

## *Supporting Information*

### **Nickel(0)-Catalyzed Enantio- and Diastereoselective Synthesis of Benzoxasiloles: Ligand-Controlled Switching from Inter- to Intramolecular Aryl-Transfer Process**

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## [1] General

All manipulations were conducted under a nitrogen atmosphere by using standard Schlenk or dry box techniques unless otherwise noted.  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded on Bruker AVANCE III 400 spectrometers at 25 °C. The chemical shifts in  $^1\text{H}$ -NMR and  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra are reported in parts per million (ppm) and are referenced to the residual solvent signal as the internal standard:  $\text{CDCl}_3$   $\delta$  = 7.26 ( $^1\text{H}$ ) and  $\delta$  = 77.0 ( $^{13}\text{C}$ ) ppm;  $\text{C}_6\text{D}_6$ :  $\delta$  = 7.16 ( $^1\text{H}$ ) and  $\delta$  = 128.1 ( $^{13}\text{C}$ ) ppm. Splitting patterns are denoted as "s" for singlet; "d" for doublet; "t" for triplet; "q" for quartet; "sext" for sextet; "sept" for septet; "m" for multiplet, "br" for broad; "dt" for doublet of triplets; "td" for triplet of doublets, and "app" for apparent. Mass spectra were obtained by using a Shimadzu GCMS-QP 2010 instrument with an ionization voltage of 70 eV. Medium-pressure column chromatography was carried out on a Biotage Flash Purification System Isolera, equipped with a 250 nm UV detector. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-2014 gas chromatograph, equipped with a flame ionization detector. High resolution mass spectrometry (HRMS) was performed at Instrumental Analysis Center, Faculty of Engineering, Osaka University. Enantioselectivities were recorded by means of either JASCO-Supercritical Fluid chromatography (SFC) equipped with PU-2080- $\text{CO}_2$  plus  $\text{CO}_2$  delivery pump and MD-2018 plus as a photodiode array detector or HPLC of Shimadzu or Lacrome manufacturer using chiral columns of Diacel Chiralpak (I and O series). Optical rotations were measured in JASCO-DIP 1000 polarimeter with a path length of 1 dm using the sodium D line, 589 nm. THF, toluene, and benzene- $d_6$  were distilled from sodium benzophenone ketyl, and other solvents were distilled and degassed prior to use. All commercially available reagents were distilled over  $\text{CaH}_2$  under reduced pressure prior to use.  $\text{Ni}(\text{cod})_2$  was recrystallized from toluene prior to use.  $\text{Ni}(\text{acac})_2$  was dried under reduced pressure (0.3 mmHg) at >100 °C prior to use. All synthesized starting materials were purified either by distillation over  $\text{CaH}_2$  or recrystallized prior to use for catalytic reactions. Chiral *N*-heterocyclic carbene (NHC) salts were synthesized according to the reported procedures. Optimized ligand **L5**· $\text{HBF}_4$  was prepared according to Grubbs protocol.<sup>S1</sup>

**[2] Preparation of Starting Materials:** All starting materials (Figure S1) employed for catalytic reactions were prepared according to experimental procedure reported in our previous communication,<sup>S2</sup> except for **1n** and **1o**. The experimental procedures for all new compounds (**1g**, **1i**,

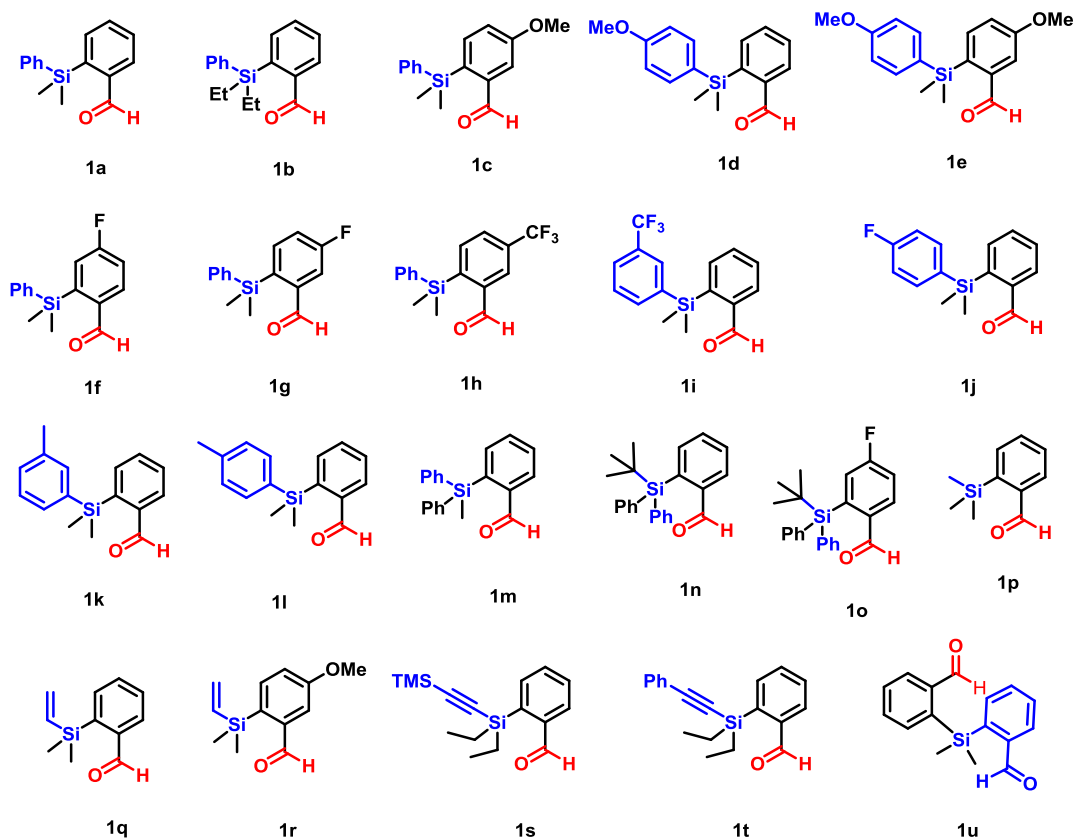
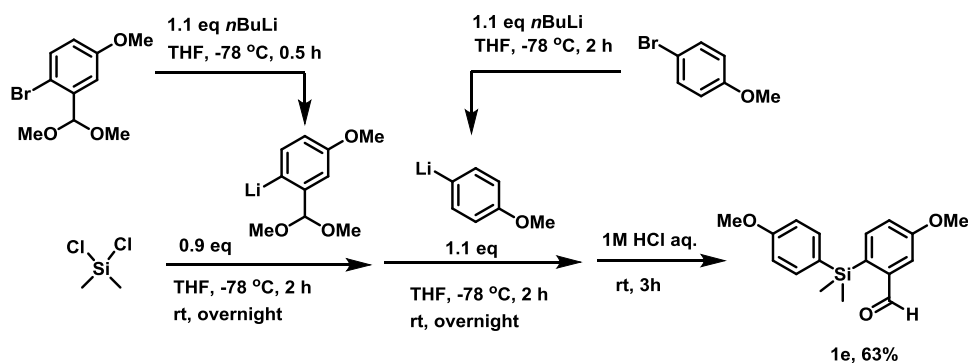


Figure S1: Substrates employed for catalytic asymmetric reactions

**1j**, **1t**, and **1u**) were described herein.

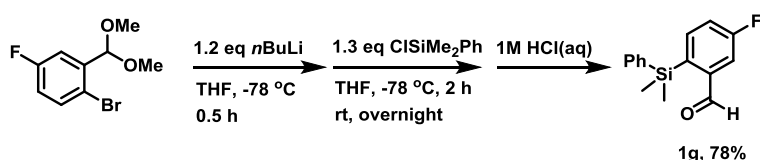
#### Synthesis of 2-dimethyl(4-methoxyphenyl)silyl-5-methoxybenzaldehyde (**1e**):



To the solution of 1-bromo-4-methoxybenzaldehyde dimethylacetal (5.9 g, 23.0 mmol) in THF (40 mL) was added  $n\text{BuLi}$  (16 mL, 25.5 mmol, 1.6 M in hexane) dropwise at  $-78\text{ }^{\circ}\text{C}$  and the mixture was stirred further for 0.5 h. This solution was transferred slowly to a flask containing a

solution of dichlorodimethylsilane (3.3 g, 25.5 mmol) in THF (40 mL) at  $-78\text{ }^{\circ}\text{C}$  using cannula. The resulting reaction mixture was stirred further for 2 h at  $-78\text{ }^{\circ}\text{C}$  and then allowed to warm to room temperature with stirring for overnight. The reaction mixture was brought to  $-78\text{ }^{\circ}\text{C}$  again and a solution of 4-methoxyphenyllithium (prepared by the reaction of 1-bromo-4-methoxybenzene (5.2 g, 27.8 mmol) with  $n\text{BuLi}$  (19 mL, 30.5 mmol, 1.6 M in hexane) in THF (40 mL) at  $-78\text{ }^{\circ}\text{C}$ ) was added slowly using cannula over 30 min and allowed to stir at  $-78\text{ }^{\circ}\text{C}$  for additional 2 h followed by warming to room temperature with overnight stirring. 1M HCl (aq.) was added and the organic layer was extracted with ether, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. It was purified by silica gel column chromatography (with 3% EtOAc:hexane) gave 2-dimethyl(4-methoxyphenyl)silyl-5-methoxybenzaldehyde (**1e**) as colorless oil in 63% overall yield (4.4 g, 14.6 mmol).  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.59 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ), 3.81 (s, 3H,  $\text{OCH}_3$ ), 3.87 (s, 3H,  $\text{OCH}_3$ ), 6.89 (d,  $J = 8.4\text{ Hz}$ , 2H, Ar-*H*), 7.11 (dd,  $J = 2.8, 8.4\text{ Hz}$ , 1H, Ar-*H*), 7.41 (d,  $J = 8.4\text{ Hz}$ , 2H, Ar-*H*), 7.47 (d,  $J = 2.4\text{ Hz}$ , 1H, Ar-*H*), 7.55 (d,  $J = 8.4\text{ Hz}$ , 1H, Ar-*H*), 10.07 (s, 1H, CHO).  **$^{13}\text{C}\{^1\text{H}\}\text{ NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.7, 55.0, 55.3, 113.7, 114.9, 119.3, 129.7, 132.7, 135.4, 137.9, 142.8, 160.4, 160.9, 192.7. **HRMS** (EI):  $m/z$  Calcd for  $\text{C}_{17}\text{H}_{20}\text{O}_3\text{Si}$ : ( $\text{M}^+$ ) 300.1182, found 300.1181.

#### Synthesis of 2-(dimethyl(phenyl)silyl)-5-fluorobenzaldehyde (**1g**):

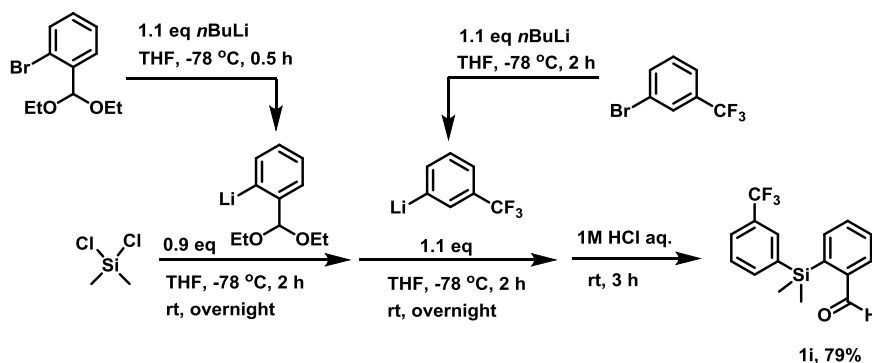


To the solution of 1-bromo-4-fluorobenzaldehyde dimethylacetal (5.9 g, 24.0 mmol) in THF (50 mL) was added  $n\text{BuLi}$  (18.2 mL, 29.2 mmol, 1.6 M in hexane) dropwise at  $-78\text{ }^{\circ}\text{C}$  and the mixture was stirred further for 0.5 h. To this reaction mixture was added chlorodimethylphenylsilane (5.4 g, 31.6 mmol) and stirred for 2 h at  $-78\text{ }^{\circ}\text{C}$  and then allowed to warm to room temperature for overnight. HCl aq. (1M) was added to the mixture and the organic layer was extracted with ether, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated and purified by silica gel column chromatography (with 5% EtOAc:hexane) to get **1g** as a colorless liquid (5.0 g, 78% yield).  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.63 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ), 7.24–7.29 (m, 2H, Ar-*H*), 7.32–7.40 (m, 3H, Ar-*H*), 7.46–7.49 (m, 2H, Ar-*H*), 7.60–7.64 (m, 2H, Ar-*H*), 10.03 (s, 1H, CHO).  **$^{13}\text{C}\{^1\text{H}\}\text{ NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -1.1, 117.5 (d,  $J_{\text{CF}} = 20.5\text{ Hz}$ ), 120.0 (d,  $J_{\text{CF}} = 20.5\text{ Hz}$ ), 128.0, 129.3, 133.9, 136.6 (d,  $J_{\text{CF}} = 3.8\text{ Hz}$ ), 138.2,



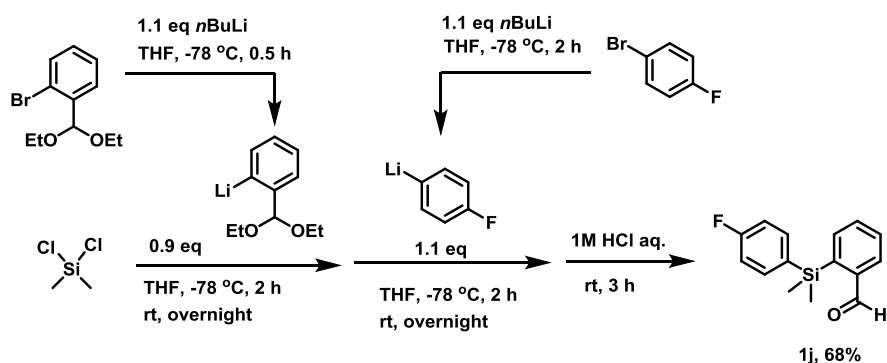
138.7 (d,  $J_{\text{CF}} = 7.1$  Hz), 143.4 (d,  $J_{\text{CF}} = 5.0$  Hz), 164.0 (d,  $J_{\text{CF}} = 255.0$  Hz), 191.5. **HRMS** (EI):  $m/z$  Calcd for  $\text{C}_{15}\text{H}_{15}\text{FOSi}$ : ( $\text{M}^+$ ) 258.0876, found 258.0875.

#### Synthesis of 2-(dimethyl(3-(trifluoromethyl)phenyl)silyl)benzaldehyde (**1i**):



To the solution of 2-bromobenzaldehyde diethyl acetal (2.0 g, 7.7 mmol) in THF (20 mL) was added *n*BuLi (5.3 mL, 8.5 mmol, 1.6 M in hexane) dropwise at -78 °C and the mixture was stirred further for 0.5 h. This solution was transferred slowly to a flask containing a solution of dichlorodimethylsilane (1.1 g, 8.5 mmol) in THF (20 mL) at -78 °C using cannula. The resulting reaction mixture was stirred further for 2 h at -78 °C and then allowed to warm to room temperature with stirring for overnight. The reaction mixture was brought to -78 °C again and a solution of 3-trifluoromethylphenyllithium (prepared by the reaction of 3-Bromobenzotrifluoride (2.0 g, 9.3 mmol) with *n*BuLi (6.4 mL, 10.2 mmol, 1.6 M in hexane) in THF (20 mL) at -78 °C) was added slowly using cannula over 0.5 h and allowed to stir at -78 °C for additional 2 h followed by warming to room temperature with overnight stirring. 1M HCl (aq.) was added and the organic layer was extracted with ether, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. It was purified by silica gel column chromatography (with 5% EtOAc:hexane) to get **1i** as a colorless liquid (1.9 g, 79% yield). **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.73 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ), 7.51 (t, 1H,  $J = 7.5$  Hz, Ar-*H*), 7.63–7.70 (m, 3H, Ar-*H*), 7.70–7.74 (m, 1H, Ar-*H*), 7.77 (d, 1H,  $J = 7.2$  Hz, Ar-*H*), 7.84 (s, 1H, Ar-*H*), 7.93–7.80 (m, 1H, Ar-*H*), 10.03 (s, 1H, CHO). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -1.5, 124.4 (q,  $J_{\text{CF}} = 271.0$  Hz), 125.5 (q,  $J_{\text{CF}} = 3.7$  Hz), 127.9, 129.8 (q,  $J_{\text{CF}} = 31.7$  Hz), 130.1, 130.2 (d,  $J_{\text{CF}} = 3.7$  Hz), 133.2, 133.6, 136.9, 137.3, 139.0, 140.5, 141.0, 192.9. **HRMS** (EI):  $m/z$  Calcd for  $\text{C}_{16}\text{H}_{15}\text{F}_3\text{OSi}$ : ( $\text{M}+\text{H}^+$ ) 309.0922, found 309.0921.

### Synthesis of 2-((4-fluorophenyl)dimethylsilyl)benzaldehyde (**1j**):

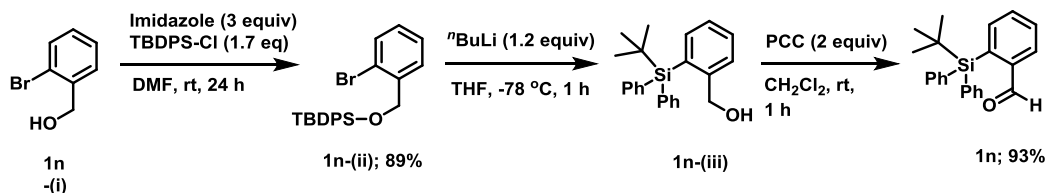


To the solution of 2-bromobenzaldehyde diethyl acetal (2.0 g, 7.7 mmol) in THF (20 mL) was added *n*BuLi (5.3 mL, 8.5 mmol, 1.6 M in hexane) dropwise at -78 °C and the mixture was stirred further for 0.5 h. This solution was transferred slowly to a flask containing a solution of dichlorodimethylsilane (1.1 g, 8.5 mmol) in THF (20 mL) at -78 °C using cannula. The resulting reaction mixture was stirred further for 2 h at -78 °C and then allowed to warm to room temperature with stirring for overnight. The reaction mixture was brought to -78 °C again and a solution of (4-fluorophenyl)lithium (prepared by the reaction of 1-bromo-4-fluorobenzene (1.6 g, 9.3 mmol) with *n*BuLi (6.4 mL, 10.2 mmol, 1.6 M in hexane) in THF (20 mL) at -78 °C) was added slowly using cannula over 0.5 h and allowed to stir at -78 °C for additional 2 h followed by warming to room temperature with overnight stirring. 1M HCl (aq.) was added and the organic layer was extracted with ether, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. It was purified by silica gel column chromatography (with 3% EtOAc:hexane) to get **1j** as a colorless liquid (1.4 g, 68% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 0.62 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 7.04 (t, *J* = 8.6 Hz, 2H, Ar-*H*), 7.48 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.50–7.65 (m, 3H, Ar-*H*), 7.89–7.93 (m, 1H, Ar-*H*), 10.01 (s, 1H, CHO).

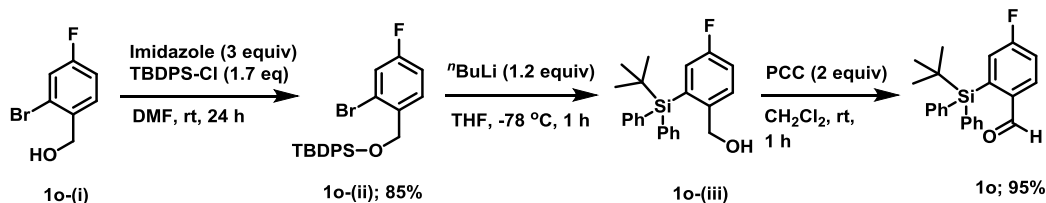
**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ -1.2, 114.9 (d, *J*<sub>CF</sub> = 19.6 Hz), 129.8, 132.6, 133.1, 134.3 (d, *J*<sub>CF</sub> = 3.8 Hz), 135.8 (d, *J*<sub>CF</sub> = 7.3 Hz), 136.7, 140.2, 141.1, 163.5 (d, *J*<sub>CF</sub> = 245.8 Hz), 191.0. **HRMS** (CI): *m/z* Calcd for C<sub>15</sub>H<sub>16</sub>FOSi: (M+H<sup>+</sup>) 259.0943, found 259.0946.

### Synthesis of 2-(*tert*-butyldiphenylsilyl)benzaldehyde (**1n**):



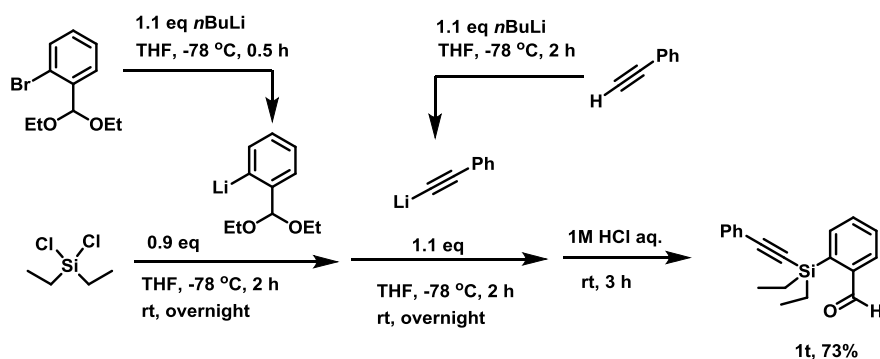
To a stirring solution of (2-bromophenyl)methanol, **1n-i** (2.8 g, 14.7 mmol) and imidazole (3.0 g, 44.1 mmol) in DMF (20 mL) was added TBDPSCl (6.39 mL, 25.0 mmol) at room temperature followed by stirring further for 24 h. Aqueous NaHCO<sub>3</sub> was added and extracted well with hexane twice. The organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated and purified through silica gel column chromatography (with 5% EtOAc:hexane) to get pure protected benzylalcohol **1n-ii** (5.5 g, 89% yield). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 1.11 (s, 9H, SiC(CH<sub>3</sub>)<sub>3</sub>), 4.78 (s, 2H, OCH<sub>2</sub>), 7.14 (td, *J* = 1.4, 7.4 Hz, 1H, Ar-*H*), 7.35–7.46 (m, 7H, Ar-*H*), 7.49 (dd, *J* = 1.1, 8.0 Hz, 1H, Ar-*H*), 7.71 (dd, *J* = 1.4, 8.0 Hz, 4H, Ar-*H*), 7.75 (d, *J* = 7.5 Hz, 1H, Ar-*H*). The spectral data was identified to that previously reported.<sup>S3</sup> TBDPSCl-protected benzylalcohol, **1n-ii** (9 g, 21.2 mmol) was dissolved in dry THF (60 mL) was cooled to -78 °C and *n*BuLi was added drop wise for 15 min. After 30 min it was allowed to warm up slowly to room temperature. Reaction mixture was quenched with NH<sub>4</sub>Cl (aqueous) and extracted with ether (3 x 100 mL). Combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to get isomerized product (O–Si to C–Si) **1n-iii** quantitatively as a very thick liquid as confirmed by <sup>1</sup>H NMR analysis of residue. It was forwarded for next step without purification. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 1.17 (s, 9H, SiC(CH<sub>3</sub>)<sub>3</sub>), 4.11 (d, *J* = 6.6 Hz, 2H, OCH<sub>2</sub>), 7.33–7.43 (m, 7H, Ar-*H*), 7.47–7.57 (m, 2H, Ar-*H*), 7.61–7.67 (m, 4H, Ar-*H*), 7.97 (dd, *J* = 1.0, 7.5 Hz, 1H, Ar-*H*). The *ortho*-TBDPSCl-benzylalcohol **1n-iii** (7.0 g, 20.2 mmol) was dissolved in DCM (60 mL) and PCC (8.7 g, 40.4 mmol) was added in a small portion-wise under N<sub>2</sub> flow and allowed to stir for 1–2 h at room temperature. After completion of reaction, DCM was evaporated completely then re-diluted with ether. The black sticky material was filtered off over celite and washed three times with ether. The ether solution was evaporated to get white solid (quantitative conversion), which was recrystallized with toluene to get pure compound **1n** (6.5 g, 93% yield). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 1.20 (s, 9H, SiC(CH<sub>3</sub>)<sub>3</sub>), 7.32–7.42 (m, 6H, Ar-*H*), 7.55–7.64 (m, 6H, Ar-*H*), 7.99 (dd, *J* = 1.8, 6.5 Hz, 1H, Ar-*H*), 8.07 (dd, *J* = 1.8, 6.5 Hz, 1H, Ar-*H*), 9.86 (s, 1H, CHO). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ 18.9, 28.7, 128.0, 128.4, 129.5, 129.9, 132.5, 135.1, 135.9, 137.7, 138.8, 141.9, 193.0. **HRMS** (EI): *m/z* Calcd for C<sub>23</sub>H<sub>24</sub>OSi: (*M*<sup>+</sup>) 344.1596, found 344.1591.

### Synthesis of 2-(*tert*-butyldiphenylsilyl)-4-fluorobenzaldehyde (**1o**):



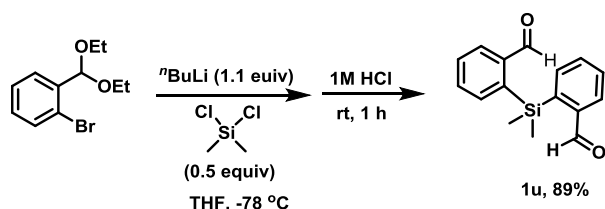
Compound **1o** was synthesized following the similar experimental procedure as employed for **1n** using (2-bromo-4-fluorophenyl)methanol (**1o-(i)**, 6.9 g, 25.0 mmol) as a starting material. **1o-(ii)**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.12 (s, 9H, SiC(CH<sub>3</sub>)<sub>3</sub>), 4.74 (s, 2H, OCH<sub>2</sub>), 7.08 (td, *J* = 2.4, 8.3 Hz, 1H, Ar-*H*), 7.22–7.27 (m, 1H, Ar-*H*), 7.35–7.48 (m, 6H, Ar-*H*), 7.64–7.74 (m, 5H, Ar-*H*). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 19.4, 26.9, 64.8, 114.4 (d, *J*<sub>CF</sub> = 20.6 Hz), 119.4 (d, *J*<sub>CF</sub> = 24.6 Hz), 121.0 (d, *J*<sub>CF</sub> = 9.3 Hz), 127.9, 128.7 (d, *J*<sub>CF</sub> = 8.0 Hz), 129.9, 133.1, 135.5, 135.8 (d, *J*<sub>CF</sub> = 3.1 Hz), 161.4 (d, *J*<sub>CF</sub> = 247.8 Hz). **HRMS** (EI): *m/z* Calcd for C<sub>23</sub>H<sub>24</sub>BrFOSiNa: (*M*<sup>+</sup>+Na) 465.0661, found 465.0666. **1o-(iii)**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.17 (s, 9H, SiC(CH<sub>3</sub>)<sub>3</sub>), 4.08 (d, *J* = 6.1 Hz, 2H, OCH<sub>2</sub>), 7.18 (td, *J* = 2.9, 8.3 Hz, 1H, Ar-*H*), 7.35–7.45 (m, 6H, Ar-*H*), 7.53 (dd, *J* = 5.5, 8.3 Hz, 1H, Ar-*H*), 7.61–7.67 (m, 5H, Ar-*H*). It was used for next oxidation-step without purification. **1o** (4.4 g, 95% yield): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.18 (s, 9H, SiC(CH<sub>3</sub>)<sub>3</sub>), 7.19 (td, *J* = 2.5, 8.3 Hz, 1H, Ar-*H*), 7.30–7.41 (m, 6H, Ar-*H*), 7.53–7.58 (m, 4H, Ar-*H*), 7.61 (dd, *J* = 2.5, 9.4 Hz, 1H, Ar-*H*), 8.09 (dd, *J* = 5.6, 8.7 Hz, 1H, Ar-*H*), 9.79 (s, 1H, CHO). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 19.0, 28.7, 117.1 (d, *J*<sub>CF</sub> = 21.1 Hz), 124.5 (d, *J*<sub>CF</sub> = 21.1 Hz), 128.2, 129.7, 131.3 (d, *J*<sub>CF</sub> = 8.6 Hz), 134.3, 135.9, 138.1 (d, *J*<sub>CF</sub> = 3.3 Hz), 142.9 (d, *J*<sub>CF</sub> = 5.7 Hz), 165.0 (d, *J*<sub>CF</sub> = 257.9 Hz), 191.2. **HRMS** (CI): *m/z* Calcd for C<sub>23</sub>H<sub>24</sub>FOSi: (*M*<sup>+</sup>+H) 363.1574, found 363.1578.

### Synthesis of 2-(diethyl(phenylethynyl)silyl)benzaldehyde (**1t**):



To a solution of 2-bromobenzaldehyde diethyl acetal (7.5 g, 29 mmol) in THF (50 mL) was added dropwise  $n\text{BuLi}$  (20 mL, 32 mmol) at  $-78\text{ }^{\circ}\text{C}$ , and the mixture was stirred for 0.5 h. This solution was slowly added to a solution of dichlorodimethylsilane (5 g, 32 mmol) in THF (100 mL), and stirred for 2 h at  $-78\text{ }^{\circ}\text{C}$ . The resulting reaction mixture was allowed to warm to room temperature for overnight. To reaction mixture at  $-78\text{ }^{\circ}\text{C}$  was added a solution of lithium phenylacetylide (prepared by the reaction of phenylacetylene (3.6 g, 35 mmol) with  $n\text{BuLi}$  (24 mL, 39 mmol) in THF (20 mL) at  $-78\text{ }^{\circ}\text{C}$ ) slowly for a period of 30 min. and further stirred for 2 h. After warming to room temperature for overnight, HCl aq. (1M) was added and stirred for 3 h. The organic layer was extracted with ether, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated and purified by silica gel column chromatography (eluted with 3% EtOAc in hexane) to get **1t** as a colorless liquid (6.0 g, 73% yield).  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.02–1.10 (m, 10H,  $\text{Si}(\text{CH}_3\text{CH}_2)_2$ ), 7.33–7.36 (m, 3H, ArH), 7.55–7.62 (m, 3H, ArH), 7.65 (td,  $J = 1.5, 7.3\text{ Hz}$ , 1H, Ar-H), 7.89 (dd,  $J = 1.5, 7.3\text{ Hz}$ , 1H, Ar-H), 8.29 (d,  $J = 7.2\text{ Hz}$ , 1H, Ar-H), 10.16 (s, 1H, CHO).  **$^{13}\text{C}\{^1\text{H}\}\text{NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.0, 8.1, 92.4, 108.5, 123.4, 128.3, 128.6, 129.9, 132.1, 133.1, 133.4, 137.0, 138.51, 141.3, 192.7. **HRMS** (CI):  $m/z$  Calcd for  $\text{C}_{19}\text{H}_{20}\text{OSi}$ : ( $\text{M}+\text{H}^+$ ) 292.1283, found 292.1279.

#### Synthesis of 2,2'-(dimethylsilanediyl)dibenzaldehyde (**1u**):



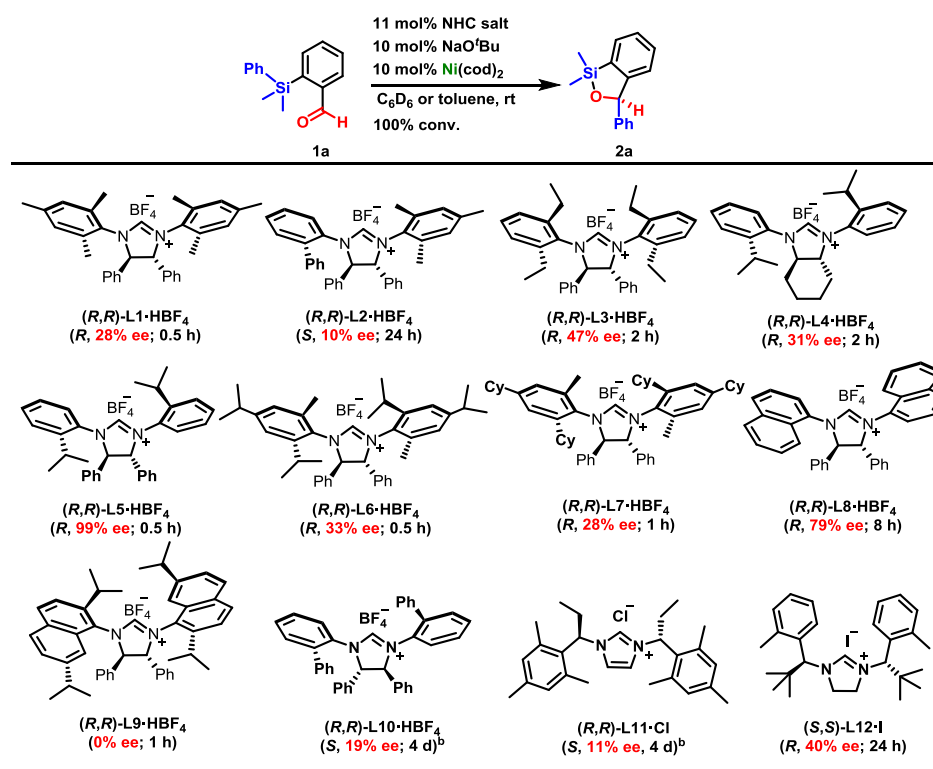
A stirring solution of 2-bromobenzaldehyde diethyl acetal (5.0 g, 19.3 mmol) in THF (60 mL) was added  $n\text{BuLi}$  (13.2 mL, 1.6 M in THF, 21.2 mmol) drop wise at  $-78\text{ }^{\circ}\text{C}$  under  $\text{N}_2$ . After 1 h, dichlorodimethylsilane (1.2 g, 9.65 mmol) was introduced drop wise to the reaction mixture at the same temperature and allowed it to stir for 1 h followed by warming to room temperature with overnight stirring. After completion of the reaction, 1 M HCl was added and stirred for 1 h. Biphasic solution was separated and aqueous layer was washed with ethyl acetate three times. The combined organic layers was dried over  $\text{Na}_2\text{SO}_4$ , concentrated, and purified by recrystallization with toluene to get required compound **1u** as a white solid (2.3 g, 89% yield).  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.66 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ), 7.55 (td,  $J = 1.3, 7.4\text{ Hz}$ , 2H, Ar-H), 7.60 (td,  $J = 1.3, 7.4\text{ Hz}$ , 2H, Ar-H), 7.81 (dd,  $J = 1.1, 7.4\text{ Hz}$ , 2H, Ar-H), 7.87 (dd,  $J = 1.1, 7.4\text{ Hz}$ , 2H, Ar-H), 9.92 (s, 2H, CHO).  **$^{13}\text{C}\{^1\text{H}\}\text{NMR}$**

(100 MHz, CDCl<sub>3</sub>):  $\delta$  0.0, 129.5, 132.1, 133.3, 136.2, 140.5, 141.6, 193.1. **HRMS** (EI):  $m/z$  Calcd for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>Si: (M<sup>+</sup>) 268.0920, found 268.0919.

### [3] Optimization for catalytic enantioselective synthesis

#### 1a. Survey of chiral NHCs (Scheme 2)

**Scheme 2. Survey of chiral NHC Ligands**



**General method:** A screw cap vial was charged with NHC-salt **L<sub>n</sub>·X** (0.022 mmol) and NaO<sup>t</sup>Bu (0.02 mmol) in toluene or C<sub>6</sub>D<sub>6</sub> (1 mL). After 10 min of stirring, Ni(cod)<sub>2</sub> (0.02 mmol) was added. To the stirring solution was added 2-(dimethylphenyl)silylbenzaldehyde (**1a**) and allowed to stir (or transferred to J. Young NMR tube) at room temperature (except in case of **L10·HBF<sub>4</sub>** and **L11·HBF<sub>4</sub>**). The progress of reaction was monitored by either GC or <sup>1</sup>H NMR. The resulting reaction mixture was filtered through small pad of silica and concentrated. Formation of **2a** was confirmed by spectroscopic data, reported previously for racemic compound.<sup>S2</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.46 (s, 3H, SiCH<sub>3</sub>), 0.54 (s, 3H, SiCH<sub>3</sub>), 6.18 (s, 1H, CHOSi), 7.01–7.07 (m, 1H, Ar-H), 7.27–7.37 (m, 7H, Ar-H), 7.60–7.65 (m, 1H, Ar-H).

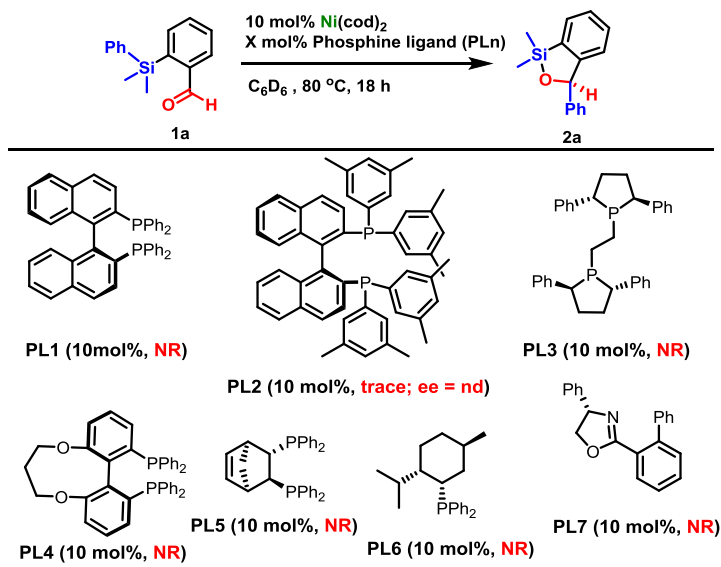
*Note:* Product **2a** was sensitive toward silica gel column chromatography as well as HPLC conditions.<sup>S4</sup> However, it could be possible to filter quickly through short silica gel column or

recycle GPC, if required. Enantioselectivity for **2a** was measured after converting it (after 100% conversion) into stable product, **3a** by Tamao-Fleming oxidation (see **Scheme S2**, *vide infra*).

**General procedure for Tamao-Fleming oxidation (TFO):** To the solution of crude benzoxasilole **2** (for 0.2 mmol) in THF/MeOH (1:1; 1 mL) were added KHCO<sub>3</sub> (40 mg, 0.4 mmol) and H<sub>2</sub>O<sub>2</sub> (35% aq, 0.19 mL, 2.0 mmol) at 0 °C. The reaction mixture was stirred to complete the reaction for overnight. The reaction was quenched carefully with aqueous NaHSO<sub>3</sub> solution at 0 °C and extracted well with ethyl acetate (3 x 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated and purified by silica gel column chromatography (isolated with 20% EtOAc:Hexane) to get **3a** as a white solid. (*R*)-2-(hydroxy(phenyl)methyl)phenol (**3a**): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 3.04 (br s, 1H, CHOH), 6.00 (s, 1H, CHOH), 6.82 (td, *J* = 1.0, 7.4 Hz, Ar-*H*, 1H), 6.84–6.92 (m, Ar-*H*, 2H), 7.19 (td, *J* = 2.0, 7.8 Hz, Ar-*H*, 1H), 7.30–7.40 (m, 5H, Ar-*H*), 7.92 (br s, 1H, Ar-OH). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ 76.9, 117.2, 119.9, 126.6, 126.8, 128.19, 128.23, 128.7, 129.3, 141.8, 155.4. **HRMS** (ESI) *m/z* calcd for C<sub>13</sub>H<sub>12</sub>O<sub>2</sub>: (M<sup>+</sup>) 200.0837, found 200.0836. The spectral data was identified to that previously reported.<sup>S5</sup> **Chiral separation:** The enantioselectivity was measured by using either chiral HPLC (Chiralpak OD-H column. (10% isopropanol in hexane, Flow rate = 0.5 mL/min, *t*<sub>R</sub> = 22.9 min (*S*-enantiomer) and 34.7 min (*R*-enantiomer)) or SFC using Chiralpak ID (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 2.0 mL/min, Flow (isopropanol) = 0.3 mL/min, 25 °C, λ = 250 nm). Retention time: *t*<sub>R</sub> = 3.7 min (*S*-enantiomer) and 4.0 min (*R*-enantiomer). The absolute stereochemistry of **2a** was assigned by analogy to **2h** (determined to be (*R*) by X-ray with Flack parameter = 0.02(3); when (*R,R*)-**L5** was employed, *vide infra*).

**1b. Survey of chiral phosphine ligands (Scheme S1):** Phosphine (mono- as well as bidentate) ligands were failed to give any conversion to required products. The reaction procedure was followed as such; To the stirring solution of phosphine ligand and Ni(cod)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> (1 mL) was added **1a** and transferred to J. Young NMR tube. The reaction was monitored by <sup>1</sup>H NMR at room temperature for 24 h followed by heating at 80 °C for 18 h.

### Scheme S1. Screening of phosphine ligands



### 1c. Further optimization with L5·HBF<sub>4</sub> (Table 1)

Table 1. Further Optimization with L5·HBF<sub>4</sub>

Reaction scheme showing the conversion of **1a** to **(R)-2a** using X mol%  $(R,R)\text{-L5}\cdot\text{HBF}_4$ , Y mol%  $\text{NaO}^t\text{Bu}$ , and Z mol%  $\text{Ni}(\text{cod})_2$  in toluene.

entry	X	Y	Z	temp (°C)	time (h)	yield (%) <sup>a</sup>	ee (%) <sup>b</sup>
1	11.0	10.0	10.0	rt	0.5	100	>99
2	11.0	10.0	10.0	rt	24	–	–
3	11.0	10.0	–	80	48	–	–
4	2.2	2.0	2.0	rt	1.0	99	99
5	1.1	1.0	1.0	rt	48	95	97
6	2.2	2.0	2.0	rt	1.0	99	99

**General Procedure:** A screw cap vial was charged with  $(R,R)\text{-L5}\cdot\text{HBF}_4$  (1–11 mol%) and  $\text{NaO}^t\text{Bu}$  (1–10 mol%) in toluene (1 mL). After 10 min of stirring,  $\text{Ni}(\text{cod})_2$  (1–11 mol%) was added. 2-Dimethylphenylsilylbenzaldehyde (**1a**; 48.0 mg, 0.2 mmol) was added to the stirring solution and allowed to stir at room temperature. The progress of reaction was monitored and yields of **2a** were



calculated by GC using *n*-pentadecane as an internal standard. The enantioselectivity was measured for corresponding TFO product, **3a** (see **Scheme S2**, *vide infra*).

**Entry 1:** Reaction was performed with (*R,R*)-**L5·HBF<sub>4</sub>** (12.0 mg, 0.022 mmol, 11 mol%), NaO<sup>t</sup>Bu (1.9 mg, 0.02 mmol, 10 mol%), and Ni(cod)<sub>2</sub> (5.5 mg, 0.02 mmol, 10 mol%) in 1 mL toluene. reaction was completed in 30 min at room temperature (100% GC yield, 99% ee).

**Entry 2:** Reaction was performed under identical reaction conditions except Ni(acac)<sub>2</sub> was used as a Ni(II) source in place of Ni(cod)<sub>2</sub> and stirred for 24 h. No reaction took place.

**Entry 3:** Reaction was performed in the absence of Ni(cod)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>. No reaction took place even at 80 °C for 24 h.

**Entry 4:** Reaction was conducted with 2 mol% catalyst loading {(*R,R*)-**L5·HBF<sub>4</sub>** (2.4 mg, 0.0044 mmol), NaO<sup>t</sup>Bu (0.38 mg, 0.004 mmol), and Ni(cod)<sub>2</sub> (1.1 mg, 0.004 mmol)}. Reaction was completed in 1 h with 99% GC yield and 99% ee.

**Entry 5:** Reaction was conducted with 1 mol% catalyst loading {(*R,R*)-**L5·HBF<sub>4</sub>** (1.2 mg, 0.0022 mmol), NaO<sup>t</sup>Bu (0.2 mg, 0.002 mmol), and Ni(cod)<sub>2</sub> (0.6 mg, 0.004 mmol)}. Reaction was relatively slow and required longer time and result is denoted as conversion of starting material (95% conversion in 2 days). Ee was measured from aliquot taken from reaction mixture of 95% conversion.

**Entry 6:** Reaction was conducted under identical reaction condition as entry 4 using with (*S,S*)-**L5·HBF<sub>4</sub>**, resulted (*S*)-**2a** with consistent efficiency.

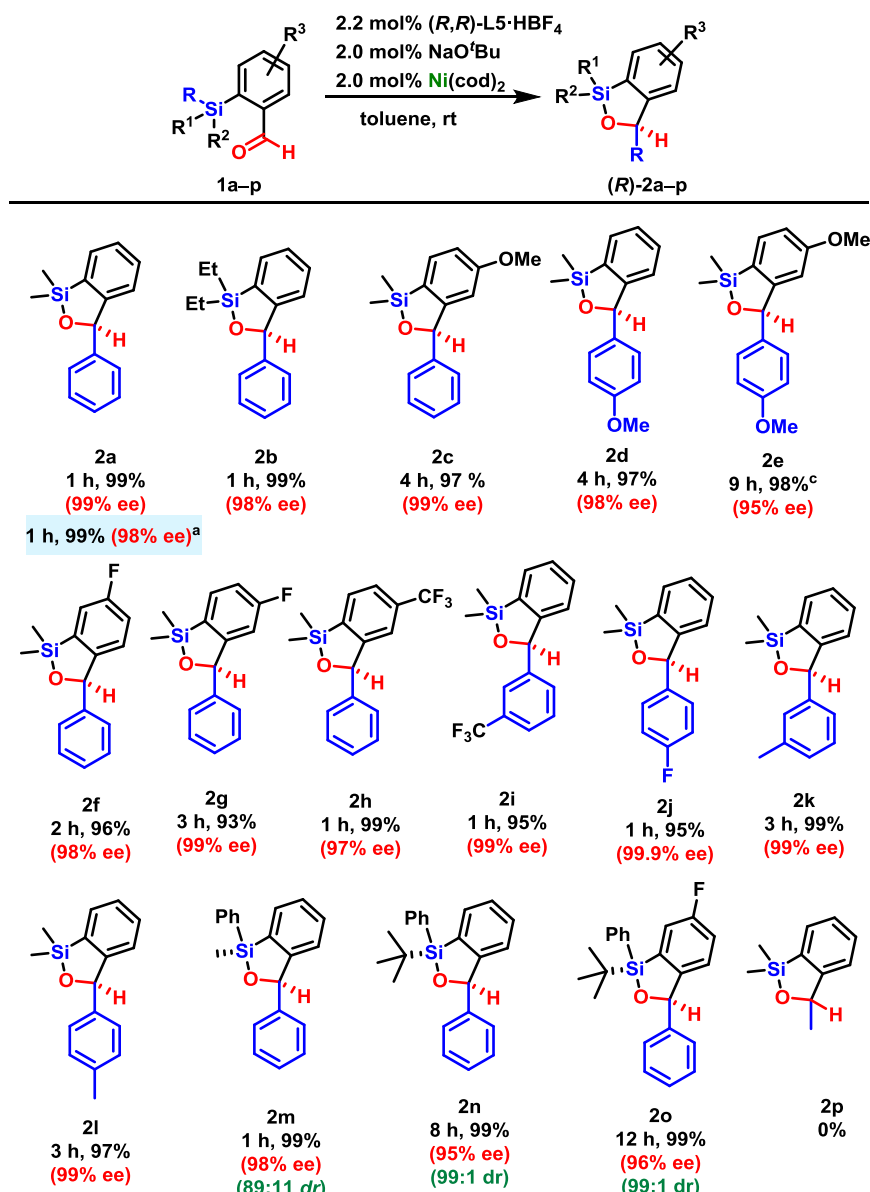
**Optimized conditions employed for study of substrate scope:** entry 4

#### [4] Substrate scope

##### Scope of 3-aryl-2,1-benzoxasilole (Table 2)

**General procedures:** A reaction tube was charged with (*R,R*)-**L5·HBF<sub>4</sub>** (2.2 mol%) and NaO<sup>t</sup>Bu (2.0 mol%) in toluene (1–10 mL; 0.2 M). After 5 to 10 min of stirring, Ni(cod)<sub>2</sub> (2.0 mol%) was added. *ortho*-Silylbenzaldehyde **1** (0.20–2.0 mmol) was added after 10 min and allowed to stir at room temperature and progress of the reaction was monitored either by GC or <sup>1</sup>H NMR. The products were isolated by short silica gel column chromatography (Wakogel<sup>®</sup> C-300, 5.0 g, eluted with ether). Further purification was carried out either by recrystallization or recycle GPC, if necessary.

**Table 2. Catalytic Enantio- and Diastereoselective Synthesis of 3-Arylbenzoxasiloles**

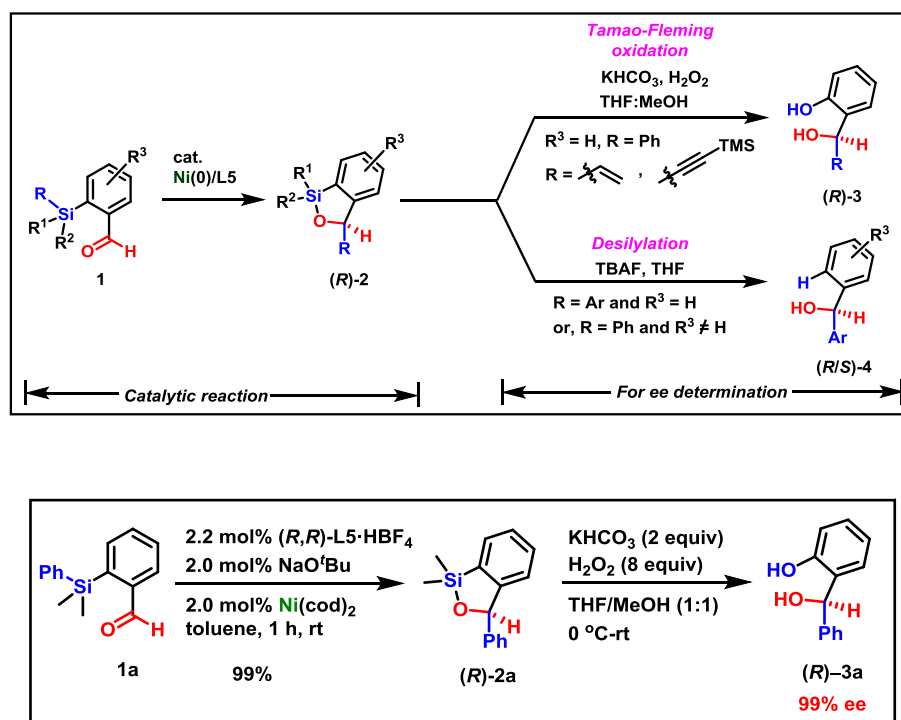


<sup>a</sup> Reaction was conducted at 5 mmol scale

Note: Since, 3-arylbenzoxasiloles **2** are sensitive to HPLC; it was converted it into either **3** (Tamao-Fleming oxidation) or **4** (desilylation) product to ascertain the enantioselectivity of corresponding benzoxasiloles, as shown below in **Scheme S2**. However, enantioselectivities measured after both transformations were consistent, as examined for **2h** (*vide infra*).

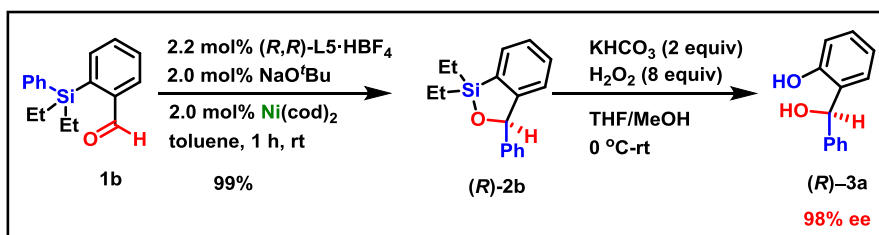
**Scheme S2. Nickel-catalyzed synthesis of benzoxasilole **2** and further transformations to **3** and**

**4**

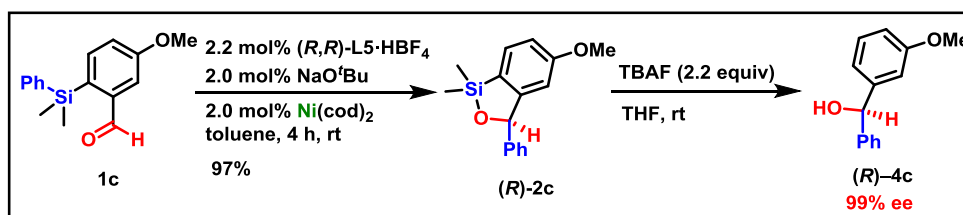


**Reaction of **1a** giving (R)-2a** (Table 1, entry 3; 99% yield, 99% ee): The general procedure was followed with 2-(dimethyl(phenyl)silyl)benzaldehyde (**1a**) (48.0 mg, 0.20 mmol) for 1.0 h at room temperature. Reaction mixture was purified by short silica gel column chromatography giving (R)-1,1-dimethyl-3-phenyl-1,3-dihydrobenzo[c][1,2]oxasilole (**2a**) in 99% yield (47.5 mg, 0.198 mmol).  $[\alpha]_D^{23} = (-) 143.3^\circ$  ( $c = 0.2$ , in CHCl<sub>3</sub>). The absolute stereochemistry of **2a** was assigned by analogy to **2h** and enantioselectivity was evaluated after converting it into corresponding oxidation product **3a**. It was synthesized from **2a** as mentioned in general procedure for TFO in 81% yield. **Chiral separation:** The enantioselectivity was determined by SFC using Chiralpak ID (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 2.0 mL/min, Flow (isopropanol) = 0.3 mL/min, 25 °C,  $\lambda = 250$  nm). Retention time:  $t_R = 3.7$  min (minor S-enantiomer) and 4.0 min (major R-enantiomer).

**Gram scale synthesis of 2a:** Reaction procedure was followed as the optimized conditions (Table 1, entry 4) using 2-dimethylphenylsilylbenzaldehyde (**1a**; 1.2 g, 5.0 mmol), (R,R)-L5·HBF<sub>4</sub> (54.0 mg, 0.10 mmol), NaO<sup>t</sup>Bu (9.6 mg, 0.10 mmol) and Ni(cod)<sub>2</sub> (27.2 mg, 0.10 mmol) in toluene (25 mL). The reaction was completed in 1 h with consistent result. Enantioselectivity was measured after converting it into **3a**.



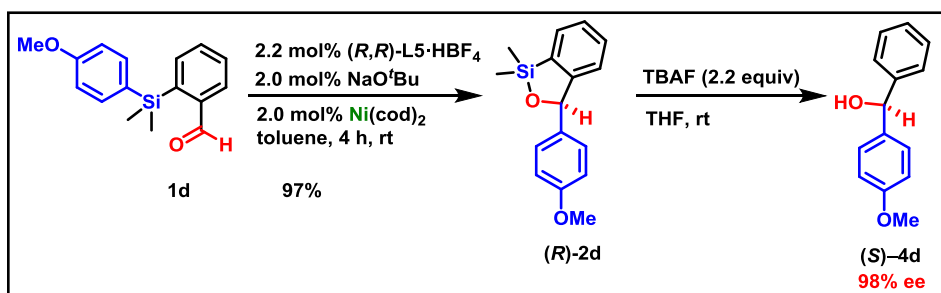
**Reaction of **1b** giving **(R)-2b**** (99% yield, 98% ee): The general procedure was followed with 2-(diethyl(phenyl)silyl)benzaldehyde (**1b**) (54.0 mg, 0.2 mmol) and reaction was completed within 1.0 h at room temperature. Purification by short silica gel column chromatography gave  $(R)$ -1,1-diethyl-3-phenyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (**2b**) as a pale yellow liquid in 99% yield (53.0 mg, 0.198 mmol). Spectroscopic data of **2b** was identified to that previously reported for racemic compound.<sup>S2</sup> **2b**: (99% yield, pale yellow liquid).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.85–1.13 (m, 10H, 2 x  $\text{SiCH}_2\text{CH}_3$ ), 6.16 (s, 1H,  $\text{CHOSi}$ ), 7.02 (d,  $J = 6.6$  Hz, 1H, Ar-*H*), 7.26–7.36 (m, 7H, Ar-*H*), 7.61 (d,  $J = 6.6$  Hz, 1H, Ar-*H*).  $[\alpha]_{\text{D}}^{23} = (-) 109.1^\circ$  ( $c = 0.1$ , in  $\text{CHCl}_3$ ). The absolute stereochemistry of **2b** was assigned by analogy to **2h** and enantioselectivity was evaluated after converting it into **3a** (80% yield, 98% ee). **Chiral separation** The enantioselectivity of **3a** was determined by SFC using chiralpak ID (Back pressure = 15 MPa, Flow ( $\text{CO}_2$ ) = 2.0 mL/min, Flow (isopropanol) = 0.3 mL/min, 25 °C,  $\lambda = 250$  nm). Retention time:  $t_{\text{R}} = 4.1$  min (minor *S*-enantiomer) and 4.4 min (major *R*-enantiomer).



**Reaction of **1c** giving **(R)-2c**** (97% yield, 99% ee): The general procedure was followed with 2-(dimethyl(phenyl)silyl)-5-methoxybenzaldehyde (**1c**) (54.0 mg, 0.2 mmol) and reaction was conducted at room temperature for 4 h. Purification by short silica gel column chromatography gave  $(R)$ -5-methoxy-1,1-dimethyl-3-phenyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (**2c**) as a white solid in 97% yield (52.0 mg, 0.192 mmol). Spectroscopic data of **2c** was identified to that previously reported for racemic compound.<sup>S2</sup>  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.40 (s, 3H,  $\text{SiCH}_3$ ), 0.48 (s, 3H,  $\text{SiCH}_3$ ), 3.68 (s, 3H,  $\text{OCH}_3$ ), 6.09 (s, 1H,  $\text{CHOSi}$ ), 6.49 (d,  $J = 2.0$  Hz, 1H, Ar-*H*), 6.86 (dd,  $J = 2.4$ , 8.0 Hz, 1H, Ar-*H*), 7.21–7.33 (m, 5H, Ar-*H*), 7.52 (d,  $J = 8.0$  Hz, 1H, Ar-*H*).  $[\alpha]_{\text{D}}^{23} = (-) 61.3^\circ$  ( $c = 0.1$ , in  $\text{CHCl}_3$ ). The absolute stereochemistry of **2c** was assigned by analogy to **2h** and

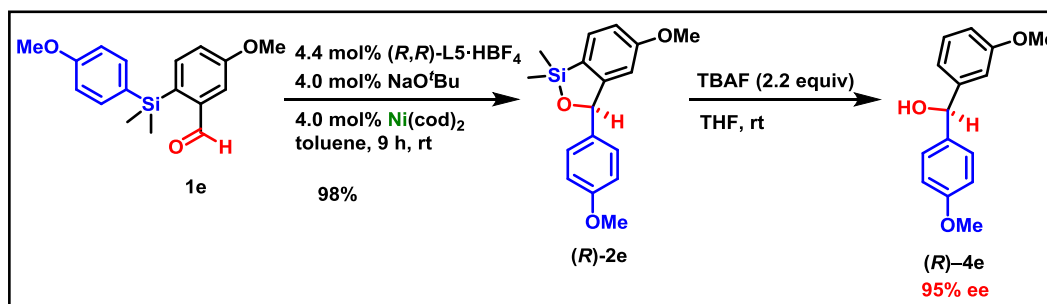
enantioselectivity was evaluated after converting it into desilylation product **4c** (75% yield, 99% ee).

**Experimental procedure for desilylation:** For example, (*R*)-(3-methoxyphenyl)(phenyl)methanol (**4c**): To a reaction tube charged with **2c** (53.0 mg, 0.19 mmol) in 0.5 mL THF was added TBAF (1 M, 0.2 mL) at room temperature and stirred for 5 h to complete the reaction. The reaction mixture was quenched by aqueous NH<sub>4</sub>Cl and stirred for 30 min. The biphasic mixture was separated and extracted with ethyl acetate (3 x 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated and purified by silica gel column chromatography (with 20% EtOAc:Hexane). Spectroscopic data of **4c** was identified to that previously reported.<sup>S6</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 2.14 (br s, CHOH, 1H), 3.68 (s, OCH<sub>3</sub>, 3H), 5.71 (s, CHOH, 1H), 6.67–6.73 (m, Ar-*H*, 1H), 6.82–6.87 (m, Ar-*H*, 2H), 7.12–7.18 (m, Ar-*H*, 2H), 7.20–7.29 (m, Ar-*H*, 4H). **Chiral separation:** The enantioselectivity was determined by SFC using Chiralpak IA (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 2.0 mL/min, Flow (IPA) = 0.3 mL/min, 25 °C, λ = 250 nm). Retention time: *t*<sub>R</sub> = 7.0 min (minor *S*-enantiomer) and 7.3 min (major *R*-enantiomer).

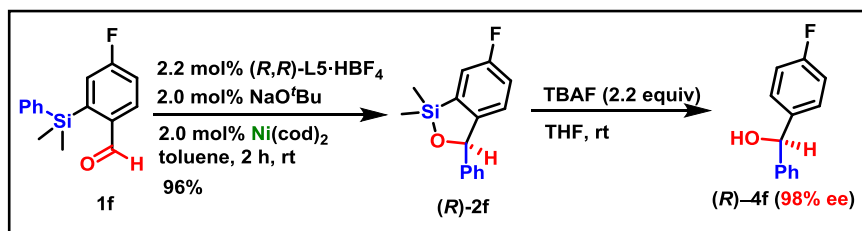


**Reaction of 1d giving (R)-2d** (97% yield, 98% ee): The general procedure was followed with 2-dimethyl(4-methoxyphenyl)silylbenzaldehyde (**1d**) (54.0 mg, 0.2 mmol) and reaction was conducted at room temperature for 4 h. Purification by short silica gel column chromatography gave (*R*)-3-(4-methoxyphenyl)-1,1-dimethyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (**2d**) as a pale yellow solid in 97% yield (52.5 mg, 0.19 mmol). Spectroscopic data of **2d** was identified to that previously reported for racemic compound.<sup>S2</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 0.47 (d, *J* = 2.4 Hz, 3H, SiCH<sub>3</sub>), 0.54 (d, *J* = 2.4 Hz, 3H, SiCH<sub>3</sub>), 3.81 (s, 3H, OCH<sub>3</sub>), 6.16 (s, 1H, CHOSi), 6.89 (dt, *J* = 2.4, 8.7 Hz, 2H, Ar-*H*), 7.01–7.05 (m, 1H, Ar-*H*), 7.21 (dt, *J* = 2.4, 8.7 Hz, 2H, Ar-*H*), 7.30–7.38 (m, 2H, Ar-*H*), 7.61–7.67 (m, 1H, Ar-*H*). [α]<sub>D</sub><sup>23</sup> = (–) 115.0 (*c* = 0.1, in CHCl<sub>3</sub>). The absolute stereochemistry of **2d** was assigned by analogy to **2h** and enantioselectivity was evaluated after converting it into desilylation product **4d** (75% yield, 98% ee). Spectroscopic data of **4d** was identified to that previously reported.<sup>S7</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 2.15 (br s, 1H, CHOH), 3.79 (s, 3H, OCH<sub>3</sub>), 5.81 (s, 1H, CHOH), 6.86 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.23–7.40 (m, 7H, Ar-*H*). **Chiral separation:**

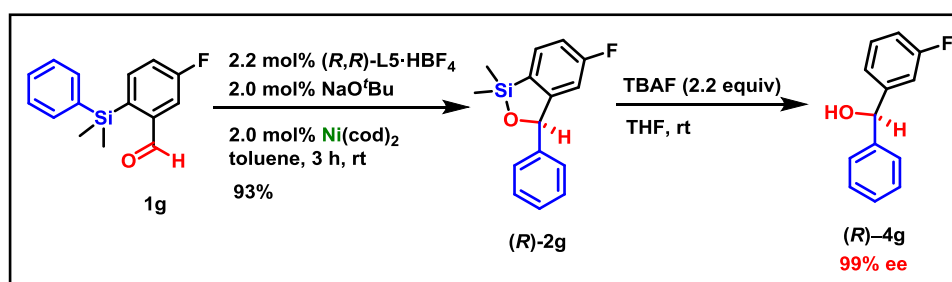
The enantioselectivity for **4d** was determined by SFC using Chiralpak ID (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 2.0 mL/min, Flow (IPA) = 0.3 mL/min, 25 °C,  $\lambda$  = 250 nm). Retention time:  $t_R$  = 5.8 min (minor *R*-enantiomer) and 6.0 min (major *S*-enantiomer).



**Reaction of 1e giving (R)-2e** (98% yield, 95% ee): The general procedure was followed with 5-methoxy-2-((4-methoxyphenyl)dimethylsilyl)benzaldehyde (**1e**) (120.0 mg, 0.4 mmol) using (*R,R*)-**L5** (10 mg, 0.018 mmol), NaO<sup>t</sup>Bu (1.6 mg, 0.016 mmol), Ni(cod)<sub>2</sub> (4.3 mg, 0.016 mmol) and reaction was conducted at room temperature for 9 h. Purification by short silica gel column chromatography gave (*R*)-5-methoxy-3-(4-methoxyphenyl)-1,1-dimethyl-1,3-dihydrobenzo[*c*][1,2]-oxasilole (**2e**) as pale yellow thick liquid in 98% yield (117 mg, 0.39 mmol). The spectroscopic data was identified to that reported data for racemic compound.<sup>S2</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.43 (s, 3H, SiCH<sub>3</sub>), 0.50 (s, 3H, SiCH<sub>3</sub>), 3.73 (s, 3H, OCH<sub>3</sub>), 3.80 (s, 3H, OCH<sub>3</sub>), 6.10 (s, 1H, CHOSi), 6.52 (s, 1H, Ar-*H*), 6.89 (dd, *J* = 2.4, 8.0 Hz, 1H, Ar-*H*), 7.20 (d, *J* = 8.8 Hz, 3H, Ar-*H*), 7.52 (d, *J* = 8.3 Hz, 1H, Ar-*H*). [ $\alpha$ ]<sub>D</sub><sup>23</sup> = (–) 27.4° (*c* = 0.1, in CHCl<sub>3</sub>). The absolute stereochemistry of **2e** was assigned by analogy to **2h** and enantioselectivity was evaluated after converting it into desilylation product **4e** (50% yield, 95% ee). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.16 (d, *J* = 3.2 Hz, 1H, CHOH), 3.76 (s, 6H, 2 x OCH<sub>3</sub>), 5.75 (d, *J* = 3.2 Hz, 1H, CHOH), 6.77 (dd, *J* = 1.9, 8.0 Hz, 1H Ar-*H*), 6.83 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.91 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.92 (s, 1H, Ar-*H*), 7.19–7.30 (m, 3H, Ar-*H*). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  55.2, 55.24, 75.7, 111.9, 112.8, 113.8, 118.7, 127.9, 129.4, 136.0, 145.7, 159.0, 159.7. **HRMS** (ESI) *m/z* calcd for C<sub>15</sub>H<sub>16</sub>O<sub>3</sub> 244.1099: (*M*<sup>+</sup>) found 244.1097. **Chiral separation**: The enantioselectivity for **4e** was determined by SFC using Chiralpak ID (Back pressure = 15MPa, Flow (CO<sub>2</sub>) = 2.0 mL/min, Flow (IPA) = 0.3 mL/min, 25 °C,  $\lambda$  = 250 nm). Retention time:  $t_R$  = 7.0 min (minor *S*-enantiomer) and 7.4 min (major *R*-enantiomer).

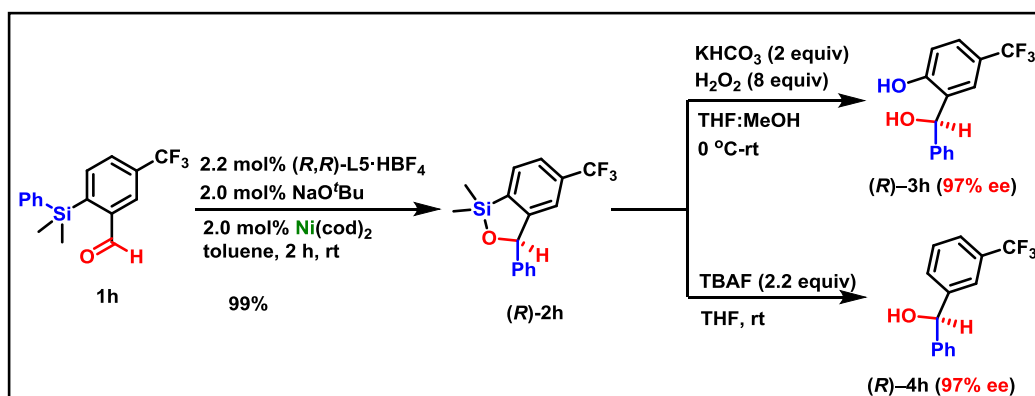


**Reaction of 1f giving (R)-2f** (96% yield, 98% ee): The general procedure was followed with 2-(dimethylphenyl)silyl-4-fluorobenzaldehyde (**1f**) (51.0 mg, 0.2 mmol) and reaction was conducted at room temperature for 2 h. Purification by short silica gel column chromatography gave *(R)*-6-fluoro-1,1-dimethyl-3-phenyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (**2f**) as pale yellow oil in 96% yield (49.0 mg, 0.19 mmol). The spectroscopic data was identified to that previously reported for racemic compound.<sup>S2</sup> **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.44 (s, 3H,  $\text{SiCH}_3$ ), 0.52 (s, 3H,  $\text{SiCH}_3$ ), 6.12 (s, 1H,  $\text{CHOSi}$ ), 6.96–6.99 (m, 2H, Ar-*H*), 7.23–7.35 (m, 6H, Ar-*H*).  $[\alpha]_D^{23} = (-) 110.9$  ( $c = 0.1$ , in  $\text{CHCl}_3$ ). The absolute stereochemistry of **2f** was assigned by analogy to **2h** and enantioselectivity was evaluated after converting it into desilylation product **4f** (70% yield, 98% ee). The spectroscopic data of **4f** was identified to that previously reported.<sup>S7</sup> **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.20 (br s, 1H,  $\text{CHOH}$ ), 5.71 (d,  $J = 2.6$  Hz, 1H,  $\text{CHOH}$ ), two set of double at 6.90 and 6.93 (d,  $J = 8.0$  Hz, 2H Ar-*H*), 7.15–7.28 (m, 7H, Ar-*H*). **Chiral separation:** The enantioselectivity for **4f** was determined by SFC using Chiralpak ID (Back pressure = 15MPa, Flow ( $\text{CO}_2$ ) = 4.0 mL/min, Flow ( $\text{CH}_2\text{Cl}_2$ ) = 0.6 mL/min, 25 °C,  $\lambda = 250$  nm). Retention time:  $t_R = 3.4$  min (major *R*-enantiomer) and 3.9 min (minor *S*-enantiomer).



**Reaction of 1g giving (R)-2g** (93% yield, 99% ee): The general procedure was followed with 2-(dimethyl(phenyl)silyl)-5-fluorobenzaldehyde (**1g**) (129 mg, 0.5 mmol) and reaction was conducted at room temperature for 3 h. Purification by short silica gel column chromatography gave *(R)*-5-fluoro-1,1-dimethyl-3-phenyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (**2g**) as pale yellow oil in 93% yield (120 mg, 0.47 mmol). **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.44 (s, 3H,  $\text{SiCH}_3$ ), 0.52 (s, 3H,  $\text{SiCH}_3$ ), 6.11 (s, 1H,  $\text{CHOH}$ ), 6.69 (d,  $J = 9.9$  Hz, 1H, Ar-*H*), 7.00 (td,  $J = 2.3, 7.6$  Hz, 1H, Ar-*H*),

7.24–7.36 (m, 5H, Ar-*H*), 7.55 (t, *J* = 6.9 Hz, 1H, Ar-*H*). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ 0.6, 1.3, 83.6, 110.7 (d, *J*<sub>CF</sub> = 21.0 Hz), 115.0 (d, *J*<sub>CF</sub> = 21.0 Hz), 127.0, 128.0, 128.6, 130.4, 132.3 (d, *J*<sub>CF</sub> = 9.0 Hz), 143.1, 155.3 (d, *J*<sub>CF</sub> = 7.3 Hz), 164.4 (d, *J*<sub>CF</sub> = 248.0 Hz). **HRMS** (EI): *m/z* Calcd for C<sub>15</sub>H<sub>15</sub>FOSi: (M<sup>+</sup>) 258.0876, found 258.0871. [α]<sub>D</sub><sup>23</sup> = (–) 131.7 (*c* = 0.1, in CHCl<sub>3</sub>). The absolute stereochemistry of **2g** was assigned by analogy to **2h** and enantioselectivity of **2g** was evaluated after converting it into desilylation product **4g** (76% yield, 99% ee). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 2.26 (d, *J* = 3.1 Hz, 1H, CHOH), 5.83 (*J* = 3.1 Hz, 1H, CHOH), 6.95 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 7.14 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 7.29–7.37 (m, 6H, Ar-*H*). Spectroscopic data of **4g** was identified to that previously reported.<sup>S8</sup> **Chiral separation:** The enantioselectivity was determined by SFC using Chiralpak IC (Back pressure = 15MPa, Flow (CO<sub>2</sub>) = 4.0 mL/min, Flow (isopropanol) = 0.2 mL/min, 25 °C, λ = 250 nm). Retention time: *t*<sub>R</sub> = 3.6 min (major *R*-enantiomer) and 3.9 min (minor *S*-enantiomer).



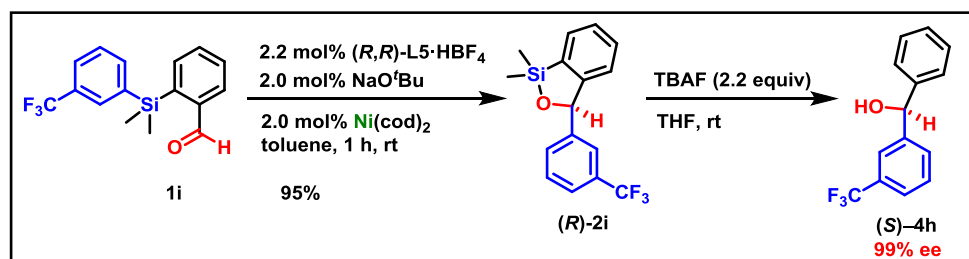
**Reaction of 1h giving (R)-2h** (99% yield, 97% ee): The general procedure was followed with 2-dimethylphenylsilyl-5-(trifluoromethyl)benzaldehyde (**1h**) (61.0 mg, 0.2 mmol) and reaction was conducted at room temperature for 2 h. Purification by silica gel column chromatography gave (R)-1,1-dimethyl-3-phenyl-5-(trifluoromethyl)-1,3-dihydrobenzo[c][1,2]oxasilole (**2h**) as a pale yellow solid in 99% yield (60.0 mg, 0.19 mmol). Spectroscopic data of **2h** was identified to that previously reported.<sup>S2</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 0.48 (s, 3H, SiCH<sub>3</sub>), 0.56 (s, 3H, SiCH<sub>3</sub>), 6.19 (s, 1H, CHOSi), 7.27–7.40 (m, 6H, Ar-*H*), 7.57 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.73 (d, *J* = 7.2 Hz, 1H, Ar-*H*). [α]<sub>D</sub><sup>23</sup> = (–) 103.8 (*c* = 0.1, in CHCl<sub>3</sub>). The absolute stereochemistry of **2h** was assigned by X-ray analysis (Flack parameter 0.02(3)) and enantioselectivity was evaluated after converting it into corresponding oxidation product **3h** as well as desilylation product **4h** prepared as described above. *Enantioselectivities were consistent in both products 3h and 4h* (97% ee).

(R)-2-(hydroxy(phenyl)methyl)-4-(trifluoromethyl)phenol (**3h**, 77% yield, 97% ee): **<sup>1</sup>H NMR** (400



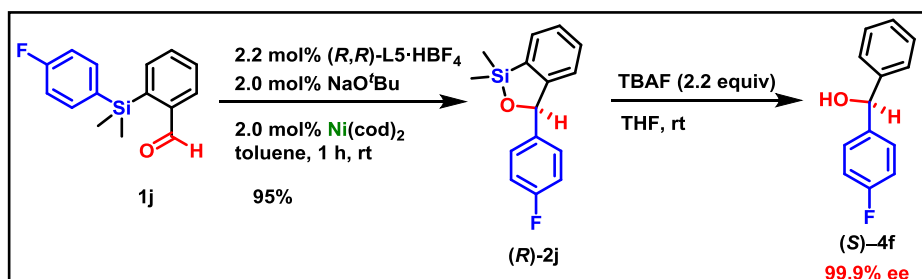
MHz, CDCl<sub>3</sub>):  $\delta$  3.12 (br s, 1H, CHOH), 6.02 (s, 1H, CHOH), 6.95 (d,  $J$  = 8.5 Hz, 1H, Ar-*H*), 7.12 (d,  $J$  = 1.6 Hz, 1H, Ar-*H*), 7.33–7.41 (m, 5H, Ar-*H*), 7.44 (dd,  $J$  = 1.6, 8.5 Hz, 1H, Ar-*H*), 8.52 (br s, 1H, Ar-OH). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  76.9, 117.6, 122.2 (q,  $J_{CF}$  = 33.1 Hz), 125.4 (q,  $J_{CF}$  = 3.7 Hz), 125.6 (q,  $J_{CF}$  = 271.0 Hz), 126.5 (q,  $J_{CF}$  = 3.7 Hz), 126.6, 126.8, 128.7, 129.0, 141.0, 158.3. **HRMS** (FAB)  $m/z$  calcd for C<sub>14</sub>H<sub>10</sub>F<sub>3</sub>O<sub>2</sub>: (M<sup>+</sup>–H) 267.0632, found 267.0632. **Chiral separation**: The enantioselectivity of **3h** was determined by HPLC using Chiralpak OD-H (IPA/Hexane 1:9; flow 0.5 mL/min,  $\lambda$  = 254 nm); retention time:  $t_R$  = 16.2 min (minor *S*-enantiomer) and 19.9 min (major *R*-enantiomer).

(*R*)-phenyl(3-(trifluoromethyl)phenyl)methanol (**4h**, 58% yield, 97% ee): Spectroscopic data of **4h** was identified to that previously reported for racemic compound.<sup>S9</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.27 (d,  $J$  = 3.5 Hz, 1H, CHOH), 5.89 (d,  $J$  = 3.5 Hz, 1H, CHOH), 7.25–7.37 (m, 5H, Ar-*H*), 7.44 (dd,  $J$  = 7.9, 7.9 Hz, 1H, Ar-*H*), 7.53 (dd,  $J$  = 8.2, 8.2 Hz, 2H, Ar-*H*), 7.70 (br s, 1H, Ar-*H*). **Chiral separation**: The enantioselectivity of **4h** was determined by HPLC using Chiralpak OB-H (IPA/Hexane 1:9; flow 1.0 mL/min,  $\lambda$  = 254 nm); retention time:  $t_R$  = 9.2 min (major *R*-enantiomer) and 21.1 min (minor *S*-enantiomer).

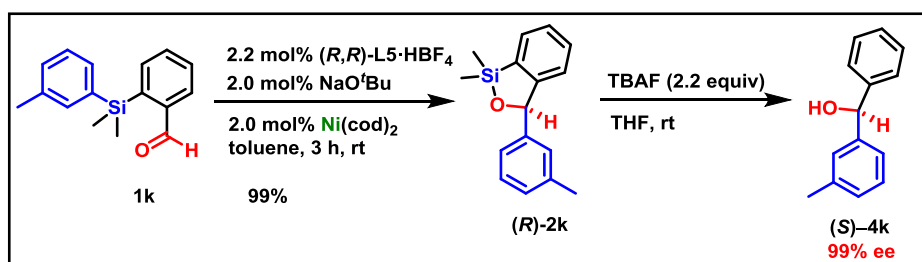


**Reaction of **1i** giving (*R*)-**2i** (95% yield, 99% ee):** The general procedure was followed with 2-(dimethyl(3-(trifluoromethyl)phenyl)silyl)benzaldehyde (**1i**) (154.0 mg, 0.5 mmol) and reaction was conducted at room temperature for 1 h. Purification by short silica gel column chromatography gave (*R*)-1,1-dimethyl-3-(3-(trifluoromethyl)phenyl)-1,3-dihydrobenzo[c][1,2]oxasilole (**2i**) as colorless liquid in 95% yield (147.0 mg, 0.48 mmol). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.47 (d,  $J$  = 2.3 Hz, 3H, SiCH<sub>3</sub>), 0.55 (d,  $J$  = 2.3 Hz, 3H, SiCH<sub>3</sub>), 6.21 (1H, CHOSi), 7.02 (br s, 1H, Ar-*H*), 7.32–7.36 (m, 2H, Ar-*H*), 7.46 (br s, 2H, Ar-*H*), 7.52–7.68 (m, 2H, Ar-*H*), 7.60–7.65 (m, 1H, Ar-*H*). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  0.4, 1.1, 83.3, 123.5, 123.8 (q,  $J_{CF}$  = 3.7 Hz), 124.0 (d,  $J_{CF}$  = 272.0 Hz), 124.6 (q,  $J_{CF}$  = 3.7 Hz), 127.5, 129.0, 130.0, 130.3, 130.8 (d,  $J_{CF}$  = 32.0 Hz), 130.9, 135.1, 144.8, 151.5 (d,  $J_{CF}$  = 9.0 Hz). **HRMS** (EI):  $m/z$  Calcd for C<sub>16</sub>H<sub>15</sub>F<sub>3</sub>OSi: (M<sup>+</sup>) 308.0844, found 308.0841.  $[\alpha]_D^{23}$  = (–) 116.3° ( $c$  = 0.1, in CHCl<sub>3</sub>). The absolute stereochemistry of **2i** was assigned by analogy to **2h** and enantioselectivity was evaluated after converting it into desilylation product **4h**.

(73% yield, 99% ee). **Chiral separation:** The enantioselectivity was determined by means of SFC using Chiralpak IB (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 5.0 mL/min, Flow (isopropanol) = 0.2 mL/min, 25 °C,  $\lambda$  = 230 nm). Retention time:  $t_R$  = 3.4 min (major *S*-enantiomer) and 3.8 min (minor *R*-enantiomer).

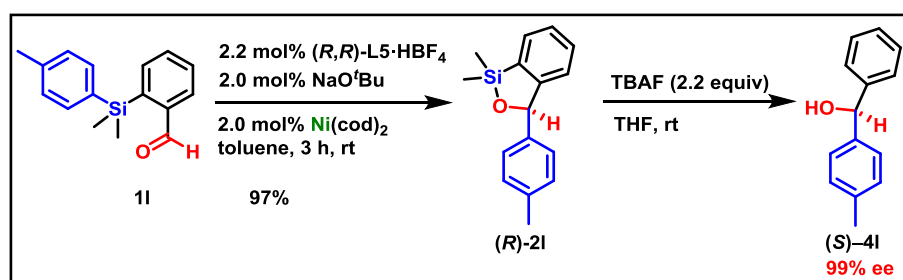


**Reaction of **1j** giving (*R*)-**2j**** (95% yield, 99.9% ee): The general procedure was followed with 2-((4-fluorophenyl)dimethylsilyl)benzaldehyde (**1j**) (129.0 mg, 0.5 mmol) and reaction was conducted at room temperature for 1 h. Purification by short silica gel column chromatography gave (*R*)-3-(4-fluorophenyl)-1,1-dimethyl-1,3-dihydrobenzo[c][1,2]oxasilole (**2j**) as pale yellow oil in 98% yield (127.0 mg, 0.47 mmol). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.45 (s, 3H, SiCH<sub>3</sub>), 0.52 (s, 3H, SiCH<sub>3</sub>), 6.15 (s, 1H, CHOSi), 6.96–7.06 (m, 3H, Ar-*H*), 7.20–7.28 (m, 2H, Ar-*H*), 7.29–7.36 (m, 2H, Ar-*H*), 7.59–7.65 (m, 1H, Ar-*H*). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  0.4, 1.2, 83.3, 115.3 (d,  $J_{CF}$  = 22.8 Hz), 123.7, 127.2, 128.8 (d,  $J_{CF}$  = 7.9 Hz), 129.8, 130.7, 135.1, 139.7 (d,  $J_{CF}$  = 3.0 Hz), 152.2, 162.3 (d,  $J_{CF}$  = 248.0 Hz). **HRMS** (EI):  $m/z$  Calcd for C<sub>15</sub>H<sub>15</sub>FOSi: (M<sup>+</sup>) 258.0876, found 258.0878.  $[\alpha]_D^{23}$  = (–) 112.2 ( $c$  = 0.16, in CHCl<sub>3</sub>). The absolute stereochemistry of **2j** was assigned by analogy to **2h** and enantioselectivity was evaluated after converting it into desilylation product **4f** (70% yield, 99.9% ee). **Chiral separation:** The enantioselectivity for **4f** was determined by SFC using Chiralpak ID (Back pressure = 15MPa, Flow (CO<sub>2</sub>) = 3.5 mL/min, Flow (CH<sub>2</sub>Cl<sub>2</sub>) = 0.6 mL/min, 25 °C,  $\lambda$  = 250 nm). Retention time:  $t_R$  = 2.8 min (minor *R*-enantiomer) and 3.1 min (major *S*-enantiomer).



**Reaction of **1k** giving (*R*)-**2k**** (99% yield, 99% ee): The general procedure was followed with 2-dimethyl(3-methylphenyl)silylbenzaldehyde (**1k**) (51.0 mg, 0.2 mmol) and reaction was conducted

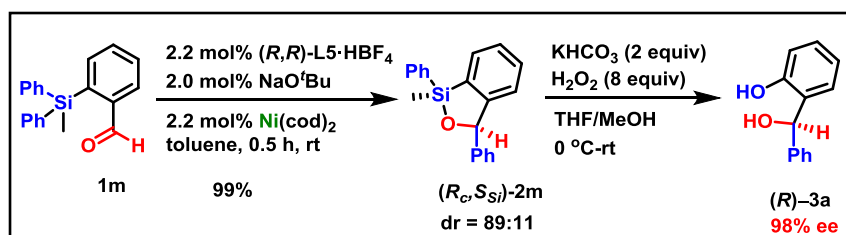
at room temperature for 3 h. Purification by short silica gel column chromatography gave (*R*)-1,1-dimethyl-3-(*m*-tolyl)-1,3-dihydrobenzo[*c*][1,2]oxasilole (**2k**) as pale yellow oil in 99% yield (50.0 mg, 0.2 mmol). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 0.44 (s, 3H, SiCH<sub>3</sub>), 0.53 (s, 3H, SiCH<sub>3</sub>), 2.33 (s, 3H, Ar-CH<sub>3</sub>), 6.13 (s, 1H, CHOSi), 7.00–7.12 (m, 4H, Ar-*H*), 7.22 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 7.28–7.35 (m, 2H, Ar-*H*), 7.58–7.64 (m, 1H, Ar-*H*). [ $\alpha$ ]<sub>D</sub><sup>23</sup> = (–) 133.3° (*c* = 0.1, in CHCl<sub>3</sub>). Spectroscopic data of **2k** was identified to that previously reported for racemic compound.<sup>S2</sup> The absolute stereochemistry of **2k** was assigned by analogy to **2h** and enantioselectivity was evaluated after converting it into desilylation product **4k**. (74% yield, 96% ee). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 2.24 (br s, 1H, CHOH), 2.33 (s, 3H, Ar-CH<sub>3</sub>), 5.79 (s, 1H, CHOH), 7.07 (d, *J* = 7.3 Hz, 1H, Ar-*H*), 7.14–7.28 (m, 4H, Ar-*H*), 7.30–7.40 (m, 4H, Ar-*H*). Spectroscopic data of **4k** was identified to that previously reported.<sup>S7</sup> **Chiral separation:** The enantioselectivity was determined by means of SFC using Chiralpak IA (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 2.0 mL/min, Flow (isopropanol) = 0.3 mL/min, 25 °C, λ = 250 nm). Retention time: *t*<sub>R</sub> = 5.6 min (major *S*-enantiomer) and 5.9 min (minor *R*-enantiomer).



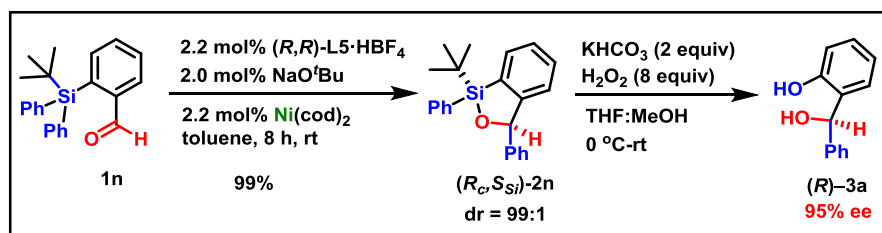
**Reaction of 1l giving (R)-2l** (97% yield, 99% ee): The general procedure was followed with 2-dimethyl(4-methylphenyl)silylbenzaldehyde (**1l**) (50.5 mg, 0.2 mmol) and reaction was conducted at room temperature for 3 h. Purification by silica gel column chromatography gave (*R*)-1,1-dimethyl-3-(*p*-tolyl)-1,3-dihydrobenzo[*c*][1,2]oxasilole (**2l**) as pale yellow oil in 97% yield (49.0 mg, 0.19 mmol). Spectroscopic data of **2l** was identified to that previously reported.<sup>S2</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 0.44 (s, 3H, SiCH<sub>3</sub>), 0.51 (s, 3H, SiCH<sub>3</sub>), 2.33 (s, 3H, Ar-CH<sub>3</sub>), 6.14 (s, 1H, CHO), 6.99–7.05 (m, 1H, Ar-*H*), 7.11–7.18 (m, 4H, Ar-*H*), 7.28–7.34 (m, 2H, Ar-*H*), 7.58–7.63 (m, 1H, Ar-*H*). [ $\alpha$ ]<sub>D</sub><sup>23</sup> = (–) 121.7 (*c* = 0.1, in CHCl<sub>3</sub>). The absolute stereochemistry of **2l** was assigned by analogy to **2h** and enantioselectivity of **2l** was evaluated after converting it into desilylation product **4l** (75% yield, 99% ee). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 2.21 (s, 1H, CHOH), 2.30 (s, 3H, CH<sub>3</sub>), 5.77 (s, 1H, CHOH), 7.11 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.19–7.25 (m, 3H, Ar-*H*), 7.26–7.37 (m, 4H, Ar-*H*). Spectroscopic data of **4l** was identified to that previously reported.<sup>S7</sup>

**Chiral separation:** The enantioselectivity was determined by SFC using Chiralpak IB (Back pressure = 15MPa, Flow (CO<sub>2</sub>) = 3.0 mL/min, Flow (isopropanol) = 0.3 mL/min, 25 °C, λ = 250 nm). Retention time: *t*<sub>R</sub> = 3.9 min (major *S*-enantiomer) and 4.2 min (minor *R*-enantiomer).

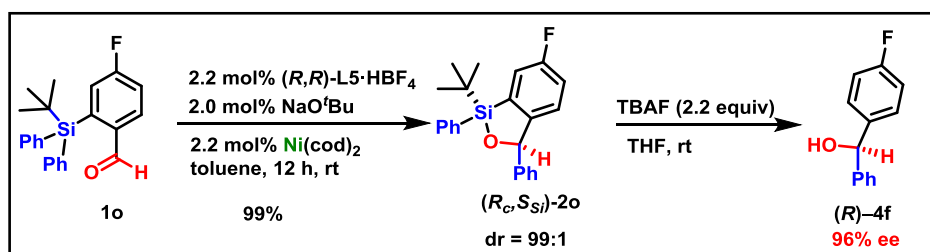
#### Diastereoselective synthesis of 3-arylbenzoxasiloles (2m–o)



**Reaction of 1m giving (R<sub>c</sub>, S<sub>si</sub>)-2m** (99% yield, 89:11 dr, 98% ee): The general procedure for catalytic reaction was slightly modified. A reaction tube charged with (R,R)-L5-HBF<sub>4</sub> (12.0 mg, 0.022 mmol), NaO<sup>t</sup>Bu (1.9 mg, 0.02 mmol) and Ni(cod)<sub>2</sub> (6.0 mg, 0.022 mmol) in toluene (5.0 mL) was stirred for 15 min. 2-Diphenylmethylsilylbenzaldehyde (**1m**) (300.0 mg, 1.0 mmol) was added and stirred at room temperature for 0.5 h. Purification by short silica gel column chromatography gave 1-methyl-1,3-diphenyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (**2m**) as pale yellow oil in 99% yield (296.0 mg, 0.2 mmol) as a mixture of diastereomers (89:11 *dr*). **<sup>1</sup>H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.43 (s, 3H, SiCH<sub>3</sub>, minor), 0.48 (s, 3H, SiCH<sub>3</sub>, major), 6.03 (s, 1H, CHOSi, major), 6.05 (s, 1H, CHOSi, major), 6.72–7.76 (m, 1H each for both diastereomers, Ar-*H*), 6.83–6.92 (m, 3H each for both diastereomers, Ar-*H*), 6.92–7.00 (m, 5H each for both diastereomers, Ar-*H*), 7.07 (d, *J* = 7.0 Hz, 2H, Ar-*H*, minor), 7.09 (d, *J* = 7.0 Hz, 2H, Ar-*H*, major), 7.23–7.29 (m, 1H each for both diastereoisomers, Ar-*H*), 7.38–7.46 (m, 2H each for both diastereomers, Ar-*H*). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ -0.7<sub>minor</sub>, -0.5<sub>major</sub>, 85.1<sub>minor</sub>, 85.3<sub>major</sub>, 124.9, 128.1, 128.2, 128.5, 128.7, 128.9, 129.2, 129.3, 130.8, 131.1, 132.1, 132.2, 134.6, 134.9, 135.2, 137.5, 144.9, 145.1, 154.5. Several carbons of phenyl groups are overlapped. [α]<sub>D</sub><sup>23</sup> = (–) 176.3 (*c* = 0.1, in CHCl<sub>3</sub>). The absolute stereochemistries of **2m** was assigned to be (R<sub>c</sub>, S<sub>si</sub>) by analogy to **2n** (determined by X-ray analysis, *vide infra*). The enantioselectivity of **2m** with respect to carbon-stereogenic centre was evaluated after converting it into **3a** using TFO conditions as employed previously (98% ee at carbon) for **2a** and **2b**. **Chiral separation:** The enantioselectivity was determined by SFC using Chiralpak ID (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 2.0 mL/min, Flow (isopropanol) = 0.3 mL/min, 25 °C, λ = 250 nm). Retention time: *t*<sub>R</sub> = 4.0 min (minor *S*-enantiomer) and 4.5 min (major *R*-enantiomer).

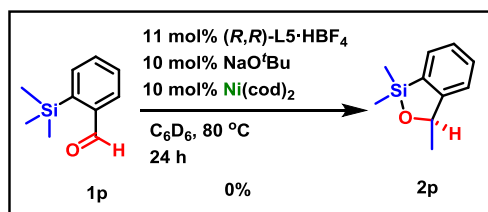


**Reaction of **1n** giving (*R<sub>C</sub>*, *S<sub>Si</sub>*)-**2n**** (99% yield, 99:1 dr, 95% ee): A reaction tube was charged with (*R,R*)-**L5**·**HBF<sub>4</sub>** (24.0 mg, 0.044 mmol), NaO<sup>*t*</sup>Bu (3.8 mg, 0.04 mmol) and Ni(cod)<sub>2</sub> (12.0 mg, 0.044 mmol) in toluene (10.0 mL) was stirred for 15 min. 2-(*tert*-Butyldiphenylsilyl)benzaldehyde (**1n**) (720.0 mg, 2.0 mmol) was added and stirred at room temperature for 8 h. Purification by short silica gel column chromatography gave 1-(*tert*-butyl)-1,3-diphenyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (**2n**) as a white solid in 99% yield (712.0 mg, 1.9 mmol) as a mixture of diastereomers (99:1 dr). It was recrystallized (in hexane, −20 °C) to a single diastereomer. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 1.14 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 6.30 (s, 1H, CHOSi), 7.06 (d, *J* = 6.0 Hz, 1H, Ar-*H*), 7.15–7.33 (m, 5H, Ar-*H*), 7.32–7.56 (m, 5H, Ar-*H*), 7.82 (d, *J* = 6.0 Hz, 2H, Ar-*H*), 7.88 (d, *J* = 6.0 Hz, 1H, Ar-*H*). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ 19.8, 25.7, 85.2, 123.9, 127.2, 127.3, 127.7, 127.8, 128.4, 129.8, 130.0, 131.7, 134.1, 134.3, 143.6, 153.5. **HRMS** (ESI): *m/z* Calcd for C<sub>23</sub>H<sub>24</sub>OSiNa: (M<sup>+</sup>+Na) 367.1494, found 367.1481. [α]<sub>D</sub><sup>23</sup> = (−) 172.2° (*c* = 0.1, in CHCl<sub>3</sub>). The absolute stereochemistries (*S<sub>Si</sub>*, *R<sub>C</sub>*) of **2n** was confirmed by X-ray analysis (Flack parameter 0.03(15)). The enantioselectivity with respect to carbon centre was evaluated after converting it into **3a** using TFO conditions as employed previously. **Chiral separation**: The enantioselectivity of **3a** was determined by SFC using Chiralpak ID (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 2.0 mL/min, Flow (isopropanol) = 0.3 mL/min, 25 °C, λ = 250 nm). Retention time: *t<sub>R</sub>* = 3.7 min (minor *S*-enantiomer) and 3.9 min (major *R*-enantiomer).



**Reaction of **1o** giving (*R<sub>C</sub>*, *S<sub>Si</sub>*)-**2o**** (99% yield, 99:1 dr, 96% ee): A reaction tube was charged with (*R,R*)-**L5**·**HBF<sub>4</sub>** (12.0 mg, 0.022 mmol), NaO<sup>*t*</sup>Bu (1.9 mg, 0.02 mmol) and Ni(cod)<sub>2</sub> (6.0 mg, 0.022 mmol) in toluene (5.0 mL) was stirred for 15 min. 2-(*tert*-Butyldiphenylsilyl)-5-fluorobenzaldehyde

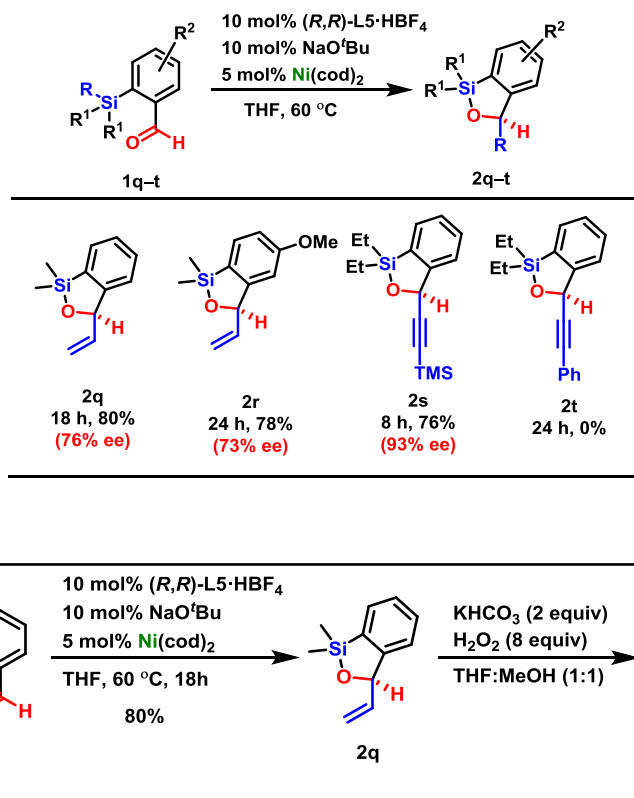
(**1o**) (362.0 mg, 1.0 mmol) was added and stirred at room temperature for 12 h. Purification by short silica gel column chromatography gave 1-(*tert*-butyl)-6-fluoro-1,3-diphenyl-1,3-dihydrobenzo[*c*]-[1,2]oxasilole (**2o**) as a white solid in 99% yield (358.0 mg, 0.99 mmol) as a mixture of diastereomers (99:1 dr). It was recrystallized (in hexane,  $-20\text{ }^{\circ}\text{C}$ ) to single diastereomer.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.06 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 6.20 (s, 1H,  $\text{CHOSi}$ ), 6.91–6.97 (m, 1H, Ar-*H*), 7.00 (td,  $J = 2.1, 8.7$  Hz, 1H, Ar-*H*), 7.10–7.17 (m, 2H, Ar-*H*), 7.19–7.27 (m, 3H, Ar-*H*), 7.35–7.48 (m, 4H, Ar-*H*), 7.73 (dd,  $J = 1.7, 7.0$  Hz, 2H, Ar-*H*).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.8, 25.7, 84.7, 117.3 (d,  $J_{\text{CF}} = 15.4$  Hz), 117.5 (d,  $J_{\text{CF}} = 17.0$  Hz), 125.6 (d,  $J_{\text{CF}} = 7.3$  Hz), 127.2, 127.9, 128.0, 128.5, 130.1, 133.6, 134.0, 134.5 (d,  $J_{\text{CF}} = 5.7$  Hz), 143.3, 148.9 (d,  $J_{\text{CF}} = 2.1$  Hz), 162.2 (d,  $J_{\text{CF}} = 246.4$  Hz). **HRMS** (EI):  $m/z$  Calcd for  $\text{C}_{23}\text{H}_{23}\text{FOSi}$ : ( $\text{M}^+$ ) 362.1502, found 362.1501.  $[\alpha]_{\text{D}}^{23} = (-) 156.8^{\circ}$  ( $c = 0.1$ , in  $\text{CHCl}_3$ ). The absolute stereochemistries of **2o** was assigned by analogy to **2n** and the enantioselectivity with respect to carbon centre was evaluated after converting it into desilylation product **4f** using TBAF (83% yield, 96% ee). The spectroscopic data of **4f** was identified to that previously reported as obtained from **2f**. **Chiral separation**: The enantioselectivity of **4f**, obtained from **2o** was determined by SFC using Chiralpak ID (Back pressure = 15 MPa, Flow ( $\text{CO}_2$ ) = 4.0 mL/min, Flow ( $\text{CH}_2\text{Cl}_2$ ) = 0.6 mL/min,  $25\text{ }^{\circ}\text{C}$ ,  $\lambda = 250$ ). Retention time:  $t_{\text{R}} = 3.1$  min (major *R*-enantiomer) and 3.9 min (minor *S*-enantiomer).



**Reaction of 1p:** A sample vial was charged with (*R,R*)-L5-HBF<sub>4</sub> (12.0 mg, 0.022 mmol) and NaO<sup>*t*</sup>Bu (1.9 mg, 0.02 mmol) and after 10 min of stirring Ni(cod)<sub>2</sub> (5.5 mg, 0.02 mmol) was added. To the stirring solution was added 2-trimethylsilylbenzaldehyde (**1p**) and transferred to J. Young NMR tube. The reaction was monitored by NMR. After 24 h (observed no reaction), it was heated to 80 °C. No reaction took place and starting material was intact as such, recovered after filtration.

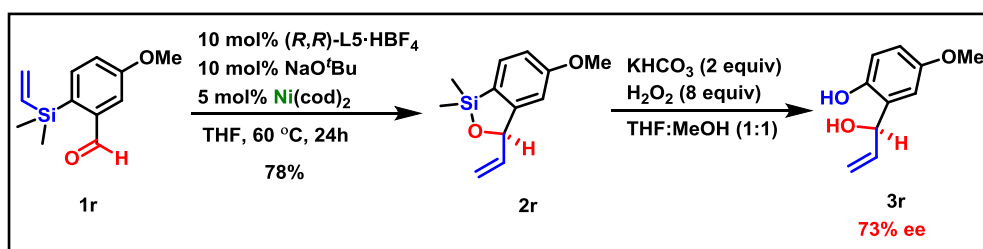
## Scope of 3-vinyl- and alkynyl-2,1-benzoxasiloles (Table 3)

**Table 3. Catalytic Enantioselective Synthesis of 3-Vinyl- and Alkynylbenzoxasiloles**



**Reaction of **1q** giving  $(R)$ -**2q**** (80% yield, 76% ee): A screwed reaction tube was charged with  $(R,R)$ -L5-HBF<sub>4</sub> (54.3 mg, 0.1 mmol) and NaO<sup>t</sup>Bu (9.6 mg, 0.1 mmol) in THF (1.5 mL). After 10 min of stirring, Ni(cod)<sub>2</sub> (13.7 mg, 0.05 mmol) was added. The resulting reaction mixture was stirred at room temperature for 1 h followed by addition of a solution of **1q** (190.0 mg, 1.0 mmol in 1 mL THF). The reaction mixture was stirred at 60 °C for 18 h. The reaction mixture was filtered through small silica column. It was further purification by recycle GPC to get  $(R)$ -1,1-dimethyl-3-vinyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (**2q**) as volatile colorless oil in 80% yield (136.0 mg, 0.36 mmol). The spectroscopic data was identified to that reported data for racemic compound. <sup>21</sup>**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 0.40 (s, 3H, SiCH<sub>3</sub>), 0.41 (s, 3H, SiCH<sub>3</sub>), 5.18 (d, *J* = 10.1 Hz, 1H, CH=CH<sub>2</sub>), 5.40 (d, *J* = 16.8 Hz, 1H, CH=CH<sub>2</sub>), 5.58 (d, *J* = 6.8 Hz, 1H, CHOSi), 5.91 (ddd, *J* = 6.8, 10.1, 16.8 Hz, 1H, CH=CH<sub>2</sub>), 7.21 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.31 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 7.40 (dt, *J* = 1.3, 7.6 Hz, 1H, Ar-*H*), 7.56 (d, *J* = 7.2 Hz, 1H, Ar-*H*). [α]<sub>D</sub><sup>23</sup> = (–) 15.1 (*c* = 0.09, in CHCl<sub>3</sub>). The absolute stereochemistry of **2q** was assigned by analogy to **2h** and enantioselectivity was evaluated after converting it into oxidation product **3q**. To the stirred solution

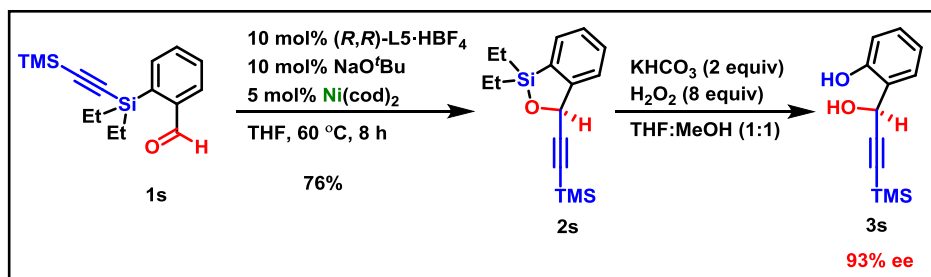
of benzoxasilole **2q** (30 mg, 0.15 mmol) in 1 mL MeOH and THF (1:1) KHCO<sub>3</sub> (30 mg) and H<sub>2</sub>O<sub>2</sub> (35% aqueous solution, 0.12 mL) was added. The reaction flask was closed with stopper and stirred at room temperature for overnight gave vinyl alcohol **3q** (isolated with 15% EtOAc:Hexane; 10 mg, 66% yield, 76% ee). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 2.80 (br s, 1H, CHOH), 5.24–5.37 (m, 3H, CHOH and CH=CH<sub>2</sub>), 6.14 (ddd, *J* = 16.9, 10.3, 6.3 Hz, 1H, CH=CH<sub>2</sub>), 6.83–6.89 (m, 2H, Ar-*H*), 7.01 (dd, *J* = 7.5, 1.6 Hz, 1H, Ar-*H*), 7.19 (td, *J* = 8.1, 1.7 Hz, 1H, Ar-*H*), 7.74 (br s, 1H, Ar-OH). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ 76.3, 116.4, 117.2, 120.0, 125.5, 127.6, 129.4, 138.0, 155.5. HRMS (ESI) *m/z* calcd for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub> 150.0681, found 150.0680. **Chiral separation:** The enantioselectivity for **3q** was determined by HPLC using Chiralpak OB-H; Isopropanol/Hexane = 3:97; Flow = 0.5 mL/min; T = 40 °C; λ = 250 nm. Retention time: *t*<sub>R</sub> = 43.1 min (minor *S*-enantiomer) and 47.4 min (major *R*-enantiomer).



**Reaction of **1r** giving **2r**** (78% yield, 73% ee): The general procedure was followed with 2-dimethylvinylsilyl-5-methoxybenzaldehyde (**1r**) (220.0 mg, 1.0 mmol) and reaction was conducted at 60 °C for 24 h. The reaction mixture was filtered through small silica column. It was further purification by recycle GPC to get (*R*)-5-methoxy-1,1-dimethyl-3-vinyl-1,3-dihydrobenzo[*c*]-[1,2]oxasilole (**2r**) as colorless and volatile oil in 78% yield (170.0 mg, 0.77 mmol). The spectroscopic data was identified to that reported data for racemic compound.<sup>S2</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 0.44 (s, 3H, SiCH<sub>3</sub>), 0.45 (s, 3H, SiCH<sub>3</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 5.22 (td, *J* = 1.2, 10.0 Hz, 1H, CH=CH<sub>2</sub>), 5.46 (td, *J* = 1.2, 17.0 Hz, 1H, CH=CH<sub>2</sub>), 5.58 (d, *J* = 6.8 Hz, 1H, CHO), 5.97 (ddd, *J* = 6.8, 10.0, 17.0 Hz, 1H, CH=CH<sub>2</sub>), 6.77 (d, *J* = 2.4 Hz, 1H, Ar-*H*), 6.93 (dd, *J* = 2.0, 8.0 Hz, 1H, Ar-*H*), 7.51 (d, *J* = 8.0 Hz, 1H, Ar-*H*). [α]<sub>D</sub><sup>23</sup> = (–) 9.7 (*c* = 0.09, in CHCl<sub>3</sub>). The absolute stereochemistry of **2r** was assigned by analogy to **2h** and enantioselectivity was evaluated after converting it into oxidation product **3r** (69 % yield, 73% ee). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 2.62 (br s, 1H, CHOH), 3.74 (s, 3H, OCH<sub>3</sub>), 5.25–5.37 (m, 3H, CHOH and CH=CH<sub>2</sub>), 6.09–6.18 (m, 1H, CH=CH<sub>2</sub>), 6.59 (s, *J* = 2.7 Hz, 1H, Ar-*H*), 6.75 (dd, *J* = 8.7, 2.5 Hz, 1H, Ar-*H*), 6.81 (d, *J* = 8.7 Hz, 1H, Ar-*H*), 7.20 (d, *J* = 2.5 Hz, 1H, Ar-OH). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ 55.9, 75.9, 113.2, 114.3, 116.5, 117.7, 126.5, 137.9, 149.2, 153.0. **HRMS** (ESI) *m/z* calcd for C<sub>10</sub>H<sub>13</sub>O<sub>3</sub> 181.0864: (M<sup>+</sup>)

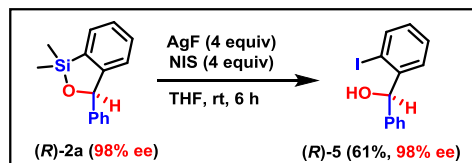


found 181.0861. **Chiral separation:** The enantioselectivity for **3r** was determined by SFC using Chiralpak IB (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 4.0 mL/min; Flow (isopropanol) = 0.2 mL/min; T = 25 °C; λ = 230 nm). Retention time: *t*<sub>R</sub> = 6.0 min (major *R*-enantiomer) and 6.9 min (minor *S*-enantiomer).

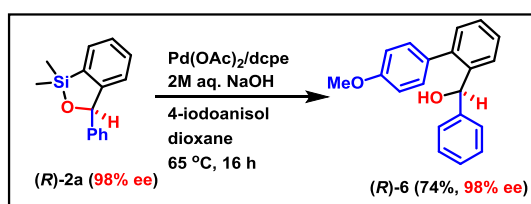


**Reaction of 1s giving 2s** (76% yield, 93% ee): A screwed reaction tube was charged with (*R,R*)-**L5**·**HBF**<sub>4</sub> (27.3 mg, 0.05 mmol) and NaO'Bu (4.8 mg, 0.05 mmol) in THF (1.5 mL). After 10 min of stirring, Ni(cod)<sub>2</sub> (6.8 mg, 0.025 mmol) was added. The resulting reaction mixture was stirred at room temperature for 1 h followed by addition of a solution of 2-diethyl(trimethylsilyl)ethynyl)silylbenzaldehyde (**1s**) (144.0 mg, 0.5 mmol) in THF (1.0 mL) was added the solution. The reaction mixture was stirred at 60 °C for 8 h. The reaction mixture was filtered through small silica column. It was further purified by Kugelrohr distillation (0.4 mmHg, 100 °C) to get (*R*)-1,1-diethyl-3-((trimethylsilyl)ethynyl)-1,3-dihydrobenzo[*c*][1,2]oxasilole (**2s**) as colorless oil in 76% (109.4 mg, 0.38 mmol). The spectroscopic data was identified to that reported data for racemic compound.<sup>S2</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 0.18 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.77–1.02 (m, 10H, Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 5.91 (s, 1H, CHO), 7.31–7.36 (m, 1H, Ar-*H*), 7.43–7.46 (m, 2H, Ar-*H*), 7.54 (dd, *J* = 0.8, 7.3 Hz 1H, Ar-*H*). [α]<sub>D</sub><sup>23</sup> = (+) 8.9 (*c* = 0.2, in CHCl<sub>3</sub>). The absolute stereochemistry of **2s** was assigned by analogy to **2h** and enantioselectivity was evaluated after converting it into oxidation product **3s** according to the previously reported procedure (68 % yield). The spectroscopic data was identified to that reported data for racemic compound.<sup>S2</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 0.22 (s, 9H, TMS), 2.59 (br s, 1H, OH), 5.66 (s, 1H, ArCH), 6.87–6.91 (m, 2H, Ar-*H*), 7.10 (br s, 1H, OH), 7.22–7.26 (m, 1H, Ar-*H*), 7.36 (dd, *J* = 1.4, 7.8 Hz, 1H, Ar-*H*). **Chiral separation:** The enantioselectivity for **3s** was determined by SFC using Chiralpak IA (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 4.0 mL/min; Flow (isopropanol) = 0.3 mL/min; T = 25 °C; λ = 220 nm). Retention time: *t*<sub>R</sub> = 3.1 min (minor *S*-enantiomer) and 3.2 min (major *R*-enantiomer).

## [5] Synthetic utilities of 3-arylbenzoxasiloles

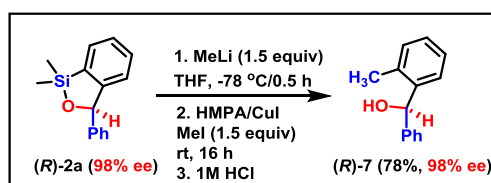


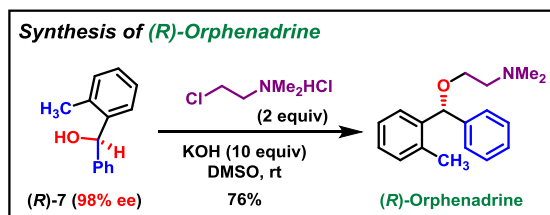
**Reaction of (R)-2a giving (R)-5** (61% yield, 98% ee): To the stirring solution of (R)-2a (86 mg, 0.4 mmol, 98% ee) in THF (2 mL) was added Ag(I)F (208 mg, 1.6 mmol) followed by *N*-iodosuccinamide (360 mg, 1.6 mmol). The reaction flask was covered with aluminum foil and allowed to stir at room temperature for overnight under N<sub>2</sub> atmosphere. After completion of reaction, it was filtered through celite and further purified by silica gel column chromatography to yield yellow oil product **6** (189.0 mg, 61% yield, isolated with 10% EtOAc:Hexane). Spectral data was identified to that previously reported.<sup>S10</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.36–2.50 (m, 1H, CHOH), 6.06 (d,  $J$  = 3.2 Hz, 1H, CHOH), 6.99 (td,  $J$  = 1.4, 7.6 Hz, 1H, Ar-*H*), 7.26–7.44 (m, 6H, Ar-*H*), 7.52 (dd,  $J$  = 1.0, 7.7 Hz, 1H, Ar-*H*), 7.83 (dd,  $J$  = 1.0, 7.7 Hz, 1H, Ar-*H*).  $[\alpha]_{\text{D}}^{23}$  = (+) 53.9° ( $c$  = 0.18, in CHCl<sub>3</sub>) (Lit.<sup>S11</sup>  $[\alpha]_{\text{D}}$  = (+) 68.2° ( $c$  = 1.5, in acetone for >95% ee, *R*-analogue). **Chiral separation:** The enantioselectivity was determined by SFC using Chiralpak IB (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 2.0 mL/min, Flow (IPA) = 0.3 mL/min, 25 °C,  $\lambda$  = 250 nm). Retention time:  $t_{\text{R}}$  = 5.8 min (major *R*-enantiomer) and 6.4 min (minor *S*-enantiomer). The absolute stereochemistry of **5** was assigned by analogy to previous report.<sup>S10</sup>



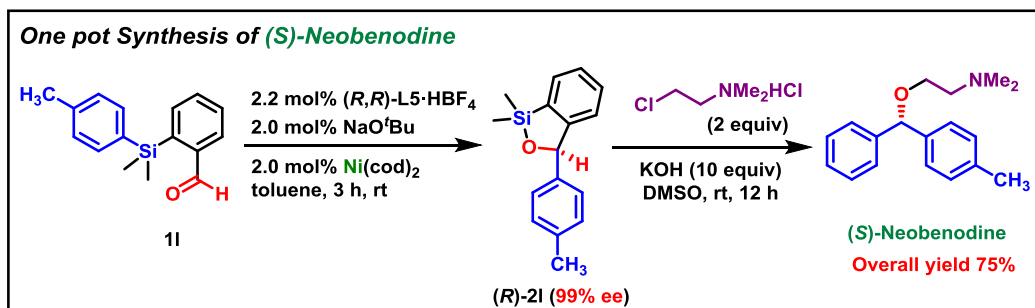
**Reaction of (R)-2a giving (R)-6** (74% yield, 98% ee): To a stirring solution of **2a** (96 mg, 0.4 mmol, 98% ee) and 4-iodoanisole (140 mg, 0.48 mmol) in dioxane (2 mL) was added a freshly prepared solution of Pd(OAc)<sub>2</sub> (9 mg, 8 mol%) and 1,2-bis(dicyclohexylphosphino)ethane (18 mg, 16 mol%) in dioxane (2 mL). After stirring the reaction mixture for 30 min at room temperature, aqueous NaOH (2M, 2.0 mmol) was added. The biphasic solution was stirred further for 30 min followed by heated at 65 °C. After completion of reaction, it was cooled to rt and then diluted with ethyl acetate, filtered through silica and concentrated. It was dried over Na<sub>2</sub>SO<sub>4</sub> and purified by silica gel column chromatography (with 15% EtOAc:hexane, 74% yield). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.18 (br s,

1H, *CHOH*), 3.77 (s, 3H, *OCH*<sub>3</sub>), 5.88 (s, 1H, *CHOH*), 6.84 (d, *J* = 8.8 Hz, 2H, *Ar-H*), 7.10–7.15 (m, 4H, *Ar-H*), 7.16–7.23 (m, 4H, *Ar-H*), 7.25 (td, *J* = 1.6, 7.5 Hz, 1H, *Ar-H*), 7.30 (td, *J* = 1.6, 7.5 Hz, 1H, *Ar-H*), 7.47 (dd, *J* = 1.6, 7.5 Hz, 1H, *Ar-H*). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ 55.4, 72.5, 113.5, 126.7, 127.2, 127.3, 127.4, 127.7, 128.3, 130.3, 130.5, 133.2, 141.1, 141.3, 144.0, 158.9. **HRMS** (EI): *m/z* Calcd for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>: (*M*<sup>+</sup>) 290.1307, found 290.1308. [ $\alpha$ ]<sub>D</sub><sup>23</sup> = (+) 160.8° (*c* = 0.2, in CHCl<sub>3</sub>). **Chiral separation**: The enantioselectivity was determined by SFC using Chiralpak IB (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 2.0 mL/min, Flow (IPA) = 0.3 mL/min, 25 °C, λ = 250 nm). Retention time: *t*<sub>R</sub> = 5.6 min (major *R*-enantiomer) and 6.1 min (minor *S*-enantiomer).



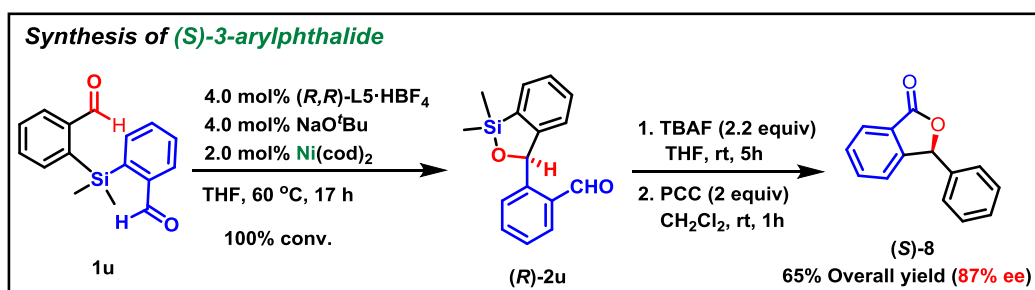


**Synthesis of (*R*)-orphenadrine from (*R*)-7:** To a suspension of (*R*)-2a (105 mg, 0.53 mmol, 98% ee) and hydrochloride salt of 2-(*N,N*-dimethylamino)ethylchloride (152.7 mg, 1.06 mmol) in DMSO (1.5 mL), a grinded KOH (excess, 297 mg, 5.3 mmol) was added. The reaction mixture was stirred at room temperature. After 16 h, it was diluted with ether and aqueous NaOH (1M, 10 mL) was added and stirred vigorously for 30 min. The biphasic mixture was extracted well and aqueous phase was extracted with ether (3 x 10 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated and purified by short silica gel column chromatography (with 20% EtOAc:hexane:1% TEA; 76% yield). The spectral data was identified to previously reported.<sup>S12,13</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 2.18 (br s, 9H, Ar-CH<sub>3</sub>, N(CH<sub>3</sub>)<sub>2</sub>), 2.51 (t, *J* = 6.1 Hz, 2H, NCH<sub>2</sub>), 3.45–3.53 (m, 2H, OCH<sub>2</sub>), 5.46 (s, 1H, CHOCH<sub>2</sub>), 7.04–7.20 (m, 5H, Ar-*H*), 7.21–7.27 (m, 3H, Ar-*H*), 7.36 (d, *J* = 7.5 Hz, 1H, Ar-*H*). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ 19.4, 46.0, 59.0, 67.6, 81.3, 125.9, 127.1, 127.3, 127.4, 127.6, 128.2, 130.5, 135.9, 139.8, 141.1. **HRMS** (CI): *m/z* Calcd for C<sub>18</sub>H<sub>24</sub>NO: (M<sup>+</sup>+H) 270.1852, found 270.1856. [α]<sub>D</sub><sup>23</sup> = (+) 3.4° (*c* = 0.1, in CHCl<sub>3</sub>) {(Lit.<sup>S13</sup> [α]<sub>D</sub><sup>27</sup> = (+) 11.0° (*c* = 3.61, in THF for 81% ee, *R*-analogue)}.



**One pot synthesis of (*S*)-neobenodine from 11 (75% yield):** In a globe box, a screw cap vial was charged with NHC-salt **L5**·HBF<sub>4</sub> (2.4 mg, 2.2 mol%) and NaO<sup>*t*</sup>Bu (0.4 mg, 2 mol%) in toluene (1 mL). After 10 min of stirring, Ni(cod)<sub>2</sub> (1.1 mg, 2 mol%) was added. After 10 min, **11** (51 mg, 0.2 mmol) was added and allowed it stir till completion of reaction, monitored by GC. Dry DMSO (1 mL) was added to the reaction mixture. To the reaction solution, freshly grinded KOH (112 mg, 2.0 mmol) and hydrochloride salt of 2-(*N,N*-dimethylamino)ethylchloride (57 mg, 0.4 mmol) were added. The reaction mixture was stirred at room temperature for 12 h. GC analysis shows a sole

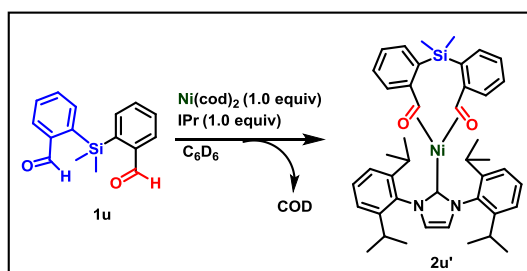
product of required product. It was diluted with ether and aqueous NaOH (1M, 5 mL) was added and stirred vigorously for 30 min. The biphasic mixture was extracted well and aqueous phase was extracted with ether (3 x 10 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated and purified by silica gel column chromatography (with 20% EtOAc:hexane:1% TEA; 45.0 mg, overall yield 75%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 2.26 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.30 (s, 3H, Ar-CH<sub>3</sub>), 2.59 (t, *J* = 6.1 Hz, 2H, NCH<sub>2</sub>), 3.55 (t, *J* = 6.1 Hz, 2H, OCH<sub>2</sub>), 5.32 (s, 1H, CHOCH<sub>2</sub>), 7.10 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.20–7.36 (m, 7H, Ar-*H*). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ 21.1, 46.0, 59.0, 67.5, 83.8, 126.9, 127.0, 127.2, 128.3, 129.0, 137.0, 139.3, 142.5. **HRMS** (FAB): *m/z* Calcd for C<sub>18</sub>H<sub>24</sub>NO: (*M*<sup>+</sup>+*H*) 270.1852, found 270.1853. [*α*]<sub>D</sub><sup>23</sup> = (–) 9.4° (*c* = 0.1, in CHCl<sub>3</sub>).



**Synthesis of (S)-3-Phenylisobenzofuran-1(3H)one (8) from 1u** (65% yield, 87% ee): In a globe box, a screw cap vial was charged with NHC-salt L5·HBF<sub>4</sub> (44 mg, 4.0 mol%) and NaO<sup>t</sup>Bu (7.7 mg, 4.0 mol%) in THF (20 mL). After 10 min of stirring, Ni(cod)<sub>2</sub> (11 mg, 2.0 mol%) was added and stirred at room temperature for additional 60 min. To a stirring solution, **1u** (536 mg, 2 mmol) was added and stirred for 30 min followed by heating at 60 °C till completion of reaction (*ca.* 16 h), monitored by GC. The reaction mixture was filtered through short silica column. **2u**: **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 0.47 (s, 3H, SiCH<sub>3</sub>), 0.55 (s, 3H, SiCH<sub>3</sub>), 6.91–6.99 (m, 1H, Ar-*H*), 6.15 (s, 1H, CHOSi), 7.27–7.36 (m, 3H, Ar-*H*), 7.46 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.53 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.59–7.67 (m, 1H, Ar-*H*), 7.90 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 10.39 (s, 1H, Ar-CHO). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ 0.5, 0.9, 78.4, 123.7, 127.3, 128.0, 128.3, 129.9, 130.9, 131.8, 133.6, 134.1, 135.2, 151.8, 192.8. **HRMS** (EI): *m/z* Calcd for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>Si: (*M*<sup>+</sup>) 268.0920, found 268.0919. [*α*]<sub>D</sub><sup>23</sup> = (–) 148.8° (*c* = 0.1, in CHCl<sub>3</sub>). It was forwarded for without further purification. To a solution of **2u** (110 mg, 0.4 mmol) in THF was added TBAF (1M, 1.0 mL, 1.0 mmol) at 0 °C allowed to stir at room temperature for 5 h. After the completion of reaction, it was quenched with aqueous NH<sub>4</sub>Cl solution and stirred vigorously for further 30 min. The reaction mixture was extracted and aqueous phase was washed with ethyl acetate (3 x 15 min). Combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated and used for next oxidation step. The compound was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> and then

PCC (172 mg, 0.8 mmol) was added. After 1 h, CH<sub>2</sub>Cl<sub>2</sub> was evaporated completely and ether was added to the black residue. It was filtered through celite, washed the residue (3 x 10 mL) and filtered, concentrated to get desired product with quantitative conversion. It was further purified by silica gel column chromatography (with 15% ethyl acetate:hexane, white solid, 65% over all yield). The spectroscopic data was identified to previously reported.<sup>S13</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.3 (s, 1H, OCHPh), 7.14–7.20 (m, 2H, Ar-*H*), 7.20–7.31 (m, 4H, Ar-*H*), 7.44 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.54 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.85 (d, *J* = 7.5 Hz, 1H, Ar-*H*). [ $\alpha$ ]<sub>D</sub><sup>23</sup> = (+) 32.8° (*c* = 0.1, in CHCl<sub>3</sub>) (Lit.<sup>S14</sup> [ $\alpha$ ]<sub>D</sub><sup>27</sup> = (+) 40.3° (*c* = 1.0, in CH<sub>2</sub>Cl<sub>2</sub> for 84% ee, *S*-analogue). **Chiral separation:** The enantioselectivity was determined by SFC using Chiralpak IA (Back pressure = 15 MPa, Flow (CO<sub>2</sub>) = 2.4 mL/min, Flow (CH<sub>2</sub>Cl<sub>2</sub>) = 0.4 mL/min, 40 °C, λ = 250 nm). Retention time: *t*<sub>R</sub> = 7.0 min (minor *R*-enantiomer) and 7.3 min (major *S*-enantiomer). The absolute stereochemistry of **8** was assigned by analogy to literature report.<sup>S14</sup>

#### [6] Isolation of ( $\eta^2$ : $\eta^2$ -dialdehyde)Ni complex (**2u'**)

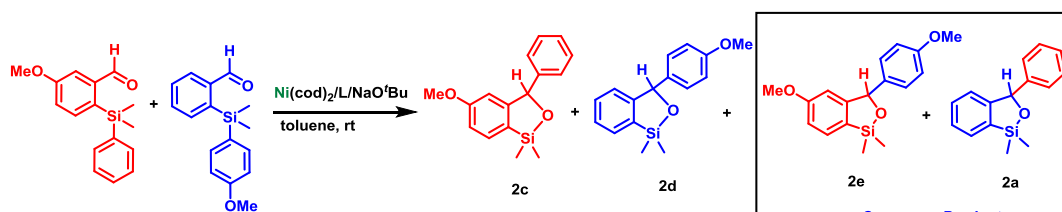


To the stirring solution of Ni(cod)<sub>2</sub> (22.0 mg, 0.08 mmol) and IPr (31.0 mg, 0.08 mmol) in C<sub>6</sub>D<sub>6</sub> (1 mL) was added 2,2'-(dimethylsilanediyl)dibenzaldehyde (21.5, 0.08 mmol). After 5 min the volatile materials were evaporated under high vacuum for a long time. A yellow crystalline solid **2u'** was obtained quantitatively and the complex was analyzed by <sup>1</sup>H, <sup>13</sup>C and X-ray analyses. **<sup>1</sup>H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.37 (s, 3H, SiCH<sub>3</sub>), 0.96 (d, *J* = 6.8 Hz, 6H, IPr-CH<sub>3</sub>), 1.08 (d, *J* = 6.8 Hz, 6H, IPr-CH<sub>3</sub>), 1.21 (d, *J* = 6.8 Hz, 6H, IPr-CH<sub>3</sub>), 1.68 (d, *J* = 6.8 Hz, 6H, IPr-CH<sub>3</sub>), 3.08 (sept, *J* = 6.8 Hz, 2H, IPr-CHCH<sub>3</sub>), 3.14 (sept, *J* = 6.8 Hz, 2H, IPr-CHCH<sub>3</sub>), 4.97 (s, 2H, CHO), 6.04 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 6.66 (s, 2H, IPr-NCHCHN), 6.96 (t, *J* = 7.2 Hz, 2H, Ar-*H*), 7.14 (t, *J* = 7.6 Hz, 4H, Ar-*H*), 7.31 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.36 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.40 (t, *J* = 7.6 Hz, 2H, Ar-*H*). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>): δ 0.4, 23.4, 23.6, 24.8, 26.0, 28.7, 29.4, 117.1, 121.6, 123.9, 124.1, 124.2, 126.5, 129.4, 129.6, 133.5, 133.8, 137.2, 146.5, 147.3, 149.3, 193.7.

## [7] Crossover experiments

**(a) Crossover experiments with 1c and 1d** (Scheme S3): To a stirring solution of NHC salt **L5·HBF<sub>4</sub>** (4.8 mg, 0.0088 mmol), NaO<sup>t</sup>Bu (0.8 mg, 0.008 mmol), and Ni(cod)<sub>2</sub> (2.2 mg, 0.008 mmol) in toluene (1 mL) was added a pre-dissolved solution of **1c** (54.0 mg, 0.2 mmol) and **1d** (54.0, 0.2 mmol) in toluene (1 mL) at room temperature. The reaction mixture was stirred at room temperature. The reaction was monitored by GC using *n*-pentadecane as an internal standard for 4 h. The corresponding benzoxasiloles **2c** and **2d** were obtained in 80% yield each, with no formation of crossover products (entry 1). The influence of salts and base on mechanism switching was studied. In all of these cases, crossover products were obtained (entries 2–5).

**Scheme S3. Crossover experiments with 1c and 1d<sup>a</sup>**



entry	Conversions	1c	1d	L = NHC/Salt	mol%	2c	2d	Crossover Products	
1	100%	100%		L = (R,R)-L5·HBF <sub>4</sub>	4	80%	80%	0%	0%
2	100%	100%		L = IPr	2	52%	60%	42%	46%
3	42%	76%		L = IPr·HCl	2	15%	50%	25%	27%
4	58%	87%		L = IPr/NaBF <sub>4</sub>	5	27%	54%	30%	32%
5	100%	100%		L = SIPr·HBF <sub>4</sub>	4	64%	56%	38%	44%

<sup>a</sup>Yields were determined by GC using *n*-pentadecane as an internal standard.

**Entry 1:** Under the optimized enantioselective reaction conditions using **L5·HBF<sub>4</sub>**.

**Entry 2:** ref. S2.

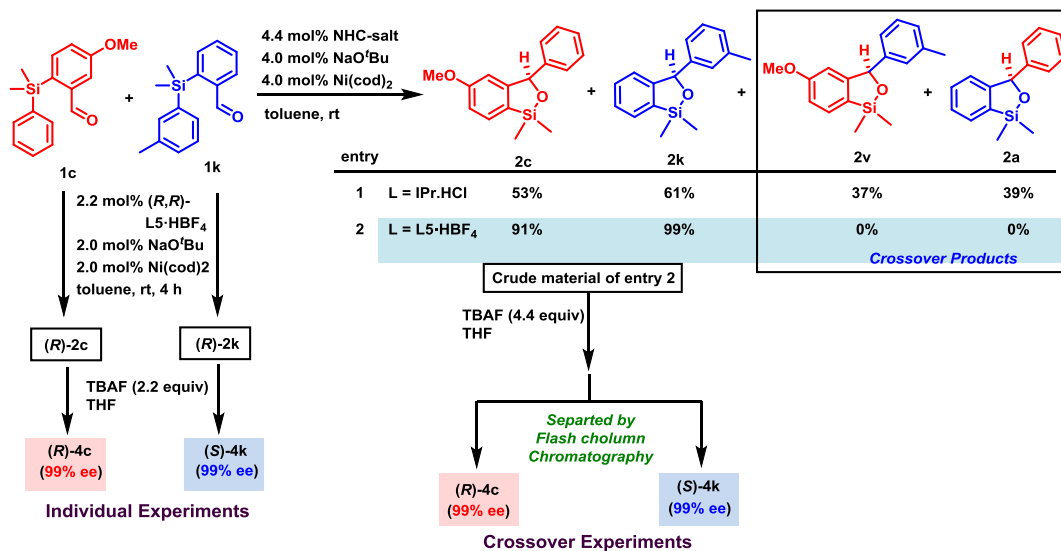
**Entry 3:** IPr·HCl salt was used for *in situ* generation of IPr (free carbene) in the presence of KO<sup>t</sup>Bu and yields were obtained after 42% and 76% conversion of **1c** and **1d**, respectively.

**Entry 4:** NaBF<sub>4</sub> was used as an additive in Ni(cod)<sub>2</sub>/IPr catalytic system. Yields were mentioned at 58% and 87% conversion of **1c** and **1d**, respectively.

**Entry 5:** Commercially available SIPr·HBF<sub>4</sub> was employed as a precursor of SIPr in the presence of NaO<sup>t</sup>Bu. Yields were mentioned after quantitative conversion of **1c** and **1d**.

**(b) Crossover experiments with 1c and 1k** (Scheme S4): The crossover experiments was examined with **1c** (54.0 mg, 0.2 mmol) and **1k** (51.0 mg, 0.2 mmol) under the identical reaction conditions

**Scheme S4: Crossover experiments with 1c and 1k<sup>a</sup>**



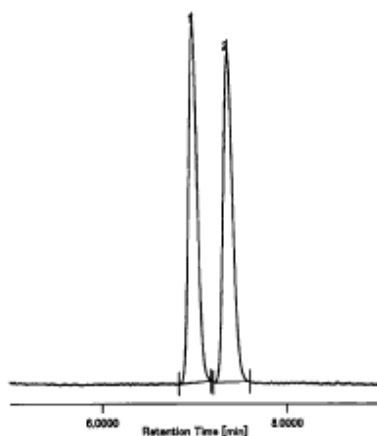
<sup>a</sup>Yields were determined by GC using *n*-pentadecane as an internal standard.

using NHC salt **L5·HBF<sub>4</sub>**. The corresponding benzoxasiloles **2c** and **2k** were obtained in 91 and 99% yields, respectively, with no crossover products (entry 2). After completion of reaction, it was passed through the small pad of silica and volatile material was evaporated. The crude material was subjected to desilylation using TBAF (0.9 mL, 0.88 mmol) in THF (2 mL). The desilylated products **4c** (31 mg, 72% yield) and **4k** (29 mg, 73% yield) were obtained after silica column chromatography (isolated with 20 and 10% EtOAc:hexane, respectively). The enantioselectivities measured for desilylation products (**4c** and **4k**) correspond to benzoxasiloles (**2c** and **2k**, respectively), which were remain consistent with the results of those of individual experiments (see below the chiral SFC charts). Entry 1 showed the results of crossover experiments, when IPr·HCl was employed.



# Comparative Chiral SFC chart of 4c correspond to 2c

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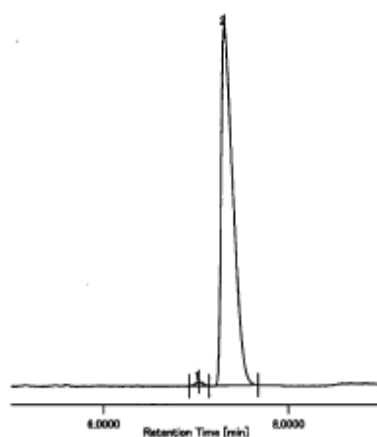
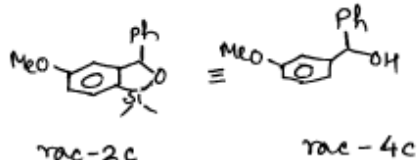


Sequence Name R-323-rac and chir-OMe-

Chromatogram m-OMe-rac

Name

#	CH	tR	Area	Height	Area%
1	9	6.9783	544771	83822	50.035
2	9	7.3533	544008	77287	49.965



Sequence Name R-323-rac and chir-OMe-

Chromatogram R-323-m

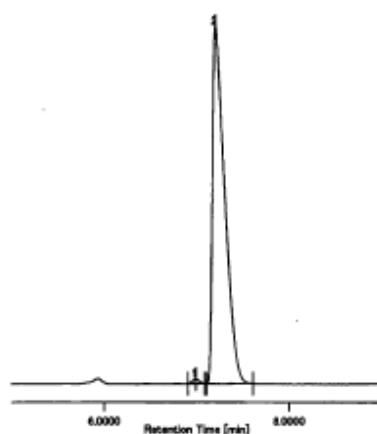
Name

#	CH	tR	Area	Height	Area%
1	9	7.0300	19436	3328	0.758
2	9	7.3133	2544898	291999	99.242

Individual Experiment

2c  $\equiv$  4c

98.6% ee



Sequence Name m-OMe and m-Me-chiral

Chromatogram R-325-2-C.O.pdt

Name

#	CH	tR	Area	Height	Area%
1	9	6.9900	35908	6908	0.704
2	9	7.2050	5067351	548771	99.296

After Crossover Experiment

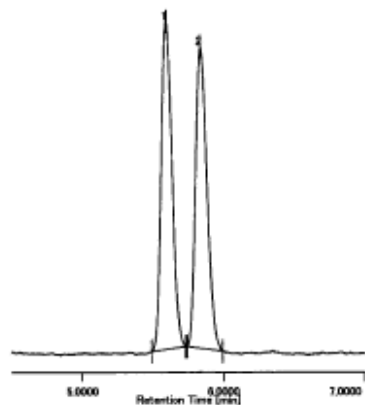
2c  $\equiv$  4c

98.6% ee

Top SFC (for racemic sample), center SFC (for individual experiment's product) and bottom SFC (for crossover experiment's product).

# Comparative Chiral SFC chart of 4k correspond to 2k

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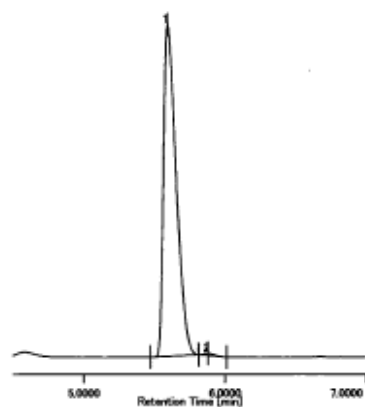
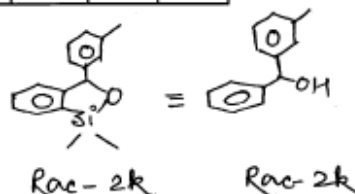


Sequence Name m-OMe and m-Me-racemic

Chromatogram m-Me-rac-317

Name

#	CH	tR	Area	Height	Area%
1	9	5.5967	324642	61381	50.471
2	9	5.8400	318580	56477	49.529



Sequence Name m-OMe and m-Me-chiral

Chromatogram R-313-m-Me

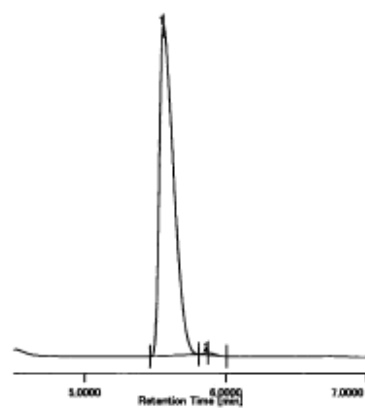
Name

#	CH	tR	Area	Height	Area%
1	9	5.5967	2755352	440426	99.515
2	9	5.8783	13428	2901	0.485

Individual Experiment

2k ≡ 4k

99% ee



Sequence Name m-OMe and m-Me-chiral

Chromatogram R-325-1- C.O.pdt

Name

#	CH	tR	Area	Height	Area%
1	9	5.5617	3794545	540715	99.573
2	9	5.8733	16289	3286	0.427

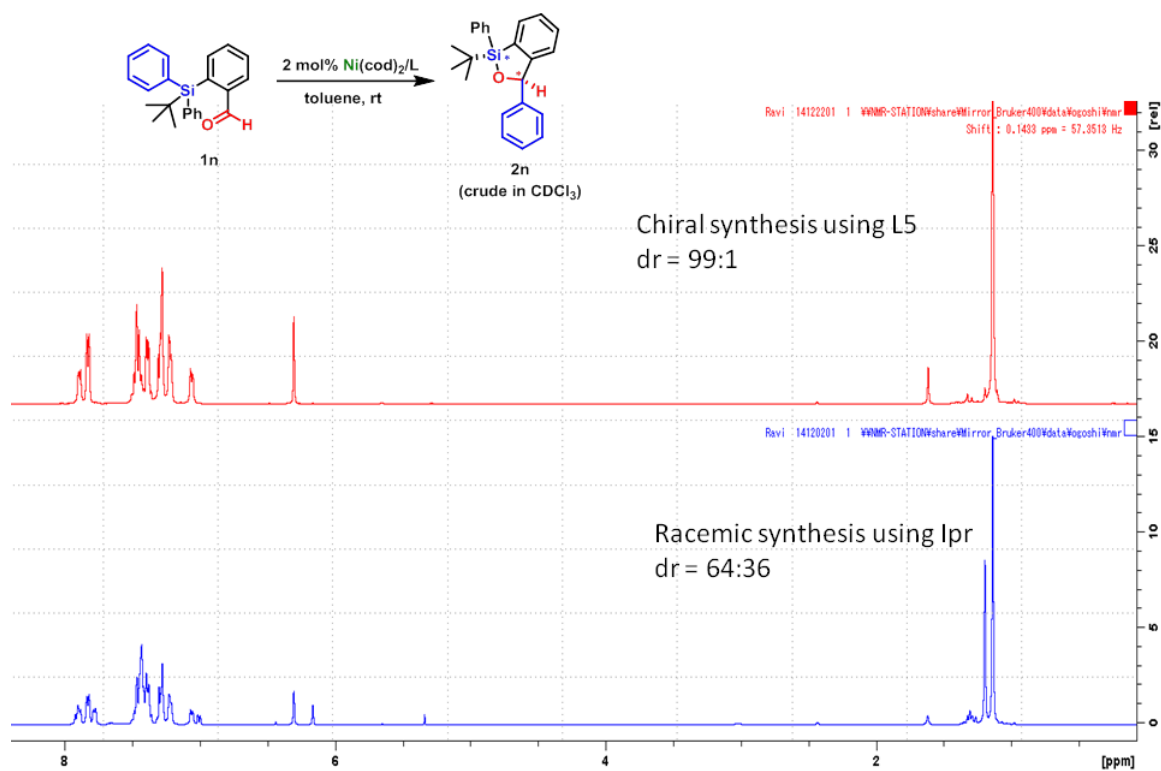
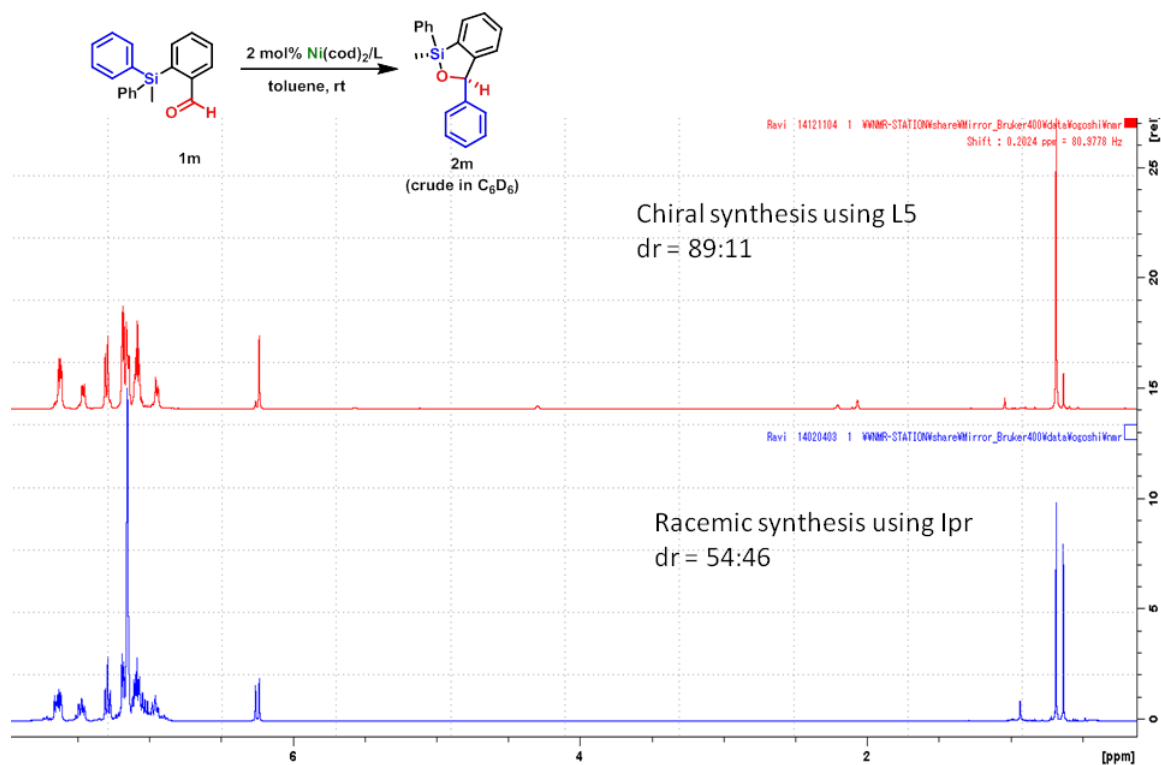
After Crossover Experiment

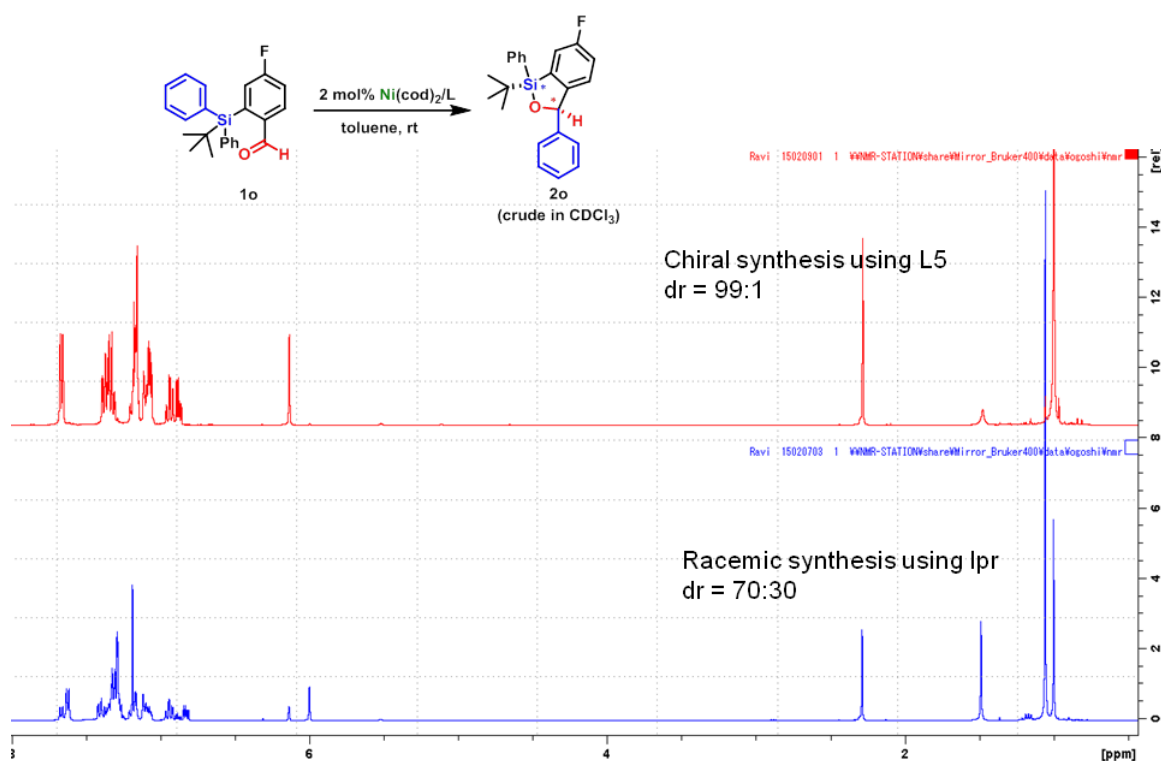
2k ≡ 4k

99% ee

Top SFC (for racemic sample), center SFC (for individual experiment's product) and bottom SFC (for crossover experiment's product).

[8] Comparative  $^1\text{H}$  NMR spectra for diastereoselectivity (IPr *versus* L5) in case of 2m–o





#### [9] Computational Details:

All calculations were performed with the Gaussian 09 package<sup>S15</sup> of programs with the hybrid B3LYP functional.<sup>S16</sup> For geometry optimizations, nickel was represented by the effective core potentials (ECPs) of Hay and Wadt with a double- $\zeta$  basis set (LANL2DZ)<sup>S17</sup> augmented with an *f*-type polarization function.<sup>S18</sup> The 6-311G(d,p) basis set was used for C, H, and N, whereas the 6-311G+(d) basis set was used for Si and O. The geometry optimizations were performed without any symmetry constraint followed by analytical frequency calculations to confirm that a minimum had been reached. The Gibbs energies were calculated at 298 K and 1 atm from the harmonic approximation for frequencies. Potential energies were also obtained by performing single point calculations using the above optimized geometries with the following basis sets: the LANL2DZ effective core potential for the inner electrons and the LANL2TZ<sup>S19</sup> basis set, augmented by an *f* polarization function, for the outer ones for Ni, the 6-311+G(2d,p) basis set for all the other atoms. Solvent effects (toluene,  $\epsilon = 2.3741$ ) were introduced through the single-point calculation at the optimized gas-phase geometries for all the minima by means of the polarizable continuum model (IEFPCM) implemented in Gaussian 09.<sup>S20</sup> Relative Gibbs energies were obtained by adding the Gibbs energy corrections derived from the analytical frequency calculations. These calculations involve a certain margin error.

Coordinates, E and G at 298 K in a.u. for all calculated extrema:

Ni(NHC\*) (NHC\* = (R,R)-L5)

**E = -1556.579862, G = -1556.649748**

N	-1.04907600	-0.52881600	0.01674300
C	-2.14893700	-1.31576900	-0.46580500
C	-3.15875400	-3.38867800	-1.14113800
C	-4.37753600	-2.74970800	-1.34023300
H	-3.08538200	-4.45257700	-1.33871900
H	-5.23633100	-3.31764400	-1.68060100
C	2.00254900	1.26731300	-0.47193600
C	3.00742300	3.36168500	-1.08527700
C	4.21399300	2.72417800	-1.35189000
H	2.93653200	4.43391700	-1.23212900
H	5.06625200	3.30111600	-1.69354000
C	0.58641000	0.39324600	1.45340100
H	0.31182400	1.39195200	1.81030300
C	-0.68148800	-0.51623400	1.45242100
H	-0.39768800	-1.52888000	1.75918300
C	1.70864000	-0.12122400	2.33351100
C	2.33969100	-1.34326300	2.07187500
C	2.11314500	0.61669500	3.44768400
C	3.34823000	-1.81410800	2.90640900
H	2.04645200	-1.92481200	1.20468100
C	3.12188500	0.14644300	4.28832900
H	1.63441000	1.56668700	3.66080700
C	3.74222600	-1.07011200	4.01943400
H	3.82970600	-2.76093100	2.68850000
H	3.42285800	0.73297000	5.14906000
H	4.52891100	-1.43704100	4.66887300
C	-1.77779100	-0.03969200	2.38496400
C	-2.14875400	-0.82251400	3.47997400
C	-2.41731200	1.19048700	2.19094800
C	-3.13297800	-0.38847800	4.36782000
H	-1.66301800	-1.77926800	3.64062700
C	-3.40149500	1.62538500	3.07276500
H	-2.15006100	1.80666100	1.33939500
C	-3.76210100	0.83652100	4.16605200
H	-3.40815700	-1.00965600	5.21272300
H	-3.89015900	2.57908200	2.90712500
H	-4.52991600	1.17536500	4.85229600
C	1.87856400	2.65844900	-0.64326300
C	-2.02115900	-2.69692300	-0.70347900

C	-0.08059700	-0.01311500	-0.80219600
C	0.56857300	3.39978400	-0.41170500
H	-0.15865900	2.67588500	-0.03998900
C	0.70775800	4.51039400	0.64508500
H	1.09043400	4.11664000	1.59056500
H	1.39059600	5.29757100	0.31293300
H	-0.26321000	4.97590000	0.83852500
C	0.00457700	3.95065100	-1.73458300
H	0.67800200	4.68887400	-2.17992300
H	-0.13873500	3.13713700	-2.45052700
H	-0.96214700	4.43512900	-1.56628700
C	-0.69948300	-3.43742100	-0.54729600
H	0.03300800	-2.72677100	-0.16061300
C	-0.79906600	-4.60069200	0.45596700
H	-1.15697400	-4.25845600	1.43075200
H	-1.48483400	-5.37685800	0.10461300
H	0.18085600	-5.06602900	0.59774300
C	-0.17041300	-3.91644200	-1.91206700
H	-0.85286800	-4.63493400	-2.37560400
H	-0.05094300	-3.06649400	-2.58903800
H	0.80286600	-4.40311000	-1.79584200
Ni	-0.10814500	0.02804100	-2.56353700
C	-4.48757400	-1.38102000	-1.10532900
H	-5.42975000	-0.86842700	-1.26191400
C	-3.37446700	-0.67413000	-0.66782100
H	-3.43630600	0.39065100	-0.48531700
C	3.21569800	0.62714100	-0.74193700
H	3.27428400	-0.44521300	-0.60966800
C	4.32011000	1.34549600	-1.18267100
H	5.25258900	0.83413700	-1.39234400

o-dimethylphenylsilylbenzaldehyde (1a)

**E = -945.9365012, G = -945.9844812**

Si	0.17666800	-1.09307300	0.00000100
O	-4.35933400	-1.33513100	-0.00000300
C	-3.15165800	-1.13886100	-0.00000300
C	-2.51658500	0.19622500	-0.00000300
C	1.92066300	-0.31302900	0.00000100
C	2.58537700	-0.02023600	-1.20082400
C	-0.61852000	1.66745500	-0.00000200
C	-1.11006000	0.35323200	-0.00000200
C	4.50047300	0.82808100	0.00000200
C	-2.85155300	2.59646900	-0.00000400

C	3.86006200	0.54397900	-1.20459900
C	3.86006300	0.54397400	1.20460300
C	-3.36861200	1.31033400	-0.00000400
C	-1.46854200	2.77243000	-0.00000300
C	2.58537800	-0.02024100	1.20082700
C	-0.00531700	-2.16377600	1.56722900
H	-2.46644300	-2.00427000	-0.00000300
H	-4.43774000	1.13464800	-0.00000400
H	-3.51485500	3.45372200	-0.00000500
H	-1.04733000	3.77191300	-0.00000400
H	0.45163000	1.83607700	-0.00000200
H	0.00034900	-1.54896500	2.47006700
H	-0.93510500	-2.73629700	1.56021500
H	0.82582400	-2.87087200	1.62989100
H	2.10763500	-0.23540800	2.15102000
H	4.35311200	0.75908000	2.14638000
H	5.49278200	1.26531700	0.00000200
H	4.35311000	0.75908900	-2.14637600
H	2.10763200	-0.23540000	-2.15101800
C	-0.00531400	-2.16377900	-1.56722700
H	0.00034900	-1.54897000	-2.47006500
H	0.82583000	-2.87087200	-1.62988800
H	-0.93510000	-2.73630300	-1.56021100

**( $\eta^2$ -1a)Ni(NHC\*) (Figure S2)**

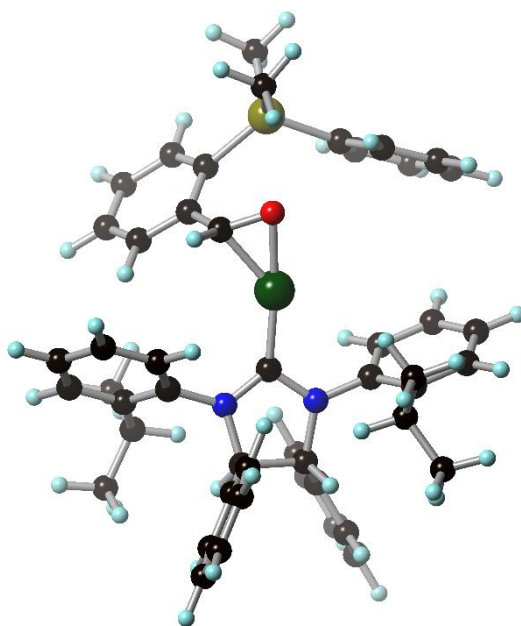
**E = -2502.569344, G = -2502.660506**

C	0.63757600	-1.59420700	-1.29109000
H	1.42116500	-2.10017900	-0.71162500
C	1.00796800	-1.27278400	-2.69077900
C	2.30943300	-0.79594900	-2.91658600
H	2.97915800	-0.68460300	-2.07138000
C	2.74141800	-0.44326800	-4.18781400
H	3.74880500	-0.06922000	-4.33461100
C	1.87158900	-0.57530400	-5.26772100
H	2.18850700	-0.30087800	-6.26813200
C	0.59454600	-1.09113400	-5.05712100
H	-0.04768400	-1.22670900	-5.91917800
C	0.12879900	-1.46414900	-3.78531500
O	-0.62274300	-1.79323500	-0.95566100
Si	-1.57902400	-2.35539900	-3.70367600
C	-2.03745400	-2.79992800	-5.51683100
H	-1.26394100	-3.41586600	-5.98358200

H	-2.96628400	-3.37722900	-5.50500700
H	-2.20585900	-1.92432900	-6.14838600
C	-1.49707700	-4.03100900	-2.80021000
H	-1.33496200	-3.90205400	-1.73207200
H	-2.42705600	-4.58348400	-2.96234800
H	-0.67763100	-4.62691500	-3.21221500
C	-3.05344800	-1.29678300	-3.09899800
C	-3.77631200	-1.63110800	-1.94547500
C	-3.51685400	-0.21696100	-3.86560500
C	-4.93004100	-0.93576800	-1.58616100
H	-3.43316400	-2.44517800	-1.31785300
C	-4.66427000	0.49034200	-3.50843800
H	-2.98506300	0.07550200	-4.76613900
C	-5.38038000	0.12520300	-2.36978900
H	-5.47547400	-1.22073300	-0.69270000
H	-5.00382000	1.31748800	-4.12341500
H	-6.28203700	0.66283700	-2.09595000
Ni	-0.07332800	-0.16658400	-0.17160400
C	0.68796100	1.33677300	0.69781800
N	-0.10774900	2.19042800	1.38939300
N	1.96970800	1.74801300	0.86981000
C	-1.54272200	2.13191900	1.35929300
C	0.61831200	3.33811500	1.98776300
C	3.12837300	1.02752300	0.42443100
C	2.10033300	2.86759000	1.84488600
C	-2.28370100	1.87753700	2.52808100
C	-2.19015500	2.34959100	0.13767300
H	0.36299700	3.42444200	3.04435400
C	0.32411200	4.66937100	1.31854700
C	4.08037900	1.63053700	-0.41839800
C	3.31286600	-0.28296500	0.87858300
H	2.69384500	3.66898800	1.40652500
C	2.74383500	2.46876100	3.16193500
C	-3.68084900	1.89026200	2.42174100
C	-1.63270000	1.54339900	3.86396300
H	-1.59372500	2.53097200	-0.74669300
C	-3.57644500	2.33507100	0.05770700
C	0.34150800	4.81499700	-0.07348300
C	0.06842400	5.79227000	2.10943100
C	5.21831300	0.88062700	-0.74943000
C	3.91207800	3.03066700	-0.99716800
C	4.43936900	-1.01046200	0.51834900
H	2.55611100	-0.72382600	1.51335000
C	3.69312600	3.31502500	3.74122400
C	2.38054800	1.30054900	3.84135700
C	-4.32506500	2.11724200	1.21119600



H	-4.27745800	1.69961900	3.30695000
H	-0.55136900	1.58468400	3.72799700
C	-2.00380200	2.55627600	4.96252700
C	-1.96721500	0.10357000	4.29919000
H	-4.06315300	2.48828100	-0.89698200
C	0.11554600	6.05823200	-0.65725500
H	0.52273400	3.95318300	-0.70554900
C	-0.15641500	7.03895100	1.52675600
H	0.04444500	5.69174200	3.18966600
C	5.40515500	-0.41872900	-0.29320100
H	5.96978600	1.32378000	-1.39329200
H	2.94007200	3.40799500	-0.67700100
C	4.99278300	3.99821300	-0.47793400
C	3.88792400	3.01532800	-2.53701700
H	4.56576500	-2.02533700	0.87685200
C	4.26343600	3.00921900	4.97615600
H	3.98855200	4.22192800	3.22373400
C	2.95026500	0.99197500	5.07354900
H	1.65665800	0.62310800	3.40393800
H	-5.40828000	2.11222700	1.16671600
H	-1.75148100	3.57813400	4.66673200
H	-3.07457900	2.53102700	5.18339500
H	-1.46805200	2.32785800	5.88822200
H	-3.03804900	-0.02050900	4.48281100
H	-1.67356100	-0.61658400	3.53153200
H	-1.43863400	-0.14609700	5.22395200
C	-0.13256700	7.17472700	0.14142000
H	0.12765200	6.15487100	-1.73699300
H	-0.35583700	7.89942800	2.15535100
H	6.29612300	-0.96857800	-0.57451800
H	5.01827500	4.02840100	0.61435400
H	5.98724700	3.69866600	-0.82089700
H	4.80547000	5.01190100	-0.84330600
H	4.84389900	2.68197900	-2.95075500
H	3.10779000	2.35105100	-2.91384800
H	3.69568000	4.02228300	-2.91893000
C	3.89273900	1.84616900	5.64567700
H	5.00022000	3.67619200	5.40926900
H	2.66222900	0.08066400	5.58533700
H	-0.31188200	8.14144200	-0.31503600
H	4.33811900	1.60236800	6.60338400



**Figure S2** Optimized structures of ( $\eta^2$ -**1a**)Ni(NHC\*)

**( $\eta^2$ : $\eta^2$ -**1a**)Ni(NHC\*) (Figure S3)**

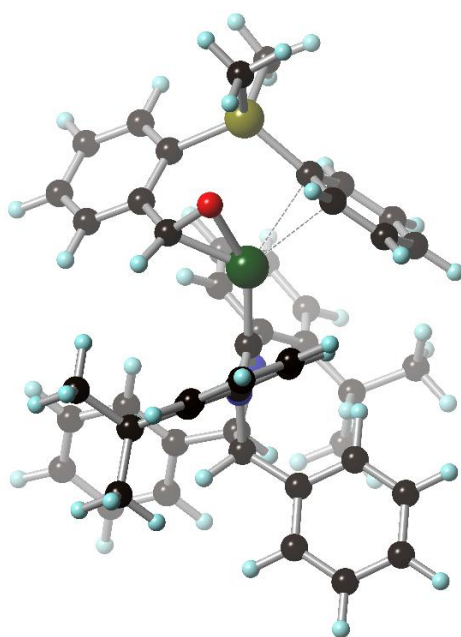
where NHC\* = (*R,R*)**L5**

**E = -2502.568039, G = -2502.657091**

C	1.29503500	-0.05654300	-2.76167200
H	2.28978800	0.40153900	-2.73056400
C	0.32739900	0.55387200	-3.69444600
C	0.62141000	1.80508200	-4.25614200
H	1.55498400	2.29361000	-3.99141400
C	-0.24757400	2.41707700	-5.15257400
H	0.00073600	3.38260700	-5.58022500
C	-1.43033400	1.77282400	-5.50567400
H	-2.11589500	2.22982000	-6.21101100
C	-1.72706200	0.52623900	-4.95011600
H	-2.65407000	0.04597400	-5.24108000
C	-0.87547100	-0.11252800	-4.03942100
O	1.18907000	-1.34762200	-2.51217900
Si	-1.39850800	-1.83279300	-3.33719000
C	-3.21800600	-2.09800700	-3.90902300
H	-3.26889900	-2.21852100	-4.99490800
H	-3.60229500	-3.01731900	-3.45826700
H	-3.88879500	-1.28256400	-3.62854900
C	-0.46568000	-3.32217500	-4.06942800
H	0.58105400	-3.31766800	-3.77449500

H	-0.93557100	-4.25279700	-3.73698300
H	-0.52673300	-3.28830600	-5.16117000
C	-1.50325100	-1.91016300	-1.40839900
C	-0.53038600	-2.55184500	-0.60794000
C	-2.66202900	-1.44999300	-0.75791500
C	-0.71549700	-2.71176700	0.77150600
H	0.34087900	-2.99157200	-1.07571800
C	-2.85630300	-1.62934800	0.60919400
H	-3.43915200	-0.95649700	-1.32967700
C	-1.88138800	-2.25794200	1.38253000
H	0.04216400	-3.22398600	1.35506000
H	-3.77366300	-1.27973200	1.06929700
H	-2.03443000	-2.40298000	2.44643300
Ni	0.59776500	-0.39900500	-0.94900900
C	0.70294000	1.05782000	0.27904000
N	-0.15034100	2.03645000	0.68309300
N	1.89954500	1.29987900	0.87969900
C	-1.50173200	2.20117600	0.22200200
C	0.53692700	3.12624000	1.42784500
C	3.02229900	0.40683000	0.80620700
C	1.86572200	2.42714400	1.84310100
C	-2.57257500	2.35321800	1.12668700
C	-1.73256900	2.23784800	-1.15605900
H	-0.02810200	3.38808600	2.31939600
C	0.74578100	4.39110300	0.61046300
C	4.26284000	0.82768400	0.29251300
C	2.86059600	-0.89876400	1.28452100
H	2.70282000	3.09907000	1.65705700
C	1.91342800	2.00051200	3.30086400
C	-3.84761600	2.57064200	0.58635600
C	-2.41813900	2.28656000	2.64346800
H	-0.89893000	2.10602700	-1.83022100
C	-3.01124300	2.43139700	-1.66246900
C	1.08342100	4.35558100	-0.74624600
C	0.64630400	5.63213800	1.24702200
C	5.31456800	-0.09938000	0.30287900
C	4.49471600	2.21635400	-0.29092200
C	3.91425800	-1.80267300	1.26427600
H	1.89576100	-1.19351200	1.67524200
C	2.71259800	2.71713000	4.19592500
C	1.14670100	0.93575400	3.78770400
C	-4.07595900	2.61074900	-0.78399400
H	-4.68644100	2.70076300	1.26096300
H	-1.39418900	1.98423600	2.86514400
C	-2.66745500	3.66018000	3.29777000
C	-3.32678000	1.21896200	3.28014600

H	-3.16342400	2.45263100	-2.73481400
C	1.32288000	5.53596500	-1.44590100
H	1.14693100	3.40574600	-1.26309300
C	0.88891300	6.81386300	0.54919600
H	0.37610600	5.67548200	2.29730300
C	5.15367200	-1.39552100	0.77708300
H	6.28125600	0.19958400	-0.08650900
H	3.53534100	2.73615200	-0.30553000
C	5.47105700	3.04082300	0.57040900
C	4.98334500	2.15290700	-1.75023500
H	3.77017100	-2.81150900	1.63310000
C	2.74172700	2.38672300	5.55001800
H	3.31834300	3.54059200	3.83157100
C	1.17529100	0.60331600	5.13954700
H	0.52969500	0.35950600	3.10836900
H	-5.07861800	2.77828800	-1.16137300
H	-2.03587300	4.43909100	2.86343000
H	-3.70709800	3.97230400	3.16318100
H	-2.46759300	3.61609500	4.37231800
H	-4.38608900	1.44964100	3.13911600
H	-3.13459400	0.23441300	2.85104600
H	-3.14127100	1.16486300	4.35692100
C	1.22889300	6.76824700	-0.80067400
H	1.57575300	5.49281400	-2.49921700
H	0.80362700	7.76742700	1.05796300
H	5.98998600	-2.08515900	0.76139300
H	5.13822200	3.10633800	1.60945200
H	6.46783400	2.59031400	0.57360400
H	5.56452400	4.05714900	0.17719700
H	5.97051000	1.68916600	-1.82597200
H	4.29586800	1.57741700	-2.37407800
H	5.05875600	3.16207200	-2.16553000
C	1.97187800	1.32844600	6.02545100
H	3.37040400	2.95149400	6.22910200
H	0.57839800	-0.22628500	5.50149500
H	1.41116400	7.68561500	-1.34865200
H	1.99594300	1.06529400	7.07673900



**Figure S3** Optimized structures of ( $\eta^2:\eta^2$ -**1a**)Ni(NHC\*)

**Ni(IPr)**

**E = -1329.115208, G = -1329.180383**

Ni	0.68413100	0.06509700	-0.50808900
N	2.32311500	1.23216700	1.50707100
N	0.86599100	2.62650500	0.72529600
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**( $\eta^2$ -1a)Ni(IPr) (Figure S4)**

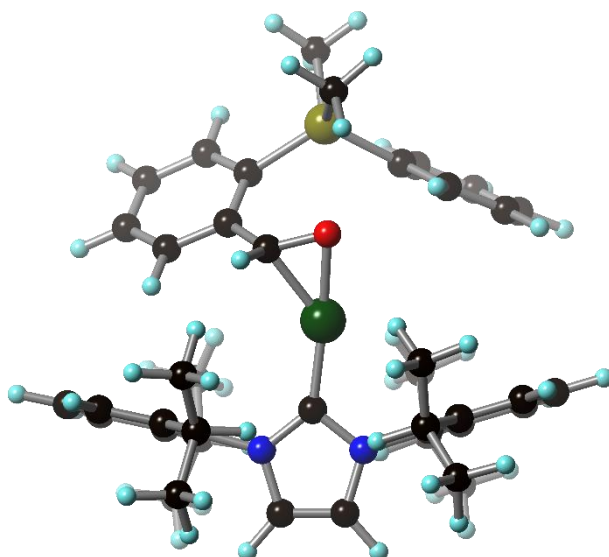
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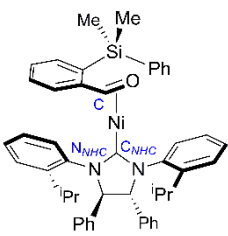
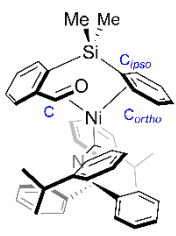
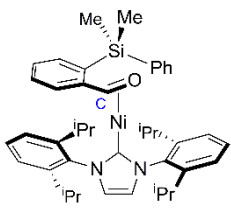


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H	-2.51049400	0.03334100	-2.98287300
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H	0.01923900	1.99108500	-6.75903700
H	-1.73199500	3.33054100	-5.61360500



**Figure S4** Optimized structures of ( $\eta^2$ -**1a**)Ni(IPr)

**Table S1.** Selected Geometries for ( $\eta^2$ -**1a**)Ni(NHC\*), ( $\eta^2$ : $\eta^2$ -**1a**)Ni(NHC\*), and ( $\eta^2$ -**1a**)Ni(IPr)

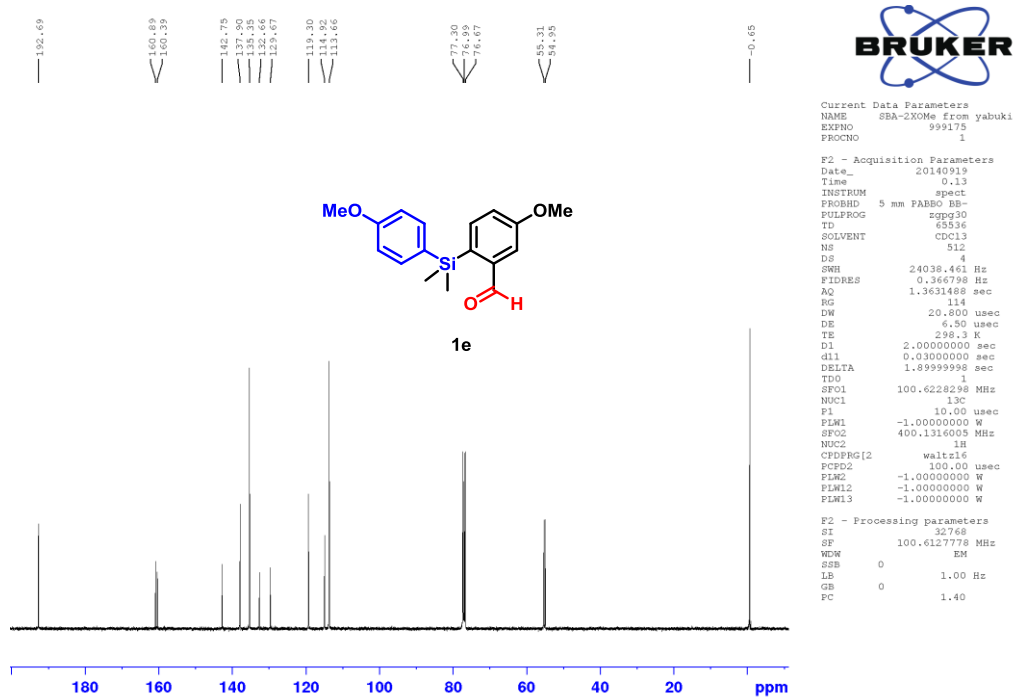
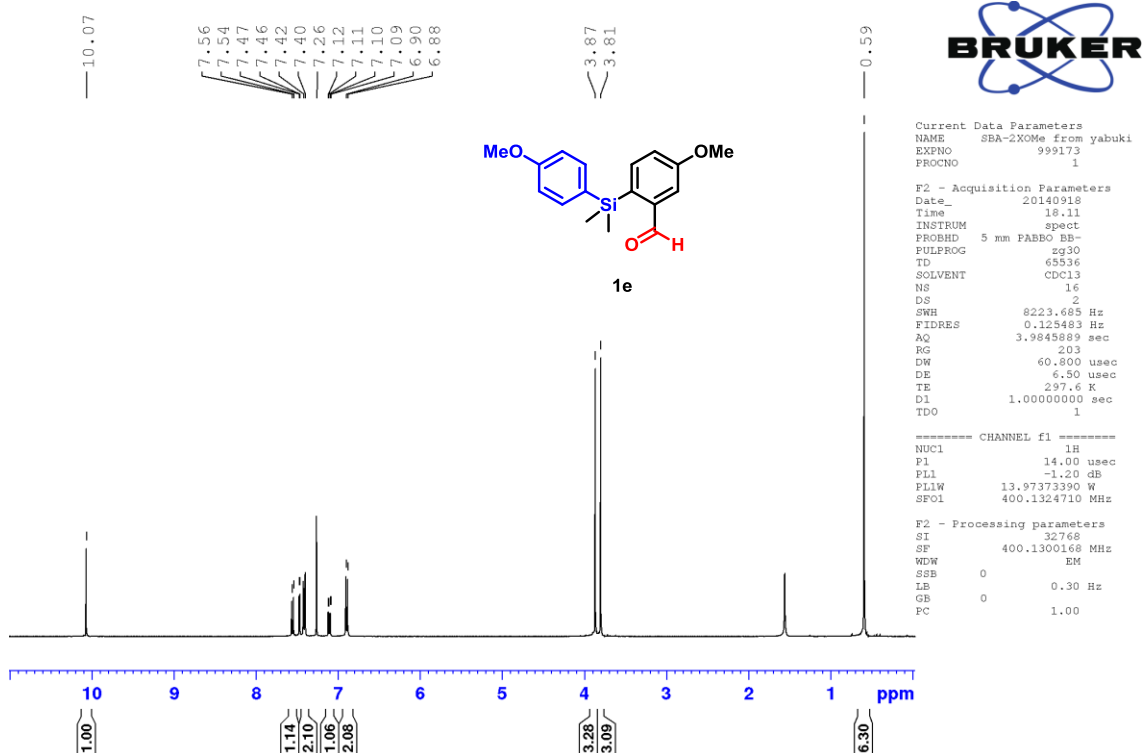
			
	( $\eta^2$ - <b>1a</b> )Ni(NHC*)	( $\eta^2$ : $\eta^2$ - <b>1a</b> )Ni(NHC*)	( $\eta^2$ - <b>1a</b> )Ni(IPr)
bond distances / Å			
Ni–O	1.8875	1.9217	1.8862
Ni–C	1.9485	1.9721	1.9542
C–O	1.3193	1.3192	1.3186
Ni–C <sub>NHC</sub>	1.8962	1.9083	1.9011
Ni–C <sub>invo</sub>	(4.3276)	2.6285	(4.1982)
Ni–C <sub>ortho</sub>	(4.3593)	2.4543	(3.9997)
Si···O	2.9635	2.7589	2.9513
Ni···Si	4.4197	3.4270	4.3609
bond angles / °			
C <sub>NHC</sub> –Ni–O	172.14	152.05	170.93
C <sub>NHC</sub> –Ni–C	134.25	116.07	135.51
torsion angles / °			
N <sub>NHC</sub> –C <sub>NHC</sub> –Ni–C	–7.23	–79.70	3.86

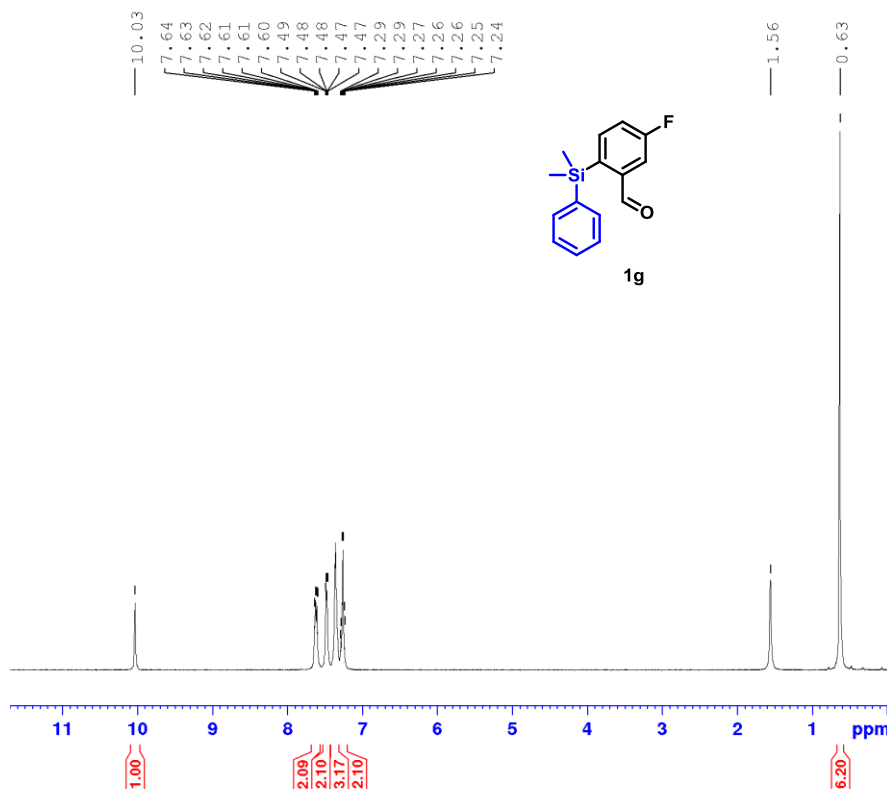
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[11]  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra and SFC/HPLC chart



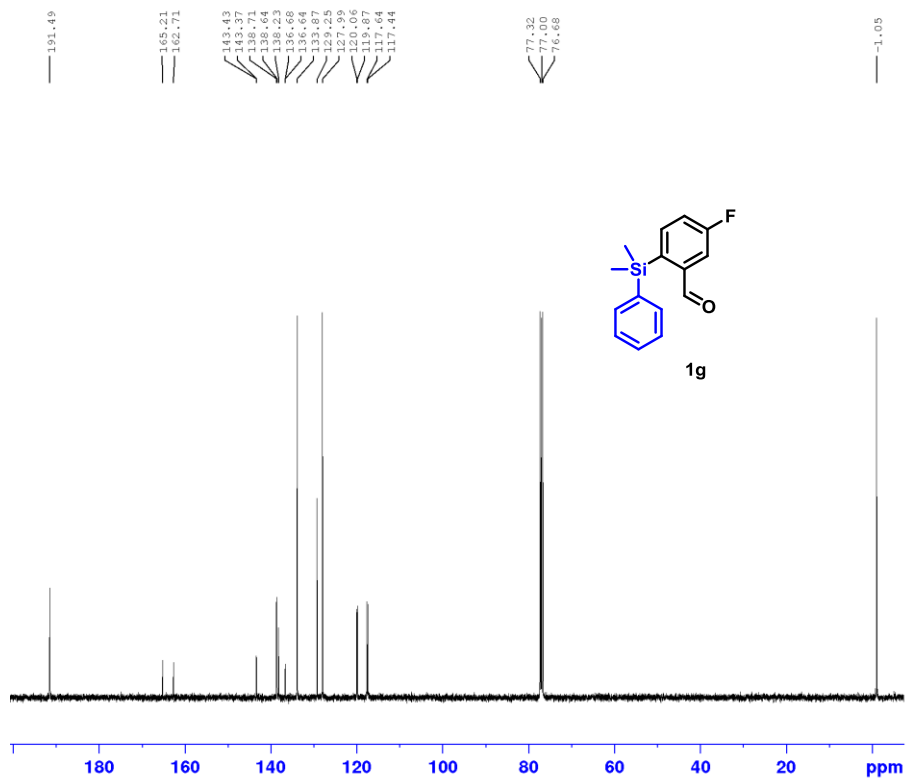


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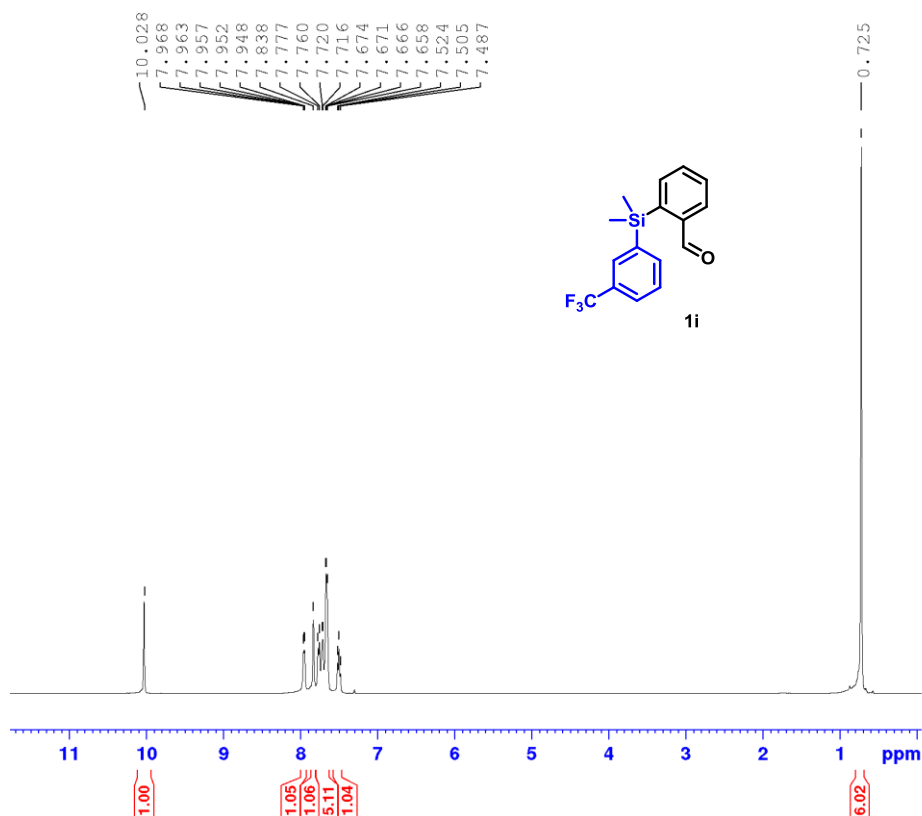
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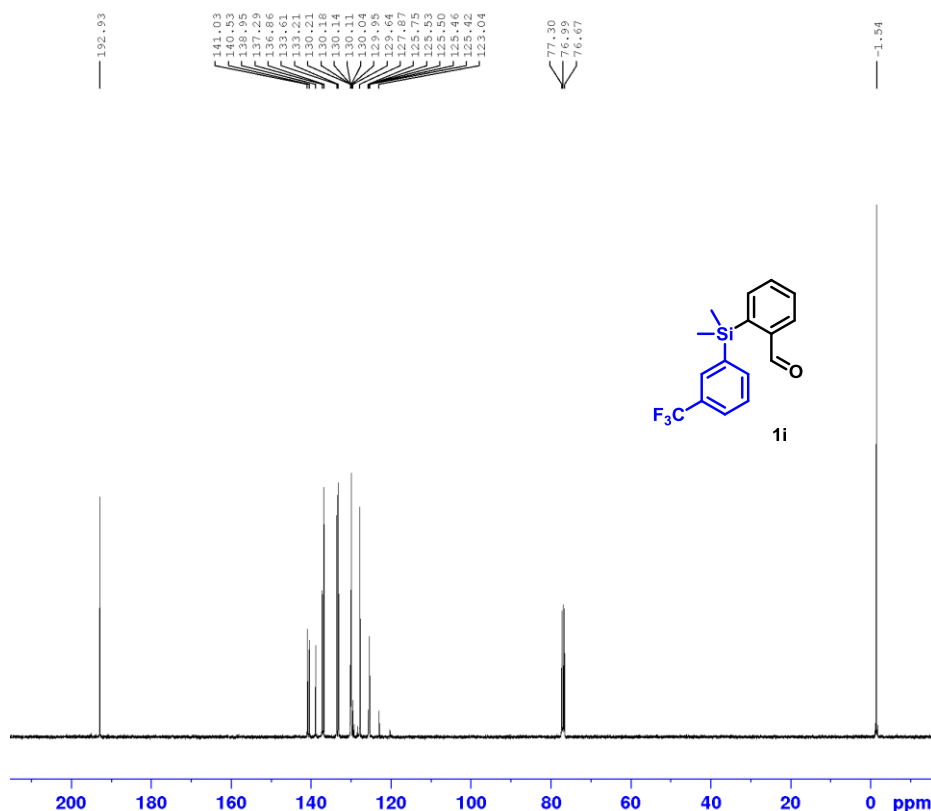


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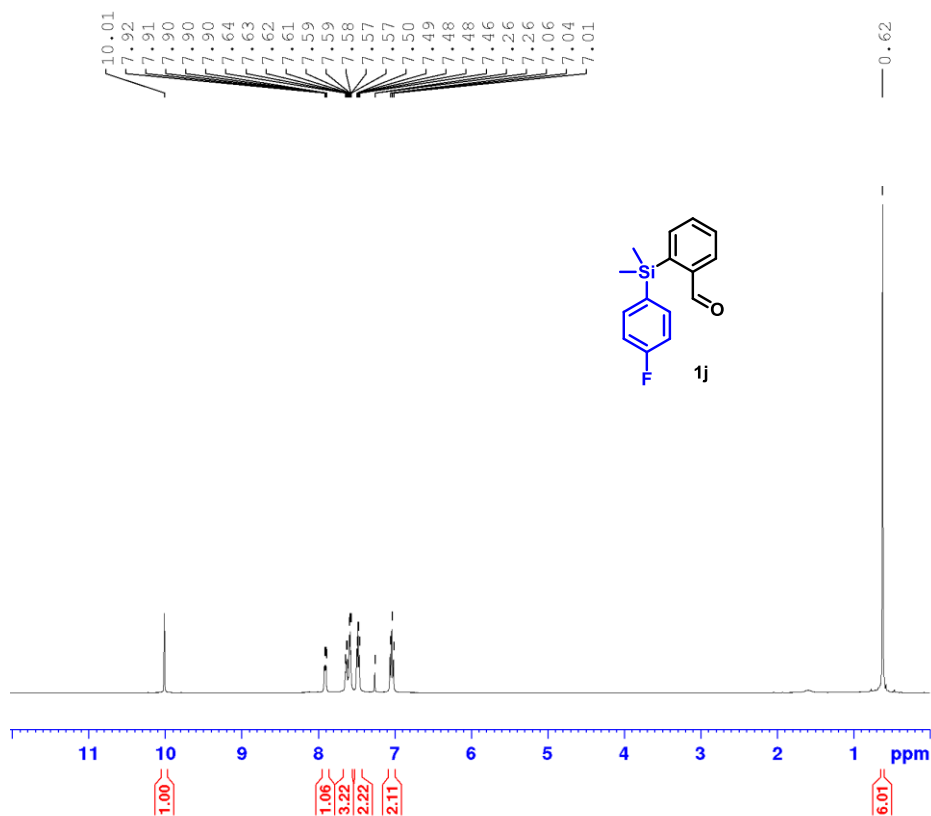
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PL12 15.88 dB  
PL13 16.00 dB  
PL12W 13.97373390 W  
PL12W 0.27372372 W  
PL13W 0.26626399 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127793 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

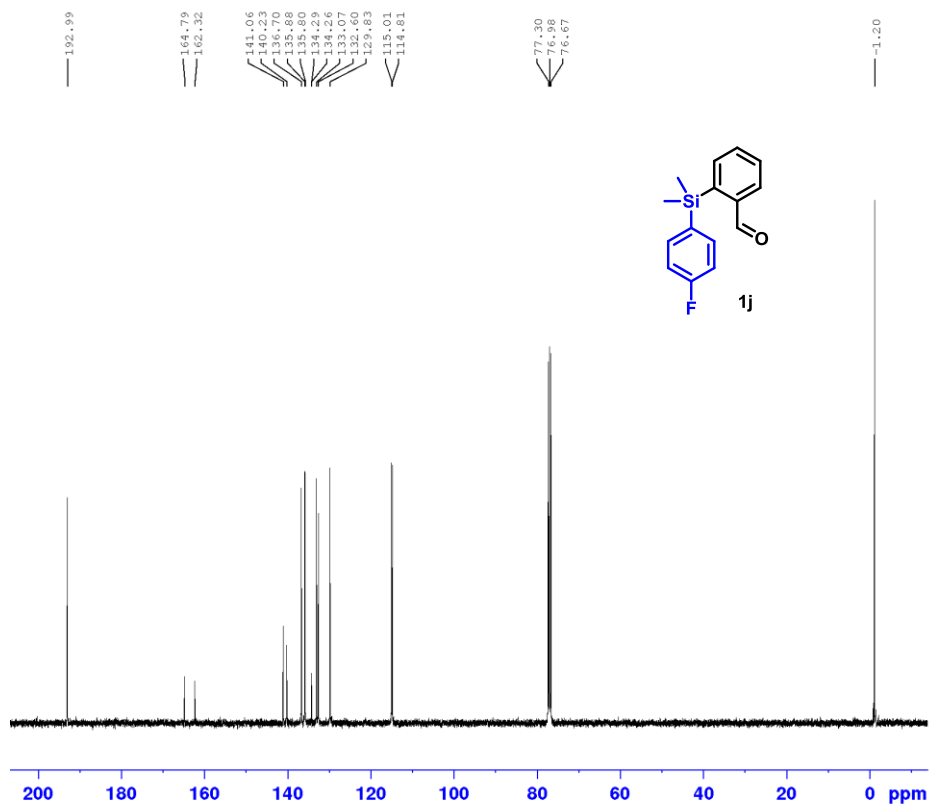


Current Data Parameters  
NAME Ravi  
EXPNO 15050901  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150509  
Time 10.40  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 203  
DW 60.800 usec  
DE 6.50 usec  
TE 296.1 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 <sup>1</sup>H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300189 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



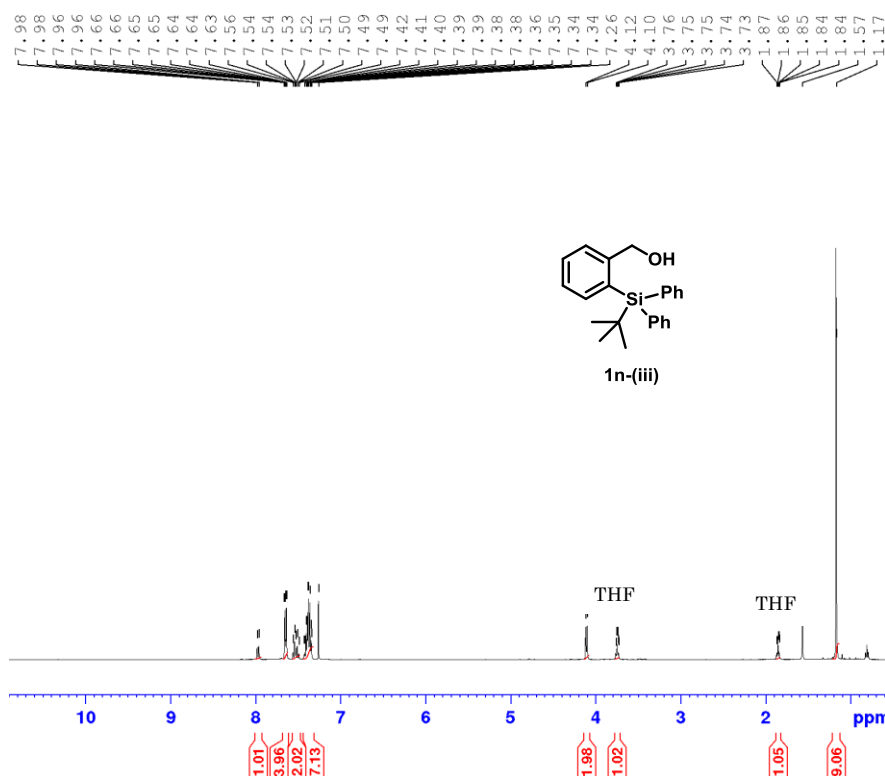
Current Data Parameters  
NAME Ravi  
EXPNO 15050902  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150509  
Time 12.19  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 512  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 203  
DW 20.800 usec  
DE 6.50 usec  
TE 297.1 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 <sup>13</sup>C  
P1 10.00 usec  
PL1 1.70 dB  
PL1W 24.62453270 W  
SFO1 100.6228298 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 <sup>1</sup>H  
PCPD2 100.00 usec  
PL2 -1.20 dB  
PL12 15.88 dB  
PL13 16.00 dB  
PL2W 13.97373390 W  
PL12W 0.27372372 W  
PL13W 0.26626399 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127774 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

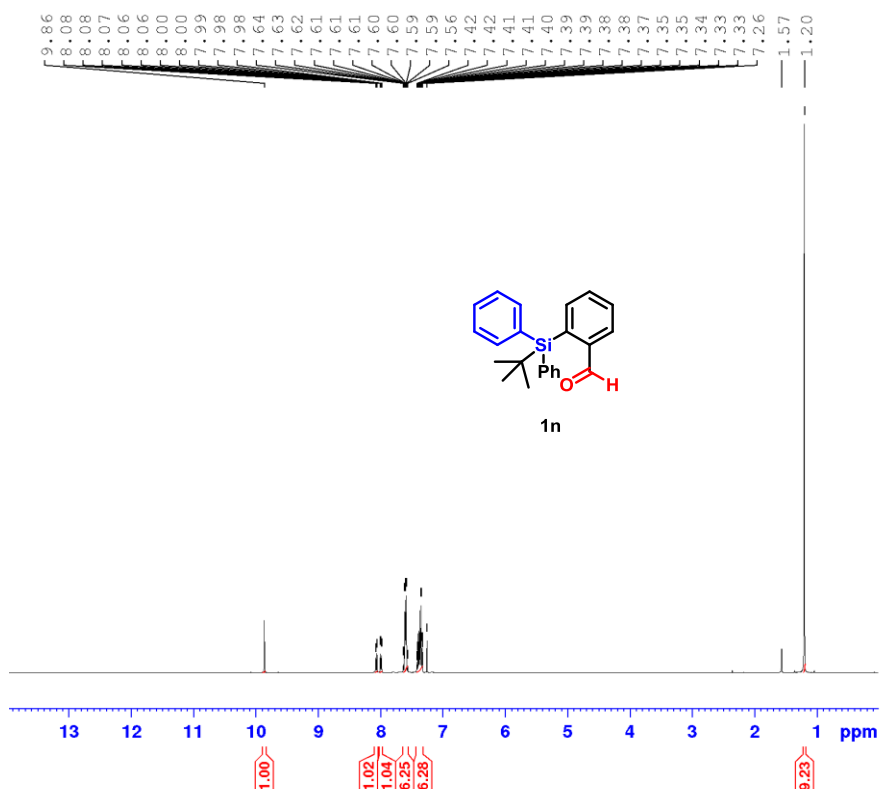


Current Data Parameters  
 NAME TBP-SBA-S.M  
 EXPNO 14111701  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20141117  
 Time 19.00  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB-  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 8223.685 Hz  
 FIDRES 0.125483 Hz  
 AQ 3.9845889 sec  
 RG 203  
 DW 60.800 usec  
 DE 6.50 usec  
 TE 296.0 K  
 D1 1.00000000 sec  
 TDO 1

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.00 usec  
 PL1 -1.20 dB  
 PL1W 13.97373390 W  
 SFO1 400.1324710 MHz

F2 - Processing parameters  
 SI 32768  
 SF 400.1300179 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



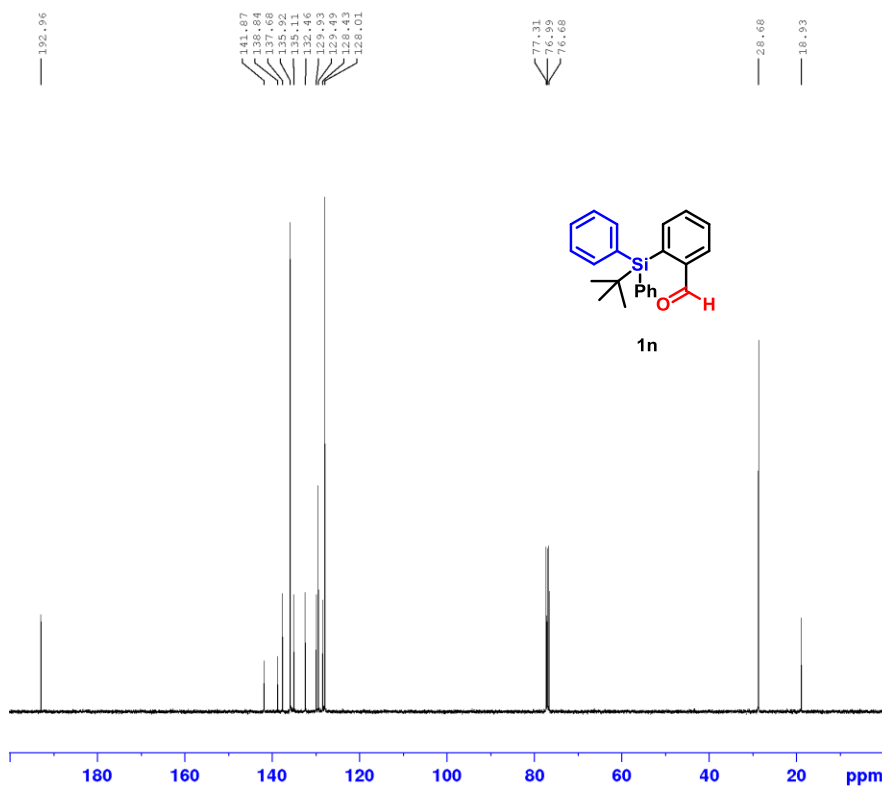
Current Data Parameters  
 NAME TBP-SBA-S.M  
 EXPNO 14112603  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20141126  
 Time 11.08  
 INSTRUM spect  
 PROBHD 5 mm PABBO BS-  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 8223.685 Hz  
 FIDRES 0.125483 Hz  
 AQ 3.9845889 sec  
 RG 181  
 DW 60.800 usec  
 DE 6.50 usec  
 TE 295.5 K  
 D1 1.00000000 sec  
 TDO 1

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.00 usec  
 PL1 -1.20 dB  
 PL1W 13.97373390 W  
 SFO1 400.1324710 MHz

F2 - Processing parameters  
 SI 32768  
 SF 400.1300191 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00





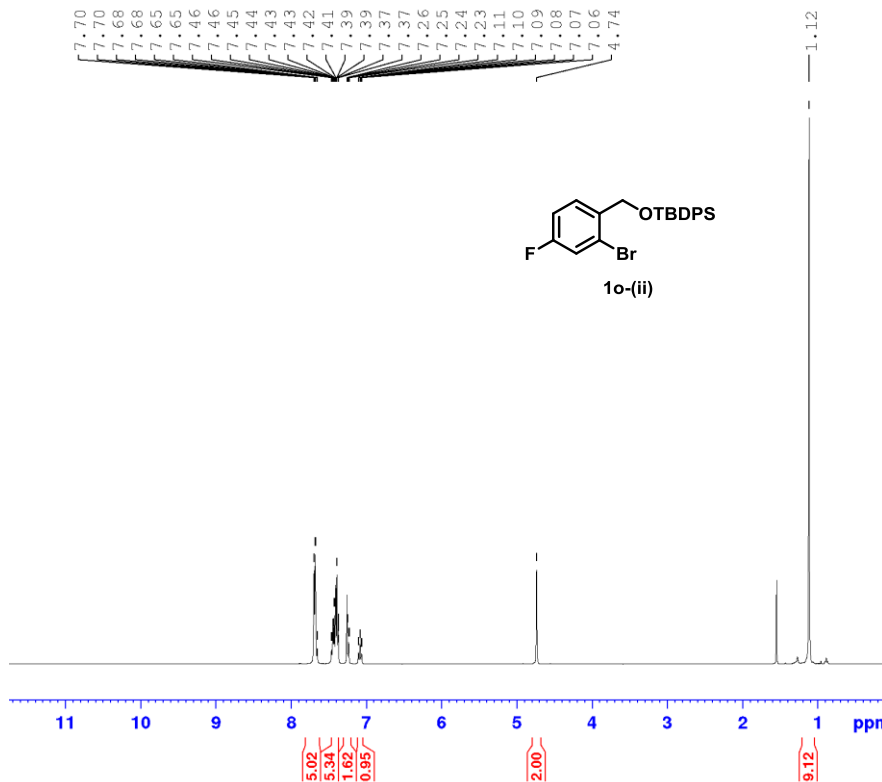
Current Data Parameters  
NAME TBDP-SBA-S.M  
EXPNO 14112604  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20141126  
Time 11.39  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 288  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 203  
DW 20.800 usec  
DE 6.50 usec  
TE 296.8 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 10.00 usec  
PL1 1.70 dB  
PL1W 24.62453270 W  
SFO1 100.6228298 MHz

===== CHANNEL f2 =====  
CPDPRG2 waitz16  
NUC2 1H  
PCPD2 100.00 usec  
PL2 -1.20 dB  
PL12 15.88 dB  
PL13 16.00 dB  
PL2W 13.97373390 W  
PL12W 0.27372372 W  
PL13W 0.26626399 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127784 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

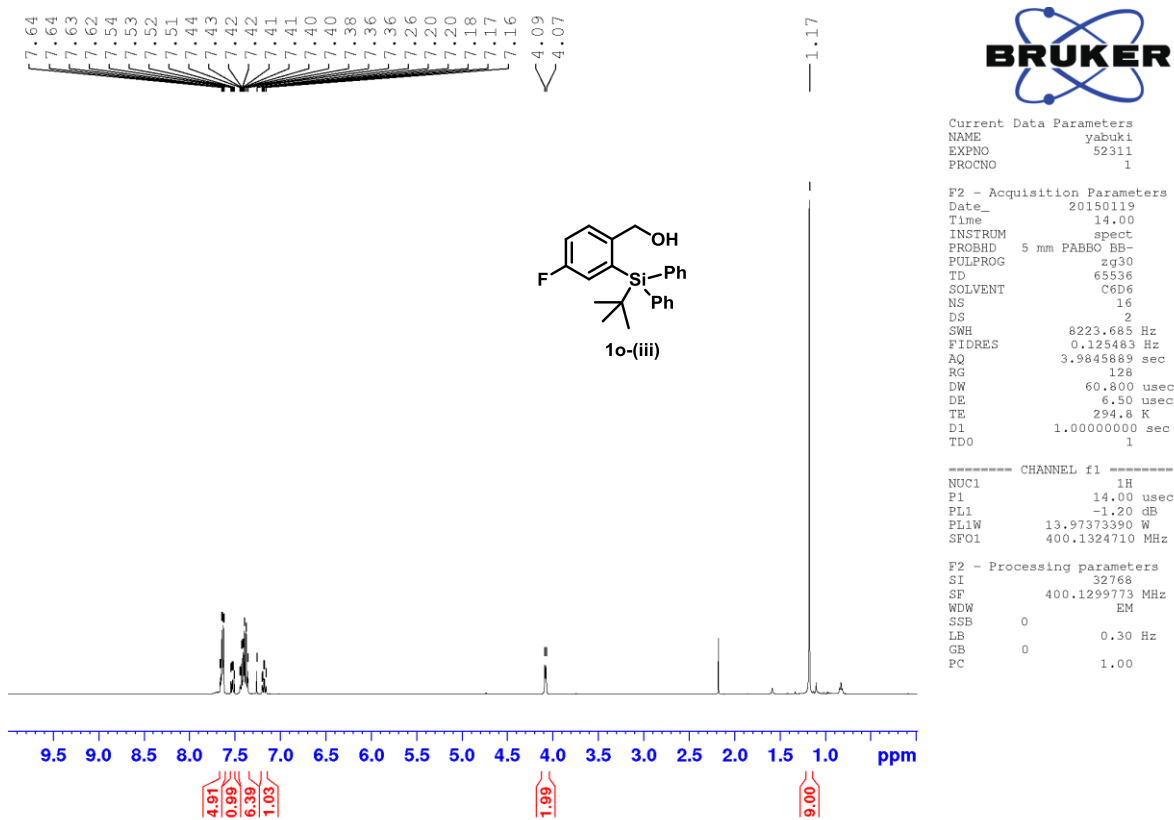
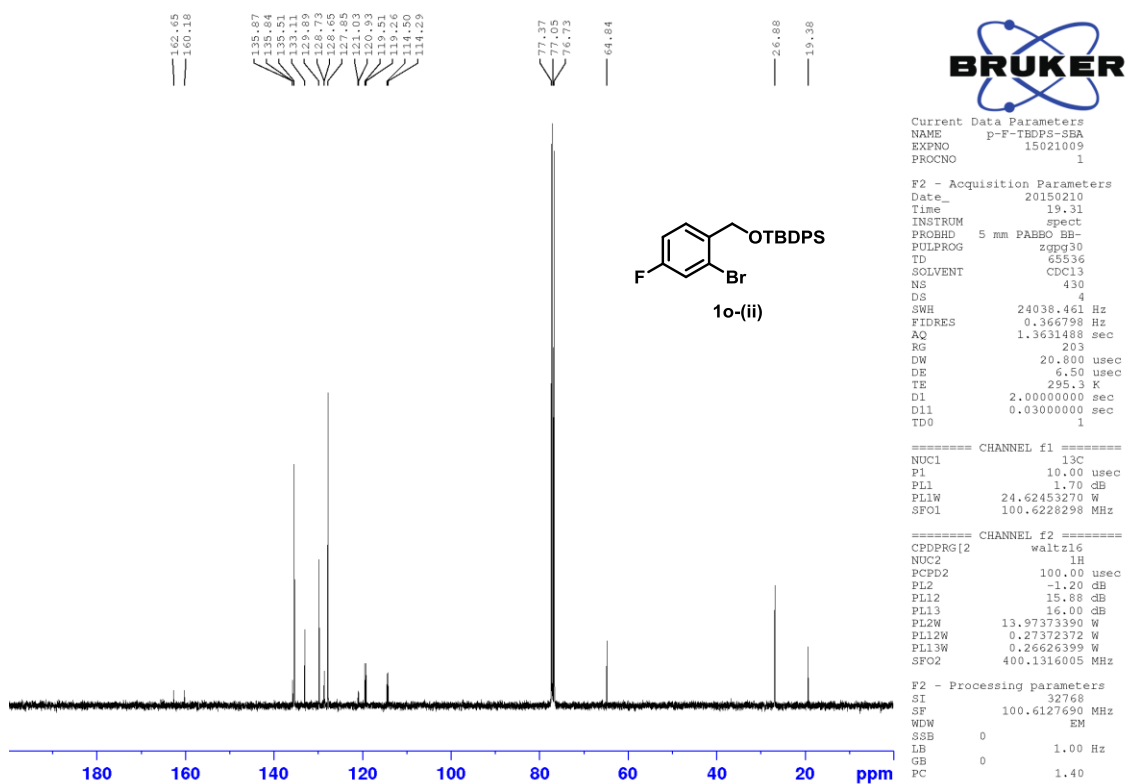


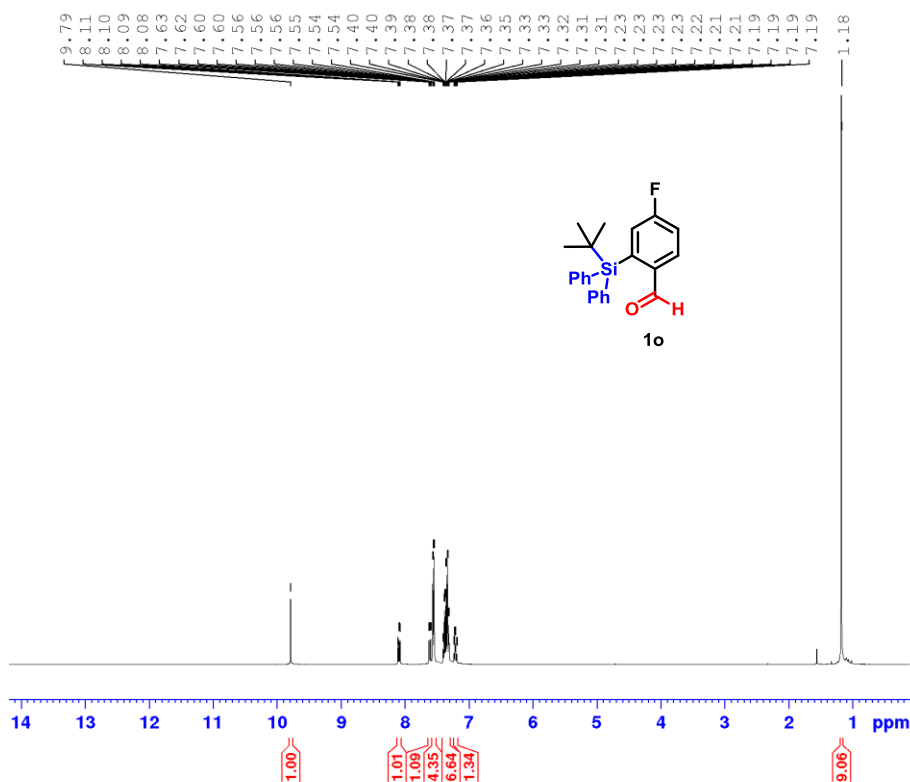
Current Data Parameters  
NAME p-F-TBDPS-SBA  
EXPNO 15021006  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150210  
Time 16.20  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 203  
DW 60.800 usec  
DE 6.50 usec  
TE 295.7 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300169 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



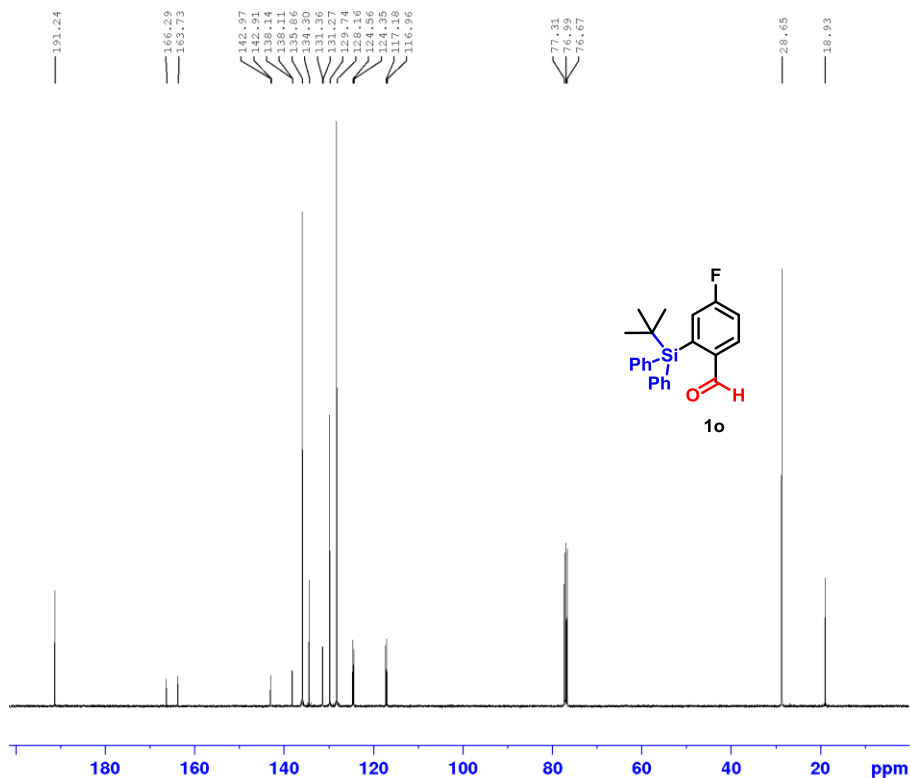


Current Data Parameters  
NAME p-F-TBDPS-SBA  
EXPNO 15020505  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150205  
Time 18.27  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845689 sec  
RG 57  
DW 60.800 usec  
DE 6.50 usec  
TE 295.1 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300347 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



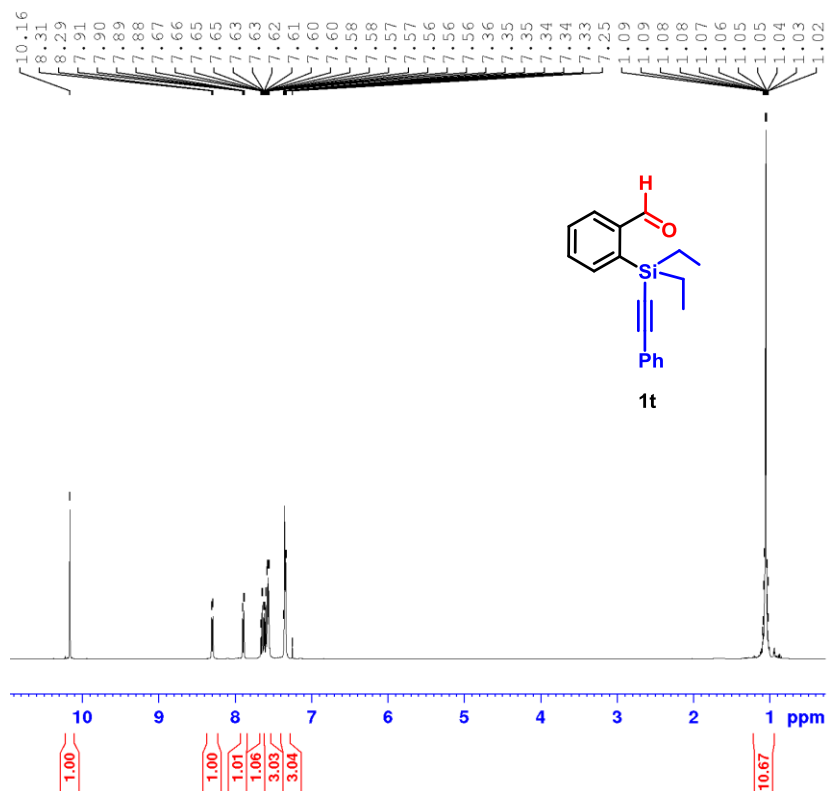
Current Data Parameters  
NAME p-F-TBDPS-SBA  
EXPNO 15020506  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150205  
Time 19.04  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 512  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 203  
DW 20.800 usec  
DE 6.50 usec  
TE 295.9 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 10.00 usec  
PL1 1.70 dB  
PL1W 24.62453270 W  
SFO1 100.6228298 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 100.00 usec  
PL2 -1.20 dB  
PL12 15.88 dB  
PL13 16.00 dB  
PL2W 13.97373390 W  
PL12W 0.27372372 W  
PL13W 0.26626399 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127791 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

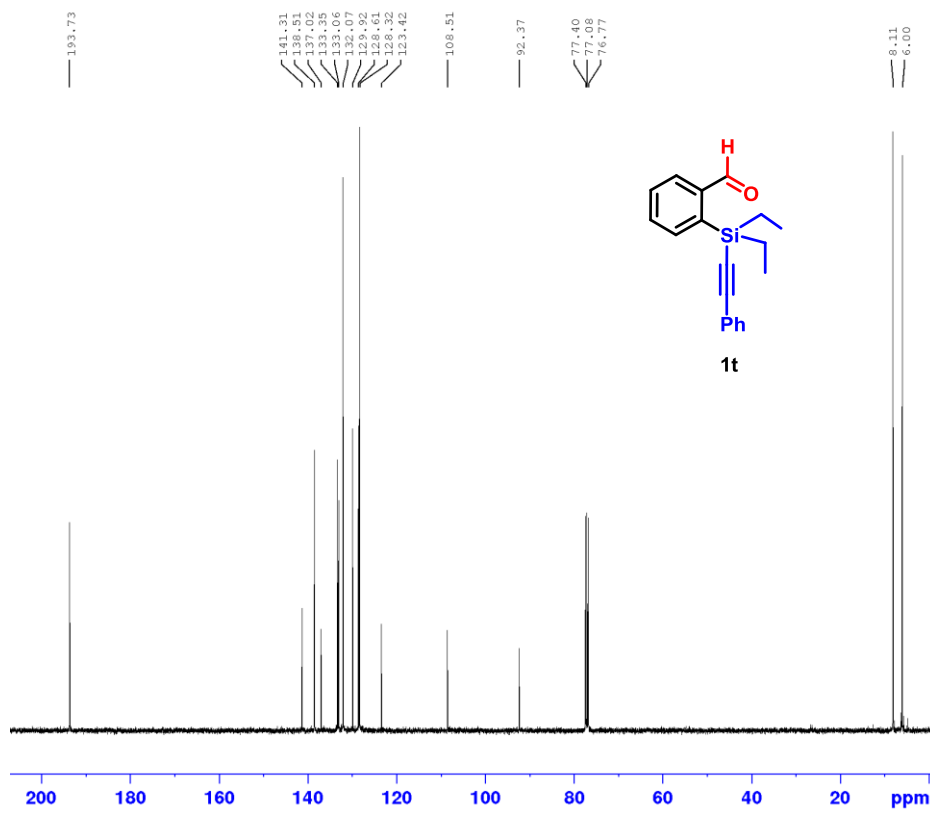


Current Data Parameters  
NAME BSA-CCPh  
EXPNO 999136  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140617  
Time 23.39  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 16  
DS 2  
SWH 8223.665 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 50.8  
DW 60.800 usec  
DE 6.50 usec  
TE 298.6 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300204 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



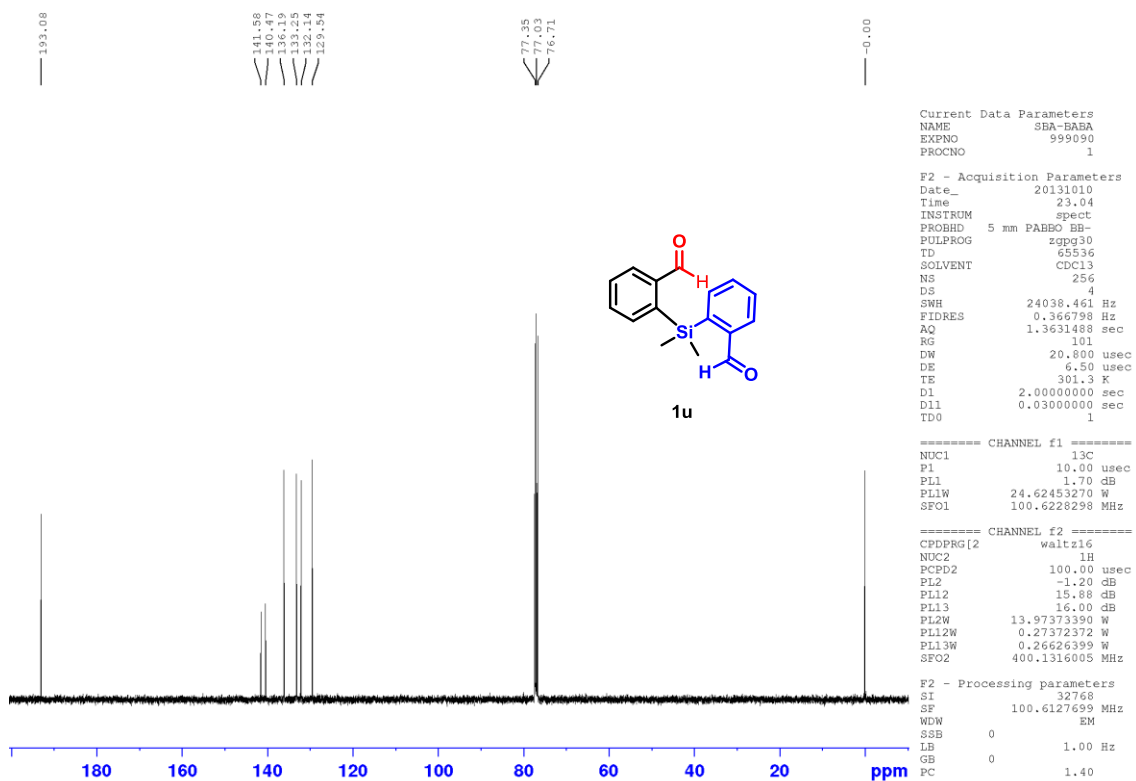
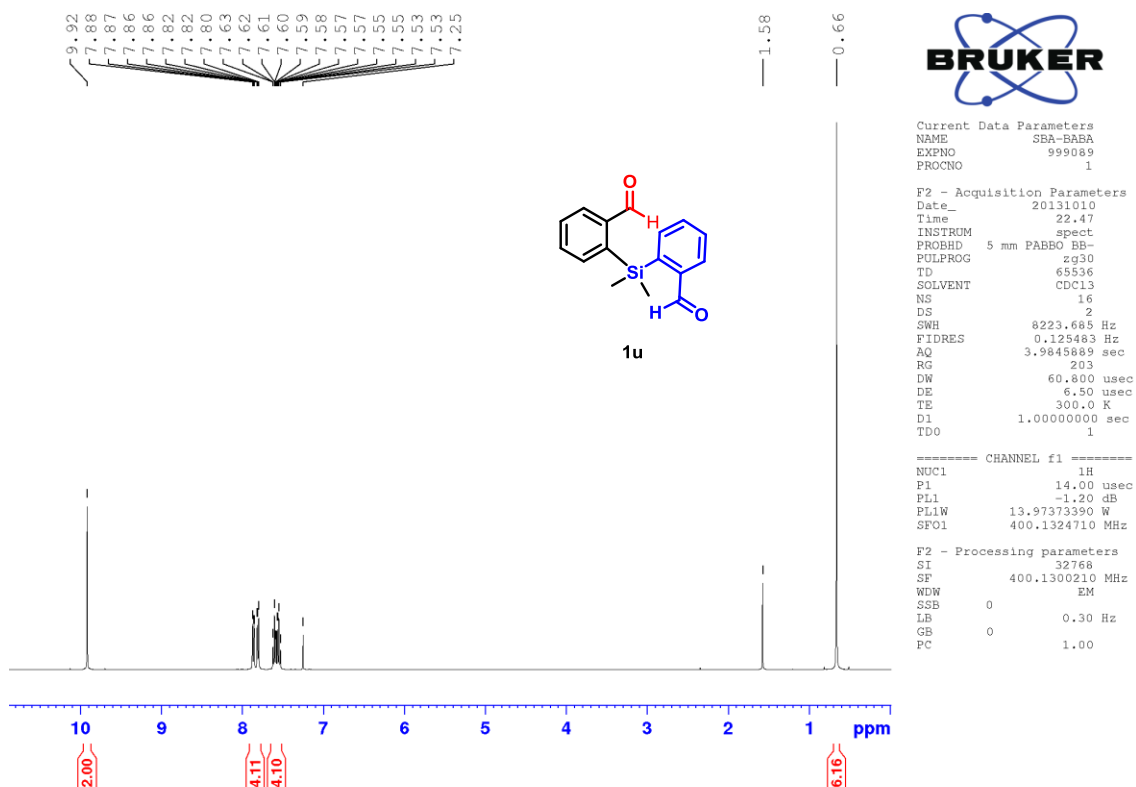
Current Data Parameters  
NAME yabukijournal  
EXPNO 999137  
PROCNO 1

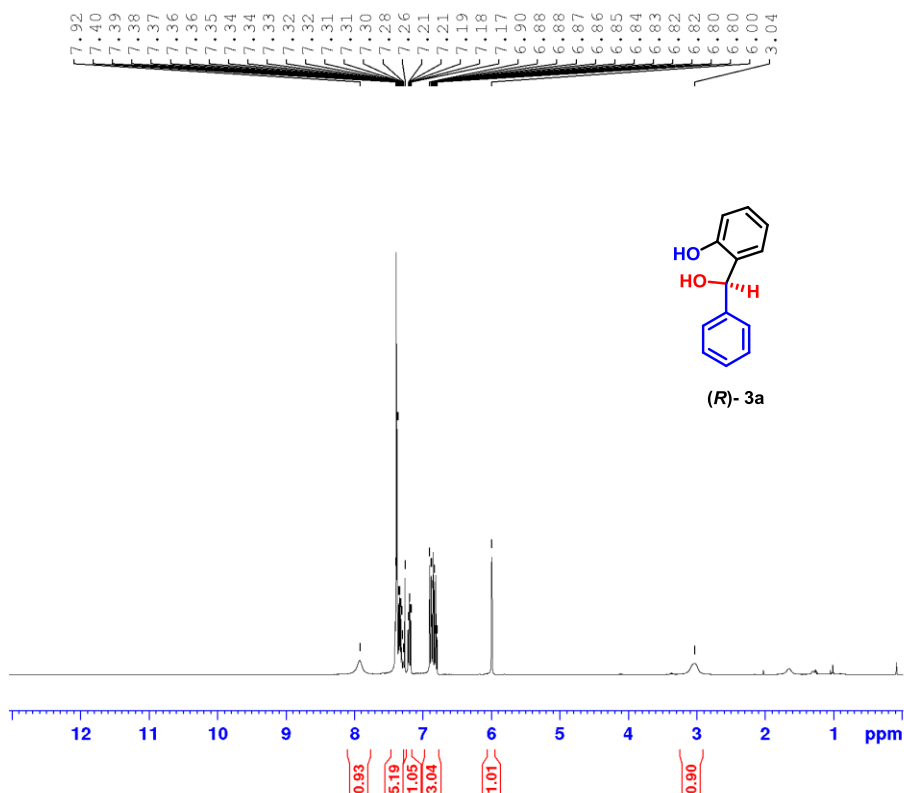
F2 - Acquisition Parameters  
Date\_ 20140618  
Time 0.05  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 238  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 114  
DW 20.800 usec  
DE 6.50 usec  
TE 299.6 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 10.00 usec  
PL1 1.70 dB  
PL1W 24.62453270 W  
SFO1 100.6228298 MHz

===== CHANNEL f2 =====  
CPDPRG[2] waltz16  
NUC2 1H  
PCPD2 100.00 usec  
PL2 -1.20 dB  
PL12 15.88 dB  
PL13 16.00 dB  
PL2W 13.97373390 W  
PL12W 0.27372372 W  
PL13W 0.26626399 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127690 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40



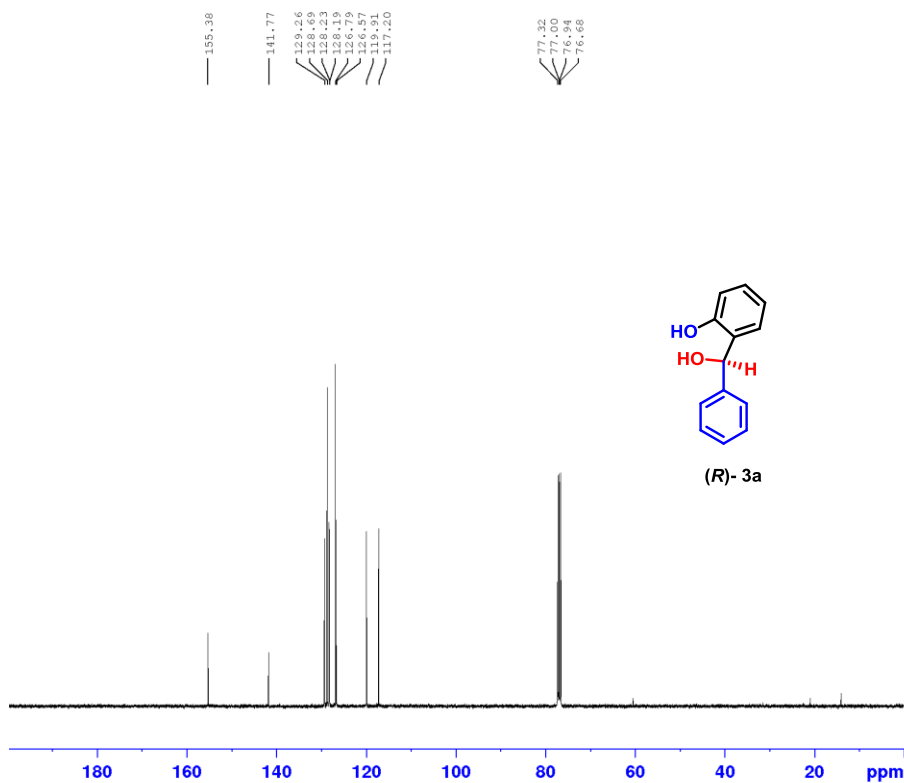


Current Data Parameters  
NAME R-423-model-TFO  
EXPNO 14120408  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20141204  
Time 20.50  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 181  
DW 60.800 usec  
DE 6.50 usec  
TE 295.9 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300176 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



Current Data Parameters  
NAME R-423-model-TFO  
EXPNO 13120203  
PROCNO 1

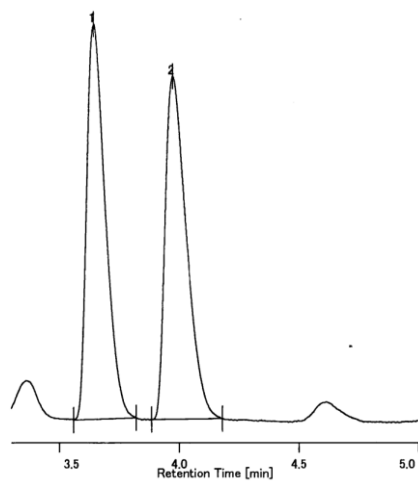
F2 - Acquisition Parameters  
Date\_ 20131202  
Time 13.21  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 512  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 90.5  
DW 20.800 usec  
DE 6.50 usec  
TE 295.4 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 10.00 usec  
PL1 1.70 dB  
PL1W 24.62453270 W  
SFO1 100.6228298 MHz

===== CHANNEL f2 =====  
CPDPRG[2] waltz16  
NUC2 1H  
PCPD2 100.00 usec  
PL2 -1.20 dB  
PL12 15.88 dB  
PL13 16.00 dB  
PL2W 13.97373390 W  
PL12W 0.27372372 W  
PL13W 0.26626399 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127772 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

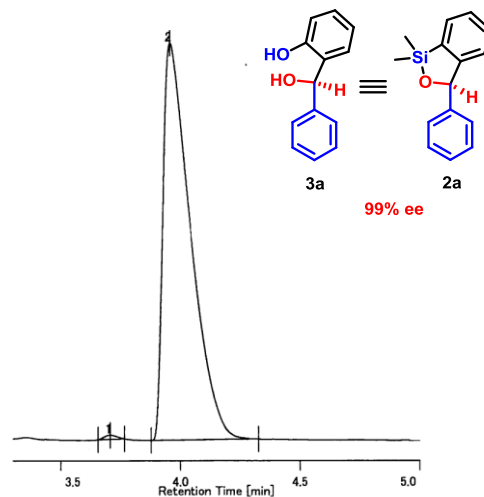
**Chiral Separation:** SFC; Chiralpak ID; Flow (CO<sub>2</sub>) = 2.0 mL/min; Flow (isopropanol) = 0.3 mL/min;  
T = 25 °C; λ = 250 nm; Back pressure = 15 Mpa



Chromatogram R-147

Name

#	CH	tR	Area	Height	Area%
1	9	3.6433	610382	114294	49.964
2	9	3.9733	611254	99098	50.036



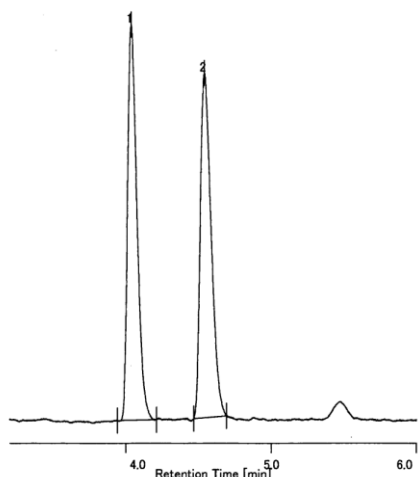
Chromatogram R-162

Name

#	CH	tR	Area	Height	Area%
1	9	3.7067	29397	8328	0.470
2	9	3.9583	6221204	777702	99.530

**Chiral Separation:** SFC; Chiralpak ID; Flow (CO<sub>2</sub>) = 2.0 mL/min; Flow (isopropanol) = 0.3 mL/min;  
T = 25 °C; λ = 250 nm; Back pressure = 15 Mpa

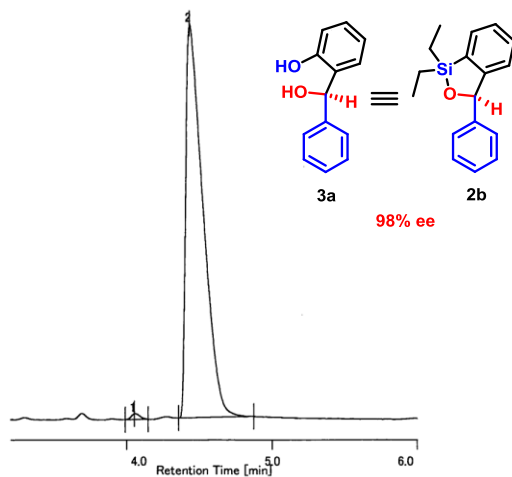
クロマトグラム+ピーク情報



Chromatogram R-147\_20140913.001

Name

#	CH	tR	Area	Height	Area%
1	9	4.0417	572491	127741	49.801
2	9	4.5450	577068	111220	50.199

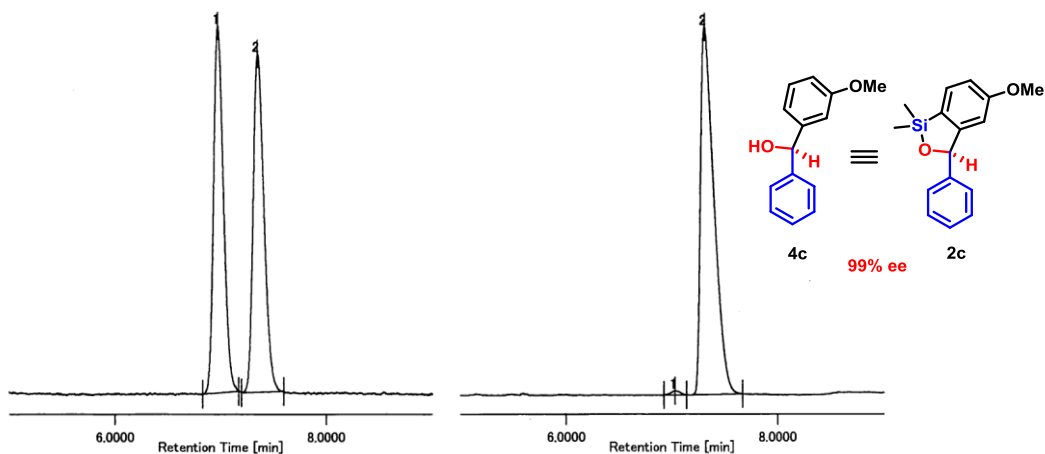


Chromatogram R-366\_20140913.001

Name

#	CH	tR	Area	Height	Area%
1	9	4.0533	41505	10384	0.678
2	9	4.4350	6076228	730603	99.322

**Chiral Separation:** SFC; Chiralpak IA; Flow (CO<sub>2</sub>) = 2.0 mL/min; Flow (isopropanol) = 0.3 mL/min;  
T = 25 °C; λ = 250 nm; Back pressure = 15 Mpa



Chromatogram m-OMe-rac

Name

#	CH	tR	Area	Height	Area%
1	9	6.9783	544771	83822	50.035
2	9	7.3533	544008	77287	49.965

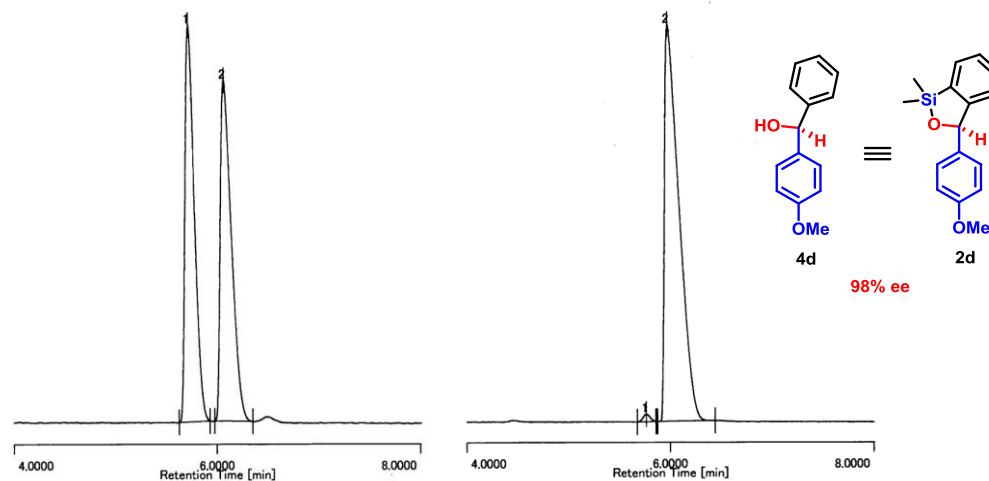
Chromatogram R-323-m

Name

#	CH	tR	Area	Height	Area%
1	9	7.0300	19436	3328	0.758
2	9	7.3133	2544898	291999	99.242

**Chiral Separation:** SFC; Chiralpak ID; Flow (CO<sub>2</sub>) = 2.0 mL/min; Flow (isopropanol) = 0.3 mL/min;  
T = 25 °C; λ = 250 nm; Back pressure = 15 Mpa

クロマトグラム+ピーク情報



Chromatogram R-440-chiralgpc\_150216\_001

Name

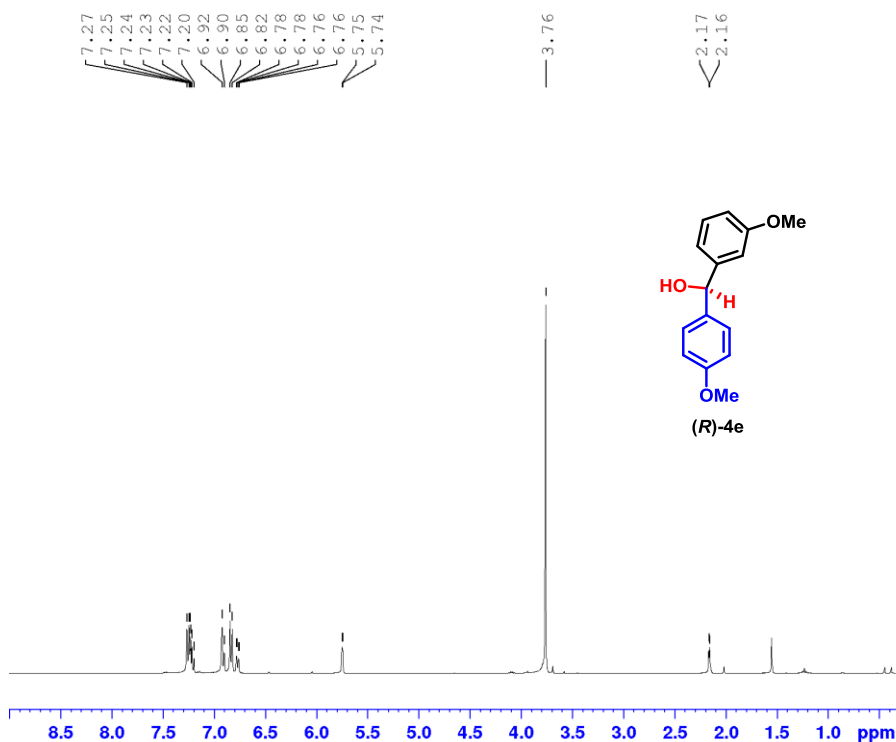
#	CH	tR	Area	Height	Area%
1	9	5.7150	2449758	380147	49.991
2	9	6.0667	2450609	326433	50.009

Chromatogram R-441-chiralgpc\_150216\_003

Name

#	CH	tR	Area	Height	Area%
1	9	5.7633	66090	13634	0.959
2	9	5.9767	6826178	699689	99.041



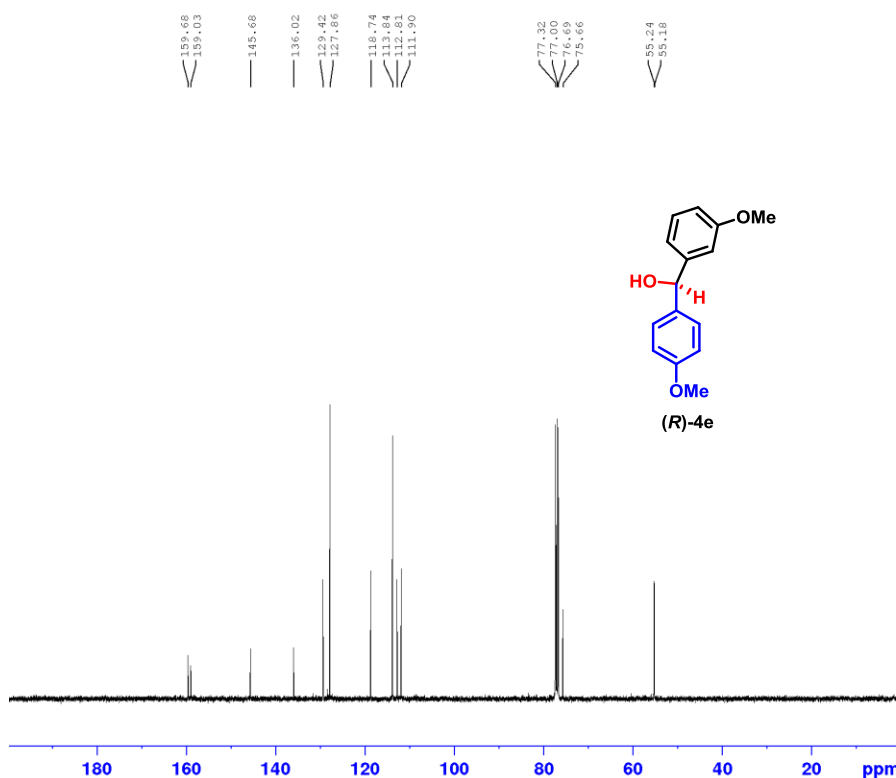


Current Data Parameters  
 NAME 2XOMe-TBAF  
 EXPNO 14112102  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20141121  
 Time 19.16  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB-  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 8223.665 Hz  
 FIDRES 0.125483 Hz  
 AQ 3.9845889 sec  
 RG 203  
 DW 60.800 usec  
 DE 6.50 usec  
 TE 295.9 K  
 D1 1.00000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.00 usec  
 PL1 -1.20 dB  
 PL1W 13.97373390 W  
 SFO1 400.1324710 MHz

F2 - Processing parameters  
 SI 32768  
 SF 400.1300292 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters  
 NAME 2XOMe-TBAF  
 EXPNO 14112201  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20141122  
 Time 10.03  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB-  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 512  
 DS 4  
 SWH 24038.461 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 161  
 DW 20.800 usec  
 DE 6.50 usec  
 TE 297.0 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

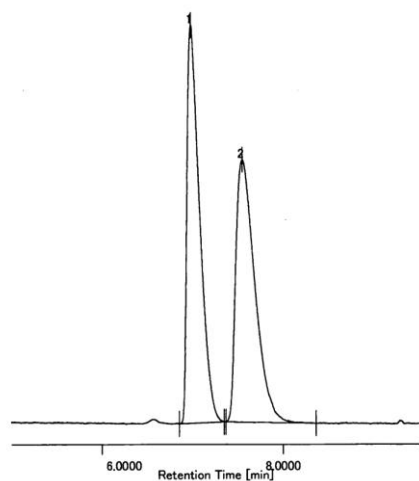
===== CHANNEL f1 =====  
 NUC1 13C  
 P1 10.00 usec  
 PL1 1.70 dB  
 PL1W 24.62453270 W  
 SFO1 100.6228298 MHz

===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 100.00 usec  
 PL2 -1.20 dB  
 PL12 15.88 dB  
 PL13 16.00 dB  
 PL2W 13.97373390 W  
 PL12W 0.27372372 W  
 PL13W 0.26626399 W  
 SFO2 400.1316005 MHz

F2 - Processing parameters  
 SI 32768  
 SF 100.6127757 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

**Chiral Separation:** SFC; Chiralpak ID; Flow (CO<sub>2</sub>) = 2.0 mL/min; Flow (isopropanol) = 0.3 mL/min;  
T = 25 °C; λ = 250 nm; Back pressure = 15 Mpa

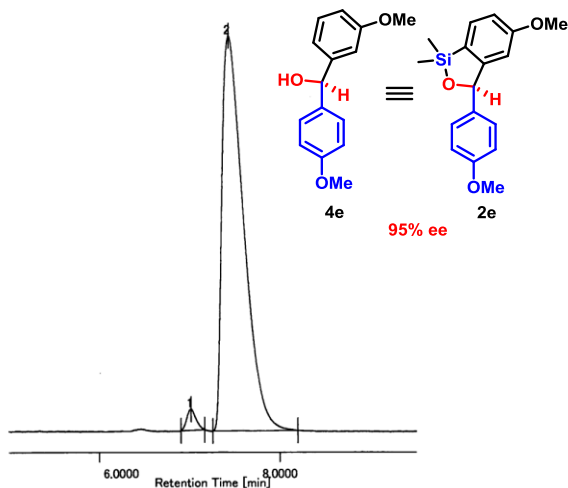
クロマトグラム+ピーク情報



Chromatogram R-411-rac\_20141205\_001

Name

#	CH	tR	Area	Height	Area%
1	9	6.9817	1848336	186846	50.722
2	9	7.5500	1795685	123130	49.278



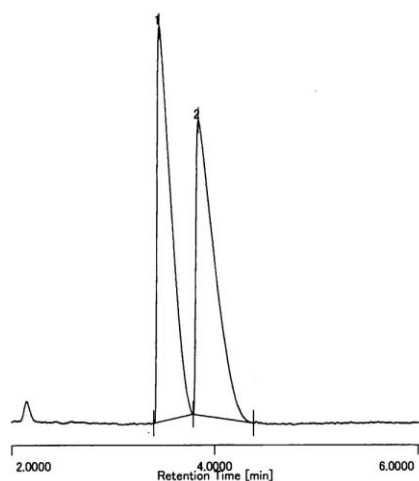
Chromatogram R-411-chiral\_20141205\_002

Name

#	CH	tR	Area	Height	Area%
1	9	7.0167	94623	13052	2.292
2	9	7.4350	4033877	243167	97.708

**Chiral Separation:** SFC; Chiralpak ID; Flow (CO<sub>2</sub>) = 4.0 mL/min; Flow (CH<sub>2</sub>Cl<sub>2</sub>) = 0.6 mL/min;  
T = 25 °C; λ = 250 nm; Back pressure = 15 Mpa

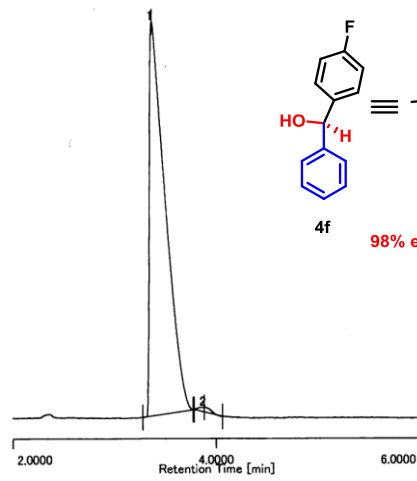
クロマトグラム+ピーク情報



Chromatogram R-442

Name

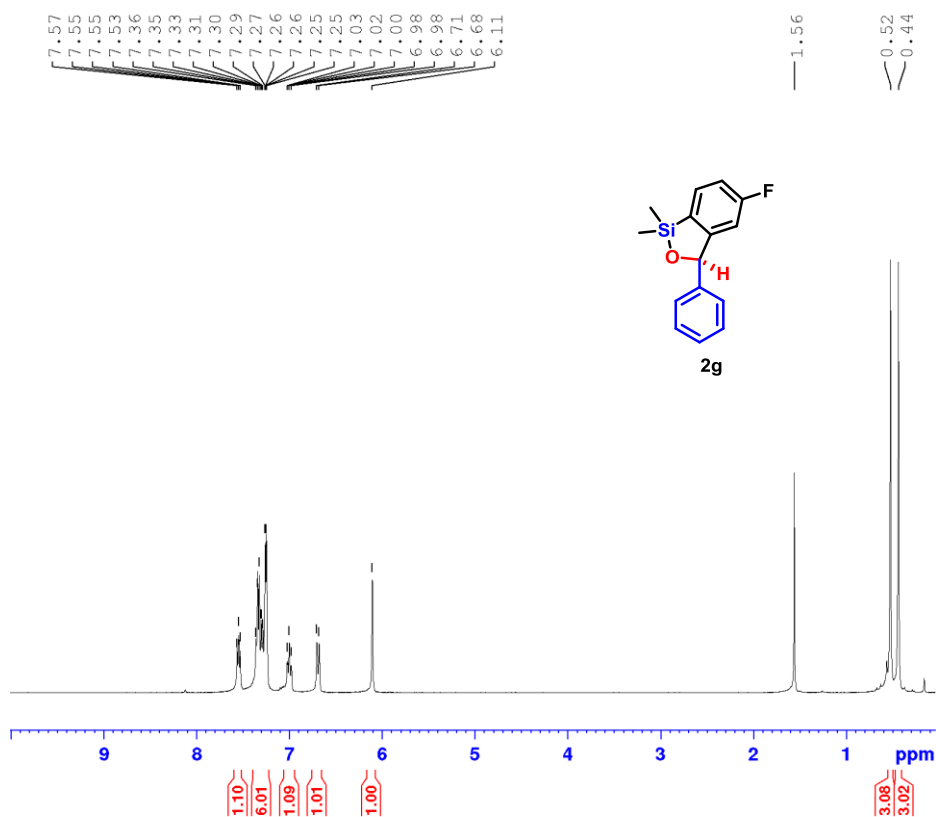
#	CH	tR	Area	Height	Area%
1	9	3.4617	1566649	166133	50.379
2	9	3.8483	1543080	123901	49.621



Chromatogram R-387

Name

#	CH	tR	Area	Height	Area%
1	9	3.3733	5257878	490293	99.132
2	9	3.8833	46057	5806	0.868

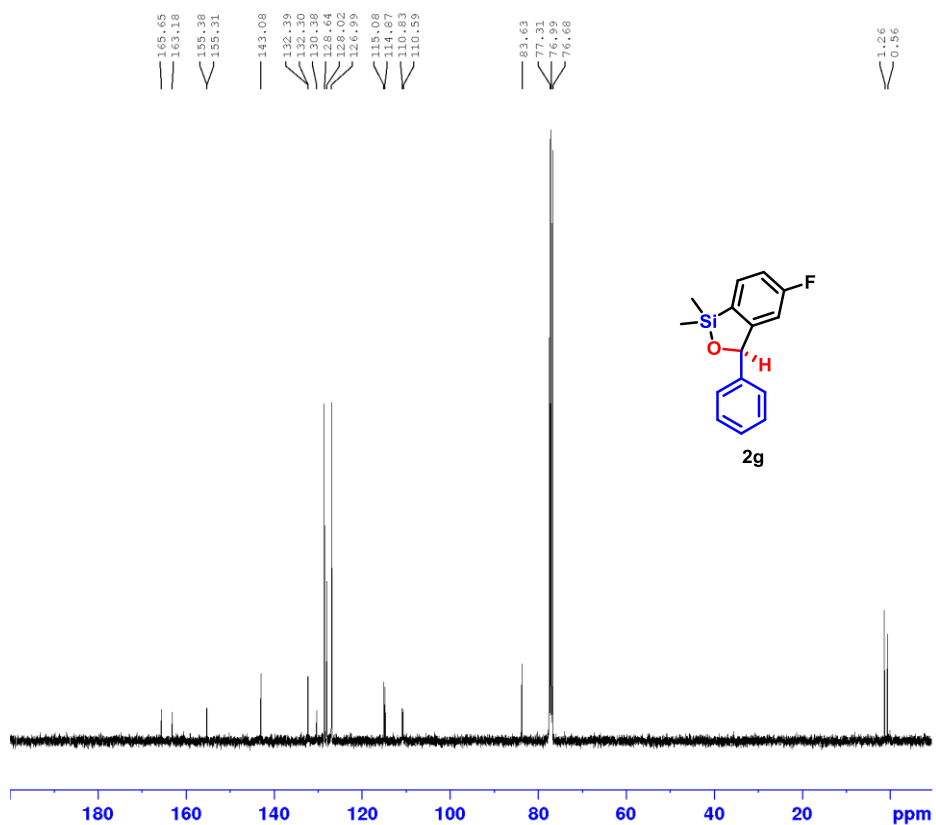


Current Data Parameters  
NAME Ravi  
EXPNO 15052302  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150523  
Time 14.22  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDC13  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 203  
DW 60.800 usec  
DE 6.50 usec  
TE 297.3 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300211 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



Current Data Parameters  
NAME Ravi  
EXPNO 15052305  
PROCNO 1

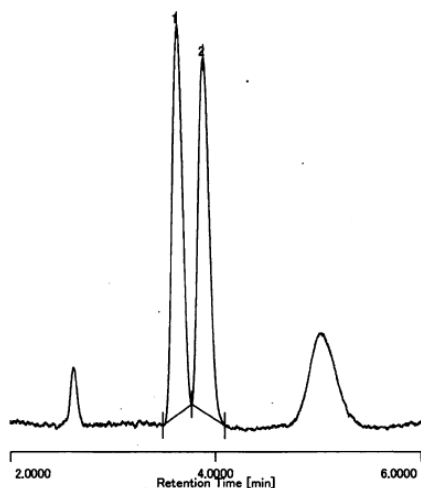
F2 - Acquisition Parameters  
Date\_ 20150523  
Time 15.07  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDC13  
NS 512  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 203  
DW 20.800 usec  
DE 6.50 usec  
TE 298.0 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 10.00 usec  
PL1 -1.70 dB  
PL1W 24.62453270 W  
SFO1 100.6228298 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 100.00 usec  
PL2 -1.20 dB  
PL12 15.88 dB  
PL13 16.00 dB  
PL2W 13.97373390 W  
PL12W 0.27372372 W  
PL13W 0.26626399 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127745 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**Chiral Separation:** SFC; Chiralpak IC; Flow (CO<sub>2</sub>) = 4.0 mL/min; Flow (isopropanol) = 0.2 mL/min;  
T = 25 °C; λ = 250 nm; Back pressure = 15 Mpa

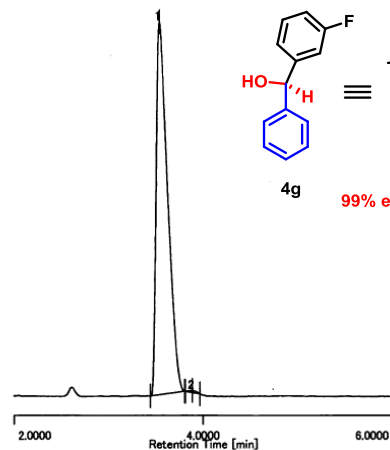


Chromatogram R-483

Name

#	CH	tR	Area	Height	Area%
1	9	3.6183	531774	77388	50.002
2	9	3.8800	531730	70289	49.998

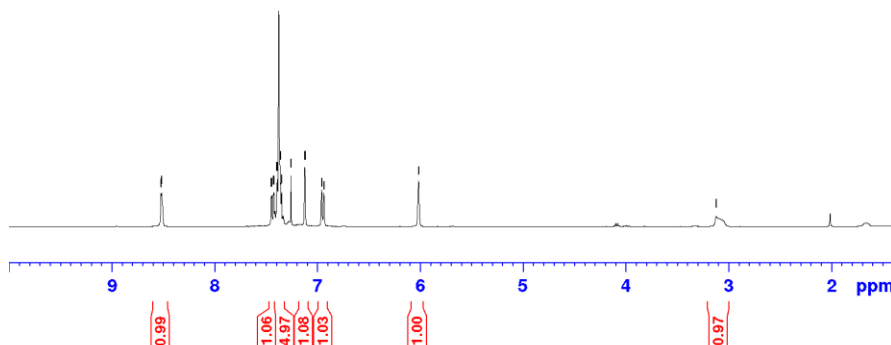
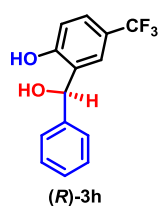
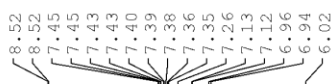
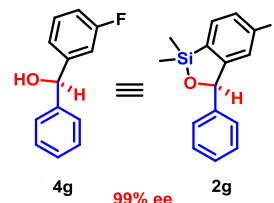
クロマトグラム+ピーク情報



Chromatogram R-506

Name

#	CH	tR	Area	Height	Area%
1	9	3.5417	5840725	708510	99.622
2	9	3.8850	22161	4295	0.378

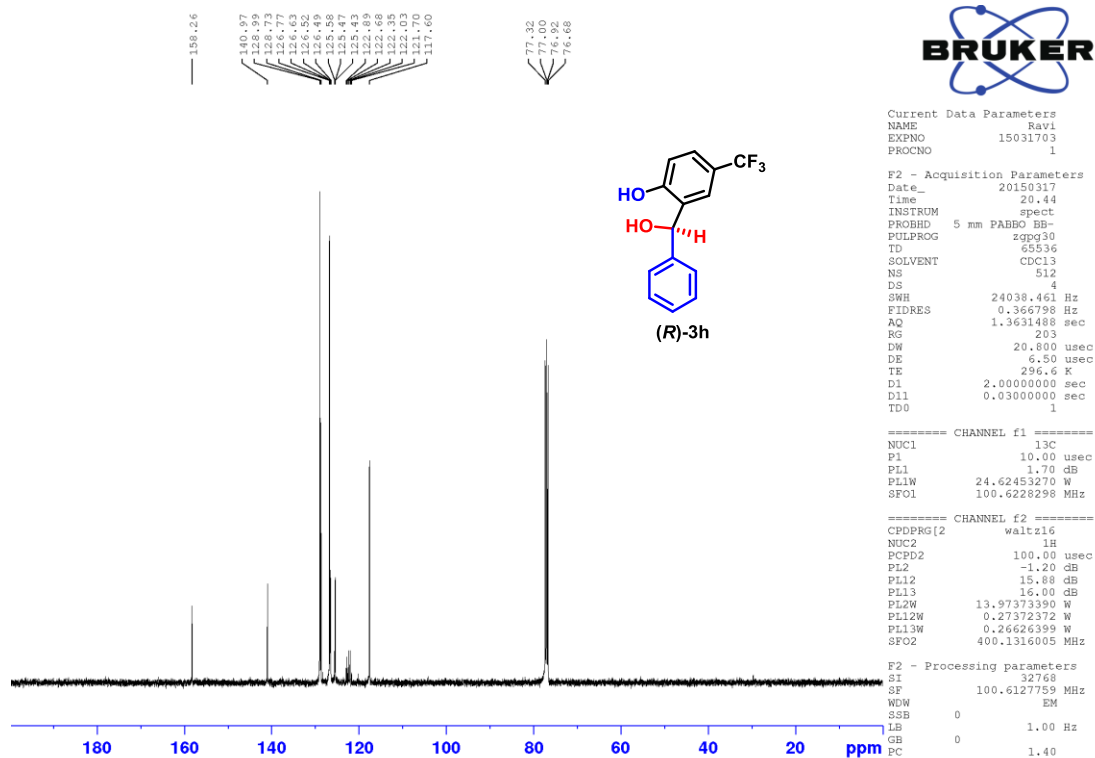


Current Data Parameters  
NAME m-CP3-TFO  
EXPNO 15021805  
PROCNO 1

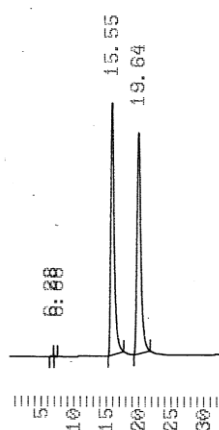
F2 - Acquisition Parameters  
Date\_ 20150218  
Time 19.02  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 203  
DW 60.800 usec  
DE 6.50 usec  
TE 294.9 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300186 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



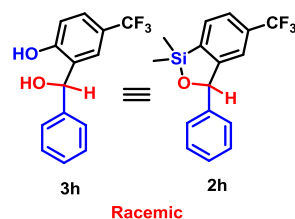
**Chiral Separation:** HPLC; Chiralpak OD-H; Isopropanol/Hexane = 1:9; Flow = 0.5 mL/min;  
T = 30 °C;  $\lambda$  = 250 nm



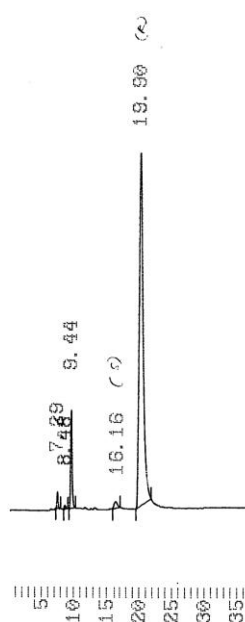
ANALYZED: 01/21/14 10:46  
SYSTEM : 1  
METHOD :  
CHANNEL : 1 <DIGITAL>  
OPERATOR: SEQ :  
FILE : 0  
CALC-METHOD: AR/HI% <AREA> COMPONENT

NO.	RT	AREA	CONC	BC
1	6.28	1341	0.091	BB
2	6.88	802	0.054	BB
3	15.55	741454	50.285	BB
4	19.64	730901	49.569	BB

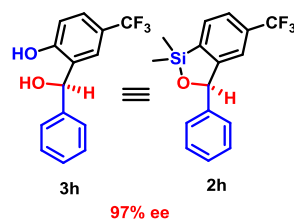
TOTAL 1474498 100.000  
PEAK REJ : 0



**Chiral Separation:** HPLC; Chiralpak OD-H; Isopropanol/Hexane = 1:9; Flow = 0.5 mL/min;  
T = 30 °C;  $\lambda$  = 250 nm



ANALYZED: 01/29/14 12:49  
SYSTEM : 1  
METHOD :  
CHANNEL : 1 <DIGITAL>



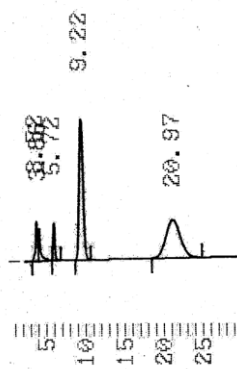
97% ee

FILE : 0  
CALC-METHOD: AR/HI% <AREA> COMPONENT

NO.	RT	AREA	CONC	BC
1	7.29	16418	1.208	BB
2	8.48	3578	0.263	BB
3	9.44	126201	9.287	BB
4	16.16	17790	1.309	BB
5	19.90	1194935	87.933	BB

TOTAL 1358922 100.000  
PEAK REJ : 0

**Chiral Separation:** HPLC; Chiralpak OB-H; Isopropanol/Hexane = 1:9; Flow = 1.0 mL/min;  
T = 30 °C;  $\lambda$  = 250 nm



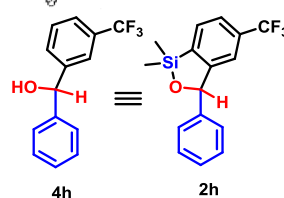
ANALYZED: 02/27/14 17:54  
SYSTEM : 1  
METHOD :  
CHANNEL : 1 <DIGITAL>

OPERATOR:  
SEQ :

FILE : 0  
CALC-METHOD: AR/HI% <AREA> COMPONENT

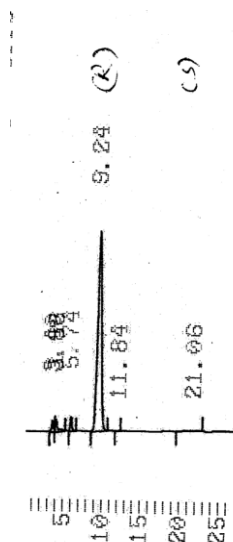
NO.	RT	AREA	CONC	BC
1	3.52	47094	6.057	BV
2	3.86	35767	4.600	VV
3	5.72	35189	4.526	VB
4	9.22	330316	42.481	BB
5	20.97	329201	42.337	BB

TOTAL 777567 100.000  
PEAK REJ : 0



Racemic

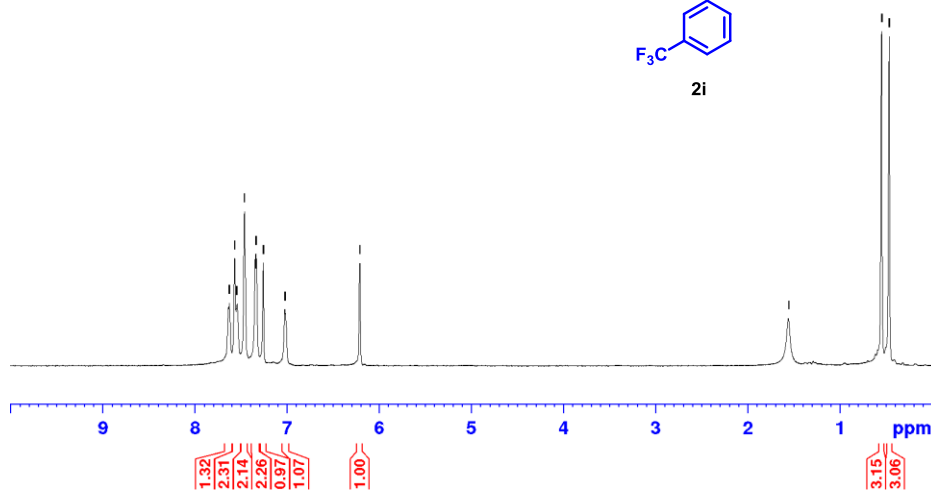
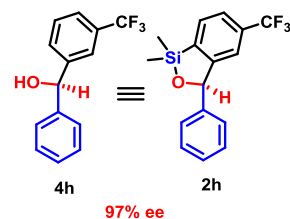
**Chiral Separation:** HPLC; Chiralpak OB-H; Isopropanol/Hexane = 1:9; Flow = 1.0 mL/min;  
T = 30 °C;  $\lambda$  = 254 nm



ANALYZED: 02/27/14 18:26  
SYSTEM : 1  
METHOD :  
CHANNEL : 1 <DIGITAL> OPERATOR: SEQ :  
FILE : 0  
CALC-METHOD: AR/HI% <AREA> COMPONENT

NO.	RT	AREA	CONC	BC
1	3.40	11128	2.162	BV
2	3.88	12114	2.354	VB
3	5.74	13056	2.537	BB
4	9.24	469607	91.240	BB
5	11.84	706	0.137	BB
6	21.06	8084	1.571	BB

TOTAL 514695 100.000  
PEAK REJ : 0

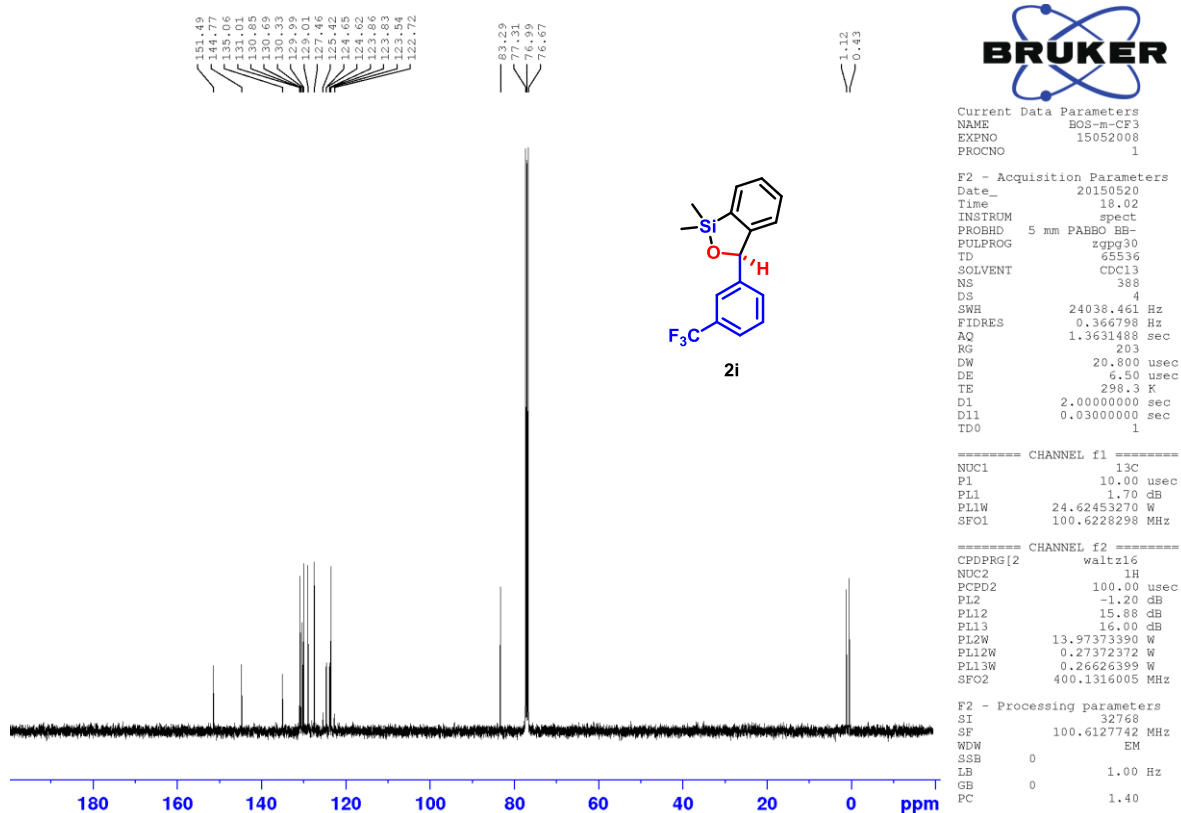


Current Data Parameters  
NAME Ravi  
EXPNO 15052007  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150520  
Time 17.23  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDC13  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 203  
DW 60.800 usec  
DE 6.50 usec  
TE 297.2 K  
D1 1.00000000 sec  
TD0 1

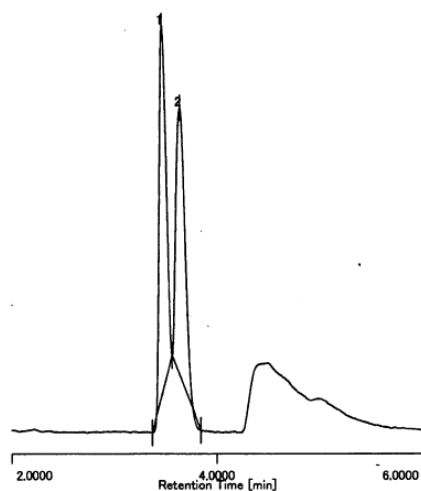
===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SF01 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300186 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



**Chiral Separation:** SFC; Chiralpak IB; Flow (CO<sub>2</sub>) = 5.0 mL/min; Flow (isopropanol) = 0.2 mL/min;  
T = 25 °C; λ = 230 nm; Back pressure = 15 Mpa

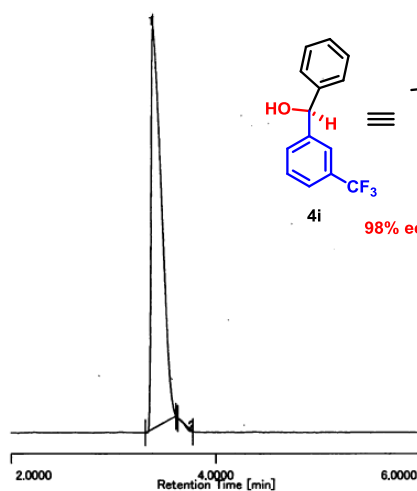
クロマトグラム+ピーク情報



Chromatogram R-495

Name

#	CH	tR	Area	Height	Area%
1	10	3.4650	1705957	380557	50.711
2	10	3.6383	1658110	277602	49.289

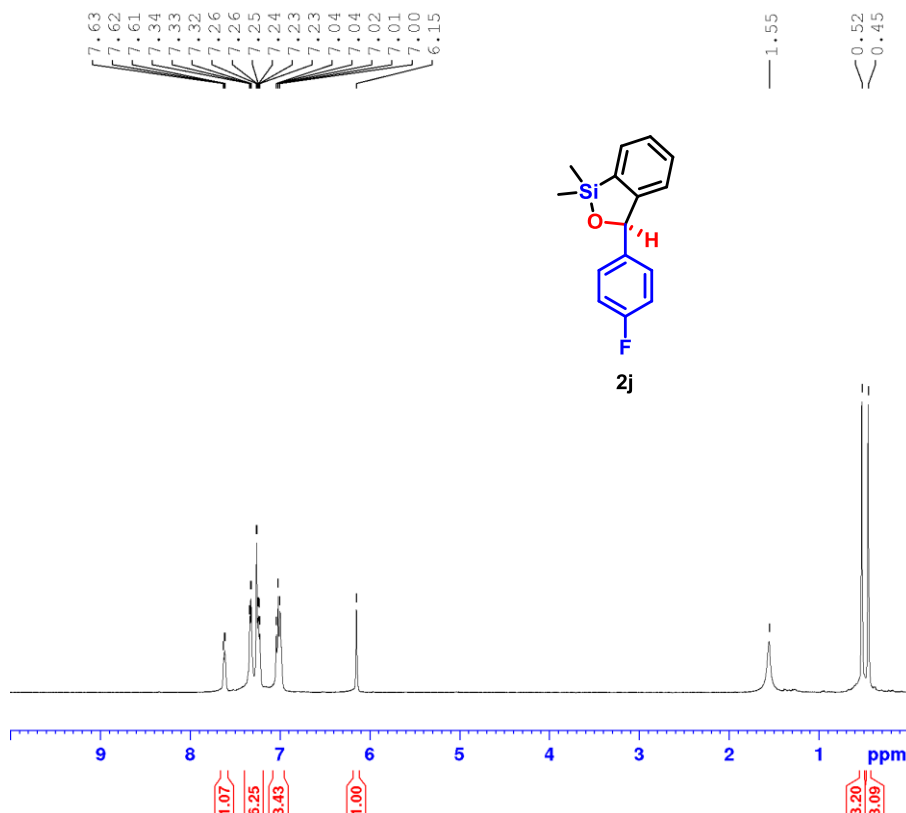


Chromatogram R-497

Name

#	CH	tR	Area	Height	Area%
1	10	3.3900	6057214	866189	99.737
2	10	3.7717	15943	1056	0.263



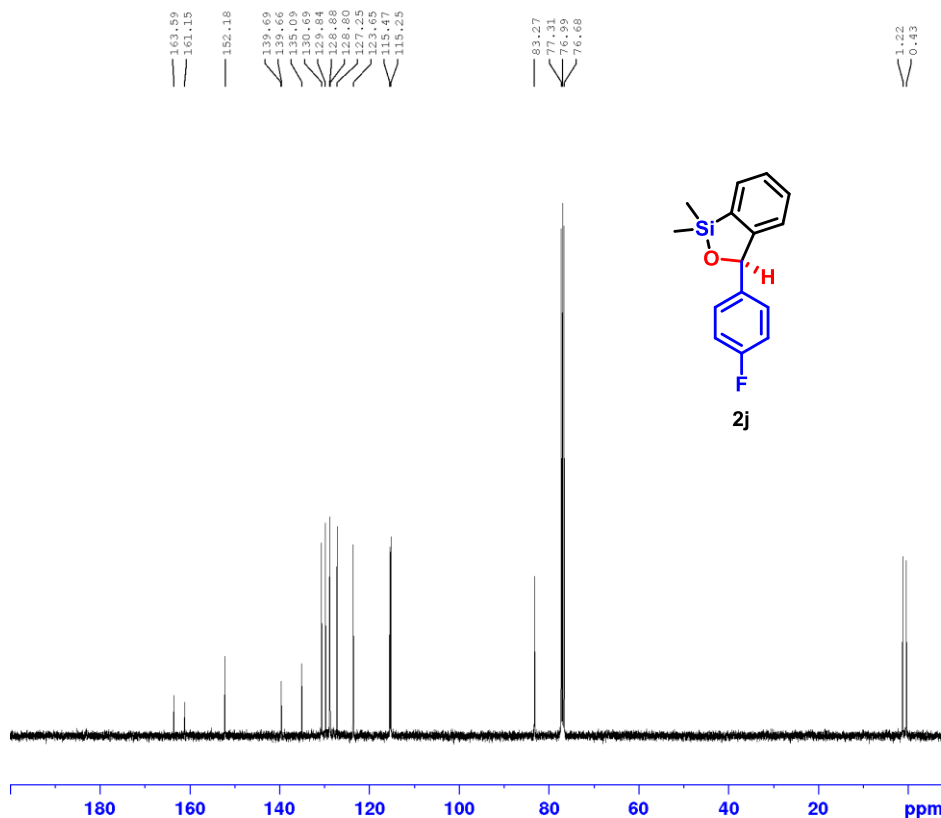


Current Data Parameters  
NAME Ravi  
EXPNO 15051304  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150513  
Time 18.22  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDC13  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 203  
DW 60.800 usec  
DE 6.50 usec  
TE 296.6 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300165 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



Current Data Parameters  
NAME BOS-p-F  
EXPNO 15051305  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150513  
Time 20.05  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDC13  
NS 512  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 203  
DW 20.800 usec  
DE 6.50 usec  
TE 297.2 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1

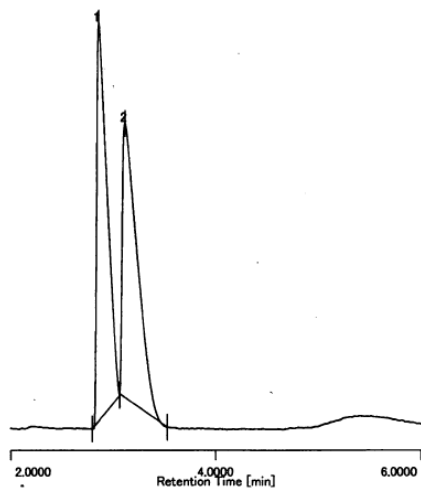
===== CHANNEL f1 =====  
NUC1 13C  
P1 10.00 usec  
PL1 1.70 dB  
PL1W 24.62453270 W  
SFO1 100.6228298 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 100.00 usec  
PL2 -1.20 dB  
PL12 15.88 dB  
PL13 16.00 dB  
PL2W 13.97373390 W  
PL12W 0.127372372 W  
PL13W 0.26626399 W  
SFO2 400.1316005 MHz

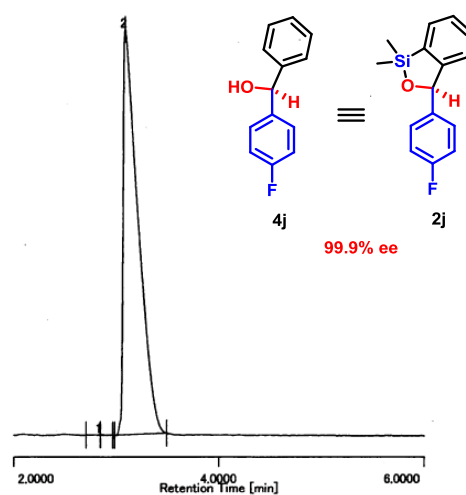
F2 - Processing parameters  
SI 32768  
SF 100.6127756 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**Chiral Separation:** SFC; Chiralpak ID; Flow (CO<sub>2</sub>) = 3.5 mL/min; Flow (CH<sub>2</sub>Cl<sub>2</sub>) = 0.6 mL/min;  
T = 25 °C; λ = 250 nm; Back pressure = 15 Mpa

クロマトグラム+ピーク情報



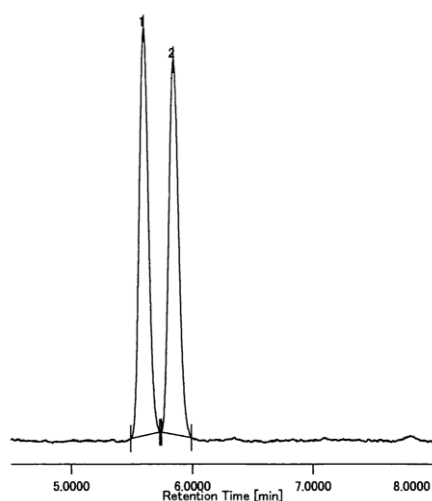
#	CH	tR	Area	Height	Area%
1	9	2.8650	1525199	219484	50.163
2	9	3.1200	1515311	151568	49.837



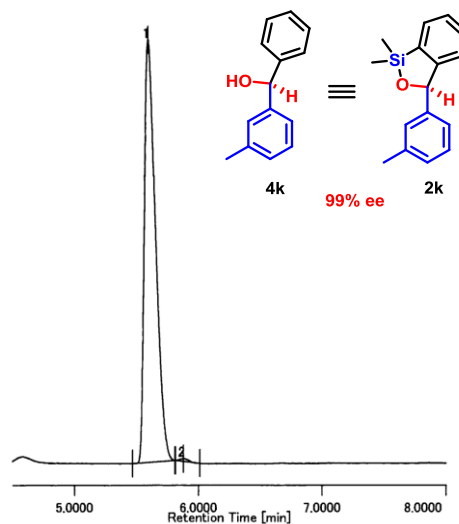
#	CH	tR	Area	Height	Area%
1	9	2.8483	1819	392	0.039
2	9	3.0967	4698388	472516	99.961

**Chiral Separation:** SFC; Chiralpak IA; Flow (CO<sub>2</sub>) = 2.0 mL/min; Flow (Isopropanol) = 0.3 mL/min;  
T = 25 °C; λ = 250 nm; Back pressure = 15 Mpa

クロマトグラム+ピーク情報

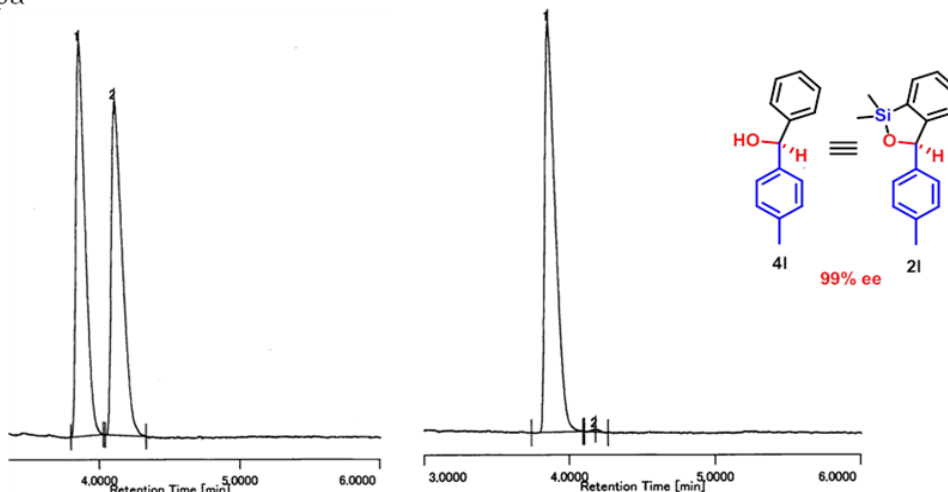


#	CH	tR	Area	Height	Area%
1	9	5.5967	324642	61381	50.471
2	9	5.8400	318580	56477	49.529



#	CH	tR	Area	Height	Area%
1	9	5.5967	2755352	440426	99.515
2	9	5.8783	13428	2901	0.485

**Chiral Separation:** SFC; Chiralpak IB; Flow (CO<sub>2</sub>) = 3.0 mL/min; Flow (Isopropanol) = 0.3 mL/min; T = 25 °C; λ = 250 nm; Back pressure = 15 Mpa

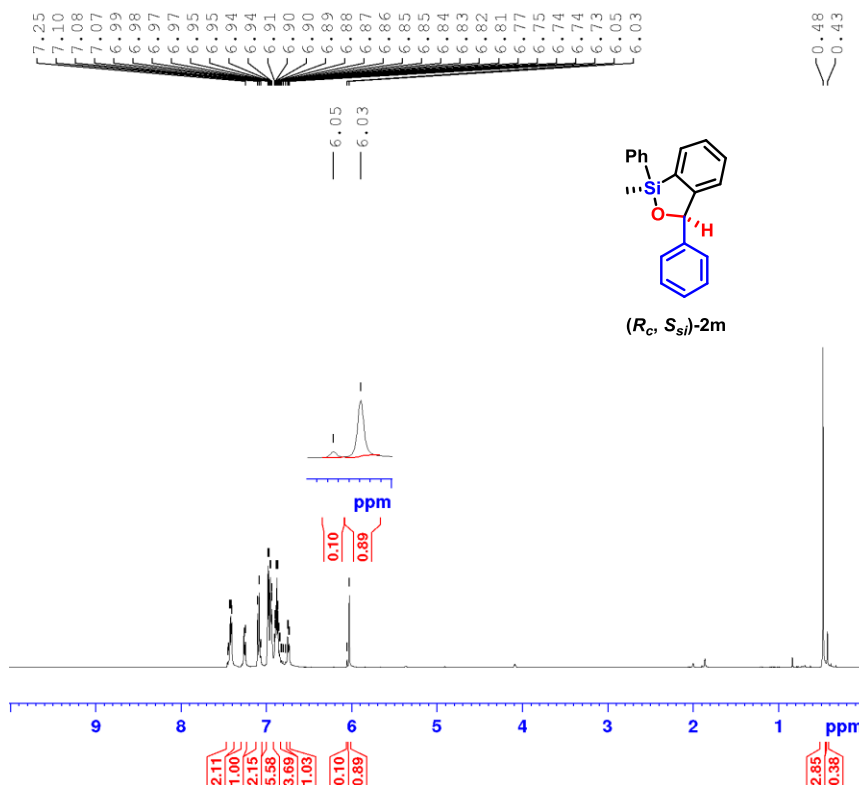


Chromatogram R-347-4\_20141001\_001

Name					
#	CH	tR	Area	Height	Area%
1	9	3.8600	801408	176611	49.975
2	9	4.1117	802202	149874	50.025

Chromatogram R-348-1\_20141001\_001

Name					
#	CH	tR	Area	Height	Area%
1	9	3.8567	1113148	221329	99.541
2	9	4.1800	5134	1674	0.459

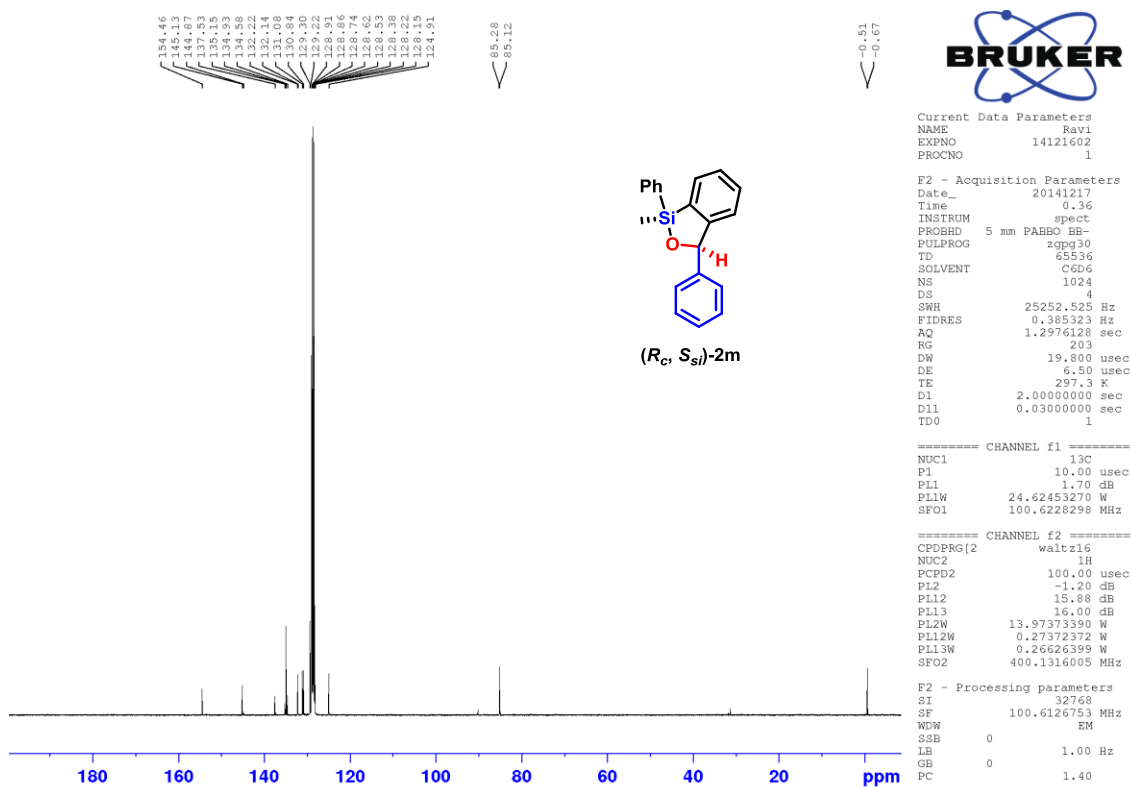


Current Data Parameters  
NAME Rav1  
EXPNO 14121601  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20141216  
Time 23.37  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT C6D6  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 64  
DW 60.800 usec  
DE 6.50 usec  
TE 295.9 K  
D1 1.00000000 sec  
TDO 1

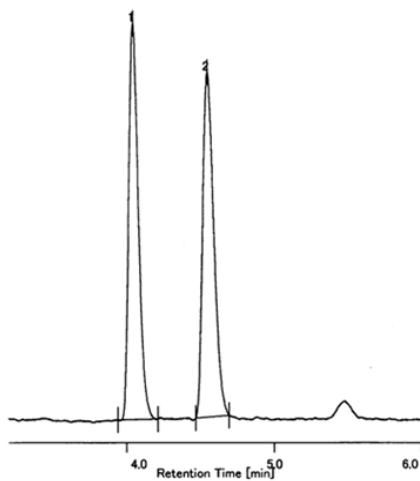
===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.9737390 W  
SF01 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300815 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



**Chiral Separation:** SFC; Chiralpak ID; Flow (CO<sub>2</sub>) = 2.0 mL/min; Flow (isopropanol) = 0.3 mL/min; T = 25 °C; λ = 250; Back pressure = 15 MPa

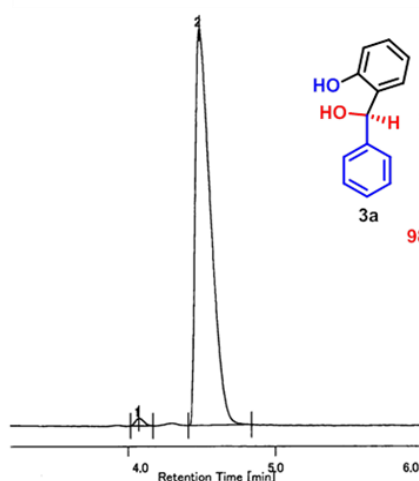
クロマトグラム+ピーク情報



Chromatogram R-147\_20140913.001

Name

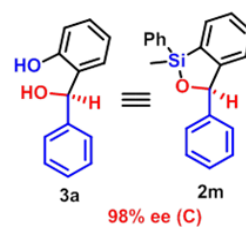
#	CH	tR	Area	Height	Area%
1	9	4.0417	572491	127741	49.801
2	9	4.5450	577068	111220	50.199

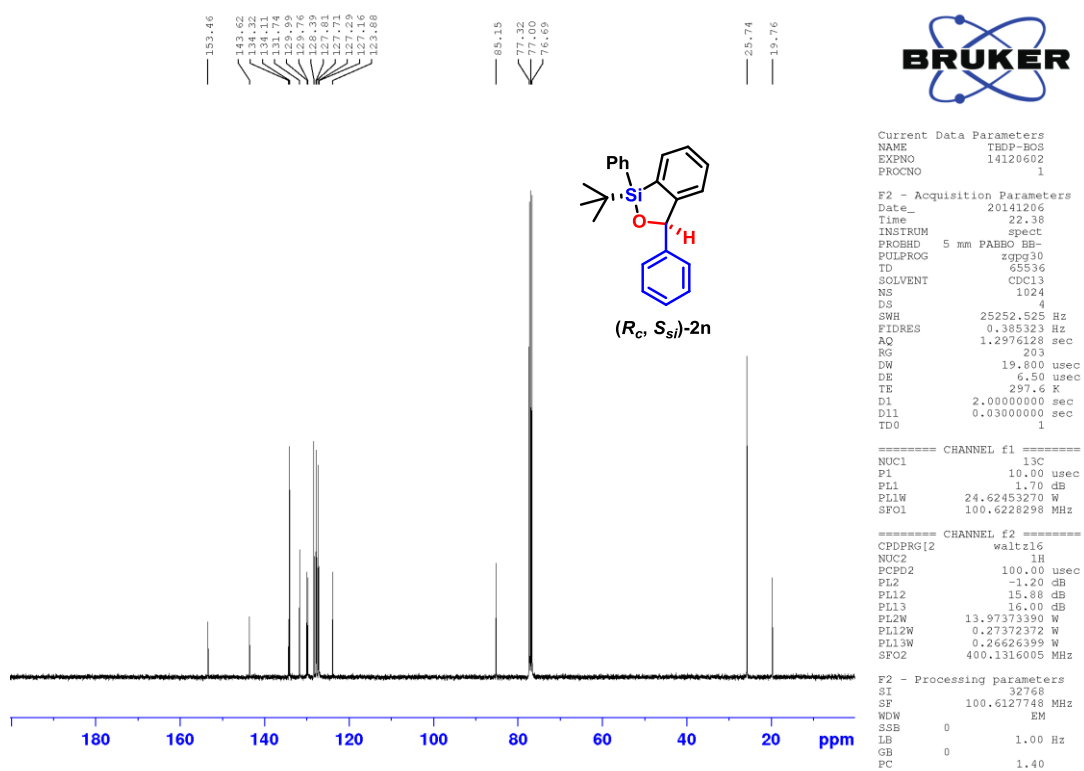
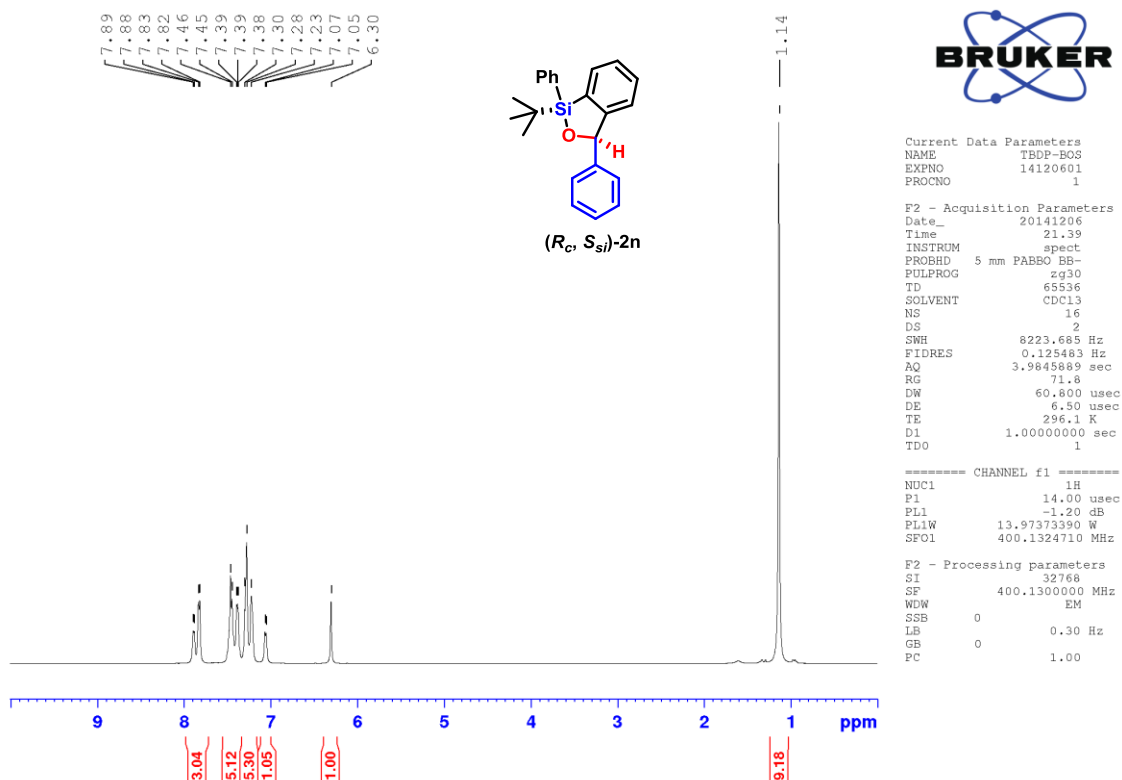


Chromatogram R-341\_20140913.001

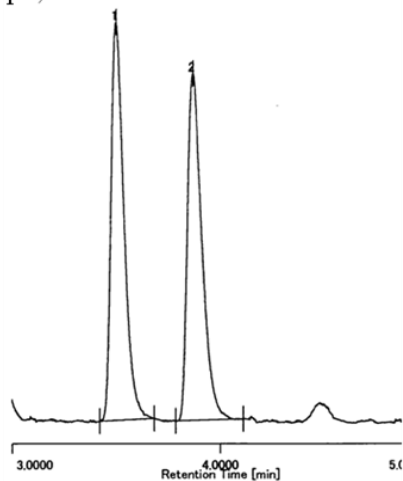
Name

#	CH	tR	Area	Height	Area%
1	9	4.0717	37987	9501	1.039
2	9	4.4883	3617895	507773	98.961





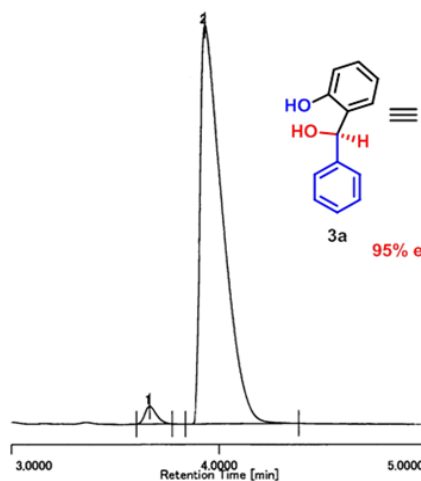
**Chiral Separation:** SFC; Chiralpak ID; Flow (CO<sub>2</sub>) = 2.0 mL/min; Flow (isopropanol) = 0.3 mL/min;  
T = 25 °C; λ = 250; Back pressure = 15 Mpa,



Chromatogram R-147\_20140926\_001

Name

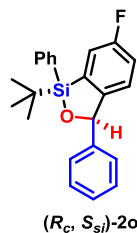
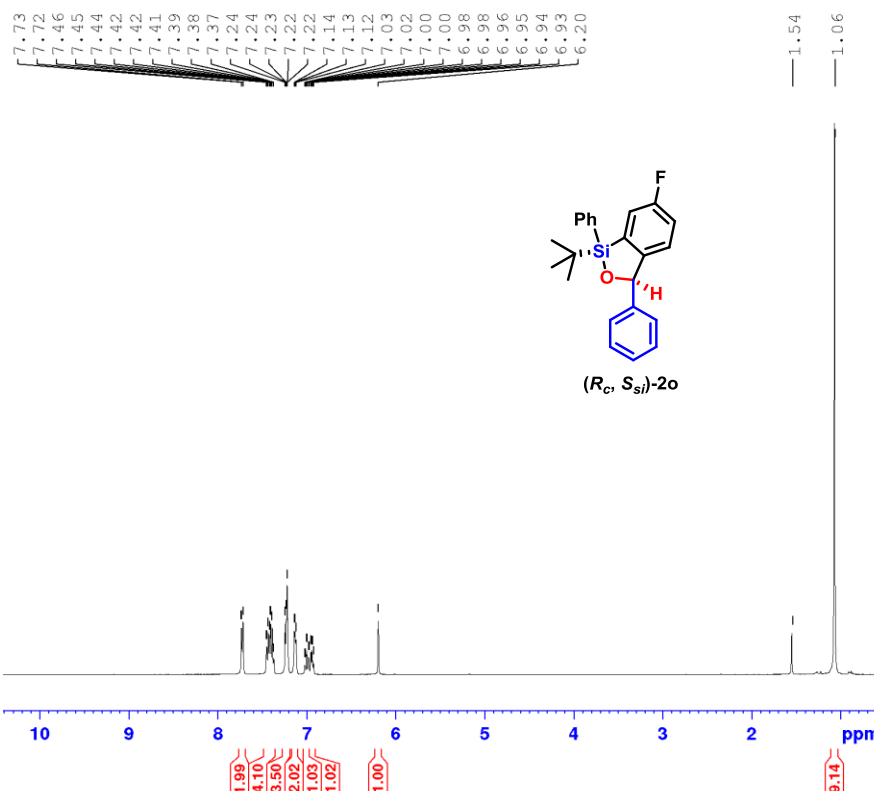
#	CH	tR	Area	Height	Area%
1	9	3.5033	285185	66991	50.041
2	9	3.8700	284717	58297	49.959



Chromatogram R-426\_20141205\_001

Name

#	CH	tR	Area	Height	Area%
1	9	3.6650	119818	30902	2.248
2	9	3.9333	5209633	700713	97.752

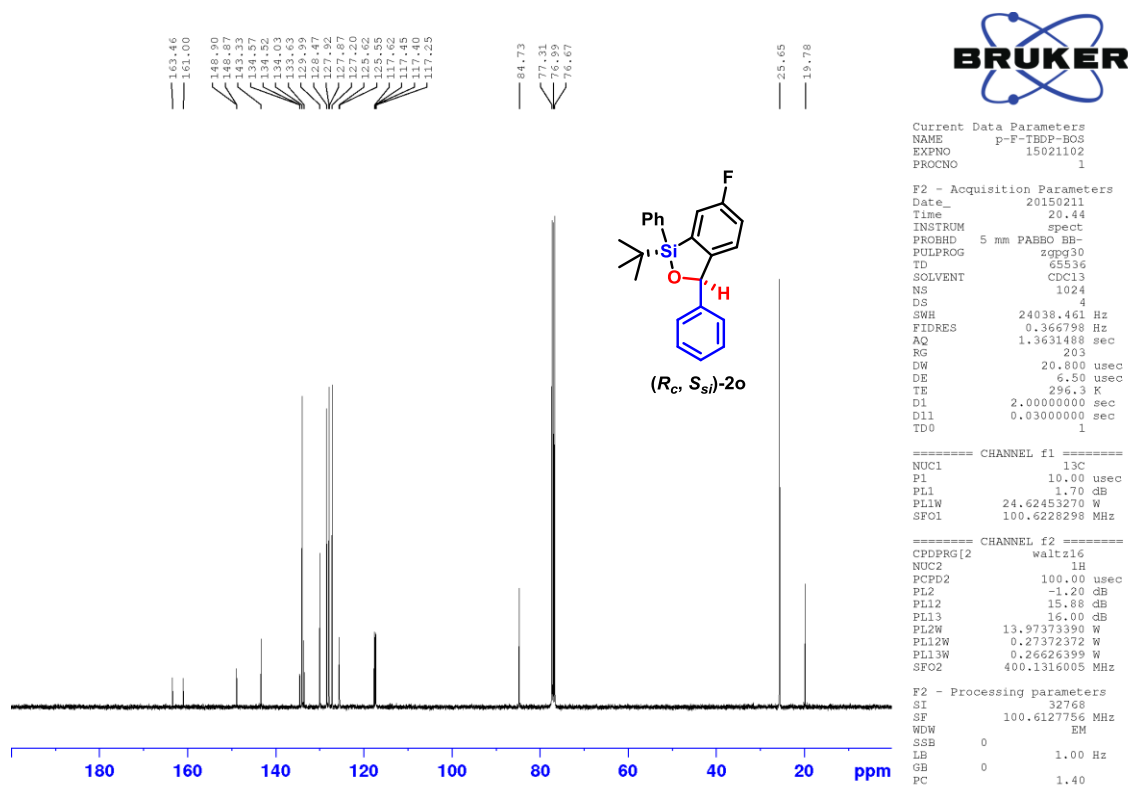


Current Data Parameters  
NAME Ravi  
EXPNO 15021007  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150210  
Time 16.29  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 181  
DW 60.800 usec  
DE 6.50 usec  
TE 295.7 K  
D1 1.00000000 sec  
TD0 1

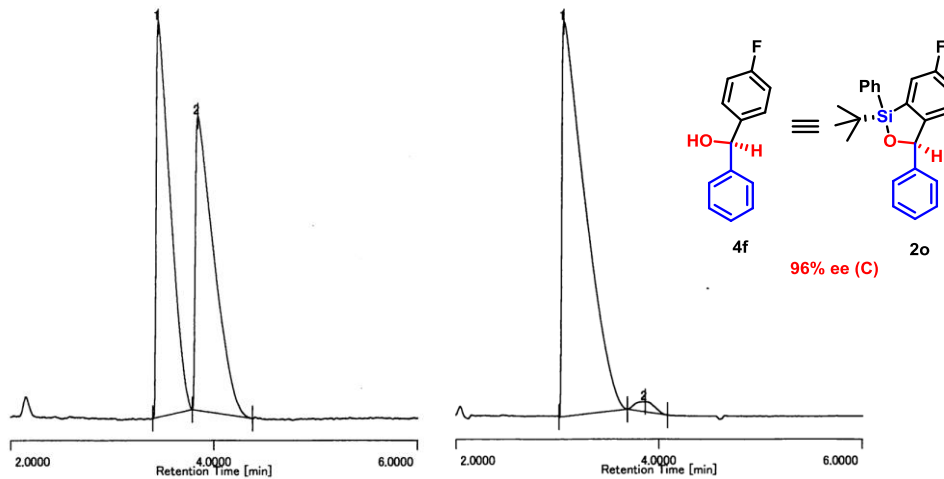
===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300227 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



**Chiral Separation:** SFC; Chiralpak ID; Flow (CO<sub>2</sub>) = 4.0 mL/min; Flow (CH<sub>2</sub>Cl<sub>2</sub>) = 0.6 mL/min;  
T = 25 °C; λ = 250; Back pressure = 15 Mpa,

クロマトグラム+ピーク情報



Chromatogram R-442

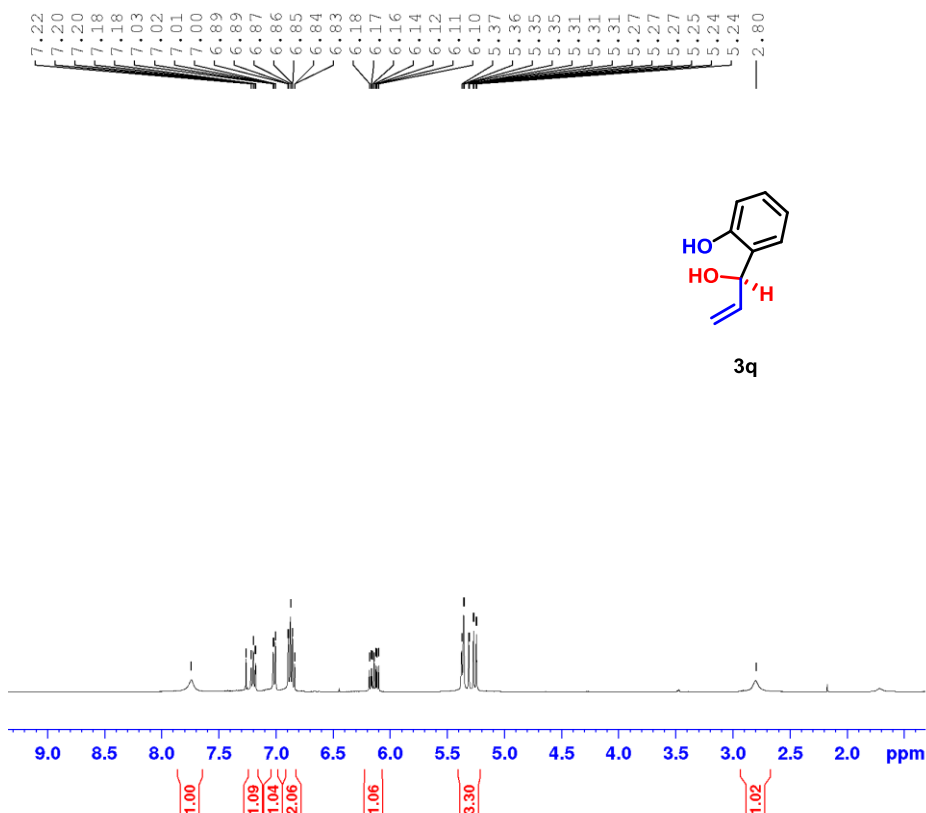
Name

#	CH	tR	Area	Height	Area%
1	9	3.4617	1566649	166133	50.379
2	9	3.8483	1543080	123901	49.621

Chromatogram R-443

Name

#	CH	tR	Area	Height	Area%
1	9	3.0733	7043766	445632	97.889
2	9	3.8667	151918	11692	2.111

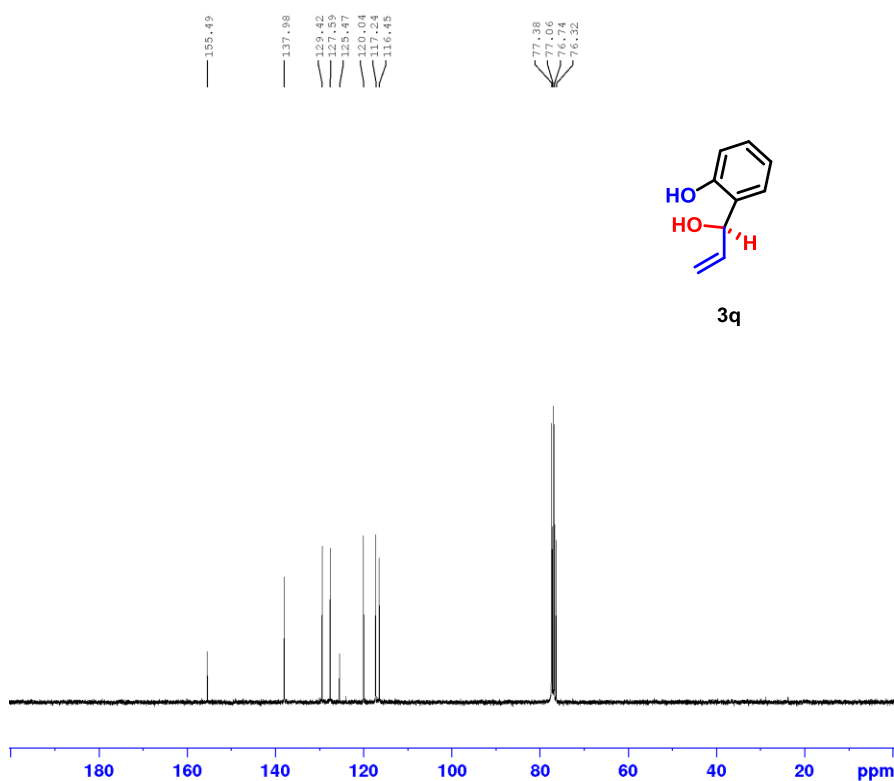


Current Data Parameters  
NAME Ravi  
EXPNO 13121202  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20131212  
Time 10.36  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 161  
DW 60.800 usec  
DE 6.50 usec  
TE 295.3 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300160 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



Current Data Parameters  
NAME Ravi  
EXPNO 13121203  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20131212  
Time 19.30  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 512  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 101  
DW 20.800 usec  
DE 6.50 usec  
TE 295.6 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1

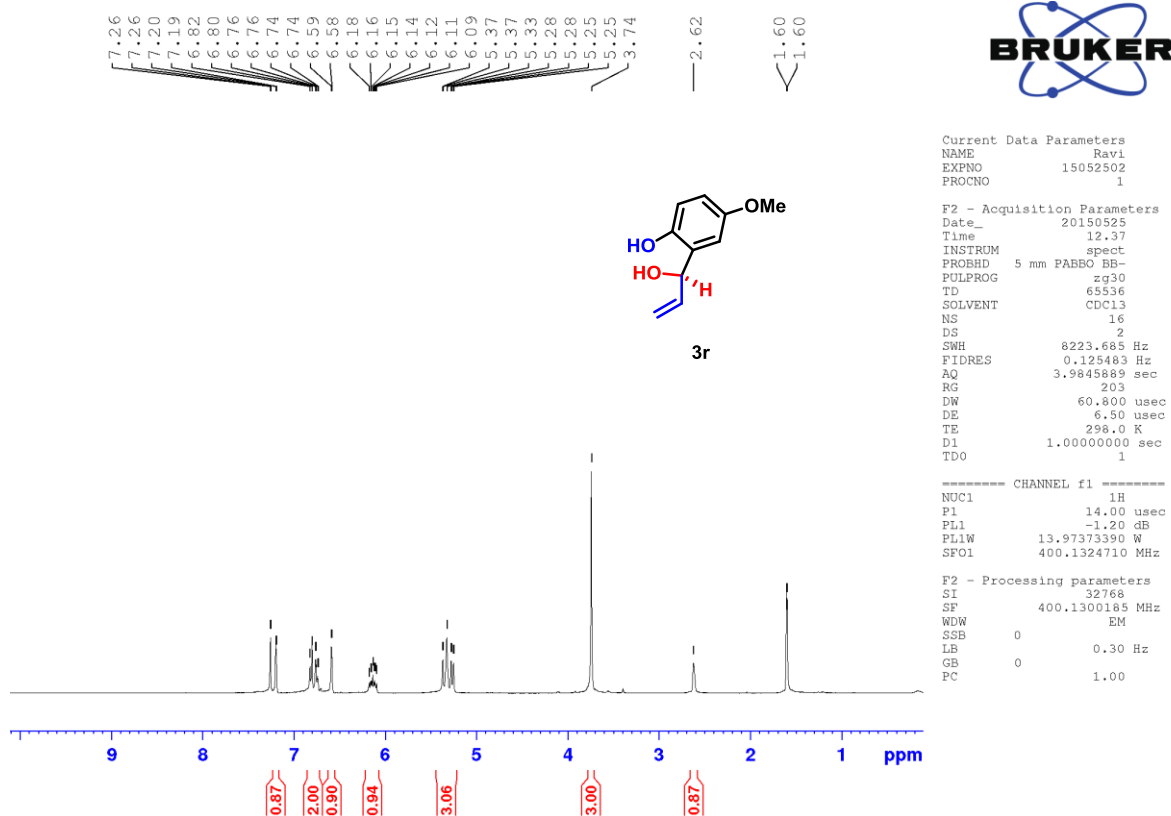
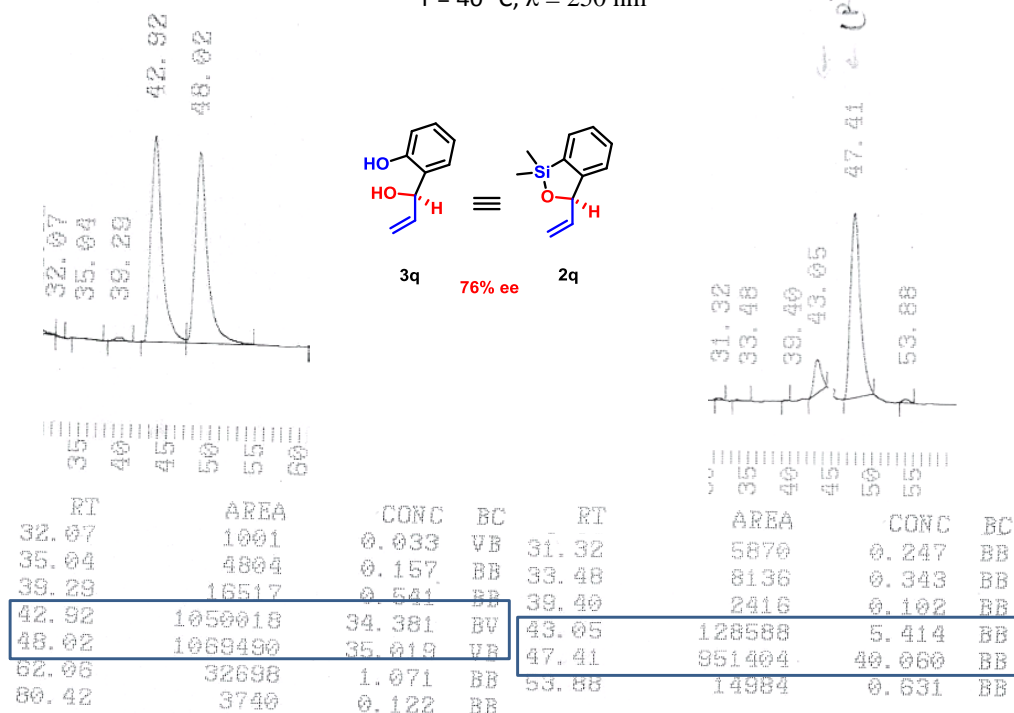
===== CHANNEL f1 =====  
NUC1 13C  
P1 10.00 usec  
PL1 1.70 dB  
PL1W 24.62453270 W  
SFO1 100.6228298 MHz

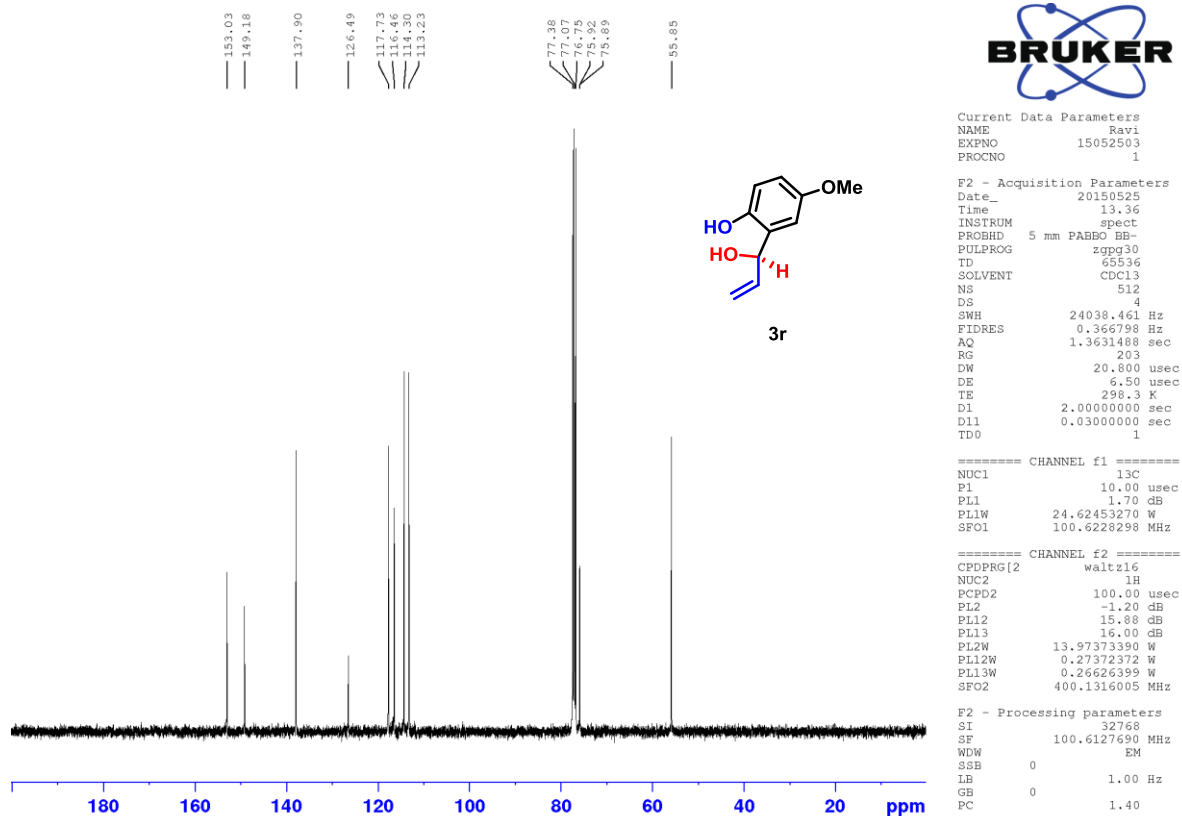
===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 100.00 usec  
PL2 -1.20 dB  
PL12 15.88 dB  
PL13 16.00 dB  
PL2W 13.97373390 W  
PL12W 0.27372372 W  
PL13W 0.26626399 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127690 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40



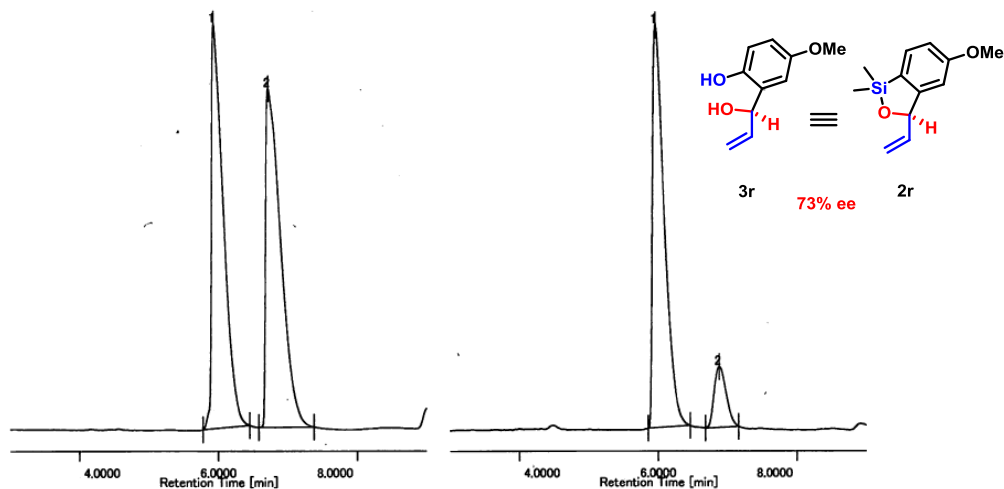
**Chiral Separation:** HPLC; Chiralpak OB-H; Isopropanol/Hexane = 3:97; Flow = 0.5 mL/min;  
T = 40 °C;  $\lambda$  = 250 nm





**Chiral Separation:** SFC; Chiralpak IB; Flow (CO<sub>2</sub>) = 4.0 mL/min; Flow (isopropanol) = 0.2 mL/min;  
 T = 25 °C; λ = 230 nm; Back pressure = 15 Mpa

クロマトグラム+ピーク情報



Chromatogram R-504

Name

#	CH	tR	Area	Height	Area%
1	10	5.9400	14029189	1178273	48.718
2	10	6.7217	14767645	986556	51.282

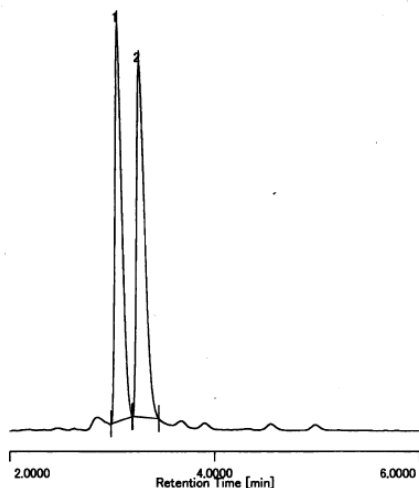
Chromatogram R-514-OMe-V

Name

#	CH	tR	Area	Height	Area%
1	10	5.9683	5714600	488809	86.539
2	10	6.8800	888902	73926	13.461

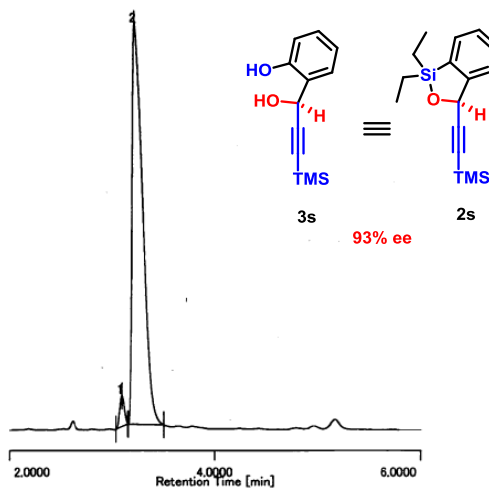
**Chiral Separation:** SFC; Chiralpak IA; Flow (CO<sub>2</sub>) = 4.0 mL/min; Flow (isopropanol) = 0.3 mL/min;  
T = 25 °C; λ = 220 nm; Back pressure = 15 Mpa

クロマトグラム+ピーク情報



Chromatogram R-480(1)-alkynyl-TMS-diol  
Name

#	CH	tR	Area	Height	Area%
1	10	3.0483	3714641	788023	49.317
2	10	3.2600	3817569	698938	50.683

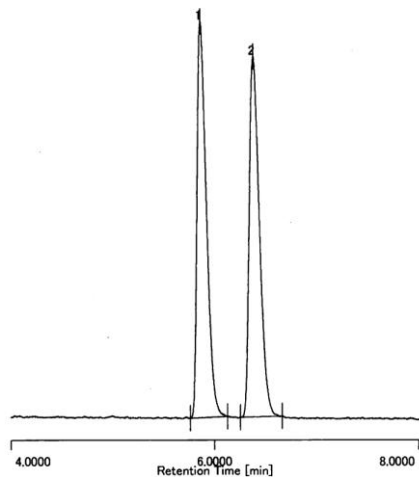


Chromatogram R-484(1)-alkynyl-TMS-diol in THF  
Name

#	CH	tR	Area	Height	Area%
1	10	3.0967	279441	90151	3.306
2	10	3.2167	8172820	1174613	96.694

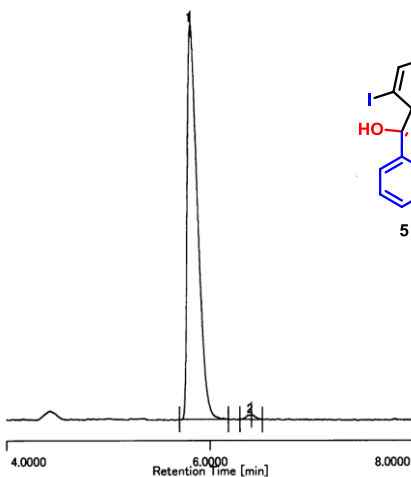
**Chiral Separation:** SFC; Chiralpak IB; Flow (CO<sub>2</sub>) = 2.0 mL/min; Flow (Isopropanol) = 0.3 mL/min;  
T = 25 °C; λ = 250; Back pressure = 15 Mpa,

クロマトグラム+ピーク情報



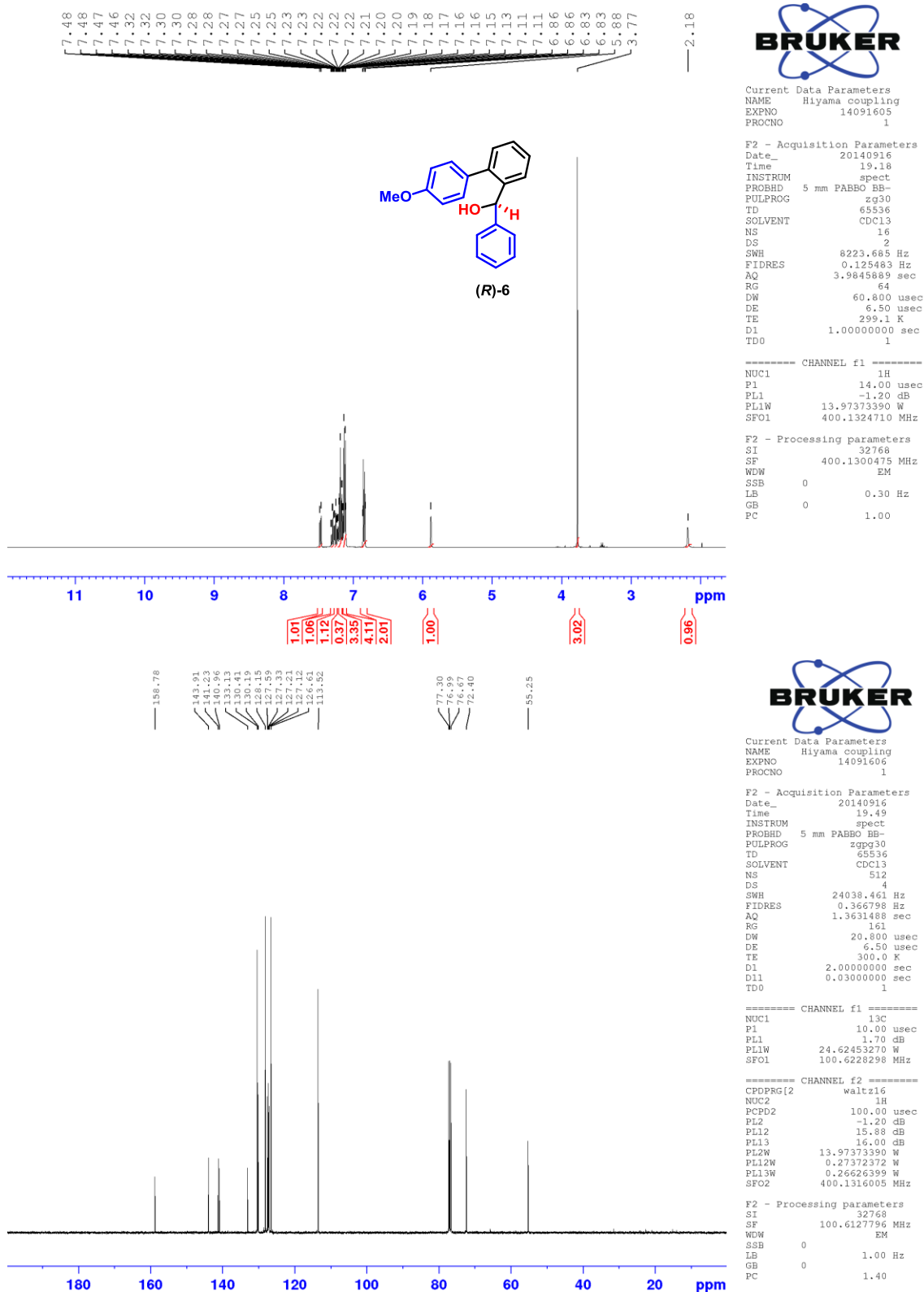
Chromatogram R-357-2\_20140930\_002  
Name

#	CH	tR	Area	Height	Area%
1	9	5.8650	1832166	290535	50.071
2	9	6.3817	1826934	264247	49.929



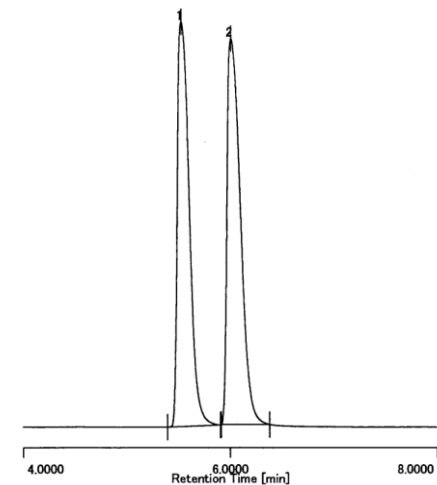
Chromatogram R-364-pure20140930\_002  
Name

#	CH	tR	Area	Height	Area%
1	9	5.8117	3271865	467411	98.955
2	9	6.4050	34553	5797	1.045



**Chiral Separation:** SFC; Chiralpak IB; Flow (CO<sub>2</sub>) = 2.0 mL/min; Flow (Isopropanol) = 0.3 mL/min;  
T = 25 °C; λ = 250; Back pressure = 15 Mpa,

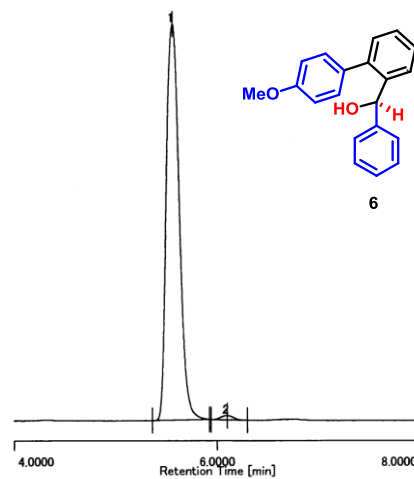
クロマトグラム+ピーク情報



Chromatogram R-360

Name

#	CH	tR	Area	Height	Area%
1	9	5.5267	18095299	2289391	48.470
2	9	6.0067	19237660	2181925	51.530

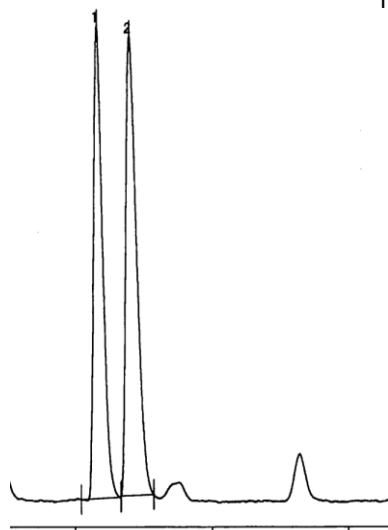


Chromatogram R-367-4

Name

#	CH	tR	Area	Height	Area%
1	9	5.5633	11742562	1336794	98.990
2	9	6.0967	119839	14440	1.010

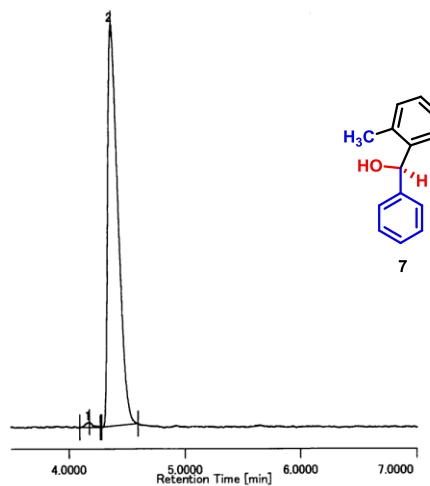
**Chiral Separation:** SFC; Chiralpak IB; Flow (CO<sub>2</sub>) = 2.0 mL/min; Flow (Isopropanol) = 0.3 mL/min;  
T = 25 °C; λ = 250; Back pressure = 15 Mpa,



Chromatogram R-390-2

Name

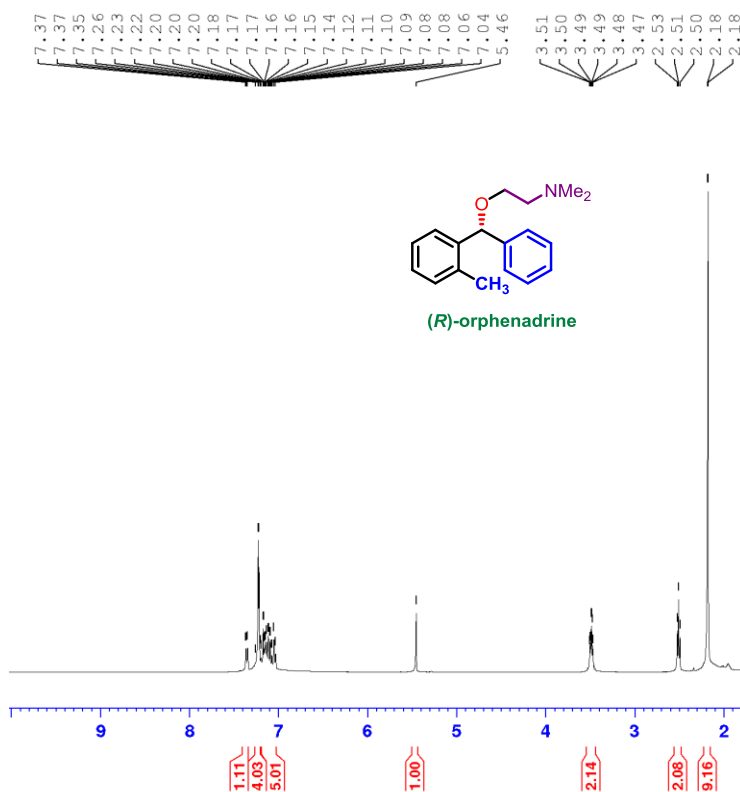
#	CH	tR	Area	Height	Area%
1	9	4.1633	970480	213161	46.327
2	9	4.3983	1124348	207166	53.673



Chromatogram R-397-1

Name

#	CH	tR	Area	Height	Area%
1	9	4.1800	11939	2844	0.882
2	9	4.3683	1341724	219554	99.118

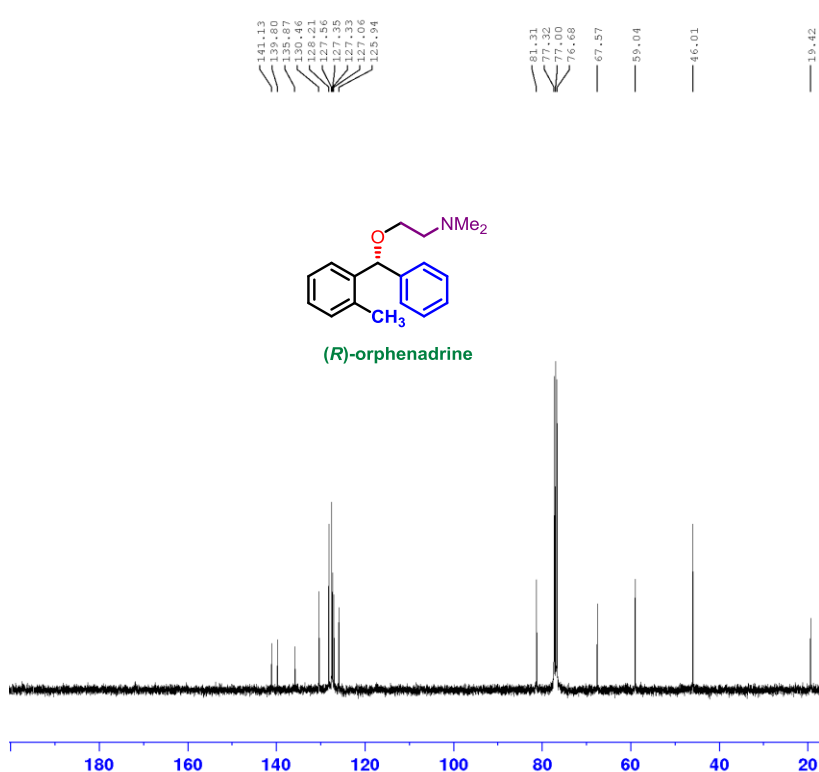


Current Data Parameters  
NAME Orphenadrine  
EXPNO 14103002  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20141030  
Time 18.36  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8223.665 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 80.6  
DW 60.800 usec  
DE 6.50 usec  
TE 295.8 K  
D1 1.0000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300497 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



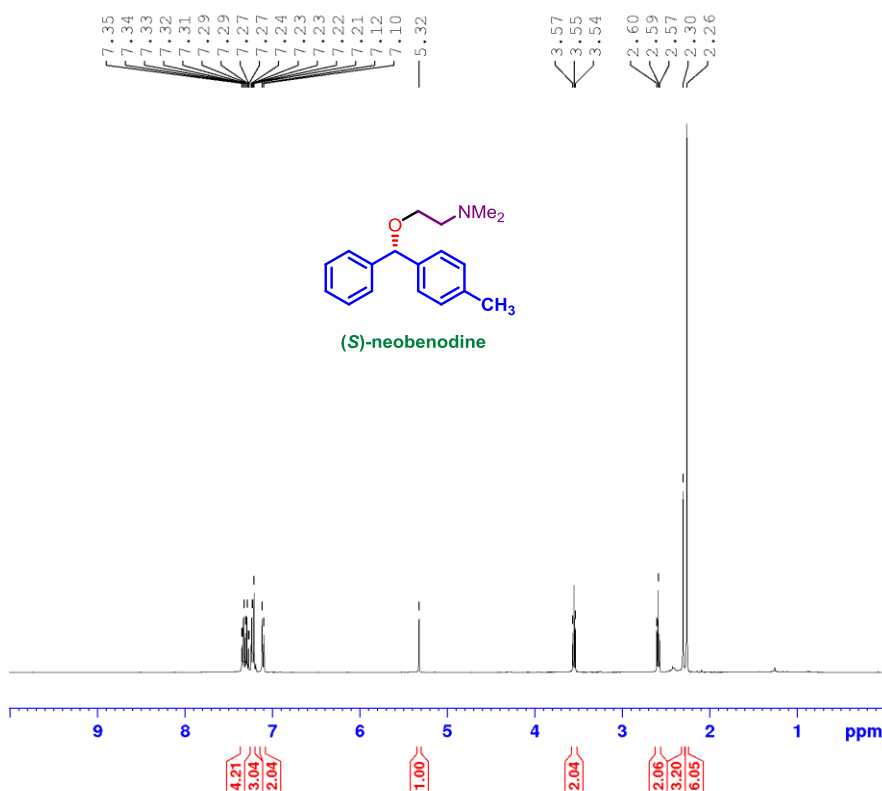
Current Data Parameters  
NAME Orphenadrine  
EXPNO 14103003  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20141030  
Time 18.57  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 330  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 203  
DW 20.800 usec  
DE 6.50 usec  
TE 298.2 K  
D1 2.0000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 10.00 usec  
PL1 1.70 dB  
PL1W 24.62453270 W  
SFO1 100.6228298 MHz

===== CHANNEL f2 =====  
CPDPRG[2] waltz16  
NUC2 1H  
PCPD2 100.00 usec  
PL2 -1.20 dB  
PL12 15.88 dB  
PL13 16.00 dB  
PL2W 13.97373390 W  
PL12W 0.27372372 W  
PL13W 0.26626399 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127751 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

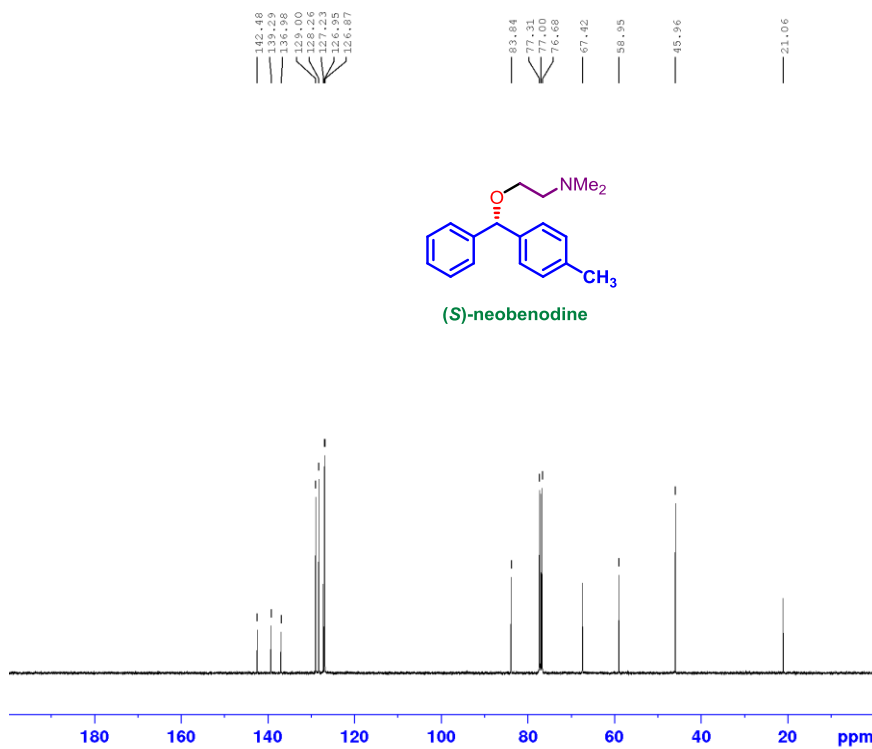


Current Data Parameters  
 NAME Neobenodine  
 EXPNO 14101201  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20141012  
 Time 17.07  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB-  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 8223.685 Hz  
 FIDRES 0.125483 Hz  
 AQ 3.9845889 sec  
 RG 71.8  
 DW 60.800 usec  
 DE 6.50 usec  
 TE 297.9 K  
 D1 1.00000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.00 usec  
 PL1 -1.20 dB  
 PL1W 13.97373390 W  
 SFO1 400.1324710 MHz

F2 - Processing parameters  
 SI 32768  
 SF 400.1300237 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



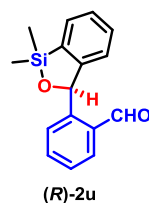
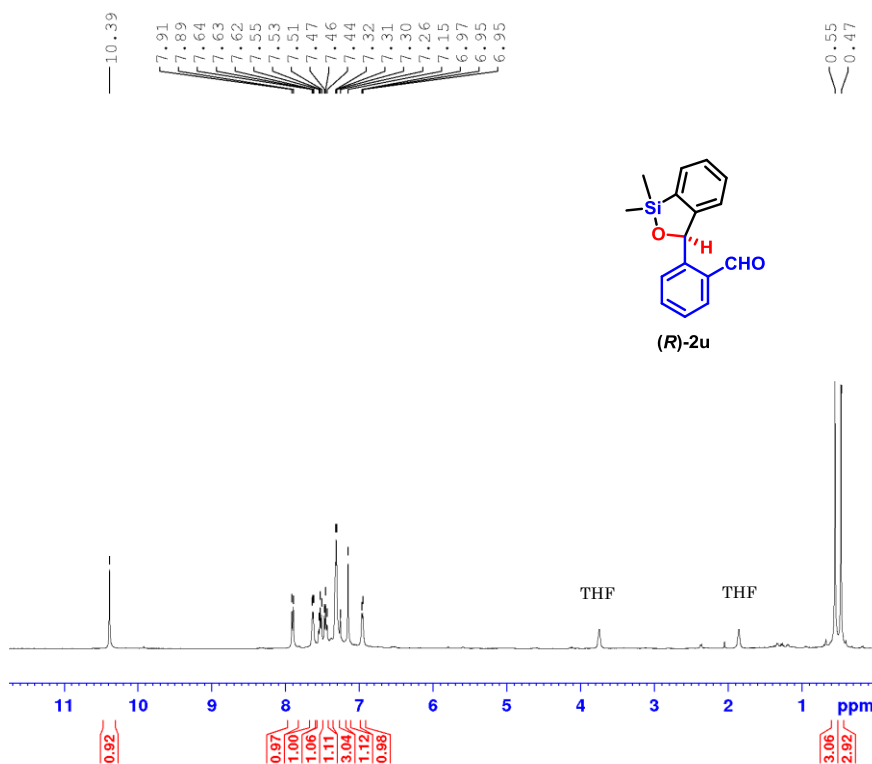
Current Data Parameters  
 NAME Neobenodine  
 EXPNO 14101202  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20141012  
 Time 17.38  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB-  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 512  
 DS 4  
 SWH 24038.461 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 128  
 DW 20.800 usec  
 DE 6.50 usec  
 TE 299.2 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 13C  
 P1 10.00 usec  
 PL1 1.70 dB  
 PL1W 24.62453270 W  
 SFO1 100.6228298 MHz

===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 100.00 usec  
 PL2 -1.20 dB  
 PL12 15.88 dB  
 PL13 16.00 dB  
 PL2W 13.97373390 W  
 PL12W 0.27372372 W  
 PL13W 0.26626399 W  
 SFO2 400.1316005 MHz

F2 - Processing parameters  
 SI 32768  
 SF 100.6127759 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

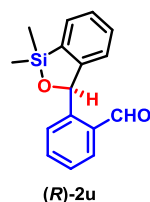
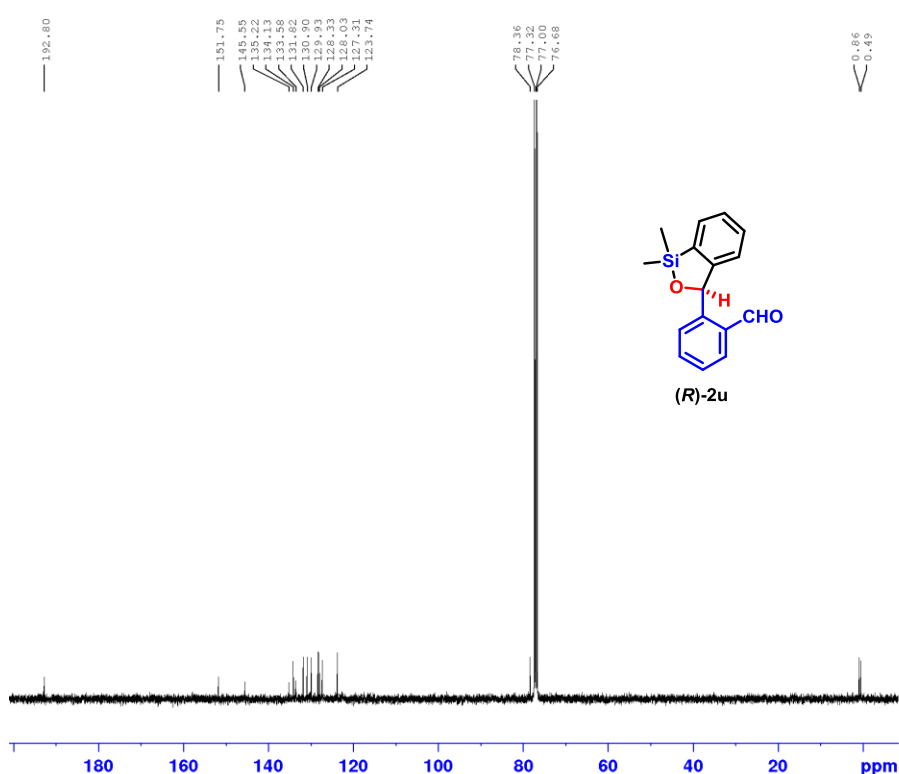


Current Data Parameters  
NAME BOS-BABA  
EXPNO 14031103  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140311  
Time 18.37  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 128  
DW 60.800 usec  
DE 6.50 usec  
TE 295.1 K  
D1 1.0000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1300178 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



Current Data Parameters  
NAME BOS-BABA  
EXPNO 15011002  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150110  
Time 16.16  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 512  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 203  
DW 20.800 usec  
DE 6.50 usec  
TE 295.7 K  
D1 2.0000000 sec  
D11 0.0300000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 10.00 usec  
PL1 1.70 dB  
PL1W 24.62453270 W  
SFO1 100.6228298 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 100.00 usec  
PL2 -1.20 dB  
PL12 15.88 dB  
PL13 16.00 dB  
PL2W 13.97373390 W  
PL12W 0.27372372 W  
PL13W 0.26626399 W  
SFO2 400.1316005 MHz

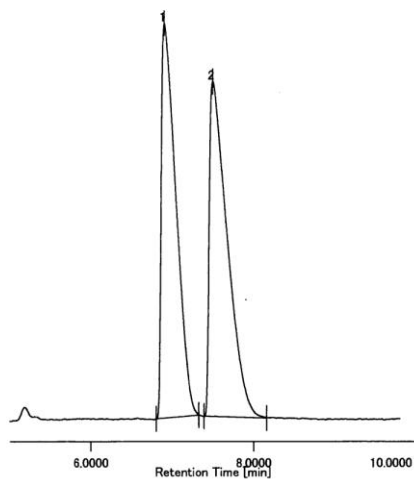
F2 - Processing parameters  
SI 32768  
SF 100.6127733 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40





**Chiral Separation:** SFC; Chiralpak IA; Flow (CO<sub>2</sub>) = 2.4 mL/min; Flow (CH<sub>2</sub>Cl<sub>2</sub>) = 0.4 mL/min;  
T = 40 °C; λ = 250; Back pressure = 15 Mpa,

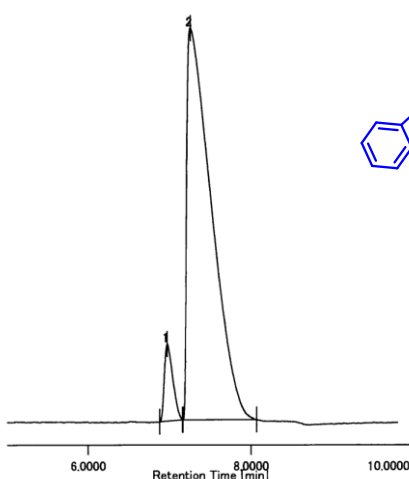
クロマトグラム+ピーク情報



Chromatogram R-223-rac-2

Name

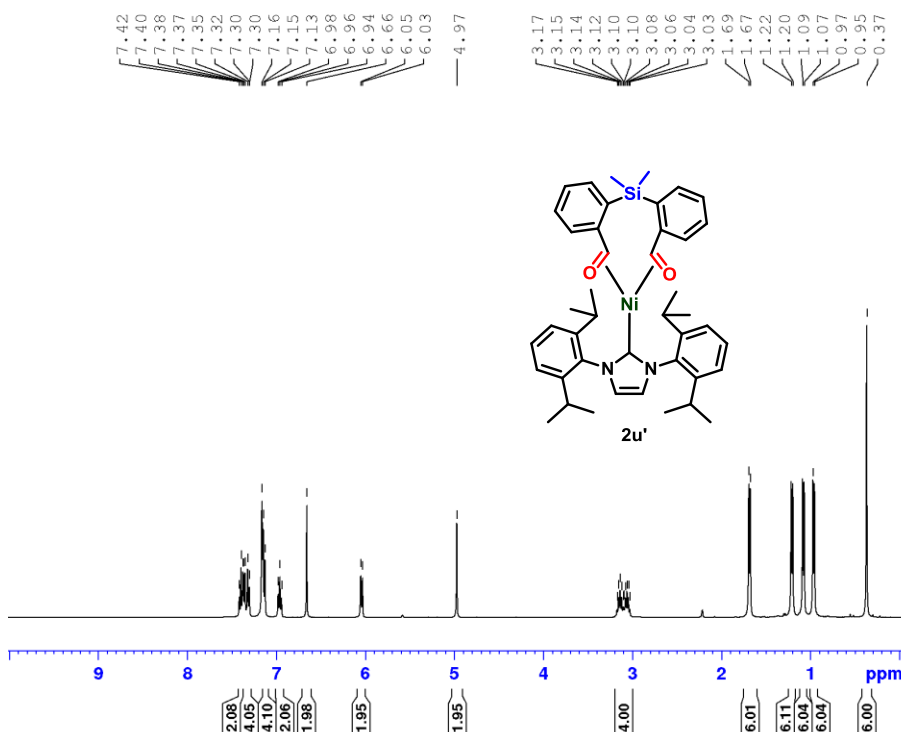
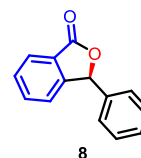
#	CH	tR	Area	Height	Area%
1	10	6.9067	7128018	573902	49.207
2	10	7.5017	7357845	486547	50.793



Chromatogram R-223-chir-2

Name

#	CH	tR	Area	Height	Area%
1	10	6.9717	1222845	171222	6.338
2	10	7.2650	18070834	870158	93.662

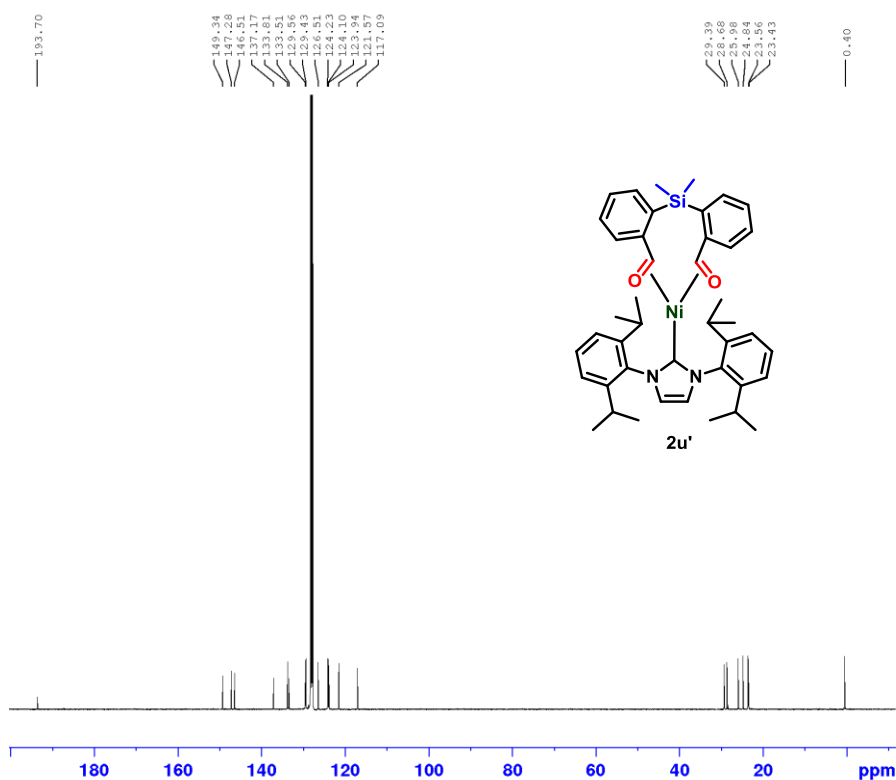


Current Data Parameters  
NAME yabukijournal  
EXPNO 999199  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150226  
Time 23.07  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT C6D6  
NS 16  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9845889 sec  
RG 64  
DW 60.800 usec  
DE 6.50 usec  
TE 294.8 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 14.00 usec  
PL1 -1.20 dB  
PL1W 13.97373390 W  
SFO1 400.1324710 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1299961 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



Current Data Parameters  
 NAME yabukijournal  
 EXPNO 999200  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20150227  
 Time 1.03  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB-  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT C6D6  
 NS 2048  
 DS 4  
 SWH 25252.525 Hz  
 FIDRES 0.385323 Hz  
 AQ 1.2976128 sec  
 RG 203  
 DW 19.800 usec  
 DE 6.50 usec  
 TE 295.8 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 DELTA 1.89999998 sec  
 TD0 1  
 SF01 100.6228298 MHz  
 NUC1 13C  
 P1 10.00 usec  
 PLW1 -1.00000000 W  
 SF02 400.1316005 MHz  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 100.00 usec  
 PLW2 -1.00000000 W  
 PLW12 -1.00000000 W  
 PLW13 -1.00000000 W

F2 - Processing parameters  
 SI 32768  
 SF 100.6127316 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40