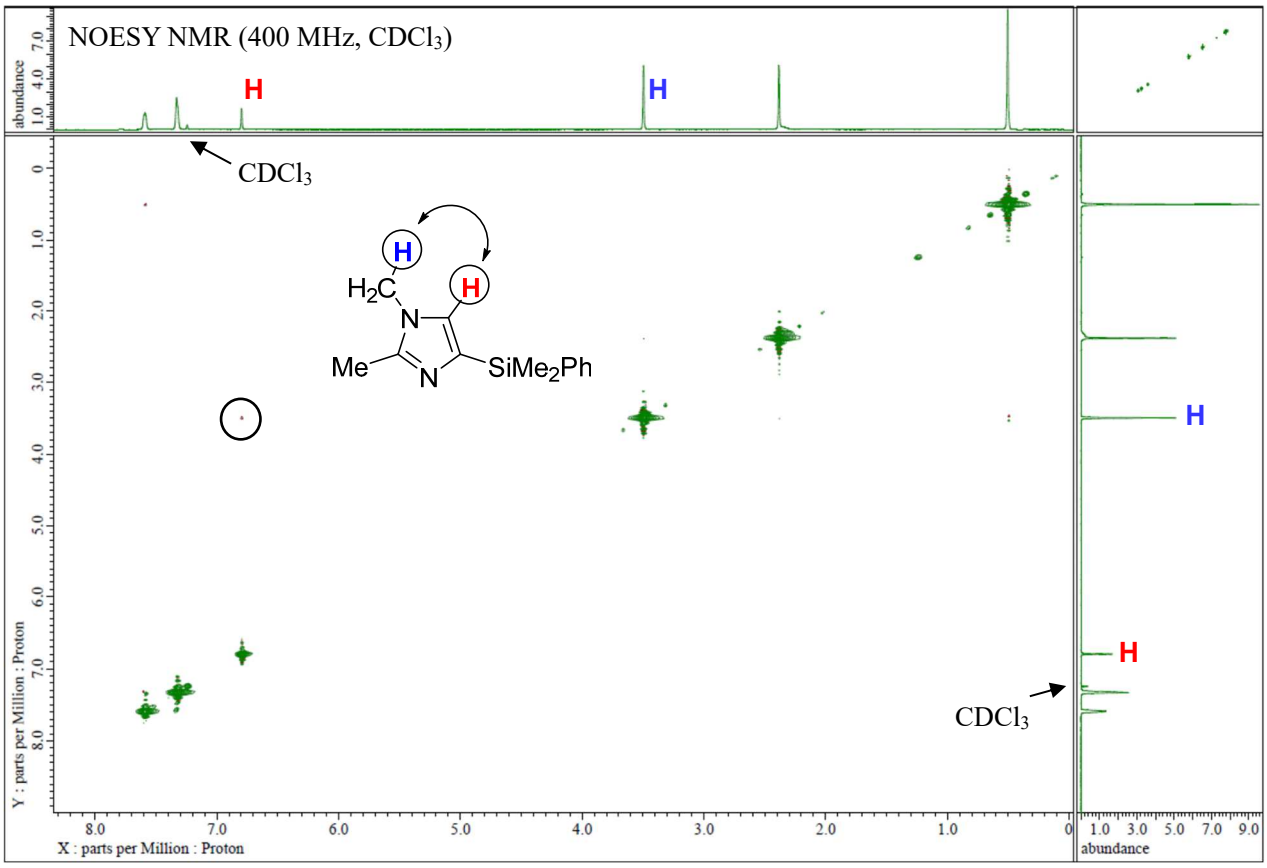


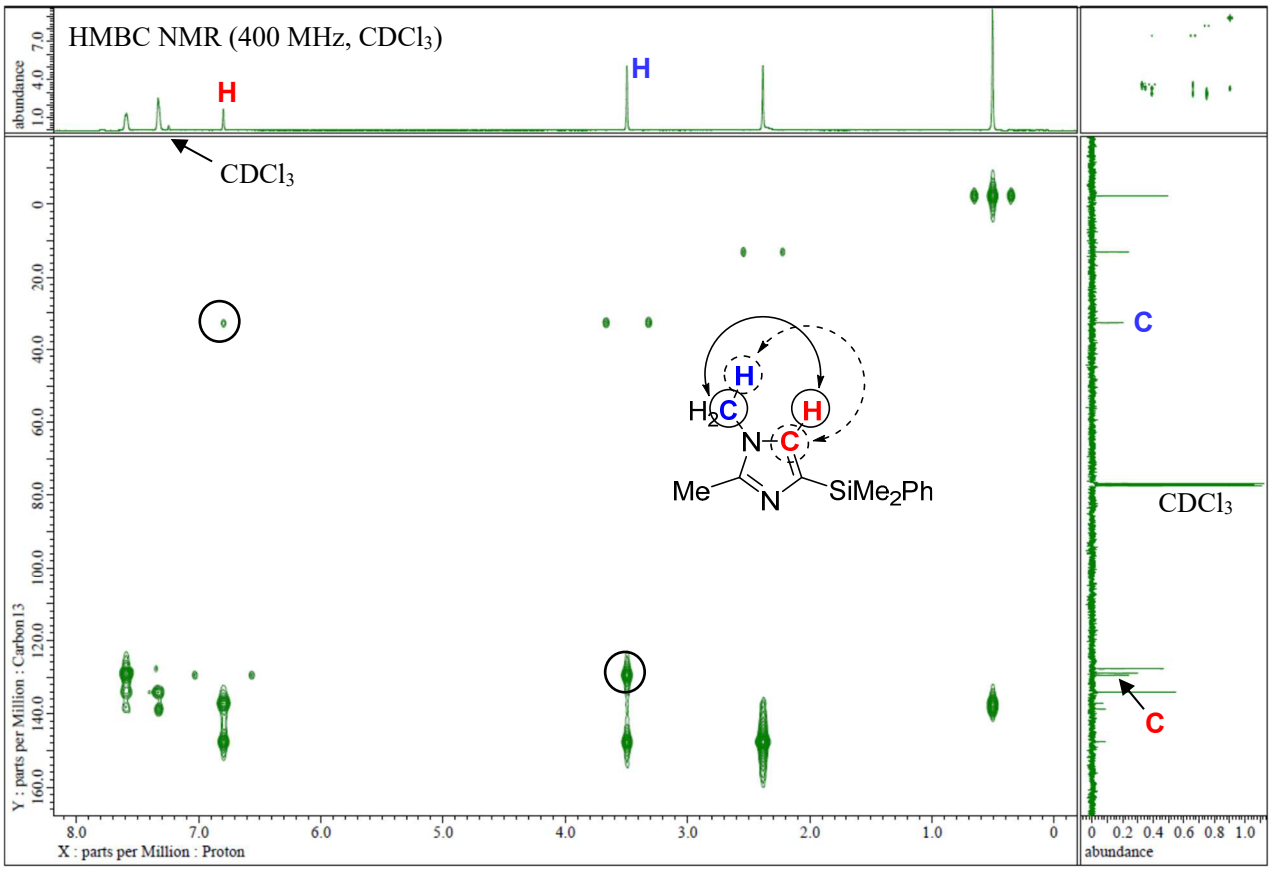
2s

^{13}C NMR (101 MHz, $CDCl_3$)

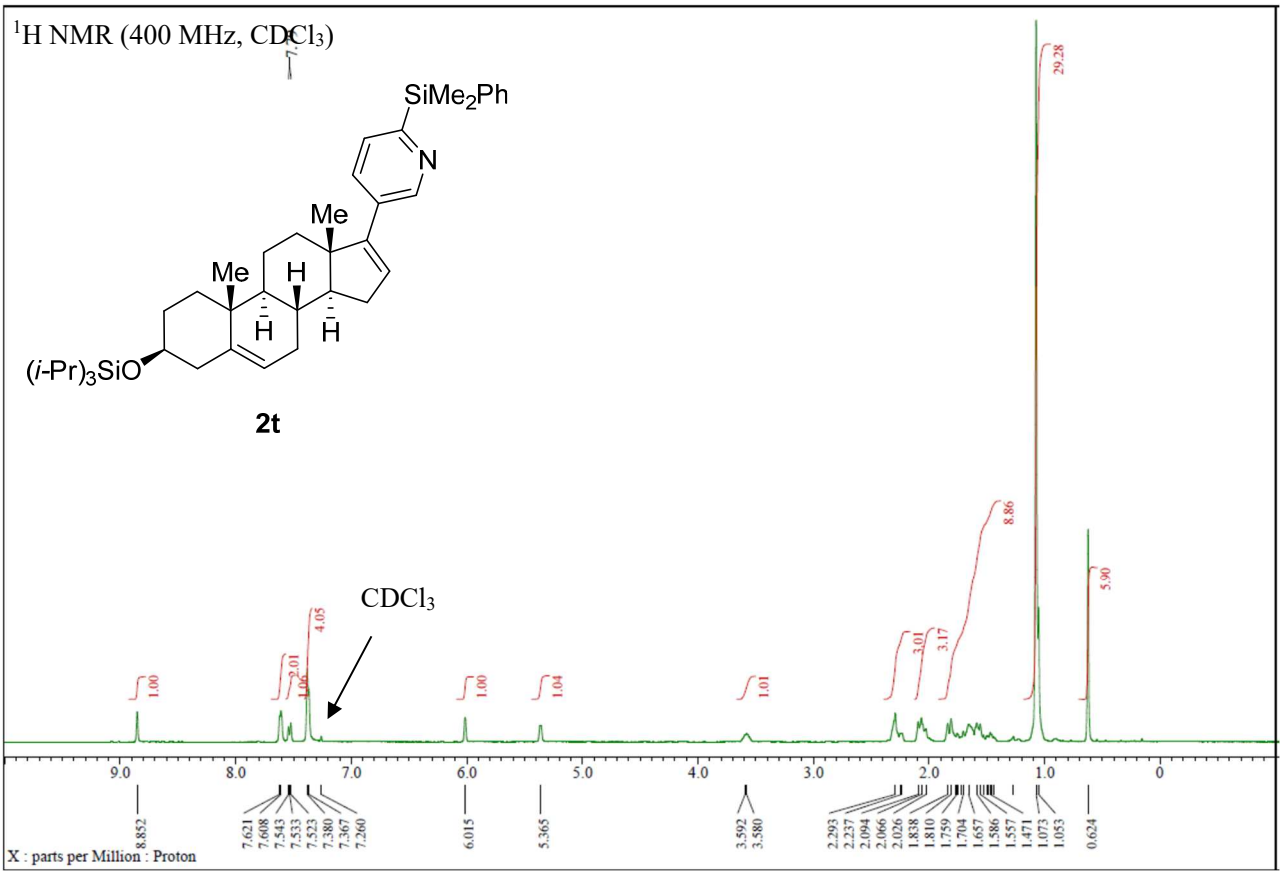


2s

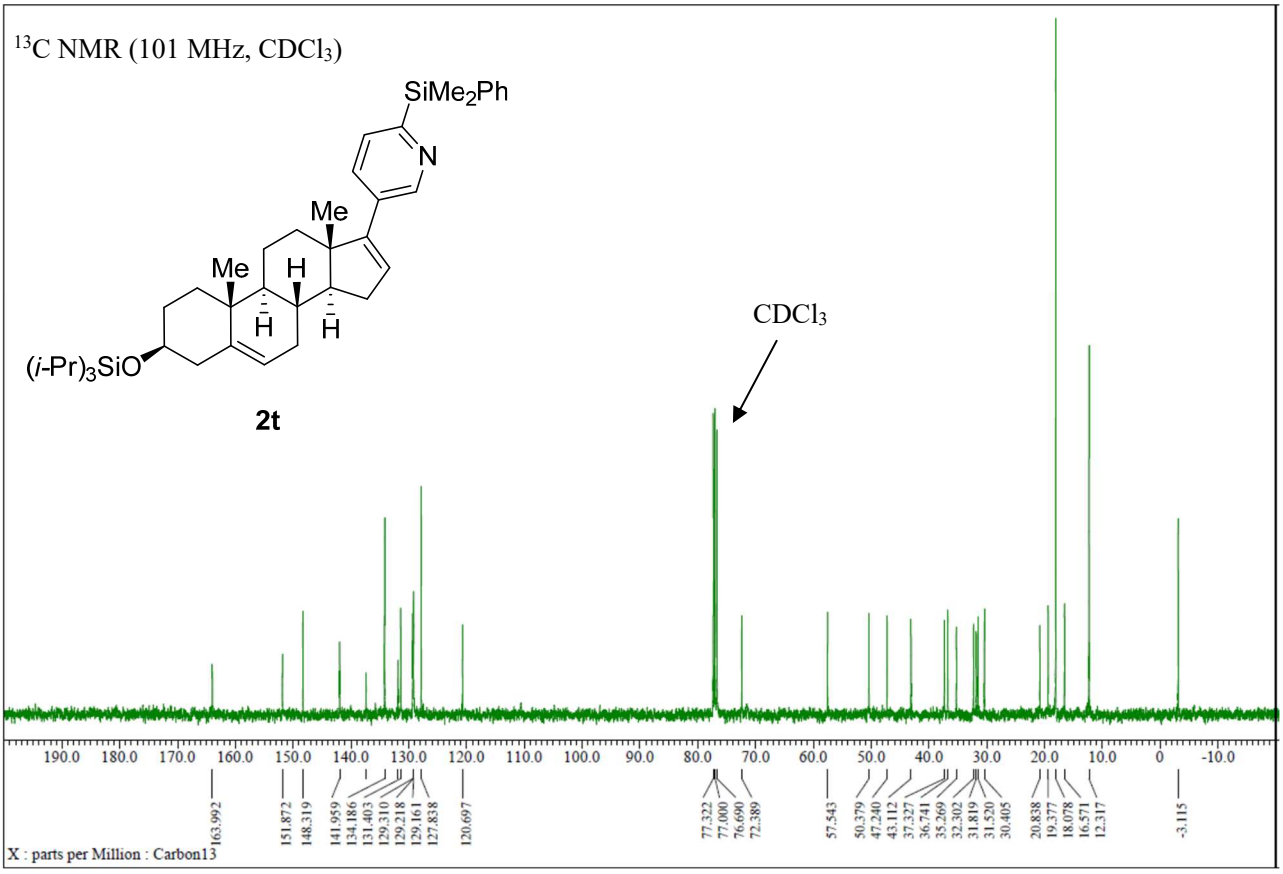

NOESY NMR (400 MHz, CDCl3)
H
H
CDCl3
H2C
N
Me
N
SiMe2Ph
H
H
CDCl3
Y : parts per Million : Proton
X : parts per Million : Proton
abundance


HMBC NMR (400 MHz, CDCl3)
H
H
CDCl3
H2C
N
C
Me
N
SiMe2Ph
C
CDCl3
C
Y : parts per Million : Carbon13
X : parts per Million : Proton
abundance

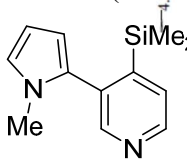
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

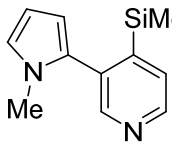


^{1}H NMR (400 MHz, $CDCl_3$)



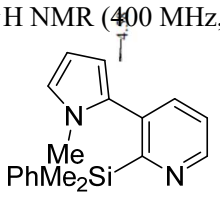
2n-4Si

^{13}C NMR (101 MHz, $CDCl_3$)



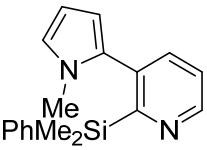
2n-4Si

^{1}H NMR (400 MHz, $CDCl_3$)

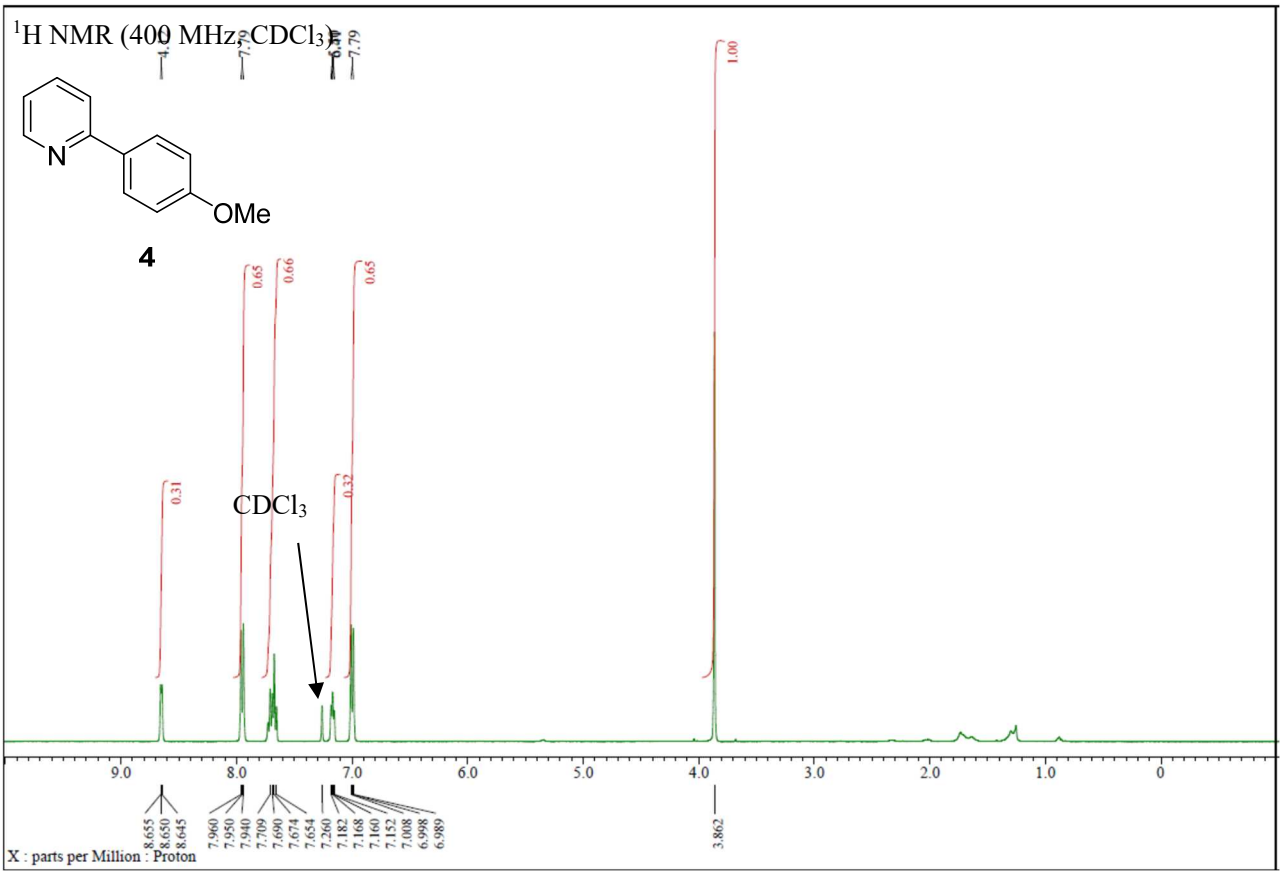


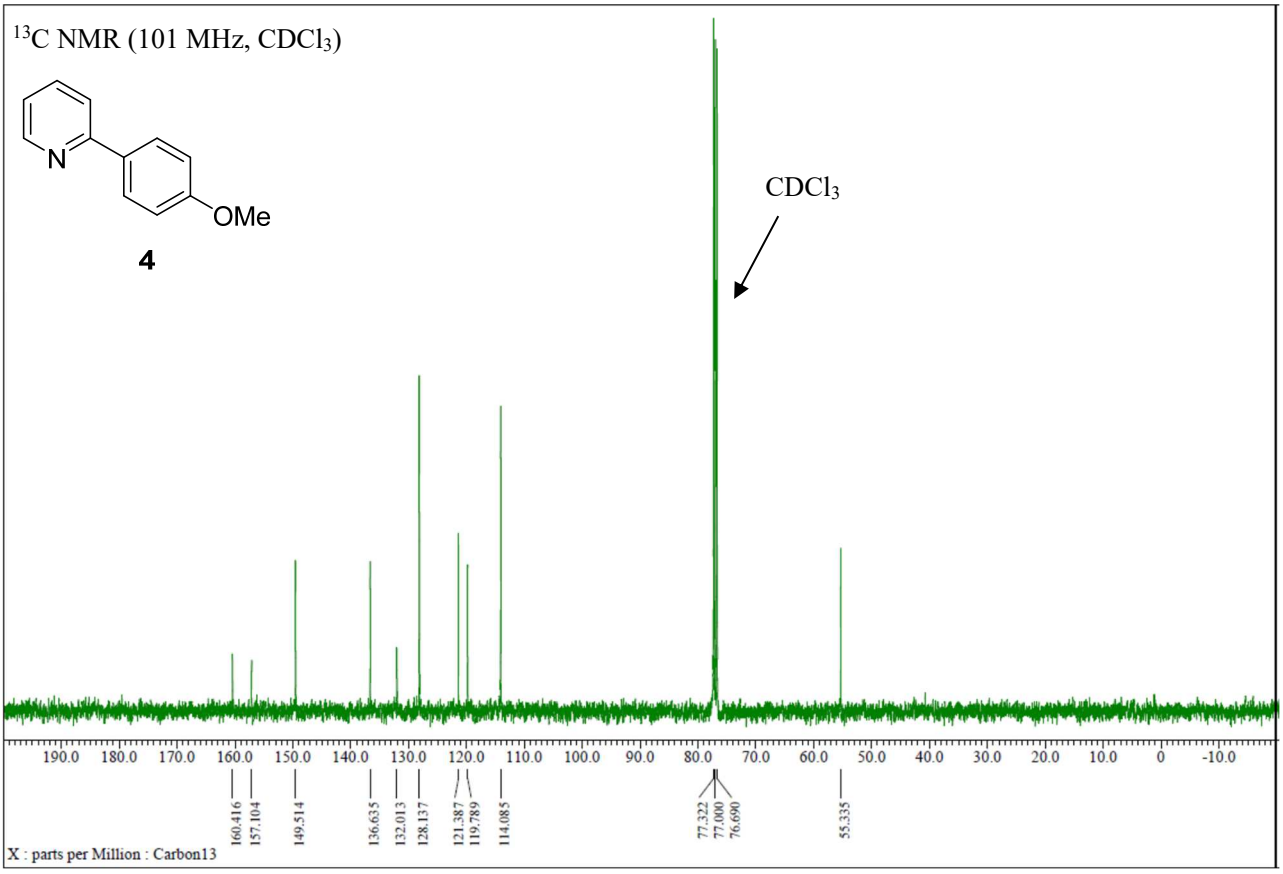
2n-2Si

^{13}C NMR (101 MHz, $CDCl_3$)

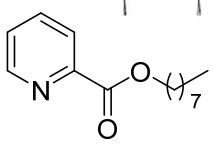


2n-2Si


^{1}H NMR (400 MHz, CDCl$_3$)
OMe
4
CDCl$_3$
X : parts per Million : Proton

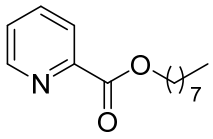

^{13}C NMR (101 MHz, CDCl$_3$)
OMe
4
CDCl$_3$
X : parts per Million : Carbon13

^{1}H NMR (400 MHz, $CDCl_3$)



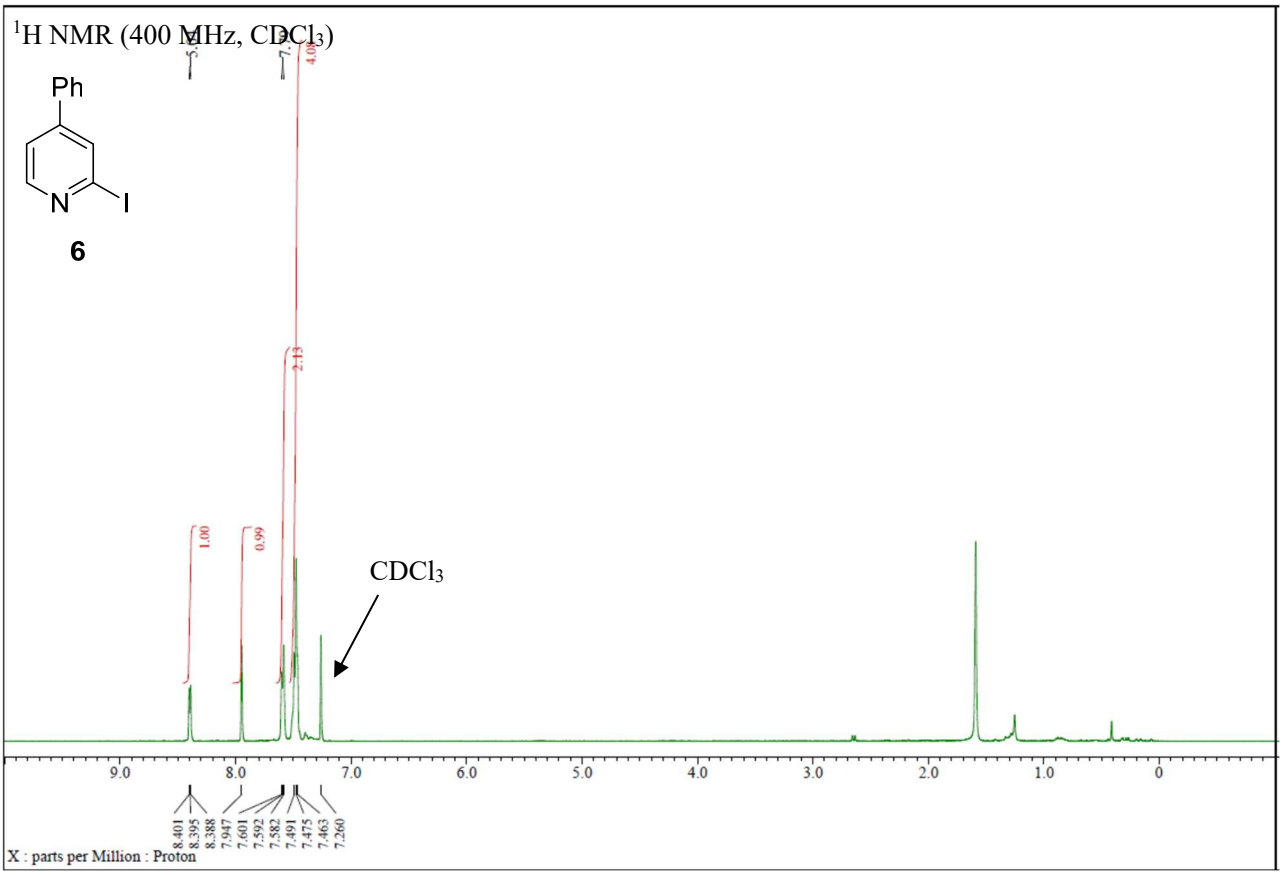
5

^{13}C NMR (101 MHz, $CDCl_3$)

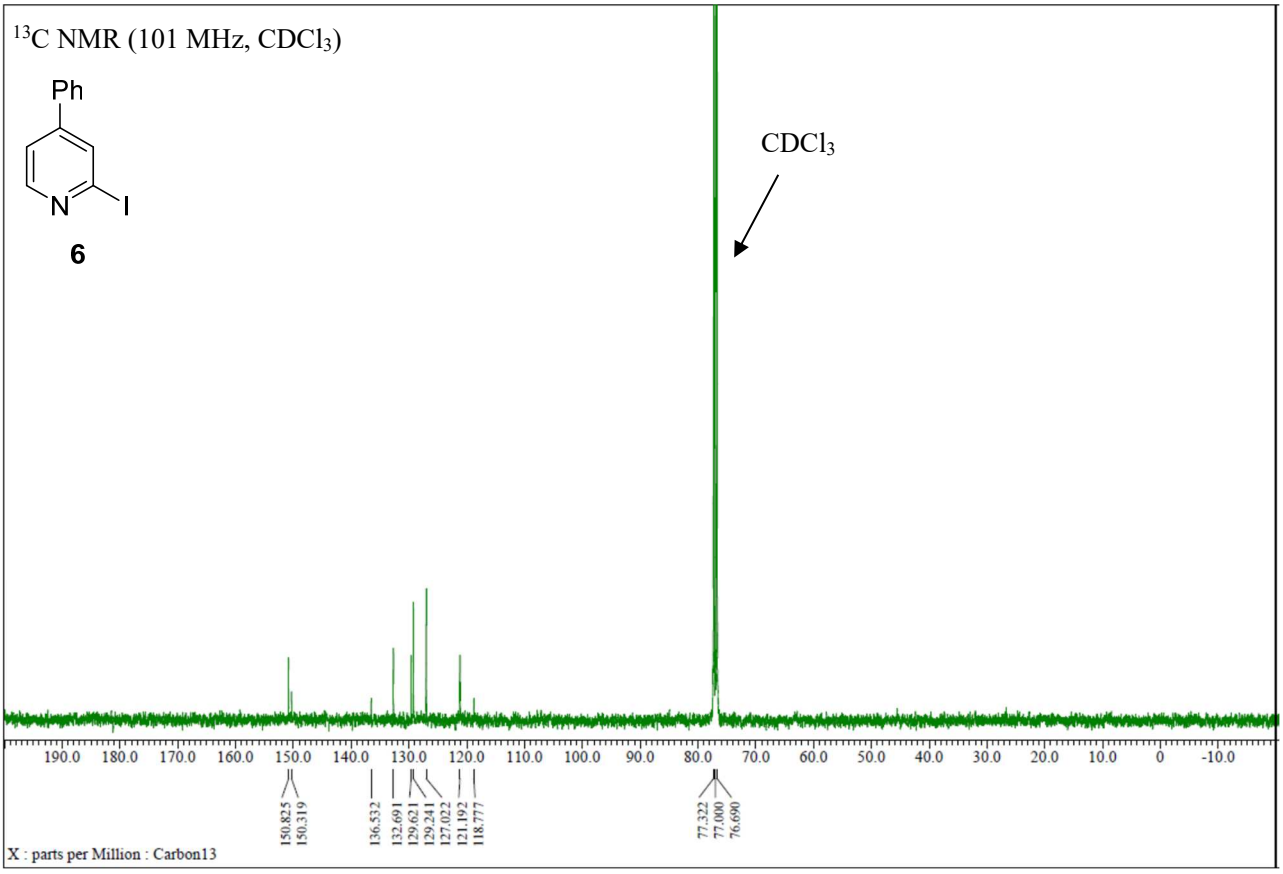


5

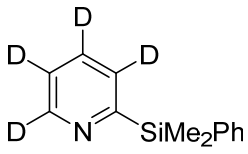
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

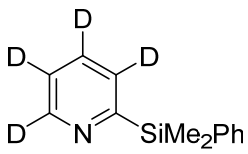


^{1}H NMR (400 MHz, $CDCl_3$)



2a-d_5

^{13}C NMR (101 MHz, $CDCl_3$)



2a-d_5