

## Synthesis of Noval Tetracycles via a Highly efficient Intramolecular Heck Reaction with anti-Hydride Elimination

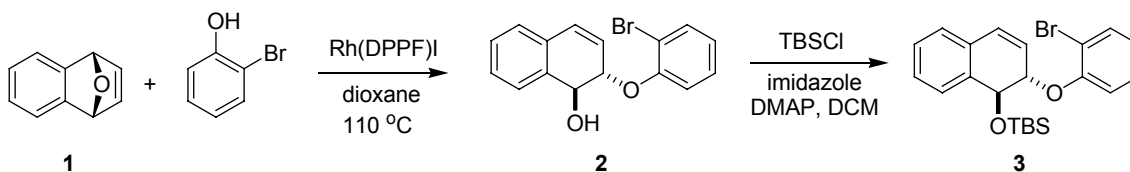
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**General** All the reactions were carried out under N<sub>2</sub>. Solvents and solutions were added with a syringe, unless otherwise noted. Analytical TLC was performed using EM separations precoated silica gel 0.2 mm layer UV fluorescent sheets. Column chromatography was carried out as “flash chromatography” as reported by Still using Merck 60 (230-400 mesh) silica gel.<sup>1</sup> Unless otherwise specified, extracts were dried over MgSO<sub>4</sub> and solvents were removed with a rotary evaporator at aspirator pressure.

Dioxane was distilled under N<sub>2</sub> from Na/benzophenone immediately prior to use. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was distilled from CaH<sub>2</sub> immediately prior to use. 2-bromo-4-methoxyphenol and 2-bromo-5-methoxyphenol were prepared *ortho*-bromination of corresponding phenols using NBS according a literature procedure.<sup>2</sup> The oxabicycles **26**, **29**, **33**, **38** were prepared by following literature procedures.<sup>3</sup> All other reagents, metal catalysts and ligands were purchased from Aldrich or Strem Chemical Company and used as received unless otherwise noted.

Melting point were taken on a Fisher-Johns melting point apparatus without correction. IR spectra were obtained using Nicolet DX FT IR spectrometer as thin films on NaCl plates. High-resolution mass spectra were obtained from a VG 70-250S (double focusing) mass spectrometer at 70 eV. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were obtained using Varian Unity 400 or Unity-500 spectrometers. <sup>1</sup>H spectra were referenced to tetramethylsilane (TMS, 0 ppm); <sup>13</sup>C spectra were referenced to solvent carbons (77.23 ppm for CDCl<sub>3</sub>). When carbons are equivalent, no special notation is used.



(±)-(1*S*\*,2*S*\*)-([2-(2-Bromo-phenoxy)-1,2-dihydro-naphthalen-1-yloxy]-*tert*-butyl-dimethyl-silane (**3**):

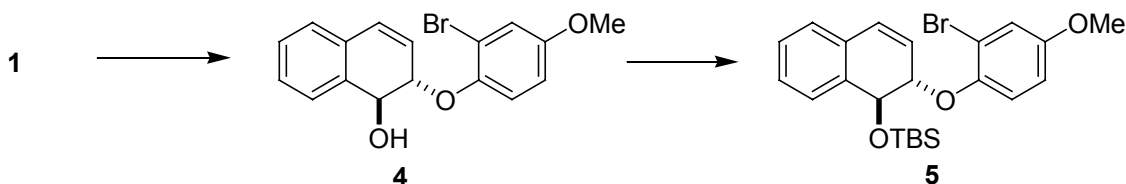
<sup>1</sup> Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-5.

<sup>2</sup> Carreno, M. C.; Garcia Ruano, J. L.; Sanz, G.; Toledo, M. A.; Urbano, A. *Synlett* **1997**, 1241-1242.

<sup>3</sup> Lautens, M.; Schmid, G. A.; Chau, A. *J. Org. Chem.* **2002**, *67*, 8043-8053.

**Typical procedure for a Rh-catalyzed ring-opening reaction:** To a flame-dried round-bottomed flask was added [Rh(COD)Cl]<sub>2</sub> (0.098 g, 0.2 mmol) and DPPF (0.222 g, 0.4 mmol), which was dissolved in 20 mL dioxane and stirred at room temperature for 10 min to produce a red solution. AgOTf (0.206 g, 0.8 mmol) was added followed by sonication for 10 min to produce an orange heterogeneous solution. Bu<sub>4</sub>NI (0.444 g, 1.2 mmol) was added followed by stirring for another 10 min to give a dark-red solution of the [Rh(DPPF)I] catalyst. To this catalyst solution was added oxabenzonorbornadiene (**1**) (2.88 g, 20 mmol) and 2-bromophenol (6.92 g, 40 mmol), which was heated to 110 °C for 1 h. The mixture was poured into NaOH solution (1M, 100 mL) and extracted with Et<sub>2</sub>O (3×100 mL). The combined organic phase was washed with NaOH (1M, 50 mL), brine (50 mL) and dried over MgSO<sub>4</sub>. After the most solvent was removed under vacuum, the brown residue was decoloured by passing through a short silica gel column (10% EtOAc: hexanes). The white product (**2**) (5.6 g, 88%) was obtained by recrystallization from 5% EtOAc:hexanes. mp 121-122 °C (hexanes). NMR spectra are identical to its enantiomerically-enriched form as previously reported.<sup>4</sup>

**Typical procedure for TBS protection:** To a round-bottomed flask was added **2** (1.59g, 5 mmol), *tert*-butyldimethyl chloride (1.13 g, 7.5 mmol), imidazole (0.511 g, 5 mmol) and DMAP (31 mg, 0.25 mmol), which was dissolved in DCM (10 mL) and stirred at rt for 30 h followed by addition of hexane (50 mL) to precipitate the imidazolium salt. The solution was filtered and the solvent was removed under vacuum. The residue was chromatographed on silica gel (1% EtOAc: hexanes) to give **3** (2.14 g, 99%) as a viscous liquid. R<sub>f</sub>=0.2 on silica gel (1% EtOAc: hexanes). IR (neat, cm<sup>-1</sup>) 3066 (w), 2954 (s), 2932 (s), 2856 (s), 1584 (m), 1475 (s), 1273 (s), 1244 (s), 1130 (s), 1079 (s), 1032 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61 (1H, d, *J*=7.1 Hz), 7.57 (1H, dd, *J*=7.9, 1.5 Hz), 7.30-7.20 (3H, m), 7.08 (1H, dd, *J*=7.0, 1.7 Hz), 6.97 (1H, dd, *J*=8.4, 1.1 Hz), 6.85 (1H, ddd, *J*=7.5, 7.5, 1.3 Hz), 6.45 (1H, dd, *J*=9.9, 2.1 Hz), 5.86 (1H, dd, *J*=9.9, 2.0 Hz), 5.33 (1H, d, *J*=10.4 Hz), 5.24 (1H, ddd, *J*=10.6, 1.8, 1.8 Hz), 0.95 (9H, s), 0.21 (3H, s), 0.09 (3H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.3, 137.6, 134.0, 132.7, 128.9, 128.6, 128.1, 127.9, 127.1, 126.4, 125.6, 122.6, 115.8, 113.7, 81.0, 73.8, 26.3, 18.6, -3.9, -4.5. HRMS calc'd for C<sub>18</sub>H<sub>18</sub>BrO<sub>2</sub>Si ([M-CMe<sub>3</sub>]<sup>+</sup>): 373.0259. Found: 373.0258.



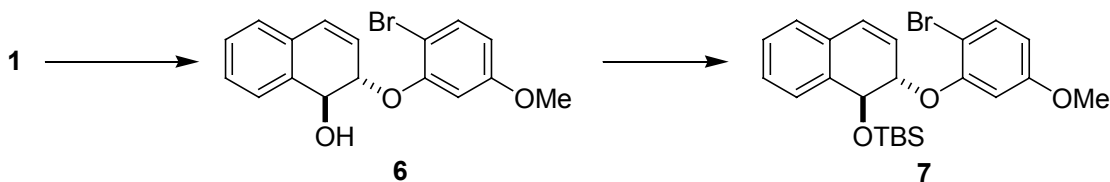
(±)-(1*S*\*,2*S*\*)-[2-(2-Bromo-4-methoxy-phenoxy)-1,2-dihydro-naphthalen-1-yloxy]-*tert*-butyl-dimethyl-silane (**5**)

Following the general procedure (80 °C, 2.5 h) for the ring-opening reaction using 2-bromo-4-methoxyphenol as the nucleophiles, **4** was obtained as a white crystalline solid

<sup>4</sup> Lautens, M.; Fagnou, K.; Taylor, M. *Org. Lett.* **2000**, 2, 1677-1679.

(67%, 5 mmol scale).  $R_f=0.18$  on silica gel (10% EtOAc: hexanes); mp 122-123 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3215 (br), 1599 (w), 1490 (s), 1460 (m), 1269 (m), 1038 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (1H, d,  $J=7.3$  Hz), 7.30-7.23 (2H, m), 7.12 (1H, d,  $J=2.9$  Hz), 7.10 (1H, dd,  $J=7.0, 1.8$  Hz), 6.91 (1H, d,  $J=9.0$  Hz), 6.78 (1H, dd,  $J=9.0, 2.9$  Hz), 6.50 (1H, dd,  $J=9.9, 2.0$  Hz), 6.04 (1H, dd,  $J=9.9, 2.2$  Hz), 5.25 (1H, dd,  $J=10.4, 3.5$  Hz), 4.97 (1H, ddd,  $J=10.4, 2.1, 2.1$  Hz), 3.75 (3H, s), 2.92 (1H, d,  $J=3.7$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 148.7, 135.7, 132.1, 129.1, 128.4, 128.2, 126.6, 126.6, 125.3, 119.0, 118.0, 114.6, 114.3, 83.3, 72.8, 56.0. HRMS calc'd for  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{NaBr}$  ( $\text{NaM}^+$ ): 369.0096. Found: 369.0115.

Followed the general procedure for TBS protection, **5** was obtained as a viscous liquid (99%).  $R_f=0.13$  on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2954 (s), 2929 (s), 2856 (s), 1603 (w), 1574 (w), 1490 (s), 1260 (s), 1215 (s), 1132 (s), 1077 (s), 1043 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (1H, d,  $J=7.1$  Hz), 7.29-7.22 (2H, m), 7.14 (1H, d,  $J=3.1$  Hz), 7.07 (1H, dd,  $J=7.0, 1.6$  Hz), 6.92 (1H, d,  $J=9.2$  Hz), 6.78 (1H, dd,  $J=9.0, 3.0$ ), 6.43 (1H, dd,  $J=9.9, 2.0$  Hz), 5.87 (1H, dd,  $J=9.9, 2.2$  Hz), 5.28 (1H, d,  $J=10.3$  Hz), 5.08 (1H, ddd,  $J=10.3, 2.0, 2.0$  Hz), 3.76 (3H, s), 0.97 (9H, s), 0.20 (3H, s), 0.11 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.7, 148.4, 137.5, 132.7, 128.7, 128.0, 127.9, 127.2, 126.4, 125.7, 119.1, 117.5, 114.5, 114.1, 81.8, 73.7, 56.1, 26.3, 18.7, -3.8, -4.5. HRMS calc'd for  $\text{C}_{19}\text{H}_{20}\text{BrO}_3\text{Si}$  ( $[\text{M}-\text{CMe}_3]^+$ ): 403.0365. Found: 403.0367.

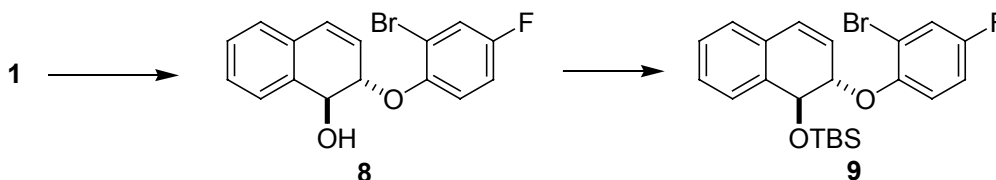


**(±)-(1S\*,2S\*)-[2-(2-Bromo-5-methoxy-phenoxy)-1,2-dihydro-naphthalen-1-yloxy]-*tert*-butyl-dimethyl-silane (7)**

Following the general procedure (90 °C, 2 h) for the ring-opening reaction using 2-bromo-5-methoxyphenol as the nucleophiles, **6** was obtained as a white crystalline solid (82%, 5 mmol scale).  $R_f=0.23$  on silica gel (10% EtOAc: hexanes); mp 79-81 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3420 (br), 1588 (s), 1484 (s), 1304 (m), 1203 (s), 1165 (s), 1058 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (1H, d,  $J=7.3$  Hz), 7.43 (1H, d,  $J=8.8$  Hz), 7.32-7.25 (2H, m), 7.11 (1H, dd,  $J=7.0, 1.8$  Hz), 6.52-6.49 (2H, m), 6.46 (1H, dd,  $J=8.8, 2.6$  Hz), 6.04 (1H, dd,  $J=9.9, 2.0$  Hz), 5.29 (1H, dd,  $J=10.7, 3.2$  Hz), 5.07 (1H, ddd,  $J=10.6, 2.1, 2.1$  Hz), 3.75 (3H, s), 2.87 (1H, d,  $J=3.5$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.3, 155.1, 135.6, 133.7, 132.0, 129.4, 128.5, 128.2, 126.6, 126.1, 125.2, 108.0, 104.3, 103.2, 82.4, 72.7, 55.8. HRMS calc'd for  $\text{C}_{17}\text{H}_{15}\text{BrO}_3$  ( $\text{M}^+$ ): 346.0205. Found: 346.0205.

Followed the general procedure for TBS protection, **7** was obtained as a viscous liquid (94%).  $R_f=0.16$  on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2954 (m), 2928 (m), 2856 (m), 1592 (s), 1484 (s), 1278 (m), 1203 (s), 1165 (s), 1134 (s), 1080 (m), 1062 (m).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (1H, d,  $J=7.4$  Hz), 7.43 (1H, d,  $J=8.7$  Hz), 7.28 (1H, ddd,  $J=7.5, 7.5, 1.3$  Hz), 7.24 (1H, dddd,  $J=7.3, 7.3, 1.7, 0.7$  Hz), 7.07 (1H, dd,  $J=7.1, 1.5$  Hz).

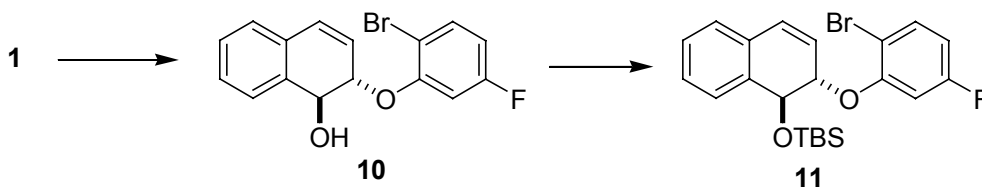
Hz), 6.54 (1H, d,  $J=2.7$  Hz), 6.45 (1H, dd,  $J=10.2, 2.2$  Hz), 6.43 (1H, dd,  $J=8.9, 2.8$  Hz), 5.86 (1H, dd,  $J=9.8, 2.0$  Hz), 5.32 (1H, d,  $J=10.5$  Hz), 5.20 (1H, ddd,  $J=10.5, 2.0, 2.0$  Hz), 3.74 (3H, s), 0.96 (9H, s), 0.22 (3H, s), 0.11 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.2, 154.9, 137.5, 133.8, 132.6, 128.9, 128.0, 127.9, 126.9, 126.4, 125.6, 107.5, 104.4, 103.0, 81.0, 73.7, 55.8, 26.4, 18.7, -3.8, -4.4. HRMS calc'd for  $\text{C}_{19}\text{H}_{20}\text{BrO}_3\text{Si}$  ( $[\text{M}-\text{CMe}_3]^+$ ): 403.0365. Found: 403.0376.



**(±)-(1S\*,2S\*)-[2-(2-Bromo-4-fluorophenoxy)-1,2-dihydro-naphthalen-1-yloxy]-tert-butyl-dimethyl-silane (9)**

Following the general procedure (90 °C, 2 h) for the ring-opening reaction using 2-bromo-4-fluorophenol as the nucleophiles, **8** was obtained as a white crystalline solid (75%, 5 mmol scale).  $R_f=0.22$  on silica gel (10% EtOAc: hexanes); mp 141-142 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3235 (br), 1592 (w), 1483 (s), 1188 (s), 1045 (m), 1035 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (1H, d,  $J=7.3$  Hz), 7.32 (1H, dd,  $J_{\text{HH}}=2.9$  Hz,  $^3J_{\text{HF}}=7.9$  Hz), 7.32-7.25 (2H, m), 7.12 (1H, dd,  $J=6.8, 1.8$  Hz), 6.97 (1H, ddd,  $J_{\text{HH}}=9.0, 2.9$  Hz,  $^3J_{\text{HF}}=7.5$  Hz), 6.92 (1H, dd,  $J_{\text{HH}}=9.2$  Hz,  $^4J_{\text{HF}}=4.9$  Hz), 6.52 (1H, dd,  $J=9.9, 2.0$  Hz), 6.02 (1H, dd,  $J=9.9, 2.2$  Hz), 5.28 (1H, dd,  $J=10.3, 2.6$  Hz), 5.03 (1H, ddd,  $J=10.4, 2.1, 2.1$  Hz), 2.78 (1H, d,  $J=3.7$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.5 ( $^1J_{\text{CF}}=245$  Hz), 151.2 ( $^4J_{\text{CF}}=2.3$  Hz), 135.6, 132.0, 129.6, 128.6, 128.3, 126.7, 125.9, 125.3, 120.8 ( $^2J_{\text{CF}}=26$  Hz), 117.0 ( $^3J_{\text{CF}}=8$  Hz), 115.4 ( $^2J_{\text{CF}}=22$  Hz), 114.1 ( $^3J_{\text{CF}}=10$  Hz), 83.1, 72.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -119.9 (1F, dd,  $J_{\text{FH}}=12.2, 7.6$  Hz). HRMS calc'd for  $\text{C}_{16}\text{H}_{12}\text{BrFO}_2$  ( $\text{M}^+$ ): 334.0005. Found: 334.0005.

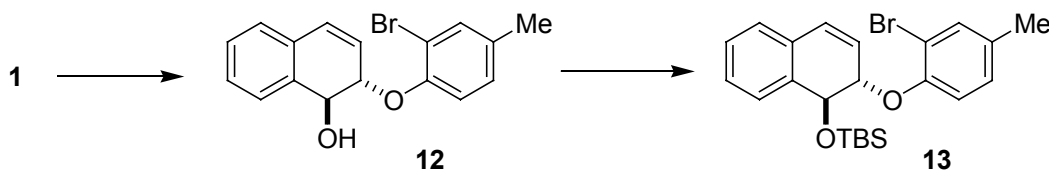
Followed the general procedure for TBS protection, **8** was obtained as a viscous liquid (98%).  $R_f=0.18$  on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2950 (w), 2930 (w), 2955 (w), 1590 (w), 1483 (s), 1252 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (1H, d,  $J=7.3$  Hz), 7.33-7.30 (1H, m), 7.30-7.22 (2H, m), 7.07 (1H, dd,  $J=7.0, 1.6$  Hz), 6.96-6.94 (2H, m), 6.45 (1H, dd,  $J=9.9, 2.0$  Hz), 5.85 (1H, dd,  $J=9.9, 2.0$  Hz), 5.29 (1H, d,  $J=10.4$  Hz), 5.13 (1H, ddd,  $J=10.4, 2.0, 2.0$  Hz), 0.96 (9H, s), 0.19 (3H, s), 0.09 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.1 ( $^1J_{\text{CF}}=244$  Hz), 151.0 ( $^4J_{\text{CF}}=2.3$  Hz), 137.4, 132.6, 129.0, 128.1, 128.0, 126.8, 126.5, 125.6, 120.8 ( $^2J_{\text{CF}}=25$  Hz), 116.7 ( $^3J_{\text{CF}}=8$  Hz), 115.0 ( $^2J_{\text{CF}}=22$  Hz), 114.0 ( $^3J_{\text{CF}}=10$  Hz), 81.9, 73.7, 26.3, 18.6, -3.9, -4.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -120.9 (1F, dd,  $J_{\text{FH}}=13.7, 6.1$  Hz). HRMS calc'd for  $\text{C}_{22}\text{H}_{26}\text{BrFO}_2\text{Si}$  ( $\text{M}^+$ ): 448.0869. Found: 448.0857.



**(±)-(1S\*,2S\*)-[2-(2-Bromo-5-fluoro-phenoxy)-1,2-dihydro-naphthalen-1-yloxy]-*tert*-butyl-dimethyl-silane (11)**

Following the general procedure (90 °C, 2 h) for the ring-opening reaction using 2-bromo-5-fluorophenol as the nucleophiles, **10** was obtained as a white crystalline solid (75%, 5 mmol scale).  $R_f=0.33$  on silica gel (10% EtOAc: hexanes); mp 135-137 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3207 (br), 1595 (m), 1580 (m), 1474 (s), 1410 (m), 1287 (m), 1261 (s), 1241 (m), 1154 (s), 1112 (m), 1038 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (1H, d,  $J=7.1$  Hz), 7.51 (1H, dd,  $J_{\text{HH}}=8.8$  Hz,  $^4J_{\text{HF}}=6.2$  Hz), 7.33-7.26 (2H, m), 7.13 (1H, dd,  $J=6.7, 2.0$  Hz), 6.69 (1H, dd,  $J_{\text{HH}}=2.7$  Hz,  $^3J_{\text{HF}}=10.3$  Hz), 6.64 (1H, ddd,  $J_{\text{HH}}=8.8, 2.7$  Hz,  $^3J_{\text{HF}}=7.9$  Hz), 6.54 (1H, dd,  $J=9.9, 2.2$  Hz), 6.01 (1H, dd,  $J=9.9, 2.2$  Hz), 5.30 (1H, dd,  $J=10.4, 2.2$  Hz), 5.06 (1H, ddd,  $J=10.4, 2.2, 2.2$  Hz), 2.79 (1H, d,  $J=3.7$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8 ( $^1J_{\text{CF}}=247$  Hz), 155.4 ( $^3J_{\text{CF}}=10$  Hz), 135.5, 134.1 ( $^3J_{\text{CF}}=10$  Hz), 131.9, 129.9, 128.6, 128.3, 126.8, 125.4, 125.3, 109.8 ( $^2J_{\text{CF}}=22$  Hz), 107.8 ( $^4J_{\text{CF}}=3.8$  Hz), 103.8 ( $^2J_{\text{CF}}=27$  Hz), 82.6, 72.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.4 (1F, ddd,  $J_{\text{FH}}=10.7, 7.6, 5.9$  Hz). HRMS calc'd for  $\text{C}_{16}\text{H}_{10}\text{BrFO}$  ( $[\text{M}-\text{H}_2\text{O}]^+$ ): 315.9899. Found: 315.9907.

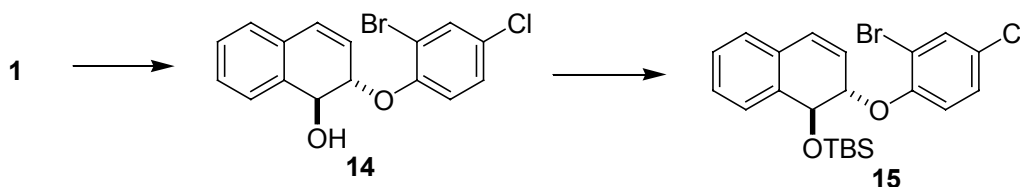
Followed the general procedure for TBS protection, **11** was obtained as a viscous liquid (98%).  $R_f=0.18$  on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3069 (w), 2954 (s), 2930 (s), 2888 (m), 2857 (s), 1602 (s), 1479 (s), 1416 (s), 1280 (s), 1254 (s), 1158 (s), 1131 (s), 1110 (s), 1079 (s), 1044 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (1H, d,  $J=7.5$  Hz), 7.50 (1H, dd,  $J_{\text{HH}}=8.8$  Hz,  $^4J_{\text{HF}}=6.2$  Hz), 7.31-7.23 (2H, m), 7.08 (1H, dd,  $J=7.0, 1.6$  Hz), 6.75 (1H, dd,  $J_{\text{HH}}=2.6$  Hz,  $^3J_{\text{HF}}=10.6$  Hz), 6.60 (1H, ddd,  $J_{\text{HH}}=8.8, 2.7$  Hz,  $^3J_{\text{HF}}=7.7$  Hz), 6.47 (1H, dd,  $J=9.9, 2.2$  Hz), 5.85 (1H, dd,  $J=9.9, 1.8$  Hz), 5.32 (1H, d,  $J=10.6$  Hz), 5.18 (1H, ddd,  $J=10.6, 2.0, 2.0$  Hz), 0.95 (9H, s), 0.20 (3H, s), 0.08 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7 ( $^1J_{\text{CF}}=246$  Hz), 155.4 ( $^3J_{\text{CF}}=10$  Hz), 137.4, 134.1 ( $^3J_{\text{CF}}=10$  Hz), 132.5, 129.2, 128.2, 128.0, 126.6, 126.5, 125.5, 109.3 ( $^2J_{\text{CF}}=22$  Hz), 107.7 ( $^4J_{\text{CF}}=3.8$  Hz), 103.8 ( $^2J_{\text{CF}}=27$  Hz), 81.5, 73.8, 26.3, 18.6, -4.0, -4.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.7 (1F, ddd,  $J_{\text{FH}}=10.9, 7.5, 6.1$  Hz). HRMS calc'd for  $\text{C}_{22}\text{H}_{26}\text{BrFO}_2\text{Si}$  ( $\text{M}^+$ ): 448.0869. Found: 448.0855.



**(±)-(1S\*,2S\*)-[2-(2-Bromo-4-methyl-phenoxy)-1,2-dihydro-naphthalen-1-yloxy]-*tert*-butyl-dimethyl-silane (13)**

Following the general procedure (90 °C, 2 h) for the ring-opening reaction using 2-bromo-4-methylphenol as the nucleophiles, **12** was obtained as a white crystalline solid (68%, 5 mmol scale).  $R_f$ =0.26 on silica gel (10% EtOAc: hexanes); mp 104-105 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3543 (w), 1599 (w), 1490 (s), 1245 (s), 1048 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (1H, d,  $J$ =7.1 Hz), 7.39 (1H, dd,  $J$ =2.0, 0.5 Hz), 7.32-7.24 (2H, m), 7.11 (1H, dd,  $J$ =7.0, 1.8 Hz), 7.03 (1H, ddd,  $J$ =8.4, 2.0, 0.5 Hz), 6.84 (1H, d,  $J$ =8.2 Hz), 6.50 (1H, dd,  $J$ =9.9, 2.2 Hz), 6.05 (1H, dd,  $J$ =9.9, 2.0 Hz), 5.28 (1H, dd,  $J$ =10.8, 3.2 Hz), 5.03 (1H, ddd,  $J$ =10.6, 2.1, 2.1 Hz), 2.85 (1H, d,  $J$ =3.5 Hz), 2.28 (3H, s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.4, 135.7, 134.2, 133.1, 132.1, 129.3, 129.2, 128.4, 128.1, 126.6, 126.5, 125.2, 116.2, 113.5, 82.7, 72.8, 20.5. HRMS calc'd for  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{NaBr}$  ( $\text{NaM}^+$ ): 353.0153. Found: 353.0162.

Followed the general procedure for TBS protection, **13** was obtained as a viscous liquid (100%).  $R_f$ =0.19 on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3031 (w), 2952 (m), 2928 (m), 2855 (m), 1602 (w), 1490 (s), 1249 (s), 1130 (s), 1079 (m), 1050 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (1H, d,  $J$ =7.1 Hz), 7.39 (1H, d,  $J$ =1.5 Hz), 7.30-7.21 (2H, m), 7.06 (1H, dd,  $J$ =7.0, 1.6 Hz), 7.01 (1H, ddd,  $J$ =8.3, 2.2, 0.7 Hz), 6.86 (1H, d,  $J$ =8.4 Hz), 6.43 (1H, dd,  $J$ =9.9, 2.0 Hz), 5.86 (1H, dd,  $J$ =9.9, 2.0 Hz), 5.31 (1H, d,  $J$ =10.4 Hz), 5.17 (1H, ddd,  $J$ =10.4, 2.0, 2.0 Hz), 2.27 (3H, s), 0.96 (9H, s), 0.21 (3H, s), 0.10 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.1, 137.6, 134.3, 132.7, 132.4, 129.1, 128.7, 128.0, 127.9, 127.2, 126.4, 125.6, 115.9, 113.5, 81.1, 73.7, 26.3, 20.4, 18.7, -3.9, -4.5. HRMS calc'd for  $\text{C}_{19}\text{H}_{20}\text{BrO}_2\text{Si}$  ( $[\text{M-CMe}_3]^+$ ): 387.0416. Found: 387.0415.

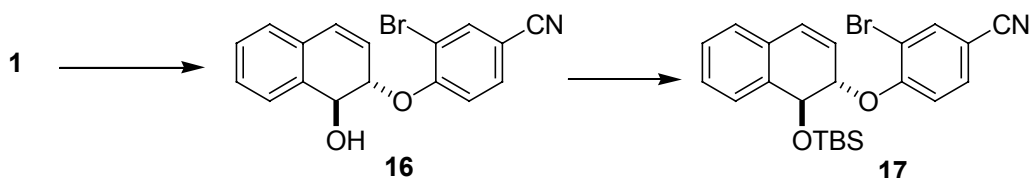


**(±)-(1S\*,2S\*)-[2-(2-Bromo-4-chloro-phenoxy)-1,2-dihydro-naphthalen-1-yloxy]-tert-butyl-dimethyl-silane (15)**

Following the general procedure (90 °C, 2 h) for the ring-opening reaction using 2-bromo-4-chlorophenol as the nucleophiles, **14** was obtained as a white crystalline solid (77%, 5 mmol scale).  $R_f$ =0.25 on silica gel (10% EtOAc: hexanes); mp: 130-131 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3222 (br), 1565 (w), 1473 (s), 1385 (m), 1262 (s), 1042 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (1H, d,  $J$ =7.1 Hz), 7.57 (1H, d,  $J$ =2.6 Hz), 7.33-7.26 (2H, m), 7.22 (1H, d,  $J$ =8.8, 2.6 Hz), 7.12 (1H, dd,  $J$ =6.8, 1.8 Hz), 6.88 (1H, d,  $J$ =8.8 Hz), 6.53 (1H, dd,  $J$ =9.9, 2.2 Hz), 6.00 (1H, dd,  $J$ =9.9, 2.0 Hz), 5.28 (1H, d,  $J$ =10.6 Hz), 5.05 (1H, ddd,  $J$ =10.4, 2.3, 2.3 Hz), 2.76 (1H, br).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 135.5, 133.4, 131.9, 129.7, 128.7, 128.6, 128.3, 127.4, 126.7, 125.6, 125.3, 116.5, 114.2, 82.7, 72.7. HRMS calc'd for  $\text{C}_{16}\text{H}_{11}\text{BrClO}$  ( $[\text{M-OH}]^+$ ): 332.9682. Found: 332.9684.

Followed the general procedure for TBS protection, **15** was obtained as a viscous liquid (98%).  $R_f$ =0.19 on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2950 (w), 2928 (w), 2953 (w), 1470 (s), 1278 (s), 1257 (s), 1244 (s), 1128 (m), 1077 (m), 1046 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (1H, d,  $J$ =7.3 Hz), 7.56 (1H, d,  $J$ =2.6 Hz), 7.30-7.23 (2H, m),

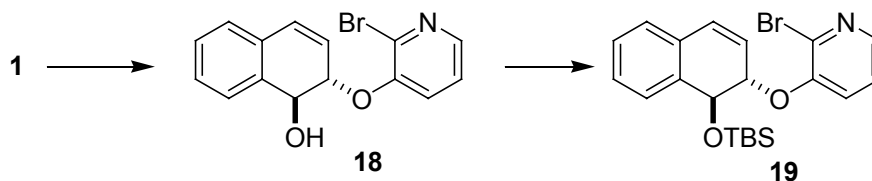
7.20 (1H, dd,  $J=8.8, 2.6$  Hz), 7.07 (1H, dd,  $J=7.0, 1.6$  Hz), 6.91 (1H, d,  $J=9.0$  Hz), 6.46 (1H, dd,  $J=9.9, 2.0$  Hz), 5.82 (1H, dd,  $J=9.9, 2.0$  Hz), 5.30 (1H, d,  $J=10.4$  Hz), 5.18 (1H, ddd,  $J=10.4, 2.0, 2.0$  Hz), 0.95 (9H, s), 0.20 (3H, s), 0.08 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.3, 137.4, 133.4, 132.5, 129.1, 128.5, 128.2, 128.0, 126.8, 126.6, 126.5, 125.6, 116.5, 114.2, 81.6, 73.7, 26.3, 18.6, -3.9, -4.5. HRMS calc'd for  $\text{C}_{18}\text{H}_{17}\text{BrClO}_2\text{Si}$  ( $[\text{M}-\text{CMe}_3]^+$ ): 406.9870. Found: 406.9862.



**(±)-(1S\*,2S\*)-3-Bromo-4-[1-(*tert*-butyl-dimethyl-silanyloxy)-1,2-dihydro-naphthalen-2-yloxy]-benzonitrile (17)**

Following the general procedure (110 °C, 2 h) for the ring-opening reaction using 2-bromo-4-cyanophenol as the nucleophiles, **16** was obtained as a white crystalline solid (52%, 5 mmol scale) by chromatographing on silica gel (20% EtOAc: hexanes).  $R_f=0.21$  on silica gel (20% EtOAc: hexanes); mp 119-121 °C (EtOAc/hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3456 (br), 2231 (m), 1593 (m), 1488 (s), 1291 (s), 1258 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (1H, d,  $J=2.0$  Hz), 7.65 (1H, d,  $J=7.1$  Hz), 7.57 (1H, dd,  $J=8.6, 2.0$  Hz), 7.35-7.28 (2H, m), 7.15 (1H, dd,  $J=6.6, 2.0$ ), 6.99 (1H, d,  $J=8.6$  Hz), 6.58 (1H, dd,  $J=9.9, 2.0$  Hz), 5.96 (1H,  $J=9.9, 2.0$  Hz), 5.32 (1H, d,  $J=10.3$  Hz), 5.19 (1H, ddd,  $J=10.3, 2.1, 2.1$  Hz), 2.72 (1H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 137.4, 135.3, 133.3, 131.8, 130.4, 128.9, 128.5, 127.0, 125.4, 124.5, 117.8, 114.8, 113.9, 106.2, 82.2, 72.5. HRMS calc'd for  $\text{C}_{17}\text{H}_{12}\text{NO}_2\text{NaBr}$  ( $\text{NaM}^+$ ): 363.9943. Found: 339.9959.

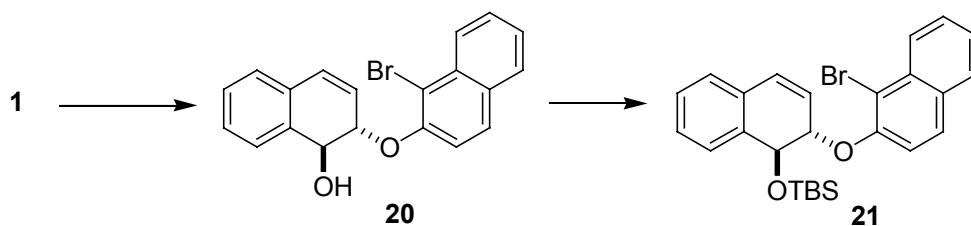
Followed the general procedure for TBS protection, **17** was obtained as a white solid (90%) by chromatographing on silica gel (2.5% EtOAc: hexanes).  $R_f=0.12$  on silica gel (2.5% EtOAc: hexanes); mp 125-126 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3070 (w), 2954 (m), 2929 (m), 2856 (m), 2228 (m), 1596 (m), 1488 (s), 1290 (m), 1258 (s), 1131 (m), 1080 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (1H, d,  $J=2.0$  Hz), 7.58 (1H, dd,  $J=7.0, 1.6$  Hz), 7.55 (1H, dd,  $J=8.8, 2.2$  Hz), 7.33-7.25 (2H, m), 7.10 (1H, dd,  $J=7.1, 1.8$  Hz), 7.05 (1H, d,  $J=8.6$  Hz), 6.50 (1H, d,  $J=9.7$ ), 5.80 (1H, d,  $J=9.5$  Hz), 5.34 (2H, s), 0.93 (9H, s), 0.18 (3H, s), 0.04 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 137.5, 137.2, 133.1, 132.4, 129.8, 128.4, 128.2, 126.7, 126.0, 125.5, 117.9, 115.0, 113.8, 105.8, 81.6, 73.7, 26.2, 18.5, -4.1, -4.5. HRMS calc'd for  $\text{C}_{19}\text{H}_{17}\text{BrNO}_2\text{Si}$  ( $[\text{M}-\text{CMe}_3]^+$ ): 398.0212. Found: 398.0220.



**(±)-(1S\*,2S\*)-2-Bromo-3-[1-(*tert*-butyl-dimethyl-silanyloxy)-1,2-dihydronaphthalen-2-yloxy]-pyridine (**19**)**

Following the general procedure (110 °C, 7 h) for the ring-opening reaction using 2-bromo-3-hydroxypyridine as the nucleophiles, **18** was obtained as a white crystalline solid (35%, 5 mmol scale) by chromatographing on silica gel (25% EtOAc: hexanes).  $R_f=0.17$  on silica gel (25% EtOAc: hexanes); mp 97-99 °C (EtOAc/hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3304 (br), 1562 (m), 1446 (m), 1412 (s), 1283 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (1H, dd,  $J=4.2, 2.0$  Hz), 7.66 (1H, d,  $J=6.6$  Hz), 7.35-7.27 (2H, m), 7.25-7.19 (2H, m), 7.14 (1H, dd,  $J=7.0, 1.7$ ), 6.56 (1H, dd,  $J=9.9, 2.2$  Hz), 5.99 (1H,  $J=9.9, 2.0$  Hz), 5.32 (1H, dd,  $J=10.4, 4.2$  Hz), 5.11 (1H, ddd,  $J=10.4, 2.2, 2.2$  Hz), 2.88 (1H, d,  $J=4.2$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.8, 142.6, 135.5, 134.4, 131.9, 130.1, 128.7, 128.4, 126.9, 125.4, 125.1, 123.7, 122.4, 82.6, 72.6. HRMS calc'd for  $\text{C}_{15}\text{H}_{12}\text{NO}_2\text{NaBr}$  ( $\text{NaM}^+$ ): 339.9943. Found: 339.9950.

Followed the general procedure for TBS protection, **18** was obtained as a viscous liquid (86%) by chromatographing on silica gel (5% EtOAc: hexanes).  $R_f=0.19$  on silica gel (5% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3063 (m), 2954 (s), 2931 (s), 2856 (s), 1560 (s), 1446 (s), 1413 (s), 1277 (s), 1202 (s), 1130 (s), 1075 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (1H, dd,  $J=4.6, 1.6$  Hz), 7.59 (1H, d,  $J=7.5$  Hz), 7.32-7.25 (3H, m), 7.18 (1H, dd,  $J=8.2, 4.6$  Hz), 7.10 (1H, dd,  $J=7.0, 1.8$  Hz), 6.49 (1H, dd,  $J=9.9, 2.2$  Hz), 5.84 (1H, dd,  $J=9.9, 2.0$  Hz), 5.34 (1H, d,  $J=10.6$  Hz), 5.23 (1H, ddd,  $J=10.6, 2.0, 2.0$  Hz), 0.94 (9H, s), 0.20 (3H, s), 0.08 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.8, 142.2, 137.3, 134.4, 132.5, 129.5, 128.3, 128.1, 126.6, 126.4, 125.5, 123.5, 122.3, 81.5, 73.8, 26.3, 18.5, -4.0, -4.5. HRMS calc'd for  $\text{C}_{21}\text{H}_{26}\text{BrNO}_2\text{Si}$  ( $\text{M}^+$ ): 431.0916. Found: 431.0914.



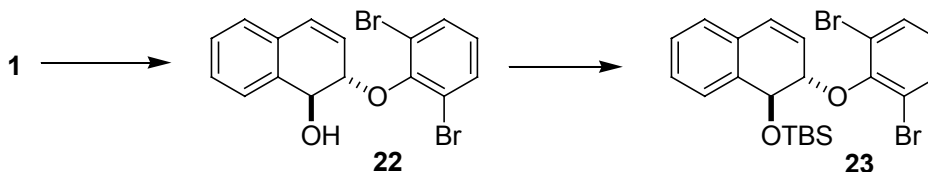
**(±)-(1S\*,2S\*)-[2-(1-Bromo-naphthalen-2-yloxy)-1,2-dihydronaphthalen-1-yloxy]-*tert*-butyl-dimethyl-silane (**21**)**

Following the general procedure (110 °C, 2 h) for the ring-opening reaction using 1-bromo-2-naphthol as the nucleophiles, **20** was obtained as a white crystalline solid (80%, 5 mmol scale).  $R_f=0.24$  on silica gel (10% EtOAc: hexanes); mp 148-149 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3208 (br), 1592 (m), 1459 (m), 1038 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (1H, d,  $J=8.6$  Hz), 7.77 (1H, dd,  $J=8.2, 0.5$  Hz), 7.76 (1H, d,  $J=9.0$  Hz), 7.67 (1H, d,



$J=6.8$  Hz), 7.58 (1H, ddd,  $J=7.7$ , 7.7, 0.7 Hz), 7.42 (1H, dd,  $J=7.3$ , 7.3 Hz), 7.32-7.25 (2H, m), 7.25 (1H, d,  $J=9.0$  Hz), 7.12 (1H, dd,  $J=6.8$ , 1.8 Hz), 6.52 (1H, dd,  $J=9.0$ , 2.0 Hz), 6.10 (1H, dd,  $J=9.9$ , 2.2 Hz), 5.38 (1H, dd,  $J=10.4$ , 3.7 Hz), 5.21 (1H, ddd,  $J=10.6$ , 2.0, 2.0 Hz), 2.95 (1H, d,  $J=3.7$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.7, 135.7, 133.4, 132.1, 130.7, 129.4, 129.4, 128.5, 128.3, 128.2, 128.1, 126.7, 126.7, 126.6, 125.3, 125.2, 117.4, 111.6, 83.5, 73.0. HRMS calc'd for  $\text{C}_{20}\text{H}_{15}\text{O}_2\text{NaBr}$  ( $\text{NaM}^+$ ): 389.0147. Found: 389.0153.

Followed the general procedure for TBS protection, **21** was obtained as a viscous liquid (99%).  $R_f=0.19$  on silica gel (1% EtOAc: hexanes); mp 81-83 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3066 (w), 2954 (s), 2928 (s), 2855 (s), 1623 (m), 1595 (m), 1501 (s), 1471 (s), 1463 (s), 1352 (m), 1260 (s), 1243 (s), 1132 (s), 1081 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (1H, d,  $J=8.4$  Hz), 7.78 (1H, dd,  $J=8.1$  Hz), 7.77 (1H, d,  $J=9.0$  Hz), 7.63 (1H, d,  $J=7.3$  Hz), 7.58 (1H, ddd,  $J=7.7$ , 7.7, 1.3 Hz), 7.42 (1H, ddd,  $J=7.5$ , 7.5, 1.1 Hz), 7.33 (1H, d,  $J=9.0$ ), 7.30-7.23 (2H, m), 7.08 (1H, dd,  $J=7.0$ , 1.5 Hz), 6.45 (1H, dd,  $J=9.9$ , 1.6 Hz), 5.91 (1H, dd,  $J=9.9$ , 1.8 Hz), 5.41-5.33 (2H, m), 0.97 (9H, s), 0.22 (3H, s), 0.10 (3H, s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.4, 137.5, 133.6, 132.7, 130.5, 129.1, 128.8, 128.3, 128.1, 128.0, 127.9, 127.3, 126.7, 126.5, 125.6, 124.9, 117.5, 111.7, 82.2, 73.9, 26.4, 18.7, -3.8, -4.5. HRMS calc'd for  $\text{C}_{22}\text{H}_{20}\text{BrO}_2\text{Si}$  ( $[\text{M}-\text{CMe}_3]^+$ ): 423.0416. Found: 423.0416.

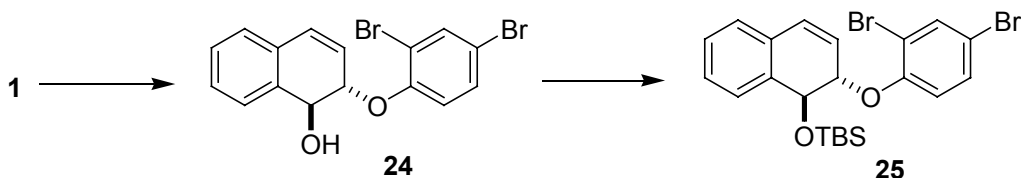


**(±)-(1S\*,2S\*)-tert-Butyl-[2-(2,6-dibromo-phenoxy)-1,2-dihydro-naphthalen-1-yloxy]-dimethyl-silane (23)**

Following the general procedure (80 °C, 2 h) for the ring-opening reaction using 2,6-dibromophenol as the nucleophiles, **22** was obtained as a white crystalline solid (74%, 5 mmol scale) after chromatographed on silica gel (10% EtOAc:hexanes).  $R_f=0.22$  on silica gel (10% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (1H, m), 7.53 (2H, d,  $J=7.9$  Hz), 7.30-7.24 (2H, m), 7.12-7.10 (1H, m), 6.87 (1H, t,  $J=7.9$  Hz), 6.51 (1H, d,  $J=9.7$  Hz), 6.07 (1H, d,  $J=9.9$  Hz), 5.37 (2H, m), 2.68 (1H, d,  $J=1.8$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.2, 135.7, 133.3, 132.0, 129.2, 128.5, 128.4, 126.8, 126.4, 126.1, 126.0, 118.8, 84.4, 73.1. HRMS calc'd for  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{NaBr}_2$  ( $\text{NaM}^+$ ): 416.9096. Found: 416.9095.

Followed the general procedure for TBS protection, **23** was obtained as a viscous liquid (91%).  $R_f=0.20$  on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2956 (s), 2929 (s), 2856 (s), 1556 (m), 1435 (s), 1238 (s), 1132 (s), 1076 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55-7.50 (1H, m), 7.52 (2H, d,  $J=8.1$  Hz), 7.29-7.23 (2H, m), 7.09 (1H, dd,  $J=6.2$ , 2.4 Hz), 6.87 (1H, t,  $J=8.5$  Hz), 6.50 (1H, dd,  $J=9.9$ , 0.9 Hz), 5.82 (1H, dd,  $J=9.9$ , 3.5 Hz), 5.43 (1H, ddd,  $J=7.1$ , 3.5, 1.5 Hz), 5.25 (1H, d,  $J=7.3$  Hz), 0.93 (9H, s), 0.25 (3H, s), 0.09 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.3, 136.9, 133.2, 132.4, 129.7, 128.1, 127.4,

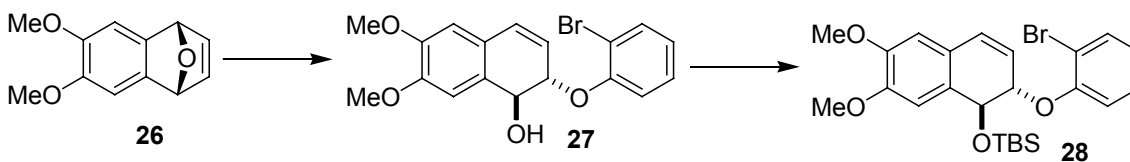
126.9, 126.3, 124.4, 119.5, 81.3, 72.7, 26.3, 18.6, -3.8, -4.3. HRMS calc'd for  $C_{22}H_{26}Br_2O_2Si$  ( $M^+$ ): 508.0069. Found: 508.0078.



**(±)-(1S\*,2S\*)-*tert*-Butyl-[2-(2,4-dibromo-phenoxy)-1,2-dihydro-naphthalen-1-yloxy]-dimethyl-silane (25)**

Following the general procedure (90 °C, 3 h) for the ring-opening reaction using 2,4-dibromophenol as the nucleophiles, **24** was obtained as a white crystalline solid (61%, 5 mmol scale).  $R_f$ =0.24 on silica gel (10% EtOAc: hexanes); mp 121-122 °C (hexanes). IR (neat,  $cm^{-1}$ ) 3299 (br), 1573 (w), 1471 (s), 1285 (m), 1261 (s), 1044 (s).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.70 (1H, d,  $J$ =2.4 Hz), 7.64 (1H, d,  $J$ =7.2 Hz), 7.35 (1H, dd,  $J$ =8.6, 2.5 Hz), 7.33-7.26 (2H, m), 7.12 (1H, dd,  $J$ =6.8, 2.0 Hz), 6.82 (1H, d,  $J$ =8.8 Hz), 6.52 (1H, dd,  $J$ =9.9, 2.0 Hz), 5.99 (1H, dd,  $J$ =9.9, 2.2 Hz), 5.27 (1H, d,  $J$ =10.5 Hz), 5.05 (1H, ddd,  $J$ =10.4, 2.4, 2.4 Hz), 2.76 (1H, br).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  153.9, 136.0, 135.5, 131.9, 131.6, 129.7, 128.6, 128.3, 126.8, 125.5, 125.3, 117.0, 114.6, 114.4, 82.6, 72.7. HRMS calc'd for  $C_{16}H_{12}Br_2O_2$  ( $M^+$ ): 393.9204. Found: 393.9209.

Followed the general procedure for TBS protection, **25** was obtained as a viscous liquid (100%).  $R_f$ =0.20 on silica gel (1% EtOAc: hexanes). IR (neat,  $cm^{-1}$ ) 3065 (w), 2952 (w), 2925 (w), 2955 (w), 1470 (s), 1243 (s), 1076 (m), 1045 (m).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.70 (1H, d,  $J$ =2.4 Hz), 7.59 (1H, d,  $J$ =7.3 Hz), 7.33 (1H, dd,  $J$ =8.8, 2.4 Hz), 7.31-7.23 (2H, m), 7.07 (1H, dd,  $J$ =7.0, 1.6 Hz), 6.86 (1H, d,  $J$ =9.0 Hz), 6.46 (1H, dd,  $J$ =9.9, 2.0 Hz), 5.82 (1H, dd,  $J$ =9.7, 1.8 Hz), 5.30 (1H, d,  $J$ =10.6 Hz), 5.18 (1H, ddd,  $J$ =10.6, 2.0, 2.0 Hz), 0.95 (9H, s), 0.20 (3H, s), 0.08 (3H, s).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  153.8, 137.4, 136.1, 132.5, 131.4, 129.2, 128.2, 128.0, 126.6, 126.5, 125.5, 116.9, 114.6, 113.8, 81.5, 73.7, 26.3, 18.6, -3.9, -4.5. HRMS calc'd for  $C_{22}H_{26}Br_2O_2Si$  ( $M^+$ ): 506.9865. Found: 506.9876.

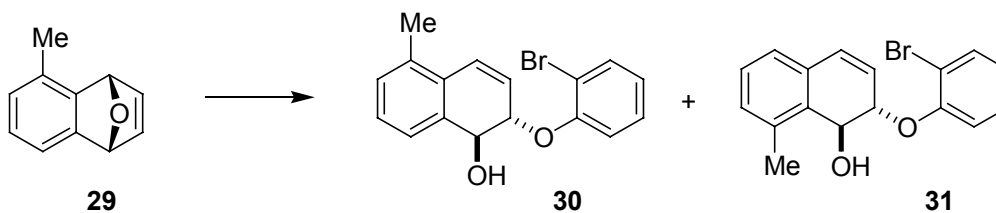


**(±)-(1S\*,2S\*)-[2-(2-Bromo-phenoxy)-6,7-dimethoxy-1,2-dihydro-naphthalen-1-yloxy]-*tert*-butyl-dimethyl-silane (28)**

The Rh(COD)I catalyst was prepared according to the general procedure. To this catalyst solution was added **26** (1.02 g, 5 mmol) and 2-bromophenol (1.73 g, 20 mmol), which

stirred at 80 °C for 1.5 h. The mixture was poured into a NaOH solution (1M, 30 mL) and extracted with Et<sub>2</sub>O (3×30 mL). The combined organic phase was washed with NaOH (1M, 20 mL), brine (20 mL) and dried over MgSO<sub>4</sub>. After the most solvent was removed, the brown residue was chromatographed on silica gel (25% EtOAc: hexanes) to give the white crystalline product **27** (1.63 g, 88%). *R*<sub>f</sub>=0.13 on silica gel (20% EtOAc: hexanes); mp 126-127 °C (EtOAc/hexanes). IR (neat, cm<sup>-1</sup>) 3500 (br), 2936 (w), 1605 (w), 1576 (m), 1514 (s), 1475 (s), 1277 (s), 1242 (s), 1125 (s), 1031 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (1H, dd, *J*=7.9, 1.6 Hz), 7.25 (1H, ddd, *J*=8.2, 8.2, 1.6 Hz), 7.23 (1H, s), 6.96 (1H, dd, *J*=8.2, 0.9 Hz), 6.89 (1H, ddd, *J*=7.9, 7.9, 1.3 Hz), 6.68 (1H, s), 6.43 (1H, *J*=9.9, 2.2 Hz), 5.97 (1H, dd, *J*=9.9, 2.0 Hz), 5.24 (1H, dd, *J*=10.6, 3.5 Hz), 5.06 (1H, ddd, *J*=10.6, 2.1, 2.1 Hz), 3.94 (3H, s), 3.89 (3H, s), 2.81 (1H, d, *J*=3.7 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.6, 149.1, 148.6, 133.8, 129.0, 128.8, 128.6, 124.9, 124.3, 123.1, 116.0, 113.7, 110.4, 109.0, 82.6, 72.8, 56.3, 56.3. HRMS calc'd for C<sub>18</sub>H<sub>17</sub>O<sub>4</sub>NaBr (NaM<sup>+</sup>): 399.0207. Found: 399.0204.

Followed the general procedure for TBS protection, **28** was obtained as a viscous liquid (99%) after chromatographed on silica gel (5% EtOAc: hexanes). *R*<sub>f</sub>=0.12 on silica gel (5% EtOAc: hexanes). IR (neat, cm<sup>-1</sup>) 2954 (s), 2932 (s), 2857 (m), 1605 (w), 1576 (m), 1513 (s), 1475 (s), 1277 (s), 1245 (s), 1131 (s), 1031 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (1H, dd, *J*=7.9, 1.6 Hz), 7.23 (1H, ddd, *J*=7.8, 7.8, 1.7 Hz), 7.22 (1H, s), 6.97 (1H, dd, *J*=8.4, 0.9 Hz), 6.85 (1H, ddd, *J*=7.7, 7.7, 1.3 Hz), 6.64 (1H, s), 6.36 (1H, dd, *J*=9.9, 2.0 Hz), 5.77 (1H, dd, *J*=9.8, 1.9 Hz), 5.30 (1H, d, *J*=10.4 Hz), 5.22 (1H, ddd, *J*=10.8, 1.8, 1.8 Hz), 3.92 (3H, s), 3.88 (3H, s), 0.98 (9H, s), 0.25 (3H, s), 0.09 (3H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.3, 148.7, 148.3, 134.0, 130.4, 128.6, 128.3, 125.3, 125.3, 122.5, 115.7, 113.7, 110.2, 109.5, 81.2, 73.9, 56.3, 56.2, 26.3, 18.6, -3.9, -4.6. HRMS calc'd for C<sub>24</sub>H<sub>31</sub>BrO<sub>4</sub>Si (M<sup>+</sup>): 490.1175. Found: 490.1187.



To the Rh(COD)I catalyst solution which was prepared according to the general procedure was added **29** (0.158 g, 1 mmol) and 2-bromophenol (0.346 g, 2 mmol), which was stirred at 90 °C for 8 h. The mixture was poured into NaOH solution (1M, 10 mL) and extracted with Et<sub>2</sub>O (2×20 mL). The combined organic phase was washed with NaOH (1M, 10 mL), brine (10 mL) and dried over MgSO<sub>4</sub>. After the most solvent was removed under vacuum, the brown residue was chromatographed on silica gel (5%→10%→25% EtOAc: hexanes) to give the first fractions (**30**) as a white crystalline product (0.096 g, 30%) and the second fractions (**31**) a viscous liquid (0.098 g, 30%).

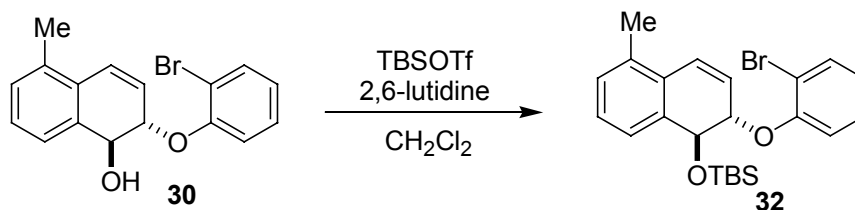
**(±)-(1S\*,2S\*)-2-(2-Bromo-phenoxy)-5-methyl-1,2-dihydro-naphthalen-1-ol (30)**

*R*<sub>f</sub>=0.31 on silica gel (10% EtOAc: hexanes); mp 139-141 °C (EtOAc/hexanes). IR (neat, cm<sup>-1</sup>) 3182 (br), 1471 (s), 1435 (m), 1265 (m), 1234 (m), 1167 (m), 1081 (m), 1028 (s).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (1H, dd,  $J=7.9, 1.6$  Hz), 7.52 (1H, d,  $J=7.3$  Hz), 7.25 (1H, m), 7.21 (1H, t,  $J=7.1$  Hz), 7.11 (1H, d,  $J=7.7$  Hz), 6.94 (1H, dd,  $J=8.2, 1.1$  Hz), 6.89 (1H, ddd,  $J=7.7, 7.7, 1.3$  Hz), 6.73 (1H, dd,  $J=10.2, 2.1$  Hz), 6.10 (1H, dd,  $J=10.3, 1.9$  Hz), 5.25 (1H, dd,  $J=11.0, 2.0$  Hz), 5.05 (1H, ddd,  $J=11.0, 2.0, 2.0$  Hz), 2.82 (1H, d,  $J=2.6$  Hz), 2.36 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.6, 135.9, 134.0, 133.9, 130.2, 130.0, 128.8, 128.2, 126.2, 126.1, 123.1, 122.8, 115.8, 113.6, 82.0, 72.9, 19.1. HRMS calc'd for  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{Br}$  ( $\text{M}^+$ ): 330.0255. Found: 330.0248.

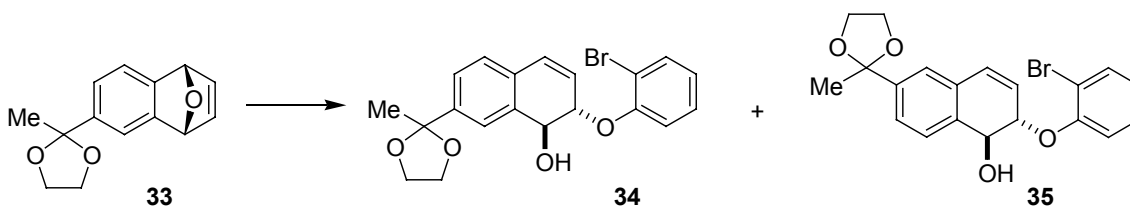
**( $\pm$ )-(1*S*\*,2*S*\*)-2-(2-Bromo-phenoxy)-8-methyl-1,2-dihydro-naphthalen-1-ol (**31**)**

$R_f=0.09$  on silica gel (10% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3317 (br), 3063 (w), 2922 (w), 1583 (m), 1474 (s), 1273 (m), 1240 (s), 1030 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (1H, dd,  $J=7.9, 1.6$  Hz), 7.26 (1H, ddd,  $J=8.2, 7.5, 1.6$  Hz), 7.20 (1H, t,  $J=7.5$  Hz), 7.14 (1H, d,  $J=7.3$  Hz), 7.10 (1H, dd,  $J=8.2, 1.3$  Hz), 7.05 (1H, d,  $J=7.3$  Hz), 6.88 (1H, ddd,  $J=7.6, 7.6, 1.4$  Hz), 6.75 (1H, d,  $J=9.7$  Hz), 6.13 (1H, ddd,  $J=9.5, 5.3, 0.9$  Hz), 5.09 (1H, d,  $J=6.8$  Hz), 4.94 (1H, dd,  $J=5.3, 2.2$  Hz), 2.44 (3H, s), 1.67 (1H, d,  $J=7.3$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.5, 137.9, 133.8, 132.6, 131.3, 131.1, 129.0, 128.6, 126.1, 123.6, 122.2, 118.1, 114.8, 76.6, 66.0, 18.5. HRMS calc'd for  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{Br}$  ( $\text{M}^+$ ): 330.0255. Found: 330.0247.



**( $\pm$ )-(1*S*\*,2*S*\*)-[2-(2-Bromo-phenoxy)-5-methyl-1,2-dihydro-naphthalen-1-yloxy]-tert-butyl-dimethyl-silane (**32**)**

To a round-bottomed flask was added the alcohol **30** (0.200 g, 0.60 mmol) and 2,6-lutidine (0.30 mL, 2.5 mmol) which was dissolved in 3 mL DCM. *tert*-Butyldimethyl triflate (0.4 mL, 1.7 mmol) was added through a syringe and the mixture was stirred at rt for 5 h followed by quenching with saturated  $\text{NH}_4\text{Cl}$  (5 mL). The mixture was extracted with hexanes ( $3 \times 10$  mL). The organic layers were combined, washed with brine and dried over  $\text{MgSO}_4$ . After removal of the solvent, the residue was chromatographed on silica gel (1% EtOAc: hexanes) to give **32** (0.250 g, 93%) as a viscous liquid.  $R_f=0.18$  on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3064 (w), 2954 (m), 2928 (m), 2856 (m), 1585 (w), 1476 (s), 1442 (m), 1275 (m), 1243 (s), 1127 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (1H, dd,  $J=7.8, 1.6$  Hz), 7.47 (1H, d,  $J=7.5$  Hz), 7.22 (1H, ddd,  $J=8.2, 7.3, 1.6$  Hz), 7.18 (1H, t,  $J=7.5$  Hz), 7.08 (1H, d,  $J=7.7$  Hz), 6.98 (1H, dd,  $J=8.2, 1.1$  Hz), 6.84 (1H, ddd,  $J=7.6, 7.6, 1.5$  Hz), 6.66 (1H, dd,  $J=10.1, 1.6$  Hz), 5.90 (1H, dd,  $J=10.1, 1.8$  Hz), 5.26 (1H, d,  $J=10.8$  Hz), 5.19 (1H, ddd,  $J=10.9, 1.9, 1.9$  Hz), 2.33 (3H, s), 0.95 (9H, s), 0.20 (3H, s), 0.09 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.4, 137.9, 133.9, 133.8, 130.8, 129.8, 128.6, 127.7, 127.4, 125.5, 123.3, 122.5, 115.9, 113.7, 80.5, 74.1, 26.3, 19.1, 18.6, -3.9, -4.5. HRMS calc'd for  $\text{C}_{23}\text{H}_{29}\text{BrO}_2\text{Si}$  ( $\text{M}^+$ ): 444.1120. Found: 444.1137.



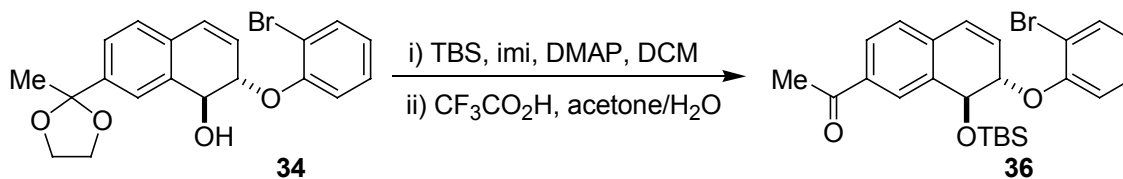
To the Rh(COD)I catalyst which was prepared according the general procedure was added **33** (1.38 g, 6 mmol) and 2-bromophenol (2.08 g, 12 mmol), which stirred at 90 °C for 4 h. The mixture was poured into NaOH solution (1M, 50 mL) and extracted with Et<sub>2</sub>O (3×40 mL). The combined organic phase was washed with NaOH (1M, 20 mL), brine (20 mL) and dried over MgSO<sub>4</sub>. After the most solvent was removed under vacuum, the brown residue was decoloured by passing through a short silica gel column (10% EtOAc: hexanes). The isomeric mixture was recrystallized from 10% EtOAc: hexanes to give the pure isomer **34** as a white crystalline product (0.92 g, 38%). The solvent of the mother solution was removed under vacuum and the residue was carefully chromatographed on silica gel (10% EtOAc: hexanes) to give the pure isomer **35** as a viscous liquid (0.94 g, 39%).

**(±)-(1S\*,2S\*)-2-(2-Bromo-phenoxy)-7-(2-methyl-[1,3]dioxolan-2-yl)-1,2-dihydro-naphthalen-1-ol (34)**

R<sub>f</sub>=0.24 on silica gel (20% EtOAc: hexanes); mp 142-143 °C (EtOAc/hexanes). IR (neat, cm<sup>-1</sup>) 3444 (br), 2986 (w), 2892 (w), 1584 (w), 1475 (s), 1442 (w), 1373 (w), 1277 (m), 1240 (s), 1199 (w), 1031 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (1H, s), 7.58 (1H, dd, *J*=8.1, 1.6 Hz), 7.40 (1H, ddd, *J*=7.9, 1.8, 0.8 Hz), 7.25 (1H, ddd, *J*=8.2, 7.4, 1.6 Hz), 7.10 (1H, d, *J*=7.7 Hz), 6.96 (1H, dd, *J*=8.2, 1.3 Hz), 6.89 (1H, ddd, *J*=7.7, 7.7, 1.4 Hz), 6.52 (1H, d, *J*=9.9, 2.2 Hz), 6.06 (1H, dd, *J*=9.9, 2.2 Hz), 5.29 (1H, dd, *J*=10.6, 3.1 Hz), 5.10 (1H, ddd, *J*=10.4, 2.3, 2.3 Hz), 4.07-4.02 (2H, m), 3.83-3.77 (2H, m), 2.90 (1H, d, *J*=3.7 Hz), 1.67 (3H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.6, 143.8, 135.8, 133.9, 131.7, 129.0, 128.8, 126.5, 126.5, 125.1, 123.2, 122.4, 116.1, 113.8, 109.0, 82.5, 72.8, 64.8, 64.7, 27.7. HRMS calc'd for C<sub>20</sub>H<sub>17</sub>BrO<sub>3</sub> ([M-H<sub>2</sub>O]<sup>+</sup>): 384.0361. Found: 384.0349.

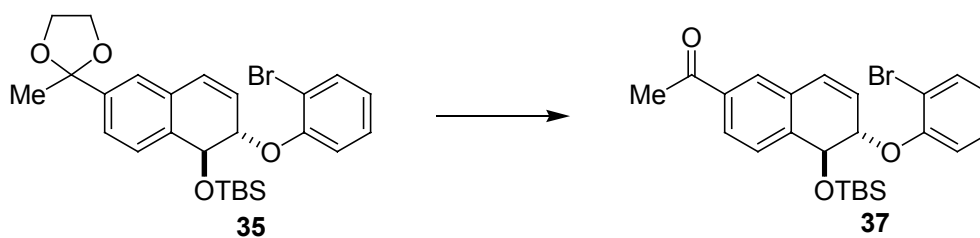
**(±)-(1S\*,2S\*)-2-(2-Bromo-phenoxy)-6-(2-methyl-[1,3]dioxolan-2-yl)-1,2-dihydro-naphthalen-1-ol (35)**

R<sub>f</sub>=0.30 on silica gel (20% EtOAc: hexanes). IR (neat, cm<sup>-1</sup>) 3444 (br), 2986 (w), 2888 (w), 1584 (w), 1475 (s), 1441 (w), 1274 (m), 1243 (s), 1199 (m), 1032 (s). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.63 (1H, d, *J*=7.9 Hz), 7.58 (1H, dd, *J*=7.9, 1.5 Hz), 7.42 (1H, dd, *J*=7.9, 1.6 Hz), 7.25 (1H, ddd, *J*=8.2, 7.8, 1.4 Hz), 7.25 (1H, s), 6.94 (1H, dd, *J*=8.3, 1.1 Hz), 6.89 (1H, t, *J*=7.7 Hz), 6.53 (1H, d, *J*=9.9, 2.1 Hz), 6.07 (1H, dd, *J*=9.8, 2.0 Hz), 5.29 (1H, dd, *J*=10.7, 3.2 Hz), 5.08 (1H, ddd, *J*=10.6, 2.1, 2.1 Hz), 4.07-4.02 (2H, m), 3.83-3.77 (2H, m), 2.87 (1H, d, *J*=3.3 Hz), 1.66 (3H, s). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 154.5, 143.5, 135.3, 133.9, 132.0, 129.4, 128.8, 126.5, 125.3, 125.2, 123.7, 123.2, 115.9, 113.7, 108.8, 82.5, 72.7, 64.7, 64.7, 27.8. HRMS calc'd for C<sub>20</sub>H<sub>20</sub>BrO<sub>4</sub> (MH<sup>+</sup>): 403.0545. Found: 403.0549.



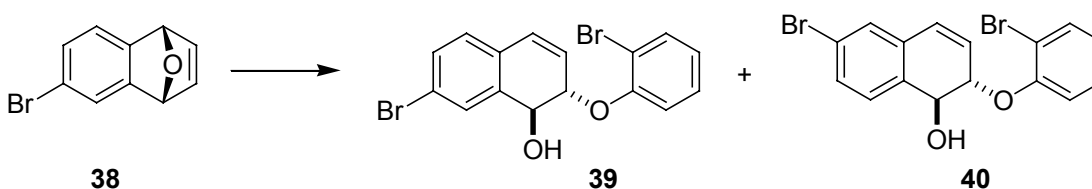
**(±)-(7S\*,8S\*)-1-[7-(2-Bromo-phenoxy)-8-(*tert*-butyl-dimethyl-silanyloxy)-7,8-dihydro-naphthalen-2-yl]-ethanone (36)**

To a round-bottomed flask was added **34** (0.605 g, 1.5 mmol), *tert*-butyldimethyl chloride (0.339 g, 2.25 mmol), imidazole (0.153 g, 2.25 mmol) and DMAP (17 mg, 0.15 mmol). DCM (3 mL) was added and the mixture was stirred at rt for 36 h followed by addition of hexane (50 mL) to precipitate the imidazolium salt. The solution was filtered and the solvent was removed under vacuum. The residue was chromatographed on silica gel (3.5% EtOAc: hexanes) to give the TBS protected acetal as a viscous liquid. The acetal was dissolved in acetone/H<sub>2</sub>O (15 mL, 5:1) and trifluoroacetic acid (0.5 mL) was added dropwise. The mixture was stirred at rt for 12 h during which the product was formed a white precipitate. Saturated NaHCO<sub>3</sub> (5 mL) was added and acetone was removed under vacuum. The residue was extracted with Et<sub>2</sub>O (2×30 mL). The combined organic phase was washed with saturated NaHCO<sub>3</sub> (20 mL), brine (20 mL) and dried over MgSO<sub>4</sub>. After removal of the solvent, the residue was chromatographed on silica gel (5% EtOAc: hexanes) to give **36** (0.653 g, 92% yield, 2 steps) as a white solid. *R*<sub>f</sub>=0.20 on silica gel (5% EtOAc: hexanes); mp 105-108 °C (hexanes). IR (neat, cm<sup>-1</sup>) 2949 (w), 2928 (m), 2854 (m), 1678 (s), 1477 (s), 1281 (m), 1239 (s). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.23 (1H, s), 7.88 (1H, dd, *J*=7.8, 1.7 Hz), 7.58 (1H, dd, *J*=7.9, 1.5 Hz), 7.24 (1H, ddd, *J*=7.8, 7.8, 1.6 Hz), 7.17 (1H, d, *J*=7.8 Hz), 6.98 (1H, dd, *J*=8.4, 1.0 Hz), 6.87 (1H, ddd, *J*=7.7, 7.7, 1.2 Hz), 6.50 (1H, dd, *J*=9.9, 2.1 Hz), 6.02 (1H, dd, *J*=9.8, 2.0 Hz), 5.35 (1H, d, *J*=10.6 Hz), 5.26 (1H, ddd, *J*=10.6, 2.0, 2.0 Hz), 2.61 (3H, s), 1.00 (9H, s), 0.26 (3H, s), 0.11 (3H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 197.5, 154.1, 137.9, 137.0, 136.5, 134.0, 130.2, 128.6, 128.1, 128.1, 126.6, 125.9, 122.8, 115.8, 113.8, 80.7, 73.5, 27.0, 26.3, 18.7, -3.9, -4.5. HRMS calc'd for C<sub>24</sub>H<sub>30</sub>BrO<sub>3</sub>Si (MH<sup>+</sup>): 473.1148. Found: 473.1166.



**(±)-(5S\*,6S\*)-1-[6-(2-Bromo-phenoxy)-5-(*tert*-butyl-dimethyl-silanyloxy)-5,6-dihydro-naphthalen-2-yl]-ethanone (35)**

Followed the procedure for preparation of **36**, **37** was obtained as a white solid (93%, 2 steps) from **35**.  $R_f=0.20$  on silica gel (5% EtOAc: hexanes); mp 122-124 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2954 (m), 2929 (m), 2856 (m), 1685 (s), 1475 (s), 1274 (s), 1242 (s), 1140 (m), 1089 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (1H, dd,  $J=7.9, 1.8$  Hz), 7.71 (1H, d,  $J=7.9$  Hz), 7.67 (1H, d,  $J=1.6$  Hz), 7.58 (1H, dd,  $J=7.9, 1.6$  Hz), 7.24 (1H, ddd,  $J=7.4, 7.4, 1.6$  Hz), 6.98 (1H, dd,  $J=8.3, 1.0$  Hz), 6.87 (1H, ddd,  $J=7.6, 7.6, 1.5$  Hz), 6.51 (1H, dd,  $J=9.9, 2.0$  Hz), 5.95 (1H, dd,  $J=9.9, 2.0$  Hz), 5.34 (1H, d,  $J=10.6$  Hz), 5.25 (1H, ddd,  $J=10.6, 1.9, 1.9$  Hz), 2.61 (3H, s), 0.96 (9H, s), 0.22 (3H, s), 0.11 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.8, 154.1, 142.9, 136.9, 134.0, 133.1, 128.6, 128.3, 128.3, 128.2, 125.8, 122.8, 115.9, 113.8, 80.5, 73.8, 26.8, 26.3, 18.6, -3.9, -4.6. HRMS calc'd for  $\text{C}_{24}\text{H}_{30}\text{BrO}_3\text{Si}$  ( $\text{MH}^+$ ): 473.1148. Found: 473.1156



To the  $\text{Rh}(\text{COD})\text{I}$  catalyst which was prepared according the general procedure was added **38** (2.23 g, 10 mmol) and 2-bromophenol (3.46 g, 20 mmol), which stirred at 90 °C for 4 h. The mixture was poured into NaOH solution (1M, 100 mL) and extracted with  $\text{Et}_2\text{O}$  (3×50 mL). The combined organic phase was washed with NaOH (1M, 20 mL), brine (20 mL) and dried over  $\text{MgSO}_4$ . After the most solvent was removed under vacuum, the brown residue was decoloured by passing through a short silica gel column (10% EtOAc: hexanes). The isomeric mixture was recrystallized from 5% EtOAc: hexanes to give the pure isomer **40** as a white crystalline product (1.07 g, 27%). The solvent of the mother solution was removed under vacuum and the residue was carefully chromatographed on silica gel (5% EtOAc: hexanes) to give the pure isomer **39** as a white crystalline solid (2.02 g, 51%).

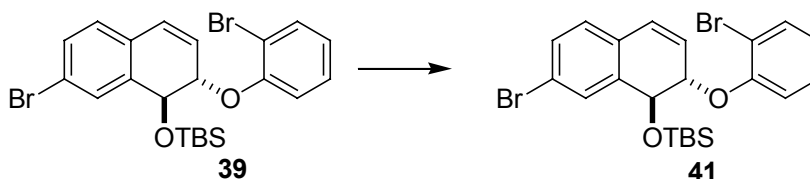
**(±)-(1S\*,2S\*)-7-Bromo-2-(2-bromo-phenoxy)-1,2-dihydro-naphthalen-1-ol (39)**

$R_f=0.17$  on silica gel (5% EtOAc: hexanes); mp 99-101 °C (EtOAc/hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3553 (br), 3433 (br), 3061 (w), 2865 (w), 1584 (m), 1475 (s), 1442 (m), 1276 (m), 1242 (s), 1050 (m), 1030 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (1H, s), 7.58 (1H, dd,  $J=7.9, 1.6$  Hz), 7.40 (1H, ddd,  $J=8.1, 2.0, 0.9$  Hz), 7.26 (1H, ddd,  $J=7.8, 7.8, 1.5$  Hz), 6.98 (1H, d,  $J=8.1$  Hz), 6.94 (1H, dd,  $J=8.2, 1.1$  Hz), 6.90 (1H, ddd,  $J=7.7, 7.7, 1.3$  Hz), 6.46 (1H, d,  $J=9.9, 2.0$  Hz), 6.08 (1H, dd,  $J=9.9, 1.8$  Hz), 5.29 (1H, dd,  $J=11.0, 3.3$  Hz), 5.07 (1H, ddd,  $J=11.0, 2.0, 2.0$  Hz), 2.91 (1H, d,  $J=3.5$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.4, 137.8, 134.0, 131.2, 131.0, 128.9, 128.5, 128.4, 128.0, 127.0, 123.3, 122.4, 115.9, 113.7, 82.2, 72.4. HRMS calc'd for  $\text{C}_{16}\text{H}_{12}\text{Br}_2\text{O}_2$  ( $\text{M}^+$ ): 393.9204. Found: 393.9201.

**(±)-(1S\*,2S\*)-6-Bromo-2-(2-bromo-phenoxy)-1,2-dihydro-naphthalen-1-ol (40)**

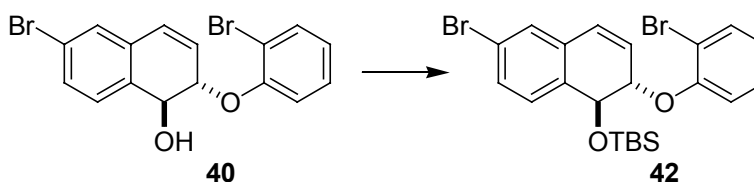
$R_f=0.13$  on silica gel (5% EtOAc: hexanes); mp 149-151 °C (EtOAc/hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3200 (br), 1585 (w), 1561 (w), 1478 (s), 1440 (m), 1268 (m), 1235 (s), 1164 (m), 1046 (s), 1028 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (1H, dd,  $J=7.9, 1.6$  Hz), 7.53 (1H, d,  $J=8.1$  Hz), 7.41 (1H, dd,  $J=8.1, 1.8$  Hz), 7.26 (1H, s), 7.25 (1H, dd,  $J=7.8, 7.8, 1.6$  Hz), 6.93 (1H, dd,  $J=7.9, 1.2$  Hz), 6.90 (1H, ddd,  $J=7.7, 7.7, 1.3$  Hz), 6.44 (1H, d,  $J=9.9, 2.2$  Hz).

Hz), 6.10 (1H, dd,  $J=9.9, 1.8$  Hz), 5.24 (1H, dd,  $J=10.8, 2.7$  Hz), 5.07 (1H, ddd,  $J=10.8, 2.1, 2.1$  Hz), 2.90 (1H, d,  $J=3.5$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.4, 134.6, 134.0, 133.9, 131.2, 129.4, 128.9, 128.2, 128.0, 127.1, 123.3, 122.1, 115.9, 113.7, 82.1, 72.5. HRMS calc'd for  $\text{C}_{16}\text{H}_{10}\text{Br}_2\text{O}$  ( $[\text{M}-\text{H}_2\text{O}]^+$ ): 375.9098. Found: 375.9102.



**(±)-(1S\*,2S\*)-[7-Bromo-2-(2-bromo-phenoxy)-1,2-dihydro-naphthalen-1-yloxy]-tert-butyl-dimethyl-silane (41)**

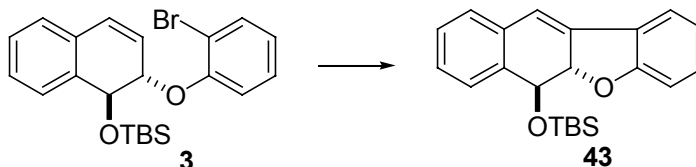
Followed the general procedure for TBS protection, **41** was obtained as a viscous liquid (100%).  $R_f=0.18$  on silica gel (100% hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3065 (w), 2954 (s), 2929 (s), 2856 (s), 1587 (m), 1474 (s), 1242 (s), 1138 (m), 1083 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (1H, s), 7.57 (1H, dd,  $J=7.9, 1.6$  Hz), 7.37 (1H, ddd,  $J=7.7, 2.2, 0.9$  Hz), 7.23 (1H, ddd,  $J=8.3, 7.3, 1.5$  Hz), 6.96 (1H, dd,  $J=8.3, 1.0$  Hz), 6.94 (1H, d,  $J=7.9$  Hz), 6.86 (1H, ddd,  $J=7.6, 7.6, 1.4$  Hz), 6.40 (1H, dd,  $J=9.9, 2.0$  Hz), 5.89 (1H, dd,  $J=9.9, 1.8$  Hz), 5.29 (1H, d,  $J=10.6$  Hz), 5.20 (1H, ddd,  $J=10.6, 1.9, 1.9$  Hz), 0.96 (9H, s), 0.22 (3H, s), 0.09 (3H, s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.2, 139.7, 134.0, 131.5, 130.9, 129.1, 128.6, 127.9, 127.8, 127.7, 122.8, 121.9, 115.8, 113.8, 80.5, 73.4, 26.3, 18.6, -3.9, -4.6. HRMS calc'd for  $\text{C}_{22}\text{H}_{26}\text{Br}_2\text{O}_2\text{Si}$  ( $\text{M}^+$ ): 508.0069. Found: 508.0070.



**(±)-(1S\*,2S\*)-[6-Bromo-2-(2-bromo-phenoxy)-1,2-dihydro-naphthalen-1-yloxy]-tert-butyl-dimethyl-silane (42)**

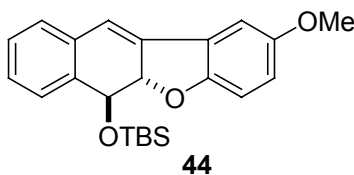
Followed the general procedure for TBS protection, **42** was obtained as a viscous liquid (98%).  $R_f=0.30$  on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2954 (s), 2928 (s), 2856 (s), 1586 (m), 1475 (s), 1275 (m), 1241 (s), 1136 (s), 1083 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (1H, dd,  $J=7.9, 1.6$  Hz), 7.45 (1H, d,  $J=8.1$  Hz), 7.40 (1H, dd,  $J=8.2, 1.9$  Hz), 7.23 (1H, ddd,  $J=8.4, 7.5, 1.6$  Hz), 7.22 (1H, d,  $J=2.0$  Hz), 6.96 (1H, dd,  $J=8.1, 2.2$  Hz), 6.86 (1H, ddd,  $J=7.6, 7.6, 1.4$  Hz), 6.38 (1H, dd,  $J=9.9, 1.8$  Hz), 5.92 (1H, dd,  $J=9.9, 1.8$  Hz), 5.26-5.18 (2H, m), 0.94 (9H, s), 0.19 (3H, s), 0.09 (3H, s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.2, 136.5, 134.6, 134.0, 130.8, 129.2, 128.7, 128.6, 127.7, 127.5, 122.8, 121.9, 115.9, 113.8, 80.5, 73.4, 26.3, 18.6, -3.9, -4.5. HRMS calc'd for  $\text{C}_{22}\text{H}_{26}\text{Br}_2\text{O}_2\text{Si}$  ( $\text{M}^+$ ): 508.0069. Found: 508.0073.





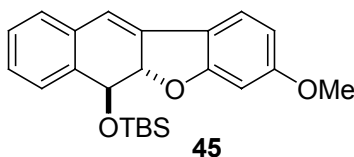
**(±)-(5S\*,6S\*)-tert-Butyl-(5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-dimethyl-silane (43)**

**General procedure for the Pd-catalyzed Heck reaction:** A vial which was charged with **3** (0.216 g, 0.5 mmol), DABCO (0.168 g, 1.5 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (4.6 mg, 0.005 mmol) and HP(*t*-Bu)<sub>3</sub>·BF<sub>4</sub> (5.8 mg, 0.02 mmol) was purged with N<sub>2</sub> for 10 min. Dioxane (1 mL) was added via a syringe and the mixture was stirred at 40 °C for 60 h under N<sub>2</sub>. The mixture was poured into saturated NaHCO<sub>3</sub> (10 mL) and extracted with hexanes (3×15 mL). The organic phase was combined, washed with brine (15 mL) and dried over MgSO<sub>4</sub>. After removal of solvent, the residue was chromatographed on silica gel (1% EtOAc: hexanes) to give a white wax-like solid (0.161 g, 92%). R<sub>f</sub>=0.28 on silica gel (1% EtOAc: hexanes). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (1H, m), 7.46 (1H, dd, *J*=7.2, 0.7 Hz), 7.28-7.21 (3H, m), 7.17-7.14 (1H, m), 6.96 (1H, ddd, *J*=7.4, 7.4, 1.1 Hz), 6.94 (1H, d, *J*=8.1 Hz), 6.58 (1H, d, *J*=2.2 Hz), 5.19-5.12 (2H, m), 1.06 (9H, s), 0.28 (3H, s), 0.21 (3H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.6, 139.2, 136.4, 134.7, 130.8, 128.0, 127.5, 126.6, 125.3, 124.9, 121.7, 121.5, 114.3, 111.2, 87.8, 74.9, 26.3, 18.7, -4.0, -4.6. HRMS calc'd for C<sub>22</sub>H<sub>26</sub>O<sub>2</sub>Si (M<sup>+</sup>): 350.1702. Found: 350.1704.



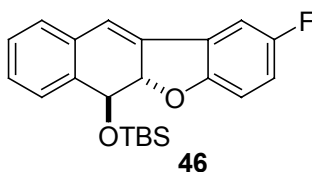
**(±)-(5S\*,6S\*)-tert-Butyl-(2-methoxy-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-dimethyl-silane (44)**

Follow the general procedure for the Heck reaction, **44** was obtained as a white wax-like solid (96%). R<sub>f</sub>=0.11 on silica gel (1% EtOAc: hexanes); mp 106-108 °C (hexanes). IR (neat, cm<sup>-1</sup>) 2953 (m), 2929 (m), 2856 (m), 1484 (s), 1262 (m), 1194 (s), 1154 (s), 1081 (m), 1036 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63-7.61 (1H, m), 7.26-7.23 (2H, m), 7.15-7.13 (1H, m), 6.98 (1H, d, *J*=2.4 Hz), 6.85 (1H, d, *J*=8.8 Hz), 6.81 (1H, dd, *J*=8.8, 2.6 Hz), 6.55 (1H, s), 5.13 (2H, s), 3.80 (3H, s), 1.06 (9H, s), 0.27 (3H, s), 0.20 (3H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.1, 154.9, 139.6, 136.4, 134.6, 128.0, 127.5, 126.6, 125.3, 125.2, 117.6, 114.2, 111.4, 105.9, 88.1, 74.9, 56.3, 26.3, 18.7, -4.0, -4.6. HRMS calc'd for C<sub>23</sub>H<sub>28</sub>O<sub>3</sub>Si (M<sup>+</sup>): 380.1808. Found: 380.1810.



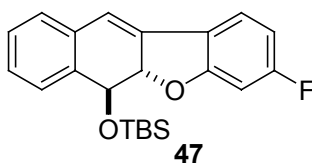
**(±)-(5S\*,6S\*)-tert-Butyl-(3-methoxy-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-dimethyl-silane (45)**

Follow the general procedure for the Heck reaction, **45** was obtained as a viscous liquid (91%).  $R_f=0.10$  on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2954 (m), 2932 (m), 2856 (m), 1619 (s), 1494 (s), 1472 (m), 1348 (m), 1273 (m), 1248 (m), 1147 (s), 1081 (m).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61-7.59 (1H, m), 7.35 (1H, d,  $J=8.3$  Hz), 7.25-7.20 (2H, m), 7.13-7.10 (1H, m), 6.54 (1H, dd,  $J=8.4, 2.3$  Hz), 6.50 (1H, d,  $J=2.2$  Hz), 6.43 (1H, d,  $J=2.9$  Hz), 5.17 (1H, dd,  $J=12.7, 2.9$  Hz), 5.12 (1H, d,  $J=12.7$  Hz), 3.83 (3H, s), 1.06 (9H, s), 0.28 (3H, s), 0.20 (3H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 162.6, 138.7, 135.8, 135.0, 127.9, 126.9, 126.2, 125.2, 122.1, 117.5, 111.7, 108.6, 96.6, 88.9, 74.9, 55.9, 26.4, 18.8, -3.8, -4.4. HRMS calc'd for  $\text{C}_{23}\text{H}_{28}\text{O}_3\text{Si}$  ( $\text{M}^+$ ): 380.1808. Found: 380.1807.



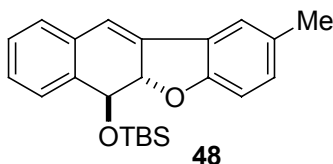
**(±)-(5S\*,6S\*)-tert-Butyl-(2-fluoro-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-dimethyl-silane (46)**

Follow the general procedure for the Heck reaction, **46** was obtained as a white wax-like solid (96%).  $R_f=0.25$  on silica gel (1% EtOAc: hexanes); mp 81-83 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2950 (m), 2928 (m), 2855 (m), 1602 (w), 1477 (s), 1178 (m), 1150 (s), 1080 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63-7.61 (1H, m), 7.30-7.24 (2H, m), 7.17-7.14 (1H, m), 7.12 (1H, dd,  $J_{\text{HH}}=2.7$  Hz,  $^3J_{\text{HF}}=7.9$  Hz), 6.91 (1H, ddd,  $J_{\text{HH}}=8.8, 2.7$  Hz,  $^3J_{\text{HF}}=8.8$  Hz), 6.84 (1H, d,  $J=8.8$  Hz,  $^4J_{\text{HF}}=4.2$  Hz), 6.57 (1H, d,  $J=2.7$  Hz), 5.17 (1H, AB,  $J=12.7, 2.7$  Hz), 5.14 (1H, AB,  $J=13.0$  Hz), 1.06 (9H, s), 0.27 (3H, s), 0.20 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.6, 158.2 ( $^1J_{\text{CF}}=239$  Hz), 138.6 ( $^4J_{\text{CF}}=3.0$  Hz), 136.4, 134.2, 128.1, 127.9, 126.9, 125.9 ( $^3J_{\text{CF}}=9$  Hz), 125.4, 117.2 ( $^2J_{\text{CF}}=24$  Hz), 115.5, 111.4 ( $^3J_{\text{CF}}=8$  Hz), 108.1 ( $^2J_{\text{CF}}=25$  Hz), 88.6, 74.8, 26.3, 18.7, -4.0, -4.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -122.8 (1F, ddd,  $J_{\text{FH}}=7.6, 7.6, 4.6$  Hz). HRMS calc'd for  $\text{C}_{22}\text{H}_{25}\text{FO}_2\text{Si}$  ( $\text{M}^+$ ): 368.1608. Found: 368.1602.



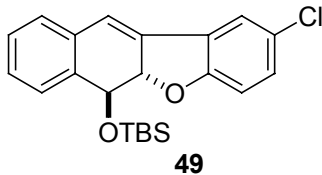
**(±)-(5S\*,6S\*)-tert-Butyl-(3-fluoro-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-dimethyl-silane (47)**

Follow the general procedure for the Heck reaction, **47** was obtained as a white wax-like solid (97%).  $R_f=0.34$  on silica gel (1% EtOAc: hexanes); mp 96-97 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2950 (m), 2928 (m), 2855 (m), 1602 (w), 1477 (s), 1178 (m), 1150 (s), 1080 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.60 (1H, m), 7.38 (1H, dd,  $J=8.1, 5.7$  Hz), 7.28-7.24 (2H, m), 7.26-7.22 (1H, m), 6.70-6.65 (2H, m), 6.52 (1H, d,  $J=3.1$  Hz), 5.21 (1H, dd,  $J=12.8, 2.9$  Hz), 5.14 (1H, dd,  $J=12.8, 0.7$  Hz), 1.06 (9H, s), 0.26 (3H, s), 0.20 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7 ( $^3J_{\text{CF}}=14$  Hz), 164.3 ( $^1J_{\text{CF}}=249$  Hz), 137.7 ( $J_{\text{CF}}=1.5$  Hz), 135.9, 134.5, 128.1, 127.6, 126.6, 125.3, 122.3 ( $^3J_{\text{CF}}=11$  Hz), 121.1 ( $J_{\text{CF}}=2.3$  Hz), 113.8 ( $J_{\text{CF}}=2.3$  Hz), 108.8 ( $^2J_{\text{CF}}=24$  Hz), 99.4 ( $^2J_{\text{CF}}=26$  Hz), 89.3, 74.7, 26.2, 18.7, -4.0, -4.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -108.9 (1F, ddd,  $J_{\text{FH}}=9.4, 8.8, 6.2$  Hz). HRMS calc'd for  $\text{C}_{22}\text{H}_{25}\text{FO}_2\text{Si}$  ( $\text{M}^+$ ): 368.1608. Found: 368.1609.



**(±)-(5S\*,6S\*)-tert-Butyl-dimethyl-(2-methyl-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-silane (48)**

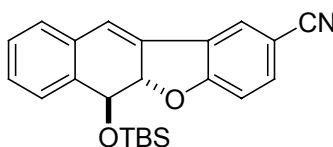
Follow the general procedure for the Heck reaction, **48** was obtained as a white wax-like solid (96%).  $R_f=0.23$  on silica gel (1% EtOAc: hexanes); mp 66-67 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2956 (s), 2929 (s), 2856 (s), 1601 (m), 1483 (s), 1253 (m), 1198 (m), 1150 (s), 1081 (s), 1003 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63-7.61 (1H, m), 7.27-7.23 (3H, m), 7.16-7.12 (1H, m), 7.04 (1H, dd,  $J=8.2, 1.3$  Hz), 6.83 (1H, d,  $J=8.2$  Hz), 6.54 (1H, d,  $J=2.2$  Hz), 5.14-5.13 (2H, m), 2.33 (3H, s), 1.06 (9H, s), 0.27 (3H, s), 0.20 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 154.9, 139.6, 136.4, 134.6, 128.0, 127.5, 126.6, 125.3, 125.2, 117.6, 114.2, 111.4, 105.9, 88.1, 74.9, 56.3, 26.3, 18.7, -4.0, -4.6. HRMS calc'd for  $\text{C}_{23}\text{H}_{28}\text{O}_2\text{Si}$  ( $\text{M}^+$ ): 364.1859. Found: 364.1861.



**(±)-(5S\*,6S\*)-tert-Butyl-(2-chloro-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-dimethyl-silane (49)**

Follow the general procedure for the Heck reaction, **49** was obtained as a white wax-like (90%).  $R_f=0.29$  on silica gel (1% EtOAc: hexanes); mp 126-128 °C (hexanes). IR (neat,

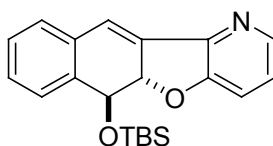
cm<sup>-1</sup>) 2950 (m), 2928 (m), 2855 (m), 1599 (w), 1465 (s), 1252 (s), 1105 (s), 1080 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63-7.60 (1H, m), 7.39 (1H, d, *J*=2.2 Hz), 7.29-7.23 (2H, m), 7.16 (1H, dd, *J*=8.6, 2.2 Hz), 7.16-7.14 (1H, m), 6.85 (1H, d, *J*=8.6 Hz), 6.57 (1H, d, *J*=2.8 Hz), 5.18 (1H, AB, *J*=12.8, 2.8 Hz), 5.14 (1H, AB, *J*=12.8 Hz), 1.05 (9H, s), 0.26 (3H, s), 0.20 (3H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.0, 137.8, 136.3, 134.2, 130.4, 128.1, 128.0, 126.9, 126.6, 126.5, 125.4, 121.6, 115.7, 112.1, 88.6, 74.7, 26.3, 18.7, -4.0, -4.6. HRMS calc'd for C<sub>22</sub>H<sub>25</sub>ClO<sub>2</sub>Si (M<sup>+</sup>): 384.1312. Found: 384.1308.



**50**

**(±)-(5S\*,6S\*)-6-(*tert*-Butyl-dimethyl-silanyloxy)-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-2-carbonitrile (50)**

Follow the general procedure for the Heck reaction, **50** was obtained as a white solid (91%) by chromatographing on silica gel (2.5% EtOAc/hexanes). R<sub>f</sub>=0.15 on silica gel (2.5% EtOAc: hexanes); mp 125-126 °C (hexanes). IR (neat, cm<sup>-1</sup>) 3065 (w), 2954 (m), 2929 (m), 2856 (m), 2225 (m), 1610 (m), 1473 (s), 1253 (m), 1213 (s), 1151 (m), 1082 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (1H, d, *J*=1.6 Hz), 7.62 (1H, d, *J*=6.0 Hz), 7.52 (1H, dd, *J*=8.6, 1.8 Hz), 7.33-7.27 (2H, m), 7.19 (1H, dd, *J*=6.4, 2.2 Hz), 6.99 (1H, d, *J*=8.4 Hz), 6.69 (1H, d, *J*=3.1 Hz), 5.27 (1H, dd, *J*=12.8, 3.1 Hz), 5.17 (1H, d, *J*=12.8 Hz), 1.06 (9H, s), 0.26 (3H, s), 0.20 (3H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.3, 136.2, 135.9, 135.0, 133.7, 128.5, 128.3, 127.3, 126.4, 125.7, 125.5, 119.3, 117.3, 112.0, 105.1, 89.4, 74.4, 26.2, 18.6, -4.1, -4.6. HRMS calc'd for C<sub>23</sub>H<sub>25</sub>NO<sub>2</sub>Si (M<sup>+</sup>): 375.1655. Found: 375.1647.

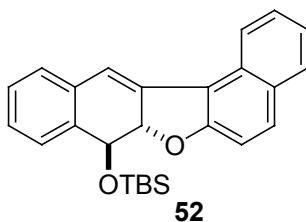


**51**

**(±)-(10S\*,10aS\*)-10-(*tert*-Butyl-dimethyl-silanyloxy)-10,10a-dihydro-11-oxa-4-aza-benzo[b]fluorene (51)**

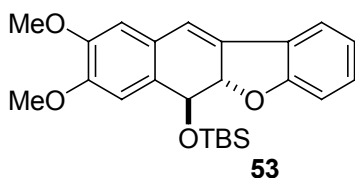
Follow the general procedure for the Heck reaction, **51** was obtained as a white solid (95%) by chromatographing on silica gel (10% EtOAc/hexanes). R<sub>f</sub>=0.12 on silica gel (10% EtOAc: hexanes); mp 146-147 °C (hexanes). IR (neat, cm<sup>-1</sup>) 3063 (w), 2954 (m), 2929 (m), 2857 (m), 1651 (w), 1594 (w), 1473 (m), 1414 (s), 1251 (m), 1205 (s), 1152 (m), 1085 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (1H, dd, *J*=4.8, 1.3 Hz), 7.63 (1H, d, *J*=6.4 Hz), 7.33-7.27 (2H, m), 7.24 (1H, dd, *J*=6.4, 2.2 Hz), 7.19 (1H, dd, *J*=8.2, 1.3 Hz), 7.11 (1H, dd, *J*=8.1, 4.9 Hz), 7.00 (1H, d, *J*=3.1 Hz), 5.28 (1H, dd, *J*=9.6, 3.1 Hz), 5.17 (1H, d, *J*=9.8 Hz), 1.06 (9H, s), 0.27 (3H, s), 0.21 (3H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.4, 145.9, 143.5, 136.9, 136.6, 134.1, 128.5, 128.2, 127.7, 125.4, 124.2, 117.5, 87.7,

74.7, 26.2, 18.7, -4.1, -4.6. HRMS calc'd for  $C_{21}H_{25}NO_2Si$  ( $M^+$ ): 351.1655. Found: 351.1653.



**(±)-(7S\*,8S\*)-tert-Butyl-(7a,8-dihydro-dinaphtho[2,1-b;2',3'-d]furan-8-yloxy)-dimethyl-silane (52)**

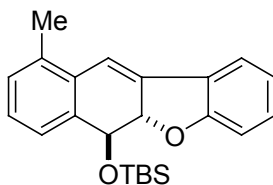
Follow the general procedure for the Heck reaction (catalyst loading  $Pd_2(dba)_3$  10 mol%,  $HP(t-Bu)_3 \cdot BF_4$  40 mol%, stirred at 80 °C for 24 h), **52** was obtained as a yellow liquid (83%).  $R_f=0.24$  on silica gel (1% EtOAc: hexanes). IR (neat,  $cm^{-1}$ ) 3061 (w), 2954 (m), 2929 (m), 2856 (m), 1626 (w), 1587 (w), 1523 (w), 1473 (m), 1460 (m), 1252 (m), 1218 (s), 1152 (m), 1080 (s), 1001 (m).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.18 (1H, d,  $J=7.7$  Hz), 7.85 (1H, d,  $J=8.1$  Hz), 7.77 (1H, d,  $J=8.8$  Hz), 7.65 (1H, d,  $J=7.0$  Hz), 7.60 (1H, ddd,  $J=8.8, 6.8, 1.1$  Hz), 7.40 (1H, ddd,  $J=8.2, 7.0, 1.1$  Hz), 7.32-7.23 (3H, m), 7.22 (1H, d,  $J=8.8$  Hz), 6.95 (1H, d,  $J=3.1$  Hz), 5.32 (1H, dd,  $J=13.0, 3.1$  Hz), 5.23 (1H, dd,  $J=13.0, 0.7$  Hz), 1.08 (9H, s), 0.31 (3H, s), 0.23 (3H, s);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  164.4, 140.0, 135.5, 135.3, 132.4, 130.1, 129.6, 129.5, 128.1, 128.1, 127.3, 126.8, 125.1, 124.0, 123.1, 116.6, 114.8, 113.1, 88.7, 74.8, 26.3, 18.8, -3.9, -4.5. HRMS calc'd for  $C_{26}H_{28}O_2Si$  ( $M^+$ ): 400.1859. Found: 400.1863.



**(±)-(5S\*,6S\*)-tert-Butyl-(8,9-dimethoxy-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-dimethyl-silane (54)**

Follow the general procedure for the Heck reaction (0.5 mmol scale, stirred at 70 °C for 60 h), the mixture was added to a solution of  $NH_2OH \cdot HCl$  (0.150 g) and NaOAc (0.160 g) in MeOH (5 mL) and stirred overnight under  $N_2$  at rt. After  $NaHCO_3$  workup and hexane extraction, **53** was obtained as a slightly yellow viscous liquid (93%) by chromatographing on silica gel (5% EtOAc: hexanes).  $R_f=0.12$  on silica gel (5% EtOAc: hexanes). IR (neat,  $cm^{-1}$ ) 2953 (m), 2931 (m), 2856 (m), 1608 (w), 1571 (w), 1506 (s), 1464 (s), 1322 (s), 1251 (s), 1214 (m), 1147 (s), 1122 (s).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.44 (1H, dd,  $J=7.5, 0.7$  Hz), 7.25 (1H, s), 7.21 (1H, ddd,  $J=7.8, 7.8, 1.3$  Hz), 6.95 (1H, ddd,  $J=7.5, 7.5, 0.8$  Hz), 6.94 (1H, d,  $J=8.1$  Hz), 6.72 (1H, s), 6.52 (1H, d,  $J=2.4$  Hz),

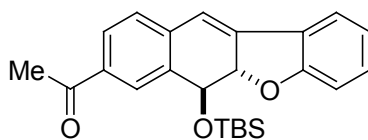
5.15-5.08 (2H, m), 3.92 (3H, s), 3.90 (3H, s), 1.07 (9H, s), 0.30 (3H, s), 0.21 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 148.4, 148.4, 137.4, 130.3, 129.2, 127.3, 125.0, 121.5, 121.4, 113.9, 111.1, 110.3, 109.2, 87.9, 74.9, 56.3, 56.2, 26.2, 18.7, -3.9, -4.7. HRMS calc'd for  $\text{C}_{24}\text{H}_{30}\text{O}_4\text{Si}$  ( $\text{M}^+$ ): 410.1913. Found: 410.1922.



**54**

**(±)-(5S\*,6S\*)-tert-Butyl-dimethyl-(10-methyl-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-silane (54)**

Follow the general procedure for the Heck reaction, **54** was obtained as a white wax-like solid (97%).  $R_f$ =0.17 on silica gel (0.5% EtOAc: hexanes); mp 76-78 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3054 (w), 2956 (s), 2929 (s), 2856 (s), 1608 (m), 1465 (s), 1366 (m), 1253 (s), 1204 (s), 1151 (s), 1093 (s), 1016 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (1H, dd,  $J$ =7.5, 0.9 Hz), 7.48 (1H, d,  $J$ =7.4 Hz), 7.23 (1H, ddd,  $J$ =7.7, 7.7, 1.4 Hz), 7.16 (1H, t,  $J$ =7.6 Hz), 7.10 (1H, d,  $J$ =7.5 Hz), 6.96 (1H, ddd,  $J$ =7.5, 7.5, 0.9 Hz), 6.94 (1H, d,  $J$ =8.1 Hz), 6.74 (1H, d,  $J$ =3.1 Hz), 5.16 (1H, dd,  $J$ =12.9, 3.0 Hz), 5.08 (1H, d,  $J$ =12.9 Hz), 2.40 (3H, s), 1.05 (9H, s), 0.27 (3H, s), 0.19 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 139.1, 136.4, 133.9, 132.9, 130.8, 129.7, 125.1, 123.0, 121.6, 121.4, 111.4, 111.1, 87.6, 75.2, 26.3, 19.5, 18.8, -4.0, -4.6. HRMS calc'd for  $\text{C}_{23}\text{H}_{28}\text{O}_2\text{Si}$  ( $\text{M}^+$ ): 364.1859. Found: 364.1867.

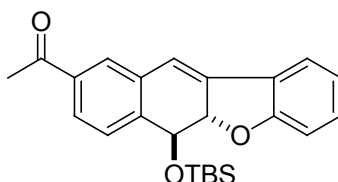


**55**

**(±)-(5S\*,6S\*)-1-[6-(tert-Butyl-dimethyl-silanyloxy)-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-8-yl]-ethanone (55)**

Follow the general procedure for the Heck reaction, **55** was obtained as a yellowish liquid (55%) by chromatographing on silica gel (2.5% EtOAc/hexane).  $R_f$ =0.25 on silica gel (2.5% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2954 (m), 2928 (m), 2856 (m), 1680 (s), 1600 (s), 1462 (s), 1357 (m), 1274 (m), 1248 (s), 1151 (s), 1089 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (1H, s), 7.89 (1H, dd,  $J$ =7.9, 1.6 Hz), 7.49 (1H, d,  $J$ =7.4 Hz), 7.28 (1H, ddd,  $J$ =7.7, 7.7, 1.3 Hz), 7.22 (1H, d,  $J$ =7.9 Hz), 6.99 (1H, ddd,  $J$ =7.5, 7.5, 0.7 Hz), 6.98 (1H, d,  $J$ =8.1 Hz), 6.62 (1H, d,  $J$ =2.4 Hz), 5.21-5.13 (2H, m), 2.61 (3H, s), 1.10 (9H, s), 0.31 (3H, s), 0.24 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.4, 165.0, 142.5, 139.4, 136.5, 135.8, 131.7, 128.2, 126.7, 125.9, 124.4, 122.1, 121.8, 113.4, 111.4, 87.7, 74.5,

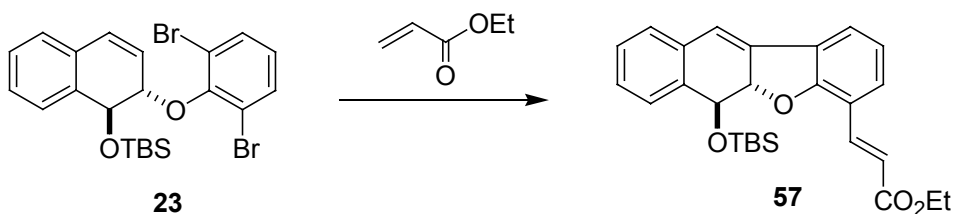
26.8, 26.2, 18.7, -4.0, -4.7. HRMS calc'd for C<sub>24</sub>H<sub>28</sub>O<sub>3</sub>Si (M<sup>+</sup>): 392.1808. Found: 392.1818.



**56**

**(±)-(5S\*,6S\*)-1-[6-(*tert*-Butyl-dimethyl-silanyloxy)-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-9-yl]-ethanone (56)**

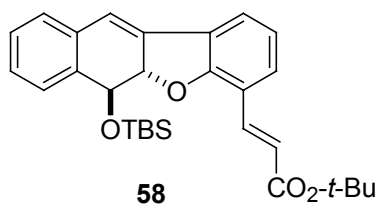
Follow the general procedure for the Heck reaction, **56** was obtained as a yellowish liquid (92%) by chromatographing on silica gel (2.5% EtOAc/hexane). R<sub>f</sub>=0.27 on silica gel (2.5% EtOAc: hexanes). IR (neat, cm<sup>-1</sup>) 2954 (m), 2928 (m), 2856 (m), 1687 (s), 1683 (s), 1609 (w), 1463 (s), 1360 (m), 1292 (m), 1257 (s), 1201 (s), 1153 (s), 1089 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (1H, dd, *J*=8.1, 1.8 Hz), 7.73 (1H, d, *J*=1.6 Hz), 7.72 (1H, d, *J*=8.1 Hz), 7.49 (1H, dd, *J*=7.5, 0.7 Hz), 7.26 (1H, ddd, *J*=7.8, 7.8, 1.6 Hz), 6.99 (1H, ddd, *J*=7.4, 7.4, 0.8 Hz), 6.96 (1H, d, *J*=8.1 Hz), 6.62 (1H, s), 5.16 (2H, d, *J*=1.3 Hz), 2.61 (3H, s), 1.06 (9H, s), 0.29 (3H, s), 0.21 (3H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.0, 164.7, 141.6, 140.5, 137.0, 135.2, 131.3, 127.6, 125.9, 125.6, 124.5, 122.0, 121.7, 113.5, 111.3, 87.3, 74.9, 26.9, 26.2, 18.7, -4.0, -4.6. HRMS calc'd for C<sub>24</sub>H<sub>28</sub>O<sub>3</sub>Si (M<sup>+</sup>): 392.1808. Found: 392.1801.



**(±)-(5S\*,6S\*)-3-[6-(*tert*-Butyl-dimethyl-silanyloxy)-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-4-yl]-acrylic acid ethyl ester (57)**

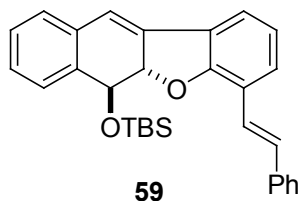
**General procedure for the Pd-catalyzed double Heck reaction:** A vial which was charged with **23** (0.102 g, 0.2 mmol), DABCO (0.112 g, 1 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (9.2 mg, 0.01 mmol) and HP(*t*-Bu)<sub>3</sub>·BF<sub>4</sub> (11.6 mg, 0.04 mmol) was purged with N<sub>2</sub> for 10 min. Dioxane (1 mL) was added and the mixture was stirred at rt for 5 min, followed by addition of ethyl acrylate (0.040g, 0.4 mmol). The mixture was stirred at 40 °C for 24 h before quenched by addition of saturated NaHCO<sub>3</sub> (10 mL). The mixture was extracted with hexanes (3×10 mL). The organic phase was combined, washed with brine (10 mL)

and dried over  $\text{MgSO}_4$ . After removal of solvent, the residue was chromatographed on silica gel (2.5% EtOAc: hexanes) to give a yellow crystalline solid (0.079 g, 88%). The single crystal for X-ray structure determination was obtained by slow evaporation of **57** in hexane.  $R_f=0.19$  on silica gel (2.5% EtOAc: hexanes); mp 121-123 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2958 (m), 2931 (m), 2854 (m), 1710 (s), 1635 (m), 1433 (s), 1312 (m), 1174 (s), 1160 (m), 1084 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (1H, d,  $J=16.1$  Hz), 7.64-7.62 (1H, m), 7.45 (1H, dd,  $J=7.5, 1.1$  Hz), 7.35 (1H, dd,  $J=7.7, 0.7$  Hz), 7.30-7.25 (2H, m), 7.18-7.16 (1H, m), 6.99 (1H, t,  $J=7.6$  Hz), 6.82 (1H, d,  $J=16.1$  Hz), 6.63 (1H, d,  $J=3.1$  Hz), 5.29 (1H, dd,  $J=12.6, 3.1$  Hz), 5.20 (1H, d,  $J=12.6$  Hz), 4.27 (2H, m), 1.34 (3H, t,  $J=7.1$  Hz), 1.10 (9H, s), 0.33 (3H, s), 0.23 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.6, 163.4, 139.2, 137.9, 136.3, 134.4, 130.7, 128.1, 127.8, 126.8, 125.9, 125.4, 122.9, 122.0, 120.8, 119.3, 115.2, 89.0, 74.7, 60.6, 26.2, 18.7, 14.5, -4.0, -4.3. HRMS calc'd for  $\text{C}_{27}\text{H}_{32}\text{O}_4\text{Si}$  ( $\text{M}^+$ ): 448.2070. Found: 448.2067.



**(±)-(5S\*,6S\*)-3-[6-(*tert*-Butyl-dimethyl-silanyloxy)-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-4-yl]-acrylic acid *tert*-butyl ester (**58**)**

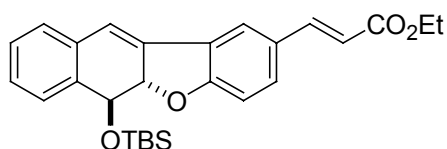
Follow the general procedure for the double Heck reaction using **23** and *t*-butyl acrylate, **58** was obtained as a yellow viscous liquid (81%).  $R_f=0.18$  on silica gel (2.5% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2952 (m), 2928 (m), 2857 (m), 1708 (s), 1633 (m), 1320 (m), 1150 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64-7.62 (1H, m), 7.63 (1H, d,  $J=16.1$  Hz), 7.44 (1H, dd,  $J=7.5, 1.1$  Hz), 7.32 (1H, dd,  $J=7.4, 0.9$  Hz), 7.29-7.25 (2H, m), 7.18-7.15 (1H, m), 6.98 (1H, t,  $J=7.6$  Hz), 6.77 (1H, d,  $J=16.1$  Hz), 6.62 (1H, d,  $J=3.1$  Hz), 5.28 (1H, dd,  $J=12.8, 3.1$  Hz), 5.20 (1H, dd,  $J=12.7, 0.7$  Hz), 1.54 (9H, s), 1.09 (9H, s), 0.34 (3H, s), 0.23 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 163.3, 138.3, 137.9, 136.3, 134.4, 131.1, 128.1, 127.8, 126.8, 125.9, 125.4, 123.1, 122.6, 121.9, 119.6, 115.1, 89.0, 80.5, 74.6, 28.5, 26.2, 18.7, -3.8, -4.4. HRMS calc'd for  $\text{C}_{29}\text{H}_{36}\text{O}_4\text{Si}$  ( $\text{M}^+$ ): 476.2383. Found: 476.2390.





**(±)-(5S\*,6S\*)-tert-Butyl-dimethyl-(4-styryl-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-silane**

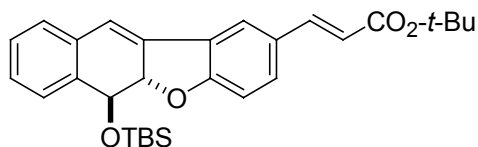
Follow the general procedure for the double Heck reaction using **23** and styrene, **59** was obtained as a yellow liquid (81%) by chromatographing on silica gel (1% EtOAc/hexanes).  $R_f=0.35$  on silica gel (2.5% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3058 (w), 3031 (w), 2950 (s), 2931 (s), 2854 (s), 1589 (m), 1470 (m), 1453 (s), 1430 (s), 1344 (m), 1150 (m), 1083 (s).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65-7.63 (1H, m), 7.54-7.24 (2H, m), 7.45 (1H, d,  $J=7.7$  Hz), 7.39-7.36 (3H, m), 7.34 (1H, d,  $J=16.4$  Hz), 7.29 (1H, d,  $J=16.7$  Hz), 7.29-7.25 (3H, m), 7.18-7.16 (1H, m), 6.99 (1H, t,  $J=7.6$  Hz), 6.61 (1H, d,  $J=3.1$  Hz), 5.28 (1H, dd,  $J=12.6, 3.1$  Hz), 5.21 (1H, dd,  $J=12.6, 0.6$  Hz), 4.27 (2H, m), 1.34 (3H, t,  $J=7.1$  Hz), 1.11 (9H, s), 0.37 (3H, s), 0.25 (3H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 138.8, 137.9, 136.3, 134.6, 130.3, 128.8, 128.0, 127.8, 127.7, 127.5, 126.6, 126.6, 125.3, 125.3, 122.9, 121.9, 120.4, 114.5, 88.3, 75.0, 26.4, 18.9, -3.6, -4.3. HRMS calc'd for  $\text{C}_{30}\text{H}_{32}\text{O}_2\text{Si}$  ( $\text{M}^+$ ): 452.2172. Found: 452.2171.



**60**

**(±)-(5S\*,6S\*)-3-[6-(tert-Butyl-dimethyl-silanyloxy)-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-2-yl]-acrylic acid ethyl ester (60)**

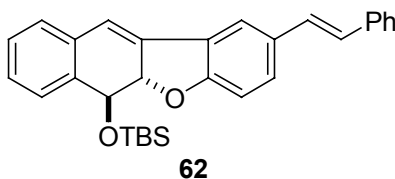
Follow the general procedure for the double Heck reaction using **25** and ethyl acrylate, **60** was obtained as a yellow solid (94%).  $R_f=0.11$  on silica gel (2.5% EtOAc: hexanes); mp 68-70 °C (hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2955 (m), 2937 (m), 2857 (m), 1708 (s), 1636 (m), 1608 (m), 1479 (m), 1257 (m), 1174 (s), 1153 (s), 1081 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (1H, d,  $J=15.9$  Hz), 7.64-7.61 (2H, m), 7.44 (1H, dd,  $J=8.4, 1.8$  Hz), 7.30-7.26 (2H, m), 7.19-7.17 (1H, m), 6.94 (1H, d,  $J=8.4$  Hz), 6.64 (1H, d,  $J=2.9$  Hz), 6.36 (1H, d,  $J=15.9$  Hz), 5.23 (1H, dd,  $J=12.8, 2.9$  Hz), 5.15 (1H, d,  $J=12.8$  Hz), 4.27 (2H, q,  $J=7.1$  Hz), 1.34 (3H, t,  $J=7.1$  Hz), 1.06 (9H, s), 0.27 (3H, s), 0.20 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 166.2, 144.4, 137.7, 136.3, 134.3, 131.5, 128.5, 128.1, 127.9, 126.9, 125.8, 125.4, 121.1, 116.5, 115.6, 111.5, 88.9, 74.7, 60.6, 26.2, 18.7, 14.6, -4.0, -4.6. HRMS calc'd for  $\text{C}_{29}\text{H}_{36}\text{O}_4\text{Si}$  ( $\text{M}^+$ ): 448.2070. Found: 448.2059.



**61**

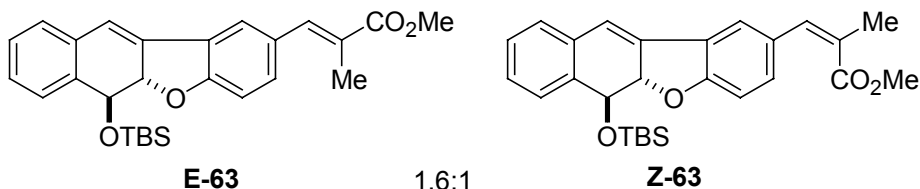
**(±)-(5S\*,6S\*)-3-[6-(*tert*-Butyl-dimethyl-silanyloxy)-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-2-yl]-acrylic acid *tert*-butyl ester (61)**

Follow the general procedure for the double Heck reaction using **25** and *t*-butyl acrylate, **61** was obtained as a yellow liquid (91%).  $R_f=0.25$  on silica gel (2.5% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2952 (m), 2931 (m), 2857 (m), 1705 (s), 1633 (m), 1609 (m), 1149 (s), 1101 (m), 1081 (m).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.61 (2H, m), 7.57 (1H, d,  $J=15.9$  Hz), 7.40 (1H, dd,  $J=8.4$ , 1.7 Hz), 7.29-7.26 (2H, m), 7.18-7.16 (1H, m), 6.93 (1H, d,  $J=8.4$  Hz), 6.63 (1H, d,  $J=3.1$  Hz), 6.29 (1H, d,  $J=15.9$  Hz), 5.22 (1H, dd,  $J=12.8$ , 3.1 Hz), 5.15 (1H, d,  $J=12.7$  Hz), 1.54 (9H, s), 1.06 (9H, s), 0.27 (3H, s), 0.20 (3H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 166.0, 143.3, 137.8, 136.3, 134.3, 131.4, 128.6, 128.1, 127.8, 126.9, 125.7, 125.3, 120.9, 118.4, 115.4, 111.4, 88.9, 80.6, 74.7, 28.5, 26.3, 18.8, -4.0, -4.5. HRMS calc'd for  $\text{C}_{29}\text{H}_{36}\text{O}_4\text{Si}$  ( $\text{M}^+$ ): 476.2383. Found: 476.2387.



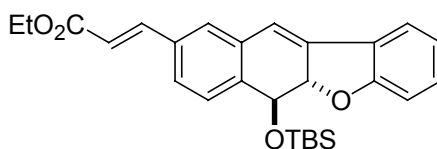
**(±)-(5S\*,6S\*)-*tert*-Butyl-dimethyl-(2-styryl-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-silane (62)**

Follow the general procedure for the double Heck reaction using **25** and styrene, **62** was obtained as a yellow liquid (92%) by chromatographing on silica gel (1% EtOAc/hexanes).  $R_f=0.17$  on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3025 (w), 2952 (s), 2925 (s), 2850 (s), 1600 (m), 1477 (s), 1150 (s), 1081 (s).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64-7.62 (2H, m), 7.50 (1H, d,  $J=8.0$  Hz), 7.39 (1H, dd,  $J=8.4$ , 2.0 Hz), 7.36 (2H, t,  $J=7.4$  Hz), 7.38-7.23 (3H, m), 7.18-7.16 (1H, m), 7.09 (1H, AB,  $J=16.2$  Hz), 7.02 (1H, AB,  $J=16.4$  Hz), 6.93 (1H, d,  $J=8.3$  Hz), 6.65 (1H, d,  $J=2.9$  Hz), 5.21 (1H, dd,  $J=12.8$ , 3.0 Hz), 5.16 (1H, dd,  $J=12.8$ , 0.7 Hz), 1.07 (9H, s), 0.28 (3H, s), 0.21 (3H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 138.7, 137.7, 136.4, 134.5, 131.4, 129.8, 128.9, 128.4, 128.0, 127.6, 127.6, 127.3, 126.7, 126.5, 125.4, 125.3, 119.2, 114.7, 111.2, 88.5, 74.8, 26.3, 18.8, -3.9, -4.5. HRMS calc'd for  $\text{C}_{30}\text{H}_{32}\text{O}_2\text{Si}$  ( $\text{M}^+$ ): 452.2171. Found: 452.2182.



**(±)-(5S\*,6S\*)-3-[6-(*tert*-Butyl-dimethyl-silanyloxy)-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-2-yl]-2-methyl-acrylic acid methyl ester**

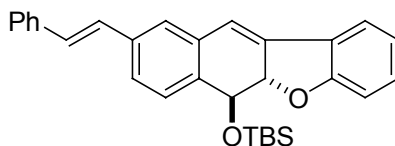
The general procedure for the double Heck reaction was employed by using **25** and methyl methacrylate. After 24 at 40 °C, workup and column chromatography (2.5% EtOAc:hexane) yielded pure **E-63** (0.020 g) as a yellowish liquid and a mixture of **E/Z-63** (0.046 g, ratio 5:6 by  $^1\text{H}$  NMR). Total yield of **63** was 0.066 g (74%, 1.6:1). Pure **E-63** sample was characterized.  $R_f=0.11$  (**E-63**),  $R_f=0.14$  (**Z-63**) on silica gel (2.5% EtOAc:hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2949 (m), 2929 (m), 2857 (m), 1711 (s), 1609 (m), 1480 (m), 1251 (s), 1211 (s), 1103 (s), 1082 (m).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (1H, s), 7.63-7.62 (1H, m), 7.53 (1H, d,  $J=1.6$  Hz), 7.31 (1H, dd,  $J=8.4, 1.7$  Hz), 7.28-7.26 (2H, m), 7.18-7.16 (1H, m), 6.96 (1H, d,  $J=8.3$  Hz), 6.62 (1H, d,  $J=3.1$  Hz), 5.22 (1H, dd,  $J=12.7, 3.1$  Hz), 5.16 (1H, dd,  $J=12.8, 0.7$  Hz), 3.83 (3H, s), 2.17 (3H, d,  $J=1.5$  Hz), 1.06 (9H, s), 0.28 (3H, s), 0.21 (3H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.4, 164.6, 138.8, 138.1, 136.3, 134.3, 133.0, 129.6, 128.1, 127.8, 126.9, 126.8, 125.3, 125.2, 122.8, 115.1, 111.1, 88.7, 74.8, 52.3, 26.3, 18.8, 14.5, -3.9, -4.5. HRMS calc'd for  $\text{C}_{27}\text{H}_{32}\text{O}_4\text{Si}$  ( $\text{M}^+$ ): 448.2070. Found: 448.2062.



**64**

**(±)-(5S\*,6S\*)-3-[6-(*tert*-Butyl-dimethyl-silanyloxy)-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-9-yl]-acrylic acid ethyl ester (**64**)**

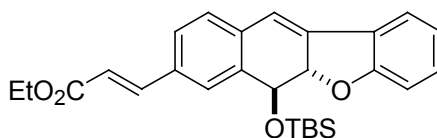
Follow the general procedure for the double Heck reaction using **42** and ethyl acrylate, **64** was obtained as a pale-yellow liquid (81%).  $R_f=0.21$  on silica gel (5% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2955 (m), 2929 (m), 2856 (m), 1713 (s), 1637 (s), 1463 (s), 1313 (m), 1272 (s), 1258 (s), 1175 (s), 1154 (s), 1084 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (1H, d,  $J=16.1$  Hz), 7.64 (1H, d,  $J=7.9$  Hz), 7.48 (1H, dd,  $J=7.5, 0.7$  Hz), 7.41 (1H, dd,  $J=7.9, 1.6$  Hz), 7.30 (1H, d,  $J=1.5$  Hz), 7.26 (1H, ddd,  $J=7.8, 7.8, 1.3$  Hz), 6.98 (1H, ddd,  $J=7.5, 7.5, 0.7$  Hz), 6.95 (1H, d,  $J=7.9$  Hz), 6.58 (1H, d,  $J=2.2$  Hz), 6.44 (1H, d,  $J=16.1$  Hz), 5.18-5.08 (2H, m), 4.28 (2H, q,  $J=7.2$  Hz), 1.35 (3H, t,  $J=7.1$  Hz), 1.06 (9H, s), 0.28 (3H, s), 0.21 (3H, s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 164.7, 144.3, 140.3, 138.7, 135.3, 134.4, 131.1, 127.3, 125.9, 125.7, 124.6, 121.9, 121.6, 118.6, 113.6, 111.3, 87.5, 74.8, 60.8, 26.3, 18.7, 14.6, -4.0, -4.6. HRMS calc'd for  $\text{C}_{27}\text{H}_{32}\text{O}_4\text{Si}$  ( $\text{M}^+$ ): 448.2070. Found: 448.2067.



**65**

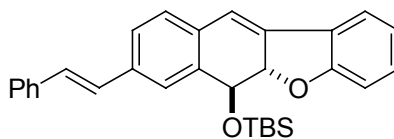
**(±)-(5S\*,6S\*)-tert-Butyl-dimethyl-(9-styryl-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-silane (65)**

Follow the general procedure for the double Heck reaction using **42** and styrene, **65** was obtained as a pale-yellow liquid (85%) by chromatographing on silica gel (1% EtOAc/hexanes).  $R_f=0.20$  on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3027 (w), 2954 (s), 2928 (s), 2855 (s), 1602 (m), 1463 (s), 1250 (m), 1150 (s), 1082 (s).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (1H, d,  $J=7.9$  Hz), 7.52 (2H, dd,  $J=8.3$ , 1.0 Hz), 7.48 (1H, dd,  $J=7.6$ , 1.7 Hz), 7.40 (1H, dd,  $J=7.9$ , 1.7 Hz), 7.37 (2H, t,  $J=7.6$  Hz), 7.31 (1H, d,  $J=1.6$  Hz), 7.27 (1H, dddd,  $J=7.3$ , 7.3, 1.2, 1.2 Hz), 7.25 (1H, ddd,  $J=7.7$ , 7.7, 1.3 Hz), 7.12 (1H, AB,  $J=16.3$  Hz), 7.10 (1H, AB,  $J=16.3$  Hz), 6.98 (1H, ddd,  $J=7.4$ , 7.4, 1.0 Hz), 6.95 (1H, d,  $J=7.9$  Hz), 6.62 (1H, d,  $J=2.6$  Hz), 5.19-5.13 (2H, m), 1.07 (9H, s), 0.29 (3H, s), 0.22 (3H, s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 139.6, 137.5, 137.2, 135.8, 135.0, 130.9, 129.1, 128.9, 128.3, 127.9, 126.7, 125.7, 125.7, 124.8, 124.5, 121.7, 121.5, 114.1, 111.2, 87.8, 74.9, 26.3, 18.8, -3.9, -4.5. HRMS calc'd for  $\text{C}_{30}\text{H}_{32}\text{O}_2\text{Si}$  ( $\text{M}^+$ ): 452.2172. Found: 452.2175.



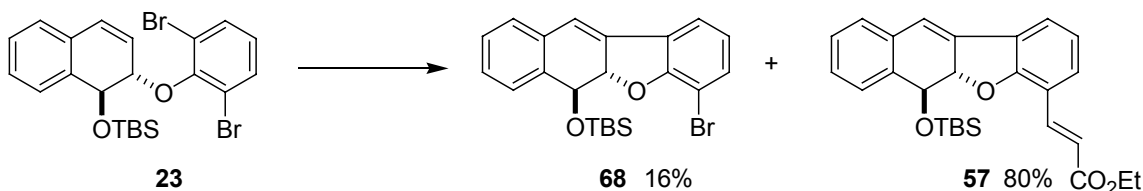
**(±)-(5S\*,6S\*)-3-[6-(tert-Butyl-dimethyl-silanyloxy)-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-8-yl]-acrylic acid ethyl ester (66)**

Follow the general procedure for the double Heck reaction using **41** and ethyl acrylate, **66** was obtained as a pale-yellow liquid (85%).  $R_f=0.24$  on silica gel (5% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 2955 (m), 2929 (m), 2856 (m), 1712 (s), 1634 (s), 1600 (m), 1463 (s), 1309 (m), 1261 (m), 1207 (s), 1175 (s), 1155 (s), 1080 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (1H, s), 7.68 (1H, d,  $J=15.9$ ), 7.47 (1H, dd,  $J=7.5$ , 0.7 Hz), 7.40 (1H, dd,  $J=7.8$ , 1.7 Hz), 7.26 (1H, dd,  $J=7.7$ , 7.7, 1.4 Hz), 7.15 (1H, d,  $J=7.9$  Hz), 6.98 (1H, ddd,  $J=7.4$ , 7.4, 0.9 Hz), 6.59 (1H, d,  $J=2.7$  Hz), 6.42 (1H, d,  $J=15.9$  Hz), 5.16 (1H, AB,  $J=12.8$ , 2.7 Hz), 5.13 (1H, AB,  $J=12.8$  Hz), 4.28 (2H, q,  $J=7.1$  Hz), 1.35 (3H, t,  $J=7.1$  Hz), 1.09 (9H, s), 0.29 (3H, s), 0.23 (3H, s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 164.9, 144.6, 141.0, 137.0, 136.9, 133.5, 131.3, 128.3, 127.0, 124.9, 124.6, 121.9, 121.7, 117.8, 113.7, 111.3, 87.7, 74.6, 60.7, 26.3, 18.8, 14.6, -4.0, -4.5. HRMS calc'd for  $\text{C}_{27}\text{H}_{32}\text{O}_4\text{Si}$  ( $\text{M}^+$ ): 448.2070. Found: 448.2085.



**(±)-(5S\*,6S\*)-tert-Butyl-dimethyl-(8-styryl-5a,6-dihydro-benzo[b]naphtho[2,3-d]furan-6-yloxy)-silane**

Follow the general procedure for the double Heck reaction using **41** and styrene, **67** was obtained as a pale-yellow liquid (85%).  $R_f=0.17$  on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3027 (m), 2955 (m), 2929 (m), 2855 (m), 1596 (m), 1463 (m), 1253 (m), 1206 (m), 1150 (s), 1077 (m).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (1H, s), 7.51 (2H, dd,  $J=7.7, 0.8$  Hz), 7.46 (1H, dd,  $J=7.4, 0.7$  Hz), 7.36 (2H, t,  $J=7.6$  Hz), 7.34 (1H, dd,  $J=8.0, 1.5$  Hz), 7.26 (1H, t,  $J=7.3$  Hz), 7.23 (1H, ddd,  $J=7.7, 7.7, 1.3$  Hz), 7.14 (1H, AB,  $J=16.2$  Hz), 7.13 (1H, d,  $J=7.7$  Hz), 7.10 (1H, AB,  $J=16.2$  Hz), 6.96 (1H, ddd,  $J=7.5, 7.5, 0.9$  Hz), 6.95 (1H, d,  $J=8.1$  Hz), 6.59 (1H, d,  $J=2.8$  Hz), 5.19 (1H, dd,  $J=12.8, 2.9$  Hz), 5.14 (1H, d,  $J=12.8$  Hz), 1.13 (9H, s), 0.31 (3H, s), 0.25 (3H, s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 139.2, 137.6, 136.7, 136.6, 134.2, 130.8, 128.9, 128.8, 128.7, 127.9, 127.0, 126.8, 126.8, 124.9, 123.0, 121.7, 121.6, 114.1, 111.2, 87.9, 74.8, 26.4, 18.8, -3.9, -4.6. HRMS calc'd for  $\text{C}_{30}\text{H}_{32}\text{O}_2\text{Si}$  ( $\text{M}^+$ ): 452.2172. Found: 452.2164.



A vial which was charged with **23** (0.114 g, 0.22 mmol), DABCO (0.099 g, 0.88 mmol),  $\text{Pd}_2(\text{dba})_3$  (5.1 mg, 0.0056 mmol) and  $\text{HP}(t\text{-Bu})_3\text{BF}_4$  (6.5 mg, 0.00224 mmol) was purged with  $\text{N}_2$  for 10 min. Dioxane (1 mL) was added and the mixture was stirred at rt for 5 min, followed by addition of ethyl acrylate (0.040g, 0.4 mmol). The mixture was stirred at 40 °C for 12 h before quenched by addition of saturated  $\text{NaHCO}_3$  (10 mL). The mixture was extracted with hexanes (3×10 mL). The organic phase was combined, washed with brine (10 mL) and dried over  $\text{MgSO}_4$ . After removal of solvent, the residue was chromatographed on silica gel (1%→2.5% EtOAc: hexanes) to give **68** as a colourless liquid (0.015 g, 16%) and **57** (0.079g, 80%). **68**:  $R_f=0.20$  on silica gel (1% EtOAc: hexanes). IR (neat,  $\text{cm}^{-1}$ ) 3063 (w), 2952 (m), 2928 (m), 2855 (m), 1470 (s), 1432 (s), 1253 (m), 1209 (s), 1151 (s), 1083 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66-7.64 (1H, m), 7.38 (2H, d,  $J=7.9$  Hz), 7.29-7.25 (2H, m), 7.17-7.15 (1H, m), 6.85 (1H, t,  $J=7.9$  Hz), 6.60 (1H, d,  $J=2.9$  Hz), 5.25 (1H, dd,  $J=12.6, 2.9$  Hz), 5.20 (1H, d,  $J=12.6$  Hz), 1.07 (9H, s), 0.36 (3H, s), 0.24 (3H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 138.4, 136.3, 134.1, 133.4, 128.1, 128.0, 126.9, 126.4, 125.4, 122.8, 120.5, 115.9, 104.3, 88.5, 74.7, 26.3, 18.8, -3.9, -4.6. HRMS calc'd for  $\text{C}_{22}\text{H}_{25}\text{BrO}_2\text{Si}$  ( $\text{M}^+$ ): 428.0807. Found: 428.0821.