Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

A General Method for Asymmetric Arylation and Vinylation of Silyl Ketene Acetals

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Supporting information: procedures and characterization

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I. General

^{1}H NMR spectra were acquired on Bruker Avance 400 or 300 MHz spectrometers and chemical shifts were recorded relative to $SiMe_4$ (δ 0.00) or residual protiated solvents ($CDCl_3$: δ 7.26; C_6D_6: δ 7.16; CD_2Cl_2: 5.30). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiple). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a J value in Hz. ^{13}C NMR spectra were obtained at 100 MHz on 400 MHz or 75 MHz on 300 MHz instruments and chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.23). ^{31}P{^{1}H} NMR spectra were recorded at 162 MHz using H_3PO_4 as an external reference. ^{19}F{^{1}H} NMR spectra were recorded at 376 MHz using $CFCl_3$ as an external reference. Proof of purity of new compounds was demonstrated with copies of ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra.

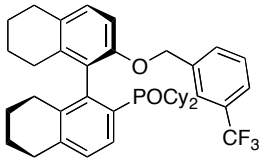
Anhydrous α,α,α–trifluorotoluene (Aldrich) was degassed by argon bubbling and then stored over activated 4 Å molecular sieve beads in the glove box before use. Dry diethyl ether, toluene, hexane and dichloromethane were collected from a solvent purification system containing a column of activated alumina (1 m x 2) under argon. Anhydrous $PhCF_3$ (Aldrich), *t*-butyl methyl ether (Aldrich) and cyclopentyl methyl ether were used without further purification and were stored in the glove box. Dry THF was freshly distilled from sodium/benzophenone under argon before use. Dry triethylamine and trimethylsilyl chloride were distilled from CaH_2 under argon before use. Diisopropylamine was distilled from anhydrous KOH under argon before use. *o*-Xylene was distilled from sodium under argon before use. All of anhydrous solvents were stored in Schlenk tubes in the glove box. The GC standard, *n*-dodecane was degassed and dried over activated 4 Å molecular sieve beads before use.

Unless noted otherwise, commercially available chemicals were used without further purification. $PdMe_2$(TMEDA)[1] and biarylphosphines L1-4[2] were prepared according to reported procedures. Anhydrous lithium acetate (Aldrich) was dissolved in acetic acid, then concentrated and dried in a vacuum oven (29 inHg of partial vacuum at 120 ^{o}C) for 12 hours before use. The treatment is important for reproducibility of catalytic arylation reactions. (*E*)-1-*t*-Butoxy-1-(trimethylsiloxy)-propene was prepared according to our reported procedure and the final aqueous workup was important![2]

Glassware was dried at 120 ^{o}C for at least 3 hours before use. Flash

chromatography was preformed using Merck 40-63D 60 Å silica gel. GC and GC/MS analysis were conducted with Agilent J&W GC column DB-5MS-UI. Chiral HPLC analysis was performed on a Shimadzu LC-20AD instrument using Daicel Chiracel columns at 25°C. Optical rotation was measured using a JASCO P-1030 Polarimeter equipped with a sodium vapor lamp at 589 nm and the concentration of samples was denoted as *c*.

II. Synthesis of chiral biarylmonophosphines



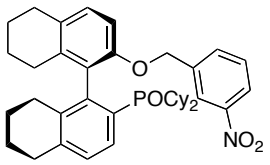
(*R*)-2-Dicyclohexylphosphinyl-2′-*m*-trifluoromethylbenzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. Under argon, to a 25 mL two-necked RBF equipped with a condenser was added (*R*)-2-dicyclohexylphosphinyl-2′-hydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (147 mg, 0.30 mmol) and anhydrous K_2CO_3 (207 mg, 1.5 mmol). Then analytical-grade acetone (6 mL) was added, followed by 3-(trifluoromethyl)benzyl bromide (358 mg, 1.5 mmol), . The resulting mixture was refluxed under argon for 1 day until all the starting material was consumed (monitored by ^{31}P NMR spectroscopy). After the mixture was cooled to 25 ^{o}C, it was filtered through a pad of Celite with ethyl acetate washings (10 mL × 2). The filtrate was concentrated on a rotary evaporator and the resulting residue was purified by flash chromatography (ethyl acetate/hexane 3:2), which afforded the desired compound (165 mg, 85%) as yellow foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.42 (m, 1H), 7.36-7.32 (m, 1H), 7.30-7.26 (m, 2H), 7.17-7.15 (m, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 4.98 (ψs, 2H), 2.88-2.71 (m, 4H), 2.54-2.48 (m, 1H), 2.27-2.21 (m, 1H), 2.17-2.09 (m, 1H), 2.05-1.98 (m, 1H), 1.88-1.06 (m, 27H), 0.95-0.70 (m, 3H).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 45.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.78.

ESI-MS: Calcd for $C_{40}H_{49}F_3O_2P$ $(M+H)^+$: 649.33. Found: 649.45.

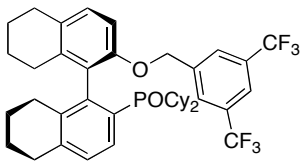


(*R*)-2-Dicyclohexylphosphinyl-2′-*m*-nitrobenzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. Under argon, to a 25-mL two-necked RBF equipped with a condenser was added (*R*)-2-dicyclohexylphosphinyl-2′-hydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (147 mg, 0.30 mmol) and anhydrous K_2CO_3 (207 mg, 1.5 mmol). Then analytical-grade acetone (6 mL) was added, followed by *m*-nitrobenzyl bromide (324 mg, 1.5 mmol). The resulting mixture was refluxed under argon for 1 day until all the starting material was consumed (monitored by ^{31}P NMR spectroscopy). After the mixture was cooled to 25 ^{o}C, it was filtered through a pad of Celite with ethyl acetate washings (10 mL × 2). The filtrate was concentrated on a rotary evaporator and the resulting residue was purified by flash chromatography (ethyl acetate/hexane 3:2), which afforded the desired compound (187 mg, quantitative) as yellow foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.03 (m, 1H), 7.83 (s, 1H), 7.45-7.39 (m, 2H), 7.30-7.25 (m, 1H), 7.20-7.18 (m, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 5.06-4.99 (m, 2H), 2.99-2.72 (m, 4H), 2.54-2.47 (m, 1H), 2.29-2.34 (m, 1H), 2.20-2.14 (m, 1H), 2.07-1.99 (m, 1H), 1.78-1.09 (m, 27H), 0.97-0.73 (m, 3H).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 44.9.

ESI-MS: Calcd for $C_{39}H_{49}NO_4P$ $(M+H)^+$: 626.33. Found: 626.44.



(*R*)-2-Dicyclohexylphosphinyl-2′-*m,m*-bis(trifluoromethyl)benzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. Under argon, to a 25-mL two-necked was added (*R*)-2-dicyclohexylphosphinyl-2′-hydroxy-5,5',6,6',7,7',8,8'-octahydro-binaphthyl (470 mg, 0.96 mmol) and *m,m*-bis(trifluoromethyl)benzyl bromide (460 mg, 1.5 mmol), then anhydrous DMF (5 mL) was added, followed by NaH (73 mg, 3.1 mmol). The resulting mixture was stirred at room temperature for 12 h until all the starting material was consumed (monitored by ^{31}P NMR spectroscopy). Then, the reaction mixture was diluted with EA (20 ml) and washed by saturated ammonium

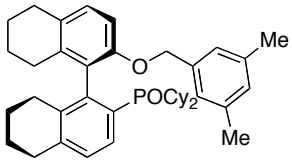
chloride solution (20 ml), water (20 ml) and brine (20 ml), then dried over anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator and the resulting residue was purified by flash chromatography (ethyl acetate/hexane 2:1 to DCM/MeOH 20:1), which afforded the desired compound (620 mg, 90%) as yellow foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.43 (s, 2H), 7.24-7.22 (m, 1H), 7.19-7.16 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 5.03 (ψs, 2H), 2.89-2.73 (m, 4H), 2.57-2.51 (m, 1H), 2.25-2.13 (m, 2H), 2.07-2.00 (m, 1H), 1.87-1.01 (m, 27H), 0.90-0.62 (m, 3H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 45.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.0.

ESI-MS: Calcd for $C_{41}H_{48}F_6O_2P$ $(M+H)^+$: 717.32. Found: 717.46.

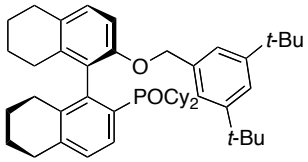


(*R*)-2-Dicyclohexylphosphinyl-2′-*m,m*-dimethylbenzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. The same procedure as above was used. (*R*)-2-Dicyclohexylphosphinyl-2′-hydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (200 mg, 0.41 mmol), *m,m*-dimethylbenzyl bromide (121 mg, 0.61 mmol), NaH (30 mg, 1.23 mmol) and DMF (3 mL) were used. The reaction was stirred at room temperature for 1 h. The crude product was purified by flash chromatography (ethyl acetate/hexane 2:1 to DCM/MeOH 20:1), which afforded the desired compound (240 mg, 97%) as white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 10.6, 8.0 Hz, 1H), 7.14 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.80 (s, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.64 (s, 2H), 4.90-4.83 (m, 2H), 2.89-2.80 (m, 3H), 2.77-2.71 (m, 1H), 2.52-2.44 (m, 1H), 2.32-2.13 (m, 10H), 2.05-1.95 (m, 1H), 1.84-0.87 (m, 28H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 45.01.

ESI-MS: Calcd for $C_{41}H_{54}O_2P$ $(M+H)^+$: 609.38. Found: 609.63.

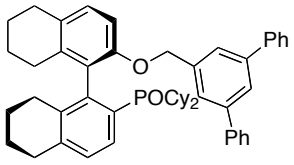


(*R*)-2-Dicyclohexylphosphinyl-2′-*m,m*-di-*t*-butylbenzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. The same procedure as above was used. (*R*)-2-Dicyclohexylphosphinyl-2′-hydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (100 mg, 0.20 mmol), *m,m*-di-*t*-butylbenzyl bromide (86 mg, 0.31 mmol), NaH (15 mg, 0.6 mmol) and DMF (2 mL) were used. The reaction was stirred at room temperature for 12 h. The crude product was purified by flash chromatography (ethyl acetate/hexane 2:1 to DCM/MeOH 20:1), which afforded the desired compound (140 mg, 99%) as white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (m, 1H), 7.19 (s, 1H), 7.13-7.10 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 1.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 4.98 (d, *J* = 12.0 Hz, 1H), 4.90 (d, *J* = 12.0 Hz, 1H), 2.87-2.72 (m, 4H), 2.49-2.42 (m, 1H), 2.37-2.29 (m, 1H), 2.19-2.13 (m, 1H), 2.00-1.94 (m, 1H), 1.75-0.85 (m, 46H), 0.65-0.59 (m, 2H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 44.9.

ESI-MS: Calcd for $C_{47}H_{66}O_2P$ $(M+H)^+$: 693.47. Found: 693.66.

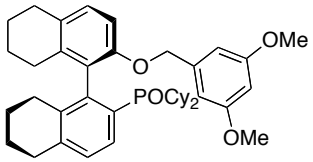


(*R*)-2-Dicyclohexylphosphinyl-2′-*m,m*-diphenylbenzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. The same procedure as above was used. (*R*)-2-Dicyclohexylphosphinyl-2′-hydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (200 mg, 0.41 mmol), *m,m*-diphenylbenzyl bromide (197 mg, 0.61 mmol), NaH (29 mg, 1.22 mmol) and DMF (4 mL) were used. The reaction was stirred at room temperature for 12 h. The crude product was purified by flash chromatography (ethyl acetate/hexane 2:1 to DCM/MeOH 20:1), which afforded the desired compound (270 mg, 91%) as white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.47-7.34 (m, 11H), 7.26-7.24 (m, 2H), 7.18-7.15 (m, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 5.10-5.02 (m, 2H), 2.88-2.71 (m, 3H), 2.68-2.60 (m, 1H), 2.50-2.45 (m, 1H), 2.33-2.25 (m, 1H), 2.15-2.10 (m, 1H), 2.01-1.95 (m, 1H), 1.97-1.03 (m, 27H), 0.91-0.74 (m, 3H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 45.2.

ESI-MS: Calcd for $C_{51}H_{58}O_2P$ $(M+H)^+$: 733.41. Found: 733.56.

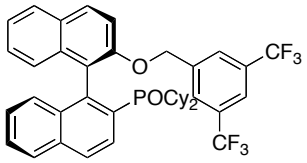


(*R*)-2-Dicyclohexylphosphinyl-2′-*m,m*-dimethoxylbenzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. The same procedure as above was used. (*R*)-2-Dicyclohexylphosphinyl-2′-hydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (100 mg, 0.20 mmol), *m,m*-dimethoxylbenzyl bromide (72 mg, 0.31 mmol), NaH (15 mg, 0.61 mmol) and DMF (2 mL) were used. The reaction was stirred at room temperature for 12 h. The crude product was purified by flash chromatography (ethyl acetate/hexane 2:1 to DCM/MeOH 20:1), which afforded the desired compound (66 mg, 51%) as white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.35 (m, 1H), 7.11-7.09 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.27 (t, *J* = 2.3 Hz, 1H), 6.23-6.22 (m, 2H), 4.91 (ψs, 2H), 3.61 (s, 6H), 2.87-2.74 (m, 4H), 2.48-2.43 (m, 1H), 2.30-2.26 (m, 1H), 2.15-2.11 (m, 1H), 2.01-1.94 (m, 1H), 1.89-1.07 (m, 27H), 0.97-0.81 (m, 3H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 44.75.

ESI-MS: Calcd for $C_{41}H_{54}O_4P$ $(M+H)^+$: 641.37. Found: 641.57.



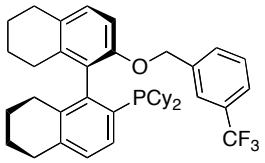
(*R*)-2-Dicyclohexylphosphinyl-2'-*m,m*-bis(trifluoromethyl)benzyloxy-1,1'-binaphthyl. Under argon, to a 25 mL two-necked RBF equipped with a condenser was added (*R*)-2-Dicyclohexylphosphinyl-2′-hydroxy-1,1'-binaphthyl (300 mg, 0.62 mmol) and *m,m*-bis(trifluoromethyl)benzyl bromide (285 mg, 0.9 mmol), then anhydrous DMF (5 mL) was added, followed by NaH (46 mg, 1.9 mmol). The resulting mixture was stirred at room temperature for 12 h until all the starting material was consumed (monitored by ^{31}P NMR spectroscopy). Then, the reaction mixture was diluted with EA (20 ml) and washed by saturated ammonium chloride solution (20 ml), water (20 ml) and brine (20 ml), then dried over anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator and the resulting residue was purified by flash chromatography (ethyl acetate/hexane 2:1 to DCM/MeOH 20:1), which afforded the desired compound (390 mg, 89%) as yellow foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-7.96 (m, 3H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.9 Hz, 1H), 7.60 (ψs, 1H), 7.55-7.51 (m, 1H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.35-7.31 (m, 1H), 7.29-7.18 (m, 5H), 7.04 (d, *J* = 8.4 Hz, 1H), 5.23 (d, *J* = 12.7 Hz, 1H), 5.08 (d, *J* = 12.7 Hz, 1H), 1.77-1.61 (m, 5H), 1.51-1.42 (m, 6H), 1.34-1.15 (m, 5H), 1.07-1.01 (m, 2H), 0.93-0.75 (m, 4H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 45.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.04.

ESI-MS: Calcd for $C_{41}H_{40}F_6O_2P$ $(M+H)^+$: 709.26. Found: 709.43.



(*R*)-2-Dicyclohexylphosphino-2′-*m*-trifluoromethylbenzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. Under argon, a 25-mL Schlenk tube was charged with the phosphine oxide (60 mg, 0.09 mmol), triethylamine (0.5 mL, 3.6 mmol) and dry toluene (2.0 mL). After the resulting solution was cooled to 0 ^{o}C, trichlorosilane (0.09 mL, 0.9 mmol) was added by syringe. The resulting mixture was heated with stirring in a 110 ^{o}C oil bath for 12 hours, until all the starting material was consumed (monitored by ^{31}P NMR spectroscopy). At the conclusion of the reaction, the mixture was cooled to 25 ^{o}C in the glove box and diluted with degassed diethyl ether (10 mL). After the resulting suspension was briefly chilled for 5 minutes in a -30 ^{o}C fridge of the glove box, a degassed, saturated Na_2CO_3 solution (1.0 mL) was added to quench the reaction. The desired ligand was obtained after the crude mixture was passed through a pad of silica gel and washed with diethyl ether in the glove box. The filtrate was concentrated under vacuum and afforded the desired compound (38 mg, 67%) as white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.43 (m, 1H), 7.36-7.24 (m, 4H), 7.11-7.06 (m, 2H), 6.70 (d, *J* = 8.3 Hz, 1H), 5.01 (d, *J* = 12.8 Hz, 1H), 4.91 (d, *J* = 12.8 Hz, 1H), 2.85-2.72 (m, 4H), 2.42-2.27 (m, 2H), 2.15-1.94 (m, 3H), 1.79-0.80 (m, 28H), 0.62-0.60 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 145.1, 144.8, 139.0, 137.9, 136.4, 135.7, 135.6, 131.9, 131.7, 130.9, 130.5, 129.7, 129.6, 129.0, 128.8, 128.4, 127.5, 123.8, 122.9, 122.8, 108.1, 67.4, 35.3, 35.1, 33.1, 33.0, 30.4, 30.3, 30.2, 30.1, 29.7, 29.6,

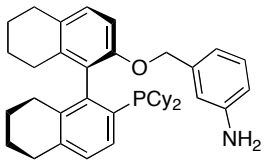
29.3, 29.1, 28.3, 27.7, 27.6, 27.5, 27.3, 27.2, 26.6, 26.2, 23.5, 23.2, 23.1, 22.9. The splitting pattern was not assigned due to complexity of the spectrum.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ -10.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.8.

$[\alpha]^{21}_{D} = +24.6^{o}$ (c = 0.3, $CHCl_3$).

ESI-MS: Calcd for $C_{40}H_{49}F_3OP$ $(M+H)^+$: 633.34. Found: 633.48.



(*R*)-2-Dicyclohexylphosphino-2′-*m*-aminobenzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. Under argon, a 25-mL Schlenk tube was charged with the phosphine oxide (100.0 mg, 0.16 mmol), triethylamine (0.89 mL, 6.4 mmol) and dry toluene (3.0 mL). After the resulting solution was cooled to 0 ^{o}C, trichlorosilane (0.16 mL, 1.6 mmol) was added by syringe. The resulting mixture was heated with stirring in a 110 ^{o}C oil bath for 12 hours, until all the starting material was consumed (monitored by ^{31}P NMR spectroscopy). At the conclusion of the reaction, the mixture was cooled to 25 ^{o}C in the glove box and diluted with degassed diethyl ether (10 mL). After the resulting suspension was briefly chilled for 5 minutes in a -30 ^{o}C fridge of the glove box, a degassed, saturated Na_2CO_3 solution (1.0 mL) was added to quench the reaction. The desired ligand was obtained after the crude mixture was passed through a pad of silica gel and washed with diethyl ether in the glove box. The filtrate was concentrated under vacuum and afforded the desired compound (47 mg, 50%) as white foam.

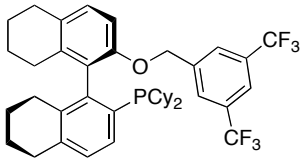
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.31 (m, 1H), 7.09-6.98 (m, 3H), 6.69 (d, J = 8.4 Hz, 1H), 6.52-6.48 (m, 2H), 6.33 (s, 1H), 4.87 (d, J = 12.8 Hz, 1H), 4.82 (d, J = 12.8 Hz, 1H), 3.48 (br s, 2H), 2.86-2.74 (m, 4H), 2.38-2.30 (m, 2H), 2.14-2.08 (m, 1H), 2.02-1.92 (m, 2H), 1.75-0.79 (m, 29H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 146.3, 145.6, 145.3, 139.4, 137.7, 136.1, 136.0, 132.3, 129.6, 129.5, 129.1, 129.0, 128.7, 127.1, 116.1, 113.6, 112.8, 108.6, 68.5, 35.3, 33.1, 33.0, 30.4, 30.3, 30.1, 29.9, 29.8, 29.4, 29.3, 29.1, 28.3, 27.8, 27.7, 27.6, 27.4, 27.3, 27.2, 26.6, 26.4, 23.6, 23.2, 23.1, 23.0. The splitting pattern was not assigned due to complexity of the spectrum.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ -10.2.

$[\alpha]^{21}_{D} = +27.3^{o}$ (c = 0.3, $CHCl_3$).

ESI-MS: Calcd for $C_{39}H_{51}NOP$ $(M+H)^{+}$: 580.36. Found: 580.55.



(*R*)-2-Dicyclohexylphosphino-2′-*m*,*m*-bis(trifluoromethyl)benzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. The same procedure as described above was used. The corresponding phosphine oxide (147 mg, 0.20 mmol), triethylamine (1.13 mL, 8.2 mmol), trichlorosilane (0.20 mL, 2.0 mmol) and dry toluene (5 mL) were used. The reaction was finished after heating at 110 ^{o}C for 12 hours. After workup, the resulting residue was purified in the glove box by flash chromatography (degassed diethyl ether), which afforded the desired compound (107 mg, 75%) as white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.45 (s, 2H), 7.34-7.31 (m, 1H), 7.13-7.08 (m, 2H), 6.70 (d, J = 8.3 Hz, 1H), 5.05 (d, J = 13.2 Hz, 1H), 4.95 (d, J = 13.2 Hz, 1H), 2.84-2.74 (m, 4H), 2.44-2.39 (m, 1H), 2.29-2.23 (m, 1H), 2.16-2.03 (m, 2H), 1.95-1.91 (m, 1H), 1.80-1.01 (m, 23H), 0.92-0.74 (m, 4H), 0.53-0.49 (m, 1H).

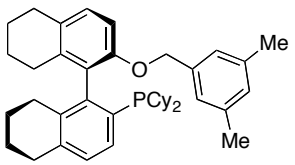
^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 144.8, 140.5, 138.1, 136.7, 136.6, 135.5, 131.8, 131.6, 131.3, 130.1, 129.8, 129.7, 128.9, 127.7, 126.0, 124.6, 121.9, 120.9, 107.9, 66.7, 35.2, 35.1, 33.2, 33.1, 30.4, 30.3, 30.2, 30.0, 29.6, 29.5, 29.4, 29.3, 29.2, 28.3, 27.7, 27.6, 27.5, 27.4, 27.3, 27.2, 26.6, 26.1, 23.5, 23.1, 23.0, 22.9. The splitting pattern was not assigned due to complexity of the spectrum.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ -10.3

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.0

$[\alpha]^{21}_{D} = +50.7^{o}$ (c = 0.3, $CHCl_3$).

ESI-MS: Calcd for $C_{41}H_{48}F_6OP$ $(M+H)^{+}$: 701.33. Found: 701.60.



(*R*)-2-Dicyclohexylphosphino-2′-*m*,*m*-dimethylbenzyloxy-5,5',6,6',7,7',8,8'-

octahydro-1,1'-binaphthyl. The same procedure as described above was used. The corresponding phosphine oxide (240 mg, 0.39 mmol), triethylamine (2.17 mL, 15.6 mmol), trichlorosilane (0.41 mL, 4.07 mmol) and dry toluene (5 mL) were used. The reaction was finished after heating at 110 ^{o}C for 12 hours. After workup, the resulting residue was purified in the glove box by flash chromatography (degassed diethyl ether), which afforded the desired compound (190 mg, 83%) as white foam.

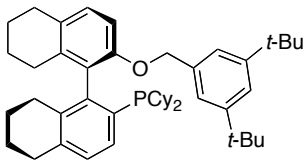
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.30 (m, 1H), 7.08-7.02 (m, 2H), 6.80 (s, 1H), 6.70-6.68 (m, 3H), 4.87 (d, *J* = 12.5 Hz, 1H), 4.81 (d, *J* = 12.5 Hz, 1H), 2.85-2.73 (m, 4H), 2.38-2.31 (m, 2H), 2.19 (s, 6H), 2.13-2.08 (m, 1H), 2.04-1.93 (m, 2H), 1.78-0.88 (m, 28H), 0.78-0.74 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 153.3, 145.6, 145.3, 137.9, 137.7, 137.5, 136.1, 136.0, 135.9, 132.2, 132.0, 129.6, 129.5, 129.0, 128.7, 128.5, 127.2, 123.9, 108.4, 68.5, 35.3, 35.2, 33.1, 33.0, 30.4, 30.3, 30.1, 29.8, 29.7, 29.4, 29.2, 29.1, 28.3, 27.8, 27.7, 27.6, 27.4, 27.3, 27.2, 26.6, 26.3, 23.6, 23.2, 21.3. The splitting pattern was not assigned due to complexity of the spectrum.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ -10.2.

$[\alpha]^{21}_{D}$ = +35.2 (*c* = 0.3, $CHCl_3$).

ESI-MS: Calcd for $C_{41}H_{54}OP$ $(M+H)^{+}$: 593.38. Found: 593.56.



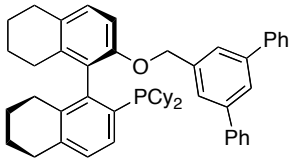
(*R*)-2-Dicyclohexylphosphino-2′-*m,m*-di-*t*-butylbenzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. The same procedure as described above was used. The corresponding phosphine oxide (200 mg, 0.29 mmol), triethylamine (1.61 mL, 11.6 mmol), trichlorosilane (0.29 mL, 2.9 mmol) and dry toluene (5 mL) were used. The reaction was finished after heating at 110 ^{o}C for 12 hours. After workup, the resulting residue was purified in the glove box by flash chromatography (degassed diethyl ether), which afforded the desired compound (158 mg, 80%) as white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.30 (m, 1H), 7.22 (s, 1H), 7.12-7.07 (m, 2H), 6.92-6.91 (m, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 5.04 (d, *J* = 12.2 Hz, 1H), 4.85 (d, *J* = 12.2 Hz, 1H), 2.89-2.74 (m, 4H), 2.46-2.34 (m, 2H), 2.19-2.12 (m, 1H), 2.05-1.98 (m, 2H), 1.75-0.79 (m, 45H), 0.66-0.47 (m, 2H).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ -10.0.

$[\alpha]^{21}_{D} = +31.3^{o}$ (c = 0.3, $CHCl_3$).

ESI-MS: Calcd for $C_{47}H_{66}OP$ $(M+H)^{+}$: 677.48. Found: 677.63.



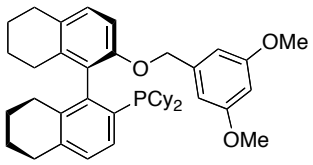
(*R*)-2-Dicyclohexylphosphino-2′-*m,m*-diphenylbenzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. The same procedure as described above was used. The corresponding phosphine oxide (200 mg, 0.27 mmol), triethylamine (1.50 mL, 10.8 mmol), trichlorosilane (0.27 mL, 2.7 mmol) and dry toluene (5 mL) were used. The reaction was finished after heating at 110 ^{o}C for 12 hours. After workup, the resulting residue was purified in the glove box by flash chromatography using degassed diethyl ether, which afforded the desired compound (165 mg, 85%) as white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.49-7.41 (m, 8H), 7.38-7.34 (m, 3H), 7.27 (d, J = 1.1 Hz, 2H), 7.13-7.08 (m, 2H), 6.78 (d, J = 8.4 Hz, 1H), 5.10 (d, J = 12.6 Hz, 1H), 5.02 (d, J = 12.6 Hz, 1H), 2.86-2.74 (m, 3H), 2.68-2.63 (m, 1H), 2.42-2.33 (m, 2H), 2.15-2.07 (m, 1H), 2.04-1.97 (m, 2H), 1.79-1.16 (m, 23H), 1.06-0.73 (m, 5H), 0.61-0.56 (m, 1H).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ -10.0.

$[\alpha]^{21}_{D} = +48.5^{o}$ (c = 0.3, $CHCl_3$).

ESI-MS: Calcd for $C_{51}H_{58}OP$ $(M+H)^{+}$: 717.41. Found: 717.55.



(*R*)-2-Dicyclohexylphosphino-2′-*m,m*-dimethoxylbenzyloxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. The same procedure as described above was used. The corresponding phosphine oxide (100 mg, 0.16 mmol), triethylamine (0.87 mL, 6.2 mmol), trichlorosilane (0.16 mL, 1.6 mmol) and dry toluene (3 mL) were used. The reaction was finished after heating at 110 ^{o}C for 12 hours. After workup, the resulting residue was purified in the glove box by flash chromatography (degassed diethyl ether), which afforded the desired compound (67 mg, 69%) as white foam.

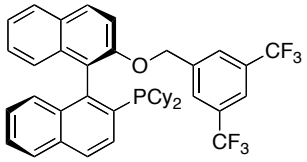
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.08-7.03 (m, 2H), 6.72 (d, *J* = 7.4 Hz, 1H), 6.29-6.26 (m, 3H), 4.94 (d, *J* = 12.8 Hz, 1H), 4.85 (d, *J* = 12.8 Hz, 1H), 3.62 (s, 6H), 2.88-2.73 (m, 4H), 2.40-2.33 (m, 2H), 2.15-2.11 (m, 1H), 2.01-1.97 (m, 2H), 1.76-0.83 (m, 28H), 0.72-0.69 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 153.1, 140.4, 137.5, 136.2, 136.1, 129.6, 129.5, 129.3, 128.8, 127.2, 108.2, 103.0, 99.9, 68.0, 55.2, 35.3, 35.2, 32.9, 32.8, 30.4, 30.3, 30.1, 30.0, 29.9, 29.4, 29.1, 29.0, 28.3, 27.7, 27.6, 27.5, 27.3, 27.2, 26.6, 26.3, 23.6, 23.2, 23.0. The splitting pattern was not assigned due to complexity of the spectrum.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ -10.2.

$[\alpha]^{21}_{D}$ = +54.6 (*c* = 0.3, $CHCl_3$).

ESI-MS: Calcd for $C_{41}H_{54}O_3P$ $(M+H)^+$: 625.37. Found: 625.54



(*R*)-2-Dicyclohexylphosphino-2′-*m*,*m*-bis(trifluoromethyl)benzyloxy- 1,1'-binaphthyl. The same procedure as described above was used. The corresponding phosphine oxide (390 mg, 0.56 mmol), triethylamine (3.10 mL, 22.5 mmol), trichlorosilane (0.57 mL, 5.6 mmol) and dry toluene (20 mL) were used. The reaction was finished after heating at 110 ^{o}C for 12 hours. After workup, the resulting residue was purified in the glove box by flash chromatography (degassed diethyl ether), which afforded the desired compound (320 mg, 84%) as yellow foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 9.0 Hz, 1H), 7.96-7.91 (m, 2H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.77 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.61 (ψs, 1H), 7.46-7.42 (m, 1H), 7.36-7.32 (m, 2H), 7.25-7.17 (m, 5H), 7.12 (d, *J* = 8.4 Hz, 1H), 5.11 (d, *J* = 12.9 Hz, 1H), 5.07 (d, *J* = 12.9 Hz, 1H), 1.88-1.81 (m, 1H), 1.75-1.69 (m, 1H), 1.61-1.42 (m, 9H), 1.21-0.73 (m, 11H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 142.8, 142.5, 140.0, 135.3, 135.1, 134.3, 133.6, 133.2, 133.1, 130.9, 129.8, 129.2, 129.1, 128.0, 127.1, 126.5, 126.3, 126.2, 126.1, 124.6, 124.5, 124.4, 124.0, 121.7, 121.2, 121.1, 113.8, 68.6, 35.2, 35.1, 34.5, 34.4, 30.5, 30.4, 30.3, 30.1, 29.8, 29.7, 27.4, 27.3, 27.2, 27.1, 26.4, 26.2. The splitting pattern was not assigned due to complexity of the spectrum.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ -8.9

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.0

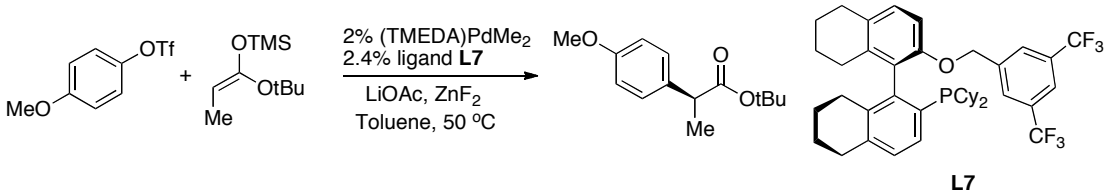
$[\alpha]^{21}_D$ = +8.6 (*c* = 0.5, $CHCl_3$).

ESI-MS: Calcd for $C_{41}H_{40}F_6OP$ $(M+H)^+$: 693.26. Found: 693.51.

III. Condition optimization of asymmetric arylation and vinylation

A typical procedure for arylation and vinylation: In an argon-filled glove box, a dry 4-mL vial was charged with $PdMe_2$(TMEDA) (0.5 mg, 0.002 mmol), ligand **L7** (1.5 mg, 0.0024 mmol) and 0.3 mL of dry toluene. After stirring at 25 ^oC for 30 minutes, the mixture was treated successively with pretreated LiOAc (13 mg, 0.20 mmol), ZnF_2 (2.1 mg, 0.02 mmol), 4-methoxylphenyl triflate (28 mg, 0.10 mmol), (*E*)-1-*tert*-butoxy-1-trimethylsiloxypropene (30 mg, 0.15 mmol) and internal standard *n*-dodecane (10 *u*L). The vial was capped tightly and the mixture was heated with stirring in a 50 ^oC heating block for 24 h, until aryl triflate was fully consumed (checked by GC). At intervals, an aliquot of the reaction mixture was taken inside the glove box and passed through a silica gel plug with diethyl ether washing (1.5 mL). The filtrate was used to determine the GC conversion of ArOTf. The solvent of the filtrate was removed and the residue was analyzed by chiral HPLC analysis (Daicel CHIRALCEL OJ-H; 1% *i*-PrOH in hexanes). To facilitate the determination of the ee, the racemic product was prepared by using an achiral ligand SPhos.

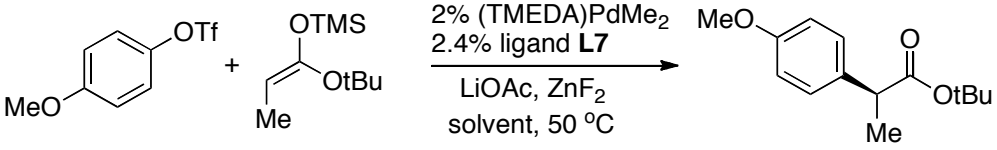
Table *S*1 Effect of palladium catalyst.



L7

Entry	Catalyst	Additive	Time (h)	Temperature (°C)	Conversion (%)	GC Yield (%)	ee (%)
1	$(TMEDA)PdMe_2$		6	50	94	92	94
			24	50	100	98	94
2	$Pd(OAc)_2$		6	50	71	67	91
			24	50	82	75	
3	$Pd(dba)_2$		6	50	19	2	
			24	50	23	5	
4	$PdCl_2$		6	50	0	0	
			24	50	0	0	
5	$Pd(acac)_2$		6	50	0	0	
			24	50	0	0	
6	$(TMEDA)PdMe_2$	No ZnF_2	6	50	85	78	94
			24	50	100	93	
7	$(TMEDA)PdMe_2$	No LiOAc	6	50	21	3	
			24	50	23	5	
8	$(TMEDA)PdMe_2$	100% ZnF_2	6	50	87	86	94
			6	50	95	94	

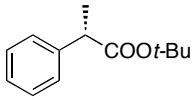
Table *S*2. Effect of solvents



Entry	Solvent	Reaction Time (h)	Temperature (°C)	Conversion (%)	GC Yield (%)	ee (%)
1	$PhCF_3$	6	50	40	25	92
		24	50	58	41	
2	Toluene	6	50	94	92	94
		24	50	100	98	
3	*o*-Xylene	6	50	89	84	93
		24	50	100	95	
4	Benzene	6	50	86	79	93
		24	50	100	93	
5	DME	6	50	27	4	28
		24	50	28	5	
6	THF	6	50	27	10	88
		24	50	48	28	
7	1,4-Dioxane	6	50	22	8	88
		24	50	45	31	
8	Et_2O	6	50	77	69	94
		6	50	92	84	
9	*t*BuOMe	6	50	69	60	94
		24	50	82	77	

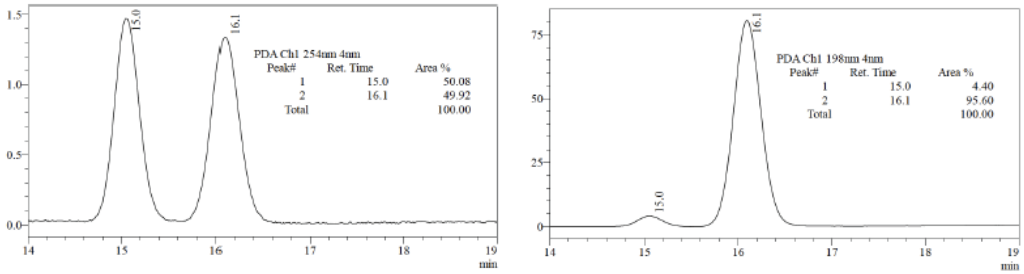
IV. Isolation of arylation and vinylation products

A general procedure for asymmetric arylation and vinylation: In an argon-filled glove box, a dry 4-mL vial was charged with $PdMe_2$(TMEDA) (2.5 mg, 0.010 mmol), ligand **L7** (8.5 mg, 0.012 mmol) and 1.5 mL of dry toluene or $PhCF_3$. After stirring at 25 ^oC for 30 minutes, the mixture was treated successively with pretreated LiOAc (66 mg, 1.0 mmol, 2 equiv), ZnF_2 (10 mg, 0.1 mmol, 0.2 equiv), aryl triflate (0.50 mmol), (*E*)-1-*tert*-butoxy-1-trimethylsiloxypropene (150 mg, 0.75 mmol, 1.5 equiv) and GC standard *n*-dodecane (50 *u*L). The vial was capped tightly and the mixture was heated with stirring in a 50 ^oC heating block. After aryl triflate was fully consumed (monitored by GC), the reaction mixture was cooled to room temperature and filtered through a pad of silica gel with diethyl ether washing (20 mL). The filtrate was concentrated and the resulting residue was purified by flash silica gel chromatography. The general procedure was used for all the isolation with 0.50 mmol of aryl triflate, unless stated otherwise. The racemic products were prepared using a similar procedure with SPhos as a supporting ligand.



(*S*)-*tert*-Butyl 2-phenylpropionate [59415-37-1]. The reaction was finished within 18 hours at 50 ^oC in $PhCF_3$. The title compound was obtained as colorless oil (91 mg, 88% yield, 91% ee) by flash chromatography using EA/hexane (1:40) as eluent. The ee of the product was determined to be 87% when PhMe was used.

The ee of the purified products was determined to be 91% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99:1; detection wave-lengths = 254 nm and 198 nm; flow rate = 0.5 mL/min). T_R = 15.0 min (minor) and 16.1 min (major).

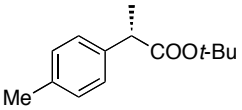


$[\alpha]^{21}_D$ = +28.5^o (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.21 (m, 5H), 3.61 (q, *J* = 7.1, 1H), 1.45 (d, *J*

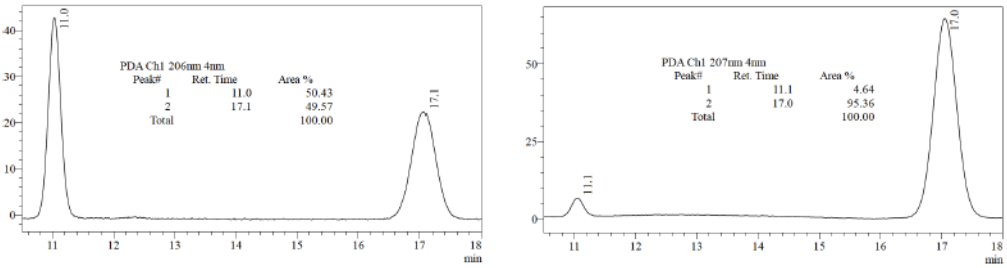
= 7.1 Hz, 3H), 1.39 (s, 9H).

GCMS (EI): calcd for $C_{13}H_{18}O_2$ M: 206.1. Found: 206.0.



(*S*)-*tert*-Butyl 2-*p*-tolylpropionate [197659-36-2 for racemate]. The reaction was finished within 12 hours at 50 ^{o}C in toluene. The title compound was obtained as yellow oil (108 mg, 98% yield) by flash chromatography using EA/hexane (1:30) as eluent.

The ee of the purified products was determined to be 91% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 98:2; detection wave-lengths = 207 nm; flow rate = 0.5 mL/min). T_R = 11.1 min (minor) and 17.0 min (major).

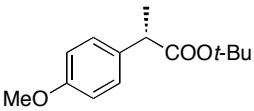


$[\alpha]^{21}_{D}$ = +26.9^{o} (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.56 (q, *J* = 7.2 Hz, 1H), 2.32 (s, 3H), 1.42 (d, *J* = 7.2 Hz, 3H), 1.39 (s, 9H).

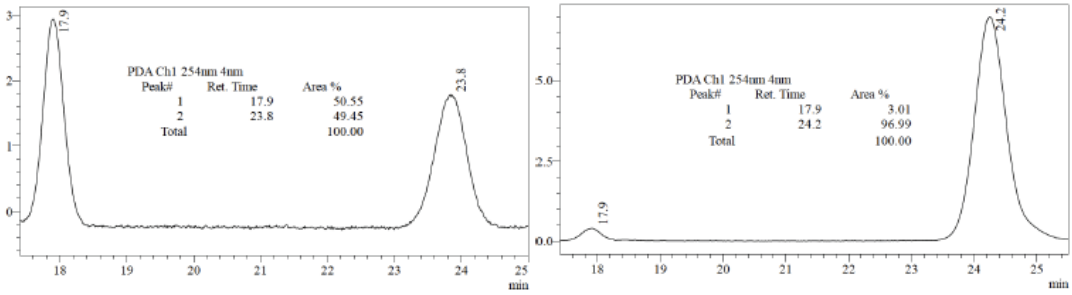
^{13}C NMR (75 MHz, $CDCl_3$): δ 174.0, 138.2, 136.3, 129.1, 127.3, 80.3, 46.1, 28.0, 21.0, 18.6.

GCMS (EI): calcd for $C_{14}H_{22}O_2$ M^+: 220.2. Found: 220.1.



(*S*)-*tert*-Butyl 2-*p*-anisylpropionate [138623-00-4 for racemate]. The reaction was finished within 24 hours at 50 ^{o}C in toluene. The title compound was obtained as yellow oil (116 mg, 98% yield, 94% ee) by flash chromatography using EA/hexane (1:30) as eluent. The ee of the product was determined to be 92% when $PhCF_3$ was used.

The ee of the purified products was determined to be 94% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99:1; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 17.9 min (minor) and 24.2 min (major).

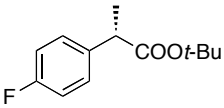


$[\alpha]^{21}_D$ = +24.5° (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.19 (m, 2H), 6.87-6.84 (m, 2H), 3.79 (s, 3H), 3.55 (q, *J* = 7.2 Hz, 1H), 1.42 (d, *J* = 7.2 Hz, 3H), 1.39 (s, 9H).

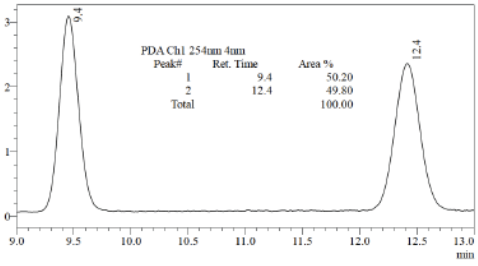
^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 158.5, 133.3, 128.4, 113.8, 80.3, 55.2, 45.6, 27.9, 18.6.

GCMS (EI): calcd for $C_{14}H_{19}O_3$ M^+: 236.1. Found: 236.1.



(*S*)-*tert*-Butyl 2-*p*-fluorophenylpropionate [1019322-29-2 for racemate]. The reaction was finished within 18 hours at 50 °C in $PhCF_3$. The title compound was obtained as yellow oil (111 mg, 99% yield, 93% ee) by flash chromatography using EA/hexane (1:30) as eluent. The ee of the product was determined to be 91% when PhMe was used.

Ee of the purified products was determined to be 93% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 9.5 min (minor) and 12.4 min (major).



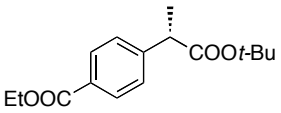
$[\alpha]^{21}_D = +34.1^o$ (c = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.23 (m, 2H), 7.01-6.97 (m, 2H), 3.59 (q, J = 7.2 Hz, 1H), 1.43 (d, J = 7.2 Hz, 3H), 1.39 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 161,8 (J_{CF} = 244.7 Hz), 136.8 (J_{CF} = 3.1 Hz), 128.9 (J_{CF} = 7.8 Hz), 115.2 (J_{CF} = 21.4 Hz), 80.6, 45.8, 27.9, 18.5.

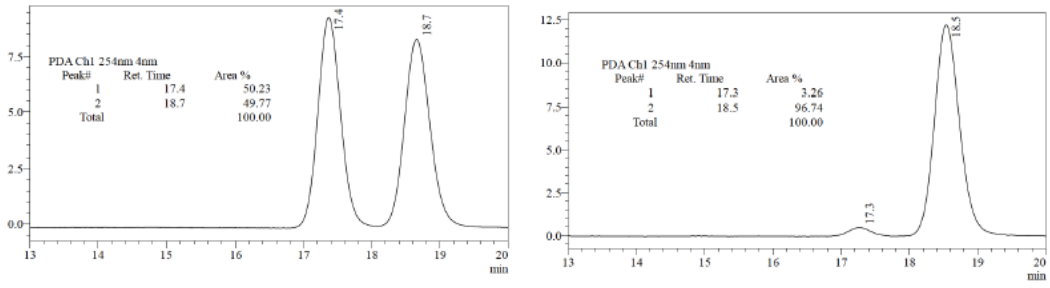
^{19}F NMR (376 MHz, $CDCl_3$): δ -116.3.

GCMS (EI): calcd for $C_{13}H_{17}FO_2$ M^+: 224.1. Found: 224.1.



(*S*)-*tert*-Butyl 2-*p*-ethoxycarbonylphenylpropionate [1334591-49-9]. The reaction was finished within 18 hours at 50 ^{o}C in $PhCF_3$. The title compound was obtained as colorless oil (133 mg, 96% yield, 94% ee) by flash chromatography using EA/hexane (1:30) as eluent. The ee of the product was determined to be 90% when PhMe was used.

Ee of the purified products was determined to be 94% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99.5:0.5; detection wave-lengths = 254 nm; flow rate = 0.5 mL/min). T_R = 17.3 min (minor) and 18.5 min (major).

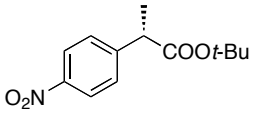


$[\alpha]^{21}_D = +23.2^o$ (c = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, CDCl3): δ 8.00-7.97 (m, 2H), 7.36-7.33 (m, 2H), 4.36 (q, J =

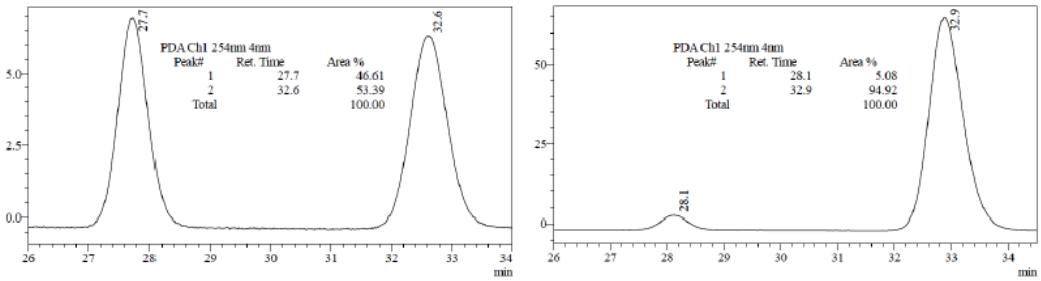
7.1 Hz, 2H), 3.65 (q, J = 7.1 Hz, 1H), 1.45 (d, J = 7.2 Hz, 3H), 1.44-1.35 (m, 12H).

GCMS (EI): calcd for $C_{16}H_{23}O_4$ $(M+H)^+$: 279.2. Found: 279.2.



(*S*)-*tert*-Butyl 2-*p*-nitrophenylpropionate [89278-22-8 for racemate]. The reaction was finished within 6 hours at 50 °C in $PhCF_3$. The title compound was obtained as yellow oil (123 mg, 98% yield, 90% ee) by flash chromatography using EA/hexane (1:30) as eluent. The ee of the product was determined to be 85% when PhMe was used.

Ee of the purified products was determined to be 90% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99.5:0.5; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 28.1 min (minor) and 32.9 min (major).

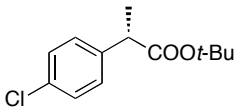


$[\alpha]^{21}_D$ = +21.7° (c = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-7.17 (m, 2H), 7.48-7.45 (m, 2H), 3.73 (q, J = 7.2 Hz, 1H), 1.49 (d, J = 7.2 Hz, 3H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 148.5, 147.0, 128.4, 123.7, 81.4, 46.5, 27.9, 18.3.

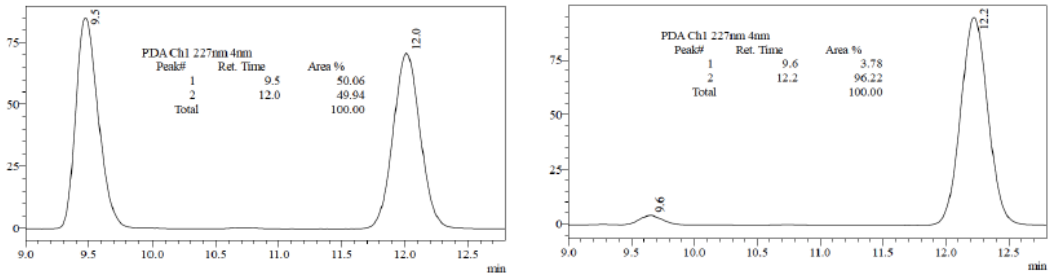
GCMS (EI): calcd for $C_{13}H_{17}NO_4$ $(M+H)^+$: 252.1. Found: 252.1.



(*S*)-*tert*-Butyl 2-*p*-chlorophenylpropionate [465529-75-3 for racemate]. The same procedure with $PdMe_2$(TMEDA) (6.5 mg, 0.025 mmol, 5 mol% Pd) and ligand **L7** (21 mg, 0.030 mmol) was used in $PhCF_3$. The reaction was finished within 40 hours at 50 °C. The title compound was obtained as colorless oil (108 mg, 90% yield,

93% ee) by flash chromatography using EA/hexane (1:30) as eluent. The ee of the product was determined to be 89% when PhMe was used.

Ee of the purified products was determined to be 93% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99:1; detection wavelengths = 227 nm; flow rate = 0.5 mL/min). T_R = 9.6 min (minor) and 12.2 min (major).

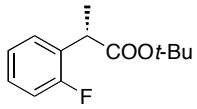


$[\alpha]^{21}_D = +25.4^o$ (c = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.23-7.21 (m, 2H), 3.58 (q, J = 7.2 Hz, 1H), 1.43 (d, J = 7.2 Hz, 3H), 1.39 (s, 9H).

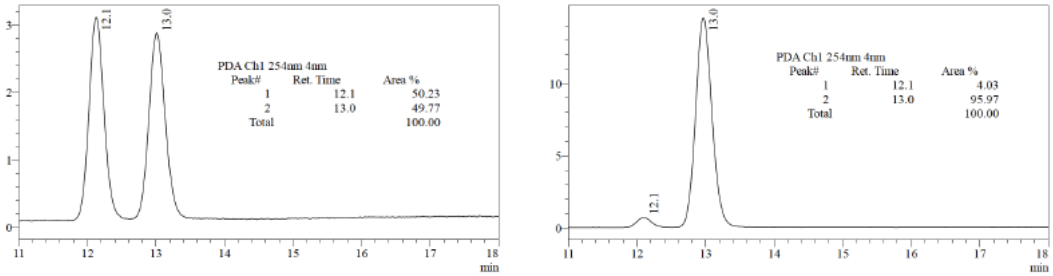
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 139.6, 132.7, 128.8, 128.6, 80.7, 45.9, 27.9, 18.4.

GCMS (EI): calcd for $C_{13}H_{17}ClO_2$ M^+: 240.1. Found: 240.1.



***(S)*-*tert*-Butyl 2-*o*-fluorophenylpropionate.** The reaction was finished within 18 hours at 50 ^{o}C in $PhCF_3$. The title compound was obtained as yellow oil (107 mg, 96% yield, 92% ee) by flash chromatography using EA/hexane (1:30) as eluent. The ee of the product was determined to be 90% when PhMe was used.

The ee of the purified products was determined to be 92% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99:1; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 12.1 min (minor) and 13.0 min (major).



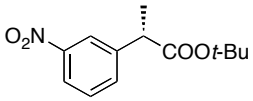
$[\alpha]^{21}_D$ = +32.9 ^{o} (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 1H), δ 7.23-7.19 (m, 1H), δ 7.12-7.08 (m, 1H), 7.05-7.00 (m, 1H), 3.92 (q, *J* = 7.2 Hz, 1H), 1.45 (d, *J* = 7.2 Hz, 3H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 160.4 (J_{CF} = 245.9 Hz), 128.56 (J_{CF} = 4.5 Hz), 128.5 (J_{CF} = 14.1 Hz), 128.3 (J_{CF} = 8.2 Hz), 124.1 (J_{CF} = 3.7 Hz), 115.3 (J_{CF}= 22.4 Hz), 80.7, 39.4 (J_{CF} = 2.4 Hz), 27.9, 17.4.

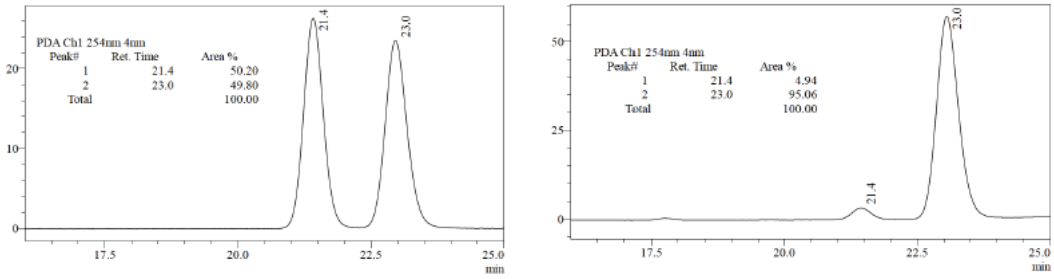
^{19}F NMR (376 MHz, $CDCl_3$): δ -118.3.

GCMS (EI): Calcd for $C_{13}H_{17}FO_2$ M^+: 224.1. Found: 224.1.



***(S)*-*tert*-Butyl 2-*m*-nitrophenylpropionate [183180-54-3 for racemate].** The reaction was finished within 20 hours at 50 ^{o}C in $PhCF_3$. The title compound was obtained as yellow oil (119 mg, 95% yield, 90% ee) by flash chromatography using EA/hexane (1:20) as eluent. The ee of the product was determined to be 83% when PhMe was used.

The ee of the purified products was determined to be 90% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99.5:0.5; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 21.4 min (minor) and 23.0 min (major).

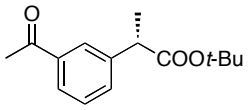


$[\alpha]^{21}_D$ = +22.3^o (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.18 (m, 1H), δ 8.14-8.11 (m, 1H), δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.50 (ψt, *J* = 7.9 Hz, 1H), 3.74 (q, *J* = 7.2 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 1.41 (s, 9H).

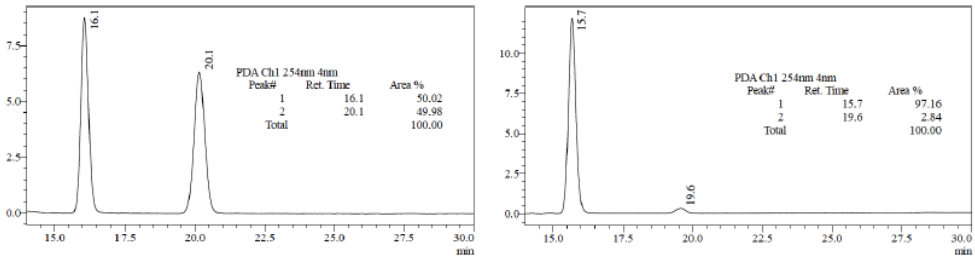
^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 148.4, 143.0, 133.7, 129.3, 122.7, 122.0, 81.4, 46.2, 27.9, 18.3.

GCMS (EI): calcd for $C_{13}H_{18}NO_4$ $(M+H)^+$: 252.1. Found: 252.1.



***(S)-tert*-Butyl 2-*m*-acetophenylpropionate.** The reaction was finished within 20 hours at 50 ^{o}C in $PhCF_3$. The title compound was obtained as yellow oil (110 mg, 89% yield, 94% ee) by flash chromatography using EA/hexane (1:20) as eluent. The ee of the product was determined to be 91% when PhMe was used.

The ee of the purified products was determined to be 94% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 98:2; detection wave-lengths = 254 nm; flow rate = 0.5 mL/min). T_R = 15.7 min (major) and 19.6 min (minor).

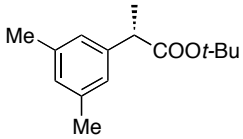


$[\alpha]^{21}_{D}$ = +31.6^{o} (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.88 (m, 1H), 7.86-7.83 (m, 1H), 7.53-7.51 (m, 1H), 7.42 (ψt, *J* = 7.7 Hz, 1H), 3.69 (q, *J* = 7.2 Hz, 1H), 2.61 (s, 3H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 173.3, 141.7, 137.4, 132.2, 128.7, 127.5, 127.0, 80.8, 46.4, 27.9, 26.7, 18.5.

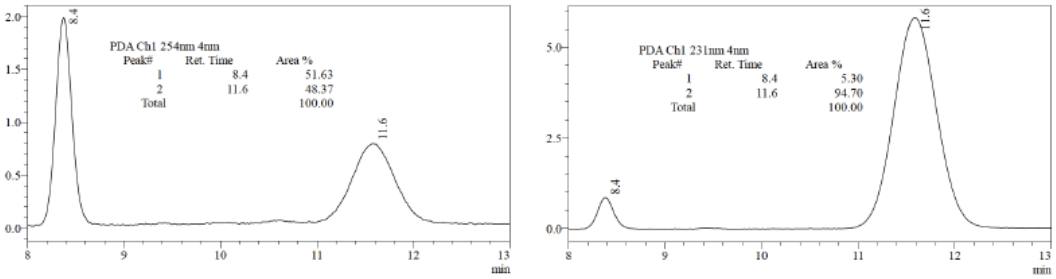
GCMS (EI): calcd for $C_{15}H_{20}O_3$ M: 248.1. Found: 248.2.



***(S)-tert*-Butyl 2-*m*-xylylpropionate [1226783-49-8 for racemate].** The reaction was finished within 24 hours at 50 ^{o}C in toluene. The title compound was obtained as colorless oil (110 mg, 94% yield) by flash chromatography using EA/hexane (1:30) as eluent.

The ee of the purified products was determined to be 89% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99:1; detection wave-

lengths = 254 nm and 231 nm; flow rate = 0.5 mL/min). T_R = 8.4 min (minor) and 11.6 min (major).

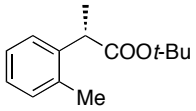


$[\alpha]^{21}_D$ = +23.9° (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (s, 2H), 6.88 (s, 1H), 3.53 (q, *J* = 7.1 Hz, 1H), 2.30 (s, 6H), 1.43-1.41 (m, 12H).

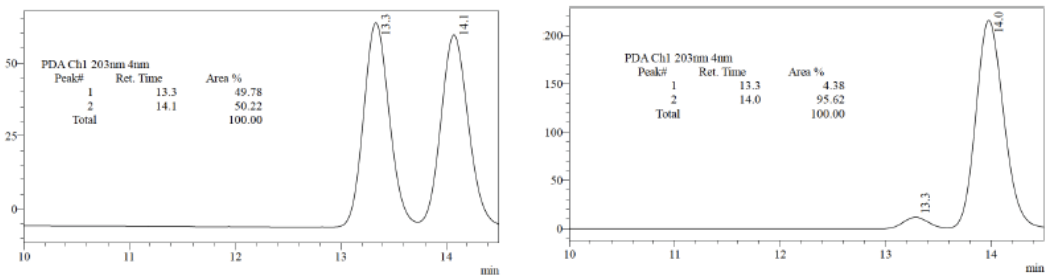
^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 141.1, 137.9, 128.5, 125.2, 80.3, 46.3, 28.0, 21.3, 18.7.

GCMS (EI): calcd for $C_{15}H_{22}O_2$ M^+: 234.2. Found: 234.1.



***(S)-tert*-Butyl 2-*o*-tolylpropionate [1334591-54-6].** The reaction was finished within 60 hours at 50 °C in $PhCF_3$. The title compound was obtained as yellow oil (106 mg, 96% yield) by flash chromatography using EA/hexane (1:30) as eluent.

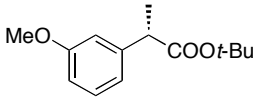
The ee of the purified products was determined to be 91% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99.5:0.5; detection wave-lengths = 203 nm; flow rate = 0.4 mL/min). T_R = 13.3 min (minor) and 14.0 min (major).



$[\alpha]^{21}_D$ = +40.9° (*c* = 0.3, $CHCl_3$).

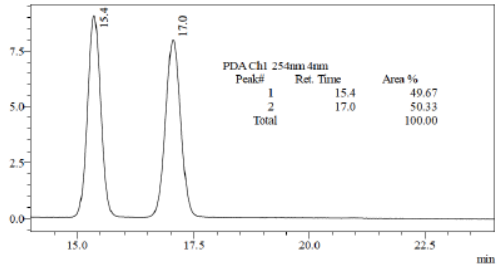
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.25 (m, 1H), 7.20-7.12 (m, 3H), 3.85 (q, *J* = 7.1 Hz, 1H), 2.36 (s, 3H), 1.42 (d, *J* = 7.1 Hz, 3H), 1.38 (s, 9H).

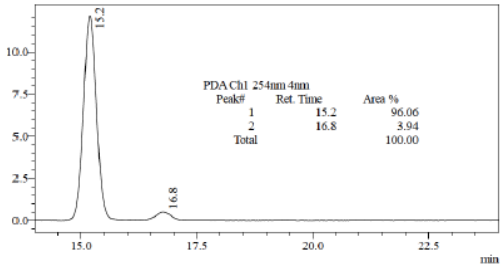
GCMS (EI): calcd for $C_{14}H_{20}O_2$ M: 220.2. Found: 220.1.



***(S)-tert*-Butyl 2-*m*-anisylpropionate [62381-22-0 for racemate].** The reaction was finished within 20 hours at 50 °C in $PhCF_3$. The title compound was obtained as yellow oil (116mg, 98% yield, 92% ee) by flash chromatography using EA/hexane (1:30) as eluent. The ee of the product was determined to be 90% when PhMe was used.

The ee of the purified products was determined to be 92% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99:1; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 15.2 min (major) and 16.8 min (minor).



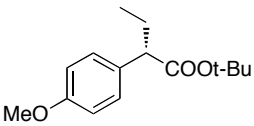


$[\alpha]^{21}_D$ = +37.6 (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.20 (m, 1H), 6.89-6.84 (m, 2H), 6.80-6.77 (m, 1H), 3.80 (s, 3H), 3.57 (q, *J* = 7.2 Hz, 1H), 1.44 (d, *J* = 7.2 Hz, 3H), 1.39 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 159.7, 142.8, 129.4, 119.8, 113.1, 112.3, 80.5, 55.2, 46.5, 27.9, 18.5.

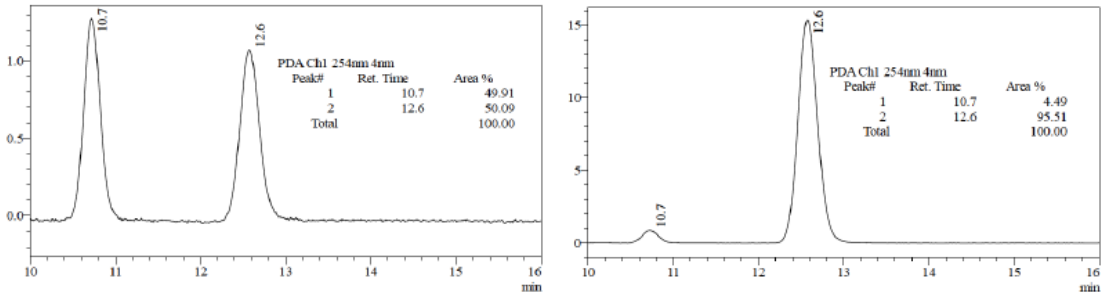
GCMS (EI): calcd for $C_{14}H_{20}O_3$ M: 236.1. Found: 236.1.



(*S*)-*tert*-Butyl 2-*p*-anisylbutanoate. The same procedure with (*E*)-1-*tert*-butoxy-1-(trimethylsiloxy)butene (216 mg, 1.5 mmol) was used in toluene. The reaction was finished within 10 hours at 50 °C. The title compound was obtained as colorless oil (124 mg, 99% yield) by flash chromatography using EA/hexane (1:30) as eluent.

Ee of the purified products was determined to be 92% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99:1; detection wavelengths = 227 nm; flow rate = 0.5 mL/min). T_R = 10.7 min (minor) and 12.6 min

(major).

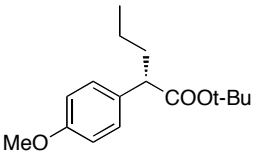


$[\alpha]^{20}_{D} = +18.0^{o}$ (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.20 (m, 2H), 6.85-6.83 (m, 2H), 3.79 (s, 3H), 3.28 (t, J = 7.7 Hz, 1H), 2.06-1.96 (m, 1H), 1.73-1.66 (m, 1H), 1.40 (s, 9H), 0.88 (t, J = 7.4 Hz, 3H).

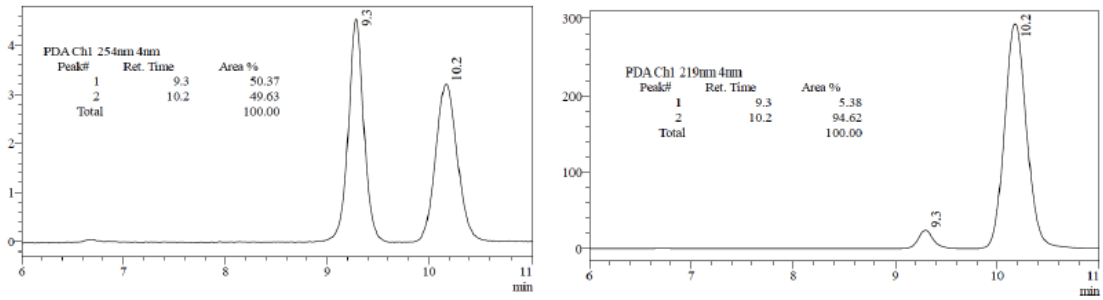
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 158.5, 131.9, 128.8, 113.8, 80.3, 55.2, 53.7, 28.0, 26.8, 12.2.

GCMS (EI): calcd for $C_{15}H_{22}O_3$ M^{+}: 250.2. Found: 250.1.



(*S*)-*tert*-Butyl 2-*p*-anisylpentanoate. The same procedure with (*E*)-1-*tert*-butoxy-1-(trimethylsiloxy)pentene (230 mg, 1.5 mmol) was used in toluene. The reaction was finished within 10 hours at 50 ^{o}C. The title compound was obtained as colorless oil (129 mg, 98% yield) by flash chromatography using EA/hexane (1:30) as eluent.

Ee of the purified products was determined to be 90% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99:1; detection wave-lengths = 227 nm; flow rate = 0.5 mL/min). T_R = 9.3 min (minor) and 10.2 min (major).



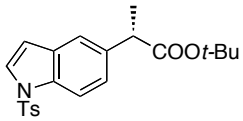
$[\alpha]^{20}_{D} = +12.3^{o}$ (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.20 (m, 2H), 6.85-6.83 (m, 2H), 3.79 (s, 3H), 3.38 (t, J = 7.7 Hz, 1H), 2.01-1.92 (m, 1H), 1.70-1.61 (m, 1H), 1.39 (s, 9H), 1.32-1.22

(m, 2H), 0.90 (t, J = 7.4 Hz, 3H).

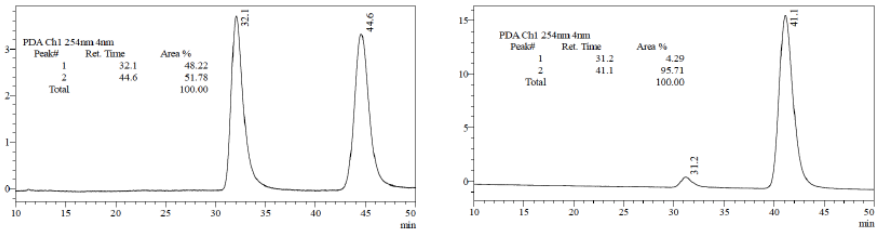
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 158.5, 132.1, 128.8, 113.8, 80.3, 55.2, 51.7, 35.8, 28.0, 20.8, 13.9.

GCMS (EI): calcd for $C_{16}H_{24}O_3$ M^+: 264.2. Found: 264.1.



(*S*)-*tert*-Butyl *N*-tosyl-2-5-indolylpropionate. The reaction was finished within 12 hours at 50 °C in toluene. The title compound was obtained as yellow oil (201 mg, 99% yield) by flash chromatography using EA/hexane (1:10) as eluent.

The ee of the purified products was determined to be 91% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 95:5; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 31.2 min (minor) and 41.1 min (major).

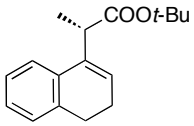


$[\alpha]^{21}_D$ = +7.9 (c = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.4 Hz, 2H), 7.54 (d, J = 3.7 Hz, 1H), 7.44 (d, J = 1.2 Hz, 1H), 7.26-7.20 (m, 3H), 6.61 (d, J = 3.6 Hz, 1H), 3.66 (q, J = 7.2 Hz, 1H), 1.45 (d, J = 7.2 Hz, 3H), 1.37 (s, 9H).

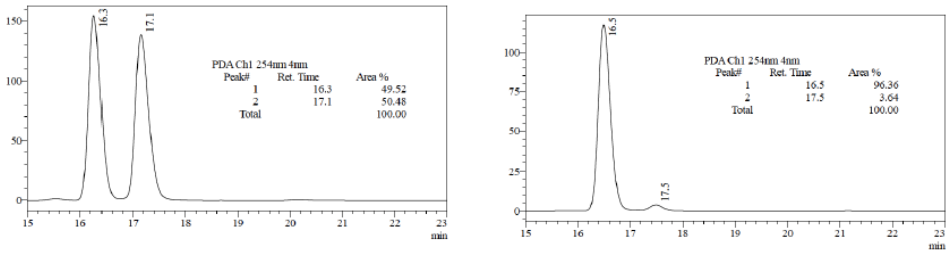
^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 144.9, 136.3, 135.4, 133.9, 130.9, 129.9, 126.8, 126.6, 124.4, 120.9, 113.4, 109.0, 80.5, 46.3, 27.9, 21.5,18.9.

GCMS (EI): calcd for $C_{22}H_{25}NO_4S$ M 399.2. Found: 399.2.



***(S)*-*tert*-Butyl 2-3′,4′-dihydro-1-naphthylpropionate [26732-57-0].** The reaction was finished within 18 hours at 50 °C in toluene. The title compound was obtained as colorless oil (116 mg, 90% yield, 93% ee) by flash chromatography using EA/hexane (1:30) as eluent. The ee of the product was determined to be 81% when $PhCF_3$ was used.

The ee of the purified products was determined to be 93% based on chiral HPLC analysis (Daicel CHIRALCEL IC; hexanes: *i*-PrOH = 99.8:0.2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 16.5 min (major) and 17.5 min (minor).

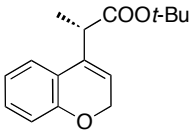


$[\alpha]^{21}_D$ = +29.1 (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.28 (m, 1H), 7.20-7.12 (m, 3H), 6.01 (t, *J* = 4.1 Hz, 1H), 3.63 (q, *J* = 7.1 Hz, 1H), 2.75-2.71 (m, 2H), 2.30-2.24 (m, 2H), 1.40-1.38 (m, 12H).

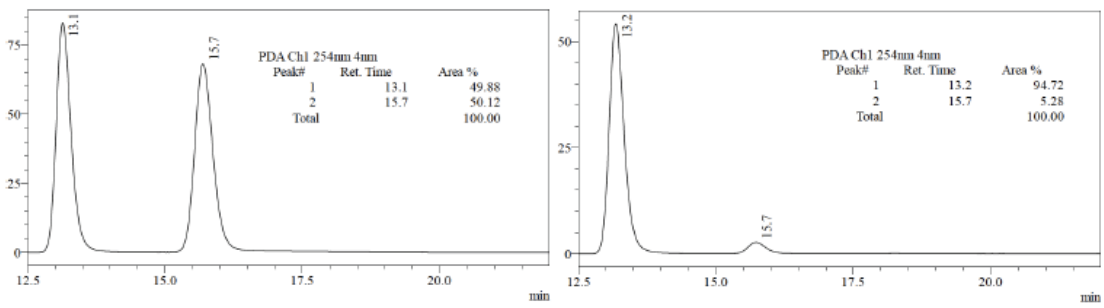
^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 136.8, 136.4, 134.5, 127.6, 126.7, 126.2, 125.4, 122.6, 80.3, 42.3, 28.3, 27.9, 23.1, 16.7.

GCMS (EI): calcd for $C_{17}H_{22}O_2$ M^+: 258.2. Found: 258.1.



***(S)-tert*-Butyl 2-(4-chromenyl)propionate.** The reaction was finished within 6 hours at 50 °C in toluene. The title compound was obtained as colorless oil (127 mg, 98% yield) by flash chromatography using EA/hexane (1:30) as eluent.

The ee of the purified products was determined to be 90% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99:1; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 13.2 min (major) and 15.7 min (minor).

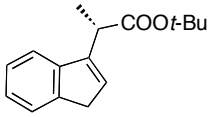


$[\alpha]^{21}_D$ = +21.7 (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.14-7.10 (m, 1H), 6.91-6.87 (m, 1H), 6.82 (dd, *J* = 8.0, 1.1 Hz, 1H), 5.73 (t, *J* = 3.8 Hz, 1H), 4.76 (d, *J* = 3.8 Hz, 2H), 3.56 (q, *J* = 7.1 Hz, 1H), 1.40-1.38 (m, 12H).

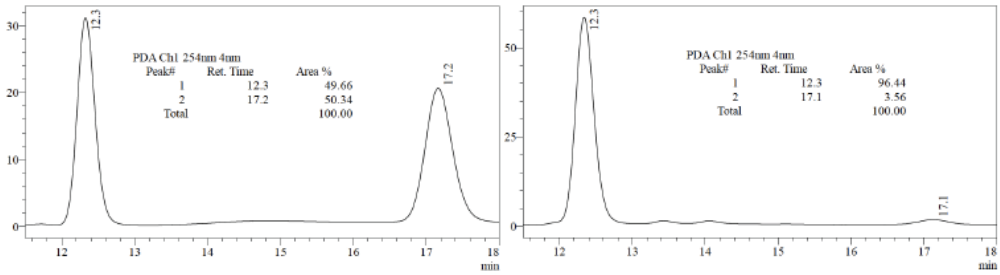
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 154.5, 134.1, 129.0, 123.3, 122.9, 121.1, 118.4, 116.1, 80.7, 65.2, 41.5, 27.9, 16.3.

GCMS (EI): calcd for $C_{16}H_{20}O_3$ M: 260.1. Found: 260.1.



***(S)*-*tert*-Butyl 2-(1-indenyl)propionate.** The reaction was finished within 30 hours at 50 °C in toluene. The title compound was obtained as colorless oil (113 mg, 93% yield) by flash chromatography using EA/hexane (1:30) as eluent.

The ee of the purified products was determined to be 93% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99:1; detection wave-lengths = 254 nm; flow rate = 0.5 mL/min). T_R = 12.3 min (major) and 17.1 min (minor).

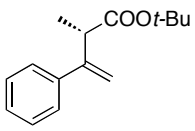


$[\alpha]^{21}_D$ = +25.1° (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.43 (m, 2H), 7.30-7.27 (m, 1H), 7.22-7.17 (m, 1H), 6.37 (d, *J* = 1.1 Hz, 1H), 3.56 (q, *J* = 7.1 Hz, 1H), 3.36 (s, 2H), 1.49 (d, *J* = 7.1 Hz, 3H), 1.42 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 144.3, 144.2, 143.6, 128.9, 125.9, 124.7, 123.8, 119.5, 80.6, 39.9, 37.8, 28.0, 16.5.

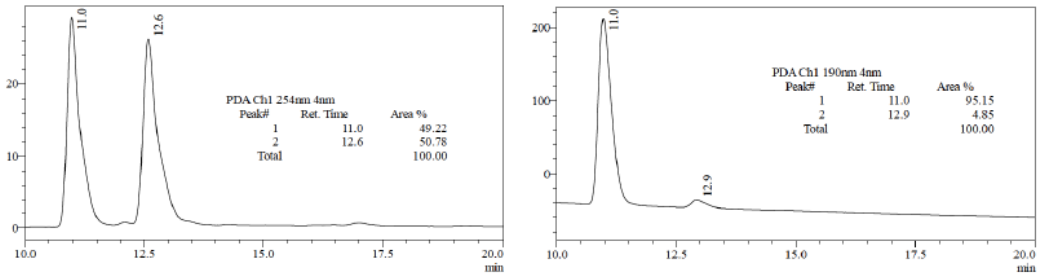
GCMS (EI): calcd for $C_{16}H_{22}O_2$ M+: 244.2. Found: 244.1.



***(S)*-*tert*-Butyl 2-α-styrylpropionate.** The same procedure with $PdMe_2$(TMEDA) (6.3 mg, 0.025 mmol, 5 mol% Pd) and ligand **L7** (21 mg, 0.030 mmol) was used in

toluene. The reaction was finished within 18 hours at 50 ^{o}C. The title compound was obtained as colorless oil (95 mg, 82% yield) by flash chromatography using EA/hexane (1:30) as eluent.

Ee of the purified products was determined to be 90% based on chiral HPLC analysis (Daicel CHIRALCEL OD-H; hexanes: *i*-PrOH = 99.8:0.2; detection wave-lengths = 254 nm and 190 nm; flow rate = 0.5 mL/min). T_R = 11.0 min (major) and 112.9 min (minor).

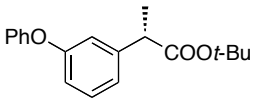


$[\alpha]^{21}_{D}$ = +9.8 (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.38 (m, 2H), 7.34-7.24 (m, 3H), 5.36 (s, 1H), 5.21 (s, 1H), 3.58 (q, *J* = 7.0 Hz, 1H), 1.37-1.33 (m, 12H).

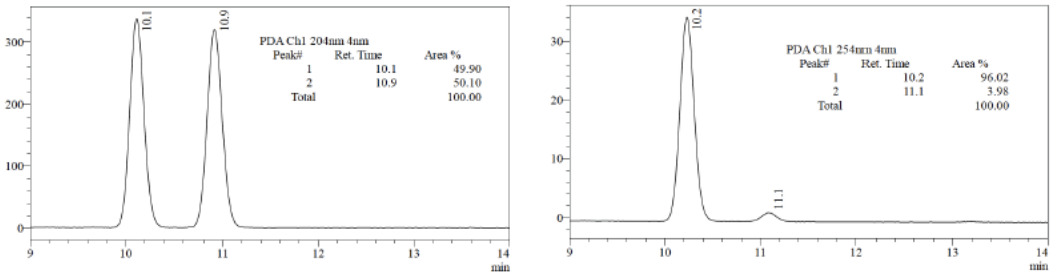
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 148.6, 141.5, 128.2, 127.4, 126.6, 113.5, 80.4, 45.4, 27.8, 16.8.

GCMS (EI): calcd for $C_{15}H_{20}O_2$ M^+: 232.2. Found: 232.1.



***(S)*-*tert*-Butyl 2-*m*-phenoxyphenylpropionate [1226783-55-6 for racemate].** The reaction was finished within 18 hours at 50 ^{o}C in $PhCF_3$. The title compound was obtained as colorless oil (144 mg, 97% yield, 92% ee) by flash chromatography using EA/hexane (1:30) as eluent. The ee of the product was determined to be 88% when PhMe was used.

The ee of the purified products was determined to be 92% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 98:2; detection wave-lengths = 254 nm and 204 nm; flow rate = 0.5 mL/min). T_R = 10.2 min (minor) and 11.1 min (major).

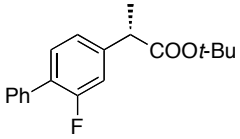


$[\alpha]^{21}_D$ = +24.2 (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (m, 2H), 7.29-7.25 (m, 1H), 7.11-7.07 (m, 1H), 7.04-6.96 (m, 4H), 6.90-6.87 (m, 1H), 3.58 (q, *J* = 7.2 Hz, 1H), 1.42 (d, *J* = 7.2 Hz, 3H), 1.38 (s, 9H).

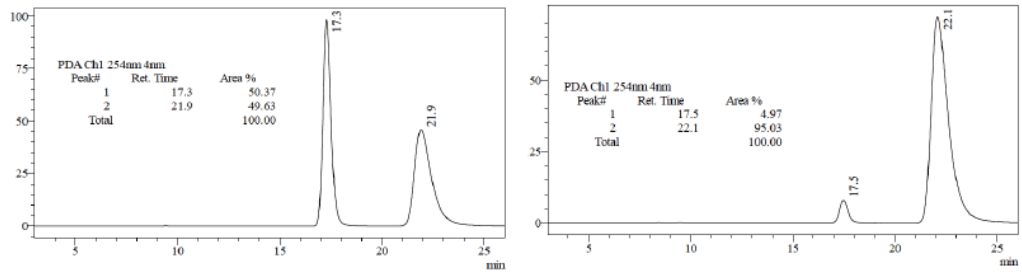
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 157.3, 143.2, 129.70, 129.67, 123.2, 122.3, 118.8 (2 overlapping signals), 118.1, 117.3, 80.6, 46.4, 27.9, 18.3

GCMS (EI): calcd for $C_{19}H_{22}O_3$ M: 298.2. Found: 298.1.



***(S)-tert*-Butyl 2-*m*-fluoro-*p*-biphenylpropionate [362523-47-5].** The reaction was finished within 6 hours at 50 ^{o}C in $PhCF_3$. The title compound was obtained as colorless oil (147 mg, 98% yield, 90% ee) by flash chromatography using EA/hexane (1:30) as eluent. The ee of the product was determined to be 83% when PhMe was used.

The ee of the purified products was determined to be 90% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*PrOH = 99:1; detection wave- lengths = 254 nm; flow rate = 0.5 mL/min). T_R = 17.5 min (minor) and 22.1 min (major).



$[\alpha]^{21}_D$ = +16.6 (*c* = 0.3, $CHCl_3$).

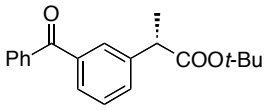
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53 (m, 2H), 7.45-7.33 (m, 4H), 7.15-7.09 (m, 2H), 3.64 (q, *J* = 7.2 Hz, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.43 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 159.7 (J_{CF} = 247.9 Hz), 142.6 (J_{CF} = 7.7 Hz), 135.7, 130.6 (J_{CF} = 3.9 Hz), 128.9 (J_{CF} = 3.0 Hz), 128.4, 127.5, 127.4, 123.5 (J_{CF}

= 3.4 Hz), 115.1 (J_{CF} = 23.5 Hz), 80.9, 46.0, 28.0, 18.4.

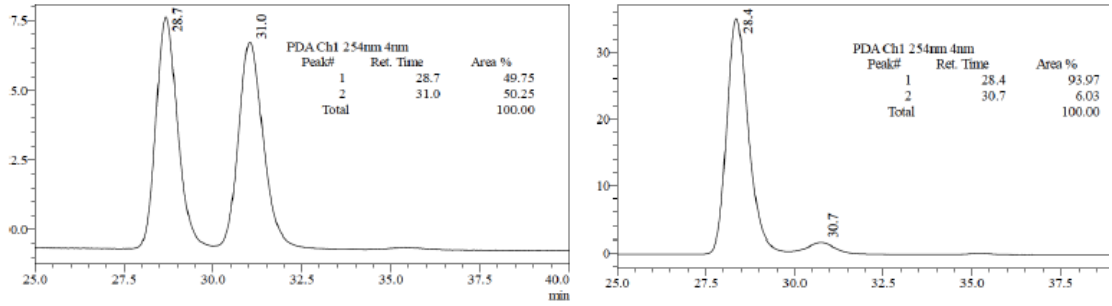
^{19}F NMR (376 MHz, $CDCl_3$): -118.0.

GCMS (EI): calcd for $C_{19}H_{21}FO_2$ M: 300.1. Found: 300.1



(*S*)-*tert*-Butyl 2-*m*-benzoylphenylpropionate [1334591-51-3]. The reaction was finished within 12 hours at 50 °C in $PhCF_3$. The title compound was obtained as colorless oil (144 mg, 97% yield) by flash chromatography using EA/hexane (1:10) as eluent.

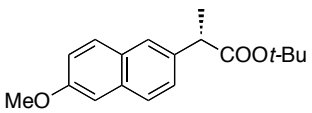
The ee of the purified products was determined to be 88% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99.5:0.5; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 28.4 min (major) and 30.7 min (minor).



$[\alpha]^{21}_D$ = +44.5 (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.82 (m, 2H), 7.76-7.75 (m, 1H), 7.72-7.69 (m, 1H), 7.64-7.60 (m, 1H), 7.58-7.56 (m, 1H), 7.53-7.45 (m, 3H), 3.68 (q, *J* = 7.2 Hz, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.40 (s, 9H).

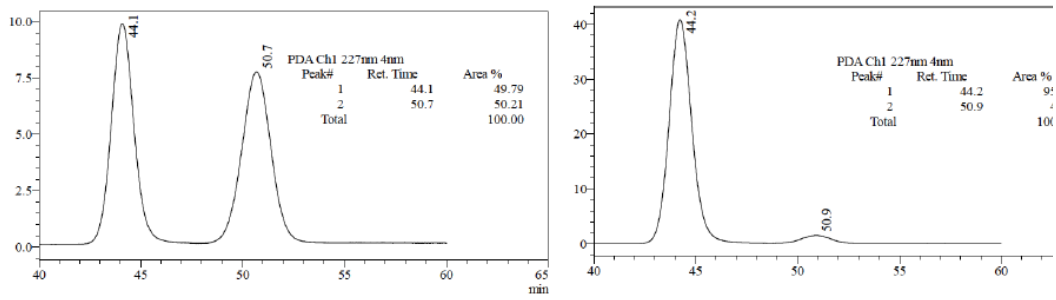
GCMS (EI): calcd for $C_{20}H_{22}O_3$ M: 310.2. Found: 310.2.



(*S*)-*tert*-Butyl 2-6′-methoxy-2′-naphthylpropionate [92455-03-3]. The reaction was finished within 36 hours at 50 °C in $PhCF_3$. The title compound was obtained as white solid (137 mg, 96% yield) by flash chromatography using EA/hexane (1:30) as eluent.

The ee of the purified products was determined to be 92% based on chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 99:1; detection wavelengths

= 227 nm; flow rate = 0.5 mL/min). T_R = 44.2 min (major) and 50.9 min (minor).



$[\alpha]^{21}_D$ = +18.9 (*c* = 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.65 (m, 3H), 7.41 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.15-7.11 (m, 2H), 3.92 (s, 3H), 3.75 (q, *J* = 7.1 Hz, 1H), 1.53 (d, *J* = 7.1 Hz, 3H), 1.40 (s, 9H).

GCMS (EI): calcd for $C_{18}H_{22}O_3$ M: 286.2. Found: 286.1.

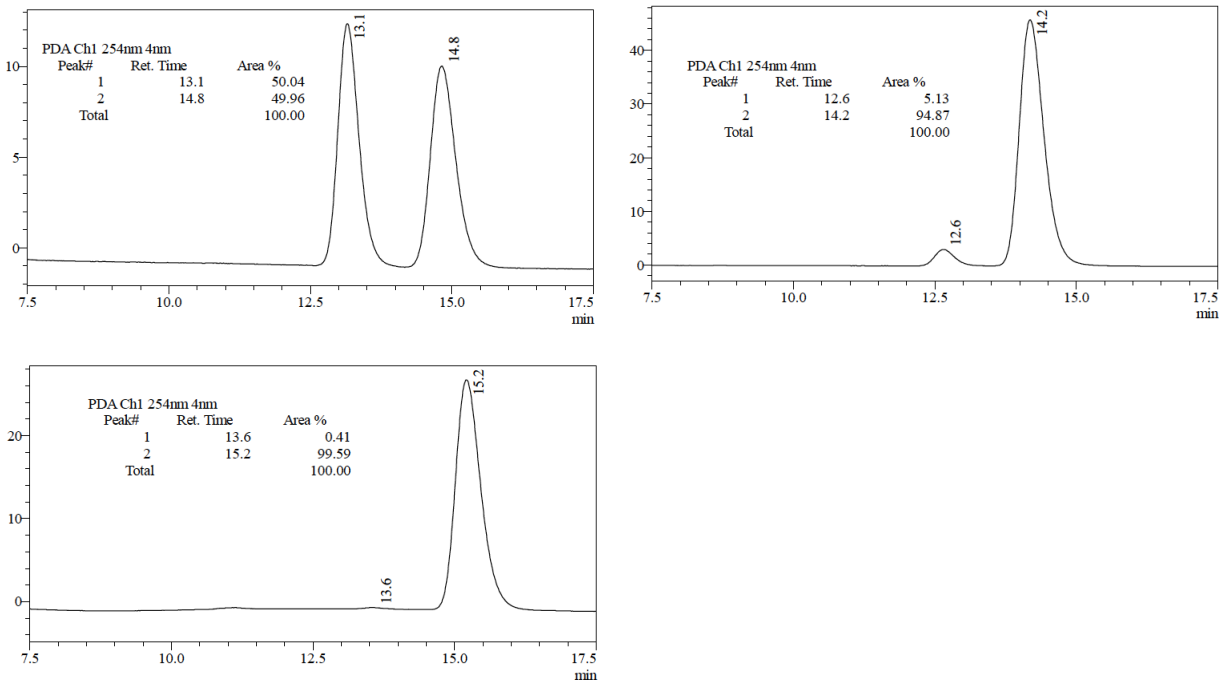
V. A gram-scale synthesis of (*S*)-Flurbiprofen

A coupling procedure without using a glove box: Under argon, a 50-mL dry Schlenk tube was charged with $PdMe_2$(TMEDA) (20 mg, 0.08 mmol), ligand **L7** (67 mg, 0.10 mmol) and dry $PhCF_3$ (12 mL). After the resulting mixture was stirred at room temperature for 30 minutes, pretreated LiOAc (528 mg, 8.0 mmol), ZnF_2 (82 mg, 0.8 mmol), *m*-fluoro-*p*-biphenyl triflate (1.28 g, 4.0 mmol) and (*E*)-1-*tert*-butoxy-1-trimethylsiloxypropene (1.21 g, 6.0 mmol) were added into the Schlenk tube against argon flow, followed by internal standard *n*-dodecane (400 *u*L). The Schlenk tube was tightly capped and the reaction mixture was heated with vigorous stirring in a 50 ^{o}C oil bath. After stirring at 50 ^{o}C for 9 hours, the reaction reached completion (monitored by GC). At the end of the reaction, the mixture was cooled to 25 ^{o}C, and filtered through a pad of silica gel (~20 g) with diethyl ether washing (50 mL). The filtrate was concentrated on a rotary evaporator and the residue was purified by flash silica gel chromatography (1:30 ethyl acetate/hexane), which afforded (*S*)-Flurbiprofen ester (1.19 g, 98% yield, 90% ee) as yellow oil.

Acidic hydrolysis. The arylation product was dissolved in analytical-grade DCM (10 mL) under argon, followed by the addition of trifluoroacetic acid (10 mL). The hydrolysis was carried out at room temperature with stirring for 4 hours. At the end of the reaction, the solvent and trifluoroacetic acid was concentrated on a rotary

evaporator. The residue was directly purified by flash chromatography (1:3 ethyl acetate/hexane), which afforded (*S*)-Flurbiprofen (1.17 g, 99% yield, 90% ee) as off-white solid.

The ee of synthetic (*S*)-Flurbiprofen was improved to 96% after one crystallization by vapor diffusion of hexane into a concentrated solution in 5 mL of Et_2O at room temperature (84% yield). Recrystalization improved the ee to 99%.



For a sample of 99% ee, $[\alpha]^{20}_D = +40.6^o$ (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.52 (m, 2H), 7.46-7.35 (m, 4H), 7.19-7.13 (m, 2H), 3.79 (q, J = 7.2 Hz, 1H), 1.56 (d, J = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$): δ -117.4

VI. Reference

(1) Biscoe, M. R.; Fors, B. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **2008**, *130*, 6686.
(2) Huang, Z.; Liu, Z.; Zhou, J. *J. Am. Chem. Soc.* **2011**, *133*, 15882.