Supporting Information

Stereoselective Synthesis of Multisubstituted Butadienes through Directed Mizoroki–Heck Reaction and Homo-Coupling Reaction of Vinyl(2-pyridyl)silane

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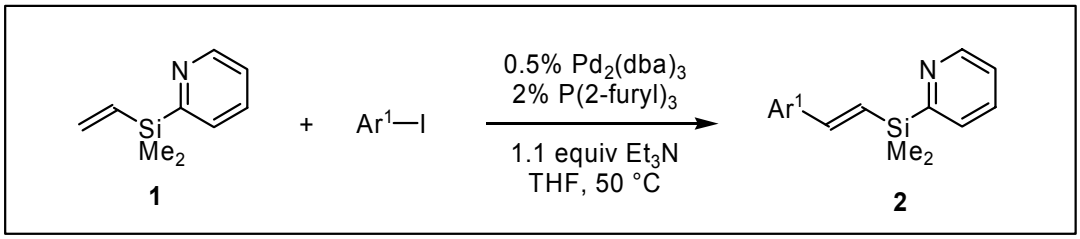
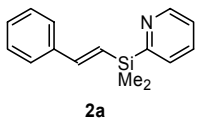
General. ^{1}H and ^{13}C NMR spectra were recorded on Varian GEMINI-2000 (^{1}H 300 MHz, ^{13}C 75 MHz), Varian MERCURYplus-400 (^{1}H 400 MHz, ^{13}C 100 MHz), and JEOL A-500 (^{1}H 500 MHz, ^{13}C 125 MHz) spectrometers in $CDCl_3$. UV/Vis spectra were recorded on Shimadzu UV-2500 spectrophotometer. Fluorescence spectra were recorded on Horiba Jobin Yvon SPEX FluoroMax-3 spectrofluorometer. IR spectra were recorded on Shimadzu FTIR-8100 spectrophotometer. EI and CI mass spectra were recorded on JMS-SX102A spectrometer. FAB mass spectra were recorded on JMS-HX110A spectrometer. Gel permeation chromatography was carried out with Japan Analytical Industry LC-918. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. $Pd[P(t\text{-}Bu)_3]_2$ and $P(t\text{-}Bu)_3$ were purchased from Strem Chemicals, Inc. and used as received. Dimethyl(2-pyridyl)(vinyl)silane (**1**) was prepared according to our previously reported procedure.[1]

Synthesis of Alkenyl(2-pyridyl)silanes 2 except 2i.



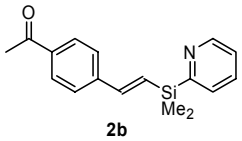
To a solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (2.6 mg, 2.5 μmol) and tri-2-furylphosphine (2.3 mg, 0.01 mmol) in THF (1.5 mL) were added iodobenzene (112 mg, 0.55 mmol), dimethyl(2-pyridyl)vinylsilane (**1**) (82 mg, 0.50 mmol), and triethylamine (61 mg, 0.60 mmol) at room temperature under argon and the reaction mixture was stirred at 50 °C for 24 h. After cooling to room temperature, toluene (5 mL) was added to the reaction mixture. This mixture was extracted with 1 N aq HCl (6 x 10 mL). The combined aqueous phase was neutralized by adding $NaHCO_3$ and then was extracted with EtOAc (3 x 30 mL). Drying over Na_2SO_4 and removal of the solvents under reduced pressure afforded **2a** (118 mg, 99%) as pale yellow oil.



2a

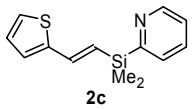
2a: 93% yield from **1** and iodobenzene. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.50 (s, 6H), 6.65 (d, *J* = 19.2 Hz, 1H), 7.02 (d, *J* = 19.2 Hz, 1H), 7.21 (ddd, *J* = 6.9, 4.8, 2.1 Hz, 1H), 7.26-7.36 (m, 3H), 7.44–7.49 (m, 2H), 7.54–7.62 (m, 2H), 8.81 (dt, *J* = 5.1, 1.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ –3.4, 122.9, 126.1, 126.6, 128.3, 128.6, 129.5, 134.1, 138.2, 145.9, 150.4, 167.0. IR (neat) 2959, 1605, 1574, 1495, 1449, 1418, 1246 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{15}H_{17}NSi$: 239.1131, found 239.1122. Anal. Calcd for $C_{15}H_{17}NSi$: C, 75.26; H, 7.16; N, 5.85. Found: C, 75.49; H, 7.25; N, 5.83.

(1) Itami, K.; Mitsudo, K.; Kamei, T.; Koike, T.; Nokami, T.; Yoshida, J. *J. Am. Chem. Soc.* **2000**, *122*, 12013.



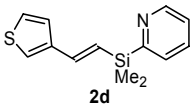
2b

2b: 71% yield from **1** and 4′-iodoacetophenone. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.52 (s, 6H), 2.59 (s, 3H), 6.80 (d, *J* = 19.2 Hz, 1H), 7.03 (d, *J* = 19.2 Hz, 1H), 7.20–7.23. (m, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.53–7.62 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 8.79–8.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –3.1, 26.7, 122.9, 126.5, 128.5, 129.3, 129.9, 134.0, 136.3, 142.2, 144.3, 150.1, 166.0, 197.2. HRMS (EI) *m*/*z* calcd for $C_{17}H_{19}NOSi$: 281.1236, found: 281.1237.



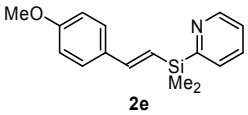
2c

2c: 92% yield from **1** and 2-iodothiophene. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.48 (s, 6H), 6.36 (d, *J* = 18.6 Hz, 1H), 6.97 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.00 (dd, *J* = 3.6, 1.7 Hz, 1H), 7.09 (d, *J* = 18.6 Hz, 1H), 7.19 (dm, *J* = 4.8 Hz, 1H), 7.22 (ddd, *J* = 7.5, 4.8, 1.8 Hz, 1H), 7.55 (ddd, *J* = 7.5, 1.8, 1.1 Hz, 1H), 7.61 (td, *J* = 7.5, 1.8 Hz, 1H), 8.80 (ddd, *J* = 4.8, 1.8, 1.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ –3.3, 122.9, 125.1, 125.5, 126.1, 127.4, 129.5, 134.1, 138.2, 144.9, 150.2, 166.5. IR (neat) 1595, 1574, 1559, 1246 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{13}H_{15}NSSi$: 245.0694, found 245.0694. Anal. Calcd for $C_{13}H_{15}NSSi$: C, 63.62; H, 6.16; N, 5.71. Found: C, 63.33; H, 6.19; N, 5.50.



2d

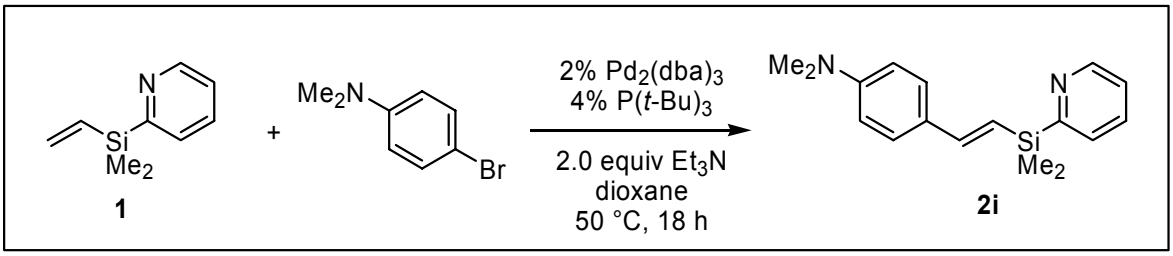
2d: 72% yield from **1** and 3-iodothiophene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.50 (s, 6H), 6.42 (d, *J* = 18.8 Hz, 1H), 7.01 (d, *J* = 18.8 Hz, 1H), 7.18–7.25 (m, 3H), 7.29–7.31 (m, 1H), 7.53–7.59 (m, 2H), 8.79–8.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –3.0, 122.7, 123.0, 124.8, 125.4, 125.7, 129.2, 133.8, 139.3, 141.7, 150.0, 166.6. HRMS (EI) *m*/*z* calcd for $C_{13}H_{15}NSSi$: 245.0694, found: 245.0693.



2e

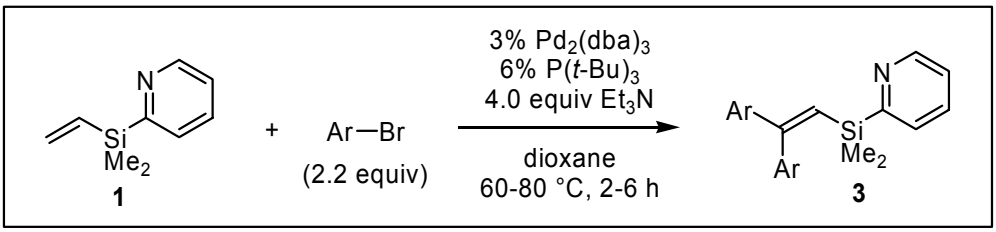
2e: 97% yield from **1** and 4-iodoanisole. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.49 (s, 6H), 3.80 (s, 3H), 6.48 (d, *J* = 18.9 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.97 (s, *J* = 18.9 Hz, 1H), 7.17–7.21 (m, 1H), 7.41 (d, *J* = 9.3 Hz, 2H), 7.53–7.61 (m, 2H), 8.79–8.81 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ –3.2, 55.2, 113.8, 122.7, 123.0, 127.8, 129.4, 131.0, 134.0, 145.2, 150.2, 159.7, 167.1. HRMS (EI) *m*/*z* calcd for $C_{16}H_{19}NOSi$: 269.1236, found: 269.1237.

Synthesis of Alkenyl(2-pyridyl)silane 2i.

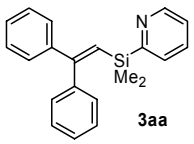


A mixture of $Pd_2(dba)_3{\cdot}CHCl_3$ (106.6 mg, 0.10 mmol), P(*t*-Bu)$_3$ (40.5 mg, 0.20 mmol), **1** (889.5 mg, 5.5 mmol), 4-bromo-*N*,*N*-dimethylaniline (1.00 g, 5.0 mmol), and Et_3N (1.01 g, 10.0 mmol) in dioxane (5 mL) was stirred at 50 °C for 18 h. After cooling to room temperature, catalyst and salts were removed by filtration through a short gel pad (EtOAc/$CHCl_3$). The filtrate was evaporated, and the residue was subjected to silica gel chromatography (hexane/EtOAc = 5/2) to afford **2i** (1.16 g, 82%) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.51 (s, 6H), 2.98 (s, 6H), 6.36 (d, *J* = 18.4 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 18.8 Hz, 1H), 7.22–7.25 (m, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.58–7.62 (m, 2H), 8.80–8.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –2.8, 40.5, 112.0, 119.8, 122.5, 126.7, 127.5, 129.3, 133.8, 145.7, 149.9, 150.4, 167.4. HRMS (EI) *m*/*z* calcd for $C_{17}H_{22}N_2Si$: 282.1552, found: 282.1546.

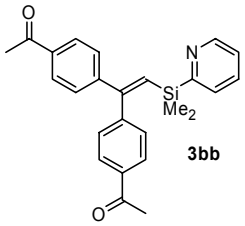
One-Pot Synthesis of Alkenyl(2-pyridyl)silanes 3 from 1 and Aryl Bromides.



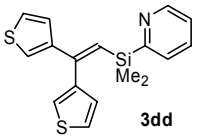
A mixture of $Pd_2(dba)_3 \cdot CHCl_3$ (9.8 mg, 9.5 μmol), P(*t*-Bu)$_3$ (3.6 mg, 0.02 mmol), **1** (47.6 mg, 0.29 mmol), 4-bromoanisole (120.5 mg, 0.64 mmol), and Et_3N (121.4 mg, 1.20 mmol) in dioxane (1 mL) was stirred at 80 °C for 3 h. After cooling to room temperature, catalyst and salts were removed by filtration through a short gel pad (EtOAc/$CHCl_3$). The filtrate was evaporated, and the residue was subjected to silica gel chromatography (hexane/EtOAc = 5/2) to afford **3ee** (99.3 mg, 91%) as pale yellow oil.



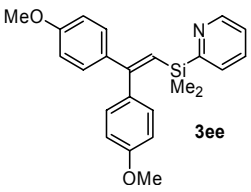
3aa: 99% yield from **1** and bromobenzene. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 6H), 6.55 (s, 1H), 7.10–7.19 (m, 3H), 7.22–7.36 (m, 8H), 7.37–7.45 (m, 1H), 7.53 (td, *J* = 7.5, 1.8 Hz, 1H), 8.78 (dm, *J* = 5.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ –2.0, 122.5, 126.34, 126.35, 127.3, 127.4, 127.8, 128.0, 129.3, 129.6, 133.9, 142.3, 142.9, 150.0, 158.8, 167.8. IR (neat) 3058, 2957, 1574, 1489, 1443, 1418, 1246 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{21}H_{21}NSi$: 315.1443, found 315.1444.



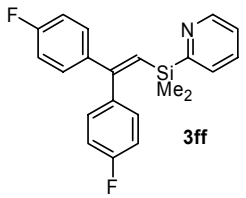
3bb: 79% yield from **1** and 4′-bromoacetophenone. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.22 (s, 6H), 2.58 (s, 3H), 2.61 (s, 3H), 6.72 (s, 1H), 7.17–7.21 (m, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.32–7.36 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.51–7.55 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 8.73–8.75 (m, 1H). ^{13}C NMR (125MHz, $CDCl_3$) δ –2.1, 26.57, 26.58, 122.7, 127.3, 128.0, 128.2, 129.2, 129.7, 130.6, 134.0, 136.22, 136.23, 146.4, 146.5, 150.0, 156.3, 166.7, 197.50, 197.55. HRMS (EI) *m*/*z* calcd for $C_{25}H_{25}NO_2Si$: 399.1655, found: 399.1656.



3dd: 72% yield from **1** and 3-bromothiophene. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 6H), 6.46 (s, 1H), 6.87 (d, *J* = 1.2 Hz, 1H), 6.90 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.05 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.15–7.26 (m, 3H), 7.31 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.42 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.55 (td, *J* = 7.5, 1.7 Hz, 1H), 8.76 (dq, *J* = 4.5, 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ –2.2, 122.5, 123.6, 123.9, 124.9, 125.4, 125.5, 126.0, 129.0, 129.2, 133.9, 142.5, 144.9, 148.0, 150.0, 167.8. HRMS (EI) *m*/*z* calcd for $C_{17}H_{17}NS_2Si$: 327.0572, found 327.0573.

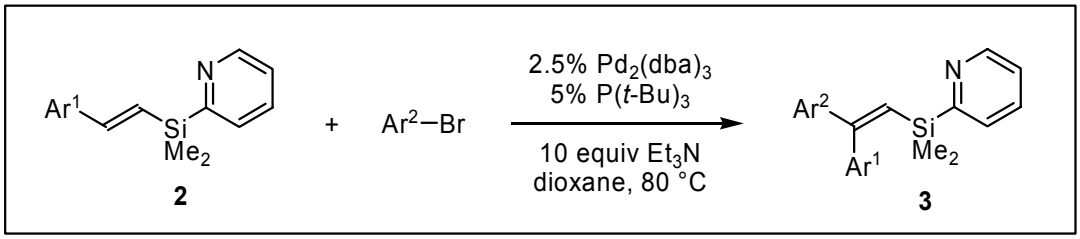


3ee: 91% yield from **1** and 4-bromoanisole. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.20 (s, 6H), 3.75 (s, 3H), 3.78 (s, 3H), 6.38 (s, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.11–7.14 (m, 1H), 7.26 (d, *J* = 9.2 Hz, 2H), 7.41–7.43 (m, 1H), 7.47–7.50 (m, 1H), 8.74–8.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.7, 55.0, 55.1, 112.9, 113.0, 122.1, 123.4, 128.4, 128.9, 130.5, 133.5, 134.7, 135.7, 149.6, 157.7, 158.7, 159.1, 167.9. HRMS (EI) *m*/*z* calcd for $C_{23}H_{25}NO_2Si$:375.1655, found: 375.1654.

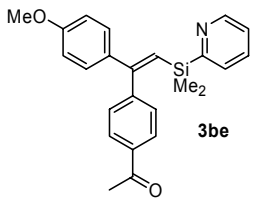


3ff: 72% yield from **1** and 1-bromo-4-fluorobenzene. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 6H), 6.46 (s, 1H), 6.88–6.97 (m, 4H), 7.02–7.07 (m, 2H), 7.15–7.27 (m, 3H), 7.35–7.38 (m, 1H), 7.51–7.56 (m, 1H), 8.74–8.76 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ –2.0, 114.8 (d, $J_{C–F}$ = 21.6 Hz), 114.9 (d, $J_{C–F}$ = 21.7 Hz), 122.7, 126.8, 129.0, 129.2 (d, $J_{C–F}$ = 9.2 Hz), 131.2 (d, $J_{C–F}$ = 8.0 Hz), 134.1, 138.0 (d, $J_{C–F}$ = 3.5 Hz), 139.0 (d, $J_{C–F}$ = 3.5 Hz), 150.0, 156.6, 162.3 (d, $J_{C–F}$ = 244.9 Hz), 162.7 (d, $J_{C–F}$ = 247.1 Hz), 167.4. HRMS (EI) *m*/*z* calcd for $C_{21}H_{19}F_2NSi$:351.1255, found: 351.1255.

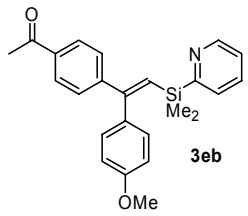
Synthesis of Alkenyl(2-pyridyl)silanes 3 from 2 and Aryl Bromides.



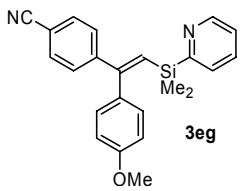
A mixture of **2b** (279.6 mg, 1.00 mmol), 4-bromoanisole (96.4 mg, 1.05 mmol), triethylamine (1.01 g, 10.0 mmol), $Pd_2(dba)_3$·$CHCl_3$ (26.0 mg, 0.025 mmol), and P(*t*-Bu)$_3$ (11.5 mg, 0.05 mmol) in dry dioxane (1.5 mL) was stirred at 80 °C for 2 h under argon. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short silica gel pad (EtOAc). The filtrate was evaporated, and the residue was chromatographed on silica gel (hexane/EtOAc) to afford **3be** (272.7 mg, 73%) as pale yellow oil.



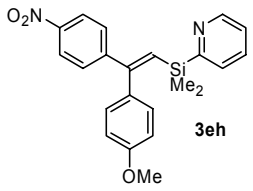
3be: 73% yield from **2b** and 4-bromoanisole. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 6H), 2.60 (s, 3H), 3.78 (s, 3H), 6.47 (s, 1H), 6.73 (d, *J* = 9.3 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.13–7.22 (m, 1H), 7.34–7.37 (m, 1H), 7.40–7.53 (m, 1H), 7.81 (d, *J* = 8.7 Hz, 2H), 8.72–8.74 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ –1.9, 26.6, 52.2, 113.4, 122.6, 125.0, 127.9, 128.5, 129.2, 129.8, 134.0, 134.9, 136.0, 147.6, 149.9, 157.0, 159.6, 167.4, 197.7. HRMS (EI) *m*/*z* calcd for $C_{24}H_{25}NO_2Si$: 387.1655, found: 387.1655.



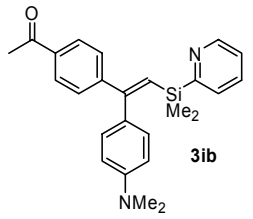
3eb: 63% yield from **2e** and 4′-bromoacetophenone. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.21 (s, 6H), 2.58 (s, 3H), 3.82 (s, 3H), 6.58 (s, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.16–7.19 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.36–7.42 (m, 1H), 7.52–7.56 (m, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 8.75–8.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.8, 26.7, 55.3, 113.3, 122.5, 127.5, 127.9, 129.0, 129.1, 130.6, 133.8, 133.9, 136.0, 147.6, 149.9, 157.3, 159.1, 167.3, 197.3. HRMS (EI) *m*/*z* calcd for $C_{24}H_{25}NO_2Si$: 387.1655, found: 387.1656.



3eg: 61% yield from **2e** and 4-bromobenzonitrile. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.21 (s, 6H), 3.82 (s, 3H), 6.58 (s, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.17–7.20 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.37–7.40 (m, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.52–7.57 (m, 1H), 8.74–8.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.8, 55.3, 111.0, 113.4, 118.8, 122.6, 127.9, 129.1, 130.2, 130.6, 131.7, 133.3, 133.9, 147.4, 149.8, 156.5, 159.2, 167.0. HRMS (EI) *m*/*z* calcd for $C_{23}H_{22}N_2OSi$: 370.1501, found: 370.1495.

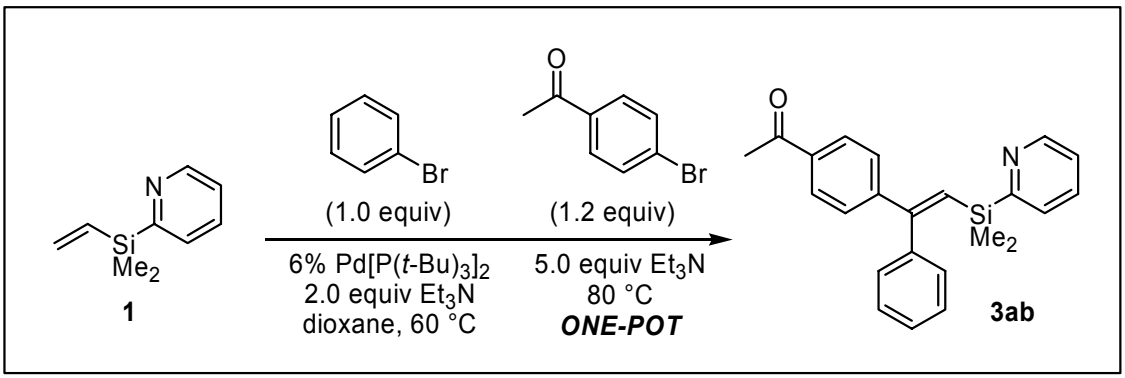


3eh: 39% yield from **2e** and 1-bromo-4-nitrobenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.23 (s, 6H), 3.82 (s, 3H), 6.64 (s, 1H), 6.79 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.18–7.21 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.38–7.45 (m, 1H), 7.53–7.58 (m, 1H), 8.10 (d, *J* = 9.2 Hz, 2H), 8.75–8.77 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.8, 55.3, 113.4, 122.6, 123.1, 128.0, 129.1, 130.6, 131.2, 133.2, 134.0, 146.9, 149.3, 149.8, 156.2, 159.3, 166.9. HRMS (EI) *m*/*z* calcd for $C_{22}H_{22}N_2O_3Si$: 390.1400, found: 390.1401.



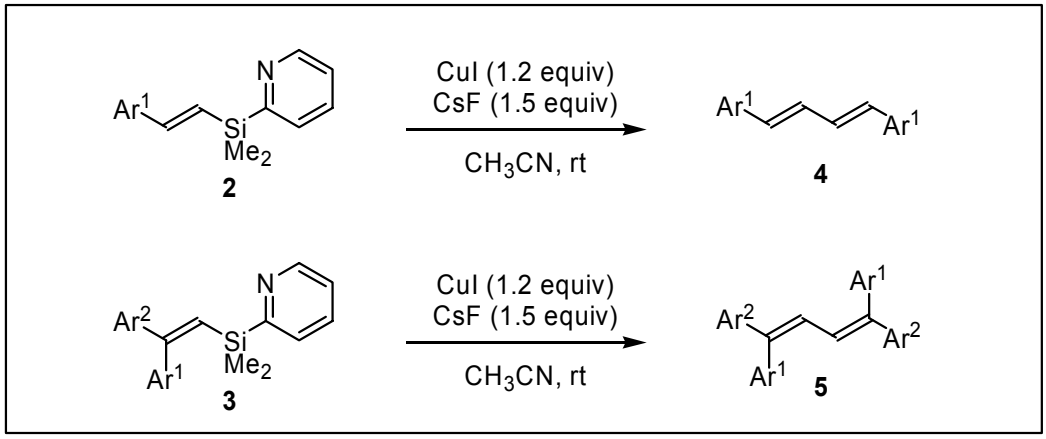
3ib: 86% yield from **2i** and 4′-bromoacetophenone. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.23 (s, 6H), 2.55 (s, 3H), 2.94 (s, 6H), 6.47 (s, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 7.12–7.16 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.43–7.45 (m, 1H), 7.50–7.54 (m, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 8.75–8.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.7, 26.6, 40.4, 111.4, 122.3, 127.5, 127.6, 127.7, 129.0, 129.3, 130.2, 133.6, 135.7, 148.3, 149.7, 149.8, 158.0, 167.7, 197.2. HRMS (EI) *m*/*z* calcd for $C_{25}H_{28}N_2OSi$: 400.1971, found: 400.1972.

Synthesis of Alkenyl(2-pyridyl)silane 3ab.

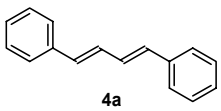


A mixture of Pd[P(*t*-Bu)$_3$]$_2$ (30.7 mg, 0.06 mmol), triethylamine (202.4 mg, 2.0 mmol), **1** (167.4 mg, 1.03 mmol), and bromobenzene (158.5 mg, 1.01 mmol) in dioxane (1.2 mL) was stirred at 60 °C for 5 h under argon. To this mixture were added 4′-bromoacetophenone (236.2 mg, 1.19 mmol), triethylamine (506.0 mg, 5.0 mmol), and dioxane (1.2 mL) the resultant mixture was further stirred at 80 °C for 2 h. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short silica gel pad (EtOAc). The subjection of the crude mixture to silica gel chromatography (hexane/EtOAc = 5/2) afforded **3ab** (241.3 mg, 68%) as pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.18 (s, 6H), 2.58 (s, 3H), 6.66 (s, 1H), 7.08–7.10 (m, 2H), 7.16–7.20 (m, 1H), 7.23–7.32 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.36–7.40 (m, 3H), 7.52–7.56 (m, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 8.75–8.77 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ –2.2, 26.4, 122.5, 127.3, 127.6, 127.9, 128.0, 129.1, 129.35, 129.38, 133.8, 136.0, 141.4, 147.1, 149.9, 157.5, 167.2, 197.4. HRMS (EI) *m*/*z* calcd for $C_{23}H_{23}NOSi$: 357.1549, found: 357.1548.

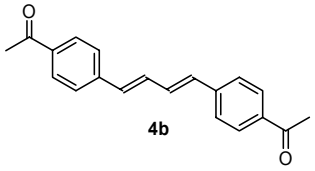
Typical Procedure for CuI/CsF-Mediated Homo-Coupling Reaction of Alkenyl(2-pyridyl)silanes (2 and 3).



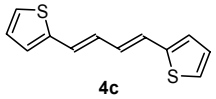
A mixture of **3bb** (120.5 mg, 0.30 mmol), CuI (69.1 mg, 0.36 mmol), and CsF (68.7 mg, 0.45 mmol) in dry CH_3CN (3.0 mL) was stirred at room temperature for 3 h under argon. Catalyst and salts were removed by filtration through a short gel pad (EtOAc/$CHCl_3$). The filtrate was evaporated, and the residue was subjected to gel permeation chromatography ($CHCl_3$) to afford **5bb** as pale yellow solid (49.3 mg, 62%).


4a

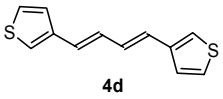
4a:[2] >99% yield from **2a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.68 (dd, *J* = 18.9, 7.2 Hz, 2H), 6.98 (dd, *J* = 18.9, 7.2 Hz, 2H), 7.20-7.50 (m, 10H). UV/Vis ($CHCl_3$): λ_{max} = 333 nm. FL ($CHCl_3$): λ_{max} = 381 nm.


4b

4b:[3] 47% yield from **2b**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 6H), 6.76 (dd, *J* = 18.9, 7.2 Hz, 2H), 7.07 (dd, *J* = 18.9, 7.2 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 4H), 7.92 (d, *J* = 8.4 Hz, 4H). UV/Vis ($CHCl_3$): λ_{max} = 368 nm. FL ($CHCl_3$): λ_{max} = 425 nm.

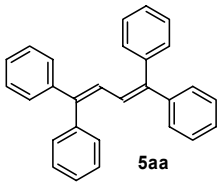

4c

4c:[4] 70% yield from **2c**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67–6.80 (m, 4H), 6.95–7.05 (m, 4H), 7.17 (dd, *J* = 4.8, 1.6 Hz, 2H). UV/Vis ($CHCl_3$): λ_{max} = 363 nm. FL ($CHCl_3$): λ_{max} = 430 nm.

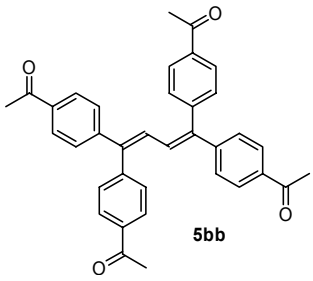

4d

4d:[5] 46% yield from **2d**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60–6.80 (m, 4H), 7.18 (dd, *J* = 4.0, 2.4 Hz, 2H), 7.25–7.30 (m, 4H). UV/Vis ($CHCl_3$): λ_{max} = 322 nm. FL ($CHCl_3$): λ_{max} = 394 nm.

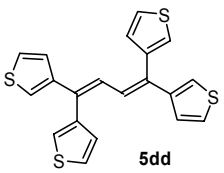
(2) Wang, Z.; Zhang, G.; Guzei, I.; Verkade, J. G. *J. Org. Chem.* **2001**, *66*, 3521.
(3) Mitsudo, T.; Fischetti, W.; Heck, R. F. *J. Org. Chem.* **1984**, *49*, 1640.
(4) Frère, P.; Raimundo, J.-M.; Blanchard, P.; Delaunay, J.; Richomme, P.; Sauvajol, J.-L.; Orduna, J.; Garin, J.; Roncali, J. *J. Org. Chem.* **2003**, *68*, 7254.
(5) Leznoff, C. C.; Lilie, W.; Manning, C. *Can. J. Chem.* **1974**, *52*, 132.



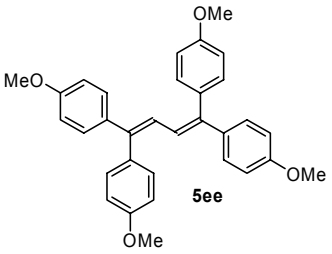
5aa:[6] 58% yield from **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 2H), 7.05-7.20 (m, 20H). UV/Vis ($CHCl_3$): λ_{max} = 348 nm. FL ($CHCl_3$): λ_{max} = 449 nm.



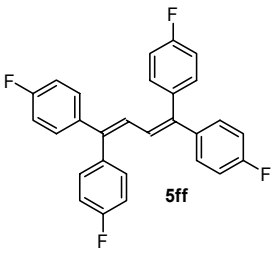
5bb: 62% yield from **3bb**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 6H), 2.68 (s, 6H), 6.84 (s, 2H), 7.21 (d, *J* = 8.4 Hz, 4H), 7.41 (d, *J* = 8.4 Hz, 4H), 7.84 (d, *J* = 8.4 Hz, 4H), 8.05 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.6, 26.7, 127.6, 127.8, 128.5, 128.6, 130.8, 136.3, 136.7, 143.7, 144.0, 145.7, 197.3, 197.6. HRMS (EI) *m*/*z* calcd for $C_{36}H_{30}O_4$: 526.2144, found: 526.2144. UV/Vis ($CHCl_3$): λ_{max} = 381 nm. FL ($CHCl_3$): λ_{max} = 480 nm.



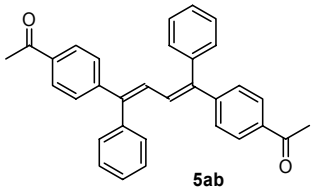
5dd: 38% yield from **3dd**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 2H), 6.96–6.97 (m, 2H), 7.09–7.10 (m, 2H), 7.12–7.13 (m, 2H), 7.23–7.25 (m, 2H), 7.33–7.34 (m, 2H), 7.38–7.40 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.7, 125.0, 125.1, 125.3, 126.1, 129.7, 133.1, 139.8, 144.1. HRMS (EI) *m*/*z* calcd for $C_{20}H_{14}S_4$: 381.9978, found: 381.9980. UV/Vis ($CHCl_3$): λ_{max} = 353 nm. FL ($CHCl_3$): λ_{max} = 435 nm.



5ee:[6] 63% yield from **3ee**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 6H), 3.86 (s, 6H), 6.65 (s, 2H), 6.78 (d, *J* = 9.6 Hz, 4H), 6.94 (d, *J* = 8.7 Hz, 4H), 7.11 (d, *J* = 8.7 Hz, 4H), 7.24 (d, *J* = 9.6 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.31, 55.32, 113.35, 113.39, 124.5, 128.7, 131.7, 132.4, 135.5, 141.9, 158.6, 158.7. UV/Vis ($CHCl_3$): λ_{max} = 365 nm. FL ($CHCl_3$): λ_{max} = 448 nm.

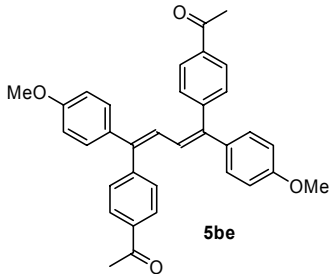


5ff: 51% yield from **3ff**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (s, 2H), 6.91–6.97 (m, 4H), 7.08–7.15 (m, 8H), 7.24–7.29 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 115.2 (d, J_{C-F} = 21.7 Hz), 115.4 (d, J_{C-F} = 20.5 Hz), 125.6, 129.2 (d, J_{C-F} = 8.0 Hz), 132.2 (d, J_{C-F} = 8.0 Hz), 135.5 (d, J_{C-F} = 3.4 Hz), 138.3 (d, J_{C-F} = 3.5 Hz), 142.2, 162.3 (d, J_{C-F} = 246.0 Hz), 162.4 (d, J_{C-F} = 247.1 Hz). HRMS (EI) *m*/*z* calcd for $C_{28}H_{18}F_4$: 430.1345, found: 430.1351. UV/Vis ($CHCl_3$): λ_{max} = 345 nm. FL ($CHCl_3$): λ_{max} = 435 nm.

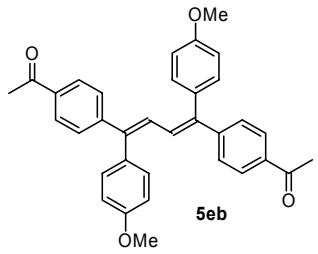


5ab: 61% yield from **3ab**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 6H), 6.88 (s, 2H), 7.25 (d, *J* = 9.2 Hz, 4H), 7.29–7.31 (m, 4H), 7.41–7.47 (m, 6H), 7.82 (d, *J* = 8.8 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.9, 127.9, 128.1, 128.4, 128.6, 128.8, 130.9, 136.2, 139.2, 144.6, 147.0, 197.8. HRMS (EI) *m*/*z* calcd for $C_{32}H_{26}O_2$: 442.1933, found: 442.1933. UV/Vis ($CHCl_3$): λ_{max} = 376 nm. FL ($CHCl_3$): λ_{max} = 472 nm.

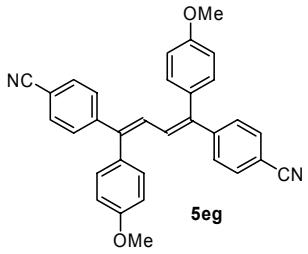
(6) Feit, B.-A.; Buzhansky, L. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1777.



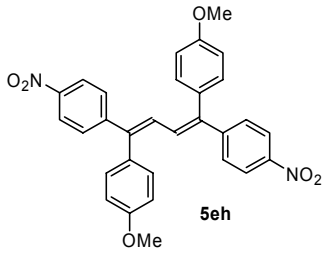
5be: 56% yield from **3be**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.66 (s, 6H), 3.78 (s, 6H), 6.65 (s, 2H), 6.78 (d, *J* = 8.7 Hz, 4H), 7.05 (d, *J* = 8.7 Hz, 4H), 7.42 (d, *J* = 8.1 Hz, 4H), 8.01 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.7, 55.3, 113.7, 124.8, 128.3, 128.8, 130.9, 134.3, 136.2, 142.5, 145.2, 159.4, 197.8. HRMS (EI) *m*/*z* calcd for $C_{34}H_{30}O_4$: 502.2144, found: 502.2145. UV/Vis ($CHCl_3$): λ_{max} = 389 nm. FL ($CHCl_3$): λ_{max} = 499 nm.



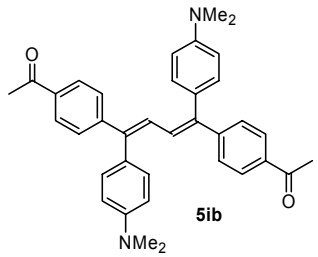
5eb: 50% yield from **3eb**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.56 (s, 6H), 3.87 (s, 6H), 6.84 (s, 2H), 6.96 (d, *J* = 8.4 Hz, 4H), 7.23 (d, *J* = 8.1 Hz, 4H), 7.28 (d, *J* = 8.1 Hz, 4H), 7.83 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 55.3, 113.8, 127.6, 127.9, 128.2, 131.2, 131.8, 135.8, 143.7, 147.3, 159.3, 197.5. HRMS (EI) *m*/*z* calcd for $C_{34}H_{30}O_4$: 502.2144, found: 502.2146. UV/Vis ($CHCl_3$): λ_{max} = 391 nm. FL ($CHCl_3$): λ_{max} = 500 nm.



5eg: 63% yield from **3eg**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 6H), 6.80 (s, 2H), 6.97 (d, *J* = 8.8 Hz, 4H), 7.20 (d, *J* = 8.8 Hz, 4H), 7.27 (d, *J* = 8.4 Hz, 4H), 7.52 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 110.6, 113.9, 118.8, 127.7, 128.1, 130.4, 131.6, 131.8, 143.3, 146.7, 159.3. HRMS (EI) *m*/*z* calcd for $C_{32}H_{24}N_2O_2$: 468.1838, found: 468.1838. UV/Vis ($CHCl_3$): λ_{max} = 383 nm. FL ($CHCl_3$): λ_{max} = 490 nm.

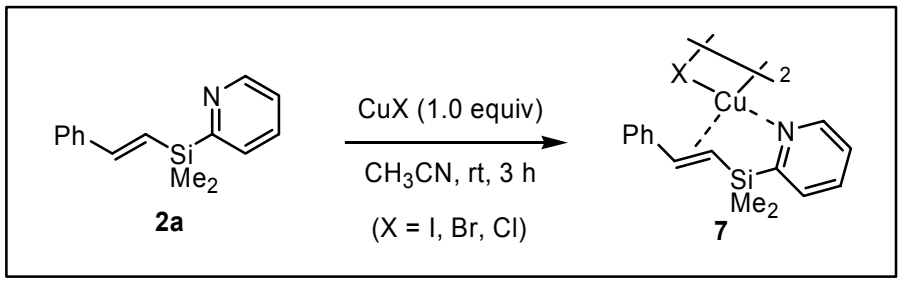


5eh: 24% yield from **3eh**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 6H), 6.85 (s, 2H), 6.98 (d, *J* = 8.8 Hz, 4H), 7.21 (d, *J* = 8.8 Hz, 4H), 7.32 (d, *J* = 8.4 Hz, 4H), 8.09 (d, *J* = 8.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 114.0, 123.4, 128.3, 130.3, 131.7, 143.5, 146.7, 148.7, 159.5. HRMS (EI) *m*/*z* calcd for $C_{30}H_{24}N_2O_6$: 508.1634, found: 508.1635. UV/Vis ($CHCl_3$): λ_{max} = 417 nm. FL ($CHCl_3$): λ_{max} = 593 nm.



5ib: 48% yield from **3ib**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 6H), 3.03 (s, 12H), 6.74 (d, *J* = 8.0 Hz, 4H), 6.85 (s, 2H), 7.18 (d, *J* = 8.4 Hz, 4H), 7.32 (d, *J* = 8.4 Hz, 4H), 7.82 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.7, 40.5, 111.7, 127.4, 128.0, 128.1, 128.3, 131.6, 135.5, 143.5, 148.1, 149.8, 197.3. HRMS (EI) *m*/*z* calcd for $C_{36}H_{36}N_2O_2$: 528.2777, found: 528.2775. UV/Vis ($CHCl_3$): λ_{max} = 322 nm. FL ($CHCl_3$): λ_{max} = 578 nm.

Typical Procedure for the Stoichiometric Reaction of 2a and CuX (X = I, Br, Cl).



To a solution of CuI (193 mg, 1.01 mmol) in dry CH_3CN (10 mL) was added **2a** (239.4 mg, 1.00 mmol) at room temperature. After stirring the resultant mixture at room temperature for 3 h (yellow solid gradually deposited), the mixture was filtered. The resultant solid was washed with CH_3CN (10 mL) and dried under reduced pressure to afford **7 (X = I)** (436.6 mg, >99% yield) as yellow solid.

7 (X = I): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.49 (s, 6H), 5.81 (d, *J* = 18.8 Hz, 1H), 6.87 (d, *J* = 18.8 Hz, 1H), 7.04 (ddd, *J* = 7.2, 4.8, 1.2 Hz, 1H), 7.34–7.42 (m, 3H), 7.46 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.58 (td, *J* = 7.6, 1.6 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.80 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –2.6, 124.1, 127.6, 127.8, 128.2, 128.4, 128.9, 134.9, 137.3, 150.4, 167.2. LRMS (FAB) *m*/*z* 733 (bridged dimer – I), 541 (bridged dimer – CuI_2), 302 (monomer – I).

7 (X = Br): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.49 (s, 6H), 5.37 (d, *J* = 16.8 Hz, 1H), 6.64 (d, *J* = 16.8 Hz, 1H), 6.95–7.20 (br, 1H), 7.30–7.45 (m, 4H), 7.50–7.70 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –3.0, 92.0, 120.8, 124.8, 127.7, 127.9, 128.1, 128.6, 129.1, 135.5, 137.8, 150.4. LRMS (FAB) *m*/*z* 685 (bridged dimer – Br), 541 (bridged dimer – $CuBr_2$), 302 (monomer – Br).

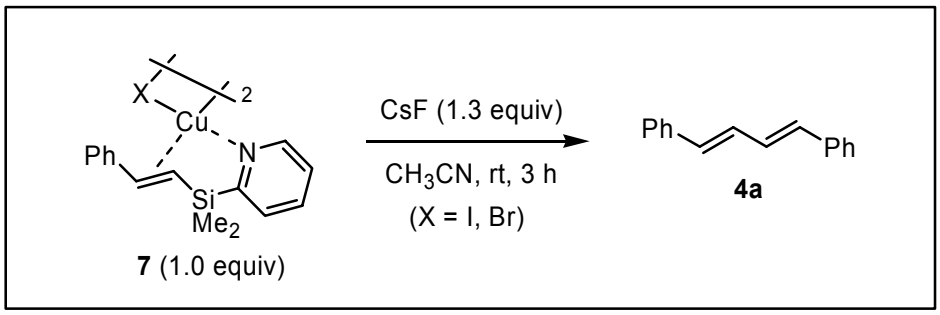
7 (X = Cl): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.62 (brs, 6H), 3.00–5.00 (br, 1H), 6.20–6.80 (m, 2H), 6.80–8.00 (m, 7H), 8.20–9.20 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –3.9, 119.6 (br), 125.8, 126.0, 127.5, 127.8, 137.4, 141.4 (br). LRMS (FAB) *m*/*z* 541 (bridged dimer – $CuCl_2$).

Copper complex **8** was obtained in quantitative yield using the similar procedure.

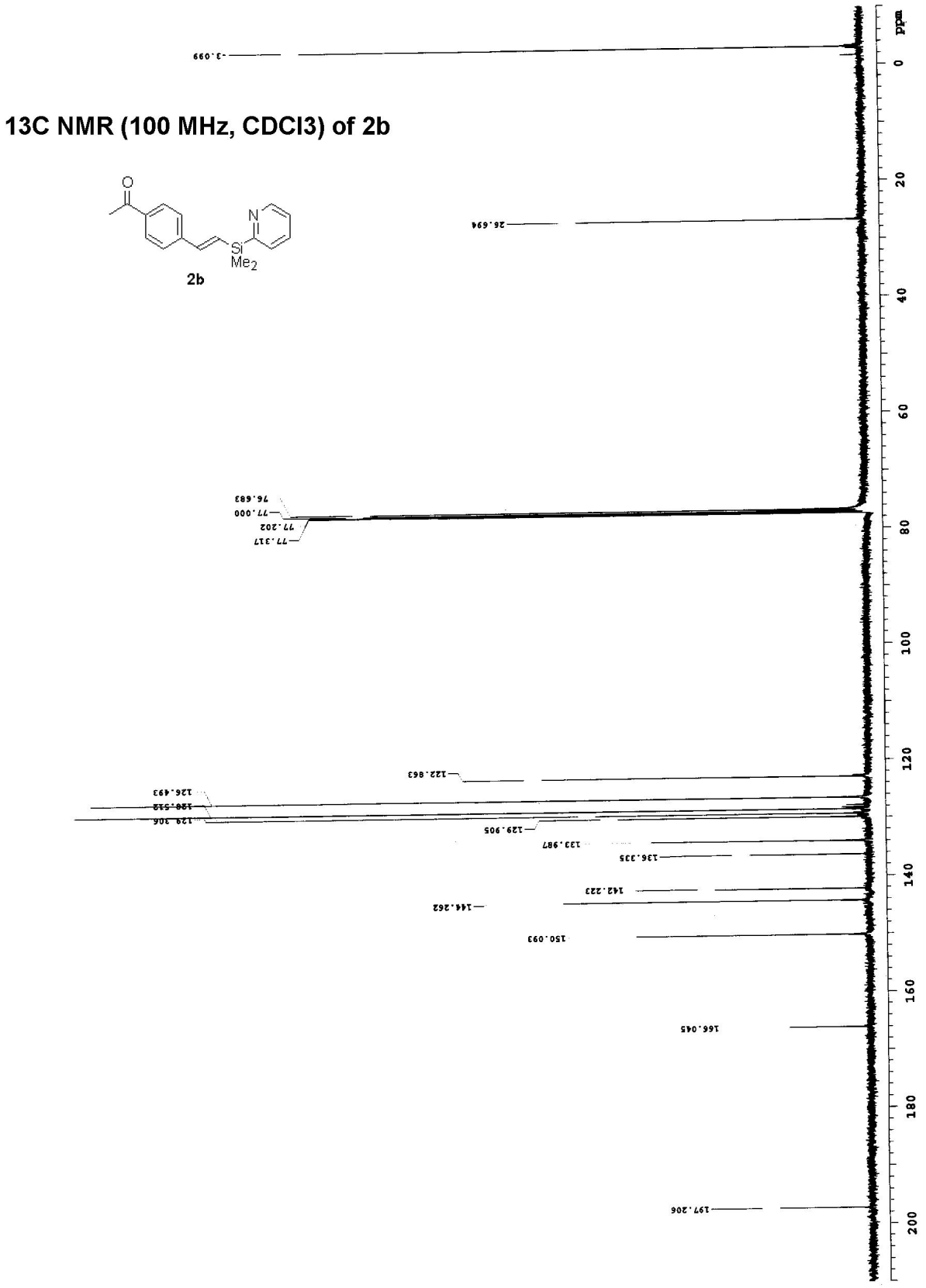
8: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.47 (s, 6H), 2.41 (s, 3H), 5.73 (d, *J* = 18.4 Hz, 1H), 6.86 (d, *J* = 18.4 Hz, 1H), 6.94 (ddd, *J* = 7.6, 5.2, 1.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.44 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.57 (td, *J* = 7.6, 1.2 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.70 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –2.8, 21.5, 101.5 (br), 124.0, 127.9, 128.8, 129.2, 131.8 (br), 134.7, 134.9, 138.1, 150.7, 167.5. LRMS (FAB) *m*/*z* 886 (M for bridged dimer), 759 (bridged dimer – I), 569 (bridged dimer – CuI_2).

X-ray data for **8**: $C_{16}H_{19}NSiICu$ (monomer unit), *M* = 443.87, triclinic, space group *P-1* (No. 2), *a* = 8.5498(5) Å, *b* = 14.413(1) Å, *c* = 14.731(2) Å, α = 89.934(4)°, β = 90.007(6)°, γ = 82.093(2)°, *V* = 1797.9(2) Å^3, *Z* = 5, D_c = 2.050 g/cm^3, μ = 37.37 cm^{-1}. Intensity data were measured on a Rigaku RAXIS imaging plate area detector with graphite-monochromated Mo-Kα radiation. The data were collected at 23 ± 1 °C to a maximum 2θ value of 54.8°. A total of 15634 reflections were collected. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement on F was based on 6446 observed reflections (I > 3.00σ (I)) and 400 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of *R* = 0.041 (R_w = 0.068). All calculations were performed using the CrystalStructure crystallographic software package.

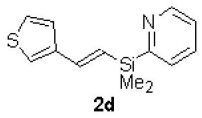
Typical Procedure for the Stoichiometric Reaction of 7 and CsF.



A mixture of **7 (X = I)** (218.6 mg, 0.51 mmol) and CsF (93.3 mg, 0.61 mmol) in dry CH_3CN (3 mL) was stirred at room temperature for 3 h. Salts were removed by filtration through a short gel pad (EtOAc). Removal of the solvent under reduced pressure afforded the crude **4a**. The yield of **4a** was determined to be >99% by GC analysis using *n*-pentadecane as an internal standard.

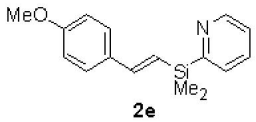

13C NMR (100 MHz, CDCl3) of 2b
O
N
Si
Me2
2b
-3.099
26.694
76.683
77.000
77.202
77.317
122.863
126.493
129.306
129.905
133.987
136.335
142.223
144.263
150.093
166.045
197.206
ppm
0
20
40
60
80
100
120
140
160
180
200

13C NMR (100 MHz, CDCl3) of 2d



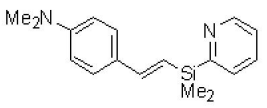
2d

13C NMR (75 MHz, CDCl3) of 2e



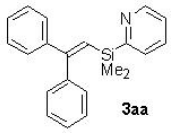
2e

13C NMR (100 MHz, CDCl3) of 2i

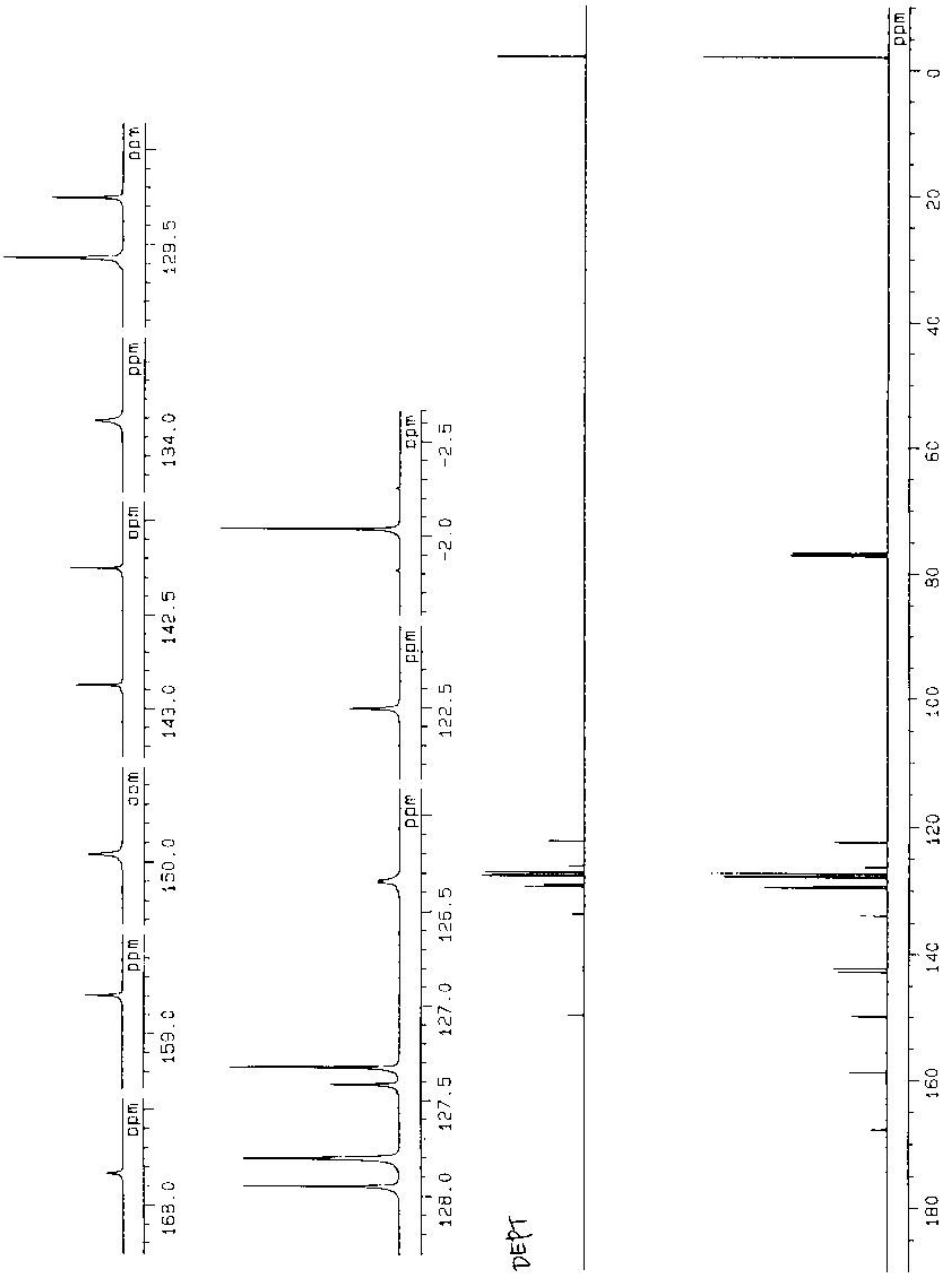


2i

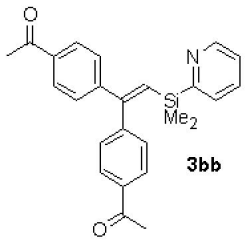
13C NMR (125 MHz, CDCl3) of 3aa



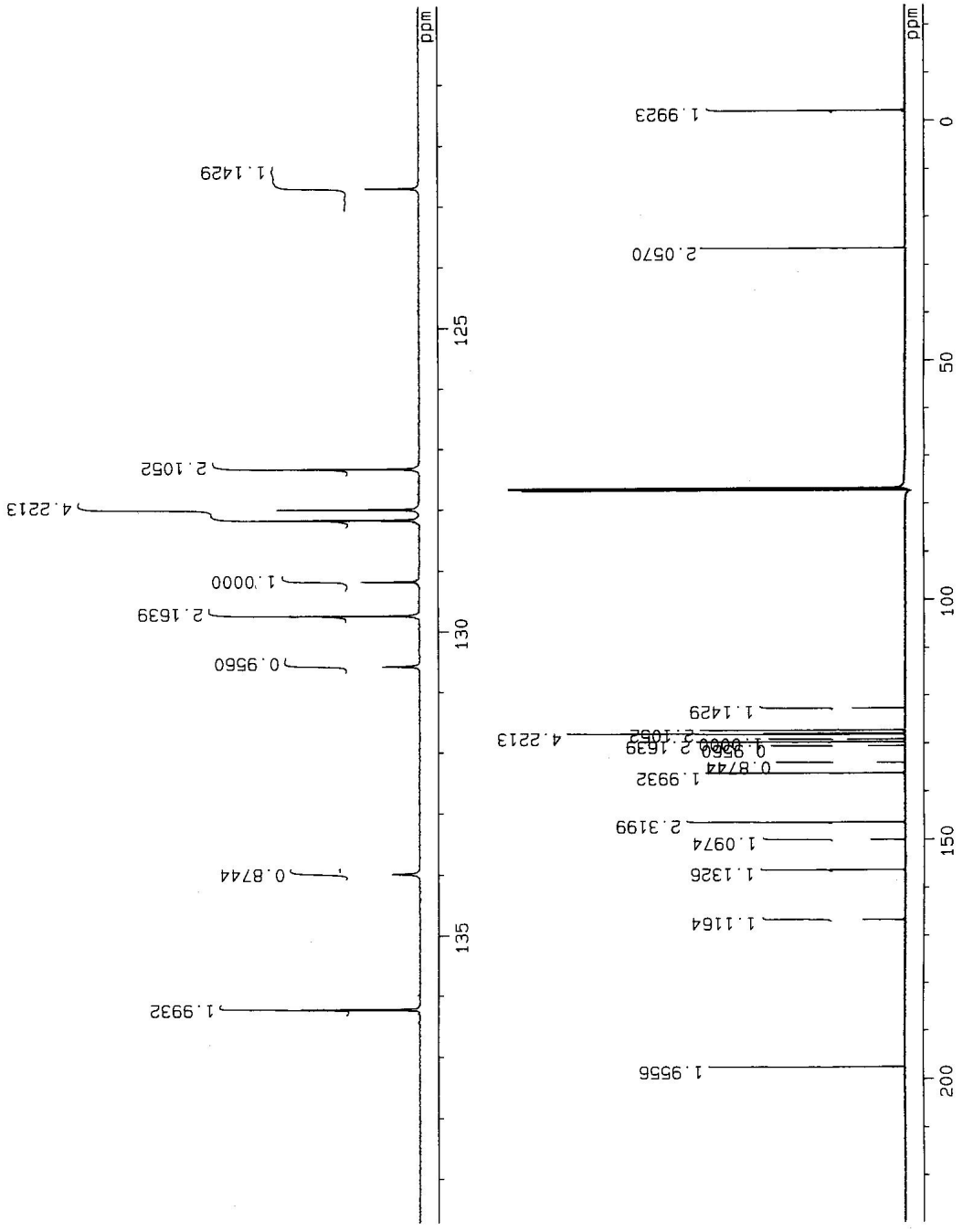
3aa



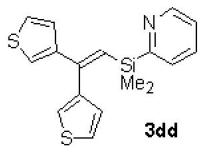
13C NMR (125 MHz, CDCl3) of 3bb



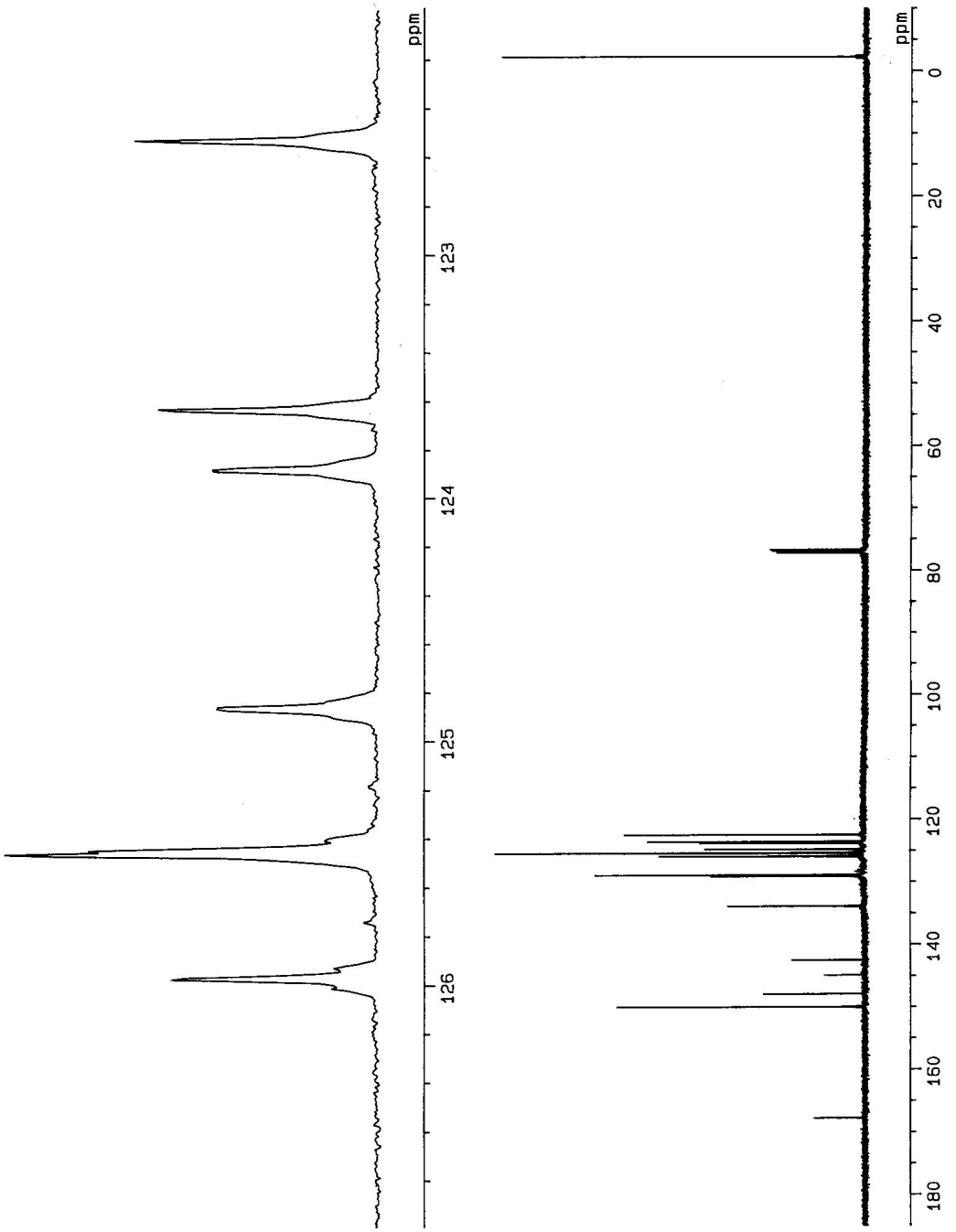
3bb



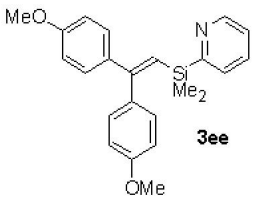
13C NMR (125 MHz, CDCl3) of 3dd



3dd

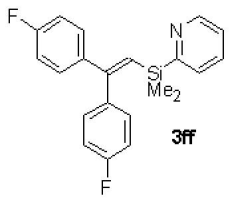


13C NMR (100 MHz, CDCl3) of 3ee



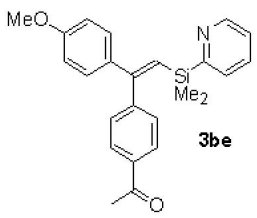
3ee

13C NMR (75 MHz, CDCl3) of 3ff



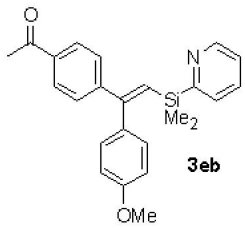
3ff

13C NMR (75 MHz, CDCl3) of 3be



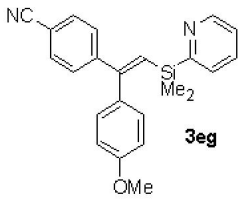
3be

13C NMR (100 MHz, CDCl3) of 3eb



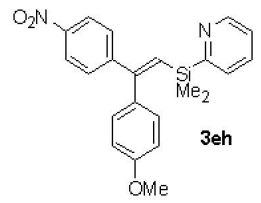
3eb

13C NMR (100 MHz, CDCl3) of 3eg



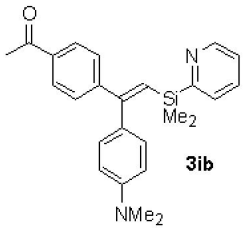
3eg

13C NMR (100 MHz, CDCl3) of 3eh



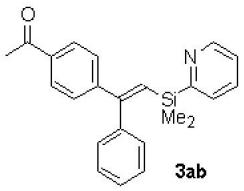
3eh

13C NMR (100 MHz, CDCl3) of 3ib



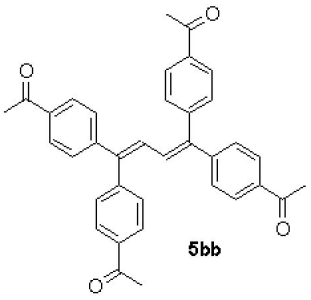
3ib

13C NMR (75 MHz, CDCl3) of 3ab



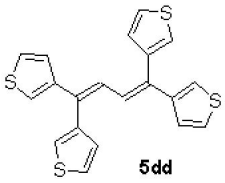
3ab

13C NMR (75 MHz, CDCl3) of 5bb



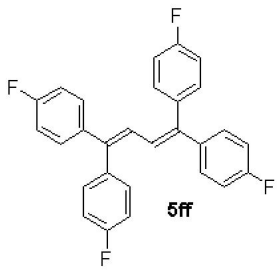
5bb

13C NMR (75 MHz, CDCl3) of 5dd



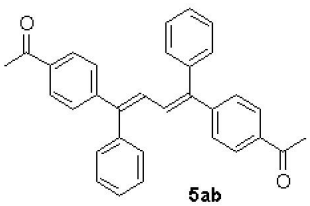
5dd

13C NMR (75 MHz, CDCl3) of 5ff

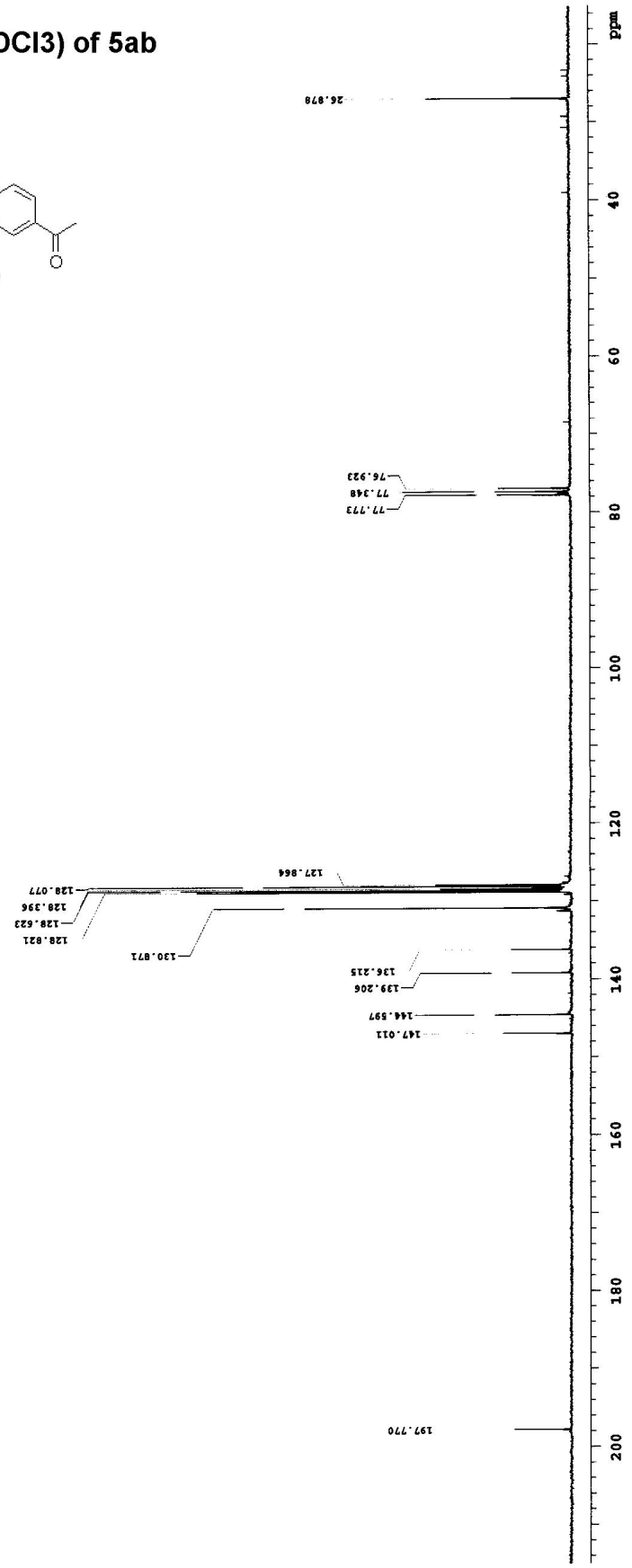


5ff

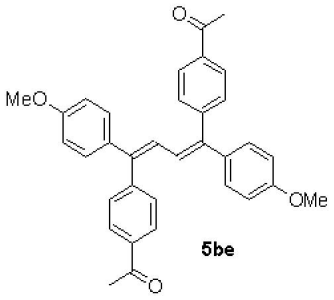
13C NMR (75 MHz, CDCl3) of 5ab



5ab

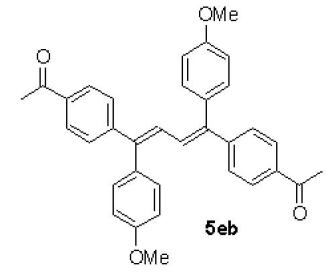


13C NMR (75 MHz, CDCl3) of 5be



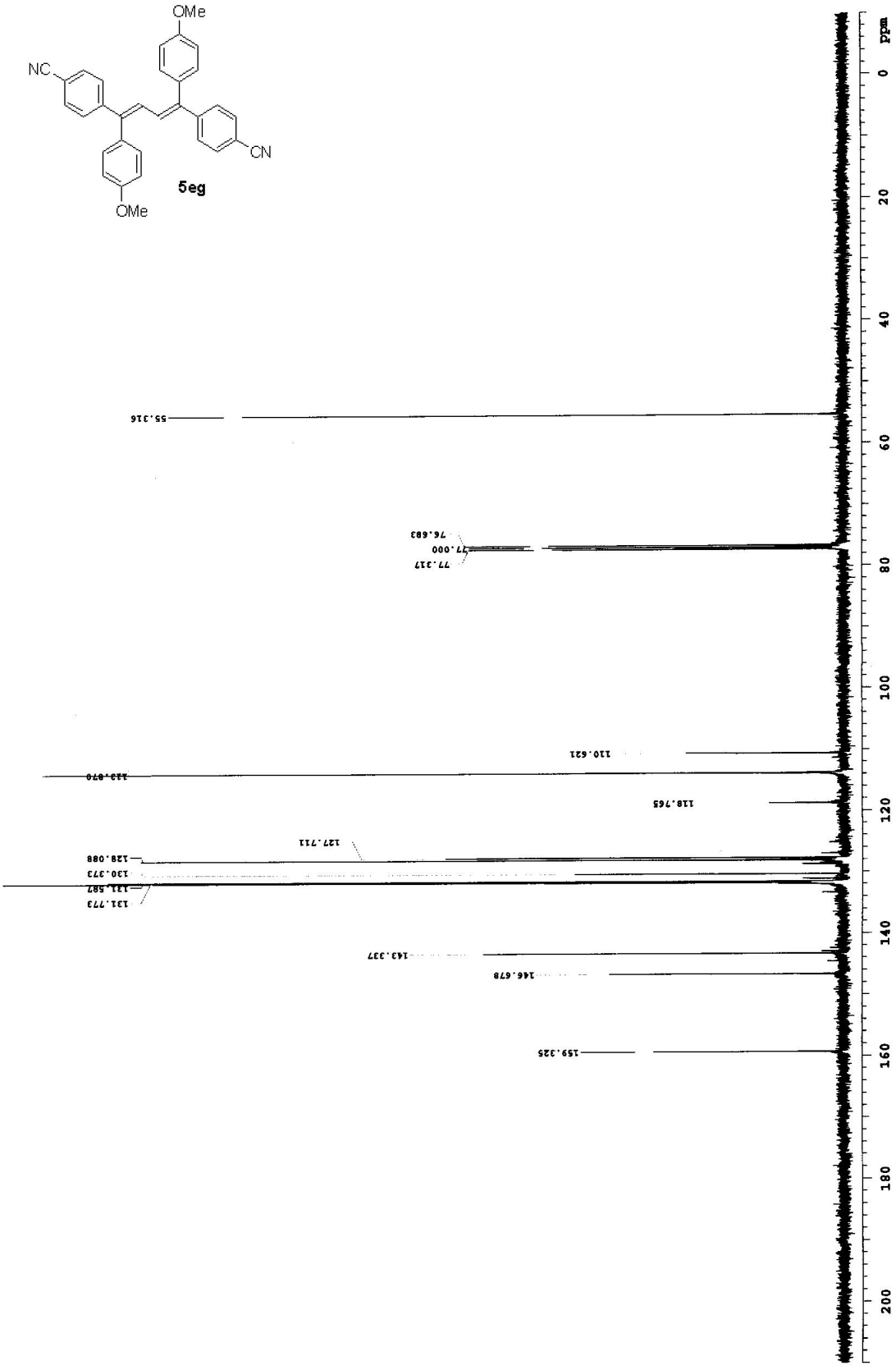
5be

13C NMR (75 MHz, CDCl3) of 5eb

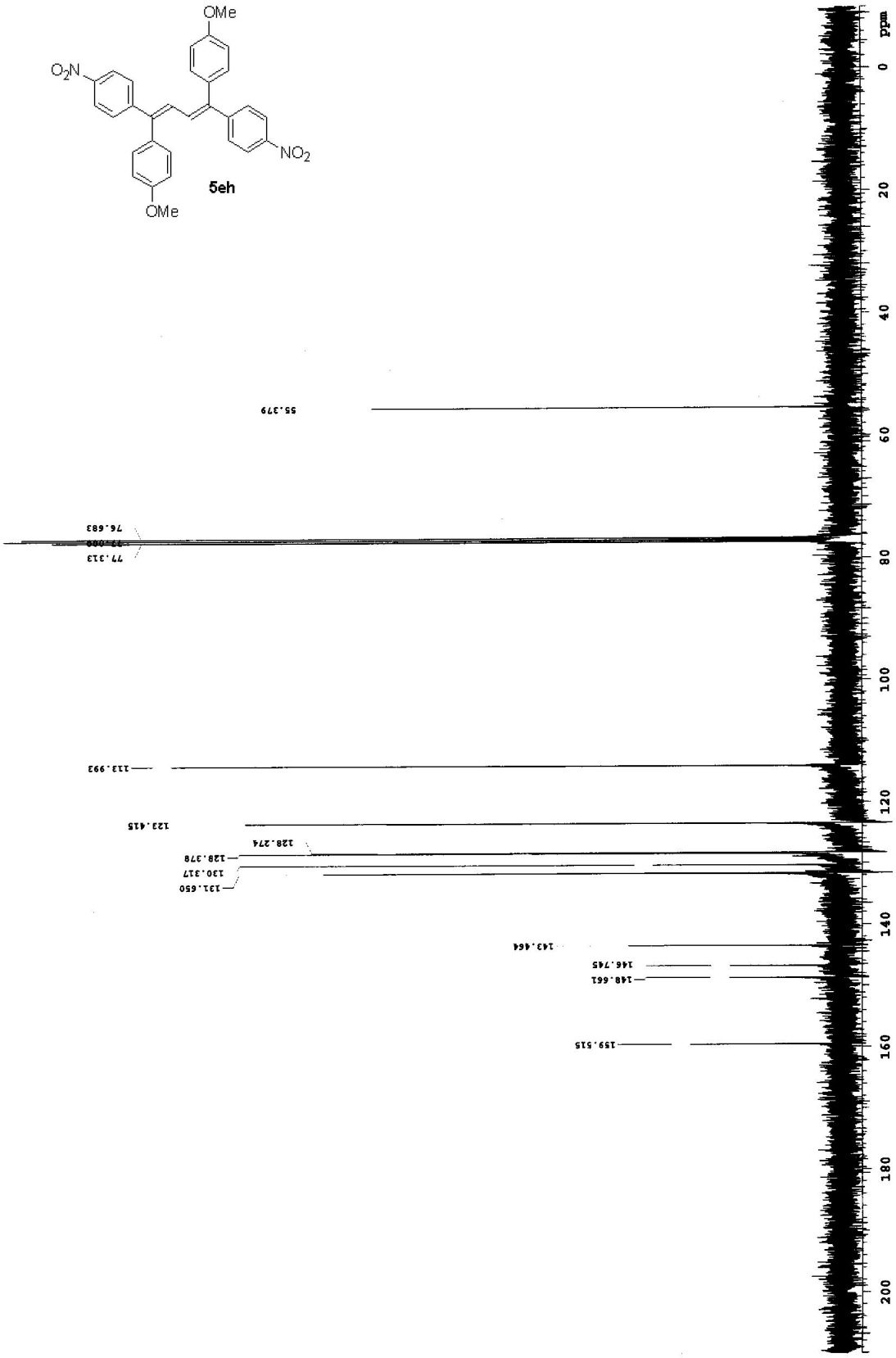


5eb

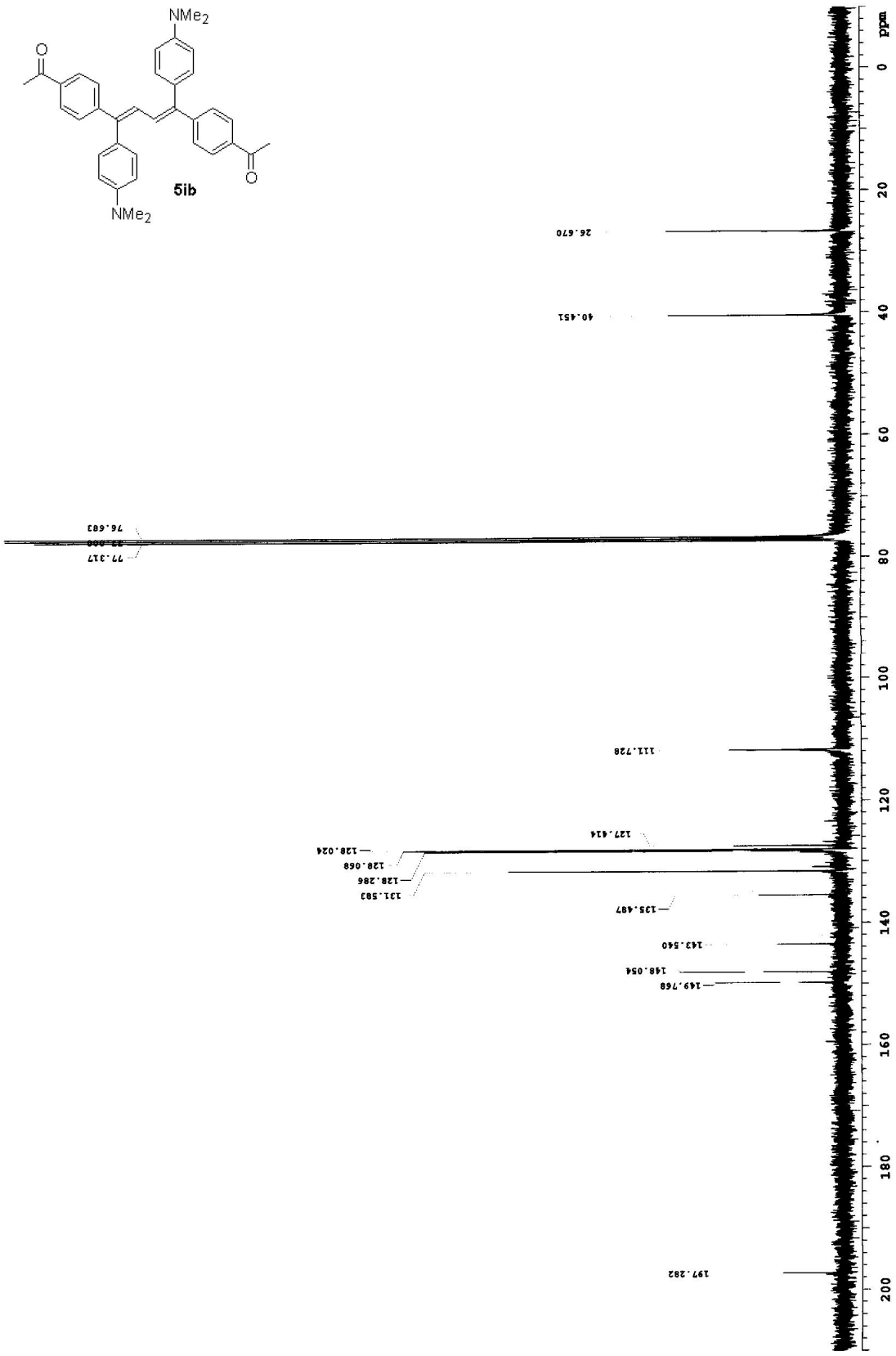
13C NMR (100 MHz, CDCl3) of 5eg



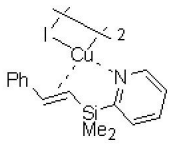
13C NMR (100 MHz, CDCl3) of 5eh



13C NMR (100 MHz, CDCl3) of 5ib

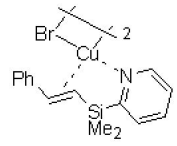


1H NMR (400 MHz, CDCl3) of 7 (X = I)



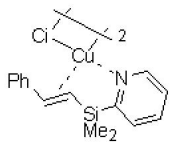
7 (X = I)

1H NMR (400 MHz, CDCl3) of 7 (X = Br)



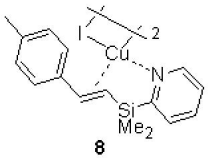
7 (X = Br)

1H NMR (400 MHz, CDCl3) of 7 (X = Cl)



7 (X = Cl)

1H NMR (400 MHz, CDCl3) of 8



8