## **Supplementary Information**

# Sodium silylsilanolate enables nickel-catalysed silylation of aryl chlorides.

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#### **Instrumentation and Chemicals**

<sup>1</sup>H NMR (600 MHz), <sup>13</sup>C NMR (151 MHz), and <sup>19</sup>F NMR (564 MHz) spectra were recorded on a JEOL ECZ-600 spectrometer. Chemical shifts in <sup>1</sup>H NMR spectra were recorded in delta ( $\delta$ ) units, parts per million (ppm) relative to residual CHCl<sub>3</sub> ( $\delta$  = 7.26 ppm). Chemical shifts in <sup>13</sup>C NMR spectra were recorded in delta ( $\delta$ ) units, parts per million (ppm) relative to CDCl<sub>3</sub> ( $\delta$ = 77.16 ppm). For <sup>19</sup>F NMR spectra, fluorobenzene (<sup>19</sup>F:  $\delta$  = –113.50 ppm) were used as an external standard. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II-KR spectrometer in Atmospheric Pressure Chemical Ionisation (APCI) method using "LC/MS tuning mix, for APCI, low concentration" (Agilent Technologies, Inc.) as the internal standard. For all spectroscopic studies, spectroscopic grade solvents were used as purchased unless otherwise noted.

All non-aqueous reactions were carried out under an inert atmosphere of N2 gas in ovendried glassware unless otherwise noted. Dehydrated solvents (toluene, hexane, MeCN, DMSO) were purchased from FUJIFILM Wako Pure Chemical Corporation and stored under nitrogen atmosphere. Dehydrated THF was purchased from Kanto Chemical Co., Inc. and stored under nitrogen atmosphere. Dehydrated 1,2-dimethoxyethane (DME) and 1,2-dichloroethane were purchased from Sigma-Aldrich Co. LLC and stored under nitrogen atmosphere. Sodium trimethylsilyldimethylsilanolate (2-Me),<sup>1</sup> sodium benzyldimethylsilyldimethylsilanolate (2-Benzyl),<sup>1</sup> sodium allyldimethylsilyldimethylsilanolate (**2-Allyl**),<sup>1</sup> 1-((tertbutyldimethylsilyl)oxy)-4-chlorobenzene (1e),<sup>2</sup> tert-butyl 4-chlorobenzoate (1h),<sup>3</sup> N-methyl-5chloroindole (1i),<sup>4</sup> 1-chloro-3,4-dihydronaphthalene (1k),<sup>5</sup> 4-*tert*-butyl-1-chlorocyclohexene (11),<sup>6</sup> 4-chlorophenyl(pinacolato)borane (1t),<sup>7</sup> and SC-560 (1u)<sup>8</sup> were prepared according to the literature. All other reagents were commercially available and used without further purification unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25-mm thick, silica gel 60 F<sub>254</sub>. Preparative flash chromatography was performed using Silica Gel (Wakosil® C-300 purchased from FUJIFILM Wako Pure Chemical Corporation, or Silica Gel 60N, spherical neutral, particle size 100-210 µm, purchased from Kanto Chemical Co., Inc.) and Alumina (activated 200 purchased from Nacalai Tesque, Inc.). Preparative recycling gel permeation chromatography (GPC) was performed on a JAI LC-9260 II NEXT system using CHCl<sub>3</sub> as the eluent.

## **Optimisation of Reaction Conditions**

MeO 14 0.20 r (0.17	A CI + Si-Si-NaO NaO nmol 2.0 equiv Y M)	10 mol% Ni catalyst toluene, 70 °C, 12 h	MeO Si 3a
entry	Ni catalyst	<b>3a</b> (%) <sup>[a]</sup>	<b>1a</b> (%) <sup>[a]</sup>
1	NiCl <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub>	47	9
2	NiCl <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub>	20	41
3	NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	28	49
4	NiCl <sub>2</sub> (dcype)	14	55
5	NiCl <sub>2</sub> (dppe)	6	65
6	NiCl <sub>2</sub> (dppf)	21	45
7	NiCl <sub>2</sub> (PPh <sub>3</sub> )(IPr)	24	14
8	NiCl <sub>2</sub> (bpy)	5	62
9	none	0	96

## Table S1. Screening of Ni catalysts

[a] Determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

MeO 0.20 (0.7	CI + -Si-Si- NaO 1a 2-Me 2.0 equiv 17 M)	10 mol% Ni(cod) <sub>2</sub> 20 mol% ligand toluene, 70 °C, 12 h	MeO 3a
entry	ligand	<b>3a</b> (%) <sup>[a]</sup>	<b>1a</b> (%) <sup>[a]</sup>
1	PCy <sub>3</sub>	47	10
2	$P(c-Pent)_3$	39	11
3	PtBu <sub>3</sub>	37	15
4	JohnPhos (10 mol%)	21	10
5	PCy <sub>2</sub> Ph	47	21
6	PEt <sub>2</sub> Ph	65	2
7	PMe <sub>2</sub> Ph	71	5
8 <sup>[b]</sup>	PMe <sub>2</sub> Ph	50	24
9	PMePh <sub>2</sub>	54	18

Table S2. Screening of ligands

[a] Determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

[b] 5 mol% Ni(cod)<sub>2</sub>, 10 mol% PMe<sub>2</sub>Ph were used.

MeO 1 0.20 (0.1	La 2-Me mmol 2.0 equiv 7 M)	10 mol% Ni(cod) <sub>2</sub> 20 mol% PMe <sub>2</sub> Ph solvent, 70 °C, 12 h	MeO 3a
entry	solvent	<b>3a</b> (%) <sup>[a]</sup>	<b>1a</b> (%) <sup>[a]</sup>
1	toluene	71	5
2	THF	52	10
3	DME	42	8
4	hexane	56	10
5	1,2-dichloroethane	0	93
6	MeCN	3	77
7	DMSO	3	71

[a] Determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

ſ		10 mol% Ni(cod) <sub>2</sub> 20 mol% PMe <sub>2</sub> Ph	Si
MeO	NaO NaO	toluene, temp., 12 h	MeO
1	a 2-Me		3a
(0.17	7 M)		
entry	temperature	<b>3a</b> (%) <sup>[a]</sup>	<b>1a</b> (%) <sup>[a]</sup>
1	60 °C	51	30
2	70 °C	71	5
3	80 °C	71	6

## Table S4. Screening of reaction temperatures

[a] Determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

## Table S5. Screening of amounts of ligand

	_CI	10 mol% Ni(cod) <sub>2</sub> X mol% PMe <sub>2</sub> Ph	Si Si
MeO	NaO	toluene, 70 °C, 12 h	MeO
<b>1a</b> 0.20 mmol (0.17 M)	<b>2-Me</b> 2.0 equiv		3a
entry	Х	<b>3a</b> (%) <sup>[a]</sup>	<b>1a</b> (%) <sup>[a]</sup>
1	10	60	13
2	20	71	5
3	30	57	12

[a] Determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

		10 mol% Ni(cod) <sub>2</sub> 20 mol% PMe <sub>2</sub> Ph	Si
MeO		toluene, 70 °C, 12 h	MeO
<b>1a</b> 0.20 mm (X M)	<b>2-Me</b> ol 2.0 equiv		3a
entry	Х	<b>3a</b> (%) <sup>[a]</sup>	<b>1a</b> (%) <sup>[a]</sup>
1	0.10	53	26
2	0.17	71	5
3	0.25	71	3
4	0.33	69	1

Table S6. Screening of reaction concentration

[a] Determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

T٤	ıb	le	<b>S7</b> .	Screening	of amounts	of 2-Me and	reaction time
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MeO	CI + -Si- <mark>Si</mark> - NaO	10 mol% Ni(cod)₂ 20 mol% PMe₂Ph toluene, 70 °C, 12 h	MeO
<b>1a</b> 0.20 mmol (0.17 M)	<b>2-Me</b> I X equiv		3a
entry	Х	<b>3a</b> (%) <sup>[a]</sup>	<b>1a</b> (%) <sup>[a]</sup>
1	1.5	64	12
2	2.0	71	5
3 <sup>[b]</sup>	2.0	77	2
4	2.5	82	0
5	3.0	81	0

[a] Determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.[b] 18 h.

#### **Experimental Procedures**

General Procedure for Silylation of Aryl Chlorides with Sodium Silylsilanolates (GP1, Scheme 1)



The synthesis of **3a** is representative. An oven-dried 20-mL Schlenk tube equipped with a septum and a magnetic stir bar was charged with Ni(cod)<sub>2</sub> (27.5 mg, 0.100 mmol) and toluene (0.50 mL). After the mixture was stirred at room temperature for 5 min, PMe<sub>2</sub>Ph (28.5 µL, 0.200 mmol) and toluene (0.50 mL) were added to the mixture. The mixture was stirred at room temperature for 5 min to give a solution of the nickel complex (0.10 M). Another oven-dried 20-mL Schlenk tube equipped with a septum and a magnetic stir bar was charged with 2-Me (213 mg, 1.25 mmol) and toluene (1.5 mL). The mixture was stirred at room temperature for 5 min. The solution of the nickel complex (0.50 mL) and 1a (60.4  $\mu$ L, 0.500 mmol) were sequentially added to the mixture, and toluene (1.0 mL) was added to wash the inner side of the tube. The septum was removed and the tube was capped with a greaseless stopcock. The resulting mixture was stirred at 70 °C on a preheated aluminum block. After 12 h, saturated aqueous NH<sub>4</sub>Cl solution (5 mL) was added. The mixture was poured into a separatory funnel with EtOAc (20 mL) and water (20 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with EtOAc (20 mL  $\times$  2). The combined organic extract was washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with an eluent (hexane/EtOAc = 99/1 to 97/3) to provide **3a** (75.9 mg, 0.421 mmol, 84 %) as a colorless oil.

## General Procedure for Silylation of Aryl Chlorides with Sodium Silylsilanolates (GP2, Scheme 2)



The synthesis of **3h** is representative. An oven-dried 20-mL Schlenk tube equipped with a septum and a magnetic stir bar was charged with Ni(cod)<sub>2</sub> (27.5 mg, 0.100 mmol), PCy<sub>2</sub>Ph (54.9 mg, 0.200 mmol), and toluene (1.0 mL). The mixture was stirred at room temperature for 5 min to give a solution of the nickel complex (0.10 M). Another oven-dried 20-mL Schlenk tube equipped with a septum and a magnetic stir bar was charged with 2-Me (213 mg, 1.25 mmol) and toluene (1.5 mL). The mixture was stirred at room temperature for 5 min. The solution of the nickel complex (0.50 mL) and 1h (106 mg, 0.498 mmol) were sequentially added to the mixture, and toluene (1.0 mL) was added to wash the inner side of the tube. The septum was removed and the tube was capped with a greaseless stopcock. The resulting mixture was stirred at 70 °C on a preheated aluminum block. After 12 h, saturated aqueous NH<sub>4</sub>Cl solution (5 mL) was added. The mixture was poured into a separatory funnel with EtOAc (20 mL) and water (20 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with EtOAc (20 mL  $\times$  2). The combined organic extract was washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with an eluent (hexane/EtOAc = 40/1) and then GPC (eluent: CHCl<sub>3</sub>) to provide **3h** (103 mg, 0.411 mmol, 82%) as a colorless oil.

### **Characterisation Data**

## (4-Methoxyphenyl)trimethylsilane (3a):



 $R_f = 0.38$  (hexane). All the resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>9</sup>

#### (2-Methoxyphenyl)trimethylsilane (3b):

Synthesized via **GP1** by using **2-Me** (298 mg, 1.75 mmol) and the solution of the nickel complex (0.10 M, 1.00 mL). Reaction time was 18 h. Obtained as a colorless oil (57.5 mg, 0.319 mmol, 64%) from **1b** (59.4  $\mu$ L, 0.500 mmol). Purification was done by column chromatography on silica gel (hexane/DCM = 19/1 to 4/1) and then GPC (eluent: CHCl<sub>3</sub>). R<sub>f</sub> = 0.45 (hexane/DCM = 4/1). All the resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>10</sup>

#### (3-Methoxyphenyl)trimethylsilane (3c):

MeO Synthesized via **GP1**. Reaction time was 18 h. Obtained as a colorless oil (59.1 mg, 0.328 mmol, 66%) from **1c** (60.9  $\mu$ L, 0.500 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 99/1 to

24/1) and then GPC (eluent; CHCl<sub>3</sub>).  $R_f = 0.32$  (hexane/EtOAc = 50/1). All the resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>9</sup>

#### (4-Butylphenyl)trimethylsilane (3d):



Synthesized via **GP1** by using **2-Me** (298 mg, 1.75 mmol) and the solution of the nickel complex (0.10 M, 1.00 mL). Reaction time was 18 h. Obtained as a colorless oil (65.5 mg, 0.317 mmol, 63%) from **1d** (84.3  $\mu$ L, 0.500

mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/0 to 99/1) and then GPC (eluent: CHCl<sub>3</sub>). R<sub>f</sub> = 0.68 (hexane). All the resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>10</sup>

#### *tert*-Butyldimethyl(4-trimethylsilylphenoxy)silane (3e):



Synthesized via **GP1**. Reaction time was 15 h. Obtained as a colorless oil (103 mg, 0.367 mmol, 74%) from **1e** (121 mg, 0.498 mmol). Purification was done by column chromatography on silica gel (hexane)

and then GPC (eluent: CHCl<sub>3</sub>).  $R_f = 0.36$  (hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.37 (td, J = 5.1, 2.7 Hz, 2H), 6.83 (td, J = 5.1, 2.7 Hz, 2H), 0.98 (s, 9H), 0.23 (s, 9H), 0.20 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  156.5, 134.8, 132.1, 119.7, 25.8, 18.3, -0.8, -4.2; HRMS (APCI-MS, positive): m/z [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>28</sub>OSi<sub>2</sub> 280.1673; Found 280.1680.

#### 4-(4-Trimethylsilylphenyl)morpholine (3f):



Synthesized via **GP1** by using **2-Me** (298 mg, 1.75 mmol) and the solution of the nickel complex (0.10 M, 1.00 mL). Reaction time was 18 h. Obtained as a white solid (85.4 mg, 0.363 mmol, 73%) from **1f** (98.8 mg, 0.500 mmol). Purification was done by column chromatography on

silica gel (hexane/EtOAc = 1/0 to 10/1). R<sub>f</sub> = 0.37 (hexane/EtOAc = 8/1). All the resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>11</sup>

#### 5-Trimethylsilyl-1,3-benzodioxole (3g):



Synthesized via **GP1**. Reaction time was 18 h. Obtained as a colorless oil (63.0 mg, 0.324 mmol, 65%) from **1g** (58.4  $\mu$ L, 0.500 mmol). Purification was done by column chromatography on silica gel (hexane/DCM = 1/0 to

10/1) and then GPC (eluent: CHCl<sub>3</sub>).  $R_f = 0.36$  (hexane/DCM = 10/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 6.99 (d, J = 7.5 Hz, 1H), 6.97 (s, 1H), 6.84 (d, J = 7.5 Hz, 1H), 5.93 (s, 2H), 0.23 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  148.3, 147.4, 133.6, 127.3, 112.8, 108.6, 100.6, -0.8; HRMS (APCI-MS, positive): m/z [M]<sup>+</sup> Calcd for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>Si 194.0758; Found 194.0754.

#### tert-Butyl 4-trimethylsilylbenzoate (3h):



Synthesized via **GP1**. Obtained as a colorless oil (69.3 mg, 0.277 mmol, 56%) from **1h** (106 mg, 0.498 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 40/1) and then GPC

(eluent: CHCl<sub>3</sub>).

Also synthesized via **GP2**. Obtained as a colorless oil (103 mg, 0.411 mmol, 82%) from **1h** (106 mg, 0.498 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 40/1) and then GPC (eluent: CHCl<sub>3</sub>).

 $R_f = 0.40$  (hexane/EtOAc = 30/1). All the resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>9</sup>

#### 1-Methyl-5-trimethylsilyl-1*H*-indole (3i):

Synthesized via **GP1**. Obtained as a colorless oil (64.3 mg, 0.316 mmol, 63%) from **1i** (82.8 mg, 0.500 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/0 to 30/1) and then GPC (eluent: CHCl<sub>3</sub>). R<sub>f</sub> = 0.43 (hexane/EtOAc = 30/1). All the resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>12</sup>

#### 5-Trimethylsilyl-3-methylbenzo[*b*]thiophene (3j):



Synthesized via **GP1** by using **2-Me** (298 mg, 1.75 mmol) and the solution of the nickel complex (0.10 M, 1.00 mL). Reaction time was 18 h. Obtained as a colorless oil (50.1 mg, 0.227 mmol, 45%) from **1**j (91.3 mg, 0.500 mmol).

Purification was done by column chromatography on silica gel (hexane) and then GPC (eluent: CHCl<sub>3</sub>).  $R_f = 0.64$  (hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.86–7.85 (m, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 2.47 (s, 3H), 0.33 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  141.2, 139.3, 135.3, 132.2, 128.8, 126.8, 122.3, 121.3, 14.0, -0.7; HRMS (APCI-MS, positive): *m/z* [M]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>16</sub>SSi 220.0737; Found 220.0736.

#### 1-Trimethylsilyl-3,4-dihydronaphthalene (3k):

Synthesized via **GP1**. Obtained as a colorless oil (58.5 mg, 0.289 mmol, 58%) from **1k** (82.3 mg, 0.500 mmol). Purification was done by column chromatography on silica gel (hexane) and then GPC (eluent: CHCl<sub>3</sub>).  $R_f = 0.62$  (hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.26–7.25 (m, 1H), 7.17 (td, J = 6.2, 2.7 Hz, 1H), 7.13–7.10 (m, 2H), 6.43 (t, J = 4.8 Hz, 1H), 2.70 (t, J = 8.2 Hz, 2H), 2.27–2.24 (td, J = 8.2, 4.8 Hz, 2H), 0.25 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  139.7, 138.2, 136.7, 136.2, 128.0, 126.5, 126.4, 126.3, 28.1, 24.3, –0.1; HRMS (APCI-MS, positive): m/z [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>19</sub>Si 203.1251; Found 203.1255.

#### 4-tert-Butyl-1-trimethylsilylcyclohexene (31):



Synthesized via **GP1**. Obtained as a colorless oil (44.1 mg, 0.210 mmol, 42%) from **11** (86.4 mg, 0.500 mmol). Purification was done by column chromatography on silica gel (hexane) and then GPC (eluent: CHCl<sub>3</sub>).  $R_f =$ 

0.83 (hexane). All the resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>9</sup>

## Ethyl 4-(8-trimethylsilyl-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11ylidene)piperidine-1-carboxylate (3m):



Synthesized via **GP1** by using **2-Me** (298 mg, 1.75 mmol) and the solution of the nickel complex (0.10 M, 1.00 mL). Reaction time was 18 h. Obtained as a white solid (160 mg, 0.380 mmol, 76%) from **1m** (191 mg, 0.500 mmol). Purification was done by column chromatography on silica gel (DCM/MeOH = 100/1 to 40/1) and then GPC (eluent: CHCl<sub>3</sub>).  $R_f = 0.32$  (DCM/MeOH = 40/1); <sup>1</sup>H NMR

(CDCl<sub>3</sub>):  $\delta$  8.37 (dd, J = 4.8, 1.4 Hz, 1H), 7.42 (dd, J = 7.5, 1.4 Hz, 1H), 7.31 (d, J = 7.5 Hz, 1H), 7.30 (s, 1H), 7.18 (d, J = 6.9 Hz, 1H), 7.06 (dd, J = 7.4, 5.0 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.82 (br, 2H), 3.46–3.33 (m, 2H), 3.14–3.09 (m, 2H), 2.88–2.82 (m, 2H), 2.47 (m, 1H), 2.39 (m, 2H), 2.31 (m, 1H), 1.24 (t, J = 7.2 Hz, 3H), 0.23 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  157.5, 155.5, 146.5, 139.7, 139.4, 137.4, 136.8, 136.7, 135.4, 134.1, 133.7, 131.0, 128.6, 122.1, 61.3, 45.0, 44.9, 31.9, 31.8, 30.8, 30.6, 14.7, –1.1; HRMS (APCI-MS, positive): m/z [M+H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub>Si 421.2306; Found 421.2302.

#### 1-(2-(Phenyl(4-trimethylsilylphenyl)methoxy)ethyl)piperidine (3n):



Synthesized via **GP1** by using **2-Me** (302 mg, 1.77 mmol) and the solution of the nickel complex (0.10 M, 1.01 mL). Reaction time was 18 h. Obtained as a pale yellow oil (109 mg, 0.297 mmol, 59%) from **1n** (167 mg, 0.506 mmol). Purification was done by column chromatography on silica gel (EtOAc/MeOH =

80/1 to 40/1).  $R_f = 0.41$  (EtOAc/MeOH = 40/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.46–7.44 (m, 2H), 7.36–7.34 (m, 2H), 7.33–7.29 (m, 4H), 7.24–7.21 (m, 1H), 5.36 (s, 1H), 3.59 (t, J = 6.2 Hz, 2H), 2.64 (t, J = 6.2 Hz, 2H), 2.44 (br, 4H), 1.56–1.55 (m, 4H), 1.41 (m, 2H), 0.23 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  143.0, 142.4, 139.5, 133.5, 128.5, 127.5, 127.1, 126.4, 84.1, 67.3, 58.8, 55.1, 26.1, 24.4, –1.0; HRMS (APCI-MS, positive): m/z [M+H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>34</sub>NOSi 368.2404; Found 368.2405.

## *N*,*N*-Dimethyl-3-(3-trimethylsilyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepin-5-yl)propan-1amine (30):

Synthesized via **GP1** by using **2-Me** (346 mg, 2.03 mmol) and the solution of the nickel complex (0.10 M, 1.02 mL). Reaction time was 24 h. Obtained as a pale yellow oil (124 mg, 0.352 mmol, 69%) from **10** (160 mg, 0.508 mmol). Purification was done by column



chromatography on silica gel (CHCl<sub>3</sub>/MeOH = 50/1 to 20/1).  $R_f$  = 0.32 (CHCl<sub>3</sub>/MeOH = 20/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.21 (s, 1H), 7.13– 7.05 (m, 5H), 6.89 (m, 1H), 3.80 (t, *J* = 7.2 Hz, 2H), 3.14 (s, 4H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.15 (s, 6H), 1.75–1.70 (m, 2H), 0.24 (s, 9H); <sup>13</sup>C

NMR (CDCl<sub>3</sub>): δ 148.4, 147.9, 138.2, 135.2, 134.2, 129.9, 129.3, 127.5, 126.4, 124.8, 122.4, 120.2, 57.9, 49.0, 45.7, 32.4, 32.3, 26.3, -0.9; HRMS (APCI-MS, positive): *m*/*z* [M+H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>33</sub>N<sub>2</sub>Si 353.2408; Found 353.2414.

#### 4-Trimethylsilylbenzonitrile (3p):



Synthesized via GP2. Obtained as a pale yellow oil (63.4 mg, 0.362 mmol, 72%) from 1p (68.8 mg, 0.500 mmol). Purification was done by column chromatography on silica gel (hexane/Et<sub>2</sub>O = 99/1 to 9/1) and then GPC

(eluent: CHCl<sub>3</sub>).  $R_f = 0.35$  (hexane/Et<sub>2</sub>O = 20/1). All the resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>10</sup>

#### 4'-Trimethylsilylacetophenone (3q):



Synthesized via **GP2**. Reaction time was 18 h. Obtained as a pale yellow oil (58.1 mg, 0.302 mmol, 60%) from **1q** (65.0  $\mu$ L, 0.500 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/0 to 30/1) and then GPC (eluent: CHCl<sub>3</sub>). R<sub>f</sub> = 0.29 (hexane/EtOAc = 30/1). All

the resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>10</sup>

#### 3-Trifluoromethyl-5-trimethylsilylbenzonitrile (3r):



Synthesized via **GP2**. Obtained as a colorless oil (73.5 mg, 0.302 mmol, 60%) from **1r** (73.4  $\mu$ L, 0.500 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/0 to 94/6) and then GPC (eluent: CHCl<sub>3</sub>). R<sub>f</sub> = 0.30 (hexane/EtOAc = 40/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.95

(s, 1H), 7.92 (s, 1H), 7.88 (s, 1H), 0.34 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  144.7, 140.1, 133.8 (d, *J* = 4.3 Hz), 131.2 (q, *J* = 33.2 Hz), 129.1 (d, *J* = 4.3 Hz), 123.3 (q, *J* = 273.1 Hz), 118.0, 113.0, -1.4; <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -63.4; HRMS (APCI-MS, positive): *m/z* [M+H]<sup>+</sup> Calcd for C<sub>11</sub>H<sub>13</sub>F<sub>3</sub>NSi 244.0764; Found 244.0773.

#### 2-Naphthyltrimethylsilane (3s):



Synthesized via **GP2**. Obtained as a colorless oil (79.9 mg, 0.399 mmol, 80%) from **1s** (81.3 mg, 0.500 mmol). Purification was done by column chromatography on silica gel (hexane).  $R_f = 0.54$  (hexane). All the

resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>9</sup>

#### Trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (3t):



Synthesized via **GP2**. Obtained as a white solid (50.7 mg, 0.184 mmol, 37%) from **1t** (119 mg, 0.499 mmol). Purification was done by column chromatography on silica gel (hexane/Et<sub>2</sub>O = 99/1 to 9/1) and then GPC (eluent: CHCl<sub>3</sub>).  $R_f = 0.40$  (hexane/Et<sub>2</sub>O = 20/1). All the resonances in

<sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>13</sup>

#### 1-(4-Methoxyphenyl)-3-trifluoromethyl-5-(4-trimethylsilylphenyl)-1*H*-pyrazole (3u):



Synthesized via **GP2**. Obtained as a white solid (143 mg, 0.366 mmol, 73%) from **1u** (176 mg, 0.499 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/0 to 30/1) and then GPC (eluent: CHCl<sub>3</sub>).  $R_f$  = 0.36 (hexane/EtOAc = 20/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.46 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.9 Hz, 2H),

7.19 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 6.73 (s, 1H), 3.83 (s, 3H), 0.26 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  159.6, 144.7, 142.9 (q, J = 37.6 Hz), 141.8, 133.7, 132.6, 129.4, 127.9, 127.0, 121.5 (q, J = 268.8 Hz), 114.4, 105.2, 55.6, -1.2; <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -62.5; HRMS (APCI-MS, positive): m/z [M+H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>22</sub>F<sub>3</sub>N<sub>2</sub>OSi 391.1448; Found 391.1452.

#### *tert*-Butyl 4-(1,1,3,3,3-pentamethyldisiloxaneyl)benzoate (4h):



Synthesized via **GP1**. Obtained as a colorless oil (29.3 mg, 0.0838 mmol, 17%, 90% purity, contaminated with **3h**) from **1h** (106 mg, 0.498 mmol). Purification was done by column chromatography on

silica gel (hexane/EtOAc = 40/1) and then GPC (eluent: CHCl<sub>3</sub>).  $R_f = 0.35$  (hexane/EtOAc = 30/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.96 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 1.59 (s, 9H), 0.32 (s, 6H), 0.08 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  166.1, 145.7, 132.9, 132.6, 128.5, 81.0, 28.3, 2.1, 0.9; HRMS (APCI-MS, positive): m/z [M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>28</sub>O<sub>3</sub>Si<sub>2</sub> 324.1571; Found 324.1579.

#### Benzyl(4-methoxyphenyl)dimethylsilane (5):



Synthesized via **GP1** by using **2-Benzyl** (308 mg, 1.25 mmol). Reaction time was 18 h. Obtained as a colorless oil (73.6 mg, 0.287 mmol, 57%) from **1a** (60.4  $\mu$ L, 0.500 mmol). Purification was done by column

chromatography on silica gel (hexane/DCM = 20/1 to 4/1) and then GPC (eluent: CHCl<sub>3</sub>). R<sub>f</sub> = 0.39 (hexane/DCM = 4/1). All the resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>14</sup>

#### Allyl(4-methoxyphenyl)dimethylsilane (6):



Synthesized via **GP1** by using **2-Allyl** (245 mg, 1.25 mmol). Obtained as a colorless oil (65.2 mg, 0.316 mmol, 63%) from **1a** (60.4  $\mu$ L, 0.500 mmol). Purification was done by column chromatography on silica gel

(hexane/DCM = 94/6 to 1/1) and then GPC (eluent: CHCl<sub>3</sub>).  $R_f = 0.33$  (hexane/DCM = 4/1). All the resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the reported values.<sup>15</sup>

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Figure S1. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3a



Figure S2. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3a



Figure S3. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **3b** 



Figure S4. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of **3b** 



Figure S5. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3c



Figure S6. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3c



Figure S7. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3d



Figure S8. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3d



Figure S9. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3e



Figure S10. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3e



Figure S11. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **3f** 



Figure S12. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3f



Figure S13. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3g



Figure S14. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3g



Figure S15. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **3h** 



Figure S16. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3h



Figure S17. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3i



Figure S18. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3i



Figure S19. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3j



Figure S20. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3j



Figure S21. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3k



Figure S22. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3k



Figure S23. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 31



Figure S24. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 31



Figure S25. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **3m** 



Figure S26. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3m



Figure S27. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3n



Figure S28. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3n



Figure S29. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 30



Figure S30. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 30



Figure S31. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **3p** 



Figure S32. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3p



Figure S33. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3q



Figure S34. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3q



Figure S35. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3r



Figure S36. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3r



Figure S37. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 3r



Figure S38. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3s



Figure S39. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3s



Figure S40. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 3t



Figure S41. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3t



Figure S42. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **3u** 



Figure S43. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 3u



Figure S44. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of **3u** 



Figure S45. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 4h



Figure S46. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 4h



Figure S47. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 5



Figure S48. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 5



Figure S49. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 6



Figure S 50. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of 6