Supplementary Information

Catalytic Asymmetric C-Si Bond Activation via Torsional Strain-Promoted Rh-Catalyzed Aryl-Narasaka Acylation

Feng et al.

Supplementary Methods

General Information

Nuclear magnetic resonances were recorded on Bruker-400 MHz and Bruker-500 MHz instruments. Reference values for residual solvents were taken as $\delta = 7.26$ ppm (CDCl₃), 2.50 ppm (DMSO-d₆) for ¹H NMR; $\delta = 77.00$ ppm (CDCl₃), $\delta = 39.00$ ppm (DMSO-d₆) for ¹³C NMR. All reactions were performed under an inert atmosphere of dry nitrogen in flame-dried glassware, unless otherwise stated. 1,4-Dioxane and tetrahydrofuran were distilled over sodium in the presence of benzophenone under an atmosphere of nitrogen. Toluene and dichloromethane were distilled over calcium hydride under an atmosphere of nitrogen.

Typical procedure for the preparation of the L7 (Typical Procedure A)



The 4-PhC₆H₄-TADDOL (2.313 g, 3.00 mmol, 1.0 equiv) was added to a flame-dried round bottom flask charged with 4 Å molecular sieves, followed by the addition of Et₃N (4.50 mL, 32.37 mmol, 11.0 equiv) and THF (30 mL). After the mixture being cooled to 0 °C, phosphorus trichloride (0.31 mL, 3.60 mmol, 1.2 equiv) was added dropwise and the mixture was stirred at for 45 of room temperature minutes. Α mixture (S)-3-methyl-1-((2,4,6-triisopropylphenyl)sulfonyl)piperazine (3.300 g, 9.00 mmol, 3.0 equiv) and Et₃N (1.80 mL, 12.95 mmol, 4.3 equiv) in THF (10 mL) was added slowly at 0 °C and the mixture was allowed to warm to room temperature and stirred overnight. Ethyl ether (10 mL) was added to the reaction flask and the mixture was filtered through a pad of Celite. The filtrate was concentrated in vacuum and the residue was purified by flash column chromatography (PE/EtOAc = 95:5) on silica gel which was pre-treated with Et₃N to afford L7 (2.640 g, 76%). $[\alpha]_{D}^{20}$ + 54.19 (c 1.13, CH₂Cl₂). ¹**H** NMR (500 MHz, CDCl₃) δ 7.89 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.67 - 7.62 (m, 4H), 7.62 - 7.61 (m, 4H), 7.61 - 7.59 (m, 4H), 7.59 - 7.56 (m, 4H), 7.56 - 7.49 (m, 4H), 7.48 - 7.45 (m, 4H), 7.45 - 7.41 (m, 4H), 7.39 - 7.32 (m, 4H), 7.23 - 7.18 (m, 2H), 5.29 (dd, J = 1008.6, 3.4 Hz, 1H), 4.89 (d, J = 8.4 Hz, 1H), 4.23 (hept, J = 6.7 Hz, 2H), 4.04 - 3.89 (m, 1H), 3.63 - 3.53 (m, 1H), 3.53 - 3.44 (m, 1H), 3.40 (dd, J = 11.3, 3.1 Hz, 1H), 3.37 - 3.30 (m, 1H), 3.18 (dd, J = 11.5, 3.1 Hz, 1H), 3.14 (dd, J =3.4 Hz, 1H), 3.14 - 3.06 (m, 1H), 2.93 (hept, J = 7.0 Hz, 1H), 1.42 (s, 3H), 1.41 (d, J = 4.7, 3H), 1.32 - 3.06 (m, 1H), 2.93 (hept, J = 7.0 Hz, 1H), 1.42 (s, 3H), 1.41 (d, J = 4.7, 3H), 1.32 - 3.06 (m, 1H), 2.93 (hept, J = 7.0 Hz, 1H), 1.42 (s, 3H), 1.41 (d, J = 4.7, 3H), 1.32 - 3.06 (m, 1H), 2.93 (hept, J = 7.0 Hz, 1H), 1.42 (s, 3H), 1.41 (d, J = 4.7, 3H), 1.32 - 3.06 (m, 1H), 2.93 (hept, J = 7.0 Hz, 1H), 1.42 (s, 3H), 1.41 (d, J = 4.7, 3H), 1.32 - 3.06 (m, 1H), 2.93 (hept, J = 7.0 Hz, 1H), 1.42 (s, 3H), 1.41 (d, J = 4.7, 3H), 1.32 - 3.06 (m, 1H), 2.93 (hept, J = 7.0 Hz, 1H), 1.42 (s, 3H), 1.41 (d, J = 4.7, 3H), 1.32 - 3.06 (m, 1H), 2.93 (hept, J = 7.0 Hz, 1H), 1.42 (s, 3H), 1.41 (d, J = 4.7, 3H), 1.32 - 3.06 (m, 1H), 1.41 (d, J = 4.7, 3H), 1.32 - 3.06 (m, 1H), 1.41 (d, J = 4.7, 3H), 1.32 - 3.06 (m, 1H), 1.32 - 3.06 (m, 1H), 1.32 - 3.06 (m, 1H), 1.41 (m, 2H), 1.41 (m, 2H), 1.32 - 3.06 (m, 2H), 1.32 - 3.06 (m, 2H), 1.32 - 3.06 (m, 2H), 1.41 (m, 2H), 1.32 - 3.06 (m, 2H), 1.32 - 31.27 (m, 18H), 0.44 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 153.4, 151.9, 145.8, 145.28, 145.27, 141.0, 140.7, 140.63, 140.62, 140.5, 140.4, 140.3, 140.04, 140.00, 139.9, 129.5, 129.3, 129.14, 129.10, 128.73, 128.71, 128.70, 127.5, 127.4, 127.3, 127.2, 127.04, 127.00, 126.9 126.5, 126.3, 125.9, 123.9, 111.9,

82.5 (d, J = 2.8 Hz), 82.3 (d, J = 16.8 Hz), 82.0, 81.4 (d, J = 7.3 Hz), 49.7 (d, J = 3.7 Hz), 48.1 (d, J = 19.4 Hz), 46.1 (d, J = 1.6 Hz), 38.9 (d, J = 10.3 Hz), 34.2, 29.5, 27.6, 25.5, 25.1, 24.8, 23.54, 23.53, 17.6 (d, J = 7.7 Hz). ³¹**P NMR** (202 MHz, CDCl₃) δ 137.5. **HRMS (ESI)** calcd for C₇₅H₇₈N₂O₆PS [M+H]⁺ 1165.5318, found 1165.5313.



L2 was prepared following the Typical Procedure A

The reaction of 4-FC₆H₄-TADDOL (0.538 g, 1.00 mmol), phosphorus trichloride (0.10 mL, 1.20 mmol), (*S*)-3-methylmorpholine (0.304 g, 3.00 mmol) and 4 Å molecular sieves afforded L2 (0.374 g, 56%). [α]_D²⁰ + 97.56 (c 1.18, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.64 (m, 2H), 7.58 – 7.51 (m, 2H), 7.41 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 7.06 – 7.01(m, 2H), 7.01 – 6.99 (m, 2H), 6.99 – 6.97 (m, 2H), 6.97 – 6.91 (m, 2H), 5.01 (dd, *J* = 8.6, 3.4 Hz, 1H), 4.60 (d, *J* = 8.4 Hz, 1H), 3.81 (dt, *J* = 10.8, 3.2 Hz, 1H), 3.68 – 3.58 (m, 2H), 3.58 – 3.49 (m, 2H), 3.49 – 3.38 (m, 1H), 3.32 – 3.22 (m, 1H), 1.33 (d, *J* = 6.4 Hz, 3H), 1.29 (s, 3H), 0.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.1 (d, *J* = 245.4 Hz), 162.0 (d, *J* = 245.6 Hz), 161.9 (d, *J* = 245.4 Hz), 142.5 (d, *J* = 3.4 Hz), 142.0, 137.64, 137.63, 137.61, 137.60, 137.04, 137.03, 130.53, 130.51, 130.47, 130.45, 130.43, 130.39, 128.8, 128.7, 128.6, 115.1 (d, *J* = 21.2 Hz), 114.7 (d, *J* = 21.1 Hz), 114.5 (d, *J* = 20.8 Hz), 114.1 (d, *J* = 21.2 Hz), 111.9, 82.2 (d, *J* = 3.7 Hz), 82.0 (d, *J* = 21.1 Hz), 81.5, 80.6 (d, *J* = 9.2 Hz), 72.6 (d, *J* = 4.8 Hz), 68.2 (d, *J* = 3.3 Hz), 48.5 (d, *J* = 21.9 Hz), 39.5 (d, *J* = 12.0 Hz), 27.50, 25.48, 16.7 (d, *J* = 9.5 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 137.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.4, -114.7, -115.2, -115.3. HRMS (ESI) calcd for C₃₆H₃₅F₄NO₅P [M+H]⁺ 668.2189, found 668.2190.



L3 : Ar = 4-PhC₆H₄

L3 was prepared following the Typical Procedure A

The reaction of 4-PhC₆H₄-TADDOL (0.280 g, 0.60 mmol), phosphorus trichloride (63 µL, 0.72 mmol), morpholine (0.375 g, 3.00 mmol) and 4 Å molecular sieves afforded L3 (0.194 g, 52%). $[\alpha]_D^{20}$ + 91.18 (c 0.99, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.65 – 7.61 (m, 4H), 7.61 – 7.59 (m, 8H), 7.59 – 7.56 (m, 4H), 7.56 – 7.51 (m, 4H), 7.47 – 7.44 (m, 2H), 7.44 – 7.42 (m, 4H), 7.42 – 7.40 (m, 2H), 7.34 (t, J = 7.2 Hz, 4H), 5.29 (dd, J = 8.6, 3.4 Hz, 1H), 4.90 (d, J = 8.4 Hz, 1H), 3.90 – 3.67 (m, 4H), 3.52 – 3.39 (m, 2H), 3.39 – 3.26 (m, 2H), 1.41 (s, 3H), 0.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.7, 145.2, 140.9, 140.69, 140.67, 140.63, 140.55, 140.4, 140.02, 139.96, 129.4, 129.14, 129.09, 128.7, 127.5, 127.4, 127.3, 127.08, 127.05, 127.01, 126.96, 126.6, 126.3, 125.9, 111.9, 82.6 (d, J = 2.8 Hz), 82.4 (d, J = 19.9 Hz), 81.9, 81.3 (d, J = 8.0 Hz), 67.9 (d, J = 5.8 Hz), 44.2 (d, J = 17.1 Hz), 27.7, 25.5. ³¹P NMR (162 MHz, CDCl₃) δ 138.0. HRMS (ESI) calcd for C₅₉H₅₃NO₅P [M+H]⁺ 886.3661, found 886.3671.



L4 was prepared following the Typical Procedure A

The reaction of 4-PhC₆H₄-TADDOL (0.771 g, 1.00 mmol), phosphorus trichloride (0.10 mL, 1.20 mmol), benzyl (*S*)-3-methylpiperazine-1-carboxylate (0.70 mL, 3.00 mmol) and 4 Å molecular sieves afforded **L4** (0.671 g, 65%). $[\alpha]_D^{20}$ + 70.31 (c 1.03, CH₂Cl₂). ¹**H NMR** (500 MHz, CDCl₃) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.66 – 7.65 (m, 1H), 7.65 – 7.63 (m, 2H), 7.63 – 7.61 (m, 4H), 7.61 – 7.60 (m, 4H), 7.60 – 7.58 (m, 4H), 7.58 – 7.56 (m, 2H), 7.56 – 7.54 (m, 2H), 7.48 – 7.45 (m, 4H), 7.45 – 7.42 (m, 4H), 7.42 – 7.40 (m, 2H), 7.40 – 7.38 (m, 2H), 7.38 – 7.36 (m, 2H), 7.36 – 7.35 (m, 2H), 7.35 – 7.32 (m, 2H), 5.31 (dd, *J* = 8.5, 3.0 Hz, 1H), 5.26 – 5.09 (m, 2H), 4.89 (d, *J* = 8.5 Hz, 1H), 4.21 – 3.86 (m, 2H), 3.80 (d, *J* = 13.0 Hz, 1H), 3.64 – 3.40 (m, 2H), 3.38 – 3.13 (m, 2H), 1.45 (s, 3H), 1.36 (s, 3H), 0.43 (s, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 155.8, 145.9, 145.4, 145.3, 141.0, 140.68, 140.65, 140.6, 140.5, 140.3, 140.02, 140.00, 139.9, 136.7, 129.4, 129.14, 129.10, 128.73, 128.70, 128.5, 128.0, 127.9, 127.5, 127.4, 127.28, 127.26, 127.2, 127.1, 127.04, 127.00, 126.99, 126.9, 126.5, 126.3, 125.9, 111.8, 82.7 (d, *J* = 3.0 Hz), 82.4 (d, *J* = 21.4 Hz), 81.8, 81.3 (d, *J* = 8.8 Hz), 67.2, 50.2, 49.8, 48.3, 47.8, 45.5, 45.2, 38.8 (d, *J* = 22.2 Hz), 27.7, 25.4, 17.0. ³¹**P NMR** (202 MHz, CDCl₃) δ 138.15. **HRMS (ESI)** calcd for C₆₈H₆₂N₂O₆P [M+H]⁺1033.4345, found 1033.4331.



L5 was prepared following the Typical Procedure A

The reaction of 4-PhC₆H₄-TADDOL (0.771 g, 1.00 mmol), phosphorus trichloride (0.10 mL, 1.20 mmol), benzyl *tert*-butyl (*S*)-3-methylpiperazine-1-carboxylate (0.601 g, 3.00 mmol) and 4 Å molecular sieves afforded **L5** (0.383 g, 38%). [α]_D²⁰ + 68.81 (c 0.89, CH₂Cl₂). ¹**H NMR** (500 MHz, CDCl₃) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.71 – 7.68 (m, 4H), 7.68 – 7.67 (m, 4H), 7.67 – 7.66 (m, 2H), 7.66 – 7.65 (m, 4H), 7.65 – 7.63 (m, 2H), 7.63 – 7.61 (m, 4H), 7.52 – 7.49 (m, 4H), 7.48 – 7.45 (m, 4H), 7.42 – 7.39 (m, 2H), 7.39 – 7.36 (m, 2H), 5.39 (d, *J* = 8.0 Hz, 1H), 4.95 (d, *J* = 8.0 Hz, 1H), 4.21 – 3.89 (m, 2H), 3.80 (d, *J* = 12.5 Hz, 1H), 3.67 – 3.45 (m, 2H), 3.34 – 3.11 (m, 2H), 1.57 (s, 9H), 1.52 (s, 3H), 1.42 (d, *J* = 7.0 Hz, 3H), 0.49 (s, 3H). ¹³C **NMR** (126 MHz, CDCl₃) δ 155.2, 145.9, 145.41, 145.39, 141.1, 140.7, 140.64, 140.59, 140.54, 140.49, 140.3, 140.0, 139.9, 129.4, 129.12, 129.08, 128.70, 128.68, 127.5, 127.4, 127.3, 127.23, 127.19, 127.03, 127.01, 126.97, 126.96, 126.9, 126.5, 126.3, 125.9, 111.7, 82.7 (d, *J* = 3.3 Hz), 82.4 (d, *J* = 21.4 Hz), 81.7, 81.3 (d, *J* = 8.7 Hz), 79.6, 50.4, 49.2, 48.2, 45.7, 44.5, 39.0, 28.4, 27.7, 25.4, 17.0. ³¹P **NMR** (202 MHz, CDCl₃) δ 138.19. **HRMS** (**ESI**) calcd for C₆₅H₆₄N₂O₆P [M+H]⁺ 999.4502, found 999.4504.



L6 : Ar = 4-PhC₆H₄

L6 was prepared following the Typical Procedure A

The reaction of 4-PhC₆H₄-TADDOL (0.385 g, 0.50 mmol), phosphorus trichloride (50 µL, 0.60 mmol), (S)-1-(mesitylsulfonyl)-3-methylpiperazine (0.424 g, 1.50 mmol) and 4 Å molecular sieves afforded L6 (0.336 g, 62%). $[\alpha]_{D}^{20}$ + 97.70 (c 1.00, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.65 – 7.63 (m, 2H), 7.63 – 7.62 (m, 2H), 7.62 - 7.61 (m, 2H), 7.61 - 7.60 (m, 2H), 7.60 - 7.59 (m, 2H), 7.59 - 7.57 (m, 4H), 7.56 - 7.53 (m, 2H), 7.53 - 7.50 (m, 2H), 7.50 - 7.46 (m, 2H), 7.46 - 7.44 (m, 4H), 7.44 - 7.43 (m, 2H), 7.43 -7.40 (m, 2H), 7.39 - 7.36 (m, 2H), 7.36 - 7.31 (m, 2H), 6.96 (s, 2H), 5.27 (dd, J = 8.4, 3.6 Hz, 1H), 4.87 (d, J = 8.4 Hz, 1H), 3.99 - 3.84 (m, 1H), 3.65 - 3.54 (m, 1H), 3.53 - 3.41 (m, 2H), 3.25-3.16 (m, 1H), 3.16 - 3.00 (m, 2H), 2.67 (s, 6H), 2.29 (s, 3H), 1.41 (s, 3H), 1.31 (d, J = 6.8 Hz, 3H), 0.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.8, 145.28, 145.26, 142.7, 140.96, 140.95, 140.7, 140.63, 140.60, 140.51, 140.49, 140.40, 140.38, 140.3, 140.03, 140.00, 139.94, 131.93, 131.0, 129.3, 129.14, 129.09, 128.73, 128.70, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 126.9, 126.6, 126.3, 125.9 111.9, 82.5 (d, J = 3.9 Hz), 82.3 (d, J = 21.3 Hz), 82.0, 81.3 (d, J = 8.8 Hz), 50.4 (d, J = 4.1 Hz), 47.8 (d, J = 23.2 Hz), 45.4 (d, J = 2.9 Hz), 38.8 (d, J = 14.3 Hz), 27.6, 25.5, 23.0, 20.9, 17.4 (d, J = 8.4 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 137.7. HRMS (ESI) calcd for C₆₉H₆₆N₂O₆PS [M+H]⁺ 1081.4379, found 1081.4391.

Typical procedure for the preparation of diiodides ¹(**Typical Procedure B**)



A mixture of dimethyl cyclic diaryliodonium² (2.980 g, 6.50 mmol, 1.0 equiv), tetrabutylammonium iodide (4.800 g, 13.00 mmol, 2.0 equiv), CuI (0.124 g, 0.65 mmol, 10 mol%), *trans*-N,N'- dimethylcyclohexane-1,2-diamine (0.185 g, 1.30 mmol, 20 mol%) in dioxane (15 mL) was stirred at room temperature for 24 hours. After complete consumption of starting material, the mixture was filtered through Celite and the filtrate was concentrated in vacuum and purified by flash column chromatography (PE/EtOAc = 95:5) on silica gel to afford **S1** (2.590 g, 92%). ¹**H NMR** (500 MHz, CDCl₃) δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.00 (t, *J* = 7.8 Hz, 2H), 2.01 (s, 6H). ¹³**C NMR** (126 MHz, CDCl₃) δ 147.4, 137.5, 136.7, 130.0, 129.4, 100.6, 21.4. **HRMS (ESI)** calcd for C₁₄H₁₂I₂Na [M+Na]⁺ 456.8926, found 456.8897.



S2 was prepared following the Typical Procedure B

The reaction of tetramethyl cyclic diaryliodonium² (4.380 g, 9.05 mmol, 1.0 equiv) and tetrabutylammonium iodide (6.690 g, 18.10 mmol, 2.0 equiv) afforded **S2** (3.747 g, 90%). ¹**H NMR** (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 6H), 1.92 (s, 6H). ¹³**C NMR** (100 MHz, CDCl₃) δ 147.8, 137.1, 136.3, 136.0, 130.8, 97.5, 20.3, 17.8. **HRMS** (**ESI**) calcd for C₁₆H₁₆I₂Na [M+Na]⁺484.9239, found 484.9247.

Typical procedure for the preparation of anhydrides³ (Typical Procedure C)



To a flask charged with benzofuran-5-carboxylic acid (0.972 g, 6.00 mmol, 2.0 equiv) and MsCl (0.26 mL, 3.30 mmol, 1.1 equiv) in THF (18 mL) at 0 °C was added a solution of Et₃N (1.40 mL, 10.26 mmol, 3.4 equiv) in THF (36 mL) dropwise. The mixture was warmed to room temperature and stirred for 1 hour. Then the mixture was concentrated under vacuum, diluted with ethyl acetate and NaHCO₃(aq.) and extracted with ethyl acetate for three times, and the combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated to afford the crude **S3** (0.933 g, 61%) without further purification. ¹H NMR (400 MHz, CDCl₃) δ 8.49 (s, 2H), 8.16 (d, *J* = 8.4 Hz, 2H), 7.80 – 7.71 (m, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 6.94 – 6.84 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 162.7, 158.2, 146.8, 127.9, 127.0, 125.0, 123.8, 111.9, 107.2. HRMS (ESI) calcd for C₁₈H₁₀O₅Na [M+Na]⁺ 329.0426, found 329.0422.



S4 was prepared following the Typical Procedure C

The reaction of 3-bromo-4-fluorobenzoic acid (2.190 g, 10.00 mmol, 2.0 equiv) with MsCl (0.43 mL, 5.50 mmol, 1.1 equiv) afforded **S4** (0.735 g, 35%). ¹**H NMR** (400 MHz, CDCl₃) δ 8.38 – 8.32 (m, 2H), 8.14 – 8.07 (m, 2H), 7.29 (d, J = 8.0 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 163.2 (¹ $J_{C-F} = 259$ Hz), 159.9, 136.4 (⁴ $J_{C-F} = 2.1$ Hz), 131.9 (³ $J_{C-F} = 9.0$ Hz), 126.0 (³ $J_{C-F} = 3.5$ Hz), 117.3 (² $J_{C-F} = 23.3$ Hz), 110.2 (² $J_{C-F} = 22.1$ Hz). ¹⁹**F NMR** (376 MHz, CDCl₃) δ -95.9. **HRMS** (**ESI**) calcd for C₁₄H₆Br₂F₂O₃Na [M+Na]⁺ 440.8549, found 440.8555.



S5 was prepared following the Typical Procedure C

The reaction of 3,4-difluorobenzoic acid (1.580 g, 10.00 mmol, 2.0 equiv) with MsCl (0.43 mL, 5.50 mmol, 1.1 equiv) afforded **S5** (0.960 g, 64%). ¹**H NMR** (400 MHz, CDCl₃) δ 8.01 – 7.95 (m, 2H), 7.95 – 7.85 (m, 2H), 7.40 – 7.29 (m, 2H). ¹³**C** NMR (100 MHz, CDCl₃) δ 159.9, 154.8 (dd, J_{C-F} = 261, 12.7 Hz), 150.4 (dd, J_{C-F} = 253, 13.2 Hz), 127.8 (dd, J_{C-F} = 7.8, 3.7 Hz), 125.4 (dd, J_{C-F} = 5.6, 3.6 Hz), 119.9 (dd, J_{C-F} = 19.0, 2.0 Hz), 118.2 (d, ² J_{C-F} = 18.3 Hz). ¹⁹**F** NMR (376 MHz, CDCl₃) δ - 126.0, - 134.7. **HRMS (ESI)** calcd for C₁₄H₆F₄O₃Na [M+Na]⁺321.0151, found 321.0150.

Typical procedure for the preparation of silafluorene (Typical Procedure D)



Under nitrogen atmosphere, to a mixture of 2,2'-dibromo-1,1'-binaphthalene (2.060 g, 5.00 mmol, 1.0 equiv) in THF (50 mL) was added *n*BuLi (2.4 M in hexanes, 4.8 mL, 11.50 mmol, 2.3 equiv) dropwise at -78 °C. After the mixture was stirred under the same temperature for 2 hours, a solution of dichlorodimethylsilane (0.73 mL, 7.50 mmol, 1.50 equiv) in THF (5 mL) was added dropwise. The resulting mixture was stirred for additional 12 hours at -78 °C before it was allowed to warm to room temperature. The mixture was quenched with water (10 mL) and extracted with ethyl acetate (15 mL*3). The combined organic layer was washed with brine and dried with Na₂SO₄, concentrated and purified by flash column chromatography (PE/EtOAc = 99:1) on silica gel which was pretreated by Et₃N to give the desired product **4a** (1.301 g, 84%). ¹**H NMR** (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.43 – 7.34 (m, 2H), 0.48 (s, 6H). ¹³**C NMR** (100 MHz, CDCl₃) δ 147.1, 139.9, 135.7, 129.7, 128.5, 128.3, 127.9, 127.8, 125.7, 124.3, -3.32. **HRMS (ESI)** calcd for C₂₂H₁₉Si [M+H]⁺ 311.1256, found 311.1256.



4b was prepared following the **Typical Procedure D** The reaction of 2,2'-dibromo-1,1'-binaphthalene (4.121 g, 10.00 mmol, 1.0 equiv), *n*BuLi (2.4 M in hexanes, 9.6 mL, 23.00 mmol, 2.3 equiv) and dichlorodiphenylsilane (3.15 mL, 15.00 mmol, 1.5 equiv) afforded **4b** (3.201 g, 73%). ¹**H NMR** (400 MHz, CDCl₃) δ 8.04 (d, J = 8.8 Hz, 2H), 7.99 – 7.89 (m, 6H), 7.68 (d, J = 7.2 Hz, 4H), 7.54 (t, J = 7.4 Hz, 2H), 7.45 – 7.38 (m, 4H), 7.34 (t, J = 7.4 Hz, 4H). ¹³**C NMR** (100 MHz, CDCl₃) δ 148.5, 136.8, 136.0, 135.6, 132.4, 130.2, 129.8, 129.3, 128.32, 128.26, 128.2, 128.0, 126.1, 124.4. **HRMS (ESI)** calcd for C₃₂H₂₃Si [M+H]⁺ 435.1569, found 435.1563.



4c

4c (known compound)⁴ was prepared following the Typical Procedure D

The reaction of 2,2'-dibromo-1,1'-biphenyl (1.560 g, 5.00 mmol, 1.0 equiv), *n*BuLi (2.4 M in hexanes, 4.4 mL, 10.50 mmol, 2.1 equiv) and dichlorodimethylsilane (0.97 mL, 10.00 mmol, 2.0 equiv) afforded **4c** (0.879 g, 84%). ¹**H** NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.0 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.27 (m, 2H), 0.43 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 148.4, 137.4, 134.6, 134.4, 133.3, 130.5, 129.8, 128.0, 127.6, 120.9, -5.1.



4d

4d was prepared following the Typical Procedure D

The reaction of 2,2'-dibromo-1,1'-binaphthalene (0.680 g, 1.65 mmol, 1.1 equiv), *n*BuLi (2.4 M in hexanes, 1.6 mL, 3.75 mmol, 2.5 equiv) and dimethoxydi-*p*-tolylsilane (0.408 g, 1.50 mmol, 1.0 equiv) afforded **4d** (0.434 g, 63%). ¹**H NMR** (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.93 (t, *J* = 7.2 Hz, 4H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 4H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 4H), 2.34 (s, 6H). ¹³**C NMR** (100 MHz, CDCl₃) δ 148.4, 140.3, 137.3, 136.0, 135.6, 129.8, 129.4, 129.0, 128.8, 128.3, 128.2, 128.0, 126.0, 124.3, 21.6. **HRMS (ESI)** calcd for C₃₄H₂₇Si [M+H]⁺ 463.1882, found 463.1880.



4e was prepared following the Typical Procedure D

The reaction of 2,2'-diiodo-6,6'-dimethyl-1,1'-biphenyl (0.651 g, 1.50 mmol, 1.0 equiv), *n*BuLi (2.4 M in hexanes, 1.40 mL, 3.45 mmol, 2.3 equiv) and dichlorodiphenylsilane (0.48 mL, 2.25 mmol, 1.5 equiv) afforded **4e** (0.163 g, 30%). ¹**H NMR** (500 MHz, CDCl₃) δ 7.62 (d, *J* = 7.0 Hz,

2H), 7.59 (d, J = 7.0 Hz, 4H), 7.38 (t, J = 7.3 Hz, 2H), 7.31 (t, J = 7.0 Hz, 6H), 7.25 – 7.23 (m, 2H), 2.40 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 149.7, 138.2, 135.4, 134.0, 133.8, 133.5, 131.1, 129.9, 128.0, 126.9, 22.7. HRMS (ESI) calcd for C₂₆H₂₃Si [M+H]⁺ 363.1569, found 363.1570.



4f was prepared following the Typical Procedure D

The reaction of 6,6'-diiodo-2,2',3,3'-tetramethyl-1,1'-biphenyl (1.620 g, 3.50 mmol, 1.0 equiv), *n*BuLi (2.4 M in hexanes, 3.40 mL, 8.05 mmol, 2.3 equiv) and dichlorodiphenylsilane (1.10 mL, 5.25 mmol, 1.5 equiv) afforded **4f** (0.167 g, 12%). ¹**H NMR** (500 MHz, CDCl₃) δ 7.64 – 7.58 (m, 4H), 7.54 (d, *J* = 7.0 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 4H), 7.14 (d, *J* = 7.0 Hz, 2H), 2.36 (s, 6H), 2.26 (s, 6H). ¹³**C NMR** (126 MHz, CDCl₃) δ 150.6, 140.4, 135.6, 135.4, 134.1, 133.3, 130.8, 129.8, 128.6, 127.9, 20.6, 20.0. **HRMS (ESI)** calcd for C₂₈H₂₇Si [M+H]⁺ 391.1882, found 391.1877.



4g was prepared following the Typical Procedure D

The reaction of 2,2'-dibromo-1,1'-binaphthalene (0.618 g, 1.50 mmol, 1.0 equiv), *n*BuLi (2.4 M in hexanes, 1.40 mL, 3.45 mmol, 2.3 equiv) and dichlorodi(*m*-tolyl)silane (0.506 g, 1.80 mmol, 1.2 equiv) afforded **4g** (0.208 g, 30%). ¹**H NMR** (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 4H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.50 – 7.44 (m, 4H), 7.43 – 7.35 (m, 2H), 7.26 – 7.18 (m, 4H), 2.28 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 148.4, 137.6, 137.0, 136.02, 135.98, 132.7, 132.3, 131.1, 129.8, 129.4, 128.3, 128.2, 128.0, 126.0, 124.3, 21.5. **HRMS** (**ESI**) calcd for C₃₄H₂₇Si [M+H]⁺ 463.1882, found 463.1886.

Typical procedure for the preparation of silafluorene (Typical Procedure E)





piece of iodine was added 1/3 amount of solution of 1-bromo-4-fluorobenzene (1.320 g, 7.50 mmol, 2.0 equiv) in THF (5 mL) to initiate the reaction. After initiation, the rest of the solution was added dropwise. After stirring at room temperature for 30 minutes, a solution of tetramethyl silicate (0.571 g, 3.75 mmol, 1.0 equiv) in THF (2 mL) was added dropwise and stirred for additional 30 minutes. The mixture was filtered via syringe and the filtrate was used directly without further purification.

To the mixture of 2,2'-dibromo-1,1'-binaphthalene (1.030 g, 2.50 mmol, 0.7 equiv) in THF (50 mL) was added nBuLi (2.4 M in hexanes, 2.20 mL, 5.25 mmol, 1.4 equiv) dropwise at -78 °C. After the same temperature for stirring at 2 hours. a solution of bis(4-fluorophenyl)dimethoxysilane (S6) in THF was added dropwise. The mixture was stirred for additional 12 hours at -78 °C before it was allowed to warm to room temperature. The reaction was quenched with water (10 mL), the resulting mixture was extracted with ethyl acetate (15 mL*3). The combined organic layer was washed with brine and dried with Na₂SO₄, concentrated and purified by flash column chromatography (PE/EtOAc = 99:1) on silica gel which was pretreated by Et₃N to give the desired product **4h** (0.599 g, 51%). ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 8.4 Hz, 2H), 7.94 (t, J = 9.2 Hz, 4H), 7.88 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.2 Hz, 4H), 7.55 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.05 (t, J = 8.8 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 164.5 (d, ¹*J*_{C-F} = 249 Hz), 148.6, 137.6 (d, ³*J*_{C-F} = 5.7 Hz), 136.2, 136.1, 129.8, 129.0, 128.5, 128.4, 128.0, 127.7 (d, ${}^{4}J_{C-F} = 3.8$ Hz), 126.3, 124.6, 115.6 (d, ${}^{2}J_{C-F} = 19.9$ Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -109.4. HRMS (ESI) calcd for C₃₂H₂₁F₂Si [M+H]⁺ 471.1381, found 471.1376.



4i was prepared following the Typical Procedure E

The reaction of 2,2'-dibromo-1,1'-binaphthalene (1.030 g, 2.50 mmol, 0.7 equiv), tetramethyl silicate (0.571 g, 3.75 mmol, 1.0 equiv) and 1-bromo-3-fluorobenzene (1.320 g, 7.50 mmol, 2.0 equiv) afforded **4i** (0.448 g, 38%). ¹**H NMR** (500 MHz, CDCl₃) δ 8.05 (d, J = 8.5 Hz, 2H), 7.98 (d, J = 5.0 Hz, 2H), 7.97 – 7.92 (m, 4H), 7.59 – 7.55 (m, 2H), 7.47 – 7.42 (m, 4H), 7.38 (dd, J = 8.5, 3.0 Hz, 2H), 7.34 (dd, J = 7.5, 5.5 Hz, 2H), 7.15 – 7.10 (m, 2H). ¹³**C NMR** (126 MHz, CDCl₃) δ 162.6 (d, ¹ J_{C-F} = 250.0 Hz), 148.8, 136.1, 135.3, 134.9 (d, ³ J_{C-F} = 4.3 Hz), 131.1 (d, ⁴ J_{C-F} = 3.2 Hz), 130.2 (d, ³ J_{C-F} = 7.1 Hz), 129.8, 129.0, 128.6, 128.4, 128.0, 126.4, 124.7, 121.8 (d, ² J_{C-F} = 19.3 Hz), 117.5 (d, ² J_{C-F} = 21.0 Hz). ¹⁹**F NMR** (471 MHz, CDCl₃) δ - 112.4. **HRMS (ESI)** calcd for C₃₂H₂I_F₂Si [M+H]⁺471.1381, found 471.1380.



4j

4j was prepared following the Typical Procedure D

The reaction of 2,2'-dibromo-1,1'-binaphthalene (0.618 g, 1.50 mmol, 1.0 equiv), *n*BuLi (2.4 M in hexanes, 1.40 mL, 3.45 mmol, 2.3 equiv) and dichloro(methyl)(phenyl)silane (0.344 g, 1.80 mmol, 1.2 equiv) afforded **4j** (0. 415 g, 74%). ¹**H NMR** (500 MHz, CDCl₃) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.94 (t, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.52 – 7.51 (m, 1H), 7.51 – 7.49 (m, 2H), 7.42 – 7.37 (m, 2H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.32 – 7.27 (m, 2H), 0.79 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 148.1, 147.9, 138.6, 138.2, 135.91, 135.86, 134.5, 134.3, 130.0, 129.8, 129.7, 129.0, 128.8, 128.3, 128.08, 128.05, 128.0, 127.9, 125.94, 125.92, 124.4, 124.3, -5.3. **HRMS (ESI)** calcd for C₂₇H₂₁Si [M+H]⁺ 373.1413, found 373.1411.

Typical procedure for Rh-catalyzed ring-opening/acylation reaction (Typical

Procedure F)



Under nitrogen atmosphere, to a Schleck tube was added [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), L1 (24.5 mg, 0.021 mmol, 10.5 mol%) and dioxane (2 mL) at room temperature and was stirred for 30 minutes. The solution was transfer via cannula carefully to another Schlenk tube charged with 4a (62 mg, 0.200 mmol, 1.0 equiv), acetic anhydride (28 µL, 0.300 mmol, 1.5 equiv), Na₂CO₃ (6.4 mg, 0.060 mmol, 30 mol%) and dioxane (2 mL). The tube was capped with a screw cap and stirred at 70 °C for 24 h. After being cooled to room temperature, the mixture was filtered through Celite and the filtrate was concentrated in vacuum and purified by flash column chromatography (PE/EtOAc = 90:10) on silica gel to afford **6a** (73 mg, 98%, 90% ee). $[\alpha]_D^{20}$ -2.25 (c 1.13, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 10:90, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹**H NMR** (500 MHz, CDCl₃) δ 8.04 (d, J = 9.0 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 9.0Hz, 1H), 7.55 - 7.50 (m, 1H), 7.49 - 7.44 (m, 1H), 7.31 - 7.26 (m, 1H), 7.26 - 7.22 (m, 1H), 7.17 (d, J = 8.5 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H), 2.70 (s, 1H), 1.94 (s, 3H), 0.13 (s, 3H), -0.47 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 205.2, 141.5, 138.3, 137.9, 137.4, 134.2, 133.7, 133.5, 132.7, 130.4, 128.7, 128.2, 128.0, 127.6, 127.5, 127.0, 126.6, 126.5, 126.2, 123.9, 30.5, 0.6. HRMS (ESI) calcd for C₂₄H₂₂O₂SiNa [M+Na]⁺ 393.1287, found 393.1288.



Compound 6b was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and benzoic anhydride (68 mg, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6b** (100 mg, 90%, 91% ee). $[\alpha]_D^{20} - 45.31$ (c 1.05, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 8.4 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.74 (d, J = 4.8 Hz, 1H), 7.73 – 7.69 (m, 2H), 7.66 – 7.60 (m, 3H), 7.52 (d, J = 8.4 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.27 (m, 2H), 7.20 (t, J = 7.8 Hz, 2H), 7.11 – 7.06 (m, 2H), 7.05 – 7.01 (m, 2H), 7.01 – 6.95 (m, 1H), 6.93 – 6.86 (m, 1H), 6.85 – 6.78 (m, 3H), 5.33 (bs, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 200.8, 142.0, 137.4, 136.73, 136.66, 136.3, 136.0, 135.2, 134.5, 133.7, 133.6, 133.5, 133.4, 132.9, 132.5, 132.0, 130.5, 129.5, 128.5, 127.9, 127.84, 127.82, 127.7, 127.5, 127.0, 126.9, 126.8, 126.6, 126.5, 126.3, 125.7, 124.0. HRMS (ESI) calcd for C₃₉H₂₈O₂SiNa [M+Na]⁺ 579.1756, found 579.1752.



Compound 6c was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and acetic anhydride (28 µL, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6c** (97 mg, 98%, 92% ee). $[\alpha]_D^{20}$ + 17.60 (c 0.98, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 15:85, flow: 1.0 mL/min, λ = 254 nm. ¹**H NMR** (400 MHz, CDCl₃) δ 7.92 – 7.88 (m, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.61 (t, *J* = 1.4 Hz, 1H), 7.61 – 7.59 (m, 1H), 7.49 – 7.44 (m, 1H), 7.42 – 7.37 (m, 1H), 7.36 – 7.33 (m, 2H), 7.33 – 7.30 (m, 1H), 7.25 – 7.19 (m, 1H), 7.09 – 7.06 (m, 2H), 7.06 – 7.01 (m, 2H), 6.99 – 6.93 (m, 1H), 6.92 – 6.89 (m, 2H), 6.89 – 6.85 (m, 1H), 3.43 (s, 1H), 1.99 (s, 3H). ¹³C NMR (100 MHz, CDC₃) δ 205.8, 143.2, 138.0, 136.5, 135.8, 134.9, 134.7, 134.4, 133.9, 133.8, 133.7, 132.9, 132.8, 132.2, 129.6, 128.9, 128.8, 128.1, 128.0, 127.7, 127.6, 127.2, 127.1, 127.0, 126.8, 126.6, 126.5, 126.2, 123.2, 30.4. **HRMS (ESI)** calcd for C₃₄H₂₆O₂SiNa [M+Na]⁺ 517.1600, found 517.1600.



Compound 6d was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and propionic anhydride (28 µL, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6d** (97 mg, 98%, 92% ee). $[\alpha]_D^{20}$ + 19.33 (c 0.97, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 15:85, flow: 1.0 mL/min, λ = 254 nm. ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.87 (m, 2H), 7.86 (d, J = 8.4 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.68 – 7.64 (m, 2H), 7.59 (d, J = 8.8 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.37 – 7.34 (m, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.08 (d, J = 8.8 Hz, 2H), 7.05 – 6.98 (m, 2H), 6.94 (t, J = 7.8 Hz, 1H), 6.87 (t, J = 7.8 Hz, 3H), 4.07 (s, 1H), 2.55 – 2.41 (m, 1H), 2.39 – 2.22 (m, 1H), 0.76 (t, J = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 209.7, 143.0, 138.4, 136.1, 135.8, 135.0, 134.9, 134.4, 133.9, 133.6, 133.5, 132.81, 132.78, 132.2, 129.6, 128.73, 128.71, 128.2, 127.8, 127.7, 127.5, 127.1, 126.9, 126.7, 126.5, 126.3, 126.2, 122.7, 36.1, 7.9. HRMS (ESI) calcd for C₃₅H₂₈O₂SiNa [M+Na]⁺ 531.1756, found 531.1757.



Compound 6e was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and butyric anhydride (49 µL, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L1** (18.9 mg, 0.021 mmol, 10.5 mol%) afforded **6e** (61 mg, 59%, 85% ee). $[\alpha]_D^{20}$ + 14.26 (c 1.00, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 10:90, flow: 1.0 mL/min, λ = 254 nm. ¹**H NMR** (400 MHz, CDCl₃) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.72 – 7.68 (m, 2H), 7.68 – 7.64 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.36 – 7.33 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.83 – 6.71 (m, 1H), 4.27 (s, 1H), 2.41 (dt, *J* = 17.6, 7.0 Hz, 1H), 2.26 (dt, *J* = 17.6, 7.0 Hz, 1H), 1.36 – 1.20 (m, 2H), 0.44 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 210.0, 142.8, 138.9, 136.2, 135.5, 135.40, 135.0, 134.4, 133.9, 133.6, 133.4, 132.8, 132.7, 132.2, 129.6, 128.72, 128.68, 128.1, 127.8, 127.7, 127.5, 127.1, 126.84, 126.82, 126.7, 126.5, 126.33, 126.27, 122.5, 44.8, 16.9, 13.1. HRMS (ESI) calcd for C₃₆H₃₀O₂SiNa [M+Na]+545.1913, found 545.1906.



Compound 6f was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and hexanoic anhydride (69 μ L, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded

6f (49 mg, 45%, 86% ee). $[\alpha]_D^{20}$ + 8.33 (c 0.93, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 10:90, flow: 1.0 mL/min, λ = 254 nm. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 7.2 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.67 – 7.63 (m, 2H), 7.53 (d, J = 8.8 Hz, 1H), 7.45 (t, J = 7.2 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.35 (d, J = 6.8 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 7.2 Hz, 2H), 6.97 (d, J = 7.6 Hz, 1H), 6.92 (t, J = 8.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 2H), 6.83 – 6.80 (m, 1H), 4.27 (s, 1H), 2.48 – 2.34 (m, 1H), 2.34 – 2.22 (m, 1H), 1.28 – 1.14 (m, 2H), 1.00 – 0.88 (m, 2H), 0.81 – 0.70 (m, 2H), 0.68 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 210.2, 142.8, 139.0, 136.2, 135.5, 135.0, 134.4, 133.9, 133.6, 133.4, 132.8, 132.7, 132.2, 129.6, 128.73, 128.68, 128.1, 127.8, 127.7, 127.5, 127.1, 126.9, 126.8, 126.7, 126.5, 126.4, 126.3, 122.5, 42.9, 34.8, 23.1, 22.1, 13.8. HRMS (ESI) calcd for C₃₈H₃₄O₂SiNa [M+Na]⁺ 573.2226, found 573.2219.



Compound 6g was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and 2-methoxyacetic anhydride (49 mg, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6g** (97 mg, 93%, 88% ee). $[\alpha]_D^{20}$ + 16.34 (c 0.98, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 254 nm. ¹**H NMR** (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.43 – 7.38 (m, 1H), 7.38 – 7.34 (m, 2H), 7.34 – 7.30 (m, 1H), 7.25 – 7.20 (m, 1H), 7.09 – 7.05 (m, 2H), 7.05 – 7.00 (m, 2H), 6.97 – 6.91 (m, 1H), 6.91 – 6.88 (m, 2H), 6.88 – 6.84 (m, 1H), 4.01 (d, *J* = 17.6 Hz, 1H), 3.72 (bs, 1H), 2.95 (s, 3H). ¹³C NMR (126 MHz, DMSO-d₆) δ 198.2, 143.2, 137.2, 136.3, 135.4, 133.7, 133.6, 133.5, 133.3, 133.2, 132.8, 132.34, 132.33, 131.4, 128.6, 128.2, 127.7, 127.4, 127.2, 127.0, 126.7, 126.6, 126.3, 126.2, 125.9, 125.8, 125.6, 125.5, 123.4, 75.4, 57.5. **HRMS (ESI)** calcd for C₃₅H₂₈O₃SiNa [M+Na]⁺ 547.1705, found 547.1699.



Compound 6h was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and cyclopropanecarboxylic anhydride (46 mg, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6h** (84 mg, 81%, 85% ee). $[\alpha]_D^{20}$ + 40.51 (c 0.98, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 254 nm. ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.72 – 7.68 (m, 2H), 7.68 – 7.64 (m,

2H), 7.63 (d, J = 8.5 Hz, 1H), 7.45 (t, J = 7.3 Hz, 1H), 7.40 – 7.38 (m, 1H), 7.38 – 7.33 (m, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.16 (d, J = 8.5 Hz, 1H), 7.02 – 6.97 (m, 2H), 6.94 (t, J = 7.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 1H), 6.79 (t, J = 7.5 Hz, 2H), 4.38 (s, 1H), 1.96 – 1.79 (m, 1H), 1.15 – 1.03 (m, 1H), 0.76 – 0.60 (m, 1H), 0.48 – 0.32 (m, 1H), 0.21 – 0.12 (m, 1H). ¹³C **NMR** (126 MHz, CDCl₃) δ 210.5, 143.2, 139.9, 136.3, 135.6, 135.5, 135.0, 134.3, 133.8, 133.5, 133.4, 133.1, 132.6, 132.4, 129.5, 128.8, 128.6, 128.0, 127.8, 127.7, 127.6, 127.1, 126.8, 126.6, 126.50, 126.46, 126.2, 122.7, 22.4, 13.5, 12.5. **HRMS** (**ESI**) calcd for C₃₆H₂₈O₂SiNa [M+Na]⁺ 543.1756, found 543.1759.



Compound 6i was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and acrylic anhydride (36 µL, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6i** (83 mg, 82%, 93% ee). $[\alpha]_D^{20}$ + 12.12 (c 0.96, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 15:85, flow: 1.0 mL/min, λ = 254 nm. ¹**H NMR** (500 MHz, CDCl₃) δ 7.89 – 7.85 (m, 1H), 7.84 (d, *J* = 4.5 Hz, 2H), 7.73 – 7.71 (m, 1H), 7.71 – 7.69 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.39 – 7.37 (m, 1H), 7.37 – 7.34 (m, 1H), 7.34 – 7.29 (m, 1H), 7.21 – 7.14 (m, 1H), 7.08 – 7.03 (m, 2H), 7.03 – 6.97 (m, 2H), 6.95 – 6.88 (m, 1H), 6.87 – 6.85 (m, 1H), 6.85 – 6.84 (m, 1H), 6.84 – 6.82 (m, 1H), 6.27 (dd, *J* = 17.5, 10.5 Hz, 1H), 5.68 (dd, *J* = 10.5, 1.0 Hz, 1H), 4.52 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 199.5, 142.3, 137.1, 136.7, 136.4, 135.72, 135.69, 135.0, 134.4, 133.9, 133.6, 132.8, 132.72, 132.69, 132.1, 129.5, 128.7, 128.3, 128.1, 127.8, 127.7, 127.6, 127.1, 127.0, 126.9, 126.6, 126.50, 126.45, 126.1, 123.5. **HRMS (ESI)** calcd for C₃₅H₂₆O₂SiNa [M+Na]⁺ 529.1600, found 529.1597.



Compound 6j was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and (*E*)-but-2-enoic anhydride (45 µL, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L1** (18.9 mg, 0.021 mmol, 10.5 mol%) afforded **6j** (104 mg, 99%, 85% ee). $[\alpha]_D^{20} - 0.41$ (c 1.00, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.85 (m, 1H), 7.85 – 7.80 (m, 2H), 7.76 – 7.72 (m, 2H), 7.70 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.41 – 7.38 (m, 2H), 7.38 – 7.34 (m, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.07 – 7.03 (m, 1H), 7.03 – 6.99 (m, 2H), 6.99 – 6.93 (m, 1H),

6.91 - 6.84 (m, 1H), 6.84 - 6.81 (m, 2H), 6.81 - 6.77 (m, 1H), 6.63 - 6.51 (m, 1H), 5.99 (d, J = 15.6 Hz, 1H), 5.18 (s, 1H), 1.56 (d, J = 6.8 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 200.3, 149.8, 142.3, 137.5, 136.6, 136.3, 135.9, 135.1, 134.4, 133.9, 133.6, 133.3, 132.68, 132.65, 132.3, 131.8, 129.5, 128.5, 128.2, 128.1, 127.7, 127.6, 127.5, 127.0, 126.8, 126.7, 126.64, 126.62, 126.43, 126.38, 125.8, 123.3, 18.3. **HRMS (ESI)** calcd for C₃₆H₂₈O₂SiNa [M+Na]⁺ 543.1756, found 543.1754.



Compound 6k was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and methacrylic anhydride (45 µL, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6k** (69 mg, 66%, 92% ee). $[\alpha]_D^{20}$ + 10.04 (c 1.00, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 230 nm. ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.84 (m, 1H), 7.84 – 7.80 (m, 2H), 7.80 – 7.75 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.41 – 7.35 (m, 2H), 7.32 – 7.27 (m, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.05 – 7.00 (m, 2H), 7.00 – 6.95 (m, 2H), 6.88 – 6.84 (m, 1H), 6.84 – 6.79 (m, 2H), 6.76 (d, *J* = 8.8 Hz, 1H), 5.70 (s, 1H), 5.61 (s, 1H), 5.37 (s, 1H), 1.59 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 203.3, 143.9, 142.1, 137.1, 136.8, 136.4, 136.1, 135.1, 134.4, 133.8, 133.6, 133.2, 132.65, 132.55, 132.1, 132.0, 129.5, 128.5, 128.0, 127.74, 127.70, 127.6, 127.4, 127.0, 126.9, 126.8, 126.6, 126.4, 126.3, 125.8, 123.7, 16.8 HRMS (ESI) calcd for C₃₆H₂₈O₂SiNa [M+Na]⁺ 543.1756, found 543.1758.



Compound 61 was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and 4-methylbenzoic anhydride (76 mg, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6l** (63 mg, 55%, 88% ee). $[\alpha]_D^{20} - 88.03$ (c 1.04, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 8.4 Hz, 1H), 7.82 – 7.79 (m, 1H), 7.79 – 7.76 (m, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.40 – 7.35 (m, 1H), 7.31 – 7.26 (m, 2H), 7.10 – 7.05 (m, 2H), 7.05 – 7.02 (m, 2H), 7.02 – 6.99 (m, 2H), 6.99 – 6.93 (m, 1H), 6.89 – 6.84 (m, 1H), 6.83 – 6.78 (m, 2H), 6.78 – 6.75 (m, 1H), 5.59 (s, 1H), 2.28 (s, 3H).¹³C NMR (100 MHz, CDCl₃) δ 200.3, 144.6, 142.0, 137.3, 136.82, 136.77, 136.0, 135.2, 134.5, 133.8, 133.7, 133.5, 133.4, 133.0, 132.5, 132.0, 130.8, 129.5, 128.7, 128.5, 127.84, 127.81, 127.7, 127.5, 126.9, 126.8, 126.6, 126.4, 126.3, 125.7, 124.1, 21.7. HRMS



Compound 6m was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and 4-fluorobenzoic anhydride (79 mg, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6m** (76 mg, 67%, 92% ee). $[\alpha]_D^{20} - 67.08$ (c 1.01, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 8.4 Hz, 1H), 7.78 – 7.76 (m, 1H), 7.76 – 7.74 (m, 2H), 7.74 – 7.70 (m, 2H), 7.66 – 7.64 (m, 1H), 7.64 – 7.59 (m, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.38 – 7.35 (m, 1H), 7.34 – 7.31 (m, 1H), 7.31 – 7.27 (m, 1H), 7.11 – 7.05 (m, 2H), 7.05 – 7.01 (m, 2H), 7.00 – 6.95 (m, 1H), 6.94 – 6.88 (m, 1H), 6.88 – 6.85 (m, 1H), 6.85 – 6.83 (m, 2H), 6.83 – 6.79 (m, 2H), 5.15 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 199.3, 165.8 (d, ¹ $J_{C-F} = 254.7$ Hz), 141.9, 137.5, 136.6, 136.4, 135.9, 135.1, 134.4, 133.7, 133.6, 133.5, 133.2, 133.1, 132.9, 132.7 (d, ⁴ $J_{C-F} = 2.8$ Hz), 132.5, 132.0, 129.5, 128.6, 128.0 (d, ³ $J_{C-F} = 4.7$ Hz), 127.8, 127.7, 127.6, 127.1, 127.0, 126.8, 126.6, 126.5, 126.4, 125.8, 123.8, 115.1 (d, ² $J_{C-F} = 21.8$ Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -103.9. HRMS (ESI) calcd for C₃₉H₂₇FO₂SiNa [M+Na]⁺ 597.1662, found 597.1672.



Compound 6n was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and 4-chlorobenzoic anhydride (89 mg, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6n** (114 mg, 96%, 88% ee). $[\alpha]_D^{20} - 98.06$ (c 1.00, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 274$ nm. ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.4 Hz, 1H), 7.78 – 7.75 (m, 2H), 7.75 – 7.74 (m, 2H), 7.74 – 7.71 (m, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.38 – 7.36 (m, 1H), 7.36 – 7.29 (m, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.12 – 7.06 (m, 2H), 7.04 (d, J = 7.6 Hz, 2H), 6.99 (t, J = 7.4 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.90 – 6.86 (m, 1H), 6.83 (t, J = 7.4 Hz, 2H), 4.97 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 199.5, 141.7, 139.8, 137.7, 136.5, 136.3, 135.9, 135.1, 134.7, 134.5, 133.7, 133.6, 133.5, 132.9, 132.5, 132.0, 131.7, 129.6, 128.6, 128.2, 128.00, 127.97, 127.8, 127.7, 127.6, 127.1, 126.8, 126.6, 126.5, 126.4, 125.9, 123.8. HRMS (ESI) calcd for C₃₉H₂₇ClO₂SiNa [M+Na]⁺ 613.1367, found 613.1360.



Compound 60 was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and 4-(trifluoromethyl)benzoic anhydride (109 mg, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **60** (109 mg, 87%, 87% ee). $[\alpha]_D^{20} - 61.55$ (c 1.05, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 254 nm. ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.72 (m, 2H), 7.72 – 7.68 (m, 2H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.38 – 7.36 (m, 2H), 7.35 – 7.33 (m, 2H), 7.33 – 7.30 (m, 1H), 7.14 – 7.10 (m, 1H), 7.10 – 7.06 (m, 1H), 7.06 – 7.03 (m, 2H), 7.03 – 6.98 (m, 2H), 6.98 – 6.95 (m, 1H), 6.85 (t, *J* = 7.5 Hz, 2H), 4.33 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 200.0, 142.0, 139.4, 138.3, 136.3, 136.2, 135.7, 135.0, 134.5, 133.84 (q, *J* = 32.6 Hz) 133.75, 133.6, 132.8, 132.6, 132.0, 130.0, 129.7, 128.8, 128.2, 128.0, 127.9, 127.7, 127.3, 127.2, 126.9, 126.8, 126.6, 126.5, 126.0, 124.7 (q, *J* = 3.7 Hz), 124.0, 121.2 (q, *J* = 273.3 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -63.2. HRMS (ESI) calcd for C₄₀H₂₇F₃O₂SiNa [M+Na]⁺ 647.1630, found 647.1639.



Compound 6p was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and 3-methylbenzoic anhydride (76 mg, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6p** (58 mg, 52%, 89% ee). $[\alpha]_D^{20} - 74.96$ (c 1.10, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 254 nm. ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, J = 8.5 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.82 – 7.80 (m, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.46 – 7.43 (m, 2H), 7.43 – 7.42 (m, 2H), 7.42 – 7.39 (m, 1H), 7.34 – 7.30 (m, 1H), 7.30 – 7.27 (m, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.14 – 7.11 (m, 1H), 7.11 – 7.09 (m, 1H), 7.09 – 7.07 (m, 1H), 7.07 – 7.04 (m, 2H), 6.99 (t, J = 7.5 Hz, 1H), 6.93 – 6.87 (m, 1H), 6.86 – 6.83 (m, 2H), 6.83 – 6.81 (m, 1H), 5.47 (bs, 1H), 2.21 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 201.2, 142.0, 137.6, 137.2, 137.0, 136.8, 136.3, 136.0, 135.1, 134.5, 134.2, 133.7, 133.6, 133.4, 132.8, 132.5, 132.0, 131.0, 129.5, 128.5, 127.84, 127.83, 127.78, 127.7, 127.5, 127.0, 126.80, 126.77, 126.7, 126.4, 126.3, 125.5, 124.0, 21.1. HRMS (ESI) calcd for C₄₀H₃₀O₂SiNa [M+Na]⁺ 593.1913, found 593.1918.



Compound 6q was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and **S4** (126 mg, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6q** (75 mg, 58%, 95% ee). $[\alpha]_D^{20} - 100.42$ (c 0.94, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 8.5 Hz, 1H), 7.76 – 7.73 (m, 2H), 7.73 – 7.72 (s, 2H), 7.72 – 7.70 (m, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 – 7.38 (m, 2H), 7.38 – 7.34 (m, 2H), 7.34 – 7.30 (m, 1H), 7.15 (t, J = 7.8 Hz, 1H), 7.07 – 7.04 (m, 1H), 7.04 – 7.01 (m, 2H), 6.99 (d, J = 7.5 Hz, 1H), 6.96 (t, J = 7.8 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 6.88 – 6.84 (m, 2H), 6.84 -6.80 (m, 1H), 4.64 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 198.4, 161.8 (d, ¹ $J_{C-F} = 255.1$ Hz), 141.8, 137.8, 136.4, 136.1, 135.91, 135.90, 135.8, 135.0, 134.5, 133.99, 133.96, 133.6 (d, ³ $J_{C-F} = 3.0$ Hz), 127.21, 127.19, 126.9, 126.8, 126.6, 126.5, 126.0, 123.5, 115.9 (d, ² $_{J_{C-F}} = 23.2$ Hz), 109.0 (d, ² $_{J_{C-F}} = 21.9$ Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ - 98.8. HRMS (ESI) calcd for C₃₉H₂₆BrFO₂SiNa [M+Na]⁺ 675.0767, found 675.0760.



Compound 6r was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and **S5** (90 mg, 0.30 mmol) with $[Rh(CO)_2CI]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6r** (102 mg, 86%, 94% ee). $[\alpha]_D^{20} - 61.38$ (c 0.99, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, J = 8.0 Hz, 1H), 7.78 – 7.75 (m, 1H), 7.75 – 7.73 (m, 2H), 7.73 – 7.68 (m, 2H), 7.61 (d, J = 8.5 Hz, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.39 – 7.36 (m, 2H), 7.36 – 7.33 (m, 2H), 7.33 – 7.30 (m, 1H), 7.14 – 7.09 (m, 1H), 7.07 – 7.04 (m, 2H), 7.04 – 7.02 (m, 1H), 7.02 – 6.98 (m, 1H), 6.98 – 6.93 (m, 1H), 6.93 – 6.88 (m, 2H), 6.84 (t, J = 7.5 Hz, 2H), 4.67 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 198.3, 153.6 (dd, $J_{C-F} = 258.8$, 13.1 Hz), 149.7 (dd, $J_{C-F} = 251.6$, 10.3 Hz), 141.8, 137.8, 136.3, 136.0, 135.8, 135.1, 134.5, 133.7, 133.63, 133.60, 133.4, 132.8, 132.5, 132.0, 129.6, 128.7, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5 (dd, $J_{C-F} = 7.3, 3.3$ Hz), 127.22, 127.16, 126.9, 126.8, 126.53, 126.49, 125.9, 123.6, 119.2 (dd, $J_{C-F} = 16.8$ Hz), 116.8 (d, $^2J_{C-F} = 17.9$ Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ - 128.8 (d), - 136.2 (d). HRMS (ESI) calcd for C₃₉H₂₆F₂O₂SiNa [M+Na]⁺ 615.1568, found 615.1575.



Compound 6s was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and 3,4,5-trimethoxybenzoic anhydride (122 mg, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6s** (69 mg, 53%, 87% ee). $[\alpha]_D^{20} - 114.06$ (c 1.10, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 230$ nm. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.0 Hz, 1H), 7.81 – 7.77 (m, 2H), 7.77 – 7.75 (m, 2H), 7.75 – 7.73 (m, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.49 – 7.35 (m, 1H), 7.39 – 7.29 (m, 2H), 7.12 – 7.07 (m, 2H), 7.07 – 7.02 (m, 2H), 7.02 – 6.97 (m, 1H), 6.93 – 6.88 (m, 2H), 6.88 – 6. 85 (m, 2H), 6.85 – 6.80 (m, 2H), 5.30 (s, 1H), 3.82 (s, 3H), 3.72 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 199.7, 152.3, 142.7, 142.0, 137.4, 136.7, 136.6, 135.9, 135.1, 134.5, 133.8, 133.6, 133.4, 132.8, 132.6, 132.0, 131.6, 129.5, 128.6, 128.0, 127.8, 127.73, 127.67, 127.6, 127.0, 126.9, 126.8, 126.5, 126.4, 125.7, 123.9, 108.1, 60.8, 56.0. HRMS (ESI) calcd for C₄₂H₃₅O₅Si [M+H]⁺ 647.2254, found 647.2249.



Compound 6t was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and 2-naphthoic anhydride (98 mg, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6t** (108 mg, 89%, 90% ee). $[\alpha]_D^{20} - 260.01$ (c 1.10, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹**H NMR** (400 MHz, CDCl₃) δ 8.11 (s, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.80 – 7.76 (m, 2H), 7.76 – 7.72 (m, 2H), 7.72 – 7.70 (m, 1H), 7.70 – 7.64 (m, 2H), 7.64 – 7.58 (m, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.44 – 7.41 (m, 2H), 7.41 – 7.37 (m, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 2H), 7.01 (t, J = 8.2 Hz, 2H), 6.92 (t, J = 7.6 Hz, 1H), 6.89 – 6.87 (m, 1H), 6.87 – 6.80 (m, 2H), 5.47 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 200.7, 142.0, 137.5, 136.9, 136.7, 136.0, 135.6, 135.1, 134.5, 133.8, 133.7, 133.62, 133.60, 133.5, 132.9, 132.5, 132.0, 131.7, 129.6, 129.5, 128.8, 128.6, 128.0, 127.9, 127.83, 127.78, 127.7, 127.61, 127.56, 127.0, 126.9, 126.8, 126.6, 126.53, 126.50, 126.3, 125.7, 124.9, 124.1. **HRMS (ESI)** calcd for C₄₃H₃₀O₂SiNa [M+Na]⁺ 629.1913, found 629.1911.



Compound 6u was prepared following the Typical Procedure F

The reaction of **4b** (87 mg, 0.20 mmol) and **S3** (92 mg, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (14.6 mg, 0.013 mmol, 6.25 mol%) afforded **6u** (75 mg, 63%, 90% ee). $[\alpha]_D^{20} - 156.59$ (c 0.98, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, J = 10.5 Hz, 2H), 7.82 (d, J = 4.5 Hz, 2H), 7.75 (d, J = 9.0 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.70 – 7.65 (m, 2H), 7.65 – 7.61 (m, 1H), 7.57 (d, J = 9.0 Hz, 2H), 7.47 – 7.37 (m, 3H), 7.32 (t, J = 9.0 Hz, 2H), 7.22 (t, J = 7.0 Hz, 1H), 7.15 (d, J = 8.5 Hz, 1H), 7.10 – 7.06 (m, 2H), 7.03 (d, J = 8.0 Hz, 1H), 6.99 (t, J = 7.0 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.88 – 6.85 (m, 1H), 6.85 – 6.80 (m, 2H), 6.66 (s, 1H), 5.64 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 200.4, 157.6, 146.3, 142.0, 137.2, 137.1, 136.8, 136.0, 135.2, 134.5, 133.7, 133.6, 133.4, 132.9, 132.4, 132.0, 131.7, 129.5, 128.5, 127.83, 127.79, 127.77, 127.7, 127.5, 127.04, 126.95, 126.9, 126.8, 126.6, 126.5, 126.3, 125.6, 125.5, 124.0, 111.0, 107.1. HRMS (ESI) calcd for C₄₁H₂₈O₃SiNa [M+Na]⁺ 619.1705, found 619.1706.



Compound 6v was prepared following the Typical Procedure F

The reaction of **4a** (62 mg, 0.20 mmol) and propionic anhydride (38 µL, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L1** (18.9 mg, 0.021 mmol, 10.5 mol%) afforded **6v** (71 mg, 92%, 85% ee). $[\alpha]_D^{20} + 4.20$ (c 0.98, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 8:92, flow: 1.0 mL/min, λ = 230 nm. ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.49 – 7.43 (m, 1H), 7.30 – 7.26 (m, 1H), 7.26 – 7.21 (m, 1H), 7.17 – 7.10 (m, 2H), 3.22 (s, 1H), 2.48 (dq, J = 18.5, 7.0 Hz, 1H), 2.55 – 2.40 (dq, J = 18.5, 7.0 Hz, 1H), 0.74 (t, J = 7.0 Hz, 3H), 0.22 (s, 3H), -0.53 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 209.3, 141.3, 138.7, 138.1, 136.5, 133.9, 133.7, 133.5, 132.6, 130.4, 128.6, 128.1, 128.0, 127.9, 127.4, 127.3, 127.0, 126.5, 126.4, 126.2, 123.4, 36.0, 7.9, 0.7, 0.6. HRMS (ESI) calcd for C₂₅H₂₄O₂SiNa [M+Na]⁺ 407.1443, found 407.1455.



Compound 6w was prepared following the Typical Procedure F

The reaction of **4a** (62 mg, 0.20 mmol) and butyric anhydride (38 µL, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L1** (18.9 mg, 0.021 mmol, 10.5 mol%) afforded **6w** (43 mg, 53%, 90% ee). $[\alpha]_D^{20} + 0.29$ (c 1.13, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 4:96, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, J = 8.4 Hz, 1H), 7.95 (t, J = 7.4 Hz, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.49 – 7.42 (m, 1H), 7.32 – 7.27 (m, 1H), 7.25 – 7.21 (m, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 3.29 (s, 1H), 2.48 – 2.32 (m, 1H), 2.28 – 2.09 (m, 1H), 1.30 – 1.20 (m, 2H), 0.41 (t, J = 7.4 Hz, 3H), 0.24 (s, 3H), -0.56 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 209.3, 141.1, 139.2, 138.3, 136.2, 133.80, 133.76, 133.5, 132.6, 130.4, 128.6, 128.1, 128.0, 127.8, 127.4, 127.3, 127.0, 126.5, 126.34, 126.30, 123.2, 44.7, 16.9, 13.1, 0.68, 0.65. HRMS (ESI) calcd for C₂₆H₂₆O₂SiNa [M+Na]⁺ 421.1600, found 407.1606.



Compound 6x was prepared following the Typical Procedure F

The reaction of **4g** (94 mg, 0.20 mmol) and acetic anhydride (28 µL, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (24.5 mg, 0.021 mmol, 10.5 mol%) afforded **6x** (99 mg, 96%, 91% ee). $[\alpha]_D^{20} + 24.07$ (c 0.97, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.0, 1H), 7.89 (d, J = 8.4, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.61 – 7.56 (m, 2H), 7.50 – 7.44 (m, 1H), 7.40 – 7.32 (m, 1H), 7.25 – 7.19 (m, 1H), 7.09 – 7.05 (m, 2H), 7.04 – 7.02 (m, 1H), 7.02 – 6.96 (m, 2H), 6.96 – 6.93 (m, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.56 – 6.47 (m, 2H), 4.12 (s, 1H), 2.06 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 207.0, 164.1 (d, ¹*J*_{C-F} = 247.6 Hz), 163.4 (d, ¹*J*_{C-F} = 247.6 Hz), 143.0, 138.3, 136.9 (d, ³*J*_{C-F} = 7.6 Hz), 135.9, 135.4 (d, ³*J*_{C-F} = 7.6 Hz), 134.6, 134.0, 133.7, 132.7, 131.9, 131.4 (d, ⁴*J*_{C-F} = 3.8 Hz), 129.8 (d, ⁴*J*_{C-F} = 3.6 Hz), 128.9, 128.2, 127.8, 127.6, 127.3, 127.1, 127.0, 126.7, 126.6, 126.1, 122.7, 115.0 (d, ²*J*_{C-F} = 19.6 Hz), 114.1 (d, ²*J*_{C-F} = 19.8 Hz), 30.6. ¹⁹F NMR (376 MHz, CDCl₃) δ - 110.7, -111.8. HRMS (ESI) calcd for C₃₄H₂₄F₂O₂SiNa [M+Na]⁺ 553.1411, found 553.1414.



Compound 6y was prepared following the Typical Procedure F

The reaction of **4c** (93 mg, 0.20 mmol) and acetic anhydride (28 µL, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (24.5 mg, 0.021 mmol, 10.5 mol%) afforded **6y** (81 mg, 78%, 92% ee). $[\alpha]_D^{20}$ + 4.23 (c 1.07, CH₂Cl₂). HPLC conditions: Chiralcel 0AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 254 nm. ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.88 (m, 2H), 7.88 – 7.83 (m, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.67 (dd, *J* = 8.4 Hz, 1.4 Hz, 1H), 7.51 (d, *J* = 6.8 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.38 – 7.32 (m, 1H), 7.25 – 7.19 (m, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 1H), 7.00 – 6.95 (m, 1H), 6.95 – 6.92 (m, 2H), 6.92 – 6.87 (m, 1H), 6.69 (d, *J* = 7.2 Hz, 2H), 3.33 (s, 1H), 2.36 (s, 3H), 2.17 (s, 3H), 1.98 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 205.6, 143.1, 139.5, 138.5, 138.0, 136.7, 135.3, 134.9, 133.8, 133.7, 132.93, 132.87, 132.29, 132.26, 131.0, 128.6, 128.5, 128.14, 128.10, 127.8, 127.5, 127.0, 126.9, 126.7, 126.5, 126.4, 126.2, 123.3, 30.4, 21.6, 21.4. HRMS (ESI) calcd for C₃₆H₃₀O₂SiNa [M+Na]⁺ 545.1913, found 545.1921.



Compound 6z was prepared following the Typical Procedure F

The reaction of **4h** (94 mg, 0.20 mmol) and acetic anhydride (28 µL, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (24.5 mg, 0.021 mmol, 10.5 mol%) afforded **6z** (100 mg, 94%, 94% ee). $[\alpha]_D^{20} + 20.87$ (c 0.99, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹**H NMR** (400 MHz, CDCl₃) δ 7.90 (dd, J = 8.6, 2.4 Hz, 2H), 7.86 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 5.6 Hz, 1H), 7.60 (d, J = 5.6 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.46 – 7.41 (m, 1H), 7.39 – 7.35 (m, 1H), 7.35 – 7.30 (m, 2H), 7.25 – 7.20 (m, 1H), 7.13 – 7.08 (m, 1H), 7.08 – 7.04 (m, 1H), 7.04 -6.98 (m, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.81 – 6.74 (m, 2H), 6.65 – 6.57 (m, 2H), 4.42 (s, 1H), 2.08 (s, 3H). ¹³C **NMR** (100 MHz, CDCl₃) δ 207.4, 162.5 (d, ¹J_{C-F} = 246.9 Hz), 161.6 (d, ¹J_{C-F} = 246.1 Hz) 138.5 (d, ³J_{C-F} = 4.3 Hz), 138.4, 136.8 (d, ³J_{C-F} = 4.3 Hz), 135.7, 134.1, 133.6, 132.7, 132.7, 131.9, 130.4 (d, ⁴J_{C-F} = 2.9 Hz), 129.74, 129.68, 129.02, 128.97 (d, ⁴J_{C-F} = 2.9 Hz), 128.8, 128.7, 128.3, 127.7, 127.6, 127.5, 127.2, 127.0, 126.72, 126.68, 126.1, 122.6, 121.2 (d, ²J_{C-F} = 19 Hz), 119.6 (d, ²J_{C-F} = 19.2 Hz), 116.8 (d, ²J_{C-F} = 20.8 Hz), 115.9 (d, ²J_{C-F} = 21 Hz), 30.7. ¹⁹F NMR (376 MHz, CDCl₃) δ - 113.2, - 113.8. **HRMS (ESI)** calcd for C₃₄H₂₄F₂O₂SiNa [M+Na]⁺ 553.1411, found 553.1411.



Compound 6aa was prepared following the Typical Procedure F

The reaction of **4f** (92 mg, 0.20 mmol) and acetic anhydride (28 µL, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (24.5 mg, 0.021 mmol, 10.5 mol%) afforded **6aa** (101 mg, 96%, 92% ee). $[\alpha]_D^{20}$ + 20.99 (c 1.05, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 254 nm. ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.87 (m, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.44 – 7.39 (m, 2H), 7.34 – 7.29 (m, 1H), 7.24 – 7.20 (m, 2H), 7.20 – 7.15 (m, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.92 – 6.86 (m, 2H), 6.83 – 6.78 (m, 2H), 6.78 – 6.75 (m, 1H), 3.53 (s, 1H), 2.32 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 205.8, 143.2, 138.0, 137.0, 136.6, 136.1, 135.6, 135.4, 135.2, 134.2, 134.1, 133.9, 133.8, 132.9, 132.8, 132.3, 132.0, 130.9, 130.4, 129.7, 128.7, 128.2, 127.9, 127.6, 127.4, 127.10, 127.08, 126.9, 126.7, 126.43, 126.39, 126.2, 123.1, 30.5, 21.6, 21.4. HRMS (ESI) calcd for C₃₆H₃₀O₂SiNa [M+Na]⁺ 545.1913, found 545.1913.



Compound 6bb was prepared following the Typical Procedure F

The reaction of **4c** (92 mg, 0.20 mmol) and 4-fluorobenzoic anhydride (79 mg, 0.30 mmol) with [Rh(CO)₂Cl]₂ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (24.5 mg, 0.021 mmol, 10.5 mol%) afforded **6bb** (78 mg, 65%, 91% ee). $[\alpha]_D^{20} - 65.65$ (c 1.10, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹H NMR (500 MHz, CDCl₃) δ 7.89 (d, J = 8.5 Hz, 1H), 7.76 – 7.74 (m, 1H), 7.74 – 7.71 (m, 2H), 7.67 – 7.64 (m, 2H), 7.64 – 7.63 (m, 1H), 7.63 – 7.62 (m, 1H), 7.62 – 7.59 (m, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.33 – 7.29 (m, 1H), 7.19 (d, J = 7.5 Hz, 2H), 7.11 – 7.02 (m, 2H), 6.96 – 6.92 (m, 1H), 6.92 – 6.90 (m, 2H), 6.88 – 6.85 (m, 1H), 6.85 – 6.80 (m, 2H), 6.62 (d, J = 7.5 Hz, 2H), 4.99 (s, 1H), 2.37 (s, 3H), 2.15 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 199.0, 165.7 (d, ¹ $J_{C-F} = 254.6$ Hz), 141.8, 139.4, 138.1, 137.7, 136.4 (d, ³ $J_{C-F} = 10.8$ Hz), 135.2, 133.7, 133.6, 133.5, 133.1, 133.01, 133.00, 132.97, 132.80, 132.77, 132.5, 132.1, 131.2, 128.5, 127.9 (d, ⁴ $J_{C-F} = 3.5$ Hz), 127.8, 127.7, 127.5, 127.0, 126.7, 126.6, 126.5, 126.3, 125.7, 123.9, 115.0 (d, ² $J_{C-F} = 22.1$ Hz), 21.5, 21.3. ¹⁹F NMR (471 MHz, CDCl₃) δ -104.2. HRMS (ESI) calcd for C₄₁H₃₁FO₂SiNa [M+Na]⁺ 625.1975, found 625.1960.



Compound 6cc was prepared following the Typical Procedure F

The reaction of **4d** (73 mg, 0.20 mmol) and acetic anhydride (28 µL, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (24.5 mg, 0.021 mmol, 10.5 mol%) afforded **6cc** (70 mg, 83%, 88% ee). $[\alpha]_D^{20}$ + 14.03 (c 1.00, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 254 nm. ¹**H NMR** (400 MHz, CDCl₃) δ 7.61 – 7.57 (m, 2H), 7.45 – 7.41 (m, 1H), 7.40 – 7.37 (m, 1H), 7.37 – 7.34 (m, 2H), 7.34 – 7.33 (m, 2H), 7.33 – 7.31 (m, 2H), 7.31 – 7.30 (m, 1H), 7.30 – 7.27 (m, 1H), 7.25 – 7.22 (m, 2H), 7.22 – 7.19 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 3.21 (s, 1H), 2.09 (s, 3H), 1.92 (s, 3H), 1.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 205.0, 145.0, 139.6, 138.8, 138.1, 136.2, 135.7, 135.4, 135.0, 134.7, 134.54, 134.49, 132.8, 131.7, 129.6, 129.3, 127.7, 127.6, 127.4, 126.7, 124.9, 29.7, 19.9, 19.6. **HRMS (ESI)** calcd for C₂₈H₂₆FO₂SiNa [M+Na]⁺ 445.1600, found 445.1602.



Compound 6dd was prepared following the Typical Procedure F

The reaction of **4d** (73 mg, 0.20 mmol) and benzoic anhydride (68 mg, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (24.5 mg, 0.021 mmol, 10.5 mol%) afforded **6dd** (68 mg, 70%, 85% ee). $[\alpha]_D^{20} - 72.17$ (c 1.00, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹H NMR (500 MHz, CDCl₃) δ 7.81 – 7.77 (m, 2H), 7.75 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.39 – 7.38 (m, 2H), 7.38 – 7.37 (m, 2H), 7.37 – 7.35 (m, 1H), 7.35 – 7.33 (m, 1H), 7.32 – 7.28 (m, 1H), 7.28 – 7.24 (m, 2H), 7.21 (t, J = 7.5 Hz, 2H), 7.10 (t, J = 7.5 Hz, 1H), 7.09 – 7.05 (m, 1H), 7.04 – 6.99 (m, 1H), 5.41 (s, 1H), 1.75 (s, 3H), 1.34 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 200.5, 143.7, 139.6, 138.4, 137.8, 137.1, 136.5, 136.4, 135.6, 135.24, 135.17, 134.5, 133.6, 132.2, 131.6, 130.8, 129.4, 129.1, 128.2, 127.6, 127.2, 126.7, 126.5, 125.7, 20.1, 19.5. HRMS (ESI) calcd for C_{33H28}O₂SiNa [M+Na]+507.1756, found 507.1763.



Compound 6ee was prepared following the Typical Procedure F

The reaction of **4d** (73 mg, 0.20 mmol) and **S5** (89 mg, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (24.5 mg, 0.021 mmol, 10.5 mol%) afforded **6ee** (69 mg, 66%, 88% ee). $[\alpha]_D^{20} - 50.35$ (c 0.90, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 6.4 Hz, 2H), 7.53 – 7.45 (m, 1H), 7.43 – 7.37 (m, 1H), 7.33 – 7.28 (m, 2H), 7.28 – 7.26 (m, 2H), 7.26 – 7.24 (m, 2H), 7.24 – 7.19 (m, 2H), 7.18 – 7.16 (m, 1H), 7.16 – 7.10 (m, 2H), 7.10 – 7.05 (m, 2H), 7.05 – 7.02 (m, 1H), 7.01 (d, J = 7.6 Hz, 1H), 4.60 (s, 1H), 1.70 (s, 3H), 1.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 197.4, 153.9 (dd, $J_{C-F} = 256.9$, 12.8 Hz), 150.0 (dd, $J_{C-F} = 249.7$, 12.9 Hz), 143.5, 139.9, 138.7, 136.9, 136.7, 135.9, 135.4, 135.3, 135.1, 134.6, 134.5, 133.69, 133.65, 133.6, 132.7, 131.6, 129.5, 129.2, 128.0 (d, $J_{C-F} = 3.6$ Hz), 127.9 (d, $J_{C-F} = 3.1$ Hz), 127.6, 127.3, 126.8, 126.7, 125.6, 119.5 (d, $J_{C-F} = 18.0$ Hz), 117.1 (d, $J_{C-F} = 17.6$ Hz), 20.1, 19.5. ¹⁹F NMR (376 MHz, CDCl₃) δ - 128.5, - 135.8. HRMS (ESI) calcd for C₃₃H₂₆F₂O₂SiNa [M+Na]⁺ 543.1568, found 543.1579.



Compound 6E was prepared following the Typical Procedure F

The reaction of **4e** (78 mg, 0.20 mmol) and acetic anhydride (28 µL, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L7** (24.5 mg, 0.021 mmol, 10.5 mol%) afforded **6ff** (40 mg, 45%, 87% ee). $[\alpha]_D^{20}$ + 35.74 (c 0.77, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 230 nm. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.42 – 7.37 (m 1H), 7.36 – 7.34 (m, 1H), 7.34 – 7.31 (m, 2H), 7.31 – 7.27 (m, 2H), 7.27 – 7.26 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 3.42 (s, 1H), 2.30 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.82 (s, 3H), 1.27 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 205.7, 145.5, 140.6, 139.0, 138.8, 138.1, 136.7, 136.4, 135.8, 135.0, 134.6, 134.4, 134.3, 132.4, 129.4, 129.1, 128.9, 128.3, 127.6, 127.2, 124.5, 29.9, 20.8, 20.7, 16.1, 16.0. HRMS (ESI) calcd for C₃₀H₃₀O₂SiNa [M+Na]⁺ 473.1913, found 473.1918.



Compound S6 was prepared following the Typical Procedure F

The reaction of **4a** (62 mg, 0.20 mmol) and benzoic anhydride (68 mg, 0.30 mmol) with $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), **L1** (18.9 mg, 0.021 mmol, 10.5 mol%) afforded **S6** (43 mg, 54%, 75% ee). $[\alpha]_D^{20}$ + 64.22 (c 1.07, CH₂Cl₂). HPLC conditions: Chiralcel AD-H,

isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 254 nm. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.60 (m, 1H), 7.60 – 7.59 (m, 1H), 7.58 – 7.57 (m, 1H), 7.56 – 7.52 (m, 1H), 7.38 – 7.34 (m, 1H), 7.34 – 7.31 (m, 1H), 7.31 – 7.28 (m, 1H), 7.23 – 7.20 (m, 1H), 7.20 – 7.16 (m, 2H), 7.16 – 7.12 (m, 1H), 7.11 – 7.05 (m, 1H), 4.24 (s, 1H), 0.40 (s, 3H), -0.59 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 200.1, 140.3, 138.7, 138.2, 136.9, 136.4, 133.8, 133.6, 133.2, 132.2, 130.3, 130.1, 128.1, 127.9, 127.8, 127.7, 127.4, 127.3, 127.0, 126.6, 126.1, 125.7, 124.7, 0.83, 0.75. HRMS (ESI) calcd for C₂₉H₂₄O₂SiNa [M+Na]⁺ 455.1443, found 455.1440.

Control Experiments



Under nitrogen atmosphere, to a Schleck tube was added $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol, 2.5 mol%), L7 (24.5 mg, 0.021 mmol, 10.5 mol%) and dioxane (2 mL) at room temperature and was stirred for 30 minutes. The solution was transfer via cannula carefully to another Schlenk tube charged with **4i** (75 mg, 0.200 mmol, 1.0 equiv), acetic anhydride (28 µL, 0.300 mmol, 1.5 equiv), Na₂CO₃ (6.4 mg, 0.060 mmol, 30 mol%) and dioxane (2 mL). The tube was capped with a screw cap and stirred at 70 °C for 24 h. After being cooled to room temperature, the mixture was filtered through Celite and the filtrate was concentrated in vacuum and purified by flash column chromatography (PE/EtOAc = 90:10) on silica gel to afford a mixture of **6gg** and **6gg'** (85 mg, 99%). A small amount of **6gg** and **6gg'** could be separated by preparative TLC, and the related configuration was determined by single crystal X-ray diffraction analysis. The ee value was determined by the mixture of **6gg** and **6gg'**.

6gg: $[\alpha]_D^{20}$ + 7.17 (c 1.06, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 10:90, flow: 1.0 mL/min, λ = 254 nm. ¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.36 – 7.30 (m, 1H), 7.23 – 7.18 (m, 1H), 7.04 – 7.00 (m, 1H), 7.00 – 6.97 (m, 1H), 6.97 – 6.94 (m, 1H), 6.92 – 6.88 (m, 2H), 6.88 – 6.86 (m, 1H), 6.86 – 6.84 (m, 1H), 6.84 – 6.80 (m, 1H), 3.33 (s, 1H), 1.92 (s, 3H), 0.40 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 205.6, 142.4, 138.0, 136.74, 136.69, 136.2, 133.93, 133.89, 133.1, 132.82, 132.79, 130.9, 128.70, 128.69, 128.1, 127.9, 127.6, 127.5, 127.2,

127.0, 126.7, 126.6, 126.5, 126.1, 123.4, 30.4, 0.5. **HRMS (ESI)** calcd for C₂₉H₂₄O₂SiNa [M+Na]⁺ 455.1443, found 455.1440.

6gg': $[\alpha]_D^{20}$ + 55.71 (c 0.42, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 10:90, flow: 1.0 mL/min, λ = 254 nm. ¹**H NMR** (500 MHz, CDCl₃) δ 8.03 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.48 – 7.45 (m, 1H), 7.45 – 7.41 (m, 2H), 7.37 – 7.32 (m, 1H), 7.32 – 7.27 (m, 2H), 7.27 – 7.26 (m, 1H), 7.25 – 7.20 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 3.28 (s, 1H), 1.98 (s, 3H), -0.27 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 205.4, 142.3, 138.3, 137.7, 137.0, 136.5, 134.1, 133.8, 133.5, 132.7, 131.6, 129.4, 128.7, 128.2, 128.00, 127.98, 127.7, 127.6, 127.3, 127.0, 126.7, 126.5, 126.1, 123.7, 30.4, 0.7. HRMS (ESI) calcd for C₂₉H₂₄O₂SiNa [M+Na]⁺ 455.1443, found 455.1440.



Under nitrogen atmosphere, a Schlenk tube was sequentially charged with Cs₂CO₃ (3.0 equiv), benzoic acid (18.0 mg, 0.150 mmol, 1.5 equiv), 4-fluorobenzoyl chloride (18 µL, 0.150 mmol, 1.5 equiv) and 1,4-dioxane (2.0 mL). After stirred at room temperature for 2 h, the mixture was filtered by syringe and transferred to a Schlenk tubu charged with [Rh(CO)₂Cl]₂ (1.0 mg, 0.0025 mmol, 2.5 mol%), **L7** (7.3 mg, 0.0625 mmol, 6.25 mol%) and Cs₂CO₃ (10 mg, 0.030 mmol, 30 mol%). The mixture was stirred at 70 °C for 24 hour. After being cooled to room temperature, the mixture was filtered through Celite and the filtrate was concentrated in vacuum and purified by flash column chromatography (PE/EtOAc = 90:10) on silica gel to afford a mixture of **6m** and **6b** (46.6 mg, 83%). The ee value was determined by the mixture of **6m** and **6b**. HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 254 nm. The spectra data was listed as followed.



Under nitrogen atmosphere, a Schlenk tube was sequentially charged with Cs_2CO_3 (3.0 equiv), benzoic acid (18.0 mg, 0.150 mmol, 1.5 equiv), Acetyl chloride (11 µL, 0.150 mmol, 1.5 equiv) and 1,4-dioxane (2.0 mL). After stirred at room temperature for 2 h, the mixture was filtered by syringe and transferred to a Schlenk tubu charged with $[Rh(CO)_2Cl]_2$ (1.0 mg, 0.0025 mmol, 2.5 mol%), **L7** (7.3 mg, 0.0625 mmol, 6.25 mol%) and Cs_2CO_3 (10 mg, 0.030 mmol, 30 mol%). The mixture was stirred at 70 °C for 24 hour. After being cooled to room temperature, the mixture was filtered through Celite and the filtrate was concentrated in vacuum and purified by flash column

chromatography (PE/EtOAc = 90:10) on silica gel to afford **6c** (6.0 mg, 11%, 92% ee) and **6b** (36.4 mg, 74%, 93% ee). **6c** HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, $\lambda = 254$ nm. **6b** HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 15:85, flow: 1.0 mL/min, $\lambda = 254$ nm.



Under nitrogen atmosphere, to a Schleck tube was added $[Rh(CO)_2Cl]_2$ (1.0 mg, 0.0025 mmol, 2.5 mol%), L7 (12.2 mg, 0.0105 mmol, 10.5 mol%) and dioxane (2 mL) at room temperature and was stirred for 30 minutes. The solution was transfer via cannula carefully to another Schlenk tube charged with **4a** (31 mg, 0.100 mmol, 1.0 equiv), **4b** (44 mg, 0.100 mmol, 1.0 equiv), acetic anhydride (5 μ L, 0.050 mmol, 0.5 equiv), Na₂CO₃ (3.2 mg, 0.030 mmol, 30 mol%). The tube was capped with a screw cap and stirred at 70 °C for 24 h. After being cooled to room temperature, the mixture was filtered through Celite and the filtrate was concentrated in vacuum and purified by flash column chromatography (PE/EtOAc = 90:10) on silica gel to afford **6a** (9.4 mg, 51%, 90% ee) and **6c** (8.4 mg, 34%, 88% ee). **6a** HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 10:90, flow: 1.0 mL/min, λ = 254 nm.

Procedure for the synthesis of Hydroxysilanol 7



To the mixture of **6b** (28 mg, 0.05 mmol) in THF (2.0 mL) was added PhMgCl (75 μ L, 0.15 mmol, 2.0 M in THF) at room temperature. Then the mixture was stirred over night before being quenched with saturated NH₄Cl (aq.). The mixture was extracted with ethyl acetate (5 mL*3), and the combined organic layer was washed with brine, dried over Na₂SO₄, filtered, concentrated and purified by flash column chromatography (PE/EtOAc/DCM = 80:10:10) on silica gel to afford **7** (30 mg, 94%, 91% ee). $[\alpha]_D^{20}$ + 110.45 (c 0.92, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 10:90, flow: 1.0 mL/min, λ = 254 nm. ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.73 (m, 2H), 7.73 – 7.70 (m, 2H), 7.70 – 7.68 (m, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.34 – 7.31 (m, 2H), 7.31 – 7.30 (m, 2H), 7.30 – 7.28 (m, 1H), 7.24 – 7.19 (m, 2H), 7.19 – 7.16 (m, 1H), 7.12 – 7.09 (m, 2H), 7.09 –

7.07 (m, 1H), 7.00 – 6.96 (m, 1H), 6.96 – 6.93 (m, 2H), 6.93 – 6.90 (m, 2H), 6.85 (d, J = 7.5 Hz, 2H), 6.69 (t, J = 7.8 Hz, 1H), 6.58 (d, J = 8.5 Hz, 1H), 6.52 (t, J = 7.5 Hz, 1H), 6.25 (d, J = 8.5 Hz, 1H), 3.24 (s, 1H), 3.21 (s, 1H). ¹³**C** NMR (125 MHz, CDCl₃) δ 147.2, 144.1, 143.9, 142.0, 136.1, 136.0, 135.3, 134.8, 134.2, 133.8, 133.73, 133.65, 132.0, 131.9, 131.6, 129.9, 129.0, 128.7, 128.3, 128.2, 128.1, 127.9, 127.6, 127.4, 127.30, 127.25, 127.2, 127.1, 126.99, 126.95, 126.9, 126.6, 126.4, 126.1, 125.9, 125.4, 84.7. **HRMS (ESI)** calcd for C₄₅H₃₅O₂Si [M+H]⁺ 635.2406, found 635.2407.

Procedure for the synthesis of Bromides 9



To the Flask tube charged with methyltriphenylphosphonium bromide (1.79 g, 5.00 mmol) in THF (8 mL) was added nBuLi (2.10 mL, 5.00 mmol, 2.4 M in hexanes) dropwise at 0 °C. Then the mixture was allowed to warm to room temperature and stirred for 1 hour. A mixture of 6b (0.278 g, 0.50 mmol) in THF (2 mL) was added slowly at room temperature and the mixture was stirred at 70 °C for 12 hours. After being cooled to room temperature, the reaction was quenched with water (5 mL) and extracted with ethyl acetate (5 mL*3), and the combined organic layer was washed with brine, dried over Na₂SO₄, filtered, concentrated and purified by flash column chromatography (PE/EtOAc = 90:10) on silica gel to afford 8 (0.259 g, 93%, 91% ee). $[\alpha]_{D}^{20}$ + 9.89 (c 0.93, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 10:90, flow: 1.0 mL/min, $\lambda = 254$ nm. ¹**H NMR** (500 MHz, CDCl₃) δ 7.96 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.58 - 7.56 (m, 1H), 7.56 – 7.52 (m, 2H), 7.40 (t, J = 7.3 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.33 – 7.31 (m, 1H), 7.30 -7.26 (m, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.11 - 7.08 (m, 2H), 7.08 - 7.04 (m, 2H), 7.02 - 6.99 (m, 2H), 6.99 – 6.96 (m, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.83 – 6.77 (m, 2H), 6.77 – 6.76 (m, 2H), 6.76 -6.73 (m, 1H), 5.19 (d, J = 9.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 149.8, 144.1, 140.9, 139.3, 136.4, 135.9, 135.5, 135.1, 134.2, 133.4, 133.3, 132.8, 132.59, 132.57, 131.4, 129.8, 129.2, 128.4, 128.2, 127.6, 127.38, 127.35, 127.24, 127.23, 126.8, 126.5, 126.4, 126.3, 126.2, 126.1, 125.4, 118.5. **HRMS (ESI)** calcd for C₄₀H₃₀OSiNa [M+Na]⁺ 577.1964, found 577.1969.



To the mixture of 8 (54 mg, 0.10 mmol) and Na₂CO₃ (42 mg, 0.40 mmol) in toluene (5.0 mL) and hexafluoroisopropanol (5.0 mL) was added NBS (19 mg, 0.105 mmol) in one portion at 0 °C. Then the mixture was stirred at the same temperature until the complete consumption of 8. Then mixture was allowed to warm to room temperature and filter through Celite, concentrated and purified by flash column chromatography (PE/DCM = 90:10) on silica gel to afford 9 (47 mg, 74%, 90% ee). $[\alpha]_D^{20}$ + 86.77 (c 1.13, CH₂Cl₂). HPLC conditions: Chiralcel AD-H, isopropanol/hexane = 6:94, flow: 1.0 mL/min, λ = 273 nm. ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 7.0 Hz, 2H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.57 -7.53 (m, 1H), 7.53 – 7.49 (m, 2H), 7.49 – 7.45 (m, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.30 – 7.28 (m, 1H), 7.28 - 7.24 (m, 2H), 7.08 - 7.05 (m, 2H), 7.05 - 6.99 (m, 2H), 6.99 - 6.95 (m, 1H), 6.89 -6.85 (m, 1H), 6.85 - 6.81 (m, 1H), 6.81 - 6.76 (m, 2H), 6.62 (t, J = 7.5 Hz, 2H), 6.58 - 6.43 (m, 1H), 6.39 (t, J = 7.0 Hz, 1H), 4.27 (d, J = 10.5 Hz, 1H), 4.19 (d, J = 10.5 Hz, 1H). ¹³C NMR (125) MHz, CDCl₃) δ 144.6, 143.3, 140.2, 137.6, 135.5, 134.0, 133.9, 133.7, 133.54, 133.46, 132.8, 132.6, 131.4, 130.2, 129.6, 128.2, 128.1, 127.8, 127.6, 127.5, 127.3, 127.1, 126.2, 126.1, 126.0, 125.8, 125.7, 125.0, 124.9, 123.9, 80.5, 44.4. HRMS (ESI) calcd for C₄₀H₂₉OSiBrNa [M+Na]⁺ 655.1069, found 655.1058.

Procedure for the application of silanol on cross-coupling reaction



To the solution of **6b** (56 mg, 0.10 mmol, 91% ee) in CF₃COOH (0.2 mL), hexafluoroisopropanol (4 mL) and DCM (2.0 mL) was added nBu₄NBr₃ (72 mg, 0.15 mmol, 1.50 equiv) at room temperature. Then the mixture was stirred at the same temperature until the complete consumption of **6b**. Then mixture was diluted with ethyl acetate (5.0 mL), extracted with ethyl acetate (5.0 mL*3), the combined organic layer was washed with brine, dried over Na₂SO₄, concentrated and purified by flash column chromatography (PE/EA = 95:5) on silica gel to afford **10** (39 mg, 90%, 92% ee). $[\alpha]_D^{20}$ + 28.2 (c 0.98, CH₂Cl₂). HPLC conditions: Chiralcel OD-H, isopropanol/hexane = 5:95, flow: 1.0 mL/min, λ = 254 nm. ¹**H NMR** (400 MHz, CDCl₃) δ 8.19 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.60 – 7.53 (m, 1H), 7.53 – 7.50 (m, 1H), 7.50 – 7.46 (m, 2H), 7.38 – 7.34 (m, 1H), 7.34 – 7.32 (m, 2H), 7.32 – 7.28 (m, 2H), 7.18 – 7.15 (m, 1H), 7.15 – 7.08 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 198.4, 137.8, 137.5, 136.2, 135.4, 134.1, 133.9, 132.6, 132.5, 131.5, 129.3, 129.1, 129.0, 128.2, 128.1, 127.8, 127.4, 127.28, 127.26, 127.21, 127.16, 127.1, 126.8, 124.9, 123.2. HRMS (ESI) calcd for C₂₇H₁₈OBr [M+H]⁺437.0541, found 437.0543.



The mixture of 10 (22 mg, 0.050 mmol, 1.0 equiv, 92% ee), 3-methoxyphenylboronic acid (12 mg, 0.075 mmol, 1.5 equiv), Pd₂(dba)₃ (0.9 mg, 0.001 mmol, 2.0 mol%), SPhos (1.6 mg, 0.004 mmol, 8.0 mol%) and K₂CO₃ (28 mg, 0.200 mmol, 4.0 equiv) in toluene (0.8 mL), ethanol (0.2 mL) and H₂O (0.2 mL) was stirred at 90 °C for 3 hours. After being cooled to room temperature, the reaction was diluted with ethyl acetate (5 mL) and extracted with ethyl acetate (5 mL*3), and the combined organic layer was washed with brine, dried over Na₂SO₄, filtered, concentrated and purified by flash column chromatography (PE/EtOAc = 90:10) on silica gel to afford 11 (22 mg, 94%, 92% ee). $[\alpha]_{D}^{20}$ + 50.0 (c 0.87, CH₂Cl₂). HPLC conditions: Chiralcel OD-H, isopropanol/hexane = 5:95, flow: 1.0 mL/min, λ = 254 nm. ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.42 – 7.40 (m, 2H), 7.40 – 7.35 (m, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.27 (m, 1H), 7.25 – 7.20 (m, 1H), 7.13 – 7.05 (m, 2H), 7.04 – 7.00 (m, 1H), 7.00 – 6.94 (m, 2H), 3.87 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 199.2, 159.4, 143.3, 142.0, 140.2, 138.0, 137.8, 137.4, 134.78, 134.75, 134.1, 133.1, 132.7, 132.0, 131.2, 130.5, 129.1, 129.03, 128.96, 128.5, 128.4, 128.1, 127.6, 127.5, 127.2, 126.9, 126.2, 125.8, 125.7, 125.4, 125.2, 122.5, 115.6, 112.9, 55.3. HRMS (ESI) calcd for C₃₄H₂₅O [M+H]⁺ 465.1855, found 465.1847.

Procedure for the synthesis of Rhodium-Ligand Complex



A mixture of $[Rh(CO)_2CI]_2$ (5.8 mg, 0.015 mmol, 1.0 equiv) and L7 (35.0 mg, 0.03 mmol, 2.0 equiv) in DCM (2 mL) was stirred at room temperature for 30 mins. Then the solvent was removed under vacuum and crystallized in mixture solvent (PE:EtOAc = 10:1) under an atmosphere of nitrogen at – 20 °C to afford orange crystal **Rh-1** (30 mg, 80%). ¹**H NMR** (400 MHz, CDCl₃) δ 7.72 – 7.67 (m, 4H), 7.67 – 7.63 (m, 4H), 7.63 – 7.60 (m, 2H), 7.58 – 7.55 (m, 2H), 7.55 – 7.52 (m, 2H), 7.52 – 7.50 (m, 2H), 7.50 – 7.47 (m, 4H), 7.47 – 7.44 (m, 2H), 7.43 – 7.38 (m, 4H), 7.38 – 7.34 (m, 4H), 7.34 – 7.32 (m, 4H), 7.32 – 7.29 (m, 2H), 7.05 (s, 2H), 5.76 (d, J = 8.0 Hz, 1H), 5.66 – 5.51 (m, 1H), 5.36 (d, J = 8.0 Hz, 1H), 4.08 – 3.94 (m, 2H), 3.65 – 3.50 (m, 1H), 3.35 – 3.26 (m, 1H), 3.13 – 3.02 (m, 1H), 2.92 – 2.78 (m, 3H), 1.99 – 1.83 (m, 1H), 1.21 (d, J = 6.8 Hz, 6H), 1.16 (d, J = 6.8 Hz, 3H), 1.12 (d, J = 6.4 Hz, 6H), 1.00 (d, J = 6.8 Hz, 6H), 0.59 (s, 3H), 0.52 (s, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 153.2, 152.0, 142.3, 142.2, 141.21, 141.17, 140.5, 140.4, 140.2, 139.9, 129.7, 129.1, 128.9, 128.83, 128.78, 128.72, 128.68, 128.4, 127.9,

127.8, 127.7, 127.4, 127.3, 127.2, 127.1, 127.01, 126.96, 125.6, 123.8, 115.1, 90.7 (d, J = 18.9 Hz), 86.8, 78.6, 78.3, 50.8, 50.6, 48.4, 45.3, 40.4, 34.1, 29.3, 26.7, 26.5, 25.0, 24.6, 23.5, 17.2. ³¹P **NMR** (162 MHz, CDCl₃) δ 115.9, 114.2.



Structure of Rh-1·EtOAc

Crystal data and structure refinement for Rh-1.

Identification code	11-15			
Empirical formula	$C_{156}H_{162}Cl_2N_4O_{16}P_2Rh_2S_2$			
Formula weight	2751.67			
Temperature/K	99.99(10)			
Crystal system	monoclinic			
Space group	P21			
a/Å	14.9883(2)			
b/Å	34.9555(5)			
c/Å	15.2977(2)			
α/°	90			
β/°	100.2050(10)			
γ/°	90			
Volume/Å ³	7888.03(19)			
Z	2			
$\rho_{calc}g/cm^3$	1.159			
µ/mm ⁻¹	2.902			
F(000)	2880.0			
Crystal size/mm ³	$0.12 \times 0.11 \times 0.1$			
Radiation	Cu Ka ($\lambda = 1.54184$)			
20 range for data collection/° 5.056 to 147.232				
Index ranges	$-18 \leqslant h \leqslant 16, -37 \leqslant k \leqslant 42, -18 \leqslant l \leqslant 17$			
Reflections collected	31702			
Independent reflections	22516 [$R_{int} = 0.0496$, $R_{sigma} = 0.0696$]			

Data/restraints/parameters	22516/8/1671
Goodness-of-fit on F ²	1.029
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0481, wR_2 = 0.1213$
Final R indexes [all data]	$R_1 = 0.0517, wR_2 = 0.1245$
Largest diff. peak/hole / e Å ⁻	³ 0.90/-0.97
Flack/Hooft parameter	-0.009(5)/0.008(5)

Supplementary Table 1. Optimization of Reaction Conditions for Bromocyclization

	Ph + SimOH PhPh	base (4. solvent,	0 eq.) temp.		Ph I Br O Si-Ph Ph
8		1.5 eq.		g)
Entry	base	solvent	temp. (°C)	yield/%	d.r.
1	NaHCO ₃	THF	0	95	2.4:1
2	NaHCO ₃	DMF	0	95	2.6:1
3	NaHCO ₃	Mesitylene	0	99	2.5:1
4	NaHCO ₃	o-Xylene	0	58	1.8:1
5	NaHCO ₃	CH ₃ OH	0	80	1:1.2
6	NaHCO ₃	CHCl ₃	0	41	1.6:1
7	NaHCO ₃	toluene	0	35	2.8:1
8	NaHCO ₃	toluene	-78	<10	5.3:1
9	Na ₂ CO ₃	toluene	-78	<10	6.0:1
10	Na ₂ CO ₃	toluene:HFIP 2:1	0	91	16.6:1
11 ^a	Na ₂ CO ₃	toluene:HFIP 1:1	0	74	>20:1

^a 1.05 eq. NBS was used;

DFT Calculations:

Computational Methods: B2PLYPD3/def2-TZVP // B3LYP-D3BJ/6-311G(d,p) Energies are given in kcal/mol

All of the DFT calculations were performed with Gaussian 16 software packages⁵. The optimization calculations were employed at B3LYP level of theory⁶ at 298.15 K with the D3 version of Grimme's dispersion (with Becke-Johnson damping)⁷. The 6-311G(d,p) basis sets⁸ were employed for the C, H, Si atoms. Vibrational frequency analysis were calculated at the same level of theory to verify whether each optimized structure is an energy minimum and to evaluate its zero-point vibrational energy. All of the product structures were fully optimized without any symmetric restrictions. For each transition state, the intrinsic reaction coordinate (IRC) analysis was conducted to ensure that it connects the right reactant and product.⁹ To obtain more accurate energies, single-point energy calculations were performed on all optimized structures applying the def2-TZVP basis set¹⁰ at the B2PLYPD3 level of theory.¹¹ A standard state of 298.15 K and 1 atm was used. All discussed energies are Gibbs free energies in gas phase (ΔG_g).

Compounds	TCG	Е	Compounds	TCG	Е
4c	0.194088	-830.318409	4c"	0.072747	-231.817104
\mathbf{H}_2	-0.001444	-1.159449	4a'	0.297727	-1138.239765
4c-HH	0.211558	-831.490834	4a'-H	0.179531	-754.224730
(<i>R</i>)- 4 a	0.281270	-1137.034077	4a"	0.115796	-385.185538
4a-HH	0.298668	-1138.226462	(S) -4a	0.281286	-1137.034072
4c'	0.210317	-831.501312	TS-rs	0.280614	-1137.000971
4c'-H	0.136044	-600.855605			



According to the Eyring equation:

$$\mathbf{k} = \frac{k_B T}{h} e^{\frac{-\Delta G}{RT}}$$

The reaction rate for the racemization of **4a**:

$$k = 7.4E-3 s^{-1}$$

For this rotation process is a first-order reaction, Equation relates half-life to rate constant for first order reactions:

$$t_{1/2} = \frac{\ln 2}{k} \approx 94 \text{ s}$$

Supplementary Table 2. Thermal correction of Gibbs free energy (TCG, hartree) and single-point energies (E, hartree) in 298.15 K and 1 atm for all species involved in this study.

Copies of NMR Spectroscopies



Supplementary Figure 1. ¹H NMR spectroscopy of L2



Supplementary Figure 2. ¹³C NMR spectroscopy of L2


Supplementary Figure 3. ³¹P NMR spectroscopy of L2



Supplementary Figure 4. ¹⁹F NMR spectroscopy of L2



Supplementary Figure 5. ¹H NMR spectroscopy of L3



Supplementary Figure 6. ¹³C NMR spectroscopy of L3





Supplementary Figure 7. ³¹P NMR spectroscopy of L3



Supplementary Figure 8. ¹H NMR spectroscopy of L4



Supplementary Figure 9. ¹³C NMR spectroscopy of L4



Supplementary Figure 10. ³¹P NMR spectroscopy of L4

150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -2£ fl (ppm)



Supplementary Figure 11. ¹H NMR spectroscopy of L5



Supplementary Figure 12. ¹³C NMR spectroscopy of L5



150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -22 f1 (ppm)

Supplementary Figure 13. ³¹P NMR spectroscopy of L5



Supplementary Figure 14. ¹H NMR spectroscopy of L6



Supplementary Figure 15. ¹³C NMR spectroscopy of L6



Supplementary Figure 16. ³¹P NMR spectroscopy of L6



Supplementary Figure 17. ¹H NMR spectroscopy of L7



Supplementary Figure 18. ¹³C NMR spectroscopy of L7



150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -2£ f1 (ppm)

Supplementary Figure 19. ³¹P NMR spectroscopy of L7



Supplementary Figure 20. ¹H NMR spectroscopy of S1



Supplementary Figure 21. ¹³C NMR spectroscopy of S1



Supplementary Figure 22. ¹H NMR spectroscopy of S2



Supplementary Figure 23. ¹³C NMR spectroscopy of S2



Supplementary Figure 24. ¹H NMR spectroscopy of S3



Supplementary Figure 25. ¹³C NMR spectroscopy of S3



Supplementary Figure 26. ¹H NMR spectroscopy of S4



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

Supplementary Figure 27. ¹³C NMR spectroscopy of S4



Supplementary Figure 28. 19F NMR spectroscopy of S4



Supplementary Figure 29. ¹H NMR spectroscopy of S5



Supplementary Figure 30. ¹³C NMR spectroscopy of S5





Supplementary Figure 31. 19F NMR spectroscopy of S5



Supplementary Figure 32. ¹H NMR spectroscopy of 4a





Supplementary Figure 33. ¹³C NMR spectroscopy of 4a



Supplementary Figure 34. ¹H NMR spectroscopy of 4b



Supplementary Figure 35. ¹³C NMR spectroscopy of 4b



Supplementary Figure 36. ¹H NMR spectroscopy of 4c



Supplementary Figure 37. ¹³C NMR spectroscopy of 4c



Supplementary Figure 38. ¹H NMR spectroscopy of 4d



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

Supplementary Figure 39. 13C NMR spectroscopy of 4d



Supplementary Figure 40. ¹H NMR spectroscopy of 4e



Supplementary Figure 41. ¹³C NMR spectroscopy of 4e



Supplementary Figure 42. ¹H NMR spectroscopy of 4f



Supplementary Figure 43. ¹³C NMR spectroscopy of 4f



Supplementary Figure 44. ¹H NMR spectroscopy of 4g



Supplementary Figure 45. ¹³C NMR spectroscopy of 4g



Supplementary Figure 46. ¹H NMR spectroscopy of 4h



Supplementary Figure 47. ¹³C NMR spectroscopy of 4h



Supplementary Figure 48. ¹⁹F NMR spectroscopy of 4h

8 0061 8 0061 8 0044 8 0044 8 0045 9 00





Supplementary Figure 49. ¹H NMR spectroscopy of 4i



Supplementary Figure 50. ¹³C NMR spectroscopy of 4i



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2 f1 (ppm)

Supplementary Figure 51. 19F NMR spectroscopy of 4i



Supplementary Figure 52. ¹H NMR spectroscopy of 4j



Supplementary Figure 53. 13C NMR spectroscopy of 4j



Supplementary Figure 54. ¹H NMR spectroscopy of 6a



Supplementary Figure 55. ¹³C NMR spectroscopy of 6a



Supplementary Figure 56. ¹H NMR spectroscopy of 6b



Supplementary Figure 57. ¹³C NMR spectroscopy of 6b



Supplementary Figure 58. ¹H NMR spectroscopy of 6c



Supplementary Figure 59. ¹³C NMR spectroscopy of 6c



Supplementary Figure 60. ¹H NMR spectroscopy of 6d



Supplementary Figure 61. ¹³C NMR spectroscopy of 6d



Supplementary Figure 62. ¹H NMR spectroscopy of 6e



Supplementary Figure 63. ¹³C NMR spectroscopy of 6e



Supplementary Figure 64. ¹H NMR spectroscopy of 6f



Supplementary Figure 65. ¹³C NMR spectroscopy of 6f



Supplementary Figure 66. ¹H NMR spectroscopy of 6g



Supplementary Figure 67. ¹³C NMR spectroscopy of 6g



Supplementary Figure 68. ¹H NMR spectroscopy of 6h



Supplementary Figure 69. ¹³C NMR spectroscopy of 6h



Supplementary Figure 70. ¹H NMR spectroscopy of 6i



Supplementary Figure 71. ¹³C NMR spectroscopy of 6i



Supplementary Figure 72. ¹H NMR spectroscopy of 6j



Supplementary Figure 73. ¹³C NMR spectroscopy of 6j



Supplementary Figure 74. ¹H NMR spectroscopy of 6k


Supplementary Figure 75. ¹³C NMR spectroscopy of 6k



Supplementary Figure 76. ¹H NMR spectroscopy of 61



Supplementary Figure 77. ¹³C NMR spectroscopy of 61



Supplementary Figure 78. ¹H NMR spectroscopy of 6m



Supplementary Figure 79. ¹³C NMR spectroscopy of 6m



Supplementary Figure 80. 19F NMR spectroscopy of 6m



Supplementary Figure 81. ¹H NMR spectroscopy of 6n



Supplementary Figure 82. ¹³C NMR spectroscopy of 6n



Supplementary Figure 83. ¹H NMR spectroscopy of 60



Supplementary Figure 84. ¹³C NMR spectroscopy of 60



Supplementary Figure 85. 19F NMR spectroscopy of 60



Supplementary Figure 86. ¹H NMR spectroscopy of 6p



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

Supplementary Figure 87. ¹³C NMR spectroscopy of 6p



Supplementary Figure 88. ¹H NMR spectroscopy of 6q



Supplementary Figure 89. ¹³C NMR spectroscopy of 6q



Supplementary Figure 90. ¹⁹F NMR spectroscopy of 6q



Supplementary Figure 91. ¹H NMR spectroscopy of 6r



Supplementary Figure 92. ¹³C NMR spectroscopy of 6r



Supplementary Figure 93. ¹⁹F NMR spectroscopy of 6r



Supplementary Figure 94. ¹H NMR spectroscopy of 6s



Supplementary Figure 95. ¹³C NMR spectroscopy of 6s



Supplementary Figure 96. ¹H NMR spectroscopy of 6t



Supplementary Figure 97. ¹³C NMR spectroscopy of 6t







Supplementary Figure 98. ¹H NMR spectroscopy of 6u



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

Supplementary Figure 99. ¹³C NMR spectroscopy of 6u



Supplementary Figure 100. ¹H NMR spectroscopy of 6v



Supplementary Figure 101.¹³C NMR spectroscopy of 6v



Supplementary Figure 102. ¹H NMR spectroscopy of 6w



Supplementary Figure 103. ¹³C NMR spectroscopy of 6w



Supplementary Figure 104. ¹H NMR spectroscopy of 6x



Supplementary Figure 105. ¹³C NMR spectroscopy of 6x



Supplementary Figure 106. 19F NMR spectroscopy of 6x



Supplementary Figure 107. ¹H NMR spectroscopy of 6y



Supplementary Figure 108. ¹³C NMR spectroscopy of 6y



Supplementary Figure 109. ¹H NMR spectroscopy of 6z



Supplementary Figure 110. ¹³C NMR spectroscopy of 6z



Supplementary Figure 111. ¹⁹F NMR spectroscopy of 6z



Supplementary Figure 112. ¹H NMR spectroscopy of 6aa



Supplementary Figure 113. ¹³C NMR spectroscopy of 6aa



Supplementary Figure 114. ¹H NMR spectroscopy of 6bb



Supplementary Figure 115. ¹³C NMR spectroscopy of 6bb



Supplementary Figure 116. 19F NMR spectroscopy of 6bb



Supplementary Figure 117. ¹H NMR spectroscopy of 6cc



Supplementary Figure 118. ¹³C NMR spectroscopy of 6cc



Supplementary Figure 119. ¹H NMR spectroscopy of 6dd



Supplementary Figure 120. ¹³C NMR spectroscopy of 6dd



Supplementary Figure 121.¹H NMR spectroscopy of 6ee



Supplementary Figure 122. ¹³C NMR spectroscopy of 6ee



Supplementary Figure 123. 19F NMR spectroscopy of 6ee



Supplementary Figure 124. ¹H NMR spectroscopy of 6ff



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

Supplementary Figure 125. 13C NMR spectroscopy of 6ff



Supplementary Figure 126. Crude ¹H NMR spectroscopy of 6gg and 6gg'



Supplementary Figure 127. Crude ¹H NMR spectroscopy of 6m and 6b



Supplementary Figure 128. Crude ¹H NMR spectroscopy of 6c and 6b



Supplementary Figure 129. Crude ¹H NMR spectroscopy of 6a and 6c



Supplementary Figure 130.¹H NMR spectroscopy of 7



Supplementary Figure 131.¹³C NMR spectroscopy of 7



Supplementary Figure 132. ¹H NMR spectroscopy of 8



Supplementary Figure 133. ¹³C NMR spectroscopy of 8



Supplementary Figure 134. ¹H NMR spectroscopy of 9



Supplementary Figure 135. ¹³C NMR spectroscopy of 9



Supplementary Figure 136. ¹H NMR spectroscopy of 10



210 200 190 180 170 160 140 130 120 110 100 90 f1 (ppm)

Supplementary Figure 137. ¹³C NMR spectroscopy of 10



Supplementary Figure 138. ¹H NMR spectroscopy of 11



Supplementary Figure 139. ¹³C NMR spectroscopy of 11



Supplementary Figure 140. ¹H NMR spectroscopy of Rh-1



Supplementary Figure 141.¹³C NMR spectroscopy of Rh-1



Supplementary Figure 142. ³¹P NMR spectroscopy of Rh-1



Supplementary Figure 143. ¹H NMR spectroscopy of S6



Supplementary Figure 144. ¹³C NMR spectroscopy of S6

Copies of HPLC traces

Data File F:\DATA\JFENG\DATA\BXF-2-34-rac(AD-H,10%,1.0).D Sample Name: BXF-2-34-rac(AD-H,10%,1.0)



LC1260 30/11/2019 09:43:56

Supplementary Figure 145. HPLC data of 6a

Page 1 of 2
Data File F:\DATA\JFENG\DATA\BXF-2-31-repeat-2(AD,10%,1.0).D Sample Name: BXF-2-31-repeat-2(AD,10%,1.0)



LC1260 30/11/2019 09:49:05

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Supplementary Figure 146. HPLC data of 6a

Data File F:\DATA\JFENG\DATA\LN-1-3(AD,20%,1.0).D Sample Name: LN-1-3(AD,20%,1.0)



LC1260 30/11/2019 10:48:02

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Supplementary Figure 147. HPLC data of 6b

Data File F:\DATA\JFENG\DATA\BXF-2-30-(2)-0911(AD,20%,1.0).D Sample Name: BXF-2-30-(2)-0911(AD,20%,1.0) ____ Acq. Operator : Location : 1 Injection Date : 11/09/2019 10:19:20 Acq. Method : JFeng.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\BXF-2-30-(2)-0911(AD,20%,1.0).D) ×188:6161.59 mAU 060-24 175 --Ph ~ Ph Ph 150 125 6b 100 75 ; 298.06A 50 533 25 0 35 10 15 20 25 30 min Area Percent Report _____ Sorted By Signal : Multiplier 1.0000 : Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area Height Area # [min] [mAU*s] [mAU] 8 1 8.533 MM 0.2184 298.06430 22.74938 4.5432 2 17.090 MM 0.5704 6262.58691 183.00049 95.4568 Totals : 6560.65121 205.74987 _____ *** End of Report ***

LC1260 30/11/2019 10:50:23

Supplementary Figure 148. HPLC data of 6b

Page 1 of 1

Data File F:\DATA\JFENG\DATA\BXF-2-73(AD,15%,1.0).D Sample Name: BXF-2-73(AD,15%,1.0)



LC1260 30/11/2019 10:05:30

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Supplementary Figure 149. HPLC data of 6c

Sample Name: BXF-2-71(AD,15%,1.0) Acq. Operator : Location : 1 Injection Date : 06/10/2019 20:30:50 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\BXF-2-71(AD,15%,1.0).D) mAU] 13-234 160 -Me 140 0 SirroH Ph Ph 120 -100 -6c 80 60 40 10.922 20 0 14 12 10 _____ Area Percent Report Sorted By : Signal Multiplier 1.0000 : : Dilution 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area # [min] [min] [mAU*s] Height Area [mAU] 8 1 10.922 BB 0.3409 199.83362 9.21795 3.9765 2 13.234 BB 0.4523 4825.53223 167.40480 96.0235 Totals : 5025.36584 176.62275 *** End of Report *** LC1260 30/11/2019 10:06:05 Page 1 of 1 Supplementary Figure 150. HPLC data of 6c

16 min

Data File F:\DATA\JFENG\DATA\BXF-2-71(AD,15%,1.0).D

Data File F:\DATA\JFENG\DATA\BXF-2-74-2(AD,5%,1.0).D Sample Name: BXF-2-74-2(AD,5%,1.0)



LC1260 30/11/2019 10:02:21

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Supplementary Figure 151. HPLC data of 6d

Data File F:\DATA\JFENG\DATA\BXF-2-81-1(AD,5%,1.0).D Sample Name: BXF-2-81-1(AD,5%,1.0) _____ Acq. Operator : Location : 1 Injection Date : 09/10/2019 16:30:49 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\BXF-2-81-1(AD,5%,1.0).D) 223.8 mAU -29-926 35 -0 30 Si. OH Ph 25 -6d 20 15 10 5 10 0 25 30 20 10 15 _____ Area Percent Report Sorted By Signal : Multiplier 1.0000 : Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [mAU*s] [mAU] 8 1 29.926 MM 1.0270 2273.98682 36.90383 92.8611 2 33.065 MM 1.2275 174.81848 2.37354 7.1389 7.1389 Totals : 2448.80530 39.27737 _____ *** End of Report ***

LC1260 30/11/2019 10:03:50

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Supplementary Figure 152. HPLC data of 6d

Data File F:\DATA\JFENG\DATA\FJ-11-17-rac(AD,10%,1.0).D Sample Name: FJ-11-17-rac(AD,10%,1.0)



LC1260 30/11/2019 15:05:07

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Supplementary Figure 153. HPLC data of 6e

Data File F:\DATA\JFENG\DATA\FJ-11-16(AD,10%,1.0).D Sample Name: FJ-11-16(AD,10%,1.0) Acq. Operator : Location : 1 Injection Date : 11/10/2019 16:11:50 Acq. Method : JFeng.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-11-16(AD,10%,1.0).D) 8. 2000 ·· mAU -5-225 700 o SivOH 600 Ph Ph 500 6e 400 300 200 14.088 100 0 10 12 14 16 min ____ ____ Area Percent Report Sorted By Signal : Multiplier 1.0000 : Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [min] [mAU*s] [mAU] 8 1 14.088 MM 0.3750 1926.70337 85.64039 8.6543 2 15.225 MM 0.4260 2.03361∈4 795.60052 91.3457 Totals : 2.22628e4 881.24091 *** End of Report ***

LC1260 30/11/2019 15:07:20

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Supplementary Figure 154. HPLC data of 6e





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Supplementary Figure 155. HPLC data of 6f

Data File F:\DATA\JFENG\DATA\FJ-11-18(AD,10%,1.0).D Sample Name: FJ-11-18(AD,10%,1.0)



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Supplementary Figure 156. HPLC data of 6f

Data File F:\DATA\JFENG\DATA\LN-1-9(AD,20%,1.0).D Sample Name: LN-1-9(AD,20%,1.0)



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Supplementary Figure 157. HPLC data of 6g

Data File F:\DATA\JFENG\DATA\BXF-2-85(AD,80%,1.0).D Sample Name: BXF-2-85(AD,80%,1.0)



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Supplementary Figure 158. HPLC data of 6g

Data File F:\DATA\JFENG\DATA\FJ-11-80(AD,20%,1.0).D Sample Name: FJ-11-80(AD,20%,1.0) Acq. Operator : Location : 1 Injection Date : 14/11/2019 20:51:16 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-11-80(AD,20%,1.0).D) mAU -44.079 12.238 120 0 Si...OH 100 Ph 80 6h : racemic 60 -40 -20 0 -20 -40 12 16 18 min 10 14 _____ Area Percent Report Sorted By : Signal 1.0000 Multiplier : 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area # [min] [min] [mAU*s] Height [mAU] Area 8
 1
 11.079 BB
 0.2995 3369.19971
 174.28862
 49.9996

 2
 12.238 BB
 0.3367 3369.25903
 154.30183
 50.0004
Totals : 6738.45874 328.59045 ------*** End of Report ***

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Supplementary Figure 159. HPLC data of 6h

Data File F:\DATA\JFENG\DATA\FJ-11-79-re(AD,20%,1.0).D Sample Name: FJ-11-79-re(AD,20%,1.0)



LC1260 30/11/2019 15:53:11

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Supplementary Figure 160. HPLC data of 6h

Data File F:\DATA\JFENG\DATA\BXF-2-28(AD-H,15%,1.0).D Sample Name: EXF-2-28(AD-H,15%,1.0)

_____ Acq. Operator : Location : 1 Injection Date : 09/09/2019 20:22:35 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\BXF-2-28(AD-H,15%,1.0).D) Area: 2011.49 mAU 15:017 100 -0 Si...OH 80 Ph 60 6i : racemic 40 20 0 2.5 12.5 20 15 17.5 7.5 10 min ____ Area Percent Report Sorted By : Signal 1.0000 Multiplier . : Dilution 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area # [min] [min] [mAU*s] Height [mAU] Area 8
 1
 15.017 MM
 0.4193 2611.48633 103.79387 49.4755

 2
 18.808 MM
 0.5307 2666.85132 83.75375 50.5245
Totals : 5278.33765 187.54762

*** End of Report ***

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Supplementary Figure 161. HPLC data of 6i

Data File F:\DATA\JFENG\DATA\BXF-2-33-repeat(AD,15%,1.0).D Sample Name: BXF-2-33-repeat(AD, 15%, 1.0) _____ Acq. Operator : Location : 1 Injection Date : 16/09/2019 21:56:43 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\BXF-2-33-repeat(AD, 15%, 1.0).D) mAU -19:120 70 O 60 SivoH Ph Ph 50 61 40 -30 20 -10 15.144 0 15 20 2.5 12.5 17.5 7.5 10 min _____ Area Percent Report _____ Sorted By : Signal Multiplier 1.0000 : Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [min] [mAU*s] [mAU] 8 1 15.144 BB 0.3823 83.10104 3.43480 3.2995 2 19.120 BB 0.4930 2435.51465 76.59618 96.7005 Totals : 2518.61569 80.03099 _____ *** End of Report ***

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Supplementary Figure 162. HPLC data of 6i

Data File F:\DATA\JFENG\DATA\FJ-11-23-rac(AD,10%,1.0).D Sample Name: FJ-11-23-rac(AD,10%,1.0)



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.877	MM	0.4289	1542.57129	59.94010	51.0402
2	31.321	BB	0.7572	1479.69543	28.24319	48.9598
Total	ls :			3022.26672	88.18329	

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Supplementary Figure 163. HPLC data of 6j

Data File F:\DATA\JFENG\DATA\FJ-10-119(AD,10%,1.0).D Sample Name: FJ-10-119(AD,10%,1.0)



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Supplementary Figure 164. HPLC data of 6j

Data File F:\DATA\JFENG\DATA\FJ-10-168(AD,20%,1.0).D Sample Name: FJ-10-168(AD,20%,1.0) Acq. Operator : Location : 1 Injection Date : 06/09/2019 10:47:06 Acq. Method : JFeng.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 D, Sig=230,4 Ref=off (F:\DATA\JFENG\DATA\FJ-10-168(AD,20%,1.0).D) Area 95423 mAU -558 600 C 500 Si OH ~ 10.443 Ph Ph 400 6k : racemic 300 200 100 0 10 mir _____ Area Percent Report : Signal 1.0000 Sorted By Multiplier : 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 D, Sig=230,4 Ref=off Height [mAU] Peak RetTime Type Width Area Area # [min] [mAU*s] % 1 6.558 MM 0.2729 9954.22949 608.02948 51.2811 2 10.443 MM 0.4187 9456.88184 376.44547 48.7189 Totals : 1.94111e4 984.47495 *** End of Report ***

LC1260 30/11/2019 16:07:52

Supplementary Figure 165. HPLC data of 6k

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Data File F:\DATA\JFENG\DATA\FJ-10-166(AD,20%,1.0).D Sample Name: FJ-10-166(AD,20%,1.0)

Acq. Operator	;		
Sample Operator	:		
Acq. Instrument	: LC1260	Locatio	on: 1
Injection Date	: 06/09/2019 11:02:35		
		Inj Volur	ne : Manually
Acq. Method	: F:\METHOD\JFeng.M		
Last changed	: 06/09/2019 10:15:53	by	
	(modified after loa	ding)	
Analysis Method	: F:\METHOD\ZK.M		
Last changed	: 14/07/2019 15:34:15	pÀ	
Additional Info	: Peak(s) manually in	tegrated	
DAD1 D, Sig	=230,4 Ref=off (F:\DATA\JFENG\DAT	FA\FJ-10-166(AD,20%,1.0).D)	
mAU			51 St
1200			Predit 2
800-	Ph Ph		
600 -	бК		
400 -			
200 -		5 5 7 7	Breed No.245
0			
	2	· · · · · · · ·	8 10 m
	2	· · ·	5 10 1
	Area Percent	Report	
Sorted By	: Signal		
Multiplier	: 1.0000		
Dilution	: 1.0000		
Use Multiplier	& Dilution Factor with	ISTDS	
Signal 1: DAD1	D, Sig=230,4 Ref=off		
Peak RetTime Ty	pe Width Area	Height Area	
# [min]	[min] [mAU*s]	[mAU] %	
			1
1 6.583 MM	0.1672 1013.44720	101.00916 4.0897	
2 10.511 MM	0.3043 2.37670e4	1301.72522 95.9103	
		1100 30100	
Totals :	2.47804e4	1402.73438	

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Supplementary Figure 166. HPLC data of 6k

Acq. Operator : Location : 1 Injection Date : 25/09/2019 20:35:22 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\LN-1-6-2(AD,20%,1.0).D) mAU 9-476 -Me 400 0 SigoH Ph Ph 14.772 300 -61 : racemic 200 100 0 16 12 8 10 14 _____ Area Percent Report Sorted By : Signal Multiplier 1.0000 : : Dilution 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area Height Area # [min] [mAU*s] [mAU] 8 1 9.476 BB 0.2499 7564.23047 464.71857 49.9657 2 14.772 BB 0.4291 7574.60352 273.54688 50.0343 Totals : 1.51388e4 738.26544 _____ *** End of Report *** LC1260 30/11/2019 09:50:47 Supplementary Figure 167. HPLC data of 61

Data File F:\DATA\JFENG\DATA\LN-1-6-2(AD,20%,1.0).D

Sample Name: LN-1-6-2(AD,20%,1.0)

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18

min

Data File F:\DATA\JFENG\DATA\BXF-2-57(AD,20%,1.0).D Sample Name: BXF-2-57(AD,20%,1.0)



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Supplementary Figure 168. HPLC data of 61

Data File F:\DATA\JFENG\DATA\LN-1-7(AD,20%,1.0).D Sample Name: LN-1-7(AD,20%,1.0)



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Supplementary Figure 169. HPLC data of 6m

Data File F:\DATA\JFENG\DATA\BXF-2-56-1(AD,20%,1.0).D Sample Name: BXF-2-56-1(AD,20%,1.0)



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Supplementary Figure 170. HPLC data of 6m

Data File F:\DATA\JFENG\DATA\BXF-2-106(AD,20%,1.0).D Sample Name: BXF-2-106(AD,20%,1.0)



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Supplementary Figure 171. HPLC data of 6n

Injection Date : 23/10/2019 21:27:47 Acq. Method : DEF_LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 B, Sig=274,4 Ref=off (F:\DATA\JFENG\DATA\BXF-2-101(AD,20%,1.0).D) 16:942 mAU_ CI 80 70 -C 10H Ph Ph 60 50 -6n 40 30 20 11.041 10 0 2.5 12.5 15 17.5 20 7.5 10 min

Area Percent Report

Sorted By		:	Sig	nal		
Multiplier		:	1.0	00C		
Dilution		:	1.0	00C		
Use Multiplier	Se.	Dilution	Factor	with	ISTDs	

Signal 1: DAD1 B, Sig=274,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.041	BB	0.2906	174.70988	9.32589	5.9194
2	16.942	BB	0.4908	2776.75806	87.85071	94.0806
Total	ls :			2951.46794	97.17660	

*** End of Report ***

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Supplementary Figure 172. HPLC data of 6n

Data File F:\DATA\JFENG\DATA\FJ-10-124-2(AD,20%,1.0).D Sample Name: FJ-10-124-2(AD,20%,1.0)

_____ Acq. Operator : Location : 1 Injection Date : 12/07/2019 17:51:20 Acq. Method : DEF_LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-10-124-2(AD,20%,1.0).D) mAU -10.682 CF₃ 17.5 12.268 0 SICOH 15 Ph Ph 12.5 -: racemic 60 10-7.5 5 2.5 0 12 10 14 min Area Percent Report Sorted By Signal : 1.0000 Multiplier : Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
			-	-		
1	10.682	BB	0.2819	349.90295	19.26788	50.9608
2	12.268	BB	0.3499	336.70950	14.77239	49.0392
Total	ls :			686.61246	34.04027	

*** End of Report ***

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Supplementary Figure 173. HPLC data of 60

Data File F:\DATA\JFENG\DATA\FJ-10-123-20190716(AD,20%,1.0).D Sample Name: FJ-10-123-20190716(AD,20%,1.0)



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Supplementary Figure 174. HPLC data of 60





Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.506	MM	0.2091	1193.75562	95.14936	49.4194
2	14.371	MM	0.4715	1221.80725	43.18851	50.5806
Tota.	ls :			2415.56287	138.33787	

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Supplementary Figure 175. HPLC data of 6p





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Supplementary Figure 176. HPLC data of 6p

Data File F:\DATA\JFENG\DATA\FJ-11-89-rac(AD,20%,1.0).D Sample Name: FJ-11-89-rac(AD,20%,1.0)



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Supplementary Figure 177. HPLC data of 6q

Acq. Operator : Location : 1 Injection Date : 19/11/2019 13:04:23 Acq. Method : JFeng.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-11-88(AD,20%,1.0).D) mAU] 12:904 Br 175 150 0 S 'OH Ph Ph 125 6q 100 75 50 25 3.999 0 10 12 8 _____ Area Percent Report _____ Sorted By : Signal 1.0000 Multiplier : 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [mAU*s] [mAU] 8 1 8.999 BB 0.2216 114.54284 7.97432 2.6437 2 12.904 BB 0.3544 4218.12646 184.70149 97.3563 Totals : 4332.66930 192.67582 ------*** End of Report *** LC1260 30/11/2019 15:47:29 Supplementary Figure 178. HPLC data of 6q

Data File F:\DATA\JFENG\DATA\FJ-11-88(AD,20%,1.0).D

Sample Name: FJ-11-88(AD,20%,1.0)

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14

min

Data File F:\DATA\JFENG\DATA\FJ-11-75(AD,20%,1.0).D Sample Name: FJ-11-75(AD,20%,1.0)



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Supplementary Figure 179. HPLC data of 6r

Data File F:\DATA\JFENG\DATA\FJ-11-74(AD,20%,1.0).D Sample Name: FJ-11-74(AD,20%,1.0)



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Supplementary Figure 180. HPLC data of 6r

Data File F:\DATA\JFENG\DATA\FJ-11-34-rac-1(AD,20%,1.0).D Sample Name: FJ-11-34-rac-1(AD,20%,1.0)



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Supplementary Figure 181. HPLC data of 6s
Data File F:\DATA\JFENG\DATA\FJ-11-33(AD,20%,1.0).D Sample Name: FJ-11-33(AD,20%,1.0)

Acq. Operator : Location : 1 Injection Date : 20/10/2019 11:55:00 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 D, Sig=230,4 Ref=off (F:\DATA\JFENG\DATA\FJ-11-33(AD,20%,1.0).D) mAU _ 13:155 OMe -OMe 1200 OSi...OH Ph Ph OMe 1000 800 6s 600 400 11.849 200 0 12 10 14 min ____ _____ Area Percent Report Sorted By : Signal 1.0000 Multiplier : : 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 D, Sig=230,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [min] [mAU*s] [mAU] 8 1 11.849 BV 0.3525 2643.01733 115.72359 6.5381 2 13.155 VBA 0.4349 3.77820e4 1348.45288 93.4619 Totals : 4.04250e4 1464.17647

*** End of Report ***

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Supplementary Figure 182. HPLC data of 6s

Data File F:\DATA\JFENG\DATA\SL-1-21-(AD,20%,1.0).D Sample Name: SL-1-21-(AD,20%,1.0) Acq. Operator : Location : 1 Injection Date : 06/11/2019 09:24:35 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\SL-1-21-(AD,20%,1.0).D) mAU _ 10.933 80 -Ó Ph Ph 60 15.932 40 6t : racemic 20 0--20 16 10 12 14 _____ _____ Area Percent Report : Signal 1.0000 Sorted By Multiplier : 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area # [min] [min] [mAU*s] Height [mAU] Area % 1 10.933 BB 0.2913 2131.81250 113.39069 50.1496 2 15.932 BB 0.4606 2119.09131 71.33137 49.8504 Totals : 4250.90381 184.72206 *** End of Report ***

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Supplementary Figure 183. HPLC data of 6t

Data File F:\DATA\JFENG\DATA\FJ-11-60-(AD,20%,1.0).D Sample Name: FJ-11-60-(AD,20%,1.0)



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Supplementary Figure 184. HPLC data of 6t





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Supplementary Figure 185. HPLC data of 6u

Data File F:\DATA\JFENG\DATA\FJ-11-69(AD,20%,1.0).D Sample Name: FJ-11-69(AD,20%,1.0) Acq. Operator : Location : 1 Injection Date : 10/11/2019 16:27:31 Acq. Method : JFeng.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-11-69(AD,20%,1.0).D) mAU – 16.683 600 C Si 'OH 500 Ph 400 6u 300 200 10.534 100 0 16 18 12 14 10 min _____ Area Percent Report _____ Sorted By Signal : Multiplier 1.0000 : Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [min] [mAU*s] [mAU] 8 1 10.534 BB 0.2671 1123.68115 65.19385 5.1705 2 16.683 BB 0.4719 2.06087e4 679.31561 94.8295 Totals : 2.17324e4 744.50946 _____ *** End of Report ***

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Supplementary Figure 186. HPLC data of 6u

Data File F:\DATA\JFENG\DATA\BXF-1-114-rac(AD,8%,1.0).D Sample Name: BXF-1-114-rac(AD,8%,1.0) _____ Acq. Operator : Location : 1 Injection Date : 20/04/2019 21:19:28 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 D, Sig=230,4 Ref=off (F:\DATA\JFENG\DATA\BXF-1-114-rac(AD,8%,1.0).D) mAU . 40-318 800 0 Si. OH Me 15.390 Me 600 6v : racemic 400 200 0 16 18 min 12 14 10 _____ Area Percent Report Sorted By Signal : Multiplier 1.0000 : : Dilution 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 D, Sig=230,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [min] [mAU*s] [mAU] 8
 1
 10.318
 BB
 0.2922
 1.80134€4
 929.00806
 50.3522

 2
 15.390
 BB
 0.4500
 1.77614€4
 605.96783
 49.6478
Totals : 3.57748e4 1534.97589 *** End of Report ***

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Supplementary Figure 187. HPLC data of 6v

Data File F:\DATA\JFENG\DATA\FJ-10-83(AD,8%,1.0).D Sample Name: FJ-10-83(AD,8%,1.0)



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Supplementary Figure 188. HPLC data of 6v

Data File F:\DATA\JFENG\DATA\FJ-12-157-2-rac-(AD,4%,1.0).D Sample Name: FJ-12-157-2-rac-(AD,4%,1.0) _____ Acq. Operator : Location : 1 Injection Date : 12/06/2020 09:34:46 Acq. Method : JFeng.M Analysis Method : C:\Chem32\1\Methods\DEF_LC.M Last changed : 13/02/2014 23:27:44 by SYSTEM Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-12-157-2-rac-(AD,4%,1.0).D) mAU -152 18.626 17.5 -0 15 -Si OH Mé 12.5 10-6w : racemic 7.5 5-2.5 -0 -2.5 2.5 15 10 12.5 17.5 7.5 ____ Area Percent Report Sorted By : Signal 1.0000 Multiplier : : 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [mAU*s] [mAU] ofo 1 17.152 BB 0.4148 524.48938 19.31630 49.8754 2 18.626 BB 0.4422 527.11066 17.96947 50.1246 Totals : 1051.60004 37.28577 -----------------*** End of Report ***

LC1260 01/07/2020 21:11:42

Supplementary Figure 189. HPLC data of 6w

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min

Data File F:\DATA\JFENG\DATA\FJ-12-161-1-(AD,4%,1.0).D Sample Name: FJ-12-161-1-(AD,4%,1.0) _____ Acq. Operator : Location : 1 Injection Date : 12/06/2020 20:02:11 Acq. Method : JFeng.M Analysis Method : C:\Chem32\1\Methods\DEF_LC.M Last changed : 13/02/2014 23:27:44 by SYSTEM Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-12-161-1-(AD,4%,1.0).D) mAU 18.890 500 0" SivoH 400 Me 1 Me 300 6w 200 100 17.524 0 20 min 2.5 12.5 17.5 15 7.5 10 Area Percent Report Sorted By Signal : Multiplier 1.0000 : Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area Height Area # [min] [mAU*s] [mAU] 8 1 17.524 BB 0.4212 747.10229 26.47641 4.6546 2 18.890 BB 0.4435 1.53038e4 532.12524 95.3454 Totals : 1.60509e4 558.60165 _____ *** End of Report *** LC1260 01/07/2020 21:12:29

Supplementary Figure 190. HPLC data of 6w

Sample Name: FJ-10-191-RAC(AD,20%,1.0) Acq. Operator : Location : 1 Injection Date : 21/09/2019 17:24:02 Acq. Method : JFeng.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-10-191-RAC(AD,20%,1.0).D) mAU 1 3.507 7.746 Me 1200 o 1000 800 6x : racemic 600 400 200 0 6 8 _____ Area Percent Report : : : Signal 1.0000 Sorted By Multiplier 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU] % 1 6.507 BV R 0.2134 1.85975e4 1388.39795 50.4683 2 7.746 VB 0.2396 1.82523e4 1198.97424 49.5317 Totals : 3.68499e4 2587.37219 *** End of Report ***

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Supplementary Figure 191. HPLC data of 6x

Data File F:\DATA\JFENG\DATA\FJ-10-191-RAC(AD,20%,1.0).D

Data File F:\DATA\JFENG\DATA\FJ-10-190(AD,20%,1.0).D Sample Name: FJ-10-190(AD,20%,1.0) Acq. Operator : Location : 1 Injection Date : 21/09/2019 17:35:46 Acq. Method : JFeng.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-10-190(AD,20%,1.0).D) mAU 0224 1200 --Me 0 1000 Si 'OH 800 600 6x 400 200 6.532 0 _____ Area Percent Report _____ : Signal 1.0000 Sorted By Multiplier 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Height Area Peak RetTime Type Width Area # [min] [mAU*s] [mAU] 8 1 6.532 VB 0.1707 746.57880 67.67377 4.4558 2 7.770 BB 0.2018 1.60088e4 1230.35925 95.5442 Totals : 1.67553e4 1298.03302 ----------------*** End of Report ***

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Supplementary Figure 192. HPLC data of 6x

Data File F:\DATA\JFENG\DATA\bxf-2-45-rac(AD,15%,1.0).D Sample Name: bxf-2-45-rac(AD,15%,1.0)

					=		
Acq. Operator :							
Sample Operator :	212.00		Teachier	. 1			
Injection Date : 1	9/09/2019 11·27·22		LOCALION	: 1			
11,0001011 2000 1 1	J/ J/ LOIJ 11.L.		Inj Volume	: No inj			
Acq. Method : C Last changed : 1	:\Chem32\1\Methods 9/09/2019 11:18:37	\DEF_LC.M by					
(I Applyzeig Mothod · F	MODIFIED After loa	ding)					
Last changed : 1	4/07/2019 15:34:15	by					
DAD1 A, Sig=254,4	Ref=off (F:\DATA\JFENG\DAT	Albxf-2-45-rac(AD	0,15%,1.0).D)				
mAU]				ř	9		
	\land						
						5	
	Me					9.62	
30 -	01					Ā	
	Si. OH					A	
25-						1	
20-					1		
	Ϋ́ Μe	•					
	Me					and an	
15-							
6)	y : racemic					1	
10-							
				1			
				11			
5-							
5-							
5-	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~						~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~						~
	5 7.5	10	12.5	15	17.5	20	
	5 7.5	10	12.5	15	17.5	20	mir
	5 7.5 Area Percent	10 Report	12.5	15	17.5	20	
Sorted By	5 7.5 Area Percent	10 Report	12.5	15	17.5	20	mir
Sorted By Multiplier	5 7.5 Area Percent : Signal	10 Report	12.5	15	17.5	20	
Sorted By Multiplier Dilution	5 7.5 Area Percent : Signal : 1.0000 : 1.0000	10 Report	12.5	15	17.5	20	, , , , , , , , , , , , , , , , , , ,
Sorted By Multiplier Dilution Use Multiplier & Dil	5 7.5 Area Percent : Signal : 1.0000 : 1.0000 lution Factor with	10 Report	12.5	15	17.5	20	, , , , , , , , , , , , , , , , , , ,
Sorted By Multiplier Dilution Use Multiplier & Dil	5 7.5 Area Percent : Signal : 1.0000 : 1.0000 lution Factor with	10 Report	12.5	15	17.5	20	, , , , , , , , , , , , , , , , , , ,
Sorted By Multiplier Dilution Use Multiplier & Dil	5 7.5 Area Percent : Signal : 1.0000 : 1.0000 lution Factor with	Report ISTDs	12.5	15	17.5	20	, , , , , , , , , , , , , , , , , , ,
Sorted By Multiplier Dilution Use Multiplier & Dil Signal 1: DAD1 A, Si	5 7.5 Area Percent : Signal : 1.0000 : 1.0000 lution Factor with ig=254,4 Ref=off	Report ISTDs	12.5	15	17.5	20	, , , , , , , , , , , , , , , , , , ,
Sorted By Multiplier Dilution Use Multiplier & Dil Signal 1: DAD1 A, Si	5 7.5 Area Percent : Signal : 1.0000 : 1.0000 lution Factor with ig=254,4 Ref=off	Report ISTDs	12.5	15	17.5	20	, , , , , , , , , , , , , , , , , , ,
Sorted By Multiplier Dilution Use Multiplier & Dil Signal 1: DAD1 A, Si Peak RetTime Type	5 7.5 Area Percent : Signal : 1.0000 : 1.0000 lution Factor with ig=254,4 Ref=off Width Area	Report ISTDs Height	12.5	15	17.5	20	, , , , , , , , , , , , , , , , , , ,
Sorted By Multiplier Dilution Use Multiplier & Dil Signal 1: DAD1 A, Si Peak RetTime Type M # [min]	5 7.5 Area Percent : Signal : 1.0000 : 1.0000 lution Factor with ig=254,4 Ref=off Width Area [min] [mAU*s]	Report ISTDs Height [mAU]	Area %	15	17.5	20	, , , , , , , , , , , , , , , , , , ,
Sorted By Multiplier Dilution Use Multiplier & Dil Signal 1: DAD1 A, S: Peak RetTime Type M # [min]	5 7.5 Area Percent : Signal : 1.0000 : 1.0000 lution Factor with ig=254,4 Ref=off Width Area [min] [mAU*s]	10 Report ISTDs Height [mAU]	Area %	15	17.5	20	, , , , , , , , , , , , , , , , , , ,
Sorted By Multiplier Dilution Use Multiplier & Dil Signal 1: DAD1 A, S: Peak RetTime Type Y # [min] 	5 7.5 Area Percent : Signal : 1.0000 : 1.0000 lution Factor with ig=254,4 Ref=off Width Area [min] [mAU*s]	10 Report ISTDs Height [mAU] 37.41811 30.15059	Area %	15	17.5	20	mir
Sorted By Multiplier Dilution Use Multiplier & Dil Signal 1: DAD1 A, S: Peak RetTime Type T # [min] 	5 7.5 Area Percent : Signal : 1.0000 : 1.0000 lution Factor with ig=254,4 Ref=off Width Area [min] [mAU*s] 0.4297 1044.59082 0.5362 1034.66772	10 Report ISTDs Height [mAU] 37.41811 30.16058	Area % 50.2386 49.7614	15	17.5	20	mir
Sorted By Multiplier Dilution Use Multiplier & Dil Signal 1: DAD1 A, S: Peak RetTime Type T # [min] 	5 7.5 Area Percent : Signal : 1.0000 : 1.0000 lution Factor with ig=254,4 Ref=off Width Area [min] [mAU*s] 0.4297 1044.59082 0.5362 1034.66772 2079.25854	10 Report ISTDs Height [mAU] 37.41811 30.16058 67.57869	Area % 50.2386 49.7614	15	17.5	20	mir
Sorted By Multiplier Dilution Use Multiplier & Dil Signal 1: DAD1 A, S: Peak RetTime Type T # [min] 	5 7.5 Area Percent : Signal : 1.0000 : 1.0000 lution Factor with ig=254,4 Ref=off Width Area [min] [mAU*s] 0.4297 1044.59082 0.5362 1034.66772 2079.25854	10 Report ISTDs Height [mAU] 37.41811 30.16058 67.57869	Area % 50.2386 49.7614	15	17.5	20	mir
Sorted By Multiplier Dilution Use Multiplier & Dil Signal 1: DAD1 A, S: Peak RetTime Type M # [min] 	5    7.5      Area Percent      :    1.0000      :    1.0000      lution Factor with      ig=254,4 Ref=off      Width Area      [min] [mAU*s]      0.4297 1044.59082      0.5362 1034.66772      2079.25854	10 Report ISTDs Height [mAU] 37.41811 30.16058 67.57869	Area % 50.2386 49.7614	15	17.5 = =	20	

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Supplementary Figure 193. HPLC data of 6y

Data File F:\DATA\JFENG\DATA\bxf-2-44(AD,15%,1.0).D Sample Name: bxf-2-44(AD,15%,1.0)

Acq. Operator : Location : 1 Injection Date : 19/09/2019 11:55:04 Acq. Method :: DEF_LC.M Analyzis Method: E: NETHONIXEM Matricol E: NETHONIXEM Additional Info : Peak(s) manually integrated $I = \frac{1}{25} \frac{1}{10} \frac{1}{10}$						
Injection bate : 19/09/2019 11:55:04 Acg. Method :: DEF_LC.M Analysis Method :: RetPONDX.M Last changed :: 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated The set of the s	Acq. Operator :					
Injoint block i DBC I DBORNOW Analysis Method : DBC IC.M Analysis Method : F:METHODXXK.M Last changed : H4/07/2019 15:134:15 by Additional Info : Peak(s) manually integrated The second A Social A Social A Social (F. DATAUFENGUDATAbd 2:44(AD, 15%, 10)D) The second A Social A	Injection Data .	19/09/2019 11.55	• 0.4	Location :	1	
Analysis Method : F:\METHOD\EX.M East changed : 14/07/2019 15:34:15 by Additional Info : Peak(9 manually integrated DOI A Sp244 Ref-df(F:DATAJFENGDATADM2-244AD,15%,10,D)	Acg. Method :	DEF LC.M	.01			
Lact changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated The second relation of the	Analysis Method :	F:\METHOD\ZK.M				
Additional Info: : Peak(a) manually integrated DADIA Sig-2544 Ref=off (FDATAUFENGDATABUK-2-44(AD,15%,10,D)	Last changed :	14/07/2019 15:34	:15 by			
DADI A Sig-254.4 Ref-off (F.DATAUFENGDATAble 2-44(AD, 15%, 10, D)	Additional Info :	Peak(s) manually	integrated			
$\frac{1}{40} \qquad \qquad$	DAD1 A, Sig=25	4,4 Ref=off (F:\DATA\JFENG	SIDATAIbxf-2-44(AD,15	%,1.0).D)		
25  5  7.5  10  12.5  15  17.5  20  m    Area Percent Report    Area Percent Report    Sorted By : Signal    Multiplier : 1.0000  1000  1000  1000  10000    Dilution : 1.0000  1000  1000  1000  1000  1000    Use Multiplier & Dilution Factor with ISTDs  Signal 1: DAD1 A, Sig=254,4 Ref=off  Area  Height Area  #  [min] [min] [mAU*s] [mAU] %  %    Feak RetTime Type Width Area Height Area    # [min] [min] [mAU*s] [mAU] %  *  *  *	mAU 40 35 30 25 20 6 15 5 5	Me Si.''OH Me We			16.208	19:01
Area Percent Report    Sorted By  :  Signal    Multiplier  :  1.0000    Dilution  :  1.0000    Use Multiplier & Dilution Factor with ISTDs    Signal 1: DADI A, Sig=254,4 Ref=off    Peak RetTime Type Width  Area    # [min]  [mAU's]  [mAU]    1  16.208 BB  0.4039  60.09991  2.23376    1  16.61 BB  0.5250  1441.64819  42.14939  95.9980    Totals :  1501.74810  44.38315		2.5 5	7.5 1	10 12.5	15	17.5 20 mii
Area Percent Report    Sorted By  :  Signal    Multiplier  :  1.0000    Dilution  :  1.0000    Use Multiplier & Dilution Factor with ISTDs    Signal 1: DAD1 A, Sig=254,4 Ref=off    Peak RetTime Type Width  Area    # [min]  [mAU]						
Sorted By : Signal Multiplier : 1.0000 Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU] % 		Area Perc	ent Report			
Multiplier : 1.0000 Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU] % 	Sorted By	: Signa	1			
Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU] % 	Multiplier	: 1.000	0			
Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU] % 	Dilution	: 1.000	0			
Signal 1: DADI A, Sig=254,4 Ref=off Peak RetTime Type Width Area Height Area # [min] [mAU*s] [mAU] % 	Use Multiplier &	Dilution Factor w	ith ISTDs			
Peak RetTime Type Width Area  Height Area    # [min]  [min]  [mAU*s]  [mAU]  %	Signal 1: DAD1 A,	Sig=254,4 Ref=of	f			
# [min]  [min]  [mAU*s]  [mAU]  %               1  16.208  BB  0.4039  60.09991  2.23376  4.0020    2  19.661  BB  0.5250  1441.64819  42.14939  95.9980    Totals :  1501.74810  44.38315	Peak RetTime Type	Width Area	Height	Area		
 1 16.208 BE 0.4039 60.09991 2.23376 4.0020 2 19.661 BB 0.5250 1441.64819 42.14939 95.9980 Totals : 1501.74810 44.38315	# [min]	[min] [mAU*s]	[mAU]	8		
1  16.208 BB  0.4039  60.09991  2.23376  4.0020    2  19.661 BB  0.5250  1441.64819  42.14939  95.9980    Totals :  1501.74810  44.38315						
Z 13.001 BB 0.5250 1441.04019 42.14559 95.9980 Totals : 1501.74810 44.38315	1 16.208 BB	0.4039 60.099	91 2.23376	4.0020		
Totals: 1501.74810 44.38315	5 19.001 BB	0.5250 1441.648	42.14939	00000		
	Totals :	1501 748	10 44.38315			
	TOORTO .	1001.140	10 11.00010			

------*** End of Report ***

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# Supplementary Figure 194. HPLC data of 6y

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Data File F:\DATA\JFENG\DATA\FJ-11-1-rac(AD,20%,1.0).D Sample Name: FJ-11-1-rac(AD,20%,1.0)



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Supplementary Figure 195. HPLC data of 6z

Data File F:\DATA\JFENG\DATA\FJ-10-200(AD,20%,1.0).D Sample Name: FJ-10-200(AD,20%,1.0)



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Supplementary Figure 196. HPLC data of 6z

Sample Name: FJ-11-3-rac(AD,20%,1.0) Acq. Operator : Location : 1 Injection Date : 02/10/2019 09:38:27 Acq. Method : JFeng.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-11-3-rac(AD,20%,1.0).D) mAU -5.972 70 Me 01 7.562 Si 60 'OH 50 Me 40 -30 -6aa : racemic 20 -10 0-8 9 min 6 _____ Area Percent Report : Signal 1.0000 Sorted By Multiplier : 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Height Peak RetTime Type Width Area # [min] [min] [mAU*s] Area [mAU] % 1 5.972 BB 0.1489 734.85309 75.92108 50.2229 2 7.562 BB 0.1906 728.33130 58.76814 49.7771 Totals : 1463.18439 134.68922 ----------------*** End of Report ***

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Supplementary Figure 197. HPLC data of 6aa

Data File F:\DATA\JFENG\DATA\FJ-11-3-rac(AD,20%,1.0).D

Data File F:\DATA\JFENG\DATA\FJ-11-2(AD,20%,1.0).D Sample Name: FJ-11-2(AD,20%,1.0)



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Supplementary Figure 198. HPLC data of 6aa

Data File F:\DATA\JFENG\DATA\BXF-2-134(AD,20%,1.0).D Sample Name: BXF-2-134(AD,20%,1.0) _____ Acq. Operator : Location : 1 Injection Date : 11/11/2019 19:48:42 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\BXF-2-134(AD,20%,1.0).D) mAU_ <del>5.6</del>99 0 80 OH 60 Me Me 6bb : racemic 40 -29.900 20 0 -20 25 30 35 40 min 20 10 15 _____ Area Percent Report Sorted By Signal : Multiplier 1.0000 : Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [min] [mAU*s] [mAU] 8 
 1
 15.699 BB
 0.4588 3717.13770
 125.04779
 50.3423

 2
 29.900 BB
 0.9877
 3666.59521
 57.52039
 49.6577
Totals : 7383.73291 182.56818 *** End of Report ***

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Supplementary Figure 199. HPLC data of 6bb

Data File F:\DATA\JFENG\DATA\BXF-2-133(AD,20%,1.0).D Sample Name: BXF-2-133(AD,20%,1.0)



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Supplementary Figure 200. HPLC data of 6bb

Data File F:\DATA\JFENG\DATA\FJ-11-11-rac(AD,20%,1.0).D Sample Name: FJ-11-11-rac(AD,20%,1.0) Acq. Operator : Sample Operator : Acq. Instrument : LC1260 Location : 1 Injection Date : 02/10/2019 09:14:50 Inj Volume : Manually Acq. Method : F:\METHOD\JFeng.M Last changed : 02/10/2019 09:02:21 by (modified after loading) Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-11-11-rac(AD,20%,1.0).D) mAU 1 1462 5.245 250 Me Me O Si Me 'OH 200 Ph 150 6cc : racemic 100 50 · 0 7 min 6 Area Percent Report _____ _____ Sorted By : Signal : 1.0000 Multiplier 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area Height # [min] [min] [mAU*s] [mAU] Peak RetTime Type Width Area 8 ----|-----|-----|------|------| 1 4.462 BB 0.1117 2335.01074 325.37936 50.2081 2 5.245 BB 0.1310 2315.65405 273.00372 49.7919 4650.66479 598.38309 Totals :

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Supplementary Figure 201. HPLC data of 6cc

Data File F:\DATA\JFENG\DATA\FJ-11-10(AD,20%,1.0).D Sample Name: FJ-11-10(AD,20%,1.0) Acq. Operator : Location : 1 Injection Date : 02/10/2019 09:26:55 Acq. Method : JFeng.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-11-10(AD,20%,1.0).D) mAU -5.248 700 Me Me 0" 600 -SigoH Me Ph Ph 500 400 6cc 300 -200 .466 100 0 _____ Area Percent Report Sorted By : Signal 1.0000 Multiplier ÷ 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [mAU*s] [mAU] 8 1 4.466 BB 0.1040 391.48196 58.51941 6.1529 2 5.248 BB 0.1231 5971.06201 748.19598 93.8471 Totals : 6362.54398 806.71540 -----------------*** End of Report ***

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Supplementary Figure 202. HPLC data of 6cc

Data File F:\DATA\JFENG\DATA\BXF-2-139(AD,20%,1.0).D Sample Name: BXF-2-139(AD,20%,1.0) Acq. Operator : Location : 1 Injection Date : 13/11/2019 20:24:19 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\BXF-2-139(AD,20%,1.0).D) mAU ] 1841 300 -Me 0 250 Me. Si 6.982 Ph 200 6dd : racemic 150 100 50 0 min 9 _____ Area Percent Report Sorted By : Signal 1.0000 Multiplier ÷ 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [mAU*s] [mAU] 8 
 1
 4.841 BB
 0.1188 2694.25537
 338.59076
 50.0765

 2
 6.982 BB
 0.1819 2686.01855
 227.27237
 49.9235
Totals : 5380.27393 565.86313 _____ *** End of Report ***

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Supplementary Figure 203. HPLC data of 6dd

Data File F:\DATA\JFENG\DATA\BXF-2-138-2(AD,20%,1.0).D Sample Name: BXF-2-138-2(AD,20%,1.0)



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Supplementary Figure 204. HPLC data of 6dd

Data File F:\DATA\JFENG\DATA\BXF-2-150(AD,20%,1.0).D Sample Name: BXF-2-150(AD,20%,1.0) Acq. Operator : Location : 1 Injection Date : 19/11/2019 15:40:14 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 F, Sig=273,4 Ref=off (F:\DATA\JFENG\DATA\BXF-2-150(AD,20%,1.0).D) Area, 18844.4 mAU ] -586 2000 -Me 1750 0 Me Si OH Ph Ph 1500 1250 6ee : racemic 1000 19372.2 750 1.637 500 250 0 10 12 14 min _____ _____ Area Percent Report Sorted By Signal : Multiplier 1.0000 : : Dilution 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 F, Sig=273,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [mAU*s] [mAU] 8 1 4.586 MM 0.1469 1.88444e4 2137.47729 49.3094 2 11.637 MM 0.6176 1.93722e4 522.74225 50.6906 Totals : 3.82166e4 2660.21954 -----------------*** End of Report ***

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Supplementary Figure 205. HPLC data of 6ee

Data File F:\DATA\JFENG\DATA\BXF-2-149(AD,20%,1.0).D Sample Name: BXF-2-149(AD,20%,1.0)



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Supplementary Figure 206. HPLC data of 6ee

Data File F:\DATA\JFENG\DATA\SL-1-16(AD,20%,1.0).D Sample Name: SL-1-16(AD,20%,1.0) Acq. Operator : Location : 1 Injection Date : 26/10/2019 16:22:16 Acq. Method : DEF LC.M Analysis Method : F:\METHOD\ZK.M Last changed : 14/07/2019 15:34:15 by Additional Info : Peak(s) manually integrated DAD1 D, Sig=230,4 Ref=off (F:\DATA\JFENG\DATA\SL-1-16(AD,20%,1.0).D) mAU --355 1600 -Me 1.887 1400 -Me Me 0" Si.voH Me. 1200 Ph 1000 -Me 6ff : racemic 800 600 400 200 0 5 9 min _____ Area Percent Report Sorted By Signal : Multiplier 1.0000 . : Dilution 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 D, Sig=230,4 Ref=off Height [mAU] Peak RetTime Type Width Area Area # [min] [mAU*s] ofo 1 4.355 BV 0.1168 1.25693e4 1650.55920 49.7878 2 4.887 VB 0.1340 1.26764e4 1449.27954 50.2122 Totals : 2.52456e4 3099.83875 ----------------*** End of Report ***

LC1260 30/11/2019 15:28:27

Supplementary Figure 207. HPLC data of 6ff

Data File F:\DATA\JFENG\DATA\FJ-11-480(AD,20%,1.0).D Sample Name: FJ-11-480(AD,20%,1.0)



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Supplementary Figure 208. HPLC data of 6ff

Data File F:\DATA\BXF\DATA\bxf-3-87(AD,90%,1.0).D Sample Name: bxf-3-87(AD,90%,1.0)



Supplementary Figure 209. HPLC data of a mixture of 6gg and 6gg'

Data File F:\DATA\BXF\DATA\bxf-3-97(AD,90%,1.0).D Sample Name: bxf-3-97(AD,90%,1.0)



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Supplementary Figure 210. HPLC data of a mixture of 6gg and 6gg'

Data File F:\DATA\JFENG\DATA\FJ-12-129-rac(AD,20%,1.0).D Sample Name: FJ-12-129-rac(AD,20%,1.0)

Acq. Operator : Location : 1 Injection Date : 30/05/2020 19:23:31 Acq. Method : DEF LC.M Analysis Method : C:\Chem32\1\Methods\DEF_LC.M Last changed : 13/02/2014 23:27:44 by SYSTEM Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-12-129-rac(AD,20%,1.0).D) mAU -078 80 -8.433 70 60 6b, racemic 6m, racemic 50 18.436 40 16.837 30 20 10 0 2.5 15 10 12.5 17.5 7.5 min Area Percent Report _____ Sorted By Signal : Multiplier 1.0000 : Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU] 90 1 8.433 BV 0.2053 975.61163 73.31185 22.3421 2 9.078 VB 0.2249 1219.14490 83.20212 27.9191 3 16.837 BB 0.5125 976.81873 29.79408 22.3697 4 18.436 BB 0.5209 1195.12402 35.66485 27.3690 Totals : 4366.69928 221.97290 *** End of Report ***

LC1260 02/07/2020 08:57:37

Supplementary Figure 211. HPLC data of a mixture of 6m and 6b

Data File F:\DATA\JFENG\DATA\FJ-12-129-(1)-(AD,20%,1.0).D Sample Name: FJ-12-129-(1)-(AD,20%,1.0)



Supplementary Figure 212. HPLC data of a mixture of 6m and 6b

Data File F:\DATA\JFENG\DATA\FJ-11-169-race-(1)(AD,10%,1.0).D Sample Name: FJ-11-169-race-(1)(AD,10%,1.0)



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### Supplementary Figure 213. HPLC data of 7

Data File F:\DATA\JFENG\DATA\FJ-11-169-chiral-0226(AD,10%,1.0).D Sample Name: FJ-11-169-chiral-0226(AD,10%,1.0)



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## Supplementary Figure 214. HPLC data of 7

Data File F:\DATA\JFENG\DATA\FJ-11-123-rac-(2)(AD,10%,1.0).D Sample Name: FJ-11-123-rac-(2)(AD,10%,1.0) _____ Acq. Operator : Location : 1 Injection Date : 01/03/2020 17:23:51 Acq. Method : JFeng.M Analysis Method : F:\METHOD\JFeng.M Last changed : 19/09/2014 20:49:49 by Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-11-123-rac-(2)(AD,10%,1.0).D) mAU -158 350 -Ph 9.680 300 SimOH PhPh 250 8 : racemic 200 150 -100 50 0 10 8 _____ _____ Area Percent Report : Signal 1.0000 Sorted By Multiplier 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area # [min] [min] [mAU*s] Height [mAU] Area % 
 1
 8.158 BB
 0.2881 6883.85938
 378.69330
 49.8741

 2
 9.680 BB
 0.3824 6918.61914
 285.77731
 50.1259
Totals : 1.38025e4 664.47061 *** End of Report ***

LC1260 01/03/2020 17:36:20

Supplementary Figure 215. HPLC data of 8

Data File F:\DATA\JFENG\DATA\FJ-11-123-chiral-(8)(AD,10%,1.0).D Sample Name: FJ-11-123-chiral-(8)(AD,10%,1.0)



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Supplementary Figure 216. HPLC data of 8

Data File F:\DATA\JFENG\DATA\FJ-11-170-rac-0225(AD,6%,1.0).D Sample Name: FJ-11-170-rac-0225(AD,6%,1.0)



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## Supplementary Figure 217. HPLC data of 9
Data File F:\DATA\JFENG\DATA\FJ-11-170-chiral-0225(AD,6%,1.0).D Sample Name: FJ-11-170-chiral-0225(AD,6%,1.0) _____ Acq. Operator : Location : 1 Injection Date : 25/02/2020 10:57:15 Acq. Method : JFeng.M Analysis Method : F:\METHOD\JFeng.M Last changed : 19/09/2014 20:49:49 by Additional Info : Peak(s) manually integrated DAD1 F, Sig=273,4 Ref=off (F:\DATA\JFENG\DATA\FJ-11-170-chiral-0225(AD,6%,1.0).D) 1484.95 mAU -026 Ph 140 1,1 Br 120 0 Şi~Ph 100 Ph 80 9 60 40 1266978 page 124 20 0 _____ _____ Area Percent Report : Signal 1.0000 Sorted By Multiplier : 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 F, Sig=273,4 Ref=off Height Area Peak RetTime Type Width Area # [min] [mAU*s] [mAU] 8 
 1
 3.424 MM
 0.1019
 82.63519
 13.52122
 5.2715

 2
 4.026 MM
 0.1654
 1484.94800
 149.61452
 94.7285
Totals : 1567.58319 163.13574 *** End of Report ***

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Supplementary Figure 218. HPLC data of 9

Data File F:\DATA\JFENG\DATA\FJ-12-195-a-race(OD,5%,1.0).D Sample Name: FJ-12-195-a-RACE(OD, 5%, 1.0) Acq. Operator : Location : 1 Injection Date : 27/06/2020 16:02:11 Acq. Method : DEF LC.M Analysis Method : C:\Chem32\1\Methods\DEF_LC.M Last changed : 13/02/2014 23:27:44 by SYSTEM Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-12-195-a-race(OD,5%,1.0).D) 171442 mAU ] 9.901 600 0440 6440 6440 Ph 02 500 Br 400 10 : racemic 300 200 100 0 6 10 min _____ _____ Area Percent Report : Signal 1.0000 Sorted By Multiplier ÷ 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area # [min] [min] [mAU*s] Height [mAU] Area ofo 1 6.901 MM 0.2046 7744.19629 630.75885 50.9401 2 9.440 MM 0.2720 7458.36865 456.97809 49.0599 Totals : 1.52026e4 1087.73694 *** End of Report ***

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Supplementary Figure 219. HPLC data of 10

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Data File F:\DATA\JFENG\DATA\FJ-12-199-(OD,5%,1.0).D Sample Name: FJ-12-199-(OD,5%,1.0)



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### Supplementary Figure 220. HPLC data of 10

Data File F:\DATA\JFENG\DATA\FJ-12-198-race(OD,5%,1.0).D Sample Name: FJ-12-198-race(OD,5%,1.0) Acq. Operator : Location : 1 Injection Date : 28/06/2020 09:24:05 Acq. Method : JFeng.M Analysis Method : C:\Chem32\1\Methods\DEF_LC.M Last changed : 13/02/2014 23:27:44 by SYSTEM Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-12-198-race(OD,5%,1.0).D) Hea 1322.39 mAU -9:939 250 0 OMe 200 11 : racemic 150 100 50 0 10 12 14 min _____ Area Percent Report Signal 1.0000 Sorted By : Multiplier ÷ 1.0000 Dilution Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area # [min] [min] [mAU*s] Height Area [mAU] 8 
 1
 9.939 MM
 0.4101 7322.38721
 297.60254
 50.9989

 2
 12.316 MM
 0.4715
 7035.55566
 248.70322
 49.0011
Totals : 1.43579e4 546.30576 ------*** End of Report ***

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## Supplementary Figure 221. HPLC data of 11

Data File F:\DATA\JFENG\DATA\FJ-12-200-(OD,5%,1.0).D Sample Name: FJ-12-200-(OD,5%,1.0) Acq. Operator : Location : 1 Injection Date : 28/06/2020 09:42:18 Acq. Method : JFeng.M Analysis Method : C:\Chem32\1\Methods\DEF_LC.M Last changed : 13/02/2014 23:27:44 by SYSTEM Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-12-200-(OD,5%,1.0).D) 1930.4 mAU -9:959 500 0 400 OMe 300 11 200 481,484,493,222 100 0 12 10 14 min 8 _____ Area Percent Report _____ Sorted By Signal : 1.0000 Multiplier : : Dilution 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Height Peak RetTime Type Width Area Area # [min] [min] [mAU*s] [mAU] 8 1 9.959 MM 0.3773 1.19304e4 527.06537 96.2938 2 12.355 MM 0.4676 459.18649 16.36664 3.7062 Totals : 1.23896e4 543.43201 ------------------*** End of Report ***

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### Supplementary Figure 222. HPLC data of 11

Data File F:\DATA\JFENG\DATA\FJ-12-132-race-(1)(AD,20%,1.0).D Sample Name: FJ-12-132-race-(1)(AD,20%,1.0) _____ Acq. Operator : Location : 1 Injection Date : 29/06/2020 21:26:16 Acq. Method : JFeng.M Analysis Method : C:\Chem32\1\Methods\DEF_LC.M Last changed : 13/02/2014 23:27:44 by SYSTEM Additional Info : Peak(s) manually integrated DAD1 A, Sig=254,4 Ref=off (F:\DATA\JFENG\DATA\FJ-12-132-race-(1)(AD,20%,1.0).D) mAU **11:525** 350 Ph O_SI.VOH 300 Me Me 17.926 250 200 -S6 : racemic 150 100 50 0 12 16 18 10 14 min _____ Area Percent Report _____ Sorted By Signal : Multiplier 1.0000 : Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=254,4 Ref=off Peak RetTime Type Width Area Height Area # [min] [mAU*s] [mAU] 8 
 1
 11.525
 BB
 0.2767
 6883.16504
 381.08438
 49.9439

 2
 17.926
 BB
 0.4543
 6898.61523
 235.11957
 50.0561
Totals : 1.37818e4 616.20395 *** End of Report ***

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Supplementary Figure 223. HPLC data of S6

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Data File F:\DATA\JFENG\DATA\FJ-12-197(AD,20%,1.0).D Sample Name: FJ-12-197(AD,20%,1.0)

Acq. Operator	:		
Sample Operator	:		
Acq. Instrument	: LC1260	Location : 1	
Injection Date	: 29/06/2020 21:48:05		
		Inj Volume : Manually	
Acq. Method	: F:\METHOD\JFeng.M		
Last changed	: 29/06/2020 21:10:13 by		
	(modified after loading)	1047 -	
Analysis Method	: C:\Chem32\1\Methods\DEF_LC.N	M	
Last changed	: 13/02/2014 23:27:44 by SYST	SM.	
Additional Info	: Peak(s) manually integrated		
DADT A, SIg=2	254,4 Ret=oft (F:\DATA\JFENG\DATA\FJ-12-197(A	AD,20%,1.0).D)	ŝ
mAU -			94
200	$\sim$		Ť
175-	Ph Ph		
1			
150			1
	Y Y I OH		
	Me Me		
125	$\sim$		
-			
100	56		
-			
75			
		547	
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<b>`</b>	. , , , ,	10 12 14	10 10 10
	Area Percent Report		
Sorted By	: Signal		
Multiplier	: 1.0000		
Dilution	: 1.0000		
Use Multiplier &	Dilution Factor with ISTDs		
Signal 1: DAD1 A	, Sig=254,4 Ref=off		
Peak RetTime Typ	e Width Area Height	Area	
# [min]	[min] [mAU*s] [mAU]	8	
	-		
1 11.547 BB	0.2694 863.20203 49.034	44 12.4029	
2 17.945 BB	0.4469 6096.48047 209.8602	26 87.5971	
Totals :	6959.68250 258.894	70	

LC1260 01/07/2020 21:10:55

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# Supplementary Figure 224. HPLC data of S6

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