

# Supporting Information

## **Palladium-catalyzed domino Heck-disilylation and Heck-monosilylation of alkene-tethered carbamoyl chlorides: synthesis of versatile silylated oxindoles**

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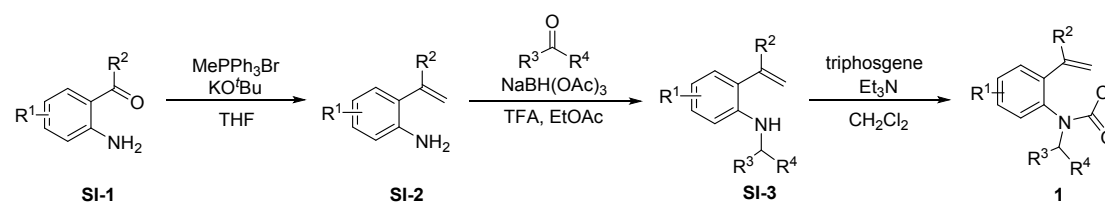
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## General information:

The  $^1\text{H}$  NMR,  $^{19}\text{F}$  NMR and  $^{13}\text{C}$  NMR were recorded with Bruker 400 MHz spectrometer instruments in  $\text{CDCl}_3$ . The chemical shifts ( $\delta$ ) of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were measured in ppm, referenced to residual  $^1\text{H}$  and  $^{13}\text{C}$  signals of nondeuterated  $\text{CDCl}_3$  ( $\delta = 7.26$  and  $77.00$ ) as internal standards. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. HRMS were recorded on VG ZAB-HS mass spectrometer with ESI resource.

## Preparation of Starting Materials:

**General Procedure 1:** (ref: *Org. Biomol. Chem.*, 2019, **17**, 8358.)

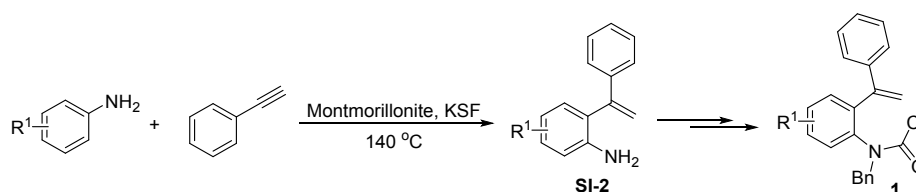


A mixture of MePPh<sub>3</sub>Br (1.5 equiv) and KO<sup>t</sup>Bu (1.5 equiv) in THF (0.3 mmol/mL) was stirred at room temperature for 1 h. Then **SI-1** (1.0 equiv) was added dropwise to the reaction mixture at 0 °C. The reaction was stirred at room temperature until the starting material was disappeared. After that the solvents were evaporated under reduced pressure. The residue was purified by column chromatography to give **SI-2**.

The **SI-2** (1.0 equiv) was dissolved in ethyl acetate (0.25 M). The aldehyde or ketone (1.2 equiv) was added followed by trifluoroacetic acid (2.0 equiv). The reaction was stirred for 30 minutes then sodium triacetoxyborohydride (2.0 equiv) was added. The reduction was stirred for 2 h then quenched with 4 M NaOH. The reaction was diluted with ethyl acetate and washed twice with brine. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude was purified by flash column chromatography to give **SI-3**.

The **SI-3** (1.0 equiv) was dissolved in dichloromethane (0.3 M) and cooled to 0 °C. Then triethylamine (2.0 equiv) was added followed by triphosgene (0.5 equiv). The reaction was warmed to room temperature and stirred until completion indicated by TLC. The reaction was quenched with water and extracted twice with dichloromethane. The organic layers were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude starting materials were purified by flash column chromatography in ethyl acetate/petroleum ether mixtures to give **1**.

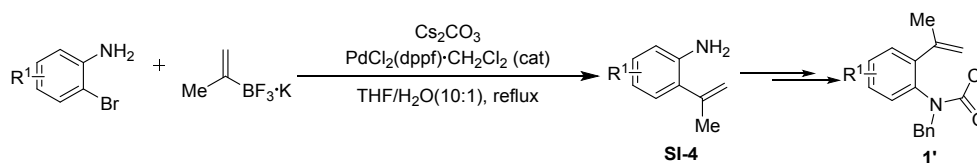
**General Procedure 2:** (ref: *Org. Biomol. Chem.*, 2019, **17**, 8358.)



Aniline (1.0 equiv), phenylacetylene (1.1 equiv) and montraorillonite KSF (100.0 mg/mmol) are introduced in a round bottomed flask equipped with magnetic stirrer and a reflux condenser. The reaction mixture is heated at 140 °C for 5 hours and then cooled to room temperature. The crude mixtures were dissolved with dichloromethane and filtered. Then the solvents were concentrated in vacuo and the crude was purified by column chromatography (silica gel, appropriate mixture of petroleum ether/ethyl acetate) to give **SI-2**.

(Note: The remaining procedure follows the **General Procedure 1**.)

**General Procedure:** (ref: *Org. lett.*, 2018, **20**, 7929.)

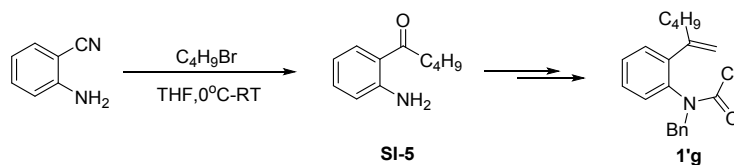


To a suspension of potassium isopropenyltrifluoroborate (1.1 equiv), Cs<sub>2</sub>CO<sub>3</sub> (3.0 equiv), PdCl<sub>2</sub>(dppf)•CH<sub>2</sub>Cl<sub>2</sub> (9.0 mol%) in a solvent mixture (THF/H<sub>2</sub>O = 10/1) was added 2-bromoaniline (1.0 equiv). The reaction mixture was stirred at reflux for 16 h, then cooled to room temperature and diluted with water (30 mL) followed by extraction with ethyl acetate (50 mL x 3). The combined organic layer was washed with saturated sodium chloride (50 mL), dried over MgSO<sub>4</sub>, concentrated under

reduced pressure and the crude product was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether as an eluent) to give the desired products **SI-4**.

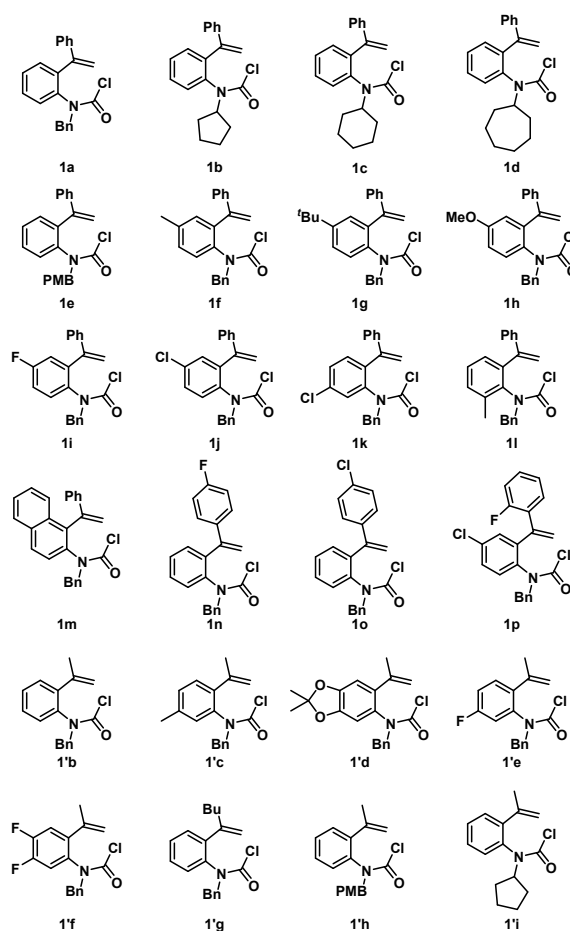
(Note: The remaining procedure follows the **General Procedure 1**.)

**General Procedure 4:** (ref: *Asian J. Org. Chem.*, 2018, 7, 1124.)



To a solution of 2-amino-benzonitrile (1.0 equiv) in dry THF (0.2 mmol/ mL). Then the solution of the Grignard reagents (2.7 equiv) in THF solution was slowly added dropwise at 0 °C over 30 min. Then the resulting mixture was stirred at ambient temperature overnight. Addition of a saturated aqueous NH<sub>4</sub>Cl solution produced a suspension mixture, then filtered, and extracted with EtOAc. The combined organics were dried over MgSO<sub>4</sub>. After that the solvents were evaporated under reduced pressure. The residue was purified by column chromatography to give **SI-5**.

(Note: The remaining procedure follows the **General Procedure 1**.)



**1a-1e, 1j, 1i-1m, 1'b, 1'h, 1'i** were synthesized by **general procedure 1**

**1f-1i, 1k-1m** were synthesized by **general procedure 2**

**1'c-1'f** were synthesized by **general procedure 3**

**1'g** was synthesized by **general procedure 4**

All of the starting materials are known compounds.

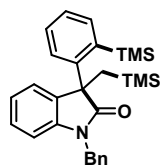
### General Procedure for the Synthesis of Disilylated Oxindoles

In a 38 mL sealed tube, the mixture of **1** (0.20 mmol), **2a** (0.60 mmol), Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol), K<sub>2</sub>CO<sub>3</sub> (82.8 mg, 0.60 mmol) were dissolved in anhydrous DMF (2.0 mL). Then, the tube was purged with N<sub>2</sub> for three times and sealed with PTEF cap. The reaction mixture was stirred at room temperature for 12 h. When the reaction was finished, the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum Ether) to give the products **3**.

### General Procedure for the Synthesis of Monosilylated Oxindoles

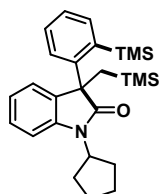
In a 38 mL sealed tube, the mixture of **1'** (0.20 mmol), **2a** (0.60 mmol), Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol), K<sub>2</sub>CO<sub>3</sub> (82.8 mg, 0.6 mmol) were dissolved in anhydrous DMF (2.0 mL). Then, the tube was purged with N<sub>2</sub> for three times and sealed with PTEF cap. The reaction mixture was heated to 100 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum Ether) to give the products **4**.

### Characterization of Products:



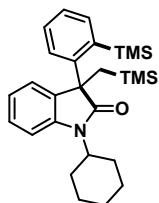
1-benzyl-3-((trimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one (**3a**)

White solid (83 mg, 91%) M.P.: 90-94 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 – 7.82 (m, 1H), 7.33 – 7.27 (m, 5H), 7.24 – 7.19 (m, 2H), 7.14 – 7.03 (m, 3H), 6.84 (d,  $J = 8.0$  Hz, 1H), 6.81 – 6.78 (m, 1H), 5.32 (d,  $J = 15.2$  Hz, 1H), 4.55 (d,  $J = 15.6$  Hz, 1H), 2.38 (d,  $J = 13.6$  Hz, 1H), 1.75 (d,  $J = 13.6$  Hz, 1H), 0.59 (s, 9H), –0.23 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.3, 148.9, 142.4, 138.7, 137.6, 136.9, 136.0, 128.7, 128.7, 128.6, 127.8, 127.5, 126.0, 125.0, 122.8, 109.1, 57.0, 43.9, 27.8, 4.4, –0.7. ESI-MS: Calcd for  $\text{C}_{28}\text{H}_{35}\text{NOSi}_2$ :  $[\text{M}+\text{H}^+]$  458.2330, found 458.2330.



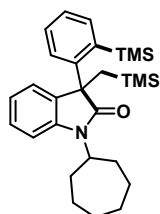
1-cyclopentyl-3-((trimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one  
**(3b)**

Yellow oil (70 mg, 81%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 7.2$  Hz, 1H), 7.30 – 7.27 (m, 1H), 7.18 (t,  $J = 7.2$  Hz, 1H), 7.11 – 7.00 (m, 4H), 6.75 (d,  $J = 8.0$  Hz, 1H), 4.96 – 4.86 (m, 1H), 2.31 (d,  $J = 13.6$  Hz, 1H), 2.18 – 1.86 (m, 6H), 1.79 – 1.70 (m, 2H), 1.69 (d,  $J = 13.6$  Hz, 1H), 0.57 (s, 9H), –0.25 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.3, 149.3, 141.4, 138.6, 137.5, 137.2, 128.5, 128.5, 127.5, 125.9, 125.4, 122.2, 110.0, 56.7, 51.9, 27.8, 27.8, 27.2, 27.0, 25.1, 25.1, 4.5, –0.7. ESI-MS: Calcd for  $\text{C}_{26}\text{H}_{37}\text{NOSi}_2$ :  $[\text{M}+\text{H}^+]$  436.2486, found 436.2496.



1-cyclohexyl-3-((trimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one **(3c)**  
Yellow oil (77 mg, 86%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 – 7.78 (m, 1H), 7.30 – 7.27 (m, 1H), 7.19 – 7.14 (m, 2H), 7.09 – 7.00 (m, 3H), 6.66 (d,  $J = 8.0$  Hz, 1H), 4.29 – 4.21 (m, 1H), 2.36 (d,  $J = 13.6$  Hz, 1H), 2.25 – 2.10 (m, 2H), 1.91 – 1.87 (m, 3H), 1.75 (d,  $J = 12.8$  Hz, 2H), 1.65 (d,  $J = 13.6$  Hz, 1H), 1.51 – 1.23 (m, 3H), 0.59 (s, 9H), –0.23 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.1, 149.7, 142.4, 138.5, 137.5, 137.3,

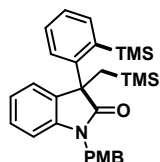
128.5, 128.4, 127.5, 125.8, 125.3, 122.1, 110.2, 56.5, 51.9, 29.1, 28.9, 27.1, 27.1, 25.9, 25.4, 4.6, -0.6. ESI-MS: Calcd for C<sub>27</sub>H<sub>39</sub>NOSi<sub>2</sub>: [M+H<sup>+</sup>] 450.2643, found 450.2648.



1-cycloheptyl-3-((trimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one

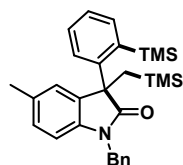
**(3d)**

Yellow oil (91 mg, 99%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 – 7.79 (m, 1H), 7.30 – 7.24 (m, 1H), 7.19 – 7.14 (m, 1H), 7.09 – 7.01 (m, 4H), 6.64 – 6.62 (m, 1H), 4.51 – 4.45 (m, 1H), 2.36 (d, *J* = 13.6 Hz, 1H), 2.26 – 2.17 (m, 2H), 2.02 – 1.95 (m, 1H), 1.83 – 1.55 (m, 10H), 0.59 (s, 9H), -0.24 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 178.3, 149.7, 142.0, 138.6, 137.5, 137.3, 128.5, 128.4, 127.5, 125.8, 125.2, 122.1, 110.2, 56.6, 53.2, 31.6, 31.1, 27.7, 27.6, 27.1, 27.1, 26.3, 26.0, 4.5, -0.6. ESI-MS: Calcd for C<sub>28</sub>H<sub>41</sub>NOSi<sub>2</sub>: [M+H<sup>+</sup>] 464.2799, found 464.2802.



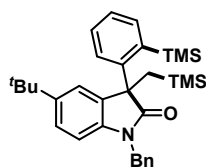
1-(4-methoxybenzyl)-3-((trimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one **(3e)**

Colourless oil (79 mg, 82%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 – 7.83 (m, 1H), 7.29 – 7.20 (m, 4H), 7.14 – 7.01 (m, 3H), 6.89 – 6.84 (m, 3H), 6.79 – 6.75 (m, 1H), 5.25 (d, *J* = 15.6 Hz, 1H), 4.50 (d, *J* = 15.2 Hz, 1H), 3.80 (s, 3H), 2.37 (d, *J* = 13.6 Hz, 1H), 1.75 (d, *J* = 14.0 Hz, 1H), 0.60 (s, 9H), -0.23 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.2, 159.0, 142.7, 142.5, 140.4, 134.6, 131.9, 131.0, 128.8, 128.1, 127.9, 127.8, 127.0, 125.1, 122.4, 114.1, 109.1, 55.2, 54.0, 43.5, 26.1, -0.6, -1.2. ESI-MS: Calcd for C<sub>29</sub>H<sub>37</sub>NO<sub>2</sub>Si<sub>2</sub>: [M+H<sup>+</sup>] 488.2436, found 488.2437.



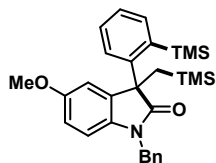
1-benzyl-5-methyl-3-((trimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one (**3f**)

Colourless oil (73 mg, 78%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.20 (m, 6H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.90 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.29 (d, *J* = 15.6 Hz, 1H), 4.54 (d, *J* = 15.2 Hz, 1H), 2.37 (d, *J* = 14.0 Hz, 1H), 2.29 (s, 3H), 1.72 (d, *J* = 13.6 Hz, 1H), 0.59 (s, 9H), –0.22 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.3, 149.0, 140.0, 138.7, 137.5, 137.0, 136.1, 132.3, 128.9, 128.6, 128.6, 128.0, 127.5, 127.5, 125.9, 125.7, 108.8, 57.1, 43.9, 27.9, 26.9, 21.0, 21.0, 4.4, –0.7. ESI-MS: Calcd for C<sub>29</sub>H<sub>37</sub>NOSi<sub>2</sub>: [M+H<sup>+</sup>] 472.2486, found 472.2486.



1-benzyl-5-(tert-butyl)-3-((trimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one (**3g**)

Yellow oil (72 mg, 70%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 – 7.83 (m, 1H), 7.31 – 7.19 (m, 7H), 7.13 – 7.08 (m, 2H), 6.79 – 6.75 (m, 2H), 5.31 (d, *J* = 15.6 Hz, 1H), 4.48 (d, *J* = 15.6 Hz, 1H), 2.36 (d, *J* = 13.6 Hz, 1H), 1.76 (d, *J* = 13.6 Hz, 1H), 1.27 (s, 9H), 0.60 (s, 9H), –0.26 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.5, 149.2, 145.8, 140.0, 138.7, 137.6, 136.2, 128.8, 128.6, 127.6, 127.5, 125.9, 124.4, 122.5, 122.5, 108.5, 108.4, 57.3, 44.0, 34.6, 31.5, 27.8, 4.5, –0.7. ESI-MS: Calcd for C<sub>32</sub>H<sub>43</sub>NOSi<sub>2</sub>: [M+H<sup>+</sup>] 514.2956, found 514.2960.

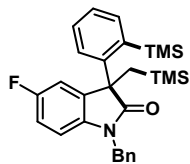


1-benzyl-5-methoxy-3-((trimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one (**3h**)

Yellow oil (81 mg, 83%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 – 7.80 (m, 1H), 7.30 – 7.27 (m, 5H), 7.23 – 7.18 (m, 1H), 7.14 – 7.09 (m, 1H), 6.80 – 6.77 (m, 1H), 6.74 – 6.71 (m, 1H), 6.70 – 6.67 (m, 1H), 5.28 (d, *J* = 15.6 Hz, 1H), 4.49 (d, *J* = 15.2 Hz,

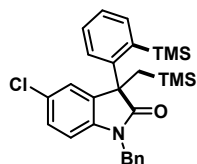


1H), 3.72 (s, 3H), 2.34 (d,  $J = 13.6$  Hz, 1H), 1.70 (d,  $J = 14.0$  Hz, 1H), 0.57 (s, 9H), -0.23 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.1, 156.2, 148.9, 138.6, 138.2, 137.6, 136.1, 136.0, 128.8, 128.7, 127.5, 126.0, 112.7, 112.1, 112.1, 109.5, 57.5, 55.8, 44.0, 27.8, 4.4, -0.7. ESI-MS: Calcd for  $\text{C}_{29}\text{H}_{37}\text{NO}_2\text{Si}_2$ :  $[\text{M}+\text{H}^+]$  488.2436, found 488.2438.



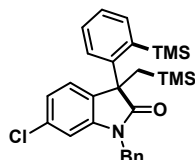
1-benzyl-5-fluoro-3-((trimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one (**3i**)

Colourless oil (70 mg, 74%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.82 (m, 1H), 7.34 – 7.21 (m, 6H), 7.16 – 7.11 (m, 1H), 6.94 – 6.88 (m, 1H), 6.84 – 6.81 (m, 1H), 6.78 – 6.72 (m, 2H), 5.30 (d,  $J = 15.6$  Hz, 1H), 4.53 (d,  $J = 15.6$  Hz, 1H), 2.37 (d,  $J = 13.6$  Hz, 1H), 1.70 (d,  $J = 13.6$  Hz, 1H), 0.57 (s, 9H), -0.20 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.1, 159.4 (d,  $J = 240.0$  Hz), 148.2, 138.6 (d,  $J = 7.0$  Hz), 138.6, 138.3 (d,  $J = 1.0$  Hz), 137.7, 135.7, 128.8, 128.7, 128.6, 127.7, 127.5, 126.2, 114.1 (d,  $J = 23.0$  Hz), 112.9 (d,  $J = 22.0$  Hz), 109.6 (d,  $J = 8.0$  Hz), 57.4, 44.0, 27.7, 4.4, -0.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -120.05. ESI-MS: Calcd for  $\text{C}_{28}\text{H}_{34}\text{FNOSi}_2$ :  $[\text{M}+\text{H}^+]$  476.2236, found 476.2236.



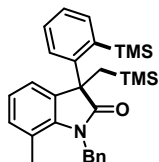
1-benzyl-5-chloro-3-((trimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one (**3j**)

Yellow oil (61 mg, 62%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 7.6$  Hz, 1H), 7.33 – 7.11 (m, 8H), 7.03 (d,  $J = 1.6$  Hz, 1H), 7.77 – 6.71 (m, 2H), 5.25 (d,  $J = 15.2$  Hz, 1H), 4.52 (d,  $J = 15.6$  Hz, 1H), 2.34 (d,  $J = 13.6$  Hz, 1H), 1.67 (d,  $J = 14.0$  Hz, 1H), 0.54 (s, 9H), -0.23 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  178.9, 148.0, 140.9, 138.8, 138.7, 137.8, 135.6, 128.8, 128.7, 128.3, 127.8, 127.5, 126.3, 125.4, 125.4, 110.1, 110.1, 57.2, 44.0, 44.0, 27.9, 27.9, 4.3, -0.7. ESI-MS: Calcd for  $\text{C}_{28}\text{H}_{34}\text{ClNOSi}_2$ :  $[\text{M}+\text{H}^+]$  492.1940, found 492.1947.



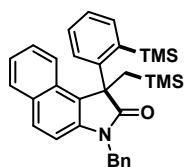
1-benzyl-6-chloro-3-((trimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one (**3k**)

Colourless oil (44 mg, 45%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.82 (m, 1H), 7.31 – 7.13 (m, 8H), 7.10 – 7.05 (m, 1H), 6.95 (d,  $J = 8.4$  Hz, 1H), 6.72 (d,  $J = 7.6$  Hz, 1H), 5.36 (d,  $J = 15.6$  Hz, 1H), 4.35 (d,  $J = 15.6$  Hz, 1H), 2.41 (d,  $J = 13.2$  Hz, 1H), 2.25 (d,  $J = 13.2$  Hz, 1H), 0.61 (s, 9H),  $-0.24$  (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  178.4, 146.9, 144.4, 138.4, 137.9, 135.6, 133.8, 131.5, 129.3, 129.2, 128.8, 127.7, 127.5, 126.2, 124.1, 124.1, 107.5, 57.9, 44.1, 22.7, 4.7,  $-1.1$ . ESI-MS: Calcd for  $\text{C}_{28}\text{H}_{34}\text{ClNOSi}_2$ :  $[\text{M}+\text{H}^+]$  492.1940, found 492.1941.



1-benzyl-7-methyl-3-((trimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one (**3l**)

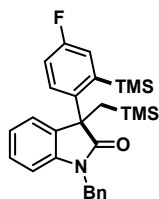
Yellow oil (64 mg, 68%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 – 7.81 (m, 1H), 7.29 – 7.13 (m, 7H), 7.01 – 6.87 (m, 4H), 5.47 (d,  $J = 16.8$  Hz, 1H), 4.91 (d,  $J = 16.4$  Hz, 1H), 2.41 (d,  $J = 13.6$  Hz, 1H), 2.38 (s, 3H), 1.67 (d,  $J = 13.6$  Hz, 1H), 0.67 (s, 9H),  $-0.22$  (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  180.2, 149.2, 140.6, 139.0, 139.0, 138.1, 137.6, 131.7, 128.9, 128.7, 128.5, 127.1, 126.0, 125.9, 123.2, 122.9, 119.7, 56.4, 44.9, 28.3, 18.9, 4.4,  $-0.6$ . ESI-MS: Calcd for  $\text{C}_{29}\text{H}_{37}\text{NOSi}_2$ :  $[\text{M}+\text{H}^+]$  472.2486, found 472.2488.



3-benzyl-1-((trimethylsilyl)methyl)-1-(2-(trimethylsilyl)phenyl)-1,3-dihydro-2H-benzo[e]indol-2-one (**3m**)

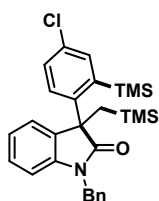
Yellow oil (61 mg, 60%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 8.8$  Hz, 1H), 7.84 (d,  $J = 7.6$  Hz, 1H), 7.61 (d,  $J = 8.4$  Hz, 1H), 7.41 – 7.36 (m, 1H), 7.32 – 7.28 (m,

1H), 7.27 – 7.19 (m, 8H), 7.10 – 7.04 (m, 1H), 6.80 – 6.77 (m, 1H), 5.73 (d,  $J = 16.8$  Hz, 1H), 5.21 (d,  $J = 17.2$  Hz, 1H), 2.50 (d,  $J = 13.6$  Hz, 1H), 1.76 (d,  $J = 13.6$  Hz, 1H), 0.58 (s, 9H), –0.30 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  181.1, 148.7, 139.2, 137.9, 137.7, 137.3, 134.5, 132.8, 129.4, 128.8, 128.6, 127.2, 126.2, 126.2, 125.9, 125.4, 123.8, 122.7, 122.1, 120.6, 56.8, 46.1, 27.8, 4.5, –0.6. ESI-MS: Calcd for  $\text{C}_{32}\text{H}_{37}\text{NOSi}_2$ :  $[\text{M}+\text{H}^+]$  508.2486, found 508.2488.



1-benzyl-3-(4-fluoro-2-(trimethylsilyl)phenyl)-3-((trimethylsilyl)methyl)indolin-2-one (**3n**)

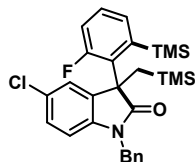
Colourless oil (61mg, 64%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 – 7.48 (m, 1H), 7.32 – 7.19 (m, 6H), 7.06 – 7.00 (m, 2H), 6.85 – 6.70 (m, 3H), 5.28 (d,  $J = 15.2$  Hz, 1H), 4.52 (d,  $J = 15.2$  Hz, 1H), 2.32 (d,  $J = 13.6$  Hz, 1H), 1.68 (d,  $J = 13.6$  Hz, 1H), 0.57 (s, 9H), –0.26 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.2, 160.8 (d,  $J = 246.0$  Hz), 144.5, 142.3, 142.3, 136.7, 136.0, 130.5 (d,  $J = 6.0$  Hz), 128.7, 128.0, 127.6, 127.5, 125.0, 124.0 (d,  $J = 19.0$  Hz), 122.9, 114.9 (d,  $J = 20.0$  Hz), 109.2, 56.4, 43.9, 43.9, 28.1, 28.1, 4.2, –0.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –117.08. ESI-MS: Calcd for  $\text{C}_{28}\text{H}_{34}\text{FNOSi}_2$ :  $[\text{M}+\text{H}^+]$  476.2236, found 476.2234.



1-benzyl-3-(4-chloro-2-(trimethylsilyl)phenyl)-3-((trimethylsilyl)methyl)indolin-2-one (**3o**)

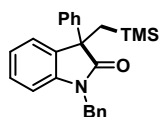
White solid (84 mg, 86%) M.P.: 140-144 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 2.4$  Hz, 1H), 7.31 – 7.26 (m, 4H), 7.26 – 7.17 (m, 2H), 7.05 – 7.00 (m, 3H), 6.82 (d,  $J = 7.6$  Hz, 1H), 6.65 (d,  $J = 8.4$  Hz, 1H), 5.26 (d,  $J = 15.6$  Hz, 1H), 4.49 (d,  $J = 15.6$  Hz, 1H), 2.29 (d,  $J = 13.6$  Hz, 1H), 1.64 (d,  $J = 13.6$  Hz, 1H), 0.55 (s, 9H), –0.29 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.0, 147.3, 142.4, 141.8, 137.2, 136.5, 135.9,

132.5, 130.2, 128.8, 128.3, 128.1, 127.7, 127.6, 125.0, 123.0, 109.3, 56.6, 44.0, 43.9, 27.9, 27.8, 4.3, -0.7. ESI-MS: Calcd for C<sub>28</sub>H<sub>34</sub>ClNOSi<sub>2</sub>: [M+H<sup>+</sup>] 492.1940, found 492.1947.



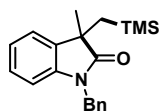
1-benzyl-5-chloro-3-(2-fluoro-6-(trimethylsilyl)phenyl)-3-((trimethylsilyl)methyl)indolin-2-one (**3p**)

Yellow oil (70 mg, 69%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.59 (m, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.21 (m, 4H), 7.11 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.97 – 6.90 (m, 2H), 6.68 (d, *J* = 8.4 Hz, 1H), 5.50 (d, *J* = 15.6 Hz, 1H), 4.41 (d, *J* = 15.2 Hz, 1H), 2.18 (d, *J* = 12.4 Hz, 1H), 1.89 (d, *J* = 12.8 Hz, 1H), 0.61 (s, 9H), -0.24 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.1 (d, *J* = 2.0 Hz), 161.2 (d, *J* = 246.0 Hz), 141.2, 140.8, 136.6, 135.6 (d, *J* = 9.0 Hz), 135.3, 133.0 (d, *J* = 3.0 Hz), 128.7, 128.2 (d, *J* = 10.0 Hz), 128.0 (d, *J* = 4.0 Hz), 127.7, 127.7, 127.5, 124.0 (d, *J* = 4.0 Hz), 117.2 (d, *J* = 26.0 Hz), 110.0, 54.2 (d, *J* = 1.0 Hz), 44.8, 27.7, 4.8, -0.9. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -103.59. ESI-MS: Calcd for C<sub>28</sub>H<sub>33</sub>ClFNOSi<sub>2</sub>: [M+H<sup>+</sup>] 510.1846, found 510.1855.



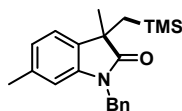
1-benzyl-3-phenyl-3-((trimethylsilyl)methyl)indolin-2-one (**4a**)

Yellow oil (42 mg, 55%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 – 7.40 (m, 2H), 7.35 – 7.20 (m, 10H), 7.10 – 7.05 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.34 (d, *J* = 15.6 Hz, 1H), 4.56 (d, *J* = 15.6 Hz, 1H), 2.03 (d, *J* = 14.4 Hz, 1H), 1.67 (d, *J* = 14.0 Hz, 1H), -0.23 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.2, 143.2, 142.7, 135.9, 134.2, 128.7, 128.4, 128.0, 127.5, 127.4, 126.9, 126.4, 125.3, 122.5, 109.2, 53.9, 44.0, 26.4, -0.6. ESI-MS: Calcd for C<sub>25</sub>H<sub>27</sub>NOSi: [M+H<sup>+</sup>] 385.1862, found 385.1860.



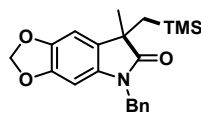
1-benzyl-3-methyl-3-((trimethylsilyl)methyl)indolin-2-one (**4b**)

Yellow oil (40 mg, 62%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.24 (m, 5H), 7.20 – 7.11 (m, 2H), 7.03 – 6.98 (m, 1H), 6.74 (d,  $J = 7.6$  Hz, 1H), 5.22 (d,  $J = 15.6$  Hz, 1H), 4.57 (d,  $J = 15.2$  Hz, 1H), 1.46 (s, 3H), 1.43 (d,  $J = 14.8$  Hz, 1H), 1.20 (d,  $J = 14.8$  Hz, 1H),  $-0.31$  (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  181.2, 141.9, 136.1, 135.5, 128.7, 127.5, 127.5, 127.4, 123.1, 122.3, 108.9, 46.2, 43.7, 28.8, 27.1,  $-0.7$ . ESI-MS: Calcd for  $\text{C}_{20}\text{H}_{25}\text{NOSi}$ :  $[\text{M}+\text{H}^+]$  324.1778, found 324.1778.



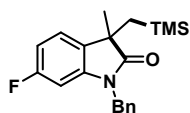
1-benzyl-3,6-dimethyl-3-((trimethylsilyl)methyl)indolin-2-one (**4c**)

Yellow oil (60 mg, 90%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J = 4.4$  Hz, 4H), 7.26 – 7.23 (m, 1H), 7.05 (d,  $J = 7.2$  Hz, 1H), 6.84 – 6.78 (m, 1H), 6.57 (s, 1H), 5.19 (d,  $J = 15.6$  Hz, 1H), 4.55 (d,  $J = 15.6$  Hz, 1H), 2.28 (s, 3H), 1.44 (s, 3H), 1.41 (d,  $J = 14.8$  Hz, 1H), 1.18 (d,  $J = 14.8$  Hz, 1H),  $-0.30$  (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  181.5, 141.9, 137.5, 136.2, 132.5, 128.6, 127.4, 127.3, 122.8, 109.7, 109.6, 45.9, 43.6, 29.0, 27.0, 21.7,  $-0.7$ . ESI-MS: Calcd for  $\text{C}_{21}\text{H}_{27}\text{NOSi}$ :  $[\text{M}+\text{H}^+]$  338.1935, found 338.1935.



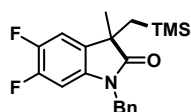
5-benzyl-7-methyl-7-((trimethylsilyl)methyl)-5,7-dihydro-6H-[1,3]dioxolo[4,5-f]indol-6-one (**4d**)

Blue oil (48 mg, 66%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.25 (m, 5H), 6.97 (s, 1H), 6.70 (s, 1H), 5.88 (d,  $J = 13.6$  Hz, 1H), 5.87 (d,  $J = 13.6$  Hz, 1H), 5.21 (d,  $J = 15.6$  Hz, 1H), 4.48 (d,  $J = 15.6$  Hz, 1H), 1.42 (s, 3H), 1.40 (d,  $J = 16.4$  Hz, 1H), 1.13 (d,  $J = 14.8$  Hz, 1H),  $-0.27$  (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  181.37, 146.74, 143.07, 135.95, 135.92, 128.76, 127.62, 127.58, 127.34, 104.74, 100.90, 92.92, 46.50, 43.88, 29.13, 27.24,  $-0.65$ . ESI-MS: Calcd for  $\text{C}_{21}\text{H}_{25}\text{NO}_3\text{Si}$ :  $[\text{M}+\text{H}^+]$  368.1676, found 368.1676.



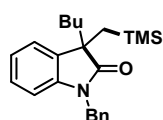
1-benzyl-6-fluoro-3-methyl-3-((trimethylsilyl)methyl)indolin-2-one (**4e**)

Colourless oil (31mg, 45%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.25 (m, 5H), 7.12 – 7.07 (m, 1H), 6.72 – 6.66 (m, 1H), 6.49 – 6.46 (m, 1H), 5.21 (d,  $J = 15.2$  Hz, 1H), 4.52 (d,  $J = 15.6$  Hz, 1H), 1.44 (s, 3H), 1.40 (d,  $J = 14.8$  Hz, 1H), 1.18 (d,  $J = 14.4$  Hz, 1H), –0.30 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  181.5, 162.6 (d,  $J = 242.0$  Hz), 143.2 (d,  $J = 12.0$  Hz), 135.6, 130.8, 128.8, 127.8, 127.4, 123.9 (d,  $J = 9.0$  Hz), 108.3 (d,  $J = 22.0$  Hz), 97.7 (d,  $J = 25.0$  Hz), 45.8, 43.9, 29.0, 27.2, –0.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –113.00. ESI-MS: Calcd for  $\text{C}_{20}\text{H}_{24}\text{FNOSi}$ :  $[\text{M}+\text{H}^+]$  342.1684, found 342.1678.



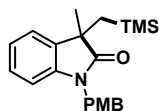
1-benzyl-5,6-difluoro-3-methyl-3-((trimethylsilyl)methyl)indolin-2-one (**4f**)

Colourless oil (33 mg, 46%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.26 (m, 5H), 7.03 – 6.98 (m, 1H), 6.57 – 6.52 (m, 1H), 5.19 (d,  $J = 15.6$  Hz, 1H), 4.51 (d,  $J = 15.6$  Hz, 1H), 1.44 (s, 3H), 1.42 (d,  $J = 14.8$  Hz, 1H), 1.14 (d,  $J = 14.8$  Hz, 1H), –0.27 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  180.9, 149.8 (dd,  $J = 244.0, 13.0$  Hz), 146.7 (dd,  $J = 241.0, 13.0$  Hz), 137.9 (dd,  $J = 9.0, 2.0$  Hz), 131.1 (dd,  $J = 5.0, 4.0$  Hz), 131.0, 128.9, 127.9, 127.4, 112.6 (dd,  $J = 19.0, 5.0$  Hz), 99.2 (dd,  $J = 23.0, 5.0$  Hz), 46.3, 44.0, 28.8, 27.1, –0.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –137.85 (d,  $J = 5.0$  Hz), –146.25 (d,  $J = 5.0$  Hz). ESI-MS: Calcd for  $\text{C}_{20}\text{H}_{23}\text{F}_2\text{NOSi}$ :  $[\text{M}+\text{H}^+]$  360.1590, found 360.1582.



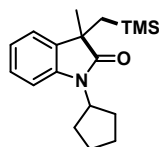
1-benzyl-3-butyl-3-((trimethylsilyl)methyl)indolin-2-one (**4g**)

Yellow oil (40 mg, 55%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.27 (m, 4H), 7.26 – 7.22 (m, 1H), 7.17 – 7.12 (m, 2H), 7.03 – 6.98 (m, 1H), 6.73 (d,  $J = 7.6$  Hz, 1H), 5.28 (d,  $J = 15.6$  Hz, 1H), 4.50 (d,  $J = 15.6$  Hz, 1H), 2.01 – 1.92 (m, 1H), 1.82 – 1.74 (m, 1H), 1.37 (d,  $J = 14.4$  Hz, 1H), 1.34 – 1.26 (m, 1H), 1.23 – 1.09 (m, 2H), 1.19 (d,  $J = 14.8$  Hz, 1H), 1.05 – 0.96 (m, 1H), 0.76 (t,  $J = 7.2$  Hz, 3H), –0.34 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  180.6, 142.8, 136.2, 133.9, 128.6, 127.6, 127.5, 123.4, 122.2, 108.7, 50.2, 43.9, 43.9, 42.4, 26.8, 26.5, 22.8, 13.8, –0.7. ESI-MS: Calcd for  $\text{C}_{23}\text{H}_{31}\text{NOSi}$ :  $[\text{M}+\text{H}^+]$  366.2248, found 366.2248.



1-(4-methoxybenzyl)-3-methyl-3-((trimethylsilyl)methyl)indolin-2-one (**4h**)

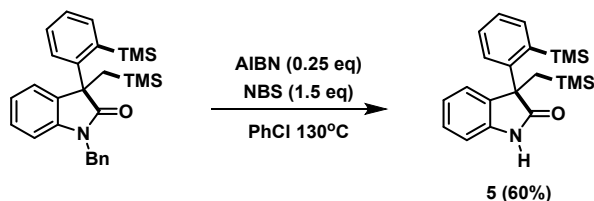
Yellow oil (41 mg, 58%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 (d, *J* = 8.8 Hz, 2H), 7.19 – 7.10 (m, 2H), 7.02 – 6.97 (m, 1H), 6.86 – 6.80 (m, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.14 (d, *J* = 15.6 Hz, 1H), 4.52 (d, *J* = 15.2 Hz, 1H), 3.76 (s, 3H), 1.44 (s, 3H), 1.42 (d, *J* = 14.8 Hz, 1H), 1.19 (d, *J* = 14.4 Hz, 1H), -0.32 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 181.1, 159.0, 141.9, 135.5, 128.8, 128.1, 127.5, 123.0, 122.2, 114.0, 108.9, 55.2, 46.1, 43.2, 28.8, 27.1, -0.8. ESI-MS: Calcd for C<sub>21</sub>H<sub>27</sub>NO<sub>2</sub>Si: [M+H<sup>+</sup>] 354.1884, found 354.1884.



1-cyclopentyl-3-methyl-3-((trimethylsilyl)methyl)indolin-2-one (**4i**)

Yellow oil (50 mg, 84%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 – 7.15 (m, 2H), 7.03 – 6.98 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 4.91 – 4.82 (m, 1H), 2.11 – 1.99 (m, 2H), 1.97 – 1.87 (m, 4H), 1.75 – 1.65 (m, 2H), 1.38 (d, *J* = 14.8 Hz, 1H), 1.38 (s, 3H), 1.14 (d, *J* = 14.4 Hz, 1H), -0.34 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 181.1, 140.8, 135.9, 127.2, 123.3, 121.7, 109.7, 51.6, 45.8, 29.1, 29.1, 27.1, 25.1, -0.8. ESI-MS: Calcd for C<sub>18</sub>H<sub>27</sub>NOSi: [M+H<sup>+</sup>] 302.1935, found 302.1935.

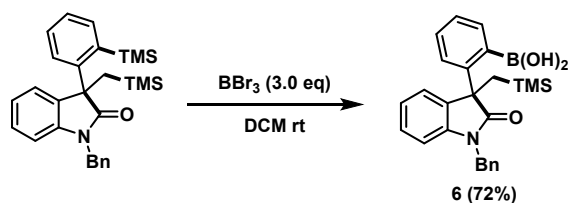
### Synthetic Transformations:



To a solution of **3a** (178.3 mg, 0.39 mmol, 1.0 equiv) in chlorobenzene (6.0 mL) containing NBS (86.0 mg, 0.46 mmol, 1.2 equiv) and AIBN (15.0 mg, 0.09 mmol, 0.2 equiv) was heated to reflux under a nitrogen atmosphere. After 4 h, AIBN (3.0 mg, 0.02 mmol, 0.05 equiv) and NBS (20.0 mg, 0.11 mmol, 0.3 equiv) were added. The solution was heated overnight then cooled to room temperature. Diethyl ether (10.0

mL) and water (20.0 mL) were added to the solution, which was stirred for 4 h, then the organic layer was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, evaporated and the crude product was purified by silica gel chromatography to give **5** (86 mg, 60%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.17 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.21 (m, 5H), 7.15 – 7.12 (m, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 1.95 (dd, *J* = 14.0, 3.2 Hz, 1H), 1.60 (dd, *J* = 14.4, 4.8 Hz, 1H), 0.22 (s, 9H), -0.22 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 181.9, 142.1, 140.6, 140.5, 134.8, 132.0, 130.9, 128.1, 127.8, 127.0, 125.5, 122.4, 110.0, 54.5, 26.3, -0.6, -1.1. ESI-MS: Calcd for C<sub>21</sub>H<sub>29</sub>NOSi<sub>2</sub>: [M+H<sup>+</sup>] 368.1860, found 368.1860.



To product **3a** (76.3 mg, 0.2 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at 0 °C under N<sub>2</sub> atmosphere was added BBr<sub>3</sub> (0.6 mmol, 3 mL, 0.2 M in CH<sub>2</sub>Cl<sub>2</sub>). After it was stirred at room temperature for 12 h, the reaction was quenched with water and extracted with EtOAc (15 mL). The combined organic layer was treated with brine (3 times), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica gel flash column chromatography to afford product **6** (61.8 mg, 72%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (s, 1H), 8.13 – 8.10 (m, 1H), 7.59 – 7.43 (m, 10H), 7.41 – 7.35 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 5.50 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 2.75 (d, *J* = 14.4 Hz, 1H), 1.98 (d, *J* = 14.0 Hz, 1H), -0.02 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 181.6, 146.0, 142.2, 135.5, 135.1, 135.0, 128.9, 128.8, 128.4, 127.8, 127.3, 126.9, 126.8, 125.8, 123.6, 109.8, 56.5, 44.2, 26.8, -0.9. ESI-MS: Calcd for C<sub>25</sub>H<sub>28</sub>BNO<sub>3</sub>Si: [M+Na<sup>+</sup>] 452.1824, found 452.1822.

### NMR Spectra:



