Stereoconvergent Negishi Arylations of Racemic Secondary Alkyl Electrophiles: Differentiating Between a CF$_3$ and an Alkyl Group

Yufan Liang and Gregory C. Fu*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

Supporting Information

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I. General Information

The following reagents were purchased and used as received: NiCl$_2$•glyme (Strem), ligand 1 (Aldrich), ZnCl$_2$ (Aldrich; reagent grade, ≥ 98%), diglyme (Aldrich; anhydrous), n-BuLi (Aldrich; 2.5 M in hexanes). All aryl bromides were purchased (Aldrich, Alfa Aesar, TCI, and Oakwood) and used as received. Anhydrous THF was purified and dried using a solvent-purification system that contained activated alumina.

All reactions were carried out in oven-dried glassware under an inert atmosphere. HPLC analyses were carried out on an Agilent 1100 Series system, using Daicel CHIRALCEL® columns or Daicel CHIRALPAK® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm).

$^1$H NMR data and $^{13}$C NMR data were collected on a Varian 500 MHz spectrometer at ambient temperature. $^{19}$F NMR data were collected on a Varian 300 MHz spectrometer at ambient temperature.
II. Preparation of Electrophiles

These procedures have not been optimized.

![Chemical structure diagram]

**General Procedure A**

**Preparation of the ketone using a Grignard reagent.** A solution of the Grignard reagent in THF (1.0 M, 40 mmol; 1.0 equiv) was added by syringe to a solution of the Weinreb amide (40 mmol) in THF (20 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min, and then it was allowed to warm to r.t. and stirred for 15 h. Next, water was added to quench the reaction at 0 °C. A solution of 1 N HCl (50 mL) was added, and then the mixture was extracted with CH₂Cl₂ (3 × 50 mL). The organic layers were combined, dried over Na₂SO₄, and concentrated. The crude product was purified by flash chromatography on silica gel.

**Reduction of the ketone to the alcohol.** NaBH₄ (2.3 g, 60 mmol; 3.0 equiv) was added in portions to a solution of the ketone (20 mmol) in Et₂O (20 mL) and MeOH (20 mL) at 0 °C (CAUTION: very exothermic). After the addition was complete, the mixture was stirred at 0 °C for 30 min, and then it was allowed to warm to r.t. and stirred for 30 min. Next, Et₂O (30 mL) was added to dilute the reaction mixture, the mixture was cooled to 0 °C, and then deionized water (30 mL) was added to quench the reaction. The mixture was extracted with CH₂Cl₂ (3 × 50 mL), and the combined organic layers were dried over Na₂SO₄ and concentrated. The crude product was purified by flash chromatography on silica gel.

**Bromination of the alcohol.** Triphenylphosphite (4.0 g, 3.4 mL; 1.3 equiv) was added over 5 min to a solution of N-bromosuccinimide (2.3 g, 13 mmol; 1.3 equiv) in CH₂Cl₂ (10 mL) at 0 °C (CAUTION: exothermic). Next, a solution of the alcohol (10 mmol) in CH₂Cl₂ (12 mL) was added to the mixture at 0 °C. The reaction mixture was heated to 40 °C and then stirred at 40 °C for 12 h. Next, the solvent was evaporated, and the product was purified by flash chromatography on silica gel.

**General Procedure B**

**Swern oxidation of the alcohol.** DMSO (2.9 mL, 40 mmol; 2.0 equiv) was added slowly to a solution of oxalyl chloride (2.0 mL, 24 mmol; 1.2 equiv) in CH₂Cl₂ (150 mL) at −78 °C. The resulting mixture was allowed to stir at −78 °C for 30 min. Next, a solution of the alcohol (20

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mmol) in CH₂Cl₂ (30 mL) was added over 5 min to the mixture. The resulting mixture was stirred at −78 °C for 45 min, and then NEt₃ (11 mL, 80 mmol; 4.0 equiv) was added in one portion. The mixture was allowed to warm to r.t., and then it was stirred at r.t. for 2 h. Next, an aqueous saturated solution of NH₄Cl (30 mL) was added to quench the reaction. The resulting mixture was extracted with CH₂Cl₂ (3 × 70 mL), and the combined organic layers were dried over Na₂SO₄ and concentrated. The crude product was purified by flash chromatography on silica gel.

**Trifluoromethylation of the aldehyde.**³ A solution of TBAF (1.0 M in THF; 0.20 mL, 0.20 mmol; 0.013 equiv) was added over 3 min to a solution of the aldehyde (15 mmol) and trifluoromethyltrimethylsilane (2.7 mL, 18 mmol; 1.2 equiv) in THF (20 mL) at 0 °C (CAUTION: very exothermic). The reaction mixture was allowed to warm to r.t., and it was stirred for 1 h. Next, an aqueous solution of 1 N HCl (30 mL) was added, and the mixture was allowed to stir at r.t. for another 2 h. Then, the mixture was extracted with CH₂Cl₂ (3 × 50 mL), and the combined organic layers were dried over Na₂SO₄ and concentrated. The crude product was purified by flash chromatography on silica gel.

The bromination step is the same as in General Procedure A.

**General Procedure C**

The first two steps are the same as in General Procedure B.

**Bromination of the alcohol.**⁴ Triphenylphosphine (4.2 g, 16 mmol; 2.0 equiv) and tetrabromomethane (5.3 g, 16 mmol; 2.0 equiv) were added to a solution of the alcohol (8.0 mmol) in toluene (20 mL). The resulting mixture was heated to 110 °C and stirred at 110 °C for 3 h, at which time it had turned into a yellow suspension. Then, CH₂Cl₂ (50 mL) was added to the reaction mixture until it became a clear solution. The solvents were then evaporated, and the crude product was purified by flash chromatography on silica gel.

(3-Bromo-4,4,4-trifluorobutyl)benzene [136832-35-4]. The title compound was synthesized according to General Procedure A, using 2,2,2-trifluoro-N-methoxy-N-methylacetamide and a Grignard reagent prepared from (2-bromoethyl)benzene. The overall yield was 34% (3 steps). The title compound was isolated as a colorless oil.

\[ \text{H NMR (500 MHz, CDCl}_3 \text{) } \delta \text{ 7.37} - \text{7.32 (m, 2H), 7.29} - \text{7.22 (m, 3H), 4.03} - \text{3.96 (m, 1H), 3.02 (ddd, 1H, J = 13.4, 8.3, 4.6 Hz), } 2.81 - \text{2.75 (m, 1H), 2.40} - \text{2.33 (m, 1H), 2.21 (ddddd, 1H, } J = 14.6, 11.0, 8.2, 4.6 \text{ Hz);} \]

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 139.2, 128.8, 128.5, 126.7, 124.0 (q, $J = 278.2$ Hz), 46.7 (q, $J = 32.6$ Hz), 32.9 (d, $J = 1.4$ Hz), 32.5;

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ −72.1 (d, 3F, $J = 7.1$ Hz);

FT-IR (film) 3029, 1258, 1168, 1111, 750, 700 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_{10}$H$_{14}$BrF$_3$: 266, found: 266, 268 (M$^+$+2).

2-Bromo-1,1,1-trifluoropropane [421-46-5]. The title compound was synthesized from 1,1,1-trifluoropropan-2-ol according to a literature procedure$^5$ in 68% yield (colorless oil; it should be stored in a refrigerator (~5 °C)).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.21 (hept, 1H, $J = 7.0$ Hz), 1.81 (d, 3H, $J = 7.0$ Hz);

The NMR spectral data are in agreement with literature data.$^6$

(2-Bromo-3,3,3-trifluoropropyl)cyclohexane. The title compound was synthesized according to General Procedure B, using 3-cyclohexyl-1,1,1-trifluoropropan-2-ol, in 46% yield (colorless oil).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.16 (dqd, 1H, $J = 3.7$, 7.1, 10.8 Hz), 1.88 – 1.65 (m, 7H), 1.65 – 1.56 (m, 1H), 1.35 – 1.24 (m, 2H), 1.23 – 1.11 (m, 1H), 1.08 – 1.00 (m, 1H), 0.87 – 0.79 (m, 1H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 124.3 (q, $J = 277.8$ Hz), 45.5 (q, $J = 32.4$ Hz), 38.4, 34.5, 33.7, 31.0, 26.3, 26.1, 25.7;

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ −72.5 (d, 3F, $J = 7.0$ Hz);

FT-IR (film) 2925, 2854, 1450, 1314, 1291, 1271, 1258, 1180, 1157, 1128, 1109, 681 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_9$H$_{14}$BrF$_3$: 258, found: 258, 260 (M$^+$+2).

2-Bromo-1,1,1-trifluorodecane [1349717-60-7]. The title compound was synthesized according to General Procedure A, using 2,2,2-trifluoro-N-methoxy-N-methylacetamide and a Grignard reagent prepared from 1-bromoocthane. The overall yield was 30% (3 steps). The title compound was isolated as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.06 (dqd, 1H, $J = 10.5$, 7.2, 3.3 Hz), 2.02 (dddd, 1H, $J = 14.6$, 9.8, 6.1, 3.3 Hz), 1.91 – 1.81 (m, 1H), 1.43 – 1.21 (m, 12H), 0.89 (t, 3H, $J = 7.2$ Hz);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 124.1 (q, $J = 278.0$ Hz), 47.7 (q, $J = 32.3$ Hz), 31.8, 31.4 (d, $J = 1.5$ Hz), 29.23, 29.15, 28.6, 26.8, 22.6, 14.1;
$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ $-72.4$ (d, 3F, $J = 7.2$ Hz);
FT-IR (film) 2956, 2928, 2857, 1266, 1173, 1124, 1105, 678 cm$^{-1}$;
GC-MS (EI) $m/z$ (M$^+$–C$_4$H$_9$) calcd for C$_6$H$_9$F$_7$BrF$_3$: 217, found: 217, 219 (M$^+$–C$_4$H$_3$+2).

OTBDPS

The title compound was synthesized according to General Procedure B from 6-((tert-butyldiphenylsilyl)oxy)hexan-1-ol.$^7$ The overall yield was 23% (3 steps). The title compound was isolated as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.70 – 7.66 (m, 4H), 7.46 – 7.37 (m, 6H), 4.04 (dqd, $J = 10.5$, 7.2, 3.4 Hz), 3.69 (t, 2H, $J = 6.3$ Hz), 2.02 (dddd, $J = 14.4$, 9.8, 5.6, 3.3 Hz), 1.90 – 1.81 (m, 1H), 1.69 – 1.54 (m, 3H), 1.49 – 1.35 (m, 3H), 1.07 (s, 9H);
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 135.6, 134.0, 129.6, 127.6, 124.1 (q, $J = 278.2$ Hz), 63.5, 47.6 (q, $J = 32.4$ Hz), 32.1, 31.4 (d, $J = 1.4$ Hz), 26.9, 26.5, 24.9, 19.2;
$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ $-72.3$ (d, 3F, $J = 7.1$ Hz);
FT-IR (film) 2932, 2858, 1428, 1259, 1113, 823, 701 cm$^{-1}$;
GC-MS (EI) $m/z$ (M$^+$–C$_4$H$_9$) calcd for C$_{19}$H$_{21}$BrF$_3$: 429, found: 429.

2-Bromo-6-chloro-1,1,1-trifluorohexane. The title compound was synthesized according to General Procedure B, using 6-chloro-1,1,1-trifluorohexan-2-ol, in 44% yield (colorless oil).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.08 (dqd, 1H, $J = 3.3$, 7.1, 10.5 Hz), 3.58 – 3.55 (m, 2H), 2.11 – 2.04 (m, 1H), 1.94 – 1.78 (m, 4H), 1.66 – 1.57 (m, 1H);
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 123.9 (q, $J = 278.1$ Hz), 47.2 (q, $J = 32.6$ Hz), 44.3, 31.5, 30.8 (d, $J = 1.5$ Hz), 24.3;
$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ $-72.3$ (d, 3F, $J = 7.1$ Hz);
FT-IR (film) 2957, 1330, 1259, 1167, 1113, 823, 701 cm$^{-1}$;
GC-MS (EI) $m/z$ (M$^+$–HBr) calcd for C$_{15}$H$_{21}$ClF$_3$: 172, found: 172.

2,10-Dibromo-1,1,1-trifluorodecane. The title compound was synthesized according to General Procedure B from 9-bromononan-1-ol. The overall yield was 50% (3 steps). The title compound was isolated as a colorless oil.

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1H NMR (500 MHz, CDCl₃) δ 7.94 – 7.90 (m, 2H), 6.93 – 6.89 (m, 2H), 4.12 – 4.05 (m, 1H), 4.03 (t, 2H, J = 6.3 Hz), 2.55 (s, 3H), 2.07 (dddd, 1H, J = 14.4, 10.1, 5.6, 3.4 Hz), 1.94 – 1.80 (m, 3H), 1.78 – 1.68 (m, 1H), 1.62 – 1.47 (m, 3H);
13C NMR (126 MHz, CDCl₃) δ 196.7, 162.9, 130.6, 130.2, 124.0 (q, J = 278.2 Hz), 114.0, 67.8, 47.4 (q, J = 32.4 Hz), 31.3 (d, J = 1.4 Hz), 28.7, 26.5, 26.3, 25.2;
19F NMR (282 MHz, CDCl₃) δ -72.3 (d, 3F, J = 7.1 Hz);
FT-IR (film) 2946, 2867, 1676, 1602, 1576, 1509, 1358, 1257, 1172, 1117, 834 cm⁻¹;
GC-MS (EI) m/z (M⁺–CH₃) calcd for C₁₄H₁₅BrF₃O₂: 351, found: 351, 353 (M⁺–CH₃+2).

1-(6-Bromo-7,7,7-trifluoroheptyl)oxy)-4-iodobenzene. The title compound was synthesized according to General Procedure B from 6-(4-iodophenoxy)hexan-1-ol. The overall yield was 33% (3 steps). The title compound was isolated as a colorless oil (it should be stored in a refrigerator (~5 °C)).

1H NMR (500 MHz, CDCl₃) δ 7.57 – 7.52 (m, 2H), 6.69 – 6.65 (m, 2H), 4.08 (dqd, 1H, J = 10.5, 7.1, 3.4 Hz), 3.93 (t, 2H, J = 6.3 Hz), 2.07 (dddd, 1H, J = 14.3, 9.9, 5.5, 3.4 Hz), 1.95 – 1.86 (m, 1H), 1.85 – 1.68 (m, 3H), 1.60 – 1.46 (m, 3H);
13C NMR (126 MHz, CDCl₃) δ 158.8, 138.2, 124.0 (q, J = 278.2 Hz), 116.9, 82.6, 67.6, 47.5 (q, J = 32.5 Hz), 31.3 (d, J = 1.4 Hz), 28.8, 26.6, 25.2;
19F NMR (282 MHz, CDCl₃) δ -72.3 (d, 3F, J = 7.1 Hz);
FT-IR (film) 2944, 1587, 1487, 1473, 1283, 1245, 1175, 1117, 820 cm⁻¹;
GC-MS (EI) m/z (M⁺) calcd for C₁₃H₁₅BrF₃IO: 450, found: 450, 452 (M⁺+2).

 tert-Butyl 4-(2-bromo-3,3,3-trifluoropropyl)piperidine-1-carboxylate. The title compound was synthesized according to General Procedure C from tert-butyl 4-(2-hydroxyethyl)piperidine-1-carboxylate. The overall yield was 26% (3 steps). The title compound was isolated as a white solid.

1H NMR (500 MHz, CDCl₃) δ 4.15 – 4.09 (m, 3H), 2.72 – 2.68 (m, 2H), 1.94 – 1.85 (m, 1H), 1.85 – 1.72 (m, 2H), 1.68 – 1.63 (m, 2H), 1.44 (s, 9H), 1.23 (tdd, 1H, J = 12.8, 11.0, 4.4 Hz), 1.03 (tdd, 1H, J = 12.7, 11.0, 4.5 Hz);
13C NMR (126 MHz, CDCl₃) δ 154.7, 124.1 (q, J = 278.1 Hz), 79.5, 44.8 (q, J = 32.7 Hz), 37.6, 33.2, 32.4, 30.0, 28.4;
19F NMR (282 MHz, CDCl₃) δ -72.5 (d, 3F, J = 7.0 Hz);
FT-IR (film) 2977, 2931, 2850, 1691, 1425, 1366, 1262, 1252, 1172, 1129, 1110, 967, 685 cm⁻¹;

(10) Prepared from 6-chlorohexan-1-ol and 4-iodophenol.
GC-MS (EI) \( m/z \) (M'–Boc) calcd for \( \text{C}_{6}\text{H}_{12}\text{BrF}_{3}\text{N} \): 258, found: 258, 260 (M'–Boc+2).

6-Bromo-7,7,7-trifluoroheptyl furan-2-carboxylate. The title compound was synthesized according to General Procedure B from 6-hydroxyhexyl furan-2-carboxylate.\(^{11}\) The overall yield was 62\% (3 steps). The title compound was isolated as a light-yellow oil (it should be stored in a refrigerator (~5 °C)).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.57 (dd, 1H, \( J = 1.8, 0.9 \) Hz), 7.17 (dd, 1H, \( J = 3.5, 0.9 \) Hz), 6.51 (dd, 1H, \( J = 3.5, 1.7 \) Hz), 4.31 (t, 2H, \( J = 6.6 \) Hz), 4.07 (dqd, 1H, \( J = 10.5, 7.1, 3.4 \) Hz), 2.05 (dddd, 1H, \( J = 14.7, 10.3, 5.6, 3.3 \) Hz), 1.93 – 1.84 (m, 1H), 1.82 – 1.68 (m, 3H), 1.55 – 1.42 (m, 3H);

\(^13\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 158.7, 146.3, 144.7, 124.0 (q, \( J = 278.1 \) Hz), 117.8, 111.8, 64.6, 47.4 (quartet, \( J = 32.5 \) Hz), 31.3 (d, \( J = 1.5 \) Hz), 28.4, 26.5, 25.1;

\(^19\)F NMR (282 MHz, CDCl\(_3\)) \( \delta \) −72.3 (d, 3F, \( J = 7.0 \) Hz);

FT-IR (film) 2949, 2866, 1726, 1582, 1571, 1475, 1400, 1297, 1260, 1180, 1118, 1014, 958, 885, 764, 677 cm\(^{-1}\);

GC-MS (EI) \( m/z \) (M') calcd for \( \text{C}_{12}\text{H}_{14}\text{BrF}_{3}\text{O}_{3} \): 342, found: 342, 344 (M'+2).

\((4,4,4\text{-Trifluoro-3-iodobutyl})\text{benzene.}\) The title compound was synthesized according to General Procedure A, using 1,1,1-trifluoro-4-phenylbutan-2-ol, in 48\% yield (colorless oil; it should be stored in a refrigerator (~5 °C)); \( N \)-iodosuccinimide, rather than \( N \)-bromosuccinimide, was used.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.35 – 7.31 (m, 2H), 7.28 – 7.22 (m, 3H), 4.09 – 4.00 (m, 1H), 3.00 (dt, 1H, \( J = 6.4, 13.4 \) Hz), 2.71 (dt, 1H, \( J = 8.2, 13.9 \) Hz), 2.23 – 2.16 (m, 2H);

\(^13\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 139.1, 128.8, 128.5, 126.7, 124.6 (quartet, \( J = 276.5 \) Hz), 34.4, 34.2 (d, \( J = 1.6 \) Hz), 23.6 (quartet, \( J = 31.1 \) Hz);

\(^19\)F NMR (282 MHz, CDCl\(_3\)) \( \delta \) −68.8 (d, 3F, \( J = 8.0 \) Hz);

FT-IR (film) 3028, 1455, 1257, 1161, 1094, 1075, 749 cm\(^{-1}\);

GC-MS (EI) \( m/z \) (M') calcd for \( \text{C}_{10}\text{H}_{10}\text{F}_{2}\text{I} \): 314, found: 314.

\((3\text{-Bromo-4,4,5,6,6-heptafluorohexyl})\text{benzene.}\) The title compound was synthesized according to General Procedure A, using 2,2,3,3,4,4,4-heptafluoro-\( N \)-methoxy-\( N \)-

(11) Prepared from hexane-1,6-diol and furan-2-carbonyl chloride.
methylbutanamide and a Grignard reagent prepared from (2-bromoethyl)benzene. The overall yield was 24% (3 steps). The title compound was isolated as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.35 – 7.32 (m, 3H), 7.28 – 7.22 (m, 2H), 4.19 – 4.08 (m, 1H), 3.06 (ddd, 1H, $J$ = 13.3, 8.4, 4.4 Hz), 2.80 (dt, 1H, $J$ = 13.9, 8.2 Hz), 2.43 – 2.36 (m, 1H), 2.27 – 2.17 (m, 1H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 139.1, 128.8, 128.5, 126.7, 121.5 – 108.5 (m), 46.5 (t, $J$ = 24.5 Hz), 32.6, 32.3;

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ −80.8 (t, 3F, $J$ = 10.7 Hz), −109.2 – −115.5 (m, 2F), −123.3 (dd, 2F, $J$ = 20.0, 8.1 Hz);

FT-IR (film) 3029, 2936, 1497, 1456, 1348, 1235, 1182, 1108, 964, 927, 750, 724, 699 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_{12}$H$_{10}$BrF$_7$: 366, found: 366, 368 (M$^+$+2).

(3-Bromo-4-chloro-4,4-difluorobutyl)benzene. The title compound was synthesized according to General Procedure A, using 1-chloro-1,1-difluoro-4-phenylbutan-2-ol, in 48% yield (colorless oil).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.35 – 7.32 (m, 2H), 7.27 – 7.23 (m, 3H), 4.12 (tdd, 1H, $J$ = 2.6, 5.6, 11.1 Hz), 3.04 (ddd, 1H, $J$ = 4.5, 8.3, 13.3 Hz), 2.78 (dt, 1H, $J$ = 8.3, 13.9 Hz), 2.50 – 2.43 (m, 1H), 2.22 (dddd, 1H, $J$ = 4.4, 8.1, 11.0, 14.5 Hz);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 139.3, 128.7, 128.5, 127.6 (dd, $J$ = 292.5, 294.2 Hz), 126.7, 53.7 (t, $J$ = 27.0 Hz), 34.2, 32.6;

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ −53.7 (dd, 1F, $J$ = 5.7, 162.3 Hz), −57.5 (dd, 1F, $J$ = 11.1, 162.4 Hz);

FT-IR (film) 3029, 2929, 1497, 1455, 1256, 1203, 1169, 1116, 1080, 1031, 947, 751, 699 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_{10}$H$_{10}$BrClF$_2$: 282, found: 282, 284 (M$^+$+2);

3-Bromo-2,2-difluoro-1,5-diphenylpentan-1-one. The title compound was synthesized according to General Procedure B, using 2,2-difluoro-3-hydroxy-1,5-diphenylpentan-1-one,$^{12}$ in 44% yield (colorless oil).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.07 – 8.05 (m, 2H), 7.67 – 7.64 (m, 1H), 7.52 – 7.48 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.22 (m, 3H), 4.46 (dtd, 1H, $J$ = 2.6, 11.1, 14.9 Hz), 3.08 (ddd, 1H, $J$ = 4.5, 8.7, 13.5 Hz), 2.80 (dt, 1H, $J$ = 8.3, 13.9 Hz), 2.45 – 2.38 (m, 1H), 2.30 – 2.22 (m, 1H);

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13C NMR (126 MHz, CDCl3) δ 188.3 (dd, J = 28.9, 30.6 Hz), 139.6, 134.4, 132.2 (t, J = 2.3 Hz), 130.0 (dd, J = 2.7, 4.1 Hz), 128.7, 128.6, 128.5, 126.4, 116.1 (dd, J = 256.9, 261.0 Hz), 49.6 (dd, J = 24.1, 26.9 Hz), 32.8, 32.2 (t, J = 2.2 Hz); 19F NMR (282 MHz, CDCl3) δ –101.1 (dd, 1F, J = 11.1, 275.8 Hz), –105.7 (dd, 1F, J = 14.9, 275.7 Hz); FT-IR (film) 3063, 3028, 2930, 1702, 1598, 1497, 1449, 1281, 1251, 1203, 1185, 1046, 923, 898, 754, 717, 700, 687 cm−1; GC-MS (EI) m/z (M+−Br) calcd for C17H15F2O: 273, found: 273.

Ethyl 3-bromo-2,2-difluoro-5-phenylpentanoate. The title compound was synthesized according to General Procedure B, using ethyl 2,2-difluoro-3-hydroxy-5-phenylpentanoate,13 in 87% yield (colorless oil).

1H NMR (500 MHz, CDCl3) δ 7.34 – 7.31 (m, 2H), 7.26 – 7.21 (m, 3H), 4.35 (q, 2H, J = 7.1 Hz), 4.23 – 4.15 (m, 1H), 3.03 (ddd, 1H, J = 4.6, 8.5, 13.5 Hz), 2.76 (dt, 1H, J = 8.3, 13.9 Hz), 2.36 – 2.29 (m, 1H), 2.20 (dddd, 1H, J = 4.6, 8.5, 11.1, 14.8 Hz), 1.34 (t, 3H, J = 7.1 Hz); 13C NMR (126 MHz, CDCl3) δ 162.2 (t, J = 32.3 Hz), 139.6, 128.7, 128.5, 126.5, 113.5 (dd, J = 253.1, 258.0 Hz), 63.4, 49.2 (dd, J = 25.5, 28.0 Hz), 32.7, 31.9, 13.8; 19F NMR (282 MHz, CDCl3) δ –105.1 (dd, 1F, J = 9.0, 255.8 Hz), –114.4 (dd, 1F, J = 15.9, 255.8 Hz); FT-IR (film) 3028, 2984, 2976, 1776, 1760, 1497, 1455, 1373, 1311, 1251, 1218, 1102, 1061, 753, 700 cm−1; GC-MS (EI) m/z (M+) calcd for C13H1579BrF2O2: 320, found: 320, 322 (M+2).

III. Stereoconvergent Negishi Cross-Couplings

**General procedure for the preparation of a solution of the arylzinc reagent (0.30 M):** ZnCl₂ (Aldrich; reagent grade, ≥98%) was fused through drying with a heat gun under high vacuum for 20 min before use. n-BuLi (Aldrich; ~2.5 M in hexanes) was titrated using diphenylacetic acid, according to Kofron’s method.¹⁴

In the air, ZnCl₂ (1.43 g, 10.5 mmol) was added quickly to an oven-dried 20 mL vial equipped with a stir bar. The vial was closed with a PTFE septum cap, and then it was evacuated and back-filled with nitrogen (three cycles). THF (6.0 mL) was added to the vial, and the resulting mixture was stirred vigorously until the ZnCl₂ had completely dissolved. THF (0.5 mL) was then added, thereby providing a 1.50 M solution of ZnCl₂. Next, an oven-dried 40 mL vial equipped with a stir bar was charged with the aryl bromide (9.00 mmol), and then it was closed with a PTFE septum cap. The vial was next evacuated and back-filled with nitrogen (three cycles), and then THF (6.5 mL) was added to this vial. The vial that contained the solution of the aryl bromide was cooled to −78 °C. A solution of n-BuLi in hexanes (2.57 M; 3.50 mL, 9.00 mmol; 1.00 equiv) was added over ~4 min to the solution of the aryl bromide. After the addition was complete, the resulting mixture was stirred at −78 °C for 7 min. Next, the solution of ZnCl₂ (1.50 M; 6.00 mL, 9.00 mmol; 1.00 equiv) was added to the vial. The resulting mixture was allowed to warm to r.t., and then it was stirred for 45 min at r.t. The solution of the arylzinc reagent was titrated using I₂, according to Knochel’s method (the concentration was typically ~0.4 M). This solution was then diluted to a 0.30 M solution using THF.

These solutions of organozinc reagents can be stored at r.t. under an inert atmosphere for several weeks without deterioration.

**General Procedure for stereoconvergent Negishi arylation**: In the air, an oven-dried 20 mL vial equipped with a stir bar was charged with the electrophile (1.00 mmol). The vial was closed with a PTFE septum cap, and then it was evacuated and back-filled with nitrogen (three cycles). In the air, NiCl₂-glyme (13.2 mg, 0.060 mmol) and (R,R)-1 (26.1 mg, 0.078 mmol) were added to an oven-dried 4 mL vial equipped with a stir bar. The vial was closed with a PTFE septum cap, and then it was evacuated and back-filled with nitrogen (three cycles). Diglyme (1.5 mL) was added to the vial, and the mixture was vigorously stirred at r.t. for 30 min. The resulting solution was transferred via syringe to the 20 mL reaction vial that contained the electrophile. The 4 mL vial was rinsed with THF three times (0.8 mL, 0.8 mL, and 0.7 mL), and the washings were transferred to the reaction vial. The resulting solution was stirred at r.t. for 3 min. Then, the joint of the reaction vial was wrapped with electrical tape, and the vial was cooled to −20 °C. Meanwhile, an oven-dried 40 mL vial that contained the solution of the arylzinc reagent was also cooled to −20 °C. Nitrogen-filled balloons were attached to both of the vials. To the vigorously stirred solution of catalyst and electrophile was added the solution of the arylzinc reagent (0.30 M; 5.0 mL, 1.5 mmol; 1.5 equiv) over 3 min, leading to an orange reaction mixture. The balloon was removed, and the puncture hole in the septum cap was covered with grease. The mixture was stirred vigorously at −20 °C for 14 h, and then the reaction was quenched by the addition of MeOH (2 mL). The resulting mixture was allowed to

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warm to r.t., and then it was diluted with Et₂O (100 mL) and washed with deionized water (20 mL × 4). The organic layer was dried over Na₂SO₄, filtered, and then concentrated, and the residue was purified by flash chromatography.

A second run was performed with (S,S)-1.

(R)-1-Methoxy-2-(1,1,1-trifluoro-4-phenylbutan-2-yl)benzene (Table 2, Entry 1). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-2-methoxybenzene were used. The reaction was run at −20 °C for 40 h. Solvent system for chromatography: 15:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 150 mg (51% yield, 88% ee); Run 2, 140 mg (48% yield, 86% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (R,R)-1: 15.5 min (minor), 16.4 min (major).

¹H NMR (500 MHz, CDCl₃) δ 7.41 – 7.39 (m, 1H), 7.33 (ddd, 1H, J = 1.7, 7.4, 8.2 Hz), 7.30 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 7.11 – 7.09 (m, 2H), 7.03 (td, 1H, J = 1.1, 7.5 Hz), 6.95 (ddd, 1H, J = 1.1, 8.3 Hz), 4.08 (dqd, 1H, J = 4.2, 9.7, 11.2 Hz), 3.82 (s, 3H), 2.57 – 2.44 (m, 2H), 2.33 (ddd, 1H, J = 4.2, 7.1, 9.8, 13.4 Hz), 2.18 (ddddd, 1H, J = 5.1, 9.5, 11.0, 13.5 Hz);

¹³C NMR (126 MHz, CDCl₃) δ 158.0, 141.1, 129.0, 128.4, 128.3, 128.2, 127.2 (q, J = 280.9 Hz), 126.0, 123.1, 120.8, 110.9, 55.6, 39.8 (q, J = 27.2 Hz), 32.6, 30.4 (d, J = 2.5 Hz);

¹⁹F NMR (282 MHz, CDCl₃) δ −69.5 (d, 3F, J = 9.6 Hz);

FT-IR (film) 2941, 1603, 1496, 1464, 1246, 1148, 1118, 1030, 753, 699 cm⁻¹;

GC-MS (EI) m/z (M⁺) calcd for C₁₇H₁₇F₃O: 294, found: 294;

[α]D²⁵ = +12° (c = 1.01, CHCl₃); 86% ee, from (S,S)-1.

(R)-1-Methoxy-3-(1,1,1-trifluoro-4-phenylbutan-2-yl)benzene (Table 2, Entry 2). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 5:1 → 4:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 268 mg (91% yield, 96% ee); Run 2, 260 mg (88% yield, 96% ee).

This compound was also prepared on a 5.00 mmol scale, using (3-bromo-4,4,4-trifluorobutyl)benzene (1.34 g, 5.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene (0.30 M; 25 mL, 7.5 mmol; 1.5 equiv). Following the General Procedure, the title compound was isolated in 91% yield (1.34 g) and 96% ee.
The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (S,S)-1: 20.4 min (minor), 32.2 min (major).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.27 (m, 3H), 7.24 – 7.20 (m, 1H), 7.13 – 7.10 (m, 2H), 6.93 – 6.89 (m, 2H), 6.87 – 6.84 (m, 1H), 3.84 (s, 3H), 3.21 (dqd, 1H, \(J = 3.9, 9.3, 11.1\) Hz), 2.61 (dd, 1H, \(J = 4.9, 9.1, 13.9\) Hz), 2.44 (dd, 1H, \(J = 7.8, 8.9, 13.8\) Hz), 2.34 (dd, 1H, \(J = 3.9, 7.7, 9.1, 13.2\) Hz), 2.21 (dd, 1H, \(J = 4.9, 9.0, 11.2, 13.8\) Hz);

\(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 159.8, 140.6, 135.9 (d, \(J = 2.0\) Hz), 129.7, 128.5, 128.4, 126.9 (q, \(J = 280.6\) Hz), 126.2, 121.5, 115.2, 113.3, 55.2, 49.2 (q, \(J = 26.5\) Hz), 32.5, 30.2 (d, \(J = 2.0\) Hz);

\(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) –69.6 (d, 3F, \(J = 9.3\) Hz);

FT-IR (film) 3028, 2956, 1603, 1586, 1496, 1454, 1258, 1157, 1110, 1044, 781, 708, 699 cm\(^{-1}\);

GC-MS (EI) \(m/z\) calcd for C\(_{17}\)H\(_{17}\)F\(_3\)O: 294, found: 294;

\([\alpha]\)^D\(_{25}\) = +48° (c = 0.97, CHCl\(_3\)); 96% ee, from (R,R)-1.

(R)-1-Methyl-3-(1,1,1-trifluoro-4-phenylbutan-2-yl)benzene (Table 2, Entry 3). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methylbenzene were used. Solvent system for chromatography: hexane. The title compound was isolated as a colorless oil.

Run 1, 247 mg (89% yield, 95% ee); Run 2, 252 mg (91% yield, 95% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (S,S)-1: 12.4 min (minor), 13.5 min (major).

\(^1\)H NMR (500 MHz, CD\(_3\)COCD\(_3\)) \(\delta\) 7.35 – 7.12 (m, 9H), 3.48 – 3.37 (m, 1H), 2.58 – 2.44 (m, 2H), 2.37 (s, 3H), 2.35 – 2.21 (m, 2H);

\(^13\)C NMR (126 MHz, CD\(_3\)COCD\(_3\)) \(\delta\) 142.0, 139.3, 135.4 (d, \(J = 2.1\) Hz), 130.9, 129.9, 129.6, 129.4, 129.3, 128.4 (q, \(J = 279.9\) Hz), 127.3, 127.1, 49.8 (q, \(J = 26.1\) Hz), 33.4, 31.1 (d, \(J = 2.2\) Hz), 21.5;

\(^19\)F NMR (282 MHz, CD\(_3\)COCD\(_3\)) \(\delta\) –70.2 (d, 3F, \(J = 9.7\) Hz);

FT-IR (film) 3028, 2955, 1496, 1454, 1259, 1171, 1147, 1110, 785, 708, 699 cm\(^{-1}\);

GC-MS (EI) \(m/z\) calcd for C\(_{17}\)H\(_{17}\)F\(_3\): 278, found: 278;

\([\alpha]\)^D\(_{25}\) = –46° (c = 0.97, CHCl\(_3\)); 95% ee, from (S,S)-1.

(R)-1-(1,1,1-Trifluoro-4-phenylbutan-2-yl)-3-(trifluoromethyl)benzene (Table 2, Entry 4). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-(trifluoromethyl)benzene were used. The reaction was run at –15 °C
for 14 h. Solvent system for chromatography: hexane. The title compound was isolated as a colorless oil.

Run 1, 287 mg (86% yield, 96% ee); Run 2, 288 mg (87% yield, 97% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (S,S)-1: 14.6 min (minor), 17.4 min (major).

1H NMR (500 MHz, CDCl$_3$) $\delta$ 7.66 – 7.63 (m, 1H), 7.56 – 7.48 (m, 3H), 7.33 – 7.27 (m, 2H), 2.65 – 2.56 (m, 1H), 2.47 – 2.36 (m, 2H), 2.30 – 2.20 (m, 1H);

13C NMR (126 MHz, CDCl$_3$) $\delta$ 140.0, 135.5 (d, $J = 2.2$ Hz), 132.5, 131.2 (q, $J = 32.5$ Hz), 129.3, 128.6, 128.3, 126.5 (q, $J = 280.7$ Hz), 126.4, 126.1 (q, $J = 3.9$ Hz), 125.2 (q, $J = 3.7$ Hz), 123.9 (q, $J = 271.4$ Hz), 49.0 (q, $J = 26.9$ Hz), 32.4, 29.9 (d, $J = 2.0$ Hz);

19F NMR (282 MHz, CDCl$_3$) $\delta$ $-62.7$ (s, 3F), $-69.7$ (d, 3F, $J = 9.2$ Hz);

FT-IR (film) 3029, 2958, 1497, 1454, 1332, 1258, 1169, 1115, 1077, 711, 698 cm$^{-1}$;

GC-MS (EI) $m/z$ (M$^+$) calcd for C$_{17}$H$_{14}$F$_6$: 332, found: 332;

[$\alpha$]$^2_5$ = +42° ($c = 0.98$, CHCl$_3$); 96% ee, from (R,R)-1.

(R)-1-Fluoro-3-(1,1,1-trifluoro-4-phenylbutan-2-yl)benzene (Table 2, Entry 5). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-fluorobenzene were used. The reaction was run at −15 °C for 14 h. Solvent system for chromatography: hexane. The title compound was isolated as a colorless oil.

Run 1, 225 mg (80% yield, 96% ee); Run 2, 220 mg (78% yield, 96% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (S,S)-1: 16.7 min (minor), 19.7 min (major).

1H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40 – 7.34 (m, 1H), 7.32 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 7.13 – 7.01 (m, 5H), 3.29 – 3.17 (m, 1H), 2.61 (ddd, 1H, $J = 4.9$, 8.8, 13.5 Hz), 2.47 – 2.32 (m, 2H), 2.20 (dddd, 1H, $J = 4.9$, 8.6, 11.2, 13.7 Hz);

13C NMR (126 MHz, CDCl$_3$) $\delta$ 162.9 (d, $J = 246.6$ Hz), 140.2, 136.9 (m), 130.2 (d, $J = 8.3$ Hz), 128.6, 128.4, 126.6 (q, $J = 280.6$ Hz), 126.3, 125.1 (d, $J = 2.9$ Hz), 116.0 (d, $J = 22.0$ Hz), 115.3 (d, $J = 21.0$ Hz), 48.9 (qd, $J = 1.9$, 26.9 Hz), 32.4, 30.1 (d, $J = 2.0$ Hz);

19F NMR (282 MHz, CDCl$_3$) $\delta$ $-69.7$ (d, 3F, $J = 9.2$ Hz), $-112.4$ (m, 1F);

FT-IR (film) 3029, 2957, 1616, 1593, 1491, 1454, 1258, 1174, 1157, 1143, 1112, 787, 709, 700 cm$^{-1}$;

GC-MS (EI) $m/z$ (M$^+$) calcd for C$_{16}$H$_{14}$F$_4$: 282, found: 282;

[$\alpha$]$^2_5$ = +49° ($c = 0.97$, CHCl$_3$); 96% ee, from (R,R)-1.
(R)-1-Chloro-3-(1,1,1-trifluoro-4-phenylbutan-2-yl)benzene (Table 2, Entry 6). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-chlorobenzene were used. The reaction was run at −15 °C for 14 h. Solvent system for chromatography: hexane. The title compound was isolated as a colorless oil.

Run 1, 260 mg (87% yield, 96% ee); Run 2, 255 mg (85% yield, 96% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (S,S)-1: 18.0 min (minor), 23.3 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.38 – 7.28 (m, 5H), 7.25 – 7.17 (m, 2H), 7.12 – 7.08 (m, 2H), 3.21 (dqd, 1H, $J$ = 3.9, 9.2, 11.0 Hz), 2.61 (ddd, 1H, $J$ = 4.9, 8.8, 13.5 Hz), 2.47 – 2.32 (m, 2H), 2.20 (dddd, 1H, $J$ = 4.9, 8.5, 11.1, 13.7 Hz);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.2, 136.4 (d, $J$ = 2.0 Hz), 134.7, 130.0, 129.3, 128.6, 128.5, 128.3, 127.4, 126.6 (q, $J$ = 280.7 Hz), 126.4, 48.9 (q, $J$ = 26.9 Hz), 32.4, 30.0 (d, $J$ = 2.1 Hz);

$^{19}$F NMR (282 MHz, CDCl$_3$) δ −69.6 (d, 3F, $J$ = 9.1 Hz);

FT-IR (film) 3028, 2957, 1599, 1576, 1497, 1479, 1454, 1257, 1170, 1157, 1113, 786, 713, 699 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_{16}$H$_{14}$ClF$_3$: 298, found: 298;

$[\alpha]^{25}_D = +54^\circ$ (c = 1.01, CHCl$_3$); 96% ee, from (R,R)-1.

(R)-(4,4,4-Trifluorobutane-1,3-diyl)dibenzene (Table 2, Entry 7). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: hexane. The title compound was isolated as a colorless oil.

Run 1, 230 mg (87% yield, 95% ee); Run 2, 225 mg (85% yield, 95% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (S,S)-1: 15.6 min (minor), 16.6 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.44 – 7.36 (m, 3H), 7.34 – 7.28 (m, 4H), 7.25 – 7.20 (m, 1H), 7.13 – 7.09 (m, 2H), 3.24 (dqd, 1H, $J$ = 3.9, 9.4, 11.0 Hz), 2.61 (ddd, 1H, $J$ = 4.9, 8.9, 13.6 Hz), 2.49 – 2.32 (m, 2H), 2.25 (dddd, 1H, $J$ = 4.8, 8.7, 11.1, 13.8 Hz);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.6, 136.4 (d, $J$ = 2.0 Hz), 134.7, 130.0, 129.2, 128.7, 128.5, 128.4, 128.2, 126.9 (q, $J$ = 280.6 Hz), 126.2, 49.2 (q, $J$ = 26.5 Hz), 32.5, 30.1 (d, $J$ = 2.0 Hz);

$^{19}$F NMR (282 MHz, CDCl$_3$) δ −69.7 (d, 3F, $J$ = 9.3 Hz);

FT-IR (film) 3028, 2957, 1599, 1576, 1497, 1479, 1454, 1434, 1257, 1170, 1157, 1113, 786, 713, 699 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_{16}$H$_{15}$F$_3$: 264, found: 264;

$[\alpha]^{25}_D = -47^\circ$ (c = 0.99, CHCl$_3$); 95% ee, from (S,S)-1.
(R)-1-Methyl-4-(1,1,1-trifluoro-4-phenylbutan-2-yl)benzene (Table 2, Entry 8). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-4-methylbenzene were used. Solvent system for chromatography: hexane. The title compound was isolated as a colorless oil.

Run 1, 246 mg (88% yield, 95% ee); Run 2, 250 mg (90% yield, 94% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min; retention times for compound obtained using (S,S)-1: 12.1 min (minor), 13.1 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.33 – 7.27 (m, 2H), 7.24 – 7.19 (m, 5H), 7.13 – 7.10 (m, 2H), 3.20 (dqd, 1H, $J$ = 3.9, 9.4, 11.2 Hz), 2.61 (ddd, 1H, $J$ = 4.9, 9.1, 13.8 Hz), 2.47 – 2.41 (m, 1H), 2.40 (s, 3H), 2.35 (dddd, 1H, $J$ = 3.9, 7.7, 9.1, 13.2 Hz), 2.22 (dddd, 1H, $J$ = 4.9, 9.0, 11.2, 13.7 Hz);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.7, 138.0, 131.3 (d, $J$ = 2.0 Hz), 129.5, 129.0, 128.5, 128.4, 127.0 (q, $J$ = 280.5 Hz), 126.2, 48.7 (q, $J$ = 26.5 Hz), 32.5, 30.1 (d, $J$ = 2.1 Hz), 21.2;

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -69.9 (d, 3F, $J$ = 9.4 Hz);

FT-IR (film) 3028, 2955, 1517, 1496, 1259, 1169, 1148, 1108, 814, 699 cm$^{-1}$;

GC-MS (EI) $m/z$ (M$^+$) calcd for C$_{17}$H$_{17}$F$_3$: 278, found: 278; 
$[\alpha]^{25}_D$ = +52$^\circ$ ($c$ = 0.99, CHCl$_3$); 95% ee, from (R,R)-1.

(R)-Methyl(4-(1,1,1-trifluoro-4-phenylbutan-2-yl)phenyl)sulfane (Table 2, Entry 9). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from (4-bromophenyl)(methyl)sulfane were used. Solvent system for chromatography: 15:1 → 5:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 162 mg (52% yield, 94% ee); Run 2, 160 mg (52% yield, 93% ee).

The ee was determined on an OD-H column (0.5% i-PrOH/hexane, flow rate 0.5 mL/min; retention times for compound obtained using (R,R)-1: 19.4 min (minor), 20.6 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.31 – 7.27 (m, 4H), 7.24 – 7.20 (m, 3H), 7.12 – 7.07 (m, 2H), 3.23 – 3.14 (m, 1H), 2.60 (ddd, 1H, $J$ = 4.9, 8.9, 13.7 Hz), 2.52 (s, 3H), 2.46 – 2.29 (m, 2H), 2.20 (dddd, 1H, $J$ = 4.8, 8.7, 11.2, 13.7 Hz);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.5, 138.7, 131.0 (d, $J$ = 2.3 Hz), 129.6, 128.5, 128.4, 126.8 (q, $J$ = 280.6 Hz), 126.6, 126.2, 48.6 (q, $J$ = 26.6 Hz), 32.4, 30.0 (d, $J$ = 2.1 Hz), 15.5;

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ −69.9 (d, 3F, $J$ = 9.3 Hz);

FT-IR (film) 3027, 2922, 1601, 1496, 1256, 1169, 1149, 1109, 816, 700 cm$^{-1}$;
GC-MS (EI) m/z (M+) calcd for C_{17}H_{17}F_{3}S: 310, found: 310; 
[α]^{25}_{D} = +68° (c = 0.98, CHCl_{3}); 94% ee, from (R,R)-1.

(R)-1-Fluoro-4-(1,1,1-trifluoro-4-phenylbutan-2-yl)benzene (Table 2, Entry 10). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-4-fluorobenzene were used. The reaction was run at −15 °C for 14 h. Solvent system for chromatography: hexane. The title compound was isolated as a colorless oil.
Run 1, 235 mg (83% yield, 96% ee); Run 2, 241 mg (85% yield, 96% ee).
The ee was determined on an OD-H column (hexane, flow rate 0.5 mL/min); retention times for compound obtained using (R,R)-1: 26.3 min (minor), 29.8 min (major).

^{1}H NMR (500 MHz, CDCl_{3}) δ 7.32 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 7.13 – 7.07 (m, 4H), 3.22 (dqd, 1H, J = 3.7, 9.2, 11.0 Hz), 2.60 (ddd, 1H, J = 4.6, 8.0, 12.2 Hz), 2.46 – 2.32 (m, 2H), 2.24 – 2.14 (m, 1H);

^{13}C NMR (126 MHz, CDCl_{3}) δ 162.6 (d, J = 247.3 Hz), 140.3, 130.8 (d, J = 8.0 Hz), 130.1 (d, J = 1.7 Hz), 128.5, 128.4, 126.7 (q, J = 280.4 Hz), 126.3, 115.7 (d, J = 21.5 Hz), 48.4 (q, J = 26.8 Hz), 32.4, 30.1 (d, J = 2.1 Hz);

^{19}F NMR (282 MHz, CDCl_{3}) δ −70.0 (d, 3F, J = 9.2 Hz), −113.9 (m, 1F);
FT-IR (film) 3028, 2956, 1609, 1513, 1497, 1455, 1258, 1230, 1163, 1111, 831, 699 cm^{-1};
GC-MS (EI) m/z (M+) calcd for C_{16}H_{14}F_{4}: 282, found: 282;
[α]^{25}_{D} = −45° (c = 1.04, CHCl_{3}); 96% ee, from (S,S)-1.

(R)-1-Bromo-4-(1,1,1-trifluoro-4-phenylbutan-2-yl)benzene (Table 2, Entry 11). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1,4-dibromobenzene were used. The reaction was run at −15 °C for 14 h. Solvent system for chromatography: hexane. The title compound was isolated as a colorless oil.
Run 1, 296 mg (86% yield, 95% ee); Run 2, 300 mg (87% yield, 95% ee).
The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (S,S)-1: 20.0 min (minor), 22.6 min (major).

^{1}H NMR (500 MHz, CDCl_{3}) δ 7.56 – 7.52 (m, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 7.10 – 7.07 (m, 2H), 3.20 (dqd, 1H, J = 3.8, 9.2, 10.9 Hz), 2.60 (ddd, 1H, J = 4.5, 7.8, 11.8 Hz), 2.46 – 2.31 (m, 2H), 2.24 – 2.13 (m, 1H);
\[^{13}\text{C}\] NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 140.2, 133.4 (d, \(J = 1.9\) Hz), 132.0, 130.8, 128.6, 128.3, 126.5 (q, \(J = 280.6\) Hz), 126.3, 122.4, 48.6 (q, \(J = 26.7\) Hz), 32.3, 29.9 (d, \(J = 2.0\) Hz);

\[^{19}\text{F}\] NMR (282 MHz, CDCl\textsubscript{3}) \(\delta\) \(-69.8\) (d, 3F, \(J = 9.3\) Hz);

FT-IR (film) 3028, 2956, 1491, 1454, 1256, 1170, 1156, 1114, 1076, 1012, 819, 699 cm\(^{-1}\);

GC-MS (EI) \(m/z\) (M\(^+\)) calcd for C\(_{16}\)H\(_{14}\)F\(_3\): 342, found: 342, 344 (M\(^+\)+2);

\([\alpha]_{D}^{25} = +61^\circ\) (\(c = 0.99\), CHCl\textsubscript{3}); 95% ee, from (R,R)-1.

(R)-5-(1,1,1-Trifluoro-4-phenylbutan-2-yl)benzofuran (Table 2, Entry 12). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 5-bromobenzofuran were used. Solvent system for chromatography: 20:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 184 mg (61% yield, 94% ee); Run 2, 178 mg (59% yield, 94% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (S,S)-1: 21.8 min (minor), 22.6 min (major).

\(^1\text{H}\) NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.67 (d, 1H, \(J = 2.2\) Hz), 7.57–7.53 (m, 2H), 7.32–7.28 (m, 2H), 7.26–7.20 (m, 2H), 7.13–7.09 (m, 2H), 6.80 (dd, 1H, \(J = 1.0, 2.2\) Hz), 3.35 (dqd, 1H, \(J = 3.7, 9.3, 11.1\) Hz), 2.66–2.57 (m, 1H), 2.50–2.38 (m, 2H), 2.34–2.24 (m, 1H);

\[^{13}\text{C}\] NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 154.7, 145.7, 140.6, 128.8 (q, \(J = 2.1\) Hz), 128.5, 128.4, 127.8, 127.0 (q, \(J = 280.7\) Hz), 126.2, 125.3, 121.8, 111.6, 106.6, 49.0 (q, \(J = 26.6\) Hz), 32.5, 30.4 (d, \(J = 2.0\) Hz);

\(^{19}\text{F}\) NMR (282 MHz, CDCl\textsubscript{3}) \(\delta\) \(-69.8\) (d, 3F, \(J = 9.4\) Hz);

FT-IR (film) 3028, 2955, 1471, 1454, 1259, 1157, 1127, 1107, 1031, 742, 699 cm\(^{-1}\);

GC-MS (EI) \(m/z\) (M\(^+\)) calcd for C\(_{18}\)H\(_{15}\)F\(_3\)O: 304, found: 304;

\([\alpha]_{D}^{25} = +56^\circ\) (\(c = 1.00\), CHCl\textsubscript{3}); 94% ee, from (R,R)-1.

(R)-1-Methyl-5-(1,1,1-trifluoro-4-phenylbutan-2-yl)-1H-indole (Table 2, Entry 13). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 5-bromo-1-methyl-1H-indole were used. Solvent system for chromatography: 20:1 → 12:1 hexane/dichloromethane. The title compound was isolated as a light-green color solid.

Run 1, 209 mg (66% yield, 94% ee); Run 2, 222 mg (70% yield, 94% ee).
The ee was determined on an OD-H column (0.5% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (R,R)-1: 23.0 min (major), 24.8 min (minor).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.61 – 7.59 (m, 1H), 7.37 (d, 1H J = 8.4 Hz), 7.33 – 7.29 (m, 2H), 7.25 – 7.18 (m, 2H), 7.15 – 7.10 (m, 3H), 6.54 (dd, 1H, J = 0.9, 3.1 Hz), 3.83 (s, 3H), 3.35 (dqd, 1H, J = 3.6, 9.3, 11.0 Hz), 2.66 – 2.60 (m, 1H), 2.51 – 2.29 (m, 3H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.0, 136.5, 129.5, 128.6, 128.43, 128.40, 127.3 (q, J = 280.5 Hz), 126.1, 125.0 (q, J = 2.0 Hz), 122.4, 121.7, 109.4, 101.0, 49.2 (q, J = 26.3 Hz), 32.9, 32.5, 30.5 (d, J = 2.0 Hz);

$^{19}$F NMR (282 MHz, CDCl$_3$) δ −69.8 (d, 3F, J = 9.4 Hz);

FT-IR (film) 3027, 2951, 1514, 1495, 1453, 1336, 1258, 1138, 1103, 799, 724, 700 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_{19}$H$_{18}$F$_3$N: 317, found: 317;

$[\alpha]_D^{25} = +63^\circ$ (c = 1.00, CHCl$_3$); 94% ee, from (R,R)-1.

(R)-4-(1,1,1-Trifluoro-4-phenylbutan-2-yl)-1,1'-biphenyl (for determination of absolute stereochemistry). (3-Bromo-4,4,4-trifluorobutyl)benzene (267 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 4-bromo-1,1'-biphenyl were used. Solvent system for chromatography: hexane → 10:1 hexane/dichloromethane. The title compound was isolated as a white solid.

Run 1, 160 mg (47% yield, 94% ee); Run 2, 158 mg (46% yield, 93% ee).

The ee was determined on an OD-H column (1.0% i-PrOH/hexane, flow rate 1.0 mL/min); retention times for compound obtained using (R,R)-1: 7.0 min (minor), 11.1 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.65 – 7.62 (m, 4H), 7.50 – 7.45 (m, 2H), 7.42 – 7.36 (m, 3H), 7.33 – 7.29 (m, 2H), 7.25 – 7.20 (m, 1H), 7.15 – 7.11 (m, 2H), 3.29 (dqd, 1H, J = 3.9, 9.3, 11.0 Hz), 2.65 (ddd, 1H, J = 4.9, 9.0, 13.8 Hz), 2.53 – 2.35 (m, 2H), 2.27 (ddddd, 1H, J = 4.9, 8.8, 11.1, 13.8 Hz);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.1, 140.6, 140.5, 133.4 (d, J = 2.0 Hz), 129.6, 128.8, 128.5, 128.4, 127.5, 127.4, 127.1, 126.9 (q, J = 280.6 Hz), 126.2, 48.8 (q, J = 26.5 Hz), 32.5, 30.1 (d, J = 2.0 Hz);

$^{19}$F NMR (282 MHz, CDCl$_3$) δ −69.6 (d, 3F, J = 9.3 Hz);

FT-IR (film) 3061, 3030, 2955, 1496, 1487, 1454, 1256, 1168, 1148, 1108, 1009, 833, 765, 737, 698 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_{22}$H$_{19}$F$_3$: 340, found: 340;

$[\alpha]_D^{25} = −69^\circ$ (c = 0.96, CHCl$_3$); 93% ee, from (S,S)-1.
(R)-1-Methoxy-3-(1,1,1-trifluoropropan-2-yl)benzene (Table 3, Entry 1). 2-Bromo-1,1,1-trifluoropropane (177 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 15:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 166 mg (81% yield, 92% ee); Run 2, 164 mg (80% yield, 90% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (S,S)-1: 19.5 min (minor), 29.0 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.30 – 7.26 (m, 1H), 6.93 – 6.91 (m, 1H), 6.89 – 6.87 (m, 2H), 3.82 (s, 3H), 3.40 (qq, 1H, J = 7.2, 9.2 Hz), 1.51 (d, 3H, J = 7.3 Hz);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.6, 137.9, 129.5, 127.1 (q, J = 280.5 Hz), 120.8, 114.6, 113.1, 55.2, 44.2 (q, J = 27.5 Hz), 14.6 (d, J = 2.8 Hz);

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ −71.4 (d, 3F, J = 9.3 Hz);

FT-IR (film) 2992, 2948, 2839, 1604, 1588, 1496, 1465, 1291, 1261, 1237, 1172, 1126, 1041, 991, 781, 703 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_{10}$H$_{11}$F$_3$O: 204, found: 204; $[\alpha]_{D}^{25} = -9.8^\circ$ (c = 1.04, CHCl$_3$); 90% ee, from (S,S)-1.

(R)-1-Methoxy-3-(1,1,1-trifluorodecan-2-yl)benzene (Table 3, Entry 2). 2-Bromo-1,1,1-trifluorodecane (275 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 15:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 265 mg (88% yield, 94% ee); Run 2, 263 mg (87% yield, 96% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (S,S)-1: 10.8 min (minor), 15.5 min (major).

$^1$H NMR (500 MHz, CD$_3$CN) $\delta$ 7.31 – 7.27 (m, 1H), 6.93 – 6.87 (m, 3H), 3.78 (s, 3H), 3.43 – 3.32 (m, 1H), 1.99 – 1.84 (m, 2H), 1.35 – 1.06 (m, 12H), 0.86 (t, 3H, J = 7.0 Hz);

$^{13}$C NMR (126 MHz, CD$_3$CN) $\delta$ 160.9, 137.6 (d, J = 2.1 Hz), 130.7, 128.5 (q, J = 279.2 Hz), 122.3, 116.1, 114.2, 56.0, 50.2 (q, J = 25.9 Hz), 32.6, 30.0, 29.9, 29.8, 29.1 (q, J = 2.3 Hz), 27.3, 23.4, 14.4;

$^{19}$F NMR (282 MHz, CD$_3$CN) $\delta$ −70.3 (d, 3F, J = 9.7 Hz);

FT-IR (film) 2926, 2856, 1604, 1587, 1496, 1456, 1436, 1259, 1161, 1125, 1104, 1047, 708 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_{17}$H$_{25}$F$_3$O: 302, found: 302; $[\alpha]_{D}^{25} = -42^\circ$ (c = 1.04, CHCl$_3$); 96% ee, from (S,S)-1.
(R)-1-(3-Cyclohexyl-1,1,1-trifluoropropan-2-yl)-3-methoxybenzene (Table 3, Entry 3). (2-Bromo-3,3,3-trifluoropropyl)cyclohexane (259 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 25:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 230 mg (80% yield, 96% ee); Run 2, 231 mg (81% yield, 96% ee).

The ee was determined on an OJ-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (R,R)-1: 9.1 min (minor), 9.7 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.30 – 7.25 (m, 1H), 6.90 – 6.81 (m, 3H), 3.82 (s, 3H), 3.33 (dqd, 1H, $J = 4.0, 9.4, 11.2$ Hz), 1.86 – 1.71 (m, 3H), 1.68 – 1.54 (m, 4H), 1.18 – 1.02 (m, 4H), 1.00 – 0.82 (m, 2H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.6, 136.6 (d, $J = 2.0$ Hz), 129.5, 127.2 (q, $J = 280.5$ Hz), 121.5, 115.2, 112.9, 55.2, 47.2 (q, $J = 26.2$ Hz), 36.0 (d, $J = 2.0$ Hz), 34.2, 33.9, 31.8, 26.4, 26.0, 25.8;

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ –69.8 (d, 3F, $J = 9.4$ Hz);

FT-IR (film) 2926, 2852, 1604, 1587, 1490, 1452, 1261, 1183, 1155, 1113, 1050, 779, 710 cm$^{-1}$;

GC-MS (EI) $m/z$ (M$^+$) calcd for C$_{16}$H$_{21}$F$_3$O: 286, found: 286; $[\alpha]^{25}_D = +52^\circ$ (c = 1.00, CHCl$_3$); 96% ee, from (R,R)-1.

(R)-tert-Butyldiphenyl((7,7,7-trifluoro-6-(3-methoxyphenyl)heptyl)oxy)silane (Table 3, Entry 4). ((6-Bromo-7,7,7-trifluorohexyl)oxy)(tert-butyl)diphenylsilane (487 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 4:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 390 mg (76% yield, 94% ee); Run 2, 395 mg (77% yield, 94% ee).

The ee was determined on an OD-H column (1.0% i-PrOH/hexane, flow rate 1.0 mL/min); retention times for compound obtained using (S,S)-1: 4.7 min (minor), 7.8 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.69 – 7.64 (m, 4H), 7.46 – 7.35 (m, 6H), 7.30 – 7.23 (m, 1H), 6.90 – 6.81 (m, 3H), 3.82 (s, 3H), 3.65 – 3.59 (m, 2H), 3.17 (dqd, 1H, $J = 4.0, 9.3, 11.0$ Hz), 2.03 – 1.92 (m, 1H), 1.90 – 1.79 (m, 1H), 1.57 – 1.27 (m, 4H), 1.23 – 1.14 (m, 2H), 1.06 (s, 9H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.7, 136.4 (d, $J = 2.0$ Hz), 135.5, 134.0 (d, $J = 1.4$ Hz), 129.6, 129.5, 127.6, 126.9 (q, $J = 280.7$ Hz), 121.4, 115.0, 113.0, 63.7, 55.2, 50.0 (q, $J = 26.3$ Hz), 32.2, 28.7 (d, $J = 2.2$ Hz), 26.9, 26.5, 25.5, 19.2;

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ –69.6 (d, 3F, $J = 9.3$ Hz);

FT-IR (film) 2933, 2858, 1603, 1587, 1490, 1472, 1428, 1260, 1161, 1113, 702 cm$^{-1}$;

GC-MS (EI) $m/z$ (M$^+-$C$_4$H$_9$) calcd for C$_{26}$H$_{28}$F$_3$O$_2$Si: 457, found: 457;
[α]^{25}\text{D} = +24^\circ \ (c = 1.03, \text{CHCl}_3); \ 94\% \ ee, \ from \ (R,R)-1.

(R)-1-(6-Chloro-1,1,1-trifluorohexan-2-yl)-3-methoxybenzene (Table 3, Entry 5). 2-Bromo-6-chloro-1,1,1-trifluorohexane (253 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 15:1 → 12:1 → 10:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 250 mg (89% yield, 96% ee); Run 2, 248 mg (88% yield, 96% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (R,R)-1: 26.1 min (minor), 27.5 min (major).

$^1\text{H} \text{NMR (500 MHz, CDCl}_3)$ \ δ 7.30 – 7.26 (m, 1H), 6.89 – 6.86 (m, 2H), 6.83 – 6.82 (m, 1H), 3.82 (s, 3H), 3.52 – 3.42 (m, 2H), 3.19 (dqd, 1H, $J = 4.1, 9.2, 11.0$ Hz), 2.05 – 1.96 (m, 1H), 1.94 – 1.68 (m, 3H), 1.43 – 1.28 (m, 2H);

$^{13}\text{C} \text{NMR (126 MHz, CDCl}_3)$ \ δ 159.7, 136.0 (d, $J = 2.3$ Hz), 129.7, 126.8 (q, $J = 280.7$ Hz), 121.3, 115.0, 113.2, 55.2, 50.0 (q, $J = 26.6$ Hz), 44.4, 32.1, 28.1 (d, $J = 2.2$ Hz), 24.1;

$^{19}\text{F} \text{NMR (282 MHz, CDCl}_3)$ \ δ −69.7 (d, 3F, $J = 9.3$ Hz);

FT-IR (film) 2954, 1603, 1490, 1456, 1257, 1159, 1109, 1043, 781, 707 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_{13}$H$_{16}$ClF$_3$O: 280, found: 280;

$[\alpha]^{25}\text{D} = +51^\circ \ (c = 0.99, \text{CHCl}_3); \ 96\% \ ee, \ from \ (R,R)-1.$

(R)-1-(10-Bromo-1,1,1-trifluorodecan-2-yl)-3-methoxybenzene (Table 3, Entry 6). 2,10-Dibromo-1,1,1-trifluorodecane (354 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 15:1 → 12:1 → 10:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 309 mg (81% yield, 96% ee); Run 2, 300 mg (79% yield, 95% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 1.0 mL/min); retention times for compound obtained using (S,S)-1: 14.9 min (minor), 25.4 min (major).

$^1\text{H} \text{NMR (500 MHz, CDCl}_3)$ \ δ 7.31 – 7.25 (m, 1H), 6.88 – 6.86 (m, 2H), 6.83 – 6.82 (m, 1H), 3.82 (s, 3H), 3.39 (t, 2H, $J = 6.8$ Hz), 3.18 (dqd, 1H, $J = 4.0, 9.3, 11.1$ Hz), 1.97 (dddd, 1H, $J = 4.1, 7.7, 9.2, 13.4$ Hz), 1.89 – 1.78 (m, 3H), 1.45 – 1.13 (m, 10H);

$^{13}\text{C} \text{NMR (126 MHz, CDCl}_3)$ \ δ 159.6, 136.5 (d, $J = 2.2$ Hz), 129.5, 126.9 (q, $J = 280.7$ Hz), 121.4, 115.1, 113.0, 55.2, 50.1 (q, $J = 26.3$ Hz), 33.9, 32.7, 29.1, 29.0, 28.64 (d, $J = 2.0$ Hz), 28.57, 28.0, 26.6;

$^{19}\text{F} \text{NMR (282 MHz, CDCl}_3)$ \ δ −69.7 (d, 3F, $J = 9.3$ Hz);

FT-IR (film) 2929, 2856, 1603, 1490, 1457, 1437, 1257, 1158, 1109, 1050, 780, 708 cm$^{-1}$;
GC-MS (EI) m/z (M+) calcd for C_{17}H_{24}^{79}BrF_{3}O: 380, found: 380, 382 (M^+-2); 
[α]^25_D = +33° (c = 0.99, CHCl₃); 96% ee, from (R,R)-1.

(R)-7,7,7-Trifluoro-6-(3-methoxyphenyl)heptyl 4-methylbenzenesulfonate (Table 3, Entry 7). 6-Bromo-7,7,7-trifluoroheptyl 4-methylbenzenesulfonate (403 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 1:1 → 1:1.5 → 1:2 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 391 mg (91% yield, 97% ee); Run 2, 393 mg (91% yield, 97% ee).
The ee was determined on an OJ-H column (10% i-PrOH/hexane, flow rate 1.0 mL/min); retention times for compound obtained using (R,R)-1: 32.0 min (minor), 34.7 min (major).

1H NMR (500 MHz, CD₃COCD₃) δ 7.80 – 7.76 (m, 2H), 7.48 – 7.44 (m, 2H), 7.33 – 7.28 (m, 1H), 6.95 – 6.90 (m, 3H), 3.99 (td, 2H, J = 1.1, 6.4 Hz), 3.80 (s, 3H), 3.46 – 3.37 (m, 1H), 2.45 (s, 3H), 1.96 – 1.83 (m, 2H), 1.63 – 1.50 (m, 2H), 1.40 – 1.06 (m, 4H);

13C NMR (126 MHz, CD₃COCD₃) δ 160.9, 145.8, 137.3 (d, J = 2.1 Hz), 134.5, 130.9, 130.6, 128.7, 128.3 (q, J = 279.9 Hz), 122.1, 116.1, 114.1, 71.4, 55.6, 50.2 (q, J = 26.1 Hz), 29.2, 29.0 (d, J = 2.2 Hz), 26.8, 25.7, 21.6;

19F NMR (282 MHz, CD₃COCD₃) δ −70.2 (d, 3F, J = 9.6 Hz);
FT-IR (film) 2945, 1600, 1457, 1358, 1258, 1176, 1118, 956, 815, 708, 663 cm⁻¹;
GC-MS (EI) m/z (M^−OTs) calcd for C_{14}H_{18}F_{3}O: 259, found: 259;
[α]^25_D = +25° (c = 0.99, CHCl₃); 97% ee, from (R,R)-1.

(R)-1-(4-((7,7,7-Trifluoro-6-(3-methoxyphenyl)heptyl)oxy)phenyl)ethan-1-one (Table 3, Entry 8). 1-(4-((6-Bromo-7,7,7-trifluoroheptyl)oxy)phenyl)ethan-1-one (367 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used.
Solvent system for chromatography: 15:1 → 10:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 357 mg (91% yield, 95% ee); Run 2, 342 mg (87% yield, 96% ee).
The ee was determined on an AD-H column (5% i-PrOH/hexane, flow rate 1.0 mL/min); retention times for compound obtained using (R,R)-1: 14.4 min (minor), 17.4 min (major).
\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.93 – 7.89 (m, 2H), 7.28 – 7.25 (m, 1H), 6.89 – 6.82 (m, 5H), 3.97 – 3.94 (m, 2H), 3.81 (s, 3H), 3.19 (dqd, 1H, \(J = 4.1, 9.3, 11.0\) Hz), 2.55 (s, 3H), 2.05 – 1.97 (m, 1H), 1.92 – 1.84 (m, 1H), 1.79 – 1.69 (m, 2H), 1.54 – 1.38 (m, 2H), 1.31 – 1.23 (m, 2H);

\(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 196.7, 162.9, 159.7, 136.3 (d, \(J = 2.0\) Hz), 130.5, 130.2, 129.6, 126.9 (q, \(J = 280.6\) Hz), 121.3, 115.1, 114.1, 113.0, 67.9, 55.2, 50.0 (q, \(J = 26.4\) Hz), 28.7, 28.6 (d, \(J = 2.2\) Hz), 26.4, 26.3, 25.7;

\(^1^9\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) –69.7 (d, 3F, \(J = 9.3\) Hz);

FT-IR (film) 2943, 1675, 1601, 1255, 1170, 1117, 834, 708 cm\(^{-1}\);

GC-MS (EI) \(m/z\) (M\(^+\)) calcd for C\(_{22}\)H\(_{25}\)F\(_3\)O\(_3\): 394, found: 394;

\([\alpha]^{25}_{\text{D}} = +34^\circ \) (\(c = 0.97\), CHCl\(_3\)); 95% ee, from (R,R)-1.

\((R)-1\)-Methoxy-3-(1,1,1-trifluoro-7-(4-iodophenoxy)heptan-2-yl)benzene (Table 3, Entry 9).

1-((6-Bromo-7,7,7-trifluorohexyl)oxy)-4-iodobenzene (451 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 10:1 \(\rightarrow\) 5:1 \(\rightarrow\) 4:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 282 mg (59% yield, 95% ee); Run 2, 292 mg (61% yield, 95% ee).

The ee was determined on an OD-H column (10% i-PrOH/hexane, flow rate 1.0 mL/min); retention times for compound obtained using (R,R)-1: 12.6 min (minor), 22.9 min (major).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.56 – 7.51 (m, 2H), 7.30 – 7.24 (m, 1H), 6.90 – 6.81 (m, 3H), 6.66 – 6.61 (m, 2H), 3.85 (t, 2H, \(J = 6.4\) Hz), 3.81 (s, 3H), 3.19 (dqd, 1H, \(J = 4.1, 9.3, 11.0\) Hz), 2.07 – 1.96 (m, 1H), 1.93 – 1.83 (m, 1H), 1.78 – 1.63 (m, 2H), 1.54 – 1.36 (m, 2H), 1.32 – 1.19 (m, 2H);

\(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 159.7, 158.8, 138.1, 136.3 (d, \(J = 2.1\) Hz), 129.6, 126.9 (q, \(J = 280.7\) Hz), 121.3, 116.9, 115.1, 113.0, 82.5, 67.7, 55.2, 50.0 (q, \(J = 26.4\) Hz), 28.8, 28.6 (d, \(J = 2.1\) Hz), 26.4, 25.7;

\(^1^9\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) –69.7 (d, 3F, \(J = 9.3\) Hz);

FT-IR (film) 2942, 1586, 1486, 1472, 1244, 1174, 1117, 834, 708 cm\(^{-1}\);

GC-MS (EI) \(m/z\) (M\(^+\)) calcd for C\(_{20}\)H\(_{22}\)F\(_3\)IO\(_2\): 478, found: 478;

\([\alpha]^{25}_{\text{D}} = +28^\circ \) (\(c = 0.98\), CHCl\(_3\)); 95% ee, from (R,R)-1.

\(\text{tert-Butyl (R)-4-}(3,3,3\text{-trifluoro-2-}(3\text{-methoxyphenyl})\text{propyl)piperidine-1-carboxylate (Table 3, Entry 10).}\quad\)\(\text{tert-Butyl 4-}\) (2-bromo-3,3,3-trifluoropropyl)piperidine-1-carboxylate (360

mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 15:1 → 10:1 hexane/dichloromethane. The title compound was isolated as a light-yellow solid.

Run 1, 320 mg (83% yield, 96% ee); Run 2, 315 mg (81% yield, 97% ee).

The ee was determined on an OJ-H column (2.0% i-PrOH/hexane, flow rate 1.0 mL/min); retention times for compound obtained using (S,S)-1: 8.5 min (minor), 13.0 min (major).

1H NMR (500 MHz, CDCl₃) δ 7.29 – 7.25 (m, 1H), 6.89 – 6.81 (m, 3H), 4.02 (br, 2H), 3.81 (s, 3H), 3.36 – 3.27 (m, 1H), 2.54 (br, 2H), 1.90 (ddd, 1H, J = 4.4, 11.4, 13.8 Hz), 1.78 (ddd, 1H, J = 4.0, 9.4, 13.7 Hz), 1.68 – 1.64 (m, 1H), 1.52 – 1.48 (m, 1H), 1.43 (s, 9H), 1.27 – 1.04 (m, 3H);

13C NMR (126 MHz, CDCl₃) δ 159.7, 154.7, 136.0 (d, J = 1.9 Hz), 129.7, 126.9 (q, J = 280.7 Hz), 121.3, 115.1, 113.0, 79.3, 55.2, 47.1 (q, J = 26.5 Hz), 35.2, 32.7, 32.5, 30.8, 28.4;

19F NMR (282 MHz, CDCl₃) δ −69.9 (d, 3F, J = 9.2 Hz);

FT-IR (film) 2932, 1690, 1456, 1424, 1366, 1259, 1162, 1118, 1098, 969, 711 cm⁻¹;

GC-MS (EI) m/z (M⁺–Boc) calcd for C₁₅H₁₉F₃NO: 286, found: 286;

[α]D²⁵ = −49° (c = 0.99, CHCl₃); 97% ee, from (S,S)-1.

(R)-7,7,7-Trifluoro-6-(3-methoxyphenyl)heptyl furan-2-carboxylate (Table 3, Entry 11). 6-Bromo-7,7,7-trifluoroheptyl furan-2-carboxylate (343 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 1:1 → 1:1.2 → 1:1.5 hexane/dichloromethane. The title compound was isolated as a yellow oil.

Run 1, 298 mg (81% yield, 96% ee); Run 2, 298 mg (81% yield, 96% ee).

The ee was determined on an OJ-H column (5% i-PrOH/hexane, flow rate 1.0 mL/min); retention times for compound obtained using (R,R)-1: 25.6 min (minor), 33.0 min (major).

1H NMR (500 MHz, CDCl₃) δ 7.57 (dd, 1H, J = 0.9, 1.8 Hz), 7.29 – 7.24 (m, 1H), 7.14 (dd, 1H, J = 0.8, 3.5 Hz), 6.89 – 6.80 (m, 3H), 6.50 (dd, 1H, J = 1.7, 3.5 Hz), 4.24 (t, 2H, J = 6.6 Hz), 3.80 (s, 3H), 3.18 (dqd, 1H, J = 4.1, 9.3, 11.0 Hz), 1.99 (ddd, 1H, J = 4.1, 7.1, 9.7, 13.7 Hz), 1.91 – 1.81 (m, 1H), 1.76 – 1.61 (m, 2H), 1.50 – 1.32 (m, 2H), 1.29 – 1.21 (m, 2H);

13C NMR (126 MHz, CDCl₃) δ 159.7, 158.7, 146.2, 144.7, 136.3 (d, J = 2.2 Hz), 129.6, 126.9 (q, J = 280.6 Hz), 121.3, 117.7, 115.0, 113.0, 111.8, 64.7, 55.2, 50.0 (q, J = 26.4 Hz), 28.6 (d, J = 2.0 Hz), 28.4, 26.4, 25.6;

19F NMR (282 MHz, CDCl₃) δ −69.7 (d, 3F, J = 9.2 Hz);

FT-IR (film) 2947, 1727, 1603, 1584, 1473, 1297, 1259, 1180, 1119, 765, 709 cm⁻¹;

GC-MS (EI) m/z (M⁺) calcd for C₁₅H₂₁F₃O₄: 370, found: 370;

[α]D²⁵ = +32° (c = 0.94, CHCl₃); 96% ee, from (R,R)-1.
(R)-1-Methoxy-3-(1,1,1-trifluoro-4-phenylbutan-2-yl)benzene (eq 3). (4,4,4-Trifluoro-3-iodobutyl)benzene (314 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 5:1 → 4:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 277 mg (94% yield, 96% ee); Run 2, 277 mg (94% yield, 96% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 ml/min); retention times for compound obtained using (S,S)-1: 20.2 min (minor), 32.3 min (major).

For the characterization data, see Table 2, Entry 2 (above).

(R)-1-(4,4,5,5,6,6,6-Heptafluoro-1-phenylhexan-3-yl)-3-methoxybenzene (eq 4). (3-Bromo-4,4,5,5,6,6,6-heptafluorohexyl)benzene (367 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 15:1 → 12:1 → 10:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 363 mg (92% yield, 99% ee); Run 2, 361 mg (92% yield, 99% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (S,S)-1: 12.8 min (minor), 15.6 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.34 – 7.28 (m, 3H), 7.24 – 7.20 (m, 1H), 7.11 – 7.09 (m, 2H), 6.93 – 6.90 (m, 2H), 6.86 – 6.85 (m, 1H), 3.84 (s, 3H), 3.34 – 3.25 (m, 1H), 2.60 – 2.53 (m, 1H), 2.45 – 2.34 (m, 2H), 2.26 – 2.17 (m, 1H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.7, 140.5, 135.5 (d, $J = 5.4$ Hz), 129.6, 128.5, 128.4, 126.2, 122.0, 119.5 – 115.2 (m), 115.6, 113.2, 112.1 – 107.0 (m), 55.2, 47.1 (t, $J = 21.0$ Hz), 32.4, 29.3;

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ –80.7 (dd, 3F, $J = 10.2, 11.9$ Hz), –112.9 – –116.8 (m, 2F), –122.6 – –125.6 (m, 2F);

FT-IR (film) 2961, 1603, 1587, 1496, 1456, 1348, 1219, 1174, 1116, 1045, 933, 728, 698 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_{19}$H$_{17}$F$_7$O: 394, found: 394;

$[\alpha]^{25}_D = +40^\circ$ (c = 0.93, CHCl$_3$); 99% ee, from (R,R)-1.
(R)-1-(1-Chloro-1,1-difluoro-4-phenylbutan-2-yl)-4-methoxybenzene (eq 5). (3-Bromo-4-chloro-4,4-difluorobutyl)benzene (283 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-4-methoxybenzene were used. Solvent system for chromatography: 6:1 → 4:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 274 mg (88% yield, 96% ee); Run 2, 278 mg (89% yield, 96% ee).

The ee was determined on an OD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (R,R)-1: 29.1 min (minor), 34.4 min (major).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.31 – 7.19 (m, 5H), 7.11 – 7.08 (m, 2H), 6.96 – 6.92 (m, 2H), 3.85 (s, 3H), 3.30 (qd, 1H, \(J = 3.1, 11.5\) Hz), 2.63 – 2.57 (m, 1H), 2.45 – 2.36 (m, 2H), 2.27 – 2.19 (m, 1H);

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 159.5, 140.7, 131.2 (t, \(J = 296.2\) Hz), 130.6, 128.5, 128.4, 126.8 (t, \(J = 2.5\) Hz), 126.2, 114.0, 55.2, 54.8 (t, \(J = 22.3\) Hz), 32.6, 30.8 (t, \(J = 2.2\) Hz);

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) –53.9 (dd, 1F, \(J = 10.9, 160.5\) Hz), –54.7 (dd, 1F, \(J = 11.9, 160.7\) Hz);

FT-IR (film) 3026, 2956, 1612, 1515, 1496, 1454, 1306, 1251, 1180, 1114, 1034, 947, 826, 699 cm\(^{-1}\);

GC-MS (EI) m/z (M\(^+\)) calcd for C\(_{17}\)H\(_{17}\)Cl\(_2\)F\(_2\): 310, found: 310;

\([\alpha]^{25}_D = +43^\circ\) (c = 0.93, CHCl\(_3\)); 96% ee, from (R,R)-1.

(R)-2,2-Difluoro-1,3,5-triphenylpentan-1-one (eq 6). 3-Bromo-2,2-difluoro-1,5-diphenylpentan-1-one (353 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 10:1 → 5:1 → 2:1 hexane/dichloromethane. The title compound was isolated as a white solid.

Run 1, 283 mg (81% yield, 98% ee); Run 2, 280 mg (80% yield, 97% ee).

The ee was determined on an AD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (R,R)-1: 20.1 min (minor), 20.9 min (major).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.88 – 7.85 (m, 2H), 7.59 – 7.55 (m, 1H), 7.43 – 7.39 (m, 2H), 7.35 – 7.24 (m, 7H), 7.20 – 7.17 (m, 1H), 7.10 – 7.07 (m, 2H), 3.62 – 3.52 (m, 1H), 2.58 (ddd, 1H, \(J = 4.7, 9.3, 13.6\) Hz), 2.46 – 2.33 (m, 2H), 2.29 – 2.22 (m, 1H);

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 190.1 (t, \(J = 30.0\) Hz), 141.0, 135.02, 134.98, 133.9, 132.8, 129.84, 129.19 (t, \(J = 3.5\) Hz), 128.6, 128.5, 128.4, 127.9, 126.0, 119.4 (t, \(J = 258.1\) Hz), 49.2 (t, \(J = 21.5\) Hz), 32.8, 29.6 (t, \(J = 3.6\) Hz);

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) –103.1 (dd, 1F, \(J = 15.4, 272.5\) Hz), –105.4 (dd, 1F, \(J = 17.3, 272.5\) Hz);

FT-IR (film) 3028, 1701, 1598, 1496, 1454, 1161, 1089, 1065, 912, 698 cm\(^{-1}\);

GC-MS (EI) m/z (M\(^+\)) calcd for C\(_9\)H\(_{20}\)F\(_2\): 350, found: 350;

\([\alpha]^{25}_D = -9.7^\circ\) (c = 0.94, CHCl\(_3\)); 97% ee, from (S,S)-1.
Ethyl (R)-2,2-difluoro-3-(3-methoxyphenyl)-5-phenylpentanoate (eq 7). Ethyl 3-bromo-2,2-difluoro-5-phenylpentanoate (321 mg, 1.00 mmol) and an arylzinc chloride reagent prepared from 1-bromo-3-methoxybenzene were used. Solvent system for chromatography: 2:1 → 1.5:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 271 mg (78% yield, 98% ee); Run 2, 278 mg (80% yield, 98% ee).

The ee was determined on an AD-H column (0.25% i-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (R,R)-1: 22.9 min (minor), 28.8 min (major).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.29 – 7.25 (m, 3H), 7.21 – 7.18 (m, 1H), 7.11 – 7.09 (m, 2H), 6.89 – 6.82 (m, 3H), 4.13 (qd, 2H, $J = 1.1, 7.2$ Hz), 3.88 (s, 3H), 3.30 (ddddd, 1H, $J = 3.6, 6.3, 9.3, 12.9, 16.2$ Hz), 2.58 (ddd, 1H, $J = 4.8, 9.3, 14.0$ Hz), 2.42 (ddd, 1H, $J = 7.5, 9.3, 13.9$ Hz), 2.25 (ddddd, 1H, $J = 3.6, 7.6, 9.3, 13.1$ Hz), 2.19 (ddddd, 1H, $J = 4.9, 9.2, 11.3, 13.9$ Hz), 1.13 (t, 3H, $J = 7.1$ Hz);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.7, 141.0, 136.3 (d, $J = 6.3$ Hz), 129.6, 128.39, 128.38, 126.1, 121.9, 116.5 (dd, $J = 254.4, 257.5$ Hz), 115.4, 113.3, 62.5, 55.2, 49.4 (dd, $J = 21.2, 23.0$ Hz), 32.7, 29.2 (dd, $J = 1.8, 4.6$ Hz), 13.7;

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -107.1 (dd, 1F, $J = 12.9, 252.1$ Hz), -113.7 (dd, 1F, $J = 19.6, 252.1$ Hz);

FT-IR (film) 2940, 1771, 1602, 1490, 1456, 1257, 1103, 1064, 774, 751, 698 cm$^{-1}$;

GC-MS (EI) m/z (M$^+$) calcd for C$_{20}$H$_{22}$F$_2$O$_3$: 348, found: 348;

$[\alpha]_D^{25} = +27^\circ$ (c = 1.05, CHCl$_3$); 98% ee, from (R,R)-1.
IV. Assignment of the Absolute Configuration of the Cross-Coupling Products

\[
\begin{align*}
&\text{Ph} \\
&\text{F}_3\text{C} \\
&\text{Ph}
\end{align*}
\]

(S)-4-(1,1,1-Trifluoro-4-phenylbutan-2-yl)-1,1'-biphenyl. This compound was prepared according to the General Procedure using (3-bromo-4,4,4-trifluorobutyl)benzene and an arylzinc chloride reagent prepared from 4-bromo-1,1'-biphenyl (run with (R,R)-1).

A suitable crystal of $\text{C}_{22}\text{H}_{19}\text{F}_3$ was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Cu-K\(\alpha\) radiation at a temperature of 120 K. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

### Table S–1. Crystal data and structure refinement for crystal01.

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Table S-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for crystal01. U(eq) is defined as one third of the trace of the orthogonalized U_ij tensor.

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Table S–3. Bond lengths [Å] and angles [°] for crystal01.

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Table S-4. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for crystal01. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^* U^{11} + \ldots + 2hk a^* b^* U^{12}]$

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Table S-5. Hydrogen coordinates ($x \times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for crystal01.

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<td>28</td>
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<td>H(8B)</td>
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<td>46</td>
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<td>8388</td>
<td>1615</td>
<td>40</td>
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(S)-2,2-Difluoro-1,3,5-triphenylpentan-1-one (eq 6). This compound was prepared with (R,R)-1.

A suitable crystal of C_{23}H_{20}F_{2}O was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Cu-Kα radiation at a temperature of 120 K. Using Olex2, the structure was solved with the ShelXS\textsuperscript{2} structure solution program using Direct Methods and refined with the ShelXL\textsuperscript{2} refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S–6. Crystal data and structure refinement for crystal02.

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<th>Value</th>
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<td><strong>Empirical formula</strong></td>
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<td><strong>Formula weight</strong></td>
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<td><strong>Temperature</strong></td>
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<tr>
<td><strong>Wavelength</strong></td>
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<tr>
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<tr>
<td><strong>Space group</strong></td>
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<tr>
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<tr>
<td>a</td>
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<tr>
<td>α</td>
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<tr>
<td>b</td>
<td>13.3182(2) Å</td>
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<tr>
<td>β</td>
<td>90°</td>
</tr>
<tr>
<td>c</td>
<td>23.7538(4) Å</td>
</tr>
<tr>
<td>γ</td>
<td>90°</td>
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<tr>
<td><strong>Volume</strong></td>
<td>1790.63(5) Å³</td>
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<td><strong>Z</strong></td>
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<tr>
<td><strong>Density (calculated)</strong></td>
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<tr>
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<tr>
<td><strong>Absorption correction</strong></td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td><strong>Max. and min. transmission</strong></td>
<td>0.7535 and 0.6828</td>
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<tr>
<td><strong>Refinement method</strong></td>
<td>Full-matrix least-squares on F²</td>
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<td><strong>Data / restraints / parameters</strong></td>
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<td><strong>Absolute structure parameter (Flack)</strong></td>
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<tr>
<td><strong>Largest diff. peak and hole</strong></td>
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Table S-7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for crystal02. U(eq) is defined as one third of the trace of the orthogonalized U_ij tensor.

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Table S–8.  Bond lengths [Å] and angles [°] for crystal02.

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C(5)-C(6)-C(7)  116.62(15)
O(1)-C(7)-C(6)  122.16(15)
O(1)-C(7)-C(8)  116.94(15)
C(6)-C(7)-C(8)  120.84(14)
F(1)-C(8)-C(7)  109.98(12)
F(1)-C(8)-C(9)  110.34(13)
F(2)-C(8)-F(1)  104.46(12)
F(2)-C(8)-C(7)  107.49(13)
F(2)-C(8)-C(9)  110.44(12)
C(9)-C(8)-C(7)  113.69(13)
C(8)-C(9)-C(16)  110.57(13)
C(10)-C(9)-C(8)  110.17(13)
C(10)-C(9)-C(16)  113.65(13)
C(11)-C(10)-C(9)  121.34(14)
C(15)-C(10)-C(9)  119.48(14)
C(15)-C(10)-C(11)  119.17(15)
C(12)-C(11)-C(10)  120.19(15)
C(13)-C(12)-C(11)  120.46(16)
C(14)-C(13)-C(12)  119.58(16)
C(13)-C(14)-C(15)  120.33(15)
C(10)-C(15)-C(14)  120.27(15)
C(17)-C(16)-C(9)  112.08(13)
C(18)-C(17)-C(16)  111.50(13)
C(19)-C(18)-C(17)  120.90(15)
C(19)-C(18)-C(23)  118.43(16)
C(23)-C(18)-C(17)  120.63(15)
C(20)-C(19)-C(18)  120.97(17)
C(19)-C(20)-C(21)  120.07(18)
C(22)-C(21)-C(20)  119.53(17)
C(21)-C(22)-C(23)  120.38(18)
C(22)-C(23)-C(18)  120.61(17)
Table S-9. Anisotropic displacement parameters (Å² x 10³) for crystal02. The anisotropic displacement factor exponent takes the form: 

\[-2\pi²[ h² a*² U^{11} + ... + 2 h k a* b* U^{12} ] \]

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Table S-10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^{-3}) for crystal02.

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Table 2, Entry 1

$^{13}$C NMR

(CDCl$_3$, 126 MHz)
Table 2, Entry 2
\(^1\text{H} \text{NMR}
(\text{CDCl}_3, \text{500 MHz})
Table 2, Entry 2
$^{13}$C NMR
(CDCl$_3$, 126 MHz)
Table 2, Entry 3
$^1$H NMR
($\text{CD}_3\text{COCD}_3$, 500 MHz)
Table 2, Entry 3
$^{13}$C NMR
$(CD_3COCD_3, 126$ MHz)
Table 2, Entry 4
$^1$H NMR
(CDCl$_3$, 500 MHz)
Table 2, Entry 4

$^{13}$C NMR
(CDCl$_3$, 126 MHz)
Table 2, Entry 5
$^1$H NMR
*(CDCl$_3$, 500 MHz)*
Table 2, Entry 5
$^{13}$C NMR
(CDCl$_3$, 126 MHz)
Table 2, Entry 6
\(^1\)H NMR
(CDCl\(_3\), 500 MHz)
Table 2, Entry 6
$^{13}$C NMR
($\text{CDCl}_3$, 126 MHz)
Table 2, Entry 7

$^1$H NMR
(CDCl$_3$, 500 MHz)
Table 2, Entry 7
$^{13}$C NMR
(CDCl$_3$, 126 MHz)
Table 2, Entry 8
$^1$H NMR
(CDCl$_3$, 500 MHz)
Table 2, Entry 8

$^{13}$C NMR

(CDCl$_3$, 126 MHz)
Table 2, Entry 9
$^1$H NMR
($\text{CDCl}_3$, 500 MHz)
Table 2, Entry 9

$^{13}$C NMR

(CDCl$_3$, 126 MHz)
Table 2, Entry 10
$^1$H NMR
(CDCl$_3$, 500 MHz)
Table 2, Entry 10

$^{13}$C NMR

(CDCl$_3$, 126 MHz)
Table 2, Entry 11
$^1$H NMR
(CDCl$_3$, 500 MHz)
Table 2, Entry 11

$^{13}$C NMR (CDCl$_3$, 126 MHz)
Table 2, Entry 12

$^1$H NMR

(CDCl$_3$, 500 MHz)
Table 2, Entry 12
$^{13}$C NMR
(CDCl$_3$, 126 MHz)
Table 2, Entry 13
^1H NMR
(CDCl$_3$, 500 MHz)
Table 2, Entry 13

$^{13}$C NMR

(CDCl$_3$, 126 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)
$^{13}$C NMR
(CDCl$_3$, 126 MHz)
Table 3, Entry 1
$^1$H NMR
(CDCl$_3$, 500 MHz)
Table 3, Entry 1

$^{13}$C NMR

(CDCl$_3$, 126 MHz)
Table 3, Entry 2

$^1$H NMR

(CD$_3$CN, 500 MHz)
Table 3, Entry 2

$^{13}$C NMR

($\text{CD}_3\text{CN, 126 MHz}$)
Table 3, Entry 3

$^1$H NMR
(CDCl$_3$, 500 MHz)
Table 3, Entry 3
$^{13}$C NMR
(CDCl$_3$, 126 MHz)
Table 3, Entry 4

$^1$H NMR
(CDCl$_3$, 500 MHz)
Table 3, Entry 4

$^{13}$C NMR

(CDCl$_3$, 126 MHz)
Table 3, Entry 5
$^1$H NMR
(CDCl$_3$, 500 MHz)
Table 3, Entry 5
$^{13}$C NMR
(CDCl$_3$, 126 MHz)
Table 3, Entry 6
$^1$H NMR
(CDCl$_3$, 500 MHz)
Table 3, Entry 6
$^{13}$C NMR
(CDCl$_3$, 126 MHz)
Table 3, Entry 7

$^1$H NMR

$(\text{CD}_3\text{COCD}_3, 500 \text{ MHz})$
Table 3, Entry 7
$^{13}$C NMR
($\text{CD}_3\text{COCD}_3$, 126 MHz)
Table 3, Entry 8
$^1$H NMR
(CDCl$_3$, 500 MHz)
Table 3, Entry 8
$^{13}$C NMR
(CDCl$_3$, 126 MHz)
Table 3, Entry 9

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(CDCl$_3$, 500 MHz)
Table 3, Entry 9

$^{13}$C NMR
(CDCl$_3$, 126 MHz)
Table 3, Entry 10

$^1$H NMR

(CDCl$_3$, 500 MHz)
Table 3, Entry 10

$^{13}$C NMR

(CDCl$_3$, 126 MHz)
Table 3, Entry 11
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Table 3, Entry 11

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(CDCl$_3$, 126 MHz)
Eq 3
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(CDCl$_3$, 500 MHz)
Eq 3

$^{13}$C NMR

($\text{CDCl}_3$, 126 MHz)
Eq 4

$^1$H NMR

(CDCl$_3$, 500 MHz)
Eq 4
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Eq 5

$^1$H NMR

(CDCl$_3$, 500 MHz)
Eq 5

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Eq 6

$^1$H NMR
(CDCl$_3$, 500 MHz)
Eq 6

$^{13}$C NMR

(CDCl$_3$, 126 MHz)
Eq 7

$^1$H NMR

(CDCl$_3$, 500 MHz)
Eq 7

$^{13}$C NMR

(CDC$_3$, 126 MHz)