

## *Supporting Information*

### **PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>-catalyzed regioselective C-H olefinations of 2-amino biaryls with vinylsilanes as unactivated alkenes**

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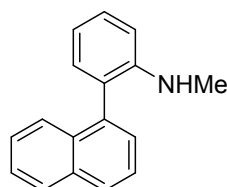
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# General Information

Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. For example, Dichloromethane, toluene, were freshly distilled from  $\text{CaH}_2$ , tetrahydrofuran (THF) and 1,4-dioxane were dried and distilled from metal sodium and benzophenone. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (300 - 400 mesh).  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in  $\text{CDCl}_3$ . Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); or m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer.

# General procedure for the synthesis of substrates 1.

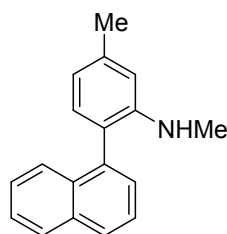
The reaction flask with 2-bromo-*N*-methylaniline (10 mmol), aryboronic acid (1.2 equiv), K<sub>2</sub>CO<sub>3</sub> (3 equiv), and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (10 mol%) was evacuated and backfilled with N<sub>2</sub>. DMF/H<sub>2</sub>O (40 mL/10 mL) was added under N<sub>2</sub> flow. The tube was closed and the mixture was stirred for 24 h at 90 °C. Then, the reaction was cooled to room temperature, diluted with H<sub>2</sub>O and extracted with EtOAc three times. The combined organic layer was washed with brine twice, dried by Na<sub>2</sub>SO<sub>4</sub>, evaporated, and purified by flash chromatography (PE/EA).



**1a**

*N*-methyl-2-(naphthalen-1-yl)aniline **1a** (81% yield)

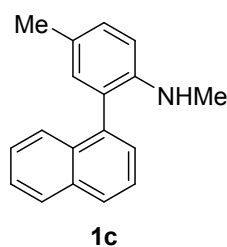
White solid. m.p. 95-99 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.81 (t, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.35 (dd, *J* = 4.9, 4.3 Hz, 1H), 7.30 (ddd, *J* = 11.2, 6.2, 1.4 Hz, 2H), 7.05 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 3.52 (s, 1H), 2.62 (d, *J* = 10.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.9, 136.9, 133.9, 131.9, 130.8, 129.0, 128.3, 128.1, 127.9, 126.3, 126.1 (d, *J* = 1.6 Hz), 125.9, 125.8, 116.8, 109.9, 30.8. HRMS (ESI) *m/z*: [M+H]<sup>+</sup>calculated for C<sub>17</sub>H<sub>16</sub>N: 234.1277, found: 234.1281.



**1b**

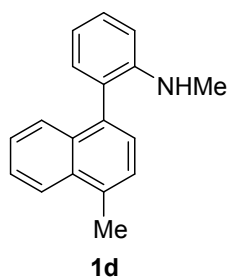
*N*,5-dimethyl-2-(naphthalen-1-yl)aniline **1b** (86% yield)

Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (dd,  $J = 11.6, 8.3$  Hz, 2H), 7.54 (d,  $J = 8.4$  Hz, 1H), 7.48 – 7.42 (m, 1H), 7.42 – 7.36 (m, 1H), 7.31 (td,  $J = 7.9, 0.8$  Hz, 2H), 6.93 (d,  $J = 7.5$  Hz, 1H), 6.58 (d,  $J = 7.5$  Hz, 1H), 6.51 (s, 1H), 3.40 (s, 1H), 2.62 (s, 3H), 2.35 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.9, 138.9, 136.9, 133.9, 132.2, 130.7, 128.3, 128.1, 127.9, 126.2 (d,  $J = 1.8$  Hz), 125.9 (d,  $J = 7.7$  Hz), 123.0, 117.5, 110.7, 30.8, 21.9. **HRMS (ESI)**  $m/z$ :  $[\text{M}+\text{H}]^+$ calculated for  $\text{C}_{18}\text{H}_{18}\text{N}$ : 248.1434, found: 248.1429.



N,4-dimethyl-2-(naphthalen-1-yl)aniline **1c** (88% yield)

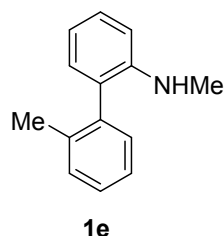
Yellow solid. m.p. 88-89 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 – 7.77 (m, 2H), 7.53 (d,  $J = 8.4$  Hz, 1H), 7.50 – 7.45 (m, 1H), 7.42 (t,  $J = 7.4$  Hz, 1H), 7.34 (dd,  $J = 12.5, 6.5$  Hz, 2H), 7.11 (dd,  $J = 8.2, 1.6$  Hz, 1H), 6.89 (d,  $J = 1.5$  Hz, 1H), 6.67 (d,  $J = 8.2$  Hz, 1H), 2.62 (s, 3H), 2.24 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 137.0, 133.8, 131.9, 131.5, 129.4, 128.3, 127.9, 127.8, 126.3 – 125.9 (m), 110.3, 31.2, 20.4. **HRMS (ESI)**  $m/z$ :  $[\text{M}+\text{H}]^+$ calculated for  $\text{C}_{18}\text{H}_{18}\text{N}$ :248.1434, found: 248.1429.



N-methyl-2-(4-methylnaphthalen-1-yl)aniline **1d** (74% yield)

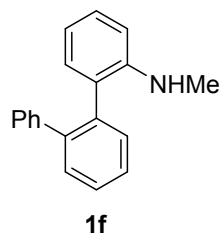
White solid. m.p. 102-108 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.3$  Hz, 1H), 7.53 (d,  $J = 8.3$  Hz, 1H), 7.45 (t,  $J = 7.4$  Hz, 1H), 7.29 (dt,  $J = 17.9, 7.7$  Hz, 4H), 7.04 (d,  $J = 7.1$  Hz, 1H), 6.75 (t,  $J = 7.2$  Hz, 1H), 6.69 (d,  $J = 8.0$  Hz, 1H), 3.55 (s, 1H), 2.67 (s, 3H), 2.62 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.9, 135.1, 134.4, 132.9, 131.9, 130.9, 128.9, 127.6, 126.7 (d,  $J =$

2.9 Hz), 125.9 (d,  $J = 13.8$  Hz), 124.4, 116.8, 109.9, 30.9, 19.6. **HRMS (ESI)**  $m/z$ :  $[M]^+$ calculated for  $C_{18}H_{17}N$ : 247.1361, found: 247.1363.



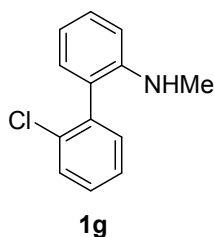
N,2'-dimethyl-[1,1'-biphenyl]-2-amine **1e** (72% yield)

White solid. m.p. 46-48 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.25 – 7.15 (m, 4H), 7.14 – 7.07 (m, 1H), 6.91 (dd,  $J = 7.3, 1.4$  Hz, 1H), 6.69 (dd,  $J = 7.3, 6.9$  Hz, 1H), 6.62 (d,  $J = 8.1$  Hz, 1H), 3.46 (s, 1H), 2.70 (s, 3H), 2.05 (s, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  146.2, 138.5, 137.3, 130.4 (d,  $J = 7.4$  Hz), 129.6, 128.6, 127.7, 127.3, 126.3, 116.7, 109.6, 30.8, 19.7. **HRMS (ESI)**  $m/z$ :  $[M+H]^+$ calculated for  $C_{14}H_{16}N$ : 198.1277, found: 198.1273.



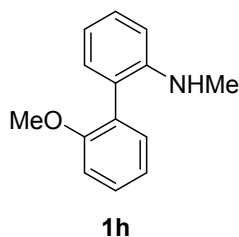
N-methyl-[1,1':2',1''-terphenyl]-2-amine **1f** (69% yield)

Purple solid. m.p. 125-128 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.43 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 7.29 (dt,  $J = 7.4, 2.8$  Hz, 1H), 7.14 – 7.05 (m, 6H), 6.86 (dd,  $J = 7.4, 1.4$  Hz, 1H), 6.57 (t,  $J = 7.3$  Hz, 1H), 6.44 (d,  $J = 8.1$  Hz, 1H), 3.54 (s, 1H), 2.46 (s, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  146.2, 141.4, 140.9, 137.6, 131.4, 130.8, 130.4, 128.9, 128.5, 127.9 (d,  $J = 3.8$  Hz), 127.8, 127.2, 126.8, 116.8, 109.9, 30.7. **HRMS (ESI)**  $m/z$ :  $[M+H]^+$ calculated for  $C_{19}H_{18}N$ : 260.1434, found: 260.1435.



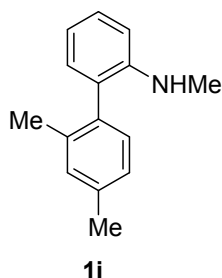
2'-chloro-N-methyl-[1,1'-biphenyl]-2-amine **1g** (69% yield)

White solid. m.p. 40-42 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 – 7.55 (m, 1H), 7.48 – 7.36 (m, 4H), 7.14 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.90 (td, *J* = 7.4, 0.8 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 3.58 (s, 1H), 2.90 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.5, 138.0, 134.3, 132.3, 130.1 (d, *J* = 1.2 Hz), 129.5, 129.2, 127.4, 125.1, 116.7, 110.0, 30.9 (d, *J* = 5.0 Hz). HRMS (ESI) *m/z*: [M+H]<sup>+</sup>calculated for C<sub>13</sub>H<sub>13</sub>ClN: 218.0731, found: 218.0734.



2'-methoxy-N-methyl-[1,1'-biphenyl]-2-amine **1h** (65% yield)

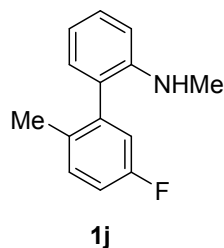
White solid. m.p. 135-138 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41 (td, *J* = 8.3, 1.7 Hz, 1H), 7.38 – 7.26 (m, 2H), 7.18 – 7.00 (m, 3H), 6.84 (td, *J* = 7.4, 0.8 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 3.83 (s, 3H), 2.86 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.9, 146.9, 132.0, 130.7, 129.0, 128.8, 128.1, 124.7, 121.2, 116.8, 111.4, 110.0, 55.8, 31.0. HRMS (ESI) *m/z*: [M+H]<sup>+</sup>calculated for C<sub>14</sub>H<sub>16</sub>NO: 214.1226, found: 214.1226.



N,2',4'-trimethyl-[1,1'-biphenyl]-2-amine **1i** (66% yield)

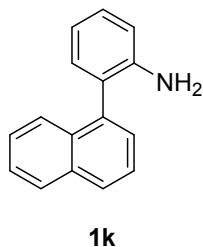
Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.31 (m, 1H), 7.17 (dd, *J* = 16.8, 9.2 Hz, 3H), 7.06 (dd, *J* = 7.3, 1.4 Hz, 1H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 3.55 (s, 1H), 2.85

(s, 3H), 2.45 (s, 3H), 2.18 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.5, 137.4, 137.1, 135.6, 131.1, 130.3, 129.8, 128.5, 127.3, 127.0, 116.6, 109.5, 30.7, 21.2, 19.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$ calculated for  $\text{C}_{15}\text{H}_{18}\text{N}$ : 212.1434, found: 212.1431.



5'-fluoro-N,2'-dimethyl-[1,1'-biphenyl]-2-amine **1j** (54% yield)

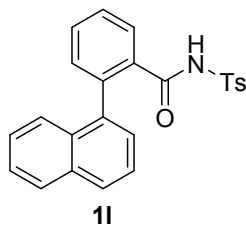
Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (t,  $J = 7.7$  Hz, 1H), 7.35 – 7.29 (m, 1H), 7.10 – 6.97 (m, 3H), 6.85 (t,  $J = 7.4$  Hz, 1H), 6.78 (d,  $J = 8.1$  Hz, 1H), 3.52 (s, 1H), 2.87 (s, 3H), 2.17 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6, 160.1, 146.1, 140.4 (d,  $J = 7.4$  Hz), 132.9 (d,  $J = 3.1$  Hz), 131.6 (d,  $J = 8.0$  Hz), 129.5, 129.0, 126.2 (d,  $J = 1.5$  Hz), 117.1 (d,  $J = 20.6$  Hz), 116.7, 114.5 (d,  $J = 20.7$  Hz), 109.7, 30.7, 18.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$ calculated for  $\text{C}_{14}\text{H}_{15}\text{NF}$ : 216.1183, found: 216.1185.



2-(naphthalen-1-yl)aniline **1k** (70% yield)

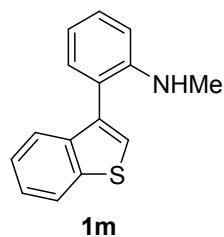
White solid. m.p. 68-70 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 – 7.72 (m, 2H), 7.57 (d,  $J = 8.3$  Hz, 1H), 7.41 (ddt,  $J = 27.6, 14.2, 7.1$  Hz, 3H), 7.19 (dd,  $J = 12.3, 4.7$  Hz, 1H), 7.09 (dd,  $J = 7.5, 1.2$  Hz, 1H), 6.88 – 6.72 (m, 2H), 3.35 (s, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.9, 136.9, 133.9, 131.7, 131.3, 128.8, 128.4, 128.1, 127.7, 126.3, 126.2, 126.1, 125.8, 118.7, 115.6. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$ calculated for  $\text{C}_{16}\text{H}_{14}\text{N}$ : 220.1121, found: 220.1121.





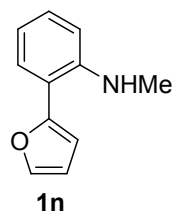
2-(naphthalen-1-yl)-N-tosylbenzamide **11** (10% yield)

White solid. m.p. 133-135 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 – 7.83 (m, 3H), 7.72 (dt, *J* = 29.7, 8.3 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.49 – 7.27 (m, 5H), 7.20 – 7.14 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 2.30 (d, *J* = 17.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.8, 164.9, 144.4, 141.9, 138.2, 136.9, 134.7, 133.7, 132.8, 132.4 – 132.1 (m), 131.6 (d, *J* = 16.1 Hz), 130.9, 130.0, 129.8, 129.4, 129.2, 128.6 (d, *J* = 2.5 Hz), 128.0, 127.6 (d, *J* = 4.7 Hz), 127.3, 126.9, 126.6, 126.4, 126.0, 125.8 – 125.5 (m), 125.1 (d, *J* = 16.3 Hz), 21.7. HRMS (ESI) *m/z*: [M+H]<sup>+</sup>calculated for C<sub>24</sub>H<sub>19</sub>NNaO<sub>3</sub>S: 424.0978, found: 424.0996.



2-(benzo[b]thiophen-3-yl)-N-methylaniline **1m** (96% yield)

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.35 – 7.20 (m, 4H), 7.09 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.79 – 6.57 (m, 2H), 3.82 (s, 1H), 2.67 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.2, 140.4, 138.4, 134.9, 130.9, 129.4, 124.9, 124.5 (d, *J* = 29.8 Hz), 123.4, 122.8, 120.8, 116.7, 110.1, 30.8. HRMS (ESI) *m/z*: [M+H]<sup>+</sup>calculated for C<sub>15</sub>H<sub>14</sub>NS: 240.0841, found: 240.0849.

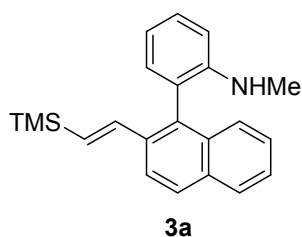


2-(furan-2-yl)-N-methylaniline **1n** (58% yield)

Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 1.1$  Hz, 1H), 7.35 (dd,  $J = 7.7, 1.4$  Hz, 1H), 7.18 – 7.10 (m, 1H), 6.64 (dd,  $J = 16.5, 8.0$  Hz, 2H), 6.45 (d,  $J = 3.1$  Hz, 1H), 6.40 (dd,  $J = 3.3, 1.8$  Hz, 1H), 5.03 (s, 1H), 2.79 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8, 145.9, 141.3, 129.3, 127.9, 116.8, 115.9, 111.3, 110.7, 106.6, 30.7. **HRMS (ESI)**  $m/z$ :  $[\text{M}+\text{H}]^+$ calculated for  $\text{C}_{11}\text{H}_{12}\text{NO}$ : 174.0913, found: 174.0919.

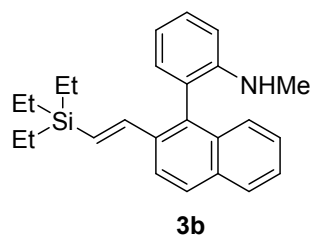
## General procedure for the synthesis of products 3.

Under air atmosphere, the substrate (0.5 mmol),  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  (3.9 mg, 3 mol%),  $\text{AgOAc}$  (167 mg, 1 mmol, 2 equiv) were added to a reaction tube containing a magnetic stir bar. After which, DCE (5.0 mL) and vinyl silane (1.5 mmol, 3 equiv) were added sequentially using a syringe. The reaction mixture was stirred at 40 °C in an oil bath for 16 hours. The reaction mixture was cooled to room temperature. The solvent was then evaporated *in vacuo* and the residue was purified by using flash silica gel column chromatography with EA and PE as eluent to afford the final products.



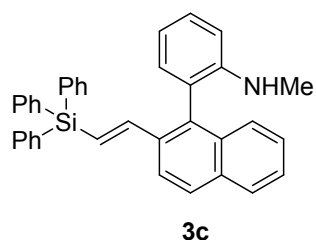
(E)-N-methyl-2-(2-(2-(trimethylsilyl)vinyl)naphthalen-1-yl)aniline **3a** (99% yield)

White solid. m.p. 70-74 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 – 7.82 (m, 3H), 7.54 (d,  $J = 8.4$  Hz, 1H), 7.51 – 7.33 (m, 3H), 7.09 – 6.96 (m, 1H), 6.93 – 6.70 (m, 3H), 6.56 (d,  $J = 19.2$  Hz, 1H), 3.27 (s, 1H), 2.72 (s, 3H), 0.14 – -0.02 (m, 9H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.6, 143.5, 135.9, 135.7, 134.9, 134.3, 132.5(d,  $J = 4.1$  Hz), 130.4, 129.3 (d,  $J = 10.8$  Hz), 128.2 – 127.2 (m), 124.2 (d,  $J = 8.0$  Hz), 117.9, 111.0, 32.1, 0.0 (d,  $J = 2.9$  Hz). **HRMS (ESI)**  $m/z$ :  $[\text{M}+\text{H}]^+$ calculated for  $\text{C}_{22}\text{H}_{26}\text{NSi}$ : 332.1829, found: 332.1836.



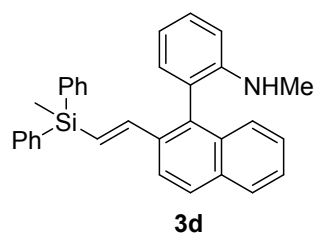
(E)-N-methyl-2-(2-(2-(triethylsilyl)vinyl)naphthalen-1-yl)aniline **3b** (71% yield)

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (dt, *J* = 8.2, 6.8 Hz, 3H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.26 (q, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.71 (dt, *J* = 17.8, 7.5 Hz, 3H), 6.37 (d, *J* = 19.4 Hz, 1H), 3.16 (s, 1H), 2.59 (s, 3H), 0.78 (t, *J* = 7.9 Hz, 9H), 0.43 (q, *J* = 7.8 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.2, 143.5, 134.7, 134.5, 133.6, 133.0, 131.1, 129.0, 127.9 (d, *J* = 10.6 Hz), 127.5, 126.7, 126.5, 126.0, 122.9 (d, *J* = 17.6 Hz), 116.7, 109.7, 30.7, 7.3, 3.6. HRMS (ESI) *m/z*: [M+H]<sup>+</sup>calculated for C<sub>25</sub>H<sub>32</sub>NSi: 374.2299, found: 374.2306.



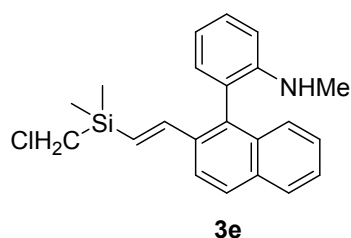
(E)-N-methyl-2-(2-(2-(triphenylsilyl)vinyl)naphthalen-1-yl)aniline **3c** (86% yield)

White solid. m.p. 46-50 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 8.6 Hz, 1H), 7.73 (dd, *J* = 13.8, 8.5 Hz, 2H), 7.51 – 7.10 (m, 19H), 6.88 (t, *J* = 12.7 Hz, 2H), 6.79 (d, *J* = 7.2 Hz, 1H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.52 (d, *J* = 8.1 Hz, 1H), 3.05 (s, 1H), 2.59 – 2.28 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.0, 146.9, 135.9, 135.3, 134.7, 134.5, 133.9, 133.0, 131.0, 129.5, 129.1, 128.3, 128.0 (d, *J* = 8.8 Hz), 126.8, 126.6, 126.4, 124.8, 123.3, 122.8, 116.9, 110.0, 30.7. HRMS (ESI) *m/z*: [M+H]<sup>+</sup>calculated for C<sub>37</sub>H<sub>32</sub>NSi: 518.2299, found: 518.2307.

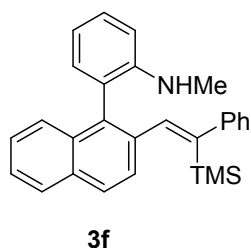


(E)-N-methyl-2-(2-(2-(methyl-diphenylsilyl)vinyl)naphthalen-1-yl)aniline **3d** (88% yield)

Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 – 7.72 (m, 3H), 7.43 – 7.33 (m, 6H), 7.24 (dt,  $J = 20.7, 7.0$  Hz, 8H), 6.89 (d,  $J = 7.2$  Hz, 1H), 6.82 (d,  $J = 19.2$  Hz, 1H), 6.75 (t,  $J = 7.2$  Hz, 1H), 6.72 – 6.64 (m, 2H), 2.53 (s, 3H), 0.47 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 136.4, 134.7 (d,  $J = 13.9$  Hz), 134.5, 133.7, 132.9, 131.1, 129.2 (d,  $J = 6.0$  Hz), 128.3, 127.9, 127.8, 126.8 – 126.5 (m), 126.3, 123.0, 31.2, -3.9. **HRMS (ESI)**  $m/z$ :  $[\text{M}]^+$ calculated for  $\text{C}_{32}\text{H}_{29}\text{NSi}$ : 455.2069, found: 455.2073.

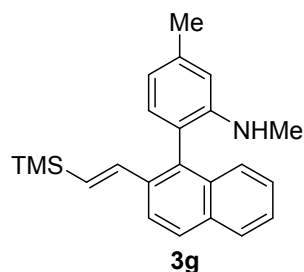


(E)-2-(2-(2-((chloromethyl)dimethylsilyl)vinyl)naphthalen-1-yl)-N-methylaniline **3e** (63% yield)  
 White solid. m.p. 61-65 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 – 7.70 (m, 3H), 7.43 (d,  $J = 8.4$  Hz, 1H), 7.35 (t,  $J = 7.4$  Hz, 1H), 7.31 – 7.21 (m, 2H), 6.89 (d,  $J = 7.3$  Hz, 1H), 6.76 (dd,  $J = 17.5, 10.6$  Hz, 2H), 6.67 (d,  $J = 8.1$  Hz, 1H), 6.39 (d,  $J = 19.4$  Hz, 1H), 3.09 (s, 1H), 2.66 (s, 2H), 2.59 (s, 3H), 0.04 (d,  $J = 1.8$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.1, 143.7, 134.1, 132.9, 132.7, 131.8, 130.1, 128.2, 127.1, 126.9, 125.7, 125.5, 125.3, 125.1, 121.6 (d,  $J = 2.6$  Hz), 115.7, 108.8, 29.7, 29.4, -5.5 (d,  $J = 5.9$  Hz). **HRMS (ESI)**  $m/z$ :  $[\text{M}+\text{H}]^+$ calculated for  $\text{C}_{22}\text{H}_{25}\text{ClNSi}$ : 366.1439, found: 366.1447.



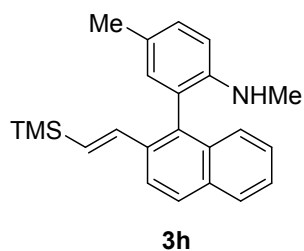
(E)-N-methyl-2-(2-(2-phenyl-2-(trimethylsilyl)vinyl)naphthalen-1-yl)aniline **3f** (74% yield)  
 Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (t,  $J = 7.2$  Hz, 1H), 7.58 (d,  $J = 8.3$  Hz, 1H), 7.46 (dd,  $J = 17.5, 8.3$  Hz, 3H), 7.37 (t,  $J = 7.6$  Hz, 1H), 7.31 (t,  $J = 7.3$  Hz, 2H), 7.23 (t,  $J = 7.3$  Hz, 1H), 7.12 (dd,  $J = 7.3, 1.2$  Hz, 1H), 7.04 (t,  $J = 7.4$  Hz, 3H), 6.94 (t,  $J = 7.2$  Hz, 1H), 6.87 (d,  $J = 8.1$  Hz, 1H), 6.71 (s, 1H), 2.82 (s, 3H), 0.00 (s, 9H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.5 (d,  $J$

= 7.9 Hz), 144.2, 138.9, 137.5, 136.4, 134.3 (d,  $J = 17.3$  Hz), 132.5, 130.7, 129.9, 129.5, 128.9, 128.3, 127.8 (d,  $J = 5.5$  Hz), 127.5, 127.3, 125.4, 118.7, 111.6, 32.5, -0.0. **HRMS (ESI)**  $m/z$ :  $[M+H]^+$ calculated for  $C_{28}H_{30}NSi$ : 408.2142, found: 408.2149.



(E)-N,5-dimethyl-2-(2-(2-(trimethylsilyl)vinyl)naphthalen-1-yl)aniline **3g** (92% yield)

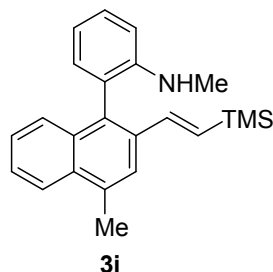
Colorless oil.  **$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  7.82 (dd,  $J = 16.0, 8.7$  Hz, 3H), 7.50 (d,  $J = 8.4$  Hz, 1H), 7.40 (t,  $J = 7.3$  Hz, 1H), 7.31 (t,  $J = 7.4$  Hz, 1H), 6.85 (d,  $J = 7.4$  Hz, 1H), 6.77 (d,  $J = 19.2$  Hz, 1H), 6.65 (d,  $J = 7.4$  Hz, 1H), 6.58 (s, 1H), 6.50 (d,  $J = 19.2$  Hz, 1H), 3.27 (s, 1H), 2.66 (s, 3H), 2.42 (s, 3H), 0.00 (s, 9H).  **$^{13}C$  NMR (101 MHz,  $CDCl_3$ )**  $\delta$  148.2, 143.6, 139.9, 135.8 (d,  $J = 9.6$  Hz), 134.8, 134.4, 132.3 (d,  $J = 4.2$  Hz), 129.2 (d,  $J = 3.2$  Hz), 128.0, 127.6, 127.2, 124.1, 121.5, 118.9, 112.0, 32.2, 23.2, -0.0. **HRMS (ESI)**  $m/z$ :  $[M+H]^+$ calculated for  $C_{23}H_{28}NSi$ : 346.1986, found: 346.1991.



(E)-N,4-dimethyl-2-(2-(2-(trimethylsilyl)vinyl)naphthalen-1-yl)aniline **3h** (78% yield)

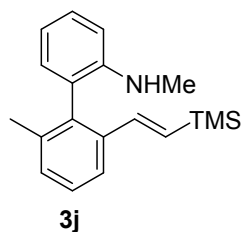
White solid. m.p. 77-80 °C.  **$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  7.83 (q,  $J = 8.8$  Hz, 3H), 7.50 (d,  $J = 8.4$  Hz, 1H), 7.42 (dd,  $J = 10.8, 3.9$  Hz, 1H), 7.33 (dd,  $J = 11.1, 4.1$  Hz, 1H), 7.16 (dd,  $J = 8.2, 1.6$  Hz, 1H), 6.81 (d,  $J = 1.7$  Hz, 1H), 6.75 (d,  $J = 19.3$  Hz, 1H), 6.70 (d,  $J = 8.2$  Hz, 1H), 6.50 (d,  $J = 19.2$  Hz, 1H), 2.65 (s, 3H), 2.27 (s, 3H), 0.00 (d,  $J = 3.1$  Hz, 9H).  **$^{13}C$  NMR (101 MHz,  $CDCl_3$ )**  $\delta$  146.2, 143.6, 135.9, 135.6, 134.8, 134.2, 133.1, 132.4, 130.7, 129.2 (d,  $J = 4.5$  Hz), 128.0, 127.7,

127.3, 124.5, 124.1, 111.6, 32.6, 21.7, 0.0 . **HRMS (ESI)** m/z: [M+H]<sup>+</sup>calculated for C<sub>23</sub>H<sub>28</sub>NSi: 346.1986, found: 346.1991.



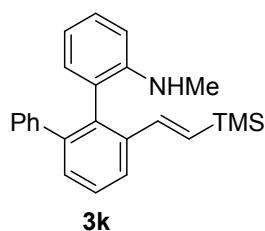
(E)-N-methyl-2-(4-methyl-2-(2-(trimethylsilyl)vinyl)naphthalen-1-yl)aniline **3i** (80% yield)

White solid. m.p. 54-58 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.71 (s, 1H), 7.58 – 7.41 (m, 2H), 7.33 (q, *J* = 6.9 Hz, 2H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.87 – 6.66 (m, 3H), 6.51 (d, *J* = 19.2 Hz, 1H), 3.25 (s, 1H), 2.73 (s, 3H), 2.66 (s, 3H), 0.00 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.7, 143.5, 135.4, 135.1, 134.5 – 133.9 (m), 132.6, 132.1, 130.2, 128.5, 127.4, 127.2, 125.4, 124.7, 124.4, 117.9, 110.9, 32.1, 20.9, -0.0. **HRMS (ESI)** m/z: [M+H]<sup>+</sup>calculated for C<sub>23</sub>H<sub>28</sub>NSi: 346.1986, found: 346.1991.



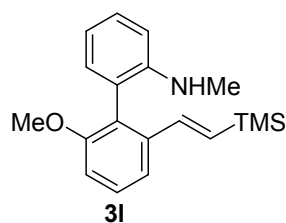
(E)-N,2'-dimethyl-6'-(2-(trimethylsilyl)vinyl)-[1,1'-biphenyl]-2-amine **3j** (99% yield)

White solid. m.p. 41-43 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.28 (dt, *J* = 16.5, 7.2 Hz, 3H), 6.91 (d, *J* = 6.6 Hz, 1H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.57 (d, *J* = 19.2 Hz, 1H), 6.38 (d, *J* = 19.2 Hz, 1H), 3.29 (s, 1H), 2.77 (s, 3H), 2.09 (s, 3H), -0.02 (d, *J* = 14.5 Hz, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.8, 143.7, 139.1 (d, *J* = 1.7 Hz), 138.4, 131.7, 131.2, 131.1, 129.9, 128.9, 125.9, 123.9, 118.2, 110.9, 32.2, 21.6, -0.0. **HRMS (ESI)** m/z: [M+H]<sup>+</sup>calculated for C<sub>19</sub>H<sub>26</sub>NSi: 296.1829, found: 296.1836.



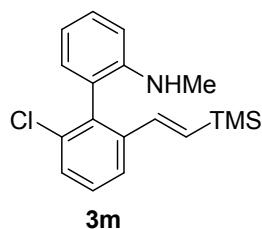
(E)-N-methyl-6'-(2-(trimethylsilyl)vinyl)-[1,1':2',1''-terphenyl]-2-amine **3k** (81% yield)

White solid. m.p. 92-94 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.48 – 7.35 (m, 2H), 7.16 – 7.10 (m, 6H), 6.71 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.63 (d, *J* = 19.2 Hz, 1H), 6.56 (t, *J* = 7.1 Hz, 2H), 6.43 (d, *J* = 19.2 Hz, 1H), 2.66 (s, 3H), 0.04 – -0.03 (m, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.4, 144.1, 143.8, 142.7, 139.6, 137.2, 132.5 (d, *J* = 7.7 Hz), 131.3, 130.4, 129.8, 129.2, 128.8, 128.7, 127.8, 125.8, 118.0, 111.0, 32.2, -0.0. HRMS (ESI) *m/z*: [M+H]<sup>+</sup>calculated for C<sub>24</sub>H<sub>28</sub>NSi: 358.1986, found: 358.1991.



(E)-2'-methoxy-N-methyl-6'-(2-(trimethylsilyl)vinyl)-[1,1'-biphenyl]-2-amine **3l** (60% yield)

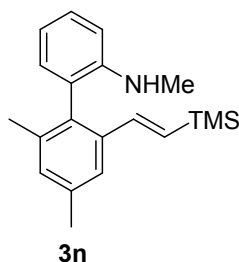
Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.29 (m, 3H), 7.01 (dd, *J* = 14.6, 7.1 Hz, 2H), 6.91 – 6.76 (m, 2H), 6.63 (d, *J* = 19.2 Hz, 1H), 6.47 (d, *J* = 19.2 Hz, 1H), 3.81 (s, 3H), 3.45 (s, 1H), 2.84 (s, 3H), 0.03 (d, *J* = 28.2 Hz, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.9, 148.4, 143.3, 140.5, 132.4 (d, *J* = 7.8 Hz), 130.0 (d, *J* = 15.1 Hz), 127.7, 122.9, 118.9, 118.0, 111.9, 111.2, 57.3, 32.3, -0.0. HRMS (ESI) *m/z*: [M+H]<sup>+</sup>calculated for C<sub>19</sub>H<sub>26</sub>NOSi: 312.1778, found: 312.1787.



(E)-2'-chloro-N-methyl-6'-(2-(trimethylsilyl)vinyl)-[1,1'-biphenyl]-2-amine **3m** (87% yield)

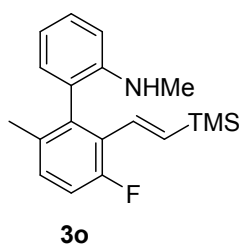
Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.38 (ddd, *J* = 12.8, 10.0, 4.6 Hz, 2H), 6.99 (dd, *J* = 7.4, 1.1 Hz, 1H), 6.87 (t, *J* = 7.3 Hz, 1H), 6.81

(d,  $J = 8.1$  Hz, 1H), 6.51 (q,  $J = 19.2$  Hz, 2H), 2.84 (s, 3H), 0.04 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.8, 142.8, 141.6, 137.4, 136.5, 133.9, 131.7, 130.8, 130.4, 130.2, 125.2, 124.2, 118.4, 111.5, 32.4, 0.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$ calculated for  $\text{C}_{18}\text{H}_{23}\text{ClNSi}$ : 316.1283, found: 316.1291.



(E)-N,2',4'-trimethyl-6'-(2-(trimethylsilyl)vinyl)-[1,1'-biphenyl]-2-amine **3n** (88% yield)

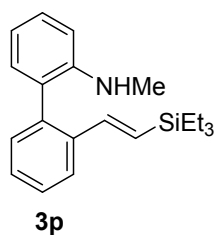
Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (s, 1H), 7.33 (dd,  $J = 14.8, 7.1$  Hz, 1H), 7.13 (s, 1H), 6.94 (d,  $J = 7.3$  Hz, 1H), 6.83 (t,  $J = 7.2$  Hz, 1H), 6.76 (d,  $J = 8.1$  Hz, 1H), 6.59 (d,  $J = 19.2$  Hz, 1H), 6.41 (d,  $J = 19.2$  Hz, 1H), 3.38 (s, 1H), 2.81 (s, 3H), 2.45 (s, 3H), 2.09 (s, 3H), 0.04 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.9, 143.8, 138.9, 138.4, 135.5, 132.1, 131.4 (d,  $J = 7.6$  Hz), 129.8, 125.9, 124.6, 118.2, 110.9, 32.2, 22.6, 21.4, 0.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$ calculated for  $\text{C}_{20}\text{H}_{28}\text{NSi}$ : 310.1986, found: 310.1991.



(E)-3'-fluoro-N,6'-dimethyl-2'-(2-(trimethylsilyl)vinyl)-[1,1'-biphenyl]-2-amine **3o** (66% yield)

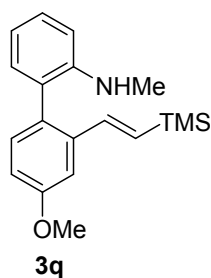
Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.30 (m, 1H), 7.20 (dd,  $J = 8.3, 5.4$  Hz, 1H), 7.06 (dd,  $J = 11.0, 8.5$  Hz, 1H), 6.91 (d,  $J = 6.3$  Hz, 1H), 6.84 (t,  $J = 7.3$  Hz, 1H), 6.77 (d,  $J = 8.1$  Hz, 1H), 6.43 (d,  $J = 5.8$  Hz, 2H), 3.40 (s, 1H), 2.82 (s, 3H), 2.07 (s, 3H), -0.00 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6, 160.2, 147.6, 140.6 (d,  $J = 3.1$  Hz), 138.7 (d,  $J = 8.7$  Hz), 138.1, 134.8 (d,  $J = 3.5$  Hz), 131.5 (d,  $J = 9.1$  Hz), 131.3, 130.4, 127.4 (d,  $J = 10.1$  Hz), 126.1, 118.7, 116.6 (d,  $J = 22.9$  Hz), 111.5, 32.4, 21.3, -0.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$ calculated for  $\text{C}_{19}\text{H}_{25}\text{FNSi}$ : 314.1735, found: 314.1741.





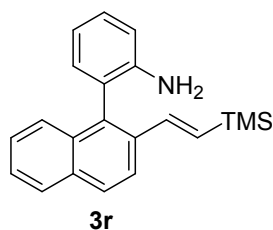
(E)-N-methyl-2'-(2-(triethylsilyl)vinyl)-[1,1'-biphenyl]-2-amine **3p** (46% yield)

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (d, *J* = 7.2 Hz, 1H), 7.32 – 7.11 (m, 4H), 6.92 (d, *J* = 6.6 Hz, 1H), 6.74 – 6.52 (m, 3H), 6.28 (d, *J* = 19.4 Hz, 1H), 2.65 (s, 3H), 0.77 (t, *J* = 7.9 Hz, 9H), 0.41 (q, *J* = 7.9 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.3, 143.2, 137.7, 137.4, 130.9, 130.3, 128.8, 128.3, 127.8, 127.2, 126.1, 125.2, 116.7, 109.5, 30.7, 7.3, 3.5. HRMS (ESI) *m/z*: [M]<sup>+</sup>calculated for C<sub>21</sub>H<sub>29</sub>NSi: 323.2069, found: 323.2071.



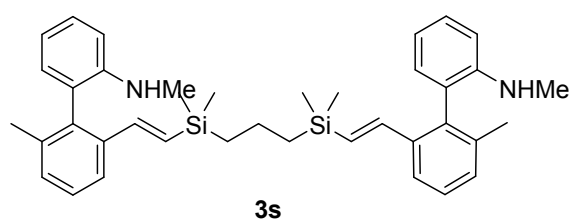
(E)-4'-methoxy-N-methyl-2'-(2-(trimethylsilyl)vinyl)-[1,1'-biphenyl]-2-amine **3q** (28% yield)

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27 (dd, *J* = 12.6, 5.3 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.01 – 6.95 (m, 1H), 6.90 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 19.2 Hz, 1H), 6.40 (d, *J* = 19.2 Hz, 1H), 3.87 (s, 3H), 2.74 (s, 3H), -0.00 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.6, 147.9, 143.2, 139.5, 133.3, 132.1 (d, *J* = 6.8 Hz), 131.7, 130.0, 127.1, 118.1, 115.9, 111.0, 56.7, 32.1, 0.0. HRMS (ESI) *m/z*: [M]<sup>+</sup>calculated for C<sub>19</sub>H<sub>25</sub>NOSi: 311.1705, found: 311.1707.



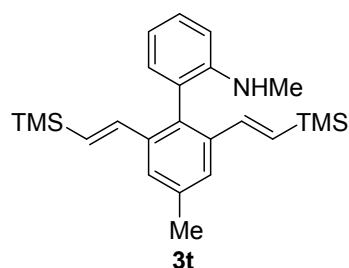
(E)-2-(2-(2-(trimethylsilyl)vinyl)naphthalen-1-yl)aniline **3r** (48% yield)

Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (dd,  $J = 17.8, 9.3$  Hz, 3H), 7.48 (d,  $J = 8.4$  Hz, 1H), 7.41 (t,  $J = 7.3$  Hz, 1H), 7.33 (t,  $J = 7.5$  Hz, 1H), 7.23 (dd,  $J = 15.6, 8.3$  Hz, 1H), 7.00 (d,  $J = 7.4$  Hz, 1H), 6.91 – 6.73 (m, 3H), 6.52 (d,  $J = 19.2$  Hz, 1H), 3.24 (s, 2H), -0.00 (s, 9H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.6, 143.3, 135.8, 135.6, 134.8, 133.9, 132.9, 132.6, 130.2, 129.3 (d,  $J = 9.6$  Hz), 127.9 (d,  $J = 10.0$  Hz), 127.4, 124.7, 124.2, 119.8, 116.7, 0.0. **HRMS (ESI)**  $m/z$ :  $[\text{M}+\text{H}]^+$ calculated for  $\text{C}_{21}\text{H}_{24}\text{NSi}$ : 318.1673, found: 318.1685.



6',6'''-((1E,1'E)-(propane-1,3-diylbis(dimethylsilanediy))bis(ethene-2,1-diyl))bis(N,2'-dimethyl-[1,1'-biphenyl]-2-amine) **3s** (66% yield)

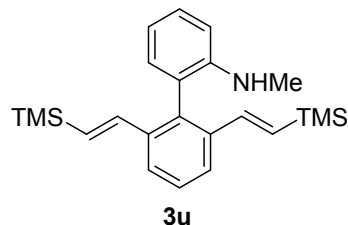
Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 7.4$  Hz, 2H), 7.40 – 7.31 (m, 6H), 6.96 (dd,  $J = 5.0, 2.3$  Hz, 2H), 6.86 (t,  $J = 7.2$  Hz, 2H), 6.79 (d,  $J = 8.0$  Hz, 2H), 6.60 (d,  $J = 19.2$  Hz, 2H), 6.40 (d,  $J = 19.2$  Hz, 2H), 3.41 (s, 2H), 2.82 (s, 6H), 2.15 (s, 6H), 1.33 – 1.25 (m, 2H), 0.68 – 0.45 (m, 4H), 0.06 – -0.07 (m, 12H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.3, 142.6, 137.8 (d,  $J = 10.0$  Hz), 136.9, 129.8 (d,  $J = 19.0$  Hz), 128.6, 127.7, 124.7, 122.7, 117.0, 109.8, 30.9, 20.1 (d,  $J = 18.6$  Hz), 18.3, -2.9 (d,  $J = 5.1$  Hz). **HRMS (ESI)**  $m/z$ :  $[\text{M}]^+$ calculated for  $\text{C}_{39}\text{H}_{50}\text{N}_2\text{Si}_2$ : 602.3513, found: 602.3498.



N,4'-dimethyl-2',6'-bis((E)-2-(trimethylsilyl)vinyl)-[1,1'-biphenyl]-2-amine **3t** (30% yield)

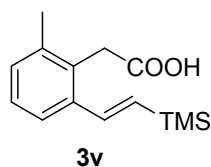
Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (s, 2H), 7.34 – 7.27 (m, 1H), 6.88 (d,  $J = 7.3$  Hz, 1H), 6.79 (t,  $J = 7.2$  Hz, 1H), 6.72 (d,  $J = 7.9$  Hz, 1H), 6.58 (d,  $J = 19.2$  Hz, 2H), 6.39 (d,  $J = 19.2$  Hz, 2H), 2.75 (s, 3H), 2.44 (s, 3H), -0.02 (d,  $J = 12.9$  Hz, 18H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )

$\delta$  143.6, 139.2, 138.5, 134.7, 132.4, 131.7, 130.1, 126.9, 32.4, 31.1, 0.0. **HRMS (ESI)**  $m/z$ :  
[M]<sup>+</sup>calculated for C<sub>24</sub>H<sub>35</sub>NSi<sub>2</sub>: 393.2308, found: 393.2309.



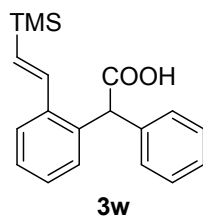
N-methyl-2',6'-bis((E)-2-(trimethylsilyl)vinyl)-[1,1'-biphenyl]-2-amine **3u** (43% yield)

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (d,  $J$  = 7.8 Hz, 2H), 7.40 – 7.26 (m, 2H), 6.88 (d,  $J$  = 7.3 Hz, 1H), 6.78 (t,  $J$  = 7.3 Hz, 1H), 6.71 (d,  $J$  = 8.2 Hz, 1H), 6.60 (d,  $J$  = 19.2 Hz, 2H), 6.39 (d,  $J$  = 19.2 Hz, 2H), 3.33 (s, 1H), 2.74 (d,  $J$  = 3.7 Hz, 3H), 0.04 – -0.05 (m, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  148.1, 143.6, 139.4, 137.5, 132.2, 132.0, 130.2, 129.1, 126.1, 124.6, 118.0, 111.0, 32.2, 0.0. **HRMS (ESI)**  $m/z$ : [M+H]<sup>+</sup>calculated for C<sub>23</sub>H<sub>34</sub>NSi<sub>2</sub>: 380.2224, found: 380.2236.



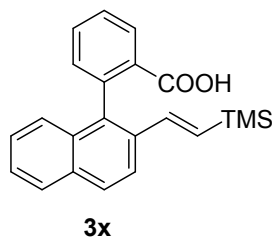
(E)-2-(2-methyl-6-(2-(trimethylsilyl)vinyl)phenyl)acetic acid **3v** (56% yield) ( $E/Z=2:1$ )

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.50 (d,  $J$  = 8.5 Hz, 1H), 7.15 (t,  $J$  = 6.7 Hz, 6H), 5.23 (d,  $J$  = 14.5 Hz, 1H), 4.85 (d,  $J$  = 8.5 Hz, 1H), 3.68 (s, 1H), 3.66 (s, 2H), 2.30 (s, 3H), 2.28 (s, 1H), 0.06 (s, 9H), 0.00 (s, 5H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.6(d,  $J$  = 5.0 Hz), 147.2, 144.8, 137.9 (d,  $J$  = 9.8 Hz), 132.9 (d,  $J$  = 6.8 Hz), 131.5, 131.3, 128.7 (d,  $J$  = 6.0 Hz), 127.3 (d,  $J$  = 5.0 Hz), 111.2, 109.9, 40.3, 40.0, 20.6 (d,  $J$  = 5.1 Hz), 0.4, 0.0. **HRMS (ESI)**  $m/z$ : [M+Na]<sup>+</sup>calculated for C<sub>14</sub>H<sub>20</sub>NaO<sub>2</sub>Si: 271.1125, found: 271.1131.



(E)-2-phenyl-2-(2-(2-(trimethylsilyl)vinyl)phenyl)acetic acid **3w** (62% yield) (*E/Z*=1:1)

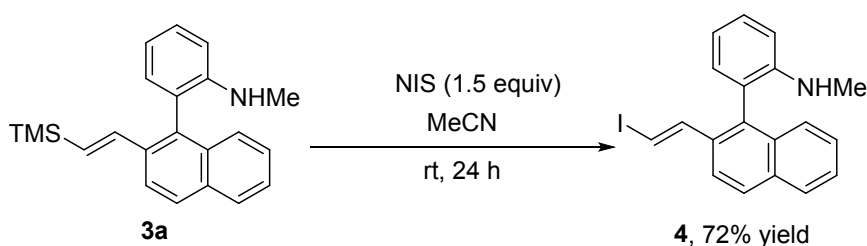
Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.4 Hz, 1H), 7.22 (t, *J* = 6.1 Hz, 14H), 7.20 – 7.15 (m, 4H), 7.13 (s, 1H), 5.20 (d, *J* = 14.5 Hz, 1H), 4.96 (s, 2H), 4.81 (d, *J* = 8.4 Hz, 1H), -0.00 (s, 9H), -0.11 (s, 7H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.7 (d, *J* = 2.0 Hz), 147.2, 144.8, 139.1, 138.9, 129.8 – 129.6 (m), 128.5 (d, *J* = 2.6 Hz), 111.6, 110.5, 58.2, 57.9, 0.4, 0.0. HRMS (ESI) *m/z*: [M+Na]<sup>+</sup>calculated for C<sub>19</sub>H<sub>22</sub>NaO<sub>2</sub>Si: 333.1281, found: 333.1284.



(E)-2-(2-(2-(trimethylsilyl)vinyl)naphthalen-1-yl)benzoic acid **3x** (54% yield) (*E/Z*=3:1)

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (d, *J* = 7.7 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.90 (t, *J* = 8.5 Hz, 3H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.60 – 7.51 (m, 3H), 7.46 (dd, *J* = 13.5, 7.2 Hz, 4H), 7.41 – 7.32 (m, 3H), 7.00 (d, *J* = 14.4 Hz, 1H), 4.83 (d, *J* = 8.6 Hz, 1H), 4.67 (d, *J* = 14.4 Hz, 1H), 0.13 (s, 3H), 0.00 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.1 (d, *J* = 9.7 Hz), 147.6, 144.6, 143.5 (d, *J* = 7.5 Hz), 140.8, 140.2, 134.5, 134.4, 133.5, 133.4 – 133.2 (m), 131.8, 131.2, 131.12, 129.5, 129.4, 128.9, 128.8 (d, *J* = 10.5 Hz), 127.2 (d, *J* = 6.3 Hz), 126.9, 126.8 (d, *J* = 5.9 Hz), 126.7, 126.5, 126.3 (d, *J* = 8.9 Hz), 111.3, 109.7, 0.7, 0.0. HRMS (ESI) *m/z*: [M+H]<sup>+</sup>calculated for C<sub>22</sub>H<sub>22</sub>NaO<sub>2</sub>Si: 369.1281, found: 369.1289.

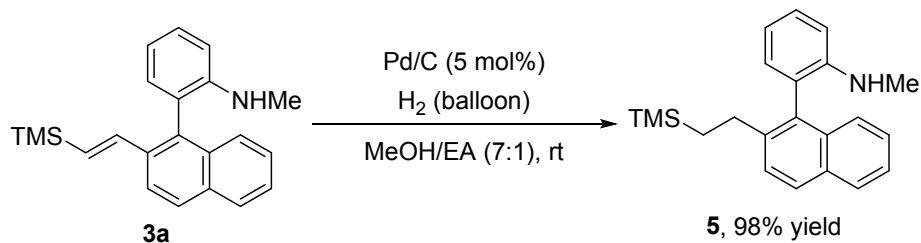
## Procedure for the synthesis of 4.



**3a** (66.2 mg, 0.2 mmol) and NIS (1.5 equiv) was added in MeCN (2 mL). The resulting mixture were degassed, purged with N<sub>2</sub> (3 times) and then stirred at room temperature for 24 h. The mixture was filtered through Celite plug and the Celite was washed with EA. The combined organic layers were concentrated under reduced pressure. The crude material was purified by silica gel column chromatography (eluent: PE/EA = 50:1) to give **4** (55.5 mg, 72% yield)<sup>[1]</sup>.

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (t, *J* = 7.5 Hz, 2H), 7.60 – 7.50 (m, 2H), 7.44 – 7.24 (m, 4H), 7.23 – 7.11 (m, 2H), 6.86 (d, *J* = 14.9 Hz, 1H), 6.46 (d, *J* = 8.6 Hz, 1H), 2.59 (d, *J* = 9.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.5, 140.6, 136.6, 135.7, 131.7, 131.2, 130.1, 129.9, 126.6, 125.8, 124.8, 124.4, 124.1, 122.6, 120.3, 109.9, 76.7, 28.3. HRMS (ESI) *m/z*: [M]<sup>+</sup>calculated for C<sub>19</sub>H<sub>16</sub>NI: 385.0322, found: 385.0317.

## Procedure for the synthesis of 5.

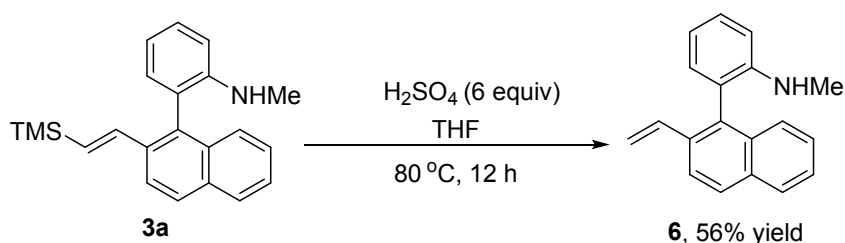


**3a** (66.2 mg, 0.2 mmol) and Pd/C (20 wt%) (5 mol%) were added in MeOH/EA (1.75 mL: 0.25 mL). The resulting mixture was degassed, purged with hydrogen (3 times) and then stirred at room temperature overnight. The mixture was filtered through Celite plug and the Celite was washed with EA. The combined organic layers were concentrated under reduced pressure. The crude

material was purified by silica gel column chromatography (eluent: PE/EA = 50:1) to give **5** (65 mg, 98% yield).

Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.93 (m, 2H), 7.62 (d,  $J = 8.5$  Hz, 1H), 7.50 (ddd,  $J = 17.5, 15.7, 7.9$  Hz, 4H), 7.14 (d,  $J = 7.2$  Hz, 1H), 6.97 (t,  $J = 7.3$  Hz, 1H), 6.90 (d,  $J = 8.2$  Hz, 1H), 3.38 (s, 1H), 2.83 (s, 3H), 2.68 – 2.51 (m, 2H), 0.92 – 0.81 (m, 2H), -0.00 (s, 9H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 144.6, 135.2, 135.0, 134.3, 132.8, 130.8, 130.1, 129.9, 129.7, 128.2, 127.9, 127.1, 126.0, 32.8, 30.1, 21.2, 0.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{22}\text{H}_{28}\text{NSi}$ : 334.1986, found: 334.1980.

## Procedure for the synthesis of **6**.

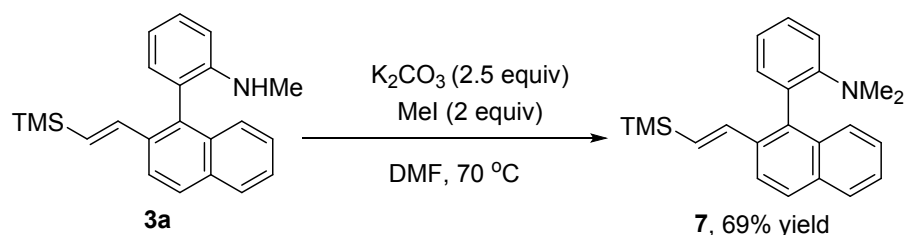


**3a** (66.2 mg, 0.2 mmol) was dissolved in THF (2 mL) in a round bottom flask equipped with a stir bar. Concentrated sulfuric acid (6 equiv) was added and the flask was fitted with a reflux condenser and placed in an oil bath at 80 °C and refluxed for 12 h. Upon cooling, the reaction mixture was quenched with water and extracted with diethyl ether. The combined organic layers were concentrated in *vacuo* and then purified by column chromatography on silica gel with 7% EtOAc in hexanes to afford **6** (29 mg, 56% yield)<sup>[2]</sup>.

Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (d,  $J = 6.8$  Hz, 3H), 7.40 – 7.34 (m, 2H), 7.30 (dd,  $J = 18.3, 8.2$  Hz, 2H), 6.93 (d,  $J = 7.3$  Hz, 1H), 6.78 (t,  $J = 7.3$  Hz, 1H), 6.71 (d,  $J = 8.1$  Hz, 1H), 6.54 (dd,  $J = 17.6, 11.0$  Hz, 1H), 5.74 (d,  $J = 17.6$  Hz, 1H), 5.14 (d,  $J = 11.0$  Hz, 1H), 3.20 (s, 1H), 2.62 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.1, 134.1, 133.3, 132.7, 132.4, 131.8, 130.1,

128.0, 127.1, 126.9, 125.5 (d,  $J = 2.1$  Hz), 125.0, 122.1, 121.6, 115.9, 114.0, 108.9, 29.8. **HRMS (ESI)** m/z:  $[M+H]^+$  calculated for  $C_{19}H_{18}N$ : 260.1434, found: 260.1429.

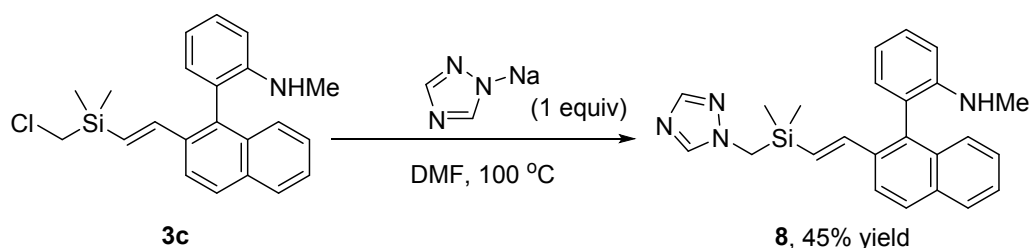
## Procedure for the synthesis of 7.



**3a** (66.2 mg, 0.2 mmol), MeI (2 equiv) and  $K_2CO_3$  (2.5 equiv) were added in DMF (2 mL). The resulting mixture was degassed, purged with  $N_2$  (3 times) and then stirred at 70 °C overnight. The mixture was filtered through Celite plug and the Celite was washed with EA. The combined organic layers were concentrated under reduced pressure. The crude material was purified by silica gel column chromatography (eluent: PE/EA = 50:1) to give **7** (47.7 mg, 69% yield).

Colorless oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.84 (d,  $J = 8.7$  Hz, 1H), 7.78 (dd,  $J = 8.1, 3.8$  Hz, 2H), 7.57 (d,  $J = 8.4$  Hz, 1H), 7.35 (ddd,  $J = 17.5, 14.6, 7.0$  Hz, 3H), 7.12 – 6.96 (m, 3H), 6.76 (d,  $J = 19.2$  Hz, 1H), 6.48 (d,  $J = 19.2$  Hz, 1H), 2.39 (s, 6H), -0.00 (s, 9H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  153.9, 144.5, 138.9, 134.7, 134.4 (d,  $J = 6.4$  Hz), 134.0, 131.4, 130.8, 129.8, 129.1, 128.5 (d,  $J = 10.6$  Hz), 127.1, 126.8, 123.9, 121.9, 118.8, 44.2, -0.0. **HRMS (ESI)** m/z:  $[M+H]^+$  calculated for  $C_{23}H_{28}NSi$ : 346.1986, found: 346.1978.

## Procedure for the synthesis of **8**.

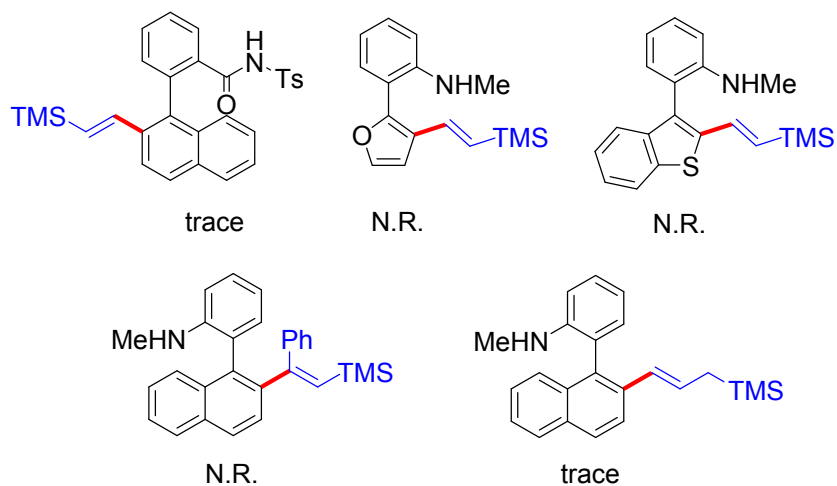
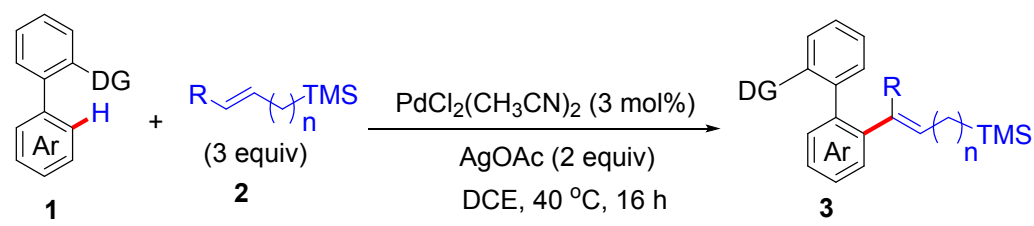


**3c** (73.2 mg, 0.2 mmol) and 1,2,4-Triazolylsodium (1 equiv) was added in DMF (2 mL). The resulting mixture were degassed, purged with N<sub>2</sub> (3 times) and then stirred at 100 °C overnight. The mixture was filtered through Celite plug and the Celite was washed with EA. The combined organic layer was concentrated under reduced pressure. The crude material was purified by silica gel column chromatography (eluent: PE/EA = 10:1) to give **8** (35.9 mg, 45% yield).

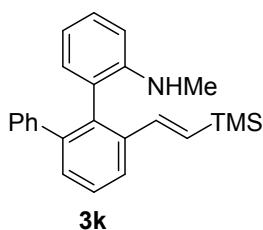
Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 (d, *J* = 7.6 Hz, 5H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.34 – 7.18 (m, 3H), 6.88 – 6.83 (m, 1H), 6.80 – 6.69 (m, 2H), 6.66 (d, *J* = 8.1 Hz, 1H), 6.31 (d, *J* = 19.4 Hz, 1H), 3.59 (s, 2H), 3.18 (s, 1H), 2.55 (s, 3H), -0.00 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.3, 147.1, 145.2, 143.1, 135.3, 133.8 (d, *J* = 6.5 Hz), 132.8, 131.2, 129.3, 128.3, 128.0, 126.7 (d, *J* = 12.6 Hz), 126.5, 125.6, 122.7 (d, *J* = 4.0 Hz), 116.9, 109.9, 40.4, 30.8, -3.8. HRMS (ESI) *m/z*: [M]<sup>+</sup> calculated for C<sub>24</sub>H<sub>26</sub>N<sub>4</sub>Si: 398.1927, found: 398.1928.

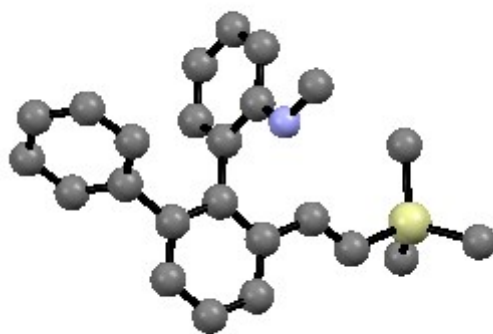


## Scheme 1 Unsuitable biaryls and silanes.



## X-ray structures of product **3k** (CCDC 1882245)





## References

- [1] C.-B Reddy, A.-K. Shil, N.-R. Guha, D. Sharma and P. Das. *Catalysis Letters*. 2014, **144**, 1530.
- [2] B.-H. Lipshutz, Z.-V. Boskovic and D.-H. Aue. *Angew. Chem. Int. Ed.* 2008, **47**, 10183.

# $^1\text{H}$ , $^{13}\text{C}$ NMR Spectra

