Electronic Supplementary Material (ESI) for Chemical Communications.

Decarboxylative C–H Silylation of *N*-Heteroarenes with Silanecarboxylic Acids

Guodong Zhang,*[a] Ye Tian,[a] Chengyu Zhang,[a] Xiang Li,*[b] and Feng Chen*[a]

[a]School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China
[b]College of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Chemical Additives for Industry, Shaanxi University of Science and Technology, Xi'an, Shaanxi 710021, China

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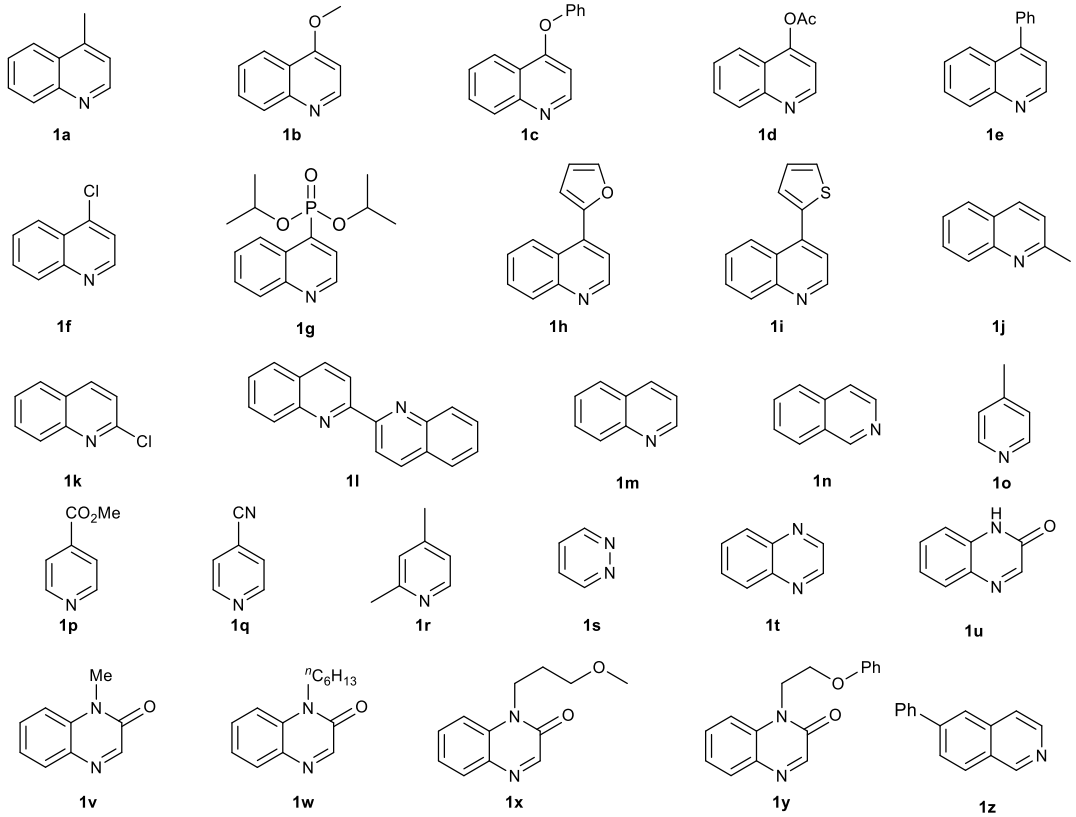
1.General Information

All new compounds were fully characterized. All reactions and manipulations involving air-sensitive compounds were performed using standard Schlenk techniques. Anhydrous MeCN was purchased from Annaiji Chemical and was used as received. ^{1}H and ^{13}C NMR spectra were recorded on an Agilent DD2 400 MHz spectrometer. The chemical shifts in ^{1}H NMR spectra were recorded relative to $CDCl_3$ (δ 7.26). The chemical shifts in ^{13}C NMR spectra were recorded relative to $CDCl_3$ (δ 77.0). Mass spectra were conducted at Bruker Dalton MAXIS. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2.Preparation of Starting Materials.



Heteroarenes **1a**, **1f**, and **1j-1u**, were commercially available.

The compounds **1b** was prepared according to **Method A**.[1]

The compounds **1c** was prepared according to **Method B**.[2]

The compounds **1d** was prepared according to **Method C**.[3]

The compounds **1e**, **1h**, **1i** and **1z** were prepared according to **Method D**.[2]

The compounds **1g** was prepared according to **Method E**.[4]

The compounds **1v-1y** were prepared according to **Method F**.[5]

Silanecarboxylic acids were synthesized according to literature report.[6]

Method A:

4-Chloroquinoline (337.32 mg, 2 mmol) was dissolved in MeOH (2 mL) followed with addition of NaOMe (562.71 mg, 10 mmol) at room temperature. The resulting mixture was heated at 70 ºC overnight before it was cooled and the solvent was removed under reduced pressure. The residue was taken up with EA and water. The organic phase was washed with brine, and the organic solution was dried over sodium sulfate. The dried solution was filtered, and the filtrate was concentrated to give the desired product **1b** (320.5 mg, 100%).

Method B:

4-Chloroquinoline (337.32 mg, 2.0 mmol), phenol (228.15 mg, 2.4 mmol, 1.2 equiv.) and K_2CO_3 (837.58 mg, 6.0 mmol, 3.0 equiv.) were suspended in dry dimethylformamide (DMF, 2.5 mL)). The resulting mixture was heated under reflux and vigorous stirring for 14 h. The reaction mass was diluted with water (12.5 mL) and extracted with dichloromethane (2 × 30 mL). Finally, the organic phases were dehydrated using Na_2SO_4, concentrated under vacuum and the crude mixture purified by flash column chromatography eluting with 25% EtOAc in petroleum ether to afford **1c** (346.4 mg, 78%) as a colorless oil.

Method C:

To an oven-dried flask (25 mL) were charged of 4-quinolinol (292.28 mg, 2 mmol) and DCM (7 mL), the mixture was cooled down to 0 °C. To the mixture was added N-ethylmorpholine (244.08 mg, 2.4 mmol). The mixture was stirred at 0 °C for 10 min, then AcCl (192.24 mg, 2.4 mmol) was added dropwise. The mixture was stirred at room temperature for 12 h, and quenched with water (10 mL), extracted with

dichloromethane (8 mL × 3), washed with brine, dried over sodium sulfate, filtered and evaporated in vacuo. The residue was purified bycolumn chromatography on silica gel (Petroleum ether /EtOAc = 2/1) to afford **1d** (141.5 mg, yield 38%) as white solid.

Method D:

A vessel was charged with 4-bromoquinoline (419.2 mg, 2.0 mmol, 1.0 equiv.) or 6-bromoisoquinoline (424.6 mg, 2.0 mmol, 1.0 equiv.), and ethanol (6 mL), water (3 mL), arylboronic acid (3.0 mmol, 1.5 equiv.), K_2CO_3 (1116.8 mg, 8.0 mmol, 4.0 equiv.), PPh_3 (21.4 mg, 0.08 mmol, 4 mol%), and $PdCl_2$ (7.2 mg, 0.04 mmol, 2 mol%) were added. The green reaction mixture was heated at 95 °C for 16 hours. After cooling to room temperature, the biphasic solution was diluted with saturated aqueous NH_4Cl (10 mL) and CH_2Cl_2 (10 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL) and the combined organic layers were washed with water (10 mL) and saturated aqueous $NaHCO_3$ (10 mL). The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel to give the desired product **1e**, **1h**, **1i** and **1z**.

Method E:

4-bromoquinoline (628.8 mg, 3.0 mmol), $HP(O)(OEt)_2$ (610.4 mg, 3.6 mmol, 1.2 equiv.), $Pd(OAc)_2$ (34.0 mg, 0.15 mmol, 5 mol%), dppf (169.7 mg, 0.3 mmol, 10 mol%), and Et_3N (366.1 mg, 3.6 mmol, 1.2 equiv.) were suspended in toluene (10 mL). The resulting mixture was heated under reflux and vigorous stirring for 20 h. The reaction mass was diluted with water (12.5 mL) and extracted with dichloromethane (2 × 30 mL). Finally, the organic phases were dehydrated using Na_2SO_4, concentrated under vacuum and the crude mixture purified by flash column chromatography eluting with 50% EtOAc in petroleum ether (40-60) to afford **1g** (698.5 mg, 79%) as a yellow oil.

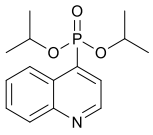
Method F:

A typical procedure: To a stirred solution of quinoxalin-2(*1H*)-ones(3 mmol) in DMF (10 mL) was added the corresponding halide (1.6 equiv) and potassium carbonate (1.2 equiv.) at room temperature, and the mixture was stirred overnight. Then the resulting

mixture was added with water (50 mL), and extracted with ethyl acetate (50 mL) for three times. The combined organic layer was dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired products **1v**-**1y**.

The characterization of new substrates listed below:

diisopropyl quinolin-4-ylphosphonate (1g)



1g

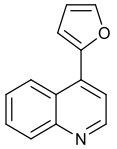
According to the ***Method E***. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 2:1), **1g** (698.5 mg, 79%) was obtained as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (t, *J* = 4.4 Hz, 1H), 8.48 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.01 (dd, *J* = 16.2, 4.2 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.66 – 7.61 (m, 1H), 4.83 – 4.71 (m, 2H), 1.41 (d, *J* = 6.2 Hz, 6H), 1.17 (d, *J* = 6.2 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4 (d, *J* = 14.1 Hz), 148.4 (d, *J* = 10.3 Hz), 135.7 (d, *J* = 180.9 Hz), 130.2 (d, *J* = 2.5 Hz), 129.7, 127.6, 126.9 (d, *J* = 4.1 Hz), 126.7 (d, *J* = 8.9 Hz), 126.5 (d, *J* = 7.6 Hz), 71.9 (dd, *J* = 1.9, 5.7 Hz), 24.1 (d, *J* = 4.0 Hz), 23.7 (d, *J* = 4.0 Hz) ppm.

HRMS (ESI) m/z: calcd for $C_{15}H_{20}NO_3P$ $(M + Na)^+$ 316.1073, found 316.1045.

4-(furan-2-yl)quinoline (1h)



1h

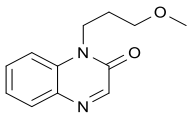
According to the ***Method D***. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 10:1), **1h** (127.9 mg, 33%) was obtained as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.6 Hz, 1H), 8.49 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.70 – 7.65 (m, 1H), 7.63 – 7.56 (m, 2H), 6.98 (d, *J* = 3.4 Hz, 1H), 6.66 – 6.59 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 149.9, 149.0, 143.9, 135.7, 130.0, 129.3, 127.0, 125.4, 124.4, 118.5, 112.1, 112.0 ppm.

HRMS (ESI) m/z: calcd for $C_{13}H_9NO$ $(M + H)^+$ 196.0757, found 196.0753.

1-(3-methoxypropyl)quinoxalin-2(1*H*)-one (1x)



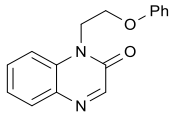
1x

According to the ***Method F***. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 5:1), **1x** (385.1 mg, 59%) was obtained as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 4.32 (t, *J* = 7.6 Hz, 2H), 3.44 (t, *J* = 5.8 Hz, 2H), 3.33 (s, 3H), 2.03 – 1.96 (m, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.8, 150.0, 133.5, 132.5, 131.0, 130.5, 123.5, 113.9, 69.6, 58.7, 39.5, 27.5 ppm.

HRMS (ESI) m/z: calcd for $C_{12}H_{14}N_2O_2$ $(M + H)^+$ 219.1128, found 219.1125.

1-(2-phenoxyethyl)quinoxalin-2(1*H*)-one (1y)



1y

According to the ***Method F***. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 5:1), **1y** (472.5 mg, 59%) was obtained as a pale yellow solid. M.P. 118-120 °C.

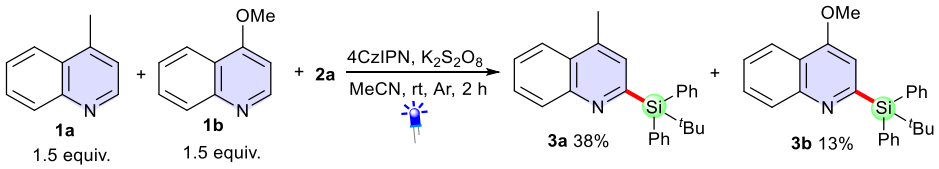
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.40 – 7.34 (m, 1H), 7.28 – 7.20 (m, 2H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.87 – 6.76 (m, 2H), 4.66 (t, *J* = 5.7 Hz, 2H), 4.35 (t, *J* = 5.7 Hz, 2H) ppm. **^{13}C NMR (101 MHz,**

$CDCl_3$) δ 158.0, 155.0, 149.9, 133.5, 133.1, 130.8, 130.5, 129.5, 123.8, 121.3, 114.6, 114.3, 64.7, 41.8 ppm.

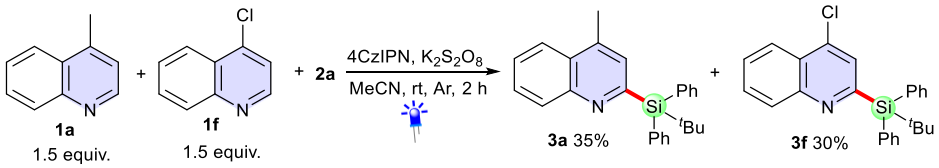
HRMS (ESI) m/z: calcd for $C_{16}H_{14}N_2O_2$ $(M + H)^+$ 267.1128, found 267.1123.

3.Mechanistic Studies

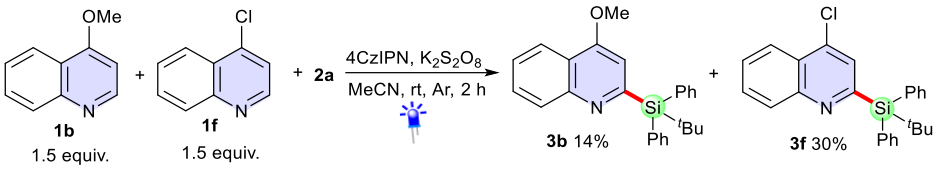
competition experiment



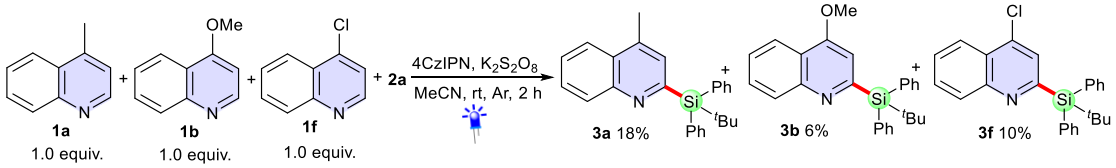
One 10 mL schlenk tubes were charged with 4CzIPN (3.9 mg, 0.005 mmol, 2.5 mol %), **1a** (0.3 mmol, 1.5 equiv.), **1b** (0.3 mmol, 1.5 equiv.), **2a** (59.9 mg, 0.2 mmol, 1 equiv.), $K_2S_2O_8$ (82.75 mg, 0.3 mmol), MeCN (2 mL), rt, Ar atmosphere. The mixture was then stirred rapidly and irradiated with a 3 W Blue LED (approximately 1-2 cm away from the light source) at room temperature for 2 h. After the reaction was completed, saturated sodium carbonate solution (10 mL) was added. The yield was determined by GC spectroscopy using dodecane as an internal standard.



One 10 mL schlenk tubes were charged with 4CzIPN (3.9 mg, 0.005 mmol, 2.5 mol %), **1a** (0.3 mmol, 1.5 equiv.), **1f** (0.3 mmol, 1.5 equiv.), **2a** (59.9 mg, 0.2 mmol, 1 equiv.), $K_2S_2O_8$ (82.75 mg, 0.3 mmol), MeCN (2 mL), rt, Ar atmosphere. The mixture was then stirred rapidly and irradiated with a 3 W Blue LED (approximately 1-2 cm away from the light source) at room temperature for 2 h. After the reaction was completed, saturated sodium carbonate solution (10 mL) was added. The yield was determined by GC spectroscopy using dodecane as an internal standard.

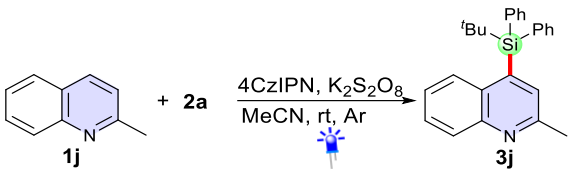


One 10 mL schlenk tubes were charged with 4CzIPN (3.9 mg, 0.005 mmol, 2.5 mol %), **1b** (0.3 mmol, 1.5 equiv.), **1f** (0.3 mmol, 1.5 equiv.), **2a** (59.9 mg, 0.2 mmol, 1 equiv.), $K_2S_2O_8$ (82.75 mg, 0.3 mmol), MeCN (2 mL), rt, Ar atmosphere. The mixture was then stirred rapidly and irradiated with a 3 W Blue LED (approximately 1-2 cm away from the light source) at room temperature for 2 h. After the reaction was completed, saturated sodium carbonate solution (10 mL) was added. The yield was determined by GC spectroscopy using dodecane as an internal standard.



One 10 mL schlenk tubes were charged with 4CzIPN (3.9 mg, 0.005 mmol, 2.5 mol %), **1a** (0.2 mmol, 1.0 equiv.), **1b** (0.2 mmol, 1.0 equiv.), **1f** (0.2 mmol, 1.0 equiv.), **2a** (59.9 mg, 0.2 mmol, 1 equiv.), $K_2S_2O_8$ (82.75 mg, 0.3 mmol), MeCN (2 mL), rt, Ar atmosphere. The mixture was then stirred rapidly and irradiated with a 3 W Blue LED (approximately 1-2 cm away from the light source) at room temperature for 2 h. After the reaction was completed, saturated sodium carbonate solution (10 mL) was added. The yield was determined by GC spectroscopy using dodecane as an internal standard.

Light/dark experiment



Eight 10 mL schlenk tubes were charged with 4CzIPN (3.9 mg, 0.005 mmol, 2.5 mol %), **1j** (87.7 mg, 0.6 mmol, 3.0 equiv.), **2a** (59.9 mg, 0.2 mmol, 1.0 equiv.), $K_2S_2O_8$ (82.8 mg, 0.3 mmol), MeCN (2 mL), rt, Ar atmosphere. The mixtures were then stirred

rapidly and irradiated with a 3 W Blue LED (approximately 1-2 cm away from the light source) at room temperature. After 20 min, the Blue LED was turned off, and one vial was removed from the irradiation setup for analysis. The remaining seven vials were stirred in the absence of light for an additional 20 min. Then, one vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining six reaction mixtures. After an additional 20 min of irradiation, the Blue LED was turned off, and one vial was removed for analysis. The remaining five vials were stirred in the absence of light for an additional 20 min. Then, a vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining four reaction mixtures. After 20 min, the Blue LED was turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light for an additional 20 min. Then, a vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining two reaction mixtures. The last vials were stirred in the absence of light for an additional 20 min, and then it was analyzed. The yield was determined by GC spectroscopy using dodecane as an internal standard.

Time/min	20	40	60	80	100	120	140	160
Yield/%	30	29	50	50	58	58	72	72

4.Synthesis and Characterization of the Corresponding Products

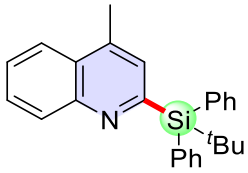
General Procedure for the Photocatalytic Decarboxylative C–H Silylation of N-Heteroarenes

One 10 mL glass vial was charged 4CzIPN (3.9 mg, 0.005 mmol, 2.5 mol %), **1** (0.6 mmol, 3equiv.), **2** (0.2 mmol, 1.0 equiv.), $K_2S_2O_8$ (82.8 mg, 0.3 mmol), MeCN (2 mL), rt, Ar atmosphere. The mixture was then stirred rapidly and irradiated with a 3 W Blue LED (approximately 1-2 cm away from the light source) at room temperature for 12 h. After the reaction was completed, saturated sodium carbonate solution (10 mL) was added and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined

organic layers were dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography to yield the corresponding product.

Characterization of products

2-(*tert*-butyldiphenylsilyl)-4-methylquinoline (3a)



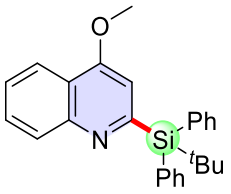
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3a** (59.5 mg, 78%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.80 – 7.71 (m, 5H), 7.60 –7.56 (m, 1H), 7.46 – 7.37 (m, 6H), 7.21 (s, 1H), 2.58 (s, 3H), 1.30 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 148.3, 140.6, 136.7, 134.5, 131.0, 129.2, 128.8, 128.5, 127.6, 127.2, 126.4, 123.7, 28.1, 19.2, 18.6 ppm.

HRMS (ESI) m/z: calcd for $C_{26}H_{27}NSi$ $(M + Na)^+$ 404.1805, found 404.1788.

2-(*tert*-butyldiphenylsilyl)-4-methoxyquinoline (3b)



According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3b** (34.8 mg, 44%) was obtained as a white solid.

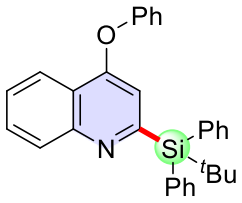
M.P. 94-96 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 6.7 Hz, 4H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.29 (m, 7H), 6.72 (s, 1H), 3.75 (s, 3H), 1.29 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 160.2, 136.7, 136.3, 134.4, 129.7, 129.3, 128.6, 127.6, 125.8, 121.5, 120.4, 107.2, 55.2, 28.2, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{26}H_{27}NOSi$ $(M + H)^+$ 398.1935, found 398.1899.

2-(*tert*-butyldiphenylsilyl)-4-phenoxyquinoline (3c)



According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3c** (48.4 mg, 53%) was obtained as a white solid.

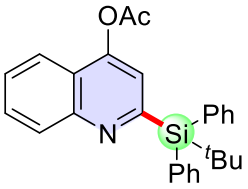
M.P. 106-108 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.3 Hz, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 4H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.32 – 7.26 (m, 6H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.60 (s, 1H), 1.25 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 159.3, 154.7, 150.5, 136.6, 134.1, 130.1, 129.8, 129.4, 129.1, 127.5, 126.2, 124.7, 121.6, 120.7, 120.2, 112.4, 28.1, 19.1 ppm.

HRMS (ESI) m/z: calcd for $C_{31}H_{29}NOSi$ $(M + K)^+$ 498.1650, found 498.1631.

2-(*tert*-butyldiphenylsilyl)quinolin-4-yl acetate (3d)



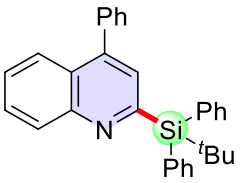
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 20:1), **3d** (35.0 mg, 41%) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.76 – 7.72 (m, 5H), 7.60 – 7.56 (m, 1H), 7.43 – 7.36 (m, 6H), 7.18 (s, 1H), 2.38 (s, 3H), 1.26 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 168.0, 152.2, 150.6, 136.7, 133.9, 130.5, 129.4, 129.4, 127.7, 127.1, 121.3, 121.0, 119.8, 28.1, 21.0, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{27}H_{27}NO_2Si$ $(M + H)^+$ 426.1884, found 426.1854.

2-(*tert*-butyldiphenylsilyl)-4-phenylquinoline (3e)



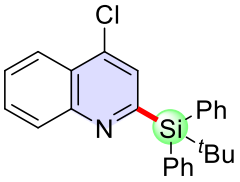
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3e** (67.1 mg, 76%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.88 – 7.82 (m, 4H), 7.80 – 7.75 (m, 1H), 7.57 – 7.52 (m, 1H), 7.51 – 7.37 (m, 12H), 1.37 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 148.9, 145.0, 138.4, 136.7, 134.3, 130.8, 129.7, 129.3, 128.7, 128.4, 128.1, 128.0, 127.6, 126.8, 125.6, 125.5, 28.2, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{31}H_{29}NSi$ $(M + H)^+$ 444.2142, found 444.2109.

2-(*tert*-butyldiphenylsilyl)-4-chloroquinoline (3f)



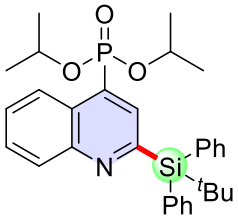
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 15:1), **3f** (57.0 mg, 71%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.75 (m, 5H), 7.71 – 7.65 (m, 1H), 7.51 –7.40 (m, 7H), 1.31 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 149.7, 140.9, 136.7, 133.7, 130.7, 129.8, 129.5, 127.8, 127.7, 127.7, 125.5, 124.0, 28.1, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{25}H_{24}{}^{35}ClNSi$ $(M + H)^+$ 402.1439, found 402.1406; calcd for $C_{25}H_{24}{}^{37}ClNSi$ $(M + H)^+$ 404.1410, found 404.1410.

diisopropyl (2-(*tert*-butyldiphenylsilyl)quinolin-4-yl)phosphonate (3g)



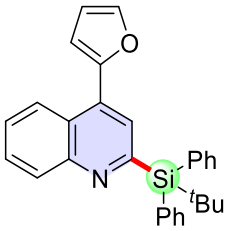
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 5:1), **3g** (66.5 mg, 63%) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.57 (m, 1H), 8.36 – 8.31 (m, 1H), 7.83 – 7.72 (m, 6H), 7.69 – 7.64 (m, 1H), 7.46 – 7.35 (m, 6H), 4.74 – 4.65 (m, 2H), 1.29 (d, *J* = 7.5 Hz, 15H), 1.10 (d, *J* = 6.2 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4 (d, *J* = 10.1 Hz), 148.6 (d, *J* = 9.6 Hz), 136.6, 133.8, 133.2 (d, *J* = 181.7 Hz), 131.6 (dd, *J* = 2.7, 6.3 Hz), 131.1 (d, *J* = 3.0 Hz), 129.4, 129.2, 127.9, 127.7, 126.8 (d, *J* = 4.6 Hz), 125.3 (d, *J* = 10.0 Hz), 71.6 (dd, *J* = 4.0, 6.1 Hz), 28.0, 24.0 (d, *J* = 4.0 Hz), 23.6 (d, *J* = 4.8 Hz), 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{31}H_{38}NO_3PSi$ $(M + H)^+$ 532.2431, found 532.2431.

2-(*tert*-butyldiphenylsilyl)-4-(furan-2-yl)quinoline (3h)



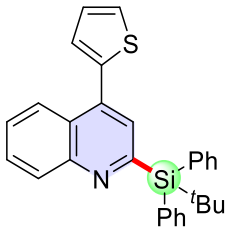
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3h** (30.4 mg, 35%) was obtained as a brownish red oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.6 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.69 (m, 5H), 7.64 – 7.54 (m, 3H), 7.47 – 7.34 (m, 6H), 6.79 – 6.73 (m, 1H), 6.57 – 6.50 (m, 1H), 1.28 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 151.8, 149.3, 143.7, 136.7, 134.2, 132.6, 131.1, 129.3, 128.8, 127.7, 127.2, 125.5, 125.4, 123.2, 111.7, 111.5, 28.1, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{29}H_{27}NOSi$ $(M + H)^+$ 434.1935, found 434.1922.

2-(*tert*-butyldiphenylsilyl)-4-(thiophen-2-yl)quinoline (3i)



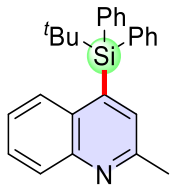
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3i** (45.9 mg, 51%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.27 (m, 2H), 7.81 – 7.70 (m, 5H), 7.60 – 7.55 (m, 1H), 7.46 – 7.33 (m, 8H), 7.26 (s, 1H), 7.17 – 7.13 (m, 1H), 1.30 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 149.1, 139.5, 137.5, 136.7, 134.2, 131.0, 129.3, 128.9, 128.5, 128.3, 127.7, 127.6, 127.1, 126.9, 125.3, 125.1, 28.1, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{29}H_{27}NSSi$ $(M + H)^+$ 450.1706, found 450.1694.

4-(*tert*-butyldiphenylsilyl)-2-methylquinoline (3j)



According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 5:1), **3j** (70.1 mg, 92%) was obtained as a white solid.

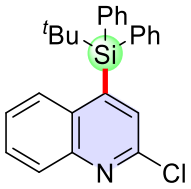
M.P. 116-118 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.74 (s, 1H), 7.65 – 7.59 (m, 5H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.37 – 7.31 (m, 4H), 7.10 (t, *J* = 7.5 Hz, 1H), 2.76 (s, 3H), 1.25 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 147.6, 143.8, 136.2, 134.1, 132.0, 130.03, 129.98, 129.4, 129.3, 128.7, 127.9, 124.6, 29.1, 25.4, 19.0 ppm.

HRMS (ESI) m/z: calcd for $C_{26}H_{27}NSi$ $(M + K)^+$ 420.1544, found 420.1572.

4-(*tert*-butyldiphenylsilyl)-2-chloroquinoline (3k)



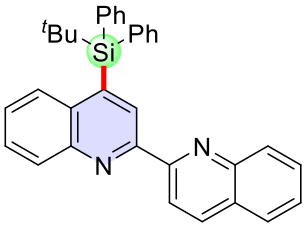
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 20:1), **3k** (48.2 mg, 60%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.78 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.53 (m, 5H), 7.45 – 7.41 (m, 2H), 7.38 – 7.33 (m, 4H), 7.20 – 7.15 (m, 1H), 1.24 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 148.8, 147.9, 136.2, 133.3, 131.7, 131.7, 130.4, 130.2, 129.8, 129.3, 128.1, 125.9, 29.0, 19.0 ppm.

HRMS (ESI) m/z: calcd for $C_{25}H_{24}{}^{35}ClNSi$ $(M + Na)^+$ 424.1259, found 424.1242; calcd for $C_{25}H_{24}{}^{37}ClNSi$ $(M + Na)^+$ 426.1229, found 426.1220.

4-(*tert*-butyldiphenylsilyl)-2,2'-biquinoline (3l)



According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 40:1), **3l** (34.1 mg, 35%) was obtained as a white solid.

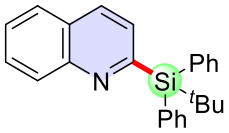
M.P. 170-172 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.88 (d, *J* = 8.6 Hz, 1H), 8.34 (d, *J* = 8.6 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.78 – 7.56 (m, 8H), 7.48 – 7.33 (m, 6H), 7.17 (t, *J* = 7.6 Hz, 1H), 1.35 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 154.3, 147.9, 147.8, 144.1, 136.6, 136.5, 136.4, 134.2, 132.1, 130.8, 130.2, 130.1, 129.5, 129.4, 128.7, 128.4, 127.9, 127.6, 126.9, 126.0, 119.3, 28.9, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{34}H_{30}N_2Si$ $(M + H)^+$ 495.2251, found 495.2226.

2-(*tert*-butyldiphenylsilyl)quinoline (3m)



According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3m** (33.2 mg, 45%) as a white solid.

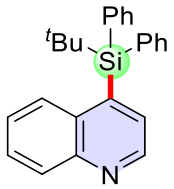
M.P. 74-76 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.65 (m, 6H), 7.58 – 7.53 (m, 1H), 7.51 – 7.30 (m, 7H), 1.28 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 148.7, 136.7, 134.4, 132.8, 130.4, 129.3, 128.9, 128.1, 127.7, 127.6, 127.1, 126.7, 28.1, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{25}H_{25}NSi$ $(M + K)^+$ 406.1388, found 406.1350.

4-(*tert*-butyldiphenylsilyl)quinoline (3m')



According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3m'** (11.8 mg, 16%) was obtained as a yellow solid.

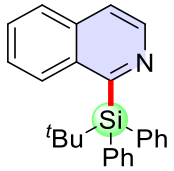
M.P. 106-108 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.2 Hz, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 4.2 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.56 (m, 5H), 7.44 – 7.39 (m, 2H), 7.37 – 7.32 (m, 4H), 7.20 – 7.16 (m, 1H), 1.24 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 148.0, 144.1, 136.3, 134.0, 132.0, 131.1, 130.3, 130.2, 129.5, 128.8, 127.9, 125.6, 29.1, 19.0 ppm.

HRMS (ESI) m/z: calcd for $C_{25}H_{25}NSi$ $(M + Na)^+$ 390.1648, found 390.1636.

1-(*tert*-butyldiphenylsilyl)isoquinoline (3n)



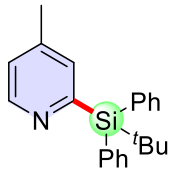
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3n** (38.2 mg, 52%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 5.6 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.73 – 7.68 (m, 4H), 7.68 – 7.63 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 4H), 7.10 (t, *J* = 7.7 Hz, 1H), 1.29 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 142.4, 136.3, 135.2, 134.7, 133.9, 129.3, 129.1, 129.0, 127.7, 127.4, 126.0, 120.5, 27.7, 19.7 ppm.

HRMS (ESI) m/z: calcd for $C_{25}H_{25}NSi$ $(M + K)^+$ 406.1388, found 406.1357.

2-(*tert*-butyldiphenylsilyl)-4-methylpyridine (3o)



According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3o** (39.6 mg, 60%) was obtained as a white solid.

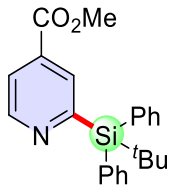
M.P. 73-75 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.9 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 4H), 7.45 – 7.34 (m, 6H), 7.14 (s, 1H), 7.06 (d, *J* = 4.7 Hz, 1H), 2.23 (s, 3H), 1.22 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 149.7, 144.4, 136.6, 134.5, 133.4, 129.2, 127.6, 123.7, 28.2, 21.1, 18.9 ppm.

HRMS (ESI) m/z: calcd for $C_{22}H_{25}NSi$ $(M + Na)^+$ 354.1648, found 354.1629.

methyl 2-(*tert*-butyldiphenylsilyl)isonicotinate (3p)



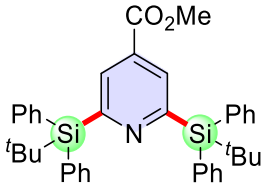
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 2:1), **3p** (58.0 mg, 77%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (d, *J* = 5.0 Hz, 1H), 7.89 (s, 1H), 7.82 – 7.77 (m, 1H), 7.72 – 7.66 (m, 4H), 7.47 – 7.37 (m, 6H), 3.87 (s, 3H), 1.23 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 166.2, 150.6, 136.5, 135.0, 133.7, 130.5, 129.4, 127.7, 121.5, 52.5, 28.1, 18.8 ppm.

HRMS (ESI) m/z: calcd for $C_{23}H_{25}NO_2Si$ $(M + H)^+$ 376.1727, found 376.1691.

methyl 2,6-bis(*tert*-butyldiphenylsilyl)isonicotinate (3p')



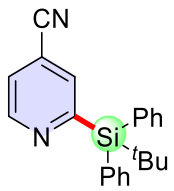
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 2:1), **3p'** (9.4 mg, 8%) was obtained as a pale-yellow solid. M.P. 179-181 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 2H), 7.69 – 7.63 (m, 8H), 7.44 – 7.39 (m, 4H), 7.36 – 7.30 (m, 8H), 3.76 (s, 3H), 1.17 (s, 18H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 166.6, 156.5, 136.6, 134.0, 132.9, 129.3, 127.6, 77.2, 28.3, 18.7 ppm.

HRMS (ESI) m/z: calcd for $C_{39}H_{43}NO_2Si_2$ $(M + H)^+$ 614.2905, found 614.2877.

2-(*tert*-butyldiphenylsilyl)isonicotinonitrile (3q)



According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3q** (37.6 mg, 60%) was obtained as a white solid.

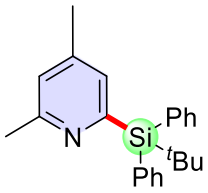
M.P. 123-125 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 – 9.05 (m, 1H), 7.68 – 7.62 (m, 4H), 7.50 – 7.36 (m, 8H), 1.21 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 150.2, 136.4, 132.8, 132.6, 129.8, 127.9, 123.7, 118.6, 117.0, 28.0, 18.8 ppm.

HRMS (ESI) m/z: calcd for $C_{22}H_{22}N_2Si$ $(M + Na)^+$ 343.1625, found 343.1596.

2-(*tert*-butyldiphenylsilyl)-4,6-dimethylpyridine (3r)



According to this *general procedure.* After column chromatography on silica (eluent: Petroleum ether: EtOAc = 100:1), **3r** (23.3 mg, 38%) was obtained as a white solid.

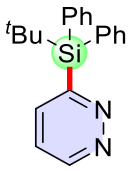
M.P. 57-59 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.3 Hz, 4H), 7.45 – 7.33(m, 6H), 6.91 (d, *J* = 6.7 Hz, 2H), 2.60 (s, 3H), 2.17 (s, 3H), 1.21 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 157.7, 144.4, 136.7, 134.9, 130.5, 129.0, 127.5, 123.1, 28.2, 24.7, 21.0, 18.8 ppm.

HRMS (ESI) m/z: calcd for $C_{23}H_{27}NSi$ $(M + Na)^+$ 368.1805, found 368.1815.

3-(*tert*-butyldiphenylsilyl)pyridazine (3s)



According to this *general procedure.* After column chromatography on silica (eluent: Petroleum ether: EtOAc = 2:1), **3s** (36 mg, 57%) was obtained as a brown solid.

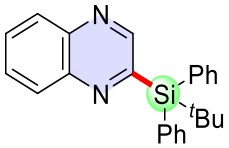
M.P. 123-125 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 9.13 (d, *J* = 4.9 Hz, 1H), 7.60 – 7.49 (m, 5H), 7.49 – 7.43 (m, 2H), 7.43 – 7.36 (m, 4H), 1.20 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 150.6, 136.2, 135.5, 134.2, 131.5, 130.1, 128.2, 28.3, 18.6 ppm.

HRMS (ESI) m/z: calcd for $C_{20}H_{22}N_2Si$ $(M + H)^+$ 319.1625, found 319.1613.

2-(*tert*-butyldiphenylsilyl)quinoxaline (3t)



According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 2:1), **3t** (39.0 mg, 53%) was obtained as a brown solid.

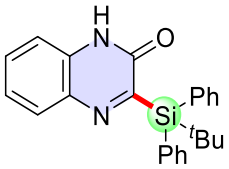
M.P. 85-87 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.30 – 8.24 (m, 1H), 8.10 – 8.03 (m, 1H), 7.89 – 7.66 (m, 6H), 7.52 – 7.32 (m, 6H), 1.28 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 150.2, 143.5, 141.3, 136.6, 133.1, 130.23, 130.20, 129.7, 129.49, 129.45, 127.9, 27.9, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{24}H_{24}N_2Si$ $(M + H)^+$ 391.1601, found 391.1588.

3-(*tert*-butyldiphenylsilyl)quinoxalin-2(1H)-one (3u)



According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 2:1), **3u** (60.2 mg, 78%) was obtained as a brown red solid.

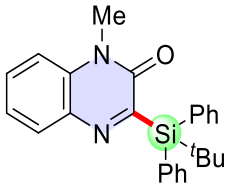
M.P. 184-186 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.73 (s, 1H), 7.97 – 7.93 (m, 1H), 7.83 – 7.74 (m, 4H), 7.46 – 7.34 (m, 7H), 7.33 – 7.28 (m, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 1.28 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 158.8, 136.3, 134.1, 133.8, 130.9, 130.7, 129.8, 129.1, 127.4, 123.6, 116.3, 28.0, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{24}H_{24}N_2OSi$ $(M + Na)^+$ 407.1550, found 407.1516.

3-(*tert*-butyldiphenylsilyl)-1-methylquinoxalin-2(1H)-one (3v)



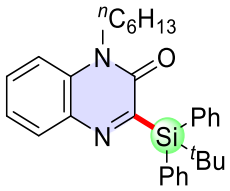
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 10:1), **3v** (39.5 mg, 50%) was obtained as a pale yellow solid. M.P. 126-128 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.9 Hz, 1H), 7.77 (d, J = 7.7 Hz, 4H), 7.57 (t, J = 7.8 Hz, 1H), 7.44 – 7.33 (m, 7H), 7.29 (d, J = 8.4 Hz, 1H), 3.57 (s, 3H), 1.28 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 156.3, 136.2, 134.2, 133.6, 133.1, 131.0, 130.9, 129.1, 127.4, 123.0, 113.5, 28.5, 28.1, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{25}H_{26}N_2OSi$ $(M + Na)^+$ 421.1707, found 421.1675.

3-(*tert*-butyldiphenylsilyl)-1-hexylquinoxalin-2(1H)-one (3w)



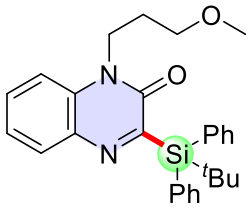
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 20:1), **3w** (67.5 mg, 72%) was obtained as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.97 (m, 1H), 7.77 – 7.72 (m, 4H), 7.59 – 7.53 (m, 1H), 7.43 – 7.29 (m, 8H), 4.14 (t, J = 7.6 Hz, 2H), 1.75 – 1.62 (m, 2H), 1.39 – 1.25 (m, 13H), 1.09 (s, 2H), 0.96 – 0.78 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 156.0, 136.2, 134.8, 134.5, 133.7, 131.3, 130.8, 129.0, 127.4, 122.7, 113.5, 41.5, 31.5, 28.1, 27.3, 26.5, 22.5, 19.2, 14.0 ppm.

HRMS (ESI) m/z: calcd for $C_{30}H_{36}N_2OSi$ $(M + H)^+$ 469.2670, found 469.2642.

3-(*tert*-butyldiphenylsilyl)-1-(3-methoxypropyl)quinoxalin-2(1H)-one (3x)



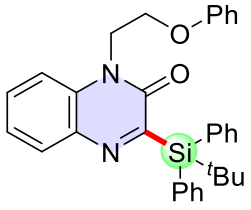
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 10:1), **3x** (47.5 mg, 52%) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 1H), 7.79 – 7.72 (m, 4H), 7.59 – 7.55 (m, 1H), 7.45 – 7.31 (m, 8H), 4.24 (t, *J* = 7.2 Hz, 2H), 3.37 (t, *J* = 5.9 Hz, 2H), 3.29 (s, 3H), 1.98 – 1.91 (m, 2H), 1.28 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 156.1, 136.2, 134.4, 133.7, 132.4, 131.2, 130.9, 129.0, 127.4, 122.8, 113.6, 69.7, 58.7, 39.0, 28.1, 27.6, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{28}H_{32}N_2O_2Si$ $(M + Na)^+$ 479.2125, found 479.2117.

3-(*tert*-butyldiphenylsilyl)-1-(3-methoxypropyl)quinoxalin-2(1H)-one (3y)



According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: EtOAc = 10:1), **3y** (66.3 mg, 66%) was obtained as a white solid.

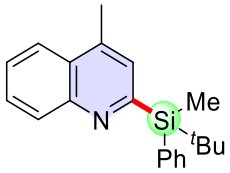
M.P. 138-140 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 1H), 7.81– 7.74 (m, 4H), 7.63 – 7.56 (m, 2H), 7.46 – 7.34 (m, 7H), 7.28 – 7.22 (m, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.81 – 6.76 (m, 2H), 4.56 (t, *J* = 5.5 Hz, 2H), 4.26 (t, *J* = 5.5 Hz, 2H), 1.31 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 158.1, 156.2, 136.2, 134.4, 133.6, 132.9, 131.1, 130.7, 129.4, 129.1, 127.4, 123.1, 121.1, 114.3, 65.1, 41.4, 28.0, 19.2 ppm.

HRMS (ESI) m/z: calcd for $C_{32}H_{32}N_2O_2Si$ $(M + H)^+$ 505.2306, found 505.2297.

2-(*tert*-butyl(methyl)(phenyl)silyl)-4-methylquinoline (3ba)



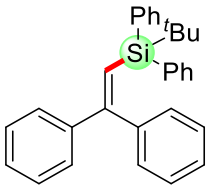
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3ba** (27.6 mg, 43%) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.69 (s, 2H), 7.62 – 7.58 (m, 1H), 7.46 – 7.42 (m, 1H), 7.31 (s, 1H), 7.30 – 7.22 (m, 3H), 2.54 (s, 3H), 1.00 (s, 9H), 0.61 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 148.3, 140.6, 135.7, 135.6, 131.0, 129.0, 128.5, 127.6, 127.4, 127.3, 126.2, 123.6, 27.1, 18.6, 18.2, 1.0 ppm.

HRMS (ESI) m/z: calcd for $C_{21}H_{25}NSi$ $(M + Na)^+$ 342.1648, found 342.1627.

***tert*-butyl(2,2-diphenylvinyl)diphenylsilane (4)**



After column chromatography on silica (eluent: Petroleum ether), **4** (26.1 mg, 31%) was obtained as a white solid.

M.P. 100-101 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 4H), 7.41 – 7.31 (m, 5H), 7.31 – 7.25 (m, 2H), 7.24 – 7.17 (m, 4H), 6.89 – 6.81 (m, 3H), 6.77 – 6.72 (m, 2H), 6.67 (s, 1H), 1.06 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 144.8, 140.9, 136.0, 134.5, 129.5, 128.6, 128.0, 127.9, 127.2, 127.1, 127.0, 123.0, 27.7, 18.8 ppm.

HRMS (ESI) m/z: calcd for $C_{32}H_{32}N_2O_2Si$ $(M + Na)^+$ 441.2009, found 441.2033.

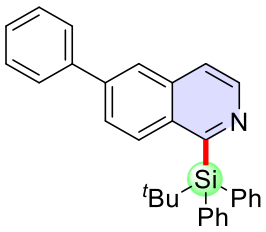
General Procedure for the Ag-catalysed Decarboxylative C–H Silylation

of N-Heteroarenes

One 10 mL glass vial was charged $AgNO_3$ (7.15 mg, 0.04 mmol, 20 mol %), **1** (0.6 mmol, 3 equiv.), **2** (0.2 mmol, 1.0 equiv.), $K_2S_2O_8$ (110.33 mg, 0.4 mmol), MeCN (2 mL), 50 °C, Ar atmosphere. The mixture was then stirred rapidly for 12 h. After the reaction was completed, saturated sodium carbonate solution (10 mL) was added and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography to yield the corresponding product.

Compounds **3a** (33.5 mg, 44%), **3e** (35.0 mg, 40%), **3f** (44.7 mg, 56%), **3g** (58.2 mg, 55%), **3j** (23.6 mg, 31%), **3p** (40.7 mg, 54%), **3s** (31.6 mg, 50%), **3u** (27.6 mg, 36%), **3v** (47.8 mg, 60%), **3w** (66.3 mg, 71%), **3y** (60.2 mg, 60%), **3z** (27.0 mg, 30%) were synthesized according to this *general procedure.*

1-(*tert*-butyldiphenylsilyl)-6-phenylisoquinoline (3z)



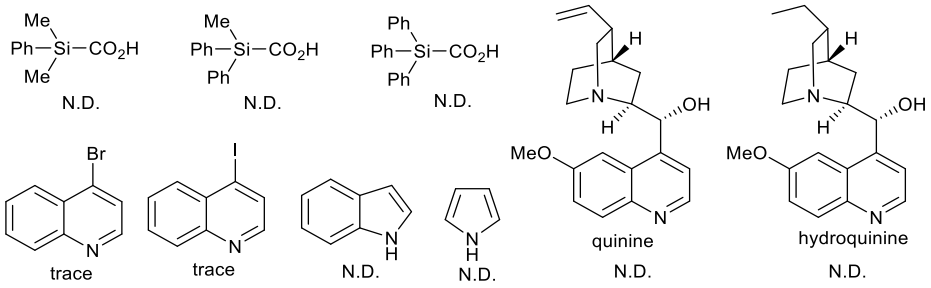
According to this *general procedure*. After column chromatography on silica (eluent: Petroleum ether: DCM = 5:1), **3z** (27.0 mg, 30%) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 5.6 Hz, 1H), 7.98 – 7.93 (m, 1H), 7.73 – 7.65 (m, 6H), 7.64 – 7.58 (m, 2H), 7.46 – 7.30 (m, 10H), 1.27 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 142.9, 141.5, 140.1, 136.4, 135.2, 135.1, 133.0, 129.8, 129.2, 128.9, 127.9, 127.7, 127.4, 125.7, 125.0, 120.7, 27.7, 19.7 ppm.

HRMS (ESI) m/z: calcd for $C_{31}H_{29}NSi$ $(M + Na)^+$ 466.1961, found 466.1932.

5. Unsuccessful Substrates



6.References

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(6) N. Xu, B. Li, C. Wang and M. Uchiyama, *Angew. Chem., Int. Ed.,* 2020, **59**, 10639–10644.

7. Spectra

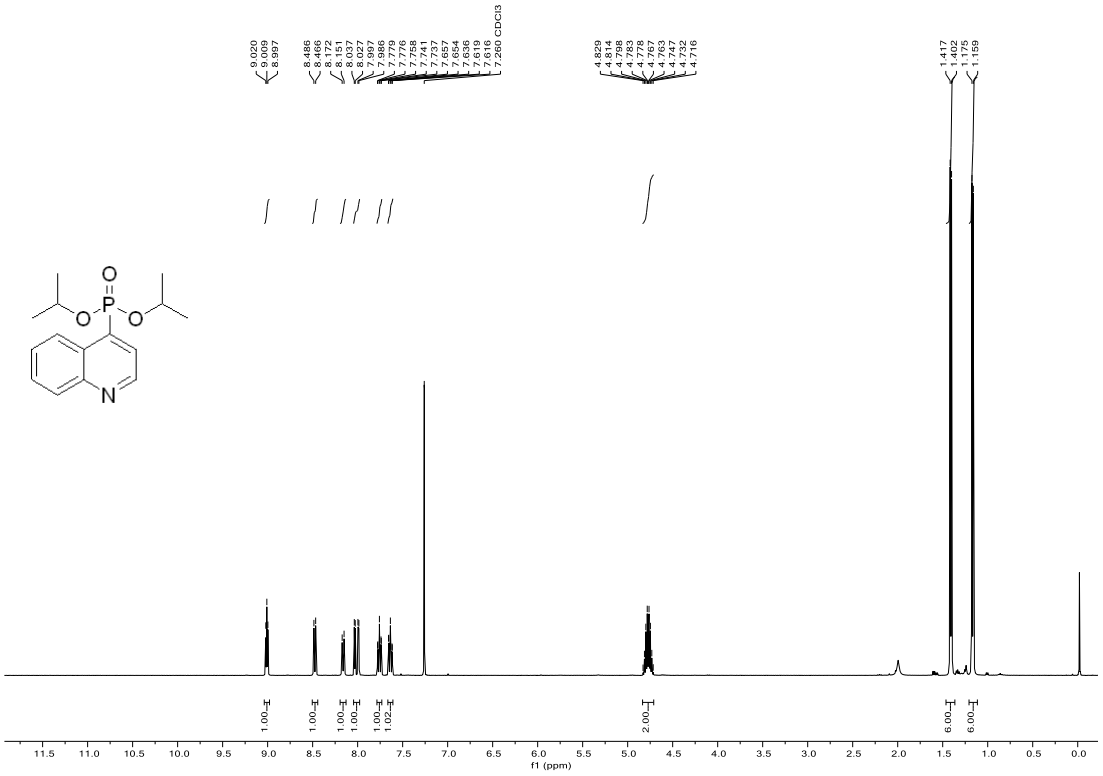

Figure S1. ^{1}H NMR spectra (400 MHz) of **1g** in $CDCl_3$.

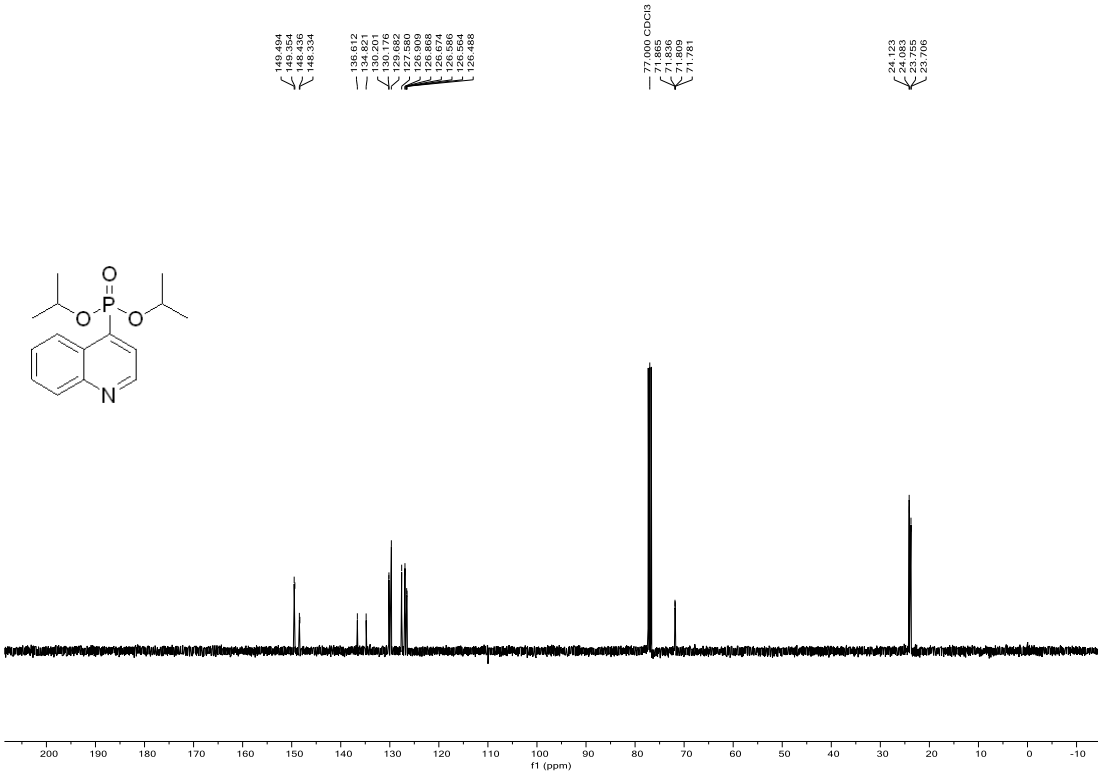

Figure S2. ^{13}C NMR spectra (101 MHz) of **1g** in $CDCl_3$.

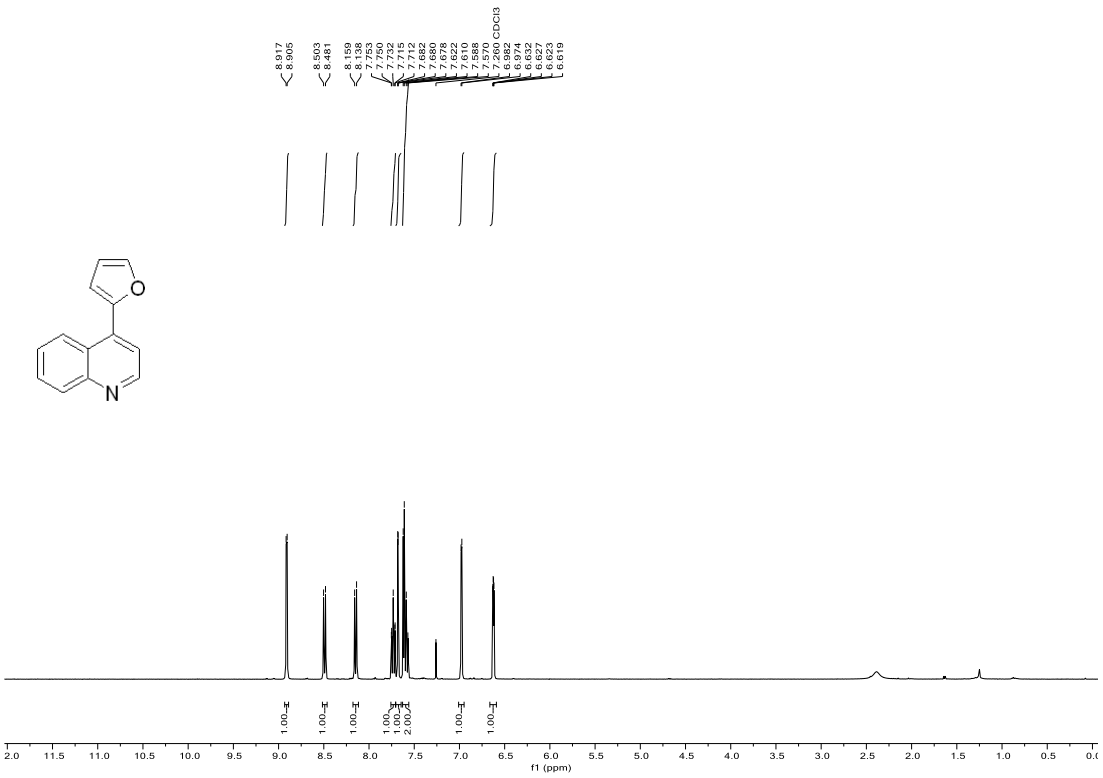

Figure S3. ^{1}H NMR spectra (400 MHz) of **1h** in $CDCl_3$.

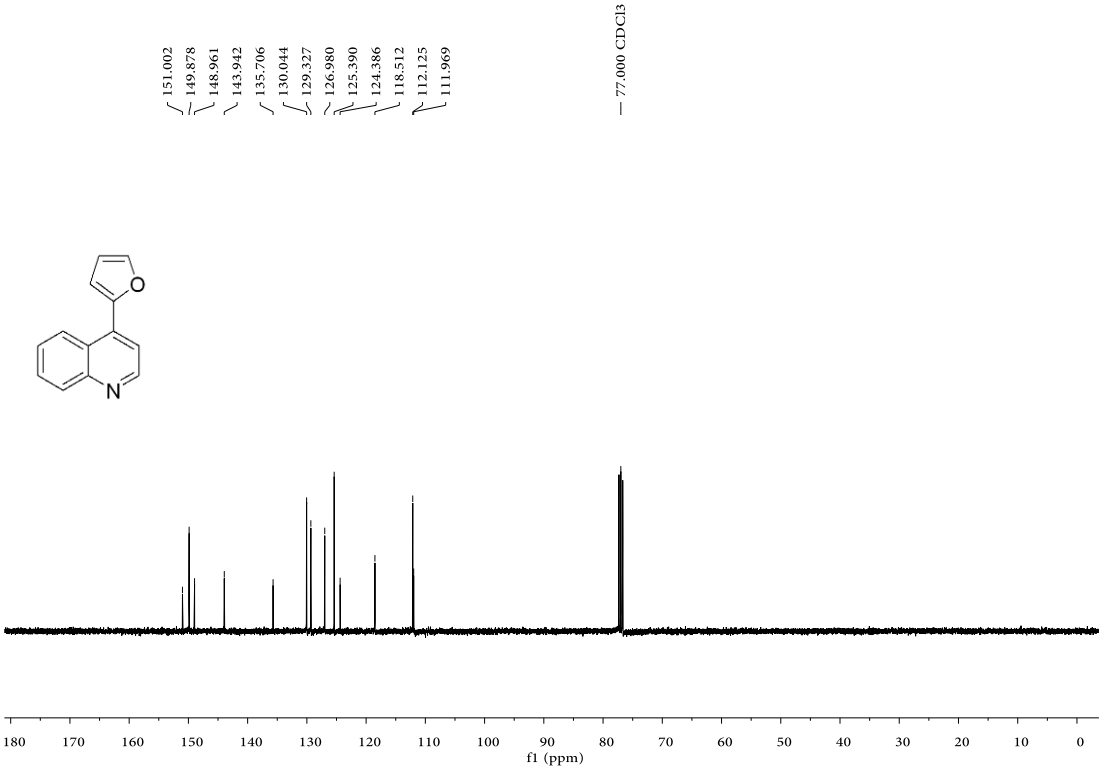

Figure S4. ^{13}C NMR spectra (101 MHz) of **1h** in $CDCl_3$.

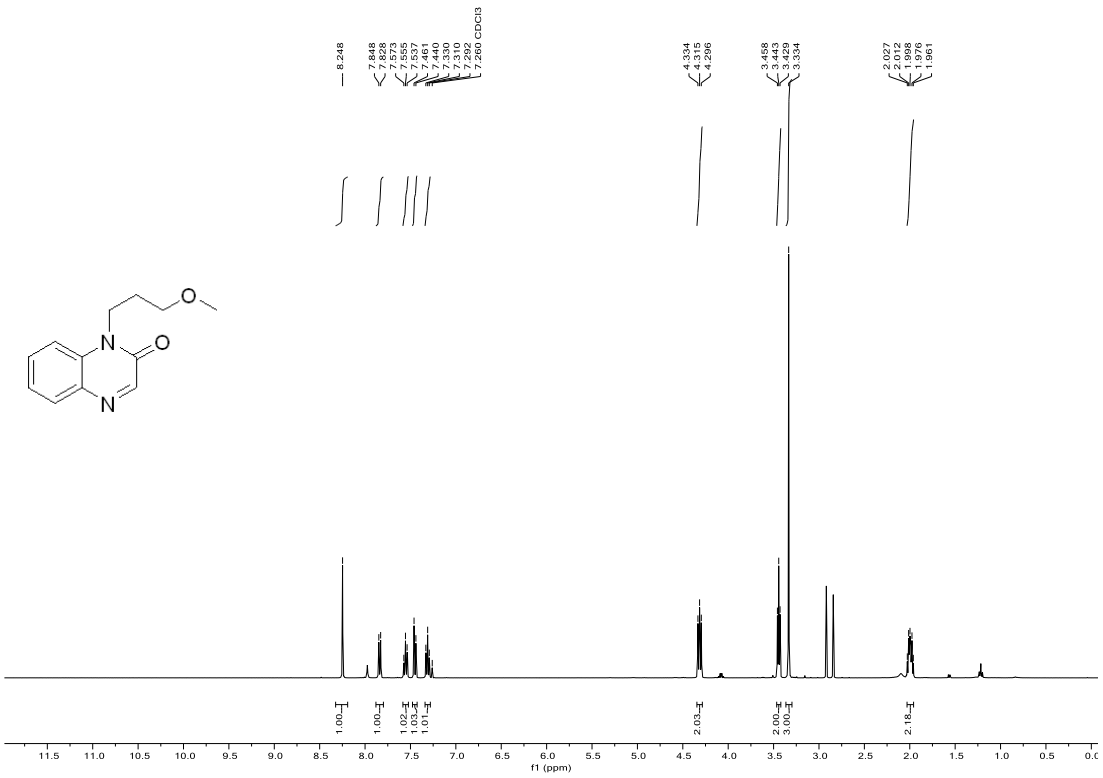

Figure S5. ^{1}H NMR spectra (400 MHz) of **1x** in $CDCl_3$.

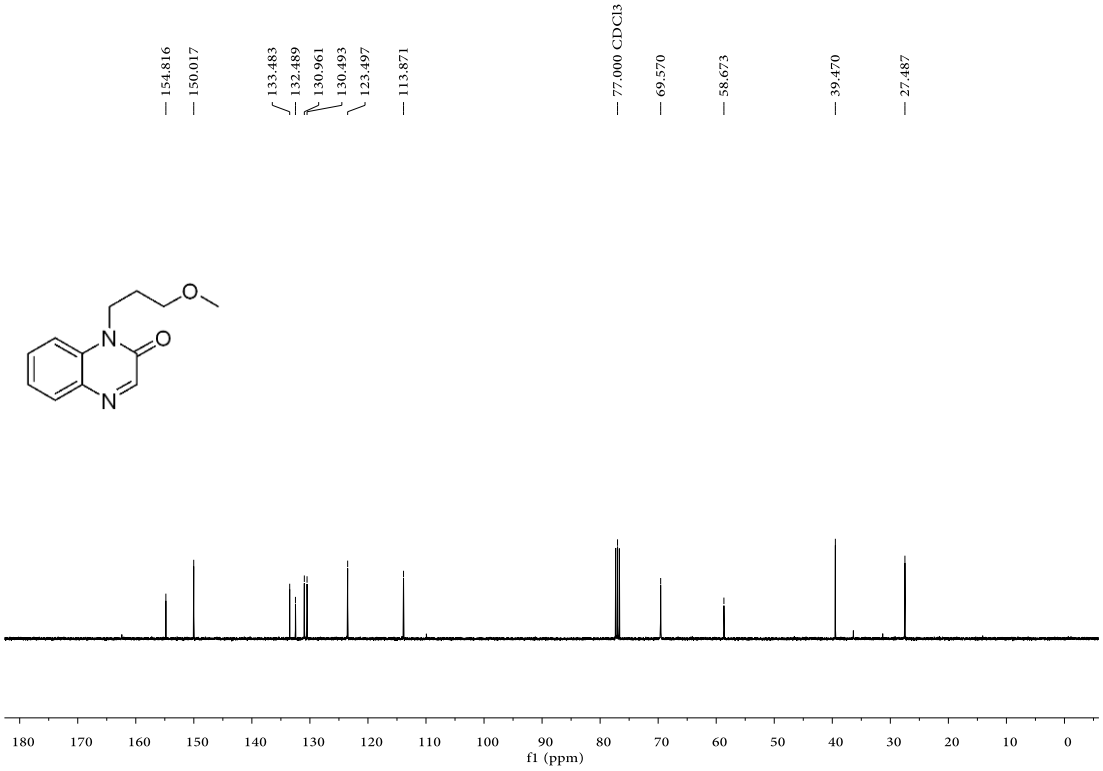

Figure S6. ^{13}C NMR spectra (101 MHz) of **1x** in $CDCl_3$.

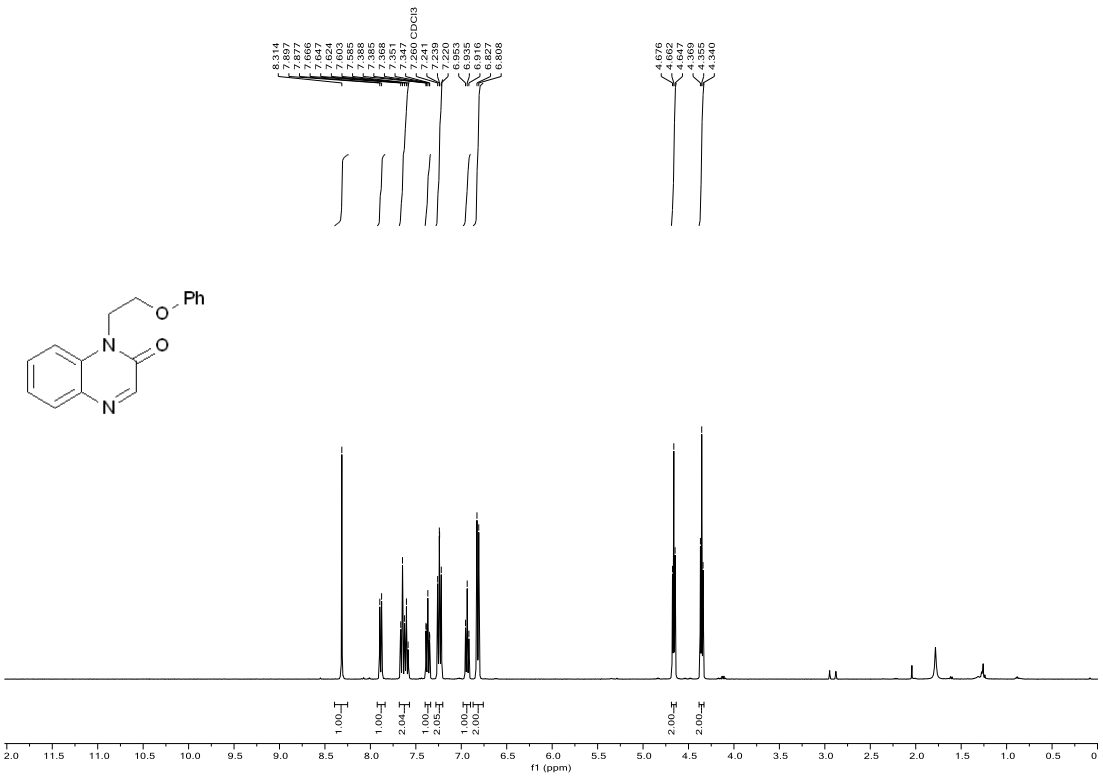

Figure S7. ^{1}H NMR spectra (400 MHz) of **1y** in $CDCl_3$.

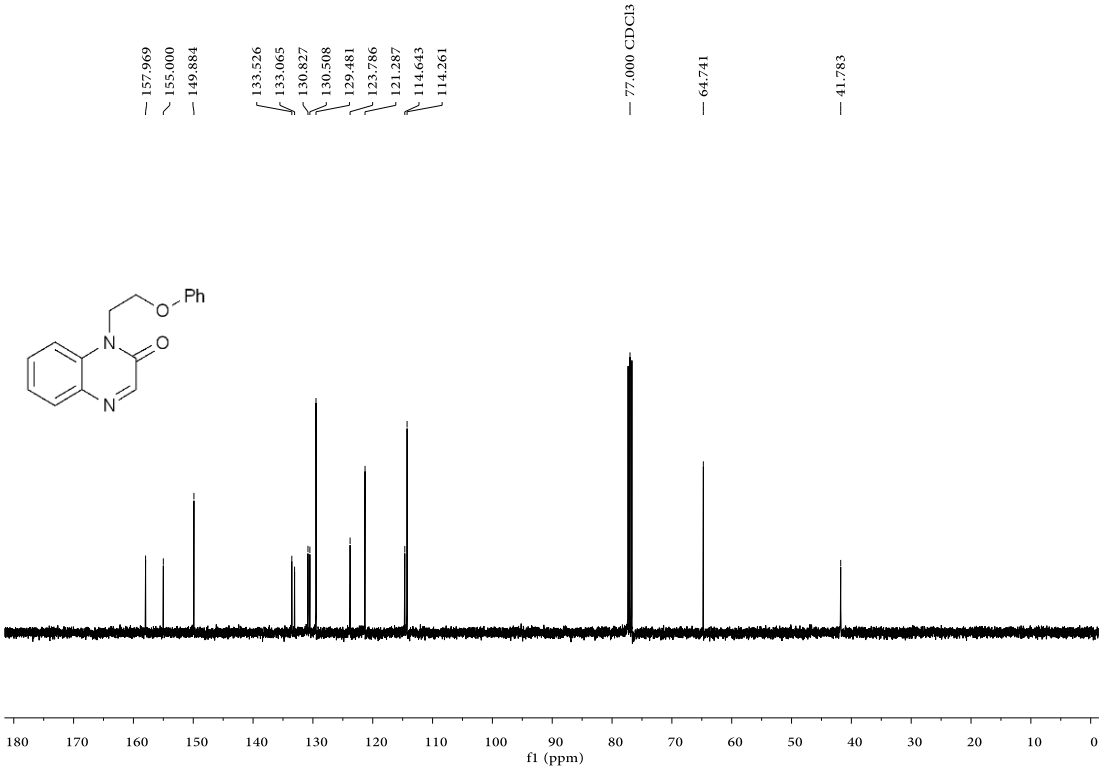

Figure S8. ^{13}C NMR spectra (101 MHz) of **1y** in $CDCl_3$.

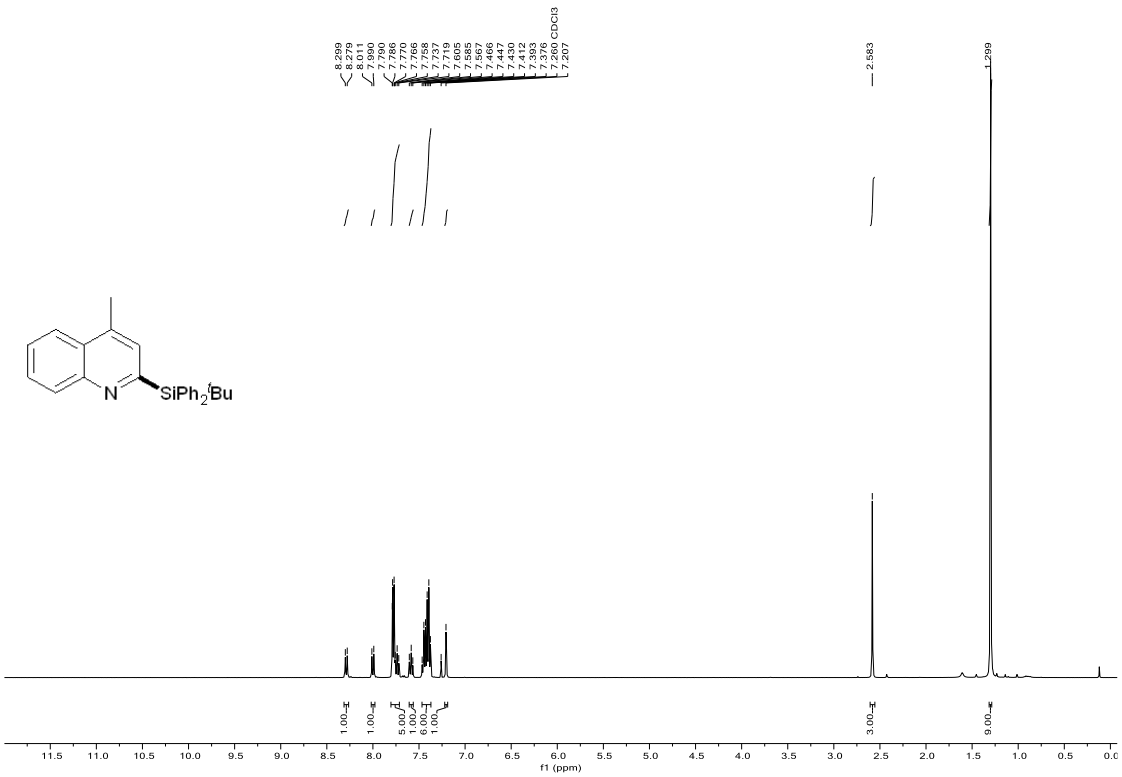

Figure S9. ^{1}H NMR spectra (400 MHz) of **3a** in $CDCl_3$.

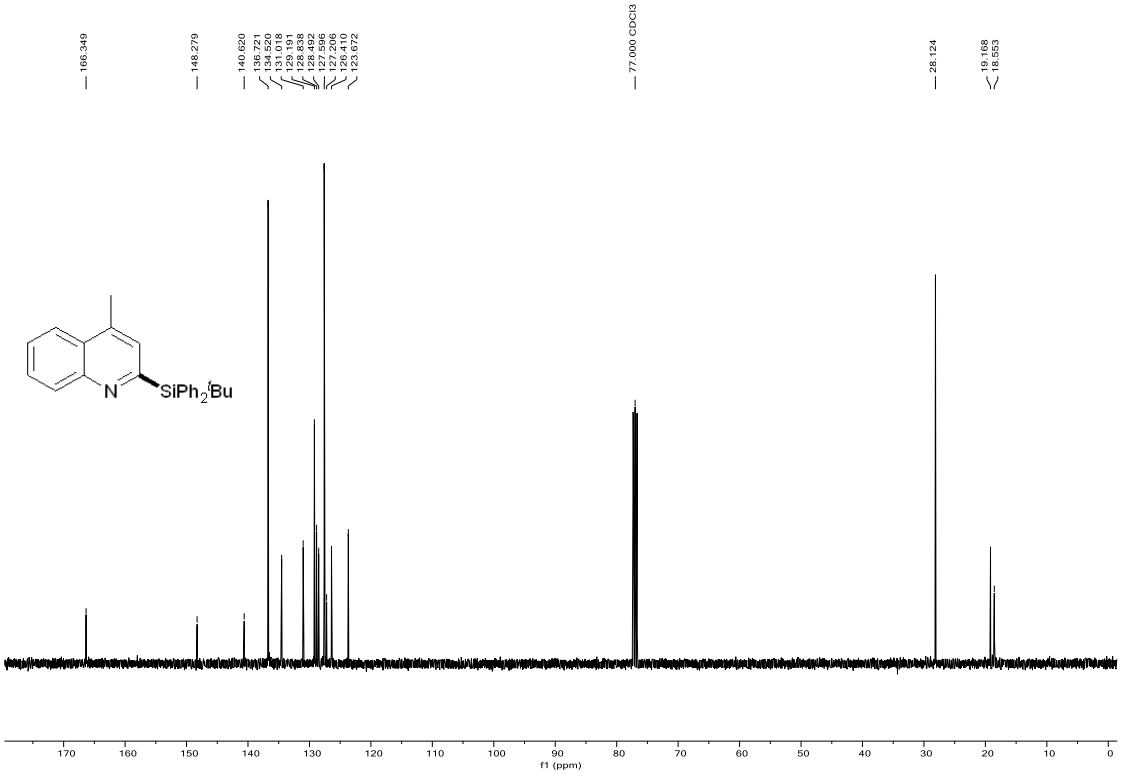

Figure S10. ^{13}C NMR spectra (101 MHz) of **3a** in $CDCl_3$.

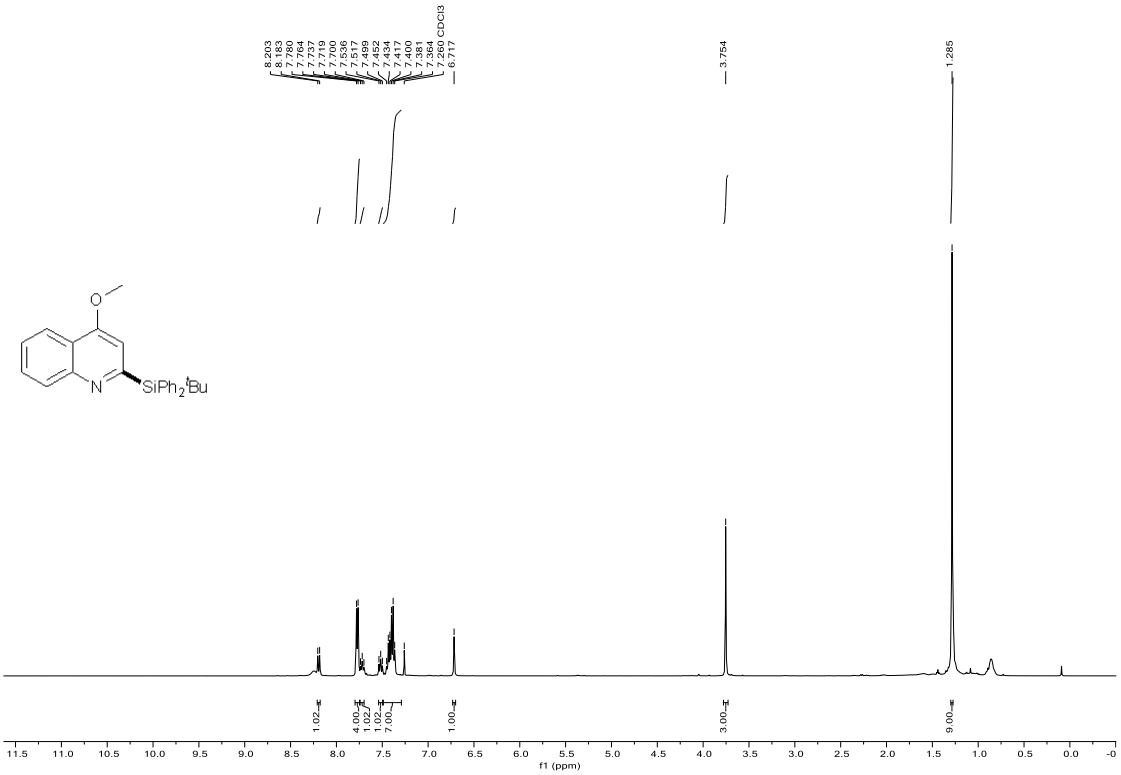

Figure S11. ^{1}H NMR spectra (400 MHz) of **3b** in $CDCl_3$.

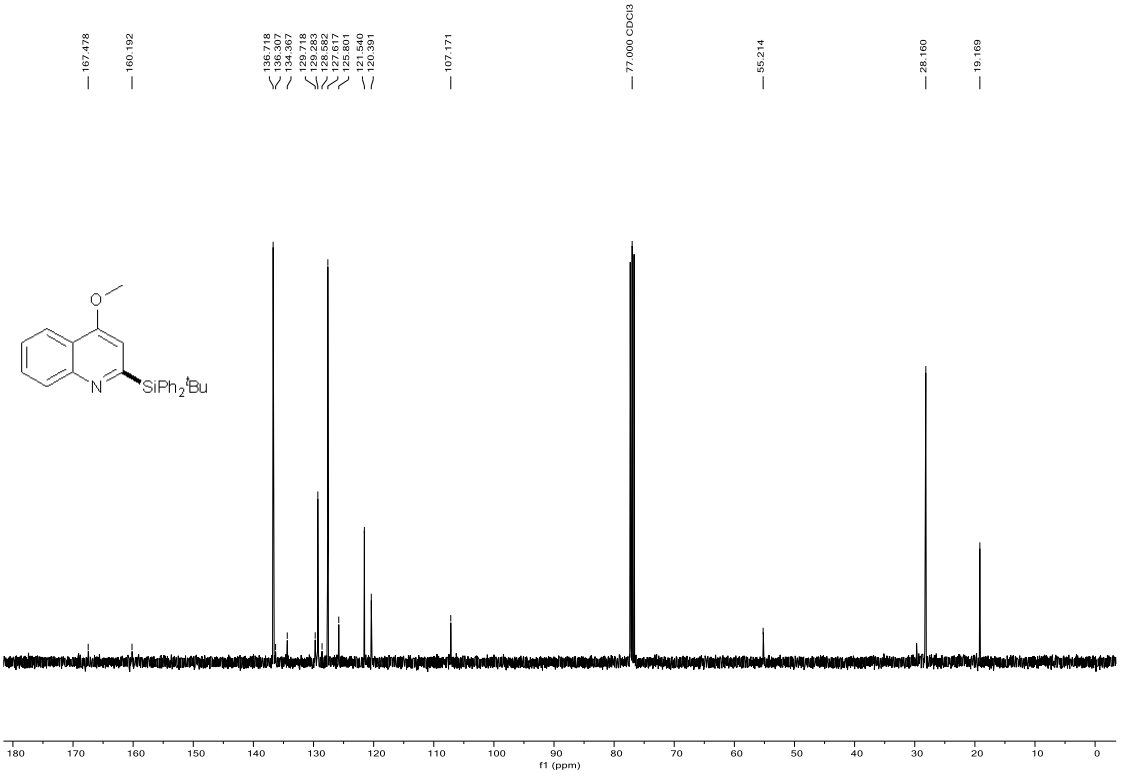

Figure S12. ^{13}C NMR spectra (101 MHz) of **3b** in $CDCl_3$.

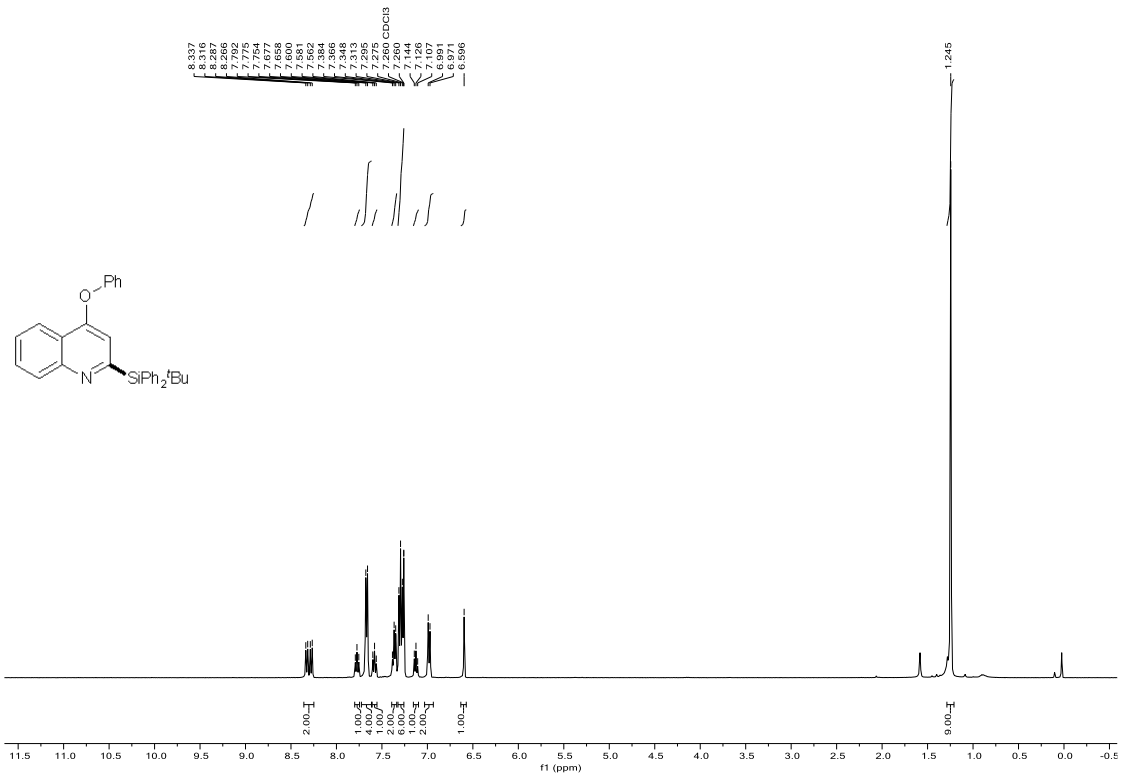

Figure S13. ^{1}H NMR spectra (400 MHz) of **3c** in $CDCl_3$.

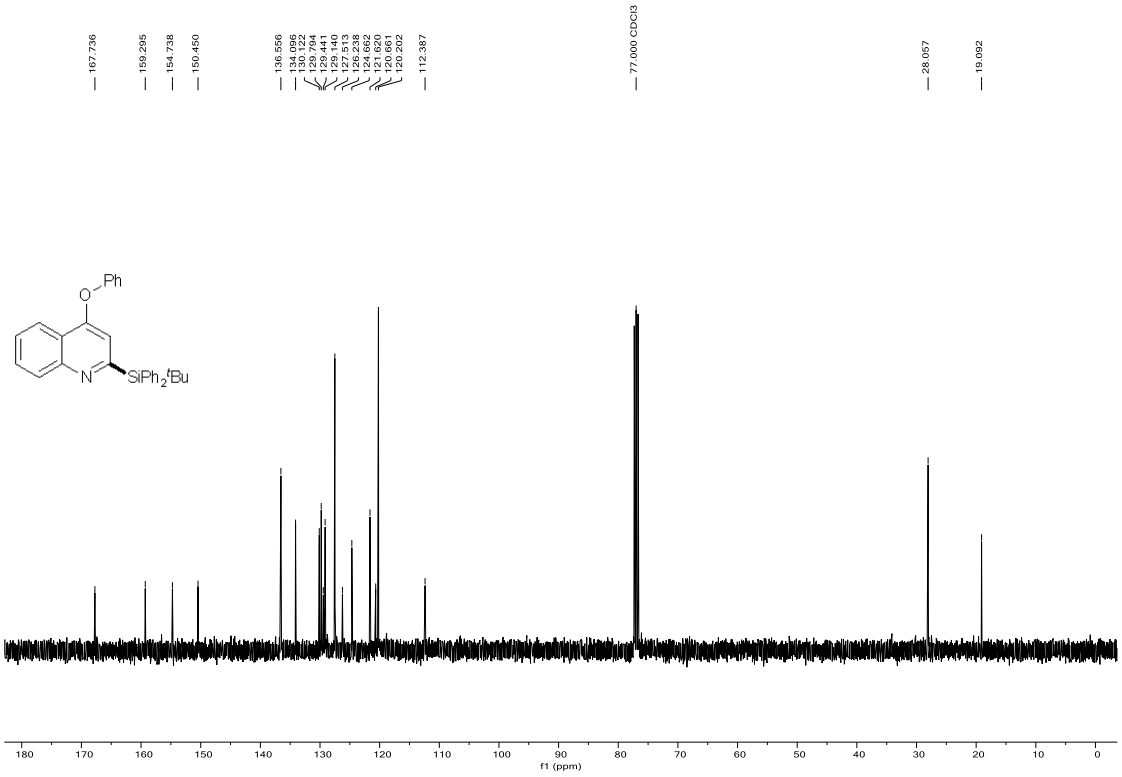

Figure S14. ^{13}C NMR spectra (101 MHz) of **3c** in $CDCl_3$.

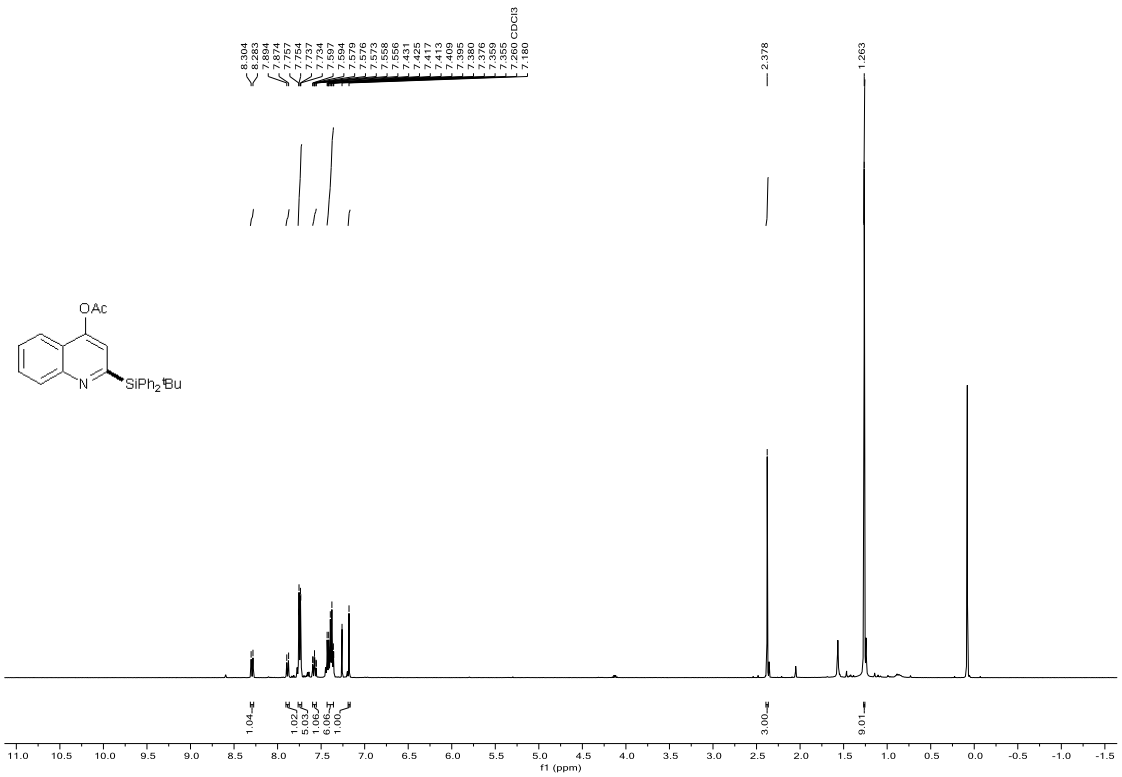

Figure S15. ^{1}H NMR spectra (400 MHz) of **3d** in $CDCl_3$.

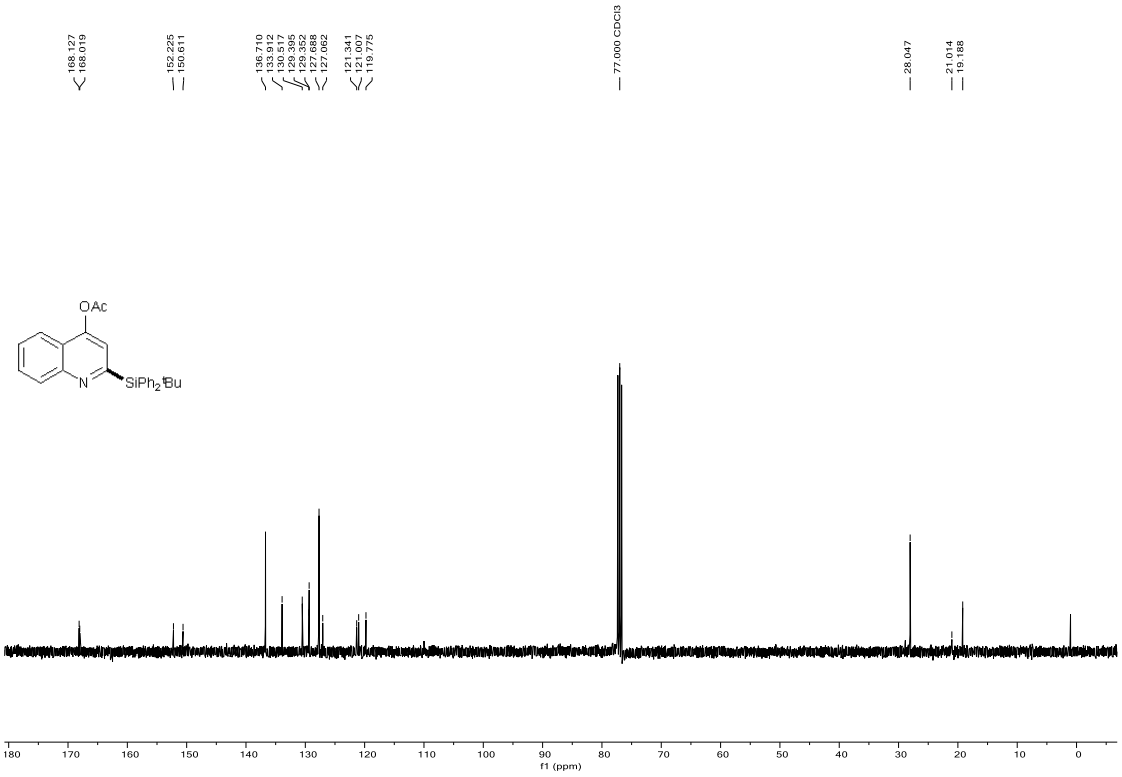

Figure S16. ^{13}C NMR spectra (101 MHz) of **3d** in $CDCl_3$.

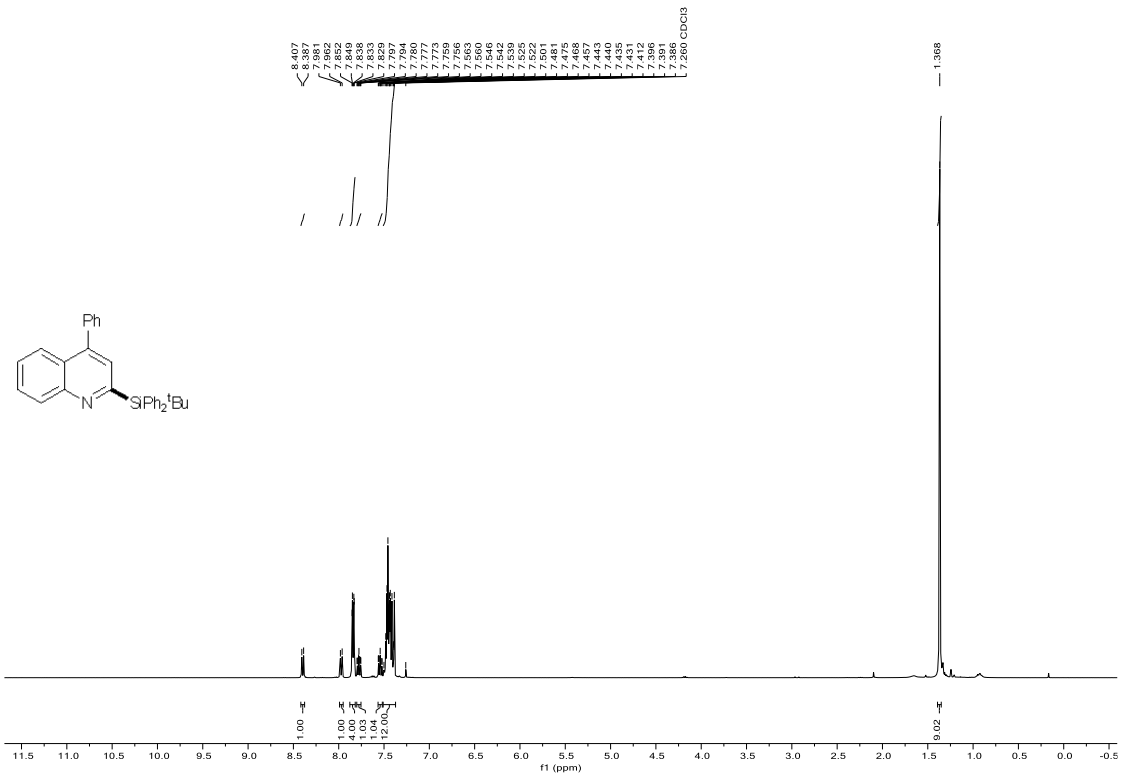

Figure S17. ^{1}H NMR spectra (400 MHz) of **3e** in $CDCl_3$.

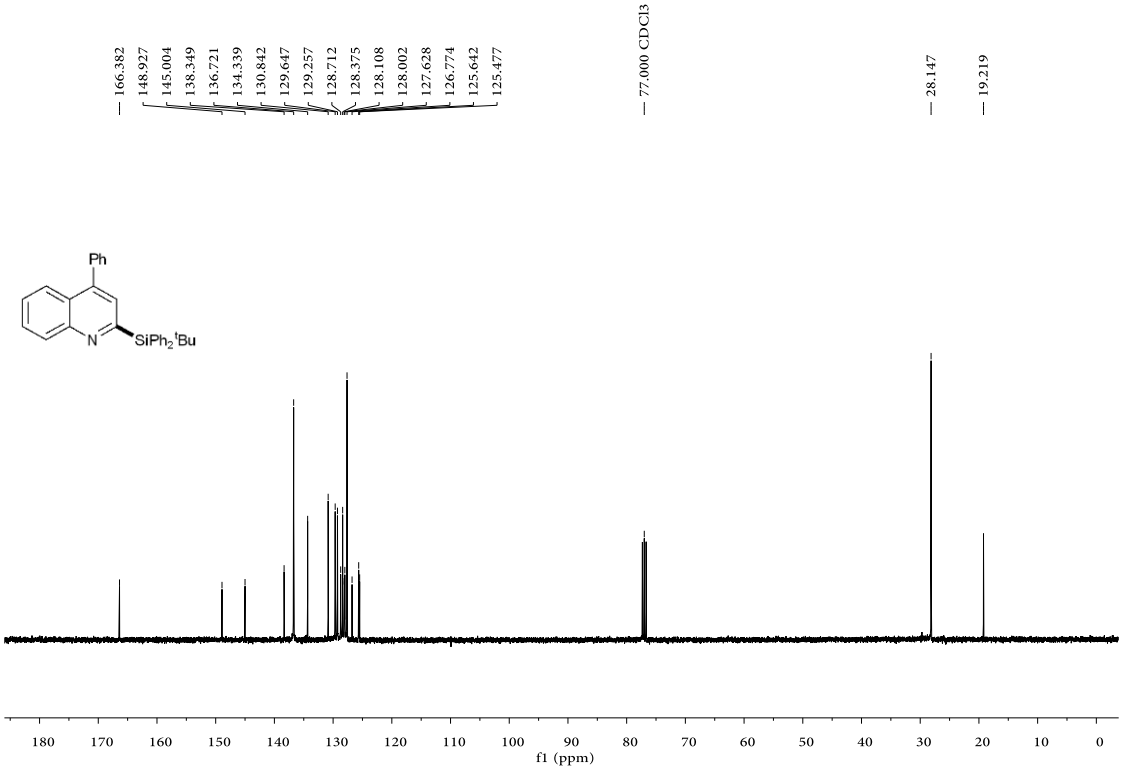

Figure S18. ^{13}C NMR spectra (101 MHz) of **3e** in $CDCl_3$.

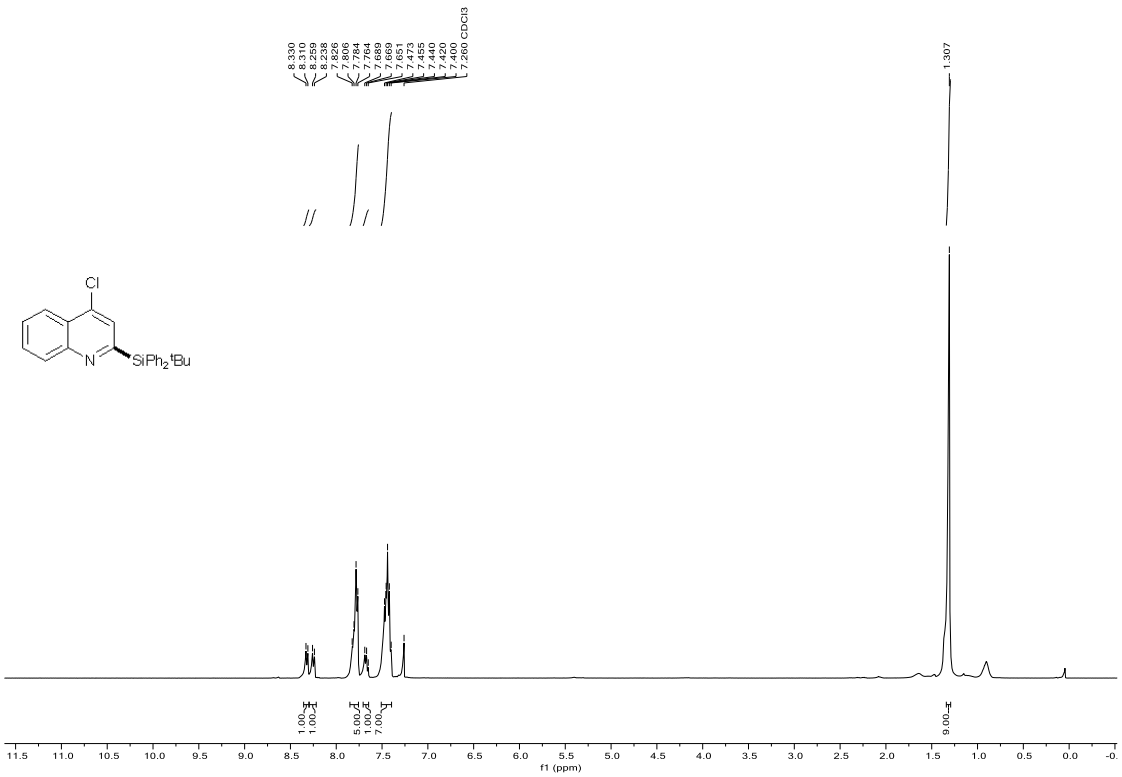

Figure S19. ^{1}H NMR spectra (400 MHz) of **3f** in $CDCl_3$.

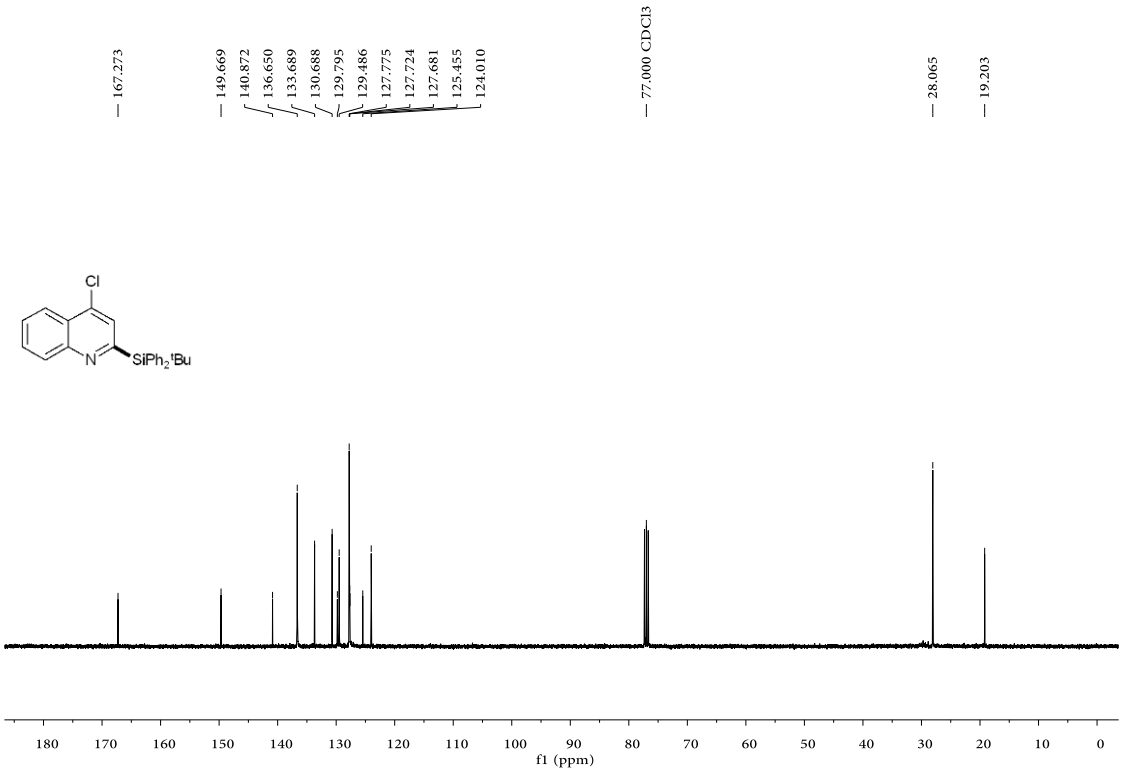

Figure S20. ^{13}C NMR spectra (101 MHz) of **3f** in $CDCl_3$.

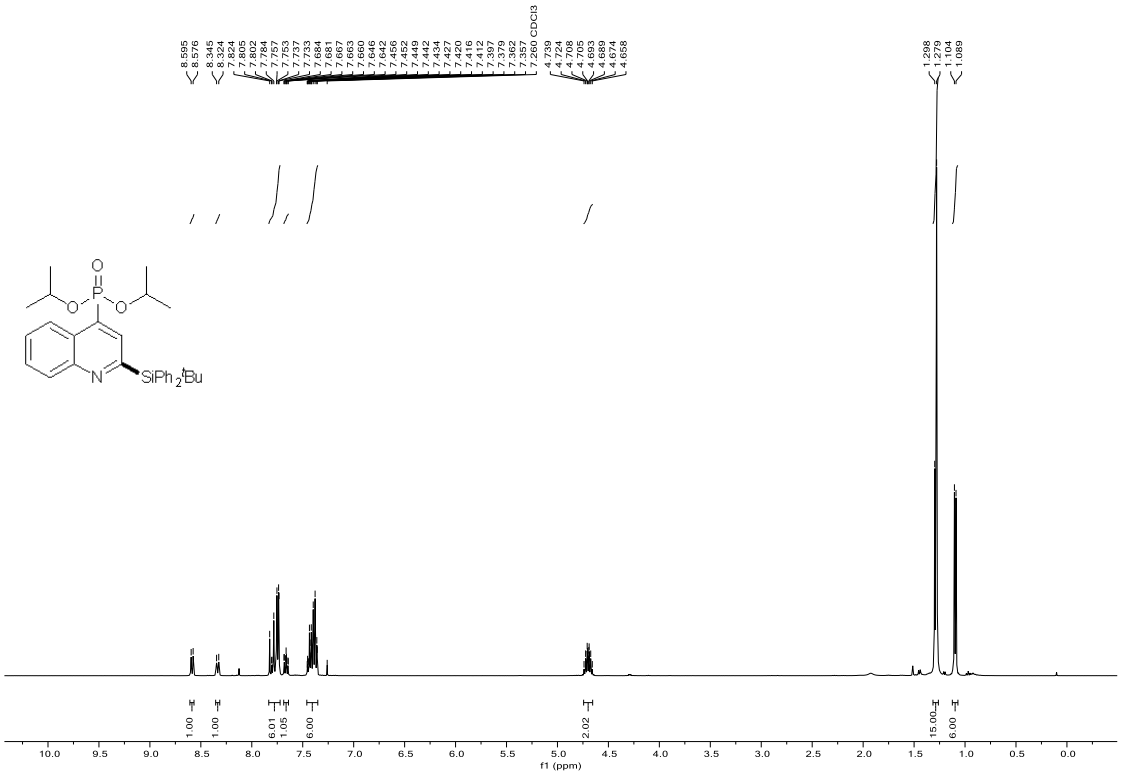

Figure S21. ^{1}H NMR spectra (400 MHz) of **3g** in $CDCl_3$.

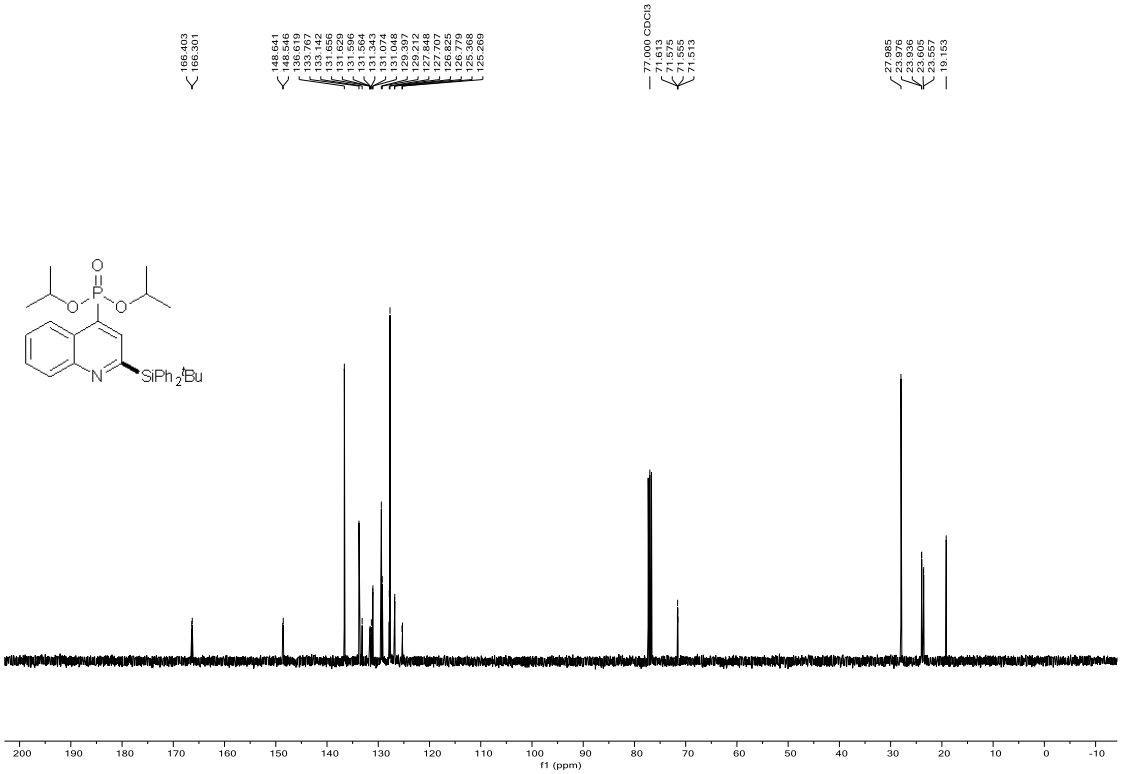

Figure S22. ^{13}C NMR spectra (101 MHz) of **3g** in $CDCl_3$.

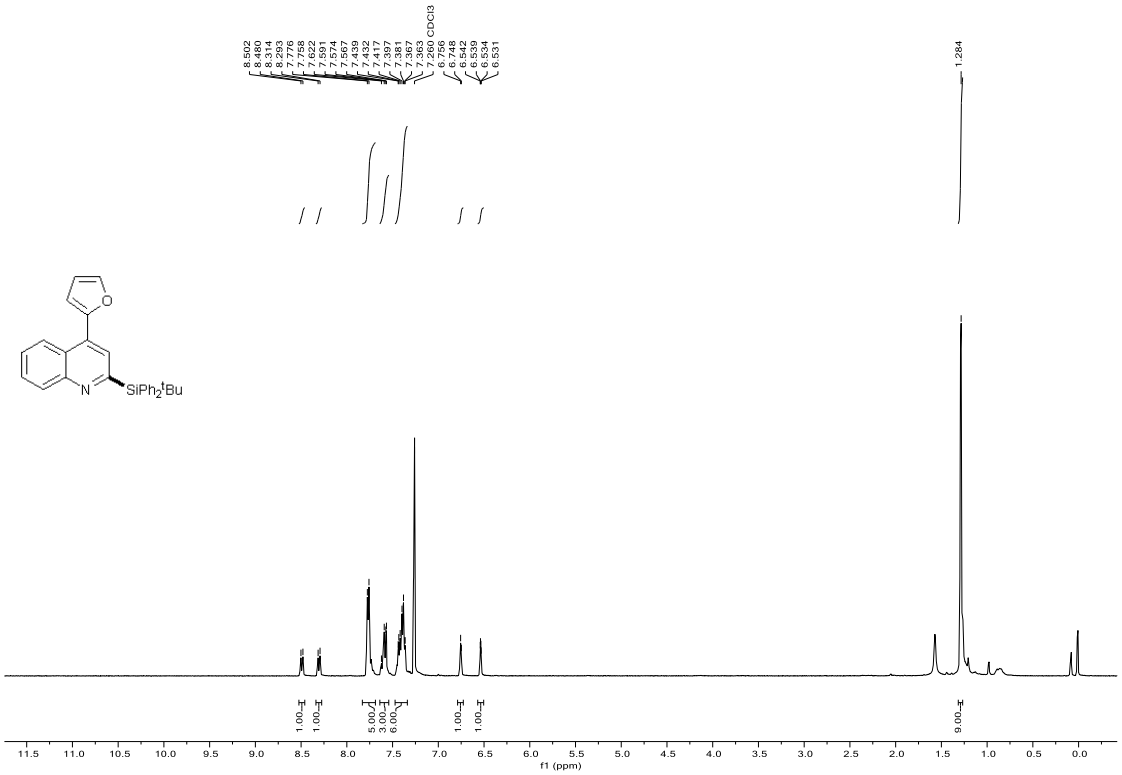

Figure S23. ^{1}H NMR spectra (400 MHz) of **3h** in $CDCl_3$.

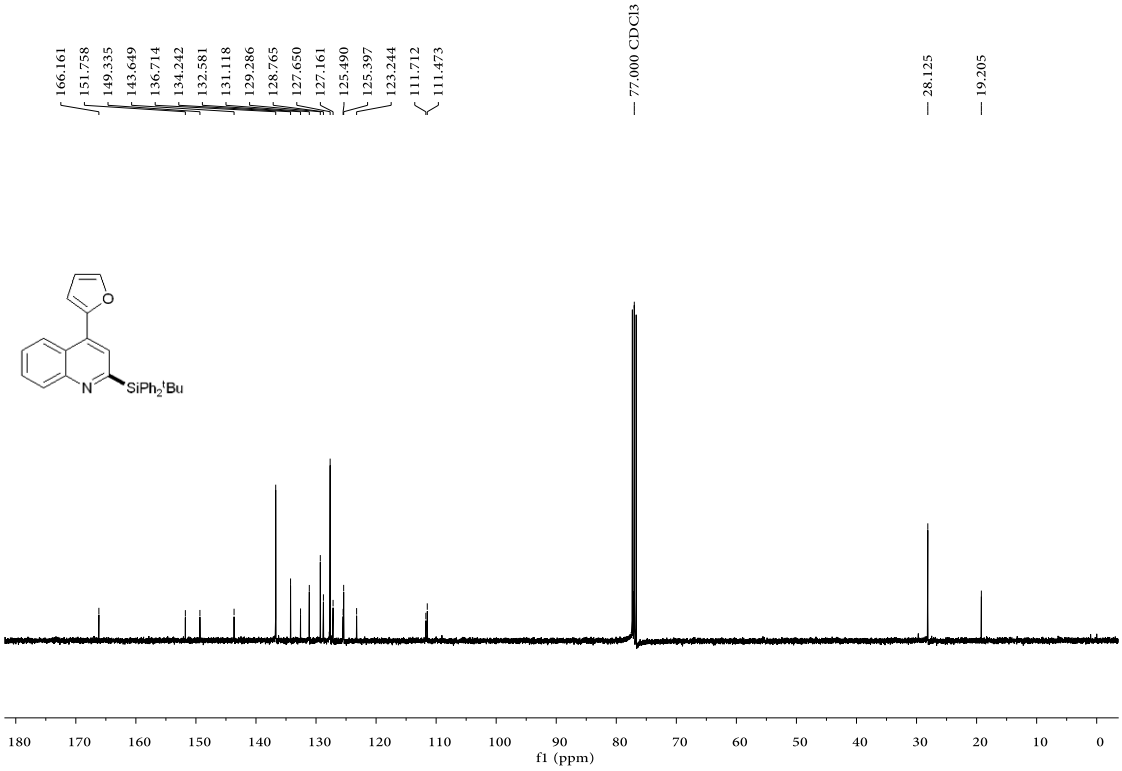

Figure S24. ^{13}C NMR spectra (101 MHz) of **3h** in $CDCl_3$.

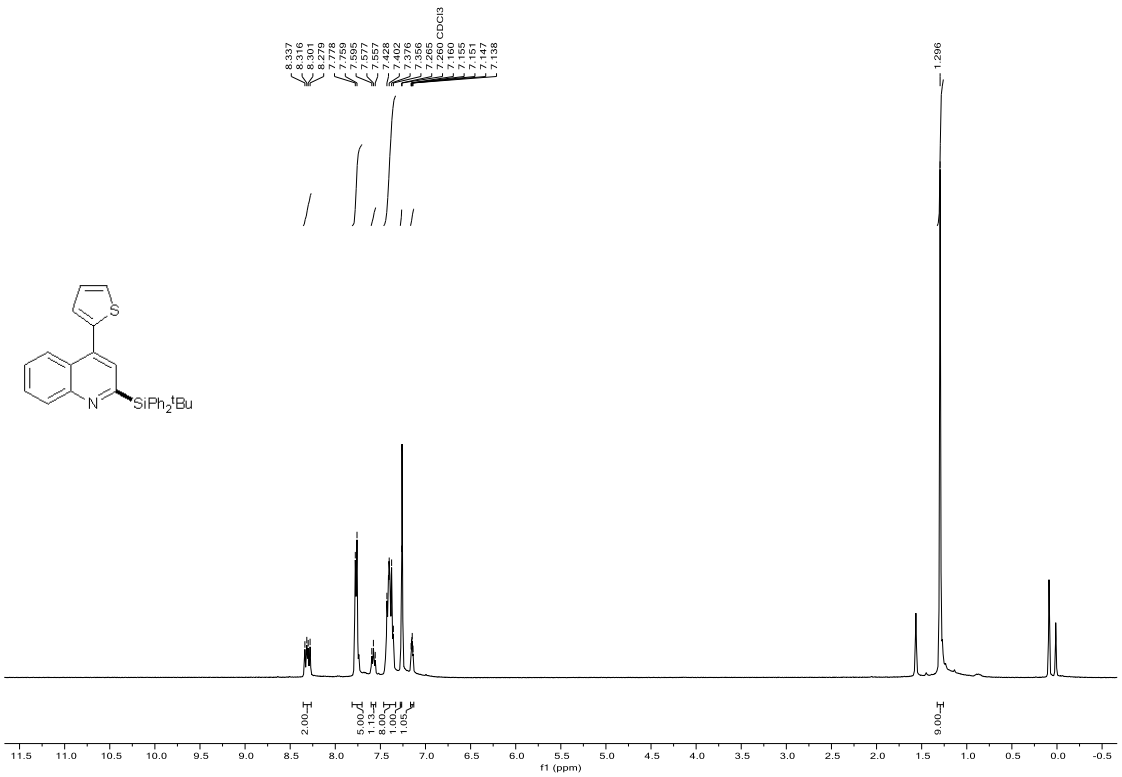

Figure S25. ^{1}H NMR spectra (400 MHz) of **3i** in $CDCl_3$.

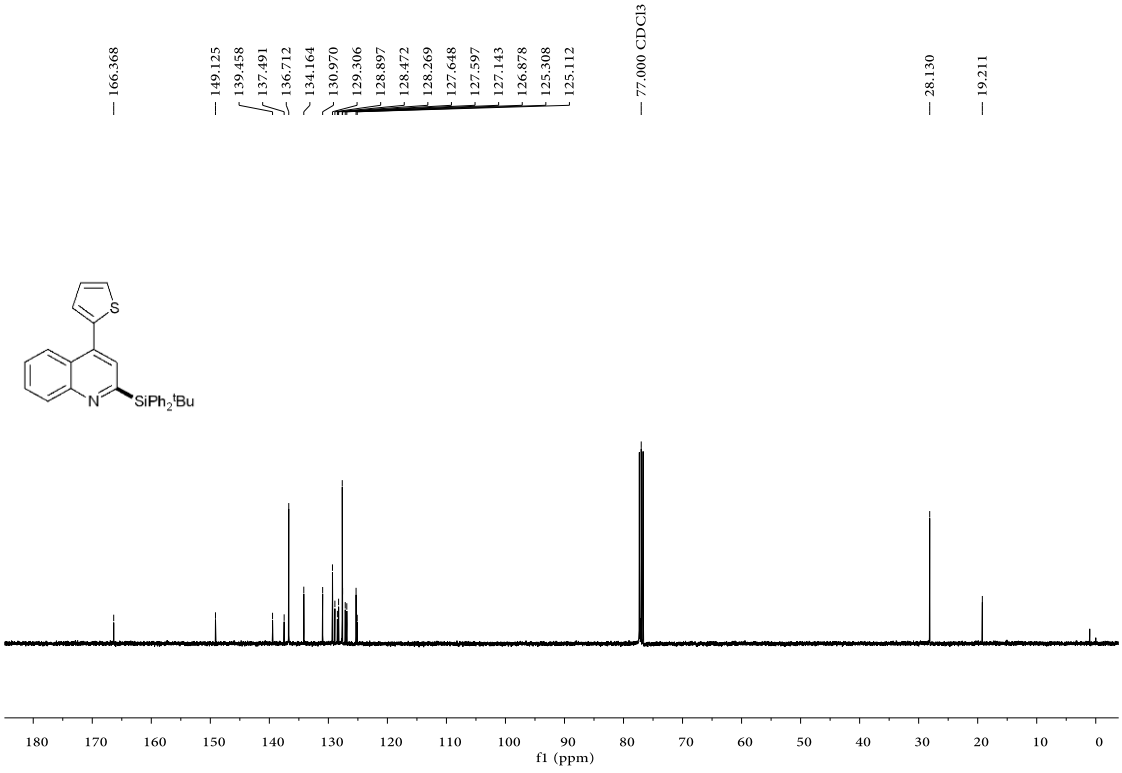

Figure S26. ^{13}C NMR spectra (101 MHz) of **3i** in $CDCl_3$.

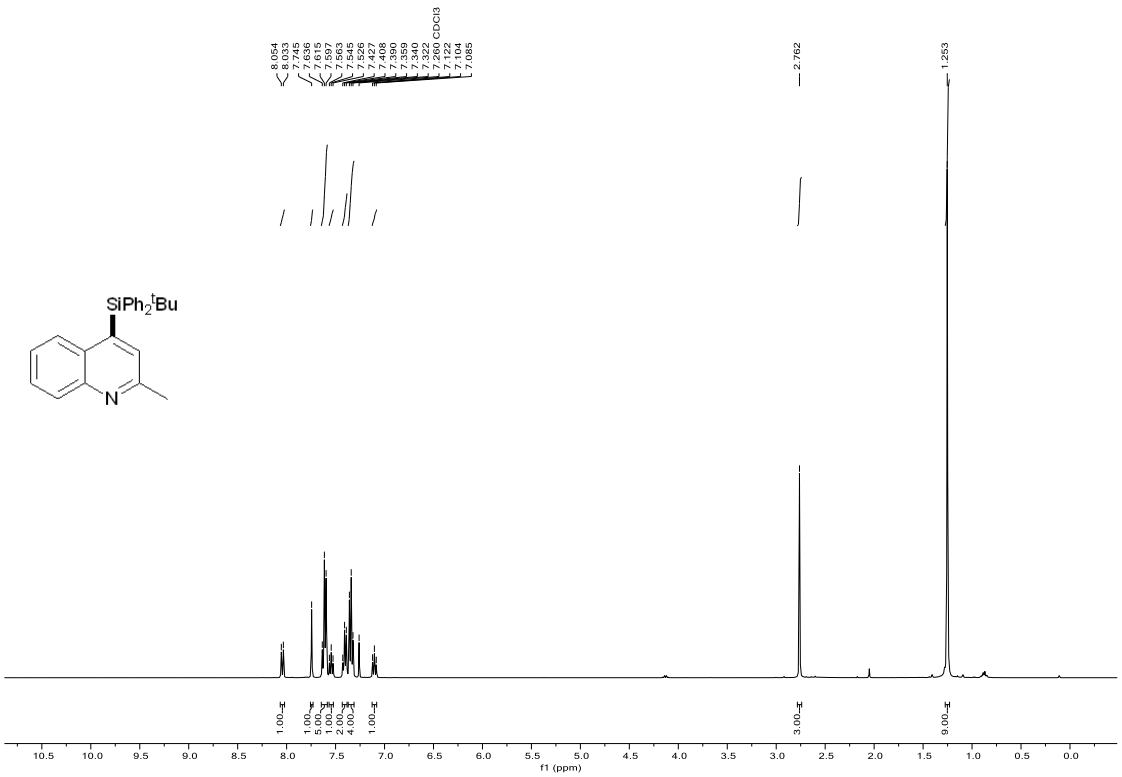

Figure S27. ^{1}H NMR spectra (400 MHz) of **3j** in $CDCl_3$.

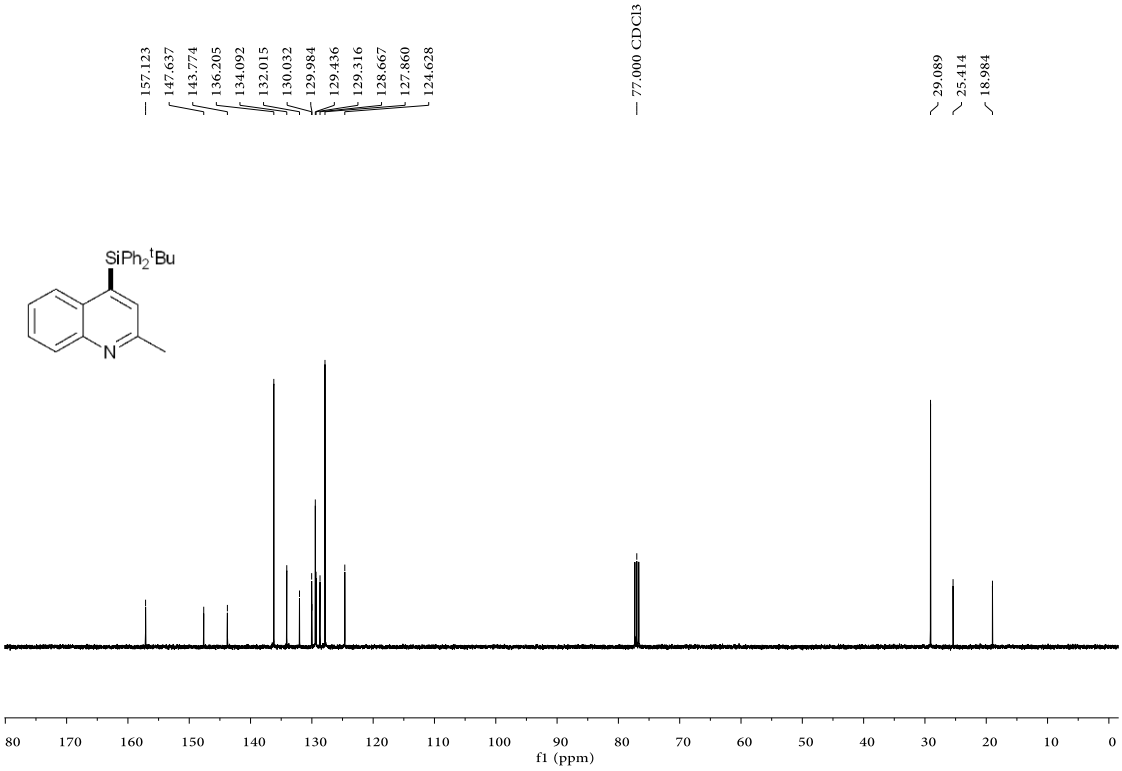

Figure S28. ^{13}C NMR spectra (101 MHz) of **3j** in $CDCl_3$.

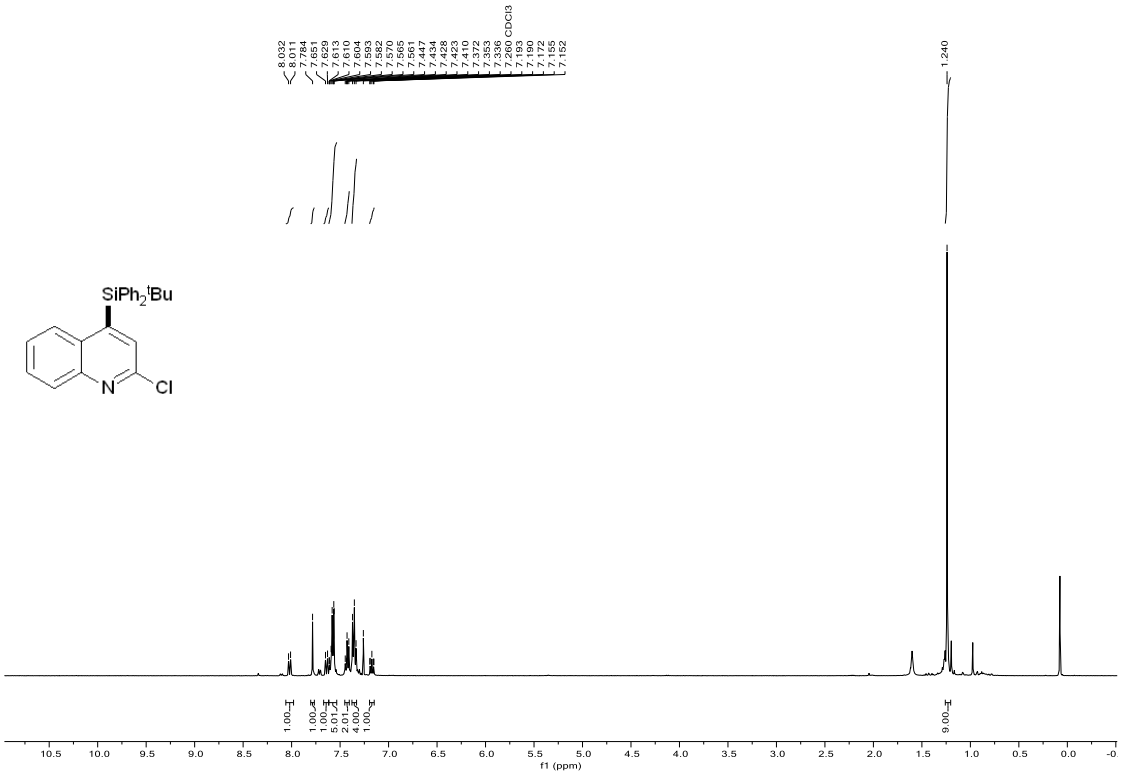

Figure S29. ^{1}H NMR spectra (400 MHz) of **3k** in $CDCl_3$.

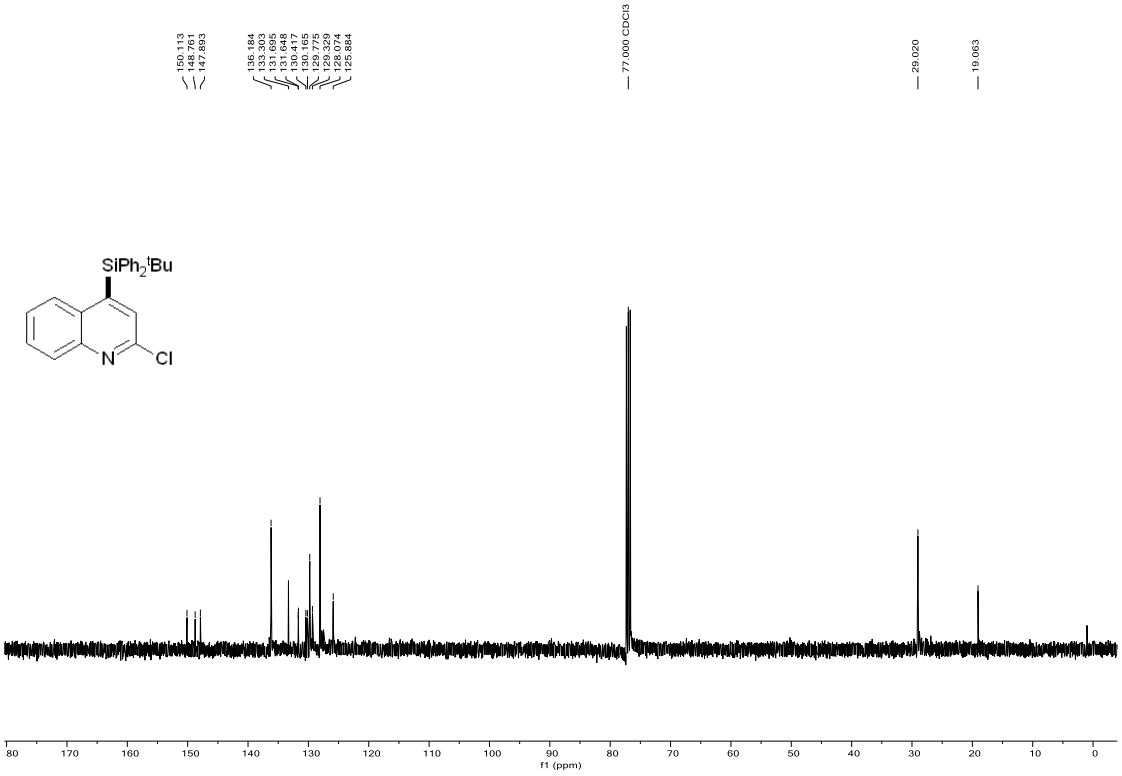

Figure S30. ^{13}C NMR spectra (101 MHz) of **3k** in $CDCl_3$.

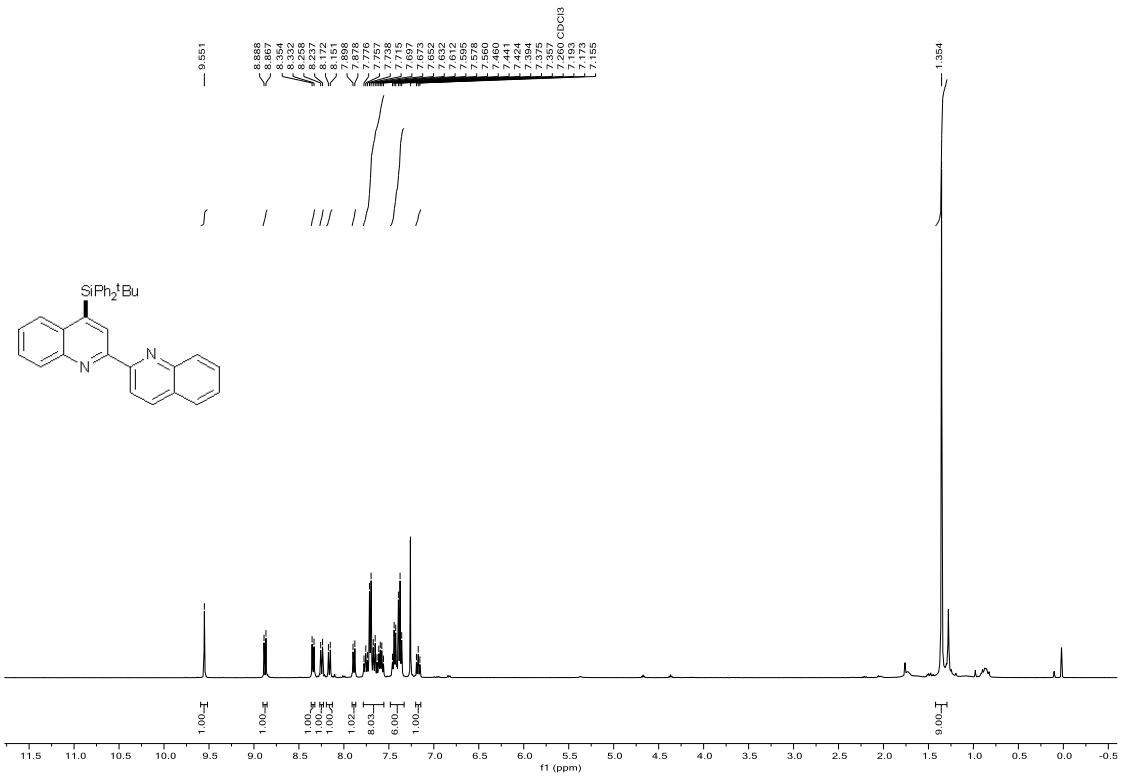

Figure S31. ^{1}H NMR spectra (400 MHz) of **3l** in $CDCl_3$.

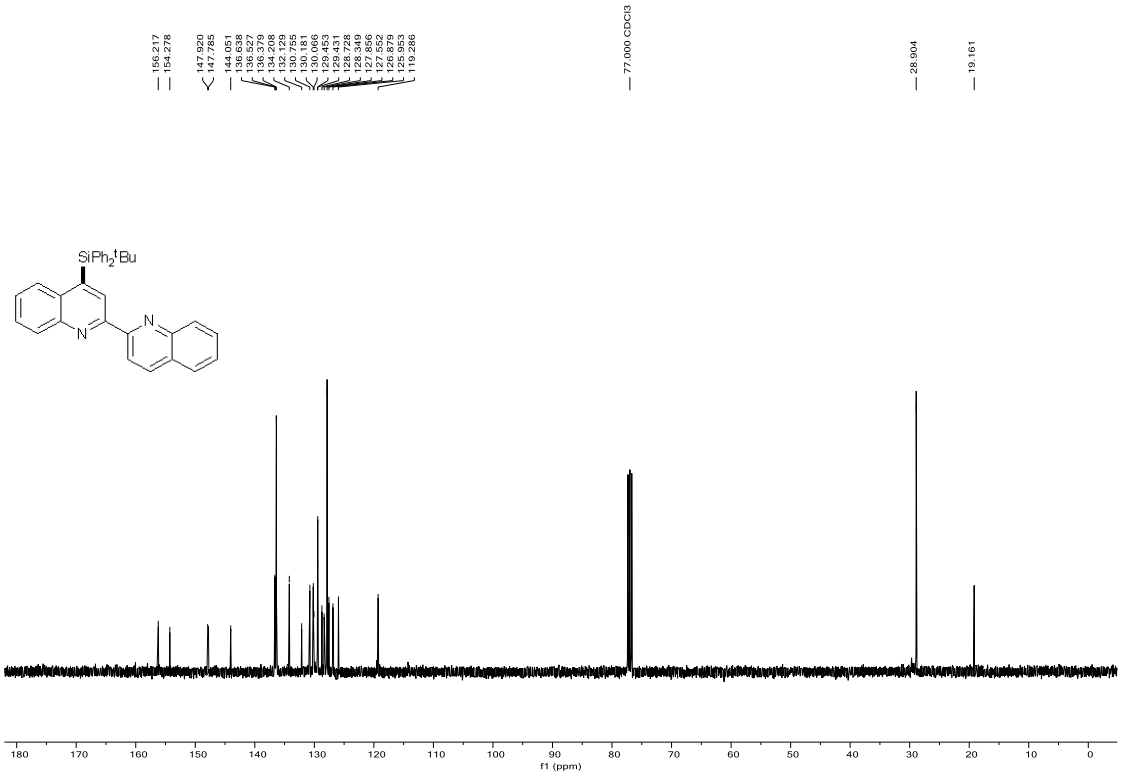

Figure S32. ^{13}C NMR spectra (101 MHz) of **3l** in $CDCl_3$.

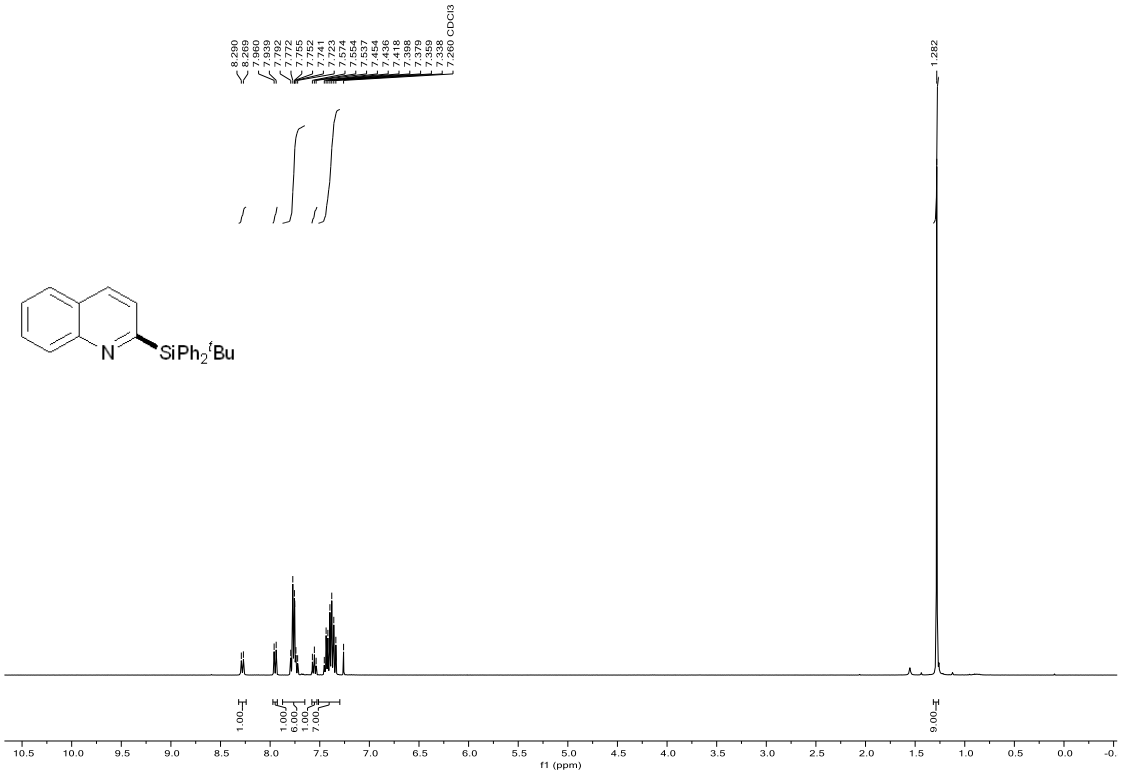

Figure S33. ^{1}H NMR spectra (400 MHz) of **3m** in $CDCl_3$.

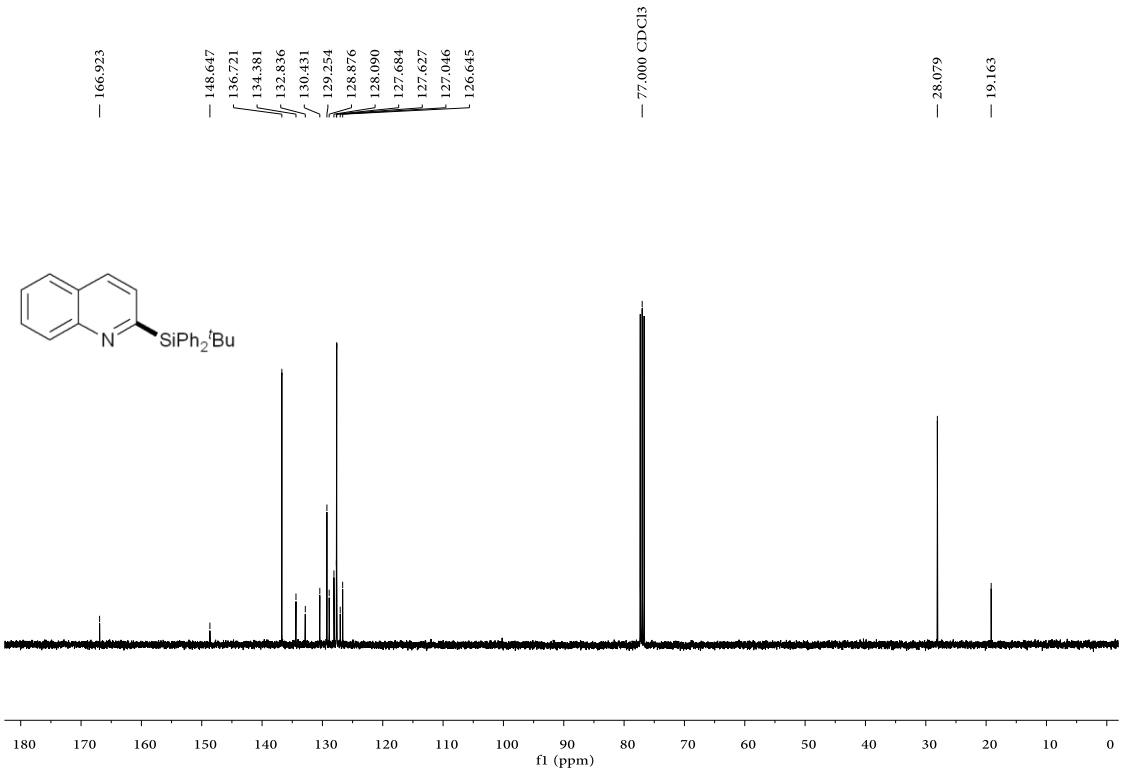

Figure S34. ^{13}C NMR spectra (101 MHz) of **3m** in $CDCl_3$.

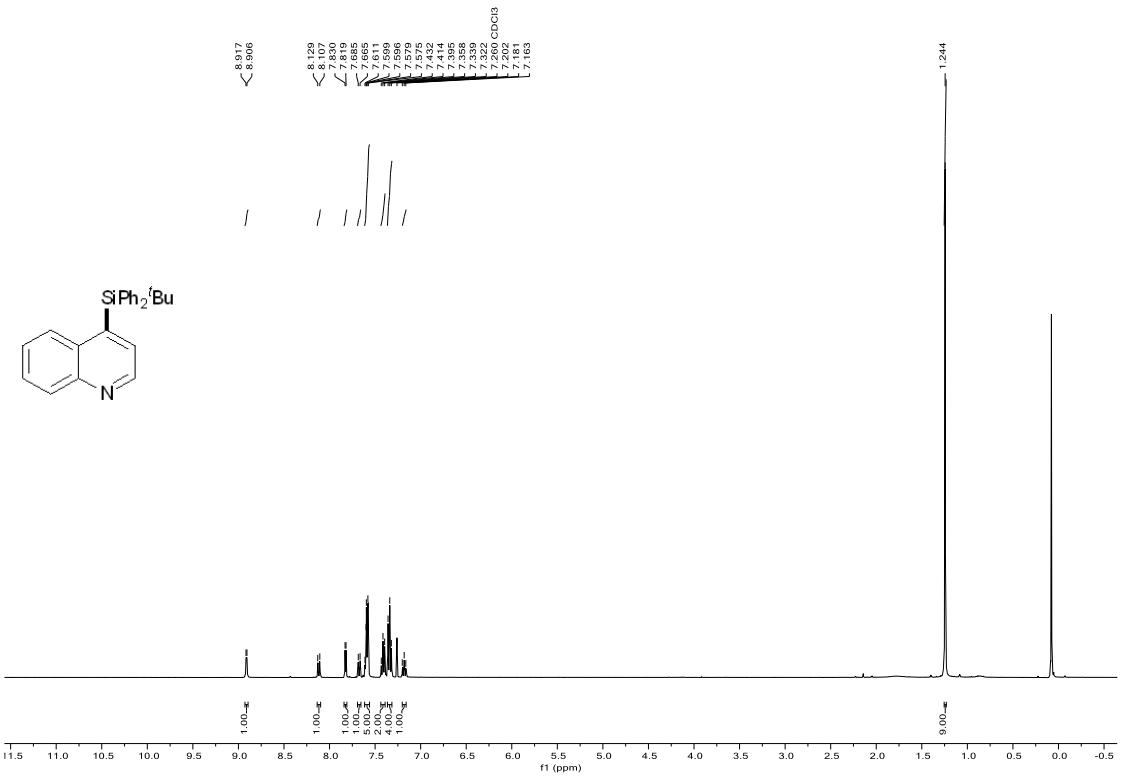

Figure S35. ^{1}H NMR spectra (400 MHz) of **3m'** in $CDCl_3$.

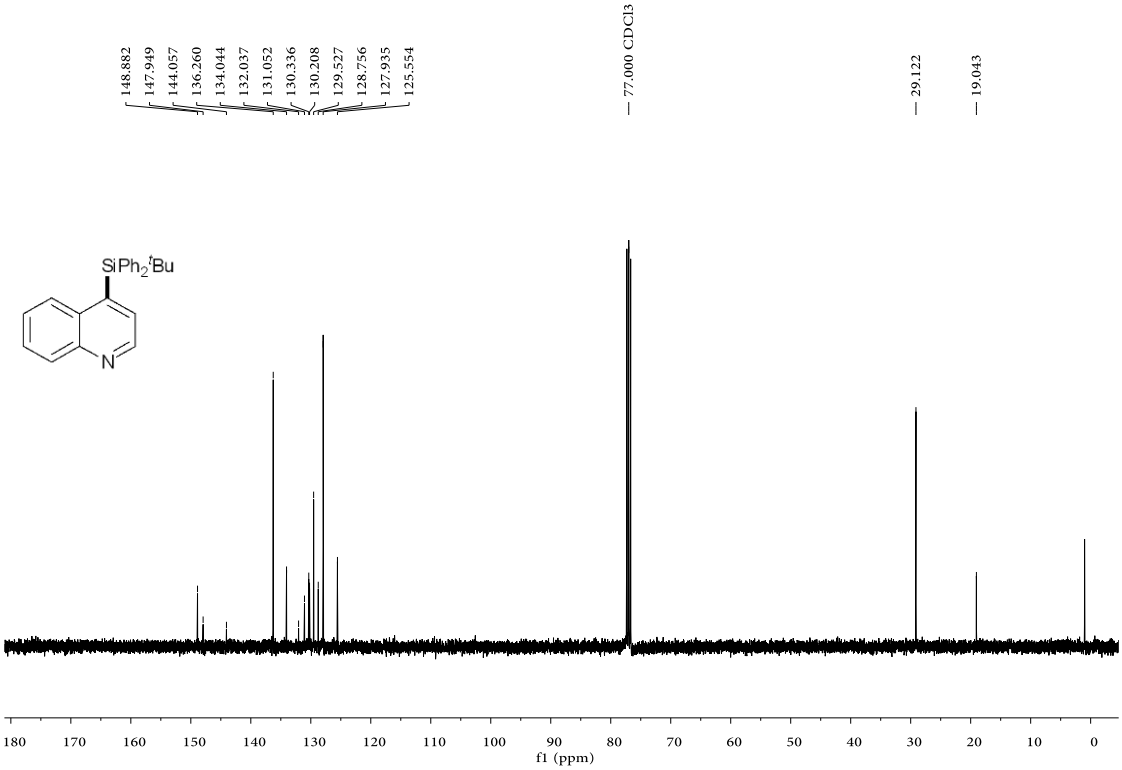

Figure S36. ^{13}C NMR spectra (101 MHz) of **3m'** in $CDCl_3$.

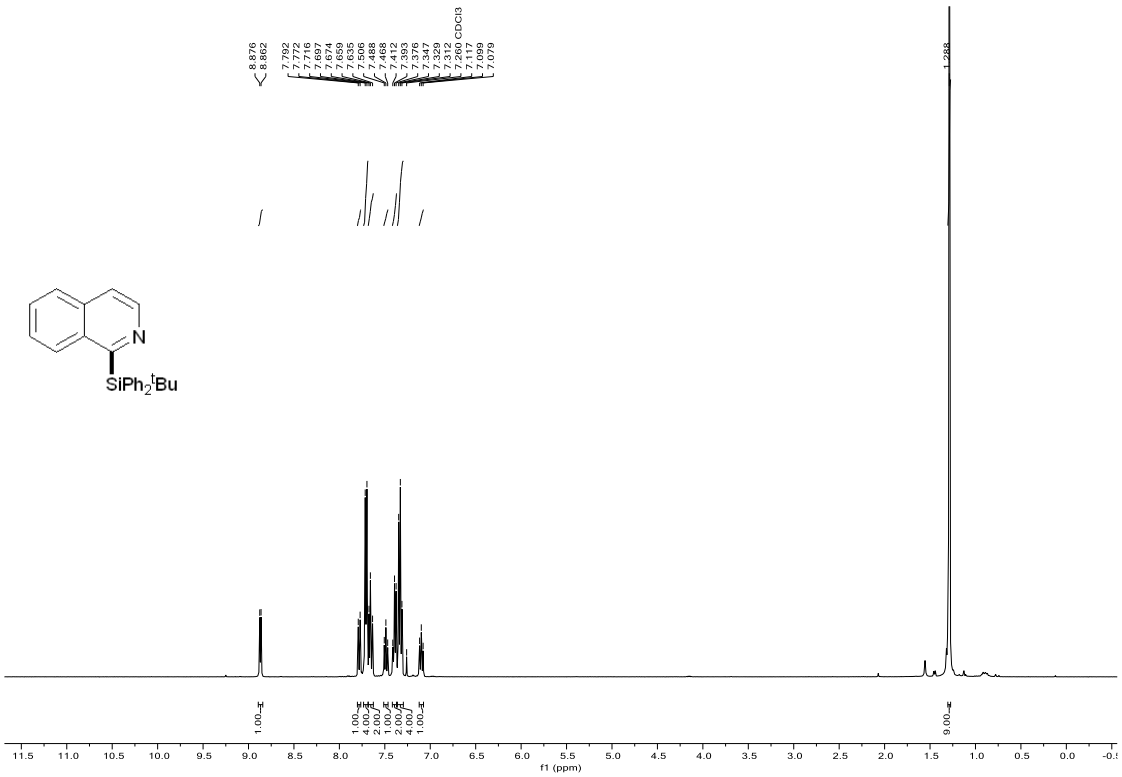

Figure S37. ^{1}H NMR spectra (400 MHz) of **3n** in $CDCl_3$.

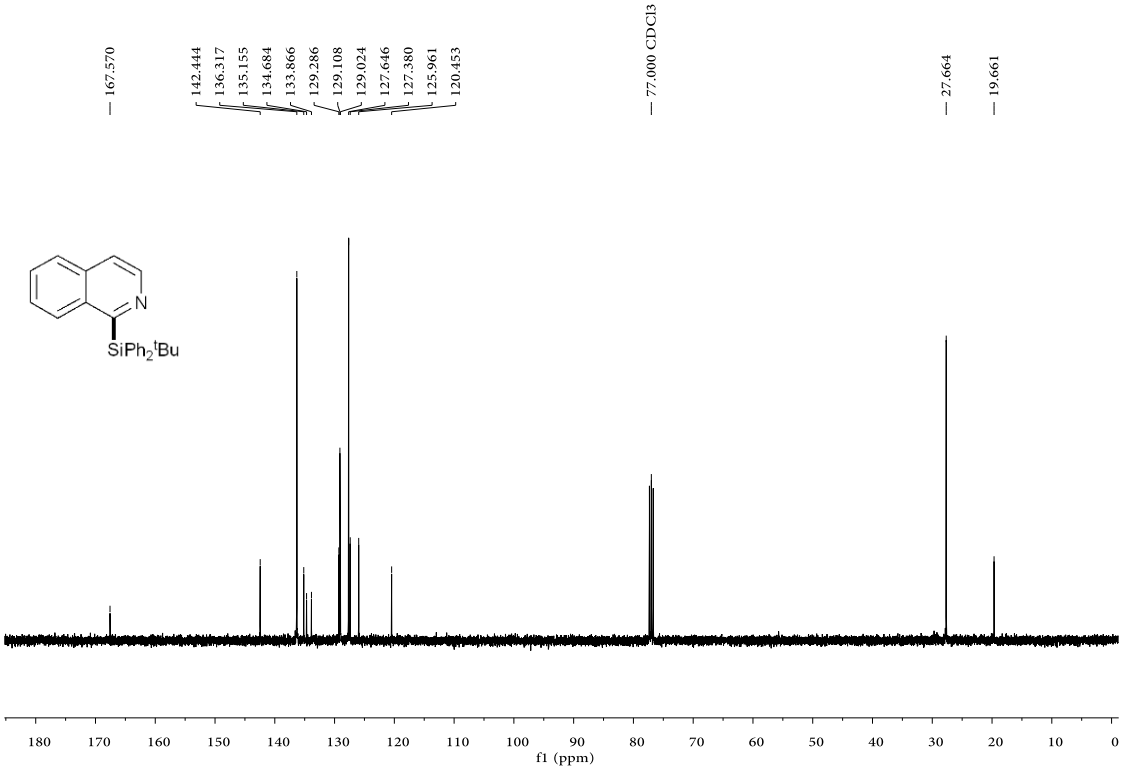

Figure S38. ^{13}C NMR spectra (101 MHz) of **3n** in $CDCl_3$.

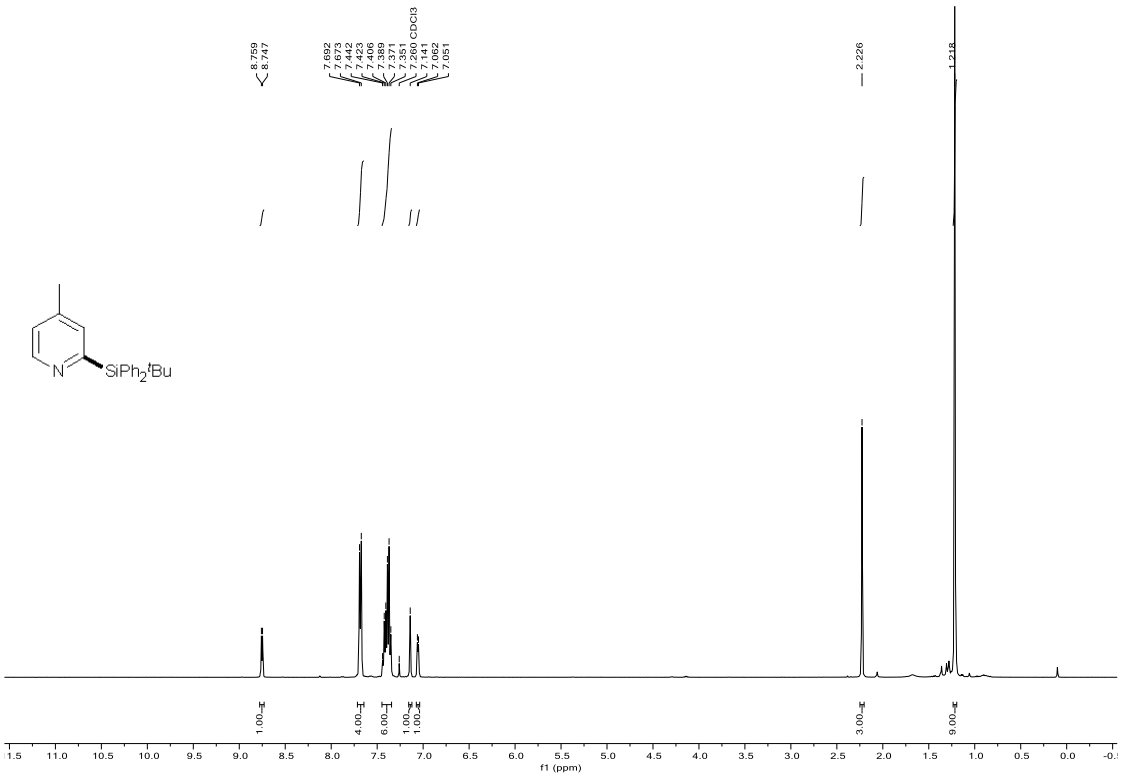

Figure S39. ^{1}H NMR spectra (400 MHz) of **3o** in $CDCl_3$.

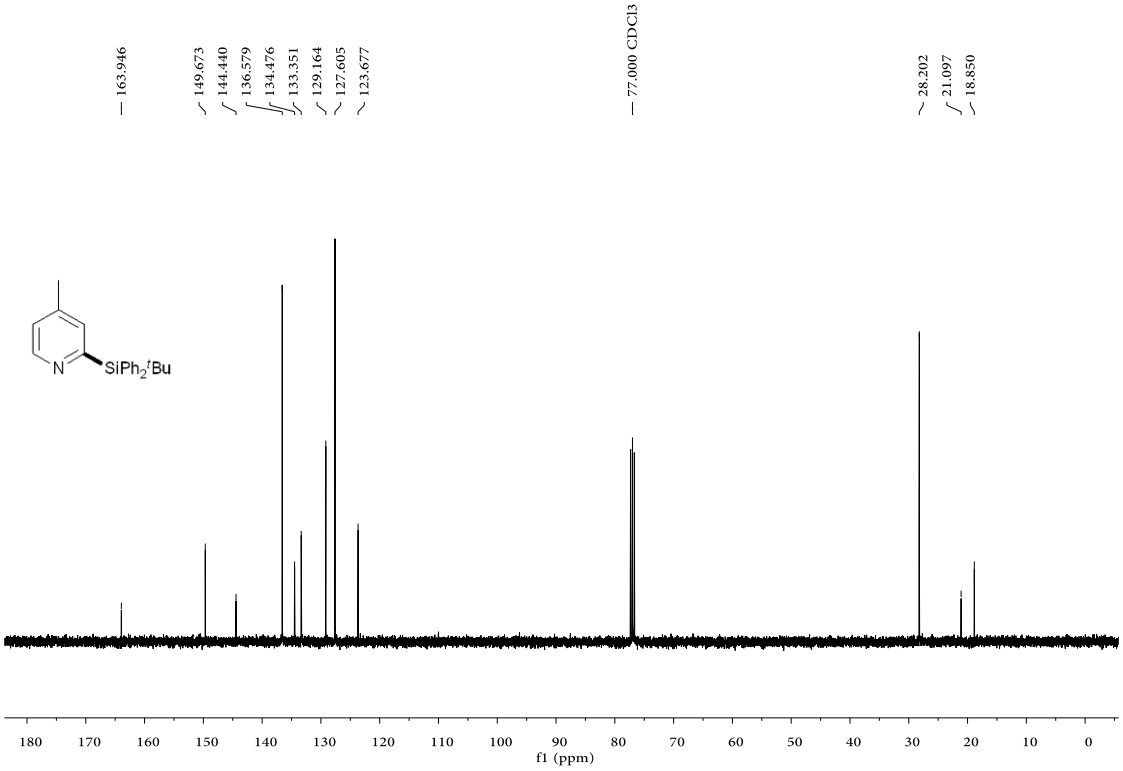

Figure S40. ^{13}C NMR spectra (101 MHz) of **3o** in $CDCl_3$.

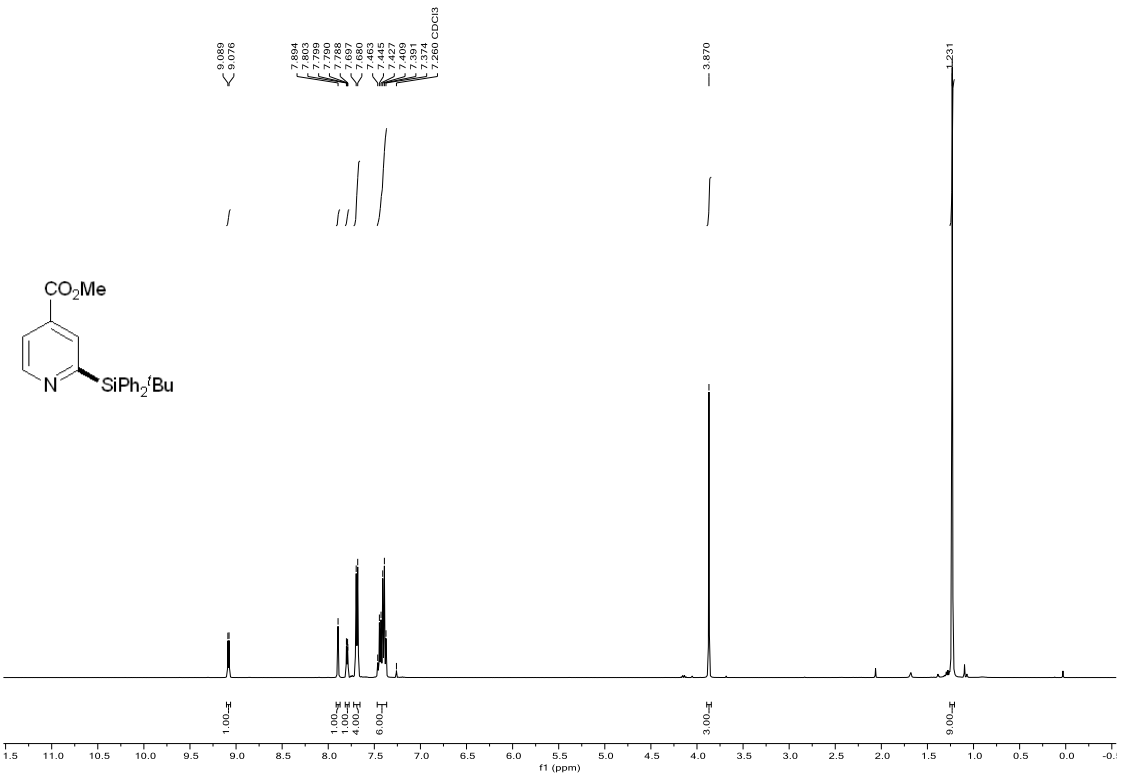

Figure S41. ^{1}H NMR spectra (400 MHz) of **3p** in $CDCl_3$.

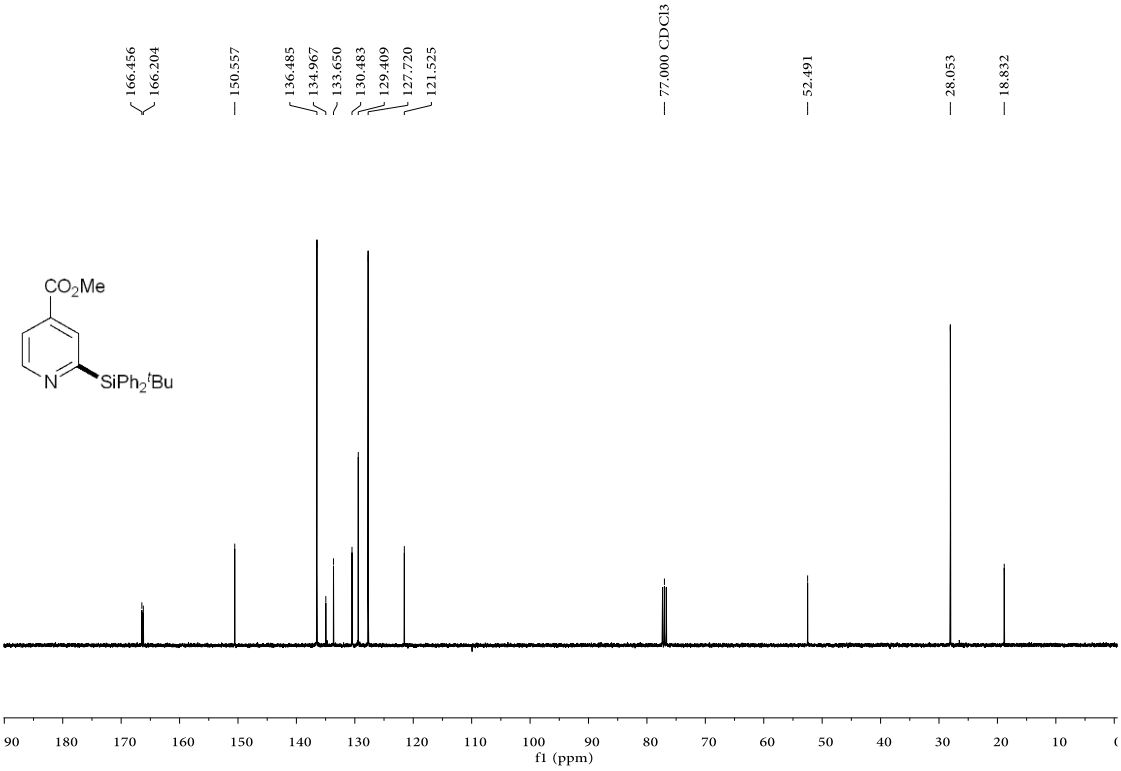

Figure S42. ^{13}C NMR spectra (101 MHz) of **3p** in $CDCl_3$.

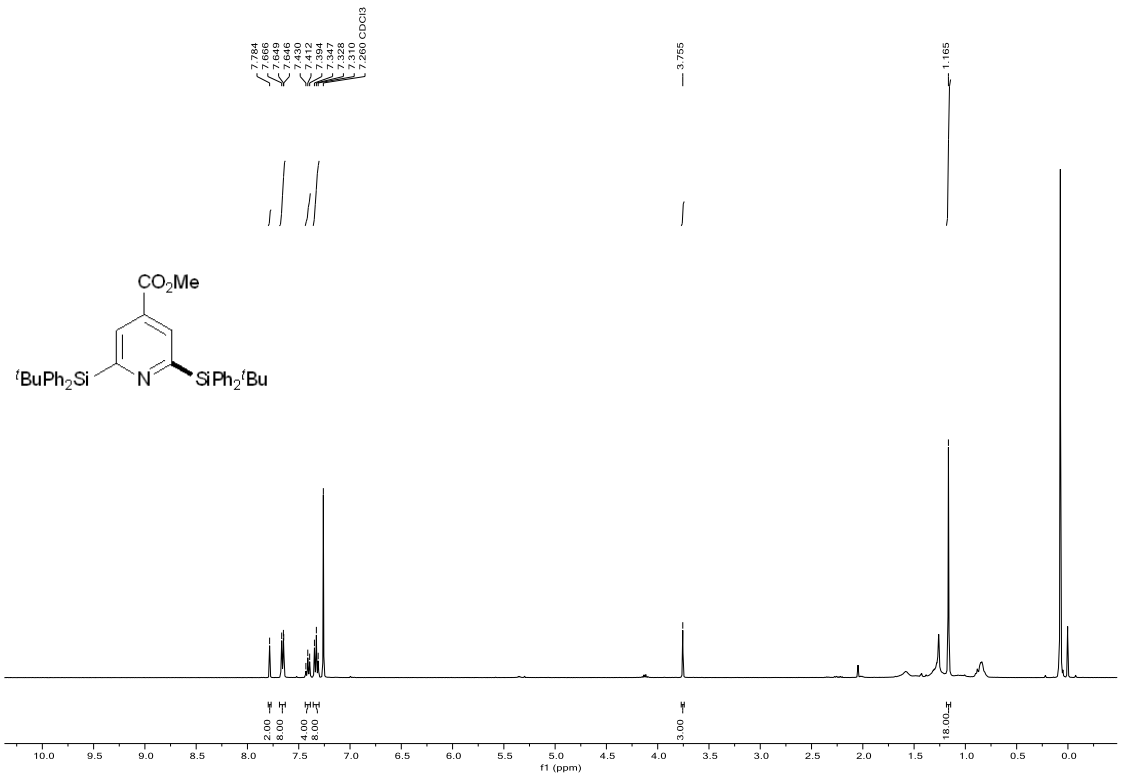

Figure S43. ^{1}H NMR spectra (400 MHz) of **3p'** in $CDCl_3$.

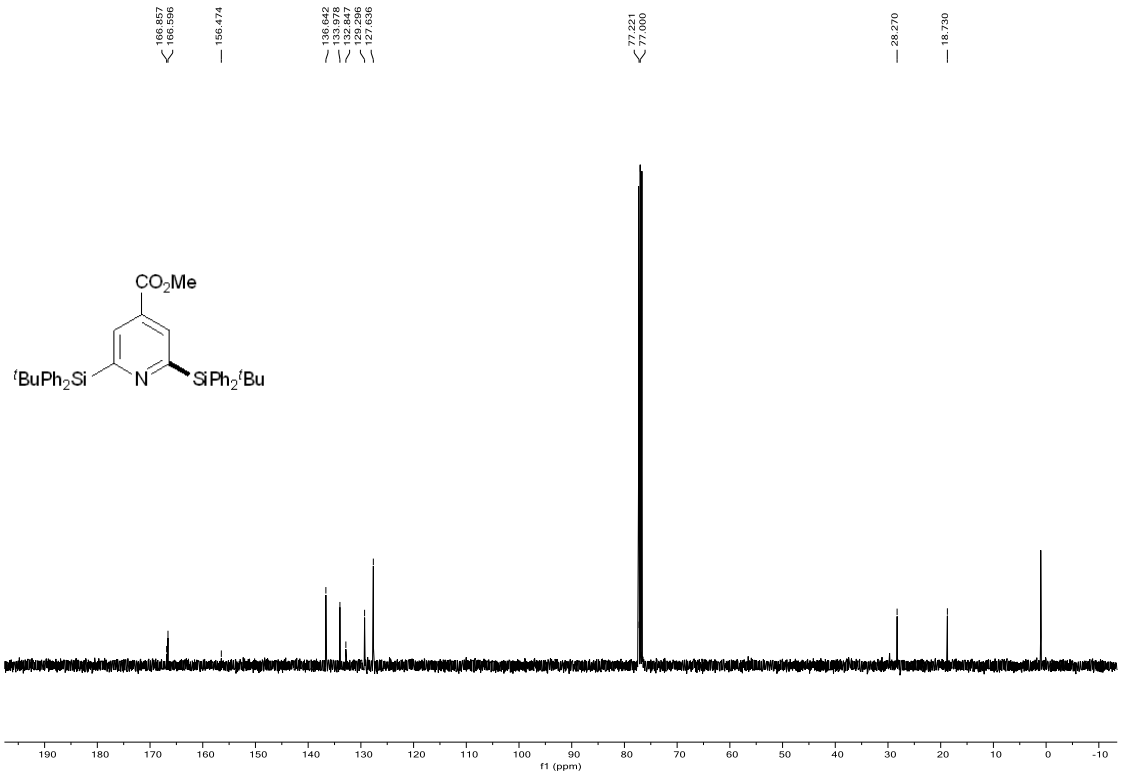

Figure S44. ^{13}C NMR spectra (101 MHz) of **3p'** in $CDCl_3$.

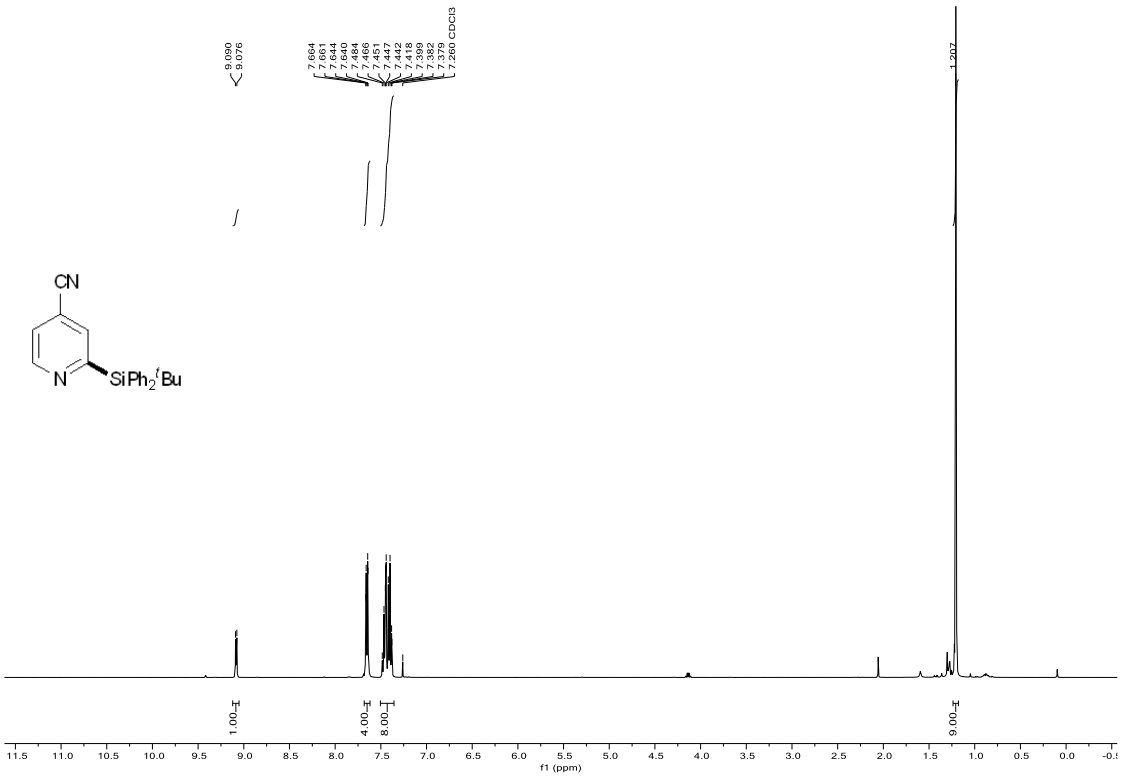

Figure S45. ^{1}H NMR spectra (400 MHz) of **3q** in $CDCl_3$.

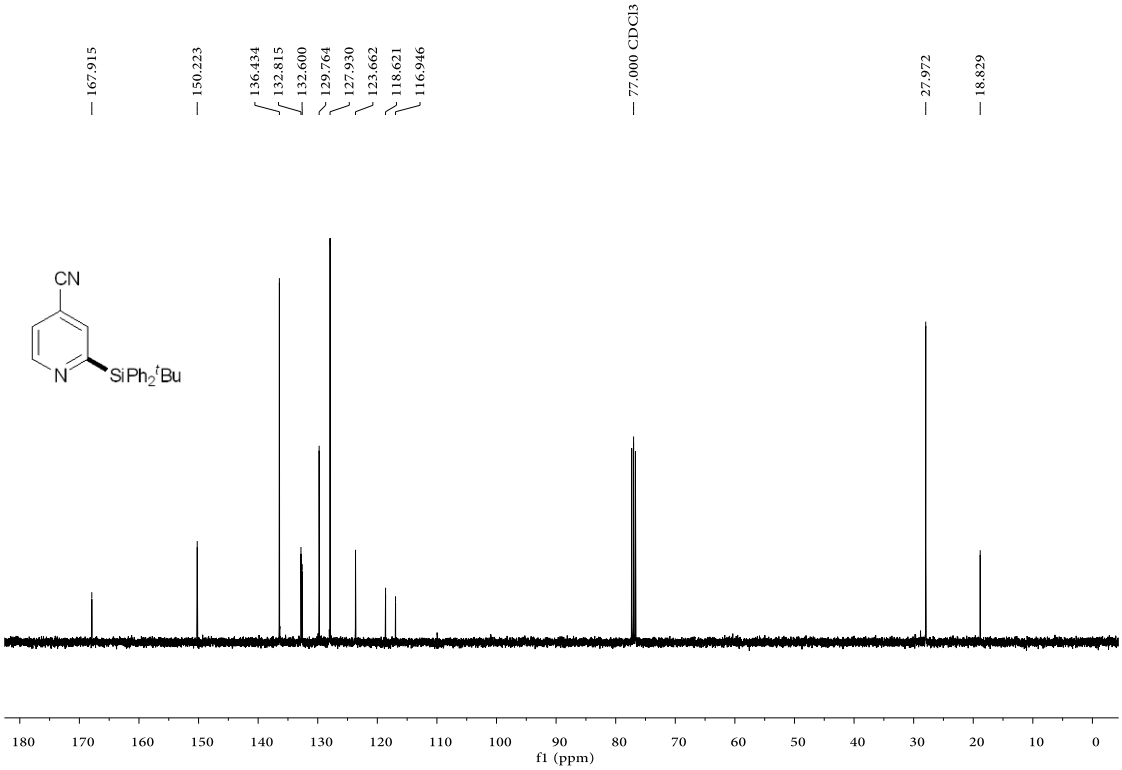

Figure S46. ^{13}C NMR spectra (101 MHz) of **3q** in $CDCl_3$.

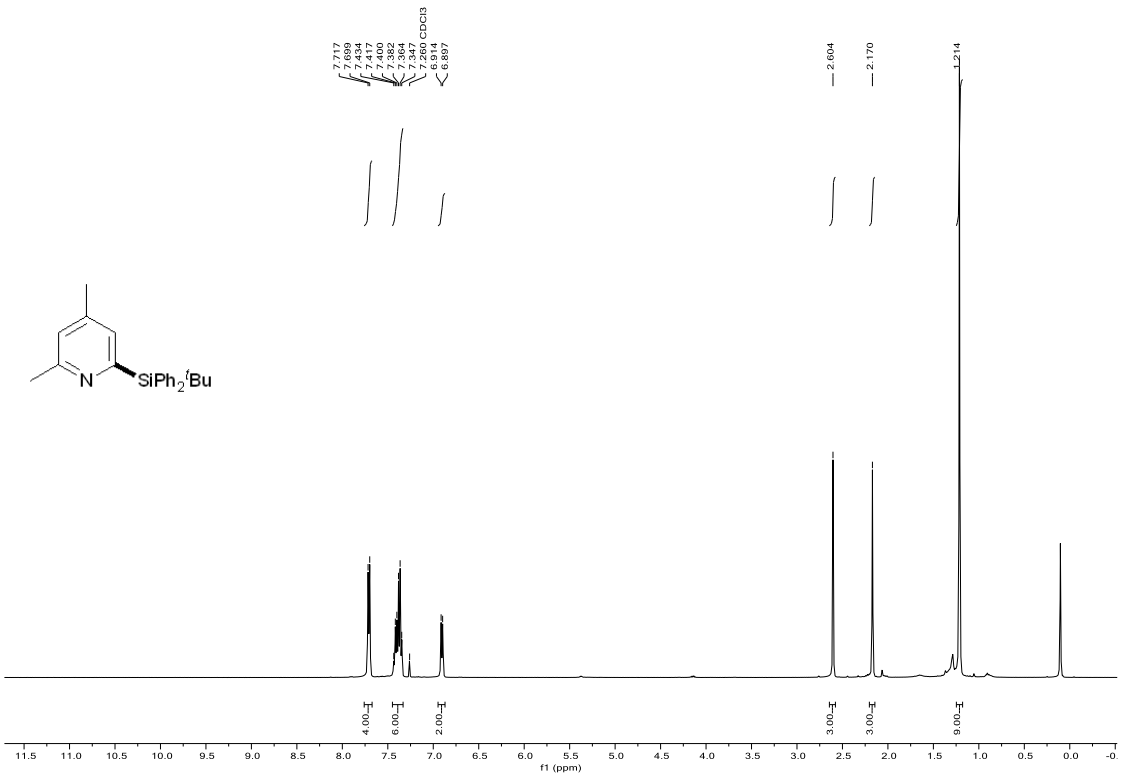

Figure S47. ^{1}H NMR spectra (400 MHz) of **3r** in $CDCl_3$.

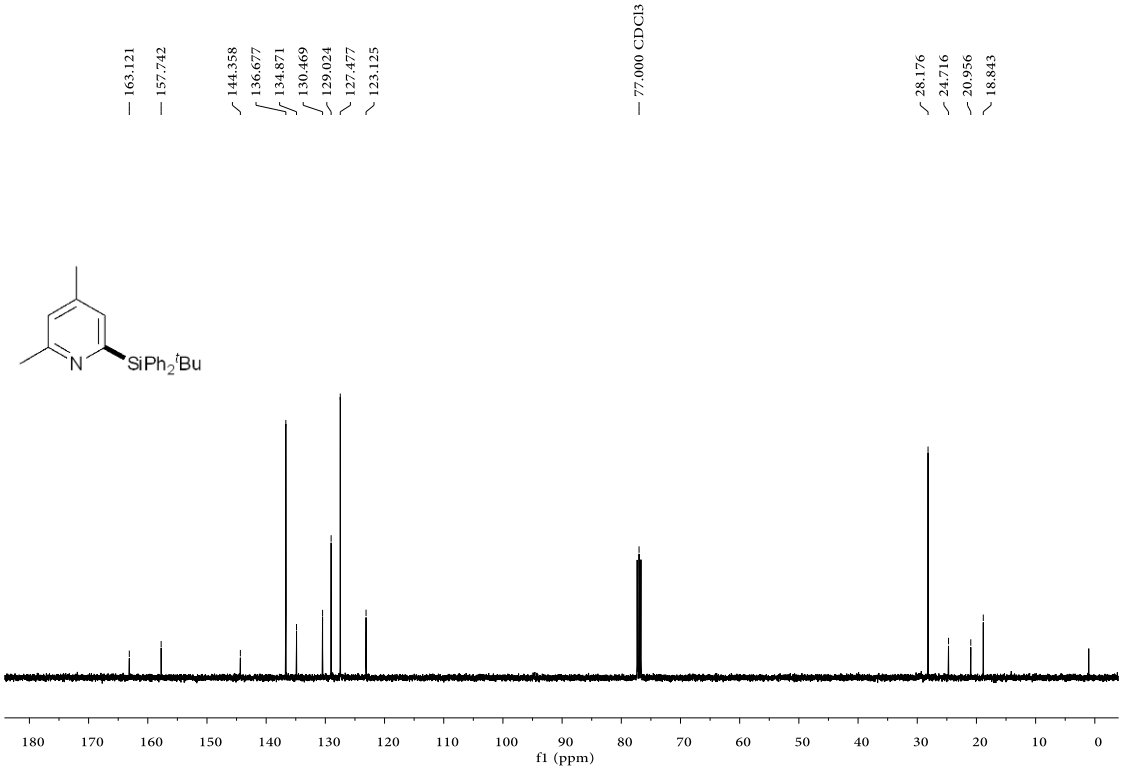

Figure S48. ^{13}C NMR spectra (101 MHz) of **3r** in $CDCl_3$.

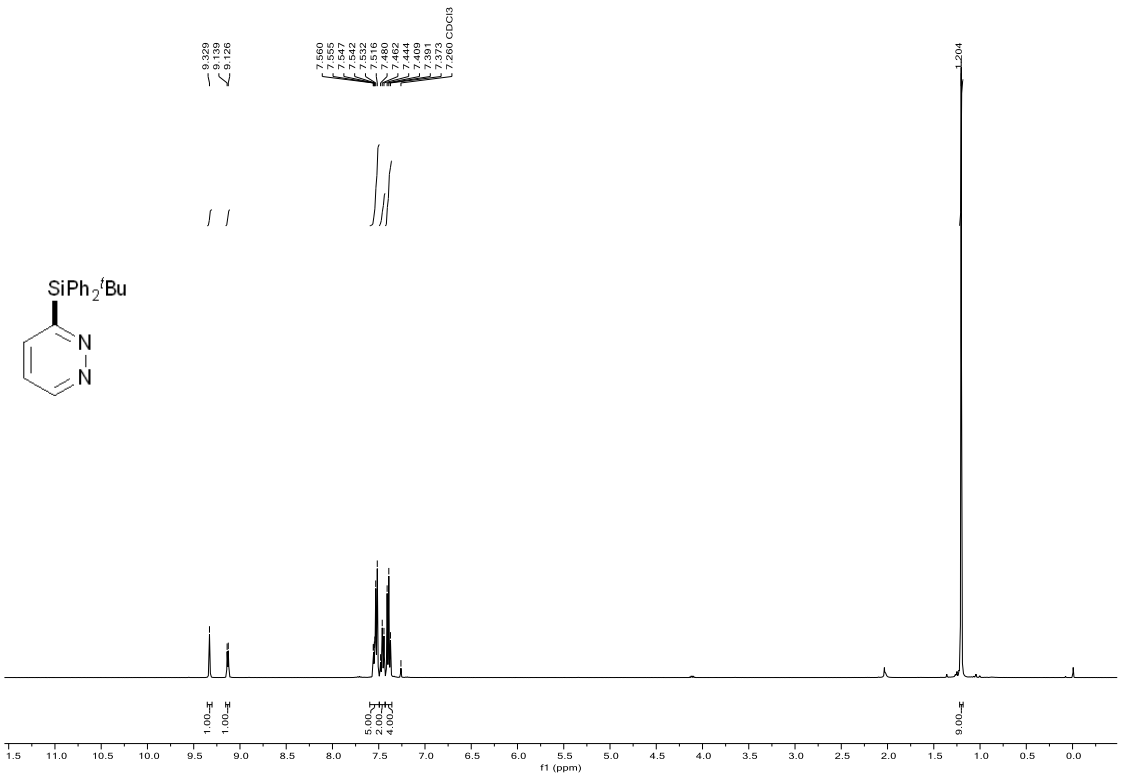

Figure S49. ^{1}H NMR spectra (400 MHz) of **3s** in $CDCl_3$.

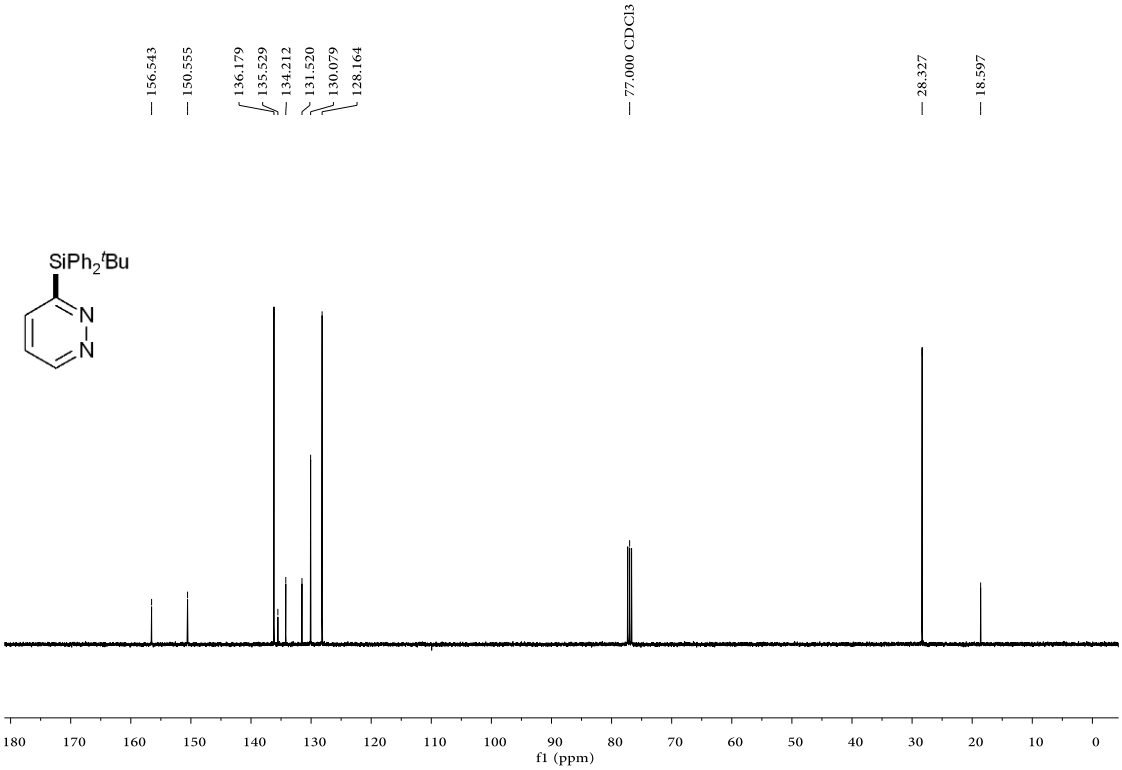

Figure S50. ^{13}C NMR spectra (101 MHz) of **3s** in $CDCl_3$

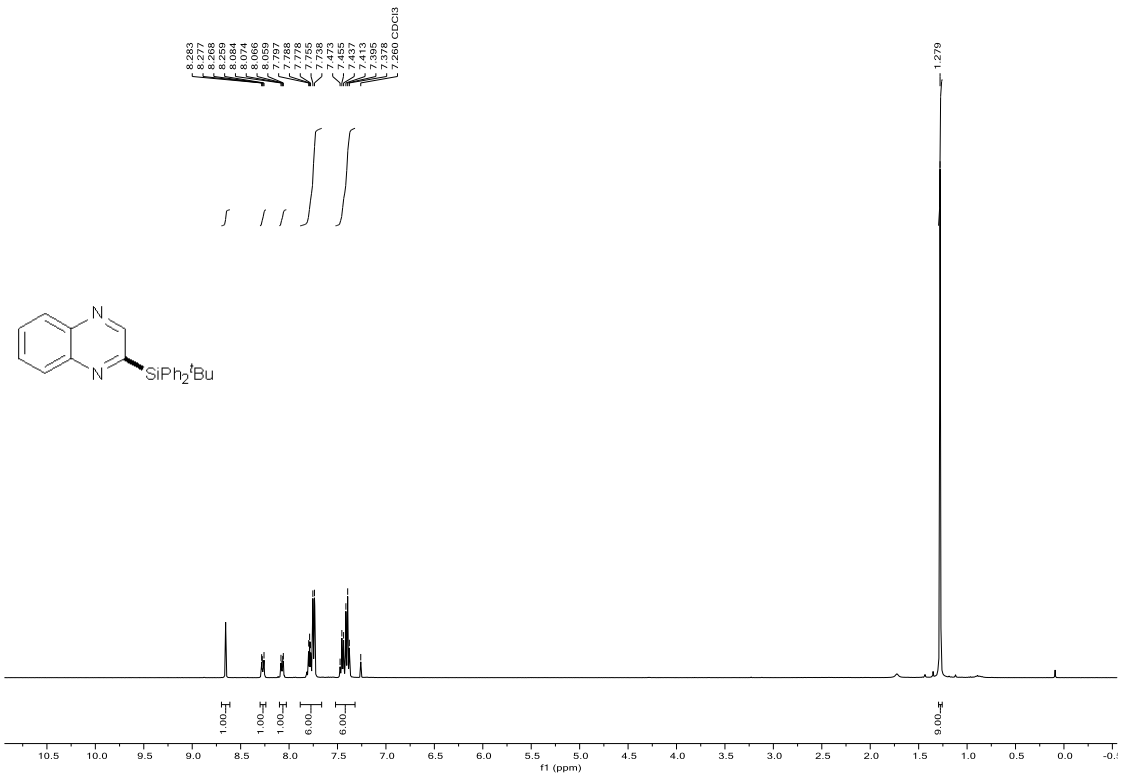

Figure S51. ^{1}H NMR spectra (400 MHz) of **3t** in $CDCl_3$.

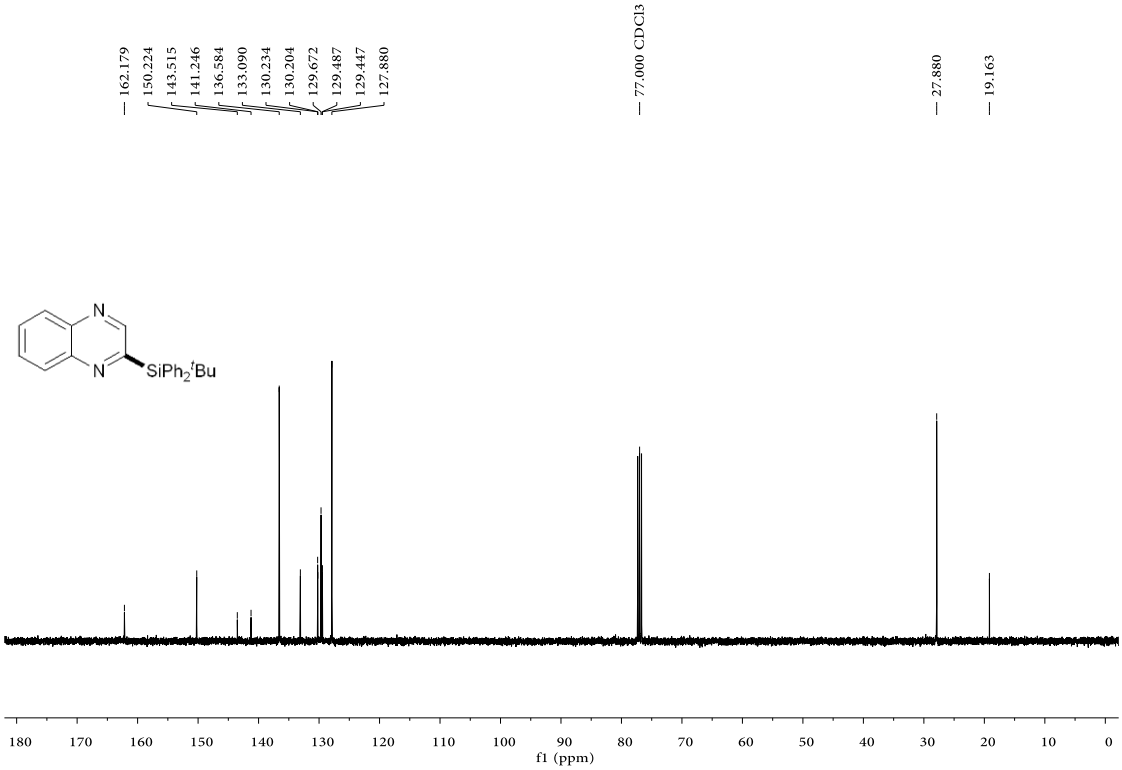

Figure S52. ^{13}C NMR spectra (101 MHz) of **3t** in $CDCl_3$.

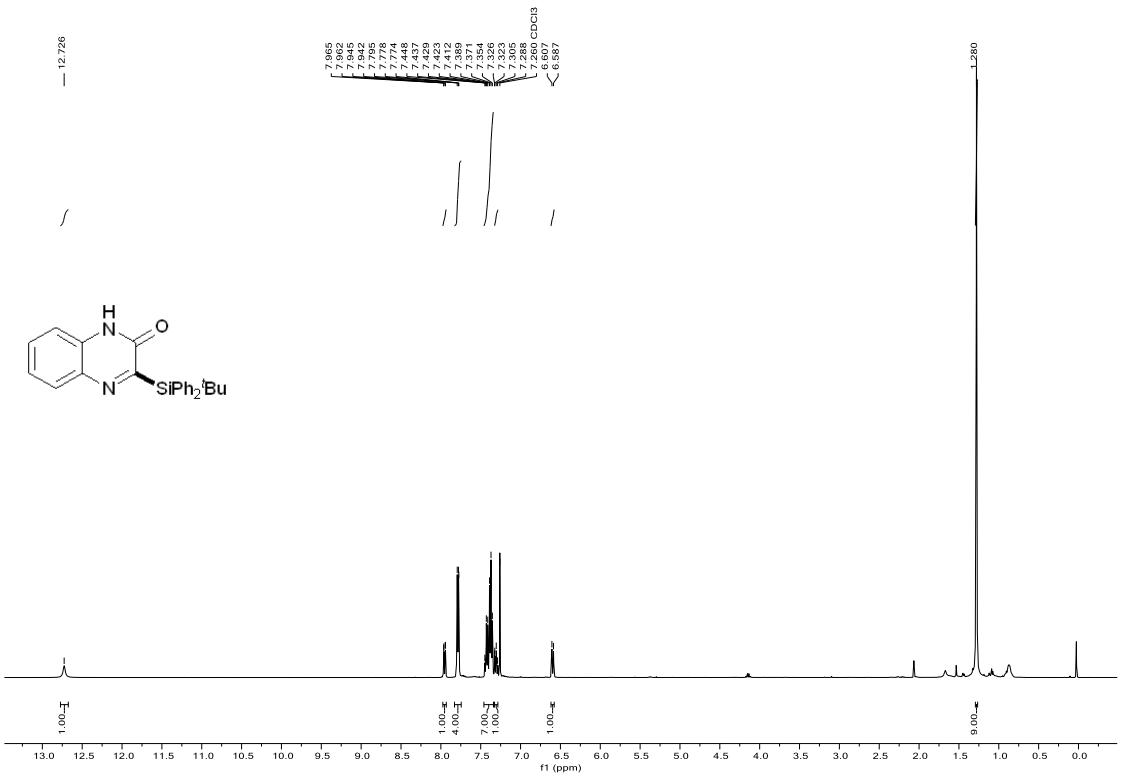

Figure S53. ^{1}H NMR spectra (400 MHz) of **3u** in $CDCl_3$.

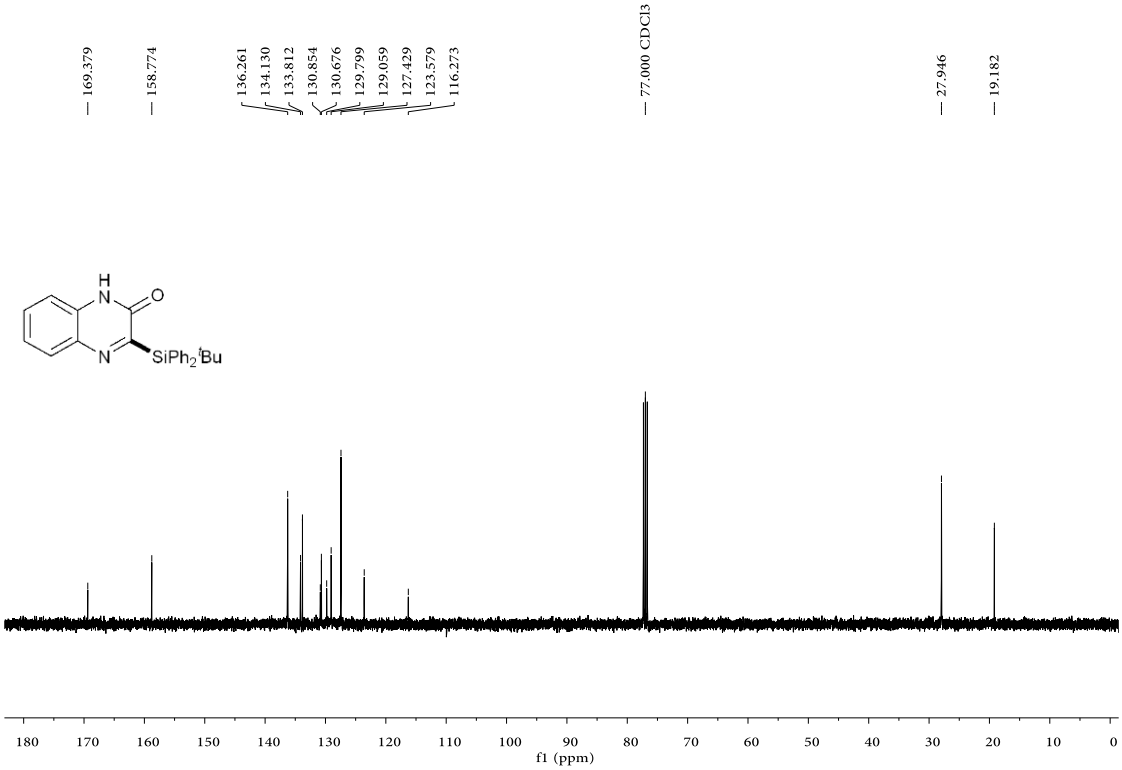

Figure S54. ^{13}C NMR spectra (101 MHz) of **3u** in $CDCl_3$.

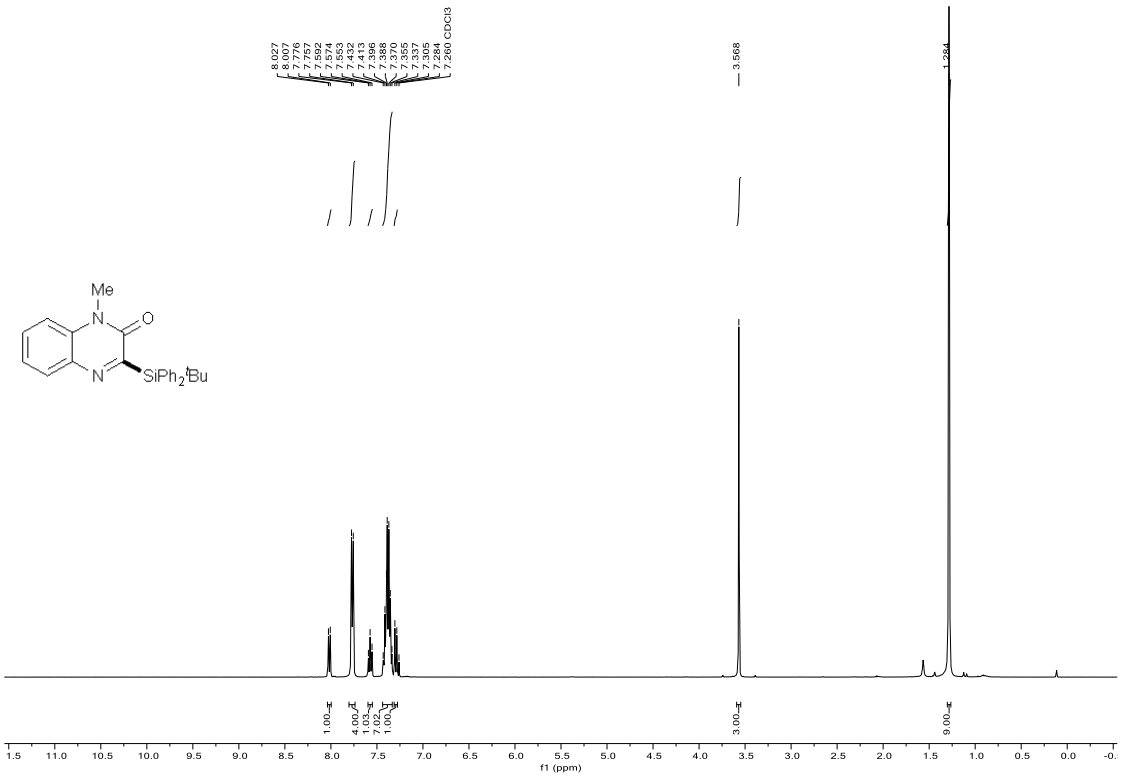

Figure S55. ^{1}H NMR spectra (400 MHz) of **3v** in $CDCl_3$.

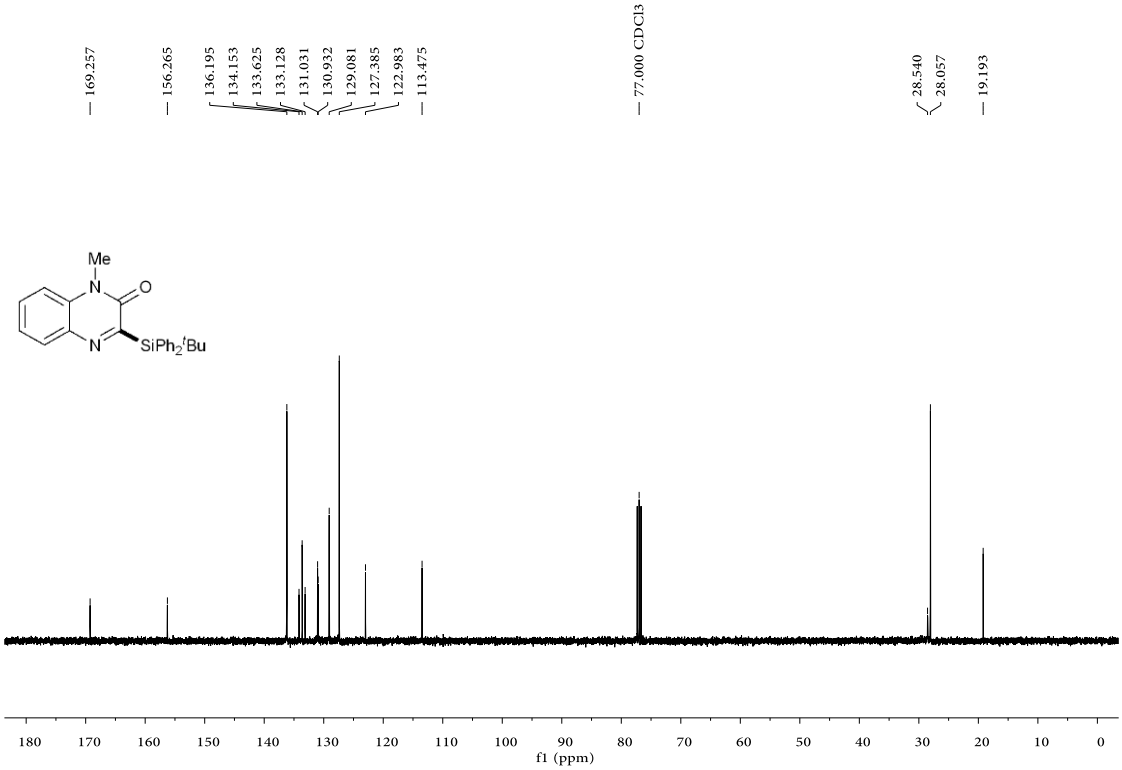

Figure S56. ^{13}C NMR spectra (101 MHz) of **3v** in $CDCl_3$.

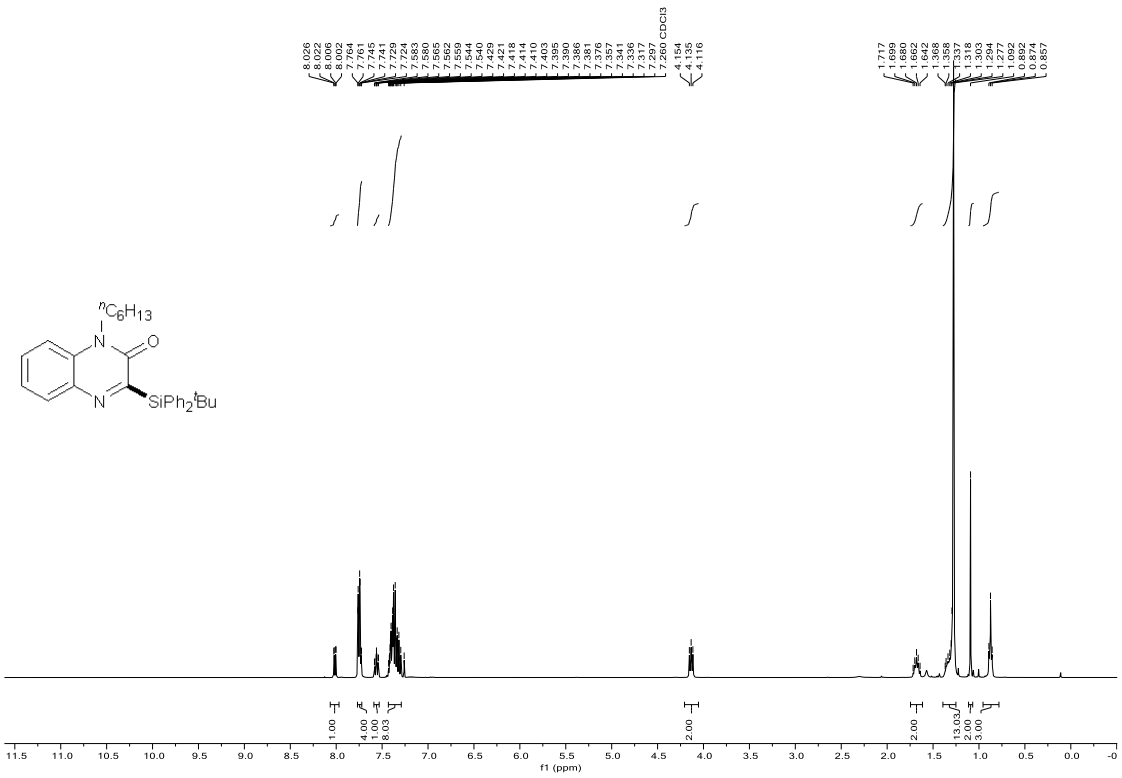

Figure S57. ^{1}H NMR spectra (400 MHz) of **3w** in $CDCl_3$.

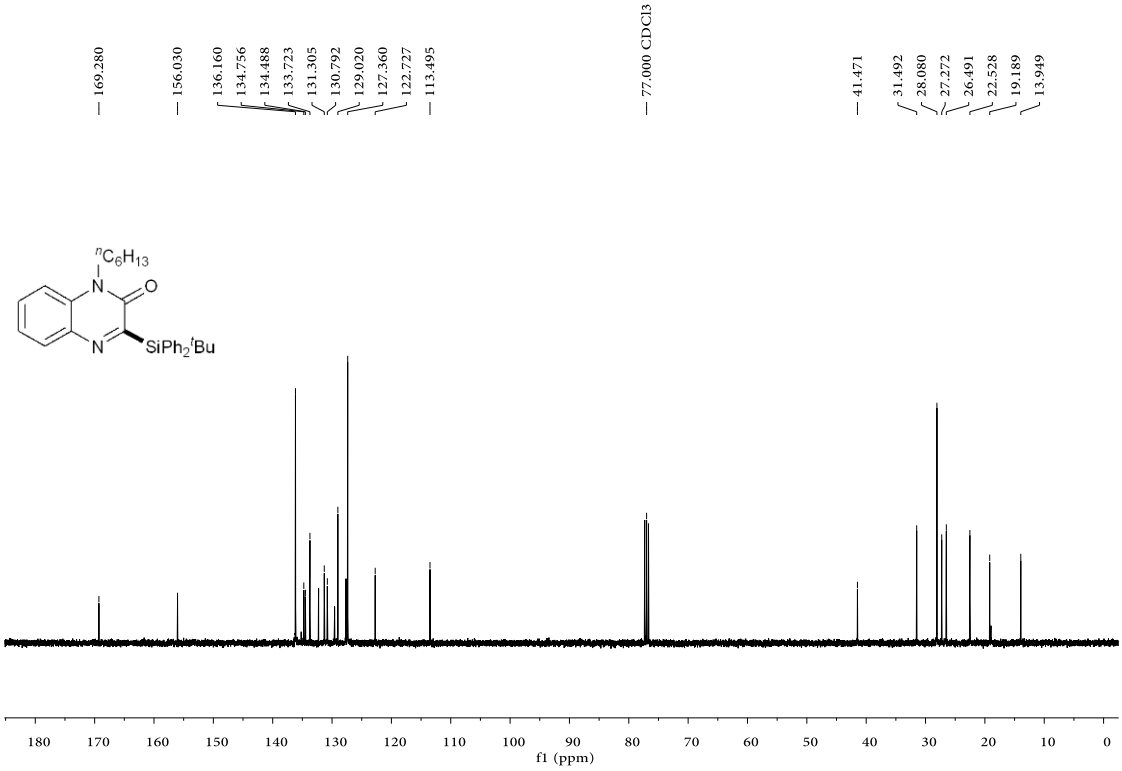

Figure S58. ^{13}C NMR spectra (101 MHz) of **3w** in $CDCl_3$.

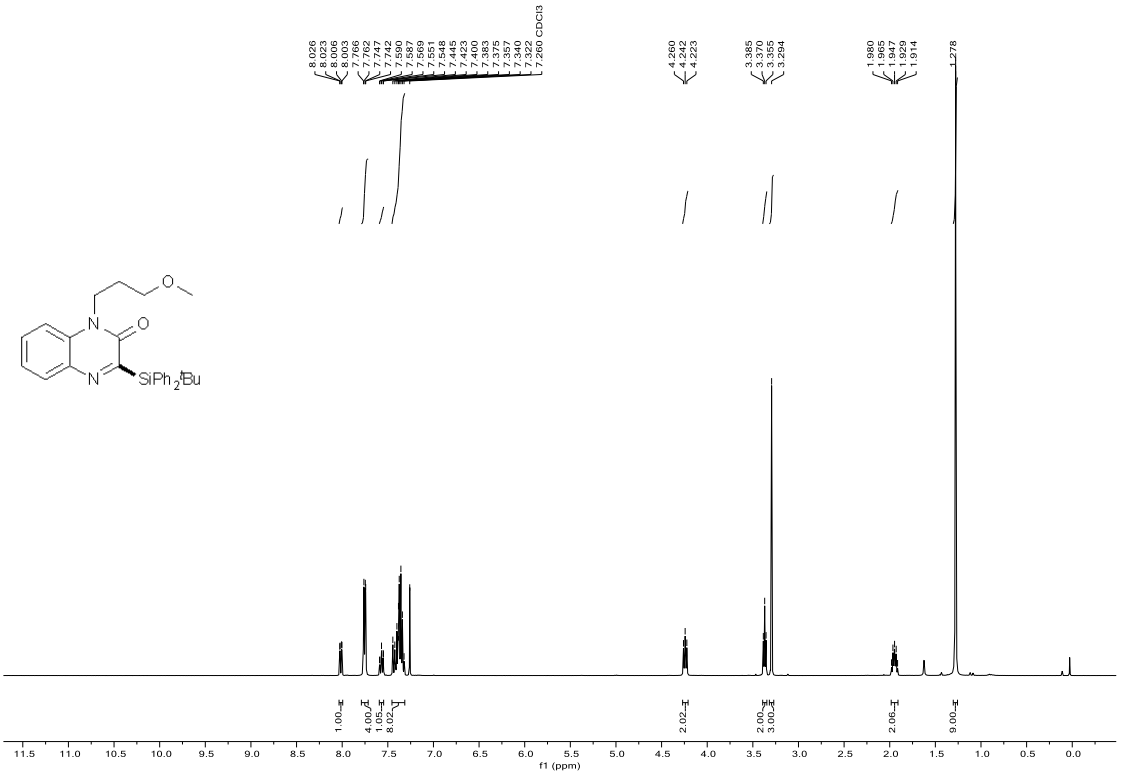

Figure S59. ^{1}H NMR spectra (400 MHz) of **3x** in $CDCl_3$.

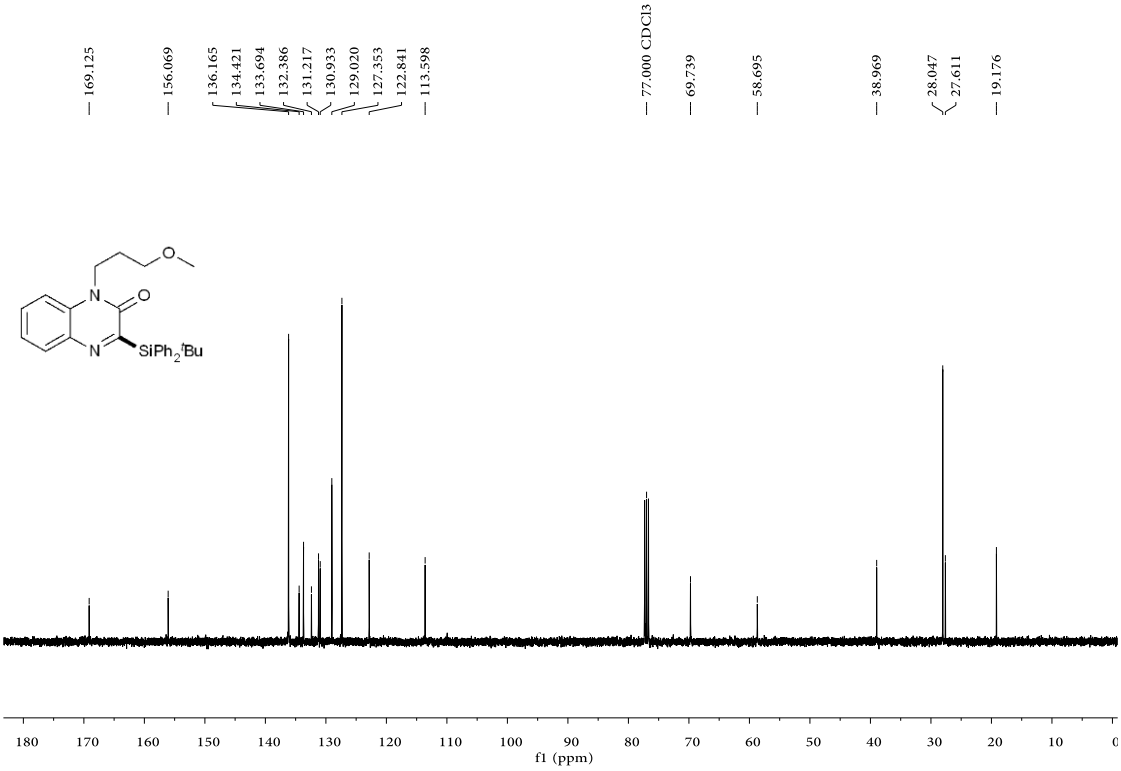

Figure S60. ^{13}C NMR spectra (101 MHz) of **3x** in $CDCl_3$.

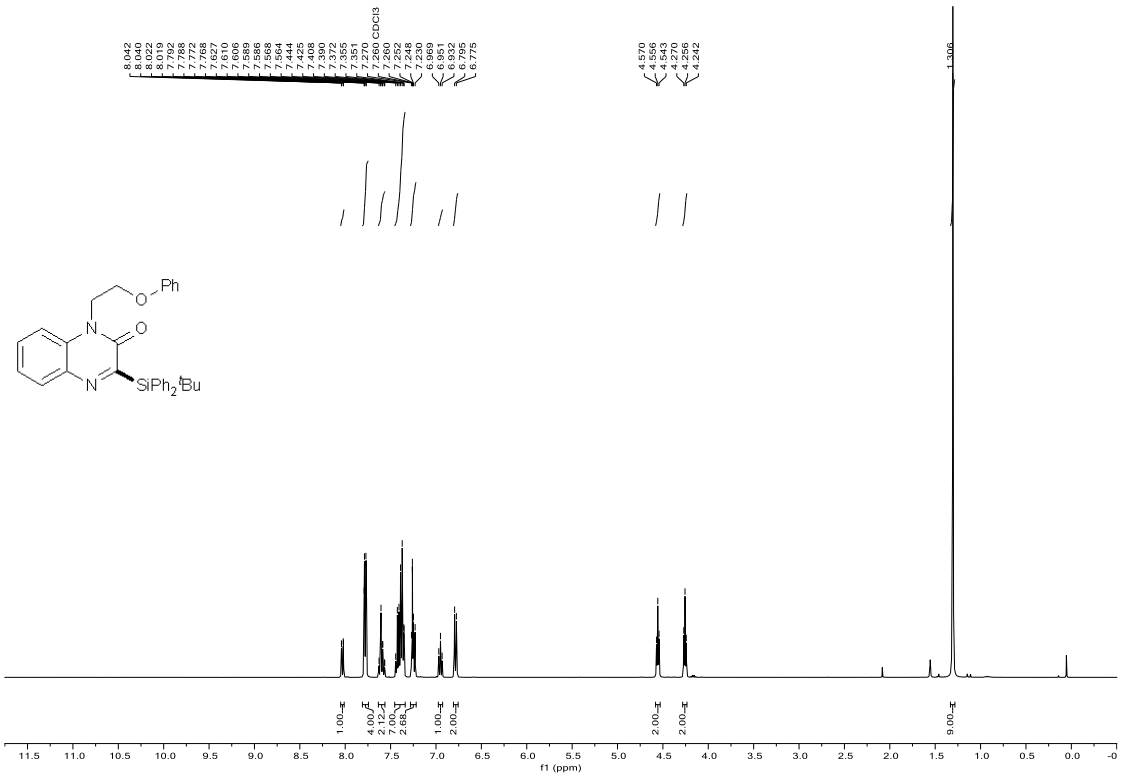

Figure S61. ^{1}H NMR spectra (400 MHz) of **3y** in $CDCl_3$.

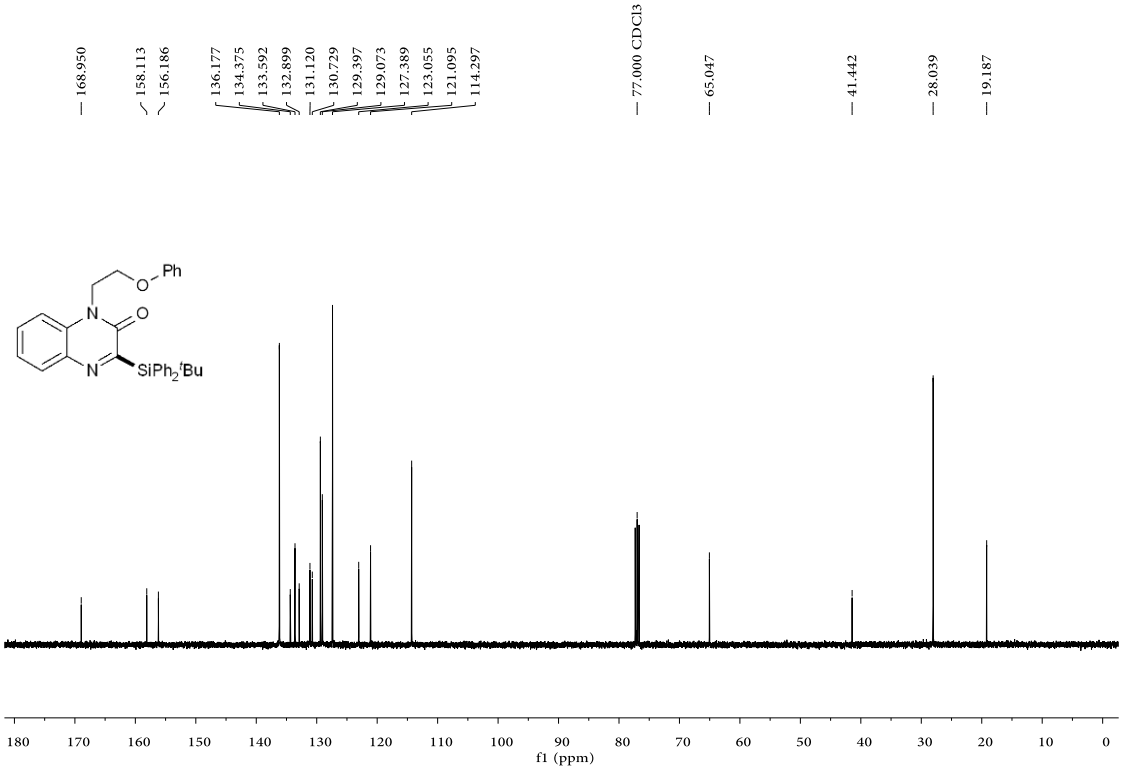

Figure 62. ^{13}C NMR spectra (101 MHz) of **3y** in $CDCl_3$.

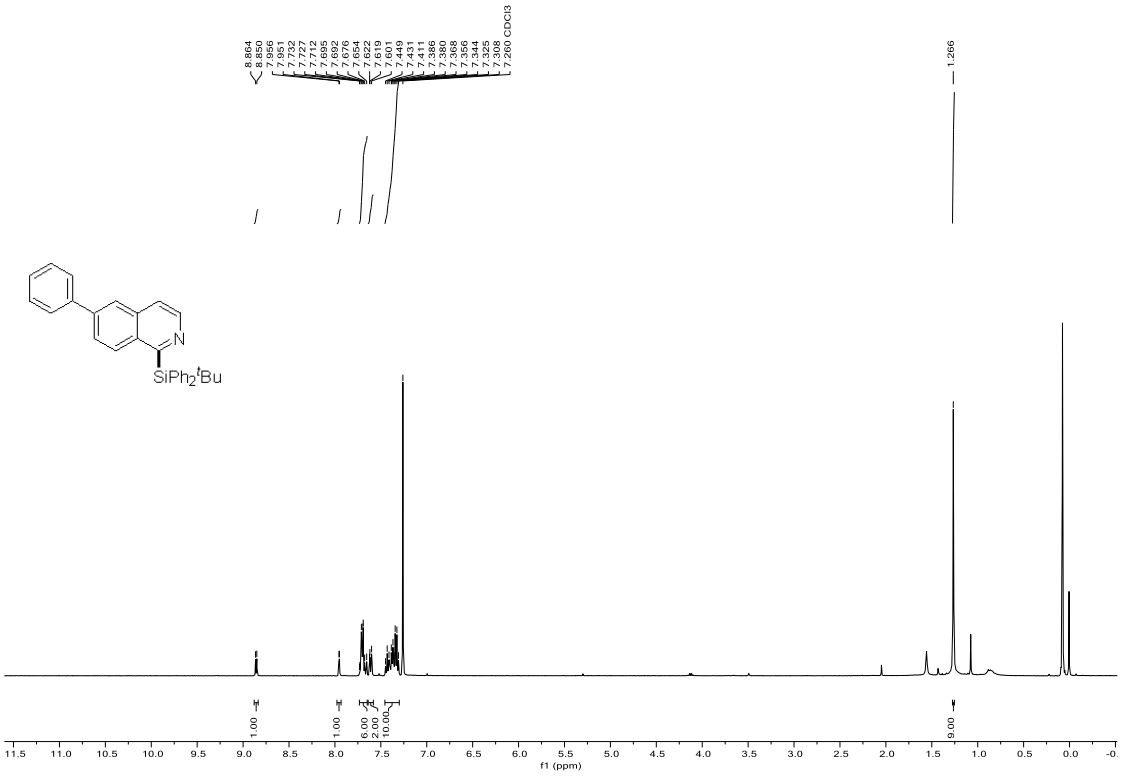

Figure S63. ^{1}H NMR spectra (400 MHz) of **3z** in $CDCl_3$.

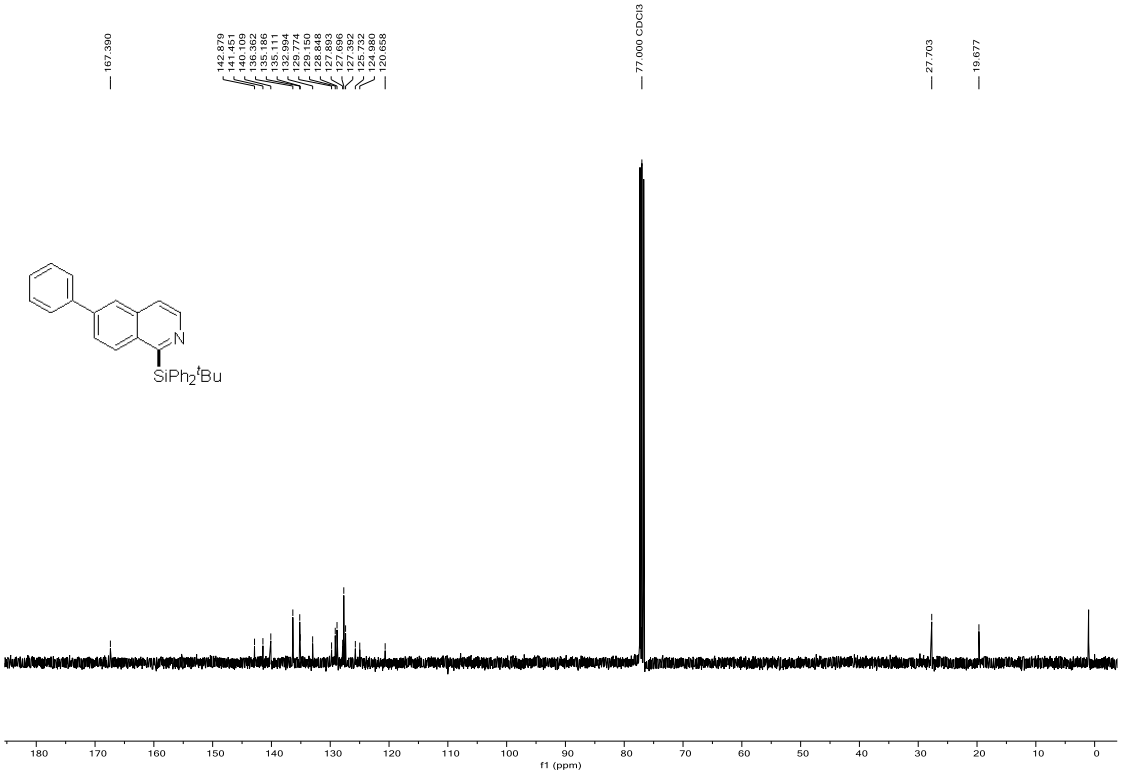

Figure S64. ^{13}C NMR spectra (101 MHz) of **3z** in $CDCl_3$.

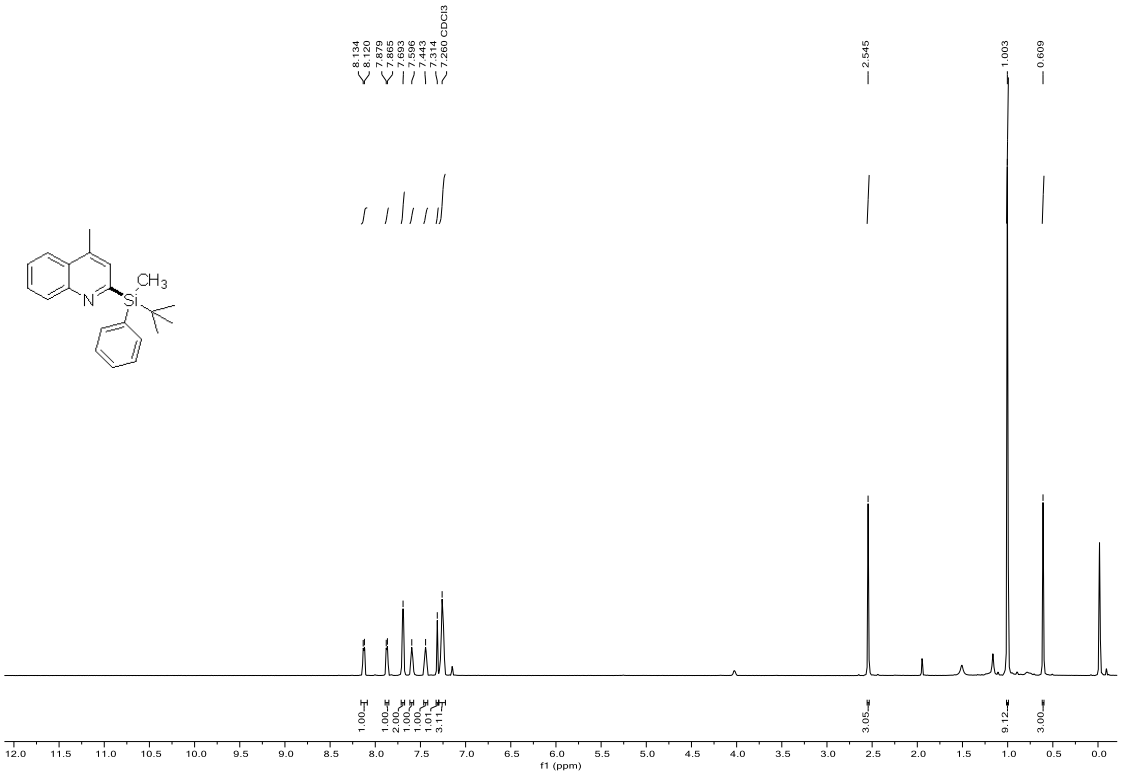

Figure S65. ^{1}H NMR spectra (400 MHz) of **3ba** in $CDCl_3$.

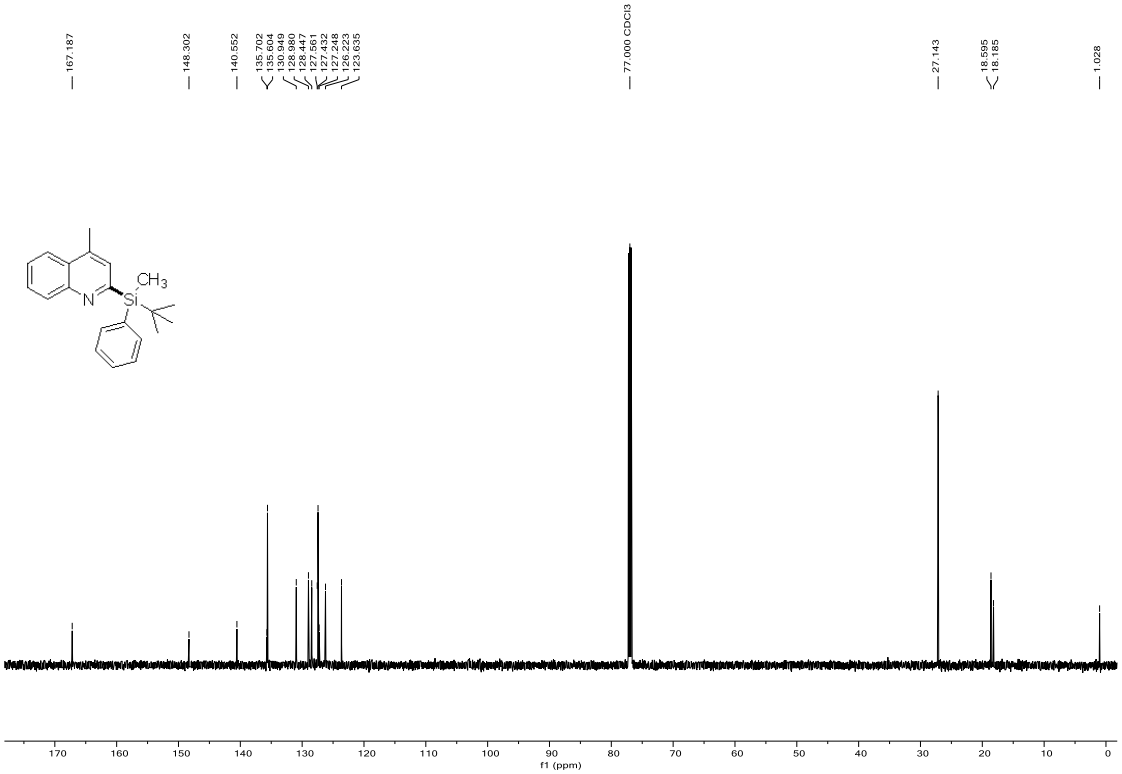

Figure S66. ^{13}C NMR spectra (101 MHz) of **3ba** in $CDCl_3$

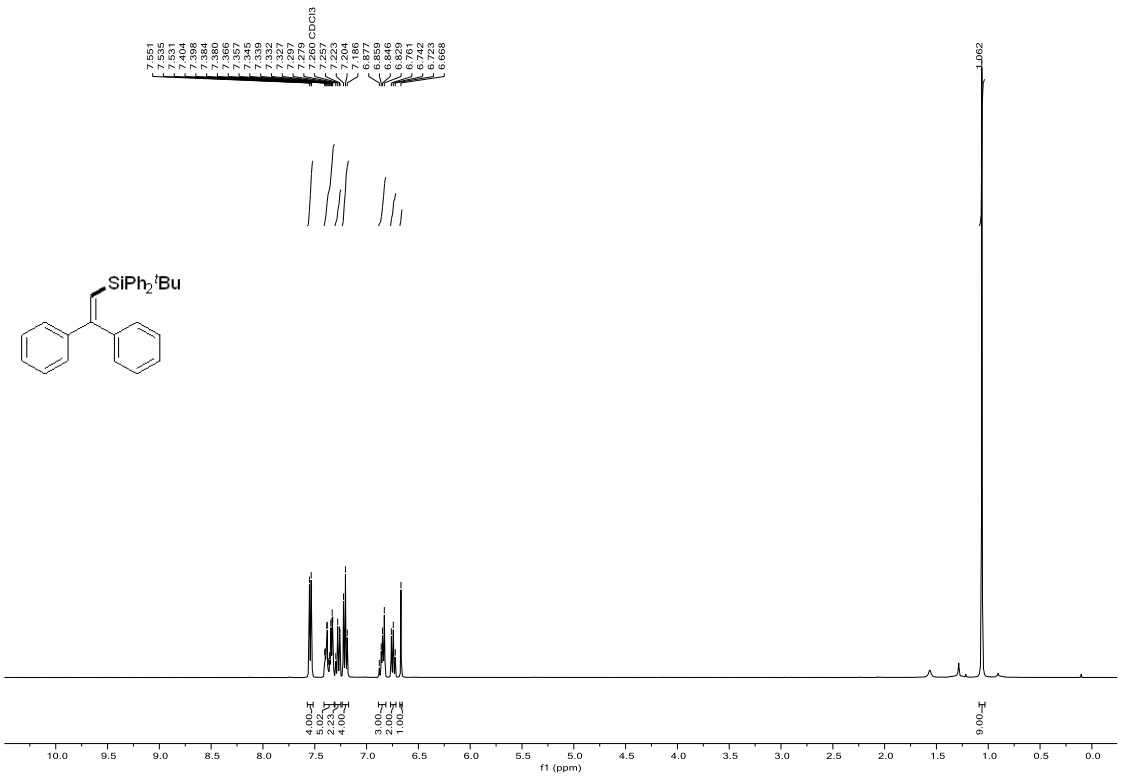

Figure S67. ^{1}H NMR spectra (400 MHz) of **4** in $CDCl_3$.

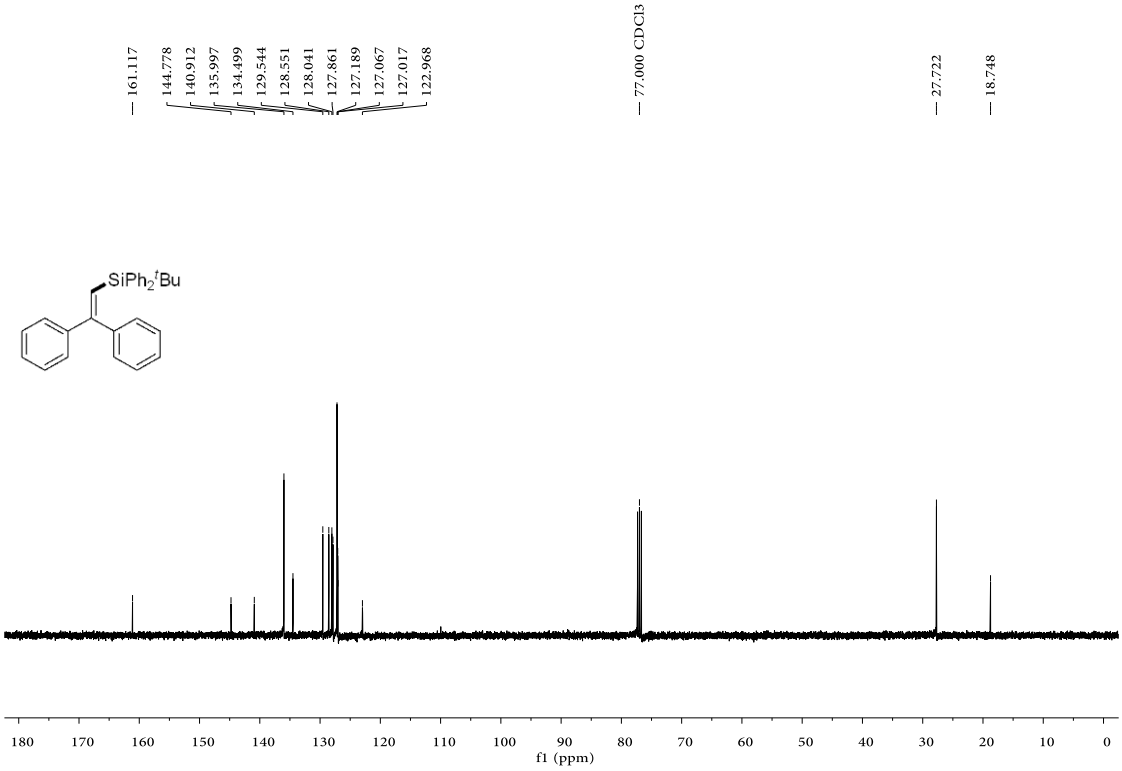

Figure S68. ^{13}C NMR spectra (101 MHz) of **4** in $CDCl_3$.